Synthesis of 2,3-Dihydrobenzofurans via Palladium Catalyzed Carboalkoxylation of 2-Allylphenols

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Supporting Information

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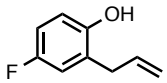
General Considerations

All reactions were carried out in flame-dried glassware under a nitrogen atmosphere unless otherwise indicated. All reagents were obtained from commercial sources and used without further purification unless otherwise indicated. Lithium *tert*-butoxide was stored in a nitrogen glovebox and removed in small portions (50-500 mg) prior to use. Trifluorotoluene was purified by distillation from P_2O_5. The following aryl triflates were prepared using the procedure developed by Frantz and co-workers;[1] compounds were consistent with previously reported spectral data: 4-fluorophenyl trifluoromethanesulfonate, [2] 4-chlorophenyl trifluoromethanesulfonate,[2] 4-methoxyphenyl trifluoromethanesulfonate,[2] 4-benzoylphenyl

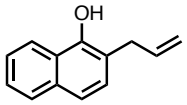
trifluoromethanesulfonate, [3] benzo[*d*][1,3]dioxol-5-yl trifluoromethanesulfonate, [4] 3-methoxyphenyl trifluoromethanesulfonate,[3] 4-cyanophenyl trifluoromethanesulfonate.[2] The following allyl phenyl ethers were prepared using the procedure developed by Zhang and co-workers;[5] compounds were consistent with previously reported spectral data: 1-(allyloxy)-4-fluorobenzene, [6] 1-(allyloxy)-4-chlorobenzene,[5] 1-(allyloxy)-4-methoxybenzene,[5] 1-(allyloxy)naphthalene, [7] (*E*)-(but-2-en-1-yloxy)benzene, [8] (cinnamyloxy)benzene, [9] [(2-methylallyl)oxy]benzene,[8] 1,4-bis(allyloxy)benzene. [10] Additionally, 2-cinnamylphenol [11] was prepared according to the reported literature procedure. Yields refer to isolated material that is determined to be >95% purity as determined by ^{1}H NMR analysis unless otherwise noted. Structural and stereochemical assignments were made on the basis of 2-D COSY and 1-D NOESY experiments. Ratios of diastereomers were determined by either ^{1}H NMR analysis, prior to and upon flash chromatography, or by gas chromatography.

Preparation and Characterization of Substrates



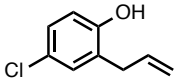
2-Allyl-4-fluorophenol (2b). Neat 1-(allyloxy)-4-fluorobenzene[6] (0.65 g, 4.3 mmol) was added to a flame dried Schlenk flask equipped with a stir bar and the neat material was heated to 200 °C for 16 h. The flask was cooled to rt and the crude product was then purified by silica gel flash chromatography to obtain 0.64 g (98%) of 2-allyl-4-fluorophenol. Spectroscopic data were consistent with those previously reported.[6]

^{1}H NMR (500 MHz, $CDCl_3$): δ 6.86 – 6.79 (m, 2H), 6.75 (dd, *J* = 8.4, 4.7 Hz, 1H), 6.06 – 5.90 (m, 1H), 5.22 – 5.12 (m, 2H), 4.75 (s, 1H), 3.38 (dt, *J* = 6.4, 1.7 Hz, 2H). **^{13}C NMR (176 MHz, $CDCl_3$):** δ 157.3 (d, *J* = 238.1 Hz), 150.1, 135.7, 127.2, 117.1, 116.8 (d, *J* = 23.2 Hz), 116.7 (d, *J* = 8.8 Hz), 114.0 (d, *J* = 8.8 Hz), 35.1.



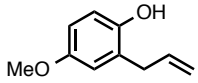
2-Allylnaphthalen-1-ol (2c). Neat 1-(allyloxy)naphthalene[7] (0.64 g, 3.5 mmol) was added to a flame dried Schlenk flask equipped with a stir bar and the neat material was heated to 200 °C for 16 h. The flask was cooled to rt and the crude product was then purified by silica gel flash chromatography to obtain 0.61 g (95%) of 2-allylnaphthalen-1-ol. Spectroscopic data were consistent with those previously reported.[7]

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.16 (ddd, *J* = 7.3, 2.2, 1.1 Hz, 1H), 7.77 (d, *J* = 7.4 Hz, 1H), 7.49 – 7.42 (m, 2H), 7.40 (d, *J* = 8.3 Hz, 1H), 7.24 – 7.19 (m, 1H), 6.13 – 6.01 (m, 1H), 5.52 (s, 1H), 5.30 – 5.19 (m, 2H), 3.56 (dd, *J* = 6.3, 1.7 Hz, 2H). **^{13}C NMR (126 MHz, $CDCl_3$):** δ 149.7, 136.3, 133.9, 128.6, 127.7, 125.9, 125.4, 125.0, 121.5, 120.5, 117.9, 117.1, 35.9.



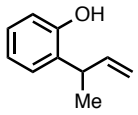
2-Allyl-4-chlorophenol (2d). Neat 1-(allyloxy)-4-chlorobenzene[5] (0.74 g, 4.4 mmol) was added to a flame dried Schlenk flask equipped with a stir bar and the neat material was heated to 200 °C for 16 h. The flask was cooled to rt and the crude product was then purified by silica gel flash chromatography to obtain 0.74 g (99%) of 2-allyl-4-chlorophenol. Spectroscopic data were consistent with those previously reported.[5]

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.09 (d, *J* = 6.6 Hz, 2H), 6.74 (d, *J* = 9.1 Hz, 1H), 5.98 (ddt, *J* = 16.7, 10.2, 6.4 Hz, 1H), 5.24 – 5.12 (m, 2H), 4.89 (s, 1H), 3.37 (d, *J* = 6.0 Hz, 2H). **^{13}C NMR (126 MHz, $CDCl_3$):** δ 152.8, 135.6, 130.2, 127.7, 127.2, 125.7, 117.3, 117.2, 35.0.



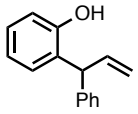
2-Allyl-4-methoxyphenol (2e). Neat 1-(allyloxy)-4-methoxybenzene[5] (0.18 g, 1.1 mmol) was added to a flame dried Schlenk flask equipped with a stir bar and the neat material was heated to 200 °C for 16 hours. The flask was cooled to rt and the resulting 0.18 g (quantitative yield) of 2-allyl-4-methoxyphenol was used without further purification. Spectroscopic data were consistent with those previously reported.[5]

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.80 – 6.72 (m, 1H), 6.68 (dd, *J* = 4.6, 2.1 Hz, 2H), 6.01 (ddt, *J* = 17.5, 9.6, 6.3 Hz, 1H), 5.21 – 5.14 (m, 1H), 5.17 – 5.11 (m, 1H), 4.61 (s, br, 1H), 3.76 (s, 3H), 3.38 (dt, *J* = 6.4, 1.7 Hz, 2H). **^{13}C NMR (176 MHz, $CDCl_3$):** δ 153.9, 148.1, 136.3, 126.7, 116.7, 116.6, 116.1, 112.8, 55.9, 35.4.



2-(But-3-en-2-yl)phenol (2f). Neat [(2-methylallyl)oxy]benzene[8] (1.0 g, 6.7 mmol) was added to a flame dried Schlenk flask equipped with a stir bar and dissolved in DMF (4.0 mL). The mixture was then heated to 200 °C for 17 h then was cooled to rt. The reaction mixture was poured into EtOAc (75 mL), extracted with water (30 mL) and brine (30 mL), dried over sodium sulfate and concentrated. The crude oil was then purified by silica gel flash chromatography to obtain 0.71 g (71%) of 2-(but-3-en-2-yl)phenol as a clear oil. Spectroscopic data were consistent with those previously reported.[12]

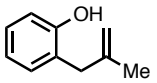
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.13 (ddd, *J* = 13.4, 7.4, 1.5 Hz, 2H), 6.91 (td, *J* = 7.5, 1.3 Hz, 1H), 6.80 (dd, *J* = 7.9, 1.3 Hz, 1H), 6.08 (ddd, *J* = 17.6, 10.3, 6.0 Hz, 1H), 5.25 – 5.12 (m, 2H), 5.02 (s, 1H), 3.70 (t, *J* = 6.8 Hz, 1H), 1.40 (dd, *J* = 7.1, 1.0 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$):** δ 153.8, 142.5, 130.4, 128.2, 127.8, 121.1, 116.3, 114.5, 37.9, 18.9.



2-(1-Phenylallyl)phenol (2g). Neat (cinnamyloxy)benzene[9] (0.69 g, 3.3 mmol) was added to a flame dried Schlenk flask equipped with a stir bar and dissolved in DMF (3.2 mL). The mixture was then heated to 200 °C for 11 h then was cooled to rt. The reaction mixture was poured into EtOAc (75 mL), extracted with water (30 mL) and brine (30 mL), dried over sodium sulfate and concentrated. The crude oil was then purified by silica gel flash chromatography to obtain 0.41 g (59%) of 2-(1-phenylallyl)phenol as a clear oil.

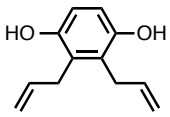
^{1}H NMR (700 MHz, C_6D_6): δ 7.19 – 7.12 (m, 2H), 7.09 (m, 3H), 7.01 (dt, *J* = 8.3, 4.0 Hz, 1H), 6.96 (tt, *J* = 7.6, 2.0 Hz, 1H), 6.78 (tt, *J* = 7.6, 1.6 Hz, 1H), 6.42 (dt, *J* = 8.1, 1.6 Hz, 1H), 6.21 – 6.12 (m,

1H), 5.07 (dd, *J* = 10.2, 1.8 Hz, 1H), 4.98 (d, *J* = 6.7 Hz, 1H), 4.93 (dq, *J* = 17.2, 1.9 Hz, 1H), 4.31 (s, 1H). **^{13}C NMR (176 MHz, C_6D_6):** δ 154.04, 142.42, 140.08, 130.03, 129.6, 129.0, 128.7, 128.3, 126.7, 121.0, 116.6, 116.2, 49.1. **HR-MS (EI):** calculated for $C_{15}H_{14}O$ $[M]^+$ 210.1044, found 210.1044. **IR (film):** 5322, 3060, 3027, 2977, 1634, 1592, 1489, 1452, 1197, 919, 750, 698 cm^{-1}.



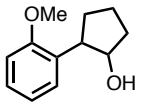
2-(2-Methylallyl)phenol (2h). Neat [(2-methylallyl)oxy]benzene[8] (1.5 g, 10 mmol) was added to a flame dried Schlenk flask equipped with a stir bar and dissolved in DMF (6.5 mL). The mixture was then heated to 210 °C for 16 h then was cooled to rt. The reaction mixture was poured into EtOAc (75 mL), extracted with water (30 mL) and brine (30 mL), dried over sodium sulfate and concentrated. The crude oil was then purified by silica gel flash chromatography to obtain 0.95 g (63%) of 2-(2-methylallyl)phenol as a clear oil. Spectroscopic data were consistent with those previously reported.[13]

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.19 – 7.10 (m, 1H), 7.09 (d, *J* = 7.4 Hz, 1H), 6.92 – 6.85 (m, 1H), 6.83 (d, *J* = 8.0 Hz, 1H), 5.17 (s, 1H), 4.89 (d, *J* = 28.2 Hz, 2H), 3.38 (s, 2H), 1.74 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 154.8, 144.8, 131.1, 128.2, 124.9, 120.9, 116.2, 112.5, 40.1, 22.2.



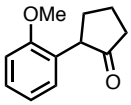
2,3-Diallylbenzene-1,4-diol (2k). Neat 1,4-bis(allyloxy)benzene[10] (1.0 g, 5.3 mmol) was added to a flame dried Schlenk flask equipped with a stir bar and dissolved in DMF (4.0 mL). The mixture was heated to 210 °C for 12 h then was cooled to rt. The reaction mixture was poured into EtOAc (75 mL), extracted with water (30 mL) and brine (30 mL), dried over sodium sulfate and concentrated. The crude material was then purified by silica gel flash chromatography (20% EtOAc/Hexanes. 2,3-diallylbenzene-1,4-diol was the lower R_f of the two major spots with the higher R_f spot being the regioisomeric 2,5-diallylbenzene-1,4-diol). This procedure afforded 0.38 g (38%) of 2,3-diallylbenzene-1,4-diol as a white solid. Spectroscopic data were consistent with those previously reported.[10]

^{1}H NMR (500 MHz, $CDCl_3$): δ 6.64 (s, 2H), 6.06 – 5.84 (m, 2H), 5.09 (dq, *J* = 10.1, 1.7 Hz, 2H), 5.01 (dq, *J* = 17.3, 1.9 Hz, 2H), 4.50 (s, 2H), 3.42 (dp, *J* = 5.0, 2.0, 1.5 Hz, 4H). **^{13}C NMR (126 MHz, $CDCl_3$):** δ 148.3, 136.1, 125.4, 115.8, 114.7, 30.9.



2-(2-Methoxyphenyl)cyclopentan-1-ol (S1a). A 50 mL round bottom flask equipped with a magnetic stir bar was charged with magnesium turnings (0.70 g, 29 mmol) and THF (20 mL). A solution of 2-bromoanisole (3.8 mL, 30 mmol) in THF (8.0 mL) was then added slowly to the magnesium suspension at room temperature. Upon initiation of the Grignard reaction the flask was cooled in an ice bath and stirred until the magnesium had been completely consumed. The flask was then cooled to –30 °C, CuCl (0.16 g, 1.6 mmol) was added, and the resulting mixture was stirred for 5 min at –30 °C. A solution of cyclopentene oxide (1.8 mL, 20 mmol, 1.0 equiv) in THF (3.0 mL) was added and the resulting solution was stirred for 1 h at –30 °C, then was warmed to 0 °C and stirred for an additional 30 min. The reaction was then quenched with saturated aqueous ammonium chloride (20 mL) and extracted into EtOAc (3 x 30 mL). The combined organic layers were then washed with brine, dried over sodium sulfate, concentrated and purified by silica gel flash chromatography, providing 2.9 g (76%) of 2-(2-methoxyphenyl)cyclopentan-1-ol as a white solid. Spectroscopic data were consistent with those previously reported.[14]

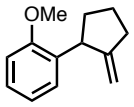
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.24 – 7.18 (m, 2H), 6.95 (td, *J* = 7.5, 1.1 Hz, 1H), 6.89 (dd, *J* = 8.5, 1.1 Hz, 1H), 4.18 (q, *J* = 6.2 Hz, 1H), 3.86 (s, 3H), 3.28 (q, *J* = 8.0 Hz, 1H), 2.47 – 2.32 (m, 1H), 2.15 – 1.97 (m, 2H), 1.94 – 1.76 (m, 2H), 1.72 (dtdd, *J* = 9.2, 7.7, 3.6, 2.6 Hz, 1H). **^{13}C NMR (126 MHz, $CDCl_3$):** δ 157.7, 131.7, 127.4, 127.1, 121.0, 110.7, 79.8, 55.6, 48.9, 34.6, 30.5, 23.1.



2-(2-Methoxyphenyl)cyclopentan-1-one (S1b). A flame-dried 250 mL round bottom flask was charged with dichloromethane (42 mL) and oxalyl chloride (1.2 mL, 14 mmol) and cooled to –78

°C. DMSO (2.0 mL, 28 mmol) was added dropwise and the resulting mixture was stirred at rt for 5 min. A solution of 2-(2-methoxyphenyl)cyclopentan-1-ol in dichloromethane (16 mL) was then added over 10 min. The resulting solution was stirred at rt for an additional 15 min, then triethylamine (8.8 mL, 63 mmol) was added. The reaction was then warmed to rt slowly and poured into water (40 mL). The layers were separated; the aqueous layer was extracted with additional dichloromethane (40 mL) and the combined organic layers were washed with 1% HCl (100 mL), saturated sodium bicarbonate (100 mL), brine (50 mL), dried over sodium sulfate and concentrated. The crude material was then purified by silica gel flash chromatography to provide 2.3 g (95%) of 2-(2-methoxyphenyl)cyclopentan-1-one as a white solid.

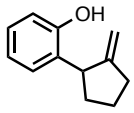
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.23 (td, *J* = 7.9, 1.7 Hz, 1H), 7.07 (dd, *J* = 7.4, 1.7 Hz, 1H), 6.91 (td, *J* = 7.5, 1.1 Hz, 1H), 6.87 (dd, *J* = 8.2, 1.1 Hz, 1H), 3.77 (s, 3H), 3.37 (dd, *J* = 11.2, 8.6 Hz, 1H), 2.50 – 2.38 (m, 2H), 2.38 – 2.29 (m, 1H), 2.25 – 2.07 (m, 2H), 1.99 – 1.76 (m, 1H). **^{13}C NMR (126 MHz, $CDCl_3$):** δ 219.3, 156.9, 130.6, 128.5, 128.4, 120.9, 111.3, 55.4, 52.6, 38.4, 31.3, 21.7. **HR-MS (ESI):** calculated for $C_{12}H_{15}O_2$ $[M+H]^+$ 191.1067, found 191.1067. **IR (film):** 2958, 2863, 1723, 1495, 1248, 1026, 753, 742 cm^{-1}. **mp** 45–47 °C.



1-Methoxy-2-(2-methylenecyclopentyl)benzene (S1c). A flame-dried 250 mL round bottom flask was charged with potassium *tert*-butoxide (1.7 g, 15 mmol), methyltriphenylphosphonium bromide (5.9 g, 16 mmol) and diethyl ether (69 mL). The mixture was then stirred at rt for 30 min, then was cooled to 0 °C in an ice bath and 2-(2-methoxyphenyl)cyclopentan-1-one (2.2 g, 11 mmol) in diethyl ether (10 mL) was added slowly. The reaction vessel was then removed from the ice bath, stirred for 1 h, diluted with pentane, filtered, concentrated and purified by silica gel flash chromatography to provide 1.9 g (89%) of 1-methoxy-2-(2-methylenecyclopentyl)benzene as a clear oil.

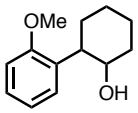
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.18 (ddd, *J* = 7.3, 4.2, 2.5 Hz, 2H), 6.96 – 6.83 (m, 2H), 4.95 (s, 1H), 4.55 (s, 1H), 3.99 (t, *J* = 7.9 Hz, 1H), 3.83 (s, 3H), 2.57 – 2.45 (m, 2H), 2.19 – 2.05 (m, 1H), 1.85 (ddt, *J* = 14.0, 6.7, 4.3 Hz, 1H), 1.71 (dddd, *J* = 20.5, 15.6, 10.3, 8.2 Hz, 2H). **^{13}C NMR (100 MHz,**

$CDCl_3$): δ 157.6, 156.4, 133.6, 128.8, 127.0, 120.7, 110.7, 106.2, 55.7, 44.4, 35.1, 33.8, 25.1. **HR-MS (EI):** calculated for $C_{13}H_{16}O$ $[M]^+$ 188.1201, found 188.1202. **IR (film):** 3069, 2952, 2867, 1652, 1599, 1490, 1462, 1238, 1030, 878, 749 cm^{-1}.



2-(2-Methylenecyclopentyl)phenol (2i). Based on a previously reported procedure,[15] a flame-dried 25 mL round bottom flask equipped with a stir bar and a reflux condenser was charged with sodium hydride (60% suspension in mineral oil) (0.33 g, 8.3 mmol). The flask was then cooled to 0 °C in an ice bath and a 2.0 M solution of ethanethiol in DMF (4.2 mL, 8.3 mmol) was added slowly. Once the addition was complete the reaction mixture was stirred for an additional 30 min then a solution of 1-methoxy-2-(2-methylenecyclopentyl)benzene (0.60 g, 3.2 mmol) in DMF (1.6 mL) was added. The reaction flask was then placed in a preheated oil bath and stirred at 150 °C for 2 h. The crude reaction mixture was poured in 1 M HCl (50 mL), extracted into EtOAc (3 x 50 mL) and the combined organic layers were washed with brine, dried over sodium sulfate, concentrated and purified by silica gel flash chromatography to obtain 0.23 g (41%) of 2-(2-methylenecyclopentyl)phenol as a clear oil.

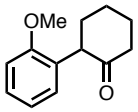
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.18 – 7.09 (m, 2H), 6.90 (td, *J* = 7.5, 1.2 Hz, 1H), 6.85 (dd, *J* = 8.4, 1.2 Hz, 1H), 5.09 (t, *J* = 2.5 Hz, 1H), 5.05 (s, 1H), 4.78 (q, *J* = 2.7 Hz, 1H), 3.72 (ddd, *J* = 10.5, 7.7, 3.1 Hz, 1H), 2.67 – 2.44 (m, 2H), 2.17 – 2.04 (m, 1H), 1.90 (tdd, *J* = 11.4, 5.9, 2.6 Hz, 1H), 1.83 (ddt, *J* = 12.0, 10.8, 5.1 Hz, 1H), 1.77 – 1.64 (m, 1H). **^{13}C NMR (126 MHz, $CDCl_3$):** δ 154.4, 153.8, 130.4, 129.6, 127.8, 121.1, 117.0, 107.5, 48.0, 34.5, 33.0, 24.7. **HR-MS (EI):** calculated for $C_{12}H_{15}O$ $[M]^+$ 175.1117, found 175.1114. **IR (film):** 3427, 3067, 2954, 2867, 1650, 1590, 1488, 1451, 1213, 879, 749 cm^{-1}.



2-(2-Methoxyphenyl)cyclohexan-1-ol (S2a). A flame-dried 50 mL round bottom flask equipped with a magnetic stir bar was charged with freshly ground magnesium (0.70 g, 29 mmol) and THF

(20 mL). A solution of 2-bromoanisole (3.8 mL, 30 mmol) in THF (8.0 mL) was then added slowly to the magnesium suspension at rt. Upon initiation of the Grignard reaction the flask was cooled in an ice bath and stirred until full consumption of the magnesium was observed. The flask was then cooled to –30 °C, CuCl (0.16 g, 1.6 mmol) was added, and the resulting mixture was stirred for 5 at –30 °C for 5 min. A solution of cyclohexene oxide (2.0 mL, 20 mmol) in THF (3.0 mL) was added and the resulting solution was stirred for 1 h at –30 °C then was warmed to 0 °C and stirred for an additional 30 min. The reaction was then quenched with concentrated aqueous ammonium chloride (20 mL) and extracted into EtOAc (3 x 30 mL). The combined organic layers were then washed with brine, dried over sodium sulfate, concentrated and purified by silica gel flash chromatography, providing 2.6 g (62%) of 2-(2-methoxyphenyl)cyclohexan-1-ol as a white solid. Spectroscopic data were consistent with those previously reported.[14]

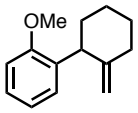
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.28 – 7.23 (m, 1H), 7.23 – 7.17 (m, 1H), 6.97 (td, *J* = 7.5, 1.2 Hz, 1H), 6.89 (dd, *J* = 8.2, 1.2 Hz, 1H), 3.83 (s, 3H), 3.74 (ddd, *J* = 10.6, 6.4, 3.8 Hz, 1H), 3.01 (ddd, *J* = 13.4, 10.4, 3.6 Hz, 1H), 2.21 – 2.08 (m, 1H), 1.89 – 1.77 (m, 2H), 1.77 – 1.70 (m, 2H), 1.50 (qd, *J* = 12.5, 3.4 Hz, 1H), 1.45 – 1.34 (m, 2H). **^{13}C NMR (126 MHz, $CDCl_3$):** δ 157.9, 131.6, 127.6, 127.4, 121.2, 111.0, 74.2, 55.7, 45.2, 35.4, 32.5, 26.3, 25.3.



2-(2-Methoxyphenyl)cyclohexan-1-one (S2b). A flame-dried 250 mL round bottom flask was charged with dichloromethane (42 mL) and oxalyl chloride (1.0 mL, 12 mmol) and cooled to –78 °C. A solution of DMSO (1.8 mL, 25 mmol) was added dropwise and the reaction mixture was stirred for 5 min at –78 °C. A solution of 2-(2-methoxyphenyl)cyclohexan-1-ol in dichloromethane (16 mL) was then added over 10 min. The resulting solution was stirred for an additional 15 min followed by the addition of triethylamine (7.9 mL, 57 mmol). The reaction was then warmed to rt slowly and poured into water (40 mL). The layers were separated; the aqueous layer was extracted with additional dichloromethane (40 mL) and the combined organic layers were washed with 1% HCl (100 mL), saturated sodium bicarbonate (100 mL),

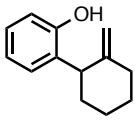
brine (50 mL), dried over sodium sulfate and concentrated. The crude material was then purified by silica gel flash chromatography to provide 2.2 g (93%) of 2-(2-methoxyphenyl)cyclohexan-1-one as a white solid. Spectroscopic data were consistent with those previously reported.[16]

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.27 (td, *J* = 7.8, 1.6 Hz, 1H), 7.15 (dt, *J* = 7.6, 1.3 Hz, 1H), 6.99 (td, *J* = 7.5, 1.1 Hz, 1H), 6.91 (d, *J* = 8.2 Hz, 1H), 3.98 (dd, *J* = 13.0, 5.5 Hz, 1H), 3.79 (s, 3H), 2.64 – 2.44 (m, 2H), 2.21 (dddt, *J* = 27.4, 11.9, 5.9, 3.1 Hz, 2H), 2.13 – 1.95 (m, 2H), 1.93 – 1.71 (m, 2H). **^{13}C NMR (126 MHz, $CDCl_3$):** δ 209.6, 156.8, 128.6, 127.8, 127.7, 120.4, 110.5, 55.3, 50.9, 42.2, 33.3, 27.5, 25.6.



1-Methoxy-2-(2-methylenecyclohexyl)benzene (S2c). A flame-dried 250 mL round bottom flask was charged with potassium *tert*-butoxide (1.6 g, 14 mmol), methyltriphenylphosphonium bromide (5.3 g, 15 mmol) and diethyl ether (63 mL). The mixture was then stirred at rt for 30 min then was cooled to 0 °C in an ice bath and a solution of 2-(2-methoxyphenyl)cyclohexan-1-one (2.2 g, 11 mmol) in diethyl ether (10 mL) was added slowly. The reaction flask was then removed from the ice bath, stirred for 1 h, diluted with pentane, filtered, concentrated and purified by silica gel flash chromatography to provide 1.9 g (88%) of 1-methoxy-2-(2-methylenecyclohexyl)benzene as a clear oil.

^{1}H NMR (401 MHz, $CDCl_3$): δ 7.21 (td, *J* = 7.4, 7.0, 1.8 Hz, 2H), 6.96 (td, *J* = 7.5, 1.2 Hz, 1H), 6.89 (dd, *J* = 8.7, 1.2 Hz, 1H), 4.61 (q, *J* = 1.9 Hz, 1H), 3.97 (q, *J* = 1.8 Hz, 1H), 3.80 (s, 3H), 3.71 (dd, *J* = 12.4, 4.1 Hz, 1H), 2.46 (dq, *J* = 13.2, 2.2 Hz, 1H), 2.30 – 2.16 (m, 1H), 2.00 – 1.83 (m, 1H), 1.77 (qd, *J* = 12.5, 3.4 Hz, 1H), 1.68 – 1.54 (m, 1H), 1.44 (tdd, *J* = 16.5, 7.9, 3.9 Hz, 1H). **^{13}C NMR (101 MHz, $CDCl_3$):** δ 157.2, 152.8, 132.2, 128.6, 127.1, 120.5, 110.8, 106.6, 55.9, 42.3, 36.9, 33.8, 28.8, 27.1. **HR-MS (EI):** calculated for $C_{14}H_{18}O$ $[M]^+$ 202.1358, found 202.1358. **IR (film):** 2927, 2854, 1644, 1600, 1492, 1461, 1437, 1236, 1029, 890, 750 cm^{-1}.

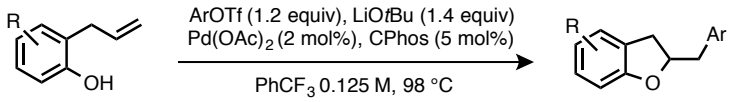


2-(2-Methylenecyclohexyl)phenol (2j). Based on a previously reported procedure.[15] A flame-dried 25 mL round bottom flask equipped with a stir bar and a reflux condenser was charged with sodium hydride (60% w/w) (0.51 g, 13 mmol). The flask was then cooled to 0 °C in an ice bath and a 2.0 M solution of ethanethiol in DMF (6.4 mL, 13 mmol) was added slowly. Once the addition was complete the reaction was stirred for an additional 30 minutes followed by the addition of 1-methoxy-2-(2-methylenecyclohexyl)benzene (1.0 g, 4.9 mmol) in DMF (2.5 mL). The reaction was placed in a preheated oil bath and stirred at 150 °C for 2 hours. The crude reaction mixture was then poured in 1 M HCl (50 mL), extracted into EtOAc (3 x 50 mL) and the combined organic layers were washed with brine, dried over sodium sulfate, concentrated and purified by silica gel flash chromatography to obtain 0.71 g (76%) of 2-(2-methylenecyclohexyl)phenol as a clear oil.

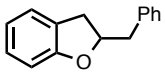
^{1}H NMR (700 MHz, $CDCl_3$): δ 7.19 – 7.13 (m, 2H), 6.95 (td, *J* = 7.5, 1.3 Hz, 1H), 6.87 (dd, *J* = 8.0, 1.2 Hz, 1H), 4.91 (s, 1H), 4.79 (q, *J* = 1.8 Hz, 1H), 4.30 (q, *J* = 1.7 Hz, 1H), 3.40 (dd, *J* = 12.1, 4.0 Hz, 1H), 2.54 – 2.46 (m, 1H), 2.22 (dddt, *J* = 13.1, 11.8, 4.7, 1.3 Hz, 1H), 2.04 – 1.88 (m, 2H), 1.82 (qd, *J* = 12.3, 3.5 Hz, 1H), 1.60 (qt, *J* = 12.8, 3.5 Hz, 1H), 1.45 (qt, *J* = 12.9, 3.8 Hz, 1H). **^{13}C NMR (126 MHz, $CDCl_3$):** δ 154.4, 153.8, 130.4, 129.6, 127.8, 121.1, 117.0, 107.5, 76.9, 48.0, 34.5, 33.0, 24.7. **HR-MS (EI):** calculated for $C_{13}H_{16}O$ $[M]^+$ 189.1274, found 189.1272. **IR (film):** 3441, 3074, 2927, 2854, 1642, 1487, 1448, 1223, 1174, 893, 749 cm^{-1}.

Preparation and Characterization of 2,3-Dihydrobenzofurans

General procedure for the synthesis of 2,3-dihydrobenzofurans

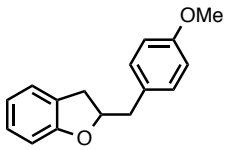


CPhos (5.0 mol%) and lithium tert-butoxide (1.4 equiv) were added to an oven-dried 5 mL test tube equipped with a stir bar that was then sealed with a septa. The test tube was then flushed with nitrogen. Benzotrifluoride (0.25 M) was then added, followed by the 2-allylphenol substrate (1 equiv) and aryl triflate (1.2 equiv) by microsyringe (solid 2-allylphenols and aryl triflates were added earlier with the other solid reagents). Palladium acetate (2.0 mol%) was then added in a freshly prepared benzotrifluoride solution (1.1 mg/mL), bringing the final 2-allylphenol substrate concentration to 0.125 M. The reaction was then heated to 98 °C for 15 hours. Upon completion the reaction was cooled to rt, quenched with concentrated aqueous ammonium chloride (3.0 mL), and then extracted with ethyl acetate (3 x 4 mL), washed with brine (6.0 mL), dried over Na_2SO_4 and concentrated. The crude material was purified by silica gel flash chromatography.



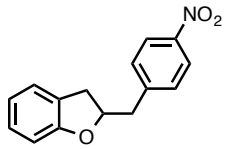
2-Benzyl-2,3-dihydrobenzofuran (4a). The coupling of 2-allylphenol (33 μL, 0.25 mmol) and phenyl trifluoromethanesulfonate (49 μL, 0.30 mmol) was performed using the general procedure. Upon purification by silica gel flash chromatography 45 mg (85%) of 2-benzyl-2,3-dihydrobenzofuran was obtained as a clear oil. Known compound, corresponds with previously reported spectra.[15]

^{1}H NMR (401 MHz, $CDCl_3$): δ 7.38 – 7.22 (m, 5H), 7.18 – 7.08 (m, 2H), 6.84 (td, *J* = 7.4, 1.1 Hz, 1H), 6.80 (d, *J* = 8.1 Hz, 1H), 5.02 (dq, *J* = 8.8, 7.0 Hz, 1H), 3.28 – 3.15 (m, 2H), 2.95 (ddd, *J* = 13.9, 10.0, 7.1 Hz, 2H). **^{13}C NMR (101 MHz, $CDCl_3$):** δ 159.5, 137.6, 129.5, 128.7, 128.1, 126.7, 126.7, 125.1, 120.4, 109.6, 83.6, 42.1, 35.1.



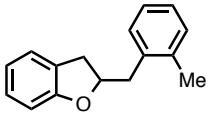
2-(4-Methoxybenzyl)-2,3-dihydrobenzofuran (4b). The coupling of 2-allylphenol (33 μL, 0.25 mmol) and 4-methoxyphenyl trifluoromethanesulfonate (77 mg, 0.30 mmol) was performed using the general procedure. Upon purification by silica gel flash chromatography 45 mg (75%) of 2-(4-methoxybenzyl)-2,3-dihydrobenzofuran was obtained as a clear oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.20 (d, *J* = 8.2 Hz, 2H), 7.18 – 7.08 (m, 2H), 6.88 (d, *J* = 8.2 Hz, 2H), 6.84 (t, *J* = 7.4 Hz, 1H), 6.80 (d, *J* = 8.0 Hz, 1H), 5.04 – 4.90 (m, 1H), 3.81 (s, 3H), 3.21 (dd, *J* = 15.6, 8.9 Hz, 1H), 3.14 (dd, *J* = 13.9, 6.8 Hz, 1H), 2.96 (dd, *J* = 15.6, 7.5 Hz, 1H), 2.89 (dd, *J* = 13.9, 6.7 Hz, 1H). **^{13}C NMR (126 MHz, $CDCl_3$):** δ 159.6, 158.5, 130.5, 129.6, 128.1, 126.8, 125.1, 120.4, 114.1, 109.6, 83.9, 55.4, 41.2, 35.0. **HR-MS (EI):** calculated for $C_{16}H_{16}O_2$ $[M]^+$ 240.1150, found 240.1152. **IR (film):** 2930, 1604, 1511, 1477, 1231, 1175, 1033, 749 cm^{-1}.



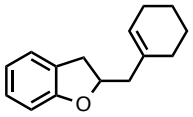
2-(4-Nitrobenzyl)-2,3-dihydrobenzofuran (4c). The coupling of 2-allylphenol (33 μL, 0.25 mmol) and 4-nitrophenyl trifluoromethanesulfonate (81 mg, 0.30 mmol) was performed using the general procedure. Upon purification by silica gel flash chromatography 45 mg (74%) of 2-(4-nitrobenzyl)-2,3-dihydrobenzofuran was obtained as a clear oil.

^{1}H NMR (401 MHz, $CDCl_3$): δ 8.18 (d, *J* = 8.7 Hz, 2H), 7.45 (d, *J* = 8.5 Hz, 2H), 7.19 – 7.06 (m, 2H), 6.84 (t, *J* = 7.4 Hz, 1H), 6.77 (d, *J* = 8.0 Hz, 1H), 5.03 (dtd, *J* = 8.9, 7.5, 5.1 Hz, 1H), 3.32 (dd, *J* = 15.6, 8.9 Hz, 1H), 3.20 (dd, *J* = 14.1, 7.8 Hz, 1H), 3.08 (dd, *J* = 14.1, 5.1 Hz, 1H), 2.95 (dd, *J* = 15.6, 7.2 Hz, 1H). **^{13}C NMR (101 MHz, $CDCl_3$):** δ 159.2, 147.0, 145.5, 130.4, 128.3, 126.2, 125.1, 123.8, 120.8, 109.7, 82.5, 42.0, 35.3. **HR-MS (EI):** calculated for $C_{15}H_{13}NO_3$ $[M]^+$ 255.0895, found 255.0895. **IR (film):** 2920, 1596, 1510, 1476, 1346, 1231, 749 cm^{-1}. **mp** 69-71 °C.



