Generation of Aryllithium Reagents from *N*-Arylpyrroles Using Lithium

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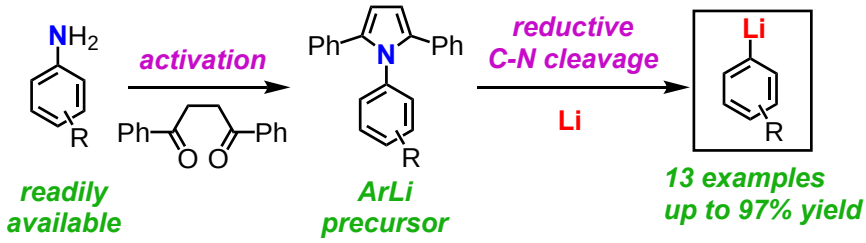

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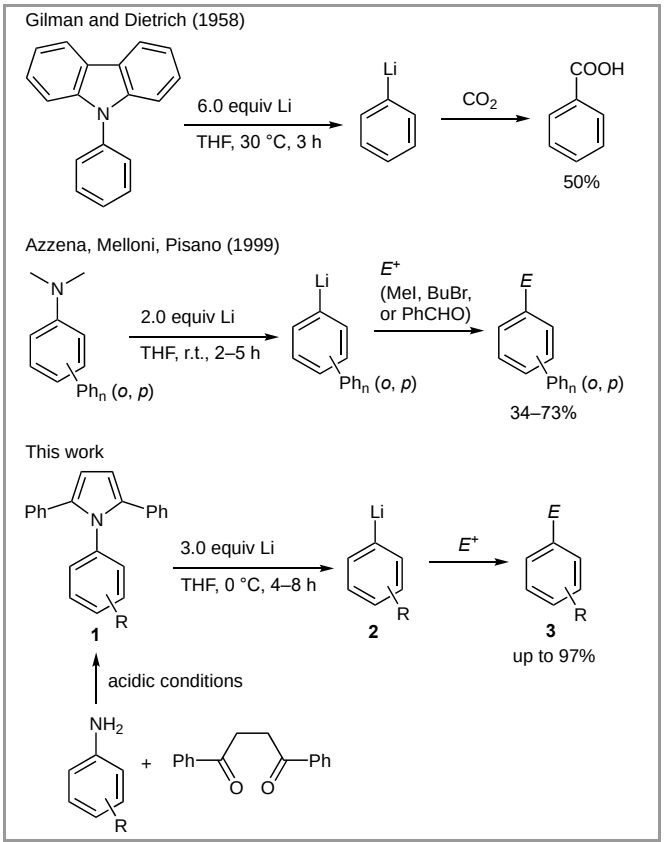
Abstract Treatment of 1-aryl-2,5-diphenylpyrroles with lithium powder at 0 °C in THF results in the generation of the corresponding aryllithium reagents through reductive C-N bond cleavage.

Key words organolithium reagent, C-N bond cleavage, lithium, pyrrole, metalation, reduction, deamination

The preparation of organolithium reagents from organic halides and lithium metal is a fundamental and important method in organic synthesis.[1] Besides the reductive cleavage of the carbon-halogen bonds, that of other carbon-heteroatom bonds is also attractive. With respect to the generation of aryllithium reagents, reductive lithiation of aryl halides prevails. Little is known about the alkali-metal-mediated cleavage of Ar–OR,[2] Ar–SR,[3] and Ar–NR_2[4] bonds because of the poorer leaving group ability of these heteroatom-centered anions and the regioselectivity of the cleavage (e.g., either Ar–OR or ArO–R). In line with the recent active research about inert bond activation,[5] the generation of aryllithium reagents from these less reactive precursors has been attracting attention.

The generation of aryllithiums from aniline derivatives has scarcely been reported (Scheme 1). The first reductive cleavage of Ar–NR_2 was reported in 1958 by Gilman and Dietrich.[4a] They treated *N*-phenylcarbazole with 6 equivalents of lithium in THF at 30 °C for 3 h to yield a 50% yield of benzoic acid after carbonation. In 1980, Cohen and co-workers observed reductive C–N bond cleavage of 1-dimethylaminonaphthalene as a minor side reaction.[4b] Azzena, Melloni, Pisano, and co-workers reported in 1999 that 2- or 4-dimethylaminobiphenyl derivatives undergo reductive lithiation to efficiently yield the corresponding biphenylyllithium reagents.[4c,d] These precedents highlight difficulty in generally preparing aryllithium reagents from aniline derivatives via C–N bond cleavage.[6]



Scheme 1 Reductive lithiation of aniline derivatives

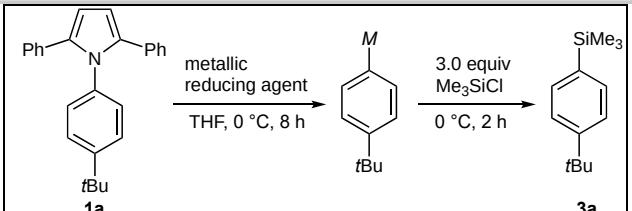
Here we report that *N*-arylpyrrole derivatives **1** efficiently undergo reductive lithiation to yield the corresponding aryllithium reagents **2** (Scheme 1). The starting pyrroles **1** were readily available from the corresponding anilines and 1,4-diphenyl-1,4-butanedione under Paal-Knorr conditions.[7] Additionally, the pyrrolic anion is the much better leaving group than dimethylamide, considering that the pK_a values of pyrrole and pyrrolidine were reported to be 23 and 44 in DMSO,

respectively.[8] The two phenyl groups at the 2 and 5 positions are expected to suppress unwanted side reactions as well as to help successive one-electron reductions from lithium surface. We thus consider the 2,5-diphenylpyrrolyl group is an attractive leaving group to generate aryllithium reagents from aniline derivatives via C–N bond cleavage.

Considering our previous conditions for the endocyclic C–N bond cleavage of *N*-phenylindoles with lithium,[6h,i] we set the reaction of **1a** with lithium powder[9] in THF as a model reaction (Table 1). The expected exocyclic C–N bond cleavage indeed proceeded smoothly with 3.0 equivalent of lithium powder at 0 ˚C to complete in 8 h (entry 1). The formation of the aryllithium was quantified by ^{1}H NMR analysis of the crude reaction mixture after treatment with chlorotrimethylsilane. The corresponding product **3a** was formed in 87% yield, along with the formation of 2,5-diphenyl-1-trimethylsilylpyrrole in 76% yield. When smaller amounts of lithium were used, the reactions did not reach full conversions (entries 2 and 3). The use of 1 equivalent of lithium resulted in 27% conversion (entry 4). Commercially available lithium granule was less effective than lithium powder probably because of the smaller surface area of the granule (entry 5). Although sodium dispersion[10,11] bearing a large surface area showed very high performance for the reduction, the relevant arylsodium reagent reacted with THF to give *t*-butylbenzene and none of **3a** (entry 6). To avoid the protonation, lithium iodide was placed in the reduction with sodium dispersion (entry 7). As expected, the transmetalation between the arylsodium and lithium iodide would proceed to eventually afforded **3a** in 84% yield. This Na-LiI protocol is advantageous in terms of the commercial availability of sodium dispersion. Magnesium powder were not reactive at all (entry 8).

Other ethereal solvents such as 1,4-dioxane and diethyl ether were examined. Notably, the solubility of **1a** was problematic and THF was found to be the optimal solvent. In 1,4-dioxane, **1a** seemed to be totally insoluble and was not converted at all. In diethyl ether, the reaction proceeded to afford **3a** in 68% yield with 88% conversion although some of **1a** remained insoluble at the beginning.

