

Supporting information for:

Ligand-Controlled Cobalt-Catalyzed Isomerization and Reductive C-O Bond Cleavage of Allylic Ethers

Lijun Chang, Cheng Cai, Ran Chen, Jianhui Chen,* Yanshu Luo, Yuanzhi Xia*

College of Chemistry and Materials Engineering, Wenzhou University, Wenzhou 325035, China

cjh@wzu.edu.cn; xyz@wzu.edu.cn

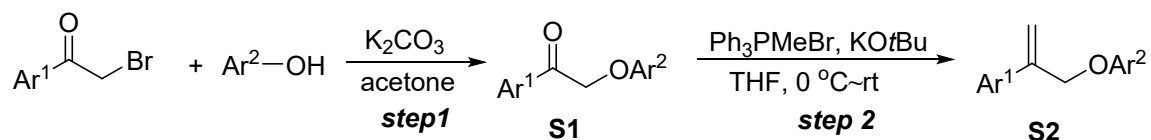
Table of Contents:

Entry	Content	Page
I	General information	S2
II	Procedures for the synthesis of starting materials	S2
III	Cobalt-catalyzed isomerization of allyl ethers	S11
IV	Cobalt-catalyzed reductive C-O bond cleavage of allyl ethers	S22
V	Gram-scale reactions	S28
VI	Further derivatizations	S28
VII	Preliminary mechanistic studies	S29
VIII	NMR Spectra	S34

I. General information

THF, xylene, anisole, 1,4-dioxane, PhCl and Hexane were purchased from Energy Chemical and used as received. Toluene was distilled from sodium benzophenone ketyl prior to use. HBpin (98%), NaBHET₃ (1.0 mol/L in THF), Xantphos, DPEPhos and CoCl₂ (99%) were purchased from Energy Chemical and used as received. Bis(2-(diphenylphosphanyl)phenyl)amine (**PNP**),¹ and phosphine-amido-oxazoline ligand (**PAO**)² were prepared according to previously reported procedures, respectively. The other commercially available chemicals were used as received. NMR spectra were recorded on a Bruker-400 or Bruker-500 instrument. ¹H NMR chemical shifts were referenced to tetramethylsilane signal (0 ppm), ¹³C NMR chemical shifts were referenced to the solvent resonance (77.00 ppm, CDCl₃), ¹⁹F NMR chemical shifts were referenced to the solvent resonance. The following abbreviations (or combinations thereof) were used to explain multiplicities: s = singlet, d = doublet, t = triplet, m = multiplet, br = broad, q = quadruplet. High-resolution mass spectra (HRMS) were recorded on a Bruker micrOTOF-Q II instrument (ESI). Melting points were obtained using a X-4 melting point apparatus (Laboratory Devices, Beijing taikē CO.; LTD.). In this report, all the reactions that require heating were using oil bath as the heating source.

II. Procedures for the synthesis of starting materials



Step 1: According to a previously reported procedure,³ a 250 mL round bottom flask equipped with a reflux condenser and a dropping funnel was charged with phenol (22 mmol), K₂CO₃ (30 mmol) and acetone (50 mL). The mixture was added dropwisely with a solution of 2-bromoacetophenone (20 mmol in 50 mL of acetone) at room temperature over 30 mins. The resulting suspension was stirred at reflux overnight, cooled to room temperature, filtered and concentrated under reduced pressure. The residue was purified by recrystallization from petroleum ether to give the desired product **S1**.

Step 2: According to a previously reported procedure,⁴ a 250 mL three-necked flask was charged with PPh₃MeBr (24 mmol), KOtBu (24 mmol) and dried THF (50 mL) under argon. The mixture was stirred at 0 °C for 1 h, added

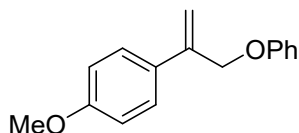
¹ L. Liang, P. Chien, J. Lin, M. Huang, Y. Huang, J. Liao, *Organometallics*. **2006**, *25*, 1399.

² H. Liu, C. Cai, Y. Ding, J. Chen, B. Liu, Y. Xia, *ACS Omega*. **2020**, *5*, 11655.

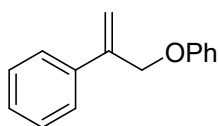
³ T. Mete, D. Laha, R. Bhat, *ChemistrySelect* **2018**, *3*, 7656.

⁴ G. Hoang, S. Zhang, J. Takacs, *Chem. Commun.* **2018**, *54*, 4838.

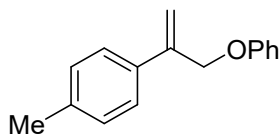
dropwisely with a solution of **S1** (20 mmol in 50 mL of dried THF). Then the resulted solution was stirred at room temperature overnight, passed through a pad of silica gel and washed with EA. The filtrate was concentrated and purified by flash column chromatography to give the desired product **S2**.



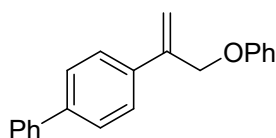
1-methoxy-4-(3-phenoxyprop-1-en-2-yl)benzene (1a).⁵ White solid was obtained by silica gel column chromatography with PE/EA (50:1). 5.78 g, 24.1 mmol, 60% yield. ¹H NMR: (500 MHz, CDCl₃): δ 7.43 (d, J = 8.5 Hz, 2H), 7.26-7.32 (m, 2H), 6.94-6.99 (m, 3H), 6.89 (d, J = 8.5 Hz, 2H), 5.53 (s, 1H), 5.37 (s, 1H), 4.87 (s, 2H), 3.82 (s, 3H).



(3-phenoxyprop-1-en-2-yl)benzene (1b).⁶ White solid was obtained by silica gel column chromatography with PE/EA (50:1). 1.51 g, 7.1 mmol, 60% yield. ¹H NMR: (500 MHz, CDCl₃): δ 7.45-7.50 (m, 2H), 7.32-7.38 (m, 2H), 7.25-7.32 (m, 3H), 6.93-6.98 (m, 3H), 5.60 (s, 1H), 5.46 (s, 1H), 4.89 (s, 2H).



1-methyl-4-(3-phenoxyprop-1-en-2-yl)benzene (1c). Colorless oil was obtained by silica gel column chromatography with PE/EA (50:1). 2.40 g, 10.6 mmol, 71% yield. ¹H NMR: (500 MHz, CDCl₃): δ 7.37 (d, J = 8.0 Hz, 2H), 7.25-7.30 (m, 2H), 7.15 (d, J = 8.0 Hz, 2H), 6.93-6.97 (m, 3H), 5.57 (s, 1H), 5.41 (s, 1H), 4.86 (s, 2H), 2.34 (s, 3H); ¹³C NMR: (125.8 MHz, CDCl₃) δ 158.7, 142.9, 137.8, 135.5, 129.4, 129.1, 125.9, 120.9, 115.0, 113.9, 69.8, 21.1. HRMS (ESI) m/z: [M + H]⁺ Calcd for C₁₆H₁₇O⁺ 225.1274, Found 225.1278.

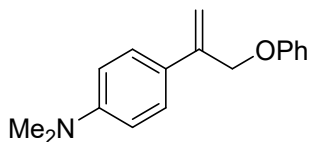


(3-phenoxyprop-1-en-2-yl)-1,1'-biphenyl (1d). White solid was obtained by silica gel column chromatography with PE/EA (50:1). 0.92 g, 3.2 mmol, 38% yield. M. P. 82.2-82.5 °C. ¹H NMR: (500 MHz, CDCl₃) δ 7.63-7.54 (m,

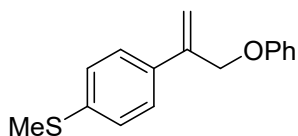
⁵ M. Organ, E. Arvanitis, C. Dixon, J. Cooper, *J. Am. Chem. Soc.* **2002**, *124*, 1288.

⁶ M. Czyz, M. Taylor, T. Hornngren, A. Polyzos, *ACS Catal.* **2021**, *11*, 5472.

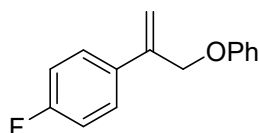
6H), 7.41-7.46 (m, 2H), 7.37-7.26 (m, 3H), 7.01 - 6.94 (m, 3H), 5.67 (s, 1H), 5.49 (s, 1H), 4.92 (s, 2H); ^{13}C NMR: (125.8 MHz, CDCl_3) δ 158.7, 142.6, 140.8, 140.6, 137.2, 129.5, 128.8, 127.4, 127.2, 126.9, 126.4, 121.1, 115.0, 114.8, 69.8. HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{21}\text{H}_{19}\text{O}^+$ 287.1430, Found 287.1439.



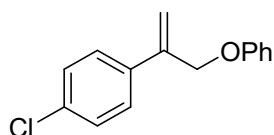
***N,N*-dimethyl-4-(3-phenoxyprop-1-en-2-yl)aniline (1e).** White solid was obtained by silica gel column chromatography with PE/EA (80:1). 0.46 g, 1.8 mmol, 46% yield. M. P. 52.7-53.0 °C. ^1H NMR: (400MHz, CDCl_3) δ 7.39 (d, $J = 8.4$ Hz, 2H), 7.23-7.31 (m, 2H), 6.92-7.00 (m, 3H), 6.70 (d, $J = 8.8$ Hz, 2H), 5.48 (s, 1H), 5.27 (s, 1H), 4.87 (s, 2H), 2.95 (s, 6H); ^{13}C NMR (101 MHz, CDCl_3) δ 158.7, 150.2, 142.2, 129.3, 126.6, 126.1, 120.8, 114.9, 112.1, 111.1, 69.9, 40.4. HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{17}\text{H}_{20}\text{NO}^+$ 254.1539, Found 254.1537.



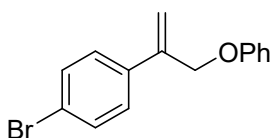
methyl(4-(3-phenoxyprop-1-en-2-yl)phenyl)sulfane (1f). White solid was obtained by silica gel column chromatography with PE/EA (50:1). 0.48 g, 1.9 mmol, 38 % yield. M. P. 39.8-40.5 °C. ^1H NMR (500 MHz, CDCl_3) δ 7.41 (d, $J = 8.5$ Hz, 2H), 7.26-7.31 (m, 2H), 7.23 (d, $J = 8.5$ Hz, 2H), 6.93-6.98 (m, 3H), 5.60 (s, 1H), 5.43 (s, 1H), 4.87 (s, 2H), 2.48 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 158.5, 142.2, 138.3, 134.9, 129.4, 126.3, 121.0, 114.8, 114.4, 69.7, 15.6; HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{16}\text{H}_{17}\text{OS}^+$ 257.0995, Found 257.0996.



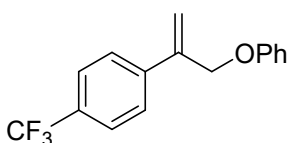
1-fluoro-4-(3-phenoxyprop-1-en-2-yl)benzene (1g). Colorless oil was obtained by silica gel column chromatography with PE/EA (50:1). 2.81 g, 12.2 mmol, 82% yield. ^1H NMR: (500 MHz, CDCl_3): δ 7.41-7.47 (m, 2H), 7.25-7.32 (m, 2H), 7.00-7.06 (m, 2H), 6.92-6.99 (m, 3H), 5.55 (s, 1H), 5.44 (s, 1H), 4.85 (s, 2H); ^{13}C NMR (125.8 MHz, CDCl_3) δ 162.6 (d, $J = 247.0$ Hz), 158.5, 142.2, 134.4 (d, $J = 3.5$ Hz), 129.5, 127.8 (d, $J = 8.0$ Hz), 121.1, 115.3 (d, $J = 20.0$ Hz), 114.9, 69.9; ^{19}F NMR (376 MHz, CDCl_3) δ -114.1; HRMS (ESI) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{15}\text{H}_{13}\text{FNaO}^+$ 251.0843, Found 251.0853.



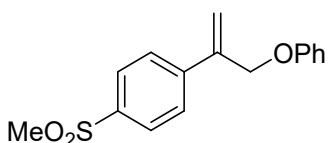
1-chloro-4-(3-phenoxyprop-1-en-2-yl)benzene (1h). Colorless oil was obtained by silica gel column chromatography with PE/EA (50:1). 2.04 g, 8.3 mmol, 88% yield. ¹H NMR: (500 MHz, CDCl₃): δ 7.40 (d, J = 8.5 Hz, 2H), 7.25-7.33 (m, 4H), 6.91-6.99 (m, 3H), 5.59 (s, 1H), 5.47 (s, 1H), 4.84 (s, 2H); ¹³C NMR: (125.8 MHz, CDCl₃) δ 158.5, 142.1, 136.8, 133.8, 129.5, 128.6, 127.4, 121.2, 115.5, 114.9, 69.8; HRMS (ESI) m/z: [M + H]⁺ Calcd for C₁₅H₁₄ClO⁺ 245.0728, Found 245.0728.



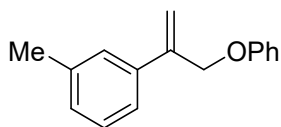
1-bromo-4-(3-phenoxyprop-1-en-2-yl)benzene (1i). Colorless oil was obtained by silica gel column chromatography with PE/EA (50:1). 2.71 g, 9.4 mmol, 94% yield. ¹H NMR: (500 MHz, CDCl₃): δ 7.45 (d, J = 8.0 Hz, 2H), 7.23-7.37 (m, 4H), 6.89-7.00 (m, 3H), 5.58 (s, 1H), 5.47 (s, 1H), 4.83 (s, 2H); ¹³C NMR: (125.8 MHz, CDCl₃) δ 158.5, 142.2, 137.2, 131.6, 129.5, 127.7, 122.0, 121.2, 115.6, 114.9, 69.7; HRMS (ESI) m/z: [M + H]⁺ Calcd for C₁₅H₁₄BrO⁺ 289.0223, Found 289.0232.



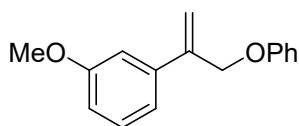
1-(3-phenoxyprop-1-en-2-yl)-4-(trifluoromethyl)benzene (1j). Colorless oil was obtained by silica gel column chromatography with PE. 0.29 g, 1.0 mmol, 26 % yield. ¹H NMR: (500 MHz, CDCl₃): δ 7.54-7.65 (m, 4H), 7.27-7.34 (m, 2H), 6.91-7.02 (m, 3H), 5.69 (s, 1H), 5.58 (s, 1H), 4.90 (s, 2H); ¹³C NMR (125.8 MHz,) δ 158.4, 142.1 (d, J = 46.5 Hz), 130.0 (d, J = 32.5 Hz), 129.5, 126.5, 125.4 (q, J = 3.5 Hz), 125.2, 123.1, 121.3, 117.1, 114.9, 69.7; ¹⁹F NMR (376 MHz, CDCl₃) δ -62.6; HRMS (ESI) m/z: [M + H]⁺ Calcd for C₁₆H₁₄F₃O⁺ 279.0991, Found 279.0987.



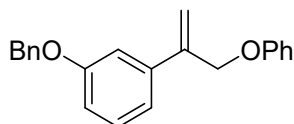
1-(methylsulfonyl)-4-(3-phenoxyprop-1-en-2-yl)benzene (1k). White solid was obtained by silica gel column chromatography with PE/EA (5:1). 0.42 g, 1.5 mmol, 48 % yield. M. P. 68.0-68.5 °C. ¹H NMR: (400 MHz, CDCl₃) δ 7.93 (d, J = 8.4 Hz, 2H), 7.67 (d, J = 8.4 Hz, 2H), 7.28-7.34 (m, 2H), 6.91-7.03 (m, 3H), 5.74 (s, 1H), 5.64 (s, 1H), 4.91 (s, 2H), 3.06 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 158.2, 143.7, 141.8, 139.6, 129.5, 127.5, 127.0, 121.3, 118.4, 114.8, 69.5, 44.4; HRMS (ESI) m/z: [M + H]⁺ Calcd for C₁₆H₁₇O₃S⁺ 289.0893, Found 289.0898.



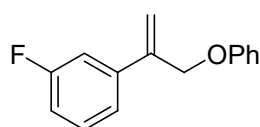
1-methyl-3-(3-phenoxyprop-1-en-2-yl)benzene (1l). Colorless oil was obtained by silica gel column chromatography with PE/EA (80:1). 2.34 g, 10.4 mmol, 70% yield. $^1\text{H NMR}$: (400 MHz, CDCl_3) δ 7.21 (m, 5H), 7.12 (d, $J = 6.8$ Hz, 1H), 6.97 (d, $J = 8.0$ Hz, 3H), 5.58 (s, 1H), 5.44 (s, 1H), 4.87 (s, 2H), 2.36 (s, 3H); $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 158.5, 143.0, 138.2, 137.8, 129.3, 128.6, 128.2, 126.6, 123.0, 120.8, 114.8, 114.2, 69.5, 21.4; HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{16}\text{H}_{17}\text{O}^+$ 225.1274, Found 225.1278.



1-methoxy-3-(3-phenoxyprop-1-en-2-yl)benzene (1m). Colorless oil was obtained by silica gel column chromatography with PE/EA (80:1). 2.04 g, 9.8 mmol, 66% yield. $^1\text{H NMR}$: (500 MHz, CDCl_3): δ 7.20-7.31 (m, 3H), 6.98-7.08 (m, 2H), 6.96 (m, 3H), 6.85 (d, $J = 9.0$ Hz, 1H), 5.60 (s, 1H), 5.46 (s, 1H), 4.86 (s, 2H), 3.80 (s, 3H); $^{13}\text{C NMR}$: (125.8 MHz, CDCl_3) δ 159.7, 158.6, 139.9, 129.4, 121.0, 118.5, 115.0, 114.9, 113.3, 112.1, 69.8, 55.2; HRMS (ESI) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{16}\text{H}_{16}\text{NaO}_2^+$ 263.1043, Found 263.1045.

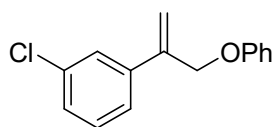


1-(benzyloxy)-3-(3-phenoxyprop-1-en-2-yl)benzene (1n). Colorless oil was obtained by silica gel column chromatography with PE/EA (100:1). 0.62 g, 2.0 mmol, 35% yield. $^1\text{H NMR}$: (400 MHz, CDCl_3) δ 7.21-7.48 (m, 8H), 7.05-7.15 (m, 2H), 7.02-6.90 (m, 4H), 5.59 (s, 1H), 5.46 (s, 1H), 5.06 (s, 2H), 4.85 (s, 2H); $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 158.7, 158.4, 142.7, 139.8, 136.8, 129.3, 128.5, 127.8, 127.4, 120.9, 118.6, 114.9, 114.8, 114.0, 112.9, 69.8, 69.5; HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{22}\text{H}_{21}\text{O}_2^+$ 317.1536, Found 317.1532.

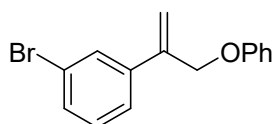


1-fluoro-3-(3-phenoxyprop-1-en-2-yl)benzene (1o). Colorless oil was obtained by silica gel column chromatography with PE. 1.02 g, 4.5 mmol, 64% yield. $^1\text{H NMR}$: (500 MHz, CDCl_3): δ 7.21-7.34 (m, 4H), 7.18 (d, $J = 10.0$ Hz, 1H), 6.90-7.03 (m, 4H), 5.62 (s, 1H), 5.50 (s, 1H), 4.85 (s, 2H); $^{13}\text{C NMR}$ (125.8 MHz,) δ 162.9 (d, $J = 245.5$ Hz), 158.5, 142.2, 140.7 (d, $J = 7.5$ Hz), 129.9 (d, $J = 8.5$ Hz), 129.5, 121.7 (d, $J = 3.5$ Hz), 121.2, 116.0,

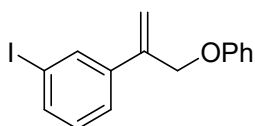
115.0, 114.8 (d, J = 21.5 Hz), 113.1 (d, J = 22.5 Hz), 69.8; ^{19}F NMR (376 MHz, CDCl_3) δ -113.1; HRMS (ESI) m/z: $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{15}\text{H}_{13}\text{FNaO}^+$ 251.0843, Found 251.0853.



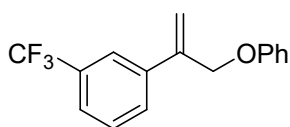
1-chloro-3-(3-phenoxyprop-1-en-2-yl)benzene (1p). Colorless oil was obtained by silica gel column chromatography with PE. 0.86 g, 3.5 mmol, 70% yield. ^1H NMR: (500 MHz, CDCl_3): δ 7.46 (s, 1H), 7.32-7.37 (s, 1H), 7.26-7.32 (m, 4H), 6.90-7.00 (m, 3H), 5.61 (s, 1H), 5.50 (s, 1H), 4.85 (s, 2H); ^{13}C NMR: (125.8 MHz, CDCl_3) δ 158.5, 142.2, 140.3, 134.5, 129.7, 129.5, 128.0, 126.3, 124.3, 121.2, 116.1, 115.0, 69.7; HRMS (ESI) m/z: $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{15}\text{H}_{14}\text{ClO}^+$ 245.0728, Found 245.0728.



1-bromo-3-(3-phenoxyprop-1-en-2-yl)benzene (1q). Colorless oil was obtained by silica gel column chromatography with PE. 0.42 g, 1.5 mmol, 50% yield. ^1H NMR: (500 MHz, CDCl_3): δ 7.62 (s, 1H), 7.43 (d, J = 8.0 Hz, 1H), 7.39 (d, J = 8.0 Hz, 1H), 7.25-7.32 (m, 2H), 7.18-7.25 (m, 1H), 6.92-7.00 (m, 3H), 5.60 (s, 1H), 5.50 (s, 1H), 4.84 (s, 2H); ^{13}C NMR: (125.8 MHz, CDCl_3) δ 158.5, 142.1, 140.6, 130.9, 130.0, 129.5, 129.2, 124.7, 122.7, 121.2, 116.2, 115.0, 69.7; HRMS (ESI) m/z: $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{15}\text{H}_{14}\text{BrO}^+$ 289.0223, Found 289.0232.

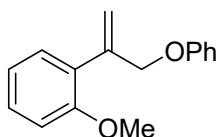


1-iodo-3-(3-phenoxyprop-1-en-2-yl)benzene (1r). Orange oil was obtained by silica gel column chromatography with PE/EA (25:1). 0.98 g, 2.9 mmol, 60% yield. ^1H NMR: (400 MHz, CDCl_3) δ 7.82 (s, 1H), 7.64 (d, J = 8.0 Hz, 1H), 7.42 (d, J = 8.0 Hz, 1H), 7.23-7.33 (m, 2H), 7.04-7.12 (m, 1H), 6.92-7.01 (m, 3H), 5.58 (s, 1H), 5.48 (s, 1H), 4.83 (s, 2H); ^{13}C NMR (101 MHz, CDCl_3) δ 158.3, 141.8, 140.5, 136.8, 135.0, 130.0, 129.4, 125.2, 121.1, 116.0, 114.8, 94.5, 69.4; HRMS (ESI) m/z: $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{15}\text{H}_{13}\text{INaO}^+$ 358.9903, Found 358.9910.

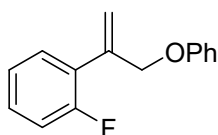


1-(3-phenoxyprop-1-en-2-yl)-3-(trifluoromethyl)benzene (1s). Colorless oil was obtained by silica gel column chromatography with PE/EA (50:1). 0.74 g, 2.7 mmol, 53% yield. ^1H NMR: (500 MHz, CDCl_3): δ 7.73 (s, 1H),

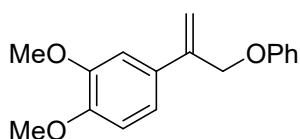
7.64 (d, J = 8.0 Hz, 1H), 7.56 (d, J = 8.0 Hz, 1H), 7.43-7.49 (m, 1H), 7.25-7.33 (m, 2H), 6.92-7.01 (m, 3H), 5.66 (s, 1H), 5.56 (s, 1H), 4.89 (s, 2H); ^{13}C NMR (125.8 MHz,) δ 158.4, 142.2, 139.2, 130.9 (q, J = 31.5 Hz), 129.5, 129.4, 128.9, 125.2, 124.6 (q, J = 3.5 Hz), 122.9 (q, J = 8.0 Hz), 121.3, 116.7, 115.0, 69.8; ^{19}F NMR (376 MHz, CDCl_3) δ -62.6; HRMS (ESI) m/z: $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{16}\text{H}_{14}\text{F}_3\text{O}^+$ 279.0991, Found 279.0987.



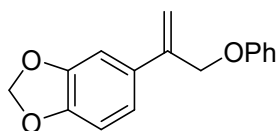
1-methoxy-2-(3-phenoxyprop-1-en-2-yl)benzene (1t). Colorless oil was obtained by silica gel column chromatography with PE/EA (50:1). 2.74 g, 11.4 mmol, 57% yield. ^1H NMR: (400 MHz, CDCl_3): δ 7.20-7.33 (m, 4H), 6.85-7.00 (m, 5H), 5.50 (s, 1H), 5.27 (s, 1H), 4.87 (s, 2H), 3.81 (s, 3H); ^{13}C NMR (125.8 MHz, CDCl_3) δ 158.7, 156.8, 143.9, 130.4, 129.2, 129.1, 128.9, 120.7, 120.6, 115.2, 114.9, 110.6, 69.6, 55.4; HRMS (ESI) m/z: $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{16}\text{H}_{17}\text{O}_2^+$ 241.1223, Found 241.1221.



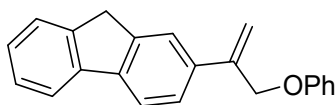
1-fluoro-2-(3-phenoxyprop-1-en-2-yl)benzene (1u). Colorless oil was obtained by silica gel column chromatography with PE/EA (80:1). 1.43 g, 6.3 mmol, 70% yield. ^1H NMR: (500 MHz, CDCl_3): δ 7.31-7.39 (m, 1H), 7.24-7.30 (m, 3H), 7.03-7.15 (m, 2H), 6.90-7.00 (m, 3H), 5.61 (s, 1H), 5.47 (s, 1H), 4.86 (s, 2H); ^{13}C NMR (125.8 MHz,) δ 160.1 (d, J = 247.5 Hz), 158.6, 140.3, 130.2 (d, J = 4.5 Hz), 129.5, 129.4, 126.8 (d, J = 14.5 Hz), 124.2 (d, J = 3.5 Hz), 120.9, 117.5 (d, J = 3.0 Hz), 115.8 (d, J = 22.5 Hz), 114.9, 69.9; ^{19}F NMR (376 MHz, CDCl_3) δ -114.5; HRMS (ESI) m/z: $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{15}\text{H}_{13}\text{FNaO}^+$ 251.0843, Found 251.0853.



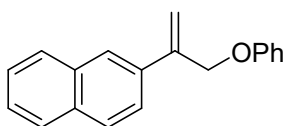
1,2-dimethoxy-4-(3-phenoxyprop-1-en-2-yl)benzene (1v). Colorless oil was obtained by silica gel column chromatography with PE/EA (20:1). 2.86 g, 10.5 mmol, 70% yield. ^1H NMR: (500 MHz, CDCl_3): δ 7.26-7.32 (m, 2H), 7.01-7.06 (m, 2H), 6.93-6.99 (m, 3H), 6.84 (d, J = 9.0 Hz, 1H), 5.53 (s, 1H), 5.39 (s, 1H), 4.86 (s, 2H), 3.87 (d, J = 2.5 Hz, 6H); ^{13}C NMR: (125.8 MHz, CDCl_3) δ 158.6, 149.1, 148.9, 142.6, 131.3, 129.4, 121.0, 118.5, 114.9, 113.5, 111.1, 109.6, 70.1, 55.8; HRMS (ESI) m/z: $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{17}\text{H}_{18}\text{NaO}_3^+$ 293.1148, Found 293.1155.



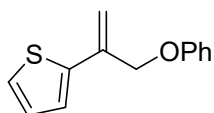
1-(3-phenoxyprop-1-en-2-yl)benzo[d][1,3]dioxole (1w). Colorless oil was obtained by silica gel column chromatography with PE/EA (150:1). 0.42 g, 1.7 mmol, 33% yield. ^1H NMR (400 MHz, CDCl_3) δ 7.22-7.33 (m, 2H), 6.90-7.02 (m, 5H), 6.78 (d, $J = 8.0$ Hz, 1H), 5.95 (s, 2H), 5.50 (s, 1H), 5.37 (s, 1H), 4.82 (s, 2H); ^{13}C NMR (101 MHz, CDCl_3) δ 158.5, 147.8, 147.4, 142.5, 132.6, 129.4, 121.0, 119.6, 114.9, 114.0, 108.2, 106.6, 101.1, 70.0; HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{16}\text{H}_{15}\text{O}_3^+$ 255.1016, Found 255.1024.



1-(3-phenoxyprop-1-en-2-yl)-9H-fluorene (1x). White solid was obtained by silica gel column chromatography with PE/EA (150:1). 0.61 g, 2.0 mmol, 34% yield. M. P. 92.1-92.4 °C. ^1H NMR (400 MHz, CDCl_3): δ 7.80-7.73 (m, 2H), 7.67 (s, 1H), 7.53 (dd, $J = 13.6, 8.0$ Hz, 2H), 7.35-7.41 (m, 1H), 7.28-7.34 (m, 3H), 6.95-7.03 (m, 3H) 5.67 (s, 1H), 5.49 (s, 1H), 4.96 (s, 2H), 3.91 (s, 2H); ^{13}C NMR (101 MHz, CDCl_3) δ 158.6, 143.4, 143.2, 141.6, 141.2, 136.8, 129.4, 126.8, 125.0, 124.8, 122.6, 121.0, 119.9, 119.7, 114.9, 114.5, 69.9, 36.9; HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{22}\text{H}_{19}\text{O}^+$ 299.1430, Found 299.1427.

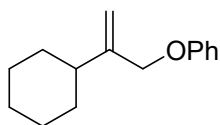


1-(3-phenoxyprop-1-en-2-yl)naphthalene (1y). White solid was obtained by silica gel column chromatography with PE/EA (50:1). 1.16 g, 4.4 mmol, 44% yield. M. P. 35.7-36.5 °C. ^1H NMR: (500 MHz, CDCl_3): δ 7.89 (s, 1H), 7.76-7.85 (m, 3H), 7.63 (dd, $J = 8.5, 1.5$ Hz, 1H), 7.41-7.50 (m, 2H), 7.25-7.35 (m, 2H), 6.93-7.04 (m, 3H), 5.75 (s, 1H), 5.56 (s, 1H), 5.00 (s, 2H); ^{13}C NMR: (125.8 MHz, CDCl_3) δ 158.7, 143.0, 135.6, 133.4, 133.1, 129.5, 128.3, 128.0, 127.6, 126.2, 126.1, 124.9, 124.2, 121.1, 115.3, 115.1, 69.9; HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{19}\text{H}_{17}\text{O}^+$ 261.1274, Found 261.1277.

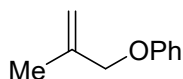


1-(3-phenoxyprop-1-en-2-yl)thiophene (1z). Yellow oil was obtained by silica gel column chromatography with PE. 0.91 g, 4.2 mmol, 52% yield. ^1H NMR: (500 MHz, CDCl_3): δ 7.24-7.32 (m, 2H), 7.19 (d, $J = 5.0$ Hz, 1H), 7.12 (d, $J = 5.0$ Hz, 1H), 6.90-7.01 (m, 4H), 5.62 (s, 1H), 5.34 (s, 1H), 4.84 (s, 2H); ^{13}C NMR: (125.8 MHz, CDCl_3) δ

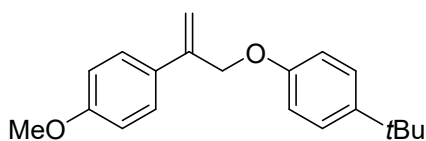
158.5, 141.9, 137.0, 129.5, 127.4, 124.7, 124.0, 121.2, 115.0, 113.3, 69.7; HRMS (ESI) m/z: [M + Na]⁺ Calcd for C₁₃H₁₂NaOS⁺ 239.0501, Found 239.0507.



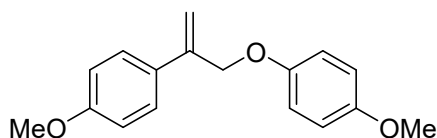
((2-cyclohexylallyl)oxy)benzene (1aa). Colorless oil was obtained by silica gel column chromatography with PE. 2.39 g, 11.7 mmol, 74% yield. ¹H NMR: (400 MHz, CDCl₃) δ 7.23-7.31 (m, 2H), 6.89-6.96 (m, 3H), 5.11 (s, 1H), 4.98 (s, 1H), 4.48 (s, 2H), 2.20-2.12 (m, 1H), 1.75-1.89 (m, 4H), 1.70 (d, J = 12.0 Hz, 1H), 1.15-1.34 (m, 5H); ¹³C NMR (126 MHz, CDCl₃) δ 158.8, 150.0, 129.3, 120.6, 114.7, 110.1, 70.0, 41.2, 32.2, 26.6, 26.2; HRMS (ESI) m/z: [M + Na]⁺ Calcd for C₁₅H₂₀NaO⁺ 239.1406, Found 239.1406.



((2-methylallyl)oxy)benzene (1ab).⁷ Colorless oil was obtained by silica gel column chromatography with PE. 3.75 g, 25.3 mmol, 67% yield. ¹H NMR: (400 MHz, CDCl₃) δ 7.22-7.31 (m, 2H), 6.89-6.98 (m, 3H), 5.09 (s, 1H), 4.98 (s, 1H), 4.42 (s, 2H), 1.82 (s, 3H).



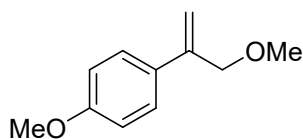
1-(tert-butyl)-4-((2-(4-methoxyphenyl)allyl)oxy)benzene (1ac). White solid was obtained by silica gel column chromatography with PE/EA (50:1). 0.30 g, 1.1 mmol, 25% yield. M. P. 62.0-62.5 °C. ¹H NMR: (500 MHz, CDCl₃): δ NMR (500 MHz,) δ 7.43 (d, J = 8.8 Hz, 2H), 7.30 (d, J = 8.8 Hz, 2H), 6.85-6.92 (m, 4H), 5.53 (s, 1H), 5.37 (s, 1H), 4.84 (s, 2H), 3.81 (s, 3H), 1.30 (s, 9H); ¹³C NMR: (125.8 MHz, CDCl₃) δ 159.5, 156.5, 143.7, 142.6, 130.9, 127.2, 126.2, 114.4, 113.8, 113.2, 70.2, 55.3, 34.1, 31.5; HRMS (ESI) m/z: [M + H]⁺ Calcd for C₂₀H₂₅O₂⁺ 297.1849, Found 297.1851.



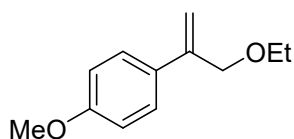
1-methoxy-4-(3-(4-methoxyphenoxy)prop-1-en-2-yl)benzene (1ad). White solid was obtained by silica gel column chromatography with PE/EA (50:1). 0.73 g, 2.7 mmol, 45% yield. M. P. 94.7-95.7 °C. ¹H NMR: (500 MHz, CDCl₃): δ 7.43 (d, J = 9.0 Hz, 2H), 6.80-6.92 (m, 6H), 5.51 (s, 1H), 5.35 (s, 1H), 4.82 (s, 2H), 3.82 (s, 3H), 3.77 (s,

⁷ W. Gao, X. Zhang, X. Xie, S. Ding, *Chem. Commun.* **2020**, 56, 2012.

3H); ^{13}C NMR: (125.8 MHz, CDCl_3) δ 159.5, 154.1, 152.9, 142.7, 130.9, 127.2, 116.1, 114.6, 113.8, 113.2, 70.9, 55.7, 55.3; HRMS (ESI) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{17}\text{H}_{18}\text{NaO}_3^+$ 293.1148, Found 293.1155.



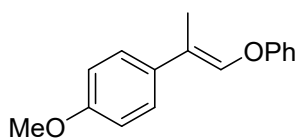
1-methoxy-4-(3-methoxyprop-1-en-2-yl)benzene (1ae).⁸ Colorless oil was obtained by silica gel column chromatography with PE/EA (50:1). 1.21 g, 6.8 mmol, 72 % yield. ^1H NMR: (500 MHz, CDCl_3): δ 7.41 (d, $J = 9.0$ Hz, 2H), 6.87 (d, $J = 9.0$ Hz, 2H), 5.44 (s, 1H), 5.23 (s, 1H), 4.29 (s, 2H), 3.80 (s, 3H), 3.36 (s, 3H).



1-(3-ethoxyprop-1-en-2-yl)-4-methoxybenzene (1af).⁹ Colorless oil was obtained by silica gel column chromatography with PE/EA (200:1). 0.0740 g, 0.41 mmol, 26% yield. ^1H NMR: (400 MHz, CDCl_3): δ 7.41 (dd, $J = 8.8, 2.4$ Hz, 2H), 6.86 (dd, $J = 8.8, 2.4$ Hz, 2H), 5.43 (s, 1H), 5.24 (s, 1H), 4.33 (s, 2H), 3.80 (s, 3H), 3.49-3.57 (m, 2H), 1.15-1.25 (m, 3H).

III. Cobalt-catalyzed isomerization of allyl ethers

General procedure for Co-catalyzed isomerization of allyl ethers: To a 10 mL flame-dried Schlenk flask cooled under argon, CoCl_2 (0.025 mmol), **PNP** (0.03 mmol), PhCl (1 mL), alkene **1** (0.5 mmol) and NaBHET_3 (0.075 mmol, 1 M in THF) were added in sequence. Then the reaction mixture was stirred at rt for 1 h, purified by flash column chromatography using PE/EtOAc as the eluent to give the desired product **2**.

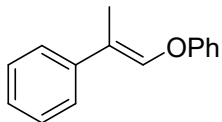


(E)-1-methoxy-4-(1-phenoxyprop-1-en-2-yl)benzene [(E)-(2a)]. Prepared according to the general procedure using 0.1187 g (0.50 mmol) of **1a**, 0.0161 g (0.03 mmol) of **PNP**, 0.0032 g (0.025 mmol) of CoCl_2 , 75 μL (0.075 mmol, 1 M in THF) of NaBHET_3 , 1 mL (0.5 M) of PhCl. Then the mixture was stirred at rt for 1 h (> 99% conv., 10/1 *E/Z*, monitored by ^1H NMR), purified by flash column chromatography using PE as the eluent to give 0.0973 g (0.40 mmol, 82% yield, >20/1 *E/Z*) of **(E)-2a** as a white solid. M. P. 56.2-56.4 $^\circ\text{C}$. ^1H NMR (CDCl_3 , 500 MHz): δ

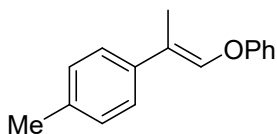
⁸ W. Kirmse, J. Rode, *Chem. Ber.* **1986**, *119*, 3694.

⁹ J. Gupton, J. Dicesare, J. Brown, J. Idoux, *Syn. Commun.* **1992**, *22*, 1067.

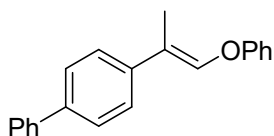
7.29-7.34 (m, 4H), 7.02-7.07 (m, 3H), 6.88 (d, $J = 9.0$ Hz, 2H), 6.76 (s, 1H), 3.80 (s, 3H), 2.11 (s, 3H); ^{13}C NMR (125.8 MHz, CDCl_3) δ 158.6, 157.7, 137.8, 132.3, 129.5, 126.5, 122.4, 120.4, 116.2, 113.9, 55.2, 13.2; HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{16}\text{H}_{17}\text{O}_2^+$ 241.1223, Found 241.1228.



(E)-(1-phenoxyprop-1-en-2-yl)benzene [(E)-(2b)]. Prepared according to the general procedure using 0.1040 g (0.50 mmol) of **1b**, 0.0162 g (0.03 mmol) of **PNP**, 0.0031 g (0.025 mmol) of CoCl_2 , 75 μL (0.075 mmol) of NaBHET_3 , 1 mL (0.5 M) of PhCl . Then the mixture was stirred at rt for 1 h ($> 99\%$ conv., 10/1 E/Z , monitored by ^1H NMR), purified by flash column chromatography using PE as the eluent to give 0.0690 g (0.33 mmol, 79% yield, $>20/1$ E/Z) of **(E)-2b** as a colorless oil. ^1H NMR (CDCl_3 , 500 MHz): δ 7.40 (d, $J = 7.5$ Hz, 2H), 7.29-7.36 (m, 4H), 7.21-7.27 (m, 1H), 7.03-7.09 (m, 3H), 6.85 (s, 1H), 2.14 (s, 3H); ^{13}C NMR: (125.8 MHz, CDCl_3) δ 157.6, 139.9, 139.0, 129.6, 128.5, 126.7, 125.5, 122.7, 120.6, 116.4, 13.0; HRMS (ESI) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{15}\text{H}_{14}\text{NaO}^+$ 233.0937, Found 233.0938.

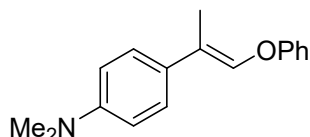


(E)-1-methyl-4-(1-phenoxyprop-1-en-2-yl)benzene [(E)-(2c)]. Prepared according to the general procedure using 0.1116 g (0.49 mmol) of **1c**, 0.0163 g (0.03 mmol) of **PNP**, 0.0033 g (0.025 mmol) of CoCl_2 , 75 μL (0.075 mmol) of NaBHET_3 , 1 mL (0.5 M) of PhCl . Then the mixture was stirred at rt for 1 h ($> 99\%$ conv., 10/1 E/Z , monitored by ^1H NMR), purified by flash column chromatography using PE as the eluent to give 0.0889 g (0.39 mmol, 80% yield, $>20/1$ E/Z) of **(E)-2c** as a colorless oil. ^1H NMR (CDCl_3 , 500 MHz): δ 7.26-7.35 (m, 4H), 7.14 (d, $J = 8.0$ Hz, 2H), 7.02-7.08 (m, 3H), 6.81 (s, 1H), 2.34 (s, 3H), 2.12 (s, 3H); ^{13}C NMR: (125.8 MHz, CDCl_3) δ 157.7, 138.4, 136.9, 136.4, 129.6, 129.1, 125.4, 122.6, 120.6, 116.3, 21.0, 13.1; HRMS (ESI) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{16}\text{H}_{16}\text{NaO}^+$ 247.1093, Found 247.1089.

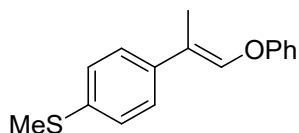


(E)-4-(1-phenoxyprop-1-en-2-yl)-1,1'-biphenyl [(E)-(2d)]. Prepared according to the general procedure using 0.1418 g (0.49 mmol) of **1d**, 0.0164 g (0.031 mmol) of **PNP**, 0.0034 g (0.026 mmol) of CoCl_2 , 75 μL (0.075 mmol)

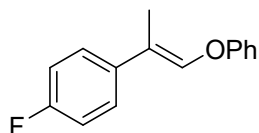
of NaBHET₃, 1 mL (0.5 M) of PhCl. Then the mixture was stirred at rt for 1 h (> 99% conv., 10/1 *E/Z*, monitored by ¹H NMR), purified by flash column chromatography using PE as the eluent to give 0.1168 g (0.41 mmol, 82% yield, >20/1 *E/Z*) of **(E)-2d** as a white solid. M. P. 122.5-122.7 °C. ¹H NMR (CDCl₃, 500 MHz): δ 7.55-7.63 (m, 4H), 7.41-7.51 (m, 4H), 7.31-7.37 (m, 3H), 7.05-7.11 (m, 3H), 6.93 (s, 1H), 2.18 (s, 3H); ¹³C NMR: (125.8 MHz, CDCl₃) δ 157.6, 140.7, 139.5, 139.1, 138.8, 129.6, 128.8, 127.2, 127.1, 126.9, 125.8, 122.7, 120.1, 116.4, 12.9; HRMS (ESI) m/z: [M + H]⁺ Calcd for C₂₁H₁₉O⁺ 287.1430, Found 287.1434.



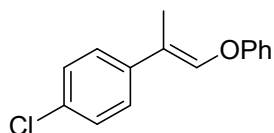
(E)-N, N-dimethyl-4-(1-phenoxyprop-1-en-2-yl)aniline [(E)-2e]. Prepared according to the general procedure using 0.0746 g (0.29 mmol) of **1e**, 0.0194 g (0.036 mmol) of **PNP**, 0.0042 g (0.03 mmol) of CoCl₂, 90 μL (0.090 mmol) of NaBHET₃, 1 mL (0.5 M) of PhCl. Then the mixture was stirred at rt for 1 h (> 99% conv., 10/1 *E/Z*, monitored by ¹H NMR), purified by flash column chromatography using PE as the eluent to give 0.0605 g (0.24 mmol, 81% yield, >20/1 *E/Z*) of **(E)-2e** as a white solid. M. P. 75.6-77.3 °C. ¹H NMR: (400 MHz, CDCl₃) δ 7.27-7.35 (m, 4H), 7.00-7.10 (m, 3H), 6.70-6.77 (m, 3H), 2.95 (s, 6H), 2.10 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 157.7, 136.7, 129.5, 126.2, 122.2, 120.9, 116.1, 112.7, 40.7, 13.0; HRMS (ESI) m/z: [M + H]⁺ Calcd for C₁₇H₂₀NO⁺ 254.1539, Found 254.1537.



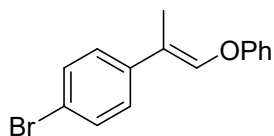
(E)-methyl(4-(1-phenoxyprop-1-en-2-yl)phenyl)sulfane [(E)-2f]. Prepared according to the general procedure using 0.1237 g (0.48 mmol) of **1f**, 0.0160 g (0.03 mmol) of **PNP**, 0.0034 g (0.026 mmol) of CoCl₂, 75 μL (0.075 mmol) of NaBHET₃, 1 mL (0.5 M) of PhCl. Then the mixture was stirred at rt for 1 h (> 99% conv., 14/1 *E/Z*, monitored by ¹H NMR), purified by flash column chromatography using PE as the eluent to give 0.1194 g (0.46 mmol, 95% yield, >20/1 *E/Z*) of **(E)-2f** as a white solid. M. P. 47.2-48.6 °C. ¹H NMR: (400 MHz, CDCl₃) δ 7.30-7.35 (m, 3H), 7.22-7.27 (m, 3H), 7.03-7.10 (m, 3H), 6.84 (s, 1H), 2.49 (s, 3H), 2.12 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 157.5, 138.7, 136.7, 136.5, 129.6, 128.1, 126.9, 125.8, 122.7, 119.9, 116.3, 16.1, 12.9; HRMS (ESI) m/z: [M + H]⁺ Calcd for C₁₆H₁₇OS⁺ 257.0995, Found 257.0997.



(E)-1-fluoro-4-(1-phenoxyprop-1-en-2-yl)benzene [(E)-(2g)]. Prepared according to the general procedure using 0.1139 g (0.50 mmol) of **1g**, 0.0161 g (0.03 mmol) of **PNP**, 0.0032 g (0.025 mmol) of CoCl_2 , 75 μL (0.075 mmol) of NaBHET_3 , 1 mL (0.5 M) of PhCl . Then the mixture was stirred at rt for 1 h (> 99% conv., 5/1 *E/Z*, monitored by ^1H NMR), purified by flash column chromatography using PE as the eluent to give 0.0917 g (0.40 mmol, 81% yield, >20/1 *E/Z*) of **(E)-2g** as a colorless oil. ^1H NMR (CDCl_3 , 500 MHz): δ 7.29-7.37 (m, 4H), 6.98-7.10 (m, 5H), 6.77 (s, 1H), 2.12 (s, 3H); ^{13}C NMR (125.8 MHz,) δ 161.9 (d, $J = 245.5$ Hz), 157.6, 138.8, 135.9 (d, $J = 3.5$ Hz), 129.7, 126.9 (d, $J = 7.5$ Hz), 122.8, 119.7, 116.4, 115.3 (d, $J = 21.0$ Hz), 13.3; ^{19}F NMR (376 MHz, CDCl_3) δ -116.1; HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{15}\text{H}_{14}\text{FO}^+$ 229.1023, Found 229.1021.

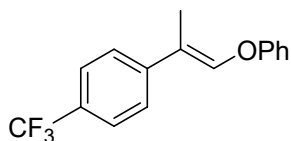


(E)-1-chloro-4-(1-phenoxyprop-1-en-2-yl)benzene [(E)-(2h)]. Prepared according to the general procedure using 0.1223 g (0.50 mmol) of **1h**, 0.0161 g (0.03 mmol) of **PNP**, 0.0032 g (0.025 mmol) of CoCl_2 , 75 μL (0.075 mmol) of NaBHET_3 , 1 mL (0.5 M) of PhCl . Then the mixture was stirred at rt for 1 h (> 99% conv., 6/1 *E/Z*, monitored by ^1H NMR), purified by flash column chromatography using PE as the eluent to give 0.0974 g (0.40 mmol, 82% yield, >20/1 *E/Z*) of **(E)-2h** as a colorless oil. ^1H NMR (CDCl_3 , 500 MHz): δ 7.26-7.36 (m, 6H), 7.01-7.10 (m, 3H), 6.83 (s, 1H), 2.11 (s, 3H); ^{13}C NMR: (125.8 MHz, CDCl_3) δ 157.5, 139.4, 138.3, 132.3, 129.6, 128.5, 126.6, 122.8, 119.3, 116.4, 12.9; HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{15}\text{H}_{14}\text{ClO}^+$ 245.0728, Found 245.0728.

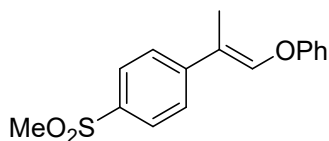


(E)-1-bromo-4-(1-phenoxyprop-1-en-2-yl)benzene [(E)-(2i)]. Prepared according to the general procedure using 0.1449 g (0.50 mmol) of **1i**, 0.0162 g (0.03 mmol) of **PNP**, 0.0033 g (0.025 mmol) of CoCl_2 , 75 μL (0.075 mmol) of NaBHET_3 , 1 mL (0.5 M) of PhCl . Then the mixture was stirred at rt for 1 h (> 99% conv., 6/1 *E/Z*, monitored by ^1H NMR), purified by flash column chromatography using PE as the eluent to give 0.1115 g (0.38 mmol, 81% yield, >20/1 *E/Z*) of **(E)-2i** as a colorless oil. ^1H NMR (CDCl_3 , 500 MHz): δ 7.44 (d, $J = 8.5$ Hz, 2H), 7.30-7.36 (m, 2H), 7.25 (d, $J = 8.5$ Hz, 2H), 7.02-7.11 (m, 3H), 6.84 (s, 1H), 2.12 (s, 3H); ^{13}C NMR: (125.8 MHz, CDCl_3) δ 157.5,

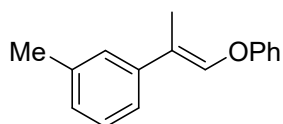
139.4, 138.8, 131.5, 129.7, 127.0, 122.9, 120.4, 119.4, 116.4, 12.9; HRMS (ESI) m/z : $[M + Na]^+$ Calcd for $C_{15}H_{13}BrNaO^+$ 311.0042, Found 311.0048.



(E)-1-(1-phenoxyprop-1-en-2-yl)-4-(trifluoromethyl)benzene [(E)-(2j)]. Prepared according to the general procedure using 0.1333 g (0.50 mmol) of **1j**, 0.0161 g (0.03 mmol) of **PNP**, 0.0032 g (0.025 mmol) of $CoCl_2$, 75 μL (0.075 mmol) of $NaBH_4Et_3$, 1 mL (0.5 M) of $PhCl$. Then the mixture was stirred at rt for 1 h ($> 99\%$ conv., 8/1 *E/Z*, monitored by 1H NMR), purified by flash column chromatography using PE as the eluent to give 0.1138 g (0.41 mmol, 85% yield, $>20/1$ *E/Z*) of **(E)-2j** as a colorless oil. 1H NMR: (500 MHz, $CDCl_3$) δ 7.57 (d, $J = 8.0$ Hz, 2H), 7.48 (d, $J = 8.0$ Hz, 2H), 7.31-7.37 (m, 2H), 7.03-7.12 (m, 3H), 6.94 (s, 1H), 2.16 (s, 3H); ^{13}C NMR (125.8 MHz,) δ 157.4, 143.6, 140.7, 129.7, 128.6 (q, $J = 32.5$ Hz), 127.9, 125.5, 125.4 (q, $J = 3.5$ Hz), 123.1, 119.0, 116.6, 12.8; ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.3; HRMS (ESI) m/z : $[M + H]^+$ Calcd for $C_{16}H_{14}F_3O^+$ 279.0991, Found 279.1001.

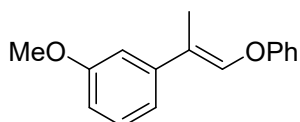


(E)-1-(methylsulfonyl)-4-(1-phenoxyprop-1-en-2-yl)benzene [(E)-(2k)]. Prepared according to the general procedure using 0.0860 g (0.30 mmol) of **1k**, 0.0194 g (0.036 mmol) of **PNP**, 0.0040 g (0.03 mmol) of $CoCl_2$, 90 μL (0.090 mmol) of $NaBH_4Et_3$, 1 mL (0.5 M) of $PhCl$. Then the mixture was stirred at rt for 1 h ($> 99\%$ conv., 14/1 *E/Z*, monitored by 1H NMR), purified by flash column chromatography using PE as the eluent to give 0.0767 g (0.27 mmol, 89% yield, $>20/1$ *E/Z*) of **(E)-2k** as a white solid. M. P. 88.4-90.0 $^{\circ}C$. 1H NMR: (400 MHz, $CDCl_3$) δ 7.89 (d, $J = 8.4$ Hz, 2H), 7.56 (d, $J = 8.4$ Hz, 2H), 7.33-7.40 (m, 2H), 7.04-7.15 (m, 3H), 7.10 (s, 1H), 3.05 (s, 3H), 2.18 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.2, 145.6, 141.8, 138.1, 129.7, 127.6, 125.8, 123.4, 118.2, 116.6, 44.6, 12.7; HRMS (ESI) m/z : $[M + H]^+$ Calcd for $C_{16}H_{17}O_3S^+$ 289.0893, Found 289.0893.

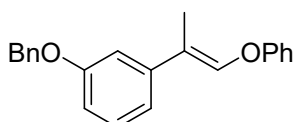


(E)-1-methyl-3-(1-phenoxyprop-1-en-2-yl)benzene [(E)-(2l)]. Prepared according to the general procedure using 0.1105 g (0.49 mmol) of **1l**, 0.0162 g (0.03 mmol) of **PNP**, 0.0035 g (0.027 mmol) of $CoCl_2$, 75 μL (0.075 mmol)

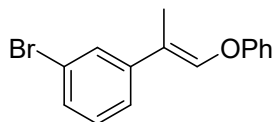
of NaBHET₃, 1 mL (0.5 M) of PhCl. Then the mixture was stirred at rt for 1 h (> 99% conv., 14/1 *E/Z*, monitored by ¹H NMR), purified by flash column chromatography using PE as the eluent to give 0.1013 g (0.45 mmol, 92% yield, >20/1 *E/Z*) of (**E**)-**2l** as a colorless oil. ¹H NMR: (400 MHz, CDCl₃) δ 7.28-7.37 (m, 2H), 7.17-7.26 (m, 3H), 7.02-7.11 (m, 4H), 6.83 (s, 1H), 2.36 (s, 3H), 2.13 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 157.6, 139.8, 138.8, 138.0, 129.6, 128.4, 127.5, 126.3, 122.6, 120.7, 116.3, 21.5, 13.1; HRMS (ESI) m/z: [M + Na]⁺ Calcd for C₁₆H₁₆NaO⁺ 247.1093, Found 247.1097.



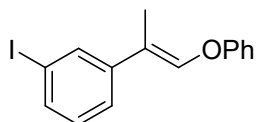
(**E**)-1-methoxy-3-(1-phenoxyprop-1-en-2-yl)benzene [(**E**)-(**2m**)]. Prepared according to the general procedure using 0.1210 g (0.50 mmol) of **1m**, 0.0161 g (0.03 mmol) of **PNP**, 0.0030 g (0.024 mmol) of CoCl₂, 75 μL (0.075 mmol) of NaBHET₃, 1 mL (0.5 M) of PhCl. Then the mixture was stirred at rt for 1 h (> 99% conv., 14/1 *E/Z*, monitored by ¹H NMR), purified by flash column chromatography using PE as the eluent to give 0.0946 g (0.39 mmol, 86% yield, >20/1 *E/Z*) of (**E**)-**2m** as a colorless oil. ¹H NMR (CDCl₃, 500 MHz): δ 7.18-7.25 (m, 2H), 7.11-7.18 (m, 1H), 6.95 (m, 3H), 6.89 (d, J = 7.5 Hz, 1H), 6.84 (s, 1H), 6.77 (s, 1H), 6.70 (d, J = 8.5 Hz, 1H), 3.71 (s, 3H), 2.04 (s, 3H); ¹³C NMR: (125.8 MHz, CDCl₃) δ 159.8, 157.6, 141.4, 139.2, 129.6, 129.4, 122.7, 120.4, 118.1, 116.4, 111.9, 111.6, 55.2, 13.1; HRMS (ESI) m/z: [M + H]⁺ Calcd for C₁₆H₁₇O₂⁺ 241.1223, Found 241.1228.



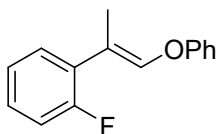
(**E**)-1-(benzyloxy)-3-(1-phenoxyprop-1-en-2-yl)benzene [(**E**)-(**2n**)]. Prepared according to the general procedure using 0.1446 g (0.46 mmol) of **1n**, 0.0160 g (0.03 mmol) of **PNP**, 0.0034 g (0.026 mmol) of CoCl₂, 75 μL (0.075 mmol) of NaBHET₃, 1 mL (0.5 M) of PhCl. Then the mixture was stirred at rt for 1 h (> 99% conv., 13/1 *E/Z*, monitored by ¹H NMR), purified by flash column chromatography using PE as the eluent to give 0.1356 g (0.43 mmol, 93% yield, >20/1 *E/Z*) of (**E**)-**2n** as a yellow oil. ¹H NMR: (400 MHz, CDCl₃) δ 7.44 (d, J = 7.2 Hz, 2H), 7.35-7.41 (m, 2H), 7.28-7.35 (m, 3H), 7.20-7.26 (m, 1H), 6.99-7.07 (m, 5H), 6.87 (d, J = 7.2 Hz, 2H), 5.07 (s, 2H), 2.12 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 158.9, 157.5, 141.3, 139.2, 137.0, 129.6, 129.4, 128.5, 127.9, 127.5, 122.7, 120.2, 118.2, 116.3, 112.6, 112.5, 70.0, 13.0; HRMS (ESI) m/z: [M + H]⁺ Calcd for C₂₂H₂₁O₂⁺ 317.1536, Found 317.1537.



(E)-1-bromo-3-(1-phenoxyprop-1-en-2-yl)benzene [(E)-(2o)]. Prepared according to the general procedure using 0.1434 g (0.50 mmol) of **1q**, 0.0161 g (0.03 mmol) of **PNP**, 0.0032 g (0.025 mmol) of CoCl_2 , 75 μL (0.075 mmol) of NaBHET_3 , 1 mL (0.5 M) of PhCl . Then the mixture was stirred at rt for 1 h (> 99% conv., 11/1 *E/Z*, monitored by ^1H NMR, >20/1 *E/Z*), purified by flash column chromatography using PE as the eluent to give 0.1062 g (0.37 mmol, 83% yield) of **(E)-2o** as a colorless oil. ^1H NMR (CDCl_3 , 500 MHz): δ 7.52 (s, 1H), 7.27-7.38 (m, 4H), 7.14-7.20 (m, 1H), 7.01-7.10 (m, 3H), 6.85 (s, 1H), 2.11 (s, 3H); ^{13}C NMR: (125.8 MHz, CDCl_3) δ 157.4, 142.1, 140.0, 129.9, 129.7, 129.5, 128.5, 124.0, 123.0, 122.7, 119.0, 116.5, 12.9; HRMS (ESI) *m/z*: $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{15}\text{H}_{13}\text{BrNaO}^+$ 311.0042, Found 311.0048.

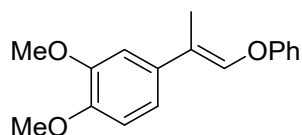


(E)-1-iodo-3-(1-phenoxyprop-1-en-2-yl)benzene [(E)-(2p)]. Prepared according to the general procedure using 0.1022 g (0.30 mmol) of **1r**, 0.0098 g (0.018 mmol) of **PNP**, 0.0020 g (0.015 mmol) of CoCl_2 , 45 μL (0.045 mmol) of NaBHET_3 , 1 mL (0.5 M) of PhCl . Then the mixture was stirred at rt for 1 h (> 99% conv., 10/1 *E/Z*, monitored by ^1H NMR), purified by flash column chromatography using PE as the eluent to give 0.0903 g (0.27 mmol, 88% yield, >20/1 *E/Z*) of **(E)-2p** as a yellow oil. ^1H NMR: (400 MHz, CDCl_3) δ 7.72 (s, 1H), 7.57 (d, $J = 8.0$ Hz, 1H), 7.30-7.37 (m, 3H), 7.04-7.11 (m, 4H), 6.83 (s, 1H), 2.10 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 157.4, 142.2, 139.9, 135.5, 134.4, 130.1, 129.7, 124.6, 122.9, 118.9, 116.5, 94.7, 12.9; HRMS (ESI) *m/z*: $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{15}\text{H}_{13}\text{NaIO}^+$ 358.9903, Found 358.9910.

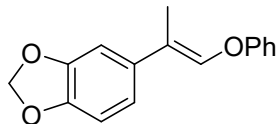


(E)-1-fluoro-2-(1-phenoxyprop-1-en-2-yl)benzene [(E)-(2q)]. Prepared according to the general procedure using 0.1163 g (0.49 mmol) of **1u**, 0.0164 g (0.031 mmol) of **PNP**, 0.0034 g (0.026 mmol) of CoCl_2 , 75 μL (0.075 mmol) of NaBHET_3 , 1 mL (0.5 M) of PhCl . Then the mixture was stirred at rt for 1 h (> 99% conv., 11/1 *E/Z*, monitored by ^1H NMR), purified by flash column chromatography using PE as the eluent to give 0.0411 g (0.18 mmol, 57% yield, >20/1 *E/Z*) of **(E)-2q** as a colorless oil. ^1H NMR (CDCl_3 , 500 MHz): δ 7.29-7.36 (m, 3H), 7.18-7.24 (m, 1H), 7.03-

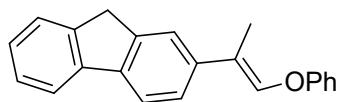
7.14 (m, 5H), 6.83 (s, 1H), 2.13 (s, 3H); ^{13}C NMR (125.8 MHz,) δ 160.4 (d, $J = 247.5$ Hz), 157.5, 141.5 (d, $J = 6.5$ Hz), 129.6, 129.4 (d, $J = 4.5$ Hz), 128.0 (d, $J = 8.5$ Hz), 127.8 (d, $J = 13.5$ Hz), 124.1 (d, $J = 3.5$ Hz), 122.7, 116.4, 115.9 (d, $J = 23.5$ Hz), 115.7, 13.8; ^{19}F NMR (376 MHz, CDCl_3) δ -114.5; HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{15}\text{H}_{14}\text{FO}^+$ 229.1023, Found 229.1021.



(E)-1,2-dimethoxy-4-(1-phenoxyprop-1-en-2-yl)benzene [(E)-(2r)]. Prepared according to the general procedure using 0.1319 g (0.5 mmol) of **1v**, 0.0164 g (0.031 mmol) of **PNP**, 0.0034 g (0.026 mmol) of CoCl_2 , 75 μL (0.075 mmol) of NaBHET_3 , 1 mL (0.5 M) of PhCl . Then the mixture was stirred at rt for 1 h ($> 99\%$ conv., 10/1 *E/Z*, monitored by ^1H NMR), purified by flash column chromatography using PE as the eluent to give 0.1152 g (0.43 mmol, 87% yield, 10/1 *E/Z*) of **(E)-2r** as a colorless oil. ^1H NMR: (500 MHz, CDCl_3) δ 7.29-7.34 (m, 2H), 7.02-7.08 (m, 3H), 6.90-6.96 (m, 2H), 6.84 (d, $J = 8.0$ Hz, 1H), 6.77 (s, 1H), 3.89 (s, 3H), 3.87 (s, 3H), 2.12 (s, 3H); ^{13}C NMR: (125.8 MHz, CDCl_3) δ 157.6, 148.9, 148.2, 138.1, 132.8, 129.6, 122.5, 120.5, 117.9, 116.3, 111.4, 109.2, 55.91, 55.86, 13.3; HRMS (ESI) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{17}\text{H}_{18}\text{NaO}_3^+$ 293.1148, Found 293.1155.

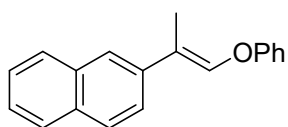


(E)-5-(1-phenoxyprop-1-en-2-yl)benzo[d][1,3]dioxole [(E)-(2s)]. Prepared according to the general procedure using 0.0756 g (0.30 mmol) of **1w**, 0.0098 g (0.018 mmol) of **PNP**, 0.0020 g (0.015 mmol) of CoCl_2 , 45 μL (0.045 mmol) of NaBHET_3 , 1 mL (0.5 M) of PhCl . Then the mixture was stirred at rt for 1 h ($> 99\%$ conv., 11/1 *E/Z*, monitored by ^1H NMR), purified by flash column chromatography using PE as the eluent to give 0.0597 g (0.24 mmol, 80% yield, $>20/1$ *E/Z*) of **(E)-2s** as a yellow oil. ^1H NMR: (400 MHz, CDCl_3) δ 7.19-7.27 (m, 2H), 6.93-7.00 (m, 3H), 6.74-6.82 (m, 2H), 6.65-6.72 (m, 2H), 5.95 (s, 2H), 2.09 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 157.6, 147.8, 146.5, 138.2, 134.1, 129.6, 122.6, 120.5, 118.9, 116.3, 108.2, 106.1, 101.0, 29.7, 13.4; HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{16}\text{H}_{15}\text{O}_3^+$ 255.1016, Found 255.1016.

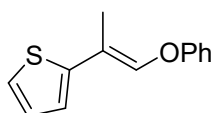


(E)-2-(1-phenoxyprop-1-en-2-yl)-9H-fluorene [(E)-(2t)]. Prepared according to the general procedure using 0.0891 g (0.30 mmol) of **1x**, 0.0098 g (0.018 mmol) of **PNP**, 0.0020 g (0.015 mmol) of CoCl_2 , 45 μL (0.045 mmol)

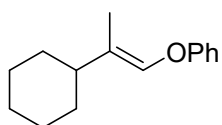
of NaBH₄Et₃, 1 mL (0.5 M) of PhCl. Then the mixture was stirred at rt for 1 h (> 99% conv., 10/1 *E/Z*, monitored by ¹H NMR), purified by flash column chromatography using PE as the eluent to give 0.0853 g (0.28 mmol, 87% yield, >20/1 *E/Z*) of (**E**)-**2t** as a yellow oil. M. P. 109.1-109.5 °C. ¹H NMR: (400 MHz, CDCl₃) δ 7.72-7.79 (m, 2H), 7.59 (s, 1H), 7.54 (d, J = 7.6 Hz, 1H), 7.43 (d, J = 8.4 Hz, 1H), 7.29-7.39 (m, 4H), 7.09 (d, J = 8.4 Hz, 3H), 6.93 (s, 1H), 3.91 (s, 2H), 2.20 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 157.6, 143.5, 143.2, 141.5, 140.4, 138.8, 138.4, 129.6, 126.7, 126.5, 125.0, 124.2, 122.6, 122.0, 120.8, 119.7, 116.6, 116.3, 36.9, 13.2; HRMS (ESI) m/z: [M + H]⁺ Calcd for C₂₂H₁₉O⁺ 299.1430, Found 244.1426.



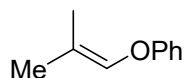
(**E**)-**2-(1-phenoxyprop-1-en-2-yl)naphthalene [(E)-(2u)]**. Prepared according to the general procedure using 0.1292 g (0.50 mmol) of **1y**, 0.0161 g (0.03 mmol) of PNP, 0.0032 g (0.025 mmol) of CoCl₂, 75 μL (0.075 mmol) of NaBH₄Et₃, 1 mL (0.5 M) of PhCl. Then the mixture was stirred at 60 °C for 12 h (> 99% conv., 5/1 *E/Z*, monitored by ¹H NMR), purified by flash column chromatography using PE as the eluent to give 0.0759 g (0.30 mmol, 60% yield, >20/1 *E/Z*) of (**E**)-**2u** as a white solid. M. P. 66.8-66.9 °C. ¹H NMR: (500 MHz, CDCl₃) δ 7.74-7.84 (m, 4H), 7.55 (d, J = 8.5 Hz, 1H), 7.39-7.48 (m, 2H), 7.29-7.37 (m, 2H), 7.04-7.11 (m, 3H), 7.01 (s, 1H), 2.25 (s, 3H); ¹³C NMR: (125.8 MHz, CDCl₃) δ 157.7, 139.7, 137.1, 133.7, 132.4, 129.7, 127.91, 127.90, 127.5, 126.2, 125.5, 123.9, 122.8, 120.3, 116.5, 13.0; HRMS (ESI) m/z: [M + H]⁺ Calcd for C₁₉H₁₇O⁺ 261.1274, Found 261.1284.



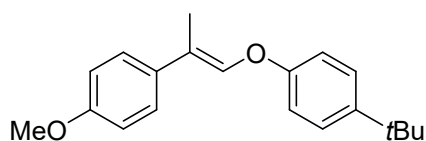
(**E**)-**2-(1-phenoxyprop-1-en-2-yl)thiophene [(E)-(2v)]**. Prepared according to the general procedure using 0.1081 g (0.50 mmol) of **1z**, 0.0164 g (0.031 mmol) of PNP, 0.0034 g (0.026 mmol) of CoCl₂, 75 μL (0.075 mmol) of NaBH₄Et₃, 1 mL (0.5 M) of PhCl. Then the mixture was stirred at 60 °C for 12 h (> 99% conv., 6/1 *E/Z*, monitored by ¹H NMR), purified by flash column chromatography using PE as the eluent to give 0.0696 g (0.32 mmol, 64% yield, >20/1 *E/Z*) of (**E**)-**2v** as a yellow oil. ¹H NMR: (500 MHz, CDCl₃) δ 7.30-7.37 (m, 2H), 7.03-7.11 (m, 4H), 6.99 (s, 3H), 2.15 (s, 3H); ¹³C NMR: (125.8 MHz, CDCl₃) δ 157.4, 143.4, 138.3, 129.7, 127.2, 122.9, 122.3, 122.3, 116.5, 115.6, 13.5; HRMS (ESI) m/z: [M + H]⁺ Calcd for C₁₃H₁₃OS⁺ 217.0682, Found 217.0678.



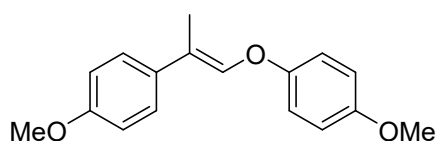
((2-cyclohexylprop-1-en-1-yl)oxy)benzene (2w). Prepared according to the general procedure using 0.1081 g (0.50 mmol) of **1aa**, 0.0161 g (0.030 mmol) of **PNP**, 0.0032 g (0.025 mmol) of CoCl_2 , 75 μL (0.075 mmol) of NaBHET_3 , 1 mL (0.5 M) of PhCl . Then the mixture was stirred at rt for 1 h (70% conv., 3/1 *E/Z*, monitored by ^1H NMR), purified by flash column chromatography using PE as the eluent to give 0.0487 g (0.23 mmol, 48% yield, 3/1 *E/Z*) of **2w** as a yellow oil. ^1H NMR (400 MHz, CDCl_3) δ 7.23-7.31 (m, 2H), 6.93-7.02 (m, 3H), 6.26 (s, 1H), 1.93 (s, 1H), 1.82-1.70 (m, 4H), 1.68 (s, 3H), 1.50-1.61 (m, 1H), 1.29 (dd, $J = 17.2, 8.8$ Hz, 4H), 1.13-1.21 (m, 1H); ^{13}C NMR (101 MHz, CDCl_3) δ 157.8, 134.9, 129.4, 126.9, 121.8, 115.8, 42.4, 31.9, 26.6, 26.3, 11.2; HRMS (ESI) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{15}\text{H}_{20}\text{NaO}^+$ 239.1406, Found 239.1406.



((2-methylprop-1-en-1-yl)oxy)benzene (2x).⁷ Prepared according to the general procedure using 0.0741 g (0.50 mmol) of **1ab**, 0.0164 g (0.031 mmol) of **PNP**, 0.0034 g (0.026 mmol) of CoCl_2 , 75 μL (0.075 mmol) of NaBHET_3 , 1 mL (0.5 M) of PhCl . Then the mixture was stirred at rt for 1 h (30 % conv., monitored by ^1H NMR), purified by flash column chromatography using PE as the eluent to give 0.0138 g (0.09 mmol, 19% yield) of **2x** as a colorless oil. ^1H NMR (500 MHz, CDCl_3) δ 7.26-7.32 (m, 2H), 7.03 - 6.93 (m, 3H), 6.20 (s, 1H), 1.71 (d, $J = 15.5$ Hz, 6H).

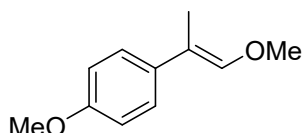


1-(tert-butyl)-4-((2-(4-methoxyphenyl)prop-1-en-1-yl)oxy)benzene (2y). Prepared according to the general procedure using 0.1423 g (0.48 mmol) of **1ac**, 0.0161 g (0.030 mmol) of **PNP**, 0.0032 g (0.025 mmol) of CoCl_2 , 75 μL (0.075 mmol) of NaBHET_3 , 1 mL (0.5 M) of PhCl . Then the mixture was stirred at rt for 1 h (> 99% conv., 10/1 *E/Z*, monitored by ^1H NMR), purified by flash column chromatography using PE as the eluent to give 0.1342 g (0.45 mmol, 88% yield, 10/1 *E/Z*) of **2y** as a yellow solid. M. P. 97.2-98.3 $^\circ\text{C}$. ^1H NMR: (400 MHz, CDCl_3) δ 7.29-7.37 (m, 4H), 6.98 (d, $J = 8.0$ Hz, 2H), 6.88 (d, $J = 8.0$ Hz, 2H), 6.76 (s, 1H), 3.81 (s, 3H), 2.10 (s, 3H), 1.31 (s, 9H); ^{13}C NMR (101 MHz, CDCl_3) δ 158.5, 155.4, 145.3, 138.2, 132.4, 128.8, 126.5, 126.4, 119.9, 115.8, 113.9, 55.3, 34.2, 31.5, 13.1; HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{20}\text{H}_{25}\text{O}_2^+$ 297.1849, Found 297.1848.

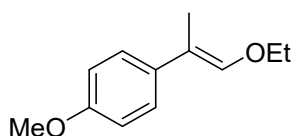


1-methoxy-4-(1-(4-methoxyphenoxy)prop-1-en-2-yl)benzene (2z). Prepared according to the general procedure using 0.1305 g (0.5 mmol) of **1ad**, 0.0161 g (0.030 mmol) of **PNP**, 0.0032 g (0.025 mmol) of CoCl_2 , 75 μL (0.075

mmol) of NaBHET₃, 1 mL (0.5 M) of PhCl. Then the mixture was stirred at rt for 1 h (> 99% conv., 10/1 *E/Z*, monitored by ¹H NMR), purified by flash column chromatography using PE as the eluent to give 0.1183 g (0.44 mmol, 88% yield, 10/1 *E/Z*) of **2z** as a yellow solid. M. P. 85.9-86.1 °C. ¹H NMR: (400 MHz, CDCl₃) δ 7.31 (d, J = 9.0 Hz, 2H), 6.98 (d, J = 9.0 Hz, 2H), 6.84-6.90 (m, 4H), 6.69 (s, 1H), 3.80 (d, J = 11.2 Hz, 6H), 2.10 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 158.4, 155.1, 151.7, 138.8, 132.3, 126.4, 119.2, 117.3, 114.6, 113.8, 55.6, 55.3, 13.1; HRMS (ESI) m/z: [M + Na]⁺ Calcd for C₁₇H₁₈NaO₃⁺ 293.1148, Found 293.1155.



1-methoxy-4-(1-methoxyprop-1-en-2-yl)benzene (2aa). Prepared according to the general procedure using 0.0888 g (0.50 mmol) of **1ae**, 0.0161 g (0.030 mmol) of **PNP**, 0.0032 g (0.025 mmol) of CoCl₂, 75 μL (0.075 mmol) of NaBHET₃, 1 mL (0.5 M) of PhCl. Then the mixture was stirred at rt for 1 h (> 99% conv., 9/1 *E/Z*, monitored by ¹H NMR), purified by flash column chromatography using PE as the eluent to give 0.0764 g (0.43 mmol, 86% yield, 9/1 *E/Z*) of **2aa** as a colorless oil. ¹H NMR: (500 MHz, CDCl₃) δ 7.22 (d, J = 8.0 Hz, 2H), 6.83 (d, J = 8.0 Hz, 2H), 6.31 (s, 1H), 3.78 (s, 3H), 3.68 (s, 3H), 1.96 (s, 3H); ¹³C NMR: (125.8 MHz, CDCl₃) δ 158.1, 144.0, 133.2, 128.6, 126.1, 113.7, 59.7, 55.2, 12.7; HRMS (ESI) m/z: [M + Na]⁺ Calcd for C₁₁H₁₄NaO₂⁺ 201.0886, Found 201.0896.

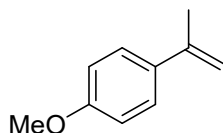


1-(1-ethoxyprop-1-en-2-yl)-4-methoxybenzene (2ab). Prepared according to the general procedure using 0.0228 g (0.12 mmol) of **1af**, 0.0039 g (0.0072 mmol) of **PNP**, 0.0008 g (0.006 mmol) of CoCl₂, 18 μL (0.018 mmol) of NaBHET₃, 0.5 mL (0.5 M) of PhCl. Then the mixture was stirred at rt for 1 h (> 99% conv., 9/1 *E/Z*, monitored by ¹H NMR), purified by flash column chromatography using PE as the eluent to give 0.0194 g (0.010 mmol, 85% yield, 9/1 *E/Z*) of **2ab** as a colorless oil. ¹H NMR: (500 MHz, CDCl₃) δ 7.14 (d, J = 8.5 Hz, 2H), 6.75 (d, J = 8.5 Hz, 2H), 6.30 (s, 1H), 3.76-3.84 (m, 2H), 3.70 (s, 3H), 1.89 (s, 3H), 1.22 (t, J = 2.0 Hz, 3H); ¹³C NMR: (125.8 MHz, CDCl₃) δ 157.9, 142.6, 133.4, 128.5, 126.0, 113.8, 67.8, 55.2, 15.4, 12.8; HRMS (ESI) m/z: [M + Na]⁺ Calcd for C₁₂H₁₆NaO₂⁺ 215.1043, Found 215.1044.

