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Supporting Information

Catalyst-Controlled 1,2- and 1,1-Arylboration of α-Alkyl Alkenyl Arenes

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General. Infrared (IR) spectra were recorded on Bruker Tensor II FT-IR Spectrometer, ν_{max} in . Bands are characterized as broad (br), strong (s), medium (m), and weak (w). ^{1}H NMR spectra were recorded at room temperature on a Varian I400 (400 MHz), Varian VXR400 (400 MHz), Varian I500 (500 MHz), or a Varian I600 (600 MHz) spectrometer. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard ($CHCl_3$: δ 7.26 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, br = broad, m = multiplet), coupling constants (Hz),and integration. ^{13}C NMR spectra were recorded on a Varian I400 (100 MHz) and Varian I500 (125 MHz) spectrometer with complete proton decoupling. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard ($CDCl_3$: δ 77.16 ppm). ^{19}F NMR spectra were recorded on a Varian VXR400 (375 MHz). ^{31}P NMR spectra were recorded on a Varian VXR400 (162 MHz). High-resolution mass spectrometry (HRMS) was performed on a Thermo Electron Corporation MAT 95XP-Trap (GC/MS). Melting points were obtained on a Thomas Hoover capillary melting point apparatus without correction. Unless otherwise noted, all reactions have been carried out with distilled and degassed solvents under an atmosphere of dry N_2 in oven- (135 °C) and flame-dried glassware with standard vacuum-line techniques. Tetrahydrofuran (THF) was purified under a positive pressure of dry argon by passage through two columns of activated alumina. Toluene was purified under a positive pressure of dry argon by passage through columns of activated alumina and Q5 (Grubbs apparatus). All work-up and purification procedures were carried out with reagent grade solvents (purchased from Sigma-Aldrich) in air. Standard column chromatography techniques using ZEOprep 60/40-63 silica gel. For difficult separations medium pressure liquid chromatography (MPLC) was performed using a Teledyne ISCO CombiFlash Rf 150 instrument. Optical rotations were measured on a PerkinElmer 241 polarimeter at 589 nm wavelength (sodium D-line) using a standard 10 cm cell (1 mL). Specific rotations, $[\alpha]_D^{20}$, are reported in degree mL/(g·dm) at the specific temperature. Concentrations (c) are given in grams per 100 mL of the specific solvent. Chiral HPLC analysis was performed on a Agilent 1220 Infinity LC system.

■ **Reagents and Catalysts:**

APhos was purchased from Sigma Aldrich and used as received.

APhosPdG3 was prepared in accordance with literature procedures. [1]

Bis[[4-(N,N-dimethylamino)phenyl]di-t-butylphosphino] palladium(0) was purchased from Strem and used as received.

Bis(pinacolato)diboron was purchased from Oakwood Chemicals and recrystallized from pentane prior to use.

Bis(tricyclohexylphosphine)palladium(0) was purchased from Strem and used as received.

4-Bromoanisole was purchased from Combi-Blocks and purified via neat filtration through a 2 cm pad of dry silica in a 5.75-inch pipette prior to use.

Bromobenzene was purchased from Sigma-Aldrich and purified via neat filtration through a 2 cm pad of dry silica in a 5.75-inch pipette prior to use.

3-Bromobenzotrifluoride was purchased from Combi-Blocks and purified via neat filtration through a 2 cm pad of dry silica in a 5.75-inch pipette prior to use.

1-Bromo-2-chlorobenzene was purchased from Combi-Blocks and purified via neat filtration through a 2 cm pad of dry silica in a 5.75-inch pipette prior to use.

5-Bromo-1H-indole was purchased from CombiBlocks and used as received.

2-Bromotoluene was purchased from Oakwood Chemicals and purified via neat filtration through a 2 cm pad of dry silica in a 5.75-inch pipette prior to use.

But-1-en-2-ylbenzene was prepared in accordance with literature procedures.[2]

1-chloro-3-(1-methylethenyl)benzene was prepared in accordance with literature procedures.[3]

3'-Chloroacetophenone was purchased from Oakwood Chemicals and used as received.

CuCl (99.99%) was purchased from Strem and purified by washing with 1M HCl (3 x 3mL), ethanol (3x 3mL), and diethyl ether (3x 3mL) and dried *in vacuo* before use.

1-Indanone was purchased from Sigma Aldrich and used as received.

Iodomethane was purchased from Sigma Aldrich and used as received.

Isopropenylboronic acid pinacol ester was purchased from Oakwood Chemicals and used as received.

2-Isopropenylnaphthalene was purchased from Combi-Blocks and used as received.

Lithium *tert*-butoxide was purchased from Strem and used as received.

((2R,3R)-6-Mesityl-2,3-diphenyl-2,3,5,6-tetrahydroimidazo[1,2-c]quinazolin-5-yl)copper(I) chloride was prepared in accordance with literature procedures.[4]

4'-Methoxyacetophenone was purchased from Combi-Blocks and used as received.

1-methoxy-4-(prop-1-en-2-yl)benzene was prepared in accordance with literature procedures.[5]

4'-Methylacetophenone was purchased from Alfa Aesar and used as received.

[1] J. Huguet Clotet, L. Ozores Viturro, S. Rodriguez Ropero, P. Dalmases Barjoan, WO 2018115362, June 28, 2018.
[2] J. J. Eish, A. A. Adeosun, *Eur. J. Org. Chem.* **2005**, *6*, 993.
[3] C. B. Tripathi, S. Mukherjee, *Angew. Chem. Int. Ed*. **2013**, *52*, 8450.
[4] K. M. Logan, M. K. Brown, *Angew. Chem. Int. Ed.* **2017**, *56*, 851.
[5] G. Bastug, S. P. Nolan, *Organometallics*, **2014,** *33*, 1253.

1-methylene-2,3-dihydro-1H-indene was prepared in accordance with literature procedures.[6]
1-methyl-4-(1-methylethenyl)benzene was prepared in accordance with literature procedures.[5]
α-Methylstyrene was purchased from Sigma Aldrich and purified via neat filtration through a 2 cm pad of dry silica in a 5.75-inch pipette prior to use.
Methyltriphenylphosphonium bromide was purchased from TCI and used as received.
Palladium(II) acetate was purchased from Strem and used as received.
PCy$_3$PdG3 was prepared in accordance with literature procedures.[7]
P*i*-Bu$_3$PdG3 was prepared in accordance with literature procedures.[7]
pent-1-en-2-ylbenzene was prepared in accordance with literature procedures.[8]
P*t*-Bu$_3$PdG3 was prepared in accordance with literature procedures.[7]
Pd G3 dimer was prepared in accordance with literature procedures.[7]
Potassium t-butoxide (1.00 M in THF) was purchased from Sigma Aldrich and used as received.
Propiophenone was purchased from Sigma Aldrich and used as received.
SIMesCuCl was prepared in accordance with literature procedures.[9]
SIMesCuO*t*-Bu was prepared in accordance with literature procedures.[10]
Sodium hydride (60% dispersion in mineral oil) was purchased from Sigma Aldrich and used as received.
***Tert*-butyl 5-bromo-1H-indole-1-carboxylate** was prepared in accordance with literature procedures.[11]
***Tert*-butyl (4-bromophenyl)carbamate** was purchased from Combi Blocks and used as received.
***Tert*-Butyl (4-bromophenyl)(methyl)carbamate** was prepared in accordance with literature procedures.[12]
4,4,5,5-Tetramethyl-2-[(1E)-2-phenyl-1-propen-1-yl]-1,3,2-dioxaborolane was prepared in accordance with literature procedures.[13]
Tricyclohexylphosphine was purchased from Sigma Aldrich and used as received.
Triisobutylphosphine was purchased from Sigma Aldrich and used as received.
Tri-*tert*-butylphosphine was purchased from Sigma Aldrich and used as received.
Tris(dibenzylideneacetone)dipalladium(0) was purchased from Strem and used as received.
Valerophenone was purchased from Combi-Blocks and used as received.

[6] M. Hisano, K. Takeda, T. Takashima, Z. Jin, A. Shiibashi, A. Matsumoto, *Macromolecules*, **2013**, *46*, 3314.
[7] N. C. Bruno, M. T. Tudge, S. L. Buchwald, *Chem. Sci.* **2013**, *4*, 916.
[8] A. Abramovitch, I. Marek, *Eur. J. Org. Chem*. **2008**, *29*, 4924.
[9] S. Diez-Gonzalez, E. C. Escudero-Adan, J. Benet-Buchholz, E. D. Stevens, A. M. Z. Slawinc, S. P. Nolan, *Dalton Trans.* **2010**, *39*, 7595.
[10] G. G. Dubinima, J. Ogikubo, D. A. Vicic, *Organometallics* **2008**, *27*, 6233.
[11] T. Furuya, A. E. Strom, T. Ritter, *J. Am. Chem. Soc.* **2009**, *131*, 1662.
[12] S. Yoshida, K. Igawa, K. Tamooka *J. Am. Chem. Soc.*, **2012**, *134*, 19358.
[13] R. Alfaro, A. Parra, J. Aleman, J. L. Garcia Ruano, M. Tortosa, *J. Am. Chem. Soc.*, **2012**, *134*, 15165.

■General Procedure A: 1,2-Arylboration of 1,1-disubstituted alkenes to form quaternary centers

In an N_2-filled glovebox, to a 13 x 100 mm screw-capped vial was added SIMes-CuCl (8.10 mg, 5.00 mol%), APhos-PdG3 precatalyst (1.30 mg, 0.500 mol%), bis(pinacolato)diboron (152 mg, 0.600 mmol, 1.50 equiv), LiO*t*-Bu (94.0 mg, 1.20 mmol, 3.00 equiv), and 3.00 mL of a solution of 10:1 toluene/THF. Alkene (0.400 mmol, 1.00 equiv) and arylbromide (0.600 mmol, 1.50 equiv) were immediately added via microsyringes, followed by another 1.00 mL of the 10:1 toluene/THF solution down the sides of the vial. The vial was sealed with a Teflon-lined screw cap then removed from the glovebox. The mixture was allowed to stir at 30°C for 12 h then was quenched upon addition of 2M HCl (4 mL). The mixture was extracted with EtOAc (3 x 4 mL). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated in vacuo. The crude mixture was purified by silica gel column chromatography to obtain the desired product or oxidized to the corresponding alcohol according to General Procedure C prior to purification.

■General Procedure B: 1,1 Arylboration of 1,1-disubstituted alkenes

In an N_2-filled glovebox, to a 13 x 100 mm screw-capped vial was added SIMes-CuCl (8.10 mg, 5.00 mol%), PCy_3-PdG3 precatalyst (2.60 mg, 1.00 mol%), bis(pinacolato)diboron (152 mg, 0.600 mmol, 1.50 equiv), LiO*t*-Bu (44.8 mg, 0.560 mmol, 1.40 equiv), and 3.00 mL of a solution of 10:1 toluene/THF. Alkene (0.400 mmol, 1.00 equiv) and arylbromide (0.600 mmol, 1.50 equiv) were immediately added via microsyringes, followed by another 1.00 mL of the 10:1 toluene/THF solution down the sides of the vial. The vial was sealed with a Teflon-lined screw cap then removed from the glovebox. The mixture was allowed to stir at 30°C for 12 h then was quenched upon addition of 2M HCl (4 mL). The mixture was extracted with EtOAc (3 x 4 mL). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated in vacuo. The crude mixture was purified by silica gel column chromatography to obtain the desired product or oxidized to the corresponding alcohol according to General Procedure C prior to purification.

■General Procedure C: Oxidation of the crude alkyl-Bpin product to the corresponding alcohol

The crude product mixture obtained by General Procedure A or B was dissolved in 2.00 mL of THF then 2M NaOH (1 mL, 2.00 mmol, 5.00 equiv) was added. The resulting biphasic mixture was stirred vigorously and cooled to 0 °C before 30% H_2O_2 (4.00 mmol, 10.0 equiv) was added. The flask was removed from the ice bath and allowed to stir at room temperature for 3 h. The reaction was diluted with H_2O (5 mL) then extracted with Et_2O (3 x 5 mL). The combined organic extract was dried with Na_2SO_4, filtered, and concentrated. The crude mixture was purified by silica gel column chromatography to obtain the desired product.

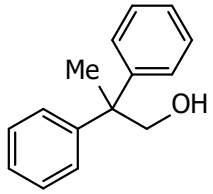
■General Procedure D: Enantioselective 1,2-Arylboration of 1,1-disubstituted alkenes to form quaternary centers

In an N_2-filled glovebox, to a 13 x 100 mm screw-capped vial was added chiral Cu catalyst **17** (10.8 mg, 5.00 mol%), APhos-Pd precatalyst (2.50 mg, 1.00 mol%),

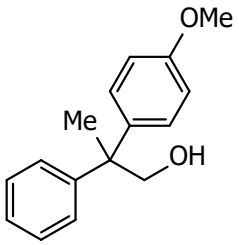
bis(pinacolato)diboron (152 mg, 0.600 mmol, 1.50 equiv), and LiO*t*-Bu (48.0 mg, 0.600 mmol, 1.50 equiv). To this, alkene (0.400 mmol, 1.00 equiv) was added via a microsyringe, immediately followed by 3.00 mL of 10:1 toluene/THF solution. Arylbromide (0.600 mmol, 1.50 equiv) was immediately added via microsyringe, followed by another 1.00 mL of the 10:1 toluene/THF solution down the sides of the vial. [Note: it is vital to add the alkene before the solvent—reaction does not perform well otherwise. If solvent is added first, followed by alkene, the reaction mixture will turn blue. If alkene is added first, the solution should turn a dark red, which indicates a potentially successful reaction]. The vial was sealed with a Teflon-lined screw cap then removed from the glovebox. The mixture was allowed to stir at 30°C for 12 h before quenching with aqueous 2 M HCl (4 mL). The mixture was extracted with EtOAc (3 x 4 mL). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated in vacuo. The crude mixture was purified by silica gel column chromatography to obtain the desired product or oxidized to the corresponding alcohol according to General Procedure C prior to purification.

■ **Characterization Data:**

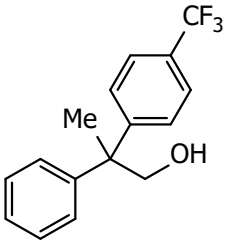
Note: In ^{13}C NMR spectra, signals of carbons directly bonded to boron were not detected because of quadrupolar relaxation.



2,2-diphenylpropan-1-ol (2): The title compound was prepared according to general procedure A. Purification by MPLC (gradient: 100% hexanes to 20:1 hexanes/ethyl acetate) yields **2** as a colorless oil (62% avg. yield of two runs). **IR (neat):** 3381 (br), 3023 (w), 2968 (w), 1493 (m), 1023 (m). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.36 – 7.25 (m, 4H), 7.25 – 7.14 (m, 6H), 4.09 (d, *J* = 6.8 Hz, 2H), 1.70 (s, 3H), 1.28 (t, *J* = 6.8 Hz, 1H). **^{13}C NMR (125 MHz, $CDCl_3$)**: δ 146.7, 128.4, 127.7, 126.3, 70.9, 48.8, 25.6. **HRMS (EI):** Calculated for $C_{15}H_{16}O$ [M^+]: 212.1201, Found: 212.1297.



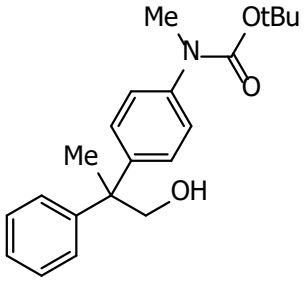
2-(4-Methoxyphenyl)-2-phenylpropan-1-ol (7): The title compound was prepared according to general procedure A using 4-bromoanisole and α-methylstyrene as coupling partners. Purification by MPLC (isocratic steps at 8% and 40% separated by gradient; hexanes/ethyl acetate) yields **7** as a colorless oil (62% avg. yield of two runs). All characterization data are in agreement with previous literature.[14] **^{1}H NMR (500 MHz, $CDCl_3$):** δ 7.36 – 7.30 (m, 2H), 7.27 – 7.21 (m, 3H), 7.21 – 7.13 (m, 2H), 6.90 – 6.83 (m, 2H), 4.10 (d, *J* = 6.2 Hz, 2H), 3.82 (s, 3H), 1.72 (s, 3H), 1.36 – 1.24 (m, 1H). **^{13}C NMR (125 MHz, $CDCl_3$)**: δ 157.9, 146.8, 138.4, 128.7, 128.3, 127.5, 126.2, 113.6, 70.9, 55.2, 48.1, 25.7.



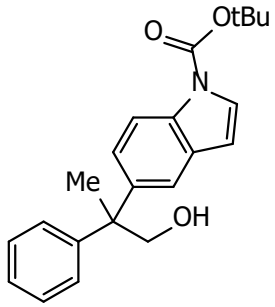
2-Phenyl-2-(4-(trifluoromethyl)phenyl)propan-1-ol (8): The title compound was prepared according to general procedure A. Purification by MPLC (0-40% gradient; hexanes/ethyl acetate) yields **8** as a colorless oil (47% avg. yield of two runs). **IR (neat):**

[14] R. P. Sonawane, V. Jheengut, C. Rabalakos, R. Larouche-Gauthier, H. K. Scott, V. K. Aggarwal, *Angew. Chem. Int. Ed.* **2011**, 50, 3760.

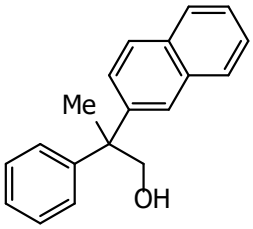
3384 (br), 3060 (w), 2939 (w), 1618 (w), 1325 (s), 1115 (s), 701 (m). **^{1}H NMR (600 MHz, $CDCl_3$):** δ 7.56 (m, 2H), 7.39 – 7.35 (m, 2H), 7.33 (m, 2H), 7.26 – 7.23 (m, 1H), 7.23 – 7.15 (m, 2H), 4.19 – 4.02 (m, 2H), 1.73 (s, 3H), 1.35 (dd, *J* = 6.6 Hz, 1H). **^{13}C NMR (125 MHz, $CDCl_3$)**: δ 151.0, 145.5, 128.5 (q, *J* = 32 Hz), 128.5, 128.1, 127.6, 126.7, 125.2 (q, *J* = 3.7 Hz), 124.2 (q, *J* = 271 Hz), 70.5, 48.9, 25.4. **HRMS (EI):** Calculated for $C_{16}H_{15}F_3O$ [M^+]: 280.1075, Found: 280.1069.



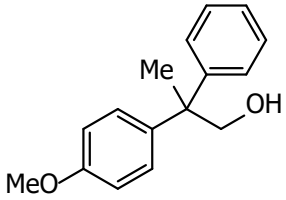
***tert*-Butyl (4-(1-hydroxy-2-phenylpropan-2-yl)phenyl)(methyl)carbamate (9):** The title compound was prepared according to general procedure A. Purification by MPLC (isocratic steps at 8% and 40% separated by gradient; hexanes/ethyl acetate) yields **9** as a colorless oil (72% avg. yield of two runs). **IR (neat):** 3440 (br), 2972 (w), 2931 (w), 1679 (s), 1365 (s), 1152 (s), 701 (m). **^{1}H NMR (600 MHz, $CDCl_3$):** δ 7.33 – 7.25 (m, 2H), 7.25 – 7.19 (m, 3H), 7.18 (m, 4H), 4.05 (s, 2H), 3.25 (s, 3H), 1.70 (s, 3H), 1.47 (s, 9H). **^{13}C NMR (125 MHz, $CDCl_3$)**: δ 154.8, 146.5, 143.6, 141.8, 128.2, 127.8, 127.6, 126.3, 125.0, 80.3, 70.7, 48.4, 37.2, 28.3, 25.5. **HRMS (ESI):** Calculated for $C_{21}H_{27}NO_3$ [M+Na]: 364.1883 Found: 364.1886.



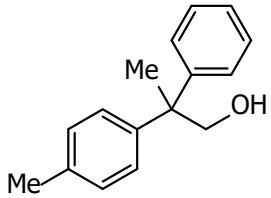
***tert*-Butyl 5-(1-hydroxy-2-phenylpropan-2-yl)-1*H*-indole-1-carboxylate (11):** The title compound was prepared according to general procedure A. Purification by MPLC (isocratic steps at 8% and 40% separated by gradient; hexanes/ethyl acetate) yields **11** as a white solid (62% avg. yield of two runs). **m.p.:** 94-97 °C. **IR (neat):** 3390 (br), 2973 (w), 2931 (w), 1731 (s), 1370 (s), 1087 (s), 700 (m). **^{1}H NMR (500 MHz, $CDCl_3$):** δ 8.05 (d, *J* = 8.8 Hz, 1H), 7.61 (d, *J* = 3.8 Hz, 1H), 7.51 (d, *J* = 2.0 Hz, 1H), 7.35 – 7.30 (m, 2H), 7.28 – 7.22 (m, 3H), 7.16 (dd, *J* = 8.8, 2.0 Hz, 1H), 6.55 (d, *J* = 3.8 Hz, 1H), 4.24 – 4.13 (m, 2H), 1.79 (s, 3H), 1.68 (s, 9H), 1.36 – 1.29 (m, 1H).**^{13}C NMR (125 MHz, $CDCl_3$)**: δ 149.7, 147.1, 140.8, 130.5, 128.3, 127.6, 126.2, 124.3, 119.7, 115.0, 107.4, 83.7, 64.4, 71.0, 48.6, 28.2, 25.9, 25.4. **HRMS (ESI):** Calculated for $C_{22}H_{25}NO_3$ [M+Na]: 374.1727, Found: 374.1729.



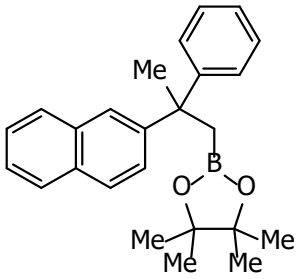
2-(Naphthalen-2-yl)-2-phenylpropan-1-ol (12): The title compound was prepared according to general procedure A using 2-bromonaphthalene and α-methylstyrene as coupling partners. Purification by MPLC (0-40% gradient; hexanes/ethyl acetate) yields **12** as a yellow oil (73% avg. yield of two runs). **IR (neat):** 3392 (br), 3056 (w), 2969 (w), 1026 (s), 701 (s), 477 (m). **^{1}H NMR (500 MHz, $CDCl_3$):** δ 7.88 – 7.80 (m, 3H), 7.77 (d, *J* = 8.7 Hz, 1H), 7.55 – 7.44 (m, 2H), 7.36 – 7.31 (m, 2H), 7.29 – 7.24 (m, 4H), 4.24 (s, 2H), 1.84 (s, 3H), 1.34 (s, 1H). **^{13}C NMR (125 MHz, $CDCl_3$)**: δ 146.4, 143.8, 133.2, 132.0, 128.4, 128.1, 128.0, 127.7, 127.4, 126.6, 126.4, 126.1, 125.8, 125.6, 70.7, 48.9, 25.5. **HRMS (EI):** Calculated for $C_{19}H_{18}O$ [M^+]: 262.1356, Found: 262.1350.



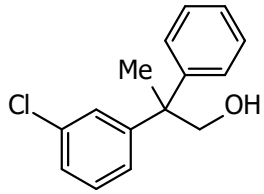
2-(4-methoxyphenyl)-2-phenylpropan-1-ol (7): The title compound was prepared according to general procedure A using 1-methoxy-4-(prop-1-en-2-yl)benzene and bromobenzene as coupling partners. Purification by MPLC (20:1 hexanes/ethyl acetate) yields **7** as a colorless oil (63% avg. yield of two runs). All characterization data are in agreement with previous literature.[14] **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.36 – 7.30 (m, 2H), 7.29 – 7.22 (m, 3H), 7.20 – 7.15 (m, 2H), 6.90 – 6.85 (m, 2H), 4.10 (s, 2H), 3.82 (s, 3H), 1.72 (s, 3H), 1.45 (m, 1H).**^{13}C NMR (125 MHz, $CDCl_3$)**: δ 157.9, 146.8, 138.4, 128.7, 128.3, 127.5, 126.2, 113.6, 70.9, 55.2, 48.1, 25.7.



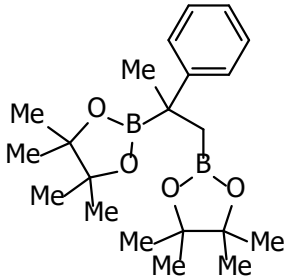
2-phenyl-2-(p-tolyl)propan-1-ol (13): The title compound was prepared according to general procedure A. Purification by MPLC (20:1 hexanes/ethyl acetate) yields **13** as a colorless oil (72% avg. yield of two runs). **IR (neat):** 3374 (br), 3055 (w), 2969 (w), 1511 (m), 1019 (s). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.36 – 7.29 (m, 2H), 7.29 – 7.20 (m, 3H), 7.14 (m, 4H), 4.11 (d, *J* = 6.6 Hz, 2H), 2.35 (s, 3H), 1.72 (s, 3H), 1.33 (t, *J* = 6.6 Hz, 1H). **^{13}C NMR (125 MHz, $CDCl_3$)**: δ 147.8, 144.5, 136.9, 130.1, 129.4, 128.7, 128.6, 127.3, 72.0, 49.5, 26.7, 22.0. **HRMS (EI):** Calculated for $C_{16}H_{18}O$ [M^+]: 226.1358, Found: 226.1351.



4,4,5,5-tetramethyl-2-(2-(naphthalen-2-yl)-2-phenylpropyl)-1,3,2-dioxaborolane (12): The title compound was prepared according to general procedure A using 2-isopropenylnaphthalene and bromobenzene as coupling partners. Purification by MPLC (gradient: 100% hexanes to 30:1 hexanes/ethyl acetate) yields **12** as a white solid (51% avg. yield of two runs). **m.p**.: 84.5-86.1 °C. **IR (neat):** 3024 (m), 2973 (w), 1357 (s), 1142 (s), 853 (s). **^{1}H NMR (400 MHz, CDCl$_3$):** δ 7.82 (s, 1H), 7.78 (m, 1H), 7.73 (m, 1H), 7.64 (m, 1H) 7.45 – 7.36 (m, 2H), 7.24 (m, 4H), 7.17 (m, 1H), 7.12 (m, 1H), 1.87 (s, 3H), 1.79 (s, 2H), 0.95 (s, 6H), 0.92 (s, 6H). **^{13}C NMR (125 MHz, CDCl$_3$)**: δ 151.0, 148.5, 133.1, 131.7, 128.0, 127.9, 127.5, 127.4, 127.2, 127.1, 125.7, 125.5, 125.3, 124.2, 82.8, 44.6, 29.8, 24.6, 24.5. **HRMS (EI):** Calculated for $C_{25}H_{29}BO_2$ [M^+]: 372.2261, Found: 372.2262.

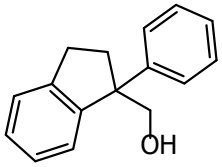


2-(3-chlorophenyl)-2-phenylpropan-1-ol (14): The title compound was prepared according to general procedure A. Purification by MPLC (20:1 hexanes/ethyl acetate) yields **14** as a colorless oil (67% avg. yield of two runs). **IR (neat):** 3392 (br), 2921 (s), 2853 (s), 1458 (m), 698 (s). **^{1}H NMR (400 MHz, CDCl$_3$):** δ 7.34 – 7.26 (m, 2H), 7.26 – 7.16 (m, 6H), 7.12 – 7.06 (m, 2H), 4.06 (d, J = 6.8 Hz, 2H), 1.68 (s, 3H), 1.28 (t, J = 6.8 Hz, 1H).**^{13}C NMR (125 MHz, CDCl$_3$)**: δ 148.9, 145.7, 134.2, 129.5, 128.5, 127.9, 127.5, 126.6, 126.5, 126.0, 70.6, 48.8, 25.4. **HRMS (EI):** Calculated for $C_{15}H_{15}ClO$ [M^+]: 246.0811, Found: 246.0809.

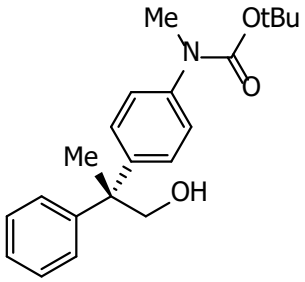


2,2'-(2-(4-methoxyphenyl)propane-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (15): The title compound was prepared according to general procedure A. Purification by MPLC (gradient: 100% hexanes to 30:1 hexanes/diethyl ether) yields **15** as a colorless oil (58% avg. yield of two runs). All characterization data are in

agreement with previous literature.[15] **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.39 (m, 2H), 7.25 (m, 2H), 7.10 (m, 1H), 1.49 (d, *J* = 15.6 Hz, 1H), 1.41 (s, 3H), 1.21 (s, 6H), 1.21 (s, 6H), 1.20 (s, 6H), 1.18 (6H, s), 1.15 (d, *J* = 15.6 Hz, 1H). **^{13}C NMR (125 MHz, $CDCl_3$)**: 149.1, 127.9, 126.4, 124.8, 83.2, 82.9, 29.7, 25.1, 24.7, 24.5, 24.4.

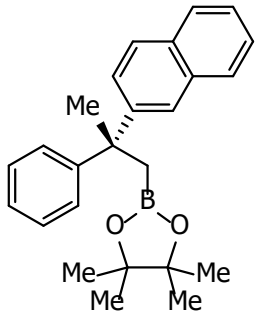


(1-phenyl-2,3-dihydro-1H-inden-1-yl)methanol (17): The title compound was prepared according to general procedure A. Purification by MPLC (gradient: 100% hexanes to 9:1 hexanes/ethyl acetate) yields **17** as a colorless oil (42% avg. yield of two runs). **IR (neat):** 3362 (br), 3020 (w), 2936 (m), 1476 (m), 1020 (s). **^{1}H NMR (600 MHz, $CDCl_3$):** δ 7.40 – 7.08 (m, 9H), 4.15 (d, *J* = 11.2 Hz, 1H), 4.00 (d, *J* = 11.2 Hz, 1H), 3.05 – 2.78 (m, 2H), 2.47 (m, 1H), 2.35 (m, 1H), 1.45 (s, 1H). **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 145.9, 145.1, 144.8, 128.4, 127.4, 127.2, 126.5, 126.4, 125.1, 125.0, 68.5, 58.5, 38.0, 30.4. **HRMS (EI):** Calculated for $C_{16}H_{16}O$ [M^+]: 224.1201, Found: 224.1195.

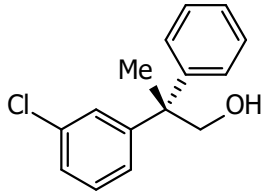


***tert*-Butyl (*R*)-(4-(1-hydroxy-2-phenylpropan-2-yl)phenyl)(methyl)carbamate ((*R*)-9):** The title compound was prepared according to general procedure D. Purification by MPLC (isocratic steps at 8% and 30% separated by gradient; hexanes/ethyl acetate) yields **(*R*)-9** as a colorless oil (40% avg. yield of two runs). All characterization data are in agreement with the racemic substrate (**9**). **^{1}H NMR (500 MHz, $CDCl_3$):** δ 7.33 – 7.25 (m, 2H), 7.25 – 7.19 (m, 3H), 7.20 (m, 4H), 4.05 (s, 2H), 3.25 (s, 3H), 1.70 (s, 3H), 1.47 (s, 9H). **^{13}C NMR (125 MHz, $CDCl_3$)**: δ 154.8, 146.5, 143.6, 141.8, 128.2, 127.8, 127.6, 126.3, 125.0, 80.3, 70.7, 48.4, 37.2, 28.3, 25.5. **Optical Rotation:** $[\alpha]_D^{20}$: +1.80 (c = 1.00, $CHCl_3$) for an enantiomerically enriched sample of 94:6 er (er in text is an average of two HPLC runs). The enantiomeric purity was established by HPLC analysis using a chiral column (Lux 3μ Cellulose-4 column, 22 °C, 0.75 mL/min, 96:4 hexane:isopropanol, 220 nm, t_{major} = 29.446 min, t_{minor} = 27.089 min). Absolute stereochemistry was determined through analogy with **(*R*)-12**. Racemic material was obtained using general procedure A (see racemic substrate 9).

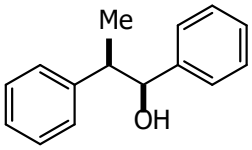
[15] D. J. Blair, D. Tanini, J. M. Bateman, H. K. Scott, E. L. Myers, V. K. Aggarwal, *Chem. Sci*. **2017**, *8*, 2898.



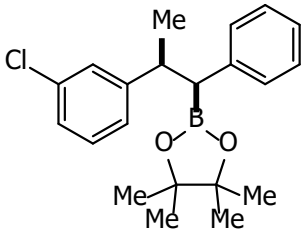
***(R)*-4,4,5,5-Tetramethyl-2-(2-(naphthalen-2-yl)-2-phenylpropyl)-1,3,2-dioxaborolane ((*R*)-12)):** The title compound was prepared according to general procedure D using 2-bromonaphthalene as a coupling partner. Purification by MPLC (isocratic steps at 1% and 5% separated by gradient; hexanes/ethyl acetate) yields **(*R*)-12** as a white solid (37% avg. yield of two runs). All characterization data are in agreement with the racemic substrate (**12**). **m.p.:** 109-113 °C. **^{1}H NMR (600 MHz, $CDCl_3$):** δ 7.85 (d, *J* = 1.8 Hz, 1H), 7.80 (d, *J* = 7.9 Hz, 1H), 7.76 (d, *J* = 7.9 Hz, 1H), 7.66 (d, *J* = 8.6 Hz, 1H), 7.50 – 7.37 (m, 3H), 7.26 (m, 3H), 7.19 (dd, *J* = 8.6, 1.6 Hz, 1H), 7.17 – 7.12 (m, 1H), 1.90 (s, 3H), 1.82 (s, 2H), 0.98 (s, 6H), 0.96 (s, 6H). **^{13}C NMR (125 MHz, $CDCl_3$)**: δ 150.9, 148.5, 133.1, 131.7, 127.9, 127.8, 127.4, 127.3, 127.1, 127.0, 125.7, 125.5, 125.2, 124.1, 82.7, 44.6, 29.7, 24.6, 24.6. **Optical Rotation:** $[\alpha]_D^{20}$: −5.80 (c = 0.73, $CHCl_3$) for an enantiomerically enriched sample of 93:7 er (er in text is an average of two HPLC runs). The enantiomeric purity was established by HPLC analysis using a chiral column (Lux 3μ Cellulose-2 column, 22 °C, 0.25 mL/min, 99:1 hexane:isopropanol, 254 nm, t_{major} = 18.331 min, t_{minor} = 16.897 min). Absolute stereochemistry was determined via X-ray crystallography. Racemic material was obtained using general procedure A (see racemic substrate **12**).



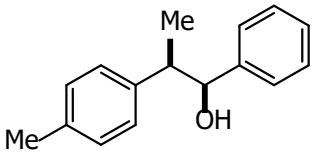
***(S)*-2-(3-Chlorophenyl)-2-phenylpropan-1-ol ((*S*)-14):** The title compound was prepared according to general procedure D. Purification by MPLC (isocratic steps at 10% and 30% separated by gradient; hexanes/ethyl acetate) yields **(*S*)-14** as a colorless oil (31% avg. yield of two runs). All relevant characterization data are in agreement with the racemic substrate (**14**). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.30 (m, 2H), 7.23 – 7.15 (m, 6H), 7.09 (m, 1H), 4.06 (s, 2H), 1.68 (s, 3H), 1.48 (m, 1H). **^{13}C NMR (125 MHz, $CDCl_3$)**: δ 149.0, 145.8, 134.3, 129.5, 128.5, 127.9, 127.6, 126.6, 126.5, 126.0, 70.6, 48.8, 25.5. **Optical Rotation:** $[\alpha]_D^{20}$: +1.90 (c = 0.96, $CHCl_3$) for an enantiomerically enriched sample of 87:13 er (er in text is an average of two HPLC runs). The enantiomeric purity was established by HPLC analysis using a chiral column (Lux 3μ Cellulose 3 column, 22 °C, 0.75 mL/min, 95:5 hexane:isopropanol, 220 nm, t_{major} = 27.677 min, t_{minor} = 35.004 min). Absolute stereochemistry was determined through analogy with **(*R*)-12**. Racemic material was obtained using general procedures A (see racemic substrate **14**).



1,2-diphenylpropan-1-ol (3): The title compound was prepared according to general procedure B. Purification by MPLC (30:1 hexanes/ethyl acetate) yields **3** as a colorless oil (64% avg. yield of two runs, >20:1 d.r.). All characterization data are in agreement with previous literature.[16] **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.30 – 7.10 (m, 10H), 4.80 (dd, *J* = 6.8, 3.4 Hz, 1H), 3.10 (app p, *J* = 6.8 Hz, 1H), 1.88 (d, *J* = 3.4 Hz, 1H), 1.30 (d, *J* = 6.8 Hz, 3H). **^{13}C NMR (125 MHz, $CDCl_3$)**: δ 143.9, 143.3, 128.6, 128.5, 128.4, 127.6, 126.8, 126.7, 79.1, 47.6, 15.3.

