Electronic Supplementary Information

Gold(I)-catalyzed diastereoselective synthesis of 1-α-oxybenzyl-1*H*-indenes

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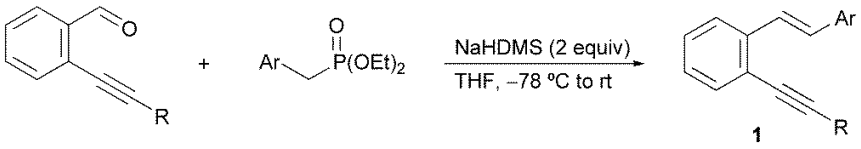
Contents:

General methods:

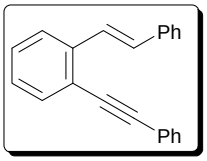
All reactions involving air-sensitive compounds were carried out under a N_2 atmosphere in oven-dried glassware with magnetic stirring. Temperatures are reported as bath temperatures. Solvents used for extraction and purification were distilled prior to use. TLC was performed on alumina-backed plates coated with silica gel 60 with F254 indicator; the chromatograms were visualized by UV light (254 nm) and/or by staining with a Ce/Mo reagent solution and subsequent heating. R_f values refer to silica gel. Flash column chromatography was carried out on silica gel 60, 230-400 mesh. ^{1}H NMR spectra were recorded at 300 or 400 MHz. Chemical shifts are reported in ppm with the residual solvent resonance as the internal standard ($CHCl_3$: δ 7.26). Data are reported as follows: chemical shift, multiplicity (s: singlet, bs: broad singlet, d: doublet, dd: doublet of doublets, ddd: doublet of doublet of doublets, td: triplet of doublets, t: triplet, dq: doublet of quartets, sex: sextet, sep: septet, m: multiplet), coupling constants (J in Hz) and integration. ^{13}C NMR spectra were recorded at 75.4 or 100.6 MHz using broadband proton decoupling. Chemical shifts are reported in ppm with the solvent resonance as internal standard ($CDCl_3$: δ 77.16). Carbon multiplicities were assigned by DEPT techniques. Gas chromatography–mass spectra (GC-MS) were recorded on an instrument equipped with a 30 m × 0.25 mm capillary apolar column (stationary phase: 5% diphenyldimethylpolysiloxane film, 0.25 μm). Low-resolution electron impact mass spectra (EI-LRMS) were obtained at 70 eV and only the molecular ions and/or base peaks as well as significant peaks in MS are given. High-resolution mass spectra (HRMS) were recorded on an instrument equipped with a magnetic sector ion analyzer using EI at 70 eV or on an instrument equipped with a QTOF analyzer using ESI (+). Melting points were measured on a microscopic apparatus using open capillary tubes and are uncorrected. All commercially available reagents were used without purification unless otherwise indicated and were purchased from standard chemical suppliers.

Synthesis and characterization data of *o*-(alkynyl)styrenes 1:

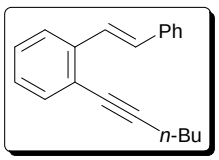


NaHMDS (10 mmol, 10 mL, 1 M in hexanes, 2 equiv) was added to a solution of the appropriate diethyl phosphonate (10 mmol, 2.0 mL, 2 equiv) in THF (20 mL) at −78 ºC and the resulting

mixture was stirred for 30 min at rt.[1] After cooling to −50 ºC, the corresponding 2-alkynylbenzaldehyde derivative[2] (5 mmol) was added to the solution, and the reaction was stirred at rt until the aldehyde was consumed as determined by GC-MS (overnight). The crude was partitioned between aqueous NH_4Cl / CH_2Cl_2 and the aqueous layer further extracted with CH_2Cl_2 (2 × 20 mL). The organic phase was dried over anhydrous Na_2SO_4 and the solvents were removed under reduce pressure. The residue was purified by flash column chromatography using a mixture of hexane/EtOAc as eluent to obtain the corresponding *o*-(alkynyl)styrene **1** as almost pure *E*-isomers. For the synthesis of selected *Z*-isomers of *o*-(alkynyl)styrenes **1**, standard Wittig reactions were carried out and the obtained crudes were carefully purified by column chromatography (yields not reported).

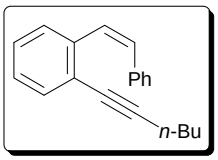


(*E*)-1-(Phenylethynyl)-2-styrylbenzene (1a): yellow oil; R_f = 0.11 (hex/EtOAc, 100/1); 88% yield; isolated as a > 20:1 mixture of *E*:*Z* isomers; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.81–7.59 (m, 2H), 7.43–7.41 (m, 4H), 7.40–7.23 (m, 10H) ppm; $^{13}C\{^1H\}$ NMR (75.4 MHz, $CDCl_3$) δ 138.8 (C), 137.5 (C), 132.9 (CH), 131.7 (2 × CH), 130.5 (CH), 128.9 (2 × CH), 128.7 (2 × CH), 128.6 (CH), 128.5 (CH), 128.0 (CH), 127.4 (CH), 126.9 (2 × CH), 124.9 (CH), 123.5 (C), 122.3 (C), 94.5 (C), 88.1 (C) ppm, one aromatic CH signal does not appear due to overlapping; LRMS (EI) *m/z* (%) 280 (M^+, 100), 202 (82); HRMS (ESI) calcd for $C_{22}H_{17}^+$ [$(M+H)^+$] 281.1325, found 281.1332.

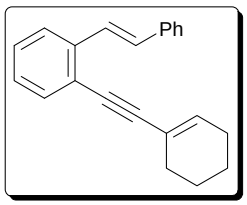


(*E*)-1-(Hex-1-yn-1-yl)-2-styrylbenzene (*E*-1b): yellow oil; R_f = 0.45 (hex/EtOAc, 100/1); 62% yield; isolated as a > 20:1 mixture of *E*/*Z* isomers; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.95 (d, *J* = 16.2 Hz, 1H), 7.87–7.84 (m, 1H), 7.78–7.75 (m, 2H), 7.69–7.66 (m, 1H), 7.59–7.54 (m, 2H), 7.49–7.33 (m, 4H), 2.71 (t, *J* = 6.8 Hz, 2H), 1.86–1.78 (m, 4H), 1.20 (t, *J* = 7.2 Hz, 3H) ppm; $^{13}C\{^1H\}$ NMR (75.4 MHz, $CDCl_3$) δ 138.6 (C), 137.6 (C), 132.7 (CH), 129.8 (CH), 128.8 (2 × CH), 127.82 (CH), 127.79 (CH), 127.24 (CH), 127.18 (CH), 126.8 (2 × CH), 124.6 (CH), 123.3 (C), 95.7 (C), 79.2 (C), 31.0 (CH_2), 22.2 (CH_2), 19.5 (CH_2), 13.8 (CH_3) ppm; LRMS (EI) *m/z* (%) 260 (M^+, 28), 215 (100); HRMS (ESI) calcd for $C_{20}H_{21}^+$ [$(M+H)^+$] 261.1638, found 261.1633.

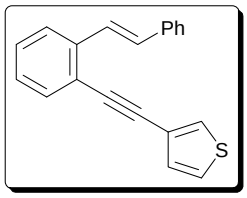
[1] K. Bera and C. Schneider, *Chem. Eur. J.,* 2016, **22**, 7074–7078.
[2] A. M. Sanjuán, M. A. Rashid, P. García-García, A. Martínez-Cuezva, M. A. Fernández-Rodríguez, F. Rodríguez and R. Sanz, *Chem. Eur. J.,* 2015, **21**, 3042–3052.



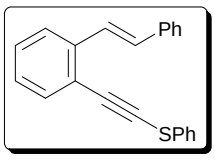
(*Z*)-1-(Hex-1-yn-1-yl)-2-styrylbenzene (*Z*-1b): yellow oil; R_f = 0.23 (hex/EtOAc, 100/1); isolated as a > 20:1 mixture of *Z:E* isomers; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.42 (d, J = 7.6 Hz, 1H), 7.21–7.70 (m, 8H), 6.83 (d, J = 12.3 Hz, 1H), 6.65 (d, J = 12.3 Hz, 1H), 2.44 (t, J = 6.9 Hz, 2H), 1.59–1.57 (m, 2H), 1.57–1.50 (m, 2H), 0.95 (t, J = 7.2 Hz, 3H) ppm; ^{13}C{^{1}H} NMR (75.4 MHz, $CDCl_3$) δ 139.3 (C), 137.2 (C), 132.4 (CH), 130.7 (CH), 129.4 (CH), 129.1 (2 × CH), 129.0 (CH), 128.2 (2 × CH), 127.2 (CH), 127.1 (CH), 127.0 (CH), 123.9 (C), 95.4 (C), 79.4 (C), 31.0 (CH_2), 22.1 (CH_2), 19.4 (CH_2), 13.8 (CH_3) ppm; LRMS (EI) *m/z* (%) 260 (M^+, 28), 215 (100).



(*E*)-1-(Cyclohex-1-en-1-ylethynyl)-2-styrylbenzene (1c): yellow oil; R_f = 0.17 (hex/EtOAc, 50/1); 70% yield; isolated as a > 20:1 mixture of *E:Z* isomers; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.78–7.23 (m, 11H), 6.37–7.35 (m, 1H), 2.40–2.27 (m, 2H), 2.26–2.25 (m, 2H), 1.81–1.72 (m, 4H) ppm; ^{13}C{^{1}H} NMR (75.4 MHz, $CDCl_3$) δ 138.4 (C), 137.6 (C), 135.2 (CH), 132.6 (CH), 130.0 (CH), 128.8 (2 × CH), 128.1 (CH), 127.8 (CH), 127.3 (CH), 127.1 (CH), 126.8 (2 × CH), 124.7 (CH), 122.8 (C), 121.0 (C), 96.6 (C), 85.5 (C), 29.4 (CH_2), 25.9 (CH_2), 22.5 (CH_2), 21.6 (CH_2) ppm; LRMS (EI) *m/z* (%) 284 (M^+, 91), 215 (100); HRMS (ESI) calcd for $C_{22}H_{21}^+$ [$(M+H)^+$] 285.1638, found 285.1640.

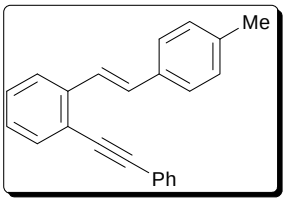


(*E*)-3-[(2-Styrylphenyl)ethynyl]thiophene (1d): brown oil; R_f = 0.27 (hex/EtOAc, 50/1); 88% yield; isolated as a > 20:1 mixture of *E:Z* isomers; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.76–7.71 (m, 2H), 7.61–7.56 (m, 4H), 7.43–7.22 (m, 8H) ppm; ^{13}C{^{1}H} NMR (75.4 MHz, $CDCl_3$) δ 138.8 (C), 137.5 (C), 132.7 (CH), 130.4 (CH), 129.9 (CH), 128.9 (2 × CH), 128.8 (CH), 128.7 (CH), 128.6 (CH), 128.0 (CH), 127.4 (CH), 126.8 (2 × CH), 125.6 (CH), 124.9 (CH), 122.5 (C), 122.2 (C), 89.6 (C), 87.6 (C) ppm; LRMS (EI) *m/z* (%) 286 (M^+, 86), 252 (100); HRMS (ESI) calcd for $C_{20}H_{15}S^+$ [$(M+H)^+$] 287.0889, found: 287.0887.

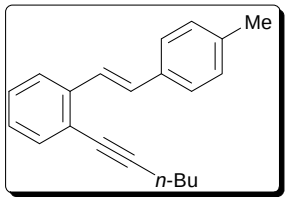


(*E*)-Phenyl[(2-styrylphenyl)ethynyl]sulfane (1e): yellow oil; R_f = 0.22 (hex/EtOAc, 50/1); 69% yield; isolated as a > 20:1 mixture of *E:Z* isomers; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.79–7.22 (m, 16H) ppm; ^{13}C{^{1}H} NMR (75.4 MHz, $CDCl_3$) δ 138.8 (C), 137.2 (C), 133.0 (C), 132.5 (CH), 130.7 (CH),

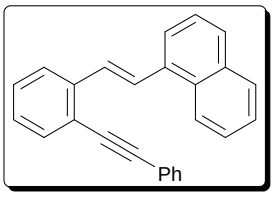
129.4 (2 × CH), 128.8 (2 × CH), 128.7 (CH), 128.0 (CH), 127.3 (CH), 126.9 (2 × CH), 126.7 (CH), 126.5 (CH), 126.4 (2 × CH), 124.8 (CH), 122.0 (C), 96.7 (C), 80.7 (C) ppm; LRMS (EI) *m/z* (%) 312 (M^+, 10), 234 (45), 203 (100).



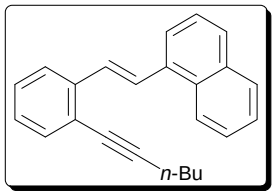
(*E*)-1-(4-Methylstyryl)-2-(phenylethynyl)benzene (1f): yellow oil; R_f = 0.25 (hex/EtOAc, 100/1); 77% yield; isolated as a > 20:1 mixture of *E:Z* isomers; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.82–7.77 (m, 2H), 7.69–7.54 (m, 3H), 7.57–7.54 (m, 2H), 7.47–7.44 (m, 4H), 7.33–7.26 (m, 4H), 2.45 (s, 3H) ppm; ^{13}C{^{1}H} NMR (75.4 MHz, $CDCl_3$) δ 139.0 (C), 137.9 (C), 134.7 (C), 132.8 (CH), 131.6 (2 × CH), 130.4 (CH), 129.6 (2 × CH), 128.7 (CH), 128.6 (2 × CH), 128.5 (CH), 127.2 (CH), 126.8 (2 × CH), 125.8 (CH), 124.8 (CH), 123.5 (C), 122.1 (C), 94.5 (C), 88.3 (C), 21.4 (CH_3) ppm; LRMS (EI) *m/z* (%) 294 (M^+, 100), 279 (88); HRMS (EI) calcd for $C_{23}H_{18}$ 294.1409, found 294.1410.



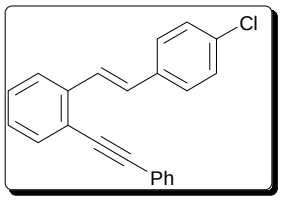
(*E*)-1-(Hex-1-yn-1-yl)-2-(4-methylstyryl)benzene (1g): yellow oil; R_f = 0.30 (hex/EtOAc, 100/1); 44% yield; isolated as a > 20:1 mixture of *E:Z* isomers; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.72–6.64 (m, 2H), 7.50–7.44 (m, 2H), 7.31–7.14 (m, 6H), 2.56 (d, J = 6.8 Hz, 2H), 2.41 (s, 3H), 1.71–1.59 (m, 4H), 1.03 (t, J = 7.2 Hz, 3H) ppm; ^{13}C{^{1}H} NMR (75.4 MHz, $CDCl_3$) δ 138.7 (C), 137.6 (C), 134.8 (C), 132.6 (CH), 129.7 (CH), 129.4 (2 × CH), 127.7 (CH), 127.0 (CH), 126.6 (2 × CH), 126.1 (CH), 124.4 (CH), 123.0 (C), 95.6 (C), 79.2 (C), 31.0 (CH_2), 22.2 (CH_2), 21.3 (CH_2), 19.4 (CH_3), 13.8 (CH_3) ppm; LRMS (EI) *m/z* (%) 274 (M^+, 49), 231 (44), 215 (100); HRMS (EI) calcd for $C_{21}H_{22}$ 274.1722, found 274.1722.



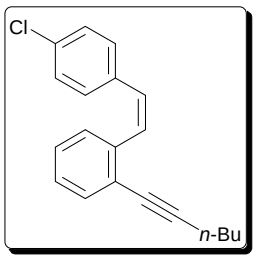
(*E*)-1-[2-(Phenylethynyl)styryl]naphthalene (1h): yellow oil; R_f = 0.21 (hex/EtOAc, 100/1); 52% yield; isolated as a > 20:1 mixture of *E:Z* isomers; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.33–8.30 (m, 1H), 8.09 (d, J = 16.2 Hz, 1H), 8.06–7.83 (m, 5H), 7.63–7.40 (m, 11H) ppm; ^{13}C{^{1}H} NMR (75.4 MHz, $CDCl_3$) δ 139.1 (C), 135.2 (C), 133.9 (C), 133.0 (CH), 131.7 (2 × CH), 131.6 (C), 129.9 (CH), 128.8 (2 × CH), 128.5 (2 × CH), 128.4 (2 × CH), 127.7 (CH), 127.5 (CH), 126.3 (CH), 126.0 (CH), 125.9 (CH), 125.5 (CH), 124.01 (CH), 123.95 (CH), 123.4 (C), 122.3 (C), 94.6 (C), 88.2 (C) ppm; LRMS (EI) *m/z* (%) 330 (M^+, 56), 313 (11), 253 (100); HRMS (ESI) calcd for $C_{26}H_{19}^+$ [$(M+H)^+$] 331.1481, found 331.1474.



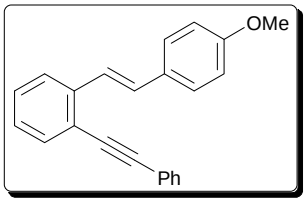
(*E*)-1-[2-(Hex-1-yn-1-yl)styryl]naphthalene (1i): orange oil; R_f = 0.27 (hex/EtOAc, 100/1); 56% yield; isolated as a > 20:1 mixture of *E:Z* isomers; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.39 (d, J = 7.8 Hz, 1H), 8.13–7.83 (m, 6H), 7.67–7.62 (m, 4H), 7.45 (t, J = 7.6 Hz, 1H), 7.35 (t, J = 7.5 Hz, 1H), 2.63 (t, J = 6.8 Hz, 2H), 1.79–1.62 (m, 4H), 1.07 (t, J = 7.2 Hz, 3H) ppm; ^{13}C{^{1}H} NMR (75.4 MHz, $CDCl_3$) δ 138.9 (C), 135.3 (C), 133.8 (C), 131.5 (CH), 130.2 (C), 128.7 (CH), 128.2 (CH), 127.9 (CH), 127.4 (CH), 127.0 (CH), 126.2 (CH), 125.9 (CH), 125.8 (CH), 125.0 (CH), 123.9 (3 × CH), 123.3 (C), 95.8 (C), 79.3 (C), 31.0 (CH_2), 22.2 (CH_2), 19.5 (CH_2), 13.8 (CH_3) ppm; LRMS (EI) *m/z* (%) 310 (M^+, 28), 268 (44), 253 (100); HRMS (ESI) calcd for $C_{24}H_{23}^+$ [(M+H)$^+$] 311.1794, found 311.1801.



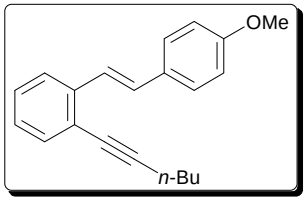
(*E*)-1-(4-Chlorostyryl)-2-(phenylethynyl)benzene (1j): yellow oil; R_f = 0.22 (hex/EtOAc, 100/1); 77% yield; isolated as a > 20:1 mixture of *E:Z* isomers; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.79–7.19 (m, 15H) ppm; ^{13}C{^{1}H} NMR (75.4 MHz, $CDCl_3$) δ 139.2 (C), 135.5 (C), 132.9 (C), 132.6 (C), 132.5 (CH), 131.7 (2 × CH), 130.4 (2 × CH), 130.0 (CH), 129.7 (CH), 129.02 (CH), 128.99 (CH), 128.55 (2 × CH), 128.51 (2 × CH), 128.1 (CH), 127.4 (CH), 123.4 (C), 123.0 (C), 94.3 (C), 88.2 (C) ppm; LRMS (EI) *m/z* (%) 314 (M^+, 32), 279 (100); HRMS (EI) calcd for $C_{22}H_{15}Cl$ 314.0862, found 314.0864.



(*Z*)-1-(4-Chlorostyryl)-2-(hex-1-yn-1-yl)benzene (*Z*-1k): yellow oil; R_f = 0.27 (hex/EtOAc, 100/1); isolated as a > 20:1 mixture of *Z:E* isomers; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.50–7.03 (m, 8H), 6.91 (d, J = 12.2 Hz, 1H), 6.64 (d, J = 12.2 Hz, 1H), 2.49 (t, J = 6.8 Hz, 2H), 2.47 (t, J = 6.8 Hz, 2H), 1.64–1.52 (m, 4H), 1.00 (t, J = 7.2 Hz, 3H) ppm; ^{13}C{^{1}H} NMR (75.4 MHz, $CDCl_3$) δ 138.9 (C), 135.6 (C), 132.8 (C), 132.5 (CH), 130.3 (2 × CH), 130.0 (C), 129.4 (CH), 128.9 (CH), 128.8 (2 × CH), 128.4 (CH), 127.8 (CH), 127.24 (CH), 127.21 (CH), 123.8 (C), 95.5 (C), 79.3 (C), 30.9 (CH_2), 22.1 (CH_2), 19.4 (CH_2), 13.8 (CH_3) ppm, two aromatic CH signals do not appear due to overlapping; LRMS (EI) *m/z* (%) 294 (M^+, 18), 215 (100); HRMS (EI) calcd for $C_{20}H_{19}Cl$ 294.1175, found 294.1172.

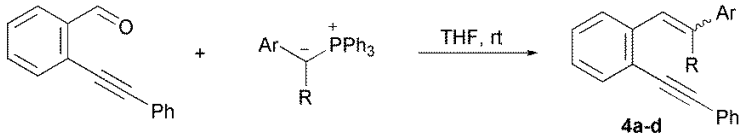


(*E*)-1-(4-Methoxystyryl)-2-(phenylethynyl)benzene (1l): yellow oil; R_f = 0.24 (hex/EtOAc, 100/1); 68% yield; isolated as a > 20:1 mixture of *E:Z* isomers; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.80–7.25 (m, 13H), 7.02 (d, J = 8.7 Hz, 2H), 3.90 (s, 3H) ppm; $^{13}C\{^1H\}$ NMR (75.4 MHz, $CDCl_3$) δ 159.6 (C), 139.1 (C), 132.7 (CH), 131.6 (2 × CH), 130.2 (C), 130.0 (CH), 128.6 (CH), 128.5 (2 × CH), 128.4 (CH), 128.0 (2 × CH), 126.9 (CH), 124.61 (CH), 124.57 (CH), 123.5 (C), 121.9 (C), 114.3 (2 × CH), 94.4 (C), 88.3 (C), 55.3 (CH_3) ppm; LRMS (EI) *m/z* (%) 310 (M^+, 100), 265 (25), 207 (21); HRMS (EI) calcd for $C_{23}H_{18}O$ 310.1358, found 310.1352.



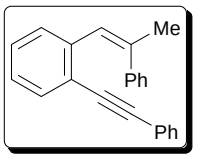
(*E*)-1-(Hex-1-yn-1-yl)-2-(4-methoxystyryl)benzene (1m): yellow oil; R_f = 0.24 (hex/EtOAc, 100/1); 64% yield; isolated as a 9:1 mixture of *E:Z* isomers. Data for the *E*-isomer: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.71 (d, J = 7.3 Hz, 1H), 7.64–7.14 (m, 7H), 6.98 (d, J = 8.8 Hz, 2H), 3.89 (s, 3H), 2.59 (t, J = 6.8 Hz, 2H), 1.73–1.62 (m, 4H), 1.06 (t, J = 7.2 Hz, 3H) ppm; $^{13}C\{^1H\}$ NMR (75.4 MHz, $CDCl_3$) δ 159.5 (C), 138.9 (C), 132.7 (CH), 130.5 (CH), 129.4 (C), 128.0 (2 × CH), 127.8 (CH), 126.8 (CH), 125.1 (CH), 124.3 (CH), 122.9 (C), 114.2 (2 × CH), 95.6 (C), 79.3 (C), 55.4 (CH_3), 31.0 (CH_2), 22.2 (CH_2), 19.5 (CH_2), 13.8 (CH_3) ppm; LRMS (EI) *m/z* (%) 290 (M^+, 100), 202 (78); HRMS (ESI) calcd for $C_{16}H_{13}O^+$ $[(M–C_5H_{10})+H]^+$ 221.0961, found 221.0958.

Synthesis and characterization data of *o*-(alkynyl)styrenes 4a-d:

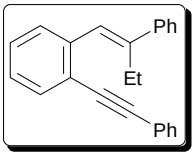


Under nitrogen atmosphere, *n*-BuLi (1.1 equiv of a 2.5 M solution in hexanes) was added to a solution of the corresponding phosphonium salt (1.1 equiv) in THF (20 mL) at 0 ºC. The resulting mixture was added for 30 min at rt. After that, 2-(phenylethynyl)benzaldehyde (1 equiv) was added to the solution at 0 ºC and the reaction mixture was stirred overnight at rt. The completion of the reaction was determined by GC-MS analysis. Then, the crude was partitioned between aqueous NH_4Cl/CH_2Cl_2, and the aqueous layer further extracted with CH_2Cl_2 (2 × 20 mL). The combined

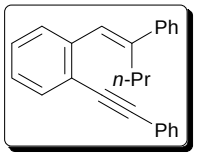
organic phase was dried over anhydrous Na_2SO_4 and the solvents were removed under reduce pressure. The residue was purified by flash chromatography using a mixture of hexane/EtOAc (100/1) as eluent to obtain the corresponding *o*-(alkynyl)styrenes **4a-d** as a variable mixture of geometrical isomers, which was carefully re-purified in order to obtain one of the geometrical isomers in pure form (yields not reported).



(*Z*)-1-(Phenylethynyl)-2-(2-phenylprop-1-en-1-yl)benzene (4a): yellow oil; R_f = 0.19 (hexane); isolated as a > 20:1 mixture of *Z:E* isomers; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.75–7.72 (m, 2H), 7.64 (d, J = 7.7 Hz, 1H), 7.51–7.49 (m, 3H), 7.39–7.36 (m, 5H), 7.20 (td, J = 7.7, 1.4 Hz, 1H), 7.09 (s, 1H), 7.05 (d, J = 7.4 Hz, 1H), 6.96 (d, J = 7.4 Hz, 1H), 2.45 (s, 3H) ppm; ^{13}C{^{1}H} NMR (75.4 MHz, $CDCl_3$) δ 141.8 (C), 140.0 (C), 139.9 (C), 132.1 (CH), 131.7 (2 × CH), 129.5 (CH), 128.50 (2 × CH), 128.47 (2 × CH), 128.4 (2 × CH), 128.3 (CH), 127.6 (CH), 127.1 (CH), 126.2 (CH), 125.4 (CH), 123.7 (C), 122.8 (C), 94.0 (C), 88.8 (C), 26.8 (CH_3) ppm; LRMS (EI) *m/z* (%) 294 (M^+, 100), 279 (98), 215 (74); HRMS (ESI) calcd for $C_{23}H_{19}^+$ [$(M+H)^+$] 295.1481, found 295.1482.

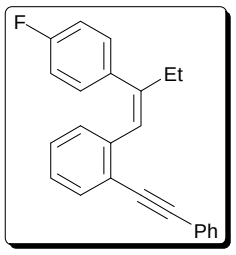


(*E*)-1-(2-Phenylbut-1-en-1-yl)-2-(phenylethynyl)benzene (4b): colourless oil; R_f = 0.21 (hexane); isolated as a 17:1 mixture of *E:Z* isomers; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.76–7.68 (m, 14H), 7.60 (s, 1H), 2.87 (q, J = 7.5 Hz, 2H), 1.18 (t, J = 7.5 Hz, 3H) ppm; ^{13}C{^{1}H} NMR (75.4 MHz, $CDCl_3$) δ 145.2 (C), 142.4 (C), 140.5 (C), 132.2 (CH), 131.6 (2 × CH), 128.7 (CH), 128.43 (2 × CH), 128.38 (2 × CH), 128.2 (CH), 128.1 (CH), 127.3 (CH), 126.8 (CH), 126.6 (CH), 126.4 (CH), 123.5 (C), 123.2 (C), 94.1 (C), 88.7 (C), 23.4 (CH_2), 13.5 (CH_3) ppm, one aromatic CH signal does not appear due to overlapping; LRMS (EI) *m/z* (%) 308 (M^+, 3), 280 (100), 215 (80); HRMS (ESI) calcd. for $C_{24}H_{21}^+$ [$(M+H)^+$] 309.1638, found 309.1634.



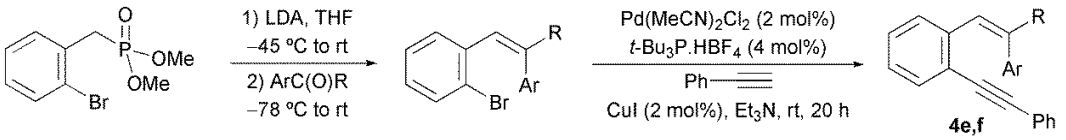
(*E*)-1-(Phenylethynyl)-2-(2-phenylpent-1-en-1-yl)benzene (4c): colorless oil; R_f = 0.35 (hexane); isolated as a 8/1 mixture of *E/Z* isomers. Data for de *E*-isomer: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.71–7.36 (m, 14H), 7.18 (s, 1H), 2.80 (t, J = 7.5 Hz, 2H), 1.63–1.45 (m, 2H), 0.97 (t, J = 7.3 Hz, 3H) ppm; ^{13}C{^{1}H} NMR (75.4 MHz, $CDCl_3$) δ 143.8 (C), 142.8 (C), 140.6 (C), 132.2 (CH), 131.7 (CH), 131.6 (2 × CH), 128.8 (CH), 128.4 (3 × CH), 128.3 (CH), 128.1 (CH), 127.30 (CH), 127.26 (CH), 126.8 (2 × CH), 126.6 (CH), 123.5 (C), 123.3 (C), 94.2 (C), 88.7 (C), 32.2 (CH_2), 21.8 (CH_2), 14.0 (CH_3) ppm;

LRMS (EI) *m/z* (%) 322 (M^+, 3), 280 (86), 204 (100); HRMS (ESI) calcd for $C_{25}H_{23}^+$ [$(M+H)^+$] 323.1806, found 323.1794.



(*Z*)-1-[2-(4-Fluorophenyl)but-1-en-1-yl]-2-(phenylethynyl)benzene (4d): yellow oil; R_f = 0.23 (hex/EtOAc, 100/1); isolated as a 7/1 mixture of *Z/E* isomers. Data for de *Z*-isomer: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.63–7.59 (m, 1H), 7.55–7.47 (m, 4H), 7.41–7.33 (m, 5H), 7.13–7.07 (m, 3H), 6.97 (s, 1H), 2.72 (q, J = 7.5 Hz, 2H), 1.05 (t, J = 7.5 Hz, 3H) ppm; $^{13}C\{^1H\}$ NMR (75.4 MHz, $CDCl_3$) δ 162.3 (d, J = 246.0 Hz, C), 144.3 (C), 140.4 (C), 138.5 (d, J = 3.0 Hz, C), 132.3 (C), 131.7 (C), 131.6 (2 × CH), 128.7 (CH), 128.5 (2 × CH), 128.4 (d, J = 8.0 Hz, 2 × CH), 128.2 (CH), 126.8 (CH), 126.5 (CH), 123.5 (CH), 123.3 (CH), 115.3 (d, J = 21.2 Hz, 2 × CH), 94.2 (C), 88.6 (C), 23.6 (CH_2), 13.5 (CH_3) ppm; LRMS (EI) *m/z* (%) 326 (M^+, 5), 298 (100), 222 (84); HRMS (ESI) calcd for $C_{24}H_{20}F^+$ [$(M+H)^+$] 327.1544, found 327.1546.

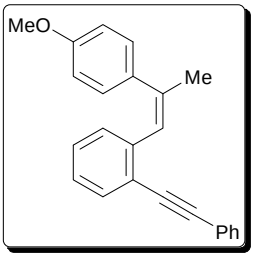
Synthesis and characterization data of *o*-(alkynyl)styrenes 4e,f:[3]



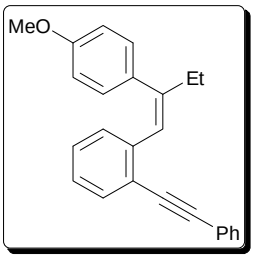
A Schlenk flask charged with a freshly made solution of LDA (12.5 mmol, 1.25 equiv) in anhydrous THF (25 mL) is cooled down to –45 ºC. A solution of dimethyl 2-bromobenzylphosphonate (2.79 g, 10 mmol, 1 equiv) in THF (5 mL) is added dropwise over 15 min. The mixture was allowed to stir 1 h and then it was allowed to warm to 0 ºC and to stir at this temperature another 1 h. After that, the reaction mixture was cooled down to –78 ºC and a solution of the corresponding ketone (11.0 mmol, 1.1 equiv) in THF (10 mL) was added dropwise over 20 min. Once the addition was finished the reaction mixture was allowed to slowly warm up to rt. After 12 h the reaction mixture was quenched by addition of aqueous NH_4Cl. The aqueous phase was extracted with Et_2O (3 × 30 mL), and the combined organic layer was dried over anhydrous Na_2SO_4, filtered through a silica plug and concentrated in vacuo affording the corresponding 2-bromostilbene derivative, which were pure enough for the next step. The 2-bromostilbene derivative (5.0 mmol, 1.0 equiv) was dissolved in dry degassed Et_3N (6 mL). Then $Pd(MeCN)_2Cl_2$ (26 mg, 0.1 mmol, 2 mol%) and phenylacetylene

[3] A. M. Sanjuán, C. Virumbrales, P. García-García, M. A. Fernández-Rodríguez and R. Sanz, *Org. Lett.,* 2016, **18**, 1072–1075.

(0.66 mL, 6.0 mmol, 1.2 equiv) were added and the mixture was allowed to stir for 5 min. After that, CuI (19 mg, 0.1 mmol, 2 mol%) was added immediately followed by (tBu)$_3$P·HBF$_4$ (58 mg, 0.2 mmol, 4 mol%).[4] The reaction mixture was allowed to stir 20 h at rt. Then, it was diluted by addition of Et_2O (20 mL) and filtered through a celite plug. The solid residue was washed with more Et_2O (3 × 10 mL) and the filtrate was poured into an extraction funnel and washed with aqueous NH_4Cl (2 × 10 mL). The organic phase was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure affording a residue of the corresponding enyne **4e,f** that was carefully purified by flash chromatography on silica gel in order to obtain one of the geometrical isomers in pure form (yields not reported).



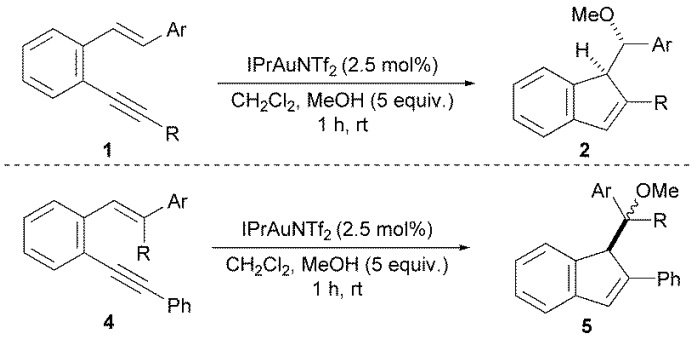
(*Z*)-1-[2-(4-Methoxyphenyl)prop-1-en-1-yl]-2-(phenylethynyl)benzene (4e): yellow oil; R_f = 0.15 (hex/EtOAc, 100/1); isolated as a > 20/1 mixture of *Z/E* isomers; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.61–7.57 (m, 2H), 7.51–7.48 (m, 1H), 7.39–7.37 (m, 3H), 7.15–7.08 (m, 3H), 6.97 (td, J = 7.6, 1.3 Hz, 1H), 6.88–6.86 (m, 2H), 6.81–6.78 (m, 2H), 3.79 (s, 3H), 2.29 (d, J = 1.5 Hz, 3H) ppm; ^{13}C{^{1}H} NMR (75.4 MHz, $CDCl_3$) δ 158.7 (C), 140.3 (C), 139.3 (C), 134.0 (C), 132.1 (CH), 131.7 (2 × CH), 129.7 (2 × CH), 129.5 (CH), 128.5 (2 × CH), 128.3 (CH), 127.7 (CH), 126.0 (CH), 124.8 (CH), 123.8 (C), 122.8 (C), 113.8 (2 × CH), 93.9 (C), 88.8 (C), 55.3 (CH_3), 26.8 (CH_3) ppm; LRMS (EI) *m/z* (%) 324 (54), 309 (60), 217 (100); HRMS (EI) calcd. for $C_{24}H_{20}O$ 324.1514, found 324.1511.



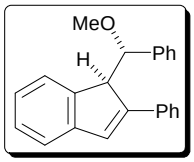
(*Z*)-1-[2-(4-Methoxyphenyl)but-1-en-1-yl]-2-(phenylethynyl)benzene (4f): yellow solid; mp 62–64 ºC; isolated as a 18/1 mixture of *Z/E* isomers; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.65–7.62 (m, 2H), 7.55–7.52 (m, 1H), 7.45–7.39 (m, 3H), 7.16–7.08 (m, 3H), 7.02–6.99 (m, 1H), 6.91 (s, 1H), 6.88–6.83 (m, 3H), 3.84 (s, 3H), 2.63 (qd, J = 7.4, 1.4 Hz, 2H), 1.21 (t, J = 7.4 Hz, 3H) ppm; ^{13}C{^{1}H} NMR (75.4 MHz, $CDCl_3$) δ 158.6 (C), 145.6 (C), 140.3 (C), 133.5 (C), 132.0 (CH), 131.6 (2 × CH), 129.9 (2 × CH), 129.4 (CH), 128.5 (2 × CH), 128.3 (CH), 127.6 (CH), 125.9 (CH), 123.8 (C), 123.5 (CH), 122.8 (C), 113.8 (2 × CH), 94.0 (C), 88.8 (C), 55.3 (CH_3), 33.1 (CH_2), 13.3 (CH_3) ppm; HRMS (EI) calcd for $C_{25}H_{22}O$ 338.1671, found 338.1673.

[4] T. Hundertmark, A. F. Littke, S. L. Buchwald and G. C. Fu, *Org. Lett.,* 2000, **2**, 1729–1731.

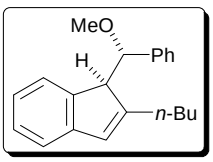
Synthesis and characterization data of methoxy-functionalized indenes 2 and 5:



MeOH (1.5 mmol, 0.06 mL) was added to a solution of $IPrAuNTf_2$ (0.025 mmol, 6 mg) in CH_2Cl_2 (0.6 mL) and the solution mixture was stirred 5 min. A solution of the corresponding starting *o*-(alkynyl)styrene **1** or **4** (0.3 mmol) in CH_2Cl_2 (0.4 mL) was subsequently added. The resulting reaction mixture was stirred at rt until complete consumption of the styrene derivative was observed by GC-MS (~1 h). The mixture was filtered through a short pad of silica gel using a 100:1 mixture of hexane/EtOAc as eluent, the solvent was removed under reduced pressure, and the crude mixture was purified by flash column chromatography on silica gel using mixtures of hexane and EtOAc as eluents to obtain the corresponding 1-(α-methoxybenzyl)-1*H*-indenes **2** and **5**, in the yields reported in Tables 2 and 4.

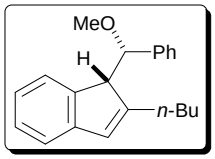


(*R)-1-[(*S**)-Methoxy(phenyl)methyl]-2-phenyl-1*H*-indene (2a):** yellow solid; mp 101–103 ºC; 93% yield (87 mg); obtained and isolated with d.r. > 20/1 starting from (*E*)-**1a**, or obtained and isolated with d.r. ~ 1/1 starting from a ~ 1/1 mixture of *E*/*Z* diastereoisomers of **1a**; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.62–7.59 (m, 2H), 7.47–7.25 (m, 10H), 7.14–7.07 (m, 2H), 6.93 (d, J = 7.5 Hz, 1H), 4.81 (d, J = 3.6 Hz, 1H), 4.41 (d, J = 3.6 Hz, 1H), 3.13 (s, 3H) ppm; ^{13}C{^{1}H} NMR (75.4 MHz, $CDCl_3$) δ 149.3 (C), 144.8 (C), 143.8 (C), 140.0 (C), 136.5 (C), 129.2 (CH), 128.5 (2 × CH), 128 .0 (2 × CH), 127.40 (2 × CH), 127.37 (CH), 127.3 (CH), 127.2 (CH), 126.9 (2 × CH), 124.8 (CH), 124.4 (CH), 121.2 (CH), 83.6 (CH), 58.0 (CH_3), 56.3 (CH) ppm; LRMS (EI) *m/z* (%) 312 (M^+, 2), 121 (100); HRMS (ESI) calcd for $C_{23}H_{21}O^+$ [$(M+H)^+$] 313.1587, found 313.1594.

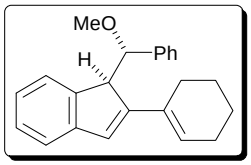


(*S)-2-Butyl-1-[(*S**)-methoxy(phenyl)methyl]-1*H*-indene (2b):** brown oil; R_f = 0.24 (hexane); 91% yield (80 mg); obtained and isolated with d.r. > 20/1 starting from (*E*)-**1b**; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.36–7.04 (m, 10H), 6.49 (s, 1H), 4.66 (d, J = 5.3 Hz, 1H), 3.81 (d, J = 5.3 Hz, 1H), 3.35 (s, 3H), 2.42–

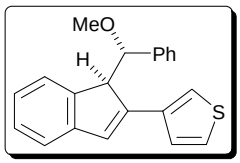
2.39 (m, 2H), 1.63–1.55 (m, 2H), 1.41–1.32 (m, 2H), 0.97 (t, J = 7.3 Hz, 3H) ppm; $^{13}C\{^1H\}$ NMR (75.4 MHz, $CDCl_3$) δ 151.7 (C), 145.1 (C), 144.0 (C), 140.6 (C), 128.0 (2 × CH), 127.60 (CH), 127.59 (CH), 127.1 (2 × CH), 126.9 (CH), 124.4 (CH), 123.5 (CH), 120.0 (CH), 84.4 (CH), 57.4 (CH_3), 57.0 (CH), 31.3 (CH_2), 30.3 (CH_2), 22.7 (CH_2), 14.1 (CH_3) ppm; LRMS (EI) *m/z* (%) 292 (M^+, 1), 121 (100); HRMS (ESI) calcd for $C_{21}H_{25}O^+$ [$(M+H)^+$] 293.1900, found 293.1903.



(*R)-2-Butyl-1-[(*S**)-methoxy(phenyl)methyl]-1*H*-indene (diast-2b):** brown solid; R_f = 0.30 (hexane); 87% yield (77 mg); obtained and isolated with d.r. > 20/1 starting from (*Z*)-**1b**; ^1H NMR (300 MHz, $CDCl_3$) δ 7.21–7.08 (m, 9H), 6.38 (s, 1H), 4.49 (d, J = 6.1 Hz, 1H), 3.89 (d, J = 6.1 Hz, 1H), 3.33 (s, 3H), 2.55 (t, J = 6.7 Hz, 2H), 1.70–1.41(m, 4H), 0.98 (t, J = 7.2 Hz, 3H) ppm; $^{13}C\{^1H\}$ NMR (75.4 MHz, $CDCl_3$) δ 151.8 (C), 145.3 (C), 143.6 (C), 138.8 (C), 127.8 (CH), 127.63 (2 × CH), 127.64 (2 × CH), 127.5 (CH), 126.8 (CH), 125.4 (CH), 123.4 (CH), 119.7 (CH), 85.1 (CH), 57.0 (CH), 56.5 (CH_3), 31.3 (CH_2), 30.6 (CH_2), 22.8 (CH_2), 14.1 (CH_3) ppm; LRMS (EI) *m/z* (%) 292 (M^+, 1), 121 (100); HRMS (ESI) calcd for $C_{21}H_{25}O^+$ [$(M+H)^+$] 293.1900, found 293.1903.

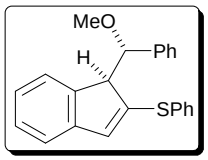


(*S)-2-Cyclohex-1-en-1-yl-1-[(*S**)-methoxy(phenyl)methyl]-1*H*-indene (2c):** yellow oil; R_f = 0.23 (hexane); 82% yield (78 mg); obtained and isolated with d.r. > 20/1 starting from (*E*)-**1c**; ^1H NMR (300 MHz, $CDCl_3$) δ 7.45–7.25 (m, 7H), 7.06 (td, J = 7.3, 1.4 Hz, 1H), 6.84 (d, J = 7.4 Hz, 1H), 6.72 (s, 1H), 6.08 (s, 1H), 4.82 (d, J = 3.9 Hz, 1H), 4.15 (d, J = 3.9 Hz, 1H), 3.31 (s, 3H), 2.63–2.49 (m, 1H), 2.25 (dd, J = 20.1, 2.7 Hz, 3H), 1.77 (ddd, J = 7.3, 5.3, 2.7 Hz, 4H) ppm; $^{13}C\{^1H\}$ NMR (75.4 MHz, $CDCl_3$) δ 150.8 (C), 145.1 (C), 144.1 (C), 140.7 (C), 132.8 (C), 128.0 (C), 127.2 (2 × CH), 127.0 (2 × CH), 126.75 (CH), 125.9 (2 × CH), 124.5 (CH), 123.8 (CH), 120.8 (CH), 84.8 (CH), 58.3 (CH), 55.4 (CH_3), 27.0 (CH_2), 26.1 (CH_2), 22.9 (CH_2), 22.4 (CH_2) ppm; LRMS (EI) *m/z* (%) 316 (M^+, 5), 121 (100); HRMS (ESI) calcd for $C_{23}H_{24}ONa^+$ [$(M+Na)^+$] 339.1719, found 339.1719.

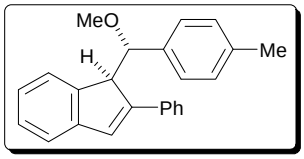


3-{(*R)-1-[(*S**)-Methoxy(phenyl)methyl]-1*H*-inden-2-yl}thiophene (2d):** white oil; R_f = 0.24 (hexane); 87% yield (83 mg); obtained and isolated with d.r. > 20/1 starting from (*E*)-**1d**; ^1H NMR (300 MHz, $CDCl_3$) δ 7.49 (dd, J = 5.0, 3.0 Hz, 1H), 7.34–7.07 (m, 11H), 6.93 (s, 1H), 4.89 (d, J = 3.7 Hz, 1H), 4.29 (d, J = 3.7 Hz, 1H), 3.23 (s, 3H) ppm; $^{13}C\{^1H\}$ NMR (75.4 MHz, $CDCl_3$) δ 144.7(C), 144.0

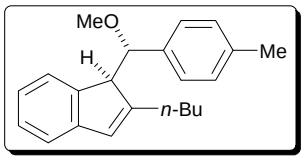
(C), 143.6 (C), 139.3 (C), 138.1 (C), 128.5 (CH), 127.8 (2 × CH), 127.4 (CH), 127.2 (CH), 126.9 (3 × CH), 125.3 (CH), 124.5 (CH), 124.4 (CH), 121.8 (CH), 121.0 (CH), 84.6 (CH), 57.8 (CH), 57.0 (CH_3) ppm; LRMS (EI) *m/z* (%) 318 (M^+, 7), 121 (100); HRMS (ESI) calcd for $C_{21}H_{18}OSNa^+$ [$(M+Na)^+$] 341.0971, found 341.0968.



{(*S)-1-[(*S**)-Methoxy(phenyl)methyl]-1*H*-inden-2-yl}(phenyl)sulfane (2e):** orange oil; R_f = 0.30 (hexane); 90% yield (93 mg); obtained and isolated with d.r. > 20/1 starting from (*E*)-**1e**; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.61 (dd, *J* = 7.7, 1.7 Hz, 2H), 7.46–7.18 (m, 10H), 7.04 (td, *J* = 7.7, 1.7 Hz, 1H), 6.81 (d, *J* = 7.7 Hz, 1H), 6.62 (s, 1H), 5.00 (d, *J* = 3.9 Hz, 1H), 3.97 (d, *J* = 3.9 Hz, 1H), 3.41 (s, 3H) ppm; $^{13}C\{^1H\}$ NMR (75.4 MHz, $CDCl_3$) δ 144.3 (C), 144.2 (C), 143.0 (C), 139.3 (C), 134.4 (C), 132.6 (2 × CH), 131.7 (CH), 129.4 (2 × CH), 128.1 (2 × CH), 127.9 (CH), 127.6 (CH), 127.2 (CH), 127.1 (2 × CH), 124.3 (CH), 124.0 (CH), 120.2 (CH), 83.2 (CH), 58.2 (CH), 58.0 (CH_3) ppm; LRMS (EI) *m/z* (%) 344 (M^+, 5), 121 (100); HRMS (ESI) calcd for $C_{23}H_{21}OS^+$ [$(M+H)^+$] 345.1308, found 345.1305.

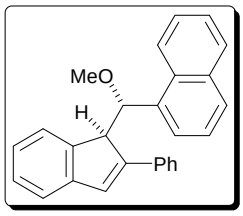


(*R)-1[(*S**)-Methoxy(*p*-tolyl)methyl]-2-phenyl-1*H*-indene (2f):** yellow oil; R_f = 0.23 (hexane); 86% yield (84 mg); obtained and isolated with d.r. > 20/1 starting from (*E*)-**1f**; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.57–7.54 (m, 2H), 7.41–7.25 (m, 5H), 7.08–7.01 (m, 6H), 6.91 (d, *J* = 7.5 Hz, 1H), 4.72 (d, *J* = 3.8 Hz, 1H), 4.33 (d, *J* = 3.8 Hz, 1H), 3.06 (s, 3H), 2.35 (s, 3H) ppm; $^{13}C\{^1H\}$ NMR (75.4 MHz, $CDCl_3$) δ 149.5 (C), 144.9 (C), 143.9 (C), 137.0 (C), 136.9 (C), 136.6 (C), 129.2 (CH), 128.8 (2 × CH), 128.5 (2 × CH), 127.4 (2 × CH), 127.2 (CH), 126.9 (2 × CH), 124.9 (CH), 124.4 (CH), 121.2 (CH), 83.6 (CH), 57.9 (CH), 56.5 (CH_3), 21.3 (CH_3) ppm; LRMS (EI) *m/z* (%) 326 (M^+, 2), 189 (7), 135 (100); HRMS (EI) calcd for $C_{24}H_{22}O$ 326.1671, found 326.1664.

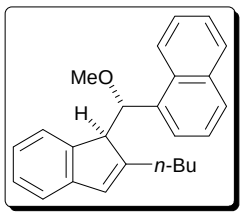


(*S)-2-Butyl-1-[(*S**)-methoxy(*p*-tolyl)methyl]-1*H*-indene (2g):** yellow oil; R_f = 0.21 (hexane); 75% yield (69 mg); obtained and isolated with d.r. > 20/1 starting from (*E*)-**1g**; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.18–7.01 (m, 8H), 6.43 (s, 1H), 4.58 (d, *J* = 5.3 Hz, 1H), 3.74 (d, *J* = 5.3 Hz, 1H), 3.28 (s, 3H), 2.34 (s, 3H), 2.27–2.22 (m, 2H), 1.56–1.51 (m, 2H), 1.34–1.27 (m, 2H), 0.91 (t, *J* = 7.3 Hz, 3H) ppm; $^{13}C\{^1H\}$ NMR (75.4 MHz, $CDCl_3$) δ 151.9 (C), 145.1 (C), 144.2 (C), 137.1 (C), 136.5 (C), 128.7 (2 × CH), 127.6 (CH), 127.1 (2 × CH), 126.8 (CH),

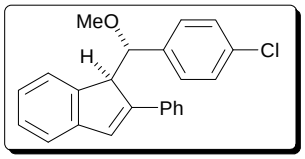
124.5 (CH), 123.4 (CH), 120.0 (CH), 84.3 (CH), 57.3 (CH), 57.1 (CH_3), 31.3 (CH_2), 30.3 (CH_2), 22.7 (CH_2), 21.3 (CH_3), 14.1 (CH_3) ppm; LRMS (EI) *m/z* (%) 306 (M^+, 1), 135 (100); HRMS (ESI) calcd for $C_{22}H_{27}O^+$ [$(M+H)^+$] 307.2056, found 307.2058.



1-[(*S)-Methoxy-(*R**)-2-phenyl-1*H*-inden-1-yl)methyl]naphthalene (2h):** yellow oil; R_f = 0.31 (hexane); 88% yield (96 mg); obtained and isolated with d.r. > 20/1 starting from (*E*)-**1h**; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.38 (d, *J*= 8.4 Hz, 1H), 8.02–7.88 (m, 2H), 7.61–7.16 (m, 14H), 6.81 (d, *J* = 7.4 Hz, 1H), 5.32 (d, *J* = 5.2 Hz, 1H), 4.65 (d, *J* = 5.2 Hz, 1H), 3.21 (s, 3H) ppm; ^{13}C{^{1}H} NMR (75.4 MHz, $CDCl_3$) δ 150.0 (C), 144.8 (C), 144.2 (C), 136.6 (C), 135.3 (C), 133.9 (C), 131.3 (C), 129.4 (CH), 129.2 (2 × CH), 128.2 (2 × CH), 127.2 (2 × CH), 127.1 (CH), 126.0 (CH), 125.7 (CH), 125.4 (2 × CH), 125.2 (CH), 124.2 (CH), 122.9 (CH), 121.2 (CH), 80.7 (CH), 57.6 (CH), 55.4 (CH_3) ppm, one aromatic CH signal does not appear due to overlapping; LRMS (EI) *m/z* (%) 362 (M^+, 11), 171 (100); HRMS (ESI) calcd for $C_{27}H_{22}ONa^+$ [$(M+Na)^+$] 385.1563, found 385.1563.

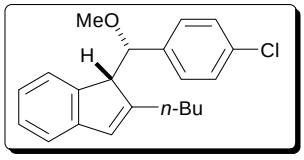


1-{(*S)-[(*S**)-2-Butyl-1*H*-indenyl-1-yl](methoxy)methyl}naphthalene (2i):** yellow oil; R_f = 0.15 (hexane); 91% yield (93 mg); obtained and isolated with d.r. > 20/1 starting from (*E*)-**1i**; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.24–8.21 (m, 1H), 7.98–7.88 (m, 2H), 7.58–7.53 (m, 4H), 7.26–7.15 (m, 2H), 6.91 (dt, *J*= 7.5, 1.3Hz, 1H), 6.66 (d, *J* = 7.5 Hz, 1H), 6.56 (s, 1H), 5.24 (d, *J* = 5.4 Hz, 1H), 3.91 (d, *J* = 5.4 Hz, 1H), 3.27 (s, 3H), 2.32–2.22 (m, 1H), 2.11–2.04 (m, 1H), 1.55–1.49 (m, 2H), 1.29–1.24 (m, 2H), 0.86 (t, *J* = 7.3 Hz, 3H) ppm; ^{13}C{^{1}H} NMR (75.4 MHz, $CDCl_3$) δ 151.5 (C), 145.2 (C), 144.1 (C), 135.6 (C), 134.1 (C), 131.4 (C), 129.3 (CH), 128.5 (CH), 127.5 (CH), 126.8 (CH), 126.2 (CH), 125.7 (CH), 125.5 (CH), 125.4 (CH), 125.3 (CH), 123.3 (CH), 123.0 (CH), 120.1 (CH), 80.7 (CH), 57.6 (CH), 56.3(CH_3), 31.3 (CH_2), 29.7 (CH_2), 22.7 (CH_2), 14.1 (CH_3) ppm; LRMS (EI) *m/z* (%) 342 (M^+, 13), 285 (100), 141 (41); HRMS (ESI) calcd for $C_{25}H_{27}O^+$ [$(M+H)^+$] 343.2056, found: 343.2057.

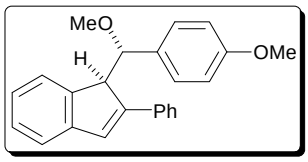


(*R)-1-[(*S**)-(4-Chlorophenyl)(methoxy)methyl]-2-phenyl-1*H*-indene (2j):** yellow oil; R_f = 0.20 (hexane); 85% yield (88 mg); obtained and isolated with d.r. > 20/1 starting from (*E*)-**1j**; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.55–7.51 (m, 2H), 7.40–7.01 (m, 12H), 4.71 (d, *J* = 4.2 Hz, 1H), 4.38 (d, *J* = 4.2 Hz, 1H), 3.13 (s, 3H) ppm; ^{13}C{^{1}H} NMR (75.4 MHz, $CDCl_3$) δ

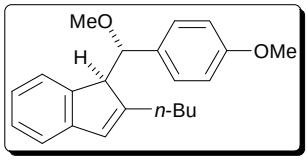
149.1 (C), 144.8 (C), 143.8 (C), 138.2 (C), 136.5 (C), 133.1 (C), 129.6 (CH), 128.5 (2 × CH), 128.4 (2 × CH), 128.0 (2 × CH), 127.4 (2 × CH), 127.3 (CH), 124.64 (CH), 124.60 (CH), 121.3 (CH), 83.7 (CH), 57.8 (CH), 55.9 (CH_3) ppm; LRMS (EI) *m/z* (%) 346 (M^+, 7), 189 (11), 155 (100); HRMS (EI) calcd for $C_{23}H_{19}ClO$ 346.1124, found: 346.1123.



(*R)-2-Butyl-1-[(*S**)-(4-chlorophenyl)(methoxy)methyl]-1*H*-indene (diast-2k):** colourless solid; mp 78–80 ºC; 88% yield (86 mg); obtained and isolated with d.r. > 20/1 starting from (*Z*)-**1k**; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.30–7.27 (m, 1H), 7.17–6.92 (m, 7H), 6.35 (s, 1H), 4.51 (d, *J* = 5.2 Hz, 1H), 3.87 (d, *J* = 5.2 Hz, 1H), 3.32 (s, 3H), 2.55–2.49 (m, 2H), 1.64–1.40 (m, 4H), 0.97 (t, *J* = 7.2 Hz, 3H) ppm; ^{13}C{^{1}H} NMR (75.4 MHz, $CDCl_3$) δ 150.8 (C), 145.2 (C), 143.2 (C), 137.0 (C), 133.3 (C), 128.8 (2 × CH), 127.9 (CH), 127.7 (2 × CH), 127.0 (CH), 125.5 (CH), 123.5 (CH), 119.9 (CH), 84.2 (CH), 57.1 (CH), 56.2 (CH_3), 31.2 (CH_2), 30.5 (CH_2), 22.8 (CH_2), 14.1 (CH_3) ppm; LRMS (EI) *m/z* (%) 326 (M^+, 12), 269 (100), 125 (28); HRMS (ESI) calcd for $C_{21}H_{24}ClO^+$ [$(M+H)^+$] 327.1510, found: 327.1509.