Table 1 Optimization of reaction conditions

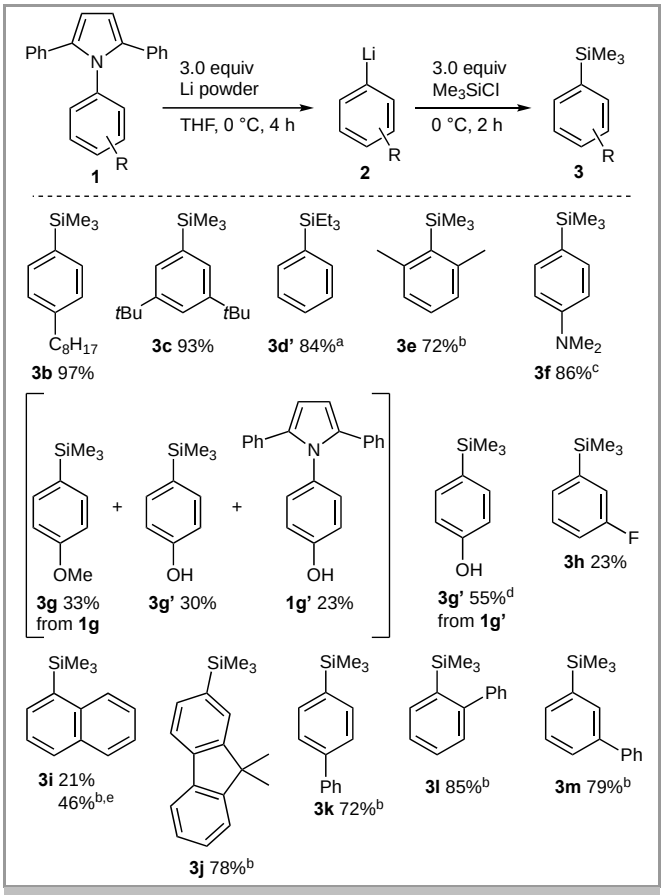


entry	metallic reducing agent	conversion of **1a** /%	NMR yield of **3a** /%[a]
1	3.0 equiv Li powder	>99	87 (87[b])
2	2.5 equiv Li powder	97	88
3	2.0 equiv Li powder	85	77
4	1.0 equiv Li powder	27	20
5	3.0 equiv Li granule	75	58
6	3.0 equiv Na dispersion	>99	<1
7	3.0 equiv Na dispersion and LiI	97	84
8	1.5 equiv Mg powder	<1	<1

[a] The efficiency of the generation of arylmetal was quantified by determining the yield of the silylated compound **3a** by ^{1}H NMR analysis. [b] Isolated yield.

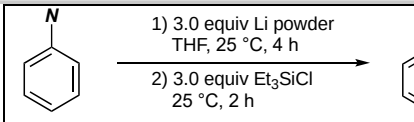
With the optimized conditions in hand (Table 1, entry 1), the scope of the lithiation with respect to the *N*-aryl unit was surveyed (Scheme 2). The lithiation reactions of **1b**, **1c**, and **1e** bearing alkyl substituents on the *N*-aryl group proceeded more smoothly than that of **1a** to go to completion within 4 h. The steric hindrance of the 2,6-dimethyl groups of **1e** did not seriously hamper the lithiation and subsequent trapping with Me_3SiCl (72%). The *p*-dimethylamino group in **1f** did not hinder the reaction to yield **3f** in 86% yield in 8 h. However, the *p*-methoxy group in **1g** have a notable influence: the reaction of **1g** with lithium powder followed by an addition of Me_3SiCl afforded **3g** in only 33% yield, along with demethylated product *p*-hydroxyphenyltrimethylsilane (**3g'**) in 30% yield and demethylated starting material *N*-(*p*-hydroxyphenyl)pyrrole **1g'** in 23% yield.[12] The demethylations should occur via fragmentation of the radical anions of **1g** and **3g** into a methyl radical and the corresponding phenoxide anion.[1f,g] Notably, when **1g'** was exposed as the unprotected starting material to a larger amount (4.0 equiv) of Li powder, **3g'** was obtained in 55% yield. A fluoro group was not compatible under the reaction conditions to afford the corresponding product **3h** in only 23% yield. Generation of naphthyllithium **2i** was not straightforward, and further reduction and silylation proceeded by means of the remaining lithium and Me_3SiCl to give **3i** in 21% yield along with several multisilylated products (detected by mass spectrometry). The selectivity in the formation of **3i** was slightly improved when the Na-LiI protocol (Table 1, entry 7) was used. *N*-fluorenylpyrrole **1j** underwent smooth lithiation to yield **3j**. The lithiation of biphenylylpyrroles **1k–m** proceeded smoothly to yield **3k–m**, respectively.

The 2,5-diphenylpyrrolyl group is the best leaving group among nitrogen-based leaving groups we tested (Table 2, entry 1). A simple pyrrolyl group served as a leaving group, while the resulting phenyllithium seemed to be partly protonated by the protons at the pyrrolic 2 and 5 positions (entry 2). A 2,5-dimethylpyrrolyl group was a poorer leaving group, and the methyl groups in the substrate may be proton sources (entry 3). As reported previously,[4b-d] *N*,*N*-dimethylaniline resisted the reductive lithiation (entry 4). Although trimethylphenylammonium triflate[13] reacted with lithium powder smoothly, none of **3d'** was formed (entry 5) and a 14% yield of *N*,*N*-dimethylaniline was obtained. The demethylation would result from the S_N2 reaction of phenyllithium with the ammonium salt and/or a single electron transfer to generate a methyl radical. The Katritzky salt[14] of aniline reacted with lithium powder to afford a complex reaction mixture (entry 6).



Scheme 2 Reaction scope with respect to the *N*-aryl group. The efficiency of the lithiation was quantified by determining the yield of the products **3** by ^{1}H NMR analysis. [a] Lithiation and silylation with Et_3SiCl were performed at 25 °C. [b] 0 °C for 1 h and 25 °C for 1 h for the silylation. [c] Lithiation for 8 h. [d] Lithiation with 4.0 equiv Li powder at 25 °C and silylation with 4.0 equiv Me_3SiCl. [e] 3.0 equiv Na dispersion and LiI.

Table 2 Effect of nitrogen-based leaving groups



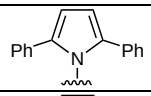
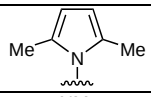
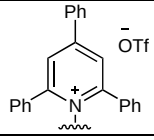
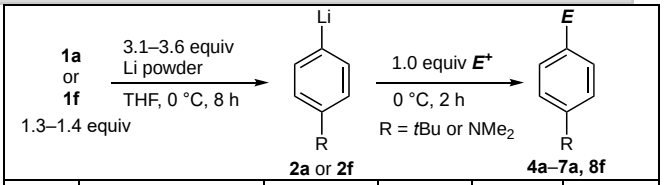
entry	*N*	conversion /%	NMR yield of **3d'** /%
1		>99	84
2		>99	56
3		74	29
4		14	<1
5		>99	<1
6		90	<1

