

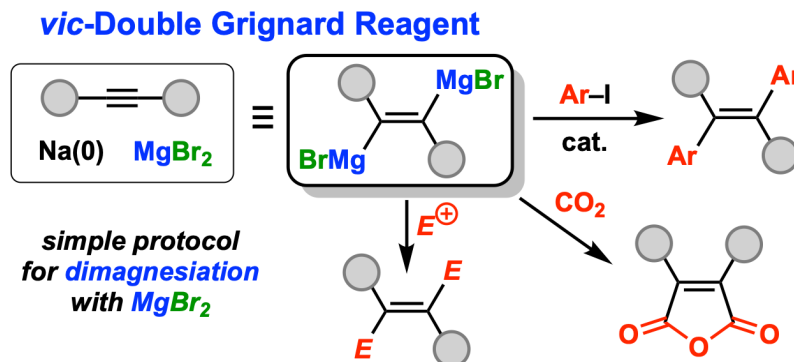
Sodium-mediated Reductive *anti*-Dimagnesiation of Diarylacetylenes with Magnesium Bromide

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This paper is dedicated to Professor Dr. Thorsten Bach on his 60th birthday.



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Abstract Diarylacetylenes undergo *anti*-dimagnesiation using magnesium bromide and Na dispersion to afford (*E*)-1,2-dimagnesioalkenes. This dimagnesiation utilizes simple MgBr_2 as a reduction-resistant electrophile, contrasting with the previously reported dimagnesiation using tricky organomagnesium halides. The resulting *vicinal* double Grignard reagents react with various electrophiles to yield multi-substituted alkenes stereoselectively.

Key words organomagnesium, sodium dispersion, alkynes, electron transfer, multi-substituted alkenes

Since the discovery of the Barbier reaction¹ and the Grignard reaction,² organomagnesium species have served as versatile reagents for various bond formations in organic synthesis for over a century.³ Naturally, methods to generate Grignard reagents have also been an important subject of investigation.⁴ Two typical approaches to the reagents include reduction of organic halides with magnesium metal⁵ and halogen-magnesium exchange⁶ (Figure 1A). However, these approaches rely on organic halide precursors, thereby limiting accesses to certain organomagnesium compounds such as *vicinal* dimagnesio species due to inevitably rapid β -elimination from 1-magnesio-2-halo intermediates (Figure 1B). While a handful of examples of 1,2-dimagnesioalkanes⁷ and -alkenes^{7,8} have been reported, the methods require intricately designed magnesium complexes to achieve the addition of $\text{Mg(I)}\text{--Mg(I)}$ complexes across C–C multiple bonds and are hence practically inconvenient for organic synthesis (Figure 1C).

Recently, we reported the synthesis of (*E*)-1,2-dimagnesioalkenes **A–R** via electron injection to alkynes from sodium metal in the presence of alkylmagnesium halide RMgX (Figure 1D).⁹ The coordination of the alkyl ligand R has been considered to make the magnesium center electron-rich to suppress its reduction with sodium metal. The reductive dimagnesiation process to generate **A–R** include the transient formation of organosodium intermediates from alkynes through single electron reduction and the subsequent transmetalation to the co-existing RMgX electrophile. Very recently, we have

achieved reductive *anti*-dizincation of alkynes using $\text{ZnCl}_2(\text{tmeda})$ as reduction-resistant zinc electrophiles (Figure 1E).¹⁰ Encouraged by the success of the dizincation using a simple zinc halide, we decided to revisit the investigation of magnesiation reagents, despite the intuition that simple magnesium halides readily undergo reduction by sodium metal to form Rieke magnesium.¹¹ Herein, we report reductive *anti*-dimagnesiation of alkynes by the use of a simple magnesium salt.

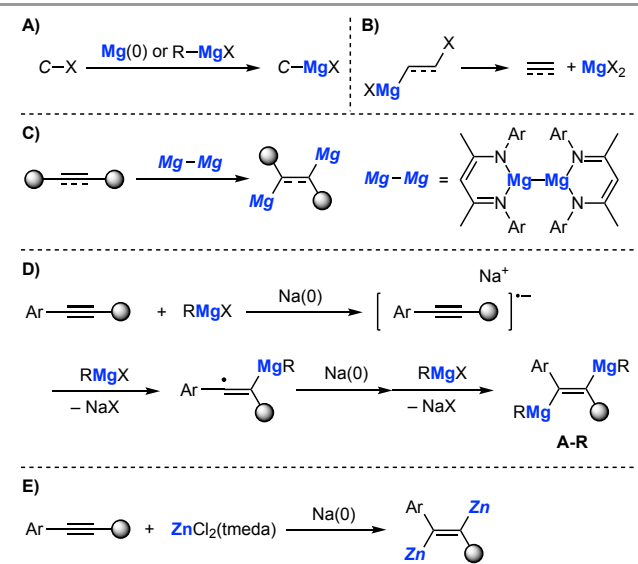


Figure 1 Generation of organomagnesium species: A) Common methods for generation of organomagnesium halides. B) β -Elimination from 1-magnesio-2-halo species. C) Addition of $\text{Mg(I)}\text{--Mg(I)}$ complex to alkenes and alkynes. D) Reductive *anti*-1,2-dimagnesiation of alkynes with RMgX as an electrophile. E) Reductive *anti*-1,2-dizincation using a zinc halide.

Our study commenced with screening magnesium salts for the model dimagnesiation of tolane (**1a**) with the aid of Na dispersion.^{12–14} The resulting dimagnesioalkene **A–X**, formed through sequential reduction and transmetalation processes similar to those of **A–R** in Figure 1D, was treated with D_2O to yield dideuterated stilbene (**2a-d₂**). Following our previous dimagnesiation with alkylmagnesium halides,⁹ the reductive

dimagnesiation of **1a** was performed using 2 equivalents of simple magnesium salts and Na dispersion (Table 1). The reactions using Mg(OTf)₂, MgF₂, and MgCl₂ afforded only trace amounts of **2a** (entries 1–3). In these cases, upon the addition of Na dispersion into the mixture of **1a** and a magnesium salt in THF, the mixture immediately turned to a black suspension, indicating the formation of Rieke magnesium. Interestingly, dimagnesiation using MgBr₂ led to formation of a reddish orange suspension (entry 4), similar to the orange-colored 1,2-dimagnesioalkene **A-R**.⁹ Quenching the resulting orange suspension with D₂O afforded **2a** in 71% yield with a high deuterium incorporation and an *E*:*Z* ratio of 89:11. However, the 14% remainder of **1a** implied that the reduction of MgBr₂ with sodium metal competitively proceeded, resulting in fruitless consumption of both MgBr₂ and sodium metal. To address the deficiency of MgBr₂ and sodium metal, larger amounts, 2.5 equivalents, of MgBr₂ and Na dispersion were used, improving the yield of **2a** (entry 5). High *E* selectivity and 97% deuterium incorporation were observed, suggesting the intermediacy of *anti*-dimagnesiated species **A-Br**. When MgI₂ was investigated as a magnesium electrophile, a much darker brown suspension was formed to eventually yield **2a** in low yield with poor stereoselectivity (entry 6).

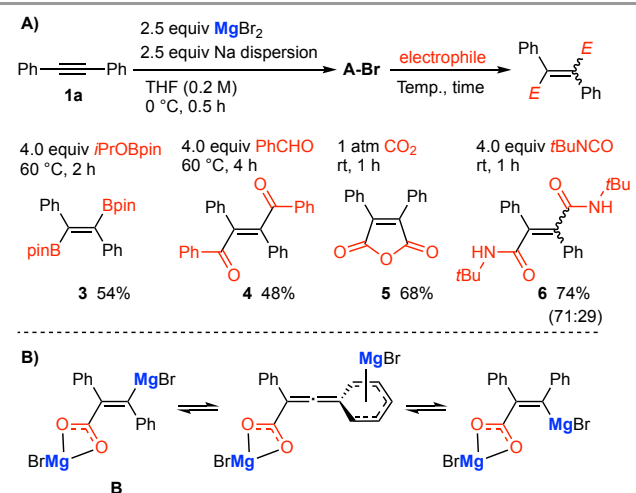
Table 1 Screening magnesium electrophiles for dimagnesiation of **1a**.

$\text{Ph}-\text{C}\equiv\text{C}-\text{Ph} \xrightarrow[\text{THF (0.2 M), 0 }^\circ\text{C, 0.5 h}]{\substack{2.0 \text{ equiv MgX}_2 \\ 2.0 \text{ equiv Na dispersion}}} \text{Ph}-\text{C}(\text{MgX})=\text{C}(\text{MgX})-\text{Ph} \xrightarrow{\text{D}_2\text{O}} \text{Ph}-\text{C}(\text{D})=\text{C}(\text{D})-\text{Ph}$				
Entry	MgX ₂	yield of 2a (%) ^a	%D ^b	<i>E</i> : <i>Z</i> ^a
1	Mg(OTf) ₂	<1	-	-
2	MgF ₂	<1	-	-
3	MgCl ₂	<1	-	-
4	MgBr ₂	71	98	89:11
5	2.5 equiv MgBr ₂ ^c	98	97	87:13
6	MgI ₂	37	- ^d	62:38

^a Yields and *E*/*Z* ratios were determined by FID-GC analysis using tetradecane as an internal standard. ^b Deuterium incorporations in (*E*)-**2a** were determined by ¹H NMR spectroscopy. ^c With 2.5 equiv Na dispersion. ^d Deuterium incorporation in (*E*)-**2a** could not be determined due to overlapping with ¹H NMR signals of other products.

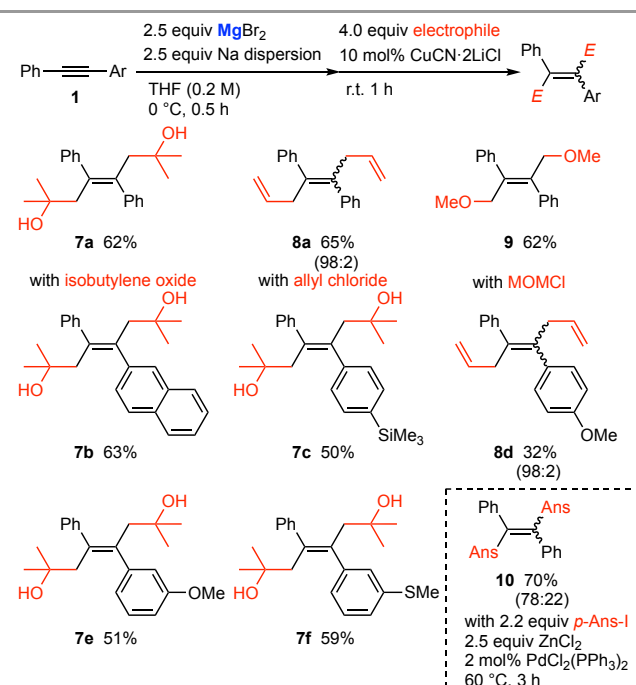
With the optimal conditions for *anti*-selective dimagnesiation with MgBr₂ (Table 1, entry 5), we have examined *vic*-double Grignard reactivity of 1,2-dimagnesioalkene **A-Br** (Scheme 1A). In our previous study,^{9a} the reaction of dimagnesioalkene **A-cPent** prepared from cyclopentylmagnesium bromide required 6.0 equivalents of isopropoxypinacolborane (*i*PrOBpin) due to the side-reaction by the cyclopentylmagnesium moiety. In contrast, fewer equivalents of *i*PrOBpin were needed for **A-Br** to afford 1,2-borylalkene **3**. Dimagnesioalkene **A-Br** also reacted with benzaldehyde. However, Oppenauer-type oxidation¹⁵ of the resulting magnesium alkoxide subsequently took place to yield 1,2-dibenzoyl alkene **4**. To our surprise, exposure of **A-Br** to an atmosphere of CO₂ resulted in formation of diphenylmaleic anhydride (**5**) in 68% yield, while expected diphenylfumarc acid was not obtained. After the reaction of **A-Br** with one equivalent of CO₂, the stereoinversion of the remaining alkenylmagnesium moiety^{8,16} in intermediate **B** could preferentially occur to introduce the second CO₂ molecule in a *syn* fashion and then to form **5** (Scheme 1B). It is noteworthy that the addition of CO₂ to dimagnesioalkene **A-cPent** afforded only a trace amount of **5**, along with a significant amount of *c*PentCO₂H. Reaction of **A-Br**

with *tert*-butyl isocyanate afforded diphenylfumaramide **6** in 74% yield with an *E*:*Z* ratio of 71:29.



Scheme 1 *vic*-Double Grignard reactivity of **A-Br**: A) Substrate scope with respect to electrophiles. C) Plausible mechanism for stereoinversion of **B**.

With the aid of a copper catalyst CuCN·2LiCl,¹⁷ 1,2-dimagnesioalkene **A-Br** reacted with other electrophiles (Scheme 2). Reactions with isobutylene oxide, allyl chloride, and methoxymethyl chloride (MOMCl) gave the corresponding tetrasubstituted alkenes **7a**, **8a**, and **9**, respectively, in good yields.



Scheme 2 Synthesis of tetrasubstituted alkenes via transmetalation to copper.

This dimagnesiation method with MgBr₂ also accommodates diarylacetylene with a π -extended naphthyl group to give **7b**. Even under strongly reducing and basic conditions for dimagnesiation, silyl (**7c**), methoxy (**8d** and **7e**), and thioether (**7f**) were well tolerated. Unfortunately, dimagnesiation of alkylarylacetylenes with MgBr₂ was not successful because the

reduction of MgBr_2 would predominate over that of the substrates that have electron-donating alkyl groups.

Transmetallation of **A-Br** to zinc chloride and subsequent Negishi coupling with aryl iodide afforded tetraarylethylene **10**. In our previous study on transmetallation of 1,2-dimagnesioalkene to zinc for Negishi coupling,^{9b} it was troublesome that the organic moiety **R** (**R** = Me, *c*Pent, *t*Bu, Me_3SiCH_2) in **A-R** from the magnesium electrophile RMgX was also transmetallated to zinc and involved in the cross-coupling reaction. To avoid such unwanted transmetallation events, preparation of **A-(Me₃Si)₂CH** from an elaborate organomagnesium halide $(\text{Me}_3\text{Si})_2\text{CHMgCl}$ was required. To our delight, the dimagnesiation method using MgBr_2 allowed the subsequent Negishi coupling to efficiently yield the product without using such a dummy alkyl ligand.

In summary, we have developed reductive *anti*-dimagnesiation of alkynes with simple magnesium bromide and Na dispersion. The choice of magnesium bromide is crucial to suppress the reduction of magnesium(II) species. This reductive dimagnesiation using MgBr_2 provides 1,2-dimagnesioalkenes **A-Br**, *vic*-double Grignard reagents. The *vic*-double nucleophiles reacted with various electrophiles to give multi-substituted alkenes. Further exploration of reductive dimetallation is in progress.

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¹H NMR (600 MHz), ¹¹B NMR (192 MHz), and ¹³C NMR (151 MHz) spectra were recorded on a JEOL ECZ-600 spectrometer. Chemical shifts in ¹H NMR spectra were recorded in delta (δ) units, parts per million (ppm) relative to residual CHCl_3 (δ = 7.26 ppm) or $\text{CD}_3\text{COCHD}_2$ (δ = 2.05 ppm). Chemical shifts in ¹³C NMR spectra were recorded in delta (δ) units, parts per million (ppm) relative to CDCl_3 (δ = 77.16 ppm) or $\text{CD}_3\text{COCOD}_3$ (δ = 29.84 ppm). For ¹¹B spectra, $\text{BF}_3\cdot\text{OEt}_2$ (δ = 0.00 ppm) was used as an external standard. Mass spectra were determined on a Bruker micrOTOF II spectrometer. TLC analyses were performed on commercial glass plates bearing a 0.25-mm layer of Merck Silica gel 60F₂₅₄. Purification was done by column chromatography using silica gel (KANTO CHEMICAL CO., INC., Silica gel 60 N, spherical neutral, particle size 100–210 μm) or monolithic silica column.¹⁸ Preparative recycling gel permeation chromatography (GPC) was done on a JAI LC-9260 II NEXT system using CHCl_3 as the eluent. FID-GC analysis was carried out using a Shimadzu GC-2025 system equipped with a Shimadzu GC column SH-Rtx-5 (30 m $\times$ 0.25 mm $\times$ 0.25 μm). Anhydrous THF was purchased from KANTO CHEMICAL CO., INC. and stored under an atmosphere of nitrogen. $\text{Mg}(\text{OTf})_2$, MgF_2 , MgCl_2 , MgBr_2 , and MgI_2 were purchased from Aldrich and dried under vacuum at 150 °C prior to use. Alkynes **1b**, **1d**, **1e**, and **1f** were prepared according to the literature.^{9a} *i*PrOBpin, isobutylene oxide, allyl chloride, and MOMCl were purchased from commercial suppliers and distilled prior to use. CO_2 gas (99.5%) was purchased from Nippon Sanso Holdings Corp. Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. Na dispersion (ca. 10 M suspension in mineral oil) was provided by KOBELCO ECO-Solutions Co., Ltd. The concentration of the Na dispersion was determined by acid-base titration. The reactions were carried out under an atmosphere of nitrogen.

Procedures and Characterization Data

General procedure for screening magnesium electrophiles (Table 1)

An oven-dried 20-mL Schlenk tube was charged with MgX_2 (2.0 mmol), **1a** (178 mg, 1.00 mmol), and THF (6.3 mL) under nitrogen atmosphere. The mixture was heated at 60 °C for 10 min to dissolve MgX_2 . After the mixture was cooled to 0 °C, Na dispersion (10 M, 0.20 mL, 2.0 mmol) was added dropwise and the resulting suspension was stirred at 0 °C for 30 min. D_2O (1.0 mL) was then added and the resulting biphasic solution was stirred additionally for 10 min. After addition of aqueous HCl (1 M, 2.5 mL), the

resulting biphasic solution was extracted with EtOAc (4 mL $\times$ 3). The combined organic layer was dried over Na_2SO_4 and filtered. The filtrate was concentrated under reduced pressure. The yield and *E/Z* ratio of **2a-d₂** were determined by FID-GC analysis with tetradecane as an internal standard.