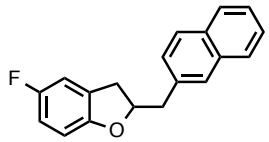
2-(2-Methylbenzyl)-2,3-dihydrobenzofuran (4d). The coupling of 2-allylphenol (33 μL, 0.25 mmol) and *o*-tolyl trifluoromethanesulfonate (72 mg, 0.30 mmol) was performed using the general procedure. Upon purification by silica gel flash chromatography 45 mg (79%) of 2-(2-methylbenzyl)-2,3-dihydrobenzofuran was obtained as a clear oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.25 – 7.21 (m, 1H), 7.22 – 7.15 (m, 4H), 7.15 – 7.10 (m, 1H), 6.85 (td, *J* = 7.4, 1.1 Hz, 1H), 6.79 (d, *J* = 8.0 Hz, 1H), 5.05 (dq, *J* = 8.7, 7.0 Hz, 1H), 3.26 (dd, *J* = 15.5, 8.8 Hz, 1H), 3.22 (dd, *J* = 14.0, 7.1 Hz, 1H), 3.00 (dd, *J* = 15.5, 7.1 Hz, 1H), 2.93 (dd, *J* = 14.1, 6.7 Hz, 1H), 2.37 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 159.5, 136.8, 135.9, 130.5, 130.0, 128.2, 126.9, 126.8, 126.2, 125.1, 120.4, 109.6, 82.9, 39.4, 35.3, 19.9. **HR-MS (EI):** calculated for $C_{16}H_{16}O$ $[M]^+$ 224.1201, found 224.1201. **IR (film):** 3023, 2921, 1597, 1478, 1228, 746 cm^{-1}.



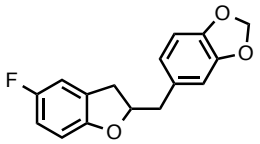
2-(Cyclohex-1-en-1-ylmethyl)-2,3-dihydrobenzofuran (4e). The coupling of 2-allylphenol (33 μL, 0.25 mmol) and cyclohex-1-en-1-yl trifluoromethanesulfonate (53 μL, 0.30 mmol) was performed using the general procedure. Upon purification by silica gel flash chromatography 13 mg (25%, ~90% purity) of 2-(cyclohex-1-en-1-ylmethyl)-2,3-dihydrobenzofuran was obtained as a clear oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.15 (dt, *J* = 7.3, 1.4 Hz, 1H), 7.13 – 7.07 (m, 1H), 6.82 (td, *J* = 7.4, 1.0 Hz, 1H), 6.77 (d, *J* = 7.9 Hz, 1H), 5.54 (dq, *J* = 3.7, 1.9 Hz, 1H), 4.97 – 4.86 (m, 1H), 3.23 (dd, *J* = 15.6, 8.9 Hz, 1H), 2.96 – 2.86 (m, 1H), 2.52 (dd, *J* = 13.7, 6.6 Hz, 2H), 2.26 (dd, *J* = 13.7, 7.6 Hz, 1H), 2.09 – 1.95 (m, 5H), 1.73 – 1.51 (m, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 159.6, 133.9, 128.0, 127.0, 125.1, 124.3, 120.2, 109.5, 81.9, 44.5, 35.2, 29.0, 25.5, 23.0, 22.5. **HR-MS (EI):** calculated for $C_{15}H_{18}O$ $[M]^+$ 214.1358, found 214.1354. **IR (film):** 2924, 2854, 1480, 1462, 1324, 1230, 747 cm^{-1}.



5-Fluoro-2-(naphthalen-2-ylmethyl)-2,3-dihydrobenzofuran (4f). The coupling of 2-allyl-4-fluorophenol (38 mg, 0.25 mmol) and naphthalen-2-yl trifluoromethanesulfonate (83 mg, 0.30 mmol) was performed using the general procedure. Upon purification by silica gel flash chromatography 55 mg (79%) of 5-fluoro-2-(naphthalen-2-ylmethyl)-2,3-dihydrobenzofuran was obtained as a white solid.

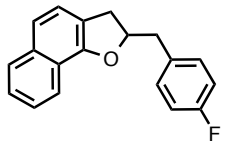
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.86 – 7.77 (m, 3H), 7.71 (s, 1H), 7.47 (dddd, *J* = 12.8, 8.1, 5.5, 1.3 Hz, 2H), 7.41 (dd, *J* = 8.4, 1.5 Hz, 1H), 6.84 (ddt, *J* = 8.0, 2.6, 1.2 Hz, 1H), 6.79 (tdt, *J* = 9.0, 2.7, 1.1 Hz, 1H), 6.69 (dd, *J* = 8.7, 4.2 Hz, 1H), 5.14 (ddt, *J* = 8.8, 7.7, 6.7 Hz, 1H), 3.34 (dd, *J* = 13.9, 6.8 Hz, 1H), 3.21 (dd, *J* = 14.6, 8.8 Hz, 1H), 3.11 (dd, *J* = 13.9, 6.7 Hz, 1H), 3.00 (ddd, *J* = 15.8, 7.5, 1.1 Hz, 1H). **^{13}C NMR (176 MHz, $CDCl_3$):** δ 157.4 (d, *J* = 236.6 Hz), 155.4, 134.7, 133.5, 132.3, 128.2, 128.0 (d, *J* = 8.8 Hz), 127.8, 127.6, 127.6, 127.5, 126.1, 125.6, 114.0 (d, *J* = 24.0 Hz), 112.1 (d, *J* = 24.7 Hz), 109.4 (d, *J* = 8.5 Hz), 84.1, 42.0, 35.2. **HR-MS (EI):** calculated for $C_{19}H_{15}FO$ $[M]^+$ 278.1107, found 278.1100. **IR (film):** 3049, 2962, 1478, 1439, 1226, 1180, 812, 743 cm^{-1}. **mp** 104-106 °C.



5-[(5-Fluoro-2,3-dihydrobenzofuran-2-yl)methyl]benzo[*d*][1,3]dioxole (4g). The coupling of 2-allyl-4-fluorophenol (38 mg, 0.25 mmol) and benzo[*d*][1,3]dioxol-5-yl trifluoromethanesulfonate (81 mg, 0.30 mmol) was performed using the general procedure. Upon purification by silica gel flash chromatography 50 mg (73%) of 5-[(5-fluoro-2,3-dihydrobenzofuran-2-yl)methyl]benzo[*d*][1,3]dioxole was obtained as a clear oil.

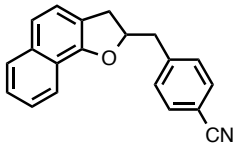
^{1}H NMR (500 MHz, $CDCl_3$): δ 6.87 – 6.81 (m, 1H), 6.82 – 6.74 (m, 3H), 6.71 (dt, *J* = 7.9, 1.8 Hz, 1H), 6.69 – 6.65 (m, 1H), 5.94 (s, 1H), 4.97 (dq, *J* = 8.6, 6.9 Hz, 1H), 3.20 (dd, *J* = 15.8, 8.8 Hz, 1H), 3.11 – 3.03 (m, 1H), 2.93 (dd, *J* = 15.9, 7.6 Hz, 1H), 2.86 (ddd, *J* = 14.0, 6.4, 1.8 Hz, 1H). **^{13}C NMR (126 MHz, $CDCl_3$):** δ 157.5 (d, *J* = 236.6 Hz), 155.5, 147.9, 146.5, 131.0, 128.1 (d, *J* = 8.7 Hz),

122.4, 114.1 (d, *J* = 23.8 Hz), 112.3, 112.1, 109.9, 109.5 (d, *J* = 8.7 Hz), 108.4, 101.1, 84.4, 41.7, 35.2. **HR-MS (EI):** calculated for $C_{16}H_{13}FO_3$ $[M]^+$ 272.0849, found 272.0856. **IR (film):** 2987, 1481, 1441, 1245, 1186, 1037, 806 cm^{-1}.



2-(4-Fluorobenzyl)-2,3-dihydronaphtho[1,2-*b*]furan (4h). The coupling of 2-allylnaphthalen-1-ol (46 mg, 0.25 mmol) and 4-fluorophenyl trifluoromethanesulfonate (73 mg, 0.30 mmol) was performed using the general procedure. Upon purification by silica gel flash chromatography 49 mg (70%) of 2-(4-fluorobenzyl)-2,3-dihydronaphtho[1,2-*b*]furan was obtained as a white solid.

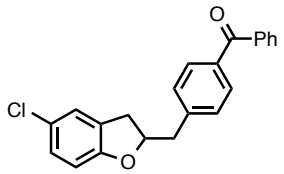
^{1}H NMR (500 MHz, $CDCl_3$): δ 8.00 – 7.92 (m, 1H), 7.82 (dt, *J* = 8.1, 1.6 Hz, 1H), 7.44 (dddd, *J* = 9.6, 6.8, 4.3, 1.7 Hz, 2H), 7.38 (dd, *J* = 8.2, 1.5 Hz, 1H), 7.34 – 7.27 (m, 3H), 7.03 (td, *J* = 8.6, 1.7 Hz, 2H), 5.23 – 5.15 (m, 1H), 3.43 (ddd, *J* = 15.3, 9.2, 1.4 Hz, 1H), 3.23 (dd, *J* = 14.0, 7.2 Hz, 1H), 3.11 (ddd, *J* = 15.2, 7.0, 1.4 Hz, 1H), 3.00 (ddd, *J* = 14.1, 6.1, 1.4 Hz, 1H). **^{13}C NMR (126 MHz, $CDCl_3$):** δ 161.9 (d, *J* = 244.6 Hz), 154.7, 134.1, 133.4 (d, *J* = 3.4 Hz), 131.1 (d, *J* = 8.0 Hz), 128.0, 125.8, 125.4, 123.1, 121.6, 120.7, 120.2, 119.5, 115.4 (d, *J* = 21.6 Hz), 84.2, 41.6, 35.9. **HR-MS (EI):** calculated for $C_{19}H_{15}FO$ $[M]^+$ 278.1107, found 278.1107. **IR (film):** 3055, 1508, 1372, 1278, 1220, 1068, 1005, 803 cm^{-1}.



4-[(2,3-Dihydronaphtho[1,2-*b*]furan-2-yl)methyl]benzonitrile (4i). The coupling of 2-allylnaphthalen-1-ol (46 mg, 0.25 mmol) and 4-cyanophenyl trifluoromethanesulfonate (75 mg, 0.30 mmol) was performed using the general procedure. Upon purification by silica gel flash chromatography 49 mg (70%) of 4-[(2,3-dihydronaphtho[1,2-*b*]furan-2-yl)methyl]benzonitrile was obtained as a white solid.

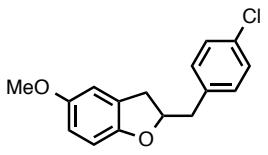
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.92 – 7.86 (m, 1H), 7.83 – 7.77 (m, 1H), 7.62 (d, *J* = 8.2 Hz, 2H), 7.49 – 7.39 (m, 4H), 7.37 (d, *J* = 8.2 Hz, 1H), 7.29 (d, *J* = 8.2 Hz, 1H), 5.21 (dddd, *J* = 9.1, 7.8, 6.8,

5.1 Hz, 1H), 3.49 (dd, *J* = 15.2, 9.3 Hz, 1H), 3.25 (dd, *J* = 14.1, 7.8 Hz, 1H), 3.09 (ddd, *J* = 13.8, 7.9, 6.0 Hz, 2H). **^{13}C NMR (126 MHz, $CDCl_3$):** δ 154.5, 143.5, 134.1, 132.4, 130.5, 128.0, 125.9, 125.6, 122.9, 121.4, 120.6, 120.5, 119.2, 119.1, 110.7, 83.3, 42.5, 36.1. **HR-MS (ESI):** calculated for $C_{20}H_{16}NO$ $[M+H]^+$ 286.1226, found 286.1228. **IR (film):** 2921, 2854, 2223, 1574, 1400, 1282, 1030, 798 cm^{-1}. **mp** 94-97 °C.



{4-[(5-Chloro-2,3-dihydrobenzofuran-2-yl)methyl]phenyl}(phenyl)methanone (4j). The coupling of 2-allyl-4-chlorophenol (42 mg, 0.25 mmol) and 4-benzoylphenyl trifluoromethanesulfonate (99 mg, 0.30 mmol) was performed using the general procedure, with the exception of the temperature, which was modified to 80 °C. Upon purification by silica gel flash chromatography 57 mg (65%) of {4-[(5-Chloro-2,3-dihydrobenzofuran-2-yl)methyl]phenyl}(phenyl)methanone obtained as a white solid.

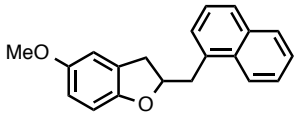
^{1}H NMR (700 MHz, Acetone-d_6): δ 7.76 (dd, *J* = 8.2, 1.4 Hz, 2H), 7.73 (d, *J* = 8.1 Hz, 2H), 7.64 (t, *J* = 7.5 Hz, 1H), 7.54 (t, *J* = 7.7 Hz, 2H), 7.51 (d, *J* = 8.1 Hz, 2H), 7.16 (dt, *J* = 2.3, 1.2 Hz, 1H), 7.08 (dd, *J* = 8.5, 2.3 Hz, 1H), 6.70 (d, *J* = 8.4 Hz, 1H), 5.15 (dtd, *J* = 8.9, 7.4, 5.6 Hz, 1H), 3.32 (dd, *J* = 16.0, 8.9 Hz, 1H), 3.19 (dd, *J* = 14.0, 7.5 Hz, 1H), 3.14 (dd, *J* = 14.0, 5.6 Hz, 1H), 3.02 (dd, *J* = 16.0, 7.4 Hz, 1H). **^{13}C NMR (176 MHz, Acetone-d_6):** δ 196.0, 159.1, 143.5, 138.6, 136.7, 133.0, 130.6, 130.3, 130.3, 130.2, 129.1, 128.3, 125.8, 125.0, 110.9, 84.6, 42.1, 35.3. **HR-MS (ESI):** calculated for $C_{22}H_{18}ClO_2$ $[M+H]^+$ 349.0990, found 349.0992. **IR (film):** 2056, 2946, 1643, 1605, 1596, 1467, 1277, 1236, 955, 927, 803 cm^{-1}. **mp** 94-97 °C.



2-(4-Chlorobenzyl)-5-methoxy-2,3-dihydrobenzofuran (4k). The coupling of 2-allyl-4-methoxyphenol (41 mg, 0.25 mmol) and 4-chlorophenyl trifluoromethanesulfonate (78 mg,

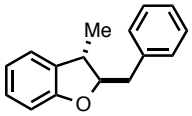
0.30 mmol) was performed using the general procedure, with the exception of the temperature, which was modified to 80 °C. Upon purification by silica gel flash chromatography 48 mg (70%) of 2-(4-chlorobenzyl)-5-methoxy-2,3-dihydrobenzofuran was obtained as a clear oil (48 mg, 0.18 mmol, 70% yield).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.32 – 7.27 (m, 2H), 7.23 – 7.16 (m, 2H), 6.73 (dt, *J* = 2.7, 0.9 Hz, 1H), 6.71 – 6.62 (m, 2H), 4.95 (dtd, *J* = 8.9, 7.3, 5.7 Hz, 1H), 3.75 (s, 2H), 3.20 (dd, *J* = 15.6, 8.8 Hz, 1H), 3.10 (dd, *J* = 14.0, 7.2 Hz, 1H), 2.95 – 2.85 (m, 2H). **^{13}C NMR (126 MHz, $CDCl_3$):** δ 154.2, 153.6, 136.2, 132.6, 130.9, 128.7, 127.6, 113.0, 111.5, 109.4, 83.5, 56.2, 41.4, 35.6. **HR-MS (EI):** calculated for $C_{16}H_{15}ClO_2$ $[M]^+$ 274.0761, found 274.0764. **IR (film):** 2915, 2831, 1485, 1197, 1182, 1031, 782 cm^{-1}.



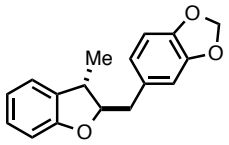
5-Methoxy-2-(naphthalen-1-ylmethyl)-2,3-dihydrobenzofuran (4l). The coupling of 2-allyl-4-methoxyphenol (41 mg, 0.25 mmol) and naphthalen-1-yl trifluoromethanesulfonate (59 μL, 0.30 mmol) was performed using the general procedure. Upon purification by silica gel flash chromatography 59 mg (81%) of 5-methoxy-2-(naphthalen-1-ylmethyl)-2,3-dihydrobenzofuran was obtained as a clear oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.10 (dq, *J* = 8.7, 0.9 Hz, 1H), 7.93 – 7.85 (m, 1H), 7.80 (dt, *J* = 7.9, 1.1 Hz, 1H), 7.53 (dddd, *J* = 19.0, 8.0, 6.8, 1.4 Hz, 2H), 7.48 – 7.40 (m, 2H), 6.80 – 6.75 (m, 1H), 6.75 – 6.66 (m, 2H), 5.27 – 5.15 (m, 1H), 3.77 (s, 3H), 3.71 (dd, *J* = 14.1, 6.5 Hz, 1H), 3.32 (dd, *J* = 14.1, 7.4 Hz, 1H), 3.17 (ddt, *J* = 15.5, 8.6, 0.9 Hz, 1H), 3.03 (ddt, *J* = 15.6, 6.9, 1.0 Hz, 1H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 154.2, 153.6, 134.0, 133.6, 132.3, 129.0, 127.8, 127.6, 127.5, 126.2, 125.8, 125.6, 123.8, 112.9, 111.6, 109.4, 83.0, 56.2, 39.1, 35.8. **HR-MS (EI):** calculated for $C_{20}H_{18}O_2$ $[M]^+$ 290.1307, found 290.1315. **IR (film):** 3053, 2968, 2919, 1488, 1196, 1180, 1026, 987, 788 cm^{-1}. **mp** 83-86 °C.



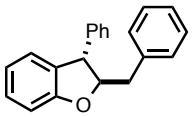
(±)-(2*R*,3*S*)-2-Benzyl-3-methyl-2,3-dihydrobenzofuran (4m). The coupling of 2-(but-3-en-2-yl)phenol (37 mg, 0.25 mmol) and phenyl trifluoromethanesulfonate (49 μL, 0.30 mmol) was performed using the general procedure except with BrettPhos (6.7 mg, 0.013 mmol) in place of CPhos as the ligand. Upon purification by silica gel flash chromatography 41 mg (73%) of (±)-(2*R*,3*S*)-2-benzyl-3-methyl-2,3-dihydrobenzofuran was obtained as a clear oil. The purified material was a 5:1 mixture of diastereomers as determined by ^{1}H NMR (crude material was a 5:1 mixture of diastereomers). Data provided are for the major diastereomer.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.39 – 7.28 (m, 4H), 7.28 – 7.22 (m, 1H), 7.18 – 7.07 (m, 2H), 6.90 – 6.83 (m, 1H), 6.79 (dd, *J* = 8.1, 2.7 Hz, 1H), 4.51 (tdd, *J* = 7.2, 5.9, 2.8 Hz, 1H), 3.29 – 3.13 (m, 2H), 2.98 (ddd, *J* = 14.0, 6.4, 2.5 Hz, 1H), 1.19 (dd, *J* = 6.9, 2.5 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$):** δ 159.1, 137.5, 132.3, 129.6, 128.6, 128.2, 126.7, 123.9, 120.5, 109.6, 91.3, 41.9, 41.3, 19.2. **HR-MS (EI):** calculated for $C_{16}H_{16}O$ $[M]^+$ 224.1201, found 224.1207. **IR (film):** 2959, 1597, 1453, 1228, 969, 746 cm^{-1}.



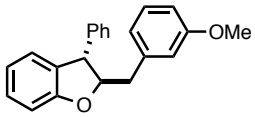
(±)-5-(2*R*,3*S*)-[(3-Methyl-2,3-dihydrobenzofuran-2-yl)methyl]benzo[*d*][1,3]dioxole (4n). The coupling of 2-(but-3-en-2-yl)phenol (37 mg, 0.25 mmol) and benzo[*d*][1,3]dioxol-5-yl trifluoromethanesulfonate (81 mg, 0.30 mmol) was performed using the general procedure modified by the use of BrettPhos (6.7 mg, 0.013 mmol) in place of CPhos as the ligand. Upon purification by silica gel flash chromatography 38 mg (57%) of (±)-5-(2*R*,3*S*)-[(3-methyl-2,3-dihydrobenzofuran-2-yl)methyl]benzo[*d*][1,3]dioxole was obtained as a clear oil. The purified material was a 7.6:1 mixture of diastereomers as determined by ^{1}H NMR (crude material was a 5:1 mixture of diastereomers). Additionally, the major diastereomer could be isolated by careful chromatography (17 mg, 0.061 mmol, 25% yield). Data provided are for the major diastereomer.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.15 – 7.05 (m, 2H), 6.86 (t, *J* = 7.4 Hz, 1H), 6.82 – 6.69 (m, 4H), 5.94 (d, *J* = 1.7 Hz, 2H), 4.43 (q, *J* = 6.8, 6.2 Hz, 1H), 3.19 (q, *J* = 7.0 Hz, 1H), 3.07 (dd, *J* = 14.0, 7.2 Hz, 1H), 2.90 (dd, *J* = 14.0, 5.7 Hz, 1H), 1.21 (d, *J* = 6.9 Hz, 2H). **^{13}C NMR (176 MHz, $CDCl_3$):** δ 159.1, 147.8, 146.4, 132.3, 131.3, 128.2, 123.9, 122.5, 120.5, 110.0, 109.7, 108.4, 101.0, 91.5, 77.3, 77.2, 77.1, 77.1, 41.7, 40.9, 19.2. **HR-MS (EI):** calculated for $C_{17}H_{16}O_3$ $[M]^+$ 268.1099, found 268.1098. **IR (film):** 2960, 2884, 1597, 1477, 1442, 1242, 1228, 1037, 926, 804, 748 cm^{-1}.



(±)-(2*R*,3*S*)-2-Benzyl-3-phenyl-2,3-dihydrobenzofuran (4o). The coupling of 2-(1-phenylallyl)phenol (53 mg, 0.25 mmol) and phenyl trifluoromethanesulfonate (49 μL, 0.30 mmol) was performed using the general procedure modified by the use of BrettPhos (6.7 mg, 0.013 mmol) in place of CPhos as the ligand. Upon purification by silica gel flash chromatography 42 mg (59%) of (±)-(2*R*,3*S*)-2-benzyl-3-phenyl-2,3-dihydrobenzofuran was obtained as a clear oil. The purified material was a 15:1 mixture of diastereomers as determined by ^{1}H NMR (crude material was a 17:1 mixture of diastereomers by ^{1}H NMR). Data provided are for the major diastereomer.

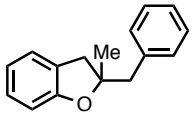
^{1}H NMR (700 MHz, $CDCl_3$): δ 7.34 – 7.26 (m, 6H), 7.26 – 7.21 (m, 2H), 7.19 – 7.15 (m, 1H), 7.07 – 7.02 (m, 2H), 6.95 (d, *J* = 7.3 Hz, 1H), 6.88 (d, *J* = 8.1 Hz, 1H), 6.85 (t, *J* = 7.4 Hz, 1H), 4.86 (td, *J* = 7.4, 5.4 Hz, 1H), 4.34 (d, *J* = 7.4 Hz, 1H), 3.19 (dd, *J* = 14.2, 7.5 Hz, 1H), 3.09 (dd, *J* = 14.2, 5.3 Hz, 1H). **^{13}C NMR (176 MHz, $CDCl_3$):** δ 159.7, 142.7, 137.3, 130.6, 129.7, 128.8, 128.7, 128.6, 128.2, 127.1, 126.8, 125.5, 120.9, 109.9, 92.1, 53.8, 41.0. **HR-MS (EI):** calculated for $C_{21}H_{18}O$ $[M]^+$ 286.1358, found 286.1359. **IR (film):** 3028, 2916, 1596, 1476, 1460, 1225, 908, 748 cm^{-1}.



(±)-(2*R*,3*S*)-2-(3-Methoxybenzyl)-3-phenyl-2,3-dihydrobenzofuran (4p). The coupling of 2-(1-phenylallyl)phenol (53 mg, 0.25 mmol) and 3-methoxyphenyl trifluoromethanesulfonate (77 mg, 0.30 mmol) was performed using the general procedure modified by the use of BrettPhos

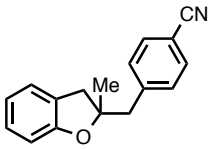
(6.7 mg, 0.013 mmol) in place of CPhos as the ligand. Upon purification by silica gel flash chromatography 41 mg (52%) of (±)-(2*R*,3*S*)-2-(3-Methoxybenzyl)-3-phenyl-2,3-dihydrobenzofuran was obtained as a clear oil. The purified material was a 29:1 mixture of diastereomers as determined by ^{1}H NMR (crude material was a 17:1 mixture of diastereomers). Data provided are for the major diastereomer.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.32 – 7.20 (m, 5H), 7.17 (tdd, *J* = 6.6, 1.7, 1.0 Hz, 1H), 7.06 (d, *J* = 7.3 Hz, 2H), 6.94 (d, *J* = 7.4 Hz, 1H), 6.90 – 6.83 (m, 2H), 6.83 – 6.74 (m, 2H), 4.85 (td, *J* = 7.4, 5.2 Hz, 1H), , 4.33 (d, *J* = 7.3 Hz, 1H), 3.78 (s, 3H), 3.16 (dd, *J* = 14.2, 7.4 Hz, 1H), 3.06 (dd, *J* = 14.1, 5.4 Hz, 1H). **^{13}C NMR (126 MHz, $CDCl_3$):** δ 159.8, 159.7, 142.7, 138.9, 130.6, 129.6, 128.9, 128.7, 128.3, 127.1, 125.5, 122.1, 120.9, 115.4, 112.2, 109.9, 92.0, 55.3, 53.8, 41.0. **HR-MS (EI):** calculated for $C_{22}H_{20}O_2$ $[M]^+$ 316.1463, found 316.1463. **IR (film):** 2927, 2853, 1598, 1584, 1491, 1460, 1238, 1052, 1029, 750 cm^{-1}.



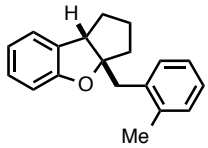
2-Benzyl-2-methyl-2,3-dihydrobenzofuran (4q). The coupling of 2-(2-methylallyl)phenol (37 mg, 0.25 mmol) and phenyl trifluoromethanesulfonate (49 μL, 0.30 mmol) was performed using the general procedure modified by the use of additional CPhos (8.2 mg, 0.019 mmol, 7.5 mol%) and lower temperature (90 °C). Upon purification by silica gel flash chromatography 45 mg (81%) of 2-benzyl-2-methyl-2,3-dihydrobenzofuran was obtained as a clear oil. Known compound corresponds to previously reported spectra.[17]

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.33 – 7.19 (m, 5H), 7.10 (td, *J* = 6.7, 1.2 Hz, 2H), 6.80 (td, *J* = 7.4, 0.9 Hz, 1H), 6.77 (d, *J* = 8.2 Hz, 1H), 3.17 (d, *J* = 15.5 Hz, 1H), 3.06 (d, *J* = 13.7 Hz, 1H), 2.95 (d, *J* = 13.7 Hz, 1H), 2.90 (d, *J* = 15.4 Hz, 1H), 1.42 (s, 3H). **^{13}C NMR (126 MHz, $CDCl_3$):** δ 158.9, 137.2, 130.7, 128.2, 128.1, 127.1, 126.7, 125.2, 120.2, 109.7, 88.6, 46.6, 41.1, 26.2.



4-[(2-Methyl-2,3-dihydrobenzofuran-2-yl)methyl]benzonitrile (4r). The coupling of 2-(2-methylallyl)phenol (37 mg, 0.25 mmol) and 4-cyanophenyl trifluoromethanesulfonate (75 mg, 0.30 mmol) was performed using the general procedure modified by the use of additional CPhos (8.2 mg, 0.019 mmol, 7.5 mol%) and lower temperature (90 °C). Upon purification by silica gel flash chromatography 46 mg (73%) of 4-[(2-methyl-2,3-dihydrobenzofuran-2-yl)methyl]benzonitrile was obtained as a clear oil.

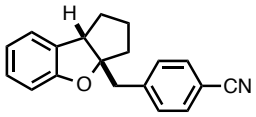
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.59 – 7.54 (m, 2H), 7.37 (d, *J* = 8.0 Hz, 2H), 7.15 – 7.07 (m, 2H), 6.82 (tt, *J* = 7.3, 1.0 Hz, 1H), 6.76 (d, *J* = 7.9 Hz, 1H), 3.11 (d, *J* = 13.7 Hz, 1H), 3.10 (d, *J* = 15.5 Hz, 1H), 2.99 (d, *J* = 15.4 Hz, 1H), 2.98 (d, *J* = 13.7 Hz, 1H), 1.41 (s, 3H). **^{13}C NMR (126 MHz, $CDCl_3$):** δ 158.6, 142.8, 131.9, 131.4, 128.3, 126.6, 125.2, 120.5, 119.1, 110.6, 109.7, 87.8, 46.8, 4.53, 26.3. **HR-MS (EI):** calculated for $C_{17}H_{15}O$ $[M]^+$ 249.1154, found 249.1151. **IR (film):** 3049, 2923, 2227, 1598, 1479, 1460, 1232, 1059, 879, 747 cm^{-1}.



(±)-(3a*R*,8b*S*)-3a-(2-Methylbenzyl)-2,3,3a,8b-tetrahydro-1*H*-cyclopenta[*b*]benzofuran (4s). The coupling of 2-(2-methylenecyclopentyl)phenol (44 mg, 0.25 mmol) and *o*-tolyl trifluoromethanesulfonate (72 mg, 0.30 mmol) was performed using the general procedure modified by the use of additional CPhos (8.2 mg, 0.019 mmol, 7.5 mol%) and lower temperature (90 °C). Upon purification by silica gel flash chromatography 58 mg (88%) of (±)-(3a*R*,8b*S*)-3a-(2-methylbenzyl)-2,3,3a,8b-tetrahydro-1*H*-cyclopenta[*b*]benzofuran was obtained as a light yellow oil.

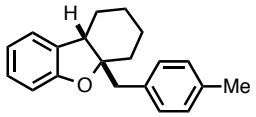
^{1}H NMR (401 MHz, $CDCl_3$): δ 7.30 (dd, *J* = 5.1, 3.8 Hz, 1H), 7.21 – 7.05 (m, 5H), 6.83 (td, *J* = 7.4, 1.0 Hz, 1H), 6.72 (d, *J* = 7.9 Hz, 1H), 3.57 (d, *J* = 8.8 Hz, 1H), 3.24 (d, *J* = 14.1 Hz, 1H), 2.98 (d, *J* = 14.1 Hz, 1H), 2.36 (s, 3H), 2.08 – 1.87 (m, 2H), 1.87 – 1.72 (m, 2H), 1.67 (dddd, *J* = 12.6, 6.3, 4.1, 2.2 Hz, 1H), 1.56 (qd, *J* = 11.9, 6.1 Hz, 1H). **^{13}C NMR (101 MHz, $CDCl_3$):** δ 159.7, 137.4, 136.0,

131.8, 131.0, 130.5, 128.1, 126.7, 125.6, 124.9, 120.3, 108.9, 100.8, 51.3, 41.3, 39.0, 35.4, 24.6, 20.5. **HR-MS (EI):** calculated for $C_{19}H_{20}O$ $[M]^+$ 264.1514, found 264.1515. **IR (film):** 2952, 1596, 1479, 1256, 1226, 892, 741, 726 cm^{-1}.



(±)-4-(3a*R*,8b*S*)-[(1,2,3,8b-Tetrahydro-3a*H*-cyclopenta[*b*]benzofuran-3a-yl)methyl]benzonitrile (4t). The coupling of 2-(2-methylenecyclopentyl)phenol (44 mg, 0.25 mmol) and 4-cyanophenyl trifluoromethanesulfonate (75 mg, 0.30 mmol) was performed using the general procedure modified by the use of additional CPhos (8.2 mg, 0.019 mmol, 7.5 mol%) and lower temperature (90 °C). The crude material was purified by silica gel chromatography, however, the product coeluted with 4-cyanophenyl trifluoromethanesulfonate. Further purification by Kugelrohr distillation was performed to remove the aryl triflate starting material that coeluted with the product, providing 60 mg (87%) of (±)-4-(3a*R*,8b*S*)-[(1,2,3,8b-tetrahydro-3a*H*-cyclopenta[*b*]benzofuran -3a-yl)methyl]benzonitrile as a clear oil.

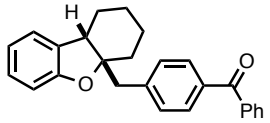
^{1}H NMR (700 MHz, $CDCl_3$): δ 7.58 – 7.51 (m, 2H), 7.44 – 7.38 (m, 2H), 7.08 (t, *J* = 7.4 Hz, 1H), 7.06 (dt, *J* = 7.4, 1.1 Hz, 1H), 6.81 (td, *J* = 7.4, 1.0 Hz, 1H), 6.71 (d, *J* = 7.9 Hz, 1H), 3.55 – 3.45 (m, 1H), 3.16 (d, *J* = 13.8 Hz, 1H), 3.04 (d, *J* = 13.8 Hz, 1H), 2.05 – 1.89 (m, 2H), 1.82 (ddq, *J* = 12.4, 5.9, 1.9 Hz, 1H), 1.73 – 1.64 (m, 2H), 1.59 – 1.49 (m, 1H). **^{13}C NMR (176 MHz, $CDCl_3$):** δ 159.5, 143.2, 131.9, 131.1, 131.1, 128.3, 124.8, 120.6, 119.2, 110.5, 108.9, 99.1, 77.3, 77.2, 77.0, 51.3, 45.5, 39.4, 35.3, 24.5. **HR-MS (EI):** calculated for $C_{19}H_{17}NO$ $[M]^+$ 275.1310, found 275.1309. **IR (film):** 2954, 2865, 2227, 1596, 1459, 1258, 1226, 892, 747, 729 cm^{-1}.



(±)-(4a*R*,9b*S*)-4a-(4-Methylbenzyl)-1,2,3,4,4a,9b-hexahydrodibenzo[*b*,*d*]furan (4u). The coupling of 2-(2-methylenecyclohexyl)phenol (47 mg, 0.25 mmol) and *p*-tolyl trifluoromethanesulfonate (54 μL, 0.30 mmol) was performed using the general procedure modified by the use of additional CPhos (8.2 mg, 0.019 mmol, 7.5 mol%) and lower

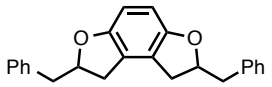
temperature (90 °C). Upon purification by silica gel flash chromatography 41 mg (59%) of (±)-(4a*R*,9b*S*)-4a-(4-methylbenzyl)-1,2,3,4,4a,9b-hexahydrodibenzo[*b*,*d*]furan was obtained as a clear oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.17 (d, *J* = 7.9 Hz, 2H), 7.14 – 7.04 (m, 4H), 6.83 (t, *J* = 7.4 Hz, 1H), 6.79 (d, *J* = 7.9 Hz, 1H), 3.15 (t, *J* = 5.3 Hz, 1H), 3.08 (d, *J* = 14.2 Hz, 1H), 2.98 (d, *J* = 14.2 Hz, 1H), 2.31 (s, 3H), 1.97 – 1.84 (m, 1H), 1.84 – 1.74 (m, 1H), 1.74 – 1.59 (m, 2H), 1.54 (h, *J* = 5.5 Hz, 2H), 1.49 – 1.29 (m, 2H). **^{13}C NMR (126 MHz, $CDCl_3$):** δ 158.6, 136.1, 134.1, 132.5, 130.6, 128.9, 127.9, 123.5, 120.2, 110.3, 90.4, 44.7, 43.4, 31.7, 26.1, 21.5, 21.2, 21.0. **HR-MS (EI):** calculated for $C_{20}H_{22}O$ $[M]^+$ 278.1761, found 278.1763. **IR (film):** 3024, 2927, 2856, 1596, 1473, 1458, 1238, 871, 746 cm^{-1}.