Table 3 Trapping aryllithium **2** with other electrophiles

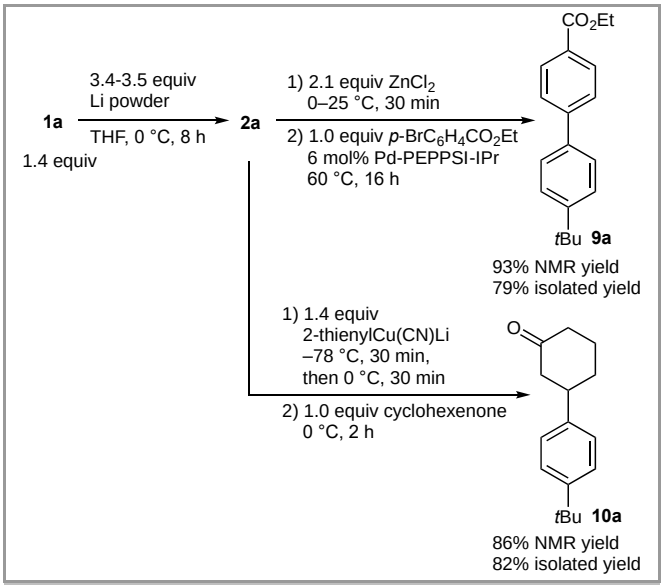


entry	E^+	*E*	product	NMR yield /%	isolated yield /%
1	$PhSO_2SPh$	SPh	**4a**	97	92
2	PhCHO	CH(OH)Ph	**5a**	91	89
3	DMF	CHO	**6a**	87	70
4	PhCONMe(OMe)	PhCO	**7a**	95	88
5[a]	$B(OiPr)_3$	Bpin	**8f**	78	56

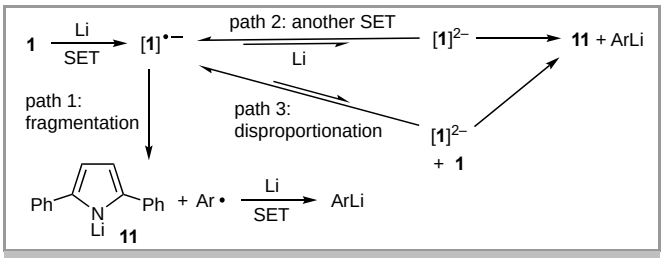
[a] $B(OiPr)_3$ was added at –40 °C and the temperature was gradually warmed up to 25 °C over 2 h. Workup after an addition of pinacol.

The aryllithium reagents thus generated were found to show reactivity similar to those generated from aryl halides, even though 2,5-diphenylpyrrolyllithium existed in the same flasks (Table 3). It is worth noting that, after transmetalation to zinc and copper, a Negishi-coupling with aryl bromide under Pd-PEPPSI-IPr catalysis[15] and conjugate addition to cyclohexenone[16] proceeded to yield biaryl **9a** and ketone **10a** in high yields (Scheme 3). In all the cases, 2,5-diphenylpyrrole was observed in more than 90% yield.

We believe that the reaction begins with a single electron transfer from lithium to **1** (Scheme 4). This first step is likely to proceed very smoothly by judging from the immediate color change of the reaction mixture (from transparent to deep blue) because of the extended π-system of **1**.[1f,g] The resulting radical anion [**1**]$^{\bullet-}$ can fragment into fairly stable pyrrolyllithium **11** and an aryl radical, which should be reduced to aryllithium via SET from lithium (path 1). Alternatively, according to the report by Cohen[17a] and Szwarc,[17b,c] the somewhat stable radical anion [**1**]$^{\bullet-}$ fragments very slowly and can undergo another single electron transfer (path 2) or disproportionation into the dianion [**1**]$^{2-}$ and neutral **1** (path 3) even though these can be in unfavorable equilibria.[18] The highly unstable dianionic species thus generated would immediately fragment into pyrrolyllithium **11** and aryllithium.



Scheme 3 Reactions of aryllithium **2a** via transmetalation.



Scheme 4 Plausible reaction mechanism.

In summary, we have developed a method to generate aryllithium species via reductive C–N bond cleavage from a class of aniline derivatives. The starting 1-aryl-2,5-diphenylpyrroles **1** are readily available from the corresponding anilines via typical Paal-Knorr synthesis. The prepared aryllithium reagents show reactivity similar to other aryllithium reagents generated from aryl halides and are expected to find applications in organic synthesis.

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^{1}H NMR (600 MHz), ^{13}C NMR (151 MHz), ^{11}B NMR (192 MHz), and ^{19}F NMR (564 MHz) were taken on JEOL ECA-600 and ECZ-600 spectrometers. Chemical shifts in ^{1}H NMR spectra were recorded in delta (δ) units, parts per million (ppm) relative to tetramethylsilane (δ = 0.00 ppm) or residual $CHCl_3$ (δ = 7.26 ppm) . Chemical shifts in ^{13}C NMR spectra were recorded in delta (δ) units, parts per million (ppm) relative to $CDCl_3$ (δ = 77.16 ppm). For the ^{11}B and ^{19}F NMR spectra, $BF_3{\cdot}OEt_2$ (^{11}B: δ = 0.00 ppm) and fluorobenzene (^{19}F: δ = –113.50 ppm) were used as external standards, respectively. High resolution mass spectra (HRMS) were obtained on a Bruker micrOTOF II-KR spectrometer in Atmospheric Pressure Chemical Ionization (APCI) method using "LC/MS tuning mix, for APCI, low concentration" (Agilent Technologies, Inc.) as an internal standard. Melting points were determined on a Stanford Research Systems MPA100 melting point apparatus.

All non-aqueous reactions were carried out under an inert atmosphere of Ar (for reactions using lithium metal) or N_2 gas in oven-dried glassware unless otherwise noted. Dehydrated THF was purchased from a commercial supplier and stored under nitrogen atmosphere.

Li powder was prepared according to a modified procedure reported by Yus.[9] The particle size (120–250 μm) of the Li powder was measured by SEM (HITACHI, Miniscope TM3030Plus). Li granule (product No. 444456) was purchased from Sigma-Aldrich and stored under an atmosphere of argon. Na dispersion (ca. 10 M suspension in mineral oil) was provided by KOBELCO ECOSolutions Co., Ltd. LiI (product No. 122-03452) was purchased from FUJIFILM Wako Pure Chemical Corporation, dried under reduced pressure at 120 °C, and then stored under an atmosphere of argon. Mg powder (product No. 135-00062) was purchased from FUJIFILM Wako Pure Chemical Corporation and stored under an atmosphere of argon. $ZnCl_2$ was purchased from FUJIFILM Wako Pure Chemical Corporation (product No. 260-01021) to prepare a 0.5 M THF solution. CuCN (product No. 09511-82) was purchased from Nacalai tesque and stored under an atmosphere of argon.

The activating agent, 1,4-diphenyl-1,4-butanedione,[19] was prepared according to the literature. Substrates, 2,5-dimethyl-1-phenylpyrrole,[20] trimethylphenylammonium triflate,[21] and the Katritzky salt of aniline[22] were prepared according to the literature procedures, while 1-phenylpyrrole [CAS:635-90-5] was obtained from a commercial supplier and used without further purification. Electrophiles Me_3SiCl, Et_3SiCl, PhCHO, $B(O\textit{i}Pr)_3$, and cyclohexenone were purchased from common commercial suppliers and distilled prior to use. PhCONMe(OMe) was prepared according to the literature.[23] All other commercially available reagents were used without further purification unless otherwise noted.

Analytical thin layer chromatography (TLC) was performed on Merck precoated analytical plates, 0.25-mm thick, silica gel 60 F_{254}. Preparative flash chromatography was performed using Silica Gel 60N, spherical neutral, particle size 100–210 μm, purchased from Kanto Chemical Co., Inc.

General procedure for the preparation of pyrroles 1

The synthesis of pyrrole **1a** is representative. A 300-mL flask was charged with 4-*tert*-butylaniline (5.8 mL, 36 mmol), 1,4-diphenyl-1,4-butanedione (7.06 g, 29.6 mmol), and toluene (120 mL). TFA (4.6 mL, 60 mmol) was added at room temperature and the mixture was stirred at 110 °C for 3 h. The reaction was quenched with saturated aqueous $NaHCO_3$ at 0 °C and pyrrole **1a** got precipitated immediately. The white precipitates were filtered off and washed with water and Et_2O to afford pyrrole **1a** (8.69 g, 24.7 mmol, 83% yield) as a white solid.