Procedure for synthesis of 1,2-diphenyl-1,2-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethene (**3**) (Scheme 1)

An oven-dried 20-mL Schlenk tube was charged with MgBr_2 (0.4 M in THF, 6.3 mL, 2.5 mmol) and **1a** (178 mg, 1.00 mmol) under nitrogen atmosphere. After the mixture was cooled to 0 °C, Na dispersion (10 M, 0.25 mL, 2.5 mmol) was added dropwise and the resulting reddish orange suspension was stirred at 0 °C for 30 min. After the addition of *i*PrOBpin (0.81 mL, 4.01 mmol), the mixture was warmed up to 60 °C and stirred for an additional 2 h. The reaction was then quenched with aqueous HCl (1 M, 2.5 mL) and the resulting biphasic solution was extracted with EtOAc (4 mL $\times$ 3). The combined organic layer was dried over Na_2SO_4 , filtered, and concentrated under reduced pressure. The yield of **3** was determined as 63% NMR yield (*E:Z* = 90:10) by ¹H NMR measurement with dibromomethane as an internal standard. Purification by column chromatography on silica gel with a hexane/EtOAc (40/1 to 20/1) eluent gave a white solid (264 mg, *R_f* = 0.2, hexane/EtOAc = 10/1). The ¹H NMR spectrum of the obtained showed a mixture of (*E*)-**3** and its reduced form, diborylalkane **3'**,^{14a} in an 88:12 ratio. The yield of (*E*)-**3** after column chromatography was calculated as 54% (232 mg, 0.537 mmol) by ¹H NMR analysis of the obtained mixture.

(*E*)-**3**: ¹H NMR (CDCl_3): δ 7.35 (d, *J* = 7.2 Hz, 4H), 7.28 (t, *J* = 7.2 Hz, 4H), 7.22 (t, *J* = 7.2 Hz, 2H), 1.08 (s, 24H); ¹³C NMR (CDCl_3): δ 147.7, 143.3, 128.2, 128.0, 126.8, 83.6, 24.6; ¹¹B NMR (CDCl_3): δ 30.4, 22.3. All the resonances in the ¹H and ¹³C NMR spectra were consistent with the reported values.^{9a}

Procedure for synthesis of (*E*)-1,2,3,4-tetraphenylbut-2-ene-1,4-dione (**4**) (Scheme 1)

An oven-dried 20-mL Schlenk tube was charged with MgBr_2 (0.4 M in THF, 6.3 mL, 2.5 mmol) and **1a** (178 mg, 0.996 mmol) under nitrogen atmosphere. After the mixture was cooled to 0 °C, Na dispersion (10 M, 0.25 mL, 2.5 mmol) was added dropwise and the resulting reddish orange suspension was stirred at 0 °C for 30 min. After the addition of benzaldehyde (0.510 mL, 5.05 mmol), the mixture was warmed up to 60 °C and stirred for an additional 4 h. The reaction was then quenched with aqueous HCl (1 M, 2.5 mL) and the resulting biphasic solution was extracted with EtOAc (4 mL $\times$ 3). The combined organic layer was dried over Na_2SO_4 , filtered, and concentrated under reduced pressure. Purification by column chromatography on silica gel with hexane (*R_f* = 0.1) and then GPC (eluent: CHCl_3) gave **4** as a white solid (186 mg, 0.479 mmol, 48%); ¹H NMR (CDCl_3): δ 7.52 (d, *J* = 6.9 Hz, 4H), 7.28–7.21 (m, 12H), 7.17–7.16 (m, 4H); ¹³C NMR (CDCl_3): δ 147.8, 133.3, 131.0, 130.5, 128.50, 128.48, 127.4, 127.3, 126.0, 125.2. All the resonances in the ¹H and ¹³C NMR spectra were consistent with the reported values.¹⁹

Procedure for synthesis of 2,3-diphenylmaleic anhydride (**5**) (Scheme 1)

An oven-dried 20-mL Schlenk tube was charged with MgBr_2 (0.4 M in THF, 19 mL, 7.6 mmol) and **1a** (536 mg, 3.08 mmol) under nitrogen atmosphere. After the mixture was cooled to 0 °C, Na dispersion (9.8 M, 0.77 mL, 7.5 mmol) was added dropwise and the resulting reddish orange suspension was stirred at 0 °C for 30 min. The headspace of the Schlenk tube was evacuated, and then an atmosphere of CO_2 (1 atm) was introduced. The mixture was warmed up to room temperature and stirred for an additional 1 h. The reaction was then quenched with aqueous HCl (2 M, 3.5 mL) and the resulting biphasic solution was extracted with EtOAc (4 mL $\times$ 3). The combined organic layer was dried over Na_2SO_4 , filtered, and concentrated under reduced pressure. Purification by column chromatography on silica gel with a hexane/EtOAc (3/1 to 0/1) eluent (*R_f* = 0.1, hexane/EtOAc = 10/1) gave **5** as a white solid (508 mg, 2.03 mmol, 68%); ¹H NMR (acetone-*d*₆): δ 7.52 (d, *J* = 7.2 Hz, 4H), 7.42–7.41 (m, 6H); ¹³C NMR (acetone-*d*₆): δ 169.4, 137.5, 136.8, 129.4, 129.2, 128.9. All the resonances in the ¹H and ¹³C NMR spectra were consistent with the reported values.²⁰

Procedure for synthesis of *N,N*-di-*tert*-butyl-2,3-diphenylfumaramide (6) (Scheme 1)

An oven-dried 20-mL Schlenk tube was charged with MgBr₂ (0.4 M in THF, 6.3 mL, 2.5 mmol) and **1a** (179 mg, 1.00 mmol) under nitrogen atmosphere. After the mixture was cooled to 0 °C, Na dispersion (10 M, 0.25 mL, 2.5 mmol) was added dropwise and the resulting reddish orange suspension was stirred at 0 °C for 30 min. After the addition of *tert*-butyl isocyanate (0.480 mL, 4.07 mmol), the mixture was warmed up to room temperature and stirred for an additional 1 h. The reaction was then quenched with aqueous HCl (1 M, 2.0 mL) and sat. aqueous NH₄Cl (0.5 mL), and the resulting biphasic solution was extracted with EtOAc (4 mL × 3). The combined organic layer was dried over Na₂SO₄, filtered, and concentrated under reduced pressure. The yield of **6** was determined as 76% NMR yield (*E:Z* = 64:36) by ¹H NMR measurement with dibromomethane as an internal standard. Purification by column chromatography on silica gel with a hexane/EtOAc (20/1 to 4/1) eluent (*R_f* = 0.2, hexane/EtOAc = 3/1) gave **6** as a white solid (282 mg, 0.745 mmol, 74%, *E:Z* = 71:29).

(*E*)-**6**: ¹H NMR (CDCl₃): δ 7.56 (d, *J* = 7.8 Hz, 4H), 7.39–7.33 (m, 6H), 5.17 (s, 2H), 1.07 (s, 18H); ¹³C NMR (CDCl₃): δ 167.7, 138.7, 136.1, 129.5, 128.6, 128.32, 51.6, 28.2.

(*Z*)-**6**: ¹H NMR (CDCl₃): δ 7.18–7.12 (m, 10H), 5.80 (s, 2H), 1.38 (s, 18H); ¹³C NMR (CDCl₃): δ 168.5, 138.4, 135.9, 128.6, 128.3, 127.9, 52.0, 28.6.

HRMS (APCI-MS, positive): *m/z* [M+H]⁺ Calcd for C₂₄H₃₁O₂N₂ 379.2380; Found 379.2377.

General procedure for Cu-catalyzed synthesis of tetrasubstituted alkenes **7, **8**, **9** (Scheme 2)**

The synthesis of **7a** is representative. An oven-dried 20-mL Schlenk tube was charged with MgBr₂ (0.4 M in THF, 6.3 mL, 2.5 mmol) and **1a** (178 mg, 0.998 mmol) under nitrogen atmosphere. After the mixture was cooled to 0 °C, Na dispersion (10 M, 0.25 mL, 2.5 mmol) was added dropwise and the resulting reddish orange suspension was stirred at 0 °C for 30 min. After the addition of CuCN·2LiCl (1.0 M in THF, 0.10 mL, 0.10 mmol) and isobutylene oxide (0.360 mL, 3.99 mmol), the mixture was allowed to warm to room temperature and stirred for an additional 1 h. The reaction was then quenched with aqueous HCl (1 M, 2.5 mL) and the resulting biphasic solution was extracted with EtOAc (4 mL × 3). The combined organic layer was dried over Na₂SO₄, filtered, and concentrated under reduced pressure. The NMR yield of **7a** was determined by ¹H NMR measurement with dibromomethane as an internal standard. Purification of the residue by column chromatography on silica gel gave **7a**.

2,7-dimethyl-4,5-diphenyloct-4-ene-2,7-diol (7a):

Compound **7a** was formed in 63% NMR yield (*E:Z* >99:1) from **1a** (178 mg, 0.998 mmol) and isobutylene oxide (0.360 mL, 3.99 mmol). Purification by column chromatography on silica gel with a hexane/EtOAc (10/1 to 3/1) eluent (*R_f* = 0.2, hexane/EtOAc = 3/1) gave **7a** as a white solid (201 mg, 0.617 mmol, 62%, *E:Z* >99:1); ¹H NMR (CDCl₃): δ 7.40 (t, *J* = 7.3 Hz, 4H), 7.32 (d, *J* = 7.3 Hz, 4H), 7.28 (t, *J* = 7.3 Hz, 2H), 2.68 (s, 4H), 1.41 (s, 2H), 0.94 (s, 12H); ¹³C NMR (CDCl₃): δ 142.9, 137.9, 129.3, 128.7, 127.0, 71.9, 47.9, 29.8. All the resonances in the ¹H and ¹³C NMR spectra were consistent with the reported values.^{9a}

4,5-diphenylocta-1,4,7-triene (8a):

Compound **8a** was formed in 71% NMR yield (*E:Z* = 98:2) from **1a** (178.0 mg, 0.999 mmol) and allyl chloride (0.330 mL, 4.05 mmol). Purification by column chromatography on silica gel with hexane (*R_f* = 0.2) and then GPC (eluent: CHCl₃) gave **8a** as a white solid (168 mg, 0.644 mmol, 65%, *E:Z* = 98:2).

(*E*)-**8a**: ¹H NMR (CDCl₃): δ 7.36 (t, *J* = 7.8 Hz, 4H), 7.29–7.25 (m, 6H), 5.63 (ddt, *J* = 6.0, 10.8, 17.4 Hz, 2H), 4.87 (dd, *J* = 1.8, 10.8 Hz, 2H), 4.82 (d, *J* = 1.8, 17.4 Hz, 2H), 2.96 (d, *J* = 6.0 Hz, 4H); ¹³C NMR (CDCl₃): δ 142.2, 137.1, 136.4, 128.9, 128.1, 126.7, 115.6, 40.4. All the resonances in the ¹H and ¹³C NMR spectra were consistent with the reported values.^{9a}

(*Z*)-**8a**: ¹H NMR (CDCl₃): δ 7.07 (t, *J* = 7.5 Hz, 4H), 7.02 (t, *J* = 7.5 Hz, 2H), 6.99 (d, *J* = 7.5 Hz, 4H), 5.85–5.80 (m, 2H), 5.11 (m, 2H), 5.02 (m, 2H), 3.33 (d, *J* = 6.1 Hz, 4H); ¹³C NMR (CDCl₃): δ 143.0, 136.7, 135.8, 129.7, 127.6,

126.0, 39.1. The rest of ¹H and ¹³C NMR resonances could not be assigned due to overlapping with the resonances of (*E*)-**8a**.

1,4-dimethoxy-2,3-diphenylbut-2-ene (9):

Compound **9** was formed in 69% NMR yield (*E:Z* >99:1) from **1a** (177.7 mg, 0.997 mmol) and MOMCl (0.300 mL, 3.99 mmol). Purification by column chromatography on silica gel with a hexane/EtOAc (20/1) eluent (*R_f* = 0.2) gave **9** as a white solid (167 mg, 0.623 mmol, 62%, *E:Z* >99:1); ¹H NMR (CDCl₃): δ 7.41–7.36 (m, 8H), 7.34–7.31 (m, 2H), 4.03 (s, 4H), 3.14 (s, 6H); ¹³C NMR (CDCl₃): δ 140.0, 139.2, 128.7, 128.1, 127.2, 73.6, 57.9. All the resonances in the ¹H and ¹³C NMR spectra were consistent with the reported values.^{9a}

2,7-dimethyl-4-(naphthalen-2-yl)-5-phenyloct-4-ene-2,7-diol (7b):

Compound **7b** was formed in 73% NMR yield (*E:Z* = 94:6) from 2-(phenylethynyl)naphthalene (228 mg, 1.00 mmol) and isobutylene oxide (0.360 mL, 3.99 mmol). Purification by column chromatography on silica gel with a hexane/EtOAc (20/1 to 2/1) eluent (*R_f* = 0.2, hexane/EtOAc = 3/1) gave **7b** as a white solid (237 mg, 0.631 mmol, 63%, *E:Z* >99:1); ¹H NMR (CDCl₃): δ 7.89 (d, *J* = 8.4 Hz, 1H), 7.86–7.85 (m, 2H), 7.77 (s, 1H), 7.53–7.48 (m, 2H), 7.46 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.44–7.41 (m, 2H), 7.37 (d, *J* = 6.6 Hz, 2H), 7.30 (t, *J* = 7.2 Hz, 1H), 2.78 (s, 2H), 2.73 (s, 2H), 1.36 (s, 2H), 0.94 (s, 6H), 0.92 (s, 6H); ¹³C NMR (CDCl₃): δ 142.9, 140.6, 138.5, 137.9, 133.3, 132.3, 129.4, 128.7, 128.3, 128.0, 127.81 (2C), 127.79, 127.0, 126.4, 126.1, 72.03, 71.98, 48.1, 48.0, 30.0, 29.9; HRMS (ESI-MS, positive): *m/z* [M+NH₄]⁺ Calcd for C₂₆H₃₄O₂N 392.2584; Found 392.2571.

4-(4-(trimethylsilyl)phenyl)-2,7-dimethyl-5-phenyloct-4-ene-2,7-diol (7c):

Compound **7c** was formed in 53% NMR yield (*E:Z* = 95:5) from 1-trimethylsilyl-4-(phenylethynyl)benzene (250 mg, 0.997 mmol) and isobutylene oxide (0.360 mL, 3.99 mmol). Purification by column chromatography on silica gel with a hexane/EtOAc (10/1 to 3/1) eluent (*R_f* = 0.2, hexane/EtOAc = 3/1) gave **7c** as a white solid (198 mg, 0.499 mmol, 50%, *E:Z* >99:1); ¹H NMR (CDCl₃): δ 7.53 (d, *J* = 7.8 Hz, 2H), 7.40 (t, *J* = 7.8 Hz, 2H), 7.32–7.27 (m, 5H), 2.69 (s, 2H), 2.66 (s, 2H), 0.95 (s, 12H), 0.27 (s, 9H); ¹³C NMR (CDCl₃): δ 143.1, 142.8, 138.8, 137.83, 137.75, 133.6, 129.3, 128.5 (2C), 126.8, 71.9 (2C), 47.9, 47.8, 29.8, 29.7, –1.0; HRMS (ESI-MS, positive): *m/z* [M+NH₄]⁺ Calcd for C₂₅H₄₀O₂NSi 414.2823; Found 414.2827.

4-(4-methoxyphenyl)-5-phenylocta-1,4,7-triene (8d):

Compound **8d** was formed in 39% NMR yield (*E:Z* = 98:2) from 1-methoxy-4-(phenylethynyl)benzene (208 mg, 0.999 mmol) and allyl chloride (0.330 mL, 4.05 mmol). Purification by column chromatography on silica gel with a hexane/EtOAc (1/0 to 40/1) eluent (*R_f* = 0.4, hexane/EtOAc = 10/1) and then GPC (eluent: CHCl₃) gave **8d** as a white solid (91.6 mg, 0.315 mmol, 32%, *E:Z* = 98:2).

(*E*)-**8d**: ¹H NMR (CDCl₃): δ 7.35 (t, *J* = 7.8 Hz, 2H), 7.28–7.23 (m, 3H), 7.18 (d, *J* = 8.4 Hz, 2H), 6.90 (d, *J* = 8.4 Hz, 2H), 5.67–5.60 (m, 2H), 4.88–4.81 (m, 4H), 3.83 (s, 3H), 2.98 (d, *J* = 6.6 Hz, 2H), 2.94 (d, *J* = 6.6 Hz, 2H); ¹³C NMR (CDCl₃): δ 158.4, 142.4, 137.0, 136.64, 136.61, 136.5, 134.5, 130.0 (2C), 128.9, 128.1, 126.6, 115.6, 113.5, 55.3, 40.4 (2C). All the resonances in the ¹H and ¹³C NMR spectra were consistent with the reported values.^{9a}

(*Z*)-**8d**: ¹H NMR (CDCl₃): δ 7.08 (t, *J* = 7.5 Hz, 2H), 7.04–7.02 (m, 1H), 6.99 (d, *J* = 7.5 Hz, 2H), 6.61 (d, *J* = 8.9 Hz, 2H), 5.84–5.78 (m, 2H), 5.12–5.08 (m, 2H), 5.02–4.99 (m, 2H), 3.70 (s, 3H), 3.32–3.30 (m, 4H); ¹³C NMR (CDCl₃): δ 130.9, 129.7, 113.0. The rest of ¹H and ¹³C NMR resonances could not be assigned due to overlapping with the resonances of (*E*)-**8d**.

4-(3-methoxyphenyl)-2,7-dimethyl-5-phenyloct-4-ene-2,7-diol (7e):

Compound **7e** was formed in 58% NMR yield (*E:Z* = 94:6) from 1-methoxy-2-(phenylethynyl)benzene (209 mg, 1.00 mmol) and isobutylene oxide (0.360 mL, 3.99 mmol). Purification by column chromatography on silica gel with a hexane/EtOAc (10/1 to 3/1) eluent (*R_f* = 0.2, hexane/EtOAc = 3/1) gave **7e** as a white solid (182 mg, 0.514 mmol, 51%, *E:Z* >99:1); ¹H NMR (CDCl₃): δ 7.39 (t, *J* = 7.8 Hz, 2H), 7.33–7.27 (m, 4H), 6.90 (d, *J* = 7.8 Hz, 1H), 6.86–6.85 (t, *J* = 2.1 Hz, 1H), 6.82 (dd, *J* = 8.4, 2.4 Hz, 1H), 3.84 (s, 3H), 2.68 (s, 2H), 2.66 (s, 2H), 0.96 (s, 6H), 0.95 (s, 6H); ¹³C NMR (CDCl₃): δ 159.6, 144.3, 142.7, 137.9, 137.6, 129.6, 129.2,

128.5, 126.8, 121.5, 115.2, 112.0, 71.8 (2C), 55.2, 48.0, 47.8, 29.8, 29.7; HRMS (ESI-MS, positive): m/z [M+NH₄]⁺ Calcd for C₂₃H₃₄O₃N 372.2533; Found 372.2535.