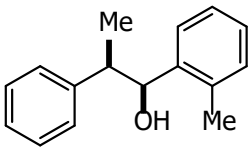


2-(2-(3-chlorophenyl)-1-phenylpropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (30): The title compound was prepared according to general procedure B. Purification by MPLC (gradient: 100% hexanes to 30:1 hexanes/ethyl acetate) yields **30** as a colorless oil (67% avg. yield of two runs, >20:1 dr, major diastereomer determined by analogy with **3**). **IR (neat):** 3029 (w), 2975 (w), 1453 (m), 783 (m), 695 (s). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.12 – 7.06 (m, 2H), 7.06 – 6.97 (m, 6H), 6.89 – 6.83 (m, 1H), 3.25 (dq, *J* = 11.1, 6.9 Hz, 1H), 2.54 (d, *J* = 11.1 Hz, 1H), 1.36 (d, *J* = 6.9 Hz, 3H), 1.22 (s, 6H), 1.20 (s, 6H). **^{13}C NMR (125 MHz, $CDCl_3$)**: δ 148.7, 140.7, 133.6, 129.1, 129.0, 128.0, 127.4, 125.8, 125.6, 125.3, 83.5, 42.6, 24.6, 22.5. **HRMS (EI):** Calculated for $C_{21}H_{26}BClO_2$ [M^+]: 356.1714, Found: 356.1715.

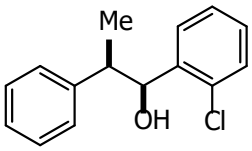


1-phenyl-2-(p-tolyl)propan-1-ol (28): The title compound was prepared according to general procedure B. Purification by MPLC (20:1 hexanes/ethyl acetate) yields **28** as a colorless oil (46% avg. yield of two runs, >20:1 dr). All characterization data are in agreement with previous literature.[17] **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.32 – 7.14 (m, 6H), 7.10 – 6.98 (m, 3H), 4.79 (dd, *J* = 5.6, 3.0 Hz, 1H), 3.16 – 2.98 (m, 1H), 2.29 (s, 3H), 1.84 (s, 1H), 1.25 (d, *J* = 7.1 Hz, 3H). **^{13}C NMR (125 MHz, $CDCl_3$)**: 142.9, 140.4, 135.9, 128.9, 127.9, 127.9, 127.1, 126.3, 78.6, 46.7, 20.9, 14.7.

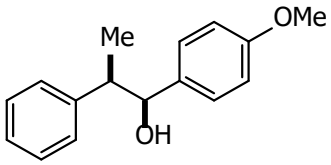
[16] B. Chen, P. Cao, Y. Liao, M. Wang, J. Liao, *Org. Lett.*, **2018**, *20*,1346.
[17] A. R. Almeida, R. D. Dias, C. J. P. Monteiro, A. R. Abreu, P. M. P. Gois, J. C. Bayon, M. M. Pereira, *Adv. Synth. Catal.* **2014**, *356*, 1223.



2-phenyl-1-(o-tolyl)propan-1-ol (27): The title compound was prepared according to general procedure B. Purification by MPLC (20:1 hexanes/ethyl acetate) yields **27** as a colorless oil (56% avg. yield of two runs, >20:1 dr, major diastereomer determined by analogy with **3**). **IR (neat):** 3416 (br), 3025 (w), 2966 (w), 1451 (m), 762 (s). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.52 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.31 – 7.23 (m, 3H), 7.24 – 7.19 (m, 3H), 7.14 (td, *J* = 7.5, 1.5 Hz, 1H), 7.06 (d, *J* = 7.5 Hz, 1H), 5.03 (dq, *J* = 7.0, 2.8 Hz, 1H), 3.10 (m, 1H), 2.18 (s, 3H), 1.34 (d, *J* = 7.0 Hz, 3H), 0.94 – 0.80 (m, 1H). **^{13}C NMR (125 MHz, $CDCl_3$)**: δ 144.1, 141.3, 134.5, 130.2, 128.3, 127.9, 127.1, 126.5, 126.2, 125.9, 74.8, 45.3, 19.1, 14.1. **HRMS (EI):** Calculated for $C_{16}H_{18}O$ [M^+]: 226.1358, Found: 226.1355.

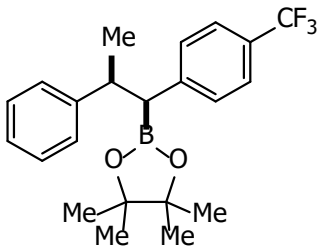


1-(2-chlorophenyl)-2-phenylpropan-1-ol (26): The title compound was prepared according to general procedure B. Purification by MPLC (20:1 hexanes/ethyl acetate) yields **26** as a colorless oil (52% avg. yield of two runs, >20:1 dr). All characterization data are in agreement with previous literature.[18] **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.55 (m, 1H), 7.37 – 7.28 (m, 6H), 7.28 – 7.21 (m, 2H), 7.21 – 7.15 (m, 1H), 5.25 – 5.22 (m, 1H), 3.32 (m, 1H), 1.80 (s, 1H), 1.20 (d, *J* = 7.1 Hz, 3H). **^{13}C NMR (125 MHz, $CDCl_3$)**: δ 144.0, 140.2, 131.8, 129.4, 128.4, 128.3, 128.2, 127.9, 126.6, 126.6, 74.8, 43.6, 12.5.

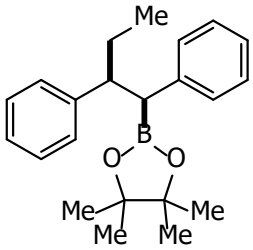


1-(4-methoxyphenyl)-2-phenylpropan-1-ol (25): The title compound was prepared according to general procedure B. Purification by MPLC (20:1 hexanes/ethyl acetate) yields **25** as a colorless oil (68% avg. yield of two runs, >20:1 dr). All characterization data are in agreement with previous literature.[19] **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.21 (m, 2H), 7.16 (d, *J* = 7.2 Hz, 1H), 7.09 (m, 4H), 6.77 (m, 2H), 4.74 (d, *J* = 6.1 Hz, 1H), 3.75 (s, 3H), 3.15 – 3.01 (m, 1H), 1.78 (s, 1H), 1.30 (d, *J* = 7.0 Hz, 3H). **^{13}C NMR (125 MHz, $CDCl_3$)**: δ 143.9, 143.3, 128.6, 128.5, 128.4, 127.6, 126.8, 126.7, 79.1, 47.6, 18.4, 15.3.

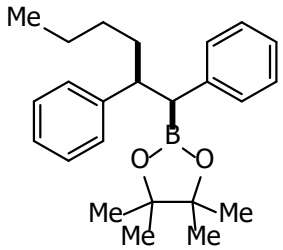
[18] C. Zhou, Z. Wang, *Synthesis* **2005**, *10*, 1649.
[19] T. Taniguchi, H. Zaimoku, H. Ishibashi, *Chem. Eur. J.* **2011**, *17*, 4307.



4,4,5,5-tetramethyl-2-(2-phenyl-1-(4-(trifluoromethyl)phenyl)propyl)-1,3,2-dioxaborolane (24): The title compound was prepared according to general procedure B. Purification by MPLC (gradient: 100% hexanes to 30:1 hexanes/ethyl acetate) yields **24** as a colorless oil (63% avg. yield of two runs, >20:1 dr, major diastereomer determined by analogy with **3**). **m.p.**: 96.8 – 101.5 °C. **IR (neat):** 3028 (w), 2981 (w), 1614 (w), 1321 (s), 851 (m). **^{1}H NMR (400 MHz, CDCl$_3$):** δ 7.29 (m 2H), 7.09 (m, 4H), 7.01 (d, *J* = 7.1 Hz, 1H), 6.96 (m, 2H), 3.26 (dq, *J* = 11.5, 6.8 Hz, 1H), 2.65 (d, *J* = 11.5 Hz, 1H), 1.37 (d, *J* = 6.8 Hz, 3H), 1.21 (s, 6H), 1.19 (s, 6H). **^{13}C NMR (125 MHz, CDCl$_3$)**: δ 146.2, 146.0, 129.5, 128.3, 127.4, 126.1, 125.1, 124.8 (q, J = 272.5 Hz), 84.0, 42.9, 24.9, 23.2. **^{19}F NMR (376 MHz, CDCl$_3$):** δ -62.26. **HRMS (EI):** Calculated for $C_{16}H_{15}F_3O$ [M^+]: 390.1978, Found: 390.1981.

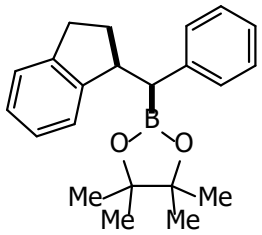


1,2-diphenylbutyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (32): The title compound was prepared according to general procedure B. Purification by MPLC (gradient: 100% hexanes to 30:1 hexanes/ethyl acetate) yields **32** as a colorless oil (73% avg. yield of two runs, >20:1 dr, major diastereomer determined by analogy with **3**). **IR (neat):** 3026 (m), 2957 (s), 2853 (m), 1493 (s), 848 (m). **^{1}H NMR (400 MHz, CDCl$_3$):** δ 7.07 (m, 2H), 7.04 – 6.89 (m, 8H), 3.02 (td, *J* = 11.3, 3.6 Hz, 1H), 2.62 (d, *J* = 11.3 Hz, 1H), 1.83 (m, 1H), 1.65 (m, 1H), 1.21 (s, 6H), 1.18 (s, 6H), 0.72 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR (125 MHz, CDCl$_3$)**: 144.0, 140.9, 129.1, 128.2, 127.7, 127.6, 125.5, 124.9, 83.4, 50.2, 29.7, 24.6, 24.5, 12.3. **HRMS (EI):** Calculated for $C_{22}H_{29}BO_2$ [M^+]: 336.2261, Found: 336.2265.

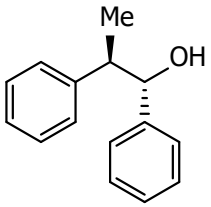


1,2-diphenylhexyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (33): The title compound was prepared according to general procedure B. Purification by column chromatography (gradient: 100% hexanes to 1:1 hexanes/dichloromethane) yields **33** as a colorless oil

(51% avg. yield of two runs, >20:1 dr, major diastereomer determined by analogy with **3**). **IR (neat):** 3018 (m), 2986 (s), 2871 (m), 1463 (s), 867 (m). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.07 (m, 2H), 7.04 – 6.89 (m, 8H), 3.02 (m, 1H), 2.62 (m, 1H), 1.97 (m, 2H), 1.83 (m, 1H), 1.65 (m, 3H), 1.20 (s, 6H), 1.17 (s, 6H), 0.72 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR (125 MHz, $CDCl_3$)**: 144.3, 141.1, 129.3, 127.8, 127.5, 127.4, 125.0, 124.9, 84.6, 50.1, 30.3, 26.7, 25.4, 24.6, 24.5, 12.2. **HRMS (EI):** Calculated for $C_{24}H_{33}BO_2$ [M^+]: 364.2574, Found: 364.2568.



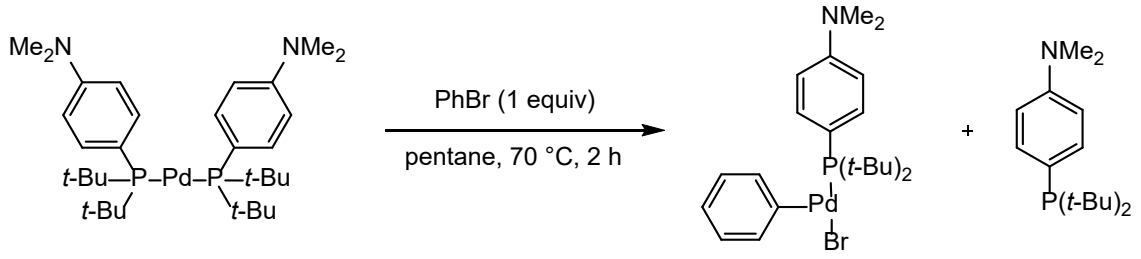
2,3-dihydro-1H-inden-1-yl)(phenyl)methyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (34): The title compound was prepared according to general procedure B. Purification by MPLC (gradient: 100% hexanes to 30:1 hexanes/ethyl acetate) yields **34** as a colorless oil (53% avg. yield of two runs, >20:1 dr, major diastereomer determined by analogy with **3**). **IR (neat):** 3023 (w), 2976 (m), 2930 (w), 1354 (s), 849 (m). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.23 (m, 4H), 7.17 – 7.12 (m, 2H), 7.03 (t, *J* = 7.5 Hz, 1H), 6.85 (t, *J* = 7.5 Hz, 1H), 6.45 (d, *J* = 7.5 Hz, 1H), 3.72 – 3.60 (m, 1H), 2.92 (m, 1H), 2.79 (m, 1H), 2.55 (m, 1H), 2.34 (m, 1H), 1.87 (m, 1H), 1.17 (s, 6H), 1.13 (s, 6H). **^{13}C NMR (125 MHz, $CDCl_3$)**: δ 147.1, 144.1, 141.7, 129.4, 128.3, 126.2, 125.5, 125.4, 124.8, 124.2, 83.4, 47.3, 32.4, 31.2, 24.6, 24.5. **HRMS (EI):** Calculated for $C_{22}H_{27}BO_2$ [M^+]: 334.2104, Found: 334.2105.



(1*S*,2*R*)-1,2-Diphenylpropan-1-ol ((*1S,2R*)-3): The title compound was prepared according to a slightly modified version of general procedure D; 3.00 equiv (1.20 mmol) of bromobenzene was added to the reaction mixture instead of 1.50 equiv (0.60 mmol), and 5 mol % PCy_3-Pd precatalyst (13.0 mg) was used instead of 1 mol %. Purification by MPLC (0-10% gradient; hexanes/ethyl acetate) yields ***(1S,2R)*-3** as an off-white solid (10% avg. yield of two runs, >20:1 d.r.). All characterization data are in agreement with the racemic substrate (**3**). **m.p.:** 49-51 °C. **^{1}H NMR (400 MHz, $CDCl_3$):** 7.23 – 7.10 (m, 8H), 7.10 – 7.03 (m, 2H), 4.75 (dd, *J* = 5.7, 3.3 Hz, 1H), 3.04 (dq, *J* = 7.0, 5.7 Hz, 1H), 1.77 (d, *J* = 3.3 Hz, 1H), 1.24 (d, *J* = 7.0 Hz, 3H). **^{13}C NMR (125 MHz, $CDCl_3$)**: δ 143.5, 142.8, 128.2, 128.0, 127.9, 127.2, 126.4, 126.2, 78.7, 47.2, 14.8. **Optical Rotation:** $[\alpha]_D^{20}$: +37.4 (c = 0.43, $CHCl_3$) for an enantiomerically enriched sample of 92:8 er (er in text is an average of two HPLC runs). The enantiomeric purity was established by HPLC analysis using a chiral column (Lux 3μ Cellulose-4 column, 22 °C, 0.75 mL/min, 95:5 hexane:isopropanol, 220 nm, t_{major} = 8.567 min, t_{minor} = 9.420 min). Absolute

stereochemistry was determined through comparison to previously reported literature values of optical rotation (literature = +47.12)[20]. Racemic material was obtained using general procedures B and C (see racemic substrate **3**).

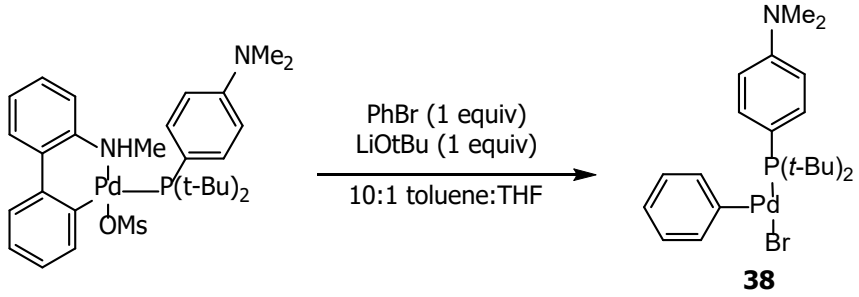
■ Mechanism Studies:



38

Synthesis of APhosPd(Ph)Br (38), procedure 1: In an N_2-filled glovebox, to an oven-dried 16 x 100 mm screw-capped vial was added $APhos_2Pd$ (100 mg, 0.141 mmol). Dry pentane (10.0 mL) was added, followed immediately by bromobenzene (0.550 mL, 5.17 mmol). The flask was sealed with a screw cap and removed from the glovebox. The reaction was stirred at 70 °C for 2 hours then was allowed to cool to room temperature. The vial cap was quickly replaced with a septum. With a N_2 line in the vial, the solvent was removed via syringe. Two more 10 mL portions of dry pentane were added then removed via syringe to eliminate any unreacted starting material and APhos byproduct, then the vial was placed under vacuum, yielding **38** as a light yellow powder (54% yield). The NMR data closely resembled that of the previously reported APhosPd(*o*-tolyl)Br.[21]

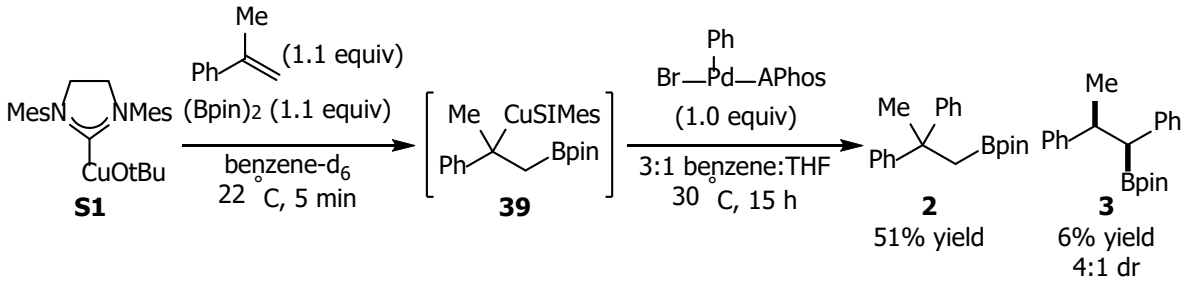
APhosPd(Ph)Br (38): ^{1}H NMR (400 MHz, C_6H_6): δ 7.88 (m, 2H), 7.68 (m, 2H), 6.87 (m, 2H), 6.73 (d, *J* = 7.0 Hz, 1H), 6.29 (m, 2H), 2.43 (d, *J* = 1.8 Hz, 6H), 1.28 (d, *J* = 13.7 Hz, 18H). **^{13}C NMR (125 MHz, C_6H_6)**: δ 150.5, 146.0, 138.1 (d, *J* = 11.1 Hz), 130.6 (d, *J* = 157.3 Hz), 126.4, 122.7, 115.3 (d, *J* = 40.8 Hz), 109.8 (d, *J* = 10.4 Hz), 39.0, 37.4 (d, *J* = 16.3 Hz), 30.5 (d, *J* = 4.2 Hz). **^{31}P NMR (162 MHz, C_6H_6)** δ 60.1. **HRMS (ESI):** Calculated for $C_{22}H_{33}NPPd^+$ [M-Br^+]: 448.1380, Found: 448.1391.



38

[20] F. A. A. Elhavez, D. J. Cram. *J. Am. Chem. Soc.* **1952**, *74*, 5846.
[21] K. Kosaka, T. Uchida, K. Mikami, Y. Ohta, T. Yokozawa, *Macromolecules* **2018**, *51*, 364.

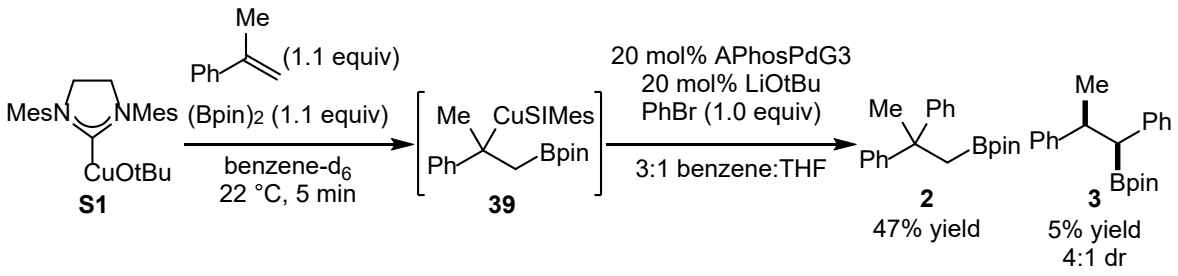
Synthesis of APhosPd(Ph)Br (38), procedure 2: In an N_2-filled glovebox, to an oven-dried 13 x 100 mm screw-capped vial was added PdG4-APhos precatalyst (17.5 mg, 0.027 mmol) and LiOtBu (2.40 mg, 0.030 mmol). A 10:1 solution of toluene-d_8/THF (0.75 mL) was added, followed immediately by bromobenzene (28.8 μL, 0.270 mmol). The solution was transferred to an NMR tube and NMR spectra were recorded to reveal the consumption of the PdG4-APhos precatalyst and formation of APhosPd(Ph)Br (**38**).



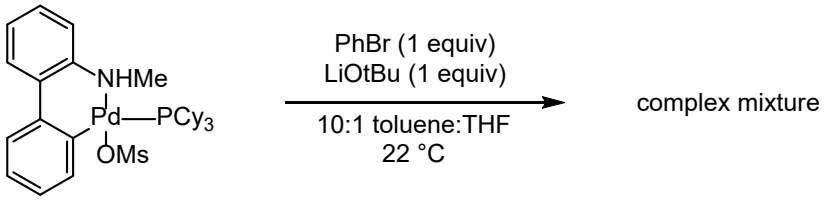
Procedure for reaction of stoichiometric copper complex (39) and stoichiometric APhosPd(Ph)Br (38): In an N_2-filled glovebox, to an oven-dried 13 x 100 mm screw-capped vial was added SIMesCuOt-Bu (22.1 mg, 0.050 mmol) and B_2pin_2 (14.1 mg, 0.055 mmol). Benzene-d_6 (0.7 mL) was added *(Note: benzene-d_6 was used in place of toluene-d_8 because it allowed for cleaner NMR spectra to be obtained*) followed immediately by α-methylstyrene (7.1 μL, 0.055 mmol) to provide a dark brown solution. The solution was transferred to an NMR tube and a ^{1}H NMR spectrum was quickly recorded to reveal that the SIMesCuOt-Bu was completely consumed *(Note: while SIMesCuOtBu was consumed, 30-40% α-methylstyrene remained unreacted, meaning not all of the SIMesCu-Bpin (formed via transmetalation of SIMesCuOt-Bu and (Bpin)$_2$) underwent migratory insertion. See the crossover experiment below in which we probed whether product was formed via reaction with the unreacted alkene and [Cu]).* The NMR tube was then brought back into the glovebox and transferred to a screw-capped vial containing a solution of Pd complex **38** (26.5 mg, 0.050 mmol, obtained by procedure 1) in a 3:1 benzene-d_6:THF solution (0.4 mL). The vial was sealed with a Teflon-lined screw cap then removed from the glovebox. The mixture was allowed to stir at 30°C for 4 h then was quenched upon addition of 2M HCl (1 mL). The mixture was extracted with EtOAc (3 x 1 mL) then dodecane (internal standard) was added and the mixture was analyzed by GC to reveal a 51% yield of **2** and a 6% yield of **3** (4:1 d.r.).

C(sp^3)-Cu complex (39): Full characterization was not possible due to the relative instability of the product and the presence of multiple compounds in the solution. The spectrum of this compound closely matches a related Csp^3-Cu complex of known confirmation.[22] **^{1}H NMR (600 MHz, C_6H_6):** δ 7.19 (m, 1H), 7.03 (m, 1H), 6.90 (m, 2H), 6.76 (m, 4H), 6.66 (s, 1H), 3.54 (d, *J* = 6.2 Hz, 2H), 3.03 (s, 3H), 2.11 (d, *J* = 3.1 Hz, 12H), 2.06 (s, 6H), 1.61 (d, *J* = 7.6 Hz, 3H), 1.45 (s, 2H), 1.01 (s, 12H).

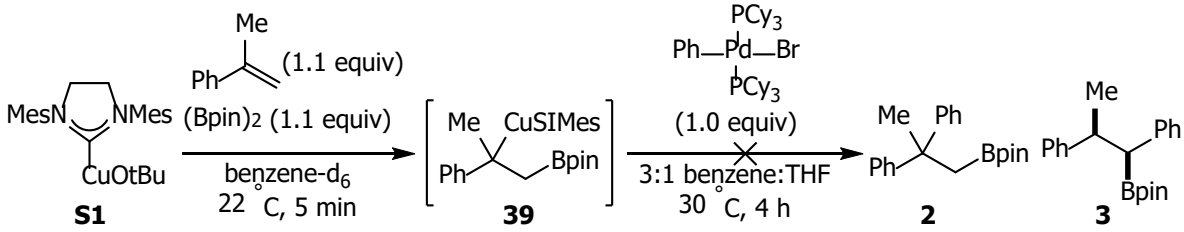
[22] D. S. Laitar, E. Y. Tsui, J. P. Sadhigi, *Organometallics* **2006**, *25*, 2405.



Generation of stoichiometric tertiary alkyl copper (39) and cross coupling using catalytic APhosPdG3: In an N_2-filled glovebox, to an oven-dried 13 x 100 mm screw-capped vial was added SIMesCuOt-Bu (22.1 mg, 0.050 mmol) and B_2pin_2 (14.1 mg, 0.055 mmol). Benzene-d_6 (0.7 mL) was added, followed immediately by α-methyl styrene (7.10 µL, 0.055 mmol) to provide a dark brown solution. The solution was transferred to an NMR tube and a ^{1}H NMR spectrum was quickly recorded to reveal that the SIMesCuOt-Bu was completely consumed. The NMR tube was then brought back into the glovebox and added to a screw-capped vial containing a solution of PhBr (8.0 µL, 0.075 mmol), Pd-APhos Precatalyst (6.40 mg, 0.01 mmol), LiOt-Bu (0.80 mg, 0.01 mmol), and a 3:1 benzene-d_6:THF solution (0.4 mL). The vial was sealed with a Teflon-lined screw cap then removed from the glovebox. The mixture was allowed to stir at 30°C for 4 h then was quenched upon addition of 2M HCl (1 mL). The mixture was extracted with EtOAc (3 x 1 mL) then dodecane (internal standard) was added and the mixture was analyzed by GC to reveal a 47% yield of **2** and a 5% yield of **3** (4:1 d.r.).

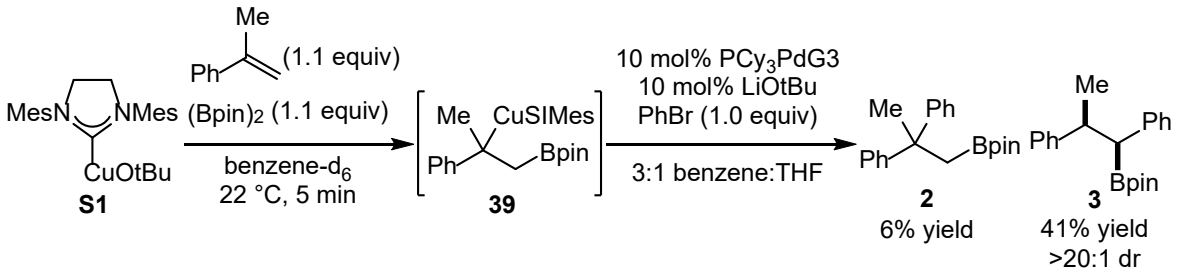


Procedure for the attempted synthesis of $(PCy_3)_nPd(Ph)Br$ (42): In an N_2-filled glovebox, to an oven-dried 13 x 100 mm screw-capped vial was added PdG4-PCy_3 precatalyst (17.9 mg, 0.027 mmol) and LiOtBu (2.40 mg, 0.030 mmol). A 10:1 solution of toluene-d_8:THF (0.75 mL) was added, followed immediately by bromobenzene (28.8 µL, 0.270 mmol). The solution was transferred to an NMR tube and NMR spectra were recorded to reveal a complex mixture of phosphorous-containing products.



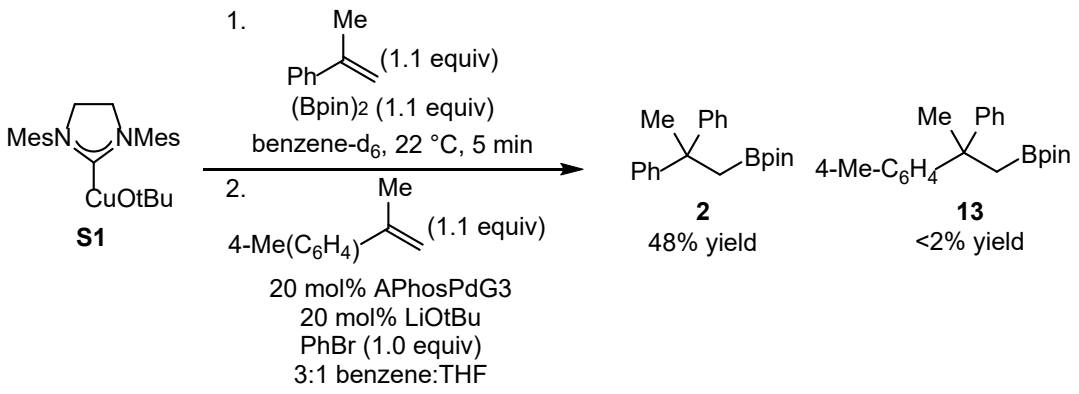
Procedure for reaction of stoichiometric copper complex (39) and stoichiometric $(PCy_3)_2Pd(Ph)Br$ (41): In an N_2-filled glovebox, to an oven-dried 13 x 100 mm screw-capped vial was added SIMesCuOt-Bu (22.1 mg, 0.050 mmol) and B_2pin_2 (14.1 mg, 0.055 mmol). Benzene-d_6 (0.7 mL) was added followed immediately by α-methylstyrene

(7.1 μL, 0.055 mmol) to provide a dark brown solution. The solution was transferred to an NMR tube and a ^{1}H NMR spectrum was quickly recorded to reveal that the SIMesCuOt-Bu was completely consumed. The NMR tube was then brought back into the glovebox and transferred to a screw-capped vial containing a solution of Pd complex **41**[23] (40.4 mg, 0.050 mmol) in a 3:1 benzene-d_6:THF solution (0.4 mL). The vial was sealed with a Teflon-lined screw cap then removed from the glovebox. The mixture was allowed to stir at 30°C for 4 h then was quenched upon addition of 2M HCl (1 mL). The mixture was extracted with EtOAc (3 x 1 mL) then dodecane (internal standard) was added and the mixture was analyzed by GC to reveal that no arylboration products were formed.

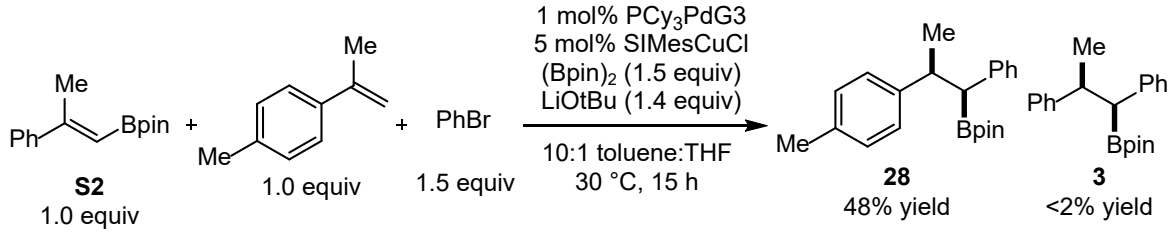


Generation of stoichiometric tertiary alkyl copper (39) and cross coupling using catalytic PCy$_3$PdG3: In an N_2-filled glovebox, to an oven-dried 13 x 100 mm screw-capped vial was added SIMesCuOt-Bu (22.1 mg, 0.050 mmol) and B_2pin_2 (14.1 mg, 0.055 mmol). Benzene-d_6 (0.7 mL) was added followed immediately by α-methylstyrene (7.10 μL, 0.055 mmol) to provide a dark brown solution. The solution was transferred to an NMR tube and a ^{1}H NMR spectrum was quickly recorded to reveal that the SIMesCuOt-Bu was completely consumed. The NMR tube was then brought back into the glovebox and added to a screw-capped vial containing a solution of PhBr (8.0 μL, 0.075 mmol), PdG3-PCy$_3$ Precatalyst (6.50 mg, 0.01 mmol), LiOt-Bu (0.80 mg, 0.01 mmol), and a 3:1 benzene-d_6:THF solution (0.4 mL). The vial was sealed with a Teflon-lined screw cap then removed from the glovebox. The mixture was allowed to stir at 30°C for 4 h then was quenched upon addition of 2M HCl (1 mL). The mixture was extracted with EtOAc (3 x 1 mL) then dodecane (internal standard) was added and the mixture was analyzed by GC to reveal a 41% yield of **3** (>20:1 dr) and a 6% yield of **2**.

[23] J. P. Stambuli, C. D. Incarvito, M. Buhl, J. F. Hartwig, *J. Am. Chem. Soc.* **2004**, *126*, 1184.

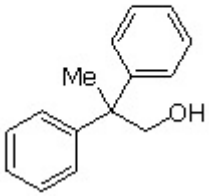


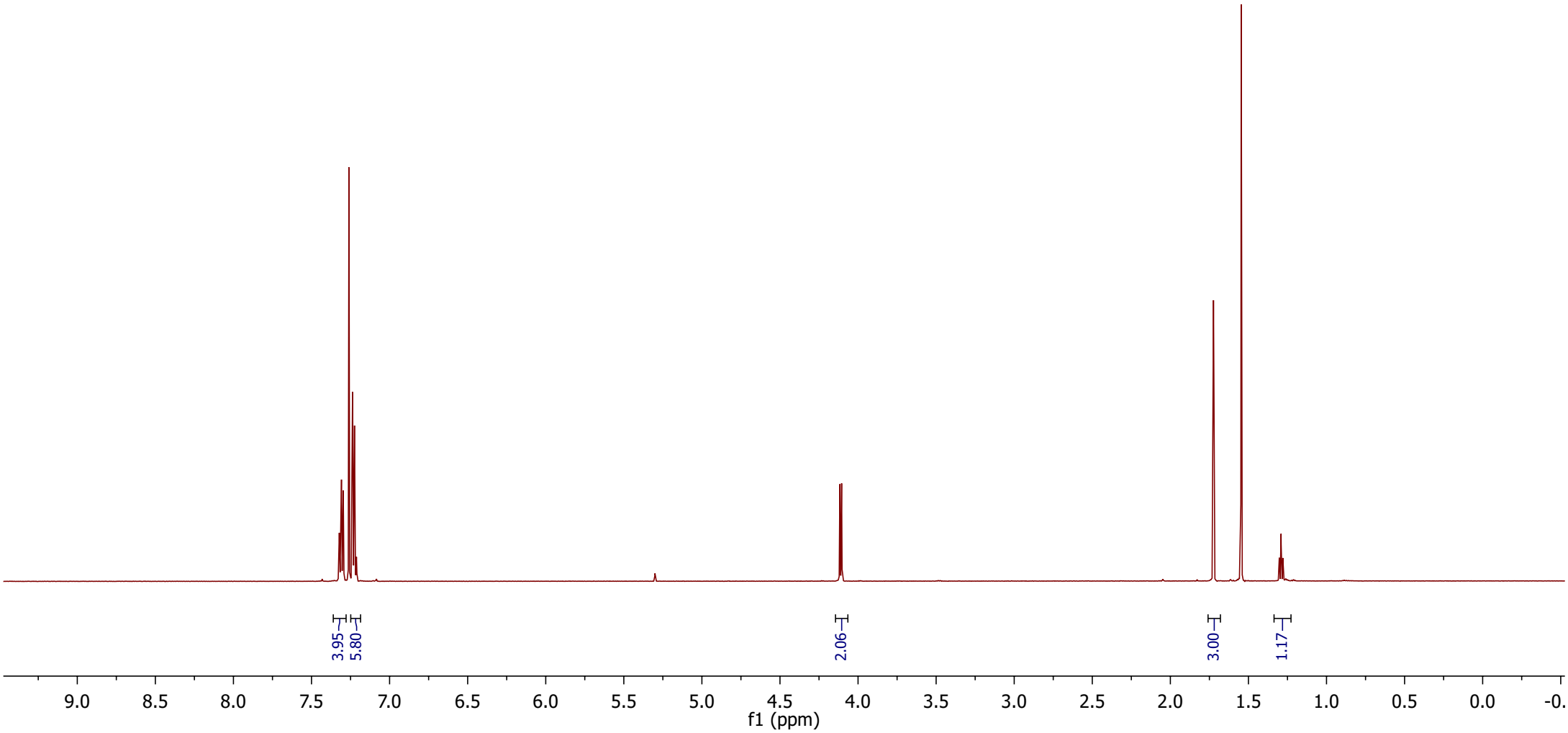
Crossover experiment to probe whether unreacted alkene is undergoing arylboration: In an N_2-filled glovebox, to an oven-dried 13 x 100 mm screw-capped vial was added SIMesCuOt-Bu (22.1 mg, 0.050 mmol) and B_2pin_2 (14.1 mg, 0.055 mmol). Benzene-d_6 (0.7 mL) was added followed immediately by α-methyl styrene (7.1 µL, 0.055 mmol) to provide a dark brown solution. The solution was transferred to an NMR tube and a ^{1}H NMR spectrum was quickly recorded to reveal that the SIMesCuOt-Bu was completely consumed. The NMR tube was then brought back into the glovebox and added to a screw-capped vial containing a solution of 1-methyl-4-(1-methylethenyl)benzene (3.6 µL, 0.025 mmol), PhBr (8.0 µL, 0.075 mmol), Pd-APhosG3 Precatalyst (6.4 mg, 0.01 mmol), LiOt-Bu (0.80 mg, 0.01 mmol), and a 3:1 benzene-d_6:THF solution (0.4 mL). The vial was sealed with a Teflon-lined screw cap then removed from the glovebox. The mixture was allowed to stir at 30°C for 4 h then was quenched upon addition of 2M HCl (1 mL). The mixture was extracted with EtOAc (3 x 1 mL) then dodecane (internal standard) was added and the mixture was analyzed by GC to reveal a 48% yield of **2** and <2% of **13**.