1-(4-*tert*-butylphenyl)-2,5-diphenyl-1*H*-pyrrole (1a)

^{1}H NMR ($CDCl_3$): δ 7.24 (d, *J* = 8.4 Hz, 2H), 7.16–7.13 (m, 6H), 7.06 (d, *J* = 6.9 Hz, 4H), 6.95 (d, *J* = 8.4 Hz, 2H), 6.48 (s, 2H), 1.28 (s, 9H).

^{13}C NMR ($CDCl_3$): δ 150.6, 136.3, 136.0, 133.5, 128.8, 128.4, 127.9, 126.2, 125.8, 109.9, 34.7, 31.5.

All the resonances in ^{1}H and ^{13}C NMR spectra were consistent with the reported values.[24]

1-(4-octylphenyl)-2,5-diphenyl-1*H*-pyrrole (1b)

Obtained as a white solid (2.36 g, 5.79 mmol, 74% yield) from the diketone (1.86 g, 7.81 mmol), purified by trituration with hexane. Reaction time: 3 h.

^{1}H NMR ($CDCl_3$): δ 7.21–7.11 (m, 6H), 7.09–7.07 (m, 4H), 7.04 (d, *J* = 7.8 Hz, 2H), 6.94 (d, *J* = 7.8 Hz, 2H), 6.49 (s, 2H), 2.59 (t, *J* = 7.9 Hz, 2H), 1.65–1.57 (m, 2H), 1.34–1.22 (m, 10H), 0.90 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR ($CDCl_3$): δ 142.2, 136.6, 135.9, 133.5, 128.9, 128.8, 128.7, 127.9, 126.2, 109.9, 35.5, 32.0, 31.3, 29.6, 29.4, 29.2, 22.8, 14.3.

mp: 133–134 °C.

HRMS (APCI-MS, positive): *m/z* = 408.2669. calcd for $C_{30}H_{34}N$: 408.2686 $[M+H]^+$.

1-(3,5-di-*tert*-butylphenyl)-2,5-diphenyl-1*H*-pyrrole (1c)

Obtained as a white solid (2.38 g, 5.84 mmol, 75% yield) from the diketone (1.86 g, 7.81 mmol), purified by trituration with hexane. Reaction time: 5 h.

^{1}H NMR ($CDCl_3$): δ 7.18–7.11 (m, 7H), 7.05 (d, *J* = 6.9 Hz, 4H), 6.73 (s, 2H), 6.49 (s, 2H), 1.06 (s, 18H).

^{13}C NMR ($CDCl_3$): δ 151.1, 137.6, 135.6, 133.7, 129.1, 127.9, 126.2, 123.5, 119.9, 109.6, 34.7, 31.2.

mp: 184–186 °C.

HRMS (APCI-MS, positive): *m/z* = 408.2699. calcd for $C_{30}H_{34}N$: 408.2686 $[M+H]^+$.

1,2,5-triphenyl-1*H*-pyrrole (1d)

Obtained as a white solid (1.23 g, 4.16 mmol, 85% yield) from the diketone (1.17 g, 4.91 mmol), purified by trituration with hexane and Et_2O. Reaction time: 2 h.

^{1}H NMR ($CDCl_3$): δ 7.25–7.22 (m, 3H), 7.19–7.12 (m, 6H), 7.06 (d, *J* = 6.6 Hz, 4H), 7.04 (d, *J* = 8.4 Hz, 2H), 6.48 (s, 2H).

^{13}C NMR ($CDCl_3$): δ 139.1, 135.9, 133.4, 129.0, 128.89, 128.86, 128.0, 127.4, 126.4, 110.1.

All the resonances in ^{1}H and ^{13}C NMR spectra were consistent with the reported values.[25]

1-(2,6-dimethylphenyl)-2,5-diphenyl-1*H*-pyrrole (1e)

Obtained as a white solid (0.994 g, 3.07 mmol, 60% yield) from the diketone (1.21 g, 5.08 mmol), purified by column chromatography on silica gel (eluent: hexane/EtOAc = 20/1). Reaction time: 4 h.

^{1}H NMR ($CDCl_3$): δ 7.19–7.11 (m, 7H), 7.05–7.01 (m, 6H), 6.60 (s, 2H), 1.88 (s, 6H).

^{13}C NMR ($CDCl_3$): δ 137.7, 137.1, 134.9, 133.4, 128.5, 128.4, 128.1, 127.3, 126.3, 109.7, 18.2.

mp: 126–127 °C.

HRMS (APCI-MS, positive): *m/z* = 324.1756. calcd for $C_{24}H_{22}N$: 324.1747 $[M+H]^+$.

1-(4-dimethylaminophenyl)-2,5-diphenyl-1*H*-pyrrole (1f)

Obtained as a pale-purple solid (3.88 g, 11.5 mmol, 59% yield) from the diketone (4.65 g, 19.5 mmol), purified by trituration with hexane and Et_2O. Reaction time: 4 h.

^1H NMR ($CDCl_3$): δ 7.19–7.16 (m, 4H), 7.13–7.11 (m, 6H), 6.88 (d, *J* = 9.0 Hz, 2H), 6.55 (d, *J* = 9.0 Hz, 2H), 6.46 (s, 2H), 2.93 (s, 6H).

^{13}C NMR ($CDCl_3$): δ 149.5, 136.1, 133.7, 129.4, 128.7, 128.1, 128.0, 126.0, 112.2, 109.5, 40.6.

mp: 214–216 °C.

HRMS (APCI-MS, positive): *m/z* = 339.1870. calcd for $C_{24}H_{23}N_2$: 339.1856 $[M+H]^+$.

1-(4-methoxyphenyl)-2,5-diphenyl-1*H*-pyrrole (1g)

Obtained as a white solid (2.05 g, 6.30 mmol, 81% yield) from the diketone (1.86 g, 7.81 mmol), purified by trituration with EtOAc. Reaction time: 3 h.

^1H NMR ($CDCl_3$): δ 7.19–7.12 (m, 6H), 7.08 (d, *J* = 6.9 Hz, 4H), 6.95 (d, *J* = 8.4 Hz, 2H), 6.75 (d, *J* = 8.4 Hz, 2H), 6.46 (s, 2H), 3.78 (s, 3H).

^{13}C NMR ($CDCl_3$): δ 158.6, 136.0, 133.5, 132.0, 129.9, 128.8, 128.0, 126.3, 114.1, 109.8, 55.5.

All the resonances in ^1H and ^{13}C NMR spectra were consistent with the reported values.[25]

1-(4-hydroxyphenyl)-2,5-diphenyl-1*H*-pyrrole (1g')

Obtained as a white solid (0.612 g, 1.97 mmol, 66% yield) from the diketone (0.714 g, 3.00 mmol), purified by trituration with hexane and Et_2O. Reaction time: 3 h.

^1H NMR ($CDCl_3$): δ 7.20–7.13 (m, 6H), 7.09–7.08 (m, 4H), 6.91 (d, *J* = 8.4 Hz, 2H), 6.70 (d, *J* = 8.4 Hz, 2H), 6.47 (s, 2H).

^{13}C NMR ($CDCl_3$): δ 154.6, 136.0, 133.4, 132.3, 130.2, 128.8, 128.0, 126.3, 115.7, 109.8.

mp: 261–263 °C.

HRMS (APCI-MS, positive): *m/z* = 311.1312, calcd for $C_{22}H_{17}NO$: 311.1305 $[M]^+$.

