

博 士 論 文

光エネルギーを利用した
有機ホウ素アート錯体の直接励起による炭素ラジカル生成

2 0 2 5 年

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目次

序論	1
第一章 2,2'-(Pyridine-2,6-diyl)diphenol (PDP) 型ホウ素アート錯体の 直接青色光励起による炭素ラジカル生成	20
第二章 PDP 型ホウ素アート錯体の直接青色光励起を鍵とする Minisci 型反応	65
第三章 PDP 型青色光励起グリコシルホウ素アート錯体を用いた C-グリコシル化反応	87
第四章 深赤色から近赤外光による azadipyrromethene (ADP) 型ホウ素 アート錯体の直接光励起を利用した触媒的炭素ラジカル生成	135
総括	197
論文目録	198
謝辞	199

略語表

Ac	Acetyl
ADP	Azadipyrromethene
Ar	Aryl
Boc	<i>tert</i> -Butoxycarbonyl
bpy	2,2'-Bipyridyl
Bn	Benzyl
Bu	Butyl
Cat	Catalyst
COD	1,5-Cyclooctadiene
CV	Cyclic Voltammetry
DBU	1,8-Diazabicyclo[5.4.0]undec-7-ene
DCM	Dichloromethane
DMAP	4-Dimethylaminopyridine
DMSO	Dimethyl Sulfoxide
DMF	<i>N,N</i> -Dimethylformamide
DR	Deep-red
dtbbpy	4,4'-Di- <i>tert</i> -butyl-2,2'-bipyridine
e	Electron
EA	Electron Acceptor
EDA	Electron Donor-Acceptor
ESR	Electron Spin Resonance
Et	Ethyl
EWG	Electron Withdrawing Group
GPC	Gel Permeation Chromatography
H ₂ O ₂	Hydrogen Peroxide
HFIP	1,1,1,3,3,3-Hexafluoro-2-Propanol
IPN	Isophthalodinitrile
L	Ligand
LED	Light Emitting Diode
Me	Methyl
Naph	Naphthyl
NIR	Near-Infrared
NMR	Nuclear Magnetic Resonance
PDP	2,2'-(Pyridine-2,6-diyl)diphenol

Ph	Phenyl
ppy	2-Phenylpyridinato
PRE	Persistent Radical Effect
SCE	Saturated Calomel Electrode
SET	Single Electron Transfer
TEMPO	2,2,6,6-Tetramethylpiperidine 1-Oxyl
<i>tert</i>	Tertiary
Tf	Trifluoromethanesulfonyl
TFA	Trifluoroacetic Acid
THF	Tetrahydrofuran
TMS	Trimethylsilyl

序論

第一節 有機ホウ素化合物

有機ホウ素化合物は湿気や空気に対して安定であることから、有機合成化学において取り扱いやすい有用な化合物群である。そのため、有機ホウ素化合物は、ホウ素部位を起点とした様々な分子変換を通じて多様な官能基に変換することができる。その代表的な例として、Brownは、有機ホウ素化合物を有機合成における重要な試薬として発展させた功績により1979年にノーベル化学賞を受賞している。また、鈴木章は、有機ホウ素化合物を用いたパラジウム触媒クロスカップリング反応の開発により2010年にノーベル化学賞を受賞している。¹ このように合成化学上重要なホウ素含有分子は、ビルディングブロックとして有用であるのみならず、医薬品合成における出発原料² や触媒³、生命化学分野における分子認識型センサー⁴の構成要素として利用されており、材料科学において多様な利用価値が見出されてきた。⁵ このような背景のもと、近年多彩な結合形成反応を志向し、有機ホウ素化合物から炭素ラジカルを発生させ、生じる炭素ラジカルを反応性中間体として用いる反応開発が積極的に行われている。⁶ 第二節より、有機ホウ素化合物からの炭素ラジカル生成手法について述べる。

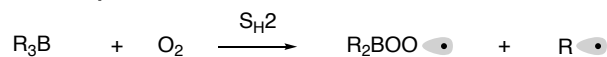
第二節 酸素や添加剤を用いた有機ホウ素化合物からの炭素ラジカル生成

1860年代にFranklandらによって行われたトリエチルボランと酸素の反応⁷を皮切りに、トリアルキルホウ素化合物から炭素ラジカルを発生させる手法の開発が、近年まで精力的に行われている。本手法において炭素ラジカル発生機構を **Figure P1** に示す。^{6a} 開始段階 (Initiation step) において、三重項酸素 (O_2) とトリアルキルホウ素化合物 (R_3B) がラジカル置換反応 (S_H2) 形式で反応し、炭素ラジカル ($R^\cdot$) が生成する。成長段階 (Propagation step) では、生じる炭素ラジカル ($R^\cdot$) が、酸素と反応することでペルオキシラジカル ($ROO^\cdot$) が生じる。ペルオキシラジカル ($ROO^\cdot$) はトリアルキルホウ素化合物 (R_3B) との S_H2 反応が進行する。生成するモノペルオキシホウ素化合物 $[(ROO)BR_2]$ はさらに酸素と反応し、ジペルオキシホウ素化合物 $[(ROO)_2BR]$ を与える。または、モノペルオキシホウ素化合物 $[(ROO)BR_2]$ はトリアルキルホウ素化合物 (R_3B) と反応し、ジアルキルホウ素化合物 $[(RO)BR_2]$ が生成する。ジアルキルホウ素化合物 $[(RO)BR_2]$ は更に酸素と反応することで、ホウ素化合物 $[(RO)_3B]$ が得られる。最終的に、自動酸化生成物に対して加水分解、酸化、還元処理を行うことで、ヒドロペルオキシドまたはアルコールが得られる。

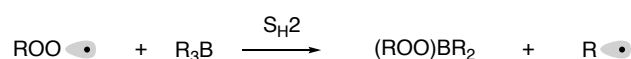
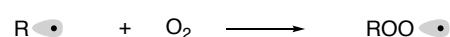
このような性質を踏まえ、1987年大畠らはトリエチルボランと酸素をラジカル開始剤として用いた、アルキン **1** に対するヒドロスタナン **2** を反応剤としたヒドロスタニル化反応を見出した (**Figure P2**)。⁸ 本反応では、トリエチルボランが反応系中に微量に存在する酸素と反応し、続く反応により目的のヒドロスタニル化生成物 **3** が得られる。反応機構を **Figure P3** に示す。トリエチルボラン (R_3B) が微量の酸素 (O_2) と反応しエチルラジカル ($Et^\cdot$) が生成する。生成したエチルラジカル ($Et^\cdot$) はヒドロスタナン

(R_3SnH) から水素引き抜きを起こし、スズラジカル ($R_3Sn^\bullet$) が生じる。スズラジカル ($R_3Sn^\bullet$) はアルキン **1** に付加しアルケニルラジカルを与える。アルケニルラジカルはヒドロスタナン (R_3SnH) から水素を引き抜き、目的のヒドロスタニル化生成物 **3** が得られる。同時に、スズラジカル ($R_3Sn^\bullet$) が再生することでラジカル連鎖反応が進行する。トリエチルボランを用いる手法は、他のラジカル開始剤と比較して加熱を必要としないことから、立体化学を制御する際に有用である。

Initiation step



Propagation steps



Further reactions

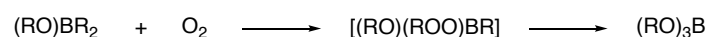
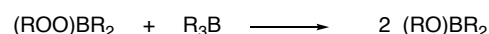
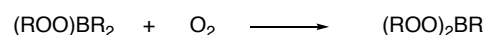


Figure P1. トリアルキルボウ素化合物の自動酸化機構

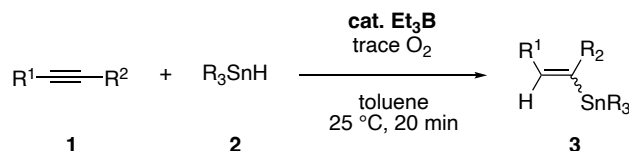


Figure P2. ヒドロスタニル化反応

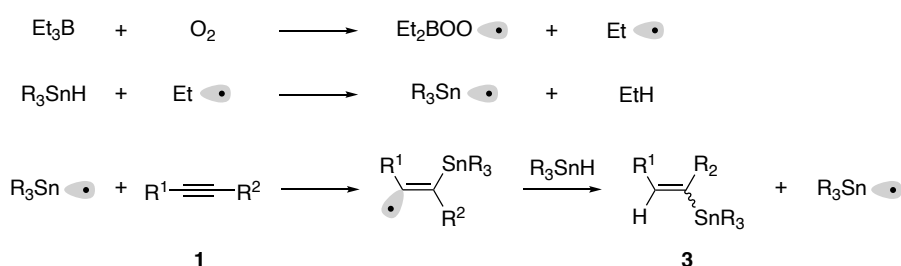


Figure P3. ヒドロスタニル化反応の反応機構

大鷗らは、トリエチルボランと酸素を用いたラジカル開始剤が低温下で炭素ラジカルを発生させ得る特性を活かし、生成物の立体選択性を自在に制御することに成功した (**Figure P4**)。⁹ 具体的には、アルキン **4** とトリフェニルゲルマン **5** において、反応温度を変えることで、異なる立体異性体の分岐的合成に成功した。 -78°C で反応を行う場合には、*Z*体のアルケニルゲルマン **6** が得られ、反応温度を 60°C に設定し反応を行うことで、*E*体の異性体 **7** のみが得られる。*E*体の異性体 **7** が得られる理由は、 60°C の

条件ではトリフェニルゲルミルラジカルの付加脱離過程によって、*Z* 体から *E* 体へ異性化するためである。

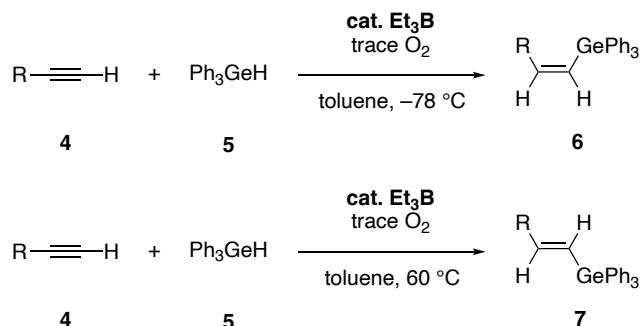


Figure P4. ヒドロゲルミル化反応

大罵らは、ハロゲン化アルキル **8** の還元反応によって還元体 **9** が得られることを報告している (Figure P5)。¹⁰ 本手法では、トリエチルボランから生じるエチルラジカルがスズラジカルを生成させ、ハロゲン化アルキル **8** のヨウ素原子引き抜きにより炭素ラジカルが生じる。生成した炭素ラジカルがトリブチルスズから水素を引き抜き、スズラジカルが発生することで、ラジカル連鎖反応が進行する。

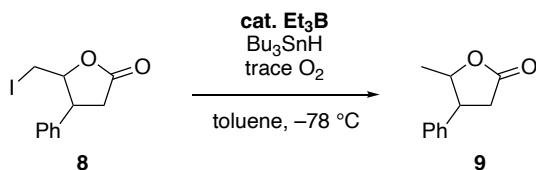


Figure P5. ハロゲン化アルキル **8** の還元反応

ここまでは、有機ホウ素化合物から生じる炭素ラジカルをラジカル開始剤として利用する反応を紹介した。ここから、有機ホウ素化合物から生じる炭素ラジカルを直接基質に導入する例を紹介する。1974 年鈴木らは、フェントン試薬 ($\text{H}_2\text{O}_2/\text{FeCl}_2$) を用いて、トリシクロヘキシルボラン **10** 由来のシクロヘキシルラジカルが電子不足オレフィン **11** に対して付加し、**12** が得られることを見出している (Figure P6)。¹¹ 同様の反応形式で、種々の電子不足オレフィンへの付加反応が報告されている。¹²

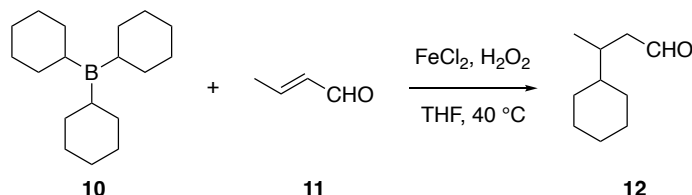


Figure P6. Giese 型ラジカル付加反応

1964 年 Matteson らは、トリメチルボロキシシン **13** と次亜塩素酸 *tert*-ブチル **14** を光照射下反応させることで、メチルラジカルが生じることを報告している (Figure P7)。

¹³ 反応機構は **Figure P8** の通りである。次亜塩素酸 *tert*-ブチル **14** から生じる *tert*-ブトキシラジカルがトリメチルボロキシシン **13** に付加し、その後メチルラジカルが生じる。生じるメチルラジカルは次亜塩素酸 *tert*-ブチル **14** と反応することでクロロメタン **15** が得られる。その際に生成する *tert*-ブトキシラジカルが続く反応を引き起こす。

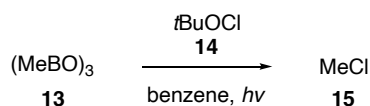


Figure P7. トリメチルボロキシシン **13** からのメチルラジカル生成

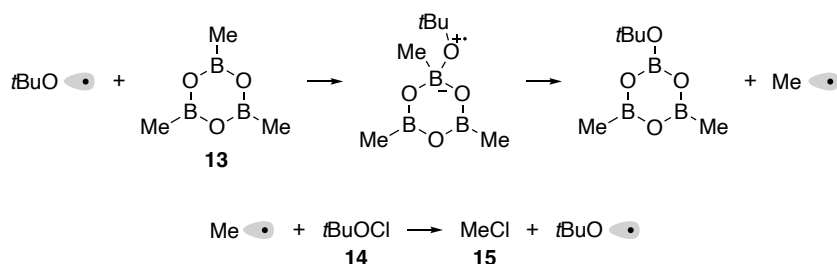


Figure P8. トリメチルボロキシシン **13** からのメチルラジカル生成機構

2000 年 Renaud らは、 Barton エステル PTOC-OMe から生じる酸素中心ラジカル ($\text{RO}^\bullet$) をアルキルボロン酸カテコールエステル **18** に反応させることで炭素ラジカルが生成することを見出した (**Figure P9**)。 ¹⁴ アルケン **16** のヒドロホウ素化により反応系中でアルキルボロン酸カテコールエステル **18** を得る。その後、光照射下で発生する酸素中心ラジカル ($\text{RO}^\bullet$) がエステル **18** と反応し炭素ラジカルが生じる (**Figure P10**)。炭素ラジカルは電子不足オレフィン **19** に付加し、さらに生じるラジカルは Barton エステル PTOC-OMe と反応することで化合物 **20** が得られるとともに、酸素中心ラジカル ($\text{RO}^\bullet$) が再生し、反応が進行する。

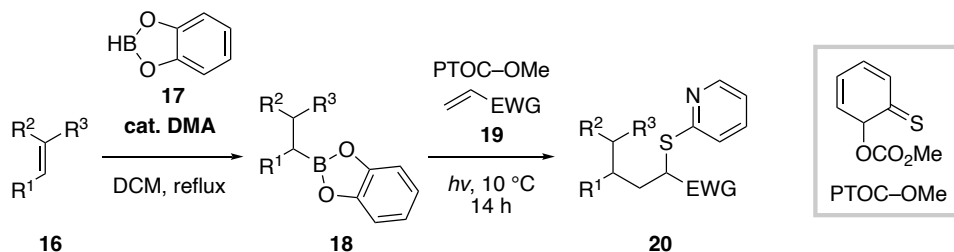


Figure P9. アルキルボロン酸カテコールエステル **18** からの炭素ラジカル生成

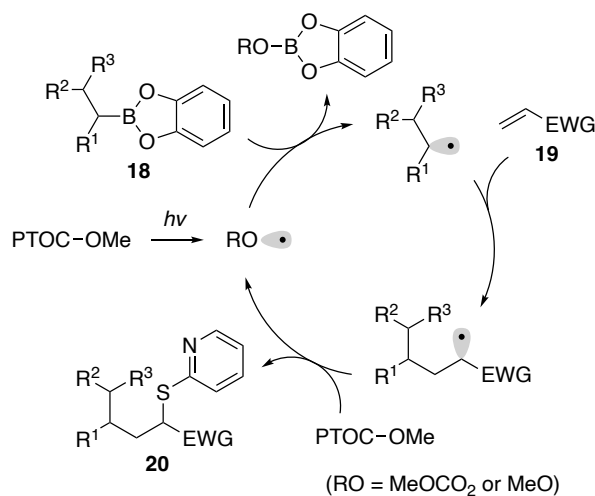


Figure P10. アルキルボロン酸カテコールエステル **18** からの炭素ラジカル生成機構

2010 年 Fensterbank らは、アルキルトリフルオロボレート塩 **21** を炭素ラジカル源として利用できる手法を開発した (**Figure P11**)。 ¹⁵ 本反応では、二塩化銅が酸化剤として働き、高温条件下で発生する炭素ラジカルと TEMPO ラジカルがラジカル-ラジカルカップリングを引き起こすことで、炭素-酸素結合形成を実現している。加えて、TEMPO ラジカルの代わりに電子不足オレフィン **23** を用いることでラジカル付加体 **24** が得られることを見出している (**Figure P12**)。その他では、種々の酸化剤を用いた反応例 ^{16a-}^{16f} や窒素中心ラジカル ^{16g} を用いた例がある。

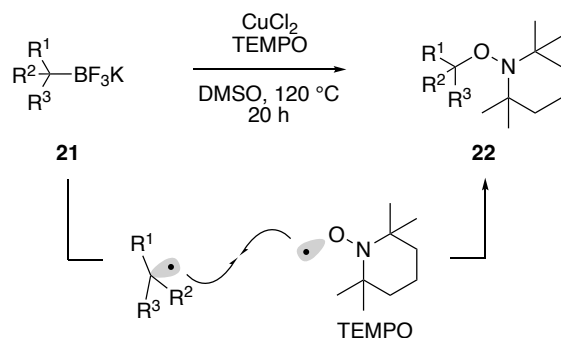


Figure P11. アルキルトリフルオロボレート塩 **21** と TEMPO ラジカルとの反応

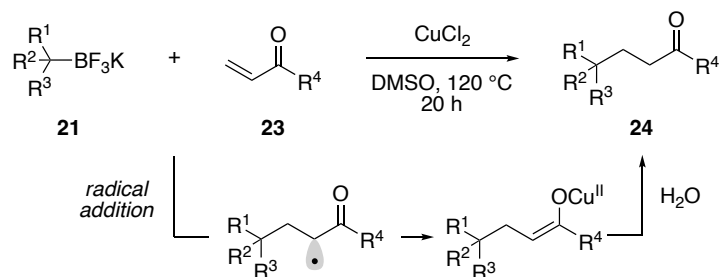


Figure P12. アルキルトリフルオロボレート塩 **21** と電子不足オレフィン **23** との反応

第三節 光酸化還元触媒を用いた有機ホウ素化合物からの炭素ラジカル生成

近年、光酸化還元触媒を用いてハロゲン化アルキルやカルボン酸といった炭素ラジカル前駆体から炭素ラジカルを生成させ、結合形成反応へ適用する手法が精力的に開発されている。¹⁷ 特に、有機ホウ素化合物は物理化学的安定性と取り扱いの容易さから、炭素ラジカル前駆体として広く利用されている。有機ホウ素化合物の酸化電位を **Figure P13** に示す。⁶ アルキルボロン酸 **27** やアルキルボロン酸ピナコールエステル **28** からの炭素ラジカル生成は、その酸化電位の高さから困難であることが知られている。そこで、ホウ素上を四配位のアニオン性に変換することで、酸化電位を低下させ、ラジカル生成を容易にする戦略がとられている (**21**, **25**, **26** and **29**)。以降、具体的な反応例を示す。

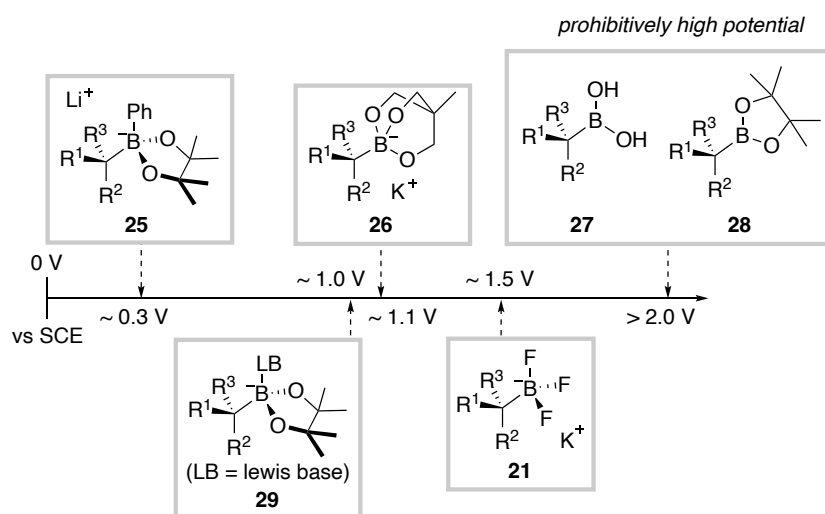


Figure P13. 炭素ラジカル前駆体として用いられる有機ホウ素化合物

2012 年穂田らは、イリジウム光酸化還元触媒を用いてアルキルトリフルオロボレート塩 **21** およびアルキルトリオールボレート塩 **26** からの炭素ラジカル発生手法を見出した (**Figure P14**)。¹⁸ 生じる炭素ラジカルは TEMPO ラジカルと反応し、ラジカルカップリング体 **30** が得られる。本報告を皮切りに、以降では様々なカップリングパートナーとの結合形成反応が報告されるようになる。

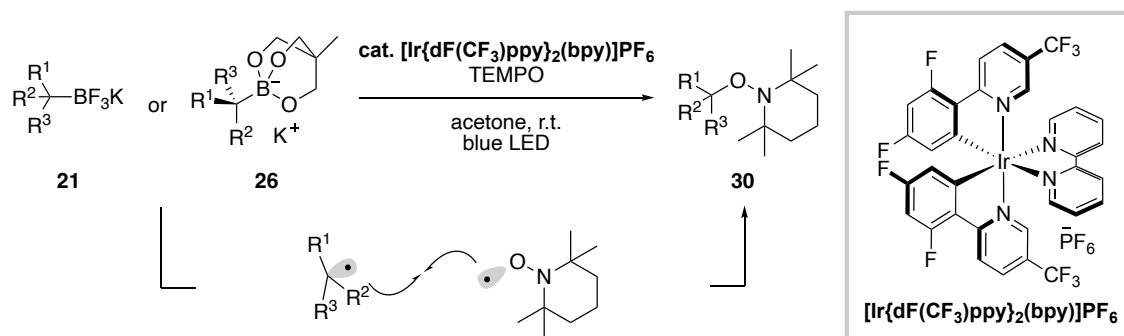


Figure P14. アルキルトリフルオロボレート塩 **21** またはアルキルトリオールボレート塩 **26** からの炭素ラジカル生成

2017 年 Martin らは、ベンジルトリフルオロボレート塩 **31** とアルケン **32**、二酸化炭素の 3 成分カップリング反応を報告した (Figure P15)。¹⁹ ベンジルトリフルオロボレート塩 **31** から生じるベンジルラジカルがアルケン **32** へ付加する。その後に生じるラジカルが二酸化炭素と反応し、一電子移動 (SET) とプロトン化を経て目的物 **33** が得られる。

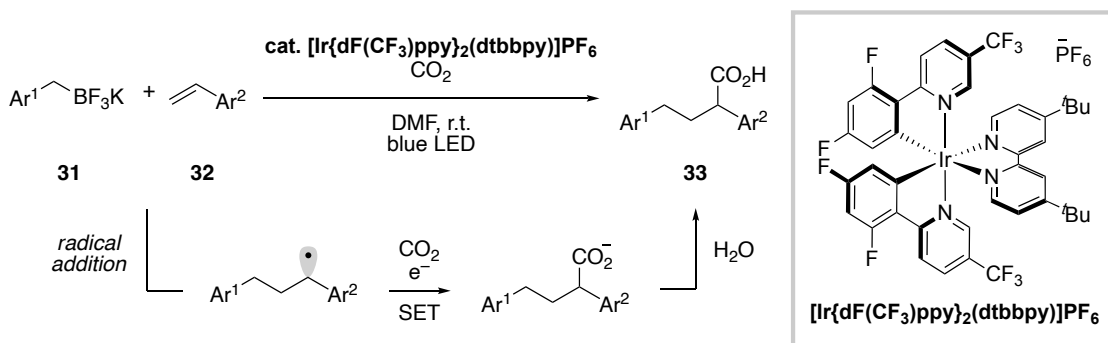


Figure P15. ベンジルトリフルオロボレート塩 **31** とアルケン **32** 及び二酸化炭素の 3 成分カップリング反応

2020 年 Sun らは、ベンジルトリフルオロボレート塩 **31** とアセテニルケトン **34** を用い、ラジカル-ラジカルカップリング反応によりプロパルギルアルコール **35** を得る手法を開発した (Figure P16)。²⁰ 本手法では短寿命なベンジルラジカルと長寿命なケチルラジカルが、交差選択的にカップリングすることにより目的物が得られる。

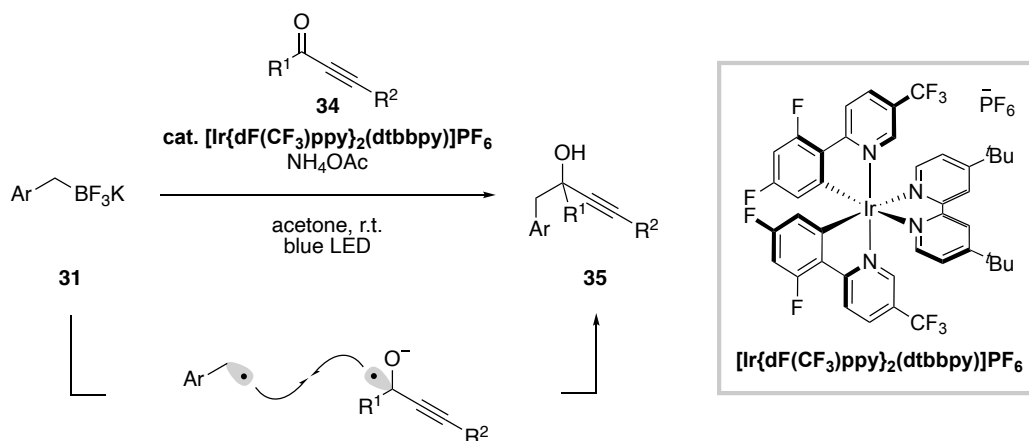


Figure P16. ラジカル-ラジカルカップリング反応

2014 年 Molander らは、光酸化還元触媒、ニッケル触媒の協働触媒系を用いて、ベンジルトリフルオロボレート塩 **31** とハロゲン化アリアル **36** のクロスカップリング反応を報告した (Figure P17)。²¹ イリジウム光酸化還元触媒、ニッケル触媒、配位子、添加剤として 2,6-lutidine を用い、アセトン/メタノール混合溶媒中、青色光を照射することで、カップリング体 **37** を得ている。反応機構は Figure P18 のとおりである。臭化ア

リール **36** がニッケル 0 価種に対して酸化的付加し、ニッケル 2 価種が生じる。ベンジルトリフルオロボレート塩 **31** が酸化されて得られるベンジルラジカルがニッケル 2 価種に対して付加し、ニッケル 3 価種が生じる。ニッケル 3 価種からの還元的脱離によってカップリング体 **37** が得られる。ニッケル 1 価種は、イリジウム触媒によって還元され、ニッケル 0 価種が再生する。その後の報告で、ベンジルトリフルオロボレート塩のみならず、第二級アルキルトリフルオロボレート塩、第三級アルキルトリフルオロボレート塩を炭素ラジカル源として用いた反応も達成されている。²²

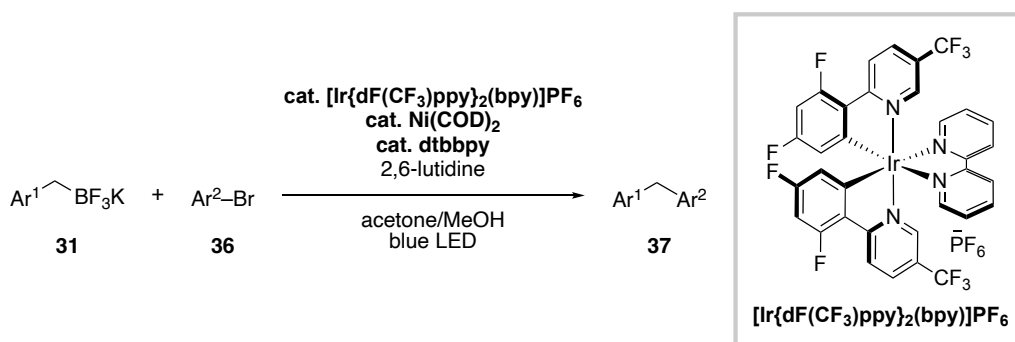


Figure P17. ニッケル触媒クロスカップリング反応

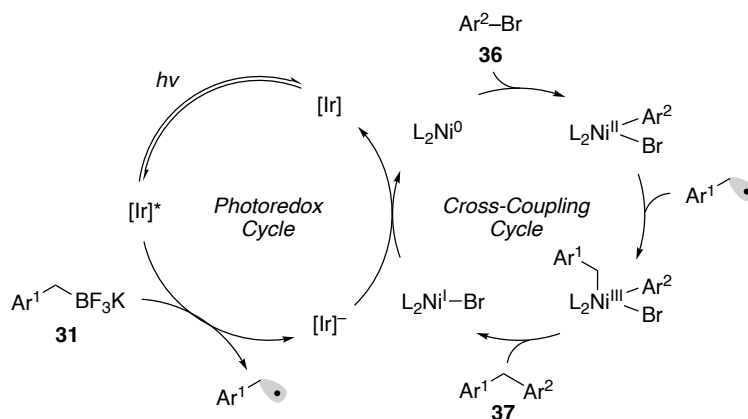


Figure P18. ニッケル触媒クロスカップリング反応の反応機構

ここまでのトリフルオロボレート塩を用いた反応に代わり、ここからは電荷中性の三配位ホウ素化合物を用いた反応例を示す。求核剤をホウ素に配位させ、反応系中でアニオンとして振る舞うことで、三配位ホウ素化合物はトリフルオロボレート塩と同様の反応性を示す。

2016 年 Ley らは、第一級、第二級ベンジルまたはアリルボロン酸ピナコールエステル **28** に対し、ピリジン系求核剤 (DMAP または **39**) と光酸化還元触媒を用いることで、ベンジルラジカルまたはアリルラジカルの生成が可能であることを見出した (Figure P19)。²³ 本手法はフロー合成法で行われており、生じるラジカルはニッケル触媒クロスカップリングやラジカル-ラジカルに適用可能であった。ニッケル触媒クロスカップリングは、先に紹介したメカニズム (Figure P18) と同様である。ラジカル-ラジ

カルカップリング反応のメカニズムを **Figure P20** に示す。ピリジン系求核剤 **39** によって活性化されたホウ素化合物 **29** は、光酸化還元触媒によって一電子酸化されることで、炭素ラジカルを与える。その際に生じるピリジニウム種は光酸化還元触媒によって還元され、長寿命なラジカルが生じる。二つのラジカルが交差選択的にカップリングすることで、目的物 **40** が得られる。Ley らは同様の形式で、保護基を持たないアルキルボロン酸からの炭素ラジカル生成法に関する報告をしている。²⁴

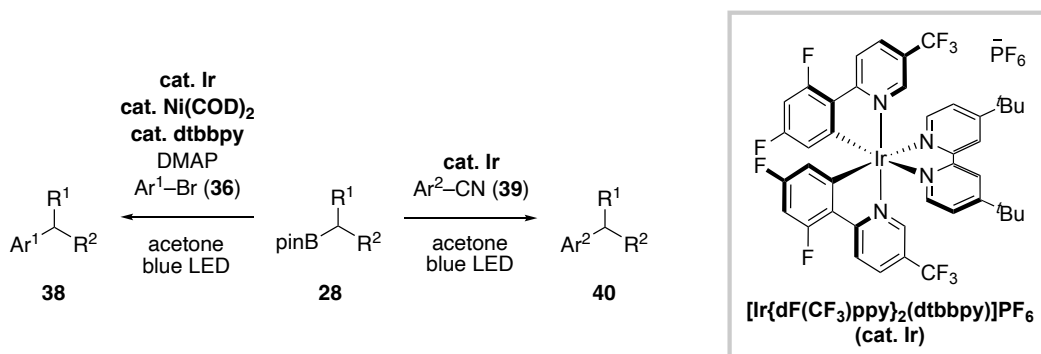


Figure P19. アルキルボロン酸ピナコールエステル **28** からの炭素ラジカル生成

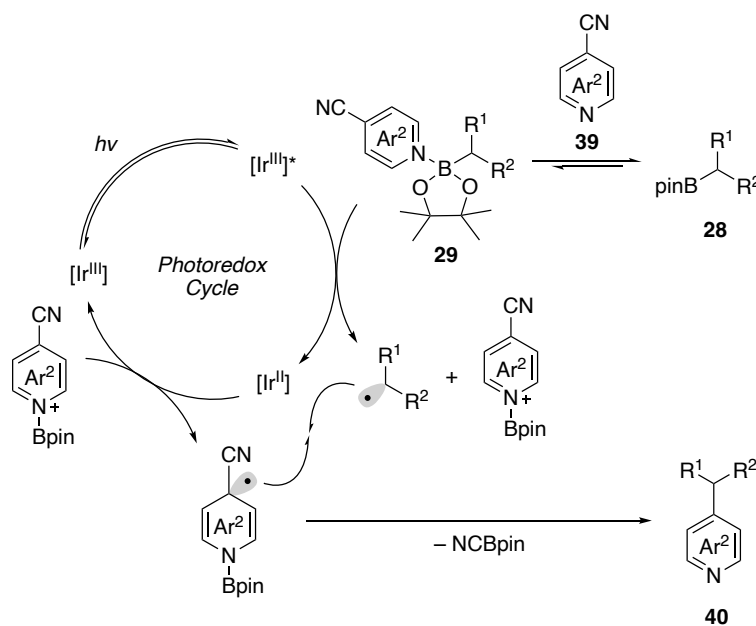


Figure P20. ラジカル-ラジカルカップリング反応の機構

2019 年 Aggarwal らは、アルキルボロン酸ピナコールエステル **28** にフェニルリチウムを作用させて調製される有機ホウ素アート錯体 **25** から炭素ラジカルを発生させる手法を開発した (**Figure P21**)。²⁵ 光酸化還元触媒として用いる **4CzIPN** が有機ホウ素アート錯体 **25** を一電子酸化することで炭素ラジカルが生じ、アルケン **41** に付加する。生じた中間体が $\text{S}_{\text{H}}2$ 機構または $\text{S}_{\text{N}}2$ 機構によって環化し、目的物 **42** が得られる。

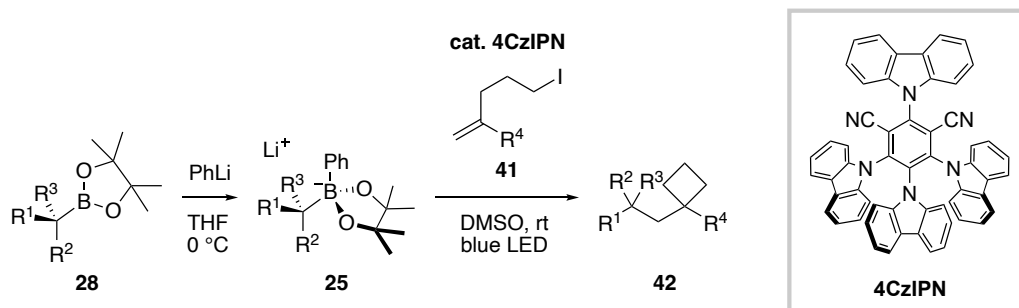


Figure P21. 有機ホウ素アート錯体 **25** からの炭素ラジカル生成

第四節 電気化学的手法を用いた有機ホウ素化合物からの炭素ラジカル生成

近年、電気化学的手法を用いて有機ホウ素化合物から炭素ラジカルを発生させる反応の開発も精力的に進められている。²⁶

先駆的な例として 2020 年 Lei らは、電気化学条件下、アルキルボロン酸からの炭素ラジカル生成法を報告した (**Figure P22**)。²⁷ アルキルボロン酸 **27** から生じる炭素ラジカルがアリールベンゾイミダゾール誘導体のアクセプター **43** に付加し、分子内環化を伴いながら目的物 **44** が得られる。その他の反応として、ラジカル付加反応²⁸、ニッケル触媒クロスカップリング反応²⁹、炭素-ヘテロ原子結合形成反応³⁰ が知られている。

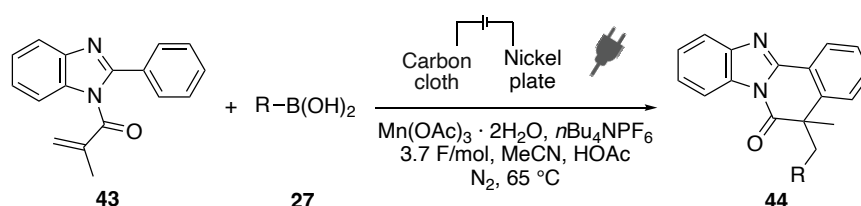


Figure P22. 電気化学的手法を用いた有機ホウ素化合物からの炭素ラジカル生成

第五節 電子ドナー・アクセプター (EDA) 錯体を介した有機ホウ素化合物からの炭素ラジカル生成

基質間の相互作用により形成される電子ドナー・アクセプター (EDA) 錯体の光励起を利用した反応開発は、外部光触媒を必要としない環境調和型の分子変換法として近年注目を集めている。³¹⁻³⁶

1990 年 Schuster らは、カウンターカチオンとして Cyanine 色素を用いることで、ホウ素アート錯体から炭素ラジカルの発生が可能であることを見出した (**Figure P23**)。³¹ 本手法では、ホウ素アート錯体 (Naph-BPh₃) とシアニン色素 (Cy⁺) のイオン対がパルスレーザー照射によって励起され、電子移動が生じることで炭素ラジカルが生成する。

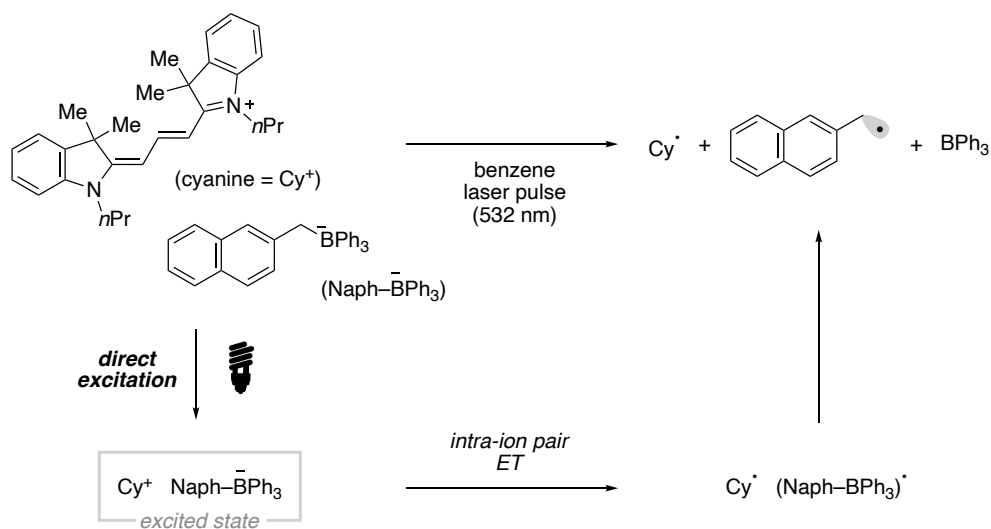


Figure P23. Cyanine 色素と有機ホウ素アート錯体から構成される EDA 錯体

2019 年 Chen らは、有機ホウ素化合物 **27** と α ケト酸 **45** が EDA 錯体を形成し、炭素ラジカルを与えることを報告した (**Figure P24**)。³² 本反応では、EDA 錯体 **I** または錯体 **II** が光によって励起され、炭素ラジカルが発生する。生じる炭素ラジカルは錯体 **II** に対して付加し、錯体 **III** から炭素ラジカルが生成し、錯体 **IV** の加水分解によって化合物 **46** が得られる。

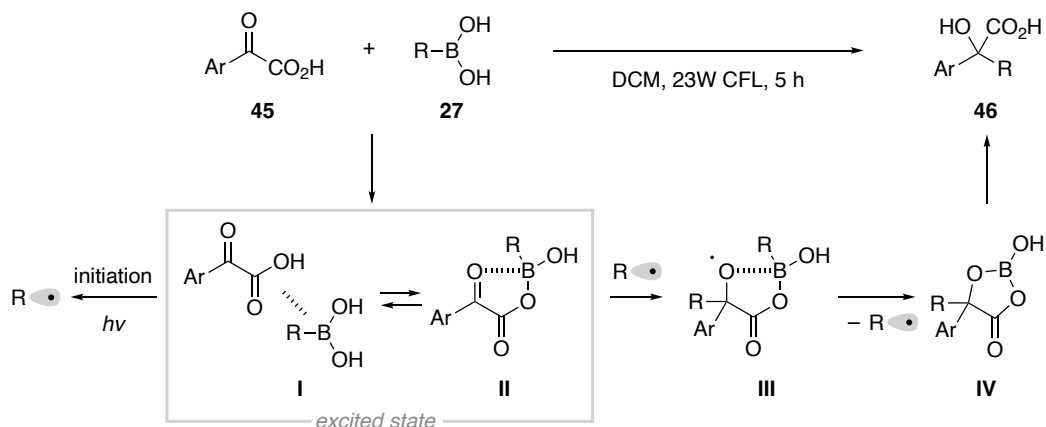


Figure P24. 有機ホウ素化合物 **27** と α ケト酸 **45** から構成される EDA 錯体

2024 年 Qin らは、イミニウム **I** と有機ホウ素アート錯体 **II** から生成する EDA 錯体が光励起され、炭素ラジカルを与えた後に複雑なアミン **50** を得ることに成功している (**Figure P25**)。³³ 本反応では、アルデヒド **47** とアミン **48** から形成されるイミニウム **I** と、カテコール **49** によってアート錯体となった有機ホウ素アート錯体 **II** が EDA 錯体を形成する。光照射によって一電子移動が生じ、窒素 α 位炭素ラジカルとホウ素由来

の炭素ラジカルが生じる。2つのラジカルが交差選択的にカップリングすることで、アミン **50** が得られる。

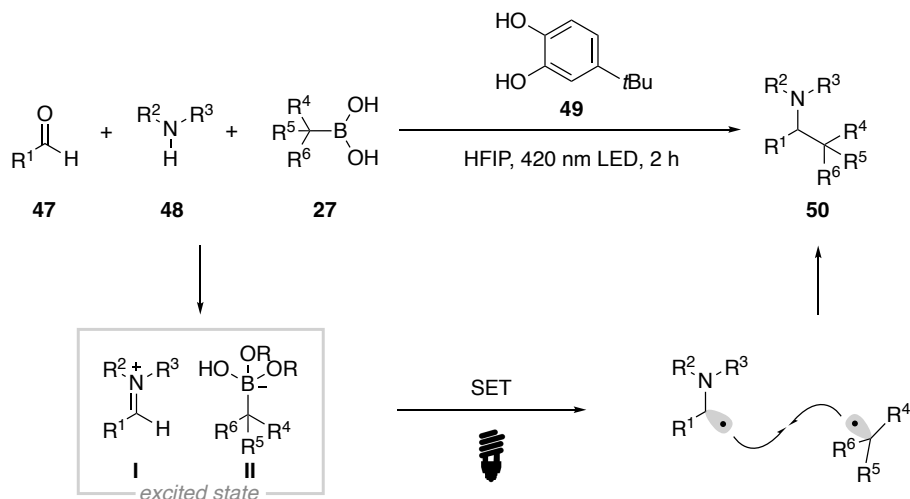


Figure P25. イミニウム **I** と有機ホウ素アート錯体 **II** から構成される EDA 錯体

第六節 直接光励起による有機ホウ素化合物からの炭素ラジカル生成

直接光で化合物を励起することで、炭素ラジカルを与える手法がある。この直接光励起の手法は、触媒や添加剤を必要とせず炭素ラジカルを与えるため反応設計が容易である。そのため直接励起の戦略は、有機合成反応のみならずポリマー合成にも利用されている。

2020 年大宮らは、光を照射するのみで炭素ラジカルを与えるボラセン型有機ホウ素アート錯体を報告した (**Figure P26**)。³⁷ ボラセン型有機ホウ素アート錯体は、ボラセンと有機リチウム試薬を -78°C で混合することで得られる。本ホウ素アート錯体は、440 nm の LED を照射することで、炭素ラジカルの生成が可能であることに加え、強力な還元剤としても機能する。生じる炭素ラジカルの電子不足オレフィン **19** に対する Giese 型ラジカル付加反応により、ラジカル付加体 **51** が得られる。また、4-シアノピリジン **52** の還元体と炭素ラジカルのカップリングによりラジカルカップリング体 **53** が得られる。ニッケル触媒を用いたクロスカップリングにより、ハロゲン化アリール **36** のアルキル化へ適用でき、化合物 **54** が得られる。

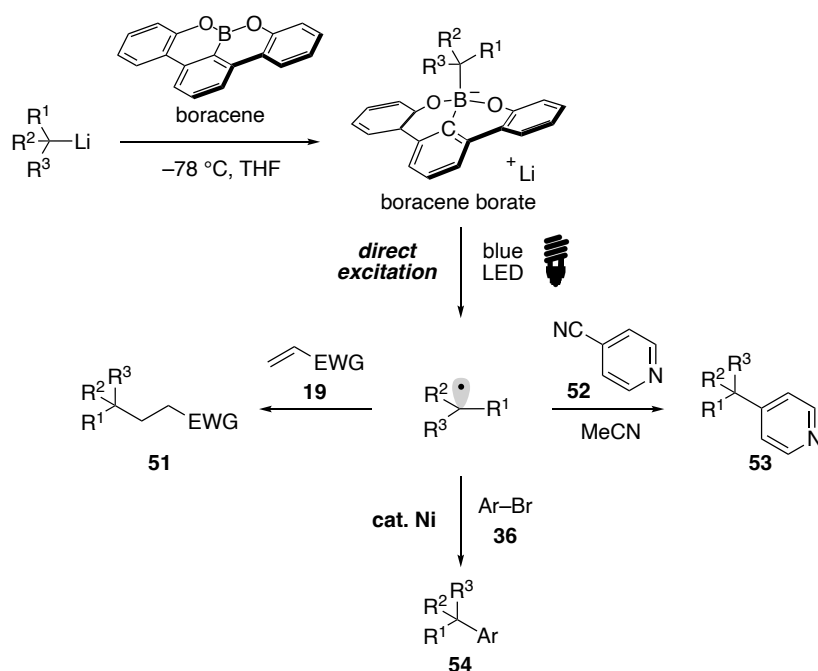


Figure P26. ボラセン型ホウ素アート錯体からの炭素ラジカル生成

2023 年 Page らは、ジピロメテン骨格を有するメチル BODIPY **55** に対し、緑色の LED を照射することで、メチルラジカルが発生することを見出した (**Figure P27**)。^{38,39} 生じるメチルラジカルは、アクリル酸誘導体 **56** のポリマー化によりポリマー **57** 合成に利用された。また、アクセプター **58** へのメチルラジカルの付加によりラジカル種 **59** が得られている。

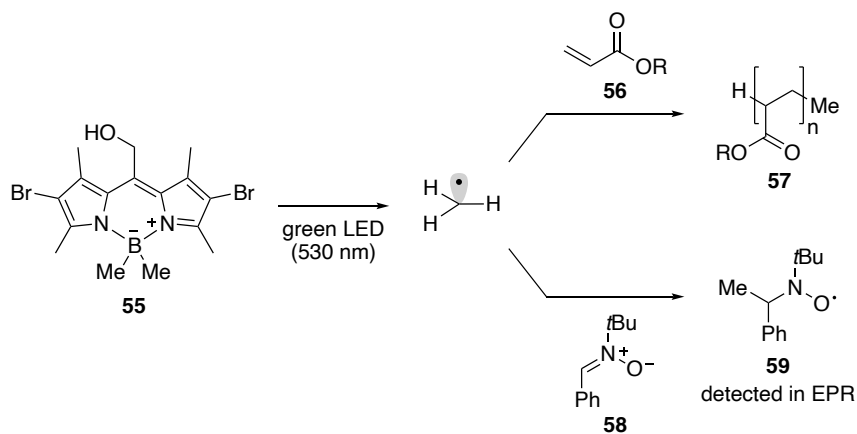


Figure P27. メチル BODIPY **55** からの炭素ラジカル生成

本論文概要

上述のように、有機ホウ素化合物は炭素ラジカル前駆体として利用することができる。しかし、通常有機ホウ素化合物から炭素ラジカルを発生する手法は、酸素や光酸化還元

触媒などの添加剤が必要であり、反応系が複雑化する傾向があった。大宮らや Page らが開発した直接光励起可能なホウ素アート錯体は、光を照射するのみで炭素ラジカルを与えることから、反応系を単純化することに成功した。³⁷⁻³⁹ 一方で、ホウ素上に置換基を導入する際に、反応性の高い有機リチウム試薬またはグリニャール試薬を用いる必要があるため、発生可能な炭素ラジカルの官能基共存性に大きな制限があった。

このような背景を踏まえ、本論文では、有機ホウ素化合物と複合体を形成し、光によって励起され、炭素ラジカルを与える有機ホウ素化合物の創出に取り組んだ。⁴⁰⁻⁴⁵ 具体的には、青色光を照射することで炭素ラジカルを与える 2,2'-(pyridine-2,6-diyl)diphenol (PDP) 型ホウ素アート錯体を創出し、生じた炭素ラジカルを用いた分子変換反応を開発した (第一章から第三章)。⁴⁰⁻⁴² さらに、赤色光を照射することで炭素ラジカルを与える azadipyrromethene (ADP) 型ホウ素アート錯体を創出し、ラジカル反応へ応用した。

43

第一章 2,2'-(Pyridine-2,6-diyl)diphenol (PDP) 型ホウ素アート錯体の直接青色光励起による炭素ラジカル生成

第一章では、直接青色光励起によって炭素ラジカルを発生させる 2,2'-(Pyridine-2,6-diyl)diphenol (PDP) 型ホウ素アート錯体を開発した (Figure P28)。⁴⁰ 以前報告されたボラセン型ホウ素アート錯体の合成には強塩基性の有機リチウム試薬やグリニャール試薬が必要だった。それと比較して PDP 型ホウ素アート錯体は、有機ホウ素化合物と PDP を加熱条件下反応させるのみで合成可能であり、ホウ素上置換基はケトン基やエステル基などが許容される。すなわち、PDP 型ホウ素アート錯体は以前に報告されたボラセン型ホウ素アート錯体と比較して、ホウ素上置換基の官能基共存性が大きく向上した。加えて、原料である有機ホウ素化合物は、ヒドロホウ素化反応、電子不足アルケンの 1,4-ホウ素化反応、宮浦ホウ素化反応、炭素-水素結合の直接活性化によるホウ素化反応などにより、幅広く合成可能である。合成した PDP 型ホウ素アート錯体は強力な還元剤としても機能するため、生じる炭素ラジカルは、脱シアノ型アルキル化反応、Giese 型ラジカル付加反応、ニッケル触媒クロスカップリング反応へ適用できた。

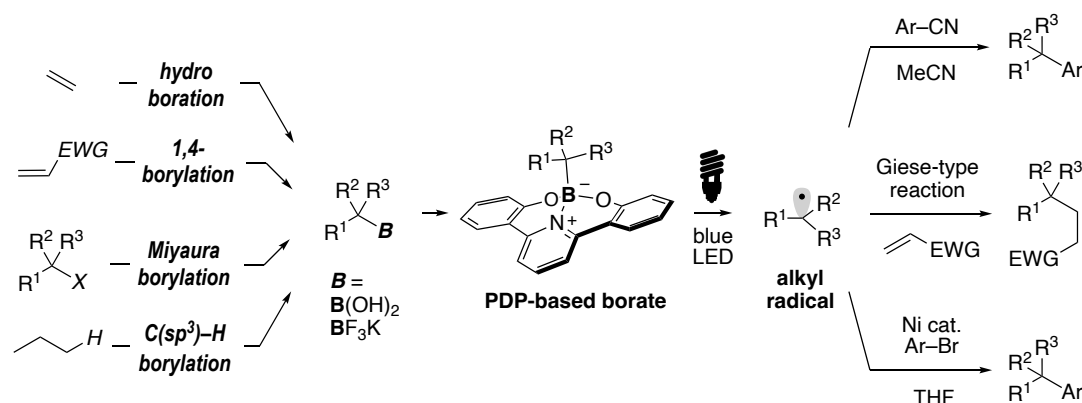


Figure P28. 直接青色光励起による PDP 型ホウ素アート錯体からの炭素ラジカル生成

第二章 PDP 型ホウ素アート錯体の直接青色光励起を鍵とする Minisci 型反応

第二章では、PDP型ホウ素アート錯体を用いて、含窒素ヘテロ芳香族化合物のMinisci型C-Hアルキル化反応を報告する（**Figure P29**）。⁴¹ 本手法では、含窒素ヘテロ芳香族化合物とPDP型ホウ素アート錯体、トリフルオロ酢酸（TFA）を用い、酸素雰囲気下、青色光を照射するのみで、目的のラジカル付加生成物が得られる。PDP型ホウ素アート錯体が青色光によって励起されて生じる炭素ラジカルが、ヘテロ芳香族化合物に付加する。その後、付加体に対して水素引き抜きが生じ、アルキル化された目的物が得られる。本反応は、外部光触媒や金属触媒を必要とせず、キニーネなどの医薬品化合物への適用も可能だった。

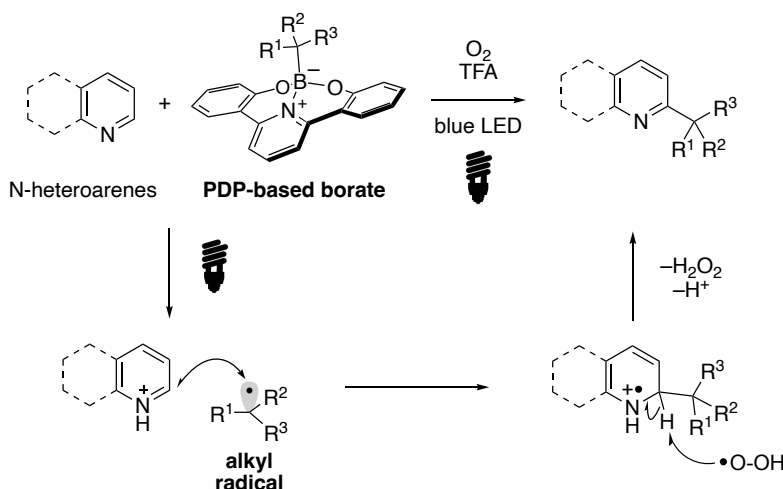


Figure P29. PDP 型ホウ素アート錯体を活用した Minisci 型反応

第三章 PDP 型青色光励起グリコシルホウ素アート錯体を用いた C-グリコシル化反応

第三章では、水酸基が無保護のグリコシルホウ素アート錯体の直接青色光励起によるC-グリコシル化反応を報告する（**Figure P30**）。⁴² グリコシルホウ素アート錯体は、グリコシルトリフルオロボレート塩から容易に合成可能であり、室温、暗所において取り扱いが可能だった。本手法では、トリフルオロメチル基を導入した PDP を有するグリコシルホウ素アート錯体が青色光によって励起されることで、アノマー位炭素ラジカルを与える。生じた炭素ラジカルは、Giese 型ラジカル付加、Minisci 型反応、アシル化反応へ適用可能だった。本手法を利用することで、無保護糖のアノマー位にアルキル基、ヘテロアリール基、アシル基の導入が可能であった。生成物の水酸基に保護基が存在せず、保護-脱保護過程を必要としないため、無保護C-グリコシドの迅速合成を実現した。

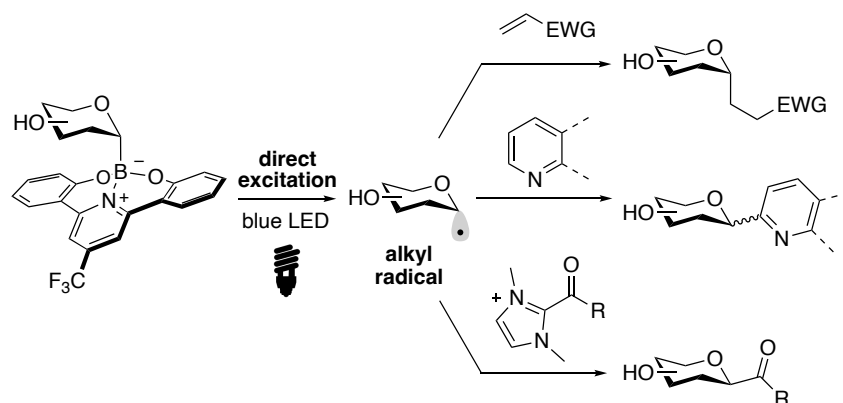


Figure P30. PDP 型ホウ素アート錯体を用いた C-グリコシル化反応

第四章 深赤色から近赤外光による azadipyrromethene(ADP) 型ホウ素アート錯体の直接光励起を利用した触媒的炭素ラジカル生成

第四章では、深赤色 (DR) から近赤外 (NIR) の光を利用した有機ホウ素化合物からの触媒的炭素ラジカル発生法を報告する (**Figure P31**)。⁴³ Azadipyrromethene (ADP) 触媒が有機ホウ素化合物と反応することで、反応系中でホウ素アート錯体を形成する。形成したホウ素アート錯体は、DR や NIR によって励起され、第三級、第二級、第一級炭素ラジカルを与える。生じる炭素ラジカルは、Giese 型ラジカル付加反応、炭素-ヘテロ原子結合形成反応、アシル化反応へ適用可能だった。本手法は、青色光吸収を有する基質においても、良好に反応が進行した。

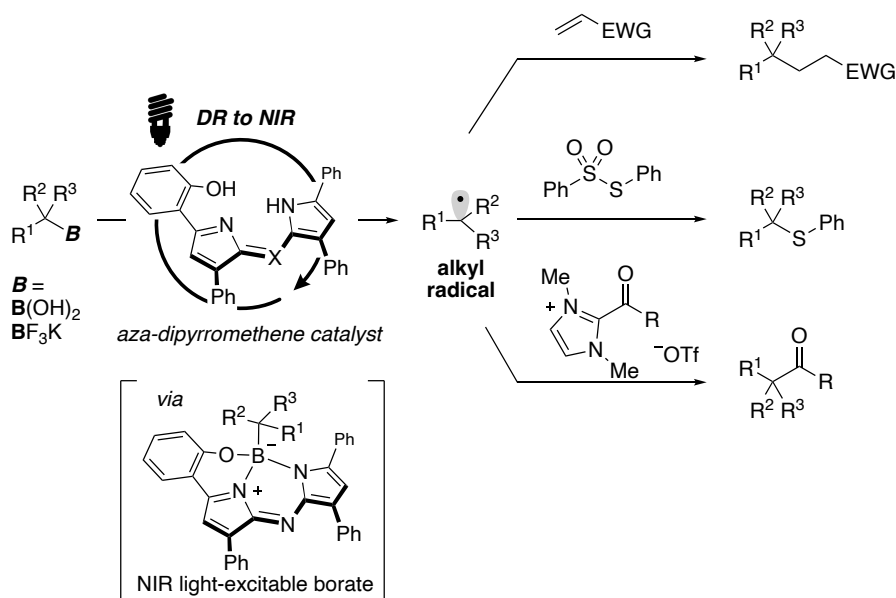


Figure P31. ADP 型ホウ素アート錯体を用いた炭素ラジカル生成反応

序論 参考文献

1. Suzuki, A. *Angew. Chem., Int. Ed.* **2011**, *50*, 6722–6737.
2. (a) Ohe, T.; Miyaura, N.; Suzuki, A. *J. Org. Chem.* **1993**, *58*, 2201–2208. (b) Miyaura, N.; Suzuki, A. *Chem. Rev.* **1995**, *95*, 2457–2483. (c) Lennox, A. J. J.; Lloyd-Jones, G. C. *Chem. Soc. Rev.* **2014**, *43*, 412–443. (d) Fyfe, J. W. B.; Watson, A. J. B. *Chem* **2017**, *13*, 31–55. (e) Grams, R. J.; Santos, W. L.; Scorei, I. R.; Abad-García, A.; Rosenblum, C. A.; Bitá, A.; Cerecetto, H.; Viñas, C.; Soriano-Ursúa, M. A. *Chem. Rev.* **2024**, *124*, 2441–2511.
3. (a) Stephan, D. W.; Erker, G. *Angew. Chem., Int. Ed.* **2015**, *54*, 6400–6441. (b) Lawson, J. R.; Melen, R. L. *Inorg. Chem.* **2017**, *56*, 8627–8643. (c) Sawamura, M.; Shimizu, Y. *Eur. J. Org. Chem.* **2022**, *26*. DOI: 10.1002/ejoc.202201249. (d) Kilic, A.; Aytar, E.; Kleij, A. W. *ChemCatChem* **2025**, *17*. DOI: 10.1002/cctc.202500002.
4. (a) Fossey, J. S.; D’Hooge, F.; van den Elsen, J. M. H.; Pereira Morais, M. P.; Pascu, S. I.; Bull, S. D.; Marken, F.; Jenkins, A. T. A.; Jiang, Y.; James, T. D. *Chem. Rec.* **2012**, *12*, 464–478. (b) Møllerup, S. K.; Wang, S. *Chem. Soc. Rev.* **2019**, *48*, 3537–3549. (c) Nakano, M.; Nakamura, R.; Sumida, Y.; Nagao, K.; Furuyama, T.; Inagaki, F.; Ohmiya, H. *Chem. Pharm. Bull.* **2021**, *69*, 526–528.
5. (a) Ji, L.; Griesbeck, S.; Marder, T. B. *Chem. Sci.* **2017**, *8*, 846–863. (b) Kothavale, S. S.; Lee, J. Y. *Adv. Opt. Mater.* **2020**, *8*, DOI: 10.1002/adom.202000922. (c) Kothavale, S. S.; Lee, J. Y. *Adv. Opt. Mater.* **2020**, *8*, DOI: 10.1002/adom.202000922. (d) Gotoh, H.; Nakatsuka, S.; Tanaka, H.; Yasuda, N.; Haketa, Y.; Maeda, H.; Hatakeyama, T. *Angew. Chem., Int. Ed.* **2021**, *60*, 12835–12840. (e) Miao, J.; Wang, Y.; Liu, J.; Wang, L. *Chem. Soc. Rev.* **2022**, *51*, 153–187. (f) Jin, C.; Yang, X.; Zhao, W.; Zhao, Y.; Wang, Z.; Tan, J. *Coord. Chem. Rev.* **2024**, *513*, 215892. (g) Hu, D.; Huang, R.; Fang, Y. *Precis. Chem.* **2024**, *3*, 10–26. (h) Grams, R. J.; Santos, W. L.; Scorei, I. R.; Abad-García, A.; Rosenblum, C. A.; Bitá, A.; Cerecetto, H.; Viñas, C.; Soriano-Ursúa, M. A. *Chem. Rev.* **2024**, *124*, 2441–2511. (i) Kozhakhmetov, Y.; Kurbanbekov, S.; Mukhamedova, N.; Urkunbay, A.; Kizatov, A.; Bayatanova, L.; Nurdillayeva, R.; Baltabayeva, D. *Crystals* **2025**, *15*, 536.
6. (a) Ollivier, C.; Renaud, P. *Chem. Rev.* **2001**, *101*, 3415–3434. (b) Marotta, A.; Adams, C. E.; Molloy, J. J. *Angew. Chem., Int. Ed.* **2022**, *61*, DOI: 10.1002/anie.202207067. (c) Pillitteri, S.; Ranjan, P.; Van der Eycken, E. V.; Sharma, U. K. *Adv. Synth. Catal.* **2022**, *364*, 1643–1665. (d) Lu, J.; Zhang, H.; Zhang, G.; Guo, R. *ChemPhotoChem* **2025**, *9*, DOI: 10.1002/cptc.202500018. (e) Wenzel, J. O.; Werner, J.; Breher, F. *Angew. Chem., Int. Ed.* **2025**, *64*, DOI: 10.1002/anie.202507060.
7. Frankland, E. *J. Chem. Soc.* **1862**, *15*, 363–381.
8. Nozaki, K.; Oshima, K.; Uchimoto, K. *J. Am. Chem. Soc.* **1987**, *109*, 2547–2549.
9. Ichinose, Y.; Nozaki, K.; Wakamatsu, K.; Oshima, K.; Utimoto, K. *Tetrahedron Lett.* **1987**, *28*, 3709–3712.
10. Miura, K.; Ichinose, Y.; Nozaki, K.; Fugami, K.; Oshima, K.; Utimoto, K. *Bull. Chem. Soc. Jpn.* **1989**, *62*, 143–147.
11. Arase, A.; Masuda, Y.; Suzuki, A. *Bull. Chem. Soc. Jpn.* **1974**, *47*, 2511–2514.
12. (a) Hawthorne, M. F.; Reintjes, M. *J. Am. Chem. Soc.* **1965**, *87*, 4585–4587. (b) Hawthorne, M. F.; Reintjes, M. *J. Am. Chem. Soc.* **1964**, *86*, 951. (c) Kabalka, G. W. *J. Organomet. Chem.* **1971**, *33*, C25–C28. (d) Suzuki, A.; Arase, A.; Matsumoto, H.; Itoh, M.; Brown, H. C.; Rogic, M. M.; Rathke, M. W. *J. Am. Chem. Soc.* **1967**, *89*, 5708–5709. (e) Brown, H. C.; Rogic, M. M.; Rathke, M. W.; Kabalka, G. W. *J. Am. Chem. Soc.* **1967**, *89*, 5709–5710. (f) Brown, H. C.; Kabalka, G. W.; Rathke, M. W.; Rogic, M. M. *J. Am. Chem. Soc.* **1968**, *90*, 4165–4166. (g) Brown, H. C.; Rathke, M. W.; Kabalka, G. W.; Rogic, M. M. *J. Am. Chem. Soc.* **1968**, *90*, 4166–4168. (h) Bieber, L. W.; Rolim Neto, P. J.; Generino, R. M. *Tetrahedron Lett.* **1999**, *40*, 4473–4476.
13. Matteson, D. S. *J. Org. Chem.* **1964**, *29*, 3399–3400.
14. Ollivier, C.; Renaud, P. *Angew. Chem., Int. Ed.* **2000**, *39*, 925–928.
15. Sorin, G.; Martinez Mallorquin, R.; Contie, Y.; Baralle, A.; Malacria, M.; Goddard, J.; Fensterbank, L. *Angew. Chem.* **2010**, *122*, 8903–8905.

16. (a) Molander, G. A.; Colombel, V.; Braz, V. A. *Org. Lett.* **2011**, *13*, 1852–1855. (b) Lockner, J. W.; Dixon, D. D.; Risgaard, R.; Baran, P. S. *Org. Lett.* **2011**, *13*, 5628–5631. (c) Fujiwara, Y.; Domingo, V.; Seiple, I. B.; Gianatassio, R.; Del Bel, M.; Baran, P. S. *J. Am. Chem. Soc.* **2011**, *133*, 3292–3295. (d) Demir, A. S.; Reis, Ö.; Emrullahoglu, M. *J. Org. Chem.* **2002**, *68*, 578–580. (e) Dickschat, A.; Studer, A. *Org. Lett.* **2010**, *12*, 3972–3974. (f) Pouliot, M.; Renaud, P.; Schenk, K.; Studer, A.; Vogler, T. *Angew. Chem.* **2009**, *121*, 6153–6156. (g) Wang, Z.; Wierich, N.; Zhang, J.; Daniliuc, C. G.; Studer, A. *J. Am. Chem. Soc.* **2023**, *145*, 8770–8775.
17. (a) Capaldo, L.; Ravelli, D. *Eur. J. Org. Chem.* **2017**, *2017*, 2056–2071. (b) Capaldo, L.; Ravelli, D.; Fagnoni, M. *Chem. Rev.* **2021**, *122*, 1875–1924. (c) Romero, N. A.; Nicewicz, D. A. *Chem. Rev.* **2016**, *116*, 10075–10166. (d) Shaw, M. H.; Twilton, J.; MacMillan, D. W. C. *J. Org. Chem.* **2016**, *81*, 6898–6926. (e) Cabanero, D. C.; Rovis, T. *Nat. Rev. Chem.* **2025**, *9*, 28–45.
18. Yasu, Y.; Koike, T.; Akita, M. *Adv. Synth. Catal.* **2012**, *354*, 3414–3420.
19. Yatham, V. R.; Shen, Y.; Martin, R. *Angew. Chem., Int. Ed.* **2017**, *56*, 10915–10919.
20. Zhang, L.; Chu, Y.; Ma, P.; Zhao, S.; Li, Q.; Chen, B.; Hong, X.; Sun, J. *Org. Biomol. Chem.* **2020**, *18*, 1073–1077.
21. Tellis, J. C.; Primer, D. N.; Molander, G. A. *Science* **2014**, *345*, 433–436.
22. (a) Tellis, J. C.; Amani, J.; Molander, G. A. *Org. Lett.* **2016**, *18*, 2994–2997. (b) Primer, D. N.; Karakaya, I.; Tellis, J. C.; Molander, G. A. *J. Am. Chem. Soc.* **2015**, *137*, 2195–2198. (c) Primer, D. N.; Molander, G. A. *J. Am. Chem. Soc.* **2017**, *139*, 9847–9850.
23. Lima, F.; Kabeshov, M. A.; Tran, D. N.; Battilocchio, C.; Sedelmeier, J.; Sedelmeier, G.; Schenkel, B.; Ley, S. V. *Angew. Chem., Int. Ed.* **2016**, *55*, 14085–14089.
24. Lima, F.; Sharma, U. K.; Grunenberg, L.; Saha, D.; Johannsen, S.; Sedelmeier, J.; Van der Eycken, E. V.; Ley, S. V. *Angew. Chem., Int. Ed.* **2017**, *56*, 15136–15140.
25. Shu, C.; Noble, A.; Aggarwal, V. K. *Angew. Chem., Int. Ed.* **2019**, *58*, 3870–3874.
26. Yin, C.; Tang, S.; Mei, J.; Hu, X.; Zhang, H. *Org. Chem. Front.* **2023**, *10*, 3361–3377.
27. Yuan, Y.; Zheng, Y.; Xu, B.; Liao, J.; Bu, F.; Wang, S.; Hu, J.-G.; Lei, A. *ACS Catal.* **2020**, *10*, 6676–6681.
28. Niu, K.; Hao, Y.; Song, L.; Liu, Y.; Wang, Q. *Green Chem.* **2021**, *23*, 302–306.
29. Luo, J.; Hu, B.; Wu, W.; Hu, M.; Liu, T. L. *Angew. Chem., Int. Ed.* **2021**, *60*, 6107–6116.
30. Go, S. Y.; Chung, H.; Shin, S. J.; An, S.; Youn, J. H.; Im, T. Y.; Kim, J. Y.; Chung, T. D.; Lee, H. G. *J. Am. Chem. Soc.* **2022**, *144*, 9149–9160.
31. (a) Lan, J. Y.; Schuster, G. B. *J. Am. Chem. Soc.* **1985**, *107*, 6710–6711. (b) Chatterjee, S.; Gottschalk, P.; Davis, P. D.; Schuster, G. B. *J. Am. Chem. Soc.* **1988**, *110*, 2326–2328.
32. Xie, S.; Li, D.; Huang, H.; Zhang, F.; Chen, Y. *J. Am. Chem. Soc.* **2019**, *141*, 16237–16242.
33. Hu, C.; Tsien, J.; Chen, S.-J.; Kong, M.; Merchant, R. R.; Kanda, Y.; Qin, T. *J. Am. Chem. Soc.* **2024**, *146*, 21769–21777.
34. Yuan, N.; Chen, S.; Liu, Y.; Chen, M. *Chem. Eur. J.* **2024**, *31*, DOI: 10.1002/chem.202403487
35. Hu, C.; Li, R.; Merchant, R. R.; Kanda, Y.; Qin, T. *J. Am. Chem. Soc.* **2025**, *147*, 44720–44726.
36. Zheng, K.; Chen, C.; Xu, H.; Mao, J.; Shen, C. *J. Org. Chem.* **2025**, *90*, 15567–15577.
37. (a) Sato, Y.; Nakamura, K.; Sumida, Y.; Hashizume, D.; Hosoya, T.; Ohmiya, H. *J. Am. Chem. Soc.* **2020**, *142*, 9938–9943. (b) Sato, Y.; Miyamoto, Y.; Sumida, Y.; Hosoya, T.; Ohmiya, H. *Org. Biomol. Chem.* **2020**, *18*, 6598–6601.
38. Chung, K.-Y.; Page, Z. A. *J. Am. Chem. Soc.* **2023**, *145*, 17912–17918.
39. Wijesooriya, C. S.; Peterson, J. A.; Shrestha, P.; Gehrmann, E. J.; Winter, A. H.; Smith, E. A. *Angew. Chem., Int. Ed.* **2018**, *57*, 12685–12689.
40. Miyamoto, Y.; Sumida, Y.; Ohmiya, H. *Org. Lett.* **2021**, *23*, 5865–5870.
41. Kemmochi, M.; Miyamoto, Y.; Sumida, Y.; Ohmiya, H. *Asian. J. Org. Chem.* **2022**, *11*, e202100640. DOI: 10.1002/ajoc.202100640
42. Miyamoto, Y.; Murakami, S.; Sumida, Y.; Hirai, G.; Ohmiya, H. *Chem. Eur. J.* **2024**, *30*, e202402256. DOI: 10.1002/chem.202402256

43. Miyamoto, Y.; Muraoka, K.; Murakami, S.; Matsudaira, T.; Ohmiya, H. *J. Am. Chem. Soc.* **2025**, *147*, 41185–41192.
44. Sato, Y.; Goto, Y.; Nakamura, K.; Miyamoto, Y.; Sumida, Y.; Ohmiya, H. *ACS Catal.* **2021**, *11*, 12886–12892.
45. Nakamura, R.; Yamazaki, T.; Kondo, Y.; Tsukada, M.; Miyamoto, Y.; Arakawa, N.; Sumida, Y.; Kiya, T.; Arai, S.; Ohmiya, H. *J. Am. Chem. Soc.* **2023**, *145*, 10651–10658.

第一章 2,2'-(Pyridine-2,6-diyl)diphenol (PDP) 型ホウ素アート錯体の 直接青色光励起による炭素ラジカル生成

第一節 着想背景および作業仮説

序章において述べたように、有機ホウ素化合物、とりわけボロン酸やボロン酸エステルは、現代有機合成化学において極めて重要な化合物の1つである。有機ホウ素化合物は空気や湿気に対して比較的安定であり、取り扱いが容易であることに加え、多種多様な官能基を有する誘導体が市販の試薬として入手可能である。さらに、Brown ヒドロホウ素化反応¹ や Miyaura ホウ素化反応²、あるいは遷移金属触媒を用いた C-H ホウ素化反応³ の進展により、その合成法は飛躍的に拡大しており、医薬品探索や材料科学の分野において必須のビルディングブロックとなっている。⁴ 近年、光酸化還元触媒を用いたラジカル反応の発展に伴い、有機ホウ素化合物をラジカル前駆体として利用する手法が注目を集めている。⁵ しかし、これら多くの手法は、貴金属触媒や外部光触媒の添加、あるいは電子ドナー・アクセプター (EDA) 錯体の形成を必要とし、反応が複雑化しやすいといった欠点があった。こうした背景の中、著者の所属研究室では、外部光触媒を用いない独自のラジカル発生法として、ボラセン(8,9-dioxa-8a-borabenzofg]tetracene) 骨格を有する有機ホウ素アート錯体の「直接光励起」による炭素-ホウ素結合の活性化を見出した (Figure 1-1A)。⁶ この手法では、ボラセン型ホウ素アート錯体が青色光を吸収して励起状態となり、炭素ラジカルを生成する。

一方で、先行研究におけるボラセン型ホウ素アート錯体の合成には課題ある。ボラセン骨格に対してアルキル基を導入する際、有機リチウム試薬や Grignard 試薬といった強力な求核剤を使用する必要があった。そのため、ケトンやエステルといった官能基を有する炭素ラジカルの発生には適用困難であった。そこで本研究では、より温和な条件下で合成可能であり、幅広い官能基許容性を有する直接光励起型ホウ素アート錯体の開発を目指した。具体的には、2,2'-(Pyridine-2,6-diyl)diphenol (以下、PDP) を三座配位子として設計した (Figure 1-1B)。PDP 配位子は、2つの酸素原子と1つの窒素原子によってホウ素中心に配位し、ボラセン型ホウ素アート錯体と同様の四配位構造を形成する。特筆すべきは、この PDP 型ホウ素アート錯体が、有機リチウム試薬を経由することなく、対応する有機ボロン酸あるいはアルキルトリフルオロボレート塩から直接合成できる点である。これにより、エステルやアミド、ケトンといった多様な官能基を有する炭素ラジカルの発生が可能となる。

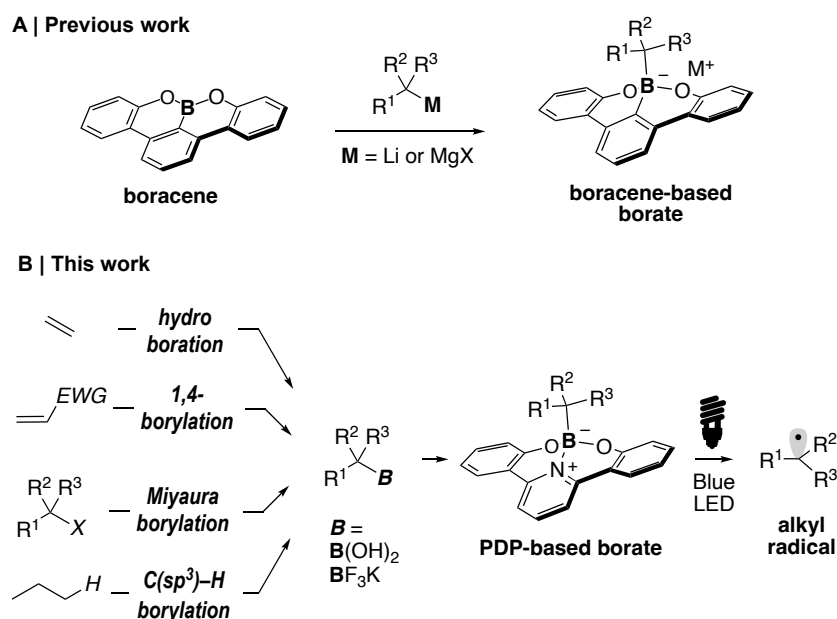


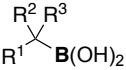
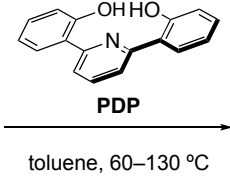
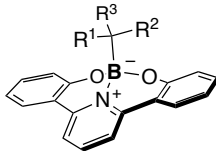
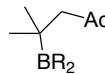
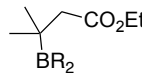
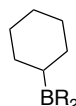
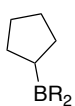
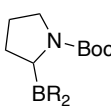
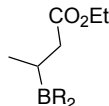
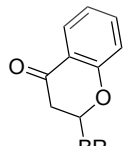
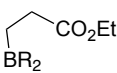
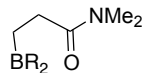
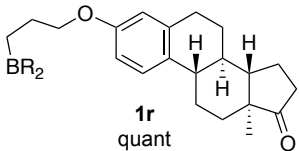
Figure 1-1. 有機ホウ素アート錯体の直接光励起：(A) 有機リチウム試薬またはグリニャール試薬から調製されるボラセン型ホウ素アート錯体 (B) 有機ホウ素化合物から調製される PDP 型ホウ素アート錯体

第二節 PDP 型ホウ素アート錯体の合成および光物理的特性

第一節で述べた配位子設計に基づき、PDP 型ホウ素アート錯体の合成を行った。PDP と *tert*-ブチルトリフルオロボレート塩、添加剤としてクロロトリメチルシラン (TMSCl) を用い、トルエン溶媒中で反応させたところ、目的とする *tert*-ブチル置換 PDP 型ホウ素アート錯体 **1a** が高収率で得られた (**Method A**)。TMSCl は、フッ素原子の引き抜き試薬として機能し、配位子交換を促進していると考えられる。また、対応するボロン酸を用いた場合でも、トルエン中、トリエチルアミン存在下で加熱を行い、モレキュラーシーブを用いて水を除去することで、同様に PDP 型ホウ素アート錯体 **1** を合成できることを確認した (**Method B**)。確立した二つの合成法 (**Method A** および **Method B**) を用いることで、PDP 型ホウ素アート錯体の基質一般性の検討を行った (**Table 1-1**)。第三級アルキル基として、*tert*-ブチル基 (**1a**) だけでなく、アダマンチル基 (**1c**) や、ケトン (**1d**)、エステル (**1e**) といった官能基を有する基質の導入が可能であった。(**1a–1e**) また、第二級アルキル基 (**1f–1j**) や第一級アルキル基 (**1k–1q**) を有するホウ素アート錯体についても、中程度から良好な収率で合成できた。ボラセン型ホウ素アート錯体の合成では適用が困難であった、アミド基 (**1o, 1p**) やニトリル基 (**1q**)、さらにはステロイド骨格を有するエストロン誘導体 **1r** のような複雑な分子の導入も可能であった。加えて、メチルボロキシンを出発原料とすることで、メチル基が置換したホウ素アート錯体 **1t** の合成も達成した。さらに、得られた PDP 型ホウ素アート錯体 **1a** は、酸、熱、および空気に対して良好な安定性を示した。特筆すべき点として、本錯体はシリカゲルカラムクロマトグラフィーによる精製が可能であり、過剰量 (7 当量) の TFA

存在下においても 2 日間は安定であった。(Figure 1-2 to 1-4)

Table 1-1. ホウ素上置換基の検討

	or				
Method A^a	Method B^b			1	
Tertiary					
					
1a 96%	1b 98%	1c quant	1d 74%	1e 79%	
Method A					
Secondary					
					
1f 97%	1g quant	1h 67%	1i quant (77%) ^c	1j 50%	
Method B		Method A			
Primary					
					
1k 84%	1l 62%	1m 47%	1n 93% (86%) ^c	1o 85%	1p 47%
Method A		Method A			
					
1q quant	1r quant	1s 54%	1t quant		
Method A		Method B			

^aStandard conditions for **Method A**: alkylBF₃K (1 equiv), TMSCl (4–15 equiv). ^bStandard conditions for **Method B**: alkylB(OH)₂ (1 equiv), Et₃N (7 equiv). ^cThe yield in parenthesis was obtained using the corresponding alkylboronic acid with **Method B**.

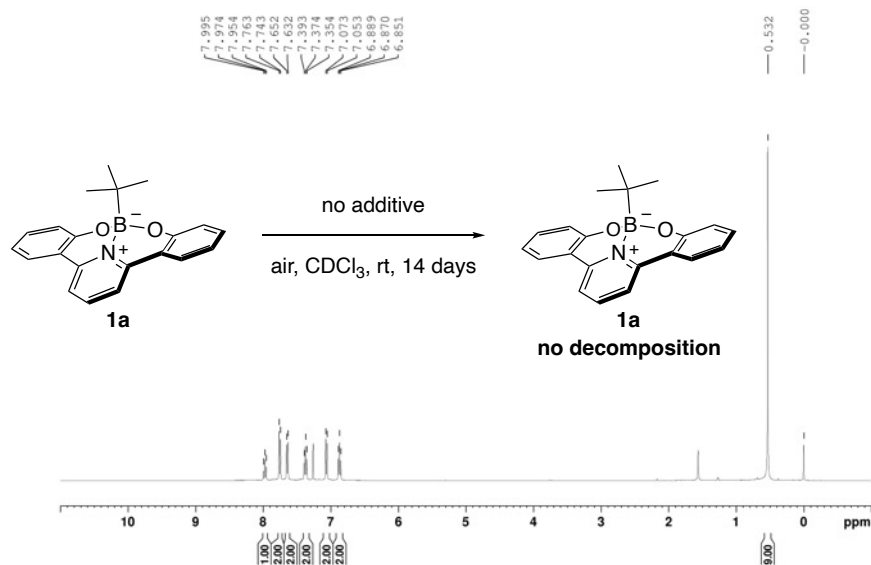


Figure 1-2. **1a** の安定性試験（添加剤なし）。14 日経過後の ^1H -NMR スペクトル^aにおいて、**1a** の分解は確認されなかった。

^aUnder an ambient atmosphere, **1a** (6.58 mg, 0.02 mmol) was placed in an oven-dried screw-top 1 mL vial and added CDCl_3 (1 mL). The solution of **1a** in CDCl_3 (0.5 mL) was moved to NMR tube. The stability of **1a** was examined by monitoring the decrease of the borate by ^1H NMR in CDCl_3 (500 μL) at room temperature.