2,7-dimethyl-4-(3-(methylsulfanyl)phenyl)-5-phenyloct-4-ene-2,7-diol (7f):

Compound **7f** was formed in 68% NMR yield (*E:Z* = 89:11) from **1a** (215 mg, 0.957 mmol) and isobutylene oxide (0.360 mL, 3.99 mmol). Purification by column chromatography on silica gel with a hexane/EtOAc (3/1) eluent (*R_f* = 0.2) gave **7f** as a white solid (209 mg, 0.564 mmol, 59%, *E:Z* >99:1); ¹H NMR (CDCl₃): δ 7.40 (t, *J* = 7.5 Hz, 2H), 7.33–7.27 (m, 4H), 7.20 (t, *J* = 1.7 Hz, 1H), 7.16 (dd, *J* = 9.3, 1.7 Hz, 1H), 7.09 (d, *J* = 7.5 Hz, 1H), 2.66 (s, 4H), 2.51 (s, 3H), 1.27 (s, 2H), 0.95 (s, 6H), 0.94 (s, 6H); ¹³C NMR (CDCl₃): δ 143.5, 142.6, 138.7, 138.2, 137.3, 129.2, 128.8, 128.5, 127.1, 126.8, 126.0, 124.6, 71.7 (2C), 48.0, 47.8, 29.8 (2C), 15.7; HRMS (ESI-MS, positive): m/z [M+NH₄]⁺ Calcd for C₂₃H₃₄O₂NS 388.2305; Found 388.2295.

Synthesis of 1,2-bis(4-methoxyphenyl)-1,2-diphenylethene (10) via Negishi coupling (Scheme 2)

An oven-dried 20-mL Schlenk tube was charged with MgBr₂ (464 mg, 2.52 mmol), **1a** (178 mg, 1.00 mmol), and THF (6.3 mL) under nitrogen atmosphere. The mixture was heated at 60 °C for 10 min to dissolve MgBr₂. After the mixture was cooled to 0 °C, Na dispersion (10 M, 0.25 mL, 2.5 mmol) was added dropwise and the resulting reddish orange suspension was stirred at 0 °C for 30 min. After the addition of ZnCl₂ (1.0 M in THF, 2.5 mL, 2.5 mmol), the mixture was warmed up to room temperature and stirred for 30 min. PdCl₂(PPh₃)₂ (14.3 mg, 0.0204 mmol) and 4-iodoanisole (519 mg, 2.22 mmol) were then added and the mixture was stirred at 60 °C for 3 h. The reaction was then quenched with aqueous HCl (1 M, 2.5 mL) and the resulting biphasic solution was extracted with EtOAc (4 mL × 3). The combined organic layer was dried over Na₂SO₄, filtered, and concentrated under reduced pressure. The yield of **10** was determined as 82% NMR yield (*E:Z* = 91:9) by ¹H NMR measurement with dibromomethane as an internal standard. Purification by column chromatography on silica gel with a hexane/EtOAc (40/1 to 20/1) eluent (*R_f* = 0.3, hexane/EtOAc = 10/1) and then GPC (eluent: CHCl₃) gave **10** as a white solid (274 mg, 0.698 mmol, 70%, *E:Z* = 78:22).

(*E*)-**10**: ¹H NMR (CDCl₃): δ 7.13–7.10 (m, 6H), 7.04 (d, *J* = 6.9 Hz, 4H), 6.91 (d, *J* = 7.5 Hz, 4H), 6.62 (d, *J* = 8.9 Hz, 4H), 3.73 (s, 6H); ¹³C NMR (CDCl₃): δ 158.0, 144.4, 139.7, 136.4, 132.64, 131.49, 127.8, 126.3, 113.1, 55.15. All the resonances in the ¹H and ¹³C NMR spectra were consistent with the reported values.¹⁰

(*Z*)-**10**: ¹H NMR (CDCl₃): δ 6.94 (d, *J* = 6.9 Hz, 4H), 6.65 (d, *J* = 8.9 Hz, 4H), 3.75 (s, 6H). The rest of ¹H NMR resonances could not be assigned due to overlapping with the resonances of (*E*)-**10**. ¹³C NMR (CDCl₃): δ 158.0, 144.3, 139.7, 136.5, 132.62, 131.51, 127.7, 126.3, 113.2, 55.18.

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Supporting Information

Supporting information for this article is available online at <https://doi.org/xx.xxxx/xxxxxx-xxxx>.

Conflict of Interest

The authors declare no conflict of interest.

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Supporting Information

Sodium-mediated Reductive *anti*-Dimagnesiumation of Diarylacetylenes with Magnesium Bromide

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NMR Spectra

S2–28

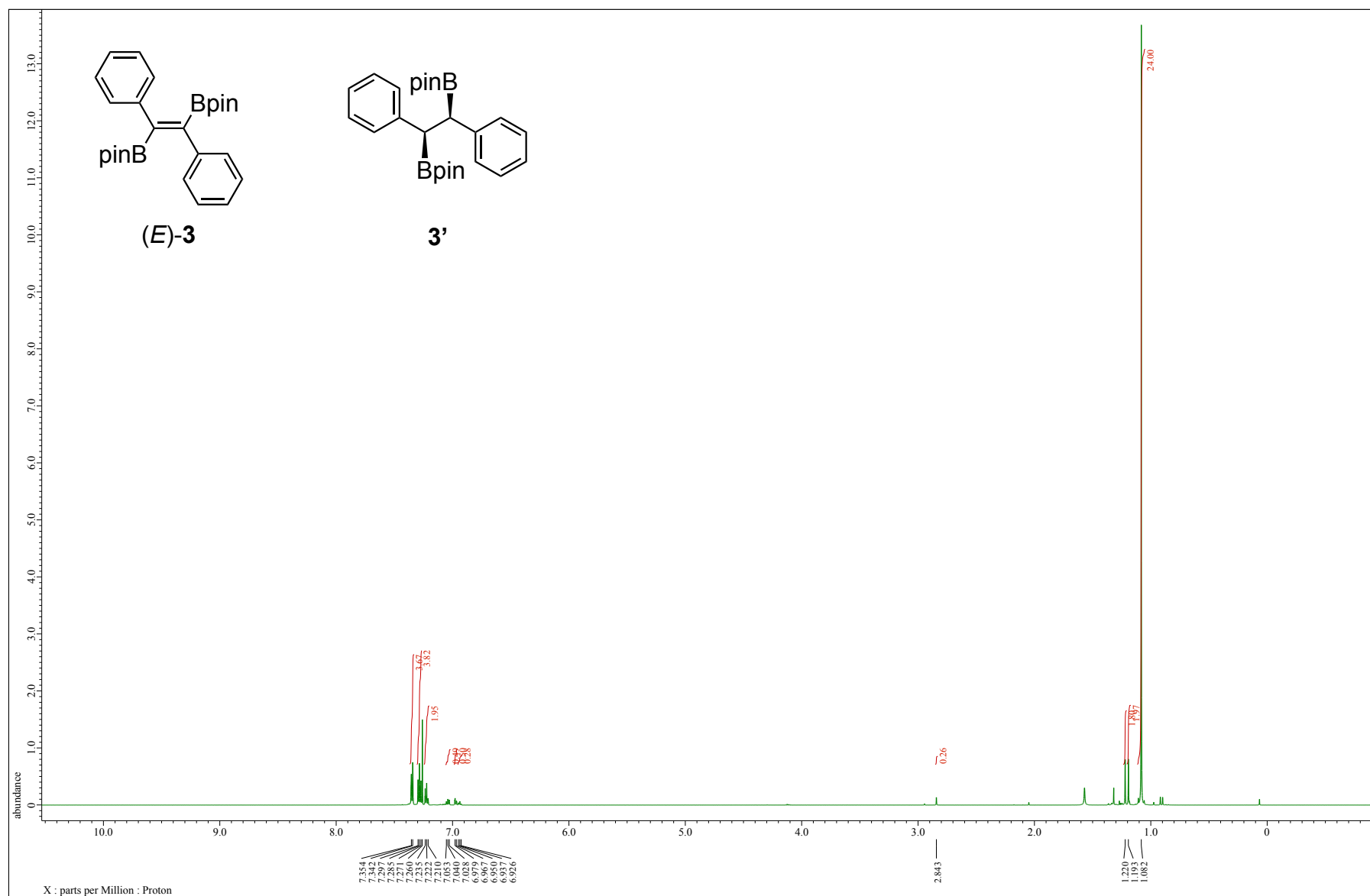
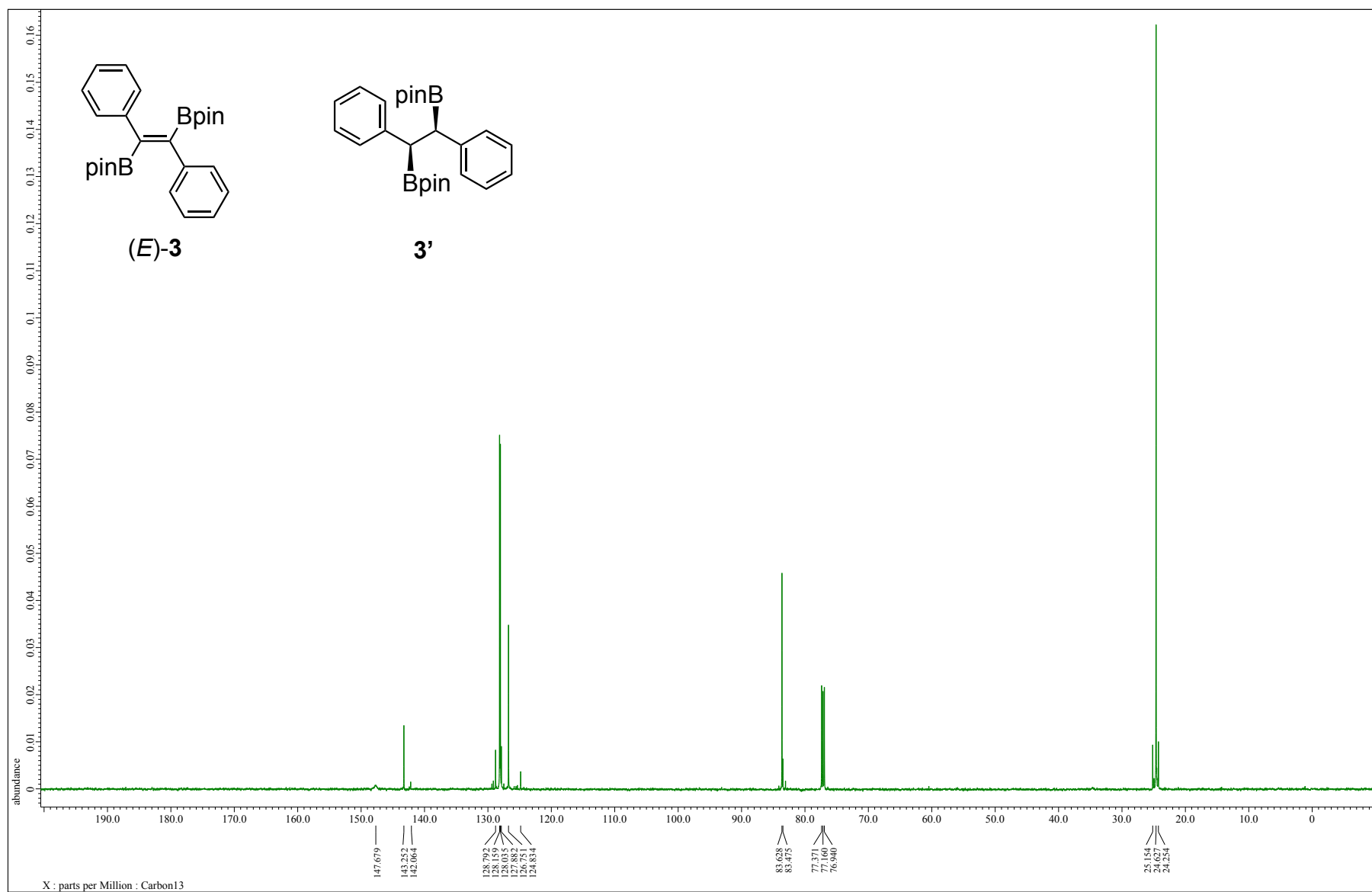


Figure S1. ¹H NMR (600 MHz, CDCl₃) spectrum of **3** ((*E*)-**3**: **3'** = 88:12).



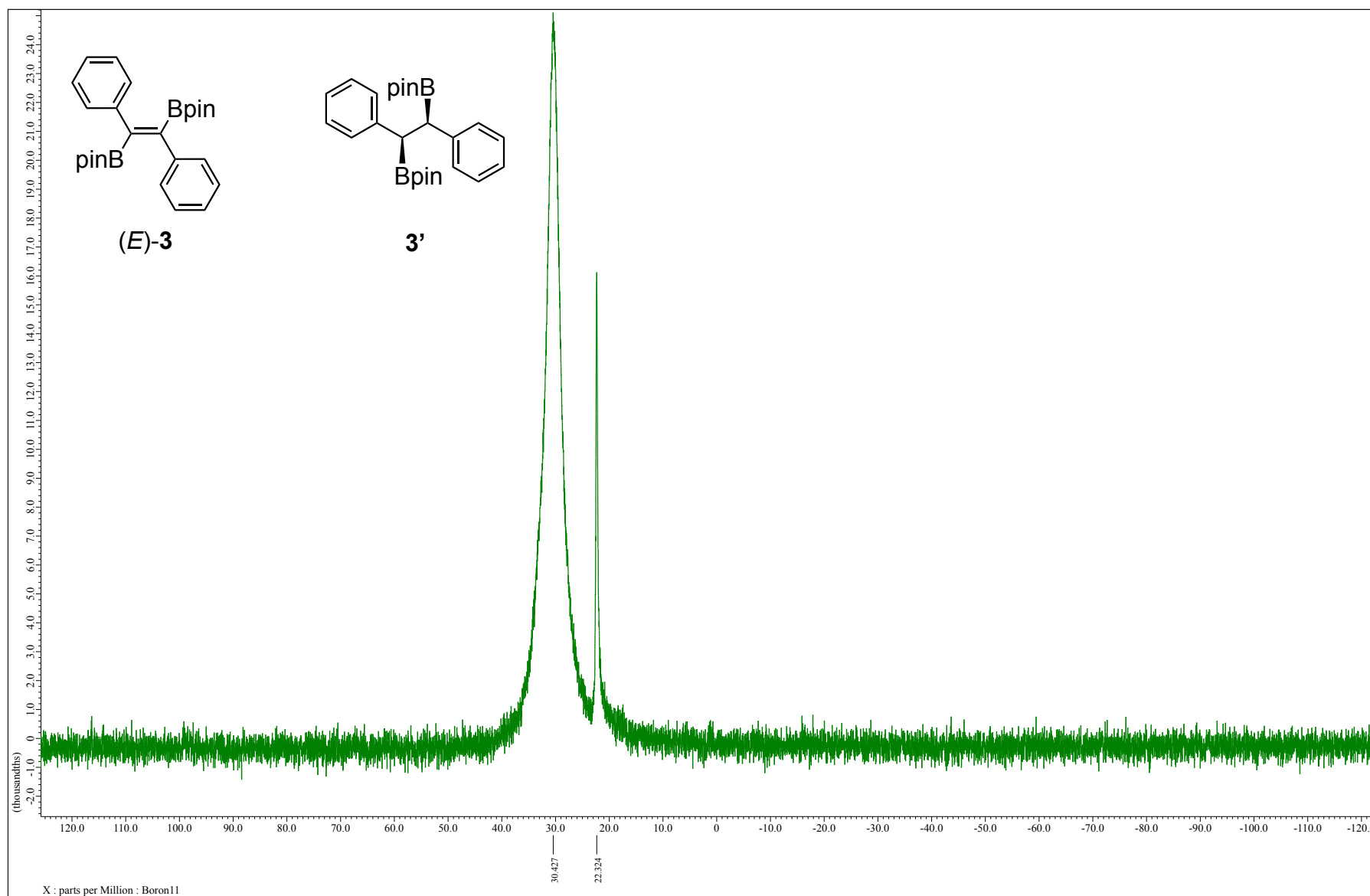


Figure S3. ^{11}B NMR (192 MHz, CDCl_3) spectrum of **3** ((*E*)-**3**: **3'** = 88:12).