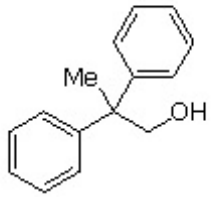
Crossover experiment to probe stability of alkene-Pd complex 36: In an N_2-filled glovebox, to a 13 x 100 mm screw-capped vial was added SIMes-CuCl (8.10 mg, 5.00 mol%), PCy_3-Pd precatalyst (1.30 mg, 0.500 mol%), bis(pinacolato)diboron (152 mg, 0.600 mmol, 1.50 equiv), NaO*t*-Bu (94.0 mg, 0.600 mmol, 1.50 equiv), and 3.00 mL of a solution of 10:1 toluene/THF. Vinylboronic ester **S2** (98.9 µL, 0.400 mmol, 1.00 equiv), α-methylstyrene (51.9 µL, 0.400 mmol, 1.00 equiv), and bromobenzene (64.1 µL, 0.600 mmol, 1.50 equiv) were immediately added via microsyringes, followed by another 1.00 mL of the 10:1 toluene/THF solution down the sides of the vial. The vial was sealed with a Teflon-lined screw cap then removed from the glovebox. The mixture was allowed to stir at 30°C for 12 h then was quenched upon addition of 2M HCl (4 mL). The mixture was extracted with EtOAc (3x 4 mL) then dodecane (internal standard) was added. The crude mixture was analyzed by GC and H NMR to reveal a 40% yield of **28** and <2% of **3**.

^{1}H NMR (600 MHz, $CDCl_3$)





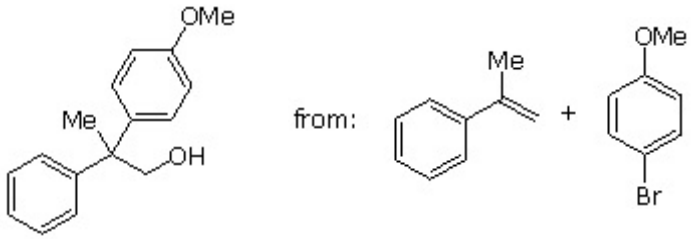
^{13}C NMR (125 MHz, $CDCl_3$)

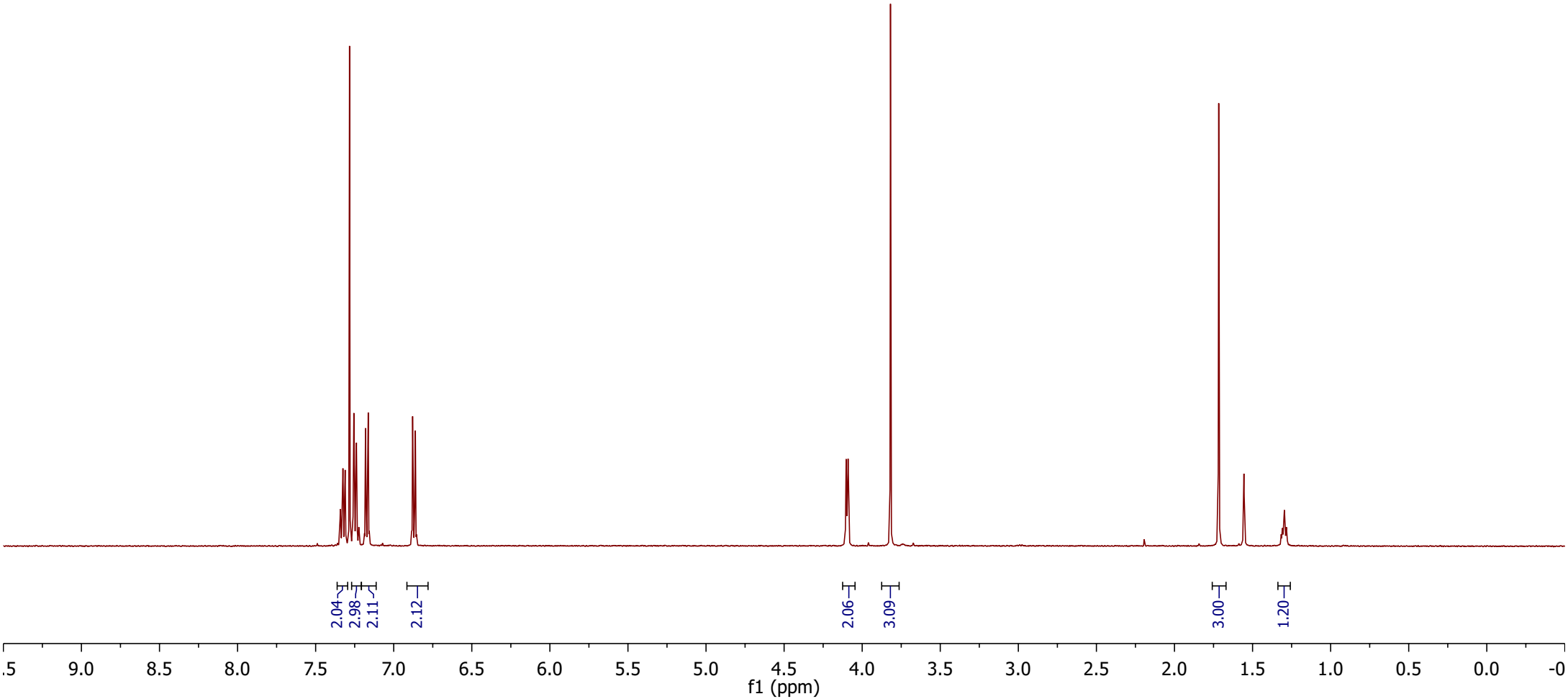


146.55
128.33
127.64
126.32
70.84
48.77
25.56

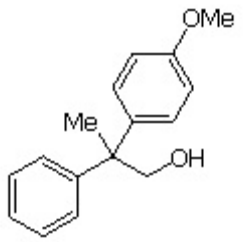
f1 (ppm)

^{1}H NMR (600 MHz, $CDCl_3$)





^{13}C NMR (125 MHz, $CDCl_3$)



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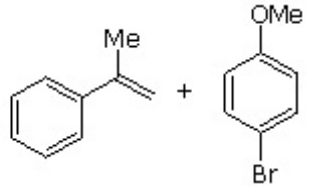
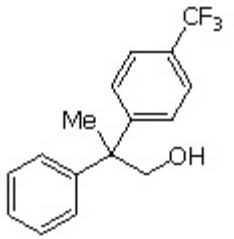
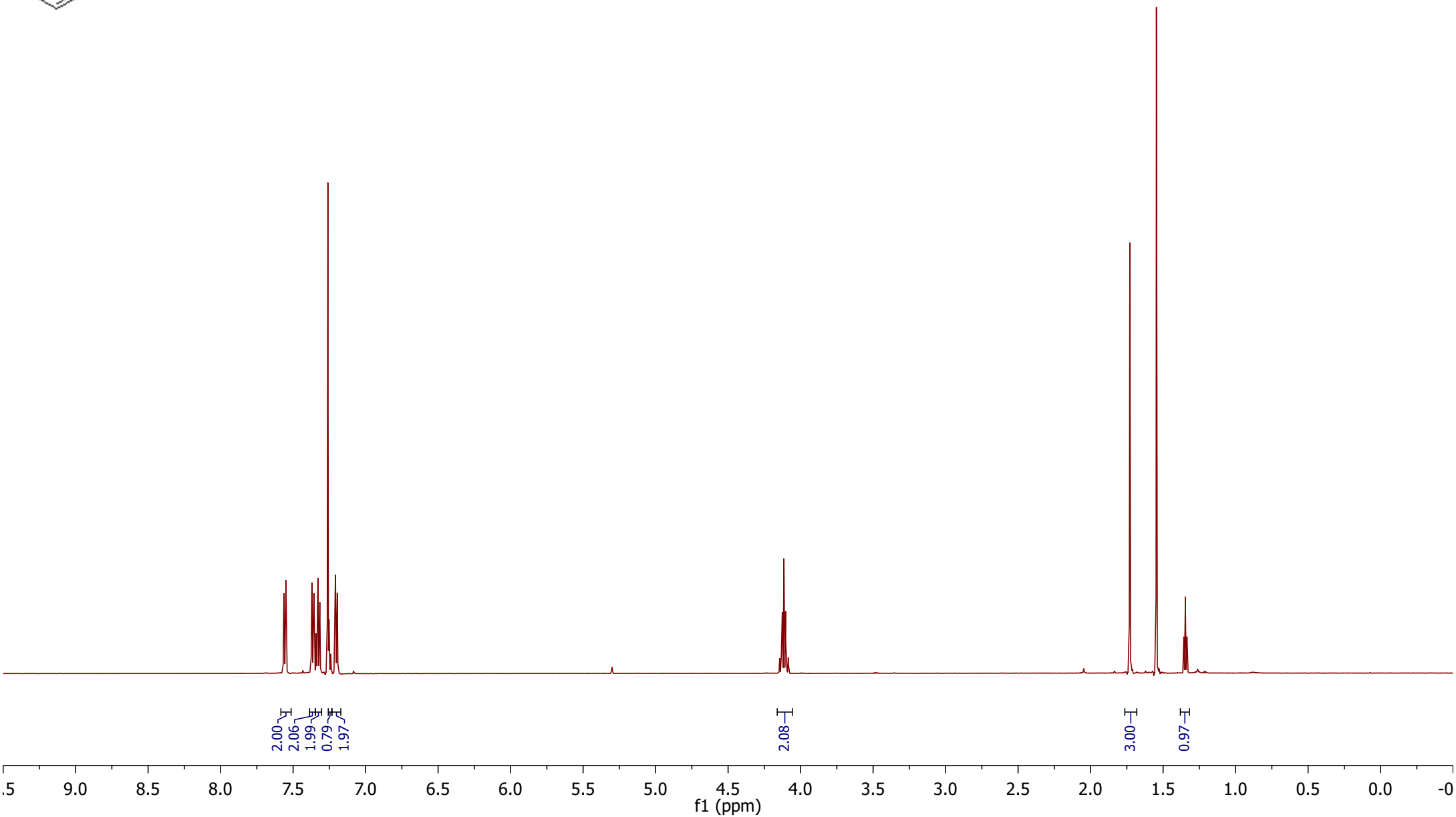


+

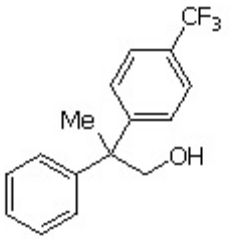
157.94
146.83
138.45
128.70
128.30
127.54
126.25
113.67
70.94
55.23
48.12
25.71

^{1}H NMR (600 MHz, $CDCl_3$)





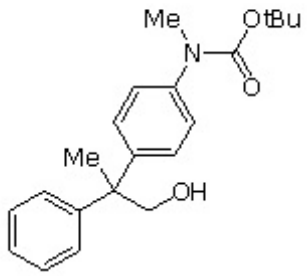
^{13}C NMR (500 MHz, $CDCl_3$)



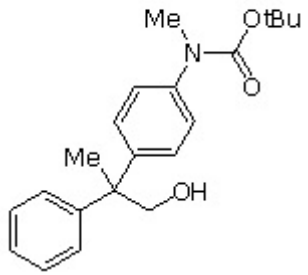
151.06
145.64
128.92
128.66
128.53
128.40
128.14
128.09
127.60
127.47
126.69
125.30
125.20
125.17
125.14
125.11
123.14
120.98
70.52
48.92
25.43
25.32

f1 (ppm)

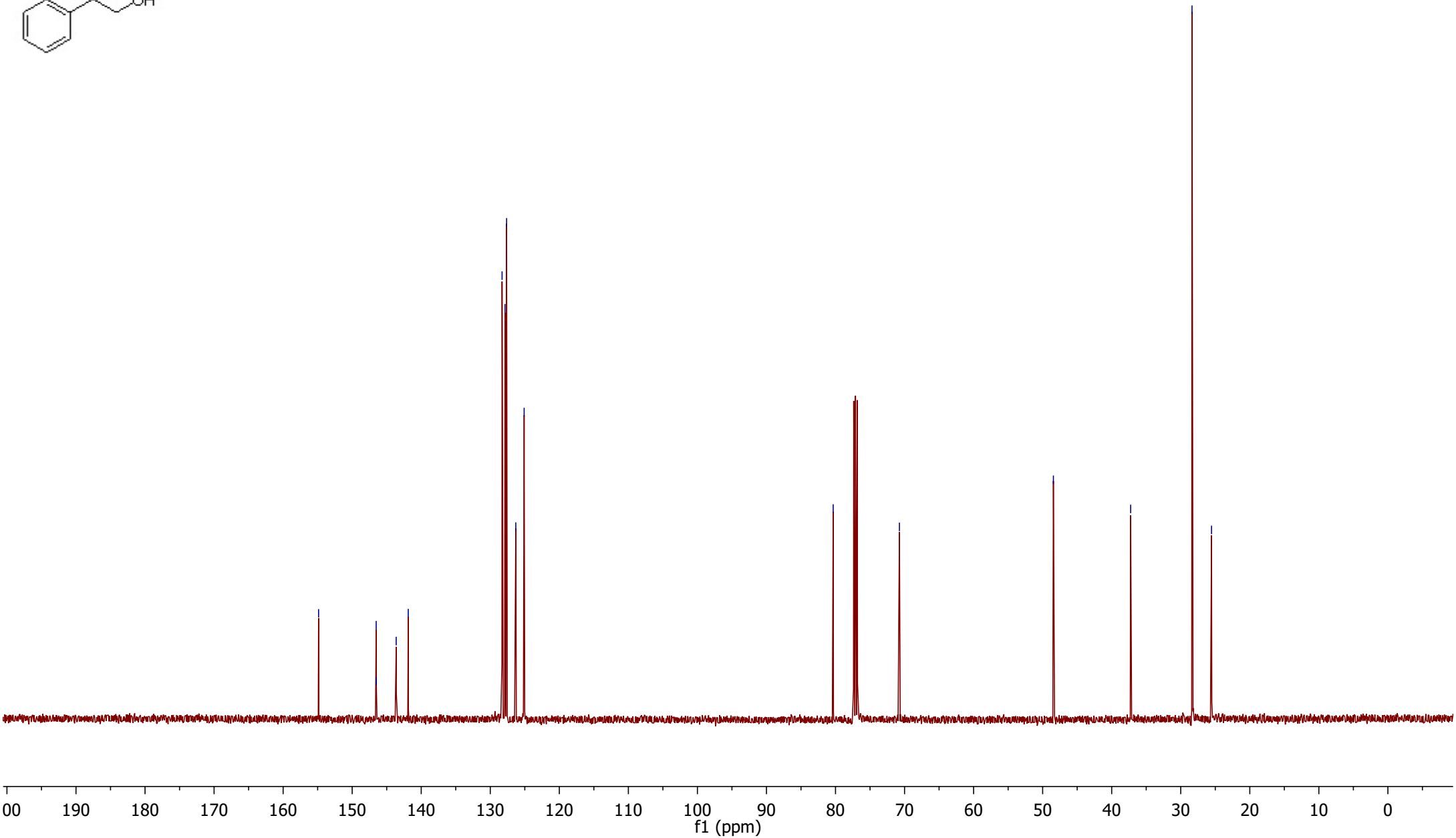
^{1}H NMR (600 MHz, $CDCl_3$)



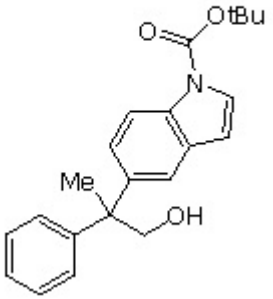
^{13}C NMR (125 MHz, $CDCl_3$)

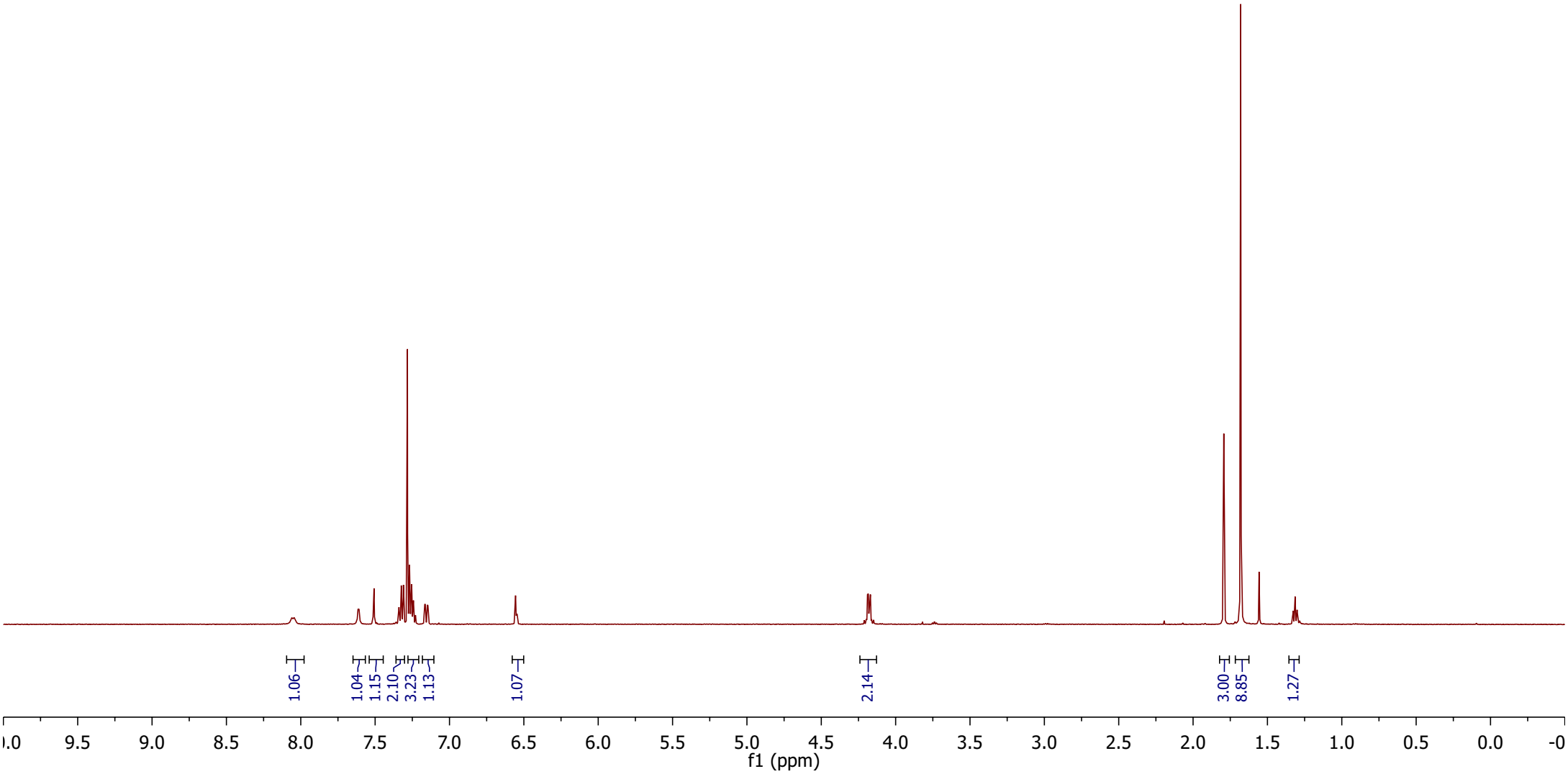


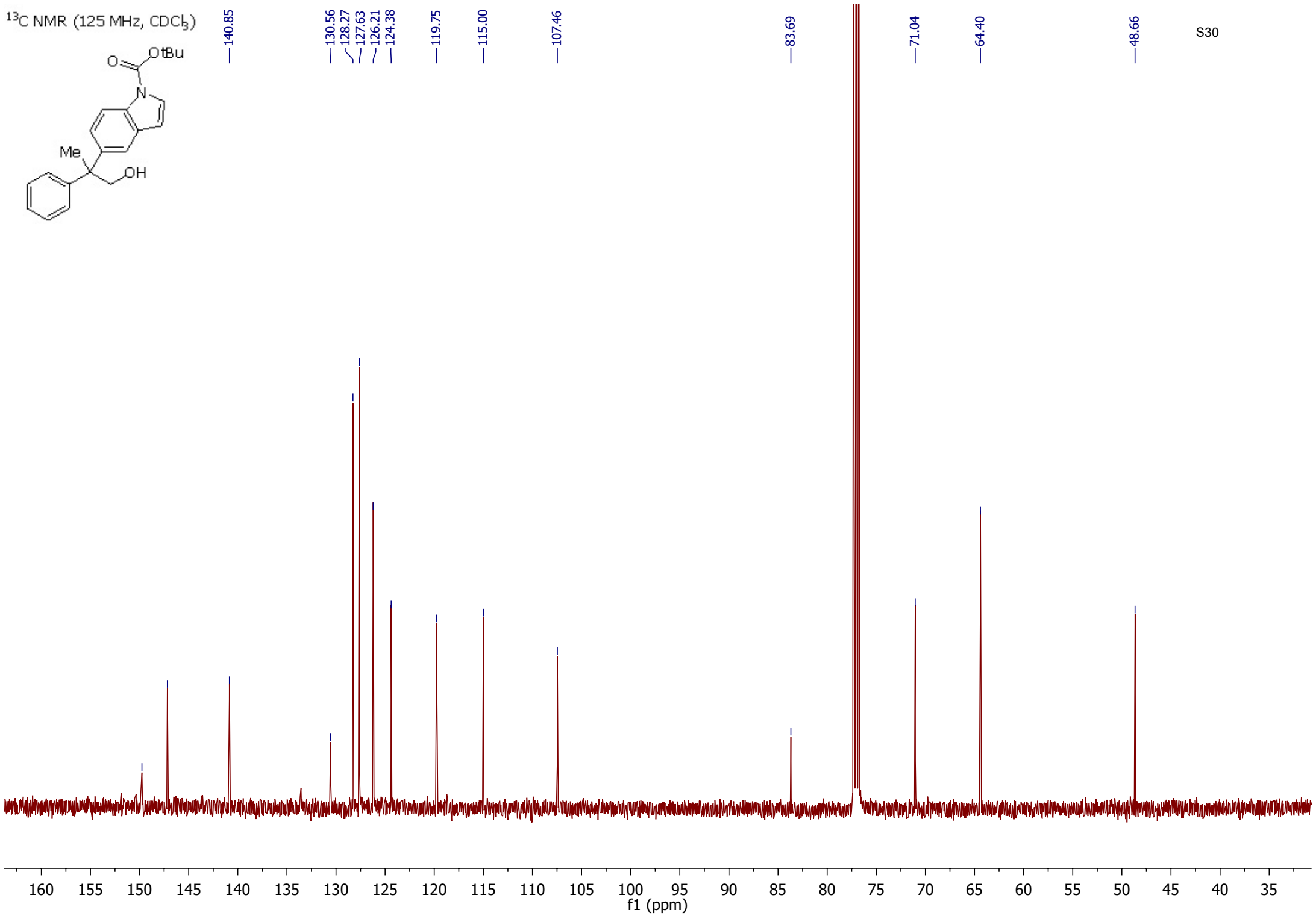
154.86
146.52
146.50
143.63
141.88
128.29
127.87
127.63
126.30
125.09
80.34
70.74
48.44
37.25
28.37
25.54



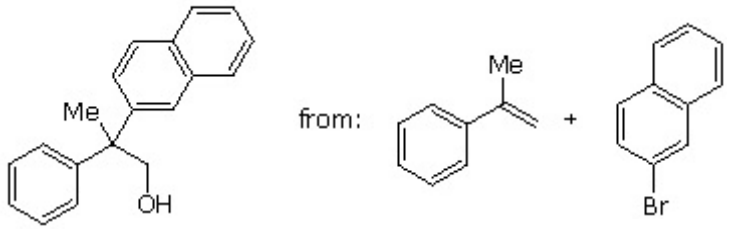
^{1}H NMR (500 MHz, $CDCl_3$)

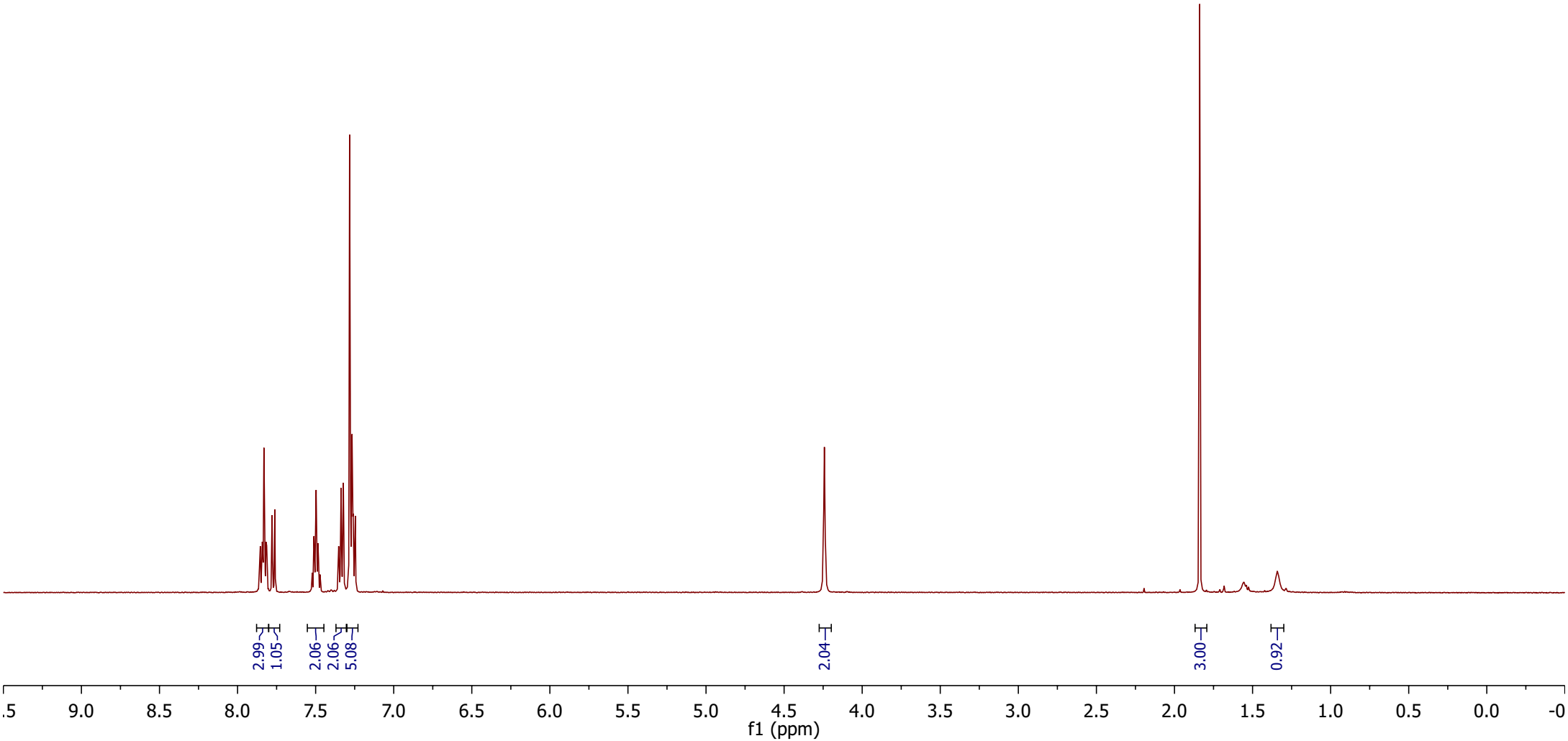




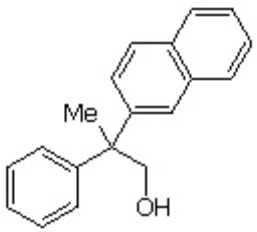

^{13}C NMR (125 MHz, CDCl$_3$)
O
OtBu
N
Me
OH
140.85
130.56
128.27
127.63
126.21
124.38
119.75
115.00
107.46
83.69
71.04
64.40
48.66
S30
160 155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35
f1 (ppm)

^{1}H NMR (500 MHz, $CDCl_3$)

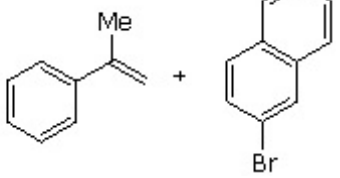




^{13}C NMR (125 MHz, $CDCl_3$)



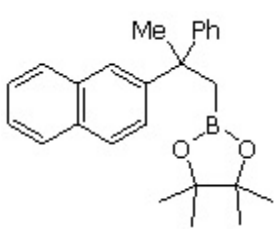
from:



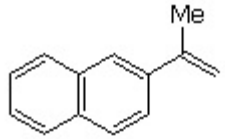
+

146.41
143.82
133.20
132.02
128.40
128.05
128.00
127.70
127.45
126.63
126.43
126.11
125.84
125.64
70.74
48.93
25.52

^{1}H NMR (400 MHz, $CDCl_3$)



from:



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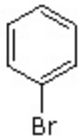
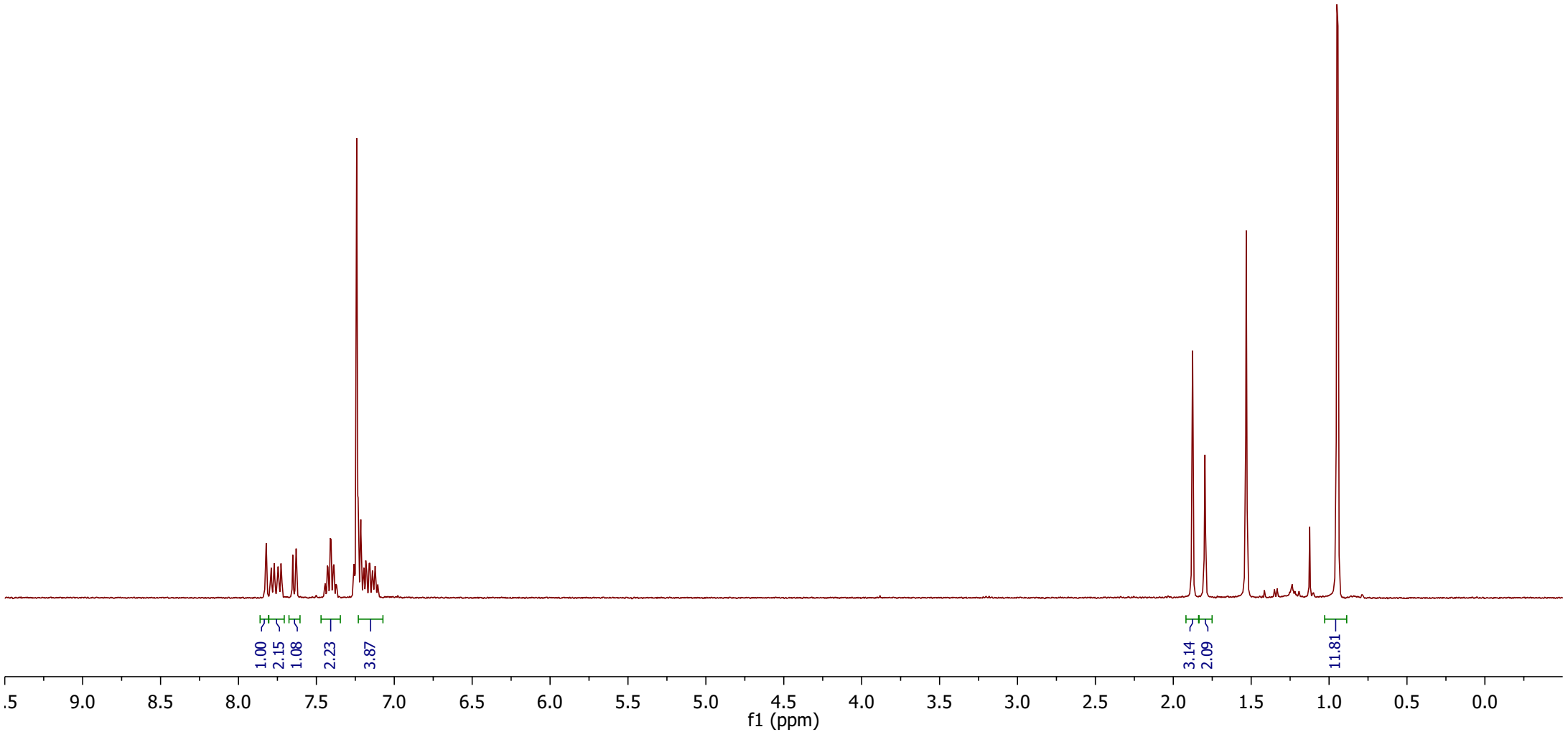
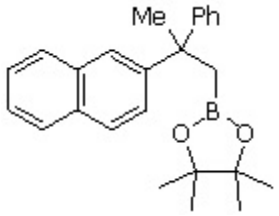




^{13}C NMR (125 MHz, $CDCl_3$)



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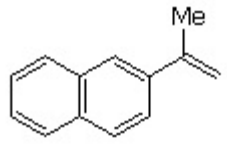