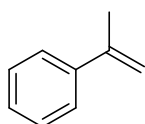
IV. Cobalt-catalyzed reductive C-O bond cleavage of allyl ethers

General procedure for cobalt-catalyzed reductive C-O bond cleavage of allyl ethers: To a 10 mL flame-dried Schlenk flask cooled under argon, added with PAO^{Me} (0.03mmol), CoCl₂ (0.025 mmol), THF (1 mL), alkene **1** (0.5

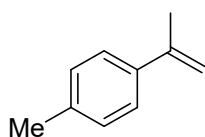
mmol), NaBHET₃ (75 μL, 0.075 mmol, 1 M in THF) and HBpin (90 μL, 0.6 mmol) in sequence. Then the reaction mixture was stirred at rt for 1 h, purified by flash column chromatography using PE/EtOAc as the eluent to give the desired product **3**.



1-methoxy-4-(prop-1-en-2-yl)benzene (3a).¹⁰ Prepared according to the general procedure using 0.1204 g (0.5 mmol) of **1a**, 0.0131 g (0.030 mmol) of PAOMe, 0.0034 g (0.025 mmol) of CoCl₂, 75 μL (0.075 mmol) of NaBHET₃, 90 μL of HBpin (0.6 mmol), 1 mL (0.5 M) of THF. After 1 h, the crude reaction mixture was purified by flash column chromatography using PE as the eluent to give 0.0646 g (0.44 mmol, 87% yield) of **3a** as a colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.41 (d, J = 8.8 Hz, 2H), 6.86 (d, J = 8.8 Hz, 2H), 5.28 (s, 1H), 4.99 (s, 1H), 3.81 (s, 3H), 2.12 (s, 3H).



prop-1-en-2-ylbenzene (3b).¹¹ Prepared according to the general procedure using 0.1051 g (0.5 mmol) of **1b**, 0.0134 g (0.030 mmol) of PAOMe, 0.0034 g (0.025 mmol) of CoCl₂, 75 μL (0.075 mmol) of NaBHET₃, 90 μL of HBpin (0.6 mmol), 1 mL (0.5 M) of THF. After 1 h, the crude reaction mixture was purified by flash column chromatography using PE as the eluent to give 0.0557 g (0.47 mmol, 87% yield) of **3b** as a colorless oil. ¹H NMR: (400 MHz, CDCl₃) δ 7.46 (d, J = 7.2 Hz, 2H), 7.28-7.35 (m, 2H), 7.22-7.28 (m, 1H), 5.35 (s, 1H), 5.07 (s, 1H), 2.14 (s, 3H).

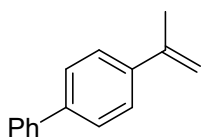


1-methyl-4-(prop-1-en-2-yl)benzene (3c).¹¹ Prepared according to the general procedure using 0.1109 g (0.50 mmol) of **1c**, 0.0140 g (0.032 mmol) of PAOMe, 0.0032 g (0.025 mmol) of CoCl₂, 75 μL (0.075 mmol) of NaBHET₃, 90 μL of HBpin (0.6 mmol), 1 mL (0.5 M) of THF. After 1 h, the crude reaction mixture was purified by flash column chromatography using PE as the eluent to give 0.0521 g (0.39 mmol, 72% yield) of **3c** as a colorless oil.

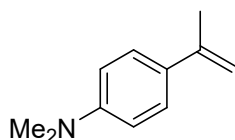
¹⁰ C. Casadevall, D. Pascual, J. Aragon, A. Call, A. Casitas, I. Casademont-Reig, J. Lloret-Fillol, *Chem. Sci.* **2022**, *13*, 4270.

¹¹ X. Wang, Z. Wang, Y. Asanuma, Y. Nishihara, *Org. Lett.* **2019**, *21*, 3640.

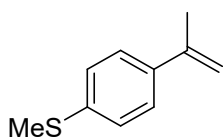
¹H NMR: (400 MHz, CDCl₃) δ 7.19-7.30 (m, 3H), 7.08 (d, J = 7.6 Hz, 1H), 5.34 (s, 1H), 5.05 (s, 1H), 2.35 (s, 3H), 2.14 (s, 3H).



4-(prop-1-en-2-yl)-1,1'-biphenyl (3d).¹¹ Prepared according to the general procedure using 0.1405 g (0.49 mmol) of **1d**, 0.0140 g (0.032 mmol) of **PAO^{Me}**, 0.0033 g (0.025 mmol) of CoCl₂, 75 μL (0.075 mmol) of NaBHET₃, 90 μL of HBpin (0.6 mmol), 1 mL (0.5 M) of THF. After 1 h, the crude reaction mixture was purified by flash column chromatography using PE as the eluent to give 0.0807 g (0.42 mmol, 84% yield) of **3d** as a white solid. ¹H NMR: (400 MHz, CDCl₃) δ 7.50-7.60 (m, 6H), 7.48-7.45 (m, 2H), 7.26-7.35 (m, 1H), 5.42 (s, 1H), 5.10 (s, 1H), 2.17 (s, 3H).

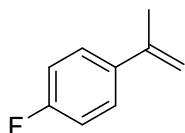


N,N-dimethyl-4-(prop-1-en-2-yl)aniline (3e).¹³ Prepared according to the general procedure using 0.0776 g (0.31 mmol) of **1e**, 0.0086 g (0.019 mmol) of **PAO^{Me}**, 0.0025 g (0.019 mmol) of CoCl₂, 45 μL (0.045 mmol) of NaBHET₃, 50 μL of HBpin (0.36 mmol), 1 mL (0.5 M) of THF. After 1 h, the crude reaction mixture was purified by flash column chromatography using PE as the eluent to give 0.0394 g (0.24 mmol, 82% yield) of **3e** as a colorless oil. ¹H NMR: (400 MHz, CDCl₃) δ 7.39 (d, J = 8.8 Hz, 2H), 6.70 (d, J = 8.8 Hz, 2H), 5.25 (s, 1H), 4.90 (s, 1H), 2.95 (s, 6H), 1.22 (s, 3H).

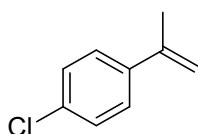


methyl(4-(prop-1-en-2-yl)phenyl)sulfane (3f).¹² Prepared according to the general procedure using 0.0757 g (0.30 mmol) of **1f**, 0.0081 g (0.018 mmol) of **PAO^{Me}**, 0.0023 g (0.017 mmol) of CoCl₂, 45 μL (0.045 mmol) of NaBHET₃, 50 μL of HBpin (0.36 mmol), 1 mL (0.5 M) of THF. After 1 h, the crude reaction mixture was purified by flash column chromatography using PE as the eluent to give 0.0415 g (0.25 mmol, 84% yield) of **3f** as a white solid. ¹H NMR: (400 MHz, CDCl₃) δ 7.40 (d, J = 8.4 Hz, 2H), 7.22 (d, J = 8.4 Hz, 2H), 5.35 (s, 1H), 5.05 (s, 1H), 2.48 (s, 3H), 2.13 (s, 3H).

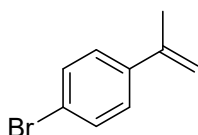
¹² U. Chakraborty, E. Reyes-Rodriguez, S. Demeshko, F. Meyer, A. Wangelin, *Angew. Chem. Int. Ed.* **2018**, *57*, 4970.



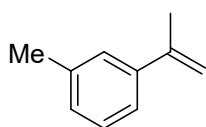
1-fluoro-4-(prop-1-en-2-yl)benzene (3g).¹¹ Prepared according to the general procedure using 0.1150 g (0.50 mmol) of **1g**, 0.0137 g (0.031 mmol) of **PAO^{Me}**, 0.0036 g (0.027 mmol) of CoCl_2 , 75 μL (0.075 mmol) of NaBHET_3 , 90 μL of HBpin (0.6 mmol), 1 mL (0.5 M) of THF. After 1 h, the crude reaction mixture was purified by flash column chromatography using PE as the eluent to give 0.0608 g (0.45 mmol, 89% yield) of **3g** as a colorless oil. ^1H NMR: (400 MHz, CDCl_3) δ 7.39-7.47 (m, 2H), 6.95-7.05 (m, 2H), 5.29 (s, 1H), 5.05 (s, 1H), 2.13 (s, 3H).



1-chloro-4-(prop-1-en-2-yl)benzene (3h).¹¹ Prepared according to the general procedure using 0.1245 g (0.51 mmol) of **1h**, 0.0132 g (0.030 mmol) of **PAO^{Me}**, 0.0036 g (0.027 mmol) of CoCl_2 , 75 μL (0.075 mmol) of NaBHET_3 , 90 μL of HBpin (0.6 mmol), 1 mL (0.5 M) of THF. After 1 h, the crude reaction mixture was purified by flash column chromatography using PE as the eluent to give 0.0720 g (0.47 mmol, 94% yield) of **3h** as a colorless oil. ^1H NMR: (400 MHz, CDCl_3) δ 7.38 (d, $J = 8.4$ Hz, 2H), 7.28 (d, $J = 8.0$ Hz, 2H), 5.34 (s, 1H), 5.08 (s, 1H), 2.11 (s, 3H).

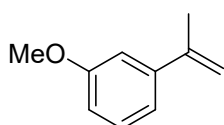


1-bromo-4-(prop-1-en-2-yl)benzene (3i).¹¹ Prepared according to the general procedure using 0.1475 g (0.51 mmol) of **1i**, 0.0133 g (0.030 mmol) of **PAO^{Me}**, 0.0034 g (0.026 mmol) of CoCl_2 , 75 μL (0.075 mmol) of NaBHET_3 , 90 μL of HBpin (0.6 mmol), 1 mL (0.5 M) of THF. After 1 h, the crude reaction mixture was purified by flash column chromatography using PE as the eluent to give 0.0916 g (0.46 mmol, 92% yield) of **3i** as a colorless oil. ^1H NMR: (400 MHz, CDCl_3) δ 7.43 (d, $J = 8.4$ Hz, 2H), 7.31 (d, $J = 8.4$ Hz, 2H), 5.34 (s, 1H), 5.09 (s, 1H), 2.11 (s, 3H).

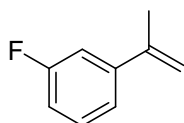


1-methyl-3-(prop-1-en-2-yl)benzene (3j).¹³ Prepared according to the general procedure using 0.0672 g (0.30

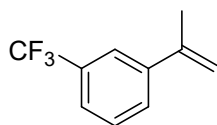
mmol) of **11**, 0.0083 g (0.018 mmol) of **PAO^{Me}**, 0.0025 g (0.018 mmol) of CoCl_2 , 45 μL (0.045 mmol) of NaBHET_3 , 50 μL of HBpin (0.36 mmol), 1 mL (0.3 M) of THF. After 1 h, the crude reaction mixture was purified by flash column chromatography using PE as the eluent to give 0.0311 g (0.24 mmol, 85% yield) of **3j** as a colorless oil. ^1H NMR: (400 MHz, CDCl_3) δ 7.18-7.30 (m, 3H), 7.08 (d, $J = 7.2$ Hz, 1H), 5.34 (s, 1H), 5.06 (s, 1H), 2.35 (s, 3H), 2.14 (s, 3H).



1-methoxy-3-(prop-1-en-2-yl)benzene (3k).¹⁵ Prepared according to the general procedure using 0.1208 g (0.50 mmol) of **1m**, 0.0136 g (0.032 mmol) of **PAO^{Me}**, 0.0035 g (0.027 mmol) of CoCl_2 , 75 μL (0.075 mmol) of NaBHET_3 , 90 μL of HBpin (0.6 mmol), 1 mL (0.5 M) of THF. After 1 h, the crude reaction mixture was purified by flash column chromatography using PE as the eluent to give 0.0640 g (0.43 mmol, 86% yield) of **3k** as a colorless oil. ^1H NMR: (400 MHz, CDCl_3) δ 7.20-7.24 (m, 1H), 7.06 (d, $J = 8.0$ Hz, 1H), 6.99 (s, 1H), 6.81 (dd, $J = 8.4, 8.0$ Hz, 1H), 5.35 (s, 1H), 5.07 (s, 1H), 3.80 (s, 3H), 2.13 (s, 3H).



1-fluoro-3-(prop-1-en-2-yl)benzene (3l).¹⁶ Prepared according to the general procedure using 0.1158 g (0.51 mmol) of **1o**, 0.0137 g (0.031 mmol) of **PAO^{Me}**, 0.0033 g (0.025 mmol) of CoCl_2 , 75 μL (0.075 mmol) of NaBHET_3 , 90 μL of HBpin (0.6 mmol), 1 mL (0.5 M) of THF. After 1 h, the crude reaction mixture was purified by flash column chromatography using PE as the eluent to give 0.0613 g (0.45 mmol, 89% yield) of **3l** as a colorless oil. ^1H NMR: (400 MHz, CDCl_3) δ 7.20-7.30 (m, 2H), 7.14 (d, $J = 10.8$ Hz, 1H), 6.90-7.00 (m, 1H), 5.37 (s, 1H), 5.11 (s, 1H), 2.12 (s, 3H).

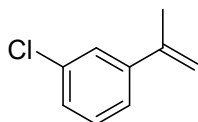


1-(prop-1-en-2-yl)-3-(trifluoromethyl)benzene (3m).¹⁴ Prepared according to the general procedure using 0.1378 g (0.49 mmol) of **1s**, 0.0131 g (0.030 mmol) of **PAO^{Me}**, 0.0035 g (0.027 mmol) of CoCl_2 , 75 μL (0.075 mmol) of

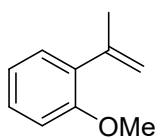
¹³ J. Li, R. He, J. Liu, Y. Liu, L. Chen, Y. Huang, Y. Li, *Org. Lett.* **2022**, *24*, 1620.

¹⁴ D. Phan, K. Kou, V. Dong, *J. Am. Chem. Soc.* **2010**, *132*, 16354.

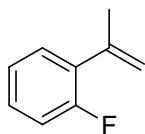
NaBHET₃, 90 μL of HBpin (0.6 mmol), 1 mL (0.5 M) of THF. After 1 h, the crude reaction mixture was purified by flash column chromatography using PE as the eluent to give 0.0764 g (0.41 mmol, 82% yield) of **3m** as a colorless oil. ¹H NMR: (400 MHz, CDCl₃) δ 7.69 (s, 1H), 7.63 (d, J = 8.0 Hz, 1H), 7.51 (d, J = 8.0 Hz, 1H), 7.39-7.45 (m, 1H), 5.41 (s, 1H), 5.17 (s, 1H), 2.12 (s, 3H);



1-chloro-3-(prop-1-en-2-yl)benzene (3n).¹⁵ Prepared according to the general procedure using 0.1227 g (0.50 mmol) of **1p**, 0.0138 g (0.032 mmol) of PAOMe, 0.0037 g (0.028 mmol) of CoCl₂, 75 μL (0.075 mmol) of NaBHET₃, 90 μL of HBpin (0.6 mmol), 1 mL (0.5 M) of THF. After 1 h, the crude reaction mixture was purified by flash column chromatography using PE as the eluent to give 0.0684 g (0.45 mmol, 88% yield) of **3n** as a colorless oil. ¹H NMR: (400 MHz, CDCl₃) δ 7.42 (s, 1H), 7.29-7.35 (m, 1H), 7.20-7.25 (m, 2H), 5.36 (s, 1H), 5.11 (s, 1H), 2.11 (s, 3H).



1-methoxy-2-(prop-1-en-2-yl)benzene (3o).¹⁶ Prepared according to the general procedure using 0.1208 g (0.50 mmol) of **1t**, 0.0140g (0.032 mmol) of PAOMe, 0.0032g (0.025 mmol) of CoCl₂, 75 μL (0.075 mmol) of NaBHET₃, 90 μL of HBpin (0.6 mmol), 1 mL (0.5 M) of THF. After 1 h, the crude reaction mixture was purified by flash column chromatography using PE as the eluent to give 0.0523 g (0.35 mmol, 72% yield) of **3o** as a colorless oil. ¹H NMR: (400 MHz, CDCl₃) δ 7.15-7.28 (m, 2H), 6.85-6.95 (m, 2H), 5.14 (s, 1H), 5.05 (s, 1H), 3.81 (s, 3H), 2.11 (s, 3H).

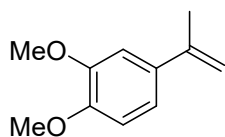


1-fluoro-2-(prop-1-en-2-yl)benzene (3p).¹⁶ Prepared according to the general procedure using 0.1156 g (0.51 mmol) of **1u**, 0.0137 g (0.031 mmol) of PAOMe, 0.0043 g (0.033 mmol) of CoCl₂, 75 μL (0.075 mmol) of NaBHET₃, 90 μL of HBpin (0.6 mmol), 1 mL (0.5 M) of THF. After 1 h, the crude reaction mixture was purified by flash

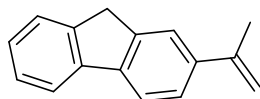
¹⁵ P. Cooper, A. Dalling, E. Farrar, T. Aldhous, S. Grelaud, E. Lester, L. Feron, P. Kemmitt, M. Grayson, J. Bower, *Chem. Sci.* **2022**, *13*, 11183.

¹⁶ M. Han, H. Pan, P. Li, L. Wang, *J. Org. Chem.* **2020**, *85*, 5825.

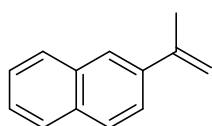
column chromatography using PE as the eluent to give 0.0574 g (0.41 mmol, 82% yield) of **3p** as a colorless oil. ¹H NMR: (400 MHz, CDCl₃) δ 7.39-7.45 (m, 2H), 6.95-7.05 (m, 2H), 5.29 (s, 1H), 5.05 (s, 1H), 2.13 (s, 3H).



1,2-dimethoxy-4-(prop-1-en-2-yl)benzene (3q).¹⁷ Prepared according to the general procedure using 0.0947 g (0.30 mmol) of **1v**, 0.0081 g (0.018 mmol) of **PAOMe**, 0.0020 g (0.018 mmol) of CoCl₂, 45 μL (0.045 mmol) of NaBHET₃, 50 μL of HBpin (0.36 mmol), 1 mL (0.3 M) of THF. After 1 h, the crude reaction mixture was purified by flash column chromatography using PE as the eluent to give 0.0580 g (0.26 mmol, 87% yield) of **3o** as a colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.05 - 6.99 (m, 2H), 6.83 (d, J = 8.8 Hz, 1H), 5.29 (s, 1H), 5.02 (s, 1H), 3.91 (s, 3H), 3.89 (s, 3H), 2.14 (s, 3H).



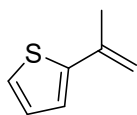
2-(prop-1-en-2-yl)-9H-fluorene (3r).¹⁸ Prepared according to the general procedure using 0.0877 g (0.29 mmol) of **1x**, 0.0083 g (0.018 mmol) of **PAOMe**, 0.0020 g (0.015 mmol) of CoCl₂, 45 μL (0.045 mmol) of NaBHET₃, 50 μL of HBpin (0.36 mmol), 1 mL (0.5 M) of THF. After 1 h, the crude reaction mixture was purified by flash column chromatography using PE as the eluent to give 0.0540 g (0.26 mmol, 87% yield) of **3r** as a white solid. ¹H NMR: (400 MHz, CDCl₃) δ 7.71-7.80 (m, 2H), 7.65 (s, 1H), 7.48-7.56 (m, 2H), 7.36 (d, J = 7.6 Hz, 1H), 7.30 (d, J = 7.6 Hz, 1H), 5.43 (s, 1H), 5.10 (s, 1H), 2.21 (s, 2H), (s, 3H).



2-(prop-1-en-2-yl)naphthalene (3s).¹¹ Prepared according to the general procedure using 0.1300 g (0.50 mmol) of **1y**, 0.0132 g (0.030 mmol) of **PAOMe**, 0.0037 g (0.028 mmol) of CoCl₂, 75 μL (0.075 mmol) of NaBHET₃, 90 μL of HBpin (0.6 mmol), 1 mL (0.5 M) of THF. After 1 h, the crude reaction mixture was purified by flash column chromatography using PE as the eluent to give 0.0699 g (0.42 mmol, 85% yield) of **3s** as a white solid. ¹H NMR: (400 MHz, CDCl₃) δ 7.74-7.86 (m, 4H), 7.61-7.68 (m, 1H), 7.39-7.46 (m, 2H), 5.51 (s, 1H), 5.17 (s, 1H), 2.25 (s, 3H).

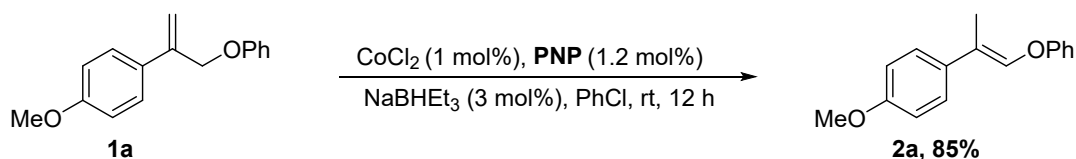
¹⁷ J. Wu, L. Gong, Y. Xia, R. Song, Y. Xie, J. Li, *Angew. Chem. Int. Ed.* **2012**, *51*, 9909.

¹⁸ L. Gao, X. Liu, G. Li, S. Chen, J. Cao, G. Wang, S. Li, *Org. Lett.* **2022**, *24*, 31, 5698.

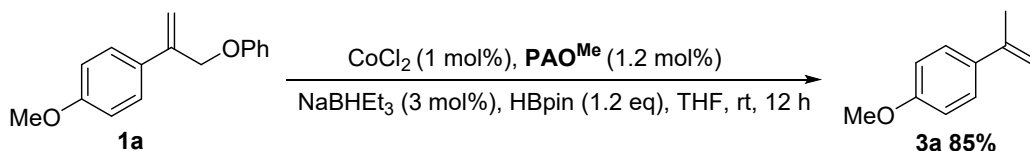


2-(prop-1-en-2-yl)thiophene (3t).¹¹ Prepared according to the general procedure using 0.1121 g (0.51 mmol) of **1z**, 0.0133 g (0.03 mmol) of **PAOMe**, 0.0040 g (0.03 mmol) of CoCl_2 , 75 μL (0.075 mmol) of NaBHET_3 , 90 μL of **HBpin** (0.6 mmol), 1 mL (0.5 M) of **THF**. After 1 h, the crude reaction mixture was purified by flash column chromatography using **PE** as the eluent to give 0.0434 g (0.35 mmol, 87% yield) of **3t** as a colorless oil. $^1\text{H NMR}$: (400 MHz, CDCl_3) δ 7.15 (s, 1H), 7.01 (s, 1H), 6.96 (s, 1H), 5.37 (s, 1H), 4.94 (s, 1H), 2.14 (s, 3H);

V. Gram-scale reactions.

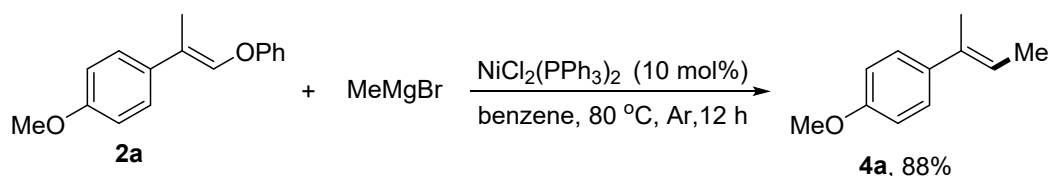


Performed according to the general procedure using 1.2026 g (5 mmol) of **1a**, 0.0323 g (0.06 mmol) of **PNP**, 0.0064 g (0.05 mmol) of CoCl_2 , 150 μL (0.15 mmol) of NaBHET_3 and 10 mL (1.0 M) of **PhCl**. The reaction mixture was stirred at rt for 12 h ($> 99\%$ conv., 10/1 *E/Z*, monitored by $^1\text{H NMR}$), passed through a pad of silica gel and washed with **EA**, concentrated under reduced pressure. Then the residue was purified by flash column chromatography using **PE/EtOAc** as the eluent to give 1.0222 g (4.3 mmol, 85% yield, $>20/1$ *E/Z*) of **2a** as a white solid.

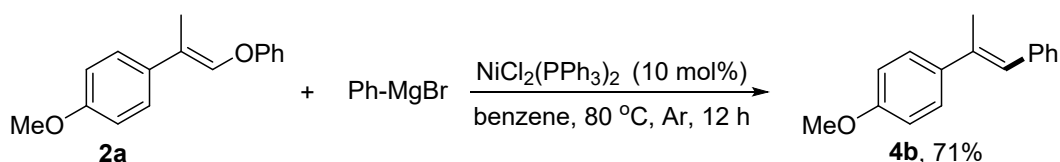


Performed according to the general procedure using 1.9233 g (8 mmol) of **1a**, 0.0419 g (0.096 mmol) of **PAOMe**, 0.0108 g (0.08 mmol) of CoCl_2 , 240 μL (0.24 mmol) of NaBHET_3 , 1.2290 g (9.6 mmol) of **HBpin** and 10 mL (1.0 M) of **THF**. The reaction mixture was stirred at rt for 12 h, passed through a pad of silica gel and washed with **PE**, concentrated under reduced pressure. Then the residue was purified by flash column chromatography using **PE** as the eluent to give 1.0200 g (6.9 mmol, 85% yield) of **3a** as a white solid.

VI. Further derivatizations.



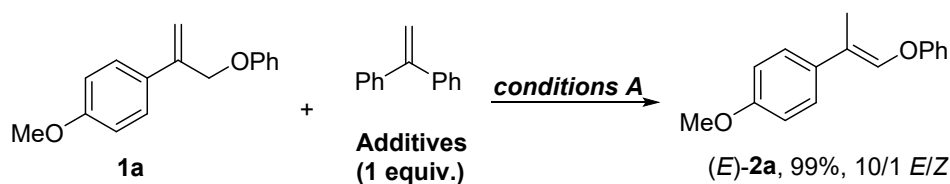
(E)-1-(but-2-en-2-yl)-4-methoxybenzene (4a):² Performed according to a previously reported procedure:¹⁹ To a 10 mL flame-dried Schlenk flask cooled under argon, 0.0597 g (0.25 mmol) of **2a**, 0.5 mL (0.5 mmol, 1 mmol/mL in THF) of MeMgBr, 0.0186 g (0.025 mmol) of NiCl₂(PPh₃)₂ and 1 mL (0.25 M) of benzene were added in sequence. Then the mixture was stirred at 80 °C for 12 h, cooled to room temperature, passed through a pad of silica gel, washed with EA, concentrated under reduced pressure. The residue was purified by flash column chromatography using PE/EtOAc as the eluent to give 0.0357 g (0.22mmol, 88% yield, >20/1 *E/Z*) of **4a** as a white solid. ¹H NMR (500 MHz, CDCl₃) δ 7.30 (d, J = 8.5 Hz, 2H), 6.84 (d, J = 8.5 Hz, 2H), 5.74-5.80 (m, 1H), 3.80 (s, 3H), 2.00 (s, 3H), 1.78 (d, J = 6.5 Hz, 3H).



(E)-1-methoxy-4-(1-phenylprop-1-en-2-yl)benzene (4b):²⁰ Performed according to a previously reported procedure:¹⁹ To a 10 mL flame-dried Schlenk flask cooled under argon, 0.0599 g (0.25 mmol) of **2a**, 0.5 mL (0.5 mmol, 1 mmol/mL in THF) of PhMgBr, 0.0328 g (0.05 mmol) of NiCl₂(PPh₃)₂ and 1 mL (0.25 M) of benzene were added in sequence. Then the mixture was stirred at 80 °C for 12 h, cooled to room temperature, passed through a pad of silica gel, washed with EA, concentrated under reduced pressure. The residue was purified by flash column chromatography using PE/EtOAc as the eluent to give 0.0400 g (0.18mmol, 71% yield, 17/1 *E/Z*) of **4b** as a white solid. ¹H NMR (500 MHz, CDCl₃) δ 7.47 (d, J = 9.0 Hz, 2H), 7.33-7.38 (m, 4H), 6.91 (d, J = 9.0 Hz, 2H), 6.78 (s, 1H), 3.84 (s, 3H), 2.26 (s, 3H).

VII. Preliminary mechanistic studies

(a) Radical Trap Experiments:

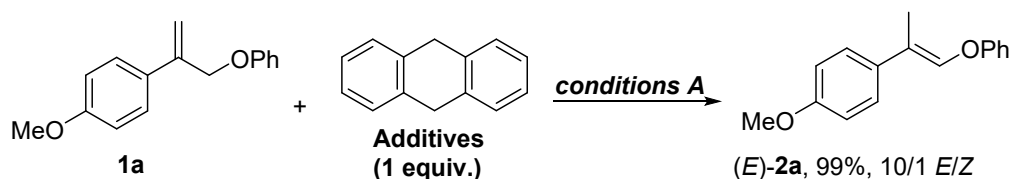


To a 10 mL flame-dried Schlenk flask cooled under argon, 0.0034 g (0.026 mmol) of CoCl₂, 0.0164 g (0.031 mmol) of PNP, 1 mL of PhCl, 0.1195 g (0.5 mmol) of **1a** and 0.0898 g (0.5 mmol) of ethene-1,1-diylidibenzene were added in sequence. The mixture was stirred at room temperature for 5 minutes, then NaBHET₃ (75 μL, 0.075 mmol)

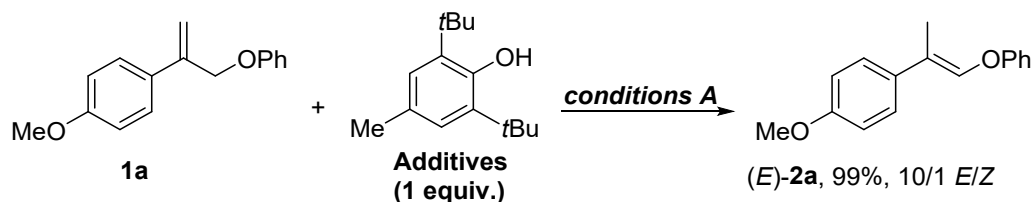
¹⁹ Y. Nassar, F. Rodier, V. Ferey, J. Cossy, *ACS Catal.* **2021**, *11*, 5736.

²⁰ X. Hu, J. He, Z. Ying, J. Zhou, J. Yu, *Chin. J. Chem.* **2021**, *39*, 2227.

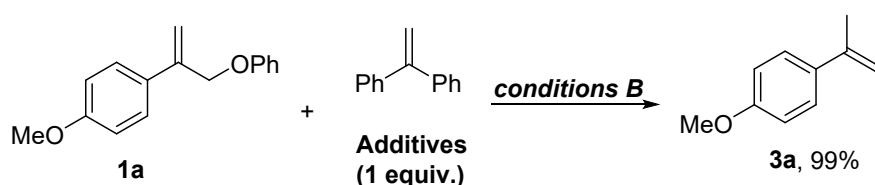
was added by dropwise. After stirring at room temperature for 1 h, the reaction was monitored by ^1H NMR (99% conv., 10/1 *E/Z*).



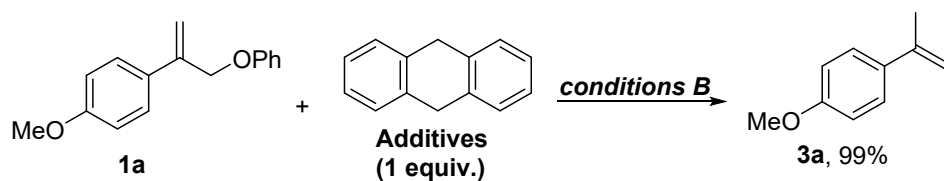
To a 10 mL flame-dried Schlenk flask cooled under argon, 0.0033 g (0.025 mmol) of CoCl_2 , 0.0168 g (0.031 mmol) of PNP, 1 mL of PhCl , 0.1202 g (0.5 mmol) of **1a** and 0.0896 g (0.5 mmol) of 9,10-dihydroanthracene were added in sequence. The mixture was stirred at room temperature for 5 minutes, then NaBHET_3 (75 μL , 0.075 mmol) was added by dropwise. After stirring at room temperature for 1 h, the reaction was monitored by ^1H NMR (99% conv., 10/1 *E/Z*).



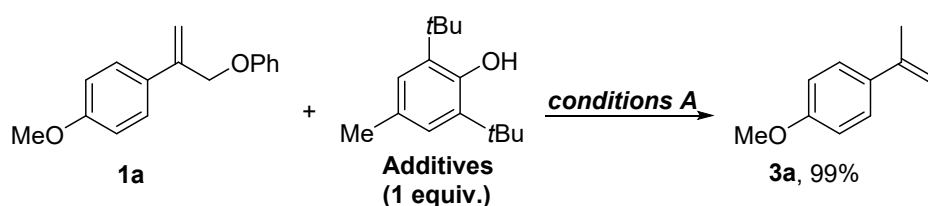
To a 10 mL flame-dried Schlenk flask cooled under argon, 0.0032 g (0.025 mmol) of CoCl_2 , 0.0164 g (0.031 mmol) of PNP, 1 mL of PhCl , 0.1205 g (0.5 mmol) of **1a** and 0.1082 g (0.49 mmol) of di-*tert*-butylhydroxytoluene were added in sequence. The mixture was stirred at room temperature for 5 minutes, then NaBHET_3 (75 μL , 0.075 mmol) was added by dropwise. After stirring at room temperature for 1 h, the reaction was monitored by ^1H NMR (99% conv., 10/1 *E/Z*).



To a 10 mL flame-dried Schlenk flask cooled under argon, 0.0036 g (0.027 mmol) of CoCl_2 , 0.0134 g (0.031 mmol) of PAO^{Me} , 1 mL of THF, 0.1203 g (0.5 mmol) of **1a** and 0.0894 g (0.50 mmol) of ethene-1,1-diyldibenzene were added in sequence. The mixture was stirred at room temperature for 5 minutes, then NaBHET_3 (75 μL , 0.075 mmol) and HBpin (90 μL , 0.60 mmol) was added by dropwise. After stirring at room temperature for 1 h, the reaction was monitored by ^1H NMR (99% conv.).

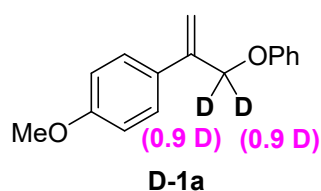


To a 10 mL flame-dried Schlenk flask cooled under argon, 0.0035 g (0.027 mmol) of CoCl_2 , 0.0134 g (0.031 mmol) of PAO^{Me} , 1 mL of THF, 0.1208 g (0.5 mmol) of **1a** and 0.0894 g (0.50 mmol) of 9,10-dihydroanthracene were added in sequence. The mixture was stirred at room temperature for 5 minutes, then NaBHET_3 (75 μL , 0.075 mmol) and HBpin (90 μL , 0.60 mmol) was added by dropwise. After stirring at room temperature for 1 h, the reaction was monitored by ^1H NMR (99% conv.).



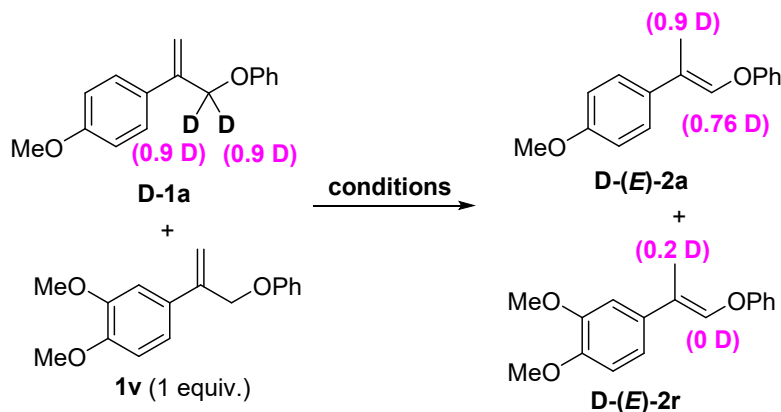
To a 10 mL flame-dried Schlenk flask cooled under argon, 0.0032 g (0.025 mmol) of CoCl_2 , 0.0141 g (0.032 mmol) of PAO^{Me} , 1 mL of THF, 0.1205 g (0.5 mmol) of **1a** and 0.1095 g (0.50 mmol) of di-tert-butylhydroxytoluene were added in sequence. The mixture was stirred at room temperature for 5 minutes, then NaBHET_3 (75 μL , 0.075 mmol) and HBpin (90 μL , 0.60 mmol) was added by dropwise. After stirring at room temperature for 1 h, the reaction was monitored by ^1H NMR (99% conv.).

(b) H/D scrambling experiments:

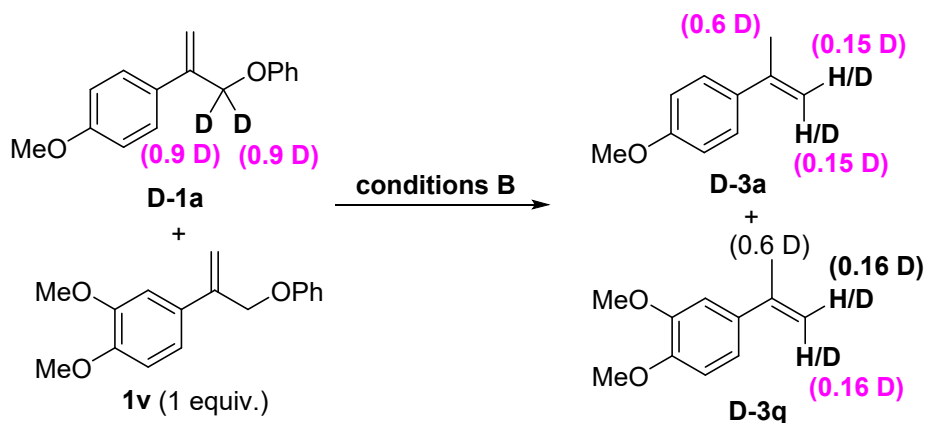


1-methoxy-4-(3-phenoxyprop-1-en-2-yl-3,3-d₂)benzene (D-1a). Prepared according to the general procedure²¹ of Wittig reaction using Ph_3PMeBr and 1-(4-methoxyphenyl)-2-phenoxyethan-1-one-2,2-d₂ (prepared according to a previously reported method, 100% D) as the starting materials, white solid. ^1H NMR (400 MHz, CDCl_3) δ 7.43 (d, $J = 8.8$ Hz, 2H), 7.27-7.31 (m, 2H), 6.94-6.99 (m, 3H), 6.89 (d, $J = 8.8$ Hz, 2H), 5.53 (s, 1H), 5.37 (s, 1H), 4.85 (s, 0.2H), 3.82 (s, 3H). ^2H NMR (61 MHz, CDCl_3): δ 4.85 (s, 1.8D).

²¹ J. Zhao, B. Cheng, C. Chen, Z. Lu, *Org. Lett.* **2020**, *22*, 837.



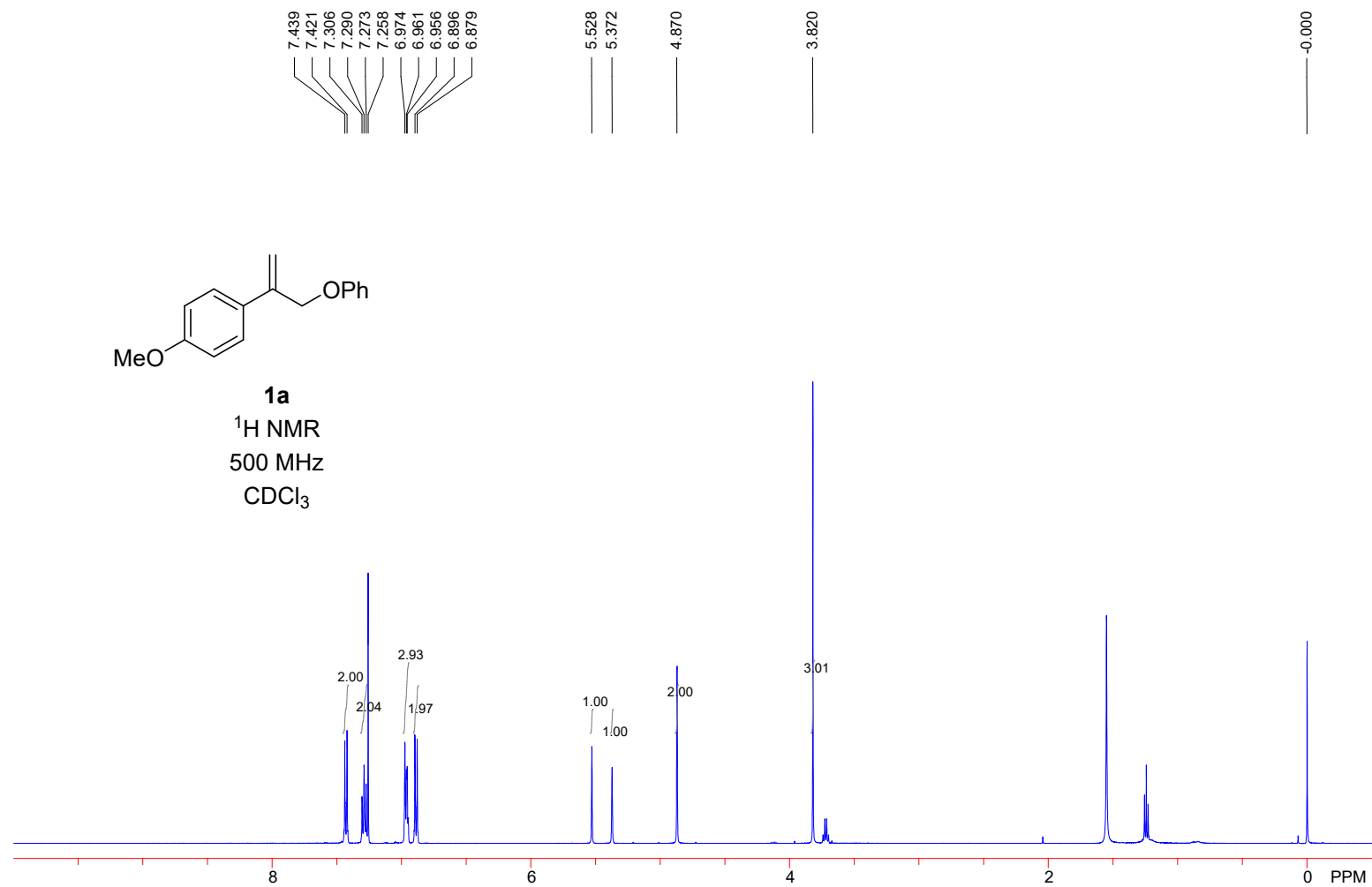
Performed according to the general procedure using 0.0603 g (0.25 mmol) of **D-1a**, 0.0681 g (0.25 mmol) of **1v**, 0.0043 g (0.030 mmol) of CoCl_2 , 0.0179 g (0.033 mmol) of **PNP**, 75 μL (1 M in THF, 0.075 mmol) of NaBHET_3 and 1 mL of PhCl. After 1 h, the crude reaction mixture was purified by flash column chromatography using PE as the eluent to give **D-(E)-2a** (0.0550 g, 0.23 mmol, 91%) and **D-(E)-2v** (0.0621 mg, 0.23 mmol, 91%), respectively. For **D-(E)-2a**: $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.30-7.35 (m, 4H), 7.04 (d, $J = 8.4$ Hz, 3H), 6.88 (d, $J = 8.4$ Hz, 2H), 6.76 (s, 0.24H), 3.81 (s, 3H), 2.11 (s, 2.1H). $^2\text{H NMR}$ (400 MHz, CHCl_3): δ 4.85 (s, 1.8D). $^2\text{H NMR}$ (61 MHz, CDCl_3) δ 6.77 (s, 0.76D), 2.09 (d, $J = 2.4$ Hz, 0.9D). For **D-(E)-2v**: $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.30-7.35 (m, 2H), 7.05 (d, $J = 8.4$ Hz, 3H), 6.95 (d, $J = 8.4$ Hz, 1H), 6.91 (s, 1H), 6.85 (d, $J = 8.3$ Hz, 1H), 6.77 (s, 1H), 3.90 (s, 3H), 3.88 (s, 3H), 2.13 (s, 3H). $^2\text{H NMR}$ (61 MHz, CDCl_3) δ 2.12 (s, 0.20D).

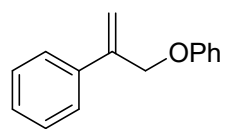


Prepared according to the general procedure using 0.0600 g (0.25 mmol) of **D-1a**, 0.0698 g (0.26 mmol) of **1v**, 0.0039 g (0.030 mmol) of CoCl_2 , 0.0139 g (0.032 mmol) of **PAOMe**, 75 μL (1 M in THF, 0.075 mmol) of NaBHET_3 and 1 mL of THF. After 1 h, the crude reaction mixture was purified by flash column chromatography using PE as the eluent to give **D-3a** (0.0277 g, 0.19 mmol, 75%) and **D-3q** (0.0387 mg, 0.22 mmol, 87%), respectively. For **D-3a**: $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.41 (d, $J = 8.8$ Hz, 2H), 6.86 (d, $J = 8.8$ Hz, 2H), 5.29 (s, 0.85H), 4.99 (s, 0.85H), 3.81 (s, 3H), 2.13 (s, 2.40H). $^2\text{H NMR}$ (61 MHz, CDCl_3) δ 5.29 (s, 0.15D), 4.99 (s, 0.15D), 2.08 (d, $J = 2.0$ Hz,

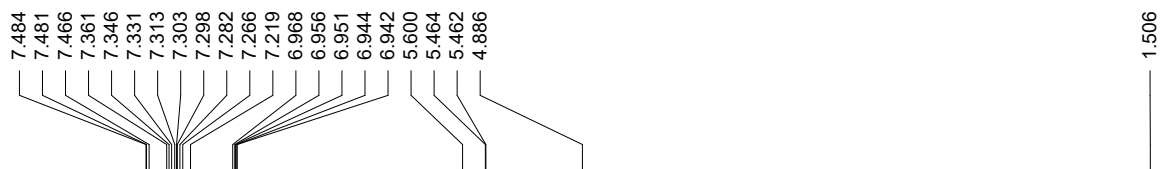
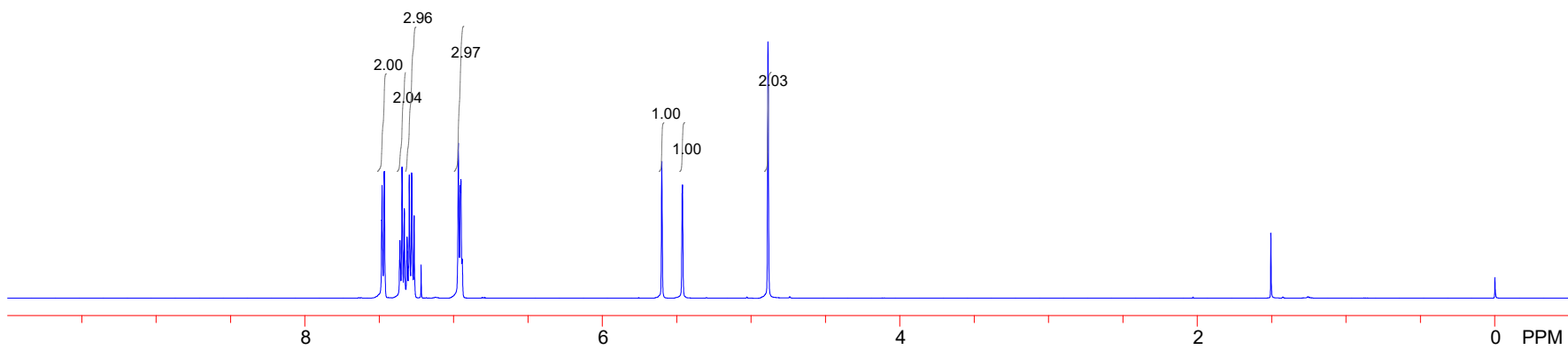
0.6D). For D-**3q**: ^1H NMR (400 MHz, CDCl_3) δ 7.04 - 7.00 (m, 2H), 6.83 (d, $J = 8.8$ Hz, 1H), 5.29 (s, 0.84H), 5.01 (s, 0.84H), 3.91 (s, 3H), 3.89 (s, 3H), 2.14 (s, 2.40H). ^2H NMR (61 MHz, CDCl_3) δ 5.32 (s, 0.16D), 5.04 (s, 0.16D), 2.12 (s, 0.6D).

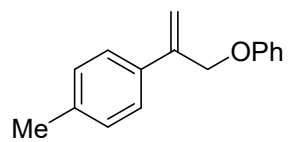
VIII. NMR Spectra





1b
¹H NMR
500 MHz
CDCl₃





1c

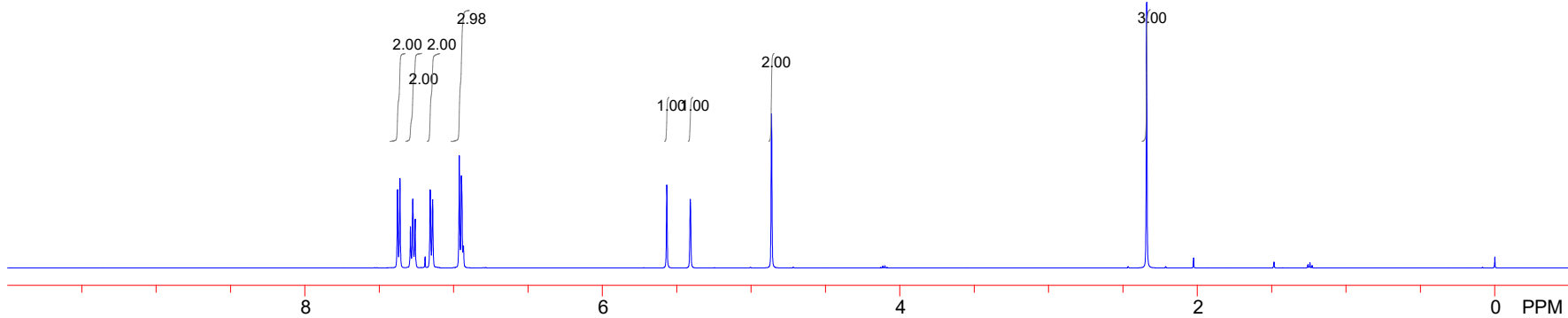
¹H NMR
500 MHz
CDCl₃

7.377
7.361
7.290
7.275
7.258
7.157
7.141
6.962
6.948

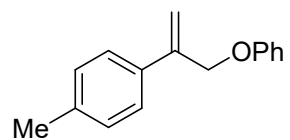
5.567
5.409

4.863

2.341



S36



1c

¹³C NMR
500 MHz
CDCl₃

158.680

142.855

137.770

135.474

129.399

129.139

125.868

120.949

114.962

113.864

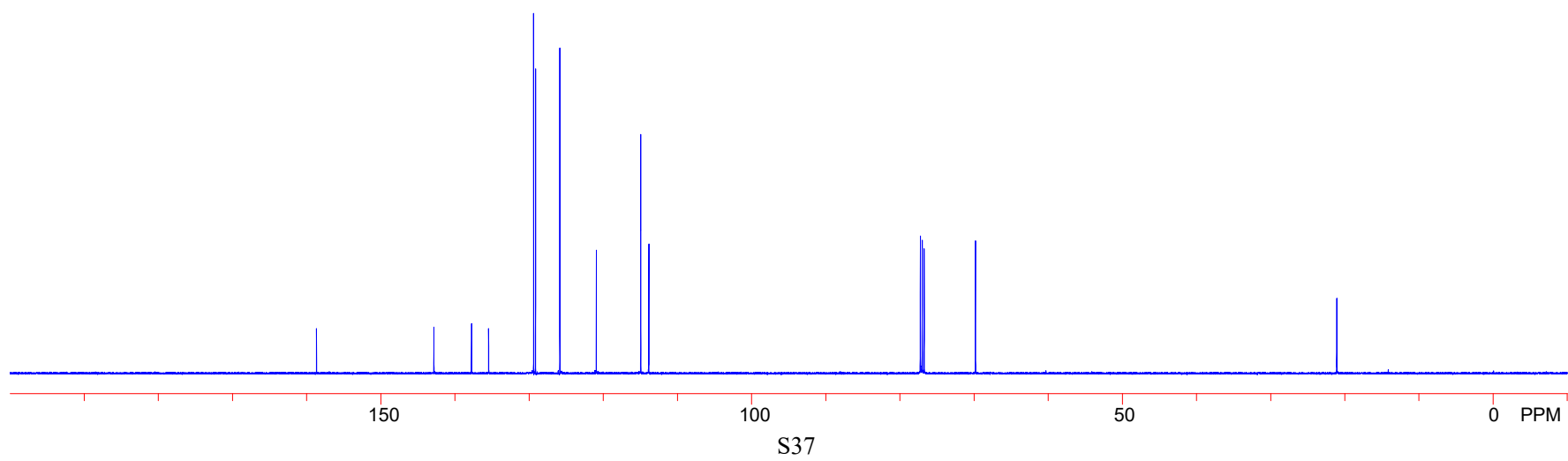
77.253

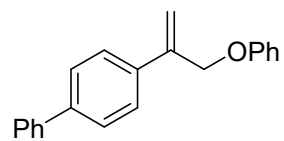
77.000

76.740

69.828

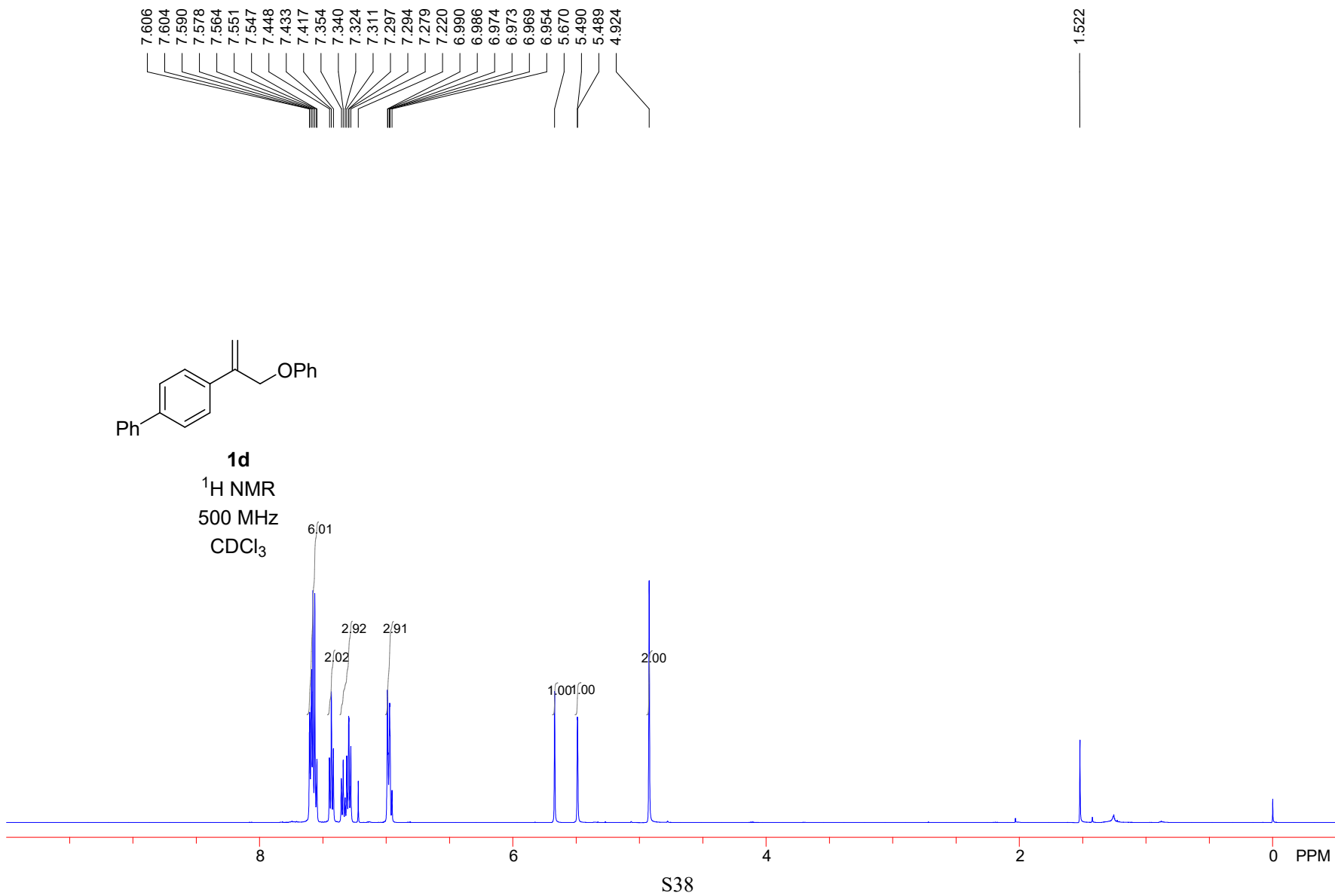
21.098

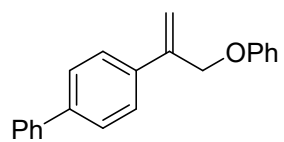




1d

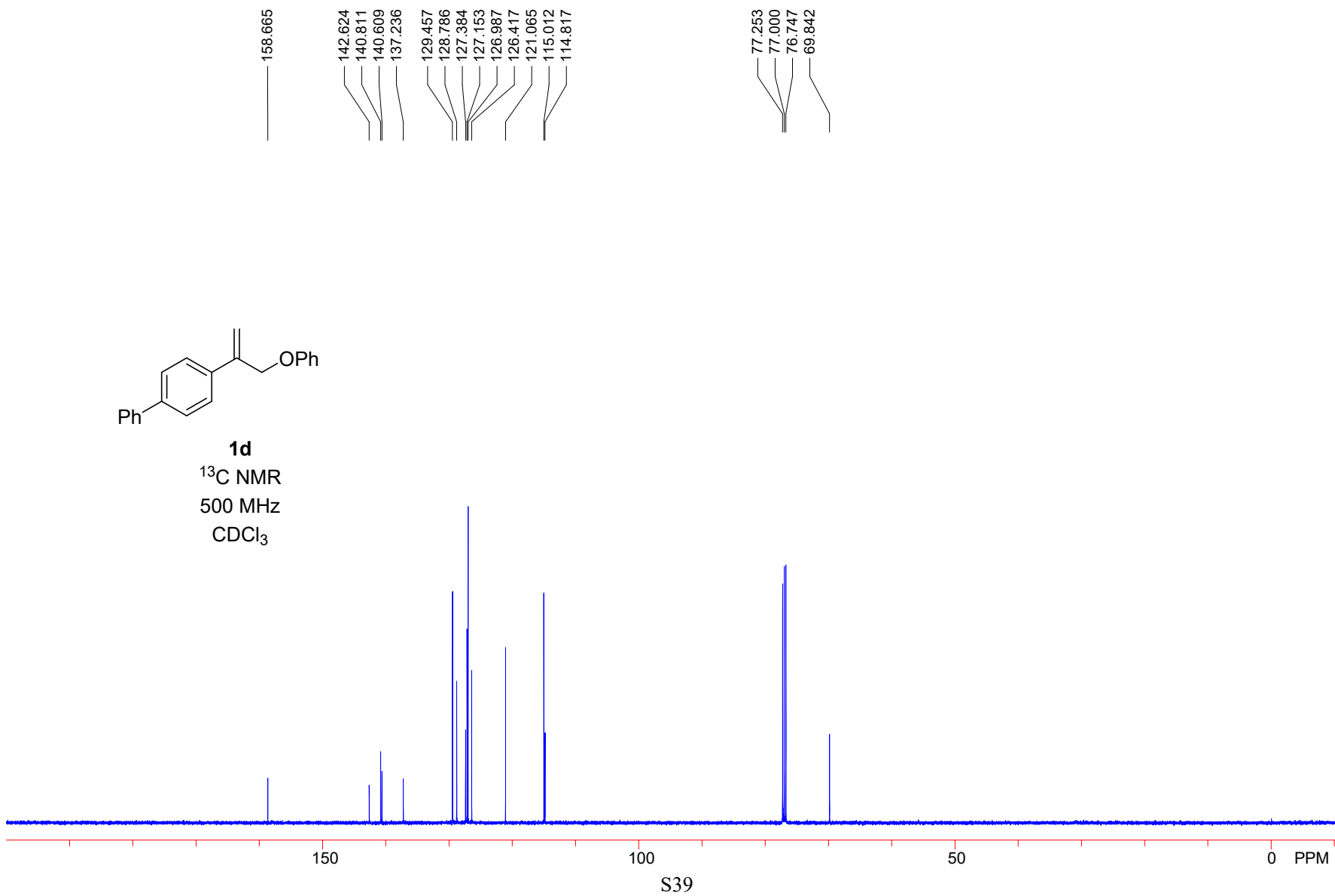
¹H NMR
500 MHz
CDCl₃

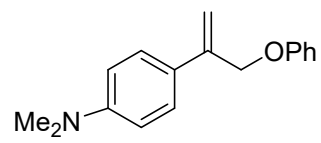




1d

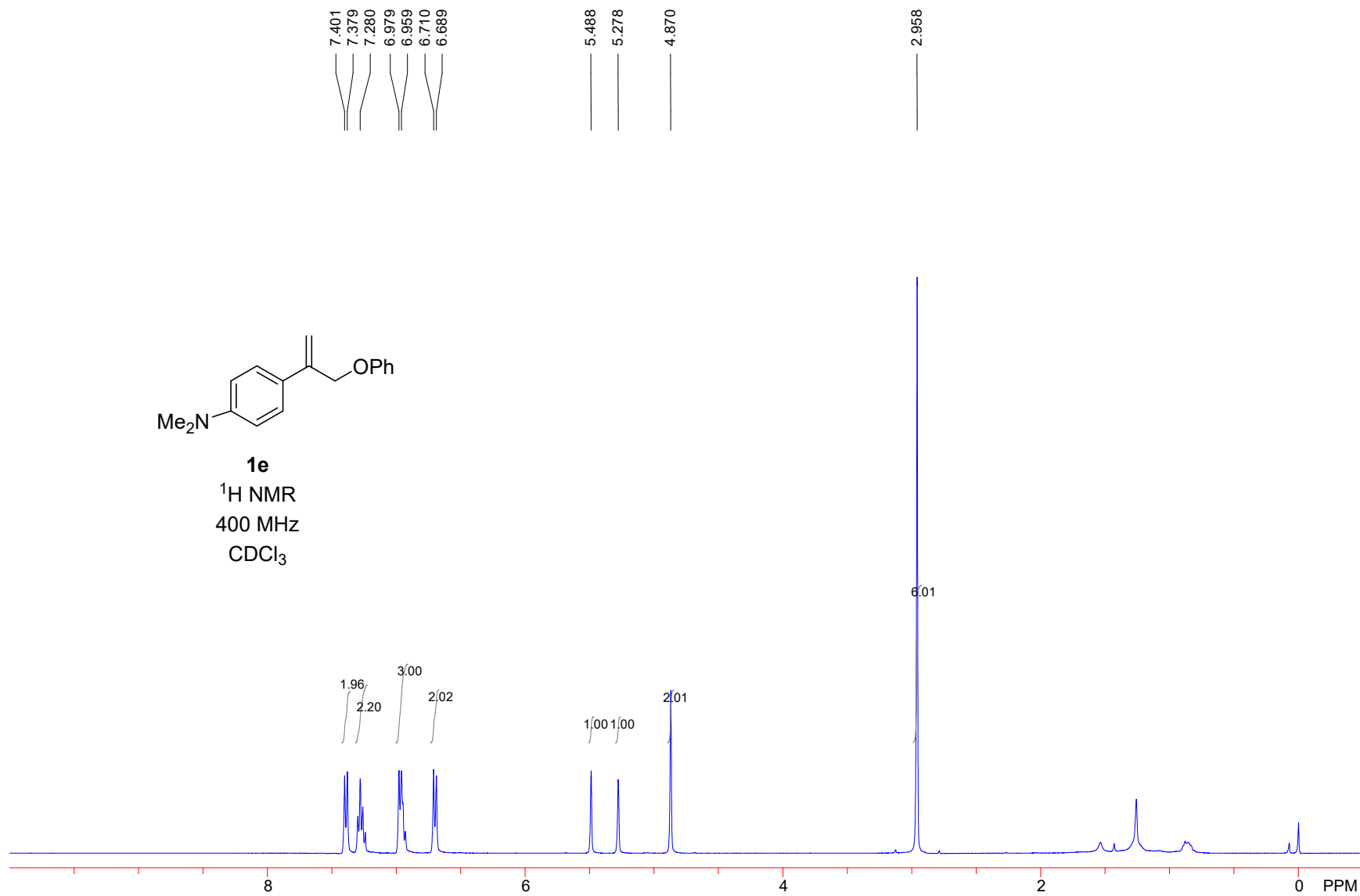
¹³C NMR
500 MHz
CDCl₃



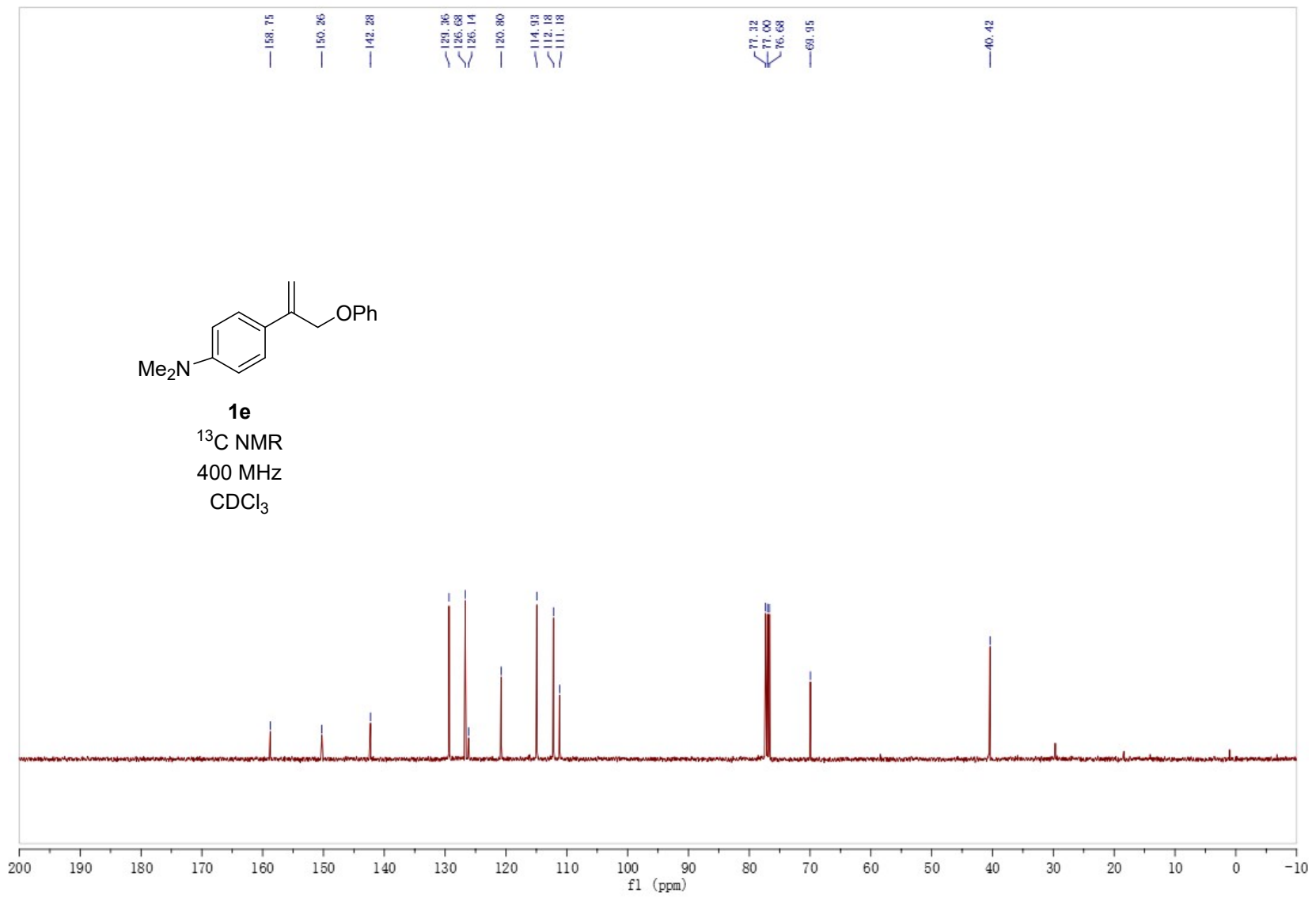


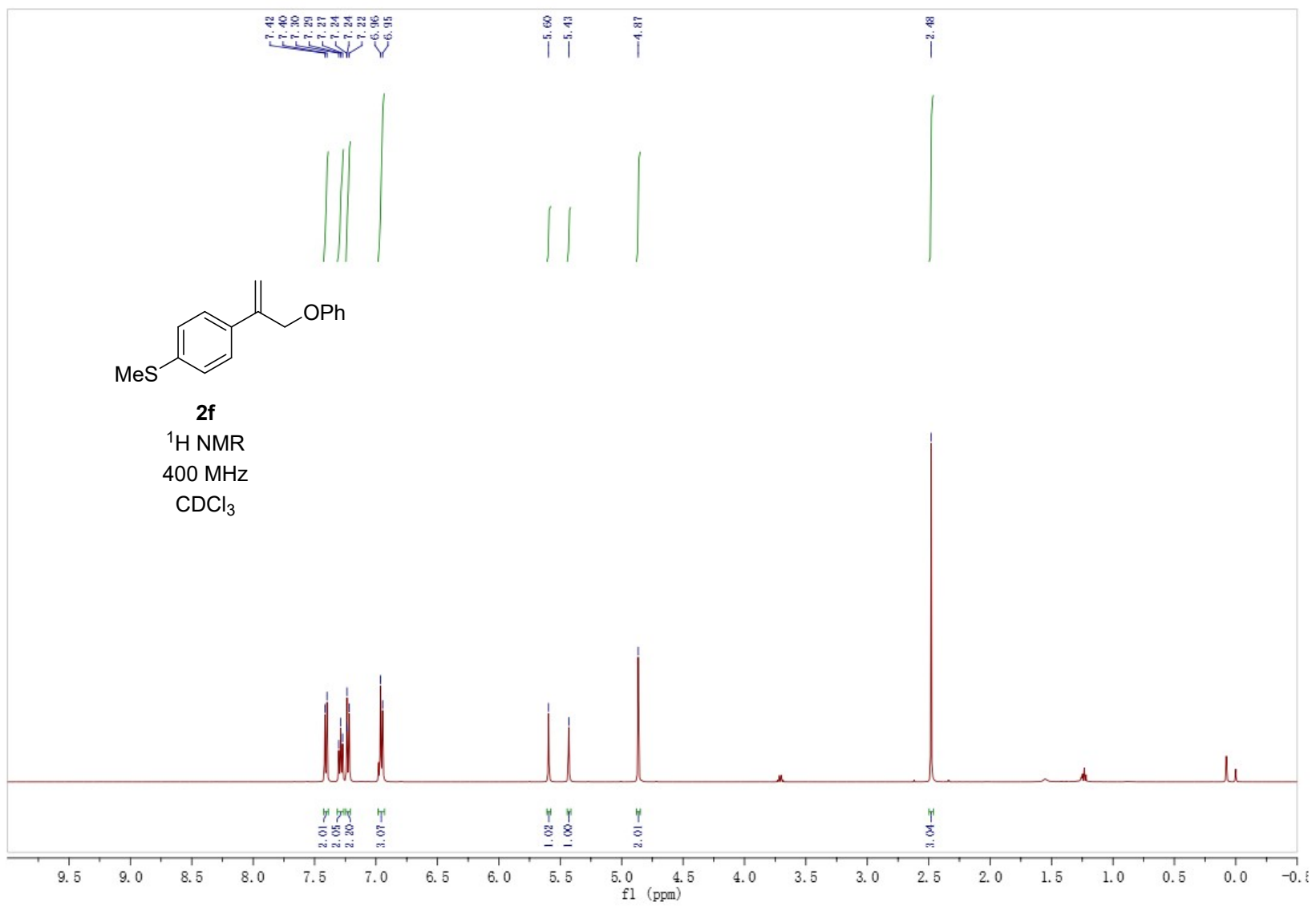
1e

¹H NMR
400 MHz
CDCl₃

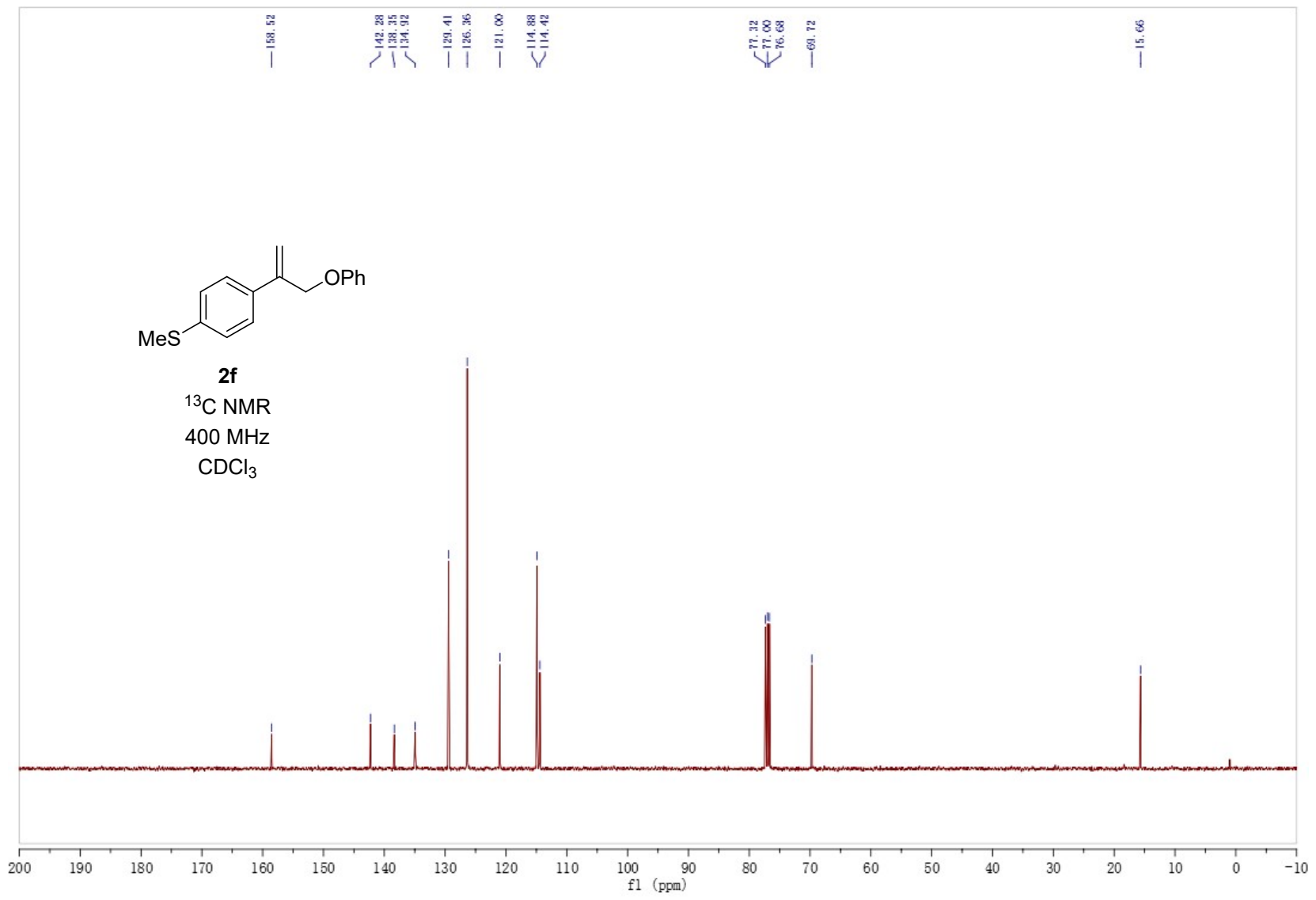


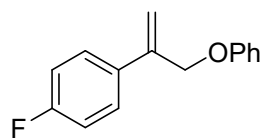
S40





S42



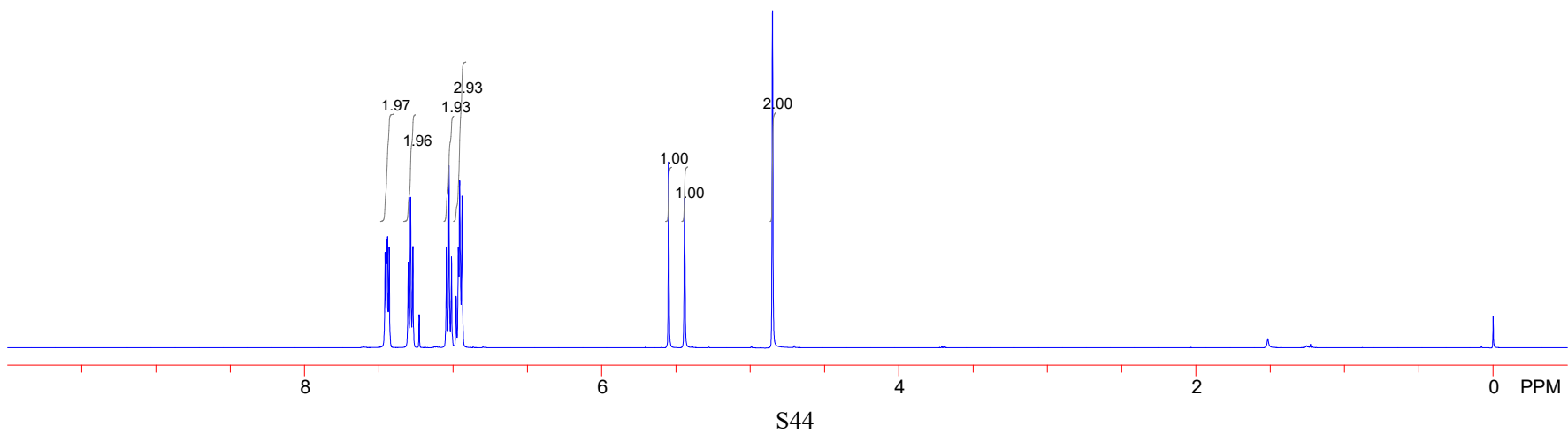
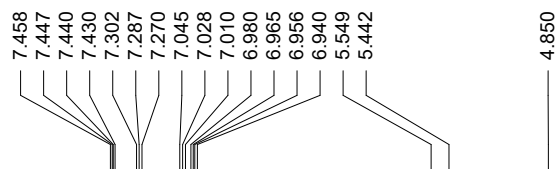