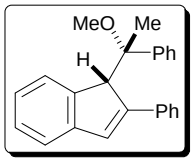


(*R)-1[(*S**)-Methoxy(4-methoxyphenyl)methyl]-2-phenyl-1*H*-indene (2l):** yellow oil; R_f = 0.20 (hexane); 86% yield (88 mg); obtained with d.r. = 16/1 and isolated with d.r. = 14/1 starting from (*E*)-**1l** or obtained and isolated with d.r. = 1/5 starting from a ~ 1/8 mixture of *E*/*Z* diastereoisomers of **1l**. Data for the *(R*,S*)* diastereoisomer; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.60–7.57 (m, 2H), 7.43–7.31 (m, 5H), 7.15–7.05 (m, 5H), 6.85 (d, *J* = 8.8 Hz, 2H), 4.74 (d, *J* = 4.2 Hz, 1H), 4.38 (d, *J* = 4.2 Hz, 1H), 3.85 (s, 3H), 3.13 (s, 3H) ppm; ^{13}C{^{1}H} NMR (75.4 MHz, $CDCl_3$) δ 158.9 (C), 149.4 (C), 144.8 (C), 144.1 (C), 136.6 (C), 131.8 (C), 129.3 (CH), 128.4 (2 × CH), 128.0 (2 × CH), 127.4 (2 × CH), 127.2 (CH), 127.1 (CH), 124.8 (CH), 124.4 (CH), 121.2 (CH), 113.3 (2 × CH), 83.6 (CH), 57.7 (CH), 56.4 (CH_3), 55.3 (CH_3) ppm; LRMS (EI) *m/z* (%) 342 (M^+, <1), 151 (100); HRMS (ESI) calcd for $C_{24}H_{22}O_2Na^+$ [$(M+Na)^+$] 365.1512, found: 365.1513.

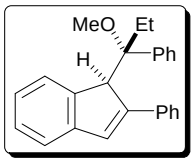


(*S)-2-Butyl-1[(*S**)-methoxy(4-methoxyphenyl)methyl]-1*H*-indene (2m):** yellow oil; R_f = 0.34 (hexane); 70% yield (68 mg); obtained and isolated with d.r. = 9/1 starting from a ~ 9/1 mixture of *E*/*Z* diastereoisomers of **1m**; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.30–7.07 (m, 6H), 6.86 (d, *J* = 8.6 Hz, 2H), 6.48 (s, 1H), 4.59 (d, *J* = 5.3 Hz, 1H), 3.84 (s, 3H), 3.79 (d, *J* = 5.3 Hz, 1H), 3.33 (s, 3H), 2.41–2.28 (m, 2H), 1.61–1.35 (m, 4H), 0.96 (t, *J* = 7.3 Hz, 3H) ppm; ^{13}C{^{1}H}

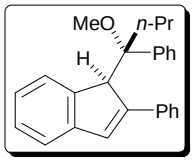
NMR (75.4 MHz, $CDCl_3$) δ 159.1 (C), 151.9 (C), 145.1 (C), 144.3 (C), 131.6 (C), 128.3 (2 × CH), 127.6 (CH), 126.8 (CH), 124.5 (CH), 123.5 (CH), 120.0 (CH), 113.3 (2 × CH), 84.2 (CH), 57.2 (CH), 57.1 (CH_3), 55.3 (CH_3), 31.3 (CH_2), 30.4 (CH_2), 22.7 (CH_2), 14.1 (CH_3) ppm; LRMS (EI) *m/z* (%) 322 (M^+, <1), 151 (100); HRMS (ESI) calcd for $C_{22}H_{26}O_2Na^+$ [$(M+Na)^+$] 345.1825, found: 345.1824.



(*S)-1-[(*S**)-1-Methoxy-1-phenylethyl]-2-phenyl-1*H*-indene (5a):** yellow oil; R_f = 0.16 (hexane/EtOAc, 100/1); 87% yield (85 mg); obtained and isolated with d.r. > 20/1 starting from (*Z*)-**4a**; ^1H NMR (300 MHz, $CDCl_3$) δ 7.68–7.65 (m, 2H), 7.45–7.26 (m, 10H), 6.94–6.89 (m, 2H), 6.17 (d, *J* = 7.6 Hz, 1H), 4.52 (s, 1H), 2.87 (s, 3H), 1.23 (s, 3H) ppm; $^{13}C\{^1H\}$ NMR (75.4 MHz, $CDCl_3$) δ 151.6 (C), 144.9 (C), 143.7 (C), 143.3 (C), 138.9 (C), 131.3 (CH), 128.5 (2 × CH), 127.74 (2 × CH), 127.71 (2 × CH), 127.69 (2 × CH), 127.5 (CH), 127.0 (CH), 126.8 (CH), 125.8 (CH), 123.9 (CH), 120.5 (CH), 81.5 (C), 61.2 (CH_3), 49.6 (CH), 17.3 (CH_3) ppm; LRMS (EI) *m/z* (%) 326 (M^+, <1), 191 (18), 135 (100); HRMS (ESI) calcd for $C_{23}H_{19}^+$ [$(M-CH_4O)+H]^+$ 295.1481, found: 295.1479.

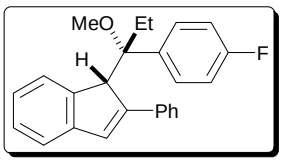


(*R)-1-[(S*)-1-Methoxy-1-phenylpropyl]-2-phenyl-1*H*-indene (5b):** yellow oil; R_f = 0.17 (hexane/EtOAc, 100/1); 78% yield (80 mg); obtained and isolated with d.r. = 3/1 starting from (*E*)-**5b**. Data for the *(R*,S*)* diastereoisomer; ^1H NMR (300 MHz, $CDCl_3$) δ 7.78 (d, *J* = 7.4 Hz, 1H), 7.51–6.91 (m, 13H), 6.69 (m, 1H), 4.62 (s, 1H), 3.08 (s, 3H), 2.46 (dq, *J* = 14.7, 7.3 Hz, 1H), 2.07 (dq, *J* = 14.7, 7.3 Hz, 1H), 0.98 (t, *J* = 7.2 Hz, 3H) ppm; $^{13}C\{^1H\}$ NMR (75.4 MHz, $CDCl_3$) δ 151.2 (C), 145.0 (C), 144.6 (C), 141.7 (C), 138.8 (C), 131.3 (CH), 127.8 (2 × CH), 127.5 (2 × CH), 127.2 (2 × CH), 127.0 (CH), 126.8 (2 × CH), 126.5 (CH), 126.3 (CH), 125.8 (CH), 124.2 (CH), 120.7 (CH), 84.1 (C), 57.5 (CH_3), 49.7 (CH), 25.8 (CH_2), 8.2 (CH_3) ppm; LRMS (EI) *m/z* (%) 340 (M^+, 26), 311 (100), 207 (97); HRMS (ESI) calcd for $C_{25}H_{24}ONa^+$ [$(M+Na)^+$] 363.1719, found 363.1720.

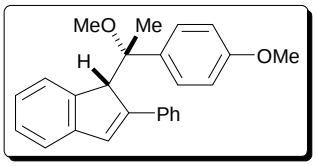


(*R)-1-[(*S**)-1-Methoxy-1-phenylbutyl]-2-phenyl-1*H*-indene (5c):** yellow oil; R_f = 0.18 (hexane/EtOAc, 100/1); 61% yield (65 mg); obtained with d.r. = 3/1 and isolated with d.r. > 20/1 starting from a ~ 8/1 mixture of *E*/*Z* diastereoisomers of **4c**. Data for the *(R*,S*)* diastereoisomer; ^1H NMR (300 MHz, $CDCl_3$) δ 7.77 (d, *J* = 7.3 Hz, 1H), 7.32–7.23 (m, 11H), 6.92 (d, *J* = 7.1 Hz, 2H), 6.68 (s, 1H), 4.60 (s, 1H), 3.07 (s, 3H), 2.46–2.36 (m, 1H), 2.00–1.90 (m, 1H), 1.45–1.37 (m, 2H), 1.03 (t, *J* =

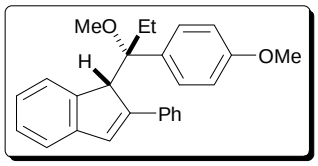
7.3 Hz, 3H) ppm; $^{13}C\{^{1}H\}$ NMR (75.4 MHz, $CDCl_3$) δ 151.2 (C), 145.1 (C), 144.6 (C), 141.8 (C), 138.8 (C), 131.2 (CH), 127.8 (2 × CH), 127.5 (2 × CH), 127.11 (2 × CH), 127.05 (CH), 126.8 (2 × CH), 126.5 (CH), 126.3 (CH), 125.8 (CH), 124.2 (CH), 120.7 (CH), 84.0 (C), 57.9 (CH_3), 49.8 (CH), 35.8 (CH_2), 16.7 (CH_2), 14.8 (CH_3) ppm; LRMS (EI) *m/z* (%) 354 (M^+, 8), 311 (100); HRMS (ESI) calcd for $C_{26}H_{26}ONa^+$ [$(M+Na)^+$]: 377.1876, found: 377.1872.



(*S)-1-[(*S**)-(1-(4-fluorophenyl)-1-methoxypropyl)]-2-phenyl-1*H*-indene (5d):** yellow oil; R_f = 0.27 (hexane/EtOAc, 100/1); 60% yield (65 mg); obtained with d.r. = 5/1 and isolated with d.r. ~ 15/1 starting from a ~ 1/15 mixture of *E*/*Z* diastereoisomers of **4d**. Data for the *(S*,S*)* diastereoisomer; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.73 (d, *J* = 7.2 Hz, 1H), 7.28–7.24 (m, 8H), 6.81–6.64 (m, 5H), 4.53 (s, 1H), 3.02 (s, 3H), 2.40 (dq, *J* = 14.6, 7.3 Hz, 1H), 2.00 (dq, *J* = 14.6, 7.3 Hz, 1H), 0.93 (t, *J* = 7.3 Hz, 3H) ppm; $^{13}C\{^{1}H\}$ NMR (75.4 MHz, $CDCl_3$) δ 161.7 (d, *J* = 244.6 Hz, C), 151.0 (C), 145.1 (C), 144.3 (C), 138.7 (C), 137.3 (d, *J* = 3.2 Hz, C), 131.3 (CH), 128.7 (d, *J* = 7.9 Hz, 2 × CH), 127.8 (2 × CH), 127.5 (2 × CH), 127.2 (CH), 126.4 (CH), 125.7 (CH), 124.3 (CH), 120.8 (CH), 113.5 (d, *J* = 21.0 Hz, 2 × CH), 83.8 (C), 57.2 (CH_3), 49.6 (CH), 25.9 (CH_2), 8.1 (CH_3) ppm; LRMS (EI) *m/z* (%) 358 (M^+, 12), 329 (100); HRMS (ESI) calcd for $C_{25}H_{23}FONa^+$ [$(M+Na)^+$]: 381.1625, found: 381.1623.

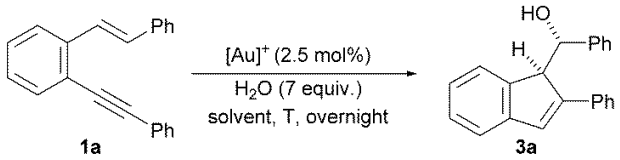


(*S)-1-[(*S**)-1-Methoxy-1-(4-methoxyphenyl)ethyl]-2-phenyl-1*H*-indene (5e):** white solid; mp 102–104 ºC; 88% yield (94 mg); obtained with d.r. = 13/1 and isolated with d.r. > 20/1 starting from (*Z*)-**4e**. Data for the *(S*,S*)* diastereoisomer; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.63–7.60 (m, 2H), 7.44–7.41 (m, 2H), 7.39–7.17 (m, 5H), 6.93–6.86 (m, 4H), 6.22 (d, *J* = 7.6 Hz, 1H), 4.46 (s, 1H), 3.88 (s, 3H), 2.81 (s, 3H), 1.16 (s, 3H); $^{13}C\{^{1}H\}$ NMR (75.4 MHz, $CDCl_3$) δ 158.9 (C), 151.7 (C), 145.0 (C), 144.0 (C), 139.0 (C), 135.5 (C), 131.2 (CH), 128.9 (2 × CH), 128.5 (2 × CH), 127.7 (2 × CH), 127.0 (CH), 126.8 (CH), 125.9 (CH), 123.9 (CH), 120.5 (CH), 113.0 (2 × CH), 81.2 (C), 61.3 (CH_3), 55.4 (CH_3), 49.4 (CH), 17.3 (CH_3); LRMS (EI) *m/z* (%) 356 (M^+, 2), 324 (100), 133 (45); HRMS (ESI) calcd for $C_{25}H_{23}O_2^+$ [$(M–H_2)+H]^+$ 355.1693, found 355.1693.



(*S)-1-[(*S**)-1-Methoxy-1-(4-methoxyphenyl)propyl]-2-phenyl-1*H*-indene (5f):** yellow oil; R_f = 0.14 (hexane/EtOAc, 10/1); 90% yield (99 mg); obtained with d.r. = 8/1 and isolated with d.r. > 20/1 starting from a ~ 1/18 mixture of *E*/*Z* diastereoisomers of **4f**. Data for the *(S*,S*)* diastereoisomer; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.78–7.76 (m, 1H), 7.45–7.35 (m, 5H), 7.23–7.18 (m, 2H), 7.10–7.07 (m, 1H), 6.75–6.72 (m, 2H), 6.58–6.54 (m, 3H), 4.53 (s, 1H), 3.73 (s, 3H), 3.30 (s, 3H), 1.97 (dq, *J* = 14.4, 7.1 Hz, 1H), 1.75 (dq, *J* = 14.4, 7.1 Hz, 1H), 0.92 (t, *J* = 7.2 Hz, 3H); ^{13}C{^{1}H} NMR (75.4 MHz, $CDCl_3$) δ 158.1 (C), 149.3 (C), 145.1 (C), 144.7 (C), 139.3 (C), 132.9 (CH), 132.3 (C), 128.3 (2 × CH), 128.0 (2 × CH), 127.8 (2 × CH), 127.2 (CH), 127.1 (CH), 126.8 (CH), 124.1 (CH), 120.5 (CH), 111.6 (2 × CH), 83.4 (C), 55.7 (CH_3), 55.1 (CH_3), 49.5 (CH), 26.4 (CH_2), 7.8 (CH_3); LRMS (EI) *m/z* (%) 370 (M^+, 4), 341 (100), 323 (48); HRMS (ESI) calcd for $C_{26}H_{26}O_2Na^+$ [$(M+Na)^+$] 393.1825, found 393.1817.

Optimization of the hydroxycyclization reaction of 1a:

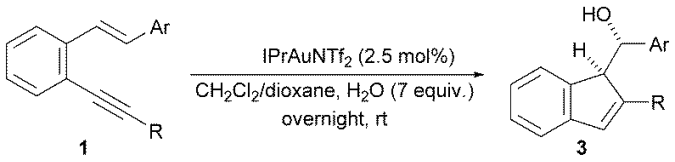


1a **3a**

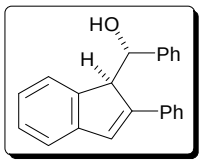
Entry[a]	**1a** (*E*/*Z*)	$[Au]^+$	Solvent	T (ºC)	Conversion (%)	Isolated yield (%)	**3a** (d.r.)
1	1/1	$IPrAuNTf_2$	CH_2Cl_2	rt	0	–	–
2	1/1	$IPrAuNTf_2$	DCE	80	–[b]	–	–
3	1/1	$IPrAuNTf_2$	CH_2Cl_2/dioxane (1/1)	rt	100	90	1/1
4	1/1	$IPrAuNTf_2$	DCE/dioxane (1/1)	80	–[b]	–	–
5	1/0	$IPrAuNTf_2$	CH_2Cl_2/dioxane (1/1)	rt	100	88	1/0
6	1/0	$Ph_3PAuNTf_2$	CH_2Cl_2/dioxane (1/1)	rt	0	–	–
7	1/0	$(PhO)_3PAuCl/AgSbF_6$	CH_2Cl_2/dioxane (1/1)	rt	0	–	–

[a]Reactions conducted using **1a** (0.1 mmol) in the corresponding solvent or solvent mixture (0.8 mL). [b]Decomposition.

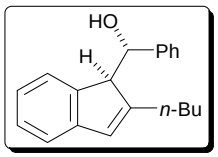
Synthesis and characterization data of hydroxy-functionalized indenes 3:



Water (2.2 mmol, 0.04 mL) was added to a solution of $IPrAuNTf_2$ (0.025 mmol, 6 mg) in a mixture of CH_2Cl_2 (0.4 mL) and dioxane (0.4 mL). After stirring at rt for 5 min, the corresponding starting *o*-(alkynyl)styrene **1** (0.3 mmol) was added in 0.8 mL of the same mixture of solvents and the resulting mixture was stirred overnight (complete consumption of starting material was confirmed by GC-MS). The mixture was diluted with water and extracted with CH_2Cl_2 (3 × 5 mL). The solvent was removed under reduced pressure, and the crude mixture was purified by flash column chromatography on deactivated silica gel using mixtures of hexane and EtOAc as eluents to obtain the corresponding 1-α-hydroxybenzyl-1*H*-indenes **3** in the yields reported in Table 3.

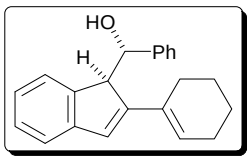


(*S)-Phenyl-[(*R**)-2-phenyl-1*H*-inden-1-yl]methanol (3a):** white oil; R_f = 0.24 (hexane/EtOAc, 50/1); 76% yield (68 mg); obtained and isolated with d.r. > 20/1 starting from (*E*)-**1a** or obtained and isolated with d.r. ~ 1/1 starting from a ~ 1:1 mixture of *E*/*Z* diastereoisomers of **1a**; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.71–7.68 (m, 2H), 7.53–7.31 (m, 10H), 7.19 (s, 1H), 7.03 (dt, J = 7.5, 1.1 Hz, 1H), 6.59 (d, J = 7.5 Hz, 1H), 5.43 (s, 1H), 4.53 (s, 1H), 1.55 (s, 1H) ppm; ^{13}C{^{1}H} NMR (75.4 MHz, $CDCl_3$) δ 148.6 (C), 145.4 (C), 142.6 (C), 142.1 (C), 135.3 (C), 129.4 (CH), 129.0 (2 × CH), 128.3 (2 × CH), 127.9 (CH), 127.7 (CH), 127.3 (CH), 127.1 (2 × CH), 125.9 (2 × CH), 125.0 (CH), 124.7 (CH), 121.5(CH), 72.6 (CH), 57.0 (CH); LRMS (EI) *m/z* (%) 298 (M^+, <1), 192 (100), 165 (38); HRMS data could not be obtained due to decomposition.

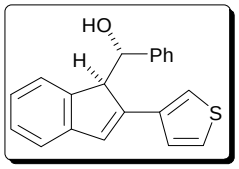


(*S)-[(*S**)-2-Butyl-1*H*-inden-1-yl](phenyl)methanol (3b):** white solid; mp 68–70 ºC; 77% yield (64 mg); obtained and isolated with d.r. > 20/1 starting from (*E*)-**1b** or obtained and isolated with d.r. ~ 1/1 starting from a ~ 1/1 mixture of *E*/*Z* diastereoisomers of **1b**; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.42–7.19 (m, 7H), 6.93 (dt, J = 7.1, 1.7 Hz, 2H), 6.60 (s, 1H), 6.51 (d, J = 3.3 Hz, 1H), 5.34 (s, 1H), 3.86 (d, J = 3.3 Hz, 1H), 2.64–2.43 (m, 2H), 1.71–1.61 (m, 2H), 1.48–1.45 (m, 2H), 1.02 (t, J = 7.3 Hz, 3H) ppm; ^{13}C{^{1}H} NMR (75.4 MHz, $CDCl_3$) δ 151.4 (C), 145.8 (C), 142.7 (C), 141.6 (C), 128.3 (2 × CH), 128.0 (CH), 127.4 (CH), 127.3 (CH), 125.9 (2 × CH), 124.7 (CH), 123.6 (CH), 120.3 (CH),

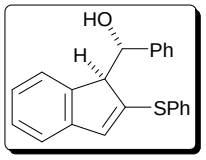
72.4 (CH), 58.3 (CH), 31.1 (CH_2), 29.4 (CH_2), 22.8 (CH_2), 14.1 (CH_3) ppm; LRMS and HRMS data could not be obtained due to decomposition.



(*S)-[(*S**)-2-(Cyclohex-1-en-1-yl)-1*H*-inden-1-yl](phenyl)methanol (3c):** yellow oil; R_f = 0.24 (hexane/EtOAc, 50/1); 70% yield (63 mg); obtained and isolated with d.r. > 20/1 starting from (*E*)-**1c**; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.47–7.19 (m, 7H), 6.94 (dt, J = 7.4, 1.3 Hz, 1H), 6.80 (s, 1H), 6.43–6.33 (m, 1H), 6.21 (bs, 1H), 5.50 (dd, J = 5.6, 2.7 Hz, 1H), 4.28 (d, J = 2.7 Hz, 1H), 2.65–2.52 (m, 1H), 2.37–2.33 (m, 3H), 1.87–1.70 (m, 4H), 1.50 (d, J = 5.6 Hz, 1H) ppm; ^{13}C{^{1}H} NMR (75.4 MHz, $CDCl_3$) δ 149.8 (C), 145.6 (C), 142.9 (C), 141.9 (C), 132.3 (C), 128.2 (2 × CH), 127.6 (CH), 127.5 (CH), 127.2 (CH), 126.5 (CH), 125.8 (2 × CH), 124.8 (CH),124.2 (CH), 121.1 (CH), 73.7 (CH), 56.1 (CH), 26.7 (CH_2), 26.2 (CH_2), 22.8 (CH_2), 22.3 (CH_2) ppm; LRMS (EI) *m/z* (%) 302 (M^+, <1), 196 (100); HRMS (ESI) calcd for $C_{22}H_{23}ONa^+$ [(M+Na)$^+$] 325.1563, found 325.1563.

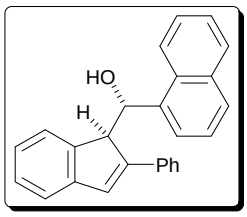


(*S)-Phenyl[(*R**)-2-(thiophen-3-yl)-1*H*-inden-1-yl]methanol (3d):** white solid; mp 140–142 ºC; 75% yield (68 mg); obtained and isolated with d.r. > 20/1 starting from (*E*)-**1d**; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.56–7.22 (m, 10H), 7.13–6.98 (m, 2H), 6.59 (d, J = 7.5 Hz, 1H), 5.53 (dd, J = 5.5, 2.6 Hz, 1H), 4.38 (d, J = 2.6 Hz, 1H), 1.69 (d, J = 5.5 Hz, 1H) ppm; ^{13}C{^{1}H} NMR (75.4 MHz, $CDCl_3$) δ 145.3 (C), 143.3 (C), 142.3 (C), 141.8 (C), 137.1 (C), 128.6 (CH), 128.2 (2 × CH), 127.7 (CH), 127.3 (CH), 126.6 (CH), 126.3 (CH), 125.8 (2 × CH), 124.8 (CH), 124.5 (CH), 121.5 (CH), 121.3 (CH), 73.2 (CH), 57.7 (CH) ppm; LRMS (EI) *m/z* (%) 304 (M^+, <1), 198 (100), 165 (45); HRMS (ESI) calcd for $C_{20}H_{17}OS^+$ [(M+H)$^+$] 305.0995, found 305.0997.

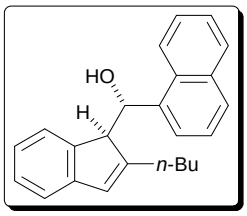


(*S)-Phenyl[(*S**)-2-(phenylthio)-1*H*-inden-1-yl]methanol (3e):** yellow oil; R_f = 0.23 (hexane/EtOAc, 50/1); 60% yield (59 mg) (~80% conversion); obtained and isolated with d.r. > 20/1 starting from (*E*)-**1e**; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.62–7.59 (m, 3H), 7.46–7.35 (m, 7H), 7.30–7.23 (m, 3H), 6.98 (ddd, J = 7.5, 5.5, 3.2 Hz, 1H), 6.77 (s, 1H), 6.52 (d, J = 7.5 Hz, 1H), 5.56 (dd, J = 5.5, 3.2 Hz, 1H), 4.03 (d, J = 3.2 Hz, 1H) ppm; ^{13}C{^{1}H} NMR (75.4 MHz, $CDCl_3$) δ 144.6 (C), 143.6 (C), 141.9 (C), 136.7 (CH), 133.7 (C), 132.6 (CH), 123.5 (2 × CH), 131.5 (C), 129.5 (2 × CH), 128.9 (CH), 128.2 (2 × CH), 127.7 (CH), 127.3 (CH), 125.8 (2 × CH), 124.6 (CH), 124.4 (CH), 120.4 (CH), 72.8 (CH), 59.0

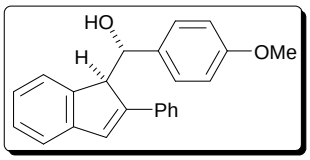
(CH) ppm; LRMS (EI) *m/z* (%) 330 (M^+, <1), 224 (78), 115 (100); HRMS (ESI) calcd for $C_{22}H_{19}OS^+$ [$(M+H)^+$]: 331.1151, found 331.1148.



(*S)-(Naphthalen-1-yl)[(*R**)-2-phenyl-1H-inden-1-yl]methanol (3h):** white solid; mp 131–133 ºC; 79% yield (82 mg); obtained and isolated with d.r. > 20/1 starting from (*E*)-**1h**; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.30 (d, J = 8.4 Hz, 1H), 8.03 (d, J = 8.0 Hz, 1H), 7.94–7.91 (m, 1H), 7.75–7.33 (m, 12H), 7.21 (s, 1H), 7.00 (t, J = 7.4 Hz, 1H), 6.21 (d, J = 7.1 Hz, 1H), 5.94 (d, J = 7.1 Hz, 1H), 4.65 (bs, 1H) ppm; ^{13}C{^{1}H} NMR (75.4 MHz, $CDCl_3$) δ 149.4 (C), 145.2 (C), 142.1 (C), 137.5 (C), 135.7 (C), 133.8 (C), 130.0 (CH), 129.4 (CH), 129.0 (2 × CH), 128.1 (CH), 128.0 (CH), 127.5 (CH), 127.2 (CH), 126.2 (2 × CH), 125.9 (CH), 125.5 (CH), 125.2 (CH),124.7 (CH), 124.3 (CH), 122.6 (CH), 121.3 (CH), 69.7 (CH), 55.7 (CH) ppm; LRMS (EI) *m/z* (%) 348 (M^+, <1), 228 (100); HRMS (ESI) calcd for $C_{26}H_{20}ONa^+$ [$(M+Na)^+$] 371.1406, found 371.1408.

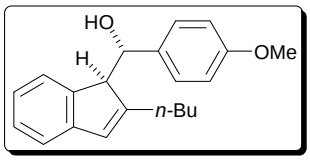


(*S)-[(*S**)-2-Butyl-1*H*-inden-1-yl](naphthalen-1-yl)methanol (3i):** white solid; mp 81–83 ºC; 53% yield (52 mg); obtained and isolated with d.r. > 20/1 starting from (*E*)-**1i**; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.19 (d, J = 8.2 Hz, 1H), 8.03–7.92 (m, 2H), 7.65–7.59 (m, 4H), 7.31–7.20 (m, 2H), 6.89 (t, J = 7.4 Hz, 1H), 6.71 (s, 1H), 6.19 (d, J = 7.5 Hz, 1H), 6.09–6.06 (m, 1H), 4.07 (s, 1H), 2.74–2.64 (m, 2H), 1.84–1.78 (m, 2H), 1.69 (d, J = 4.8 Hz, 1H), 1.57–1.50 (m, 2H), 1.06 (t, J = 7.3 Hz, 3H); ^{13}C{^{1}H} NMR (75.4 MHz, $CDCl_3$) δ 151.4 (C), 145.9 (C), 141.4 (C), 137.7 (C), 133.9 (C), 130.0 (C), 129.5 (CH), 128.3 (CH), 128.2 (CH), 127.4 (CH), 126.3 (CH), 125.7 (CH), 125.5 (CH), 125.4 (CH), 124.4 (CH), 123.5 (CH), 122.4 (CH), 120.3 (CH), 69.3 (CH), 57.0 (CH), 31.2 (CH_2), 29.3 (CH_2), 22.8 (CH_2), 14.2 (CH_3); LRMS (EI) *m/z* (%) 328 (M^+, <1), 308 (100); HRMS (ESI) calcd for $C_{24}H_{25}O^+$ [$(M+H)^+$] 327.1743, found 327.1758.



(*S)-(4-Methoxyphenyl)[(*R**)-2-phenyl-1*H*-inden-1-yl]methanol (3l):** yellow oil; R_f = 0.20 (hexane/EtOAc, 50/1); 65% yield (60 mg); obtained with d.r. ~ 3.5/1 and isolated with d.r. = 7/1 starting from (*E*)-**1l**. Data for the *(S*,R*)* diastereoisomer; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.67–7.64 (m, 2H), 7.47–7.31 (m, 7H), 7.29 (s, 1H), 7.17 (s, 1H), 7.03 (td, J = 7.5, 7.5, 1.2 Hz, 1H), 6.94 (d, J = 8.8 Hz, 1H), 6.66 (d, J = 7.5 Hz, 1H), 5.38–5.36 (m, 1H), 4.49 (d, J = 3.0 Hz, 1H), 3.88 (s, 3H), 1.47 (d, J = 5.5 Hz, 1H) ppm; ^{13}C{^{1}H} NMR (75.4 MHz, $CDCl_3$) δ 158.8 (C), 148.5

(C), 145.2 (C), 142.2 (C), 135.4 (C), 134.6 (C), 129.3 (CH), 128.9 (2 × CH), 127.8 (CH), 127.6 (CH), 127.0 (2 × CH), 126.9 (2 × CH), 124.9 (CH), 124.6 (CH), 121.3 (CH), 113.5 (2 × CH), 72.4 (CH), 57.0 (CH), 55.3 (CH_3) ppm; LRMS (EI) *m/z* (%) 308 (M^+, <1), 288 (100), 165 (91); HRMS data could not be obtained due to decomposition.



(*S)-[(*S**)-2-Butyl-1*H*-inden-1-yl](4-methoxyphenyl)methanol (3m):** yellow oil; R_f = 0.26 (hexane/EtOAc, 50/1); 63% yield (58 mg); obtained and isolated with d.r. > 20/1 starting from (*E*)-**1m**; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.36–7.24 (m, 4H), 6.99–6.96 (m, 3H), 6.65–6.61 (m, 2H), 5.33–5.30 (m, 1H), 3.89–3.84 (m, 4H), 2.59–2.49 (m, 2H), 1.69–1.61 (m, 3H), 1.49–1.46 (m, 2H), 1.02 (t, J = 7.3 Hz, 3H) ppm; ^{13}C{^{1}H} NMR (75.4 MHz, $CDCl_3$) δ 158.8 (C), 151.5 (C), 145.8 (C), 141.9 (C), 134.7 (C), 128.0 (CH), 127.3 (CH), 127.0 (2 × CH), 124.8 (CH), 123.6 (CH), 120.0 (CH), 113.6 (2 × CH), 72.3 (CH), 58.3 (CH), 55.4 (CH_3), 31.1 (CH_2), 29.5 (CH_2), 22.7 (CH_2), 14.1 (CH_3) ppm; LRMS and HRMS data could not be obtained due to decomposition.

ORTEP plot and crystallographic data for compound 3i:

Complete crystallographic data for compound **3i** has been deposited in the Cambridge Crystallographic Data Centre (CCDC) with deposition number 1585617.

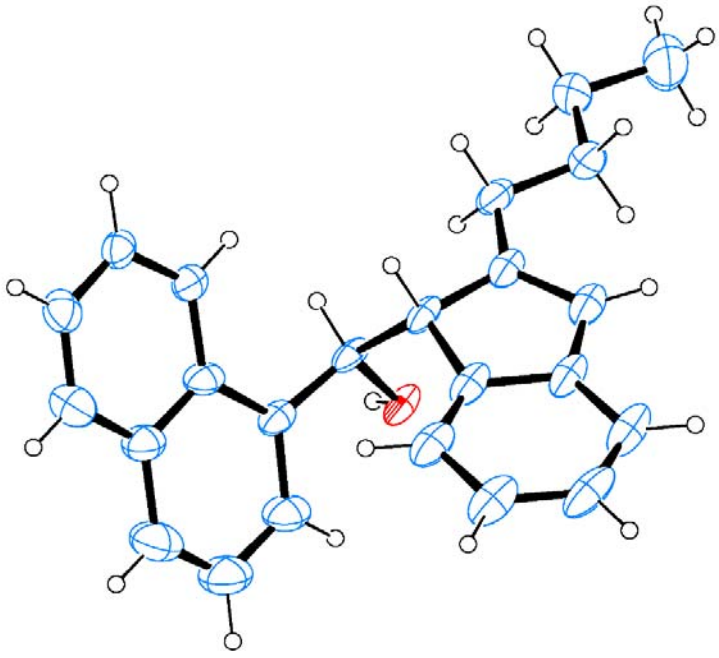


Figure S1. The ORTEP plot of the crystal structure of **3i**.

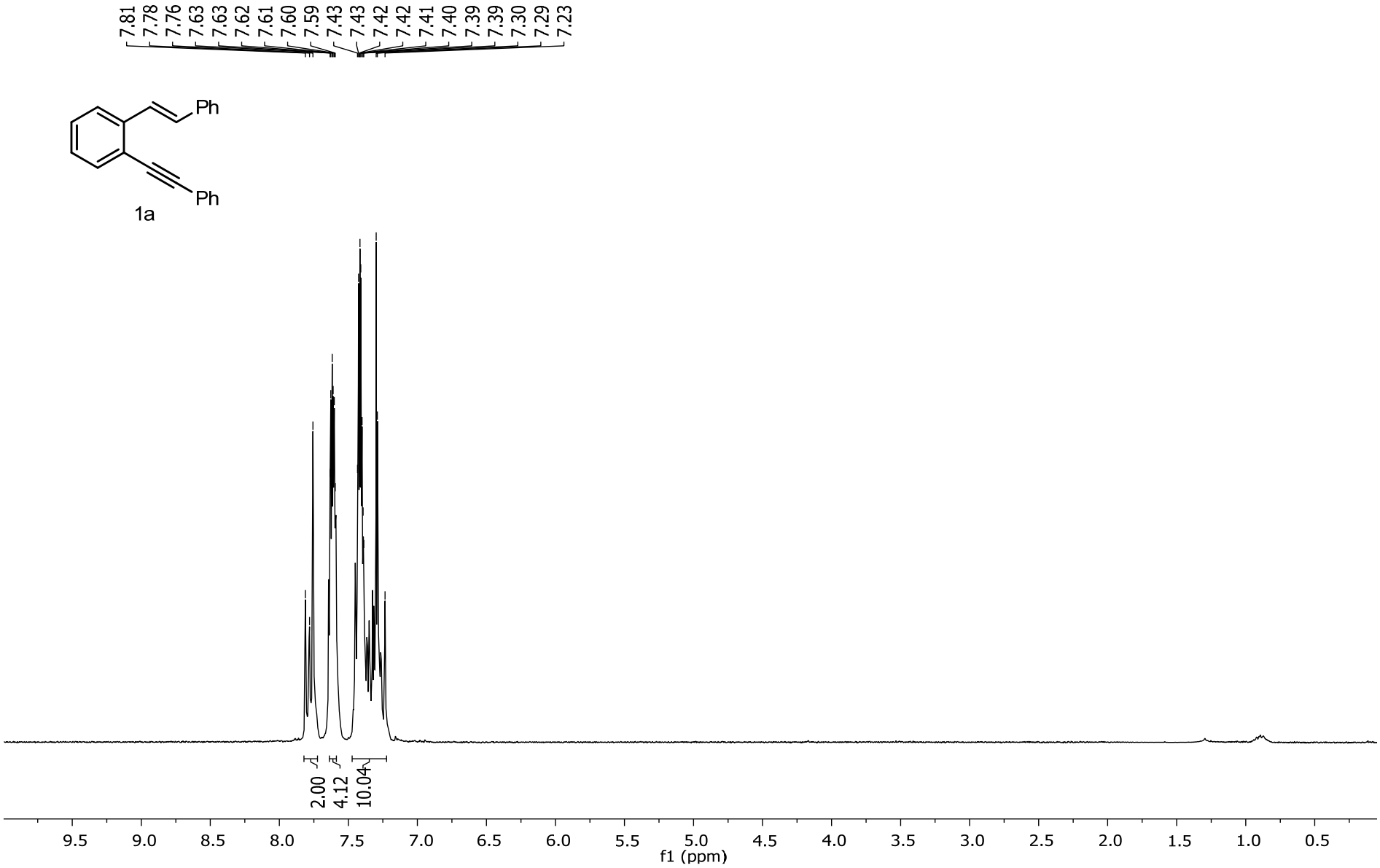
A clear colourless plate-like specimen of C24H24O, approximate dimensions 0.102 mm × 0.268 mm × 0.337 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured on a κ-geometry diffractometer system equipped with a graphite monochromator and a MoKα sealed x-ray tube (λ = 0.71073 Å). A total of 2414 frames were collected. The total exposure time was 26.82 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a triclinic unit cell yielded a total of 24985 reflections to a maximum θ angle of 25.41° (0.83 Å resolution), of which 24985 were independent (average redundancy 1.000, completeness = 99.7%, Rsig = 10.89%) and 12296 (49.21%) were greater than 2σ(F2). The final cell constants of a = 16.3273(7) Å, b = 16.8364(8) Å, c = 17.1138(8) Å, α = 89.826(2)°, β = 66.421(2)°, γ = 65.168(2)°, volume = 3835.3(3) $Å^3$, are based upon the refinement of the XYZ-centroids of 7611 reflections above 20 σ(I) with 4.816° < 2θ < 43.21°. Data were corrected for absorption effects using the Multi-Scan method (TWINABS). The ratio of minimum to maximum apparent transmission was 0.863. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.9780 and 0.9930.

Crystal system triclinic Space group P-1 Unit cell dimensions a = 16.3273(7) Å α = 89.826(2)° b = 16.8364(8) Å β = 66.421(2)° c = 17.1138(8) Å γ = 65.168(2)° Volume 3835.3(3) $Å^3$ Z 8 Density (calculated) 1.138 g/cm^3 Absorption coefficient 0.067 mm^{-1}; F(000) 1408.

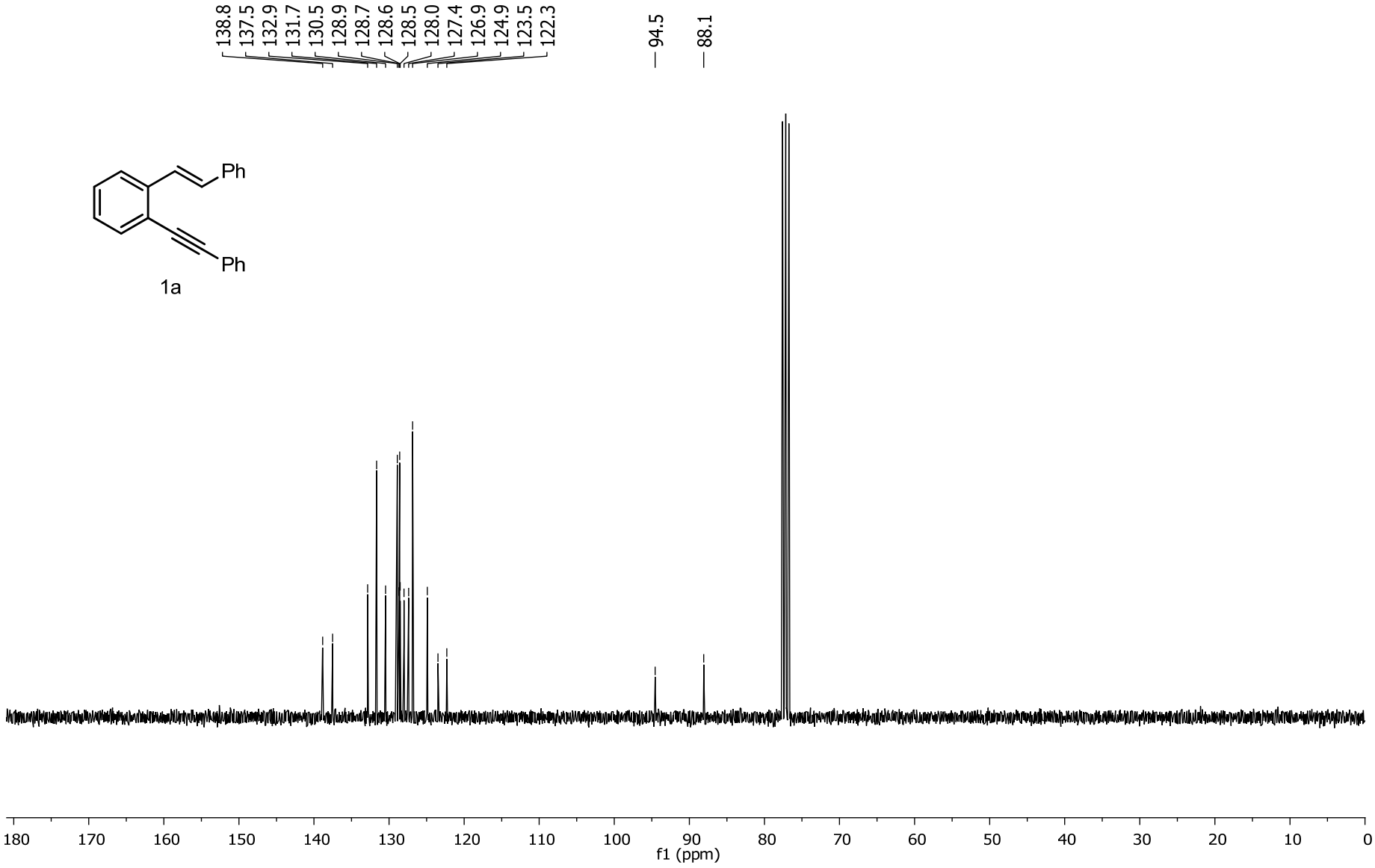
Diffractometer κ-geometry diffractometer Radiation source sealed x-ray tube, MoKα Theta range for data collection 1.32 to 25.41° Reflections collected 24985 Coverage of independent reflections 99.7% Absorption correction Multi-Scan Max. and min. transmission 0.9930 and 0.9780 Structure solution technique direct methods Structure solution program SHELXT-2014 (Sheldrick, 2014) Data / restraints / parameters 24985 / 831 / 950 Goodness-of-fit on F2 1.010 Final R indices 12296 data; I>2σ(I) R1 = 0.0676, wR2 = 0.1614 all data R1 = 0.1647, wR2 = 0.2016 Weighting scheme w=1/[σ2(Fo 2)+(0.0962P)2] where P=(Fo 2+2Fc 2)/3 Largest diff. peak and hole 0.267 and -0.254 eÅ-3 R.M.S. deviation from mean 0.050 eÅ-3.

^{1}H, ^{13}C and selected 2D NMR Spectra

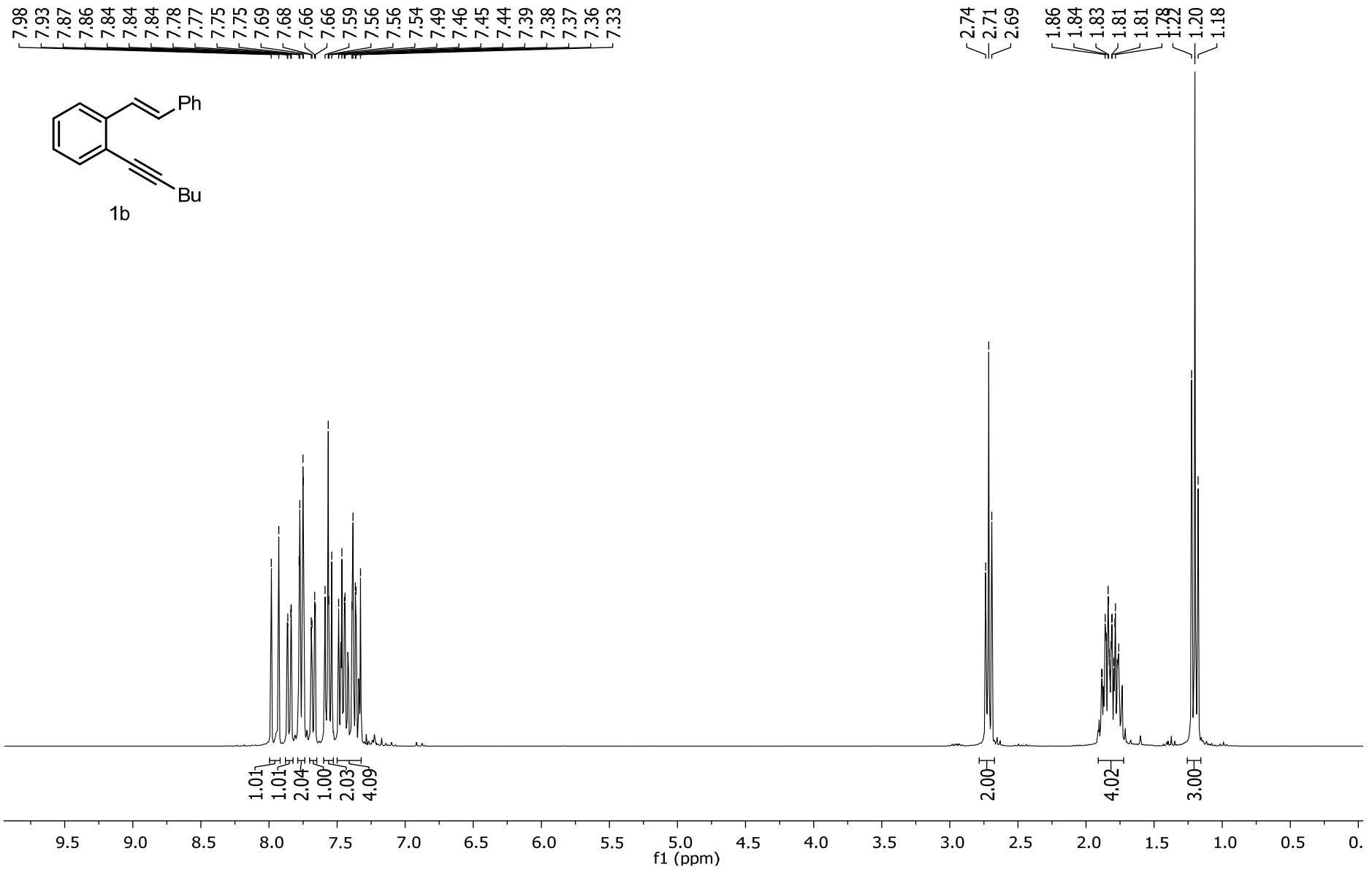
^{1}H NMR (300 MHz, $CDCl_3$)



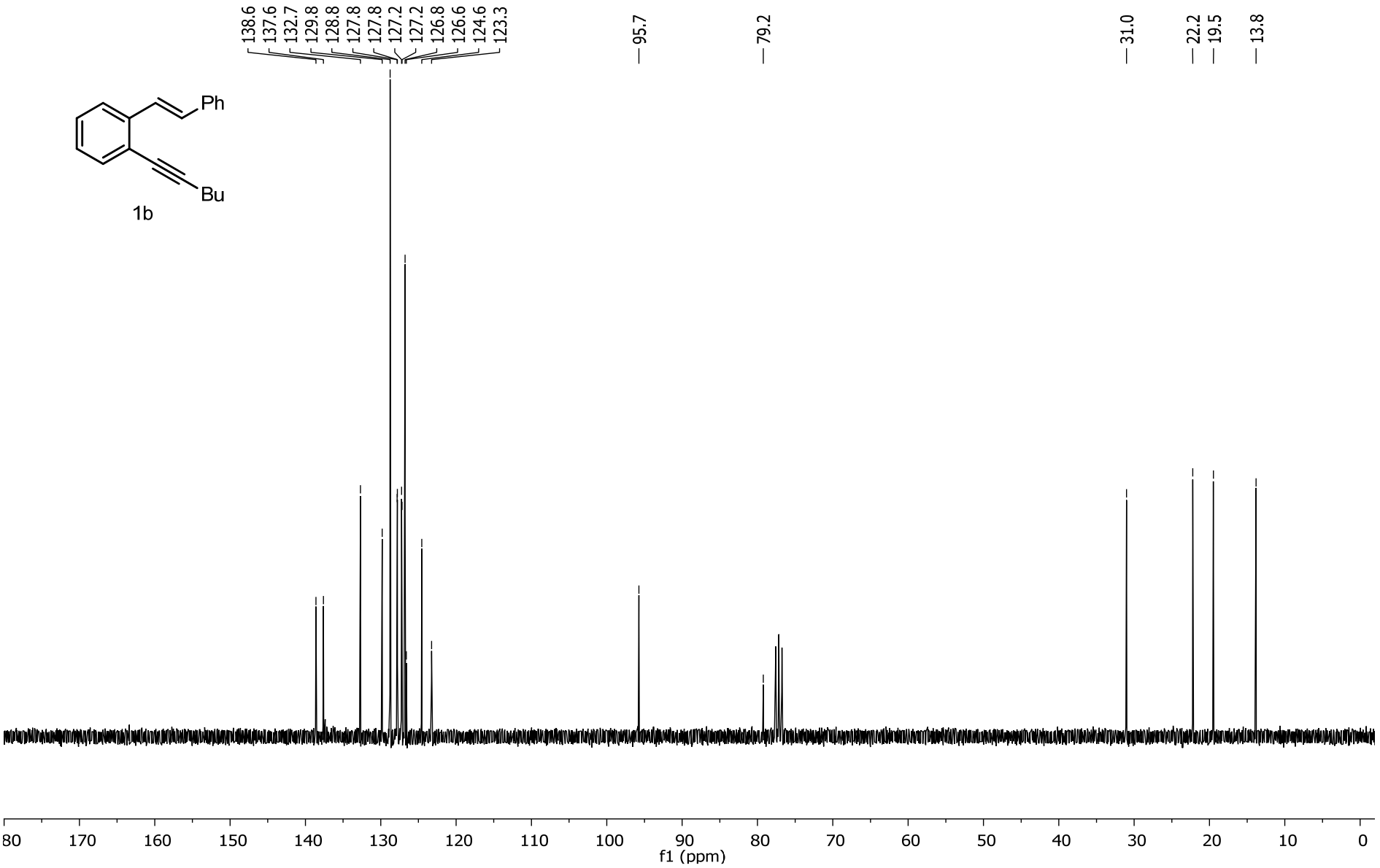
$^{13}C\{^{1}H\}$NMR (75.4 MHz, $CDCl_3$)



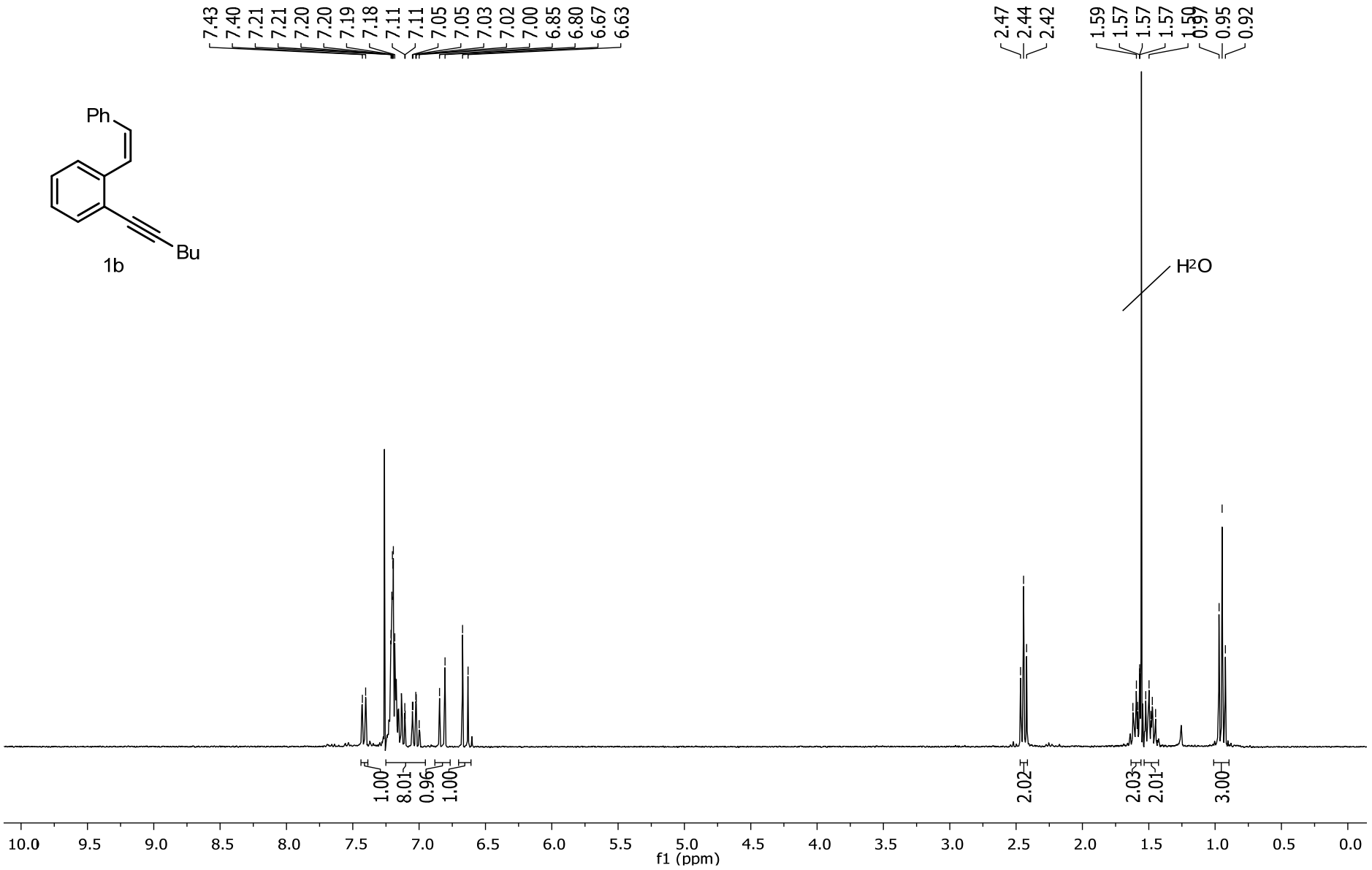
^{1}H NMR (300 MHz, $CDCl_3$)



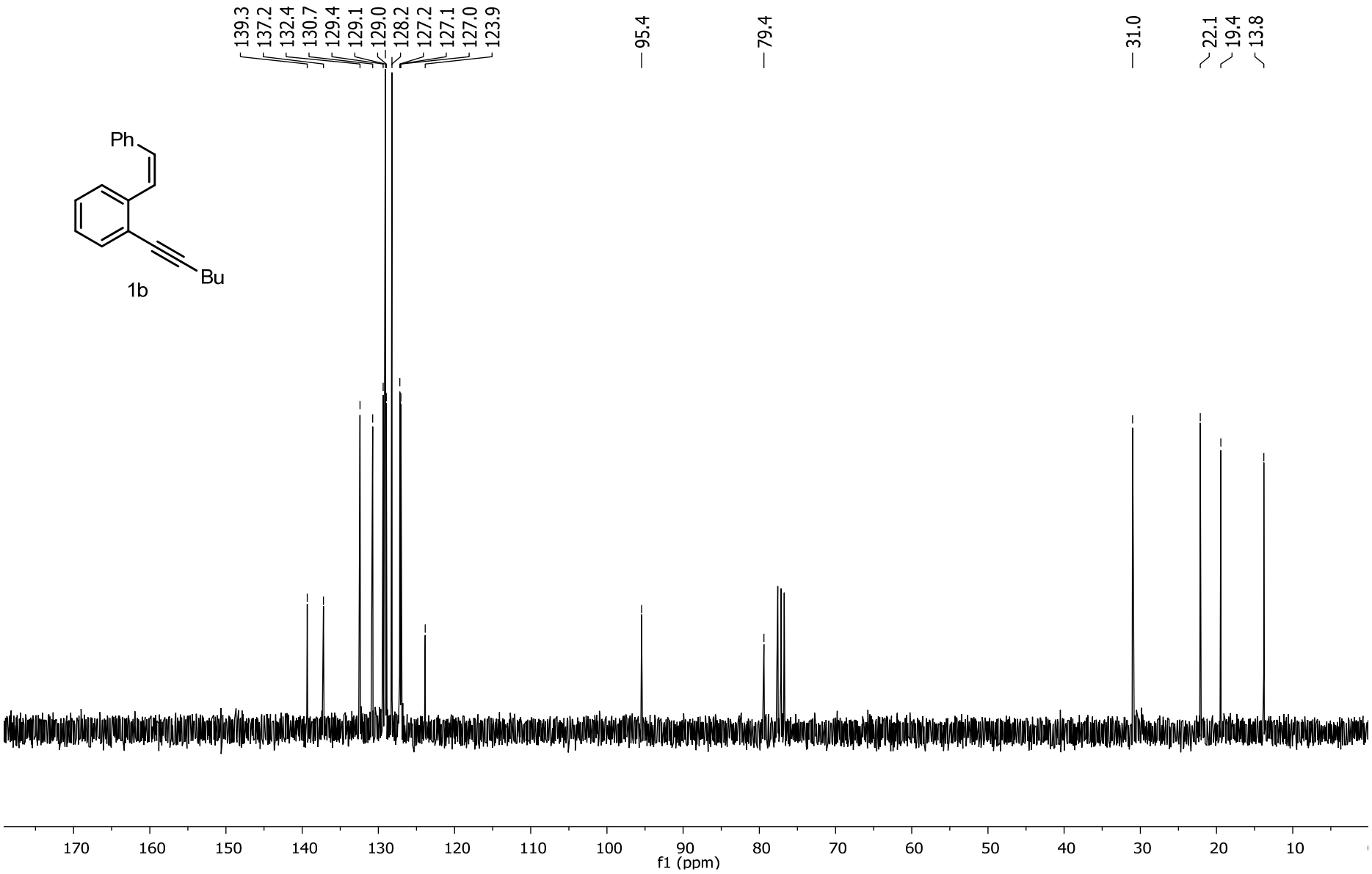
$^{13}C\{^{1}H\}$NMR (75.4 MHz, $CDCl_3$)



