Supporting Information

for

Trifluoromethanesulfonic Acid Catalyzed Friedel-Crafts Alkylation of 1,2,4-Trimethoxybenzene with Aldehydes or Benzylic Alcohols

Michael Wilsdorf, Daniel Leichnitz and Hans-Ulrich Reissig*

Institut für Chemie und Biochemie, Freie Universität Berlin
Takustr. 3, D-14195 Berlin, Germany

*Corresponding author

hreissig@chemie.fu-berlin.de

General Methods, Experimental Procedures, Characterization Data
^{1}H-NMR and ^{13}C-NMR Spectra of Synthesized Compounds

General Methods

Reactions were, in general, performed at normal atmosphere in a round bottom flask and were sealed with a cap after additon of substrates, solvent and acid. Acetonitrile was purchased from Sigma Aldrich (CHROMASOLV® Plus for HPLC, >99.9%). Trifluoromethansulfonic acid was purchased from Merck. All other reagents were purchased from commercial suppliers and used without further purification or were prepared according literature known procedures. Thin layer chromatography (TLC) analyses were performed on TLC plates purchased from Merck (silica gel 60, fluorescence indicator F254, 0.25 mm layer thickness). Products were purified by flash chromatography on silica gel 60 (230–400 mesh, Machery-Nagel). NMR spectra were recorded with Bruker (AC 500) and JOEL (ECX 400, Eclipse 500) instruments. Chemical shifts are reported relative to solvent residual peaks: ^{1}H: δ = 7.26 ppm ($CDCl_3$), ^{13}C: δ = 77.0 ppm ($CDCl_3$) and ^{1}H: δ = 2.49 ppm (DMSO-d_6), ^{13}C: δ = 39.5 ppm (DMSO-d_6). Integrals are in accordance with assignments, and coupling constants are given in Hz. All ^{13}C-NMR spectra are proton-decoupled. IR spectra were measured with a Jasco FT/IR-4100 spectrometer. HRMS analyses were performed with a Varian Ionspec QFT-7 (ESI-FT ICRMS) instrument. Melting points were measured with a Reichert apparatus (Thermovar) and are uncorrected.

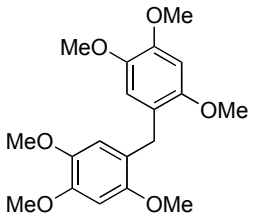
Experimental Procedures

Experimental Procedure A: To a solution of 1,2,4-trimethoxybenzene (1.0 equiv.) and aldehyde (0.7 equiv.) in MeCN (2.5 mL/mmol) at 0 °C was added F_3CSO_3H (0.1 equiv), and the resulting mixture was stirred at room temperature until complete conversion of the arene. The reaction was quenched by addition of sat. aqueous sodium bicarbonate solution (Na_2CO_3, aq.). The resulting mixture was extracted twice with EtOAc. The combined organic phases were dried (Na_2SO_4) and the solvent is removed in vacuo. The residue was purified by column chromatography on silica gel.

Experimental Procedure B: To a solution of 1-(4-methoxyphenyl)but-3-en-1-ol (1.0 equiv.) and nucleophile (1.0 – 2.0 equiv.) in MeCN (2.5 mL/mmol) at 0 °C was added F_3CSO_3H (0.1 equiv), and the resulting mixture was stirred at room temperature until complete conversion of the alcohol. The reaction was quenched by addition of sat. aqueous sodium bicarbonate solution (Na_2CO_3, aq.). The resulting mixture was extracted twice with EtOAc. The combined organic phases were dried (Na_2SO_4) and the solvent was removed in vacuo. The residue was purified by column chromatography on silica gel.

Characterization Data

Bis(2,4,5-trimethoxyphenyl)methane (5)

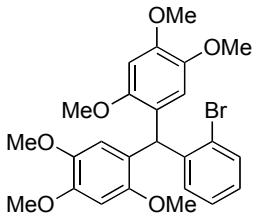


According to experimental procedure **A**: 1,2,4-trimethoxybenzene (336 mg, 2.00 mmol), paraformaldehyde (42 mg, 1.40 mmol), MeCN (5 mL), F_3CSO_3H (18 µL, 0.20 mmol), 1 h, rt; purification by column chromatography (silica gel, ethyl acetate/hexane = 1:2) afforded **5** (399 mg, 99%) as colorless solid.

M. p. 97 – 98 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 3.75, 3.80 (2 s, 6 H each, OMe), 3.83 (s, 2 H, CH_2), 3.87 (s, 6 H, OMe), 6.53, 6.66 (2 s, 2 H each, Ar) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 28.7 (t, CH_2), 56.1, 56.4, 56.5 (3 q, OMe), 97.7, 114.5 (2 d, Ar), 121.0, 142.8, 147.7, 151.5 (4 s, Ar) ppm. IR (film): υ = 2995 – 2830 (C-H), 1610, 1515, 1465, 1440, 1395 cm^{-1}. ESI-TOF: m/z calc. for $[M+Na]^+$: 371.1471, found 371.1457. Anal. calc. for $C_{19}H_{24}O_6$ (348.4): C 65.50, H 6.94; found: C 65.49, H 6.93.

Compound is literature known, see: [1].

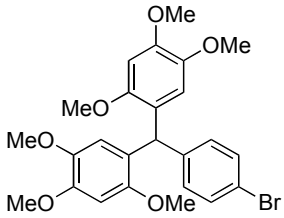
5,5'-[(2-Bromophenyl)methylene]bis(1,2,4-trimethoxybenzene) (6a)



According to experimental procedure **A**: 1,2,4-trimethoxybenzene (356 mg, 2.12 mmol), 2-bromobenzaldehyde (259 mg, 1.40 mmol), MeCN (5 mL), F_3CSO_3H (18 µL, 0.20 mmol), 24 h, rt; purification by column chromatography (silica gel, ethyl acetate/hexane = 1:4 → 1:2) afforded **6a** (520 mg, 97%) as colorless solid.

M. p. 162 – 164 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 3.61, 3.67, 3.88 (3 s, 6 H each, OMe), 6.27 (s, 1 H, CH), 6.31, 6.54 (2 s, 2 H each, Ar), 6.87 (dd, *J* = 1.7, 7.7 Hz, 1 H, Ar), 7.04 (dt, *J* = 1.7, 7.6 Hz, 1 H, Ar), 7.16 (dt, *J* = 1.4, 7.6 Hz, 1 H, Ar m, 1 H, Ph), 7.53 (dd, *J* = 1.4, 8.0 Hz, 1 H, Ar) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 43.0 (d, CH), 56.0, 56.6, 57.0 (3 q, OMe), 98.4, 114.3 (2 d, Ar), 123.0, 125.4 (2 s, Ar), 126.7, 127.5, 130.1, 132.9 (4 d, Ar), 142.6, 143.7, 148.2, 151.7 (4 s, Ar) ppm. IR (film): υ = 3000 – 2845 (C-H), 1610, 1510, 1465, 1440 cm^{-1}. ESI-TOF: m/z calc. for $[M+Na]^+$: 525.0883; 527.0868, found 525.0900; 527.0884. Anal. calc. for $C_{25}H_{27}BrO_6$ (503.4): C 59.65, H 5.41; found: C 59.74, H 5.41.

5,5'-[(4-Bromophenyl)methylene]bis(1,2,4-trimethoxybenzene) (6b)

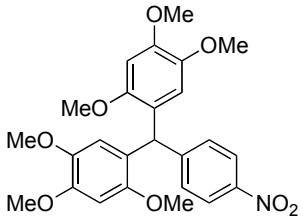


According to experimental procedure **A**: 1,2,4-trimethoxybenzene (336 mg, 2.00 mmol), 4-bromobenzaldehyde (259 mg, 1.40 mmol), MeCN (5 mL), F_3CSO_3H (18 µL, 0.20 mmol), 24 h, rt; purification by column chromatography (silica gel, ethyl acetate/hexane = 1:4 → 1:2) afforded **6b** (486 mg, 96%) as colorless solid.

M. p. 165 – 167 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 3.63, 3.66, 3.88 (3 s, 6 H each, OMe), 6.00 (s, 1 H, CH), 6.39, 6.53 (2 s, 2 H each, Ar), 6.91, 7.34 (2 d, *J* = 8.4 Hz, 2 H each, Ar) ppm. Anal. calc. for $C_{25}H_{27}BrO_6$ (503.4): C 59.65, H 5.41; found: C 59.72, H 5.48.

Compound is literature known, see: [2].

5,5'-[(4-Nitrophenyl)methylene]bis(1,2,4-trimethoxybenzene) (6c)

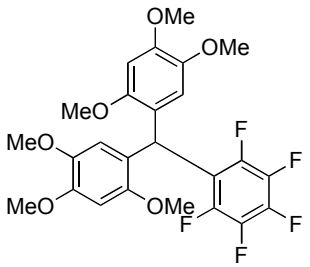


According to experimental procedure **A**: 1,2,4-trimethoxybenzene (336 mg, 2.00 mmol), 4-nitrobenzaldehyde (211 mg, 1.40 mmol), MeCN (5 mL), F_3CSO_3H (18 µL, 0.20 mmol), 24 h, rt; purification by column chromatography (silica gel, ethyl acetate/hexane = 1:4 → 1:1) afforded **6c** (456 mg, 97%) as bright yellow solid.

M. p. 121 – 124 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 3.64, 3.66, 3.89 (3 s, 6 H each, OMe), 6.10 (s, 1 H, CH), 6.38, 6.55 (2 s, 2 H each, Ar), 7.19, 8.08 (2 d, *J* = 8.7 Hz, 2 H each, Ar) ppm. Anal. calc. for $C_{25}H_{27}NO_8$ (514.4): C 63.96, H 5.80, N 2.98; found: C 63.95, H 6.12, N 2.97.

Compound is literature known, see: [2].

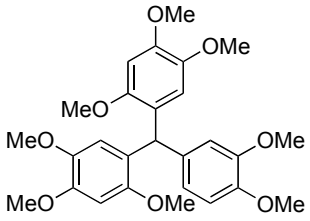
5,5'-[(Perfluorophenyl)methylene]bis(1,2,4-trimethoxybenzene) (6d)



According to experimental procedure **A**: 1,2,4-trimethoxybenzene (400 mg, 2.38 mmol), 2,3,4,5,6-pentafluorobenzaldehyde (326 mg, 1.66 mmol), MeCN (6 mL), F_3CSO_3H (21 µL, 0.24 mmol), 2 h, rt; purification by column chromatography (silica gel, ethyl acetate/hexane = 1:4 → 3:2) afforded **6d** (563 mg, 92%) as colorless solid.

M. P. 127 – 129 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 3.69, 3.70, 3.88 (3 s, 6 H each, OMe), 6.24 (s, 1 H, CH), 6.52, 6.56 (2 s, 2 H each, Ar) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 33.7 (d, CH), 56.0, 56.5, 56.8 (3 q, OMe), 97.6, 114.0 (2 d, Ar), 119.8, 142.7, 148.9, 151.4 (4 s, Ar) ppm. ^{19}F NMR (376 MHz, $CDCl_3$) δ = -163.1 (dt, *J* = 7.2, 21.2 Hz, 3-F), -157.7 (t, *J* = 21.2 Hz, 4-F), -140.7 (dd, *J* = 7.2, 22.0 Hz, 2-F) ppm. IR (film): υ = 3015 – 2850 (C-H), 1735, 1610, 1520, 1500, 1465, 1440 cm^{-1}. ESI-TOF: m/z calc. for $[M+Na]^+$: 537.1312, found 537.1303. Anal. calc. for $C_{25}H_{23}F_5O_6$ (514.4): C 58.37, H 4.51; found: C 59.06, H 4.57.

5,5'-[(3,4-Dimethoxyphenyl)methylene]bis(1,2,4-trimethoxybenzene) (6e)

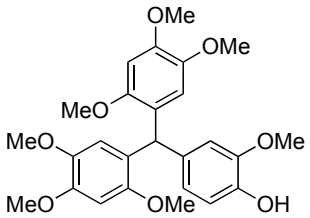


According to experimental procedure **A**: 1,2,4-trimethoxybenzene (354 mg, 2.10 mmol), 3,4-dimethoxybenzaldehyde (244 mg, 1.47 mmol), MeCN (5 mL), F_3CSO_3H (18 µL, 0.20 mmol), 24 h, rt; purification by column chromatography (silica gel, ethyl acetate/hexane = 1:2 → 1:1) afforded **6e** (320 mg, 63%) as colorless solid.

M. p. 112 – 115 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 3.62, 3.66 (2 s, 6 H each, OMe), 3.74, 3.82 (2 s, 3 H each, OMe), 3.86 (s, 6 H, OMe), 6.00 (s, 1 H, CH), 6.41 (s, 2 H, Ar), 6.49 (dd, *J* = 1.4, 8.2 Hz, 1 H, Ar), 6.53 (s, 2 H, Ar), 6.63 (d, *J* = 1.4 Hz, 1 H, Ar), 6.72 (d, *J* = 8.2 Hz, 1 H, Ar) ppm. Anal. calc. for $C_{27}H_{32}O_8$ (484.5): C 66.93, H 6.66; found: C 66.92, H 6.66.

Compound is literature known, see: [2].

4-[Bis(2,4,5-trimethoxyphenyl)methyl]-2-methoxyphenol (6f)

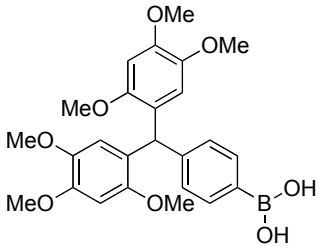


According to experimental procedure **A**: 1,2,4-trimethoxybenzene (336 mg, 2.00 mmol), vanilin (214 mg, 1.40 mmol), MeCN (5 mL), F_3CSO_3H (18 µL, 0.20 mmol), 24 h, rt; purification by column chromatography (silica gel, ethyl acetate/hexane = 1:3 → 1:1) afforded **6f** (294 mg, 62%) as colorless solid.

M. p. 188 – 190 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 3.64, 3.67 (2 s, 6 H each, OMe), 3.74 (s, 3 H, OMe), 3.88 (s, 6 H, OMe), 5.49 (s, 1 H, OH), 5.99 (s, 1 H, CH), 6.43 (s, 2 H, Ar), 6.47 (ddd, *J* = 0.7, 2.0, 8.2 Hz, 1 H, Ar), 6.54 (s, 2 H, Ar), 6.61 (d, *J* = 2.0 Hz, 1 H, Ar), 6.78 (d, *J* = 8.2 Hz, 1 H, Ar) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 42.1 (d, CH), 55.8, 56.1, 56.7, 57.0 (4 q, OMe), 98.4, 111.9, 113.7, 114.4, 121.5 (5 d, Ar), 124.8, 136.1, 142.7, 143.6, 146.2, 147.9, 151.5 (7 s, Ar) ppm. IR (film): υ = 3440 (OH), 3000 – 2835 (C-H), 1610, 1510, 1465, 1440 cm^{-1}. ESI-TOF: m/z calc. for $[M+Na]^+$: 493.1838, found 493.1847. Anal. calc. for $C_{26}H_{30}O_8$ (470.2): C 66.37, H 6.43; found: C 66.40, H 6.43.

Compound is literature known, see: [3].

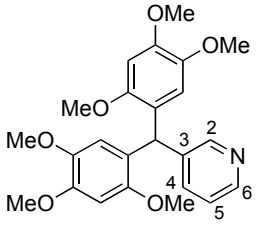
{4-[Bis(2,4,5-trimethoxyphenyl)methyl]phenyl}boronic acid (6g)



According to experimental procedure **A**: 1,2,4-trimethoxybenzene (672 mg, 4.00 mmol), (4-formyl-phenyl)boronic acid (150 mg, 1.00 mmol), MeCN (5 mL), F_3CSO_3H (9 µL, 0.10 mmol), 24 h, rt; purification by precipitation (diethylether/hexane) afforded **6g** (407 mg, 92%) as colorless solid.

M. p. 100 – 120 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 3.63, 3.67, 3.89 (3 s, 6 H each, OMe), 6.13 (s, 1 H, CH), 6.44, 6.55 (2 s, 2 H each, Ar), 7.18, 8.08 (2 d, *J* = 7.9 Hz, 2 H each, Ph) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 43.0 (d, CH), 56.0, 56.6, 56.9 (3 q, OMe), 98.2, 114.4 (2 d, Ar), 123.9 (s, Ar), 128.7, 135.3 (2 d, Ar), 142.7, 148.1, 149.4, 151.6 (4 s, Ar) ppm. IR (film): υ = 3480 (OH), 3000 – 2830 (C-H), 1605, 1510, 1460 cm^{-1}. Anal. calc. for $C_{25}H_{29}BO_8$ (468.3): C 64.12, H 6.24; found: C 64.43, H 6.08.

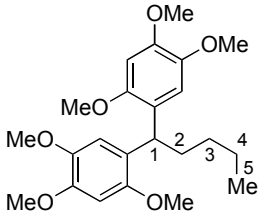
3-[Bis(2,4,5-trimethoxyphenyl)methyl]pyridine (6h)



According to experimental procedure **A**: 1,2,4-trimethoxybenzene (164 mg, 0.98 mmol), nicotinaldehyde (75 mg, 0.70 mmol), MeCN (2.5 mL), F_3CSO_3H (97 µL, 1.10 mmol), 24 h, rt; purification by column chromatography (silica gel, ethyl acetate/hexane = 1:2 → 1:1) afforded **6h** (207 mg, 99%) as colorless solid.

M. p. 114 – 116 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 3.63, 3.66, 3.88 (3 s, 6 H each, OMe), 6.04 (s, 1 H, CH), 6.40, 6.54 (2 s, 2 H each, Ar), 7.17 (dd, *J* = 4.8, 7.9 Hz, 5-H), 7.33 (dt, *J* = 2.0, 7.9 Hz, 1 H, 4-H), 8.32 (d, *J* = 2.3 Hz, 1 H, 2-H), 8.41 (dd, *J* = 1.7, 4.8 Hz, 1 H, 6-H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 40.6 (d, CH), 56.0, 56.6, 56.7 (3 q, OMe), 98.1, 114.4 (2 d, Ar), 122.7 (s, Ar), 122.9 (d, C-5), 136.3 (d, C-4), 139.8, 142.7 (2 s, Ar), 147.0 (d, C-6), 148.4 (s, Ar), 150.5 (d, C-2), 151.4 (s, Ar) ppm. IR (film): υ = 3000 – 2835 (C-H), 1510, 1465, 1440 cm^{-1}. ESI-TOF: m/z calc. for $[M+Na]^+$: 426.1911, found 426.1919. Anal. calc. for $C_{24}H_{27}NO_6$ (425.5): C 67.75, H 6.40, N 3.29; found: C 67.75, H 6.47, N 3.30.