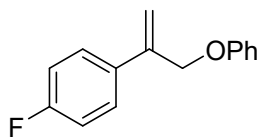
1g

¹H NMR

500 MHz

CDCl₃



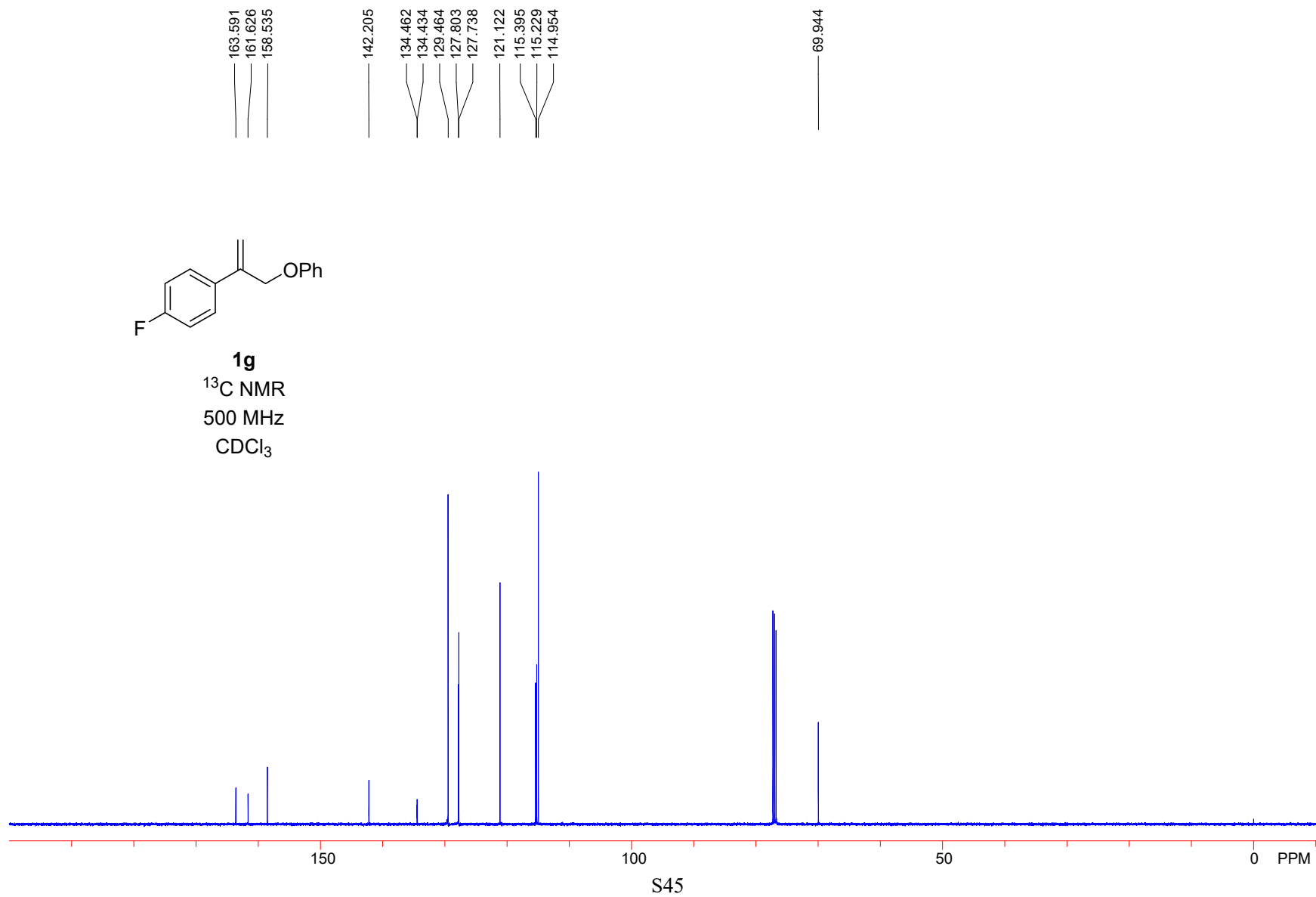


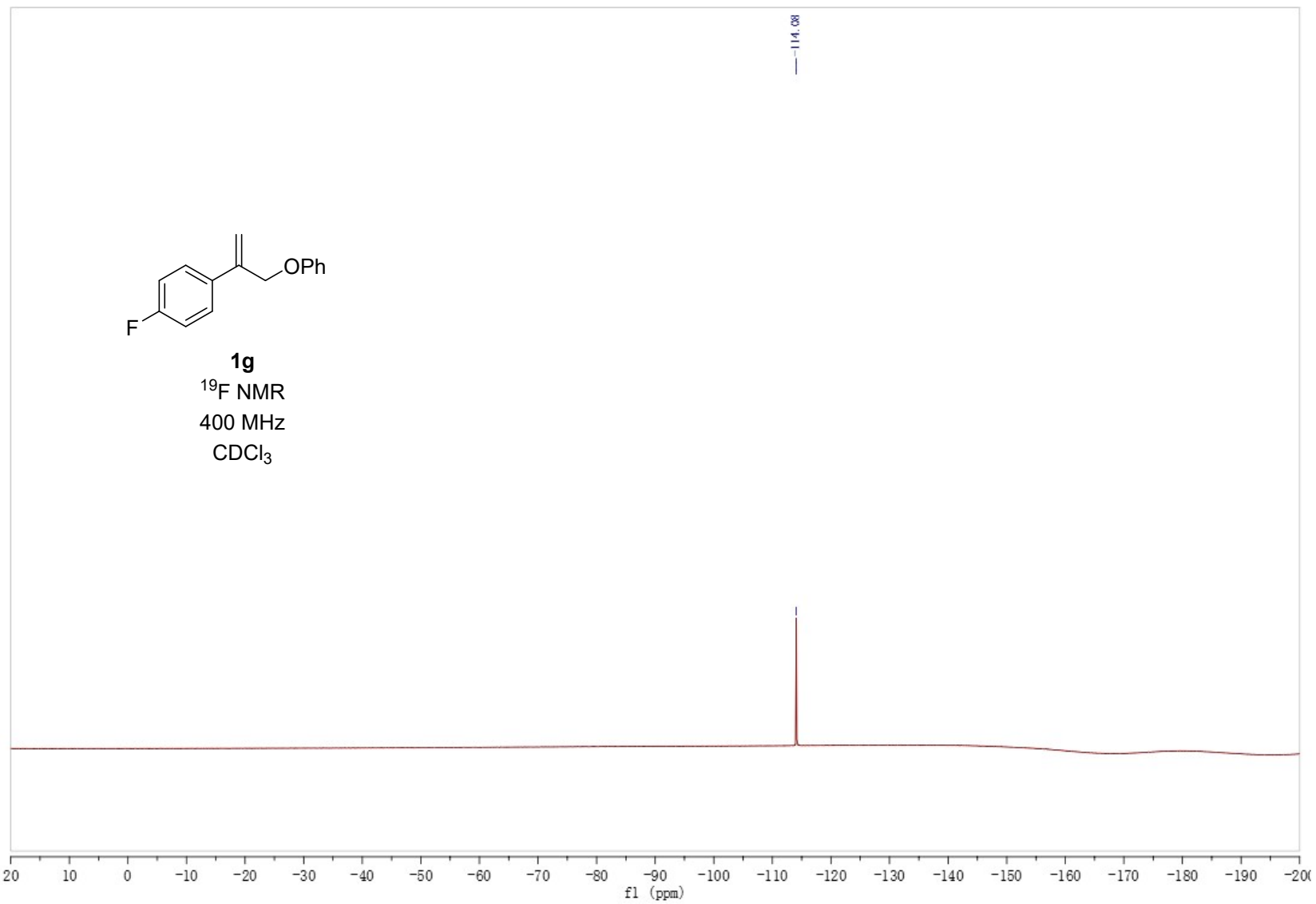
1g

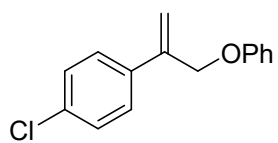
¹³C NMR

500 MHz

CDCl₃

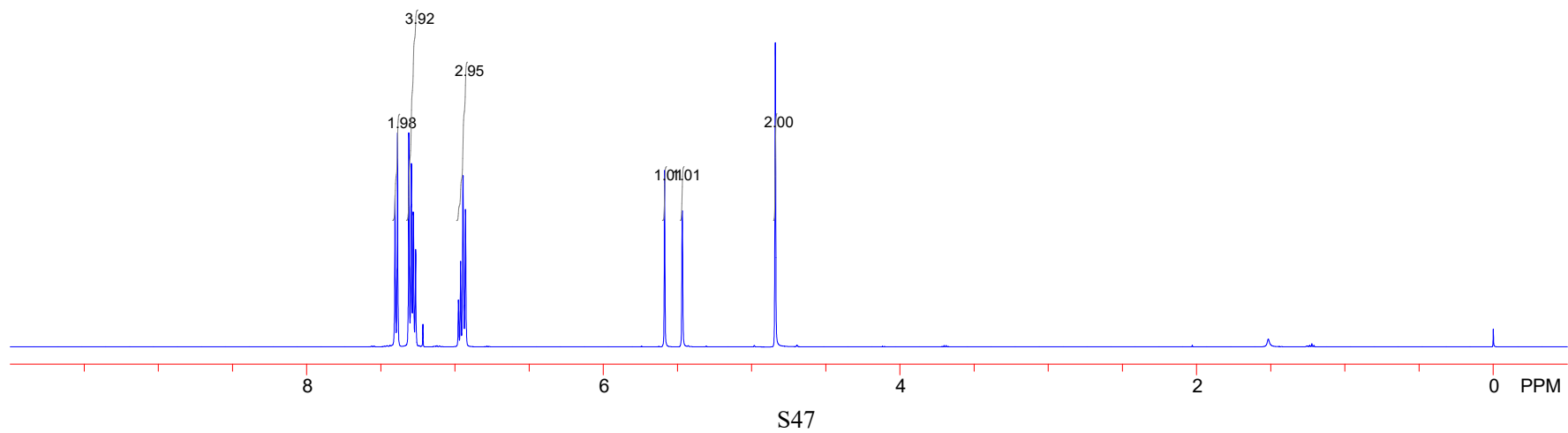
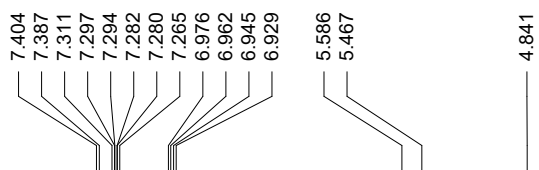


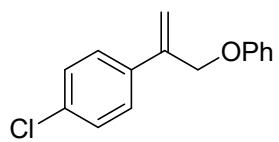




1h

¹H NMR
500 MHz
CDCl₃





1h

^{13}C NMR

500 MHz

CDCl_3

158.477

142.126

136.759

133.834

129.464

128.598

127.384

121.151

115.547

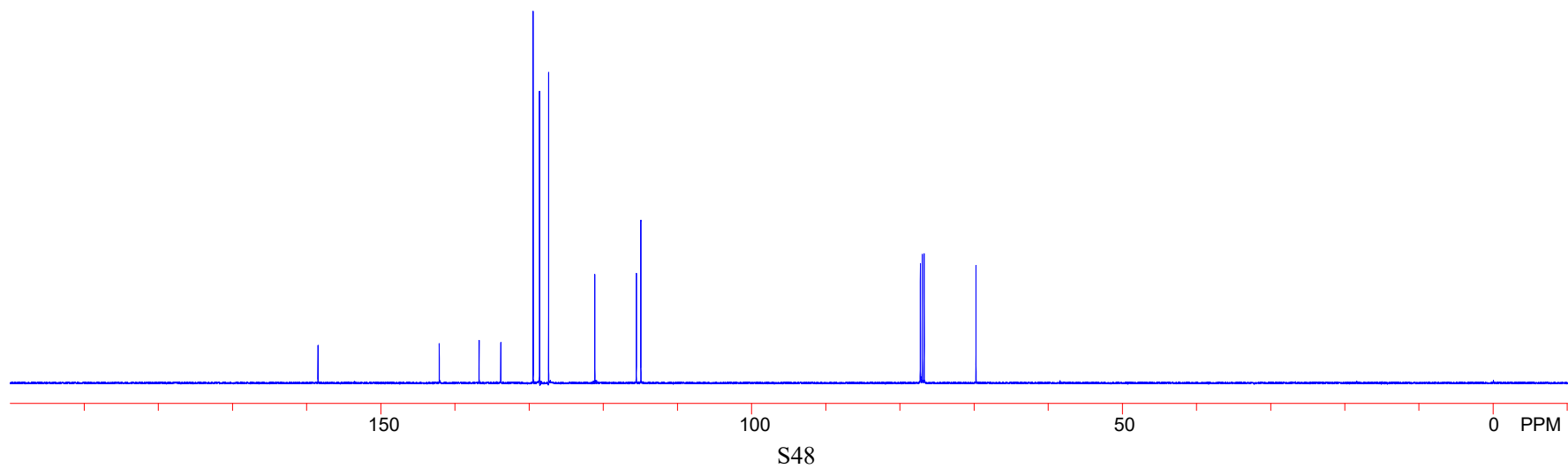
114.940

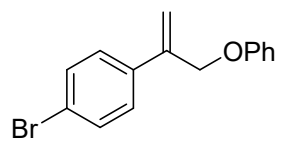
77.253

77.000

76.747

69.756



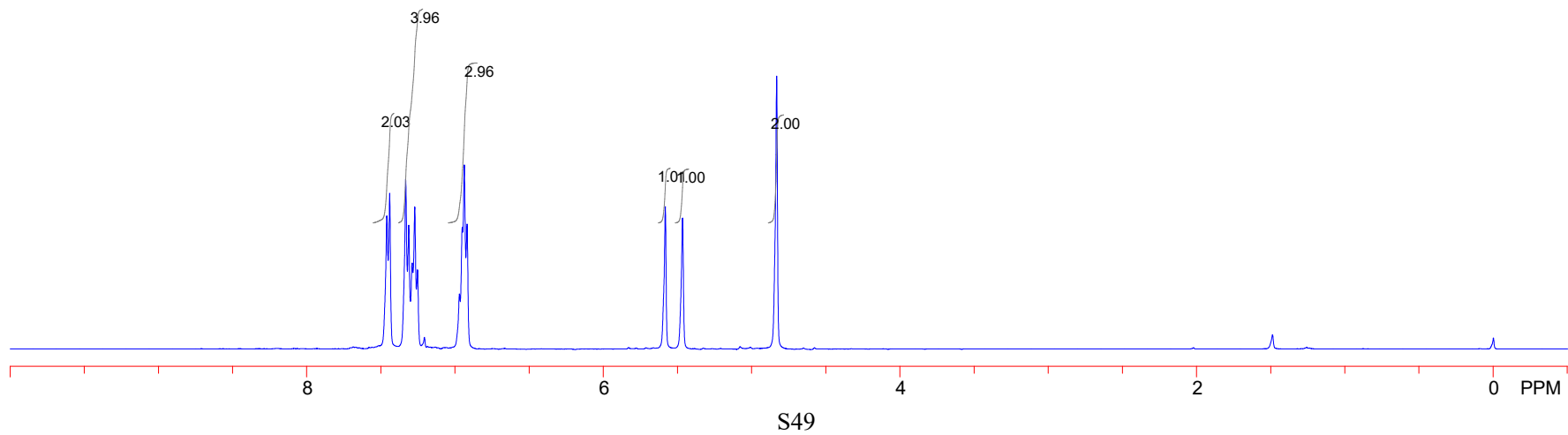


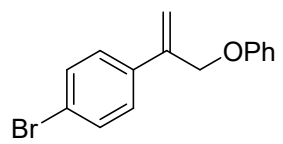
1i
¹H NMR
500 MHz
CDCl₃

7.460
7.440
7.333
7.313
7.289
7.272
7.253
6.971
6.951
6.937
6.918

5.582
5.466

4.831





1i
 ^{13}C NMR
500 MHz
 CDCl_3

158.456

142.169

137.214

131.552

129.457

127.702

122.004

121.151

115.619

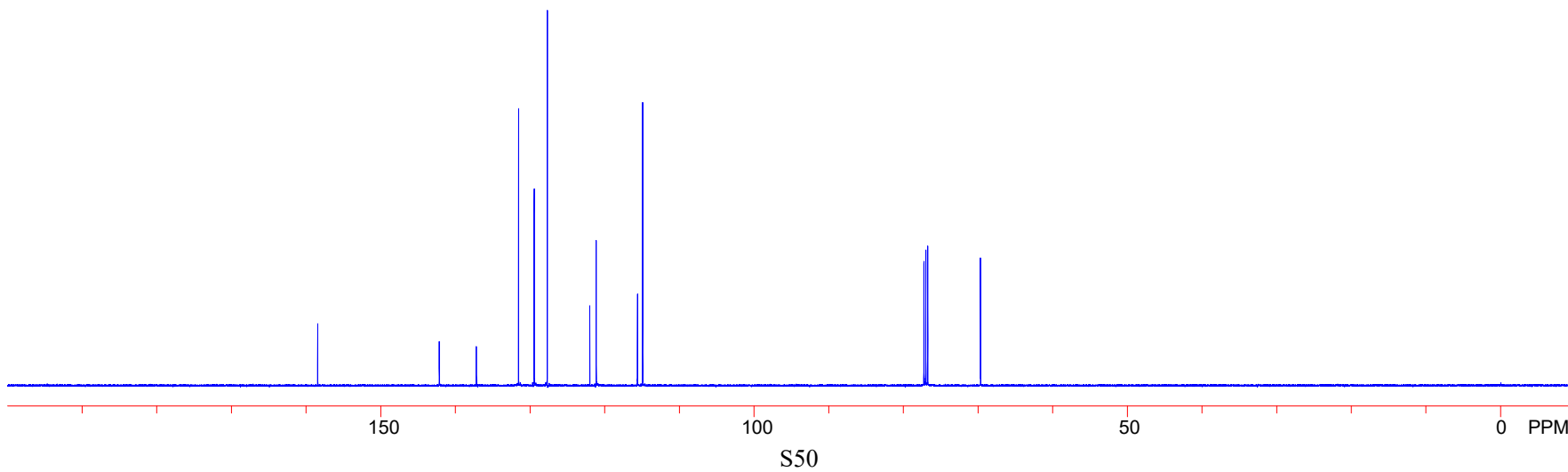
114.933

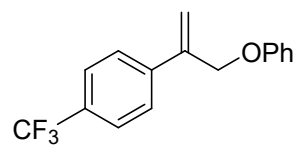
77.253

77.000

76.747

69.676





1j

¹H NMR
500 MHz
CDCl₃

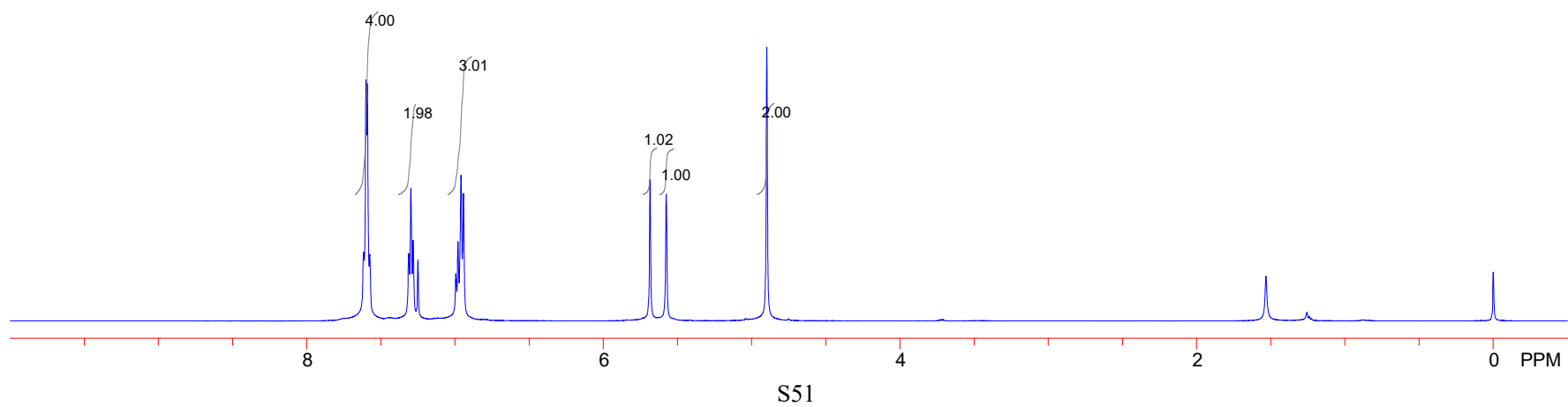
7.616
7.601
7.591
7.575
7.311
7.297
7.282
7.250
6.995
6.980
6.959
6.943

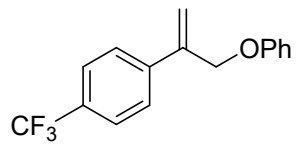
5.685
5.576

4.898

1.533

0.001





1j

¹³C NMR

500 MHz

CDCl₃

158.448

142.289

141.931

130.136

129.876

129.522

126.460

125.463

125.434

125.405

125.376

123.065

121.296

117.114

114.983

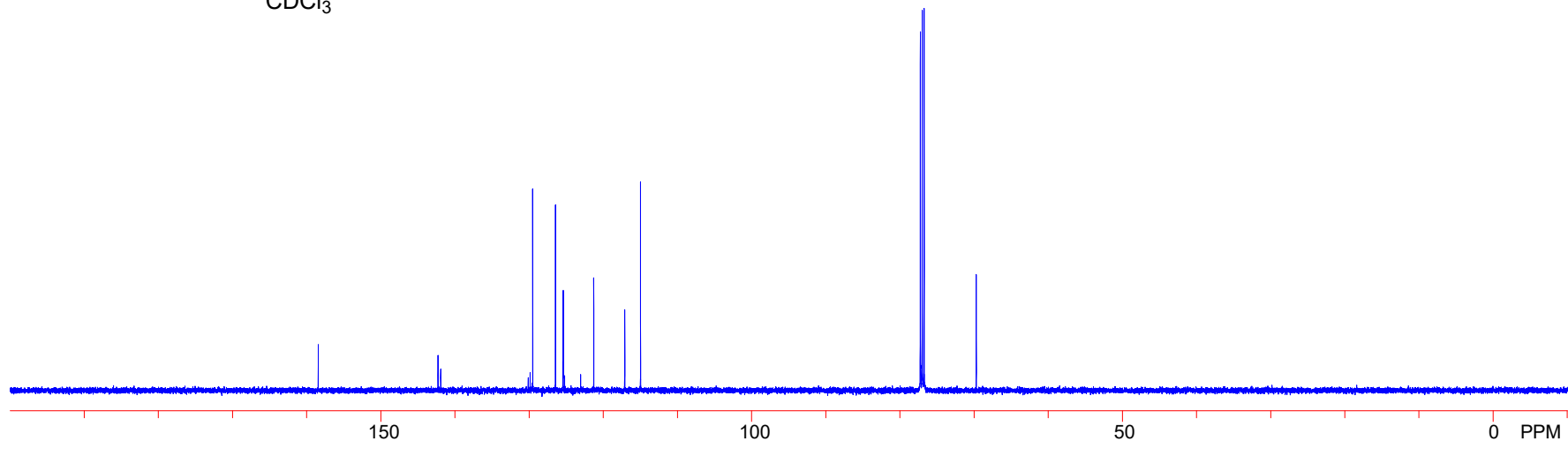
77.253

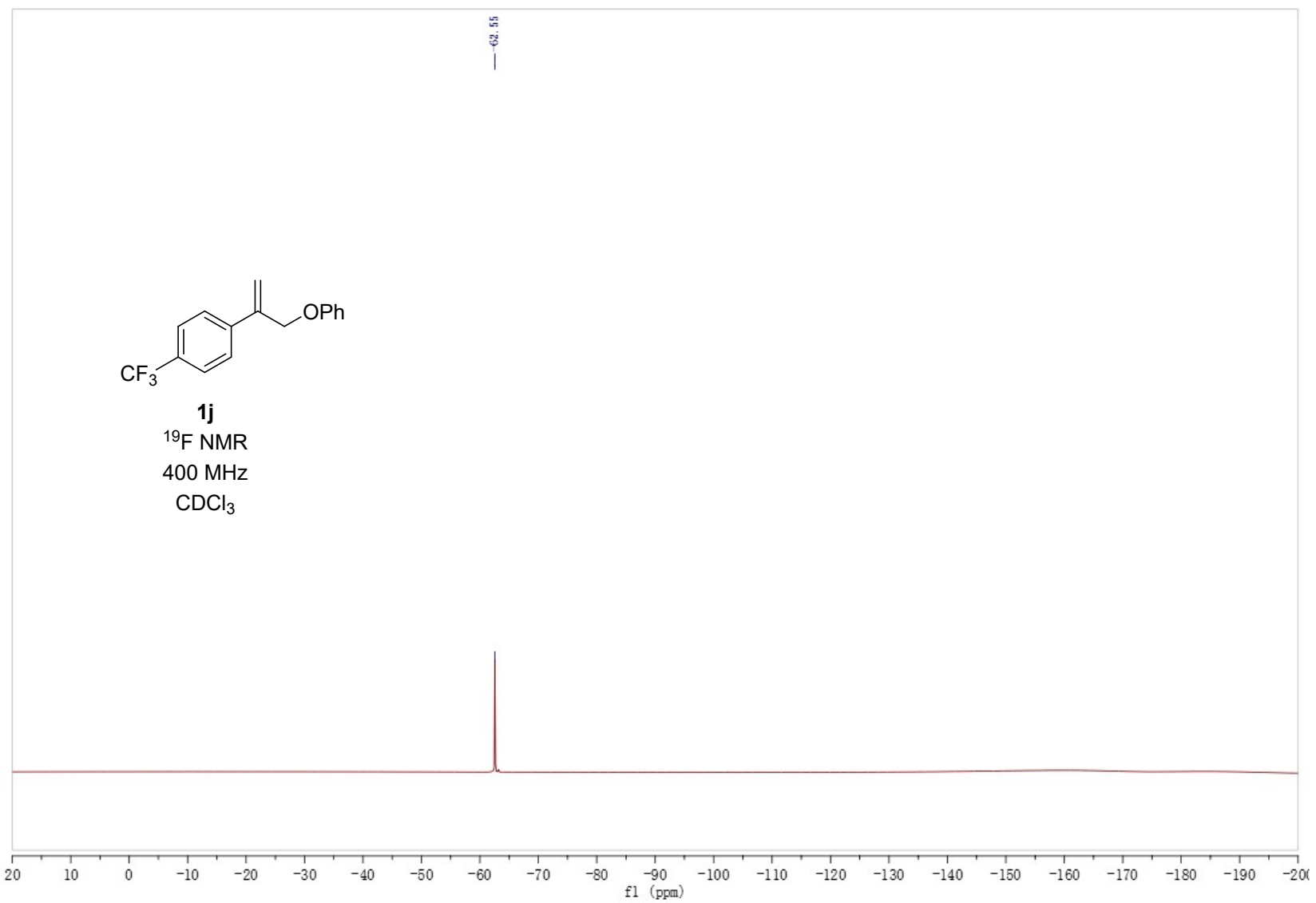
77.000

76.747

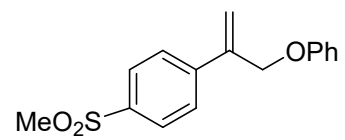
76.617

69.720



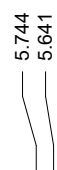
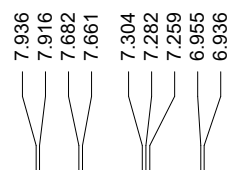
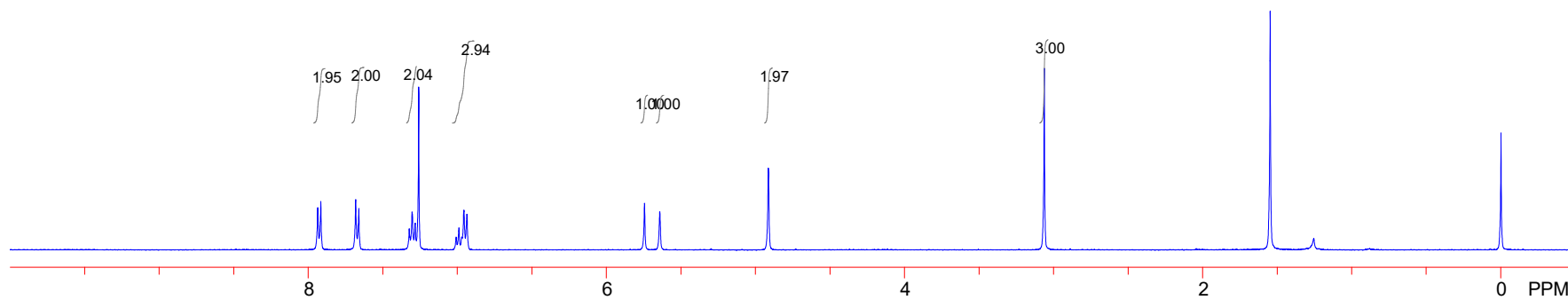


S53

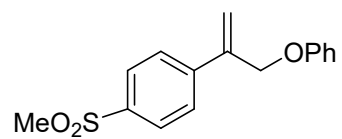


1k

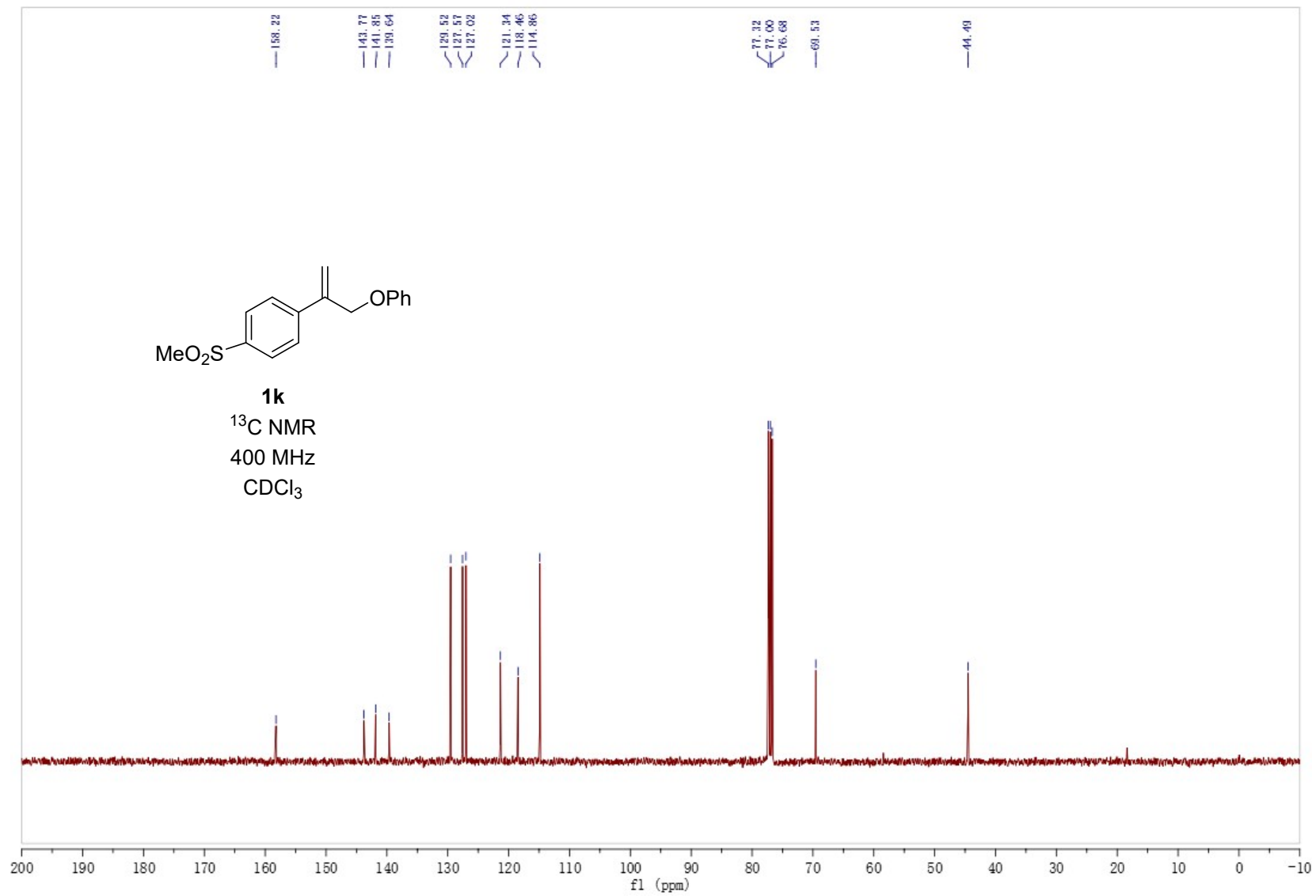
¹H NMR
400 MHz
CDCl₃

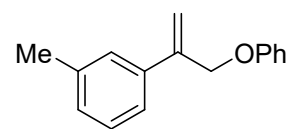


S54

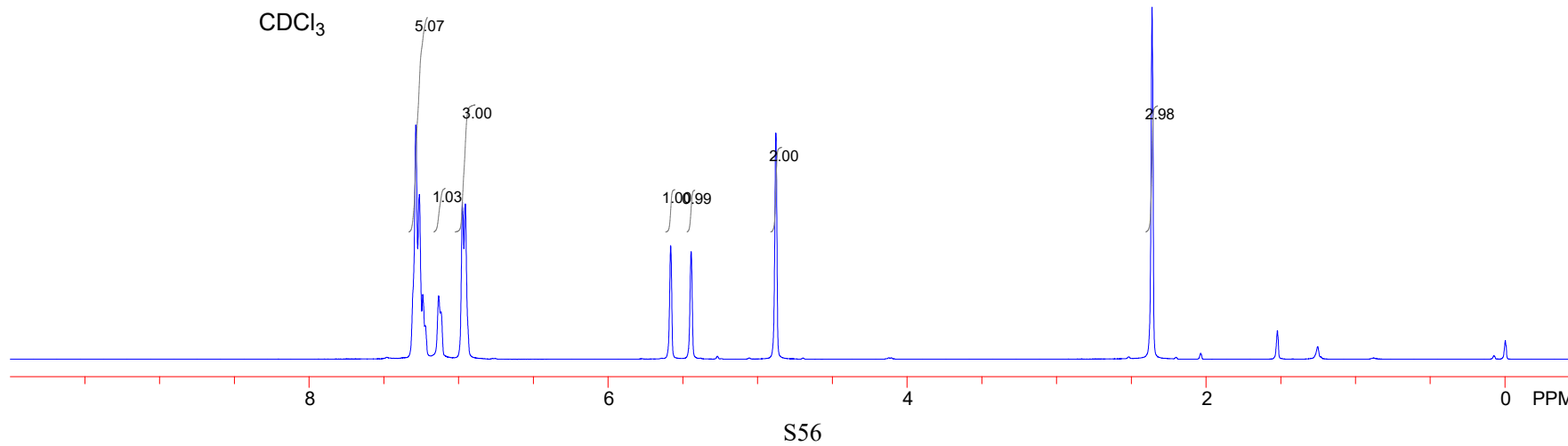


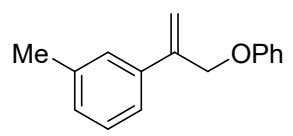
1k
¹³C NMR
400 MHz
CDCl₃





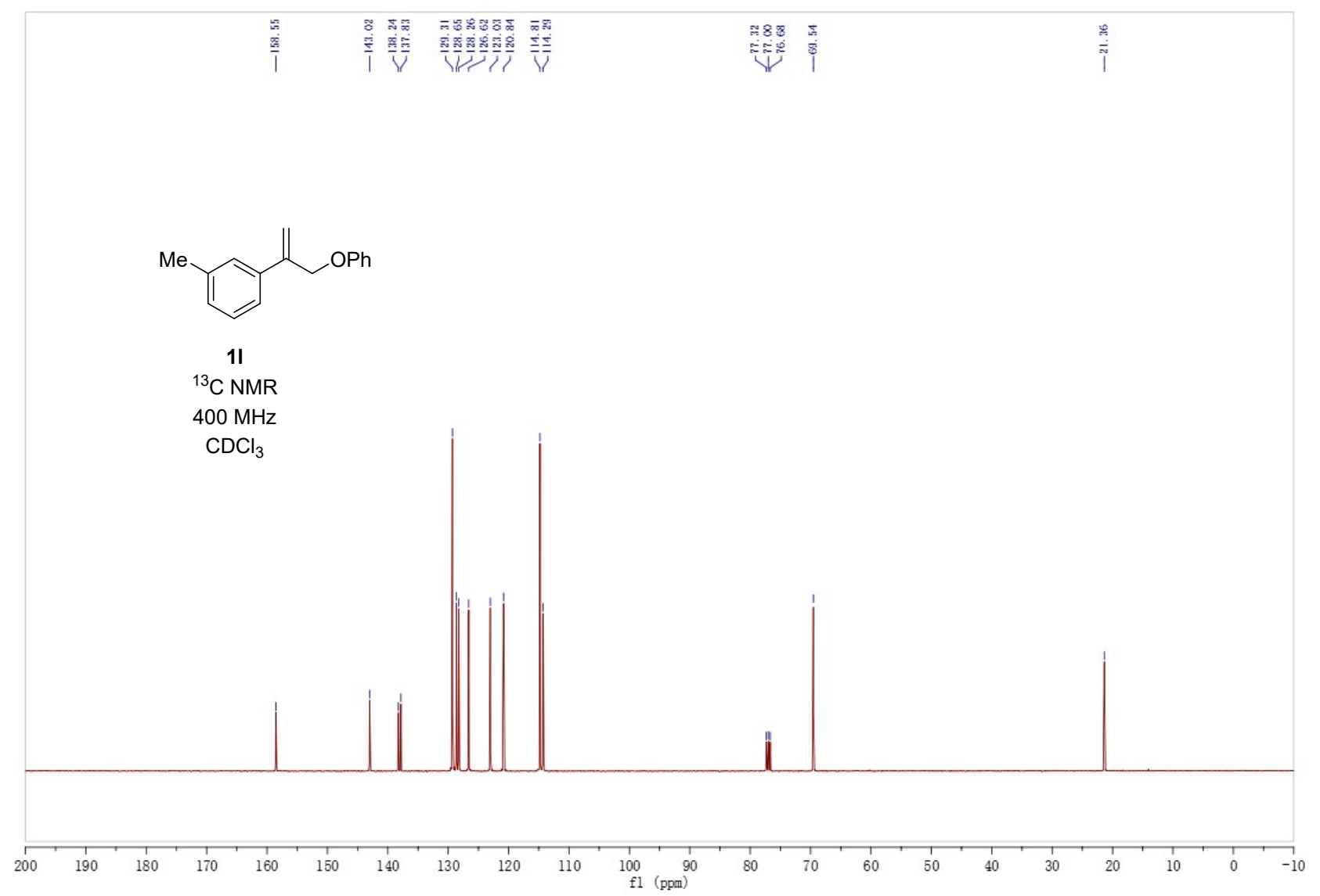
11
¹H NMR
400 MHz
CDCl₃



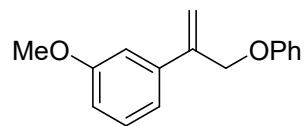


11

¹³C NMR
400 MHz
CDCl₃



S5/

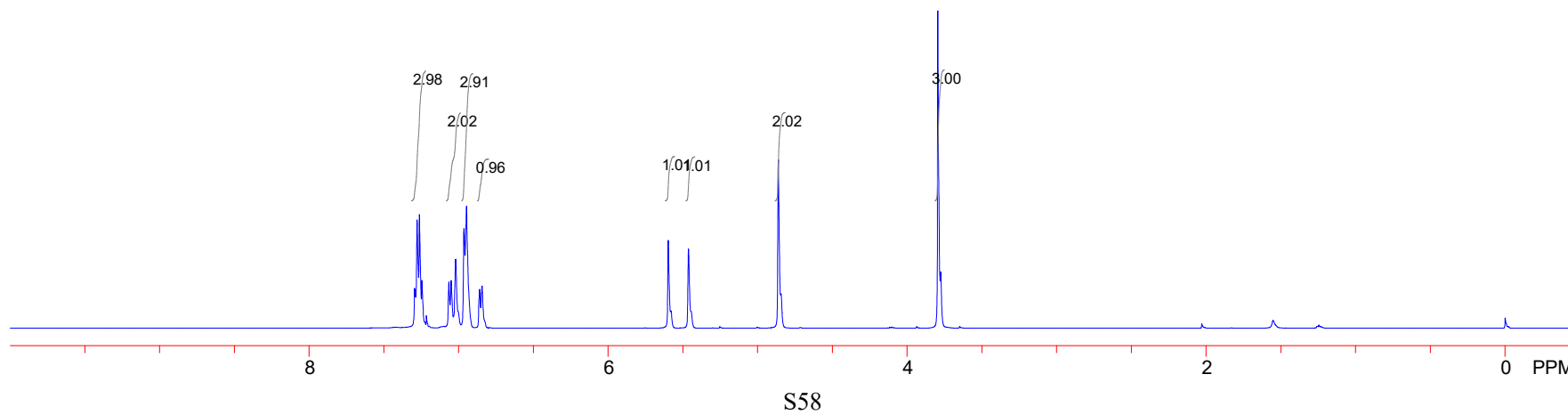
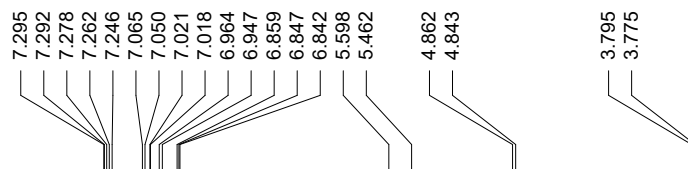


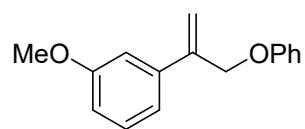
1m

¹H NMR

500 MHz

CDCl₃



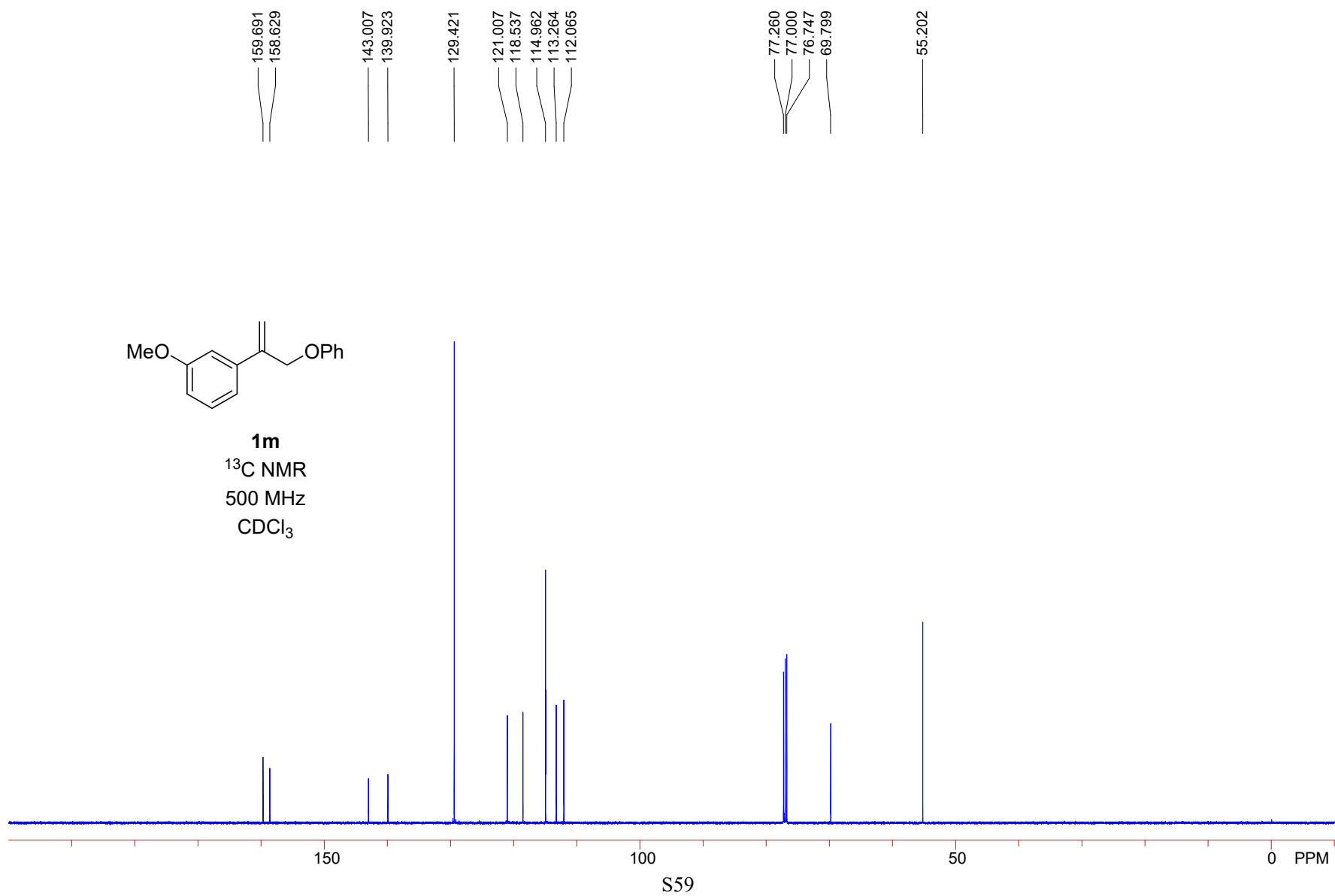


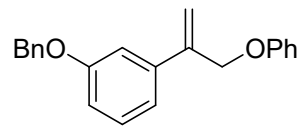
1m

¹³C NMR

500 MHz

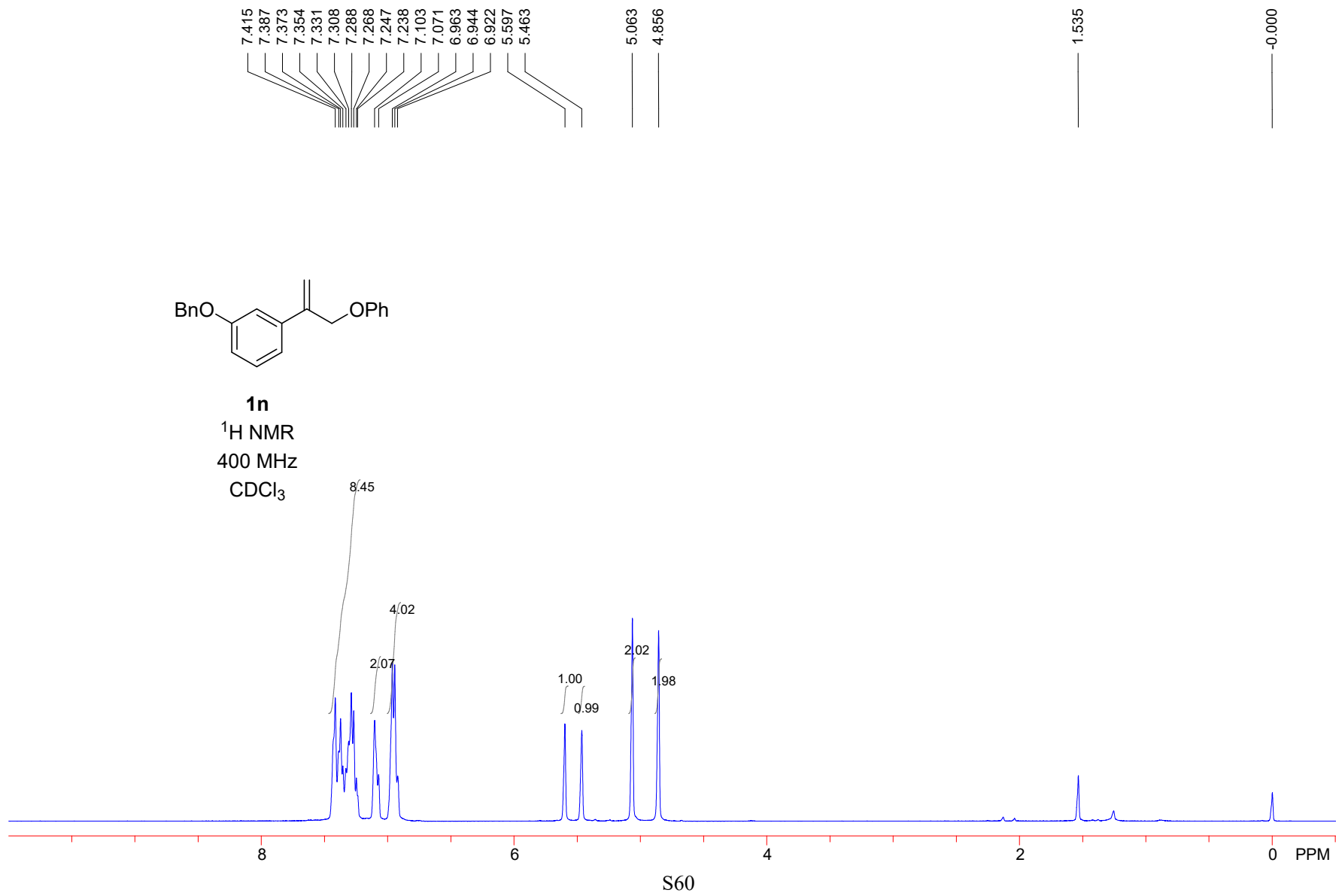
CDCl₃

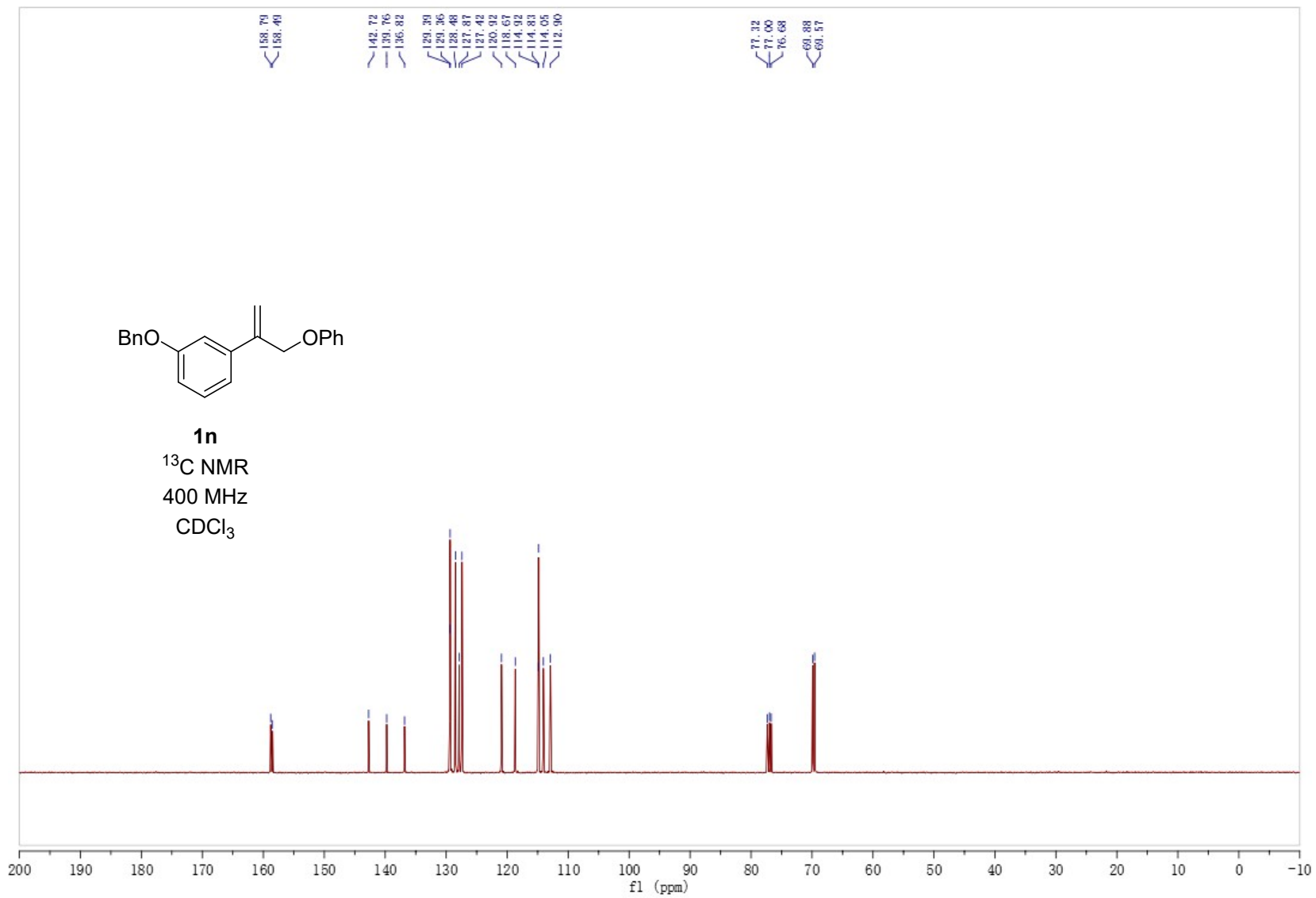




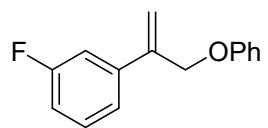
1n

¹H NMR
400 MHz
CDCl₃



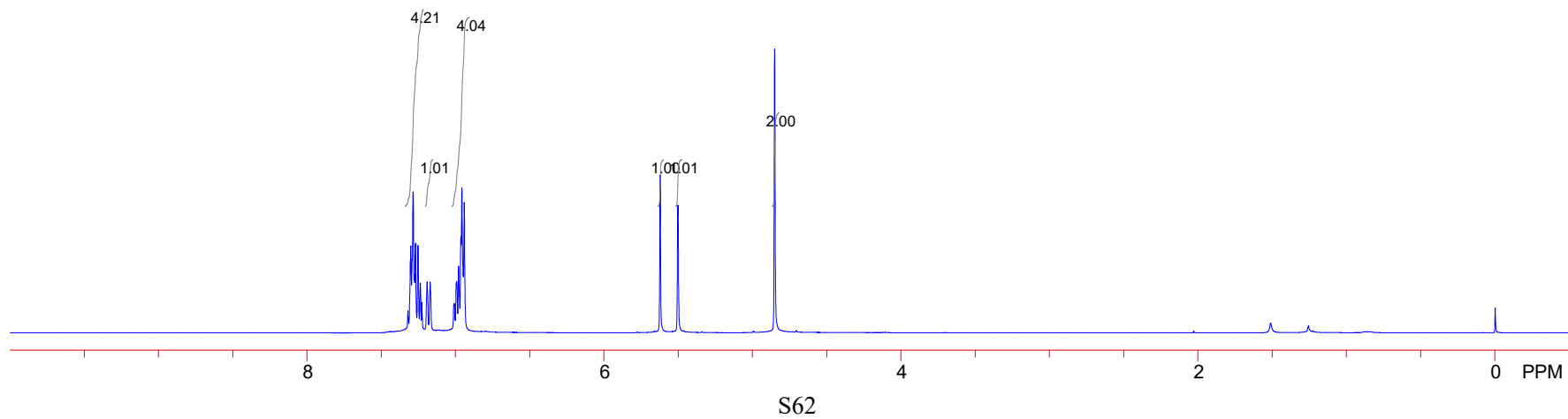


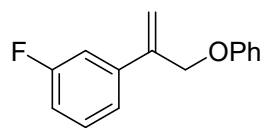
7.301
7.292
7.286
7.285
7.277
7.269
7.253
7.237
7.226
7.191
7.170
7.011
7.008
6.995
6.992
6.979
6.963
6.957
6.941
5.622
5.502
4.851



1o

¹H NMR
500 MHz
CDCl₃





1o

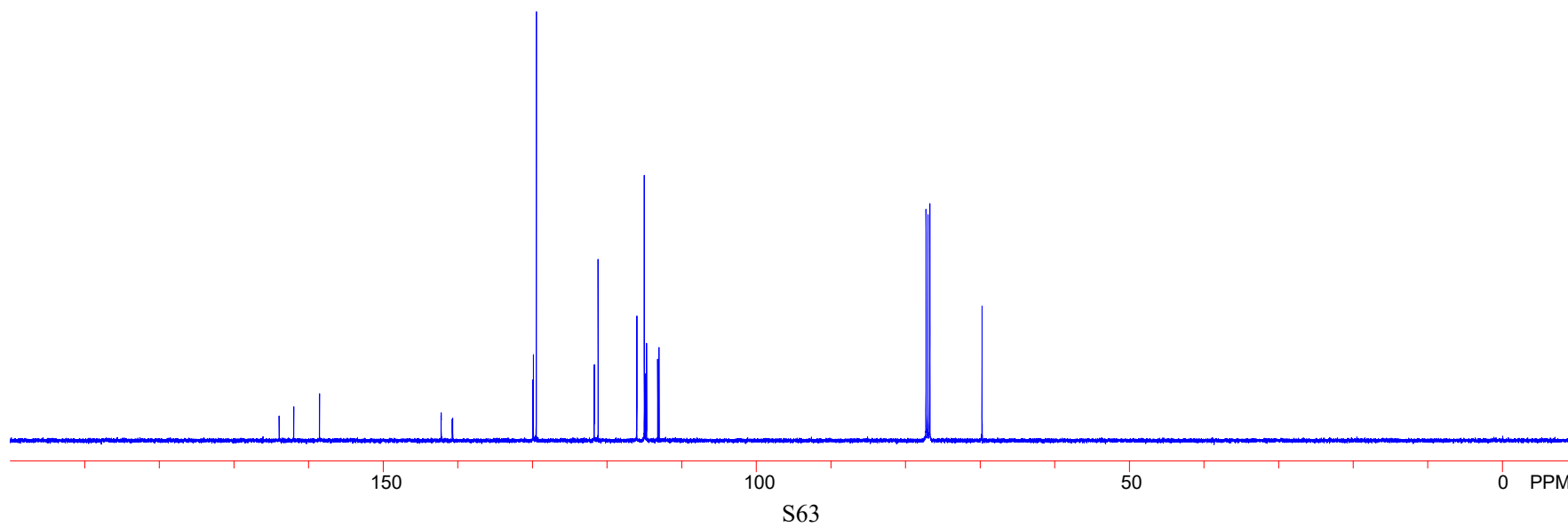
¹³C NMR
500 MHz
CDCl₃

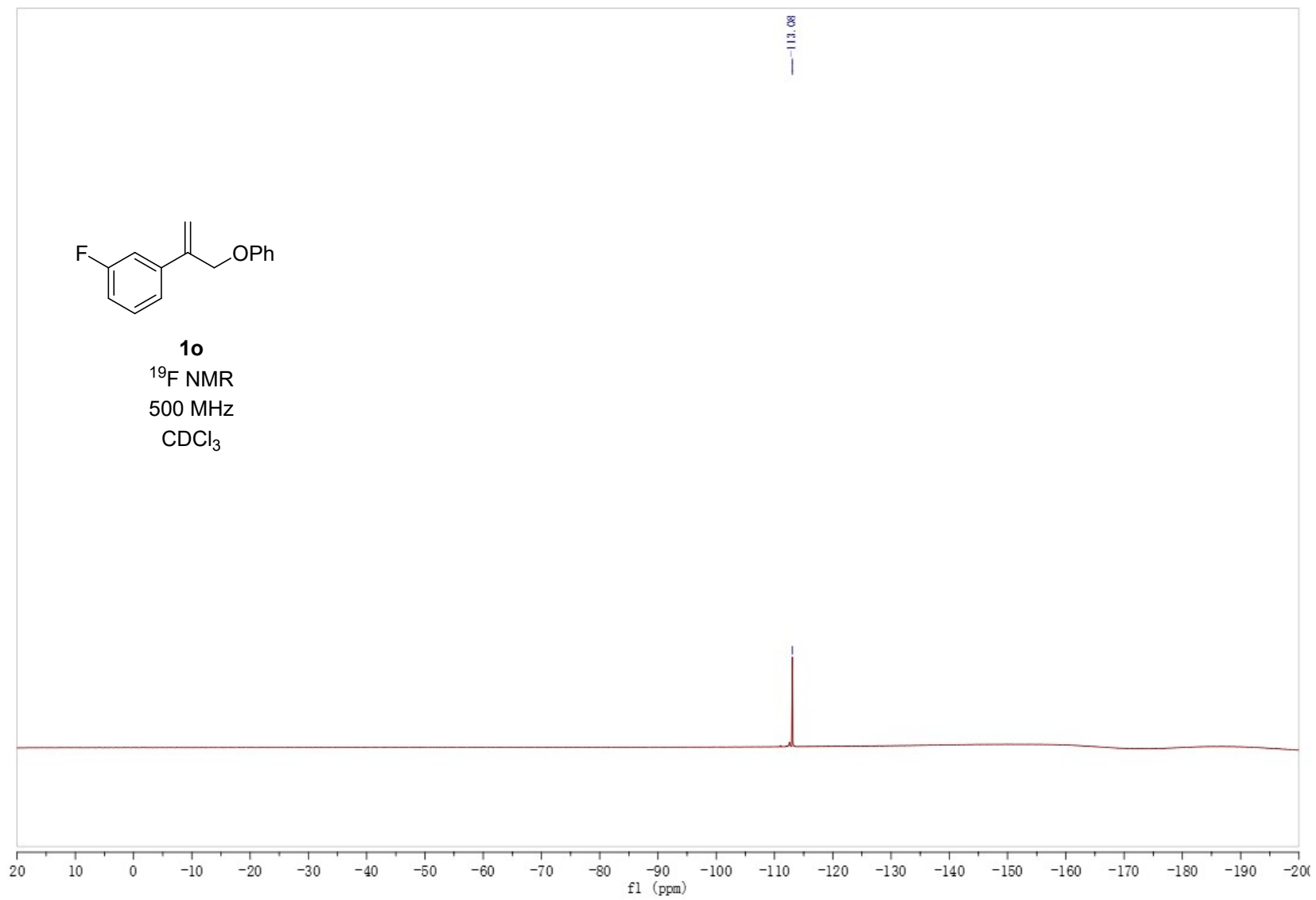
163.945
161.995
158.550

142.248
140.753

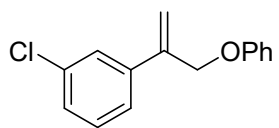
129.934
129.869
129.486
121.751
121.722
121.202
116.009
115.019
114.868
114.702
113.221
113.040

77.260
77.000
76.747
69.756

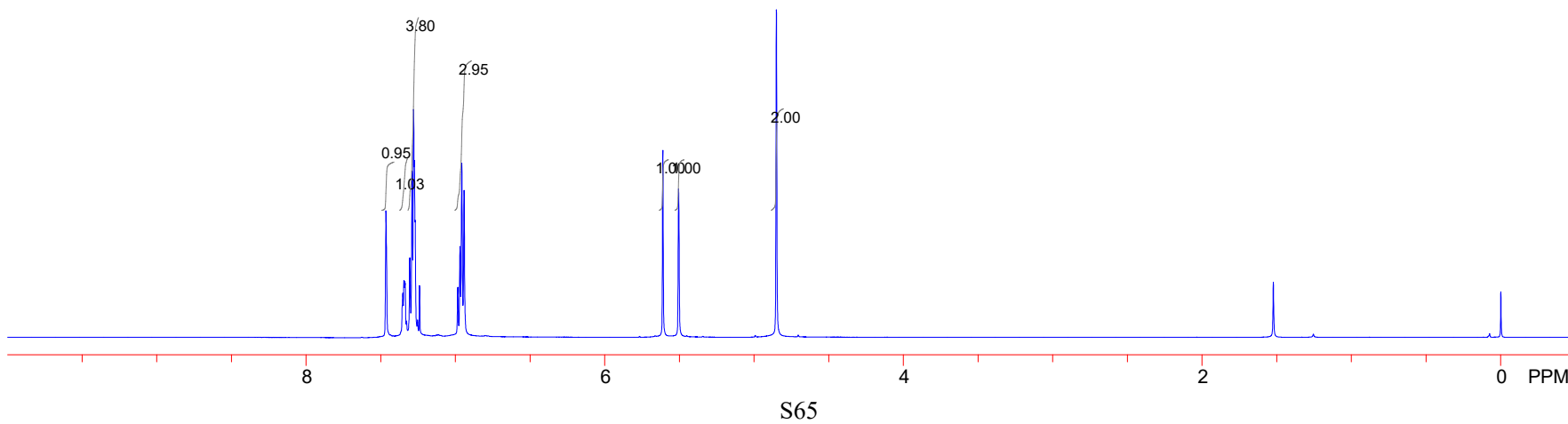
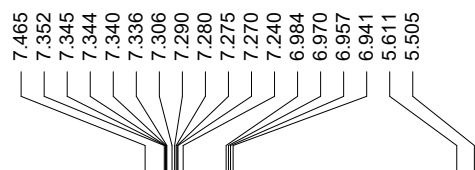


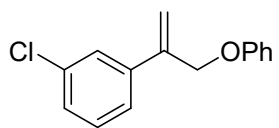


S64



1p
¹H NMR
500 MHz
CDCl₃



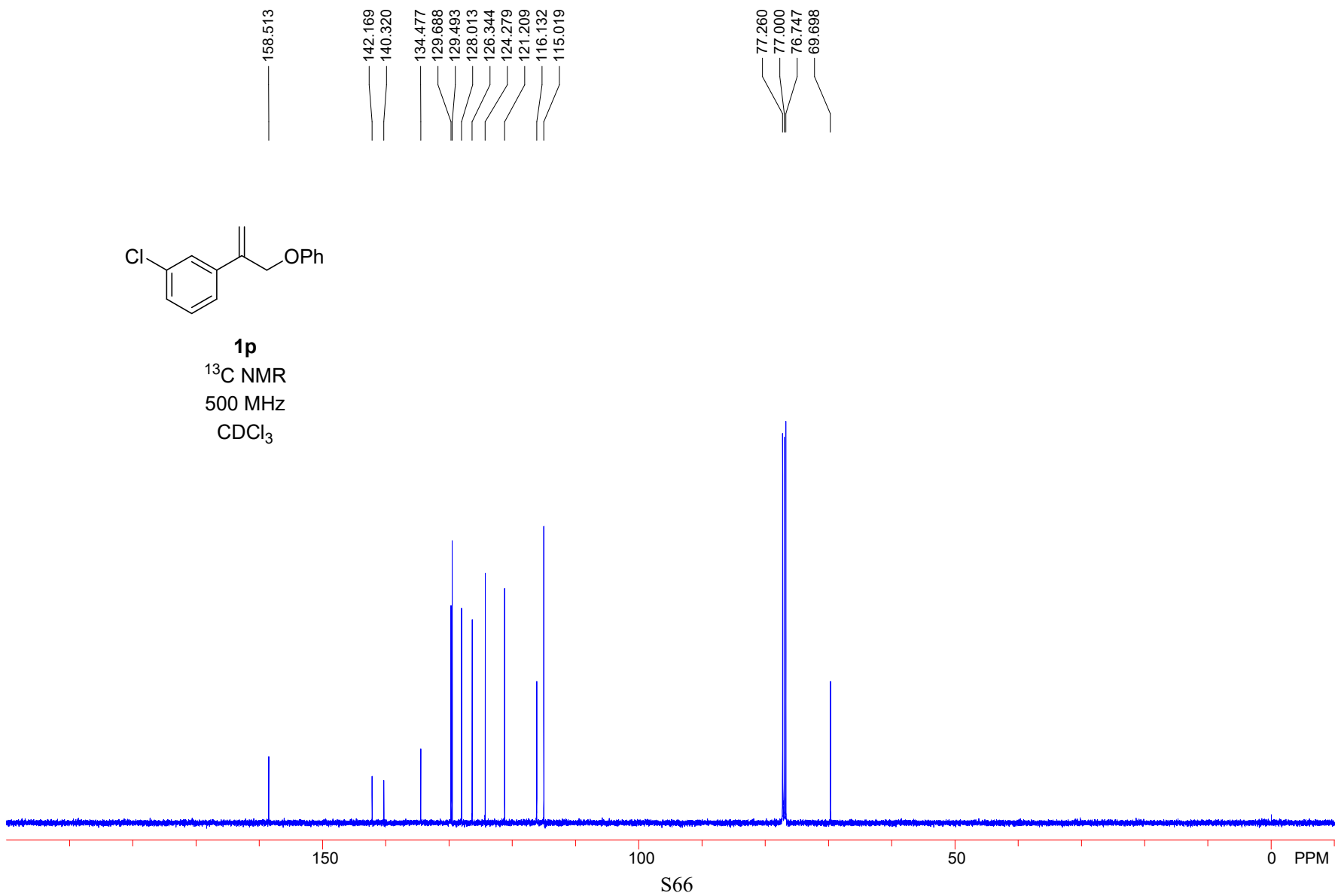


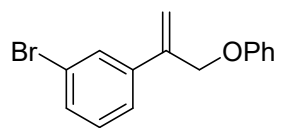
1p

¹³C NMR

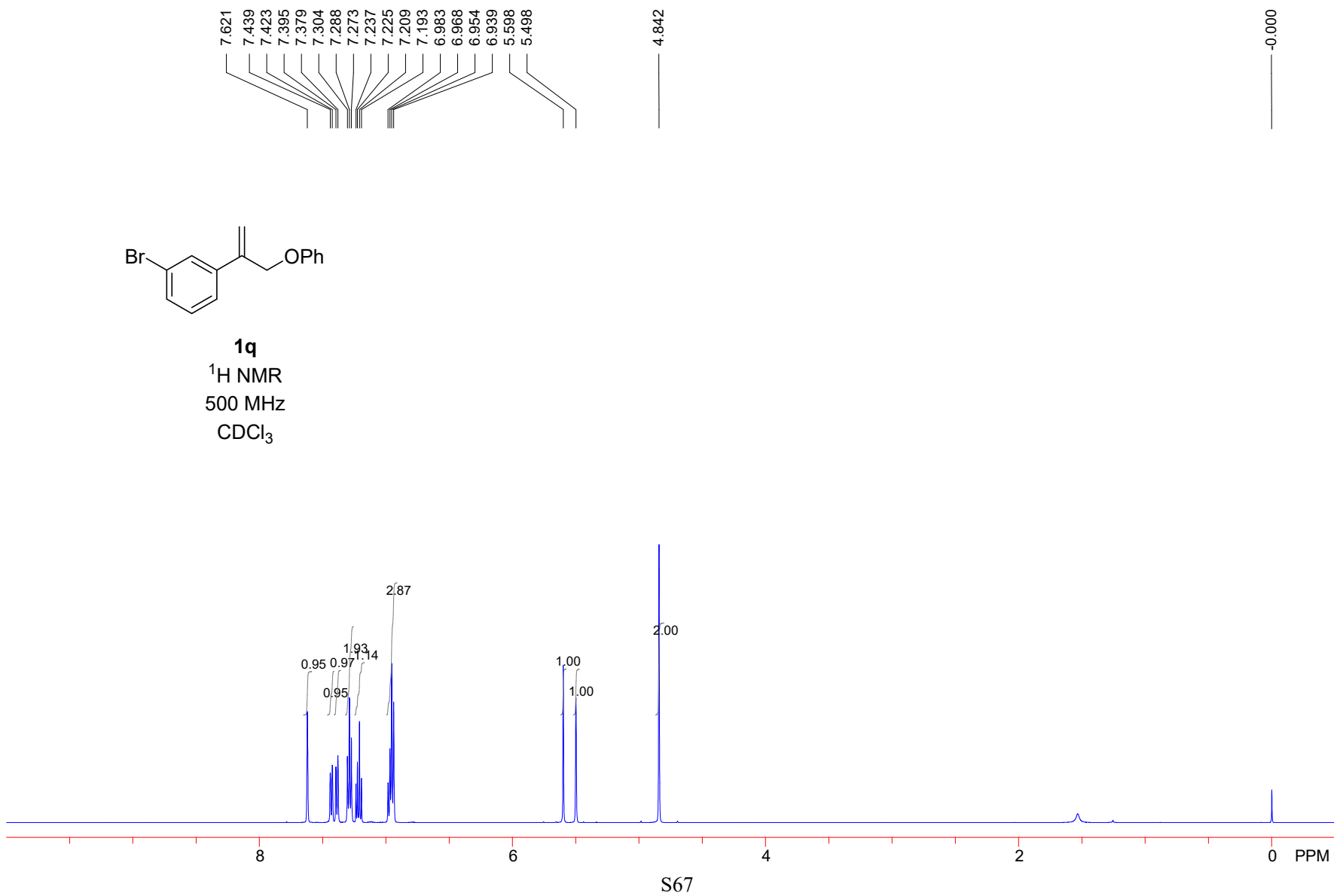
500 MHz

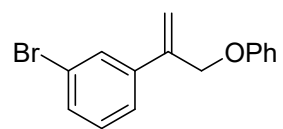
CDCl₃





1q
¹H NMR
500 MHz
CDCl₃





1q

¹³C NMR
500 MHz
CDCl₃

158.499

142.097

140.609

130.938

129.963

129.479

129.241

124.741

122.682

121.209

116.161

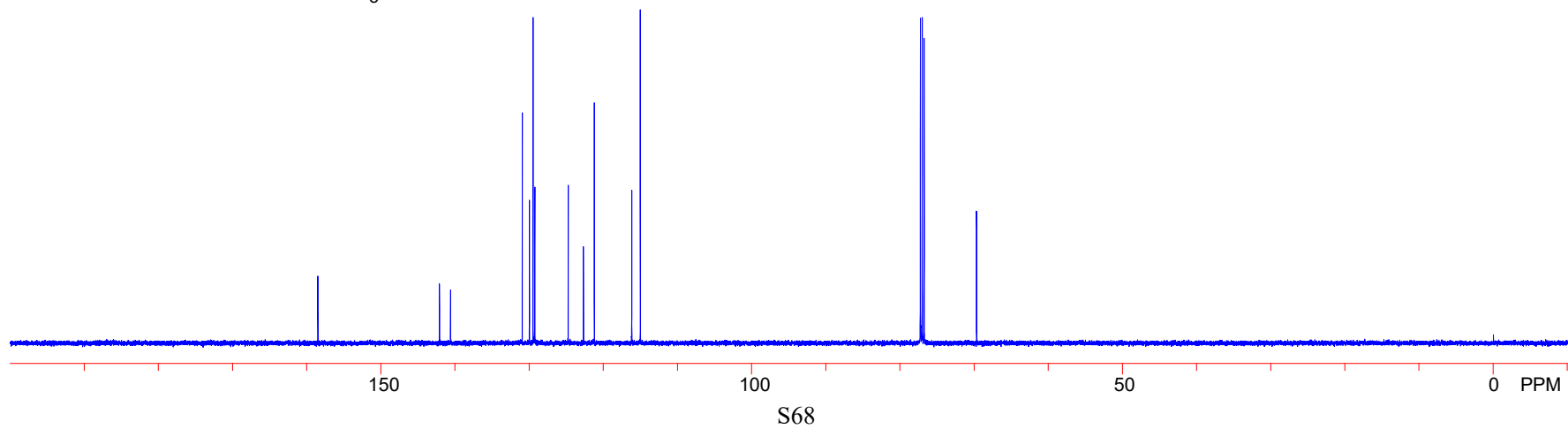
115.019

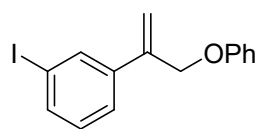
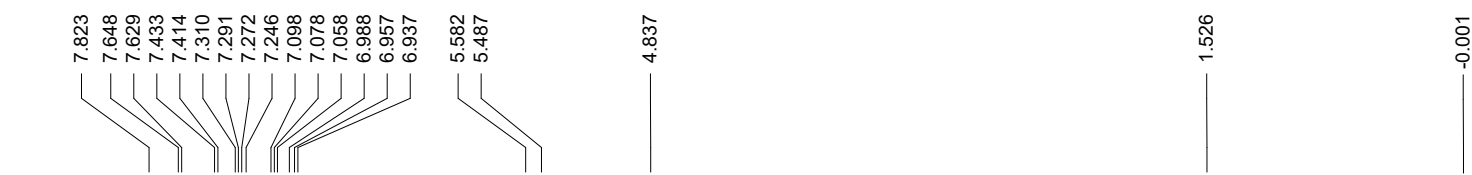
77.253