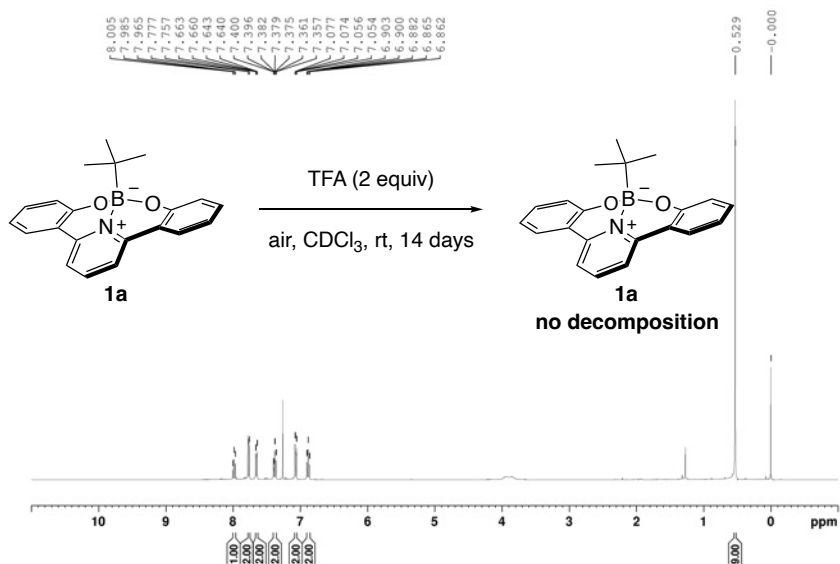


Figure 1-3. **1a** の安定性試験（2 当量の TFA 添加）。14 日経過後の ^1H -NMR スペクトルにおいて、**1a** の分解は確認されなかった。

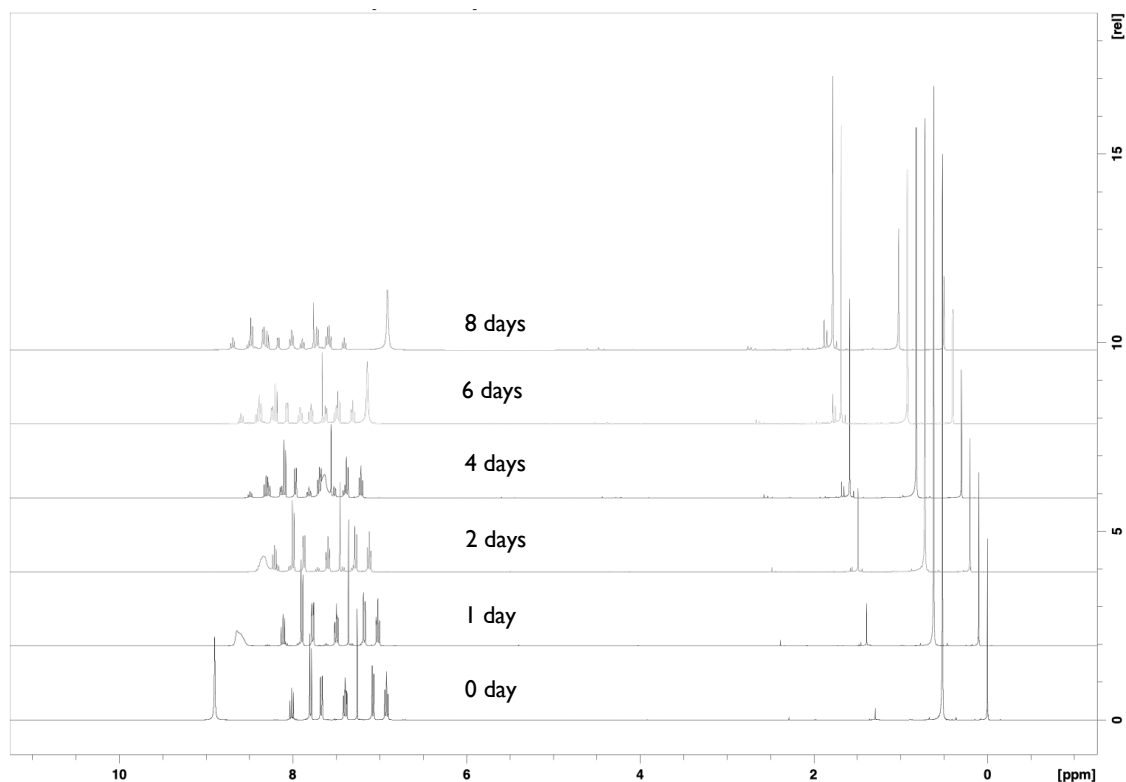


Figure 1-4. **1a** の分解の経時変化の追跡。TFA (7 当量) 存在下、 ^1H -NMR スペクトルにおいて、部分的な分解が観測された。

次に、得られた PDP 型ホウ素アート錯体の構造および光物理的特性の評価を行った。単結晶 X 線構造解析の結果、PDP 型ホウ素アート錯体 **1a**, **1k**, **1n** はホウ素原子を中心とした四配位構造をとっていることが確認された (**Figure 1-5A**)。また、PDP 型ホウ素アート錯体 **1a** に付いて密度汎関数法 (DFT) 計算により分子軌道を解析したところ、最高被占軌道 (HOMO) はホウ素-炭素結合に分布しているのに対し、最低空軌道 (LUMO) は PDP 配位子全体に広がっていることが明らかとなった (**Figure 1-5B**)。

続いて、紫外可視吸光スペクトル測定を行った。PDP 型ホウ素アート錯体 **1a** は、先行研究であるボラセン型ホウ素アート錯体 **2a** と比較して、吸収端が長波長側にシフトしており、青色光領域 (>400 nm) においても十分な吸光度を有していた (**Figure 1-5C**)。これは、PDP 配位子により HOMO-LUMO エネルギーギャップが小さくなったことに起因すると考えられる。

さらに、サイクリックボルタンメトリー (CV) 測定および蛍光スペクトル測定の結果から、励起状態における還元電位を算出したところ、以下のように見積もられた。⁷ ホウ素アート錯体 **1a** について、紫外可視吸収スペクトル、蛍光スペクトル、およびサイクリックボルタンメトリーから得られたデータに基づき、以下の Rehm-Weller 式を用いて光励起ボレートの酸化還元電位を近似的に算出した。なお、サイクリックボルタンメトリー (**Figure 1-6**) において、ボレート **1a** の電気化学的酸化過程は不可逆過程で

あった。したがって、酸化電位 E ($=+1.0537$ V vs. SCE) を $E(1a^{+}/1a)$ として用いた。ホウ素アート錯体 **1a** 励起状態におけるエネルギー $E_{00}(1a^{*}/1a)$ は吸収スペクトル及び蛍光スペクトルの波長 (406 nm, **Figure 1-7**) から推定し 3.054 eV とした。

For the excited state of borate **1a***

Rehm-Weller equation:

$$E(1a^{+}/1a^{*}) = E(1a^{+}/1a) - E_{00}(1a^{*}/1a)$$

$$E(1a^{+}/1a^{*}) = 1.0537 - 3.054 = -2.00 \text{ V vs. SCE.}$$

ホウ素アート錯体 **1i** について、紫外可視吸収スペクトル、蛍光スペクトル、およびサイクリックボルタンメトリーから得られたデータに基づき、以下の Rehm-Weller 式を用いて光励起ボレートの酸化還元電位を近似的に算出した。なお、サイクリックボルタンメトリー (**Figure 1-6**) において、ボレート **1i** の電気化学的酸化過程は不可逆過程であった。したがって、酸化電位 E ($=+1.2631$ V vs. SCE) を $E(1i^{+}/1i)$ として用いた。ホウ素アート錯体 **1i** 励起状態におけるエネルギー $E_{00}(1i^{*}/1i)$ は吸収スペクトル及び蛍光スペクトルの波長 (406 nm, **Figure 1-7**) から推定し 3.054 eV とした。

For the excited state of borate **1i***

Rehm-Weller equation:

$$E(1i^{+}/1i^{*}) = E(1i^{+}/1i) - E_{00}(1i^{*}/1i)$$

$$E(1i^{+}/1i^{*}) = 1.2631 - 3.054 = -1.79 \text{ V vs. SCE.}$$

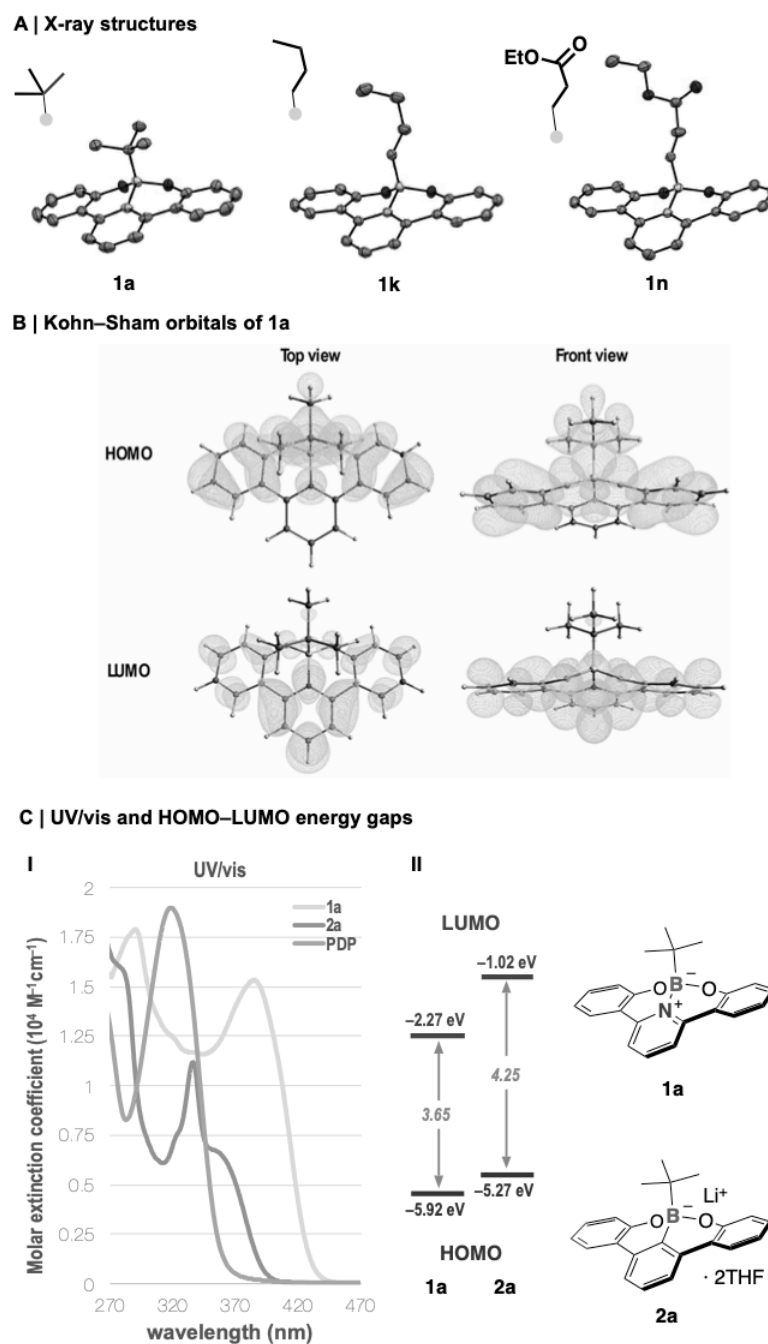


Figure 1-5. (A) **1a**, **1k** 及び **1n** の ORTEP 図 (CCDC 2080640, 2080643, 2080645)。熱振動楕円体は 50%の確率で描画した。水素原子は省略している (B) B3LYP/6-31++G(dp) level で計算した S_0 状態における **1a** の Kohn–Sham 軌道 (C) **I**: **1a**, **2a** 及び PDP の紫外可視吸収スペクトル **II**: DFT 法 (B3LYP/6-31++G(dp) level) により計算した **1a** と **2a** のエネルギー準位の比較

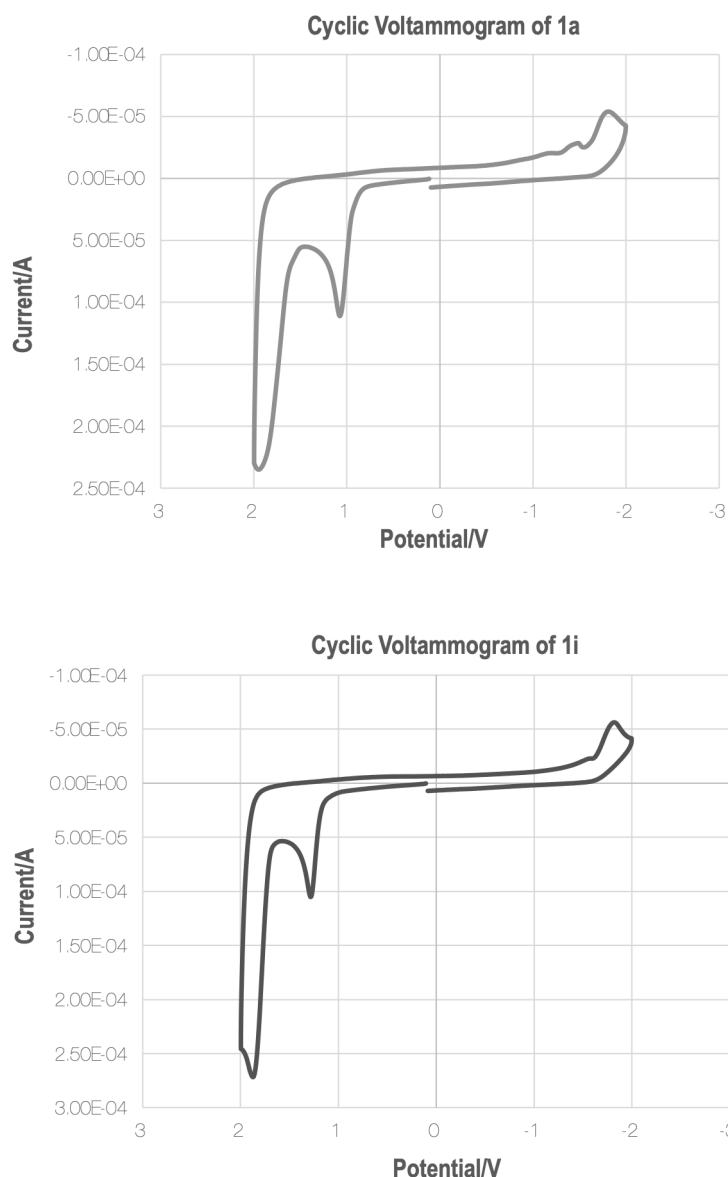


Figure 1-6. 1a と 1i のサイクリックボルタモグラム ^a

^aCyclic voltammogram of alkylborate **1a** and **1i** were recorded in dry, degassed MeCN solution with 0.1 M of tetrabutylammonium hexafluorophosphate ($[\text{N}(\text{nBu})_4]\text{PF}_6$) as a supporting electrolyte. Measurements used a glassy carbon working electrode (area = 0.07 cm²), a Ag/AgCl reference electrode, and a Pt wire counter electrode. The concentration of the sample solution was fixed at 2 mM and the sweep rates were set to 100 mV/s. For conversion to the SCE couple, it is known that Fc/Fc^+ is 380 mV more positive than SCE in MeCN⁸ and we measured the Fc/Fc^+ in MeCN to determine potentials against SCE respectively calculated according to Fc/Fc^+ ($E_{1/2} = +0.403$ V vs Ag/AgCl).

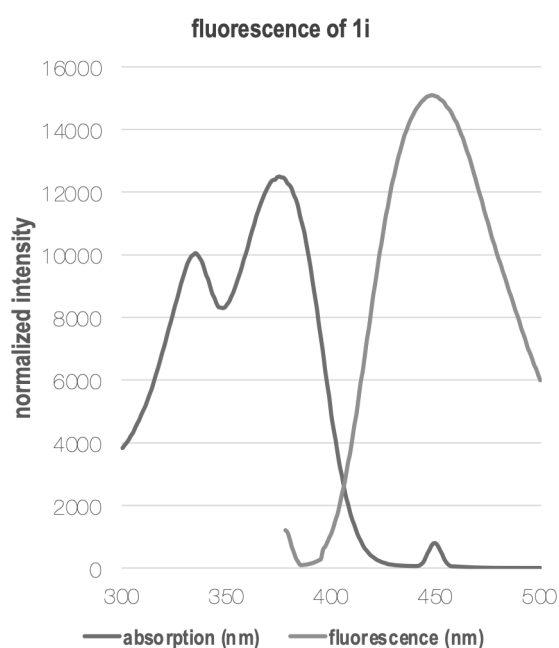
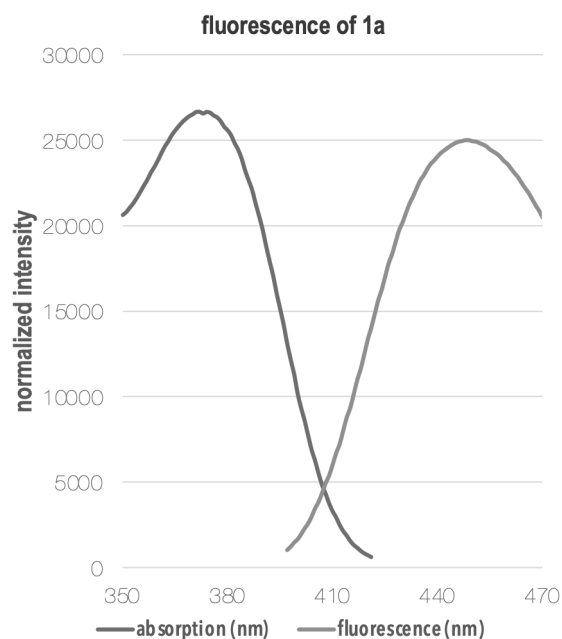


Figure 1-7. 1a と 1i の吸収スペクトル及び蛍光スペクトル^a

^a Absorption and fluorescence spectra of borate **1a** and **1i** were measured with 20 μ M DMA solution.

第三節 反応開発および基質適用範囲の検討

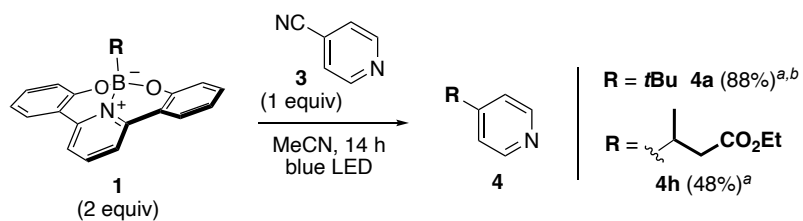
第二節で明らかにした PDP 型ホウ素アート錯体 **1** の青色光領域における吸収特性と励起状態における強力な還元力に基づき、青色光駆動型の反応開発を行った。まず、励起状態のホウ素アート錯体 **1** の有する強力な一電子還元剤としての機能 ($E(1a^+/1a^*) = -$

2.00 V vs. SCE.) を評価するため、高い還元電位を有する 4-シアノピリジン **3** ($E_{1/2} = -1.75$ V vs. SCE.) に対する脱シアノ型アルキル化反応を検討した (Figure 1-8A)。⁹ PDP 型ホウ素アート錯体 **1a** と 4-シアノピリジン **3** をアセトニトリル中で混合し、青色 LED (440 nm) を照射したところ、脱シアノ型アルキル化体 **4a** が 88% の収率で得られた。この結果は、励起されたホウ素アート錯体 **1a** から 4-シアノピリジン **3** への一電子移動 (SET) が効率的に進行したことを示唆している。また、より還元力の低いエステル置換ホウ素アート錯体 **1i** ($E(1i^{+}/1i^{*}) = -1.79$ V vs. SCE.) を用いた場合でも、中程度ながら反応は進行した。

次に、PDP 型ホウ素アート錯体 **1** をラジカル前駆体として利用する Giese 型ラジカル付加反応への適用を検討した (Figure 1-8B)。¹⁰ 電子不足アルケンであるフマル酸ジメチル **5** とホウ素アート錯体 **1** を用い、アセトニトリル/メタノール混合溶媒中、青色 LED (440 nm) を照射した。その結果、第三級炭素ラジカルのみならず、反応性が高く生成が困難とされる第一級炭素ラジカルやメチルラジカルも効率的に発生し、対応する付加体を良好な収率で与えた (**6a**, **6k** and **6t**)。さらに、アミド基を有するホウ素アート錯体 **1o** や、ステロイド骨格を持つホウ素アート錯体 **1r** を用いた場合でも、複雑な骨格を有する付加体が得られた (**6o** and **6r**)。これらの結果は、本手法が官能基許容性に優れ、医薬品の後期修飾にも適用可能であることを示している。また、本反応の副生成物として、ホウ素アート錯体のアルキル基がメトキシ基に置換されたホウ素錯体 **7** が単離された。この錯体 **7** の構造は X 線結晶構造解析により決定された。

さらに、ニッケル触媒によるハロゲン化アリールとのクロスカップリング反応が進行することを見出した (Figure 1-9)。¹¹ ハロゲン化アリール **8** とホウ素アート錯体 **1** の反応において、ニッケル触媒として $NiBr_2(diglyme)$ 、配位子として $dtbbpy$ を用い、青色 LED 照射下で目的のクロスカップリング体 **9** を得た。医薬品であるインドメタシン誘導体やベザフィブラート誘導体に対して、第一級アルキル基、第二級アルキル基の導入に成功した (**9na**, **9hb** and **9qb**)。化合物 **9ta** と **9ha** の合成においては、対応するホウ素化合物から、PDP 型ホウ素アート錯体の調製とカップリング反応をワンポットで行うことができた。

A | Decyanoalkylation



B | Giese addition

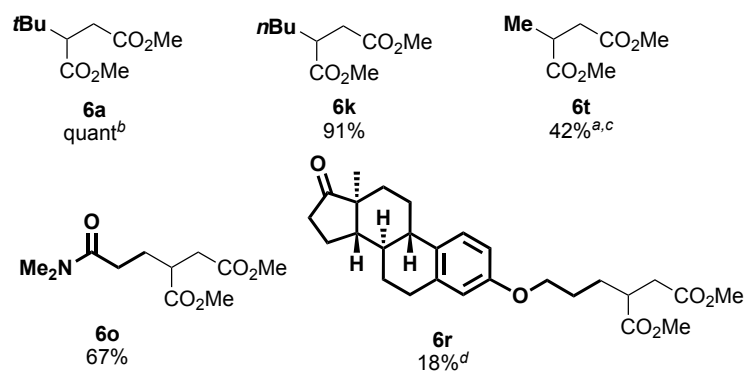
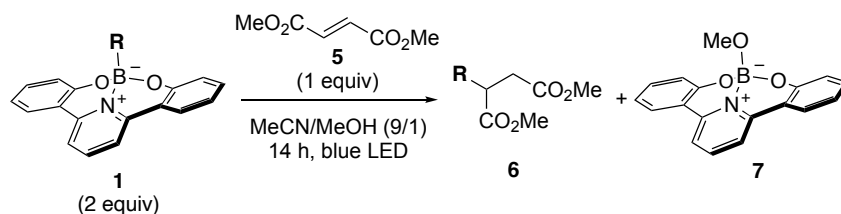


Figure 1-8. (A) 一電子還元による 4-シアノピリジンの脱シアノ型アルキル化反応 (B) Giese 型ラジカル付加反応

^aNMR yield. ^bNo reaction was observed under dark. ^c1.25 equiv of borate was used. ^d1 equiv of borate was used.

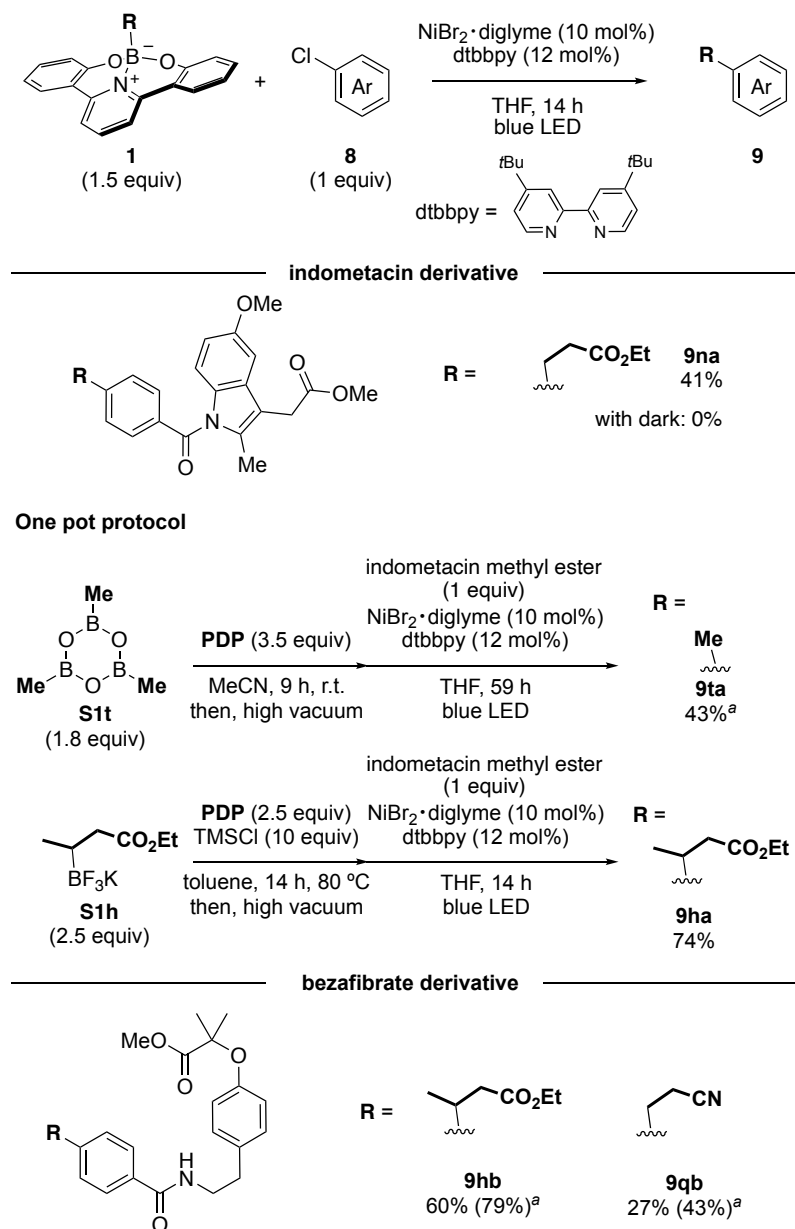


Figure 1-9. PDP 型ホウ素アート錯体とニッケル触媒クロスカップリングを組み合わせた生理活性物質の後期修飾

^aNMR yield.

第四節 結論

本章では、PDP を配位子とするホウ素アート錯体の直接青色光励起を活用した炭素ラジカル生成法を開発した。PDP 型ホウ素アート錯体の合成法は、有機ホウ素化合物を用いた温和な条件の反応であり、エステルやアミドなどの多様な官能基を有する PDP 型ホウ素アート錯体を合成可能であった。励起状態のホウ素アート錯体は強力な還元剤かつ炭素ラジカル源として機能し、脱シアノ型アルキル化反応や Giese 型ラジカル付加反応、さらにニッケル触媒によるクロスカップリング反応といった多彩な分子変換を実現した。

以降第二章、第三章では PDP 型ホウ素アート錯体を用いた種々の反応を説明する。PDP 型ホウ素アート錯体はホウ素周辺の幾何学的歪みが小さく、極めて高い化学的安定性を有する。そのため、反応中でホウ素を放出し、別のホウ素化合物と PDP 型ホウ素アート錯体を形成することは困難であった。したがって、反応の進行には当量以上の錯体を必要とし、結果として PDP 由来の副生成物が定量的に生じる点に問題があった。そこで第四章では、原子効率の課題を克服しつつ、より長波長の光によって励起される ADP 型ホウ素アート錯体の設計と開発について述べる。

第一章 参考文献

1. (a) Brown, H. C.; Rao, B. C. S. *J. Am. Chem. Soc.* **1956**, 78, 5694–5695. (b) Brown, H. C.; Jadhav, P. K.; Mandal, A. K. *Tetrahedron* **1981**, 37, 3547–3587. (c) Crudden, C. M.; Edwards, D. *Eur. J. Org. Chem.* **2003**, 2003, 4695–4712.
2. (a) Ishiyama, T.; Murata, M.; Miyaura, N. *J. Org. Chem.* **1995**, 60, 7508–7510. (b) Takagi, J.; Takahashi, K.; Ishiyama, T.; Miyaura, N. *J. Am. Chem. Soc.* **2002**, 124, 8001–8006. (c) Ito, H.; Kubota, K. *Org. Lett.* **2012**, 14, 890–893.
3. (a) Cho, J.-Y.; Tse, M. K.; Holmes, D., Jr.; Maleczka, R. E., III; Smith, M. R. *Science* **2002**, 295, 305–308. (b) Ishiyama, T.; Takagi, J.; Ishida, K.; Miyaura, N.; Anastasi, N. R.; Hartwig, J. F. *J. Am. Chem. Soc.* **2002**, 124, 390–391. (c) Mkhaliid, I. A. I.; Barnard, J. H.; Marder, T. B.; Murphy, J. M.; Hartwig, J. F. *Chem. Rev.* **2010**, 110, 890–931. (d) Kuroda, Y.; Nakao, Y. *Chem. Lett.* **2019**, 48, 1092–1100.
4. (a) Ji, L.; Griesbeck, S.; Marder, T. B. *Chem. Sci.* **2017**, 8, 846–863. (b) Kothavale, S. S.; Lee, J. Y. *Adv. Opt. Mater.* **2020**, 8, DOI: 10.1002/adom.202000922. (c) Kothavale, S. S.; Lee, J. Y. *Adv. Opt. Mater.* **2020**, 8, DOI: 10.1002/adom.202000922. (d) Gotoh, H.; Nakatsuka, S.; Tanaka, H.; Yasuda, N.; Haketa, Y.; Maeda, H.; Hatakeyama, T. *Angew. Chem., Int. Ed.* **2021**, 60, 12835–12840. (e) Miao, J.; Wang, Y.; Liu, J.; Wang, L. *Chem. Soc. Rev.* **2022**, 51, 153–187. (f) Jin, C.; Yang, X.; Zhao, W.; Zhao, Y.; Wang, Z.; Tan, J. *Coord. Chem. Rev.* **2024**, 513, 215892. (g) Hu, D.; Huang, R.; Fang, Y. *Precis. Chem.* **2024**, 3, 10–26. (h) Grams, R. J.; Santos, W. L.; Scorei, I. R.; Abad-García, A.; Rosenblum, C. A.; Bitá, A.; Cerecetto, H.; Viñas, C.; Soriano-Ursúa, M. A. *Chem. Rev.* **2024**, 124, 2441–2511. (i) Kozhakhmetov, Y.; Kurbanbekov, S.; Mukhamedova, N.; Urkunbay, A.; Kizatov, A.; Bayatanova, L.; Nurdillayeva, R.; Baltabayeva, D. *Crystals* **2025**, 15, 536.
5. (a) Marotta, A.; Adams, C. E.; Molloy, J. J. *Angew. Chem., Int. Ed.* **2022**, 61, DOI: 10.1002/anie.202207067. (b) Pillitteri, S.; Ranjan, P.; Van der Eycken, E. V.; Sharma, U. K. *Adv. Synth. Catal.* **2022**, 364, 1643–1665. (c) Lu, J.; Zhang, H.; Zhang, G.; Guo, R. *ChemPhotoChem* **2025**, 9, DOI: 10.1002/cptc.202500018. (d) Wenzel, J. O.; Werner, J.; Breher, F. *Angew. Chem., Int. Ed.* **2025**, 64, DOI: 10.1002/anie.202507060.
6. (a) Sato, Y.; Nakamura, K.; Sumida, Y.; Hashizume, D.; Hosoya, T.; Ohmiya, H. *J. Am. Chem. Soc.* **2020**, 142, 9938–9943. (b) Sato, Y.; Miyamoto, Y.; Sumida, Y.; Hosoya, T.; Ohmiya, H. *Org. Biomol. Chem.* **2020**, 18, 6598–6601.
7. Rehm, D.; Weller, A. *Isr. J. Chem.* **1970**, 8, 259–271.
8. Connelly, N. G.; Geiger, W. E. *Chem. Rev.* **1996**, 96, 877–910. (a) Andrieux, C. P.; Gelis, L.; Medebielle, M.; Pinson, J.; Saveant, J. M. *J. Am. Chem. Soc.* **1990**, 112, 3509–3520. (b) Buzzetti, L.; Prieto, A.; Roy, S. R.; Melchiorre, P. *Angew. Chem., Int. Ed.* **2017**, 56, 15039–15043.
10. Giese, B. *Angew. Chem., Int. Ed. Engl.* **1983**, 22, 753–764.
11. (a) Tellis, J. C.; Primer, D. N.; Molander, G. A. *Science* **2014**, 345, 433–436. (b) Tellis, J. C.; Amani, J.; Molander, G. A. *Org. Lett.* **2016**, 18, 2994–2997. (c) Primer, D. N.; Karakaya, I.; Tellis, J. C.; Molander, G. A. *J. Am. Chem. Soc.* **2015**, 137, 2195–2198. (d) Primer, D. N.; Molander, G. A. *J. Am. Chem. Soc.* **2017**, 139, 9847–9850.

第一章 実験項

■ Instrumentation and Chemicals Synthesis ■

NMR spectra were recorded on Bruker AVANCE NEO 400N spectrometer, operating at 400 MHz for ^1H NMR, 100.6 MHz for ^{13}C NMR, and 127 MHz for ^{11}B NMR. Chemical shifts were reported in ppm. DART-Mass and ESI-Mass spectra were measured with JMS-T100TD (JEOL Ltd.). Chloroform- d_1 (CDCl_3) containing 0.03% tetramethylsilane (TMS) (>99.8%D, Cambridge Isotope Laboratories, Inc., Cat. No. DLM-7), acetone- d_6 (99.96%D, Cambridge Isotope Laboratories, Inc., Cat. No. DLM-38) and dimethyl sulfoxide- d_6 (99.9%D, Cambridge Isotope Laboratories, Inc., Cat. No. DLM-10) were used as solvents for NMR measurements at ambient temperature. Chemical shifts (δ) for ^1H NMR are given in parts per million (ppm) relative to TMS (δ 0.00 ppm in CDCl_3), or residual acetone (δ 2.07 ppm). Chemical shifts (δ) for ^{13}C NMR are given in ppm relative to CDCl_3 (δ 77.0 ppm), or residual acetone (δ 30.6 ppm) or residual dimethyl sulfoxide (δ 39.5 ppm). Chemical shifts (δ) for ^{19}F NMR are given in ppm relative to a,a,a-trifluorotoluene (δ -63.0 ppm in CDCl_3) used as the external standard. Chemical shifts (δ) for ^{11}B NMR are given in ppm relative to $\text{BF}_3\cdot\text{OEt}_2$ (δ 0.0 ppm in CDCl_3) used as the external standard. The abbreviations s, d, t, q, hep, br s, and m signify singlet, doublet, triplet, quartet, heptet, broad singlet, and multiplet, respectively.

TLC analyses were performed on commercial glass plates bearing 0.25-mm layer of Merck Silica gel 60F₂₅₄. Silica gel (Wakosil[®] 60, 64~210 μm) was used for column chromatography. Biotage Selekt and LaboACE LC-5060 (for Gel Permeation Chromatography) were used for purification. IR spectra were measured with a Thermo Scientific iD7 ATR Accessory for the Thermo Scientific Nicolet iS5 FT-IR Spectrometer. Melting points were measured on a Stanford Research Systems MPA100. Cyclic voltammetry measurements were recorded with a Hokuto Denko HZ-7000 potentiostat. UV-Vis absorption spectra were recorded on a Shimadzu UV-1900. Fluorescence spectra were recorded on a Shimadzu RF-6000. Single-crystal X-ray diffraction data were collected on R-Axis RAPID II. Kessil PR-160 440 nm (highest blue and intensity setting) was used as a light source. TEKNOS MG9 was used as a fan.

All reactions unless otherwise noted were carried out under nitrogen atmosphere. All reactions unless otherwise noted were carried out under nitrogen atmosphere. Materials were obtained from commercial suppliers or prepared according to standard procedures unless otherwise noted. Hexane, ethylacetate, dichloromethane, acetonitrile (Super Dehydrated), diethylether, methanol (Super Dehydrated), ethanol (Super Dehydrated), tetrahydrofuran (Super Dehydrated), acetone, dimethylformamide (Super Dehydrated), toluene (Super Dehydrated), benzene (Super Dehydrated), cyclooctane (Super Dehydrated), [1,3-Bis(diphenylphosphino)propane]nickel(II) Dichloride, Bis(pinacolato)diboron, Manganese(IV) oxide, Tetrahydrofuran-Borane (Tetrahydrofuran Solution), Sodium *tert*-butoxide, acrylonitrile and Copper(I) iodide were purchased from FUJIFILM Wako Pure Chemical Co., 1-bromo-2-methoxybenzene, pyridine Hydrochloride, 1,10-phenanthroline, Potassium Hydrogenfluoride, 2,3-Dimethyl-2-butene, 1-bromoadamantane, ethyl acrylate, Ethyl Crotonate, Ethyl 3-Methylcrotonate, 1,4-dibromobutane, potassium 1,3-dioxoisindolin-2-ide, *N,N*-Dimethylacrylamide, Benzyl Bromide, estrone, 1,3-dibromopropane and Triphenylphosphine were purchased from Tokyo Chemical Industry Co., and Apollo Scientific Ltd., *tert*-Butyllithium (in *n*-pentane, 1.6mol/L), Methyllithium (in diethyl ether) and Copper(I) Chloride were purchased from Kanto Chemical Co., 2,6-dibromopyridine was purchased from Tokyo Chemical Industry Co. and

BLD Pharmatech Ltd., 1-N-Boc-Pyrrolidin-2-ylboronic acid was purchased from BLD Pharmatech Ltd., [(2-Biphenyl)dicyclohexylphosphine], Di- μ -methoxobis(1,5-cyclooctadiene)diiridium(I) and lithium methoxide were purchased from Sigma-Aldrich Japan., Mg turnings and 4-Methyl-3-penten-2-one were purchased from Nacalai Tesque, Inc., tetrahydroxydiboron and chromone were purchased from BLD Pharmatech Ltd. All reagents were used as received. The substrates listed in Figure S1-1 were prepared according to the literatures (**PDP**,¹ **S1a**,² **S1b**,³ **S1c**,⁴ **S1d**,⁵ **S1e**,⁶ **S1h**,⁵ **S1i**,⁷ **S1l**,^{8, 9} **S1m**,¹⁰ **S1n**,⁵ **S1p**,¹¹ **8a**,¹² **8b**¹³).

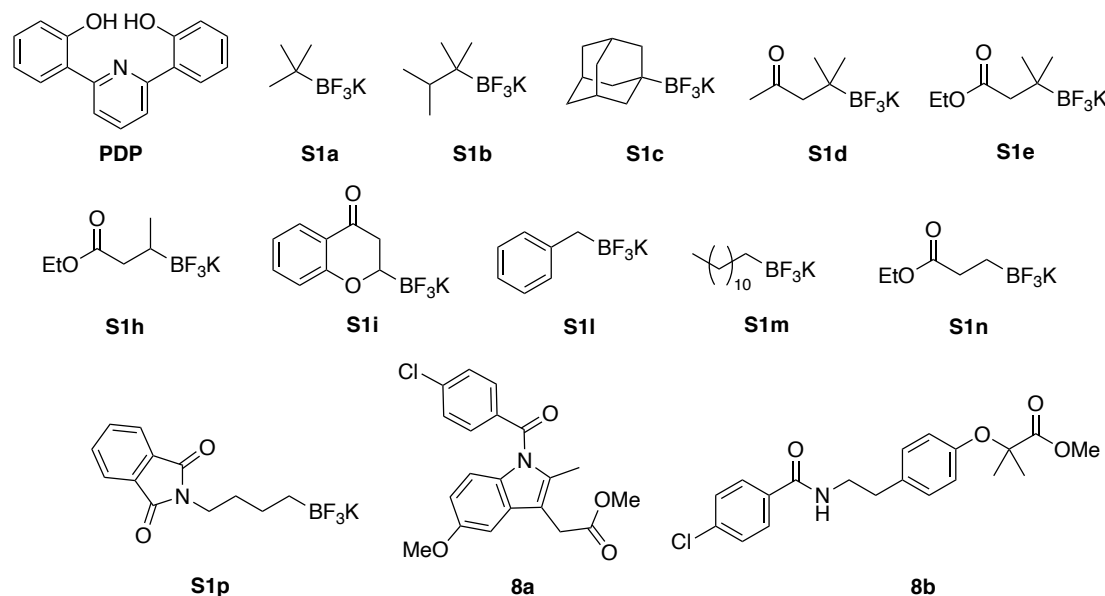
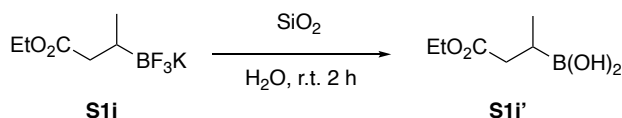


Figure S1-1. Prepared starting materials.

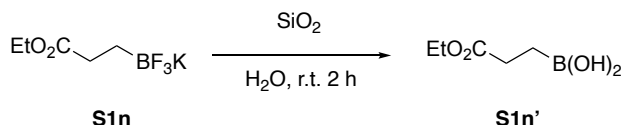
■ Characterization Data for Alkylboronic Acids and Alkyltrifluoroborates ■

(4-ethoxy-4-oxobutan-2-yl)boronic acid (**S1i'**)



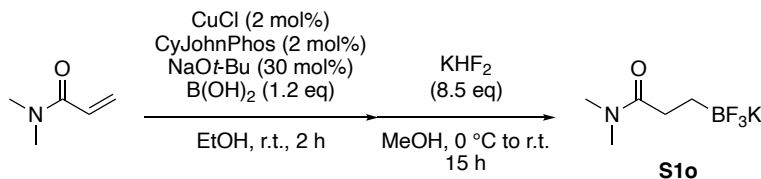
Alkylboronic acid **S1i'** was synthesized according to the literature procedure¹⁴. Under an ambient atmosphere, a round-bottom flask was charged with potassium (4-ethoxy-4-oxobutan-2-yl)trifluoroborate (666.2 mg, 3.0 mmol) and silica gel (180 mg, 3.0 mmol), this was 3 times evacuated and purged with N₂. Degassed H₂O (9 mL) were added via syringe and the mixture was stirred for 2 h. The reaction mixture was filtered, which was subsequently rinsed with EtOAc. The filtrate was extracted with AcOEt three times. The organic layer was dried over sodium sulfate, filtered, concentrated to gave **S1i'** (544.9 mg, 3.41 mmol, quantitative) as a colorless oil. The product **S1i'** was included corresponding boroxine. **IR** (neat) 1176, 1289, 1345, 1369, 1462, 1709, 2959, 3403 cm⁻¹. **¹H NMR** (400 MHz, CDCl₃) δ 4.21–4.06 (m, 2H), 2.56–2.36 (m, 2H), 1.47–1.35 (m, 1H), 1.31–1.19 (m, 3H), 1.09–0.94 (m, 3H). **¹³C NMR** (100.6 MHz, CDCl₃) δ 174.8, 60.6, 37.7, 17.2, 14.5, 14.2. **¹¹B NMR** (128 MHz, CDCl₃) δ 32.5. **HRMS–DART** (*m/z*): [M+H]⁺ calcd for C₆H₁₄BO₄⁺, 161.0980; found, 161.0979.

(3-ethoxy-3-oxopropyl)boronic acid (**S1n'**)



Alkylboronic acid **S1n'** was synthesized according to the literature procedure¹⁴. Under an ambient atmosphere, a round-bottom flask was charged with potassium (3-ethoxy-3-oxopropyl)trifluoroborate (624.1 mg, 3.0 mmol) and silica gel (180 mg, 3.0 mmol), this was 3 times evacuated and purged with N₂. Degassed H₂O (9 mL) were added via syringe and the mixture was stirred for 2 h. The reaction mixture was filtered, which was subsequently rinsed with EtOAc. The filtrate was extracted with AcOEt three times. The organic layer was dried over sodium sulfate, filtered, concentrated to gave **S1n'** (400.8 mg, 2.75 mmol, 92%) as a colorless oil. The product **S1n'** was included corresponding boroxine. **IR** (neat) 1095, 1144, 1178, 1217, 1365, 1707, 2983, 3379 cm⁻¹. **¹H NMR** (400 MHz, CDCl₃) δ 4.13 (q, *J* = 6.8 Hz, 2H), 2.48 (t, *J* = 6.8 Hz, 2H), 1.25 (t, *J* = 6.8 Hz, 3H), 1.17–1.00 (m, 2H). **¹³C NMR** (100.6 MHz, CDCl₃) δ 175.4, 60.6, 28.7, 14.2, 10.4. **¹¹B NMR** (128 MHz, CDCl₃) δ 32.7. **HRMS–DART** (*m/z*): [M+H]⁺ calcd for C₅H₁₂BO₄⁺, 147.0823; found, 147.0825.

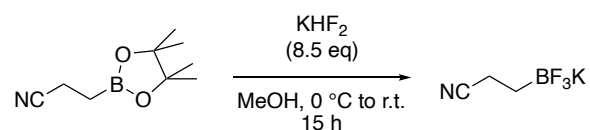
(2-Cyanoethyl)trifluoroborate potassium salt (**S1o**)



Trifluoroborate potassium salts were prepared according to the modified conditions of the literature⁵. Under an ambient atmosphere, a round-bottom flask was charged sequentially with CuCl (39.6 mg,

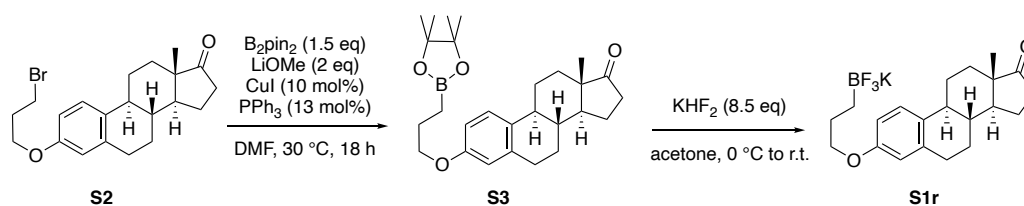
0.4 mmol), CyJhonPhos (140.2 mg, 0.4 mmol), bisboronic acid (2.2 g, 24 mmol) and NaOt-Bu (576.6 mg, 6 mmol), and was 3 times evacuated and purged with nitrogen. To the mixture, EtOH (200 mL) and *N,N*-dimethylacrylamide (2.0 g, 20 mmol, 2.2 mL) were added via syringe and the mixture was stirred for 2 h. The reaction mixture was passed through a short pad of Celite and rinsed with EtOAc. The filtrate was concentrated, and the resultant oil was dissolved in MeOH (150 mL). The solution was cooled in an ice-bath and to the solution, an aqueous saturated KHF₂ (170 mmol, 4.5 M) solution was added dropwise. The mixture was warmed to room temperature and stirred for 1 h followed by evaporation to dryness completely. The residue was triturated with acetone and filtered. The solution was concentrated to a minimal volume. To this solution was added Et₂O until the trifluoroborate precipitated. The precipitate was filtered, washed with Et₂O and dried to yield the desired product as a white solid (3.32 g, 16.0 mmol, 80%). The ¹H, ¹³C, ¹¹B, and ¹⁹F NMR spectra data of product **S1o** were consistent with the literatures.^{15, 16} **NMR data in acetone-*d*₆** ¹H NMR (400 MHz, acetone-*d*₆) δ 2.98 (s, 3H), 2.79 (s, 3H), 2.20 (t, *J* = 8.0 Hz, 2H), 0.41–0.30 (m, 2H). ¹¹B NMR (128 MHz, acetone-*d*₆) δ 4.81. ¹⁹F NMR (376 MHz, acetone-*d*₆) δ –142.2. **NMR data in DMSO-*d*₆** ¹H NMR (400 MHz, DMSO-*d*₆) δ 2.91 (s, 3H), 2.74 (s, 3H), 2.03–1.96 (m, 2H), 0.17–0.08 (m, 2H). ¹³C NMR (100.6 MHz, DMSO-*d*₆) δ 176.2, 36.9, 34.6, 30.2. The signal for the carbon attached to the boron atom was not observed. ¹¹B NMR (128 MHz, DMSO-*d*₆) δ 4.70. ¹⁹F NMR (376 MHz, DMSO-*d*₆) δ –138.6.

Synthesis of (2-cyanoethyl)trifluoroborate potassium salt (**S1q**)



Under an ambient atmosphere, 3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propanenitrile¹⁷ (1.8 g, 10 mmol) was placed in an oven-dried round-bottom flask and dissolved in MeOH (100 mL). The solution was cooled in an ice-bath and to the solution, an aqueous saturated KHF₂ (85 mmol, 4.5 M) solution was added dropwise. The mixture was warmed to room temperature and stirred for 15 h followed by evaporation to dryness completely. The residue was triturated with acetone and filtered. The aqueous solution was azeotropically concentrated with MeOH and H₂O to a minimal volume. To this solution was added Et₂O until the trifluoroborate precipitated. The precipitate was filtered, washed with Et₂O and dried to yield **S1q** as a white solid (823 mg, 5.11 mmol, 51%). **M.p.** 230–232 °C (decomp.). **IR** (neat) 859, 898, 978, 1011, 1237, 1432, 2249, 2940 cm^{–1}. ¹H NMR (400 MHz, acetone-*d*₆) δ 2.12 (t, *J* = 8.4 Hz, 2H), 0.43 (br, 2H). ¹³C NMR (100.6 MHz, acetone-*d*₆) δ 124.5, 13.2. The signal for the carbon attached to the boron atom was not observed. ¹¹B NMR (128 MHz, acetone-*d*₆) δ 4.04. ¹⁹F NMR (376 MHz, acetone-*d*₆) δ –144.2. **HRMS–ESI** (*m/z*): [*M*–K][–] calcd for C₃H₄BF₃N[–], 122.0394; found, 122.0394.

Synthesis of **S1r**



Step 1: preparation of **S3**

In a glovebox, CuI (38.1 mg, 0.20 mmol), PPh₃ (68.2 mg, 0.26 mmol), LiOMe (151.9 mg, 4.0 mmol), bis(pinacolato)diboron (761.8 mg, 3.0 mmol) and alkyl bromide **S2**¹⁸ (782.7 mg, 2.0 mmol) were placed in an oven-dried screw-top 20 mL vial with a stirring bar. To the mixture, DMF (8 mL) was added and the vial was removed from the glovebox. After the reaction mixture was stirred vigorously at 30 °C for 18 h, diluted with water and CH₂Cl₂. The suspension was washed with saturated brine. The organic layer was dried over sodium sulfate, filtered, concentrated and purified by flash column chromatography on silica gel (7/1/2–6/2/2, hexane/AcOEt/CH₂Cl₂) to afford the pinacol ester **S3** as a white solid (485.4 mg, 1.11 mmol, 55%).

Step 2: preparation of **S1r**

Under an ambient atmosphere, **S3** (485.4 mg, 1.1 mmol) was placed in an oven-dried round-bottom flask and dissolved in acetone (10 mL). The solution was cooled in an ice-bath and to the solution, an aqueous saturated KHF₂ (9.4 mmol, 4.5 M) solution was added dropwise. The mixture was warmed to room temperature and stirred overnight followed by evaporation to dryness completely. The residue was triturated with acetone and filtered. The aqueous solution was azeotropically concentrated with MeOH and H₂O to a minimal volume. To this solution was added Et₂O until the trifluoroborate precipitated. The precipitate was filtered, washed with Et₂O and CH₂Cl₂. The collected product was dried to yield the desired product **S1r** as a white solid (249.2 mg, 0.596 mmol, 54%). **M.p.** 200–202 °C (decomp.). **IR** (neat) 778, 805, 924, 1056, 1077, 1228, 1727, 2862, 2935 cm⁻¹. **¹H NMR** (400 MHz, DMSO-*d*₆) δ 7.13 (d, *J* = 8.4 Hz, 1H) 6.62 (d, *J* = 8.4 Hz, 1H), 6.56 (s, 1H), 3.77 (t, *J* = 7.6 Hz, 2H), 2.85–2.75 (m, 2H), 2.43 (dd, *J* = 18.8, 8.8 Hz, 1H), 2.38–2.29 (m, 1H), 2.21–2.13 (m, 1H), 2.10–2.00 (m, 1H), 2.00–1.86 (m, 2H), 1.75 (d, *J* = 8.0 Hz, 1H), 1.63–1.45 (m, 5H), 1.42–1.27 (m, 3H), 0.83 (s, 3H), –0.03 (m, 2H). **¹³C NMR** (100.6 MHz, DMSO-*d*₆) δ 219.7, 156.9, 137.2, 131.0, 126.0, 114.1, 112.1, 70.8, 49.6, 47.3, 43.5, 37.9, 35.4, 31.4, 29.2, 26.1, 25.5, 25.4, 21.1, 13.5. The signal for the carbon attached to the boron atom was not observed. **¹¹B NMR** (128 MHz, DMSO-*d*₆) δ 5.07. **¹⁹F NMR** (376 MHz, DMSO-*d*₆) δ –136.9. **HRMS–ESI** (*m/z*): [M–K][–] calcd for C₂₁H₂₇BF₃O₂[–], 379.2062; found, 379.2062.

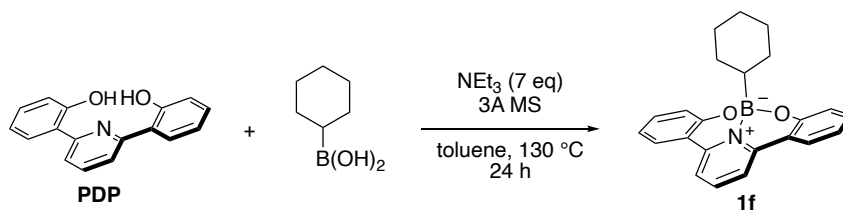
■ Characterization Data for Alkylborates 1a–1s and 7 ■

Method A (synthesis of 1a as a representative)



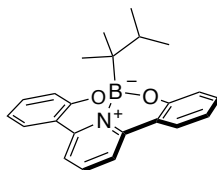
Under an ambient atmosphere, to an oven-dried screw-top 20 mL vial with a stirring bar was added 2,2'-(pyridine-2,6-diyl)diphenol (263.3 mg, 1.0 mmol), *t*-BuBF₃K **S1a** (164.0 mg, 1.0 mmol). The vial was brought to a glovebox, and added toluene (10 mL) and TMSCl (884 μ L, 7.0 mmol). After the vial was removed from the glovebox and sealed with Teflon tape, the vial was placed in aluminum heating block at 130 °C and stirred for 14 h. After cooling to room temperature, the reaction crude was passed through a short pad of N–H silica gel with toluene followed by evaporation and vacuum pump to remove the solvent to give PDP-borate **1a** as a yellow solid (315.9 mg, 0.960 mmol, 96% yield). **Rf** = 0.30 (hexane/AcOEt = 7/3). **M.p.** 220–222 °C. **IR** (neat) 748, 993, 1027, 1043, 1456, 1605, 2850, 2923 cm⁻¹. **¹H NMR** (400 MHz, CDCl₃) δ 7.98 (t, *J* = 8.0 Hz, 1H), 7.76 (d, *J* = 8.0 Hz, 2H), 7.65 (dd, *J* = 8.0, 1.6 Hz, 2H), 7.38 (ddd, *J* = 8.4, 7.2, 1.6 Hz, 2H), 7.06 (dd, *J* = 8.4, 1.2 Hz, 2H), 6.87 (ddd, *J* = 8.0, 7.0, 1.2 Hz, 2H), 0.53 (s, 9H). **¹³C NMR** (100.6 MHz, CDCl₃) δ 158.3, 149.4, 140.7, 134.2, 124.8, 120.2, 119.1, 118.7, 117.3, 28.2. The signal for the carbon attached to the boron atom was not observed. **¹¹B NMR** (128 MHz, CDCl₃) δ 7.65. **HRMS–DART** (*m/z*): [M+NH₄]⁺ calcd for C₂₁H₂₄BN₂O₂⁺, 347.1925; found, 347.1925.

Method B (synthesis of 1f as a representative)



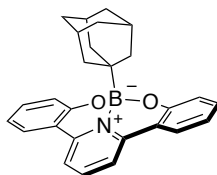
Under an ambient atmosphere, to an oven-dried screw-top 20 mL vial with a stirring bar was added 2,2'-(pyridine-2,6-diyl)diphenol (263.3 mg, 1.0 mmol), cyclohexylboronic acid (114.0 mg, 1.0 mmol). The vial was brought to a glovebox, and added molecular sieve 3A (100 mg), toluene (3.3 mL) and triethylamine (976 μ L, 7.0 mmol). After the vial was removed from the glovebox and sealed with Teflon tape, the vial was placed in aluminum heating block at 130 °C and stirred for 24 h. After cooling to room temperature, the reaction crude was passed through a short pad of Celite followed by evaporation and vacuum pump remove the solvent to give PDP-borate **1f** as a yellow solid (344 mg, 0.968 mmol, 97%). **Rf** = 0.36 (hexane/AcOEt = 7/3). **M.p.** 237–239 °C. **IR** (neat) 744, 1001, 1275, 1456, 1603, 2841, 2902, 3073 cm⁻¹. **¹H NMR** (400 MHz, CDCl₃) δ 7.98 (t, *J* = 8.0 Hz, 1H), 7.76 (d, *J* = 8.0 Hz, 2H), 7.68 (d, *J* = 8.0 Hz, 2H), 7.40 (t, *J* = 7.6 Hz, 2H), 7.08 (d, *J* = 8.0 Hz, 2H), 6.92 (t, *J* = 7.6 Hz, 2H), 1.52–1.42 (m, 3H), 1.36–1.28 (m, 2H), 1.05–0.78 (m, 5H), 0.54 (t, *J* = 11.2 Hz, 1H). **¹³C NMR** (100.6 MHz, CDCl₃) δ 157.7, 148.6, 140.6, 134.1, 125.2, 120.5, 119.3, 118.4, 117.4, 28.1, 27.1. The signal for the carbon attached to the boron atom was not observed. **¹¹B NMR** (128 MHz, CDCl₃) δ 7.65. **HRMS–DART** (*m/z*): [M+NH₄]⁺ calcd for C₂₃H₂₆BN₂O₂⁺, 373.2082; found, 373.2082.

Synthesis of 1b



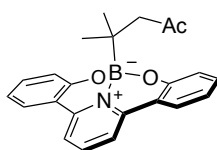
The product was synthesized according to **Method A** using potassium (2,3-dimethylbutan-2-yl)trifluoroborate **S1b** (115.2 mg, 0.6 mmol), 2,2'-(pyridine-2,6-diyl)diphenol (158.0 mg, 0.6 mmol), TMSCl (1.14 mL, 9 mmol), benzene (2 mL) at 110 °C for 14.5 h. After cooling to room temperature, the reaction crude was passed through a short pad of N–H silica gel with benzene. The solvent was removed by evaporation and vacuum pump to give PDP-borate **1b** as a yellow solid (209.9 mg, 0.588 mmol, 98% yield). **M.p.** 211–213 °C. **IR** (neat) 754, 1023, 1277, 1304, 1459, 1557, 1608, 2941 cm⁻¹. **¹H NMR** (400 MHz, CDCl₃) δ 7.99 (t, J = 8.0 Hz, 1H), 7.78 (d, J = 8.0 Hz, 2H), 7.66 (d, J = 8.0 Hz, 2H), 7.41–7.34 (m, 2H), 7.04 (d, J = 8.4 Hz, 2H), 6.88 (t, J = 7.6 Hz, 2H), 1.69 (hep, J = 6.8 Hz, 1H), 0.89 (d, J = 6.8 Hz, 6H), 0.28 (s, 6H). **¹³C NMR** (100.6 MHz, CDCl₃) δ 158.1, 149.5, 140.6, 134.1, 124.7, 120.2, 119.1, 118.9, 117.4, 34.3, 23.5, 18.9. The signal for the carbon attached to the boron atom was not observed. **¹¹B NMR** (128 MHz, CDCl₃) δ 8.38. **HRMS–DART** (m/z): [M+NH₄]⁺ calcd for C₂₃H₂₈BN₂O₂⁺, 375.2238; found, 375.2238.

Synthesis of 1c



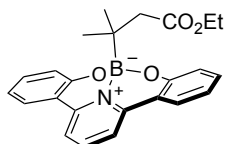
The product was synthesized according to **Method A** using potassium adamantan-1-yltrifluoroborate **S1c** (242.1 mg, 1.0 mmol), 2,2'-(pyridine-2,6-diyl)diphenol (263.3 mg, 1.0 mmol), TMSCl (1.9 mL, 15 mmol), toluene (3.3 mL) at 120 °C for 12 h. After cooling to room temperature, the reaction crude was passed through a short pad of alumina with THF. The solvent was removed by evaporation and vacuum pump to give PDP-borate **1c** as a yellow solid (413.9 mg, 1.02 mmol, quantitative, containing <5% impurities, without further purification). **M.p.** 203–205 °C. **IR** (neat) 728, 742, 992, 1020, 1041, 1275, 1457, 1605, 2842, 2883, 3064 cm⁻¹. **¹H NMR** (400 MHz, CDCl₃) δ 7.96 (t, J = 8.0 Hz, 1H), 7.77 (d, J = 8.0 Hz, 2H), 7.65 (dd, J = 8.0, 1.2 Hz, 2H), 7.40–7.35 (m, 2H), 7.06 (dd, J = 8.0, 0.8 Hz, 2H), 6.90–6.84 (m, 2H), 1.64–1.55 (m, 4H), 1.52–1.41 (m, 5H), 1.34 (d, J = 2.4 Hz, 6H). **¹³C NMR** (100.6 MHz, CDCl₃) δ 158.3, 149.4, 140.6, 134.2, 124.8, 120.2, 119.0, 118.5, 117.1, 38.6, 37.7, 28.1. The signal for the carbon attached to the boron atom was not observed. **¹¹B NMR** (128 MHz, CDCl₃) δ 7.06. **HRMS–DART** (m/z): [M+H]⁺ calcd for C₂₇H₂₇BNO₂⁺, 408.2129; found, 408.2129.

Synthesis of 1d



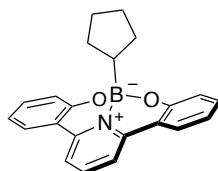
The product was synthesized according to **Method A** using potassium trifluoro(2-methyl-4-oxopent-2-yl)borate **S1d** (20.6 mg, 0.1 mmol), 2,2'-(pyridine-2,6-diyl)diphenol (26.3 mg, 0.1 mmol), TMSCl (51 μ L, 0.4 mmol), toluene (333 μ L) at 130 $^{\circ}$ C for 12 h. After cooling to room temperature, the reaction crude was concentrated under reduced pressure, and purified by flash column chromatography on silica gel (100/0–50/50, $\text{CH}_2\text{Cl}_2/\text{AcOEt}$) gave PDP-borate **1d** (27.4 mg, 73.8 μ mol, 74%) as a yellow solid. **Rf** = 0.65 ($\text{CH}_2\text{Cl}_2/\text{AcOEt}$ = 98/2). **M.p.** 135–137 $^{\circ}$ C. **IR** (neat) 755, 1043, 1275, 1458, 1556, 1610, 1694, 2937 cm^{-1} . **^1H NMR** (400 MHz, CDCl_3) δ 8.01 (t, J = 8.0 Hz, 1H), 7.78 (d, J = 8.0 Hz, 2H), 7.66 (dd, J = 8.0, 1.6 Hz, 2H), 7.40 (ddd, J = 8.4, 7.2, 1.6 Hz, 2H), 7.06 (dd, J = 8.4, 1.2 Hz, 2H), 6.93–6.87 (m, 2H), 2.25 (s, 2H), 1.97 (s, 3H), 0.58 (s, 6H). **^{13}C NMR** (100.6 MHz, CDCl_3) δ 211.6, 157.7, 149.4, 141.0, 134.4, 125.0, 120.1, 119.5, 118.6, 117.6, 52.3, 32.6, 25.7. The signal for the carbon attached to the boron atom was not observed. **^{11}B NMR** (128 MHz, CDCl_3) δ 7.13. **HRMS–DART** (m/z): $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{23}\text{H}_{23}\text{BNO}_3^+$, 372.1766; found, 372.1764.

Synthesis of **1e**



The product was synthesized according to **Method A** using potassium (4-ethoxy-2-methyl-4-oxobutan-2-yl)trifluoroborate **S1e** (271.1 mg, 1.03 mmol), 2,2'-(pyridine-2,6-diyl)diphenol (263.3 mg, 1.0 mmol), TMSCl (884 μ L, 7 mmol), benzene (5 mL) at room temperature for 1.5 h and then, warmed up at 100 $^{\circ}$ C for 12 h. After cooling to room temperature, the reaction crude was passed through a short pad of N–H silica gel with benzene. The solvent was removed by evaporation and vacuum pump to give PDP-borate **1e** as a yellow solid (316.8 mg, 0.789 mmol, 79%, containing <5% impurities, without further purification). **M.p.** 158–160 $^{\circ}$ C. **IR** (neat) 730, 749, 999, 1025, 1456, 1700, 1720, 2944 cm^{-1} . **^1H NMR** (400 MHz, CDCl_3) δ 8.00 (t, J = 8.0 Hz, 1H), 7.78 (d, J = 8.0 Hz, 2H), 7.66 (d, J = 8.0 Hz, 2H), 7.39 (t, J = 8.0 Hz, 2H), 7.07 (d, J = 8.0 Hz, 2H), 6.89 (t, J = 8.0 Hz, 2H), 3.96 (q, J = 7.2 Hz, 2H), 2.15 (s, 2H), 1.14 (t, J = 7.2 Hz, 3H), 0.59 (s, 6H). **^{13}C NMR** (100.6 MHz, CDCl_3) δ 173.9, 157.8, 149.5, 140.1, 134.5, 124.9, 120.2, 119.5, 118.5, 117.5, 59.3, 42.9, 24.6, 14.4. The signal for the carbon attached to the boron atom was not observed. **^{11}B NMR** (128 MHz, CDCl_3) δ 7.34. **HRMS–DART** (m/z): $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{24}\text{H}_{25}\text{BNO}_4^+$, 402.1871; found, 402.1873

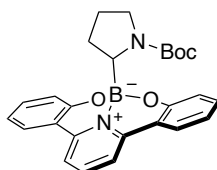
Synthesis of **1g**



The product was synthesized according to **Method B** using cyclopentylboronic acid (114.0 mg, 1.0 mmol), 2,2'-(pyridine-2,6-diyl)diphenol (263.3 mg, 1.0 mmol), molecular sieve 3A (100 mg), triethylamine (976 μ L, 7.0 mmol), toluene (3.3 mL) at 130 $^{\circ}$ C for 16 h. After cooling to room temperature, the reaction crude was filtrated followed by evaporation and vacuum pump remove the solvent to give PDP-borate **1g** as a yellow solid (349 mg, 1.02 mmol, quantitative, containing <5%

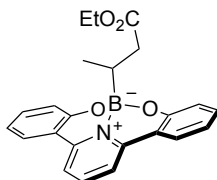
impurities, without further purification). **M.p.** 188–190 °C. **IR** (neat) 729, 748, 998, 1037, 1555, 1605, 2855, 2941 cm^{-1} . **^1H NMR** (400 MHz, CDCl_3) δ 7.99 (t, J = 8.0 Hz, 1H), 7.77 (d, J = 8.0 Hz, 2H), 7.69 (d, J = 8.0 Hz, 2H), 7.39 (t, J = 7.6 Hz, 2H), 7.08 (d, J = 8.0 Hz, 2H), 6.92 (t, J = 7.6 Hz, 2H), 1.42–1.04 (m, 8H), 0.89 (m, 1H). **^{13}C NMR** (100.6 MHz, CDCl_3) δ 157.9, 148.5, 140.6, 134.1, 125.2, 120.5, 119.4, 118.3, 117.5, 28.5, 26.2. The signal for the carbon attached to the boron atom was not observed. **^{11}B NMR** (128 MHz, CDCl_3) δ 7.72. **HRMS–DART** (m/z): $[\text{M}+\text{NH}_4]^+$ calcd for $\text{C}_{22}\text{H}_{24}\text{BN}_2\text{O}_2^+$, 359.1925; found, 359.1924.

Synthesis of **1h**



The product was synthesized according to **Method B** using 1-N-Boc-Pyrrolidin-2-ylboronic acid (21.5 mg, 0.1 mmol), 2,2'-(pyridine-2,6-diyl)diphenol (26.3 mg, 0.1 mmol), molecular sieve 3A (30 mg), triethylamine triethylamine (97.6 μL , 0.7 mmol), benzene (1 mL) at 80 °C for 14 h. After cooling to room temperature, the crude product was passed through a short pad of alumina with THF. The reaction crude was concentrated under reduced pressure, and purified by flash column chromatography on silica gel (100/0–95/5, $\text{CH}_2\text{Cl}_2/\text{AcOEt}$) gave **1h** (29.6 mg, 66.9 μmol , 67%) as a yellow solid. **M.p.** 225–227 °C (decomp.) **IR** (neat) 1300, 1394, 1458, 1585, 1614, 1677, 2925, 2973 cm^{-1} . Signals for two rotamers were given: **^1H NMR** (400 MHz, CDCl_3) δ 8.05 (t, J = 8.0 Hz, $0.30 \times 1\text{H}$), 7.97 (t, J = 8.0 Hz, $0.70 \times 1\text{H}$), 7.83–7.74 (m, 2H), 7.74–7.59 (m, 2H), 7.46–7.31 (m, 2H), 7.12–6.85 (m, 4H), 3.31 (d, J = 9.2 Hz, $0.70 \times 1\text{H}$), 3.26 (d, J = 9.2 Hz, $0.30 \times 1\text{H}$), 3.14 (q, J = 8.8 Hz, $0.30 \times 1\text{H}$), 2.97 (q, J = 8.8 Hz, $0.70 \times 1\text{H}$), 2.34–1.98 (m, 3H), 1.75–1.64 (m, 1H), 1.61–1.51 (m, 1H), 1.14 (s, $0.70 \times 9\text{H}$), 1.03 (s, $0.30 \times 9\text{H}$). **^{13}C NMR** (100.6 MHz, CDCl_3) δ 156.9, 156.8, 156.5, 154.6, 154.0, 149.2, 148.6, 148.53, 148.47, 141.0, 140.9, 134.1, 134.0, 133.8, 133.5, 126.0, 125.6, 125.24, 125.17, 120.4, 120.13, 120.07, 119.9, 119.5, 119.4, 119.1, 119.0, 118.4, 117.84, 117.79, 117.2, 46.3, 45.9, 28.5, 28.3, 26.6, 25.9, 25.2, 24.3. (Only observed peaks) **^{11}B NMR** (128 MHz, CDCl_3) δ 5.52. **HRMS–DART** (m/z): $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{26}\text{H}_{28}\text{BN}_2\text{O}_4^+$, 443.2137; found, 443.2138.

Synthesis of **1i**

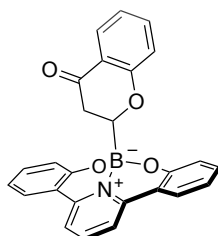


Method A: the product was synthesized using potassium (4-ethoxy-4-oxobutan-2-yl)trifluoroborate **S1i** (222.1 mg, 1.0 mmol), 2,2'-(pyridine-2,6-diyl)diphenol (263.3 mg, 1.0 mmol), TMSCl (505 μL , 4.0 mmol), toluene (3.3 mL) at 80 °C for 14 h. After cooling to room temperature, the reaction crude was passed through a short pad of alumina. The solvent was removed by evaporation and vacuum pump to give PDP-borate **1i** as a yellow solid (390 mg, 1.01 mmol, quantitative, containing <5% impurities, without further purification).

Method B: the product was synthesized using (4-ethoxy-4-oxobutan-2-yl)boronic acid (16.0 mg,

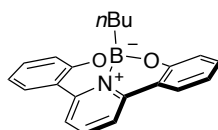
0.1 mmol), 2,2'-(pyridine-2,6-diyl)diphenol (26.3 mg, 0.1 mmol), molecular sieve 3A (30 mg), triethylamine triethylamine (97.6 μ L, 0.7 mmol), benzene (1 mL) at 80 °C for 14 h. After cooling to room temperature, the reaction crude was purified by flash column chromatography on N-H silica gel (benzene, 100%) gave **1i** (30.7 mg, 77.3 μ mol, 77%) as a yellow solid. **M.p.** 150–152 °C. **IR** (neat) 752, 1022, 1456, 1605, 1717, 2865, 2945, 3068 cm^{-1} . **^1H NMR** (400 MHz, CDCl_3) δ 8.00 (t, J = 8.0 Hz, 1H), 7.76 (dd, J = 8.0, 5.6 Hz, 2H), 7.68 (d, J = 8.0 Hz, 2H), 7.43–7.37 (m, 2H), 7.09 (dd, J = 8.0, 0.8 Hz, 2H), 6.97–6.88 (m, 2H), 3.99–3.86 (m, 2H), 2.19 (dd, J = 14.8, 4.0 Hz, 1H), 1.93 (dd, J = 14.8, 11.2 Hz, 1H), 1.20 (m, 1H), 1.11 (t, J = 7.2 Hz, 3H), 0.64 (dd, J = 7.2 Hz, 3H). **^{13}C NMR** (100.6 MHz, CDCl_3) δ 175.4, 157.4, 157.2, 148.8, 148.5, 141.0, 134.4, 134.3, 125.4, 120.5, 120.4, 119.8, 119.7, 118.3, 118.0, 117.8, 117.7, 59.6, 37.2, 14.9, 14.3. The signal for the carbon attached to the boron atom was not observed. **^{11}B NMR** (128 MHz, CDCl_3) δ 6.94. **HRMS–DART** (m/z): $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{23}\text{H}_{23}\text{BNO}_4^+$, 388.1715; found, 388.1715.

Synthesis of **1j**



The product was synthesized according to **Method A** using potassium trifluoro(4-oxochroman-2-yl)borate **S1j** (152.4 mg, 0.6 mmol), 2,2'-(pyridine-2,6-diyl)diphenol (131.7 mg, 0.5 mmol), TMSCl (303 μ L, 2.4 mmol), benzene (1.67 mL) at 60 °C for 12 h. The reaction crude was concentrated under reduced pressure, and purified by flash column chromatography on silica gel (CH_2Cl_2 , 100%) gave PDP-borate **1j** (103.9 mg, 0.248 mmol, 50%, containing <5% impurities, without further purification) as a yellow solid. **M.p.** 193–194 °C (decomp.). **IR** (neat) 727, 755, 1069, 1276, 1455, 1603, 1681, 2838 cm^{-1} . **^1H NMR** (400 MHz, CDCl_3) δ 8.09 (t, J = 8.0 Hz, 1H), 7.90 (d, J = 8.0 Hz, 1H), 7.81 (d, J = 8.0 Hz, 1H), 7.74 (d, J = 8.0 Hz, 1H), 7.69 (d, J = 7.6 Hz, 2H), 7.42 (t, J = 7.6 Hz, 1H), 7.36 (t, J = 7.6 Hz, 1H), 7.16 (t, J = 7.6 Hz, 1H), 7.08 (t, J = 8.0 Hz, 2H), 7.00–6.90 (m, 2H), 6.75 (t, J = 7.6 Hz, 1H), 6.32 (d, J = 8.4 Hz, 1H), 4.04 (d, J = 16.0 Hz, 1H), 2.84 (t, J = 16.0 Hz, 1H), 2.54 (d, J = 16.0 Hz, 1H). **^{13}C NMR** (100.6 MHz, CDCl_3) δ 194.6, 163.4, 156.5, 156.4, 149.5, 148.3, 141.7, 134.8, 134.6, 134.4, 126.7, 125.5, 125.0, 121.0, 120.51, 120.46, 120.22, 120.0, 119.7, 118.22, 118.15, 118.07, 117.6, 117.5, 38.2. The signal for the carbon attached to the boron atom was not observed. **^{11}B NMR** (128 MHz, CDCl_3) δ 4.73. **HRMS–DART** (m/z): $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{26}\text{H}_{19}\text{BNO}_4^+$, 420.1402; found, 420.1402.

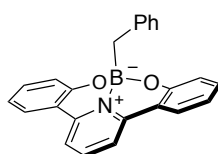
Synthesis of **1k**



The product was synthesized according to **Method A** using potassium butyltrifluoroborate (507.4 mg, 3.09 mmol), 2,2'-(pyridine-2,6-diyl)diphenol (790 mg, 3.0 mmol), TMSCl (2.7 mL, 21 mmol),

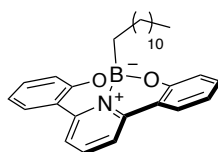
toluene (10 mL) at 100 °C for 14 h. After cooling to room temperature, the reaction crude was passed through a short pad of N–H silica gel to give PDP-borate **1k** as a yellow solid (831.5 mg, 2.53 mmol, 84%, without further purification). **M.p.** 163–164 °C. **IR** (neat) 748, 1273, 1454, 1555, 1604, 2844, 2904, 2955 cm⁻¹. **¹H NMR** (400 MHz, CDCl₃) δ 7.97 (t, J = 8.0 Hz, 1H), 7.74 (d, J = 8.0 Hz, 2H), 7.69 (d, J = 8.0 Hz, 2H), 7.41 (t, J = 7.6 Hz, 2H), 7.10 (d, J = 8.0 Hz, 2H), 6.94 (t, J = 7.6 Hz, 2H), 1.21–1.04 (m, 4H), 0.69 (t, J = 6.8 Hz, 3H), 0.40 (t, J = 7.2 Hz, 2H). **¹³C NMR** (100.6 MHz, CDCl₃) δ 157.5, 148.2, 140.7, 134.0, 125.3, 120.8, 119.6, 118.3, 117.6, 26.7, 25.8, 14.1. The signal for the carbon attached to the boron atom was not observed. **¹¹B NMR** (128 MHz, CDCl₃) δ 7.28. **HRMS–DART** (m/z): [M+NH₄]⁺ calcd for C₂₁H₂₄BN₂O₂⁺, 347.1925; found, 347.1924.

Synthesis of **1l**



The product was synthesized according to **Method A** using potassium benzyltrifluoroborate **S1l** (118.8 mg, 0.6 mmol), 2,2'-(pyridine-2,6-diyl)diphenol (158.0 mg, 0.6 mmol), TMSCl (303 μ L, 2.4 mmol), toluene (2 mL) at 80 °C for 14 h. After cooling to room temperature, the reaction crude was washed on a short pad of N–H silica gel with toluene (24 mL), then dissolved out with dry-THF. THF was removed by evaporation and vacuum pump to give PDP-borate **1l** as a pale yellow solid (136.1 mg, 0.374 mmol, 62%, containing <7% impurities). **M.p.** 219–221 °C. **IR** (neat) 697, 750, 1021, 1037, 1280, 1454, 1606, 2885 cm⁻¹. **¹H NMR** (400 MHz, CDCl₃) δ 7.98 (t, J = 8.0 Hz, 1H), 7.72 (d, J = 8.0 Hz, 2H), 7.61 (d, J = 8.0 Hz, 2H), 7.42 (t, J = 7.6 Hz, 2H), 7.08 (d, J = 8.0 Hz, 2H), 7.00–6.88 (m, 4H), 6.87–6.82 (m, 1H), 6.63 (t, J = 7.2 Hz, 2H), 1.94 (s, 2H). **¹³C NMR** (100.6 MHz, CDCl₃) δ 157.2, 148.4, 142.8, 140.9, 134.2, 128.4, 127.4, 125.3, 123.1, 120.8, 119.7, 118.2, 117.5. The signal for the carbon attached to the boron atom was not observed. **¹¹B NMR** (128 MHz, CDCl₃) δ 6.72. **HRMS–DART** (m/z): [M+NH₄]⁺ calcd for C₂₄H₂₂BN₂O₂⁺, 381.1769; found, 381.1769.

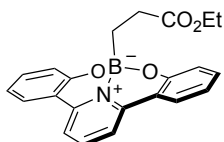
Synthesis of **1m**



The product was synthesized according to **Method A** using potassium dodecyltrifluoroborate **S1m** (27.6 mg, 0.10 mmol), 2,2'-(pyridine-2,6-diyl)diphenol (26.3 mg, 0.10 mmol), TMSCl (50 μ L, 0.4 mmol), toluene (333 μ L) at 80 °C for 12 h. After cooling to room temperature, the reaction crude was passed through a short pad of alumina to give PDP-borate **1m** as a yellow oil (20.6 mg, 46.7 μ mol, 47%, containing <5% impurities, without further purification). **IR** (neat) 755, 1277, 1301, 1457, 1584, 1609, 2850, 2920 cm⁻¹. **¹H NMR** (400 MHz, CDCl₃) δ 7.96 (t, J = 8.0 Hz, 1H), 7.73 (d, J = 8.0 Hz, 2H), 7.68 (d, J = 8.0 Hz, 2H), 7.40 (t, J = 7.6 Hz, 2H), 7.09 (d, J = 8.0 Hz, 2H), 6.93 (t, J = 7.6 Hz, 2H), 1.33–1.00 (m, 20H), 0.87 (t, J = 6.4 Hz, 3H), 0.38 (t, J = 7.6 Hz, 2H). **¹³C NMR** (100.6 MHz, CDCl₃) δ 157.5, 148.2, 140.7, 134.0, 125.3, 120.8, 119.6, 118.3, 117.6, 32.8, 31.9, 29.7, 29.64, 29.61,

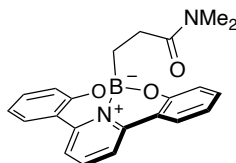
29.4, 24.3, 22.7 14.1. The signal for the carbon attached to the boron atom was not observed. **¹¹B NMR** (128 MHz, CDCl₃) δ 8.25. **HRMS–DART** (m/z): [M+H]⁺ calcd for C₂₉H₃₇BNO₂⁺, 442.2912; found, 442.2910.

Synthesis of **1n**



Method A: The product was synthesized using potassium (3-ethoxy-3-oxopropyl)trifluoroborate **S1n** (208.0 mg, 1.0 mmol), 2,2'-(pyridine-2,6-diyl)diphenol (263.3 mg, 1.0 mmol), TMSCl (505 μ L, 4.0 mmol), toluene (3.3 mL) at 80 °C for 14 h. After cooling to room temperature, the reaction crude was passed through a short pad of alumina. The solvent was removed by evaporation and vacuum pump to give PDP-borate **1n** as a yellow solid (347.4 mg, 0.931 mmol, 93%, containing <5% impurities, without further purification). **Method B:** The product was synthesized using (3-ethoxy-3-oxopropyl) boronic acid (24.2 mg, 0.17 mmol), 2,2'-(pyridine-2,6-diyl)diphenol (26.3 mg, 0.1 mmol), molecular sieve 3A (30 mg), triethylamine triethylamine (97.6 μ L, 0.7 mmol), benzene (1 mL) at 80 °C for 14 h. After cooling to room temperature, the reaction crude was purified by flash column chromatography on N-H silica gel (benzene, 100%) gave **1n** (32.2 mg, 86.3 μ mol, 86%) as a yellow solid. **M.p.** 183–186 °C. **IR** (neat) 760, 1057, 1193, 1268, 1458, 1557, 1717, 2910 cm⁻¹. **¹H NMR** (400 MHz, CDCl₃) δ 7.98 (t, J = 8.0 Hz, 1H), 7.74 (d, J = 8.0 Hz, 2H), 7.68 (d, J = 8.0 Hz, 2H), 7.41 (t, J = 7.6 Hz, 2H), 7.09 (d, J = 8.0 Hz, 2H), 6.94 (t, J = 7.6 Hz, 2H), 3.95 (q, J = 7.2 Hz, 2H), 2.22 (t, J = 8.4 Hz, 2H), 1.13 (t, J = 7.2 Hz, 3H), 0.72 (t, J = 8.4 Hz, 2H). **¹³C NMR** (100.6 MHz, CDCl₃) δ 176.4, 156.9, 148.2, 141.0, 134.3, 125.5, 120.7, 119.9, 118.1, 117.7, 59.8, 29.2, 14.2. The signal for the carbon attached to the boron atom was not observed. **¹¹B NMR** (128 MHz, CDCl₃) δ 7.12. **HRMS–DART** (m/z): [M+H]⁺ calcd for C₂₃H₂₃BNO₄⁺, 374.1558; found, 374.1559.

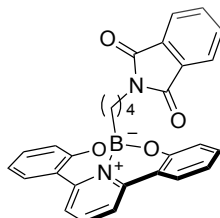
Synthesis of **1o**



The product was synthesized according to **Method A** using potassium (3-(dimethylamino)-3-oxopropyl)trifluoroborate **S1o** (124.2 mg, 0.6 mmol), 2,2'-(pyridine-2,6-diyl)diphenol (158.0 mg, 0.6 mmol), TMSCl (319 μ L, 4.2 mmol), benzene (2 mL) at room temperature for 2 h and then, warmed up at 100 °C for 12 h in an oven-dried 20 ml two-necked round-bottom flask instead of an oven-dried screw-top 20 mL vial. After cooling to room temperature, the reaction crude was washed on a short pad of N–H silica gel with benzene (150 mL), then dissolved out with dry-THF. THF was removed by evaporation and vacuum pump to give PDP-borate **1o** as a pale yellow solid (189.2 mg, 0.508 mmol, 85%, without further purification). **M.p.** 203–204 °C. **IR** (neat) 756, 1022, 1041, 1454, 1555, 1603, 1639, 2887 cm⁻¹. **¹H NMR** (400 MHz, CDCl₃) δ 8.00 (t, J = 8.0 Hz, 1H), 7.77 (d, J = 8.0 Hz, 2H), 7.69 (d, J = 8.0 Hz, 2H), 7.40 (t, J = 7.6 Hz, 2H), 7.09 (d, J = 8.0 Hz, 2H), 6.94 (t, J = 7.6 Hz, 2H),

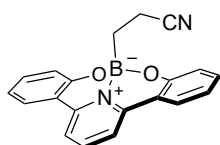
2.83 (s, 3H), 2.79 (s, 3H), 2.26 (t, $J = 8.4$ Hz, 2H), 0.72 (t, $J = 8.4$ Hz, 2H). ^{13}C NMR (100.6 MHz, CDCl_3) δ 175.9, 157.0, 148.2, 141.0, 134.2, 125.6, 120.6, 120.0, 118.3, 117.8, 37.2, 35.3, 28.4. The signal for the carbon attached to the boron atom was not observed. ^{11}B NMR (128 MHz, CDCl_3) δ 6.67. HRMS–DART (m/z): $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{22}\text{H}_{22}\text{BN}_2\text{O}_3^+$, 373.1718; found, 373.1718.

Synthesis of **1p**



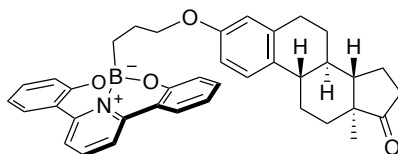
The product was synthesized according to **Method A** using potassium (4-(1,3-dioxoisindolin-2-yl)butyl)trifluoroborate **S1p** (30.9 mg, 0.10 mmol), 2,2'-(pyridine-2,6-diyl)diphenol (26.3 mg, 0.10 mmol), TMSCl (50 μL , 0.4 mmol), toluene (333 μL) at 80 $^\circ\text{C}$ for 14 h. After cooling to room temperature, the reaction crude was concentrated under reduced pressure, and purified by flash column chromatography on silica gel (CH_2Cl_2 , 100%) gave PDP-borate **1p** (22.2 mg, 46.8 μmol , 47%) as a yellow solid. **Rf** = 0.28 (CH_2Cl_2 , 100%) **M.p.** 75–77 $^\circ\text{C}$. **IR** (neat) 716, 754, 1392, 1456, 1606, 1702, 1769, 2923 cm^{-1} . ^1H NMR (400 MHz, CDCl_3) δ 7.98 (t, $J = 7.6$ Hz, 1H), 7.79–7.73 (m, 4H), 7.70–7.64 (m, 4H), 7.38 (t, $J = 7.6$ Hz, 2H), 7.07 (d, $J = 8.0$ Hz, 2H), 6.93 (t, $J = 7.6$ Hz, 2H), 3.48 (t, $J = 7.6$ Hz, 2H), 1.53–1.40 (m, 2H), 1.29–1.17 (m, 2H), 0.45 (t, $J = 7.6$ Hz, 2H). ^{13}C NMR (100.6 MHz, CDCl_3) δ 168.4, 157.3, 148.2, 140.8, 134.2, 133.6, 132.2, 125.4, 123.0, 120.8, 119.7, 118.2, 117.7, 38.2, 31.4, 21.6. The signal for the carbon attached to the boron atom was not observed. ^{11}B NMR (128 MHz, CDCl_3) δ 7.58. HRMS–DART (m/z): $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{28}\text{H}_{22}\text{BN}_2\text{O}_4^+$, 475.1824; found, 475.1825.

Synthesis of **1q**



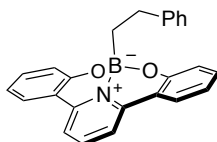
The product was synthesized according to **Method A** using potassium (2-cyanoethyl)trifluoroborate **S1q** (161.0 mg, 1.0 mmol), 2,2'-(pyridine-2,6-diyl)diphenol (263.3 mg, 1.0 mmol), TMSCl (505 μL , 4 mmol), toluene (3.3 mL) at 80 $^\circ\text{C}$ for 14 h. After cooling to room temperature, the reaction crude was passed through a short pad of alumina. The solvent was removed by evaporation and vacuum pump to give PDP-borate **1q** as a pale yellow solid (329.2 mg, 1.01 mmol, quantitative, without further purification). **M.p.** 186–187 $^\circ\text{C}$ (decomp.). **IR** (neat) 758, 1038, 1273, 1454, 1556, 1605, 2231, 2909 cm^{-1} . ^1H NMR (400 MHz, CDCl_3) δ 8.06 (t, $J = 8.0$ Hz, 1H), 7.81 (d, $J = 8.0$ Hz, 2H), 7.73 (d, $J = 8.0$ Hz, 2H), 7.46 (t, $J = 7.6$ Hz, 2H), 7.16 (d, $J = 8.0$ Hz, 2H), 7.00 (t, $J = 7.6$ Hz, 2H), 2.25 (t, $J = 8.4$ Hz, 2H), 0.78 (t, $J = 8.4$ Hz, 2H). ^{13}C NMR (100.6 MHz, CDCl_3) δ 156.4, 148.1, 141.5, 134.6, 125.6, 122.7, 120.7, 120.4, 118.03, 117.96, 11.6. The signal for the carbon attached to the boron atom was not observed. ^{11}B NMR (128 MHz, CDCl_3) δ 6.33. HRMS–DART (m/z): $[\text{M}+\text{NH}_4]^+$ calcd for $\text{C}_{20}\text{H}_{19}\text{BN}_3\text{O}_2^+$, 344.1565; found, 344.1563.

Synthesis of 1r



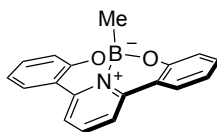
The product was synthesized according to **Method A** using potassium trifluoro(3-(((8*R*,9*S*,13*S*,14*S*)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[*a*]phenanthren-3-yl)oxy)propyl)borate **S1r** (41.8 mg, 0.1 mmol), 2,2'-(pyridine-2,6-diyl)diphenol (26.3 mg, 0.1 mmol), TMSCl (50 μ L, 0.4 mmol), toluene (1 mL) at 110 °C for 16 h. After cooling to room temperature, the reaction crude was passed through a short pad of alumina. The solvent was removed by evaporation and vacuum pump to give PDP-borate **1r** as a pale yellow solid (62.3 mg, 0.107 mmol, quantitative, containing <7% impurities, without further purification). **M.p.** 249–250 °C (decomp.). **IR** (neat) 752, 1070, 1279, 1455, 1608, 1733, 2859, 2926 cm^{-1} . **¹H NMR** (400 MHz, CDCl_3) δ 8.00 (t, J = 8.0 Hz, 1H), 7.77 (d, J = 8.0 Hz, 2H), 7.70 (d, J = 7.6 Hz, 2H), 7.40 (t, J = 7.6 Hz, 2H), 7.10 (m, 3H), 6.95 (t, J = 7.6 Hz, 2H), 6.57 (d, J = 8.4 Hz, 1H), 6.52 (s, 1H), 3.74 (t, J = 7.2 Hz, 2H), 2.92–2.75 (m, 2H), 2.49 (dd, J = 9.2, 8.8 Hz, 1H), 2.41–2.33 (m, 1H), 2.27–1.87 (m, 5H), 1.73–1.33 (m, 8H), 0.89 (s, 3H), 0.49 (t, J = 8.0 Hz, 2H). **¹³C NMR** (100.6 MHz, CDCl_3) δ 221.1, 157.3, 157.2, 148.2, 140.9, 137.4, 134.2, 131.3, 126.1, 125.4, 120.8, 119.8, 118.2, 117.7, 114.6, 112.2, 70.7, 50.4, 48.0, 44.0, 38.4, 35.9, 31.6, 29.6, 26.6, 25.9, 24.1, 21.6, 13.9. The signal for the carbon attached to the boron atom was not observed. **¹¹B NMR** (128 MHz, CDCl_3) δ 6.75. **HRMS–ESI** (m/z): $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{38}\text{H}_{39}\text{BNO}_4^+$, 584.2967; found, 584.2966.

Synthesis of 1s



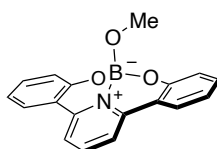
The product was synthesized according to **Method B** using phenethylboronic acid (114.0 mg, 1.0 mmol), 2,2'-(pyridine-2,6-diyl)diphenol (263.3 mg, 1.0 mmol), molecular sieve 3A (50 mg), toluene (5.0 mL) at 100 °C for 14 h. After cooling to room temperature, the reaction crude was washed on a short pad of alumina with Et_2O , then dissolved out with benzene. The benzene was removed by evaporation and vacuum pump to give PDP-borate **1s** as a pale yellow solid (204 mg, 0.541 mmol, 54%, containing <5% impurities, without further purification). **M.p.** 151–152 °C. **IR** (neat) 741, 1049, 1276, 1453, 1557, 1606, 2894, 3060 cm^{-1} . **¹H NMR** (400 MHz, CDCl_3) δ 7.99 (t, J = 8.0 Hz, 1H), 7.74 (d, J = 8.0 Hz, 2H), 7.68 (d, J = 8.0 Hz, 2H), 7.41 (t, J = 8.0 Hz, 2H), 7.13–7.06 (m, 4H), 7.03–6.92 (m, 5H), 2.56 (t, J = 8.4 Hz, 2H), 0.77 (t, J = 8.4 Hz, 2H). **¹³C NMR** (100.6 MHz, CDCl_3) δ 157.2, 148.2, 146.3, 140.9, 134.1, 127.82, 127.80, 125.4, 124.7, 120.8, 119.8, 118.3, 117.7, 30.3. The signal for the carbon attached to the boron atom was not observed. **¹¹B NMR** (128 MHz, CDCl_3) δ 7.66. **HRMS–DART** (m/z): $[\text{M}+\text{NH}_4]^+$ calcd for $\text{C}_{25}\text{H}_{24}\text{BN}_2\text{O}_2^+$, 395.1925; found, 395.1925.