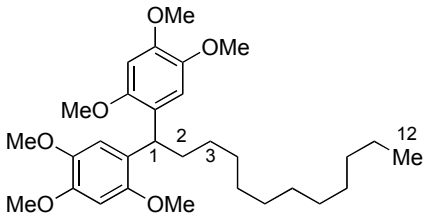
5,5'-(Pentane-1,1-diyl)bis(1,2,4-trimethoxybenzene) (7a)



According to experimental procedure **A**: 1,2,4-trimethoxybenzene (168 mg, 1.00 mmol), pentanal (60 mg, 0.70 mmol), MeCN (5 mL), F_3CSO_3H (9 µL, 0.10 mmol), 6 h, rt; purification by column chromatography (silica gel, ethyl acetate/hexane = 1:4 → 1:2) afforded **7a** (181 mg, 89%) as colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.86 (t, *J* = 7.4 Hz, 3 H, 5-H), 1.23 – 1.27 (m, 2 H, 4-H), 1.32 (m_c, 2 H, 3-H), 1.89 (m_c, 2 H, 2-H), 3.74, 3.79, 3.85 (3 s, 6 H each, OMe), 4.57 (t, *J* = 7.8 Hz, 1 H, 1-H), 6.50, 6.79 (2 s, 2 H each, Ar) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.0 (q, C-5), 22.6 (t, C-4), 30.1 (t, C-3), 34.2 (t, C-2), 36.5 (d, C-1), 56.0, 56.7, 56.9 (3 q, OMe), 98.4, 112.9 (2 d, Ar), 125.6, 142.8, 147.5, 151.6 (4 s, Ar) ppm. IR (film): υ = 2995 – 2830 (C-H), 1610, 1510, 1465, 1395 cm^{-1}. ESI-TOF: m/z calc. for $[M+Na]^+$: 427.2097, found 427.2065. Anal. calc. for $C_{23}H_{32}O_6$ (404.5): C 68.29, H 7.97; found: C 68.16, H 7.90.

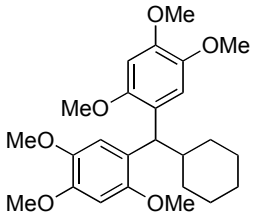
5,5'-(Dodecane-1,1-diyl)bis(1,2,4-trimethoxybenzene) (7b)



According to experimental procedure **A**: 1,2,4-trimethoxybenzene (339 mg, 2.02 mmol), dodecanal (258 mg, 1.40 mmol), MeCN (5 mL), F_3CSO_3H (18 µL, 0.20 mmol), 24 h, rt; purification by column chromatography (silica gel, ethyl acetate/hexane = 1:4 → 1:1) afforded **7b** (398 mg, 79%) as slightly brownish oil.

^{1}H NMR (500 MHz, DMSO-d_6): δ = 0.84 (t, *J* = 7.1 Hz, 3 H, 12-H), 1.12 – 1.26 (m, 18 H, 3-H to 11-H), 1.78 – 1.87 (m, 2 H, 2-H), 3.64, 3.70, 3.74 (3 s, 6 H each, OMe), 4.51 (t, *J* = 7.9 Hz, 1 H, 1-H), 6.60, 6.78 (2 s, 2 H each, Ar) ppm. ^{13}C NMR (126 MHz, DMSO-d_6): δ = 13.9 (q, C-12), 22.1, 27.5, 28.7, 28.8, 28.9, 28.97, 29.00, 31.3, 34.0, 35.3 (10 t, C-2 to C-11), 55.7, 56.4, 56.6 (3 q, OMe), 98.9, 113.6 (2 d, Ar), 124.5, 142.4, 147.6, 151.3 (4 s, Ar) ppm (the signal of C-1 overlaps with solvent residue peak). IR (film): υ = 2990 – 2850 (C-H), 1610, 1510, 1465, 1440 cm^{-1}. ESI-TOF: m/z calc. for $[M+Na]^+$: 525.3192, found 525.3198. Anal. calc. for $C_{30}H_{46}O_6$ (502.7): C 71.68, H 9.22; found: C 71.68, H 9.20.

5,5'-(Cyclohexylmethylene)bis(1,2,4-trimethoxybenzene) (7c)



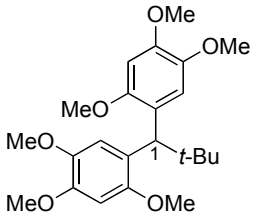
According to experimental procedure **A**: 1,2,4-trimethoxybenzene (336 mg, 2.00 mmol), cyclohexyl-aldehyde (244 mg, 1.47 mmol), MeCN (5 mL), F_3CSO_3H (18 µL, 0.20 mmol), 24 h, rt; purification by column chromatography (silica gel, ethyl acetate/hexane = 1:4 → 1:3) afforded **7c** (320 mg, 83%) as brownish highly viscous oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.87 – 0.93 (m, 2 H, Cy), 1.10 – 1.21 (m, 3 H, Cy), 1.54 – 1.70 (m, 5 H, Cy), 2.04 – 2.11 (m, 1 H, Cy), 3.76, 3.818, 3.824 (3 s, 3 H each, OMe), 4.28 (d, *J* = 11.3 Hz, 1 H, CH),

6.46, 6.93 (2 s, 2 H each, Ar) ppm. Anal. calc. for $C_{25}H_{34}O_6$ (430.5): C 69.74, H 7.96 found: C 69.75, H 7.79.

Compound is literature known, see: [2].

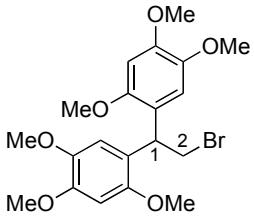
5,5'-(2,2-Dimethylpropane-1,1-diyl)bis(1,2,4-trimethoxybenzene) (7d)



According to experimental procedure **A**: 1,2,4-trimethoxybenzene (321 mg, 1.91 mmol), pivaldehyde (115 mg, 1.34 mmol), MeCN (5 mL), F_3CSO_3H (17 µL, 0.19 mmol), 24 h, rt; purification by column chromatography (silica gel, ethyl acetate/hexane = 1:3) afforded **7d** (233 mg, 58%) as colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.02 (s, 9 H, *t*-Bu), 3.76, 3.83, 3.84 (3 s, 6 H each, OMe), 5.00 (s, 1 H, 1-H), 6.50, 7.15 (2 s, 2 H each, Ar) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 29.2, 35.7 (q, s, *t*-Bu), 41.4 (d, C-1), 55.9, 56.7, 57.4 (3 q, OMe), 98.8, 114.6 (2 d, Ar), 124.5, 142.5, 147.5, 152.4 (4 s, Ar) ppm. IR (film): υ = 2950 – 2835 (C−H), 1610, 1590, 1510, 1465, 1440 cm^{-1}. ESI-TOF: m/z calc. for $[M+Na]^+$: 427.2097, found 427.2091. Anal. calc. for $C_{23}H_{32}O_6$ (404.5): C 68.29, H 7.97; found: C 68.31, H 7.98.

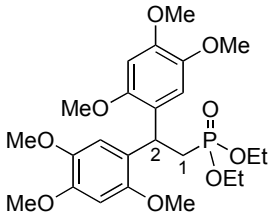
5,5'-(2-Bromoethane-1,1-diyl)bis(1,2,4-trimethoxybenzene) (7e)



According to experimental procedure **A**: 1,2,4-trimethoxybenzene (336 mg, 2.00 mmol), 2-bromo-1,1-diethoxyethane (275 mg, 1.40 mmol), MeCN (5 mL), F_3CSO_3H (18 µL, 0.20 mmol), 2 h, rt; purification by column chromatography (silica gel, ethyl acetate/hexane = 1:4 → 1:2) afforded **7e** (334 mg, 76%) as colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 3.76, 3.77, 3.85 (3 s, 6 H each, OMe), 3.90 (d, *J* = 8.0 Hz, 2 H, 2-H), 4.92 (t, *J* = 8.0 Hz, 1 H, 1-H), 6.51, 6.73 (2 s, 2 H each, Ar) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 34.4 (t, C-2), 41.1 (d, C-1), 55.8, 56.4, 56.6 (3 q, OMe), 97.8, 113.1 (2 d, Ar), 121.0, 142.5, 148.3, 151.6 (4 s, Ar) ppm. IR (film): υ = 2995 – 2830 (C−H), 1615, 1610, 1510, 1465, 1440 cm^{-1}. ESI-TOF: m/z calc. for $[M+Na–HBr]^+$: 383.1471, found 383.1489. Anal. calc. for $C_{20}H_{25}BrO_6$ (441.3): C 54.43, H 5.71; found: C 54.35, H 5.48.

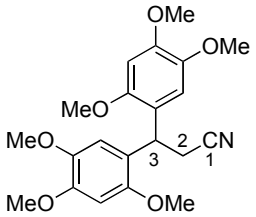
Diethyl [2,2-bis(2,4,5-trimethoxyphenyl)ethyl]phosphonate (7f)



According to experimental procedure **A**: 1,2,4-trimethoxybenzene (336 mg, 2.00 mmol), diethyl(2,2-diethoxyethyl)phosphonate (356 mg, 1.40 mmol), MeCN (5 mL), F_3CSO_3H (18 µL, 0.20 mmol), 24 h, rt; purification by column chromatography (silica gel, ethyl acetate/hexane = 1:3 → dichloromethane/diethylether 1:1) afforded **7f** (298 mg, 60%) as brownish oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.12 (t, J = 7.1 Hz, 6 H, P(OEt), 2.61 (dd, $^1J_{PH}$ = 18.0 Hz, J = 7.6, 2 H, 1-H), 3.74, 3.78, 3.82 (3 s, 6 H each, OMe), 4.83 (dt, $^2J_{PH}$ = 15.3, J = 7.6, 1 H, 2-H), 6.45, 6.87 (2 s, 2 H each, Ar) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 16.2 (dq, $^3J_{PC}$ = 6.3 Hz, $P(OEt)_2$), 29.6 (dt, $^1J_{PC}$ = 138.0 Hz, C-1), 34.4 (dd, $^2J_{PC}$ = 2.5 Hz, C-2), 56.0, 56.3, 56.6 (3 q, OMe), 61.1 (dt, $^2J_{PC}$ = 6.4 Hz, $P(OEt)_2$), 97.8, 113.8 (2 d, Ar), 123.2 (d, $^3J_{PC}$ = 10.3 Hz, Ar), 142.4, 148.0, 151.3 (3 s, Ar) ppm. ^{31}P NMR (162 MHz, $CDCl_3$): δ = 31.3 ppm. IR (film): υ = 2985 – 2835 (C−H), 1610, 1510, 1465, 1440 cm^{-1}. ESI-TOF: m/z calc. for $[M+Na]^+$: 521.1916, found 521.1917. Anal. calc. for $C_{24}H_{35}O_9P$ (498.5): C 57.82, H 7.08; found: C 57.73, H 7.13.

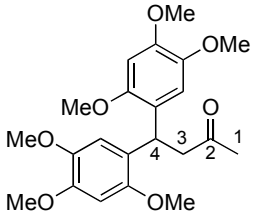
3,3-Bis(2,4,5-trimethoxyphenyl)propanenitrile (7g)



According to experimental procedure **A**: 1,2,4-trimethoxybenzene (345 mg, 2.05 mmol), 3,3-dimethoxypropanenitrile (165 mg, 1.43 mmol), MeCN (5 mL), F_3CSO_3H (18 µL, 0.20 mmol), 24 h, rt; purification by column chromatography (silica gel, ethyl acetate/hexane = 1:2 → 1:1) afforded **7g** (233 mg, 55%) as colorless highly viscous oil.

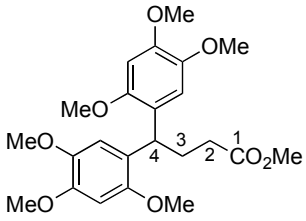
^{1}H NMR (500 MHz, $CDCl_3$): δ = 3.05 (d, J = 7.7 Hz, 2 H, 2-H), 3.76, 3.79, 3.87 (3 s, 6 H each, OMe), 4.87 (t, J = 7.7 Hz, 1 H, 3-H), 6.52, 6.73 (2 s, 2 H each, Ar) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 21.7 (t, C-2), 35.8 (d, C-3), 56.0, 56.3, 56.7 (3 q, OMe), 97.7, 113.1 (2 d, Ar), 119.3 (s, C-1), 120.6, 142.8, 148.7, 151.3 (4 s, Ar) ppm. IR (film): υ = 3000 – 2835 (C−H), 2245, 1610, 1510, 1465, 1440 cm^{-1}. ESI-TOF: m/z calc. for $[M+Na]^+$: 410.1580, found 410.1616. Anal. calc. for $C_{21}H_{25}NO_6$ (387.4): C 65.10, H 6.50; found: C 65.15, H 6.54.

4,4-Bis(2,4,5-trimethoxyphenyl)butan-2-one (7h)



According to experimental procedure **A**: 1,2,4-trimethoxybenzene (336 mg, 2.00 mmol), 4,4-dimethoxy-butan-2-one (185 mg, 1.40 mmol), MeCN (5 mL), F_3CSO_3H (18 µL, 0.20 mmol), 24 h, rt; purification by column chromatography (silica gel, ethyl acetate/hexane = 2:3) afforded **7h** (339 mg, 84%) as yellow solid. M. p. 98 – 100 °C. ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 2.08 (s, 3 H, 1-H), 3.07 (d, *J* = 7.9 Hz, 2 H, 3-H), 3.76 (s, 12 H, OMe), 3.84 (s, 6 H, OMe), 5.06 (t, *J* = 7.9 Hz, 1 H, 4-H), 6.49, 6.71 (2 s, 2 H each, Ar) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 29.6 (q, C-1), 34.4 (d, C-4), 48.4 (t, C-3), 56.1, 56.5, 56.7 (3 q, OMe), 98.1, 113.2 (2 d, Ar), 123.2, 142.7, 148.0, 151.3 (4 s, Ar), 208.1 (s, C-2) ppm. IR (film): υ = 2995 – 2835 (C−H), 1710 (C=O), 1610, 1510, 1465, 1440 cm^{-1}. ESI-TOF: m/z calc. for $[M+Na]^+$: 427.1733, found 427.1745. Anal. calc. for $C_{22}H_{28}O_7$ (404.5): C 65.33, H 6.98; found: C 65.45, H 6.67.

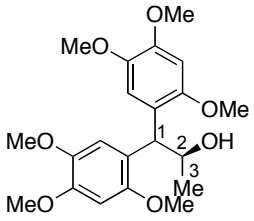
Methyl 4,4-bis(2,4,5-trimethoxyphenyl)butanoate (7i)



According to experimental procedure **A**: 1,2,4-trimethoxybenzene (336 mg, 2.00 mmol), methyl 2-(trimethylsiloxy)cyclopropanecarboxylate (263 mg, 1.40 mmol), MeCN (5 mL), F_3CSO_3H (18 µL, 0.20 mmol), 30 min, 0 °C; purification by column chromatography (silica gel, ethyl acetate/hexane = 1:3 → 1:1) afforded **7i** (421 mg, 97%) as colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.21 – 2.30 (m, 4 H, 2-H, 3-H), 3.61 (3 H, CO_2Me), 3.72, 3.78, 3.84 (3 s, 6 H each, OMe), 4.55 (t, *J* = 7.3 Hz, 1 H, 4-H), 6.48, 6.78 (2 s, 2 H each, Ar) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 29.4 (t, C-2), 32.6 (t, C-3), 36.2 (d, C-4), 51.3, 56.0, 56.66, 56.68 (4 q, OMe), 98.2, 112.7 (2 d, Ar), 124.2, 142.8, 147.8, 151.6 (4 s, Ar), 174.2 (s, C-1) ppm. IR (film): υ = 2995 – 2830 (C-H), 1735 (C=O), 1610, 1510, 1465, 1455, 1440, 1395 cm^{-1}. ESI-TOF: m/z calc. for $[M+Na]^+$: 457.1838, found 457.1838. Anal. calc. for $C_{23}H_{30}O_8$ (434.5): C 63.58, H 6.96; found: C 63.60, H 7.00.

(*S*)-1,1-Bis(2,4,5-trimethoxyphenyl)propan-2-ol (Tatarinoid C)

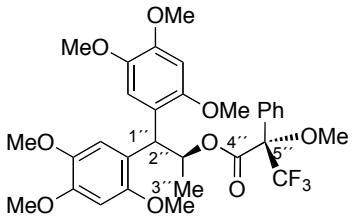


According to experimental procedure **A**: 1,2,4-trimethoxybenzene (673 mg, 4.00 mmol), (*S*)-2-(*tert*-butyldimethylsiloxy)propanal (452 mg, 2.40 mmol), MeCN (20 mL), F_3CSO_3H (18 µL, 0.20 mmol), 6 h, rt; purification by column chromatography (silica gel, ethyl acetate/hexane = 1:1) afforded (-)-tatarinoid C (343 mg, 44%) as colorless oil.

$[\alpha]_D^{22}$ = -6.2 (c = 2.55, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.17 (d, *J* = 5.7 Hz, 3 H, 3-H), 1.95 (bs, 1 H, OH), 3.758, 3.761, 3.77, 3.81, 3.83, 3.84 (6 s, 3 H each, OMe), 4.51 – 4.58 (m, 2 H, 1-H, 2-H), 6.48, 6.51, 6.91, 7.06 (4 s, 1 H each, Ar) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 21.5 (q, C-3), 45.7 (d, C-1), 55.90,

55.91, 56.53, 56.54, 56.6, 56.7 (6 q, OMe), 69.5 (d, C-2), 98.1, 98.3, 113.6, 113.7 (4 d, Ar), 121.3, 122.9, 142.7, 142.9, 147.8, 148.0, 151.3, 152.0 (8 s, Ar) ppm. IR (film): υ = 3490 (OH), 2950 – 2830 (C-H), 1610, 1510, 1465, 1440, 1395 cm^{-1}. ESI-TOF: m/z calc. for $[M+Na]^+$: 415.1733, found 415.1754. Anal. calc. for $C_{21}H_{28}O_7$ (392.4): C 64.27, H 7.19; found: C 64.23, H 7.18.

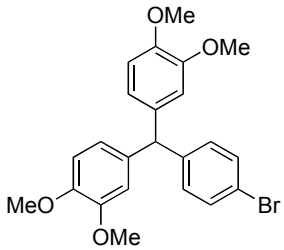
(*S*)-(*S*)-1,1-Bis(2,4,5-trimethoxyphenyl)propan-2-yl-3,3,3-trifluoro-2-methoxy-2-phenylpropanoate



To a solution of (–)-tatarinoid C (60 mg, 0.15 mmol) in dichloromethane (2.0 mL) was added *i*-Pr_2NEt (51 µL, 0.31 mmol), (*R*)-(-)-α-methoxy-α-(trifluoromethyl)phenylacetylchloride (62 mg, 0.26 mmol) and DMAP (4 mg, 0.03 mmol), and the resulting mixture was stirred for 6 h until complete conversion of (-)-tatarinoid. The reaction was quenched by addition of water; the resulting mixture was extracted twice with dichloromethane. The combined organic layers were dried (Na_2SO_4) and the solvent was removed in vavuo. The diastereomeric ratio (d. r.) was determined to be >98:2 by analysis of crude product by ^{1}H- and ^{19}F-NMR spectroscopy. Further purification by column chromatography (silica gel, ethyl acetate/hexane = 1:4 → 1:1) afforded Mosher ester derivative (70 mg, 75%) as colorless solid.

M. p. 34 – 36 °C. $[\alpha]_D^{22}$ = -70.9 (c = 0.22, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.23 (d, *J* = 6.2 Hz, 3 H, 3´´-H), 3.23 (s, 3 H, C(5´´)-OMe), 3.687, 3.690, 3.73, 3.846, 3.850, 3.852 (6 s, je 3 H, OMe), 4.87 (d, *J* = 8.9 Hz, 1 H, 1´´-H), 6.18 (m_c, 1 H, 2´´-H), 6.47, 6.50, 6.79 (3 s, je 1 H, Ar), 7.10 – 7.12 (m, 2 H, Ph), 7.16 – 7.21 (m, 3 H, Ar, Ph), 7.28 – 7.31 (m, 1 H, Ph) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 18.6 (q, C-3´´), 42.9 (d, C-1´´), 54.9 (d, C(5´´)-OMe), 55.9*, 56.30, 56.32, 56.4, 56.6 (6 q, OMe), 74.9 (d, C-2´´), 84.4 (q, $^2J_{CF}$ = 27.7 Hz, C-5´´), 97.7, 98.1, 113.1, 114.1 (4 d, Ar), 120.6, 120.8 (2 s, Ar), 123.3 (q, $^1J_{CF}$ = 288.5 Hz, CF_3), 127.1, 128.1, 129.3 (3 d, Ph), 132.3 (s, Ph), 142.7, 142.8, 148.0, 148.2, 151.3, 151.7 (6 s, Ar), 166.2 (s, C-4´´) ppm; * signal with higher intensitiy. ^{19}F NMR (470 MHz, $CDCl_3$): δ = -71.0 (CF_3) ppm. IR (film): υ = 2995 – 2830 (C-H), 1740 (C=O), 1610, 1510, 1465, 1455, 1440 cm^{-1}. ESI-TOF: m/z calc. for $[M+Na]^+$: 631.2131, found 631.2095. Anal. calc. for $C_{31}H_{35}F_3O_9$ (608.5): C 61.18, H 5.80; found: C 61.38, H 5.95.