77.000

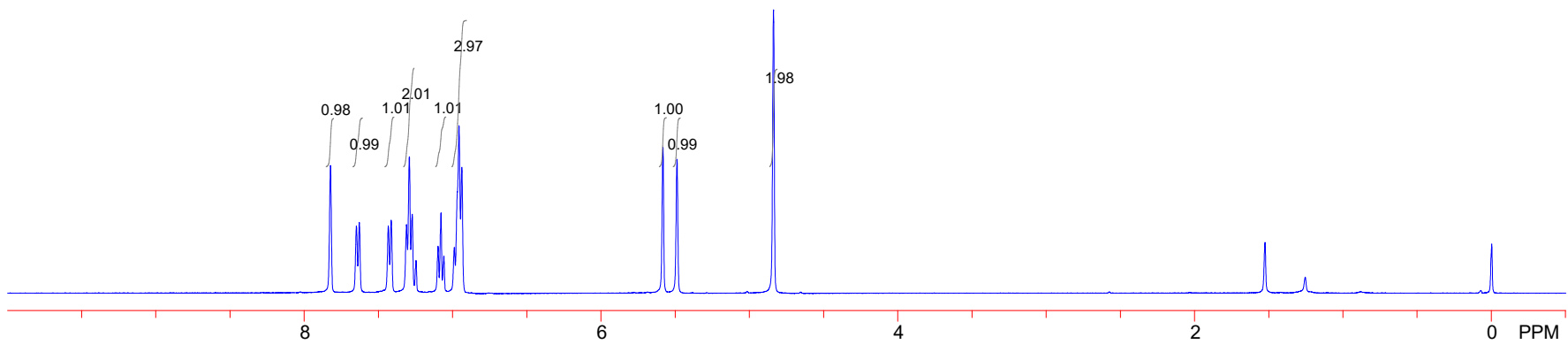
76.747

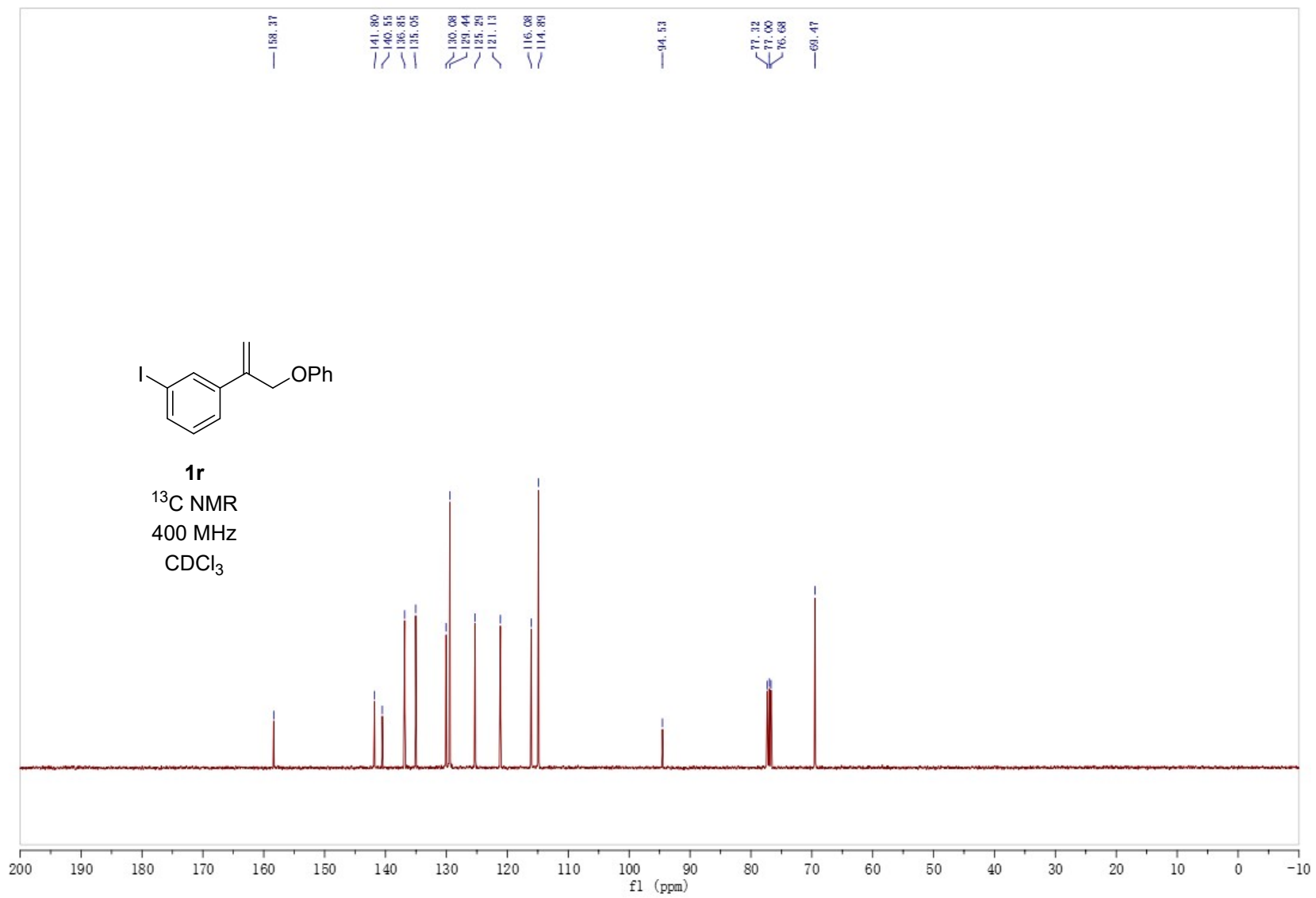
69.676

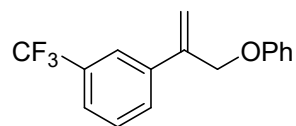




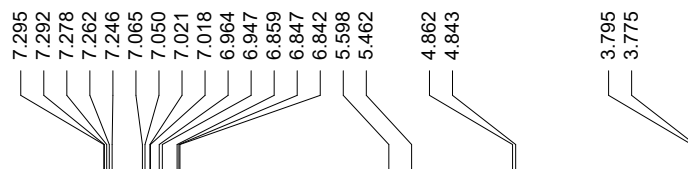
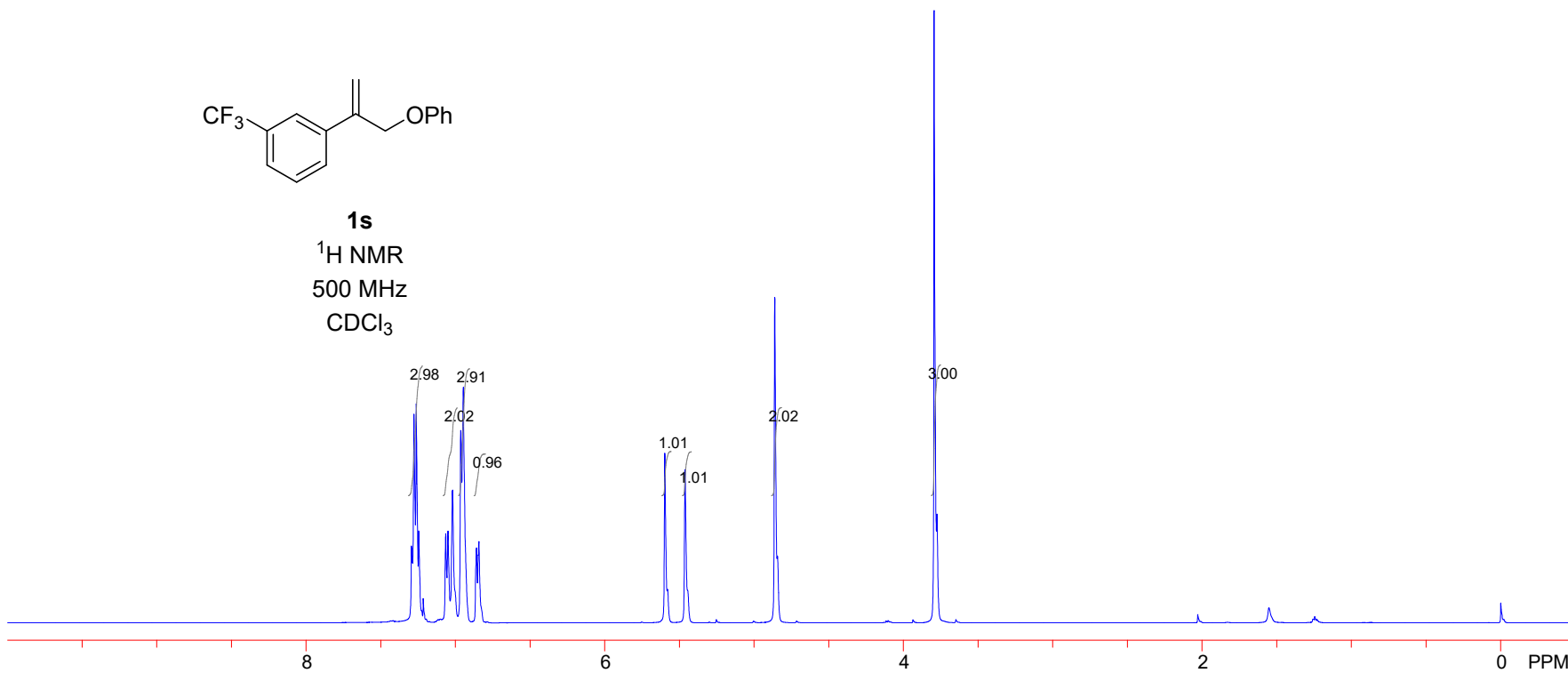
1r
¹H NMR
 400 MHz
 CDCl₃



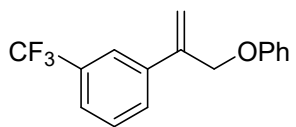




1s
¹H NMR
500 MHz
CDCl₃



S71

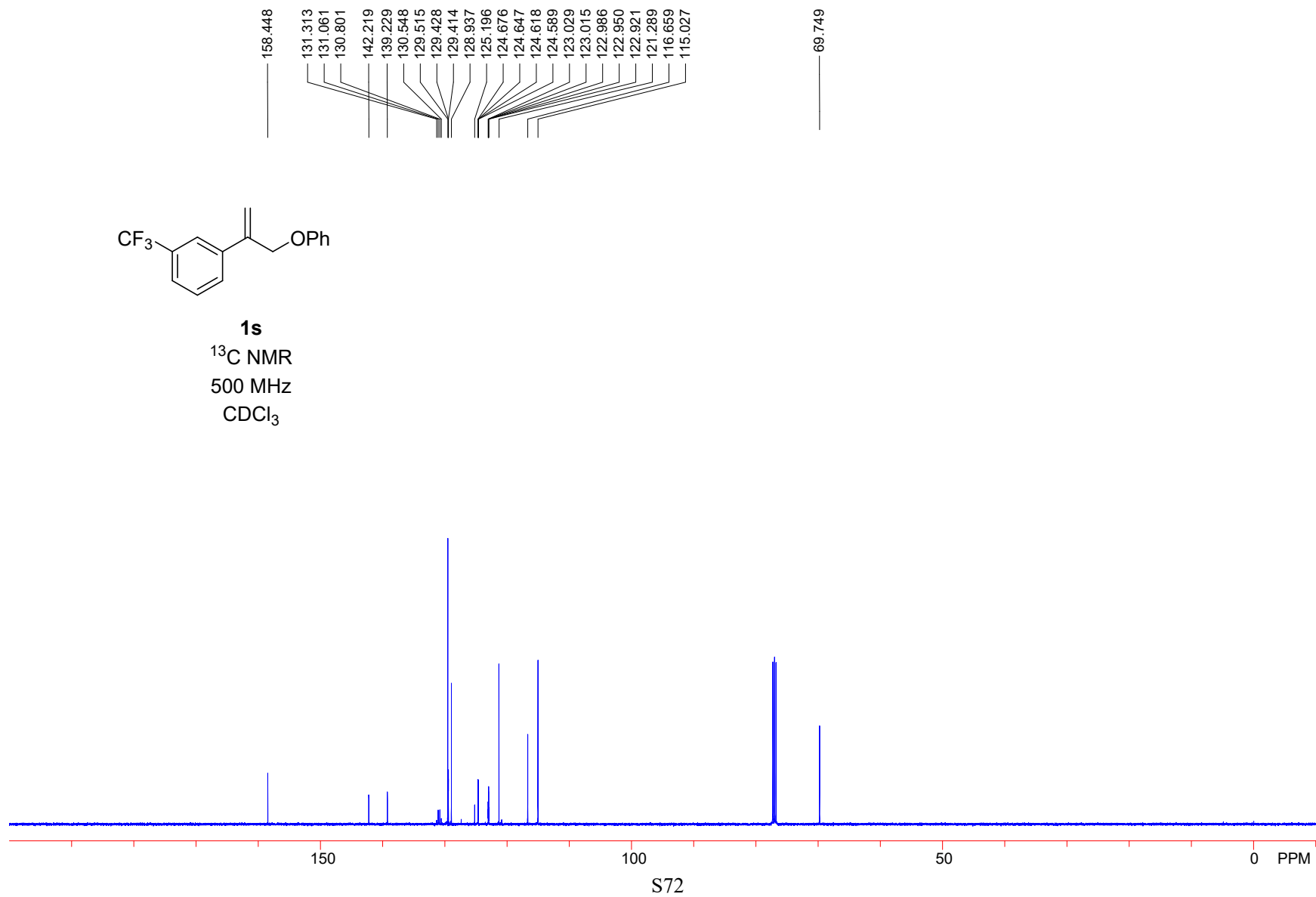


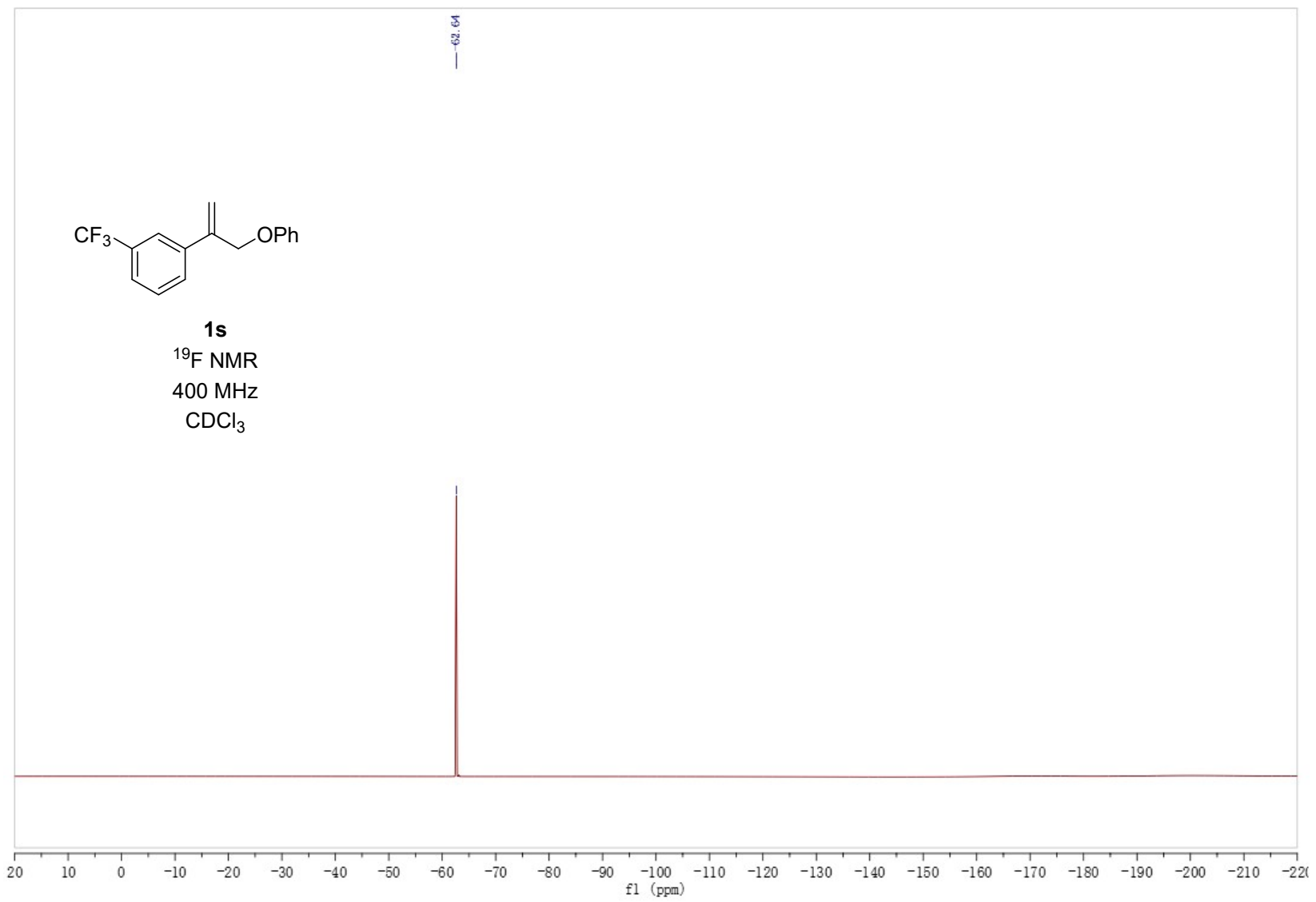
1s

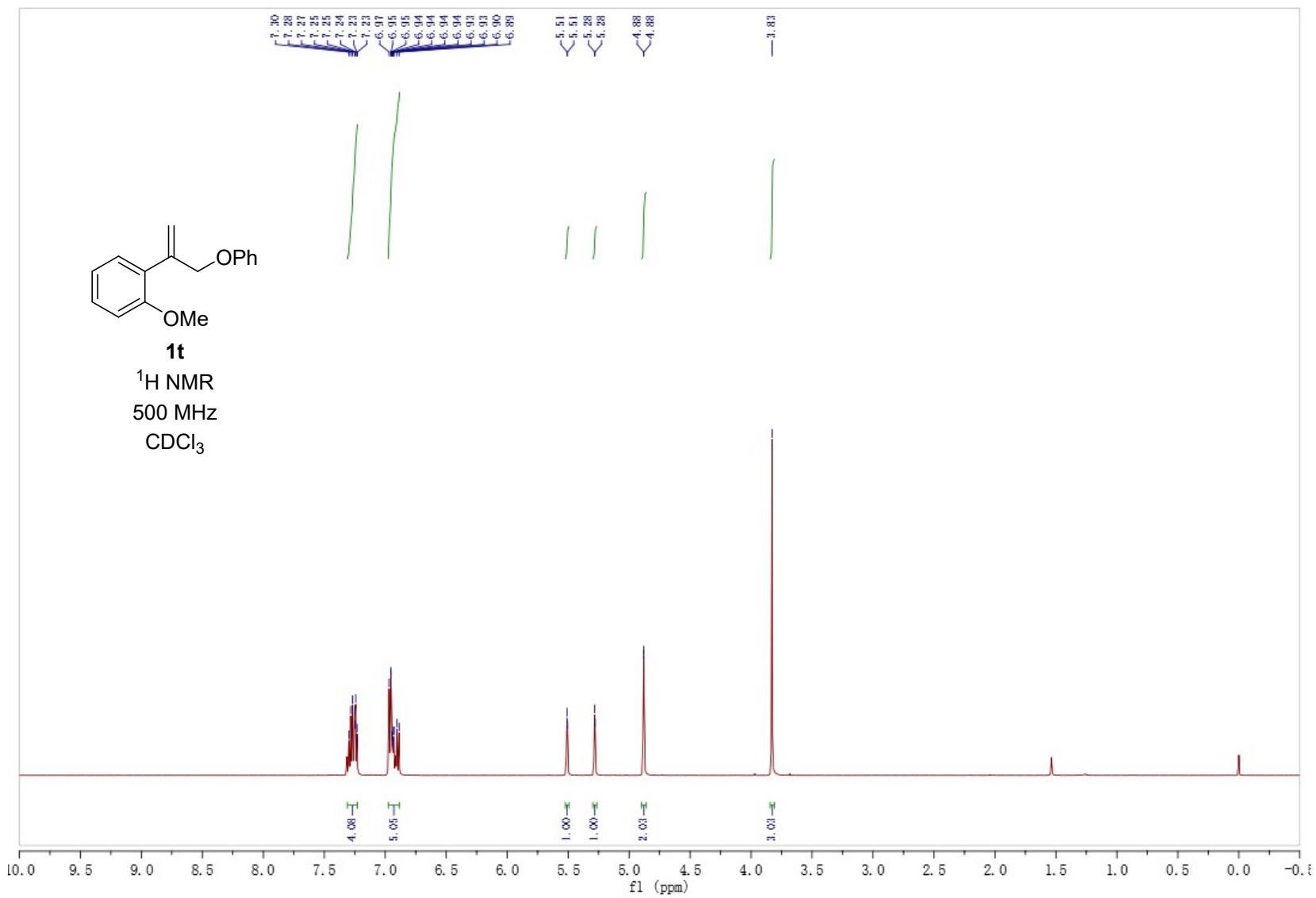
¹³C NMR

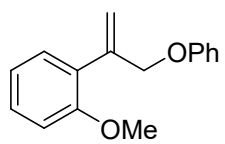
500 MHz

CDCl₃



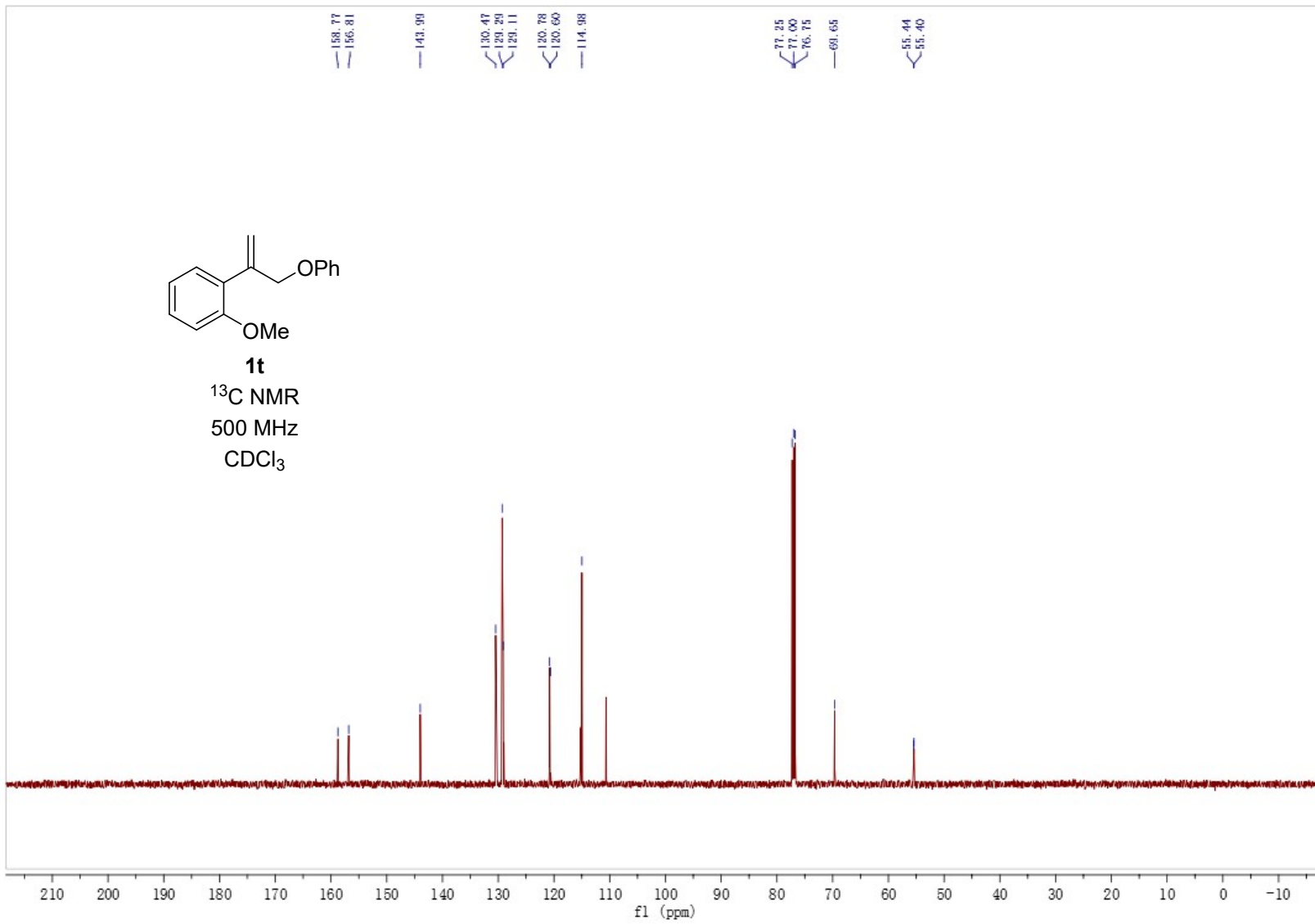


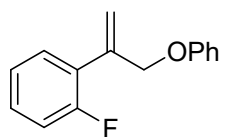
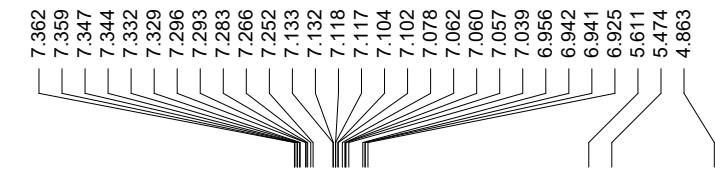




1t

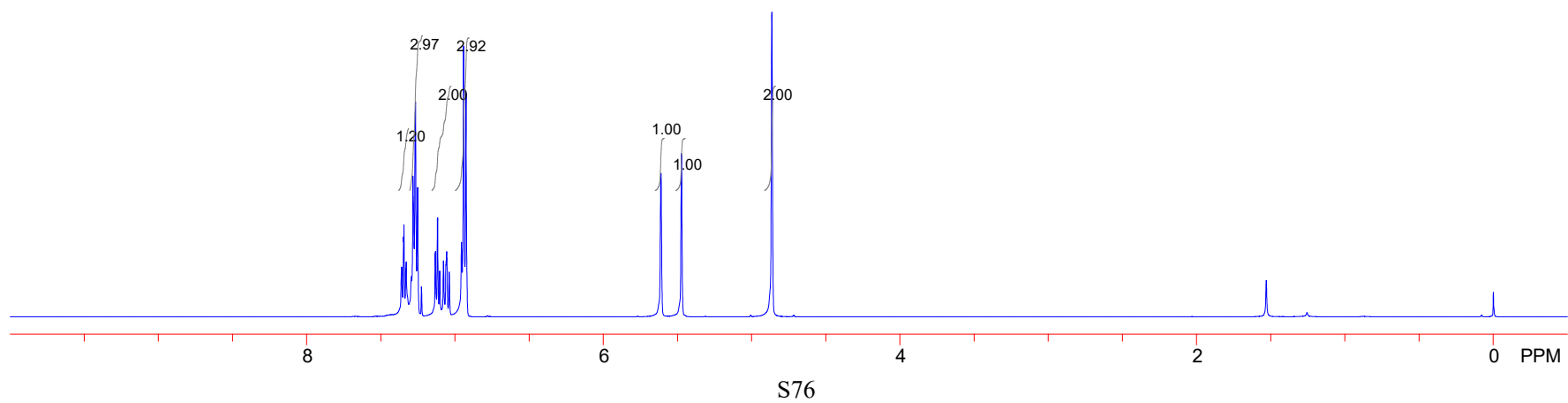
¹³C NMR
500 MHz
CDCl₃

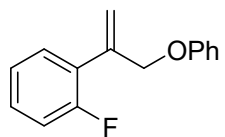




1u

¹H NMR
500 MHz
CDCl₃





1u

¹³C NMR

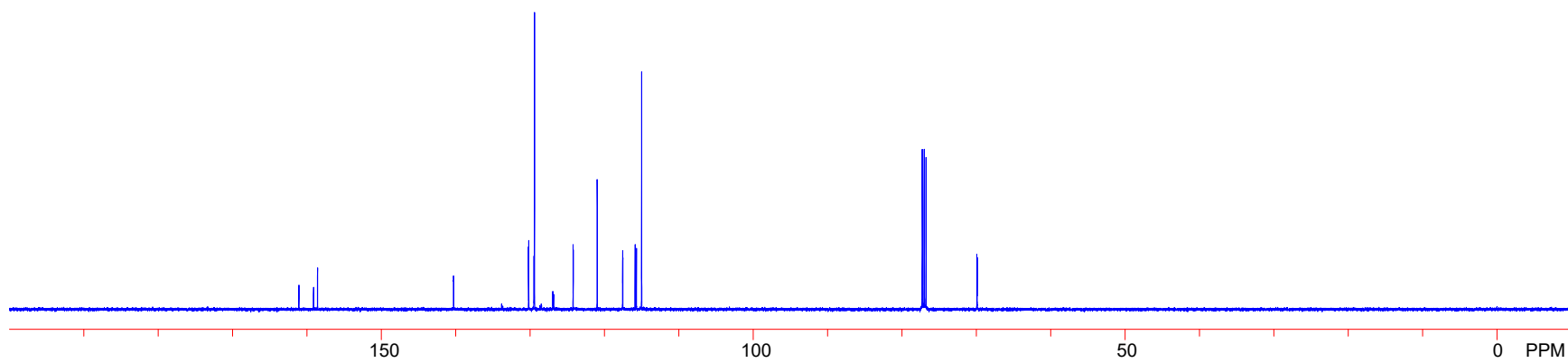
500 MHz

CDCl₃

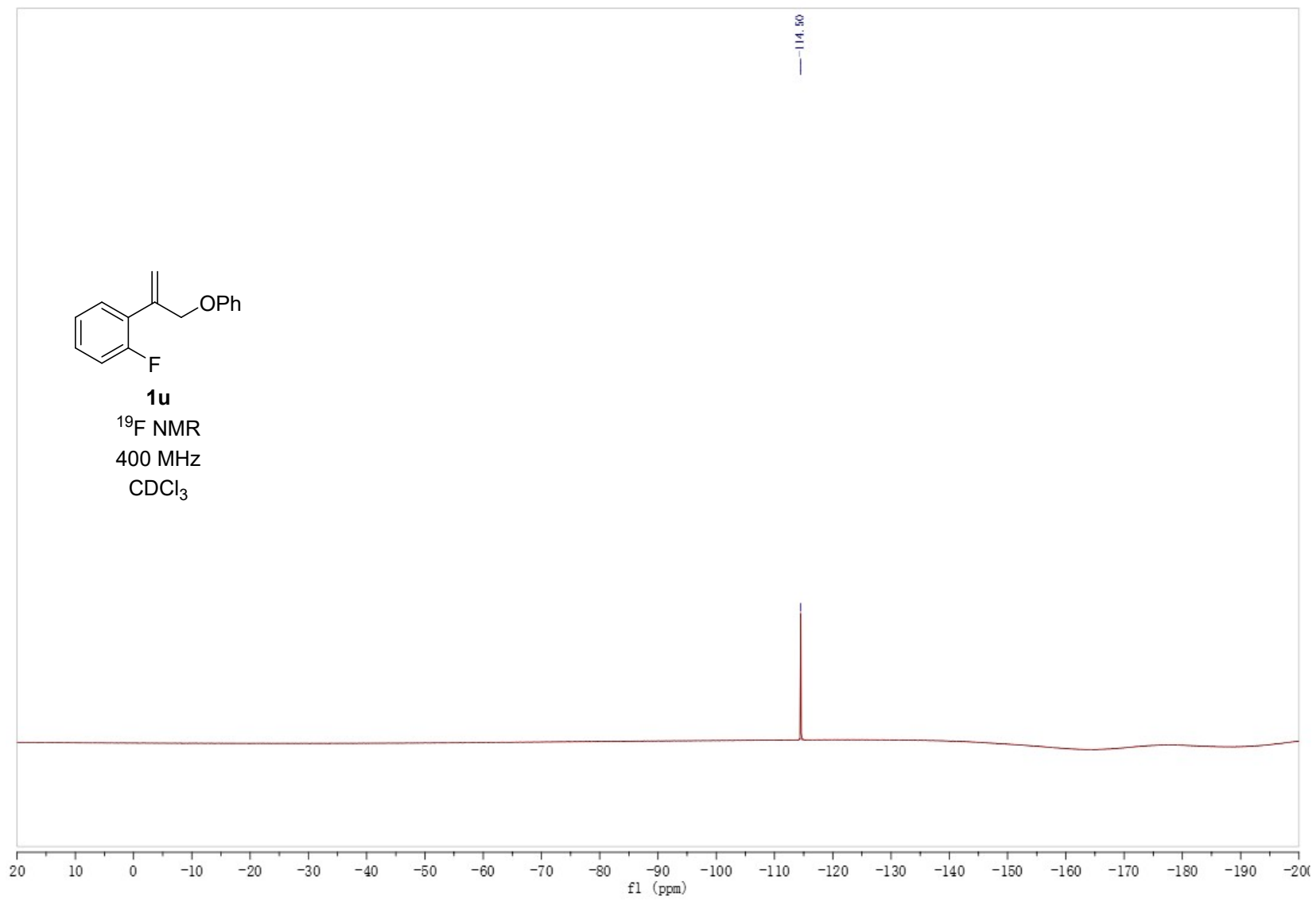
161.070
159.098
158.564

140.277
130.194
130.158
129.457
129.392
126.929
126.821
124.206
124.178
120.964
117.540
117.511
115.864
115.684
114.990

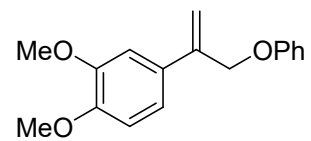
77.253
77.000
76.747
69.907



S77

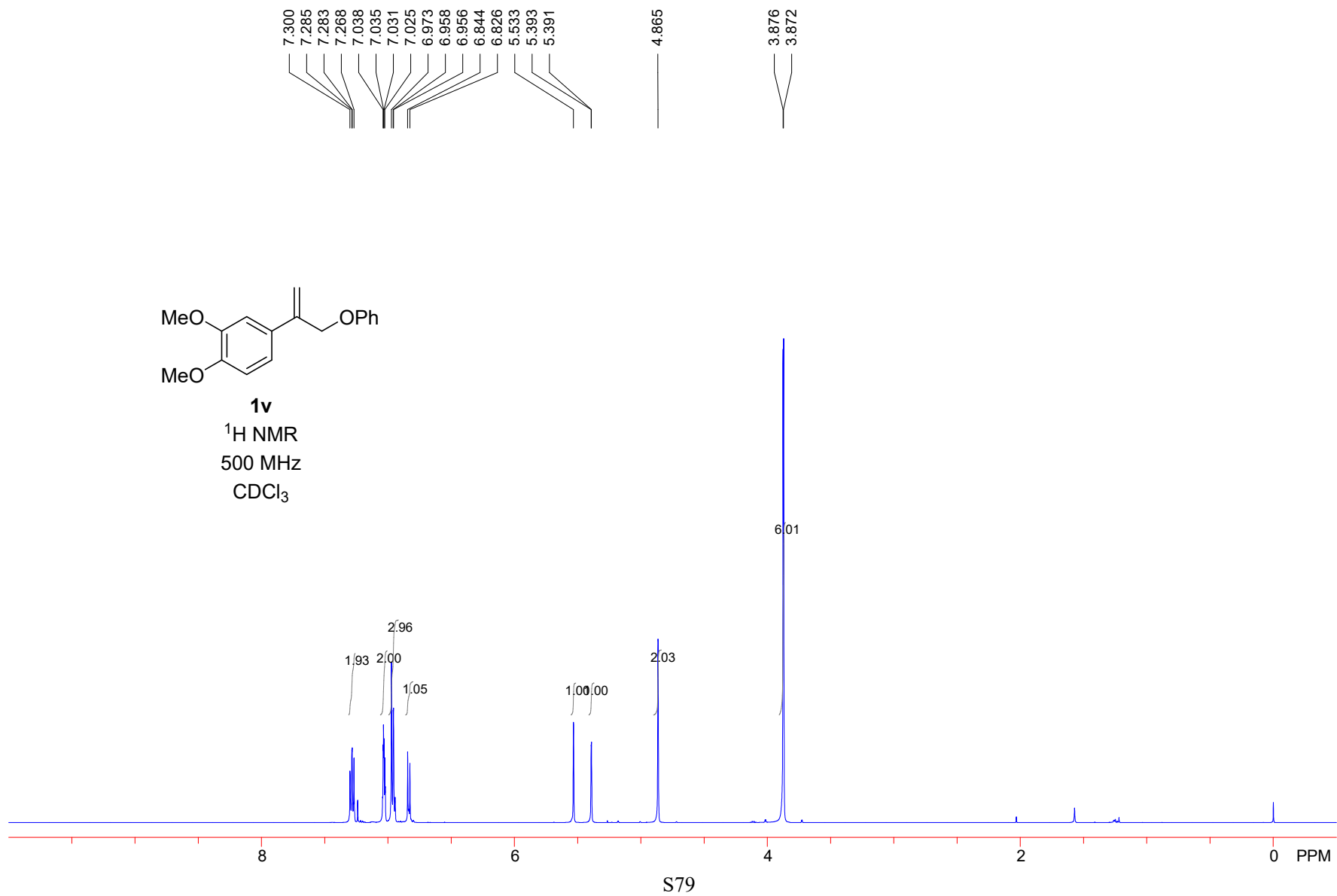


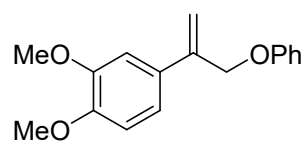
S78



1v

¹H NMR
500 MHz
CDCl₃

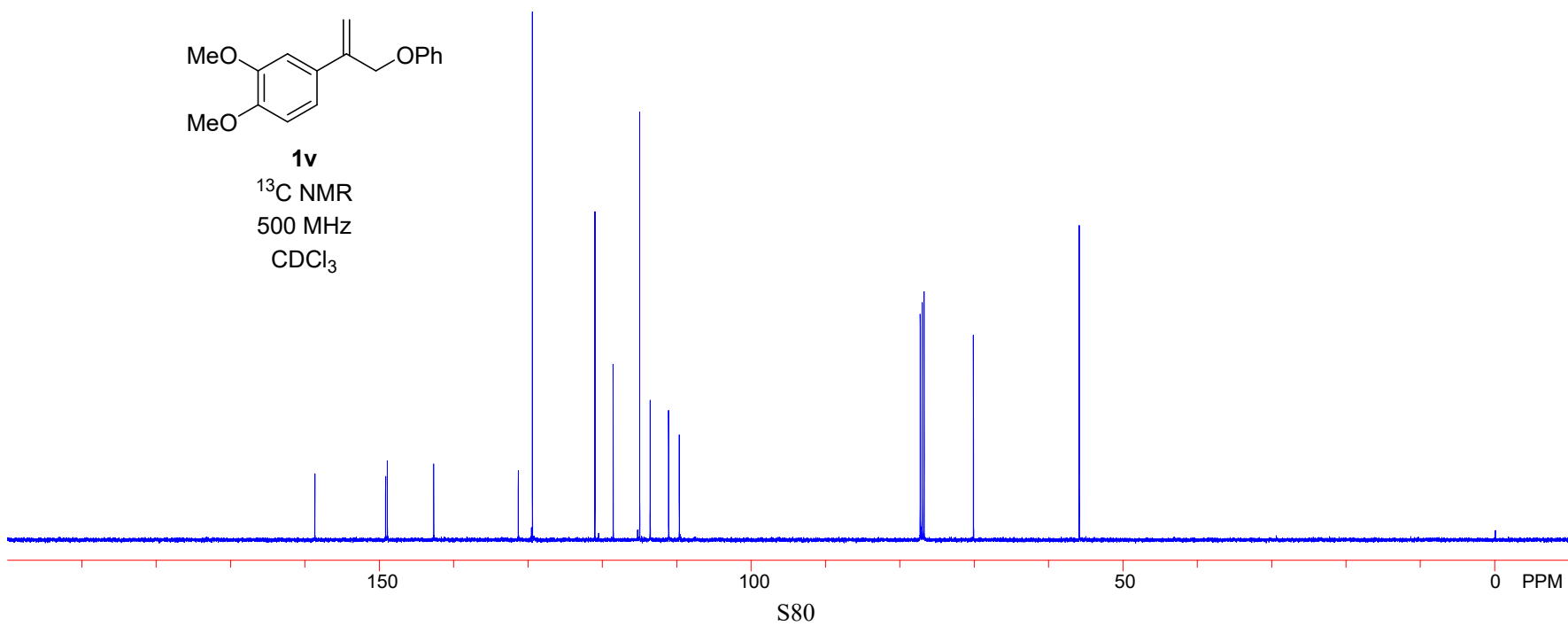


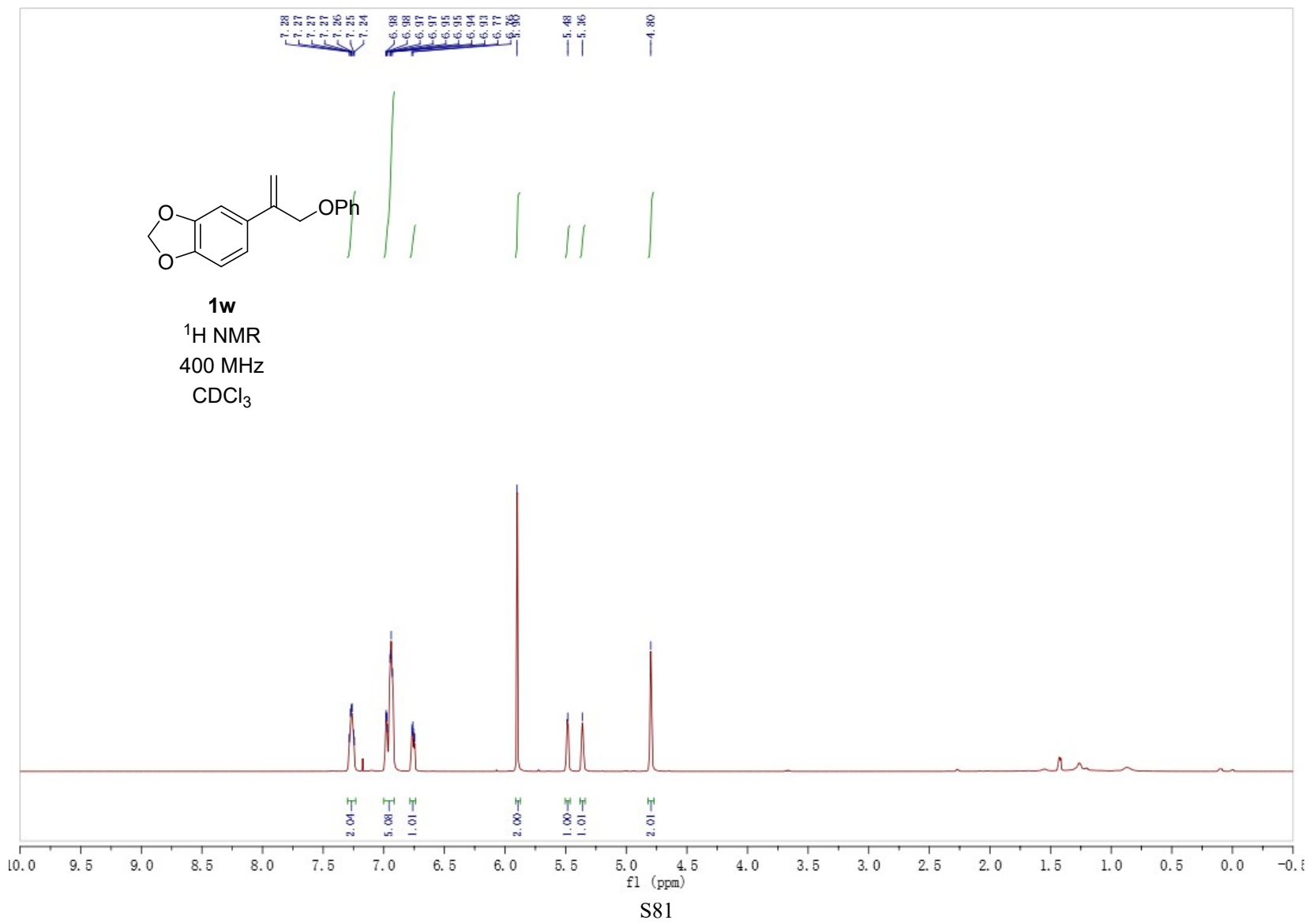


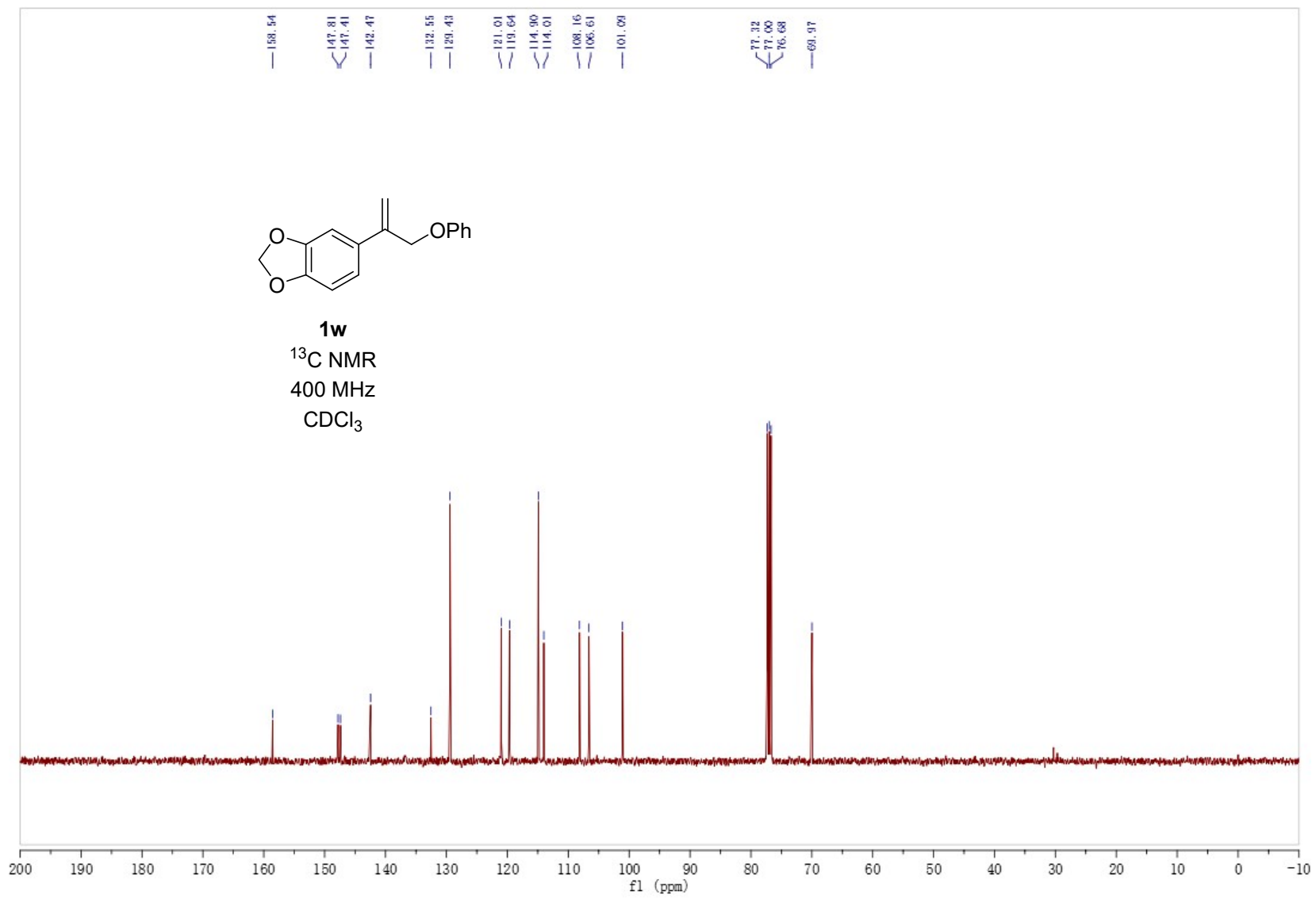
1v

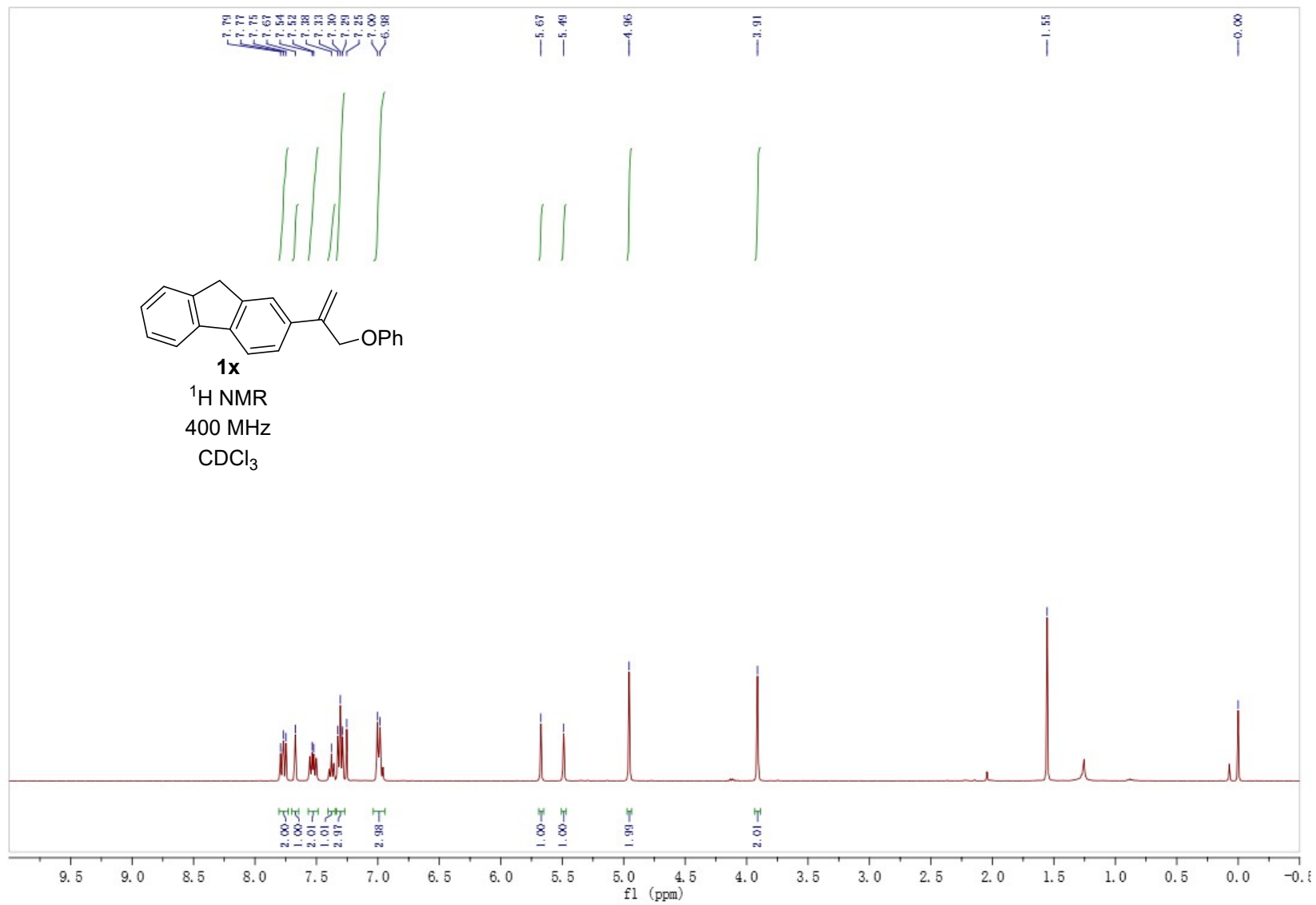
¹³C NMR
500 MHz
CDCl₃

158.665
149.146
148.915
142.689
131.306
129.407
121.007
118.551
114.990
113.568
111.098
109.660
77.260
77.000
76.747
70.110
55.889

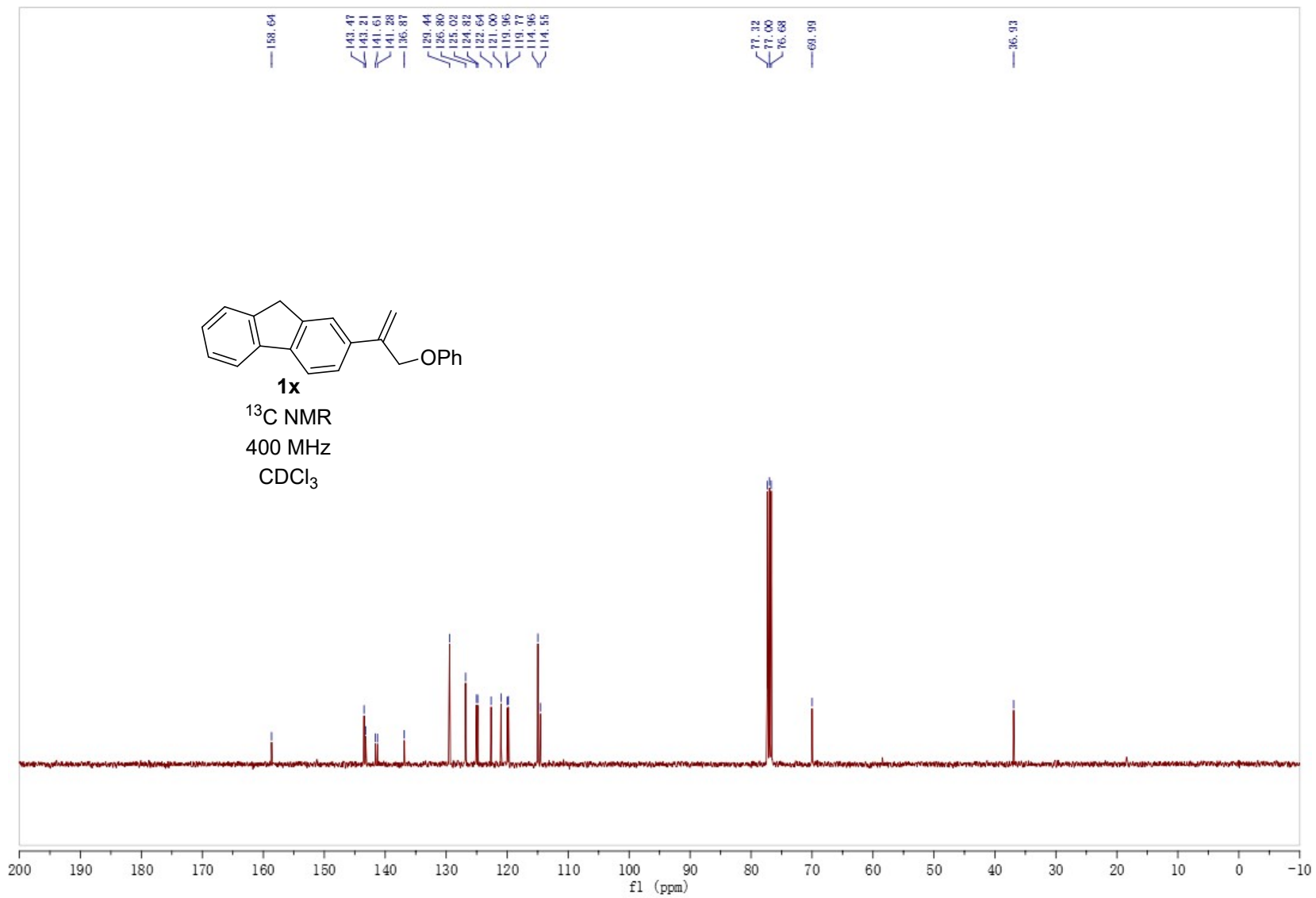


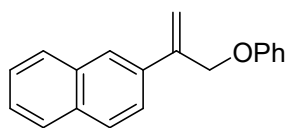
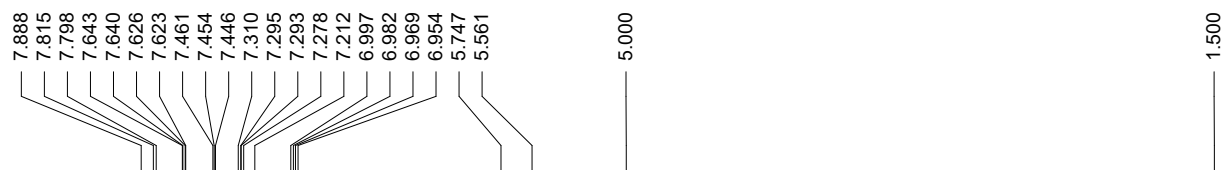




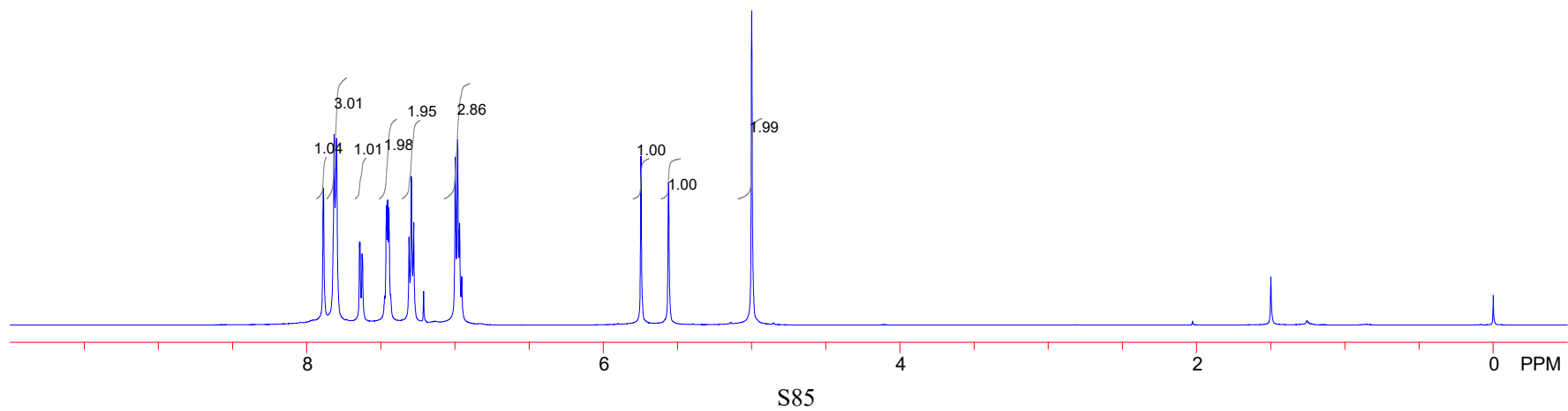


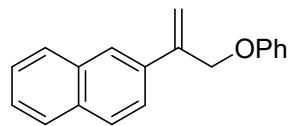
S83





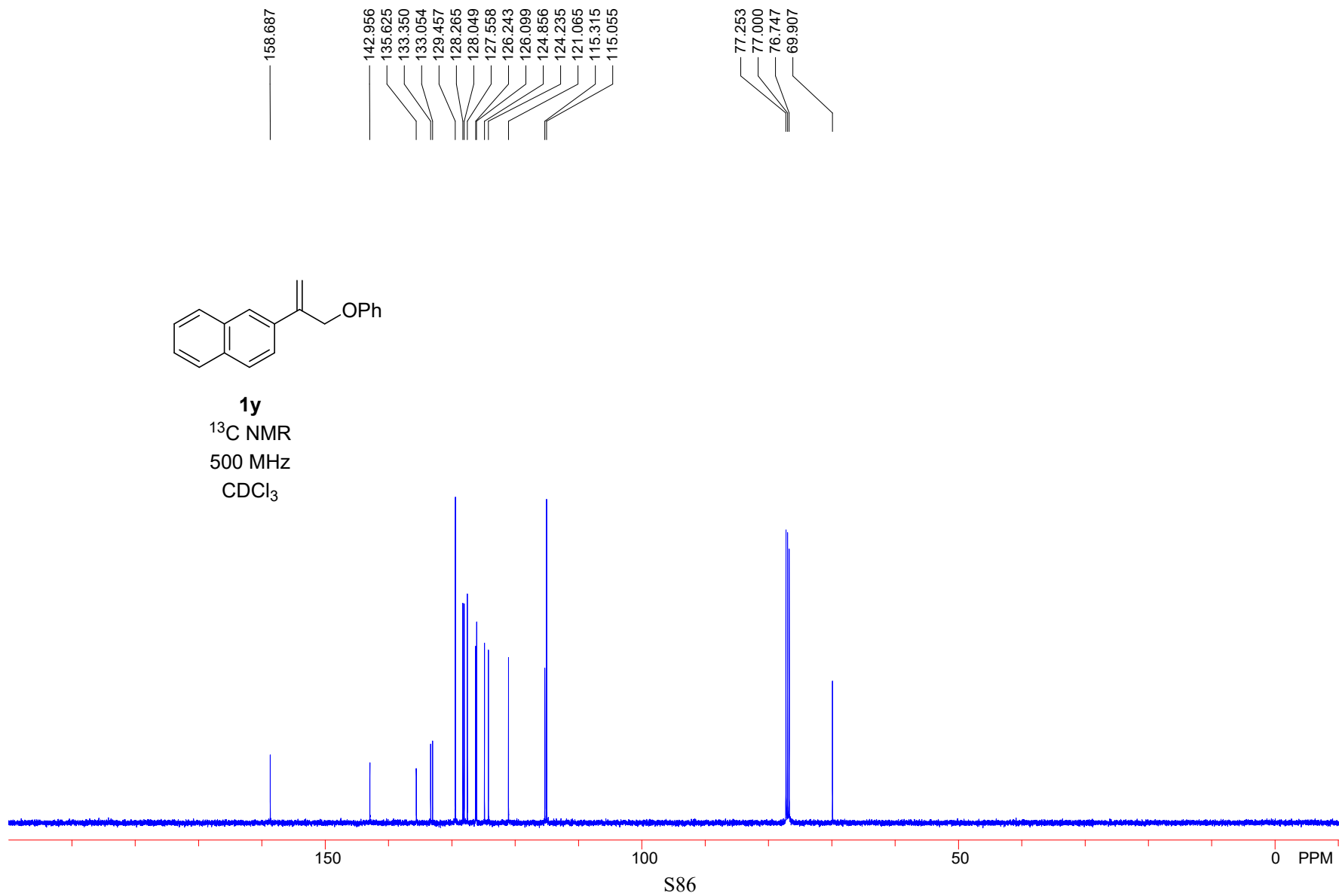
1y
¹H NMR
 500 MHz
 CDCl₃



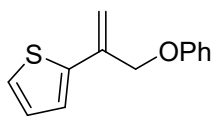


1y

¹³C NMR
500 MHz
CDCl₃

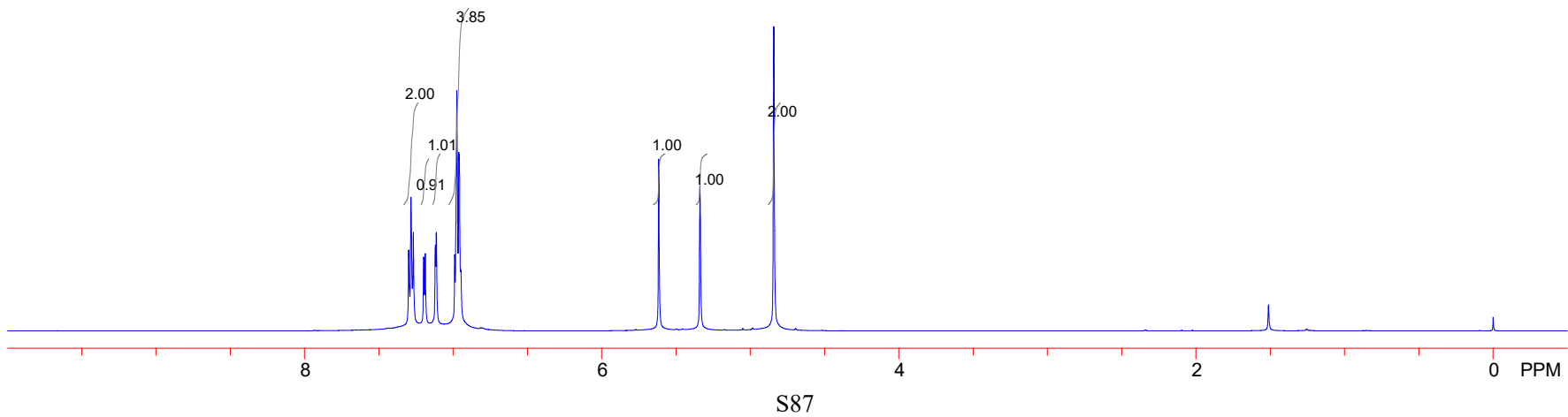


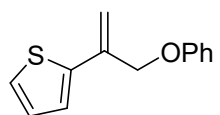
7.299
7.283
7.273
7.267
7.198
7.197
7.188
7.187
7.119
7.113
6.989
6.975
6.961
6.959
6.949
6.947
5.616
5.338
4.841