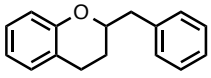
(±)-(4a*R*,9b*S*)-Phenyl{4-[(1,3,4,9b-tetrahydrodibenzo[*b*,*d*]furan-4a(2*H*)-yl)methyl]phenyl]methanone (4v). The coupling of 2-(2-methylenecyclohexyl)phenol (47 mg, 0.25 mmol) and 4-benzoylphenyl trifluoromethanesulfonate (99 mg, 0.30 mmol) was performed using the general procedure modified by the use of additional CPhos (8.2 mg, 0.019 mmol, 7.5 mol%) and lower temperature (90 °C). Upon purification by silica gel flash chromatography 63 mg (68%) of (±)-(4a*R*,9b*S*)-phenyl{4-[(1,3,4,9b-tetrahydrodibenzo[*b*,*d*]furan-4a(2*H*)-yl)methyl]phenyl]methanone was obtained as a clear oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.85 – 7.77 (m, 2H), 7.77 – 7.71 (m, 2H), 7.58 (td, *J* = 7.5, 1.5 Hz, 1H), 7.53 – 7.44 (m, 2H), 7.44 – 7.36 (m, 2H), 7.12 (t, *J* = 7.8 Hz, 1H), 7.09 (d, *J* = 7.3 Hz, 1H), 6.86 (t, *J* = 7.4 Hz, 1H), 6.80 (d, *J* = 7.9 Hz, 1H), 3.21 (d, *J* = 14.0 Hz, 1H), 3.16 (t, *J* = 5.4 Hz, 1H), 3.07 (d, *J* = 14.0 Hz, 1H), 1.98 – 1.78 (m, 2H), 1.71 (q, *J* = 5.3, 3.9 Hz, 2H), 1.57 (dq, *J* = 9.6, 6.4, 5.8 Hz, 1H), 1.52 – 1.31 (m, 3H). **^{13}C NMR (126 MHz, $CDCl_3$):** δ 196.6, 158.4, 142.4, 137.9, 135.9, 132.4, 132.3, 130.7, 130.1, 130.1, 128.4, 128.1, 123.6, 120.5, 110.4, 90.0, 77.4, 77.2, 76.9, 45.0, 44.0, 31.8, 26.3, 21.4, 20.9. **HR-MS (EI):** calculated for $C_{26}H_{24}O_2$ $[M]^+$ 368.1776, found 378.1781. **IR (film):** 2930, 2857, 1655, 1597, 1493, 1277, 1240, 908, 728 cm^{-1}.



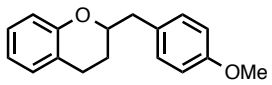
2,7-Dibenzyl-1,2,7,8-tetrahydrobenzo[1,2-*b*:4,3-*b'*]difuran (4w). The coupling of 2,3-diallylbenzene-1,4-diol (48 mg, 0.25 mmol) and phenyl trifluoromethanesulfonate (97 μL, 0.60 mmol) was performed using a modified general procedure with additional phenyl trifluoromethanesulfonate, lithium *tert*-butoxide (48 mg, 0.6 mmol, 2.4 mmol) and benzotrifluoride (3 mL, 0.08 M). After workup the crude reaction mixture was subjected to dihydroxylation conditions to facilitate the separation of olefin containing impurities. The crude material was dissolved in 3:1 Acetone/water (2.0 mL, 0.13 M), osmium tetroxide (25 wt. % in tert-butanol) (42 μL, 3.3 μmol, 0.01 equiv) and *N*-methylmorpholine *N*-oxide (44 mg, 0.38 mmol, 1.5 equiv) were added and the reaction was stirred at rt 20 hours. The reaction was quenched with concentrated aqueous sodium sulfite (4 mL), extracted into EtOAc (2 x 10 mL), washed with brine, dried with sodium sulfate and concentrated. Upon purification by silica gel flash chromatography 33 mg (38%) of 2,7-dibenzyl-1,2,7,8-tetrahydrobenzo[1,2-*b*:4,3-*b'*]difuran was obtained as a clear oil (33 mg, 0.10 mmol, 38% yield). Product was found to be a 1.1:1 mixture of diastereomers by GC analysis. The diastereomers were indistinguishable by ^{1}H NMR, however some duplicate peaks were observed in the ^{13}C NMR spectrum.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.33 (td, *J* = 7.3, 4.4 Hz, 4H), 7.26 (dt, *J* = 5.7, 4.4 Hz, 6H), 6.52 (s, 2H), 4.99 (ddq, *J* = 14.1, 7.0, 3.6, 2.9 Hz, 2H), 3.20 (ddd, *J* = 13.8, 6.6, 5.0 Hz, 2H), 3.05 (ddd, *J* = 15.0, 8.6, 1.6 Hz, 2H), 2.92 (dt, *J* = 14.1, 7.3 Hz, 2H), 2.81 (ddd, *J* = 15.1, 7.5, 2.1 Hz, 2H). **^{13}C NMR (126 MHz, $CDCl_3$):** δ 154.05, (137.61, 137.60), (129.51, 129.49), 128.7, 126.7, 123.6, (107.35, 107.34), 83.9, (42.13, 42.09), 34.3. **HR-MS (ESI):** calculated for $C_{24}H_{23}O_2$ $[M+H]^+$ 343.1693, found 343.1693. **IR (film):** 2927, 2852, 1455, 1217, 1196, 953, 796, 746 cm^{-1}.



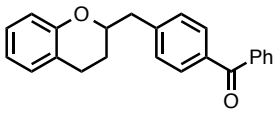
2-Benzylchroman (3a). The coupling of 2-(but-3-en-1-yl)phenol (37 mg, 0.25 mmol) and phenyl trifluoromethanesulfonate (49 μL, 0.30 mmol) was performed using the general procedure. Upon purification by silica gel flash chromatography 38 mg (68%) of 2-benzylchroman was obtained as a clear oil.

^{1}H NMR (401 MHz, $CDCl_3$): δ 7.38 – 7.21 (m, 5H), 7.14 – 7.07 (m, 1H), 7.07 – 7.00 (m, 1H), 6.84 (dd, *J* = 7.7, 5.9 Hz, 2H), 4.29 – 4.18 (m, 1H), 3.16 (dd, *J* = 13.7, 6.1 Hz, 1H), 2.88 (dd, *J* = 13.6, 7.1 Hz, 1H), 2.87 – 2.68 (m, 2H), 1.99 (dddd, *J* = 13.6, 5.9, 3.7, 2.3 Hz, 1H), 1.72 (dtd, *J* = 13.5, 10.2, 6.2 Hz, 1H). **^{13}C NMR (101 MHz, $CDCl_3$):** δ 155.0, 138.0, 129.7, 129.6, 128.5, 127.3, 126.5, 122.1, 120.1, 116.9, 76.7, 41.9, 26.6, 24.7. Spectroscopic data were consistent with those previously reported.[15]



2-(4-Methoxybenzyl)chroman (3b). The coupling of 2-(but-3-en-1-yl)phenol (37 mg, 0.25 mmol) and 4-methoxyphenyl trifluoromethanesulfonate (77 mg, 0.30 mmol) was performed using the general procedure. Upon purification by silica gel flash chromatography 26 mg (41%) of 2-(4-methoxybenzyl)chroman was obtained as a clear oil.

^{1}H NMR (401 MHz, $CDCl_3$): δ 7.19 (d, *J* = 8.4 Hz, 2H), 7.08 (t, *J* = 7.7 Hz, 1H), 7.03 (d, *J* = 7.4 Hz, 1H), 6.90 – 6.77 (m, 4H), 4.22 – 4.12 (m, 1H), 3.80 (s, 3H), 3.09 (dd, *J* = 13.8, 6.0 Hz, 1H), 2.82 (dd, *J* = 13.8, 7.0 Hz, 1H), 2.78 – 2.66 (m, 2H), 1.98 (dddd, *J* = 13.4, 5.9, 3.7, 2.3 Hz, 1H), 1.69 (dtd, *J* = 13.5, 10.2, 6.2 Hz, 1H). **^{13}C NMR (101 MHz, $CDCl_3$):** δ 158.4, 155.0, 130.7, 130.0, 129.6, 127.3, 122.1, 120.2, 116.9, 113.9, 76.9, 55.4, 41.0, 26.6, 24.7. Spectroscopic data were consistent with those previously reported.[15]



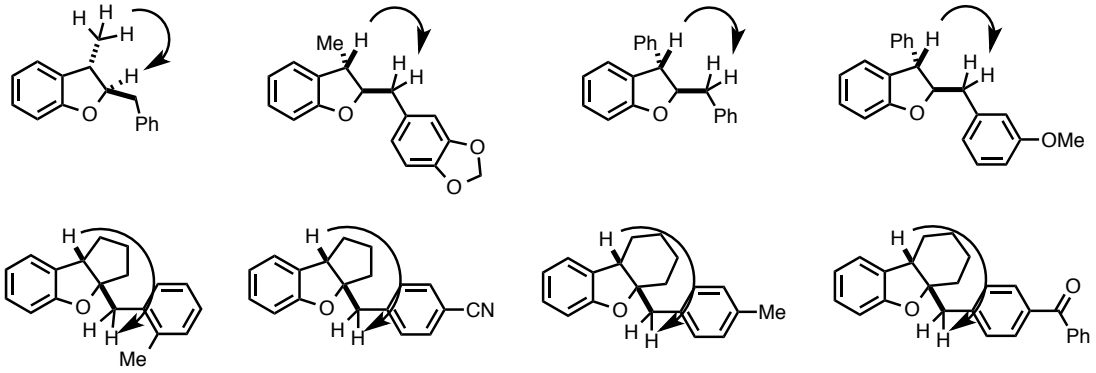
[4-(Chroman-2-ylmethyl)phenyl](phenyl)methanone (3c). The coupling of 2-(but-3-en-1-yl)phenol (37 mg, 0.25 mmol) and 4-methoxyphenyl trifluoromethanesulfonate (99 mg, 0.30 mmol) was performed using the general procedure. Upon purification by silica gel flash chromatography 64 mg (78%) of (4-(chroman-2-ylmethyl)phenyl)(phenyl)methanone was obtained as a clear oil.

^{1}H NMR (401 MHz, $CDCl_3$): δ 7.85 – 7.74 (m, 4H), 7.64 – 7.56 (m, 1H), 7.49 (dd, *J* = 8.3, 6.9 Hz, 2H), 7.41 (d, *J* = 8.1 Hz, 2H), 7.09 (t, *J* = 7.8 Hz, 1H), 7.05 (d, *J* = 8.0 Hz, 1H), 6.89 – 6.78 (m, 2H),

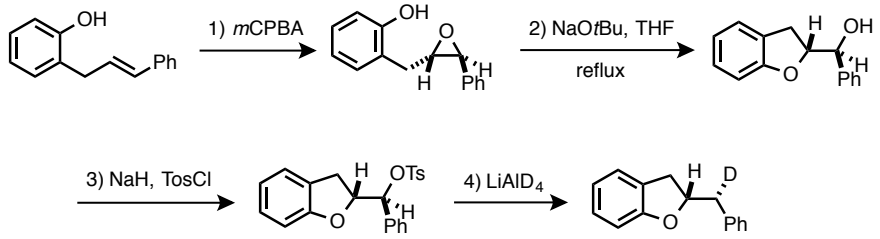
4.28 (dtd, *J* = 10.0, 6.3, 2.2 Hz, 1H), 3.19 (dd, *J* = 13.8, 6.6 Hz, 1H), 3.00 (dd, *J* = 13.8, 6.1 Hz, 1H), 2.81 (qdd, *J* = 13.0, 8.4, 4.2 Hz, 2H), 2.03 (dddd, *J* = 13.5, 5.9, 3.6, 1.7 Hz, 1H), 1.76 (dtd, *J* = 13.4, 10.4, 5.9 Hz, 1H). **^{13}C NMR (101 MHz, $CDCl_3$):** δ 196.6, 154.8, 143.1, 137.9, 135.9, 132.4, 130.4, 130.1, 129.6, 128.4, 127.4, 121.9, 120.4, 116.9, 76.2, 41.9, 26.9, 24.7. Spectroscopic data were consistent with those previously reported.[15]

Assignment of Stereochemistry

The relative stereochemical configuration of compounds **4m-p** and **4s-v** were assigned on the basis of signals observed in ^{1}H NMR nOe experiments. Relevant nOe data is shown below.



Synthesis of (2*S*,2'*R*)-*d*-4a via classical reactions.



(±)-(2*S*,2'*R*)-2-(2-Phenylmethyl-*d*)-2,3-dihydrobenzofuran (*d*-4a). A flame-dried round bottom flask equipped with a magnetic stir bar was charged with 2-cinnamylphenol[11] (0.14 g, 0.65 mmol) and dichloromethane (2.4 mL). The reaction was then cooled to 0 °C in an ice water bath and a solution of *m*CPBA (77%, 0.16 g, 0.73 mmol) in dichloromethane (1.2 mL) was added. The

reaction was removed from the bath and stirred at room temperature for three hours. The reaction was then diluted with dichloromethane (5 mL), filtered through glass wool, washed with saturated aqueous sodium bicarbonate (5 mL), dried over sodium sulfate and concentrated. The crude material was purified by flash chromatography to obtain 0.15 g (quantitative) of (±)-(2*S*,3*S*)-2-(3-phenyloxiran-2-yl)methylphenol.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.38 – 7.29 (m, 3H), 7.28 – 7.23 (m, 2H), 7.20 (td, *J* = 7.8, 1.7 Hz, 1H), 7.13 (dd, *J* = 7.5, 1.7 Hz, 1H), 6.95 (dd, *J* = 8.1, 1.3 Hz, 1H), 6.93 – 6.87 (m, 2H), 3.87 (d, *J* = 2.2 Hz, 1H), 3.36 (dt, *J* = 7.2, 2.5 Hz, 1H), 3.31 (dd, *J* = 15.0, 2.7 Hz, 1H), 2.92 (dd, *J* = 14.9, 7.2 Hz, 1H). **^{13}C NMR (126 MHz, $CDCl_3$):** δ 155.6, 136.2, 131.2, 129.0, 128.7, 128.7, 125.8, 123.3, 120.9, 117.3, 63.8, 59.8, 34.8.

The base induced intramolecular five-*endo* epoxide opening was based on a related procedure by Hirooka *et al.*[18] A flame-dried round bottom flask equipped with a magnetic stir bar and reflux condenser was charged with (±)-(2*S*,3*S*)-2-(3-phenyloxiran-2-yl)methylphenol (0.37 g, 1.6 mmol), tetrahydrofuran (16 mL) and sodium *tert*-butoxide (0.17 g, 1.8mmol). The reaction was then heated to reflux for 15 hours. The reaction was quenched with saturated aqueous ammonium chloride (5 mL), diluted with dichloromethane (30 mL) and separated. The organic layer was washed with brine (10 mL), dried with sodium sulfate and concentrated to provide 0.37 g (quantitative yield) of (±)-(2*S*,2'*R*)-2,3-dihydrobenzofuran-2-yl(phenyl)methanol as a clear oil. The material was moved forward without further purification.

^{1}H NMR (700 MHz, $CDCl_3$): δ 7.45 (d, *J* = 7.3 Hz, 2H), 7.40 (t, *J* = 7.7 Hz, 2H), 7.35 – 7.30 (m, 1H), 7.17 – 7.07 (m, 2H), 6.85 (td, *J* = 7.4, 0.9 Hz, 1H), 6.80 (d, *J* = 8.0 Hz, 1H), 5.17 (d, *J* = 3.9 Hz, 1H), 4.99 (td, *J* = 8.8, 3.9 Hz, 1H), 3.34 (dd, *J* = 15.7, 8.4 Hz, 1H), 2.91 (dd, *J* = 15.7, 9.3 Hz, 1H), 2.38 (bs, 1H). **^{13}C NMR (176 MHz, $CDCl_3$):** δ 159.5, 139.4, 128.6, 128.0, 128.0, 127.1, 126.3, 125.1, 120.9, 109.3, 86.5, 73.9, 29.3.

A flame-dried round bottom flask equipped with a magnetic stir bar was charged with (±)-(2*S*,2'*R*)-2,3-dihydrobenzofuran-2-yl(phenyl)methanol (50 mg, 0.26 mmol) and dichloromethane (1.3 mL). Sodium hydride (60% in mineral oil, 11 mg, 0.26 mmol) was added and the reaction was cooled to 0 °C in an ice water bath. *p*-Toluenesulfonyl chloride (55 mg, 0.29 mmol) was added and the reaction was stirred at 0 °C for one hour then warmed to room

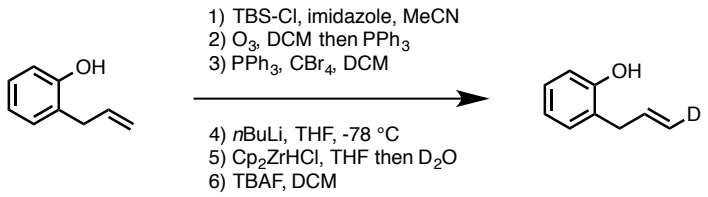
temperature and stirred for an additional three hours. The mixture was then diluted with diethyl ether, filtered and concentrated. The crude material was purified by silica flash chromatography to remove excess *p*-toluenesulfonyl chloride, however the starting material and product co-eluted to afford a 1:1 mixture of (±)-(2*S*,2'*R*)-2,3-dihydrobenzofuran-2-yl(phenyl)methyl 4-methylbenzenesulfonate and unreacted starting material as determined by NMR and mass spectrometry, that was effectively inseparable by silica gel flash chromatography. The material was carried on without further purification. Data are shown for the desired product only.

^{1}H NMR (700 MHz, $CDCl_3$): δ 7.56 – 7.51 (m, 2H), 7.44 (dd, *J* = 7.9, 1.5 Hz, 2H), 7.38 (dd, *J* = 8.5, 6.9 Hz, 2H), 7.34 – 7.29 (m, 1H), 7.26 (d, *J* = 5.6 Hz, 5H), 7.14 – 7.07 (m, 5H), 7.04 (td, *J* = 7.7, 1.3 Hz, 1H), 6.87 – 6.77 (m, 3H), 6.55 (d, *J* = 8.0 Hz, 1H), 5.59 (d, *J* = 5.4 Hz, 1H), 5.17 (d, *J* = 3.9 Hz, 1H), 5.03 – 4.93 (m, 2H), 3.31 (m, 2H), 3.18 (dd, *J* = 15.8, 9.5 Hz, 1H), 2.89 (dd, *J* = 15.7, 9.3 Hz, 1H), 2.37 (s, 3H).

A flame-dried round bottom flask equipped with a magnetic stir bar was charged with the crude (±)-(2*S*,2'*R*)-2,3-dihydrobenzofuran-2-yl(phenyl)methyl 4-methylbenzenesulfonate described above and diethyl ether (1.0 mL). Lithium aluminum hydride (29 mg, 0.69 mmol) was added to the reaction at 0 °C. The reaction was then warmed to room temperature and stirred for fifteen hours at room temperature. The reaction was diluted with diethyl ether and quenched with water (29 μL), 15% aqueous sodium hydroxide (29 μL) and water (87 μL). The reaction was then filtered through glass wool, dried with sodium sulfate and concentrated. The crude material was purified by flash chromatography to provide 7.1 mg (13% over two steps, 99.0% *d*-incorporation by MS) (±)-(2*S*,2'*R*)-2-(2-phenylmethyl-*d*)-2,3-dihydrobenzofuran as a clear oil.

^{1}H NMR (700 MHz, CD_3CN): δ 7.36 – 7.28 (m, 4H), 7.24 (tt, *J* = 6.6, 2.0 Hz, 1H), 7.16 (dd, *J* = 7.3, 1.4 Hz, 1H), 7.10 – 7.05 (m, 1H), 6.80 (td, *J* = 7.4, 1.0 Hz, 1H), 6.70 (d, *J* = 7.9 Hz, 1H), 5.01 (ddd, *J* = 9.0, 7.6, 6.0 Hz, 1H), 3.22 (dd, *J* = 15.6, 8.9 Hz, 1H), 3.00 – 2.91 (m, 2H). **^{13}C NMR (176 MHz, CD_3CN):** δ 160.4, 138.9, 130.4, 129.3, 128.8, 128.1, 127.4, 126.1, 121.2, 109.8, 84.4, 42.0 (t, J = 19.4 Hz), 35.3. **HR-MS (EI):** calculated for $C_{15}H_{14}DO$ $[M]^+$ 211.1107, found 21109. **IR (film):** 3026, 2919, 2850, 1596, 1480, 1463, 1231, 748, 700 cm^{-1}.

Synthesis of *d*-2a



(*E*)-2-(Allyl-3-*d*)phenol (*d*-2a). Conditions were based on a procedure reported by de Koning and coworkers.[19] A flame dried round-bottom flask was charged with MeCN (200 mL), 2-allylphenol (4.90 mL, 37.3 mmol), and imidazole (3.05 g, 44.8 mmol). *tert*-Butyldimethylsilyl chloride (6.75 g, 44.8 mmol) was then added to the solution in one portion and the reaction was stirred at rt for 18 h. The reaction mixture was concentrated *in vacuo* and the resulting material was transferred to a separatory funnel using EtOAc (200 mL). The organic suspension was then washed with water (200 mL) and the aqueous layer was washed with additional portions of EtOAc (2 x 200 mL). The combined organic layers were then washed with brine (300 mL), dried over anhydrous sodium sulfate, filtered and concentrated. The resulting crude product was purified by flash chromatography to obtain 8.75 g (94%) of (2-allylphenoxy)(*tert*-butyl)dimethylsilane as a clear oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.17–7.04 (m, 2 H), 6.89 (t, *J* = 7.4 Hz, 1 H), 6.79 (dd, *J* = 8.0, 1.2 Hz, 1 H), 5.98 (ddt, *J* = 18.9, 9.4, 6.6 Hz, 1 H), 5.11–4.97 (m, 2 H), 3.37 (d, *J* = 6.5 Hz, 2 H), 1.02 (s, 9 H), 0.23 (s, 6 H). Spectroscopic data were consistent with those previously reported.[19]

A flame dried round-bottom flask was charged with (2-allylphenoxy)(*tert*-butyl)dimethylsilane (3.00 g, 12.1 mmol), and dichloromethane (173 mL). The solution was then cooled to –78 °C and ozone was bubbled through the reaction mixture until a blue color persisted (ca. 30 min). The mixture was then sparged with nitrogen and PPh_3 6.33 g (24.2 mmol, 2 equiv) was added. The solution was warmed to rt and stirred for 12 h. The mixture was then concentrated *in vacuo* and the crude product was triturated with hexanes, filtered and concentrated. The crude product was then purified by flash chromatography to obtain 2.56 g (85%) of 2-(2-((*tert*-butyldimethylsilyl)oxy)phenyl)acetaldehyde as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.69 (t, *J* = 2.2 Hz, 1 H), 7.19 (td, *J* = 7.8, 1.8 Hz, 1 H), 7.15 (dd, *J* = 7.5, 1.8 Hz, 1 H), 6.95 (td, *J* = 7.4, 1.2 Hz, 1 H), 6.87 (dd, *J* = 8.0, 1.2 Hz, 1 H), 3.63 (d, *J* = 2.2 Hz, 2 H), 0.99 (s, 9 H), 0.25 (s, 6 H). Spectroscopic data were consistent with those previously reported.[19]

Conditions were based on a procedure reported by Corey and coworkers.[20] A flame dried round-bottom flask was charged with PPh_3 (2.32 g, 37.1 mmol), CBr_4 (6.14 g, 18.5 mmol) and dichloromethane (46 mL). The mixture was then cooled to 0 °C and 2-{2-[(*tert*-butyldimethylsilyl)oxy]phenyl}acetaldehyde (2.32 g, 9.26 mmol) was added slowly via syringe. The mixture was stirred for 40 min at 0 °C and then filtered through a plug of silica using dichloromethane as the eluent. The resulting solution was concentrated and the crude product was then purified by flash chromatography to obtain 3.63 g (97%) of *tert*-butyl[2-(3,3-dibromoallyl)phenoxy]dimethylsilane as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.14 (ddd, *J* = 15.5, 7.5, 1.8 Hz, 2 H), 6.91 (td, *J* = 7.5, 1.2 Hz, 1 H), 6.81 (dd, *J* = 8.0, 1.2 Hz, 1 H), 6.58 (t, *J* = 7.1 Hz, 1 H), 3.40 (d, *J* = 7.1 Hz, 2 H), 1.02 (s, 9 H), 0.26 (s, 6 H).

Conditions were based on a procedure reported by Corey and coworkers.[20] A flame dried round-bottom flask was charged with *tert*-butyl[2-(3,3-dibromoallyl)phenoxy]dimethylsilane (3.62 g, 8.86 mmol) and THF (58 mL). The mixture was then cooled to –78 °C and *n*BuLi (2.5 M in hexanes, 7.27 mL, 18.18 mmol) was added slowly. The resulting mixture was stirred at –78 °C for 1 h, then was warmed to rt and stirred for an additional 1 h. The mixture was then poured into water (150 mL) and the aqueous layer was extracted with hexanes (3 x 150 mL). The combined organic layers were washed with brine, dried over anhydrous sodium sulfate, filtered and concentrated. The crude product was purified by flash chromatography and the resulting product was further purified by kuglerohr distillation to obtain 1.13 g (52%) of *tert*-butyldimethyl[2-(prop-2-yn-1-yl)phenoxy]silane as a colorless oil.

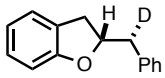
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50 (d, *J* = 7.7 Hz, 1 H), 7.12 (t, *J* = 7.0 Hz, 1 H), 6.95 (t, *J* = 7.5 Hz, 1 H), 6.78 (d, *J* = 8.1 Hz, 1 H), 3.56 (d, *J* = 2.7 Hz, 2 H), 2.16 (t, *J* = 2.7 Hz, 1 H), 1.02 (s, 9 H), 0.24 (s, 6 H).

Conditions were based on a procedure reported by Chemler and coworkers.[21] A flame dried round-bottom flask was charged with bis(cyclopentadienyl)zirconium chloride hydride (704 mg, 2.73 mmol) followed by a solution of *tert*-butyldimethyl[2-(prop-2-yn-1-yl)phenoxy]silane (538 mg, 2.18 mmol) in THF (1.10 mL). The resulting mixture was stirred at rt for 2.5 h at which time D_2O (58 mL, 3.2 mmol) was added via syringe. The reaction mixture was stirred at rt for an additional 18 h then was diluted with 1:1 Et_2O/hexanes (20 mL), dried over anhydrous sodium sulfate, filtered and concentrated. The crude product was purified by flash chromatography to obtain 507 mg (93%) of (*E*)-[2-(allyl-3-*d*)phenoxy](*tert*-butyl)dimethylsilane as a colorless oil. This material contained ca 12% of an inseparable side product that resulted from over reduction of the alkyne to the alkane. Data are for the major product.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.17–7.04 (m, 2 H), 6.89 (td, *J* = 7.5, 1.2 Hz, 1 H), 6.79 (dd, *J* = 8.0, 1.2 Hz, 1 H), 6.04–5.91 (m, 1 H), 5.03 (dt, *J* = 17.0, 1.7 Hz, 1 H), 3.37 (dd, *J* = 6.5, 1.6 Hz, 2 H), 1.01 (s, 9 H), 0.23 (s, 6 H).

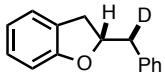
A flame dried round-bottom flask was charged with (*E*)-[2-(allyl-3-*d*)phenoxy](*tert*-butyl)dimethylsilane (300 mg, 1.20 mmol), dichloromethane (2.4 mL) and TBAF (1 M in THF, 2.4 mL, 2.4 mmol). The mixture was stirred at rt for 1.5 h then was poured into saturated aqueous ammonium chloride (20 mL) and extracted with Et_2O (3 x 30 mL). The combined organic layers were then washed with brine (30 mL), dried over anhydrous sodium sulfate, filtered and concentrated. The crude product was then purified by flash chromatography to obtain 116 mg (72%, 88.4% *d*-incorporation by MS) of (*E*)-2-(allyl-3-*d*)phenol as a colorless oil. This material contained ca 12% of an inseparable side product that resulted from over reduction of the alkyne to the alkane in the previous step. Data are for the major product.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.19–7.10 (m, 2 H), 6.90 (td, *J* = 7.4, 1.2 Hz, 1 H), 6.82 (dd, *J* = 8.0, 1.2 Hz, 1 H), 6.04 (dtt, *J* = 17.1, 6.4, 1.5 Hz, 1 H), 5.16 (dt, *J* = 17.1, 1.7 Hz, 1 H), 4.96 (s, br, 1 H), 3.43 (dd, *J* = 6.3, 1.6 Hz, 2 H). **^{13}C NMR (176 MHz, $CDCl_3$):** δ 154.2, 136.4, 130.6, 128.0, 125.40, 121.1, 116.4 (d, *J* = 24.3 Hz), 116.0, 35.2. **HR-MS (EI):** calculated for C_9H_9DO $[M]^+$ 135.0789, found 135.0789. **IR (film):** 3535, 3033, 1454, 1212, 980, 748 cm^{-1}.



(±)-(2*S*,2'*R*)-2-(2-Phenylmethyl-*d*)-2,3-dihydrobenzofuran (*d*-4a). The coupling of (*E*)-2-(allyl-3-*d*)phenol (15 mg, 0.10 mmol) and phenyl trifluoromethanesulfonate (19 μL, 0.12 mmol) was performed using the general procedure. Upon purification by flash chromatography 17 mg (81% yield, ca. 20:1 dr, 85.6% *d*-incorporation by MS) of (±)-(2*S*,2'*R*)-2-(2-phenylmethyl-*d*)-2,3-dihydrobenzofuran (*d*-4a). was obtained as a clear oil. Comparison with the independently prepared **(±)-(2*S*,2'*R*)-2-(2-Phenylmethyl-*d*)-2,3-dihydrobenzofuran (*d*-4a).** demonstrated that the reaction proceeds predominantly through an *anti*-oxypalladation mechanism. No significant loss or migration of the isotope was observed.

^{1}H NMR (700 MHz, CD_3CN): 7.36 – 7.28 (m, 4H), 7.26 – 7.21 (m, 1H), 7.16 (dd, *J* = 7.3, 1.4 Hz, 1H), 7.08 (td, *J* = 7.7, 1.2 Hz, 1H), 6.81 (td, *J* = 7.4, 1.0 Hz, 1H), 6.70 (d, *J* = 8.0 Hz, 1H), 5.01 (ddd, *J* = 9.1, 7.6, 6.1 Hz, 1H), 3.22 (dd, *J* = 15.6, 8.9 Hz, 1H), 3.00 – 2.86 (m, 2H). **^{13}C NMR (176 MHz, CD_3CN):** δ 160.4, 139.0, 130.5, 129.3, 128.8, 128.1, 127.4, 126.1, 121.2, 109.9, 84.5, 42.0 (d, *J* = 19.5 Hz), 35.4. **HR-MS (EI):** calculated for $C_{15}H_{13}DO$ $[M]^+$ 211.1102, found 211.1103. **IR (film):** 3026, 2916, 1595, 1478, 1462, 1229, 747, 700 cm^{-1}.



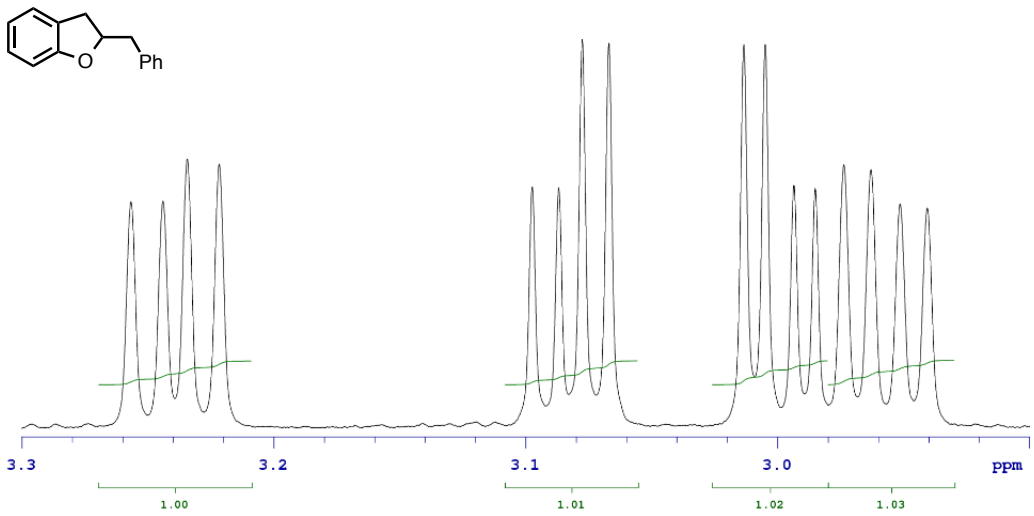
(+/-)-(2*S*,2'*S*)-2-(Phenylmethyl-*d*)-2,3-dihydrobenzofuran (*d*-4a). The coupling of (*E*)-2-(allyl-3-*d*)phenol (31 mg, 0.23 mmol) and bromobenzene (49 μL, 0.46 mmol) was performed using the general procedure for the synthesis of chromans that was previously reported by our group.[15] Upon purification by flash chromatography 7.9 mg (16%, ca. 2:1 dr, 87.1% *d*-incorporation by MS) of (+/-)-(2*S*,2'*S*)-2-(Phenylmethyl-*d*)-2,3-dihydrobenzofuran was obtained as a clear oil. Comparison with the independently prepared (±)-(2*S*,2'*R*)-2-(phenylmethyl-*d*)-2,3-dihydrobenzofuran demonstrated that the reaction proceeds through both *syn*- and *anti*-oxypalladation mechanisms, with the *syn*- mechanism being predominant. No significant loss or migration of the isotope was observed.

^{1}H NMR (700 MHz, CD_3CN): δ 7.36 – 7.26 (m, 4H), 7.27 – 7.20 (m, 1H), 7.16 (d, *J* = 7.3 Hz, 1H), 7.08 (t, *J* = 7.7 Hz, 1H), 6.80 (td, *J* = 7.4, 1.0 Hz, 1H), 6.70 (d, *J* = 7.9 Hz, 1H), 5.01 (q, *J* = 7.8 Hz, 1H), 3.22 (dd, *J* = 15.7, 8.8 Hz, 1H), 3.05 (dt, *J* = 7.5, 2.0 Hz, 1H), 2.94 (dd, *J* = 15.7, 7.7 Hz, 1H). **^{13}C NMR (176 MHz, CD_3CN):** δ 160.4, 139.0, 130.5, 129.3, 128.8, 128.1, 127.4, 126.1, 121.2, 109.9, 84.5, 42.0 (t, *J* = 19.7 Hz), 35.4. **HR-MS (EI):** calculated for $C_{15}H_{13}DO$ $[M]^+$ 211.1102, found 211.1103. **IR (film):** 3026, 2916, 1595, 1478, 1462, 1229, 747, 700 cm^{-1}.