4,4'-[(4-Bromophenyl)methylene]bis(1,2-dimethoxybenzene) (11)

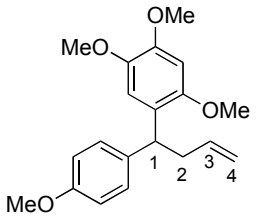


According to experimental procedure **A**: 1,2,-dimethoxybenzene (276 mg, 2.00 mmol), 4-bromo-benzaldehyde (250 mg, 1.35 mmol), MeCN (2.5 mL), F_3CSO_3H (18 µL, 0.20 mmol), 24 h, rt; purification by column chromatography (silica gel, ethyl acetate/hexane = 1:6 → 1:2) afforded **11** (147 mg, 34%) as colorless solid.

M. p. 149 – 152 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 3.76, 3.86 (2 s, 6 H each, OMe), 5.39 (s, 1 H, CH), 6.56 (ddd, *J* = 0.7, 2.0, 8.2 Hz, 2 H, Ar), 6.63 (d, *J* = 2.0 Hz, 2 H, Ar), 6.78 (d, *J* = 8.2 Hz, 2 H, Ar), 6.98 (d, *J* = 7.8 Hz, 2 H, Ar), 7.40 (d, *J* = 8.4 Hz, 2 H, Ar) ppm. Anal. calc. for $C_{23}H_{23}BrO_4$ (443.3): C 62.31, H 5.23; found: C 62.31, H 5.44.

Compound is literature known, see: [4].

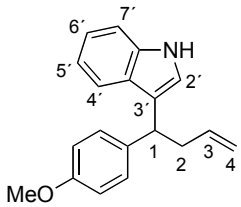
1,2,4-Trimethoxy-5-[1-(4-methoxyphenyl)but-3-en-1-yl]benzene (14a)



According to experimental procedure **B**: 1-(4-methoxyphenyl)but-3-en-1-ol (201 mg, 1.13 mmol), 1,2,4-trimethoxybenzene (172 mg, 1.02 mmol), MeCN (2.5 mL), F_3CSO_3H (9 µL, 0.10 mmol), 45 min, 0 °C; purification by column chromatography (silica gel, ethyl acetate/hexane = 1:4) afforded **14a** (338 mg, 99%) as colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.73 (m_c, 2 H, 2-H), 3.75, 3.77, 3.80, 3.86 (4 s, 3 H each, OMe), 4.39 (t, *J* = 8.0 Hz, 1 H, 1-H), 4.93, 5.02 (2 m_c, 1 H each, 4-H), 5.73 (m_c, 1 H, 3-H), 6.50, 6.75 (2 s, 1 H each, Ar), 6.74 – 6.82 (m, 2 H, Ar), 7.15 – 7.19 (m, 2 H, Ar) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 39.4 (t, C-2), 42.1 (d, C-1), 55.1, 56.1, 56.6, 56.8 (4 q, OMe), 98.1, 112.4, 113.5 (3 d, Ar), 115.8 (t, C-4), 125.0 (s, Ar), 128.8 (d, Ar), 136.8 (s, Ar), 137.3 (d, C-3), 143.0, 147.8, 151.2, 157.6 (4 s, Ar) ppm. IR (film): υ = 3005 – 2835 (C-H), 1610, 1510, 1465, 1440 cm^{-1}. ESI-TOF: m/z calc. for $[M+Na]^+$: 351.1567, found 351.1585. Anal. calc. for $C_{20}H_{24}O_4$ (328.4): C 59.65, H 5.41; found: C 59.72, H 5.48.

3-[1-(4-Methoxyphenyl)but-3-en-1-yl]-1*H*-indole (14b)

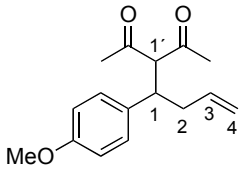


According to experimental procedure **B**: 1-(4-methoxyphenyl)but-3-en-1-ol (364 mg, 2.04 mmol), indole (242 mg, 2.07 mmol), MeCN (5 mL), F_3CSO_3H (18 µL, 0.10 mmol), 16 h, rt; purification by column chromatography (silica gel, ethyl acetate/hexane = 1:7) afforded **14b** (343 mg, 60%) as colorless highly visous oil which slowly decomposes.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.78, 2.96 (2 m_c, 1 H each, 2-H), 3.79 (s, 3 H, OMe), 4.26 (t, *J* = 7.4 Hz, 1 H, 1-H), 4.99, 5.09 (2 m_c, 1 H each, 4-H), 5.85 (m_c, 1 H, 3-H), 6.84, 7.23 (2 d, *J* = 8.7 Hz, 2 H each, Ar), 7.03 – 7.06 (m, 2 H, Indole), 7.17 (m_c, 1 H, Indole), 7.33 (m_c, 1 H, Indole), 7.45 (m_c, 1 H, Indole), 7.97 (bs, 1 H, NH) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 40.6 (t, C-2), 42.1 (d, C-1), 55.1 (q, OMe), 111.0 (d, Indole), 113.6 (d, Ar), 115.9 (t, C-4), 119.2, 119.5 (2 d, Indole), 120.0 (s, Indole), 121.2, 121.9 (2 d, Indole), 126.9 (s, Ar), 128.8 (d, Ar), 136.5, 136.9 (2 s, Indole), 137.4 (d, C-3), 157.8 (s, Ar) ppm. IR (film): υ = 3420 (N-H),

3000 – 2835 (C-H), 1610, 1510, 1455, 1440 cm^{-1}. ESI-TOF ($C_{19}H_{19}NO$ (277.4): m/z calc. for $[M+Na]^+$: 300.1364, found 300.1382.

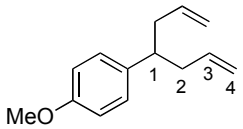
3-[1-(4-Methoxyphenyl)but-3-en-1-yl]pentane-2,4-dione (14c)



According to experimental procedure **B**: 1-(4-methoxyphenyl)but-3-en-1-ol (358 mg, 2.01 mmol), pentan-2,4-dione (401 mg, 4.01 mmol), MeCN (5 mL), F_3CSO_3H (18 µL, 0.10 mmol), 16 h, rt; purification by column chromatography (silica gel, ethyl acetate/hexane = 1:6 → 1:4) afforded **14c** (387 mg, 74%) as colorless oil.

^1H NMR (500 MHz, $CDCl_3$): δ = 1.80, 2.24 (2 s, 3 H each, Me), 2.20 – 2.27 (m, 2 H, 2-H), 3.53 (m_c, 1 H, 1-H), 3.75 (s, 3 H, OMe), 4.09 (d, *J* = 11.5 Hz, 1 H, 1´-H), 4.86 – 4.92 (m, 2 H, 4-H), 5.49 (m_c, 1 H, 3-H), 6.80, 7.04 (2 d, *J* = 8.7 Hz, 2 H each, Ar) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 29.2, 30.1 (2 q, Me), 39.4 (t, C-2), 44.6 (d, C-1), 55.1 (q, OMe), 75.4 (d, C-3), 114.0 (d, Ar), 117.1 (t, C-4), 129.1 (d, Ar), 132.2 (s, Ar), 135.0 (d, C-3), 158.4 (s, Ar), 203.2, 203.2 (2 s, C=O) ppm. IR (film): υ = 3075 – 2840 (C-H), 1700 (C=O), 1610, 1515, 1465, 1440 cm^{-1}. ESI-TOF: m/z calc. for $[M+Na]^+$: 283.1310, found 283.1329. Anal. calc. for $C_{16}H_{20}O_3$ (260.3): C 73.82, H 7.74; found: C 73.07, H 7.68.

1-(Hepta-1,6-dien-4-yl)-4-methoxybenzene (14d)

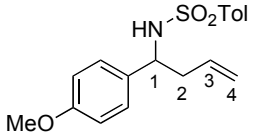


According to experimental procedure **B**: 1-(4-methoxyphenyl)but-3-en-1-ol (80 mg, 0.45 mmol), allyltrimethylsilane (103 mg, 0.90 mmol), MeCN (1.3 mL), F_3CSO_3H (2 µL, 0.02 mmol), 2 h, rt; purification by column chromatography (silica gel, ethyl acetate/hexane = 1:20) afforded **14d** (61 mg, 67%) as colorless oil.

^1H NMR (400 MHz, $CDCl_3$): δ = 2.37 (m_c, 4 H, 2-H), 2.70 (m_c, 1 H, 1-H), 3.80 (s, 3 H, OMe), 4.94 – 5.02 (m, 4 H, 4-H), 5.69 (m_c, 2 H, 3-H), 6.86, 7.10 (2 d, *J* = 8.3 Hz, 2 H each, Ar) ppm.

Compound is literature known, see: [5].

***N*-[1-(4-Methoxyphenyl)but-3-en-1-yl]-4-methylbenzenesulfonamide (14e)**



According to experimental procedure **B**: 1-(4-methoxyphenyl)but-3-en-1-ol (81 mg, 0.45 mmol), *p*-toluolsulfonamide (154 mg, 0.90 mmol), MeCN (1.3 mL), F_3CSO_3H (2 µL, 0.02 mmol), 24 h, rt; purification by column chromatography (silica gel, ethyl acetate/hexane = 1:6 → 1:4) afforded **14e** (92 mg, 62%) as colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.38 (s, 3 H, Me), 2.39 – 2.50 (m, 2 H, 2-H), 3.75 (s, 3 H, OMe), 4.31 (m_c, 1 H, 1-H), 4.87 (bd, *J* = 6.1 Hz, 1 H, NH), 5.01 – 5.08 (m, 2 H, 4-H), 5.50 (m_c, 1 H, 3-H), 6.70, 6.98 (2 d, *J* = 8.7 Hz, 1 H, each, Ar), 7.15, 7.54 (2 d, *J* = 8.3 Hz, 1 H, each, Ar) ppm.

Compound is literature known, see: [6].

[1] Govindachari, T. R.; Nagarajan, K.; Parthasarathy, P. C. *J. Chem. Soc*. **1958**, 899–916.

[2] Jaratjaroonphong, J.; Sathalalai, S.; Techasauvapak, P.; Reutrakul, V. *Tetrahedron Lett.* **2009**, *50*, 6012-6015.

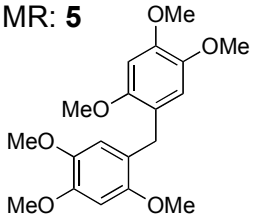
[3] Szeki, T. *Ber. dtsch. Chem. Ges.* **1911**, *44*, 1476-1481.

[4] Mohammadpoor-Baltork, I.; Moghadam, M.; Tangestaninejad, S.; Mirkhani, V.; Mohammadiannejad-Abbasabadi, K.; Khavasi, H. R. *Eur. J. Org. Chem*. **2011**, 1357-1366.

[5] Vennall, G. P.; Aggarwal, V. K. *Synthesis* **1998**, *12*, 1822-1826.

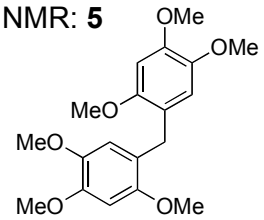
[6] Thiruphati, P.; Kim, S. S. *Tetrahedron* **2010**, *66*, 8623-8628.

^{1}H NMR: **5**

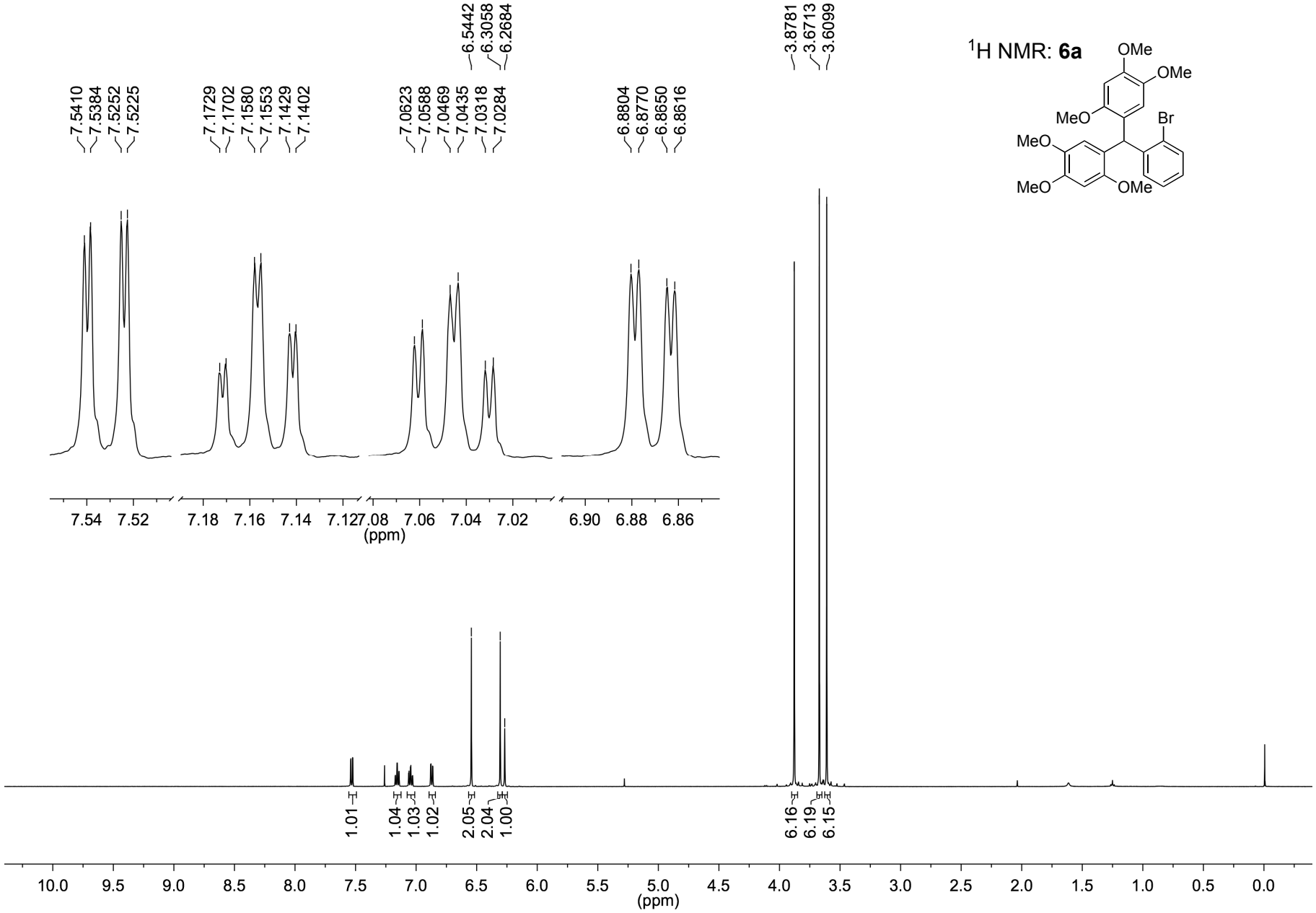

OMe
OMe
MeO
MeO
MeO
OMe

6.6591
6.5326
3.8696
3.8345
3.8040
3.7473
2.00
2.00
6.03
2.06
6.02
6.03
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
(ppm)

^{13}C NMR: **5**


OMe
OMe
MeO
MeO
MeO
OMe

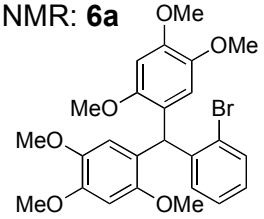
151.49
147.68
142.77
120.97
114.52
97.74
56.49
56.40
56.12
28.71
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
(ppm)


7.5410
7.5384
7.5252
7.5225
7.1729
7.1702
7.1580
7.1553
7.1429
7.1402
7.0623
7.0588
7.0469
7.0435
7.0318
7.0284
6.8804
6.8770
6.8650
6.8616
6.5442
6.3058
6.2684
3.8781
3.6713
3.6099
7.54 7.52
7.18 7.16 7.14 7.12
7.08 7.06 7.04 7.02
6.90 6.88 6.86
(ppm)
1.01
1.04
1.03
1.02
2.05
2.04
1.00
6.16
6.19
6.15
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
(ppm)

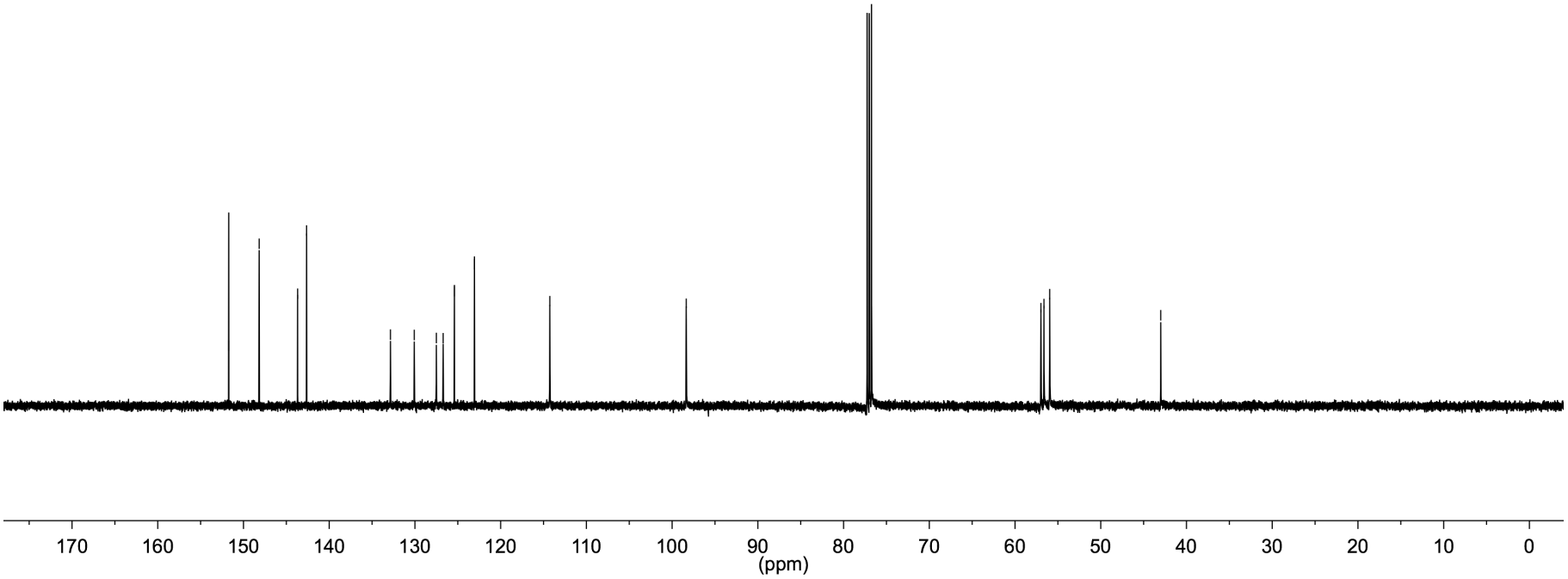
^{1}H NMR: **6a**

OMe
OMe
MeO
Br
MeO
MeO
OMe

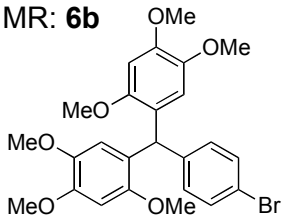
^{13}C NMR: **6a**



151.72
148.17
143.68
142.64
132.86
130.08
127.50
126.71
125.40
123.06
114.26
98.35
56.98
56.62
55.96
43.00