Synthesis of 1t



The product was synthesized according to **Method B** using 2,4,6-trimethyl-1,3,5,2,4,6-trioxatriborinane (71.5 μL , 0.5 mmol), 2,2'-(pyridine-2,6-diyl)diphenol (263.3 mg, 1.0 mmol), molecular sieve 3A (100 mg), toluene (10 mL) at 80 $^{\circ}\text{C}$ for 14 h. After cooling to room temperature, the reaction crude was passed through a short pad of Celite. The solvent was removed by evaporation and vacuum pump to give PDP-borate **1t** as a yellow solid (290.5 mg, 1.01 mmol, quantitative, without further purification). **M.p.** 200–203 $^{\circ}\text{C}$. **IR** (neat) 747, 1045, 1277, 1303, 1455, 1555, 1605, 2931 cm^{-1} . **^1H NMR** (400 MHz, CDCl_3) δ 7.99 (t, J = 8.0 Hz, 1H), 7.76 (d, J = 8.0 Hz, 2H), 7.71 (d, J = 8.0 Hz, 2H), 7.41 (t, J = 7.6 Hz, 2H), 7.11 (d, J = 8.0 Hz, 2H), 6.95 (t, J = 7.6 Hz, 2H), -0.12 (s, 3H). **^{13}C NMR** (100.6 MHz, CDCl_3) δ 157.4, 148.1, 140.7, 134.1, 125.4, 120.9, 119.7, 118.1, 117.7. The signal for the carbon attached to the boron atom was not observed. **^{11}B NMR** (128 MHz, CDCl_3) δ 7.48. **HRMS–DART** (m/z): $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{18}\text{H}_{15}\text{BNO}_2^+$, 288.1190; found, 288.1190.

Synthesis of **7**



The product was synthesized according to **Method B** using trimethyl borate (13.4 μL , 0.10 mmol), 2,2'-(pyridine-2,6-diyl)diphenol (26.3 mg, 0.10 mmol), triethylamine (97.6 μL , 0.70 mmol), and toluene (1 mL) at 100 $^{\circ}\text{C}$ for 20 h. After cooling to room temperature, the reaction crude was concentrated under reduced pressure, and purified by flash column chromatography on silica gel (100/0–90/10, $\text{CH}_2\text{Cl}_2/\text{AcOEt}$) gave **7** (19.0 mg, 62.7 μmol , 63%) as a white solid. **Rf** = 0.40 ($\text{CH}_2\text{Cl}_2/\text{AcOEt}$ = 9/1). **M.p.** 250–251 $^{\circ}\text{C}$. **IR** (neat) 1091, 1200, 1281, 1396, 1459, 1498, 1557, 1610 cm^{-1} . **^1H NMR** (400 MHz, CDCl_3) δ 8.06 (t, J = 8.0 Hz, 1H), 7.85 (d, J = 8.0 Hz, 2H), 7.79 (d, J = 8.0 Hz, 2H), 7.46 (t, J = 7.6 Hz, 2H), 7.20 (d, J = 8.0 Hz, 2H), 7.01 (t, J = 7.6 Hz, 2H), 3.26 (s, 3H). **^{13}C NMR** (100.6 MHz, CDCl_3) δ 156.5, 148.7, 141.1, 134.1, 125.7, 120.6, 120.2, 117.8, 117.6, 49.1. **^{11}B NMR** (128 MHz, CDCl_3) δ 2.74. **HRMS–DART** (m/z): $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{18}\text{H}_{15}\text{BNO}_3^+$, 304.1140; found, 304.1142.

■ X-ray Diffraction Analysis for 1a, 1k, and 1n ■

Molecular structure of **1a** (CCDC 2080640)

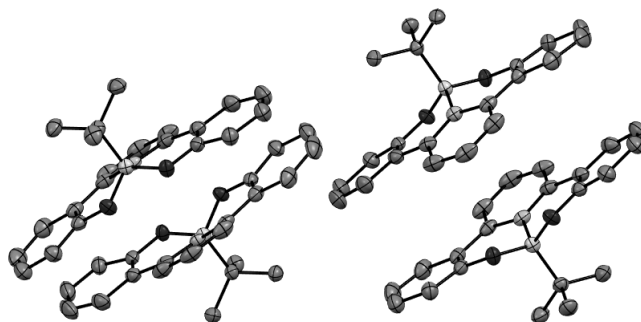


Figure S1-2. ORTEP diagram of **1a**. Ellipsoids are drawn at 50% probability. A single crystal used for the analysis was obtained by recrystallization from *n*-hexane and tetrahydrofuran. Hydrogen atoms are omitted for clarity.

Table S1-1. Crystal data and structure refinement for **1a**

Identification code	compound 1a	
Empirical formula moiety	C ₂₁ H ₂₀ BNO ₂	
Empirical formula sum	C ₂₁ H ₂₀ BNO ₂	
Formula weight sum	329.20	
Temperature	133 K	
Wavelength	0.71075 Å	
Crystal system	Triclinic	
Space group	<i>P</i> −1	
Unit cell dimensions	<i>a</i> = 8.0216(5) Å	α = 90.00000°
	<i>b</i> = 17.2263(9) Å	β = 90.00000°
	<i>c</i> = 24.8701(12) Å	γ = 90.00000°
	<i>V</i> = 3436.6(3) Å ³	
<i>Z</i>	8	
<i>D</i> _x	1.272 g/m ³	
μ	0.080 mm ^{−1}	
<i>F</i> (000)	1392.00	
Crystal size	0.100 × 0.100 × 0.100 mm ³	
Theta range for data collection	2.02 to 27.47°	
Reflections collected	224284	
Independent reflections	13012 [<i>R</i> _{int} = 0.0573]	
Completeness	99.8%	
Absorption correction	none	
Refinement method	Full-matrix least-squares on <i>F</i> ²	
Data / restraints / parameters	15669 / 0 / 901	
Goodness-of-fit on <i>F</i> ²	1.058	
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> (<i>F</i>) = 0.0524, <i>wR</i> (<i>F</i> ²) = 0.1348	
<i>R</i> indices (all data)	<i>R</i> (<i>F</i>) = 0.0948, <i>wR</i> (<i>F</i> ²) = 0.1531	
Largest diff. peak and hole	0.45 and −0.21 e Å ^{−3}	

Molecular structure of **1k** (CCDC 2080643)

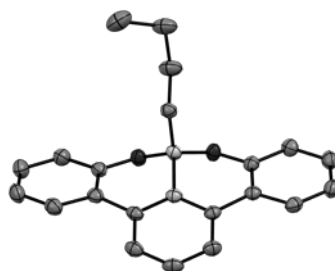


Figure S1-3. ORTEP diagram of **1k**. Ellipsoids are drawn at 50% probability. A single crystal used for the analysis was obtained by recrystallization from *n*-hexane and tetrahydrofuran. Hydrogen atoms are omitted for clarity.

Table S1-2. Crystal data and structure refinement for **1k**

Identification code	compound 1k	
Empirical formula moiety	C ₂₁ H ₂₀ BMO ₂	
Empirical formula sum	C ₂₁ H ₂₀ BMO ₂	
Formula weight sum	329.20	
Temperature	133K	
Wavelength	0.71075 Å	
Crystal system	Monoclinic	
Space group	<i>P</i> 1 2 ₁ / <i>n</i> 1	
Unit cell dimensions	<i>a</i> = 9.4640(7) Å <i>b</i> = 11.6859(6) Å <i>c</i> = 16.0891(9) Å <i>V</i> = 1700.99 Å ³	<i>β</i> = 107.069 (8)°
<i>Z</i>	4	
<i>D</i> _x	1.285 g/m ³	
<i>μ</i>	0.081 mm ⁻¹	
<i>F</i> (000)	696.00	
Crystal size	0.200 × 0.200 × 0.200 mm ³	
Theta range for data collection	2.189 to 27.484°	
Reflections collected	33631	
Independent reflections	15669 [<i>R</i> _{int} = 0.0284]	
Completeness	99.8%	
Absorption correction	multi-scan	
Refinement method	Full-matrix least-squares on <i>F</i> ²	
Data / restraints / parameters	3894 / 0 / 226	
Goodness-of-fit on <i>F</i> ²	1.017	
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> (<i>F</i>) = 0.0518, <i>wR</i> (<i>F</i> ²) = 0.1052	
<i>R</i> indices (all data)	<i>R</i> (<i>F</i>) = 0.0818, <i>wR</i> (<i>F</i> ²) = 0.11563	
Largest diff. peak and hole	0.258 and -0.295 e Å ⁻³	

Molecular structure of **1n** (CCDC 2080645)

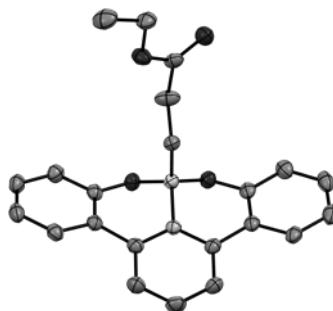


Figure S1-4. ORTEP diagram of **1n**. Ellipsoids are drawn at 50% probability. A single crystal used for the analysis was obtained by recrystallization from *n*-hexane and tetrahydrofuran. Hydrogen atoms are omitted for clarity.

Table S1-3. Crystal data and structure refinement for **1n**

dentification code	compound 1n	
Empirical formula moiety	C ₂₂ H ₂₀ BNO ₄	
Empirical formula sum	C ₂₂ H ₂₀ BNO ₄	
Formula weight sum	373.21	
Temperature	123 K	
Wavelength	0.71075 Å	
Crystal system	orthorhombic	
Space group	<i>P b c a</i>	
Unit cell dimensions	<i>a</i> = 13.0888(15) Å	$\alpha = 90.0000^\circ$
	<i>b</i> = 15.1668(14) Å	$\beta = 90.0000^\circ$
	<i>c</i> = 18.8778(17) Å	$\gamma = 90.0000^\circ$
	<i>V</i> = 3747.5(6) Å ³	
<i>Z</i>	8	
<i>D</i> _x	1.323 g/cm ⁻³	
μ	0.090 mm ⁻¹	
<i>F</i> (000)	1568.0	
Crystal size	0.100 × 0.100 × 0.100 mm ³	
Theta range for data collection	1.72 to 27.45°	
Index ranges	−16 ≤ <i>h</i> ≤ 16, −19 ≤ <i>k</i> ≤ 19, −24 ≤ <i>l</i> ≤ 23	
Reflections collected	32937	
Independent reflections	4283 [<i>R</i> _{int} = 0.0594]	
Completeness	99.9%	
Absorption correction	multi-scan	
Max. and min. transmission	0.991 and 0.520	
Refinement method	Full-matrix least-squares on <i>F</i> ²	
Data / restraints / parameters	4283 / 0 / 253	
Goodness-of-fit on <i>F</i> ²	1.048	
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> (<i>F</i>) = 0.0495, <i>wR</i> (<i>F</i> ²) = 0.1182	
<i>R</i> indices (all data)	<i>R</i> (<i>F</i>) = 0.0643, <i>wR</i> (<i>F</i> ²) = 0.1271	
Largest diff. peak and hole	0.470 and −0.223 e Å ⁻³	

■ Computational Study of 1a ■

Computational Method. The calculations were performed at RIKEN on Hokusai Big Waterfall (BW) using Gaussian 16 (revision C.01) program packages.¹⁹ The DFT method was employed using the B3LYP hybrid functional. Structures were optimized with the 6-31++G(d,p) basis set.

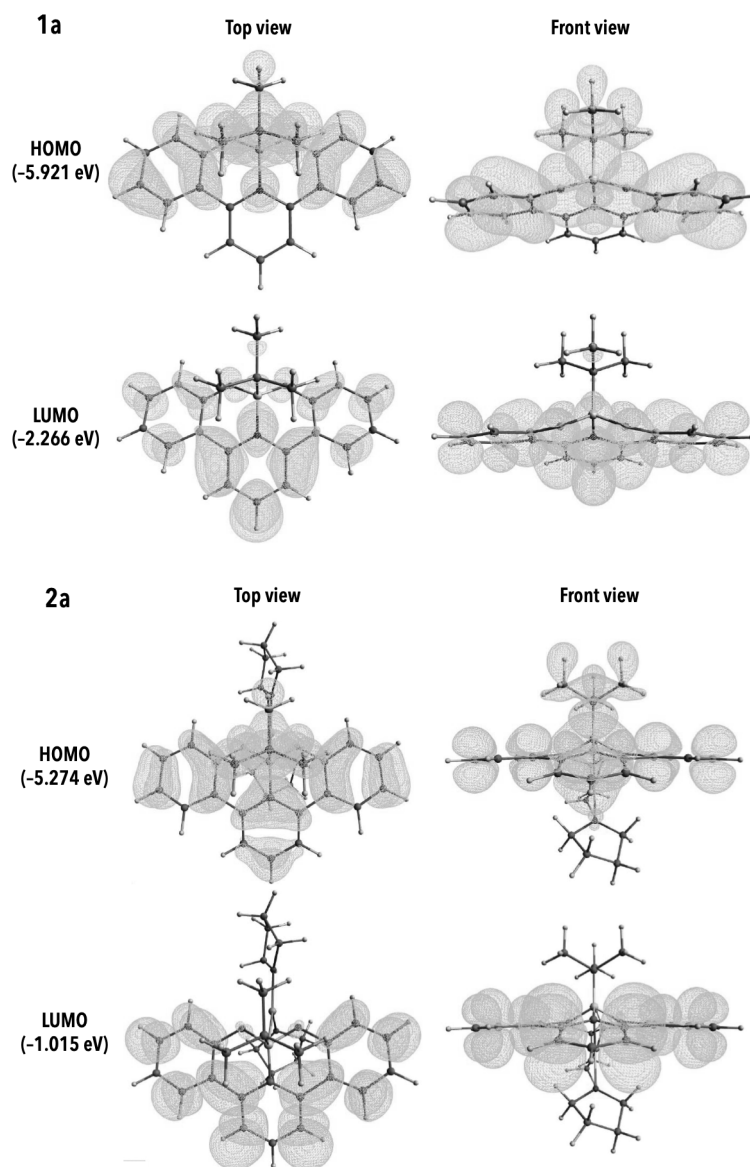


Figure S1-5. Kohn-Sham orbitals of **1a** and **2a** in the S_0 states, calculated at the B3LYP/6-31++G(d,p) level. Orbital energies are shown in parentheses.

Cartesian coordinates of 1a

C	-2.4235274296	0.6778368183	-0.1911333492
C	-2.3311000366	-0.5875637057	-0.8177046940
O	1.1644243631	-1.1930936550	-0.9960504574
O	-1.1644872823	-1.1931525841	-0.9959939677
B	-0.0000160600	-0.8670836163	-0.1568494993

N	-0.0000375900	0.7517553652	0.0248636299
C	0.0001175500	-1.6744897703	1.2779266247
C	1.2432369526	-1.3788784752	2.1467196369
H	2.1768129075	-1.6409954725	1.6432610706
H	1.3047402561	-0.3256345282	2.4410464285
H	1.1998453158	-1.9663710489	3.0723965636
C	-1.2428787949	-1.3790455046	2.1469565918
H	-1.3045190812	-0.3257931385	2.4412226180
H	-2.1765144092	-1.6413831636	1.6437292019
H	-1.1991714563	-1.9664608396	3.0726676452
C	0.0001934800	-3.1862722656	0.9471620876
H	0.0003290600	-3.7801666505	1.8696345129
H	-0.8818809880	-3.4687087152	0.3664754684
H	0.8821931232	-3.4685803103	0.3662988380
C	-3.4966272104	-1.2169689717	-1.2876940930
H	-3.3896071949	-2.1692071070	-1.7926551785
C	-4.7363687041	-0.6409910295	-1.0761397768
H	-5.6288115558	-1.1475192839	-1.4270153233
C	-4.8477106156	0.5798193348	-0.3951908282
H	-5.8208481655	1.0158588673	-0.2058055292
C	-3.7014111539	1.2272197216	0.0301645899
H	-3.8006529523	2.1704413970	0.5527983295
C	-1.1987248148	2.7826758257	0.3955665181
H	-2.1349712308	3.3166274242	0.4496917578
C	-0.0000680000	3.4554461638	0.5656099478
H	-0.0000811600	4.5162998102	0.7890508435
C	1.1986036121	2.7827012050	0.3955790882
H	2.1348380369	3.3166727218	0.4497064076
C	1.1936678916	1.4141773520	0.1073457997
C	-1.1937600055	1.4141539147	0.1073325094
C	2.4234459681	0.6778808776	-0.1911302593
C	2.3310282061	-0.5874879275	-0.8177667982
C	3.4965577029	-1.2168552833	-1.2878019340
H	3.3895442652	-2.1690717488	-1.7928053326
C	4.7362937356	-0.6408704564	-1.0762370131
H	5.6287382648	-1.1473691722	-1.4271508139
C	4.8476283550	0.5799100570	-0.3952328280
H	5.8207622801	1.0159561142	-0.2058440189
C	3.7013262792	1.2272735919	0.0301706899
H	3.8005632886	2.1704761004	0.5528390391

Cartesian coordinates of 2a

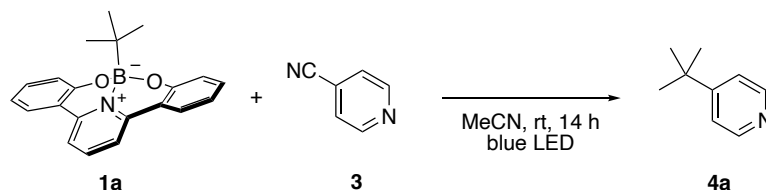
C	1.8627378205	-2.2621754408	-0.2957013950
C	0.4800365379	-2.2874682751	-0.6197092790
O	-0.4785196044	1.1869454519	-0.6080663221
B	0.4802007803	0.1388919020	-1.1842333235
C	0.5787044431	0.2597808832	-2.8285311845
C	1.1985341682	1.6060613258	-3.2682803551
H	0.5918050981	2.4636478305	-2.9590984268
H	2.2047492254	1.7446179268	-2.8560964698
H	1.2854271984	1.6476568928	-4.3641406455
C	1.4508793210	-0.8661002145	-3.4301368403
H	2.4714156333	-0.8473211230	-3.0303720667
H	1.0364198784	-1.8610402994	-3.2364149282

H	1.5251041081	-0.7515837636	-4.5217174736
C	-0.8314918399	0.1566863746	-3.4520394849
H	-0.7844065039	0.2417298813	-4.5476201317
H	-1.3020780503	-0.8055488532	-3.2171095541
H	-1.4883415483	0.9564726748	-3.0883216225
C	-0.1879522649	-3.5094992502	-0.7795903192
H	-1.2469026002	-3.4876857719	-1.0201874734
C	0.4995592827	-4.7169101332	-0.6658213947
H	-0.0296619557	-5.6550007476	-0.8086064920
C	1.8714283655	-4.7118859025	-0.3937571078
H	2.4236015620	-5.6444959979	-0.3277305859
C	2.5303800716	-3.4965628254	-0.2103743298
H	3.5955294728	-3.5057809018	-0.0006055182
C	3.7147638666	-0.8813804710	0.7427945959
H	4.2575952862	-1.7774641308	1.0273666354
C	4.2044720065	0.3629171866	1.1433611840
H	5.1365796957	0.4209783834	1.6991515661
C	3.4765758869	1.5268117682	0.8905540437
H	3.8365004113	2.4705046388	1.2886709382
C	2.2705193853	1.4606523032	0.1692122913
C	2.5109386672	-0.9654852559	0.0194184660
C	1.3753607961	2.6330775347	0.0103498828
C	0.0087829588	2.4237094189	-0.3156985943
C	-0.8901541021	3.4991625672	-0.3269444037
H	-1.9281410489	3.2974673304	-0.5754158608
C	-0.4515571414	4.7956040494	-0.0619211228
H	-1.1576339771	5.6208800891	-0.0908002329
C	0.8995430764	5.0291167325	0.2142737652
H	1.2581757257	6.0374720417	0.3975842348
C	1.7885819587	3.9553422402	0.2504903824
H	2.8348554925	4.1493270582	0.4657596131
C	1.8257389725	0.2175629202	-0.3275429656
Li	-1.4748633730	-0.1668552010	0.3873005680
O	-0.2451045491	-1.1455282335	-0.7695746034
C	-4.0060790207	-0.7099442326	-1.1313108136
O	-3.3897731661	-0.3867146725	0.1448031988
C	-4.4002818613	0.0093321010	1.1065603012
C	-5.7430594863	-0.3384490692	0.4603137033
C	-5.4348626056	-0.1754710839	-1.0375182492
H	-3.4062304185	-0.2527359888	-1.9205703752
H	-3.9875198394	-1.7998222118	-1.2557590793
H	-4.2058276421	-0.5217862103	2.0419968855
H	-4.3040701369	1.0875152453	1.2862136086
H	-6.0198571083	-1.3751501465	0.6831248491
H	-6.5506622773	0.3109857352	0.8092971900
H	-6.1259118939	-0.7247862404	-1.6827437018
H	-5.4687332278	0.8816243423	-1.3241080520
C	-0.7881864220	-1.5729098660	2.9052599324
O	-1.1427011043	-0.2853988609	2.3206665301
C	-0.4979180147	0.7858687846	3.0617773053
C	0.6591264933	0.1182734815	3.7985299040
C	0.0634131543	-1.2577498069	4.1408495758
H	-1.7136087827	-2.1080492715	3.1418878288
H	-0.2291120736	-2.1413025133	2.1554817266

H	-0.1894161337	1.5510448564	2.3469567788
H	-1.2291294798	1.2170455331	3.7593053155
H	1.5216527350	0.0156034192	3.1323496055
H	0.9695418808	0.6829563326	4.6823203591
H	0.8238760432	-2.0232217999	4.3165748007
H	-0.5644181085	-1.1908846523	5.0368062330

■ Procedure for Decyanoalkylation ■

Synthesis of 4a



Under an ambient atmosphere, to an oven-dried screw-top 5 mL vial with a stirring bar was added PDP-borate **1a** (49.0 mg, 0.15 mmol), 4-cyanopyridine (**3**) (10.4 mg, 0.1 mmol) and the vial was brought to a glovebox. To the vial was added MeCN (1 ml) and removed from the glovebox. After sealing the vial with Teflon tape, the vial was placed in EvoluChem photoreactor (PhotoRedOx Duo) equipped with a 45W blue LED (Figure S1-7). After stirred for 14 h, volatiles were removed under reduced pressure. The residue was dissolved in CDCl₃ and added 1,1,2,2-tetrachloroethane (33.1 mg, 0.197 mmol) as an internal standard. ¹H NMR (400 MHz) yield (88%) was obtained by comparing the relative value of integration for the peak observed at 8.51 ppm of **4a**¹⁹ with that of 1,1,2,2-tetrachloroethane observed at 5.96 ppm (Figure S1-6). The generation of **4a** was also confirmed by observation of the corresponding molecular ion peak with GC-MS analysis.

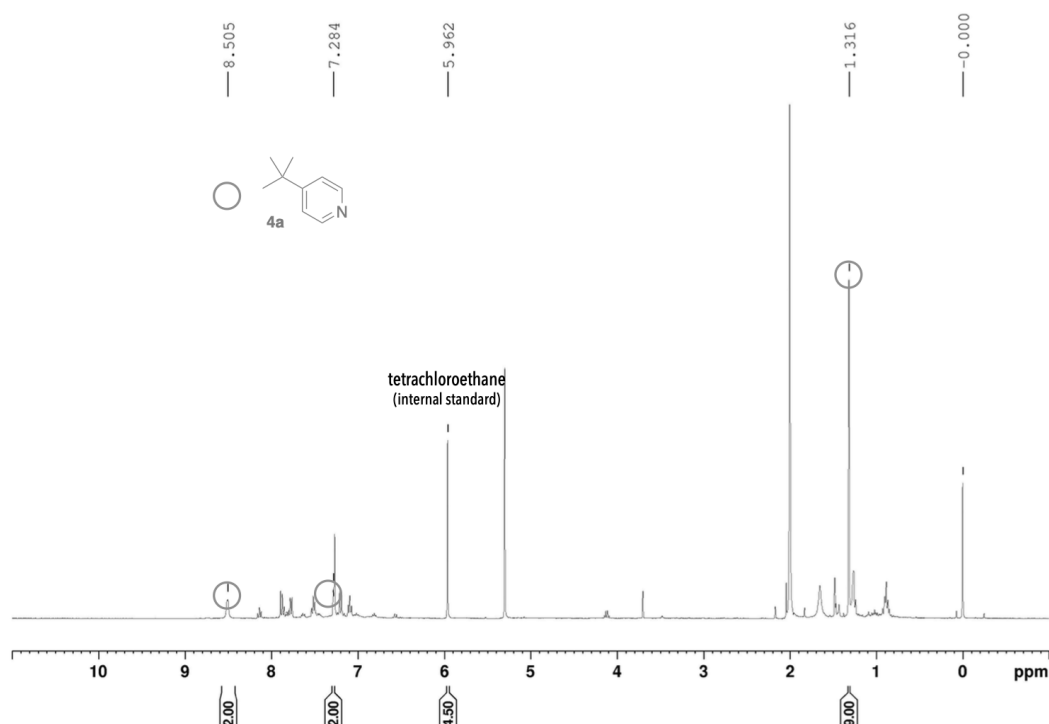


Figure S1-6. ¹H NMR analysis

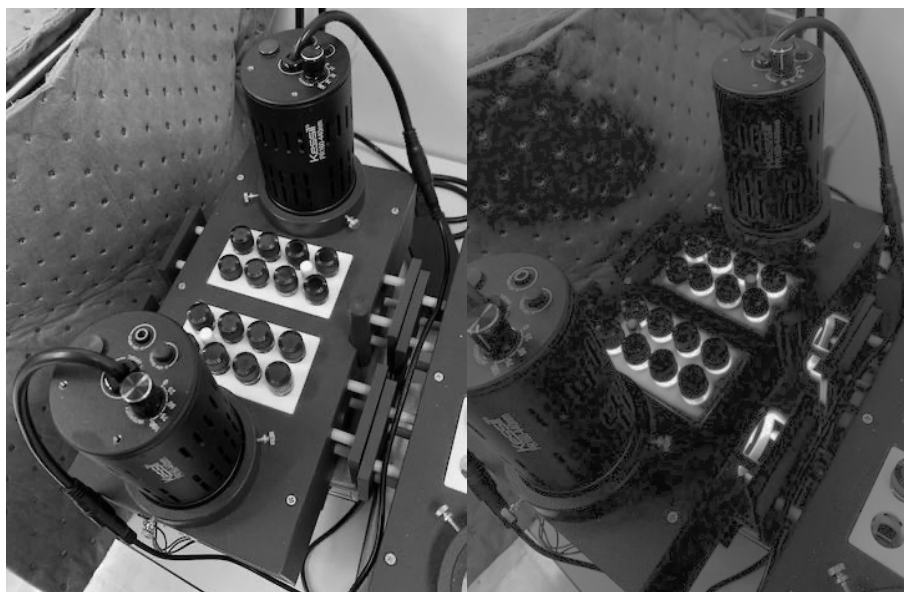
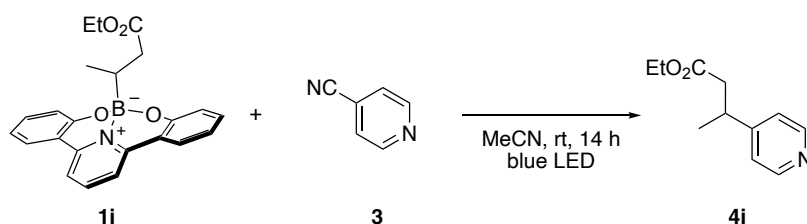


Figure S1-7. Light set up

Synthesis of **4i**



Under an ambient atmosphere, to an oven-dried screw-top 5 mL vial with a stirring bar was added PDP-borate **1i** (77.4 mg, 0.20 mmol), 4-cyanopyridine (**3**) (10.4 mg, 0.10 mmol) and the vial was brought to a glovebox. To the vial was added MeCN (1 mL) and removed from the glovebox. After sealing the vial with Teflon tape, the vial was placed in EvoluChem photoreactor (PhotoRedOx Duo) equipped with a 45W blue LED. After stirred for 14 h, volatiles were removed under reduced pressure. The residue was dissolved in CDCl₃ and added 1,1,2,2-tetrachloroethane (33.5 mg, 0.20 mmol) as an internal standard. ¹H NMR (400 MHz) yield (48%) was obtained by comparing the relative value of integration for the peak observed at 8.52 ppm of **4i**²¹ with that of 1,1,2,2-tetrachloroethane observed at 5.96 ppm (Figure S1-8). The generation of **4i** was also confirmed by observation of the corresponding molecular ion peak with GC-MS analysis.

The reaction mixture was treated with trifluoro acetic acid (375 μL, 1 mmol). After stirred for 1 h, the volatiles were removed under reduced pressure, purification by flash column chromatography on silica gel (100/0–50/50, hexane/AcOEt) and GPC (eluent: EtOAc) gave the **4i** (3.7 mg, 19% isolated yield). The ¹H and ¹³C NMR spectra data of product **4i** were consistent with the literature.²¹

¹H NMR (400 MHz, CDCl₃) δ 8.52 (br s, 2H), 7.16 (d, *J*=4.1 Hz, 2H), 4.08 (q, *J*= 7.0 Hz, 2H), 3.27 (m, 1H), 2.67–2.51 (m, 2H), 1.31 (d, *J*= 6.9 Hz, 3H), 1.18 (t, *J*=7.0 Hz, 3H).

¹³C NMR (100.6 MHz, CDCl₃) δ 171.7, 154.6, 149.9, 122.3, 60.5, 41.9, 35.8, 21.2, 14.1.

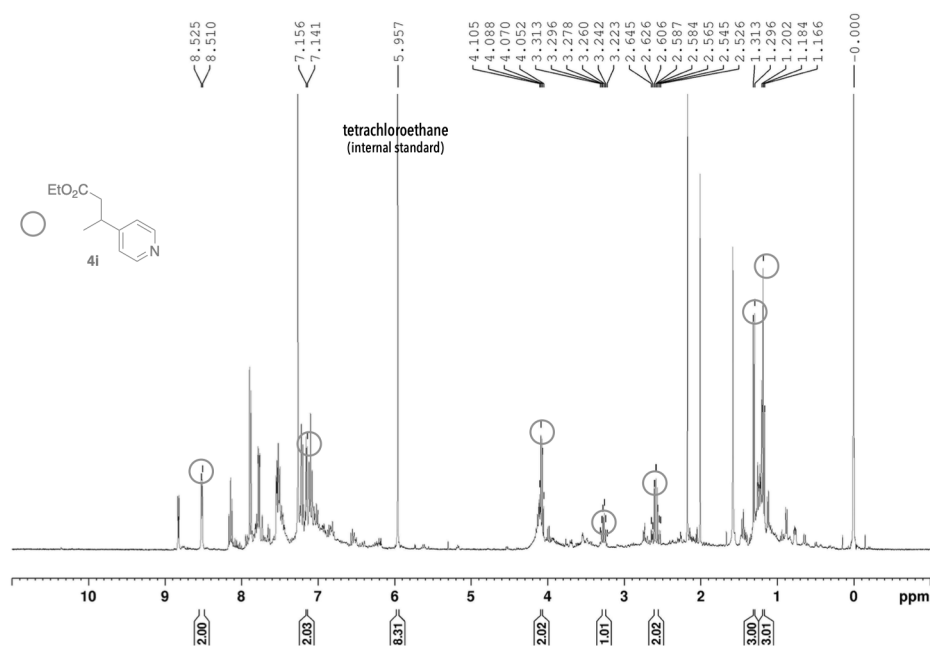
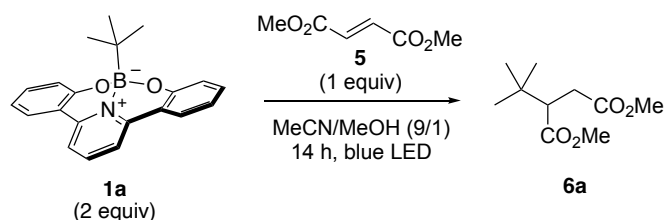


Figure S1-8. ^1H NMR analysis

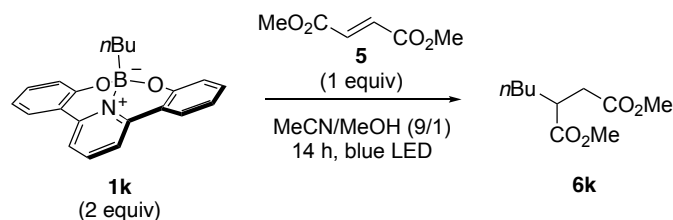
■ Procedure for Giese Addition ■

Synthesis of **6a**



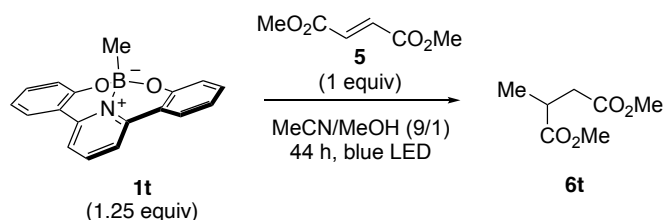
Under an ambient atmosphere, to an oven-dried screw-top 5 mL vial with a stirring bar was added PDP-borate **1a** (65.8 mg, 0.20 mmol), dimethylfumarate **5** (14.4 mg, 0.10 mmol) and the vial was brought to a glovebox. To the vial was added MeCN/MeOH (9/1, 1 mL) and removed from the glovebox. After sealing the vial with Teflon tape, the vial was placed in EvoluChem photoreactor (PhotoRedOx Duo) equipped with a 45W blue LED. After stirred for 14 h, volatiles were removed under reduced pressure, purification by flash column chromatography on silica gel (100/0–80/20, hexane/Et₂O) to give **6a** (20.2 mg, quantitative). The ^1H and ^{13}C NMR spectra data of product **6a** were consistent with the literature.²⁰ ^1H NMR (400 MHz, CDCl₃) δ 3.70 (s, 3H), 3.66 (s, 3H), 2.80 (m, 1H), 2.64 (d, J = 12.0 Hz, 1H), 2.48 (d, J = 16.4 Hz, 1H), 0.96 (s, 9H). ^{13}C NMR (100.6 MHz, CDCl₃) δ 174.7, 173.2, 51.8, 51.4, 51.2, 32.6, 27.8.

Synthesis of 6k



Under an ambient atmosphere, to an oven-dried screw-top 5 mL vial with a stirring bar was added PDP-borate **1k** (65.8 mg, 0.20 mmol), dimethylfumarate (**5**) (14.4 mg, 0.10 mmol) and the vial was brought to a glovebox. To the vial was added MeCN/MeOH (9/1, 1 mL) and removed from the glovebox. After sealing the vial with Teflon tape, the vial was placed in EvoluChem photoreactor (PhotoRedOx Duo) equipped with a 45W blue LED. After stirred for 14 h, volatiles were removed under reduced pressure, purification by flash column chromatography on silica gel (100/0–80/20, hexane/Et₂O) to give **6k** (18.4 mg, 91.0 μ mol, 91%). The ¹H and ¹³C NMR spectra data of product **6k** were consistent with the literature.²⁰ ¹H NMR (400 MHz, CDCl₃) δ 3.70 (s, 3H), 3.67 (s, 3H), 2.83 (m, 1H), 2.72 (dd, *J* = 16.4, 9.6 Hz, 1H), 2.44 (dd, *J* = 16.4, 4.0 Hz, 1H), 1.70–1.45 (m, 2H), 1.38–1.21 (m, 4H), 0.92–0.83 (m, 3H). ¹³C NMR (100.6 MHz, CDCl₃) δ 175.6, 172.5, 51.81, 51.76, 41.2, 35.8, 31.7, 29.1, 22.5, 13.9.

Synthesis of 6t



According to **Method B** using 2,4,6-trimethyl-1,3,5,2,4,6-trioxatriborinane (7 μ L, 0.10 mmol), 2,2'-(pyridine-2,6-diyl)diphenol (26.3 mg, 0.10 mmol), MeCN (1 mL) in a screw-top 5 mL vial at room temperature for 24 h. The solvent was removed by evaporation and vacuum pump to give PDP-borate **1t** and to the vial was added MeCN (800 μ L) to prepare a stock solution.

In a glovebox, to another screw-top 5 mL vial was added the stock solution (200 μ L, 0.025 mmol), dimethylfumarate (**5**) (2.8 mg, 0.02 mmol) and MeOH (20 μ L). After sealing the vial with Teflon tape, the vial was placed in EvoluChem photoreactor (PhotoRedOx Duo) equipped with a 45W blue LED. After stirred for 48 h, volatiles were removed under reduced pressure. The residue was dissolved in CDCl₃ and added 1,1,2,2-tetrachloroethane (33.6 mg, 0.20 mmol) as an internal standard. ¹H NMR (400 MHz) yield (42%) was obtained by comparing the relative value of integration for the doublet peak observed at 1.22 ppm of **6t**²² with that of 1,1,2,2-tetrachloroethane observed at 5.96 ppm (Figure S1-9). The generation of **6t** was also confirmed by observation of the corresponding molecular ion peak with GC-MS analysis.

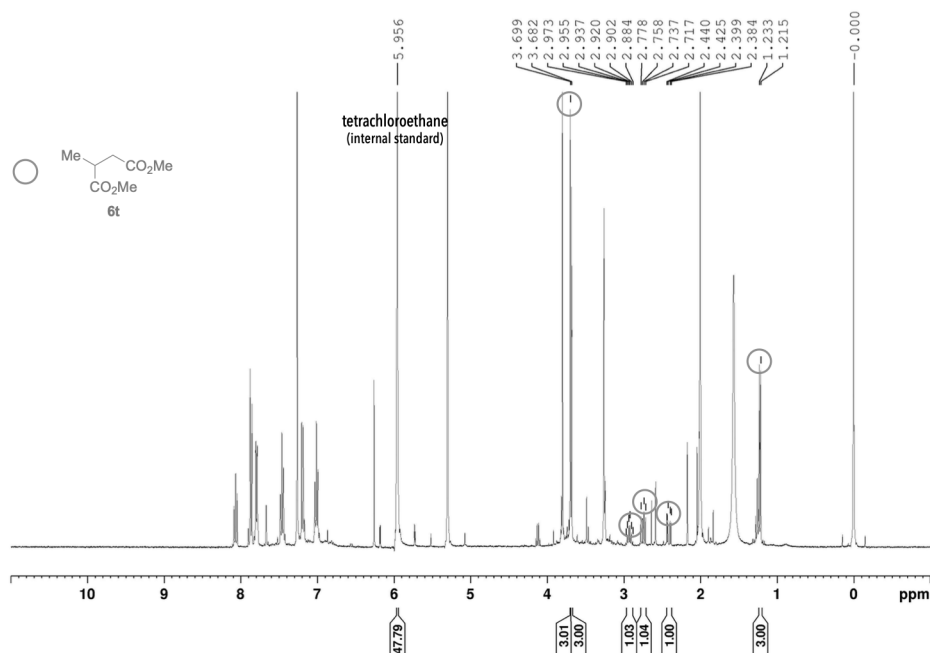
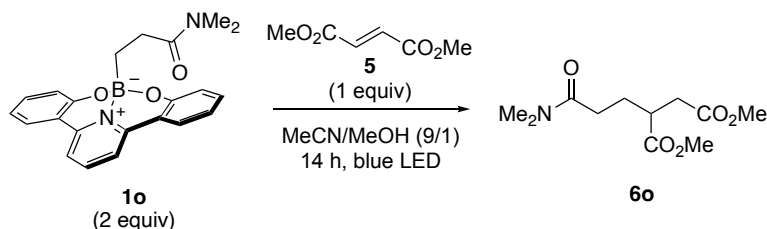


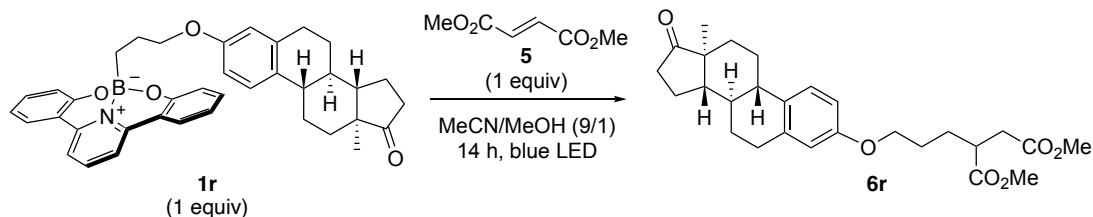
Figure S1-9. ^1H NMR analysis.

Synthesis of **6o**



Under an ambient atmosphere, to an oven-dried screw-top 5 mL vial with a stirring bar was added PDP-borate **1o** (74.5 mg, 0.20 mmol), dimethylfumarate (**5**) (14.4 mg, 0.10 mmol) and the vial was brought to a glovebox. To the vial was added MeCN/MeOH (9/1, 1 mL) and removed from the glovebox. After sealing the vial with Teflon tape, the vial was placed in EvoluChem photoreactor (PhotoRedOx Duo) equipped with a 45W blue LED. After stirred for 14 h, volatiles were removed under reduced pressure, purification by flash column chromatography on silica gel (100/0–50/50, hexane/AcOEt) to give colorless oil **6o** (16.5 mg, 67.3 μmol , 67%). **IR** (neat) 1044, 1162, 1263, 1365, 1437, 1636, 1729, 2953 cm^{-1} . **^1H NMR** (400 MHz, CDCl_3) δ 3.70 (s, 3H), 3.67 (s, 3H), 3.02–2.87 (m, 7H), 2.76 (dd, J = 16.4, 8.8 Hz, 1H), 2.50 (dd, J = 8.8, 5.2 Hz, 1H), 2.35 (t, J = 7.6 Hz, 2H), 2.03–1.87 (m, 2H). **^{13}C NMR** (100.6 MHz, CDCl_3) δ 175.0, 172.2, 171.7, 51.9, 51.8, 40.6, 37.1, 36.1, 35.4, 30.5, 27.1. **HRMS–DART** (m/z): $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{11}\text{H}_{20}\text{NO}_5^+$, 246.1336; found, 246.1335.

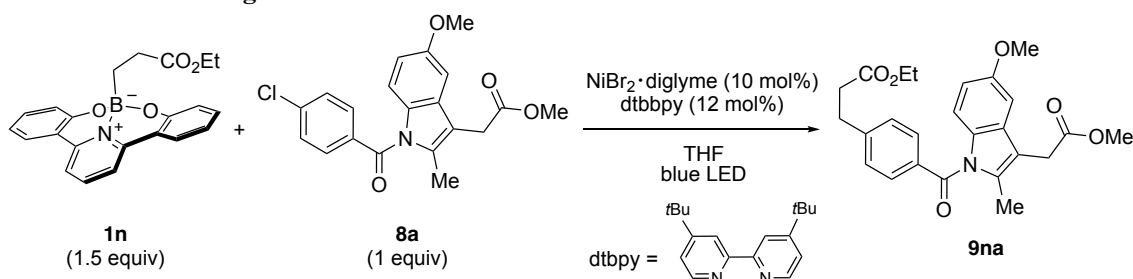
Synthesis of 6r



Under an ambient atmosphere, to an oven-dried screw-top 5 mL vial with a stirring bar was added PDP-borate **1r** (58.4 mg, 0.10 mmol), dimethylfumarate dimethylfumarate (**5**) (14.4 mg, 0.10 mmol) and the vial was brought to a glovebox. To the vial was added MeCN/MeOH (9/1, 1 mL) and removed from the glovebox. After sealing the vial with Teflon tape, the vial was placed in EvoluChem photoreactor (PhotoRedOx Duo) equipped with a 45W blue LED. After stirred for 14 h, volatiles were removed under reduced pressure, purification by flash column chromatography on silica gel (100/0–50/50, CH₂Cl₂/AcOEt) to give colorless oil **6r** (8.3 mg, 18.2 μ mol, 18%). **IR** (neat) 1164, 1254, 1281, 1436, 1500, 1610, 1737, 2943 cm⁻¹. **¹H NMR** (400 MHz, CDCl₃) δ 7.19 (d, J = 8.4 Hz, 1H), 6.69 (d, J = 8.4 Hz, 1H), 6.62 (s, 1H), 3.93 (br s, 2H), 3.71 (s, 3H), 3.68 (s, 3H), 2.98–2.85 (m, 3H), 2.76 (dd, J = 16.4, 9.2 Hz, 1H), 2.55–2.37, (m, 3H), 2.29–1.59 (m, 10H), 1.55–1.37 (m, 5H), 0.91 (s, 3H). **¹³C NMR** (100.6 MHz, CDCl₃) δ 221.0, 175.2, 172.3, 156.9, 137.8, 132.1, 126.3, 114.5, 112.1, 67.2, 51.9, 51.8, 50.4, 48.0, 44.0, 40.9, 38.4, 35.92, 35.89, 31.6, 29.7, 28.5, 26.8, 26.6, 25.9, 21.6, 13.9. **HRMS–DART** (m/z): [M+H]⁺ calcd for C₂₇H₃₇O₆⁺, 457.2585; found, 457.2585.

■ Procedure for Ni-catalyzed Alkylation ■

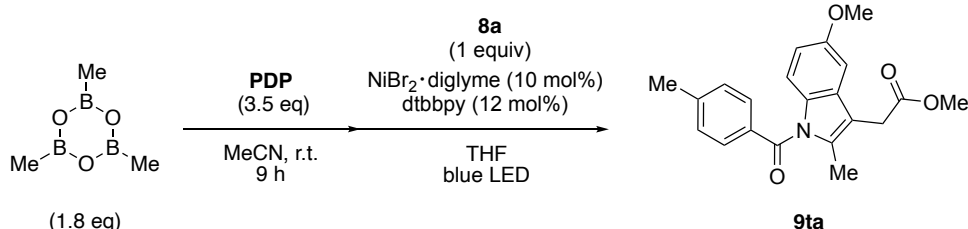
Indomethacin analog **9na**



Under an ambient atmosphere, to an oven-dried screw-top 5 mL vial with a stirring bar was added NiBr₂·diglyme (3.6 mg, 10 μ mol), dtbbpy (4,4'-di-*tert*-butyl-2,2'-bipyridyl) (3.2 mg, 12 μ mol), PDP-borate **1n** (56.0 mg, 0.15 mmol) and indomethacin methyl ester **8a** (37.2 mg, 0.10 mmol). The vial was brought to a glovebox and added THF (1 mL). After sealing the vial with Teflon tape, the vial was placed in EvoluChem photoreactor (PhotoRedOx Duo) equipped with a 45W blue LED. After stirred for 14 h, the crude product was concentrated under reduced pressure, purified by flash column chromatography on silica gel (100/0–70/30, hexane/AcOEt) and GPC (eluent: EtOAc) gave yellow oil **9na** (17.8 mg, 40.7 μ mol, 41%) as a yellow oil. **R_f** = 0.21 (hexane/AcOEt = 7/3). **IR** (neat) 1167, 1225, 1319, 1478, 1683, 1733, 2362, 2954 cm⁻¹. **¹H NMR** (400 MHz, CDCl₃) δ 7.65 (d, J = 7.2 Hz, 2H) 7.32 (d, J = 7.2 Hz, 2H), 6.96 (s, 1H), 6.87 (d, J = 8.8 Hz, 1H), 6.65 (d, J = 8.8 Hz, 1H), 4.14 (q, J = 6.8 Hz, 2H), 3.84 (s, 3H), 3.70 (s, 3H), 3.67 (s, 2H), 3.05 (t, J = 7.6 Hz, 2H), 2.68 (t, J = 7.6 Hz, 2H), 2.37 (s, 3H), 1.25 (t, J = 6.8 Hz, 3H). **¹³C NMR** (100.6 MHz, CDCl₃) δ 172.4, 171.5, 169.3, 155.9, 146.1, 136.1, 133.6, 131.0, 130.5, 130.1, 128.7, 115.0, 112.0, 111.5, 101.1, 60.6, 55.7, 52.1, 35.4, 30.9,

30.2, 14.2, 13.3. **HRMS–DART** (m/z): $[M+H]^+$ calcd for $C_{25}H_{28}NO_6^+$, 438.1911; found, 438.1912.

Indomethacin analog **9ta**



According to **Method B** using 2,4,6-trimethyl-1,3,5,2,4,6-trioxatriborinane (24.5 μ L, 0.18 mmol), 2,2'-(pyridine-2,6-diyl)diphenol (92.2 mg, 0.35 mmol), MeCN (3.5 mL) in a screw-top 5 mL vial at room temperature for 9 h. The solvent was removed by evaporation and vacuum pump to give PDP-borate **1t** and used for next step without further purification. Under an ambient atmosphere, to the screw-top 5 mL vial with a stirring bar was added $NiBr_2 \cdot diglyme$ (3.6 mg, 10 μ mol), dtbbpy (4,4'-di-*tert*-butyl-2,2'-bipyridyl) (3.2 mg, 12 μ mol) and indomethacin methyl ester **8a** (37.2 mg, 0.10 mmol). The vial was brought to a glovebox, and added THF (1 mL). After sealing the vial with Teflon tape, the vial was placed in EvoluChem photoreactor (PhotoRedOx Duo) equipped with a 45W blue LED. After stirred for 59 h, volatiles were removed under reduced pressure. The residue was dissolved in $CDCl_3$ and added 1,1,2,2-tetrachloroethane (31.5 mg, 0.188 mmol) as an internal standard. 1H NMR (400 MHz) yield (43%) was obtained by comparing the relative value of integration for the singlet peak observed at 2.46 ppm of **9ta**²⁰ with that of 1,1,2,2-tetrachloroethane observed at 5.96 ppm (Figure S1-10). The generation of **9ta** was also confirmed by observation of the corresponding molecular ion peak with GC-MS and HRMS–DART analysis. **HRMS–DART** (m/z): $[M+H]^+$ calcd for $C_{21}H_{22}NO_4^+$, 352.1543; found, 352.1545.

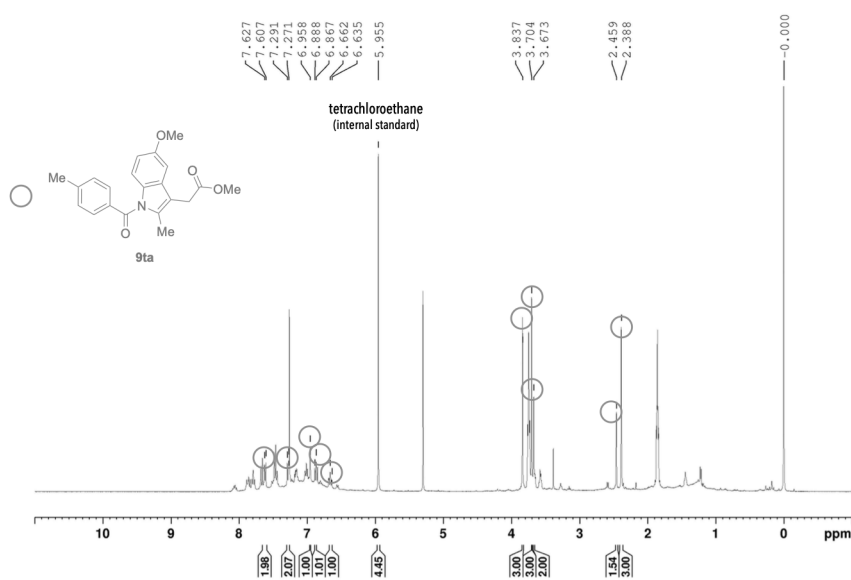
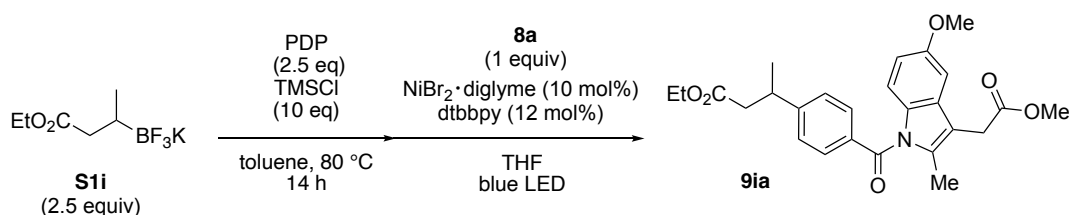


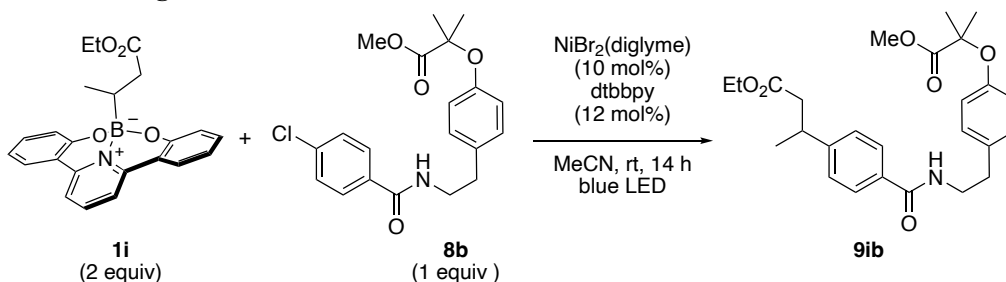
Figure S1-10. 1H NMR analysis

Indomethacin analog **9ia**



Under an ambient atmosphere, to an oven-dried screw-top 5 mL vial with a stirring bar was added 2,2'-(pyridine-2,6-diyl)diphenol (65.8 mg, 0.25 mmol), potassium (4-ethoxy-4-oxobutan-2-yl)trifluoroborate **S1i** (55.5 mg, 0.25 mmol). The vial was brought to a glovebox, and added toluene (833 μ L) and TMSCl (126 μ L 7.0 mmol). After sealing the vial with Teflon tape, the reaction was placed in aluminum heating block at 80 °C. After stirred for 14 h, the solvent was removed by evaporation and vacuum pump. To the mixture was added NiBr₂·diglyme (3.6 mg, 10 μ mol), dtbbpy (4,4'-di-*tert*-butyl-2,2'-bipyridyl) (3.2 mg, 12 μ mol) and indomethacin methyl ester **8a** (37.2 mg, 0.10 mmol) under an ambient atmosphere. The vial was brought to a glovebox, and added THF (500 μ L). After sealing the vial with Teflon tape, the reaction was placed in EvoluChem photoreactor (PhotoRedOx Duo) equipped with a 45W blue LED. After stirred for 14 h, the reaction crude was concentrated under reduced pressure, and purified by flash column chromatography on silica gel (80/0/20–60/20/20, hexane/AcOEt/CH₂Cl₂) gave **9ia** (33.4 mg, 74.0 μ mol, 74%) as a yellow oil. **Rf** = 0.21 (hexane/AcOEt/ CH₂Cl₂ = 7/1/2). **IR** (neat) 1034, 1165, 1224, 1263, 1313, 1680, 1731, 2961 cm⁻¹. **¹H NMR** (400 MHz, CDCl₃) δ 7.66 (d, *J* = 8.0 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 6.96 (d, *J* = 2.4 Hz, 1H), 6.88 (d, *J* = 9.2 Hz, 1H), 6.65 (dd, *J* = 9.2, 2.4 Hz, 1H), 4.09 (q, *J* = 7.2 Hz, 2H), 3.84 (s, 3H), 3.70 (s, 3H), 3.67 (s, 2H), 3.38 (m, 1H), 2.69–2.55 (m, 2H), 2.36 (s, 3H), 1.35 (d, *J* = 7.2 Hz, 3H), 1.20 (t, *J* = 7.2 Hz, 3H). **¹³C NMR** (100.6 MHz, CDCl₃) δ 171.9, 171.5, 169.3, 155.9, 151.2, 136.1, 133.7, 131.0, 130.5, 130.1, 127.2, 115.0, 112.0, 111.5, 101.1, 60.5, 55.7, 52.1, 42.6, 36.6, 30.2, 21.7, 14.2, 13.3. **HRMS–DART** (*m/z*): [M+H]⁺ calcd for C₂₆H₃₀NO₆⁺, 452.2068; found, 452.2068.

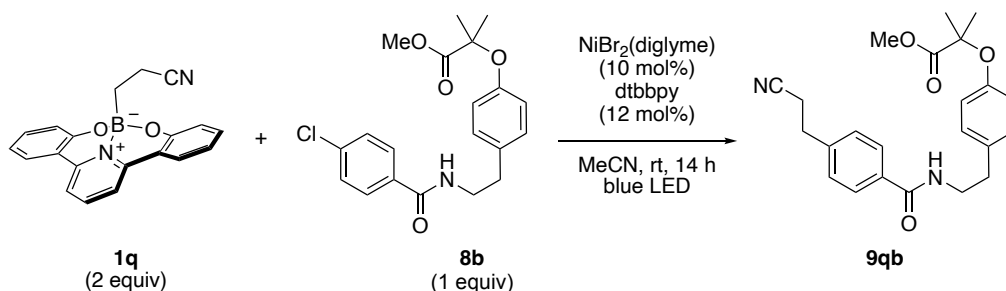
Bezafibrate analog **9ib**



Under an ambient atmosphere, to an oven-dried screw-top 5 mL vial with a stirring bar was added NiBr₂·diglyme (3.6 mg, 10 μ mol), dtbbpy (4,4'-di-*tert*-butyl-2,2'-bipyridyl) (3.2 mg, 12 μ mol), PDP-borate **1i** (77.5 mg, 0.20 mmol) and bezafibrate methyl ester **8b** (37.6 mg, 0.10 mmol). The vial was brought to a glovebox, and added THF (500 μ L). After sealing the vial with Teflon tape, the vial was placed in EvoluChem photoreactor (PhotoRedOx Duo) equipped with a 45W blue LED. After stirred for 14 h, the reaction mixture was quenched with a short pad of silica gel using ethyl acetate and CH₂Cl₂. The reaction crude was concentrated under reduced pressure and purified by flash column chromatography on silica gel (70/10/20–40/40/20, hexane/AcOEt/CH₂Cl₂) gave **9ib** (27.2 mg, 59.7 μ mol, 60%) as a pale yellow solid. **Rf** = 0.30 (hexane/AcOEt/ CH₂Cl₂ = 5/3/2). **M.p.** 76–77 °C. **IR**

(neat) 1140, 1176, 1487, 1508, 1638, 1735, 2948, 3322 cm^{-1} . ^1H NMR (400 MHz, CDCl_3) δ 7.61 (d, J = 8.1 Hz, 2H) 7.26 (d, J = 8.1 Hz, 2H), 7.10 (d, J = 8.5 Hz, 2H), 6.80 (d, J = 8.5 Hz, 2H), 6.07 (m, 1H), 4.11–4.01 (m, 2H), 3.77 (s, 3H), 3.67 (q, J = 6.7 Hz, 2H), 3.31 (m, 1H), 2.86 (t, J = 6.7 Hz, 2H), 2.64–2.51 (m, 2H), 1.59 (s, 6H), 1.29 (d, J = 7.0 Hz, 3H), 1.18 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100.6 MHz, CDCl_3) δ 174.8, 172.0, 167.2, 154.0, 149.4, 132.8, 132.7, 129.6, 127.1, 127.0, 119.5, 79.2, 60.4, 52.5, 42.6, 41.1, 36.4, 34.9, 25.4, 21.7, 14.2. HRMS–DART (m/z): $[\text{M}+\text{NH}_4]^+$ calcd for $\text{C}_{26}\text{H}_{37}\text{N}_2\text{O}_6^+$, 473.2646; found, 473.2648.

Bezafibrate analog 9qb



Under an ambient atmosphere, to an oven-dried screw-top 5 mL vial with a stirring bar was added $\text{NiBr}_2 \cdot \text{diglyme}$ (3.6 mg, 10 μmol), dtbbpy (4,4'-di-*tert*-butyl-2,2'-bipyridyl) (3.2 mg, 12 μmol), PDP-borate **1q** (65.2 mg, 0.20 mmol) and bezafibrate methyl ester **8b** (37.6 mg, 0.10 mmol). The vial was brought to a glovebox, and added THF (1 mL). After sealing the vial with sealtape, the reaction was placed in EvoluChem photoreactor (PhotoRedOx Duo) equipped with a 45W blue LED. After stirred for 14 h, the crude product was concentrated under reduced pressure, and purified by flash column chromatography on silica gel (100/0–0/100, hexane/AcOEt) gave **9qb** (10.8 mg, 27.4 μmol , 27%) as a colorless oil. Rf = 0.43 (hexane/AcOEt = 1/3). IR (neat) 1140, 1289, 1507, 1542, 1639, 1737, 2157, 3356 cm^{-1} . ^1H NMR (400 MHz, CDCl_3) δ 7.66 (d, J = 7.7 Hz, 2H) 7.32–7.25 (m, 2H), 7.11 (d, J = 7.0 Hz, 2H), 6.80 (d, J = 7.0 Hz, 2H), 6.06 (br s, 1H), 3.77 (s, 3H), 3.71–3.63 (m, 2H), 2.99 (t, J = 7.1 Hz, 2H), 2.87 (t, J = 6.7 Hz, 2H), 2.64 (t, J = 7.1 Hz, 2H), 1.59 (s, 6H). ^{13}C NMR (100.6 MHz, CDCl_3) δ 174.8, 166.9, 154.0, 141.5, 133.7, 132.6, 129.6, 128.6, 127.4, 119.6, 118.7, 79.2, 52.5, 41.1, 34.8, 31.3, 25.4, 19.1. HRMS–DART (m/z): $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{23}\text{H}_{27}\text{N}_2\text{O}_4^+$, 395.1965; found, 395.1964.

第一章 實驗項 参考文献

1. Zhang, H.; Huo, C.; Ye, K.; Zhang, P.; Tian, W.; Wang, Y. *Inorg. Chem.* **2006**, *45*, 2788–2794.
2. Huo, H.; Harms, K.; Meggers, E. *J. Am. Chem. Soc.* **2016**, *138*, 6936–6939.
3. Huang, H.; Zhang, G.; Gong, L.; Zhang, S.; Chen, Y. *J. Am. Chem. Soc.* **2014**, *136*, 2280–2283.
4. Chinzei, T.; Miyazawa, K.; Yasu, Y.; Koike, T.; Akita, M. *RSC Adv.* **2015**, *5*, 21297–21300.
5. Molander, G. A.; McKee, S. A. *Org. Lett.* **2011**, *13*, 4684–4687.
6. Verbelen, B.; Cunha Dias Rezende, L.; Boodts, S.; Jacobs, J.; Van Meervelt, L.; Hofkens, J.; Dehaen, W. *Chem. Eur. J.* **2015**, *21*, 12667–12675.
7. Matsui, J. K.; Molander, G. A. *Org. Lett.* **2017**, *19*, 436–439.
8. Sorin, G.; Martinez Mallorquin, R.; Contie, Y.; Baralle, A.; Malacria, M.; Goddard, J.; Fensterbank, L. *Angew. Chem., Int. Ed.* **2010**, *49*, 8721–8723.
9. Luo, J.; Hu, B.; Wu, W.; Hu, M.; Liu, T. L. *Angew. Chem. Int. Ed.* **2021**, *60*, 6107–6116.
10. Oeschger, R.; Su, B.; Yu, I.; Ehinger, C.; Romero, E.; He, S.; Hartwig, J. *Science* **2020**, *368*, 736–741.
11. Dai, J.-J.; Zhang, W.-M.; Shu, Y.-J.; Sun, Y.-Y.; Xu, J.; Feng, Y.-S.; Xu, H.-J. *Chem. Commun.* **2016**, *52*, 6793–6796.
12. Zhao, D.; Xu, P.; Ritter, T. *Chem* **2019**, *5*, 97–107.
13. Margrey, K. A.; Levens, A.; Nicewicz, D. A. *Angew. Chem., Int. Ed.* **2017**, *56*, 15644–15648.
14. Molander, G. A.; Cavalcanti, L. N.; Canturk, B.; Pan, P.-S.; Kennedy, L. E. *J. Org. Chem.* **2009**, *74*, 7364–7369.
15. Ding, S.; Xu, L.; Li, P. *ACS Catal.* **2016**, *6*, 1329–1333.
16. Molander, G. A.; Petrillo, D. E. *Org. Lett.* **2008**, *10*, 1795–1798.
17. Larouche-Gauthier, R.; Fletcher, C. J.; Couto, I.; Aggarwal, V. K. *Chem. Commun.* **2011**, *47*, 12592–12594.
18. Kvasnica, M.; Rarova, L.; Oklestkova, J.; Budesinsky, M.; Kohout, L. *Bioorg. Med. Chem.* **2012**, *20*, 6969–6978.
19. Gaussian 16, Revision C.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2016.
20. Sato, Y.; Nakamura, K.; Sumida, Y.; Hashizume, D.; Hosoya, T.; Ohmiya, H. *J. Am. Chem. Soc.* **2020**, *142*, 9938–9943.
21. Li, J.; He, L.; Liu, X.; Cheng, X.; Li, G. *Angew. Chem., Int. Ed.* **2019**, *58*, 1759–1763.
22. Liu, J.; Dong, K.; Franke, R.; Neumann, H.; Jackstell, R.; Beller, M. *Chem. Commun.* **2018**, *54*, 12238–12241.

第二章 PDP 型ホウ素アート錯体の直接青色光励起を鍵とする Minisci 型反応

第一節 着想背景および作業仮説

含窒素ヘテロ芳香族化合物は、医薬品や天然生理活性物質によく見られる重要な骨格である。そのため、ヘテロ芳香環の C-H 結合を直接的に修飾し、新たな分子を作り出す手法の開発は、創薬化学における重要な課題の一つである。¹ この課題に対し、炭素ラジカルを用いた Minisci 型反応は、ヘテロ芳香環にアルキル基を導入する最も直接的かつ強力な手法として広く利用されてきた (Figure 2-1A)。² Minisci 型反応は、ヘテロ芳香環に炭素ラジカルが付加し、その後酸化されることで、C-H 結合を直接修飾できる反応である。

近年、光酸化還元触媒の台頭により、穏和な条件下で多様なラジカル前駆体を利用可能な Minisci 型反応が数多く開発されている (Figure 2-1B)。³ 具体的には、有機ホウ素化合物、有機ケイ素化合物、カルボン酸、ハンチュエステルなど、多数の前駆体を用いた例が知られている。しかしながら、いずれも強力な酸化剤や触媒を必要とする点、官能基許容性に問題があるなどの課題があった。

一方、著者の所属研究室では、外部光触媒を用いない独自のラジカル発生法として、PDP 型ホウ素アート錯体の「直接光励起」に着目してきた。⁴ ボラセン型ホウ素アート錯体や第一章で述べた PDP 型ホウ素アート錯体は、青色光照射下で励起状態となり、極めて高い還元力 (約 -2.0 V vs. SCE.) を有すると同時に、炭素ラジカルを与える。

そこで、この直接光励起可能な有機ホウ素アート錯体の特性を活かすことで、外部触媒や強力な酸化剤を必要としない Minisci 型反応の開発を目指した (Figure 2-1C)。具体的には、ボラセン型ホウ素アート錯体または PDP 型ホウ素アート錯体から青色光照射によって発生した炭素ラジカルがヘテロ芳香環へ付加することで、Minisci 型反応が可能であると考えた。酸素分子が還元されて生じるヒドロペルオキシラジカルが、ラジカル付加体から水素を引き抜くことで、目的のアルキル化ヘテロ芳香族化合物が得られる。本手法が確立されれば、触媒を用いることなく、第三級から第一級アルキル基、さらにはメチル基に至るまで、多様なアルキル基をヘテロ芳香環へ導入する新たな手法になると期待される。

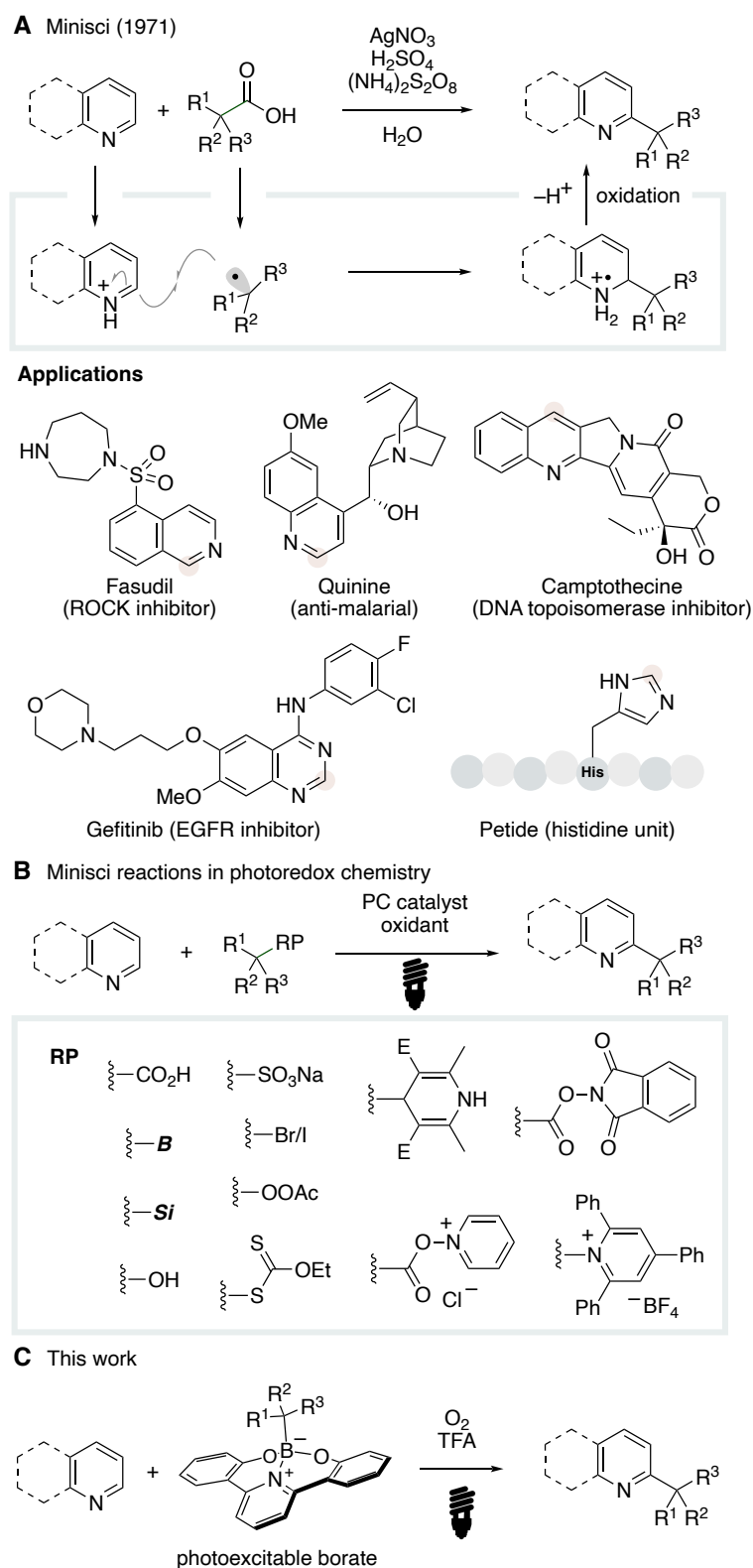


Figure 2-1. (A) Minisci 型反応：推定反応機構及び医薬品修飾への応用 (B) 光酸化還元触媒を用いた Minisci 型反応とラジカル前駆体 (RP) (C) 本研究

第二節 反応条件の最適化および基質適用範囲の検討

第一節の作業仮説に基づき、Minisci型アルキル化反応の条件検討を行った。モデル基質としてレピジン (4-メチルキノリン) **3a** と、序論で述べたボラセン型ホウ素アート錯体 **1a** を用いて検討を開始した (Table 2-1, Figure 2-2 and Figure 2-3)。DMSO/水混合溶媒中、空気雰囲気下で青色光を照射したところ、目的のアルキル化体 **4aa** が36%の収率で得られた (entry 1)。TFAを反応させていないレピジンを用いた場合、反応は進行しなかった (entry 2)。ここで、酸素で満たされた風船を用いて反応系内を酸素雰囲気下とすることで、定量的に **4aa** が得られた。(entry 3)。興味深いことに、不活性ガス (窒素) 雰囲気下においても反応は進行し、**4aa** を与えた (entries 4–8)。この結果は、ボラセン型ホウ素アート錯体 **1a** の直接光励起によるホモリティックな結合開裂が反応の起点となっていることを示唆している。しかしながら、ボラセン型ホウ素アート錯体 **1a** を用いた系では、反応後に副生するボラセン残渣の除去が困難であり、生成物の単離精製が困難であった。

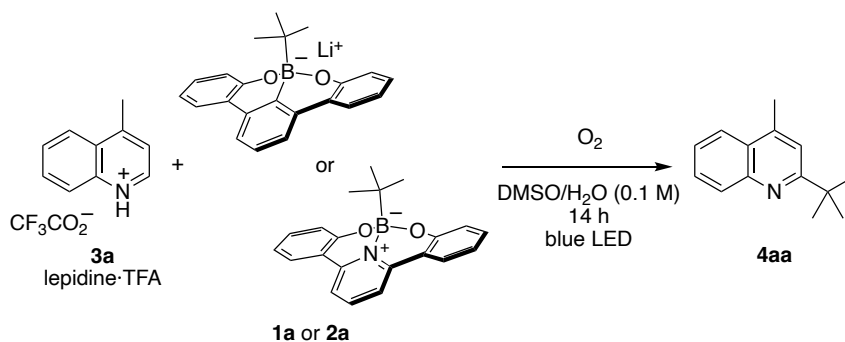
そこで、より取り扱いが容易で酸性条件に対する耐性も高いPDP型ホウ素アート錯体 **2a** を用いて、さらなる検討を行った。酸添加剤としてトリフルオロ酢酸 (TFA) を加え、レピジンを活性化させた状態で酸素雰囲気下、DMSO/水混合溶媒中で反応を行ったところ、目的物 **4aa** を81% (単離収率73%) の良好な収率で得ることができた (entry 12)。TFAを反応させていない場合、反応時間が短い場合は収率が低下した (entries 9 and 10)。最適条件の entry 12 では、EvoluChem photoreactorを用いて光を照射しているが、直接光を当てる条件、また濃度が高い条件では収率が低下した (entries 11, 13 and 14)。溶媒を変更すると収率が低下した (entry 15)。

得られた最適条件を用いて、PDP型ホウ素アート錯体 **2** の基質適用範囲を検討した (Figure 2-4A)。本反応系は、第三級アルキル基のみならず、シクロペンチル基などの第二級アルキル基の導入にも有効であり、対応するアルキル化体を中程度の収率で与えた (**4ab**, **4ac**, **4ad** and **4ae**)。さらに、第一級アルキル基についても適用可能であり、*n*-ブチル基やベンジル基、エステル官能基を有するアルキル鎖の導入に成功した (**4af**, **4ag** and **4ah**)。特筆すべきことに、最も発生が困難とされるメチルラジカルが発生と導入も可能であった (**4ai**)。メチル化反応においては、PDP型ホウ素アート錯体由来のピリジン環の2位へのメチル化に伴う副生成物の生成が確認された。X線結晶構造解析によりその構造を決定した (Figure 2-4B)。

続いて、ラジカル受容体となるヘテロ芳香環の適用範囲を検討した (Figure 2-4C)。キノリン誘導体だけでなく、キノキサリン、キナゾリノン、フェナントリジン、フェナントロリンといった多様なヘテロ芳香環に対して、位置選択的なアルキル化が進行した (**4ba**, **4ca**, **4da**, **4ea** and **4fa**)。また、抗マラリア薬であるキニーネに対しても本手法を適用でき、複雑な骨格を有する分子への直接的な官能基導入が可能であった (**4ha**)。

以上の結果より、本手法は第一級から第三級アルキル基、さらにはメチル基に至るまで、触媒を用いることなく幅広いアルキル基を含窒素ヘテロ芳香環化合物へ導入できる手法であることが示された。

Table 2-1. 条件検討



entry ^a	borate	solvent (concentration)	Reaction set up	Yield of 4aa (%) ^b	Yield of 3a (%) ^b
1	1a	DMSO/H ₂ O (9/1, 0.1 M)	A	36	-
2 ^c	1a	DMSO/H ₂ O (9/1, 0.1 M)	A	0	6
3	1a	DMSO/H ₂ O (9/1, 0.1 M)	A	quant	
4	1a	DMSO (0.1 M)	C	17	-
5	1a	DMF (0.1 M)	C	28	6
6	1a	DMF/H ₂ O (9/1, 0.1 M)	C	47	7
7	1a	DMSO/H ₂ O (9/1, 0.1 M)	C	80	-
8 ^c	1a	DMSO/H ₂ O (9/1, 0.1 M)	C	5	13
9 ^d	2a	DMSO/H ₂ O (9/1, 0.1 M)	A	17	80
10 ^e	2a	DMSO/H ₂ O (9/1, 0.1 M)	D	67	1
11	2a	DMSO/H ₂ O (9/1, 0.1 M)	E	57	30
12 ^f	2a	DMSO/H ₂ O (9/1, 0.05 M)	B	81 (73) ^g	2
13	2a	DMSO/H ₂ O (9/1, 0.05 M)	E	70	3
14	2a	DMSO/H ₂ O (9/1, 0.33 M)	D	35	48
15	2a	MeCN/H ₂ O (9/1, 0.1 M)	D	26	11

^aReaction was carried out with **1a** or **2a** (0.15 mmol), **3a**·TFA (0.1 mmol) in DMSO under oxygen atmosphere and photoirradiation for 14 h. ^b¹H NMR yield. ^cReaction was carried out using TFA-untreated lepidine. ^dReaction was carried out using TFA-untreated lepidine with coexistence of TFA (1.5 equiv). ^eThe reaction time was 1 h. ^fThe reaction time was 4 h. ^gIsolated yield.



Figure 2-2. 条件 A^a , B^b 及び C^c の光反応セットアップ (EvoluChem photoreactor)

^a**A:** The vial with O₂ balloon was fixed in EvoluChem photoreactor.

^b**B:** The vial was fixed in EvoluChem photoreactor without O₂ balloon (only O₂ babbling).

^c**C:** The vial was fixed in EvoluChem photoreactor without O₂ balloon.

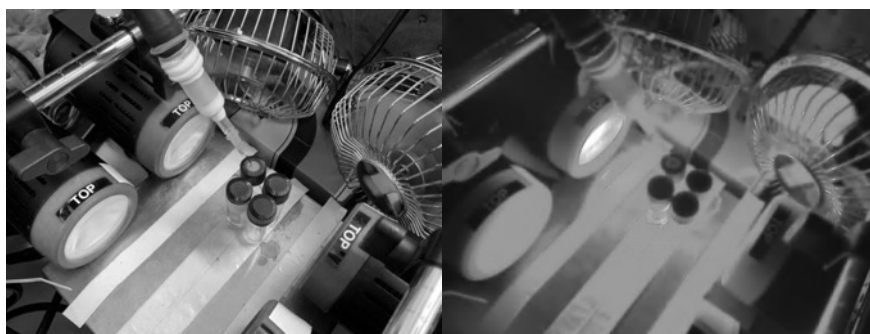


Figure 2-3. 条件 D^a 及び E^b の光反応セットアップ (direct irradiation)

^a**D:** The vial with O₂ balloon was directly irradiated.

^b**E:** The vial was directly irradiated without O₂ balloon (only O₂ babbling).

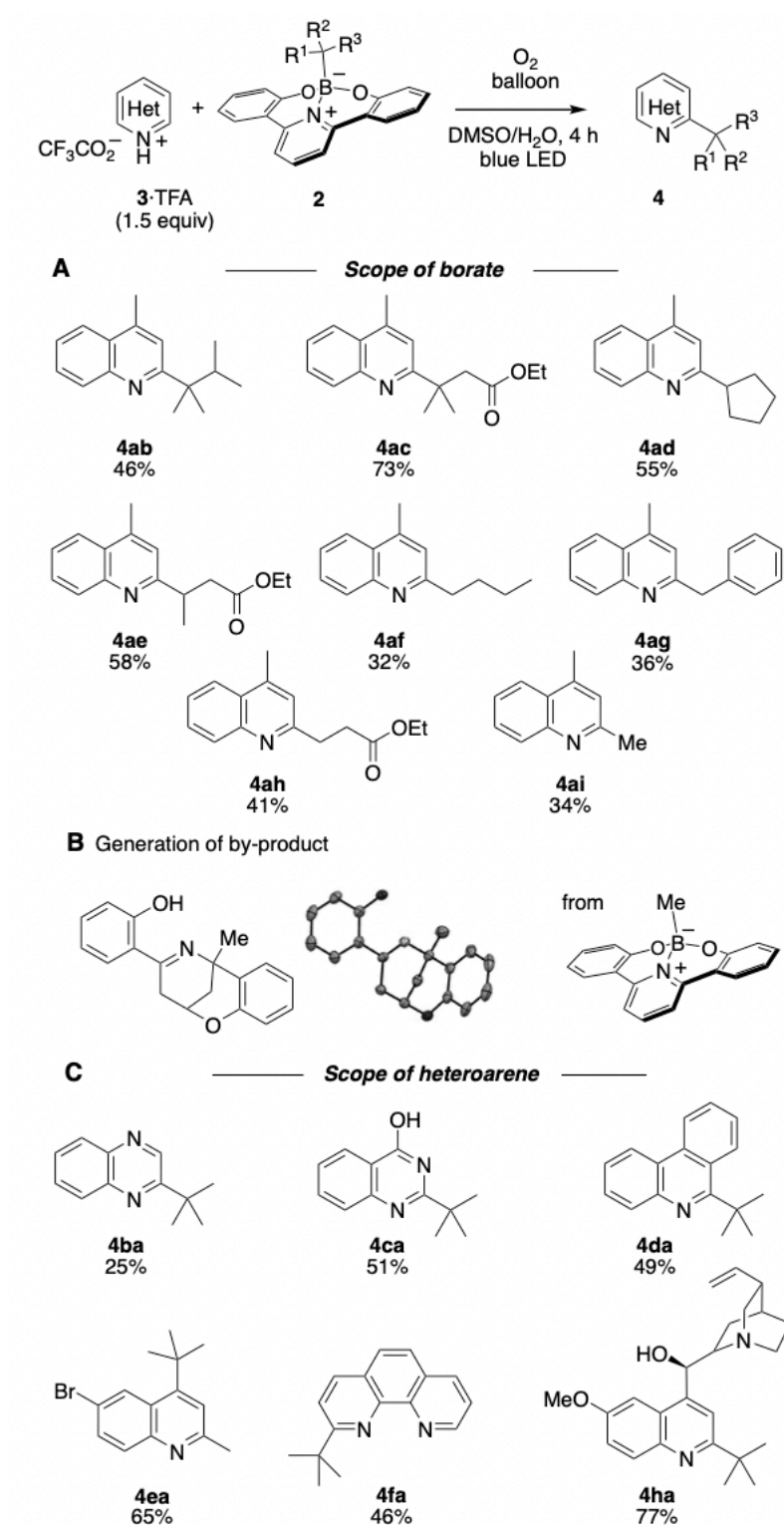
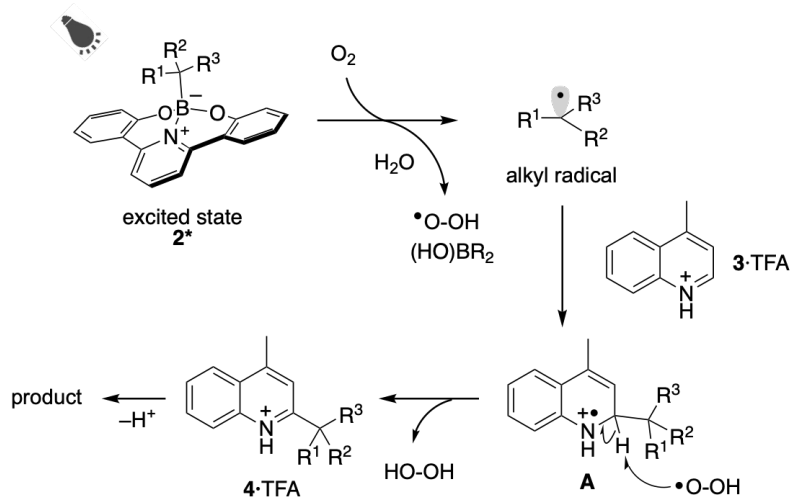


Figure 2-4. (A) PDP 型ホウ素アート錯体の基質適用範囲 (B) メチル基置換ホウ素アート錯体 **2i** から得られた副生成物の構造式および X 線結晶構造。X 線結晶構造の水素原子は省略している (CCDC 2114101)。 (C) ヘテロ芳香族化合物の基質適用範囲

第三節 推定反応機構

第二章第二節までの実験結果および PDP 型ホウ素アート錯体を用いた反応の機構解析⁴に基づき、本反応の推定反応機構を以下に示す (Figure 2-5)。まず、基底状態の PDP 型ホウ素アート錯体 **2** が青色光を吸収し、励起状態 **2*** となる。この励起種 **2*** から酸素分子への電子移動が生じ、炭素-ホウ素結合の開裂が進行し、アルキルラジカル ($R^{\bullet}$) とヒドロペルオキシラジカルが発生する。生成した炭素ラジカルは、酸 (TFA) によってプロトン化され活性化されたヘテロ芳香環 **3** に対して付加し、ラジカルカチオン中間体 **A** を与える。続いて、この中間体 **A** に対して、系中の酸化剤 (ヒドロペルオキシラジカルまたはヒドロキシラジカル⁵) が水素引き抜きを引き起こし、目的とするアルキル化体 **4** が生成する (Figure 2-5A)。一方で、PDP 型ホウ素アート錯体の炭素-ホウ素結合のホモリティック開裂から進行する経路もあると考えられる (Figure 2-5B)。

A Initiated by oxidative quenching of borate



B Initiated by homolytic cleavage

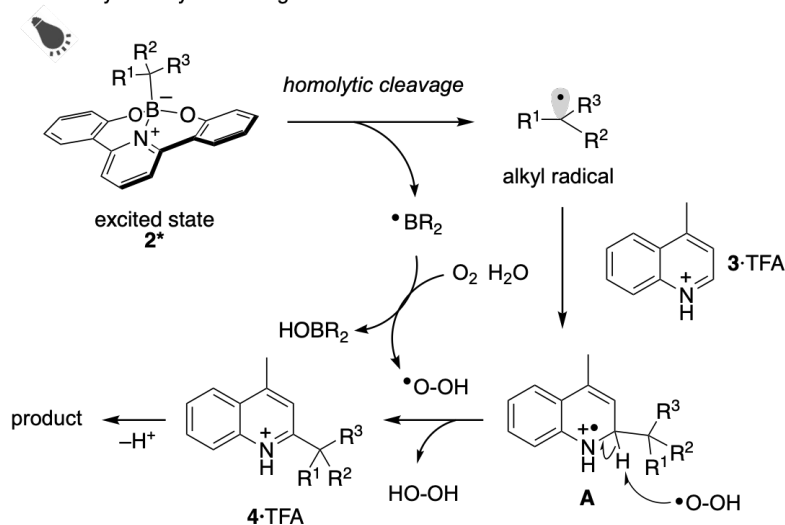


Figure 2-5. 推定反応機構 (A) 酸素による PDP 型ホウ素アート錯体の消光により開始される機構 (B) 炭素-ホウ素結合の均等開裂により開始される機構

第四節 結論

PDP 型有機ホウ素アート錯体の直接青色光励起を活用することで、外部光触媒や金属触媒を一切必要としない、含窒素ヘテロ芳香族化合物の Minisci 型アルキル化反応を開発した。本反応は、青色光照射下、励起状態のホウ素アート錯体から炭素-ホウ素結合の開裂を経て炭素ラジカルが発生する。炭素ラジカルはプロトン化されたヘテロ芳香環へ付加した後、酸素を末端酸化剤として再芳香環化が進行し、アルキル化生成物が得られる。本手法により、第三級から第一級炭素ラジカル、さらには発生困難なメチルラジカルに至るまで、多様な炭素ラジカルをヘテロ芳香環へ効率的に導入することができた。

第二章 参考文献

1. (a) Baumann, M.; Baxendale, I. R. *Beilstein J. Org. Chem.* **2013**, *9*, 2265–2319. (b) Welsch, M. E.; Snyder, S. A.; Stockwell, B. R. *Curr. Opin. Chem. Biol.* **2010**, *14*, 347–361. (c) Vitaku, E.; Smith, D. T.; Njardarson, J. T. *J. Med. Chem.* **2014**, *57*, 10257–10274. (d) Martins, P.; Jesus, J.; Santos, S.; Raposo, L.; Roma-Rodrigues, C.; Baptista, P.; Fernandes, A. *Molecules* **2015**, *20*, 16852–16891.
2. (a) Duncton, M. A. *J. Med. Chem. Commun.* **2011**, *2*, 1135. (b) Minisci, F.; Bernardi, R.; Bertini, F.; Galli, R.; Perchinummo, M. *Tetrahedron* **1971**, *27*, 3575–3579. (c) Minisci, F.; Vismara, E.; Fontana, F. *J. Org. Chem.* **1989**, *54*, 5224–5227. (d) Seiple, I. B.; Su, S.; Rodriguez, R. A.; Gianatassio, R.; Fujiwara, Y.; Sobel, A. L.; Baran, P. S. *J. Am. Chem. Soc.* **2010**, *132*, 13194–13196. (e) Fujiwara, Y.; Dixon, J. A.; O'Hara, F.; Funder, E. D.; Dixon, D. D.; Rodriguez, R. A.; Baxter, R. D.; Herlé, B.; Sach, N.; Collins, M. R.; Ishihara, Y.; Baran, P. S. *Nature* **2012**, *492*, 95–99. (f) O'Hara, F.; Blackmond, D. G.; Baran, P. S. *J. Am. Chem. Soc.* **2013**, *135*, 12122–12134.
3. (a) Proctor, R. S. J.; Phipps, R. J. *Angew. Chem., Int. Ed.* **2019**, *58*, 13666–13699. (b) Jin, J.; MacMillan, D. W. C. *Nature* **2015**, *525*, 87–90. (c) Chen, X.; Ye, F.; Luo, X.; Liu, X.; Zhao, J.; Wang, S.; Zhou, Q.; Chen, G.; Wang, P. *J. Am. Chem. Soc.* **2019**, *141*, 18230–18237. (d) Fu, M.-C.; Shang, R.; Zhao, B.; Wang, B.; Fu, Y. *Science* **2019**, *363*, 1429–1434. (e) Dong, J.; Lyu, X.; Wang, Z.; Wang, X.; Song, H.; Liu, Y.; Wang, Q. *Chem. Sci.* **2019**, *10*, 976–982. (f) Matsui, J. K.; Primer, D. N.; Molander, G. A. *Chem. Sci.* **2017**, *8*, 3512–3522. (g) Garza-Sanchez, R. A.; Tlahuext-Aca, A.; Tavakoli, G.; Glorius, F. *ACS Catal.* **2017**, *7*, 4057–4061. (h) Nuhant, P.; Oderinde, M. S.; Genovino, J.; Juneau, A.; Gagné, Y.; Allais, C.; Chinigo, G. M.; Choi, C.; Sach, N. W.; Bernier, L.; Fobian, Y. M.; Bundesmann, M. W.; Khunte, B.; Frenette, M.; Fadeyi, O. O. *Angew. Chem., Int. Ed.* **2017**, *56*, 15309–15313. (i) Proctor, R. S. J.; Davis, H. J.; Phipps, R. J. *Science* **2018**, *360*, 419–422. (j) Pitre, S. P.; Muuronen, M.; Fishman, D. A.; Overman, L. E. *ACS Catal.* **2019**, *9*, 3413–3418. (k) Ikarashi, G.; Morofuji, T.; Kano, N. *Chem. Commun.* **2020**, *56*, 10006–10009. (l) Proctor, R. S. J.; Chuentragool, P.; Colgan, A. C.; Phipps, R. J. *J. Am. Chem. Soc.* **2021**, *143*, 4928–4934. (m) Zhang, X.; Li, S.; Qiu, F.; Ang, H. T.; Wu, J.; Jia, P. *Green Chem.* **2024**, *26*, 3595–3626. (n) Tiwari, P. C.; Pulcinella, A.; Hodžić, E.; Noël, T. *ACS Cent. Sci.* **2025**, *11*, 910–917. (o) Liu, Z.; Peng, L.; Huang, H. *Chem. Commun.* **2025**, *61*, 14490–14509.
4. (a) Sato, Y.; Nakamura, K.; Sumida, Y.; Hashizume, D.; Hosoya, T.; Ohmiya, H. *J. Am. Chem. Soc.* **2020**, *142*, 9938–9943. (b) Sato, Y.; Miyamoto, Y.; Sumida, Y.; Hosoya, T.; Ohmiya, H. *Org. Biomol. Chem.* **2020**, *18*, 6598–6601. (c) Miyamoto, Y.; Sumida, Y.; Ohmiya, H. *Org. Lett.* **2021**, *23*, 5865–5870. (d) Sato, Y.; Goto, Y.; Nakamura, K.; Miyamoto, Y.; Sumida, Y.; Ohmiya, H. *ACS Catal.* **2021**, *11*, 12886–12892. (e) Nakamura, R.; Sumida, Y.; Ohmiya, H. *Bull. Chem. Soc. Jpn.* **2022**, *95*, 1001–1005. (f) Nakamura, R.; Yamazaki, T.; Kondo, Y.; Tsukada, M.; Miyamoto, Y.; Arakawa, N.; Sumida, Y.; Kiya, T.; Arai, S.; Ohmiya, H. *J. Am. Chem. Soc.* **2023**, *145*, 10651–10658. (g) Miyamoto, Y.; Murakami, S.; Sumida, Y.; Hirai, G.; Ohmiya, H. *Chem. Eur. J.* **2024**, *30*, DOI: 10.1002/chem.202402256.
5. Zhao, H.; Li, Z.; Jin, J. *New J. Chem.* **2019**, *43*, 12533–12537.