1-(3-fluorophenyl)-2,5-diphenyl-1*H*-pyrrole (1h)

Obtained as a white solid (1.22 g, 3.89 mmol, 80% yield) from the diketone (1.16 g, 4.87 mmol), purified by trituration with Et_2O. Reaction time: 3 h.

^1H NMR ($CDCl_3$): δ 7.22–7.16 (m, 7H), 7.07 (m, 4H), 6.97 (dt, *J* = 8.4, 3.0 Hz, 1H), 6.83 (d, *J* = 8.4 Hz, 1H), 6.75 (dt, *J* = 9.6 Hz, 2.4 Hz, 1H), 6.47 (s, 2H).

^{13}C NMR ($CDCl_3$): δ 162.5 (d, *J* = 247.5 Hz, 1C), 140.5 (d, *J* = 9.5 Hz, 1C), 135.9, 133.0, 129.9 (d, *J* = 9.5 Hz, 1C), 128.8, 128.2, 126.6, 125.0 (d, *J* = 2.9 Hz, 1C), 116.4 (d, *J* = 22.5 Hz, 1C), 114.6 (d, *J* = 22.5 Hz, 1C), 110.4.

^{19}F NMR ($CDCl_3$): δ –112.0 (app. dd, *J* = 9.0 Hz, 15.2 Hz).

mp: 219–220 °C.

HRMS (APCI-MS, positive): *m/z* = 314.1337. calcd for $C_{22}H_{17}FN$: 314.1340 $[M+H]^+$.

1-(naphthalen-1-yl)-2,5-diphenyl-1*H*-pyrrole (1i)

Obtained as a white solid (1.45 g, 4.20 mmol, 84% yield) from the diketone (1.19 g, 4.99 mmol), purified by column chromatography on silica gel (eluent: hexane/EtOAc = 20:1). Reaction time: 2 h.

^1H NMR ($CDCl_3$): δ 7.81–7.77 (m, 2H), 7.41–7.36 (m, 4H), 7.29 (d, *J* = 7.5 Hz, 1H), 7.03–6.99 (m, 10H), 6.62 (s, 2H).

^{13}C NMR ($CDCl_3$): δ 137.4, 136.1, 134.0, 133.4, 131.9, 128.7, 128.1, 128.0, 127.9, 127.8, 127.1, 126.5, 126.3, 125.1, 123.6, 109.8.

mp: 149–150 °C.

HRMS (APCI-MS, positive): *m/z* = 346.1590. calcd for $C_{26}H_{20}N$: 346.1590$[M+H]^+$.

1-(9,9-dimethyl-9*H*-fluoren-2-yl)-2,5-diphenyl-1*H*-pyrrole (1j)

Obtained as a white solid (1.88 g, 4.57 mmol, 91% yield) from the diketone (1.20 g, 5.04 mmol), purified by column chromatography on silica gel (eluent: hexane/EtOAc = 50:1). Reaction time: 1.5 h.

^1H NMR ($CDCl_3$): δ 7.67 (d, *J* = 6.5 Hz, 1H), 7.55 (d, *J* = 7.9 Hz, 1H), 7.39 (d, *J* = 6.5 Hz, 1H), 7.34–7.31 (m, 2H), 7.16–7.09 (m, 10H), 6.99 (d, *J* = 1.4 Hz, 1H), 6.96 (dd, *J* = 7.9, 1.4 Hz, 1H), 6.51 (s, 2H), 1.22 (s, 6H).

^{13}C NMR ($CDCl_3$): δ 154.3, 154.0, 138.6, 137.9, 137.8, 135.8, 133.5, 129.0, 128.0, 127.6, 127.2, 126.3, 123.6, 122.8, 120.2, 120.1, 110.0, 46.8, 26.8. (One signal is missing probably because of overlapping.)

mp: 68–70 °C.

HRMS (APCI-MS, positive): *m/z* = 412.2052. calcd for $C_{31}H_{26}N$: 412.2060$[M+H]^+$.

1-(4-bromophenyl)-2,5-diphenyl-1*H*-pyrrole (1k')

The precursor of **1k** (*vide infra*). Obtained as a white solid (3.15 g, 8.42 mmol, 86% yield) from the diketone (2.32 g, 9.74 mmol), purified by trituration with Et_2O. Reaction time: 4.5 h.

^1H NMR ($CDCl_3$): δ 7.35 (d, *J* = 8.4 Hz, 2H), 7.22–7.16 (m, 6H), 7.06–7.05 (d, *J* = 7.2 Hz, 4H), 6.89 (d, *J* = 8.4 Hz, 2H), 6.47 (s, 2H).

^{13}C NMR ($CDCl_3$): δ 138.1, 135.8, 133.0, 132.1, 130.5, 128.9, 128.2, 126.6, 121.1, 110.4.

mp: 217–219 °C.

HRMS (APCI-MS, positive): *m/z* = 374.0531. calcd for $C_{22}H_{17}{}^{79}BrN$: 374.0539 $[M+H]^+$.

1-(2-bromophenyl)-2,5-diphenyl-1*H*-pyrrole (1l')

The precursor of **1l** (*vide infra*). Obtained as a white solid (1.44 g, 3.85. mmol, 76% yield) from the diketone (1.21 g, 5.08 mmol), purified by trituration with hexane. Reaction time: 4.0 h.

^1H NMR ($CDCl_3$): δ 7.51–7.49 (m, 1H), 7.30 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.26 (t, *J* = 7.2 Hz, 1H), 7.19–7.13 (m, 7H), 7.12–7.10 (m, 4H), 6.52 (s, 2H).

^{13}C NMR ($CDCl_3$): δ 138.8, 136.2, 133.5, 133.2, 131.9, 129.8, 128.5, 128.1, 128.0, 126.6, 124.6, 109.9.

mp: 165–167 °C.

HRMS (APCI-MS, positive): *m/z* = 374.0556. calcd for $C_{22}H_{17}{}^{79}BrN$: 374.0539 $[M+H]^+$.

1-([1,1'-biphenyl]-3-yl)-2,5-diphenyl-1*H*-pyrrole (1m)

Obtained as a white solid (2.33 g, 6.27 mmol, 80% yield) from the diketone (1.86 g, 7.81 mmol), purified by trituration with hexane and EtOAc. Reaction time: 3.5 h.

^1H NMR ($CDCl_3$): δ 7.46 (d, *J* = 8.2 Hz, 1H), 7.34 (t, *J* = 7.2 Hz, 2H), 7.30–7.28 (m, 2H), 7.24–7.19 (m, 7H), 7.17–7.15 (m, 2H), 7.12 (m, 4H), 6.99–6.98 (m, 1H), 6.51 (s, 2H).

^{13}C NMR ($CDCl_3$): δ 141.8, 140.2, 139.3, 135.9, 133.4, 129.2, 129.0, 128.9, 128.1, 127.73, 127.71, 127.6, 127.1, 126.5, 125.9, 110.1.

mp: 183–184 °C.

HRMS (APCI-MS, positive): *m/z* =372.1740. calcd for $C_{28}H_{22}N$: 372.1747 $[M+H]^+$.

Preparation of 1k

A 100-mL flask was charged with 1-(4-bromophenyl)-2,5-diphenyl-1*H*-pyrrole (**1k'**, 1.12 g, 2.99 mmol), phenylboronic acid (0.549 g, 4.50 mmol), potassium carbonate (0.821 g, 5.94 mmol), and a mixture of toluene and methanol (6:1, v/v, 35 mL). The reaction mixture was degassed by bubbling with N_2 gas over 15 min and then $Pd(OAc)_2$ (33.1 mg, 0.147 mmol) was introduced. The reaction mixture was heated at 60 ℃ for 0.5 h. The reaction was quenched with H_2O. The resulting biphasic solution was extracted three times with EtOAc. The combined organic layer was washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by trituration with hexane to afford **1k** (0.951 g, 2.56 mmol, 86% yield) as a white solid.