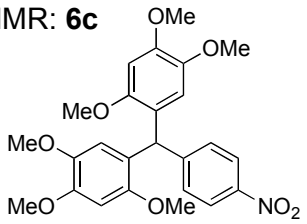


^{1}H NMR: **6b**


OMe
OMe
MeO
MeO
MeO
OMe
Br

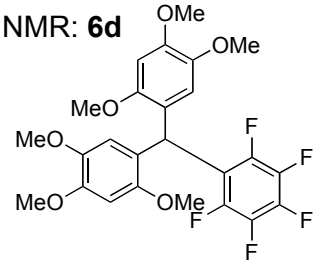
7.3511
7.3343
6.9233
6.9066
6.5341
6.3914
6.0013
3.8777
3.6593
3.6380
2.03
2.04
2.06
2.04
1.00
6.16
6.11
6.17
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
(ppm)

^{1}H NMR: **6c**

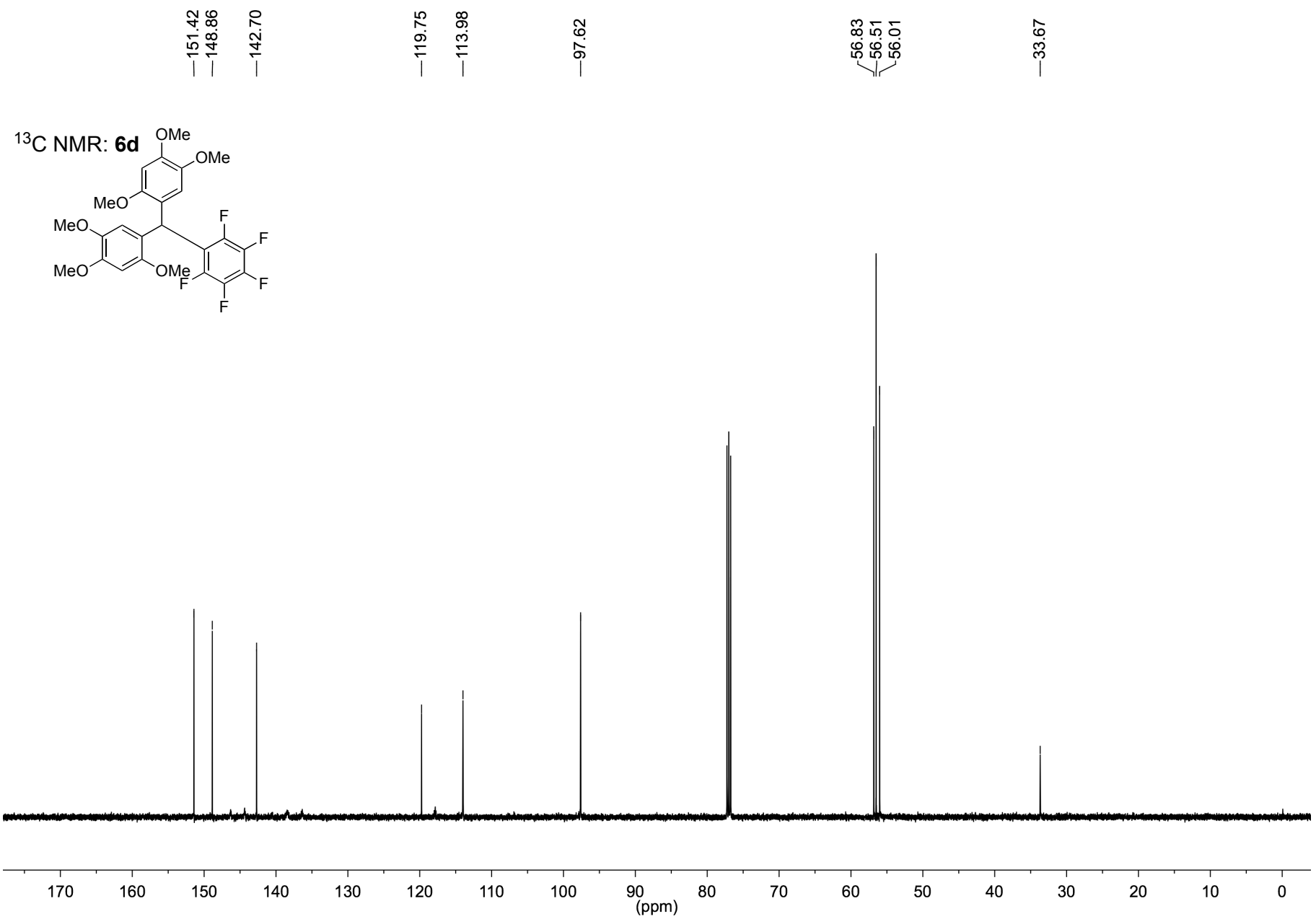

OMe
OMe
MeO
MeO
MeO
OMe
NO2

8.0926
8.0752
7.2006
7.1832
6.5487
6.3817
6.0975
3.8870
3.6626
3.6354
2.05
2.07
2.07
2.06
1.00
6.36
12.78
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
(ppm)

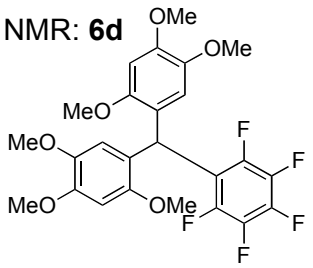
^{1}H NMR: **6d**


OMe
OMe
MeO
MeO
MeO
OMe
F
F
F
F
F

6.5602
6.5193
6.2360
3.8839
3.6977
3.6918
2.03
2.10
1.00
6.21
12.29
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
(ppm)

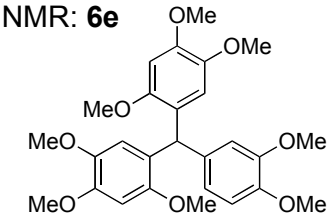

151.42
148.86
142.70
119.75
113.98
97.62
56.83
56.51
56.01
33.67
13C NMR: 6d
OMe
OMe
MeO
MeO
MeO
OMe
F
F
F
F
F
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
(ppm)

^{19}F NMR: **6d**

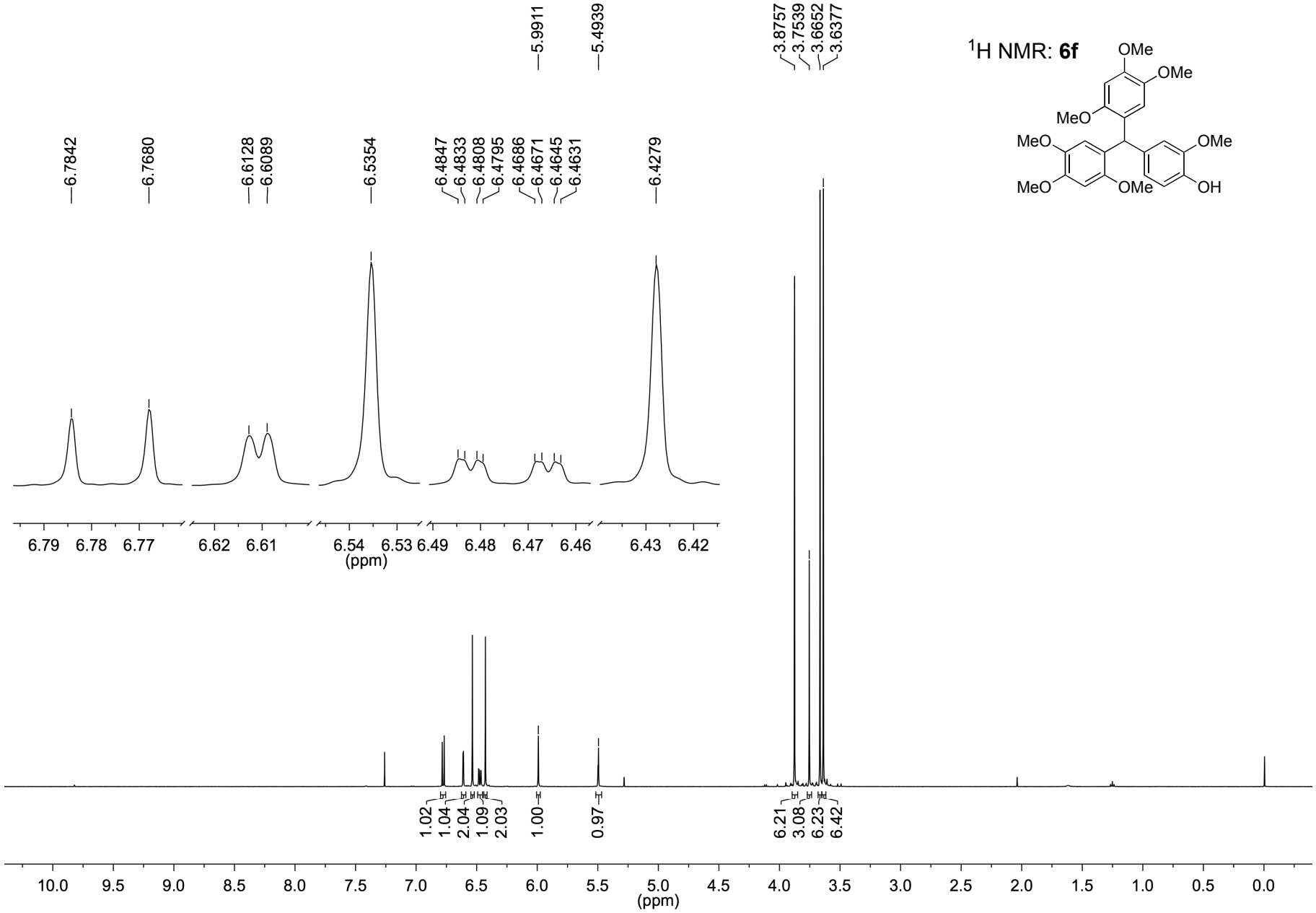

OMe
OMe
MeO
MeO
MeO
OMe
F
F
F
F
F

-140.6777
-140.6974
-140.7366
-140.7558
-157.6014
-157.6577
-157.7135
-163.0274
-163.0461
-163.0845
-163.1026
-163.1408
-163.1601
-140.6 -140.7 -140.8 -140.9
-157.5 -157.6 -157.7 -157.8 -157.9
-162.8 -162.9 -163.0 -163.1 -163.2 -163.3
(ppm)
190 170 150 130 110 90 70 50 30 10 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190
(ppm)

^{1}H NMR: **6e**

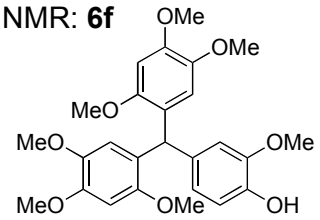

OMe
OMe
MeO
MeO
OMe
MeO
OMe
OMe

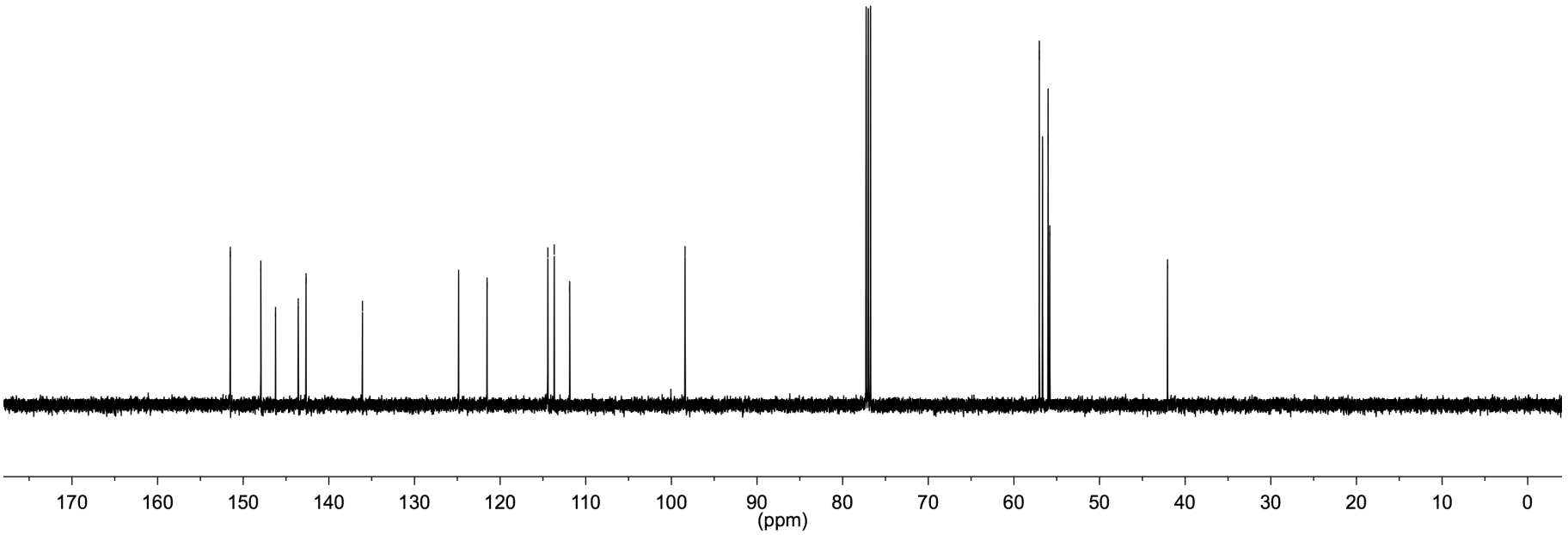
6.7297
6.7132
6.6331
6.6304
6.5260
6.5010
6.4847
6.4096
5.9950
3.8636
3.8248
3.7401
3.6572
3.6201
1.05
1.04
2.07
1.08
2.01
0.99
6.32
3.26
3.21
6.26
6.39
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
(ppm)


^{1}H NMR: **6f**
OMe
OMe
MeO
MeO
OMe
MeO
OMe
OH
6.7842
6.7680
6.6128
6.6089
6.5354
6.4847
6.4833
6.4808
6.4795
6.4686
6.4671
6.4645
6.4631
6.4279
5.9911
5.4939
3.8757
3.7539
3.6652
3.6377
6.79 6.78 6.77
6.62 6.61
6.54 6.53
6.49 6.48 6.47 6.46
6.43 6.42
(ppm)
1.02
1.04
2.04
1.09
2.03
1.00
0.97
6.21
3.08
6.23
6.42
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
(ppm)

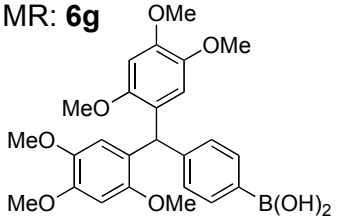
151.51
147.94
146.22
143.57
142.66
136.07
124.84
121.52
114.43
113.68
111.87
98.40
57.03
56.66
56.01
55.81
42.06