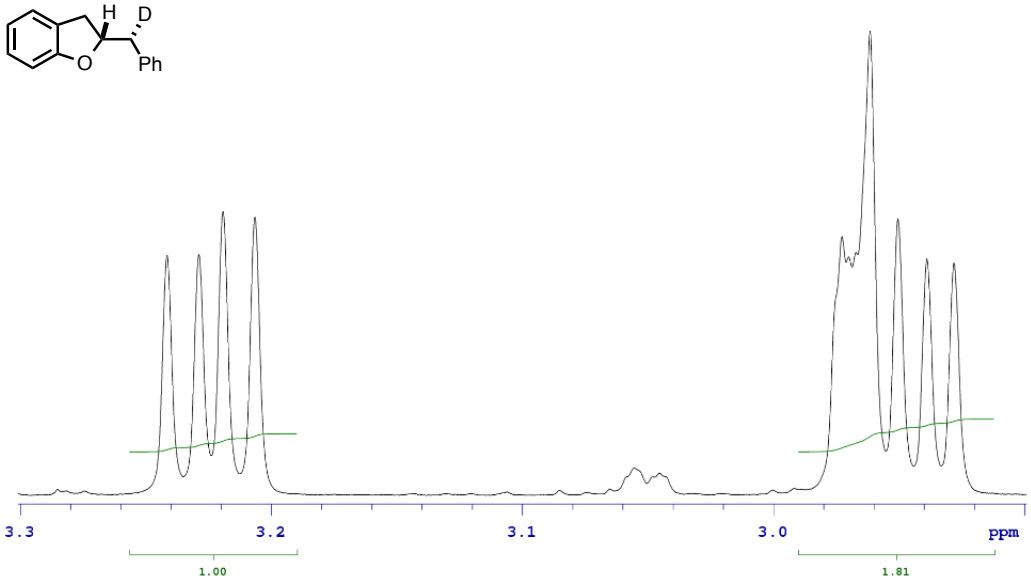
Assignment of Stereochemistry

The stereochemical assignments of the products generated from the coupling of (*E*)-2-(allyl-3-*d*)phenol and phenyl trifluoromethanesulfonate/bromobenzene were determined by comparison of ^{1}H-NMR spectra in CD_3CN with the independently prepared (±)-(2*S*,2'*R*)-2-(phenylmethyl-*d*)-2,3-dihydrobenzofuran.

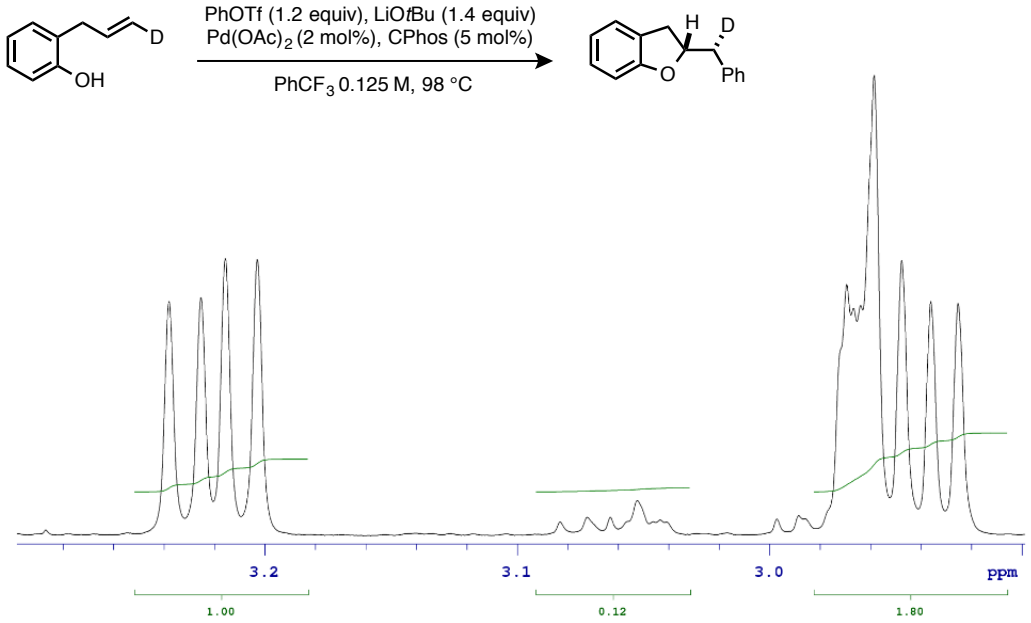
2-Benzyl-2,3-dihydrobenzofuran



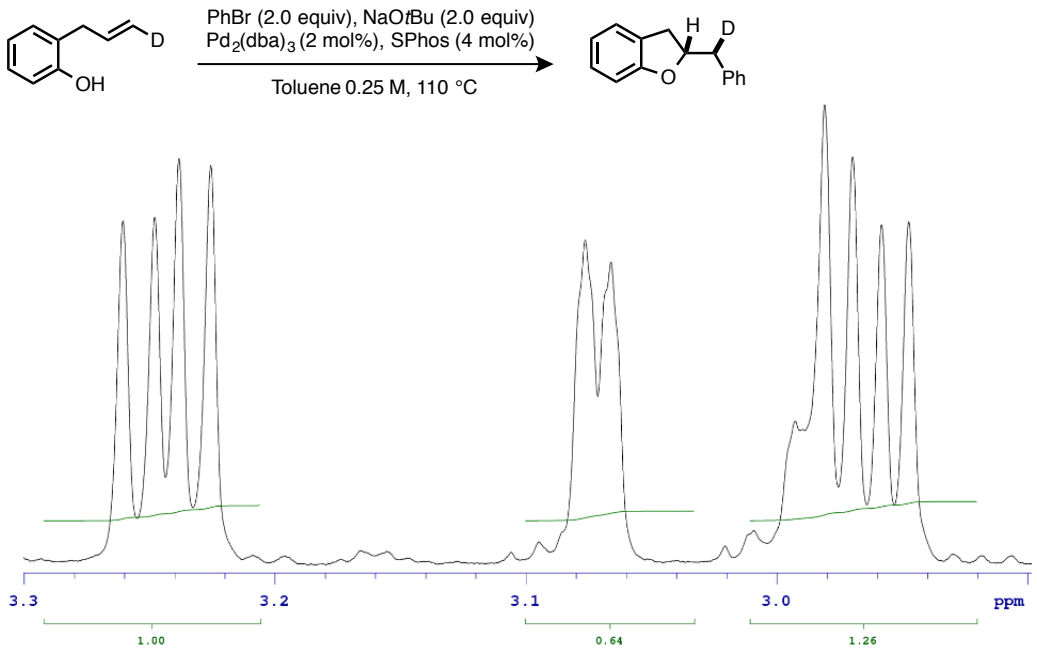
(±)-(2*S*,2'*R*)-2-(Phenylmethyl-*d*)-2,3-dihydrobenzofuran (standard)



(±)-(2*S*,2'*R*)-2-(Phenylmethyl-*d*)-2,3-dihydrobenzofuran (via Pd-catalyzed carboalkoxylation)



(±)-(2*S*,2'*S*)-2-(-Phenylmethyl-*d*)-2,3-dihydrobenzofuran (Chroman conditions)



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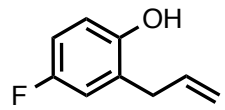

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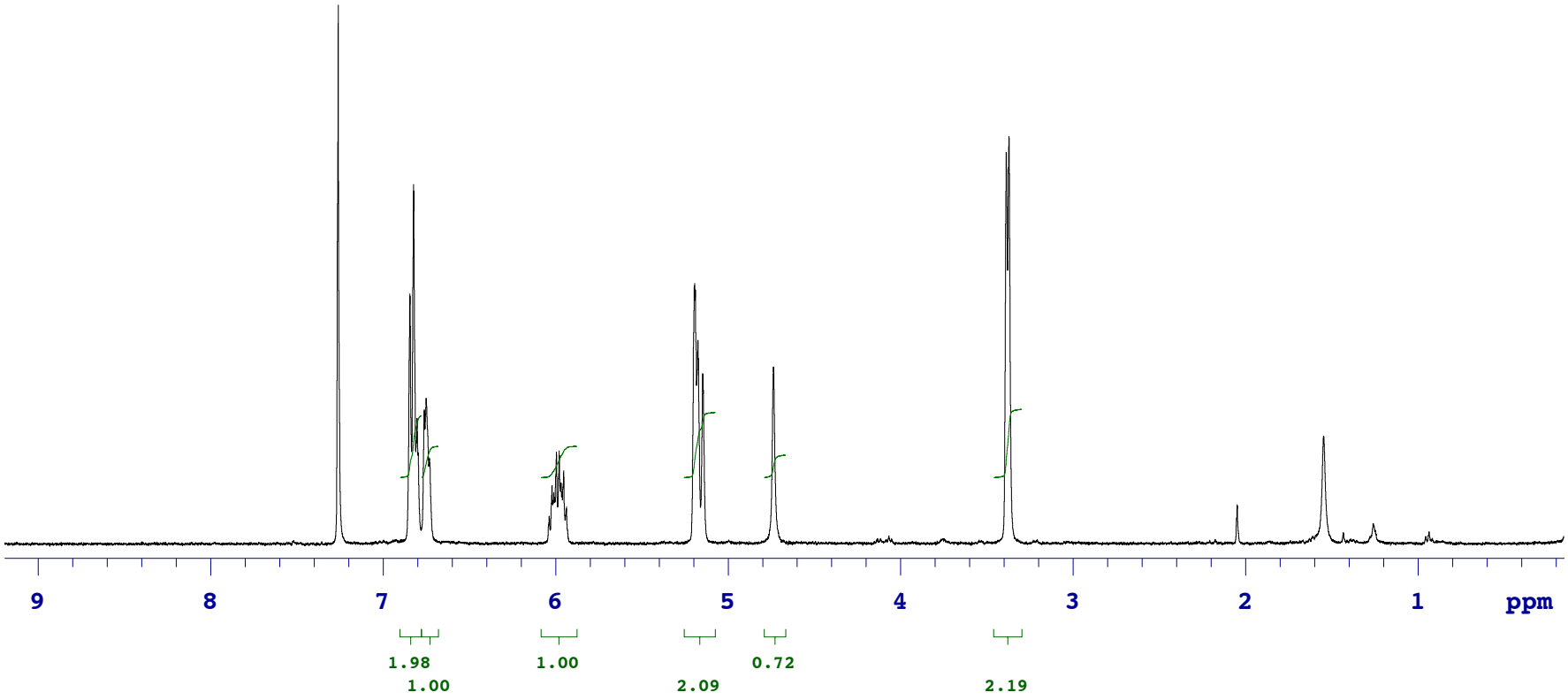

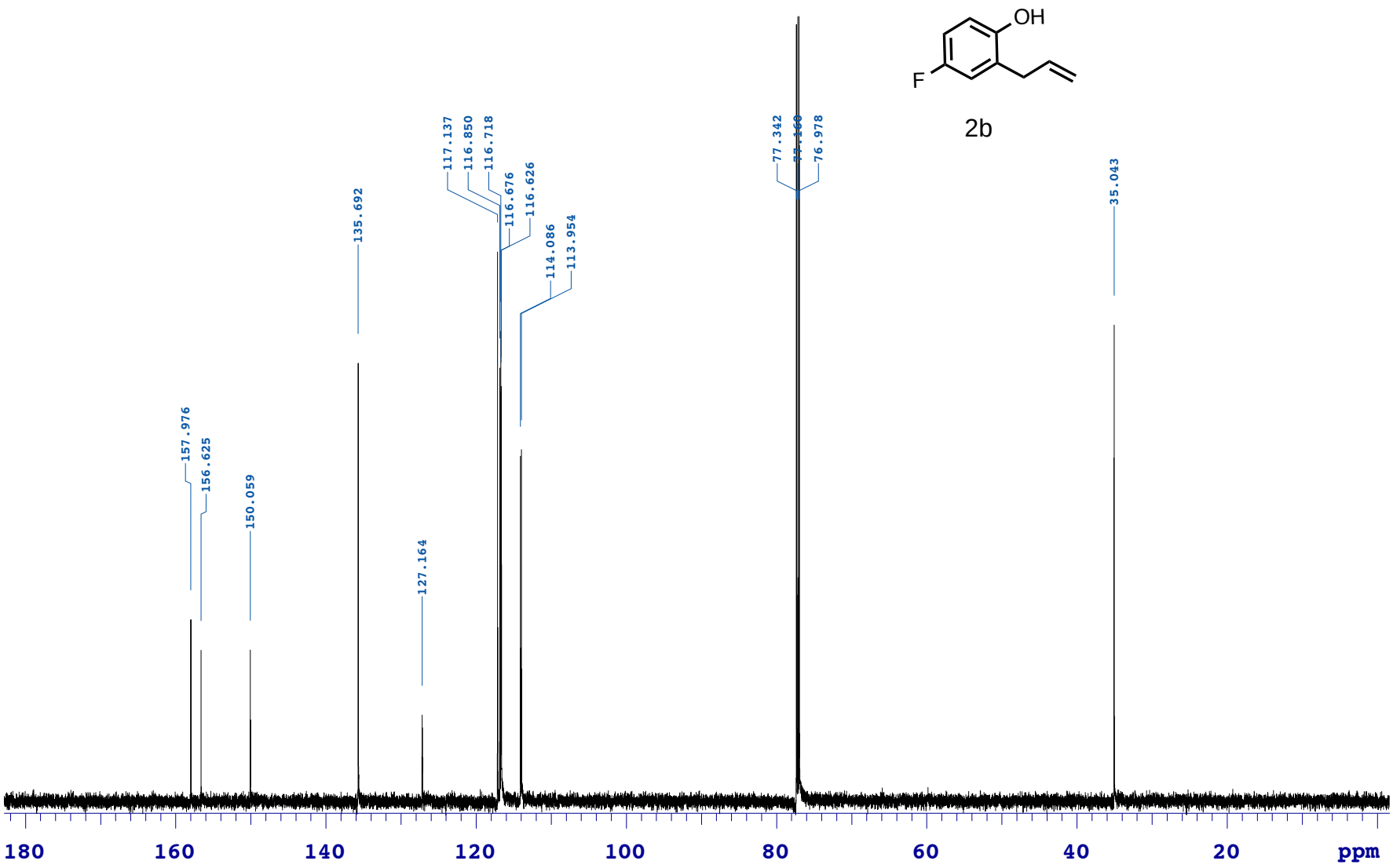
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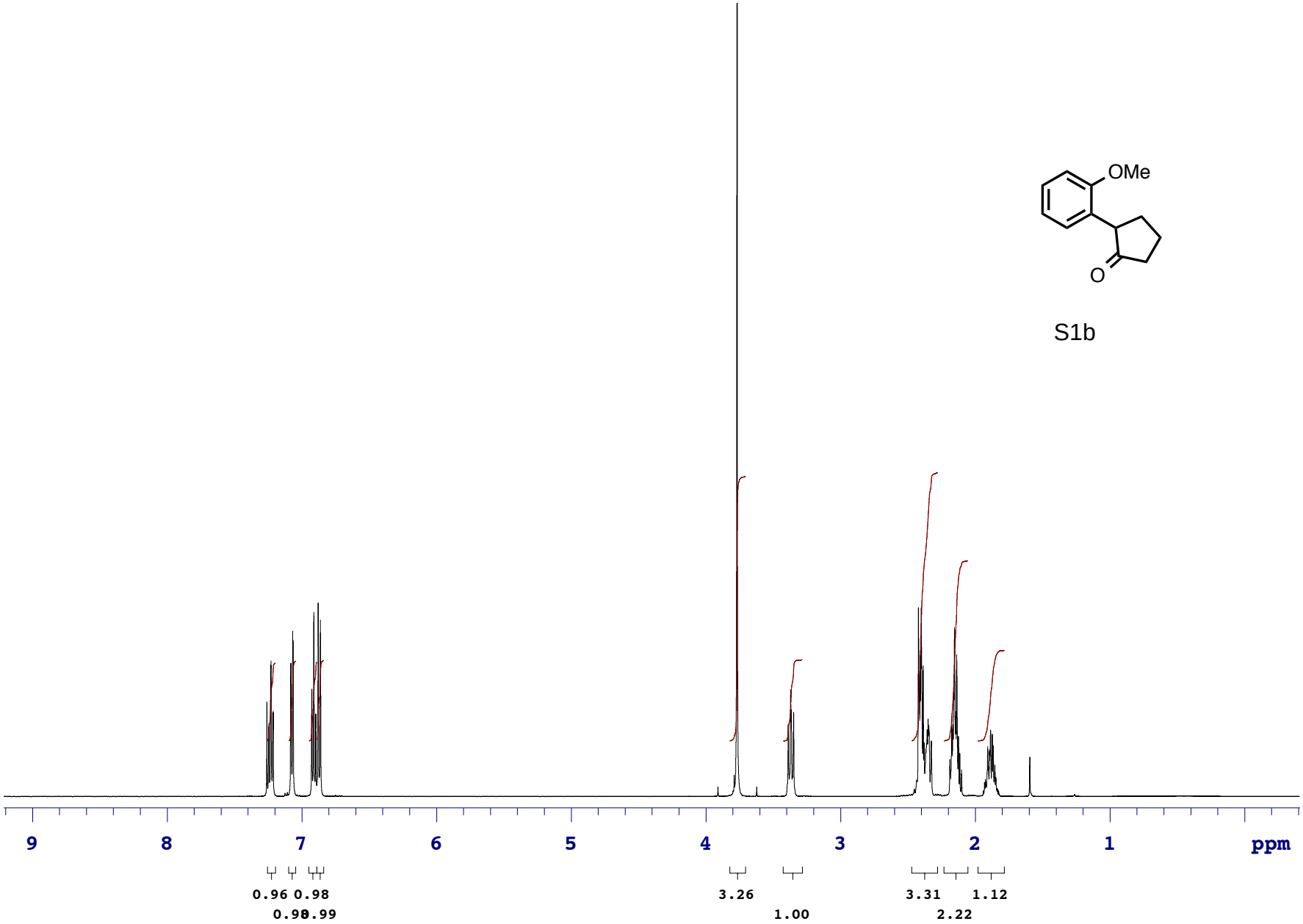
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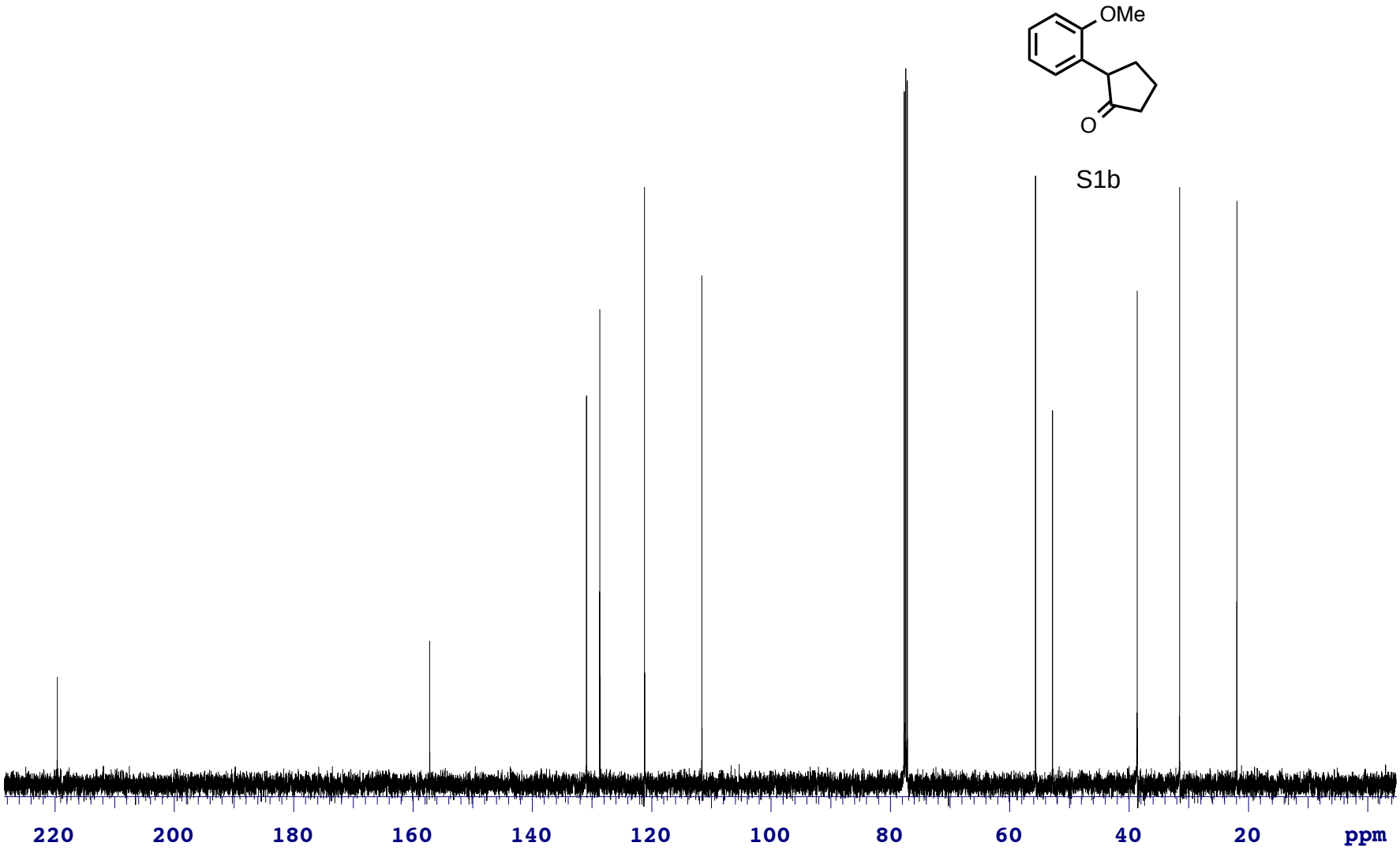
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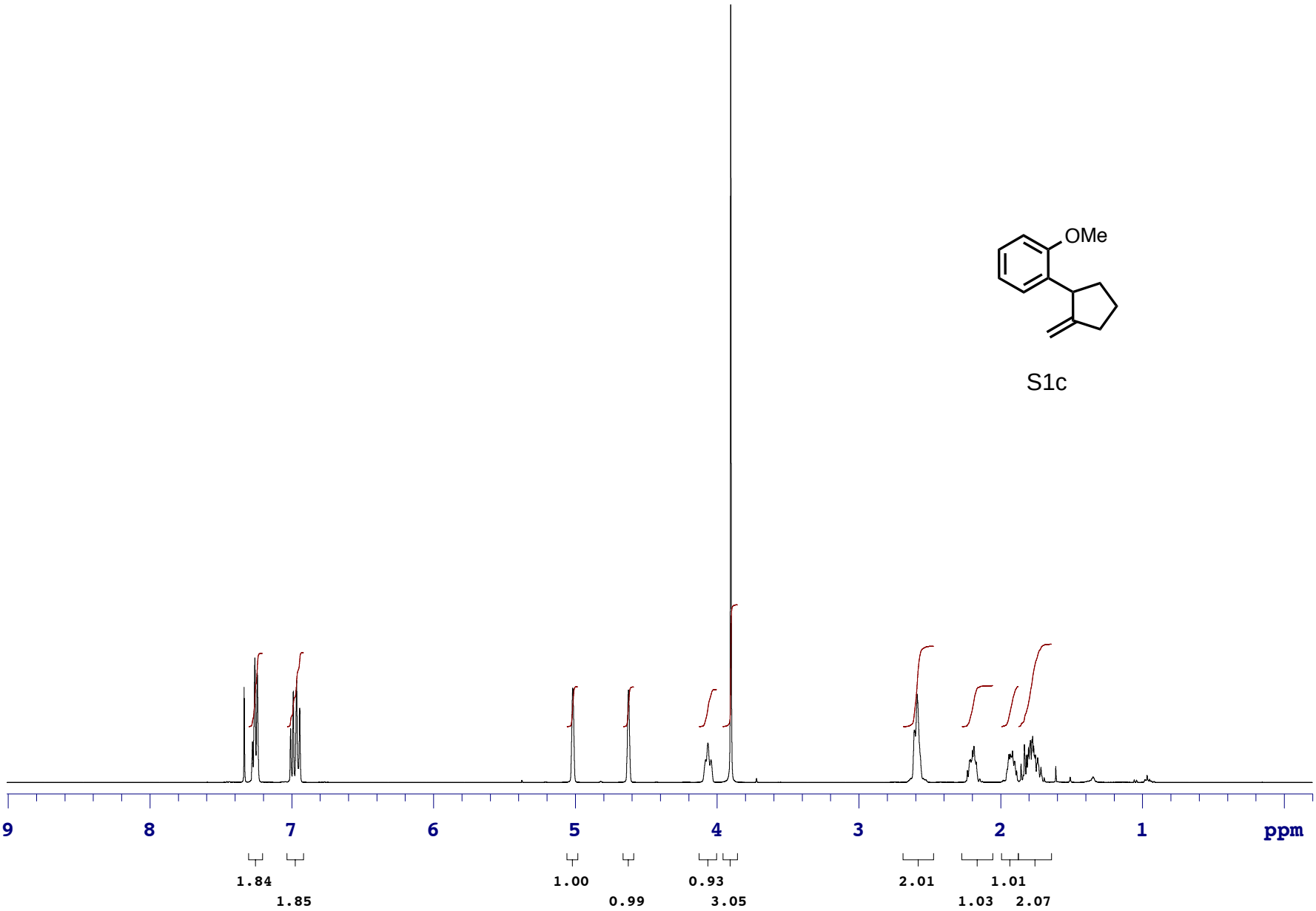
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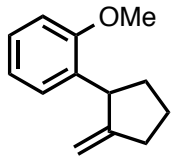

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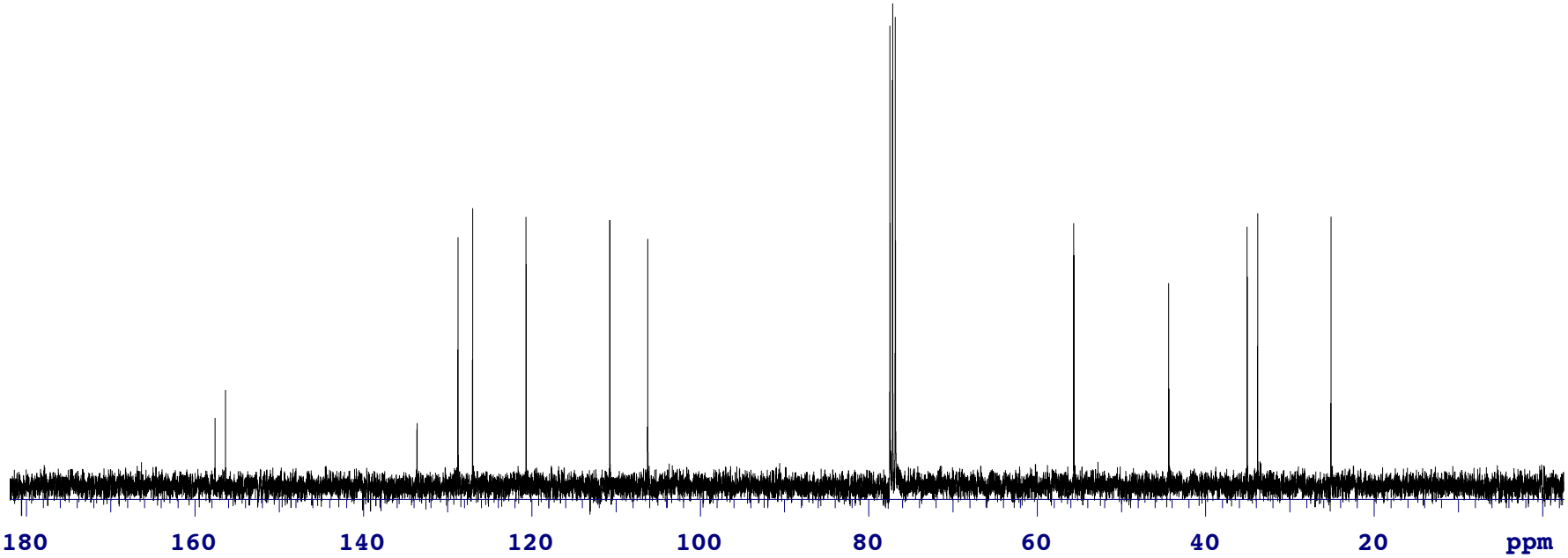

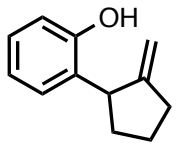

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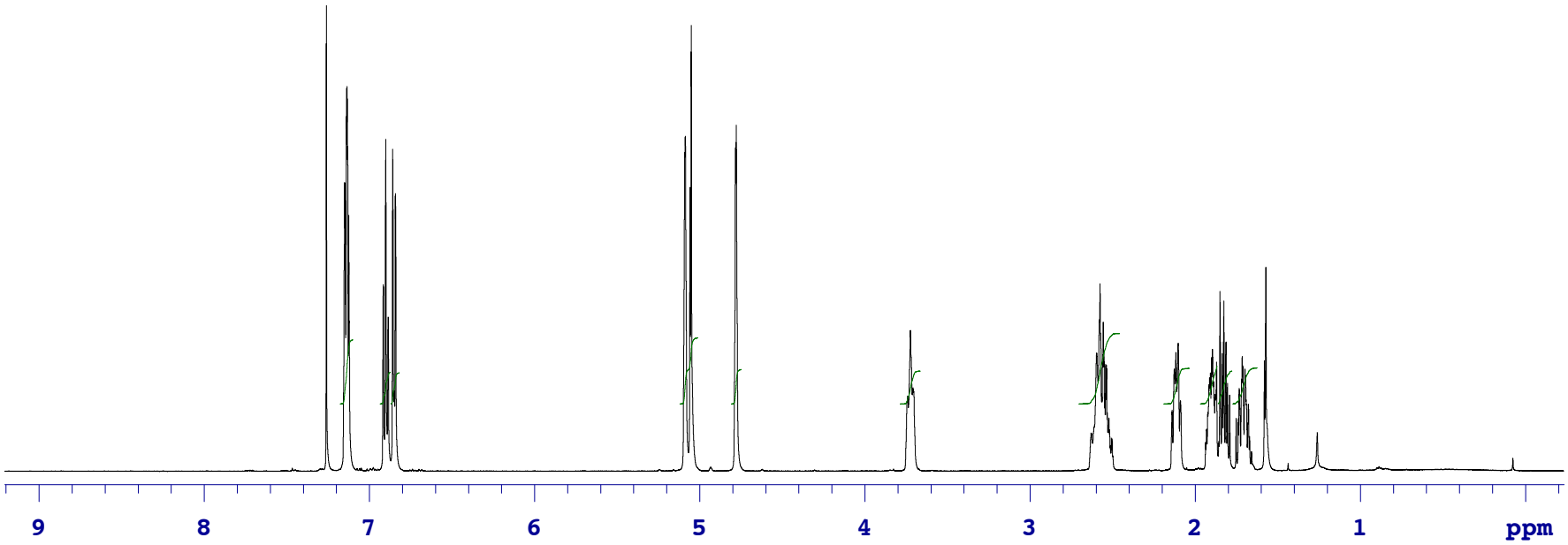