1z

¹H NMR
500 MHz
CDCl₃





1z

¹³C NMR
500 MHz
CDCl₃

158.499

141.894

137.019

129.457

127.406

124.654

123.968

121.151

114.954

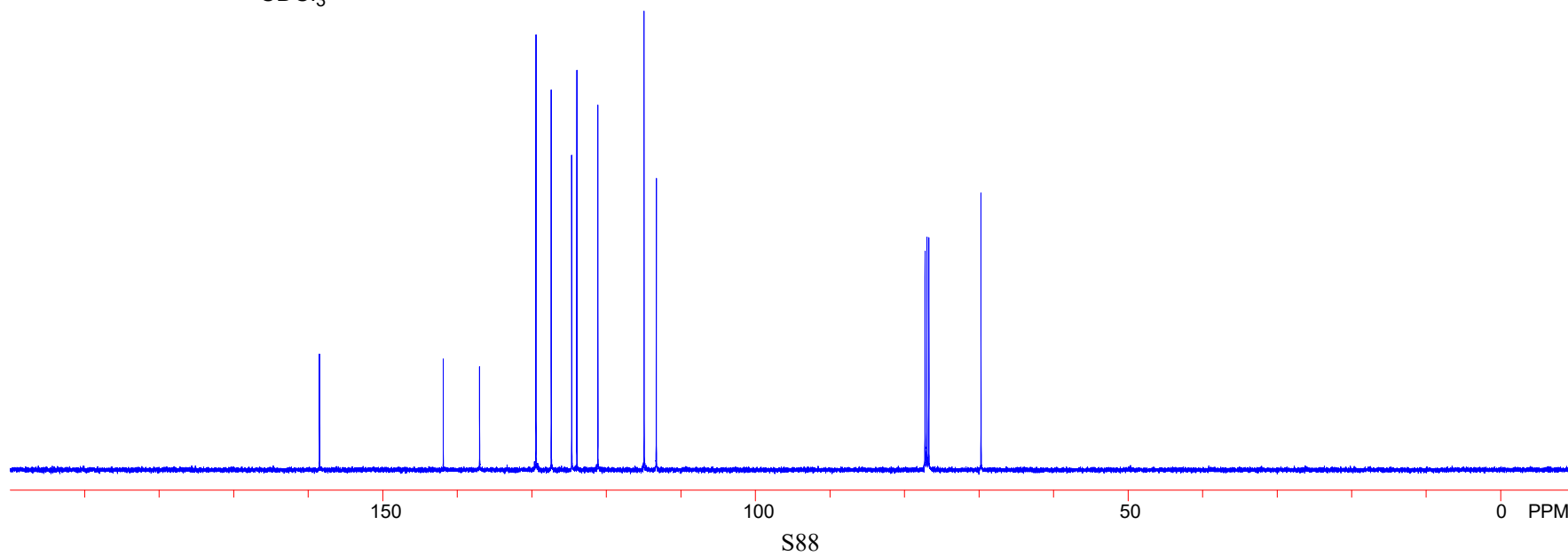
113.308

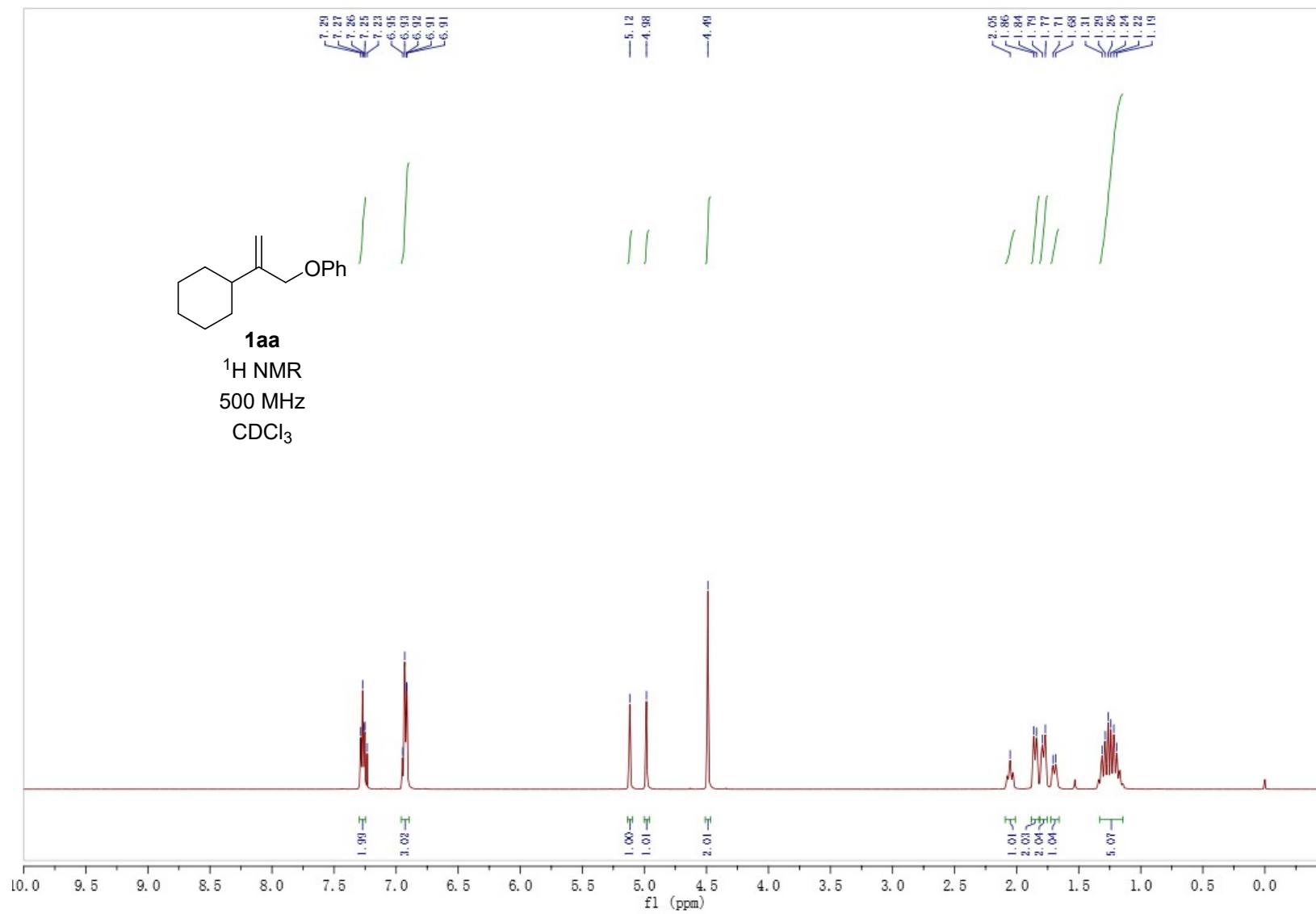
77.253

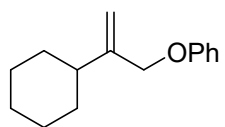
77.000

76.747

69.749

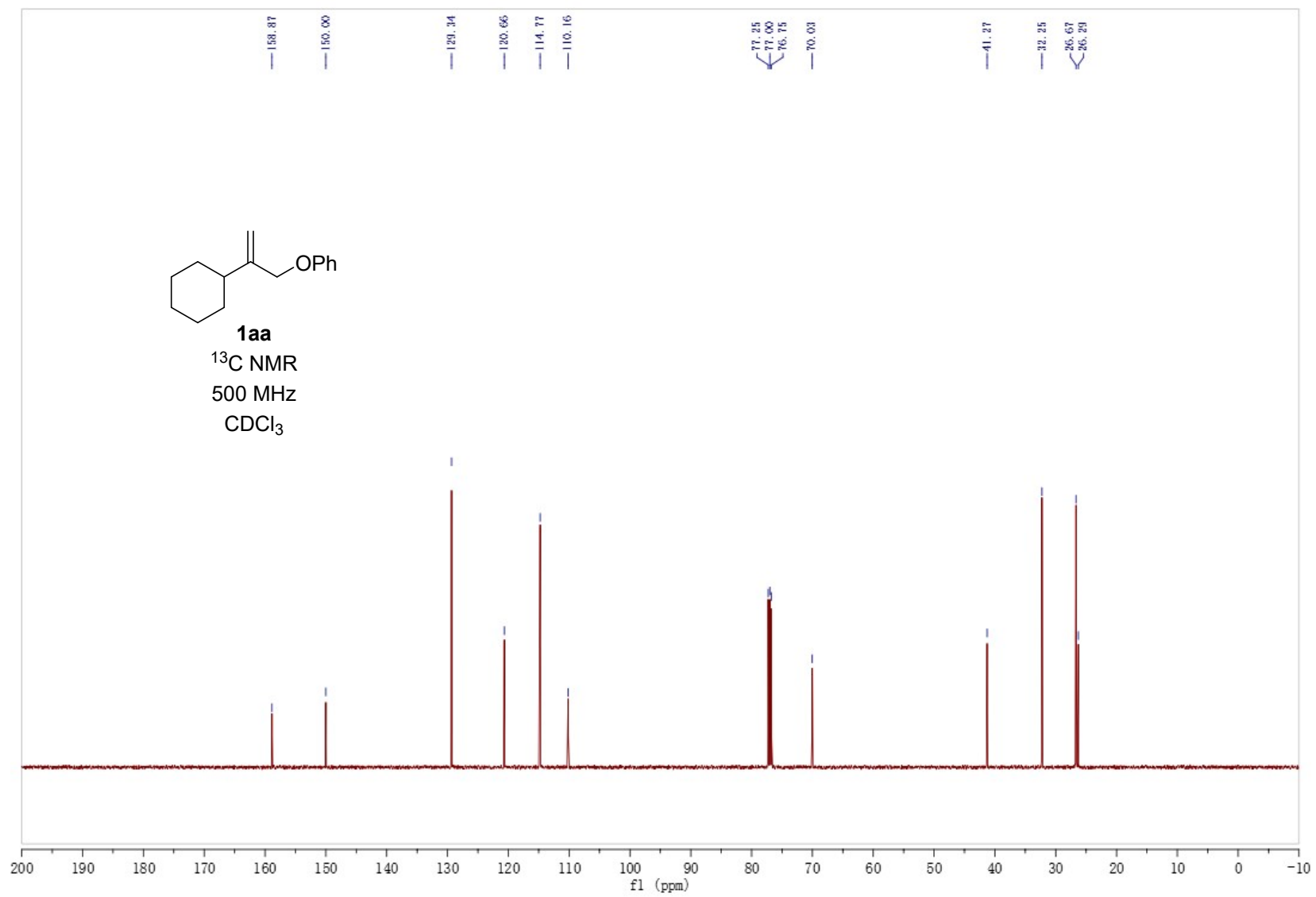




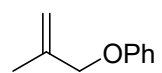


1aa

¹³C NMR
500 MHz
CDCl₃

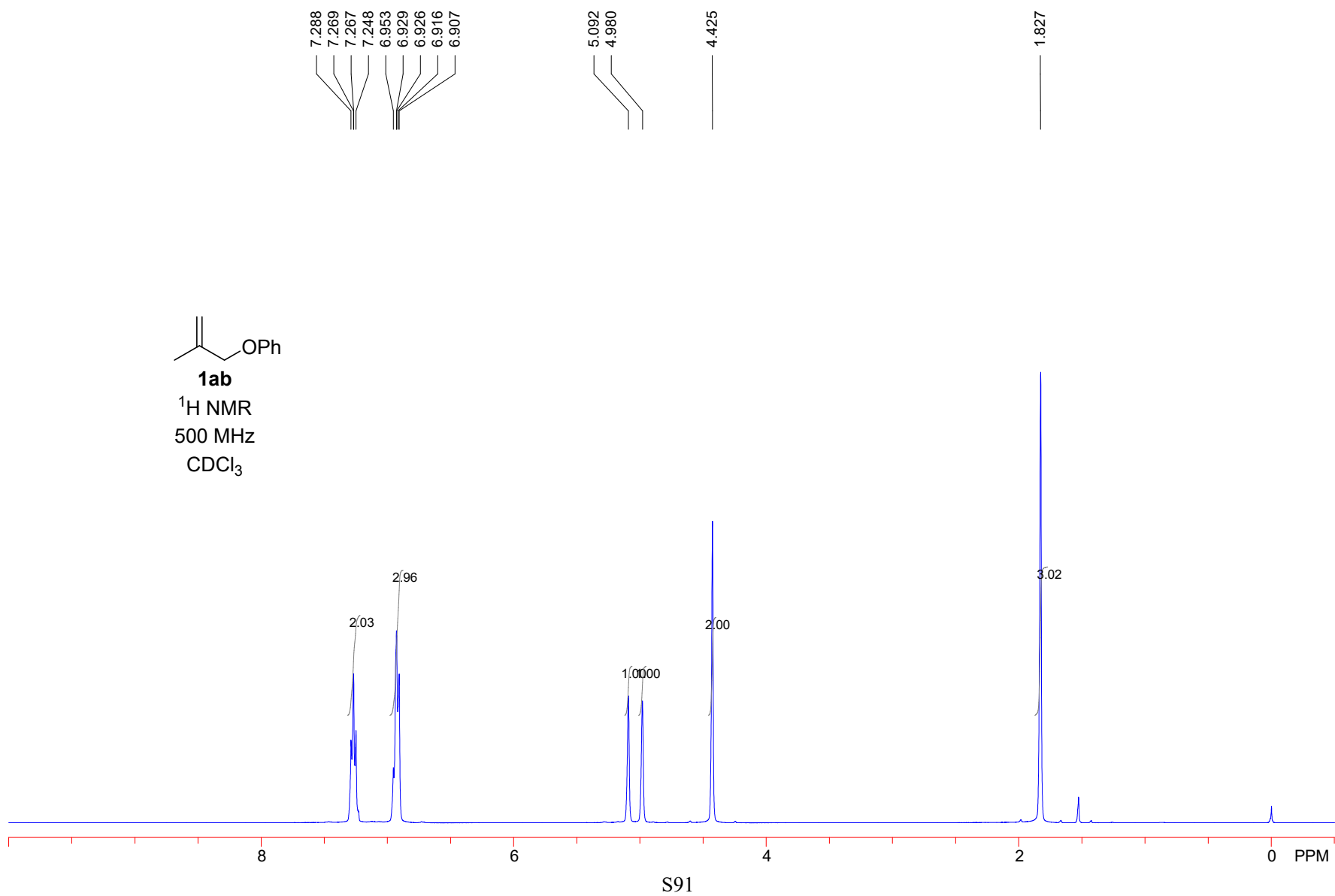


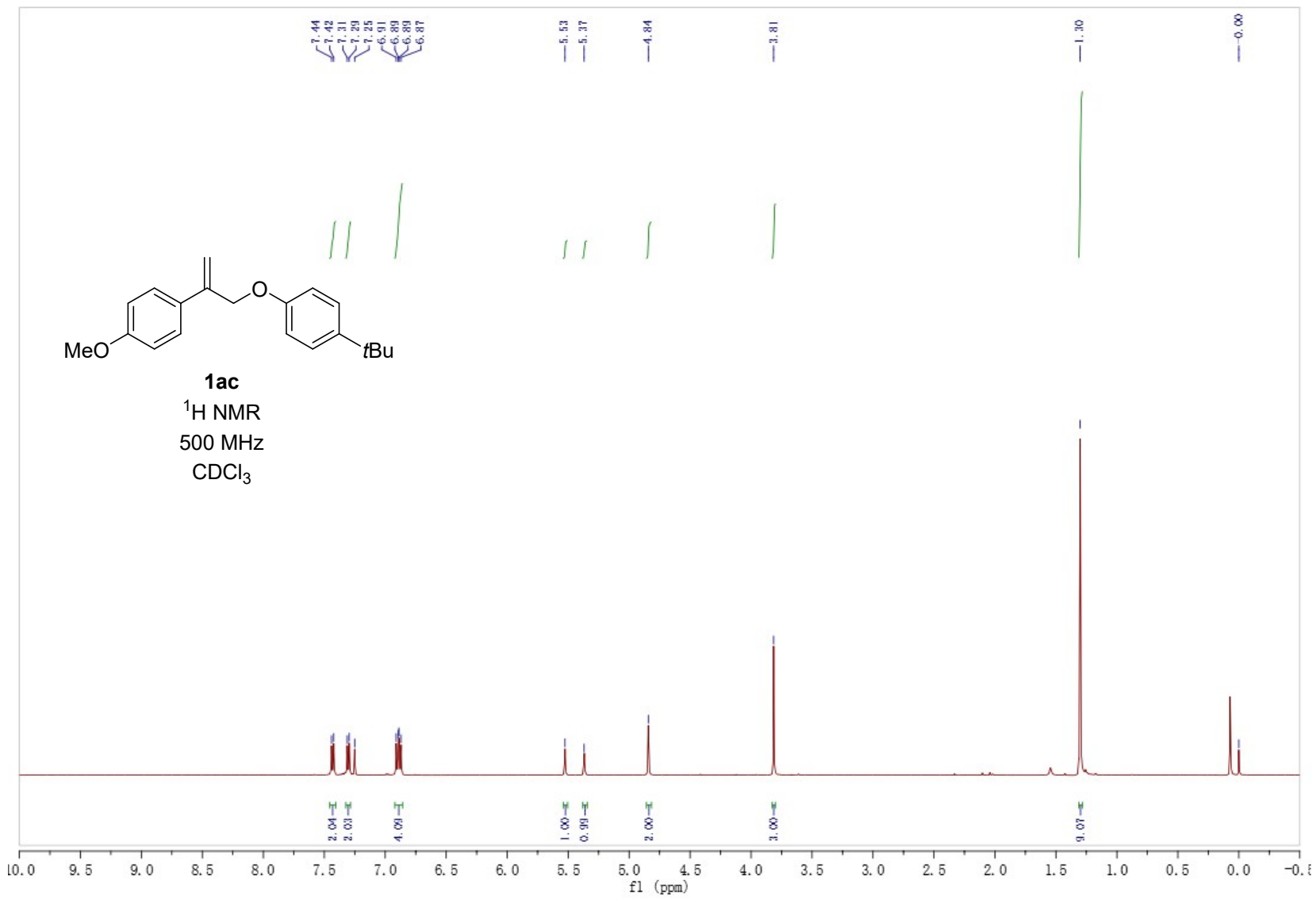
S90

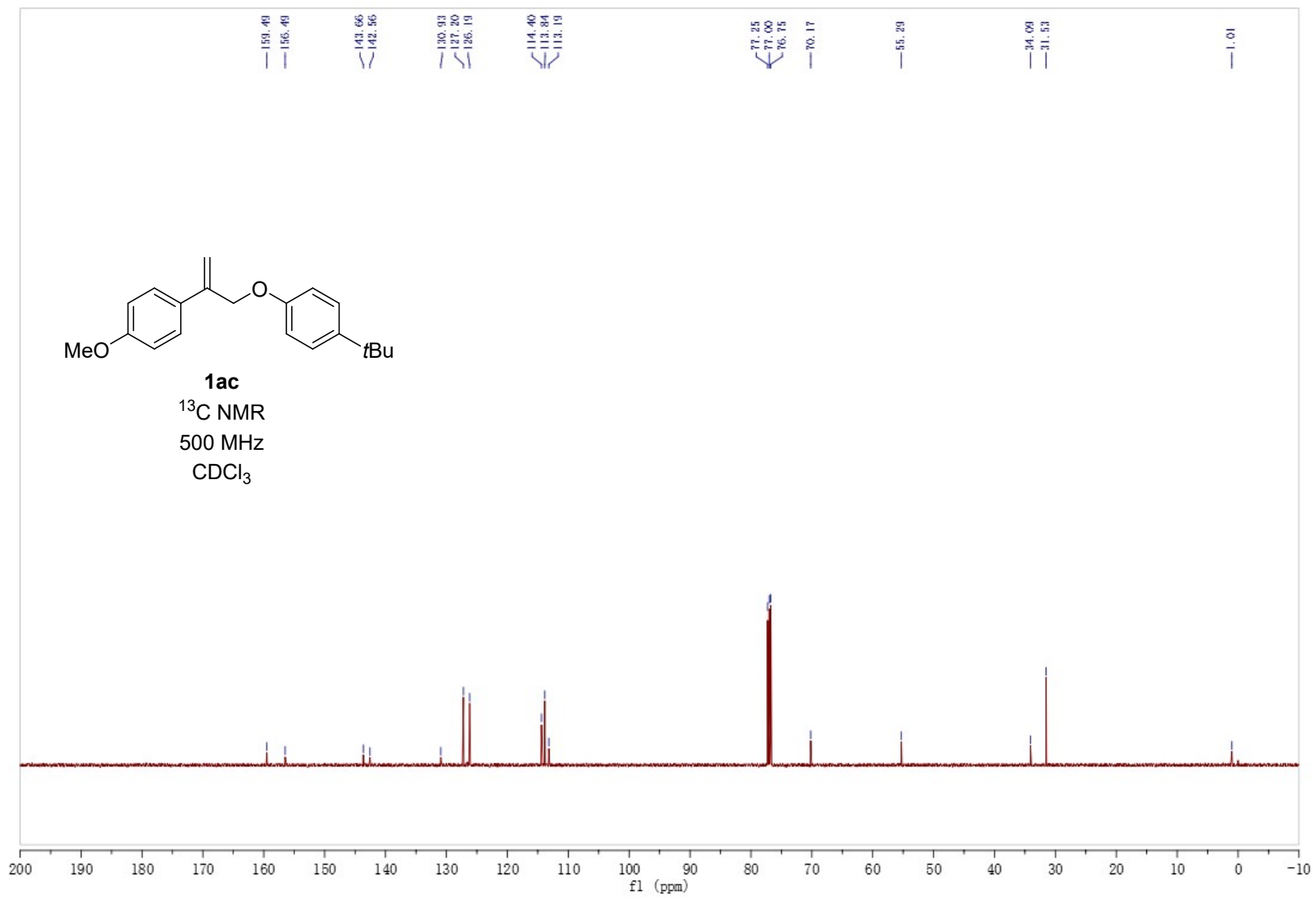


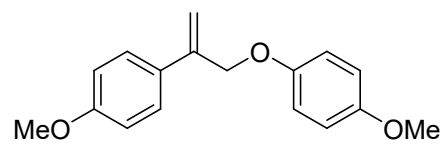
1ab

¹H NMR
500 MHz
CDCl₃







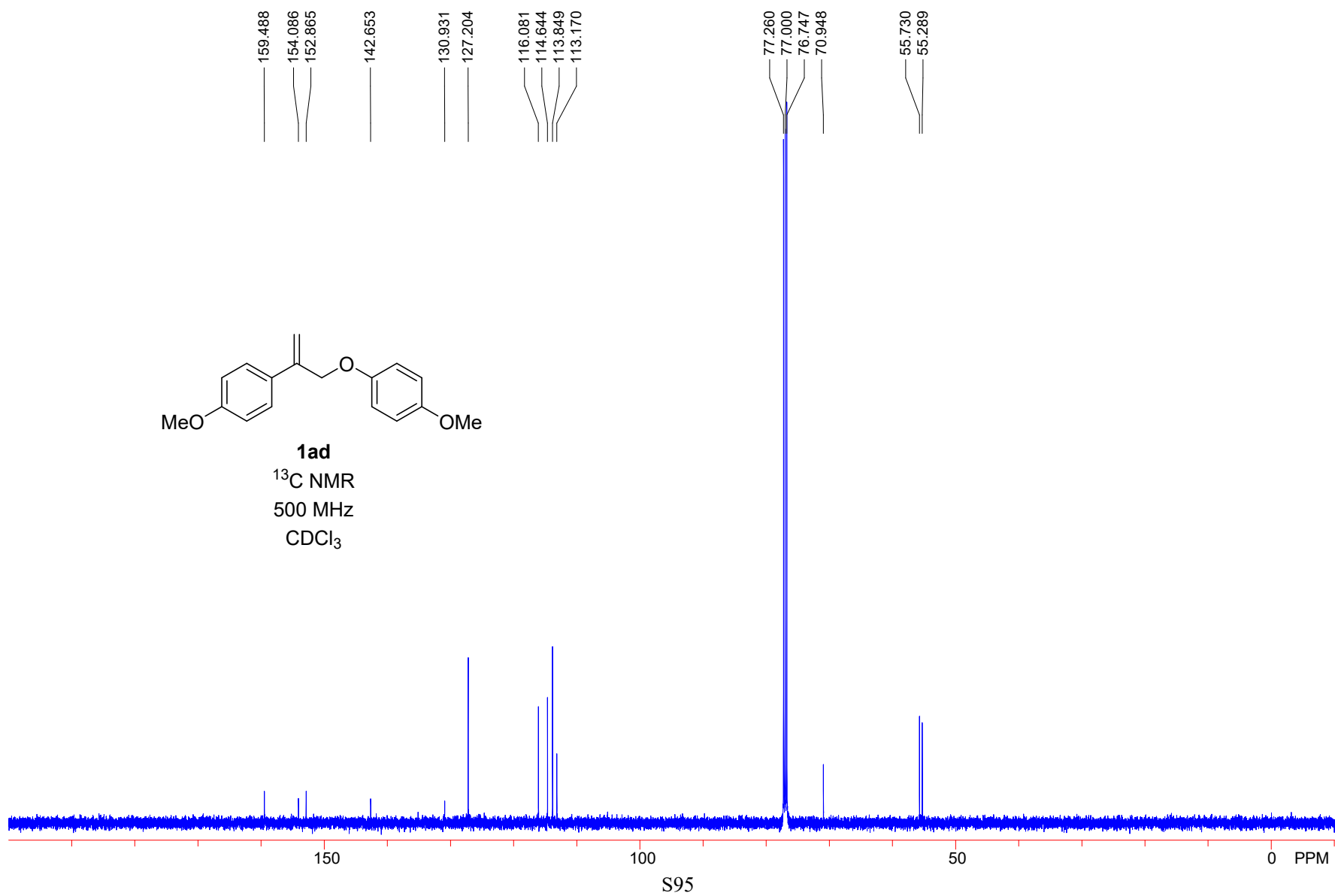


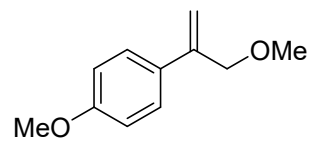
1ad

¹³C NMR

500 MHz

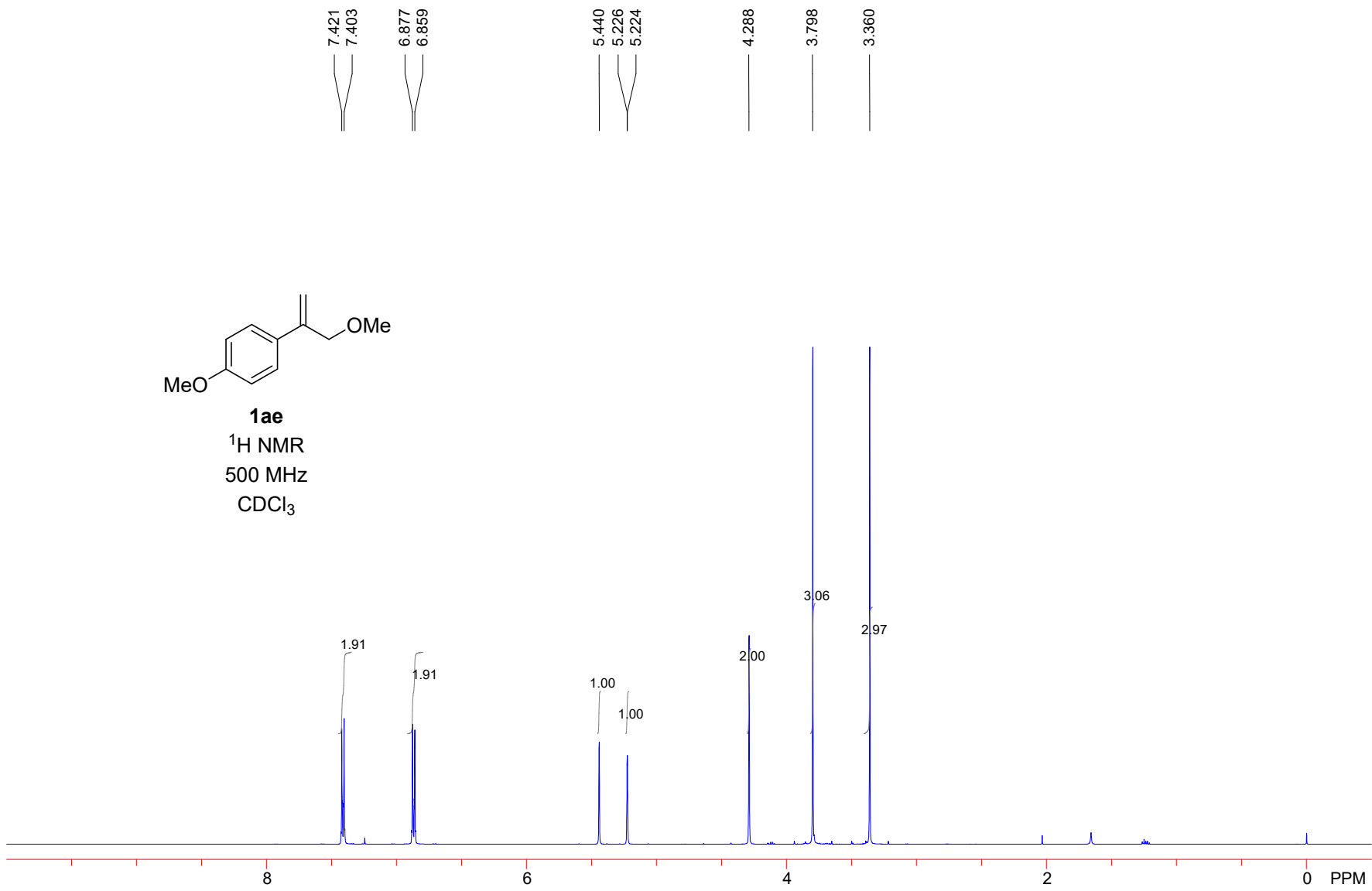
CDCl₃



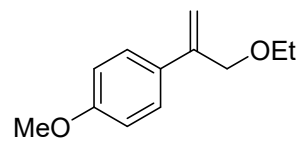


1ae

¹H NMR
500 MHz
CDCl₃

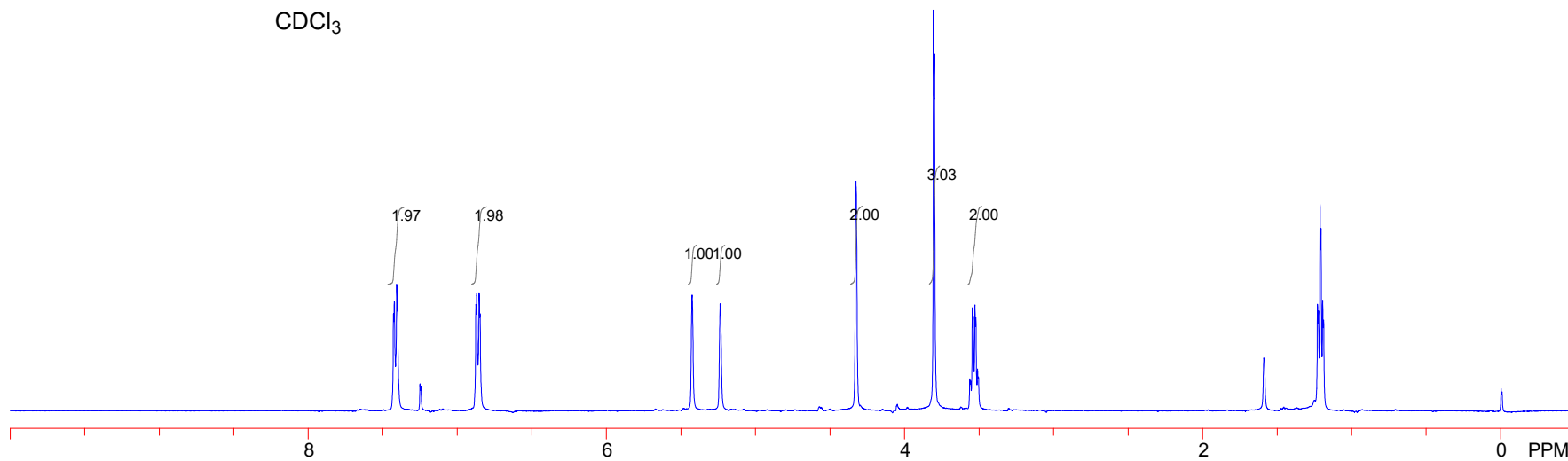
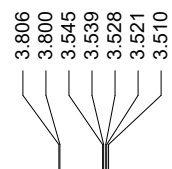
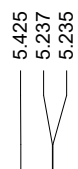
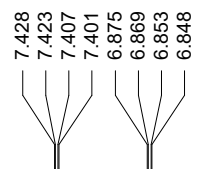


S96

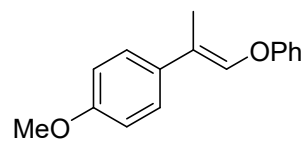


1af

¹H NMR
500 MHz
CDCl₃



S97



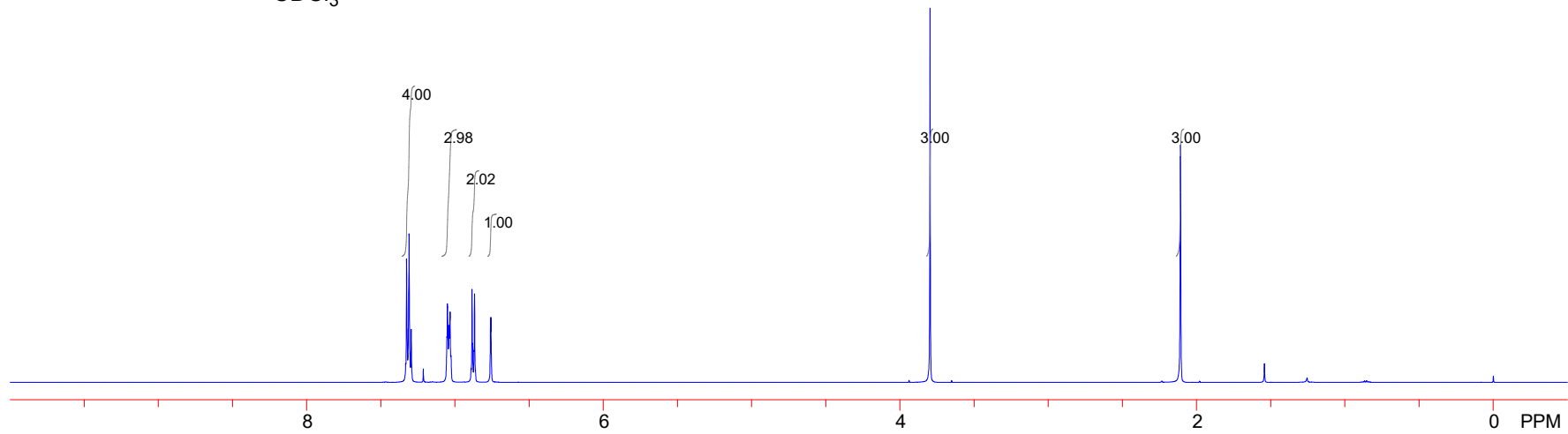
2a

¹H NMR
500 MHz
CDCl₃

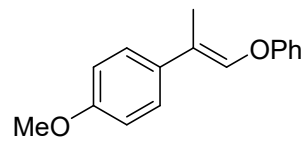
7.327
7.309
7.295
7.055
7.051
7.050
7.041
7.039
7.034
7.033
6.886
6.881
6.868
6.760
6.758

3.797

2.111
2.109

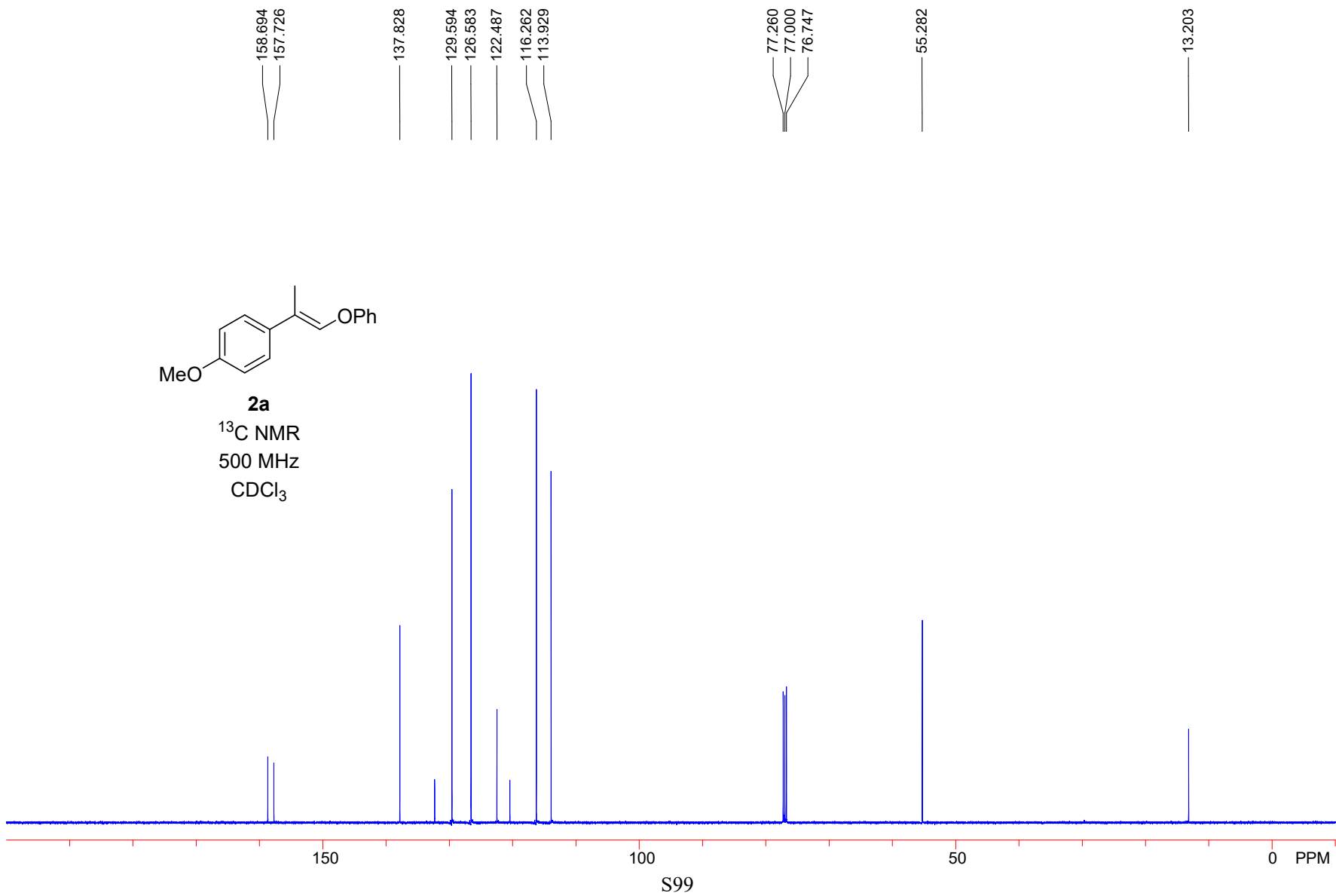


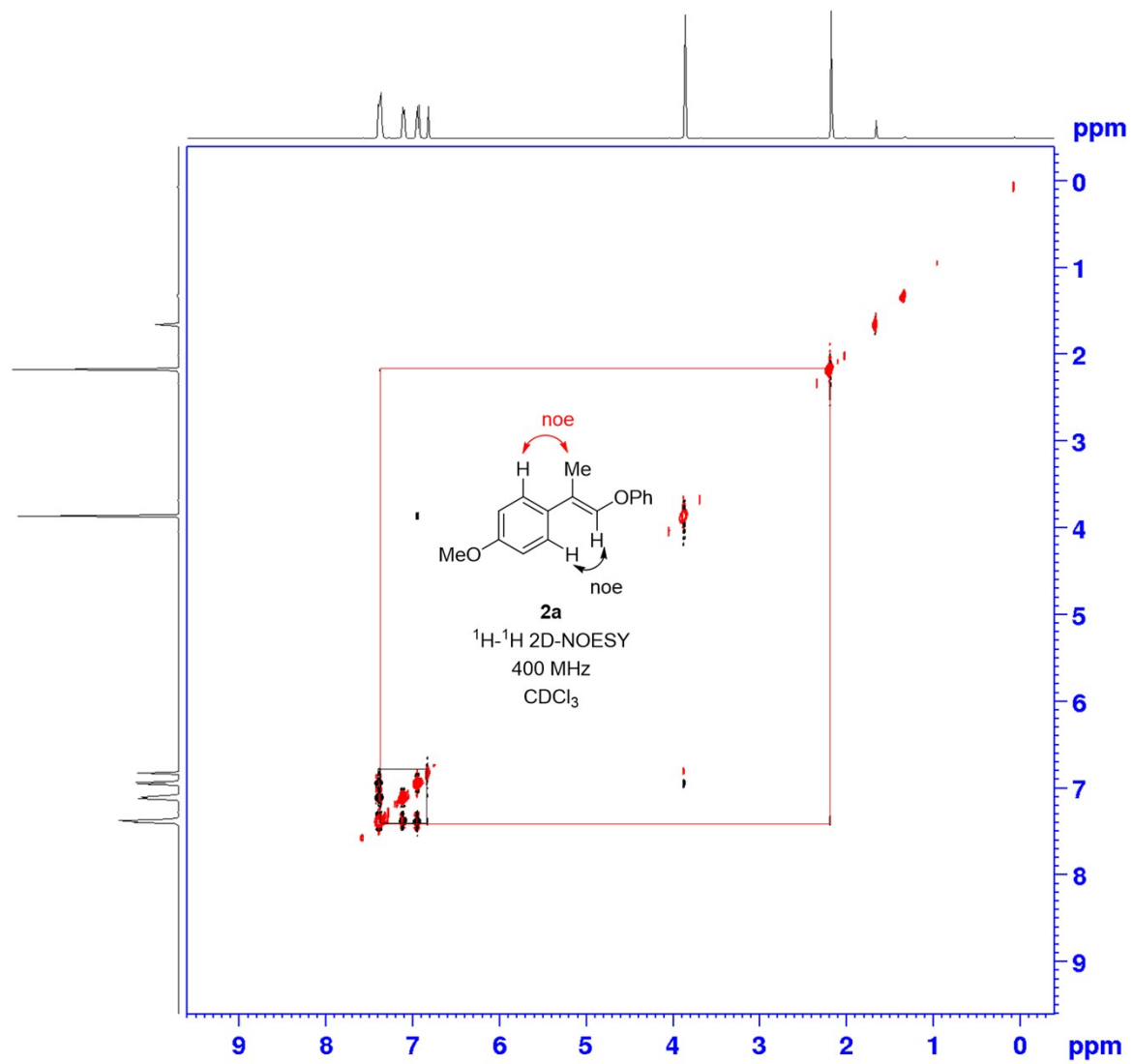
S98



2a

¹³C NMR
500 MHz
CDCl₃

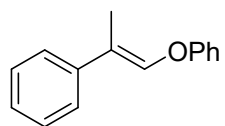




S100

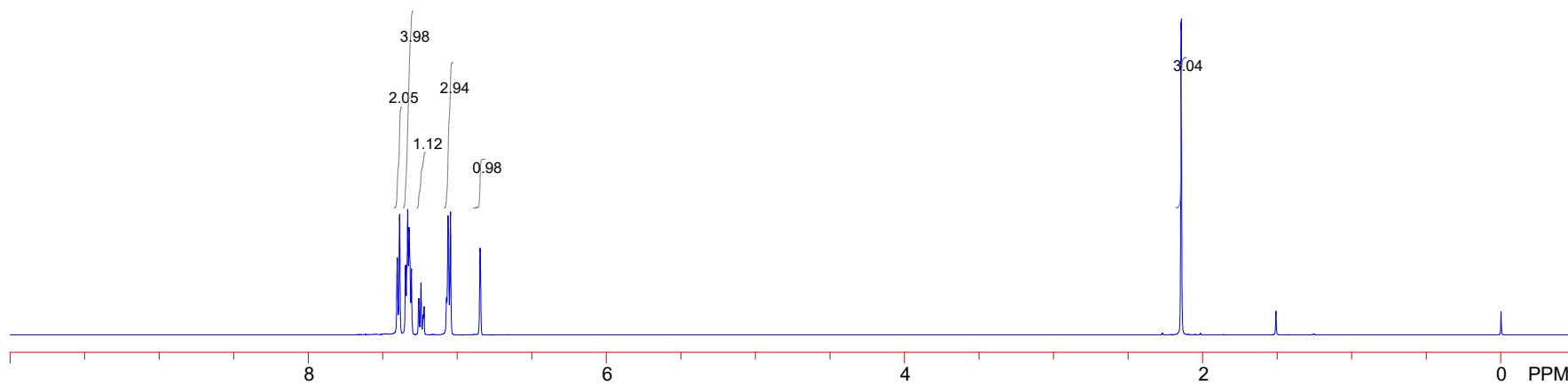
7.402
7.387
7.348
7.339
7.333
7.324
7.308
7.259
7.244
7.072
7.063
7.059
7.046
6.848
6.846

2.146
2.144

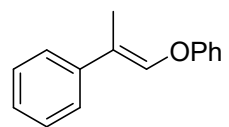


2b

¹H NMR
500 MHz
CDCl₃

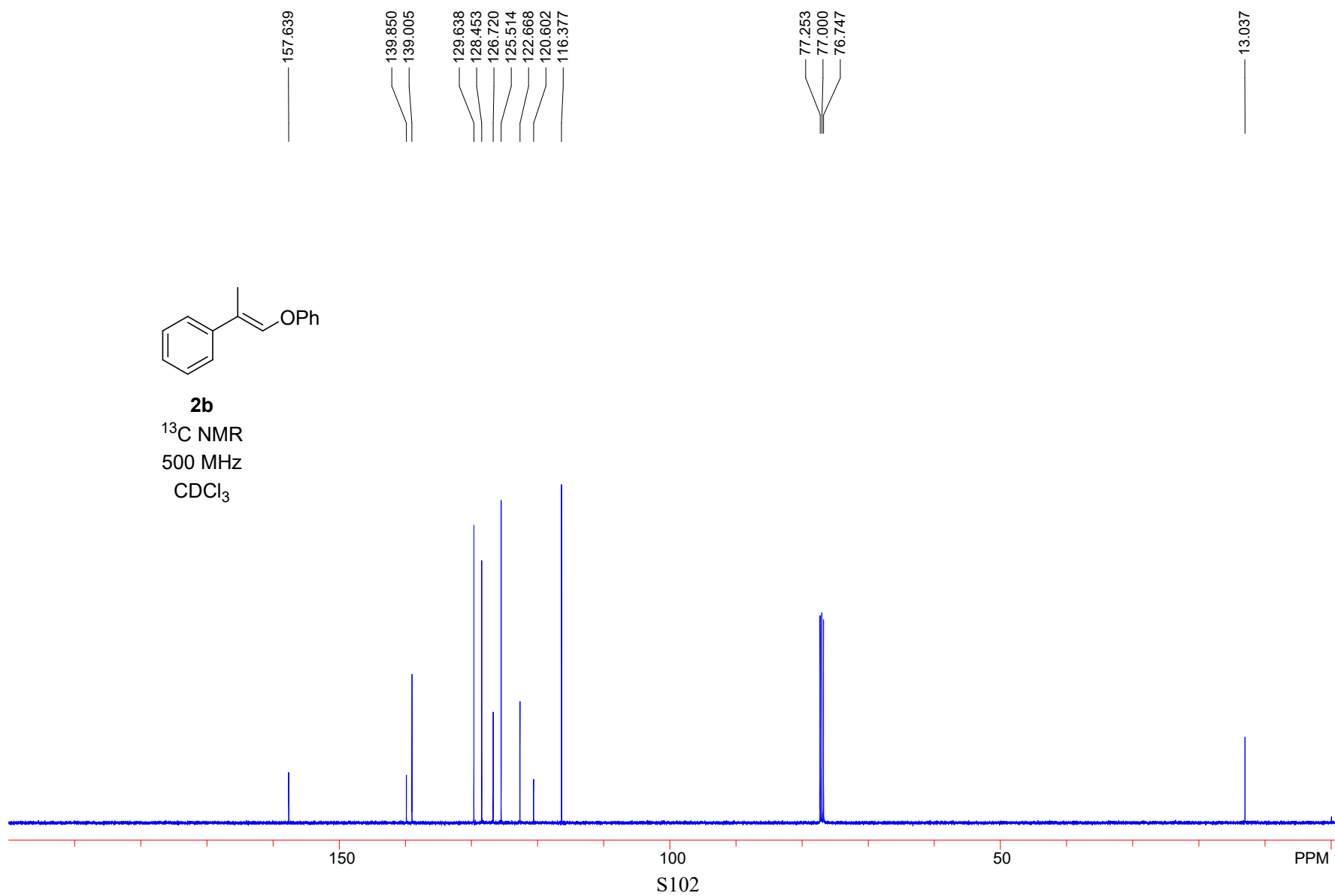


S101



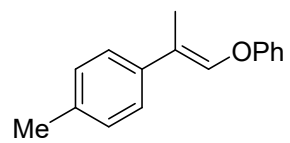
2b

¹³C NMR
500 MHz
CDCl₃



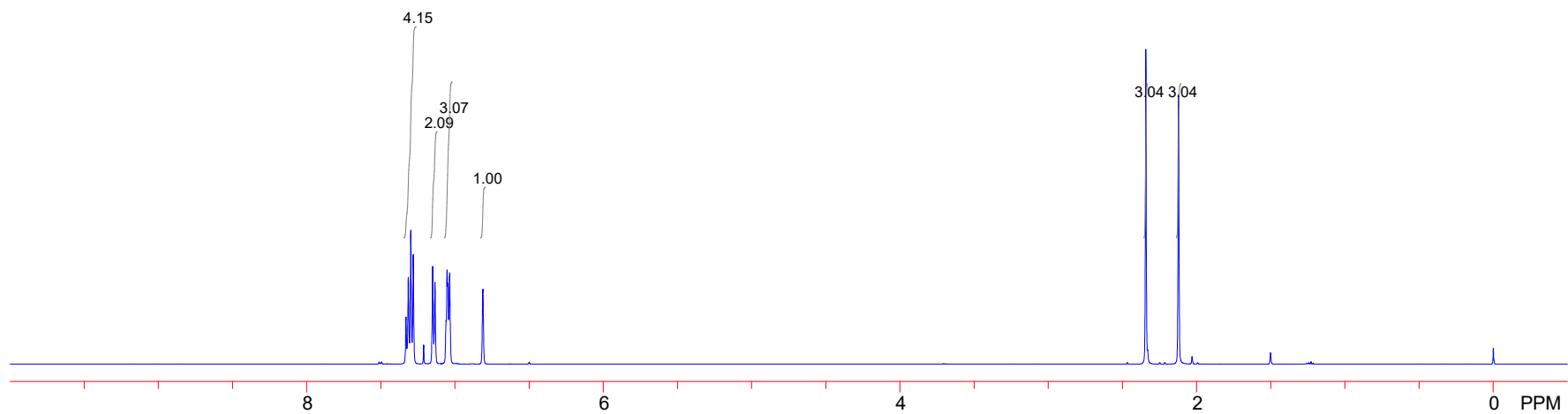
7.331
7.315
7.298
7.281
7.150
7.135
7.060
7.053
7.049
7.047
7.036
6.813
6.811

2.343
2.124
2.121

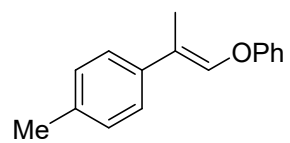


2c

¹H NMR
500 MHz
CDCl₃

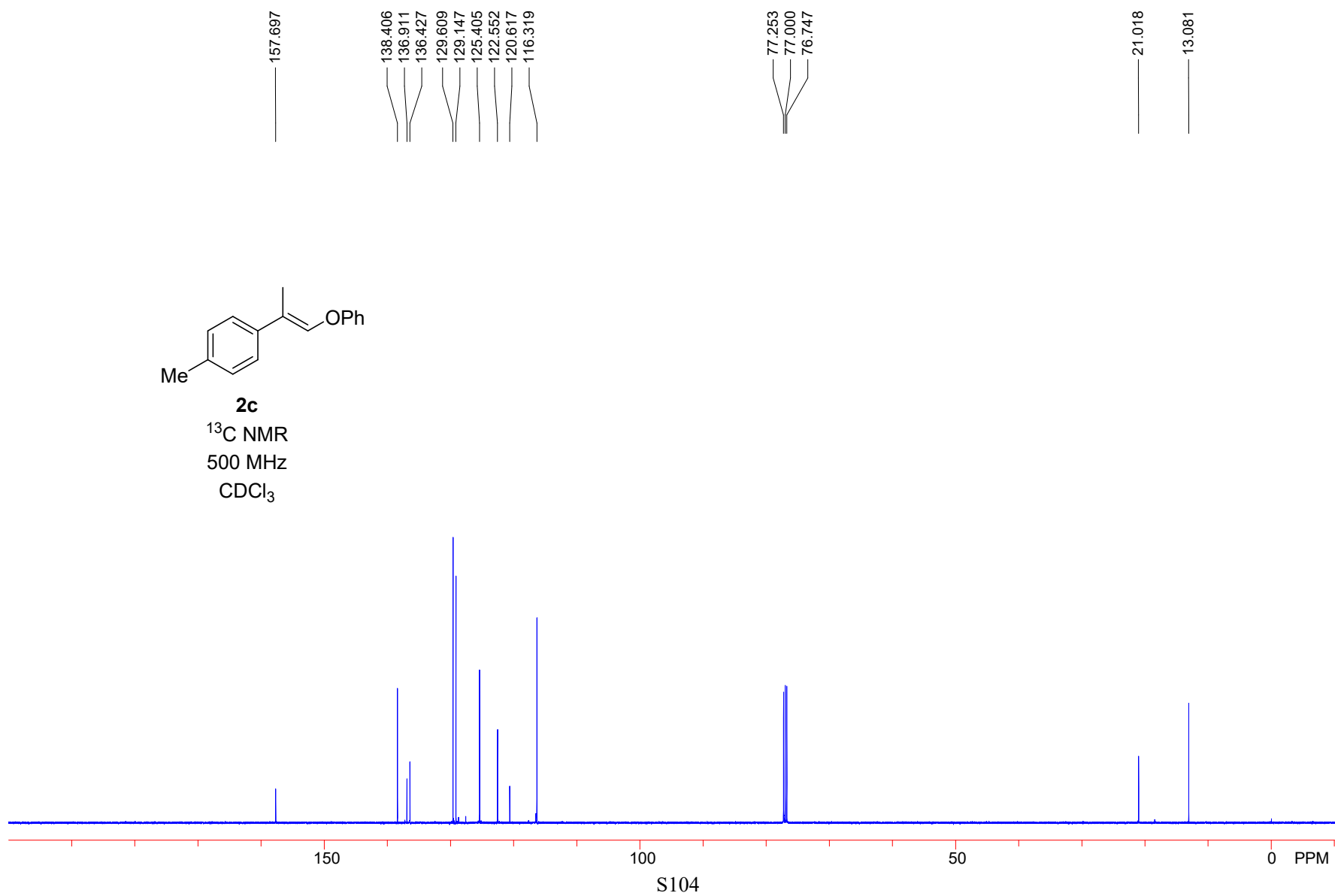


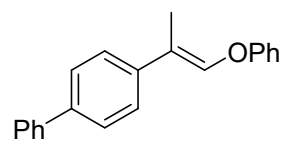
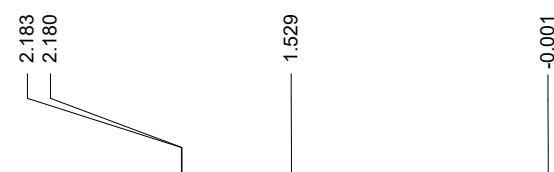
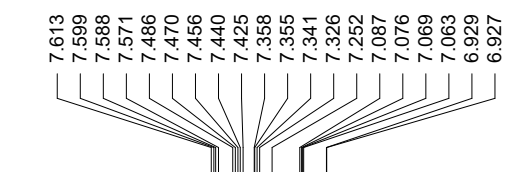
S103



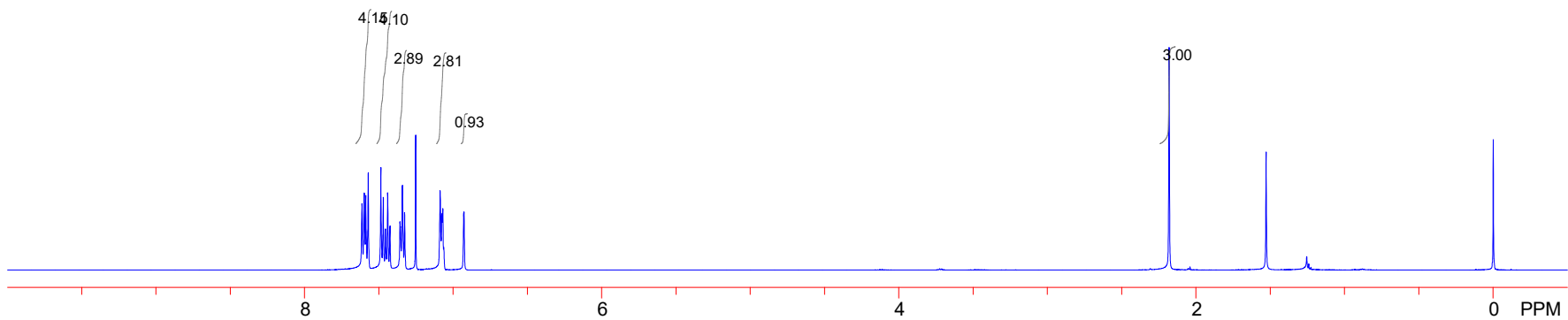
2c

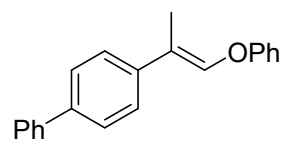
^{13}C NMR
500 MHz
 CDCl_3



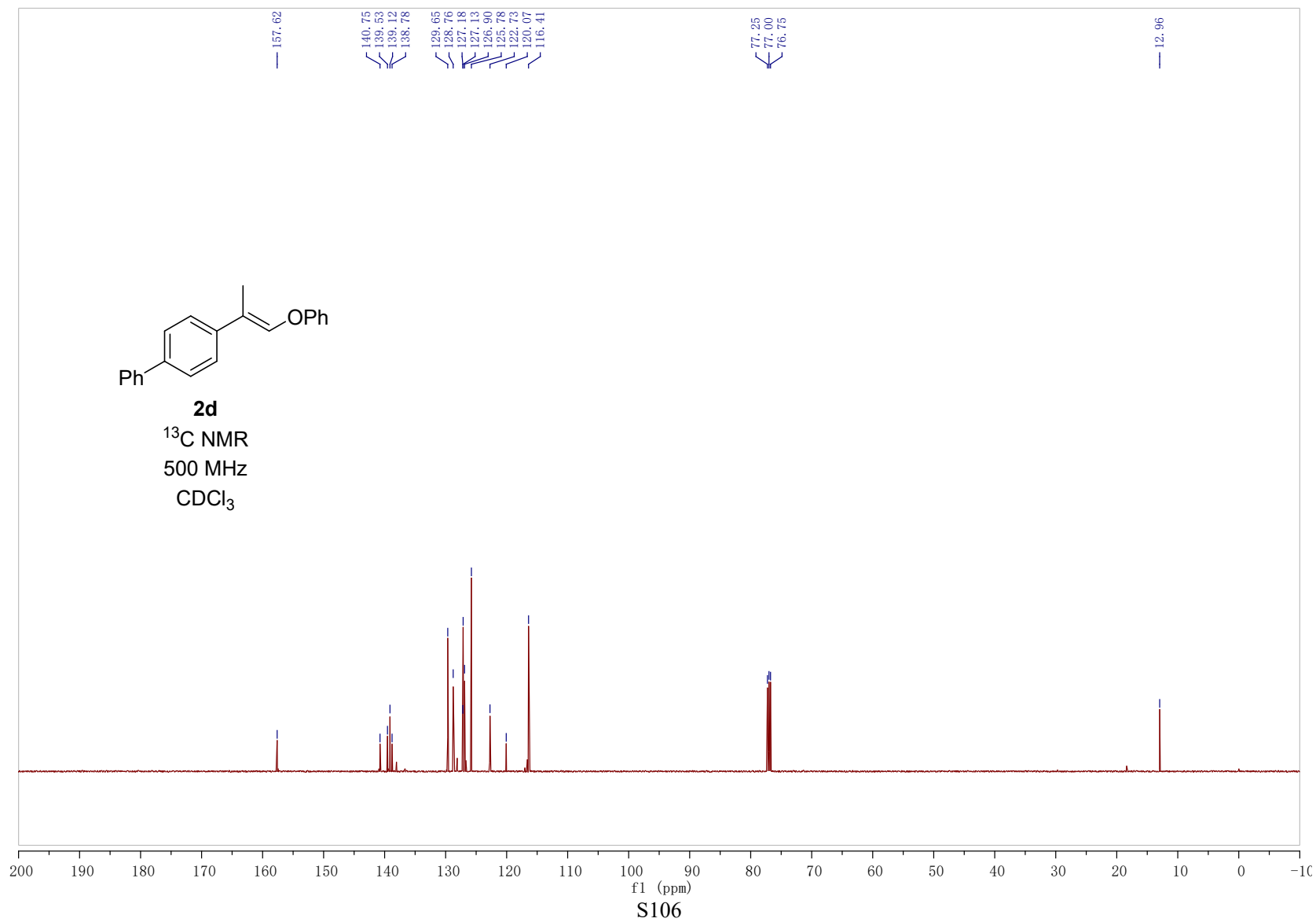


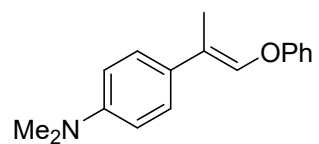
2d
¹H NMR
 500 MHz
 CDCl₃



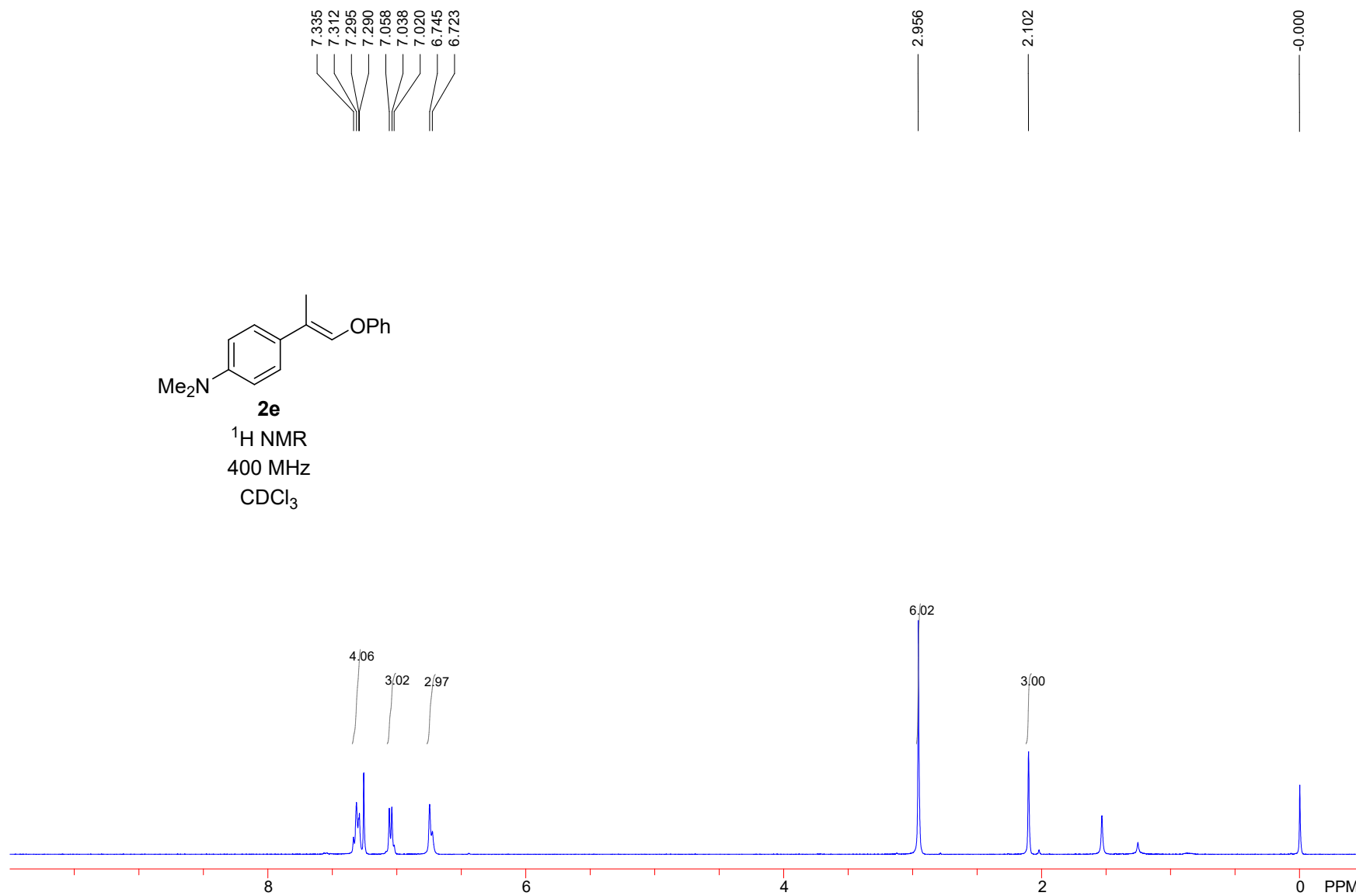


2d
¹³C NMR
500 MHz
CDCl₃

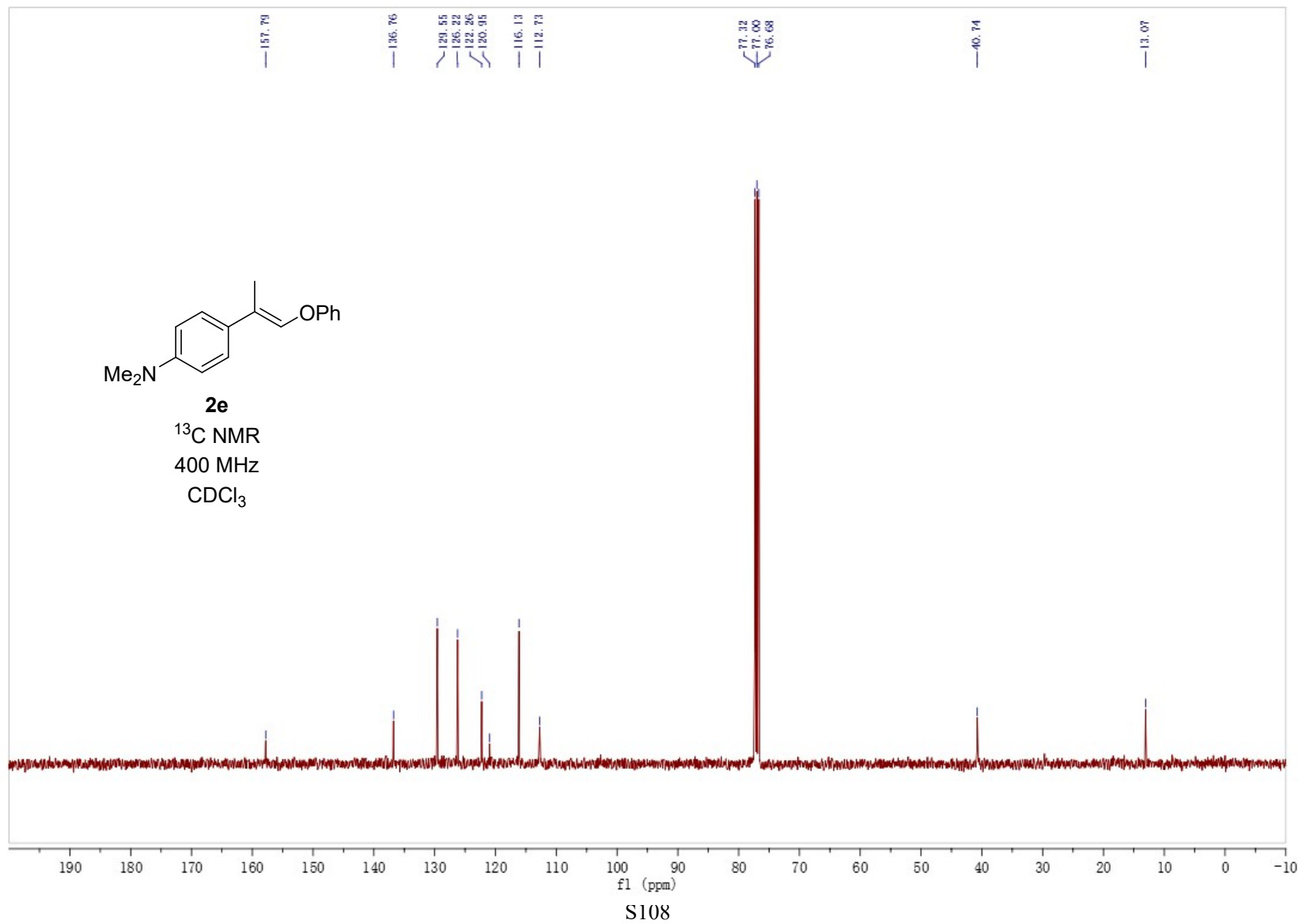


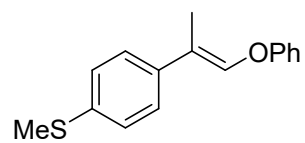


¹H NMR
400 MHz
CDCl₃



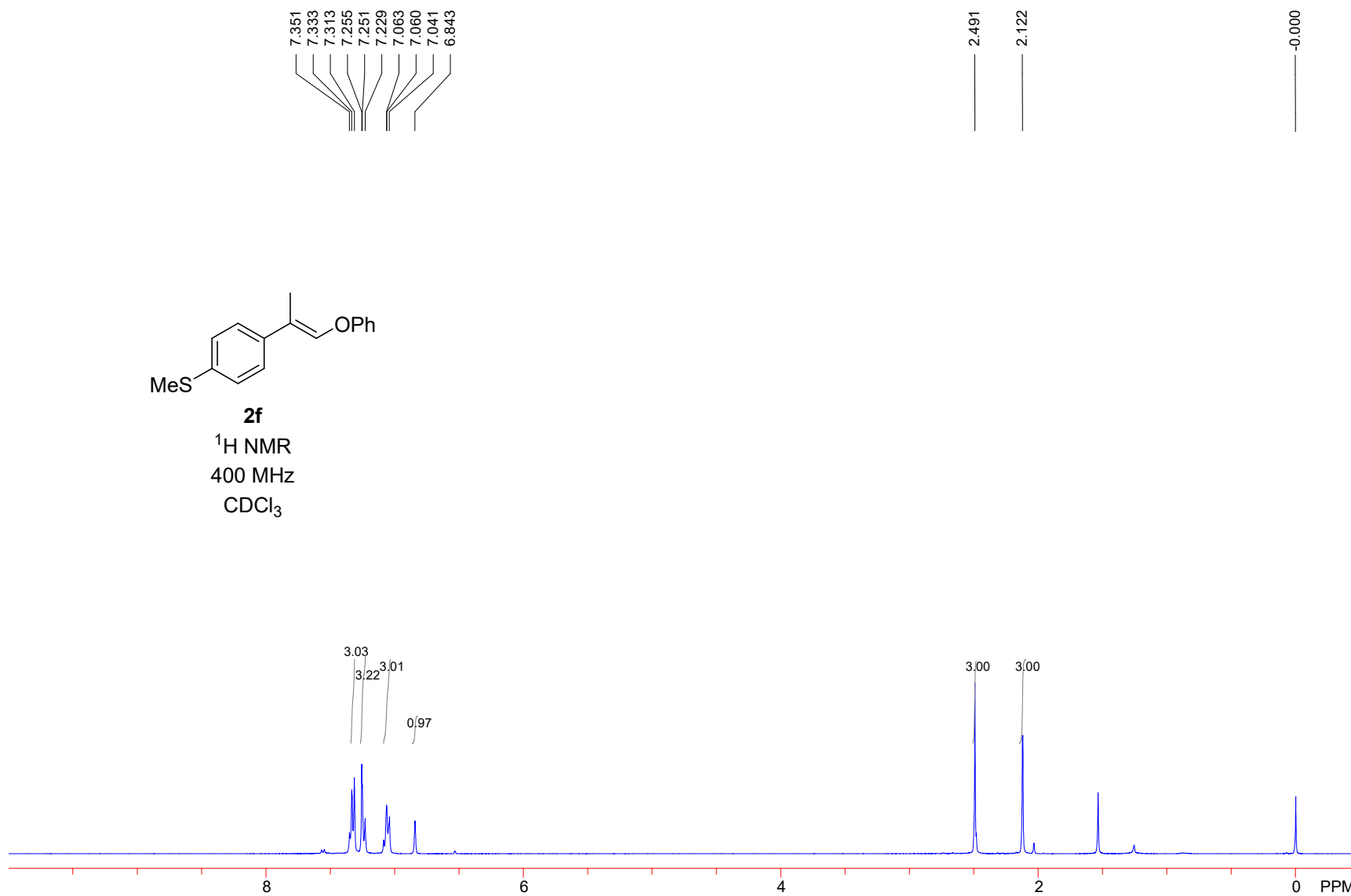
S107



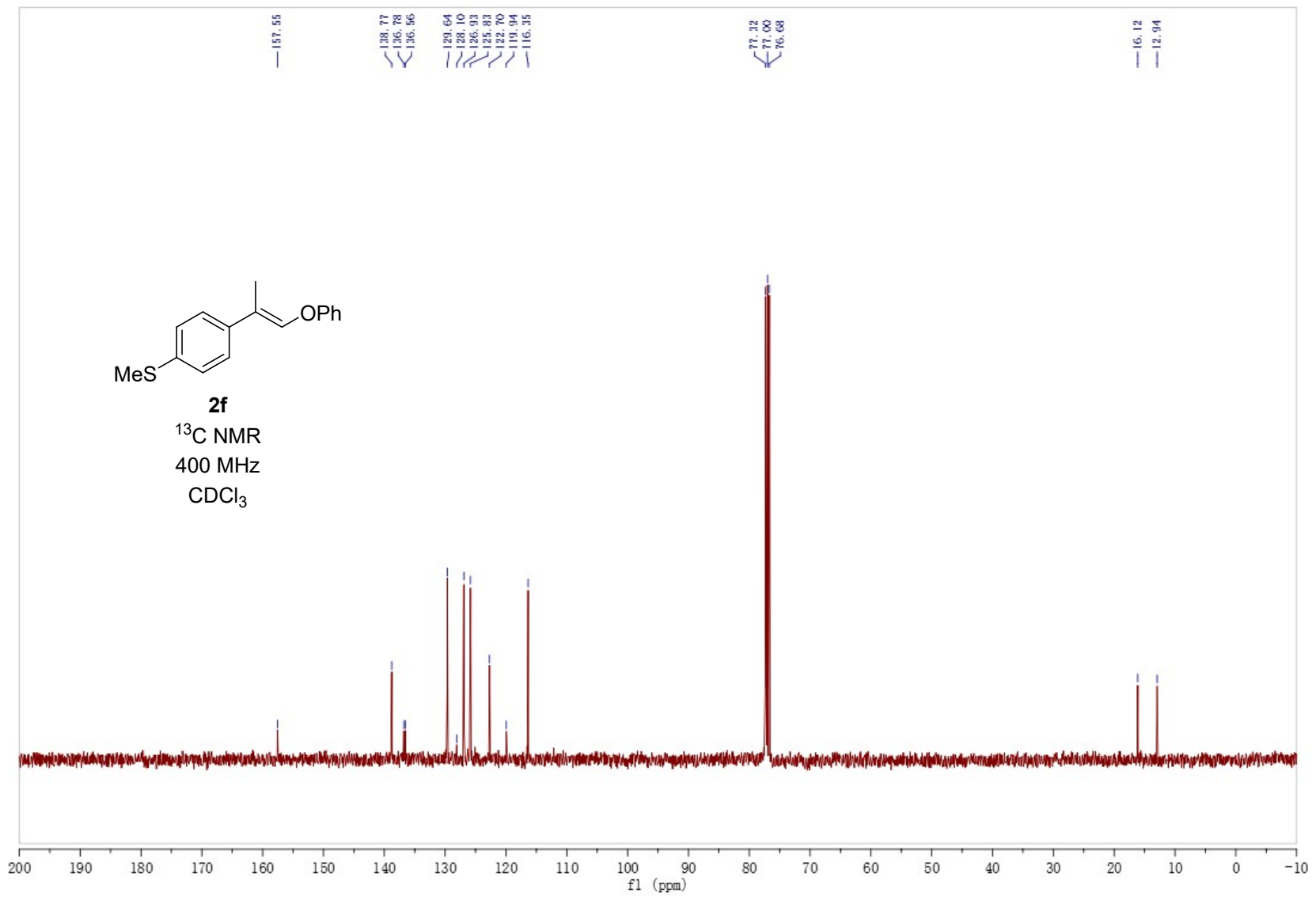


2f

¹H NMR
400 MHz
CDCl₃

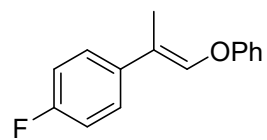


S109



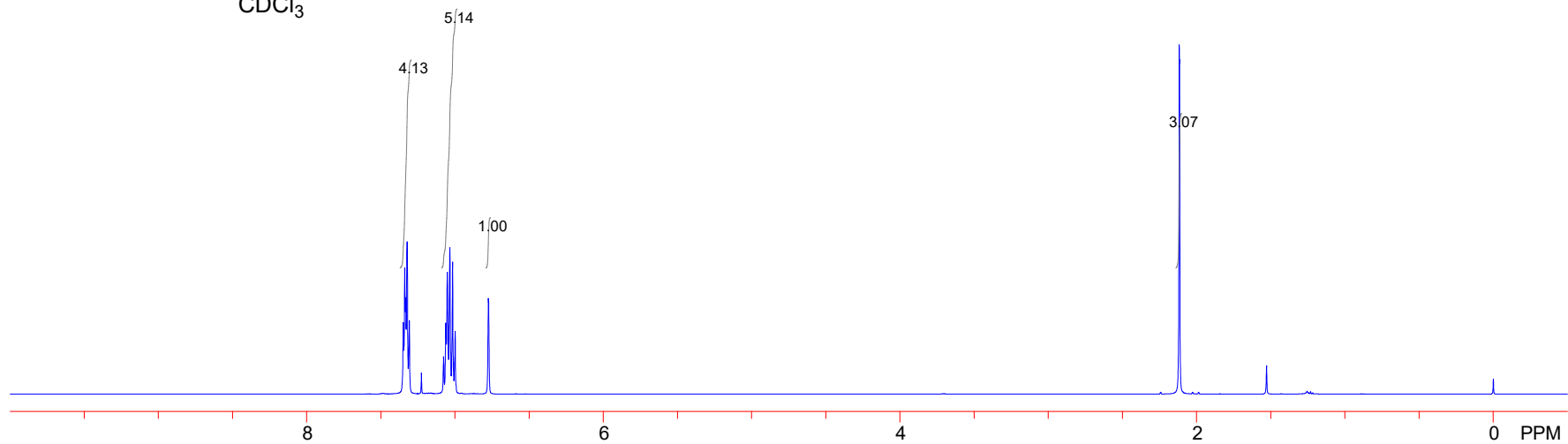
7.349
7.345
7.339
7.331
7.324
7.322
7.307
7.077
7.062
7.051
7.034
7.016
6.999
6.775
6.773

2.117
2.115

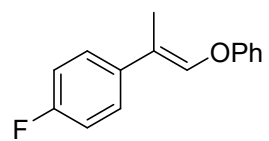


2g

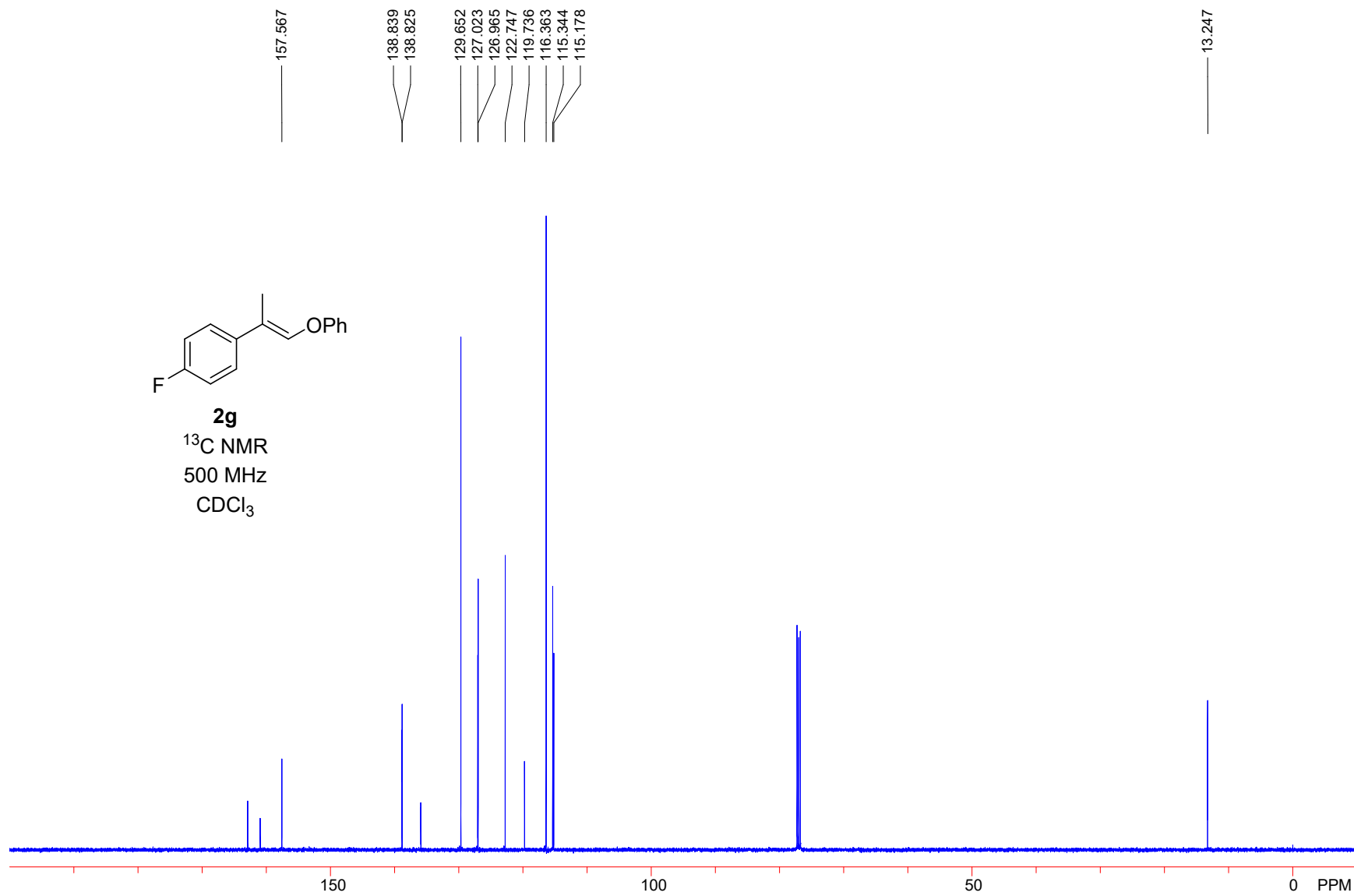
¹H NMR
500 MHz
CDCl₃



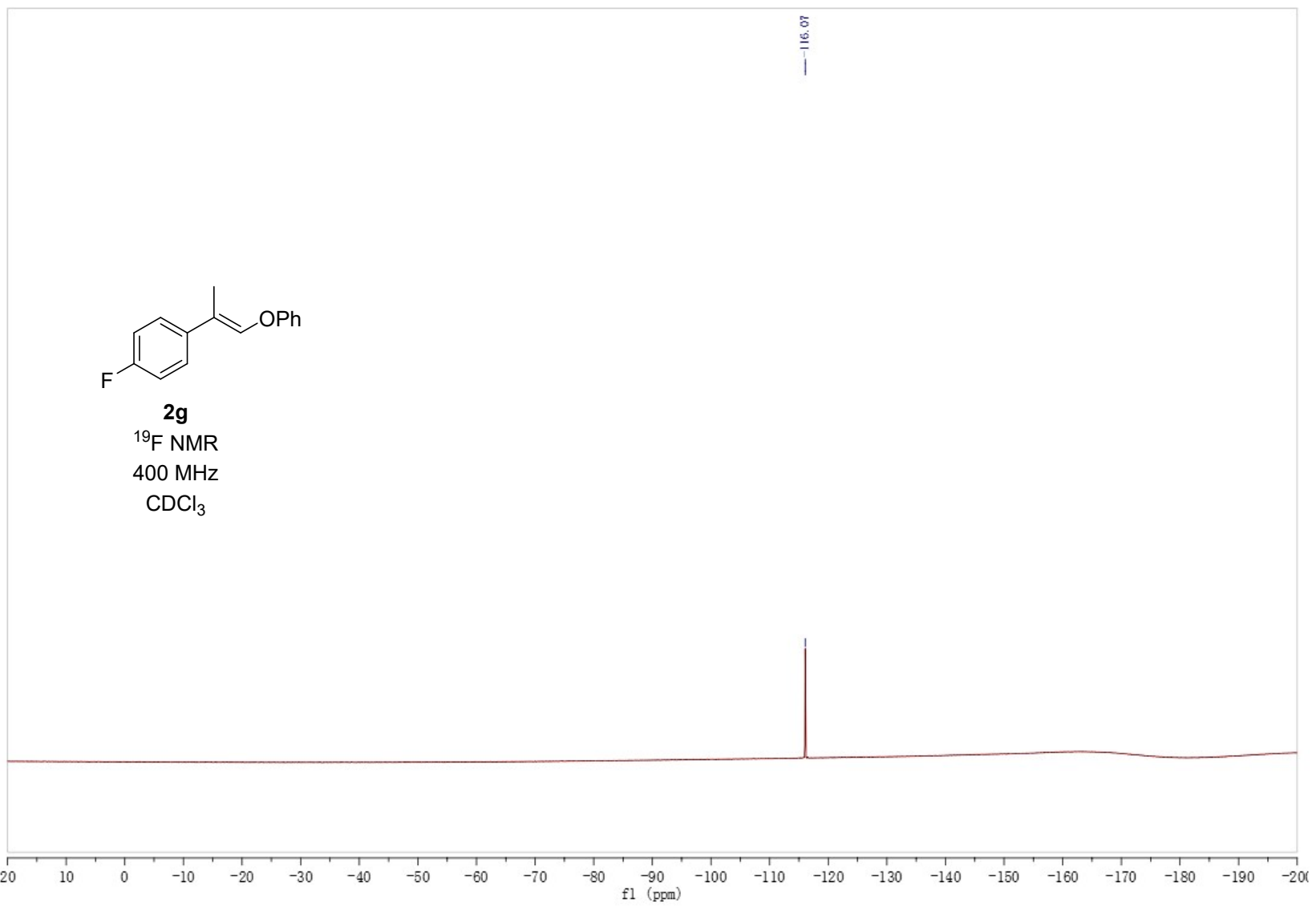
S111



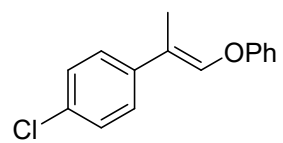
2g
¹³C NMR
500 MHz
CDCl₃



S112

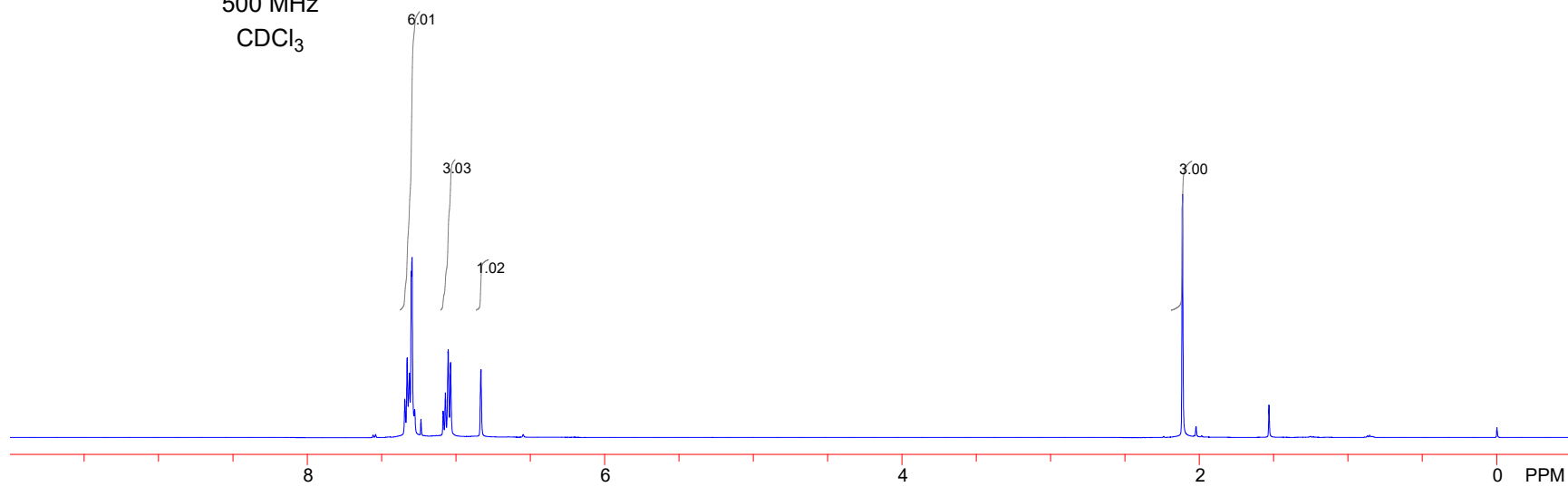


S113



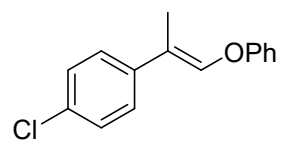
2h

¹H NMR
500 MHz
CDCl₃



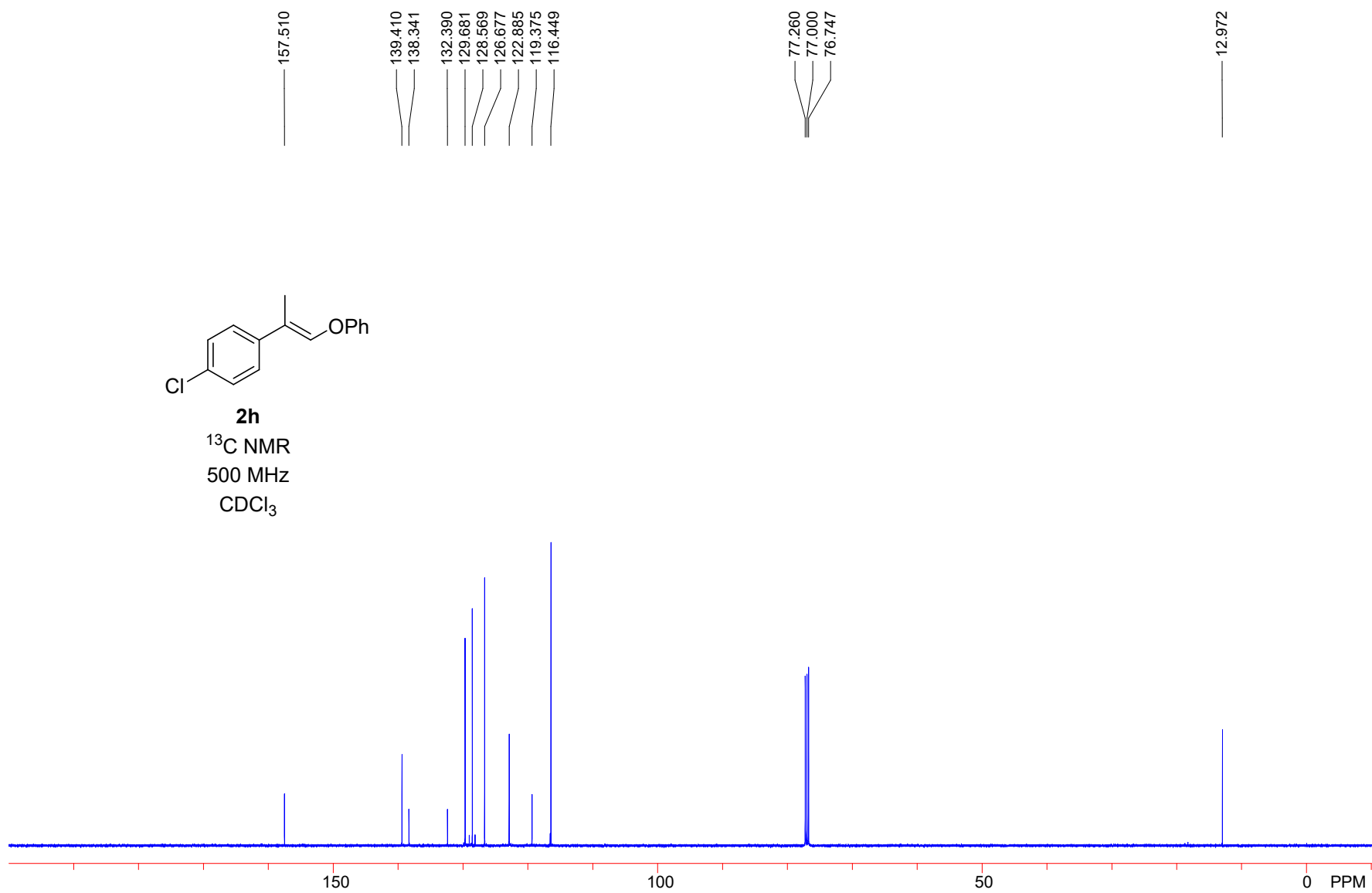
7.344
7.343
7.327
7.312
7.300
7.295
7.278
7.277
7.086
7.071
7.053
7.051
7.036
6.833
6.831

2.113

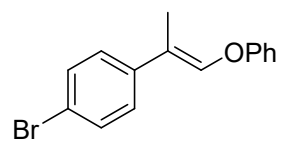


2h

¹³C NMR
500 MHz
CDCl₃



S115

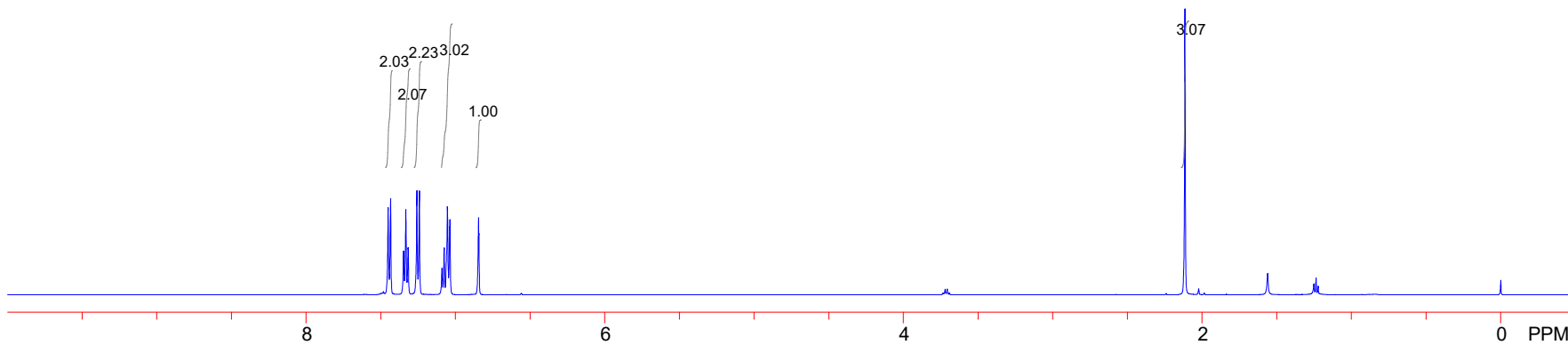


2i

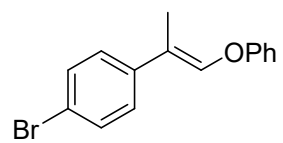
¹H NMR
500 MHz
CDCl₃

7.451
7.433
7.347
7.332
7.317
7.316
7.258
7.241
7.075
7.054
7.052
7.038
7.036
6.845
6.843