^{13}C NMR: **6f**





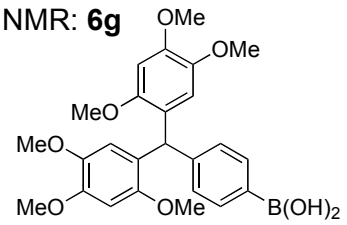
^{1}H NMR: **6g**

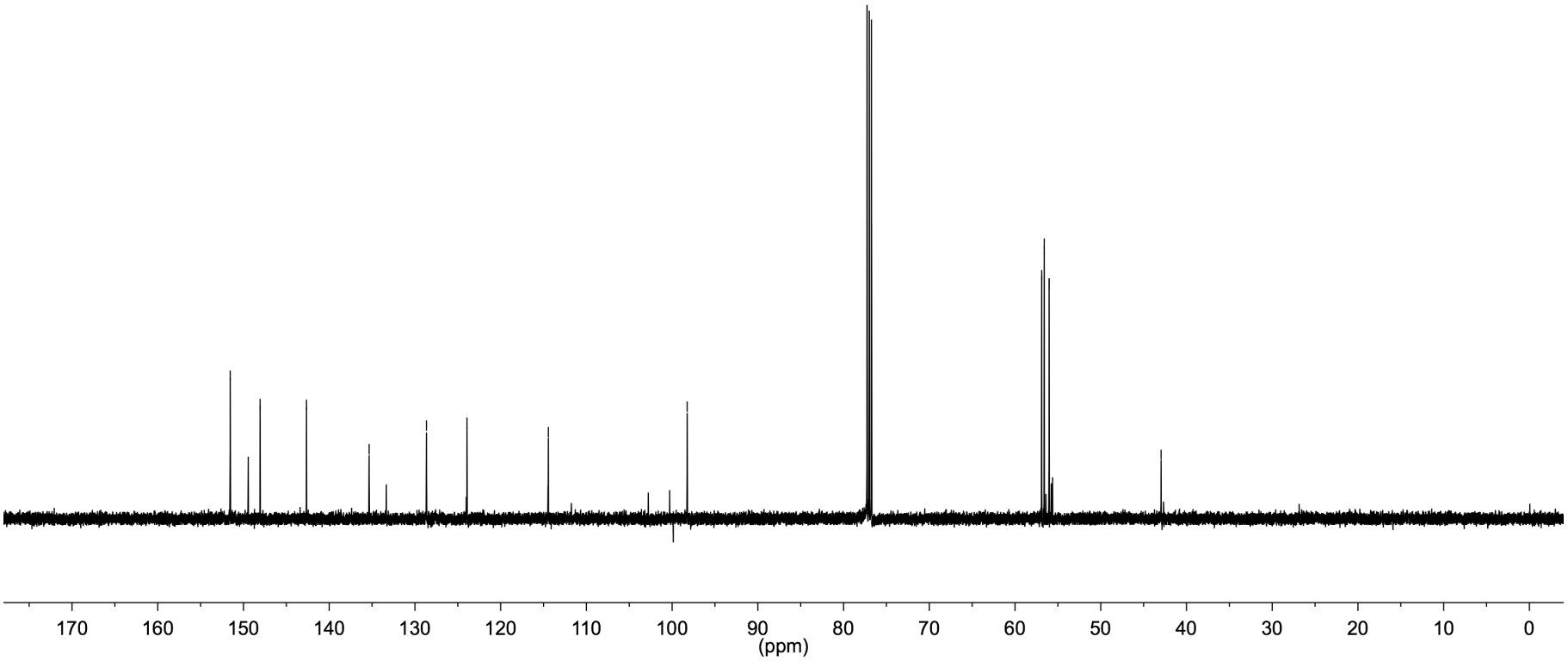

OMe
OMe
MeO
MeO
MeO
OMe
B(OH)2

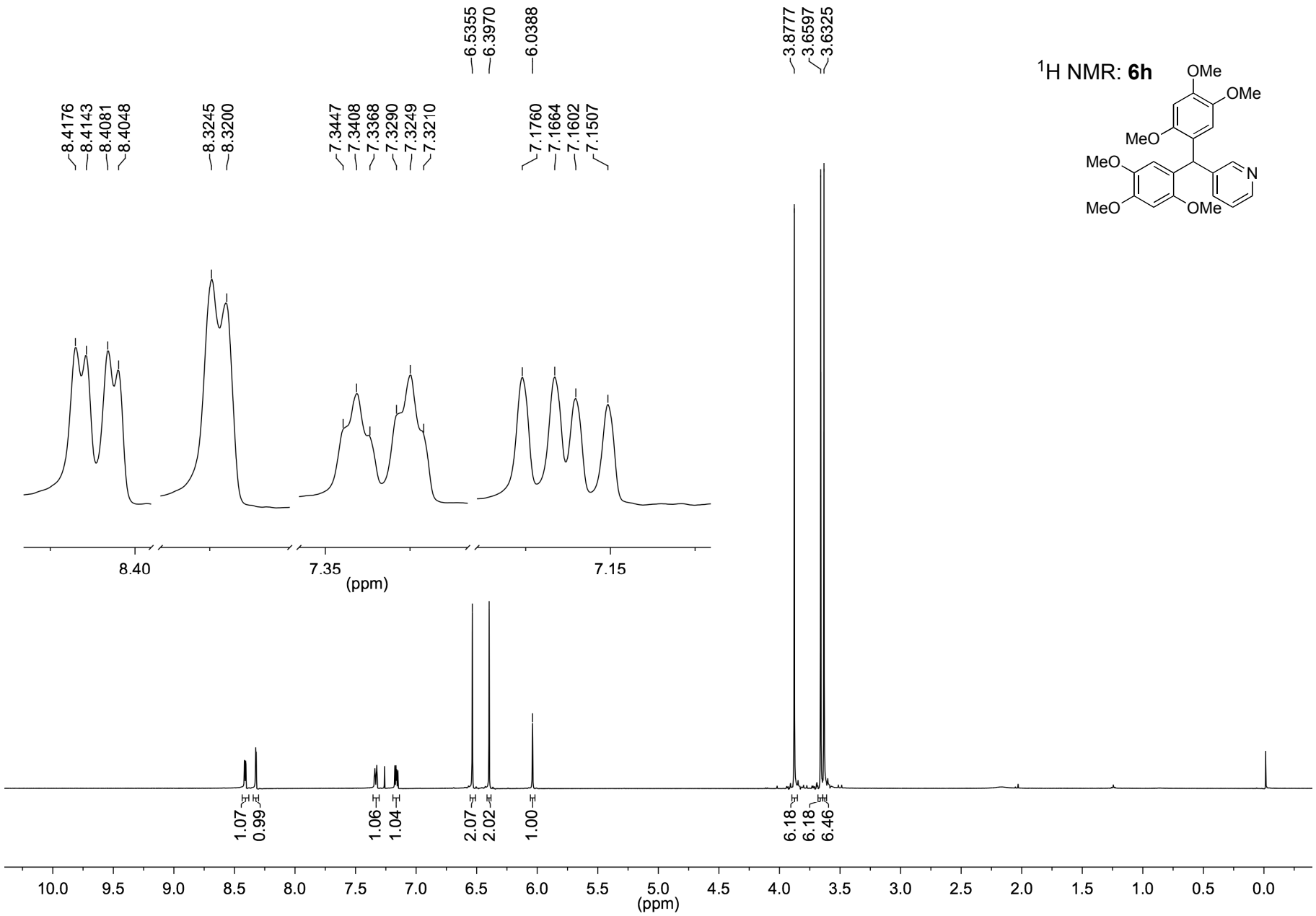
8.0862
8.0701
7.1828
7.1671
6.5538
6.4346
6.1250
3.8890
3.6657
3.6286
1.90
1.94
2.02
1.98
1.00
6.06
6.18
6.03
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
(ppm)

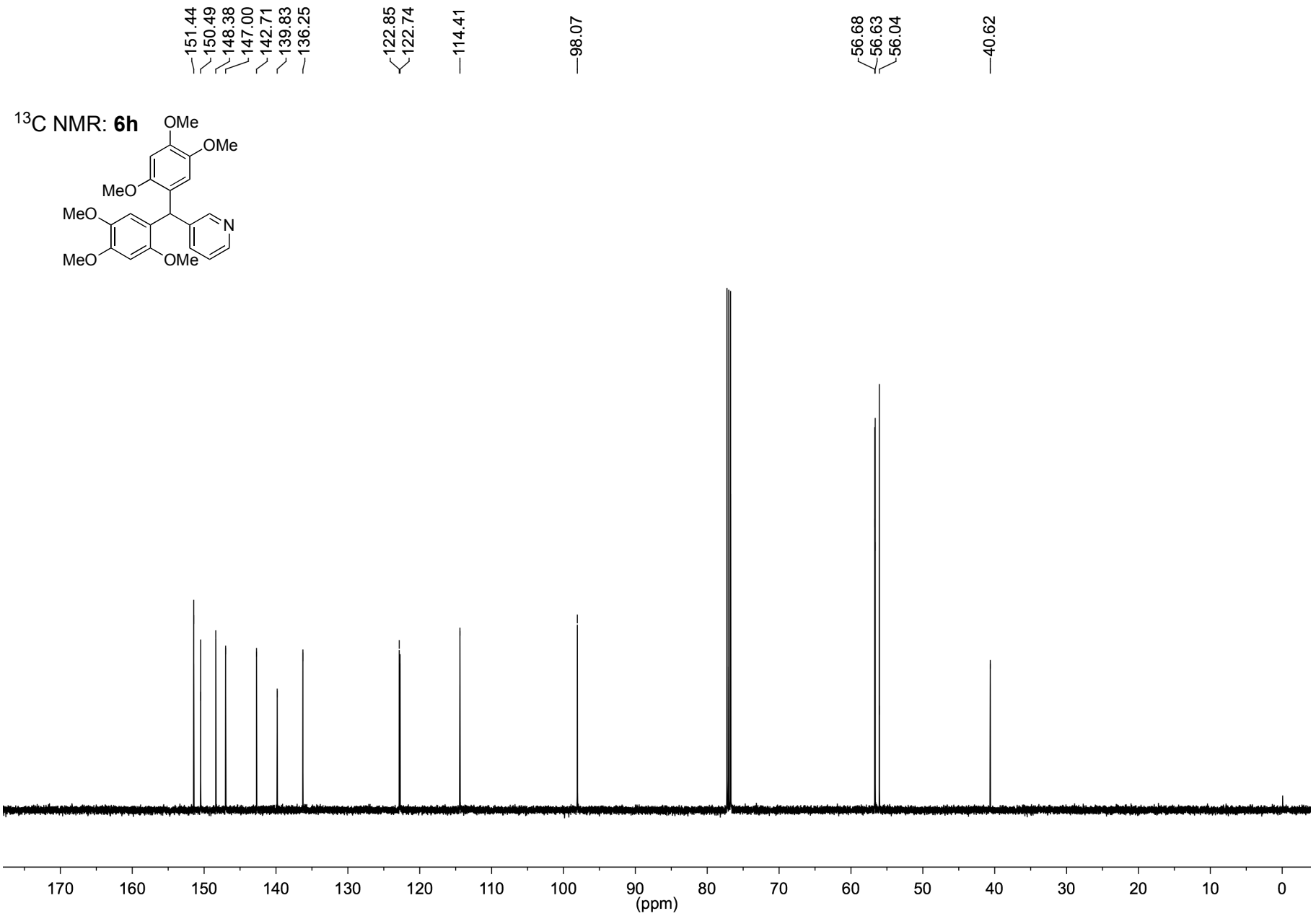
151.55
149.44
148.06
142.65
135.34
128.66
123.93
114.44
98.24
56.89
56.59
56.03
42.96

^{13}C NMR: **6g**

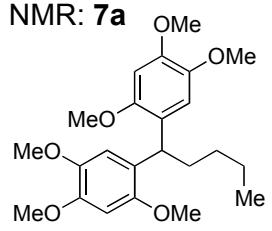





^{1}H NMR: **6h**
OMe
OMe
MeO
MeO
MeO
OMe
N
8.4176
8.4143
8.4081
8.4048
8.3245
8.3200
7.3447
7.3408
7.3368
7.3290
7.3249
7.3210
6.5355
6.3970
6.0388
7.1760
7.1664
7.1602
7.1507
3.8777
3.6597
3.6325
8.40
7.35
7.15
(ppm)
1.07
0.99
1.06
1.04
2.07
2.02
1.00
6.18
6.18
6.46
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
(ppm)

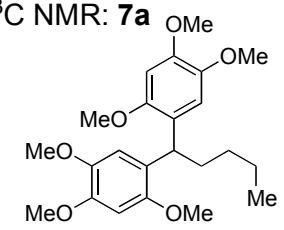

151.44
150.49
148.38
147.00
142.71
139.83
136.25
122.85
122.74
114.41
98.07
56.68
56.63
56.04
40.62
13C NMR: 6h
OMe
OMe
MeO
MeO
MeO
OMe
N
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
(ppm)

^{1}H NMR: **7a**

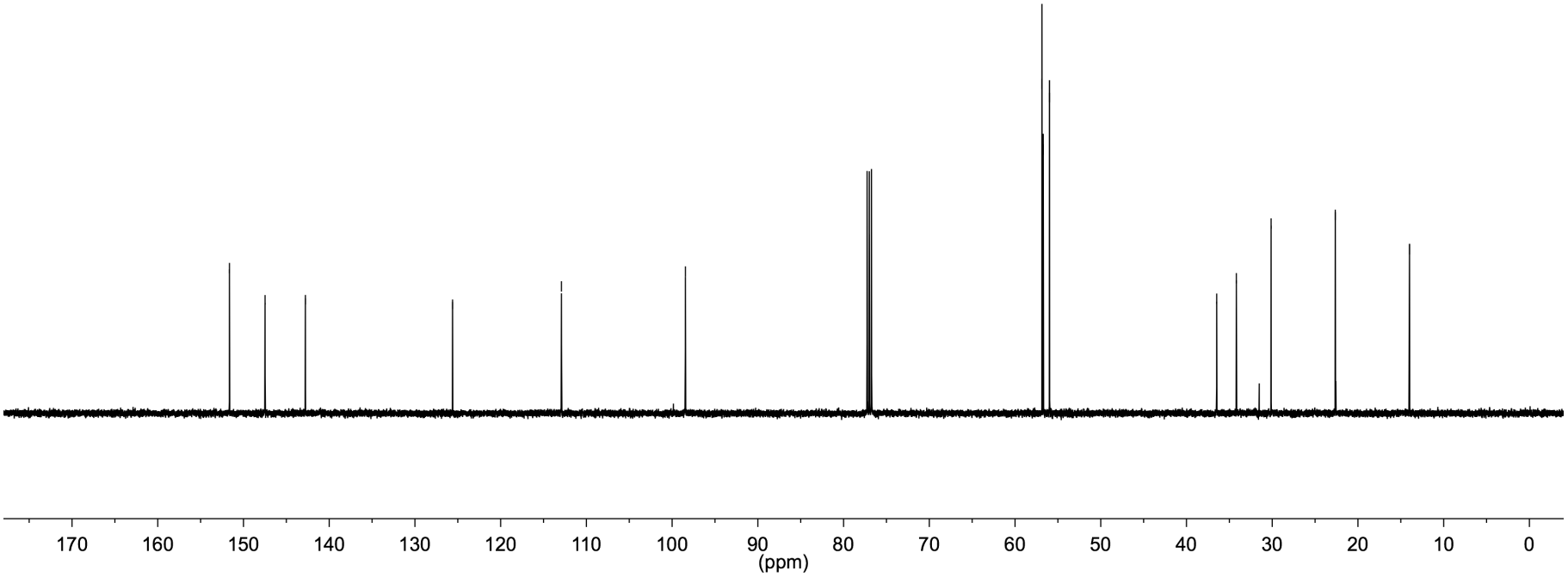

OMe
OMe
MeO
MeO
MeO
OMe
Me

6.7903
6.4961
4.5810
4.5653
4.5498
3.8491
3.7904
3.7384
1.9192
1.8731
1.3511
1.2907
1.2730
1.2275
0.8771
0.8629
0.8483
1.99
2.00
1.00
6.16
6.16
6.17
2.02
2.22
2.47
3.47
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
(ppm)

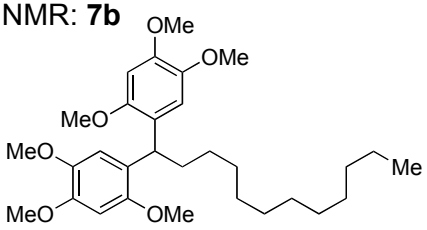
^{13}C NMR: **7a**



151.63
147.48
142.78
125.61
112.91
98.45
56.86
56.71
55.98
36.47
34.18
30.13
22.64
13.98

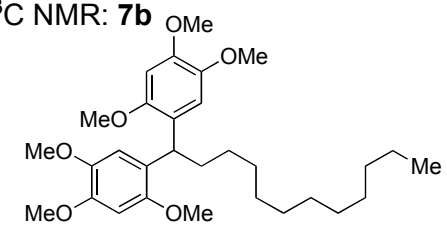


^{1}H NMR: **7b**


OMe
OMe
MeO
MeO
MeO
OMe
Me

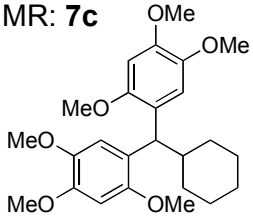
6.7795
6.6028
4.5254
4.5097
4.4940
3.7382
3.6990
3.6413
1.8654
1.7815
1.2659
1.1203
0.8531
0.8394
0.8253
1.99
1.98
1.00
6.30
6.20
6.08
1.96
18.37
3.15
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
(ppm)

^{13}C NMR: **7b**


OMe
OMe
MeO
MeO
MeO
OMe
Me

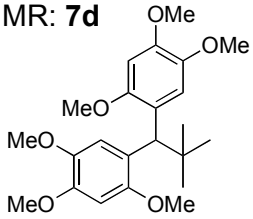
151.28
147.56
142.41
124.54
113.55
98.88
56.57
56.44
55.73
35.25
33.97
31.29
29.00
28.97
28.85
28.81
28.71
27.48
22.09
13.93
29.00
28.97
28.85
28.81
28.71
9.2 29.1 29.1 29.0 29.0 28.9 28.9 28.8 28.8 28.7 28.7 28.6 28.6
(ppm)
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
(ppm)

^{1}H NMR: **7c**


OMe
OMe
MeO
MeO
MeO
OMe

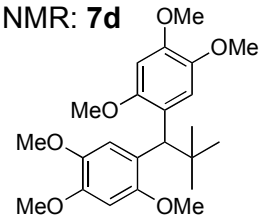
6.9264
6.4621
4.2939
4.2713
3.8242
3.8179
3.7598
2.1120
2.0396
1.6970
1.5358
1.2082
1.0952
0.9341
0.8678
2.02
2.05
1.00
12.22
6.24
0.99
5.65
3.13
2.23
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
(ppm)

^{1}H NMR: **7d**

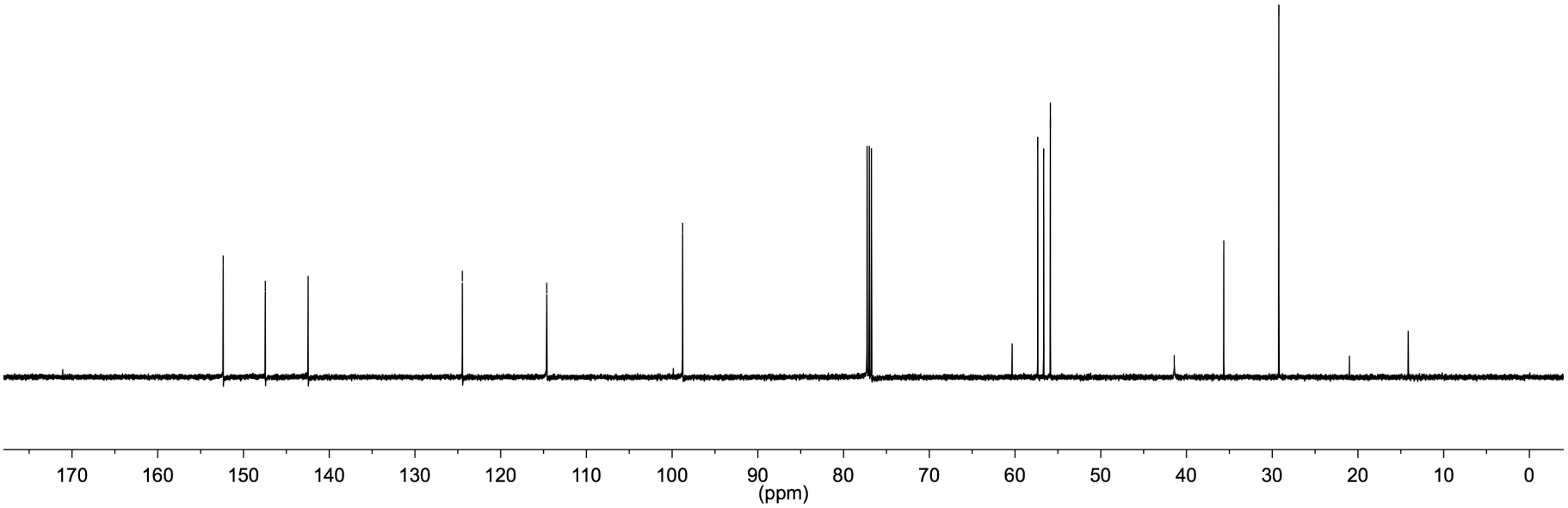

OMe
OMe
MeO
MeO
MeO
OMe

7.1484
6.4970
4.9989
3.8393
3.8267
3.7596
1.0244
2.07
2.08
1.00
12.74
6.36
9.65
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
(ppm)

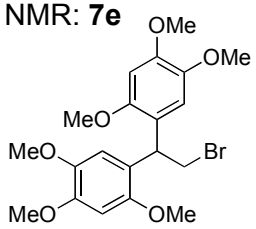
^{13}C NMR: **7d**



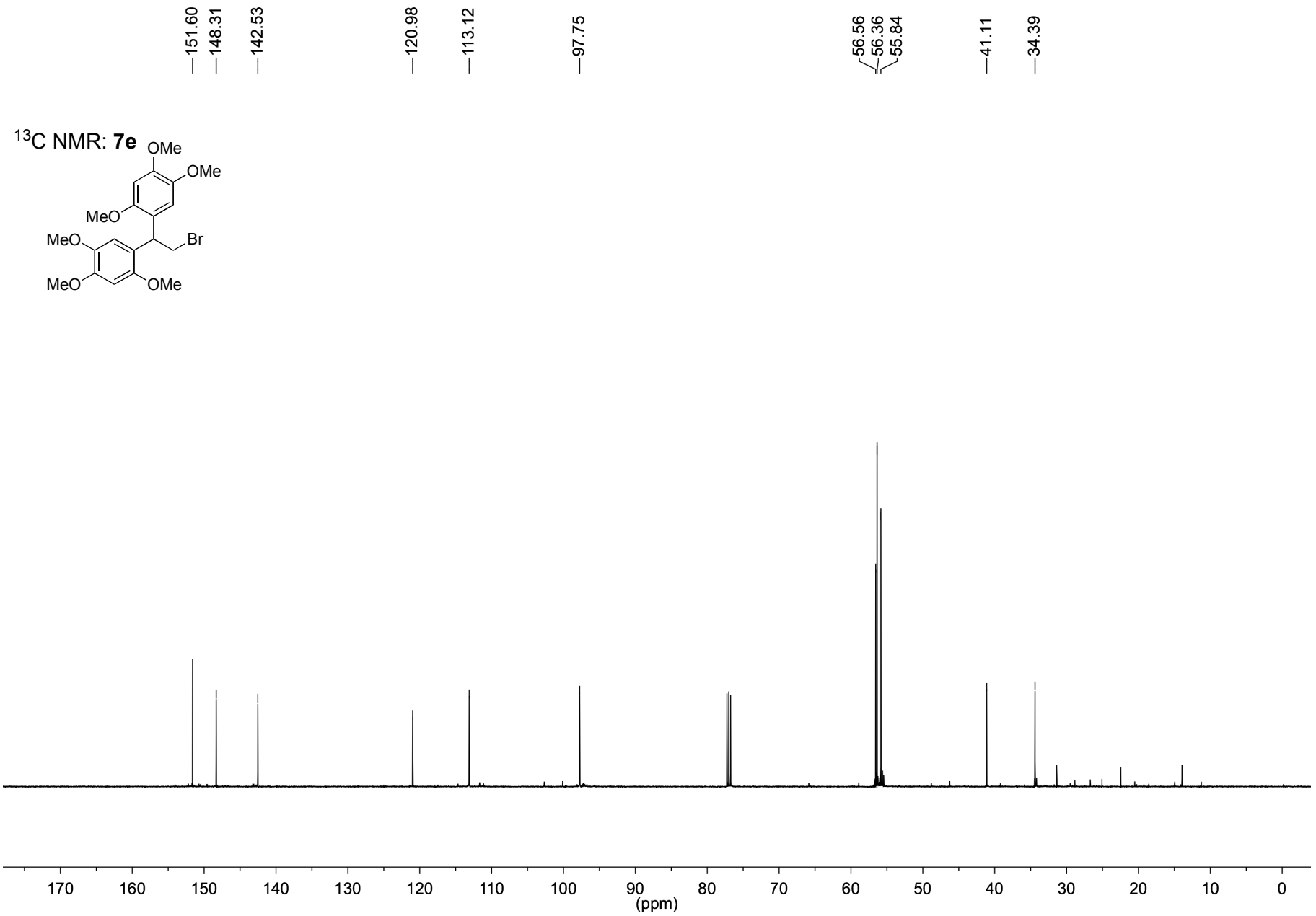
152.37
147.45
142.46
124.47
114.62
98.77
57.36
56.66
55.88
41.43
35.65
29.23