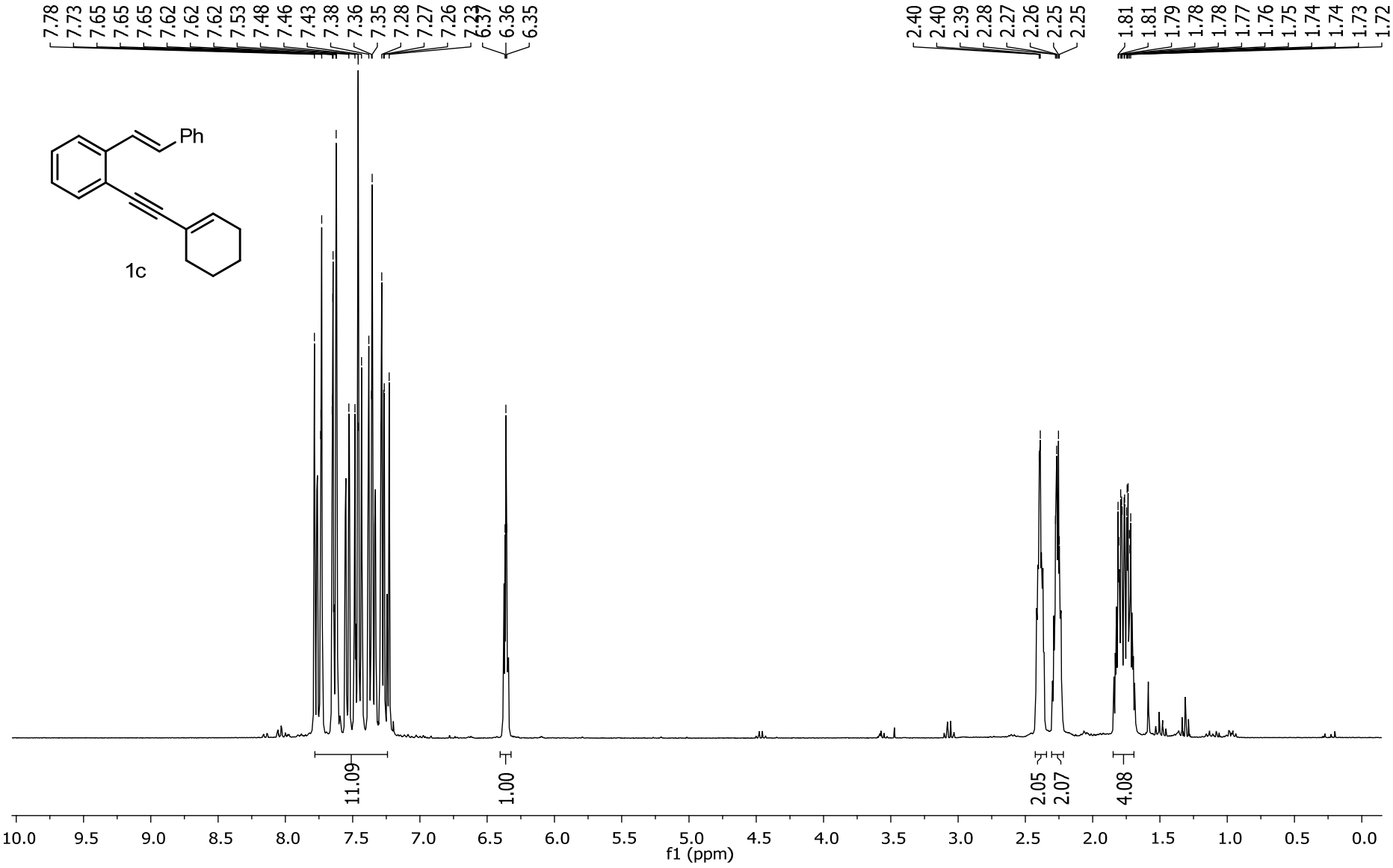
^{1}H NMR (300 MHz, $CDCl_3$)



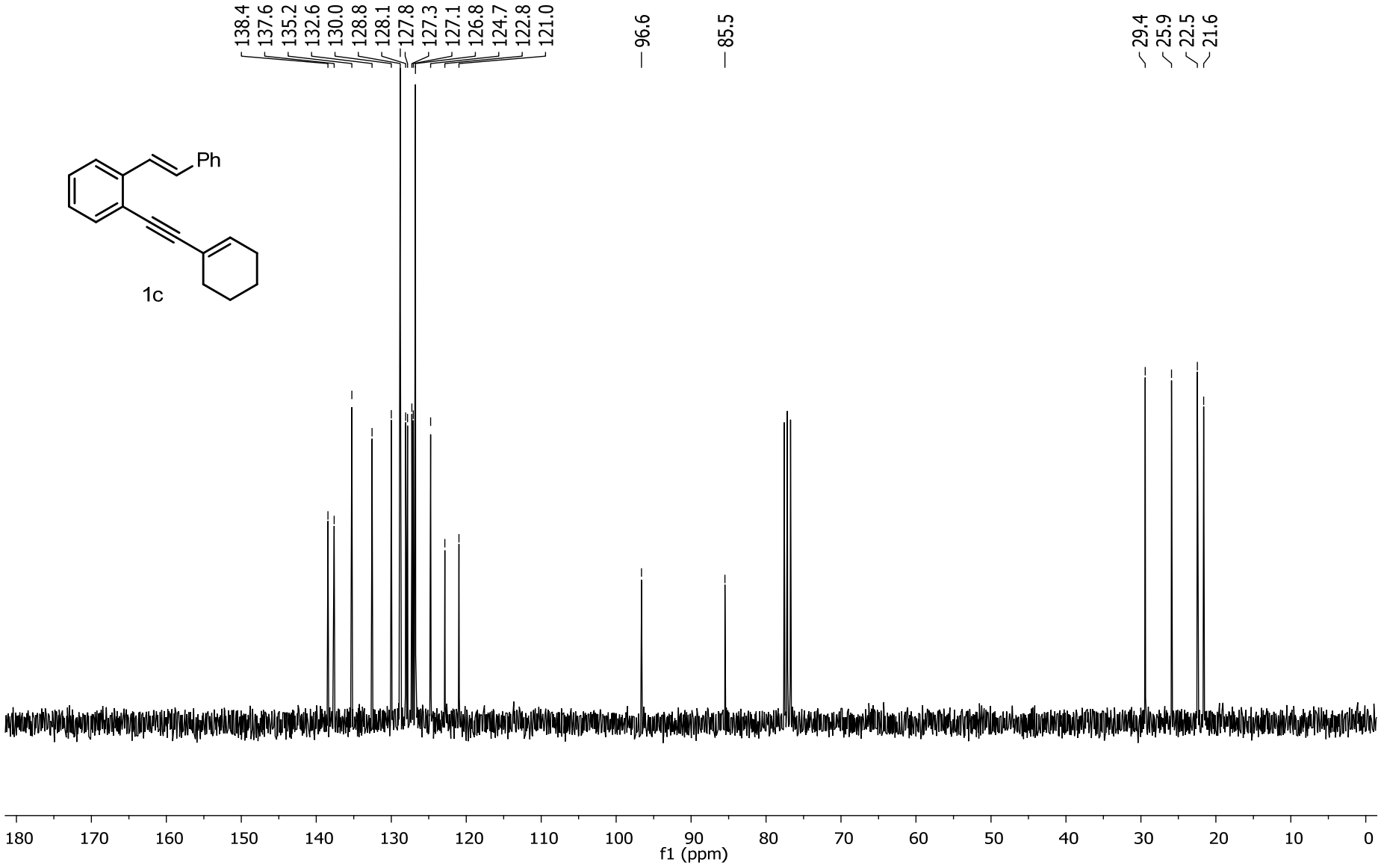
$^{13}C\{^{1}H\}$NMR (75.4 MHz, $CDCl_3$)



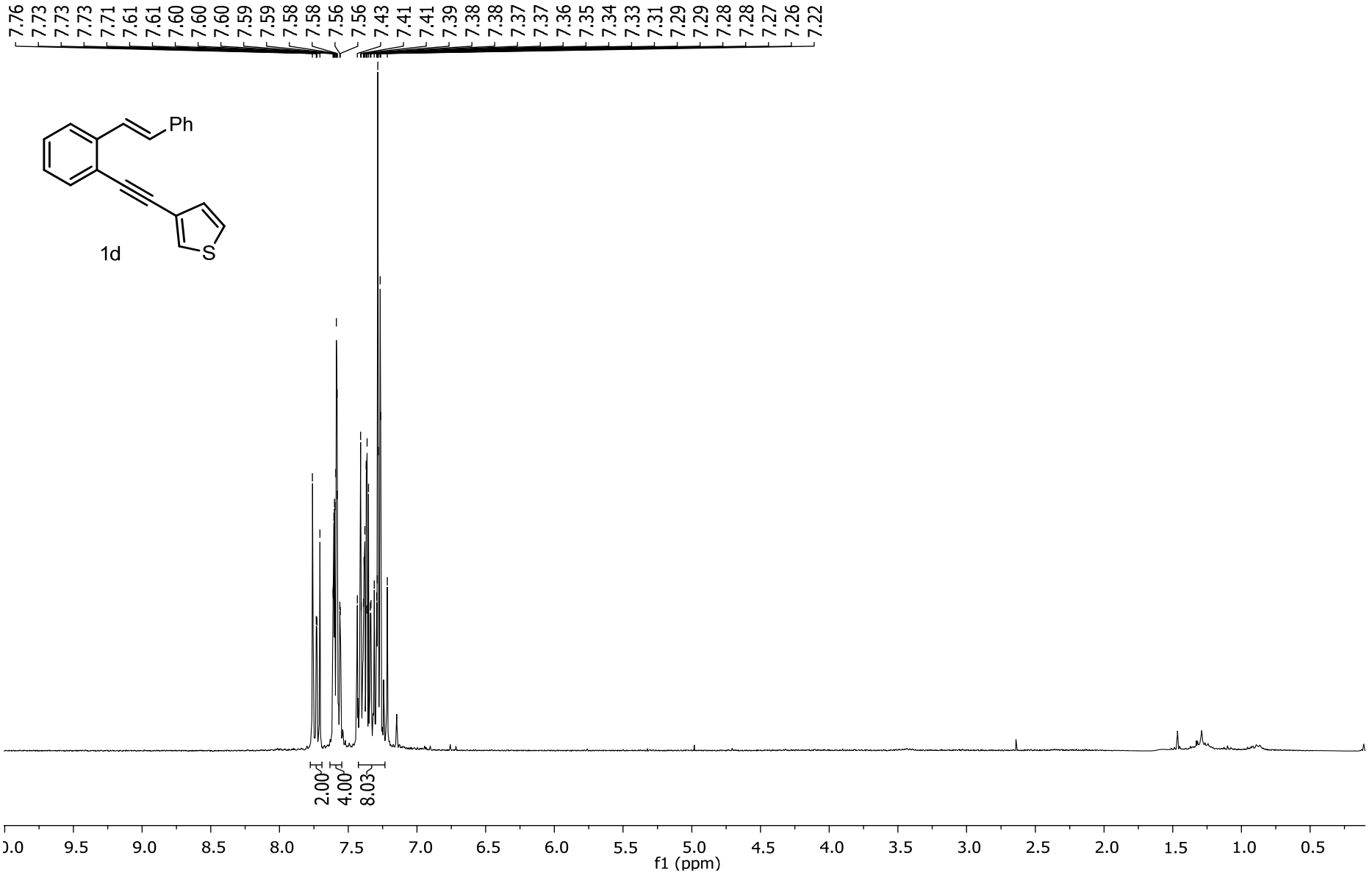
^{1}H NMR (300 MHz, $CDCl_3$)



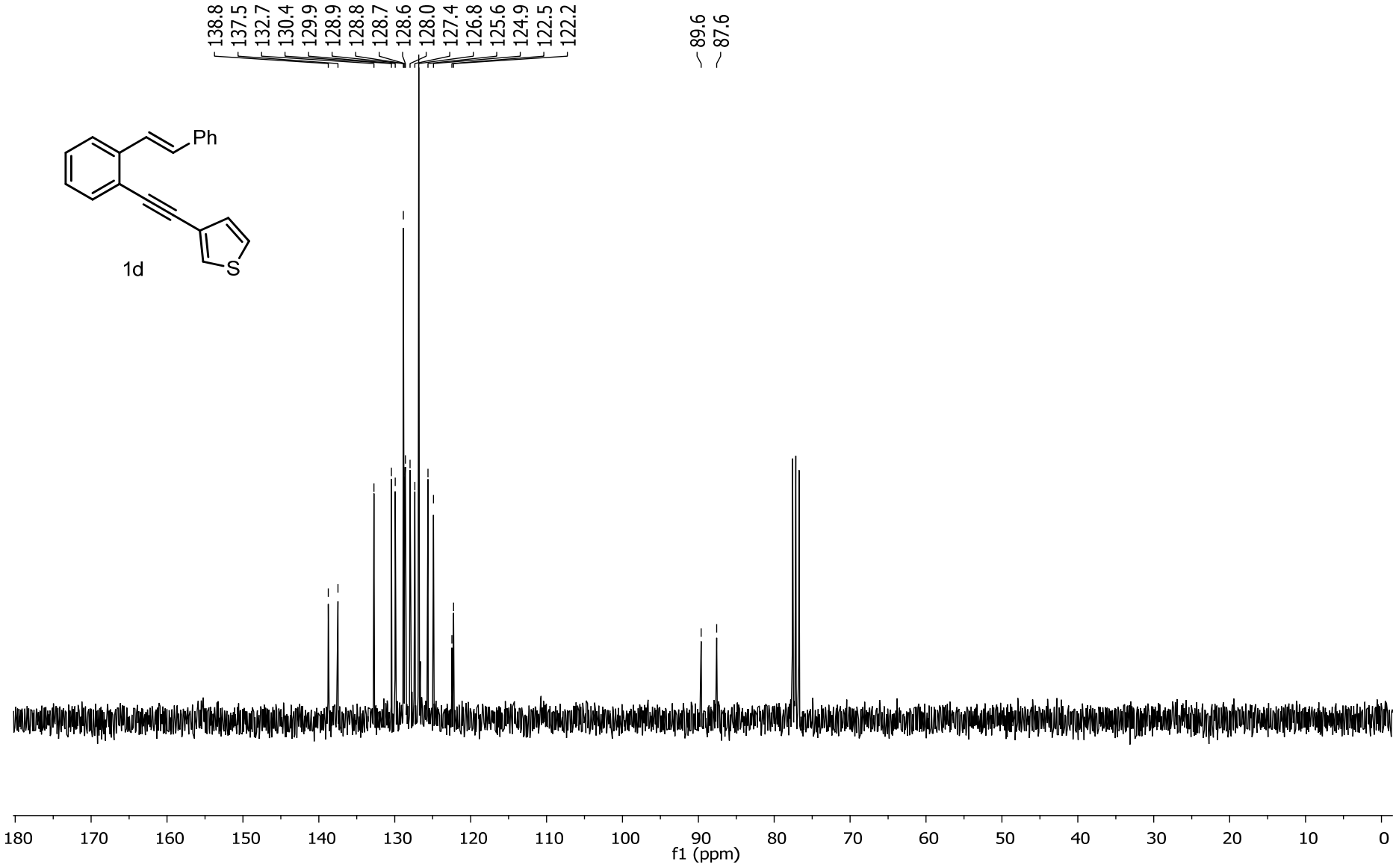
$^{13}C\{^{1}H\}$NMR (75.4 MHz, $CDCl_3$)



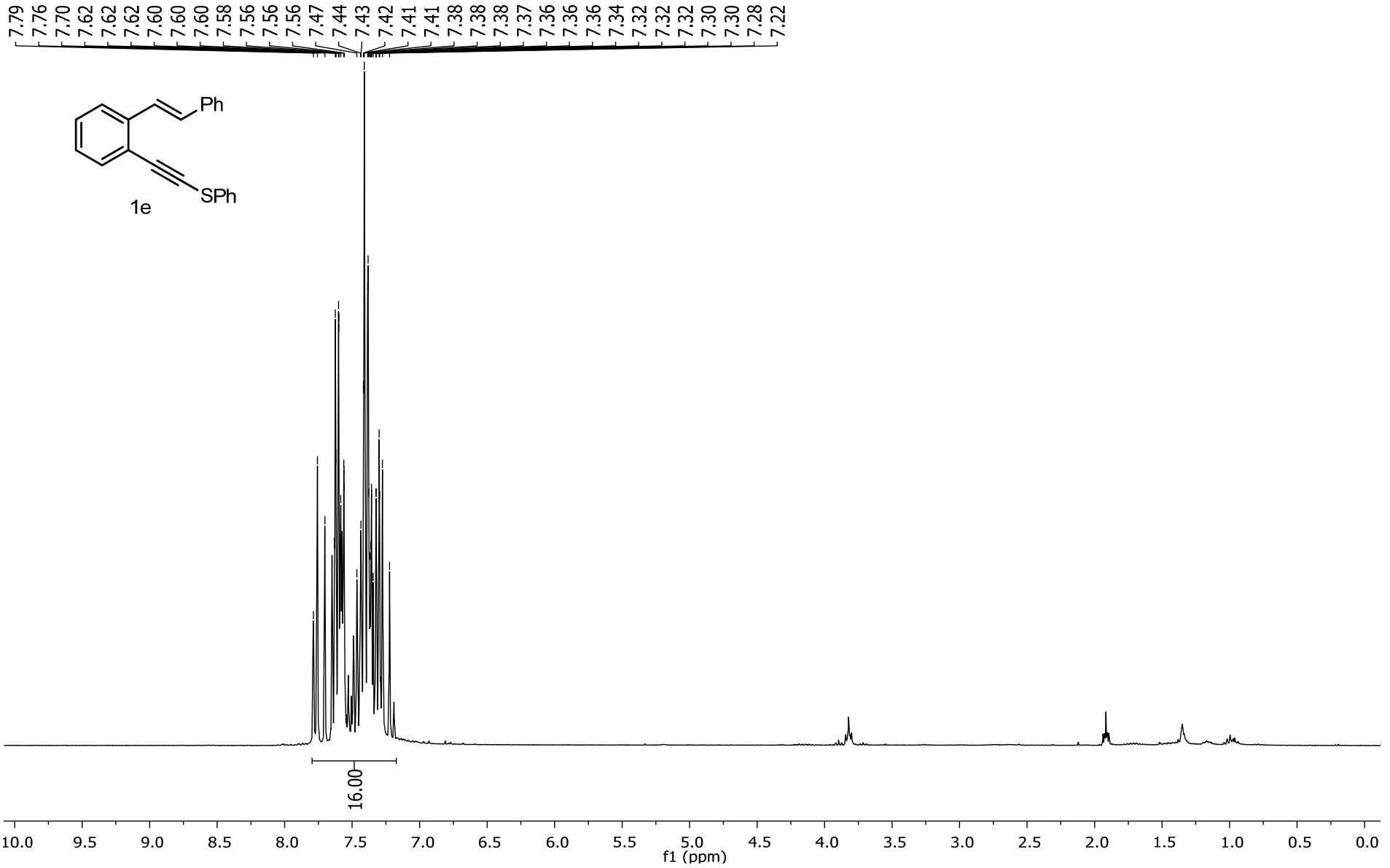
^{1}H NMR (300 MHz, $CDCl_3$)



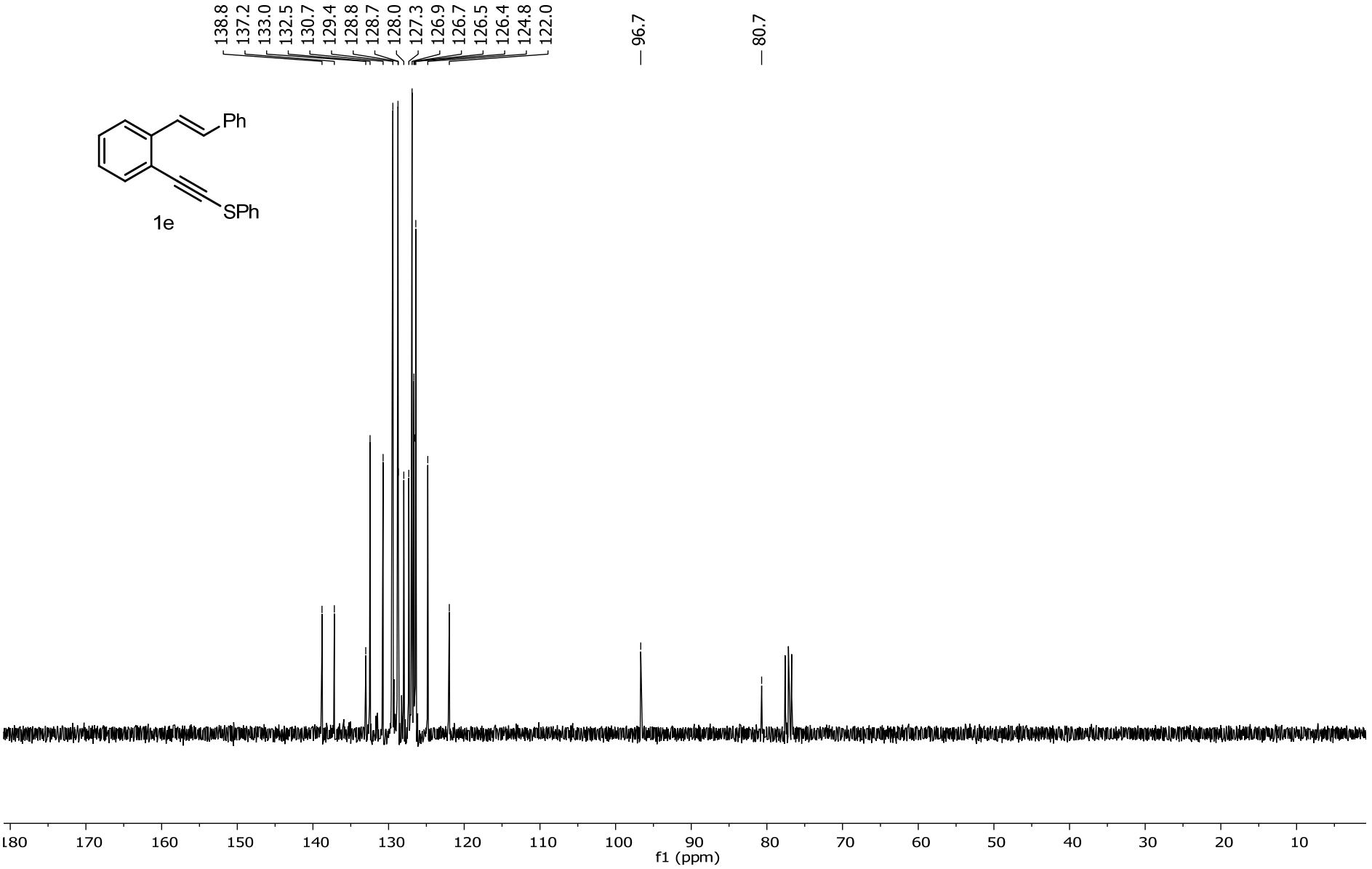
$^{13}C\{^{1}H\}$NMR (75.4 MHz, $CDCl_3$)



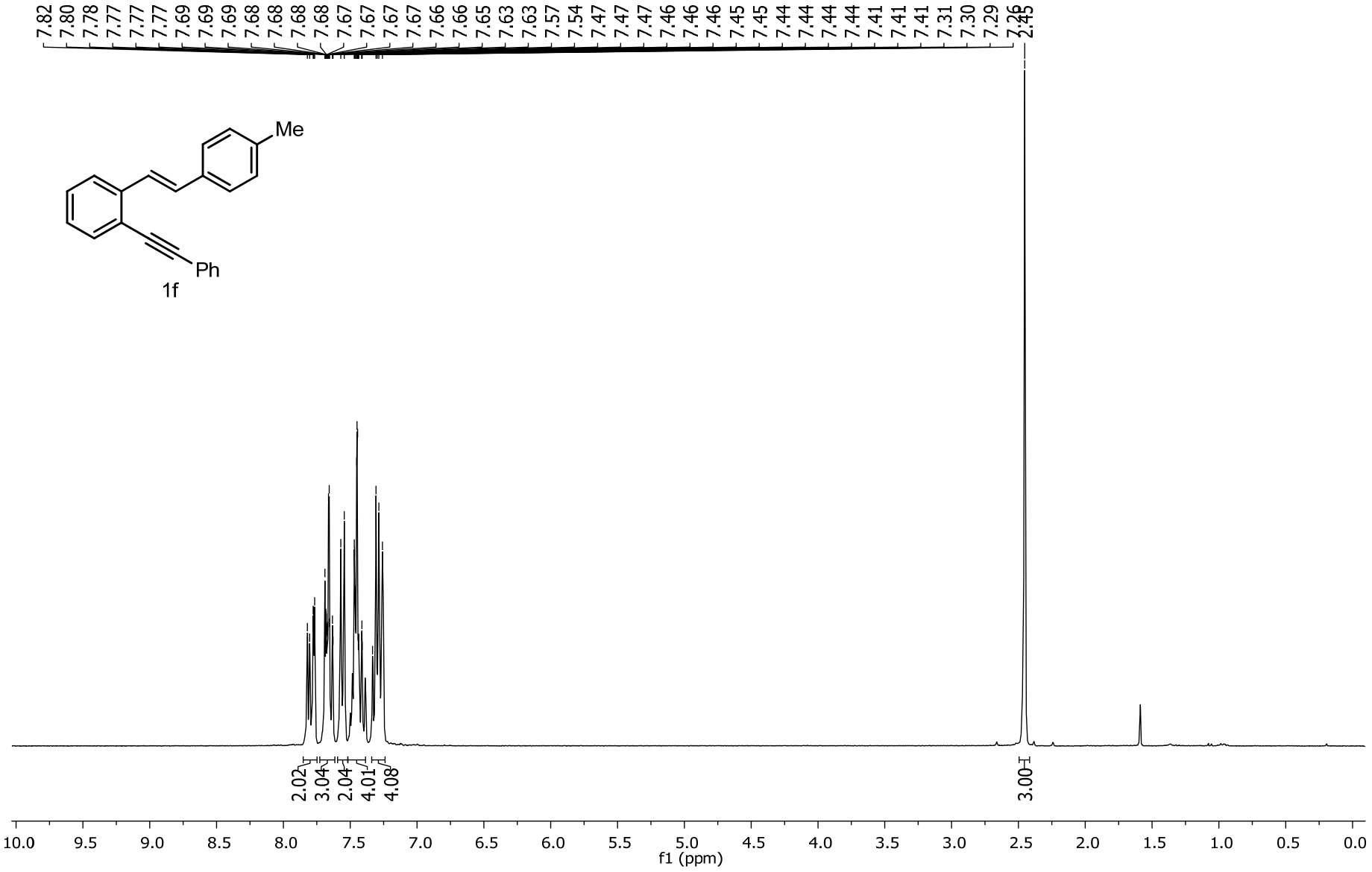
^{1}H NMR (300 MHz, $CDCl_3$)



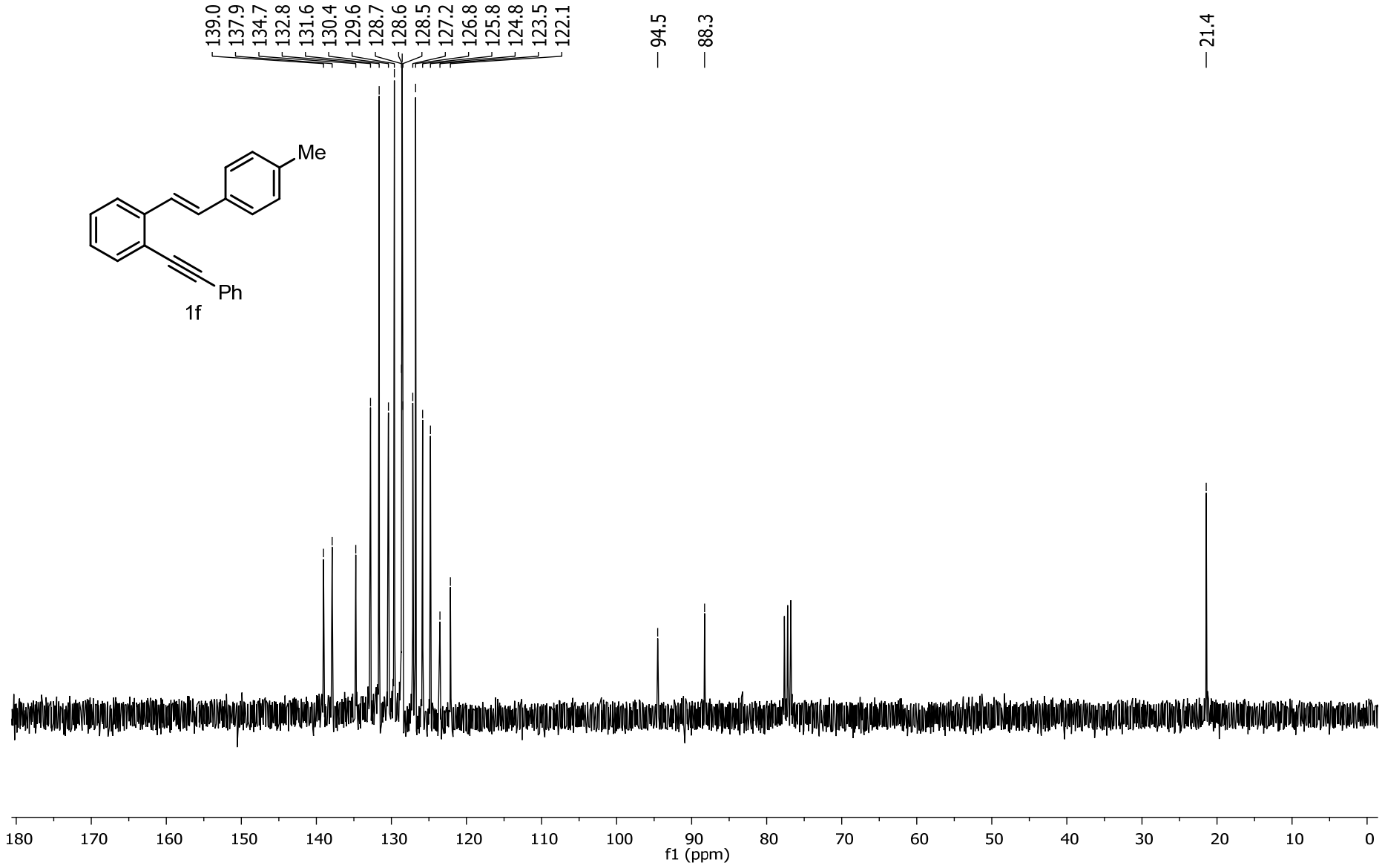
$^{13}C\{^{1}H\}$NMR (75.4 MHz, $CDCl_3$)



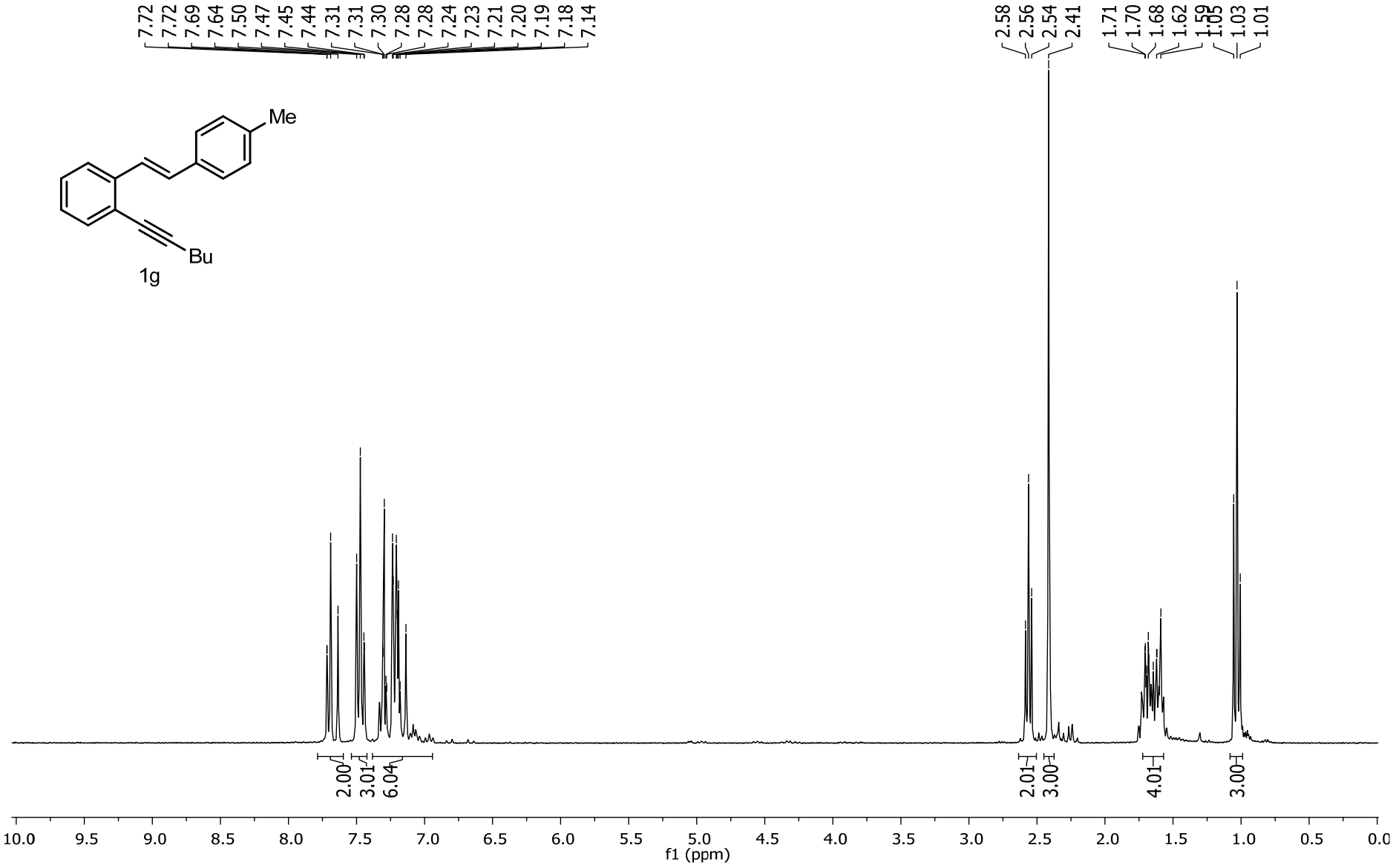
^{1}H NMR (300 MHz, $CDCl_3$)



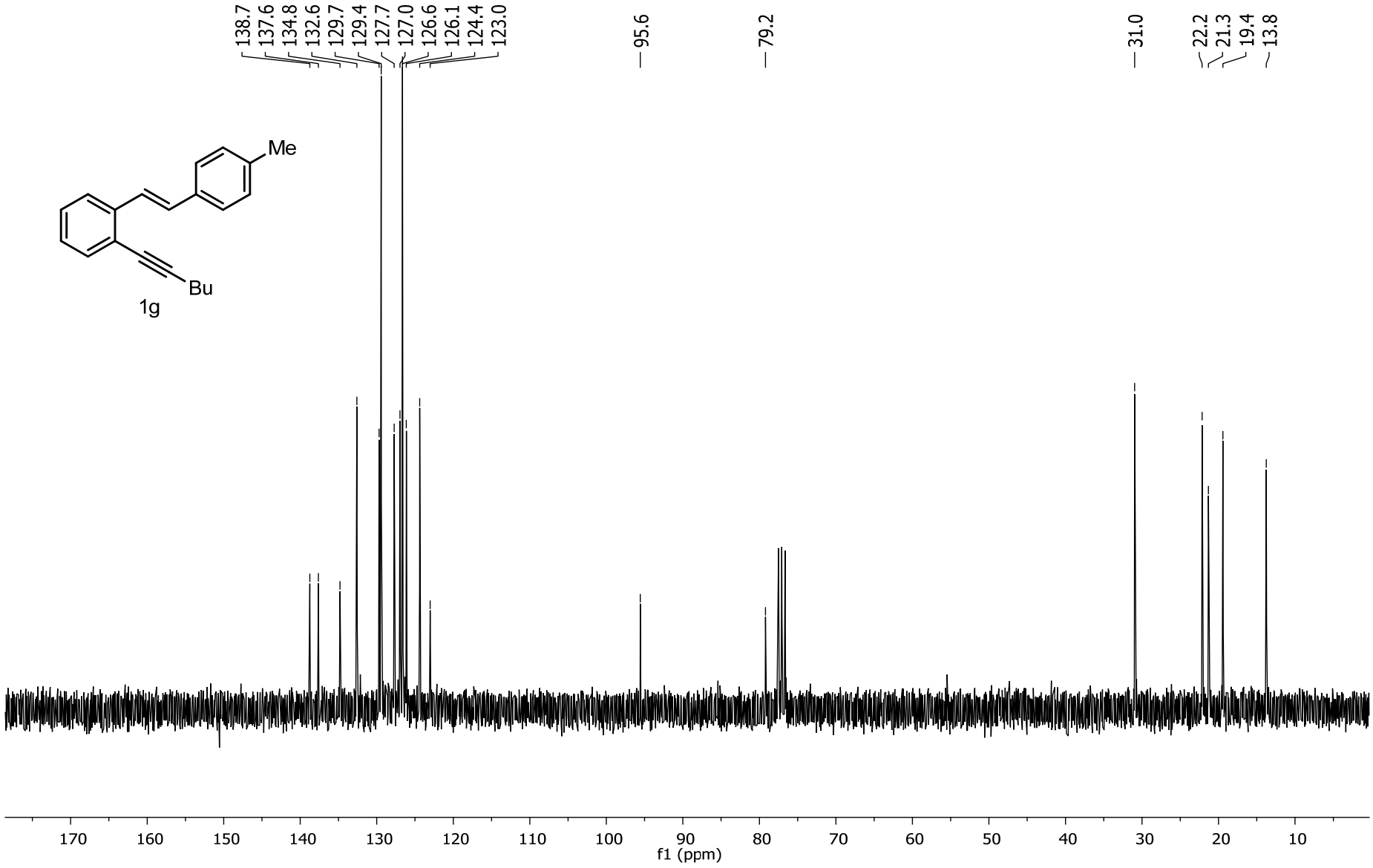
$^{13}C\{^{1}H\}$NMR (75.4 MHz, $CDCl_3$)



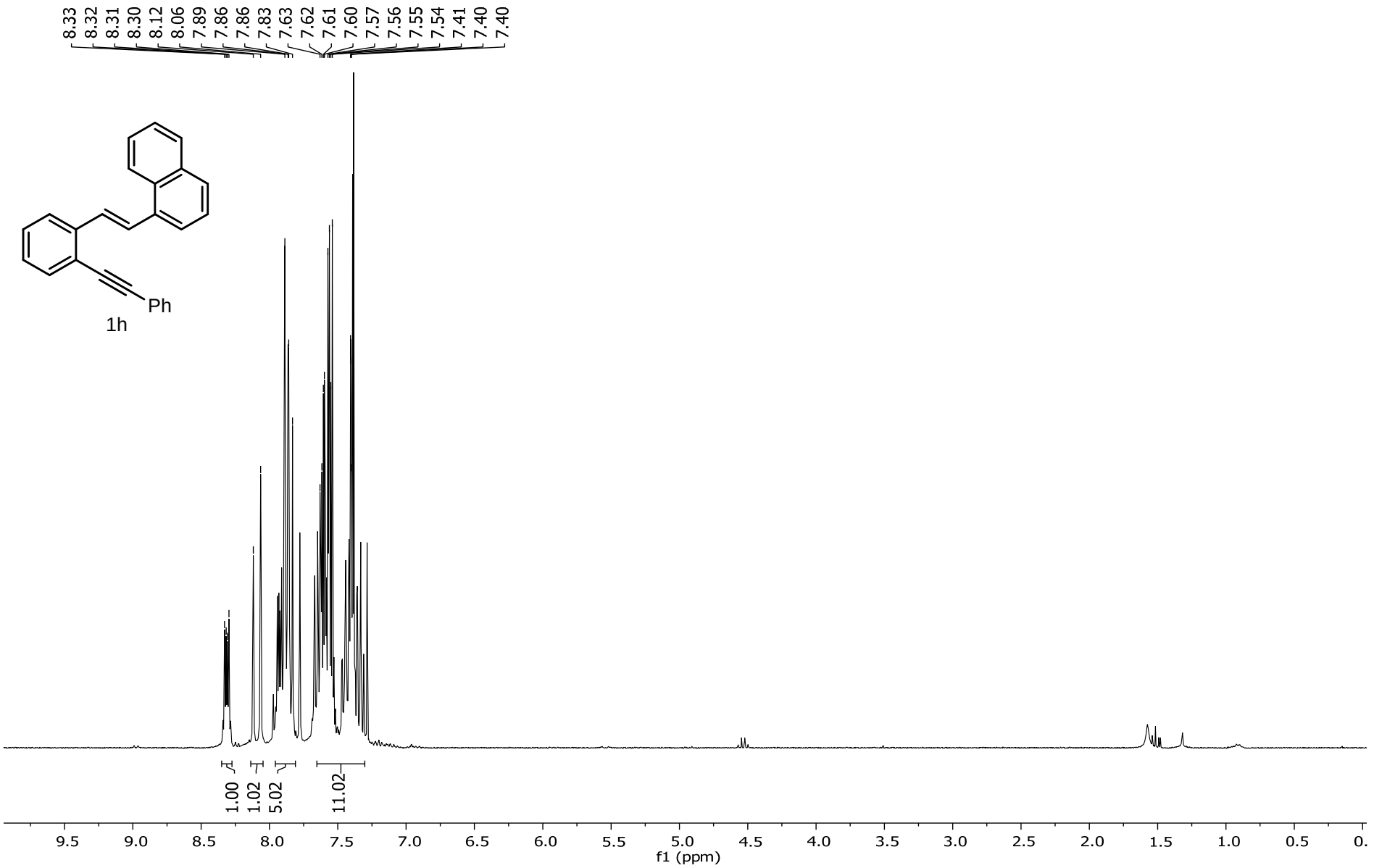
^{1}H NMR (300 MHz, $CDCl_3$)



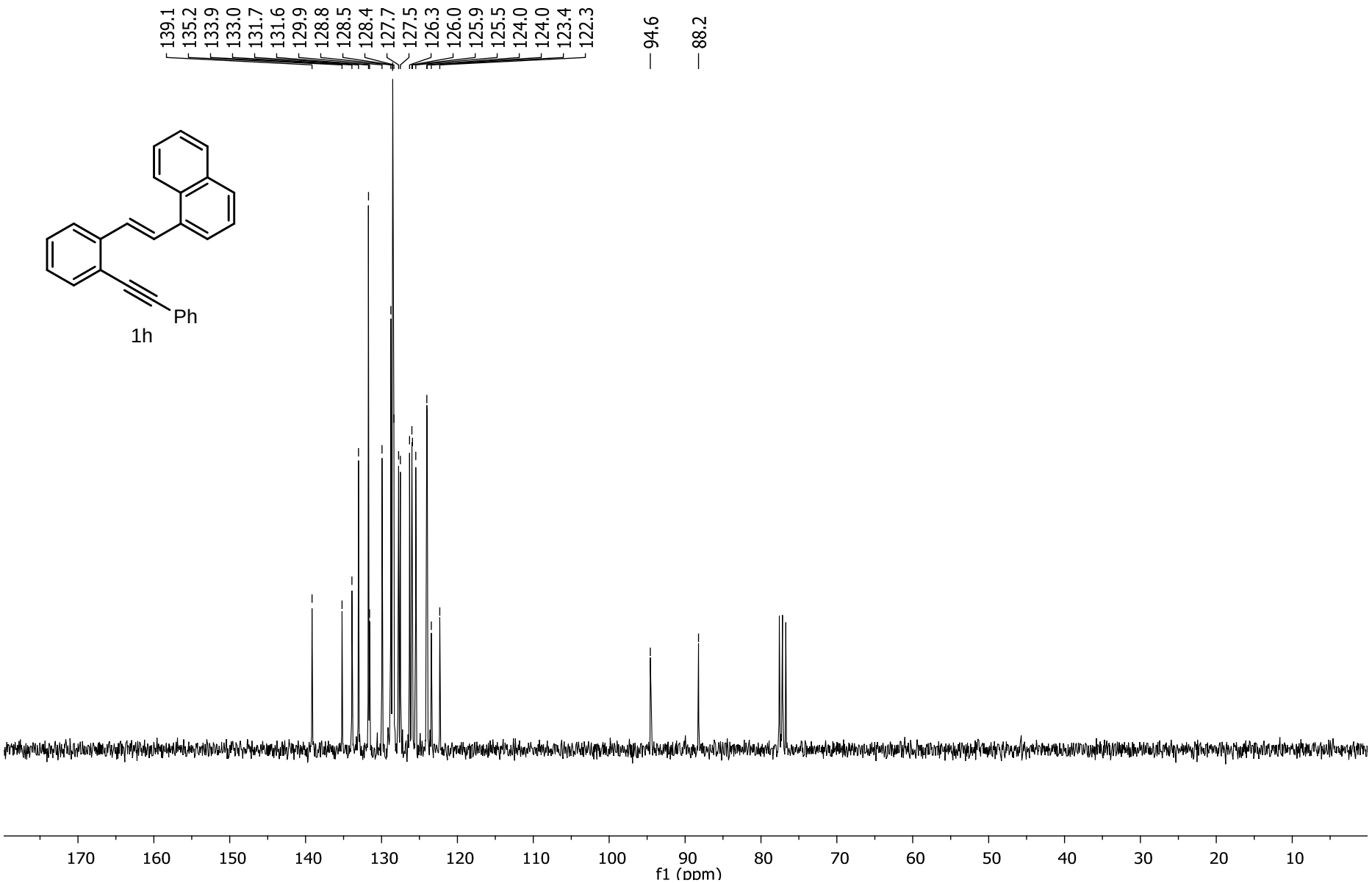
$^{13}C\{^{1}H\}$NMR (75.4 MHz, $CDCl_3$)



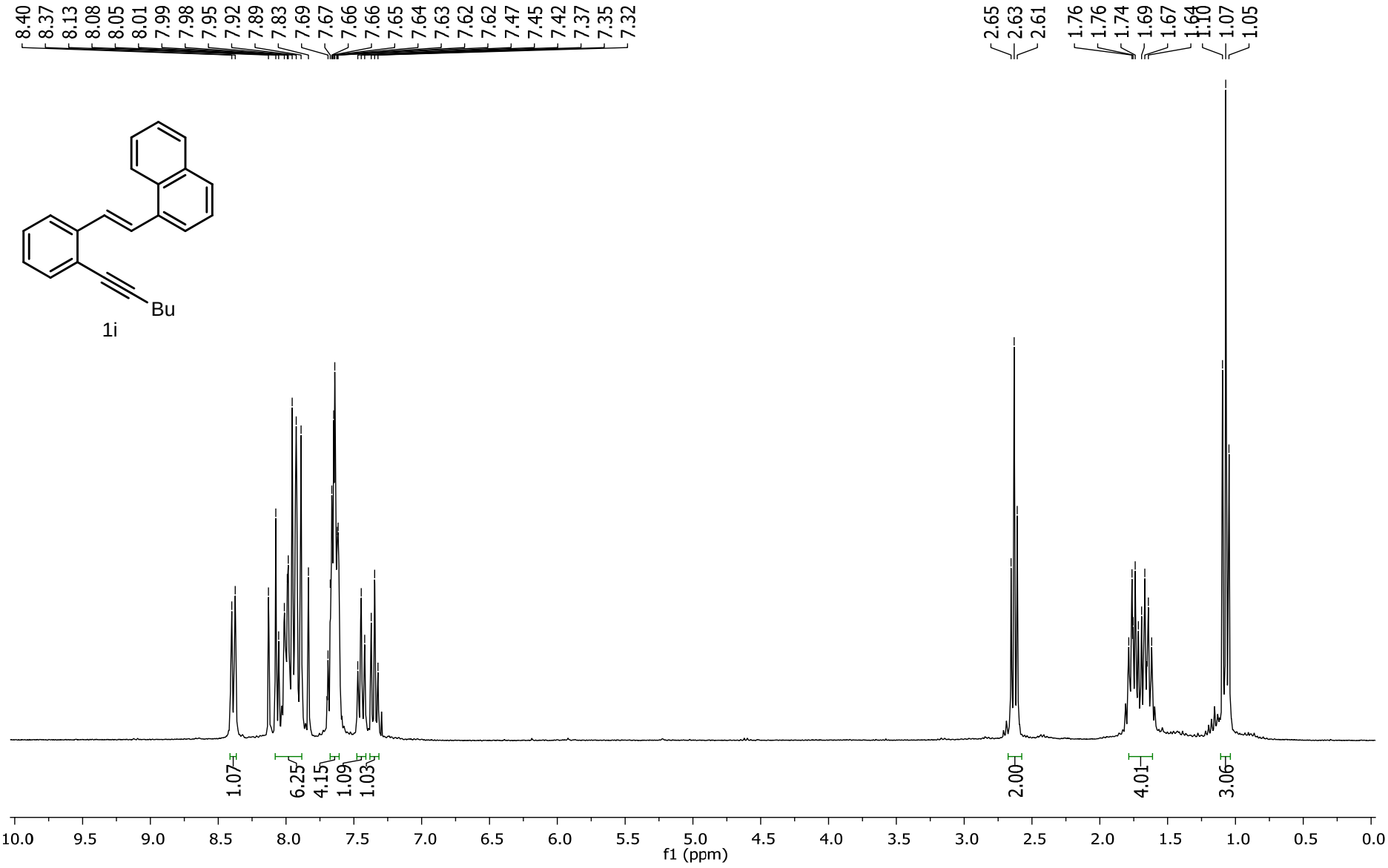
^{1}H NMR (300 MHz, $CDCl_3$)



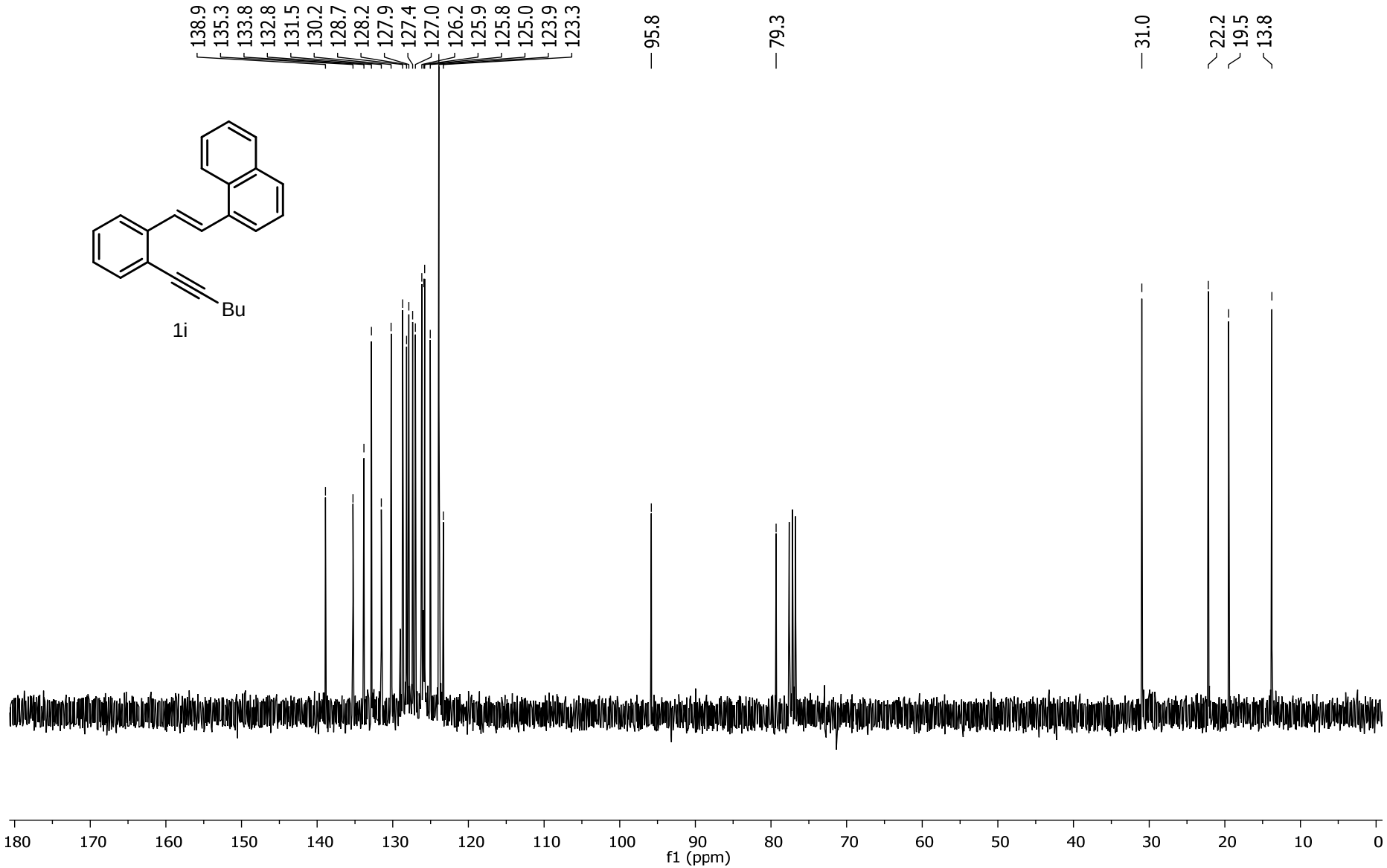
$^{13}C\{^{1}H\}$NMR (75.4 MHz, $CDCl_3$)



^{1}H NMR (300 MHz, $CDCl_3$)



$^{13}C\{^{1}H\}$NMR (75.4 MHz, $CDCl_3$)



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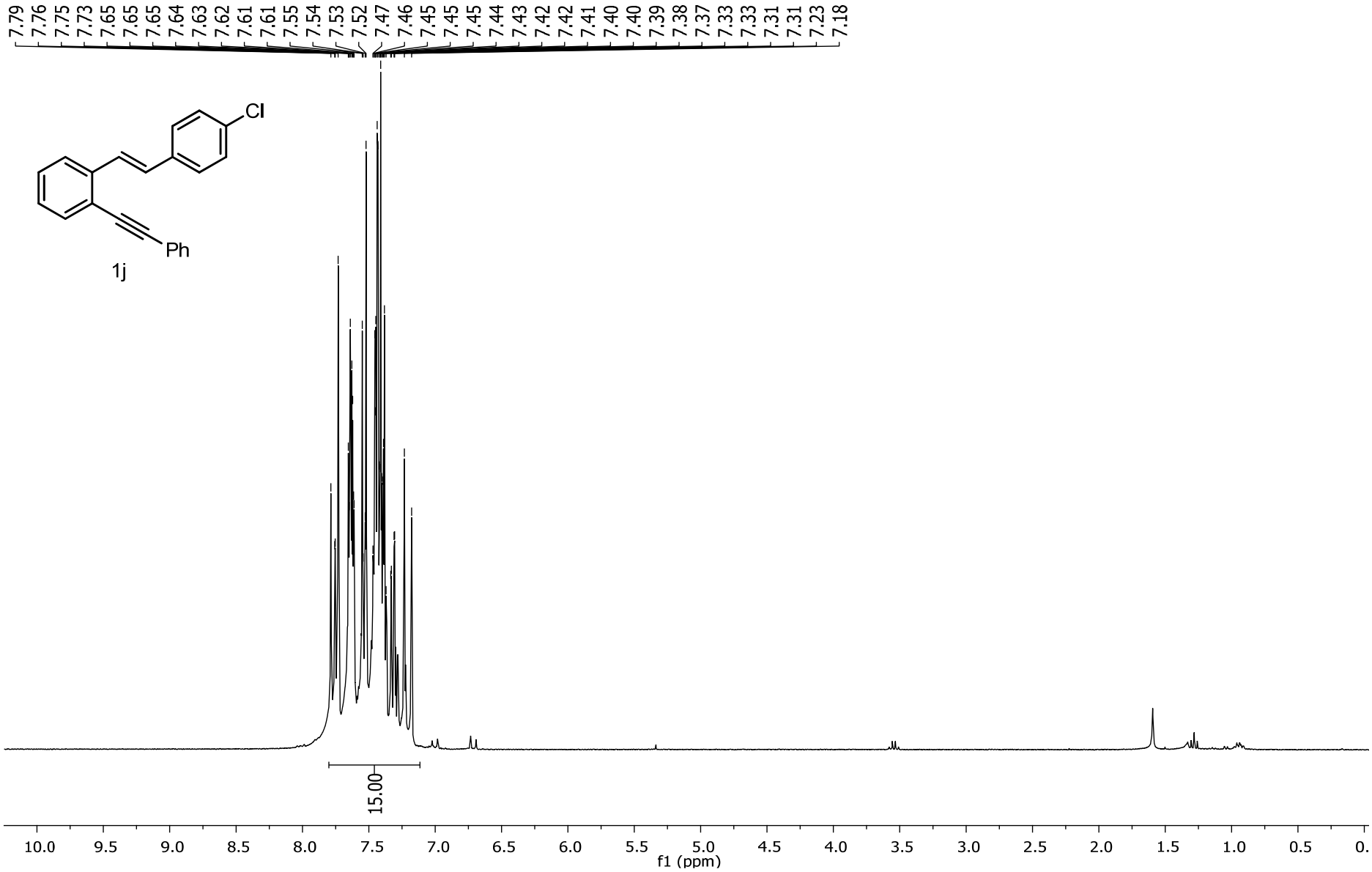

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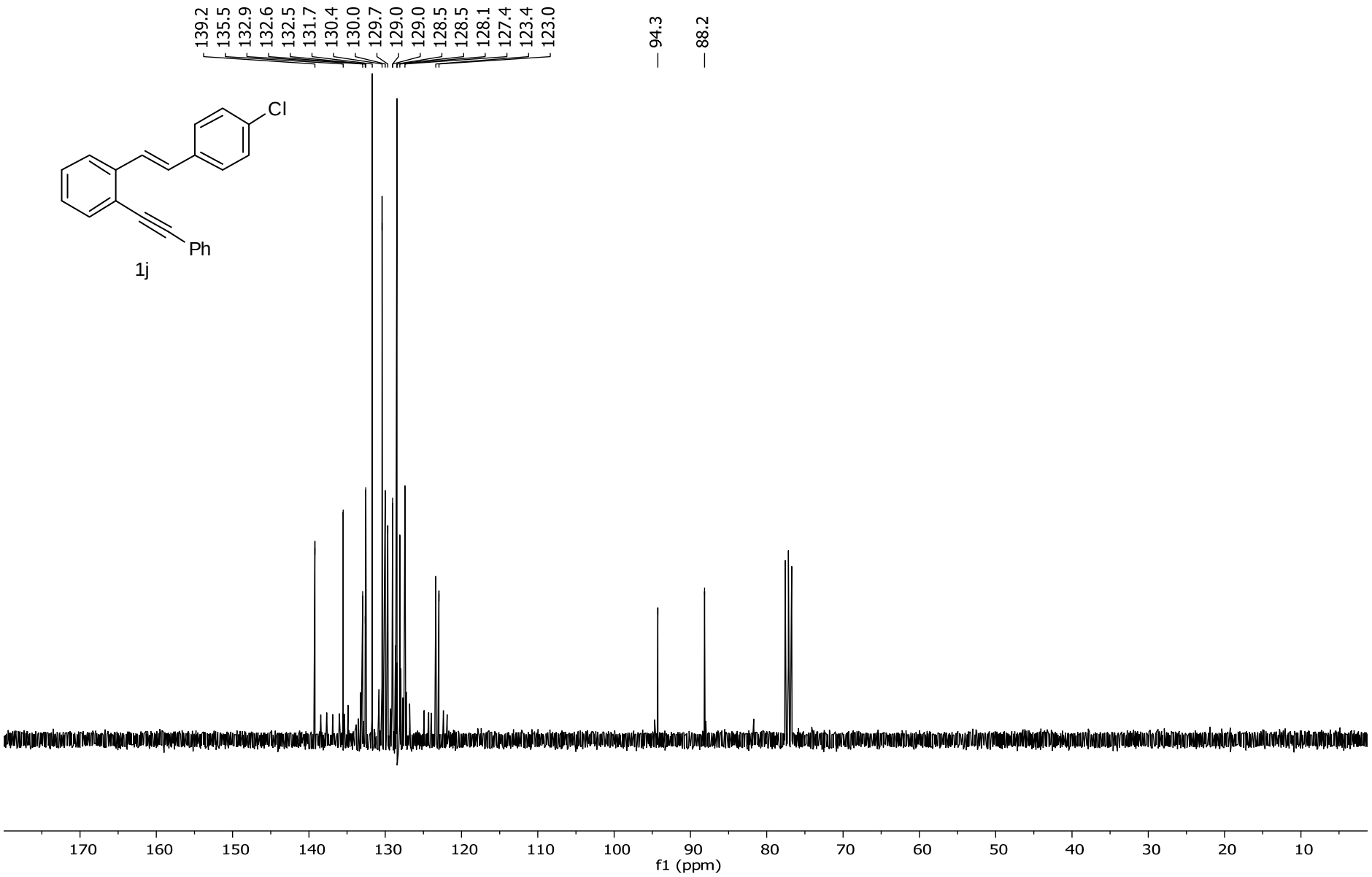