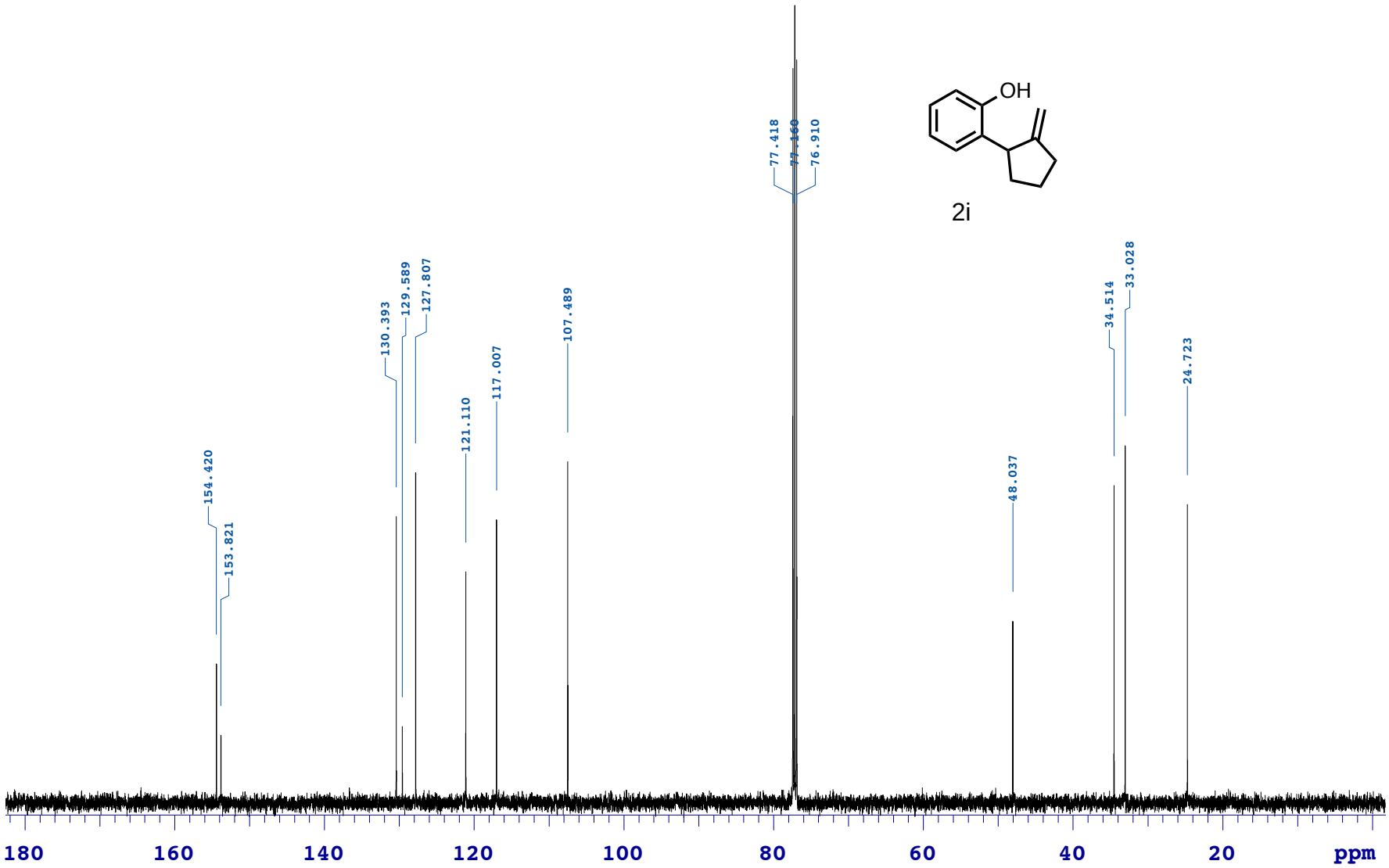
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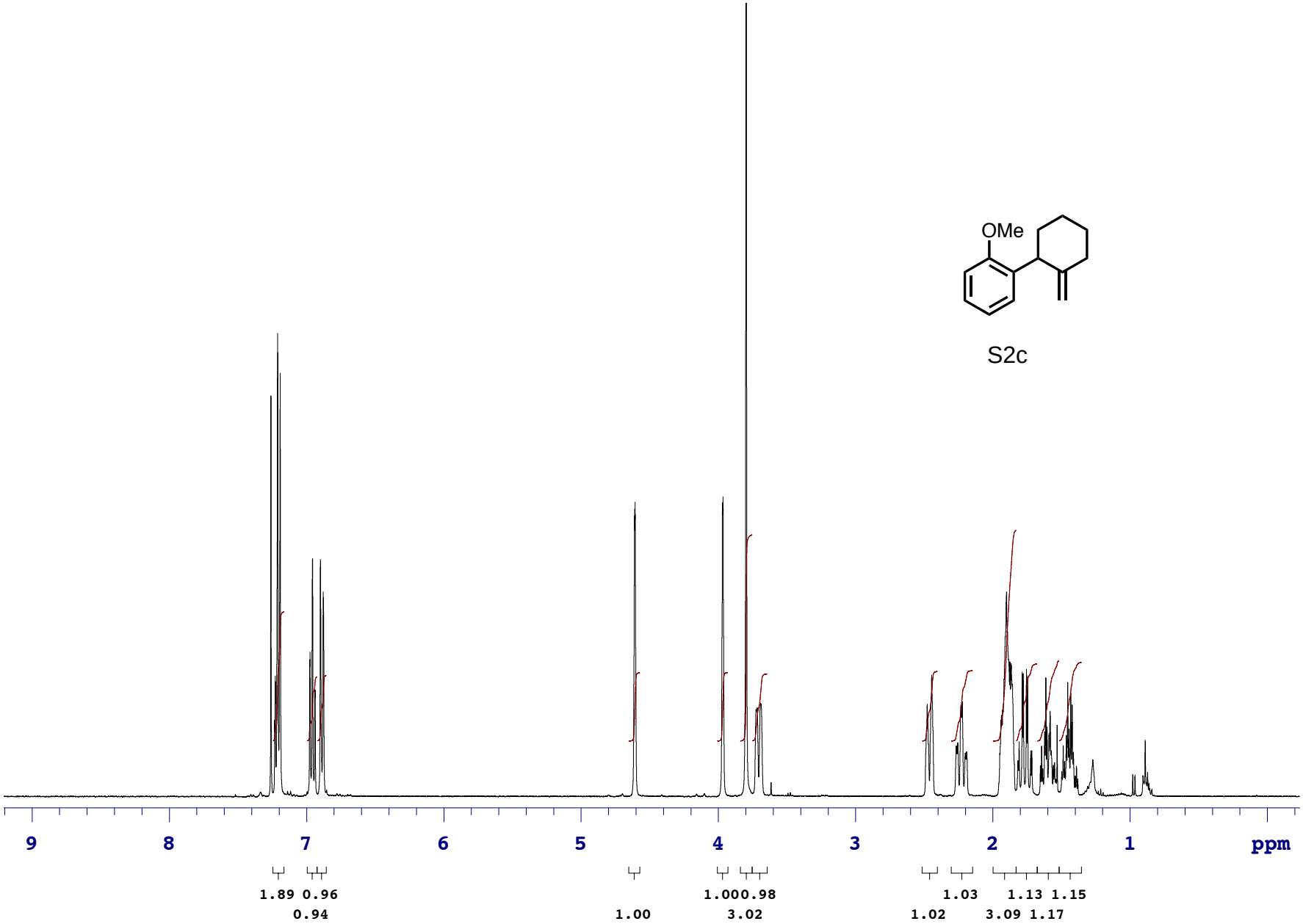
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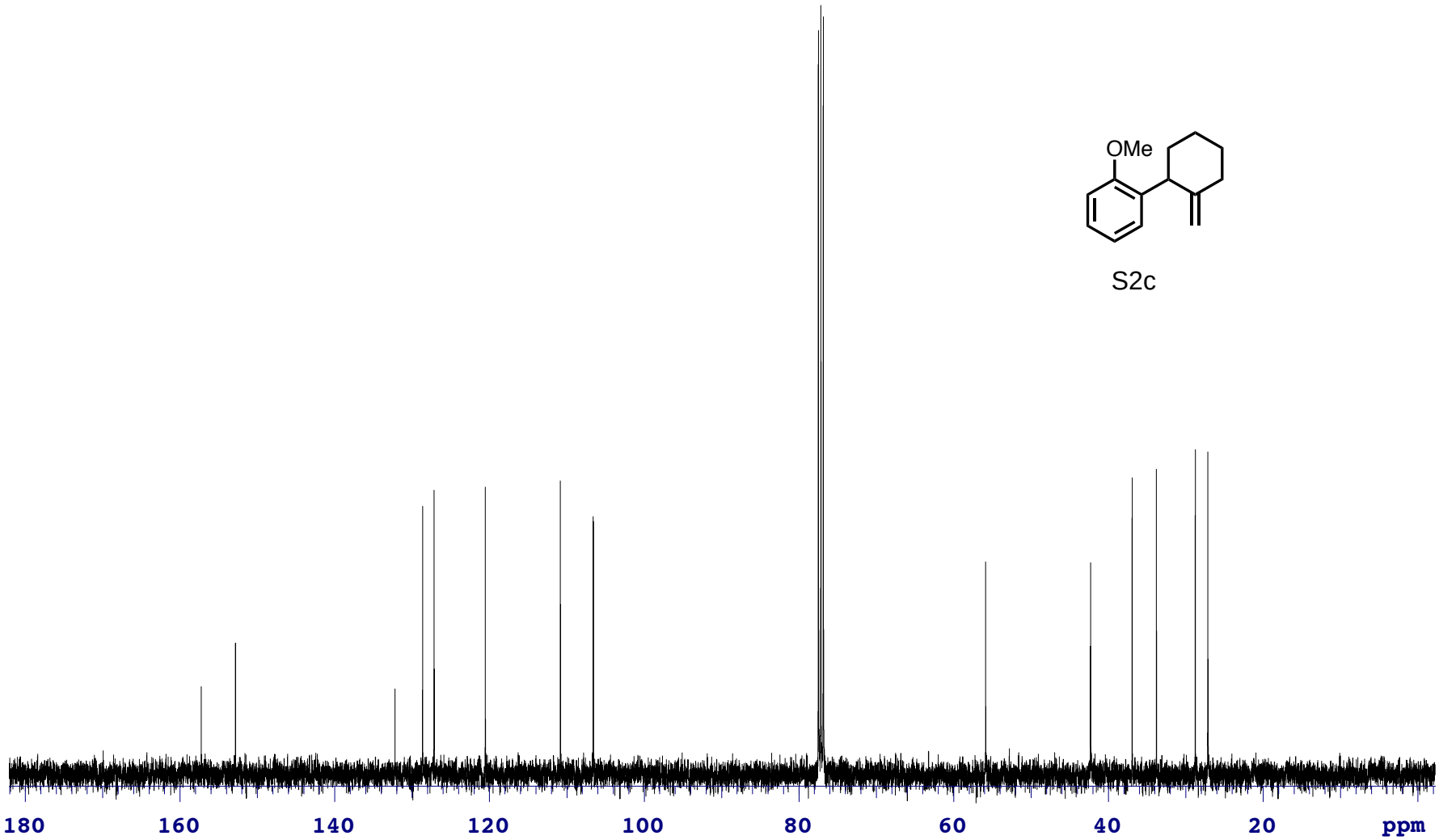
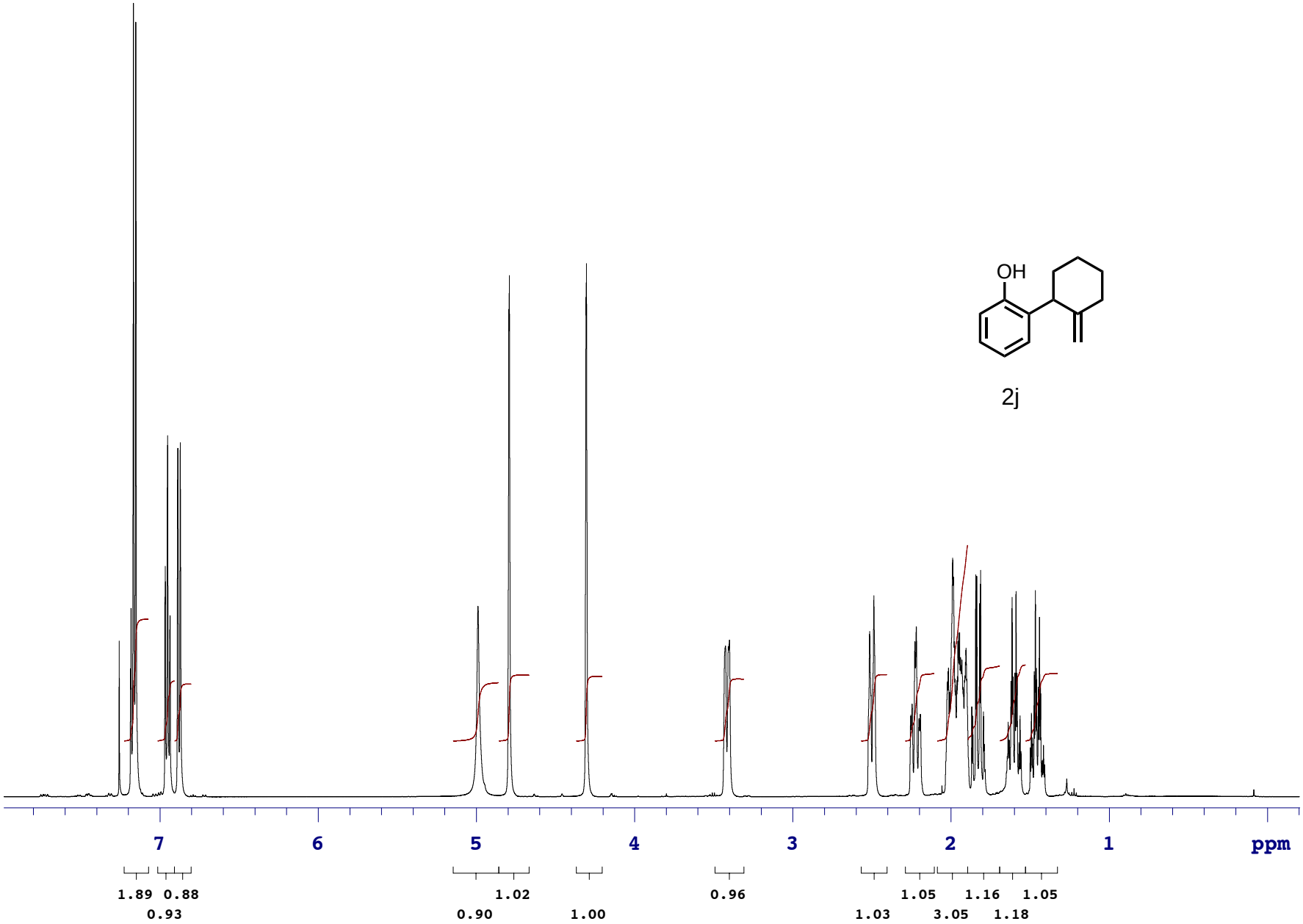
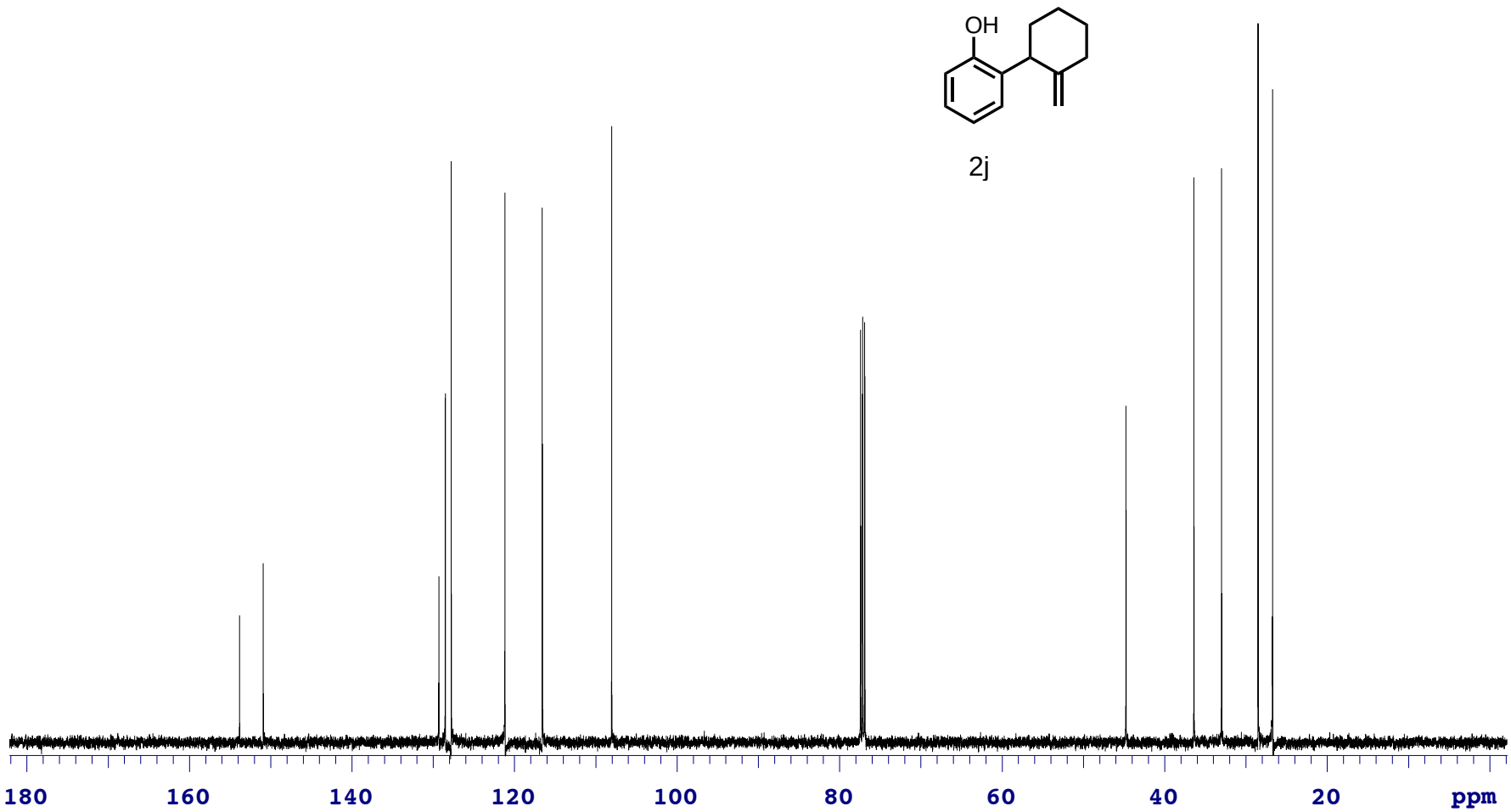
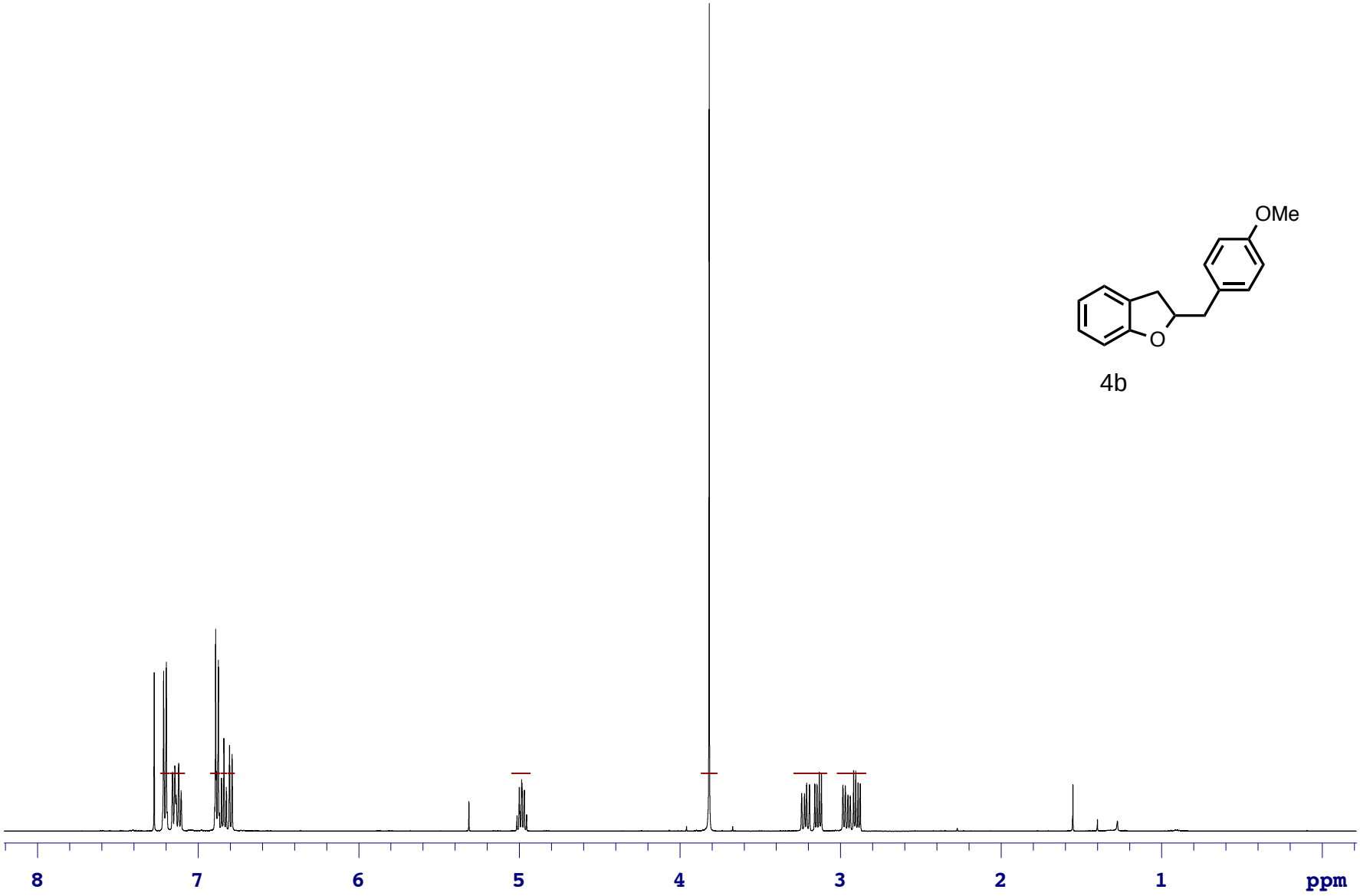
1.02
1.03
1.13 1.15
3.09 1.17

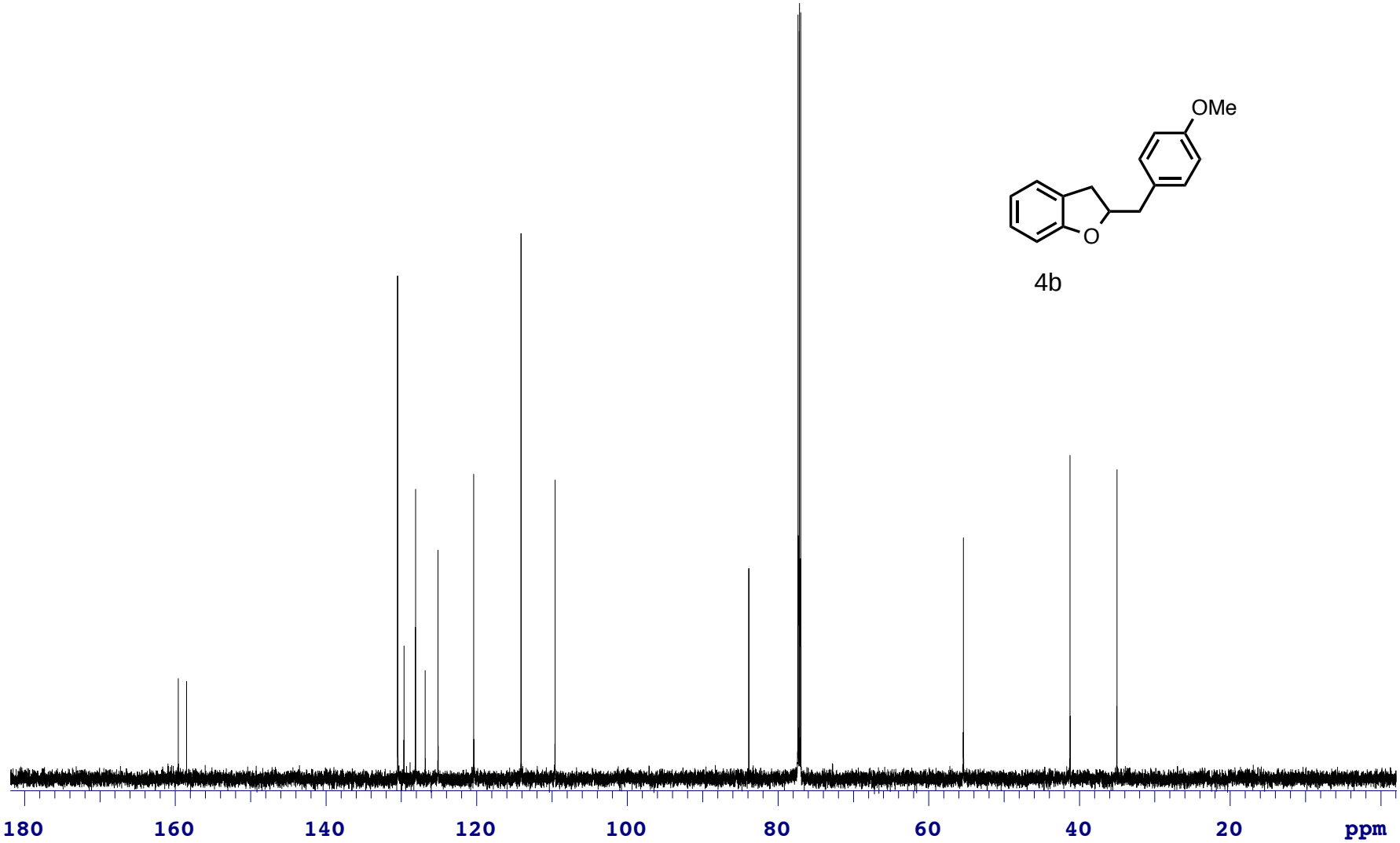


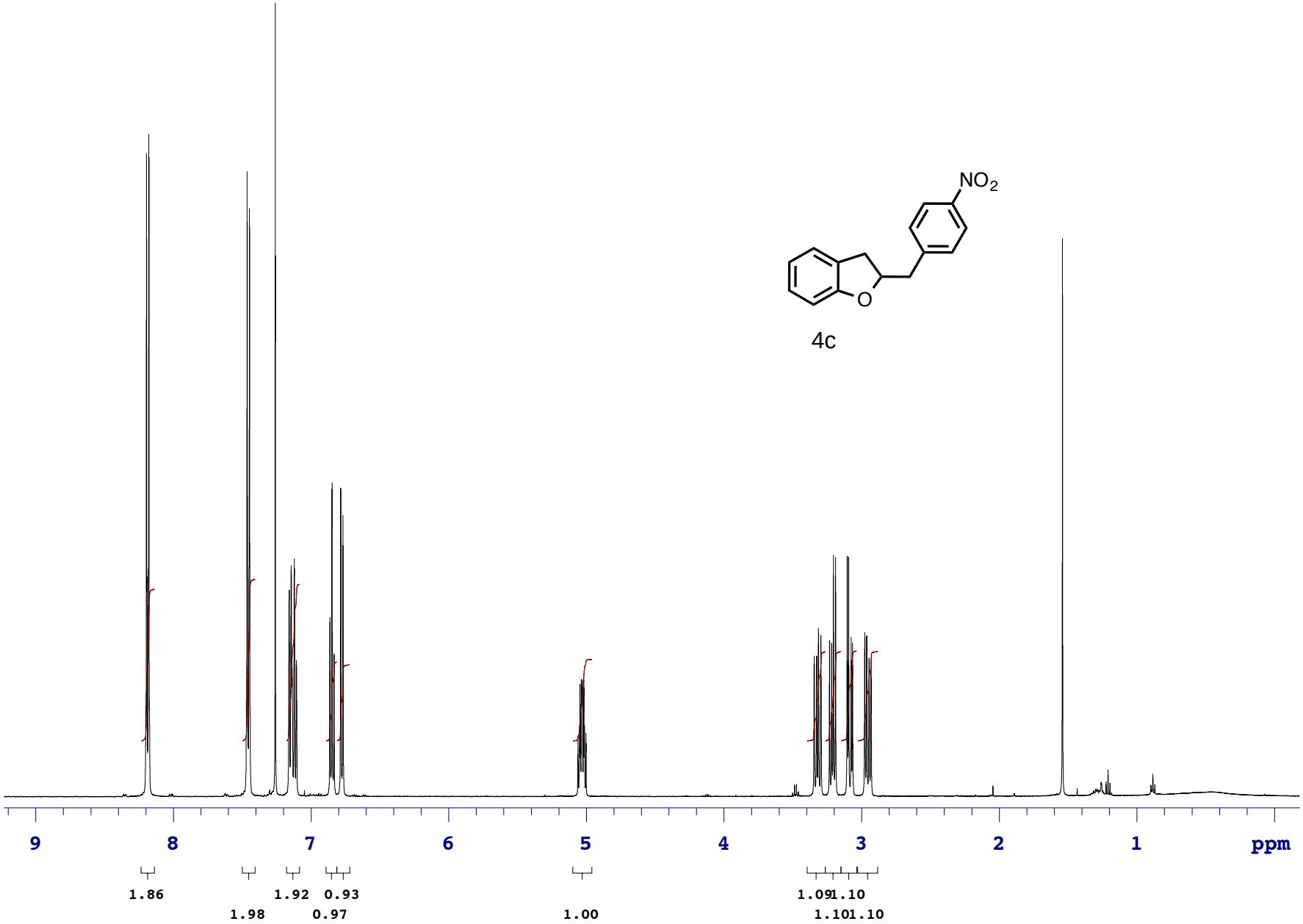
S2c

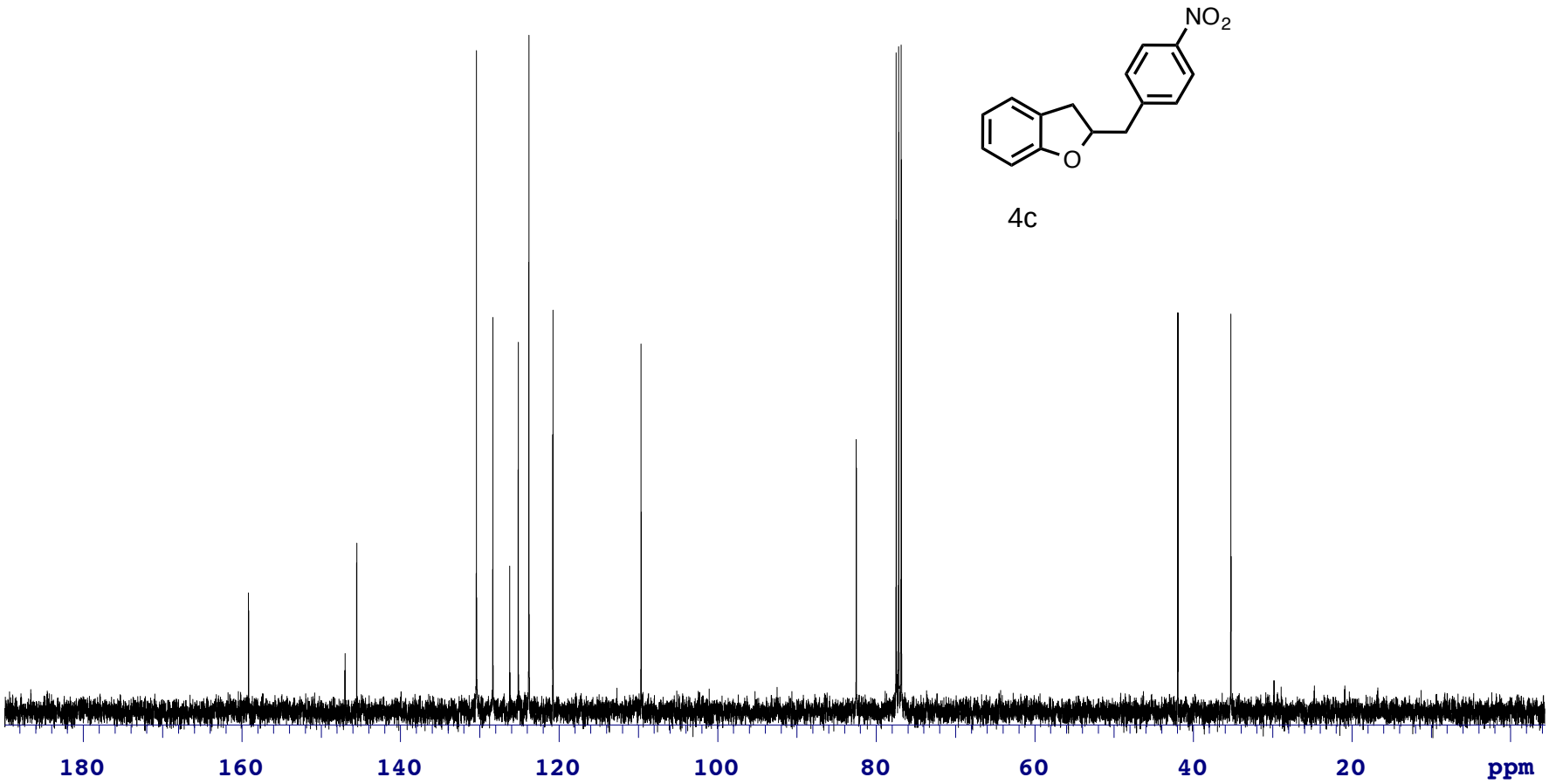

OH
2j
7
6
5
4
3
2
1
ppm
1.89
0.88
0.93
0.90
1.02
1.00
0.96
1.03
1.05
3.05
1.16
1.18
1.05