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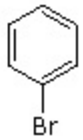
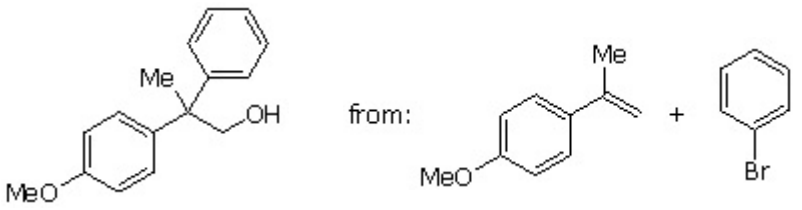
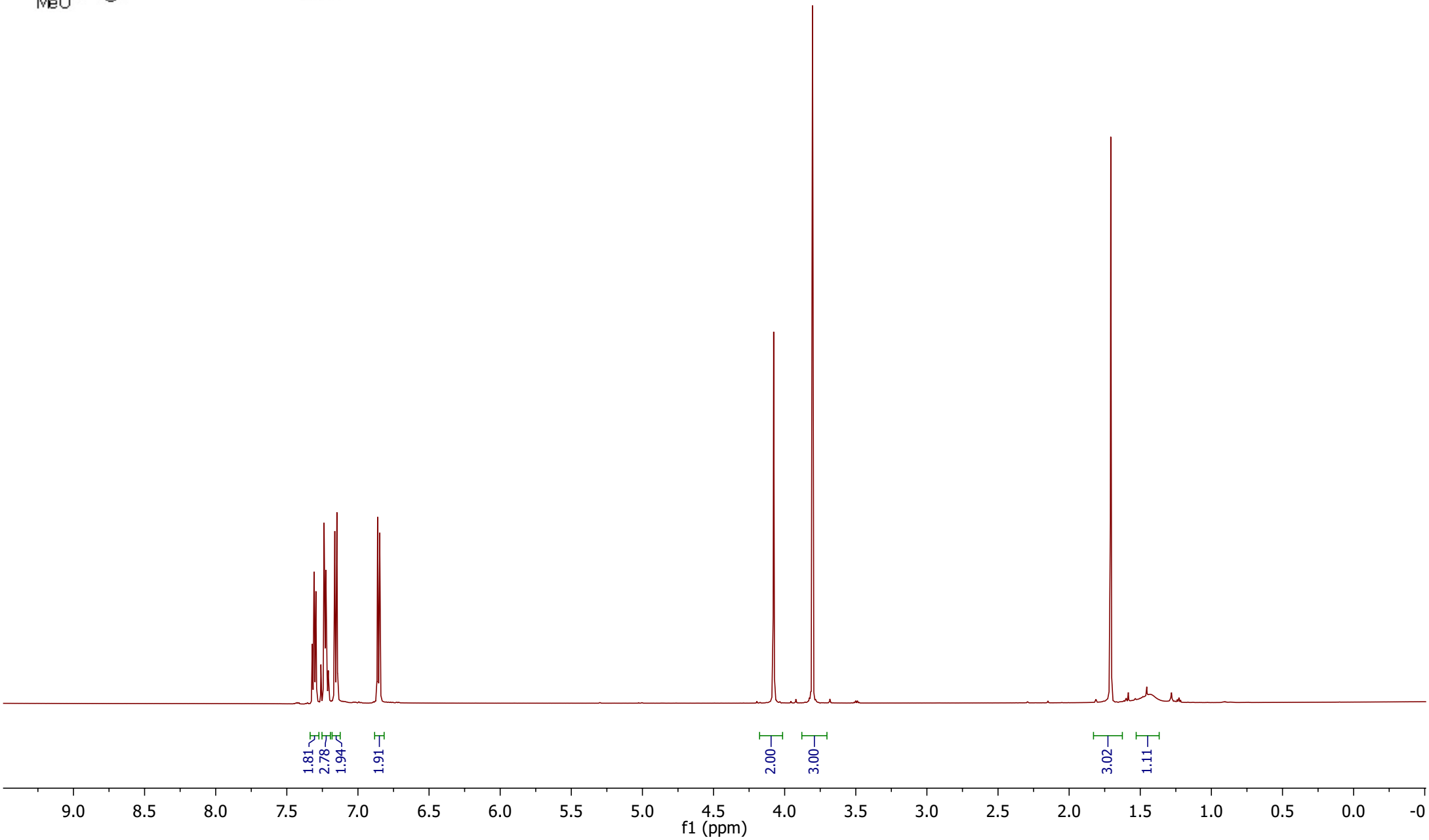


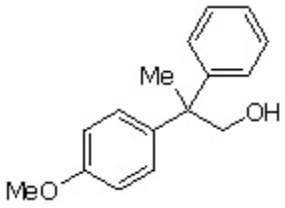
150.96
148.54
133.14
131.70
127.98
127.85
127.41
127.35
127.16
127.05
125.72
125.52
125.28
124.17
82.79
44.64
29.77
24.63
24.60

^{1}H NMR (400 MHz, $CDCl_3$)

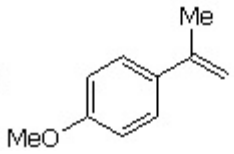




^{13}C NMR (125 MHz, $CDCl_3$)



from:



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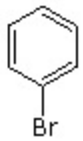
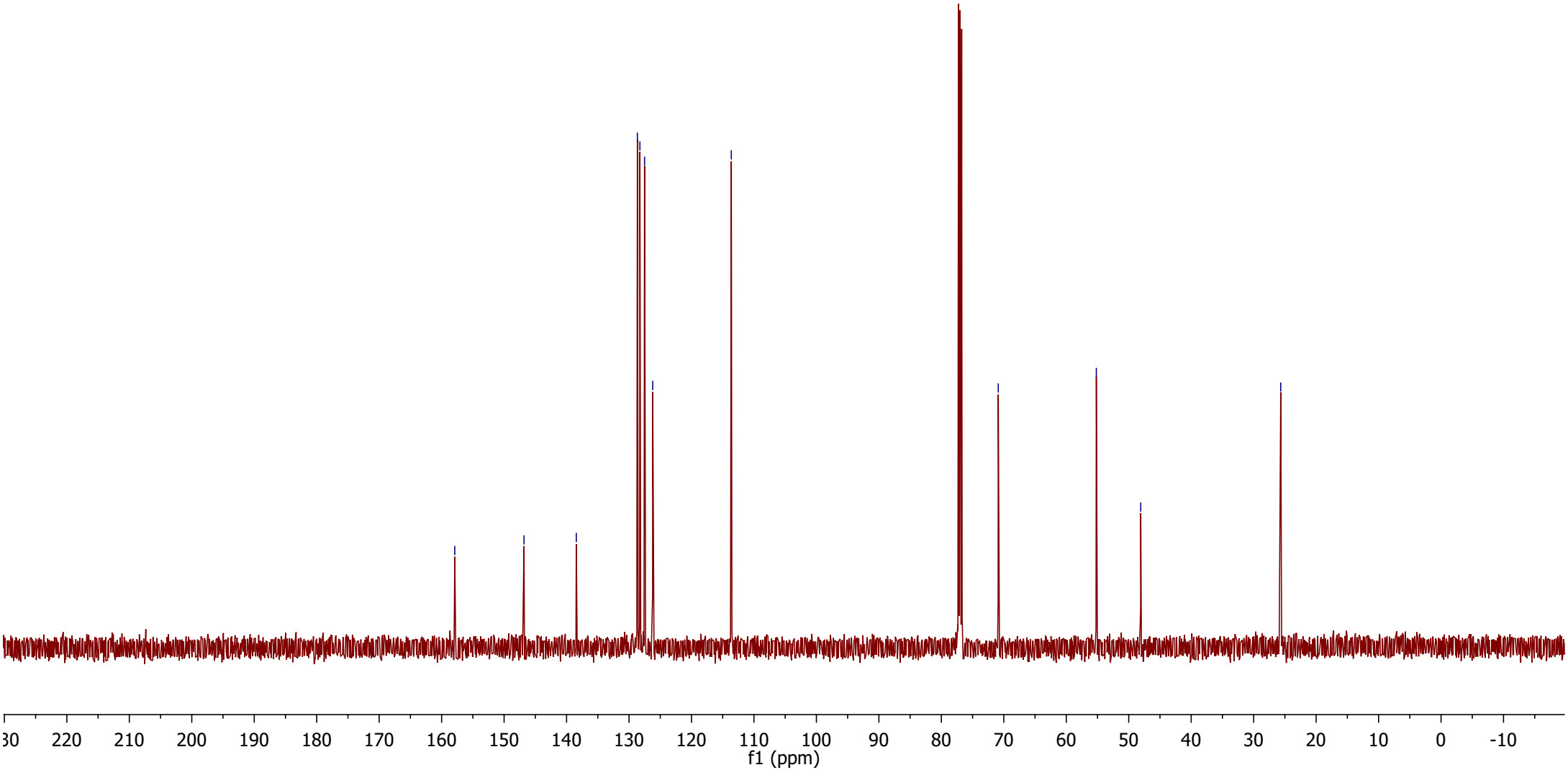
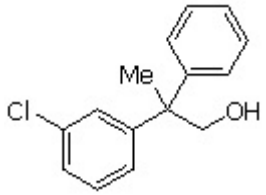
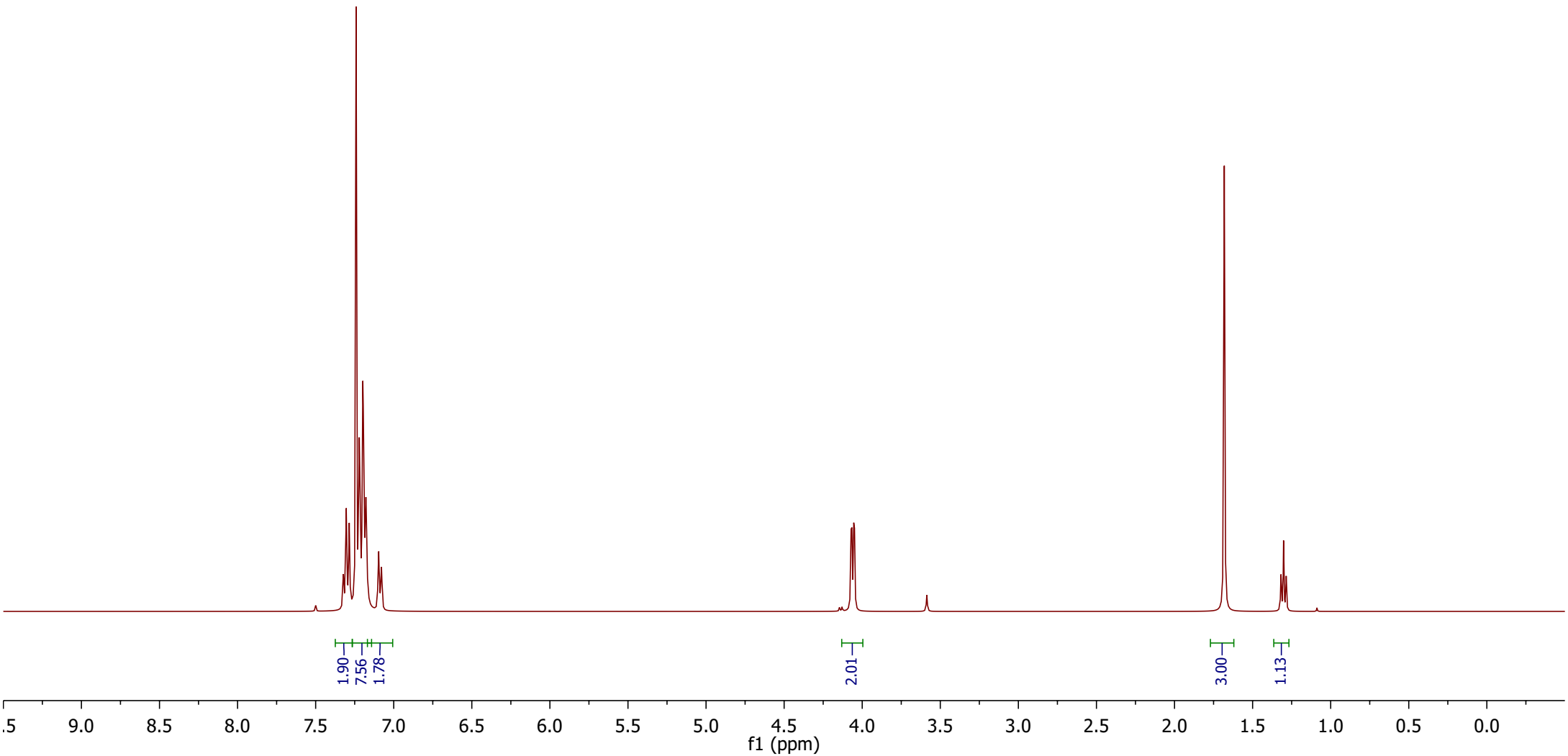


157.90
146.81
138.44
128.66
128.26
127.51
126.21
113.63
70.89
55.19
48.08
25.66

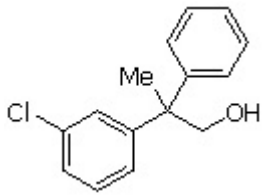


^{1}H NMR (400 MHz, $CDCl_3$)





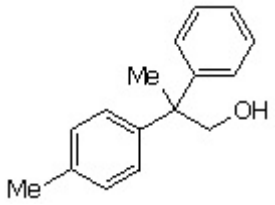
^{13}C NMR (125 MHz, $CDCl_3$)

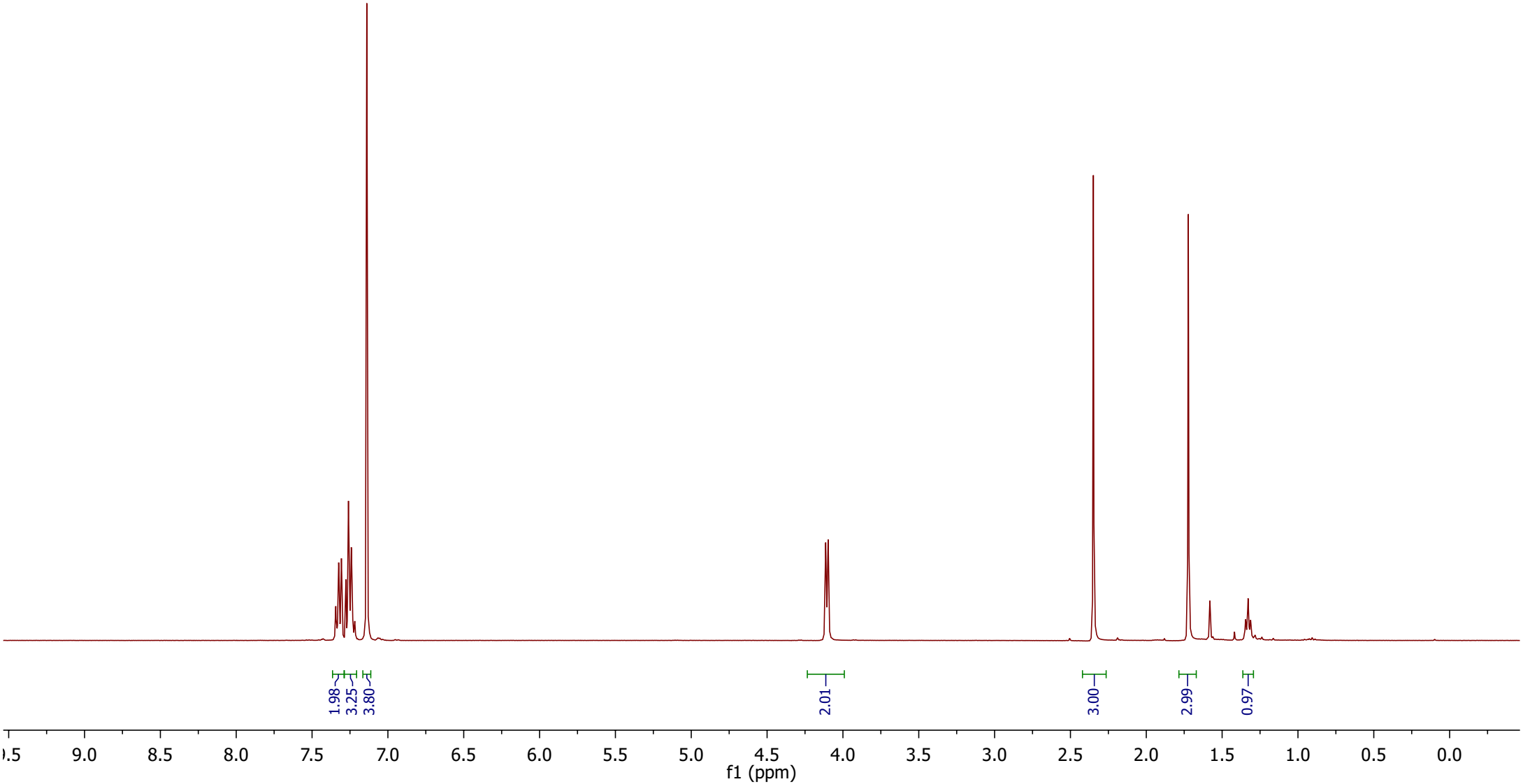


148.94
145.72
134.22
129.47
128.45
127.86
127.51
126.56
126.49
125.95
70.56
48.75
25.42

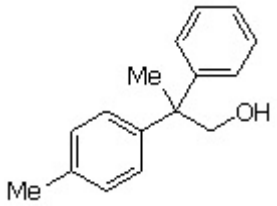
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

^{1}H NMR (400 MHz, $CDCl_3$)

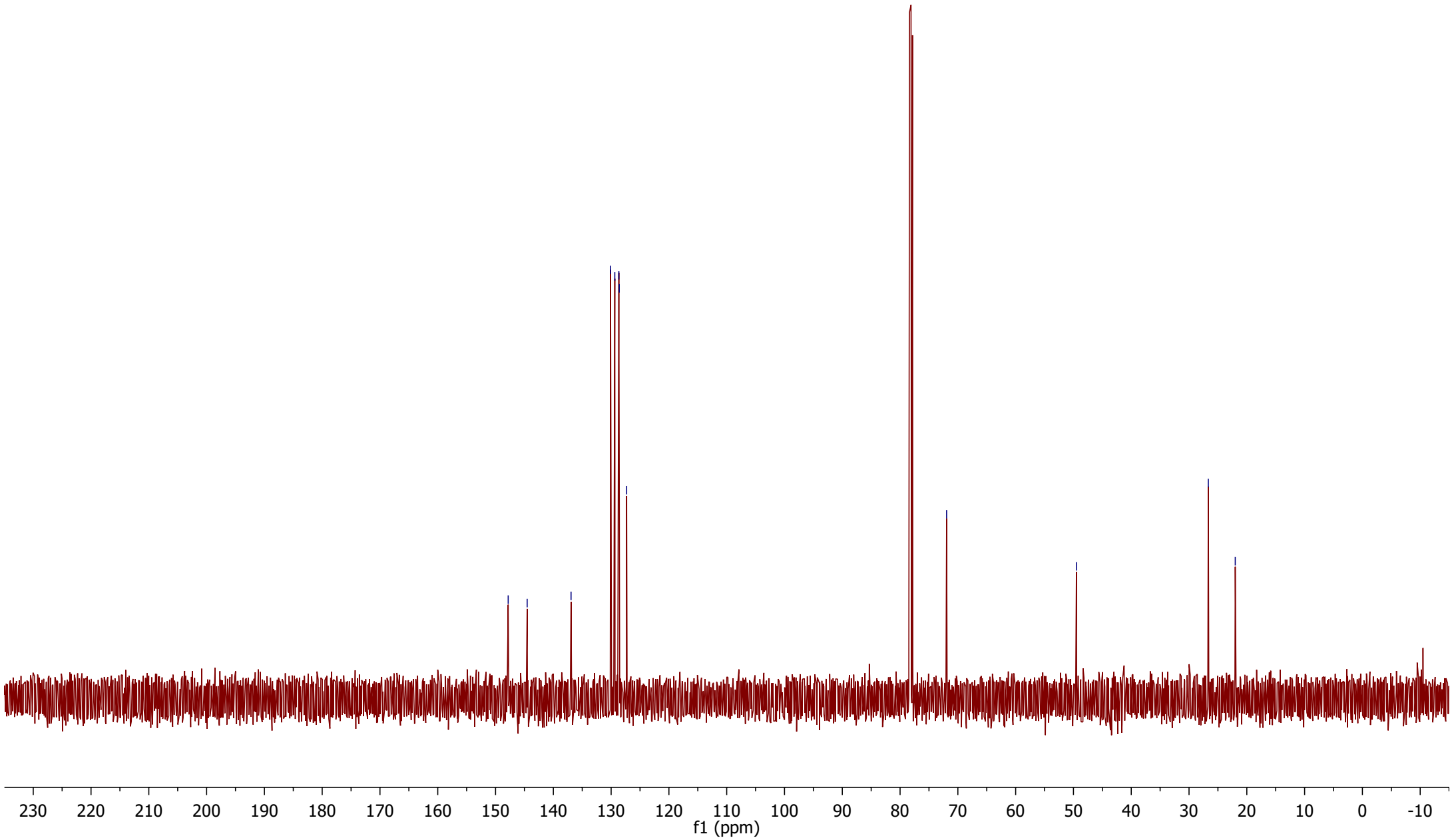




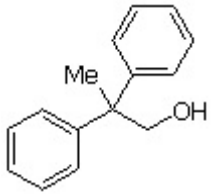
^{13}C NMR (125 MHz, $CDCl_3$)

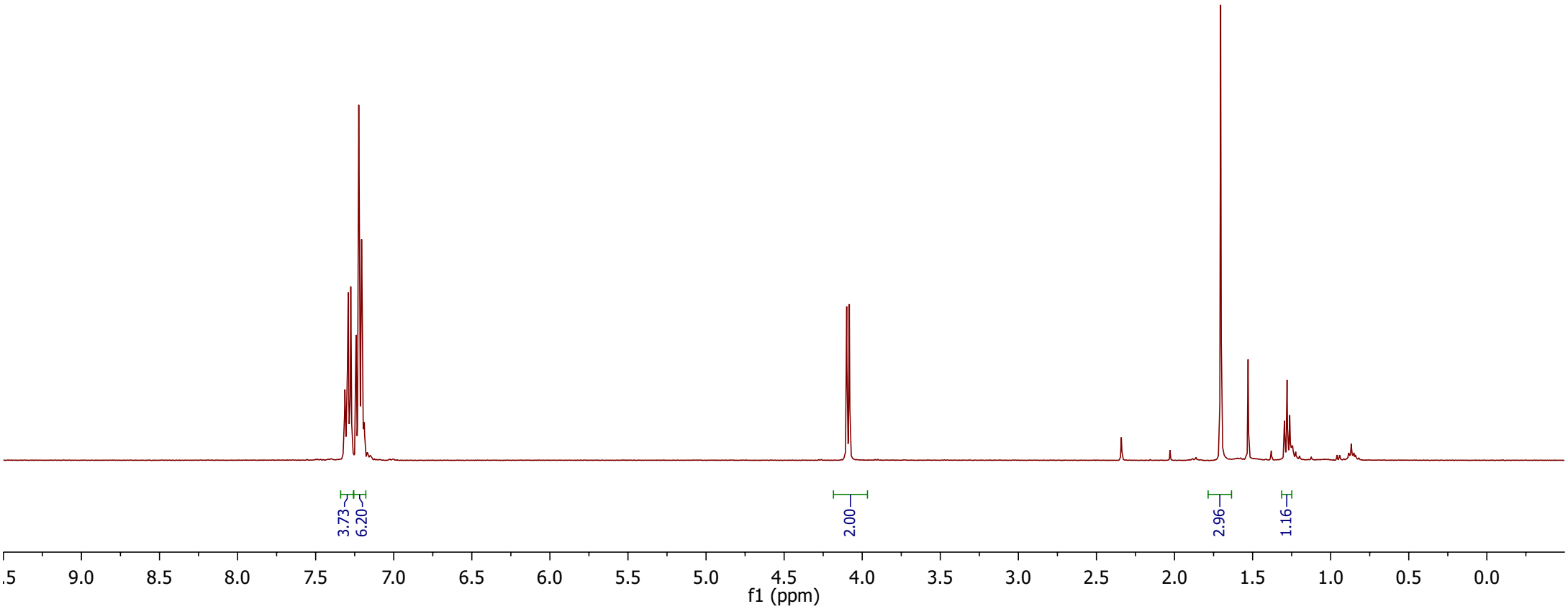


147.81
144.53
136.94
130.11
129.36
128.67
128.59
127.32
71.95
49.48
26.66
22.00

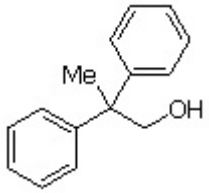


^{1}H NMR (400 MHz, $CDCl_3$)

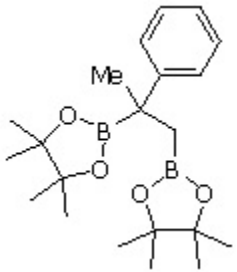


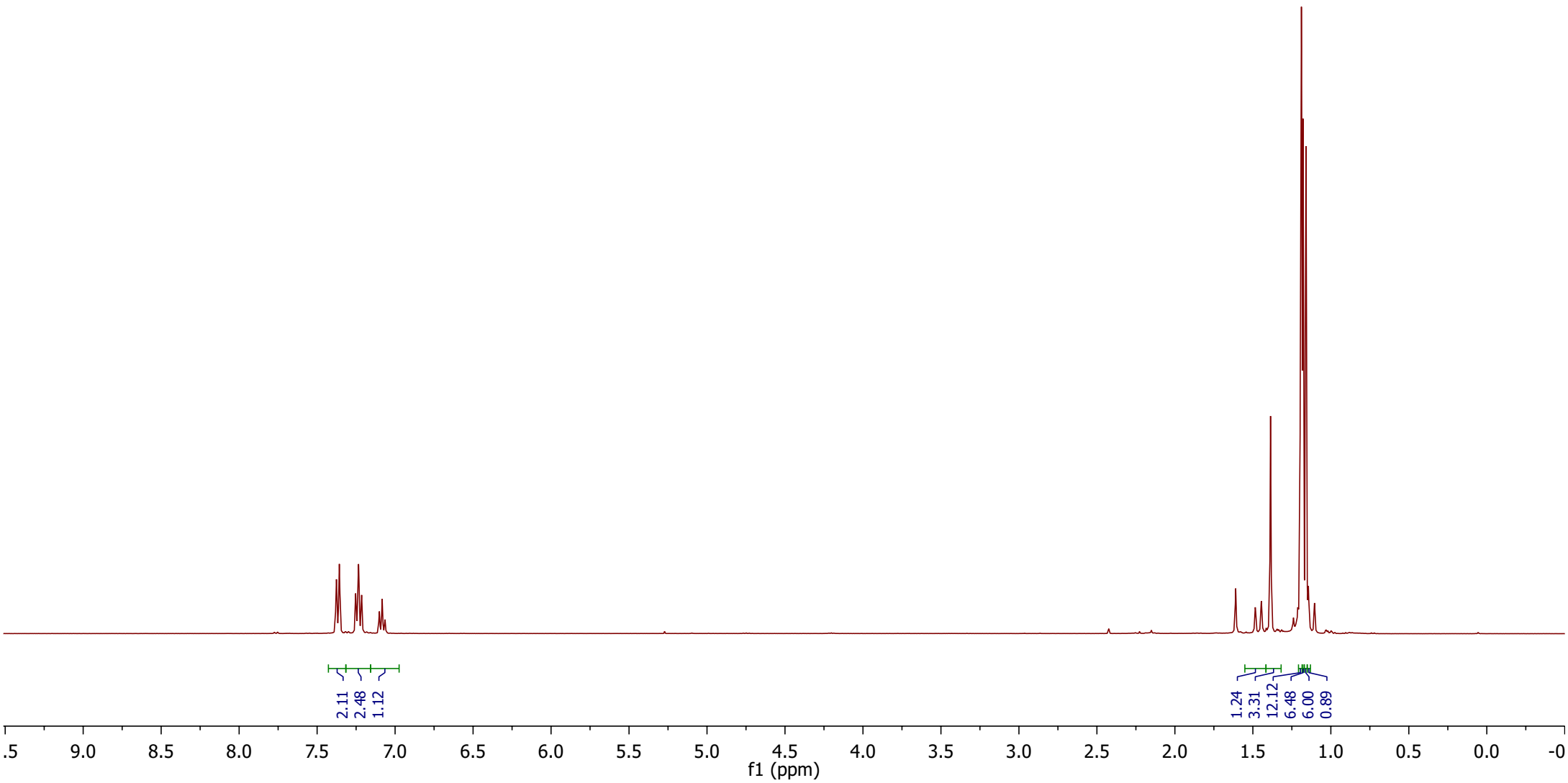


^{13}C NMR (125 MHz, $CDCl_3$)

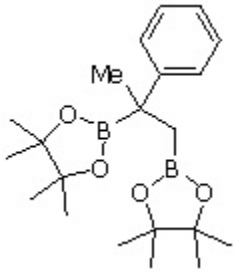


^{1}H NMR (400 MHz, $CDCl_3$)





^{13}C NMR (125 MHz, $CDCl_3$)

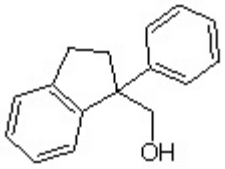


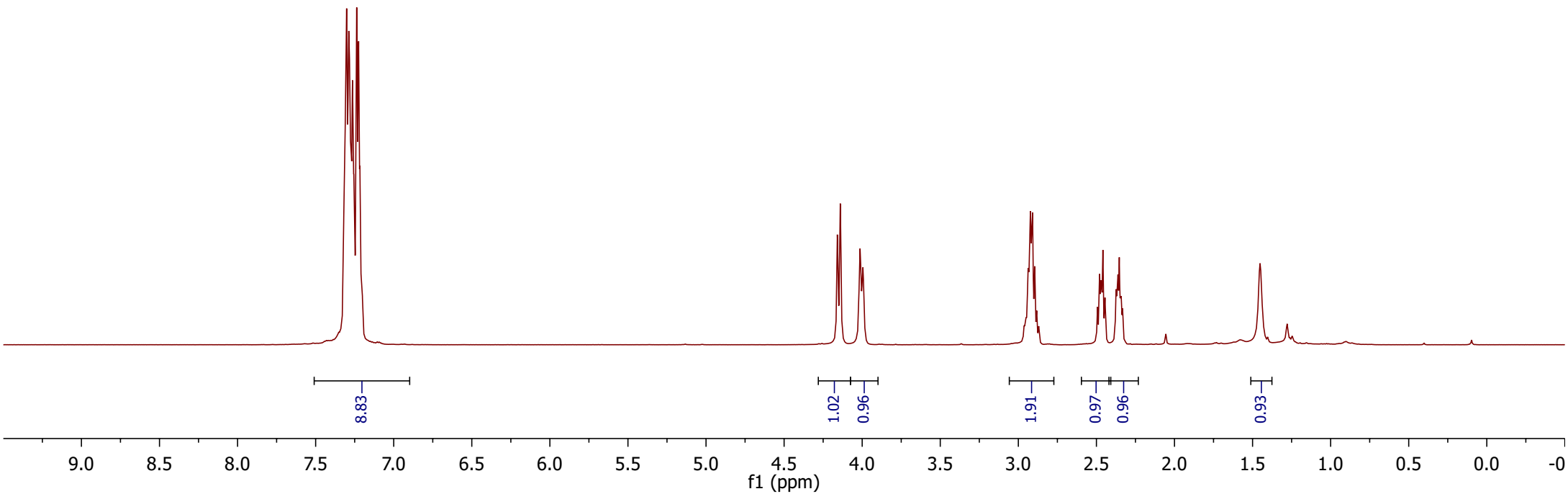
149.15
127.86
126.45
124.79
83.24
82.96
29.71
25.09
24.70
24.68
24.55
24.45

230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

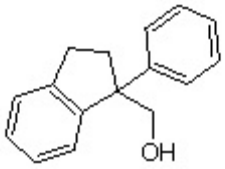
f1 (ppm)

^{1}H NMR (600 MHz, $CDCl_3$)

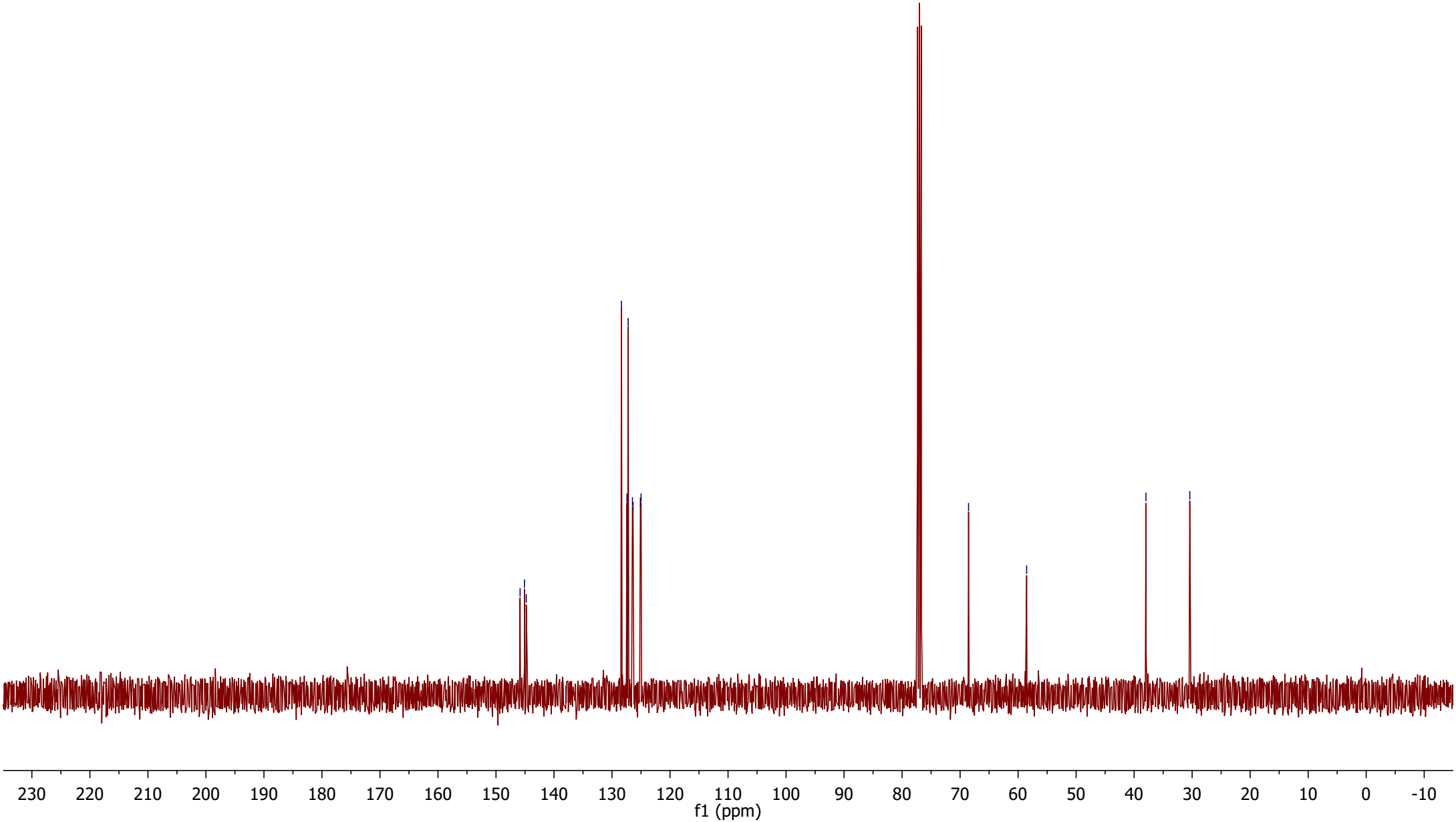




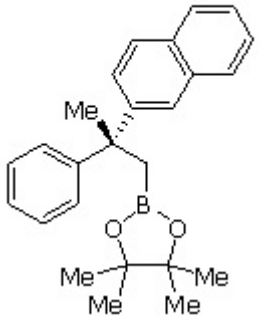
^{13}C NMR (100 MHz, $CDCl_3$)



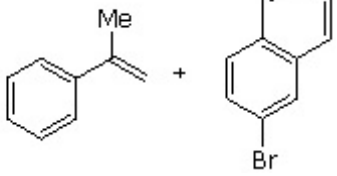
145.85
145.08
144.78
128.37
127.43
127.21
126.48
126.38
125.11
124.99
68.54
58.53
37.96
30.41



^{1}H NMR (400 MHz, $CDCl_3$)



from:



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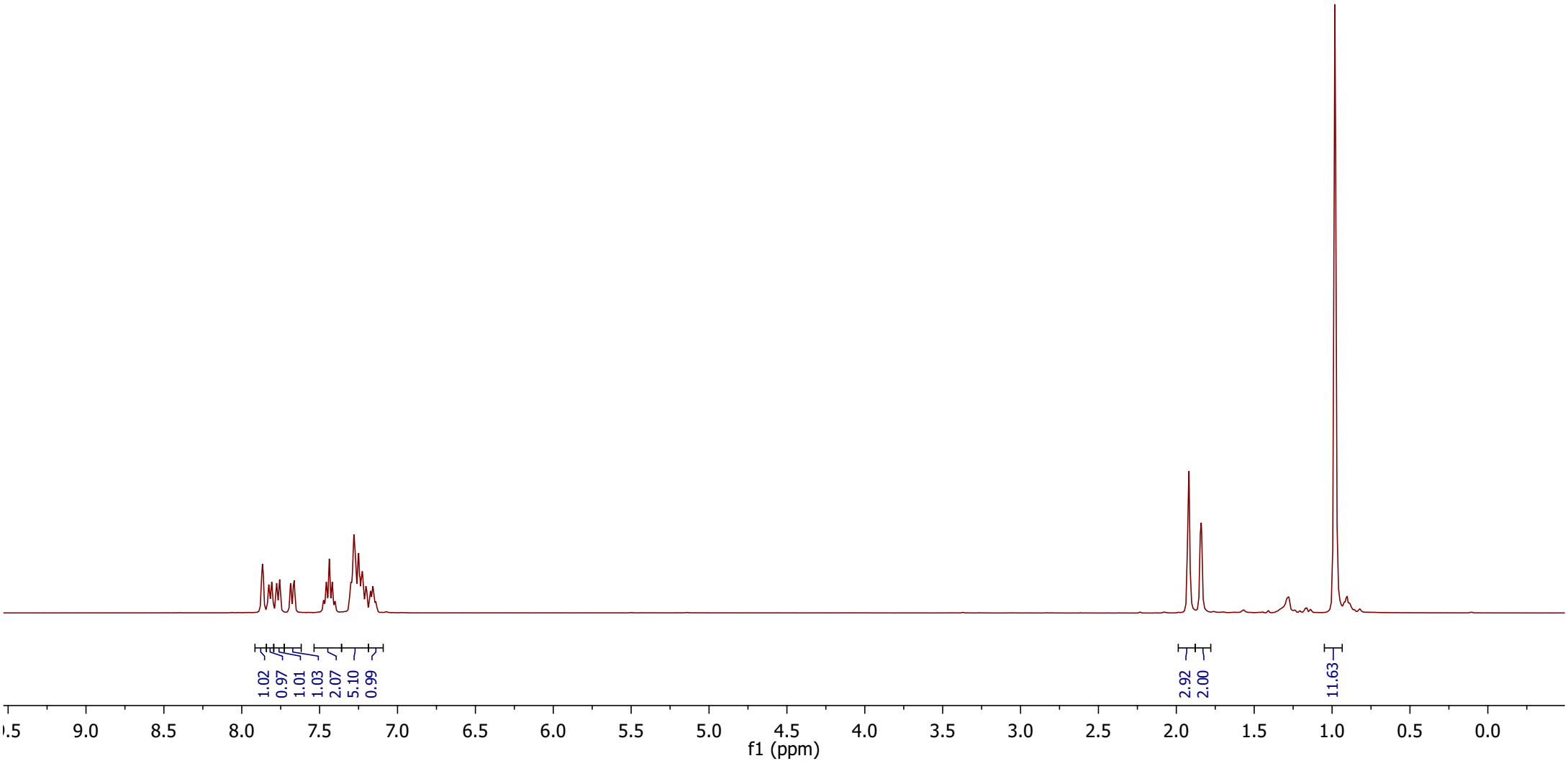
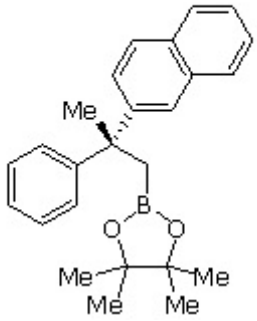
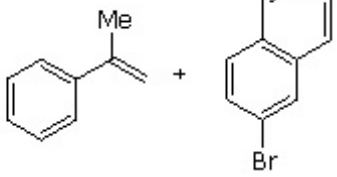