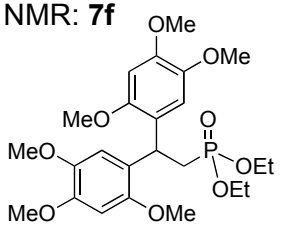
^{1}H NMR: **7e**


OMe
OMe
MeO
MeO
Br
MeO
OMe

6.7303
6.5065
4.9382
4.9221
4.9060
3.9032
3.8872
3.8470
3.7686
3.7600
2.04
2.14
1.00
2.12
6.10
12.02
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
(ppm)


151.60
148.31
142.53
120.98
113.12
97.75
56.56
56.36
55.84
41.11
34.39
13C NMR: 7e
OMe
OMe
MeO
MeO
Br
MeO
OMe
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
(ppm)

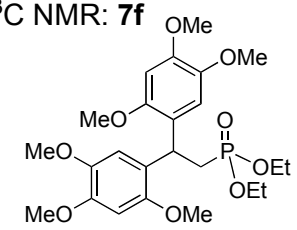
^{1}H NMR: **7f**

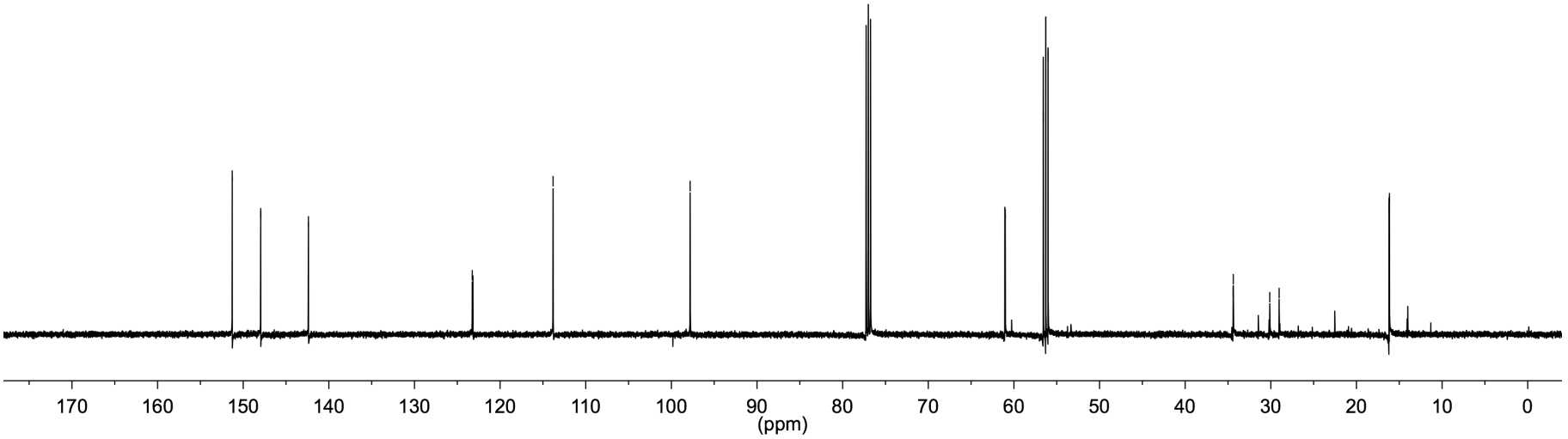

OMe
OMe
MeO
O
P
OEt
OEt
MeO
MeO
OMe

6.8717
6.4467
5.2642
4.8566
4.8414
4.8328
4.8260
4.8175
4.8022
3.8197
3.7829
3.7412
2.6301
2.6149
2.5942
2.5790
1.1338
1.1197
1.1056
2.03
1.97
1.00
2.17
5.97
8.22
6.06
1.98
6.32
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
(ppm)

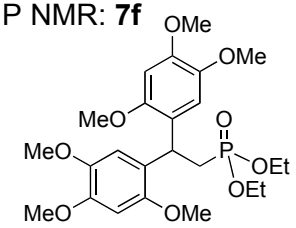
151.28
147.96
142.38
123.25
123.17
113.82
97.81
61.06
61.01
56.58
56.28
56.01
34.40
34.38
30.13
29.03
16.20
16.15

^{13}C NMR: **7f**



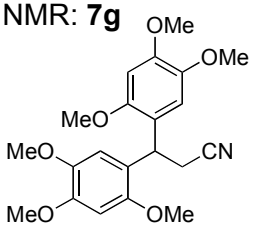


^{31}P NMR: **7f**

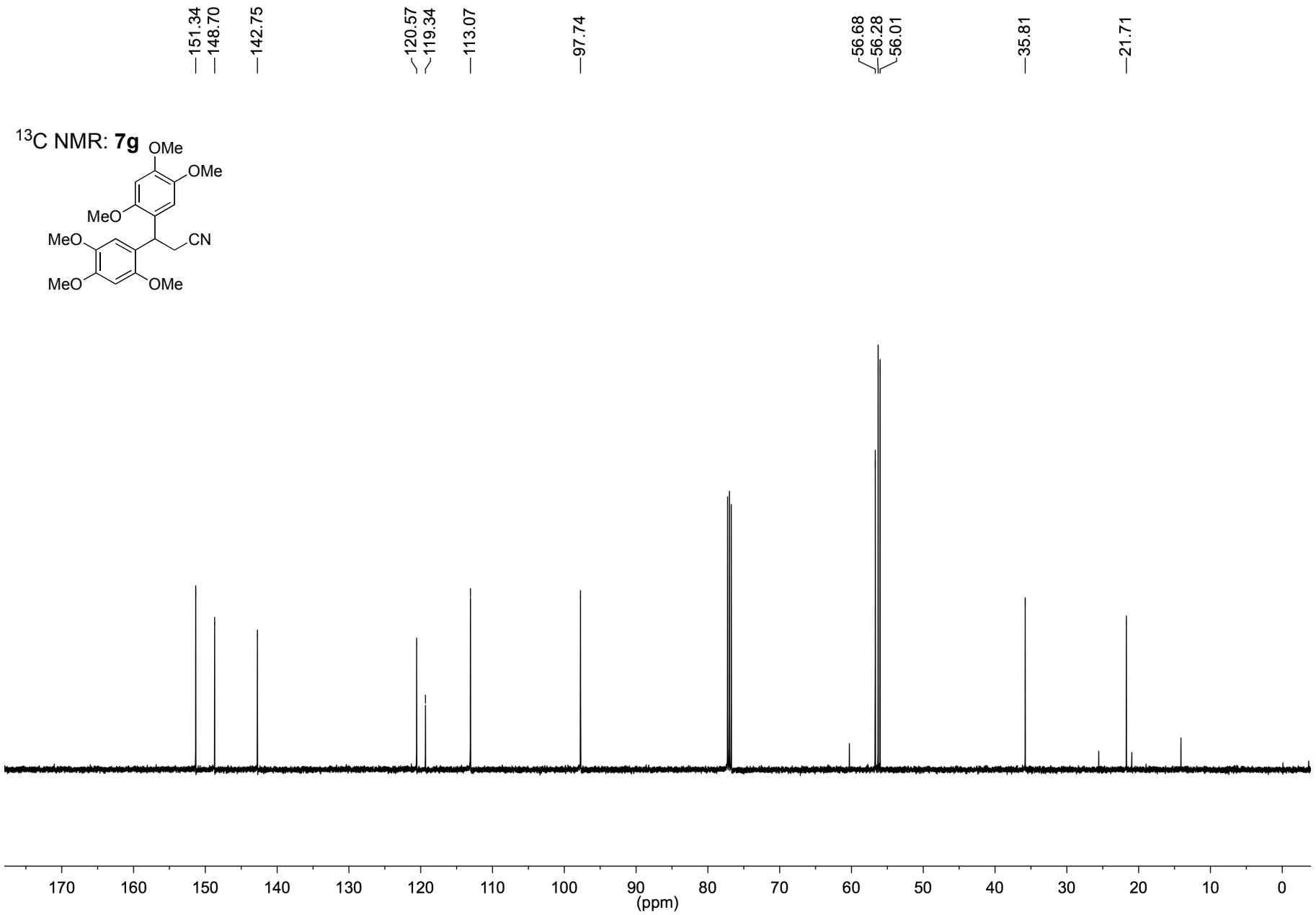

OMe
OMe
MeO
O
P
OEt
OEt
MeO
MeO
OMe

31.33
400
350
300
250
200
150
100
50
0
(ppm)
-50
-100
-150
-200
-250
-300
-350
-400

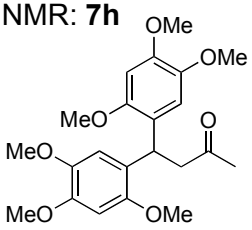
^{1}H NMR: **7g**


OMe
OMe
MeO
MeO
CN
MeO
OMe

6.7285
6.5204
4.8822
4.8668
4.8514
3.8666
3.7898
3.7640
3.0549
3.0394
1.97
1.97
1.00
6.05
6.19
6.25
2.03
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
(ppm)


151.34
148.70
142.75
120.57
119.34
113.07
97.74
56.68
56.28
56.01
35.81
21.71
13C NMR: 7g
OMe
OMe
MeO
MeO
CN
MeO
OMe
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
(ppm)

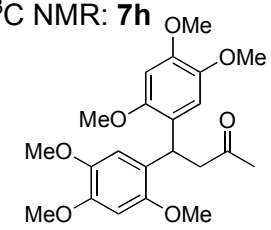
^{1}H NMR: **7h**

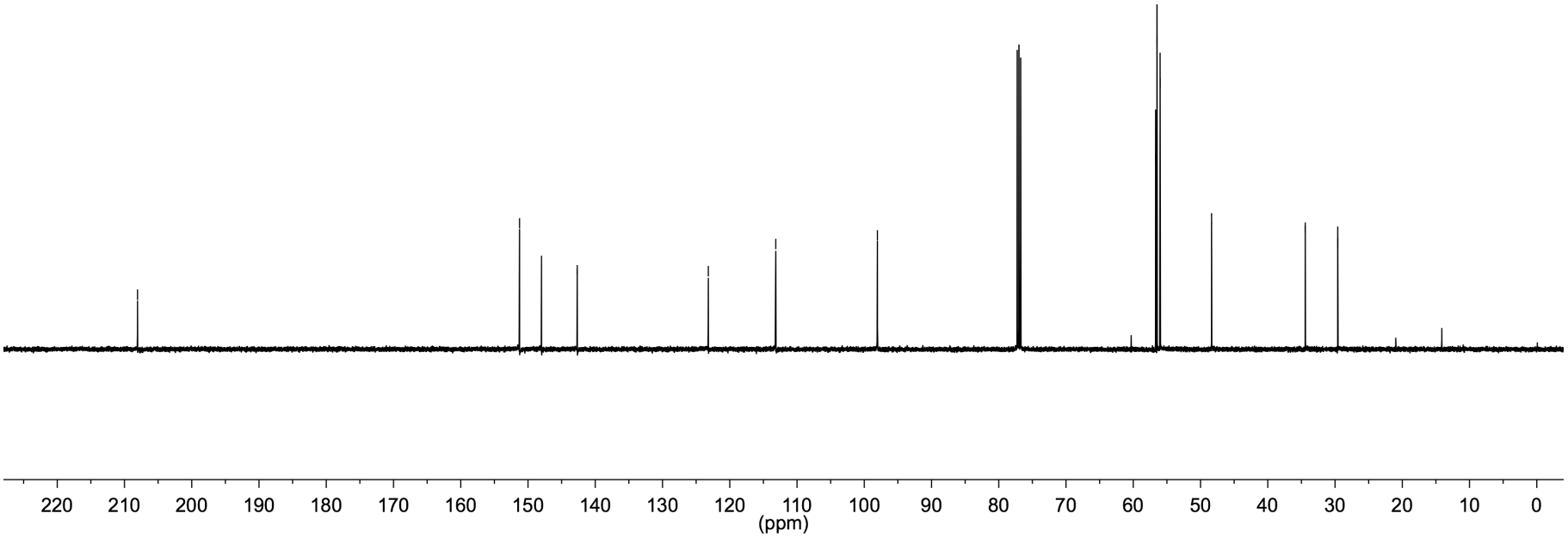

OMe
OMe
MeO
O
MeO
MeO
OMe

6.7147
6.4879
5.0722
5.0565
5.0407
3.8446
3.7585
3.0792
3.0635
2.0804
1.99
1.99
1.00
6.00
12.07
2.04
3.01
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
(ppm)

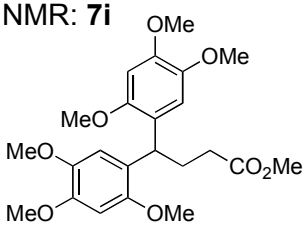
208.06
151.26
147.99
142.67
123.19
113.16
98.05
56.68
56.47
56.01
48.36
34.42
29.60

^{13}C NMR: **7h**

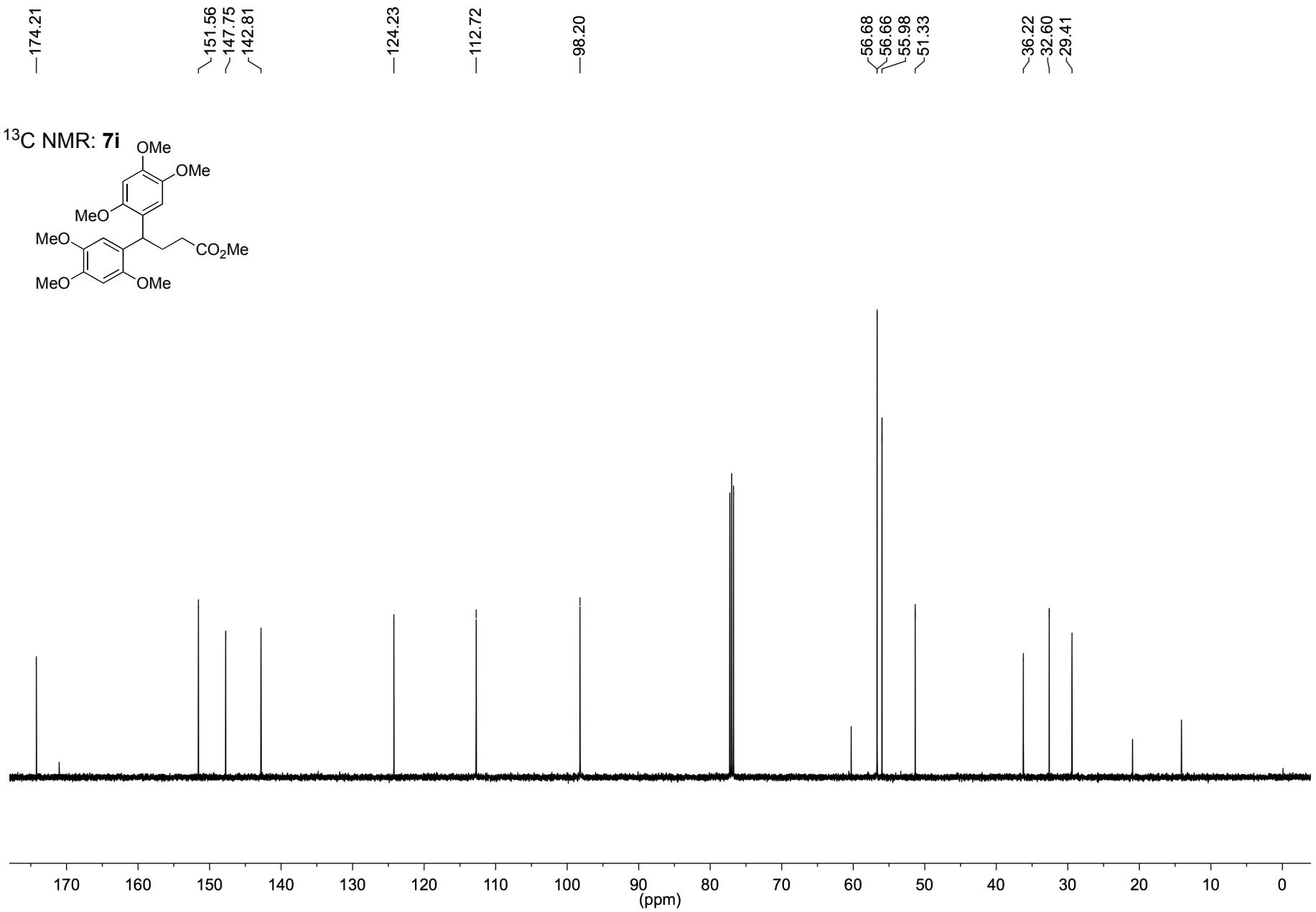




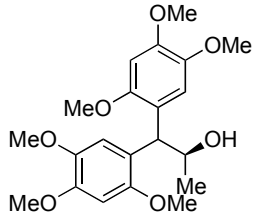
^{1}H NMR: **7i**


OMe
OMe
MeO
MeO
CO2Me
MeO
OMe

6.7802
6.4763
4.5650
4.5500
4.5353
3.8377
3.7769
3.7221
3.6076
2.2965
2.2139
2.05
2.06
1.00
5.93
6.19
6.29
3.12
4.10
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
(ppm)

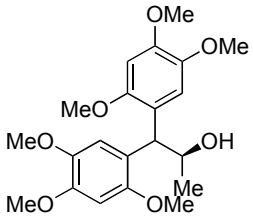

174.21
151.56
147.75
142.81
124.23
112.72
98.20
56.68
56.66
55.98
51.33
36.22
32.60
29.41
13C NMR: 7i
OMe
OMe
MeO
MeO
CO2Me
MeO
OMe
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
(ppm)