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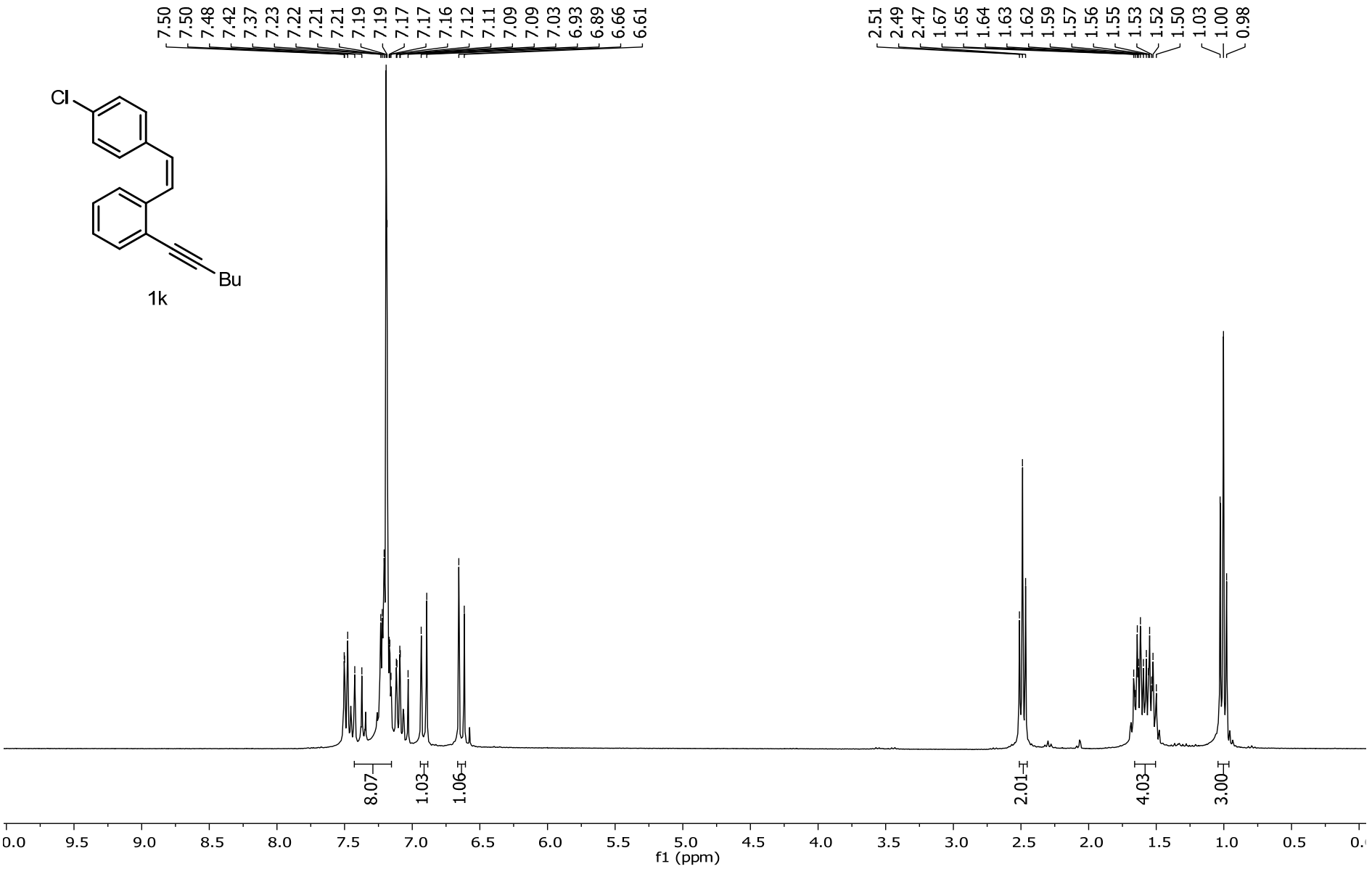
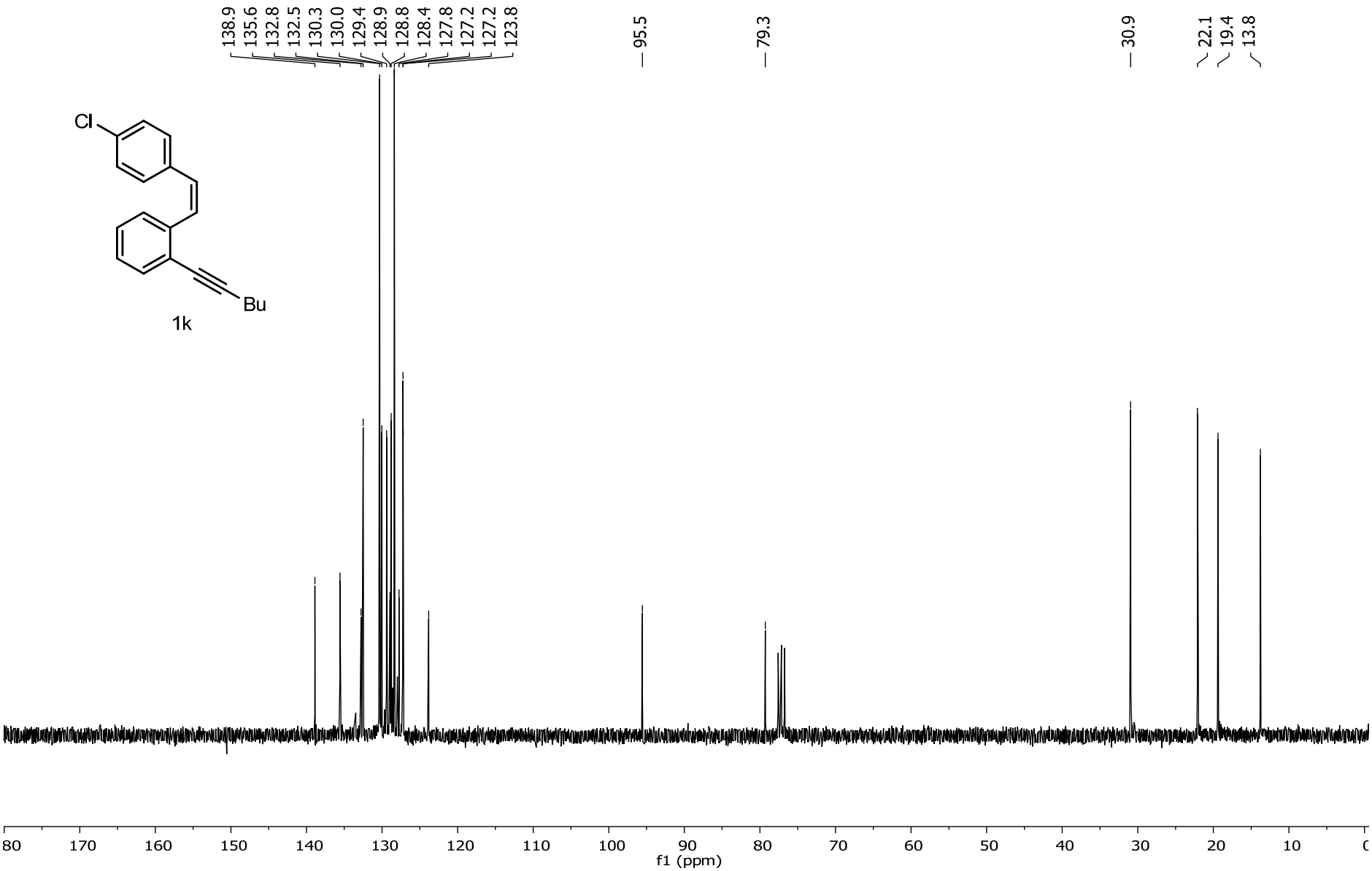
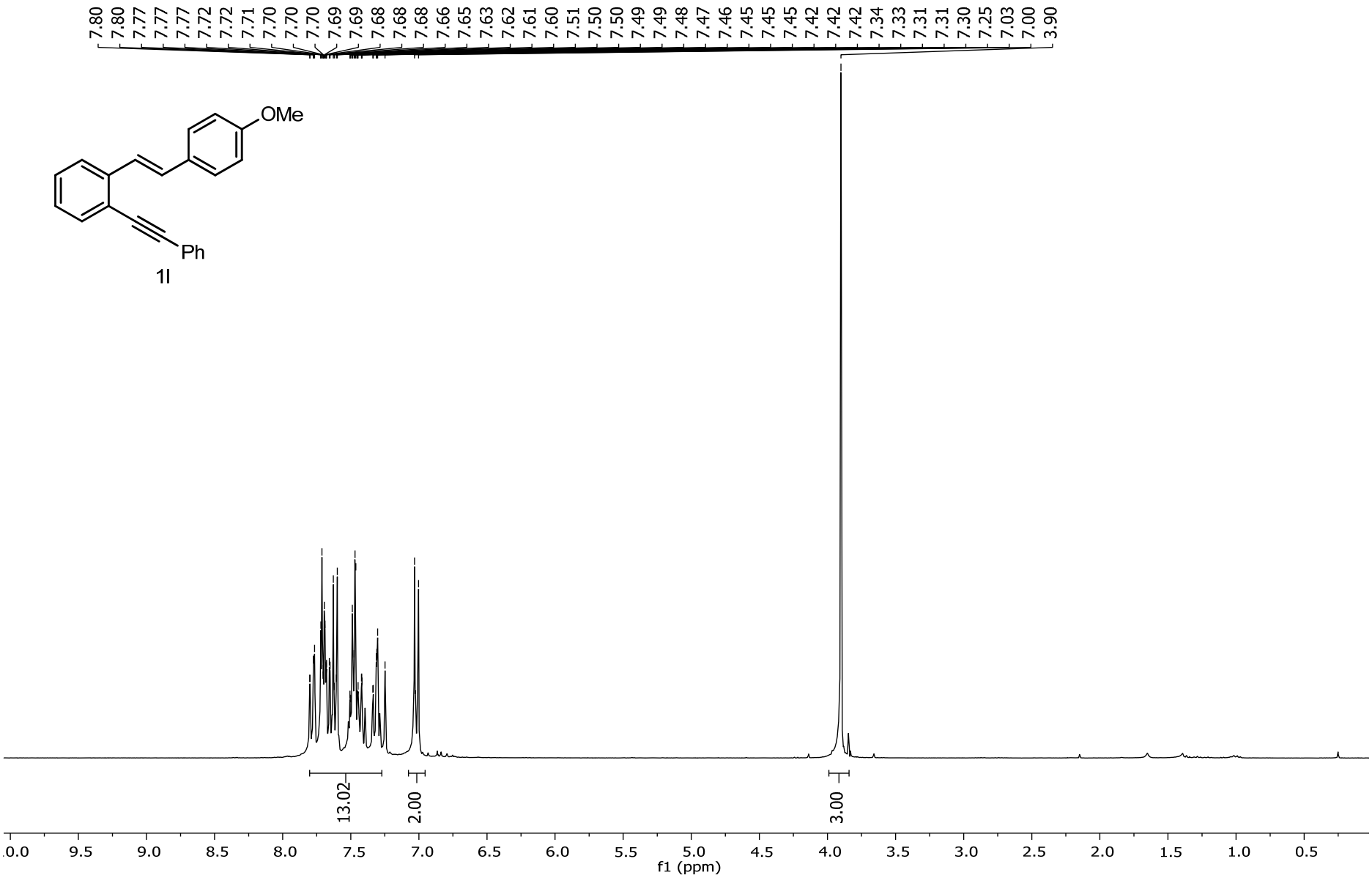


$^{13}C\{^{1}H\}$NMR (75.4 MHz, $CDCl_3$)

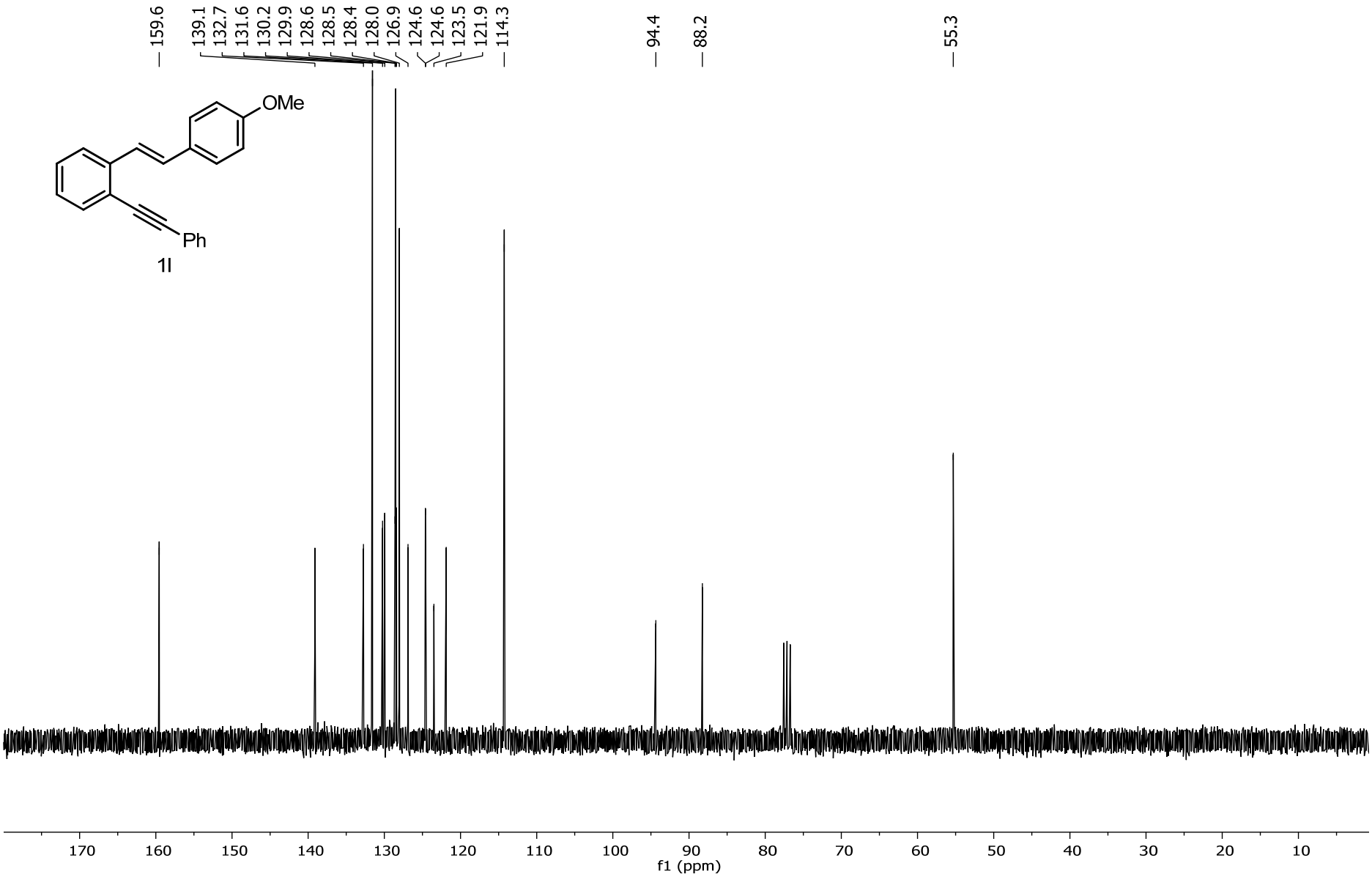


^{1}H NMR (300 MHz, $CDCl_3$)

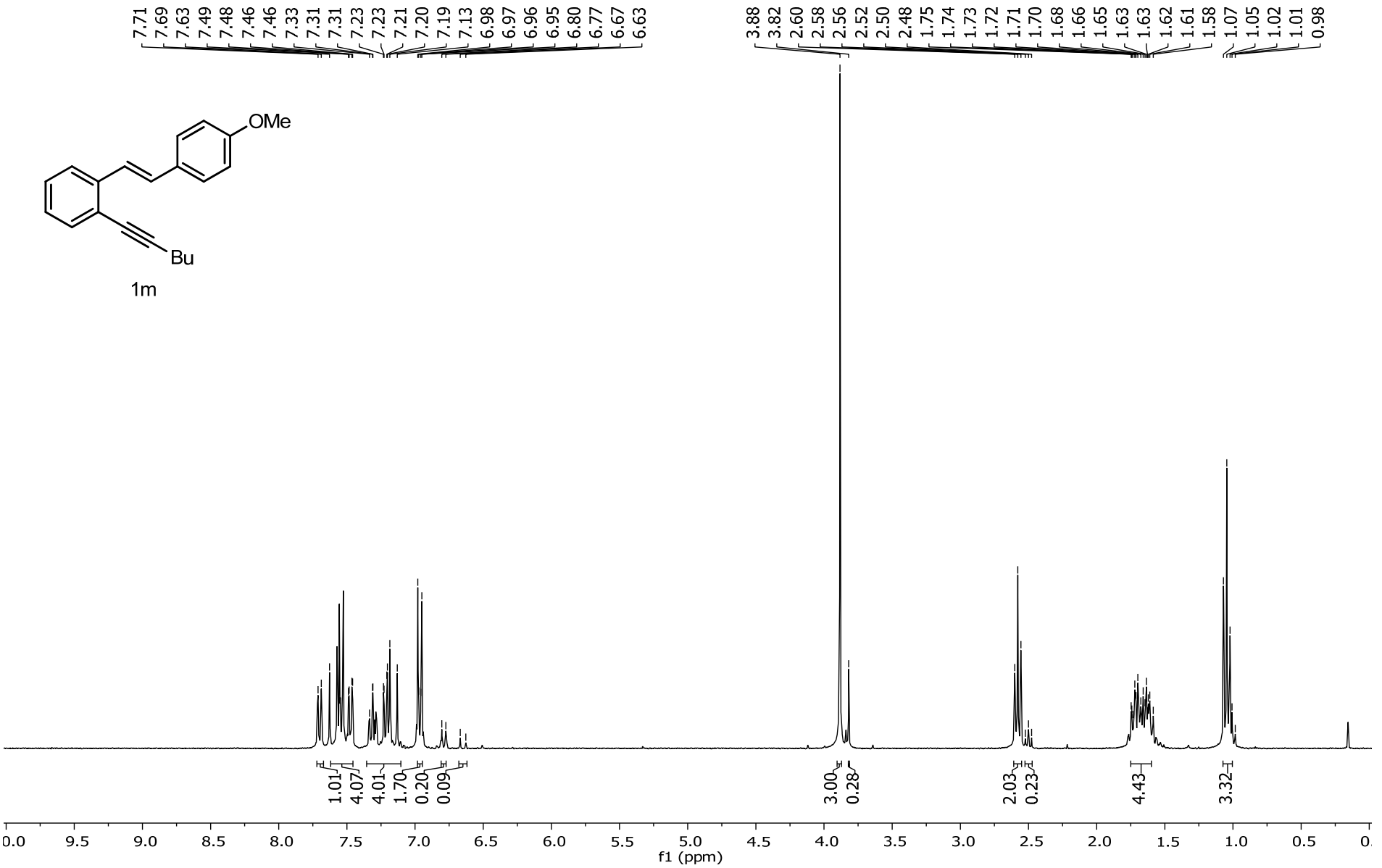


1l

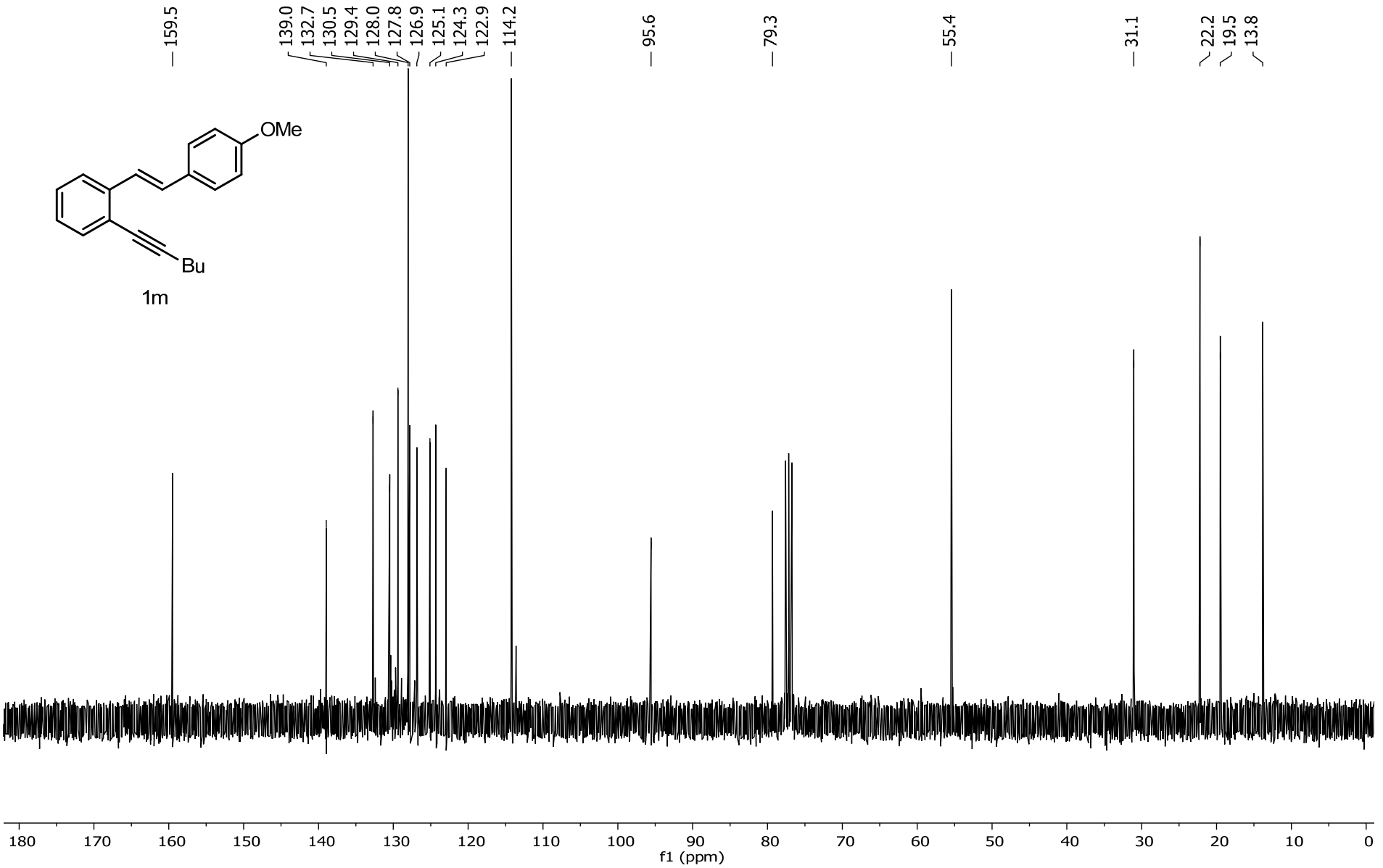
$^{13}C\{^{1}H\}$NMR (75.4 MHz, $CDCl_3$)



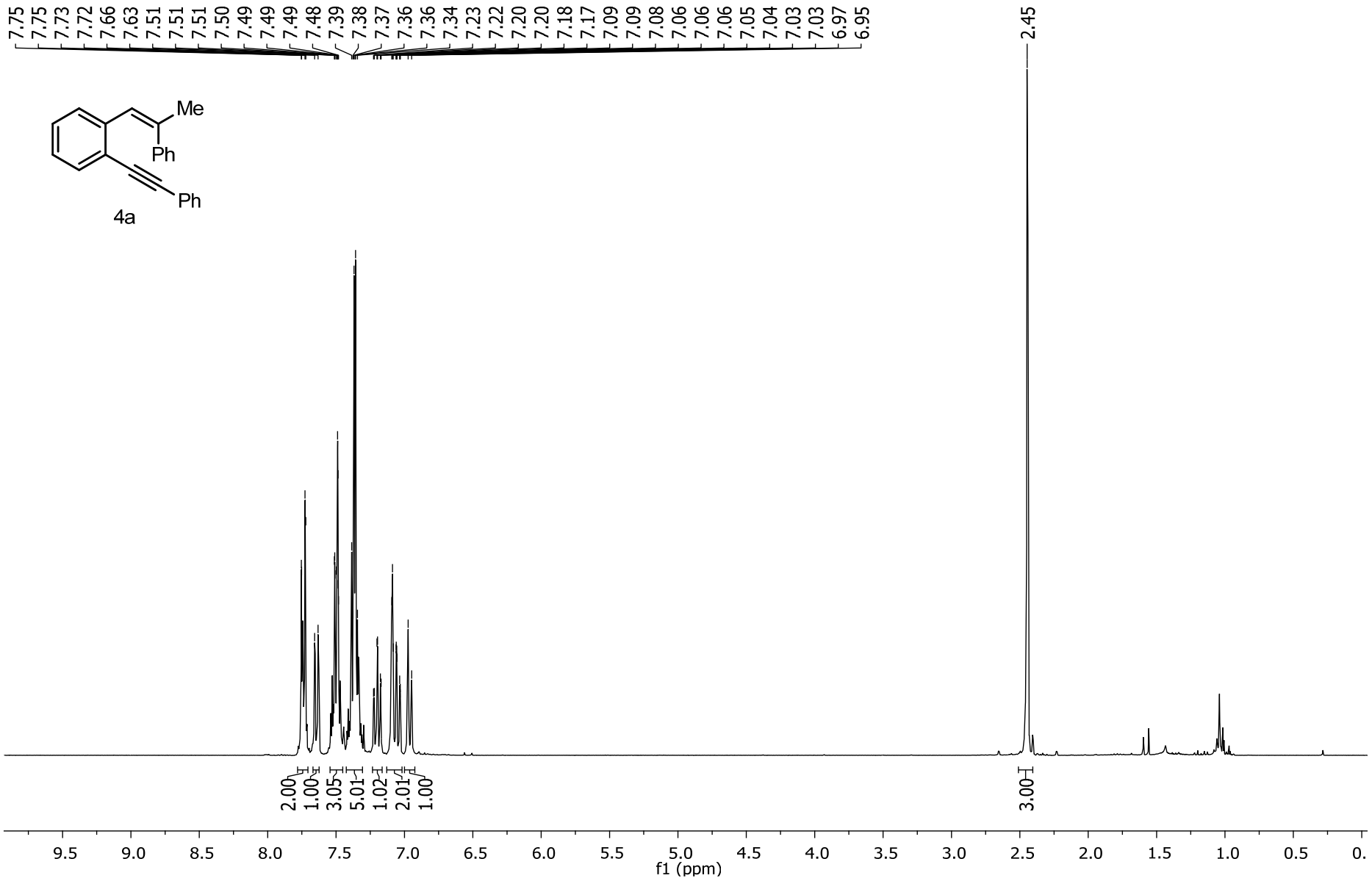
^{1}H NMR (300 MHz, $CDCl_3$)



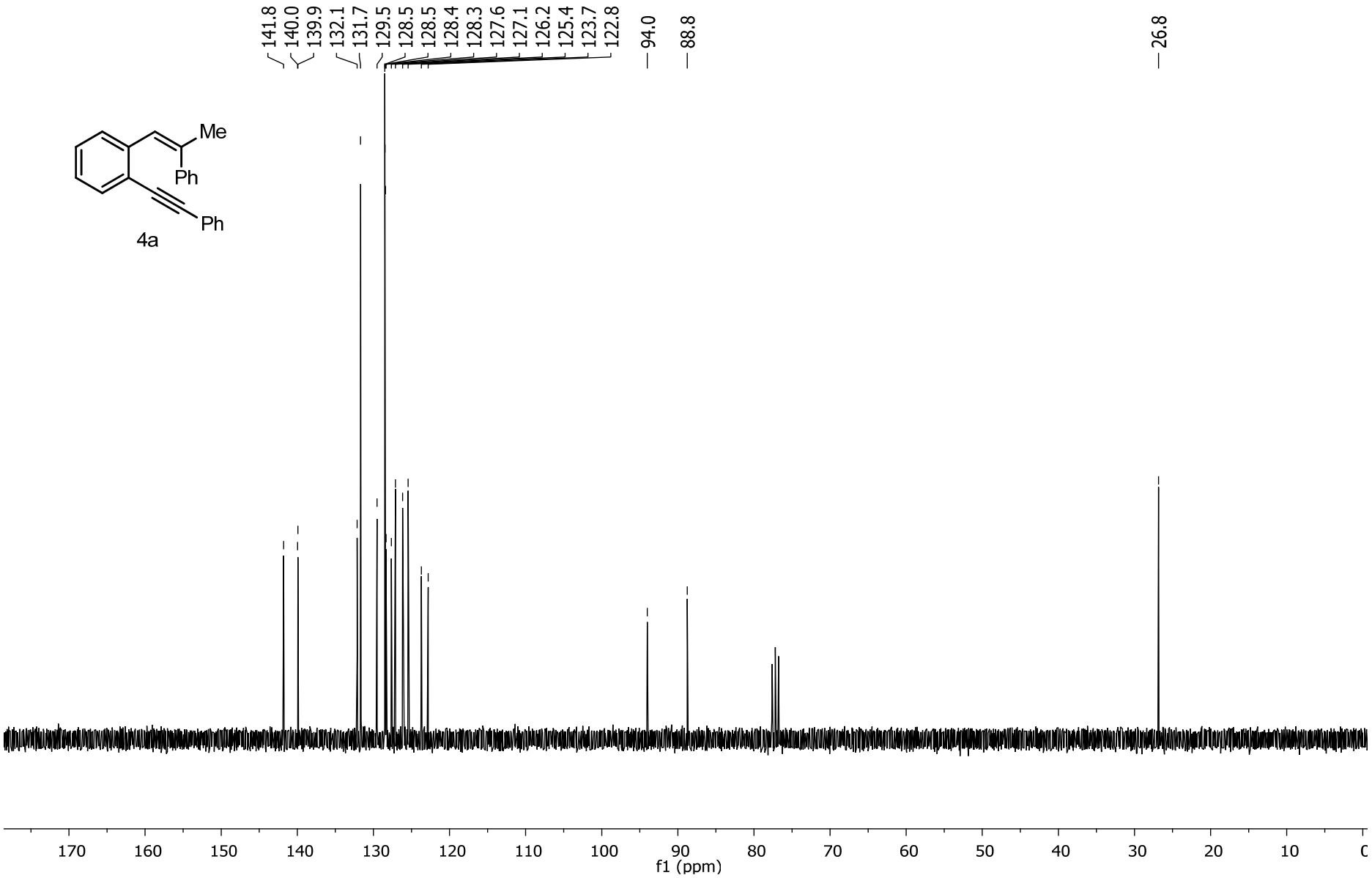
$^{13}C\{^{1}H\}$NMR (75.4 MHz, $CDCl_3$)



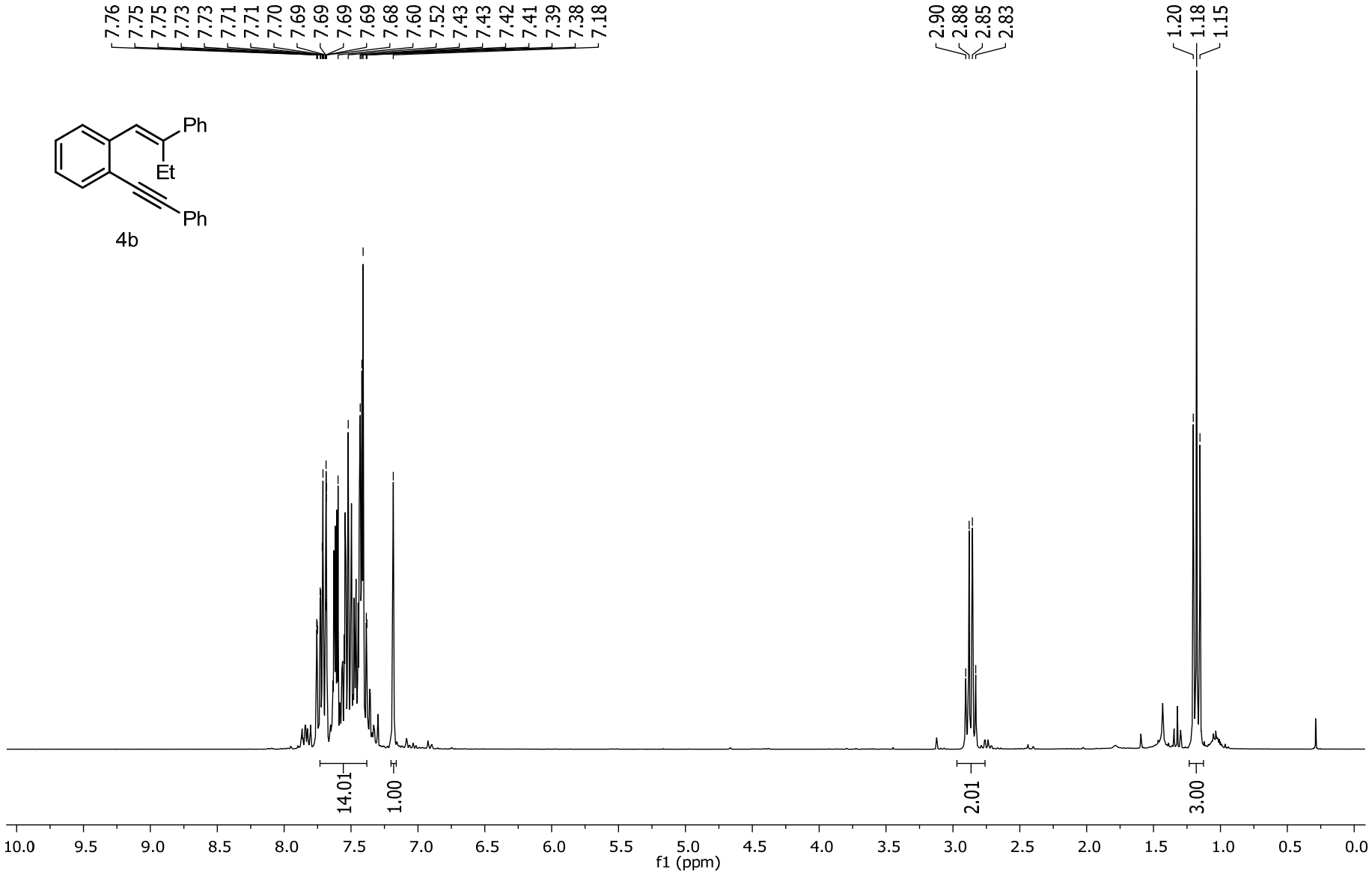
^{1}H NMR (300 MHz, $CDCl_3$)



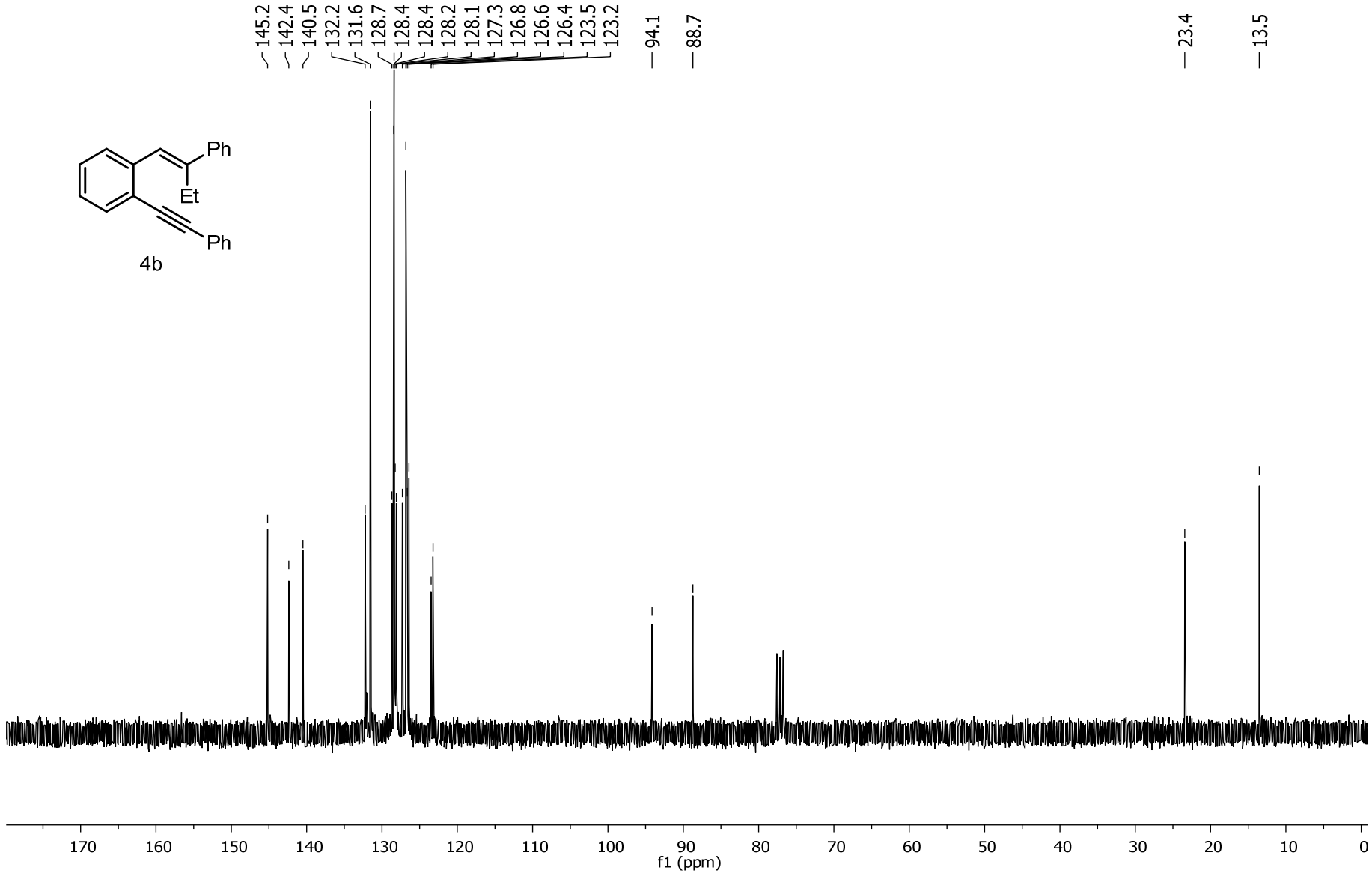
$^{13}C\{^{1}H\}$NMR (75.4 MHz, $CDCl_3$)



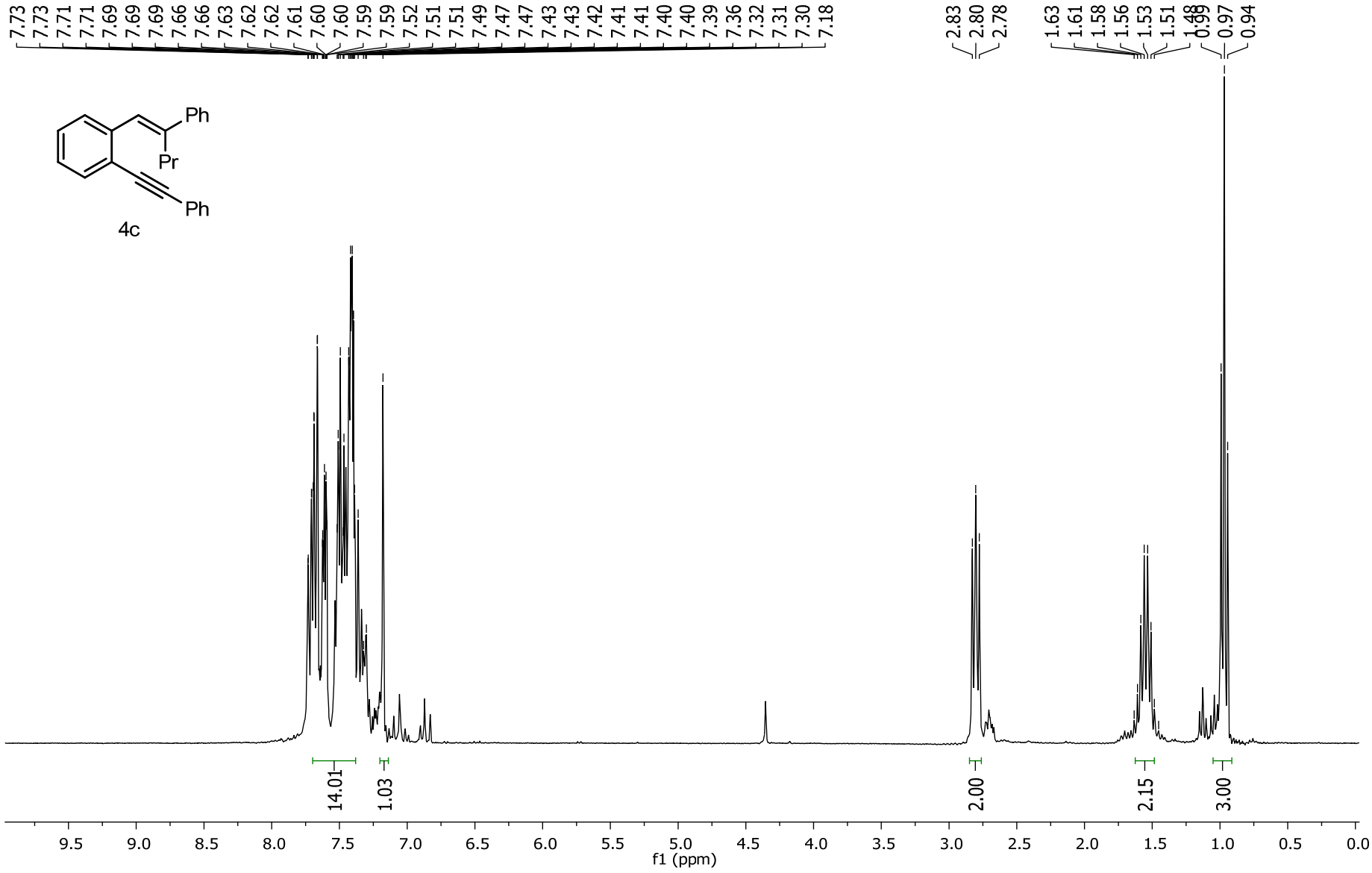
^{1}H NMR (300 MHz, $CDCl_3$)



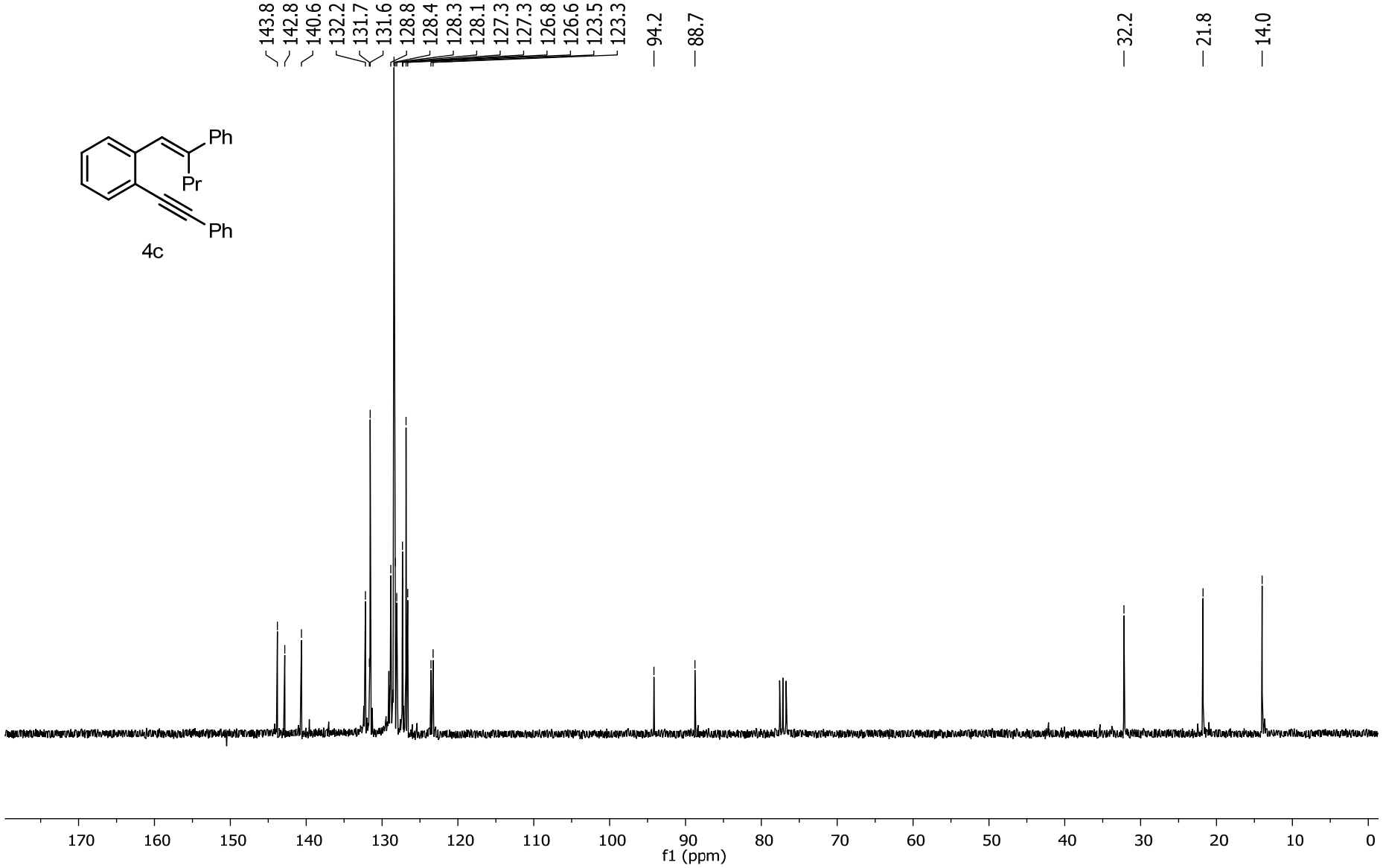
$^{13}C\{^{1}H\}$NMR (75.4 MHz, $CDCl_3$)



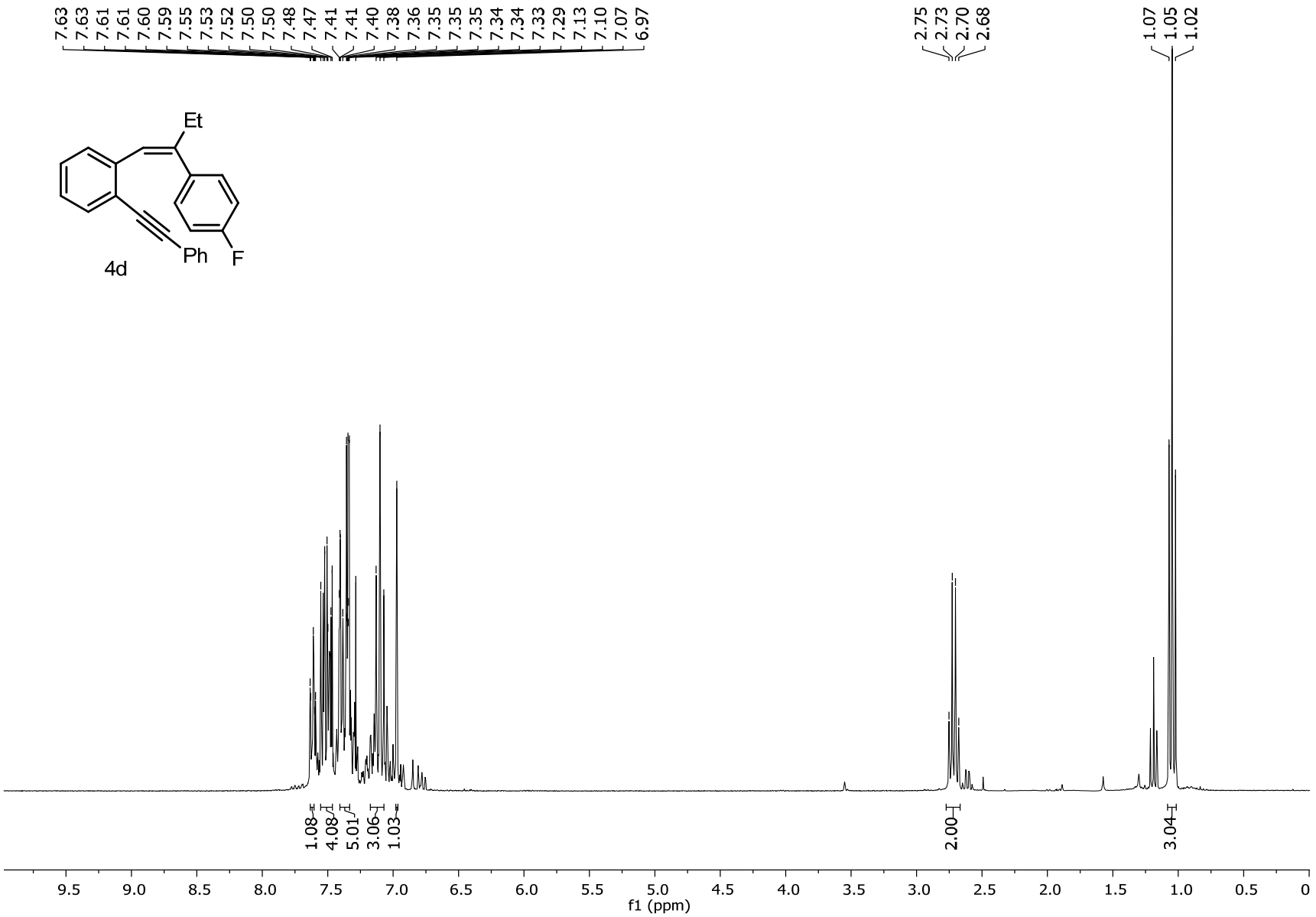
^{1}H NMR (300 MHz, $CDCl_3$)



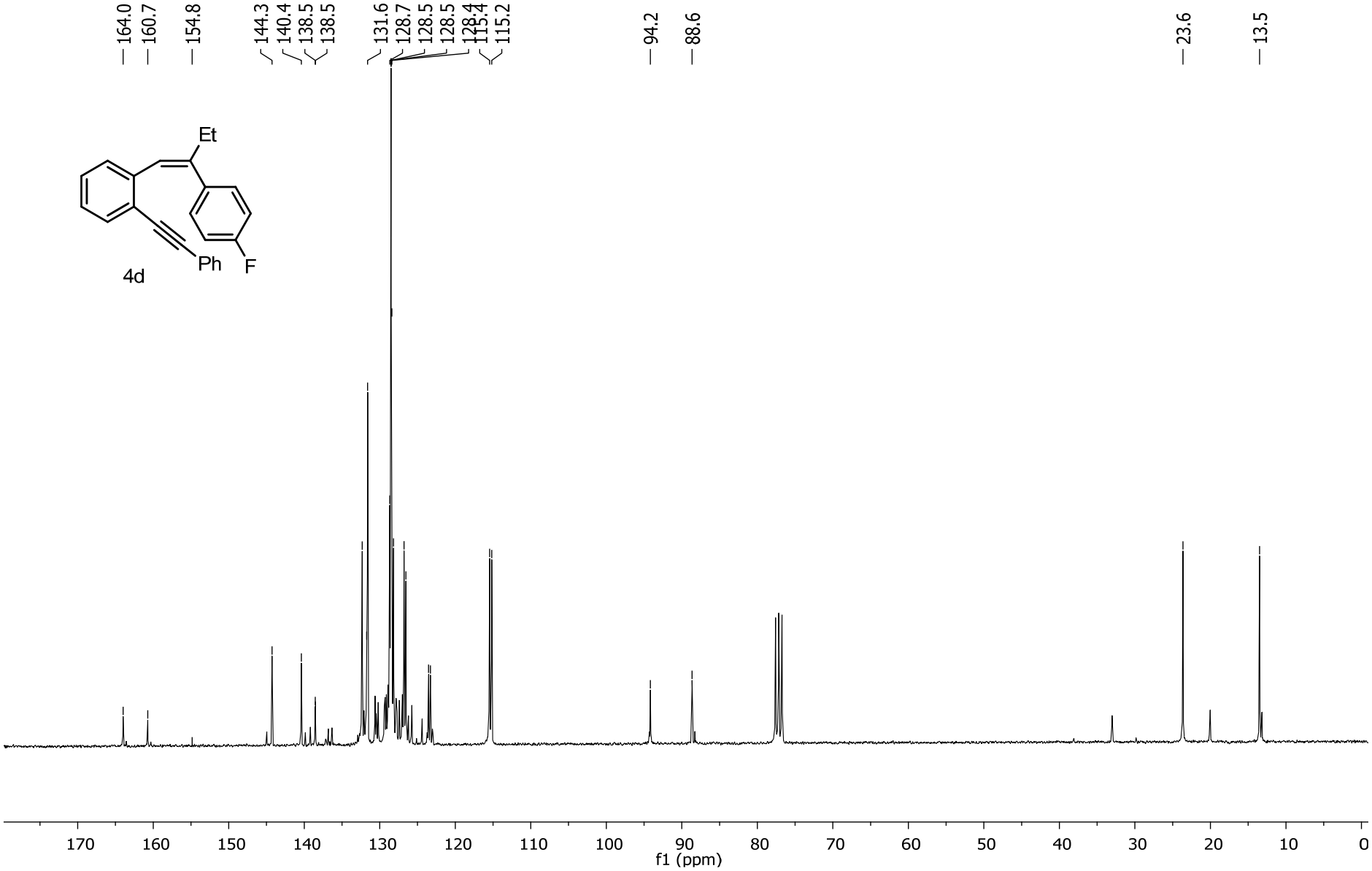
$^{13}C\{^{1}H\}$NMR (75.4 MHz, $CDCl_3$)



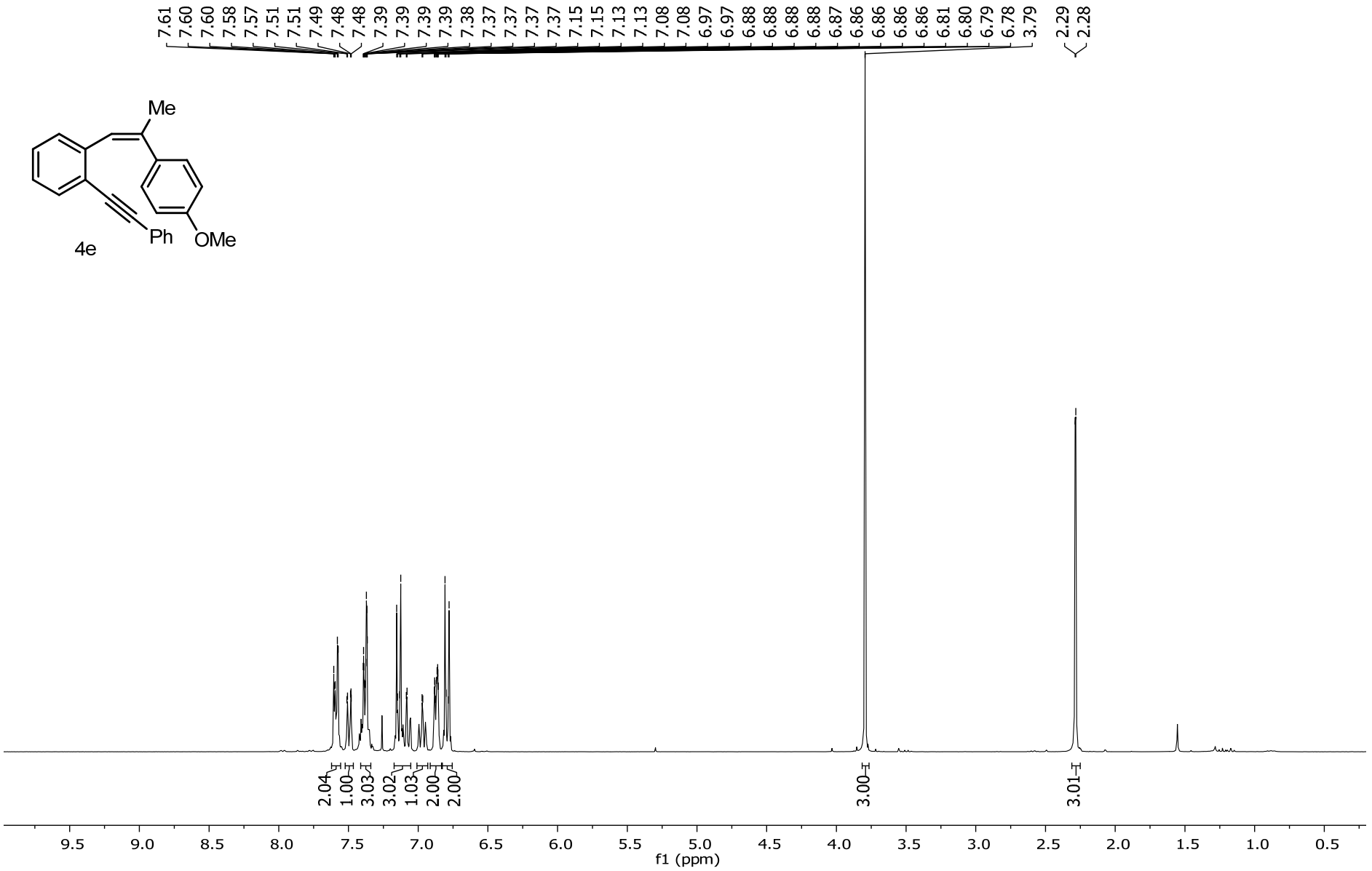
^{1}H NMR (300 MHz, $CDCl_3$)