^{13}C NMR (125 MHz, $CDCl_3$)

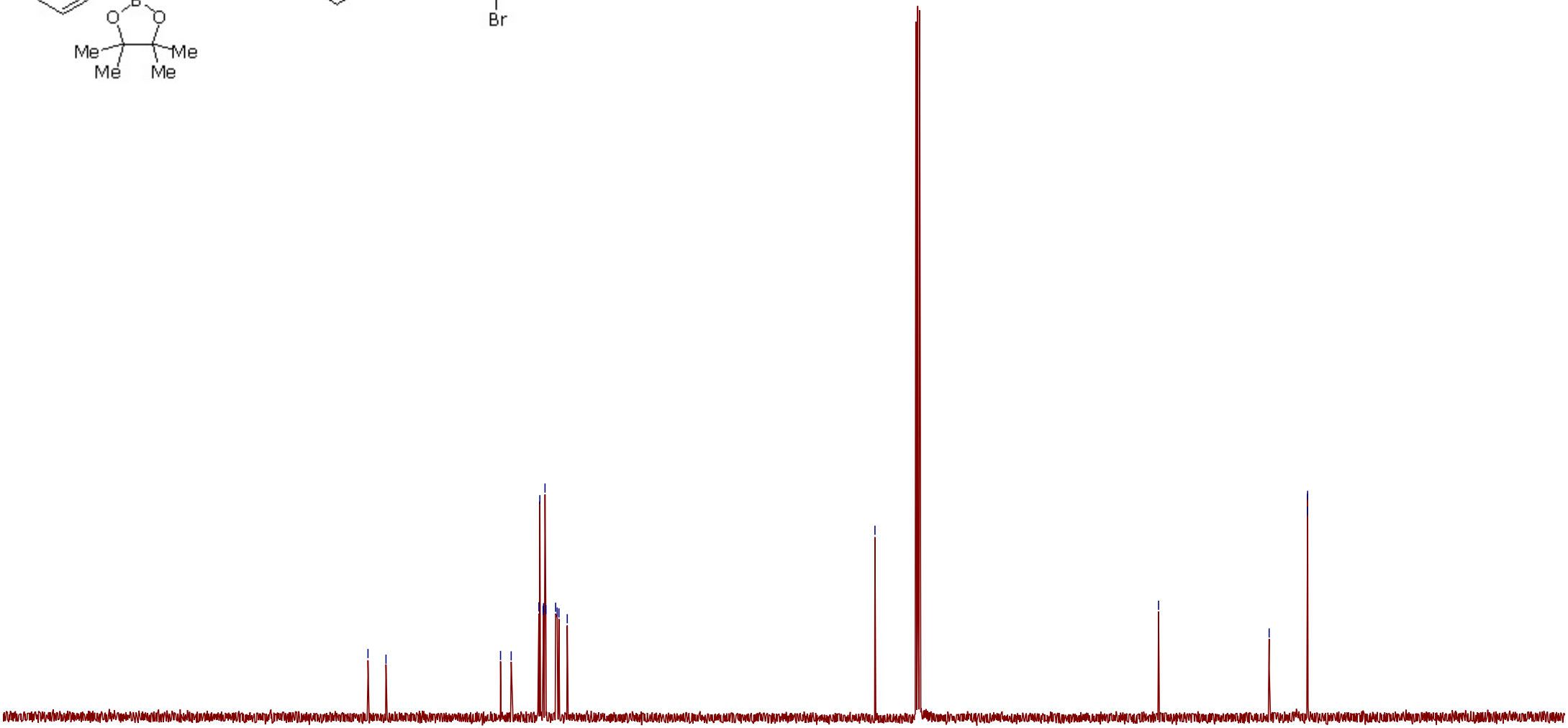


from:

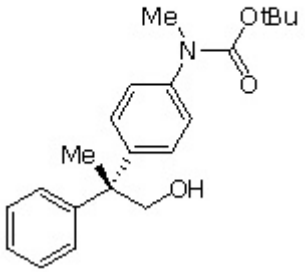


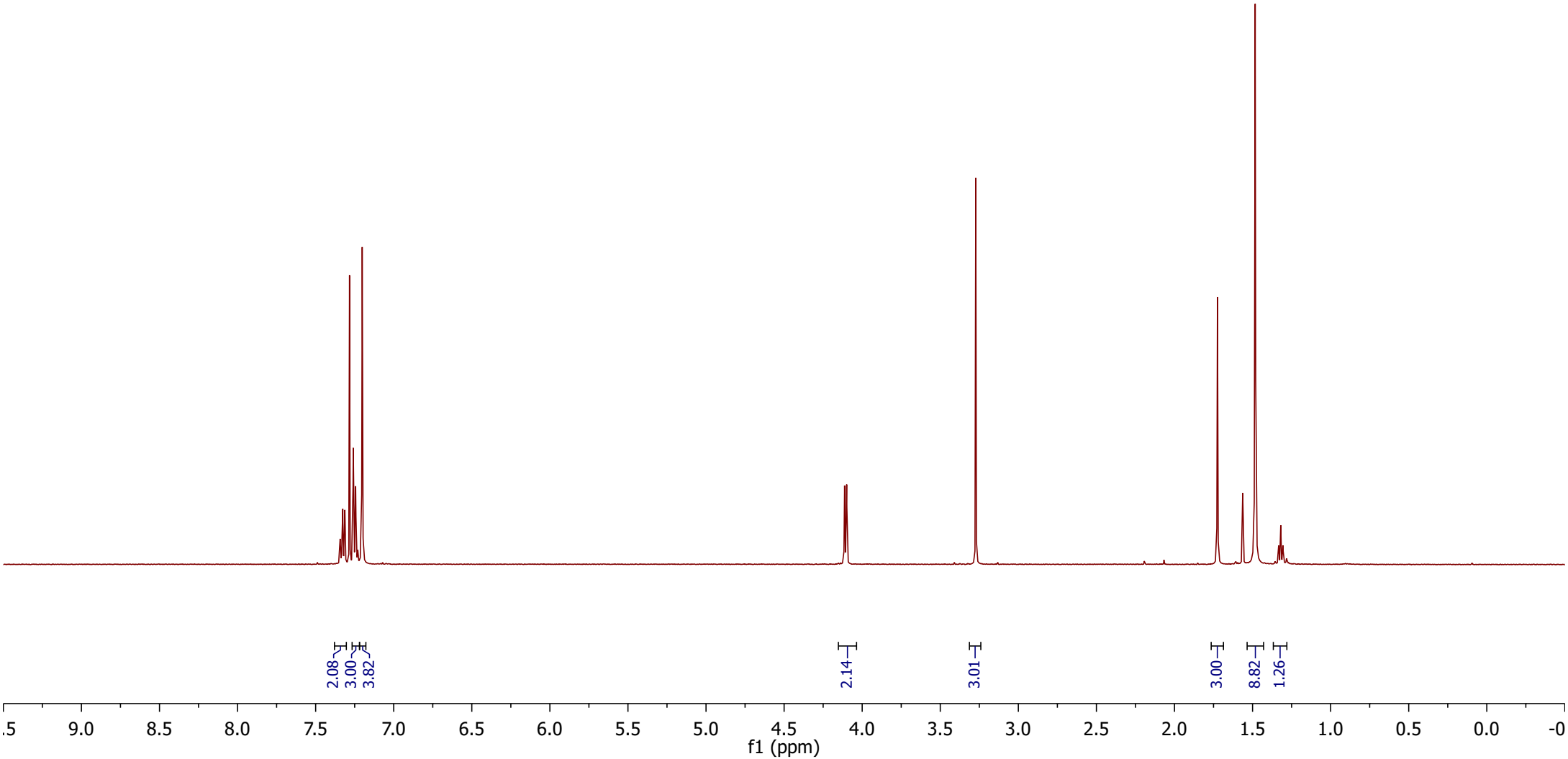
+

150.96
148.54
133.13
131.70
127.98
127.85
127.41
127.35
127.15
127.04
125.72
125.51
125.28
124.16
82.78
44.64
29.77
24.63
24.60

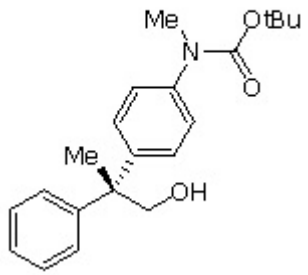


^{1}H NMR (500 MHz, $CDCl_3$)

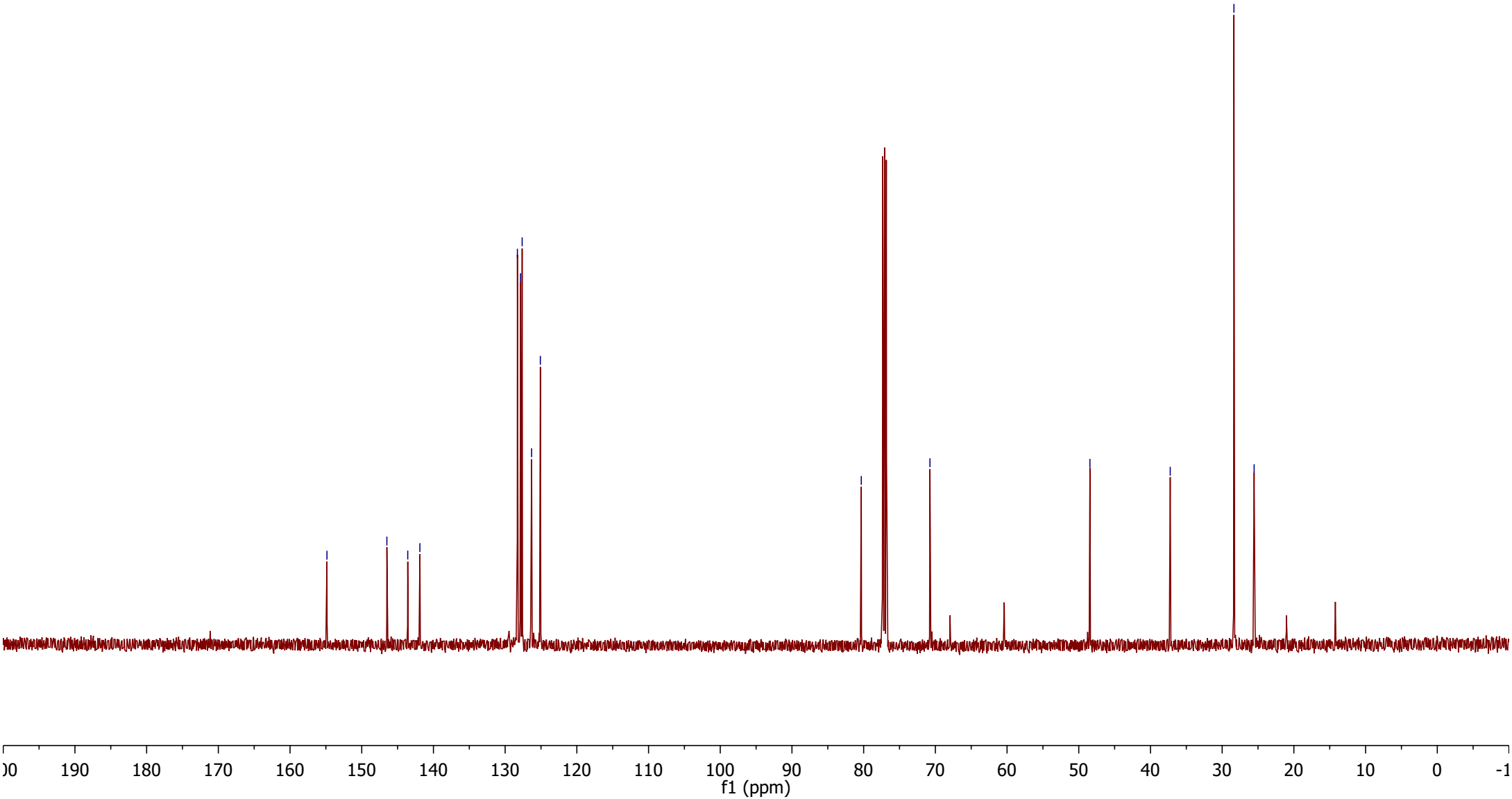




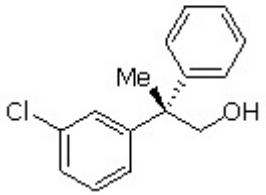
^{13}C NMR (125 MHz, $CDCl_3$)

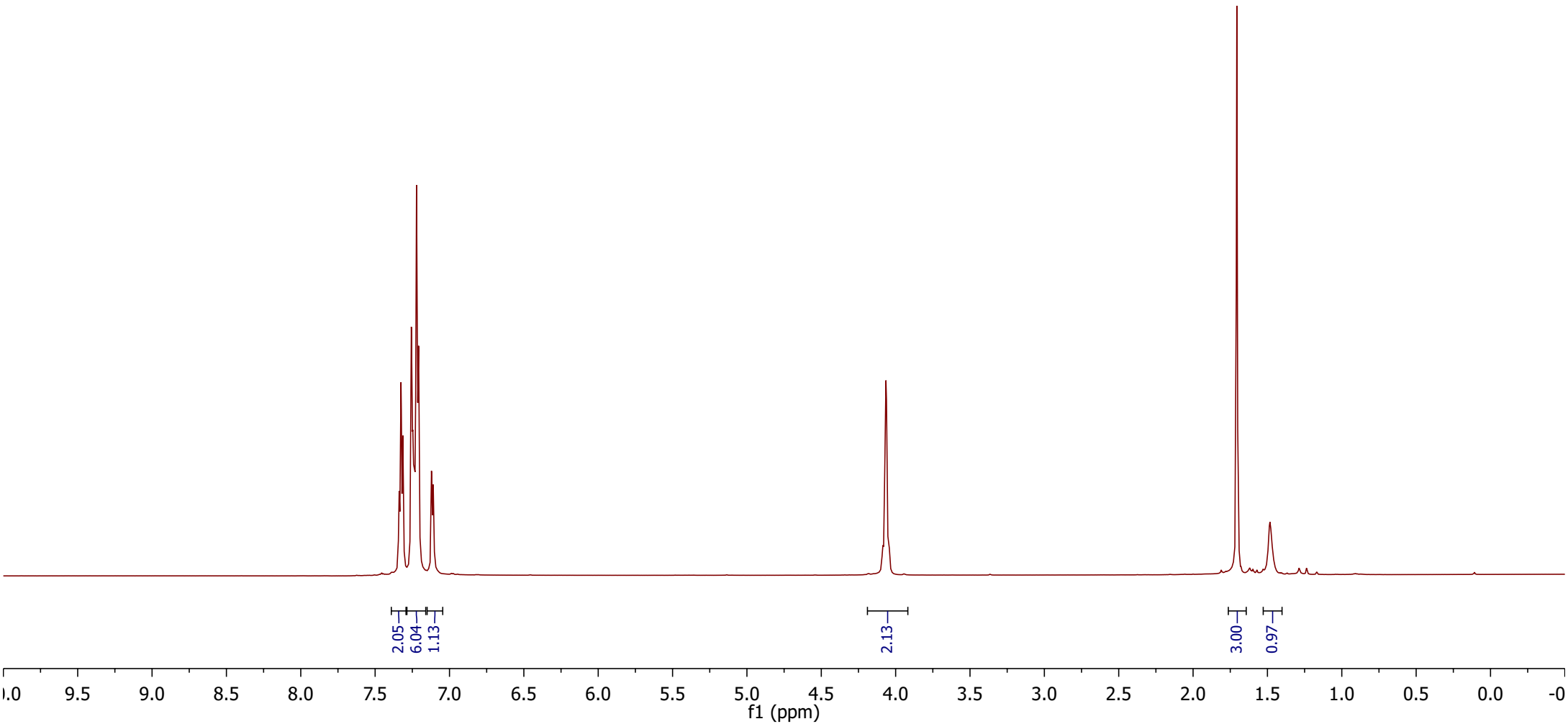


154.85
146.49
143.58
141.89
128.29
127.86
127.63
126.31
125.09
80.33
70.75
48.44
37.24
28.36
25.54

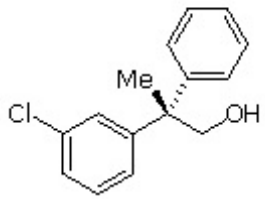


^{1}H NMR (600 MHz, $CDCl_3$)

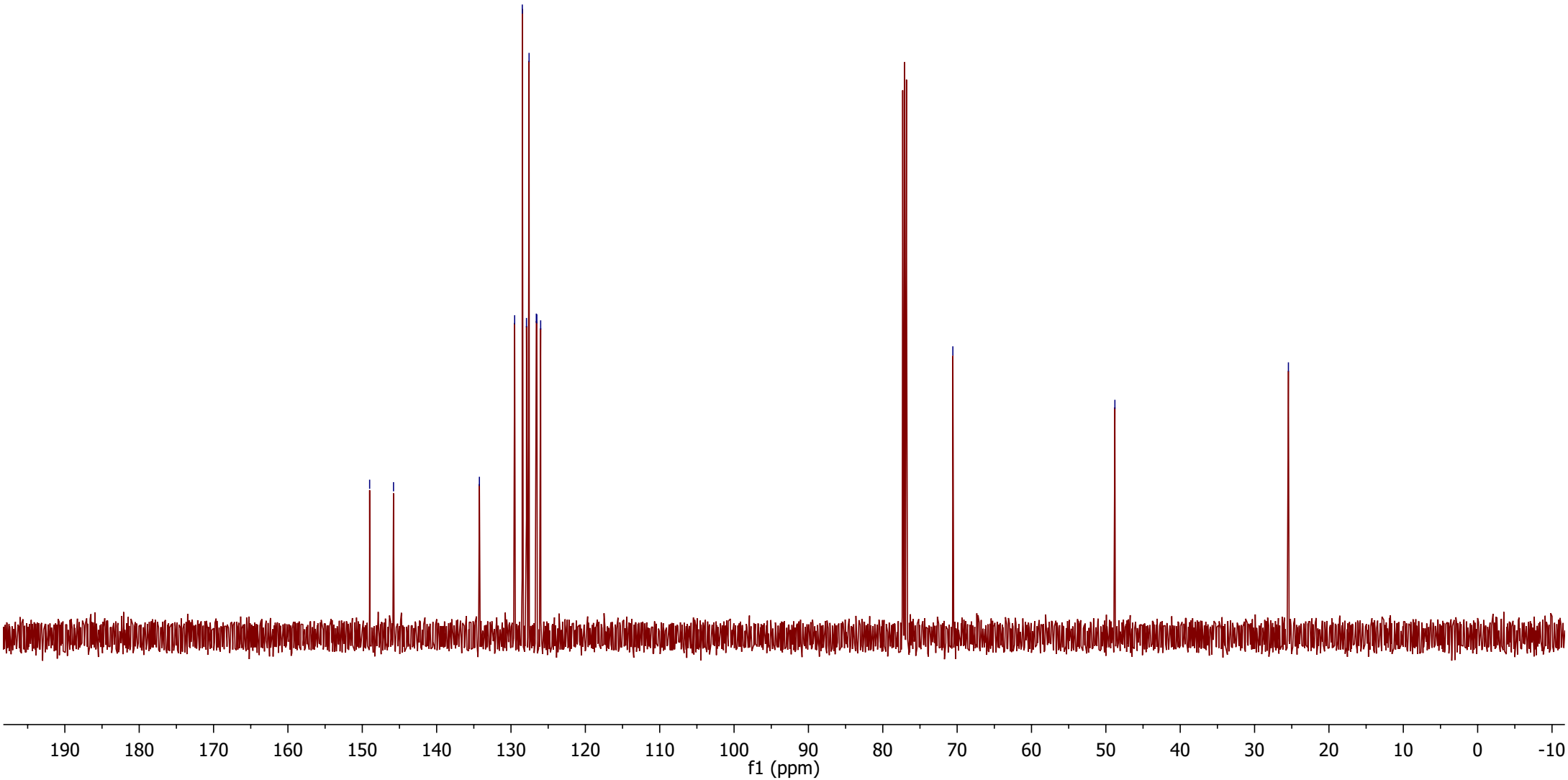




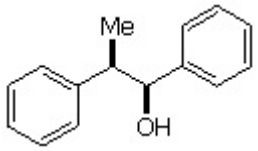
^{13}C NMR (500 MHz, $CDCl_3$)

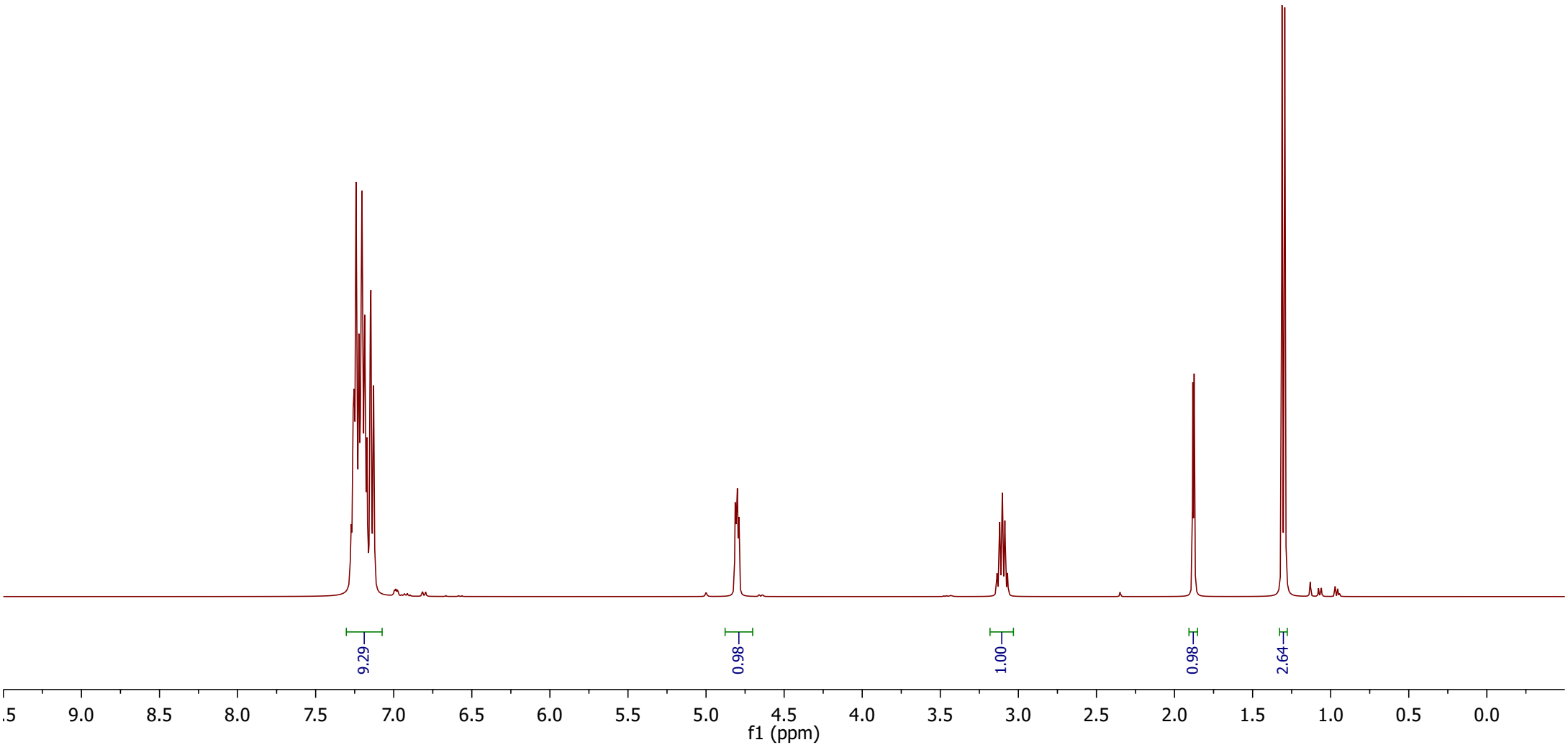


149.01
145.80
134.25
129.51
128.48
127.92
127.57
126.60
126.52
126.01
70.58
48.79
25.45

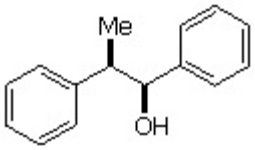


^{1}H NMR (400 MHz, $CDCl_3$)

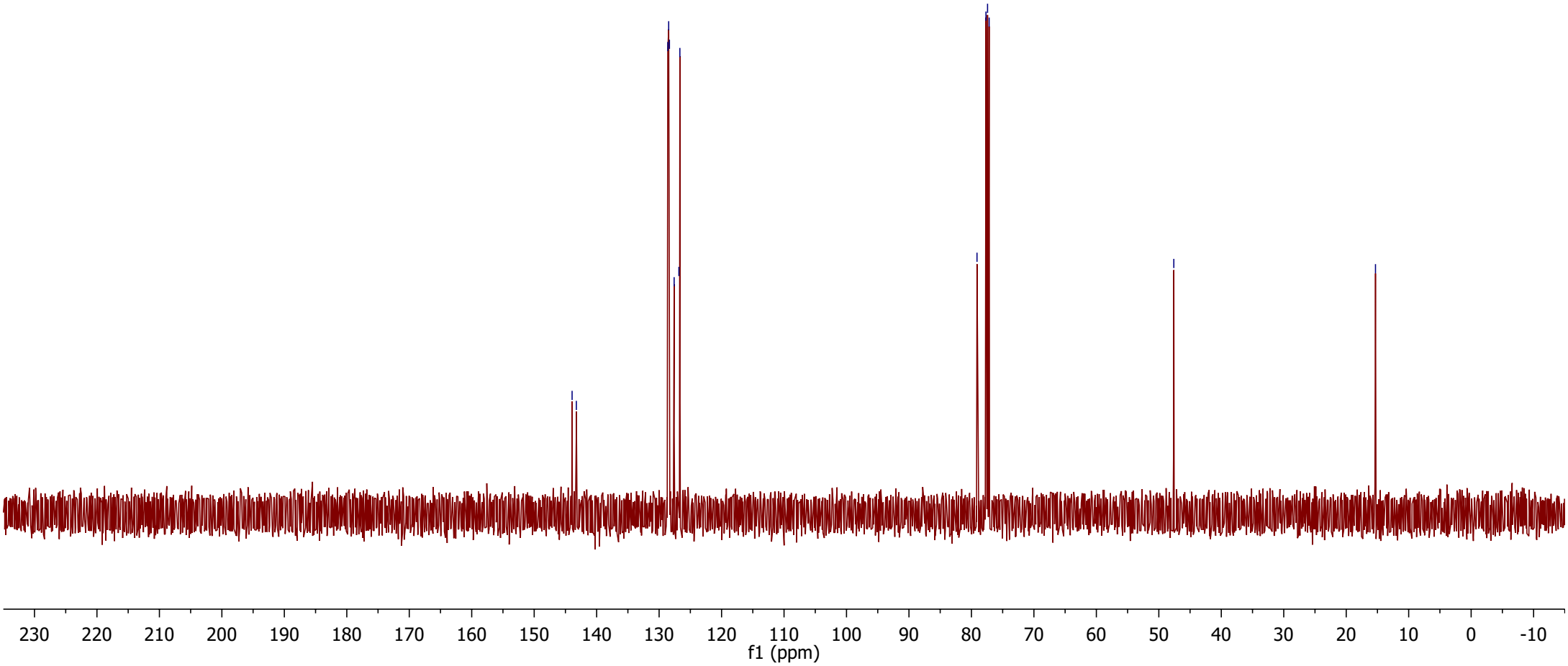




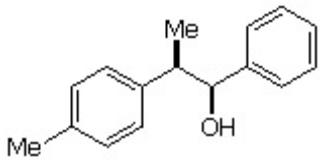
^{13}C NMR (125 MHz, $CDCl_3$)

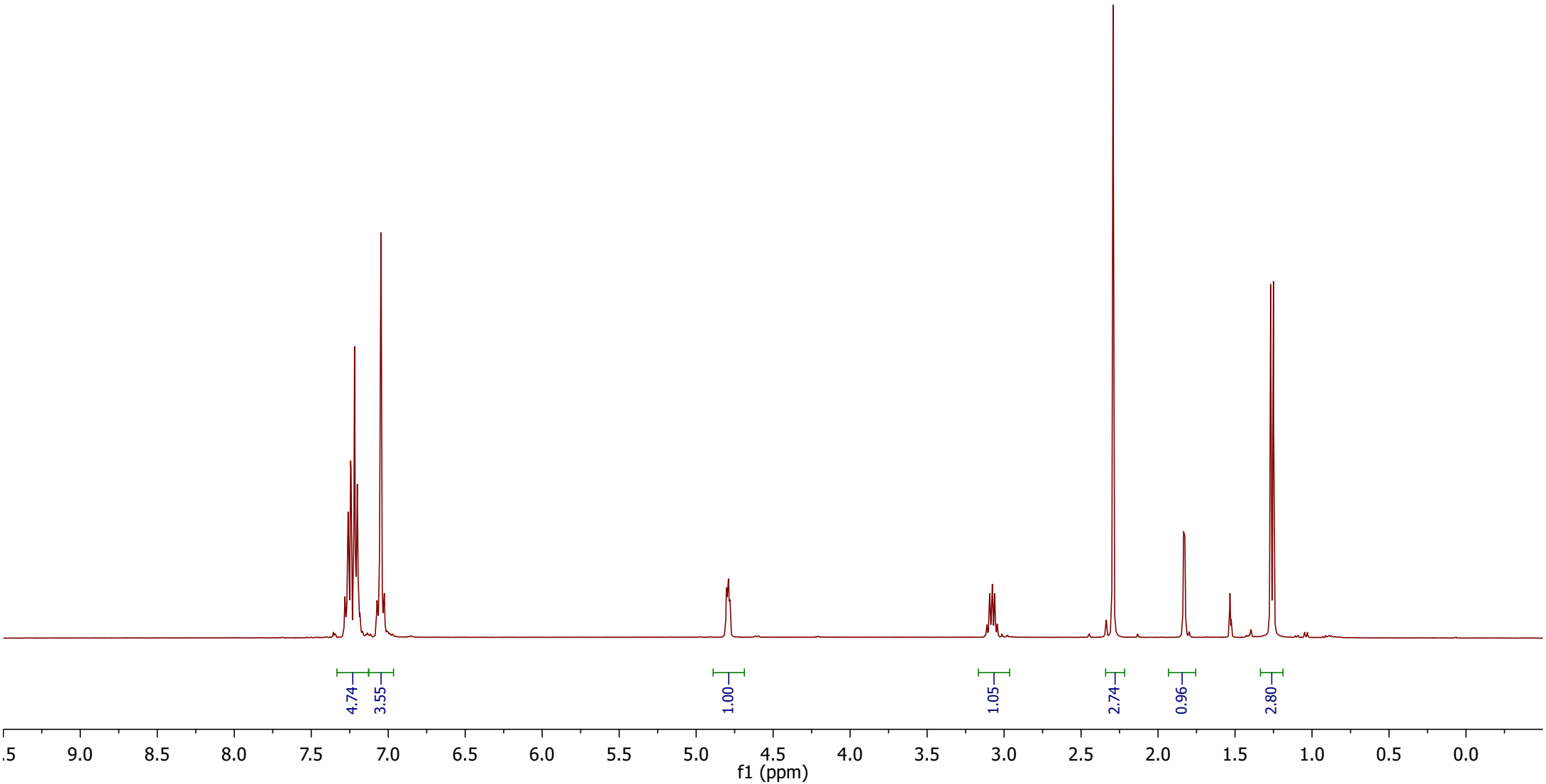


143.93
143.25
128.61
128.47
128.35
127.59
126.83
126.68
79.11
77.67
77.42
77.16
47.60
15.31

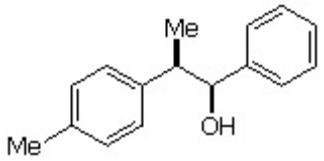


^{1}H NMR (400 MHz, $CDCl_3$)

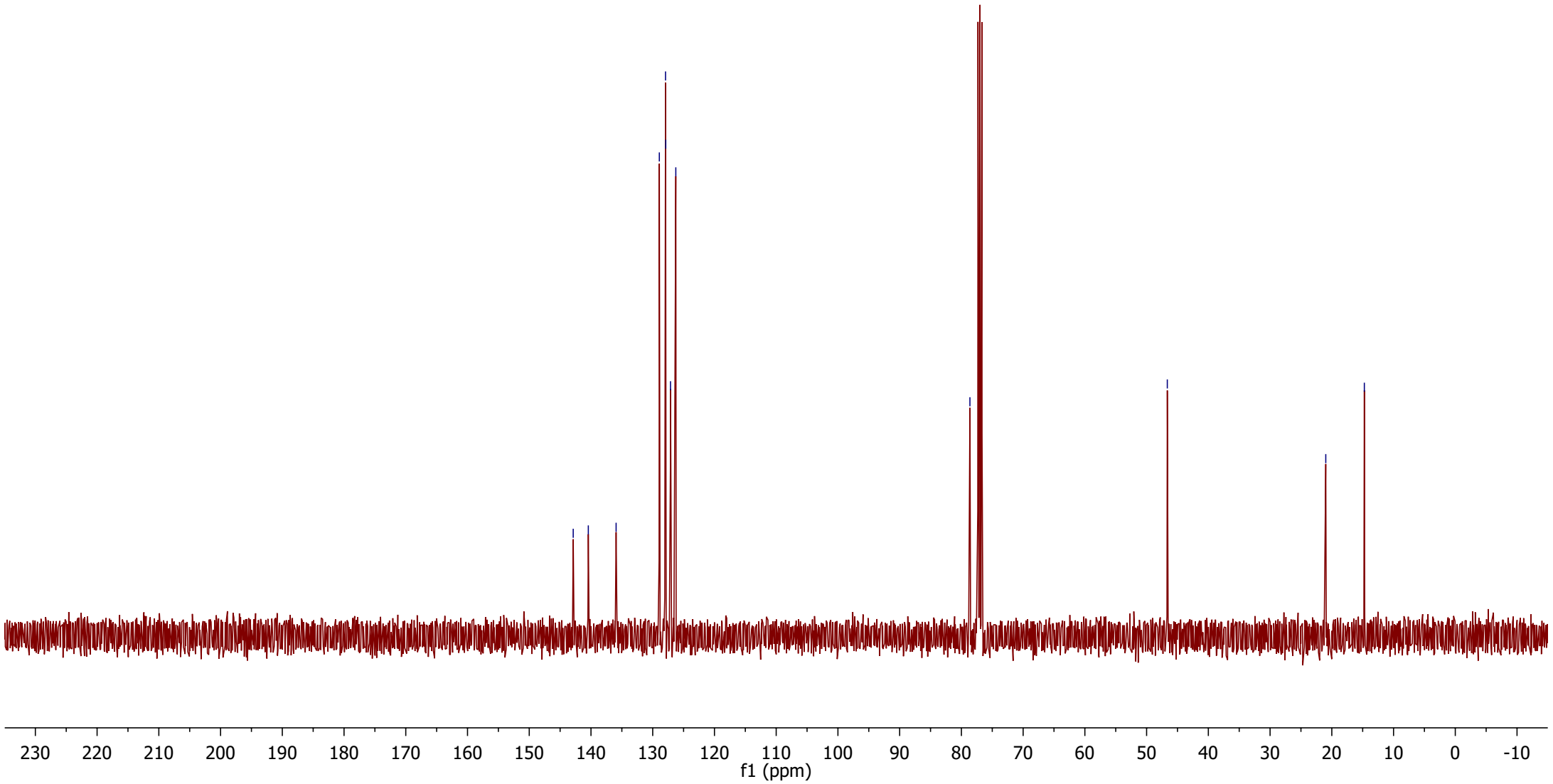




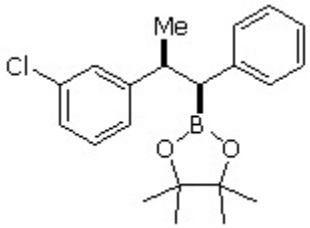
^{13}C NMR (125 MHz, $CDCl_3$)