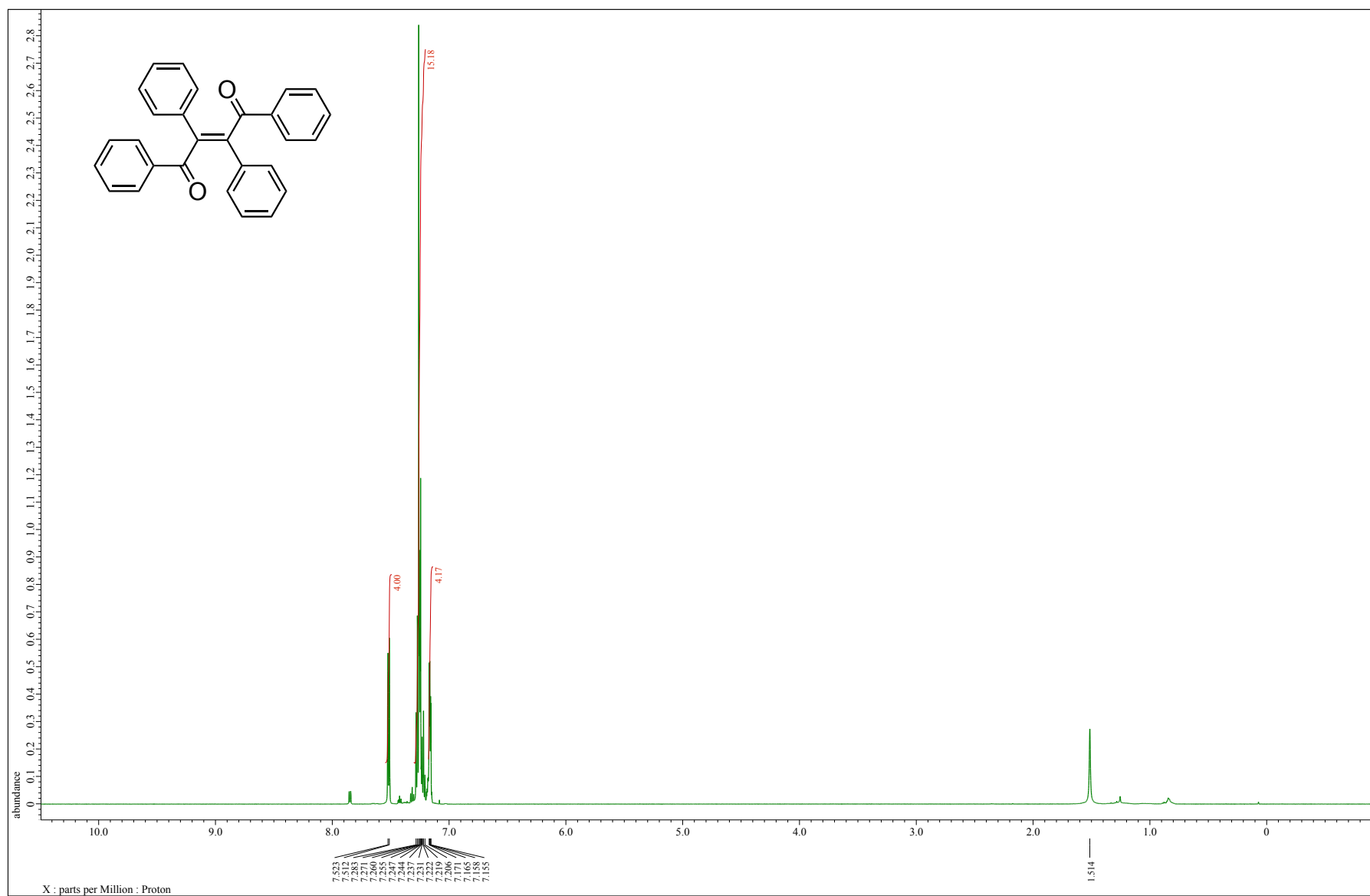


Figure S4. ¹H NMR (600 MHz, CDCl₃) spectrum of **4**.

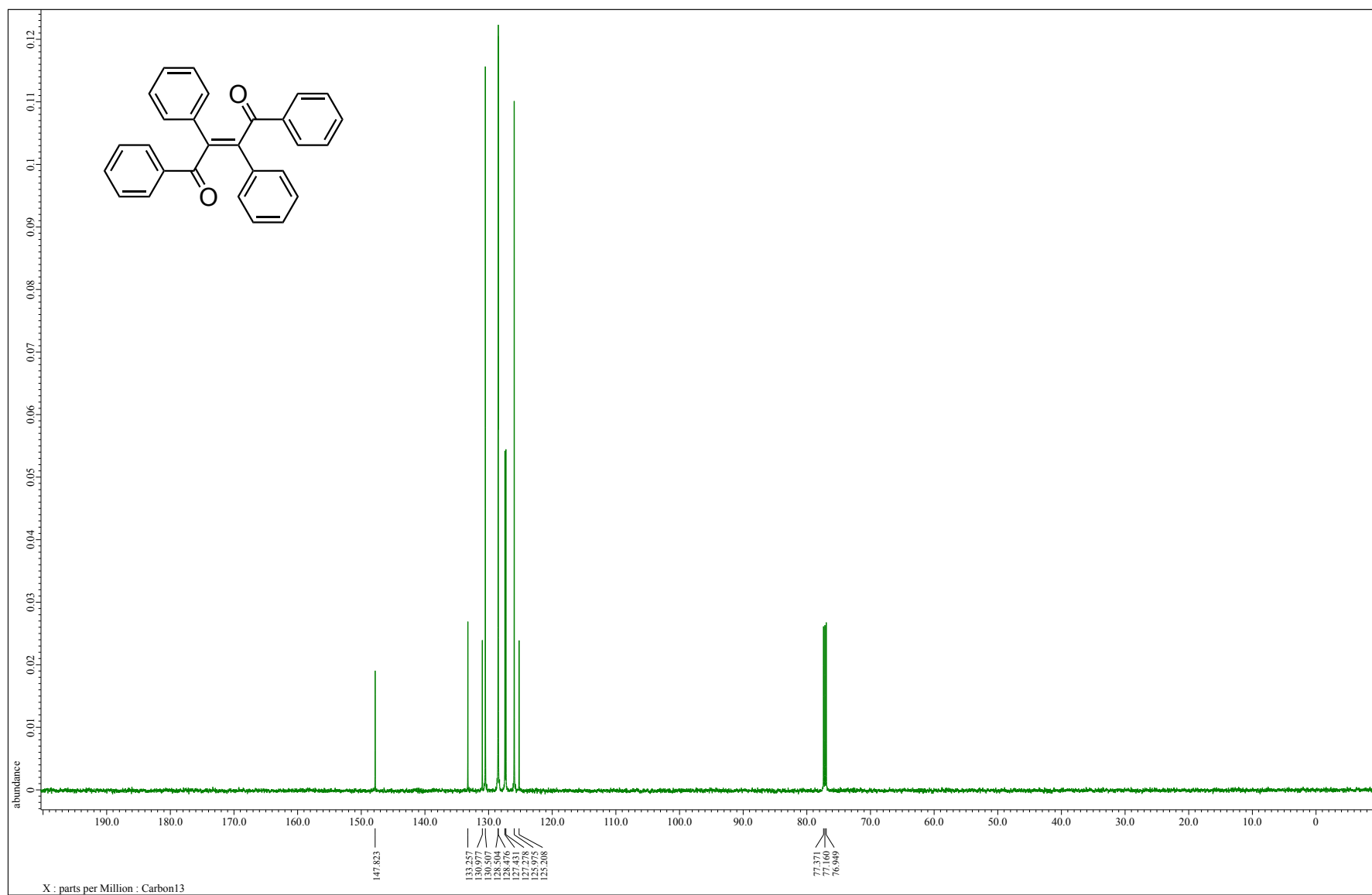


Figure S5. ¹³C NMR (151 MHz, CDCl₃) spectrum of 4.

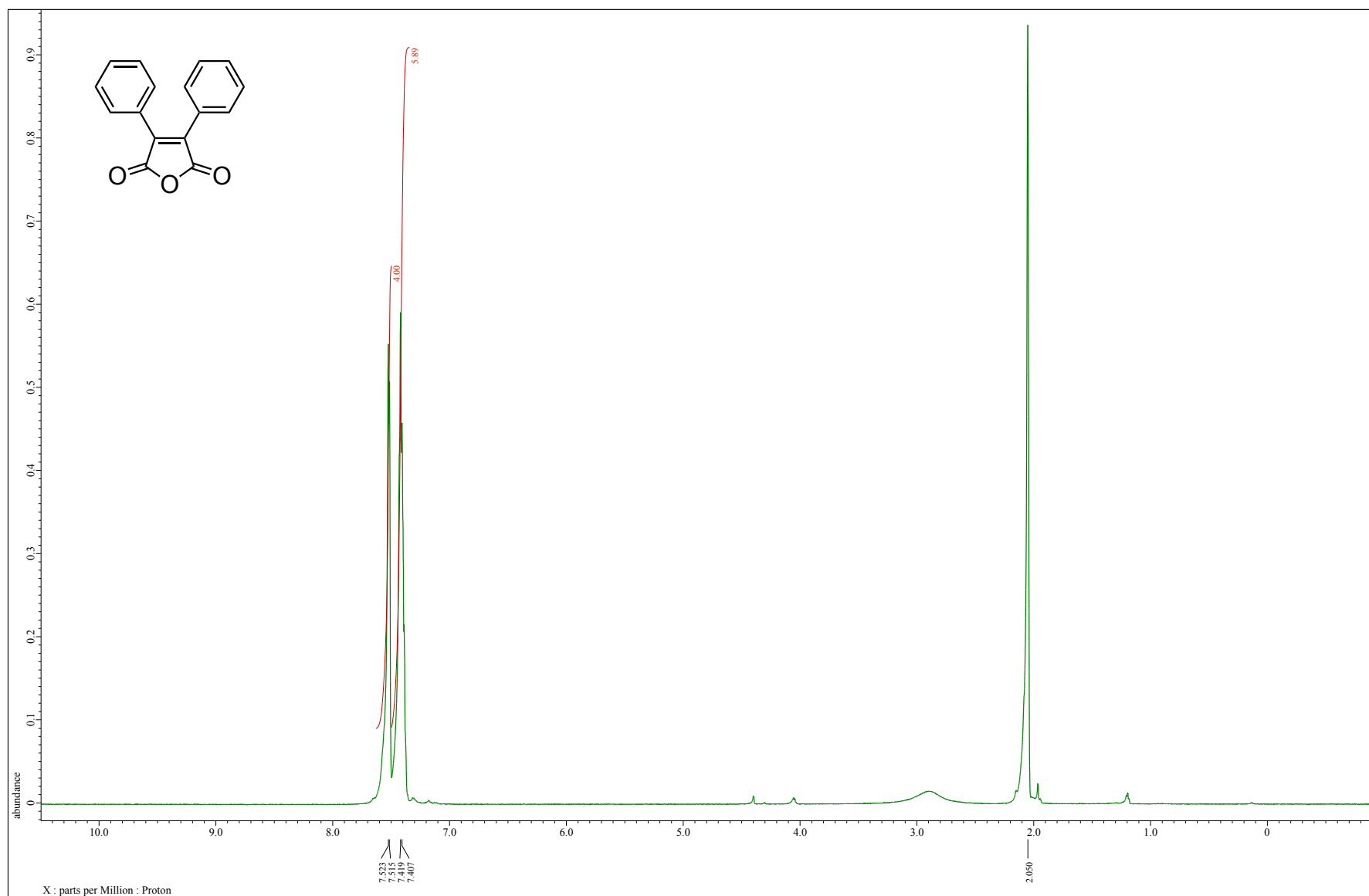


Figure S6. ^1H NMR (600 MHz, $\text{acetone-}d_6$) spectrum of **5**.

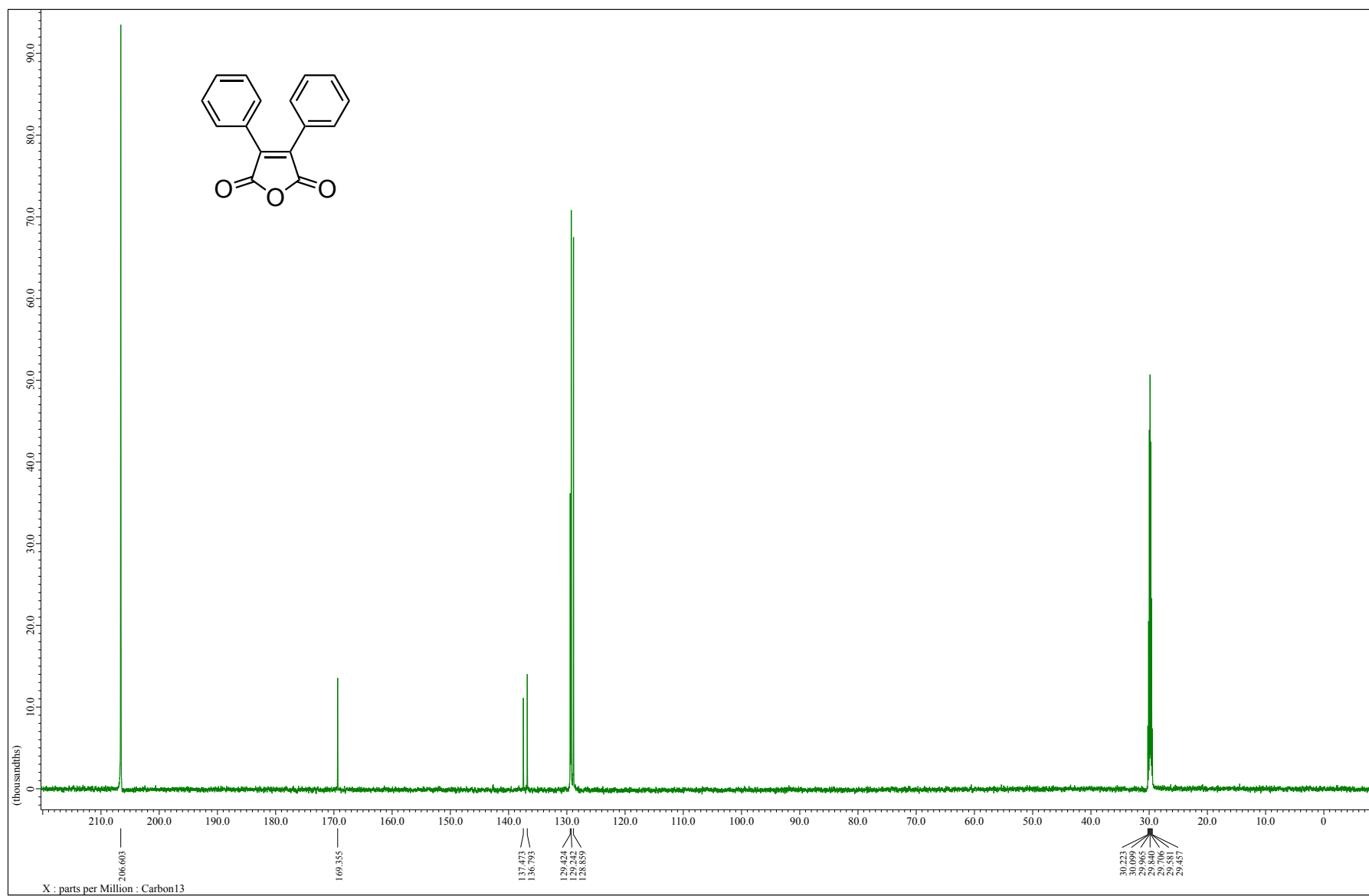


Figure S7. ¹³C NMR (151 MHz, acetone-*d*₆) spectrum of 5.

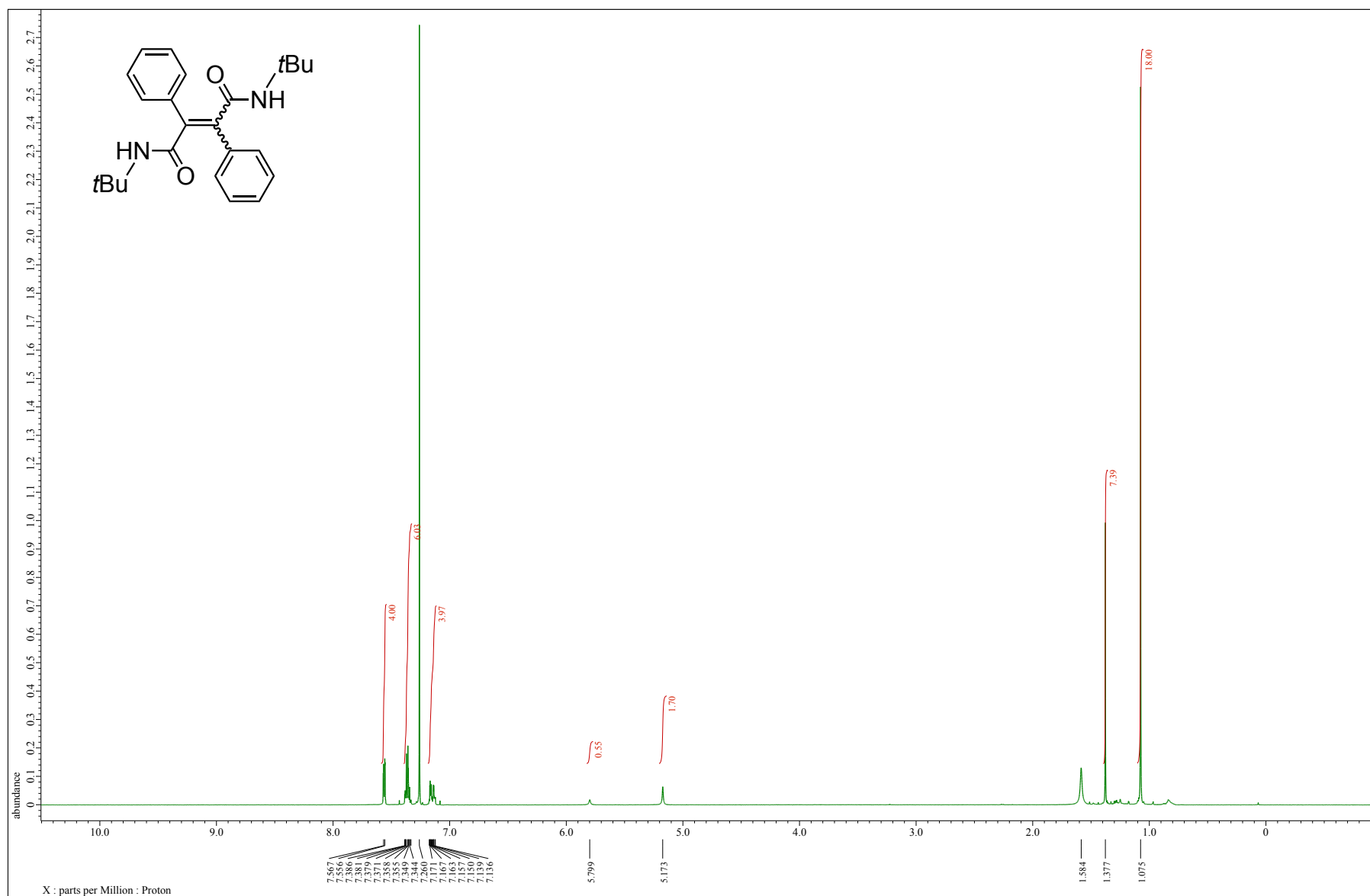


Figure S8. ^1H NMR (600 MHz, CDCl_3) spectrum of **6** (*E:Z* = 71:29).