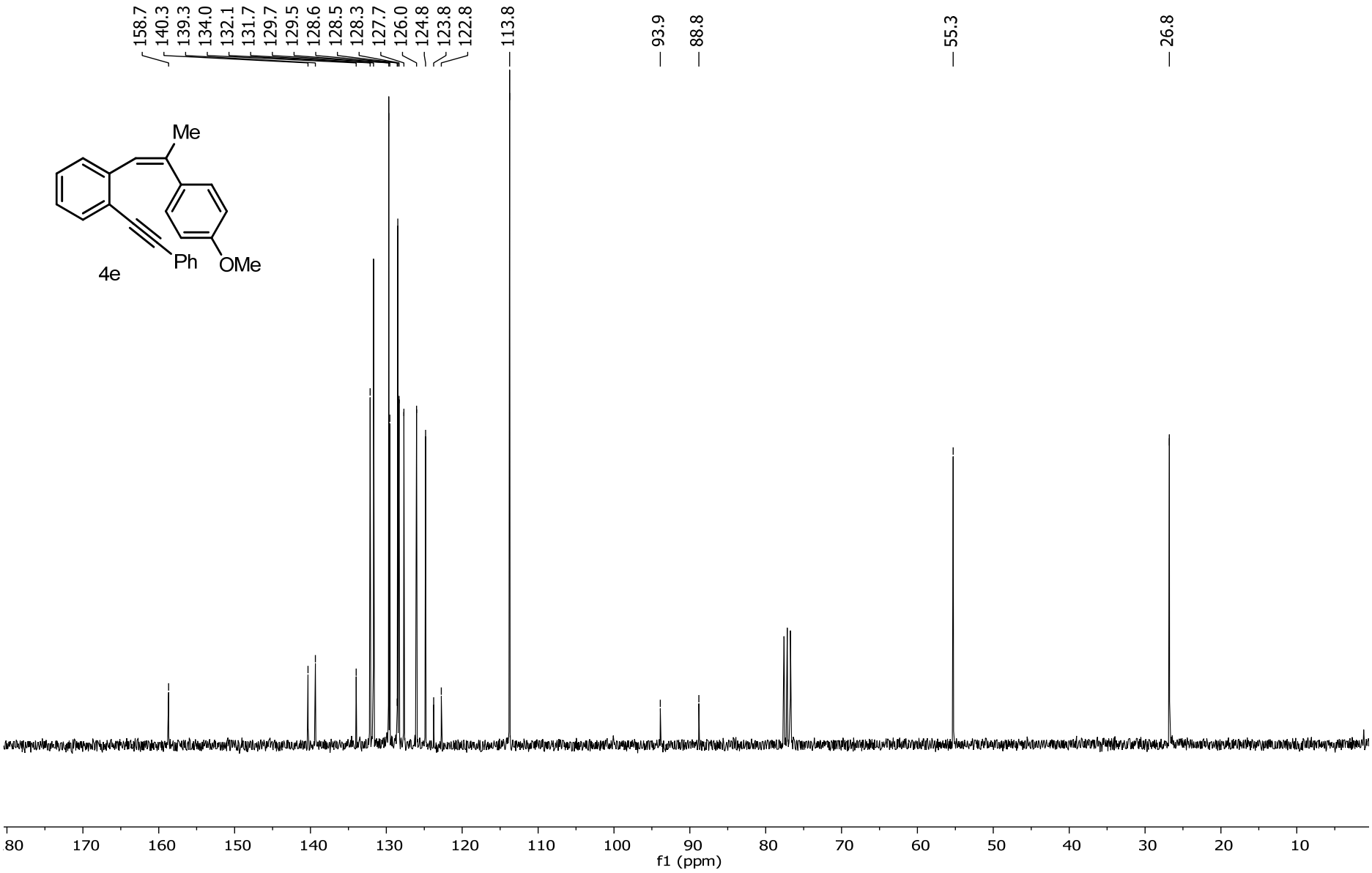
$^{13}C\{^{1}H\}$NMR (75.4 MHz, $CDCl_3$)



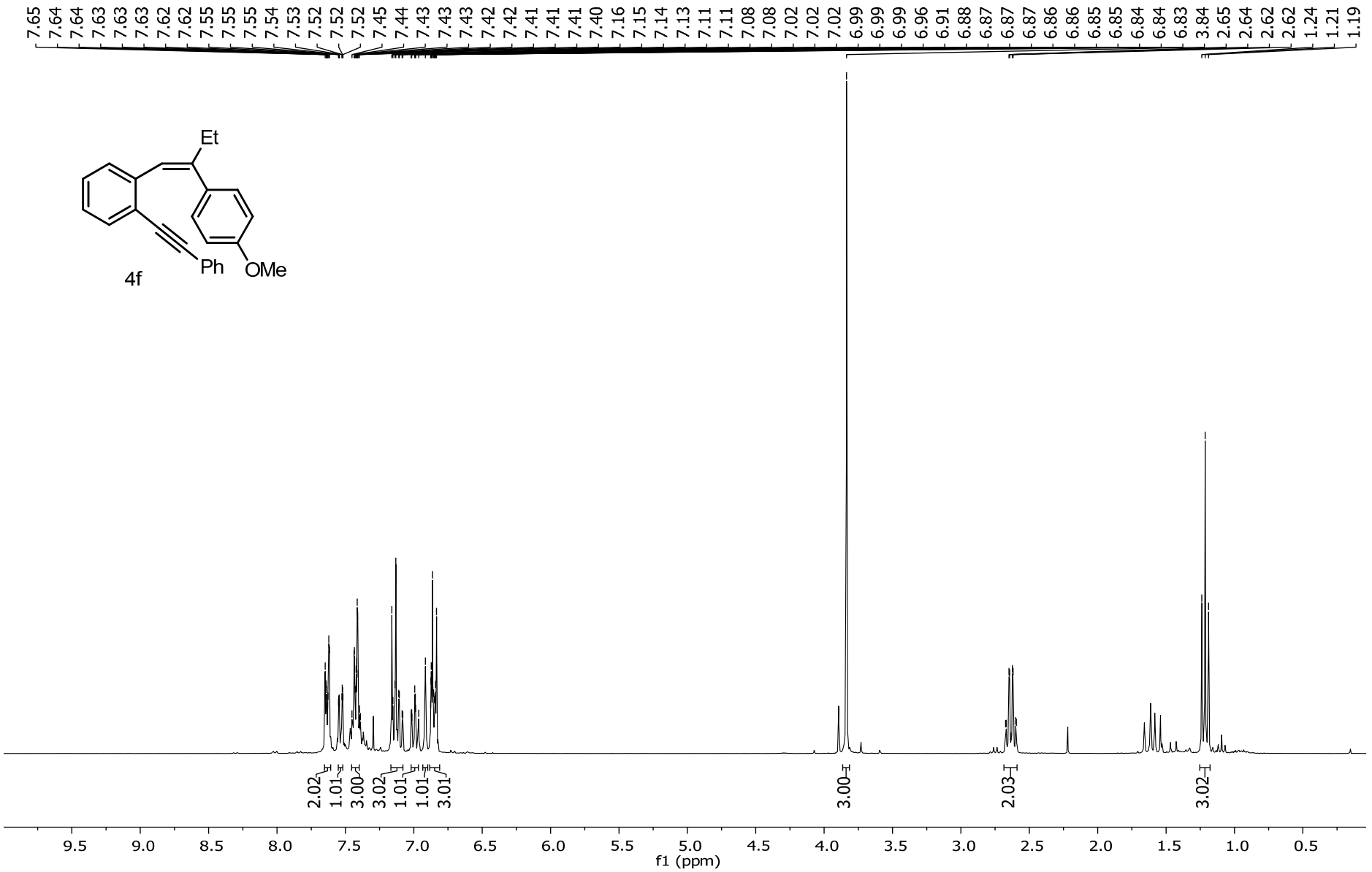
^{1}H NMR (300 MHz, $CDCl_3$)



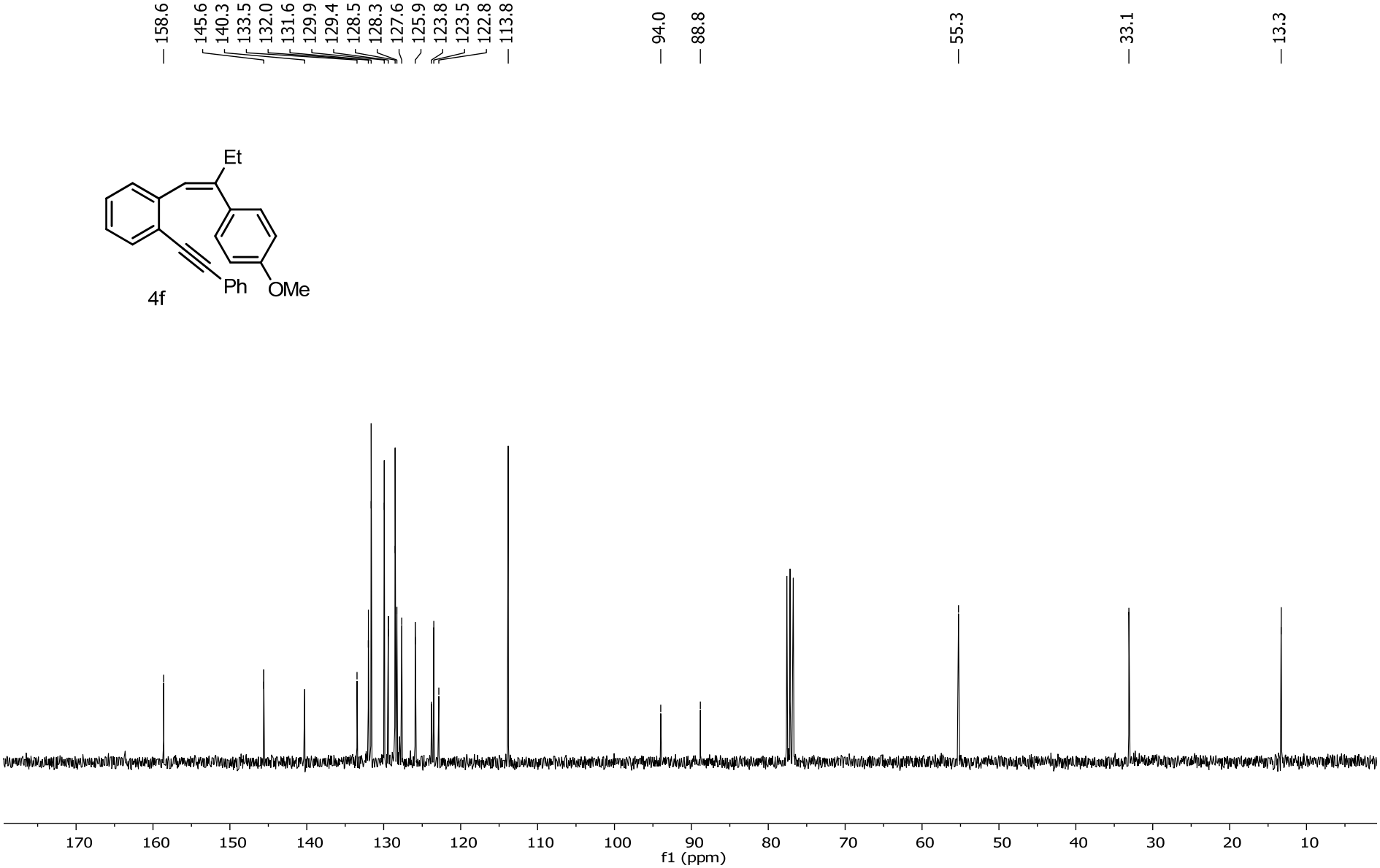
$^{13}C\{^{1}H\}$NMR (75.4 MHz, $CDCl_3$)



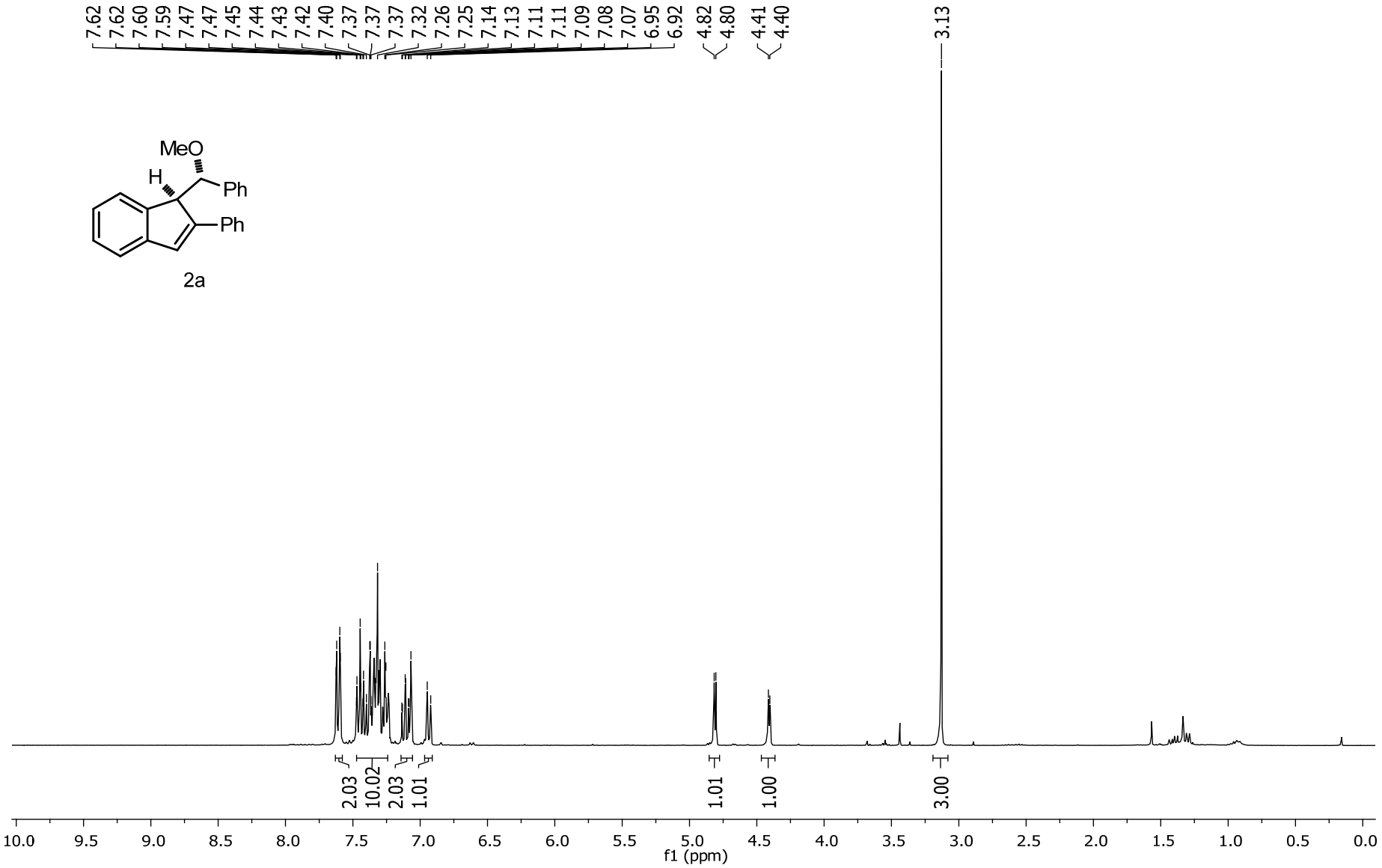
^{1}H NMR (300 MHz, $CDCl_3$)



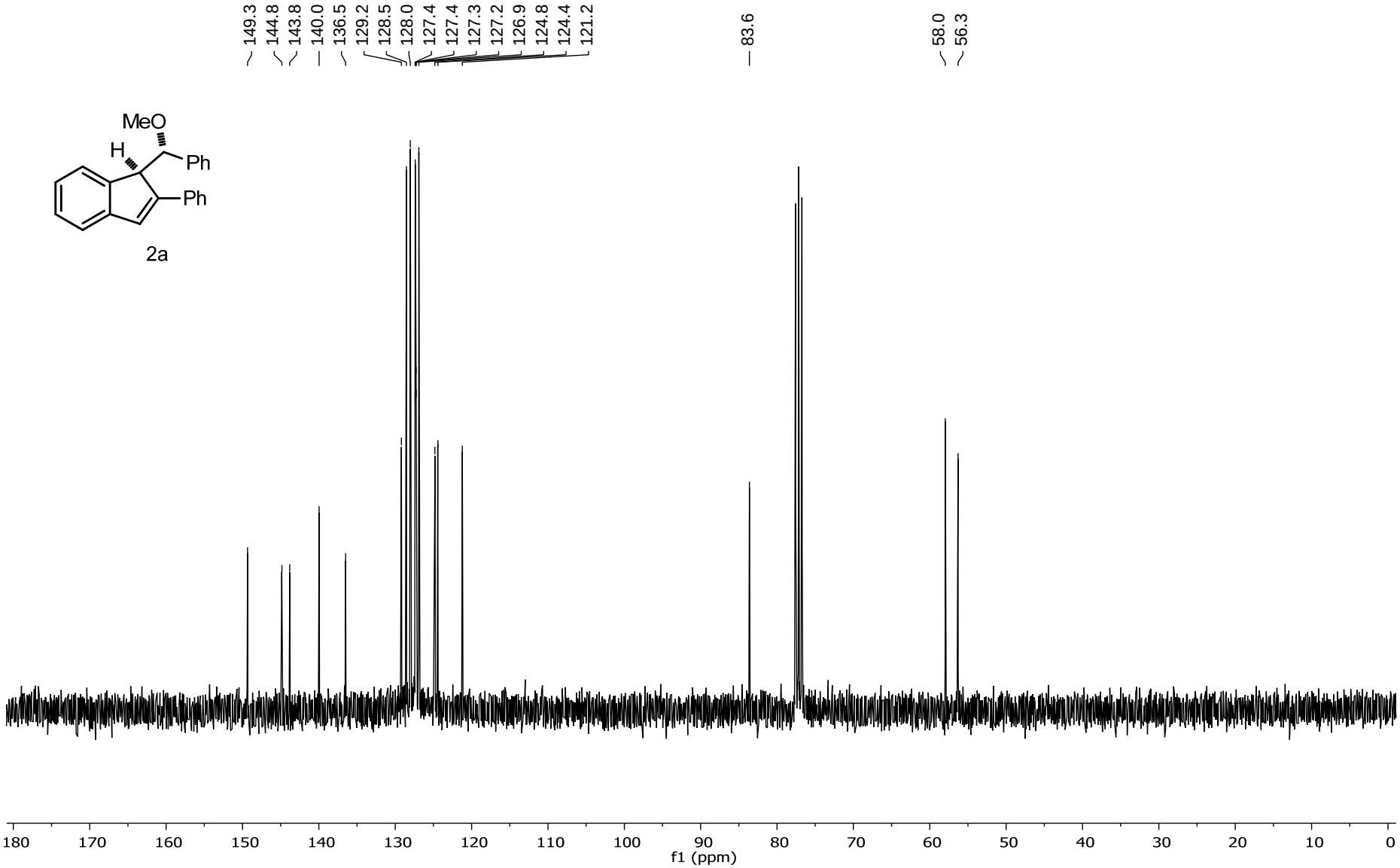
$^{13}C\{^{1}H\}$NMR (75.4 MHz, $CDCl_3$)



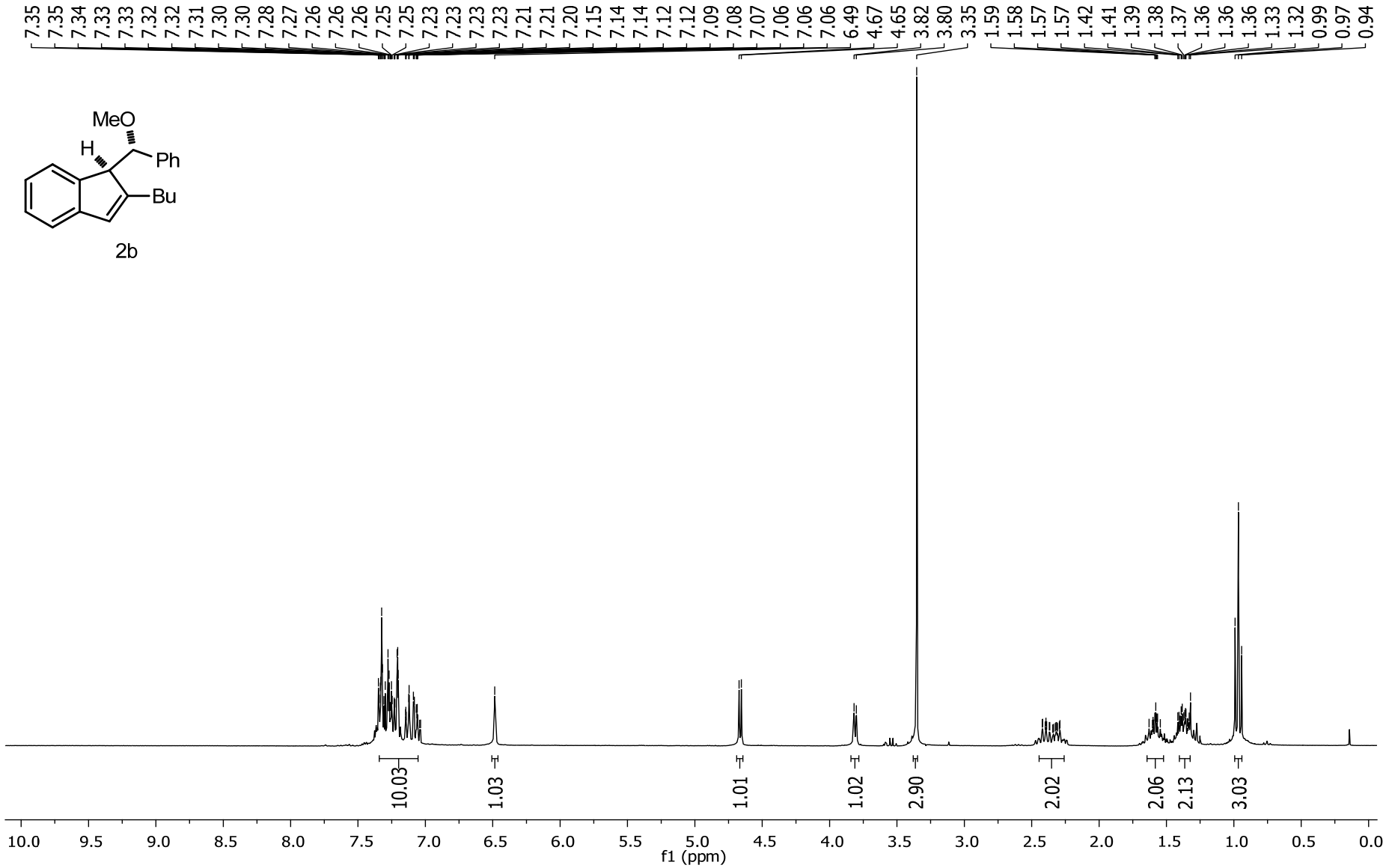
^{1}H NMR (300 MHz, $CDCl_3$)



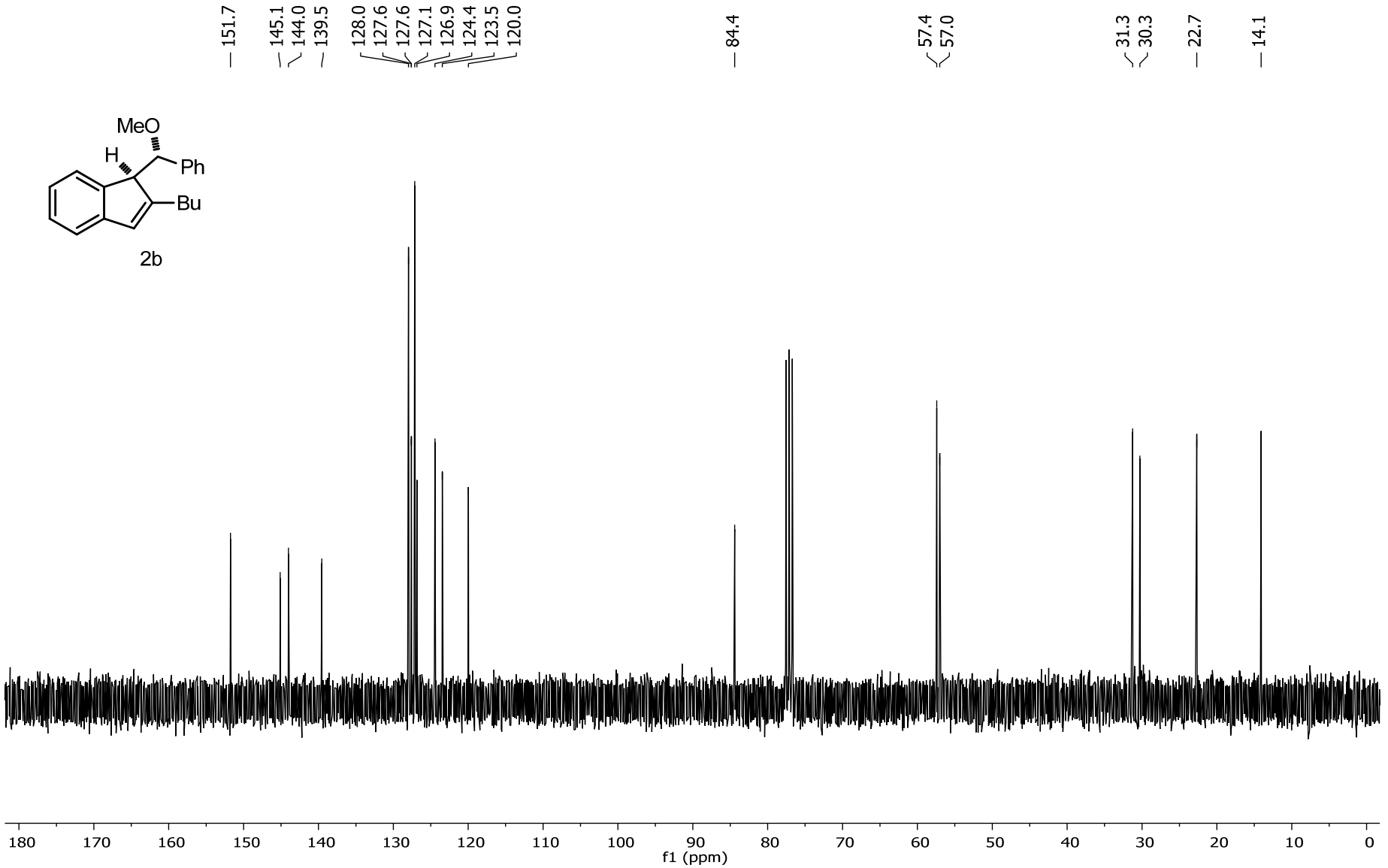
$^{13}C\{^{1}H\}$NMR (75.4 MHz, $CDCl_3$)



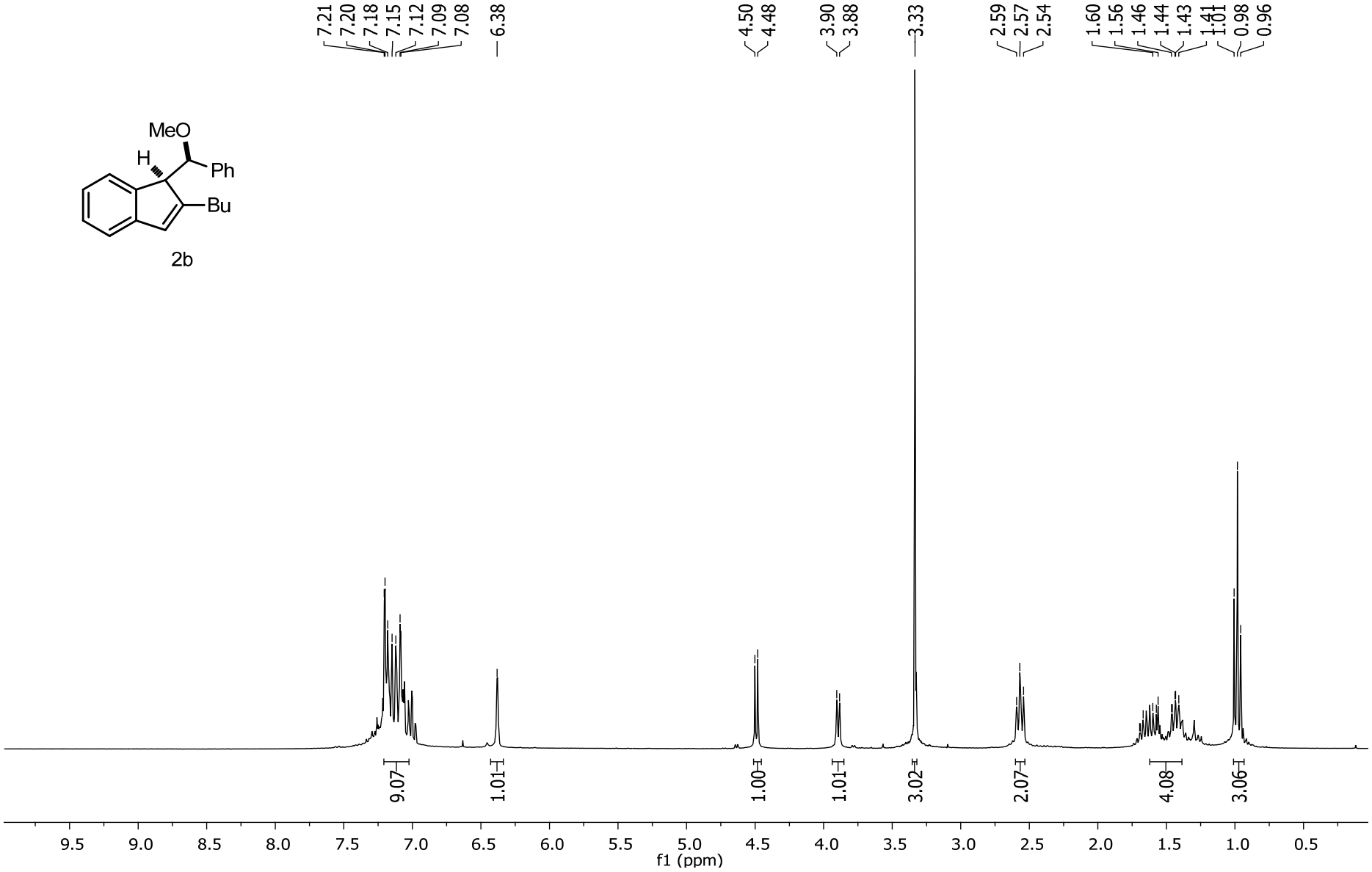
^{1}H NMR (300 MHz, $CDCl_3$)



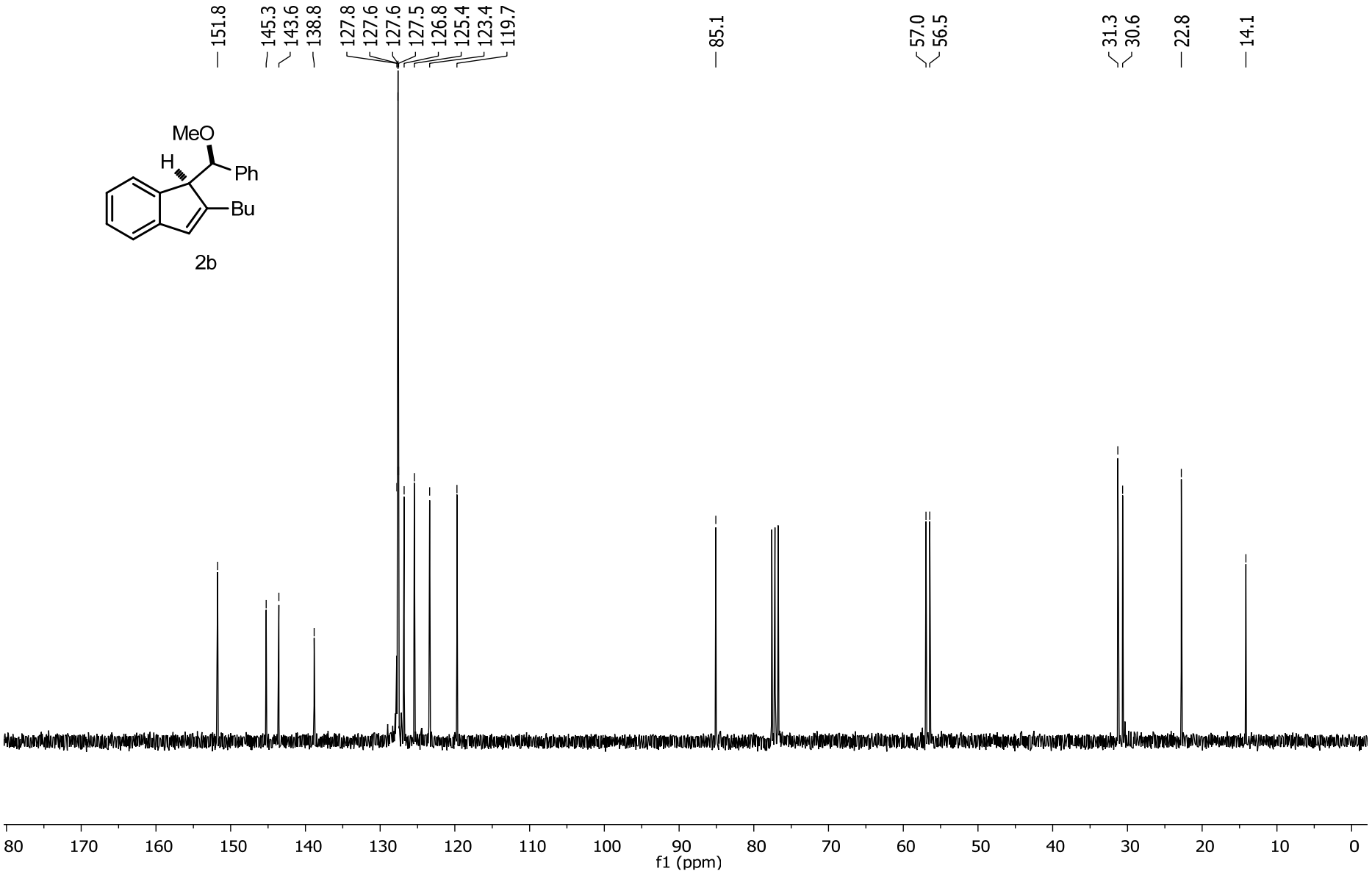
$^{13}C\{^{1}H\}$NMR (75.4 MHz, $CDCl_3$)



^{1}H NMR (300 MHz, $CDCl_3$)



$^{13}C\{^{1}H\}$NMR (75.4 MHz, $CDCl_3$)



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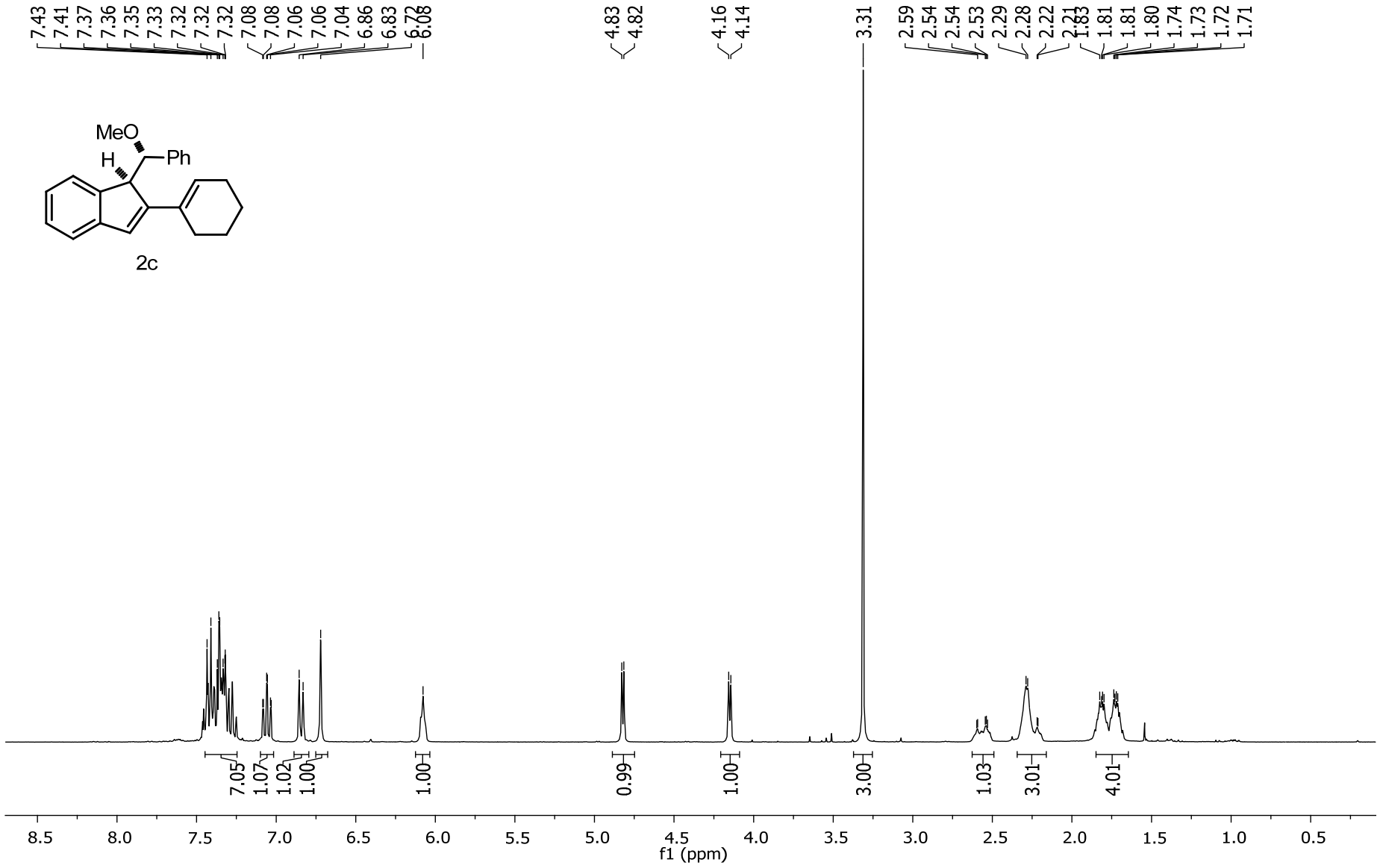
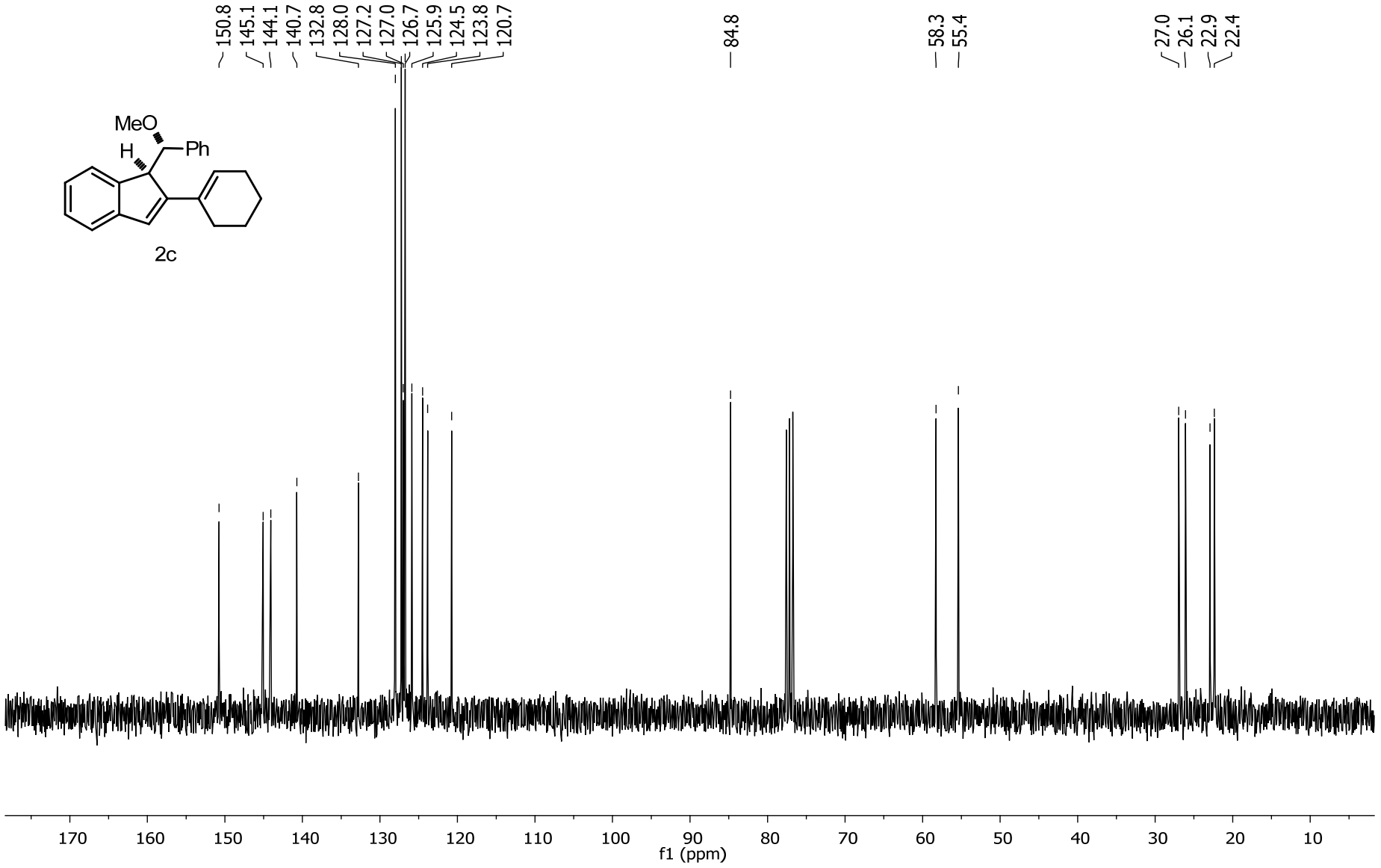
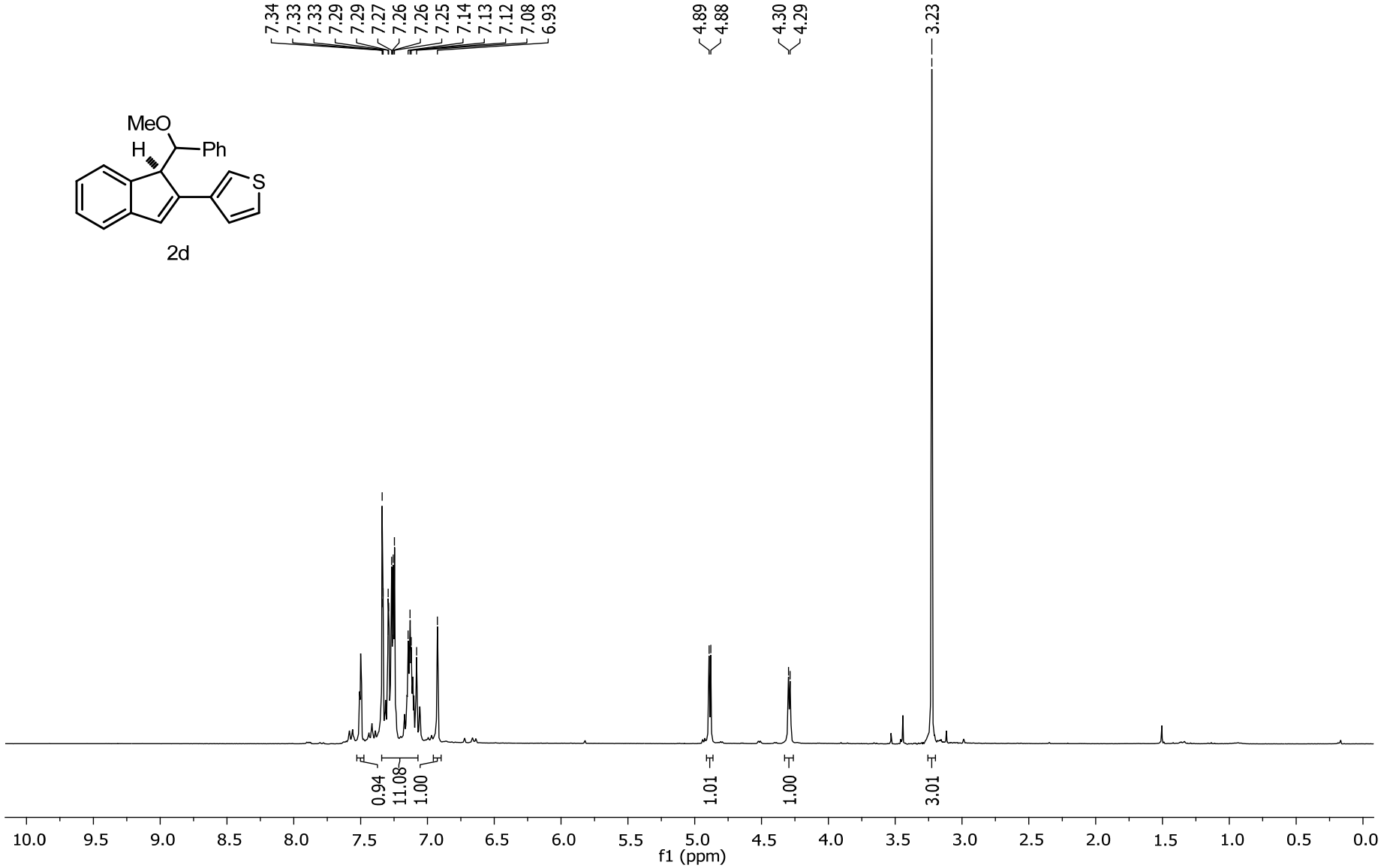


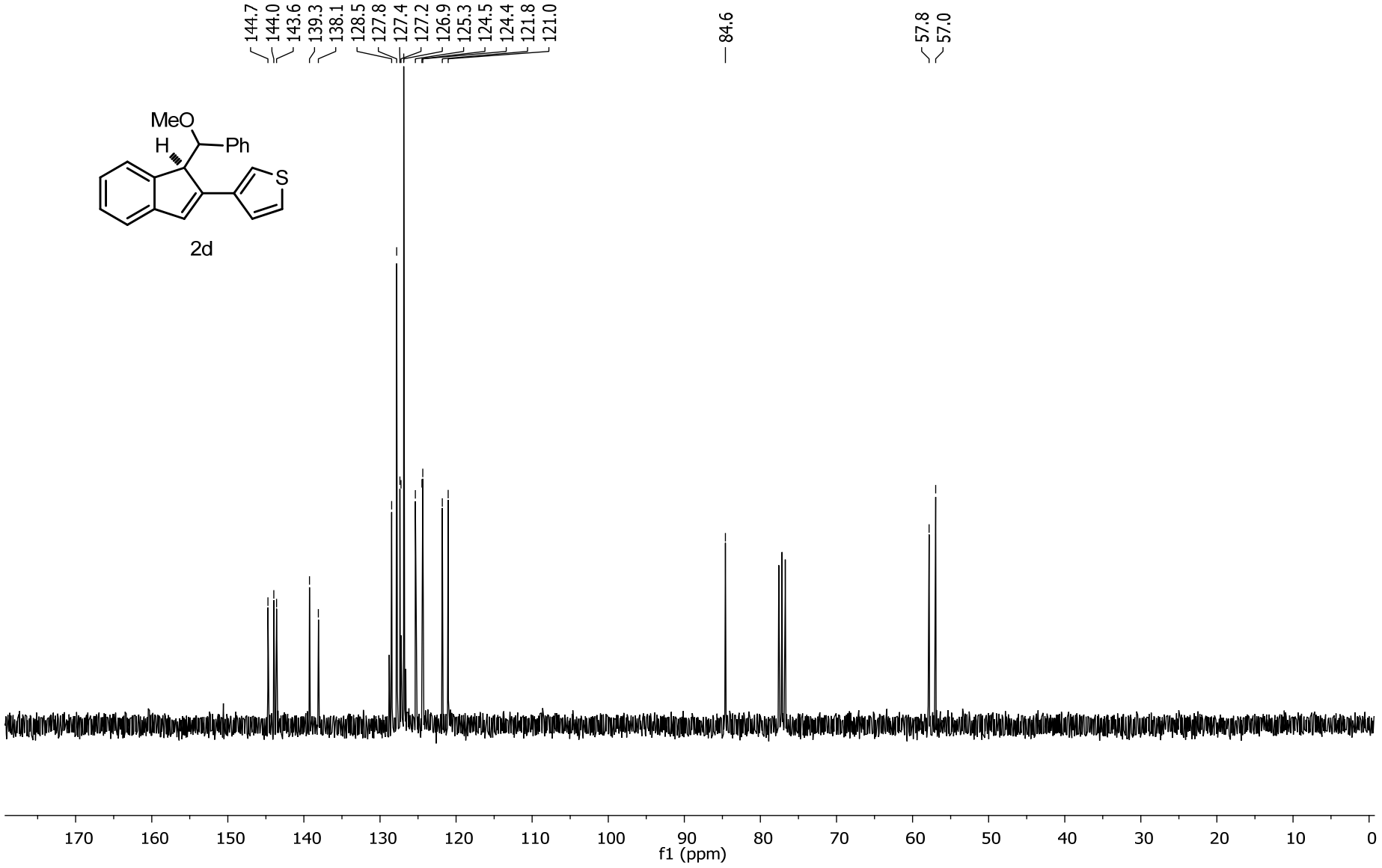
$^{13}C\{^{1}H\}$NMR (75.4 MHz, $CDCl_3$)



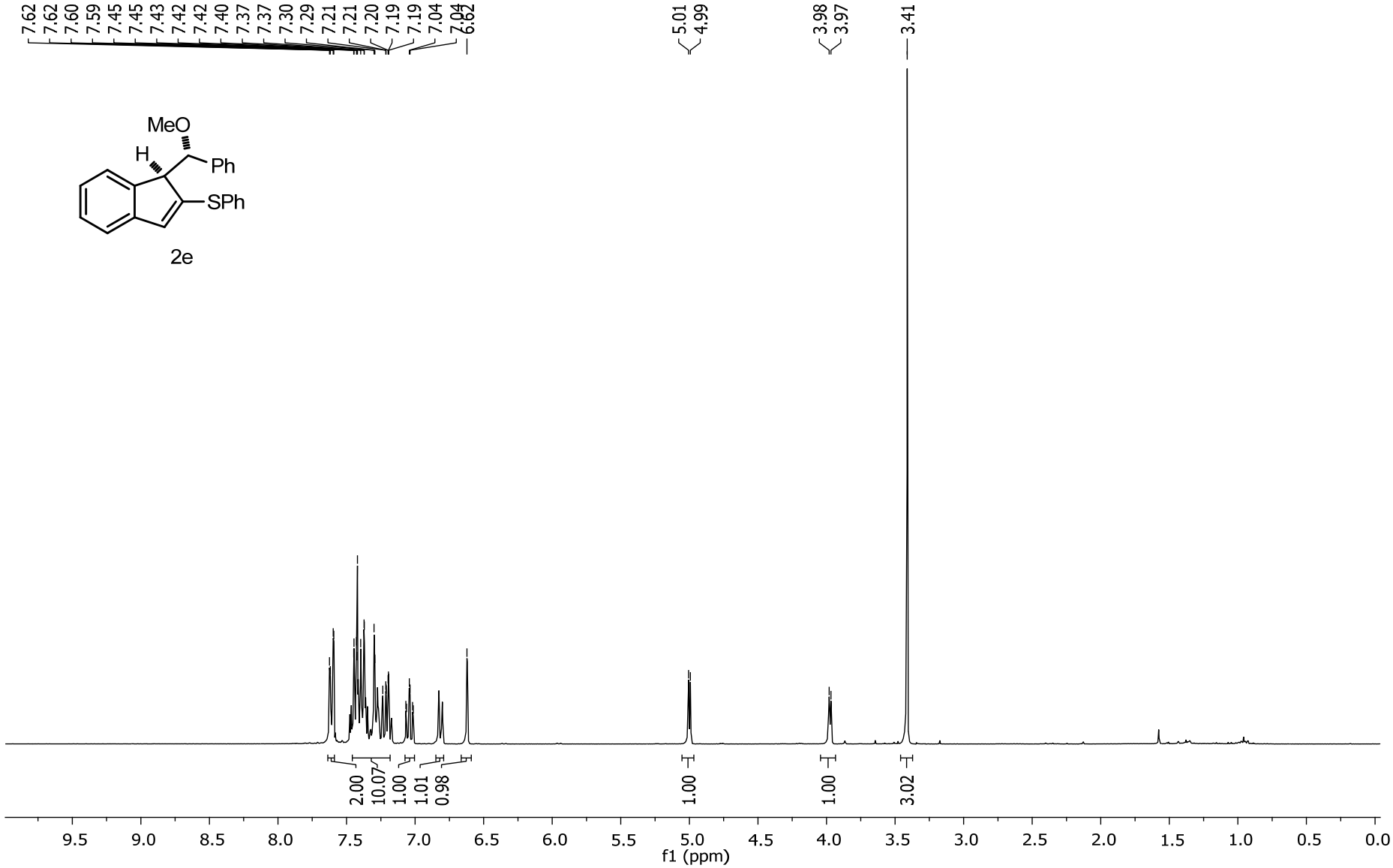
^{1}H NMR (300 MHz, $CDCl_3$)



$^{13}C\{^{1}H\}$NMR (75.4 MHz, $CDCl_3$)



^{1}H NMR (300 MHz, $CDCl_3$)



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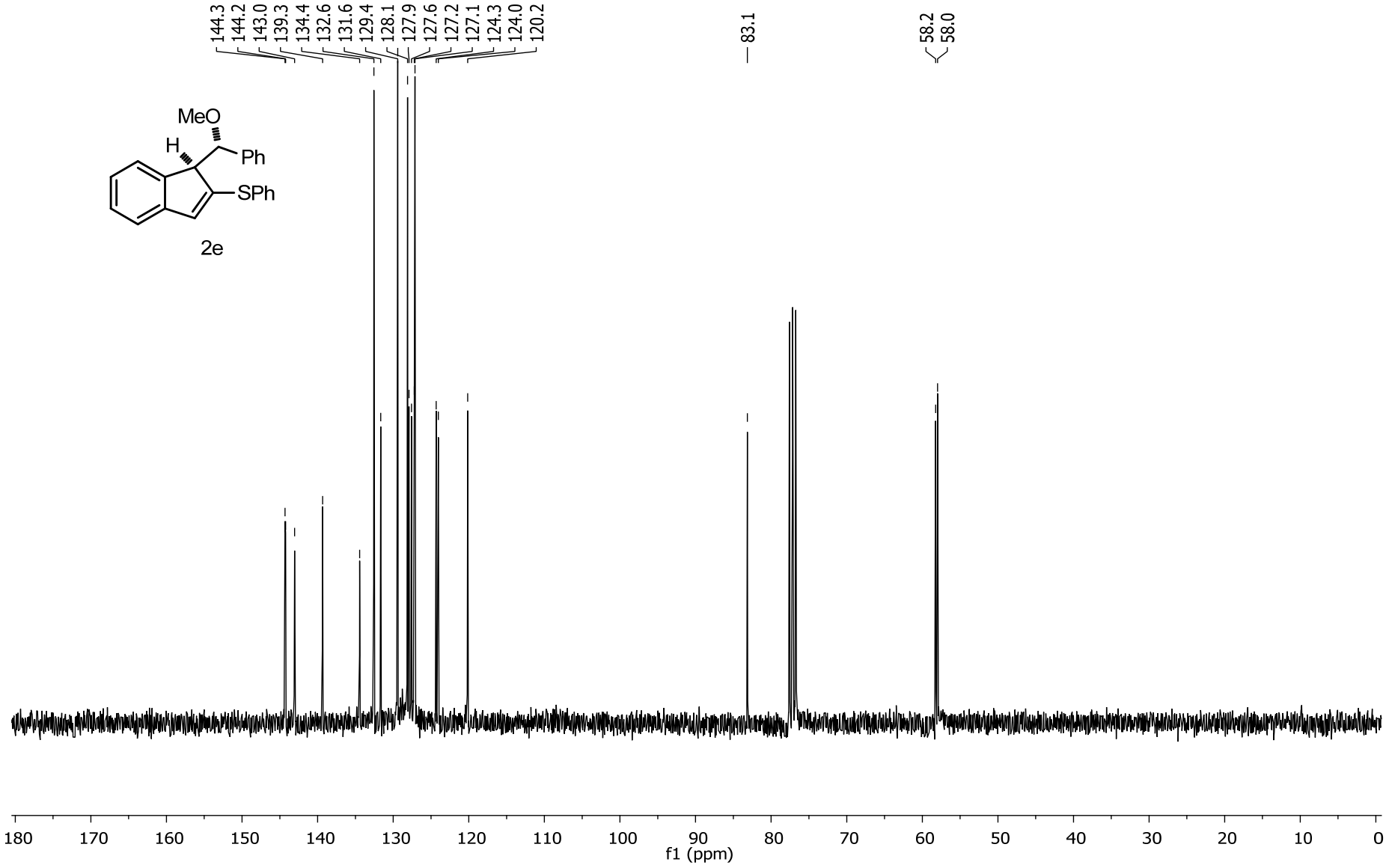