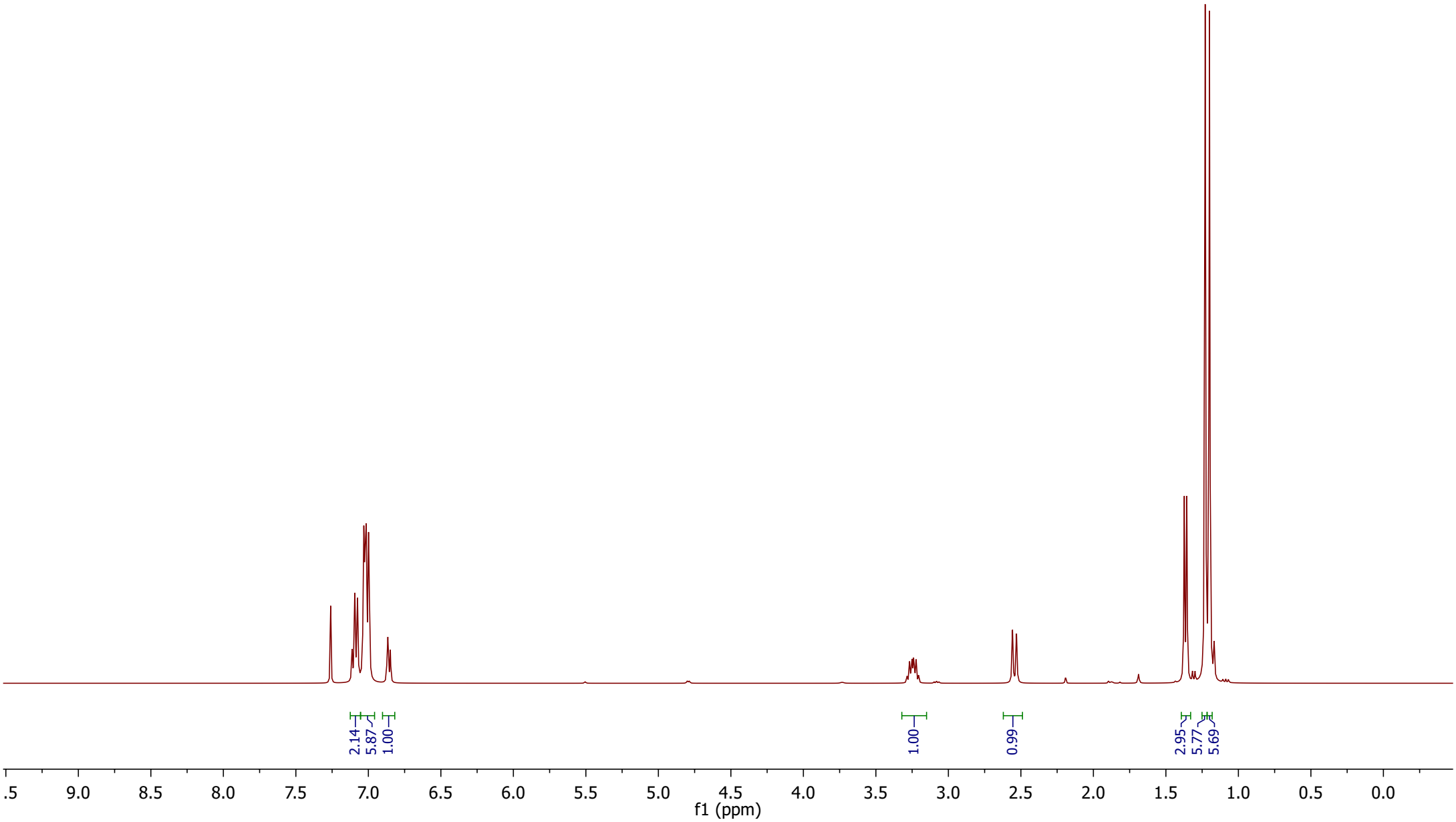


142.88
140.43
135.93
128.93
127.92
127.89
127.12
126.26
78.62
46.65
20.98
14.73

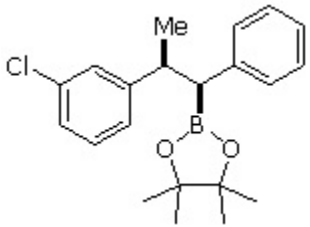


^{1}H NMR (400 MHz, $CDCl_3$)

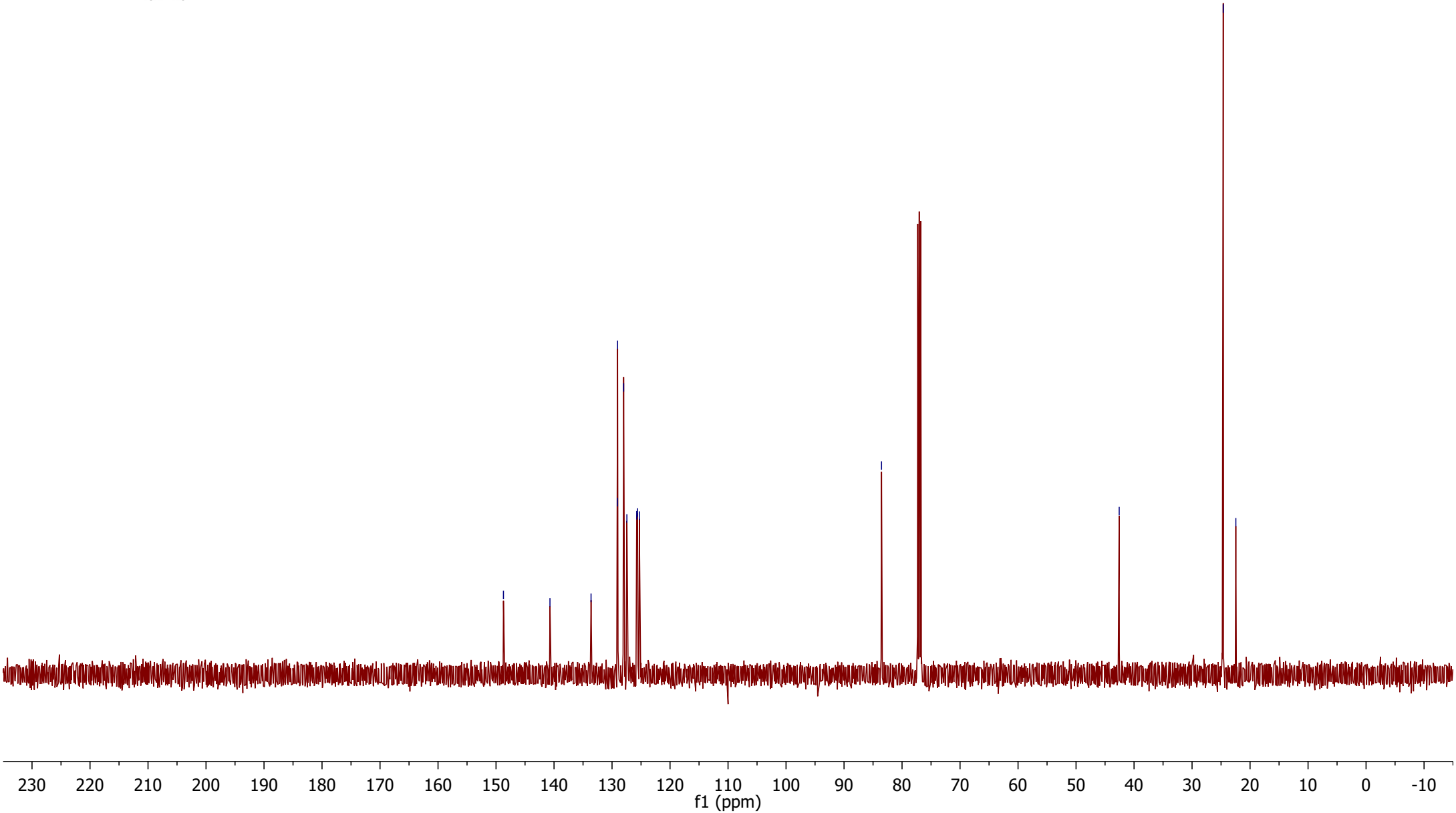




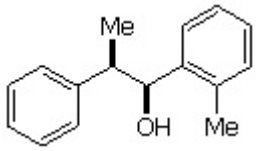
^{13}C NMR (125 MHz, $CDCl_3$)

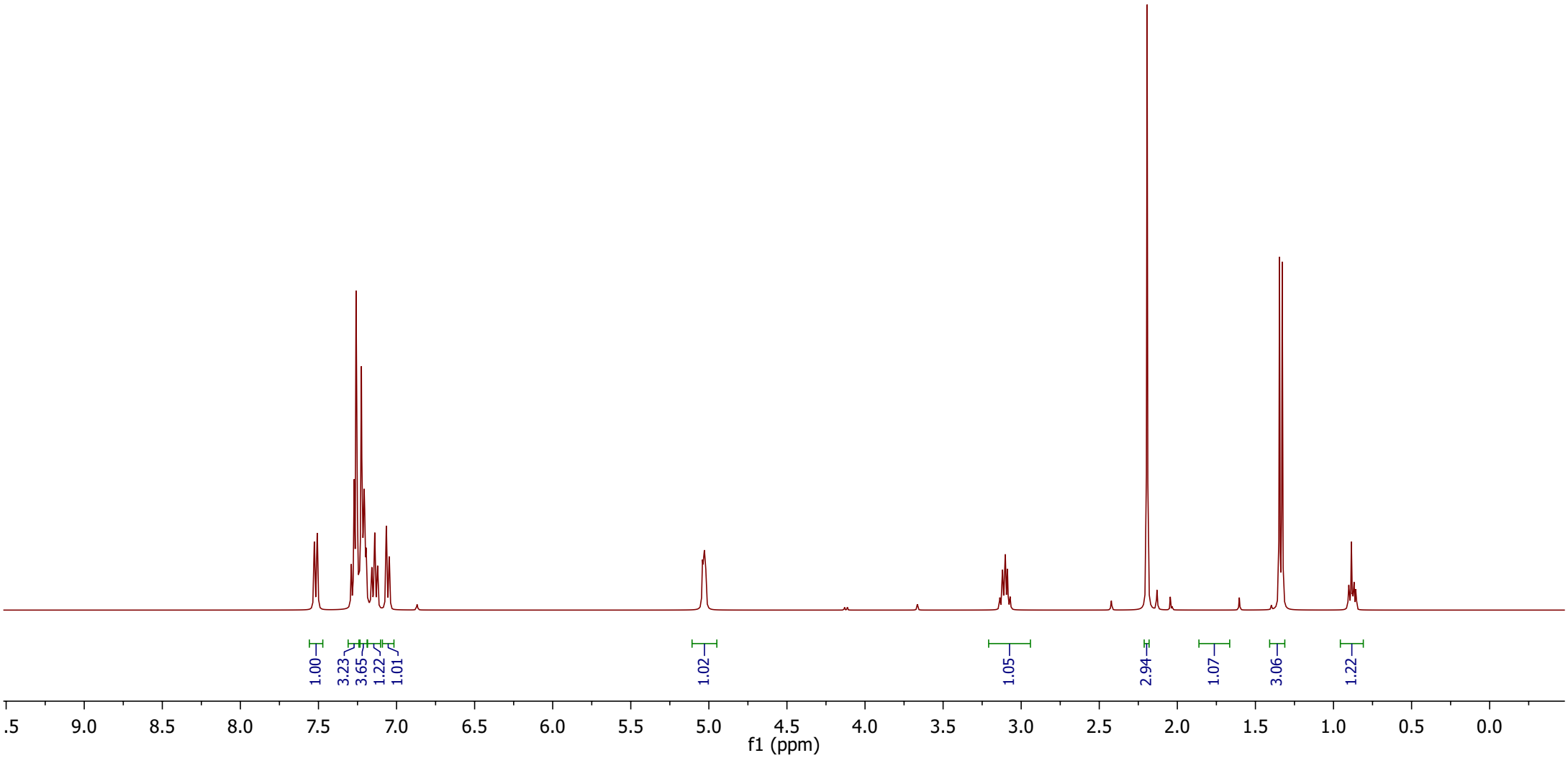


148.72
140.70
133.62
129.08
129.05
128.00
127.44
125.75
125.60
125.28
83.54
42.56
24.62
22.45

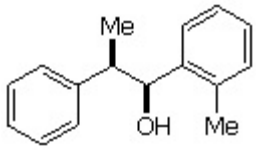


^{1}H NMR (400 MHz, $CDCl_3$)





^{13}C NMR (125 MHz, $CDCl_3$)

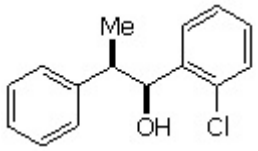


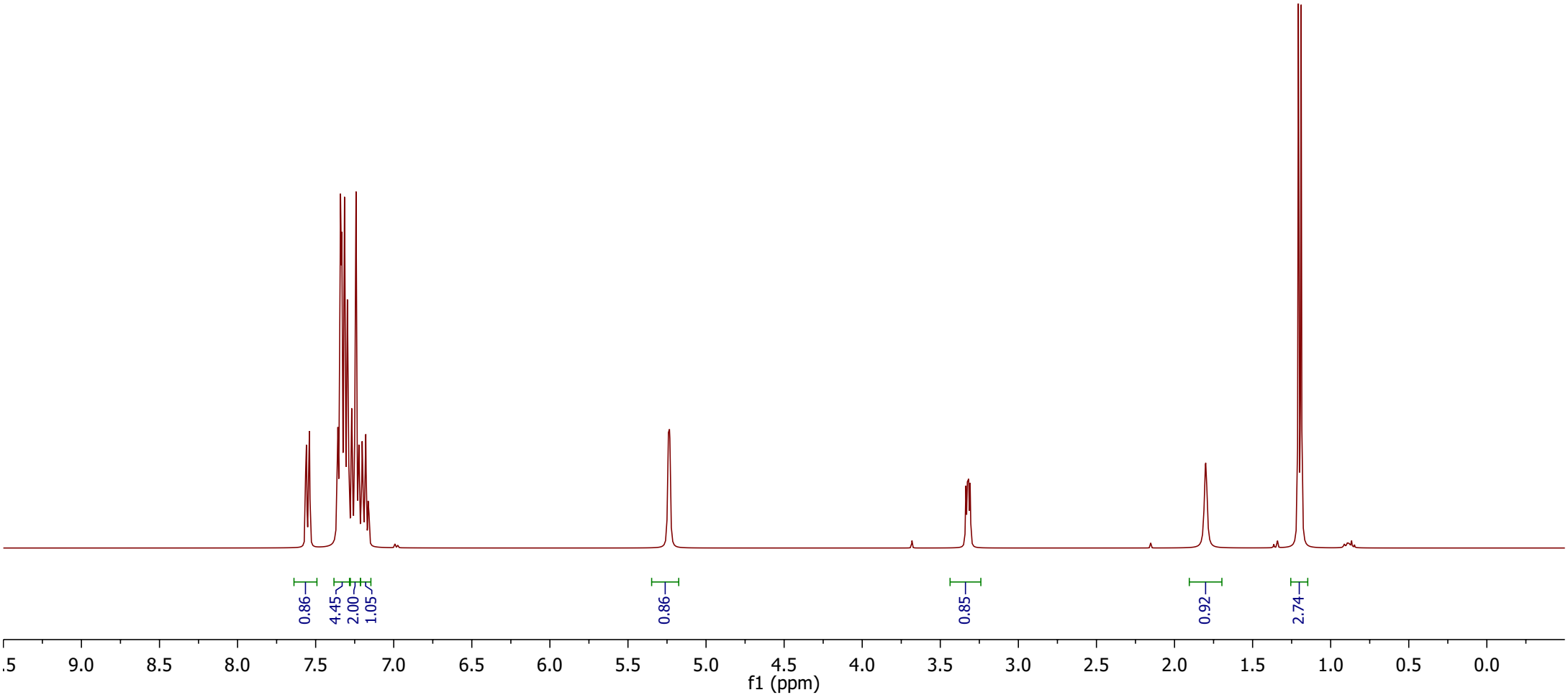
144.09
141.33
134.46
130.19
128.30
127.88
127.05
126.48
126.21
125.85
74.82
45.27
19.13
14.06

230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

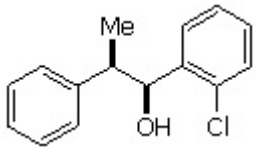
f1 (ppm)

^{1}H NMR (400 MHz, $CDCl_3$)

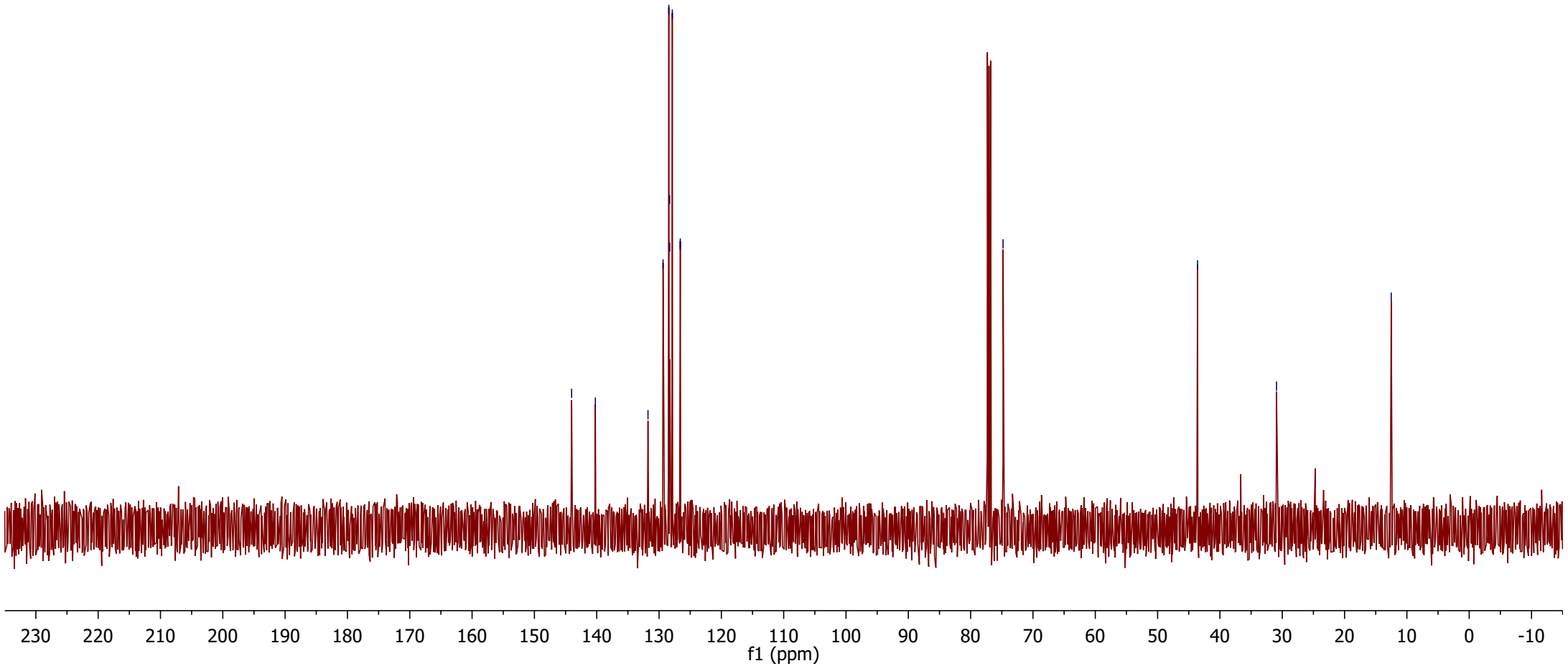




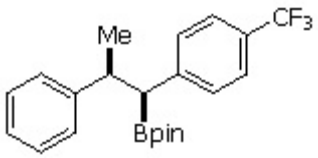
^{13}C NMR (125 MHz, $CDCl_3$)

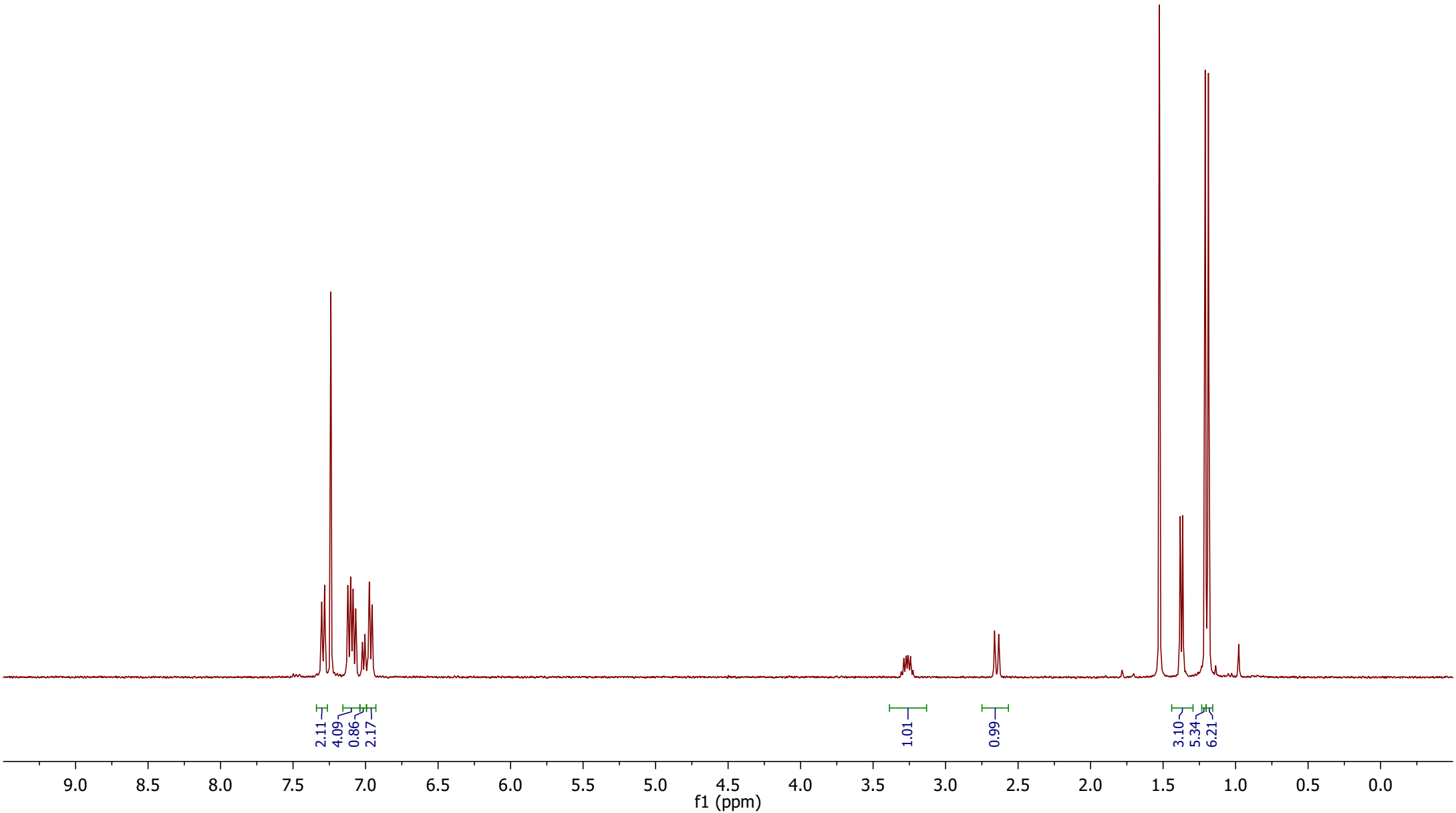


144.03
140.22
131.77
129.36
128.43
128.30
128.28
127.87
126.61
126.59
74.80
43.59
30.92
12.51

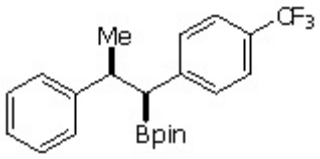


^{1}H NMR (400 MHz, $CDCl_3$)

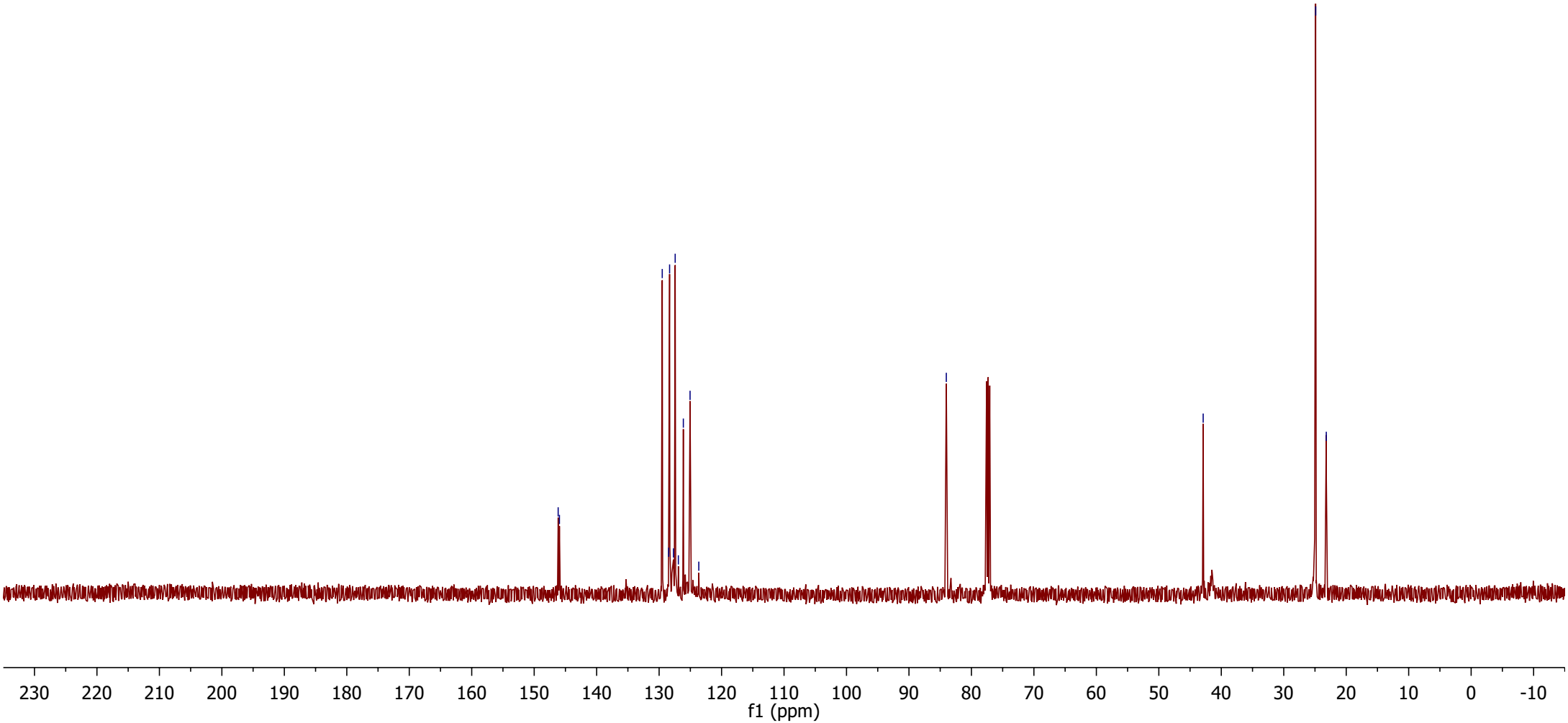




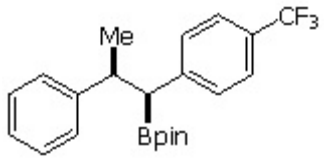
^{13}C NMR (125 MHz, $CDCl_3$)



146.16
145.96
129.50
128.47
128.32
127.71
127.43
126.92
126.12
125.05
123.65
84.02
42.90
24.89
23.19



^{19}F NMR (376 MHz, CDCl3)

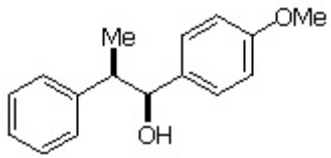


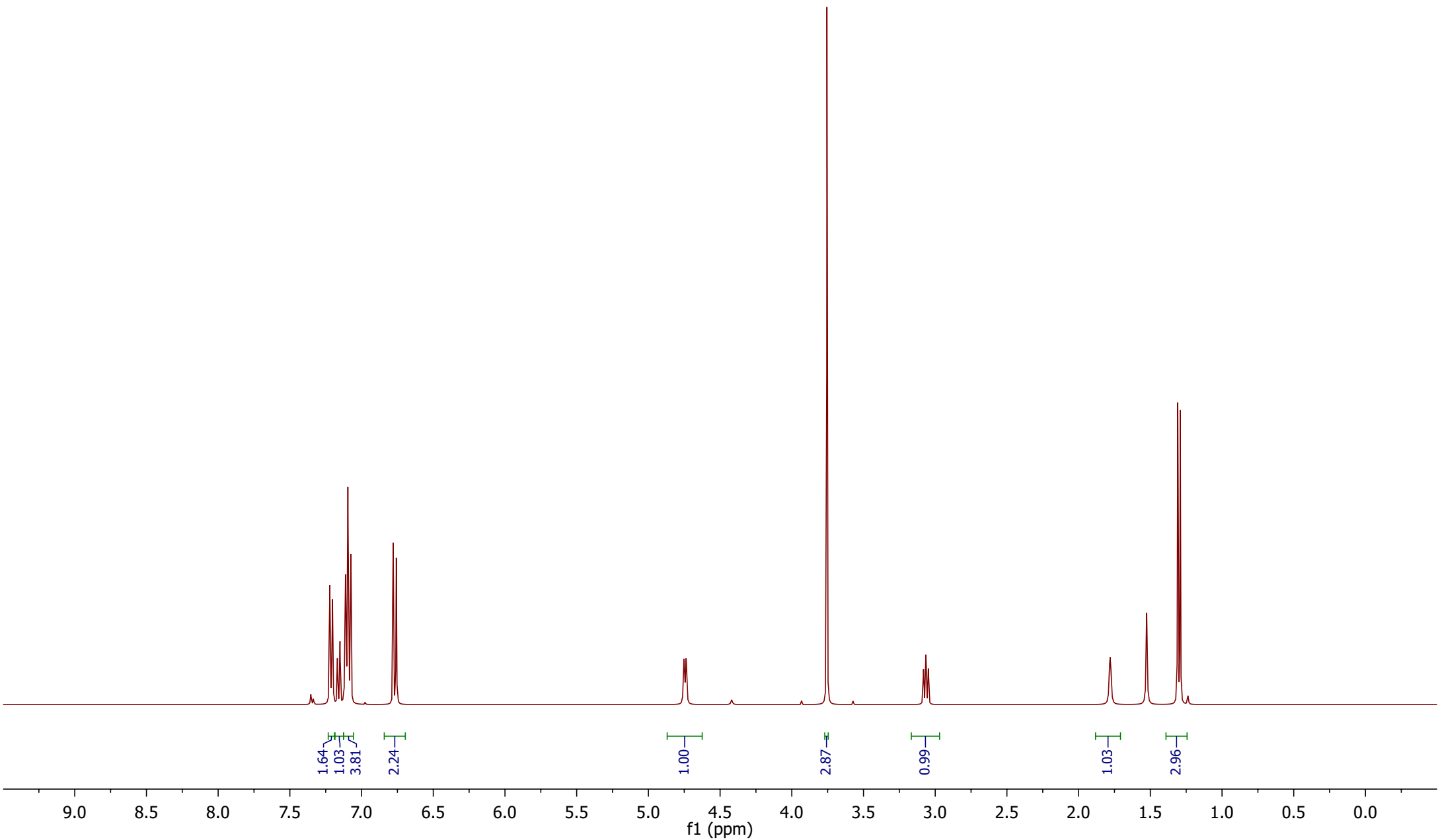
-62.26

0 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -2(

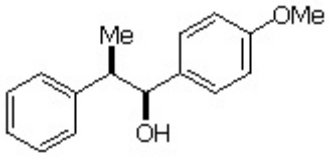
f1 (ppm)

^{1}H NMR (400 MHz, $CDCl_3$)

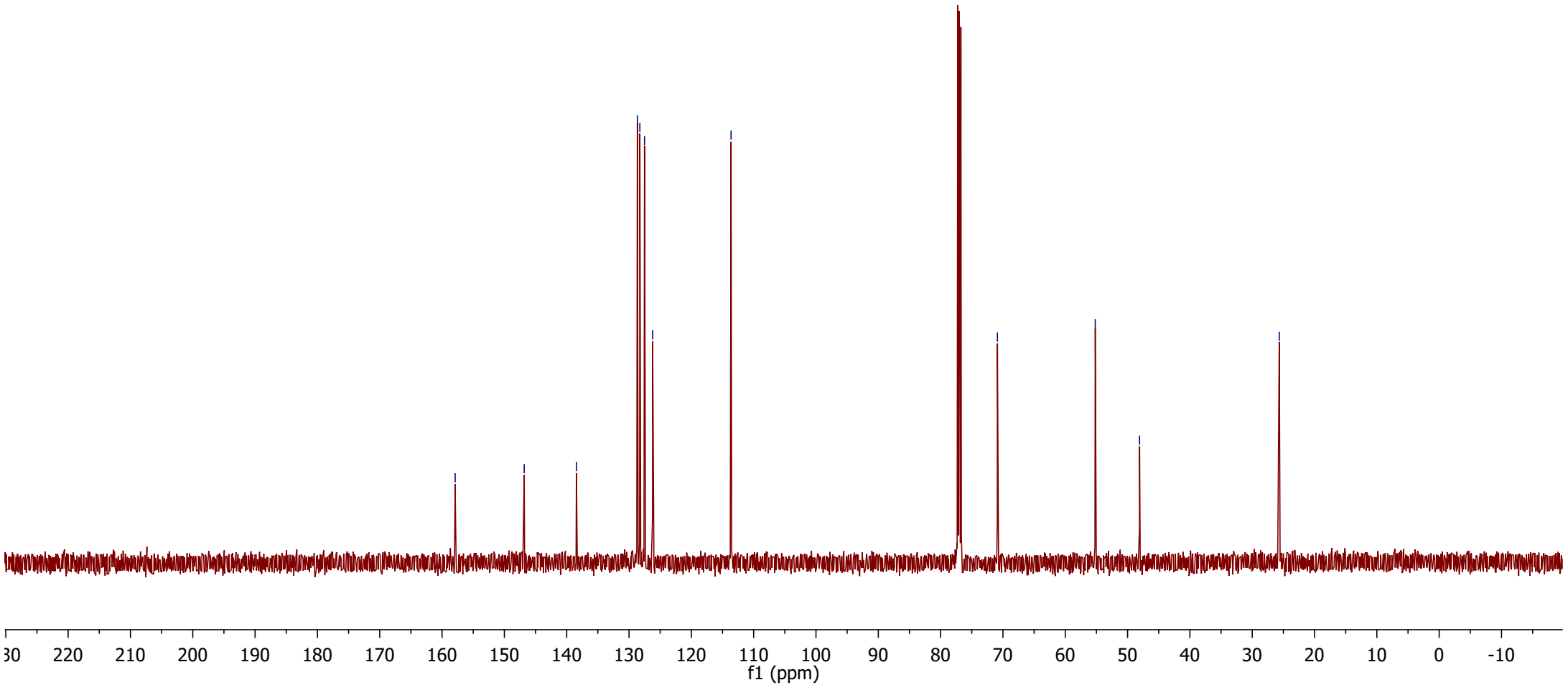




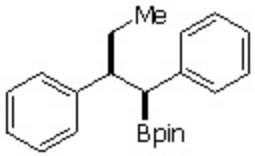
^{13}C NMR (125 MHz, $CDCl_3$)