第二章 実験項

■ Instrumentation and Chemicals Synthesis ■

NMR spectra were recorded on Bruker AVANCE NEO 400N spectrometer, operating at 400 MHz for ^1H NMR, 100.6 MHz for ^{13}C NMR, and 376.5 MHz for ^{19}F NMR. Chemical shifts were reported in ppm. Chloroform- d_1 (CDCl_3) containing 0.03% tetramethylsilane (TMS) (>99.8%D, Cambridge Isotope Laboratories, Inc., Cat. No. DLM-7) was used as solvents for NMR measurements at ambient temperature. Chemical shifts (δ) for ^1H NMR are given in parts per million (ppm) relative to relative to TMS (δ 0.00 ppm in CDCl_3). Chemical shifts (δ) for ^{13}C NMR are given in ppm relative to CDCl_3 (δ 77.0 ppm). The abbreviations s, d, t, q, br s, and m signify singlet, doublet, triplet, quartet, broad singlet, and multiplet, respectively. **DART-Mass (HRMS)** were measured with JMS-T100TD (JEOL Ltd.). **TLC analyses** were performed on commercial glass plates bearing 0.25-mm layer of Merck Silica gel 60F₂₅₄. Silica gel (Kanto Chemical Co., Silica gel 60 N, spherical, neutral) was used for column chromatography. **IR spectra** were measured with a Thermo Scientific iD7 ATR Accessory for the Thermo Scientific Nicolet iS5 FT-IR Spectrometer. **Single-crystal X-ray diffraction** data were collected on R-Axis RAPID II. Kessil PR160L 440 nm (highest blue and intensity setting) was used as a light source equipped with EvoluChem photoreactor (PhotoRedOx Duo, HepatoChem).

All reactions unless otherwise noted were carried out under nitrogen atmosphere. Materials were obtained from commercial suppliers or prepared according to standard procedures unless otherwise noted. Hexane, ethylacetate, dichloromethane, acetonitrile (Super Dehydrated), diethylether, methanol (Super Dehydrated), ethanol, dimethylformamide (Super Dehydrated), dimethyl sulfoxide (Deoxidized) toluene (Super Dehydrated), benzene (Super Dehydrated), [1,3-Bis(diphenylphosphino)propane]-nickel(II) Dichloride, Tetrahydrofuran-Borane (Tetrahydrofuran Solution), Sodium tert-butoxide, Distilled Water, (-)-Quinine Sulfate Dihydrate and Copper(I) iodide were purchased from FUJIFILM Wako Pure Chemical Co., 1-bromo-2-methoxybenzene, pyridine Hydrochloride, Potassium Hydrogenfluoride, 2,3-Dimethyl-2-butene, ethyl acrylate, Ethyl Crotonate, Ethyl 3-Methylcrotonate, Lepidine, 4-Hydroxyquinazoline, 6-bromo-2-methylquinoline, 1,10-phenanthroline and Benzyl Bromide were purchased from Tokyo Chemical Industry Co., and Apollo Scientific Ltd., tert-Butyllithium (in n-pentane, 1.6mol/L) and Copper(I) Chloride were purchased from Kanto Chemical Co., 2,6-dibromopyridine was purchased from Tokyo Chemical Industry Co. and BLD Pharmatech Ltd., [(2-Biphenyl)dicyclohexylphosphine], phenanthridine and quinoxaline were purchased from Sigma-Aldrich Japan., trifluoroacetic acid was purchased from Tokyo Chemical Industry Co. and FUJIFILM Wako Pure Chemical Co., Mg was purchased from Nacalai Tesque, Inc., tetrahydroxydiboron was purchased from BLD Pharmatech Ltd. 8,9-Dioxa-8a-borabenzof[*g*]tetracene (boracene) was prepared by the reported procedures^{1,2} 2,2'-(pyridine-2,6-diyl)diphenol (PDP) was prepared according to the literature.³ The alkylborates listed in Figure S2-1 were prepared according to the literatures.^{4,5}

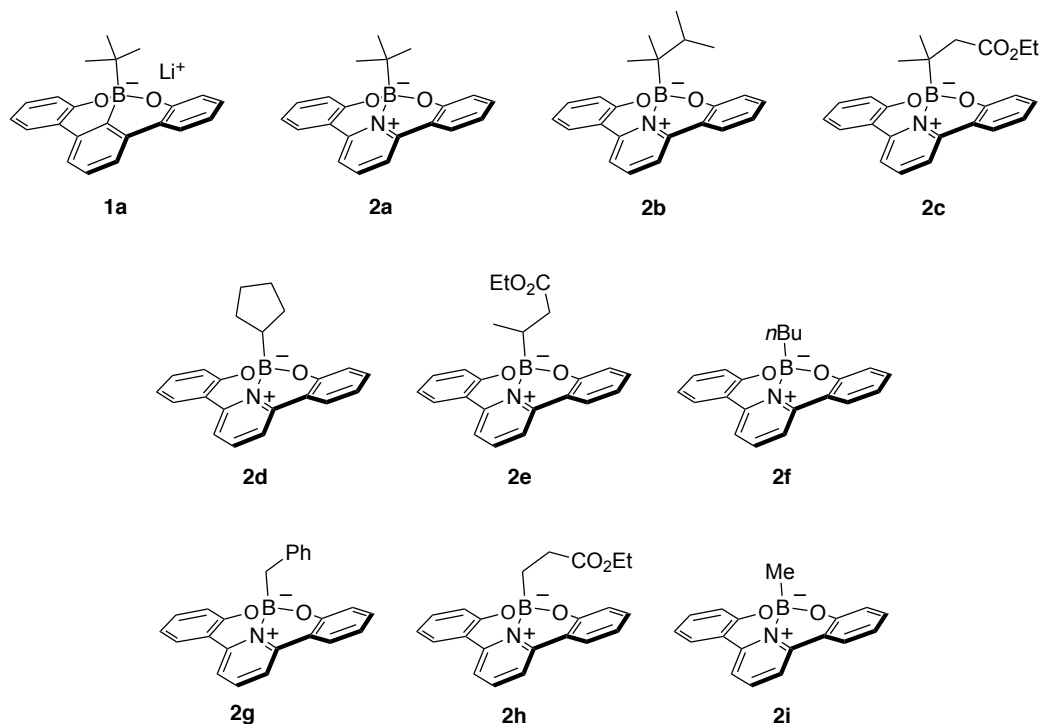
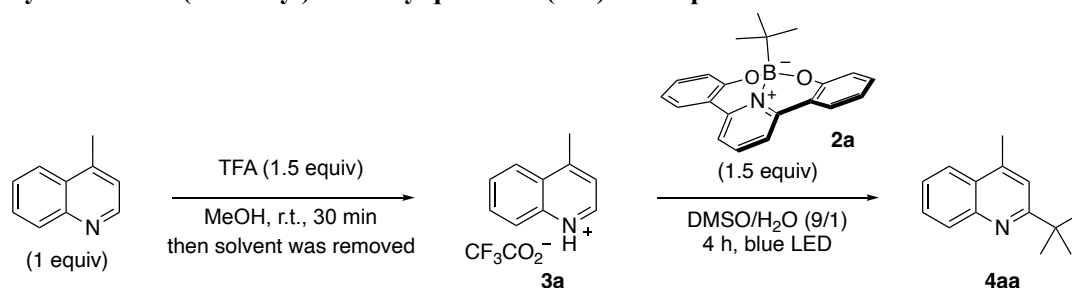


Figure S2-1. Prepared starting materials.

■ General Procedure for Minisci-type Reaction ■

Synthesis of 2-(*tert*-butyl)-4-methylquinoline (**4aa**) as a representative



Under an ambient atmosphere, to an oven-dried screw-top 4 mL vial with a stirring bar was added lepidine (14.3 mg, 0.1 mmol), MeOH (200 μL) and trifluoroacetic acid (11.5 μL , 0.15 mmol). After the vial was removed from the glovebox and stirred for 30 min. Then, the solvent was removed by N_2 bubbling. The vial was added alkylborate **2a** (49.4 mg, 0.15 mmol) and DMSO/ H_2O (9/1, 2 mL) under an ambient atmosphere. After O_2 bubbling for 1 min, and sealing the vial with Teflon tape, the reaction was placed in EvoluChem photoreactor (PhotoRedOx Duo) equipped with a 45W blue LED (Figure 2-2). After stirred for 4 h, the reaction was quenched with saturated NaHCO_3 water (ca. 10 mL) and extracted with diethyl ether (ca. 2 mL $\times$ 10). The organic layer was wash with brine and dried over Na_2SO_4 and after filtration, the filtrate was concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (100:0–95:5, hexane/AcOEt) gave **4aa** (14.6 mg, 0.0733 mmol, 73% isolated yield) as a green oil. ^1H NMR (400 MHz, CDCl_3) δ 8.05 (d, J = 8.4 Hz, 1H), 7.94 (d, J = 8.4 Hz, 1H), 7.65 (t, J = 7.6 Hz, 1H), 7.49 (t, J = 7.6 Hz, 1H), 7.35 (s, 1H), 2.69 (s, 3H), 1.46 (s, 9H). ^{13}C NMR (100.6 MHz, CDCl_3) δ 168.9, 147.3, 143.6, 129.9, 128.7, 126.5, 125.4,

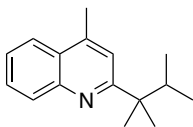
123.4, 118.9, 37.9, 30.1, 19.0. The ^1H and ^{13}C NMR spectra data of **4aa** were consistent with the literature.⁶

Large scale experiment

Under an ambient atmosphere, to two sets of oven-dried screw-top 20 mL vial with a stirring bar were added lepidine (71.6 mg, 0.5 mmol), MeOH (1 mL) and trifluoroacetic acid (57.4 μL , 0.5 mmol), respectively. After the vial was removed from the glovebox and stirred over 5 min. Then, the solvent was removed by rotary evaporator. The vials were added **2a** (246.9 mg, 0.75 mmol) and DMSO/H₂O (9/1, 10 mL) respectively under an ambient atmosphere. After O₂ bubbling for 1 min, and sealing the vial with Teflon tape and equipped with O₂ balloon. The reaction was placed in EvoluChem photoreactor (PhotoRedOx Duo) equipped with a 45W blue LED (Figure 2-2). After stirred for 19 h, the reaction was quenched with saturated NaHCO₃ water (ca. 70 mL) and extracted with diethyl ether (ca. 50 mL, over 5 times), respectively. The organic layer was combined and dried over Na₂SO₄ and after filtration, the filtrate was concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (100:0–94:6, hexane/Et₂O) gave **4aa** (152.1 mg, 0.763 mmol, 76%) as a colorless oil.

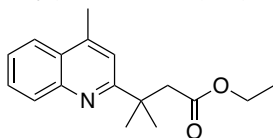
■ Characterization Data for Minisci-type adducts ■

2-(2,3-Dimethylbutan-2-yl)-4-methylquinoline (4ab)



The product **4ab** was synthesized according to general procedure using lepidine (14.3 mg, 0.1 mmol) and alkylborate **2b** (53.6 mg, 0.15 mmol). The residue was purified by flash chromatography on silica gel (100:0–95:5, hexane/AcOEt) gave **4ab** as an orange oil. (10.8 mg, 0.0474 mmol, 47% isolated yield). IR (neat) 757, 1392, 1448, 1462, 1507, 1557, 1603, 2968 cm^{-1} . ^1H NMR (400 MHz, CDCl₃) δ 8.05 (d, J = 8.4 Hz, 1H), 7.93 (d, J = 8.4 Hz, 1H), 7.65 (t, J = 7.6 Hz, 1H), 7.48 (t, J = 7.6 Hz, 1H), 7.29 (s, 1H), 2.68 (s, 3H), 2.28 (m, 1H), 1.37 (s, 6H), 0.80 (d, J = 6.8 Hz, 6H). ^{13}C NMR (100.6 MHz, CDCl₃) δ 168.9, 147.2, 143.1, 130.0, 128.5, 126.5, 125.3, 123.4, 119.6, 43.8, 37.1, 23.7, 19.0, 17.9. HRMS–DART (m/z): $[\text{M}+\text{H}]^+$ calcd for C₁₆H₂₂N⁺, 228.1747; found, 228.1747.

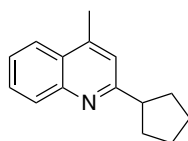
Ethyl 3-Methyl-3-(4-methylquinolin-2-yl)butanoate (4ac)



The product **4ac** was synthesized according to general procedure using lepidine (19.8 μL , 0.15 mmol). The vial was brought to a glovebox, and added MeOH (300 μL) and trifluoroacetic acid (23.1 μL , 0.3 mmol). After the vial was removed from the glovebox and stirred over 5 min. Then, the solvent was removed by rotary evaporator. The vial was added alkylborate **2c** (40.1 mg, 0.1 mmol) and DMSO/H₂O (9/1, 2 mL) under an ambient atmosphere. After O₂ bubbling for 1 min, and sealing the vial with Teflon tape, the reaction was placed in EvoluChem photoreactor (PhotoRedOx Duo) equipped with a 45W blue LED. After stirred for 4 h, the reaction was quenched with saturated NaHCO₃ water (ca. 10 mL) and extracted with diethyl ether (ca. 2 mL, over 5 times). The organic

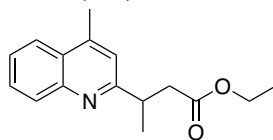
layer was dried over Na₂SO₄ and after filtration, the filtrate was concentrated under reduced pressure. The residue was purified by recycling preparative HPLC (CHCl₃) gave **4ac** (19.8 mg, 0.0730 mmol, 73% isolated yield) as a colorless oil. **IR** (neat) 759, 1035, 1198, 1508, 1559, 1602, 1731, 2975 cm⁻¹. **¹H NMR** (400 MHz, CDCl₃) δ 7.99 (d, *J* = 8.4 Hz, 1H), 7.93 (d, *J* = 8.4 Hz, 1H), 7.64 (t, *J* = 7.6 Hz, 1H), 7.48 (t, *J* = 7.6 Hz, 1H), 7.33 (s, 1H), 4.01 (q, *J* = 6.8 Hz, 2H), 2.91 (s, 2H), 2.69 (s, 3H), 1.55 (s, 6H), 1.12 (t, *J* = 6.8 Hz, 3H). **¹³C NMR** (100.6 MHz, CDCl₃) δ 172.4, 166.6, 147.2, 143.8, 129.9, 128.7, 126.6, 125.5, 123.4, 118.7, 59.8, 46.3, 40.3, 30.9, 28.3, 19.0, 14.2. **HRMS–DART** (*m/z*): [M+H]⁺ calcd for C₁₇H₂₂NO₂⁺, 272.1645; found, 272.1646.

2-Cyclopentyl-4-methylquinoline (4ad)



The product **4ad** was synthesized according to general procedure using lepidine (14.3 mg, 0.1 mmol). The vial was brought to a glovebox, and added MeOH (200 μ L) and trifluoroacetic acid (11.5 μ L, 0.15 mmol). After the vial was removed from the glovebox and stirred for 30 min. Then, the solvent was removed by N₂ bubbling. The vial was added alkylborate **2d** (51.2 mg, 0.15 mmol) and DMSO/H₂O (9/1, 2 mL) under an ambient atmosphere. After O₂ bubbling for 1 min, and sealing the vial with Teflon tape, the reaction was placed in EvoluChem photoreactor (PhotoRedOx Duo) equipped with a 45W blue LED. After stirred for 4 h, the reaction was quenched with saturated NaHCO₃ water (ca. 10 mL) and extracted with diethyl ether (ca. 2 mL $\times$ 10). The organic layer was wash with brine and dried over Na₂SO₄ and after filtration, the filtrate was concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (100:0–95:5, hexane/AcOEt) gave **4ad** (11.5 mg, 0.0545 mmol, 54% isolated yield) as an orange oil. **¹H NMR** (400 MHz, CDCl₃) δ 8.04 (d, *J* = 8.0 Hz, 1H), 7.94 (d, *J* = 8.0 Hz, 1H), 7.66 (t, *J* = 7.2 Hz, 1H), 7.49 (t, *J* = 7.2 Hz, 1H), 7.18 (s, 1H), 3.34 (m, 1H), 2.68 (s, 3H), 2.23–2.12 (m, 2H), 1.95–1.83 (m, 4H), 1.80–1.68 (m, 2H). **¹³C NMR** (100.6 MHz, CDCl₃) δ 165.9, 147.4, 144.2, 129.4, 129.0, 126.9, 125.4, 123.5, 120.6, 48.8, 33.6, 26.0, 18.8. The ¹H and ¹³C NMR spectra data of product **4ad** were consistent with the literature.⁷

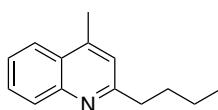
Ethyl 3-(4-methylquinolin-2-yl)butanoate (4ae)



The product **4ae** was synthesized according to general procedure using lepidine (19.8 μ L, 0.15 mmol). The vial was brought to a glovebox, and added MeOH (300 μ L) and trifluoroacetic acid (23.1 μ L, 0.3 mmol). After the vial was removed from the glovebox and stirred over 5 min. Then, the solvent was removed by rotary evaporator. The vial was added alkylborate **2e** (38.7 mg, 0.1 mmol) and DMSO/H₂O (9/1, 2 mL) under an ambient atmosphere. After O₂ bubbling for 1 min, and sealing the vial with Teflon tape, the reaction was placed in EvoluChem photoreactor (PhotoRedOx Duo) equipped with a 45W blue LED. After stirred for 4 h, the reaction was quenched with saturated

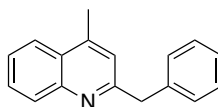
NaHCO₃ water (ca. 10 mL) and extracted with diethyl ether (ca. 2 mL, over 5 times). The organic layer was dried over Na₂SO₄ and after filtration, the filtrate was concentrated under reduced pressure. The residue was purified by recycling preparative HPLC (CHCl₃) gave **4ae** (15.0 mg, 0.0583 mmol, 58% isolated yield) as a colorless oil. **IR** (neat) 760, 1163, 1450, 1508, 1561, 1604, 1731, 2976 cm⁻¹. **¹H NMR** (400 MHz, CDCl₃) δ 8.02 (d, *J* = 8.4 Hz, 1H), 7.94 (d, *J* = 8.4 Hz, 1H), 7.66 (t, *J* = 7.6 Hz, 1H), 7.50 (t, *J* = 7.6 Hz, 1H), 7.17 (s, 1H), 4.08 (q, *J* = 7.2 Hz, 2H), 3.56 (m, 1H), 3.03 (dd, *J* = 15.6, 7.6 Hz, 1H), 2.73–2.62 (m, 4H), 1.40 (d, *J* = 6.8 Hz, 3H), 1.18 (t, *J* = 7.2 Hz, 3H). **¹³C NMR** (100.6 MHz, CDCl₃) δ 172.8, 164.4, 147.6, 144.3, 129.7, 128.9, 127.0, 125.6, 123.6, 121.0, 60.2, 40.5, 38.6, 20.7, 18.8, 14.2. **HRMS–DART** (*m/z*): [M+H]⁺ calcd for C₁₆H₂₀NO₂⁺, 258.1489; found, 258.1490.

2-Butyl-4-methylquinoline (4af)



The product **4af** was synthesized according to general procedure using lepidine (19.8 μ L, 0.15 mmol). The vial was brought to a glovebox, and added MeOH (300 μ L) and trifluoroacetic acid (23.1 μ L, 0.3 mmol). After the vial was removed from the glovebox and stirred over 5 min. Then, the solvent was removed by rotary evaporator. The vial was added alkylborate **2f** (32.9 mg, 0.1 mmol) and DMSO/H₂O (9/1, 2 mL) under an ambient atmosphere. After O₂ bubbling for 1 min, and sealing the vial with Teflon tape, the reaction was placed in EvoluChem photoreactor (PhotoRedOx Duo) equipped with a 45W blue LED. After stirred for 4 h, the reaction was quenched with saturated NaHCO₃ water (ca. 10 mL) and extracted with diethyl ether (ca. 2 mL, over 5 times). The organic layer was dried over Na₂SO₄ and after filtration, the filtrate was concentrated under reduced pressure. The residue was purified by recycling preparative HPLC (CHCl₃) gave **4af** (6.4 mg, 0.0321 mmol, 32% isolated yield) as a yellow oil. **¹H NMR** (400 MHz, CDCl₃) δ 8.04 (m, 1H), 7.95 (m, 1H), 7.67 (m, 1H), 7.50 (m, 1H), 7.15 (s, 1H), 2.92 (t, *J* = 8.0 Hz, 2H), 2.68 (s, 1H), 1.83–1.74 (m, 3H, including 1H of H₂O), 1.50–1.40 (m, 2H), 0.96 (t, *J* = 7.2 Hz, 3H). **¹³C NMR** (100.6 MHz, CDCl₃) δ 162.8, 147.7, 144.1, 129.3, 129.0, 126.8, 125.4, 123.6, 122.1, 39.0, 32.2, 22.7, 18.7, 14.0. The ¹H and ¹³C NMR spectra data of **4af** were consistent with the literature.⁸

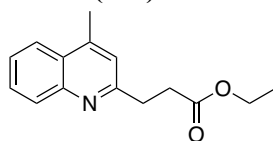
2-Benzyl-4-methylquinoline (4ag)



The product **4ag** was synthesized according to general procedure using lepidine (14.3 mg, 0.1 mmol). The vial was brought to a glovebox, and added MeOH (200 μ L) and trifluoroacetic acid (11.5 μ L, 0.15 mmol). After the vial was removed from the glovebox and stirred for 30 min. Then, the solvent was removed by N₂ bubbling. The vial was added alkylborate **2g** (54.5 mg, 0.15 mmol) and DMSO/H₂O (9/1, 2 mL) under an ambient atmosphere. After O₂ bubbling for 1 min, and sealing the vial with Teflon tape, the reaction was placed in EvoluChem photoreactor (PhotoRedOx Duo) equipped with a 45W blue LED. After stirred for 4 h, the reaction was quenched with saturated NaHCO₃ water (ca. 10 mL) and extracted with diethyl ether (ca. 2 mL $\times$ 10). The organic layer was

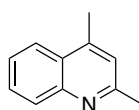
wash with brine and dried over Na₂SO₄ and after filtration, the filtrate was concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (100:0–90:10, hexane/AcOEt) gave **4ag** (8.6 mg, 0.0369 mmol, 37%) as a pale yellow solid. ¹H NMR (400 MHz, CDCl₃) δ 8.09 (d, *J* = 8.4 Hz, 1H), 7.94 (d, *J* = 8.4 Hz, 1H), 7.70 (t, *J* = 7.6 Hz, 1H), 7.52 (t, *J* = 7.6 Hz, 1H), 7.33–7.29 (m, 4H), 7.23 (m, 1H), 7.06 (s, 1H), 4.30 (s, 2H), 2.61 (s, 3H). ¹³C NMR (100.6 MHz, CDCl₃) δ 160.8, 147.6, 144.6, 139.4, 129.5, 129.21, 129.17, 128.6, 126.9, 126.4, 125.7, 123.6, 122.2, 45.5, 18.7. The ¹H and ¹³C NMR spectra data of product **4ag** were consistent with the literature.⁹

Ethyl 3-(4-methylquinolin-2-yl)propanoate (**4ah**)



The product **4ah** was synthesized according to general procedure using lepidine (19.8 μL, 0.15 mmol). The vial was brought to a glovebox, and added MeOH (300 μL) and trifluoroacetic acid (23.1 μL, 0.3 mmol). After the vial was removed from the glovebox and stirred over 5 min. Then, the solvent was removed by rotary evaporator. The vial was added alkylborate **2h** (37.3 mg, 0.1 mmol) and DMSO/H₂O (9/1, 2 mL) under an ambient atmosphere. After O₂ bubbling for 1 min, and sealing the vial with Teflon tape, the reaction was placed in EvoluChem photoreactor (PhotoRedOx Duo) equipped with a 45W blue LED. After stirred for 12.5 h, the reaction was quenched with saturated NaHCO₃ water (ca. 10 mL) and extracted with diethyl ether (ca. 2 mL, over 5 times). The organic layer was dried over Na₂SO₄ and after filtration, the filtrate was concentrated under reduced pressure. The residue was purified by recycling preparative HPLC (CHCl₃) gave **4ah** (9.9 mg, 0.0407 mmol, 41% isolated yield) as a colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 8.01 (d, *J* = 8.4 Hz, 1H), 7.95 (d, *J* = 8.4 Hz, 1H), 7.67 (t, *J* = 7.6 Hz, 1H), 7.51 (t, *J* = 7.6 Hz, 1H), 7.17 (s, 1H), 4.14 (q, *J* = 6.8 Hz, 2H), 3.25 (t, *J* = 7.2 Hz, 2H), 2.90 (t, *J* = 7.2 Hz, 2H), 2.68 (s, 3H), 1.24 (t, *J* = 6.8 Hz, 3H). ¹³C NMR (100.6 MHz, CDCl₃) δ 173.2, 160.2, 147.7, 144.3, 129.4, 129.1, 126.9, 125.6, 123.6, 122.2, 60.4, 33.5, 33.3, 18.7, 14.2. The ¹H and ¹³C NMR spectra data of product **4ah** were consistent with the literature.⁸

Synthesis of **4ai**



The product **4ai** was synthesized according to general procedure using lepidine (14.3 mg, 0.1 mmol). The vial was brought to a glovebox, and added MeOH (200 μL) and trifluoroacetic acid (11.5 μL, 0.15 mmol). After the vial was removed from the glovebox and stirred for 30 min. Then, the solvent was removed by N₂ bubbling. The vial was added alkylborate **2i** (43.1 mg, 0.15 mmol) and DMSO/H₂O (9/1, 2 mL) under an ambient atmosphere. After O₂ bubbling for 1 min, and sealing the vial with Teflon tape, the reaction was placed in EvoluChem photoreactor (PhotoRedOx Duo) equipped with a 45W blue LED. After stirred for 4 h, the reaction was quenched with saturated NaHCO₃ water (ca. 10 mL) and extracted with diethyl ether (ca. 2 mL × 10). The organic layer was dried over Na₂SO₄ and after filtration, the filtrate was concentrated under reduced pressure. The residue was dissolved in CDCl₃ and added 1,1,2,2-tetrachloroethane (23.4 mg, 0.139 mmol) as an internal standard. ¹H NMR (400

MHz) yield (31%) was obtained by comparing the relative value of integration for the singlet peak observed at 2.70 ppm of **4ai**¹⁰ with that of 1,1,2,2-tetrachloroethane observed at 5.96 ppm (Figure S2-2). The generation of **4ai** was also confirmed by observation of the corresponding molecular ion peak with HRMS–DART analysis. **HRMS–DART** (m/z): $[M+H]^+$ calcd for $C_{11}H_{12}N^+$, 158.0964; found, 158.0963.

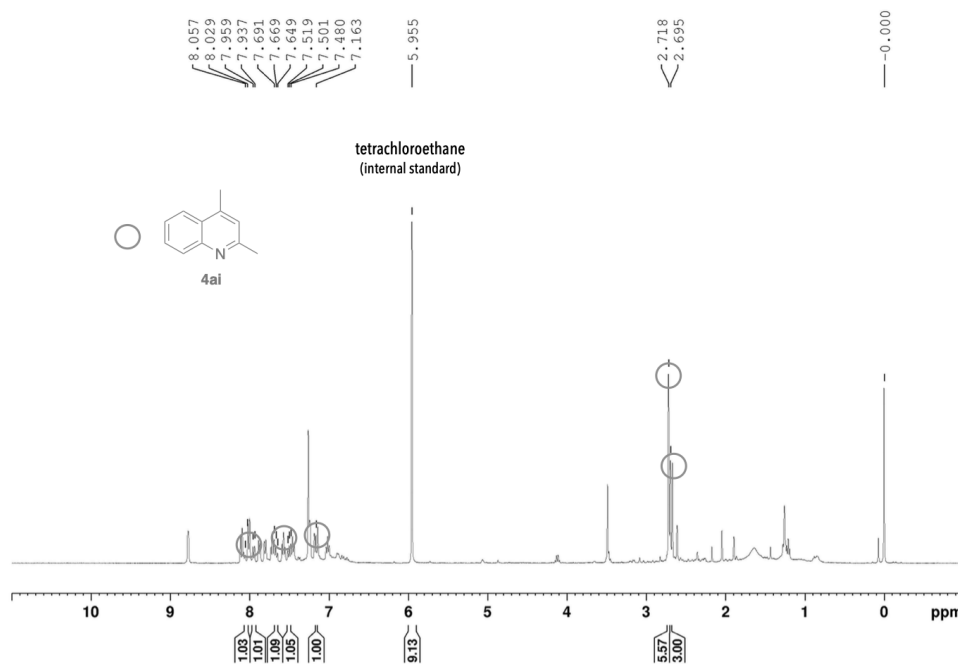
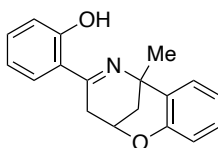


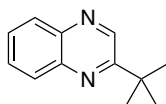
Figure S2-2. ¹H NMR analysis

By-product obtained from **4ai**



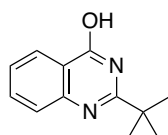
¹H NMR (400 MHz, $CDCl_3$) δ 15.22 (br s, 1H), 7.45 (d, $J = 7.6$ Hz, 1H), 7.38 (d, $J = 7.6$ Hz, 1H), 7.24 (m, 1H), 7.14 (t, $J = 7.6$ Hz, 1H), 6.92–6.86 (m, 2H), 6.83 (d, $J = 8.0$ Hz, 1H), 6.78 (d, $J = 7.6$ Hz, 1H), 5.07 (m, 1H), 3.19 (m, 1H), 3.06 (m, 1H), 2.28 (d, $J = 12.7$ Hz, 1H), 1.93–1.84 (m, 4H). **¹³C NMR** (100.6 MHz, $CDCl_3$) δ 169.1, 161.9, 151.7, 132.4, 128.8, 127.1, 126.8, 125.6, 120.4, 118.7, 118.1, 117.7, 116.9, 66.5, 50.3, 35.0, 33.1, 26.6.

2-(*tert*-Butyl)quinoxaline (**4ba**)



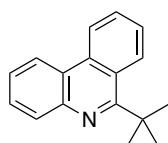
The product **4ba** was synthesized according to general procedure using quinoxaline (19.5 mg, 0.15 mmol). The vial was brought to a glovebox, and added MeOH (300 μ L) and trifluoroacetic acid (23.1 μ L, 0.3 mmol). After the vial was removed from the glovebox and stirred over 5 min. Then, the solvent was removed by rotary evaporator. The vial was added alkylborate **2a** (32.9 mg, 0.1 mmol) and DMSO/H₂O (9/1, 2 mL) under an ambient atmosphere. After O₂ bubbling for 1 min, and sealing the vial with Teflon tape, the reaction was placed in EvoluChem photoreactor (PhotoRedOx Duo) equipped with a 45W blue LED. After stirred for 4 h, the reaction was quenched with saturated NaHCO₃ water (ca. 10 mL) and extracted with diethyl ether (ca. 2 mL, over 5 times). The organic layer was dried over Na₂SO₄ and after filtration, the filtrate was concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (100:0–95:5, hexane/Et₂O) gave **4ba** (4.6 mg, 0.0247 mmol, 25% isolated yield) as a yellow oil. ¹H NMR (400 MHz, CDCl₃) δ 8.99 (s, 1H), 8.09–8.03 (m, 2H), 7.77–7.67 (m, 2H), 1.52 (s, 9H). ¹³C NMR (100.6 MHz, CDCl₃) δ 163.7, 143.4, 141.6, 140.7, 129.6, 129.3, 128.89, 128.88, 37.2, 29.7. The ¹H and ¹³C NMR spectra data of product **4ba** were consistent with the literature.¹¹

2-(*tert*-Butyl)quinazolin-4-ol (**4ca**)



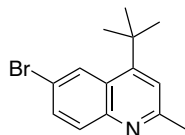
The product **4ca** was synthesized according to general procedure using quinazolin-4(3*H*)-one (20.3 mg, 0.14 mmol). The vial was brought to a glovebox, and added MeOH (200 μ L) and trifluoroacetic acid (13.8 μ L, 0.18 mmol). After the vial was removed from the glovebox and stirred for 30 min. Then, the solvent was removed by N₂ bubbling. The vial was added alkylborate **2a** (32.9 mg, 0.1 mmol) and DMSO/H₂O (9/1, 2 mL) under an ambient atmosphere. After O₂ bubbling for 1 min, and sealing the vial with Teflon tape, the reaction was placed in EvoluChem photoreactor (PhotoRedOx Duo) equipped with a 45W blue LED. After stirred for 4 h, the reaction was quenched with saturated NaHCO₃ water (ca. 10 mL) and concentrated under reduced pressure by Smart Evaporator C1 (BioChromato). The residue was passed through a short pad of NH-silica gel with diethyl ether to remove most of borate fragments and diethyl ether was removed under reduced pressure. The residue was purified by flash column chromatography on silica gel (100:0–90:10, hexane/AcOEt), and then purified by recycling preparative HPLC (CHCl₃). After the volatiles were removed, the residue was passed through a short pad of silica gel with hexane/AcOEt (9/1) and CH₂Cl₂/AcOEt (1/1) gave **4ca** (10.3 mg, 0.0509 mmol, 51% isolated yield) as a white solid. ¹H NMR (400 MHz, CDCl₃) δ 10.2 (s, 1H), 8.27 (d, *J* = 7.6 Hz, 1H), 7.79–7.68 (m, 2H), 7.46 (t, *J* = 7.2 Hz, 1H), 1.47 (s, 9H). ¹³C NMR (100.6 MHz, CDCl₃) δ 163.2, 161.7, 149.1, 134.5, 127.7, 126.4, 126.2, 120.6, 37.3, 28.3. The ¹H and ¹³C NMR spectra data of product **4ca** were consistent with the literature.¹²

6-(*tert*-Butyl)phenanthridine (**4da**)



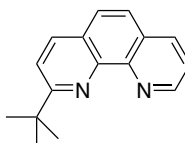
The product **4da** was synthesized according to general procedure using phenanthridine (26.9 mg, 0.15 mmol). The vial was brought to a glovebox, and added MeOH (300 μ L) and trifluoroacetic acid (23.1 μ L, 0.3 mmol). After the vial was removed from the glovebox and stirred over 5 min. Then, the solvent was removed by rotary evaporator. The vial was added alkylborate **2a** (32.9 mg, 0.1 mmol) and DMSO/H₂O (9/1, 2 mL) under an ambient atmosphere. After O₂ bubbling for 1 min, and sealing the vial with Teflon tape, the reaction was placed in EvoluChem photoreactor (PhotoRedOx Duo) equipped with a 45W blue LED. After stirred for 4 h, the reaction was quenched with saturated NaHCO₃ water (ca. 10 mL) and extracted with diethyl ether (ca. 2 mL, over 5 times). The organic layer was dried over Na₂SO₄ and after filtration, the filtrate was concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (100:0–95:5, hexane/Et₂O) gave **4da** (11.6 mg, 0.0493 mmol, 49% isolated yield) as a yellow oil. ¹H NMR (400 MHz, CDCl₃) δ 8.69 (d, *J* = 8.4 Hz, 1H), 8.63 (d, *J* = 8.4 Hz, 1H), 8.53 (t, *J* = 8.0 Hz, 1H), 8.12 (d, *J* = 8.0 Hz, 1H), 7.78 (t, *J* = 7.2 Hz, 1H), 7.73–7.57 (m, 3H), 1.73 (s, 9H). ¹³C NMR (100.6 MHz, CDCl₃) δ 166.6, 142.9, 134.0, 130.3, 129.2, 128.3, 128.2, 126.4, 125.9, 124.3, 123.4, 123.0, 121.6, 40.2, 31.2. The ¹H and ¹³C NMR spectra data of product **4da** were consistent with the literature.¹³

6-Bromo-4-(*tert*-butyl)-2-methylquinoline (**4ea**)



The product **4ea** was synthesized according to general procedure using 6-bromo-2-methylquinoline (33.3 mg, 0.15 mmol). The vial was brought to a glovebox, and added MeOH (300 μ L) and trifluoroacetic acid (23.1 μ L, 0.3 mmol). After the vial was removed from the glovebox and stirred over 5 min. Then, the solvent was removed by rotary evaporator. The vial was added alkylborate **2a** (32.9 mg, 0.1 mmol) and DMSO/H₂O (9/1, 2 mL) under an ambient atmosphere. After O₂ bubbling for 1 min, and sealing the vial with Teflon tape, the reaction was placed in EvoluChem photoreactor (PhotoRedOx Duo) equipped with a 45W blue LED. After stirred for 4 h, the reaction was quenched with saturated NaHCO₃ water (ca. 10 mL) and extracted with diethyl ether (ca. 2 mL, over 5 times). The organic layer was dried over Na₂SO₄ and after filtration, the filtrate was concentrated under reduced pressure. The residue was purified by recycling preparative HPLC (CHCl₃) gave **4ea** (18.2 mg, 0.0654 mmol, 65% isolated yield) as a pale yellow oil. IR (neat) 776, 831, 1078, 1383, 1461, 1485, 1594, 2968 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 8.49 (s, 1H), 7.92 (d, *J* = 8.8 Hz, 1H), 7.70 (d, *J* = 8.8 Hz, 1H), 7.25 (s, 1H), 2.70 (s, 3H), 1.59 (s, 9H). ¹³C NMR (100.6 MHz, CDCl₃) δ 159.1, 154.9, 147.8, 131.9, 131.5, 128.6, 126.4, 119.8, 118.3, 36.0, 31.2, 25.5. HRMS–DART (*m/z*): [M+H]⁺ calcd for C₁₄H₁₇BrN⁺, 278.0539; found, 278.0538.

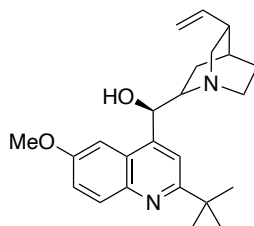
2-(*tert*-Butyl)-1,10-phenanthroline (**4fa**)



The product **4fa** was synthesized according to general procedure using 1,10-phenanthroline (36.0

mg, 0.2 mmol). The vial was brought to a glovebox, and added MeOH (400 μ L) and trifluoroacetic acid (15.4 μ L, 0.2 mmol). After the vial was removed from the glovebox and stirred over 5 min. Then, the solvent was removed by rotary evaporator. The vial was added alkylborate **2a** (32.9 mg, 0.1 mmol) and DMSO/H₂O (9/1, 2 mL) under an ambient atmosphere. After O₂ bubbling for 1 min, and sealing the vial with Teflon tape and equipped with O₂ balloon, the reaction was placed in EvoluChem photoreactor (PhotoRedOx Duo) equipped with a 45W blue LED. After stirred for 4 h, the reaction was quenched with saturated NaHCO₃ water (ca. 10 mL) and extracted with diethyl ether (ca. 2 mL, over 5 times). The organic layer was dried over Na₂SO₄ and after filtration, the filtrate was concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (100:0–70:30, hexane/AcOEt) gave **4fa** (10.8 mg, 0.0457 mmol, 46% isolated yield) as a yellow solid. ¹H NMR (400 MHz, CDCl₃) δ 9.23 (dd, J = 4.4, 1.6 Hz, 1H), 8.23 (dd, J = 8.0, 1.6 Hz, 1H), 8.18 (d, J = 8.4 Hz, 1H), 7.79–7.72 (m, 3H), 7.60 (dd, J = 8.0, 4.4 Hz, 1H), 1.61 (s, 9H). ¹³C NMR (100.6 MHz, CDCl₃) δ 169.8, 150.4, 146.5, 145.0, 136.10, 136.05, 128.9, 126.7, 126.4, 125.6, 122.4, 120.0, 38.6, 30.5. The ¹H and ¹³C NMR spectra data of product **4fa** were consistent with the literature.¹⁴

(1*R*)-(2-(*tert*-Butyl)-6-methoxyquinolin-4-yl)((1*S*,4*S*,5*R*)-5-vinylquinuclidin-2-yl)methanol (4ha**)**



The product **4ha** was synthesized according to general procedure using (-)-quinine sulfate dihydrate (39.2 mg, 0.1 mmol). The vial was brought to a glovebox, and added MeOH (400 μ L) and trifluoroacetic acid (15.5 μ L, 0.2 mmol). After the vial was removed from the glovebox and stirred for 5 min. Then, the solvent was removed by rotary evaporator. The vial was added alkylborate **2a** (49.4 mg, 0.1 mmol) and DMSO/H₂O (9/1, 2 mL) under an ambient atmosphere. After O₂ bubbling for 1 min, and sealing the vial with Teflon tape and equipped with O₂ balloon. The reaction was placed in EvoluChem photoreactor (PhotoRedOx Duo) equipped with a 45W blue LED. After stirred for 4 h, the reaction was quenched with additional TFA (155 μ L, 2 mmol) and CH₂Cl₂ (5 mL). After stirred for 30 min, the solvent was removed by Smart Evaporator C1 (BioChromato). The residue was passed through a short pad of silica gel with CH₂Cl₂/MeOH (9/1) and solvent was removed by rotary evaporator. The residue was dissolved in CDCl₃ and added 1,1,2,2-tetrachloroethane (16.3 mg, 97 μ mol) as an internal standard. ¹H NMR (400 MHz) yield (55%) was obtained by comparing the relative value of integration for the singlet peak observed at 1.45 ppm of **4ha**¹⁵ with that of 1,1,2,2-tetrachloroethane observed at 5.96 ppm (Figure S2-3). The generation of **4ha** was also confirmed by observation of the corresponding molecular ion peak with HRMS–DART analysis. **HRMS–DART** (m/z): [M+H]⁺ calcd for C₂₄H₃₃N₂O₂⁺, 381.2537; found, 381.2537.

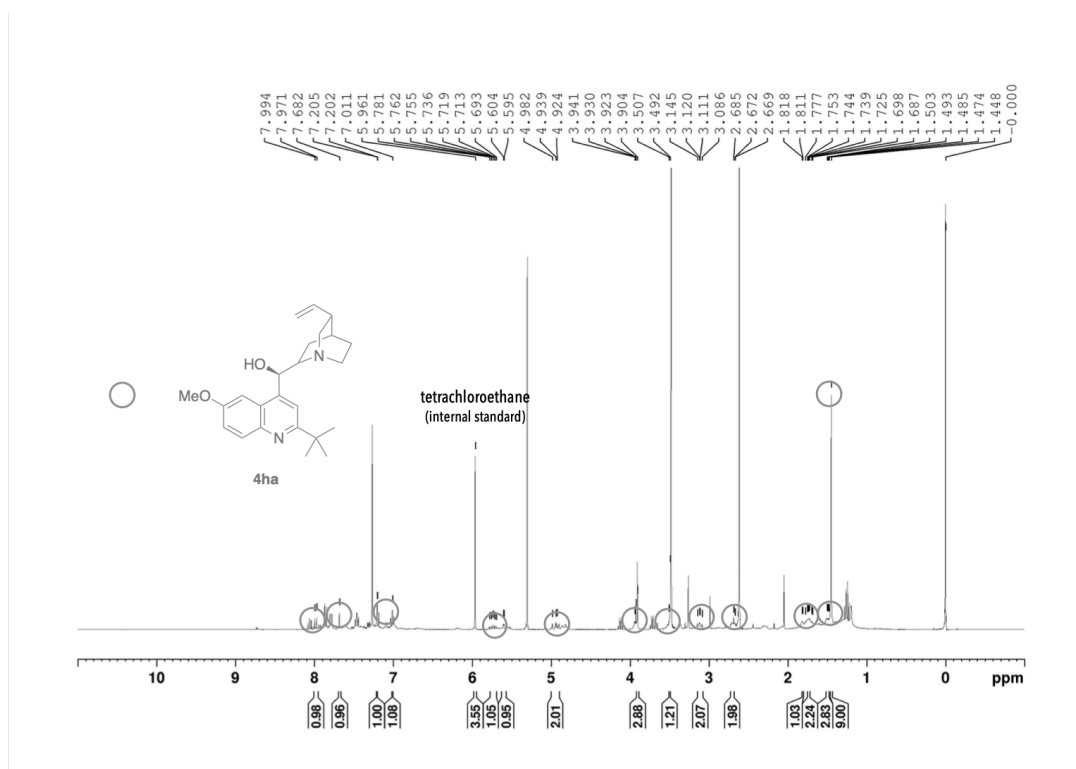


Figure S2-3. ¹H NMR analysis

■ X-ray Diffraction Analysis for By-product (CCDC 2114101) ■

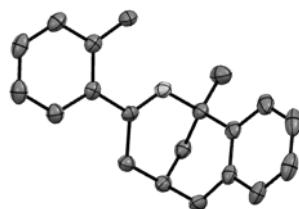


Figure S2-4. ORTEP diagram of 1a. Ellipsoids are drawn at 50% probability. A single crystal used for the analysis was obtained by recrystallization from *n*-hexane and tetrahydrofuran. Hydrogen atoms are omitted for clarity.

Table S2-1. Crystal data and structure refinement for the by-product (CCDC 2114101)

Bond precision:	C-C = 0.0031 Å		Wavelength=0.71075
Cell:	a=13.0982 (15)	b=11.3014 (15)	c=9.6381 (11)
	alpha=90	beta=102.452 (7)	gamma=90
Temperature:	123 K		
	Calculated	Reported	
Volume	1393.2 (3)	1393.2 (3)	
Space group	P 21/c	P 1 21/c 1	
Hall group	-P 2ybc	-P 2ybc	
Moiety formula	C18 H17 N O2	C18 H17 N O2	
Sum formula	C18 H17 N O2	C18 H17 N O2	
Mr	279.33	279.34	
Dx, g cm-3	1.332	1.332	
Z	4	4	
Mu (mm-1)	0.087	0.087	
F000	592.0	592.0	
F000'	592.26		
h,k,lmax	17,14,12	16,14,12	
Nref	3193	3186	
Tmin,Tmax	0.991,0.991	0.570,0.991	
Tmin'	0.991		
Correction method= # Reported T Limits: Tmin=0.570 Tmax=0.991			
AbsCorr = MULTI-SCAN			
Data completeness=	0.998	Theta(max)= 27.479	
R(reflections)=	0.0577(1990)	wR2(reflections)=	
		0.1406(3186)	
S =	1.048	Npar= 193	

第二章 実験項 参考文献

1. Numano, M.; Nagami, N.; Nakatsuka, S.; Katayama, T.; Nakajima, K.; Tatsumi, S.; Yasuda, N.; Hatakeyama, T. *Chem. Eur. J.* **2016**, *22*, 11574-11577.
2. Zhang, H.; Huo, C.; Ye, K.; Zhang, P.; Tian, W.; Wang, Y. *Inorg. Chem.* **2006**, *45*, 2788-2794.
3. Sato, Y.; Nakamura, K.; Sumida, Y.; Hashizume, D.; Hosoya, T.; Ohmiya, H. *J. Am. Chem. Soc.* **2020**, *142*, 9938-9943.
4. Miyamoto, Y.; Sumida, Y.; Ohmiya, H. *Org. Lett.* **2021**, *23*, 5865-5870.
5. Liu, Y.; Xue, L.; Shi, B.; Bu, F.; Wang, D.; Lu, L.; Shi, R.; Lei, A. *Chem. Commun.* **2019**, *55*, 14922-14925.
6. Molander, G. A.; Colombel, V.; Braz, V. A. *Org. Lett.* **2011**, *13*, 1852-1855.
7. McCallum, T.; Barriault, L. *Chem. Sci.* **2016**, *7*, 4754-4758.
8. Dong, J.; Wang, X.; Wang, Z.; Song, H.; Liu, Y.; Wang, Q. *Org. Chem. Front.* **2019**, *6*, 2902-2906.
9. Cao, D.; Chen, Z.; Lv, L.; Zeng, H.; Peng, Y.; Li, C.-J. *iScience* **2020**, *23*, 101419.
10. Putta, R. R.; Chun, S.; Lee, S. B.; Hong, J.; Oh, D.-C.; Hong, S. *RSC Advances* **2021**, *11*, 18225-18230.
11. Dubey, A. V.; Kumar, A. V. *ACS Sustain. Chem. Eng.* **2018**, *6*, 14283-14291.
12. Chen, Y.-F.; Hsieh, J.-C. *Org. Lett.* **2014**, *16*, 4642-4645.
13. Gimeno, L.; Blart, E.; Rebilly, J. N.; Coupeau, M.; Allain, M.; Roisnel, T.; Quarré De Verneuil, A.; Gourlaouen, C.; Daniel, C.; Pellegrin, Y. *Chem. - Eur. J.* **2020**, *26*, 11887-11899.
14. Matsui, J. K.; Primer, D. N.; Molander, G. A. *Chem. Sci.* **2017**, *8*, 3512-3522.
15. Sumida, Y.; Harada, R.; Kato-Sumida, T.; Johmoto, K.; Uekusa, H.; Hosoya, T. *Org. Lett.* **2014**, *16*, 6240-6243.

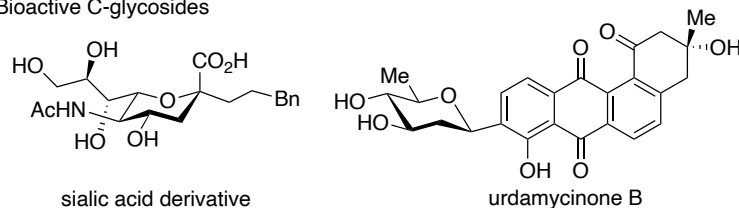
第三章 PDP 型青色光励起グリコシルハウ素アート錯体を用いた C-グリコシル化反応

第一節 着想背景および作業仮説

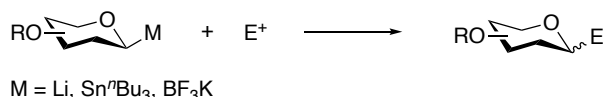
配糖体 (グリコシド) は医薬品や生理活性物質に普遍的に存在する重要な構造単位である。中でも、グリコシドのアノマー炭素とアグリコンが炭素-炭素結合で繋がった C-グリコシドは、天然に豊富に存在する O-グリコシドと比較して、酵素による加水分解に対して高い安定性を示す (Figure 3-1A)。¹ また、その特異的な立体配座や生物学的活性から、糖鎖認識酵素やタンパク質を標的とした創薬研究において重要な合成ターゲットとなっている。^{1b, 1c} これまでに、C-グリコシドを構築するために様々なグリコシルドナーが開発されてきた。² 特に、グリコシルリチウム、³ グリコシルスズ、⁴ グリコシルハウ素⁵ といったグリコシル金属化合物は、アノマー位における炭素-炭素結合形成に有効な試薬として利用されてきた (Figure 3-1B)。しかし、これらの金属試薬を用いた従来法の多くは、糖の複数の水酸基を保護した基質を用いる必要があり、保護-脱保護操作が反応工程を増加させる要因となっていた。そのため、保護-脱保護操作を必要としない「無保護グリコシル金属化合物」を用いた C-グリコシル化反応の開発が強く望まれている。⁶ しかし、一般に無保護糖の金属種は合成が困難であり、また反応の制御も難しい。そのため、無保護グリコシルドナーの合成と活用は、Walczak らによる無保護グリコシルスズを用いた Pd 触媒クロスカップリング反応のみにとどまっていた。⁴

一方、著者の所属研究室では、第一章および第二章で述べたように、PDP 配位子を有する PDP 型ハウ素アート錯体が、青色光照射下で強力な還元剤として機能すると同時に、炭素ラジカルを発生させることを見出している。⁷ この PDP 型ハウ素アート錯体は、高い官能基許容性を有しており、ハウ素上に多様なアルキル基の導入が可能である。そこで、この PDP 配位子を用いた炭素ラジカル生成戦略を無保護の糖を用いたグリコシル化反応に適用することで、新たなラジカル的 C-グリコシル化法が開発できると考えた (Figure 3-1C)。具体的には、グリコシルトリフルオロボレート塩と PDP 配位子から無保護グリコシルハウ素アート錯体 **2** を調製し、このハウ素アート錯体 **2** を直接青色光励起する。これにより、外部光触媒を用いることなくアノマー位炭素ラジカルを発生させることができ、Giese 型ラジカル付加反応や Minisci 型反応、さらにはラジカル-ラジカルカップリングを経由して、保護基フリーでアルキル、アリール、およびアシル C-グリコシドを合成できると考えた。本手法が確立されれば、煩雑な保護基の脱着を必要としない迅速かつ多様な C-グリコシド合成法になると期待される。

A | Bioactive C-glycosides



B | Glycosyl metals for C-glycoside synthesis



C | This work

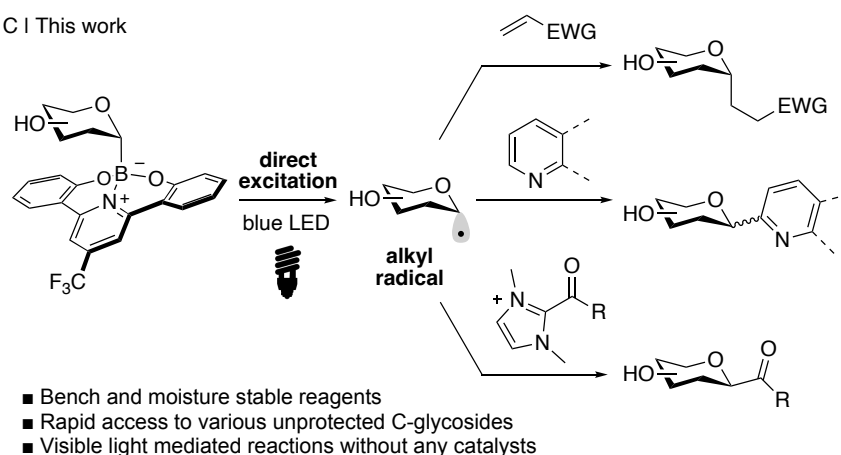


Figure 3-1. C-グリコシド合成に関する本研究の概要

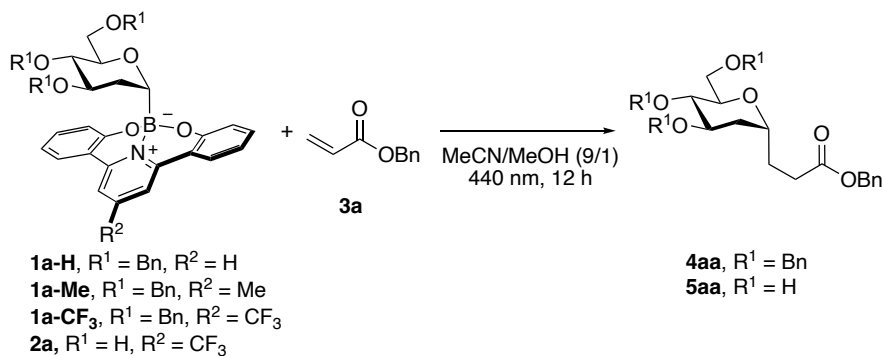
第二節 反応条件の最適化および基質適用範囲の検討

第一節の作業仮説に基づき、まず Giese 型 C-グリコシル化反応の条件検討を行った (Table 3-1)。モデル基質として、全ての水酸基をベンジル基で保護したグリコシルホウ素アート錯体 **1a** とアクリル酸ベンジル **3a** を用いた。アセトニトリル/メタノール混合溶媒中、青色 LED (440 nm) を照射したところ、無置換の PDP 配位子を持つ **1a-H** では目的とする C-グリコシド **4aa** の収率は 10%にとどまった (entry 1)。PDP 配位子にメチル基を導入した **1a-Me** を用いた場合も収率は 10%であった (entry 2)。そこで、PDP 配位子に電子求引性のトリフルオロメチル基を導入した **1a-CF₃** を用いることで、収率が 27%まで向上することを見出した (entry 3)。さらに、反応濃度を検討したところ、2.8 mM という低濃度条件において反応効率が劇的に改善され、**4aa** が 94%の収率で得られた (entry 4)。

これらの知見を基に、無保護グリコシルホウ素アート錯体 **2a** を用いた反応を検討した。最適化された条件下、**2a** と アクリル酸ベンジル **3a** を反応させたところ、保護基を持たないアルキル C-グリコシド **5aa** が 73%の単離収率 (NMR 収率 97%) で得られた (entry 5)。得られた生成物の立体は完全な α 体であった。なお、この無保護ホウ

素アート錯体 **2a** は、遮光下、室温で 6 ヶ月以上安定に保存可能であり、取り扱いが容易な試薬である。

Table 3-1. Giese 型ラジカル付加反応の条件検討 ^a



entry	borate	Concentration (mM)	Yields (%)
1	1a-H	100	10
2	1a-Me	100	10
3	1a-CF₃	100	27
4	1a-CF₃	2.8	94 (90) ^b
5	2a	2.8	97 (73) ^b

^aReaction was carried out with glycosyl borate (0.08 mmol), benzyl acrylate **3a** (0.05 mmol) in 9:1 mixture of acetonitrile and methanol under 440 nm (Kessil lamp) irradiation for 12 h. ^bIsolated yield.

続いて、Giese 型ラジカル付加反応における基質適用範囲の検討を行った (Table 3-2)。⁸ ラジカルアクセプターとして、アクリル酸エステル **3b** だけでなく、アクリルアミド **3c**、ビニルスルホン **3d**、アクリロニトリル **3e** といった種々の電子不足アルケンが適用可能であり、対応する無保護 C-グリコシドを良好な収率かつ完全な α 選択性で与えた (**5ab**, **5ac**, **5ad** and **5ae**)。ペプチド側鎖を有するアルケンを用いた場合でも、69%の収率で目的物 **5af** が得られた。また、糖の基質適用範囲の検討として、C2 位に水酸基を持つグルコース由来のハウ素アート錯体 **2b** や、C4 位の水酸基の立体化学が異なるガラクトース由来のハウ素アート錯体 **2c**、さらには二糖類由来のハウ素アート錯体 **2d** も本反応に適用可能であり、それぞれ対応する C-グリコシドを与えた (**5bb**, **5ca** and **5da**)。デヒドロアラニン **3g** を用いた際にも、対応するアミノ酸誘導体 **5bg** が得られた。

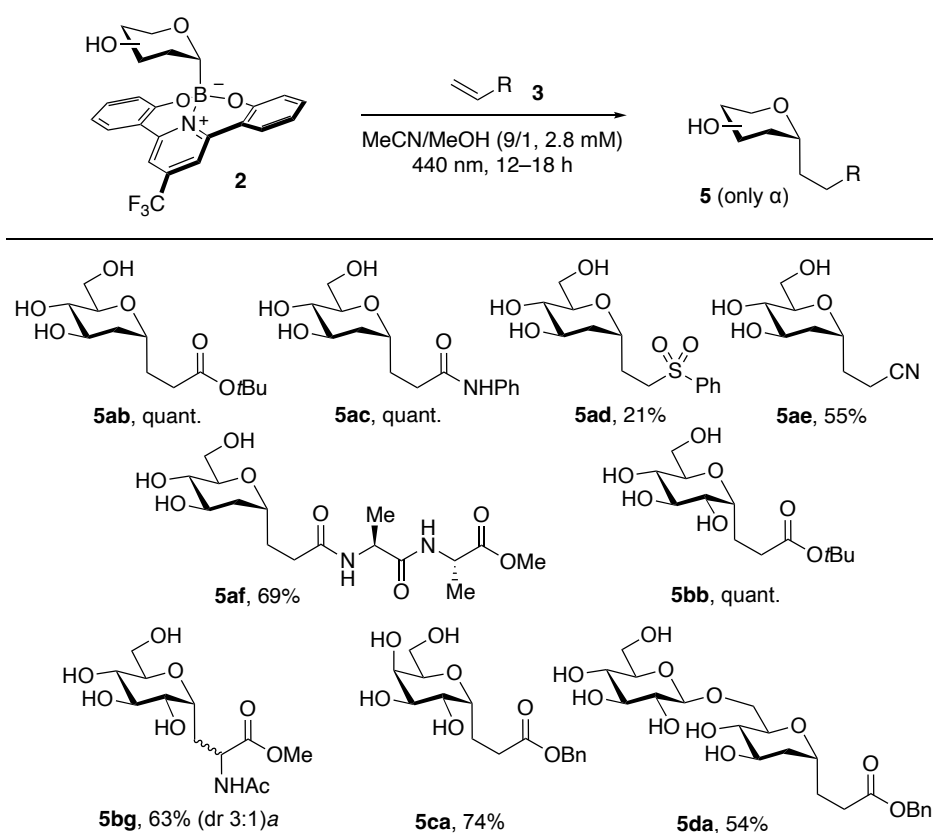
次に、ヘテロ芳香環への Minisci 型反応によるアリール C-グリコシド合成を検討した (Table 3-3)。⁹ 無保護グリコシルハウ素アート錯体 **2a** と TFA を反応させたイソキノリン **6a** に対し、過硫酸カリウムを用い、DMSO/水混合溶媒中で光照射を行ったところ、

目的物 **7aa** が定量的に得られた ($\alpha:\beta=10:1$)。レピジン **6b** を用いた反応では、反応温度によって立体選択性が変化した。0 °Cでは α 選択的、50 °Cでは β 選択的に生成物が得られた。本手法は、医薬品であるファスジル **6c** やフェナントリジン **6d** にも適用可能であり、医薬品骨格を含むアリール C-グリコシドの合成に成功した (**7bc and 7bd**)。

さらに、従来法では合成困難とされてきた「無保護アシル C-グリコシド」の直接的合成を行った (Table 3-4)。¹⁰ カップリングパートナーとしてアシルアゾリウム **8** を用いることとした。¹¹ PDP 型ホウ素アート錯体 **2** 由来のアノマー位炭素ラジカルとアシルアゾリウム **8** 由来のケチルラジカルのカロスカップリングにより目的のカップリング体が得られると考えた。ジクロロエタン中、青色光照射下でホウ素アート錯体 **2a** とアシルイミダゾリウム **8a** を反応させ、DBU により処理したところ、アシル C-グリコシド **9aa** が 41%の収率で得られた。この反応では、Giese 型ラジカル付加反応や Minisci 型反応とは対照的に、 β 体が得られた。脂肪族アシル基を有するアシルアゾリウム **8b** も適用可能であり、対応するケトン **9ab** を与えた。

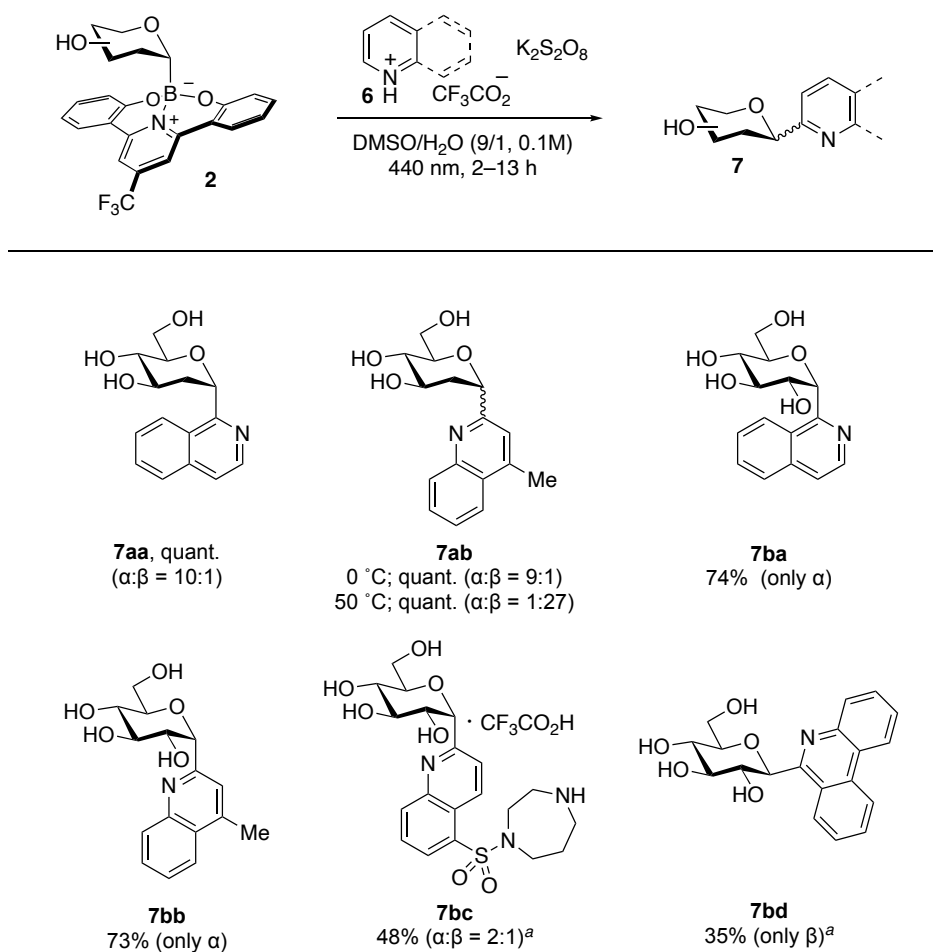
以上の結果より、本手法は煩雑な保護基の脱着を一切必要とせず、アルキル、アリール、アシル基といった多様な炭素官能基を糖のアノマー位に導入できる汎用性の高い C-グリコシル化法であることが示された。

Table 3-2. Giese 型ラジカル付加反応の基質適用範囲



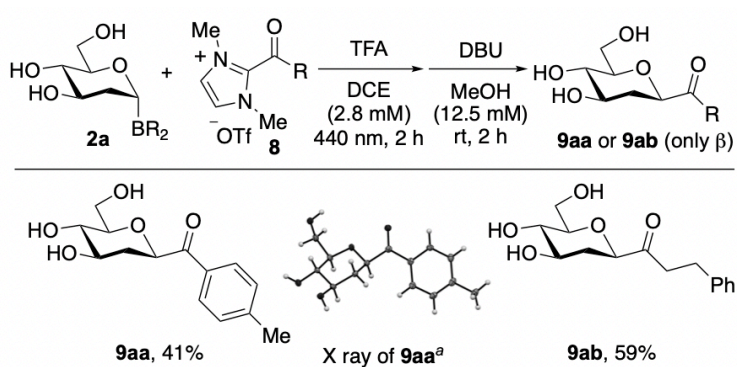
^a**5bg** was purified after acetyl protection of hydroxy groups.

Table 3-3. Minisci 型反応の基質適用範囲



^aThis reaction was conducted at 50 °C.

Table 3-4. アシル化反応の基質適用範囲



^aThe CCDC number of **9aa** is 2353967.

第三節 推定反応機構

本反応の反応機構を理解するために、まずグリコシルホウ素アート錯体の光物理的特性の評価を行った。PDP 型ホウ素アート錯体 (**1a-H**, **1a-Me**, **1a-CF₃**, **2a** and **10**) の吸収スペクトルと蛍光スペクトルは、 **Figure 3-2** から **Figure 3-6** に示す通りであった。さらに、サイクリックボルタンメトリー (CV) 測定の結果、これらのホウ素アート錯体の酸化電位には大きな差が見られなかった (**Figure 3-7** から **Figure 3-10**)。なお、**2a** は溶解性に問題があり CV の測定ができていない。以下のように PDP 型ホウ素アート錯体 (**1a-H**, **1a-Me** and **1a-CF₃**) の還元力を推定したが、収率との相関は見られなかった。

ホウ素アート錯体 **1a-H** について、紫外可視吸収スペクトル、蛍光スペクトル、およびサイクリックボルタンメトリーから得られたデータに基づき、以下の Rehm-Weller 式を用いて光励起ボレートの酸化還元電位を近似的に算出した。なお、サイクリックボルタンメトリー (**Figure 3-7**) において、ボレート **1a-H** の電気化学的酸化過程は不可逆過程であった。したがって、酸化電位 $E (= +0.805 \text{ V vs. SCE})$ を $E(\mathbf{1a-H}^+/\mathbf{1a-H})$ として用いた。ホウ素アート錯体 **1a-H** 励起状態におけるエネルギー $E_{00}(\mathbf{1a-H}^*/\mathbf{1a-H})$ は吸収スペクトル及び蛍光スペクトルの波長 (406 nm, **Figure 3-2**) から推定し 3.054 eV とした。

For the excited state of borate **1a-H***

Rehm-Weller equation:

$$E(\mathbf{1a-H}^+/\mathbf{1a-H}^*) = E(\mathbf{1a-H}^+/\mathbf{1a-H}) - E_{00}(\mathbf{1a-H}^*/\mathbf{1a-H})$$

$$E(\mathbf{1a-H}^+/\mathbf{1a-H}^*) = 0.805 - 3.061 = -2.256 \text{ V vs. SCE.}$$

ホウ素アート錯体 **1a-Me** について、紫外可視吸収スペクトル、蛍光スペクトル、およびサイクリックボルタンメトリーから得られたデータに基づき、以下の Rehm-Weller 式を用いて光励起ボレートの酸化還元電位を近似的に算出した。なお、サイクリックボルタンメトリー (**Figure 3-8**) において、ボレート **1a-Me** の電気化学的酸化過程は不可逆過程であった。したがって、酸化電位 $E (= +0.931 \text{ V vs. SCE})$ を $E(\mathbf{1a-Me}^+/\mathbf{1a-Me})$ として用いた。ホウ素アート錯体 **1a-Me** 励起状態におけるエネルギー $E_{00}(\mathbf{1a-Me}^*/\mathbf{1a-Me})$ は吸収スペクトル及び蛍光スペクトルの波長 (397 nm, **Figure 3-3**) から推定し 3.123 eV とした。

For the excited state of borate **1a-Me***

Rehm-Weller equation:

$$E(\mathbf{1a-Me}^+/\mathbf{1a-Me}^*) = E(\mathbf{1a-Me}^+/\mathbf{1a-Me}) - E_{00}(\mathbf{1a-Me}^*/\mathbf{1a-Me})$$

$$E(\mathbf{1a-Me}^+/\mathbf{1a-Me}^*) = 0.931 - 3.123 = -2.192 \text{ V vs. SCE.}$$

ホウ素アート錯体 **1a-CF₃** について、紫外可視吸収スペクトル、蛍光スペクトル、およびサイクリックボルタンメトリーから得られたデータに基づき、以下の Rehm-Weller 式を用いて光励起ボレートの酸化還元電位を近似的に算出した。なお、サイクリックボルタンメトリー (**Figure 3-9**) において、ボレート **1a-CF₃** の電気化学的酸化過程は不可逆過程であった。したがって、酸化電位 $E (= +0.951 \text{ V vs. SCE})$ を $E(\mathbf{1a-CF_3}^+/\mathbf{1a-CF_3})$ として用いた。ホウ素アート錯体 **1a-CF₃** 励起状態におけるエネルギー $E_{00}(\mathbf{1a-CF_3}^*/\mathbf{1a-CF_3})$

は吸収スペクトル及び蛍光スペクトルの波長（449 nm, **Figure 3-4**）から推定し 2.761 eV とした。

For the excited state of borate **1a-CF₃***

Rehm-Weller equation:

$$E(1a-CF_3^{+}/1a-CF_3^*) = E(1a-CF_3^{+}/1a-CF_3) - E_{00}(1a-CF_3^*/1a-CF_3)$$

$$E(1a-CF_3^{+}/1a-CF_3^*) = 0.952 - 2.761 = -1.809 \text{ V vs. SCE.}$$

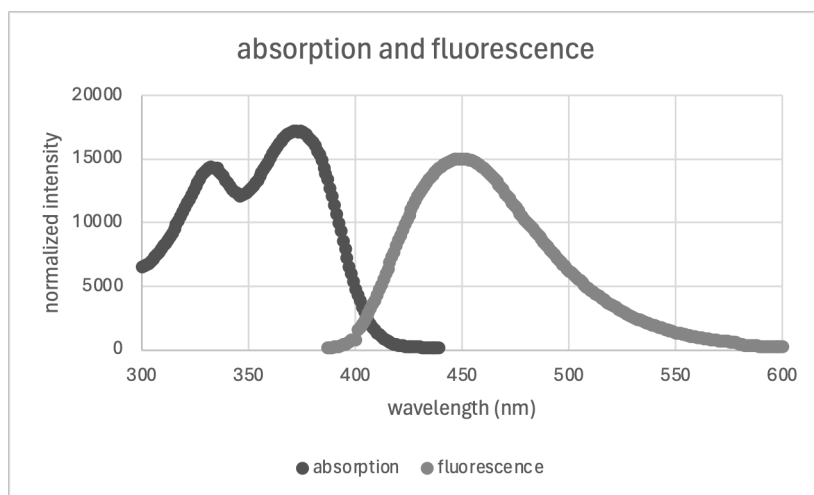


Figure 3-2. **1a-H** の吸収スペクトル及び蛍光スペクトル ^a

^aAbsorption and fluorescence spectra of **1a-H** was measured with 20 μ M acetonitrile solution.

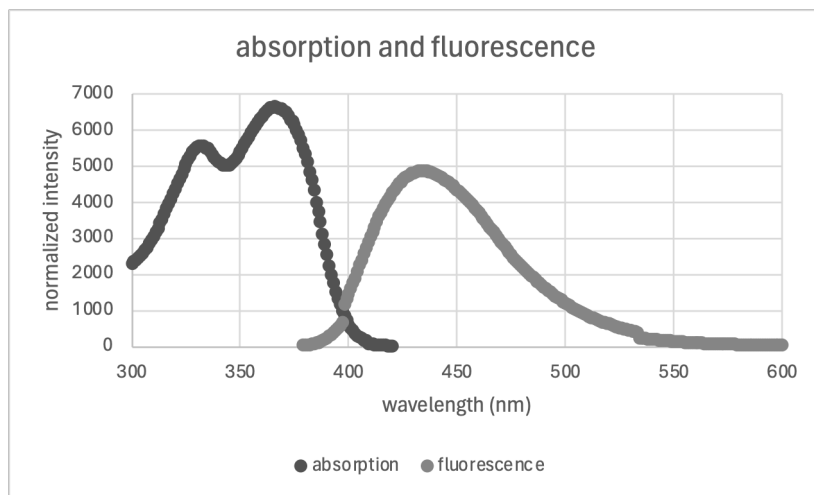


Figure 3-3. **1a-Me** の吸収スペクトル及び蛍光スペクトル ^a

^aAbsorption and fluorescence spectra of **1a-Me** was measured with 20 μ M acetonitrile solution.

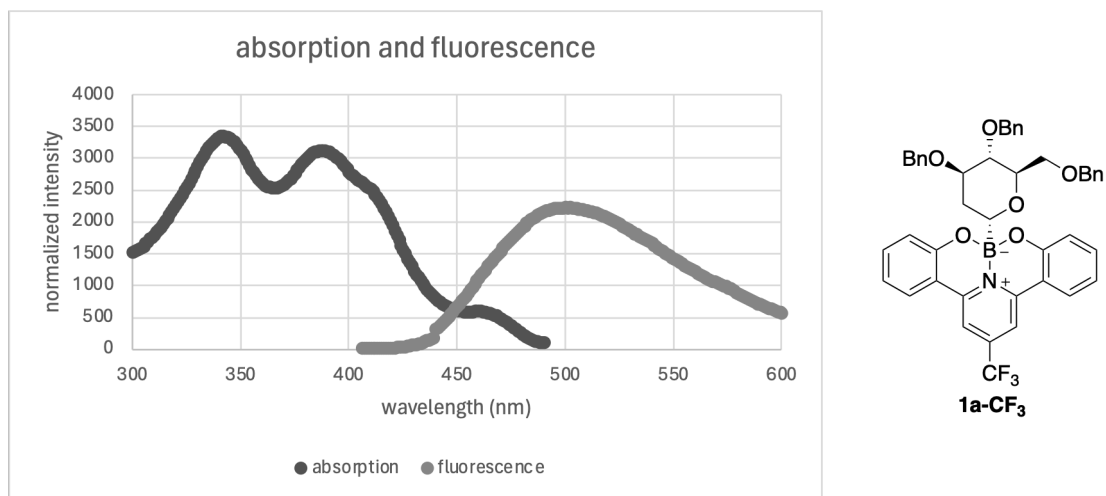


Figure 3-4. **1a-CF₃** の吸収スペクトル及び蛍光スペクトル^a

^aAbsorption and fluorescence spectra of **1a-CF₃** was measured with 20 μ M acetonitrile solution.

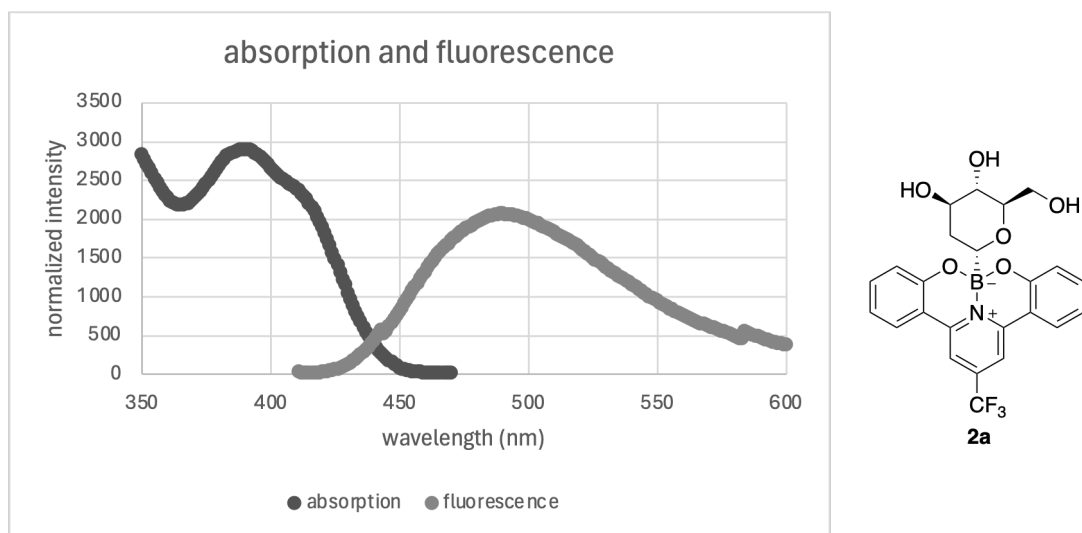


Figure 3-5. **2a** の吸収スペクトル及び蛍光スペクトル^a

^aAbsorption and fluorescence spectra of **2a** was measured with 20 μ M (9/1, DCM/MeOH) solution.

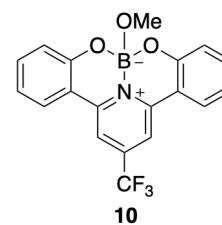
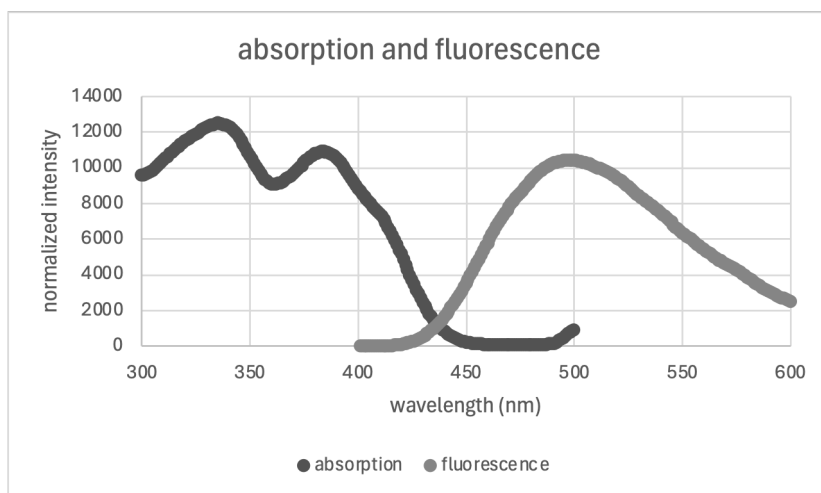
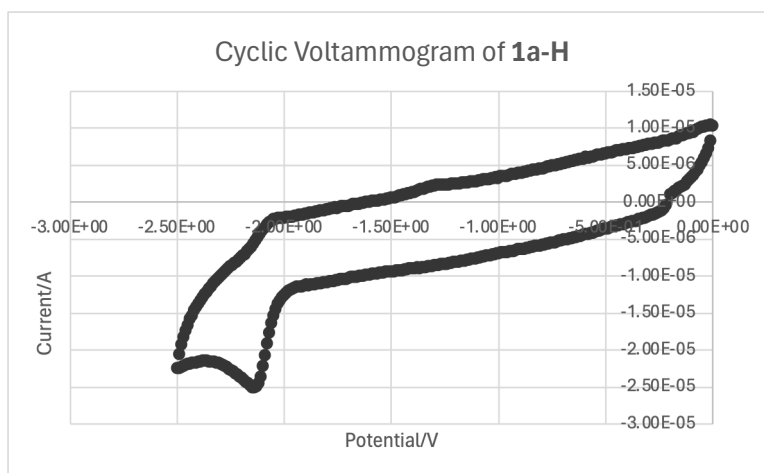
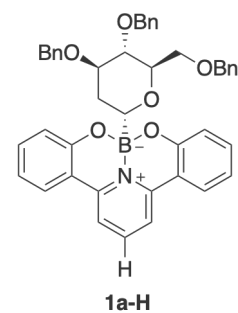
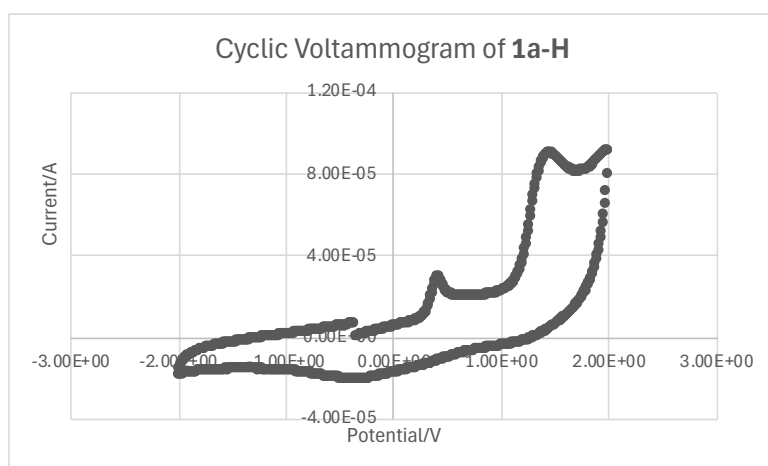


Figure 3-6. **10** の吸収スペクトル及び蛍光スペクトル^a

^aAbsorption and fluorescence spectra of **10** was measured with 20 μ M acetonitrile solution.



1a-H: $E_{pa} = +0.410$ V vs Ag/AgNO₃ = +0.805 V vs. SCE

Calculated according to Fc/Fc⁺ ($E_{1/2} = -0.0149$ V vs Ag/AgNO₃)

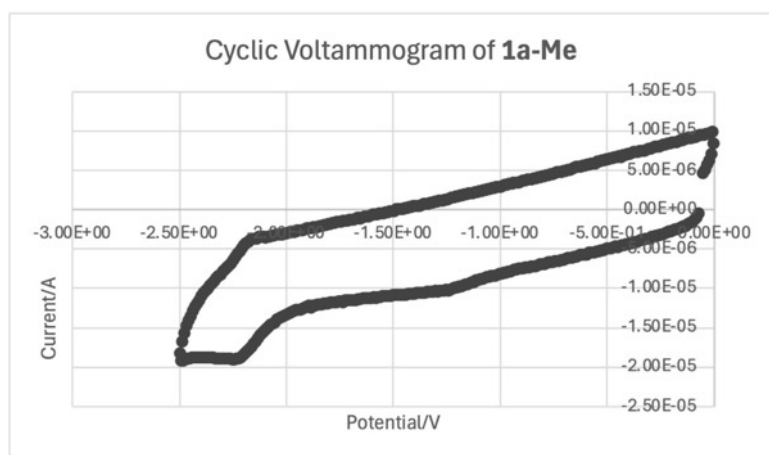
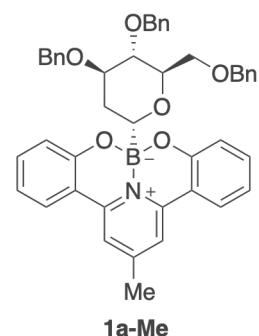
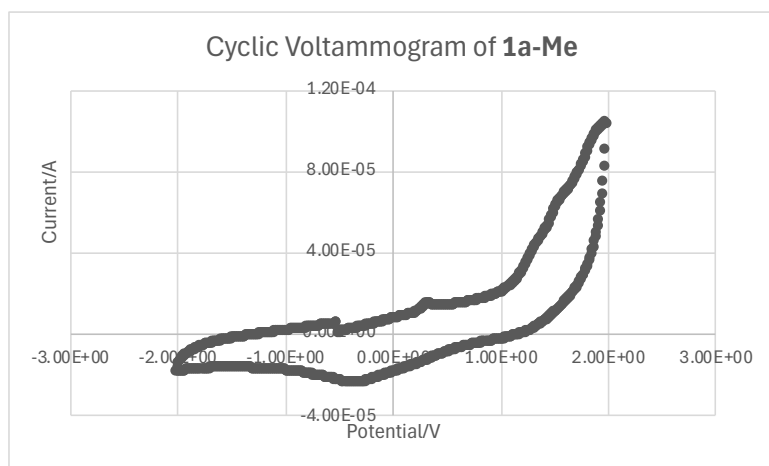
1a-H: $E_{pc} = -2.139$ V vs Ag/AgNO₃ = -1.739 V vs. SCE

Calculated according to Fc/Fc⁺ ($E_{1/2} = -0.0196$ V vs Ag/AgNO₃)

These peaks are not reversible.

Figure 3-7. 1a-H のサイクリックボルタモグラム ^a

^aIn an ambient atmosphere, **1a-H** (0.5 mM in anhydrous MeCN) and tetrabutylammonium perchlorate ([N(ⁿBu)]₄ClO₄) (0.1 M in anhydrous MeCN) as a supporting electrolyte were added to a measuring vessel. Then, the electrochemical property was measured. Measurements used a glassy carbon working electrode, a Ag/AgNO₃ reference electrode, and a Pt wire counter electrode. The sweep rates were set to 100 mV/s. For conversion to the SCE couple, it is known that Fc/Fc⁺ is 380 mV more positive than SCE in MeCN¹² and we measured the Fc/Fc⁺ in MeCN to determine potentials against SCE respectively.