2.115
2.113

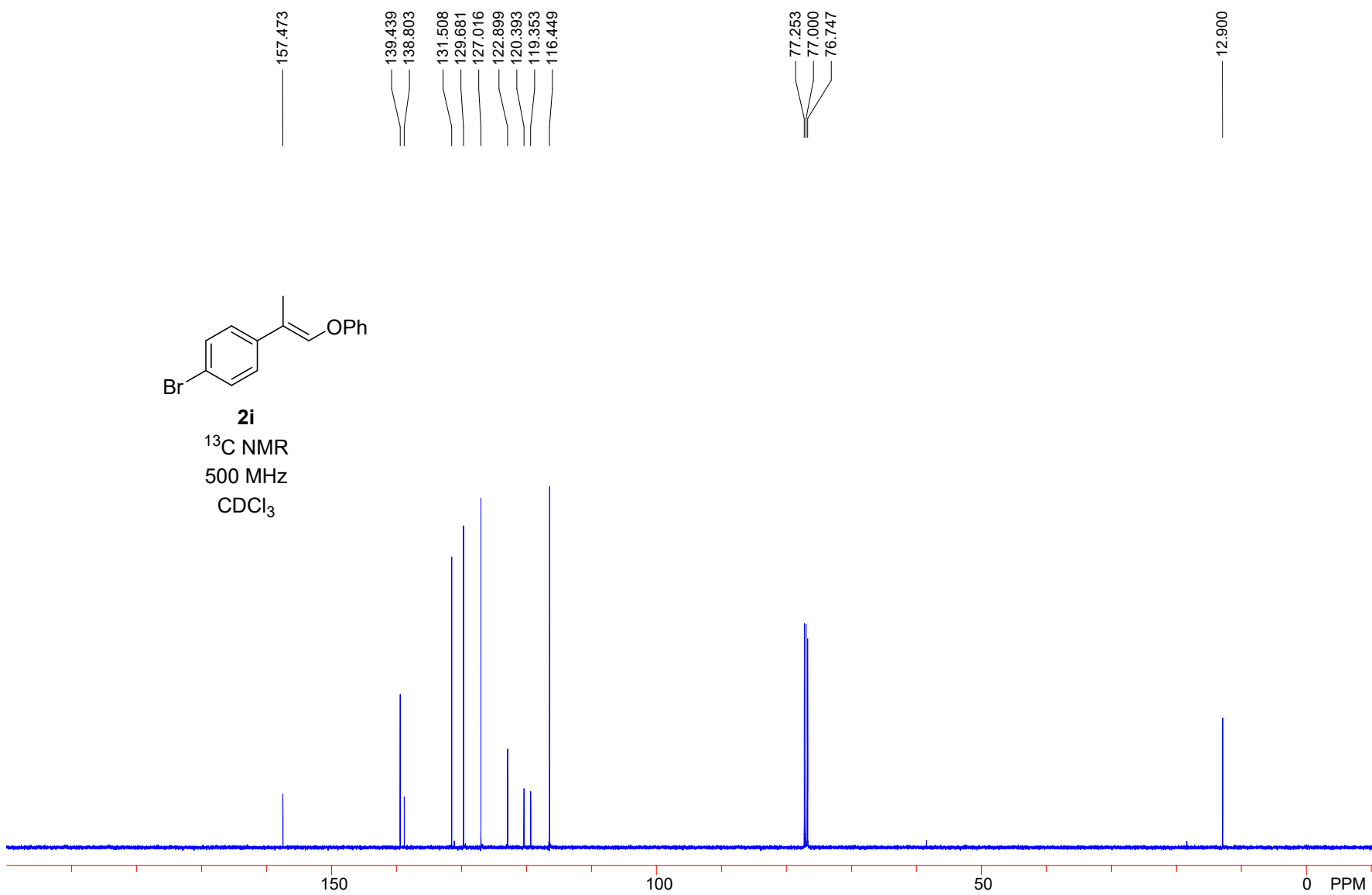


S116

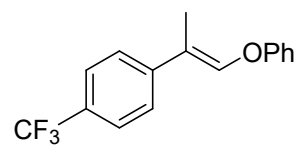


2i

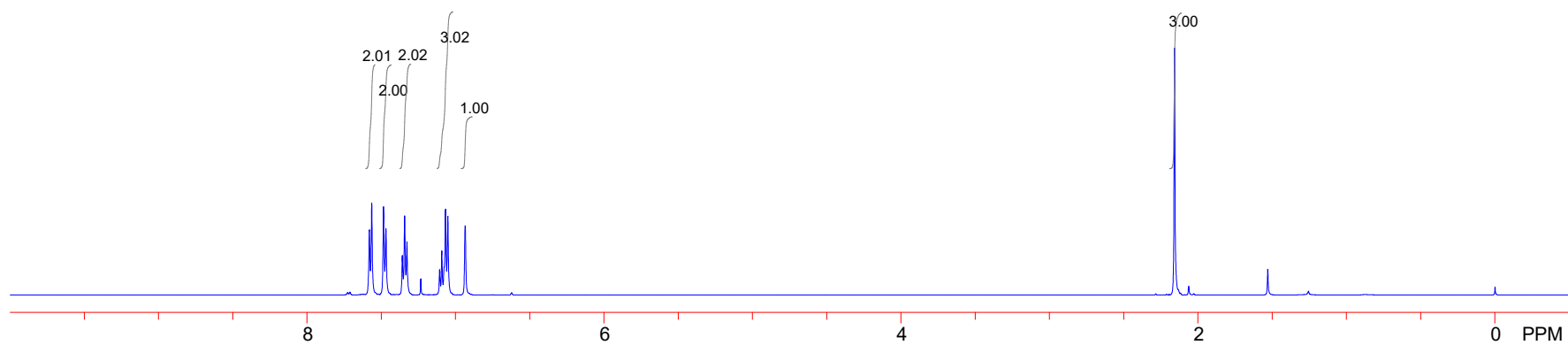
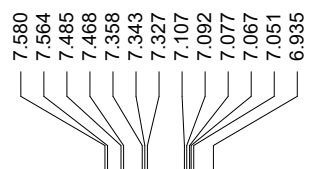
^{13}C NMR
500 MHz
 CDCl_3



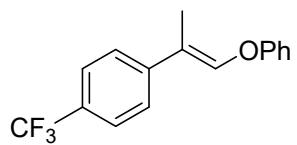
S117



2j
¹H NMR
500 MHz
CDCl₃

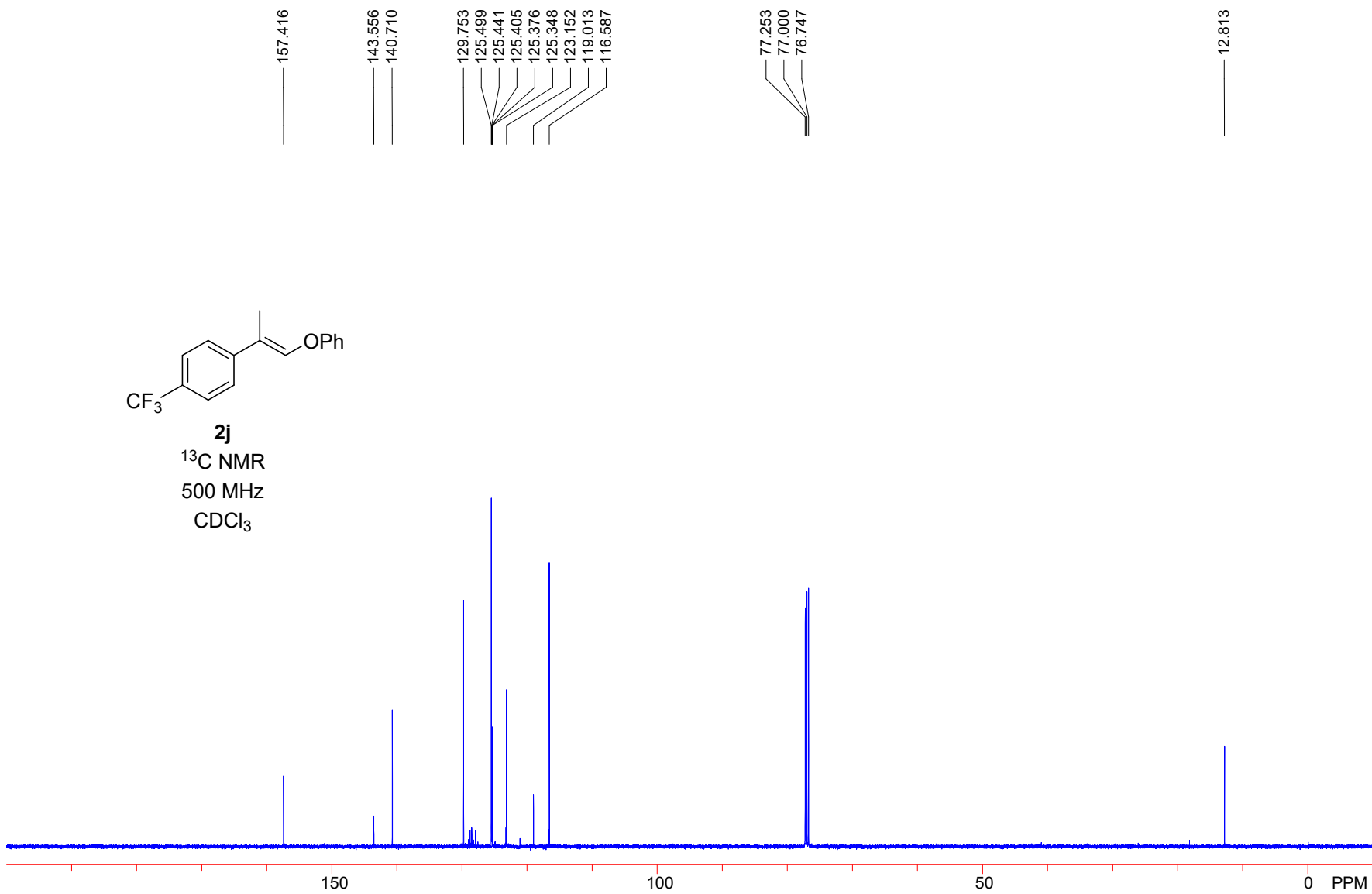


S118

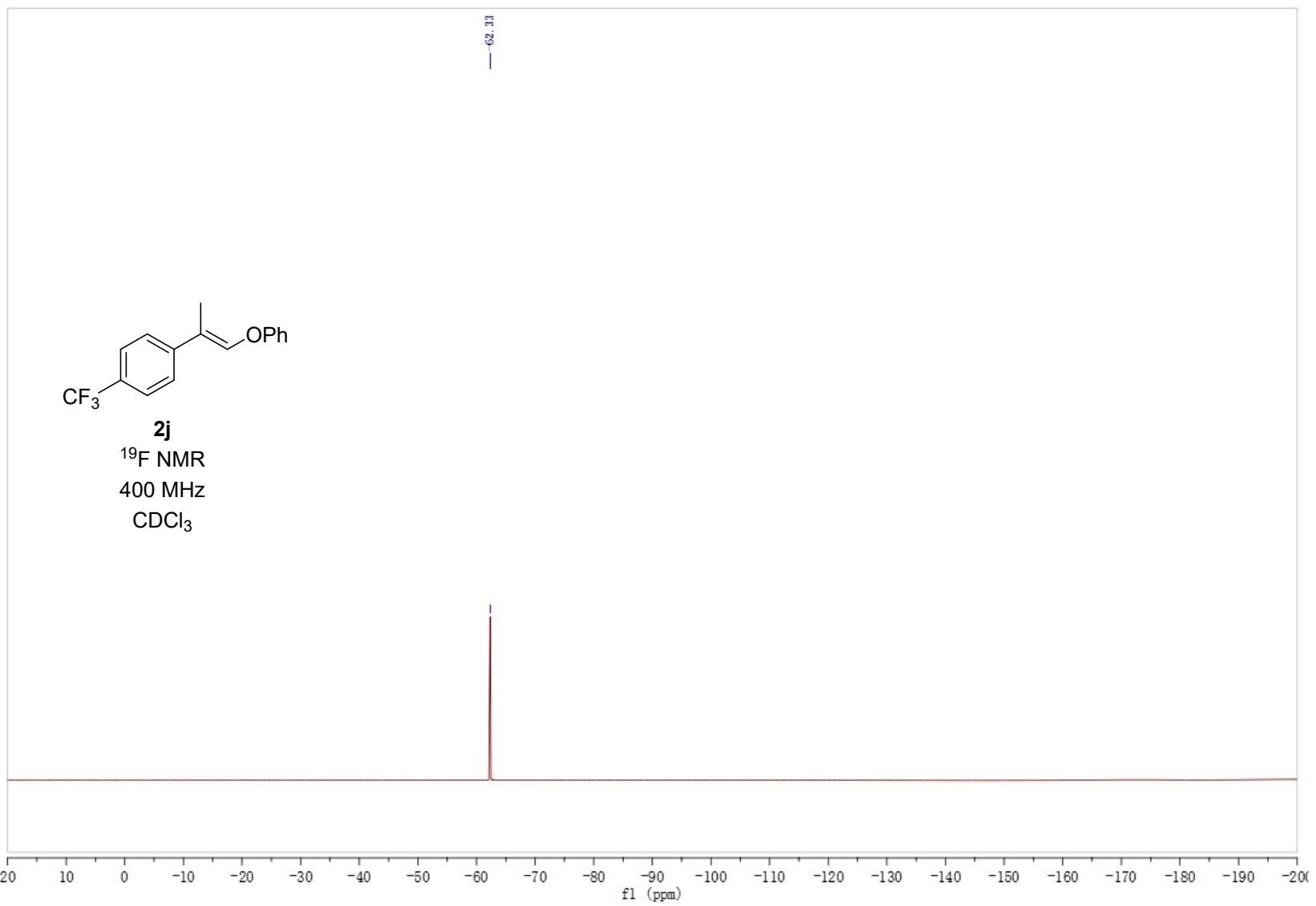


2j

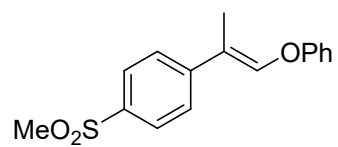
¹³C NMR
500 MHz
CDCl₃



S119

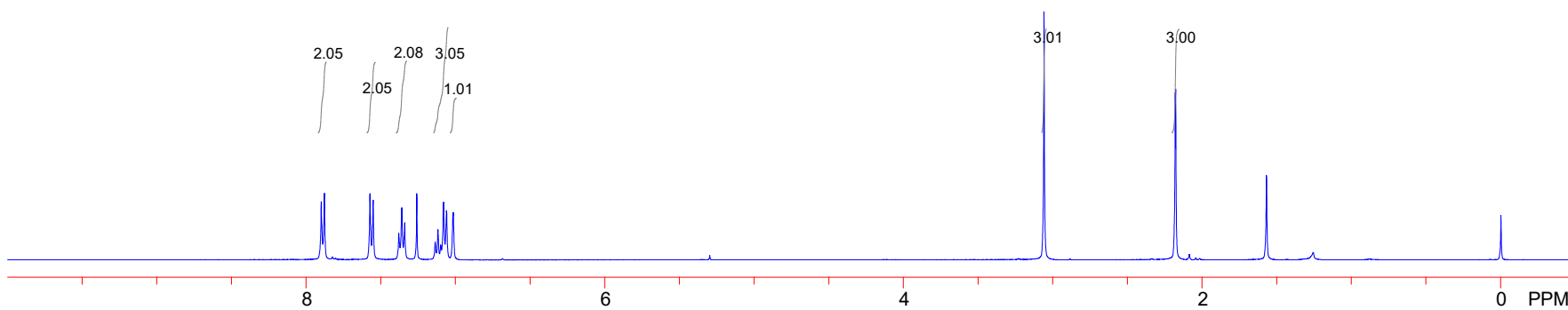
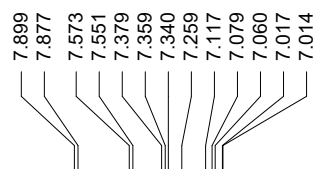


S120

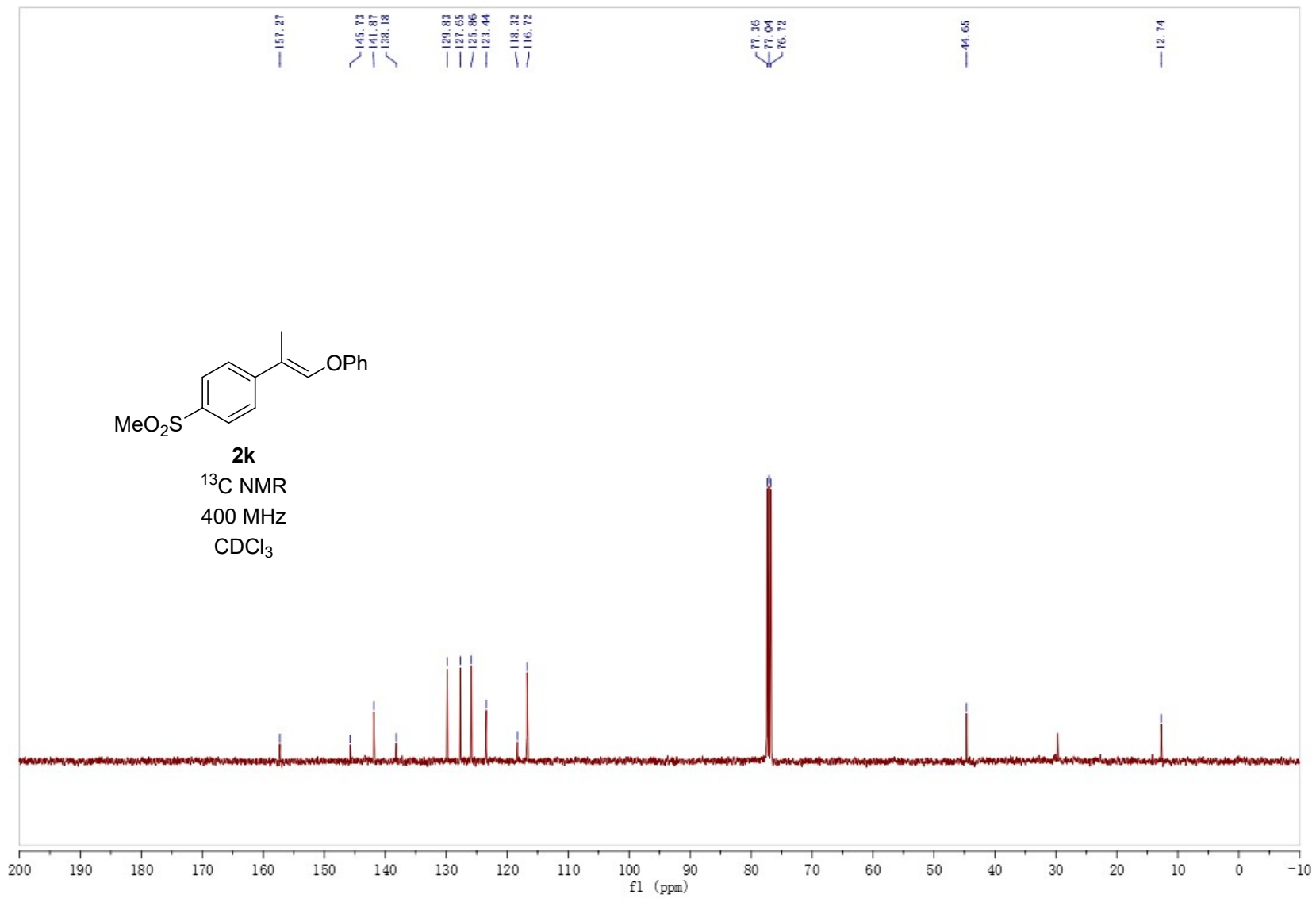


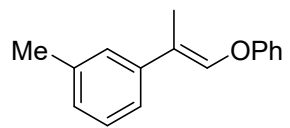
2k

¹H NMR
400 MHz
CDCl₃



S121



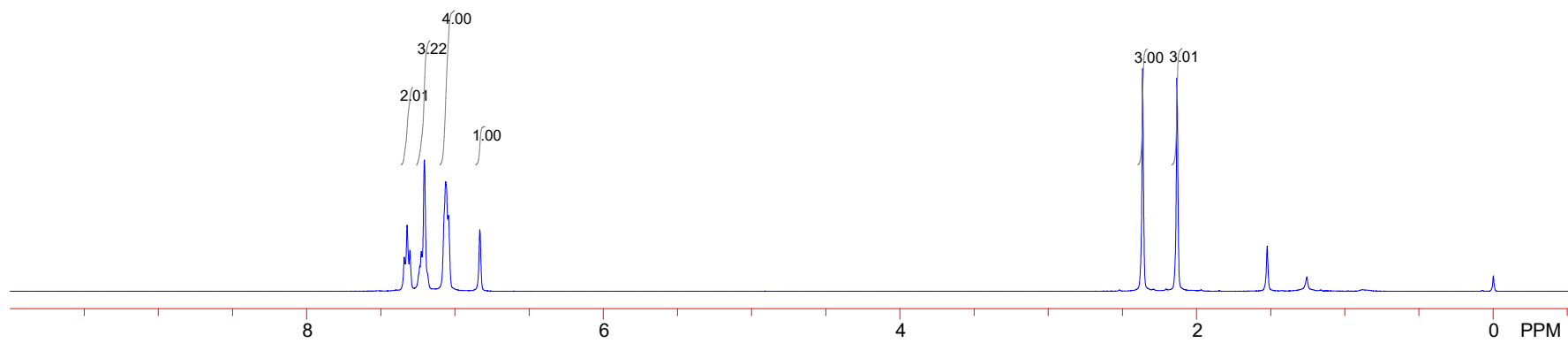


21

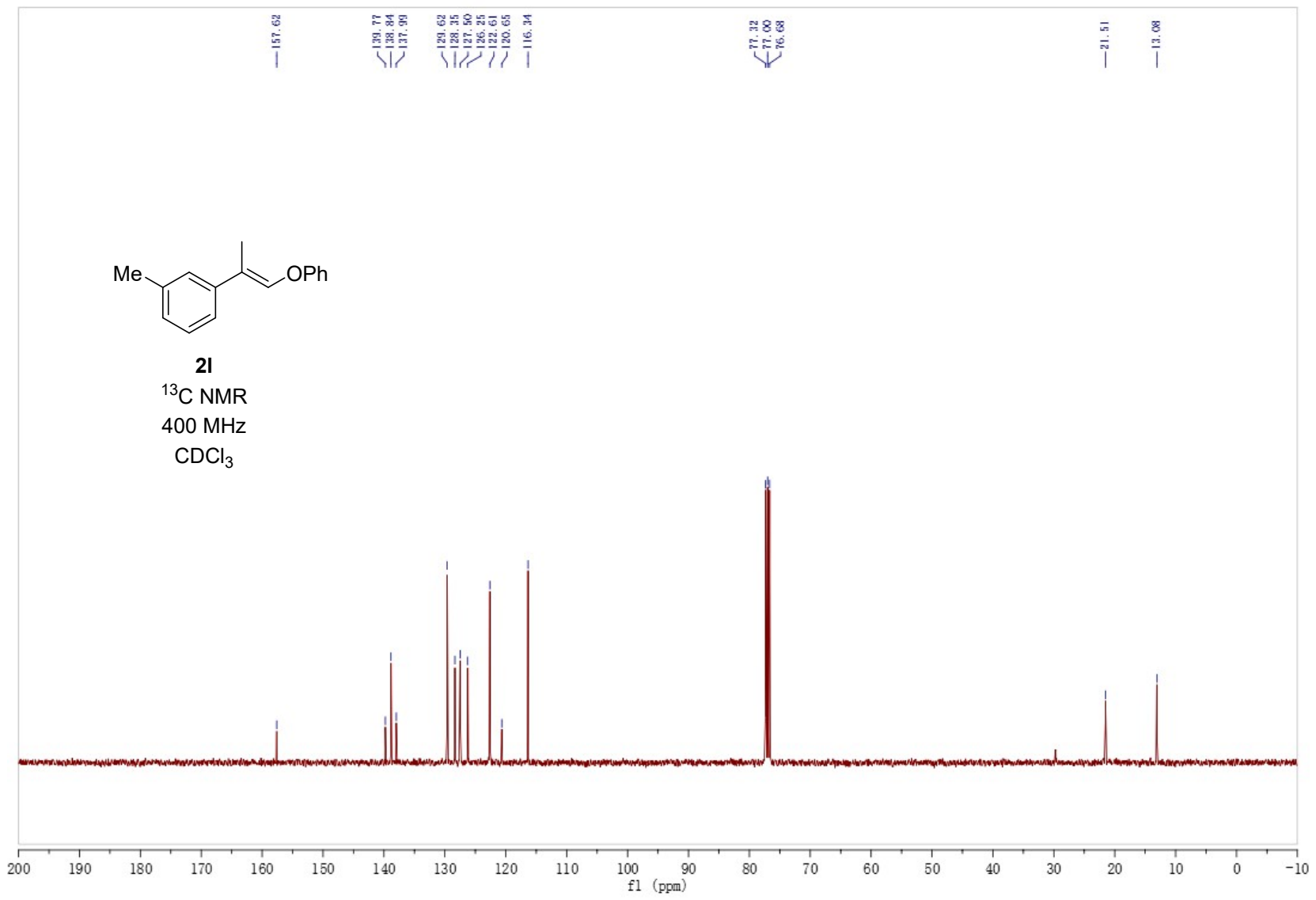
¹H NMR
400 MHz
CDCl₃

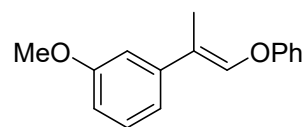
7.342
7.323
7.304
7.237
7.227
7.206
7.064
7.062
7.059
7.044
6.832

2.364
2.133
1.524



S123





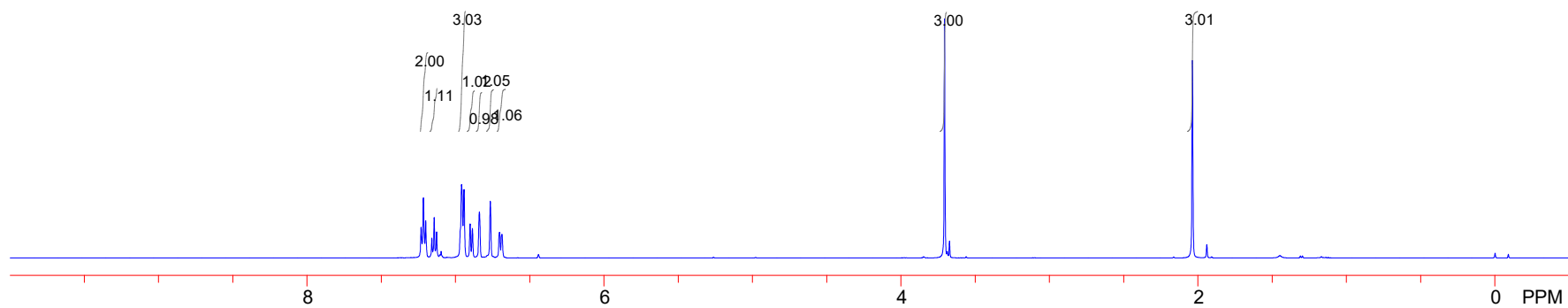
2m

¹H NMR
500 MHz
CDCl₃

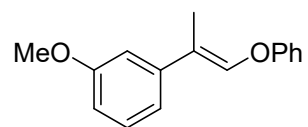
7.232
7.216
7.200
7.144
7.127
6.959
6.942
6.901
6.886
6.838
6.766
6.705
6.703

3.707

2.038



S125

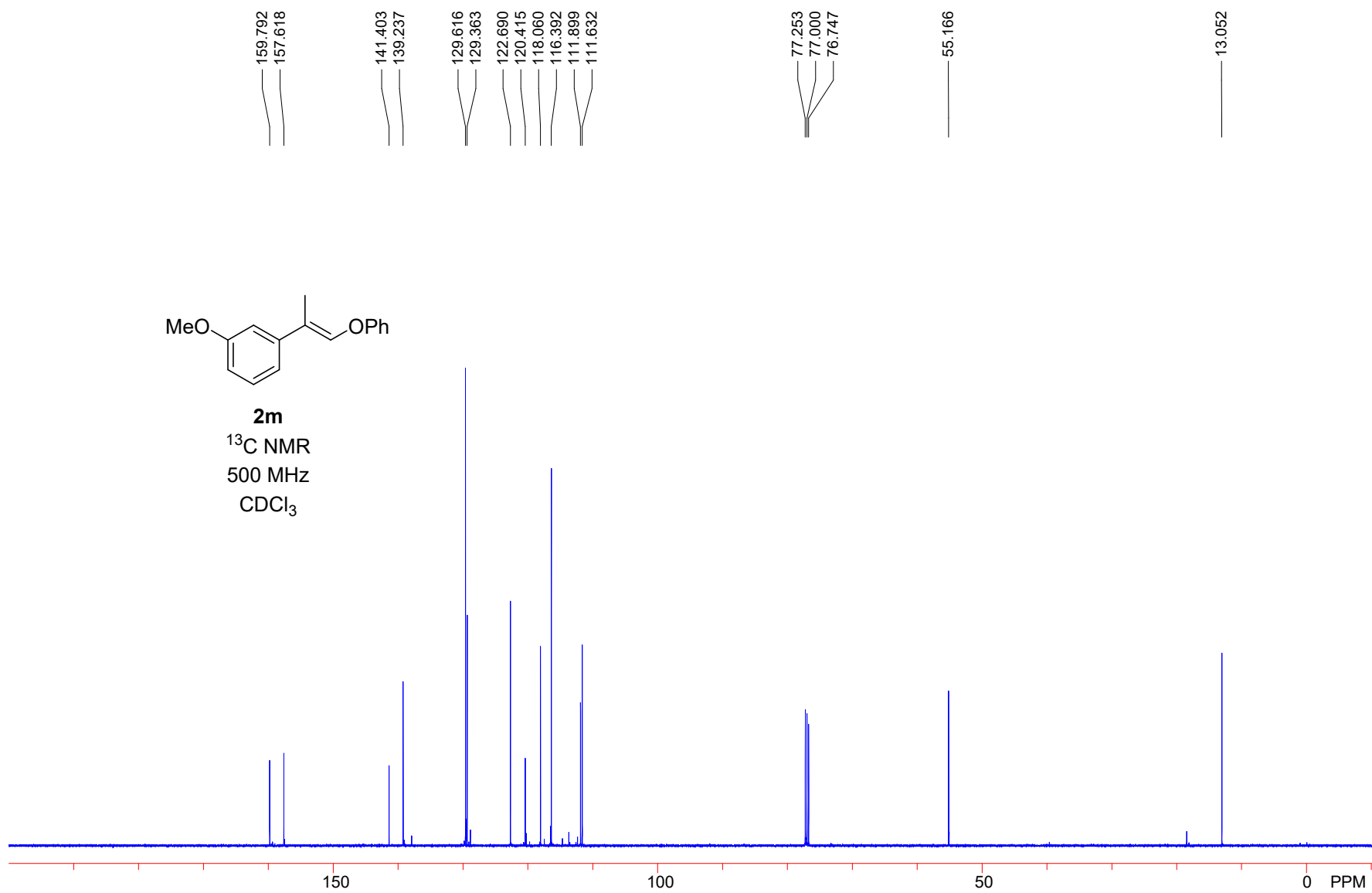


2m

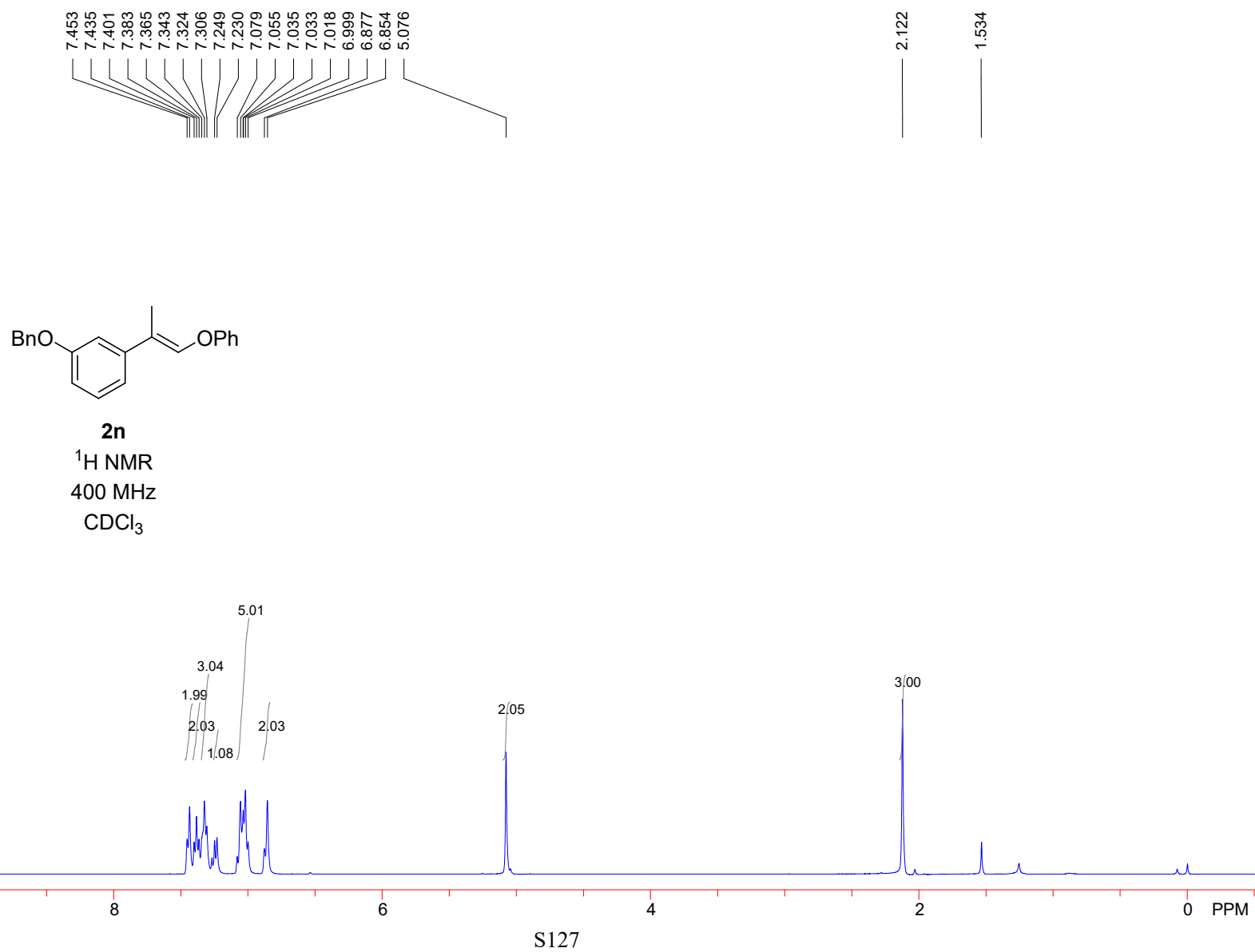
¹³C NMR

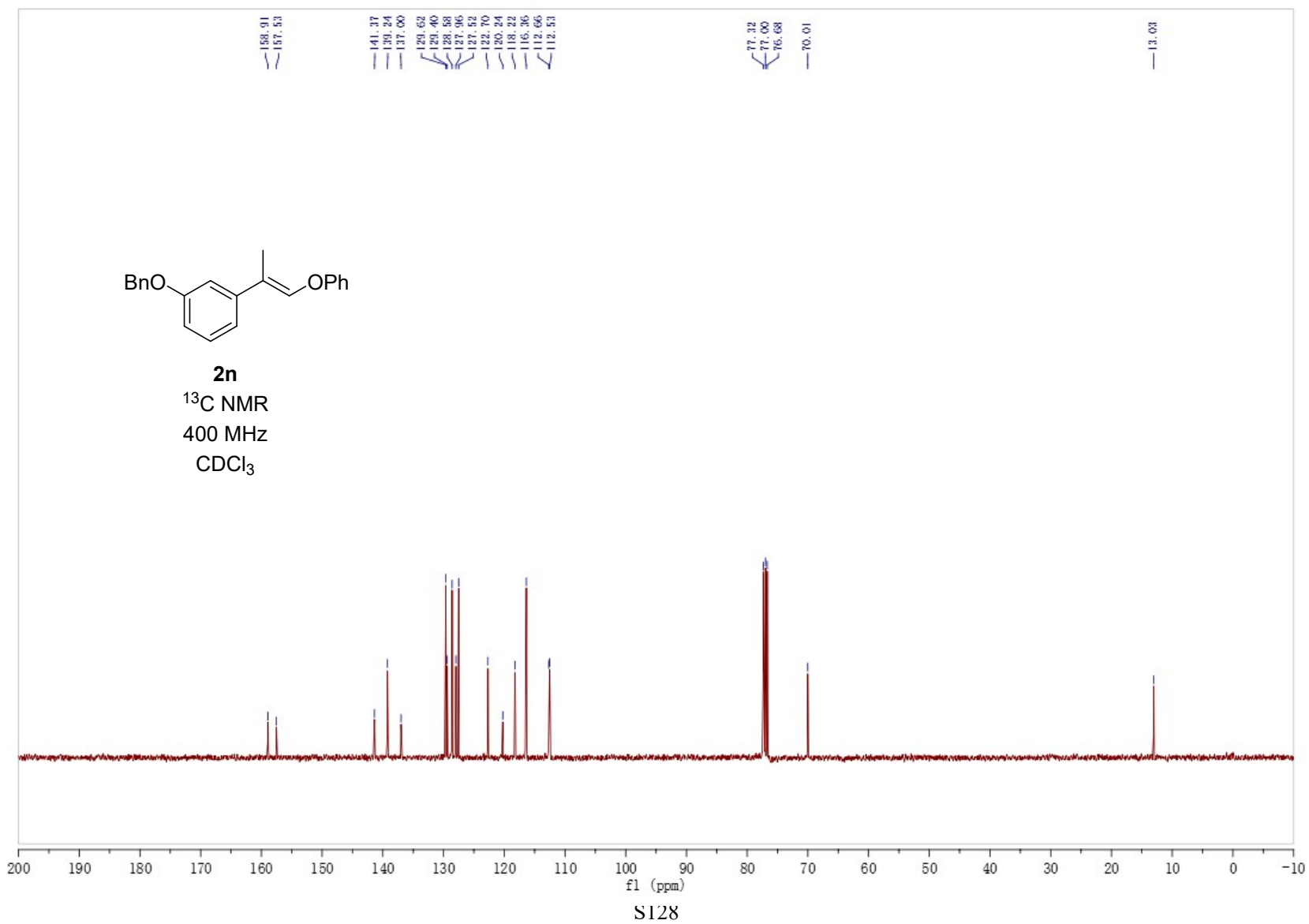
500 MHz

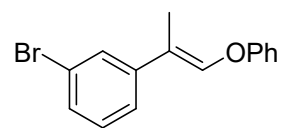
CDCl₃



S126







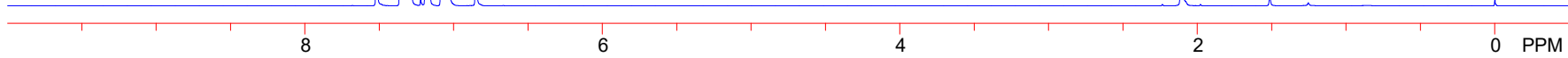
2o
¹H NMR
500 MHz
CDCl₃

7.521
7.518
7.361
7.344
7.342
7.326
7.309
7.305
7.304
7.287
7.191
7.176
7.071
7.050
7.034
6.851
6.848

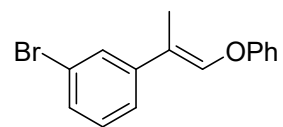
2.110

3.96
2.96
0.99
1.03
1.00

3.01

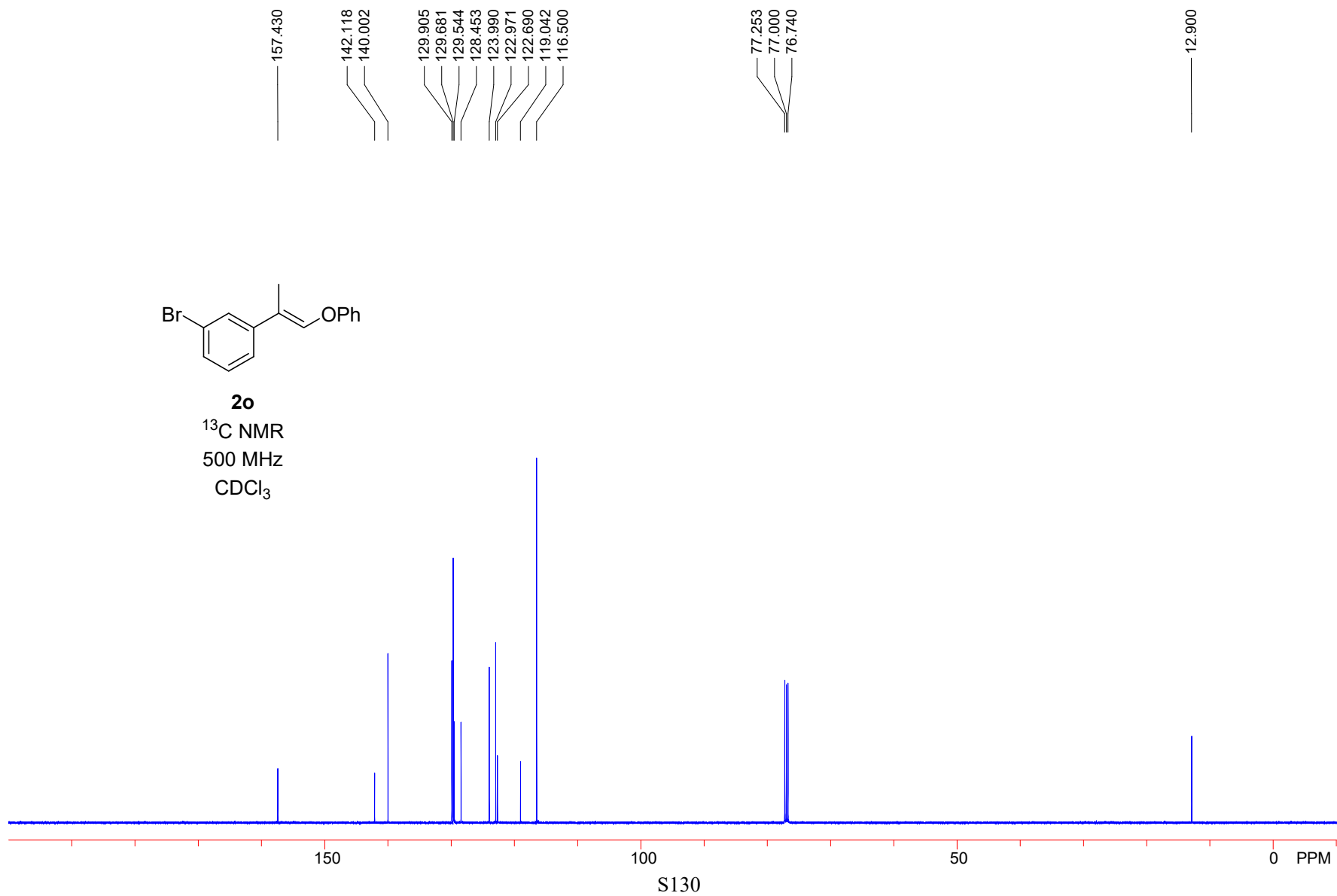


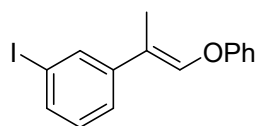
S129



2o

^{13}C NMR
500 MHz
 CDCl_3





2p

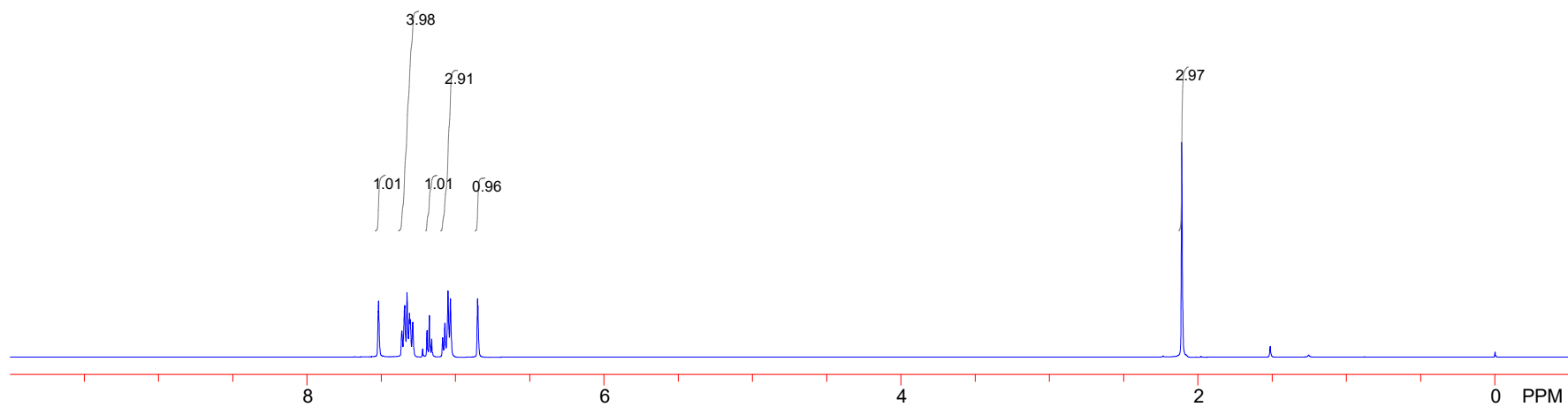
¹H NMR

500 MHz

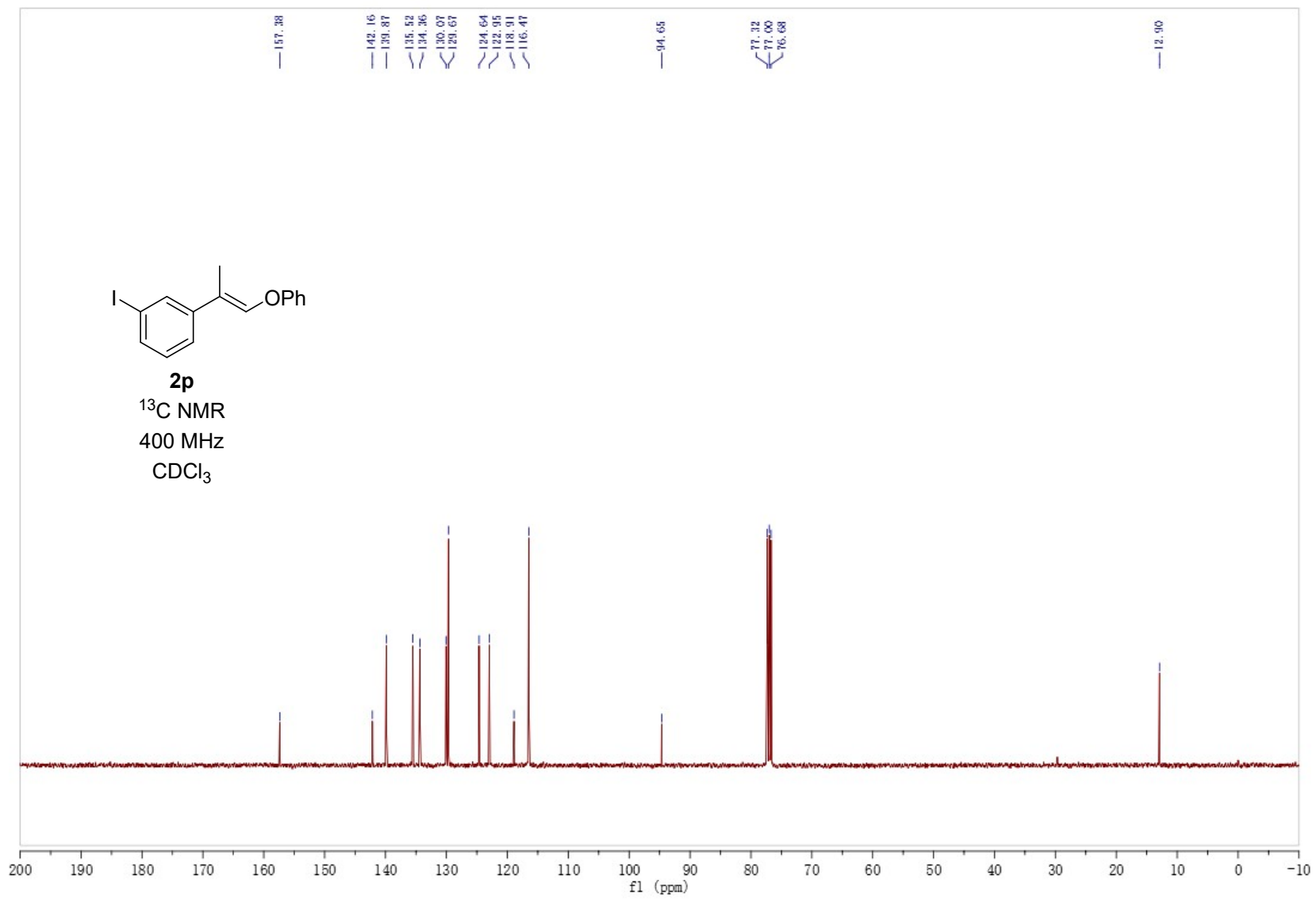
CDCl₃

7.521
7.518
7.361
7.344
7.342
7.326
7.309
7.305
7.304
7.287
7.191
7.176
7.071
7.050
7.034
6.851
6.848

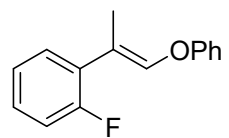
2.110



S131



S132

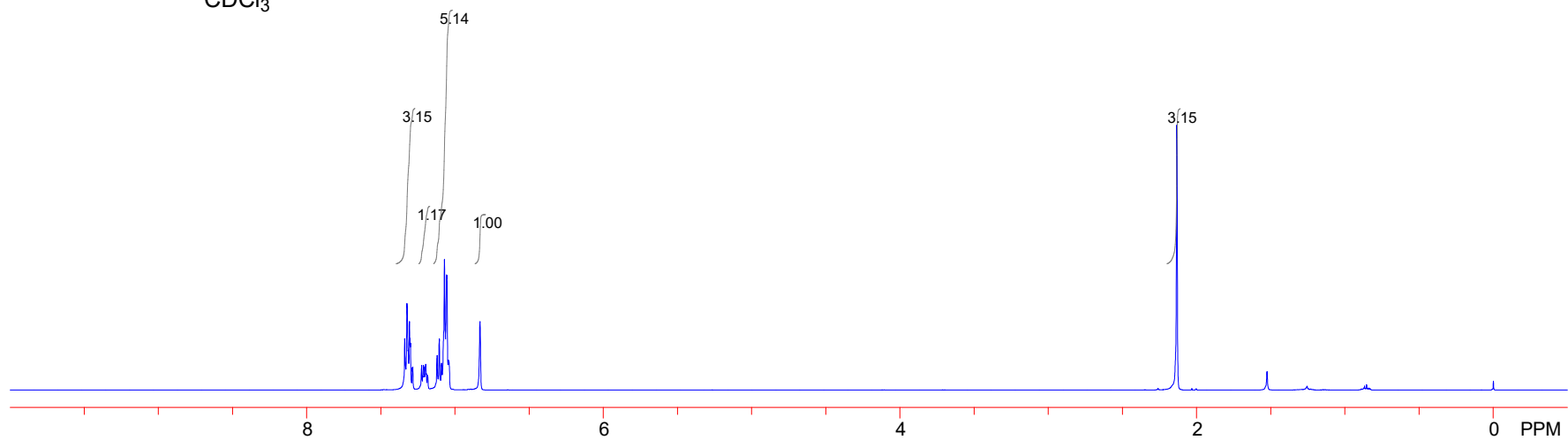


2q

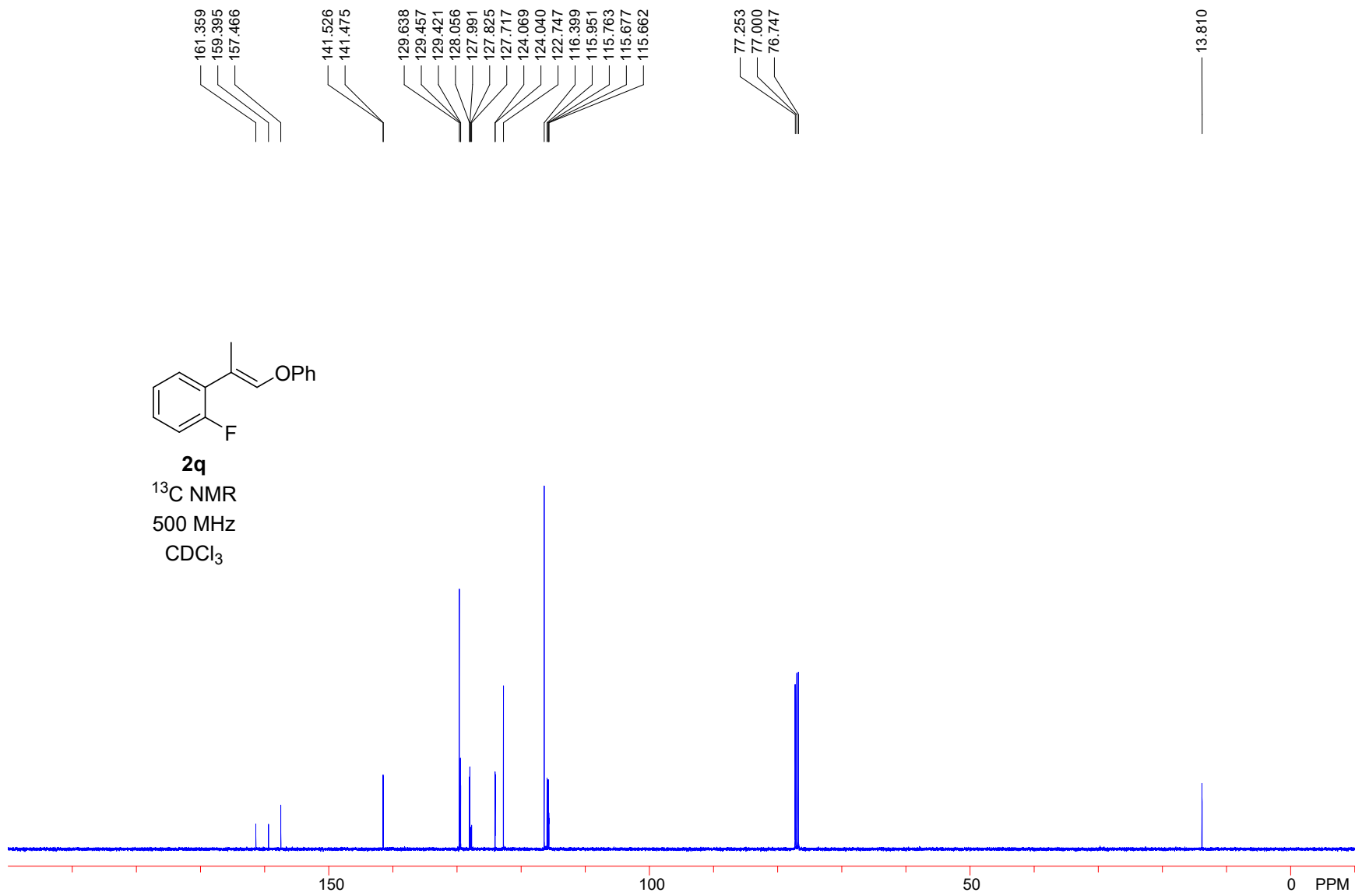
¹H NMR
500 MHz
CDCl₃

7.339
7.324
7.316
7.307
7.304
7.300
7.120
7.105
7.090
7.071
7.058
7.055
7.044
7.040
6.832
6.831

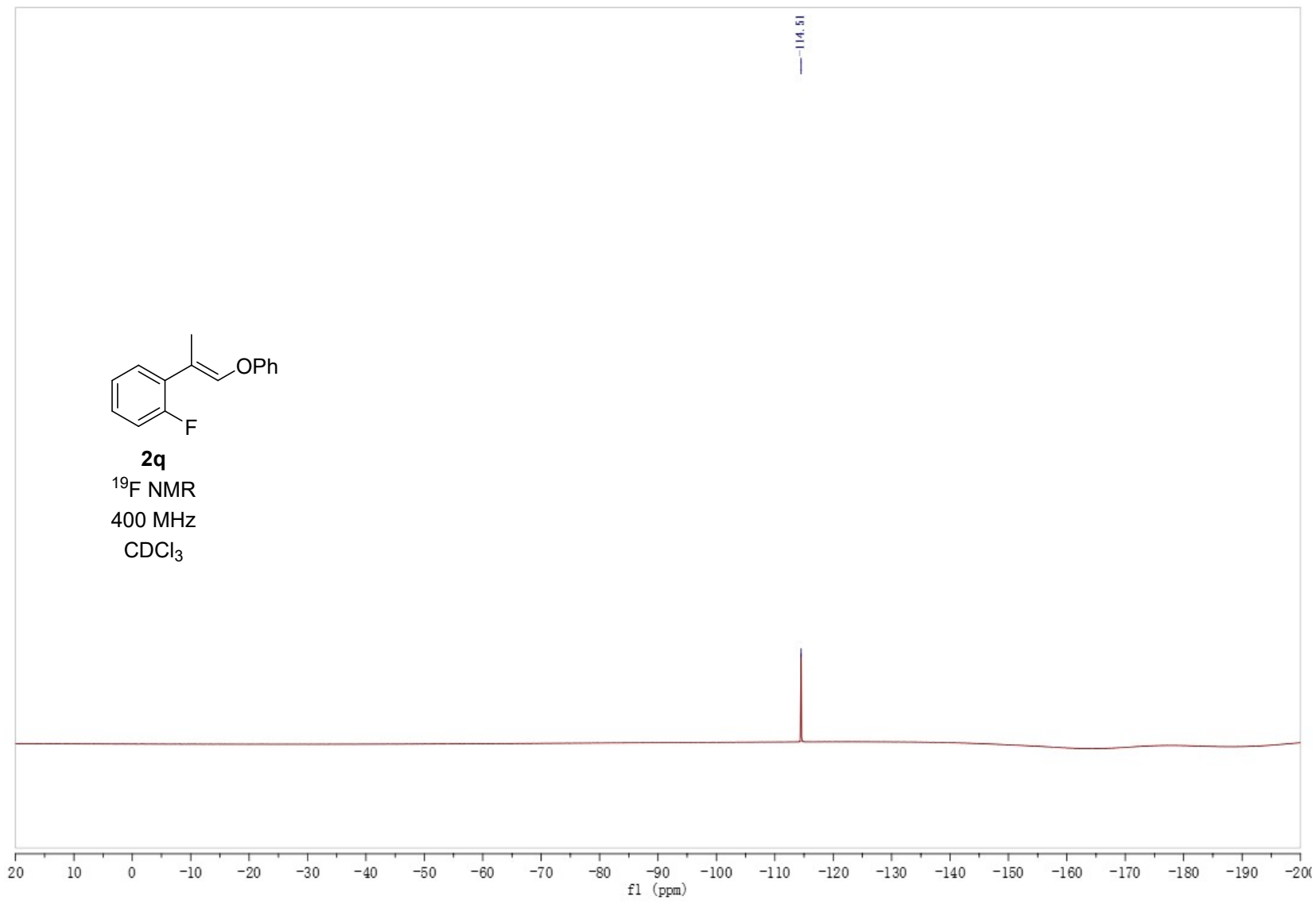
2.133



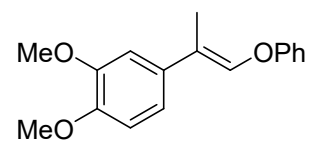
S133



S134



S135



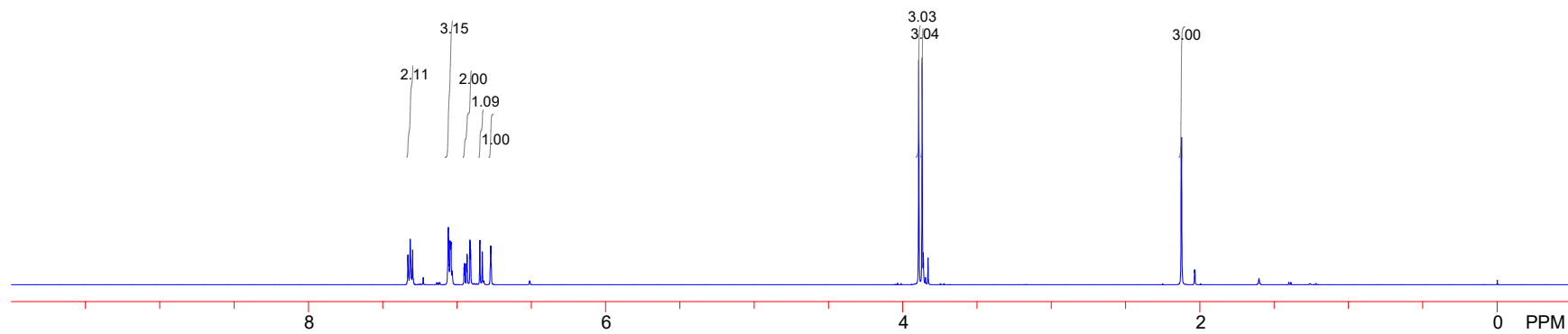
2r

¹H NMR
500 MHz
CDCl₃

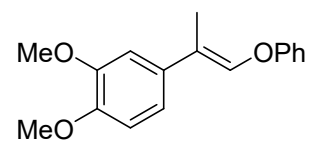
7.331
7.315
7.299
7.058
7.046
7.041
7.039
6.932
6.912
6.908
6.846
6.830
6.774
6.772

3.892
3.869

2.124

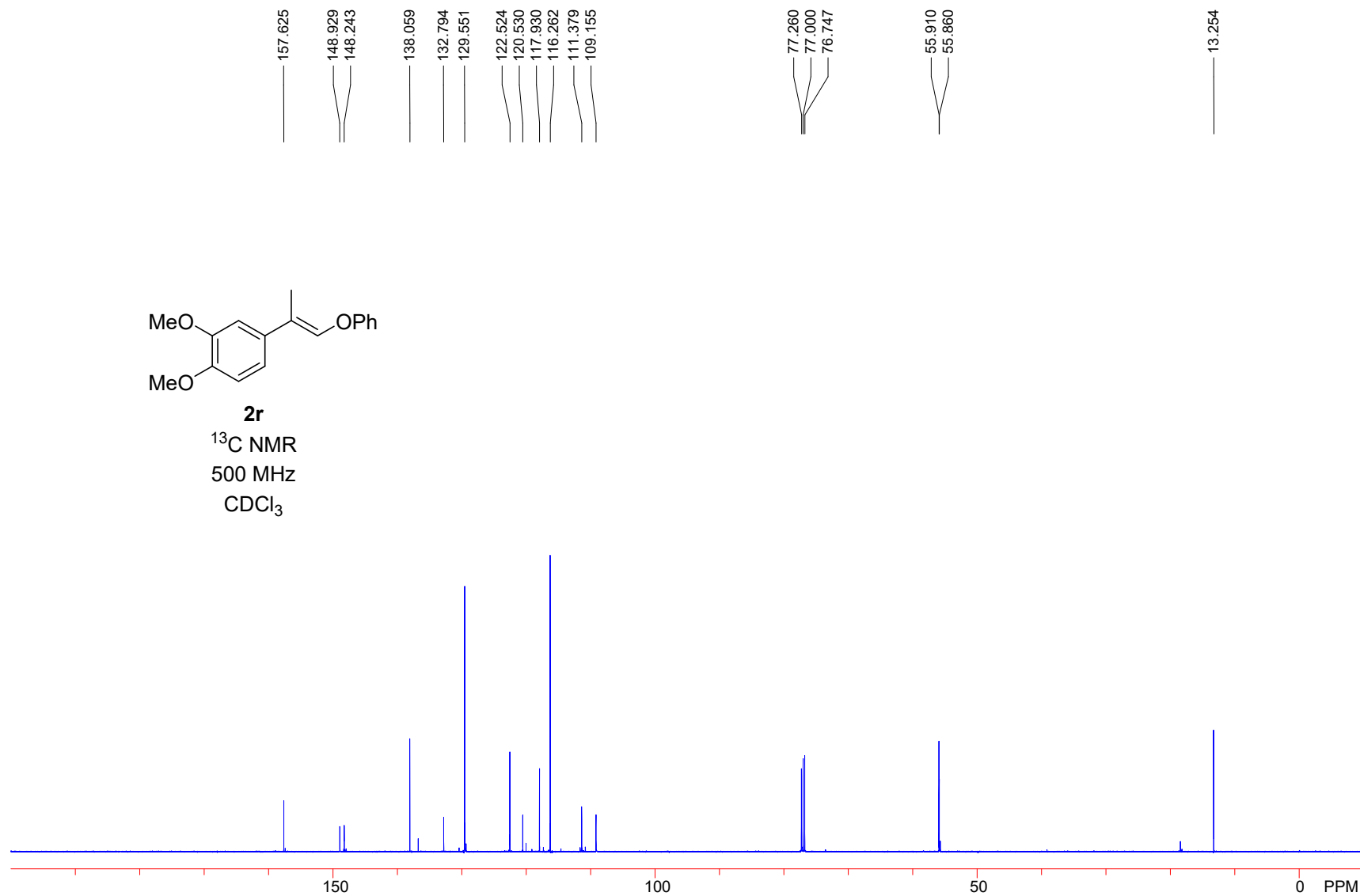


S136

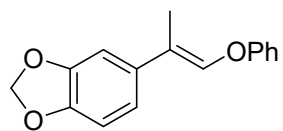


2r

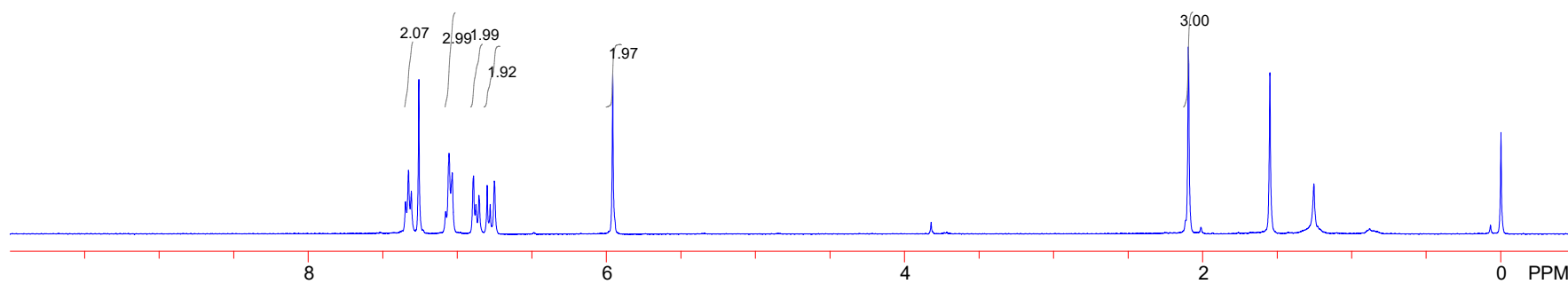
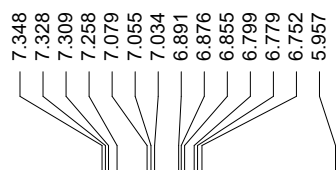
¹³C NMR
500 MHz
CDCl₃

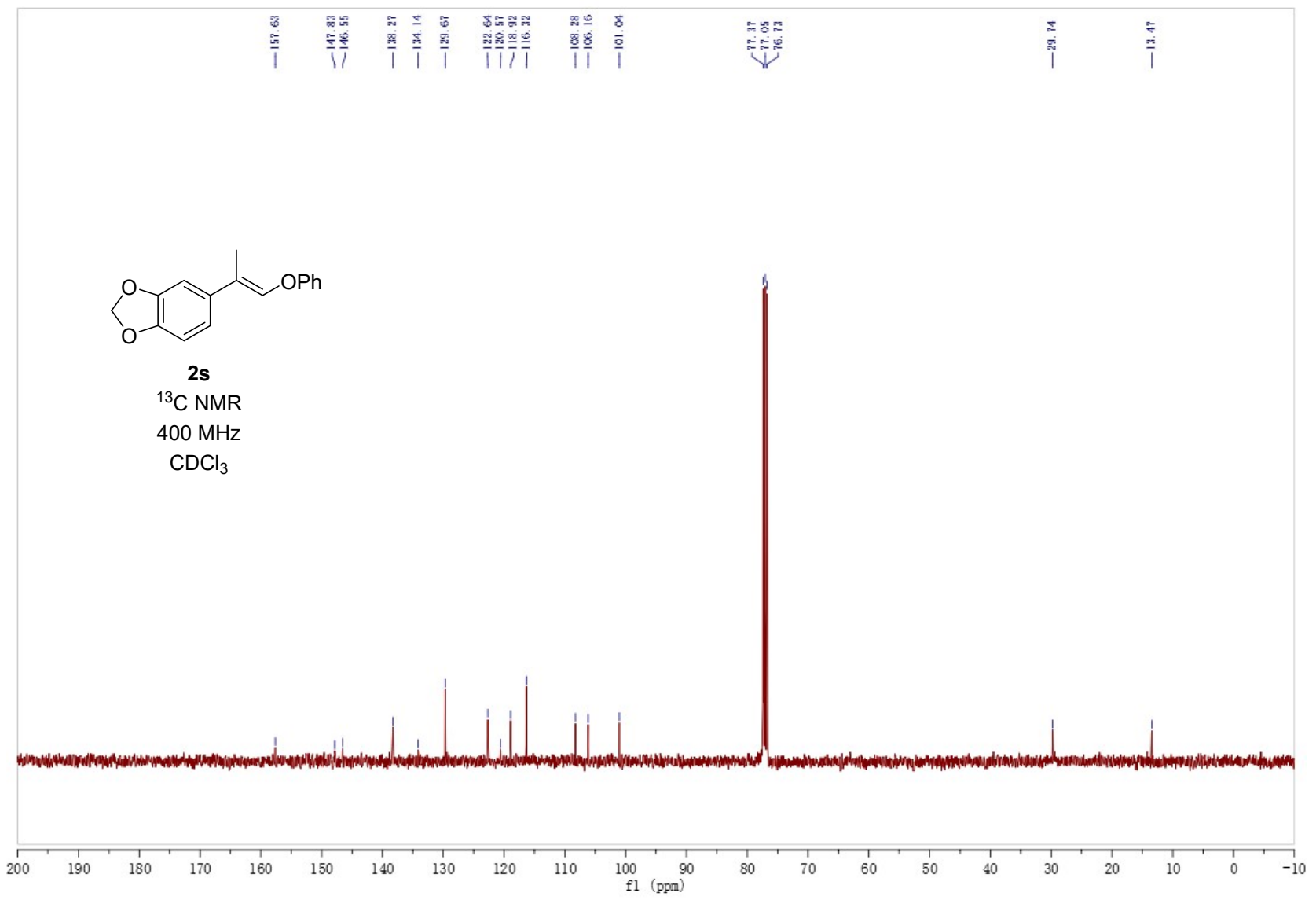


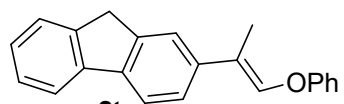
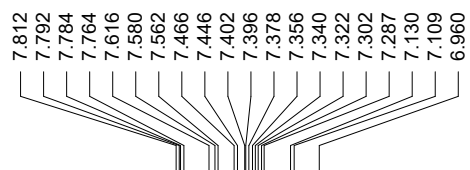
S137



2s
¹H NMR
400 MHz
CDCl₃

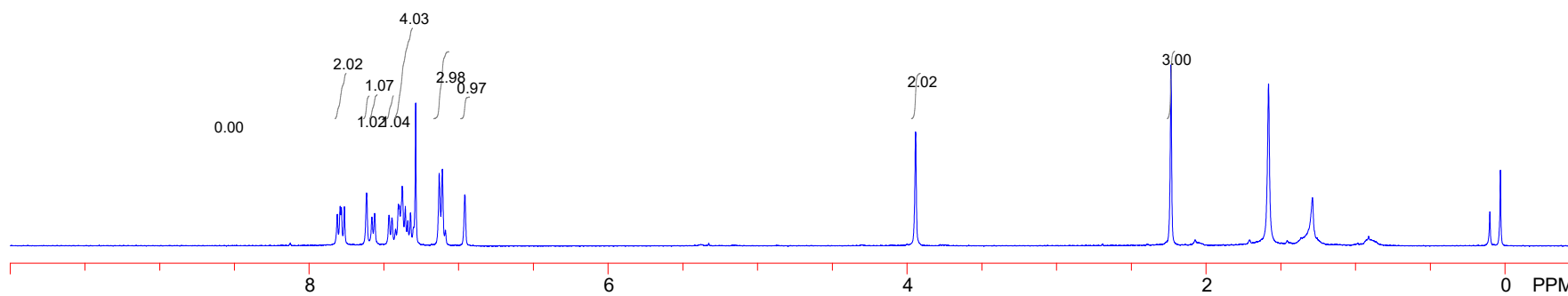


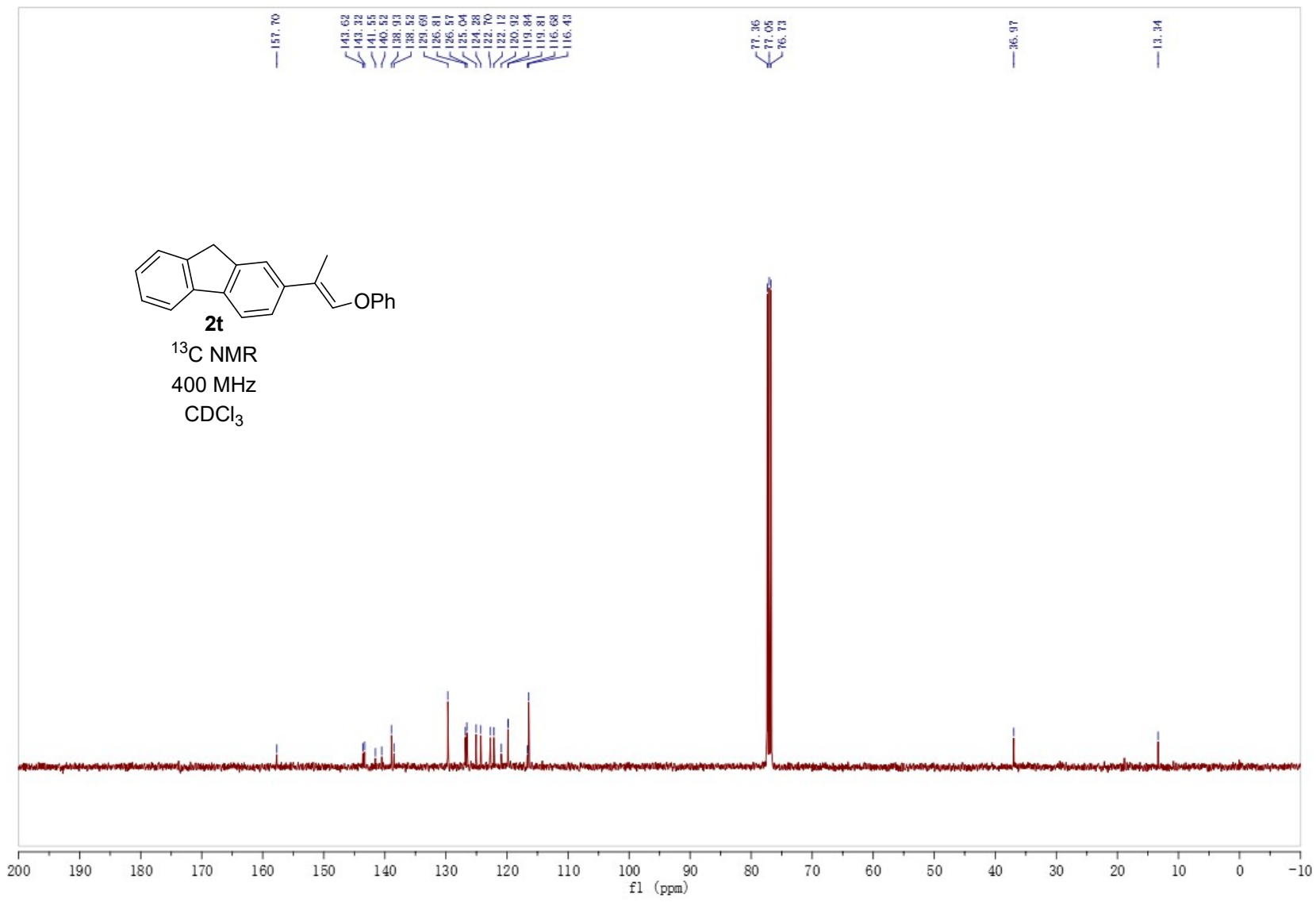




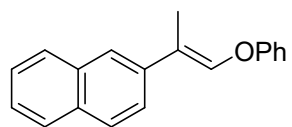
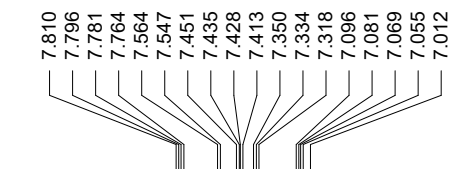
2t

¹H NMR
400 MHz
CDCl₃



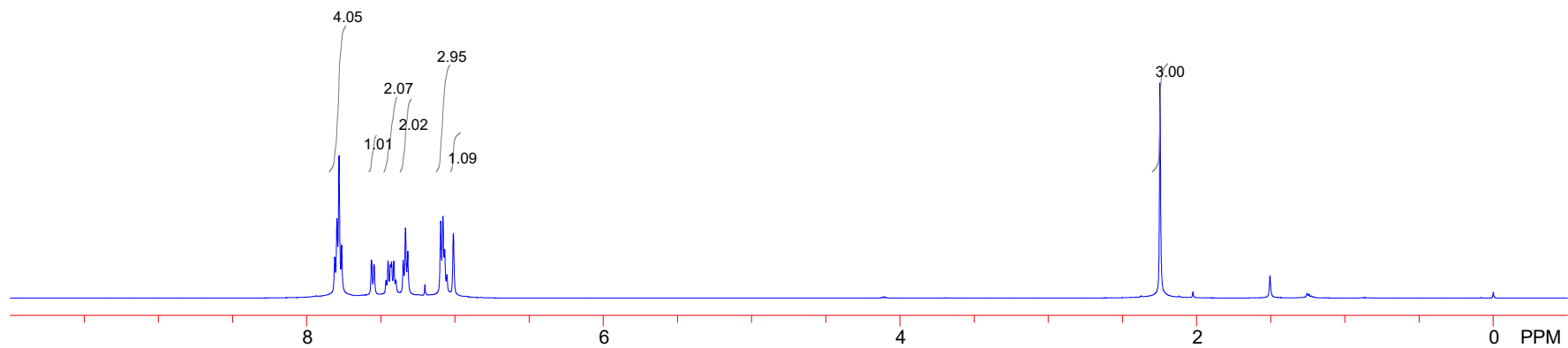


S141

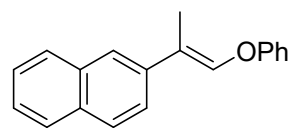


2u

¹H NMR
500 MHz
CDCl₃

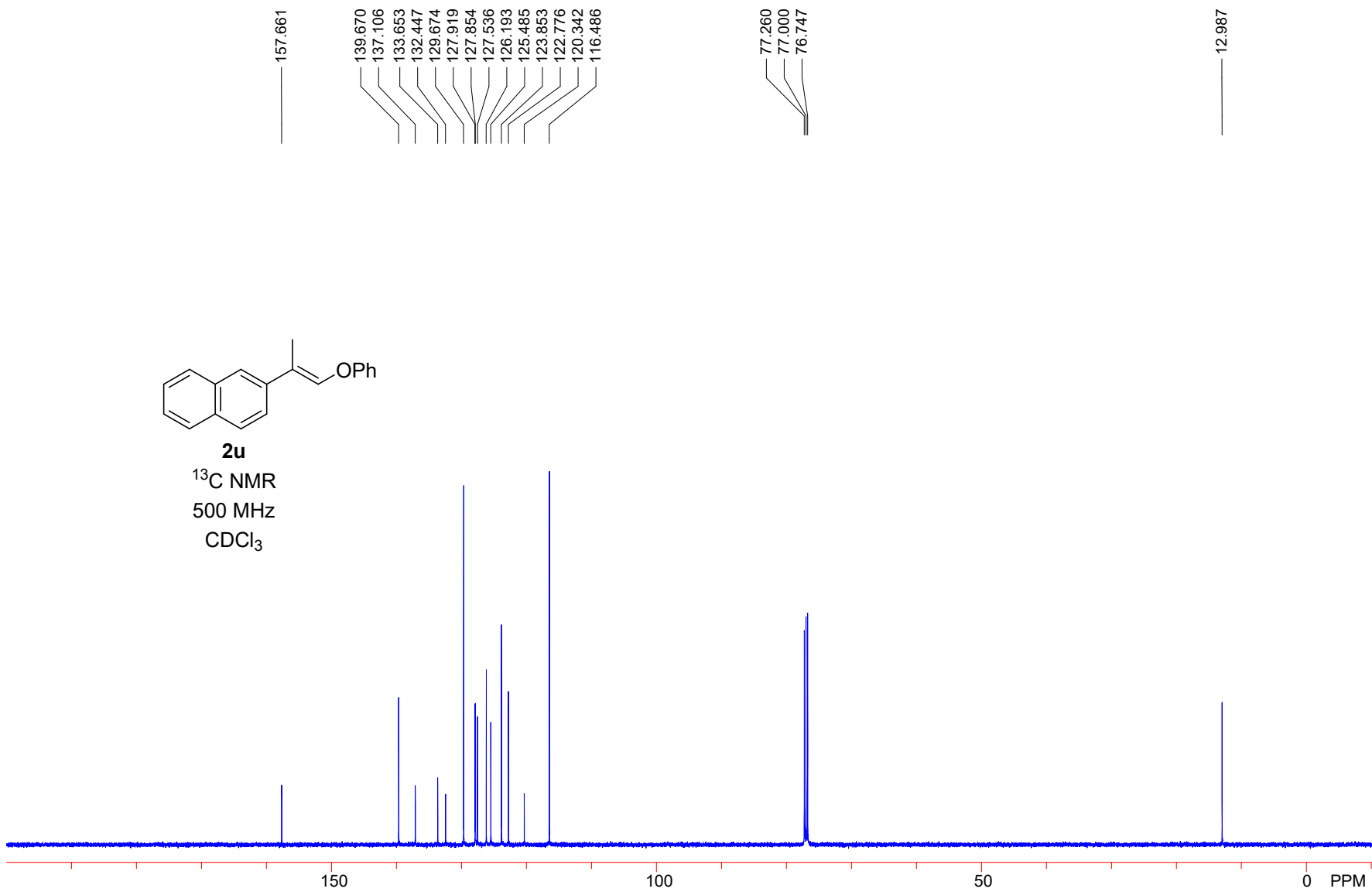


S142

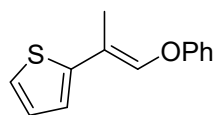


2u

¹³C NMR
500 MHz
CDCl₃



S143



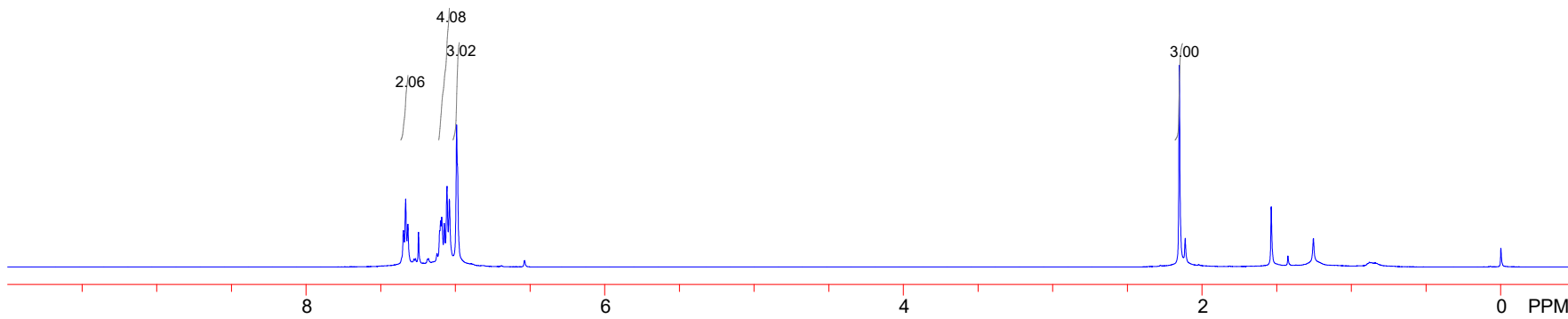
2v

¹H NMR
500 MHz
CDCl₃

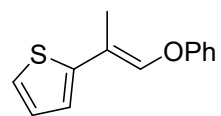
7.348
7.333
7.318
7.248
7.106
7.099
7.092
7.075
7.057
7.041
6.992
6.987