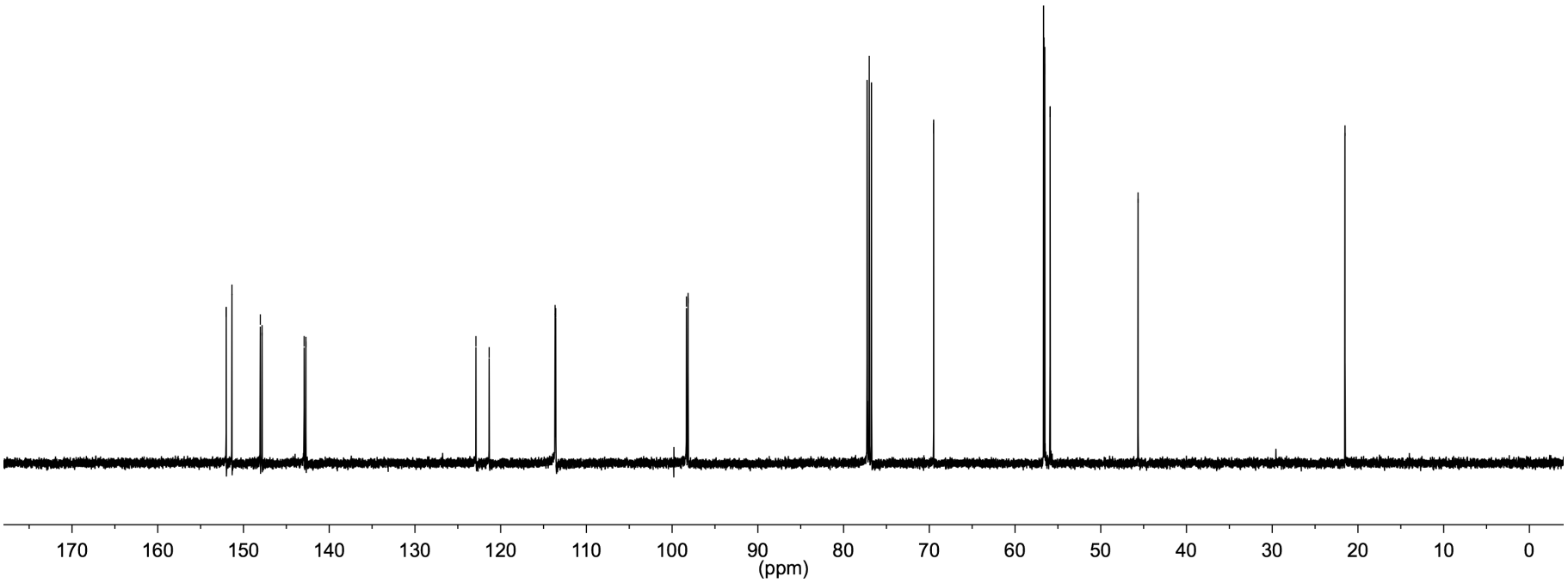
^{1}H NMR: **Tatarinoid C**



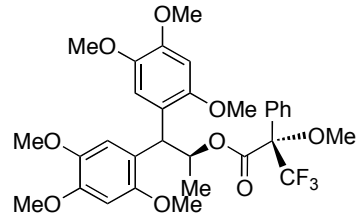
152.01
151.34
148.03
147.82
142.92
142.72
122.89
121.34
113.65
113.58
98.32
98.14
69.49
56.67
56.62
56.54
56.53
55.91
55.90
45.65
21.51

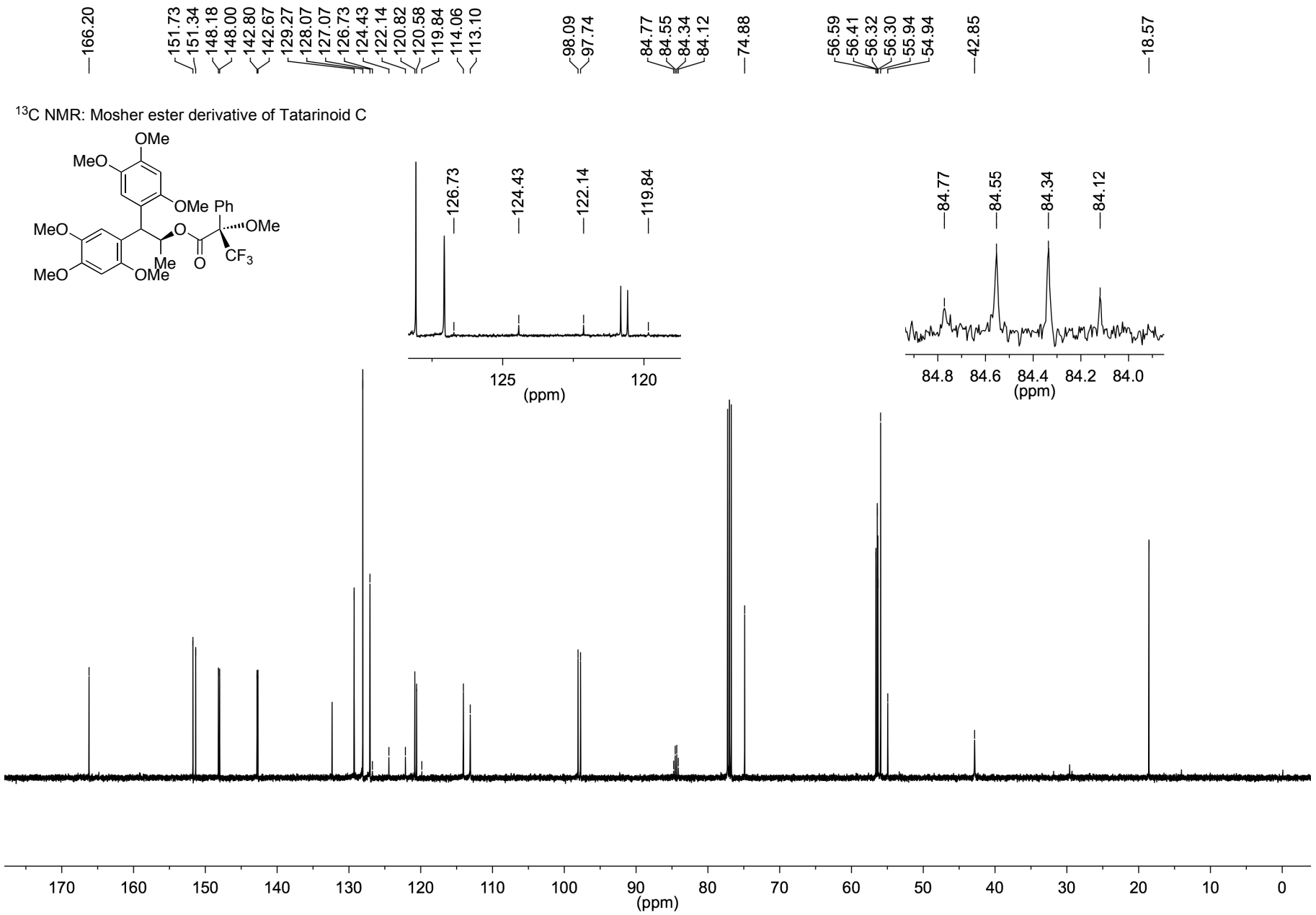
^{13}C NMR: **Tatarinoid C**



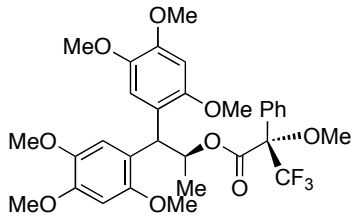


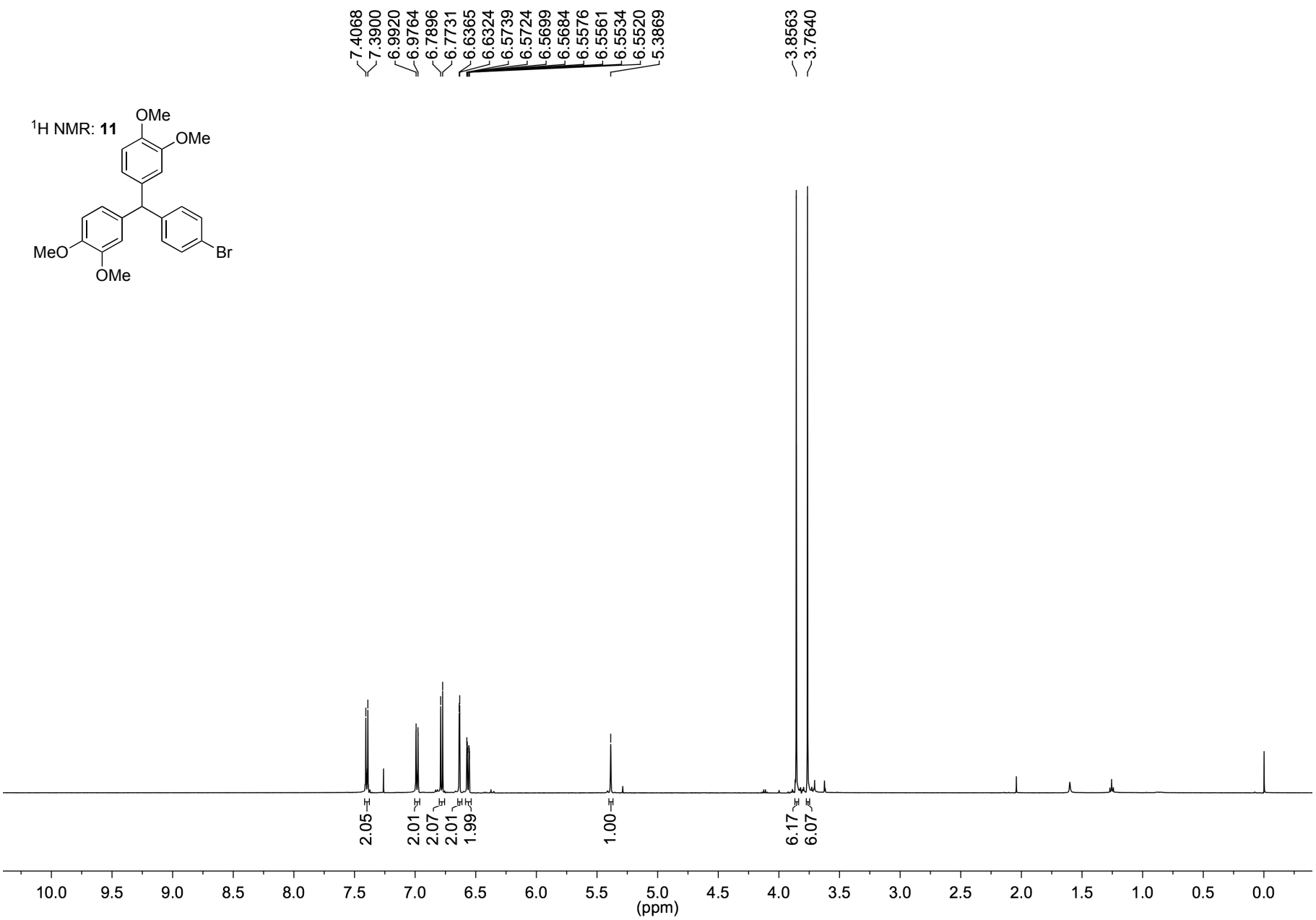
^{1}H NMR: Mosher ester derivative of Tatarinoid C

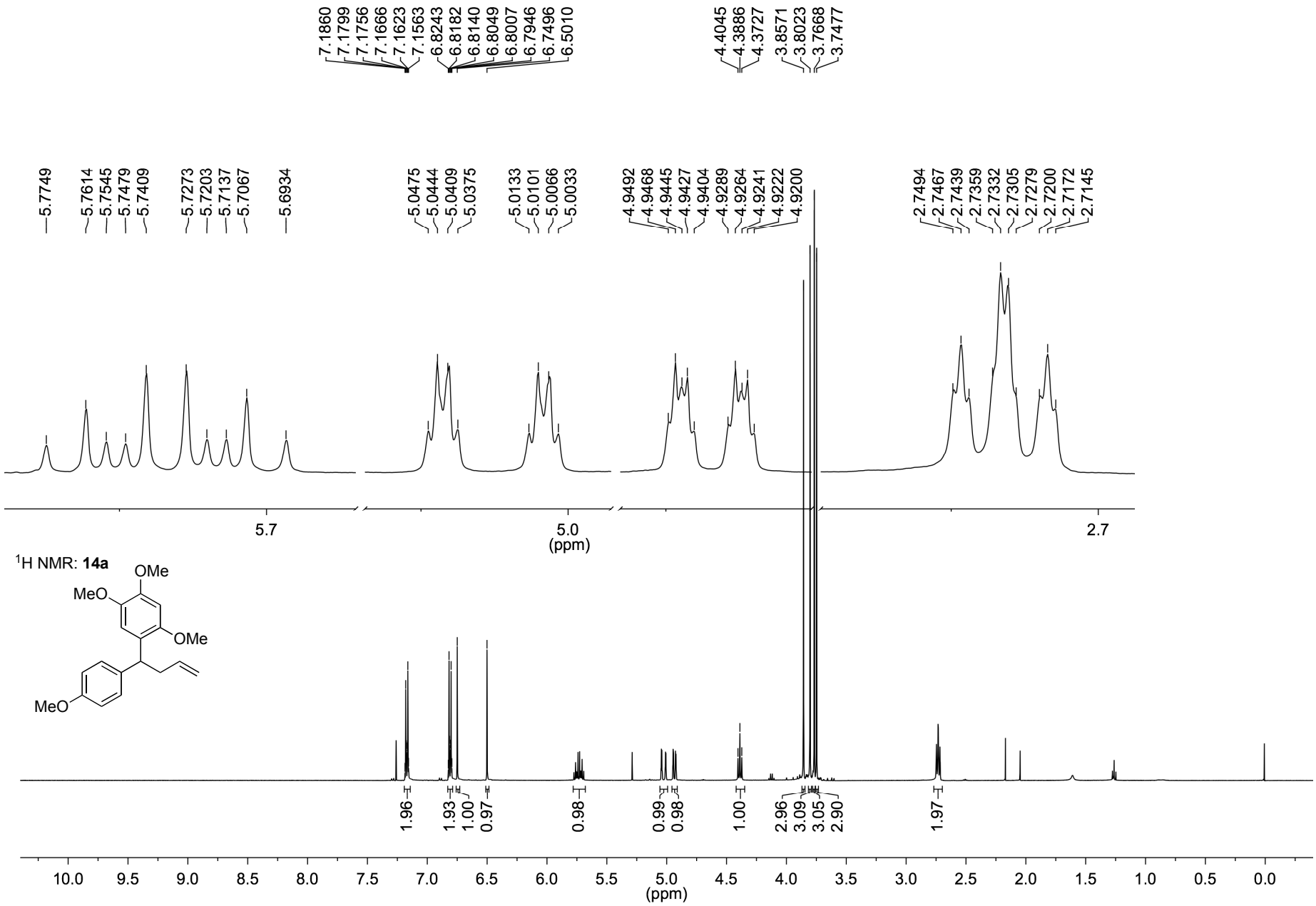


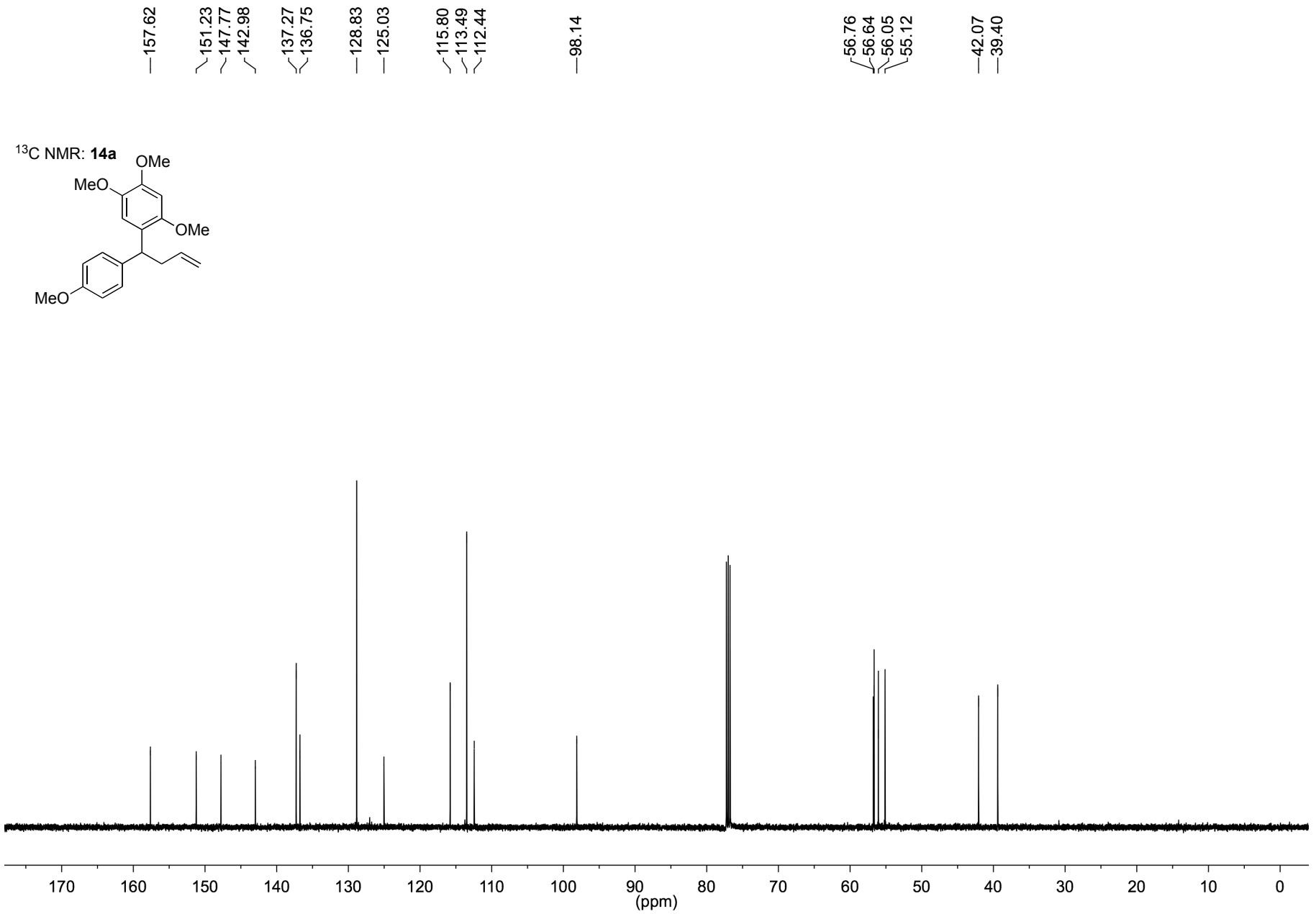

166.20
151.73
151.34
148.18
148.00
142.80
142.67
129.27
128.07
127.07
126.73
124.43
122.14
120.82
120.58
119.84
114.06
113.10
98.09
97.74
84.77
84.55
84.34
84.12
74.88
56.59
56.41
56.32
56.30
55.94
54.94
42.85
18.57
13C NMR: Mosher ester derivative of Tatarinoid C
OMe
MeO
OMe
Ph
MeO
O
OMe
Me
O
CF3
MeO
OMe
126.73
124.43
122.14
119.84
125
120
(ppm)
84.77
84.55
84.34
84.12
84.8
84.6
84.4
84.2
84.0
(ppm)
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
(ppm)