1a-Me: $E_{pa} = +0.536$ V vs Ag/AgNO₃ = +0.931 V vs. SCE

Calculated according to Fc/Fc⁺ ($E_{1/2} = -0.0149$ V vs Ag/AgNO₃)

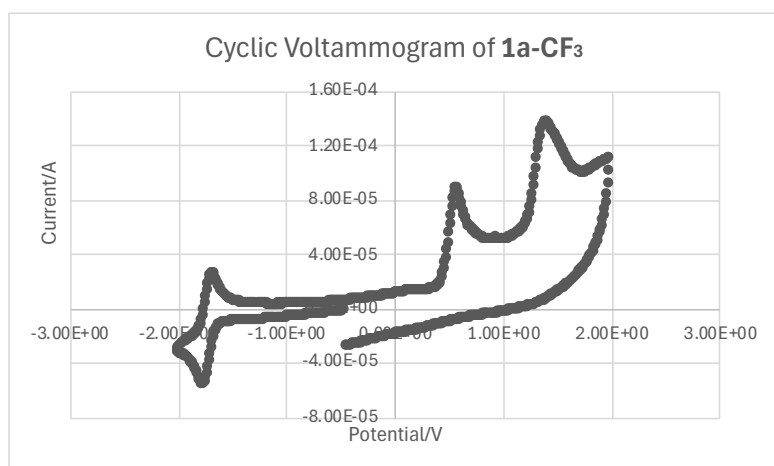
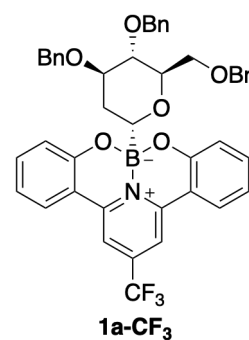
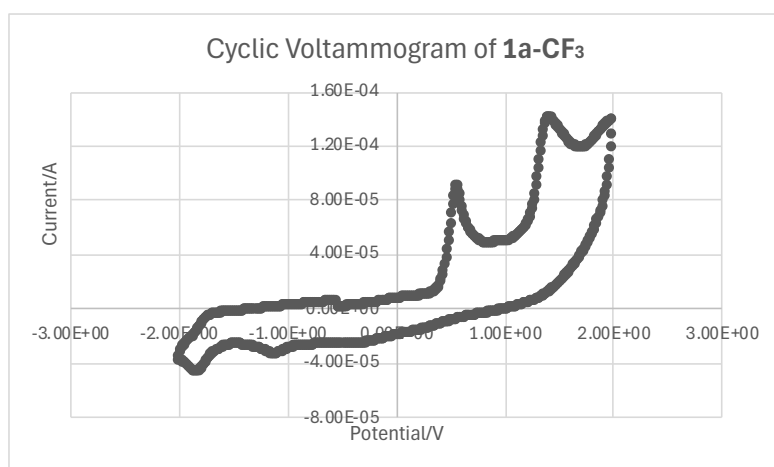
1a-Me: $E_{pc} = -2.254$ V vs Ag/AgNO₃ = -1.854 V vs. SCE

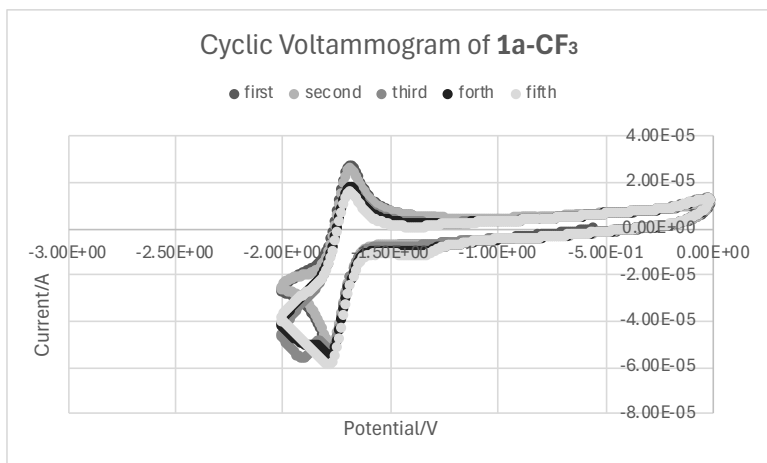
Calculated according to Fc/Fc⁺ ($E_{1/2} = -0.0196$ V vs Ag/AgNO₃)

These peaks are not reversible.

Figure 3-8. 1a-Me のサイクリックボルタモグラム ^a

^aIn an ambient atmosphere, **1a-Me** (0.5 mM in anhydrous MeCN) and tetrabutylammonium perchlorate ($[N(^tBu)_4]ClO_4$) (0.1 M in anhydrous MeCN) as a supporting electrolyte were added to a measuring vessel. Then, the electrochemical property was measured. Measurements used a glassy carbon working electrode, a Ag/AgNO₃ reference electrode, and a Pt wire counter electrode. The sweep rates were set to 100 mV/s. For conversion to the SCE couple, it is known that Fc/Fc⁺ is 380 mV more positive than SCE in MeCN¹² and we measured the Fc/Fc⁺ in MeCN to determine potentials against SCE respectively.



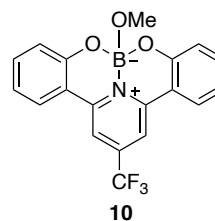
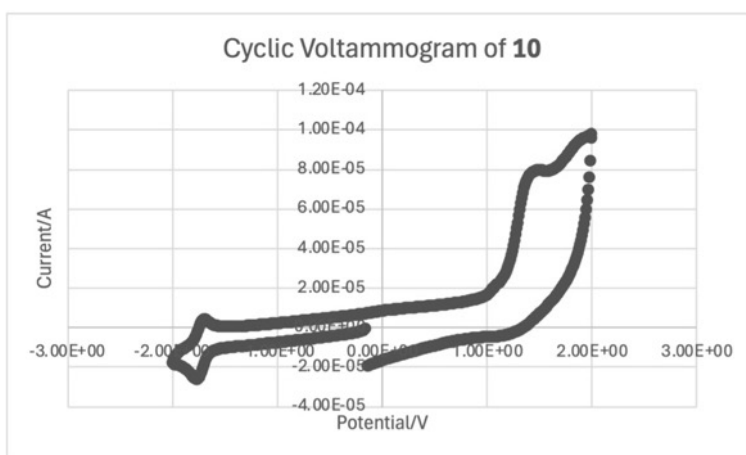


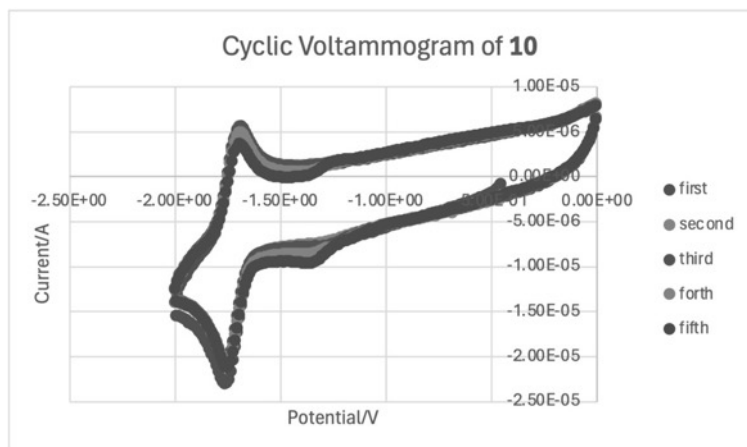
1a- CF₃: $E_{pa} = +0.557$ V vs Ag/AgNO₃ = +0.952 V vs. SCE
 Calculated according to Fc/Fc⁺ ($E_{1/2} = -0.0149$ V vs Ag/AgNO₃)

1a- CF₃: $E_{1/2}$ (1a- CF₃/1a- CF₃ radical anion)
 = -1.720 V vs Ag/AgNO₃ = -1.325 V vs. SCE
 Calculated according to Fc/Fc⁺ ($E_{1/2} = -0.0149$ V vs Ag/AgNO₃)
 The cathodic peak was reversible at least five times.

Figure 3-9. 1a-CF₃ のサイクリックボルタモグラム ^a

^aIn an ambient atmosphere, **1a-CF₃** (0.5 mM in anhydrous MeCN) and tetrabutylammonium perchlorate ([N(ⁿBu)]₄ClO₄) (0.1 M in anhydrous MeCN) as a supporting electrolyte were added to a measuring vessel. Then, the electrochemical property was measured. Measurements used a glassy carbon working electrode, a Ag/AgNO₃ reference electrode, and a Pt wire counter electrode. The sweep rates were set to 100 mV/s. For conversion to the SCE couple, it is known that Fc/Fc⁺ is 380 mV more positive than SCE in MeCN¹² and we measured the Fc/Fc⁺ in MeCN to determine potentials against SCE respectively.





10: $E_{1/2}$ (**10/10** radical anion) = -1.725 V vs Ag/AgNO₃ = -1.331 V vs. SCE

Calculated according to Fc/Fc⁺ ($E_{1/2}$ = -0.0142 V vs Ag/AgNO₃)

The cathodic peak was reversible at least five times.

These results indicate that **10** could act as photoredox catalyst.

Figure 3-10. **10** のサイクリックボルタモグラム^a

^aIn an ambient atmosphere, **10** (0.5 mM in anhydrous MeCN) and tetrabutylammonium perchlorate ([N⁺(ⁿBu)]₄ClO₄) (0.1 M in anhydrous MeCN) as a supporting electrolyte were added to a measuring vessel. Then, the electrochemical property was measured. Measurements used a glassy carbon working electrode, a Ag/AgNO₃ reference electrode, and a Pt wire counter electrode. The sweep rates were set to 100 mV/s. For conversion to the SCE couple, it is known that Fc/Fc⁺ is 380 mV more positive than SCE in MeCN¹² and we measured the Fc/Fc⁺ in MeCN to determine potentials against SCE respectively.

PDP 型ホウ素アート錯体 (**1a-H**, **1a-Me** and **1a-CF₃**) の紫外可視吸光スペクトルを比較したところ、トリフルオロメチル基を有する **1a-CF₃** は、他の誘導体と比較して長波長側に吸収帯がシフトしていることが確認された (**Figure 3-11A**)。したがって、ホウ素アート錯体のより効率的な光吸収が収率の改善に寄与していることが示唆される。

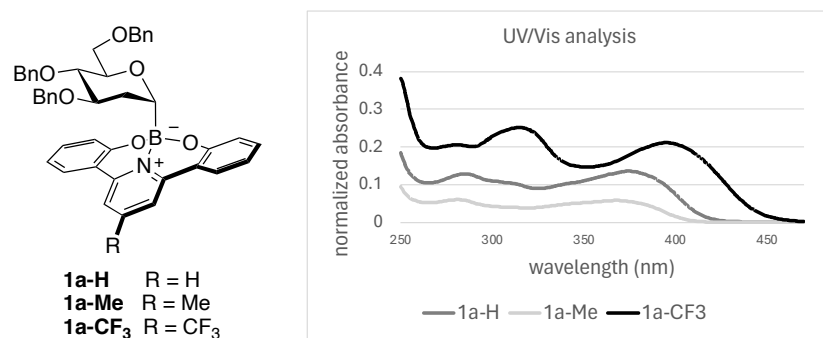
次に、反応系中で生成する副生成物に着目した。グリコシルホウ素アート錯体 **1a-CF₃** とアクリル酸ベンジル **3a** の反応混合物を詳細に解析したところ、目的の C-グリコシドに加え、ホウ素アート錯体のグリコシル基がメトキシ基に置換されたホウ素アート錯体 **10** が 88% の高収率で生成していることが確認できた (**Figure 3-11B**)。CV 測定により、可逆的なピークが確認されたため、この副生成物 **10** および基質であるグリコシルホウ素アート錯体 **1a-CF₃** は適切な電子の授受が可能であることが示された (**Figure 3-9** and **Figure 3-10**)。そのため、これらのホウ素アート錯体は、光酸化還元触媒として機能し得ることが明らかとなった。

以上の実験事実に基づき、Giese 型 C-グリコシル化反応の推定反応機構を以下に示す (**Figure 3-11C**)。反応は、青色光照射によるグリコシルホウ素アート錯体 **2** の励起状態 **2*** の形成から開始される。この **2*** からの炭素-ホウ素結合のホモリティック開裂により、アノマー位炭素ラジカル **A** が生成する。また、励起状態の **2*** あるいは **10***

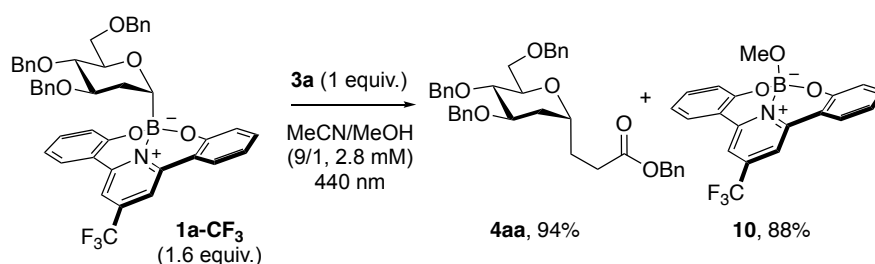
が酸化剤として機能し、基底状態のホウ素アート錯体 **2** を一電子酸化することでラジカル **A** を生じる機構も並行して進行している可能性がある。発生したアノマー位炭素ラジカル **A** は、電子不足アルケン **3** に対して付加し、炭素ラジカル中間体 **B** を形成する。最後に、この中間体 **B** が、励起状態のホウ素アート錯体 (**2*** and **10***) あるいは反応系中で生じたラジカルアニオン種から一電子還元を受け、プロトン化されることで、目的とする C-グリコシド **5** が生成すると推測される。ラジカル放出後のホウ素化合物は、溶媒であるメタノールと反応して安定なメトキシ置換ホウ素アート錯体 **10** となる。

Minisci 型反応の反応機構は、第二章に示したとおりである。最後に、アシル C-グリコシド合成における推定反応機構を示す (**Figure 3-11D**)。励起状態のグリコシルホウ素アート錯体 **2*** からアシルイミダゾリウム **8** への一電子移動 (SET) が進行し、アノマー位炭素ラジカル **A** とアシルアゾリウム由来のケチルラジカル **C** が同時に発生する。ここで、長寿命ラジカル効果 (PRE: persistent radical effect) に基づき、短寿命なアノマー位炭素ラジカル **A** と長寿命なケチルラジカル **C** の選択的なラジカル-ラジカルカップリングが進行し、中間体 **D** を形成する。最後に、塩基によるアゾリウムの脱離とアノマー位の立体反転を経て、アシル C-グリコシド **9** が生成する。アシル C-グリコシドのアノマー位の水素は塩基によって引き抜かれるため、安定な立体である β 体が得られると考えている。

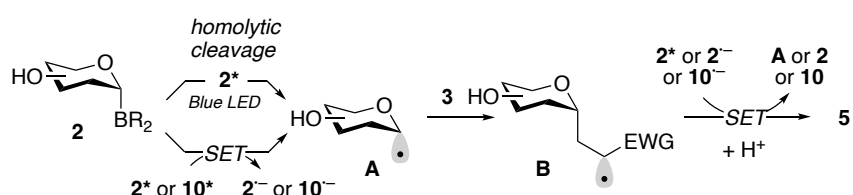
A | Physical properties of glycosyl borates



B | Byproduct derived from glycosyl borate



C | Proposed pathway of Giese-type reaction



D | Proposed pathway of Giese-type reaction for C-glycoside synthesis

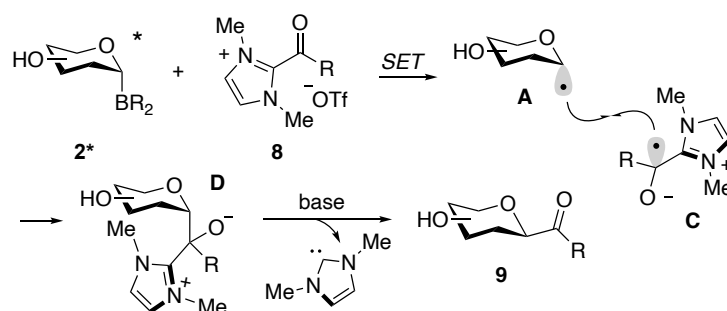


Figure 3-11. 機構実験と推定反応機構

第四節 結論

PDP 配位子を有する無保護グリコシルホウ素アート錯体の直接光励起を活用することで、外部光触媒や金属触媒を一切必要としない、ラジカル C-グリコシル化反応を見出した。本反応は、トリフルオロボレート塩から調製可能な無保護グリコシルホウ素アート錯体を用いることで簡便に実施可能である。青色光照射下、励起状態のホウ素ア

ト錯体からアノマー位炭素ラジカルが発生し、これが種々のラジカル受容体と反応することで、保護-脱保護操作を経ることなく、アルキル、アリール、およびアシル C-グリコシドを一挙に構築できる。本手法は高い立体選択性を示し、ペプチドや医薬品を含む複雑な基質に対しても適用可能である。

第三章 参考文献

1. (a) Hocek, M. *Chem. Rev.* **2009**, *109*, 6729–6764. (b) Meinke, S.; Schroven, A.; Thiem, J. *Org. Biomol. Chem.* **2011**, *9*, 4487. (c) Yang, Y.; Yu, B. *Chem. Rev.* **2017**, *117*, 12281–12356. (d) Bokor, É.; Kun, S.; Goyard, D.; Tóth, M.; Praly, J.-P.; Vidal, S.; Somsák, L. *Chem. Rev.* **2017**, *117*, 1687–1764. (e) Liao, H.; Ma, J.; Yao, H.; Liu, X.-W. *Org. Biomol. Chem.* **2018**, *16*, 1791–1806.
2. (a) Kitamura, K.; Ando, Y.; Matsumoto, T.; Suzuki, K. *Chem. Rev.* **2017**, *118*, 1495–1598. (b) Kiya, N.; Hidaka, Y.; Usui, K.; Hirai, G. *Org. Lett.* **2019**, *21*, 1588–1592. (c) Xu, L.-Y.; Fan, N.-L.; Hu, X.-G. *Org. Biomol. Chem.* **2020**, *18*, 5095–5109. (d) Hidaka, Y.; Kiya, N.; Yoritake, M.; Usui, K.; Hirai, G. *Chem. Commun.* **2020**, *56*, 4712–4715. (e) Liu, J.; Ye, Y.; Sessler, J. L.; Gong, H. *Acc. Chem. Res.* **2020**, *53*, 1833–1845. (f) Wei, Y.; Ben-zvi, B.; Diao, T. *Angew. Chem., Int. Ed.* **2021**, *60*, 9433–9438. (g) Mou, Z.; Wang, J.; Zhang, X.; Niu, D. *Adv. Synth. Catal.* **2021**, *363*, 3025–3029. (h) Ghosh, T.; Nokami, T. *Carbohydr. Res.* **2022**, *522*, 108677. (i) Parida, S. P.; Das, T.; Ahemad, M. A.; Pati, T.; Mohapatra, S.; Nayak, S. *Carbohydr. Res.* **2023**, *530*, 108856. (j) Shang, W.; Niu, D. *Acc. Chem. Res.* **2023**, *56*, 2473–2488. (k) Wei, Y.; Lin, L. Q. H.; Lee, B. C.; Koh, M. J. *Acc. Chem. Res.* **2023**, *56*, 3292–3312. (l) Jiang, Y.; Wei, Y.; Zhou, Q.-Y.; Sun, G.-Q.; Fu, X.-P.; Levin, N.; Zhang, Y.; Liu, W.-Q.; Song, N.; Mohammed, S.; Davis, B. G.; Koh, M. J. *Nature* **2024**, *631*, 319–327.
3. (a) Wittmann, V.; Kessler, H. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1091–1093. (b) Schäfer, A.; Thiem, J. *J. Org. Chem.* **1999**, *65*, 24–29. (c) Baryal, K. N.; Zhu, D.; Li, X.; Zhu, J. *Angew. Chem., Int. Ed.* **2013**, *52*, 8012–8016.
4. (a) Lesimple, P.; Beau, J.-M.; Sinaÿ, P. *J. Chem. Soc., Chem. Commun.* **1985**, 894–895. (b) Koester, D. C.; Kriemen, E.; Werz, D. B. *Angew. Chem., Int. Ed.* **2013**, *52*, 2985–2989. (c) Zhu, F.; Rodriguez, J.; Yang, T.; Kevlishvili, I.; Miller, E.; Yi, D.; O'Neill, S.; Rourke, M. J.; Liu, P.; Walczak, M. A. *J. Am. Chem. Soc.* **2017**, *139*, 17908–17922. (d) Walczak, M.; Zhu, F.; Yang, T. *Synlett* **2017**, *28*, 1510–1516. (e) Zhu, F.; Rodriguez, J.; O'Neill, S.; Walczak, M. A. *ACS Cent. Sci.* **2018**, *4*, 1652–1662.
5. (a) Molander, G. A.; Wisniewski, S. R. *J. Am. Chem. Soc.* **2012**, *134*, 16856–16868. (b) Takeda, D.; Yoritake, M.; Yasutomi, H.; Chiba, S.; Moriyama, T.; Yokoo, A.; Usui, K.; Hirai, G. *Org. Lett.* **2021**, *23*, 1940–1944. (c) Miller, E. M.; Walczak, M. A. *Org. Lett.* **2021**, *23*, 4289–4293.
6. (a) Li, G.; Noguchi, M.; Arisaka, G.; Tanaka, Y.; Shoda, S. *Org. Biomol. Chem.* **2021**, *19*, 3134–3138. (b) Wang, Q.; Lee, B. C.; Tan, T. J.; Jiang, Y.; Ser, W. H.; Koh, M. J. *Nat. Synth.* **2022**, *1*, 967–974. (c) Zhang, C.; Xu, S.-Y.; Zuo, H.; Zhang, X.; Dang, Q.-D.; Niu, D. *Nat. Synth.* **2023**, *2*, 251–260. (d) Xu, S.; Zhang, W.; Li, C.; Li, Y.; Zeng, H.; Wang, Y.; Zhang, Y.; Niu, D. *Angew. Chem., Int. Ed.* **2023**, *62*, DOI: 10.1002/anie.202218303. (e) Miura, T.; Yoritake, M.; Hirai, G. *Chem. Commun.* **2023**, *59*, 8564–8567. (f) Jiang, Y.; Zhang, Y.; Lee, B. C.; Koh, M. J. *Angew. Chem., Int. Ed.* **2023**, *62*, DOI: 10.1002/anie.202305138. (g) Talukdar, R.; Chong, D.; Fairbanks, A. J. *Org. Lett.* **2024**, *26*, 10536–10541. (h) Sun, D.; Dou, X.; Wang, F.; Wu, J.; Wang, W.; He, G. *J. Am. Chem. Soc.* **2025**, *147*, 38879–38888.
7. (a) Sato, Y.; Nakamura, K.; Sumida, Y.; Hashizume, D.; Hosoya, T.; Ohmiya, H. *J. Am. Chem. Soc.* **2020**, *142*, 9938–9943. (b) Sato, Y.; Miyamoto, Y.; Sumida, Y.; Hosoya, T.; Ohmiya, H. *Org. Biomol. Chem.* **2020**, *18*, 6598–6601. (c) Miyamoto, Y.; Sumida, Y.; Ohmiya, H. *Org. Lett.* **2021**, *23*, 5865–5870. (d) Sato, Y.; Goto, Y.; Nakamura, K.; Miyamoto, Y.; Sumida, Y.; Ohmiya, H. *ACS Catal.* **2021**, *11*, 12886–12892. (e) Kemmochi, M.; Miyamoto, Y.; Sumida, Y.; Ohmiya, H. *Asian J. Org. Chem.* **2021**, *11*, DOI: 10.1002/ajoc.202100640. (f) Nakamura, R.; Sumida, Y.; Ohmiya, H. *Bull. Chem. Soc. Jpn.* **2022**, *95*, 1001–1005. (g) Nakamura, R.; Yamazaki, T.; Kondo, Y.; Tsukada, M.; Miyamoto, Y.; Arakawa, N.; Sumida, Y.; Kiya, T.; Arai, S.; Ohmiya, H. *J. Am. Chem. Soc.* **2023**, *145*, 10651–10658.
8. (a) Shang, W.; Su, S.; Shi, R.; Mou, Z.; Yu, G.; Zhang, X.; Niu, D. *Angew. Chem., Int. Ed.* **2020**, *60*, 385–390. (b) Jiang, Y.; Wang, Q.; Zhang, X.; Koh, M. J. *Chem.* **2021**, *7*, 3377–3392. (c) Wu, J.; Wei, W.; Pöhlmann, J.; Purushothaman, R.; Ackermann, L. *Angew. Chem.*,

- Int. Ed.* **2023**, *62*, DOI: 10.1002/anie.202219319.
9. (a) Xia, L.; Fan, W.; Yuan, X.-A.; Yu, S. *ACS Catal.* **2021**, *11*, 9397–9406. (b) Xie, D.; Wang, Y.; Zhang, X.; Fu, Z.; Niu, D. *Angew. Chem., Int. Ed.* **2022**, *61*, DOI: 10.1002/anie.202204922.
 10. (a) Bakhtiar, C.; Smith, E. H. *J. Chem. Soc., Perkin Trans.* **1994**, *1*, 239–243. (b) Zou, L.-J.; Pan, Q.; Li, C.-Y.; Zhang, Z.-T.; Zhang, X.-W.; Hu, X.-G. *Org. Lett.* **2020**, *22*, 8302–8306. (c) Jiang, Y.; Yang, K.; Wei, Y.; Wang, Q.; Li, S.; Lan, Y.; Koh, M. J. *Angew. Chem., Int. Ed.* **2022**, *61*, DOI: 10.1002/anie.202211043.
 11. (a) Zhu, J. L.; Scheidt, K. A. *Tetrahedron* **2021**, *92*, 132288. (b) Bay, A. V.; Scheidt, K. A. *Trends Chem.* **2022**, *4*, 277–290. (c) Rourke, M. J.; McGill, M. J.; Scheidt, K. A.; Yang, D.; Farnam, E. J.; Zhu, J. L. *Synlett* **2023**, *34*, 2175–2180. (d) Zhu, J. L.; Schull, C. R.; Tam, A. T.; Rentería-Gómez, Á.; Gogoi, A. R.; Gutierrez, O.; Scheidt, K. A. *J. Am. Chem. Soc.* **2023**, *145*, 1535–1541. (e) Rourke, M. J.; Wang, C. T.; Schull, C. R.; Scheidt, K. A. *ACS Catal.* **2023**, *13*, 7987–7994. (f) Cao, J.; Zhu, J. L.; Scheidt, K. A. *Chem. Sci.* **2024**, *15*, 154–159.
 12. Connelly, N. G.; Geiger, W. E. *Chem. Rev.* **1996**, *96*, 877–910.

第三章 実験項

■ Instrumentation and Chemicals Synthesis ■

NMR spectra were recorded on a Bruker AVANCE NEO 400N spectrometer, operating at 400 MHz for ^1H NMR, 100.6 MHz for ^{13}C NMR, 376.5 MHz for ^{19}F NMR and 128.4 MHz for ^{11}B NMR. Chloroform- d_1 (CDCl_3) containing 0.03% tetramethylsilane (TMS) (>99.8%D, Cambridge Isotope Laboratories, Inc., Cat. No. DLM-7), Methanol- d_4 (99.9%D, Cambridge Isotope Laboratories, Inc., Cat. No. DLM-51) Deuterium oxide (99.9%D, Cambridge Isotope Laboratories, Inc., Cat. No. DLM-4) were used as solvents for NMR measurements at ambient temperature. Chemical shifts (δ) for ^1H NMR are given in parts per million (ppm) relative to TMS (δ 0.00 ppm in CDCl_3), or residual methanol (δ 3.31 ppm in CD_3OD), H_2O (δ 4.79 ppm in D_2O). Chemical shifts (δ) for ^{13}C NMR are given in ppm relative to CDCl_3 (δ 77.0 ppm), or residual methanol (δ 49.0 ppm in CD_3OD). Chemical shifts were reported in δ ppm. The abbreviations s, d, t, q, quin, and m signify singlet, doublet, triplet, quartet, quintet and multiplet, respectively. Mass spectra were obtained with a Bruker timsTOF mass spectrometer (ESI). TLC analyses were performed on commercial glass plates of Merck Silica gel 60F₂₅₄. Silica gel (Wakosil[®] 60, 64~210 μm) was used for column chromatography. Biotage[®] Selekt, Biotage[®] Isolera[™] One and LaboACE LC-5060 (for Gel Permeation Chromatography) and were used for purification. IR spectra were measured with a ATR Accessory (QATR-S) for the Shimadzu IRSpirit FT-IR Spectrometer. Melting points were measured on a Stanford Research Systems MPA100. UV-Vis absorption spectra were recorded on a Shimadzu UV-1900. Fluorescence spectra were recorded on a Shimadzu RF-6000. Cyclic voltammetry measurements were recorded with a Hokuto Denko HZ-7000 potentiostat. Single-crystal X-ray diffraction data were collected on a Bruker Single Crystal CCD X-ray Diffractometer (SMART APEX II). Kessil PR-160 440 nm was used as a light source. TEKNOS MG9 was used as a fan. Optical rotations were measured on a JASCO P-2200.

All reactions were carried out under nitrogen atmosphere. Materials were obtained from commercial suppliers or prepared according to standard procedures unless otherwise noted. Before reactions, liquid olefines (*tert*-butyl acrylate, benzyl acrylate, acrylonitrile) were passed through a short pad of Aluminium oxide 60.

Fujifilm Wako Pure Chemical Co.

DCM (super dehydrated), silica gel (Wakosil[®] 60, 64~210 μm), tetrahydrofuran (super dehydrated, stabilizer free), ethyl acetate, hexane, DCM, diethyl ether, methanol, acetone, chloroform, *N,N*-dimethylformamide, acetonitrile, methanol (super special grade), DCM (for spectrochemical analysis), *N,N*-dimethylformamide (super dehydrated), dimethyl sulfoxide (super dehydrated), toluene (super dehydrated), methanol (super dehydrated), diethyl ether (super dehydrated), acetonitrile (super dehydrated), H_2O , HCl in H_2O , lithium (shot), *tert*-butyl acrylate, acetic anhydride, chloro(triphenylphosphine)gold (I), 1,8-diazabicyclo[5.4.0]-7-undecene (DBU), acetic acid.

Tokyo Chemical Industry Co., Ltd.

N-(*tert*-Butoxycarbonyl)-*L*-alanine, 1-hydroxybenzotriazole, hydrogen chloride (ca. 4 mol/L in 1,4-dioxane), acryloyl chloride (stabilized with MEHQ), (4-dimethylaminophenyl)di-*tert*-butylphosphine, pyridine·HCl, sodium methoxide, benzyl bromide, sodium hydride (60%, dispersion in paraffin liquid), potassium peroxymonosulfate [$>$ ca. 45% (T) as KHSO_5], trimethyl borate, potassium hydrogenfluoride, benzyl acrylate (stabilized with MEHQ), acrylonitrile (stabilized with MEHQ), methyl 2-acetamidoacrylate, sodium acetate, isoquinoline, lepidine, 4-methylbenzoyl chloride, *N*-

methylimidazole, methyl trifluoromethanesulfonate, *tert*-butyldiphenylchlorosilane, *D*-galactal, 2,6-dichloropyridine.

Kanto Chemical Co.

n-Butyllithium in *n*-hexane (1.6 mol/L), 1,2-dichloroethane (dehydrated).

Merk Sigma-Aldrich Japan Inc.

Pd(OAc)₂, Pd(OH)₂/C (20 wt.% loading (dry basis), matrix carbon, wet support), almina (aluminium oxide 60), *N*-phenylacrylamide.

Nacalai Tesque Inc.

Triethylamine, NaHCO₃, sodium sulfate, K₂CO₃, naphthalene, TFA, potassium persulfate, sodium thiosulfate, Molecular Sieves 4A.

BLD Pharmatech Ltd.

2,6-Dichloro-4-methylpyridine, silver trifluoromethanesulfonate, 2,6-dichloro-4-methylpyridine.

Angene

L-Alanine methyl ester hydrochloride, 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride, 2-hydroxyphenyl boronic acid, tri-*O*-acetyl-*D*-glucal, *N*-methyliminodiacetic acid, fasudil (1*H*-1,4-Diazepine, hexahydro-1-(5-isoquinolinylsulfonyl)-).

Acros Organics

Vinylsulfonylbenzene.

The substrates listed in Figure S3-1 were prepared according to the literatures (**S1**,¹ **S2**,² **S3**,³ **S4**,³ **S5**,³ **S6**,³ **S7**,⁴ **8a**,⁵ and **8b**⁶).

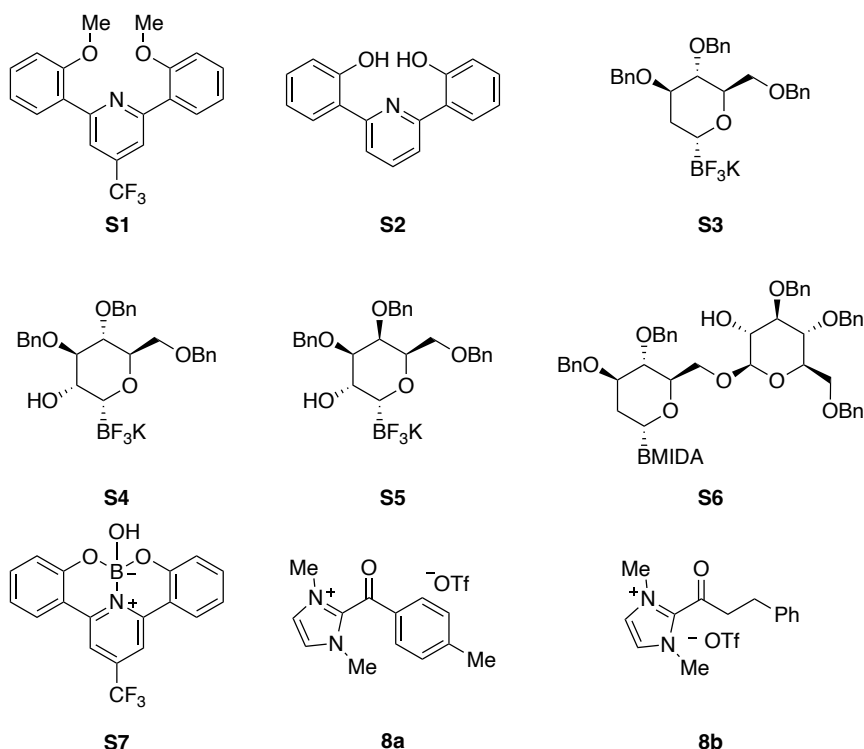
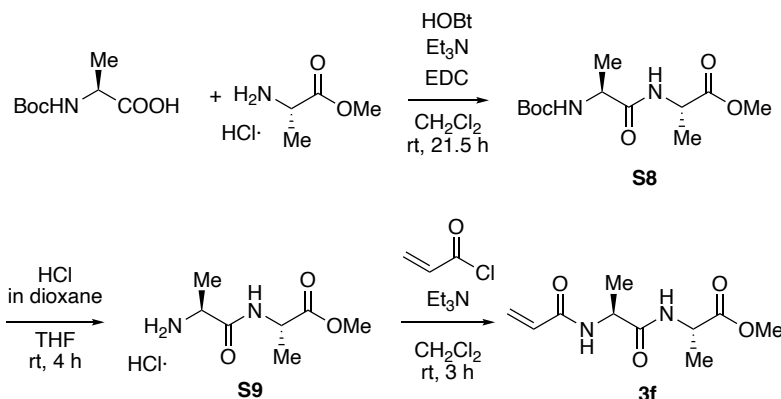


Figure S3-1. Prepared starting materials.

■ Characterization Data for Substrates ■

Methyl Acryloyl-*L*-alanyl-*L*-alaninate (**3f**)



Step 1: preparation of **S8**

A 500 mL round-bottom flask was charged sequentially with *L*-alanine methyl ester hydrochloride (1.4 g, 10 mmol) and super dehydrated CH₂Cl₂ (100 mL). The solution was cooled in an ice-bath, and triethylamine (1.7 mL, 12 mmol), *N*-(*tert*-butoxycarbonyl)-*L*-alanine and 1-hydroxybenzotriazole were added. The mixture was stirred, and then 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride was added slowly. The mixture was warmed to room temperature and stirred for 21.5 h. The mixture was quenched with water and extracted with CH₂Cl₂ over three times. The organic layer was dried over sodium sulfate and filtrated. The crude material was concentrated under reduced pressure. After volatiles were removed, flash column chromatography on silica gel (Biotage Selekt, 90:10–50:50, hexane/EtOAc) gave **S8** (2.26 g, 8.2 mmol, 82%). The spectrum data of product **S8** was consistent with the literature.⁷

Step 2: preparation of **S9**

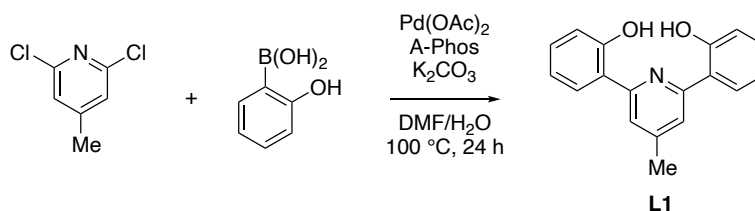
A 100 mL round-bottom flask was charged sequentially with **S8** (1.1 g, 4 mmol) and dry THF (20 mL). The solution was cooled in an ice-bath, and HCl in dioxane (20 mL, 4 M) was added slowly. The mixture was warmed to room temperature and stirred for 4 h. The resulting solution was concentrated under reduced pressure to give **S9**, which was used without further purification.

Step 3: preparation of **3f**

A 100 mL round-bottom flask was charged sequentially with **S9** and dry CH₂Cl₂ (20 mL, 0.2 M). The solution was cooled in an ice-bath, and then triethylamine (1.1 mL, 8 mmol) and acryloyl chloride (485 μ L, 6 mmol) were added dropwisely. The mixture was warmed to room temperature and stirred for 3 h. The solution was concentrated under reduced pressure and diluted with EtOAc (ca. 50 mL). The organic layer was washed with saturated NaHCO₃ aq (ca. 50 mL), 1N HCl aq (ca. 50 mL) and brine (ca. 50 mL). The organic layer was dried over sodium sulfate and filtrated. The crude material was concentrated under reduced pressure. After volatiles were removed, flash column chromatography on silica gel (50:50–0:100, hexane/EtOAc) gave **3f** (360.2 mg, 1.58 mmol, 39%, over 2 steps) as a white solid. **Rf** = 0.5 (only EtOAc) **M.p.** 150–155 °C [α]_D²⁶ –99.6 (*c* = 0.1, CH₂Cl₂) **IR** (neat) 3285, 1751, 1647, 1622, 1540, 1456, 1410, 1208, 1165, 1056 cm^{–1}. **¹H NMR** (400 MHz, CDCl₃) δ 6.88 (d, *J* = 6.8 Hz, 1H), 6.47 (d, *J* = 6.8 Hz, 1H), 6.31 (dd, *J* = 16.8, 1.6 Hz, 1H), 6.13 (dd, *J* = 16.8, 10.4 Hz, 1H), 5.68 (dd, *J* = 10.4, 1.6 Hz, 1H), 4.66 (quin, *J* = 7.2 Hz, 1H), 4.55 (quin, *J* = 7.2 Hz, 1H), 3.76 (s, 3H), 1.44 (d, *J* = 7.2 Hz, 3H), 1.42 (d, *J* = 7.2 Hz, 3H). **¹³C NMR** (100.6 MHz, CDCl₃) δ 173.0, 171.8, 165.1, 130.3, 127.2, 52.5, 48.7, 48.1, 18.6, 18.1.

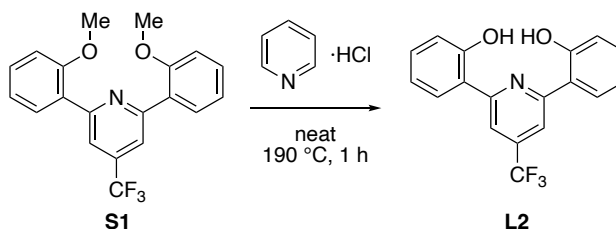
HRMS–ESI (*m/z*): [M+H]⁺ calcd for C₁₀H₁₇N₂O₄⁺, 229.1183; found, 229.1190.

2,2'-(4-Methylpyridine-2,6-diyl)diphenol (**L1**)



A round-bottom flask was charged sequentially with 2-hydroxyphenyl boronic acid (5.5 g, 40 mmol), 2,6-dichloro-4-methylpyridine (1.6 g, 10 mmol), K_2CO_3 (8.3 g, 60 mmol), $Pd(OAc)_2$ (112.3 mg, 0.5 mmol) and A-Phos (265.4 mg, 1.0 mmol) in a glovebox. The septum capped round-bottom flask was removed from the glovebox, and then dry DMF (56 mL) and H_2O (44 mL) were added under N_2 atmosphere. After stirring at 100 °C for 24 h, the reaction mixture was transferred to a separatory funnel, diluted with diethyl ether and extracted with diethyl ether over three times (ca. 100 mL $\times$ 3). The organic extract was dried over sodium sulfate, filtrated and concentrated under reduced pressure. Flash column chromatography on silica gel (100:0–60:40, hexane/EtOAc) gave **L1** (2.01 g, 7.26 mmol, 73%) as a yellow solid. Note: The product was generally eluted with hexane/EtOAc (70:30). **Rf** = 0.19 (80:20, hexane/EtOAc) **M.p.** 108–113 °C **IR** (neat) 3255, 3051, 1603, 1554, 1448, 1400, 1363, 1281, 1254, 1227 cm^{-1} . **1H NMR** (400 MHz, $CDCl_3$) δ 7.67 (dd, J = 8.0, 1.6 Hz, 2H), 7.53 (d, J = 0.4 Hz, 2H), 7.36 (ddd, J = 8.0, 7.2, 1.6 Hz, 2H), 7.05 (dd, J = 8.0, 1.2 Hz, 2H), 7.01–6.97 (ddd, J = 8.0, 7.2, 1.2 Hz, 2H), 2.54 (m, 3H). **^{13}C NMR** (100.6 MHz, $CDCl_3$) δ 156.7, 156.1, 151.2, 131.4, 128.0, 121.6, 120.8, 120.0, 118.0, 21.9. **HRMS–ESI** (m/z): $[M+H]^+$ calcd for $C_{18}H_{16}NO_2^+$, 278.1176; found, 278.1171.

2,2'-(4-Methylpyridine-2,6-diyl)diphenol (**L2**)

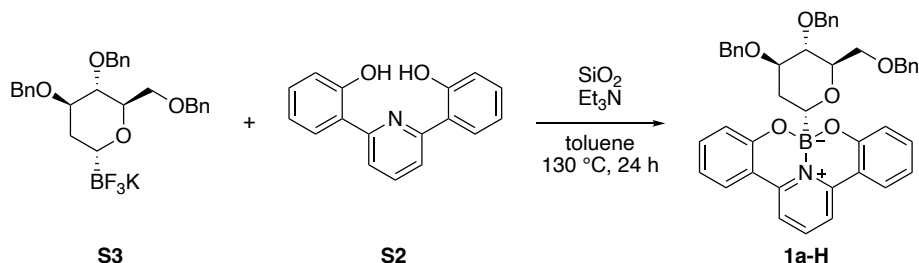


A round-bottom flask was charged sequentially with **S1** (4.0 g, 11.2 mmol) and pyridine·HCl (7.8 g, 67.2 mmol) in a glovebox. The septum capped round-bottom flask was removed from the glovebox and stirred at 190 °C for 1 h. While the mixture was warmed to room temperature, CH_2Cl_2 (ca. 50 mL) and H_2O (ca. 50 mL) were added to the solution carefully. Then the reaction mixture was transferred to a separatory funnel, diluted with CH_2Cl_2 and extracted with CH_2Cl_2 over five times (ca. 50 mL $\times$ 5). The organic extract was dried over sodium sulfate, filtrated and concentrated under reduced pressure. The residue was washed with hexane to give **L2** (3.79 g, 11.4 mmol, quant.) as an orange solid. **M.p.** 170–175 °C **IR** (neat) 3302, 1617, 1590, 1590, 1560, 1375, 1286, 1178, 1136, 758 cm^{-1} . **1H NMR** (400 MHz, $CDCl_3$) δ 7.93 (s, 2H), 7.76–7.73 (m, 2H), 7.42–7.37 (m, 2H), 7.07–7.03 (m, 4H). **1H NMR** (400 MHz, CD_3OD) δ 8.18 (d, J = 0.4 Hz, 2H), 7.88–7.85 (m, 2H), 7.36–7.32 (m, 2H), 7.02–6.98 (m, 4H). **^{13}C NMR** (100.6 MHz, CD_3OD) δ 158.8, 158.4, 141.0 (q, J_{C-F} = 33.4 Hz), 132.8, 129.6, 124.5 (q, J_{C-F} = 272.9 Hz) 122.3, 120.9, 118.5, 116.4 (q, J_{C-F} = 3.6 Hz). **^{19}F NMR** (376.5 MHz,

CD₃OD) δ –66.3. HRMS–ESI (m/z): $[M+H]^+$ calcd for C₁₈H₁₃F₃NO₂⁺, 332.0893; found, 332.0880.

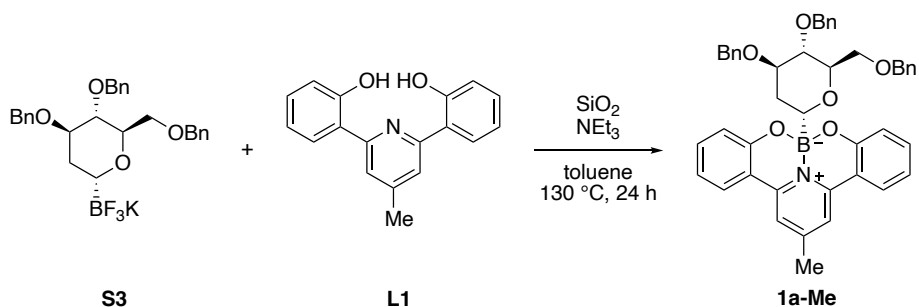
■ Characterization Data for Borates ■

8a-((2*R*,4*R*,5*S*,6*R*)-4,5-Bis(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2*H*-pyran-2-yl)-8*aH*-8,9-dioxa-3*a*¹ λ^4 -aza-8*a*⁴-borabenzofg]tetracene (1a-H)



A screw-top 20 mL vial was charged with a stirring bar, **S3** (314.7 mg, 0.6 mmol), **S2** (131.7 mg, 0.5 mmol) and SiO₂ (60.1 mg, 1.0 mmol) under ambient atmosphere. The vial was brought to a glovebox, and dry toluene (5 mL) and Et₃N (485 μ L, 3.5 mmol) were added. After the vial was removed from the glovebox and sealed with Teflon tape, the vial was placed in an aluminum heating block at 130 °C and stirred for 24 h. The reaction mixture was passed through a short pad of Celite with THF, and filtrate was concentrated under reduced pressure. This series of experiments was repeated twice and all crude material were combined. After volatiles were removed under reduced pressure, flash column chromatography on silica gel (90:10–60:40, hexane/EtOAc) gave **1a-H** (616.9 mg, 0.89 mmol, 89%) as a pale yellow solid. A small amount of THF was included. Note: The product was generally eluted with hexane/EtOAc (60:40). **Rf** = 0.37 (40:60, hexane/EtOAc) **M.p.** 170–175 °C **[α]_D²⁶** +21.0 (c = 0.25, CH₂Cl₂) **IR** (neat) 1586, 1612, 1558, 1495, 1458, 1393, 1301, 1277, 1198, 1093 cm^{–1}. **¹H NMR** (400 MHz, CDCl₃) δ 7.88 (m, 1H), 7.70–7.59 (m, 4H), 7.39–7.31 (m, 2H), 7.30–7.13 (m, 15H), 7.08 (dd, J = 8.4, 1.2 Hz, 1H), 7.04 (dd, J = 8.4 Hz, 1.2 Hz, 1H), 6.93 (m, 1H), 6.87 (m, 1H), 4.58 (d, J = 11.6 Hz, 1H), 4.40–4.17 (m, 5H), 3.78–3.73 (m, 1H), 3.55 (m, 1H), 3.48–3.41 (m, 2H), 3.33 (m, 1H), 3.16 (m, 1H), 2.10 (m, 1H), 1.66 (m, 1H). **¹¹B NMR** (128.4 MHz, CDCl₃) δ 6.01. **¹³C NMR** (100.6 MHz, CDCl₃) δ 156.9, 156.8, 149.0, 148.0, 141.0, 139.1, 139.0, 138.8, 134.2, 134.1, 128.2, 128.06, 128.03, 127.6, 127.5, 127.4, 127.2, 127.1, 125.4, 125.1, 120.5, 120.4, 119.9, 119.5, 118.3, 118.1, 117.7, 117.6, 77.6, 77.5, 77.2, 74.1, 72.9, 72.4, 70.4, 69.4, 28.2 (only observed peaks). HRMS–ESI (m/z): $[M+H]^+$ calcd for C₄₄H₄₁BNO₆⁺, 690.3029; found, 690.3047.

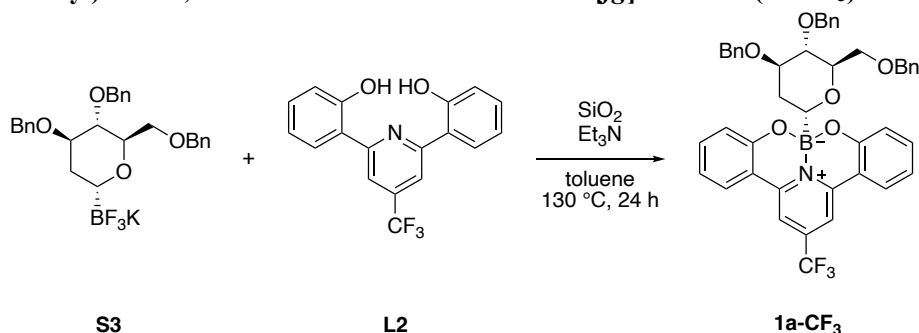
8a-((2*R*,4*R*,5*S*,6*R*)-4,5-Bis(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2*H*-pyran-2-yl)-2-methyl-8*aH*-8,9-dioxa-3*a*¹ λ^4 -aza-8*a*⁴-borabenzofg]tetracene (1a-Me)



A screw-top 20 mL vial was charged with a stirring bar, **S3** (314.7 mg, 0.6 mmol), **L1** (138.7 mg,

0.5 mmol) and SiO₂ (60.1 mg, 1.0 mmol) under ambient atmosphere. The vial was brought to a glovebox, and dry toluene (5 mL) and Et₃N (485 µL, 3.5 mmol) were added. After the vial was removed from the glovebox and sealed with Teflon tape, the vial was placed in an aluminum heating block at 130 °C and stirred for 24 h. The reaction mixture was passed through a short pad of Celite with THF, and filtrate was concentrated under reduced pressure. After volatiles were removed, flash column chromatography on silica gel (Only CH₂Cl₂, then 100:0–70:30, hexane/AcOEt) gave **1a-Me** (341.1 mg, 0.485 mmol, 97%) as a white solid. Note: The product was generally eluted with hexane/EtOAc (70:30). **R_f** = 0.07 (80:20, hexane/EtOAc) **M.p.** 207–212 °C [α]_D²⁶ +4.0 (*c* = 0.1, CH₂Cl₂) **IR** (neat) 1624, 1606, 1577, 1551, 1497, 1454, 1300, 1280, 1028, 772 cm⁻¹. **¹H NMR** (400 MHz, CDCl₃) δ 7.67 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.62 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.52 (m, 2H), 7.38–7.13 (m, 17H), 7.08 (dd, *J* = 8.4, 1.2 Hz, 1H), 7.03 (dd, *J* = 8.4, 1.2 Hz, 1H), 6.92 (m, 1H), 6.87 (m, 1H), 4.59 (d, 12.0 Hz, 1H), 4.41–4.18 (m, 5H), 3.77 (m, 1H), 3.55–3.43 (m, 3H), 3.31 (m, 1H), 3.19 (m, 1H), 2.44 (s, 3H), 2.09 (m, 1H), 1.64 (m, 1H). **¹¹B NMR** (128.4 MHz, CDCl₃) δ 6.01. **¹³C NMR** (100.6 MHz, CDCl₃) δ 157.1, 157.0, 153.2, 148.5, 147.5, 139.2, 139.1, 138.9, 134.0, 133.9, 128.2, 128.1, 127.6, 127.5, 127.4, 127.2, 127.1, 125.3, 125.0, 120.51, 120.46, 119.8, 119.4, 118.4, 118.3, 118.2, 118.0, 77.7, 77.6, 74.3, 72.9, 72.4, 70.5, 69.5, 30.9, 28.3, 22.1 (only observed peaks). **HRMS–ESI** (*m/z*): [M+H]⁺ calcd for C₄₅H₄₃BNO₆⁺, 704.3186; found, 703.3208.

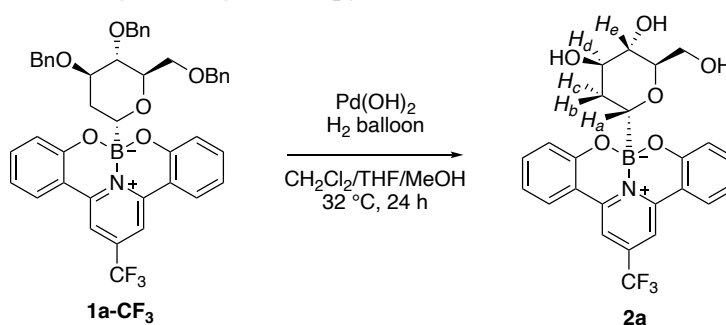
8a-((2*R*,4*R*,5*S*,6*R*)-4,5-Bis(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2*H*-pyran-2-yl)-2-(trifluoromethyl)-8*aH*-8,9-dioxo-3*a*¹ λ ⁴-aza-8*a* λ ⁴-borabenzof[*fg*]tetracene (1a-CF₃)



A screw-top 20 mL vial was charged with a stirring bar, **S3** (314.7 mg, 0.6 mmol), **L2** (165.6 mg, 0.5 mmol) and SiO₂ (60.1 mg, 1.0 mmol) under ambient atmosphere. The vial was brought to a glovebox, and toluene (5 mL) and Et₃N (485 µL, 3.5 mmol) were added. After the vial was removed from the glovebox and sealed with Teflon tape, the vial was placed in an aluminum heating block at 130 °C and stirred for 24 h. The reaction mixture was passed through a short pad of Celite with THF, and filtrate was concentrated under reduced pressure. This series of experiments was repeated four times and all crude material were combined. After volatiles were removed under reduced pressure, flash column chromatography on silica gel (100:0–85:15, hexane/EtOAc) gave **1a-CF₃** (1.42 g, 1.88 mmol, 94%) as yellow oil. Note: The product was generally eluted with hexane/EtOAc (85:15). **R_f** = 0.07 (90:10, hexane/EtOAc) [α]_D²⁶ +16.7 (*c* = 0.1, CH₂Cl₂) **IR** (neat) 1636, 1607, 1584, 1558, 1491, 1458, 1435, 1373, 1300, 1191 cm⁻¹. **¹H NMR** (400 MHz, CDCl₃) δ 7.81 (s, 1H), 7.78 (s, 1H), 7.60 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.52 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.39–7.30 (m, 2H), 7.26–7.10 (m, 15H), 7.06 (dd, *J* = 8.4, 0.8 Hz, 1H), 7.02 (dd, *J* = 8.4, 0.8 Hz, 1H), 6.90 (m, 1H), 6.84 (m, 1H), 4.53 (m, 1H), 4.40–4.28 (m, 3H), 4.22–4.15 (m, 2H), 3.76 (m, 1H), 3.56 (dd, *J* = 8.0, 5.2 Hz, 1H, **anomeric H**), 3.43–3.31 (m, 3H), 3.10 (m, 1H), 2.11 (m, 1H), 1.69 (m, 1H). **¹¹B NMR** (128.4 MHz, CDCl₃) δ 6.39.

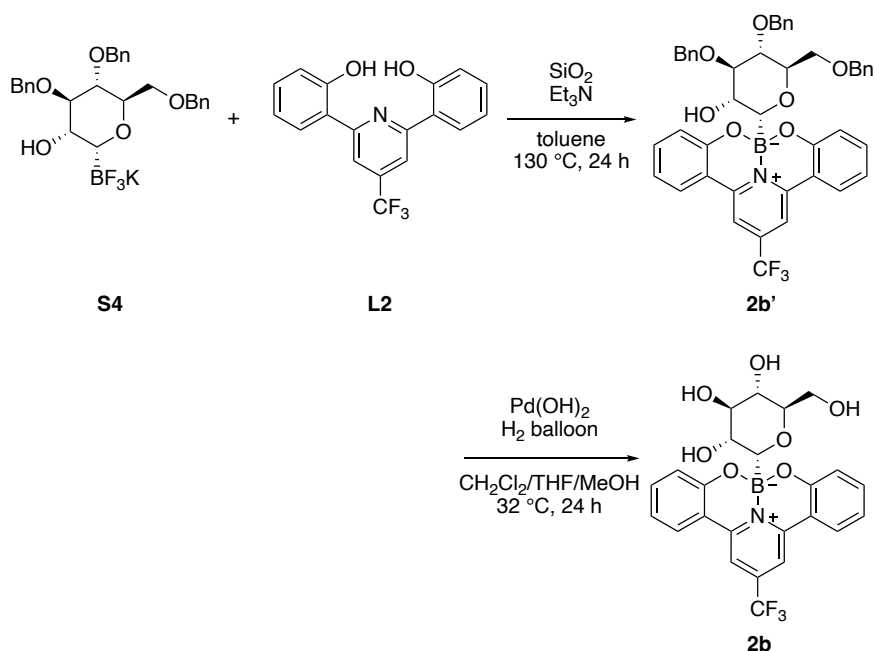
^{13}C NMR (100.6 MHz, CDCl_3) δ 157.0, 156.9, 150.7, 149.6, 142.1 (q, $J_{\text{C-F}} = 36.7$ Hz), 138.8, 138.7, 138.4, 135.1, 135.0, 128.0, 127.9, 127.4, 127.3, 127.2, 127.12, 127.06, 127.0, 125.6, 125.4, 123.1, 120.7, 120.4, 120.34, 120.33, 120.2, 119.7, 117.5, 117.2, 113.39, 113.34, 113.33, 113.20, 113.17, 113.14, 77.2, 76.9, 76.7, 73.7, 72.7, 72.0, 70.3, 69.0, 27.4 (only observed peaks). ^{19}F NMR (376.5 MHz, CDCl_3) δ -65.5. HRMS-ESI (m/z): $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{45}\text{H}_{40}\text{BF}_3\text{NO}_6^+$, 758.2903; found, 758.2922.

(2*R*,3*S*,4*R*,6*R*)-2-(Hydroxymethyl)-6-(2-(trifluoromethyl)-8,9-dioxa-3a¹ λ^4 -aza-8a λ^4 -borabenzofg]tetracen-8a-yl)tetrahydro-2*H*-pyran-3,4-diol (2a)



A round-bottom flask was charged sequentially with **1a-CF₃** (75.8 mg, 0.1 mmol), $\text{Pd}(\text{OH})_2$ on carbon (7.6 mg, 10% w/w), CH_2Cl_2 (10 mL), dry THF (10 mL) and MeOH (10 mL). The septum capped round-bottom flask was evacuated over three times, purged with H_2 and stirred at 32 °C for 24 h. The reaction mixture was passed through a short pad of Celite and rinsed with $\text{CH}_2\text{Cl}_2/\text{MeOH}$ (85:15). The filtrate was concentrated under reduced pressure. After volatiles were removed, flash column chromatography on silica gel (99.9:0.1–90:10, $\text{CH}_2\text{Cl}_2/\text{MeOH}$) gave **2a** (42.6 mg, 0.087 mmol, 87%) as a yellow solid. Note: The product was generally eluted with $\text{CH}_2\text{Cl}_2/\text{MeOH}$ (97:3). The structure of **2a** was confirmed by X-ray diffraction analysis. **R_f** = 0.37 (90:10, $\text{CH}_2\text{Cl}_2/\text{MeOH}$) **M.p.** 221–226 °C (decomp.) $[\alpha]_{\text{D}}^{26} +72.0$ ($c = 0.1$, MeOH) **IR** (neat) 3393, 1636, 1607, 1586, 1557, 1491, 1458, 1436, 1301, 1192 cm^{-1} . ^1H NMR (400 MHz, CD_3OD) δ 8.37 (d, $J = 7.2$ Hz, 2H), 8.08–8.04 (m, 2H), 7.52–7.47 (m, 2H), 7.07–7.00 (m, 4H), 3.72 (ddd, $J = 8.8, 7.2, 4.8$ Hz, 1H, H_d), 3.47 (dd, $J = 6.8, 4.8$ Hz, 1H, H_a , anomeric H), 3.39 (dd, $J = 11.4, 4.8$ Hz, 1H), 3.24 (dd, $J = 11.4, 3.2$ Hz, 1H), 3.12 (dd, $J = 8.0, 7.2$ Hz, 1H, H_e), 3.05 (ddd, $J = 8.0, 4.8, 3.2$ Hz, 1H), 1.92 (dt, $J = 13.2, 4.8$ Hz, 1H, H_c), 1.40 (ddd, $J = 13.2, 8.8, 6.8$ Hz, 1H, H_b). ^{11}B NMR (128.4 MHz, CD_3OD) δ 6.40. ^{13}C NMR (100.6 MHz, CD_3OD) δ 158.03, 158.01, 152.0, 151.4, 144.2 (q, $J_{\text{C-F}} = 35.6$ Hz), 136.43, 136.35, 127.8, 127.7, 124.9, 122.2, 121.8, 121.6, 121.3, 121.1, 119.1, 118.9, 115.90, 115.86, 115.76, 115.73, 78.1, 72.8, 71.4, 62.6, 33.1 (only observed peaks). ^{19}F NMR (376.5 MHz, CD_3OD) δ -66.9. HRMS-ESI (m/z): $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{24}\text{H}_{21}\text{BF}_3\text{NO}_6\text{Na}^+$, 510.1310; found, 510.1302.

(2*R*,3*S*,4*R*,5*S*,6*R*)-2-(Hydroxymethyl)-6-(2-(trifluoromethyl)-8,9-dioxa-3a¹ λ^4 -aza-8a λ^4 -borabenzofg]tetracen-8a-yl)tetrahydro-2*H*-pyran-3,4,5-triol (2b)



Step 1: preparation of **2b'**

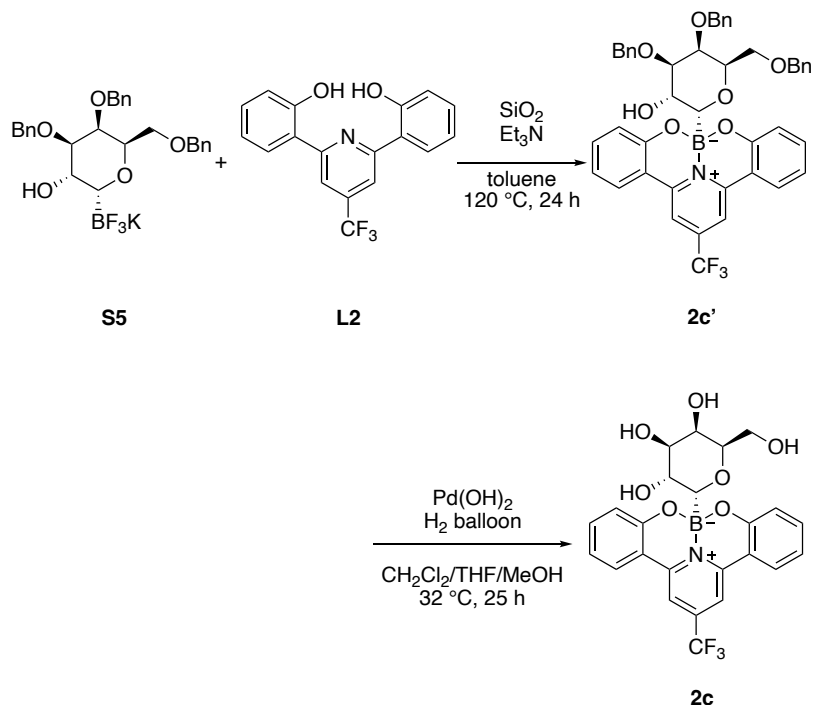
A screw-top 20 mL vial was charged with a stirring bar, **S4** (432.3 mg, 0.8 mmol), **L2** (265.0 mg, 0.8 mmol) and SiO₂ (96.1 mg, 1.6 mmol) under ambient atmosphere. The vial was brought to a glovebox, and dry toluene (7 mL) and Et₃N (776 μ L, 5.6 mmol) were added. After the vial was removed from the glovebox and sealed with Teflon tape, the vial was placed in an aluminum heating block at 130 °C and stirred for 24 h. The reaction mixture was passed through a short pad of Celite and rinsed with CH₂Cl₂/MeOH (9:1). The filtrate was concentrated under reduced pressure. This series of experiments was repeated three times and all crude material were combined. After volatiles were removed under reduced pressure, flash column chromatography on silica gel (90:10–50:50, hexane/EtOAc) gave **2b'** (1.25 g, 1.6 mmol, 67%). Note: The product was generally eluted with hexane/EtOAc (50:50).

Step 2: preparation of **2b**

A round-bottom flask was charged sequentially with **2b'** (1.25 g, 1.6 mmol), Pd(OH)₂ on carbon (125 mg, 10% w/w), CH₂Cl₂ (160 mL), dry THF (160 mL) and MeOH (160 mL). The septum capped round-bottom flask was evacuated over three times, purged with H₂ and stirred at 32 °C for 24 h. The reaction mixture was passed through a short pad of Celite and rinsed with CH₂Cl₂/MeOH (85:15). The filtrate was concentrated under reduced pressure and washed with CH₂Cl₂ to give **2b** (582.8 mg, 1.2 mmol, 72%) as a yellow solid. **R_f** = 0.26 (90:10, CH₂Cl₂/MeOH) [α]_D²⁶ –22.3 (*c* = 0.1, MeOH) **M.p.** 200–205 °C (decomp.) **IR** (neat) 3368, 1636, 1607, 1586, 1558, 1491, 1436, 1373, 1301, 1192 cm^{–1}. **¹H NMR** (400 MHz, CD₃OD) δ 8.34 (d, *J* = 11.2 Hz, 2H), 8.07–8.04 (m, 2H), 7.50–7.45 (m, 2H), 7.07–6.99 (m, 4H), 3.60–3.45 (m, 6H), 3.20 (m, 1H). **¹¹B NMR** (128.4 MHz, CD₃OD) δ 6.28. **¹³C NMR** (100.6 MHz, CD₃OD) δ 158.5, 157.6, 152.1, 152.0, 144.0 (q, *J*_{C–F} = 34.5 Hz), 136.2, 136.0, 127.5, 127.4, 125.0, 121.6, 121.4, 121.1, 120.9, 119.7, 119.1, 115.65, 115.61, 115.44, 115.41, 78.0, 74.8, 74.1, 71.9, 62.6 (only observed peaks). **¹⁹F NMR** (376.5 MHz, CD₃OD) δ –66.8. **HRMS–ESI** (*m/z*): [M+Na]⁺ calcd for C₂₄H₂₁BF₃NO₇Na⁺, 526.1255; found, 526.1245.

(2*R*,3*R*,4*R*,5*S*,6*R*)-2-(Hydroxymethyl)-6-(2-(trifluoromethyl)-8,9-dioxo-3a¹ λ ⁴-aza-8a λ ⁴-

borabenzo[fg]tetracen-8a-yl)tetrahydro-2H-pyran-3,4,5-triol (2c**)**



Step 1: preparation of **2c'**

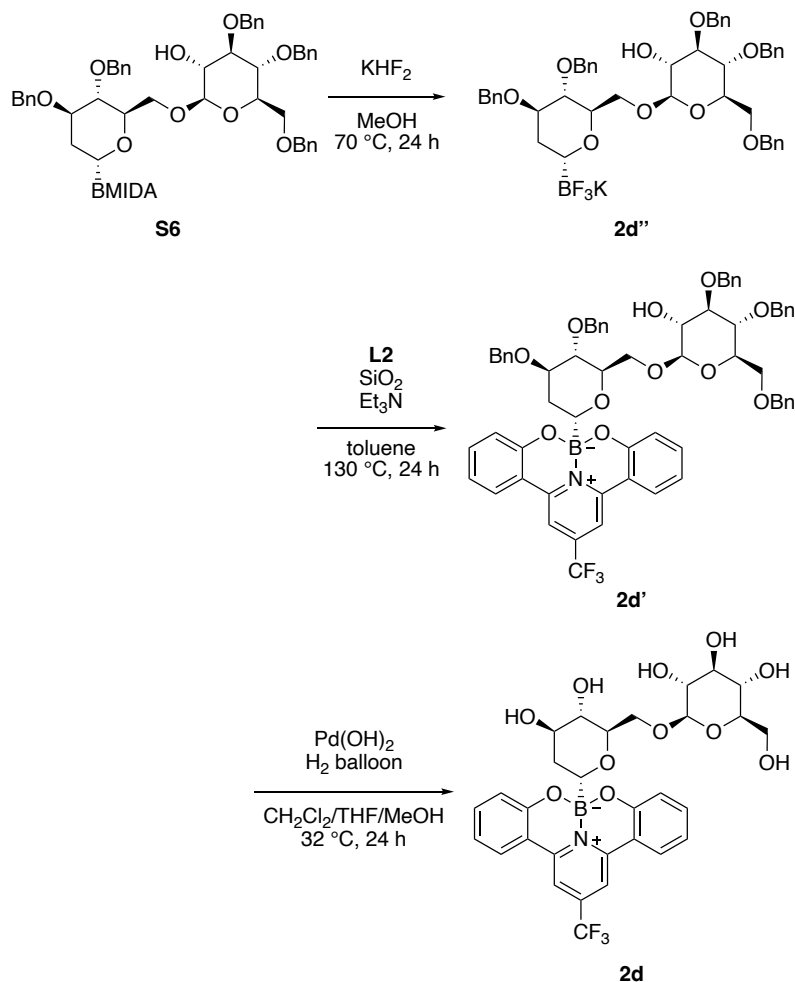
A screw-top 20 mL vial was charged with a stirring bar, **S5** (557.2 mg, 1.03 mmol), **L2** (341.2 mg, 1.03 mmol) and SiO₂ (123.8 mg, 2.06 mmol) under ambient atmosphere. The vial was brought to a glovebox, and dry toluene (7 mL) and Et₃N (998 μL, 7.2 mmol) were added. After the vial was removed from the glovebox and sealed with Teflon tape, the vial was placed in an aluminum heating block at 120 °C and stirred for 24 h. The reaction mixture was passed through a short pad of Celite with THF and rinsed with CH₂Cl₂/MeOH (9:1). The filtrate was concentrated under reduced pressure. After volatiles were removed, flash column chromatography on silica gel (90:10–50:50, hexane/EtOAc) gave **2c'** (301.8 mg, 0.39 mmol, 38%) as pale yellow oil. Note: The product was generally eluted with hexane/EtOAc (80:20).

Step 2: preparation of **2c**

A round-bottom flask was charged sequentially with **2c'** (301.8 mg, 0.39 mmol), Pd(OH)₂ on carbon (30.2 mg, 10% w/w), CH₂Cl₂ (39 mL), dry THF (39 mL) and MeOH (39 mL). The septum capped round-bottom flask was evacuated over three times, purged with H₂ and stirred at 32 °C for 25 h. The reaction mixture was passed through a short pad of Celite and rinsed with CH₂Cl₂/MeOH (85:15). The filtrate was concentrated under reduced pressure and washed with CH₂Cl₂/Et₂O (1:1) to give **2c** (50.8 mg) as a yellow solid. After volatiles were removed under reduced pressure, flash column chromatography on silica gel (99.9:0.1–90:10, CH₂Cl₂/MeOH) gave **2c** (93.0 mg) as a yellow solid. Note: The product was generally eluted with CH₂Cl₂/MeOH (95:5). The total amount of **2c** was 143.8 mg (0.286 mmol, 73%). **Rf** = 0.27 (90:10, CH₂Cl₂/MeOH) [**α**]_D²⁶ –93.9 (*c* = 0.1, MeOH) **M.p.** 193–198 °C **IR** (neat) 3408, 1636, 1607, 1586, 1557, 1436, 1373, 1300, 1250, 1191 cm^{–1}. **¹H NMR** (400 MHz, CD₃OD) δ 8.34 (d, *J* = 10.4 Hz, 2H), 8.07–8.04 (m, 2H), 7.50–7.46 (m, 2H), 7.07–7.00 (m, 4H), 3.60–3.45 (m, 6H), 3.20 (m, 1H). **¹¹B NMR** (128.4 MHz, CD₃OD) δ 5.42. **¹³C NMR** (100.6 MHz, CD₃OD) δ 158.5, 157.6, 152.1, 152.0, 144.0 (q, *J*_{C–F} = 34.8 Hz), 136.2, 136.1, 127.5, 127.4, 125.0,

121.6, 121.4, 121.0, 120.9, 119.7, 119.1, 115.6, 115.4, 78.0, 74.8, 74.1, 71.9, 62.6, 54.8 (only observed peaks). ^{19}F NMR (376.5 MHz, CD_3OD) δ -62.9. HRMS-ESI (m/z): $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{24}\text{H}_{21}\text{BF}_3\text{NO}_7\text{Na}^+$, 526.1255; found, 526.1283.

(2*R*,3*R*,4*S*,5*S*,6*R*)-2-(((2*R*,3*S*,4*R*,6*R*)-3,4-Dihydroxy-6-(2-(trifluoromethyl)-8,9-dioxa-3*a*¹ λ ⁴-aza-8*a* λ ⁴-borabenzof[*g*]tetracen-8*a*-yl)tetrahydro-2*H*-pyran-2-yl)methoxy)-6-(hydroxymethyl)tetrahydro-2*H*-pyran-3,4,5-triol (2*d*)



Step 1: preparation of **2d''**

A round-bottom flask was charged sequentially with **S6** (396.5 mg, 0.43 mmol), MeOH (8.7 mL), and KHF_2 (480 μL , 2.2 mmol, 4.5 M in H_2O). The septum capped round-bottom flask was degassed by N_2 bubbling over 1 min and stirred at $70\text{ }^\circ\text{C}$ for 24 h. The reaction mixture was concentrated under reduced pressure and dissolved in acetone. The suspended solution was passed through a short pad of Celite and rinsed with acetone. The crude mixture was concentrated under reduced pressure to give **2d''** (430.2 mg), which was used without further purification.

Step 2: preparation of **2d'**

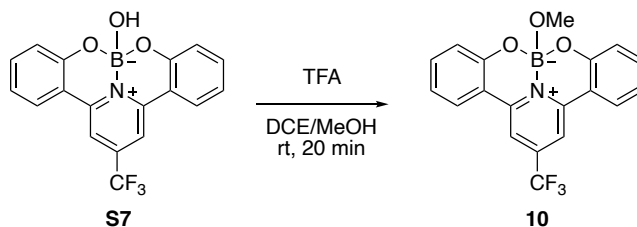
A screw-top 20 mL vial was charged with a stirring bar, **2d''** (430.2 mg, 0.43 mmol), **L2** (139.1 mg, 0.43 mmol) and SiO_2 (50.5 mg, 0.84 mmol) under ambient atmosphere. The vial was brought to a glovebox, and dry toluene (4.2 mL) and Et_3N (408 μL , 2.9 mmol) were added. After the vial was

removed from the glovebox and sealed with Teflon tape, the vial was placed in an aluminum heating block at 130 °C and stirred for 22 h. The reaction mixture was passed through a short pad of Celite and rinsed with CH₂Cl₂/MeOH (85:15). The filtrate was concentrated under reduced pressure. After volatiles were removed, flash column chromatography on silica gel (100:0–75:25, hexane/EtOAc) gave **2d'** (259.7 mg, 0.236 mmol, 56%, over 2 steps). Note: The product was generally eluted with hexane/EtOAc (85:15).

Step 3: preparation of **2d**

A round-bottom flask was charged sequentially with **2d'** (214.5 mg, 0.195 mmol), Pd(OH)₂ on carbon (21.5 mg, 10% w/w), CH₂Cl₂ (19.5 mL), dry THF (19.5 mL) and MeOH (19.5 mL). The septum capped round-bottom flask was evacuated over three times, purged with H₂ and stirred at 32 °C for 24 h. The reaction mixture was passed through a short pad of Celite and rinsed with CH₂Cl₂/MeOH (80:20). The filtrate was concentrated under reduced pressure. After volatiles were removed, flash column chromatography on silica gel (99.9:0.1–85:15, CH₂Cl₂/MeOH) gave **2d** (88.7 mg, 0.137 mmol, 70%) as a yellow solid. Note: The product was generally eluted with CH₂Cl₂/MeOH (85:15). **R_f** = 0.25 (80:20, CH₂Cl₂/MeOH) [**α**]_D²⁶ +119.7 (*c* = 0.1, MeOH) **M.p.** 170–175 °C **IR** (neat) 3383, 2924, 1636, 1607, 1586, 1556, 1491, 1458, 1436, 1300 cm⁻¹. **¹H NMR** (400 MHz, CD₃OD) δ 8.34 (m, 2H), 8.09–8.06 (m, 2H), 7.53–7.48 (m, 2H), 7.08–7.02 (m, 4H), 4.05 (d, *J* = 7.6 Hz, 1H), 3.81 (dd, *J* = 12.0, 2.4 Hz, 1H), 3.77–3.46 (m, 5H), 3.28–3.04 (m, 6H), 1.95 (m, 1H), 1.41 (m, 1H). **¹¹B NMR** (128.4 MHz, CD₃OD) δ 6.88. **¹³C NMR** (100.6 MHz, CD₃OD) δ 157.9, 157.8, 152.0, 151.3, 136.5, 127.9, 127.8, 121.9, 121.7, 121.4, 121.1, 119.1, 118.8, 116.0, 104.4, 99.9, 99.3, 77.9, 77.8, 77.1, 75.4, 75.0, 73.0, 71.5, 71.3, 70.2, 62.7, 33.1 (only observed peaks). **¹⁹F NMR** (376.5 MHz, CD₃OD) δ -66.8. **HRMS–ESI** (*m/z*): [**M**+Na]⁺ calcd for C₃₀H₃₁BF₃NO₁₁Na⁺, 672.1840; found, 672.1871.

8a-Methoxy-2-(trifluoromethyl)-8a*H*-8,9-dioxo-3a¹λ⁴-aza-8aλ⁴-borabenzofg]tetracene (**10**)



A round-bottom flask was charged with a stirring bar, **S7** (30.8 mg, 0.086 mmol), MeOH (3 mL) and TFA in DCE (0.1 M, 2 mL) under ambient atmosphere and stirred for 20 min. The reaction mixture was concentrated under reduced pressure to give **10** (29.6 mg, 80.6 μmol, 93%) as a yellow solid. The structure of **10** was confirmed by X-ray diffraction analysis. Note: This compound was gradually decomposed to **S7**. **M.p.** 242–247 °C **IR** (neat) 1637, 1607, 1581, 1492, 1458, 1435, 1316, 1301, 1275, 1250 cm⁻¹. **¹H NMR** (400 MHz, CDCl₃) δ 8.01 (s, 2H), 7.84 (dd, *J* = 8.0, 1.6 Hz, 2H), 7.53 (ddd, *J* = 8.4, 7.2, 1.6 Hz, 2H), 7.21 (dd, *J* = 8.4, 0.8 Hz, 2H), 7.07 (ddd, *J* = 8.4, 7.2, 0.8 Hz, 2H), 3.26 (s, 3H). **¹¹B NMR** (128.4 MHz, CDCl₃) δ 2.77. **¹³C NMR** (100.6 MHz, CDCl₃) δ 156.8, 150.4, 142.6 (q, *J*_{C-F} = 34.6 Hz), 135.2, 125.9, 123.2, 120.8, 120.6, 120.5, 117.0, 113.4 (q, *J*_{C-F} = 113.4 Hz), 49.1 (only observed peaks). **¹⁹F NMR** (376.5 MHz, CDCl₃) δ -65.5. **HRMS–ESI** (*m/z*): [**M**+Na]⁺ calcd for C₁₉H₁₃BF₃NO₃Na⁺, 394.0836; found, 394.0814.

■ Light Set Up ■

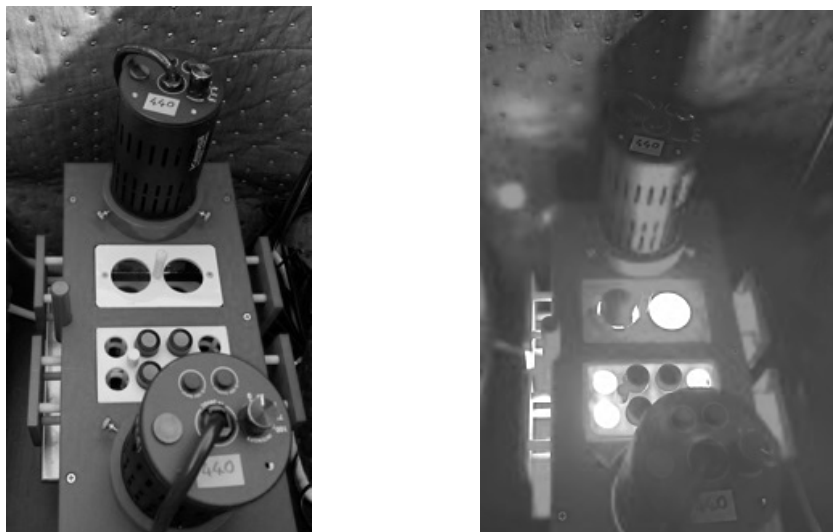


Figure S3-2. EvoluChem photoreactor

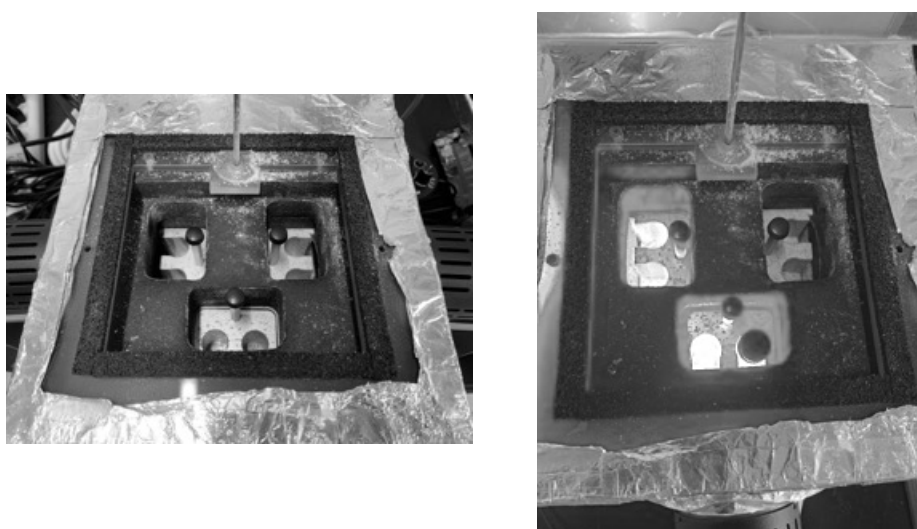
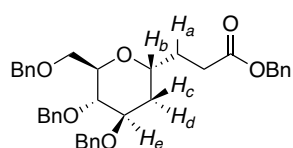


Figure S3-3. UC Reactor

■ Procedure for Giese-type Reaction ■

Benzyl 3-((2*R*,4*R*,5*S*,6*R*)-4,5-Bis(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2*H*-pyran-2-yl)propanoate (4aa)



A screw-top 20 mL vial was charged with a stirring bar and PDP-borate **1a**-CF₃ (60.6 mg, 0.08 mmol) under ambient atmosphere. The vial was brought to a glovebox, and dry MeCN (15.7 mL), dry MeOH (1.8 mL) and benzyl acrylate **3a** (8.1 mg, 0.05 mmol) in dry MeCN (500 μ L) were added. After the vial was removed from the glovebox and sealed with Teflon tape, the vial was placed in EvoluChem photoreactor (PhotoRedOx Duo) equipped with two 45W blue LEDs and stirred for 12 h. The residue was dissolved in CDCl₃ and added 1,1,2,2-tetrachloroethane (19.5 mg, 0.116 mmol) as an internal standard. ¹H NMR (400 MHz) yield of borate **10** (88%) was obtained by comparing the relative value of integration for the peak observed at 7.98 ppm of **10** with that of 1,1,2,2-tetrachloroethane observed at 5.94 ppm (Figure S3-4). ¹H NMR (400 MHz) yield of **4aa** (94%) was obtained by comparing the relative value of integration for the peak observed at 5.09 ppm of **4aa** with that of 1,1,2,2-tetrachloroethane observed at 5.94 ppm (Figure S3-4).

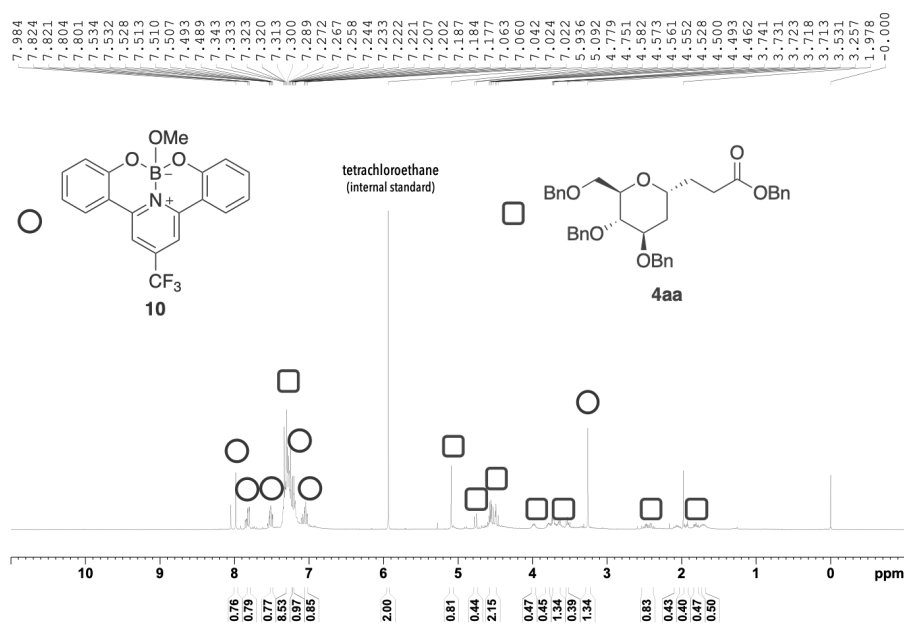
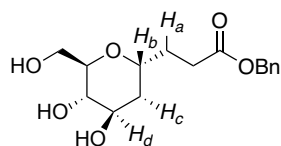


Figure S3-4. ¹H NMR analysis.

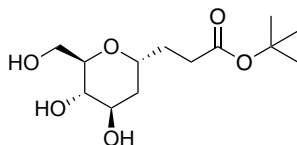
After volatiles were removed under reduced pressure, flash column chromatography on silica gel (95:5–70:30, hexane/EtOAc) and GPC (eluent: CHCl₃) gave **4aa** (26.2 mg, 45 μ mol, 90%) as colorless oil. **Rf** = 0.18 (80:20, hexane/EtOAc) [α]_D²⁶ +21.1 (*c* = 0.1, MeOH) **IR** (neat) 2926, 2865, 1732, 1497, 1454, 1365, 1257, 1207, 1162, 1094 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 7.35–7.18 (m, 20H), 5.09 (s, 2H), 4.77 (d, *J* = 11.2 Hz, 1H), 4.60–4.46 (m, 5H), 3.98 (dq, *J* = 9.6, 4.8 Hz, 1H, *H_b*, anomeric H), 3.79 (ddd, *J* = 9.2, 7.2, 4.4 Hz, 1H, *H_e*), 3.75–3.70 (m, 2H), 3.64 (m, 1H), 3.53 (m, 1H), 2.53–2.36 (m, 2H), 2.06 (dddd, *J* = 14.4, 10.4, 9.6, 5.6 Hz, 1H, *H_a*), 1.94 (dt, *J* = 13.2, 4.8 Hz, 1H, *H_d*), 1.81 (ddd, *J* = 13.2, 9.2, 4.8 Hz, 1H, *H_c*), 1.70 (dddd, *J* = 14.4, 8.8, 6.8, 4.8 Hz, 1H). ¹³C NMR (100.6 MHz, CDCl₃) δ 173.2, 138.4, 138.3, 138.2, 135.9, 128.5, 128.4, 128.32, 128.29, 128.18, 127.85, 127.76, 127.60, 127.57, 127.53, 76.6, 76.5, 73.9, 73.3, 72.5, 71.4, 69.9, 68.9, 66.2, 33.4, 30.6, 27.1 (only observed peaks). **HRMS–ESI** (*m/z*): [M+NH₄]⁺ calcd for C₃₇H₄₄NO₆⁺, 598.3163; found, 598.3184.

Benzyl **3-((2R,4R,5S,6R)-4,5-Dihydroxy-6-(hydroxymethyl)tetrahydro-2H-pyran-2-yl)propanoate (5aa)**



A screw-top 20 mL vial was charged with a stirring bar and PDP-borate **2a** (39.0 mg, 0.08 mmol) under ambient atmosphere. The vial was brought to a glovebox, and dry MeCN (15.3 mL), dry MeOH (1.7 mL) and benzyl acrylate **3a** (8.1 mg, 0.05 mmol) in dry MeCN/dry MeOH (9:1, 1 mL) were added. After the vial was removed from the glovebox and sealed with Teflon tape, the vial was placed in EvoluChem photoreactor (PhotoRedOx Duo) equipped with two 45W blue LEDs and stirred for 12 h. After volatiles were removed under reduced pressure, flash column chromatography on silica gel (100:0–90:10, CH₂Cl₂/ MeOH) and GPC (eluent: CHCl₃) gave **5aa** (11.4 mg, 36.7 μmol, 73%) as colorless oil. **R_f** = 0.18 (80:20, CH₂Cl₂/MeOH) [**α**]_D²⁶ +43.5 (*c* = 0.2, MeOH) **IR** (neat) 3397, 2924, 2360, 2341, 1734, 1456, 1260, 1163, 1096, 1067 cm⁻¹ **¹H NMR** (400 MHz, CD₃OD) δ 7.37–7.28 (m, 5H), 5.11 (s, 2H), 3.96 (dtd, *J* = 10.8, 4.8, 2.4 Hz, 1H, *H_b*, anomeric H), 3.75 (td, *J* = 11.6, 2.4 Hz, 1H, *H_d*), 3.74 (m, 1H), 3.66 (m, 1H), 3.39 (ddd, *J* = 8.8, 6.0, 2.8 Hz, 1H), 3.19 (m, 1H), 2.55–2.40 (m, 2H), 2.17 (dddd, *J* = 14.4, 10.8, 8.0, 6.4 Hz, 1H, *H_a*), 1.87 (ddd, *J* = 13.2, 4.8, 2.4 Hz, 1H, *H_c*), 1.75–1.67 (m, 2H). **¹³C NMR** (100.6 MHz, CD₃OD) δ 175.0, 137.7, 129.5, 129.24, 129.18, 75.4, 73.4, 72.6, 70.1, 67.3, 63.1, 37.3, 31.7, 27.3. **HRMS–ESI** (*m/z*): [*M*+Na]⁺ calcd for C₁₆H₂₂O₆Na⁺, 333.1309; found, 333.1313.