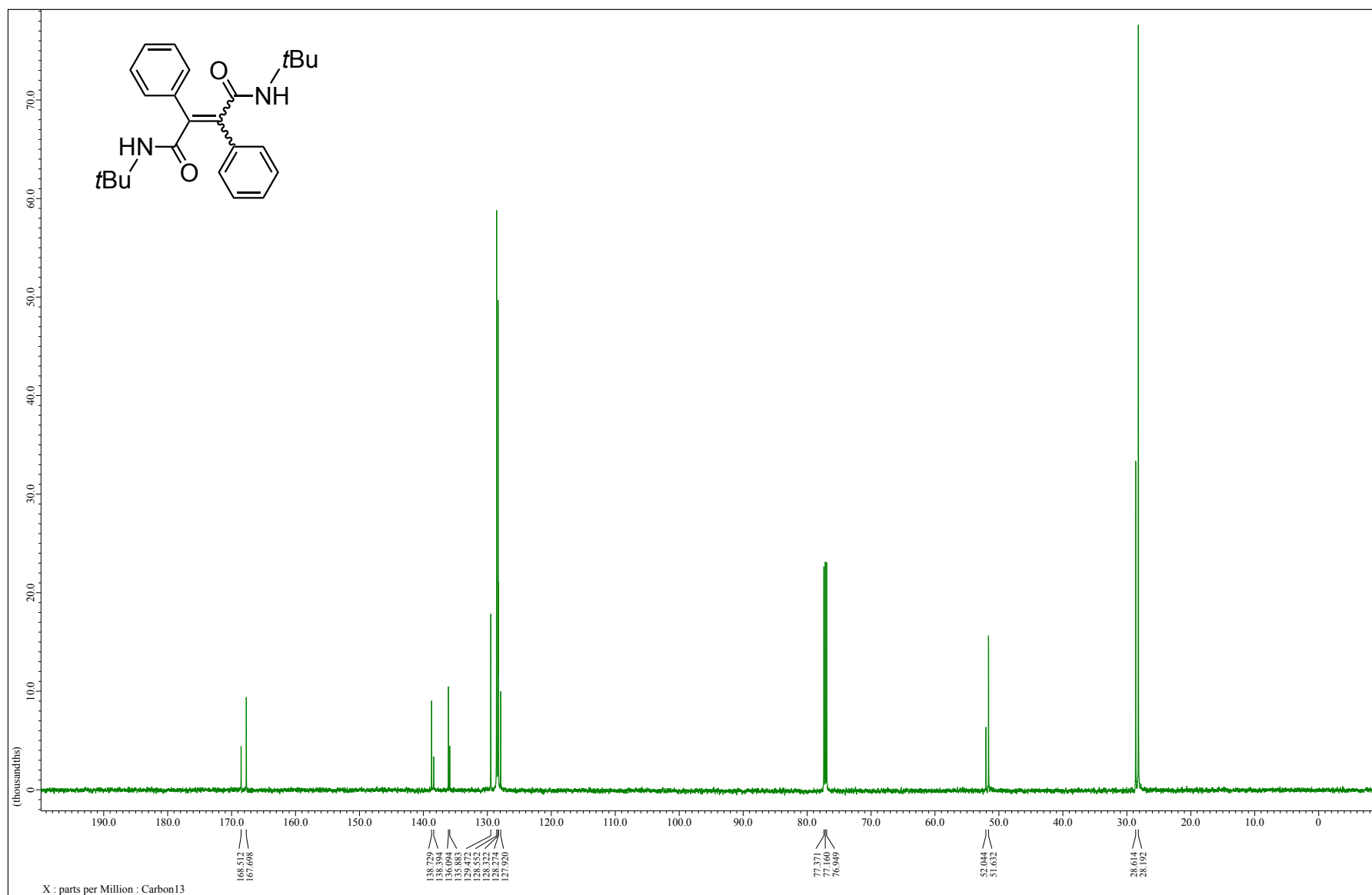


Figure S9. ¹³C NMR (151 MHz, CDCl₃) spectrum of **6** (E:Z = 71:29).

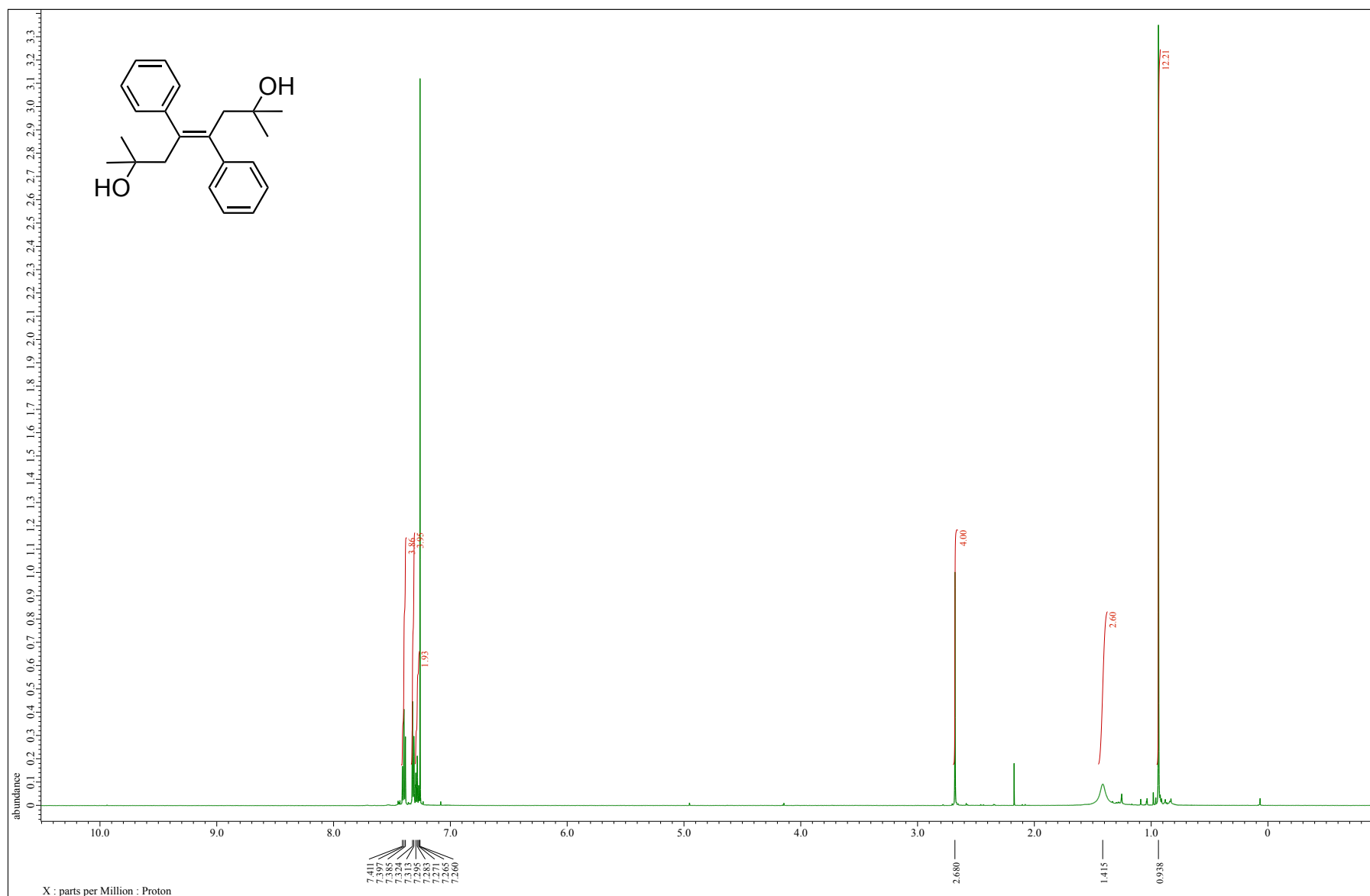


Figure S10. ¹H NMR (600 MHz, CDCl₃) spectrum of **7a**.

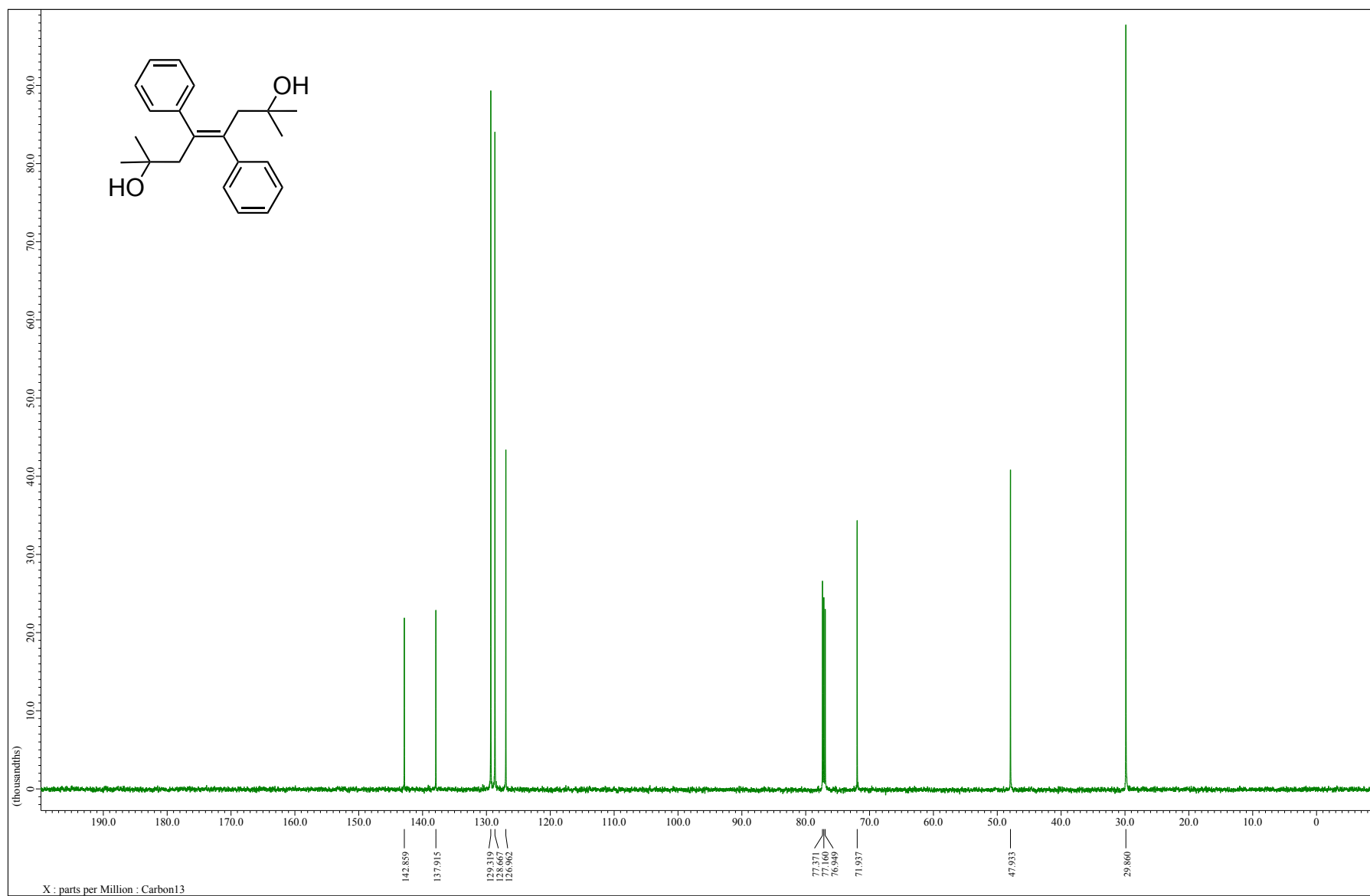
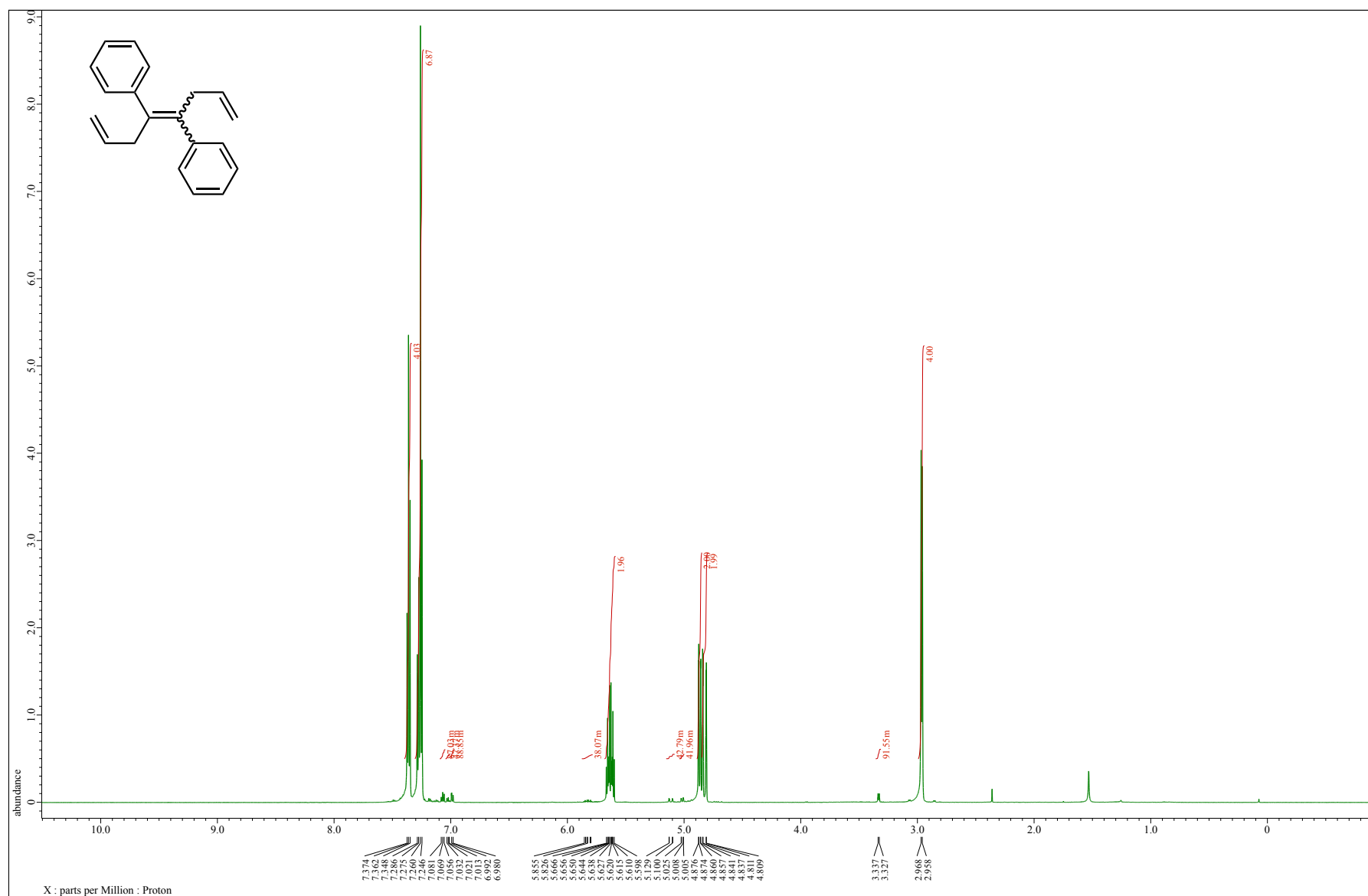


Figure S11. ¹³C NMR (151 MHz, CDCl₃) spectrum of **7a**.



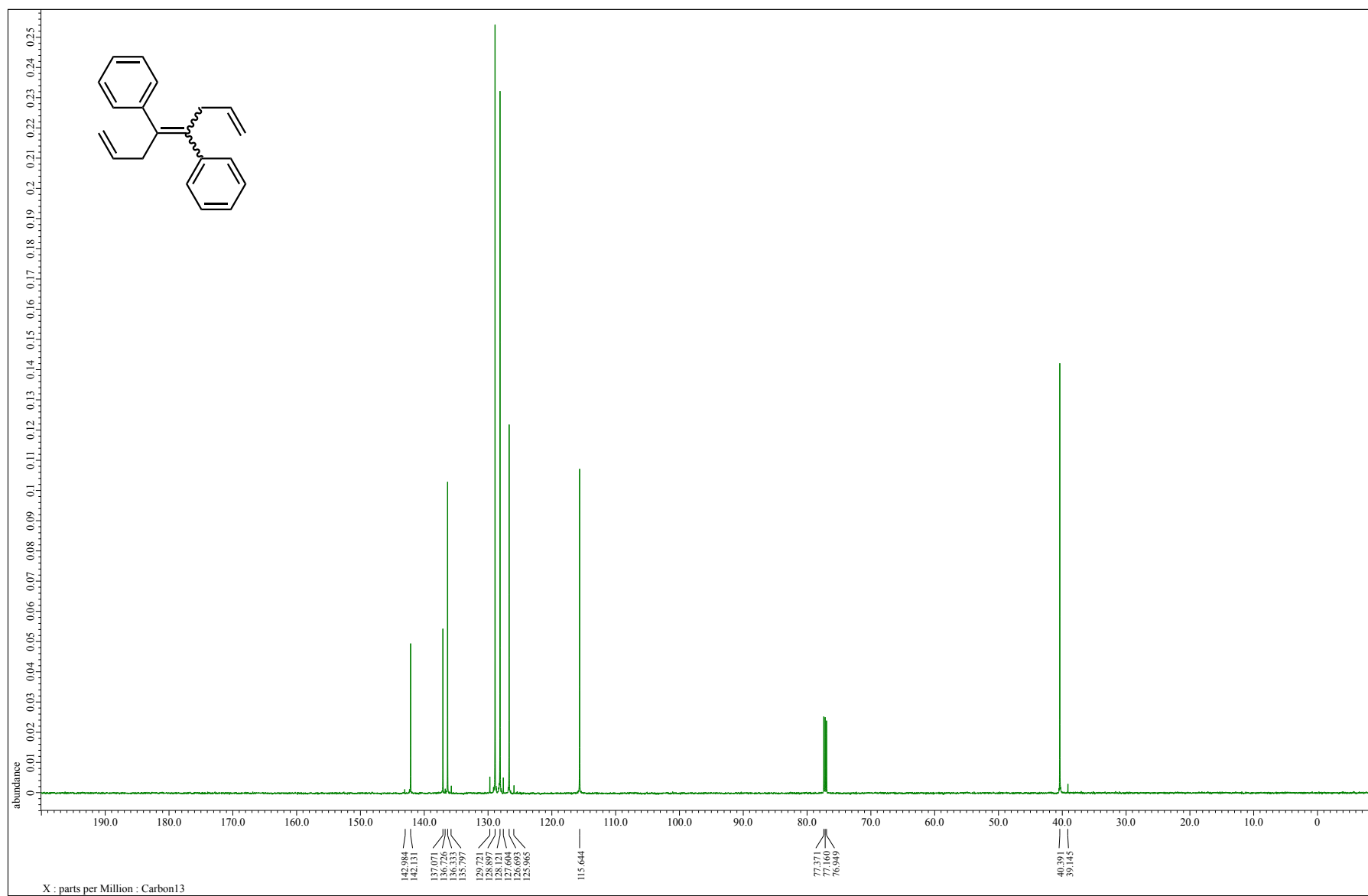


Figure S13. ^{13}C NMR (151 MHz, CDCl_3) spectrum of **8a** (E:Z = 98:2).