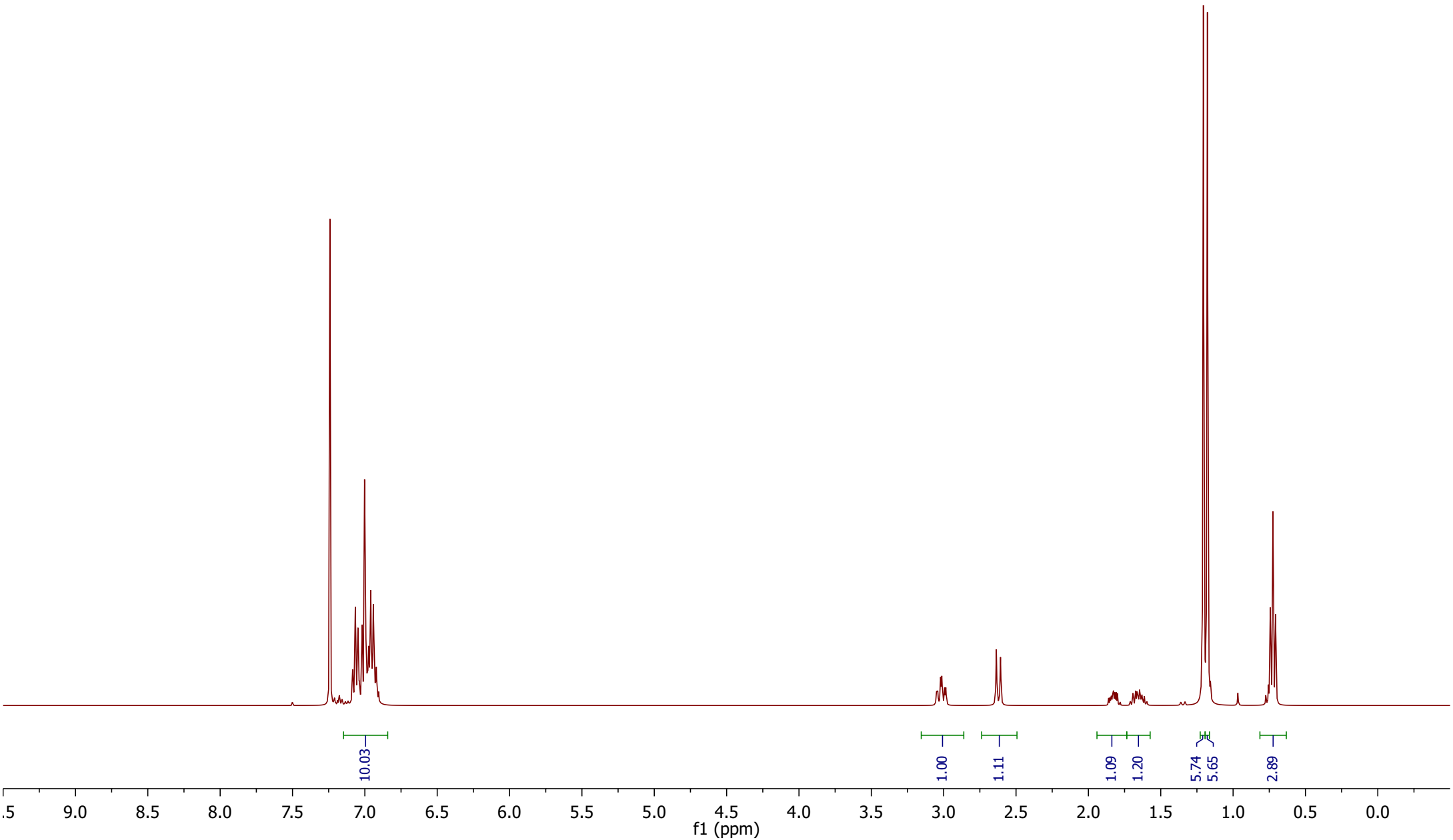


157.90
146.81
138.44
128.66
128.26
127.51
126.21
113.63
70.89
55.19
48.08
25.66

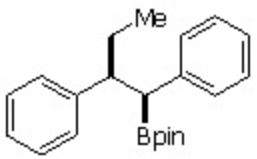


^{1}H NMR (400 MHz, $CDCl_3$)



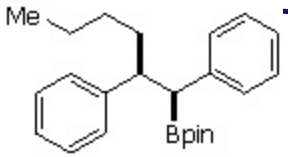


^{13}C NMR (125 MHz, $CDCl_3$)



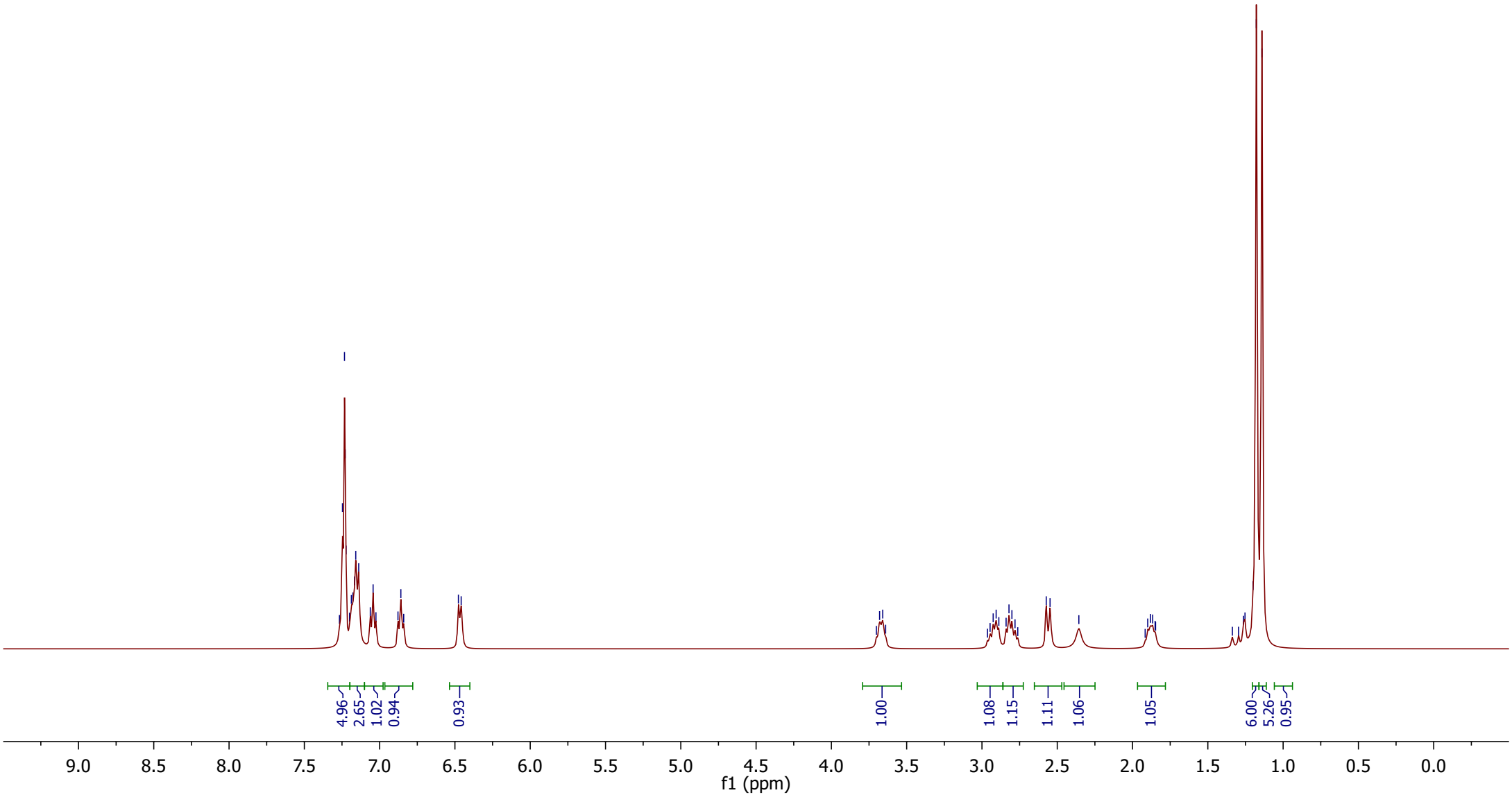
144.04
140.93
129.12
128.18
127.72
127.64
125.46
124.88
83.40
50.16
29.72
24.61
24.58
12.29

^{1}H NMR (400 MHz, CDCl$_3$)

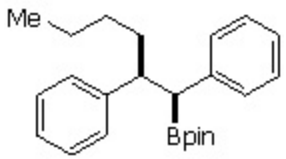


7.27 7.26 7.23 7.22 7.20 7.19 7.18 7.17 7.16 7.14 7.06 7.04 7.02 6.88 6.86 6.84 6.48 6.46

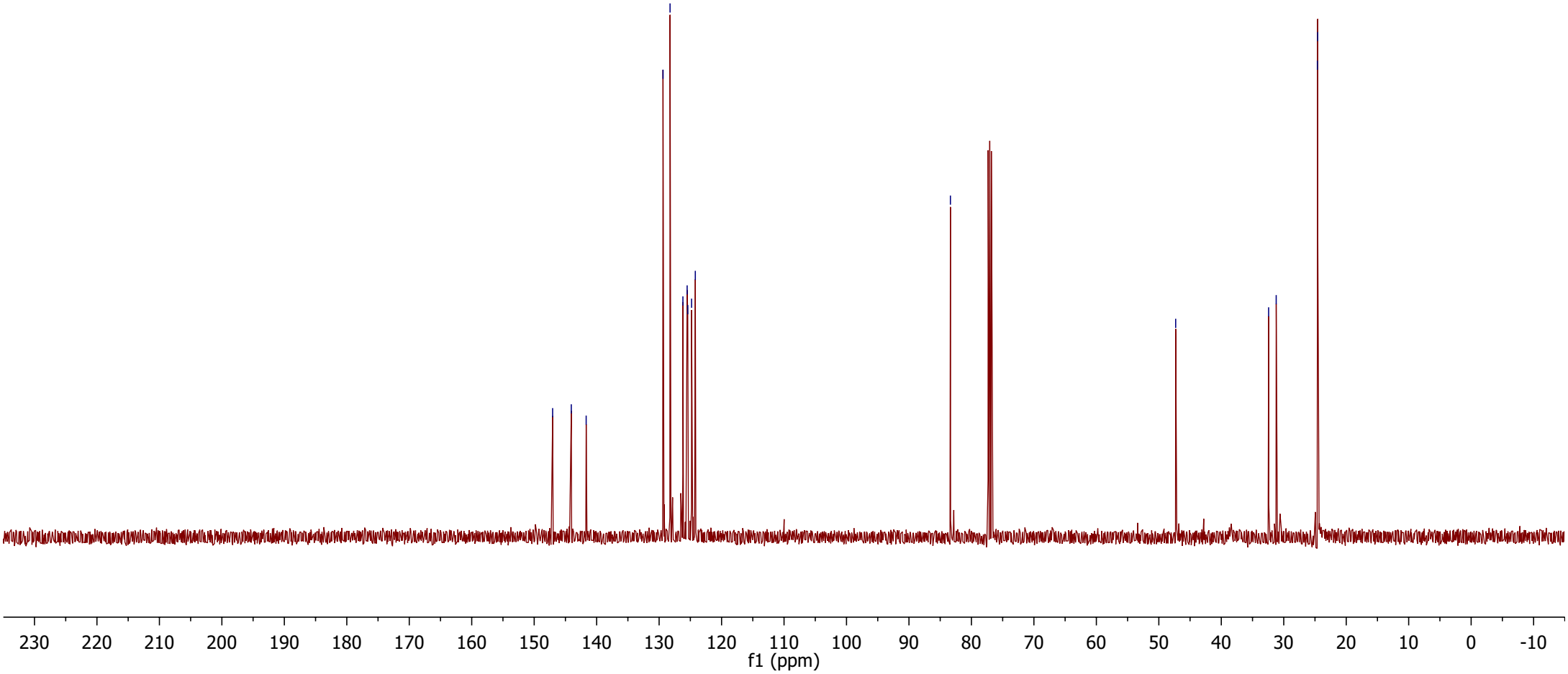
3.70 3.68 3.66 3.64 2.96 2.95 2.93 2.91 2.89 2.84 2.82 2.80 2.78 2.76 2.57 2.55 2.36 1.92 1.90 1.88 1.87 1.85 1.85 1.34 1.30 1.26 1.25 1.20 1.18 1.14



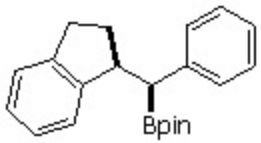
^{13}C NMR (125 MHz, $CDCl_3$)

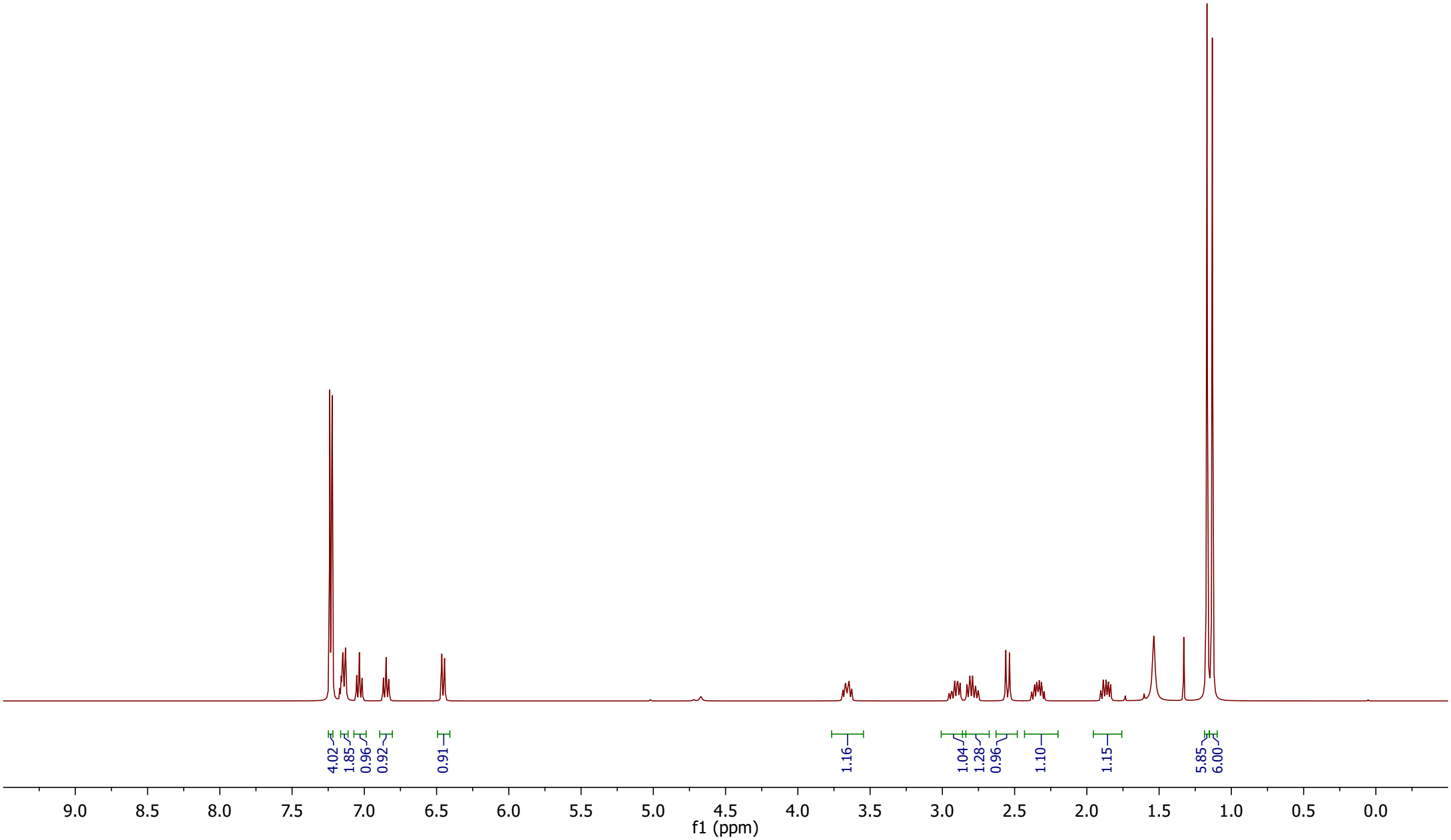


147.05
144.06
141.68
129.37
128.25
126.19
125.51
125.41
124.80
124.21
83.37
47.30
32.42
31.21
24.62
24.57

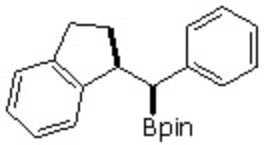


^{1}H NMR (400 MHz, $CDCl_3$)

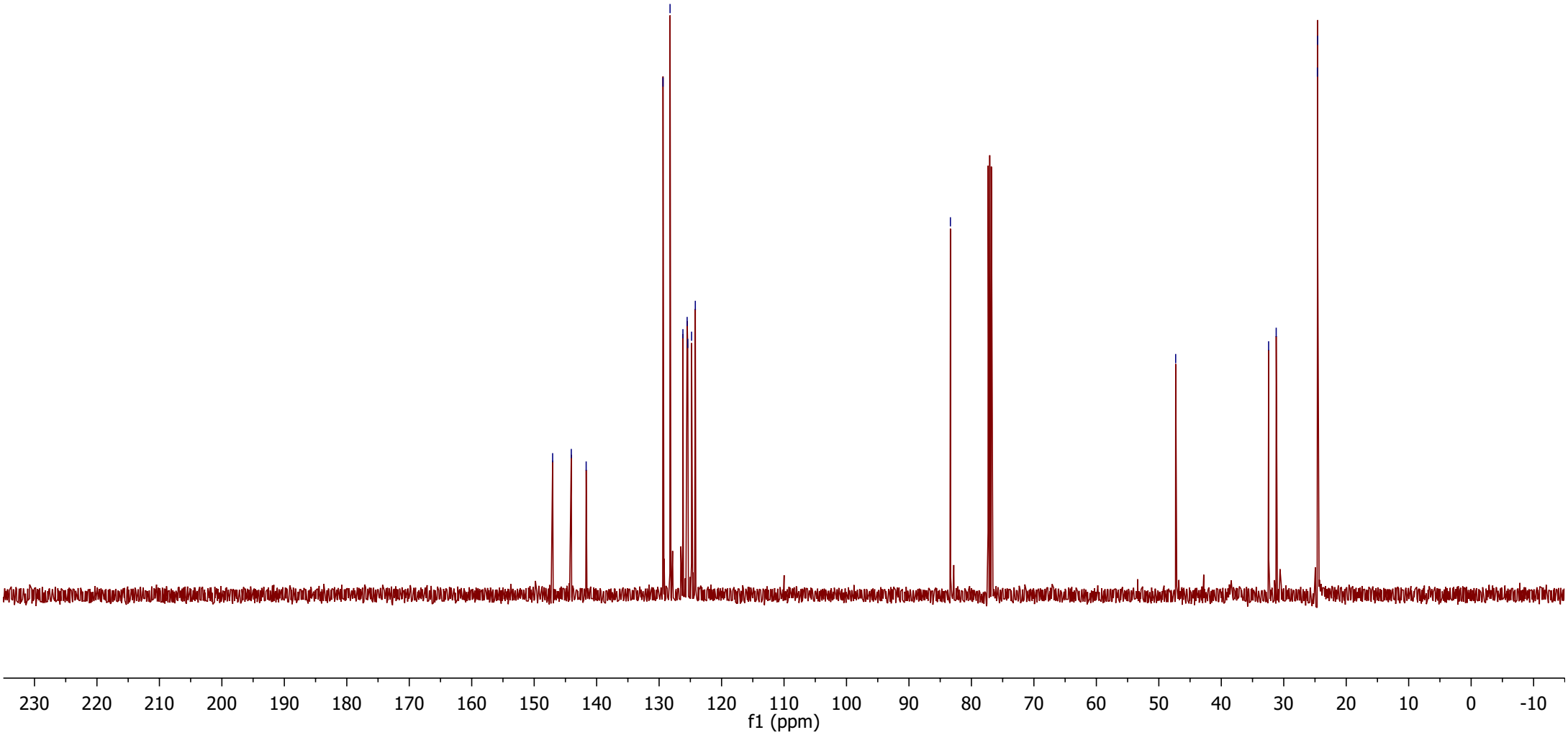




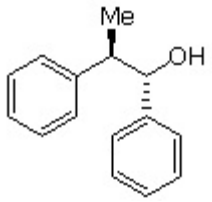
^{13}C NMR (125 MHz, $CDCl_3$)

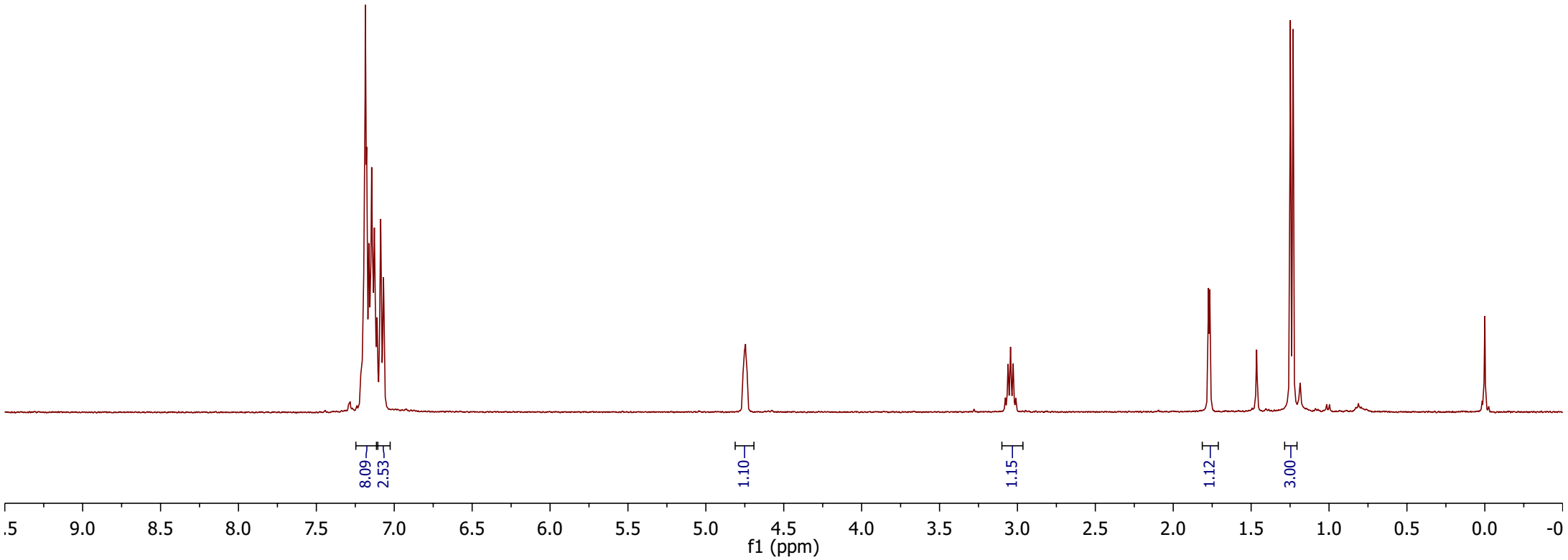


147.05
144.06
141.68
129.37
128.25
126.19
125.51
125.41
124.80
124.21
83.37
47.30
32.42
31.21
24.62
24.57

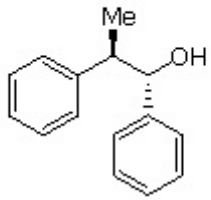


^{1}H NMR (400 MHz, $CDCl_3$)





^{13}C NMR (125 MHz, $CDCl_3$)

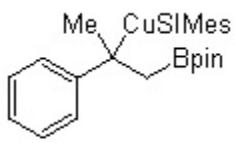


143.55
142.86
128.24
128.08
127.97
127.22
126.46
126.29
78.72
47.22
14.89

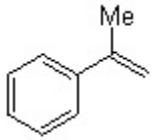
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1

f1 (ppm)

^{1}H NMR (600 MHz, C6H6)

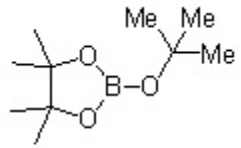


a



unreacted
starting material

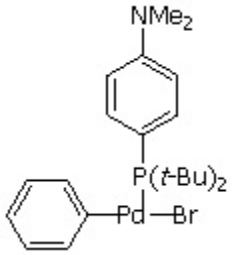
b

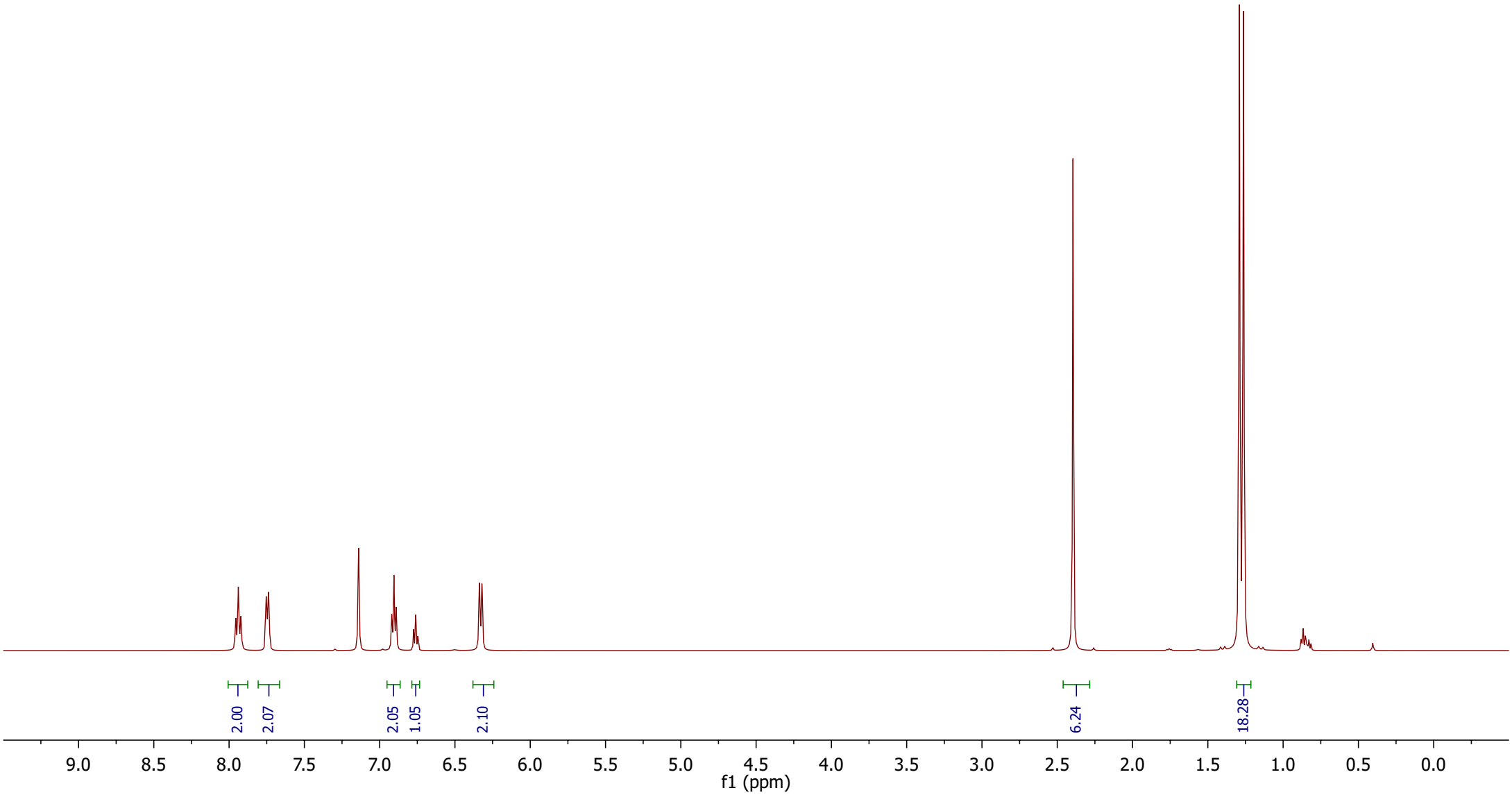


side product

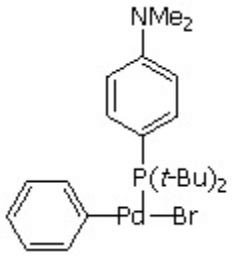
c

^{1}H NMR (400 MHz, C6D6)



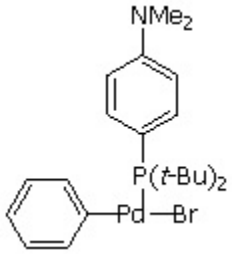


^{13}C NMR (125 MHz, C6D6)

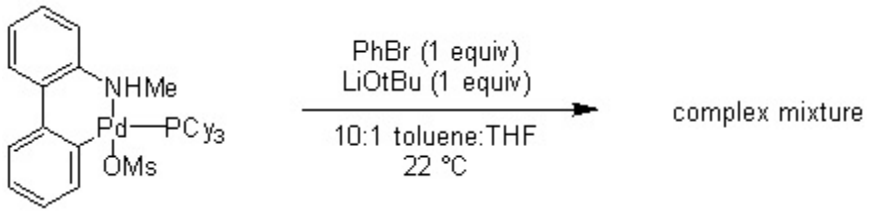


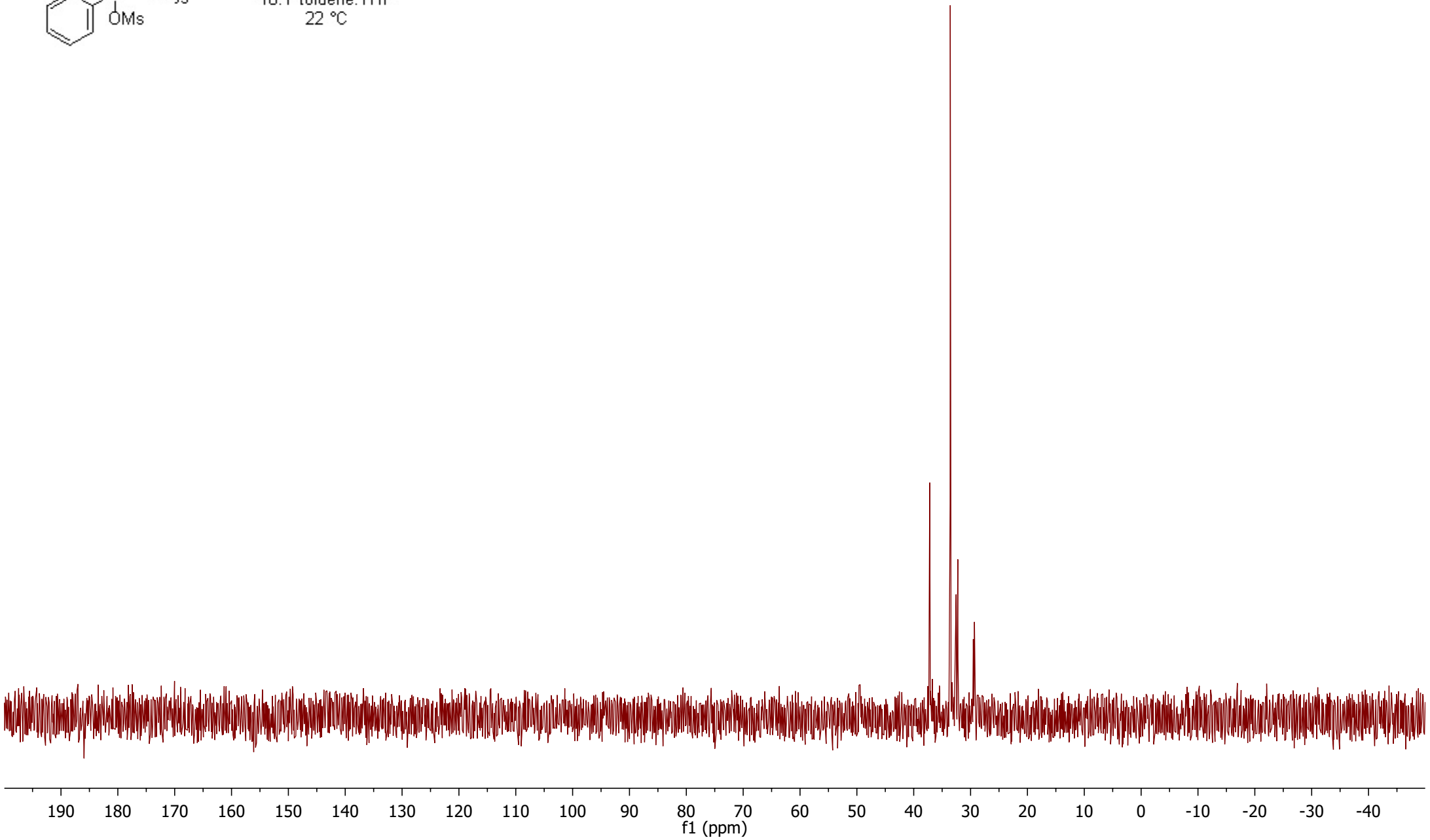
150.50
146.09
138.15
138.06
131.38
129.87
126.48
122.72
115.38
115.06
109.82
109.73
39.04
37.54
37.41
30.59
30.56

^{31}P NMR (162 MHz, C6H6)



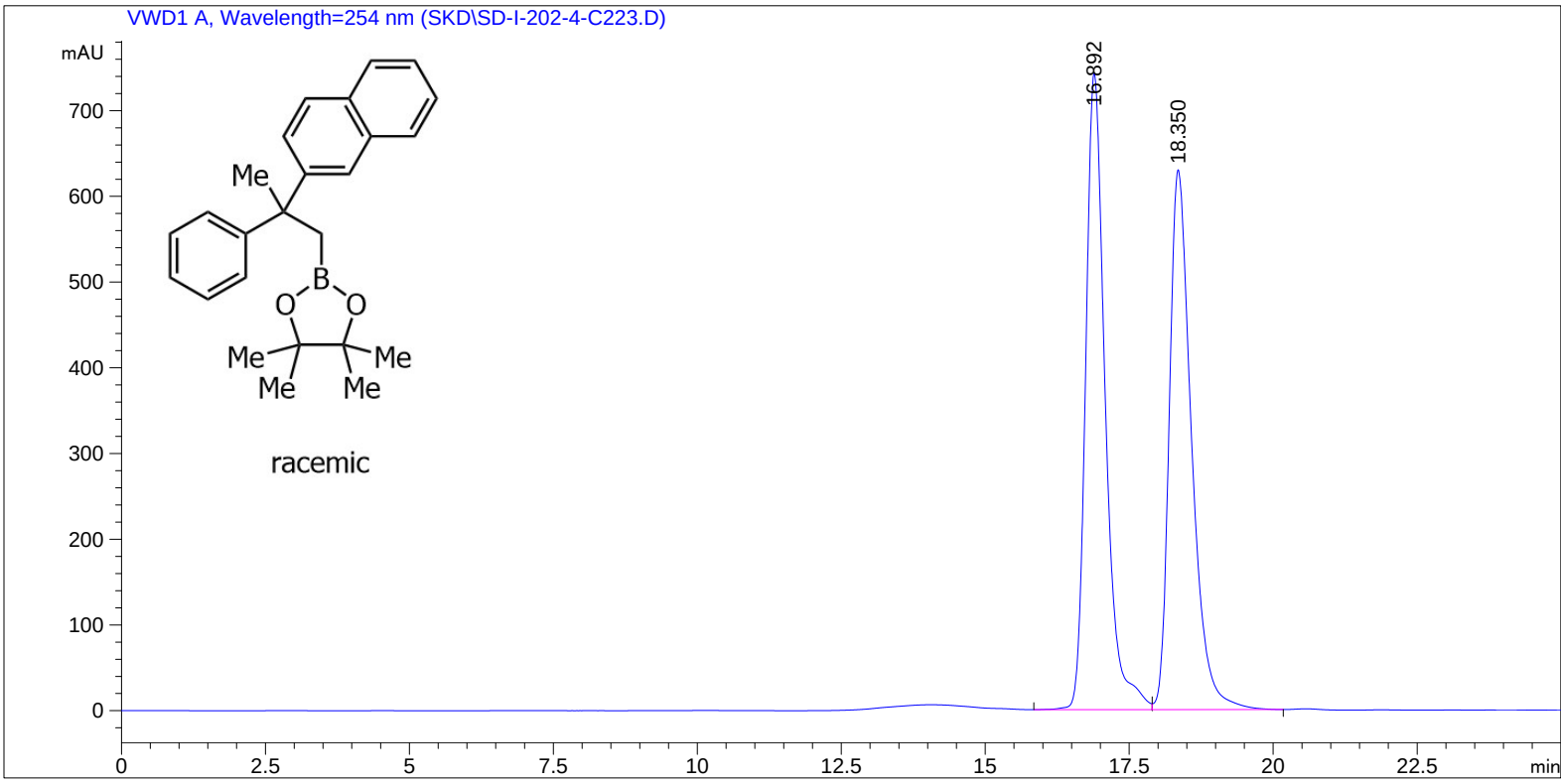
^{31}P NMR (162 MHz, tol-d8)