1-([1,1'-biphenyl]-4-yl)-2,5-diphenyl-1*H*-pyrrole (1k)[26]

^{1}H NMR ($CDCl_3$): δ 7.60–7.59 (d, *J* = 8.4 Hz, 2H), 7.49 (dd, *J* = 8.6, 2.4 Hz, 2H), 7.43 (t, *J* = 7.5 Hz, 2H), 7.35 (t, *J* = 7.2 Hz, 1H), 7.20–7.14 (m, 6H), 7.12–7.08 (m, 6H), 6.51 (s, 2H).

^{13}C NMR ($CDCl_3$): δ 140.0, 139.8, 138.2, 135.9, 133.3, 129.2, 129.0, 128.9, 128.1, 127.7, 127.4, 127.1, 126.4, 110.2.

mp: 218–220 °C

HRMS (APCI-MS, positive): *m/z* = 372.1733. calcd for $C_{28}H_{22}N$: 372.1747 $[M+H]^+$.

Preparation of 1l

A 100-mL flask was charged with **1l'** (1.13 g, 3.02 mmol), phenylboronic acid (0.489 g, 4.01 mmol), potassium carbonate (0.828 g, 5.99 mmol), and a mixture of toluene and methanol (3:1, v/v, 20 mL). The reaction mixture was degassed by bubbling with N_2 gas over 15 min and then $Pd(OAc)_2$ (35.4 mg, 0.158 mmol) was introduced. The reaction mixture was heated at 60 °C for 0.5 h. The reaction was quenched with H_2O. The resulting biphasic solution was extracted three times with EtOAc. The combined organic layer was washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (eluent: hexane/EtOAc = 20:1 then 10:1) to afford pyrrole **1l** (0.803 g, 2.16 mmol, 72% yield) as a white solid.

1-([1,1'-biphenyl]-2-yl)-2,5-diphenyl-1*H*-pyrrole (1l)[26]

^{1}H NMR ($CDCl_3$): δ 7.41–7.38 (m, 1H), 7.32–7.27 (m, 2H), 7.23–7.22 (m, 1H), 7.13 (t, *J* = 7.2 Hz, 1H), 7.09–7.01 (m, 8H), 6.83 (m, 4H), 6.58–6.57 (m, 2H), 6.37 (s, 2H).

^{13}C NMR ($CDCl_3$): δ 139.9, 138.5, 136.5, 135.7, 133.2, 131.0, 130.4, 128.5, 128.1, 128.0, 127.97, 127.93, 127.8, 126.9, 126.0, 110.0.

mp: 189–191 °C.

HRMS (APCI-MS, positive): *m/z* = 372.1755. calcd for $C_{28}H_{22}N$: 372.1747$[M+H]^+$.

General procedure for the generation of aryllithiums 2 and subsequent synthesis of silanes 3 (Table 1 and 2, Scheme 2)

The synthesis of silane **3a** is representative. A Schlenk tube was charged with lithium powder (20.7 mg, 2.98 mmol) and THF (2.0 mL). After the mixture was stirred at 0 °C for 10 min, pyrrole **1a** (349 mg, 0.993 mmol) was added and was rinsed out of the inside wall with THF (2.0 mL). After the mixture was stirred vigorously at 0 °C for 8 h, Me_3SiCl (0.38 mL, 2.98 mmol) was added. The mixture was stirred at 0 °C for 2 h and the reaction was quenched with water at 0 °C. The resulting biphasic solution was extracted three times with EtOAc. The combined organic layer was washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The resulting crude material was analyzed by ^{1}H NMR spectroscopy with 1,1,2,2-tetrachloroethane (165 mg, 0.981 mmol) as an internal standard, which indicated an 87% NMR yield of silane **3a**. The residue was purified by column chromatography on silica gel (eluent: hexane) to provide silane **3a** (179 mg, 0.867 mmol, 87% yield) as a pale-yellow solid.

General procedure for the synthesis of silanes 3 using Na dispersion (Table 1, Scheme 2)

The synthesis of silane **3a** is representative. A Schlenk tube was charged with pyrrole **1a** (353 mg, 1.00 mmol) and THF (4.0 mL). After the mixture was stirred at 0 °C for 10 min, Na dispersion (9.9 M, 0.30 mL, 3.0 mmol) was added dropwise, and the resulting suspension was stirred vigorously at 0 °C for 8 h. Me_3SiCl (0.38 mL, 2.98 mmol) was then added, and the mixture was stirred at 0 °C for 2 h. Similar aqueous workup and NMR analysis of the mixture were performed. LiI was added at first if necessary.

(4-*tert*-butylphenyl)trimethylsilane (3a)

^{1}H NMR ($CDCl_3$): δ 7.47 (d, *J* = 7.5 Hz, 2H), 7.39 (d, *J* = 7.5 Hz, 2H), 1.32 (s, 9H), 0.26 (s, 9H).

^{13}C NMR ($CDCl_3$): δ 151.8, 137.0, 133.4, 124.8, 34.8, 31.4, –0.9.

All the resonances in ^{1}H and ^{13}C NMR spectra were consistent with the reported values.[27]

trimethyl(4-octylphenyl)silane (3b)

The resulting crude material was analyzed by ^{1}H NMR spectroscopy with 1,1,2,2-tetrachloroethane (180 mg, 1.07 mmol) as an internal standard, which indicated a 97% NMR yield of silane **3b** from **1b** (408 mg, 1.00 mmol). The ^{1}H NMR spectra of **3b** was consistent with the reported values.[28]

(3,5-di-*tert*-butylphenyl)trimethylsilane (3c)

The resulting crude material was analyzed by ^{1}H NMR spectroscopy with 1,1,2,2-tetrachloroethane (177 mg, 1.05 mmol) as an internal standard, which indicated a 93% NMR yield of silane **3c** from **1c** (411 mg, 1.01 mmol).

Obtained as a colorless oil.

^{1}H NMR ($CDCl_3$):δ 7.48 (t, *J* = 2.1 Hz, 1H), 7.42 (d, *J* = 2.1 Hz, 2H), 1.38 (s, 18H), 0.31 (s, 9H).

^{13}C NMR ($CDCl_3$): δ 149.7, 139.4, 127.4, 123.3, 35.0, 31.6, –0.8.

HRMS (APCI-MS, positive): *m/z* = 262.2111, calcd for $C_{17}H_{30}Si$: 262.2111 $[M]^+$.

triethylphenylsilane (3d')

The resulting crude material was analyzed by ^{1}H NMR spectroscopy with 1,1,2,2-tetrachloroethane (167 mg, 0.995 mmol) as an internal standard, which indicated an 84% NMR yield of silane **3d'** from **1d** (298 mg, 1.01 mmol). The ^{1}H NMR spectra of **3d** was consistent with the reported values.[29]

(2,6-dimethylphenyl)trimethylsilane (3e)

The resulting crude material was analyzed by ^{1}H NMR spectroscopy with 1,1,2,2-tetrachloroethane (175 mg, 1.04 mmol) as an internal standard, which indicated a 72% NMR yield of silane **3e** from **1e** (324 mg, 1.00 mmol). The ^{1}H NMR spectra of **3e** was consistent with the reported values.[30]

***N*,*N*-dimethyl-4-(trimethylsilyl)aniline (3f)**

The resulting crude material was analyzed by ^{1}H NMR spectroscopy with 1,1,2,2-tetrachloroethane (183 mg, 1.09 mmol) as an internal standard, which indicated an 86% NMR yield of silane **3f** from **1f** (341 mg, 1.01 mmol). The ^{1}H NMR spectra of **3f** was consistent with the reported values.[31]

(4-methoxyphenyl)trimethylsilane (3g), 4-(trimethylsilyl)phenol (3g'), and 1-(4-hydroxyphenyl)-2,5-diphenyl-1*H*-pyrrole (1g')

The resulting crude material was analyzed by ^{1}H NMR spectroscopy with 1,1,2,2-tetrachloroethane (162 mg, 0.965 mmol) as an internal standard, which indicated 33%, 30% and 23% NMR yields of silanes **3g** and **3g'** and phenol **1g'**, respectively, from **1g** (325 mg, 0.999 mmol). The ^{1}H NMR spectra of **3g**[27] and **3g'**[32] were consistent with the reported values.