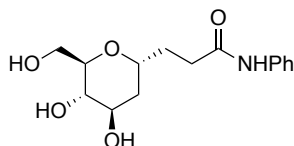
***tert*-Butyl** **3-((2R,4R,5S,6R)-4,5-Dihydroxy-6-(hydroxymethyl)tetrahydro-2H-pyran-2-yl)propanoate (5ab)**



A screw-top 20 mL vial was charged with a stirring bar and PDP-borate **2a** (60.6 mg, 0.12 mmol) under ambient atmosphere. The vial was brought to a glovebox, and dry MeCN (15.3 mL), dry MeOH (1.7 mL) and *tert*-butyl acrylate **3b** (8.1 mg, 0.05 mmol) in dry MeCN/dry MeOH (9:1, 1 mL) were added. After the vial was removed from the glovebox and sealed with Teflon tape, the vial was placed in EvoluChem photoreactor (PhotoRedOx Duo) equipped with two 45W blue LEDs and stirred for 14 h. After volatiles were removed under reduced pressure, flash column chromatography on silica gel (100:0–85:15, CH₂Cl₂/ MeOH) gave **5ab** (13.9 mg, 50.3 μmol, quantitative) as pale yellow oil. **R_f** = 0.3 (90:10, CH₂Cl₂/MeOH) [**α**]_D²⁶ +41.3 (*c* = 0.1, MeOH) **IR** (neat) 3398, 2978, 2934, 1728, 1458, 1367, 1286, 1257, 1155, 1094, 1066 cm⁻¹. **¹H NMR** (400 MHz, CD₃OD) δ 3.94 (dtd, *J* = 10.4, 5.2, 2.4 Hz, 1H, anomeric H), 3.79–3.64 (m 3H), 3.39 (ddd, *J* = 8.8, 6.0, 2.8 Hz, 1H), 3.19 (m, 1H), 2.41–2.25 (m, 2H), 2.08 (dddd, *J* = 14.2, 10.4, 8.0, 6.0 Hz, 1H), 1.87 (ddd, *J* = 13.2, 4.8, 2.4 Hz, 1H), 1.75–1.60 (m, 2H), 1.45 (s, 9H). **¹³C NMR** (100.6 MHz, CD₃OD) δ 174.7, 81.5, 75.4, 73.4, 72.5, 70.1, 63.1, 37.2, 32.9, 28.3, 27.5. **HRMS–ESI** (*m/z*): [*M*+Na]⁺ calcd for C₁₃H₂₄O₆Na⁺, 299.1465; found,

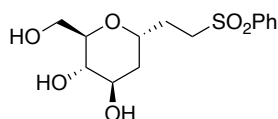
299.1471.

3-((2*R*,4*R*,5*S*,6*R*)-4,5-Dihydroxy-6-(hydroxymethyl)tetrahydro-2*H*-pyran-2-yl)-*N*-phenylpropanamide (5ac**)**



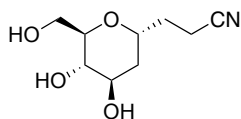
A screw-top 20 mL vial was charged with a stirring bar, PDP-borate **2a** (39.0 mg, 0.08 mmol) and *N*-phenylacrylamide **3c** (8.1 mg, 0.05 mmol) under ambient atmosphere. The vial was brought to a glovebox, and dry MeCN (16.2 mL) and dry MeOH (1.8 mL) were added. After the vial was removed from the glovebox and sealed with Teflon tape, the vial was placed in EvoluChem photoreactor (PhotoRedOx Duo) equipped with two 45W blue LEDs and stirred for 18 h. After volatiles were removed under reduced pressure, flash column chromatography on silica gel (99:9: 0.1–82:18, CH₂Cl₂/ MeOH) gave **5ac** (19.6 mg, 66 μmol, quantitative) as brown oil. *R*_f = 0.07 (90:10, CH₂Cl₂/MeOH) [*α*]_D²⁶ +47.2 (*c* = 0.2, MeOH) **IR** (neat) 3312, 2930, 1663, 1600, 1545, 1450, 1444, 1092, 1066, 757 cm⁻¹. **¹H NMR** (400 MHz, CD₃OD) δ 7.55–7.53 (m, 2H), 7.32–7.27 (m, 2H), 7.08 (m, 1H), 4.00 (dtd, *J* = 12.4, 4.0, 2.4 Hz, 1H, anomeric H), 3.81–3.75 (m, 2H), 3.69 (dd, *J* = 11.6, 6.0 Hz, 1H), 3.46 (m, 1H), 3.20 (t, *J* = 17.2 Hz, 1H), 2.52–2.39 (m, 2H), 2.22 (m, 1H), 1.91 (ddd, *J* = 13.2, 4.8, 2.4 Hz, 1H), 1.83–1.70 (m, 2H). **¹³C NMR** (100.6 MHz, CD₃OD) δ 174.2, 139.9, 129.8, 125.1, 121.2, 75.4, 73.5, 72.7, 70.2, 63.1, 37.4, 34.5, 28.1. **HRMS–ESI** (*m/z*): [M+Na]⁺ calcd for C₁₅H₂₁NO₅Na⁺, 318.1312; found, 318.1324.

(2*R*,3*S*,4*R*,6*S*)-2-(Hydroxymethyl)-6-(2-(phenylsulfonyl)ethyl)tetrahydro-2*H*-pyran-3,4-diol (5ad**)**



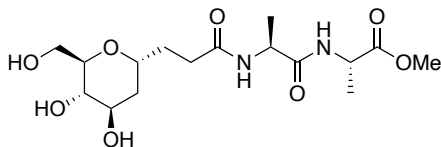
A screw-top 20 mL vial was charged with a stirring bar, PDP-borate **2a** (39.0 mg, 0.08 mmol) and vinylsulfonylbenzene **3d** (8.4 mg, 0.05 mmol) under ambient atmosphere. The vial was brought to a glovebox, and dry MeCN (16.2 mL) and dry MeOH (1.8 mL) were added. After the vial was removed from the glovebox and sealed with Teflon tape, the vial was placed in EvoluChem photoreactor (PhotoRedOx Duo) equipped with two 45W blue LEDs and stirred for 14 h. After volatiles were removed under reduced pressure, flash column chromatography on silica gel (95:5–70:30, hexane/EtOAc then 85:15, CH₂Cl₂/ MeOH) and reverse phase column chromatography on Sfär C18 D –Duo 100 Å 30 μm 30 g (100:0–60:40, H₂O/MeCN) gave **5ad** (3.4 mg, 10.7 μmol, 21%) as a pale yellow oil. The ¹H and ¹³C NMR spectra data of product **5ad** were consistent with the literature.⁸ *R*_f = 0.07 (90:10, CH₂Cl₂/MeOH), 0.5 (70:30, H₂O/MeCN) **¹H NMR** (400 MHz, CD₃OD) δ 7.55–7.53 (m, 2H), 7.32–7.27 (m, 2H), 7.08 (m, 1H), 4.00 (dddd, *J* = 11.6, 6.0, 3.6, 2.4 Hz, 1H, anomeric H), 3.81–3.75 (m, 2H), 3.69 (dd, *J* = 11.6, 6.0 Hz, 1H), 3.46 (m, 1H), 3.20 (t, *J* = 17.2 Hz, 1H), 2.52–2.39 (m, 2H), 2.22 (m, 1H), 1.91 (ddd, *J* = 13.2, 4.8, 2.4 Hz, 1H), 1.83–1.70 (m, 2H). **¹³C NMR** (100.6 MHz, CD₃OD) δ 140.5, 135.1, 130.6, 129.1, 75.9, 73.1, 71.1, 69.9, 63.0, 53.6, 37.0, 25.6.

3-((2*R*,4*R*,5*S*,6*R*)-4,5-Dihydroxy-6-(hydroxymethyl)tetrahydro-2*H*-pyran-2-yl)propanenitrile (5ae)



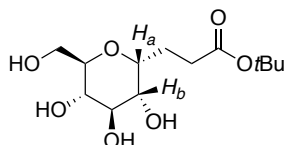
A screw-top 20 mL vial was charged with a stirring bar and PDP-borate **2a** (60.6 mg, 0.12 mmol) under ambient atmosphere. The vial was brought to a glovebox, and dry MeCN (15.3 mL), dry MeOH (1.7 mL) and acrylonitrile **3e** (2.7 mg, 0.05 mmol) in dry MeCN/dry MeOH (9:1, 1 mL) were added. After the vial was removed from the glovebox and sealed with Teflon tape, the vial was placed in EvoluChem photoreactor (PhotoRedOx Duo) equipped with two 45W blue LEDs and stirred for 13 h. After volatiles were removed under reduced pressure, flash column chromatography on silica gel (99.9:0.1–85:15, CH₂Cl₂/ MeOH) gave **5ae** (5.5 mg, 27.3 μmol, 55%) as pale yellow oil. *R_f* = 0.06 (90:10, CH₂Cl₂/MeOH) [*α*]_D²⁶ +53.3 (*c* = 0.1, MeOH) **IR** (neat) 3385, 2930, 2888, 1624, 1609, 1560, 1491, 1458, 1096, 1066 cm⁻¹. **¹H NMR** (400 MHz, CD₃OD) δ 4.03 (dddd, *J* = 11.2, 6.0, 3.2, 2.4 Hz, 1H, **anomeric H**), 3.81 (dd, *J* = 11.6, 2.8 Hz, 1H), 3.75–3.67 (m, 2H), 3.78 (m, 1H), 3.21, (m, 1H), 2.60–2.46 (m, 2H), 2.21 (m, 1H), 1.89 (ddd, *J* = 13.2, 4.8, 2.4 Hz, 1H), 1.79–1.66 (m, 2H). **¹³C NMR** (100.6 MHz, CD₃OD) δ 121.1, 75.7, 73.2, 71.6, 70.0, 62.9, 36.9, 28.1, 14.2. **HRMS–ESI** (*m/z*): [*M*+Na]⁺ calcd for C₉H₁₅NO₄Na⁺, 224.0893; found, 224.0905.

Methyl 3-((2*R*,4*R*,5*S*,6*R*)-4,5-Dihydroxy-6-(hydroxymethyl)tetrahydro-2*H*-pyran-2-yl)propanoyl)-*L*-alanyl-*L*-alaninate (5af)



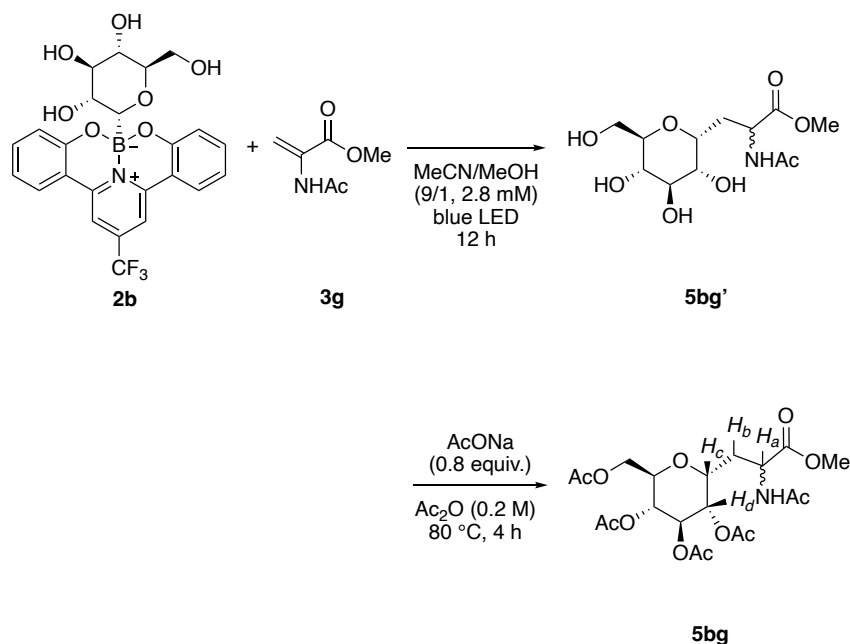
A screw-top 20 mL vial was charged with a stirring bar, PDP-borate **2a** (39.0 mg, 0.08 mmol) and **3f** (11.4 mg, 0.05 mmol) under ambient atmosphere. The vial was brought to a glovebox, and MeCN (16.2 mL) and MeOH (1.8 mL) were added. After the vial was removed from the glovebox and sealed with Teflon tape, the vial was placed in EvoluChem photoreactor (PhotoRedOx Duo) equipped with two 45W blue LEDs and stirred for 14 h. After volatiles were removed under reduced pressure, flash column chromatography on silica gel (99.9:0.1–85:15, CH₂Cl₂/ MeOH) gave **5af** (13.1 mg, 34.8 μmol, 69%) as pale yellow oil. *R_f* = 0.21 (80:20, CH₂Cl₂/MeOH) [*α*]_D²⁶ –26.9 (*c* = 0.1, MeOH) **IR** (neat) 3287, 3074, 2917, 1735, 1653, 1541, 1458, 1375, 1286, 1218 cm⁻¹. **¹H NMR** (400 MHz, CD₃OD) δ 4.43–4.32 (m, 2H), 3.99 (dddd, *J* = 10.4, 7.2, 3.2, 2.4 Hz, 1H, **anomeric H**), 3.82 (dd, *J* = 11.6, 2.4 Hz, 1H), 3.84–3.64 (m, 5H), 3.43 (m, 1H), 3.15 (m, 1H), 2.31 (dd, *J* = 8.0, 6.8 Hz, 2H), 2.13 (m, 1H), 1.87 (ddd, *J* = 13.2, 4.8, 2.4 Hz, 1H), 1.76–1.67 (m, 2H), 1.42–1.37 (m, 3H), 1.35 (d, *J* = 7.2 Hz, 3H). **¹³C NMR** (100.6 MHz, CD₃OD) δ 175.6, 175.2, 174.5, 75.5, 73.6, 72.2, 70.2, 63.2, 52.7, 50.2, 49.8, 37.3, 33.1, 28.0, 18.0, 17.4. **HRMS–ESI** (*m/z*): [*M*+Na]⁺ calcd for C₁₆H₂₈N₂O₈Na⁺, 399.1738; found, 399.1724.

***tert*-Butyl 3-((2*R*,3*R*,4*R*,5*S*,6*R*)-3,4,5-Trihydroxy-6-(hydroxymethyl)tetrahydro-2*H*-pyran-2-yl)propanoate (5bb)**



A screw-top 20 mL vial was charged with a stirring bar and PDP-borate **2b** (40.3 mg, 0.08 mmol) under ambient atmosphere. The vial was brought to a glovebox, and dry MeCN (15.3 mL), dry MeOH (1.7 mL) and *tert*-butyl acrylate **3b** (6.4 mg, 0.05 mmol) in dry MeCN/dry MeOH (9:1, 1 mL) were added. After the vial was removed from the glovebox and sealed with Teflon tape, the vial was placed in EvoluChem photoreactor (PhotoRedOx Duo) equipped with two 45W blue LEDs and stirred for 13.5 h. After volatiles were removed under reduced pressure, flash column chromatography on silica gel (90:10–80:20, CH₂Cl₂/ MeOH) gave **5bb** (16.1 mg, 55 μ mol, quantitative) as colorless oil. The ¹H and ¹³C NMR spectra data of product **5bb** were consistent with the literature.⁹ ¹H NMR (400 MHz, D₂O) δ 3.98 (dt, J = 9.6, 5.6 Hz, 1H, H_a , anomeric H), 3.82 (dd, J = 12.4, 2.4 Hz, 1H), 3.71 (dd, J = 10.0, 6.0 Hz, 1H), 3.70 (dd, J = 12.4, 5.6 Hz, 1H, H_b), 3.63 (dd, J = 10.0, 8.8 Hz, 1H), 3.49 (ddd, J = 10.0, 5.6, 2.4 Hz, 1H), 3.35 (dd, J = 10.0, 8.8 Hz, 1H), 2.48–2.30 (m, 2H), 1.97–1.90 (m, 2H), 1.45 (s, 9H). ¹³C NMR (100.6 MHz, D₂O) δ 175.4, 82.6, 75.0, 73.1, 72.5, 71.0, 70.1, 60.9, 31.2, 27.2, 19.5 .

(2*R*,3*S*,4*R*,5*R*,6*R*)-2-(2-Acetamido-3-methoxy-3-oxopropyl)-6-(acetoxymethyl)tetrahydro-2*H*-pyran-3,4,5-triyl Triacetate (5bg**)**



Step 1: Synthesis of **5bg'**

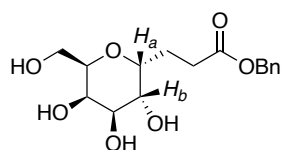
A screw-top 20 mL vial was charged with a stirring bar, PDP-borate **2b** (40.3 mg, 0.08 mmol) and methyl 2-acetamidoacrylate **3g** (7.2 mg, 0.05 mmol) under ambient atmosphere. The vial was brought to a glovebox, and dry MeCN (16.2 mL) and dry MeOH (1.8 mL) were added. After the vial was removed from the glovebox and sealed with Teflon tape, the vial was placed in EvoluChem photoreactor (PhotoRedOx Duo) equipped with two 45W blue LEDs and stirred for 12 h. The reaction mixture was passed through a short pad of silica gel and rinsed with CH₂Cl₂. The crude material was

washed on a short pad of silica gel with CH₂Cl₂, then dissolved out with CH₂Cl₂/MeOH (8:2). The filtrate in CH₂Cl₂/MeOH (8:2) was concentrated under reduced pressure and the crude material of **5bg'** was used without further purification.

Step 2: Synthesis of **5bg**

A screw-top 4 mL vial was charged with a stirring bar, the crude of **5bg'**, NaOAc (3.3 mg, 0.04 mmol) and Ac₂O (250 μ L) under ambient atmosphere. After the vial was filled with nitrogen and sealed with Teflon tape, the vial was placed in aluminum heating block at 80 °C and stirred for 4 h. The reaction mixture was diluted with diethyl ether and extracted with diethyl ether over three times. The organic extract was washed with saturated NaHCO₃ aq and brine. The organic layer was dried over sodium sulfate, filtrated and concentrated under reduced pressure. After volatiles were removed, GPC (eluent: CHCl₃) gave **5bg** (14.9 mg, 31.3 μ mol, 63%, dr 3:1) as pale yellow oil. $[\alpha]_D^{26} +54.0$ ($c = 0.2$, MeOH) **IR** (neat) 1747, 1701, 1683, 1558, 1540, 1507, 1436, 1370, 1224, 1036 cm⁻¹. **¹H NMR** (400 MHz, CDCl₃) δ 6.30 (d, $J = 6.8$ Hz, 0.75 $\times$ 1H, N-H), 6.17 (d, $J = 8.0$ Hz, 0.25 $\times$ 1H, N-H), 5.23 (t, $J = 8.8$ Hz, 0.75 $\times$ 1H), 5.22 (t, $J = 8.8$ Hz, 0.25 $\times$ 1H), 5.05–4.95 (m, 2H), 4.72 (ddd, $J = 14.4, 8.0, 4.4$ Hz, 0.25 $\times$ 1H, H_a), 4.71 (ddd, $J = 14.4, 6.8, 4.0$ Hz, 0.75 $\times$ 1H, H_a), 4.39 (ddd, $J = 11.2, 5.6, 2.8$ Hz, 0.75 $\times$ 1H, H_c , **anomeric H**), 4.35 (dd, $J = 12.4, 4.8$ Hz, 0.75 $\times$ 1H), 4.27 (ddd, $J = 11.2, 5.6, 2.8$ Hz, 0.25 $\times$ 1H, H_c , **anomeric H**), 4.26 (dd, $J = 12.4, 5.6$ Hz, 0.25 $\times$ 1H), 4.11 (dd, $J = 12.4, 2.8$ Hz, 0.25 $\times$ 1H, H_d), 4.02 (dd, $J = 11.8, 2.8$ Hz, 0.75 $\times$ 1H, H_d), 3.99 (ddd, $J = 9.2, 4.4, 2.8$ Hz, 0.75 $\times$ 1H), 3.93 (ddd, $J = 11.2, 5.6, 2.8$ Hz, 0.25 $\times$ 1H), 3.78 (s, 0.75 $\times$ 3H), 3.76 (s, 0.25 $\times$ 3H), 2.30 (ddd, $J = 14.8, 11.2, 4.0$ Hz, 0.25 $\times$ 1H, H_b), 2.29 (ddd, $J = 14.8, 11.2, 4.0$ Hz, 0.75 $\times$ 1H, H_b), 2.13–2.03 (m, 16H). (Peaks for two diastereomers were given.) **¹³C NMR** (100.6 MHz, CHCl₃) δ 172.1, 172.0, 170.8, 170.7, 169.93, 169.99, 169.8, 169.64, 169.61, 169.56, 169.50, 169.47, 69.9, 69.72, 69.68, 69.67, 69.32, 68.62, 68.15, 68.11, 61.8, 61.6, 52.75, 52.69, 49.5, 49.2, 28.0, 27.8, 23.2, 23.1, 20.8, 20.75, 20.68, 20.65 (only observed peaks). **HRMS–ESI** (m/z): $[M+H]^+$ calcd for C₂₀H₃₀NO₁₂⁺, 476.1763; found, 476.1779.

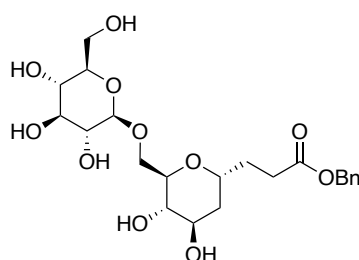
Benzyl 3-((2*R*,3*R*,4*R*,5*R*,6*R*)-3,4,5-Trihydroxy-6-(hydroxymethyl)tetrahydro-2*H*-pyran-2-yl)propanoate (**5ca**)



A screw-top 20 mL vial was charged with a stirring bar and PDP-borate **2c** (40.8 mg, 0.08 mmol) under ambient atmosphere. The vial was brought to a glovebox, and dry MeCN (15.2 mL), dry MeOH (1.8 mL) and benzyl acrylate **3a** (8.1 mg, 0.05 mmol) in dry MeCN (1 mL) were added. After the vial was removed from the glovebox and sealed with Teflon tape, the vial was placed in EvoluChem photoreactor (PhotoRedOx Duo) equipped with two 45W blue LEDs and stirred for 14 h. The reaction mixture was passed through a short pad of silica gel and rinsed with CH₂Cl₂ and then dissolved out with CH₂Cl₂/MeOH (8:2). The crude material in CH₂Cl₂/MeOH (8:2) was concentrated under reduced pressure. After volatiles were removed, reverse phase column chromatography on Sfär C18 D –Duo 100 Å 30 μ m 12 g (75:25–60:40, H₂O/MeCN) gave **5ca** (12.0 mg, 36.8 μ mol, 74%) as colorless oil. Note: The product was generally eluted with H₂O/MeCN (73:27). **Rf** = 0.50 (70:30, H₂O/MeCN) $[\alpha]_D^{26} +48.3$ ($c = 0.1$, MeOH) **IR** (neat) 3390, 2921, 2360, 1734, 1456, 1419, 1387, 1354, 1258, 1168 cm⁻¹. **¹H NMR** (400 MHz, CD₃OD) δ 7.37–7.29 (m, 5H), 5.12 (s, 2H), 3.90 (dt, $J = 9.6, 5.6$ Hz, 1H,

H_a , anomeric H), 3.75 (dd, $J = 11.6, 2.4$ Hz, 1H), 3.61 (dd, $J = 7.2, 5.6$ Hz, 1H), 3.59 (t, $J = 5.6$ Hz, 1H, H_b), 3.52 (m, 1H), 3.39 (m, 1H), 3.23 (dd, $J = 9.6, 8.4$ Hz, 1H), 2.56 (m, 1H), 2.43 (m, 1H), 2.03–1.97 (m, 2H). ^{13}C NMR (100.6 MHz, CD_3OD) δ 173.1, 135.7, 127.5, 127.22, 127.16, 74.6, 73.2, 72.6, 70.9, 70.3, 65.3, 61.1, 29.3, 19.3. HRMS–ESI (m/z): $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{16}\text{H}_{22}\text{O}_7\text{Na}^+$, 349.1258; found, 349.1262.

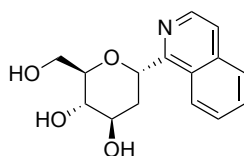
Benzyl **3-((2R,4R,5S,6R)-4,5-Dihydroxy-6-(((2R,3R,4S,5S,6R)-3,4,5-trihydroxy-6-(hydroxymethyl)tetrahydro-2H-pyran-2-yl)oxy)methyl)tetrahydro-2H-pyran-2-yl)propanoate (5da)**



A screw-top 20 mL vial was charged with a stirring bar and PDP-borate **2d** (52.0 mg, 0.08 mmol) under ambient atmosphere. The vial was brought to a glovebox, and dry MeCN (15.2 mL), dry MeOH (1.8 mL) and benzyl acrylate **3a** (8.1 mg, 0.05 mmol) in dry MeCN (1 mL) were added. After the vial was removed from the glovebox and sealed with Teflon tape, the vial was placed in EvoluChem photoreactor (PhotoRedOx Duo) equipped with two 45W blue LEDs and stirred for 14 h. The reaction mixture was passed through a short pad of silica gel and rinsed with $\text{CH}_2\text{Cl}_2/\text{MeOH}$ (99.9:0.1) and then dissolved out with $\text{CH}_2\text{Cl}_2/\text{MeOH}$ (1:1). The crude material in $\text{CH}_2\text{Cl}_2/\text{MeOH}$ (1:1) was concentrated under reduced pressure. After volatiles were removed, reverse phase column chromatography on Sfar C18 D–Duo 100 Å 30 μm 12 g (100:0–60:40, $\text{H}_2\text{O}/\text{MeCN}$) gave **5da** (12.7 mg, 26.9 μmol , 54%) as colorless oil. Note: The product was generally eluted with $\text{H}_2\text{O}/\text{MeCN}$ (90:10). $[\alpha]_D^{26} +8.1$ ($c = 0.08$, MeOH) IR (neat) 3385, 2924, 2358, 1734, 1456, 1419, 1375, 1261, 1165, 1073, 751 cm^{-1} . ^1H NMR (400 MHz, CD_3OD) δ 7.38–7.29 (m, 5H), 5.12 (s, 2H), 4.31 (d, $J = 7.6$ Hz, 1H), 4.08 (dd, $J = 10.8, 2.4$ Hz, 1H), 3.96 (m, 1H), 3.88 (m, 1H), 3.79–3.72 (m, 2H), 3.66–3.56 (m, 3H), 3.36 (m, 1H), 3.29–3.25 (m, 3H), 3.21 (dd, $J = 9.2, 8.0$ Hz, 1H), 2.56–2.41 (m, 2H), 2.17 (m, 1H), 1.88 (m, 1H), 1.77–1.68 (m, 1H). ^{13}C NMR (100.6 MHz, CD_3OD) δ 174.9, 137.7, 129.6, 129.3, 129.2, 104.8, 78.0, 77.9, 75.1, 74.6, 73.1, 72.7, 71.6, 70.4, 69.9, 67.3, 62.8, 37.0, 31.7, 27.4. HRMS–ESI (m/z): $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{22}\text{H}_{32}\text{O}_{11}\text{Na}^+$, 495.1860; found, 495.1837.

■ Procedure for Minisci-type Reaction ■

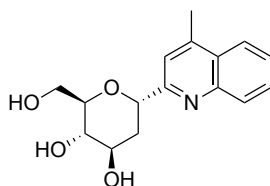
(2R,3S,4R,6S)-2-(Hydroxymethyl)-6-(isoquinolin-1-yl)tetrahydro-2H-pyran-3,4-diol (7aa)



A screw-top 4 mL vial was charged with a stirring bar, isoquinoline **6a** (6.5 mg, 0.05 mmol), and TFA (8.6 mg, 0.075 mmol) in MeOH (500 μL) under ambient atmosphere and stirred for 30 min. After

volatiles were removed under reduced pressure, $K_2S_2O_8$ (27.0 mg, 0.1 mmol), dry DMSO/H₂O (9/1, 500 μ L), and **2a** (36.5 mg, 0.075 mmol) were added. The vial was sealed with Teflon tape, placed in EvoluChem photoreactor (PhotoRedOx Duo) equipped with two 45W blue LEDs and stirred for 12 h. The reaction mixture was quenched with saturated $Na_2S_2O_3$ aq (81 μ L), saturated $NaHCO_3$ aq (227 μ L) and water (ca. 250 μ L) at 0 °C. The residue was purified by reverse phase column chromatography on Sfär C18 D –Duo 100 Å 30 μ m 30 g (100:0–5:95, H₂O/MeCN) to give **7aa** (α : β = 10:1, 15.3 mg, 55.6 μ mol, quantitative) as pale yellow oil. **Rf** = 0.33 (7:3, H₂O/MeCN) $[\alpha]_D^{26} +122.4$ (c = 0.2, MeOH) **IR** (neat) 3342, 2926, 1587, 1564, 1501, 1456, 1410, 1330, 1093, 1066 cm^{-1} . **¹H NMR** (400 MHz, CD₃OD) δ 8.66 (m, 0.91 $\times$ 1H), 8.43 (d, J = 5.6 Hz, 0.91 $\times$ 1H), 8.37 (m, 0.09 $\times$ 1H), 8.31 (m, 0.09 $\times$ 1H), 7.94 (m, 0.09 $\times$ 1H), 7.89 (d, J = 8.0 Hz, 0.91 $\times$ 1H), 7.74–7.62 (m, 3H), 5.86 (dd, J = 5.6, 2.0 Hz, 0.91 $\times$ 1H, **anomeric H**, major), 5.51 (dd, J = 11.6, 2.0 Hz, 0.09 $\times$ 1H, **anomeric H**, minor), 4.47 (ddd, J = 10.2, 8.4, 5.2 Hz, 0.91 $\times$ 1H), 3.99 (ddd, J = 8.8, 4.4, 1.6 Hz, 0.09 $\times$ 1H), 3.67 (dd, J = 12.0, 5.2 Hz, 1H), 3.60 (dd, J = 12.0, 2.8 Hz, 1H), 3.43 (m, 1H), 2.96–2.91 (m, 0.91 $\times$ 2H), 2.32 (ddd, J = 13.2, 4.8, 2.0 Hz, 0.09 $\times$ 1H), 2.10 (m, 0.09 $\times$ 1H), 2.00 (m, 1H). (Peaks for two diastereomers were given.) **¹³C NMR** (100.6 MHz, CD₃OD) δ 159.7, 141.6, 138.1, 131.3, 128.41, 128.37, 128.28, 127.6, 122.3, 77.0, 74.4, 73.6, 70.8, 62.8, 35.2. (Signals for the major diastereomer were detected). **HRMS–ESI** (m/z): $[M+Na]^+$ calcd for C₁₅H₁₇NO₄Na⁺, 298.1050; found, 298.1035.

(2*R*,3*S*,4*R*,6*S*)-2-(Hydroxymethyl)-6-(4-methylquinolin-2-yl)tetrahydro-2*H*-pyran-3,4-diol (7ab)

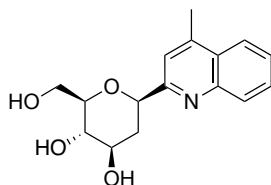


A screw-top 4 mL vial was charged with a stirring bar, lepidine **6b** (7.2 mg, 0.05 mmol), and TFA (8.6 mg, 0.075 mmol) in MeOH (500 μ L) under ambient atmosphere and stirred for 30 min. After volatiles were removed under reduced pressure, $K_2S_2O_8$ (27.0 mg, 0.1 mmol), DMSO/H₂O (9/1, 500 μ L), and **2a** (36.5 mg, 0.075 mmol) were added. The vial was sealed with Teflon tape, placed in UC reactor equipped with a 45W blue LED to keep temperature 0 °C and stirred for 12 h. The reaction mixture was quenched with saturated $Na_2S_2O_3$ aq (81 μ L), saturated $NaHCO_3$ aq (227 μ L) and water (ca. 250 μ L) at 0 °C. The residue was purified by reverse phase column chromatography on Sfär C18 D –Duo 100 Å 30 μ m 30 g (100:0–5:95, H₂O/MeCN) to give **7ab** (α : β = 9:1, 19.2 mg, 66.4 μ mol, quantitative) as pale yellow oil. **Rf** = 0.15 (7:3, H₂O/MeCN)

$[\alpha]_D^{26} +74.5$ (c = 0.3, MeOH) **IR** (neat) 3312, 2923, 2874, 1603, 1566, 1510, 1448, 1413, 1090, 1067 cm^{-1} . **¹H NMR** (400 MHz, CD₃OD) δ 8.07 (m, 1H), 8.02 (m, 1H), 7.71 (m, 1H), 7.67 (s, 0.9 $\times$ 1H), 7.62 (s, 0.1 $\times$ 1H), 7.58 (m, 1H), 5.22 (dd, J = 5.6, 2.4 Hz, 0.9 $\times$ 1H, **anomeric H**, major), 4.75 (dd, J = 12.0, 2.0 Hz, 0.1 $\times$ 1H, **anomeric H**, minor), 3.97 (dd, J = 12.0, 2.0 Hz, 0.1 $\times$ 1H), 3.87 (dd, J = 12.0, 2.4 Hz, 0.9 $\times$ 1H), 3.79–3.73 (m, 2H), 3.46 (m, 0.1 $\times$ 1H), 3.40 (m, 0.1 $\times$ 1H), 3.35 (dd, J = 4.4, 4.4 Hz, 0.9 $\times$ 1H), 3.31 (m, 0.9 $\times$ 1H), 3.12 (ddd, J = 12.8, 4.8, 2.4 Hz, 0.9 $\times$ 1H), 2.751–2.749 (m, 0.1 $\times$ 3H), 2.733–2.731 (m, 0.9 $\times$ 3H), 2.38 (ddd, J = 12.8, 4.8, 2.0 Hz, 0.1 $\times$ 1H), 1.95 (m, 0.9 $\times$ 1H), 1.65 (dt, J = 12.8, 11.6 Hz, 0.1 $\times$ 1H). (Peaks for two diastereomers were given.) **¹³C NMR** (100.6 MHz, CD₃OD) δ 161.4, 148.6, 146.8, 130.4, 130.3, 128.5, 127.5, 124.9, 121.1, 77.8, 75.8, 73.4, 70.4, 63.3, 34.9, 18.9. (Signals for the major diastereomer were detected). **HRMS–ESI** (m/z): $[M+Na]^+$

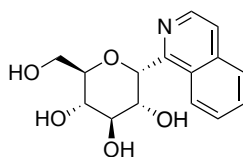
calcd for C₁₆H₁₉NO₄Na⁺, 312.1206; found, 312.1222.

(2*R*,3*S*,4*R*,6*R*)-2-(Hydroxymethyl)-6-(4-methylquinolin-2-yl)tetrahydro-2*H*-pyran-3,4-diol (7ab)



A screw-top 4 mL vial was charged with a stirring bar, lepidine **6b** (7.2 mg, 0.05 mmol), and TFA (8.6 mg, 0.075 mmol) in MeOH (500 μ L) under ambient atmosphere and stirred for 30 min. After volatiles were removed under reduced pressure, K₂S₂O₈ (27.0 mg, 0.1 mmol), DMSO/H₂O (9/1, 500 μ L), and **2a** (36.5 mg, 0.075 mmol) were added. The vial was sealed with Teflon tape, placed in UC reactor equipped with a 45W blue LED to keep temperature 50 °C and stirred for 13 h. The reaction mixture was quenched with saturated Na₂S₂O₃ aq (81 μ L), saturated NaHCO₃ aq (227 μ L) at 0 °C. The residue was purified by reverse phase column chromatography on Sfär C18 D –Duo 100 Å 30 μ m 30 g (100:0–5:95, H₂O/MeCN) to give **7ab** (α : β = 1:27, 15.0 mg, 51.8 μ mol, quantitative) as yellow oil. **Rf** = 0.21 (7:3, H₂O/MeCN) $[\alpha]_D^{26}$ +71.5 (c = 0.2, MeOH) **IR** (neat) 3337, 2921, 2870, 1603, 1566, 1510, 1448, 1413, 1353, 1300, 1092 cm⁻¹. **¹H NMR** (400 MHz, CD₃OD) δ 8.09 (m, 1H), 8.00 (m, 1H), 7.74 (m, 1H), 7.66 (s, 0.04 $\times$ 1H), 7.62–7.58 (m, 0.96 $\times$ 2H + 0.04 $\times$ 1H), 5.22 (dd, J = 5.6, 2.4 Hz, 0.04 $\times$ 1H, **anomeric H**, minor), 4.75 (dd, J = 11.6, 2.0 Hz, 0.96 $\times$ 1H, **anomeric H**, major), 3.97 (dd, J = 12.0, 2.0 Hz, 0.96 $\times$ 1H), 3.87–3.78 (m, 0.96 $\times$ 2H + 0.04 $\times$ 3H), 3.47–3.38 (m, 2H), 3.11 (m, 0.04 $\times$ 1H), 2.743–2.741 (m, 0.96 $\times$ 3H), 2.708–2.707 (m, 0.04 $\times$ 3H), 2.38 (ddd, J = 12.8, 4.8, 2.0 Hz, 0.96 $\times$ 1H), 1.98 (m, 0.04 $\times$ 1H), 1.64 (q, J = 12.0 Hz, 0.96 $\times$ 1H). (Peaks for two diastereomers were given.) **¹³C NMR** (100.6 MHz, CD₃OD) δ 162.2, 147.9, 147.8, 130.8, 129.3, 128.9, 127.6, 125.1, 120.4, 82.2, 79.5, 74.0, 72.9, 63.1, 41.6, 18.8. (Signals for the major diastereomer were detected). **HRMS–ESI** (m/z): [M+Na]⁺ calcd for C₁₆H₁₉NO₄Na⁺, 312.1206; found, 312.1215.

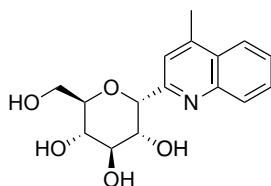
(2*R*,3*S*,4*R*,5*R*,6*R*)-2-(Hydroxymethyl)-6-(isoquinolin-1-yl)tetrahydro-2*H*-pyran-3,4,5-triol (7ba)



A screw-top 4 mL vial was charged with a stirring bar, isoquinoline **6a** (6.5 mg, 0.05 mmol), and TFA (8.6 mg, 0.075 mmol) in MeOH (500 μ L) under ambient atmosphere and stirred for 30 min. After volatiles were removed under reduced pressure, K₂S₂O₈ (27.0 mg, 0.1 mmol), DMSO/H₂O (9/1, 500 μ L), and **2a** (37.7 mg, 0.075 mmol) were added. The vial was sealed with Teflon tape, placed in EvoluChem photoreactor (PhotoRedOx Duo) equipped with two 45W blue LEDs and stirred for 13 h. The reaction mixture was quenched with saturated Na₂S₂O₃ aq (81 μ L), saturated NaHCO₃ aq (227 μ L) and water (ca. 1 mL) at 0 °C. The residue was purified by reverse phase column chromatography on Sfär C18 D –Duo 100 Å 30 μ m 30 g (100:0–5:95, H₂O/MeCN) to give **7ba** (only α , 10.8 mg, 37.1 μ mol, 74%) as pale yellow oil. **Rf** = 0.34 (7:3, H₂O/MeCN) **M.p.** 104–109 °C (decomp.) $[\alpha]_D^{26}$ +236.6 (c = 0.1, MeOH) **IR** (neat) 3486, 3329, 3245, 1560, 1412, 1324, 1066, 1033, 835, 753 cm⁻¹. **¹H NMR**

(400 MHz, CD₃OD) δ 8.68 (m, 1H), 8.42 (d, J = 5.6 Hz, 1H), 7.94 (d, J = 8.4 Hz, 1H), 7.79–7.75 (m, 2H), 7.68 (ddd, J = 8.4, 7.2, 1.2 Hz, 1H), 5.87 (d, J = 6.0 Hz, 1H, **anomeric H**), 4.47 (t, J = 9.2 Hz, 1H), 3.98 (dd, J = 9.2, 6.0 Hz, 1H), 3.61–3.59 (m, 2H), 3.46 (dd, J = 9.2, 8.6 Hz, 1H), 2.94 (ddd, J = 9.2, 4.4, 3.6 Hz, 1H). ¹³C NMR (100.6 MHz, CD₃OD) δ 159.4, 140.5, 138.4, 131.9, 129.1, 128.8, 128.5, 127.4, 122.7, 76.9, 76.0, 75.4, 75.3, 72.4, 62.6. **HRMS–ESI** (m/z): [M+Na]⁺ calcd for C₁₅H₁₇NO₄Na⁺, 314.0999; found, 314.1012.

(2*R*,3*S*,4*R*,5*R*,6*R*)-2-(Hydroxymethyl)-6-(4-methylquinolin-2-yl)tetrahydro-2*H*-pyran-3,4,5-triol (7bb)



EvoluChem photoreactor (PhotoRedOx Duo)

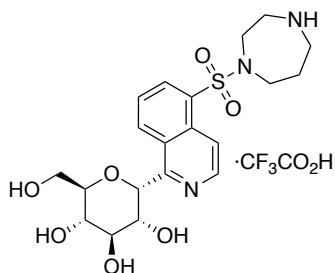
A screw-top 4 mL vial was charged with a stirring bar, lepidine **6b** (7.2 mg, 0.05 mmol), and TFA (8.6 mg, 0.075 mmol) in MeOH (500 μ L) under ambient atmosphere and stirred for 30 min. After volatiles were removed under reduced pressure, K₂S₂O₈ (27.0 mg, 0.1 mmol), DMSO/H₂O (9/1, 500 μ L), and **2b** (37.7 mg, 0.075 mmol) were added. The vial was sealed with Teflon tape, placed in EvoluChem photoreactor (PhotoRedOx Duo) equipped with two 45W blue LEDs and stirred for 2 h. The reaction mixture was quenched with saturated Na₂S₂O₃ aq (81 μ L) and saturated NaHCO₃ aq (227 μ L) at 0 °C. The residue was purified by reverse phase column chromatography on Sfär C18 D –Duo 100 Å 30 μ m 30 g (100:0–5:95, H₂O/MeCN) and decanted with H₂O (ca. 1 mL $\times$ 2) to give **7bb** (only α , 11.1 mg, 36.4 μ mol, 73%) as an off white solid.

UC reactor (50 °C)

A screw-top 4 mL vial was charged with a stirring bar, lepidine **6b** (7.2 mg, 0.05 mmol), and TFA (8.6 mg, 0.075 mmol) in MeOH (500 μ L) under ambient atmosphere and stirred for 30 min. After volatiles were removed under reduced pressure, K₂S₂O₈ (27.0 mg, 0.1 mmol), DMSO/H₂O (9/1, 500 μ L), and **2b** (37.7 mg, 0.075 mmol) were added. The vial was sealed with Teflon tape, placed in UC reactor equipped with a 45W blue LED to keep temperature 50 °C and stirred for 2 h. The reaction mixture was quenched with saturated Na₂S₂O₃ aq (81 μ L) and saturated NaHCO₃ aq (227 μ L) at 0 °C. The residue was purified by reverse phase column chromatography on Sfär C18 D –Duo 100 Å 30 μ m 30 g (100:0–5:95, H₂O/MeCN) to give **7bb** (only α , 14.9 mg, 49.0 μ mol, 98%) as an off white solid. The structure of **7bb** was confirmed by X-ray diffraction analysis. **Rf** = 0.30 (7:3, H₂O/MeCN) **M.p.** 168–173 °C [α]_D²⁶ +33.1 (c = 0.1, MeOH) **IR** (neat) 3357, 2917, 1602, 1560, 1508, 1448, 1412, 1100, 1072, 1030 cm⁻¹. ¹H NMR (400 MHz, CD₃OD) δ 8.11 (dd, J = 8.4, 0.8 Hz, 1H), 7.97 (m, 1H), 7.75 (ddd, J = 8.4, 6.8, 1.2 Hz, 1H), 7.68 (s, 1H), 7.63 (ddd, J = 8.4, 6.8, 1.2 Hz, 1H), 5.26 (d, J = 5.2 Hz, 1H, **anomeric H**), 3.94–3.83 (m, 3H), 3.71 (m, 1H), 3.39–3.33 (m, 2H), 3.39–3.33 (d, J = 0.8 Hz, 3H). ¹³C NMR (100.6 MHz, CD₃OD) δ 162.1, 147.9, 147.0, 130.9, 129.8, 128.6, 128.0, 125.1, 122.1, 77.8, 75.9, 75.8, 75.7, 72.4, 63.2, 18.9. **HRMS–ESI** (m/z): [M+Na]⁺ calcd for C₁₆H₁₉NO₅Na⁺, 328.1155; found, 328.1137.

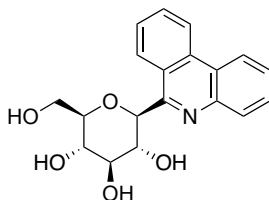
(2*S*,3*R*,4*R*,5*S*,6*R*)-2-(5-((1,4-Diazepan-1-yl)sulfonyl)isoquinolin-1-yl)-6-

(hydroxymethyl)tetrahydro-2H-pyran-3,4,5-triol (7bc)



A screw-top 4 mL vial was charged with a stirring bar, Fasudil **6c** (14.6 mg, 0.05 mmol) in MeOH (250 μ L), and TFA (17.1 mg, 0.15 mmol) in MeOH (750 μ L) under ambient atmosphere and stirred for 30 min. After volatiles were removed under reduced pressure, $K_2S_2O_8$ (27.0 mg, 0.1 mmol), DMSO/H₂O (9/1, 500 μ L), and **2b** (37.7 mg, 0.075 mmol) were added. The vial was sealed with Teflon tape, placed in UC reactor equipped with a 45W blue LED to keep temperature 50 °C and stirred for 2 h. The reaction mixture was quenched with saturated $Na_2S_2O_3$ aq (81 μ L) and saturated $NaHCO_3$ aq (227 μ L) at 0 °C. The residue was purified by reverse phase column chromatography on Sfar C18 D–Duo 100 Å 30 μ m 30 g (100:0–5:95, 0.1% TFA in H₂O/0.1% TFA in MeCN) to give **7bc** (α : β = 2:1, 10.8 mg, 23.8 μ mol, 48%) as brown oil. **Rf** = 0.42 (7:3, 0.1% TFA in H₂O / 0.1% TFA in MeCN) [α]_D²⁶ +60.2 (c = 0.2, MeOH) **IR** (neat) 3368, 1636, 1607, 1586, 1558, 1491, 1436, 1373, 1301, 1192 cm^{-1} . **¹H NMR** (400 MHz, CD₃OD) δ 8.92 (m, 1H), 8.79–8.72 (m, 0.67 $\times$ 2H), 8.66 (d, J = 6.4 Hz, 0.33 $\times$ 2H), 8.55–8.53 (m, 1H), 7.99–7.94 (m, 1H), 6.11 (d, J = 4.0 Hz, 0.67 $\times$ 1H, **anomeric H**, major), 5.47 (m, 0.33 $\times$ 1H, **anomeric H**, minor), 4.32 (t, J = 6.8 Hz, 0.67 $\times$ 1H), 4.04 (dd, J = 6.8, 4.4 Hz, 0.67 $\times$ 1H), 3.94–3.85 (m, 0.67 $\times$ 1H + 0.33 $\times$ 2H), 3.78–3.76 (m, 0.67 $\times$ 1H + 0.33 $\times$ 5H), 3.73 (m, 0.67 $\times$ 1H), 3.70–3.66 (m, 0.67 $\times$ 2H + 0.33 $\times$ 1H), 3.64–3.58 (m, 0.67 $\times$ 4H + 0.33 $\times$ 3H), 3.41 (m, 4H), 2.21–2.15 (m, 2H). (Peaks for two diastereomers were given.) **¹³C NMR** (100.6 MHz, CD₃OD) δ 160.5, 159.9, 140.0, 139.6, 139.1, 136.4, 136.3, 136.0, 135.9, 135.8, 134.8, 137.4, 133.2, 129.6, 129.0, 128.7, 128.6, 120.8, 120.6, 82.4, 79.4, 79.3, 78.6, 75.8, 74.7, 74.1, 73.0, 71.4, 70.8, 62.2, 61.9, 48.0, 46.1, 45.5, 27.4 (only observed peaks). **¹⁹F NMR** (376.4 MHz, CD₃OD) δ –77.2. **HRMS–ESI** (m/z): [$M+H$]⁺ calcd for C₂₀H₂₈N₃O₇S⁺, 454.1642; found, 454.1648.

(2R,3S,4R,5R,6S)-2-(Hydroxymethyl)-6-(phenanthridin-6-yl)tetrahydro-2H-pyran-3,4,5-triol (7bd)

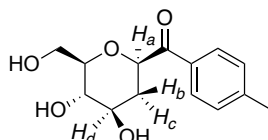


A screw-top 4 mL vial was charged with a stirring bar, phenanthridine **6d** (9.0 mg, 0.05 mmol) in MeOH (625 μ L), and TFA (8.6 mg, 0.075 mmol) in MeOH (375 μ L) under ambient atmosphere and stirred for 30 min. After volatiles were removed under reduced pressure, $K_2S_2O_8$ (27.0 mg, 0.1 mmol), DMSO/H₂O (9/1, 500 μ L), and **2b** (37.7 mg, 0.075 mmol) were added. The vial was sealed with Teflon tape, placed in UC reactor equipped with a 45W blue LED to keep temperature 50 °C and stirred for 2 h. The reaction mixture was quenched with saturated $Na_2S_2O_3$ aq (81 μ L) and saturated $NaHCO_3$ aq

(227 μL) at 0 $^{\circ}\text{C}$. The residue was purified by reverse phase column chromatography on Sfar C18 D –Duo 100 Å 30 μm 30 g (100:0–5:95, $\text{H}_2\text{O}/\text{MeCN}$) to give **7bd** (only β , 6.0 mg, 17.6 μmol , 35%) as pale yellow oil. **Rf** = 0.27 (7:3, $\text{H}_2\text{O}/\text{MeCN}$) [α]_D²⁶ –4.5 (c = 0.1, MeOH) **IR** (neat) 3355, 2077, 2923, 2867, 2360, 2346, 1087, 1063, 1018, 760 cm^{-1} . **¹H NMR** (400 MHz, CD_3OD) δ 8.81 (d, J = 8.0 Hz, 1H), 8.73 (dd, J = 8.0, 1.6 Hz, 1H), 8.57 (d, J = 8.0 Hz, 1H), 8.18 (m, 1H), 7.93 (ddd, J = 8.0, 7.2, 1.2 Hz, 1H), 7.79–7.71 (m, 3H), 5.23 (d, J = 9.2 Hz, 1H, **anomeric H**), 4.21 (t, J = 9.2 Hz, 1H), 3.93 (dd, J = 12.4, 2.0 Hz, 1H), 3.76 (m, 1H), 3.74 (t, J = 9.2 Hz, 1H), 3.69–3.59 (m, 2H). **¹³C NMR** (100.6 MHz, CD_3OD) δ 159.1, 144.2, 134.6, 132.2, 130.5, 129.9, 128.7, 128.6, 128.3, 126.8, 125.6, 123.4, 82.7, 80.2, 79.6, 74.6, 71.5, 62.9 (only observed peaks). **HRMS–ESI** (m/z): [$\text{M}+\text{Na}$]⁺ calcd for $\text{C}_{19}\text{H}_{19}\text{NO}_5\text{Na}^+$, 364.1155; found, 364.1180.

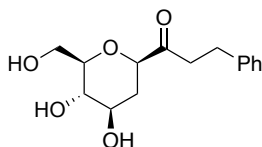
■ Procedure for Acylation ■

((2*R*,4*R*,5*S*,6*R*)-4,5-Dihydroxy-6-(hydroxymethyl)tetrahydro-2*H*-pyran-2-yl)(*p*-tolyl)methanone (9aa**)**



A screw-top 20 mL vial was charged with a stirring bar, PDP-borate **2a** (36.5 mg, 0.075 mmol) and **8a** (18.2 mg, 0.05 mmol) under ambient atmosphere. The vial was brought to a glovebox, and dry 1,2-dichloroethane (DCE, 17 mL) and TFA (11.4 mg, 0.1 mmol) in DCE (1 mL) were added. After the vial was removed from the glovebox and sealed with Teflon tape, the vial was placed in EvoluChem photoreactor (PhotoRedOx Duo) equipped with two 45W blue LEDs and stirred for 2 h. After volatiles were removed under reduced pressure, MeOH (1 mL) and TFA (22.8 mg, 0.2 mmol) in dry DCE (2 mL) were added and stirred for 20 min. The crude material was concentrated under reduced pressure and MeOH (4 mL) and DBU (75 μL , 0.5 mmol) were added. The resulting solution was stirred for 2 h and AcOH (57 μL , 1.0 mmol) was added. After stirring for 1 min, the reaction mixture was concentrated under reduced pressure. The residue was purified by reverse phase column chromatography on Sfar C18 D –Duo 100 Å 30 μm 30 g (100:0–60:40, $\text{H}_2\text{O}/\text{MeCN}$) and decanted with MeOH (ca. 500 $\mu\text{L} \times 2$) at –78 $^{\circ}\text{C}$ to room temperature to give **9aa** (5.5 mg, 20.7 μmol , 41%) as a white solid. The structure of **9aa** was confirmed by X-ray diffraction analysis. **Rf** = 0.25 (7:3, $\text{H}_2\text{O}/\text{MeCN}$) [α]_D²⁶ +22.0 (c = 0.1, MeOH) **IR** (neat) 3324, 2360, 2343, 1685, 1560, 1508, 1255, 1096, 1067, 1057 cm^{-1} . **¹H NMR** (400 MHz, CD_3OD) δ 7.93 (d, J = 8.0 Hz, 2H), 7.34 (d, J = 8.0 Hz, 2H), 5.05 (dd, J = 12.0, 2.0 Hz, 1H, H_a , **anomeric H**), 3.89 (dd, J = 12.0, 2.4 Hz, 1H), 3.78 (ddd, J = 12.0, 8.8, 4.8 Hz, 1H, H_d), 3.74 (dd, J = 12.4, 5.2 Hz, 1H), 3.41 (ddd, J = 9.6, 5.2, 2.4 Hz, 1H), 3.28 (m, 1H), 2.42 (s, 3H), 2.22 (ddd, J = 12.8, 4.8, 2.0 Hz, 1H, H_c), 1.52 (dt, J = 12.8, 12.0 Hz, 1H, H_b). **¹³C NMR** (100.6 MHz, CD_3OD) δ 198.9, 146.3, 133.3, 130.5, 130.1, 82.1, 78.1, 73.6, 72.7, 62.8, 38.0, 21.7. **HRMS–ESI** (m/z): [$\text{M}+\text{Na}$]⁺ calcd for $\text{C}_{14}\text{H}_{18}\text{O}_5\text{Na}^+$, 289.1046; found, 289.1057.

1-((2*R*,4*R*,5*S*,6*R*)-4,5-Dihydroxy-6-(hydroxymethyl)tetrahydro-2*H*-pyran-2-yl)-3-phenylpropan-1-one (9ab**)**



A screw-top 20 mL vial was charged with a stirring bar, PDP-borate **2a** (36.5 mg, 0.075 mmol) and **8b** (18.9 mg, 0.05 mmol) under ambient atmosphere. The vial was brought to a glovebox, and 1,2-dichloroethane (DCE, 17 mL) and TFA (11.4 mg, 0.1 mmol) in DCE (1 mL) were added. After the vial was removed from the glovebox and sealed with Teflon tape, the vial was placed in EvoluChem photoreactor (PhotoRedOx Duo) equipped with two 45W blue LEDs and stirred for 2 h. After volatiles were removed under reduced pressure, MeOH (1 mL) and TFA (22.8 mg, 0.2 mmol) in DCE (2 mL) were added and stirred for 20 min. The crude material was concentrated under reduced pressure and MeOH (4 mL) and DBU (75 μ L, 0.5 mmol) were added. The resulting solution was stirred for 2 h and AcOH (57 μ L, 1.0 mmol) was added. After stirring for 1 min, the reaction mixture was concentrated under reduced pressure. The residue was purified by reverse phase column chromatography on Sfar C18 D –Duo 100 Å 30 μ m 30 g (100:0–60:40, H₂O/MeCN) and passed through a short pad of silica gel with THF to give **9ab** (8.3 mg, 29.6 μ mol, 59%) as a colorless oil. The anomeric position of **9ab** was easily deuterated in CD₃OD. The ratio of the non-deuterated compound of **9ab** and the deuterated compound of **9ab** was 1:1 analyzed by ¹H NMR. All data of **9ab** was measured using the mixture of the non-deuterated **9ab** and the deuterated **9ab**. **Rf** = 0.30 (7:3, H₂O/MeCN) [α]_D²⁴ +18.6 (*c* = 0.1, MeOH) **IR** (neat) 3362, 2344, 1718, 1701, 1685, 1653, 1560, 1541, 1507, 1064 cm⁻¹. **¹H NMR** (400 MHz, CD₃OD) δ 7.26–7.13 (m, 5H), 3.99 (dd, *J* = 12.0, 2.4 Hz, 0.5 $\times$ 1H, **anomeric H**), 3.87 (dd, *J* = 12.0, 2.4 Hz, 1H), 3.69 (dd, *J* = 12.0, 5.6 Hz, 1H), 3.59 (ddd, *J* = 11.2, 8.4, 5.2 Hz, 1H), 3.23 (ddd, *J* = 9.6, 5.6, 2.4 Hz, 1H), 3.18–2.96 (3H), 2.88–2.84 (m, 2H), 2.17 (m, 1H), 1.32 (m, 1H). **¹³C NMR** (100.6 MHz, CD₃OD) δ 210.70, 210.65, 142.6, 129.45, 129.40, 127.0, 81.95, 81.90, 81.5, 73.6, 72.8, 63.0, 40.8, 36.7, 36.6, 30.1 (only observed peaks). **HRMS–ESI** (*m/z*): [M+Na]⁺ calcd for C₁₅H₂₀O₅Na⁺, 303.1203; found, 303.1199. **HRMS–ESI** (*m/z*): [M+Na]⁺ (deuterated **9ab**) calcd for C₁₅H₁₉DO₅Na⁺, 304.1266; found, 304.1258.

■ X-ray Diffraction Analysis ■

A suitable crystal obtained by recrystallization was mounted with mineral oil on a Cargille Immersion Oil Type B and transferred to Bruker Single Crystal CCD X-ray Diffractometer (SMART APEX II) (Graphite-monochromated Mo K α radiation (λ = 0.71073 Å)). Cell parameters were determined and refined, and raw frame data were integrated using APEX 3 (Bruker) and a multi-scan absorption correction using an empirical method was applied. The structures were solved by direct methods with SHELXT and refined by full-matrix least-squares techniques against *F*² (SHELXL-2018/3) by using Yadokari-XG software package. Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre.

Molecular structure of 2a (CCDC 2353960)

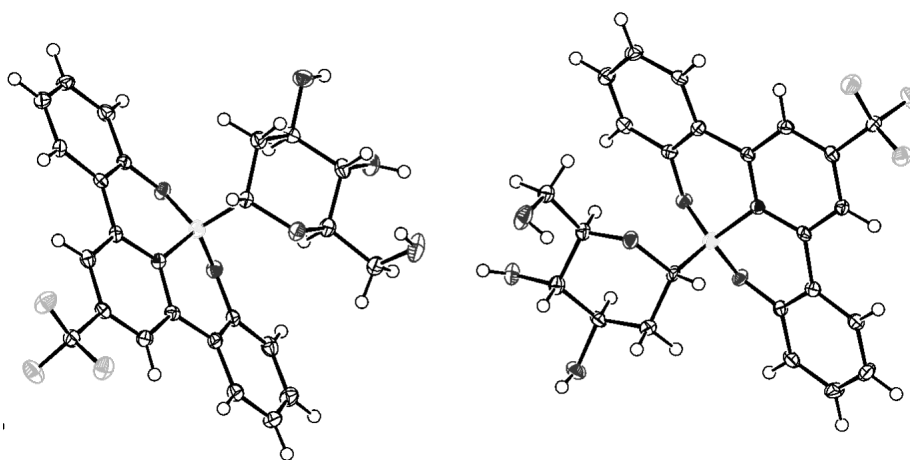


Figure S3-5. ORTEP diagram of **2a**. Ellipsoids are drawn at 50% probability. A single crystal used for the analysis was obtained by recrystallization from CH₂Cl₂/MeOH (9:1).

	2a
CCDC No.	2353960
formula	C ₂₄ H ₂₁ BF ₃ NO ₆
fw	487.23
<i>T</i> (K)	87(2)
λ (Å)	0.71073
cryst syst	orthorhombic
space group	P 2 ₁ 2 ₁ 2 ₁
<i>a</i> (Å)	5.099 (2)
<i>b</i> (Å)	24.054 (5)
<i>c</i> (Å)	33.257 (7)
α (deg)	90
β (deg)	90
γ (deg)	90
<i>V</i> (Å ³)	4079 (2)
<i>Z</i>	8
<i>D</i> _{calc} (g·cm ⁻³)	1.587
μ (mm ⁻¹)	0.130
<i>F</i> (000)	2016
cryst size (mm ³)	0.04 × 0.144 × 0.186
2 θ range (deg)	2.50 to 24.83
reflns collected	19621
params	637
GOF on <i>F</i> ²	1.024
<i>R</i> ₁ , <i>wR</i> ₂ (all data)	0.0362, 0.0787

Table S3-1. Crystallographic data and structure refinement details of **2a**.

Molecular structure of 10 (CCDC 2353968)

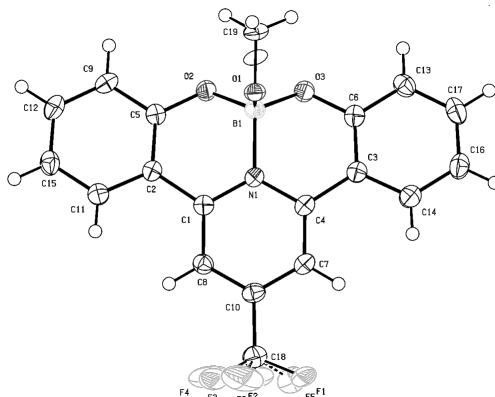


Figure S3-6. ORTEP diagram of **10**. Ellipsoids are drawn at 50% probability. A single crystal used for the analysis was obtained by recrystallization from hexane and CDCl_3 .

	10
CCDC No.	2353968
formula	$\text{C}_{19}\text{H}_{13}\text{BF}_3\text{NO}_3$
fw	371.11
T (K)	87 (2)
λ (Å)	0.71073
cryst syst	monoclinic
space group	$P2_1/c$
a (Å)	10.9367 (13)
b (Å)	18.470 (2)
c (Å)	7.9045 (9)
α (deg)	90
β (deg)	98.987 (2)
γ (deg)	90
V (Å ³)	1577.1 (3)
Z	4
D_{calc} (g·cm ⁻³)	1.563
μ (mm ⁻¹)	0.128
$F(000)$	760
cryst size (mm ³)	$0.068 \times 0.149 \times 0.233$
2θ range (deg)	2.83 to 25.03
reflns collected	7609
params	280
GOF on F^2	1.029
R_1, wR_2 (all data)	0.0376, 0.0992

Table S3-2. Crystallographic data and structure refinement details of **10**.

Molecular structure of 7bb (CCDC 2353969)

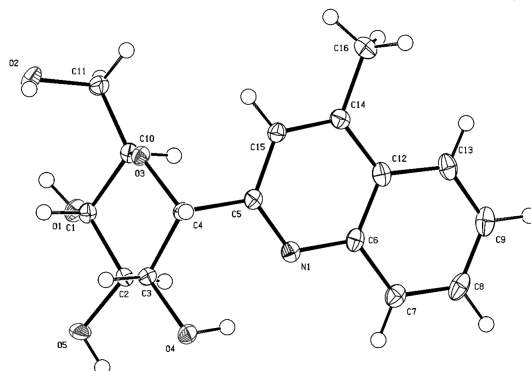


Figure S3-7. ORTEP diagram of **7bb**. Ellipsoids are drawn at 50% probability. A single crystal used for the analysis was obtained by recrystallization from MeOH.

	7bb
CCDC No.	2353969
formula	C ₁₆ H ₁₉ NO ₅
fw	305.32
<i>T</i> (K)	87 (2)
λ (Å)	0.71073
cryst syst	orthorhombic
space group	P2 ₁ 2 ₁ 2 ₁
<i>a</i> (Å)	5.216 (3)
<i>b</i> (Å)	13.319 (8)
<i>c</i> (Å)	20.795 (12)
α (deg)	90
β (deg)	90
γ (deg)	90
<i>V</i> (Å ³)	1444.7 (14)
<i>Z</i>	4
<i>D</i> _{calc} (g·cm ⁻³)	1.390
μ (mm ⁻¹)	0.104
<i>F</i> (000)	636
cryst size (mm ³)	0.06 × 0.09 × 0.18
2 θ range (deg)	2.49 to 24.73
reflns collected	14104
params	206
GOF on <i>F</i> ²	1.023
<i>R</i> ₁ , <i>wR</i> ₂ (all data)	0.0290, 0.0641

Table S3-3. Crystallographic data and structure refinement details of **7bb**.

Molecular structure of 9aa (CCDC 2353967)

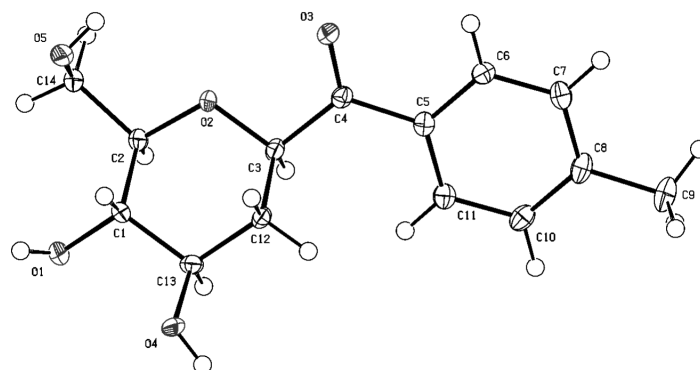


Figure S3-8. ORTEP diagram of **9aa**. Ellipsoids are drawn at 50% probability. A single crystal used for the analysis was obtained by recrystallization from EtOAc and MeOH.

	9aa
CCDC No.	2353967
formula	C ₁₄ H ₁₈ O ₅
fw	266.28
<i>T</i> (K)	87 (2)
λ (Å)	0.71073
cryst syst	monoclinic
space group	C2
<i>a</i> (Å)	15.778 (12)
<i>b</i> (Å)	6.366 (5)
<i>c</i> (Å)	14.449 (11)
α (deg)	90
β (deg)	115.544 (9)
γ (deg)	90
<i>V</i> (Å ³)	1309.5 (17)
<i>Z</i>	4
<i>D</i> _{calc} (g·cm ⁻³)	1.351
μ (mm ⁻¹)	0.102
<i>F</i> (000)	568
cryst size (mm ³)	0.05 × 0.09 × 0.25
2 θ range (deg)	2.61 to 25.04
reflns collected	3088
params	178
GOF on <i>F</i> ²	1.080
<i>R</i> ₁ , <i>wR</i> ₂ (all data)	0.0301, 0.0706

Table S3-4. Crystallographic data and structure refinement details of **9aa**.

第三章 実験項 参考文献

1. Nakamura, R.; Sumida, Y.; Ohmiya, H. *Bull. Chem. Soc. Jpn.* **2022**, *95*, 1001–1005.
2. Zhang, H.; Huo, C.; Ye, K.; Zhang, P.; Tian, W.; Wang, Y. *Inorg. Chem.* **2006**, *45*, 2788–2794.
3. Miller, E. M.; Walczak, M. A. *Org. Lett.* **2021**, *23*, 4289–4293.
4. Nakamura, R.; Yamazaki, T.; Kondo, Y.; Tsukada, M.; Miyamoto, Y.; Arakawa, N.; Sumida, Y.; Kiya, T.; Arai, S.; Ohmiya, H. *J. Am. Chem. Soc.* **2023**, *145*, 10651–10658.
5. Zhu, J. L.; Schull, C. R.; Tam, A. T.; Rentería-Gómez, Á.; Gogoi, A. R.; Gutierrez, O.; Scheidt, K. A. *J. Am. Chem. Soc.* **2023**, *145*, 1535–1541.
6. Rodríguez, R. I.; Mollari, L.; Alemán, J. *Angew. Chem. Int. Ed.* **2021**, *60*, 4555–4560.
7. Muramatsu, W.; Hattori, T.; Yamamoto, H. *J. Am. Chem. Soc.* **2019**, *141*, 12288–12295.
8. Wang, Q.; Lee, B. C.; Tan, T. J.; Jiang, Y.; Ser, W. H.; Koh, M. J. *Nat. Synth.* **2022**, *1*, 967–974.
9. Miura, T.; Yoritake, M.; Hirai, G. *Chem. Commun.* **2023**, *59*, 8564–8567

第四章 深赤色から近赤外光による azadipyrromethene (ADP) 型ホウ素アート錯体の直接光励起を利用した触媒的炭素ラジカル生成

第一節 着想背景および作業仮説

光を活用した分子変換反応は、穏和な条件下でのラジカル反応を可能にする強力な手法であるが、第三章まで述べたように、その多くは青色光 (390–500 nm) のような比較的高いエネルギーを持つ光に依存している。¹ 高エネルギー光の利用は、基質や生成物の予期せぬ分解や副反応を誘発する懸念があるため、より低エネルギー (<47 kcal/mol) である深赤色から近赤外 (DR to NIR、>600 nm) 領域の光を利用する反応の開発が求められている。² DR から NIR 光は、生体透過性が高く散乱が少ないため、大規模合成や生命化学分野への応用にも適している。³ これまでに、Os(II)錯体などの遷移金属触媒や有機色素を用いた DR から NIR 光駆動型の反応系が報告されているが、その多くは外部光触媒の励起状態を経由した外圏電子移動 (outer-sphere electron transfer) やエネルギー移動に基づいている (**Figure 4-1A**)。⁴ しかし、DR から NIR の光のエネルギーは低いいため、酸化還元電位の高い基質の活性化は困難であり、適用可能な炭素ラジカル前駆体は著しく制限されていた。

この課題に対し、基質と触媒が複合体を形成することで光吸収帯が長波長シフトする「基質-触媒複合体の直接励起」戦略が、青色光領域において報告されている (**Figure 4-1B**)。⁵ しかし、この戦略を DR から NIR 領域へ拡張し、ラジカル発生へと応用した例は報告されていない。そこで著者は、有機ホウ素化合物に対し、適切なルイス塩基触媒を作用させることで、DR から NIR 光を吸収可能な光活性錯体を系中で形成させ、その直接励起によって炭素ラジカルを生成する手法を着想した。具体的には、アザジピロメテン (ADP) 骨格を有する触媒 **A1** を設計した。序論で述べた通り、2023 年 Page らは BODIPY 型のホウ素アート錯体からの炭素ラジカル生成を報告しており、その構造を参考に ADP 骨格を設計した。⁶ ADP 配位子はホウ素原子に配位することで、光を吸収しない有機ホウ素化合物が DR から NIR の光を吸収できるようになる。

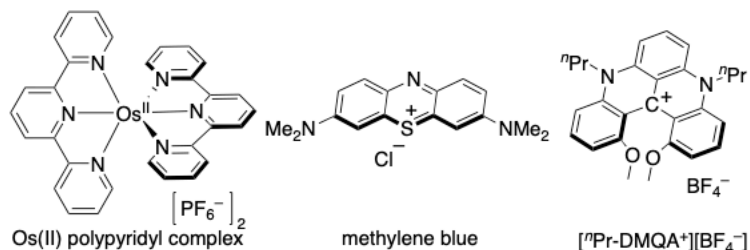
本研究の作業仮説を以下に示す (**Figure 4-1C**)。まず、ADP 触媒 **A1** が有機ホウ素化合物と脱水縮合し、四配位の有機ホウ素アート錯体 **I** を形成する。この有機ホウ素アート錯体 **I** は、DR から NIR 領域に吸収を持ち、光照射によって励起状態 **I*** となる。励起種 **I*** は、電子受容体への一電子移動 (SET) または直接的なホモリティック開裂を経て、炭素ラジカルを生成すると考えた。本手法が確立されれば、安定な有機ホウ素化合物から低エネルギー光を用いて炭素ラジカルを発生させる汎用的な手法となる。これまで困難であった近赤外光領域での炭素-炭素結合形成、炭素-ヘテロ原子結合形成反応が可能となる。

A. Reported DR to NIR light-induced photochemical activations

■ Outer-sphere electron or energy transfer



■ Reported catalysts

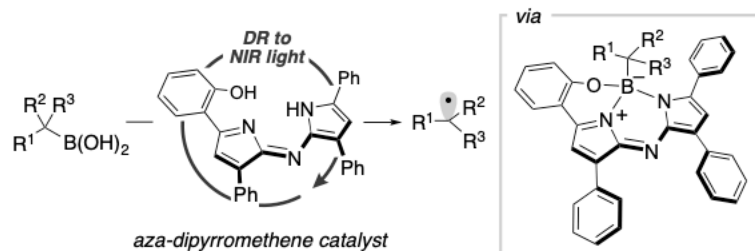


B. DR to NIR light-driven ligand-induced photochemical activation (this work)

■ Direct excitation of a substrate–catalyst complex



■ Lewis base-catalyzed radical generation strategy via direct excitation



C. Hypothesis: catalytic carbon radical generation from organoboron

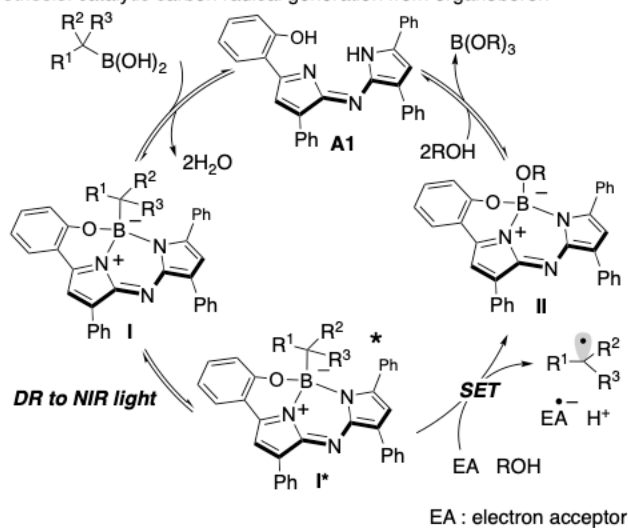


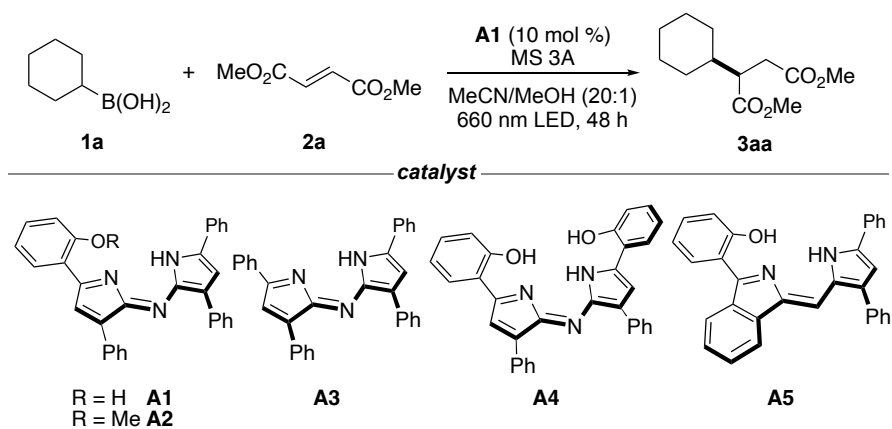
Figure 4-1. DR から NIR 光駆動による触媒的炭素ラジカル生成戦略

第二節 反応条件の最適化および基質適用範囲の検討

第一節の作業仮説に基づき、ADP 触媒を用いた有機ホウ素化合物からのラジカル発生および Giese 型ラジカル付加反応の検討を行った。モデル反応として、シクロヘキシルボロン酸 **1a** とフマル酸ジメチル **2a** を用いて反応条件の最適化を行った (Table 4-1)。フェノール性水酸基を有する ADP 触媒 **A1** (10 mol%) およびモレキュラーシーブス **3A** の存在下、アセトニトリル/メタノール混合溶媒中で 660 nm の赤色 LED を照射したところ、目的とするアルキル化体 **3aa** を 77%の収率で与えた (entry 1)。一方、ホウ素への配位部位であるフェノール性水酸基を持たない触媒 **A2** や **A3** を用いた場合、反応は全く進行しなかった (entries 2 and 3)。これは、ホウ素上での四配位ホウ素アート錯体の形成が本反応に必須であることを示唆している。2つのフェノール部位を有する触媒 **A4** を用いた場合、**3aa** の収率は 13%と低収率であった (entry 4)。また、ADP 触媒の1つの窒素原子を炭素に置換したジピロメテン型触媒 **A5** を用いた場合も、収率は 15%にとどまった (entry 5)。また、触媒や光照射を用いない条件では反応は進行しなかった (entries 6 and 7)。モレキュラーシーブス **3A** を添加しない場合、収率は大幅に低下した (entry 8)。これは、反応系内で生成する水分子を除去し、ボロン酸と触媒間の脱水縮合平衡を錯体形成側へ偏らせるために、脱水過程が必要であることを示している。より長波長な 740 nm の LED を用いた場合でも、52%の収率で目的物を得ることができた (entry 9)。

さらに、シクロヘキシルトリフルオロボレート塩 **1a'** とフマル酸ジメチル **2a** を用いて反応条件の最適化を行った (Table 4-2)。ADP 触媒 **A1** (10 mol%)、 SiO_2 およびモレキュラーシーブス **3A** の存在下、アセトニトリル/メタノール混合溶媒中で 660 nm の赤色 LED を照射したところ、目的とするアルキル化体 **3aa** を 86%の収率で与えた (entry 1)。トリフルオロボレート塩と ADP 触媒との縮合を促進するため、フッ化物イオンの捕捉剤として当量の二酸化ケイ素 (SiO_2) を添加した。フェノール性水酸基を持たない触媒 **A2** や **A3** を用いた場合、また触媒 **A1** を用いない場合、反応はほとんど進行しなかった (entries 2, 3 and 6)。2つのフェノール部位を有する触媒 **A4** を用いた場合及びジピロメテン型触媒 **A5** を用いた場合、**3aa** の収率は 58%と中程度の収率であった (entries 4 and 5)。より長波長な 740 nm の LED を用いた場合、85%の収率で目的物を得ることができた (entry 7)。

Table 4-1. アルキルボロン酸を用いる反応の条件の最適化^a

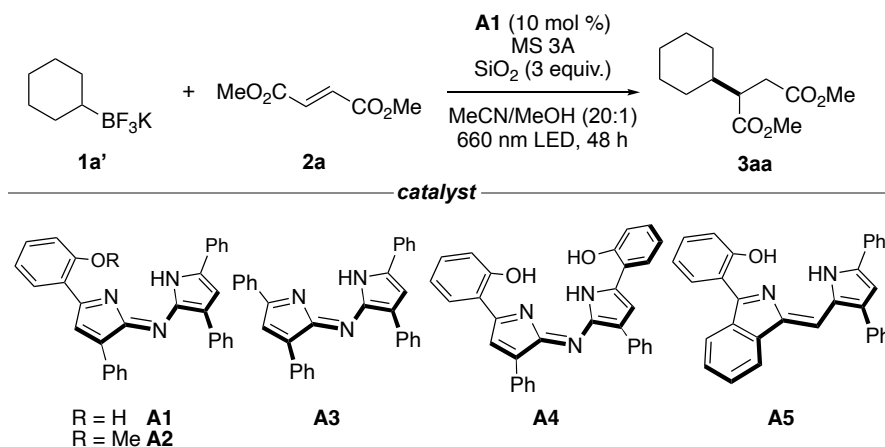


entry	change from standard conditions	yield of 3aa (%) ^{a,b}
1	none	81 (77)
2	A2 instead of A1	0
3	A3 instead of A1	0
4	A4 instead of A1	13
5	A5 instead of A1	15
6	under dark	0
7	w/o A1	0
8	w/o MS 3A	18
9	740 nm LED instead of 660 nm LED	52

^aEach reaction was carried out with **1a** (0.15 mmol), **2a** (0.10 mmol), **A1** (0.01 mmol) and MS 3A (100 mg) in MeCN/MeOH (2.0 mL/100 mL) under red LED (660 nm) irradiation for 48 h. ^b

¹H NMR yields. The number in parenthesis is isolated yield.

Table 4-2. アルキルトリフルオロボレート塩を用いる反応の条件の最適化 ^a



entry	change from standard conditions	yield of 3aa (%) ^{a,b}
1	none	86
2	A2 instead of A1	trace
3	A3 instead of A1	0
4	A4 instead of A1	58
5	A5 instead of A1	51
6	w/o A1	0
7	740 nm LED instead of 660 nm LED	85

^aEach reaction was carried out with **1a** (0.15 mmol), **2a** (0.10 mmol), **A1** (0.01 mmol), SiO₂ (0.3 mmol) and MS 3A (100 mg) in MeCN/MeOH (2.0 mL/100 mL) under red LED (660 nm) irradiation for 48 h. ^b¹H NMR yields.

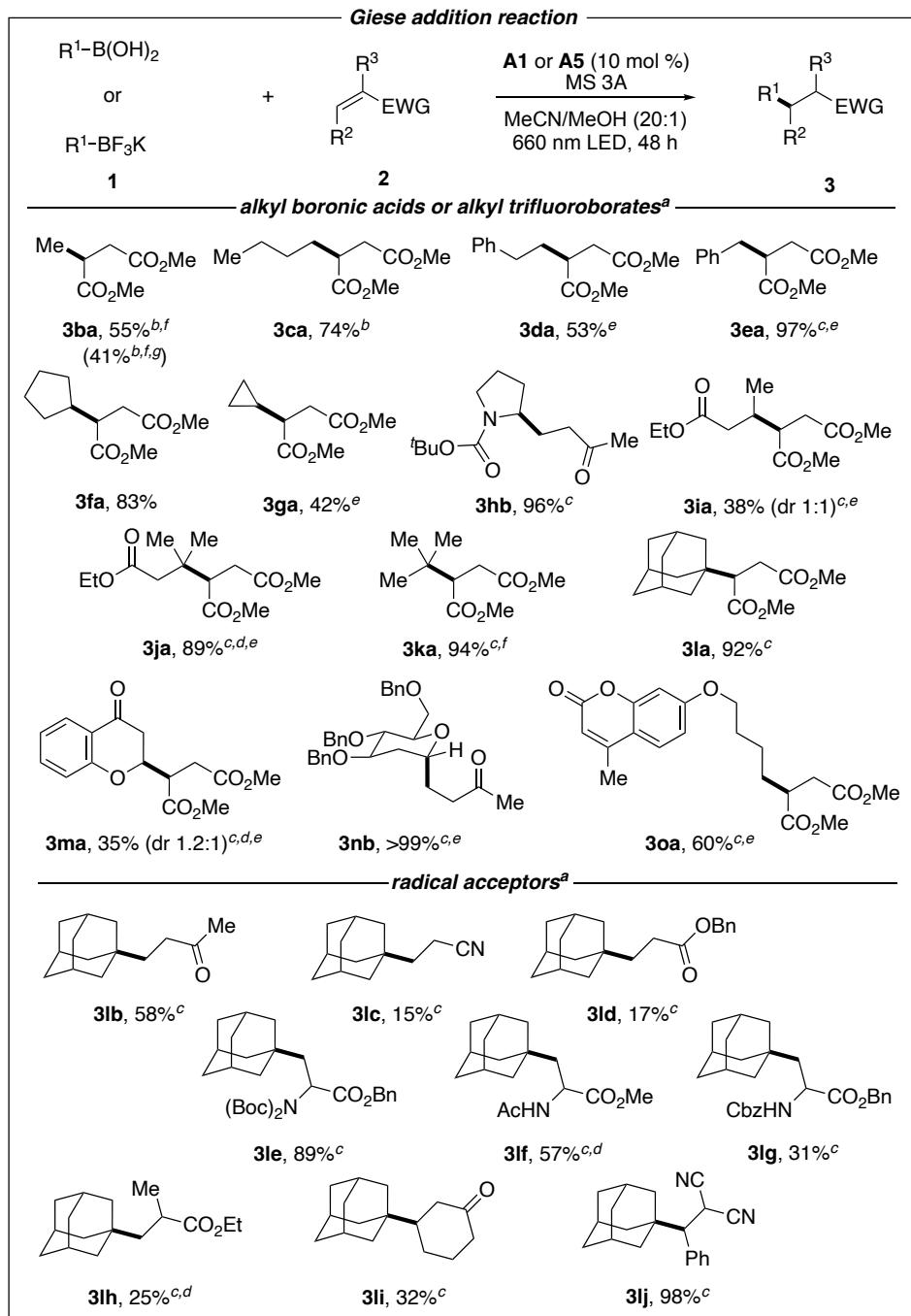
最適化された条件を用いて、有機ホウ素化合物の基質適用範囲を検討した (Table 4-3)。まず、トリメチルボロキシシン **1a** を用いたメチルラジカルの生成を試みたところ、中程度の収率で目的の付加体 **3ba** が得られた。励起光の波長を 740 nm に変更した場合でも 41%の収率が得られた。一級アルキル基を有する *n*-ブチルボロン酸 **1c** や 2-フェニルエチルボロン酸 **1d** を用いた場合、中程度の収率で対応する Giese 付加体を得られた (**3ca** and **3da**)。ベンジルトリフルオロボレート塩 **1e** を用いた場合、高収率で生成物 **3ea** が得られた。さらに、第二級アルキルホウ素化合物や、不飽和エステルヒドロホウ素化により誘導可能な二級・三級アルキルホウ素化合物、さらにはアダマンタン骨格を有する嵩高い三級アルキル基を有するホウ素化合物についても、良好な収率でラジカル生成および炭素-炭素結合形成が進行した (**3fa-3la**)。α-オキシ炭素ラジカル前駆体や糖誘導体といった複雑な構造を有するホウ素化合物を用いても反応が進行した (**3ma** and **3nb**)。青色光を吸収するクマリン骨格を有する基質においても、中程度の収

率で反応が進行した (**30a**)。

次に、ラジカル受容体となるアルケンの基質適用範囲について検討した。メチルビニルケトン **2b** のような電子不足アルケンを用いた場合は中程度の収率でラジカル付加体が得られた (**31b**)。一方で、アクリル酸エステルやアクリロニトリルを用いた場合、収率は低下した (**31c and 31d**)。これは、生成するラジカル付加体の中間体の還元電位が、励起状態にあるハウ素アート錯体の還元電位と比較して高いためであると考えられる。デヒドロアラニン誘導体や環状アルケンなどに対しては、中程度から良好な収率で付加体が得られた (**31e-31j**)。

本手法の有用性をさらに拡張するため、Giese 型付加反応以外の結合形成反応への展開を試みた (**Figure 4-2**)。チオスルホン酸エステル **4** や TEMPO **6** をラジカル捕捉剤として用いることで、C-S 結合および C-O 結合形成反応が進行した (**5, 7b and 7e**)。また、アシルアゾリウム **8** との反応では、ラジカル-ラジカルカップリングを経てケトン **9** を低収率ではあるが合成できた。さらに、アルケニルスルホン **10a** やアルキニルスルホン **10b** を用いた C(sp³)-C(sp²)および C(sp³)-C(sp)結合形成も達成した (**11aa and 11ab**)。なお、一部の反応では触媒 **A1** ではなく触媒 **A5** を用いている。後述するように、触媒 **A5** 由来のハウ素アート錯体は、触媒 **A1** 由来のハウ素アート錯体よりも還元力が高いためである。

Table 4-3. Giese 型ラジカル付加反応の基質適用範囲



^aEach Reaction was carried out with **1** (0.15 mmol), **2** (0.10 mmol), **A1** (0.01 mmol) and MS 3A (100 mg) in MeCN/MeOH (2.0 mL/100 mL) under red LED (660 nm) irradiation for 48 h.

^bNMR yield. ^cTrifluoroborate salts (0.15 mmol) with SiO₂ (0.30 mmol) were used instead of boronic acids. ^d**A5** was used instead of **A1**. ^eReaction time was 72 h. ^f20 mol % of catalyst was used. ^g740 nm LED was used instead of 660 nm LED.