OH
2j
180
160
140
120
100
80
60
40
20
ppm

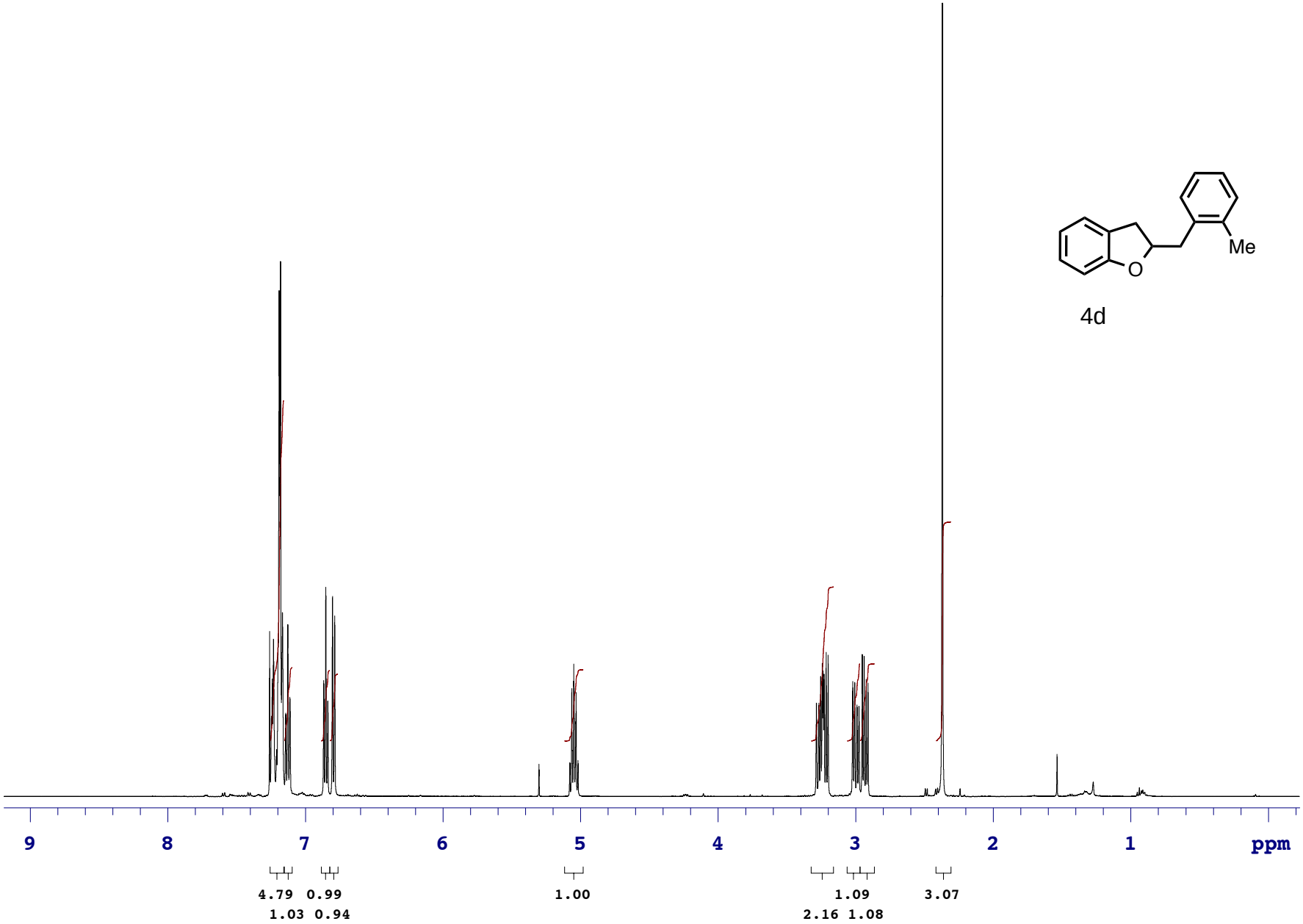

OMe
O
4b
8
7
6
5
4
3
2
1
ppm

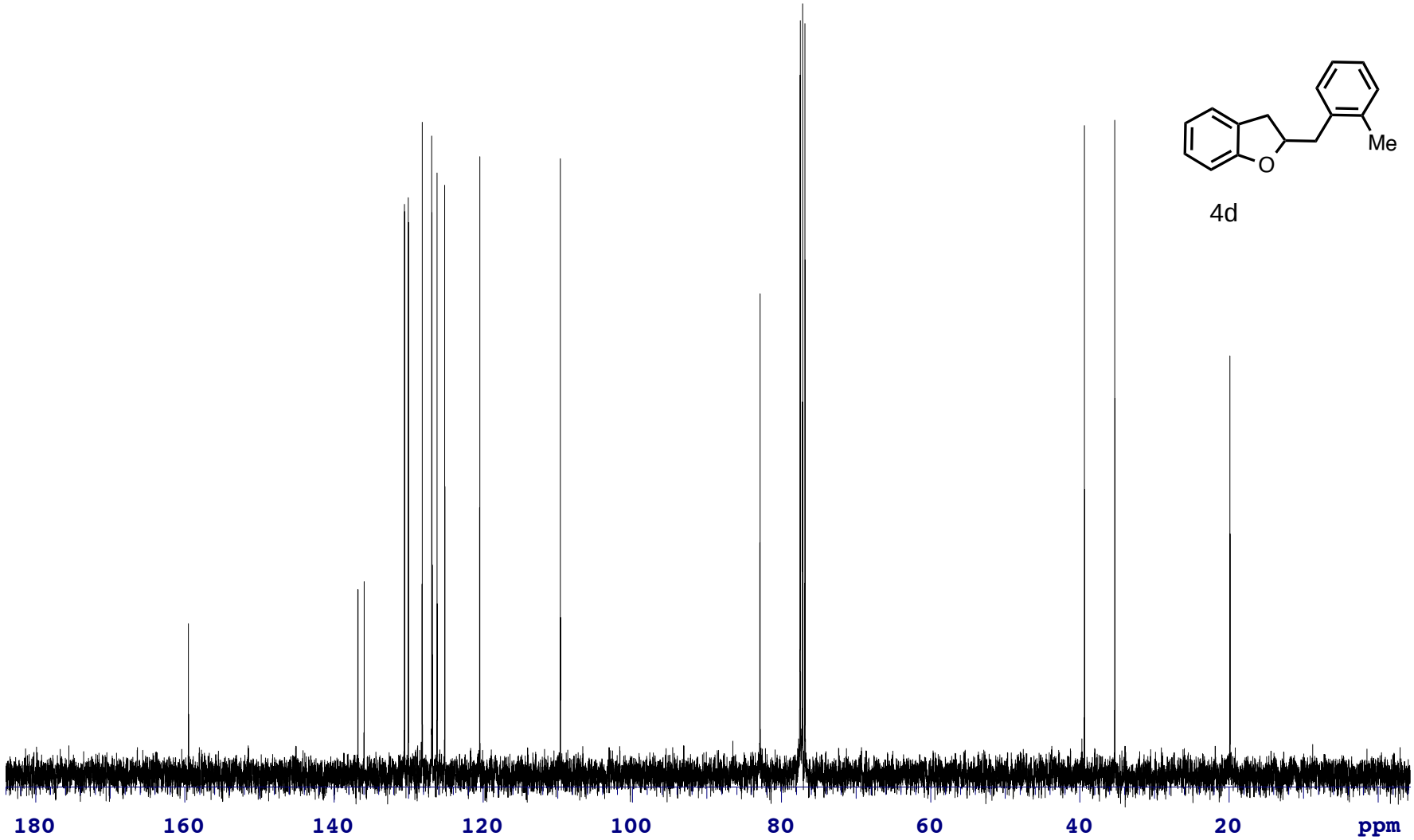

OMe
O
4b
180
160
140
120
100
80
60
40
20
ppm

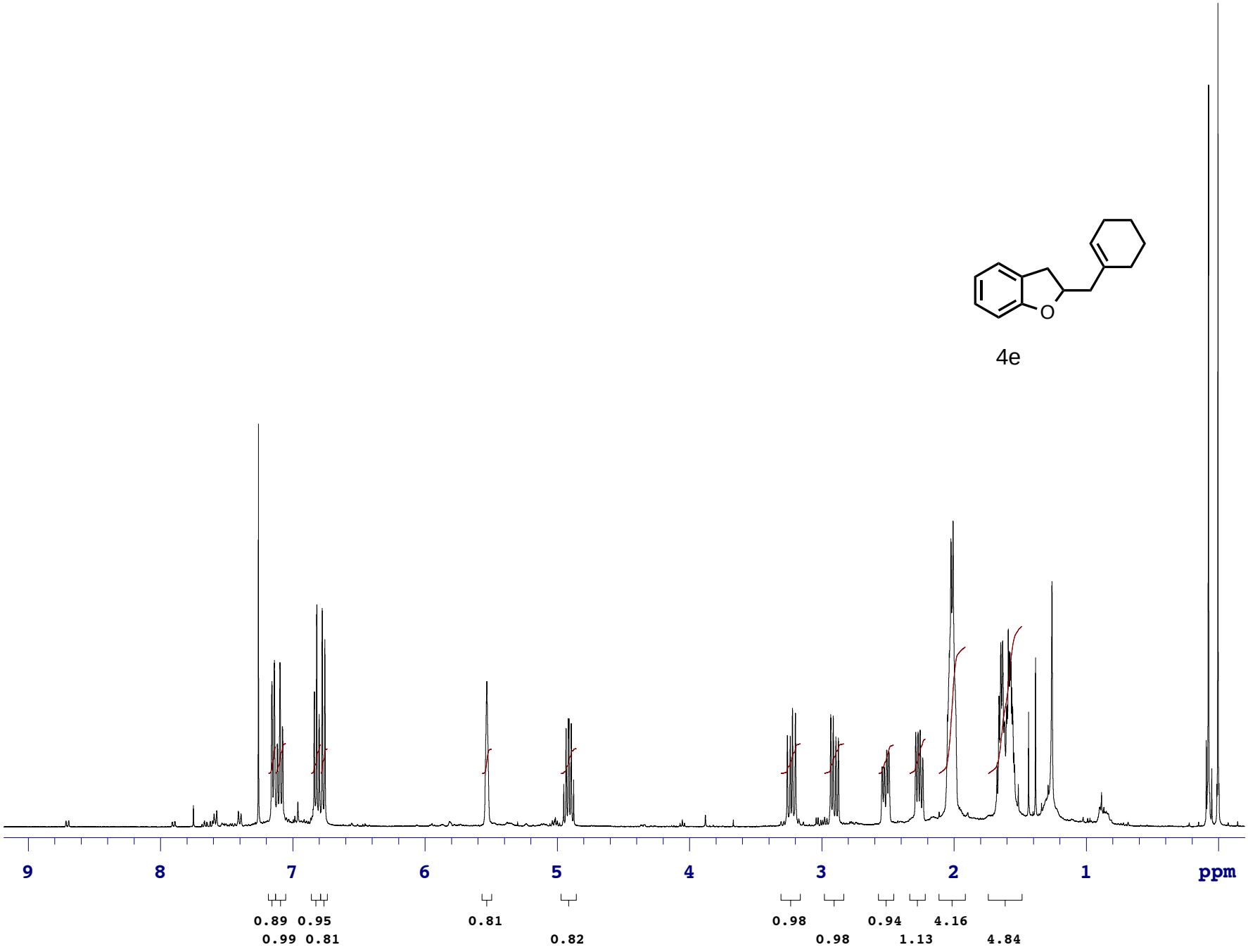

NO2
O
4c
9
8
7
6
5
4
3
2
1
ppm
1.86
1.98
1.92
0.97
0.93
1.00
1.09
1.10
1.10
1.10

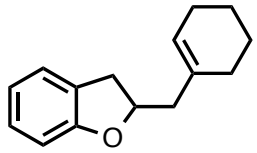


4c

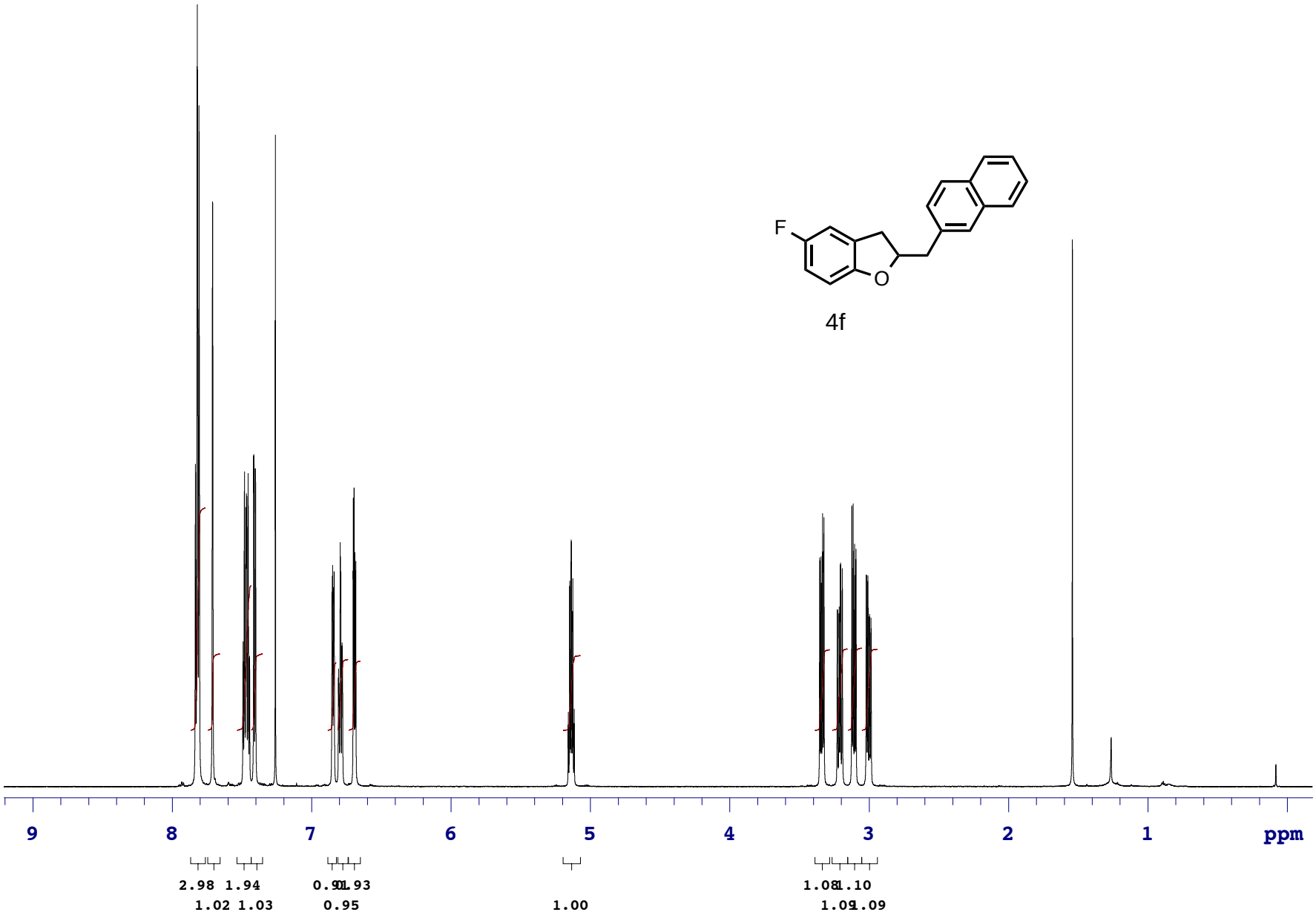

Me
O
4d
9
8
7
6
5
4
3
2
1
ppm
4.79
1.03
0.99
0.94
1.00
2.16
1.09
1.08
3.07

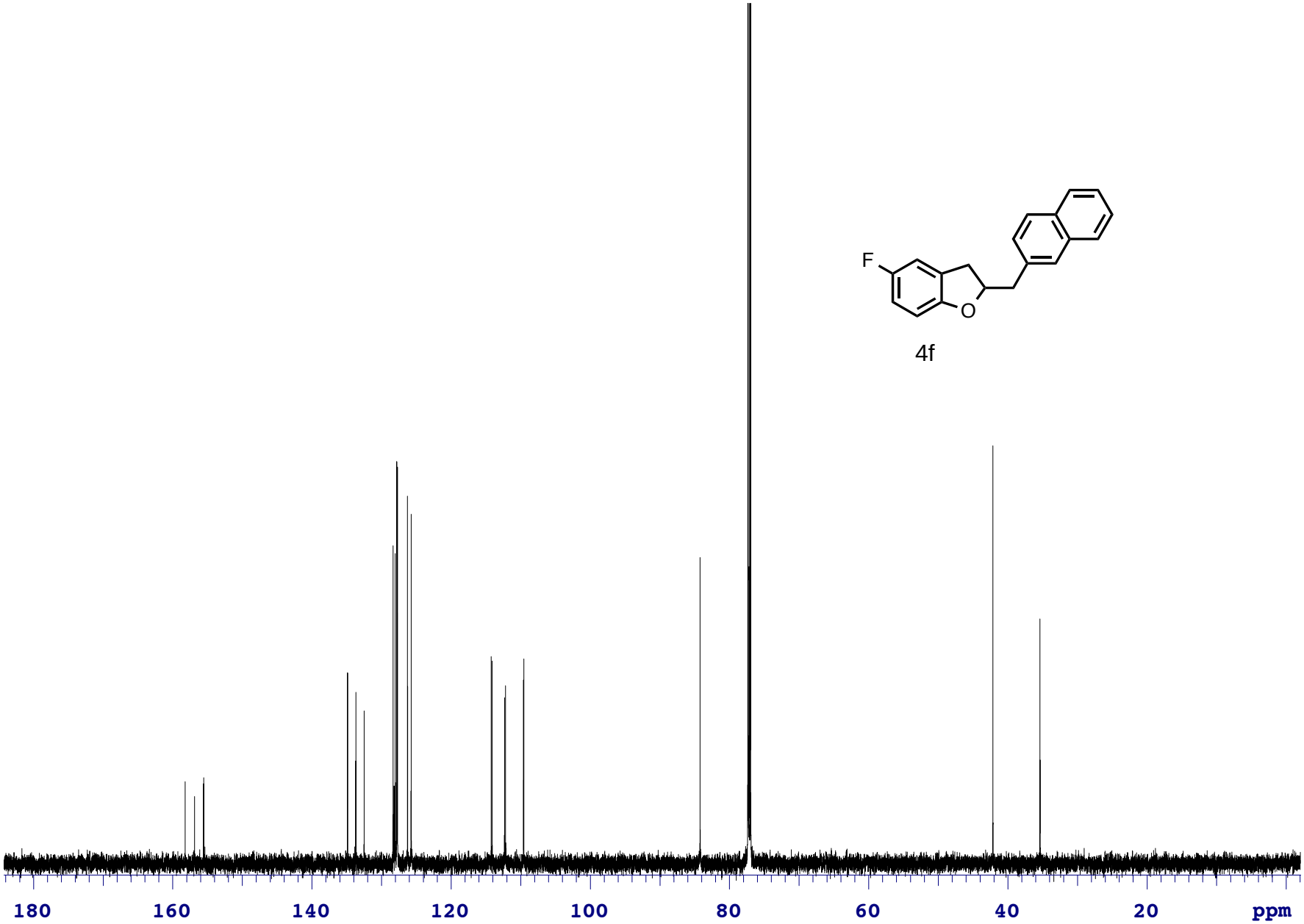

Me
O
4d
180
160
140
120
100
80
60
40
20
ppm

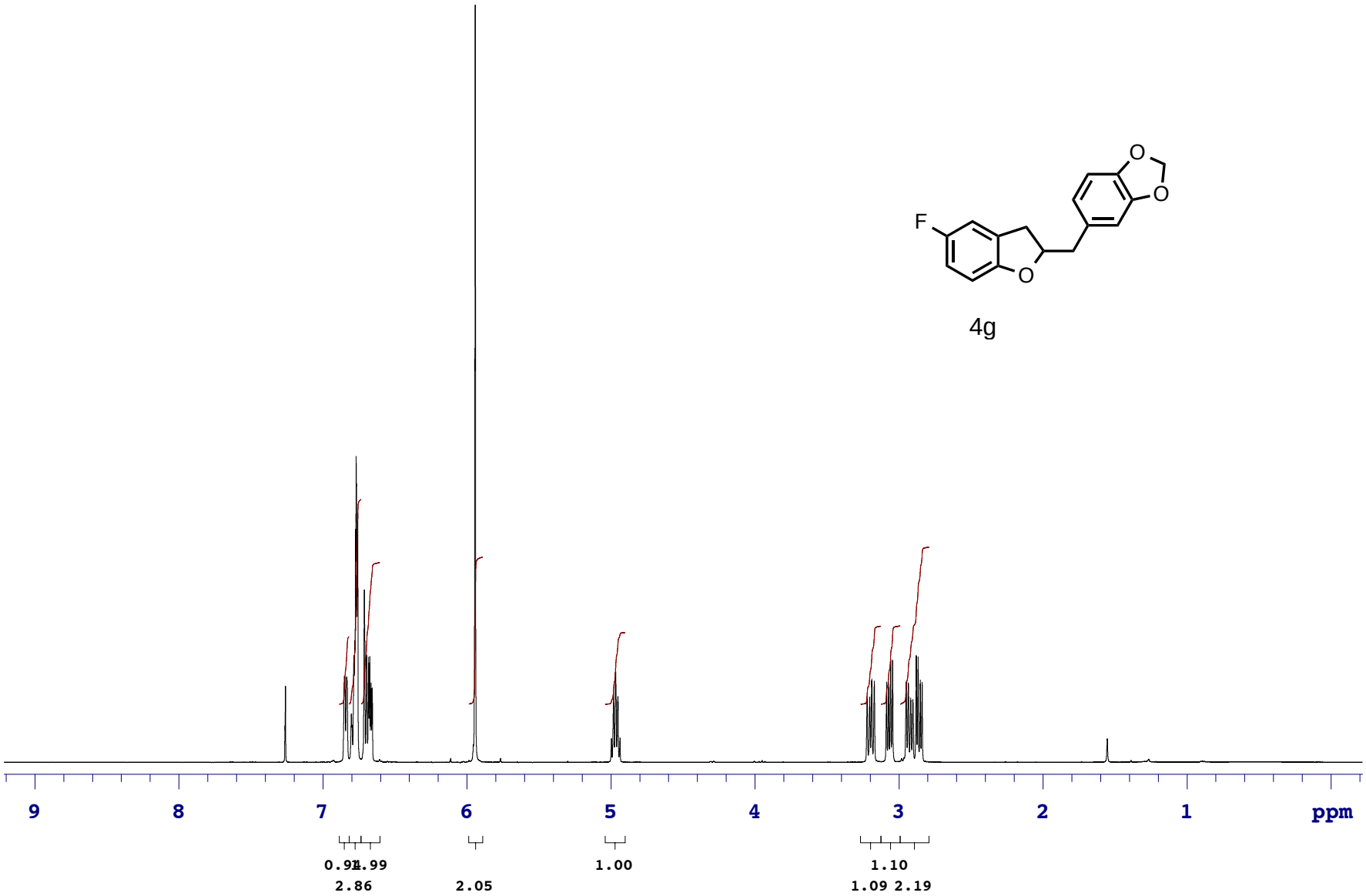

O
4e
9
8
7
6
5
4
3
2
1
ppm
0.89
0.95
0.99
0.81
0.81
0.82
0.98
0.98
0.94
1.13
4.16
4.84

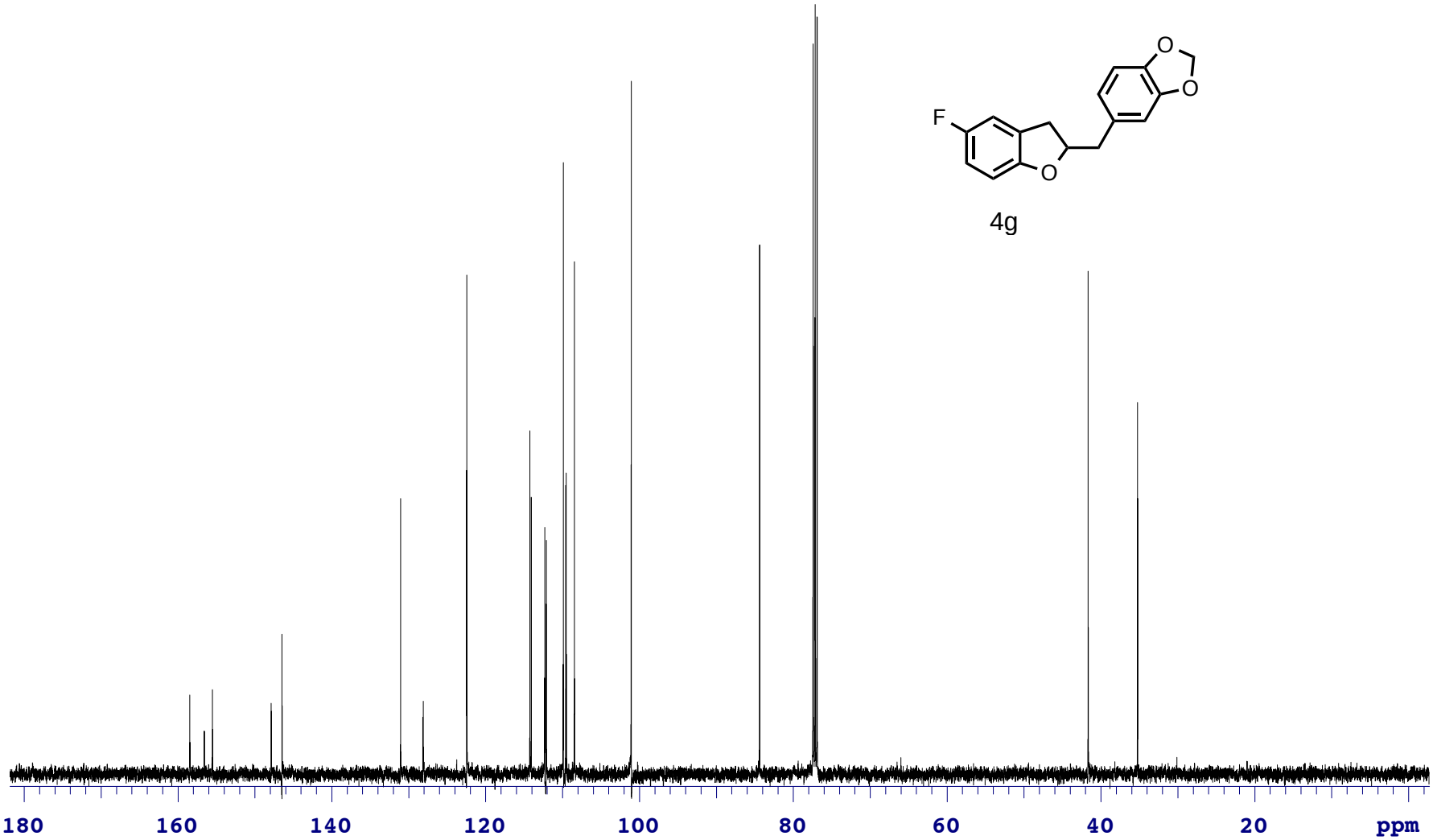


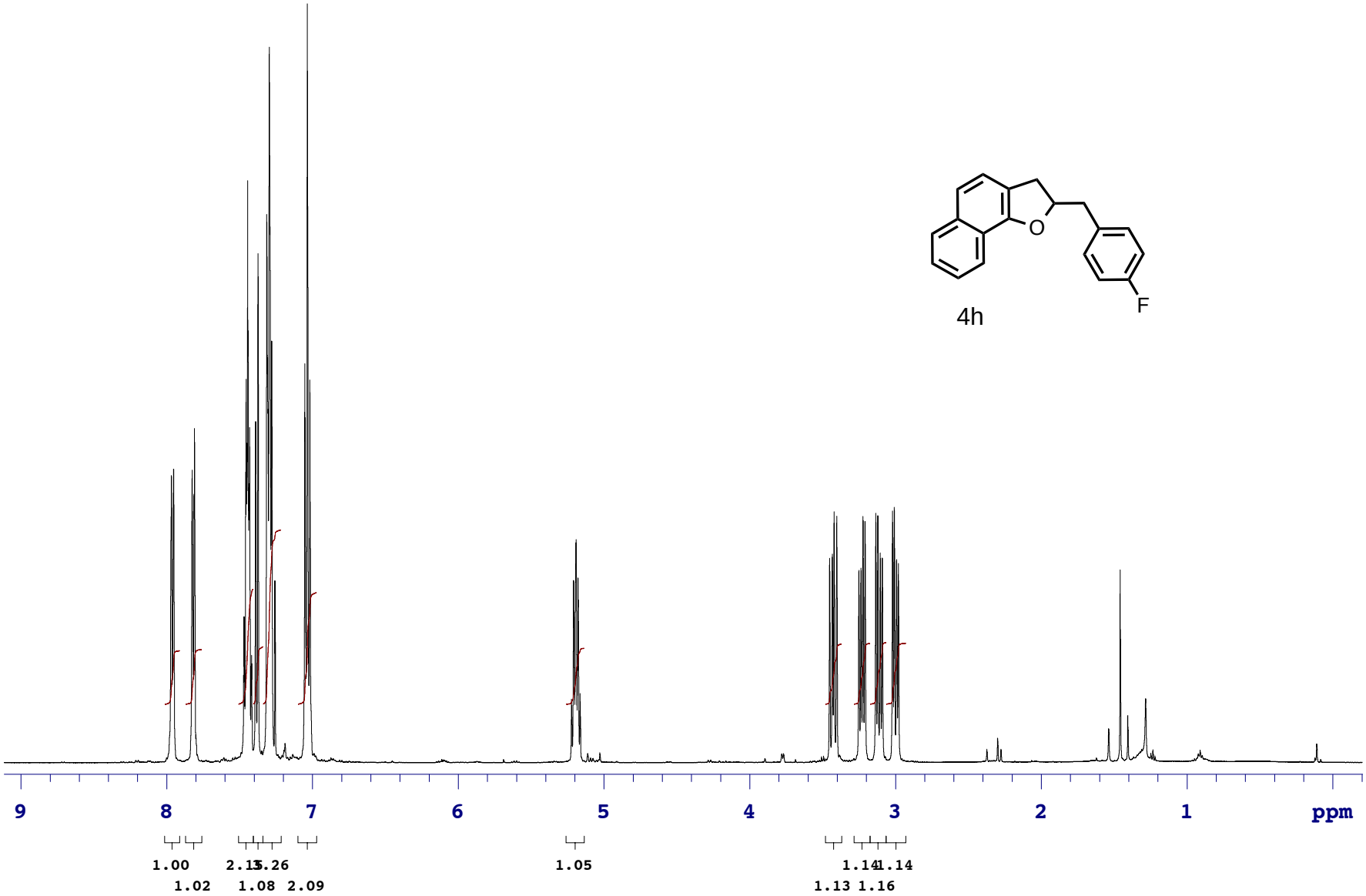
4e

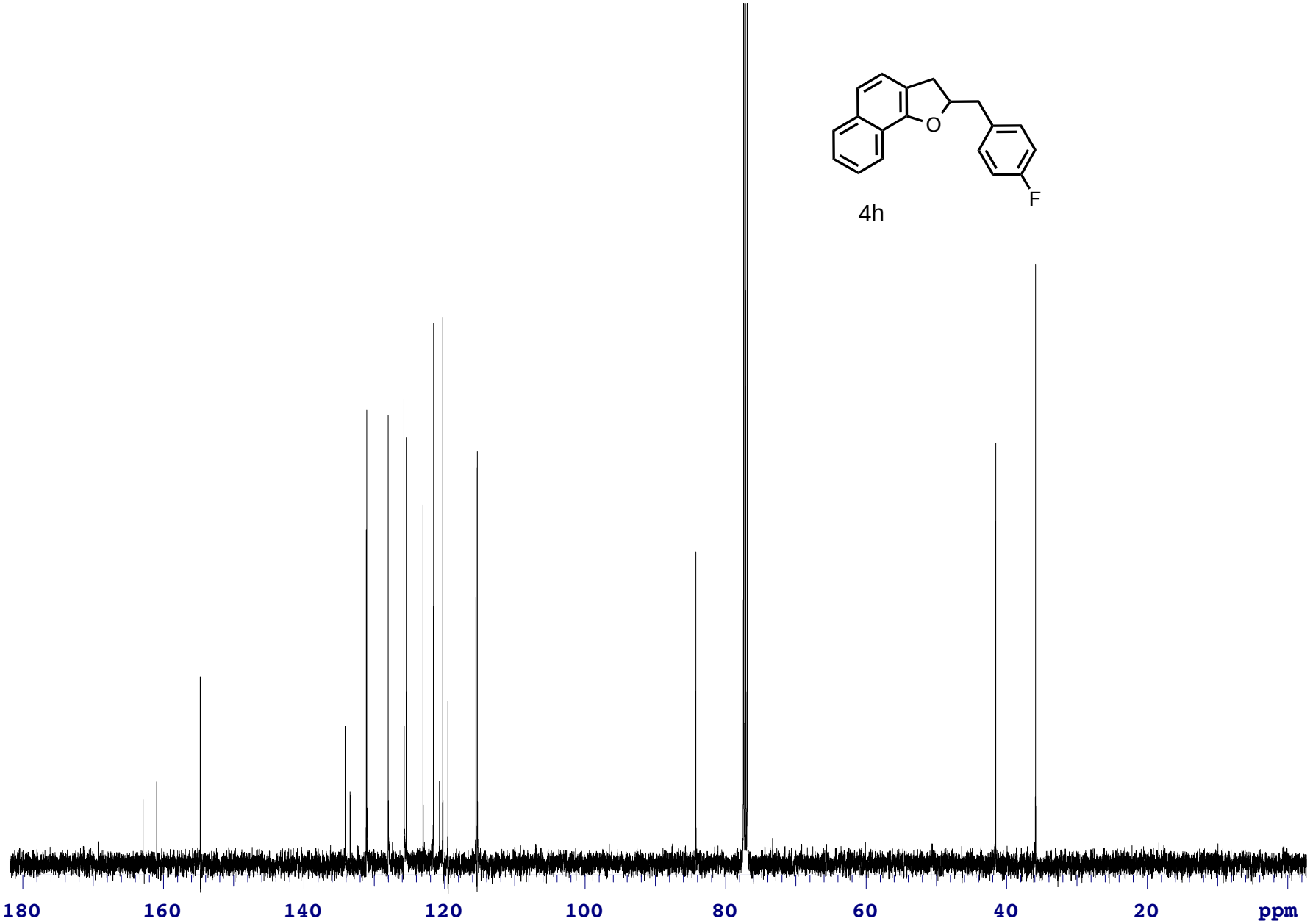

F
O
4f
9
8
7
6
5
4
3
2
1
ppm
2.98
1.02
1.94
1.03
0.91
0.95
1.93
1.00
1.08
1.09
1.10
1.09