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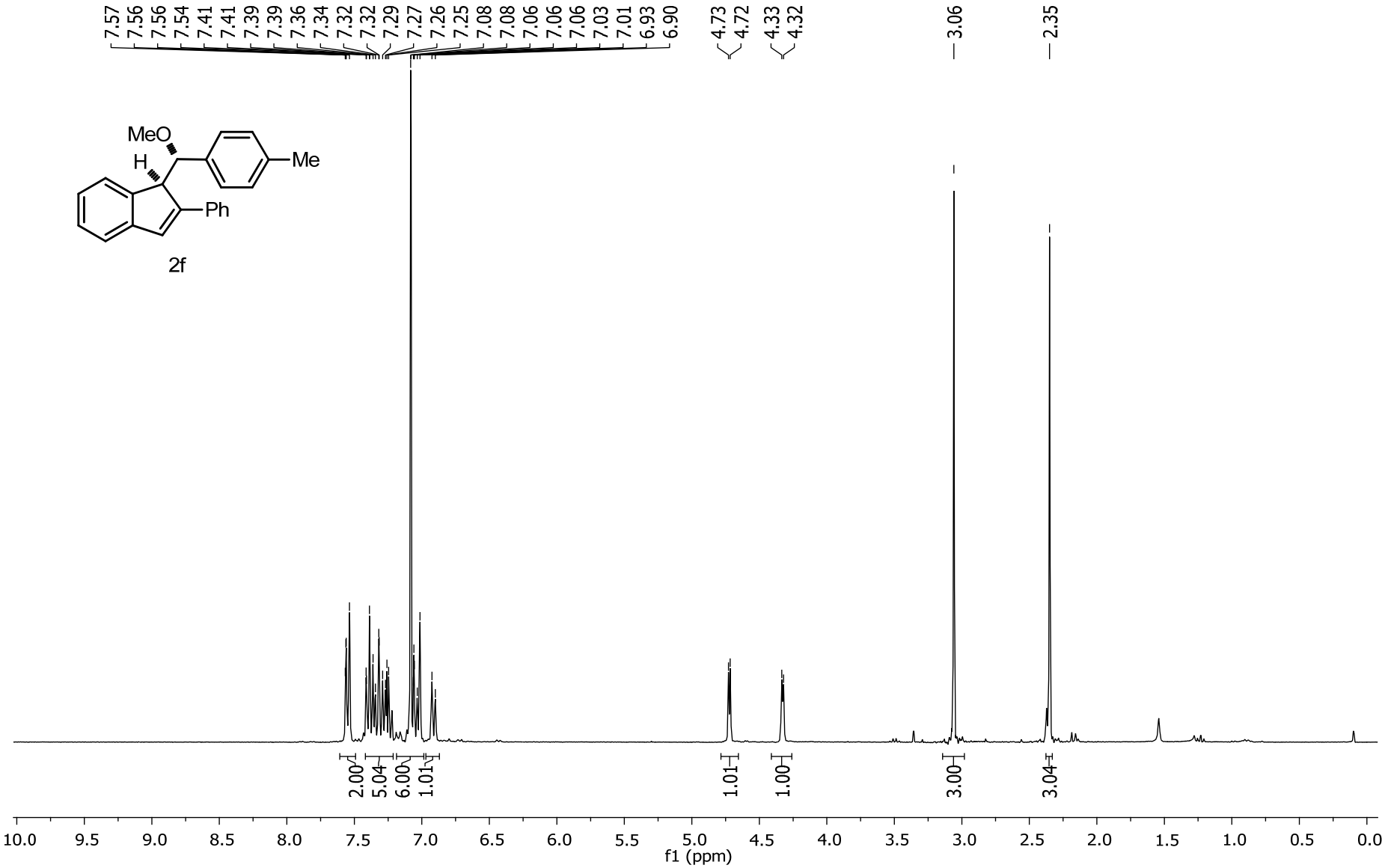
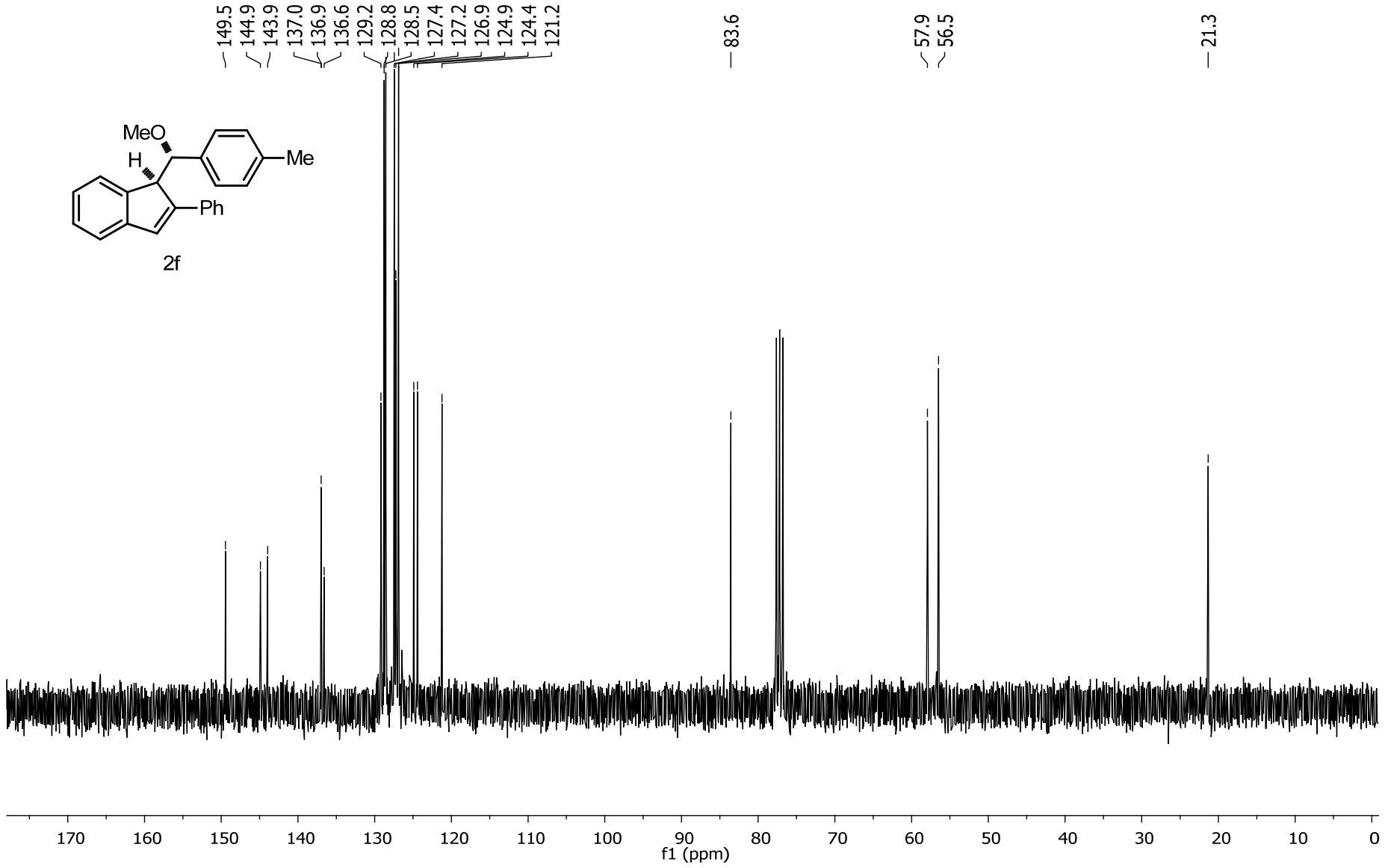


$^{13}C\{^{1}H\}$NMR (75.4 MHz, $CDCl_3$)



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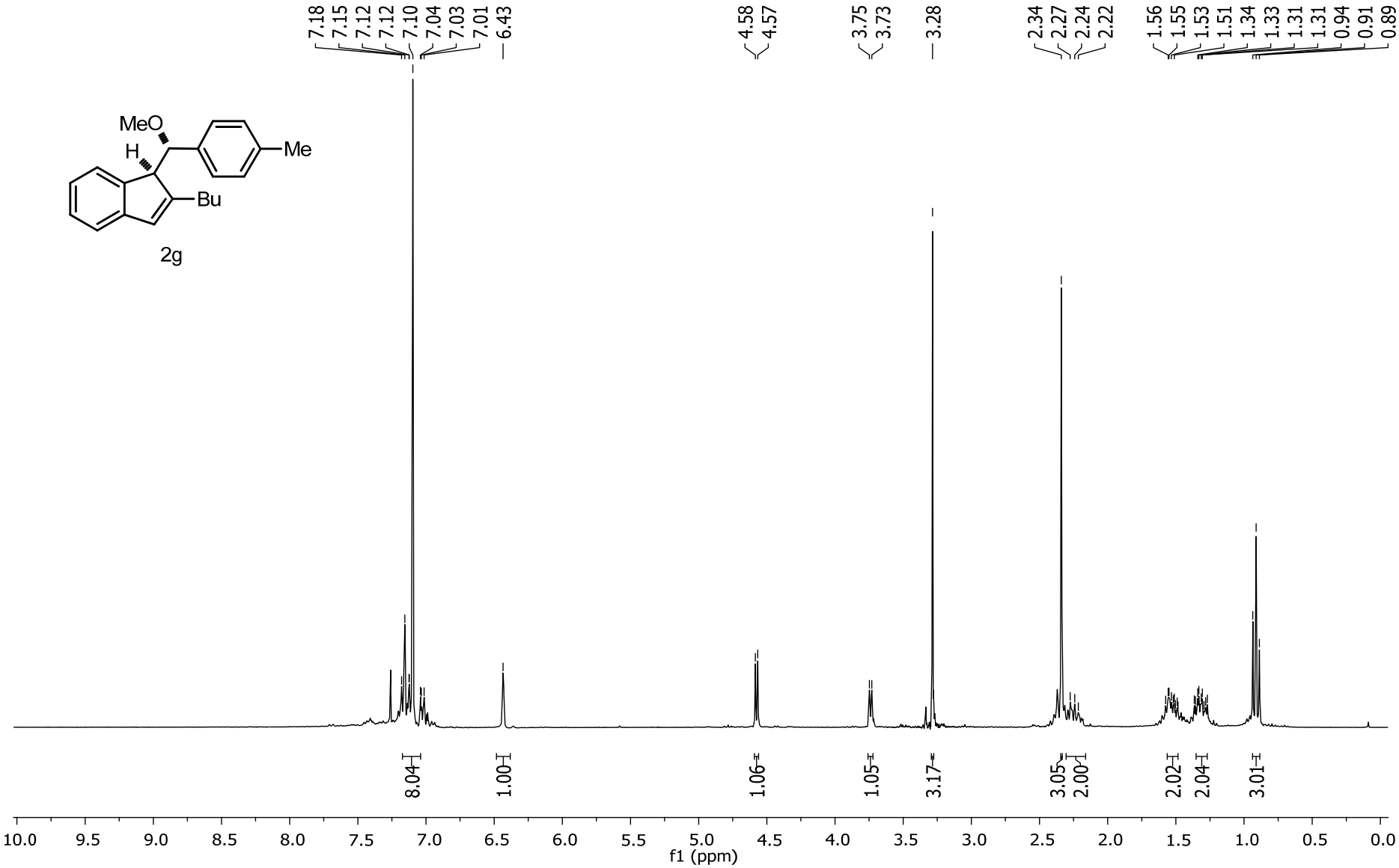
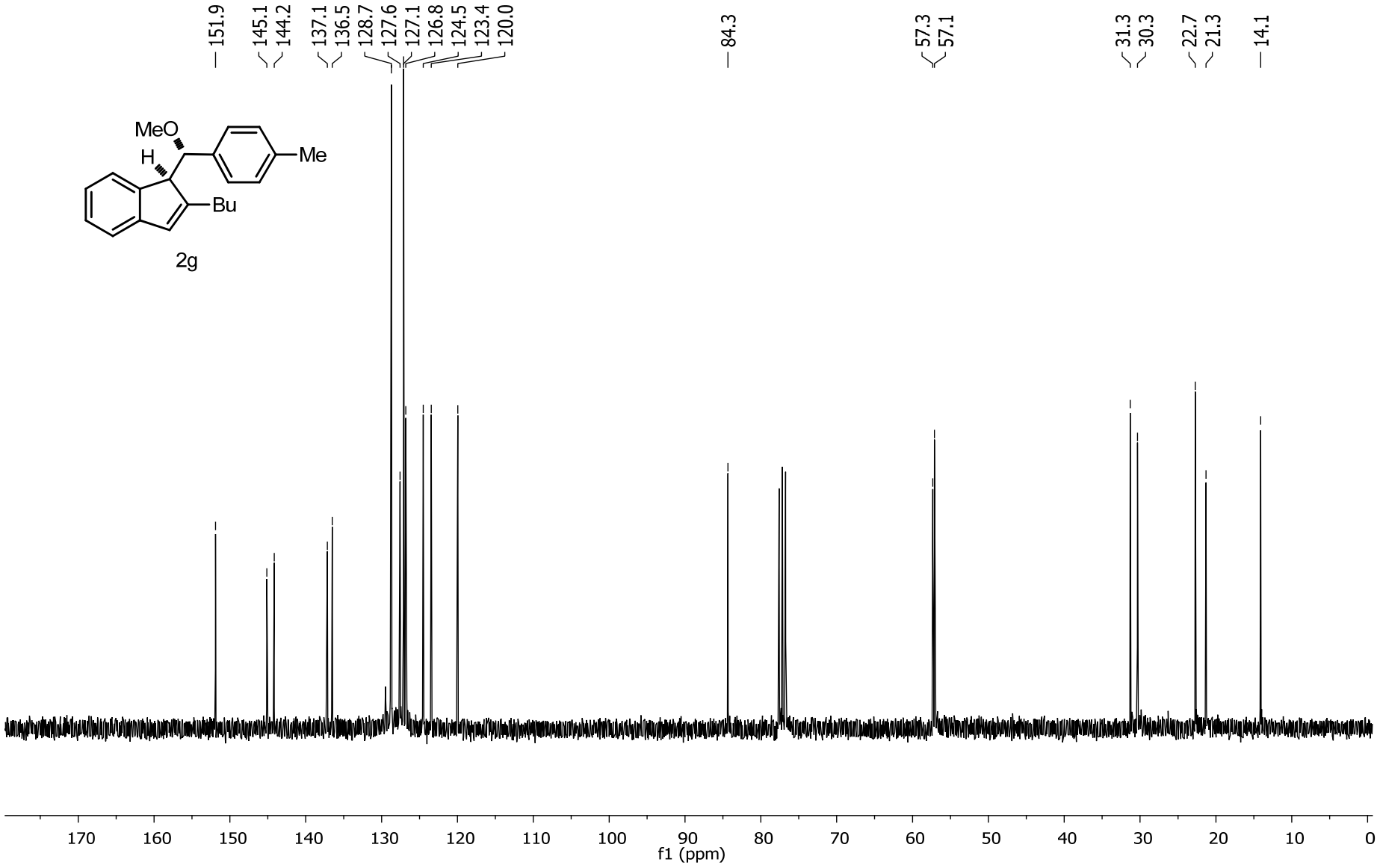


$^{13}C\{^{1}H\}$NMR (75.4 MHz, $CDCl_3$)



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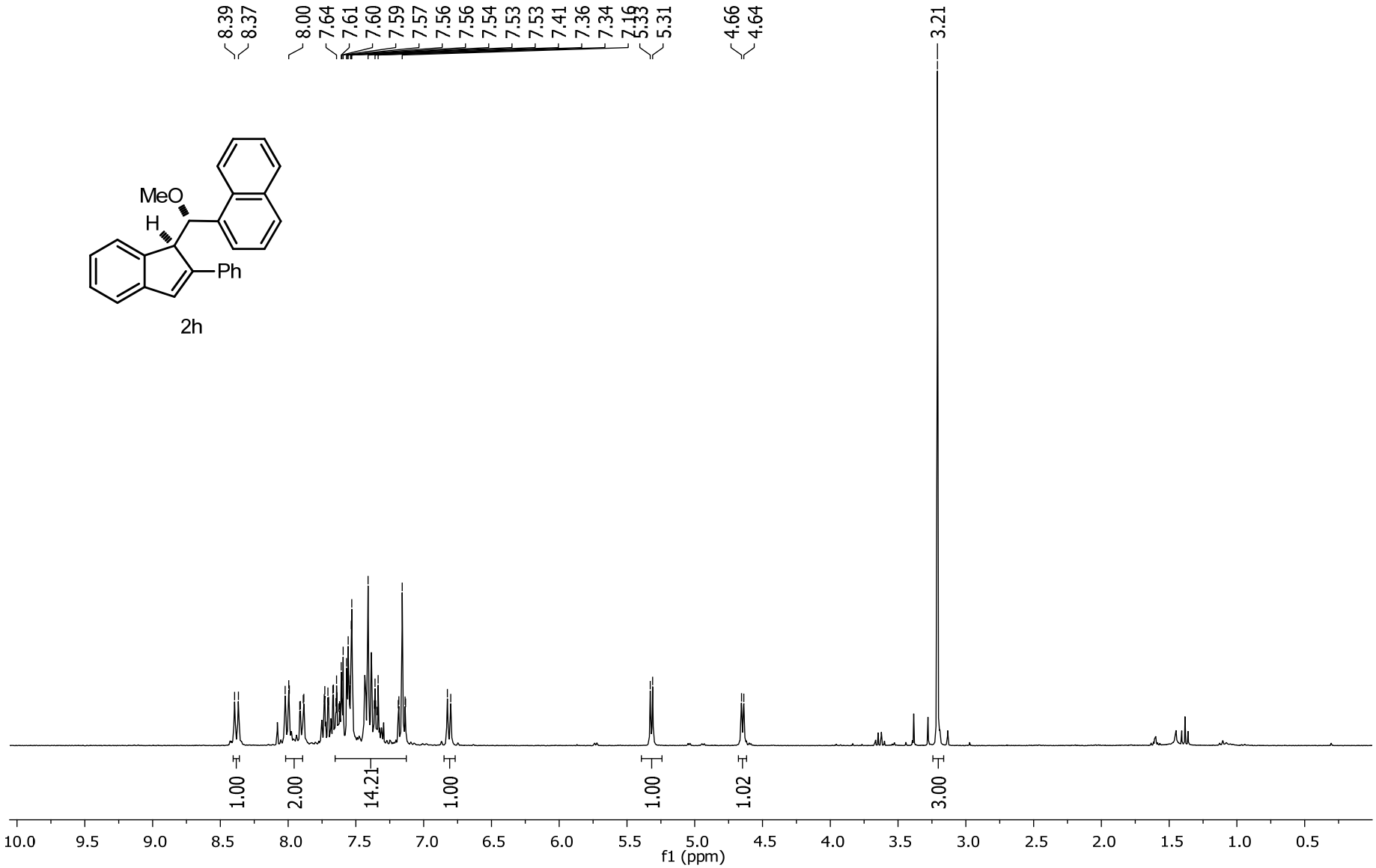
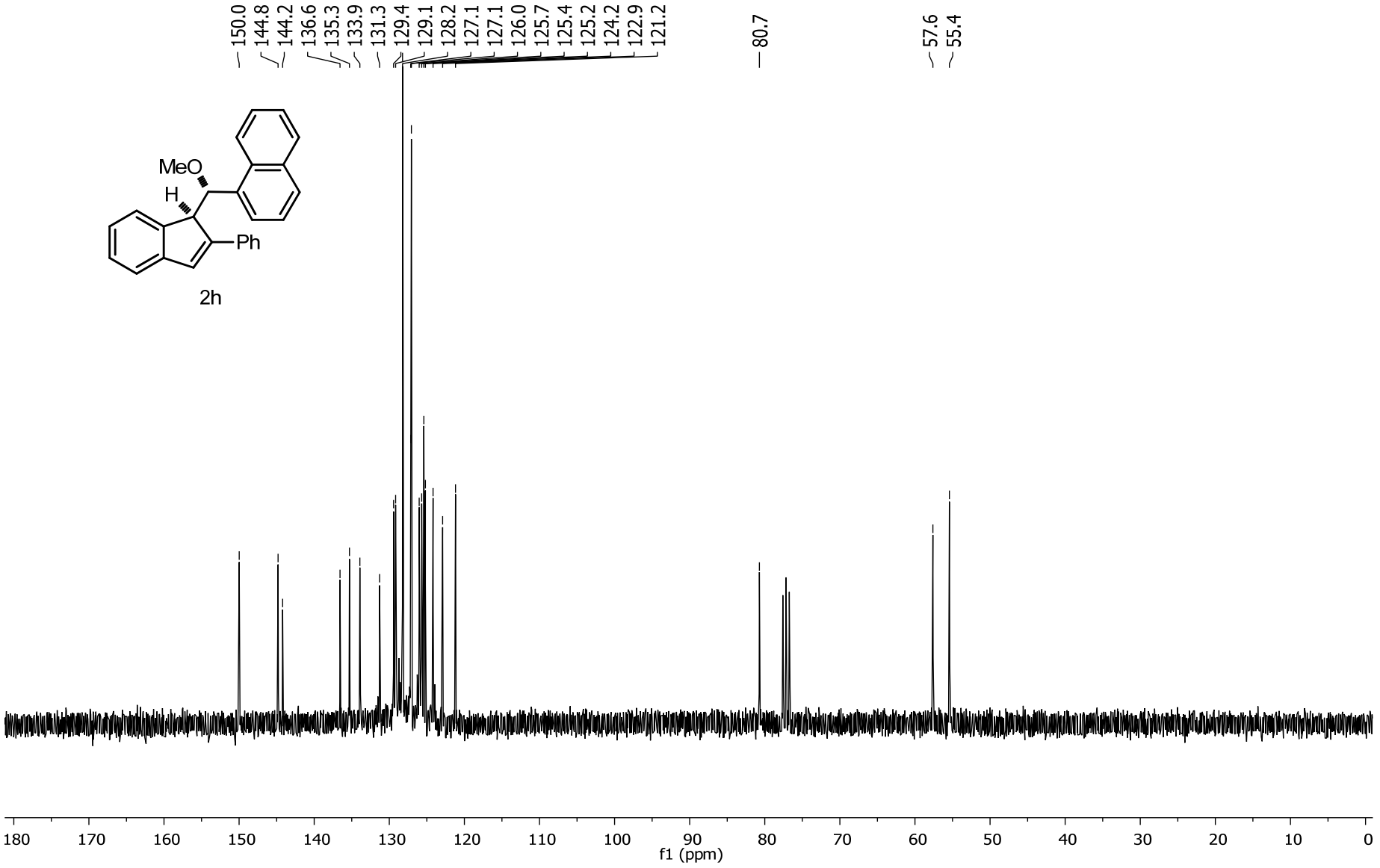


$^{13}C\{^{1}H\}$NMR (75.4 MHz, $CDCl_3$)



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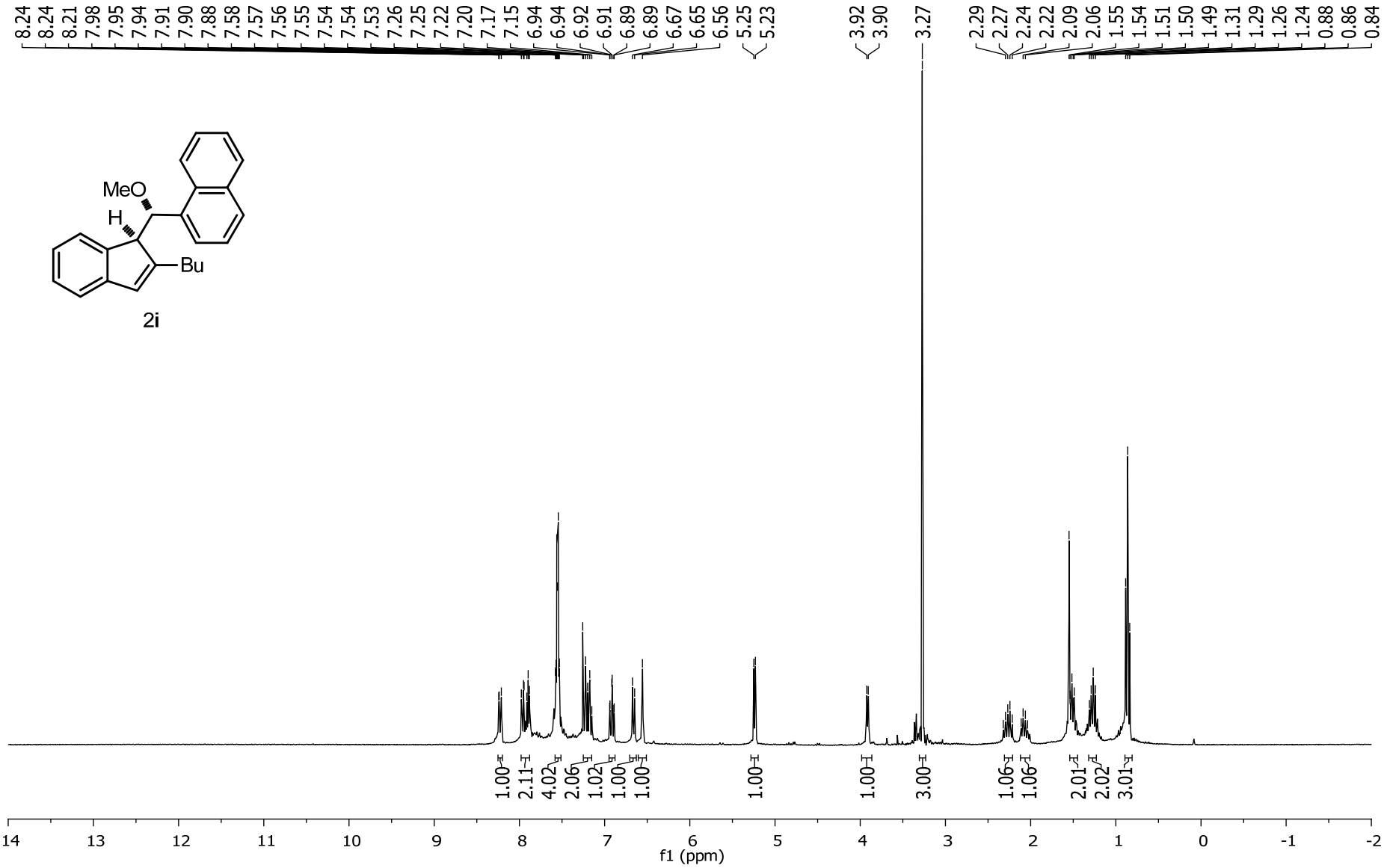

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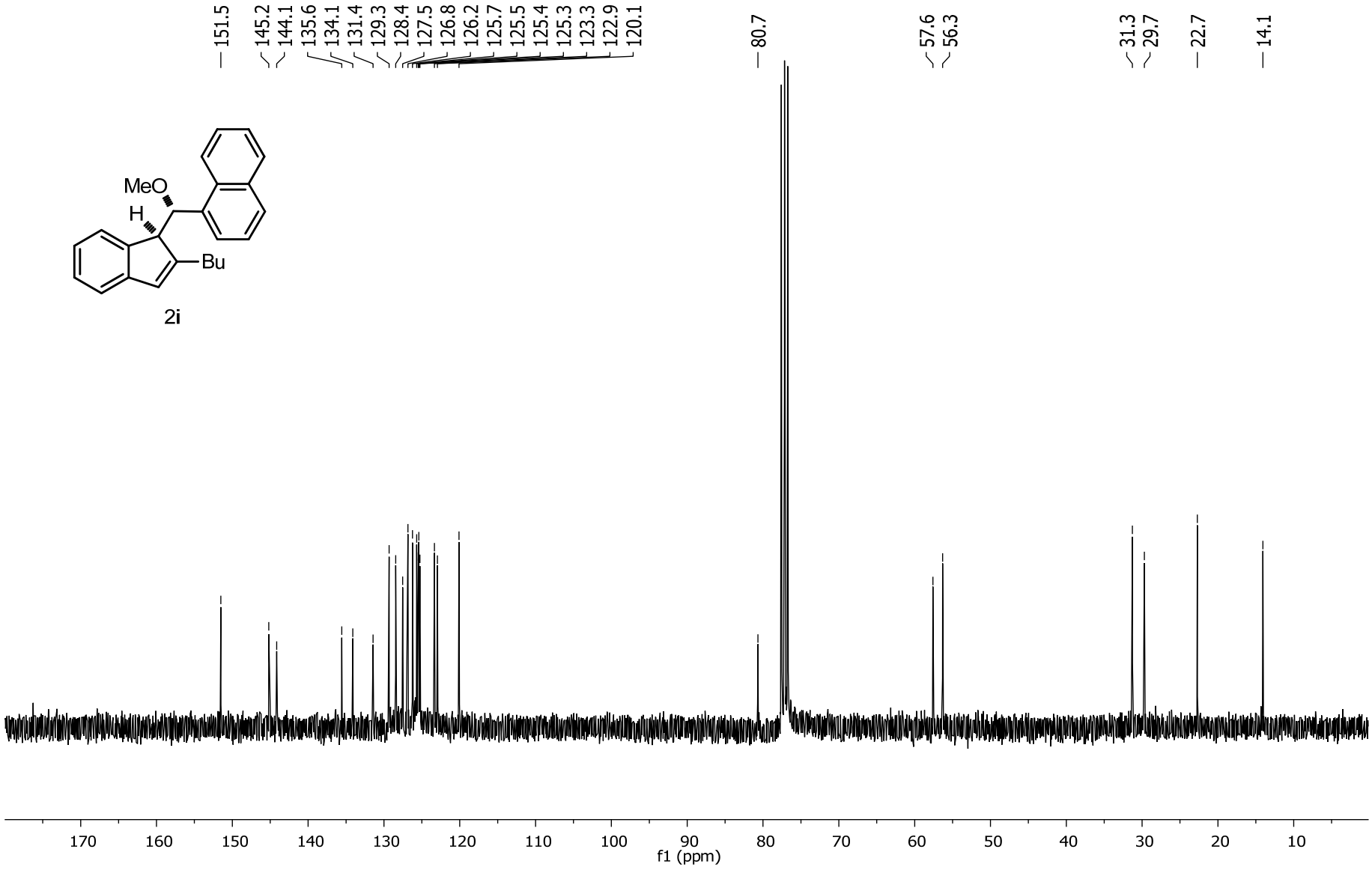

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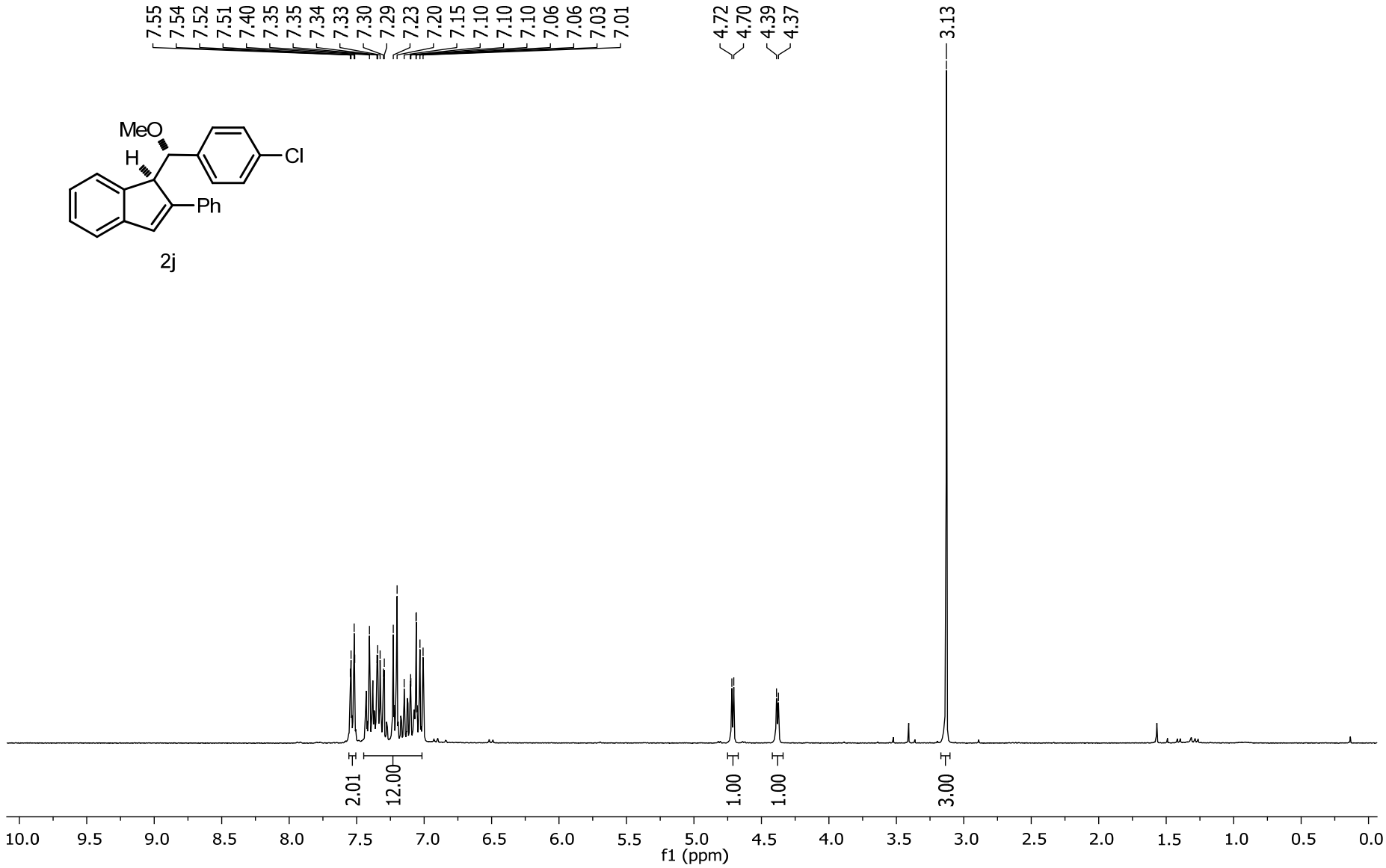
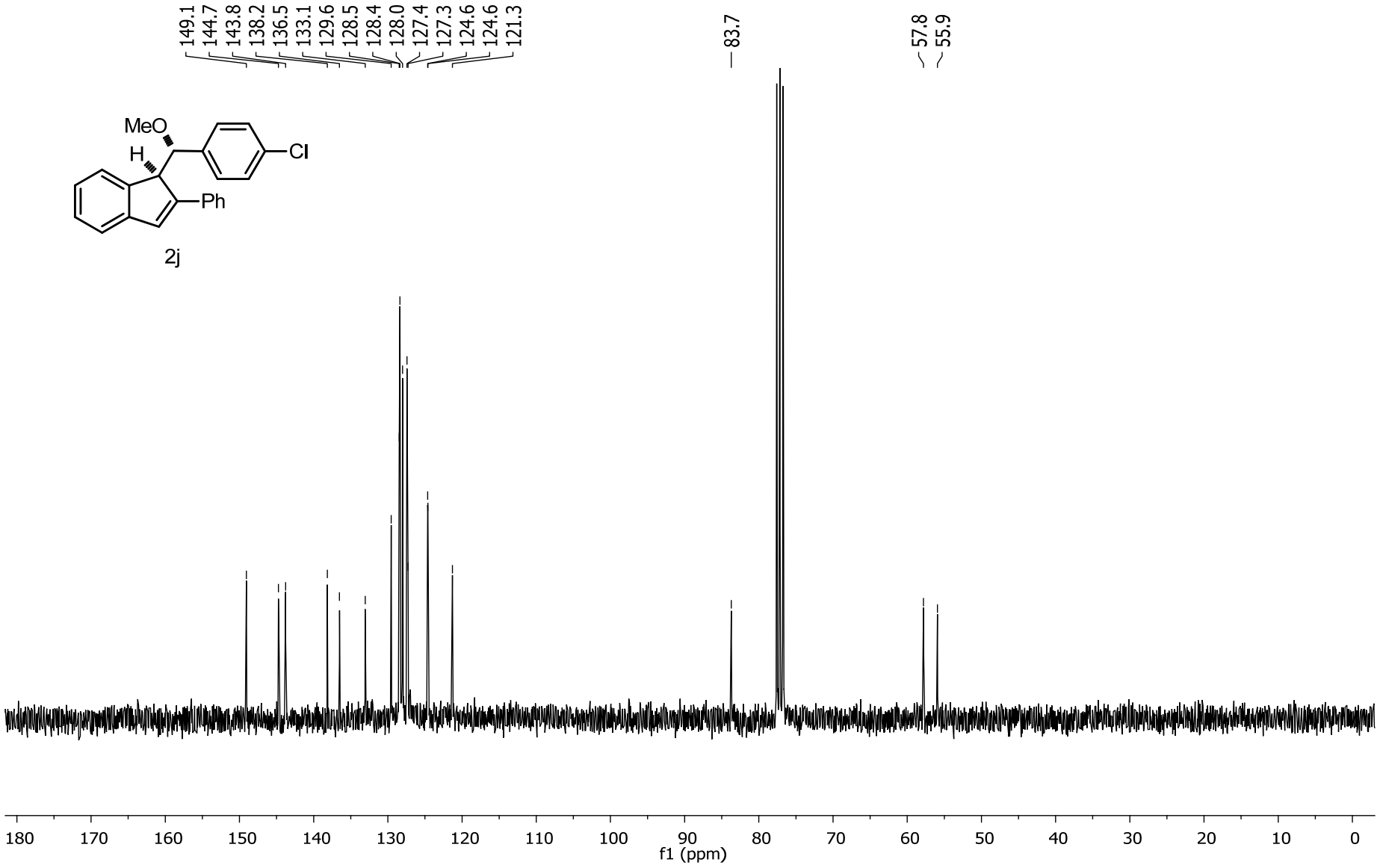


$^{13}C\{^{1}H\}$NMR (75.4 MHz, $CDCl_3$)



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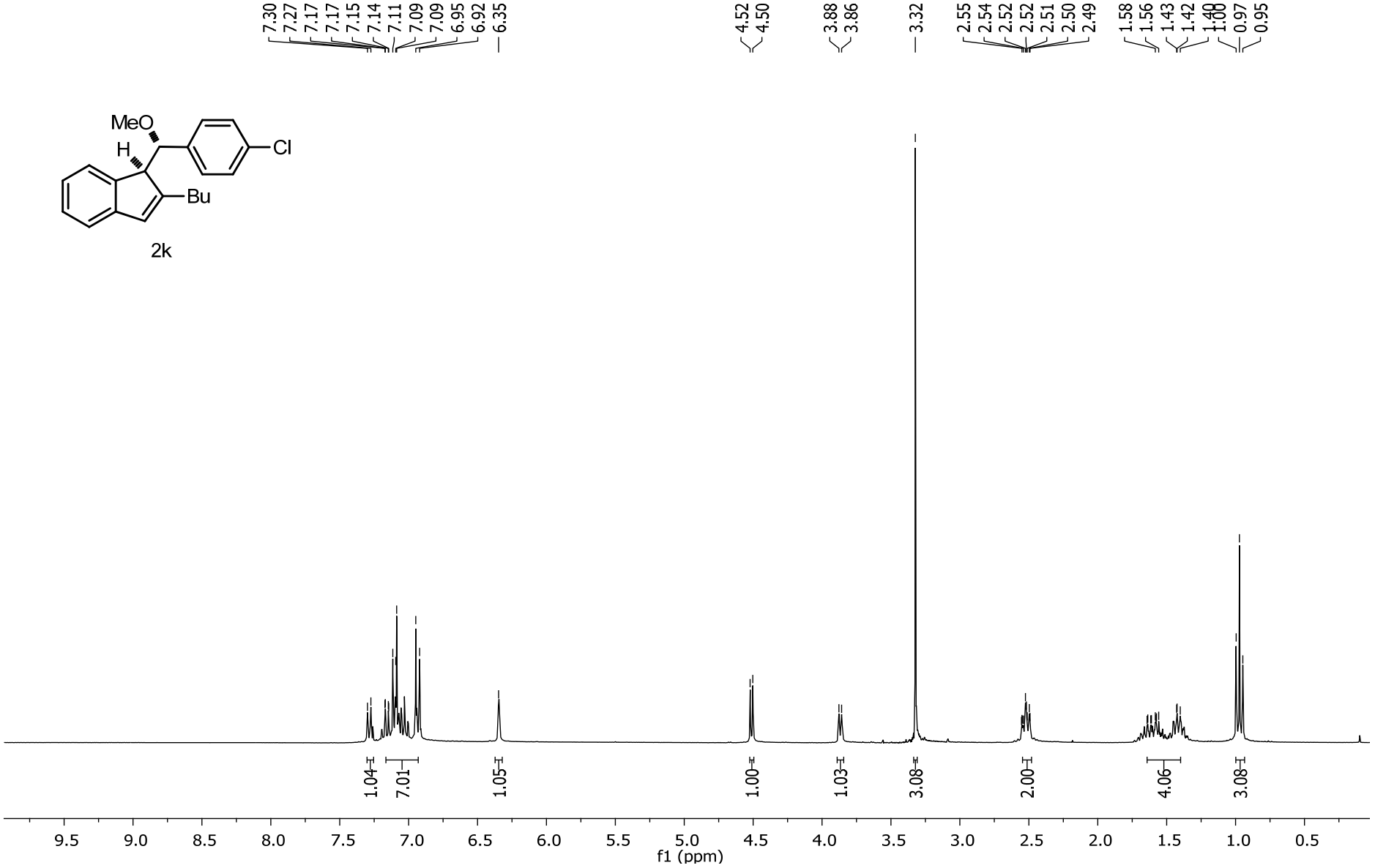
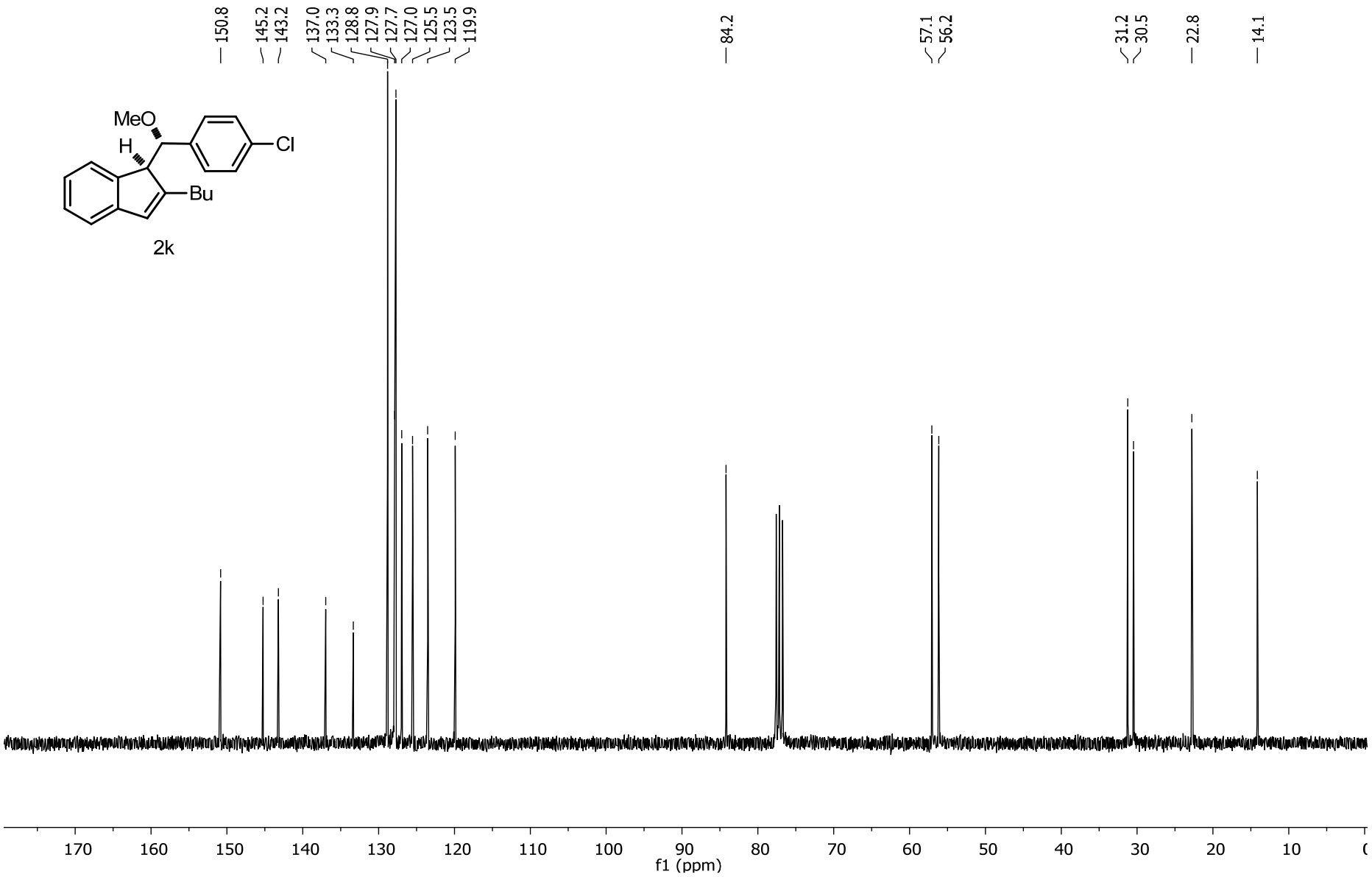


$^{13}C\{^{1}H\}$NMR (75.4 MHz, $CDCl_3$)



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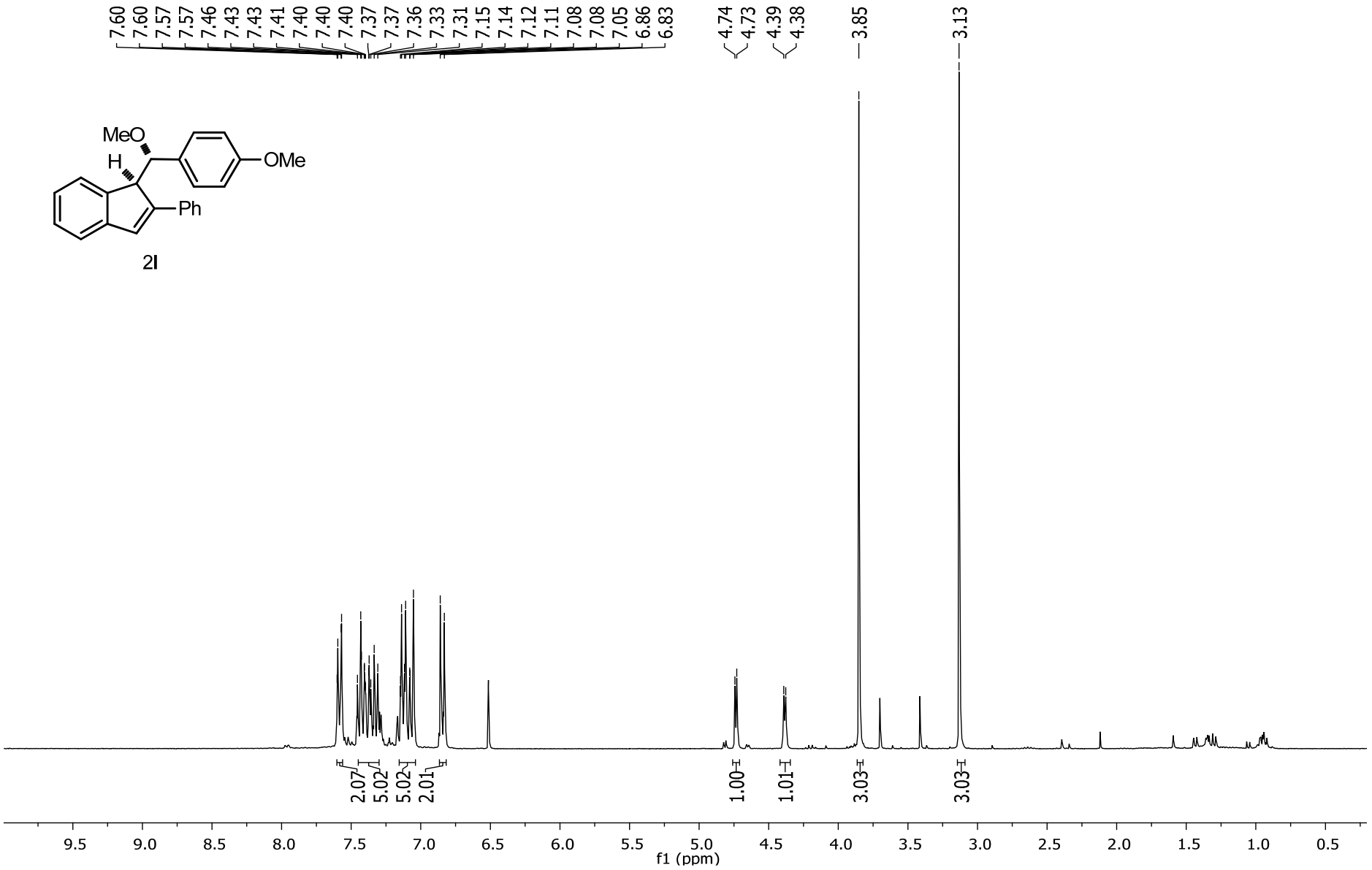
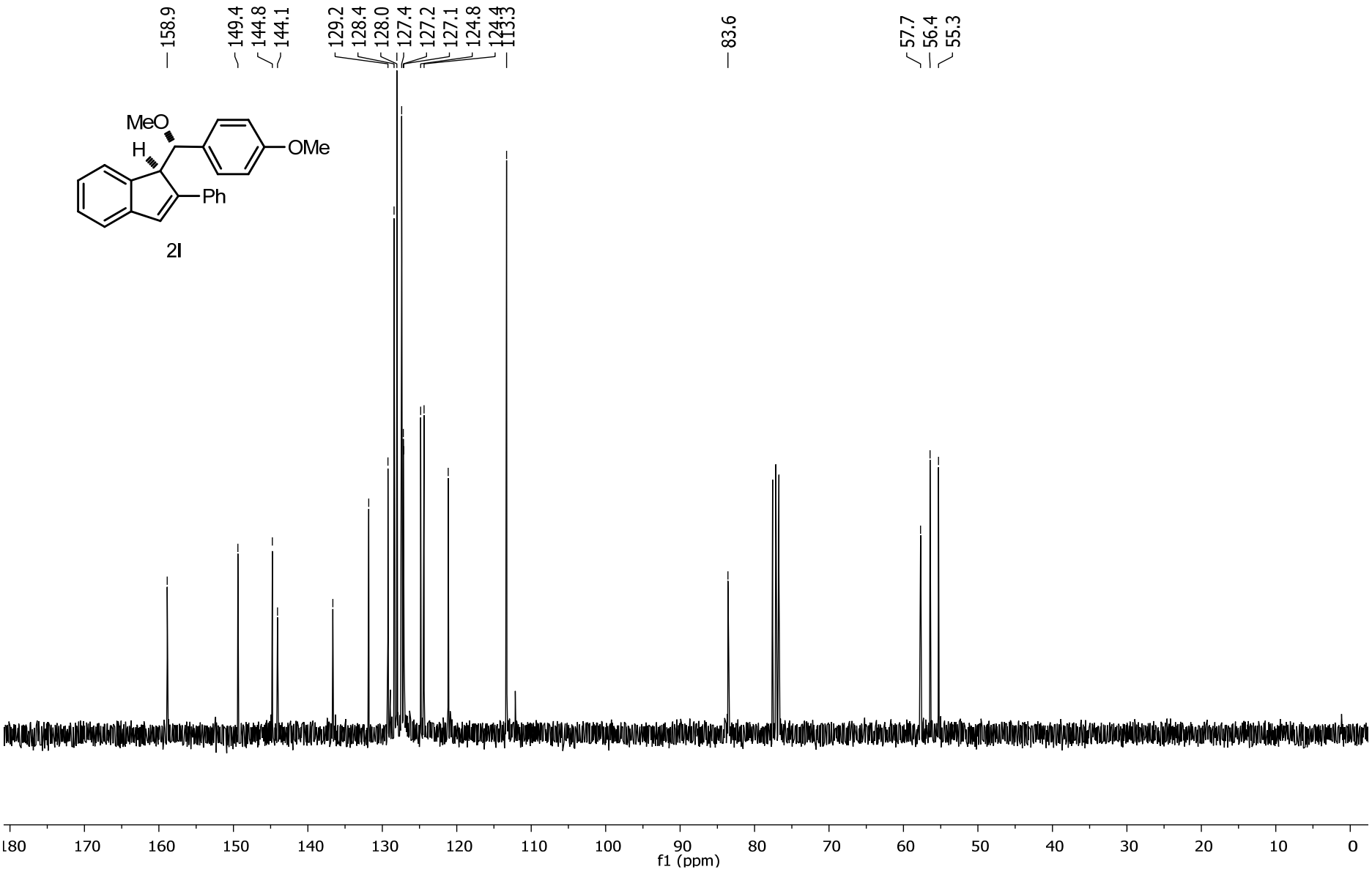


2l

$^{13}C\{^{1}H\}$NMR (75.4 MHz, $CDCl_3$)



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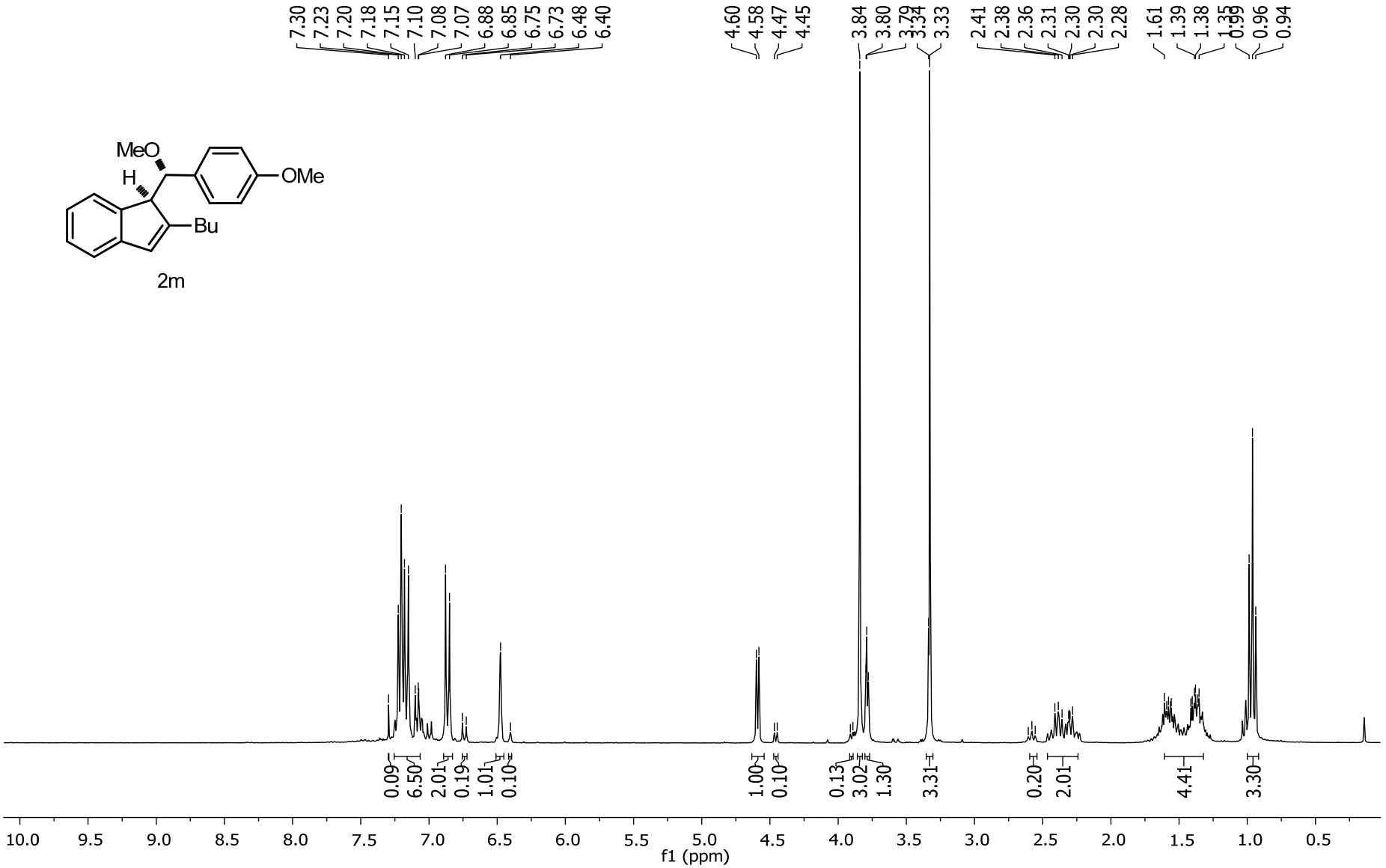
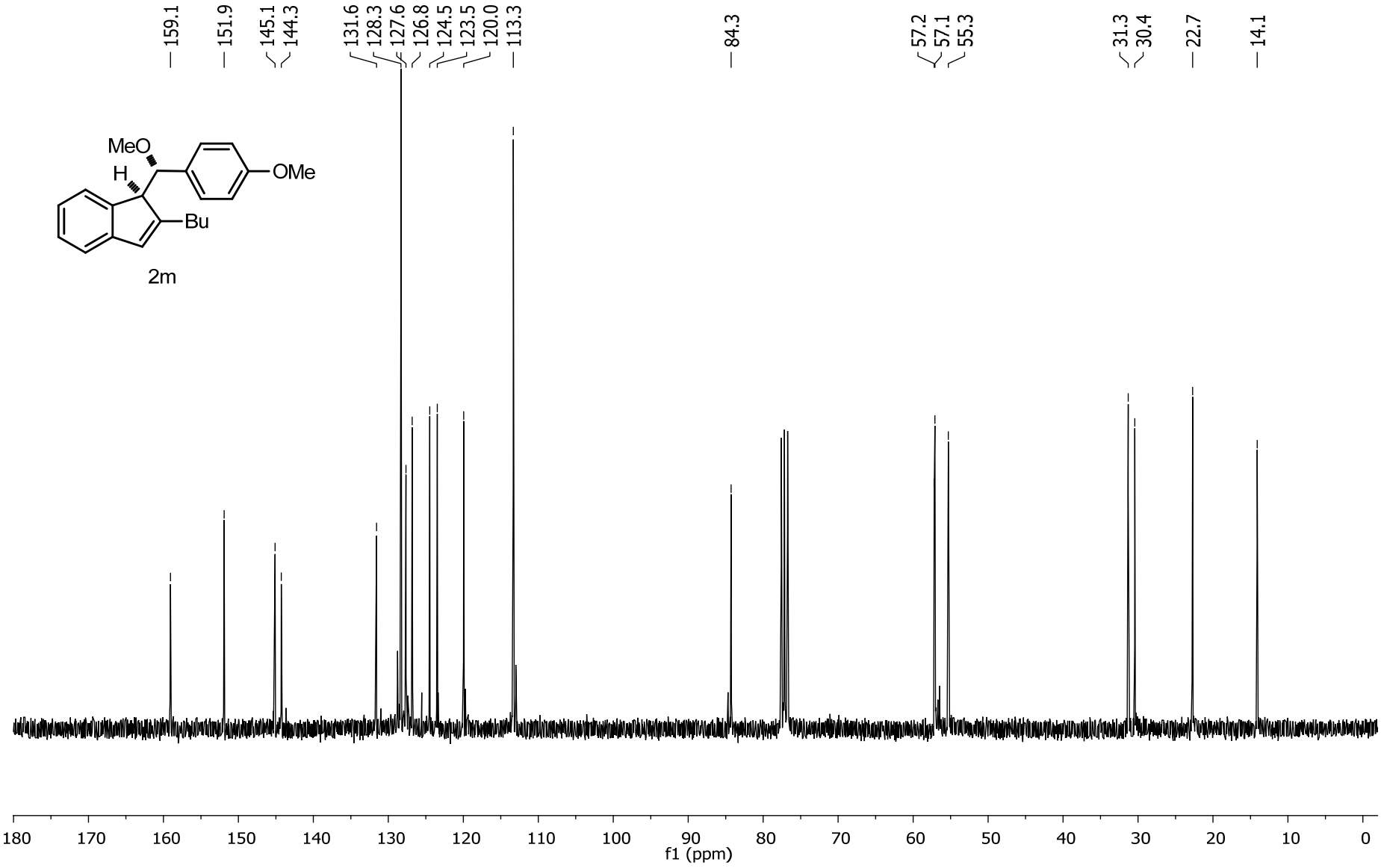
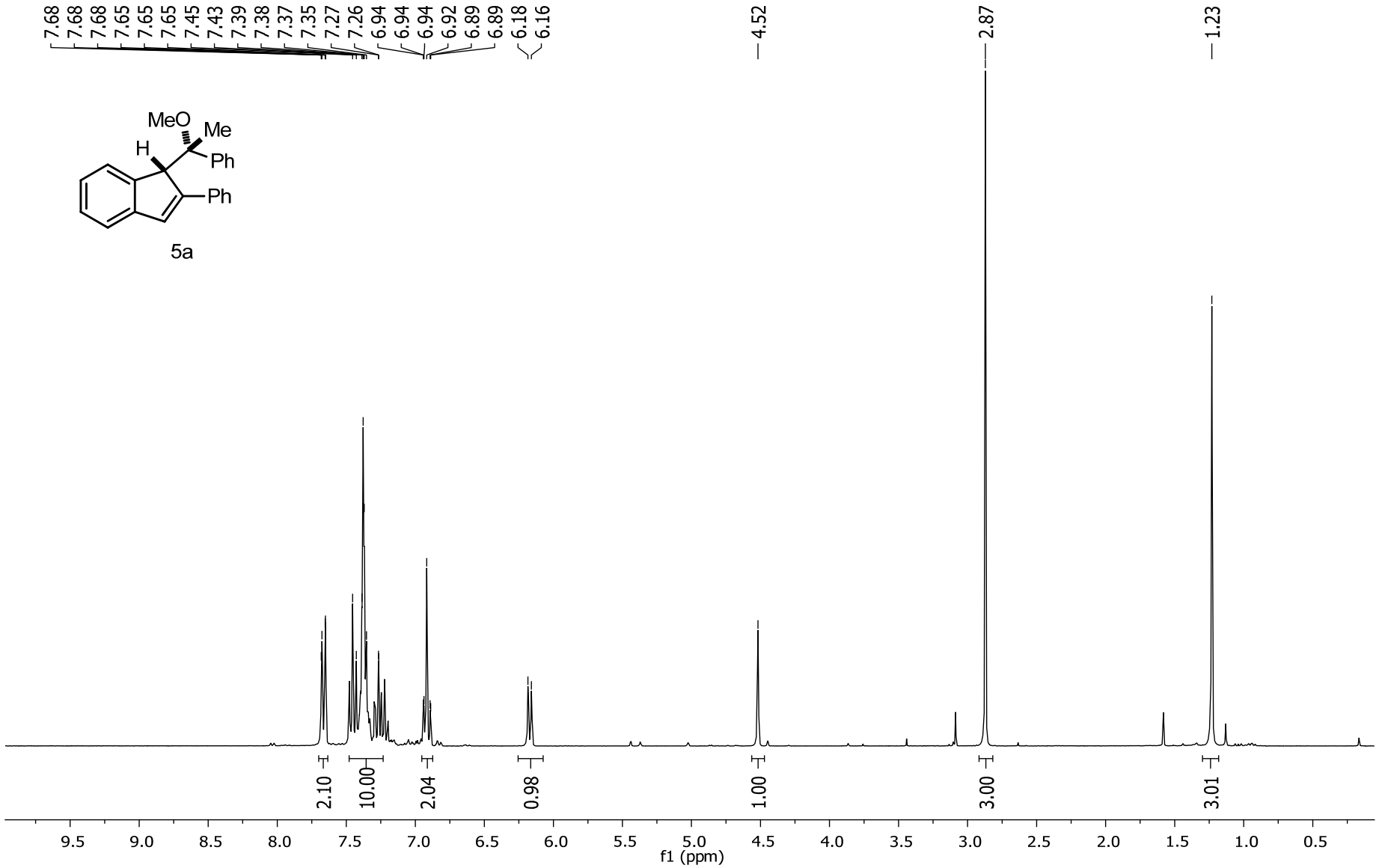