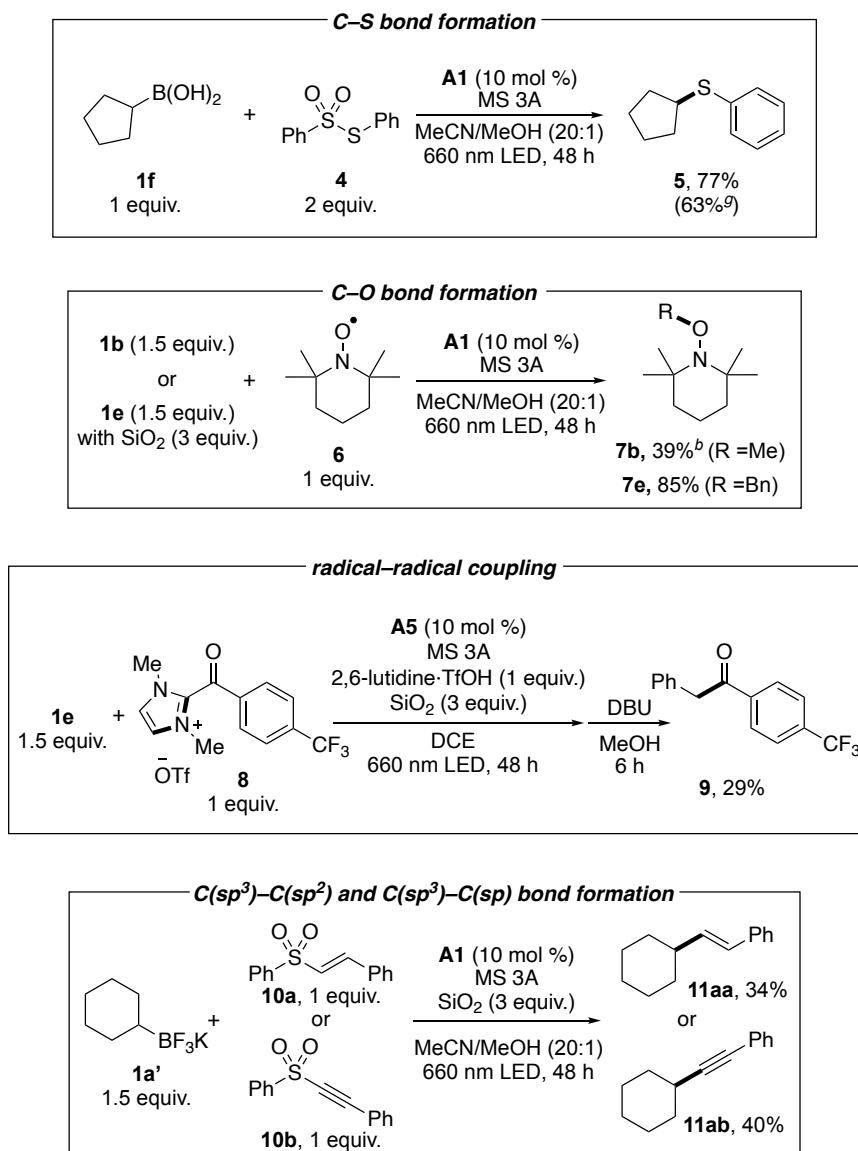


Figure. 4-2. 種々の結合形成反応

第三節 反応機構の解析

反応機構、とりわけ反応中間体に関する知見を得るため、機構解析および密度汎関数法 (DFT) 計算を実施した。まず有機ホウ素化合物とアザジピロメテン (ADP) 触媒 **A1** から生成すると考えられる反応中間体 **B1** の単離を試みた。触媒 **A1** に対し化学量論量以上のトリメチルボロキシシ **1b** を加え、酢酸エチル中、遮光条件下で反応させたところ、**B1** が定量的に得られた (Figure 4-3A)。単離した **B1** は空気下では十分な安定性を有するものの、シリカゲル精製においては不安定であった。**B1** の構造を明らかにするため、X線結晶構造解析を行った。その結果、ホウ素中心が四面体構造をとった錯体 **B1** の形成が確認された (Figure 4-3B)。

錯体 **B1**、触媒 **A1**、ジピロメテン骨格 **A5** から合成した錯体 **B3** の吸収スペクトル及び発光スペクトルを調査した (Figure 4-4, Figure 4-5 and Figure 4-6)。錯体 **B1** の吸収スペクトルは 690 nm 付近に極大波長を示し、その吸収末端は 800 nm を超える領域まで広がっていた。また、対応する蛍光スペクトルでは、720 nm 付近に極大波長が観測された。錯体 **B3** の吸収スペクトルと蛍光スペクトルは、錯体 **B1** と比較して短波長側であった。UV/vis、蛍光、およびサイクリックボルタンメトリーの結果から、錯体 **B1** と錯体 **B3** の励起状態における還元力を算出したところ、還元力は 以下のように見積もられた。⁷

ホウ素アート錯体 **B1** について、紫外可視吸収スペクトル、蛍光スペクトル、およびサイクリックボルタンメトリーから得られたデータに基づき、以下の Rehm-Weller 式を用いて光励起ボレートの酸化還元電位を近似的に算出した。なお、サイクリックボルタンメトリー (Figure 4-9) において、ボレート **B1** の電気化学的酸化過程は不可逆過程であった。したがって、酸化電位 $E(=+1.0671 \text{ V vs. SCE})$ を $E(\text{B1}^{+}/\text{B1})$ として用いた。ホウ素アート錯体 **B1** 励起状態におけるエネルギー $E_{00}(\text{B1}^{*}/\text{B1})$ は吸収スペクトル及び蛍光スペクトルの波長 (707 nm, Figure 4-7) から推定し 1.753666 eV とした。

For the excited state of **B1***

Rehm-Weller equation:

$$E(\text{B1}^{+}/\text{B1}^{*}) = E(\text{B1}^{+}/\text{B1}) - E_{00}(\text{B1}^{*}/\text{B1})$$

$$E(\text{B1}^{+}/\text{B1}^{*}) = 1.0671 - 1.753666 = -0.687 \text{ V vs SCE.}$$

さらに、ジピロメテン型のホウ素アート錯体 **B3** について、同様に励起状態における還元力を算出した。紫外可視吸収スペクトル、蛍光スペクトル、およびサイクリックボルタンメトリーから得られたデータに基づき、以下の Rehm-Weller 式を用いて光励起ボレートの酸化還元電位を近似的に算出した。なお、ホウ素アート錯体 **B3** の溶解性の問題から、サイクリックボルタンメトリーではなく DPV 解析 (Figure 4-10) を用いて酸化電位を測定した。酸化電位 $E(=+0.87265 \text{ V vs. SCE})$ を $E(\text{B3}^{+}/\text{B3})$ として用いた。ホウ素アート錯体 **B3** 励起状態におけるエネルギー $E_{00}(\text{B3}^{*}/\text{B3})$ は吸収スペクトル及び蛍光スペクトルの波長 (635 nm, Figure 4-8) から推定し 1.9525 eV とした。

For the excited state of **B3***

Rehm-Weller equation:

$$E(\text{B3}^{+}/\text{B3}^{*}) = E(\text{B3}^{+}/\text{B3}) - E_{00}(\text{B3}^{*}/\text{B3})$$

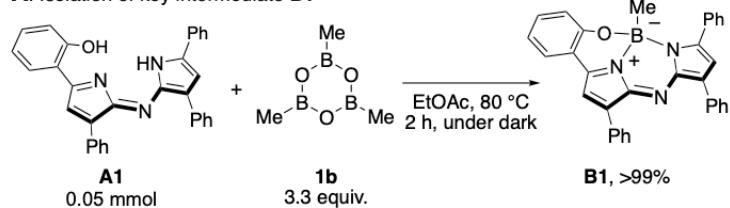
$$E(\text{B3}^{+}/\text{B3}^{*}) = 0.87265 - 1.9525 = -1.07985 \text{ V vs SCE.}$$

これらの結果から、錯体 **B3** は錯体 **B1** よりも還元力が高いことがわかり、Table 4-3 と Figure 4-2 の一部の反応では、触媒 **A1** の代わりに触媒 **A5** を用いている。

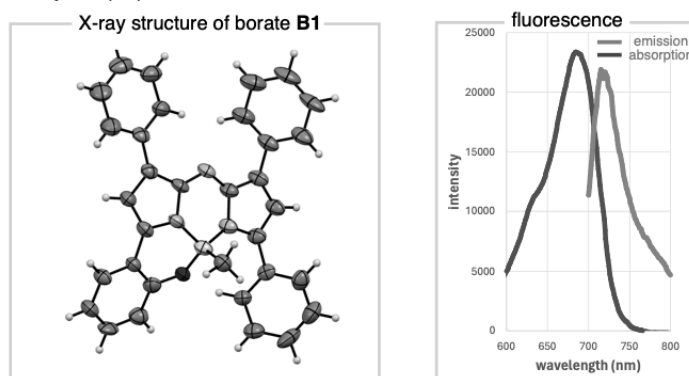
錯体 **B1** を用いて、近赤外 (NIR) 光照射下における炭素ラジカル生成が可能であるかどうかを調べた (Figure 4-3C)。740 nm LED 照射下、錯体 **B1** とフマル酸ジメチル **2a** を用いて Giese 型ラジカル付加反応を行ったところ、目的生成物 **3ba** が収率 43% で得られた。なお、メチルラジカルの生成には 740 nm の光照射が不可欠であった。また、660 nm 照射下での錯体 **B1** と TEMPO を用いたラジカル捕捉実験により、ラジカ

ルカップリング体 **7b** が得られた (Figure 4-3D)。

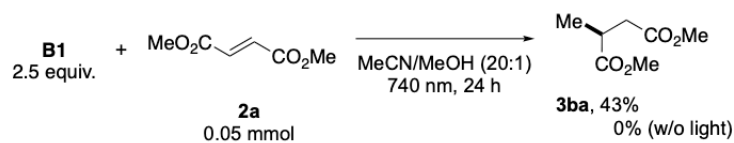
A. Isolation of key intermediate B1



B. Physical properties of B1



C. Giese addition from B1



D. Reaction with TEMPO

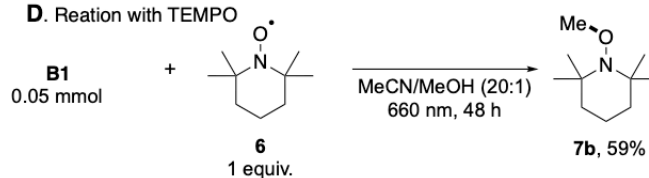


Figure 4-3. 機構実験

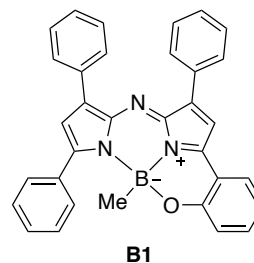
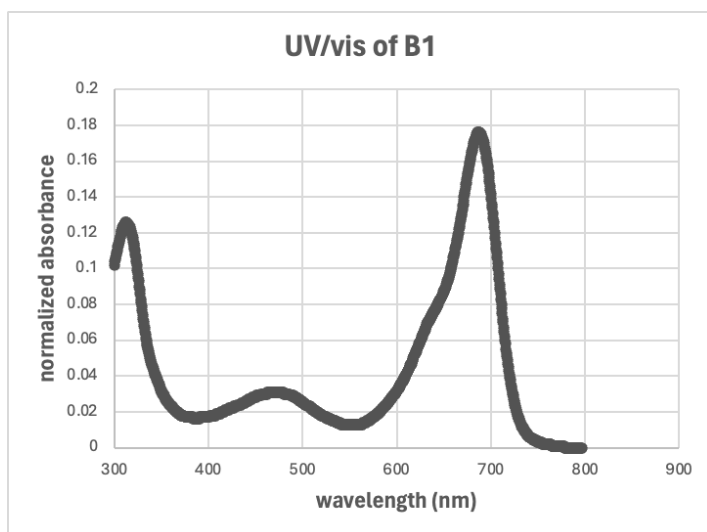


Figure 4-4. B1 の吸収スペクトル^a

^aUV-Vis spectra of **B1** was measured with 5 μ M acetonitrile solution.

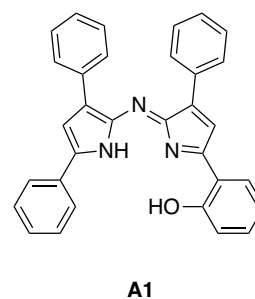
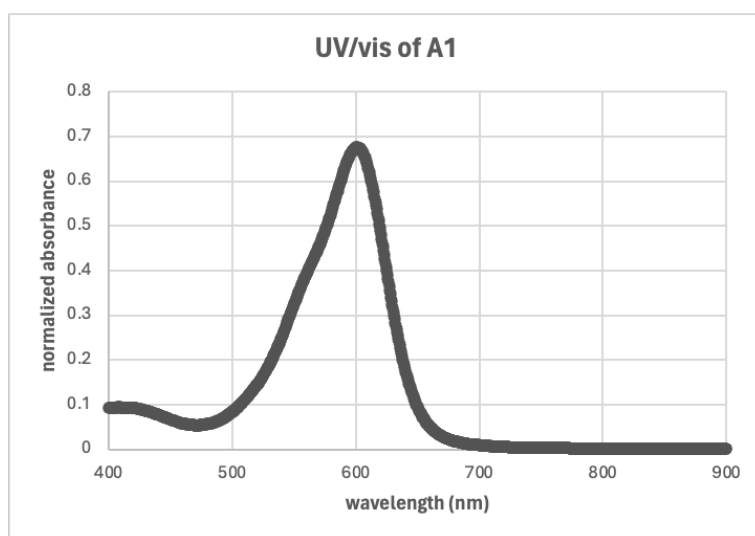


Figure 4-5. A1 の吸収スペクトル^a

^aUV-Vis spectra of **A1** was measured with 20 μ M acetonitrile solution.

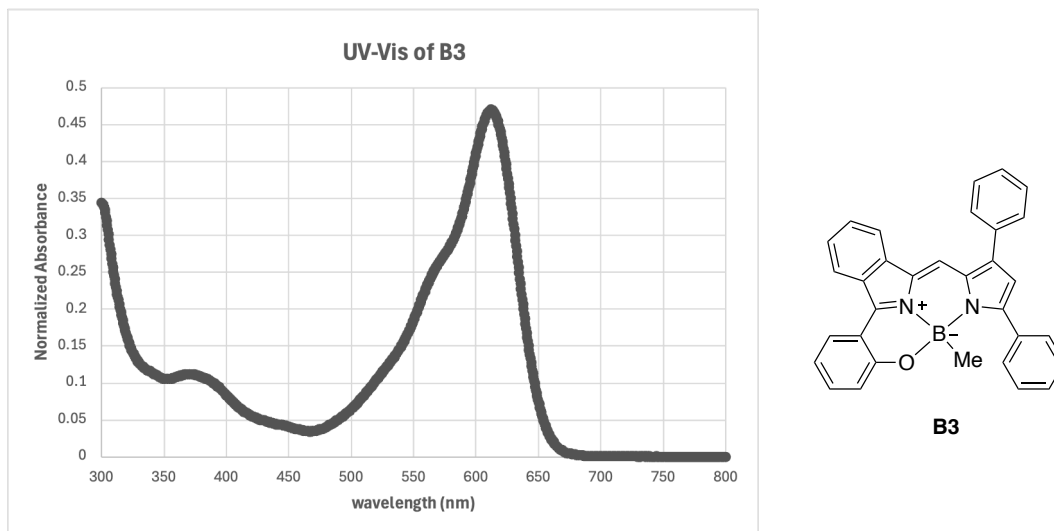


Figure 4-6. B3 の吸収スペクトル^a

^aUV-Vis spectra of **B3** was measured with 20 μ M acetonitrile solution.

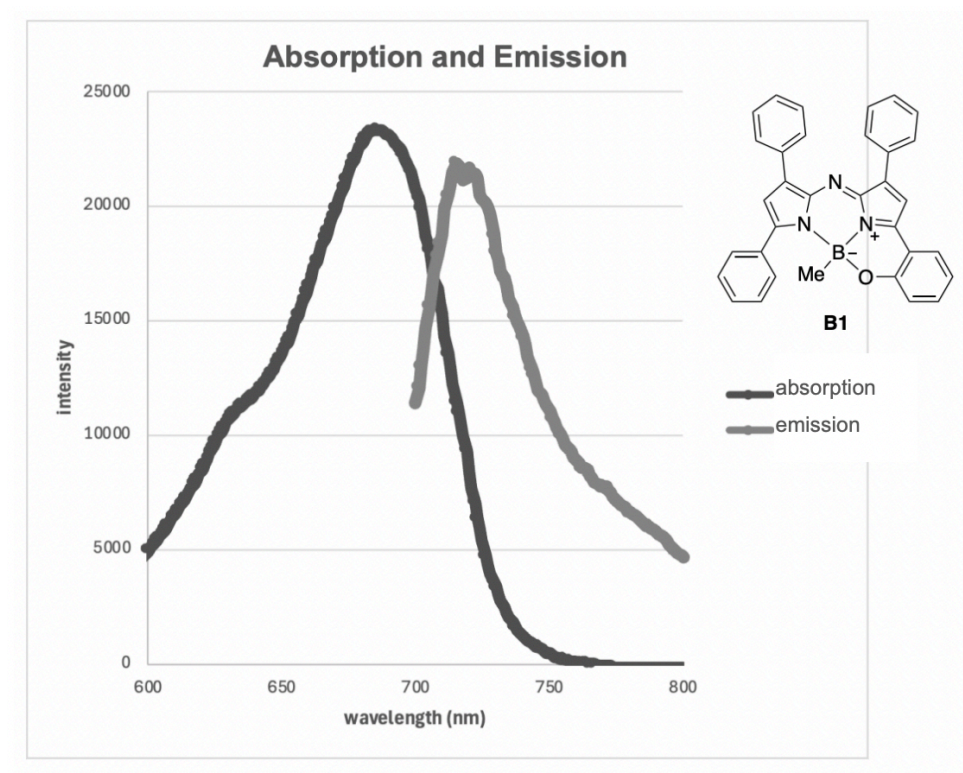


Figure 4-7. B1 の吸収スペクトル及び蛍光スペクトル^a

^aAbsorption and emission spectra of **B1** was measured with 20 μ M acetonitrile solution. The emission intensity was measured excited by each absorption maximum ($\lambda_{\text{max}} = 690$ nm).

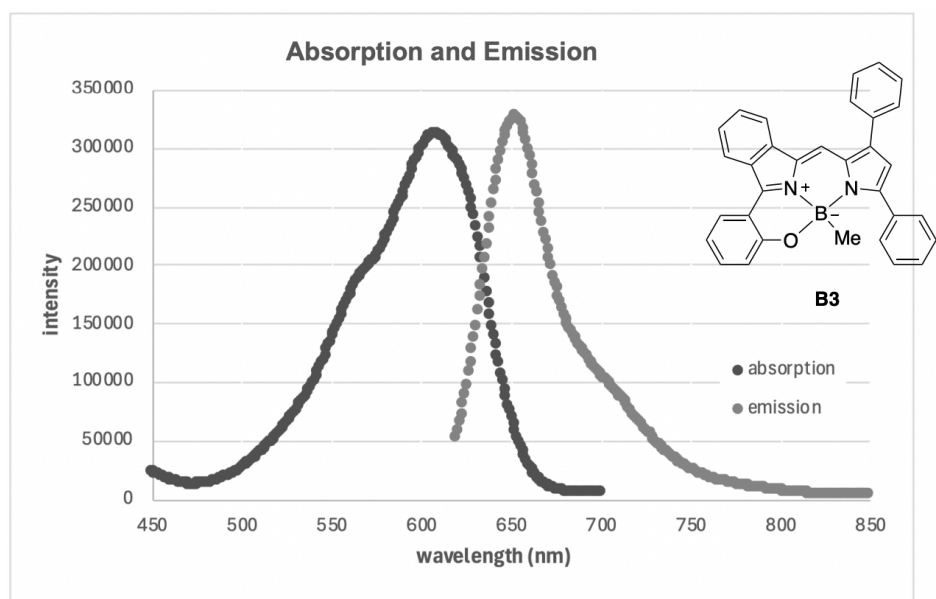
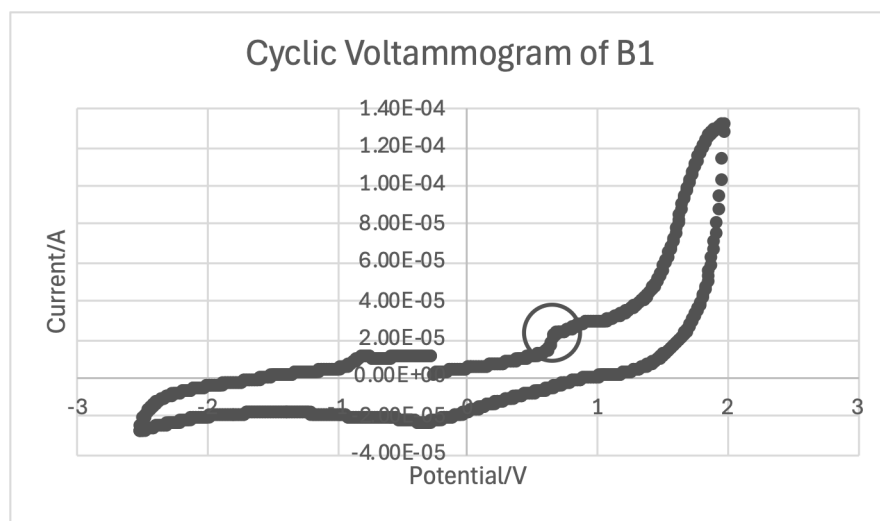


Figure 4-8. B3 の吸収スペクトル及び蛍光スペクトル^a

^a Absorption and emission spectra of **B3** was measured with 20 μM acetonitrile solution. The fluorescence intensity was measured excited by each absorption maximum ($\lambda_{\text{max}} = 610 \text{ nm}$).



B1: $E_{\text{pa}} = +0.73324 \text{ V}$ vs $\text{Ag}/\text{AgNO}_3 = +1.067 \text{ V}$ vs. SCE

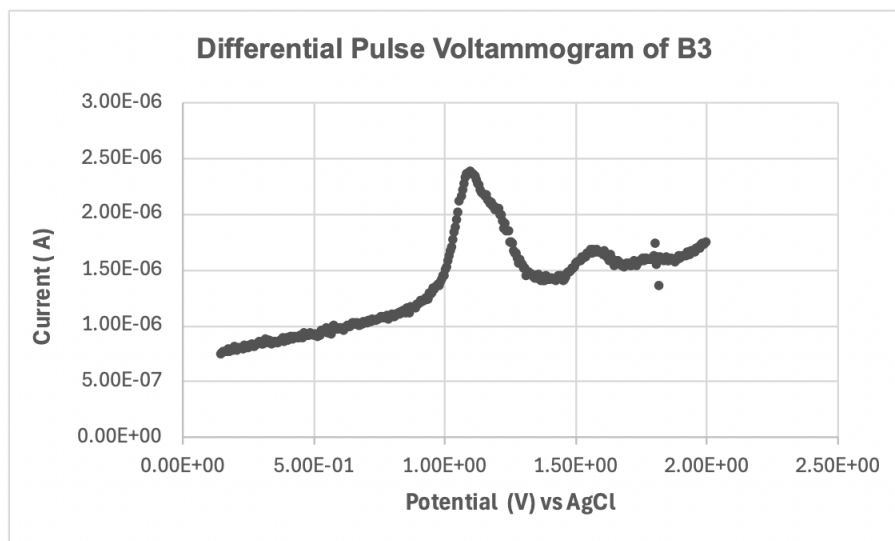
Calculated according to Fc/Fc^+ ($E_{1/2} = +0.046145 \text{ V}$ vs Ag/AgNO_3)

These peak is not reversible.

Figure 4-9. B1 のサイクリックボルタモグラム^a

^aIn an ambient atmosphere, borate (0.5 mM in anhydrous MeCN) and tetrabutylammonium perchlorate ($[\text{N}(\text{tBu})_4]\text{ClO}_4$) (0.1 M in anhydrous MeCN) as a supporting electrolyte were added to a measuring vessel. Then, the electrochemical property was measured. Measurements used a glassy carbon working electrode, a Ag/AgNO_3 reference electrode, and a Pt wire counter electrode. The sweep rates were set to 100 mV/s. For conversion to the SCE couple, it is known that Fc/Fc^+

is 380 mV more positive than SCE in MeCN and we measured the Fc/Fc^+ in MeCN to determine potentials against SCE respectively.



B3: $E_{pa} = +1.0983 \text{ V vs Ag/AgCl} = +0.87265 \text{ V vs. SCE}$

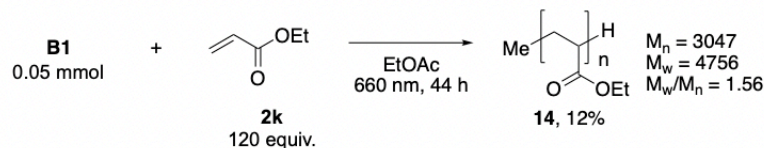
Calculated according to Fc/Fc^+ ($E_{pa} = +0.60565 \text{ V vs Ag/AgCl}$)

Figure 4-10. B3 の DPV 解析^a

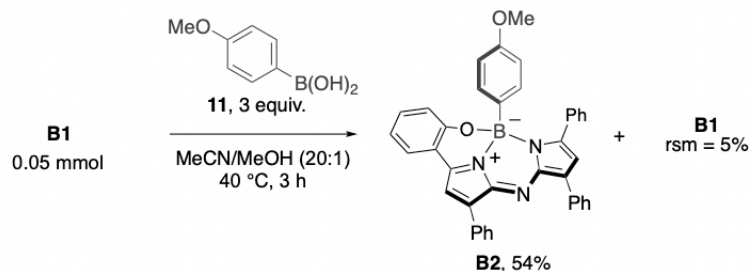
^aIn an ambient atmosphere, borate (0.5 mM in anhydrous MeCN) and tetrabutylammonium perchlorate ($[\text{N}^{\text{t}}\text{Bu}]_4\text{ClO}_4$) (0.1 M in anhydrous MeCN) as a supporting electrolyte were added to a measuring vessel. The solution was degassed for 5 min. Then, the electrochemical property was measured. Measurements used a glassy carbon working electrode, a Ag/AgCl reference electrode, and a Pt wire counter electrode. The sweep rates were set to 100 mV/s. For conversion to the SCE couple, it is known that Fc/Fc^+ is 380 mV more positive than SCE in MeCN and we measured the Fc/Fc^+ in MeCN to determine potentials against SCE respectively.

ラジカル開始剤として錯体 **B1** を用いて、660 nm LED の光照射下、アクリル酸エステルの重合反応を行った。その結果、ポリマー **14** が得られた (**Figure 4-11A**)。これらの結果は錯体 **B1** からの炭素ラジカル生成を示唆している。配位子とホウ素化合物が可逆的に交換するかどうかを調べるため、**Figure 4-11B** に示すような反応を行った。錯体 **B1** と 4-メトキシフェニルボロン酸をアセトニトリル/メタノール混合溶媒中、反応させることで、ホウ素上が 4-メトキシフェニル基に置換した ADP 型ホウ素アート錯体 **B2** が得られた。この結果は、ADP 配位子上の有機ホウ素化合物は交換可能であることを示唆している。直接励起による C–B 結合開裂の可能性を評価するため、錯体 **B1** の DFT 計算を行った (**Figure 4-11C**)。一重項励起状態にある錯体 **B1** の LUMO は主に ADP 骨格上に分布している一方、HOMO は C–B 結合領域および配位子上に存在することがわかった。HOMO-LUMO ギャップは 1.9 eV と算出された。この結果は、赤色光励起に伴い C–B 結合が弱くなることを示唆している。最後に、スケールアップ実験を行い、1 mmol スケールでの反応も可能であることが示された (**Figure 4-11D**)。

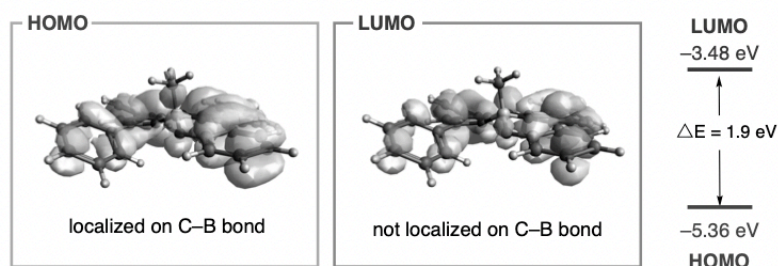
A. Radical polymerization



B. Exchange experiment between borate **A** and aryl boronic acid



C. Computational analysis : calculated HOMO and LUMO of excited state of **B1**



D. Scale up experiment

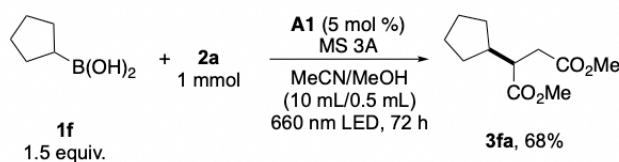


Figure 4-11. 機構実験及びスケールアップ実験

第四節 推定反応機構

前節までの実験結果から、本反応の推定反応機構を **Figure 4-12** に示す。まず、ADP 触媒 **A1** と炭素ラジカル前駆体であるホウ素化合物が脱水縮合し、ホウ素アート錯体 **I** が形成される。ホウ素アート錯体 **I** は、DR から NIR 領域の光を吸収し、励起され、励起状態 **I*** となる。炭素-ホウ素(C-B)結合の開裂および炭素ラジカルの生成に関しては、これまでの実験結果から、以下の 2 つの経路が示唆されている。第一の経路は、励起されたホウ素アート錯体 **I*** からの直接的な C-B 結合のホモリシス開裂である。第二の経路は、電子を受け取るアクセプターが存在する場合に進行する経路であり、**I*** から 電子受容体 (EA) への電子移動を経て C-B 結合が開裂する経路である。C-B 結合の開裂後、アルコールが反応し、ホウ素アート錯体 **II** を形成する。最後に、ホウ素

アート錯体 **II** の加溶媒分解によって触媒 **A1** が再生する。なお、触媒 **A1** 単独で光酸化還元触媒として作用する可能性は、サイクリックボルタンメトリー (CV) において関連する電位窓で可逆的な酸化還元波がみられないこと、および配位子の蛍光がほとんど観測できないことから否定されている。

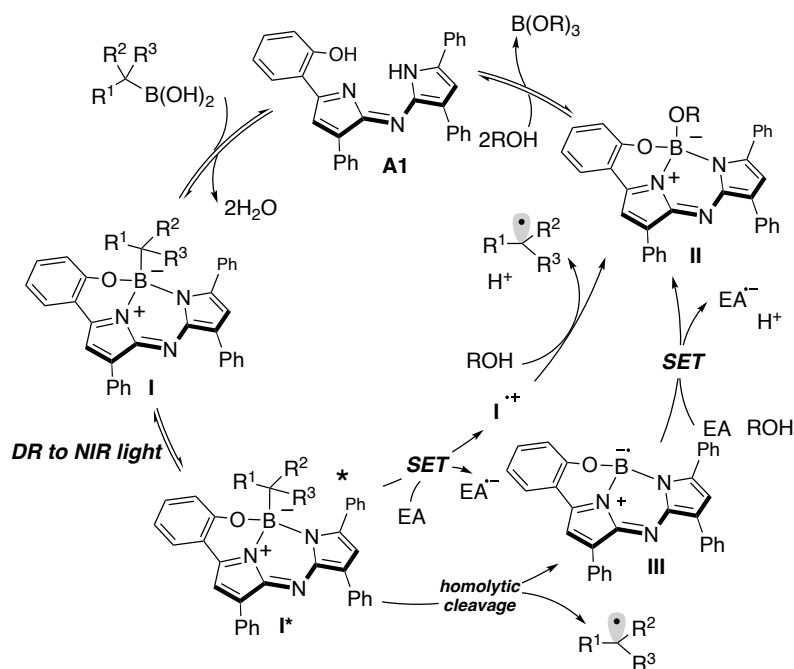


Figure 4-12. 推定反応機構

ホウ素上がメチル基で置換された **B-Me** を用いて、炭素-ホウ素結合の開裂過程の詳細な計算を行った (Figure 4-13)。まず、ホウ素アート錯体 **B-Me** が光によって励起され、一重項励起状態の $^1\text{B-Me}^*$ となる。その後、2つの経路が考えられる。1つ目は、項間交差によって三重項状態の $^3\text{B-Me}^*$ が生じる経路である。2つ目は、 $^1\text{B-Me}^*$ から一電子移動が生じ、ラジカルカチオンの $\text{B-Me}^{\bullet+}$ が生じる経路である。その後、TS-1 または TS-2 を経由し、メチルラジカルが生じる。 $^3\text{B-Me}^*$ から TS-1 を経由する経路の活性化エネルギー (14.7 kcal/mol) と $\text{B-Me}^{\bullet+}$ から TS-2 を経由する経路の活性化エネルギー (15.7 kcal/mol) の差は 1 kcal/mol 程度である。そのため、電子受容体が存在しない場合は先にメチルラジカルを与える TS-1 を経由する経路、電子受容体が存在する場合は電子移動が先に生じる TS-2 を経由する経路であると考えている。

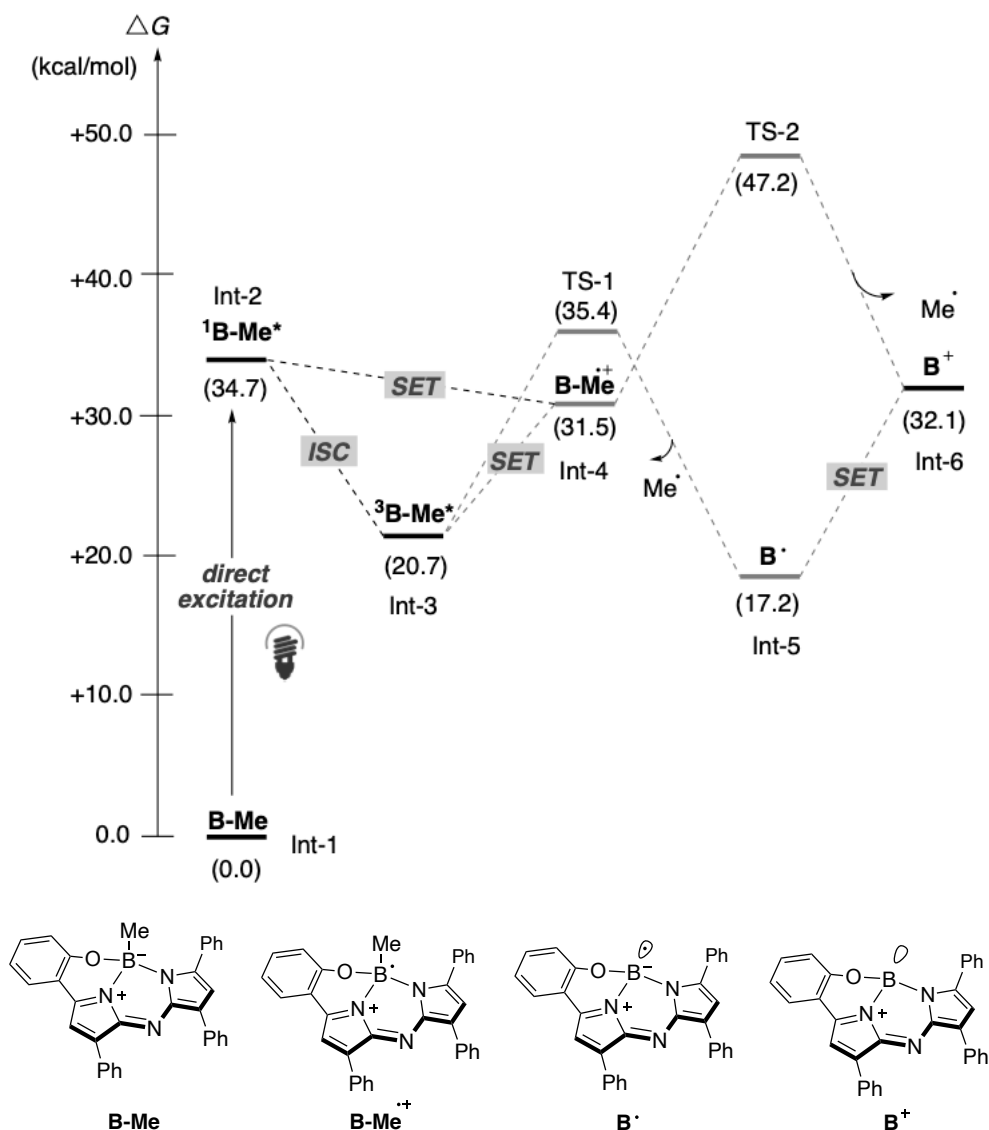


Figure 4-13. 炭素-ホウ素結合の開裂におけるエネルギーダイアグラム ^a

^aThe method TD-B3LYP method with 6-31+G(d,p) basis set with SMD model (MeCN) was used for the geometry optimization, normal vibrational mode analysis of singlet excited states of **B1** (**B-Me**). The method (UO)B3LYP functional with the 6-31+G(d,p) basis set with SMD model (MeCN) was used for the geometry optimization, normal vibrational mode analysis of triplet excited states of **B1** (**B-Me**). The method (U)B3LYP functional with the 6-31+G(d,p) basis set with SMD model (MeCN) was used for the TS calculations and the geometry optimization, normal vibrational mode analysis other than singlet and triplet excited states of **B1** (**B-Me**). The IRC calculations were performed for each transition state to confirm the transition state connecting the reaction pathway between the starting materials and the products.

第五節 結論

ADP 触媒を用いた配位子誘起型直接光励起戦略により、深赤色 (DR) から近赤外光 (NIR)

駆動型の有機ホウ素化合物からのラジカル発生法を開発した。本反応は、系中で形成される ADP 型ホウ素アート錯体が長波長光を吸収し、炭素-ホウ素結合の活性化を可能にする。本手法は、第一級から第三級までの幅広い炭素ラジカルの発生に適用でき、Giese 型ラジカル付加反応や炭素-ヘテロ原子結合形成に展開可能である。本研究により、従来困難な低エネルギー光を用いた高い酸化電位を有する基質の活性化法を確立し、光反応の新たな可能性を拓いた。

第四章 参考文献

1. (a) Kärkäs, M. D.; Porco, J. A., Jr.; Stephenson, C. R. *J. Chem. Rev.* **2016**, *116*, 9683–9747. (b) Romero, N. A.; Nicewicz, D. A. *Chem. Rev.* **2016**, *116*, 10075–10166. (c) Shaw, M. H.; Twilton, J.; MacMillan, D. W. C. *J. Org. Chem.* **2016**, *81*, 6898–6926.
2. (a) Cabanero, D. C.; Rovis, T. *Nat. Rev. Chem.* **2025**, *9*, 28–45. (b) Han, C.; Kundu, B. K.; Liang, Y.; Sun, Y. *Adv. Mater.* **2024**, *36*, 2307759 (c) Zhong, M.; Sun, Y. *Chem Catal.* **2024**, *4*, 100973. (d) Zhang, T.; Pradhan, S.; Das, S. *Angew. Chem., Int. Ed.* **2025**, *64*, e202501194, DOI: 10.1002/anie.202501194.
3. Cox, A. J.; DeWeerd, A. J.; Linden, J. *Am. J. Phys.* **2002**, *70*, 620–625.
4. (a) Ravetz, B. D.; Pun, A. B.; Churchill, E. M.; Congreve, D. N.; Rovis, T.; Campos, L. M. *Nature* **2019**, *565*, 343–346 (b) Han, G.; Li, G.; Huang, J.; Han, C.; Turro, C.; Sun, Y. *Nat. Commun.* **2022**, *13*, 2288. (c) Mato, M.; Bruzzese, P. C.; Takahashi, F.; Leutzsch, M.; Reijerse, E. J.; Schnegg, A.; Cornella, J. *J. Am. Chem. Soc.* **2023**, *145*, 18742–18747. (d) Zeng, L.; Huang, L.; Lin, W.; Jiang, L.-H.; Han, G. *Nat. Commun.* **2023**, *14*, 1102. (e) Yamamoto, H.; Yamaoka, K.; Shinohara, A.; Shibata, K.; Takao, K.; Ogura, A. *Chem. Sci.* **2023**, *14*, 11243–11250. (f) Zhang, T.; Rabeah, J.; Das, S. *Nat. Commun.* **2024**, *15*, 5208. (g) Kai, U.; Katsurayama, Y.; Nishida, R.; Kameyama, T.; Torimoto, T.; Furuyama, T. *J. Org. Chem.* **2024**, *89*, 8178–8184. (h) Stamoulis, A.; Mato, M.; Bruzzese, P. C.; Leutzsch, M.; Cadranel, A.; Gil-Sepulcre, M.; Neese, F.; Cornella, J. *J. Am. Chem. Soc.* **2025**, *147*, 6037–6048.
5. (a) Brimiouille, R.; Bach, T. *Science* **2013**, *342*, 840–843. (b) Brenninger, C.; Jolliffe, J. D.; Bach, T. *Angew. Chem., Int. Ed.* **2018**, *57*, 14338–14349. (c) Leverenz, M.; Merten, C.; Dreuw, A.; Bach, T. *J. Am. Chem. Soc.* **2019**, *141*, 20053–20057. (d) Stegbauer, S.; Jandl, C.; Bach, T. *Chem. Sci.* **2022**, *13*, 11856–11862. (e) Sherbrook, E. M.; Genzink, M. J.; Park, B.; Guzei, I. A.; Baik, M.-H.; Yoon, T. P. *Nat. Commun.* **2021**, *12*, 5735. (f) Plachinski, E. F.; Qian, R. Z.; Villanueva, R.; Poole, D. L.; Rosenthal, T.; Yoon, T. P. *J. Am. Chem. Soc.* **2024**, *146*, 31400–31404. (g) Cahoon, S. B.; Chapman, S. J.; Fiala, T. A.; Genzink, M. J.; Yoon, T. P. *J. Org. Chem.* **2024**, *89*, 17615–17620.
6. Chung, K.-Y.; Page, Z. A. *J. Am. Chem. Soc.* **2023**, *145*, 17912–17918.
7. Rehm, D.; Weller, A. *Isr. J. Chem.* **1970**, *8*, 259–271.

第四章 実験項

■ Instrumentation and Chemicals Synthesis ■

NMR spectra were recorded on a Bruker AVANCE NEO 400N spectrometer, operating at 400 MHz or a JMTC-400/54/JJ/YH, operating at 400 MHz for ^1H NMR, 100.6 MHz for ^{13}C NMR, 376.5 MHz for ^{19}F NMR and 128.4 MHz for ^{11}B NMR. Chloroform- d_1 (CDCl_3) containing 0.03% tetramethylsilane (TMS) (>99.8%D, Cambridge Isotope Laboratories, Inc., Cat. No. DLM-7), Methanol- d_4 (99.9%D, Cambridge Isotope Laboratories, Inc., Cat. No. DLM-51) and DMSO- d_6 (99.9%D, Cambridge Isotope Laboratories, Inc., Cat. No. DLM-10-1000) were used as solvents for NMR measurements at ambient temperature. Chemical shifts (δ) for ^1H NMR are given in parts per million (ppm) relative to TMS (δ 0.00 ppm in CDCl_3), or residual methanol (δ 3.31 ppm in CD_3OD), DMSO (δ 2.50 ppm in DMSO- d_6). Chemical shifts (δ) for ^{13}C NMR are given in ppm relative to CDCl_3 (δ 77.0 ppm), or residual methanol (δ 49.0 ppm in CD_3OD) or residual DMSO (δ 39.5 ppm in DMSO- d_6). Chemical shifts were reported in δ ppm. The abbreviations s, brs, d, t, q, quin, and m signify singlet, doublet, triplet, quartet, quintet and multiplet, respectively.

Mass spectra were obtained with a Bruker timsTOF mass spectrometer (ESI), a Thermo Scientific Exactive Plus orbitrap mass spectrometer (ESI) and a JEOL JMS-MS700 (EI). TLC analyses were performed on commercial glass plates of Merck Silica gel 60F₂₅₄. Silica gel (Wakosil® 60, 64~210 μm) was used for column chromatography. Biotage® Selekt, Biotage® and LaboACE LC-5060 (for Gel Permeation Chromatography) and were used for purification. IR spectra were measured with a ATR Accessory (QATR-S) for the Shimadzu IRSpirit FT-IR Spectrometer. Melting points were measured on a Stanford Research Systems MPA100. UV-Vis absorption spectra were recorded on a Shimadzu UV-1900. Fluorescence spectra were recorded on a Shimadzu RF-6000. Cyclic voltammetry measurements were recorded with a Hokuto Denko HZ-7000 potentiostat. Single-crystal X-ray diffraction data were collected on a Bruker Single Crystal CCD X-ray Diffractometer (SMART APEX II). Kessil PR-160 660 nm and Kessil PR-160 740 nm was used as a light source. TEKNOS MG9 was used as a fan. Polymer was analyzed by SHIMADZU Model: Prominence501AC, LC-20AD, SIL-20AHT, SPD-20A, CTO-20A, CBM-20A, DAWN HELEOS II AC and ViscoStar III AC.

All reactions were carried out under nitrogen atmosphere. Materials were obtained from commercial suppliers or prepared according to standard procedures unless otherwise noted. Before reactions, liquid olefines were passed through a short pad of Aluminium oxide 60.

Fujifilm Wako Pure Chemical Co.

Silica gel (Wakosil® 60, 64~210 μm), acetonitrile (super dehydrated), methanol (super dehydrated), dimethyl fumarate, ethanol, ammonium acetate.

Tokyo Chemical Industry Co., Ltd.

1-Cyclopentenylboronic acid, 4-methoxyphenylboronic Acid, (*E*)-chalcone, elemental sulfur, morpholine, 2,6-lutidine, methyl 4-bromobenzoate, 4-bromobenzophenone.

Merk Sigma-Aldrich Japan Inc.

2,4,6-Trimethyl-1,3,5,2,4,6-trioxatriborinane, $\text{NiBr}_2 \cdot \text{diglyme}$, 4,4'-di-*tert*-butyl-2,2'-bipyridyl, 4'-bromoacetophenone.

Nacalai Tesque Inc.

Molecular Sieves 3A.

Angene

(*E*)-1-(2-Hydroxyphenyl)-3-phenylprop-2-en-1-one, diethyl 1,4-dihydro-2,6-dimethyl-3,5-pyridinedicarboxylate, 4-bromobenzotrifluoride, potassium cyclohexyltrifluoroborate.

The substrates listed in Figure S4-1 were prepared according to the literatures (**S1**,¹ **S2**,² **S3**,³ **S4**,⁴ **A3**,⁵ **A4**,⁶ **1e**,⁷ **1i**,⁸ **1j**,⁹ **1k**,⁷ **1l**,¹⁰ **1m**,¹¹ **1n**,¹² **S5**,¹³ **2e**,¹⁴ **8**,¹⁵ **S6**,¹⁶ **10b**,¹⁷).

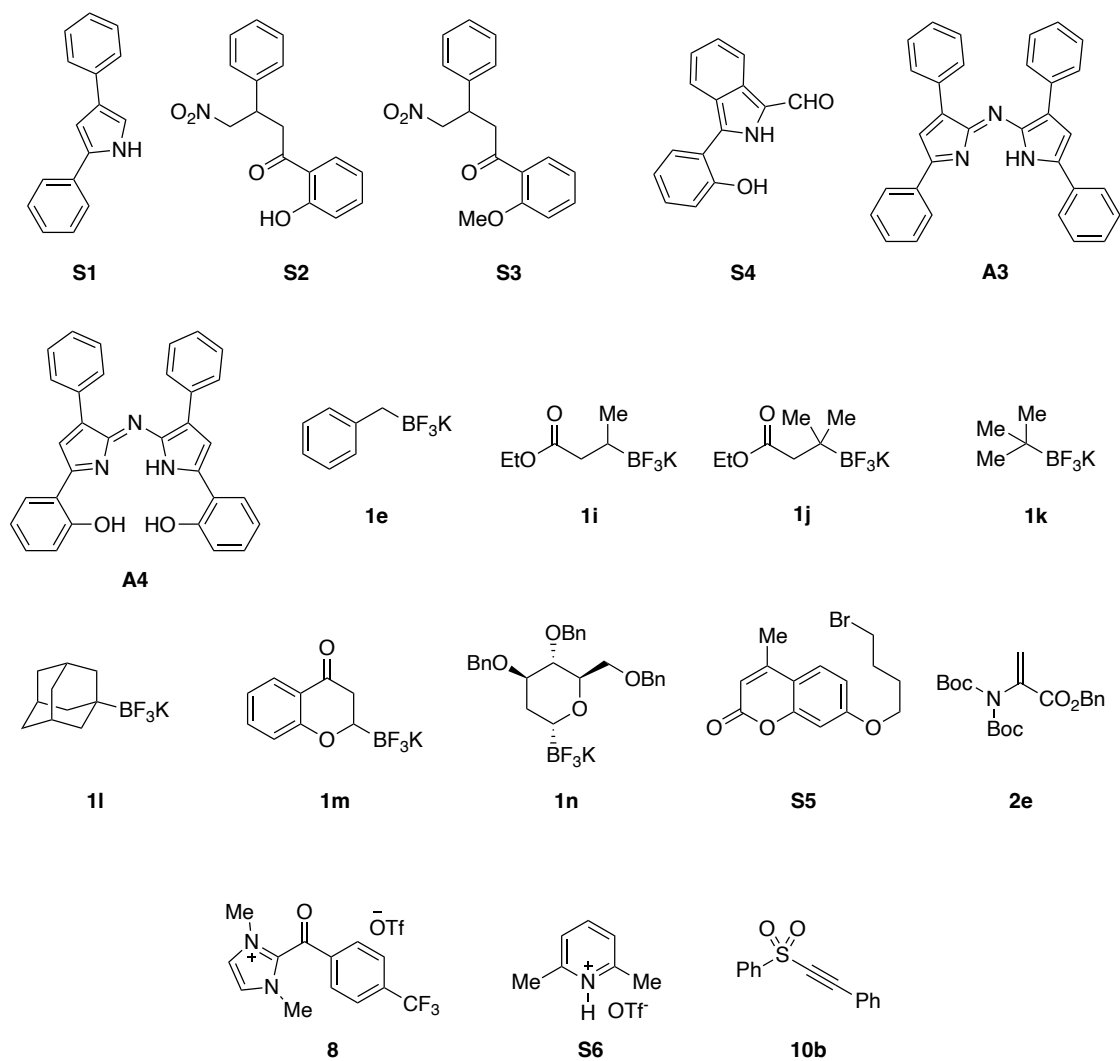


Figure S4-1. Prepared starting materials.

■ Light Set Up ■

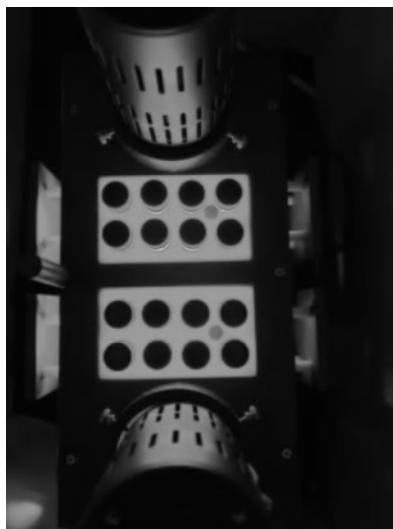


Figure S4-2. EvoluChem photoreactor

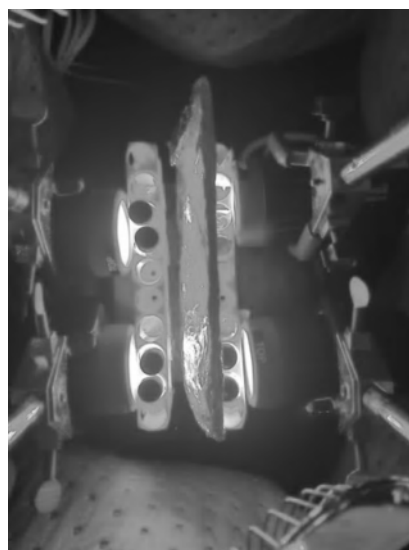
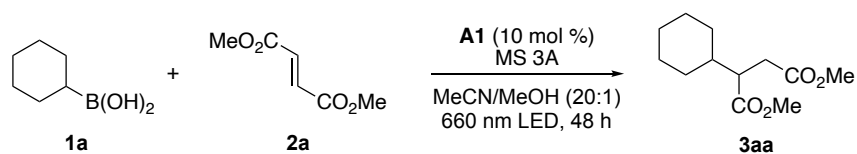


Figure S4-3. Photoreactor (Direct)

■ Procedure for Giese-type Reaction ■

Reaction optimization using boronic acids



A1 (4.7 mg, 10 μ mol), **1a** (19.2 mg, 0.15 mmol) and dimethyl fumarate **2a** (14.4 mg, 0.1 mmol) were placed in an oven-dried screw-top 4 mL vial containing a magnetic stirring bar. The vial was then

introduced into the nitrogen-filled glovebox and to this was added MS 3A (100 mg), dry MeCN (2 mL), and dry MeOH (100 μ L). The vial was sealed with Teflon[®]-coated silicon rubber septum and Teflon tape, and the vial was then brought outside the glovebox. After 48 h stirring under photoirradiation (Kessil PR160L 660 nm), the solvent was removed under reduced pressure. The residue was dissolved in CDCl₃ and 1,1,2,2-tetrachloroethane (17.8 mg, 0.11 mmol) was added as an internal standard. The ¹H NMR (400 MHz) yield of **3aa** was obtained in 81% yield by comparing the relative integration value of the peak observed at 3.67 ppm of **3aa** with that of 1,1,2,2-tetrachloroethane observed at 5.94 ppm (Figure S4-4).

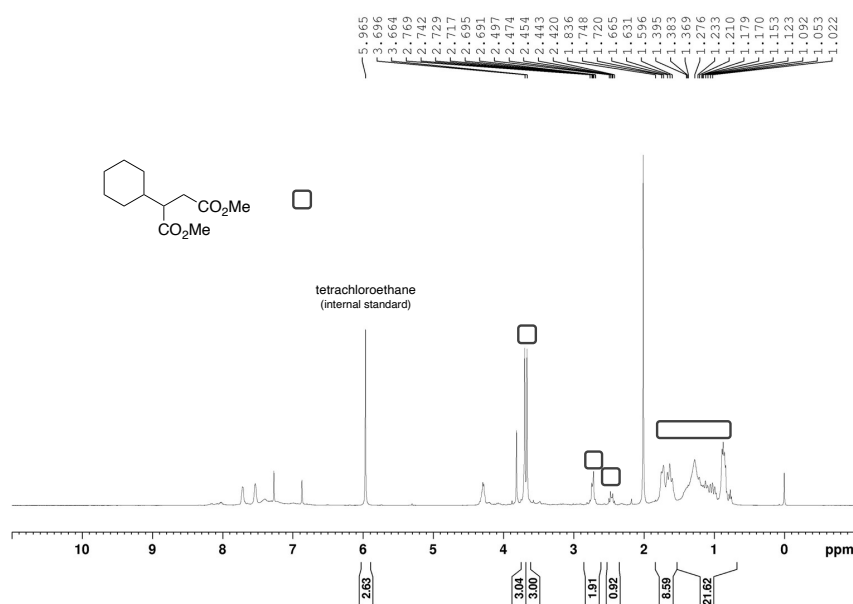
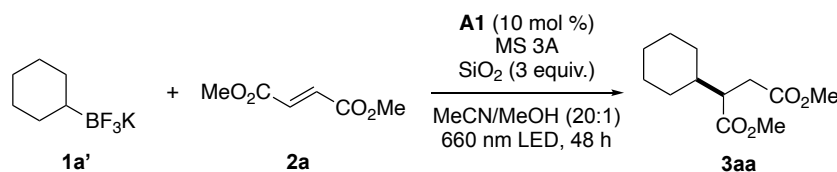


Figure S4-4. ¹H NMR analysis.

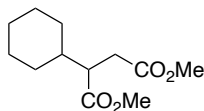
Reaction optimization using trifluoroborate salt



A1 (4.7 mg, 10 μ mol), SiO₂ (0.3 mmol), **1a'** (28.5 mg, 0.15 mmol) and dimethyl fumarate **2a** (14.4 mg, 0.1 mmol) were placed in an oven-dried screw-top 4 mL vial containing a magnetic stirring bar. The vial was then introduced into the nitrogen-filled glovebox and to this was added MS 3A (100 mg), dry MeCN (2 mL), and dry MeOH (100 μ L). The vial was sealed with Teflon[®]-coated silicon rubber septum and Teflon tape, and the vial was then brought outside the glovebox. After 48 h stirring under photoirradiation (Kessil PR160L 660 nm), the solvent was removed under reduced pressure. The residue was dissolved in CDCl₃ and 1,1,2,2-tetrachloroethane (15.3 mg, 0.091 mmol) was added as an internal standard. The ¹H NMR (400 MHz) yield of **3aa** was obtained in 86% yield by comparing the relative integration value of the peak observed at 3.67 ppm of **3aa** with that of 1,1,2,2-

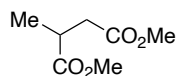
tetrachloroethane observed at 5.94 ppm.

Dimethyl 2-cyclohexylsuccinate (**3aa**)



A1 (4.7 mg, 10 μ mol), **1a** (19.2 mg, 0.15 mmol) and dimethyl fumarate **2a** (14.4 mg, 0.1 mmol) were placed in an oven-dried screw-top 4 mL vial containing a magnetic stirring bar. The vial was then introduced into the nitrogen-filled glovebox and to this was added MS 3A (100 mg), dry MeCN (2 mL), and dry MeOH (100 μ L). The vial was sealed with Teflon[®]-coated silicon rubber septum, and the vial was then brought outside the glovebox. After 48 h stirring under light irradiation (Figure S4-2), the solvent was removed under reduced pressure. The crude was purified by flash column chromatography on silica gel (100:0–85:15, Hexane/Et₂O) to give **3aa** (17.6 mg, 77.1 μ mol, 77% isolated yield). Pale yellow oil. ¹H NMR (400 MHz, CDCl₃) δ 3.70 (s, 3H), 3.67 (s, 3H), 2.77–2.69 (m, 2H), 2.46 (m, 1H), 1.75–1.72 (m, 2H), 1.67–1.58 (m, 4H), 1.28–0.99 (m, 5H). ¹³C NMR (100.6 MHz, CDCl₃) δ 175.0, 173.0, 51.8, 51.6, 47.0, 39.9, 33.2, 30.6, 30.1, 26.3, 26.1. This data is in full agreement with the data previously published in the literature.¹⁸

Dimethyl 2-methylsuccinate (**3ba**)



A1 (9.3 mg, 20 μ mol) and dimethyl fumarate **2a** (14.4 mg, 0.1 mmol) were placed in an oven-dried screw-top 4 mL vial containing a magnetic stirring bar. The vial was then introduced into the nitrogen-filled glovebox and to this was added MS 3A (100 mg), **1b** (13.9 μ L, 0.1 mmol), dry MeCN (2 mL), and dry MeOH (100 μ L). The vial was sealed with Teflon[®]-coated silicon rubber septum, and the vial was then brought outside the glovebox. After 48 h stirring under light irradiation (Figure S4-3), the solvent was removed under reduced pressure. The residue was dissolved in CDCl₃ and 1,1,2,2-tetrachloroethane (16.9 mg, 0.1 mol) was added as an internal standard. The ¹H NMR (400 MHz) yield of **3ba** was obtained by comparing the relative integration value of the peak observed at 3.68 ppm of **3ba** with that of 1,1,2,2-tetrachloroethane observed at 5.97 ppm (Figure S4-5). **3ba** was obtained in 55% NMR yield (41% yield using 740 nm LED instead of 660 nm LED). This data is in full agreement with the data previously published in the literature.¹⁹

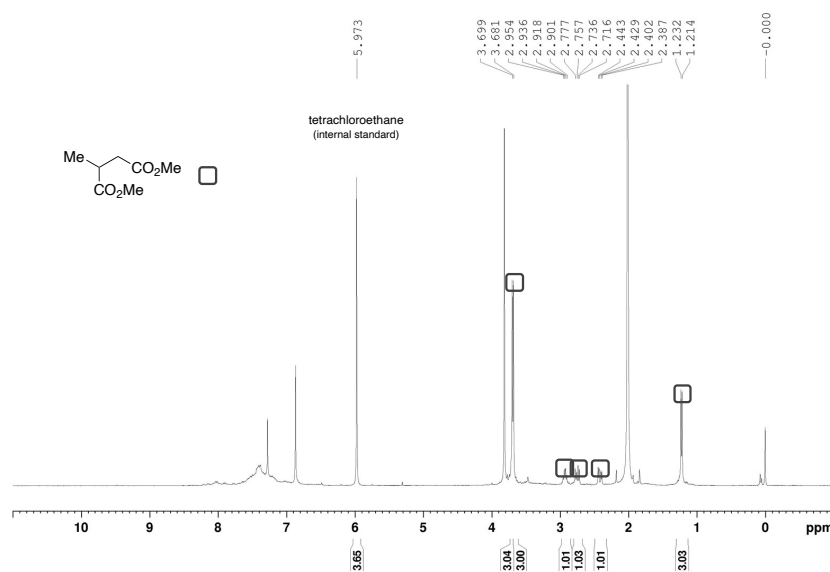
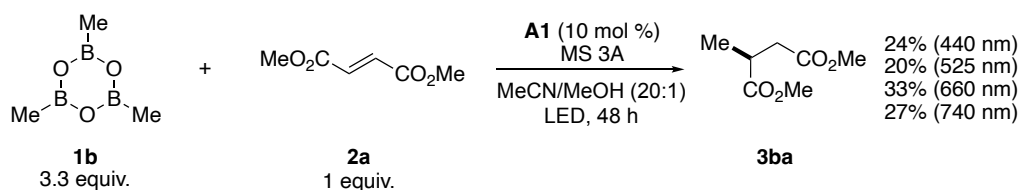
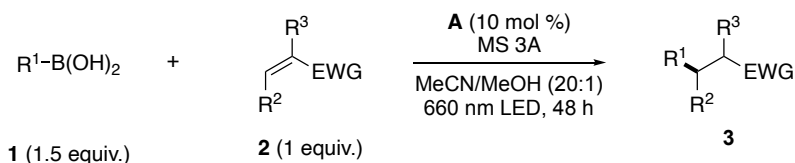


Figure S4-5. ^1H NMR analysis.



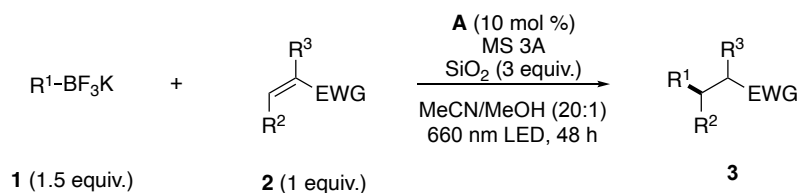
The reaction using **1b**, **2a**, and 10 mol % of **A1** under irradiation at different wavelengths was demonstrated : 440 nm (24% yield), 525 nm (20% yield), 660 nm (33% yield), and 740 nm (27% yield).

General procedure A for Giese reaction



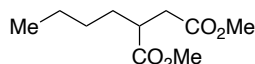
A (4.7 mg, 10 μmol), **1** (0.15 mmol) and **2** (0.1 mmol) were placed in an oven-dried screw-top 4 mL vial containing a magnetic stirring bar. The vial was then introduced into the nitrogen-filled glovebox and to this was added MS 3A (100 mg), dry MeCN (2 mL), and dry MeOH (100 μL). The vial was sealed with Teflon[®]-coated silicon rubber septum, and the vial was then brought outside the glovebox. After 48 h stirring under photoirradiation (Kessil PR160L 660 nm), the solvent was removed under reduced pressure. The volatiles were purified by flash column chromatography on silica gel to give **3**.

General procedure B for Giese reaction



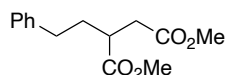
A (10 μmol), **1** (0.15 mmol), SiO_2 (0.3 mmol) and **2** (0.1 mmol) were placed in an oven-dried screw-top 4 mL vial containing a magnetic stirring bar. The vial was then introduced into the nitrogen-filled glovebox and to this was added MS 3A (100 mg), dry MeCN (2 mL), and dry MeOH (100 μL). The vial was sealed with Teflon[®]-coated silicon rubber septum, and the vial was then brought outside the glovebox. After 48 h stirring under photoirradiation (Kessil PR160L 660 nm), the solvent was removed under reduced pressure. The volatiles were purified by flash column chromatography on silica gel to give **3**.

Dimethyl 2-butylsuccinate (**3ca**)



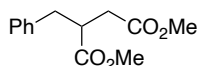
Following the general procedure **A** using catalyst **A1** (10 mol %) under light irradiation (Figure S4-3), the crude was purified by flash column chromatography on silica gel (100:0–70:30, Hexane/ Et_2O) to give **3ca** (6.4 mg, 31.8 μmol , 32% isolated yield). Brown oil. ^1H NMR (400 MHz, CDCl_3) δ 3.70 (s, 3H), 3.68 (s, 3H), 2.84 (m, 1H), 2.72 (dd, J = 16.4, 9.2 Hz, 1H), 2.44 (dd, J = 16.4, 5.2 Hz, 1H), 1.64 (m, 1H), 1.51 (m, 1H), 1.34–1.23 (m, 4H), 0.89 (t, J = 6.8 Hz, 3H). ^{13}C NMR (100.6 MHz, CDCl_3) δ 175.6, 172.5, 51.80, 51.76, 41.1, 35.8, 31.6, 29.1, 22.5, 13.9. This data is in full agreement with the data previously published in the literature.¹⁹

Dimethyl 2-phenethylsuccinate (**3da**)



Following the general procedure **A** using catalyst **A1** (10 mol %) under light irradiation (Figure S4-3) (reaction time was changed from 48 h to 72 h), the crude was purified by flash column chromatography on silica gel (100:0–70:30, Hexane/ Et_2O) to give **3da** (13.3 mg, 53.1 μmol , 53% isolated yield). Brown oil. ^1H NMR (400 MHz, CDCl_3) δ 7.30–7.26 (m, 2H), 7.21–7.16 (m, 3H), 3.71 (s, 3H), 3.67 (s, 3H), 2.90 (m, 1H), 2.77 (dd, J = 16.4, 9.2 Hz, 1H), 2.69–2.57 (m, 2H), 2.49 (dd, J = 16.4, 5.2 Hz, 1H), 2.00 (m, 1H), 1.83 (m, 1H). ^{13}C NMR (100.6 MHz, CDCl_3) δ 175.1, 172.2, 141.0, 128.4, 128.3, 126.1, 51.9, 51.8, 40.8, 35.9, 33.5, 33.2. This data is in full agreement with the data previously published in the literature.²⁰

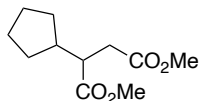
Dimethyl 2-benzylsuccinate (**3ea**)



Following the general procedure **B** using catalyst **A1** (10 mol %) (reaction time was changed from 48 h to 72 h) under light irradiation (Figure S4-3), the crude was purified by flash column chromatography on silica gel (100:0–70:30, Hexane/ Et_2O) to give **3ea** (23.0 mg, 97.2 μmol , 97%

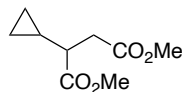
isolated yield). Blueish oil. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.31–7.26 (m, 2H), 7.22 (m, 1H), 7.16–7.14 (m, 2H), 3.67 (s, 3H), 3.64 (s, 3H), 3.14 (m, 1H), 3.05 (dd, J = 13.2, 6.0 Hz, 1H), 2.76 (dd, J = 13.2, 8.4 Hz, 1H), 2.68 (dd, J = 16.8, 9.2 Hz, 1H), 2.41 (dd, J = 16.8, 4.8 Hz, 1H). $^{13}\text{C NMR}$ (100.6 MHz, CDCl_3) δ 174.6, 172.2, 138.1, 129.0, 128.5, 126.7, 51.9, 51.7, 43.0, 37.7, 34.8. This data is in full agreement with the data previously published in the literature.²⁰

Dimethyl 2-cyclopentylsuccinate (**3fa**)



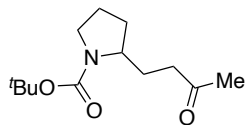
Following the general procedure **A** using catalyst **A1** (10 mol %) under light irradiation (Figure S4-2), the crude was purified by flash column chromatography on silica gel (100:0–70:30, Hexane/ Et_2O) to give **3fa** (17.7 mg, 82.7 μmol , 83% isolated yield). Brown oil. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 3.70 (s, 3H), 3.67 (s, 3H), 2.76 (dd, J = 16.0, 10.8 Hz, 1H), 2.68 (ddd, J = 10.8, 8.4, 3.2 Hz, 1H), 2.50 (dd, J = 16.0, 3.2 Hz, 1H), 1.96 (m, 1H), 1.78 (m, 1H), 1.72–1.59 (m, 3H), 1.58–1.50 (m, 2H), 1.29 (m, 1H), 1.18 (m, 1H). $^{13}\text{C NMR}$ (100.6 MHz, CDCl_3) δ 175.4, 172.6, 51.7, 51.6, 46.2, 42.3, 35.4, 30.44, 30.38, 24.9, 24.8. This data is in full agreement with the data previously published in the literature.²¹

Dimethyl 2-cyclopropylsuccinate (**3ga**)



Following the general procedure **A** using catalyst **A1** (10 mol %) (reaction time was changed from 48 h to 72 h) under light irradiation (Figure S4-3), the crude was purified by flash column chromatography on silica gel (100:0–80:20, Hexane/ Et_2O) to give **3ga** (6.4 mg, 34.1 μmol , 34% isolated yield). Red oil. **IR** (neat) 3006, 2953, 2924, 1735, 1436, 1344, 1268, 1204, 1165, 1026, 1000 cm^{-1} . $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 3.73 (s, 3H), 3.67 (s, 3H), 2.86 (dd, J = 16.4, 9.6 Hz, 1H), 2.59 (dd, J = 16.4, 4.8 Hz, 1H), 2.07 (ddd, J = 9.6, 9.6, 4.8 Hz, 1H), 0.90 (m, 1H), 0.59–0.51 (m, 2H), 0.43 (m, 1H), 0.18 (m, 1H). $^{13}\text{C NMR}$ (100.6 MHz, CDCl_3) δ 174.9, 172.4, 51.9, 51.7, 46.1, 36.3, 13.5, 4.19, 4.16. **HRMS–ESI** (m/z): $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_9\text{H}_{14}\text{O}_4\text{Na}^+$, 209.0784, found, 209.0776.

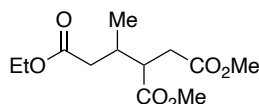
tert-Butyl 2-(3-oxobutyl)pyrrolidine-1-carboxylate (**3hb**)



Following the general procedure **B** using catalyst **A1** (10 mol %) under light irradiation (Figure S4-2), the crude was purified by flash column chromatography on silica gel (100:0–88:12, Hexane/ EtOAc) to give **3hb** (23.2 mg, 96.1 μmol , 96%, isolated yield). Blue oil. **IR** (neat) 2973, 2933, 1715, 1688, 1392, 1365, 1255, 1169, 1125, 1103 cm^{-1} . Peaks for two rotamers (56:44) were given. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 3.83 (s, $0.56 \times 1\text{H}$), 3.77 (s, $0.44 \times 1\text{H}$), 3.43–3.30 (m, 2H), 2.47–2.44 (m, 2H), 2.16 (s, 3H), 1.91–1.79 (m, 4H), 1.69–1.60 (m, 2H), 1.46 (s, 9H). (Signals for two rotamers were given.) $^{13}\text{C NMR}$ (100.6 MHz, CDCl_3) δ 208.8, 208.3, 154.9, 154.7, 79.3, 78.9, 56.5, 46.4, 46.1, 40.7,

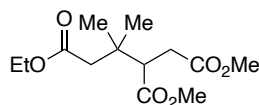
40.5, 30.7, 30.3, 29.9, 28.6, 28.5, 23.6, 23.0. (Only observed peaks) **HRMS–ESI** (m/z): $[M+H]^+$ calcd for $C_{13}H_{24}NO_3^+$, 242.1751, found, 242.1742.

4-Ethyl 1,2-dimethyl 3-methylbutane-1,2,4-tricarboxylate (**3ia**)



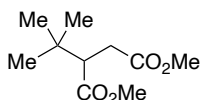
Following the general procedure **B** using catalyst **A1** (10 mol %) (reaction time was changed from 48 h to 72 h) under light irradiation (Figure S4-2), the crude was purified by flash column chromatography on silica gel (100:0–80:20, Hexane/EtOAc) and GPC ($CHCl_3$) to give **3ia** (9.9 mg, 38.0 μ mol, 38%, isolated yield, dr 1:1). Pale yellow oil. **IR** (neat) 1732, 1438, 1375, 1301, 1258, 1228, 1166, 1105, 1030, 1000 cm^{-1} . **1H NMR** (400 MHz, $CDCl_3$) δ 4.14 (q, J = 7.2 Hz, 2H), 3.71 (s, 3H), 3.68 (s, 3H), 2.93 (m, 1H), 2.82 (dd, J = 16.4, 10.8 Hz, $0.5 \times 1H$), 2.76 (dd, J = 16.4, 10.8 Hz, $0.5 \times 1H$), 2.48–2.31 (m, 3H), 2.18 (m, 1H), 1.26 (t, J = 7.2 Hz, 3H), 0.96 (d, J = 6.8 Hz, 3H). (Peaks for two diastereomers were given.) **^{13}C NMR** (100.6 MHz, $CDCl_3$) δ 174.2, 173.9, 172.54, 172.47, 172.24, 172.09, 60.53, 60.47, 51.92, 51.88, 51.87, 51.80, 45.4, 45.3, 39.13, 38.94, 33.5, 32.11, 31.9, 31.7, 16.9, 16.7, 14.20, 14.19. **HRMS–ESI** (m/z): $[M+Na]^+$ calcd for $C_{12}H_{20}O_6Na^+$, 283.1152, found, 283.1165.

4-Ethyl 1,2-dimethyl 3,3-dimethylbutane-1,2,4-tricarboxylate (**3ja**)



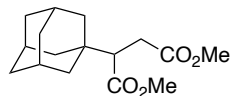
Following the general procedure **B** using catalyst **A5** (10 mol %) (reaction time was changed from 48 h to 72 h) under light irradiation (Figure S4-3), the crude was purified by GPC ($CHCl_3$) to give **3ja** (24.5 mg, 89.3 μ mol, 89% isolated yield). Brown oil. **IR** (neat) 1728, 1436, 1370, 1352, 1263, 1191, 1159, 1119, 1034, 846 cm^{-1} . **1H NMR** (400 MHz, $CDCl_3$) δ 4.13 (q, J = 7.2 Hz, 2H), 3.70 (s, 3H), 3.66 (s, 3H), 2.94 (dd, J = 12.0, 2.8 Hz, 1H), 2.80 (dd, J = 16.4, 12.0 Hz, 1H), 2.53 (m, 1H), 2.37–2.24 (m, 2H), 1.26 (t, J = 7.2 Hz, 3H), 1.08 (s, 3H), 1.07 (s, 3H). **^{13}C NMR** (100.6 MHz, $CDCl_3$) δ 174.2, 172.7, 171.3, 60.2, 51.8, 51.5, 49.5, 44.4, 34.9, 32.2, 25.3, 25.1, 14.2. **HRMS–ESI** (m/z): $[M+Na]^+$ calcd for $C_{13}H_{22}O_6Na^+$, 297.1309, found, 297.1323.

Dimethyl 2-(*tert*-butyl)succinate (**3ka**)



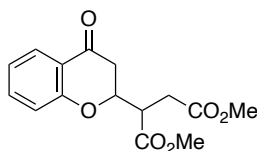
Following the general procedure **B** using catalyst **A1** (20 mol %) under light irradiation (Figure S4-3), the crude was purified by GPC ($CHCl_3$) to give **3ka** (22.1 mg, 109.3 μ mol, >99%). Pale purple oil. **1H NMR** (400 MHz, $CDCl_3$) δ 3.70 (s, 3H), 3.66 (s, 3H), 2.80 (dd, J = 16.4, 12.0 Hz, 1H), 2.64 (dd, J = 12.0, 2.8 Hz, 1H), 2.48 (dd, J = 16.4, 2.8 Hz, 1H), 0.96 (s, 9H). **^{13}C NMR** (100.6 MHz, $CDCl_3$) δ 174.7, 173.2, 51.8, 51.4, 51.1, 32.6, 27.8. This data is in full agreement with the data previously published in the literature.¹⁹

Dimethyl 2-(adamantan-1-yl)succinate (**3la**)



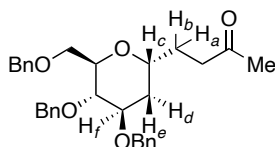
Following the general procedure **B** using catalyst **A1** (10 mol %) under light irradiation (Figure S4-2), the crude was purified by flash column chromatography on silica gel (100:0–70:30, Hexane/AcOEt) to give **3la** (25.9 mg, 92.4 μ mol, 92% isolated yield). Brown oil. ^1H NMR (400 MHz, CDCl_3) δ 3.70 (s, 3H), 3.65 (s, 3H), 2.76 (m, 1H), 2.53–2.48 (m, 2H), 1.98 (brs, 3H), 1.71–1.60 (m, 9H), 1.46 (m, 3H). ^{13}C NMR (100.6 MHz, CDCl_3) δ 174.3, 173.4, 52.2, 51.7, 51.3, 39.9, 36.7, 34.4, 30.9, 28.4. This data is in full agreement with the data previously published in the literature.²²

Dimethyl 2-(2,3-dihydro-4H-1-benzopyran-4-on-2-yl)succinate (**3ma**)



Following the general procedure **B** using catalyst **A5** (10 mol %) (reaction time was changed from 48 h to 72 h) under light irradiation (Figure S4-3), the crude was purified by preparative thin layer chromatography on silica gel (50:50, Hexane/AcOEt) and GPC (eluent: AcOEt) to give **3ma** (10.3 mg, 35.2 μ mol, 35% isolated yield, dr 1.2:1). Colorless oil. IR (neat) 1735, 1695, 1607, 1465, 1438, 1307, 1263, 1227, 1166, 767 cm^{-1} . ^1H NMR (400 MHz, CDCl_3) δ 7.88 (d, J = 8.0 Hz, 1H), 7.49 (dd, J = 8.0, 8.0 Hz, 1H), 7.05 (dd, J = 8.0, 8.0 Hz, 1H), 6.99–6.95 (m, 1H), 4.77–4.72 (m, 1H), 3.78 (s, $0.46 \times 3\text{H}$), 3.77 (s, $0.54 \times 3\text{H}$), 3.73 (s, 3H), 3.46–3.41 (m, $0.46 \times 1\text{H}$), 3.32–3.27 (m, $0.54 \times 1\text{H}$), 3.03–2.63 (m, 4H). ^{13}C NMR (100.6 MHz, CDCl_3) δ 191.3, 191.1, 172.0, 171.8, 171.7, 171.1, 160.9, 160.8, 136.19, 136.17, 127.04, 127.02, 121.92, 121.87, 120.8, 120.7, 117.9, 117.8, 76.9, 76.8, 52.5, 52.4, 52.1, 45.9, 45.2, 41.1, 40.2, 31.8, 31.7. (One carbon signal is missing due to the overlapping) HRMS–ESI (m/z): $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{15}\text{H}_{17}\text{O}_6^+$, 293.1020, found, 293.1012.

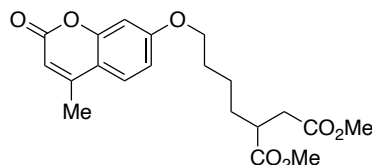
4-((2R,4R,5S,6R)-4,5-Bis(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2H-pyran-2-yl)butan-2-one (**3nb**)



Following the general procedure **B** using catalyst **A1** (10 mol %) (reaction time was changed from 48 h to 72 h) under light irradiation (Figure S4-3), the crude was purified by flash column chromatography on silica gel (100:0–80:20, Hexane/ EtOAc) to give **3nb** (51.5 mg, 105.4 μ mol, >99% isolated yield). IR (neat) 2922, 2865, 1714, 1497, 1363, 1094, 1072, 1028, 735, 697 cm^{-1} . ^1H NMR (400 MHz, CDCl_3) δ 7.32–7.19 (m, 15H), 4.78 (d, J = 11.2 Hz, 1H), 4.62–4.49 (m, 5H), 3.94 (ddt, J = 10.4, 4.8, 4.0 Hz, 1H, H_c , anomeric H), 3.79 (ddd, J = 9.2, 7.2, 4.0 Hz, 1H, H_f), 3.75–3.60 (m, 3H),

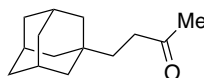
3.49 (t, $J = 7.2$ Hz, 1H), 2.54 (tdd, $J = 17.6, 8.4, 6.0$ Hz, 1H), 2.50 (tt, $J = 18.0, 7.2$ Hz, 1H), 2.11 (s, 3H), 1.97 (dddd, $J = 14.0, 10.4, 8.0, 6.4$ Hz, 1H, H_b), 1.95 (dtd, $J = 8.8, 4.8, 4.0$ Hz, 1H, H_d), 1.80 (ddd, $J = 14.0, 9.2, 4.8$ Hz, 1H, H_e), 1.64 (ddt, $J = 18.0, 6.4, 4.0$ Hz, 1H, H_a). ^{13}C NMR (100.6 MHz, CDCl_3) δ 208.4, 138.4, 138.3, 138.2, 128.35, 128.29, 128.27, 128.26, 127.8, 127.7, 127.57, 127.56, 127.54, 76.7, 76.6, 73.9, 73.3, 72.3, 71.4, 70.0, 69.0, 39.6, 33.5, 30.1, 25.6. HRMS–ESI (m/z): $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{31}\text{H}_{37}\text{O}_5^+$, 489.2636, found, 489.2641.

Dimethyl 2-((4-((4-methyl-2-oxo-2H-chromen-7-yl)oxy)butyl)succinate (30a)



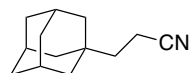
Following the general procedure **B** using catalyst **A1** (10 mol %) (reaction time was changed from 48 h to 72 h) under light irradiation (Figure S4-3), the crude was purified by flash column chromatography on silica gel (100:0–0:100, Hexane/DCM and 100:0–90:10, DCM/EtOAc) to give **30a** (22.7 mg, 60.3 μmol , 60% isolated yield). IR (neat) 1735, 1613, 1448, 1436, 1389, 1369, 1294, 1280, 1155, 1072 cm^{-1} . ^1H NMR (400 MHz, CDCl_3) δ 7.49 (d, $J = 8.8$ Hz, 1H), 6.84 (dd, $J = 8.8, 2.0$ Hz, 1H), 6.79 (m, 1H), 6.14 (s, 1H), 4.01 (t, $J = 6.4$ Hz, 2H), 3.71 (s, 3H), 3.68 (s, 3H), 2.89 (m, 1H), 2.75 (dd, $J = 16.4, 9.2$ Hz, 1H), 2.47 (dd, $J = 16.4, 5.2$ Hz, 1H), 2.40 (s, 3H), 1.86–1.47 (m, 6H). ^{13}C NMR (100.6 MHz, CDCl_3) δ 175.2, 172.3, 162.0, 161.4, 155.2, 152.6, 125.5, 113.5, 112.6, 111.9, 101.3, 68.0, 51.9, 51.8, 41.0, 35.8, 31.5, 28.7, 23.5, 18.7. HRMS–ESI (m/z): $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{20}\text{H}_{25}\text{O}_7^+$, 377.1595, found, 377.1588.

4-((3r,5r,7r)-Adamantan-1-yl)butan-2-one (31b)



Following the general procedure **B** using catalyst **A1** (10 mol %) under light irradiation (Figure S4-3), the crude was purified by flash column chromatography on silica gel (100:0–83:17, Hexane/AcOEt) to give **31b** (12.0 mg, 58.3 μmol , 58% isolated yield). Pale purple oil. ^1H NMR (400 MHz, CDCl_3) δ 2.40–2.36 (m, 2H), 2.15 (s, 3H), 1.95 (s, 3H), 1.70 (d, $J = 12.0$ Hz, 3H), 1.61 (d, $J = 12.0$ Hz, 3H), 1.45 (d, $J = 2.0$ Hz, 6H), 1.37–1.33 (m, 2H). ^{13}C NMR (100.6 MHz, CDCl_3) δ 210.1, 42.1, 37.7, 37.5, 37.0, 31.7, 29.9, 28.6. This data is in full agreement with the data previously published in the literature.²³

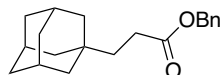
3-(Adamantan-1-yl)propanenitrile (31c)



Following the general procedure **B** using catalyst **A1** (10 mol %) under light irradiation (Figure S4-3), the crude was purified by flash column chromatography on silica gel (100:0–90:10, Hexane/AcOEt) and GPC (eluent: AcOEt) to give **31c** (2.8 mg, 14.8 μmol , 15% isolated yield). White solid. ^1H NMR (400 MHz, CDCl_3) δ 2.30–2.26 (m, 2H), 1.99 (br s, 3H), 1.72 (d, $J = 12.4$ Hz, 3H), 1.62 (d, $J = 12.4$ Hz, 3H), 1.51–1.47 (m, 8H). ^{13}C NMR (100.6 MHz, CDCl_3) δ 121.0, 41.6, 39.4, 36.8,

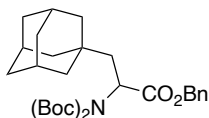
32.1, 28.3, 11.0. This data is in full agreement with the data previously published in the literature.²⁴

Phenylmethyl 3-(adamantan-1-yl)propanoate (**3ld**)



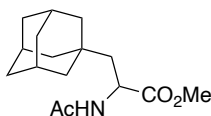
Following the general procedure **B** using catalyst **A1** (10 mol %) under light irradiation (Figure S4-3), the crude was purified by flash column chromatography on silica gel (100:0–70:30, Hexane/Et₂O) and GPC (eluent: AcOEt) to give **3ld** (5.0 mg, 16.8 μ mol, 17% isolated yield). Pink oil. ¹H NMR (400 MHz, CDCl₃) δ 7.39–7.31 (m, 5H), 5.11 (s, 2H), 2.34–2.30 (m, 2H), 1.94 (brs, 3H), 1.69 (d, J = 12.0 Hz, 3H), 1.60 (d, J = 12.0 Hz, 3H), 1.46–1.42 (m, 8H). ¹³C NMR (100.6 MHz, CDCl₃) δ 174.6, 136.1, 128.5, 128.22, 128.16, 66.1, 42.0, 38.9, 37.0, 31.9, 28.5, 28.2. This data is in full agreement with the data previously published in the literature.²⁵

Phenylmethyl 3-(adamantan-1-yl)-2-[bis[(1,1-dimethylethoxy)carbonyl]amino]propanoate (**3le**)



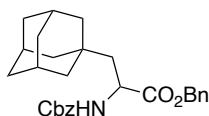
Following the general procedure **B** using catalyst **A1** (10 mol %) under light irradiation (Figure 4-S2), the crude was purified by flash column chromatography on silica gel (100:0–90:10, Hexane/AcOEt) to give **3le** (45.5 mg, 88.6 μ mol, 89% isolated yield). Brown oil. ¹H NMR (400 MHz, CD₃OD) δ 7.34 (m, 5H), 5.17–5.07 (m, 2H), 5.02 (d, J = 8.0 Hz, 1H), 2.06 (d, J = 15.2 Hz, 1H), 1.94 (brs, 3H), 1.74 (d, J = 12.0 Hz, 3H), 1.65 (d, J = 12.4 Hz, 3H), 1.59–1.50 (m, 7H), 1.43(s, 18H). ¹³C NMR (100.6 MHz, CD₃OD) δ 172.7, 153.5, 137.2, 129.5, 129.2, 129.1, 84.4, 68.0, 55.6, 45.1, 43.3, 38.0, 33.2, 30.0, 28.3. This data is in full agreement with the data previously published in the literature.²⁶

Methyl 2-acetylamino-3-(adamantan-1-yl)propanoate (**3lf**)



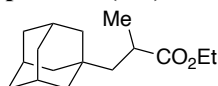
Following the general procedure **B** using catalyst **A5** (10 mol %) under light irradiation (Figure S4-3), the crude was purified by flash column chromatography on silica gel (100:0–0:100, Hexane/AcOEt) to give **3lf** (15.9 mg, 56.9 μ mol, 57% isolated yield). Dark green oil. IR (neat) 3283, 2901, 2848, 1748, 1653, 1436, 1375, 1219, 1201, 1175 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 5.73 (d, J = 8.0 Hz, 1H), 4.66 (ddd, J = 8.8, 8.8, 3.6 Hz, 1H), 3.72 (s, 3H), 2.00 (s, 3H), 1.96 (brs, 3H), 1.70 (d, J = 12.0 Hz, 3H), 1.63–1.59 (m, 4H), 1.53 (s, 6H), 1.34 (dd, J = 14.4, 8.8 Hz, 1H). ¹³C NMR (100.6 MHz, CDCl₃) δ 174.2, 169.4, 52.3, 48.4, 47.0, 42.3, 36.7, 32.7, 28.5, 23.3. HRMS–ESI (m/z): [M+H]⁺ calcd for C₁₆H₂₆NO₃⁺, 280.1907, found, 280.1893.

Phenylmethyl 3-(adamantan-1-yl)-2-phenylmethoxycarbonylaminopropanoate (**3lg**)



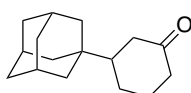
Following the general procedure **B** using catalyst **A1** (10 mol %) under light irradiation (Figure S4-3), the crude was purified by preparative thin layer chromatography on silica gel (75:25, Hexane/AcOEt) and GPC (eluent: AcOEt) to give **3lg** (13.8 mg, 30.8 μ mol, 31% isolated yield). Pale blue oil. **IR** (neat) 3345, 2901, 2847, 1724, 1454, 1344, 1310, 1214, 1185, 1049 cm^{-1} . **^1H NMR** (400 MHz, CDCl_3) δ 7.34–7.31 (m, 10H), 5.19–5.02 (m, 5H), 4.66 (ddd, $J = 8.8, 8.8, 3.2$ Hz, 1H), 1.92 (br s, 3H), 1.67 (d, $J = 12.0$ Hz, 3H), 1.63–1.57 (m, 4H), 1.51 (s, 6H), 1.32 (dd, $J = 14.4, 8.8$ Hz, 1H). **^{13}C NMR** (100.6 MHz, CDCl_3) δ 173.5, 155.6, 136.3, 135.4, 128.55, 128.49, 128.3, 128.14, 128.13, 128.0, 67.0, 66.9, 50.4, 46.9, 42.3, 36.7, 32.6, 28.4. **HRMS–ESI** (m/z): $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{28}\text{H}_{34}\text{NO}_4^+$, 448.2482, found, 448.2466.

Ethyl 3-(adamantan-1-yl)-2-methylpropanoate (**3lh**)



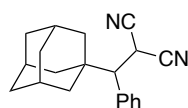
Following the general procedure **B** using catalyst **A5** (10 mol %) under light irradiation (Figure S4-3), the crude was purified by flash column chromatography on silica gel (100:0–95:5, Hexane/AcOEt) and GPC (eluent: AcOEt) to give **3lh** (6.3 mg, 25.2 μ mol, 25% isolated yield). Pale orange oil. **IR** (neat) 2975, 2901, 2848, 1735, 1452, 1377, 1303, 1217, 1184, 1155 cm^{-1} . **^1H NMR** (400 MHz, CDCl_3) δ 4.15–4.08 (m, 2H), 2.57–2.49 (m, 1H), 1.93 (brs, 3H), 1.76–1.59 (m, 7H), 1.50 (dd, $J = 12.0, 2.0$ Hz, 3H), 1.41 (d, $J = 12.0$ Hz, 3H), 1.26 (t, $J = 7.2$ Hz, 3H), 1.13 (d, $J = 7.2$ Hz, 3H), 1.02 (dd, $J = 14.0, 3.2$ Hz, 1H). **^{13}C NMR** (100.6 MHz, CDCl_3) δ 178.0, 60.1, 48.5, 42.3, 37.0, 34.3, 32.6, 28.6, 20.5, 14.2. **HRMS–ESI** (m/z): $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{16}\text{H}_{27}\text{O}_2^+$, 251.2006, found, 251.2017.