4-(trimethylsilyl)phenol (3g')

The resulting crude material was analyzed by ^{1}H NMR spectroscopy with 1,1,2,2-tetrachloroethane (175 mg, 1.04 mmol) as an internal standard, which indicated a 55% NMR yield of silane **3g'** from **1g'** (234 mg, 0.751 mmol). The ^{1}H NMR spectrum of **3g'** was consistent with the reported values.[32]

(3-fluorophenyl)trimethylsilane (3h)

The resulting crude material was analyzed by ^{1}H NMR spectroscopy with 1,1,2,2-tetrachloroethane (176 mg, 1.05 mmol) as an internal standard, which indicated a 23% NMR yield of silane **3h** from **1h** (313 mg, 0.999 mmol). The ^{1}H NMR spectra of **3h** was consistent with the reported values.[33]

trimethyl(naphthalen-1-yl)silane (3i)

The resulting crude material was analyzed by ^{1}H NMR spectroscopy with 1,1,2,2-tetrachloroethane (168 mg, 1.00 mmol) as an internal standard, which indicated a 46% NMR yield of silane **3i** from **1i** (345 mg, 0.999 mmol). The ^{1}H NMR spectra of **3i** was consistent with the reported values.[31]

(9,9-dimethyl-9*H*-fluoren-2-yl)trimethylsilane (3j)

The resulting crude material was analyzed by ^{1}H NMR spectroscopy with 1,1,2,2-tetrachloroethane (168 mg, 1.00 mmol) as an internal standard, which indicated a 78% NMR yield of silane **3j** from **1j** (413 mg, 1.00 mmol).

Obtained as a colorless oil.

^{1}H NMR ($CDCl_3$): δ 7.74–7.71 (m, 2H), 7.57 (s, 1H), 7.51 (d, *J* = 7.5 Hz, 1H), 7.44–7.43 (m, 1H), 7.35–7.32 (m, 2H), 1.50 (s, 6H), 0.32 (s, 9H).

^{13}C NMR ($CDCl_3$): δ 153.9, 152.8, 140.1, 139.5, 139.3, 132.2, 127.5, 127.4, 127.0, 122.7, 120.3, 119.5, 46.9, 27.3, −0.7.

HRMS (APCI-MS, positive): *m/z* = 266.1482, calcd for $C_{18}H_{22}Si$: 266.1485 $[M]^+$.

[1,1'-biphenyl]-4-yltrimethylsilane (3k)

The resulting crude material was analyzed by ^{1}H NMR spectroscopy with 1,1,2,2-tetrachloroethane (177 mg, 1.05 mmol) as an internal standard, which indicated a 72% NMR yield of silane **3k** from **1k** (371 mg, 0.999 mmol). The ^{1}H NMR spectra of **3k** was consistent with the reported values.[34]

[1,1'-biphenyl]-2-yltrimethylsilane (3l)

The resulting crude material was analyzed by ^{1}H NMR spectroscopy with 1,1,2,2-tetrachloroethane (158 mg, 0.941 mmol) as an internal standard, which indicated an 85% NMR yield of silane **3l** from **1l** (378 mg, 1.02 mmol). The ^{1}H NMR spectra of **3l** was consistent with the reported values.[35]

[1,1'-biphenyl]-3-yltrimethylsilane (3m)

The resulting crude material was analyzed by ^{1}H NMR spectroscopy with 1,1,2,2-tetrachloroethane (165 mg, 0.983 mmol) as an internal standard, which indicated a 79% NMR yield of silane **3m** from **1m** (372 mg, 1.00 mmol).

Obtained as a colorless oil.

^{1}H NMR ($CDCl_3$): δ 7.72 (s, 1H), 7.60 (d, *J* = 8.2 Hz, 2H), 7.57 (d, *J* = 7.3 Hz, 1H), 7.52 (d, *J* = 7.3 Hz, 1H), 7.46–7.43 (m, 3H), 7.35 (t, *J* = 7.2 Hz, 1H), 0.31 (s, 9H).

^{13}C NMR ($CDCl_3$): δ 141.8, 141.2, 140.7, 132.4, 132.3, 128.9, 128.3, 127.9, 127.5, 127.3, −0.9.

HRMS (APCI-MS, positive): *m/z* = 226.1165, calcd for $C_{15}H_{18}Si$: 226.1172 $[M]^+$.

General procedure for the trapping with other electrophiles (Table 3)

The synthesis of sulfide **4a** is representative. A Schlenk tube was charged with lithium powder (17.2 mg, 2.48 mmol) and THF (2.0 mL). After the mixture was stirred at 0 °C for 10 min, pyrrole **1a** (348 mg, 0.990 mmol) was added and was rinsed out of the inside wall with THF (2.0 mL). After the mixture was stirred vigorously at 0 °C for 8 h, a solution of $PhSO_2SPh$ (173 mg, 0.691 mmol) in THF (1.0 mL) was added. The mixture was stirred at 0 °C for 2 h and the reaction was quenched with water at 0 °C. The resulting biphasic solution was extracted three times with EtOAc. The combined organic layer was washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (eluent: hexane) to provide sulfide **4a** (154 mg, 0.635 mmol, 92% yield) as a pale-yellow oil.

(4-*tert*-butylphenyl)(phenyl)sulfane (4a)

^{1}H NMR ($CDCl_3$): δ 7.34 (d, *J* = 7.8 Hz, 2H), 7.31–7.26 (m, 6H), 7.21 (t, *J* = 7.8 Hz, 1H), 1.31 (s, 9H).

^{13}C NMR ($CDCl_3$): δ 150.7, 136.7, 131.7, 131.6, 130.3, 129.2, 126.7, 126.4, 34.7, 31.4.

All the resonances in ^{1}H and ^{13}C NMR spectra were consistent with the reported values.[36]

(4-*tert*-butylphenyl)(phenyl)methanol (5a)

Obtained as a pale-yellow solid (147 mg, 0.612 mmol, 89% yield) from PhCHO (72.8 mg, 0.686 mmol), purified by column chromatography on silica gel (eluent: hexane/EtOAc = 20/1 then 15/1).

^{1}H NMR ($CDCl_3$): δ 7.40 (d, *J* = 6.8 Hz, 2H), 7.36–7.32 (m, 4H), 7.30 (d, *J* = 8.2 Hz, 2H), 7.27 (t, *J* = 7.8 Hz, 1H), 5.82 (d, *J* = 3.4 Hz, 1H), 2.21 (d, *J* = 3.4 Hz, 1H), 1.30 (s, 9H).

^{13}C NMR ($CDCl_3$): δ 150.6, 144.0, 141.0, 128.6, 127.6, 126.6, 126.4, 125.6, 76.2, 34.6, 31.5.

All the resonances in ^{1}H and ^{13}C NMR spectra were consistent with the reported values.[37]

4-*tert*-butylbenzaldehyde (6a)

Obtained as a pale-yellow oil (86.5 mg, 0.533 mmol, 70% yield) from DMF (55.7 mg, 0.762 mmol), purified by the liquid−liquid extraction protocol according to the literature procedure.[38]

^{1}H NMR ($CDCl_3$): δ 9.99 (s, 1H), 7.83 (d, *J* = 8.9 Hz, 2H), 7.56 (d, *J* = 8.9 Hz, 2H), 1.36 (s, 9H).