2.152
2.113

1.538
1.255



S144

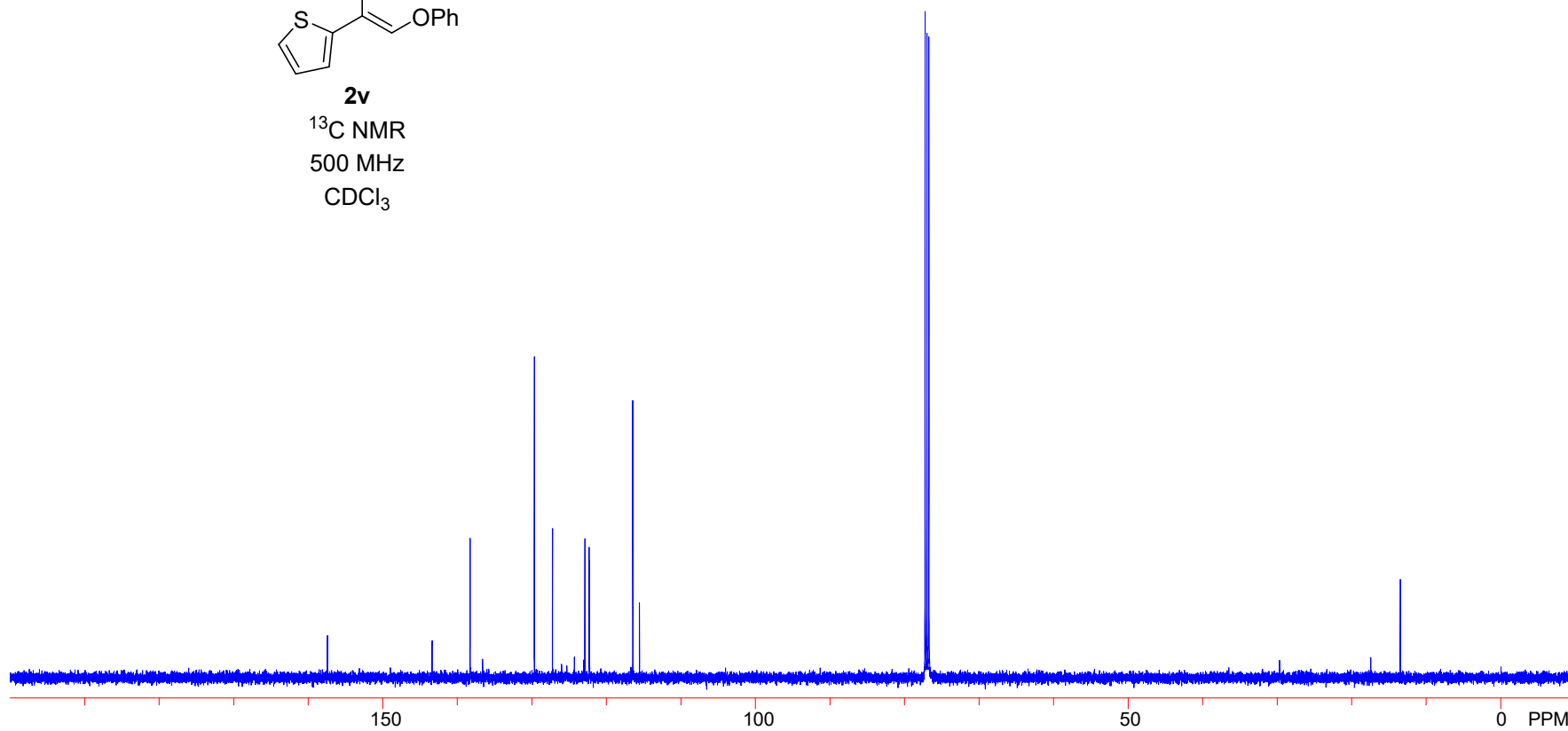


2v

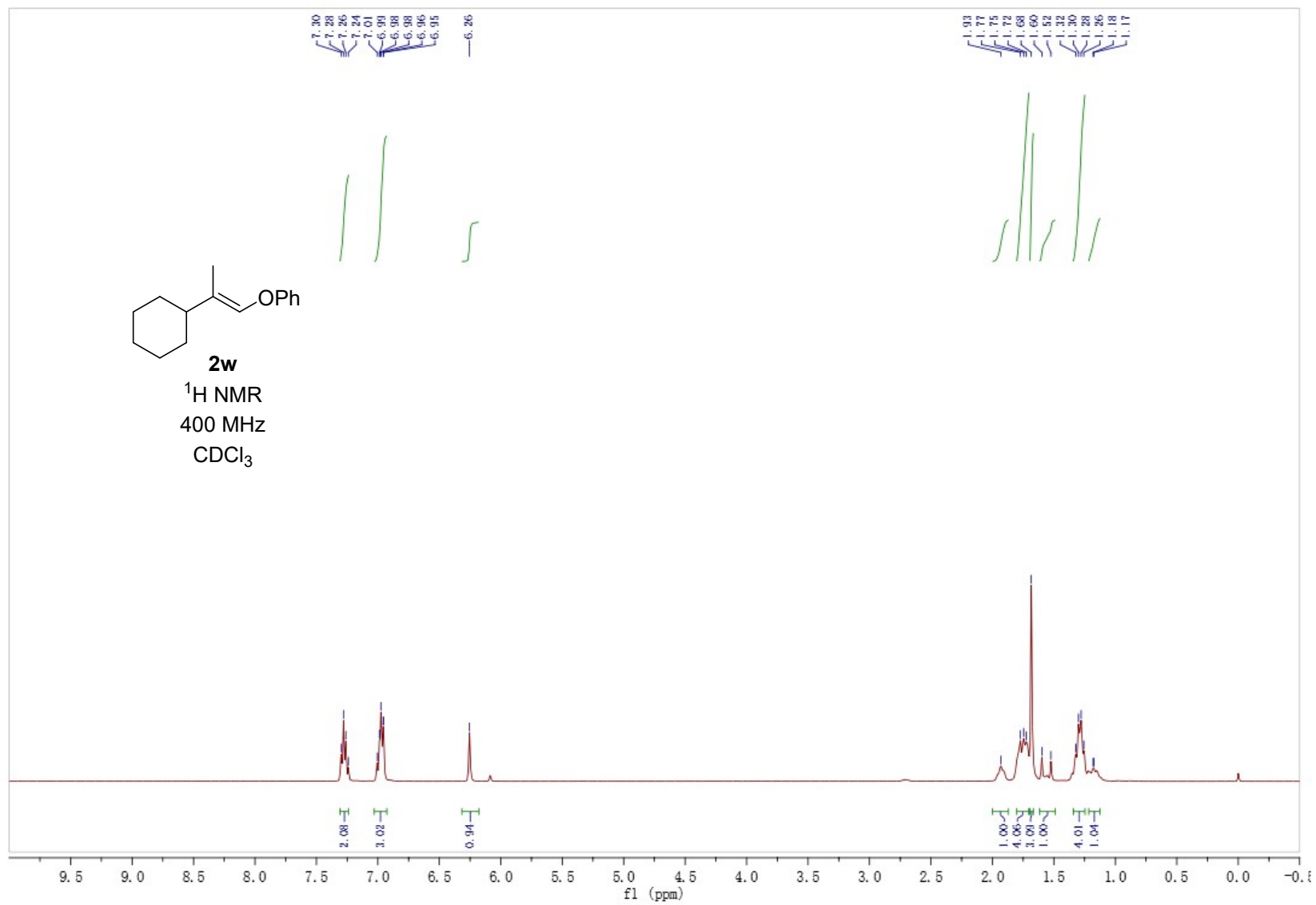
¹³C NMR
500 MHz
CDCl₃

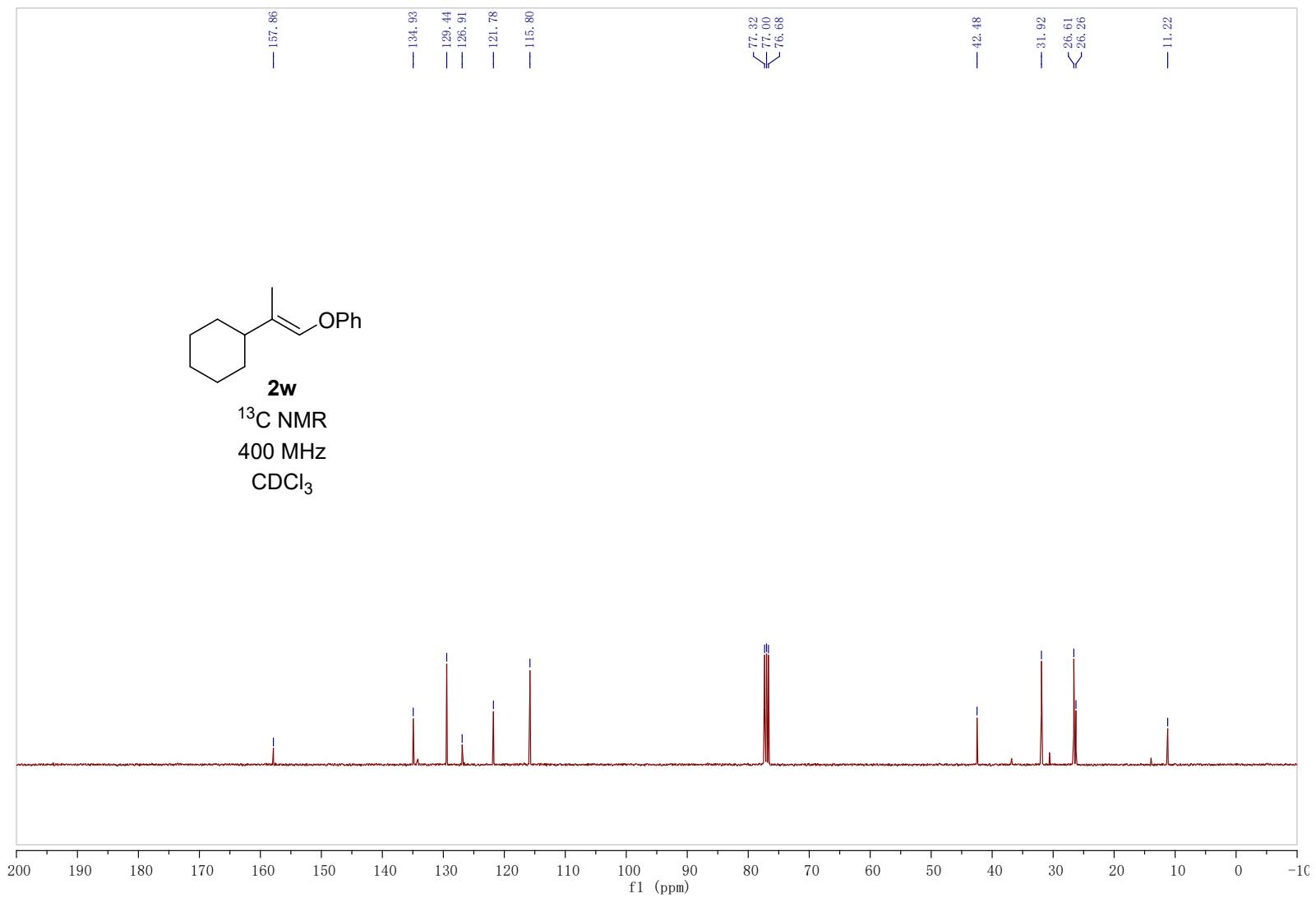
138.290
129.674
127.240
122.892
122.329
122.264
116.464
115.568

13.485

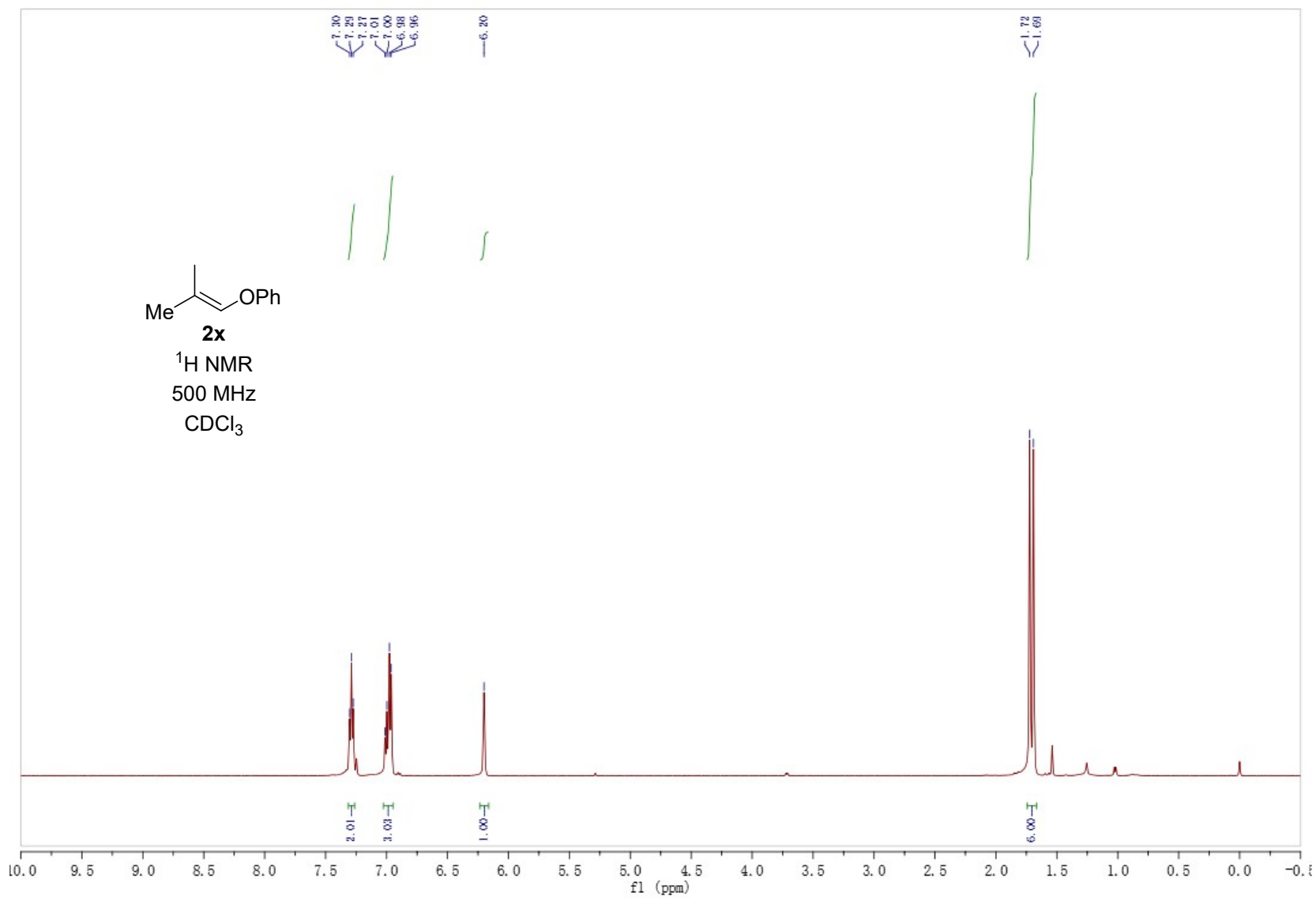


S145

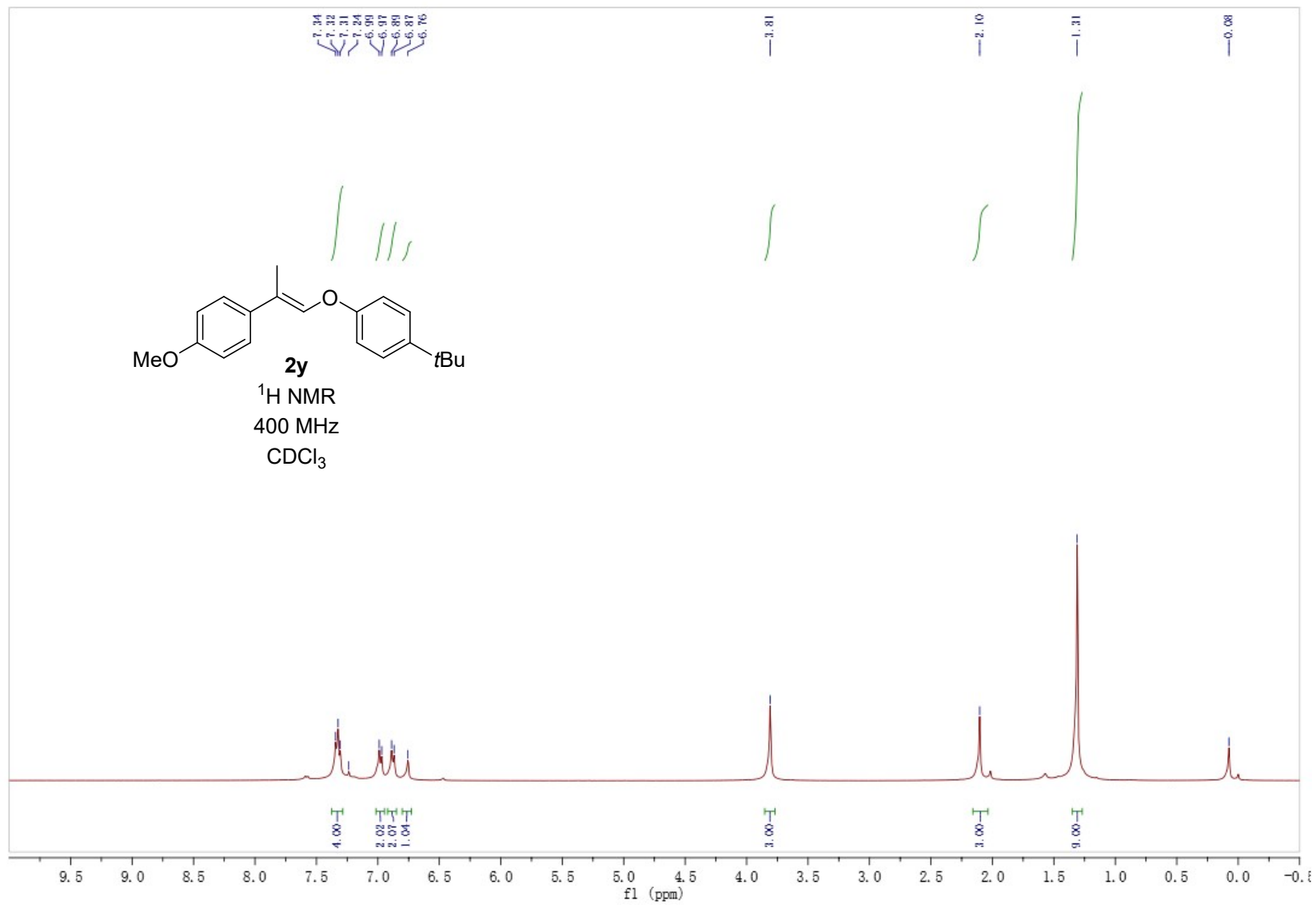




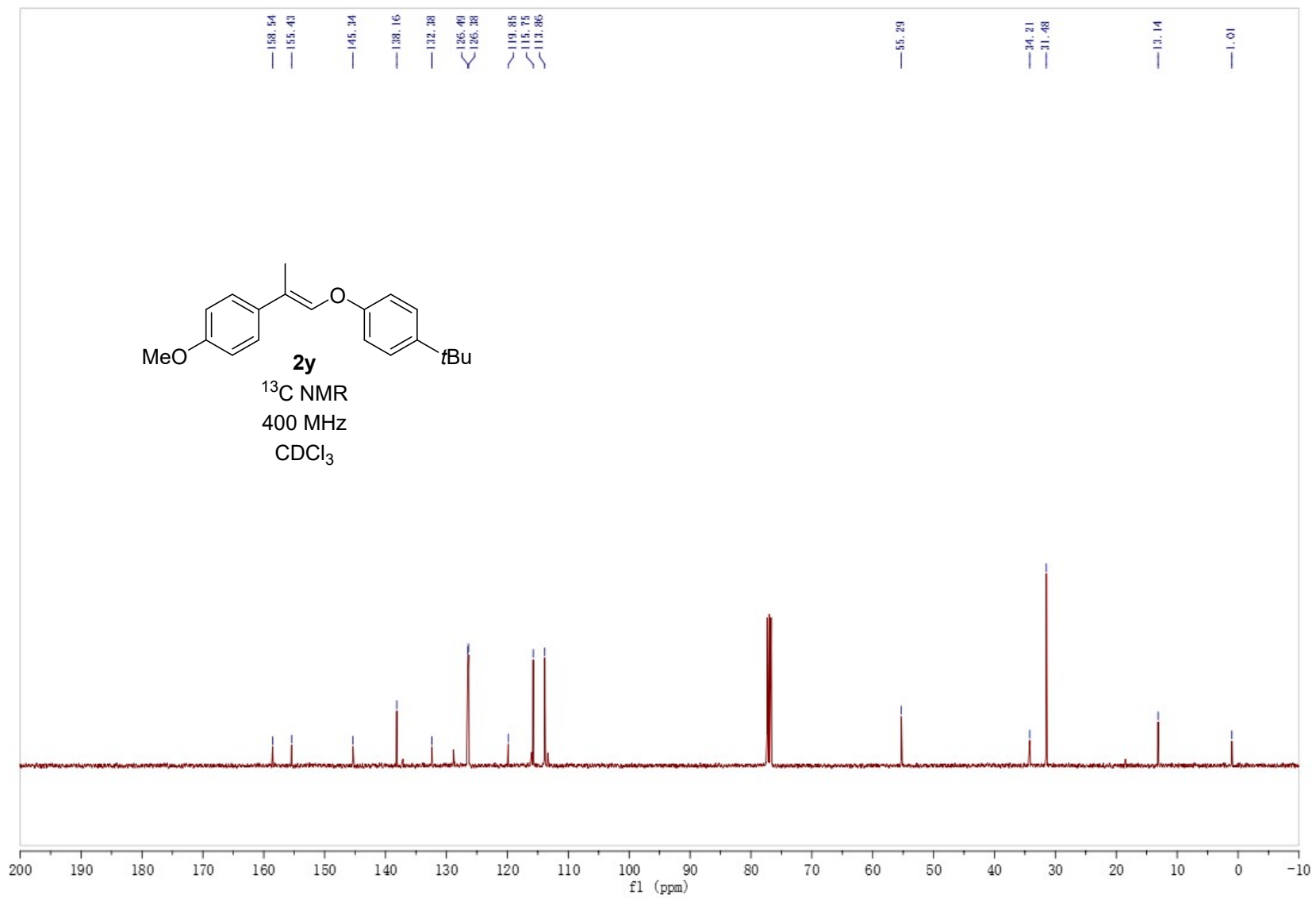
S147



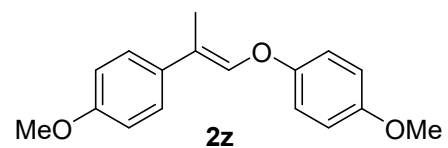
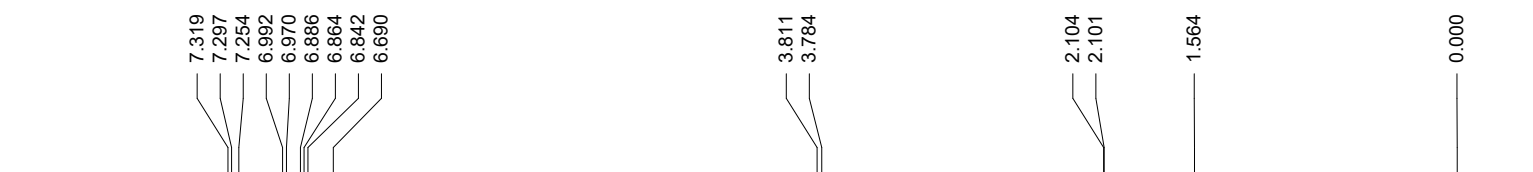
S148



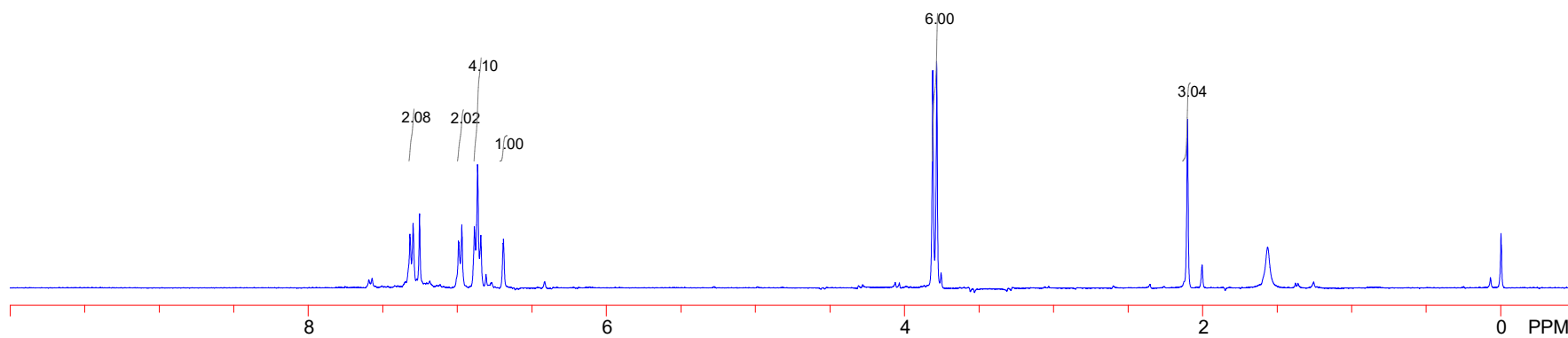
S149



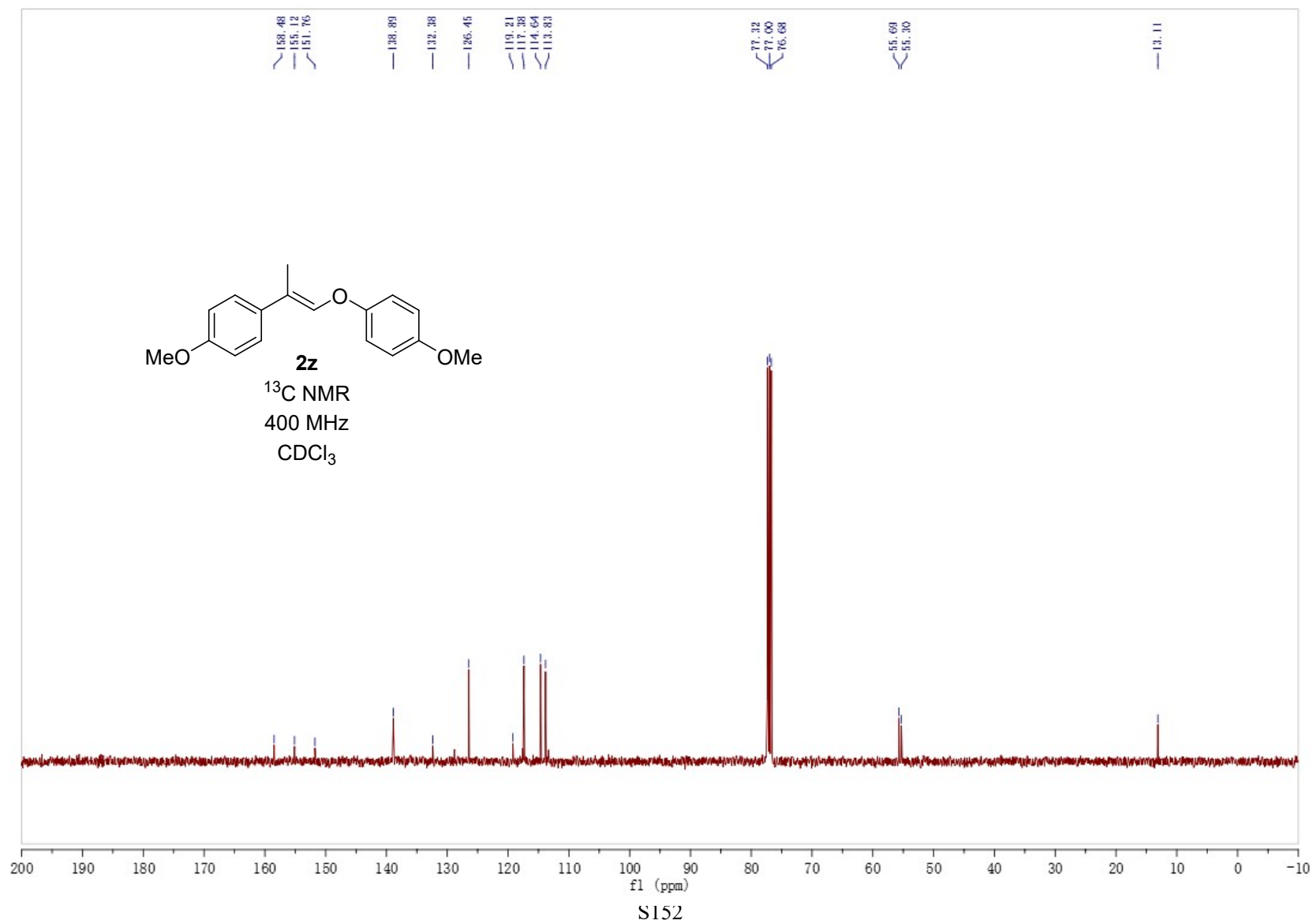
S150

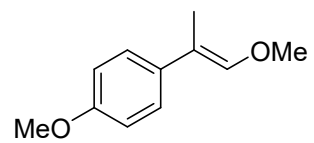


¹H NMR
 400 MHz
 CDCl₃



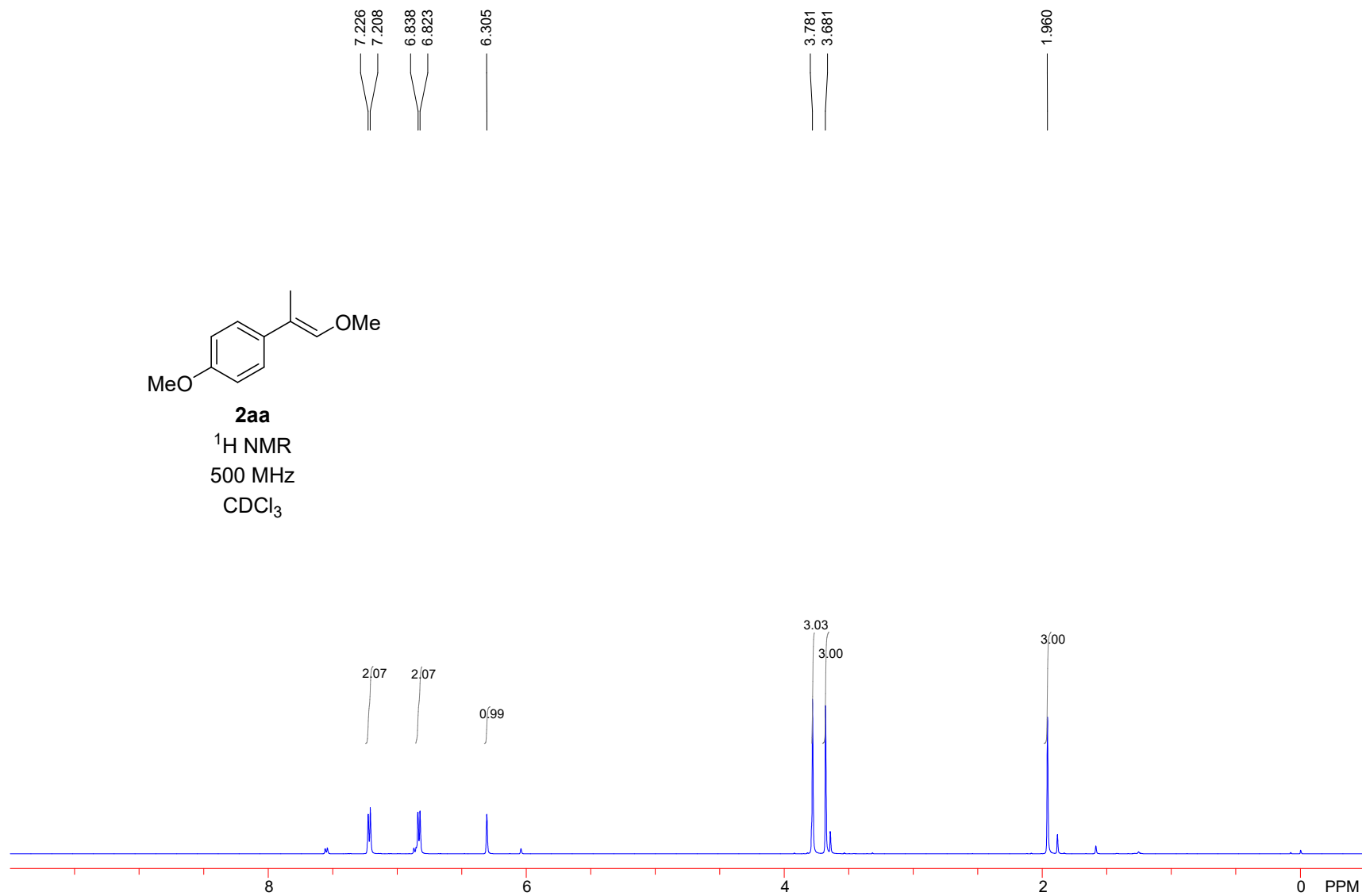
S151



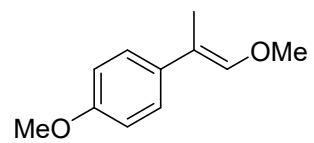


2aa

¹H NMR
500 MHz
CDCl₃



S153

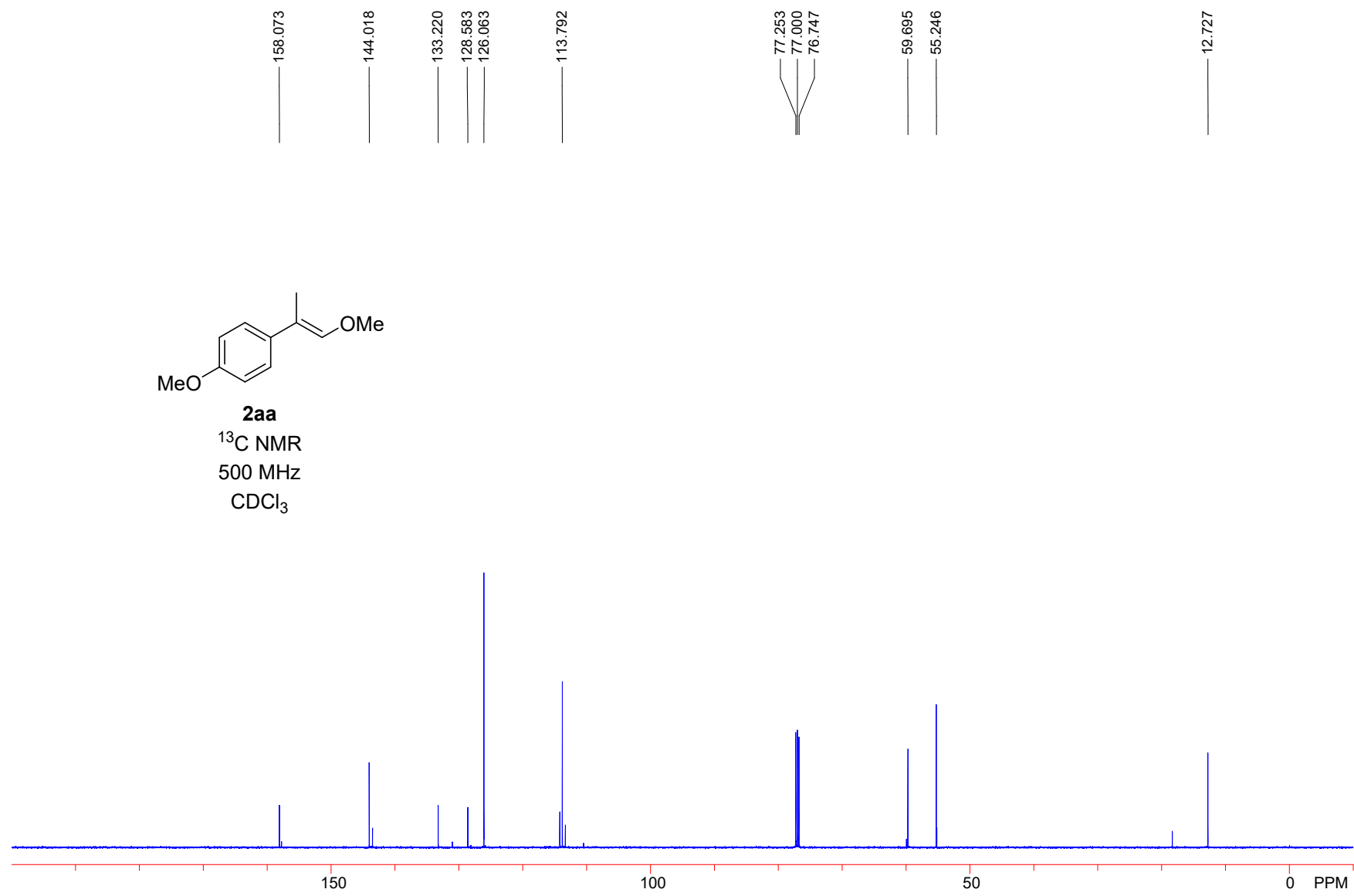


2aa

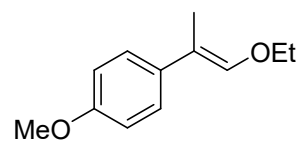
¹³C NMR

500 MHz

CDCl₃

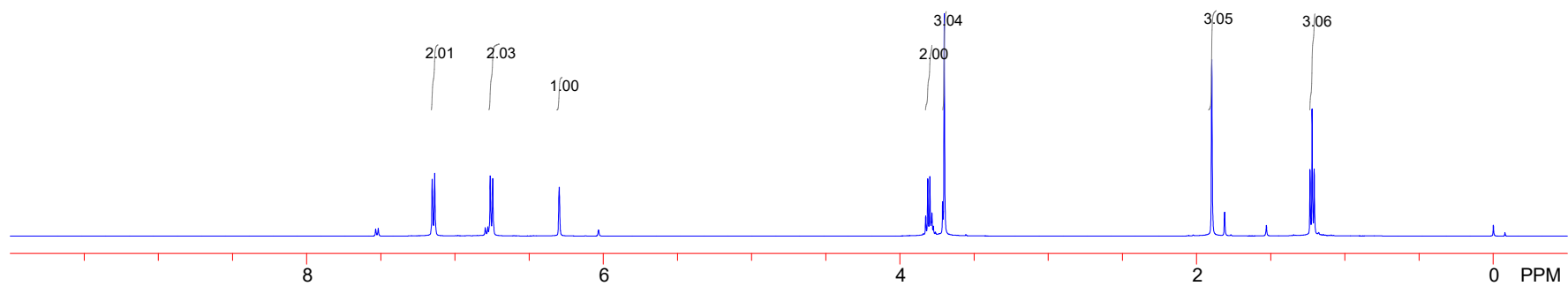
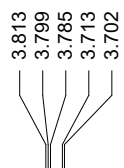
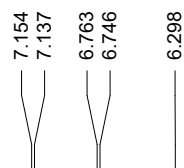


S154

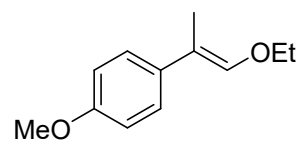


2ab

¹H NMR
500 MHz
CDCl₃

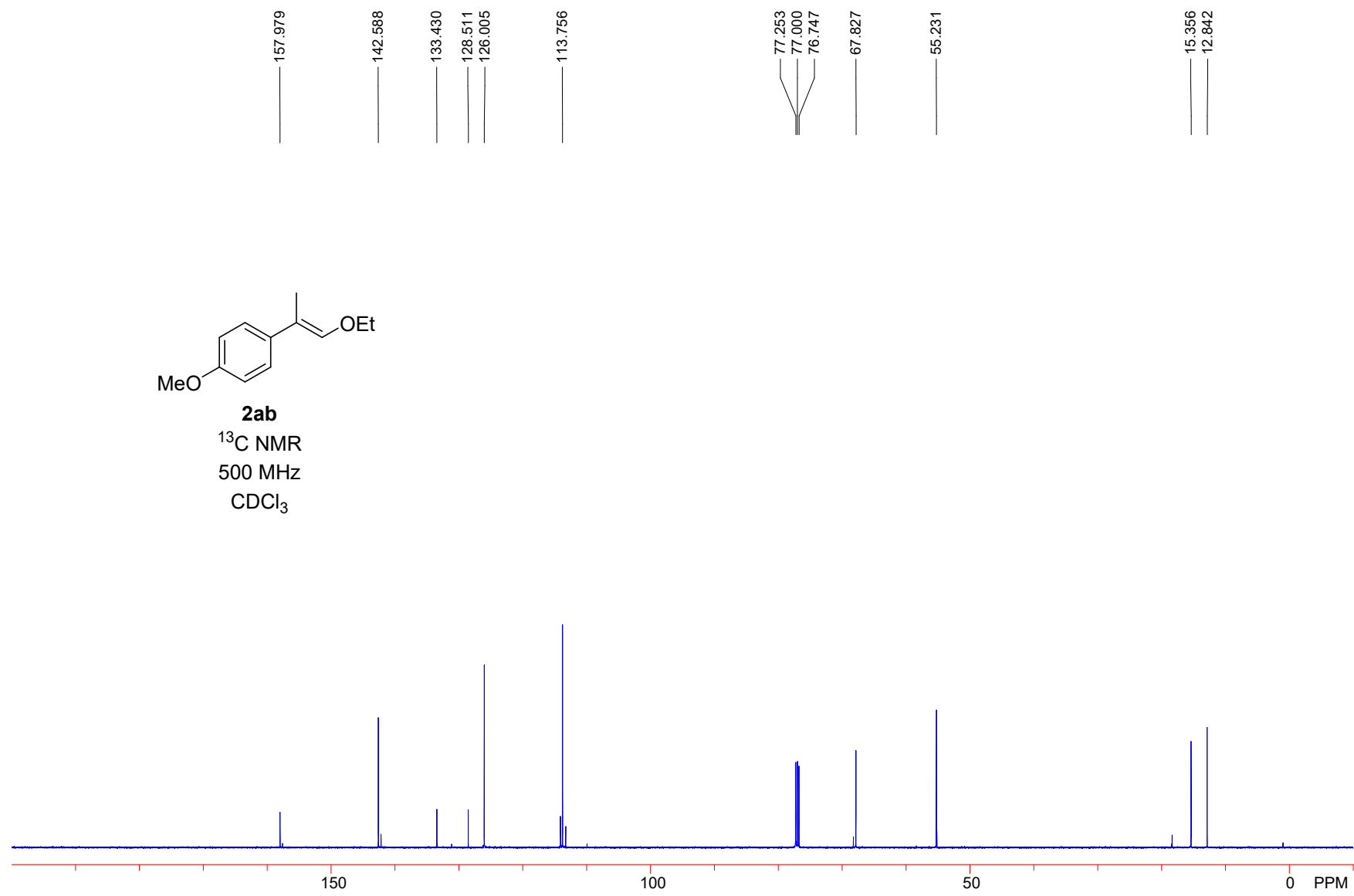


S155

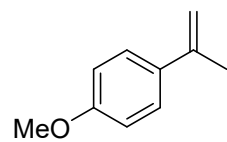


2ab

¹³C NMR
500 MHz
CDCl₃

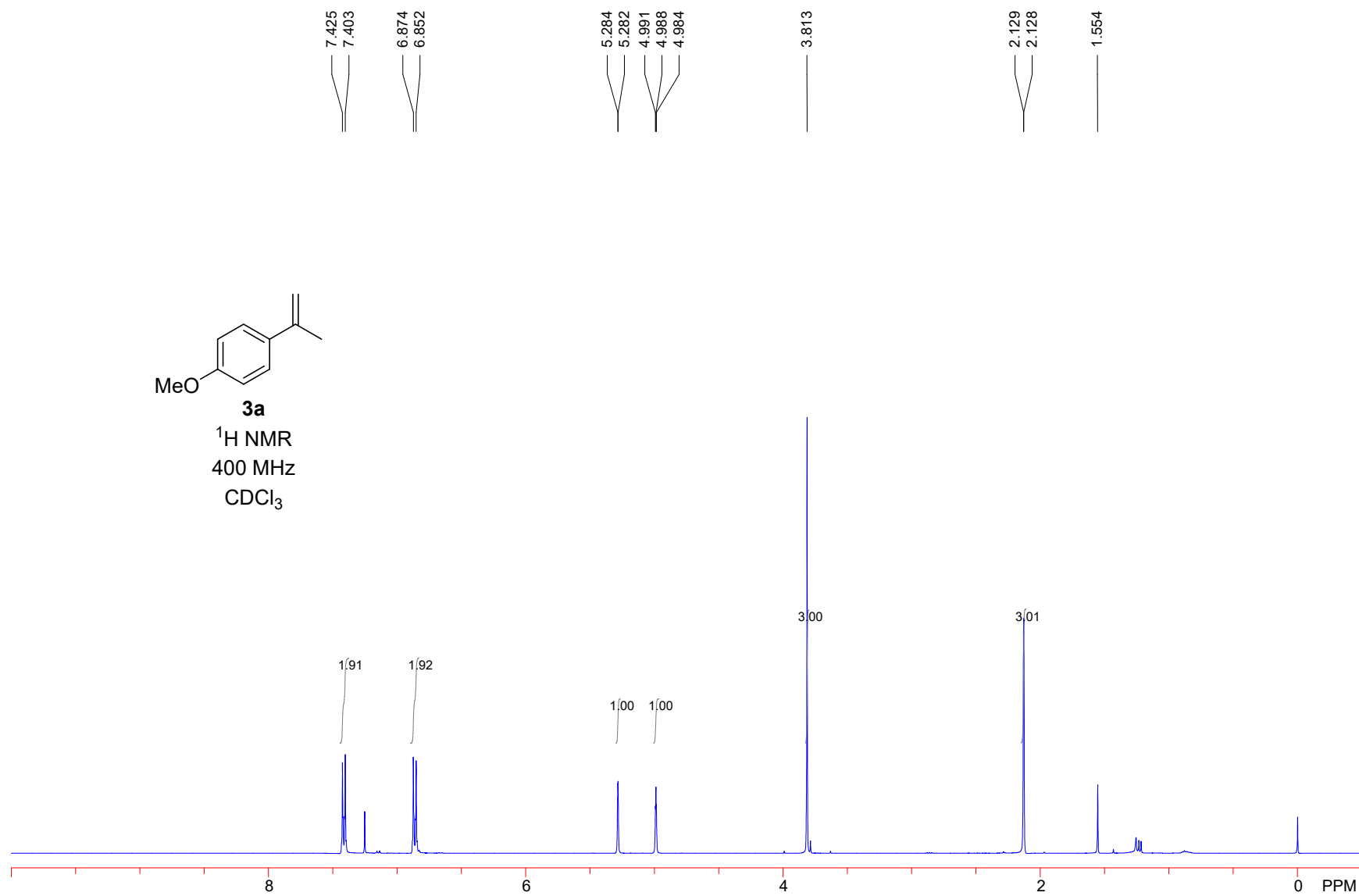


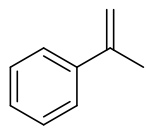
S156



3a

¹H NMR
400 MHz
CDCl₃



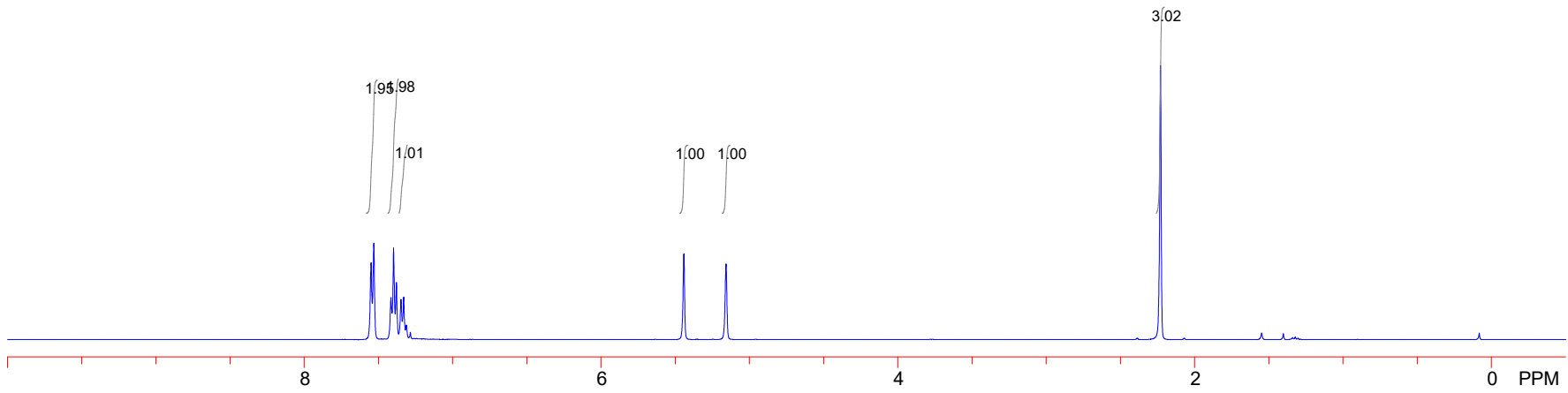


3b
¹H NMR
400 MHz
CDCl₃

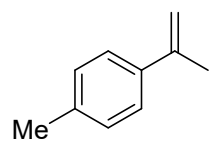
7.550
7.531
7.416
7.398
7.378
7.348
7.330