Data File C:\CHEM32\2\DATA\SKD\SD-I-202-4-C223.D
Sample Name: SKD-I-202-4-C22c

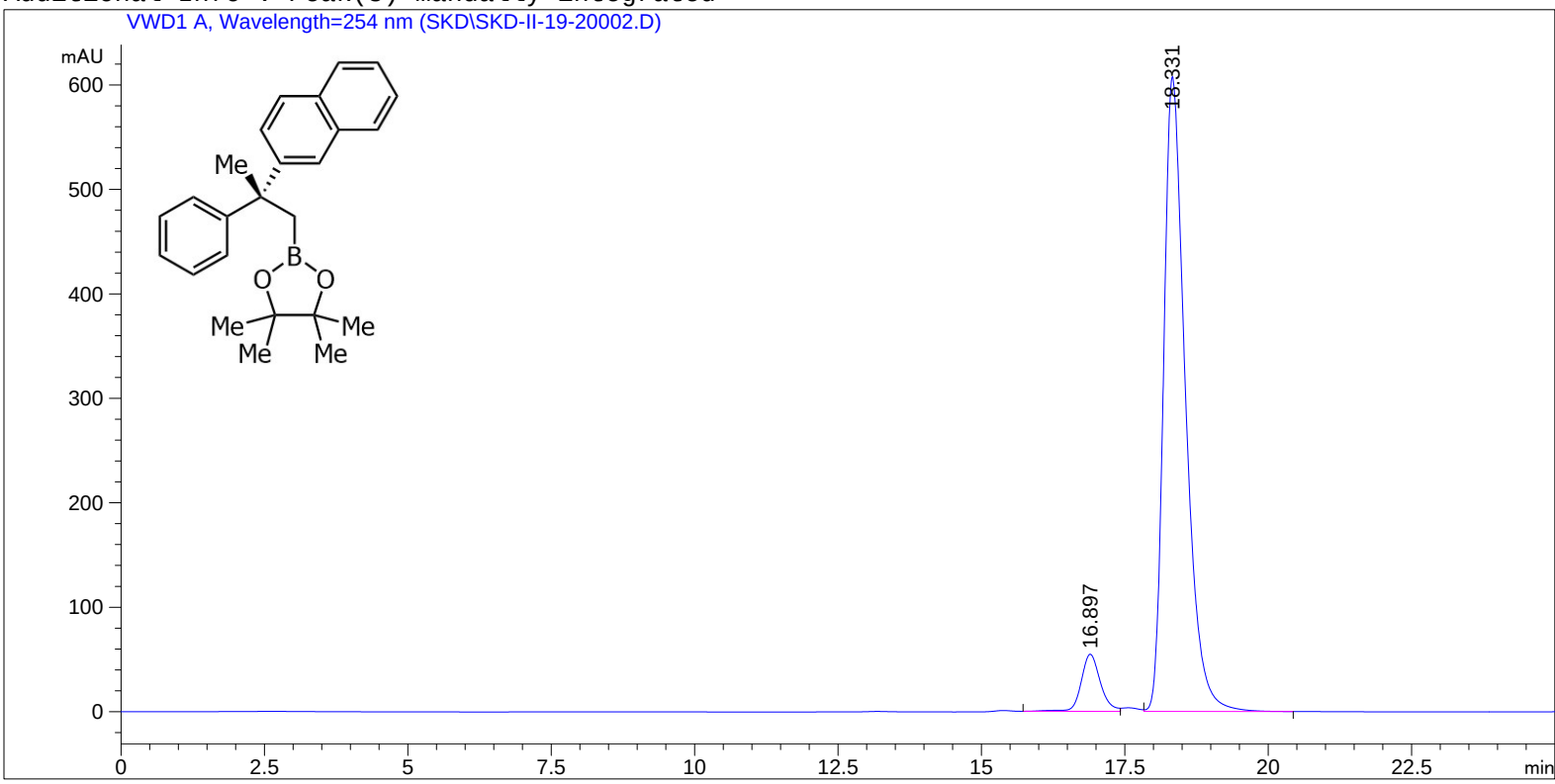

```
==========================================================================
Acq. Operator   : SYSTEM                          Seq. Line :   3
Acq. Instrument : 1220 HPLC                        Location : Vial 21
Injection Date  : 10/26/2018 11:51:09 PM               Inj :   1
                                                  Inj Volume : 10.000 µl
Acq. Method     : C:\CHEM32\2\METHODS\SKD_TRY.M
Last changed    : 10/26/2018 11:46:04 PM by SYSTEM
                  (modified after loading)
Analysis Method : C:\CHEM32\2\METHODS\DEF_LC.M
Last changed    : 10/2/2018 2:47:22 PM by SYSTEM
Sample Info     : Lux 3u Cellulose-2, 99:1 Hex:IPA, 0.25 mL/min, 254 nm,
                  25 min
```




```
==========================================================================
                        Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  16.892 BV    0.3570 1.75757e4   742.83716  50.9642
   2  18.350 VB    0.4073 1.69106e4   629.79803  49.0358

Totals :                  3.44863e4  1372.63519


==========================================================================
                        *** End of Report ***
```

Data File C:\CHEM32\2\DATA\SKD\SKD-II-19-20002.D
Sample Name: SKD-II-19-2b

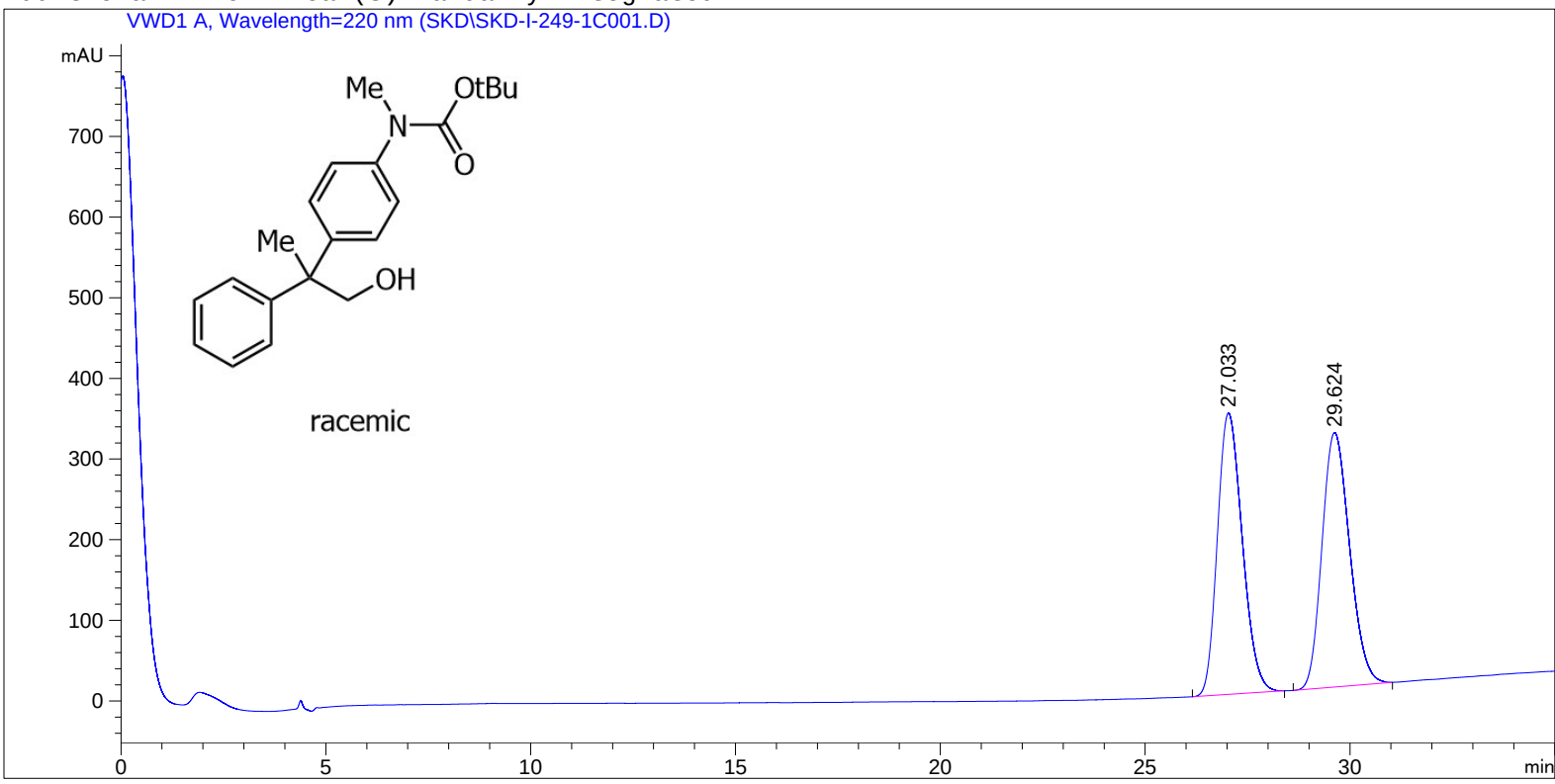

```
==========================================================================
Acq. Operator   : SYSTEM                          Seq. Line :   2
Acq. Instrument : 1220 HPLC                        Location : Vial 21
Injection Date  : 10/27/2018 1:47:40 AM                Inj :   1
                                                 Inj Volume : 10.000 µl
Acq. Method     : C:\CHEM32\2\METHODS\SKD_TRY.M
Last changed    : 10/27/2018 12:17:24 AM by SYSTEM
Analysis Method : C:\CHEM32\2\METHODS\DEF_LC.M
Last changed    : 10/2/2018 2:47:22 PM by SYSTEM
Sample Info     : Lux 3u Cellulose-2, 99:1 Hex:IPA, 0.25 mL/min, 254 nm,
                  30 min


Additional Info : Peak(s) manually integrated
```




```
==========================================================================
                          Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  16.897 BV    0.3537 1269.42810   54.71751   7.3624
   2  18.331 VB    0.4036 1.59727e4   607.74768  92.6376

Totals :                  1.72421e4   662.46519


==========================================================================
                          *** End of Report ***
```

Data File C:\CHEM32\2\DATA\SKD\SKD-I-249-1C001.D
Sample Name: SKD-I-249-1c

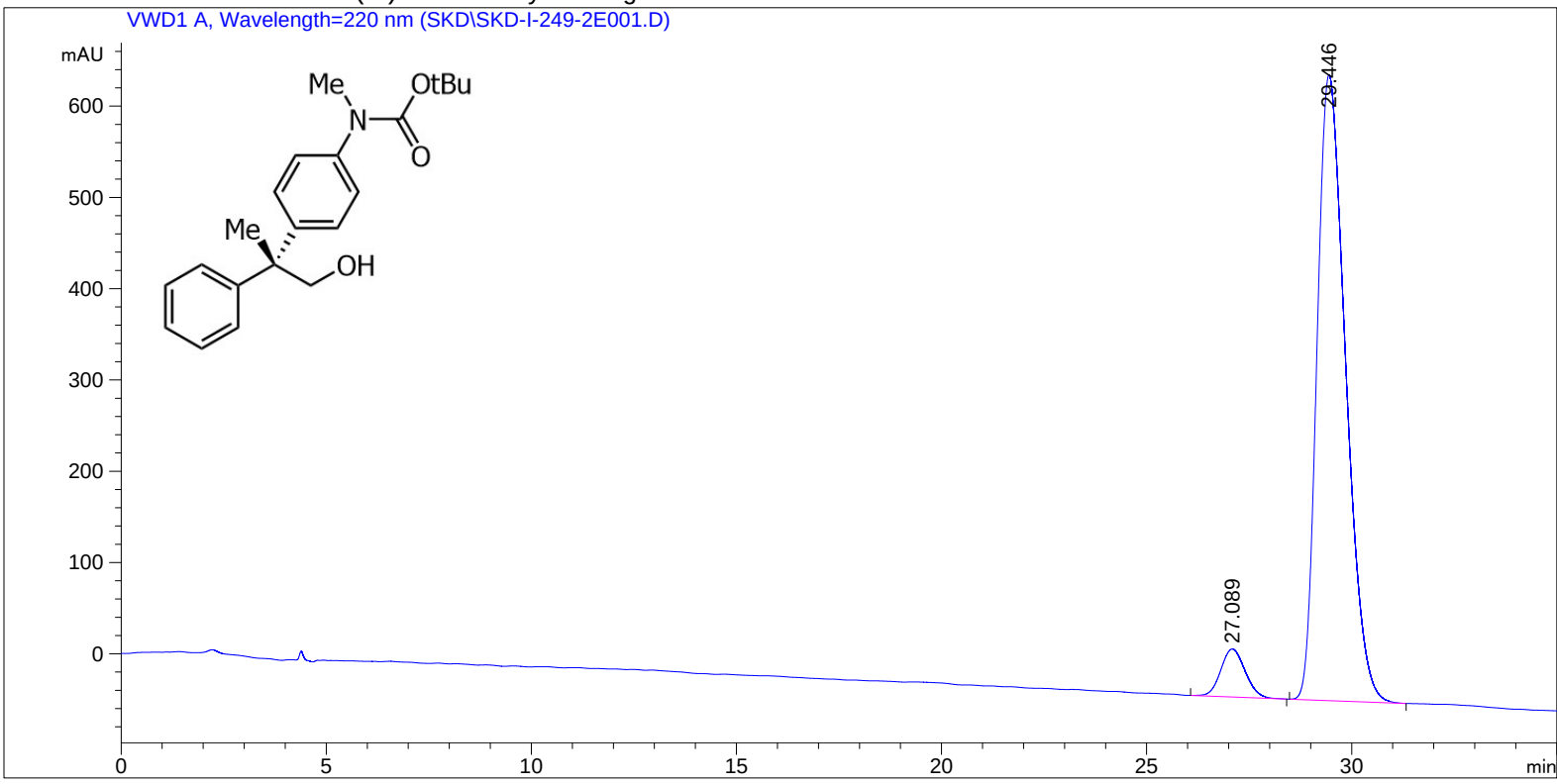

```
==========================================================================
Acq. Operator   : SYSTEM                          Seq. Line :   1
Acq. Instrument : 1220 HPLC                        Location : Vial 31
Injection Date  : 8/3/2018 3:36:45 PM                   Inj :   1
                                                 Inj Volume : 10.000 µl
Acq. Method     : C:\CHEM32\2\METHODS\SKD_TRY.M
Last changed    : 8/3/2018 4:03:59 PM by SYSTEM
                  (modified after loading)
Analysis Method : C:\CHEM32\2\METHODS\DEF_LC.M
Last changed    : 10/2/2018 2:47:22 PM by SYSTEM
Sample Info     : Lux 3u Cellulose 4, 96:4 Hex:IPA, 0.75 mL/min, 220 nm,
                  20 min


Additional Info : Peak(s) manually integrated
```




```
==========================================================================
                        Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=220 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  27.033 BB    0.6400 1.47541e4   348.78790  49.9611
   2  29.624 BB    0.7099 1.47771e4   315.53693  50.0389

Totals :                  2.95312e4   664.32483


==========================================================================
```

Data File C:\CHEM32\2\DATA\SKD\SKD-I-249-2E001.D
Sample Name: SKD-I-249-2e

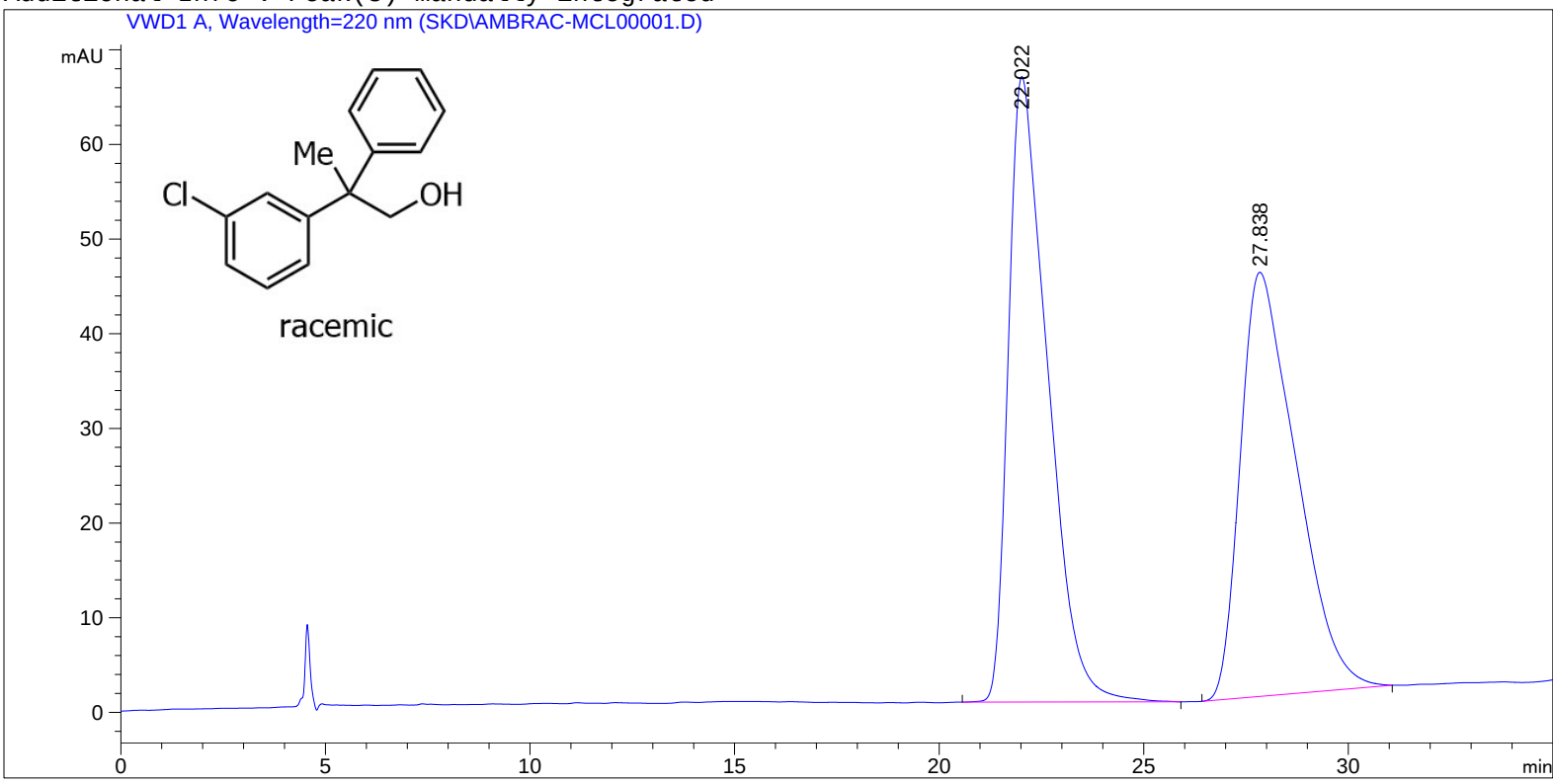

```
==========================================================================
Acq. Operator   : SYSTEM                          Seq. Line :   1
Acq. Instrument : 1220 HPLC                        Location : Vial 41
Injection Date  : 8/3/2018 4:56:23 PM                  Inj :   1
                                                 Inj Volume : 10.000 µl
Acq. Method     : C:\CHEM32\2\METHODS\SKD_TRY.M
Last changed    : 8/3/2018 4:12:41 PM by SYSTEM
Analysis Method : C:\CHEM32\2\METHODS\DEF_LC.M
Last changed    : 10/2/2018 2:47:22 PM by SYSTEM
Sample Info     : Lux 3u Cellulose 4, 96:4 Hex:IPA, 0.75 mL/min, 220 nm,
                  35 min


Additional Info : Peak(s) manually integrated
```




```
==========================================================================
                          Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=220 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  27.089 BB    0.5170 2177.48462   52.64716   6.1768
   2  29.446 BB    0.7143 3.30750e4   685.67694  93.8232

Totals :                  3.52525e4   738.32410


==========================================================================
                          *** End of Report ***
```

Data File C:\CHEM32\2\DATA\SKD\AMBRAC-MCL00001.D
Sample Name: AMBrac-mCl-a

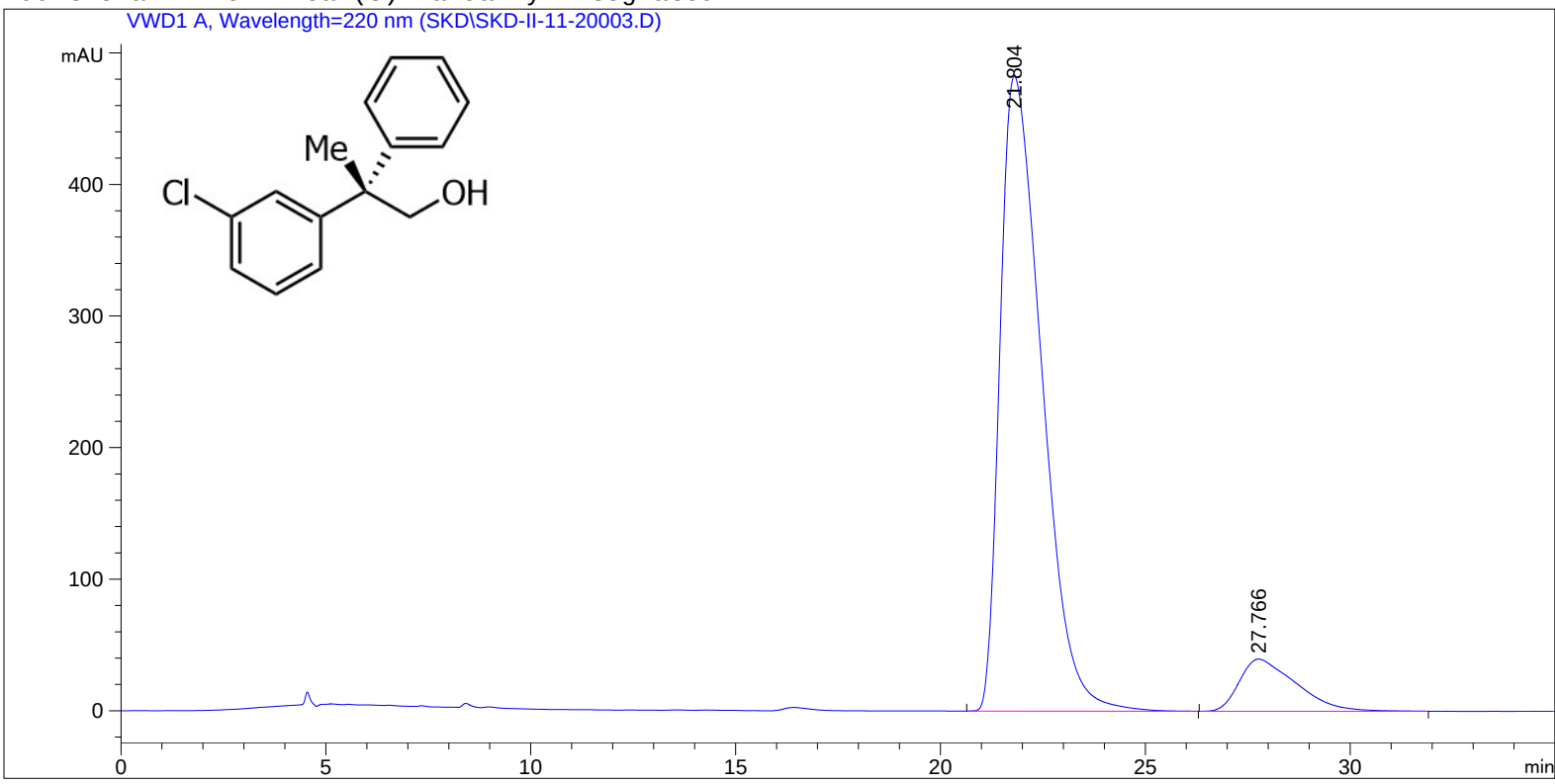

```
==========================================================================
Acq. Operator   : SYSTEM                          Seq. Line :   1
Acq. Instrument : 1220 HPLC                        Location : Vial 21
Injection Date  : 10/30/2018 11:05:31 PM               Inj :   1
                                                  Inj Volume : 10.000 µl
Acq. Method     : C:\CHEM32\2\METHODS\SKD_TRY.M
Last changed    : 10/30/2018 10:54:30 PM by SYSTEM
Analysis Method : C:\CHEM32\2\METHODS\DEF_LC.M
Last changed    : 10/2/2018 2:47:22 PM by SYSTEM
Sample Info     : Lux3u Cellulose-3, 95:5 Hex:IPA, 0.75 mL/min, 220 nm,40
                  min


Additional Info : Peak(s) manually integrated
```




```
==========================================================================
                          Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=220 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  22.022 BB    0.9515 4404.32715   66.08842  51.0363
   2  27.838 BB    1.3442 4225.47266   44.80743  48.9637

Totals :                  8629.79980  110.89585


==========================================================================
                          *** End of Report ***
```

Data File C:\CHEM32\2\DATA\SKD\SKD-II-11-20003.D
Sample Name: SKD-II-11-2c

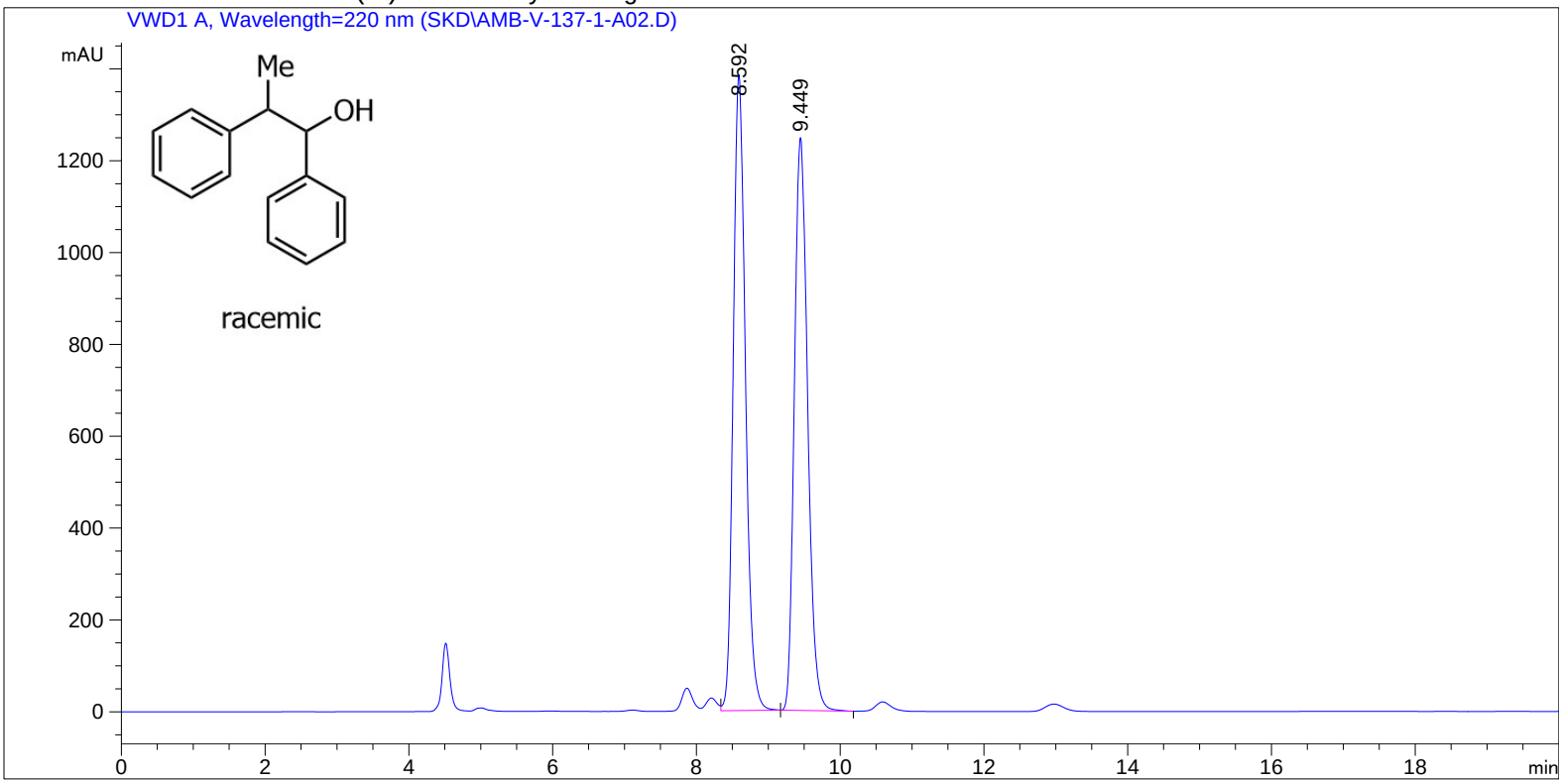

```
==================================================================
Acq. Operator   : SYSTEM                        Seq. Line :   3
Acq. Instrument : 1220 HPLC                      Location : Vial 21
Injection Date  : 10/30/2018 10:17:06 PM              Inj :   1
                                               Inj Volume : 10.000 µl
Acq. Method     : C:\CHEM32\2\METHODS\SKD_TRY.M
Last changed    : 10/30/2018 10:44:31 PM by SYSTEM
                  (modified after loading)
Analysis Method : C:\CHEM32\2\METHODS\DEF_LC.M
Last changed    : 10/2/2018 2:47:22 PM by SYSTEM
Sample Info     : Lux3u Cellulose-3, 95:5 Hex:IPA, 0.75 mL/min, 220 nm,40
                   min


Additional Info : Peak(s) manually integrated
```




```
==================================================================
                        Area Percent Report
==================================================================

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=220 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  21.804 BB    1.1016 3.40720e4   482.66177  90.0031
   2  27.766 BB    1.3436 3784.48901   39.61389   9.9969

Totals :                  3.78565e4   522.27566


==================================================================
```

Data File C:\CHEM32\2\DATA\SKD\AMB-V-137-1-A02.D
Sample Name: AMB-V-137-1-A-b

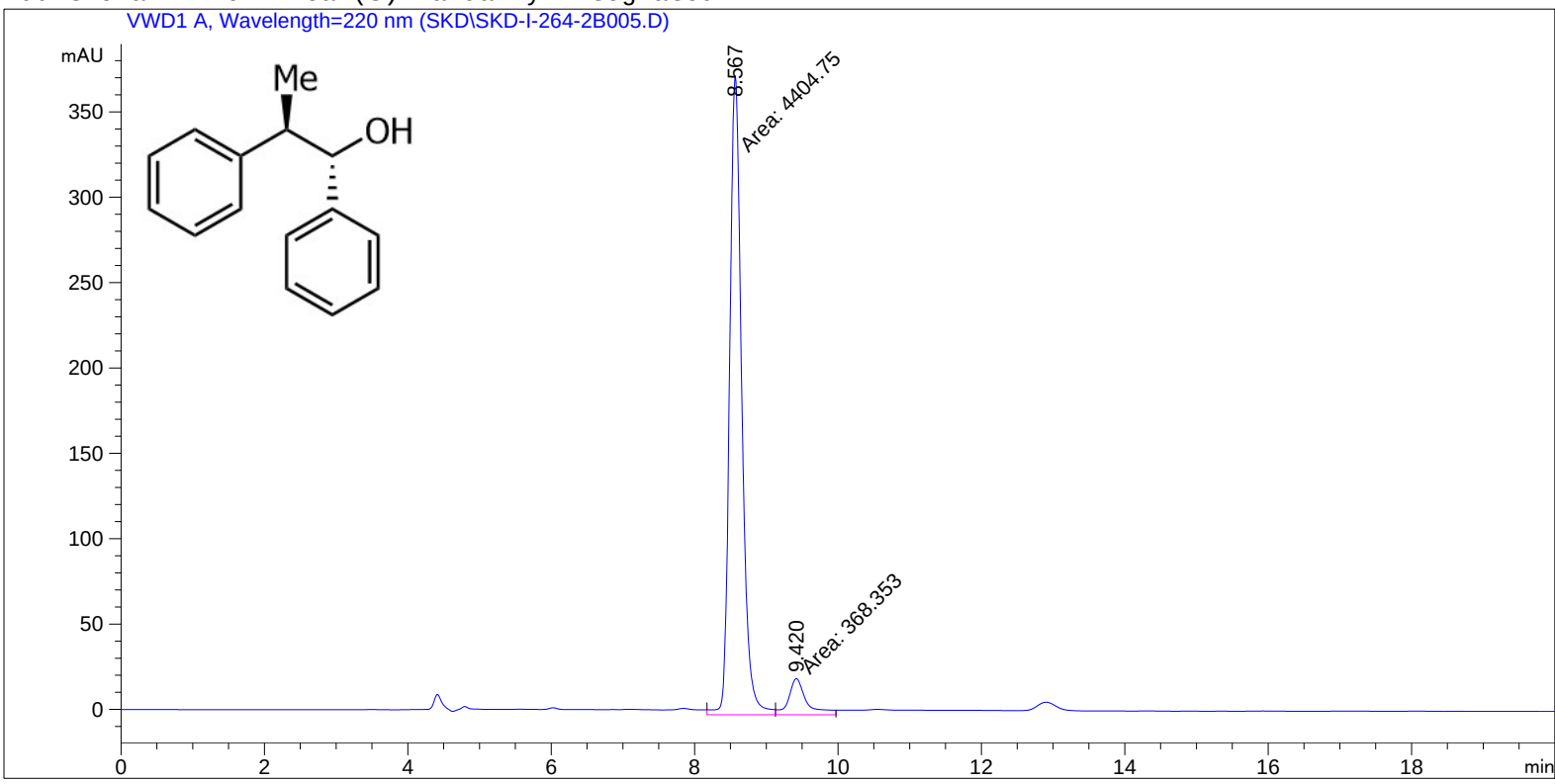

```
==========================================================================
Acq. Operator   : SYSTEM                          Seq. Line :   2
Acq. Instrument : 1220 HPLC                        Location : Vial 21
Injection Date  : 10/25/2018 1:03:54 AM                 Inj :   1
                                                 Inj Volume : 10.000 µl
Acq. Method     : C:\CHEM32\2\METHODS\SKD_TRY.M
Last changed    : 10/25/2018 12:34:56 AM by SYSTEM
Analysis Method : C:\CHEM32\2\METHODS\DEF_LC.M
Last changed    : 10/2/2018 2:47:22 PM by SYSTEM
Sample Info     : Lux3u Cellulose-4, 95:5 Hex:IPA, 0.75 mL/min, 220 nm, 2
                  0 min


Additional Info : Peak(s) manually integrated
```




```
==========================================================================
                          Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=220 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   8.592 VB    0.1844 1.64291e4  1384.48035  50.5578
   2   9.449 BB    0.2013 1.60665e4  1247.48218  49.4422

Totals :                  3.24956e4  2631.96252


==========================================================================
                          *** End of Report ***
```

Data File C:\CHEM32\2\DATA\SKD\SKD-I-264-2B005.D
Sample Name: SKD-I-264-2d


```
==================================================================
Acq. Operator   : SYSTEM                        Seq. Line :   5
Acq. Instrument : 1220 HPLC                      Location : Vial 21
Injection Date  : 10/25/2018 12:02:00 AM              Inj :   1
                                               Inj Volume : 10.000 µl
Acq. Method     : C:\CHEM32\2\METHODS\SKD_TRY.M
Last changed    : 10/24/2018 10:54:04 PM by SYSTEM
                  (modified after loading)
Analysis Method : C:\CHEM32\2\METHODS\DEF_LC.M
Last changed    : 10/2/2018 2:47:22 PM by SYSTEM
Sample Info     : Lux3u Cellulose-4, 95:5 Hex:IPA, 0.75 mL/min, 220 nm, 2
                  0 min


Additional Info : Peak(s) manually integrated
```




```
==================================================================
                        Area Percent Report
==================================================================

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=220 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   8.567 MF    0.1962 4404.74756  374.11041  92.2827
   2   9.420 FM    0.2900  368.35257   21.16996   7.7173

Totals :                  4773.10013  395.28037

==================================================================
```