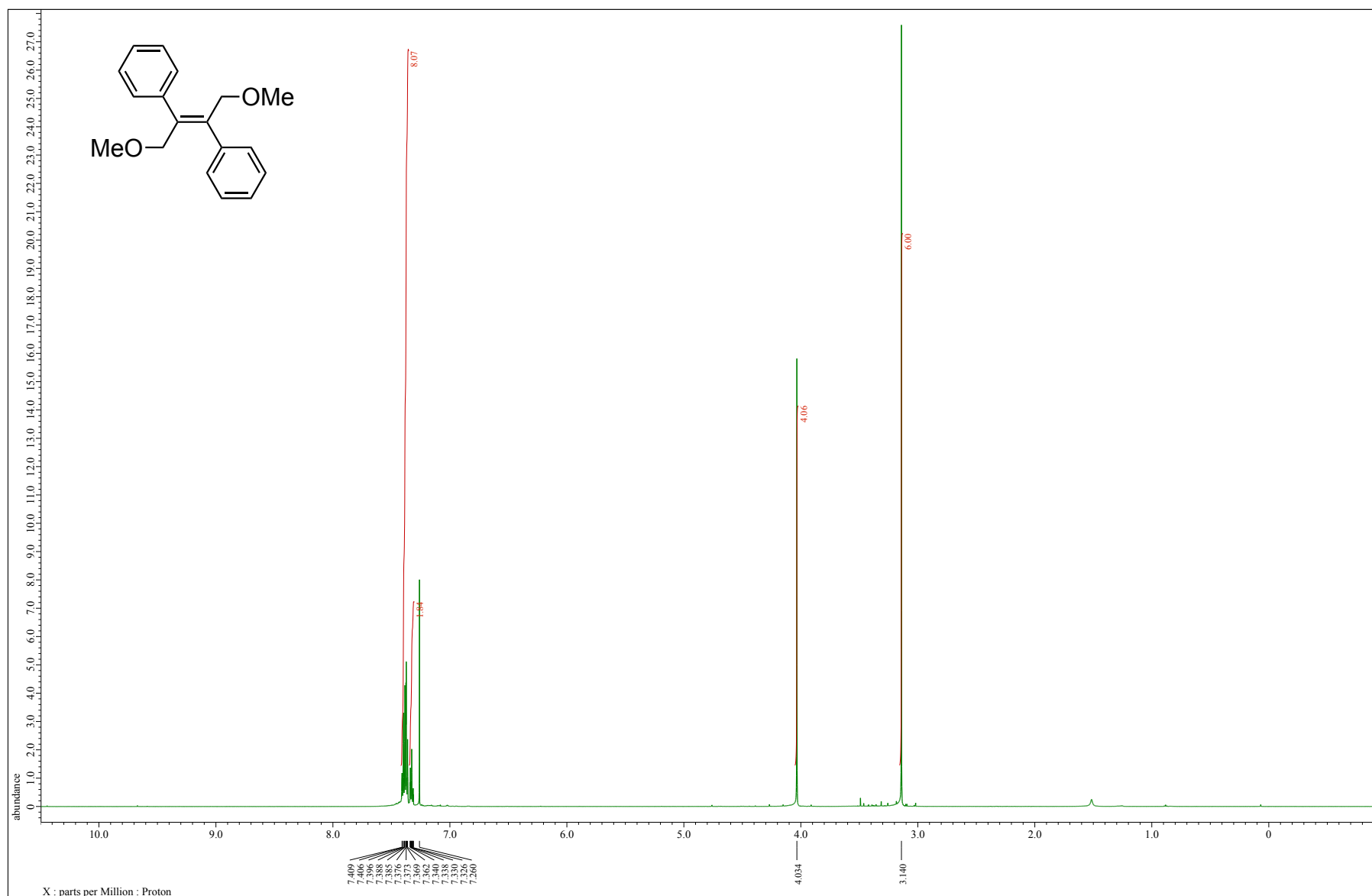


Figure S14. ¹H NMR (600 MHz, CDCl₃) spectrum of **9**.

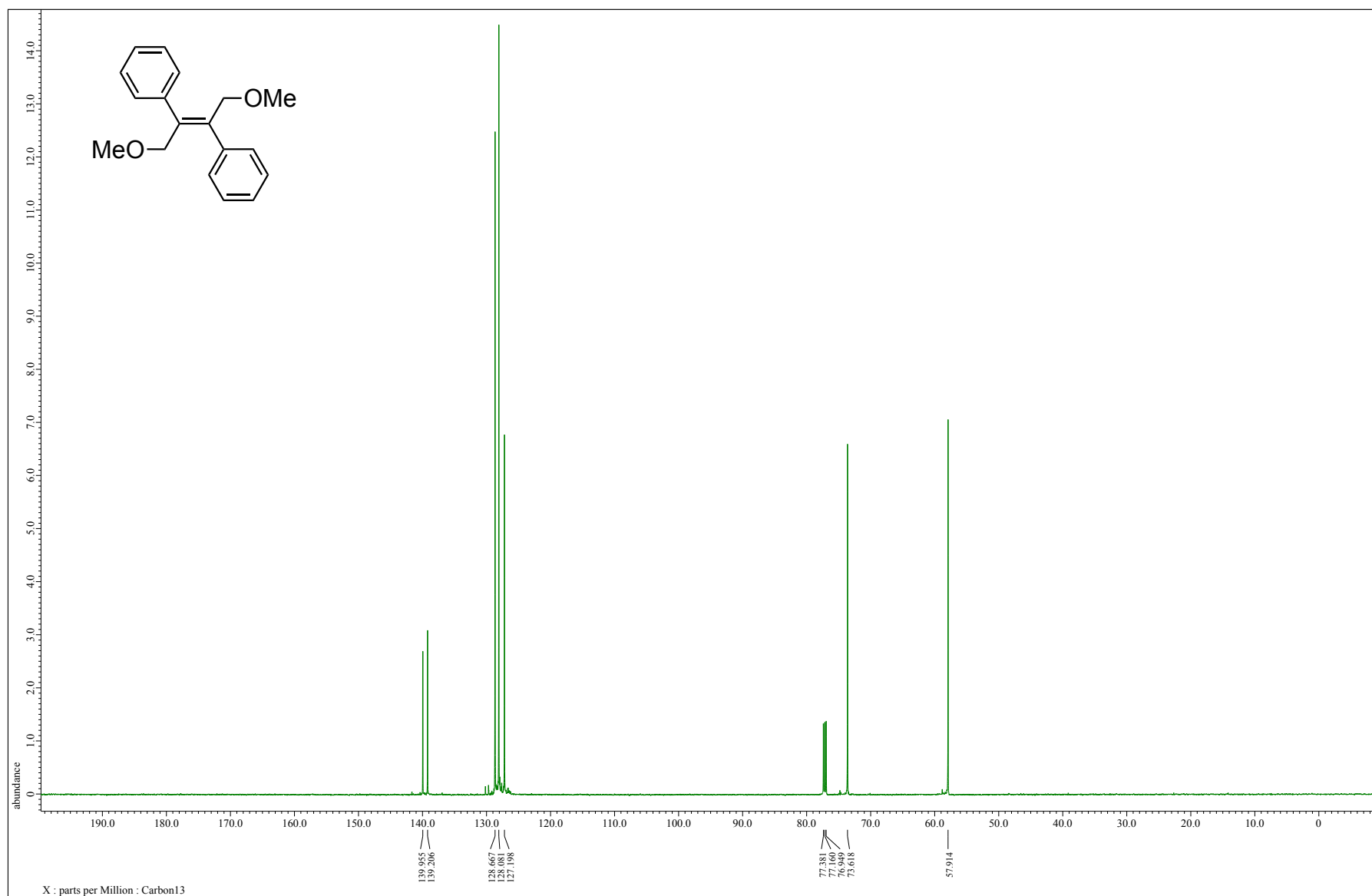


Figure S15. ^{13}C NMR (151 MHz, CDCl_3) spectrum of **9**.

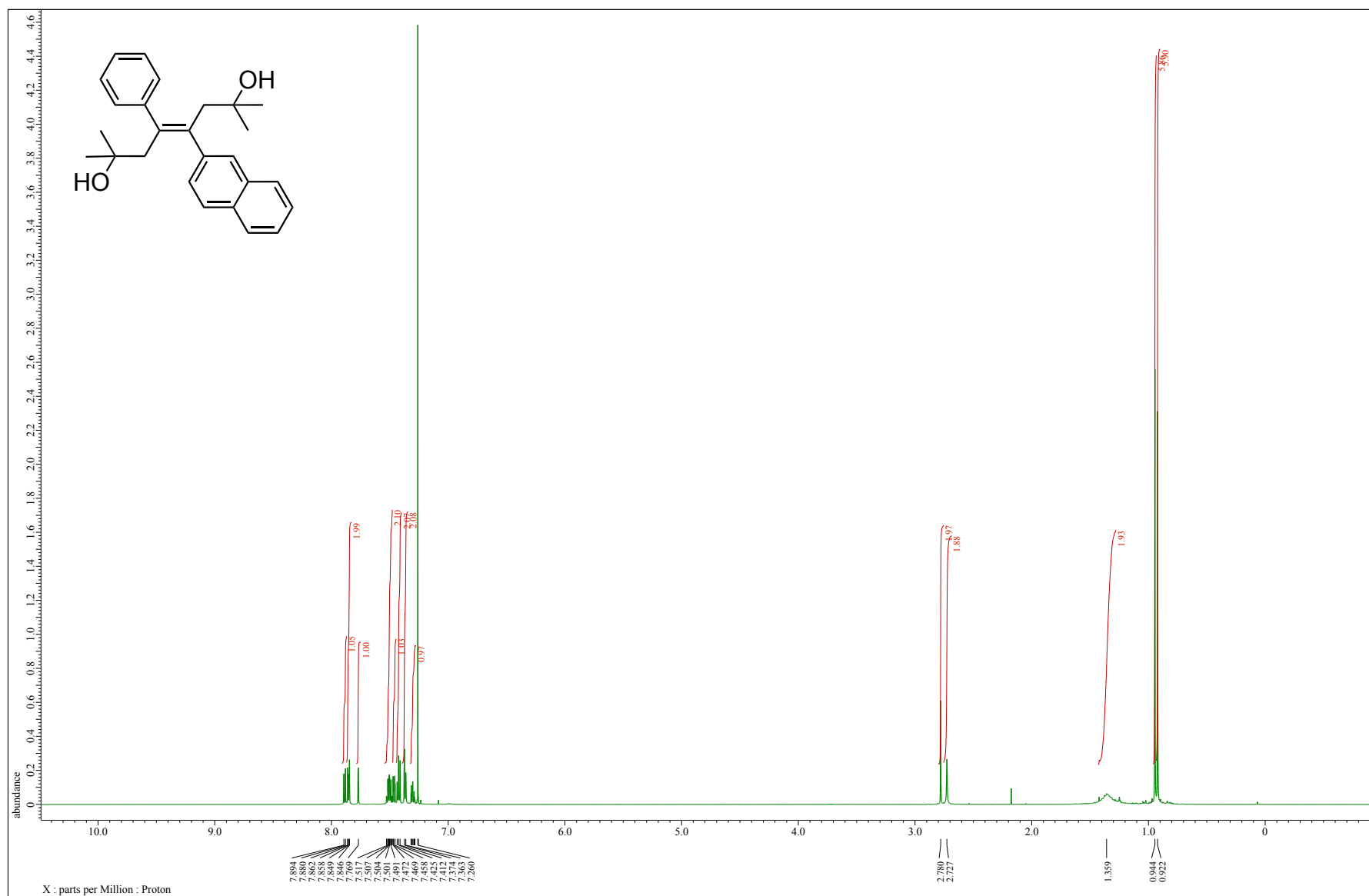


Figure S16. ¹H NMR (600 MHz, CDCl₃) spectrum of **7b**.

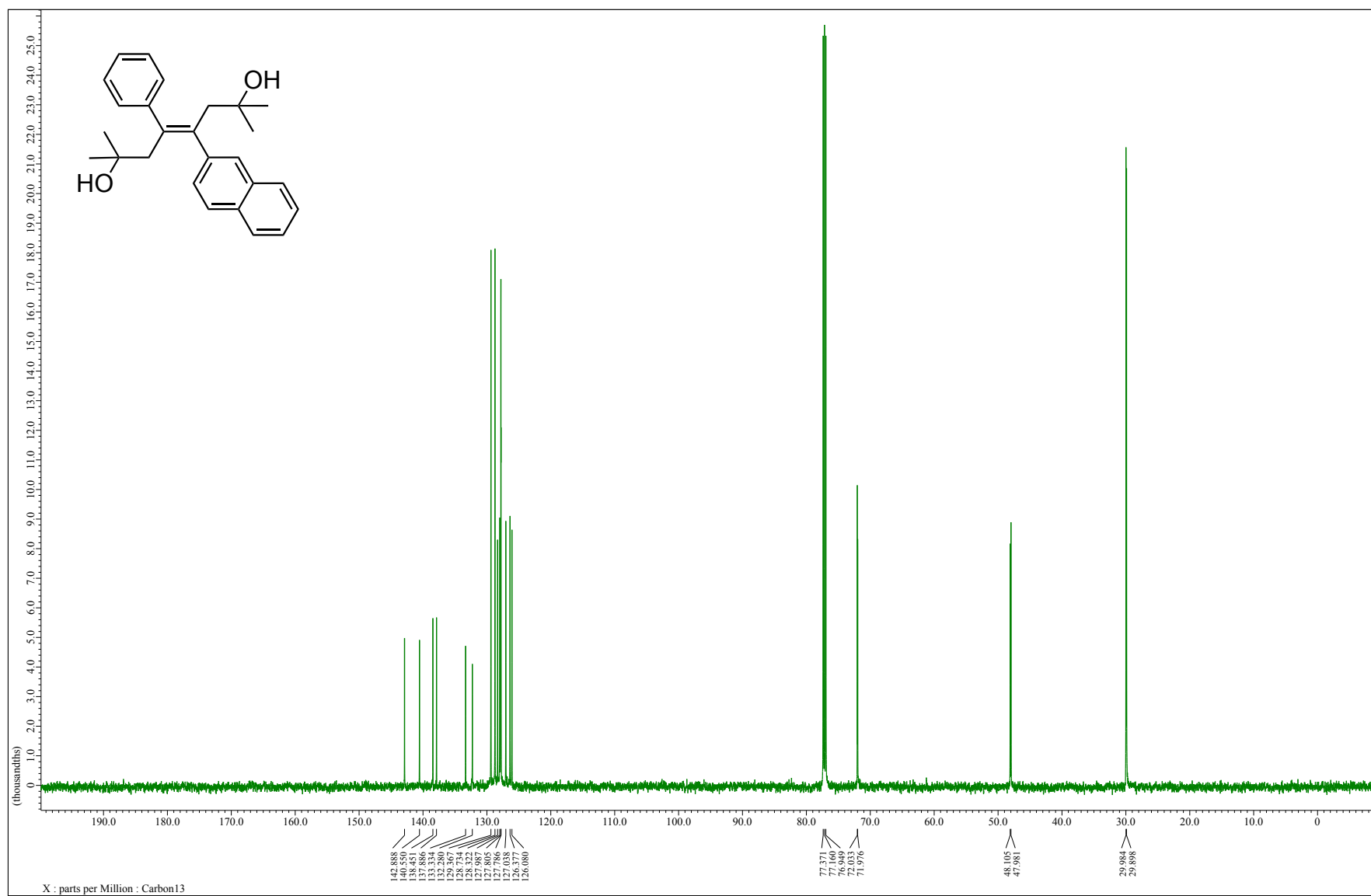


Figure S17. ¹³C NMR (151 MHz, acetone-*d*₆) spectrum of **7b**.

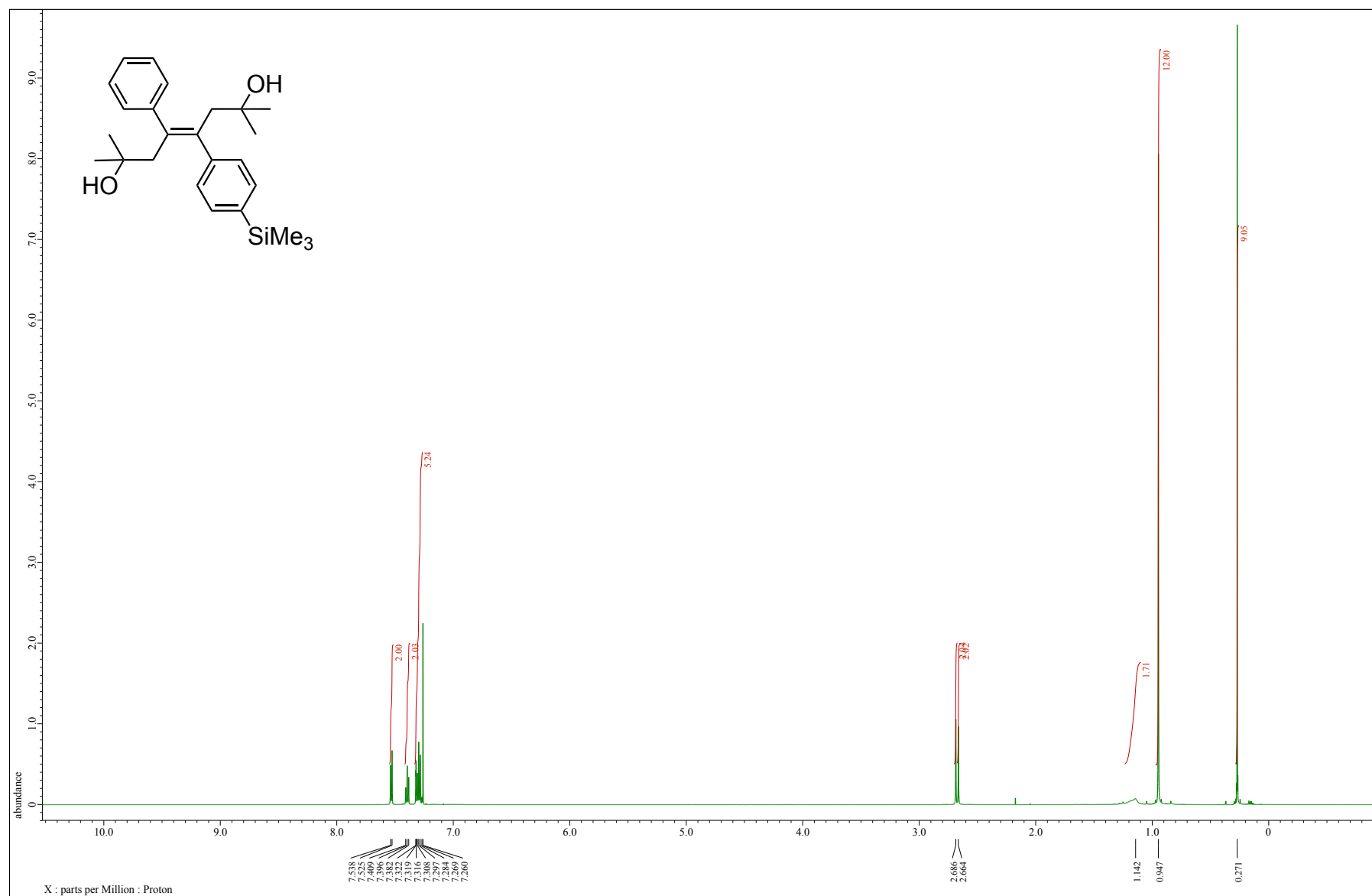


Figure S18. ¹H NMR (600 MHz, CDCl₃) spectrum of **7c**.