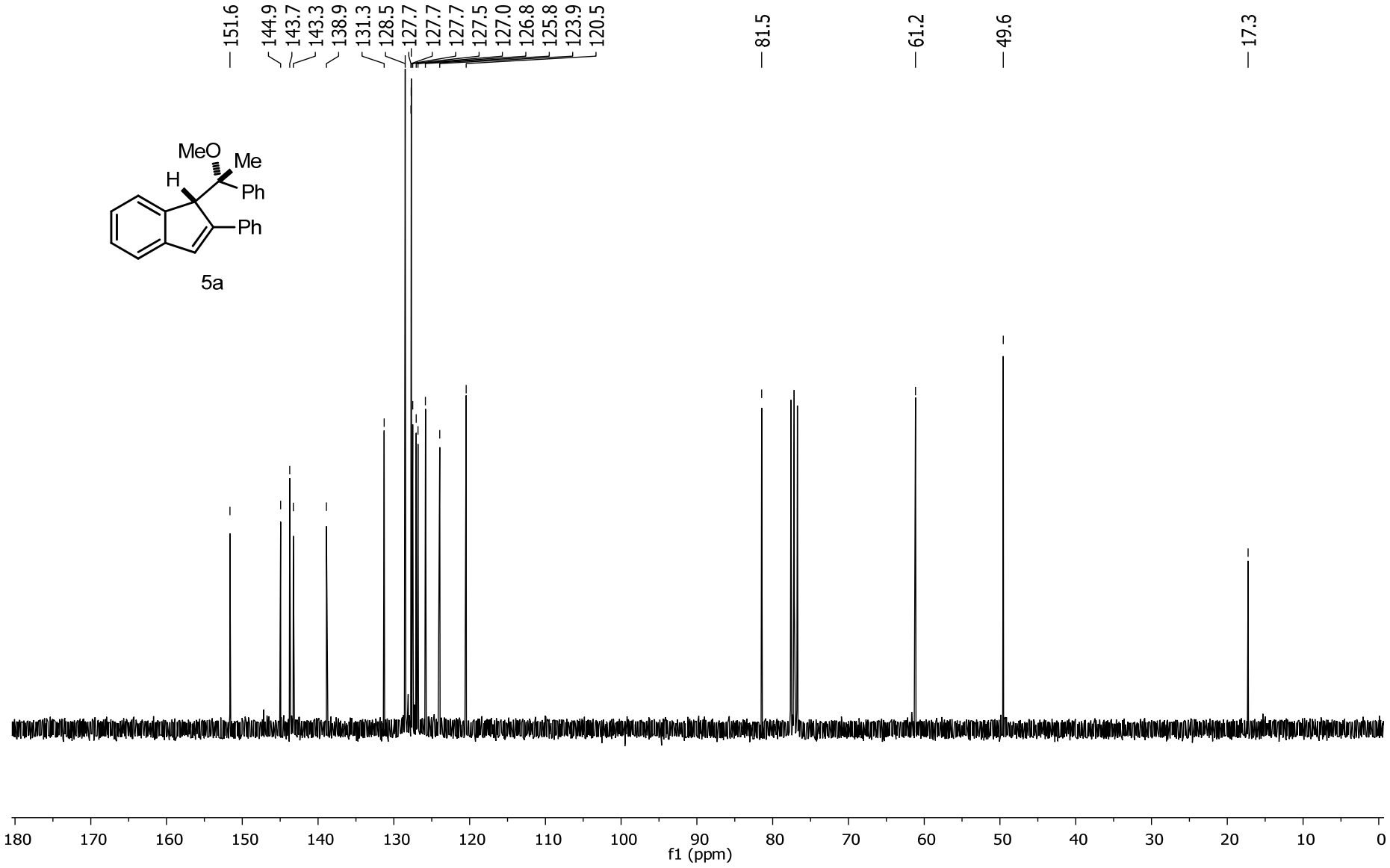
$^{13}C\{^{1}H\}$NMR (75.4 MHz, $CDCl_3$)



^{1}H NMR (300 MHz, $CDCl_3$)



$^{13}C\{^{1}H\}$NMR (75.4 MHz, $CDCl_3$)



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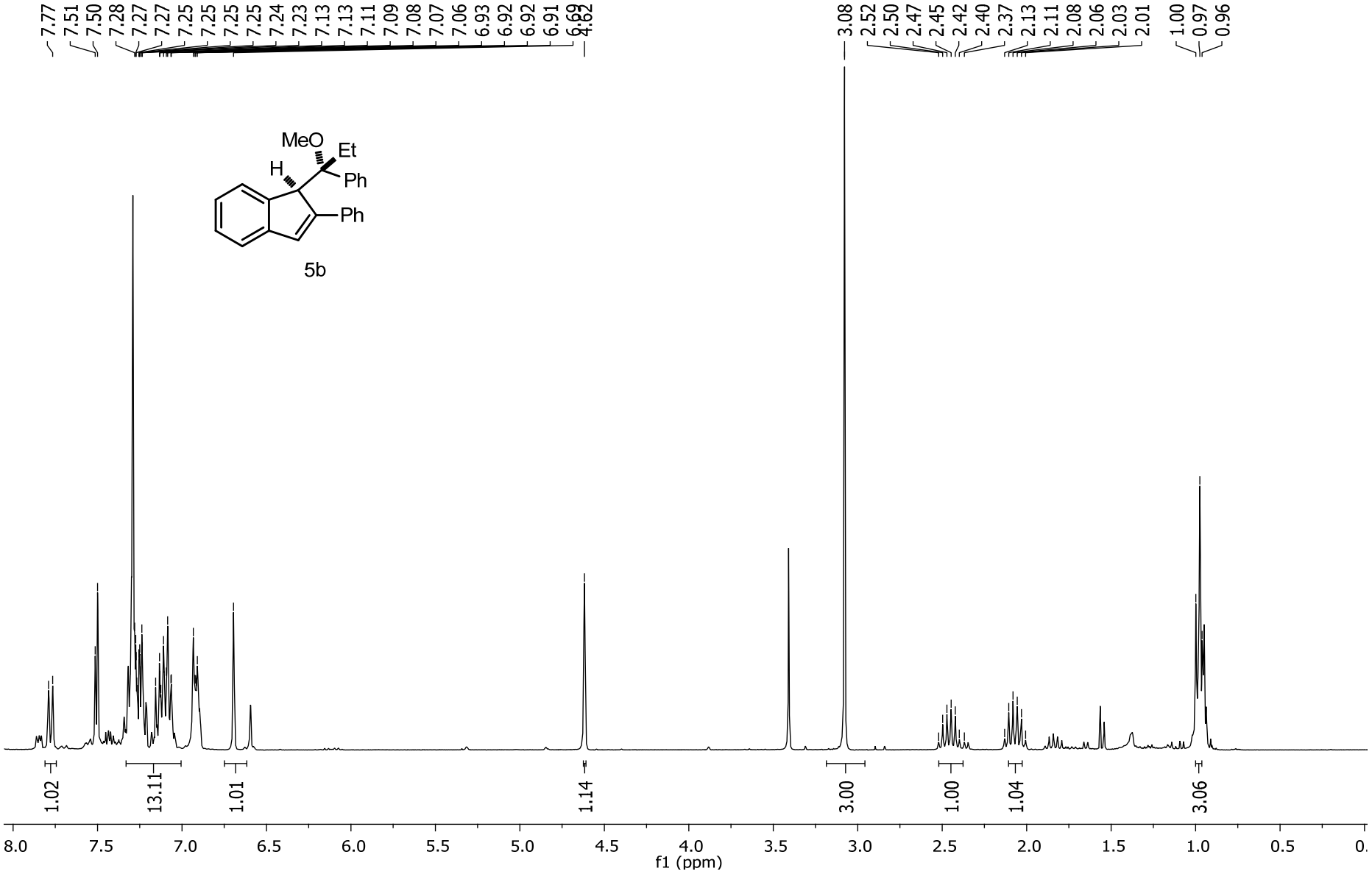
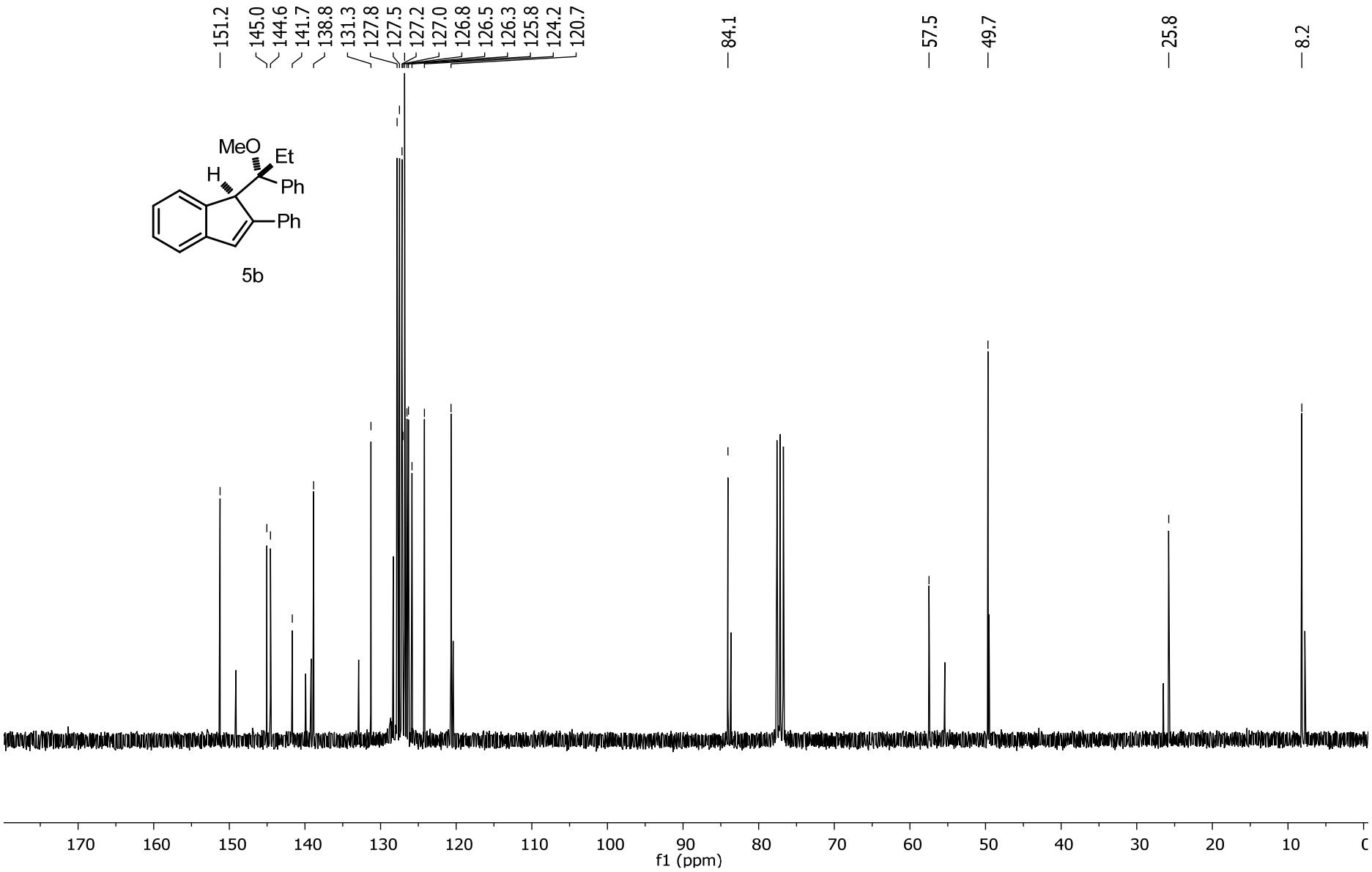
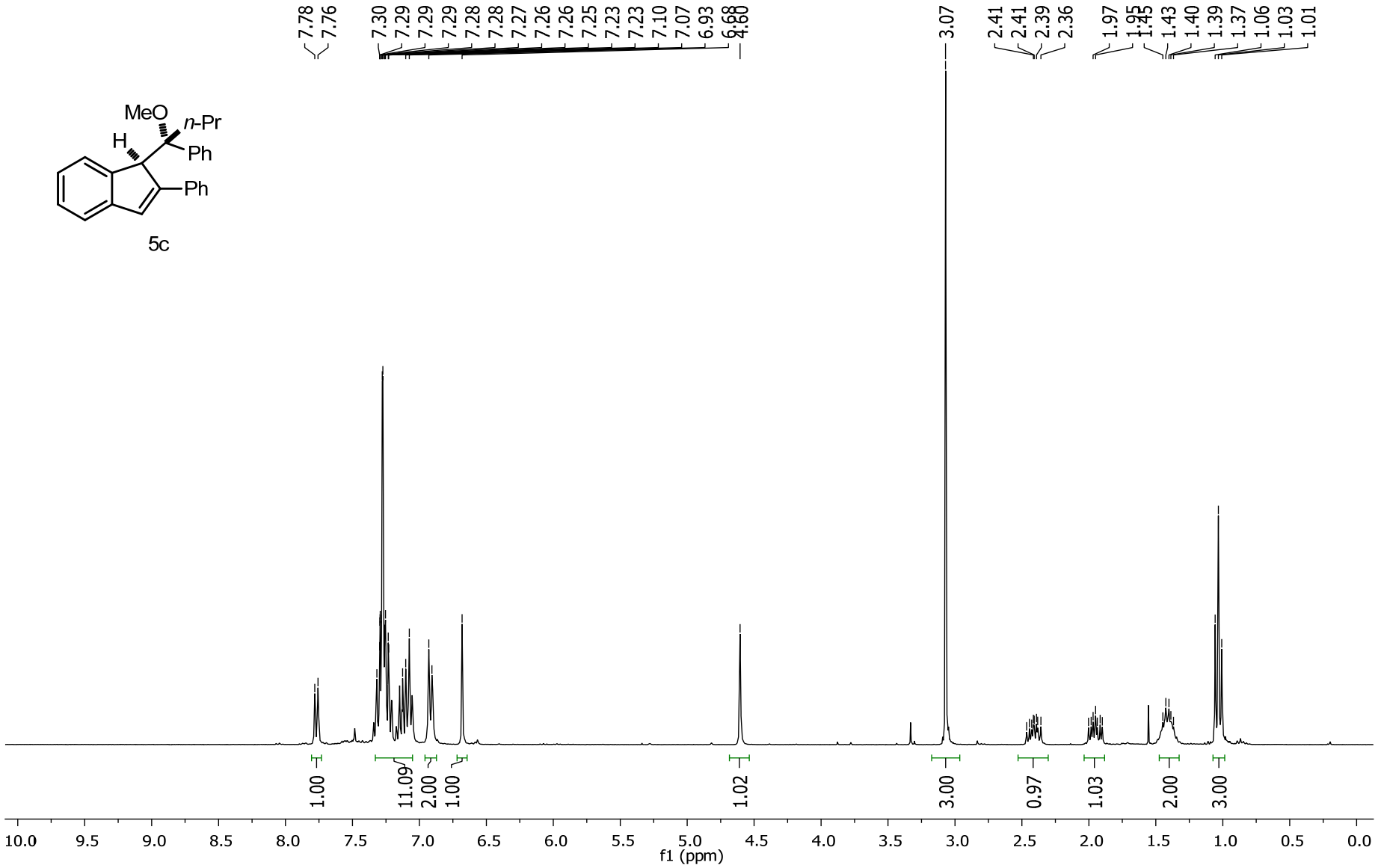


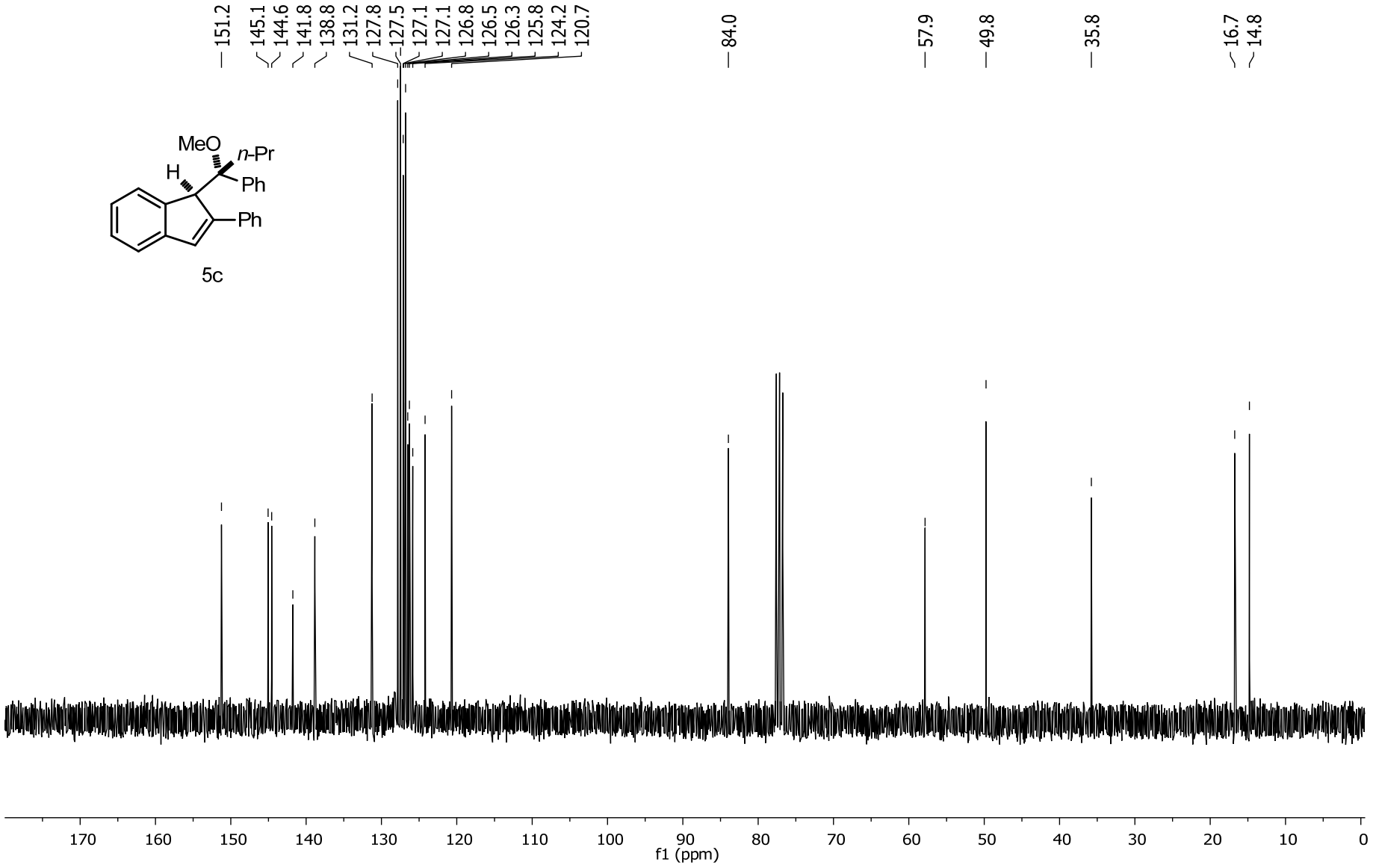
$^{13}C\{^{1}H\}$NMR (75.4 MHz, $CDCl_3$)



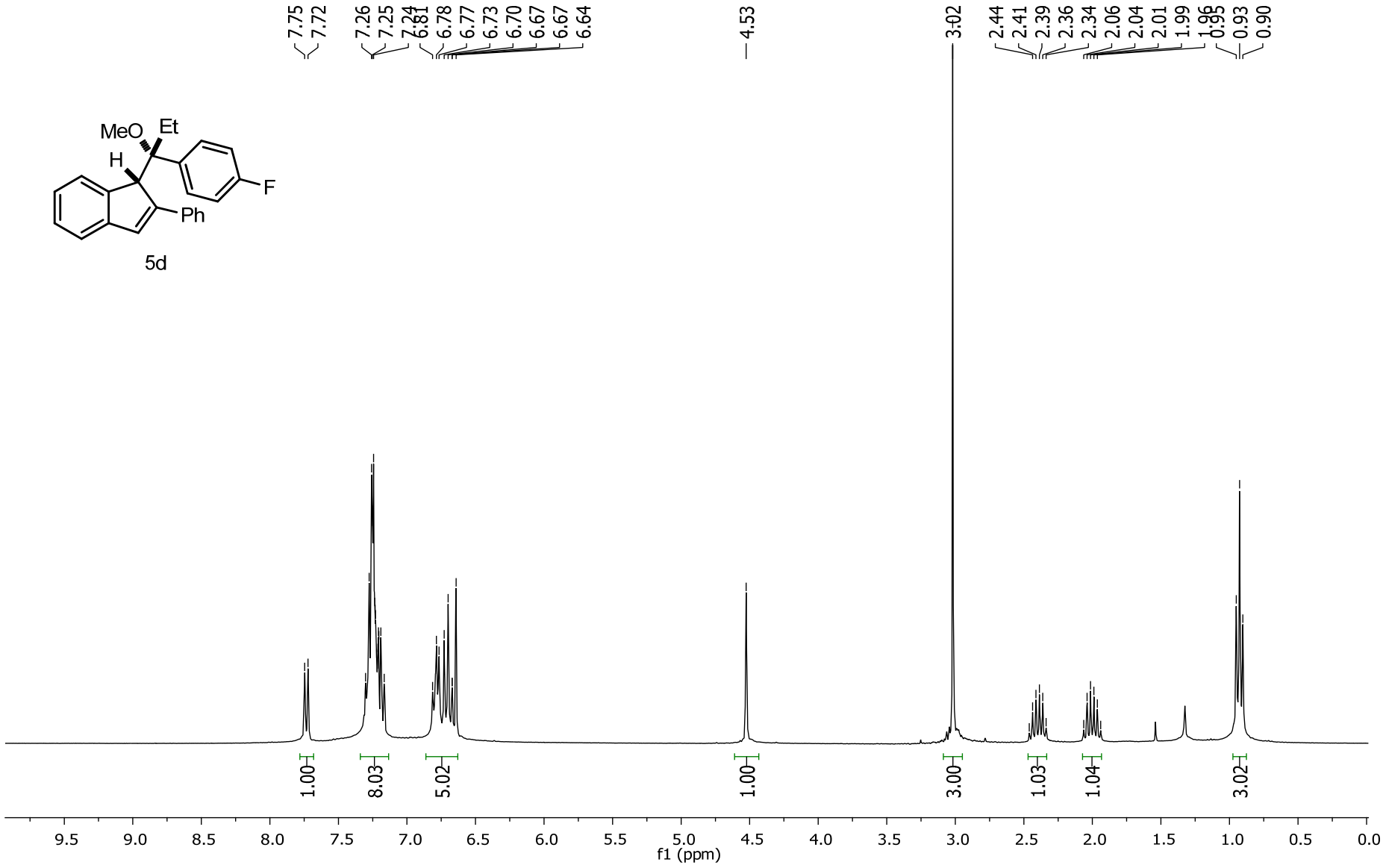
^{1}H NMR (300 MHz, $CDCl_3$)



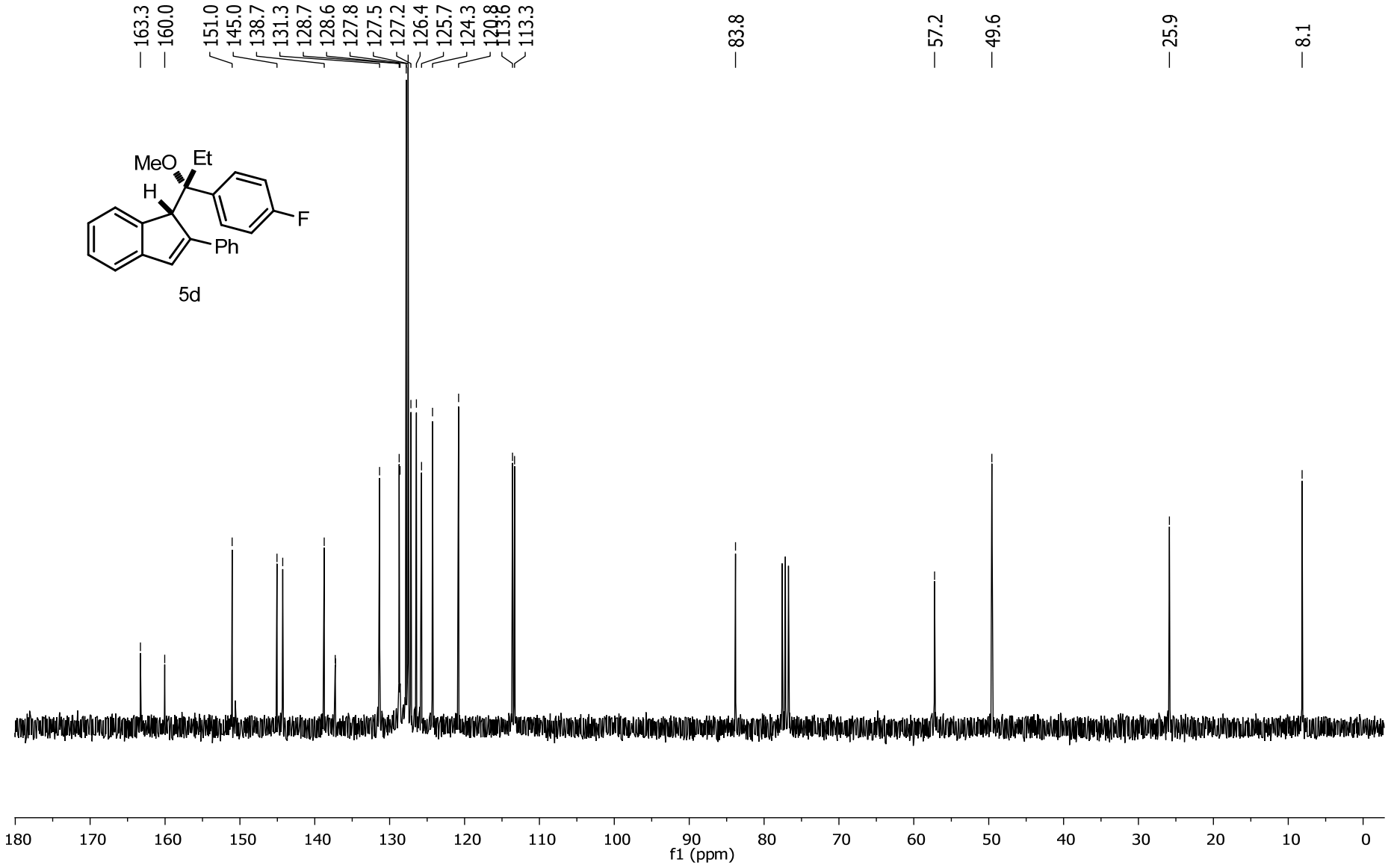
$^{13}C\{^{1}H\}$NMR (75.4 MHz, $CDCl_3$)



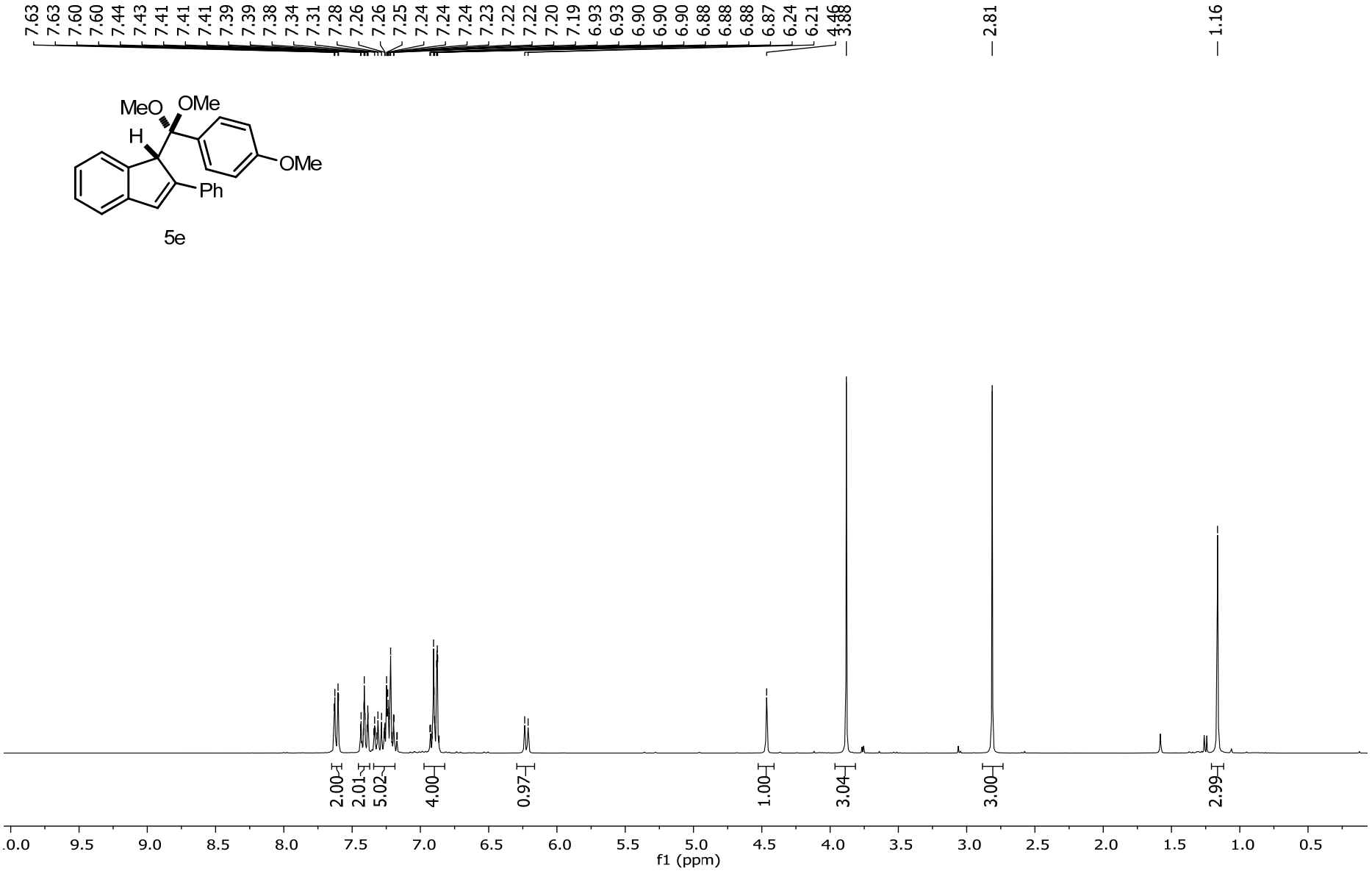
^{1}H NMR (300 MHz, $CDCl_3$)



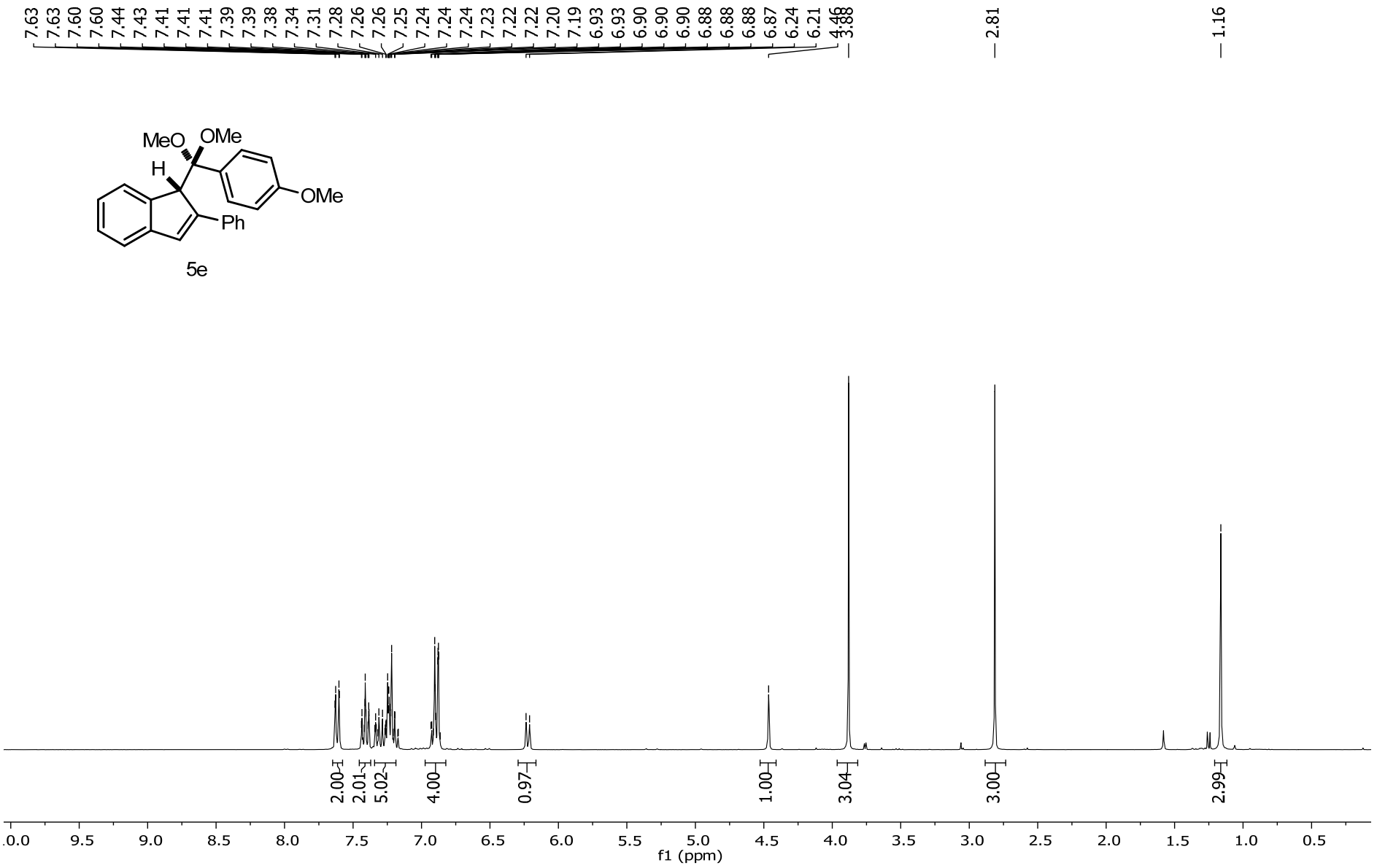
$^{13}C\{^{1}H\}$NMR (75.4 MHz, $CDCl_3$)



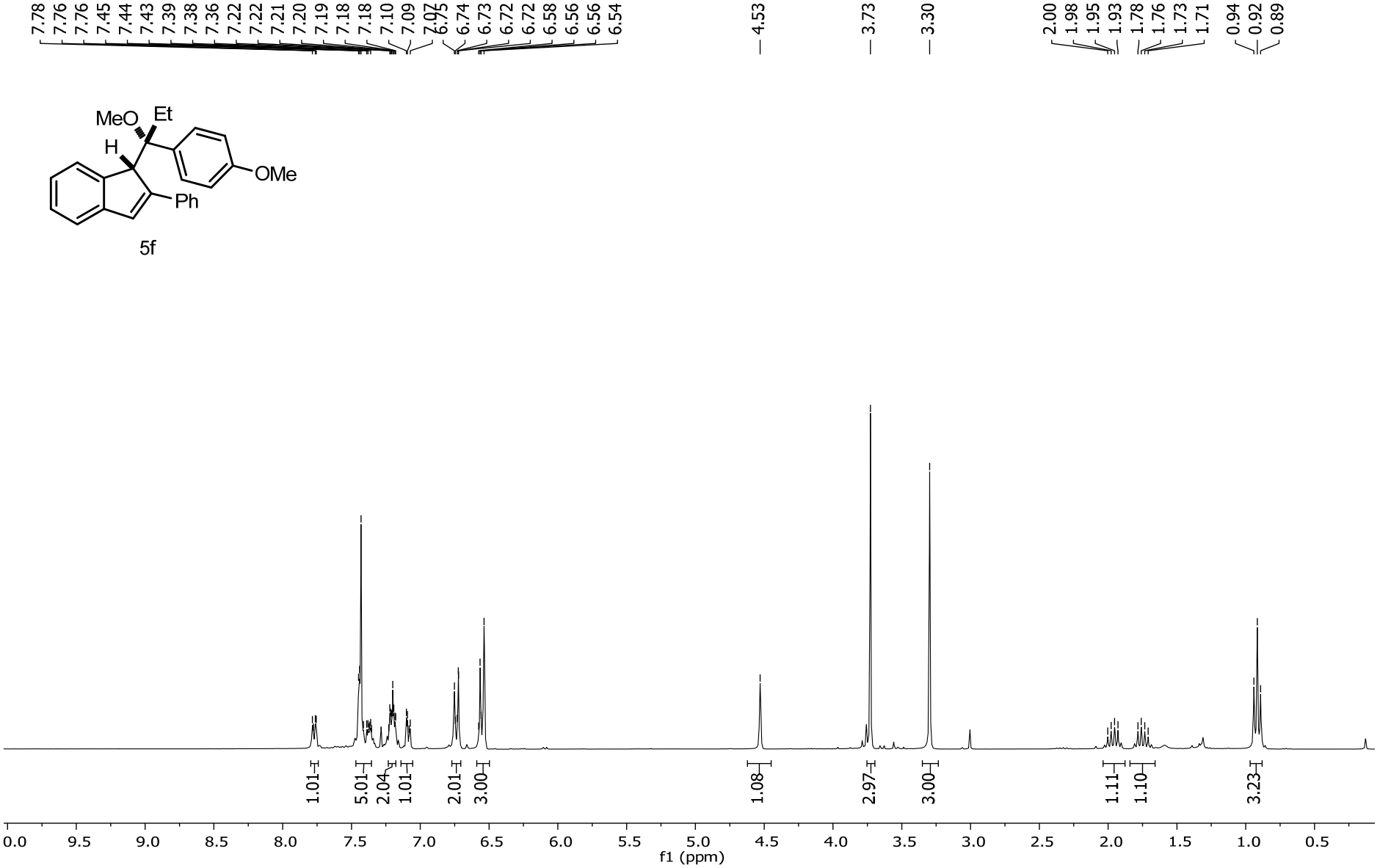
^{1}H NMR (300 MHz, $CDCl_3$)



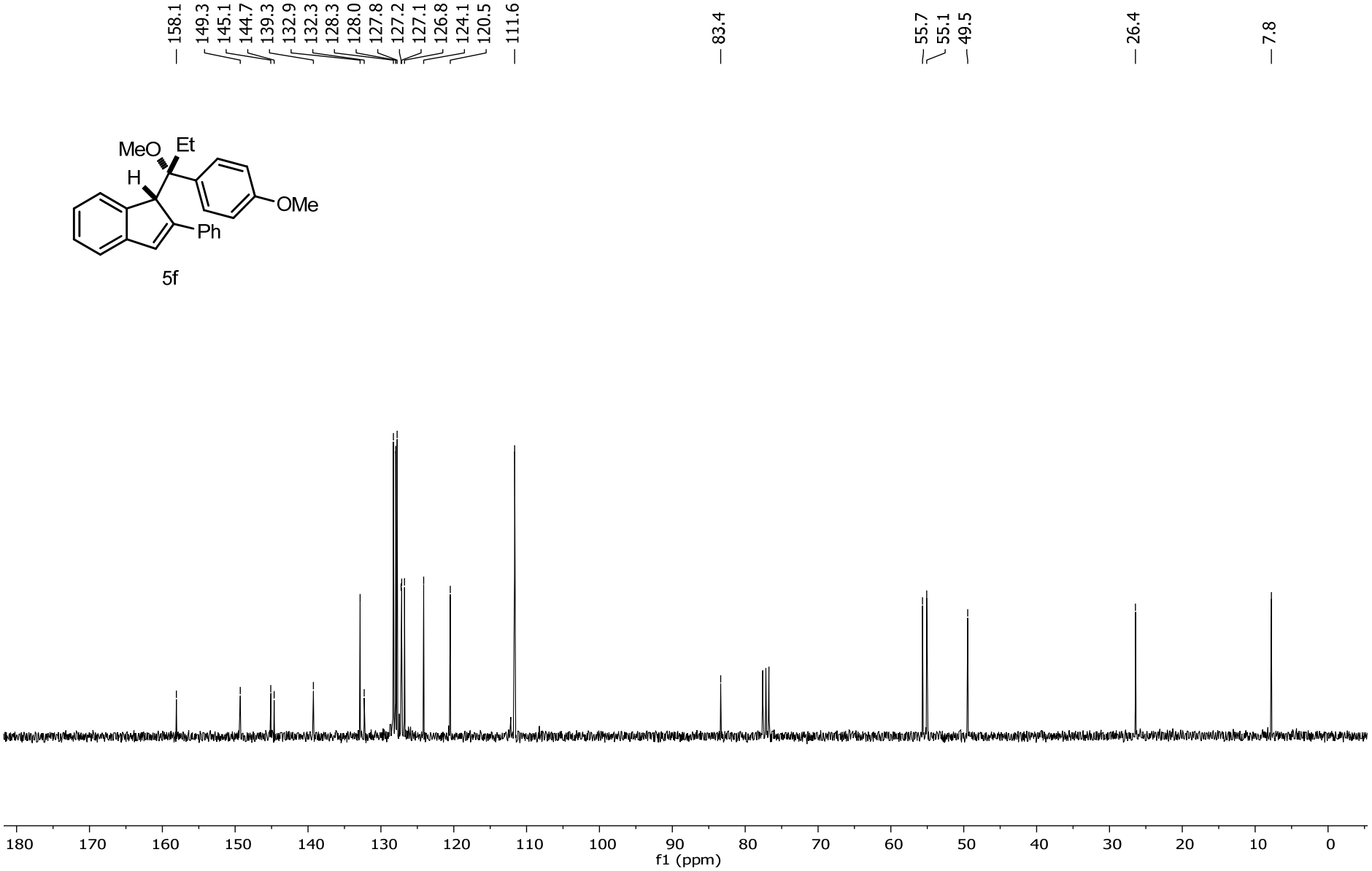
$^{13}C\{^{1}H\}$NMR (75.4 MHz, $CDCl_3$)



^{1}H NMR (300 MHz, $CDCl_3$)

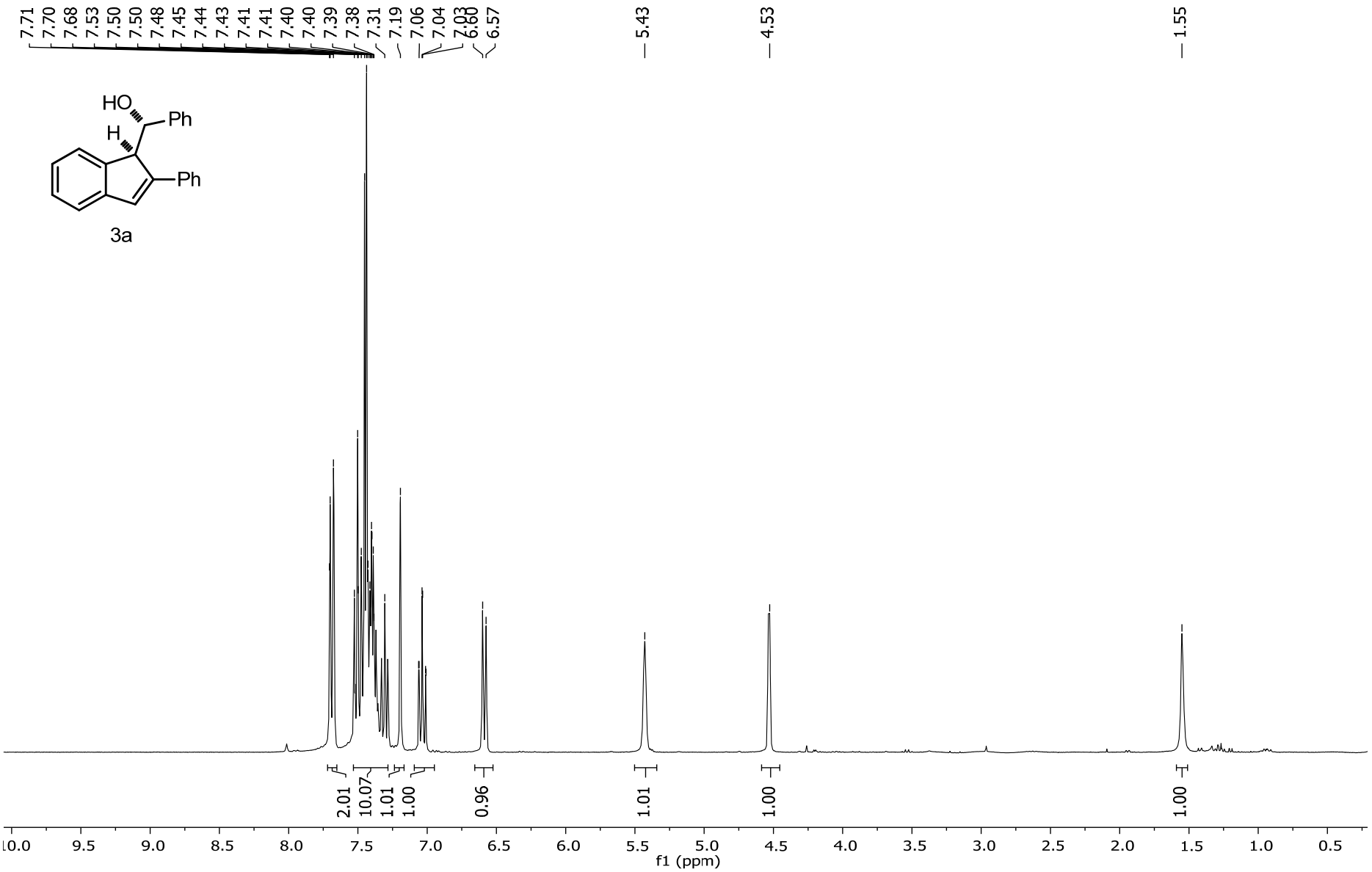


$^{13}C\{^{1}H\}$NMR (75.4 MHz, $CDCl_3$)

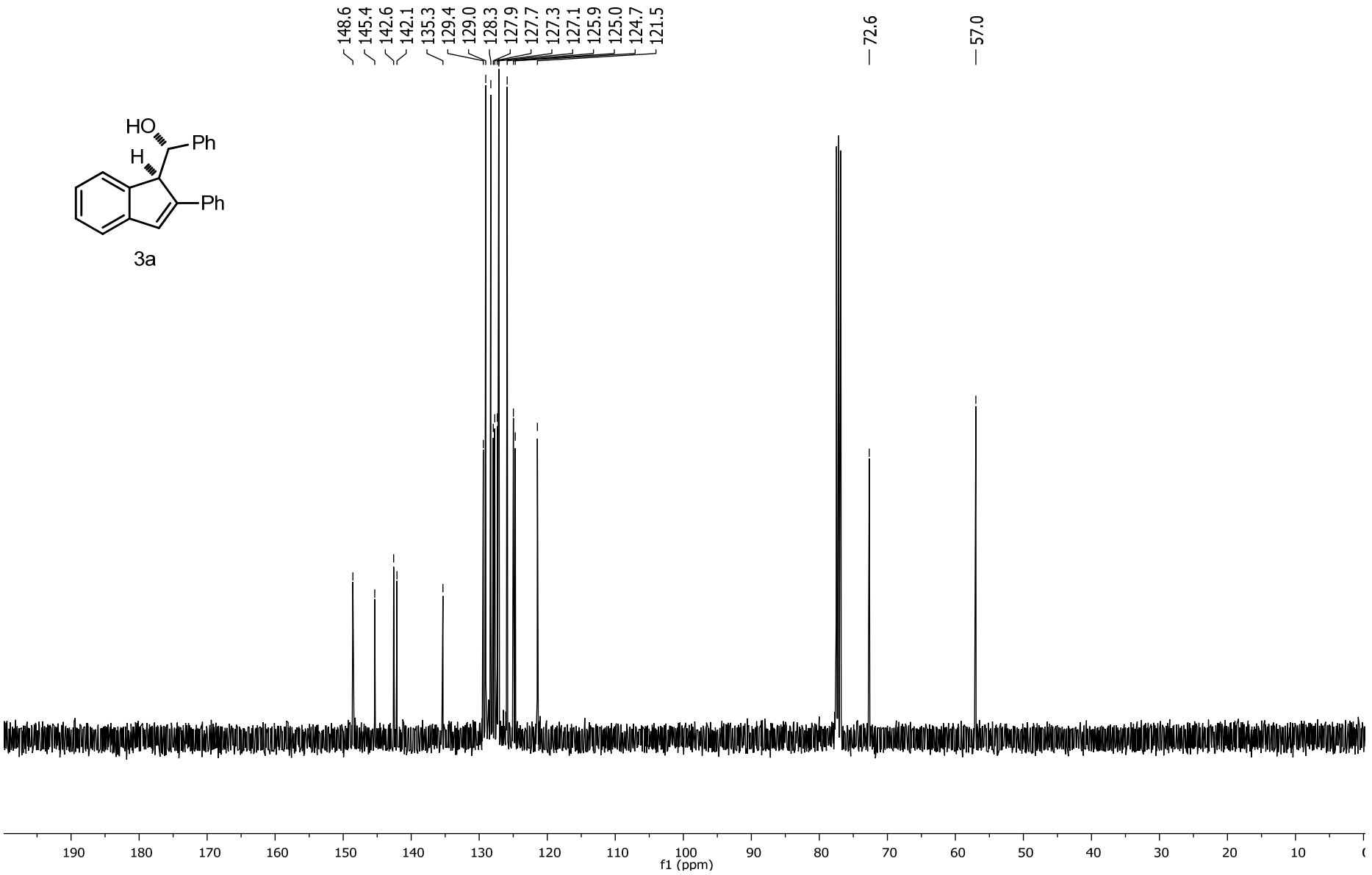


5f

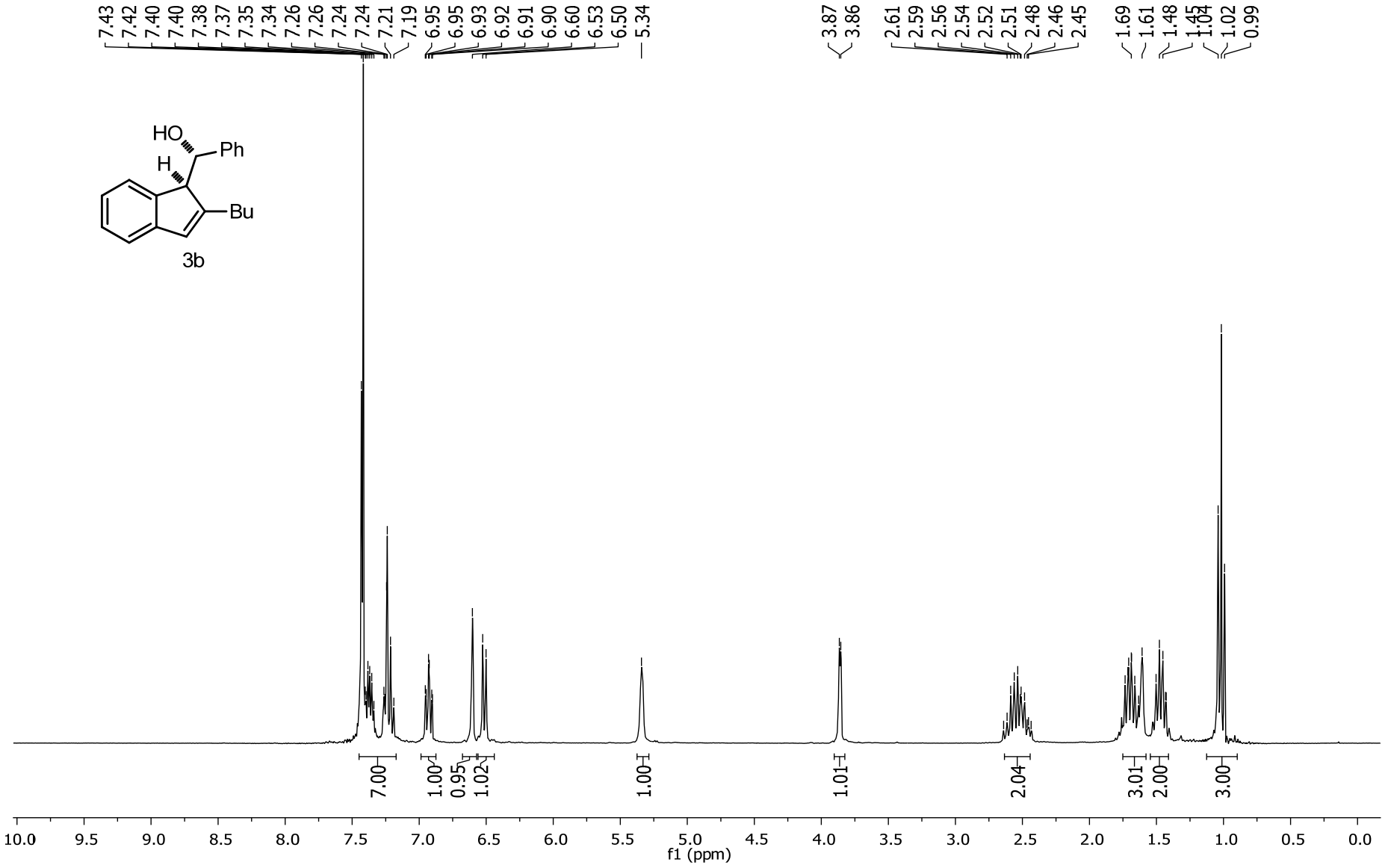
^{1}H NMR (300 MHz, $CDCl_3$)



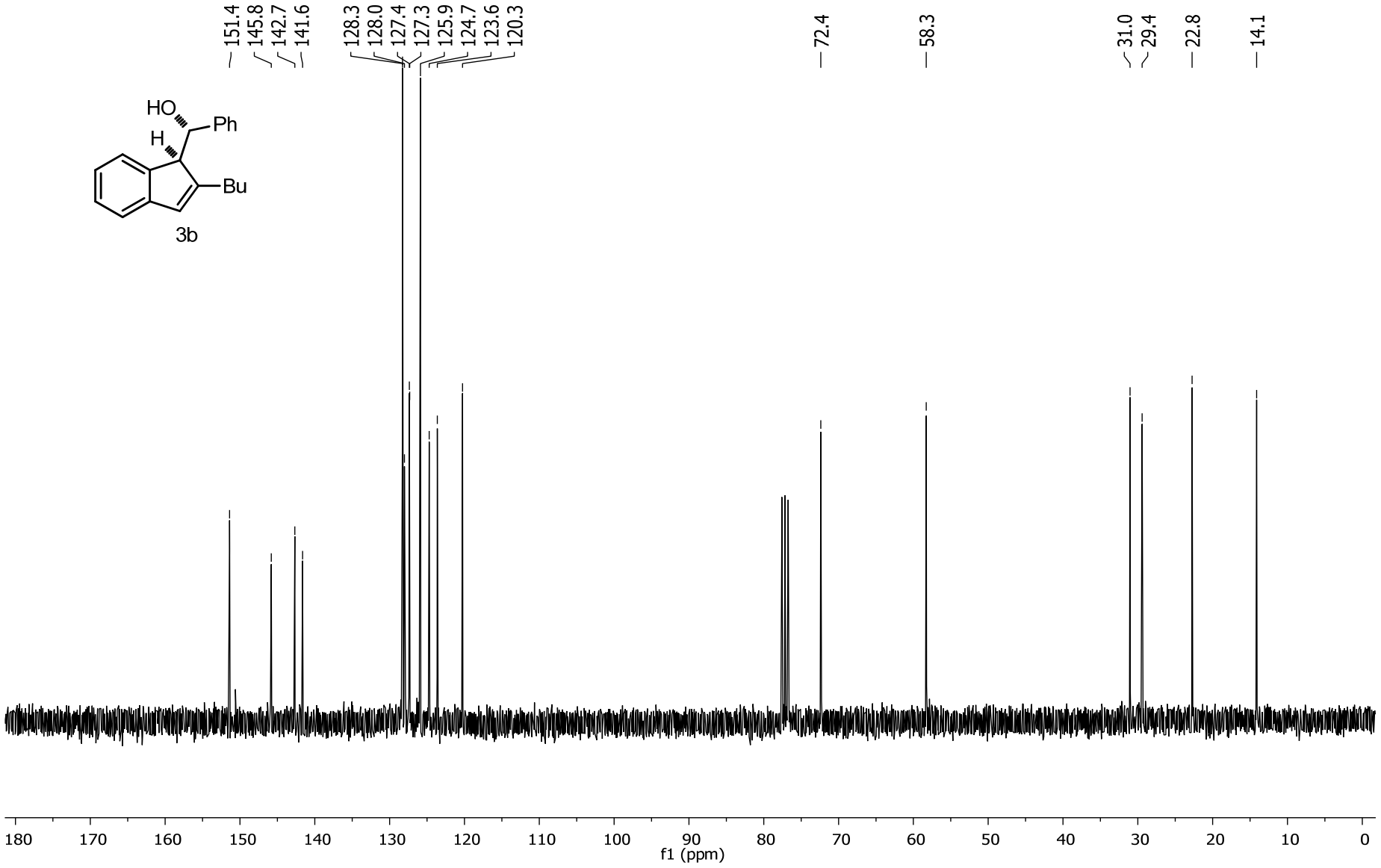
$^{13}C\{^{1}H\}$NMR (75.4 MHz, $CDCl_3$)