^{19}F NMR: Mosher ester derivative of Tatarinoid C

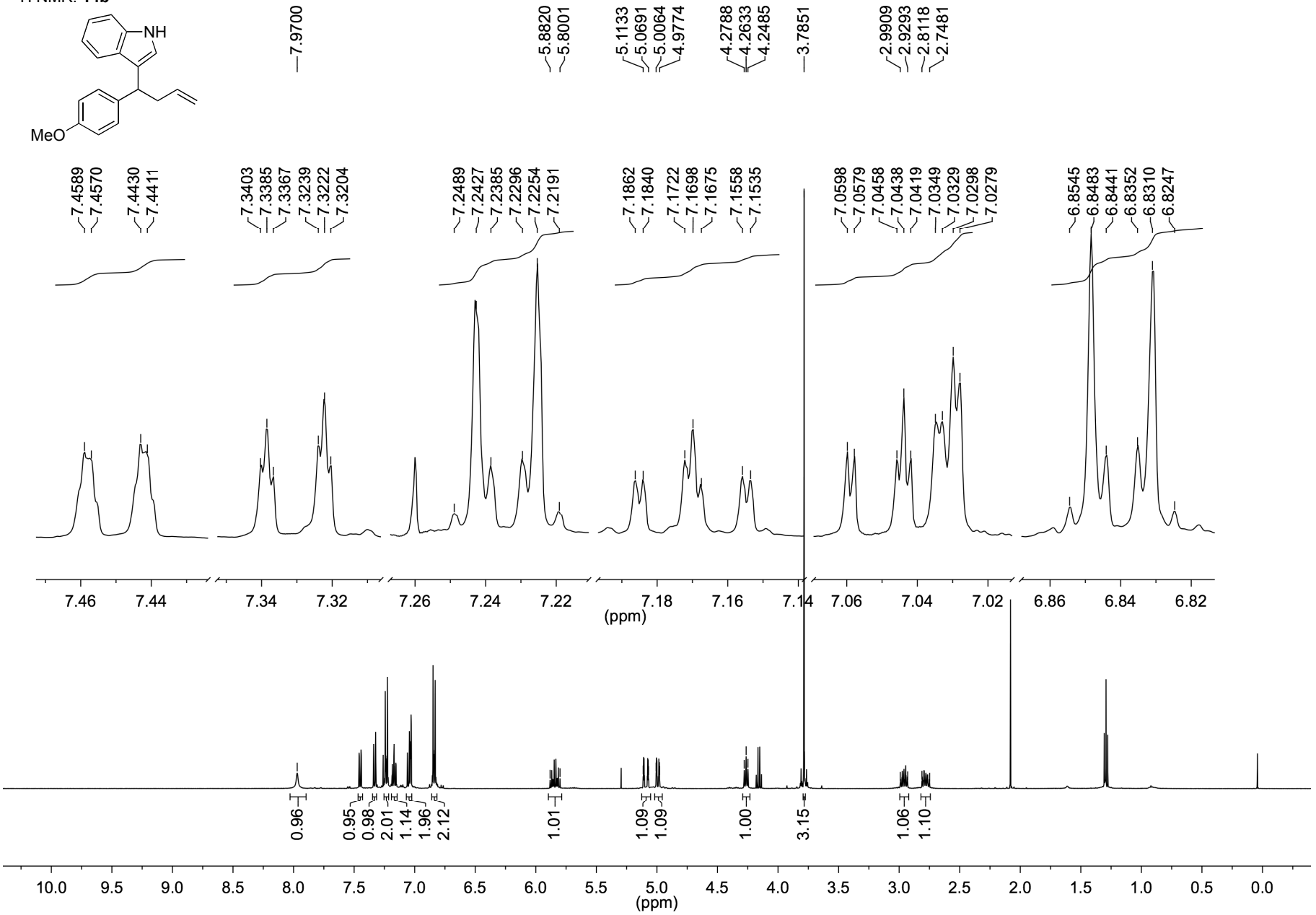


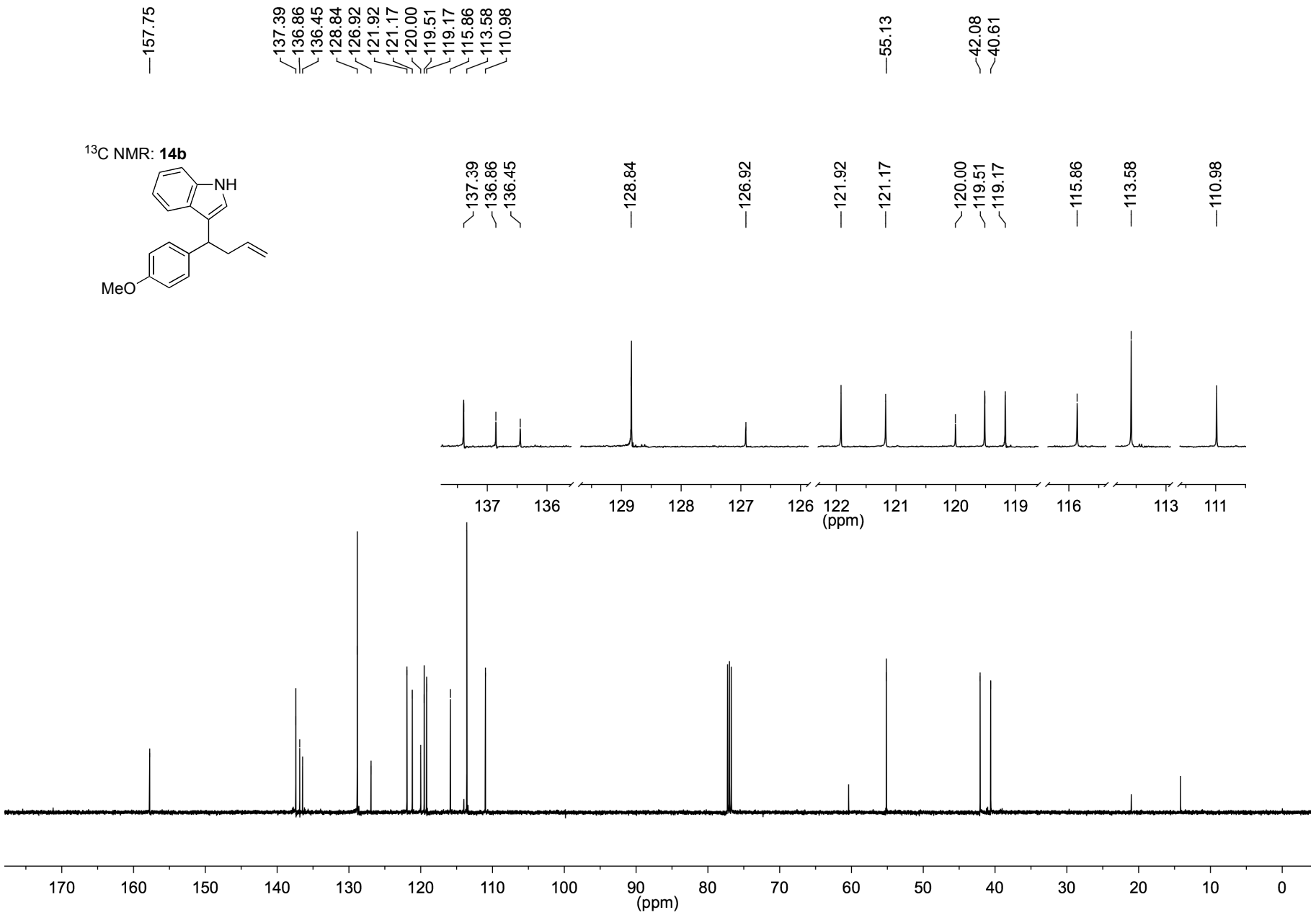

7.4068
7.3900
6.9920
6.9764
6.7896
6.7731
6.6365
6.6324
6.5739
6.5724
6.5699
6.5684
6.5576
6.5561
6.5534
6.5520
5.3869
3.8563
3.7640
1H NMR: 11
OMe
OMe
MeO
OMe
Br
2.05
2.01
2.07
2.01
1.99
1.00
6.17
6.07
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
(ppm)


7.1860
7.1799
7.1756
7.1666
7.1623
7.1563
6.8243
6.8182
6.8140
6.8049
6.8007
6.7946
6.7496
6.5010
4.4045
4.3886
4.3727
3.8571
3.8023
3.7668
3.7477
5.7749
5.7614
5.7545
5.7479
5.7409
5.7273
5.7203
5.7137
5.7067
5.6934
5.0475
5.0444
5.0409
5.0375
5.0133
5.0101
5.0066
5.0033
4.9492
4.9468
4.9445
4.9427
4.9404
4.9289
4.9264
4.9241
4.9222
4.9200
2.7494
2.7467
2.7439
2.7359
2.7332
2.7305
2.7279
2.7200
2.7172
2.7145
5.7
5.0
2.7
(ppm)
1H NMR: 14a
OMe
MeO
OMe
MeO
1.96
1.93
1.00
0.97
0.98
0.99
0.98
1.00
2.96
3.09
3.05
2.90
1.97
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
(ppm)

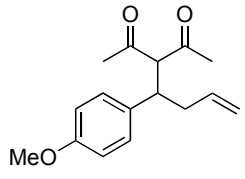

157.62
151.23
147.77
142.98
137.27
136.75
128.83
125.03
115.80
113.49
112.44
98.14
56.76
56.64
56.05
55.12
42.07
39.40
13C NMR: 14a
OMe
MeO
OMe
MeO
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
(ppm)

^{1}H NMR: **14b**

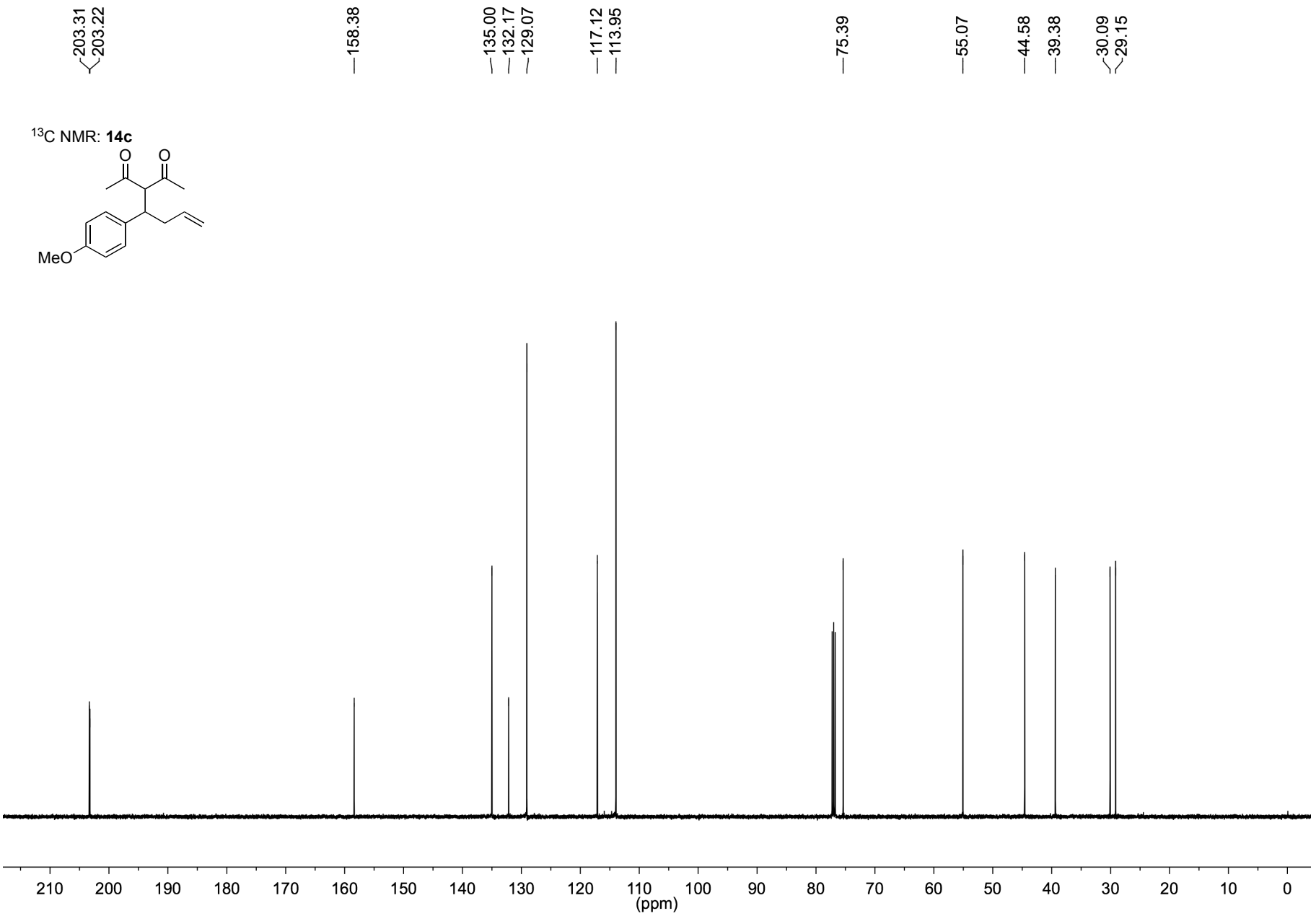

NH
MeO
7.9700
5.8820
5.8001
5.1133
5.0691
5.0064
4.9774
4.2788
4.2633
4.2485
3.7851
2.9909
2.9293
2.8118
2.7481
7.4589
7.4570
7.4430
7.4411
7.3403
7.3385
7.3367
7.3239
7.3222
7.3204
7.2489
7.2427
7.2385
7.2296
7.2254
7.2191
7.1862
7.1840
7.1722
7.1698
7.1675
7.1558
7.1535
7.0598
7.0579
7.0458
7.0438
7.0419
7.0349
7.0329
7.0298
7.0279
6.8545
6.8483
6.8441
6.8352
6.8310
6.8247
(ppm)
0.96
0.95
0.98
2.01
1.14
1.96
2.12
1.01
1.09
1.09
1.00
3.15
1.06
1.10
(ppm)


157.75
137.39
136.86
136.45
128.84
126.92
121.92
121.17
120.00
119.51
119.17
115.86
113.58
110.98
55.13
42.08
40.61
13C NMR: 14b
NH
MeO
(ppm)
(ppm)

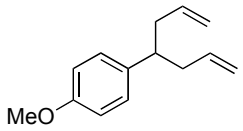
^{1}H NMR: **14c**


O
O
MeO

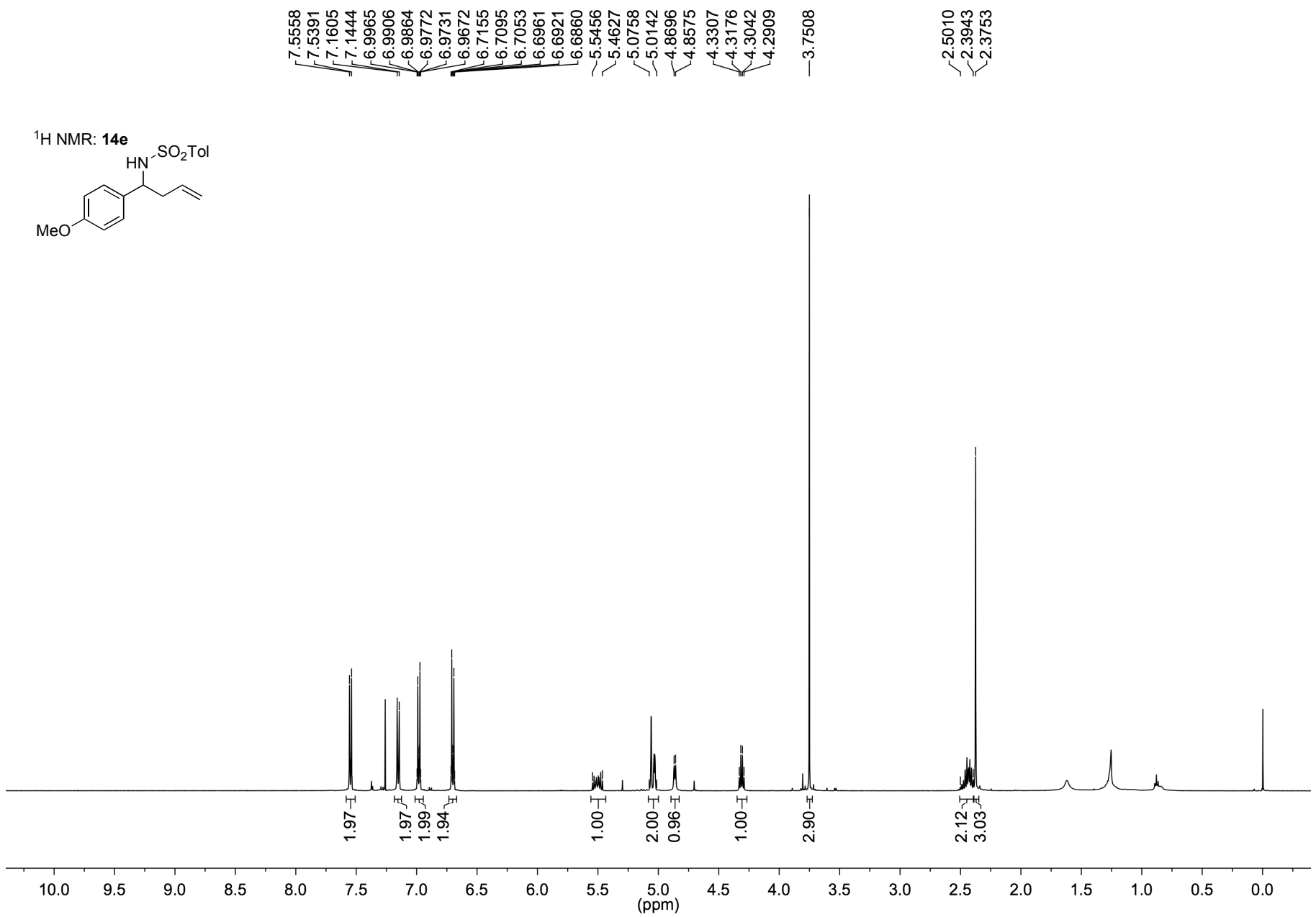
7.0588
7.0529
7.0487
7.0396
7.0355
7.0295
6.8130
6.8070
6.8028
6.7937
6.7896
6.7835
5.5304
5.4478
4.9151
4.8565
4.0960
4.0731
3.7472
3.5469
3.4963
2.2681
2.2444
2.1976
1.7986
7.08
7.06
7.04
7.02
6.84
6.82
6.80
6.78
6.76
(ppm)
2.02
2.01
0.99
2.02
0.99
3.05
1.00
4.97
2.92
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
(ppm)


203.31
203.22
158.38
135.00
132.17
129.07
117.12
113.95
75.39
55.07
44.58
39.38
30.09
29.15
^{13}C NMR: **14c**
O
O
MeO
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
(ppm)

^{1}H NMR: **14d**


MeO

7.1092
7.0884
6.8738
6.8530
5.7406
5.6374
5.0183
4.9414
3.8056
2.7355
2.6635
2.4578
2.3020
2.08
2.17
2.09
4.33
3.06
1.00
4.09
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
(ppm)


7.5558
7.5391
7.1605
7.1444
6.9965
6.9906
6.9864
6.9772
6.9731
6.9672
6.7155
6.7095
6.7053
6.6961
6.6921
6.6860
5.5456
5.4627
5.0758
5.0142
4.8696
4.8575
4.3307
4.3176
4.3042
4.2909
3.7508
2.5010
2.3943
2.3753
1H NMR: 14e
HN
SO2Tol
MeO
1.97
1.97
1.99
1.94
1.00
2.00
0.96
1.00
2.90
2.12
3.03
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
(ppm)