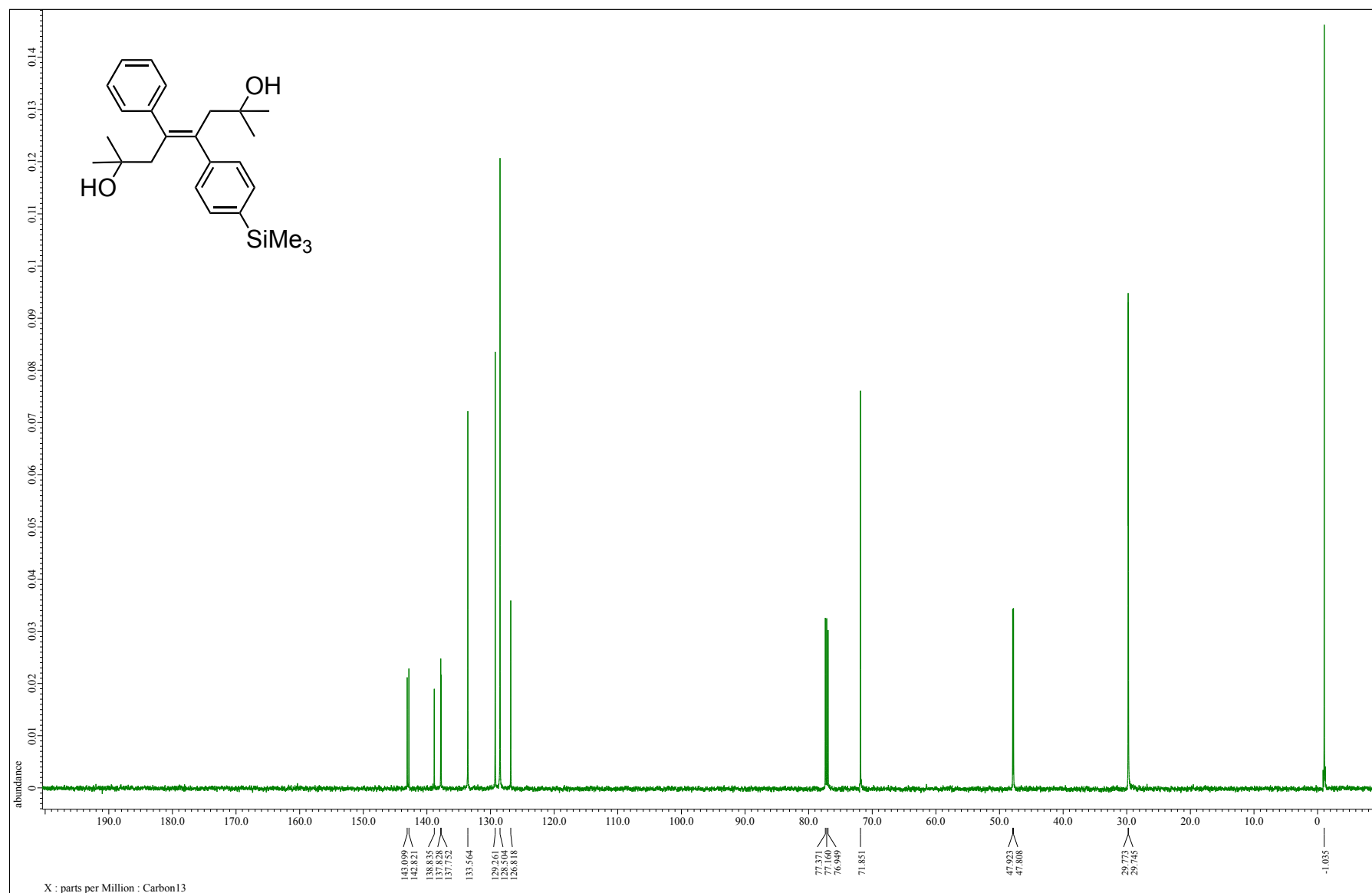


Figure S19. ¹³C NMR (151 MHz, CDCl₃) spectrum of **7c**.

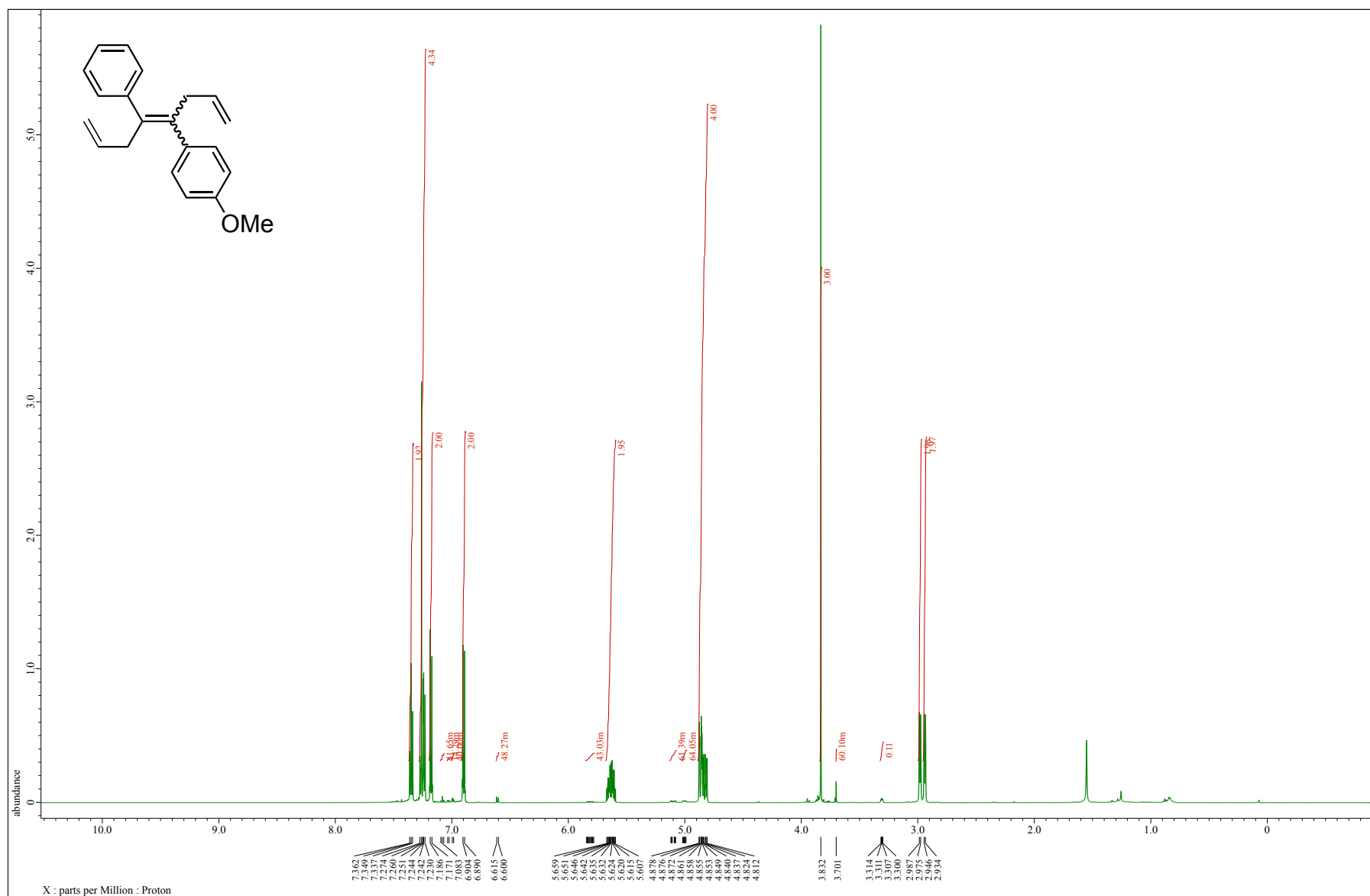


Figure S20. ¹H NMR (600 MHz, CDCl₃) spectrum of **8d** (E:Z = 98:2).

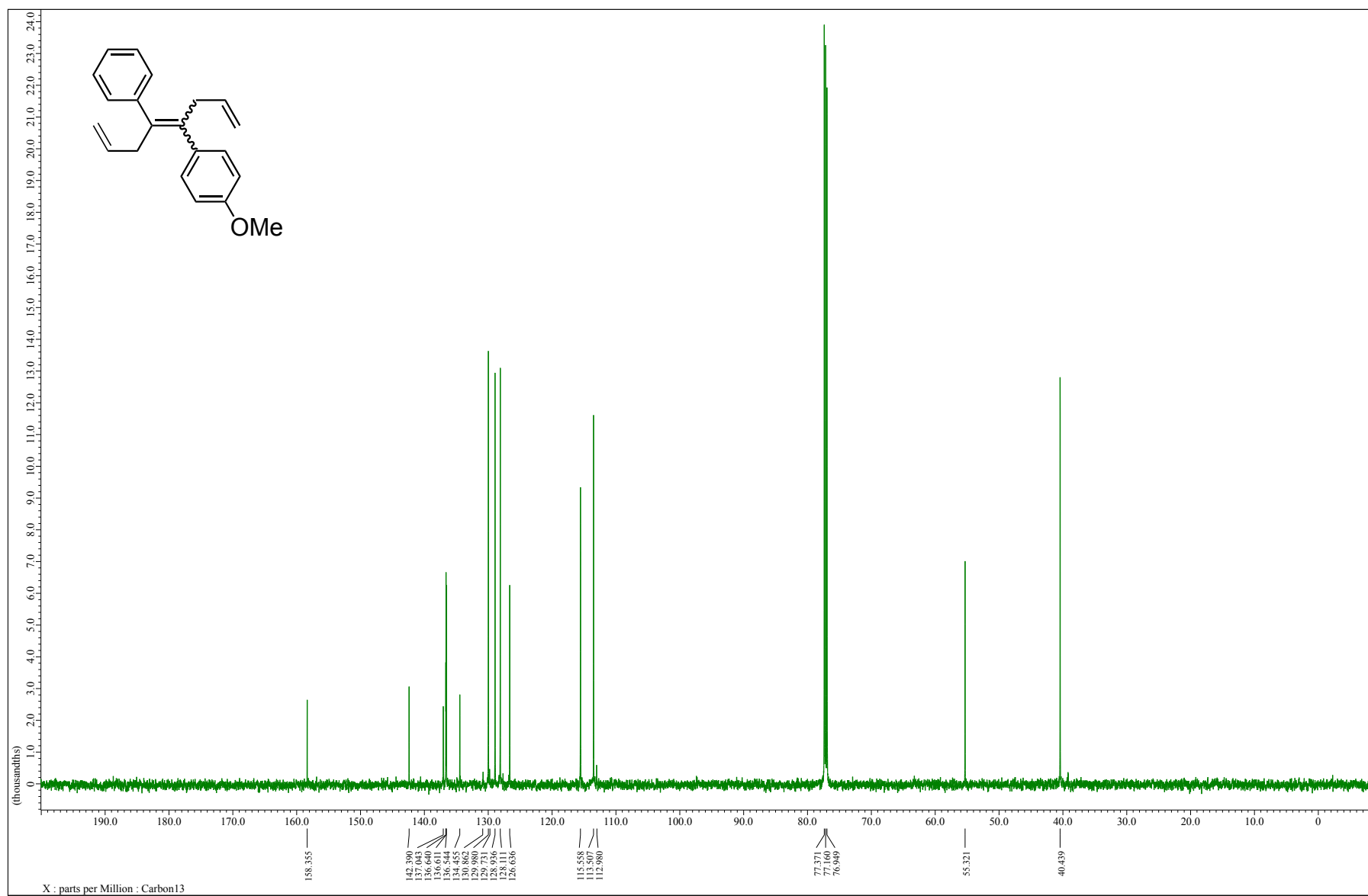


Figure S21. ¹³C NMR (151 MHz, CDCl₃) spectrum of **8d** (E:Z = 98:2).

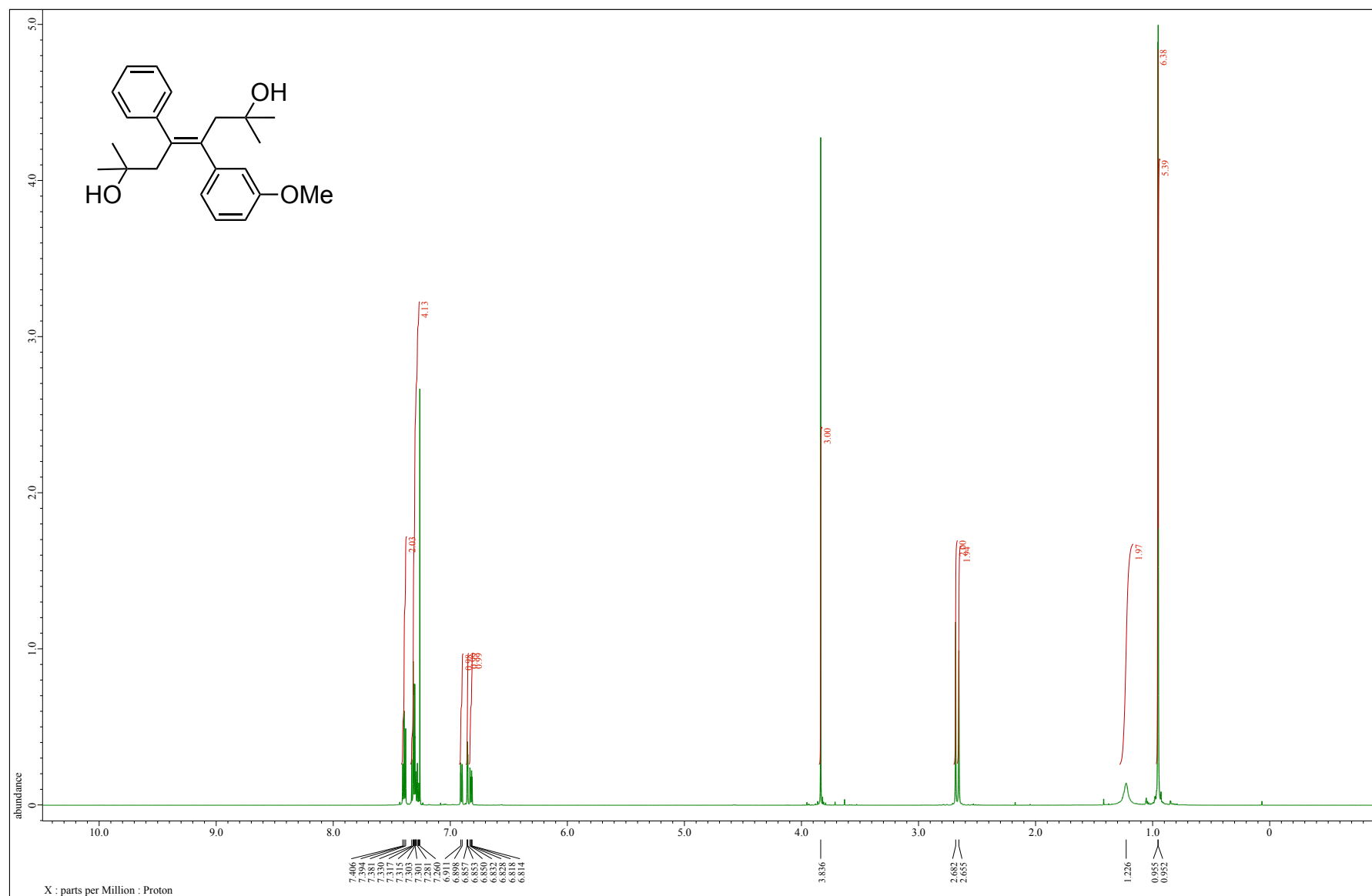


Figure S22. ¹H NMR (600 MHz, CDCl₃) spectrum of 7e.