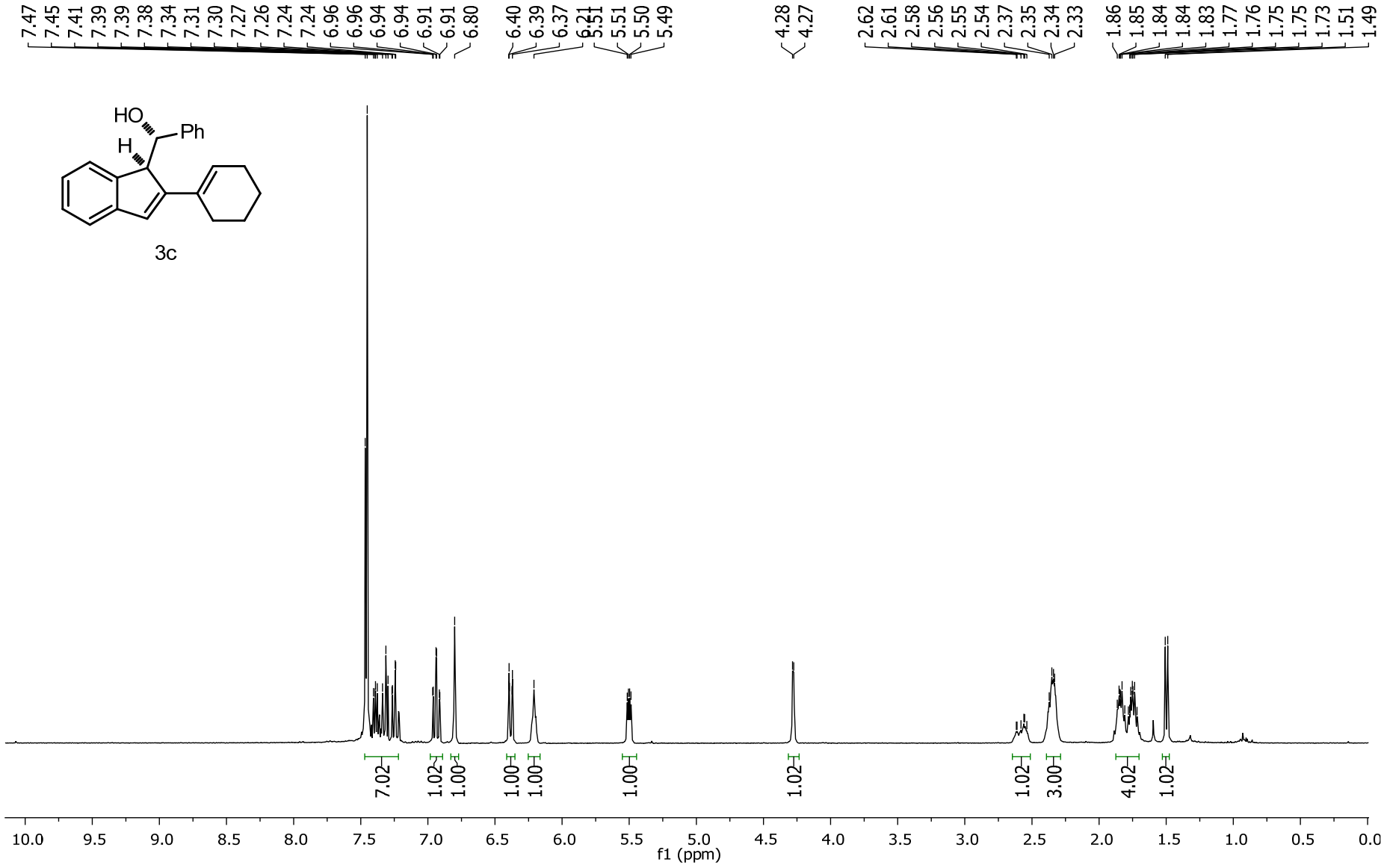
^{1}H NMR (300 MHz, $CDCl_3$)



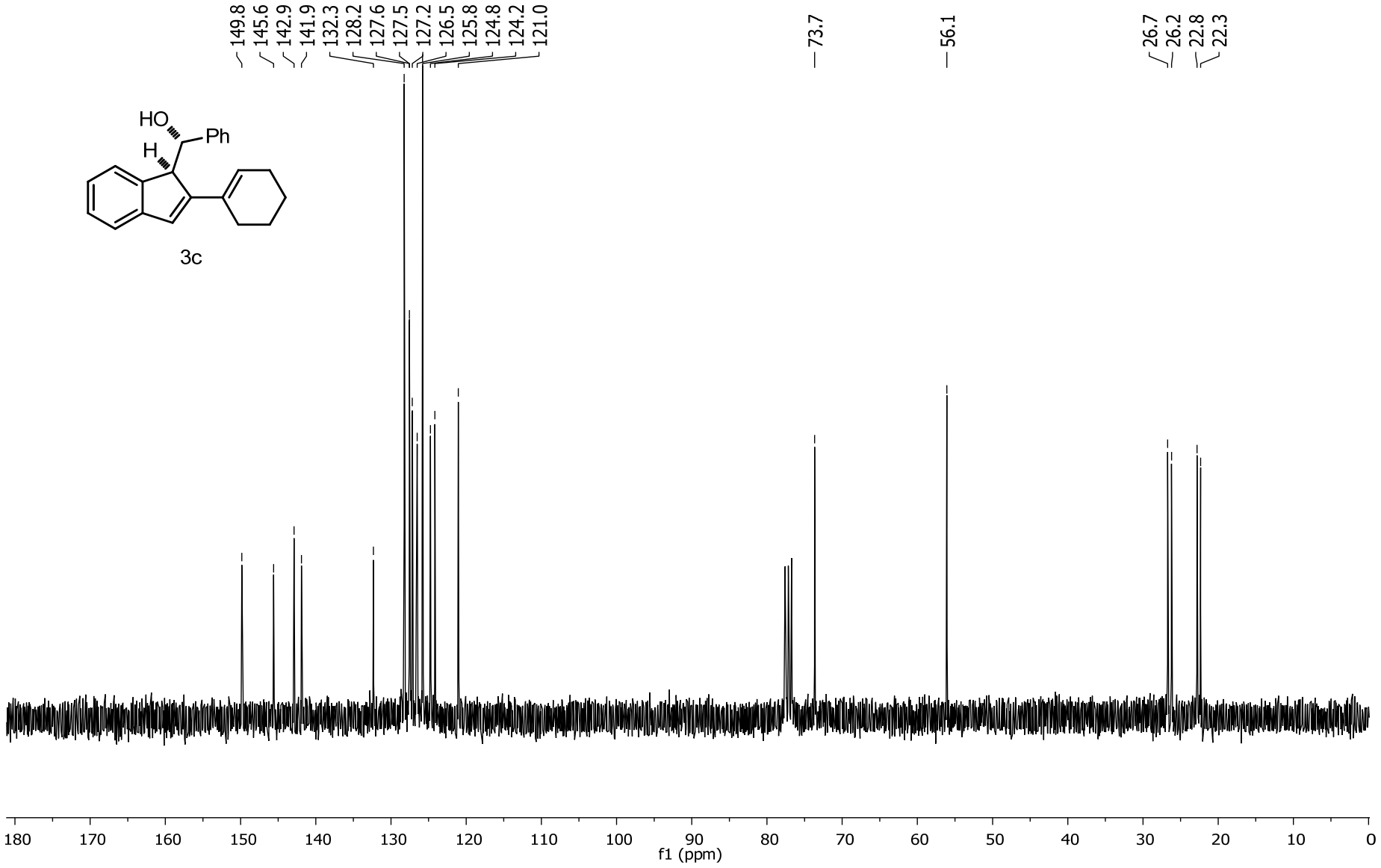
$^{13}C\{^{1}H\}$NMR (75.4 MHz, $CDCl_3$)



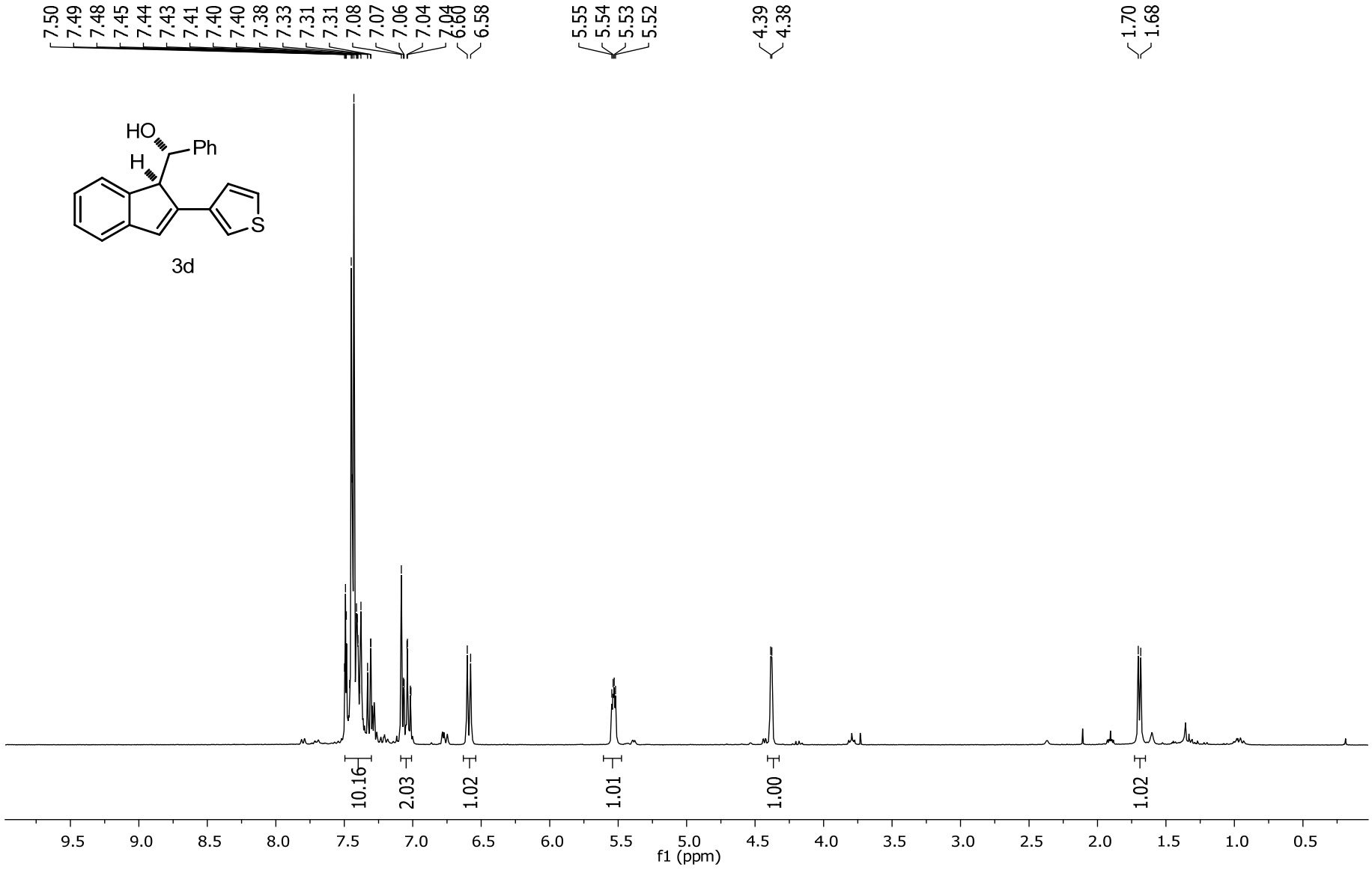
^{1}H NMR (300 MHz, $CDCl_3$)



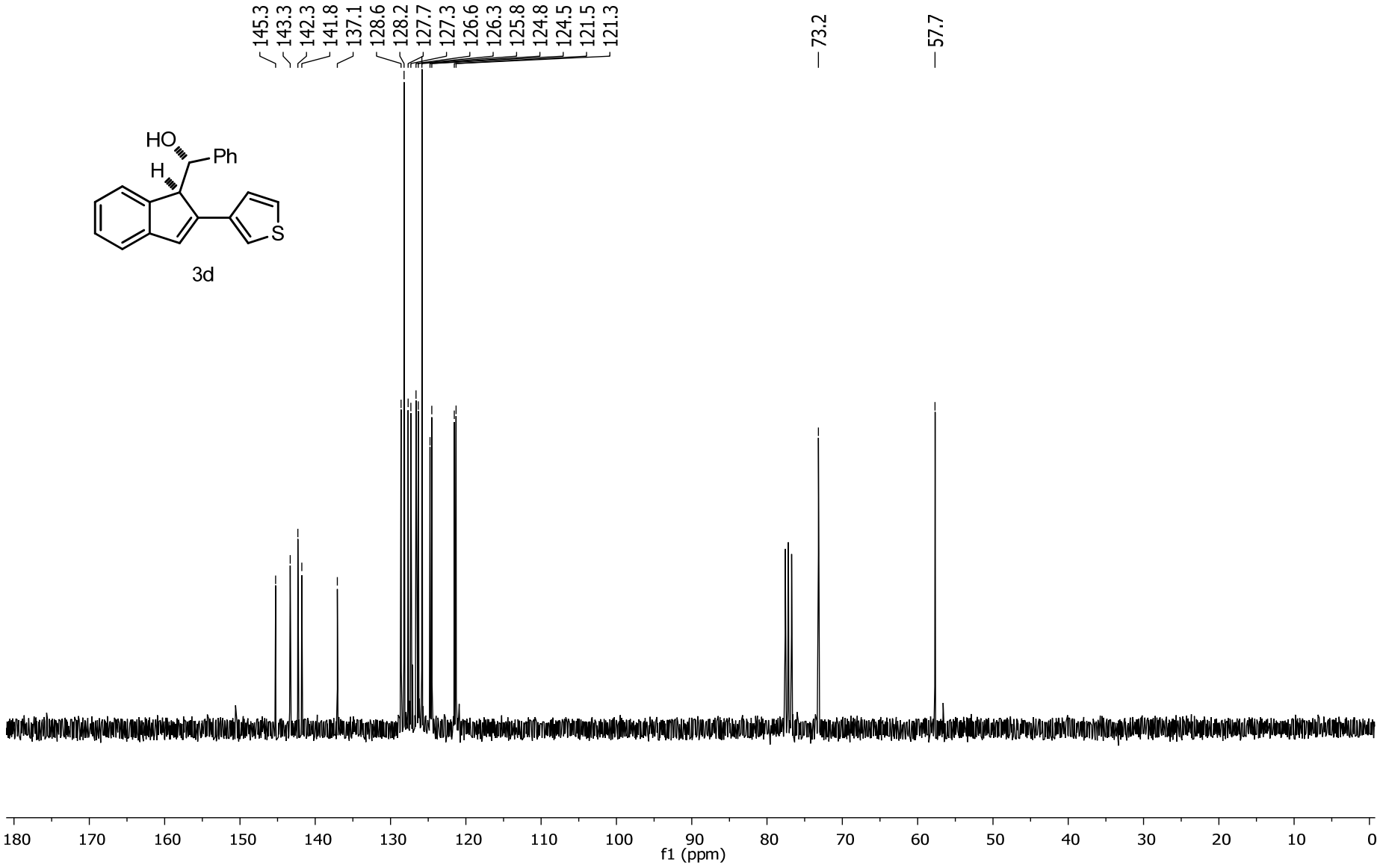
$^{13}C\{^{1}H\}$NMR (75.4 MHz, $CDCl_3$)



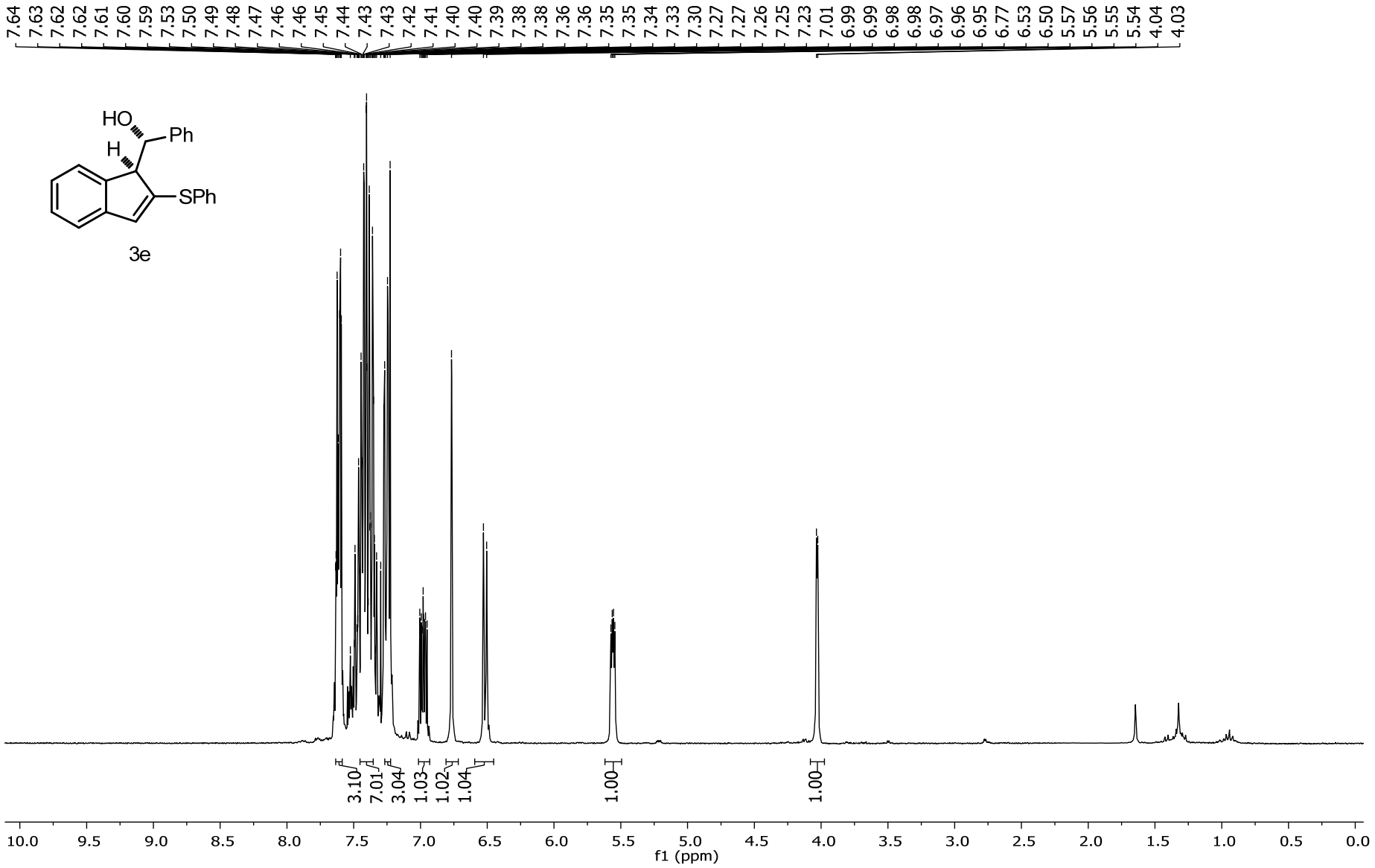
^{1}H NMR (300 MHz, $CDCl_3$)



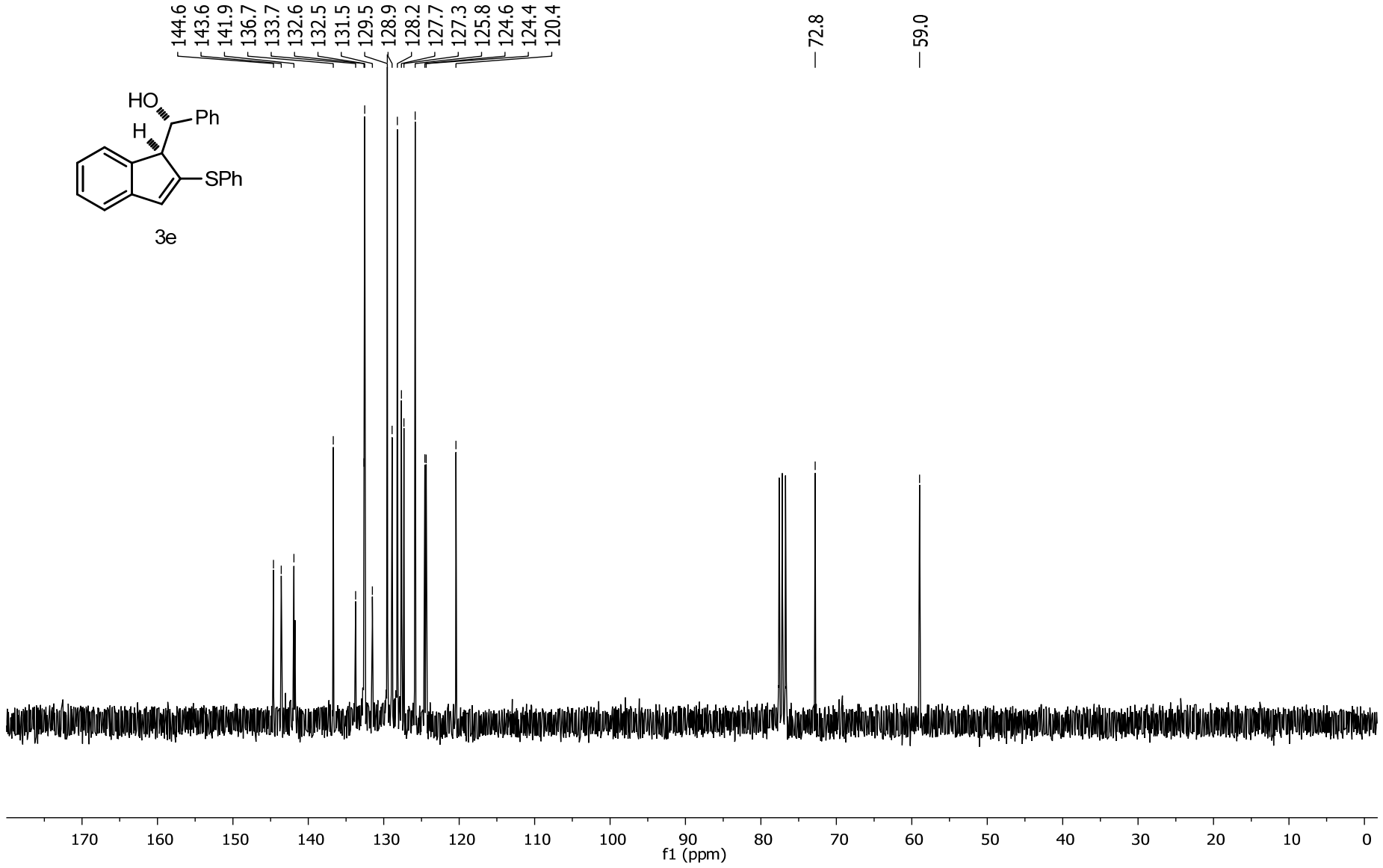
$^{13}C\{^{1}H\}$NMR (75.4 MHz, $CDCl_3$)



^{1}H NMR (300 MHz, $CDCl_3$)



$^{13}C\{^{1}H\}$NMR (75.4 MHz, $CDCl_3$)



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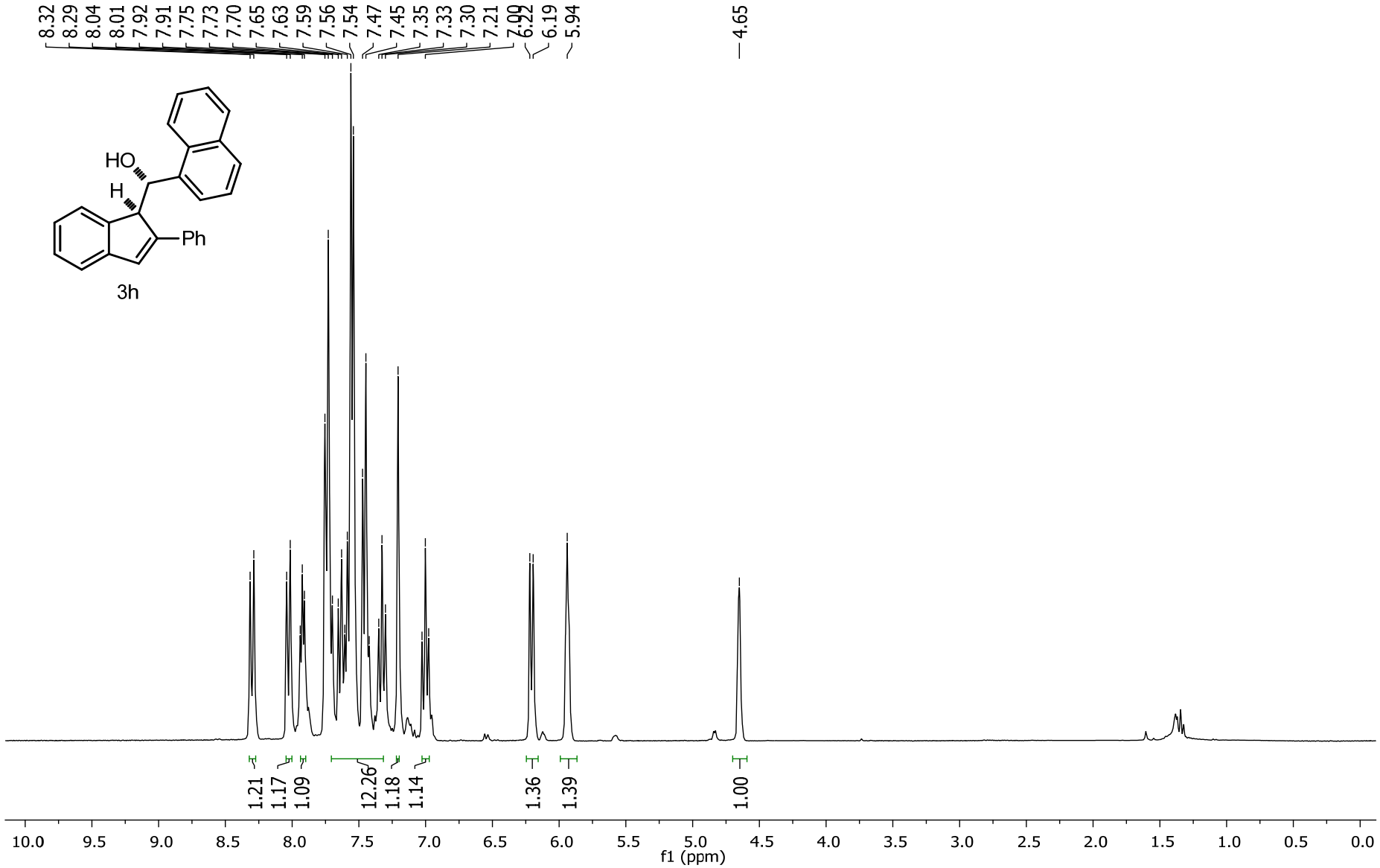
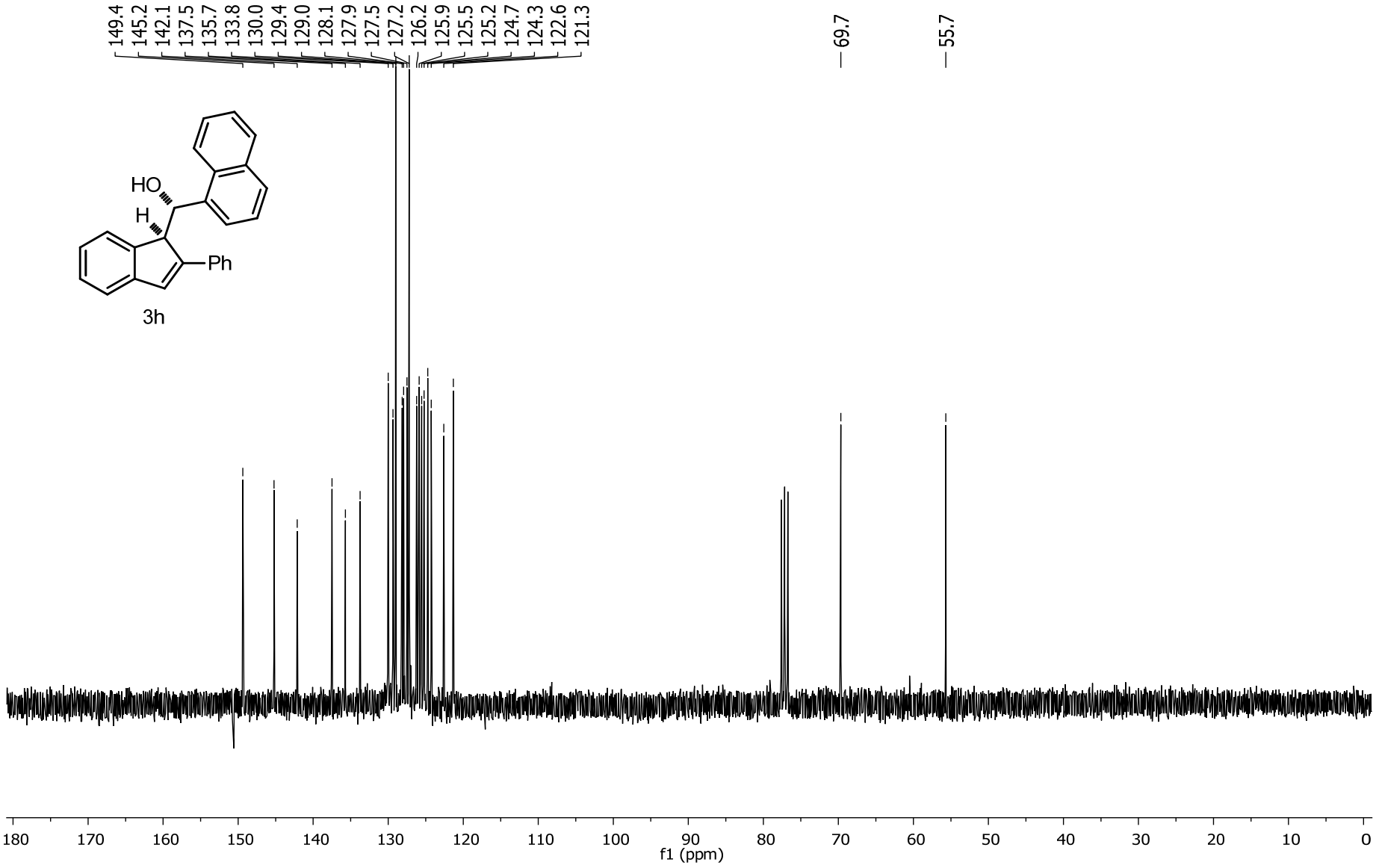
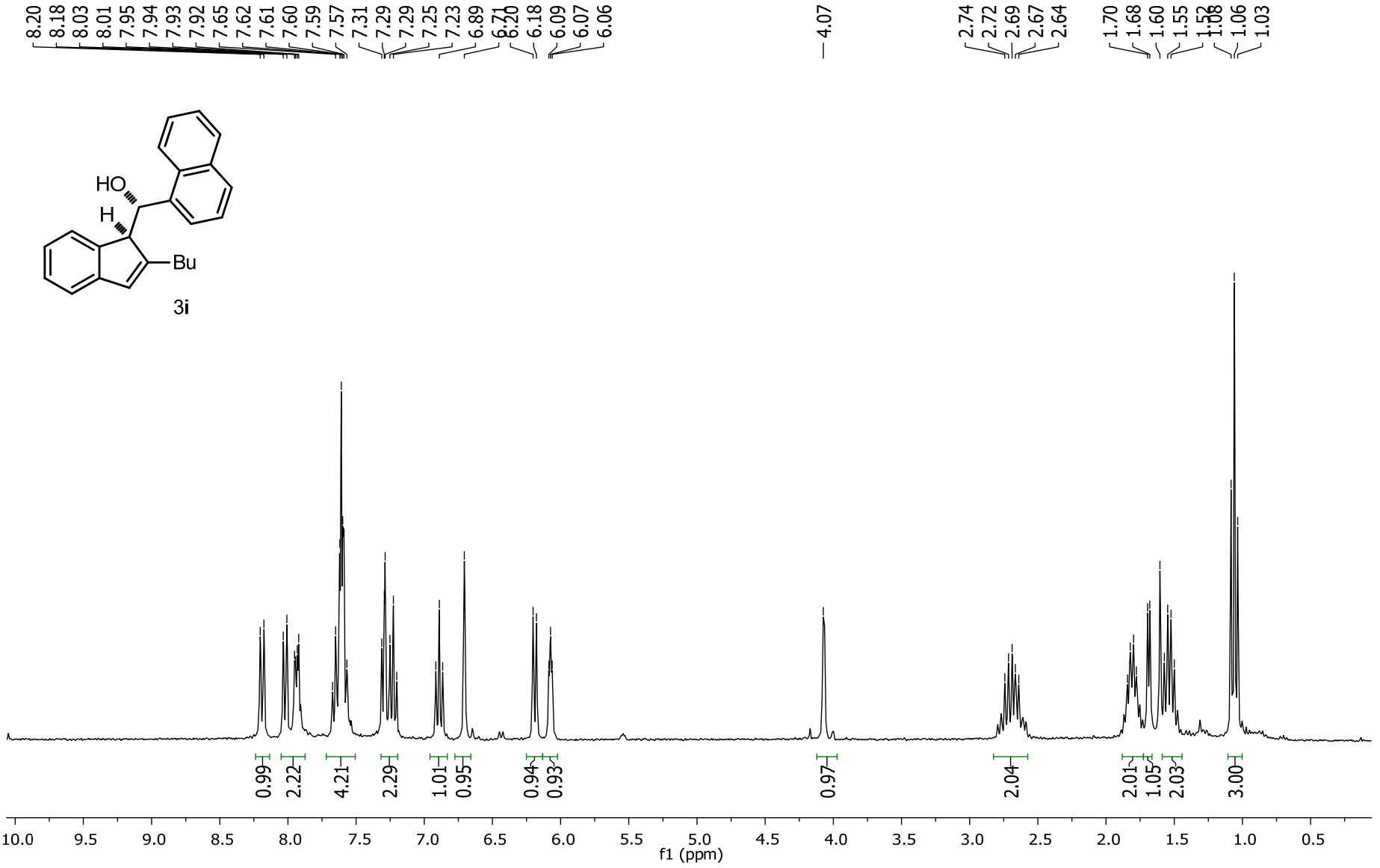


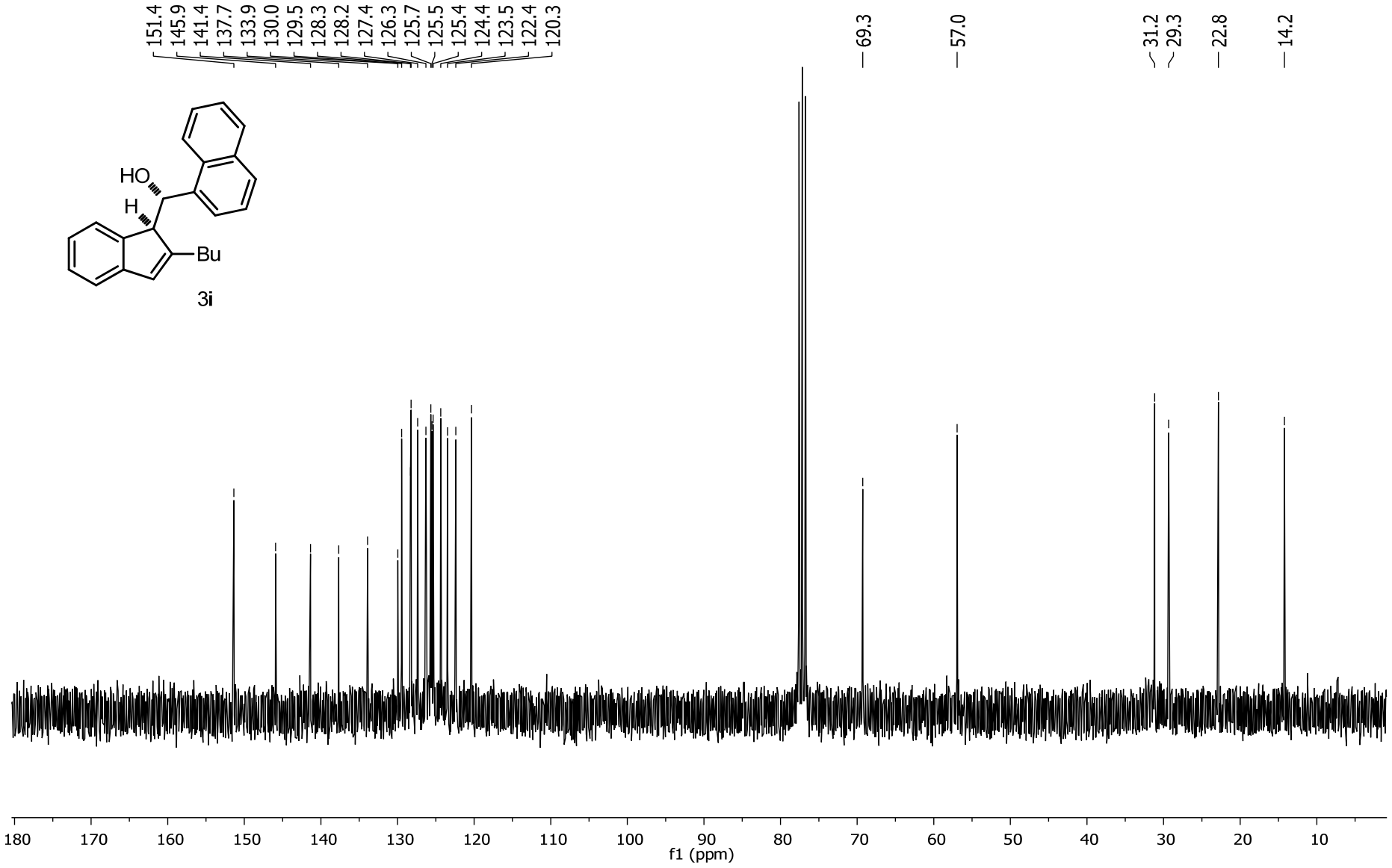
$^{13}C\{^{1}H\}$NMR (75.4 MHz, $CDCl_3$)



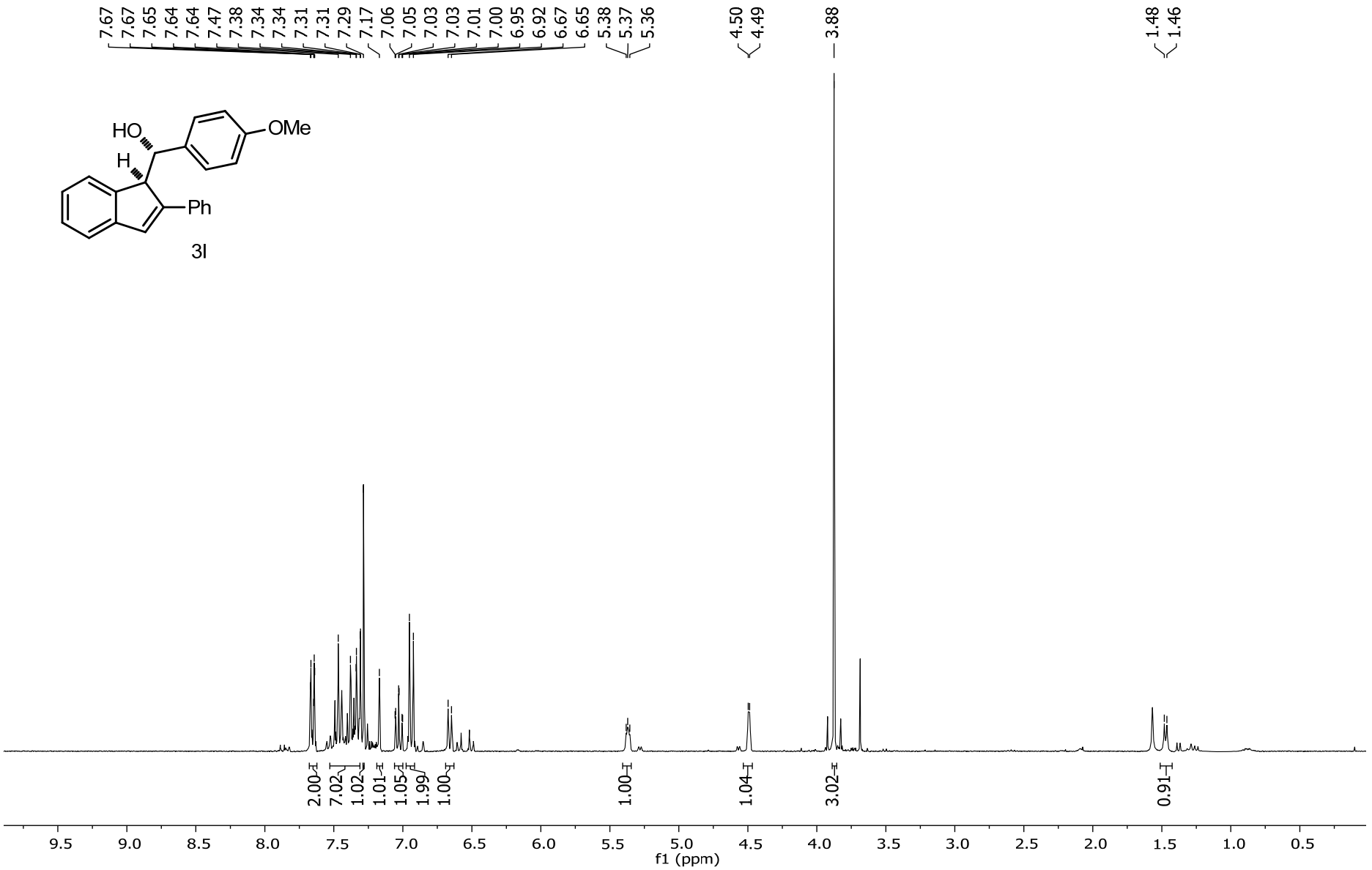
^{1}H NMR (300 MHz, $CDCl_3$)



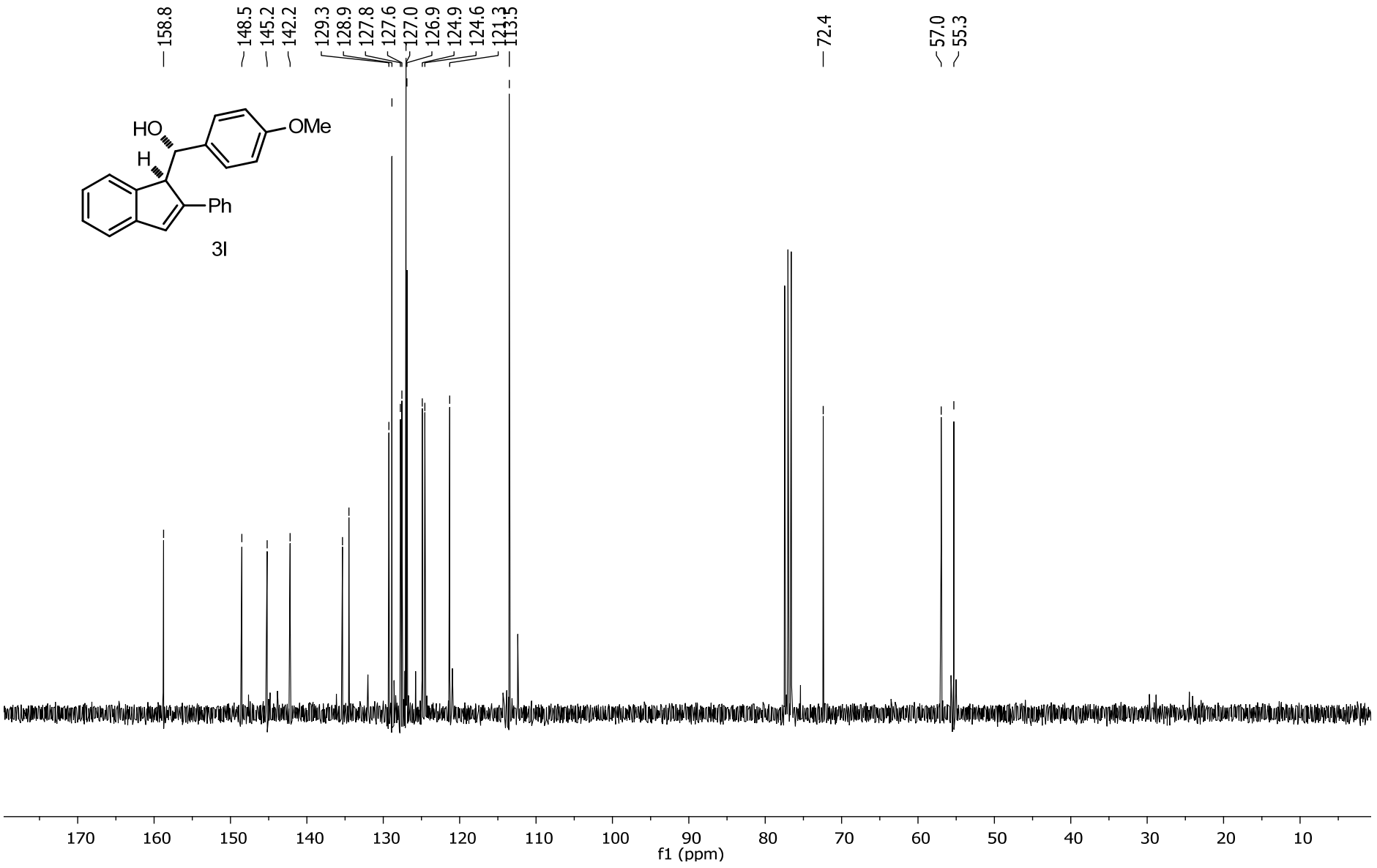
$^{13}C\{^{1}H\}$NMR (75.4 MHz, $CDCl_3$)



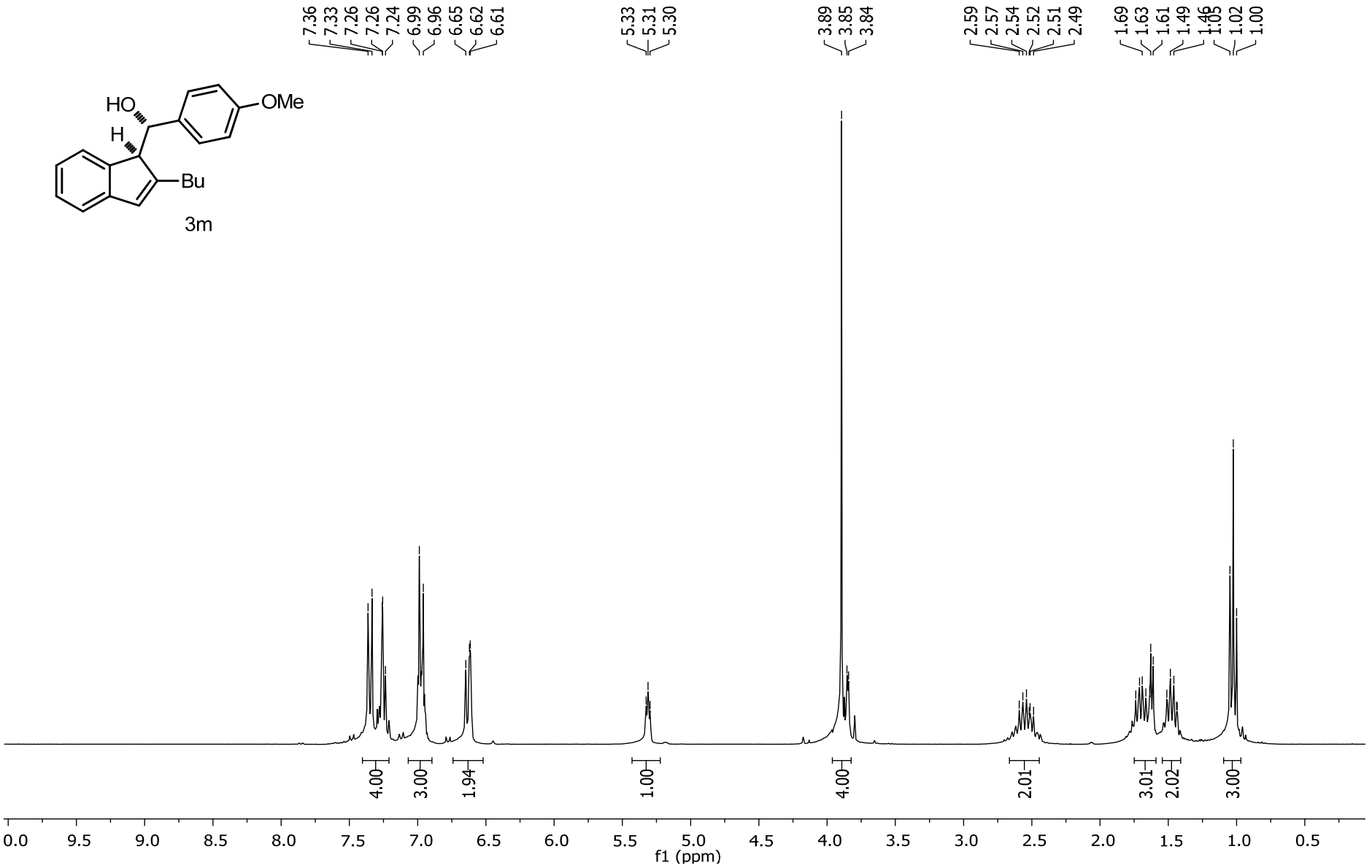
^{1}H NMR (300 MHz, $CDCl_3$)



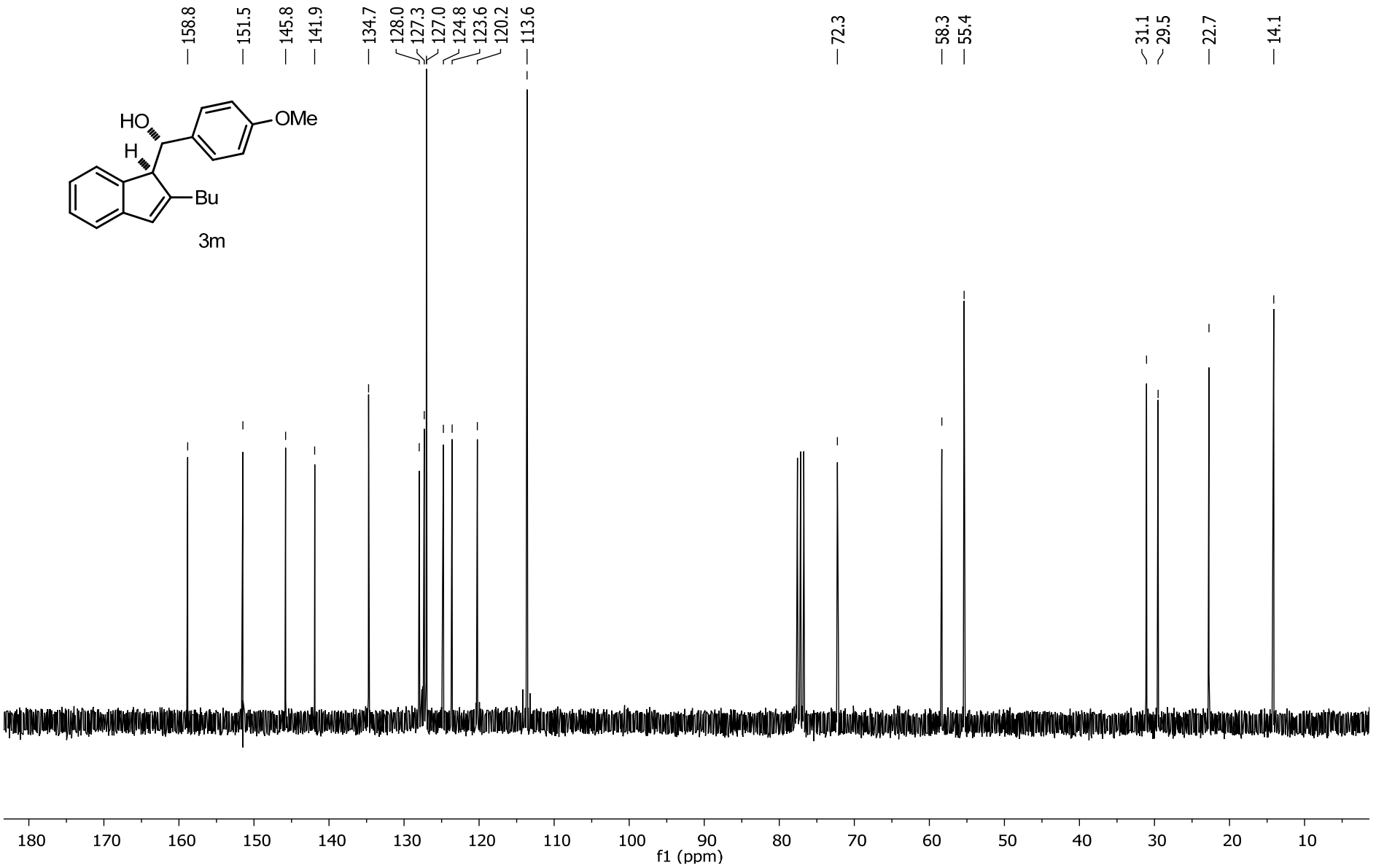
$^{13}C\{^{1}H\}$NMR (75.4 MHz, $CDCl_3$)



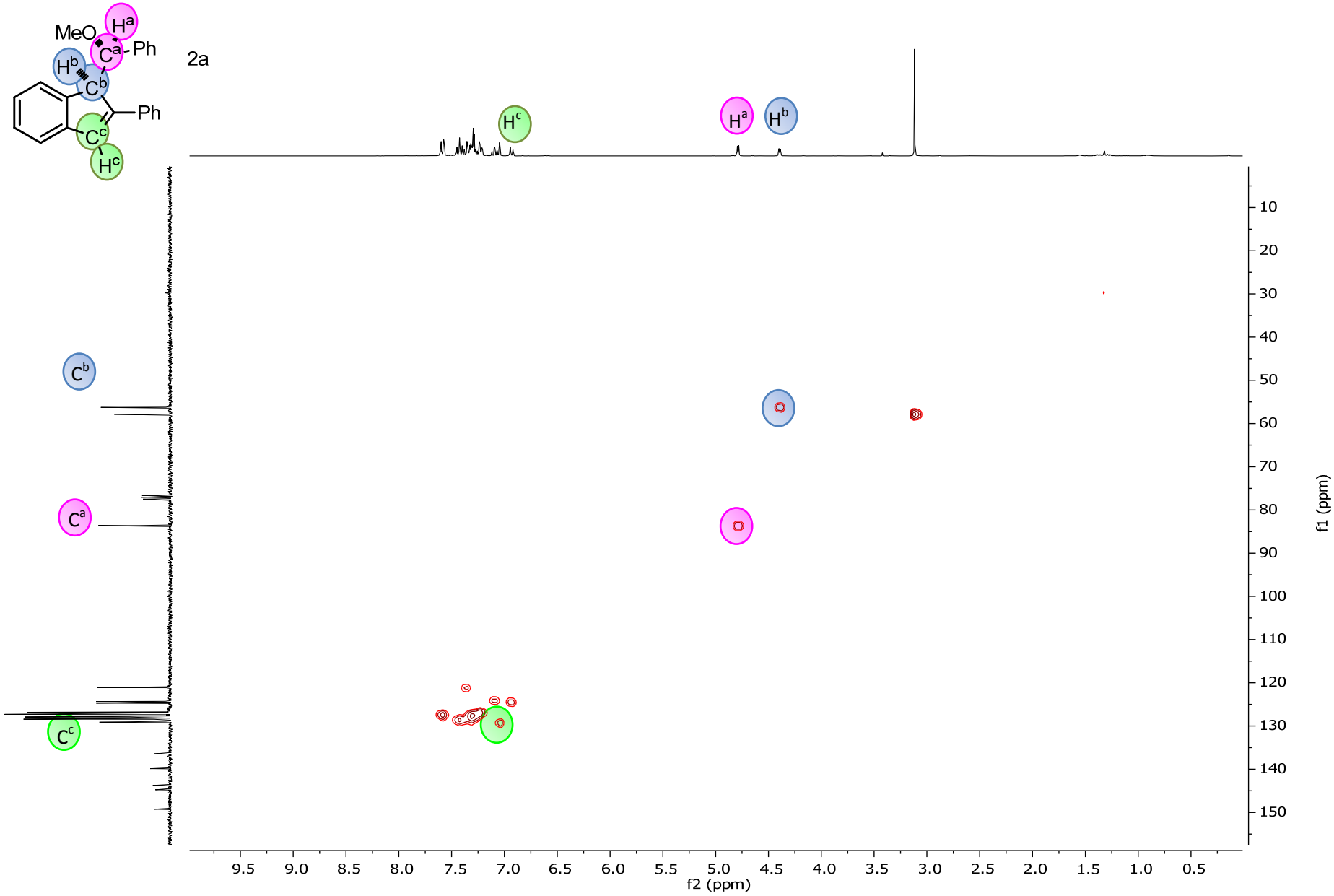
^{1}H NMR (300 MHz, $CDCl_3$)



$^{13}C\{^{1}H\}$NMR (75.4 MHz, $CDCl_3$)



HSQC NMR (300 MHz, $CDCl_3$)



HMBC NMR (300 MHz, $CDCl_3$)