^{13}C NMR ($CDCl_3$): δ 192.2, 158.6, 134.2, 129.8, 126.1, 35.5, 31.2.

All the resonances in ^{1}H and ^{13}C NMR spectra were consistent with the reported values.[39]

(4-*tert*-butylphenyl)(phenyl)methanone (7a)

Obtained as a pale-yellow oil (168 mg, 0.705 mmol, 88% yield) from PhCONMe(OMe) (133 mg, 0.805 mmol), purified by column chromatography on silica gel (eluent: hexane/CH_2Cl_2 = 3/1 then 1/1).

^{1}H NMR ($CDCl_3$): δ 7.82–7.80 (m, 2H), 7.78–7.77 (m, 2H), 7.58 (t, *J* = 7.2 Hz, 1H), 7.51–7.47 (m, 4H), 1.37 (s, 9H).

^{13}C NMR ($CDCl_3$): δ 196.6, 156.3, 138.0, 134.9, 132.3, 130.3, 130.1, 128.3, 125.4, 35.2, 31.3.

All the resonances in ^{1}H and ^{13}C NMR spectra were consistent with the reported values.[40]

Procedure for the synthesis of boronate 8f (Table 3)

A Schlenk tube was charged with lithium powder (17.4 mg, 2.51 mmol) and THF (2.0 mL). After the mixture was stirred at 0 °C for 10 min, pyrrole **1f** (339 mg, 1.00 mmol) was added and was rinsed out of the inside wall with THF (2.0 mL). After the mixture was stirred vigorously at 0 °C for 8 h, a solution of $B(O\textit{i}Pr)_3$ (138 mg, 0.734 mmol) in THF (1.0 mL) was added at −40 °C and the resulting mixture was gradually warmed up to room temperature over 2 h. After the mixture was stirred for 2 h, pinacol (95.8 mg, 0.811 mmol) was added. The mixture was stirred for 0.5 h at room temperature and sat. aq. NH_4Cl was then added. The resulting biphasic solution was extracted three times with EtOAc. The combined organic layer was washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (eluent: hexane/CH_2Cl_2 = 3/1 then 1/3) to provide boronate **8f** (101 mg, 0.409 mmol, 56% yield) as a pale-yellow solid.

***N*,*N*-dimethyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline (8f)**

^{1}H NMR ($CDCl_3$): δ 7.69 (d, *J* = 8.4 Hz, 2H), 6.69 (d, *J* = 8.4 Hz, 2H), 2.99 (s, 6H), 1.32 (s, 12H).

^{13}C NMR ($CDCl_3$): δ 152.6, 136.3, 111.3, 83.3, 40.2, 25.0. (The carbon bearing the boron atom was hardly observed due to the quadrupolar relaxation mechanism of ^{11}B nucleus).

^{11}B NMR ($CDCl_3$): δ 30.8 (br).

All the resonances in ^{1}H, ^{13}C, and ^{11}B NMR spectra were consistent with the reported values.[41]

Procedure for the synthesis of biaryl 9a (Scheme 3)

A Schlenk tube was charged with lithium powder (17.4 mg, 2.51 mmol) and THF (2.0 mL). After the mixture was stirred at 0 °C for 10 min, pyrrole **1a** (353 mg, 1.00 mmol) was added and was rinsed out of the inside wall with THF (2.0 mL). After the mixture was stirred vigorously at 0 °C for 8 h, a THF solution of $ZnCl_2$ (1.5 mmol) was added and the resulting mixture was warmed up to room temperature. After the mixture was stirred for 0.5 h, Pd-PEPPSI-IPr (26.3 mg, 0.039 mmol) and *p*-$BrC_6H_4CO_2Et$ (168 mg, 0.733 mmol) were added sequentially. The mixture was stirred at 60 °C for 16 h and the reaction was terminated by adding sat. aq. NH_4Cl. The resulting biphasic solution was extracted three times with EtOAc. The

combined organic layer was washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (eluent: hexane/CH_2Cl_2 = 5/1 then 1/1) to provide biaryl **9a** (164 mg, 0.581 mmol, 79% yield) as a white solid.

ethyl 4'-*tert*-butyl-[1,1'-biphenyl]-4-carboxylate (9a)

^{1}H NMR ($CDCl_3$): δ 8.11 (d, *J* = 8.2 Hz, 2H), 7.66 (d, *J* = 8.2 Hz, 2H), 7.59 (d, *J* = 8.5 Hz, 2H), 7.50 (d, *J* = 8.5 Hz, 2H), 4.41 (q, *J* = 7.1 Hz, 2H), 1.42 (t, *J* = 7.1 Hz, 3H), 1.38 (s, 9H).

^{13}C NMR ($CDCl_3$): δ 166.7, 151.4, 145.5, 137.2, 130.2, 129.1, 127.1, 126.9, 126.0, 61.1, 34.8, 31.5, 14.5.

All the resonances in ^{1}H and ^{13}C NMR spectra were consistent with the reported values.[42]

Procedure for the synthesis of ketone 10a (Scheme 3)

2-ThienylCu(CN)Li was prepared according to a modified procedure reported by Lipshutz.[16] A Schlenk tube was charged with a solution of thiophene (89.0 mg, 1.06 mmol) in THF (1.0 mL). Butyllithium (1.0 mmol, 1.6 M in hexane, 0.63 mL) was then added at –78 °C. The mixture was stirred at –78 °C for 15 min and at 0 °C for an additional 2 h. The solution was transferred into a slurry of CuCN (89.7 mg, 1.00 mmol) and THF (2.0 mL), with a rinse with 1.0 mL of THF.

A Schlenk tube was charged with lithium powder (17.4 mg, 2.51 mmol) and THF (2.0 mL). After the mixture was stirred at 0 °C for 10 min, pyrrole **1a** (352 mg, 1.00 mmol) was added and was rinsed out of the inside wall with THF (2.0 mL). After the mixture was stirred vigorously at 0 °C for 8 h, the THF solution of 2-thienylCu(CN)Li prepared as above was added at –78 °C. After the mixture was stirred at –78 °C for 30 min and at 0 °C for an additional 30 min, a solution of cyclohexenone (67.8 mg, 0.705 mmol) in THF (1.0 mL) was added. The mixture was stirred at 0 °C for 2 h and the reaction was quenched with sat. aq. NH_4Cl at 0 °C. The resulting biphasic solution was extracted three times with EtOAc. The combined organic layer was washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (eluent: hexane/CH_2Cl_2 = 3:1 then 1:3) to provide ketone **10a** (133 mg, 0.577 mmol, 82% yield) as a pale-yellow solid.

3-(4-(*tert*-butyl)phenyl)cyclohexan-1-one (10a)

^{1}H NMR ($CDCl_3$): δ 7.35 (d, *J* = 8.2 Hz, 2H), 7.15 (d, *J* = 8.2 Hz, 2H), 2.99 (tt, *J* = 12.6, 3.6 Hz, 1H), 2.61–2.35 (m, 4H), 2.16–2.07 (m, 2H), 1.87–1.76 (m, 2H), 1.31 (s, 9H).

^{13}C NMR ($CDCl_3$): δ 211.4, 149.6, 141.4, 126.3, 125.6, 49.1, 44.3, 41.3, 34.5, 32.9, 31.5, 25.7.

All the resonances in ^{1}H and ^{13}C NMR spectra were consistent with the reported values.[43]

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Supporting Information

Yes

Primary Data

No

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