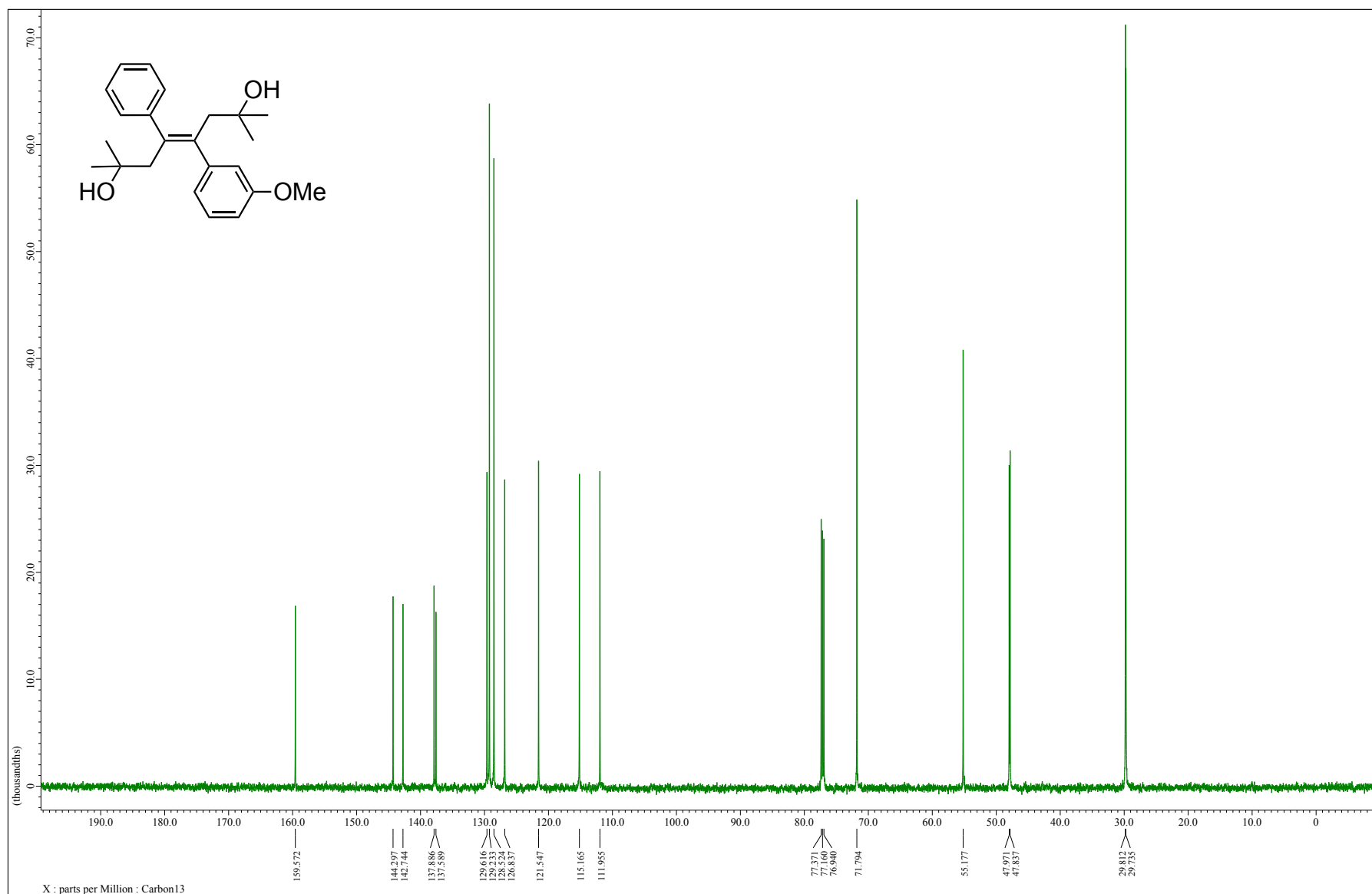


Figure S23. ¹³C NMR (151 MHz, CDCl₃) spectrum of **7e**.

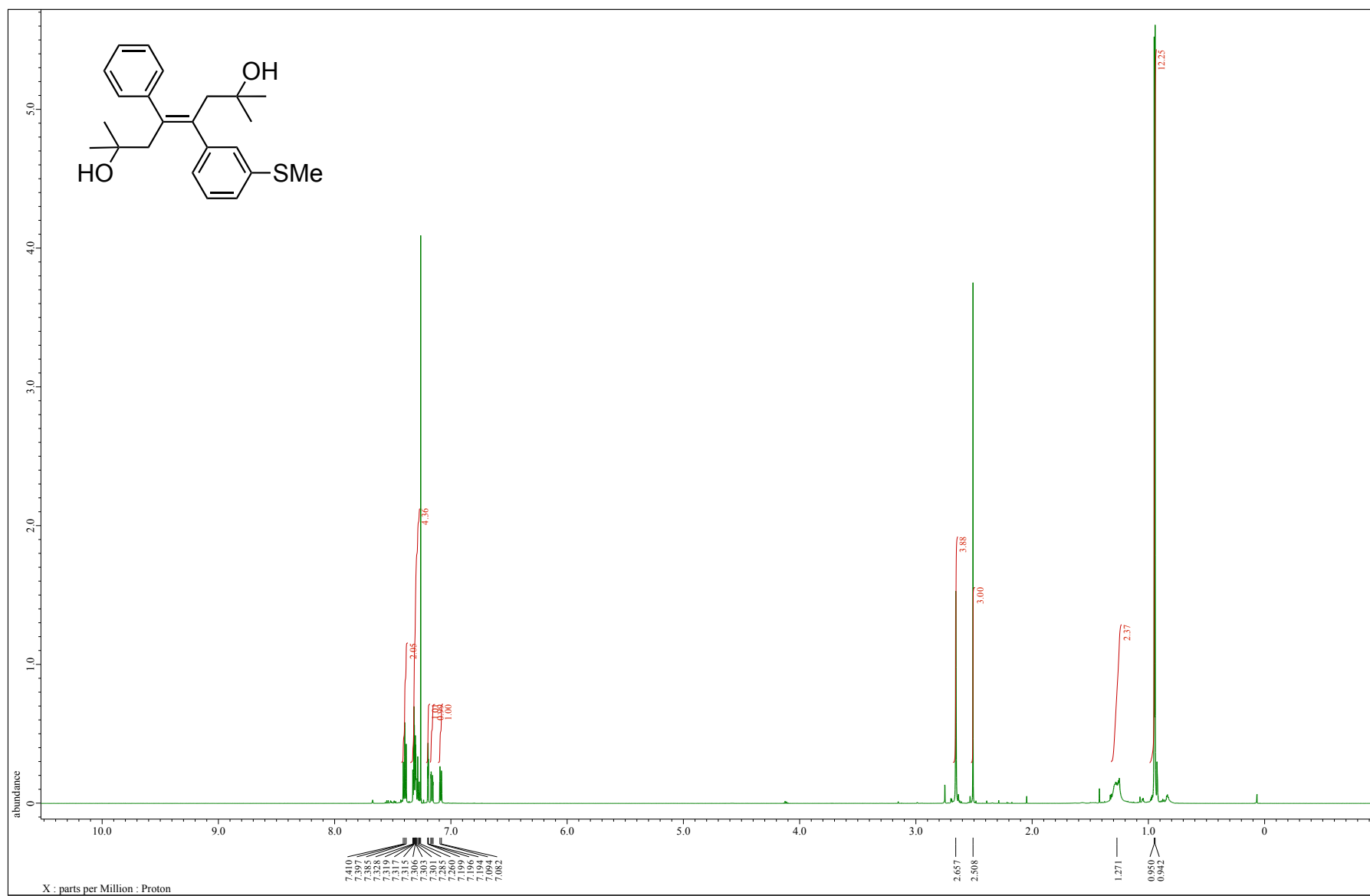


Figure S24. ¹H NMR (600 MHz, CDCl₃) spectrum of 7f.

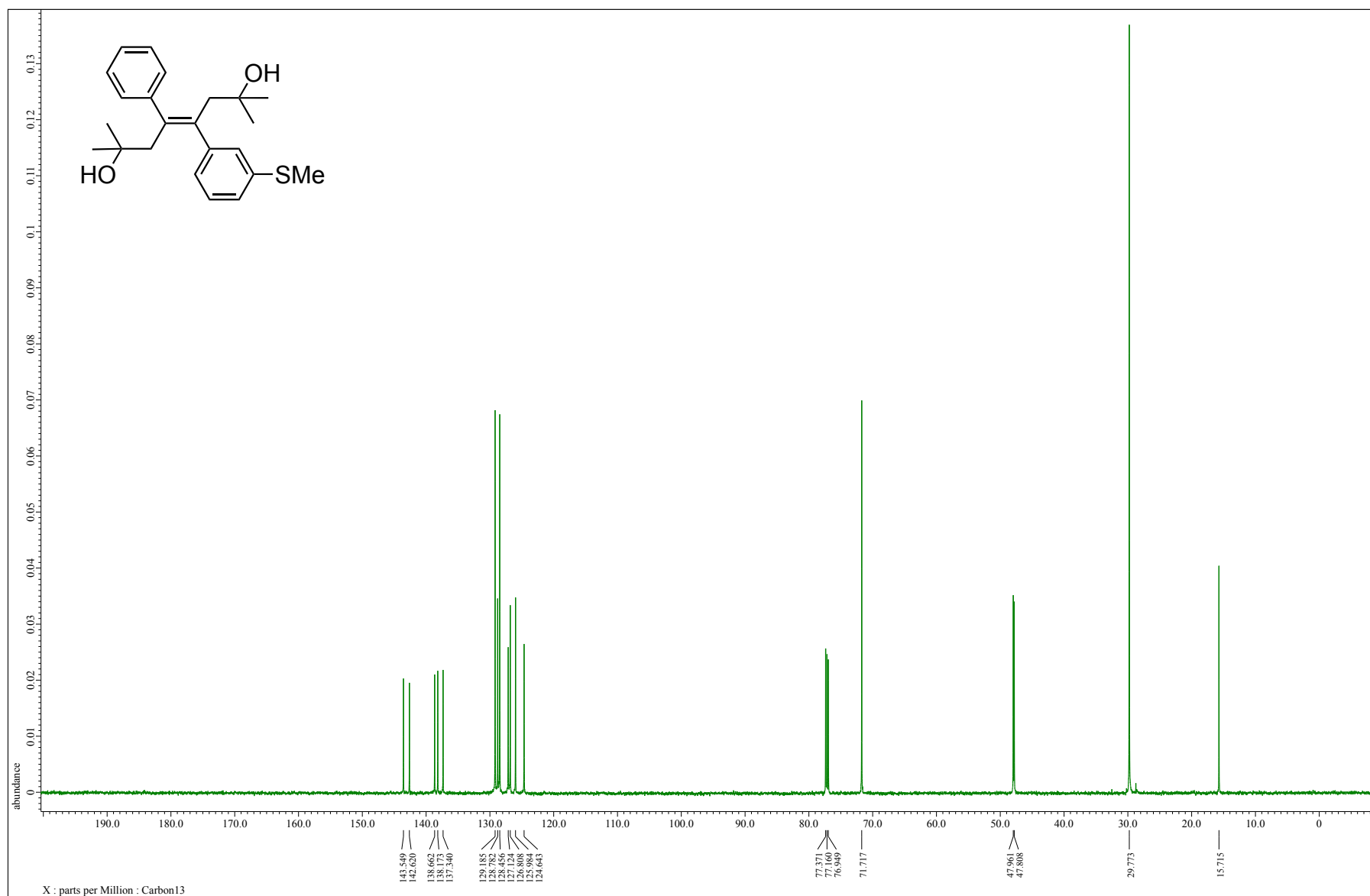


Figure S25. ¹³C NMR (151 MHz, CDCl₃) spectrum of **7f**.

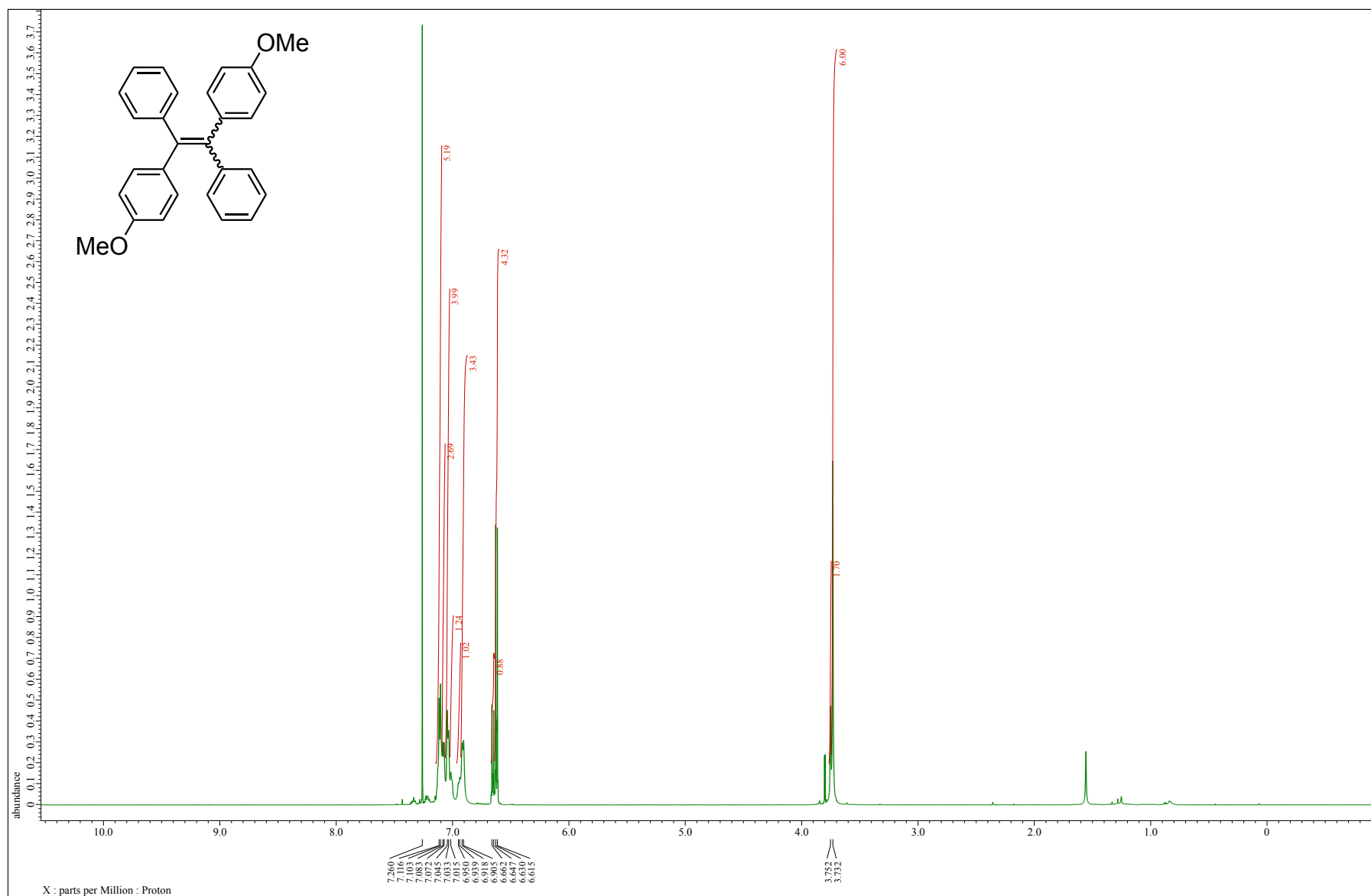


Figure S26. ^1H NMR (600 MHz, CDCl_3) spectrum of **10** ($E:Z = 78:22$).

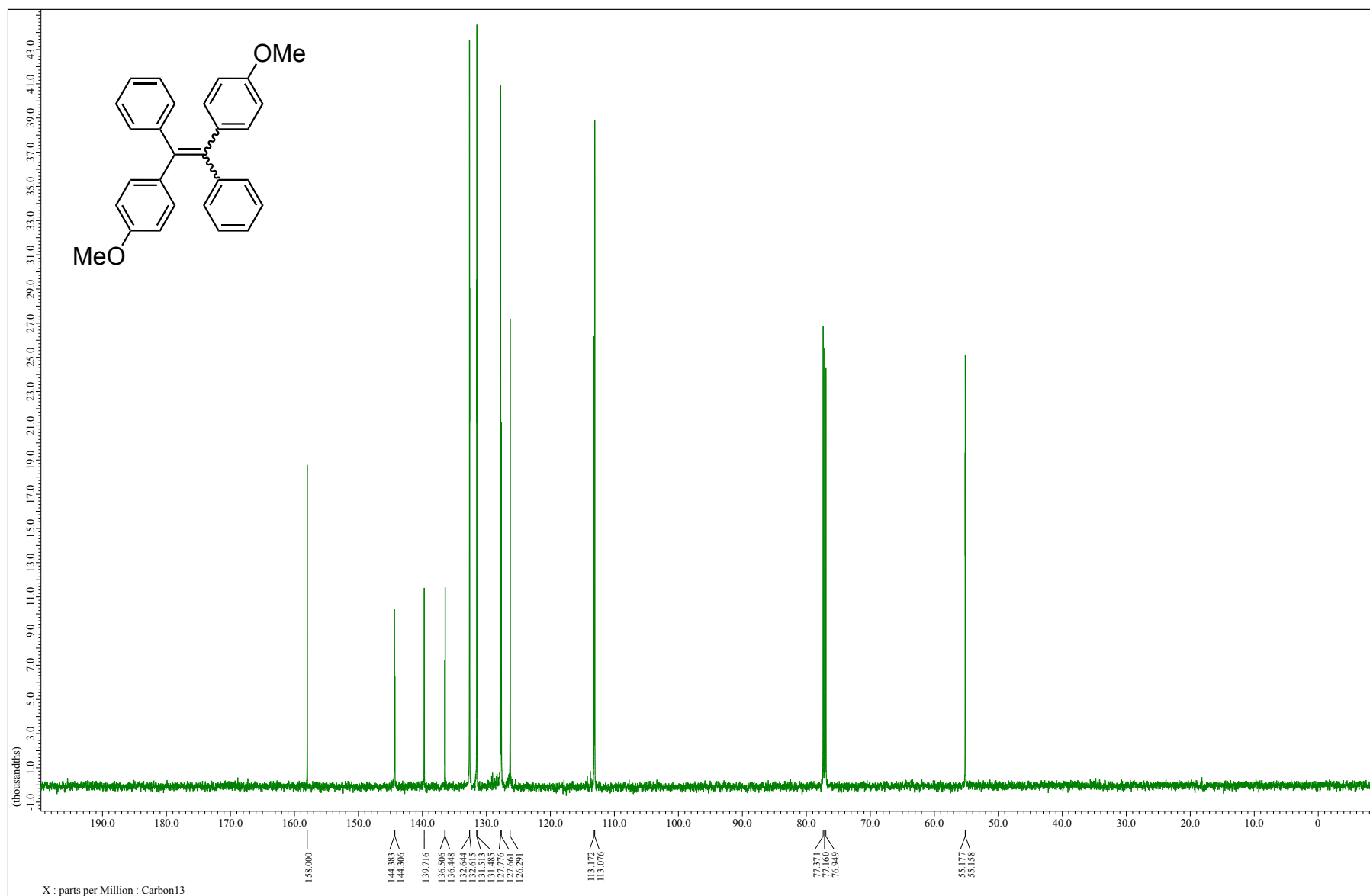


Figure S27. ^{13}C NMR (151 MHz, CDCl_3) spectrum of **10** (*E*:*Z* = 78:22).