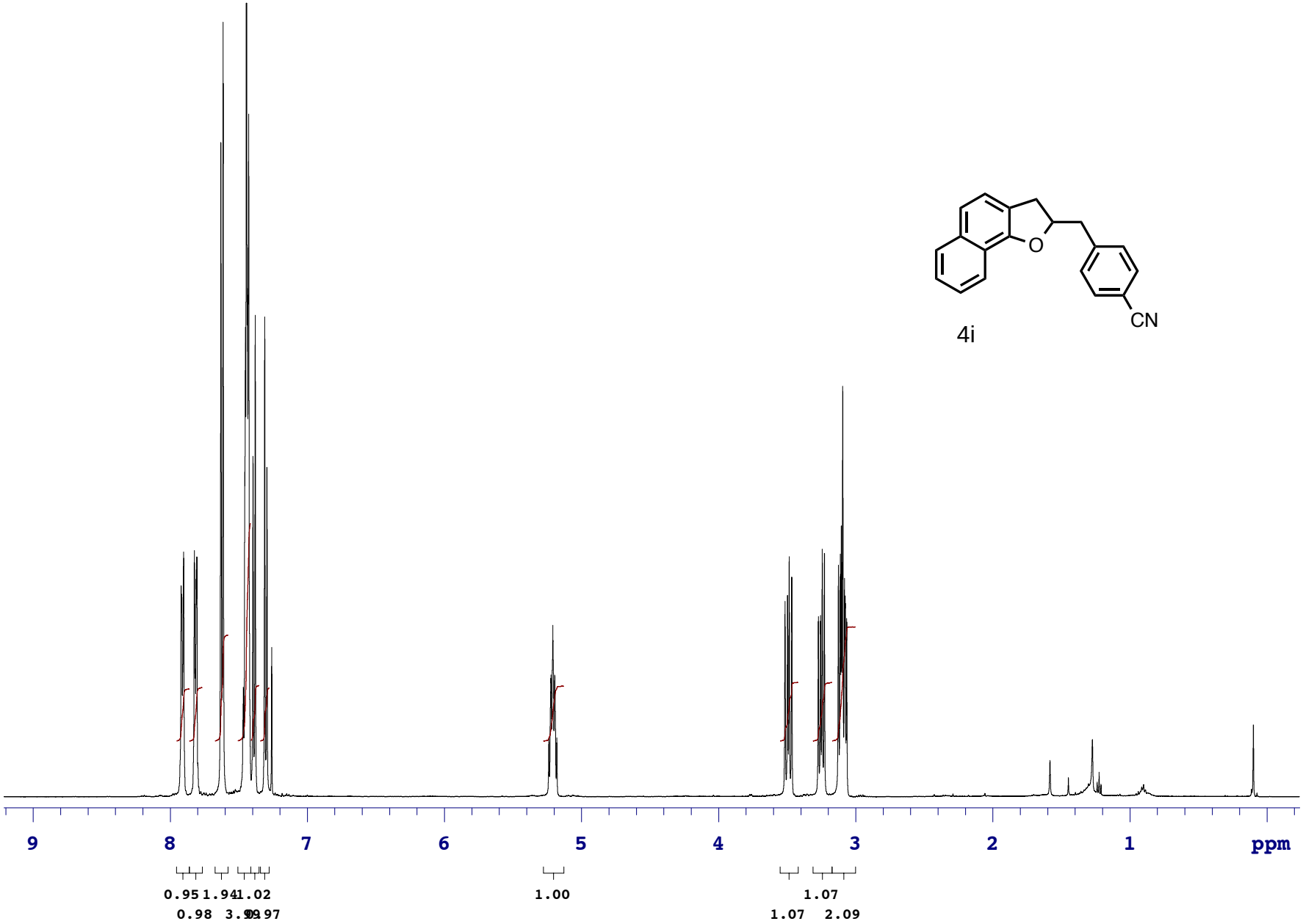

F
O
4f
180
160
140
120
100
80
60
40
20
ppm

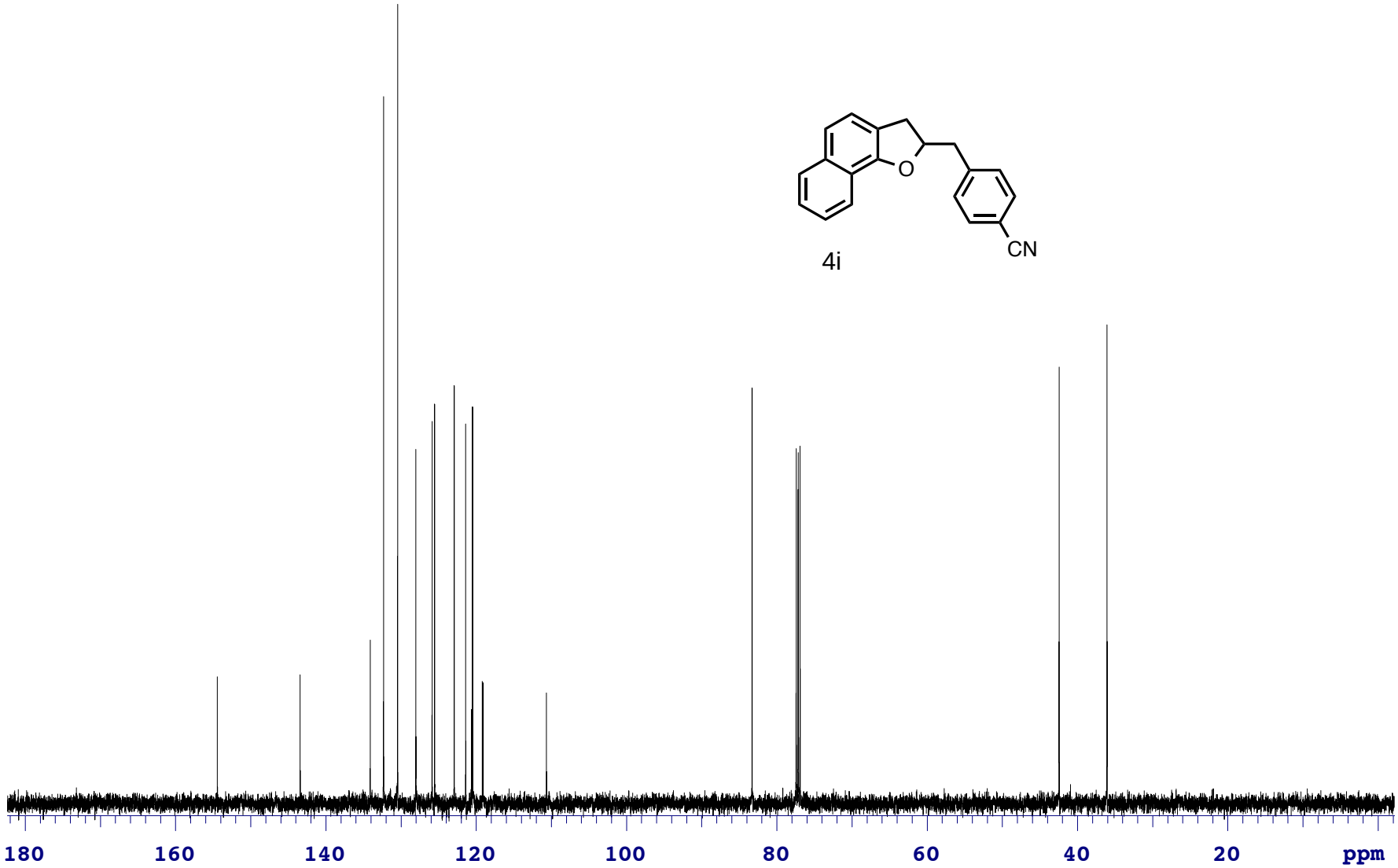

F
O
O
O
4g
9
8
7
6
5
4
3
2
1
ppm
0.91
1.99
2.86
2.05
1.00
1.10
1.09
2.19

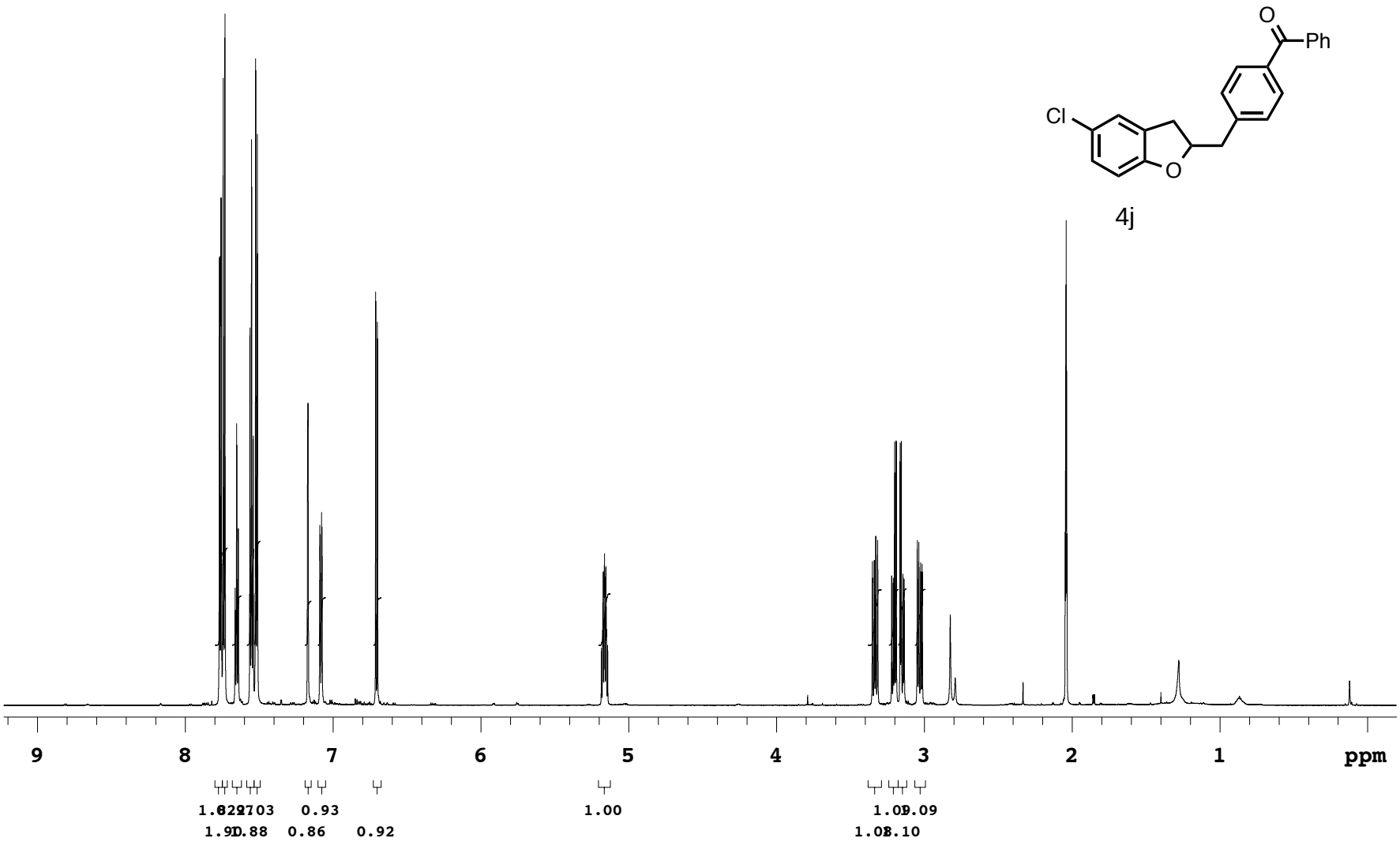

F
O
O
O
4g
180
160
140
120
100
80
60
40
20
ppm

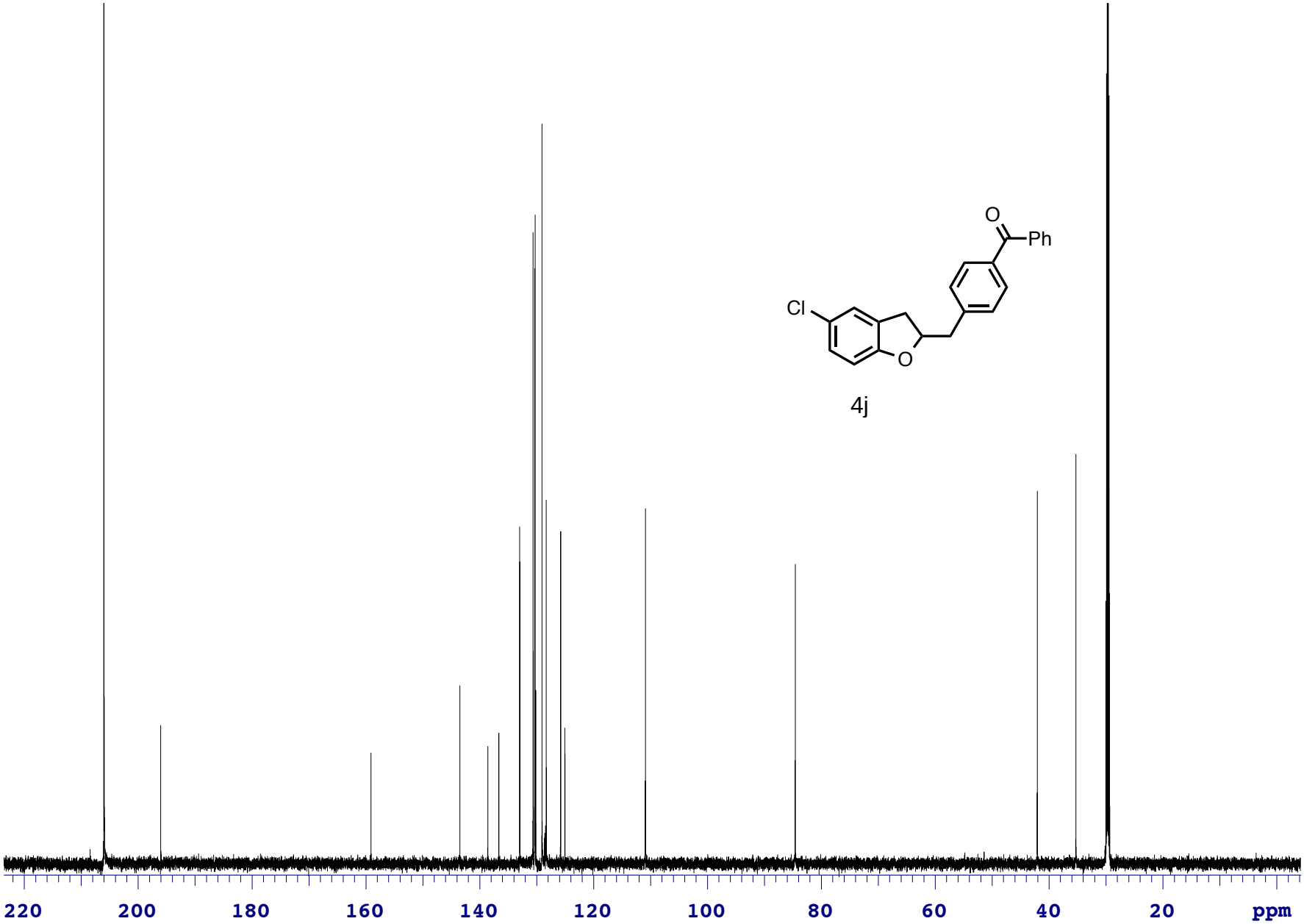

O
F
4h
9
8
7
6
5
4
3
2
1
ppm
1.00
1.02
2.13
1.08
5.26
2.09
1.05
1.13
1.14
1.16
1.14

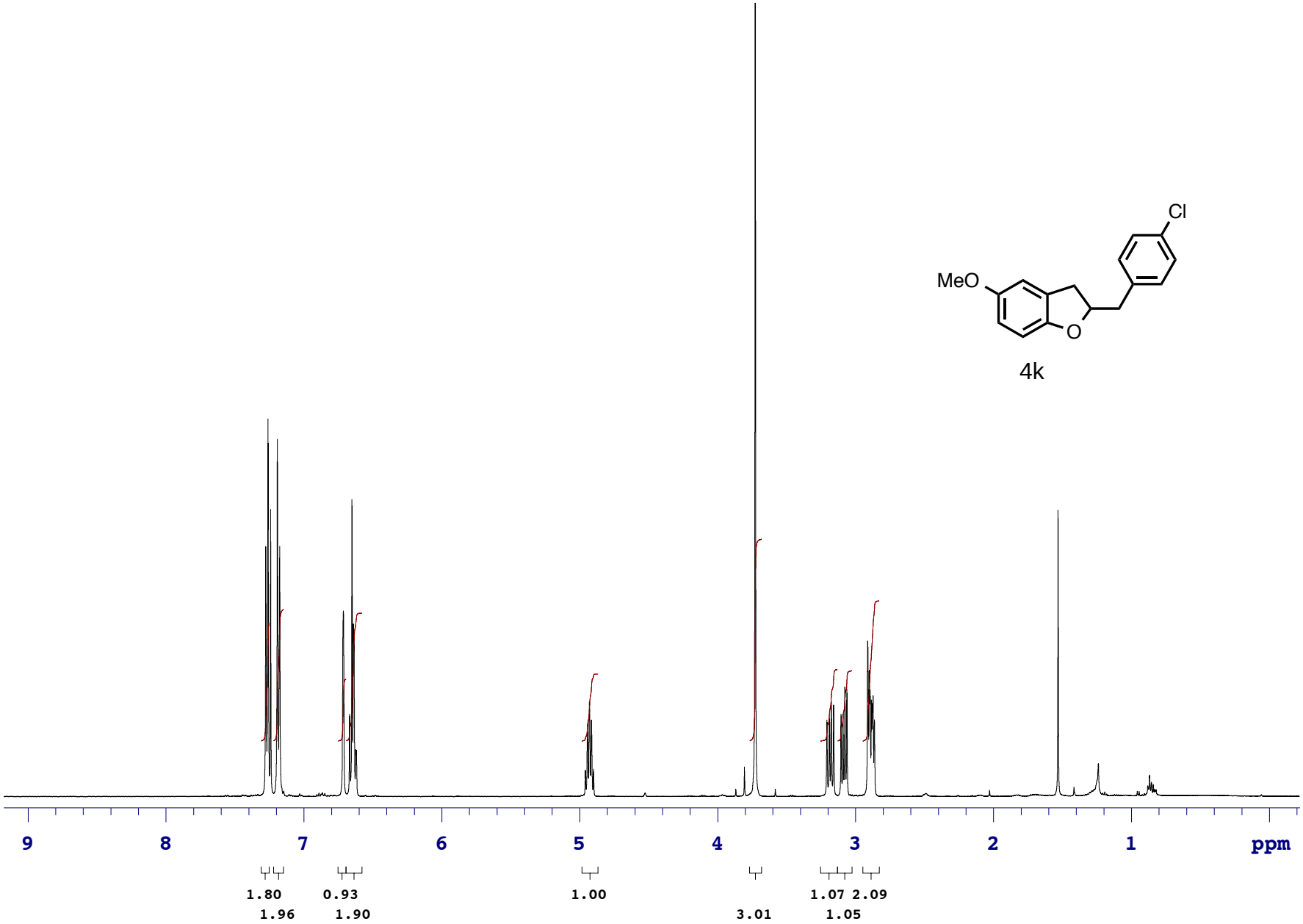

O
F
4h
180
160
140
120
100
80
60
40
20
ppm

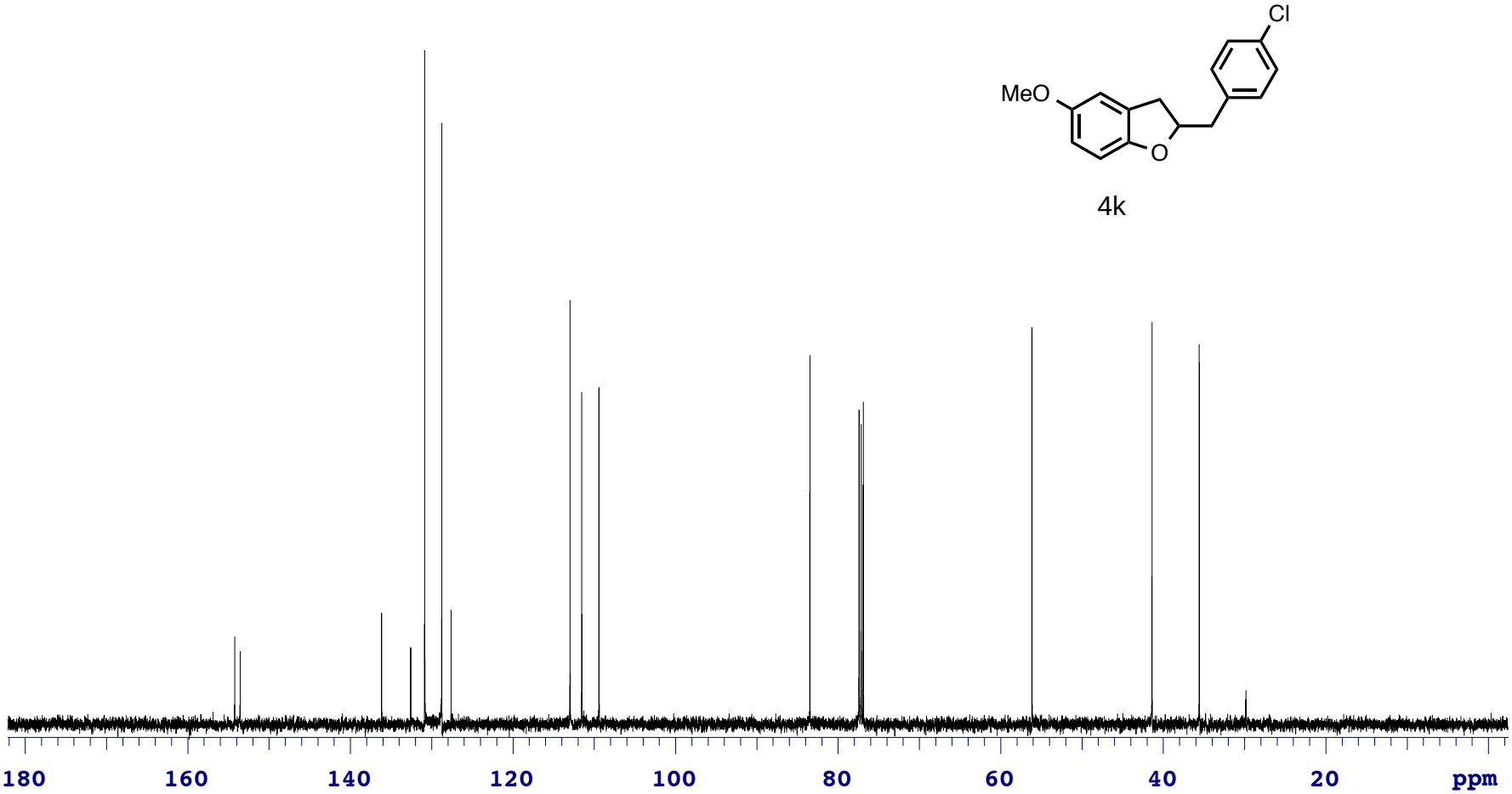

O
CN
4i
9
8
7
6
5
4
3
2
1
ppm
0.95
1.94
1.02
1.00
1.07
0.98
1.07
2.09


O
CN
4i
180
160
140
120
100
80
60
40
20
ppm

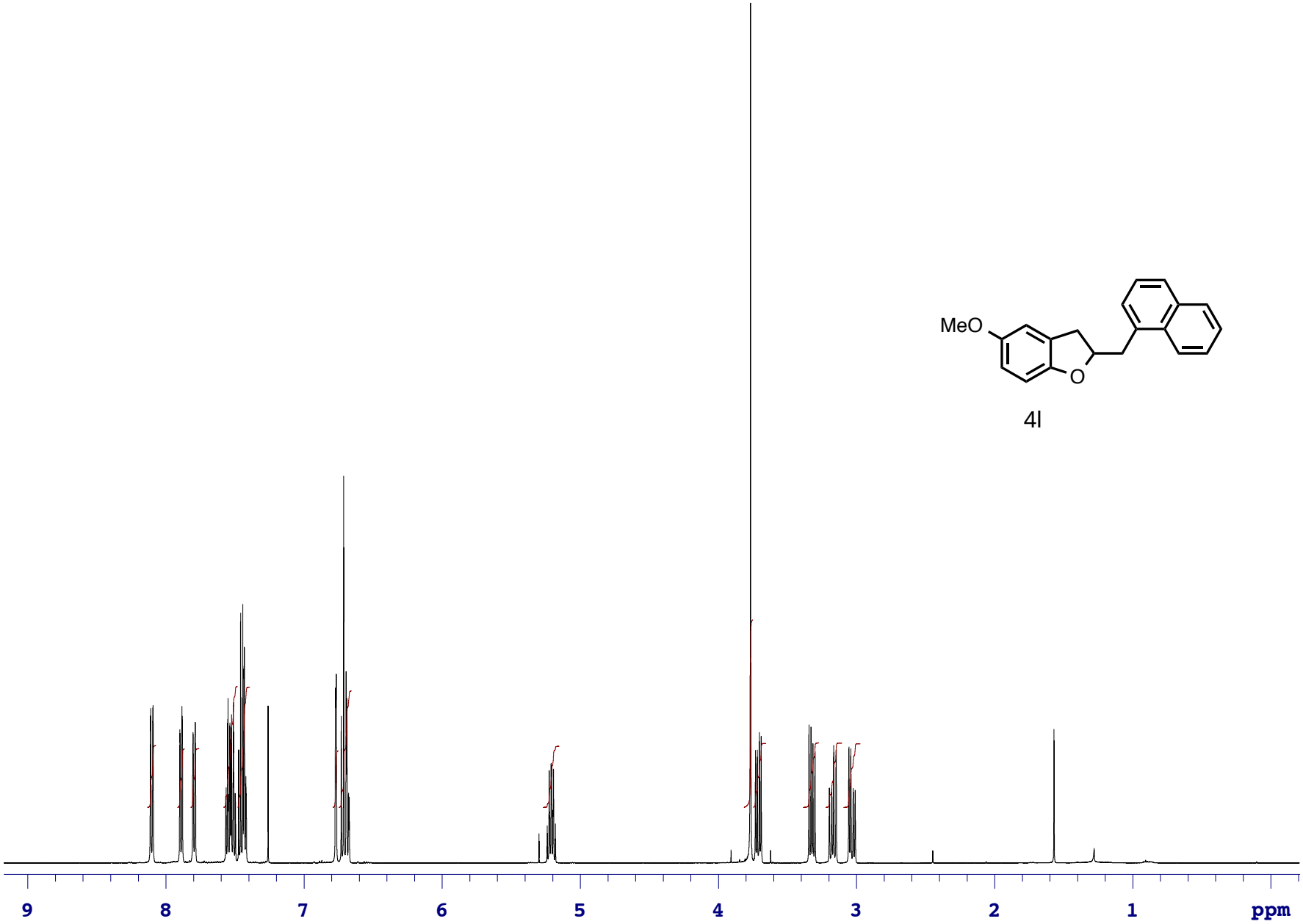

O
Ph
Cl
O
4j
9
8
7
6
5
4
3
2
1
ppm
1.00
0.93
0.92
0.88
0.86
1.10
1.09


O
Ph
Cl
O
4j
220
200
180
160
140
120
100
80
60
40
20
ppm

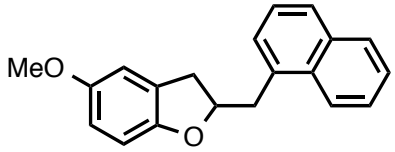

Cl
MeO
O
4k
9
8
7
6
5
4
3
2
1
ppm
1.80
1.96
0.93
1.90
1.00
3.01
1.07
1.05
2.09



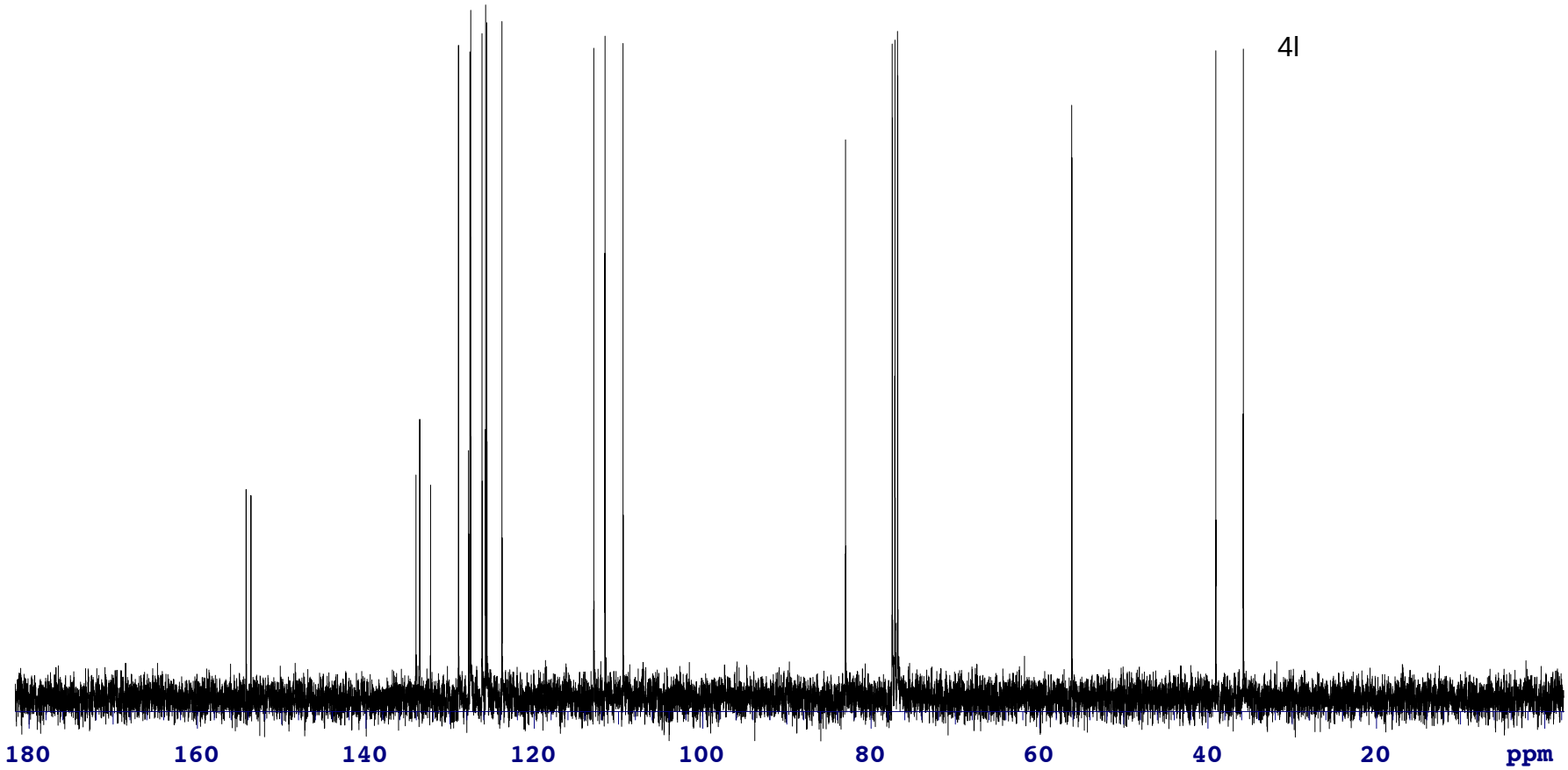
4k

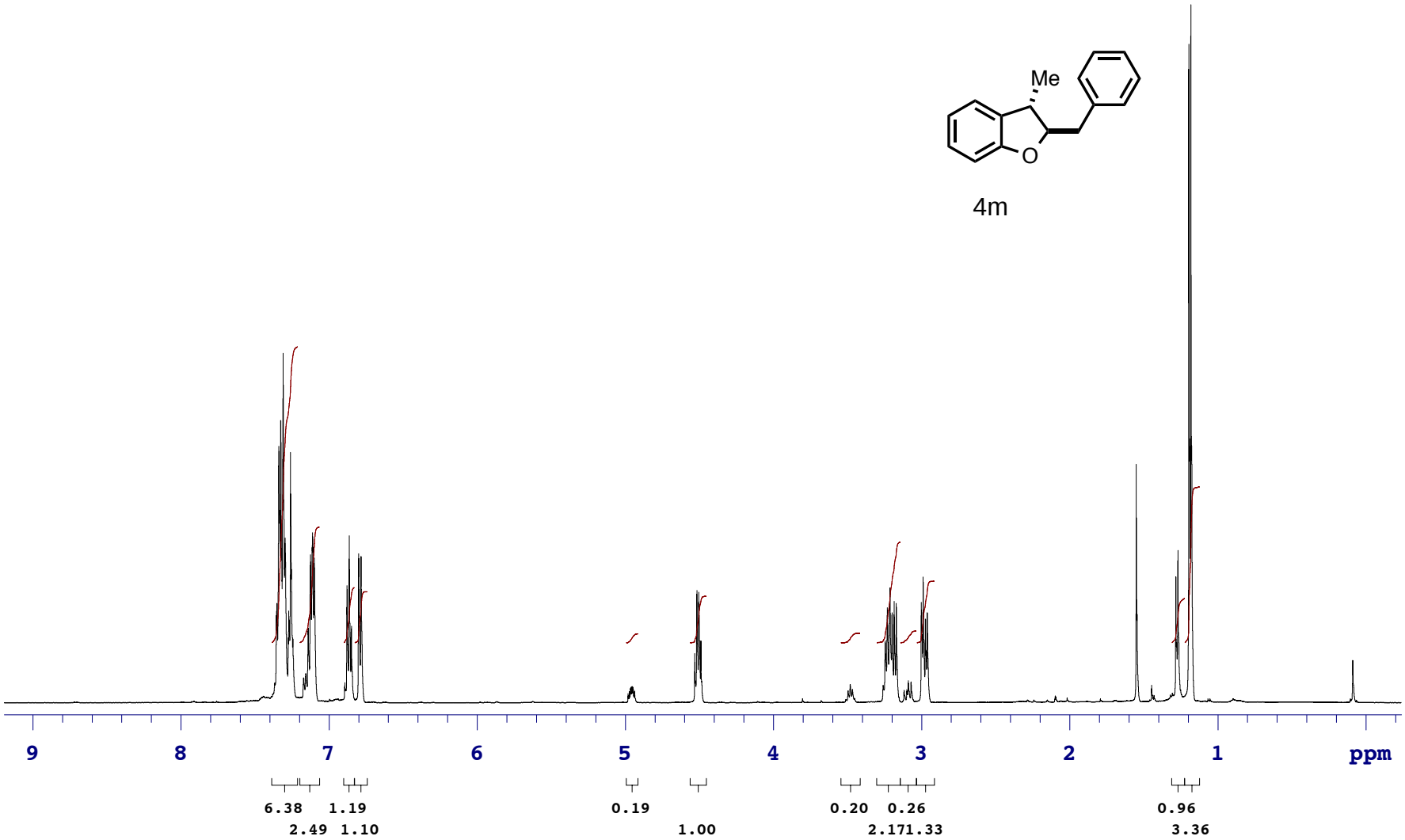


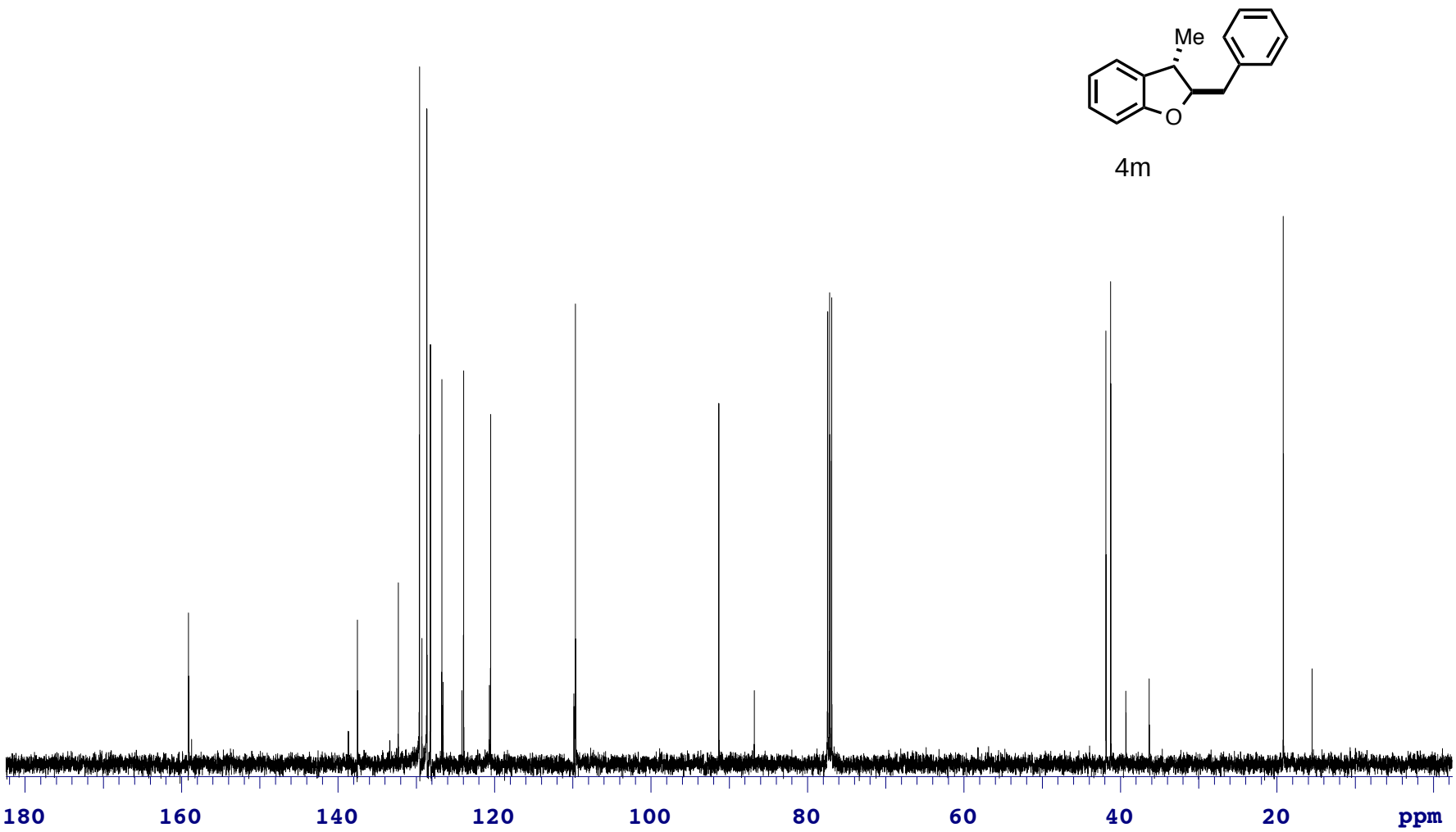
4l



4l




Me
O
4m
9
8
7
6
5
4
3
2
1
ppm
6.38
2.49
1.19
1.10
0.19
1.00
0.20
0.26
2.17
1.33
0.96
3.36


Me
O
4m
180
160
140
120
100
80
60
40
20
ppm

Proton Spectrum

Sample Name:

Data Collected on:
yb.chem.lsa.umich.edu-vnmrs700
Archive directory:

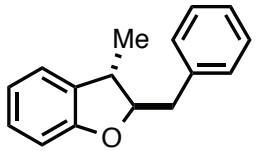
Sample directory:

FidFile: JTH-II-71-COSY

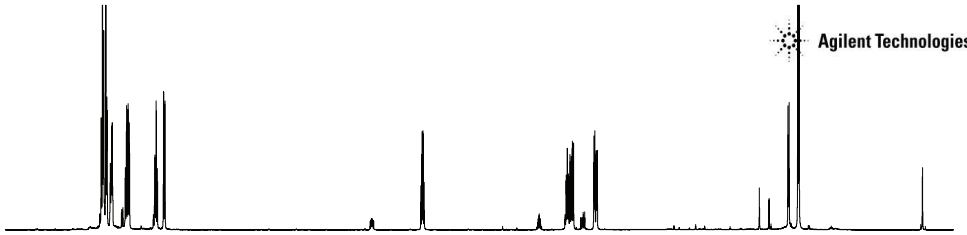
Pulse Sequence: gCOSY
Solvent: cdcl3
Data collected on: Jul 7 2014

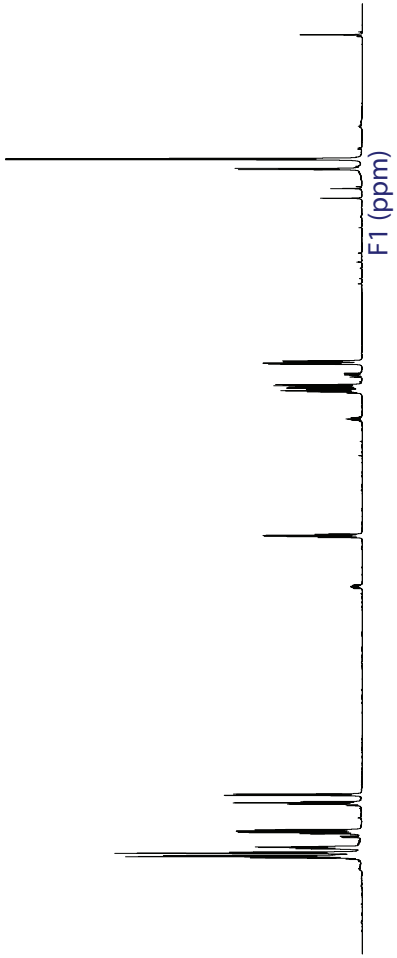
Temp. 25.0 C / 298.1 K
Operator: jhutt

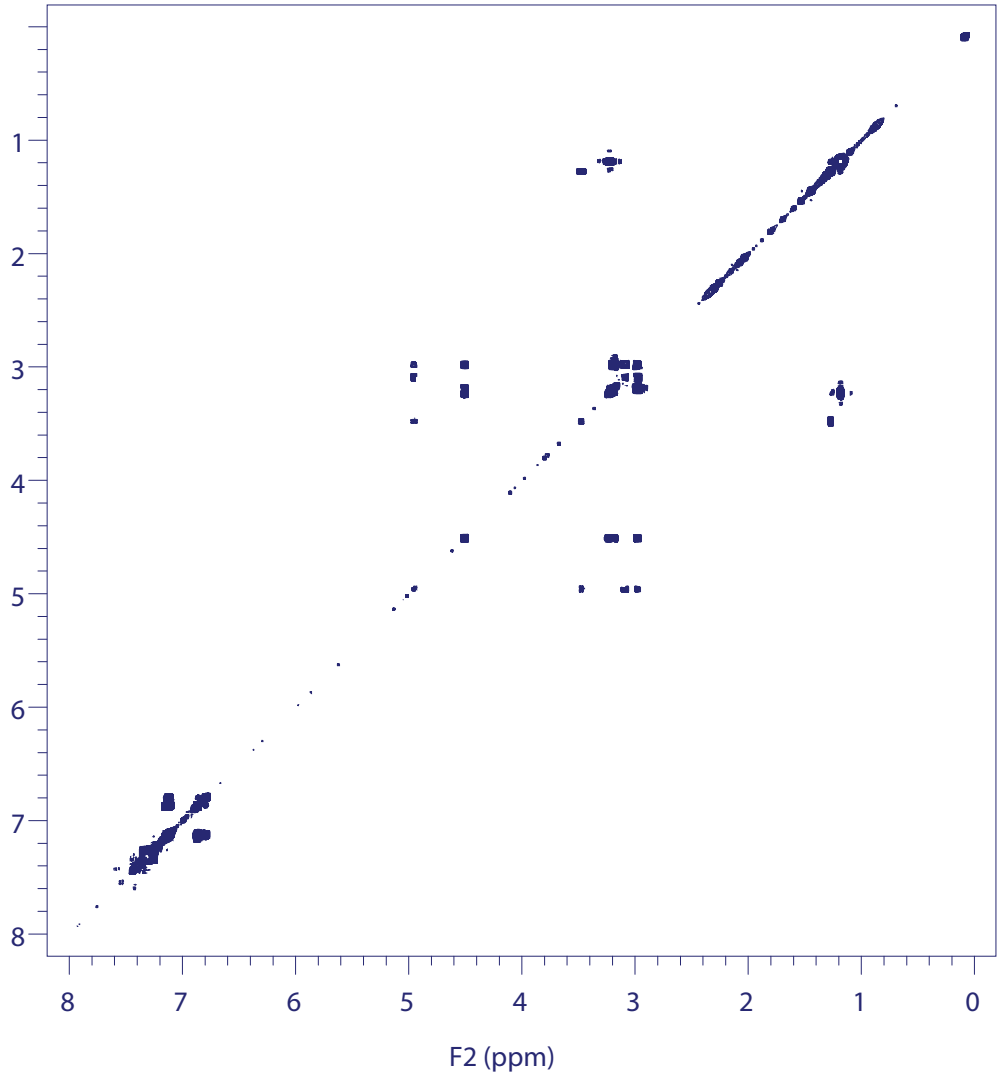
Relax. delay 1.000 sec
Acq. time 0.150 sec
Width 5868.5 Hz
2D Width 5868.5 Hz
2 repetitions
128 increments
OBSERVE H1, 699.7567747 MHz
DATA PROCESSING
Sq. sine bell 0.075 sec
F1 DATA PROCESSING
Sq. sine bell 0.022 sec
FT size 4096 x 4096
Total time 5 min 42 sec