5.442
5.157

2.230



S158



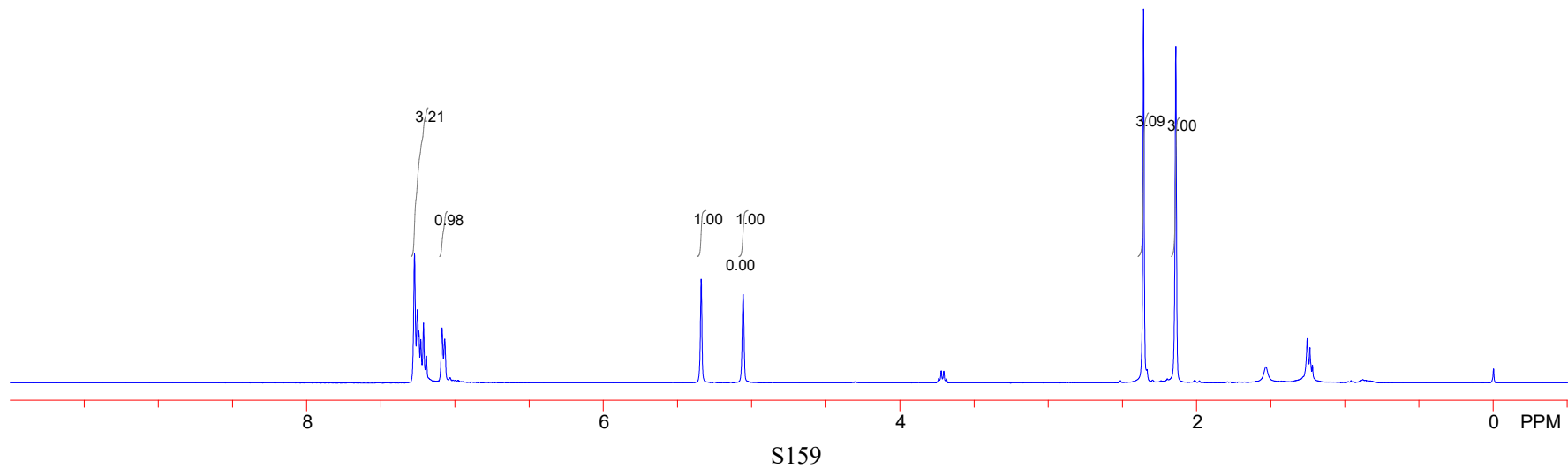
3c

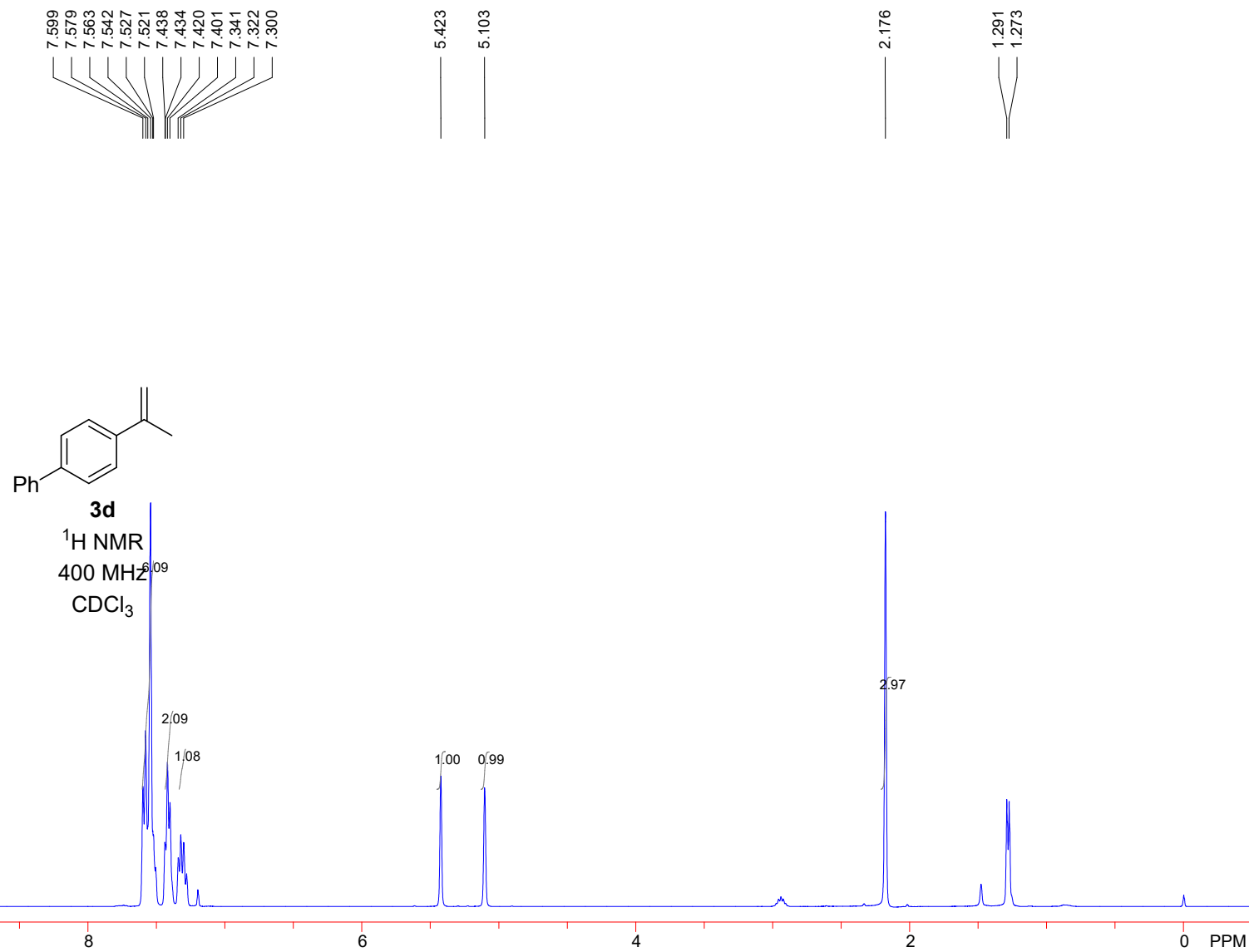
¹H NMR
400 MHz
CDCl₃

7.272
7.254
7.244
7.230
7.212
7.087
7.070

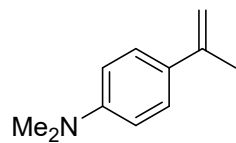
5.340
5.058
5.056

2.358
2.140



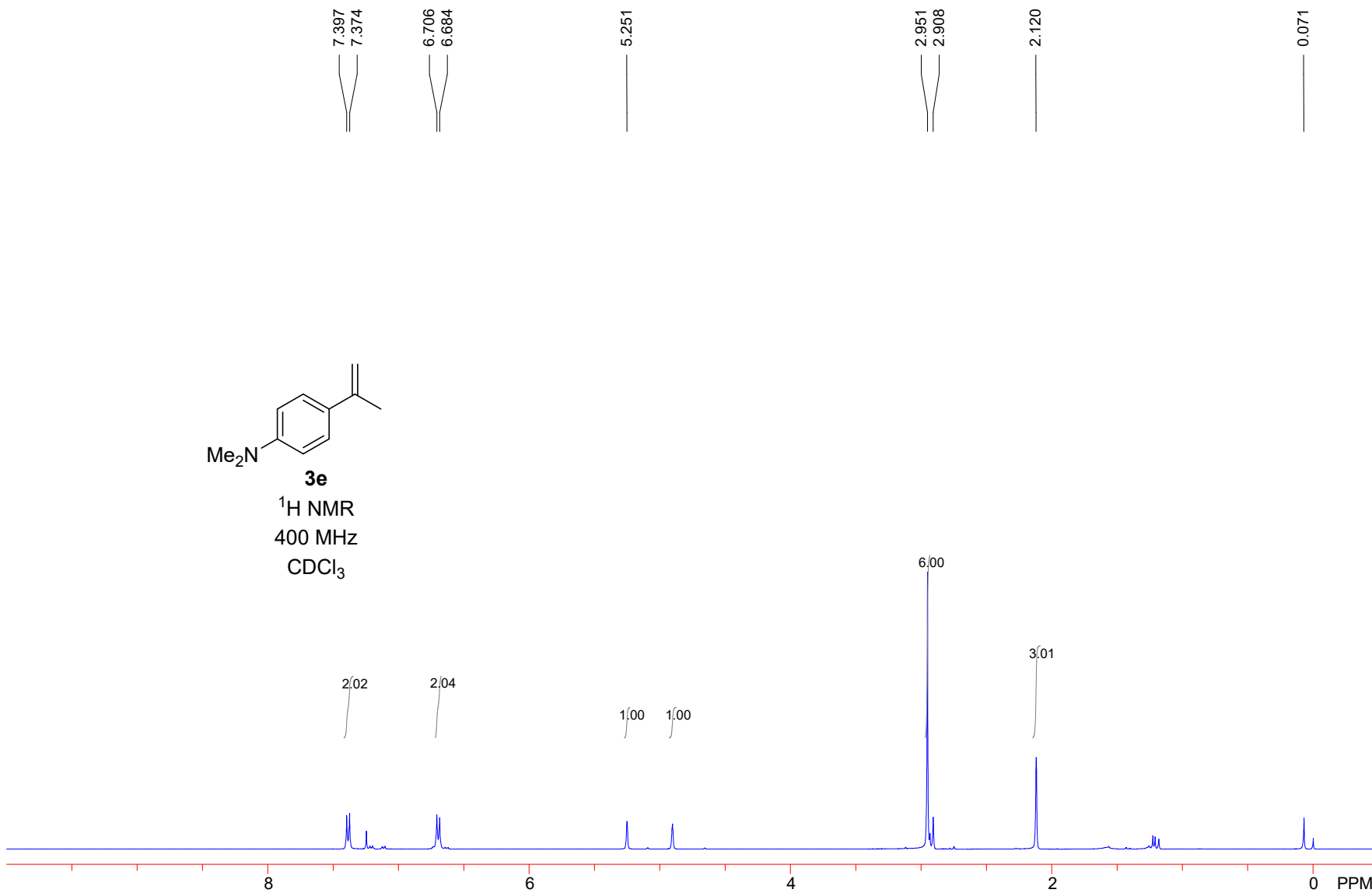


S160

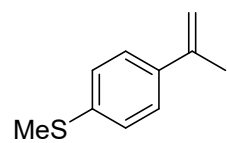


3e

¹H NMR
400 MHz
CDCl₃



S161



3f

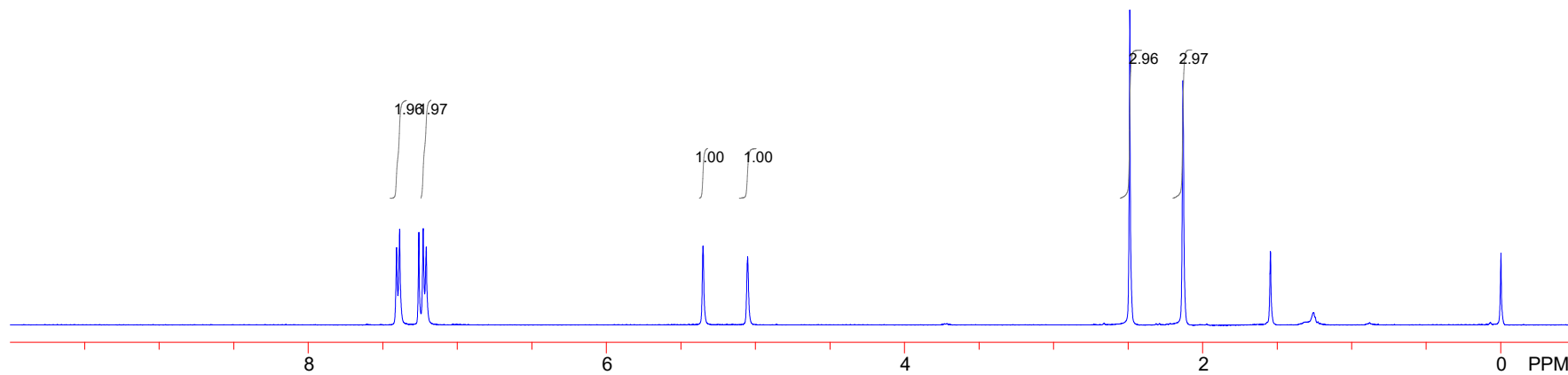
¹H NMR
400 MHz
CDCl₃

7.408
7.387
7.258
7.229
7.208

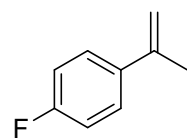
5.352
5.052

2.488
2.132
1.546

-0.000

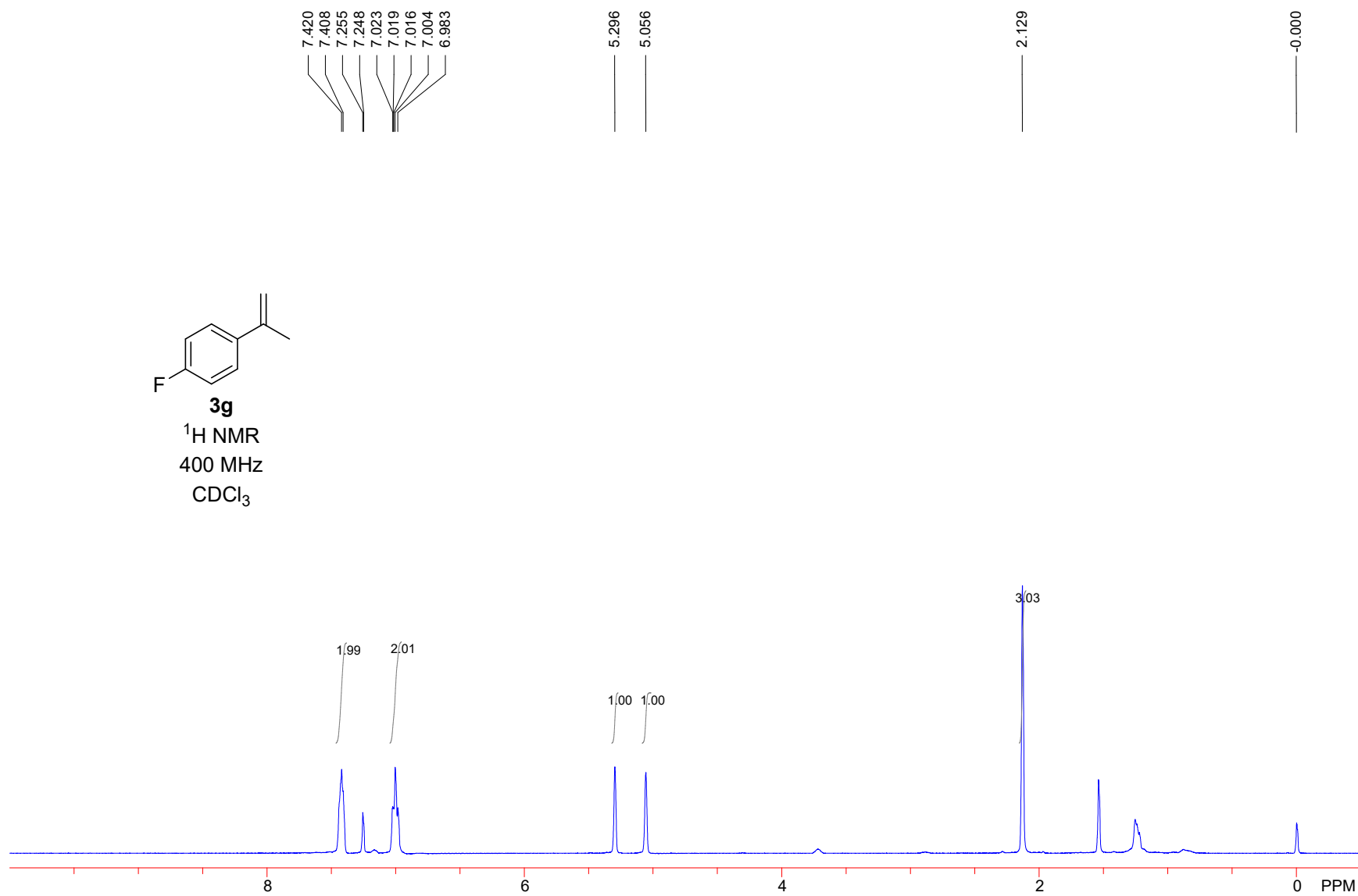


S162

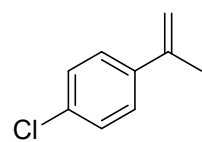


3g

¹H NMR
400 MHz
CDCl₃

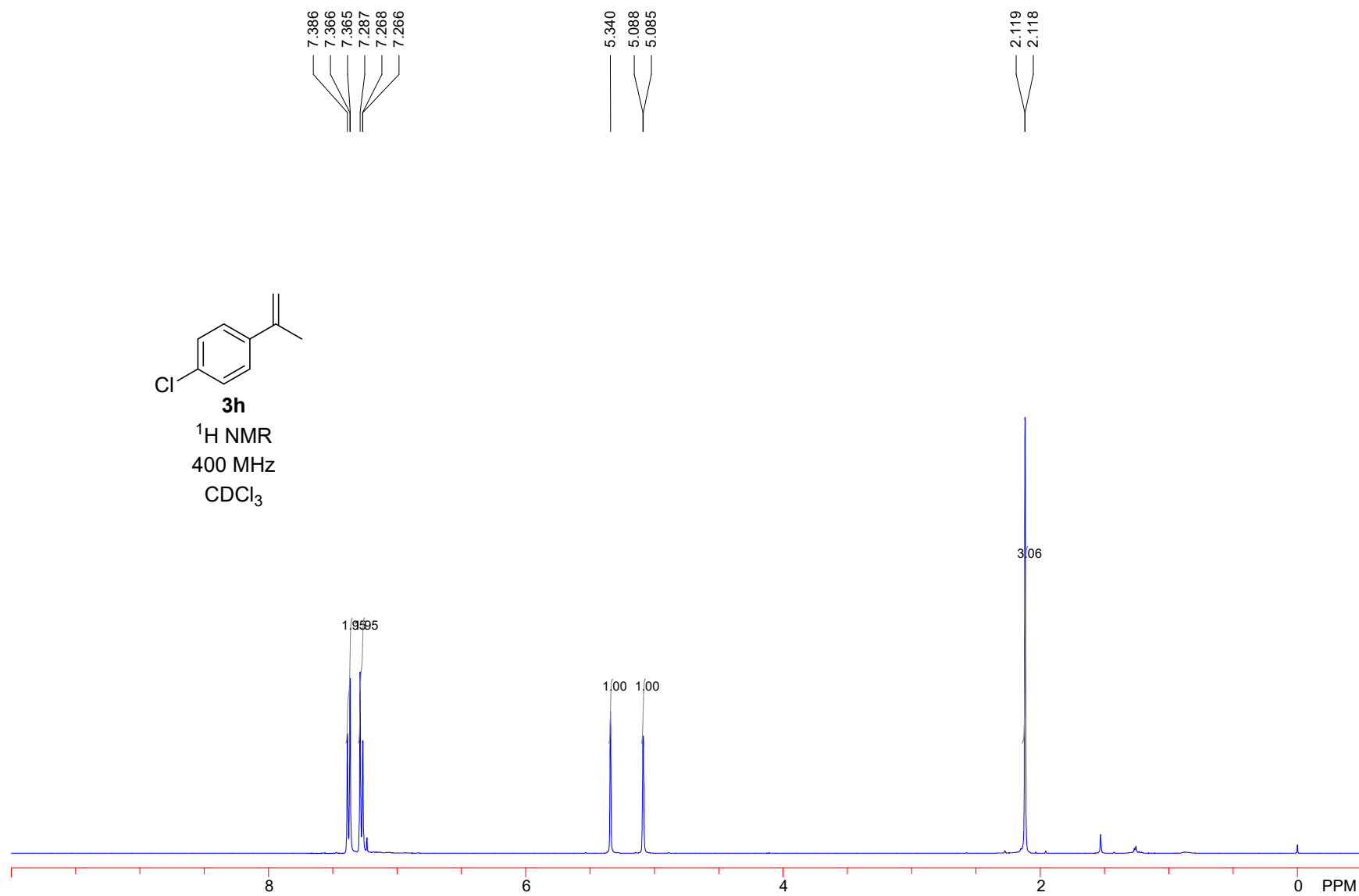


S163

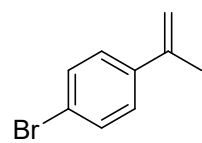


3h

¹H NMR
400 MHz
CDCl₃

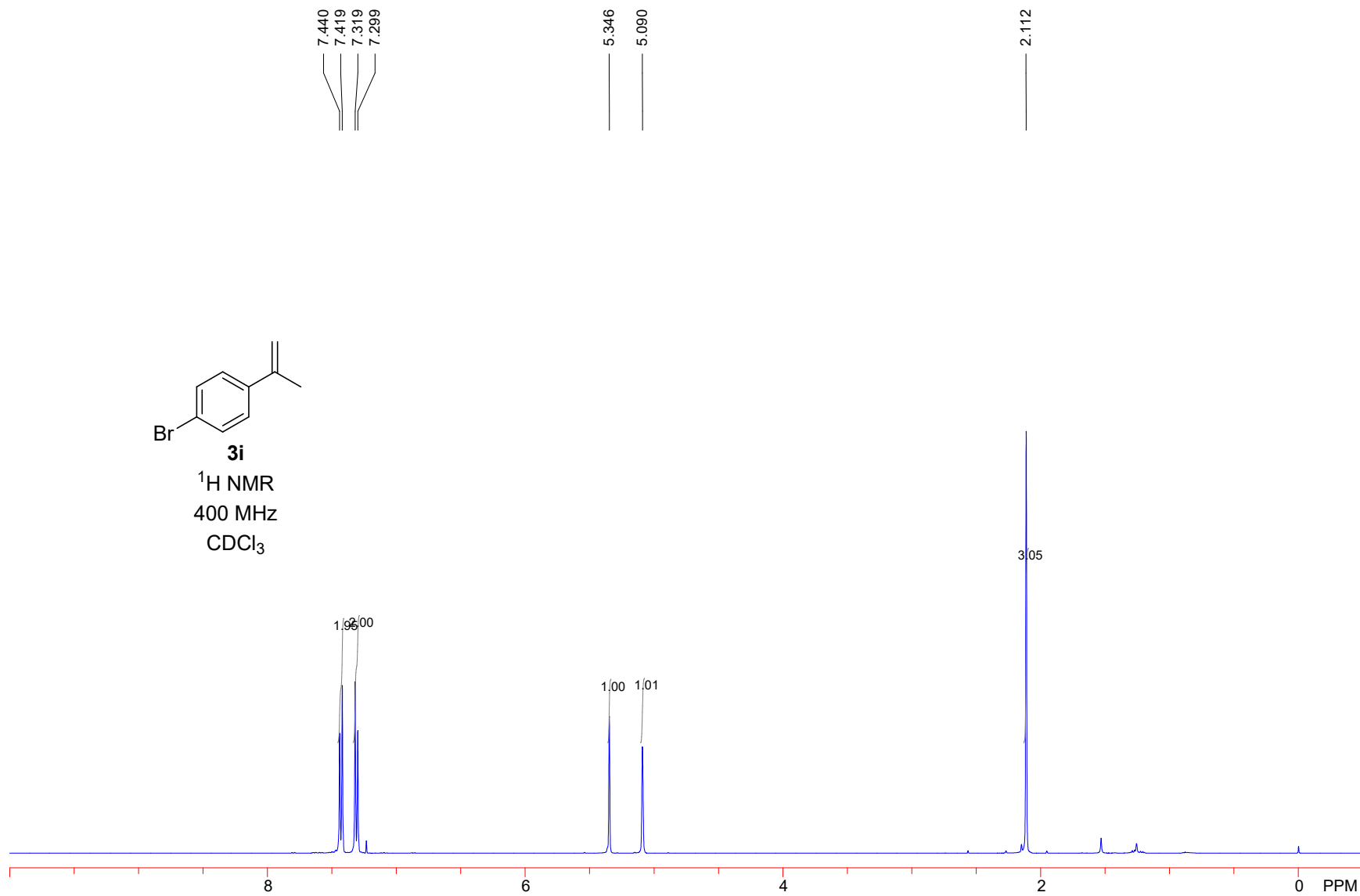


S164

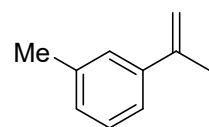


3i

¹H NMR
400 MHz
CDCl₃

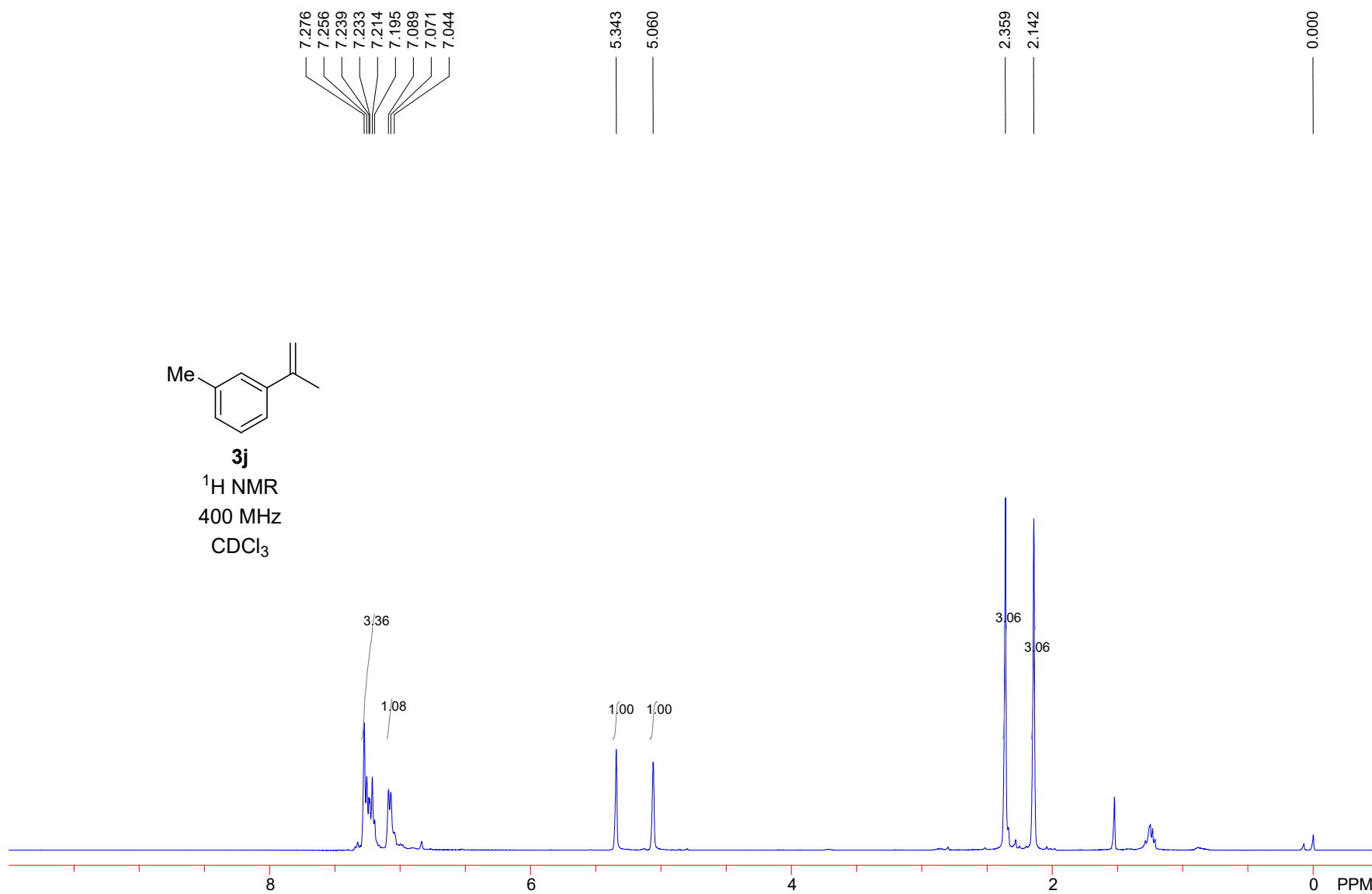


S165

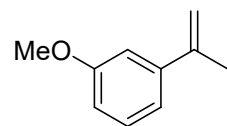


3j

¹H NMR
400 MHz
CDCl₃

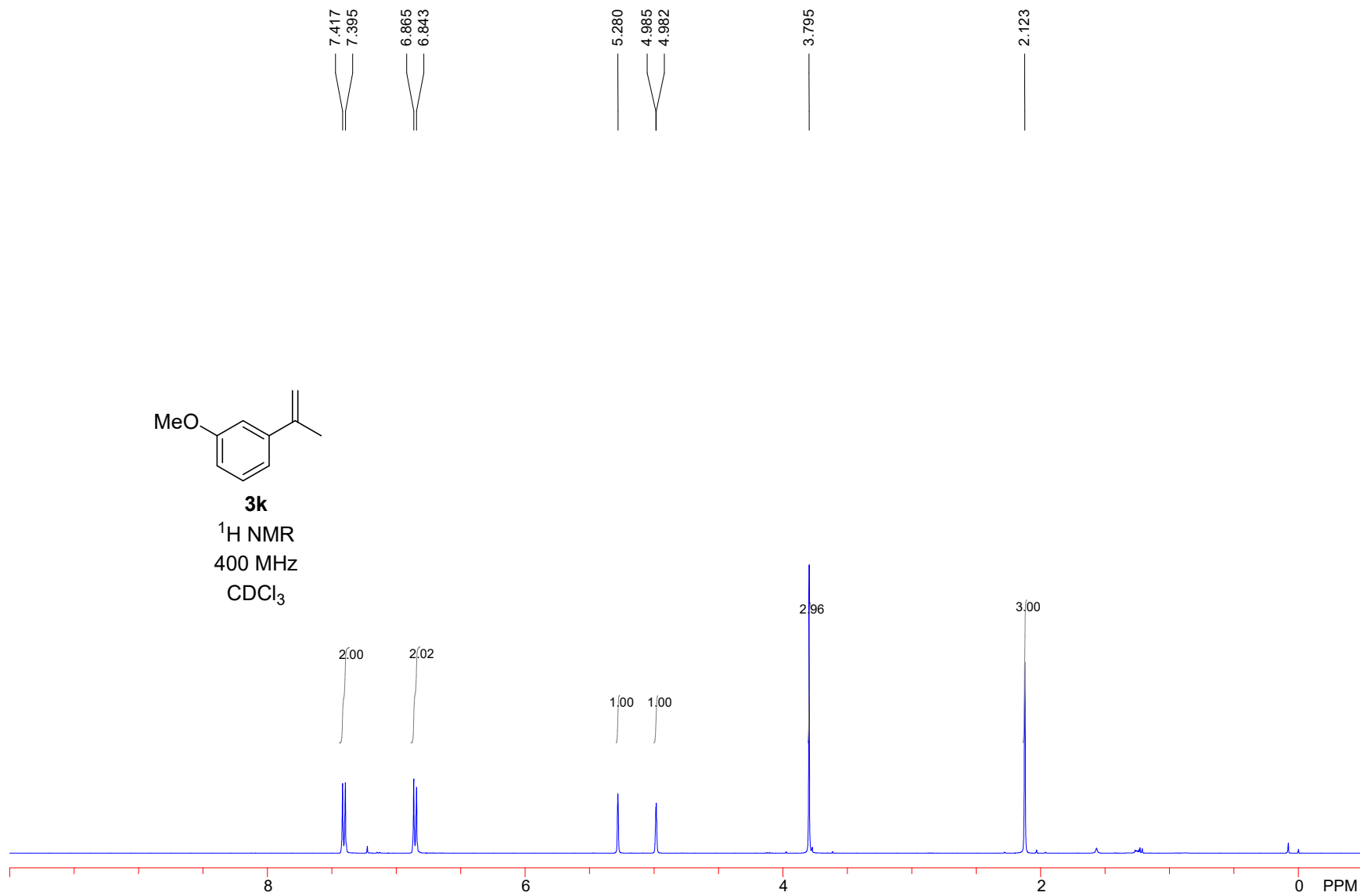


S166

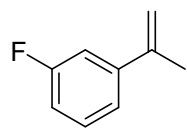


3k

¹H NMR
400 MHz
CDCl₃

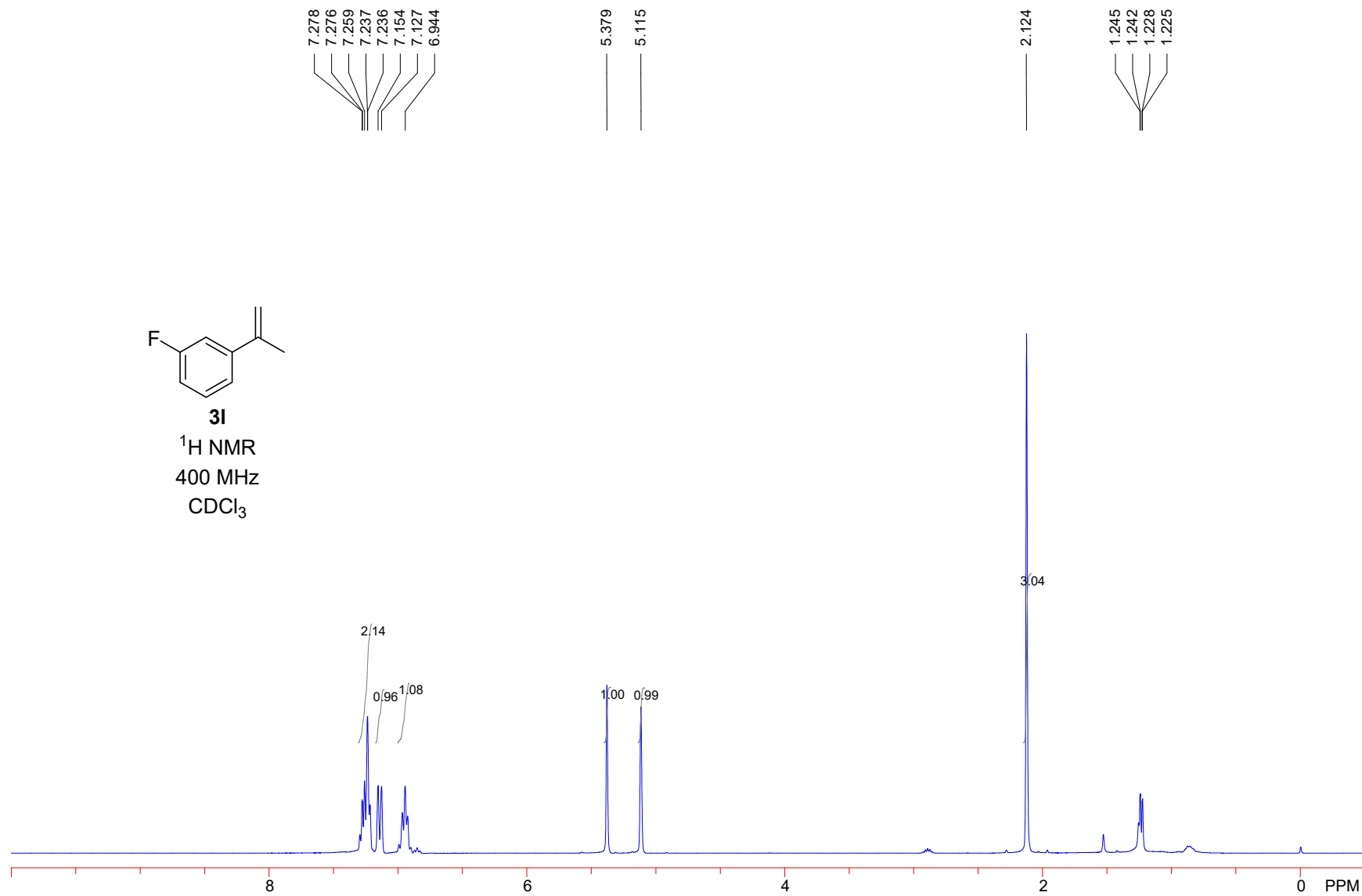


S167

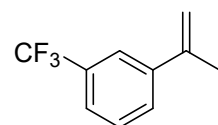


3I

¹H NMR
400 MHz
CDCl₃



S168



3m

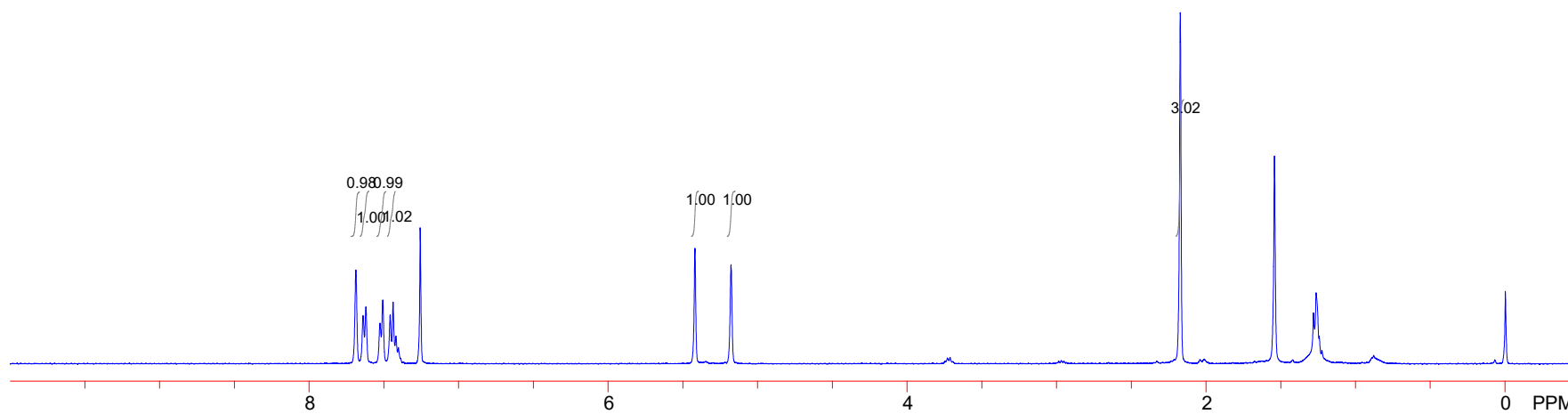
¹H NMR
400 MHz
CDCl₃

7.687
7.639
7.620
7.526
7.507
7.458
7.438
7.257

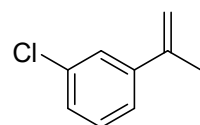
5.419
5.178

2.173

-0.001

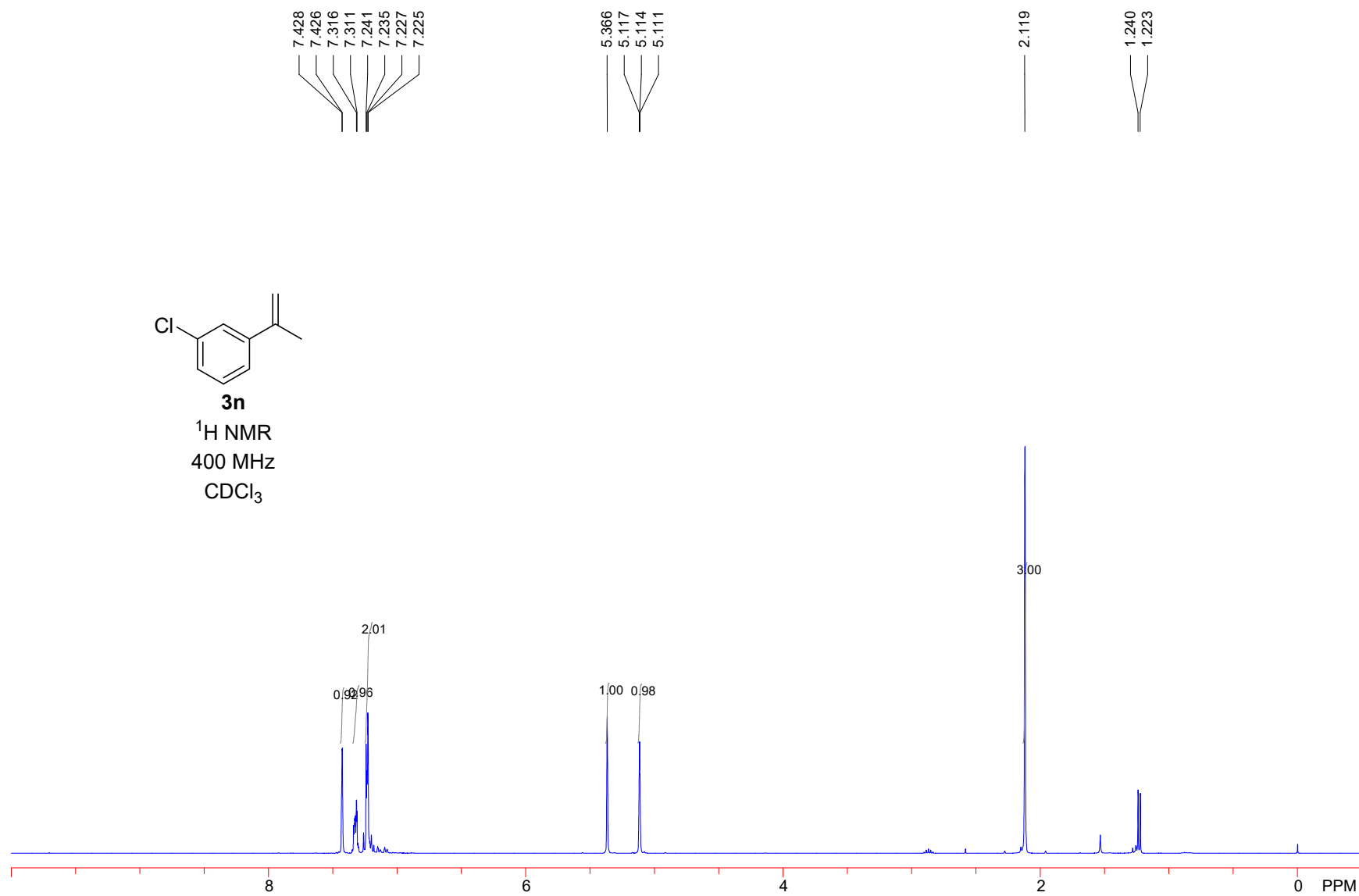


S169

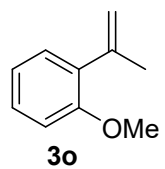


3n

¹H NMR
400 MHz
CDCl₃



S170



¹H NMR
400 MHz
CDCl₃

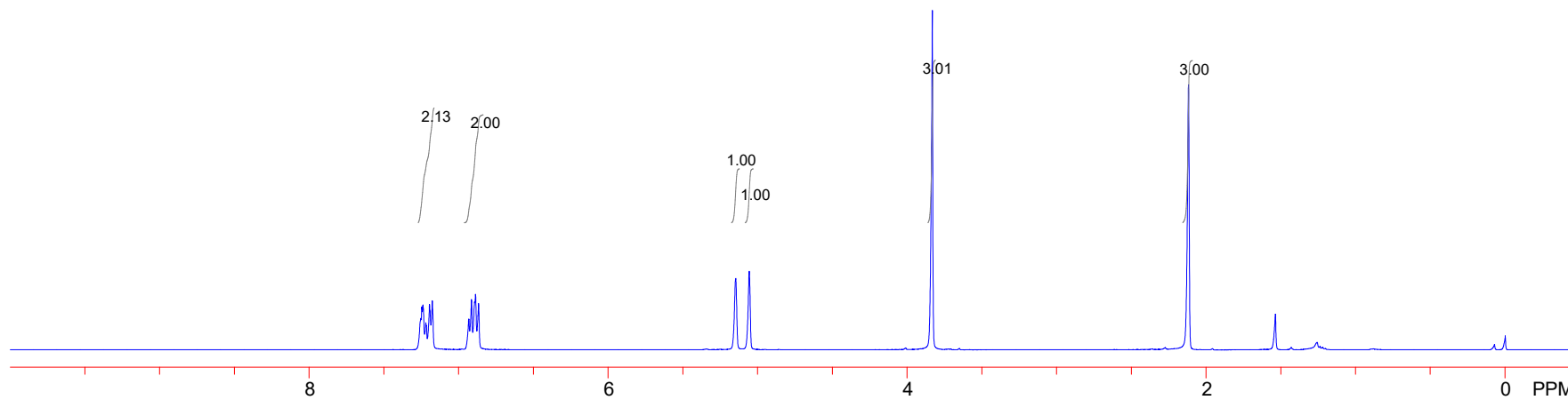
7.246
7.238
7.195
7.176
6.914
6.893
6.887
6.867

5.145
5.055

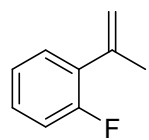
3.831

2.117

1.536



S171



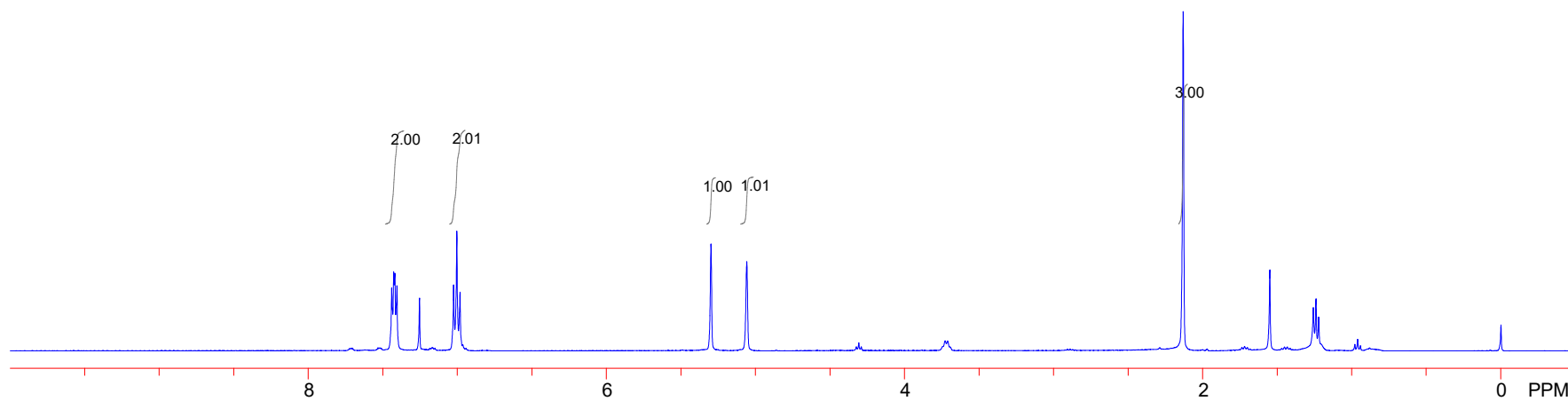
3p

¹H NMR
400 MHz
CDCl₃

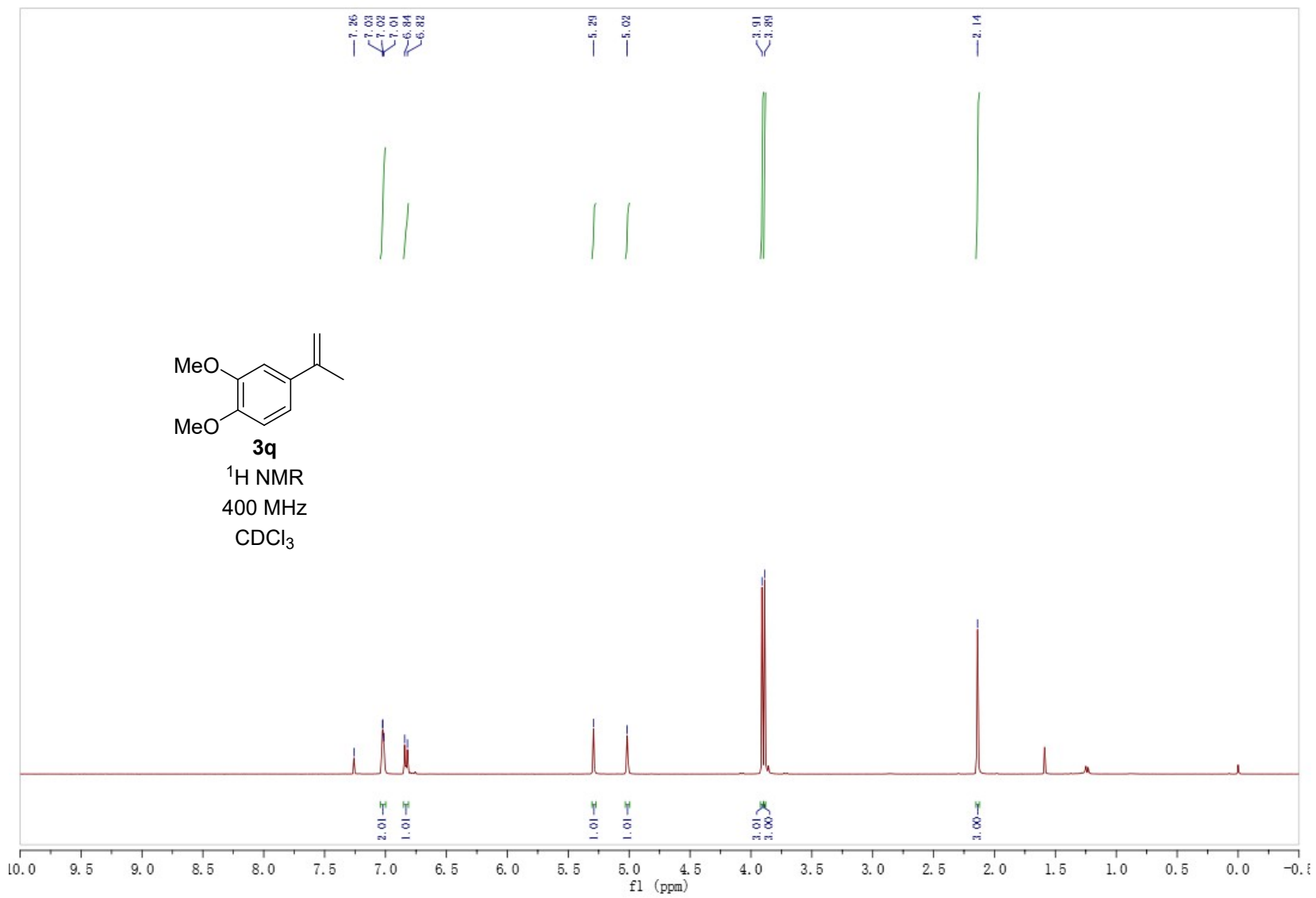
7.441
7.427
7.419
7.405
7.254
7.025
7.003
6.981

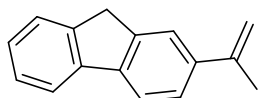
5.298
5.058

2.131



S172





3r

¹H NMR
400 MHz
CDCl₃

7.782
7.764
7.741
7.722
7.657
7.547
7.529
7.513
7.491
7.370
7.311
7.292
7.258

5.430

5.105

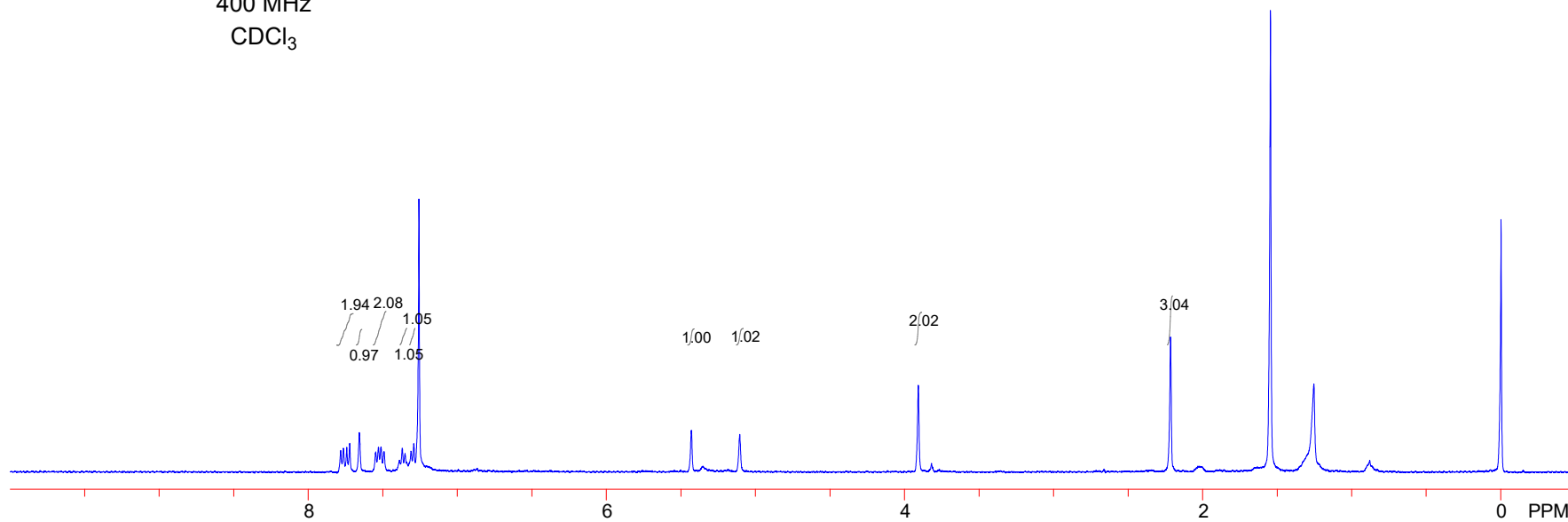
3.907

2.216

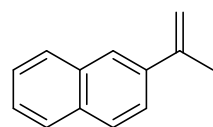
1.546

1.254

-0.001

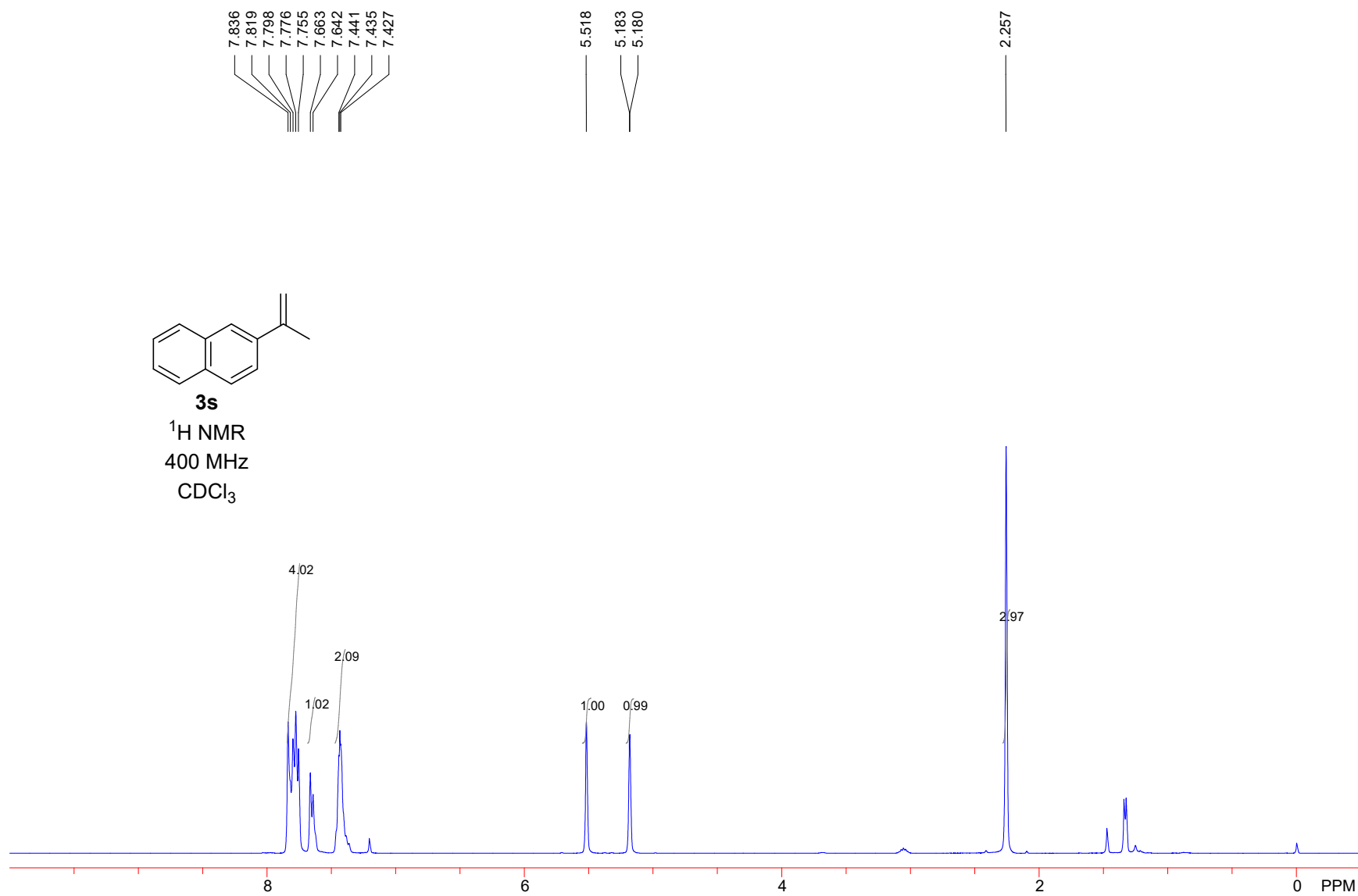


S174

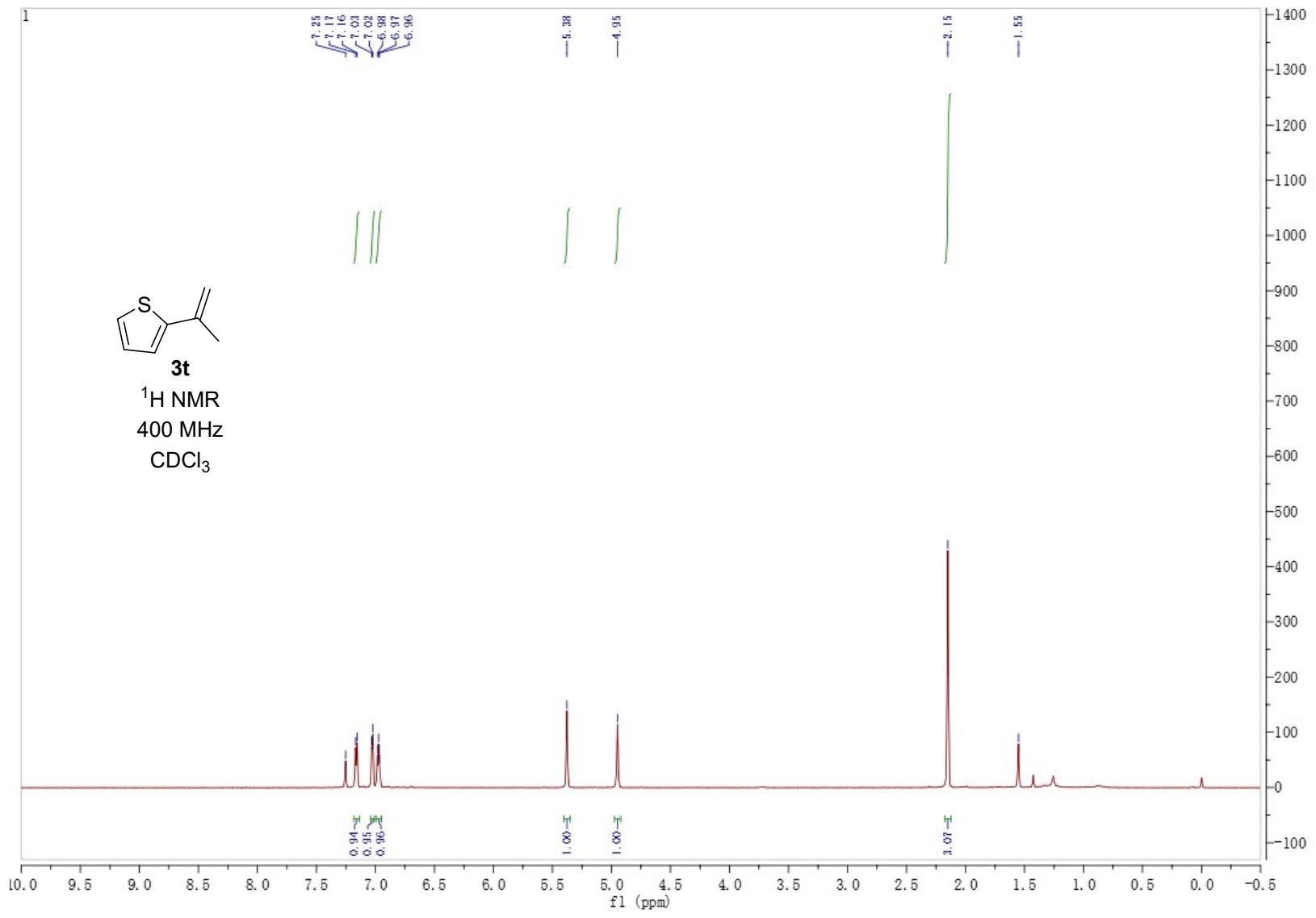


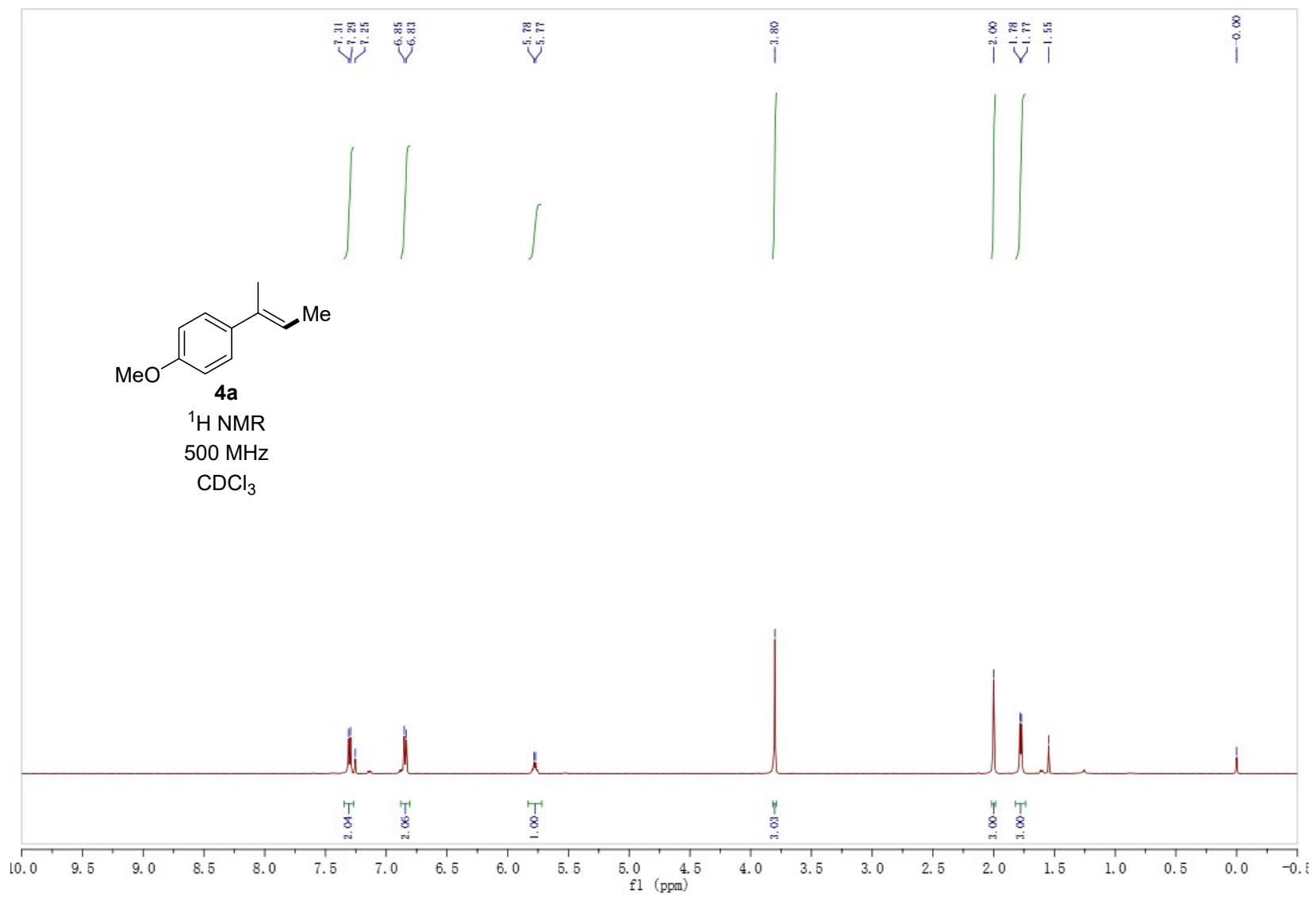
3s

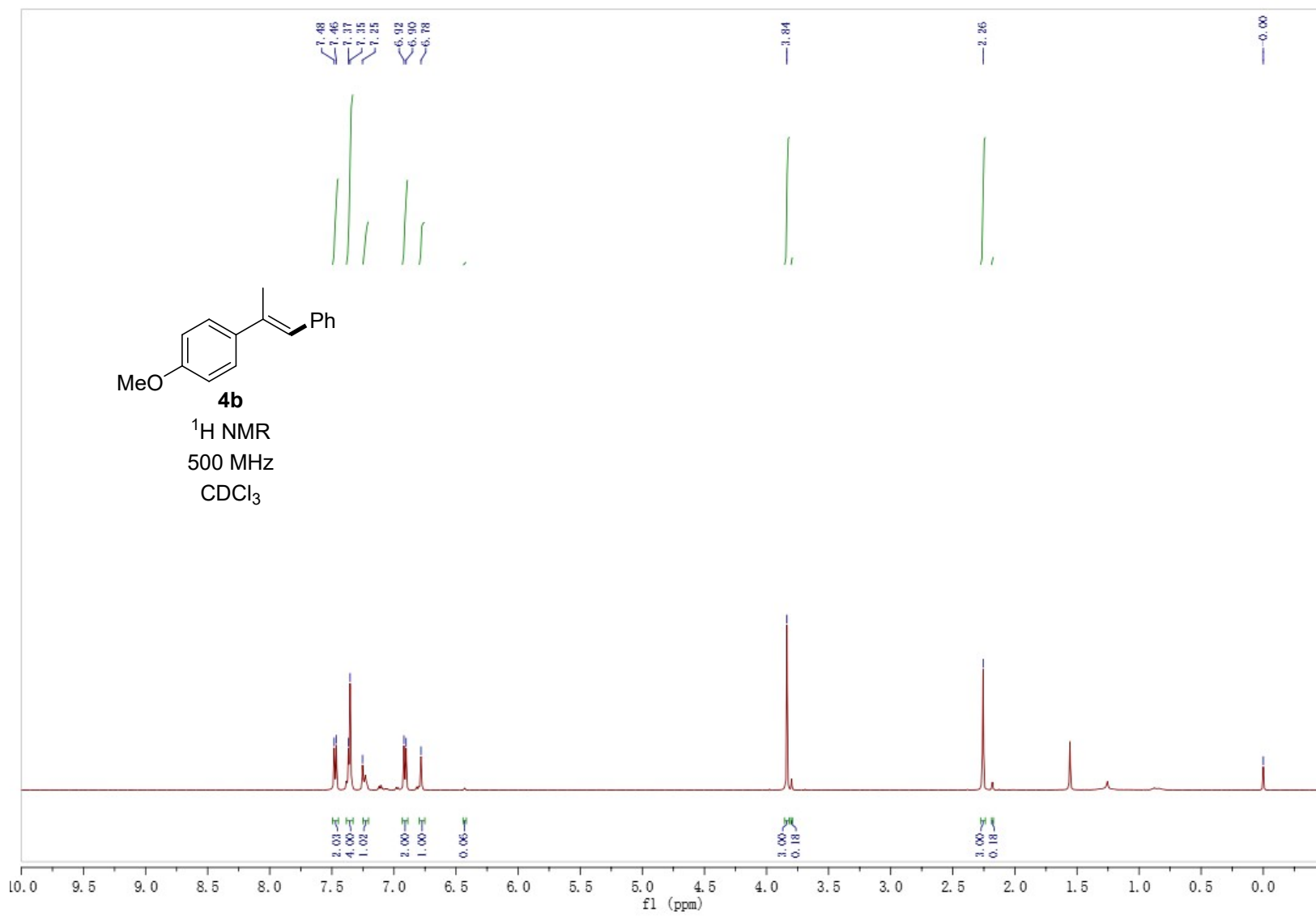
¹H NMR
400 MHz
CDCl₃

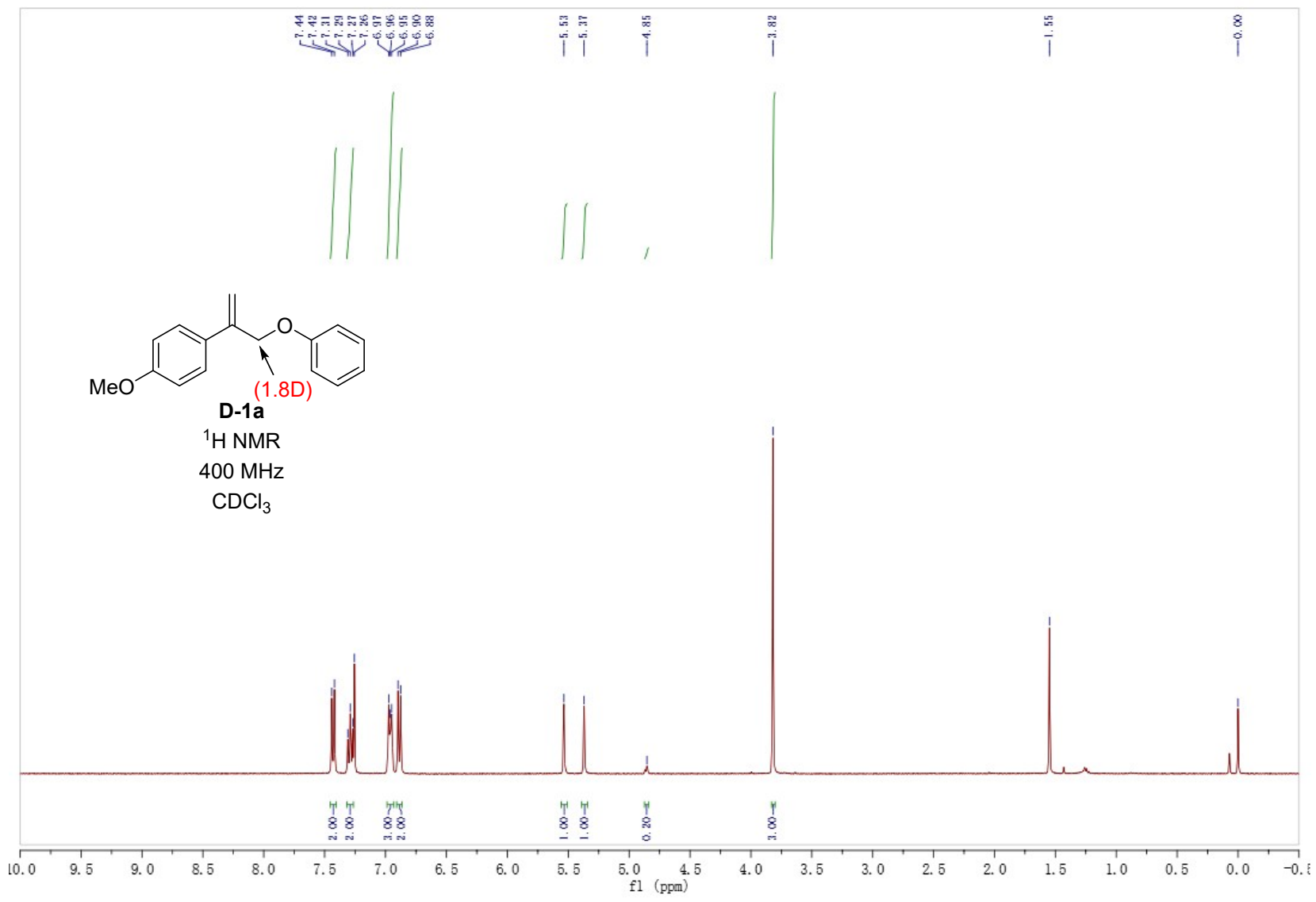


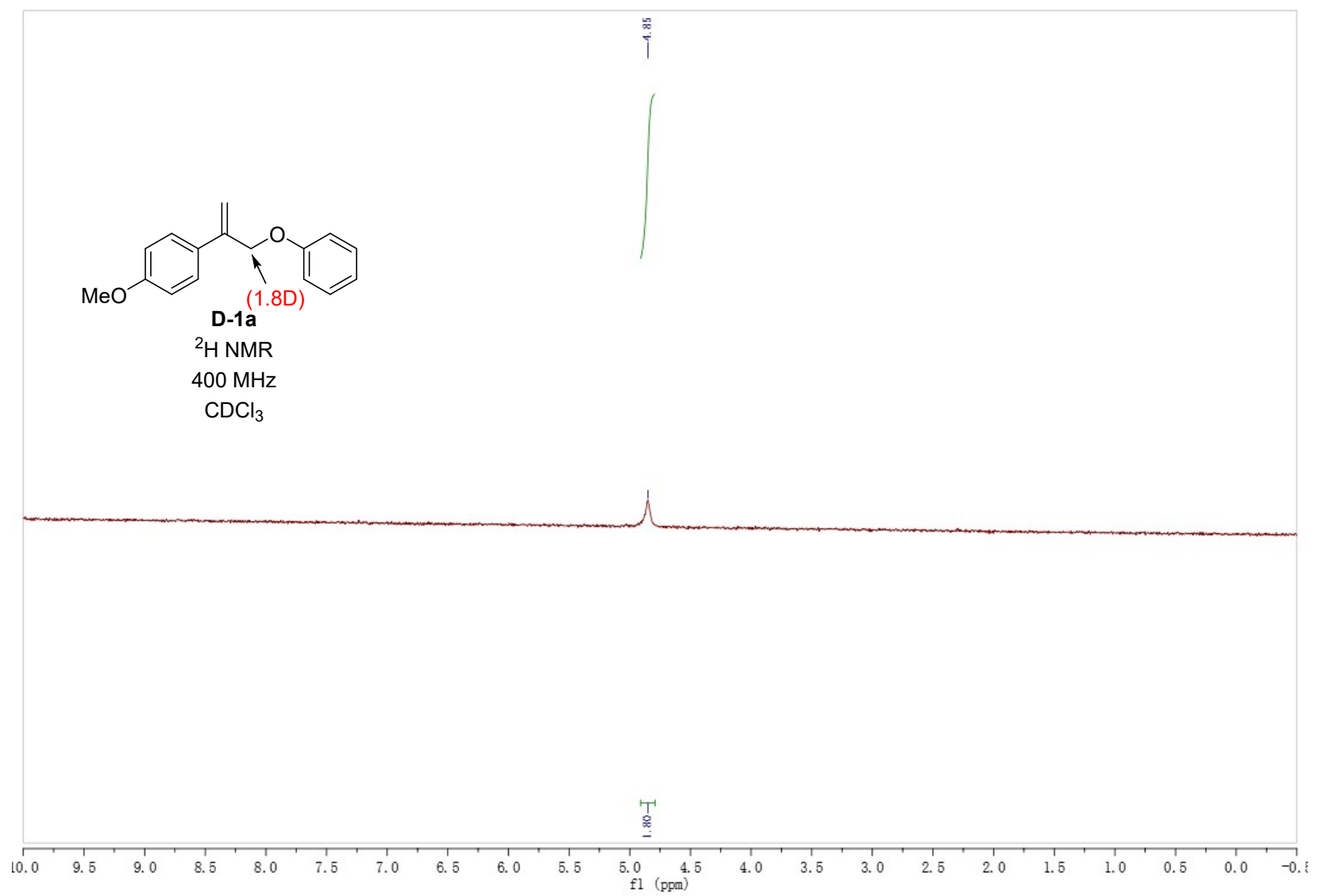
S175



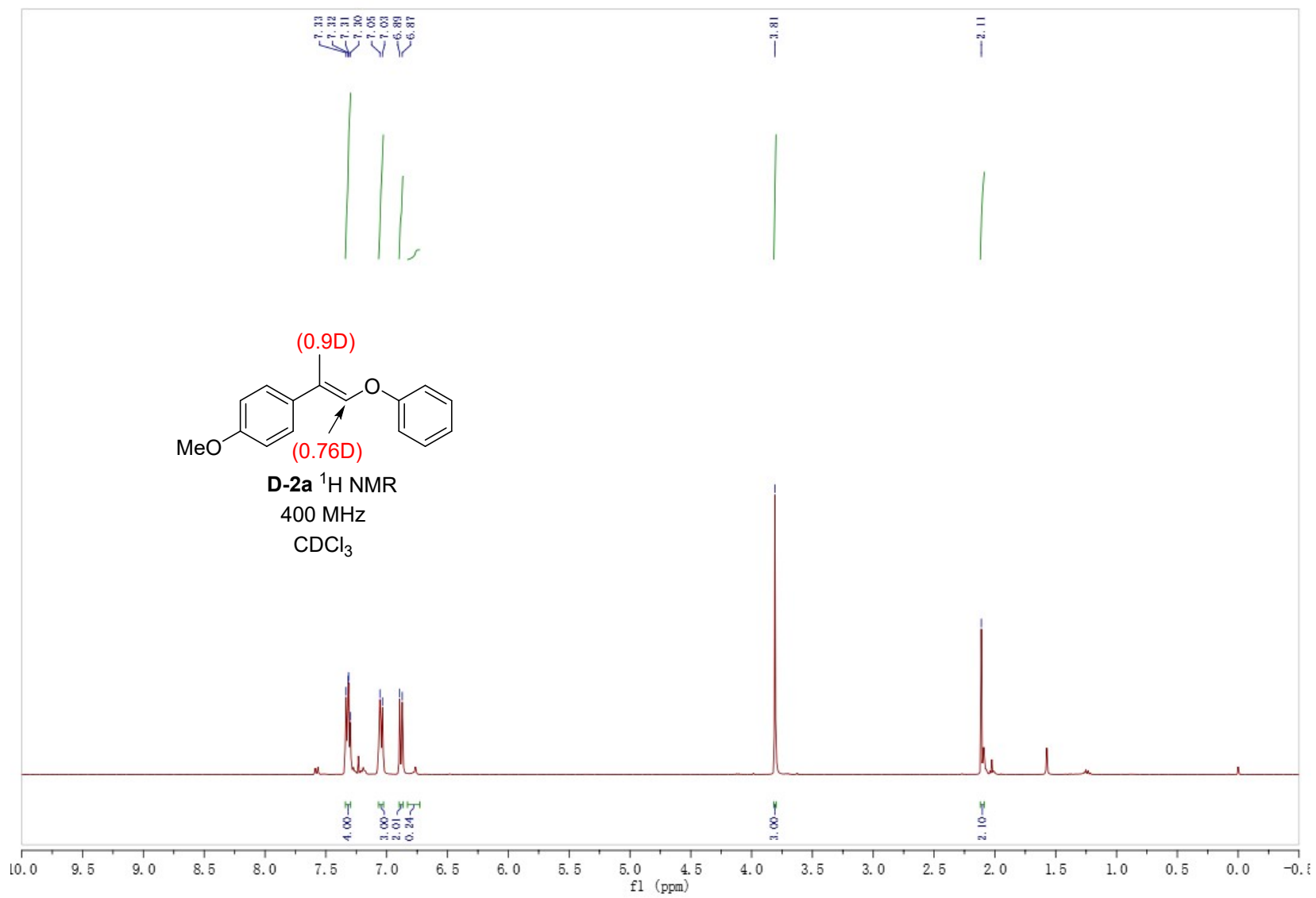


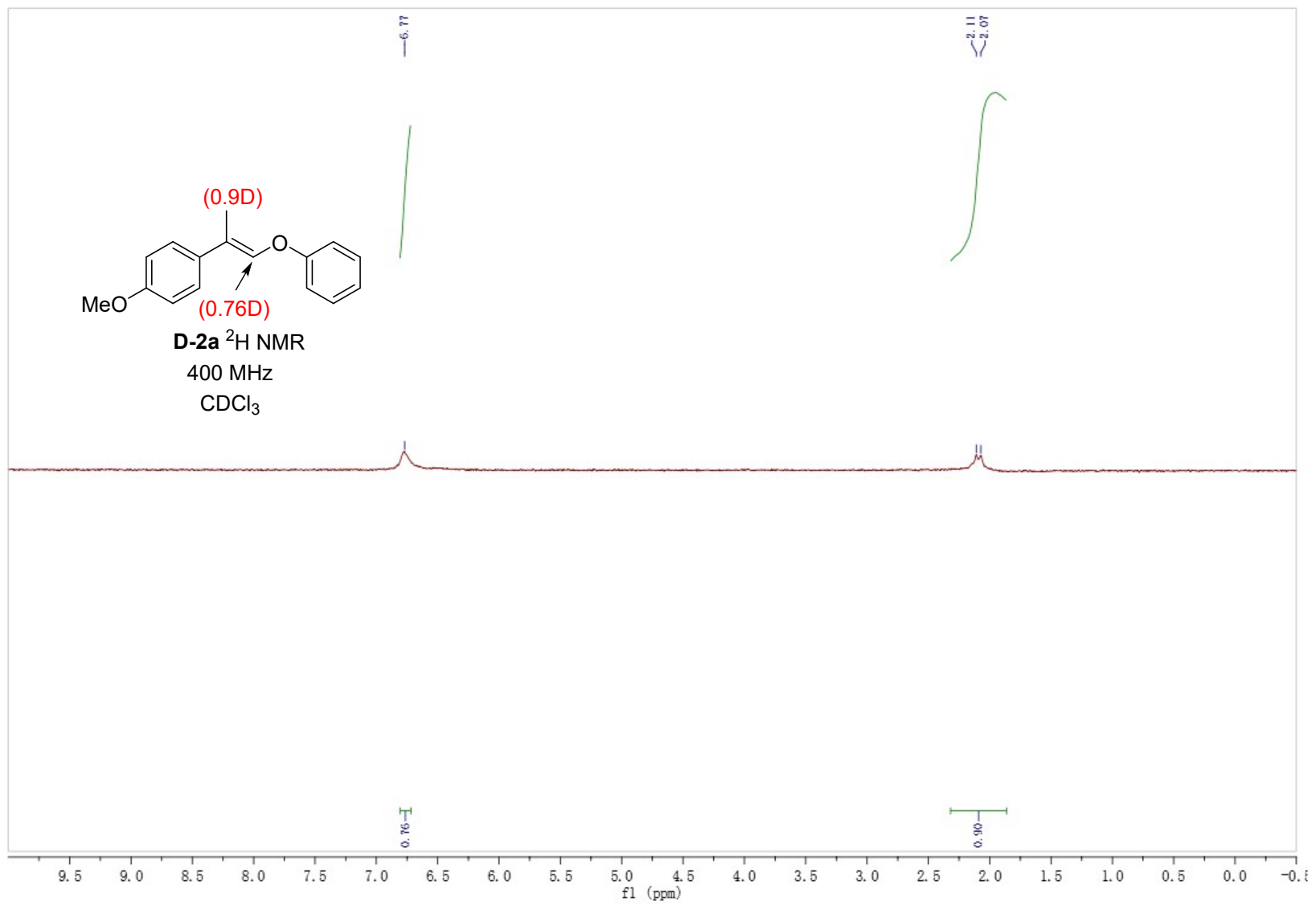




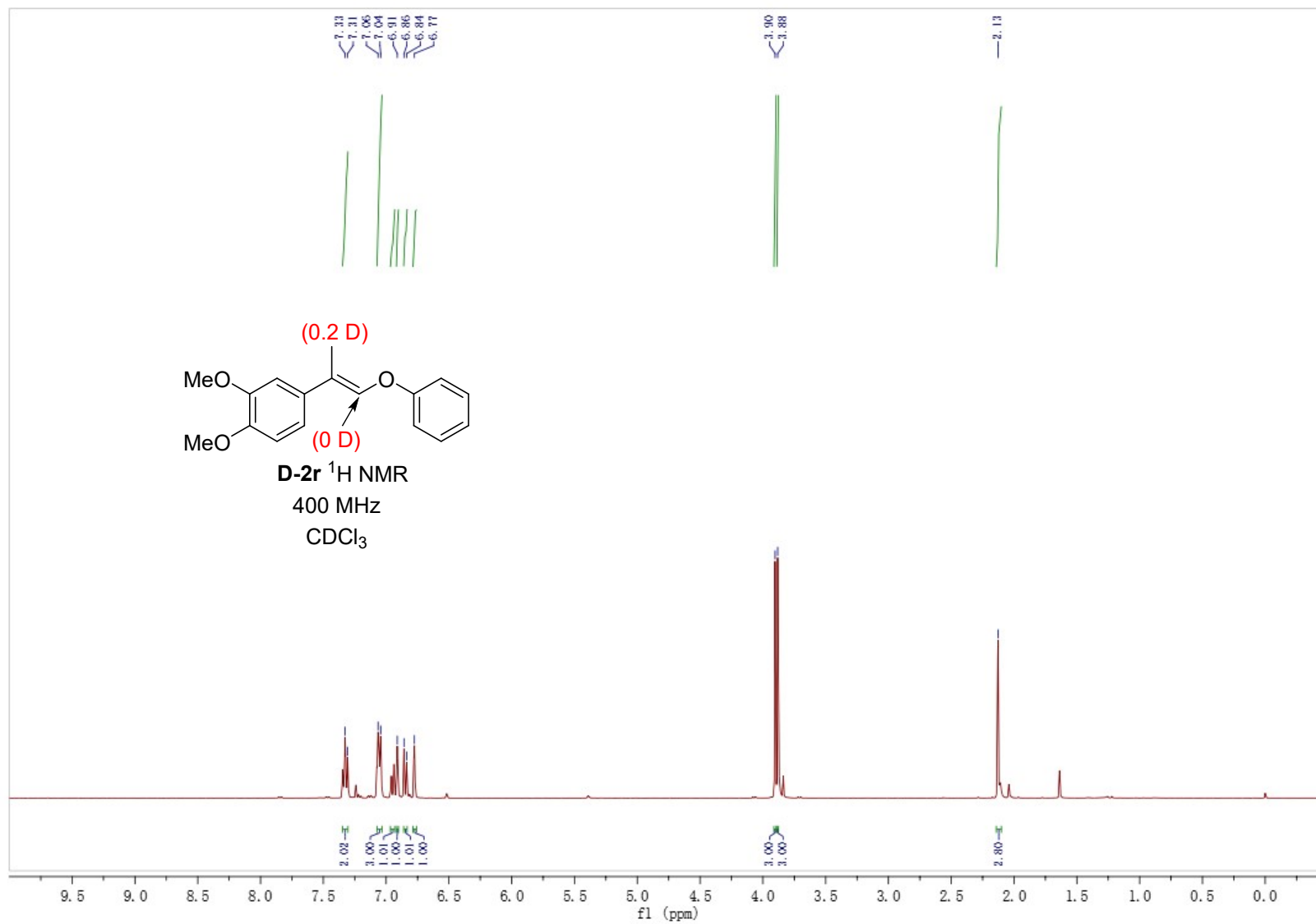


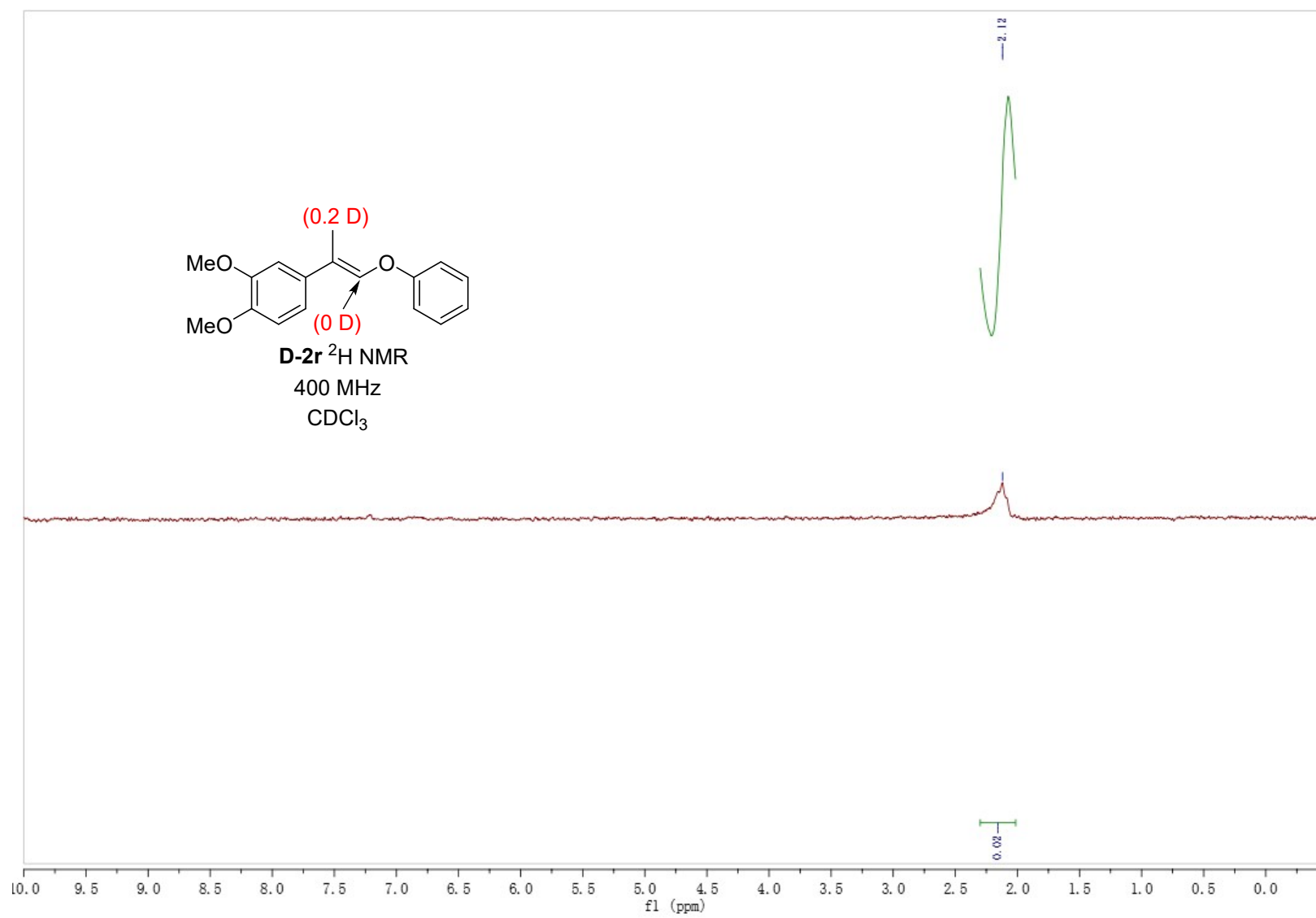
S180

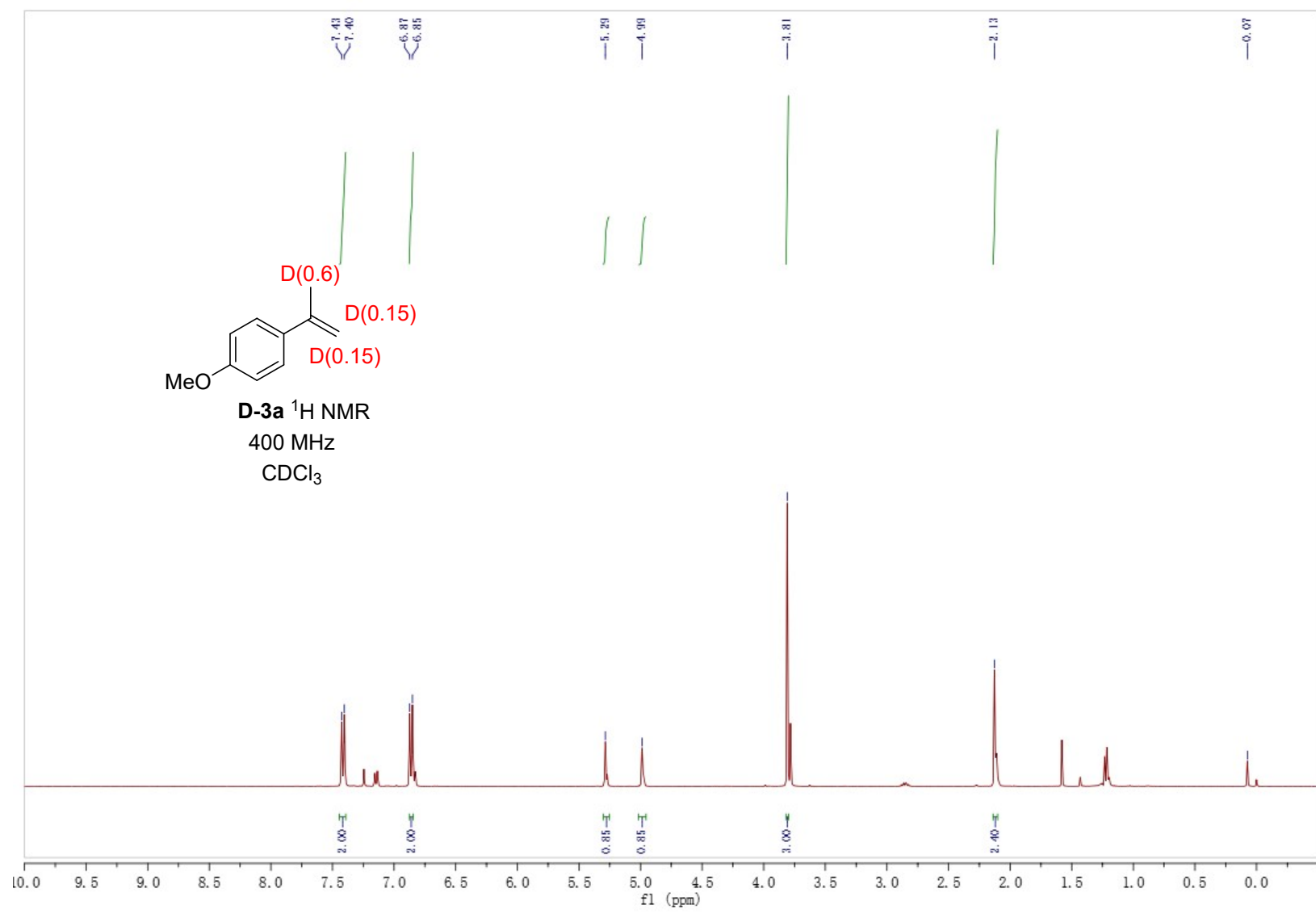


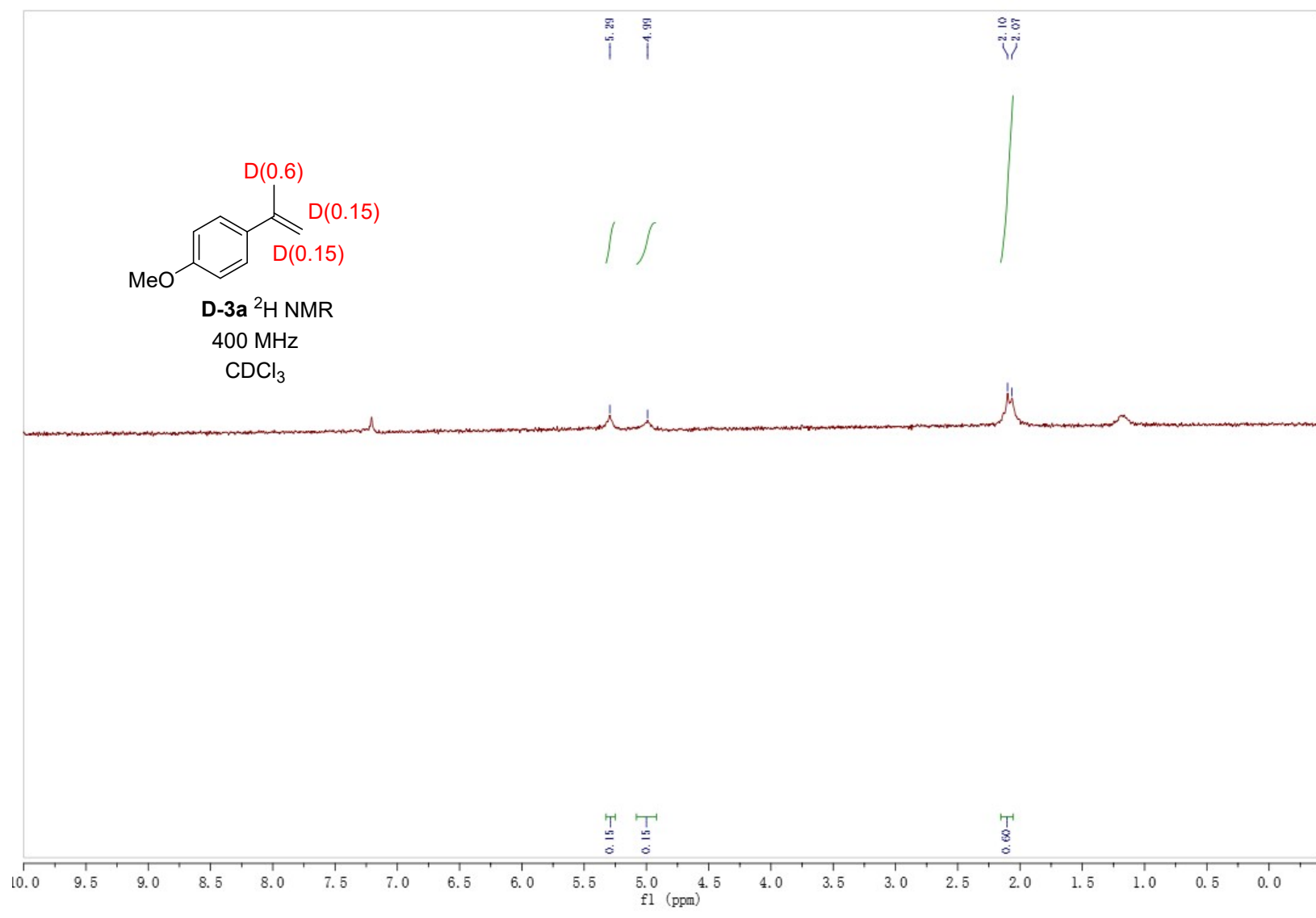


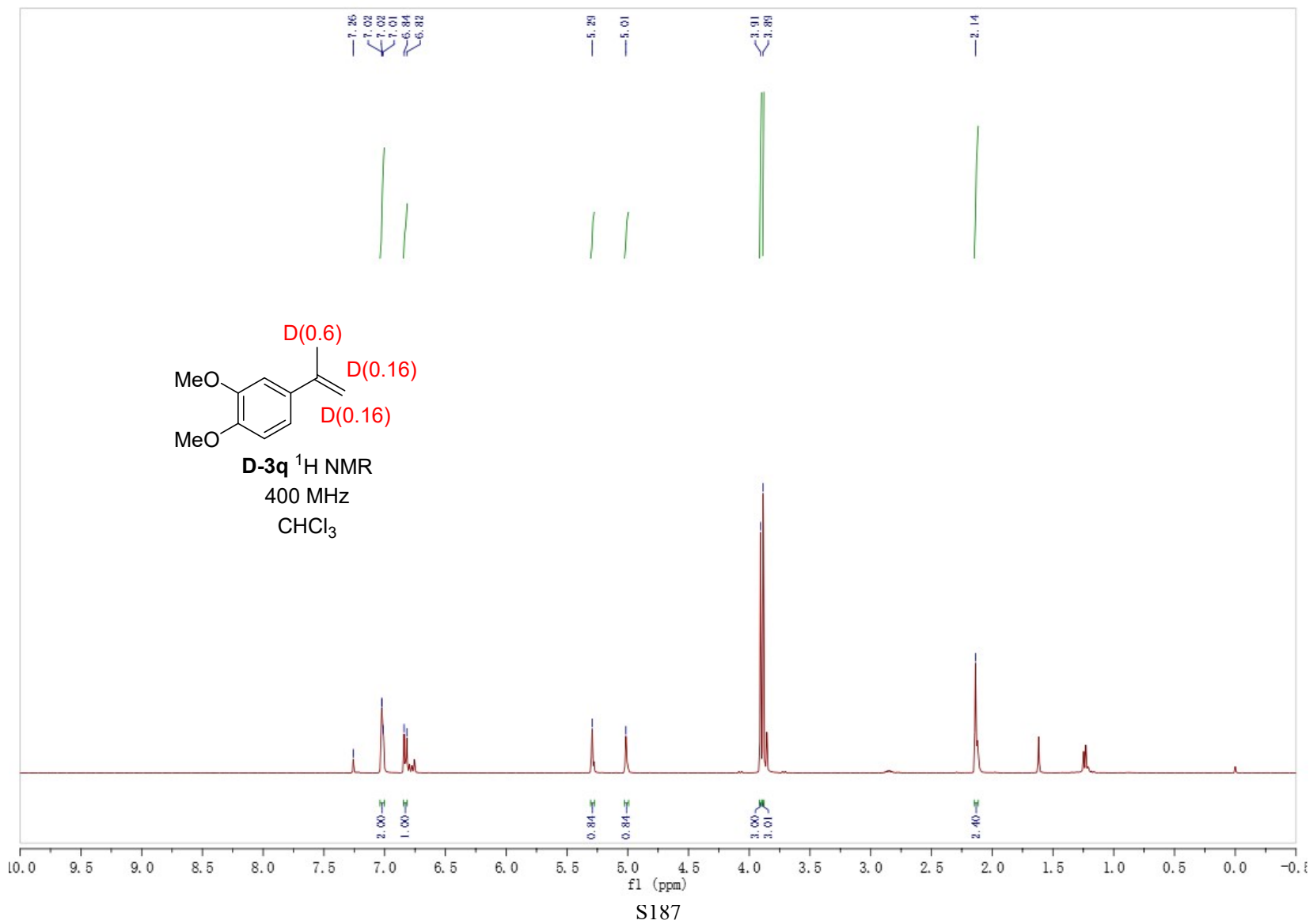
S182

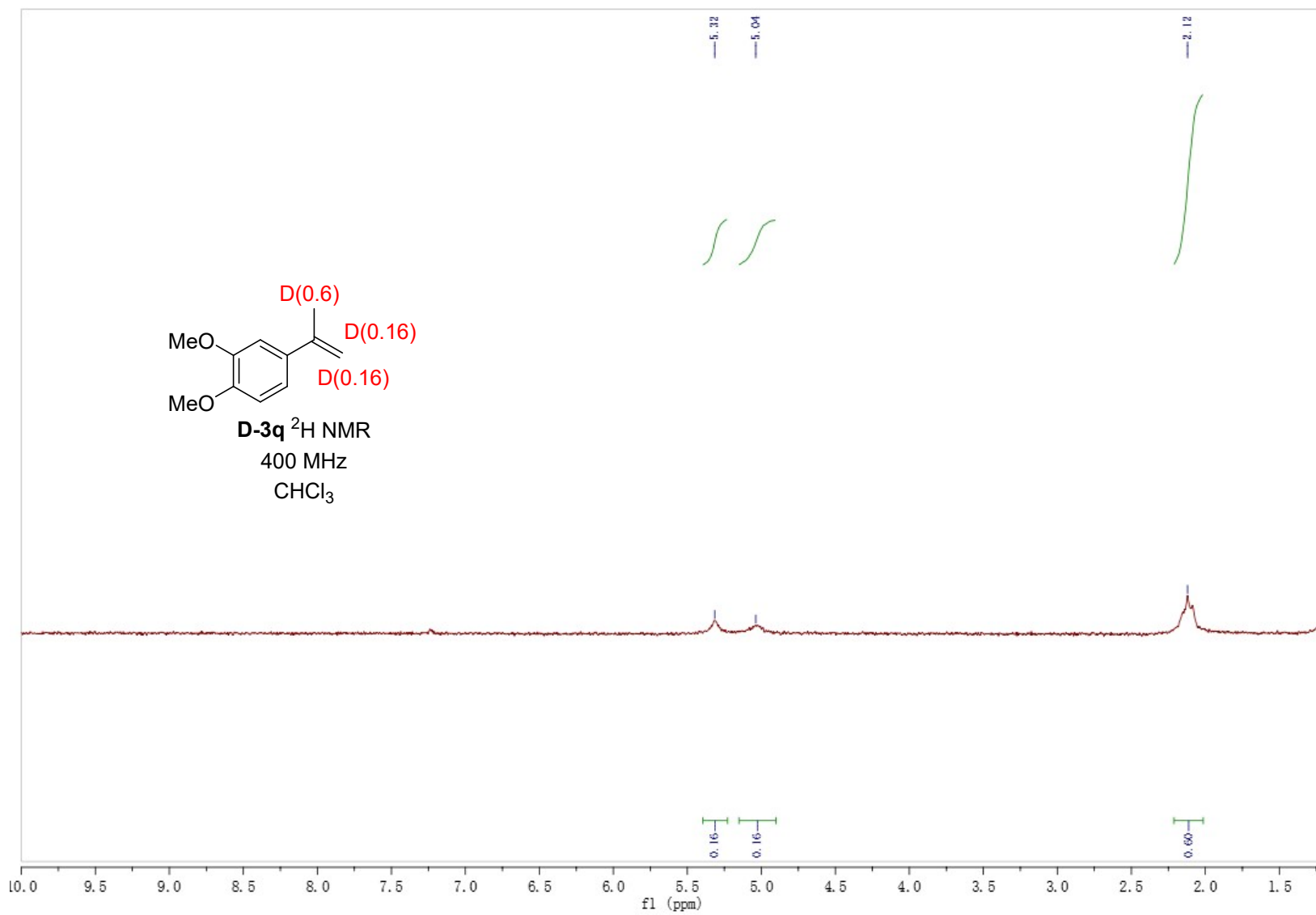












S188