3-((3*r*,5*r*,7*r*)-Adamantan-1-yl)cyclohexan-1-one (**3li**)



Following the general procedure **B** using catalyst **A1** (10 mol %) under light irradiation (Figure S4-3), the crude was purified by flash column chromatography on silica gel (100:0–70:30, Hexane/AcOEt) and GPC (AcOEt) to give **3li** (7.35 mg, 43.2 μ mol, 32% isolated yield). White solid. **^1H NMR** (400 MHz, CDCl_3) δ 2.44 (m, 1H), 2.35 (m, 1H), 2.23 (m, 1H), 2.12–2.03 (m, 2H), 1.98–1.94 (m, 4H), 1.73–1.70 (m, 3H), 1.64–1.61 (m, 3H), 1.55–1.48 (m, 7H), 1.37–1.29 (m, 2H). **^{13}C NMR** (100.6 MHz, CDCl_3) δ 213.7, 49.7, 42.1, 41.6, 39.4, 37.2, 34.4, 28.6, 25.7, 24.6. This data is in full agreement with the data previously published in the literature.²⁷

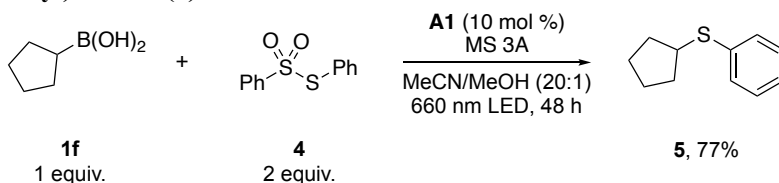
2-((Adamantan-1-yl)(phenyl)methyl)malononitrile (**3lj**)



Following the general procedure **B** using catalyst **A1** (10 mol %) under light irradiation (Figure S4-2), the crude was purified by flash column chromatography on silica gel (100:0–50:50, Hexane/Et₂O) give **3li** (28.7 mg, 98.8 μ mol, 98% isolated yield). Reddish brown solid. ¹H NMR (400 MHz, CDCl₃) δ 7.39 (brs, 5H), 4.25 (d, J = 5.2 Hz, 1H), 2.80 (d, J = 5.2 Hz, 1H), 2.02 (brs, 3H), 1.71–1.58 (m, 12H). ¹³C NMR (100.6 MHz, CDCl₃) δ 135.2, 129.6, 128.6, 128.5, 113.4, 113.3, 58.0, 40.3, 36.5, 36.3, 28.3, 23.7. This data is in full agreement with the data previously published in the literature.²⁸

■ Procedure for C–S bond formation procedure ■

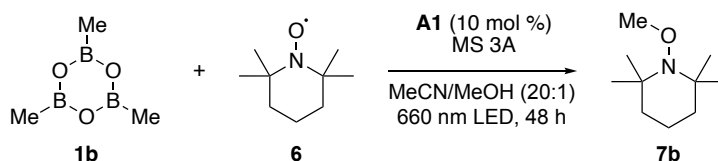
Cyclopentyl(phenyl)sulfane (**5**)



A1 (4.8 mg, 10 μ mol), **1f** (11.5 mg, 0.1 mmol) and **4** (50.4 mg, 0.2 mmol) were placed in an oven-dried screw-top 4 mL vial containing a magnetic stirring bar. The vial was then introduced into the nitrogen-filled glovebox and to this was added MS 3A (100 mg), dry MeCN (2 mL), and dry MeOH (100 μ L). The vial was sealed with Teflon[®]-coated silicon rubber septum, and the vial was then brought outside the glovebox. After 48 h stirring under photoradiation (Kessil PR160L 660 nm) (Figure S4-2), the solvent was removed under reduced pressure. The volatiles were purified by flash column chromatography on silica gel (100:0–95:5, Hexane/AcOEt) to give **5** (13.9 mg, 78.0 μ mol, 77% isolated yield). (63% isolated yield using 740 nm LED instead of 660 nm LED) Pink oil. ¹H NMR (400 MHz, CDCl₃) δ 7.36 (d, J = 8.0 Hz, 2H), 7.28 (t, J = 7.6 Hz, 2H), 7.17 (t, J = 7.6 Hz, 1H), 3.60 (quin, J = 6.4 Hz, 1H), 2.09–2.03 (m, 2H), 1.81–1.75 (m, 2H), 1.66–1.60 (m, 4H). ¹³C NMR (100.6 MHz, CDCl₃) δ 137.2, 129.9, 128.7, 125.8, 45.8, 33.5, 24.8. This data is in full agreement with the data previously published in the literature.²⁹

■ Procedure for C–O bond formation procedure ■

1-Methoxy-2,2,6,6-tetramethylpiperidine (**7b**)



A screw-top 4 mL vial was charged with a stirring bar and **A1** (4.7 mg, 10 μ mol) under ambient atmosphere. The vial was brought to a glovebox, MS 3A (100 mg), TEMPO **6** (15.6 mg, 0.1 mmol), dry MeCN (2 mL), and dry MeOH (100 μ L) and trimethylboroxine **1b** (13.9 μ L, 0.1 mmol) were added. After the vial was removed from the glovebox and sealed with Teflon tape, the vial was placed in EvoluChem photoreactor equipped with two red LEDs (660 nm) and stirred for 48 h. The volatiles were removed under reduced pressure. The residue was dissolved in CDCl₃ and added 1,1,2,2-tetrachloroethane (14.3 mg, 85.2 μ mol) as an internal standard. ¹H NMR (400 MHz) yield of **7b** (40%) was obtained by comparing the relative value of integration for the peak observed at 3.61 ppm of **7b** with that of 1,1,2,2-tetrachloroethane observed at 5.98 ppm (Figure S4-6).³⁰

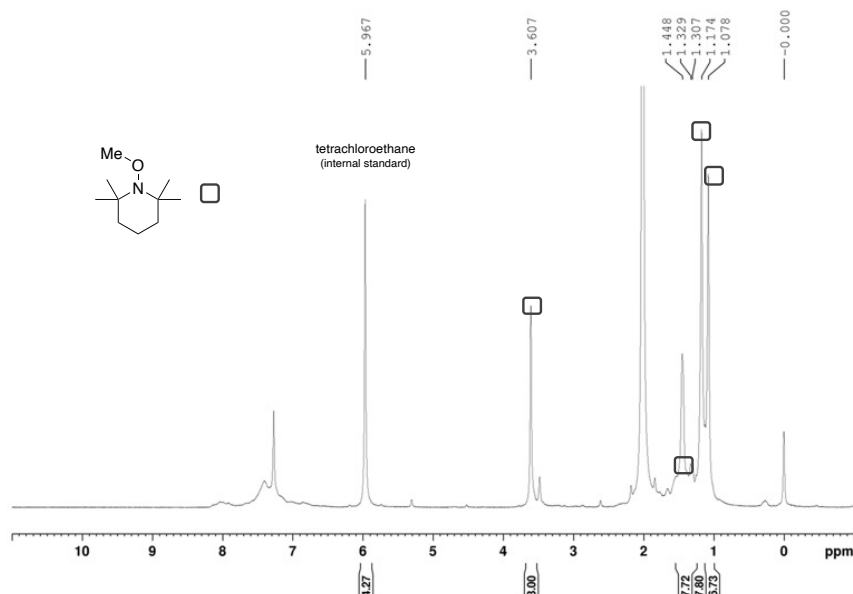
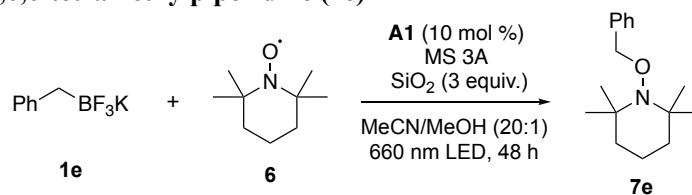


Figure S4-6. ^1H NMR analysis.

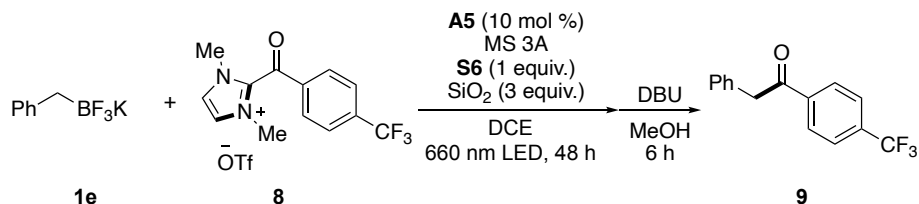
1-(Benzyloxy)-2,2,6,6-tetramethylpiperidine (7e)



A screw-top 4 mL vial was charged with a stirring bar, **A1** (4.7 mg, 10 μmol), **1e** (24.6 mg, 0.15 mmol) and SiO_2 (18.0 mg, 0.30 mmol) under ambient atmosphere. The vial was brought to a glovebox, MS 3A (100 mg), TEMPO **6** (15.6 mg, 0.1 mmol), dry MeCN (2 mL), and dry MeOH (100 μL) were added. After the vial was removed from the glovebox and sealed with Teflon tape, the vial was placed in EvoluChem photoreactor equipped with two red LEDs (660 nm) and stirred for 48 h. The volatiles were purified by flash column chromatography on silica gel (100:0–85:15, Hexane/ Et_2O) to give **5** (21.0 mg, 85.0 μmol , 85% isolated yield). Colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 7.37–7.26 (m, 5H), 4.83 (s, 2H), 1.60–1.46 (m, 5H), 1.34 (m, 1H), 1.26 (s, 6H), 1.15 (s, 6H). ^{13}C NMR (100.6 MHz, CDCl_3) δ 138.3, 128.2, 127.4, 127.3, 78.7, 60.0, 39.7, 33.1, 20.3, 17.1. This data is in full agreement with the data previously published in the literature.³¹

■ Procedure for Radical–radical Coupling Reaction ■

2-Phenyl-1-(4-(trifluoromethyl)phenyl)ethan-1-one (9)

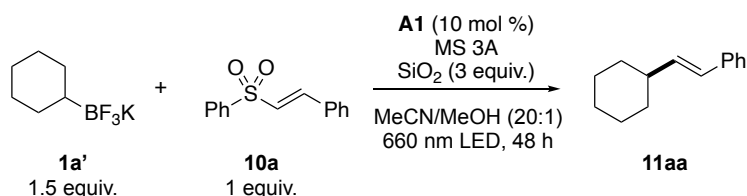


A5 (4.4 mg, 10 μ mol), **1e** (29.7 mg, 0.15 mmol), **8** (41.8 mg, 0.1 mmol), and SiO_2 (18.0 mg, 0.3 mmol) were placed in an oven-dried screw-top 4 mL vial containing a magnetic stirring bar. The vial was then introduced into the nitrogen-filled glovebox and to this was added MS 3A (100 mg), **S6** (25.7 mg, 0.1 mmol), and dry DCE (2 mL). The vial was sealed with Teflon[®]-coated silicon rubber septum and Teflon tape, and the vial was then brought outside the glovebox. After 48 h stirring under photoirradiation (Kessil PR160L 660 nm), the reaction was then added MeOH (2 mL) and stirred for 20 min. The reaction mixture was azeotroped twice with MeOH. Then, this was added MeOH (8 mL) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 1 mmol). After 6 h stirring, the reaction mixture was quenched with AcOH (2 mmol), then the solvent was removed under reduced pressure. The crude was purified by flash column chromatography on silica gel (100:0–95:5, Hexane/AcOEt) to give **9** in 29% yield. Pale orange solid. ¹H NMR (400 MHz, CDCl_3) δ 8.11 (d, J = 8.4 Hz, 2H), 7.72 (d, J = 8.4 Hz, 2H), 7.36–7.33 (m, 2H), 7.29–7.25 (m, 2H), 4.31 (s, 3H). ¹³C NMR (100.6 MHz, CDCl_3) δ 196.6, 139.1, 134.4 (d, $J_{\text{C-F}}$ = 32.7 Hz), 133.7, 129.4, 128.9, 128.8, 127.2, 125.7 (q, $J_{\text{C-F}}$ = 3.7 Hz), 123.5 (d, $J_{\text{C-F}}$ = 272.6 Hz), 45.8. ¹⁹F NMR (376.5 MHz, CDCl_3) δ –63.1. This data is in full agreement with the data previously published in the literature.³²

■ Procedure for C(sp²)–C(sp³) and C(sp)–C(sp³) bonds formation ■

C(sp²)–C(sp³) bond formation procedure

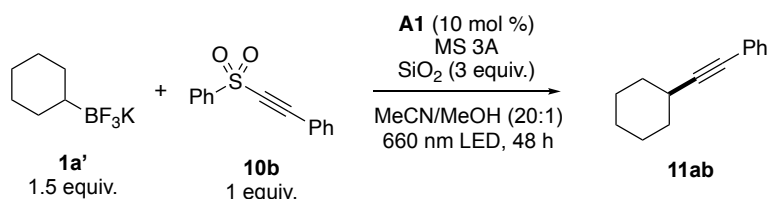
(E)-(2-Cyclohexylvinyl)benzene (11aa)



1a' (28.5 mg, 0.15 mmol), **10a** (24.4 mg, 0.1 mmol), **A1** (4.8 mg, 10 μ mol), and SiO_2 (0.3 mmol) were placed in an oven-dried screw-top 4 mL vial containing a magnetic stirring bar. The vial was then introduced into the nitrogen-filled glovebox and to this was added MS 3A (100 mg), dry MeCN (2 mL), and dry MeOH (100 μ L). The vial was sealed with Teflon[®]-coated silicon rubber septum, and the vial was then brought outside the glovebox. After 48 h stirring under photoirradiation (Kessil PR160L 660 nm) (Figure S4-3), the solvent was removed under reduced pressure. The volatiles were purified by flash column chromatography on silica gel (Hexane only) to give **11aa** (6.3 mg, 33.8 μ mol, 34% isolated yield). Colorless oil. ¹H NMR (400 MHz, CDCl_3) δ 7.36–7.26 (m, 4H), 7.18 (m, 1H), 6.34 (d, J = 16.0 Hz, 1H), 6.17 (dd, J = 16.0, 6.8 Hz, 1H), 2.13 (m, 1H), 1.82–1.65 (m, 5H), 1.38–1.13 (m, 5H). ¹³C NMR (100.6 MHz, CDCl_3) δ 138.0, 136.9, 128.4, 127.2, 126.7, 125.9, 41.1, 32.9, 26.2, 26.0. This data is in full agreement with the data previously published in the literature.³³

C(sp²)-C(sp) bond formation procedure

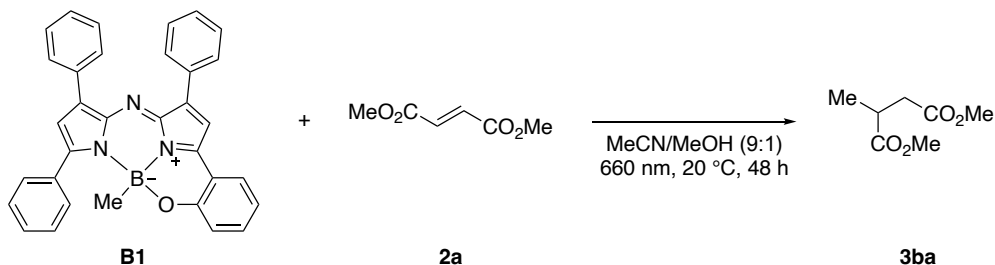
1-Cyclohexyl-2-phenylethyne (**11ab**)



1a' (28.5 mg, 0.15 mmol), **10b** (24.2 mg, 0.1 mmol), **A1** (4.8 mg, 10 μmol), and SiO_2 (0.3 mmol) were placed in an oven-dried screw-top 4 mL vial containing a magnetic stirring bar. The vial was then introduced into the nitrogen-filled glovebox and to this was added MS 3A (100 mg), dry MeCN (2 mL), and dry MeOH (100 μL). The vial was sealed with Teflon[®]-coated silicon rubber septum, and the vial was then brought outside the glovebox. After 48 h stirring under photoirradiation (Kessil PR160L 660 nm) (Figure S4-3), the solvent was removed under reduced pressure. The volatiles were purified by flash column chromatography on silica gel (Hexane only) to give **11ab** (7.37 mg, 40.0 μmol , 40% isolated yield). Colorless oil. ¹H NMR (400 MHz, CDCl_3) δ 7.41–7.38 (m, 2H), 7.30–7.25 (m, 3H), 2.58 (m, 1H), 1.89–1.86 (m, 2H), 1.78–1.74 (m, 2H), 1.58–1.50 (m, 3H), 1.38–1.33 (m, 3H). ¹³C NMR (100.6 MHz, CDCl_3) δ 131.6, 128.1, 127.4, 124.1, 94.5, 80.5, 32.7, 29.7, 25.9, 24.9. This data is in full agreement with the data previously published in the literature.³⁴

■ Mechanistic Studies ■

Giese addition from B1



A screw-top 4 mL vial was charged with a stirring bar and borate **B1** (24.5 mg, 50 μmol) and **2a** (2.9 mg, 20 μmol) under ambient atmosphere. The vial was brought to a glovebox, and dry MeCN (400 μL) and dry MeOH (20 μL) were added. After the vial was removed from the glovebox and sealed with Teflon tape, the vial was placed in UC Reactor equipped with two red LEDs (740 nm) and stirred for 48 h at 20 °C. The volatiles were removed under reduced pressure. The residue was dissolved in CDCl_3 and added 1,1,2,2-tetrachloroethane (12.2 mg, 72.7 μmol) as an internal standard. ¹H NMR (400 MHz) yield of **3ba** (46%) was obtained by comparing the relative value of integration for the peak observed at 3.70 ppm of **3ba** with that of 1,1,2,2-tetrachloroethane observed at 5.98 ppm (Figure S4-7).¹⁹ The generation of **3ba** was also confirmed by observation of the corresponding molecular ion peak with GC-MS analysis.

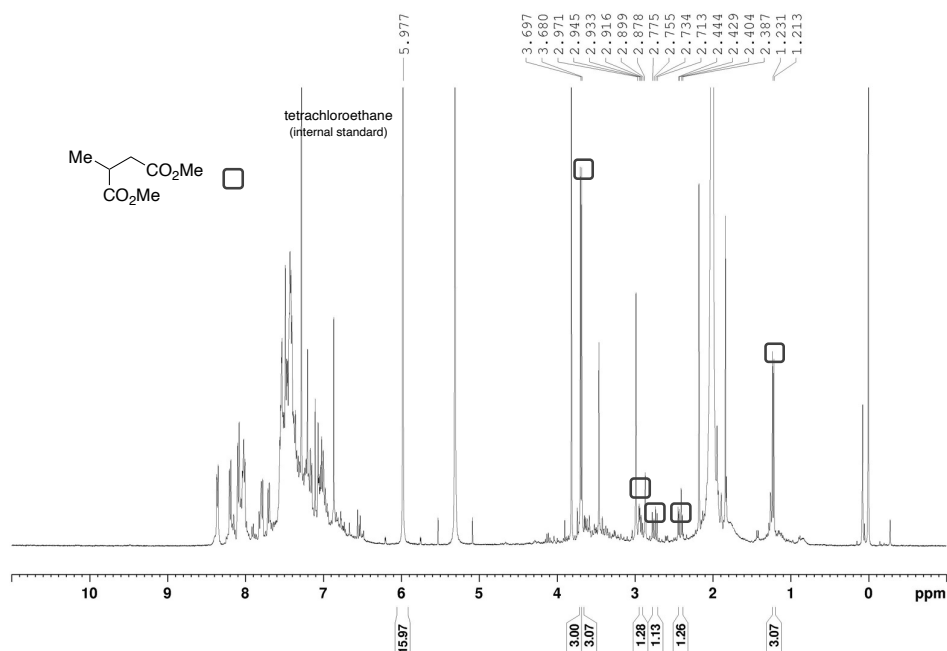
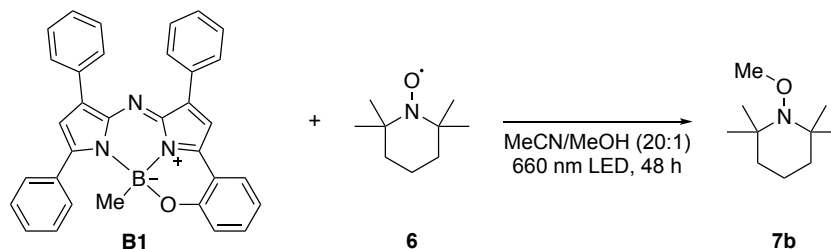


Figure S4-7. ^1H NMR analysis.

*C–O bond formation using **B1** and TEMPO*



A screw-top 4 mL vial was charged with a stirring bar and **B1** (24.5 mg, 50 μmol) under ambient atmosphere. The vial was brought to a glovebox, TEMPO (7.8 mg, 50 μmol), dry MeCN (1 mL), and dry MeOH (50 μL) were added. After the vial was removed from the glovebox and sealed with Teflon tape, the vial was placed in EvoluChem photoreactor equipped with two red LEDs (660 nm) and stirred for 48 h. The volatiles were removed under reduced pressure. The residue was dissolved in CDCl_3 and added 1,1,2,2-tetrachloroethane (17.5 mg, 104.3 μmol) as an internal standard. ^1H NMR (400 MHz) yield of **7b** (59%) was obtained by comparing the relative value of integration for the peak observed at 3.61 ppm of **7b** with that of 1,1,2,2- tetrachloroethane observed at 6.03 ppm (Figure S4-8).³⁰ The generation of **3aa** was also confirmed by observation of the corresponding molecular ion peak with GC-MS analysis.

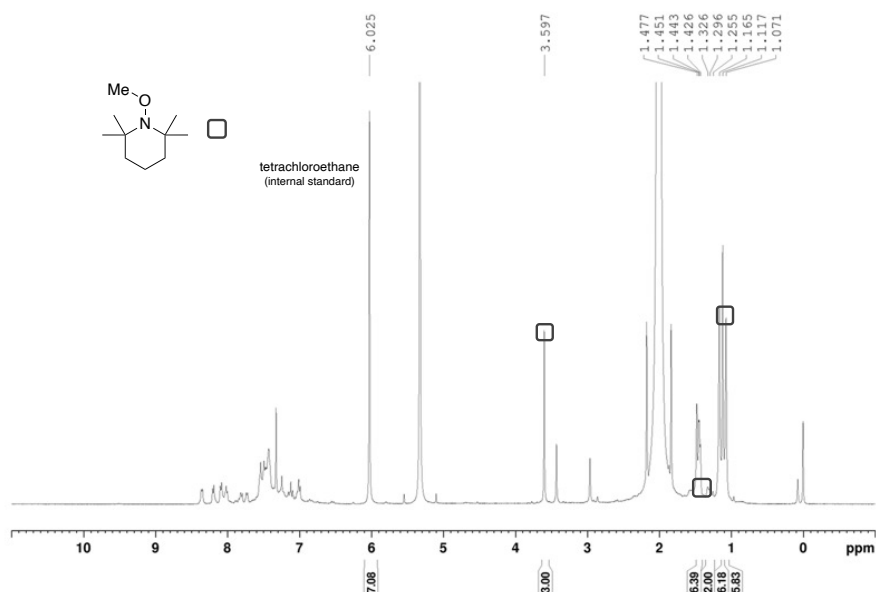
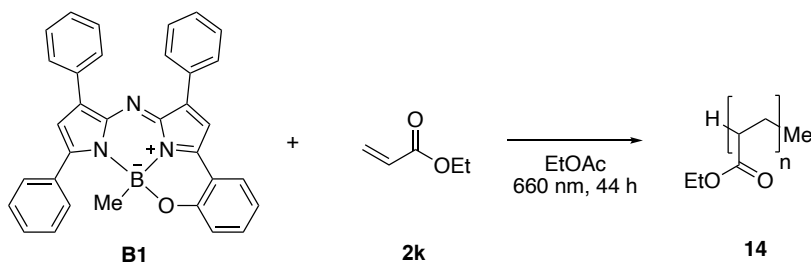


Figure S4-8. ^1H NMR analysis.

Radical polymerization



A screw-top 4 mL vial was charged with a stirring bar and borate **B1** (23.3 mg, 0.05 mmol) and **2k** (636 μL , 6.0 mmol) under ambient atmosphere. The vial was brought to a glovebox, and dry EtOAc (400 μL) was added. After the vial was removed from the glovebox and sealed with Teflon tape, the vial was placed in EvoluChem photoreactor equipped with two red LEDs (660 nm) for 44 h. The volatiles were removed under reduced pressure. GPC (CHCl_3) to give **14** (17.8 mg, 6.0 μmol , 12%, isolated yield). M_n and M_w are determined by GPC analysis.

$$M_n = 3047$$

$$M_w = 4756$$

$$M_w/M_n = 1.56$$

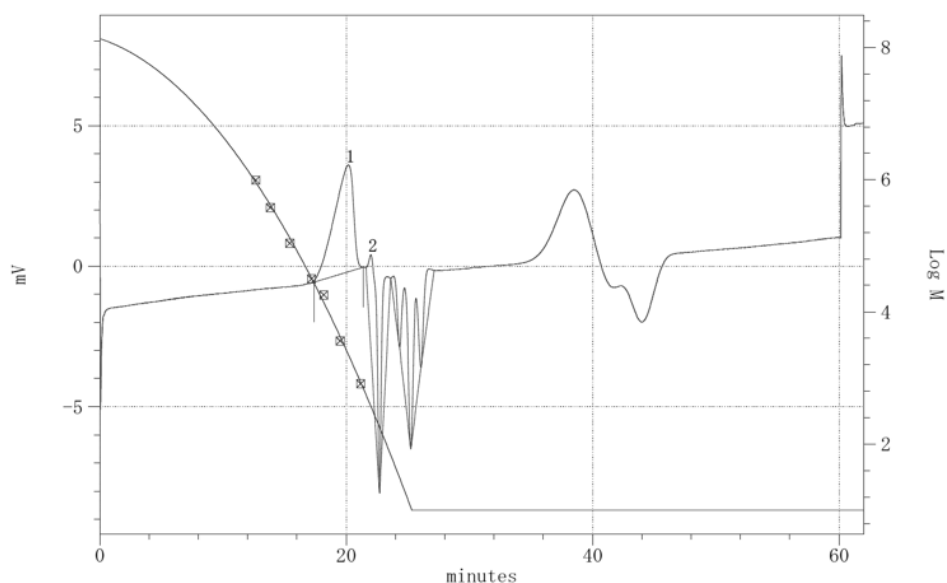
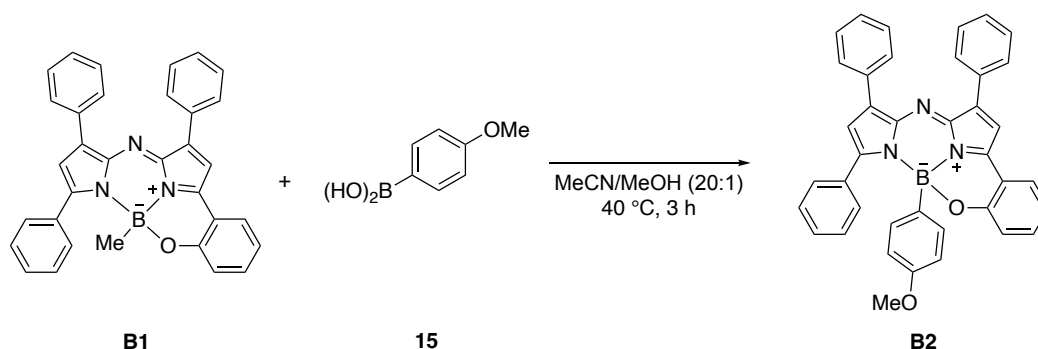


Figure S4-9. GPC analysis.

Exchange experiment between **B1** and ary boronic acid **1b**.



B1 (24.5 mg, 50 μmol) and 4-methoxyphenyl boronic acid **15** (22.8 mg, 150 μmol) were placed in an oven-dried screw-top 4 mL vial containing a magnetic stirring bar. The vial was then introduced into the nitrogen-filled glovebox and to this was added dry MeCN (2 mL), and dry MeOH (100 μL). The vial was sealed with Teflon[®]-coated silicon rubber septum and Teflon tape, and the vial was then brought outside the glovebox. The vial was placed in aluminum heating block at 40 $^{\circ}\text{C}$ and stirred for 3 h. After cooling to room temperature, the reaction crude was concentrated under reduced pressure. The residue was dissolved in CDCl_3 and added 1,1,2,2-tetrachloroethane (14.5 mg, 86.4 μmol) as an internal standard. ^1H NMR (400 MHz) yield of **B2** (54%) was obtained by comparing the relative value of integration for the peak observed at 3.60 ppm of **7b** with that of 1,1,2,2-tetrachloroethane observed at 5.95 ppm (Figure S4-10).

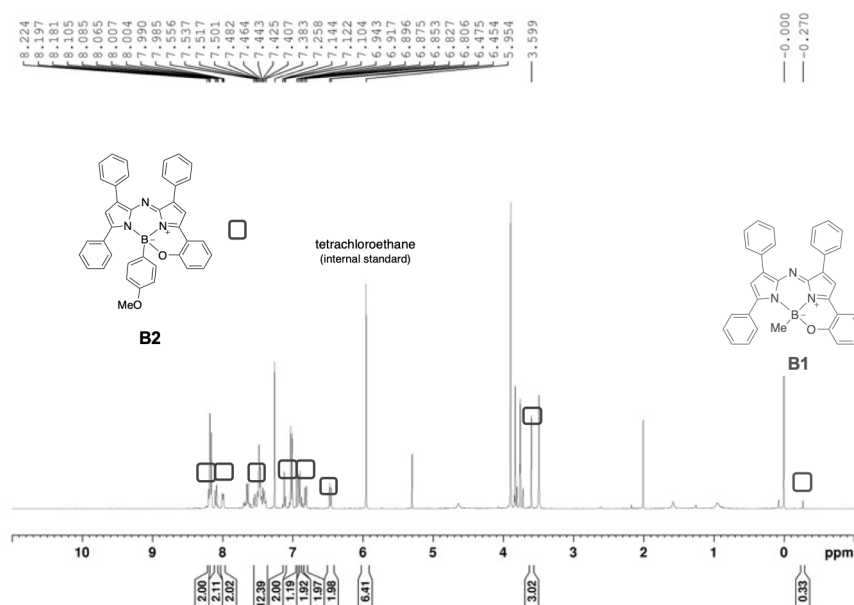
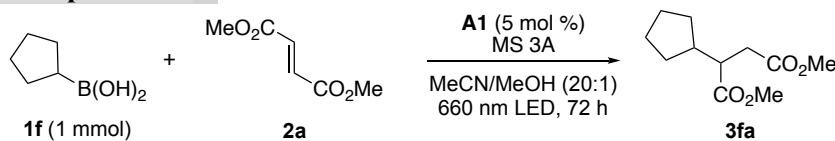


Figure S4-10. ^1H NMR analysis.

Large-scale Experiments



A1 (23.3 mg, 50 μmol), **1f** (170.9 mg, 1.5 mmol) and dimethyl fumarate **2a** (144.1 mg, 1.0 mmol) were placed in an oven-dried screw-top 4 mL vial containing a magnetic stirring bar. The vial was then introduced into the nitrogen-filled glovebox and to this was added MS 3A (100 mg), dry MeCN (2 mL), and dry MeOH (100 μL). The vial was sealed with Teflon[®]-coated silicon rubber septum and Teflon tape, and the vial was then brought outside the glovebox. After 72 h stirring under photoirradiation (Kessil PR160L 660 nm), the solvent was removed under reduced pressure. The crude was purified by flash column chromatography on silica gel (95:5–85:15, Hexane/Et₂O) to give **3fa** (145.2 mg, 677.7 μmol , 68% isolated yield).



Figure S4-11. Light set up for large-scale reaction.

■ X-ray Diffraction Analysis ■

A suitable crystal obtained by recrystallization was mounted with mineral oil on a Cargille Immersion Oil Type B and transferred to Bruker Single Crystal CCD X-ray Diffractometer (SMART APEX II) (Graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å)). Cell parameters were determined and refined, and raw frame data were integrated using APEX 3 (Bruker) and a multi-scan absorption correction using an empirical method was applied. The structures were solved by direct methods with SHELXT and refined by full-matrix least-squares techniques against F^2 (SHELXL-2018/3) by using Yadokari-XG software package. Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre.

Molecular structure of borate **B1** (CCDC2455734)

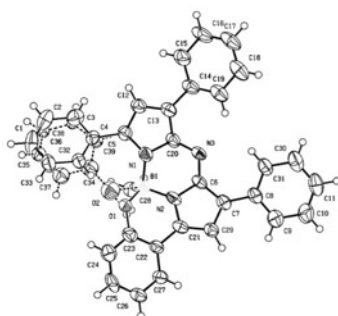


Figure S4-12. ORTEP diagram of **borate B1**. Ellipsoids are drawn at 50% probability. A single crystal used for the analysis was obtained by recrystallization from Hexane/DCM.

	borate B1
CCDC No.	2455734
formula	C ₃₃ H ₂₄ BN ₃ O
fw	489.36
<i>T</i> (K)	87(2)
λ (Å)	0.71073
cryst syst	monoclinic
space group	P2 ₁ /n
<i>a</i> (Å)	10.46(2)
<i>b</i> (Å)	15.06(3)
<i>c</i> (Å)	15.58(3)
α (deg)	90
β (deg)	104.32(3)
γ (deg)	90
<i>V</i> (Å ³)	2378(8)
<i>Z</i>	4
<i>D</i> _{calc} (g·cm ⁻³)	1.367
μ (mm ⁻¹)	0.083
<i>F</i> (000)	1024
cryst size (mm ³)	0.050 × 0.120 × 0.170
2 θ range (deg)	2.39 to 24.94
reflns collected	9299
params	349
GOF on F^2	1.075
<i>R</i> ₁ , <i>wR</i> ₂ (all data)	0.1067, 0.2460

Table S4-1. Crystallographic data and structure refinement details of borate **B1**.

Molecular structure of A2 (CCDC2455736)

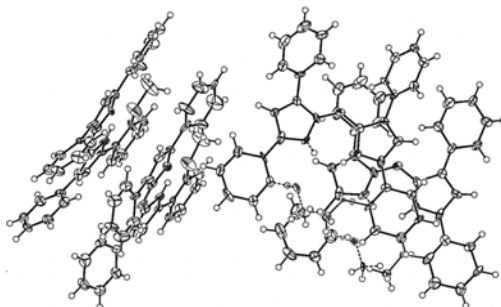


Figure S4-13. ORTEP diagram of **A2**. Ellipsoids are drawn at 50% probability. A single crystal used for the analysis was obtained by recrystallization from DCM.

	A2
CCDC No.	2455736
formula	C ₃₃ H ₂₅ N ₃ O
fw	479.56
<i>T</i> (K)	86(2)
λ (Å)	0.71073
cryst syst	monoclinic
space group	Cc
<i>a</i> (Å)	38.421(11)
<i>b</i> (Å)	9.881(3)
<i>c</i> (Å)	25.891(8)
α (deg)	90
β (deg)	98.581(4)
γ (deg)	90
<i>V</i> (Å ³)	9719(5)
<i>Z</i>	4
<i>D</i> _{calc} (g·cm ⁻³)	1.311
μ (mm ⁻¹)	0.080
<i>F</i> (000)	4032
cryst size (mm ³)	0.080 × 0.100 × 0.130
2 θ range (deg)	2.48 to 25.02
reflns collected	22936
params	1381
GOF on <i>F</i> ²	0.804
<i>R</i> ₁ , <i>wR</i> ₂ (all data)	0.0683, 0.2440

Table S4-2. Crystallographic data and structure refinement details of **A2**.

Molecular structure of A5 (CCDC 2455735)

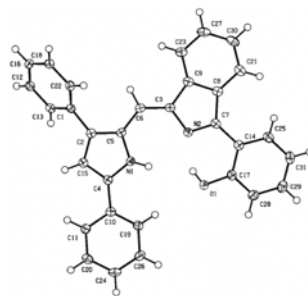


Figure S4-14. ORTEP diagram of **A5**. Ellipsoids are drawn at 50% probability. A single crystal used for the analysis was obtained by recrystallization from DCM.

	A5
CCDC No.	2455735
formula	C ₃₁ H ₂₂ N ₂ O
fw	438.51
<i>T</i> (K)	86(2)
λ (Å)	0.71073
cryst syst	triclinic
space group	P-1
<i>a</i> (Å)	7.4678(8)
<i>b</i> (Å)	11.6036(13)
<i>c</i> (Å)	13.0974(15)
α (deg)	82.6550(10)
β (deg)	74.6990(10)
γ (deg)	87.6980(10)
<i>V</i> (Å ³)	1085.7(2)
<i>Z</i>	2
<i>D</i> _{calc} (g·cm ⁻³)	1.341
μ (mm ⁻¹)	0.081
<i>F</i> (000)	460
cryst size (mm ³)	0.082 × 0.236 × 0.254
2 θ range (deg)	2.25 to 25.10
reflns collected	10707
params	316
GOF on <i>F</i> ²	1.028
<i>R</i> ₁ , <i>wR</i> ₂ (all data)	0.0326, 0.0841

Table S4-3. Crystallographic data and structure refinement details of **A5**.

■ Computational Analysis ■

To gain the deep mechanistic insight into C–B bond cleavage, the computational studies were performed. All the restricted and unrestricted density functional theory (DFT) calculations were performed with the Gaussian 16 package.³⁶

■ Computational Study of the excited singlet state of **B1** ■

Kohn–Sham orbitals of singlet excited state of **B1** was calculated using the TD-B3LYP³⁷ method with 6-311++G(d,p) basis set with SMD model (MeCN).

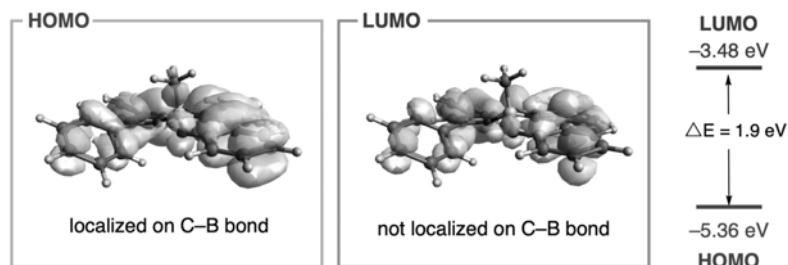


Figure S4-15. Kohn–Sham orbitals of **B1** in the singlet excited states, calculated at the TD-B3LYP/6-311++G(d,p) level.

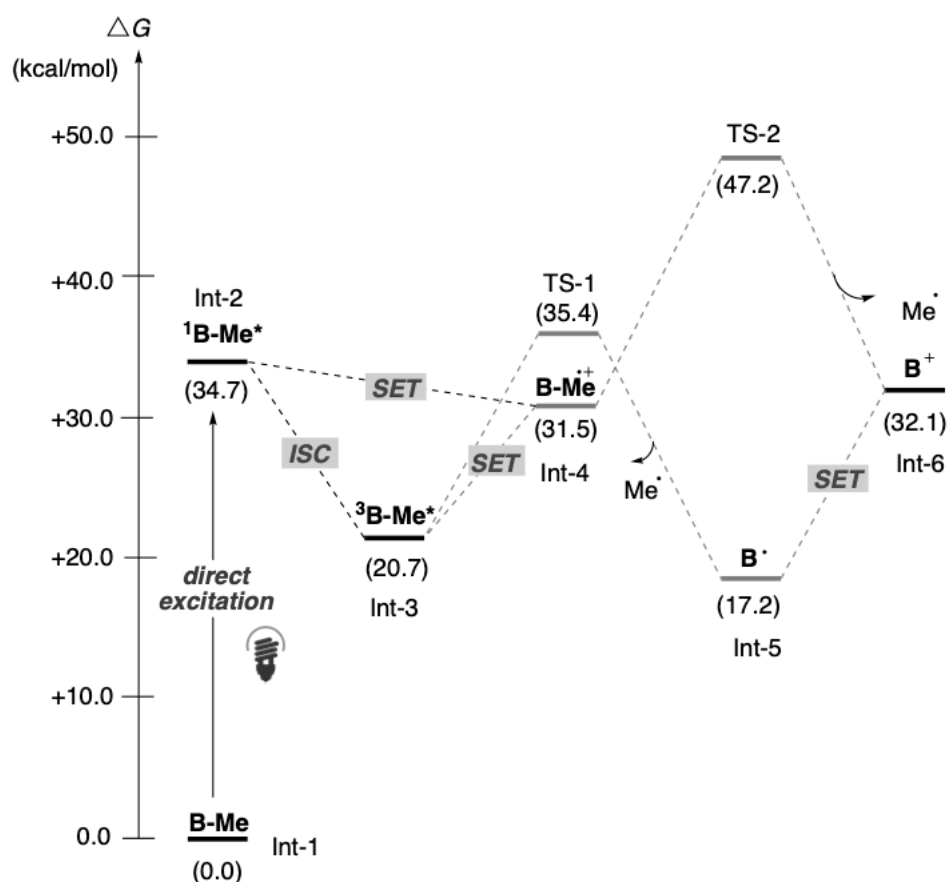
Cartesian coordinates of excited singlet state of **B1**

C	1.07453300	-1.04635400	0.23470100
N	1.43729800	0.24872400	0.17797400
C	0.47024100	1.15758700	0.04947000
C	1.87660800	-2.25893300	0.11591000
C	0.95810900	-3.31702100	0.10194100
C	-0.33826900	-2.77719700	0.21513400
N	-0.22438700	-1.41015400	0.32745200
C	0.67489600	2.59292400	-0.03250000
N	-0.91055200	0.89627800	0.02504600
C	-1.55436600	2.11643600	-0.04217900
C	-0.59740900	3.15216500	-0.05555300
C	-1.65271900	-3.32173500	0.10436100
C	-1.91338500	-4.70940100	0.05048800
C	-3.19356400	-5.18364700	-0.15572200
C	-4.26052700	-4.27677100	-0.32474100
C	-4.04312100	-2.91092100	-0.27347000
C	-2.75123300	-2.40224000	-0.05001300
O	-2.58982500	-1.08159800	-0.02066600
B	-1.39409400	-0.47097100	0.64901800
C	-1.69390900	-0.31935300	2.23220600
C	-2.98638600	2.32541600	-0.18465600
C	-3.80905600	1.46759200	-0.94432800
C	-5.16249900	1.74285300	-1.10213100
C	-5.73012500	2.87309200	-0.50980300
C	-4.92595600	3.73843300	0.23801500
C	-3.57183000	3.47517400	0.39380600
C	1.94307700	3.31267400	-0.08800000
C	1.99933600	4.66153400	0.32738600
C	3.18469200	5.38362800	0.26180600
C	4.35090000	4.78363900	-0.22138800
C	4.31297200	3.45210200	-0.63845700
C	3.12905700	2.72320300	-0.57329500
C	3.32572900	-2.35083900	-0.01445500
C	4.17306300	-1.27181500	0.31696100
C	5.55563300	-1.38904000	0.20748500
C	6.13369500	-2.57940600	-0.23571600
C	5.30916400	-3.65808900	-0.56944600
C	3.92857000	-3.54757700	-0.46220600
H	1.18338900	-4.36634600	-0.00616800
H	-0.83797700	4.19666300	-0.18015600
H	-1.08789800	-5.40155200	0.17204800
H	-3.38029700	-6.25053700	-0.19000400
H	-5.26430300	-4.65253400	-0.48958900
H	-4.85857100	-2.20781400	-0.39648800
H	-3.37650500	0.60254600	-1.42512000
H	-5.77647200	1.07865000	-1.70061600
H	-6.78676900	3.08231900	-0.63482500
H	-5.35889800	4.61710700	0.70326500
H	-2.96008300	4.14413200	0.98758900
H	1.10845200	5.13822800	0.71986300
H	3.20243000	6.41587600	0.59444200

H	5.27592300	5.34736700	-0.27076100
H	5.21010600	2.97858100	-1.02270000
H	3.11283200	1.69581100	-0.90859100
H	3.73935500	-0.34516200	0.66707100
H	6.18486900	-0.54642600	0.47351500
H	7.21105900	-2.66738400	-0.32186500
H	5.74602700	-4.58682300	-0.92041700
H	3.30832400	-4.39166700	-0.73978800
H	-0.82982700	0.07937000	2.77633700
H	-2.53693300	0.35943900	2.40608100
H	-1.95120700	-1.28481100	2.68415300

■Computational Study of TS calculation ■

The method TD-B3LYP³⁷ method with 6-31+G(d,p) basis set with SMD model (MeCN) was used for the geometry optimization, normal vibrational mode analysis of singlet excited states of **B1 (B-Me)**. The method (UO)B3LYP³⁷ functional with the 6-31+G(d,p) basis set with SMD model (MeCN) was used for the geometry optimization, normal vibrational mode analysis of triplet excited states of **B1 (B-Me)**. The method (U)B3LYP³⁷ functional with the 6-31+G(d,p) basis set with SMD model (MeCN) was used for the TS calculations and the geometry optimization, normal vibrational mode analysis other than singlet and triplet excited states of **B1 (B-Me)**. The IRC calculations were performed for each transition state to confirm the transition state connecting the reaction pathway between the starting materials and the products.



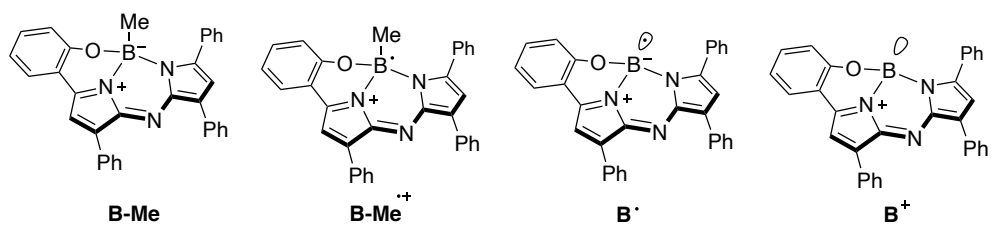
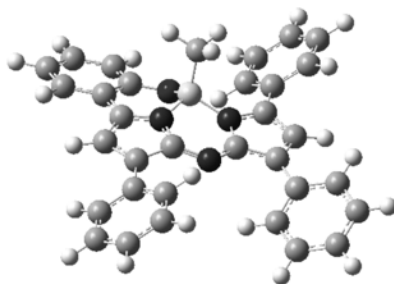


Figure S4-16. Energy diagram of C–B bond cleavage.

	E (hartree)	G _{corr} (hartree)	Gibbs (hartree)	Gibbs (kcal/mol)	Δ G (kcal/mol)
B-Me	-1536.553085	0.425788	-1536.127297	-963935.2401	
EA radical	-574.286146	0.133758	-574.152388	-360286.365	
Int-1 total				-1324221.605	0
¹ B-Me*	-1536.494899	0.422839	-1536.07206	-963900.5784	
EA radical	-574.286146	0.133758	-574.152388	-360286.365	
Int-2 total				-1324186.943	34.66176987
³ B-Me*	-1536.516969	0.422615	-1536.094354	-963914.5681	
EA radical	-574.286146	0.133758	-574.152388	-360286.365	
Int-3 total				-1324200.933	20.67206193
TS-1	-1536.491017	0.420093	-1536.070924	-963899.8655	
EA radical	-574.286146	0.133758	-574.152388	-360286.365	
TS-1 total				-1324186.231	35.37462123
B-Me ^{•+}	-1536.365256	0.42502	-1535.940236	-963817.8575	
EA anion	-574.423027	0.133819	-574.289208	-360372.2209	
Int-4 total				-1324190.078	31.52672991
TS-2	-1536.337744	0.422416	-1535.915328	-963802.2275	
EA anion	-574.423027	0.133819	-574.289208	-360372.2209	
TS-2 total				-1324174.448	47.15674899
B [•]	-1496.655197	0.389476	-1496.265721	-938921.7026	
Me radical	-39.845686	0.011516	-39.83417	-24996.34002	
EA radical	-574.286146	0.133758	-574.152388	-360286.365	
Int-5 total				-1324204.408	17.19753906
B ⁺	-1496.49804	0.392811	-1496.105229	-938820.9922	
Me radical	-39.845686	0.011516	-39.83417	-24996.34002	
EA anion	-574.423027	0.133819	-574.289208	-360372.2209	
Int-6 total				-1324189.553	32.05195578

Table S4-4. Gibbs energies of each intermediate.

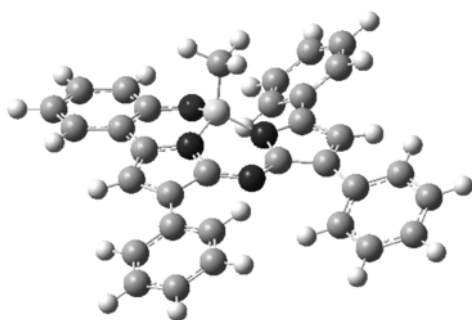
Cartesian coordinates of **B-Me**



0 1			
C	1.08887800	-1.01505200	0.28783000
N	1.39879800	0.25974200	0.14464400
C	0.42235900	1.15922100	0.00135300
C	1.93004900	-2.19924400	0.22350300
C	1.05480100	-3.27893900	0.15562400
C	-0.27873200	-2.76732300	0.20240300
N	-0.22475200	-1.42895400	0.32877700
C	0.61633600	2.57468300	-0.13940400
N	-0.96258200	0.88398300	0.03364500
C	-1.60668100	2.08683700	-0.03814500
C	-0.65902400	3.13203300	-0.14163100
C	-1.57662000	-3.36834600	0.01442200
C	-1.78716300	-4.76273500	-0.00009100
C	-3.03162500	-5.29013100	-0.31920500
C	-4.08567800	-4.42018700	-0.65081900
C	-3.90331900	-3.03956000	-0.64773500
C	-2.65965300	-2.48740600	-0.29686900
O	-2.51801300	-1.14849700	-0.31498200
B	-1.46288500	-0.52904300	0.54669200
C	-1.92699400	-0.44954500	2.09249700
C	-3.06144600	2.30111300	-0.04172500
C	-3.95426800	1.47799500	-0.75392300
C	-5.32042300	1.76620700	-0.77247600
C	-5.82144400	2.87380800	-0.08121700
C	-4.94249200	3.70261100	0.62583300
C	-3.57610400	3.42480800	0.63990500
C	1.88934600	3.29794400	-0.26678800
C	1.99543000	4.61378500	0.23035100
C	3.18285300	5.33483600	0.10065700
C	4.29175100	4.75890100	-0.52980400
C	4.19914100	3.45625200	-1.03128900
C	3.01252500	2.73158000	-0.90335800
C	3.39594000	-2.23704800	0.17425600
C	4.17596800	-1.22100500	0.76356900
C	5.57010600	-1.28418800	0.72905300
C	6.21420700	-2.35989100	0.10888200
C	5.45129100	-3.37605700	-0.47867800
C	4.05825400	-3.31585500	-0.44800600
H	1.31869900	-4.32325300	0.06562200
H	-0.91076600	4.17431500	-0.27853400
H	-0.95785600	-5.42180000	0.24089600
H	-3.18752900	-6.36436100	-0.31923100
H	-5.06021900	-4.82641000	-0.90771200
H	-4.71840800	-2.36822700	-0.90002100
H	-3.57703200	0.62158100	-1.29725400
H	-5.99395200	1.12534400	-1.33473900
H	-6.88557700	3.09204500	-0.09586900
H	-5.32105000	4.56451900	1.16804800
H	-2.90239600	4.06865900	1.19709700
H	1.14664400	5.06593900	0.73499600
H	3.24398000	6.34472400	0.49680500
H	5.21651000	5.32000500	-0.63091200
H	5.05111300	3.00320200	-1.53081300

H	2.94913200	1.72880700	-1.30950300
H	3.68798000	-0.38967100	1.25985200
H	6.15349900	-0.49410000	1.19361000
H	7.29926500	-2.40688100	0.08352200
H	5.94211000	-4.21294100	-0.96762600
H	3.47757900	-4.10077400	-0.92313500
H	-1.13652200	-0.04605200	2.74014100
H	-2.80800100	0.19474100	2.21280700
H	-2.19433900	-1.44023900	2.48505800

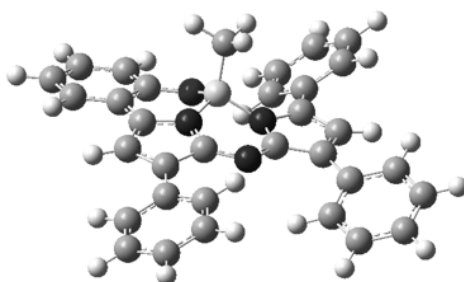
Cartesian coordinates of singlet excited state of **B-Me**



0 1			
C	1.07359800	-1.05252100	0.22836800
N	1.44268200	0.24440800	0.17684400
C	0.47588000	1.15866200	0.05133300
C	1.87178800	-2.26822900	0.10633600
C	0.94675100	-3.32482500	0.09096400
C	-0.34863200	-2.77855600	0.20713100
N	-0.22921000	-1.41026600	0.32053800
C	0.68559900	2.59466000	-0.02804300
N	-0.90718700	0.89924700	0.02412900
C	-1.54861100	2.12214400	-0.04500100
C	-0.58813300	3.15797400	-0.05465500
C	-1.66901900	-3.31737900	0.10505200
C	-1.93803700	-4.70576500	0.05091200
C	-3.22703300	-5.17393300	-0.14142100
C	-4.29373800	-4.25924200	-0.29511800
C	-4.06734300	-2.89106600	-0.24293300
C	-2.76676200	-2.39098200	-0.03423200
O	-2.59698400	-1.06786700	-0.00411400
B	-1.39159100	-0.46623700	0.64956900
C	-1.67541500	-0.31275800	2.24003200
C	-2.98220400	2.33161000	-0.19253500
C	-3.80259500	1.47591100	-0.96282000
C	-5.15846900	1.75303800	-1.12718900
C	-5.73003100	2.88433600	-0.53243600
C	-4.92727000	3.74837700	0.22485300
C	-3.57077100	3.48228100	0.38784000
C	1.95736800	3.31240200	-0.07942100
C	2.01464400	4.66369900	0.33812200
C	3.20420900	5.38601800	0.27525500
C	4.37361400	4.78297400	-0.20647100

C	4.33434400	3.44825400	-0.62504600
C	3.14598100	2.71962600	-0.56341900
C	3.32245900	-2.36620900	-0.02415400
C	4.17635000	-1.28880300	0.30913600
C	5.56178300	-1.41250800	0.19901500
C	6.13594800	-2.60794500	-0.24682300
C	5.30425200	-3.68503500	-0.58236600
C	3.92068700	-3.56801700	-0.47390800
H	1.16805200	-4.37701300	-0.01811500
H	-0.82654500	4.20479100	-0.18210900
H	-1.11334600	-5.40365400	0.16121200
H	-3.41940900	-6.24176900	-0.17615300
H	-5.30330300	-4.62956100	-0.44880400
H	-4.88125500	-2.18144400	-0.35386500
H	-3.36643100	0.61153300	-1.44625900
H	-5.77012700	1.09007600	-1.73284500
H	-6.78762200	3.09531100	-0.66309400
H	-5.36222000	4.62756400	0.69172300
H	-2.96008100	4.14922800	0.98850400
H	1.12215400	5.14175700	0.73056000
H	3.22220900	6.41983000	0.60930900
H	5.30137400	5.34615800	-0.25346300
H	5.23286700	2.97212600	-1.00826700
H	3.12833700	1.69074400	-0.90051800
H	3.74617800	-0.35908300	0.66152100
H	6.19549300	-0.57139100	0.46699100
H	7.21481600	-2.70072600	-0.33367800
H	5.73682100	-4.61723500	-0.93541000
H	3.29537900	-4.41009700	-0.75347500
H	-0.80182400	0.08013500	2.77663400
H	-2.51339500	0.37272700	2.42258000
H	-1.93540600	-1.27875200	2.69337900

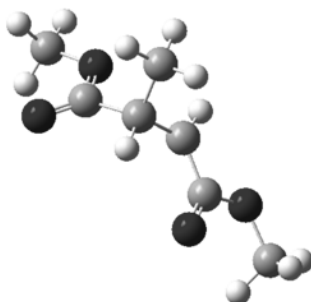
Cartesian coordinates of triplet excited state of **B-Me**



0 3			
C	1.07345400	-1.03905700	0.25558200
N	1.43726200	0.25945200	0.19391900
C	0.45091000	1.15626700	0.05024300
C	1.89485800	-2.24857100	0.14394100
C	0.99200200	-3.31444900	0.12803200
C	-0.31769200	-2.78542500	0.23004800
N	-0.21836900	-1.41322300	0.34842600
C	0.65250800	2.59575900	-0.05496900
N	-0.91947100	0.88731800	0.03004600

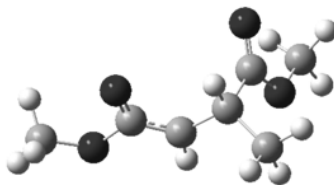
C	-1.57408300	2.11089700	-0.04789500
C	-0.61994100	3.15174300	-0.08423000
C	-1.62572400	-3.34196000	0.09317000
C	-1.87026900	-4.73710600	0.05146700
C	-3.14262400	-5.22848900	-0.18278400
C	-4.20977100	-4.32953800	-0.39589600
C	-4.00321500	-2.95581300	-0.36198500
C	-2.72192200	-2.43294500	-0.10724800
O	-2.56528500	-1.10310400	-0.10324500
B	-1.41611200	-0.48780500	0.63355200
C	-1.77133800	-0.34820800	2.20505200
C	-3.01614500	2.31496100	-0.15886000
C	-3.85130900	1.46913800	-0.91894100
C	-5.21098800	1.74981300	-1.05070500
C	-5.76808100	2.87259900	-0.42830300
C	-4.94929600	3.72480700	0.32296100
C	-3.58829600	3.45580500	0.45055800
C	1.92570200	3.31652800	-0.12307900
C	1.99352900	4.65545800	0.32422600
C	3.18139900	5.38037800	0.24234400
C	4.33457300	4.78888600	-0.28834000
C	4.28318800	3.46468400	-0.73621000
C	3.09622300	2.73419300	-0.65510100
C	3.35133600	-2.31892200	0.02281100
C	4.18328900	-1.25510400	0.43556800
C	5.57237600	-1.35450800	0.33724100
C	6.16677800	-2.51210000	-0.17517400
C	5.35458200	-3.57560200	-0.58977300
C	3.96757000	-3.48165600	-0.49366100
H	1.23042200	-4.36355600	0.02490000
H	-0.86528600	4.19595000	-0.21842100
H	-1.03912300	-5.41863000	0.20742200
H	-3.31997400	-6.29916000	-0.20554700
H	-5.20848900	-4.71384400	-0.58335900
H	-4.82262100	-2.26198700	-0.52187300
H	-3.42849200	0.60547400	-1.41496900
H	-5.83660500	1.09363200	-1.64935400
H	-6.82842100	3.08495200	-0.53162300
H	-5.37252400	4.59790500	0.81142800
H	-2.96302600	4.11652900	1.04301100
H	1.11230000	5.12245000	0.75392700
H	3.20977400	6.40616700	0.59948300
H	5.26067700	5.35338200	-0.35030600
H	5.16985000	2.99774900	-1.15643700
H	3.06775000	1.71244600	-1.01309300
H	3.73605000	-0.35485000	0.83982700
H	6.19168300	-0.52453500	0.66645200
H	7.24781900	-2.58588600	-0.25289500
H	5.80384400	-4.47798100	-0.99540700
H	3.35431600	-4.31032500	-0.83414200
H	-0.93056100	0.05490900	2.78587800
H	-2.62746900	0.32225400	2.35960500
H	-2.03651400	-1.31879000	2.64644200

Cartesian coordinates of EA radical



0 2			
C	0.57519100	0.95120300	-0.00992800
H	0.23854600	1.45872700	-0.91599400
C	-0.53413300	0.11375800	0.52922300
H	-0.38065500	-0.47003000	1.43102700
C	1.77440100	0.09675000	-0.43307000
O	2.31988200	0.18441200	-1.51908000
O	2.17433000	-0.73934500	0.53570000
C	-1.83622100	0.07270200	-0.10470200
O	-2.14964200	0.68045700	-1.12928200
O	-2.69838800	-0.72731300	0.57073000
C	-4.03015100	-0.84081400	0.02705300
H	-4.56124200	-1.51429500	0.69979700
H	-4.51984800	0.13628900	0.00440600
H	-3.99817800	-1.26049400	-0.98186100
C	3.32157400	-1.57606300	0.24788100
H	4.19991400	-0.95855500	0.04692700
H	3.47392700	-2.17346700	1.14626600
H	3.11308900	-2.22105500	-0.60868600
C	1.03525100	2.01294000	1.02536500
H	0.20875700	2.69721200	1.23746300
H	1.34913700	1.54253800	1.96148900
H	1.87162200	2.59458500	0.62370000

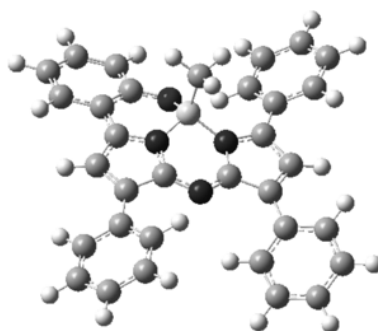
Cartesian coordinates of EA anion



-1 1			
C	0.60144900	0.97296200	-0.23463700
H	0.24372000	1.22662700	-1.23724400
C	-0.55191400	0.35233200	0.52220200
H	-0.40808700	0.09829700	1.56912900
C	1.66943600	-0.08663800	-0.46032200
O	1.83393800	-0.71735000	-1.49842900
O	2.42482100	-0.31285900	0.64031300
C	-1.77187700	0.07567500	-0.08240000

O	-2.14622200	0.27612900	-1.27095500
O	-2.70405100	-0.51024100	0.81716200
C	-4.00466000	-0.76230200	0.29604000
H	-4.57453100	-1.20906300	1.11604200
H	-4.50439900	0.15883400	-0.02808900
H	-3.98237100	-1.46043000	-0.54897800
C	3.39654600	-1.37479700	0.55787200
H	4.12307600	-1.17514700	-0.23409300
H	3.89385700	-1.39152000	1.52842100
H	2.90424800	-2.33318800	0.37105200
C	1.17717900	2.24032300	0.42892900
H	0.41206800	3.02460700	0.43595600
H	1.47234100	2.04691100	1.46548600
H	2.05523900	2.62331700	-0.10850300

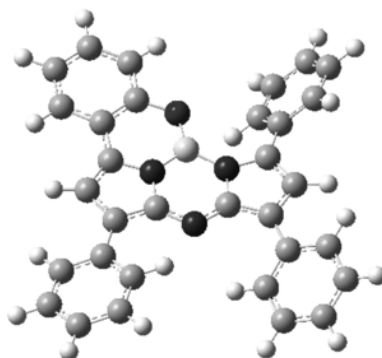
Cartesian coordinates of B-Me radical cation



1 2			
C	1.06247400	-1.00891300	0.29760400
N	1.36938800	0.27558700	0.16603700
C	0.38163800	1.14862400	0.01476400
C	1.94039200	-2.19246700	0.23655900
C	1.08929200	-3.27567700	0.17910800
C	-0.26250500	-2.78229200	0.22068900
N	-0.22762000	-1.43091900	0.35367700
C	0.57740200	2.59096400	-0.13344500
N	-0.99516600	0.86550700	0.04164300
C	-1.64077400	2.07051700	-0.02146900
C	-0.68403600	3.13350800	-0.11439300
C	-1.52165700	-3.39775400	0.01347700
C	-1.69023400	-4.80584500	-0.06940200
C	-2.91007300	-5.34160800	-0.42102500
C	-3.99244900	-4.47964900	-0.72633900
C	-3.86192100	-3.10156700	-0.66470700
C	-2.63869400	-2.52728400	-0.26945800
O	-2.54430500	-1.20106800	-0.21722200
B	-1.47150300	-0.54972900	0.59973700
C	-1.89915200	-0.44807600	2.14602700
C	-3.07760700	2.29205300	-0.03908300
C	-3.98581500	1.40297400	-0.65492400
C	-5.34650800	1.69676700	-0.67936200
C	-5.82886600	2.86743800	-0.08220300
C	-4.93823100	3.76032100	0.52758900

C	-3.57464300	3.48759000	0.53608200
C	1.85167700	3.29603400	-0.27531400
C	1.96286700	4.62381000	0.19153900
C	3.15353300	5.33139700	0.04160200
C	4.25457800	4.73179000	-0.58234900
C	4.15491600	3.41887600	-1.05463800
C	2.96754600	2.70272500	-0.90214900
C	3.40173700	-2.18902700	0.18201700
C	4.15343800	-1.14161000	0.75439600
C	5.54780400	-1.17475300	0.72418400
C	6.21562800	-2.24537800	0.12086300
C	5.47961700	-3.28996400	-0.45261700
C	4.08715700	-3.26446300	-0.42284000
H	1.36346300	-4.31726000	0.09264200
H	-0.94681200	4.17312100	-0.24555500
H	-0.84425400	-5.44906600	0.15134300
H	-3.04412600	-6.41688200	-0.47302000
H	-4.94928900	-4.90807600	-1.01053500
H	-4.69534000	-2.44659500	-0.89586600
H	-3.62062700	0.50442500	-1.13232200
H	-6.03296000	1.01405100	-1.17094800
H	-6.89230100	3.08761900	-0.09896100
H	-5.30824100	4.66912900	0.99215500
H	-2.89207900	4.18182400	1.01444900
H	1.11930100	5.09152700	0.68993600
H	3.22537300	6.34861000	0.41542900
H	5.18216200	5.28464200	-0.69997700
H	5.00215500	2.95152400	-1.54804500
H	2.89733100	1.69154800	-1.28435900
H	3.64664400	-0.31379200	1.23670900
H	6.11280200	-0.36509600	1.17680400
H	7.30139700	-2.26652800	0.09615000
H	5.99216400	-4.12066100	-0.92889700
H	3.52499800	-4.06958800	-0.88576900
H	-1.09954200	-0.01950100	2.76425900
H	-2.78789600	0.18342700	2.27095600
H	-2.13974200	-1.43678600	2.55833000

Cartesian coordinates of B radical

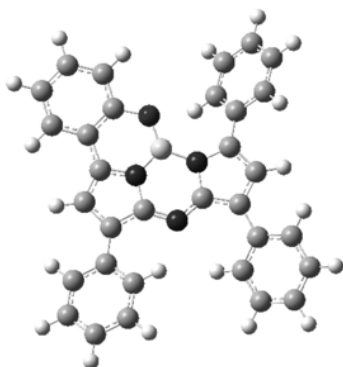


O 2			
C	-1.10401400	-1.02912800	0.02356600
N	-1.43349600	0.26557300	0.05012300

C	-0.45311400	1.18172200	0.05870000
C	-1.88404300	-2.23080500	0.00862800
C	-0.95714100	-3.31051000	-0.04243700
C	0.33510400	-2.79362800	-0.06517300
N	0.22930400	-1.41320300	-0.01157800
C	-0.58282700	2.59397600	-0.00504500
N	0.94542300	0.87434500	0.07148800
C	1.65285200	2.08054000	0.02488100
C	0.73331700	3.11625000	-0.04446700
C	1.67818200	-3.32435500	-0.15587900
C	1.96447400	-4.70316900	-0.21543200
C	3.27549300	-5.15894000	-0.31347700
C	4.33633900	-4.24287100	-0.35556400
C	4.08191300	-2.87144100	-0.29704600
C	2.76918200	-2.41631800	-0.19689900
O	2.58867500	-1.04074400	-0.13916600
B	1.32920300	-0.51318300	-0.02497700
C	3.11272200	2.20762700	0.13029500
C	3.86670300	1.45804400	1.05462200
C	5.24259300	1.65767000	1.17686500
C	5.89379600	2.60974600	0.38444400
C	5.15444100	3.36616700	-0.53156400
C	3.77849100	3.16849200	-0.65794300
C	-1.81945200	3.38544500	-0.02374800
C	-1.82353600	4.66526200	-0.62059100
C	-2.97701100	5.45030100	-0.63334400
C	-4.15925300	4.97882200	-0.05104800
C	-4.17074400	3.71352800	0.54620700
C	-3.01816500	2.92558700	0.56201500
C	-3.34517200	-2.34957000	0.03356700
C	-4.18569700	-1.26804900	-0.30982300
C	-5.57456800	-1.40731800	-0.29452000
C	-6.16328200	-2.62546700	0.06192200
C	-5.34341000	-3.70700000	0.40536600
C	-3.95517900	-3.57213900	0.39290000
H	-1.20736400	-4.36092500	-0.08972700
H	0.99975300	4.16428900	-0.04701800
H	1.14087700	-5.41039000	-0.18556500
H	3.47401100	-6.22547100	-0.35841800
H	5.36059400	-4.59468500	-0.43347300
H	4.88963200	-2.14704100	-0.32830900
H	3.37432400	0.73370400	1.69466500
H	5.80544800	1.07459100	1.90065100
H	6.96492200	2.76243300	0.48220800
H	5.64951000	4.10663600	-1.15378100
H	3.21331900	3.75026100	-1.38021900
H	-0.91945600	5.04051300	-1.09092200
H	-2.95373400	6.42942000	-1.10423100
H	-5.05781400	5.58937100	-0.06148900
H	-5.07977400	3.33872700	1.00915800
H	-3.03963800	1.95259000	1.03845400
H	-3.74401300	-0.32082500	-0.59622200
H	-6.19863000	-0.56062700	-0.56790000
H	-7.24443300	-2.73119900	0.07260800

H	-5.78619100	-4.65786800	0.68952000
H	-3.33933400	-4.41946100	0.67811700

Cartesian coordinates of B cation



1 1			
C	-1.07980700	-1.02154400	0.03057700
N	-1.39363000	0.26106100	0.06058300
C	-0.42923300	1.17166200	0.08012000
C	-1.87582600	-2.22723300	-0.00104700
C	-0.96719200	-3.29975000	-0.03324300
C	0.34072000	-2.78068500	-0.04135600
N	0.25085000	-1.41400600	0.01221300
C	-0.57483300	2.59223300	0.01597000
N	0.97284900	0.87407700	0.08548800
C	1.65460300	2.07726500	0.02515800
C	0.72289100	3.11840500	-0.04861100
C	1.66578300	-3.33162300	-0.12271500
C	1.92219400	-4.71868000	-0.18195600
C	3.22337300	-5.19083400	-0.27002900
C	4.29858700	-4.28665800	-0.30306800
C	4.07640200	-2.91189700	-0.24623500
C	2.77114200	-2.43594900	-0.15515200
O	2.60701000	-1.06456400	-0.09715500
B	1.36163300	-0.51964800	0.00277100
C	3.10860800	2.22784100	0.10005700
C	3.89414800	1.46908500	0.99002200
C	5.26744100	1.69226300	1.07985000
C	5.87867700	2.66574600	0.28180300
C	5.10580800	3.42875100	-0.60084900
C	3.73023800	3.22030000	-0.68615900
C	-1.82196000	3.35899600	0.02017900
C	-1.86415100	4.61633100	-0.61966600
C	-3.03288300	5.37571000	-0.61843300
C	-4.18014600	4.90035800	0.02770800
C	-4.14856400	3.65923200	0.67297700
C	-2.98350700	2.89225900	0.67046600
C	-3.33479900	-2.32450000	-0.00450100
C	-4.14433700	-1.25793600	-0.45046900
C	-5.53310800	-1.38229500	-0.46413900
C	-6.14109900	-2.56600700	-0.03193500
C	-5.34897000	-3.63095900	0.41379600
C	-3.96068600	-3.51471100	0.42604500

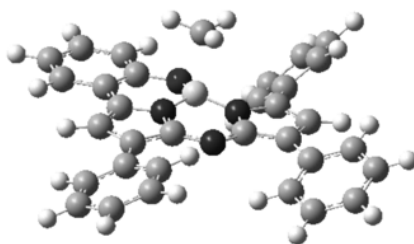
H	-1.21688800	-4.34943700	-0.08527900
H	0.98754200	4.16600300	-0.06530300
H	1.08515400	-5.40935300	-0.16053500
H	3.41054700	-6.25876100	-0.31523800
H	5.31639100	-4.65772700	-0.37373700
H	4.89884400	-2.20481400	-0.27140400
H	3.43034500	0.73165600	1.63566700
H	5.85981400	1.11039600	1.77984300
H	6.94961100	2.83298800	0.35191300
H	5.57419700	4.18576500	-1.22287800
H	3.13479200	3.81021800	-1.37601200
H	-0.98372600	4.98704800	-1.13547100
H	-3.05015900	6.33653900	-1.12462900
H	-5.08980200	5.49404000	0.03101400
H	-5.03170500	3.28965000	1.18618900
H	-2.96547900	1.94052600	1.18812000
H	-3.68370100	-0.34193500	-0.80090200
H	-6.14144100	-0.55529800	-0.81867300
H	-7.22324600	-2.65917500	-0.04321500
H	-5.81417800	-4.55075300	0.75608900
H	-3.35873600	-4.34179900	0.78883800

Cartesian coordinates of methyl radical



0 2			
C	0.00000000	0.00000000	0.00000000
H	0.00000000	1.08494700	0.00000000
H	-0.93959200	-0.54247400	0.00000000
H	0.93959200	-0.54247400	0.00000000

Cartesian coordinates of TS1

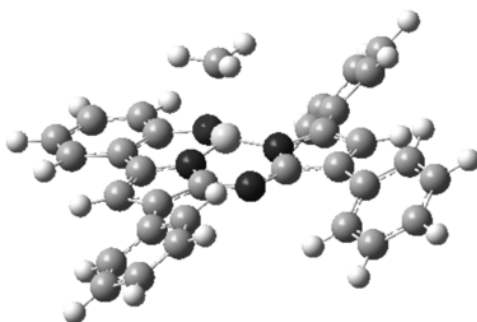


imaginary frequency (cm-1) = -355.72

0 3			
C	1.12580200	-1.03713000	0.06696500
N	1.48331900	0.25336000	0.02933000
C	0.51760100	1.18780400	-0.03806200
C	1.89343200	-2.25203600	0.02443000
C	0.95169900	-3.31737500	0.01693400
C	-0.33224500	-2.77711800	0.06563200
N	-0.20242700	-1.39755500	0.10167500
C	0.68553100	2.59676900	-0.05651100

N	-0.88344500	0.91157600	-0.06371900
C	-1.55813200	2.12884700	-0.08681300
C	-0.61812000	3.15141400	-0.06918700
C	-1.68016500	-3.29523100	0.04480500
C	-1.97828600	-4.67412200	0.04560600
C	-3.29291400	-5.12286100	-0.00321500
C	-4.35024700	-4.19942400	-0.05477400
C	-4.08667900	-2.83128300	-0.05321000
C	-2.76593600	-2.37469300	-0.00475300
O	-2.57604300	-1.01643700	-0.02207800
B	-1.31058400	-0.47149100	0.24974800
C	-1.49183900	-0.34961600	2.32402100
C	-3.01573600	2.29010300	-0.20256200
C	-3.78393600	1.53764200	-1.11226200
C	-5.15396500	1.76868600	-1.24710900
C	-5.78489900	2.75655400	-0.48255000
C	-5.03104500	3.51691000	0.41818100
C	-3.66092400	3.28738300	0.55692400
C	1.94058800	3.35920000	-0.07655100
C	1.96770700	4.67738300	0.42993700
C	3.13863300	5.43595800	0.40440700
C	4.31711800	4.89967400	-0.12731100
C	4.30637200	3.59585900	-0.63505500
C	3.13618000	2.83426000	-0.61236400
C	3.35069100	-2.38541700	-0.03653900
C	4.21017500	-1.33271600	0.34876500
C	5.59672000	-1.48566600	0.30064700
C	6.16470300	-2.68907500	-0.13187600
C	5.32640200	-3.74211000	-0.51761500
C	3.94049600	-3.59371400	-0.47196200
H	1.18285000	-4.37257400	-0.01856400
H	-0.86197200	4.20246000	-0.14375500
H	-1.15984500	-5.38683600	0.08545300
H	-3.50032200	-6.18866800	-0.00066600
H	-5.37800000	-4.54779200	-0.09288200
H	-4.89049300	-2.10263100	-0.08921500
H	-3.30454000	0.78427900	-1.72731300
H	-5.72797200	1.18218600	-1.95938500
H	-6.85134200	2.93381000	-0.59010800
H	-5.51011900	4.28547000	1.01854500
H	-3.08461600	3.87335100	1.26703800
H	1.06692900	5.10498300	0.86042200
H	3.13153900	6.44591800	0.80566900
H	5.22918400	5.48964200	-0.14663300
H	5.21207300	3.16965400	-1.05853700
H	3.14109700	1.83009700	-1.01929000
H	3.78441500	-0.39737200	0.69266200
H	6.23551500	-0.66165000	0.60722400
H	7.24419600	-2.80533400	-0.16881000
H	5.75318000	-4.68066600	-0.86094700
H	3.30976600	-4.41784100	-0.79057700
H	-0.52043500	0.02534400	2.63651500
H	-2.32273700	0.34651900	2.40787300
H	-1.70792000	-1.38421600	2.58032400

Cartesian coordinates of TS2



imaginary frequency (cm⁻¹) = -263.42

1 2			
C	1.10485200	-1.02846800	0.08140500
N	1.43513400	0.25006400	0.01641200
C	0.48546200	1.17247400	-0.05717100
C	1.89566800	-2.23984500	0.04707200
C	0.98076500	-3.30209800	0.01115600
C	-0.32553800	-2.76753900	0.04559300
N	-0.22409200	-1.40668400	0.10108800
C	0.66621100	2.59127100	-0.09139800
N	-0.92218400	0.90305800	-0.06714600
C	-1.57134000	2.11568400	-0.08995300
C	-0.61669600	3.14668700	-0.08461400
C	-1.65321000	-3.31665800	0.00744300
C	-1.91239100	-4.70424000	-0.00668300
C	-3.21397100	-5.17711000	-0.08160200
C	-4.28819200	-4.27168300	-0.14908600
C	-4.06390000	-2.89786500	-0.13726500
C	-2.75612400	-2.41480100	-0.05574500
O	-2.58999600	-1.05570500	-0.06015600
B	-1.34717100	-0.49068800	0.21874500
C	-1.54758600	-0.35876200	2.34224800
C	-3.02247200	2.30678800	-0.16574600
C	-3.84146000	1.52203900	-1.00049600
C	-5.20825600	1.78439800	-1.09270800
C	-5.77978500	2.82491400	-0.35253000
C	-4.97316800	3.61505100	0.47450200
C	-3.60436900	3.36631100	0.56153300
C	1.93273100	3.32712700	-0.13871000
C	2.00326600	4.62017800	0.42177600
C	3.18902000	5.35191600	0.37559200
C	4.32614300	4.81156200	-0.23632600
C	4.26678400	3.53339000	-0.80215200
C	3.08407500	2.79468400	-0.75483500
C	3.35463000	-2.33859400	0.01982400
C	4.17068100	-1.31760100	0.55155300
C	5.55969400	-1.44220600	0.53577500
C	6.16087000	-2.58106600	-0.01114300
C	5.36185900	-3.60104600	-0.54179600

C	3.97344400	-3.48396300	-0.52574800
H	1.21984400	-4.35506600	-0.02611900
H	-0.86052600	4.19725100	-0.15454600
H	-1.07777700	-5.39644700	0.04395400
H	-3.40340600	-6.24560500	-0.08838500
H	-5.30639600	-4.64389300	-0.20830100
H	-4.88533400	-2.19076800	-0.18637800
H	-3.40718700	0.72915000	-1.59747800
H	-5.82623600	1.17959600	-1.74991100
H	-6.84539800	3.02289900	-0.42420700
H	-5.41003800	4.42467500	1.05166600
H	-2.98390200	3.97899300	1.20812200
H	1.13080700	5.04218600	0.91137200
H	3.22709100	6.34229500	0.82010400
H	5.24903900	5.38322900	-0.27424700
H	5.14189800	3.11183000	-1.28845300
H	3.04512500	1.81267100	-1.21109900
H	3.71550500	-0.43773100	0.99135000
H	6.17340800	-0.65098600	0.95659500
H	7.24301600	-2.67436300	-0.02314700
H	5.82169900	-4.48554900	-0.97296900
H	3.36438900	-4.27331300	-0.95490400
H	-0.57910400	0.03051700	2.64460600
H	-2.38886500	0.32763400	2.39204500
H	-1.75001700	-1.40076500	2.57679200

第四章 实验项 参考文献

1. Adib, M.; Ayashi, N.; Heidari, F.; Mirzaei, P. *Synlett* **2016**, 27, 1738–1742.
2. Klausfelder, B.; Blach, P.; de Jonge, N.; Kempe, R. *Chem. Eur. J.* **2022**, 28, e202201307.
3. Loudet, A.; Bandichhor, R.; Wu, L.; Burgess, K. *Tetrahedron* **2008**, 64, 3642–3654.
4. Chen, N.; Zhang, W.; Chen, S.; Wu, Q.; Yu, C.; Wei, Y.; Xu, Y.; Hao, E.; Jiao, L. *Org. Lett.* **2017**, 19, 2026–2029.
5. Amin, A. N.; El-Khouly, M. E.; Subbaiyan, N. K.; Zandler, M. E.; Fukuzumi, S.; D'Souza, F. *Chem. Commun.* **2012**, 48, 206–208.
6. Godard, A.; Galán, L. A.; Rouillon, J.; Al Shehimi, S.; Tajani, W.; Cave, C.; Malacea-Kabbara, R.; Rousselin, Y.; Le Gendre, P.; Fihey, A.; Bendellaa, M.; Busser, B.; Sancey, L.; Le Guennic, B.; Bucher, C.; Maury, O.; Goze, C.; Bodio, E. *Inorg. Chem.* **2022**, 62, 5067–5080.
7. Huo, H.; Harms, K.; Meggers, E. *J. Am. Chem. Soc.* **2016**, 138, 6936–6939.
8. Molander, G. A.; McKee, S. A. *Org. Lett.* **2011**, 13, 4684–4687.
9. Verbelen, B.; Cunha Dias Rezende, L.; Boodts, S.; Jacobs, J.; Van Meervelt, L.; Hofkens, J.; Dehaen, W. *Chem. Eur. J.* **2015**, 21, 12667–12675.
10. Chinzei, T.; Miyazawa, K.; Yasu, Y.; Koike, T.; Akita, M. *RSC Adv.* **2015**, 5, 21297–21300.
11. Matsui, J. K.; Molander, G. A. *Org. Lett.* **2017**, 19, 436–439.
12. Miller, E. M.; Walczak, M. A. *Org. Lett.* **2021**, 23, 4289–4293.
13. Yang, C.; Zhang, Z.; Tajuddin, H.; Wu, C.; Liang, J.; Liu, J.; Fu, Y.; Czyzewska, M.; Steel, P. G.; Marder, T. B.; Liu, L. *Angew. Chem. Int. Ed.* **2011**, 51, 528–532.
14. Sim, J.; Campbell, M. W.; Molander, G. A. *ACS Catal.* **2019**, 9, 1558–1563.
15. Zhu, J. L.; Schull, C. R.; Tam, A. T.; Rentería-Gómez, Á.; Gogoi, A. R.; Gutierrez, O.; Scheidt, K. A. *J. Am. Chem. Soc.* **2023**, 145, 1535–1541.
16. Nakagawa, M.; Matsuki, Y.; Nagao, K.; Ohmiya, H. *J. Am. Chem. Soc.* **2022**, 144, 7953–7959.
17. Luque, A.; Groß, J.; Zähringer, T. J. B.; Kerzig, C.; Opatz, T. *Chem. Eur. J.* **2022**, 28, e202104329. DOI: 10.1002/chem.202104329.
18. Carré, V.; Godard, P.; Méreau, R.; Jacquot de Rouville, H.; Jonusauskas, G.; McClenaghan, N.; Tassaing, T.; Vincent, J. *Angew. Chem. Int. Ed.* **2024**, 63, e202402964. DOI: 10.1002/anie.202402964.
19. Miyamoto, Y.; Sumida, Y.; Ohmiya, H. *Org. Lett.* **2021**, 23, 5865–5870.
20. Gualandi, A.; Mazzarella, D.; Ortega-Martínez, A.; Mengozzi, L.; Calcinelli, F.; Matteucci, E.; Monti, F.; Armaroli, N.; Sambri, L.; Cozzi, P. G. *ACS Catal.* **2017**, 7, 5357–5362.
21. Rohe, S.; Morris, A. O.; McCallum, T.; Barriault, L. *Angew. Chem. Int. Ed.* **2018**, 57, 15664–15669.
22. El-Hage, F.; Schöll, C.; Pospesch, J. *J. Org. Chem.* **2020**, 85, 13853–13867.
23. Lackner, G. L.; Quasdorf, K. W.; Overman, L. E. *J. Am. Chem. Soc.* **2013**, 135, 15342–15345.
24. Qin, T.; Malins, L. R.; Edwards, J. T.; Merchant, R. R.; Novak, A. J. E.; Zhong, J. Z.; Mills, R. B.; Yan, M.; Yuan, C.; Eastgate, M. D.; Baran, P. S. *Angew. Chem. Int. Ed.* **2016**, 56, 260–265.
25. Chowdhury, R.; Yu, Z.; Tong, M. L.; Kohlhepp, S. V.; Yin, X.; Mendoza, A. *J. Am. Chem. Soc.* **2020**, 142, 20143–20151.
26. Shah, A. A.; Kelly, M. J., III; Perkins, J. J. *Org. Lett.* **2020**, 22, 2196–2200.
27. Sämman, C.; Dhayalan, V.; Schreiner, P. R.; Knochel, P. *Org. Lett.* **2014**, 16, 2418–2421.
28. Zhang, K.; Chang, L.; An, Q.; Wang, X.; Zuo, Z. *J. Am. Chem. Soc.* **2019**, 141, 10556–10564.
29. Du, B.; Jin, B.; Sun, P. *Org. Lett.* **2014**, 16, 3032–3035.
30. Norcott, P. L.; Hammill, C. L.; Noble, B. B.; Robertson, J. C.; Olding, A.; Bissember, A. C.; Coote, M. L. *J. Am. Chem. Soc.* **2019**, 141, 15450–15455.
31. Innocent, M.; Tanguy, C.; Gavelle, S.; Aubineau, T.; Guérinot, A. *Chem. Eur. J.* **2024**, 30, e202401252.
32. Buzzetti, L.; Prieto, A.; Roy, S. R.; Melchiorre, P. *Angew. Chem. Int. Ed.* **2017**, 56, 15039–15043.

33. Sakamoto, R.; Kinoshita, H.; Miura, K. *Org. Lett.* **2025**, *27*, 5241–5246.
34. Egi, M.; Kawai, T.; Umemura, M.; Akai, S. *J. Org. Chem.* **2012**, *77*, 7092–7097.
35. Connelly, N. G.; Geiger, W. E. *Chem. Rev.* **1996**, *96*, 877–910.
36. M. J. Frisch *et al.* Gaussian 16, Revision C.01, Gaussian, Inc., Wallingford CT (**2016**).
37. (a) Becke, A.D. *J. Chem. Phys.* **1993**, *98*, 1372–1377. (b) Becke, A.D. *J. Chem. Phys.* **1993**, *98*, 5648–5652. (c) Lee, C.; Yang, W.; Parr, R.G. *Phys. Rev. B* **1988**, *37*, 785–789. (d) Stephens, P.J.; Devlin, F.J.; Chabalowski, C.F.; Frisch, M.J. *J. Phys. Chem.* **1994**, *98*, 11623–11627.

総括

第一章 青色光照射下において、2,2'-(pyridine-2,6-diyl)diphenol (PDP) を三座配位子とする PDP 型ホウ素アート錯体が、炭素ラジカルを与えることを見出した。以前に報告されたボラセン型ホウ素アート錯体の合成には強塩基性の試薬が必要であったのに対し、PDP 型ホウ素アート錯体は、有機ホウ素化合物と PDP を加熱条件下反応させるのみで合成可能であり、ホウ素上置換基の官能基許容性が向上した。PDP 型ホウ素アート錯体は、強力な還元剤としても機能し脱シアノ型アルキル化反応、Giese 型ラジカル付加反応、ニッケル触媒クロスカップリング反応へと適用できた。

第二章 第一章で確立したPDP型ホウ素アート錯体の直接励起戦略を用い、含窒素ヘテロ芳香族化合物の官能基化反応であるMinisci型C-Hアルキル化反応を開発した。具体的には、青色光照射下、PDP型ホウ素アート錯体と酸素、基質である含窒素ヘテロ芳香族化合物のみを用いて、含窒素ヘテロ芳香族化合物のアルキル化反応を達成した。本反応は、医薬品化学において重要性の高いアルキル置換ヘテロ芳香環化合物を、温和な条件下かつ触媒を用いない条件で合成する手法を提供するものである。

第三章 水酸基が無保護であるグリコシルラジカルの生成に本戦略を応用した。糖供与体として PDP 型グリコシルホウ素アート錯体を合成し、その青色光直接励起により、アノマー位炭素ラジカル生成を発生させ、種々の反応に適用した。具体的には、Giese 型ラジカル付加反応、Minisci 型反応、ラジカル-ラジカルカップリング反応により、アノマー位にアルキル基、ヘテロアリール基、アシル基の導入が可能であった。本手法は、保護-脱保護過程を必要としないため、簡便な手法である。

第四章 光の波長と反応形式におけるさらなる改良を目指し、深赤色から近赤外 (DR to NIR) 領域の光を利用した触媒的反応系の構築を行った。配位子骨格を従来の PDP 型から azadipyrromethene (ADP) 型へと変更することで、錯体の吸収波長を長波長側へと劇的にシフトさせた。さらに、系中で可逆的に形成される ADP 型ホウ素アート錯体の直接励起を利用することで、触媒量の ADP を用いた炭素ラジカル生成機構を確立した。生じた炭素ラジカルを用いて、Giese 型ラジカル付加反応、炭素-ヘテロ原子結合形成反応、アシル化反応が可能であった。

以上、本論文では、配位子を用いた有機ホウ素アート錯体の直接励起が、炭素ラジカル生成のための強力な戦略となることを明らかにした。青色光による化学量論的反応から、近赤外光による触媒的反応への展開は、光エネルギーを自在に活用し分子変換へと応用する有機合成化学の可能性を提示するものである。

論文目録

第一章

“Generation of Functionalized Alkyl Radicals via the Direct Photoexcitation of 2,2'-(Pyridine-2,6-diyl)diphenol-Based Borates”

Yusuke Miyamoto, Yuto Sumida, Hirohisa Ohmiya

Org. Lett. **2021**, 23, 5865–5870.

DOI: 10.1021/acs.orglett.1c01996

第二章

“Direct Photoexcitation of Borate Enabling Minisci Reaction”

Marin Kemmochi, Yusuke Miyamoto, Yuto Sumida, Hirohisa Ohmiya

Asian. J. Org. Chem. **2022**, 11, e202100640.

DOI: 10.1002/ajoc.202100640

第三章

“Radical C-Glycosylation Using Photoexcitable Unprotected Glycosyl Borate”

Yusuke Miyamoto, Sho Murakami, Yuto Sumida, Go Hirai, Hirohisa Ohmiya

Chem. Eur. J. **2024**, 30, e202402256.

DOI: 10.1002/chem.202402256

第四章

“Deep-Red to Near-Infrared Light-Driven Radical Generation from Organoboron Compounds via Ligand-Induced Direct Excitation Catalysis”

Yusuke Miyamoto, Kanji Muraoka, Sho Murakami, Tadachika Matsudaira, Hirohisa Ohmiya

J. Am. Chem. Soc. **2025**, 147, 41185–41192.

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