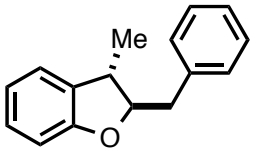


4m

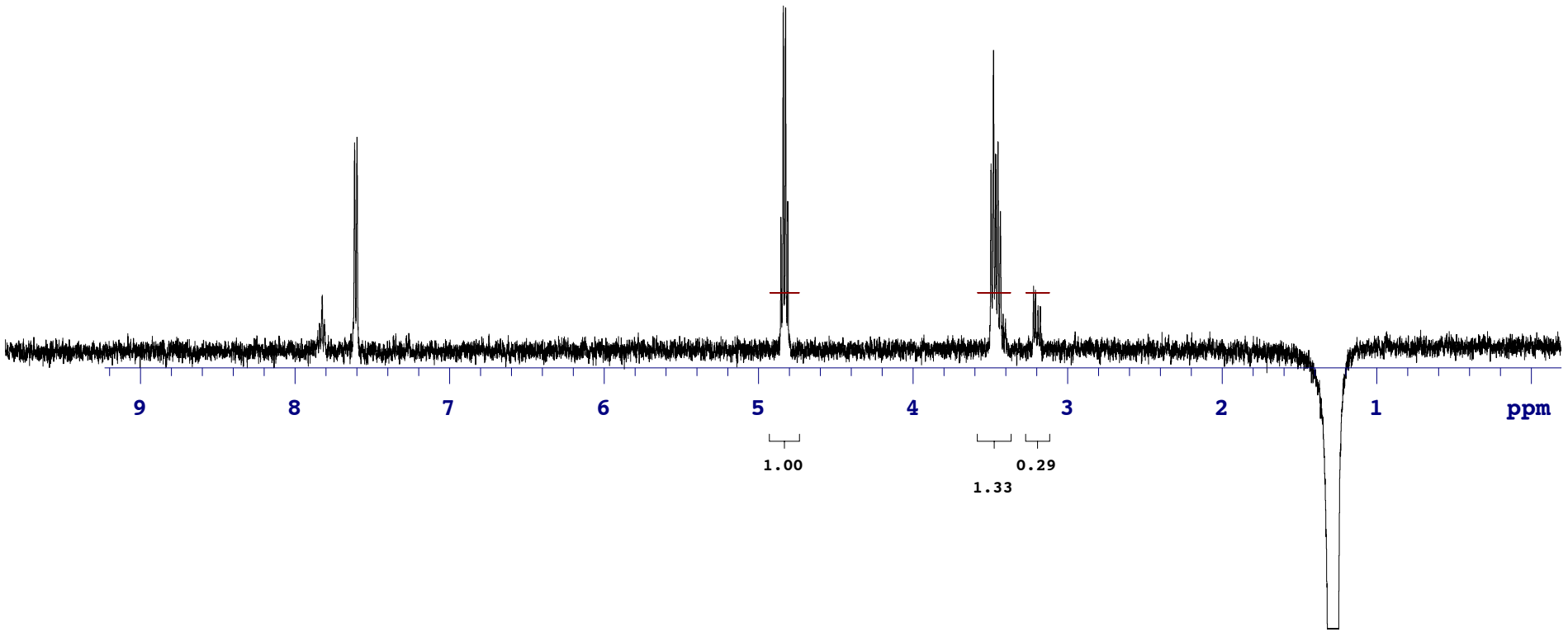


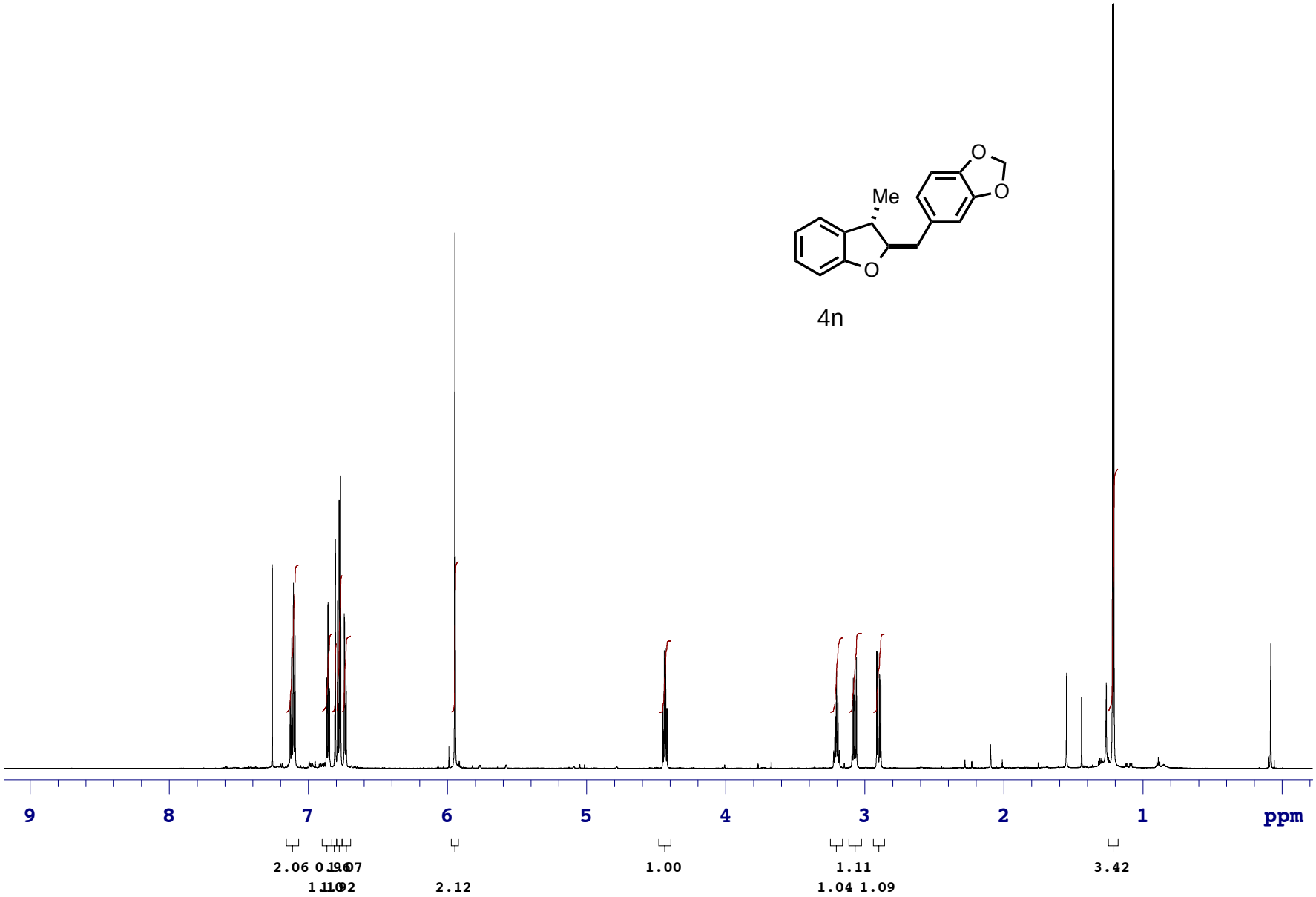




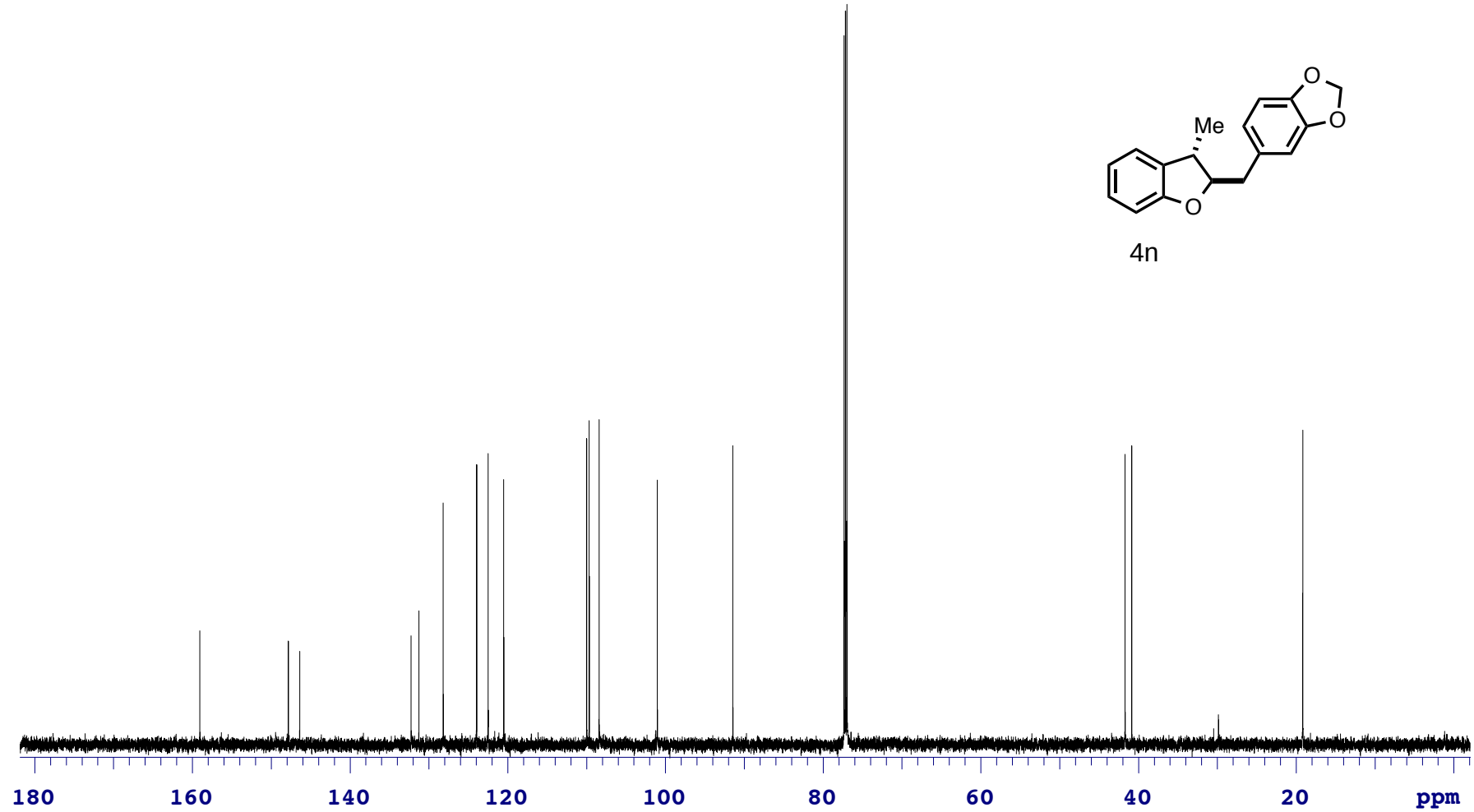


4m





4n



4n

new experiment

Sample Name:

Data Collected on:
yb.chem.lsa.umich.edu-vnmrs700
Archive directory:

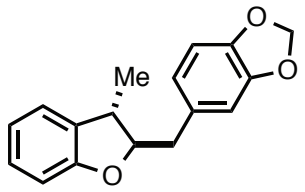
Sample directory:

FidFile: JTH-II-70-MF-COSY

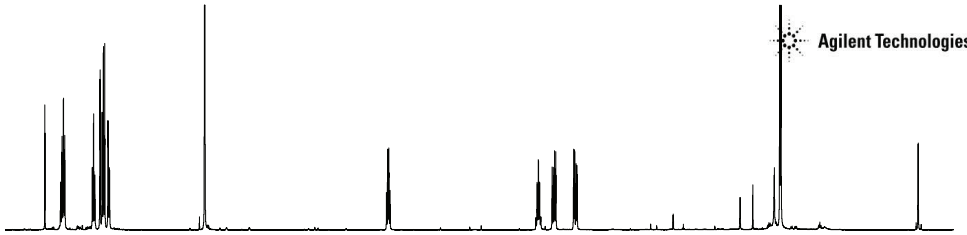
Pulse Sequence: gCOSY
Solvent: cdcl3
Data collected on: Jul 2 2014

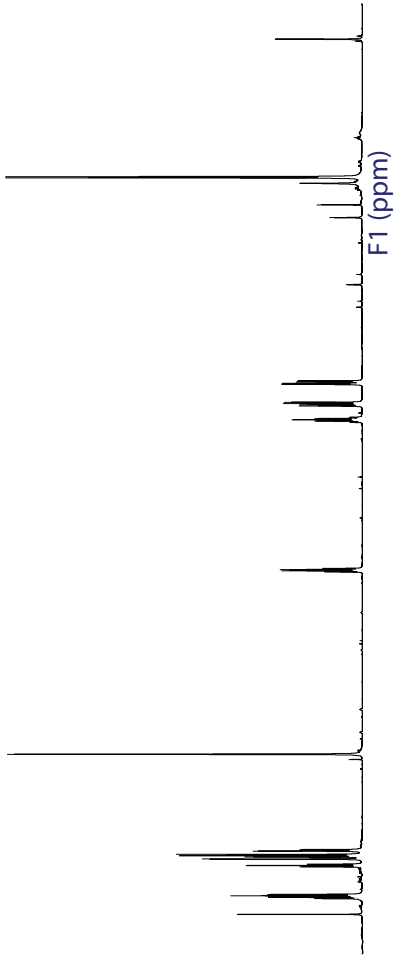
Temp. 25.0 C / 298.1 K
Operator: jhutt

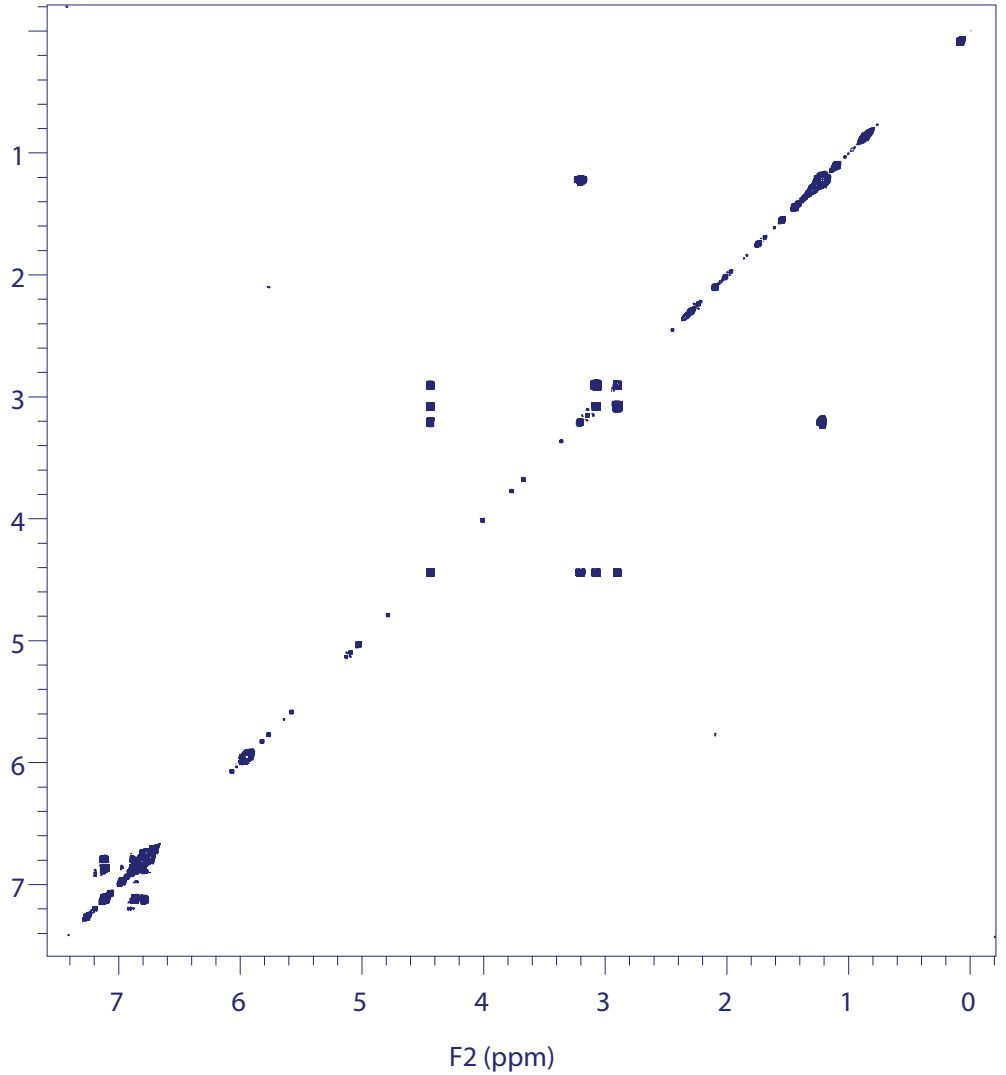
Relax. delay 1.000 sec
Acq. time 0.150 sec
Width 5458.5 Hz
2D Width 5458.5 Hz
2 repetitions
128 increments
OBSERVE H1, 699.7567663 MHz
DATA PROCESSING
Sq. sine bell 0.075 sec
F1 DATA PROCESSING
Sq. sine bell 0.023 sec
FT size 4096 x 4096
Total time 5 min 42 sec

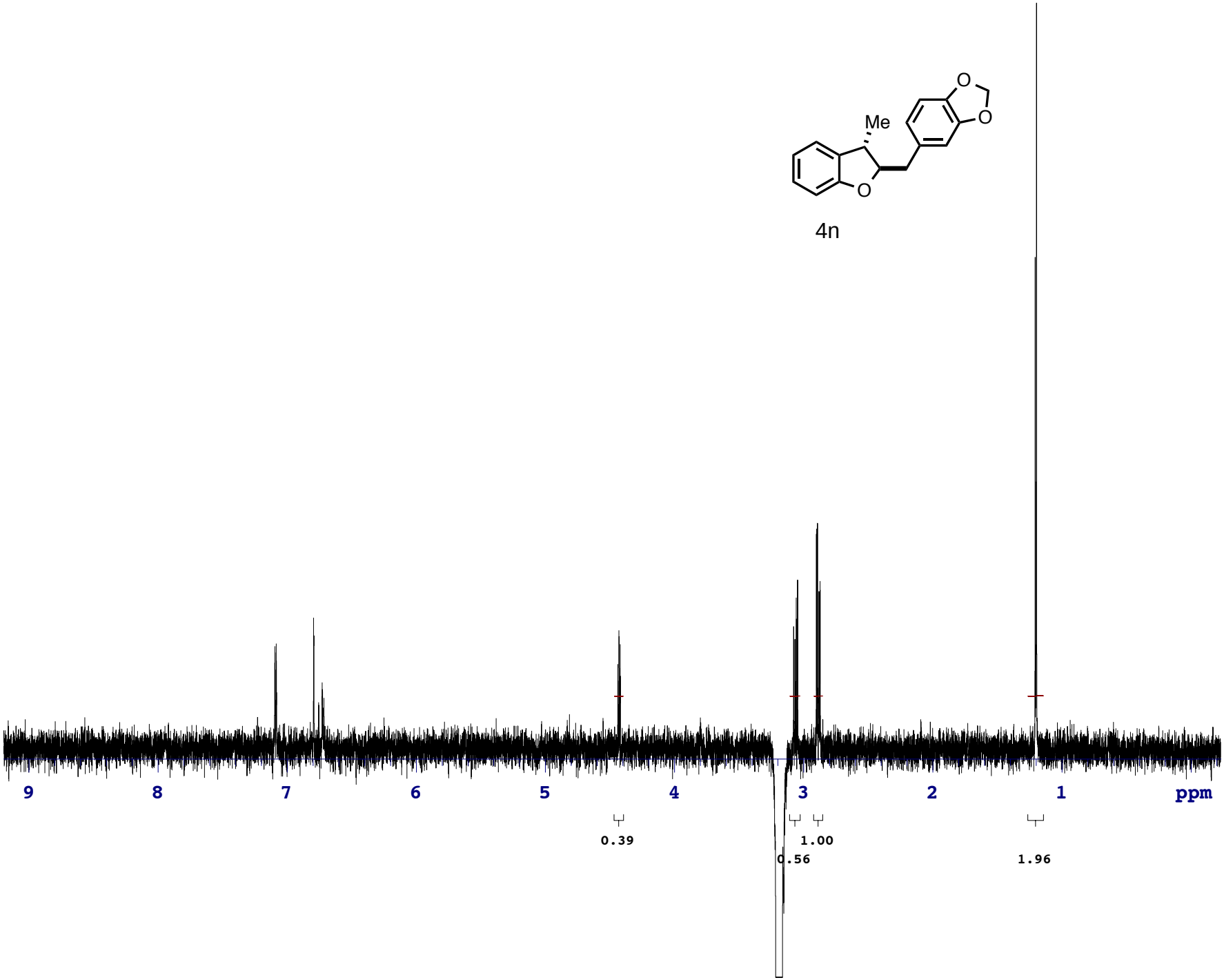


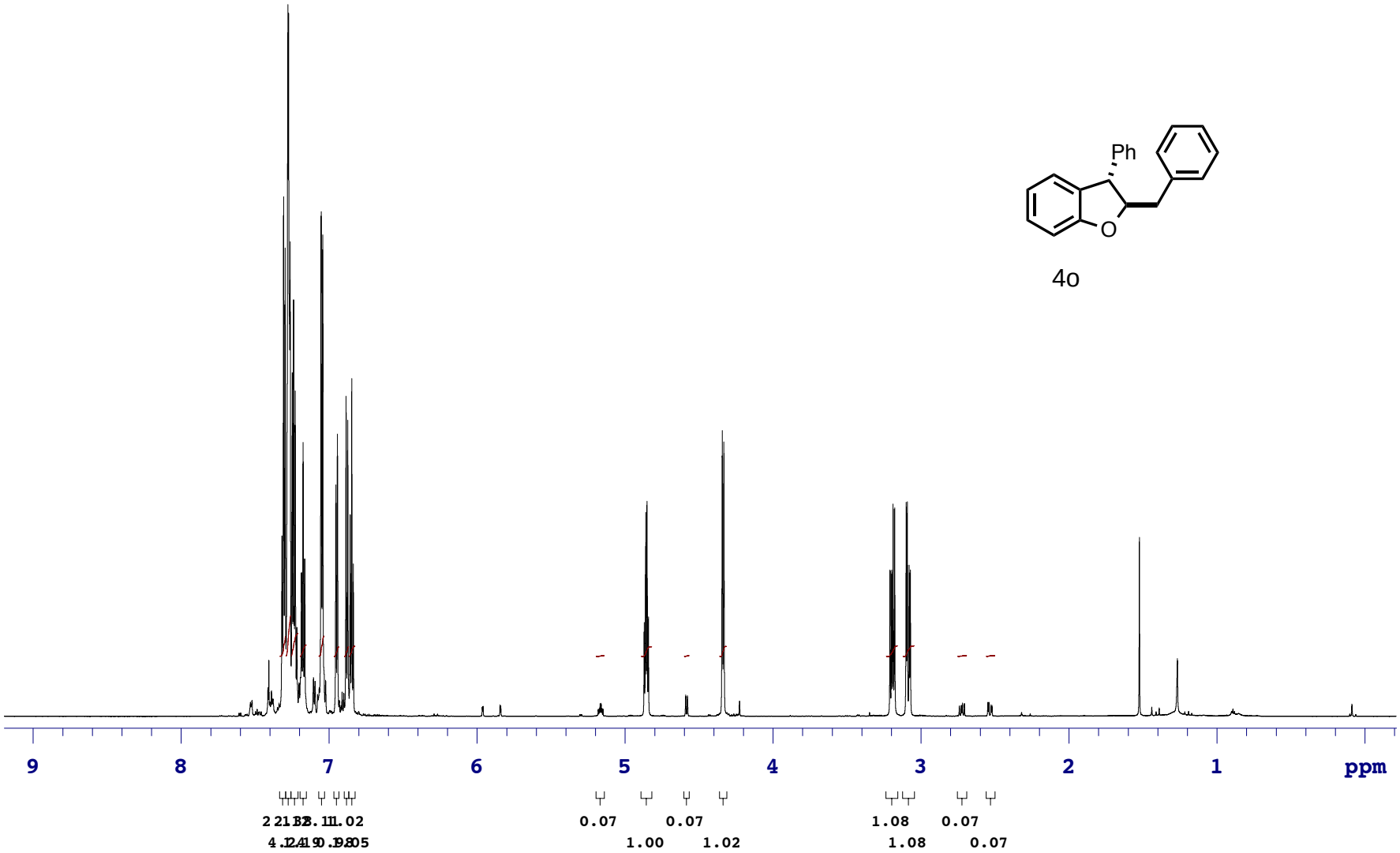
4n



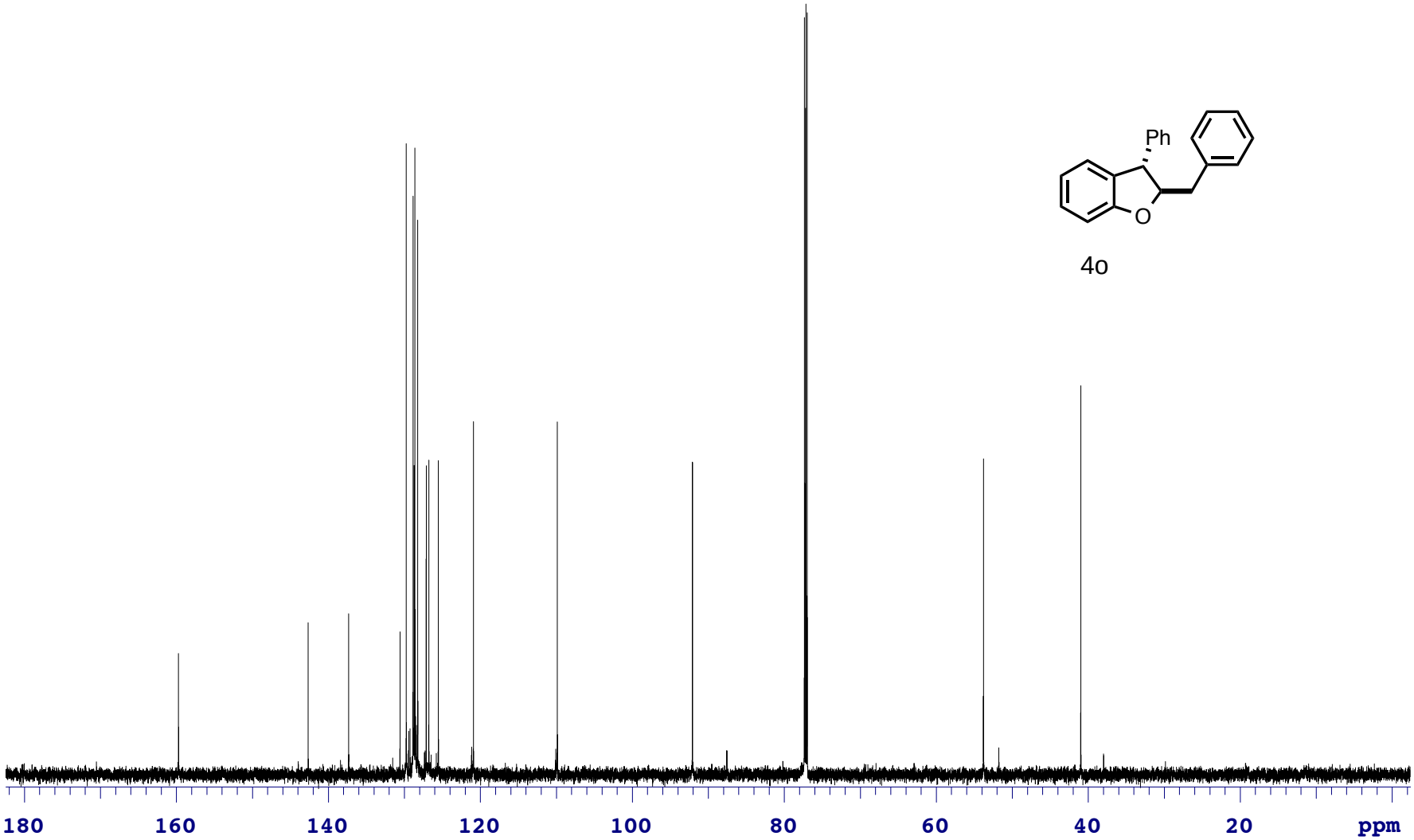





Me
O
O
O
4n
9
8
7
6
5
4
3
2
1
ppm
0.39
0.56
1.00
1.96



4o


Ph
O
4o
180
160
140
120
100
80
60
40
20
ppm

Proton Spectrum

Sample Name:

Data Collected on:
yb.chem.lsa.umich.edu-vnmrs700
Archive directory:

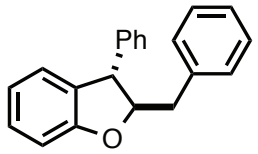
Sample directory:

FidFile: JTH-II-65-COSY

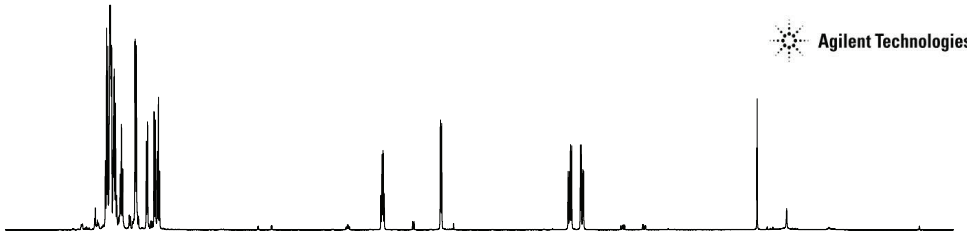
Pulse Sequence: gCOSY
Solvent: cdcl3
Data collected on: Jul 7 2014

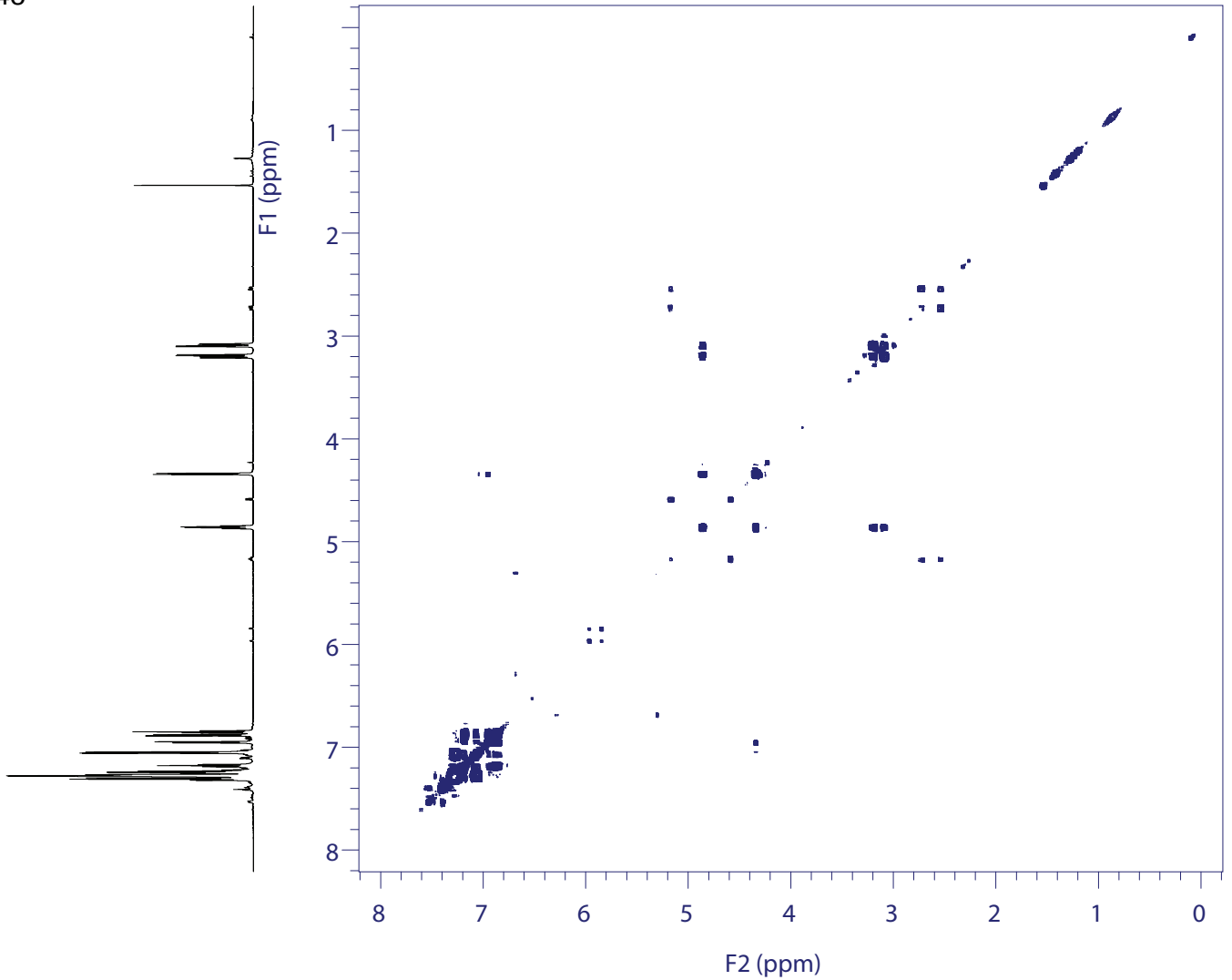
Temp. 25.0 C / 298.1 K
Operator: jhutt

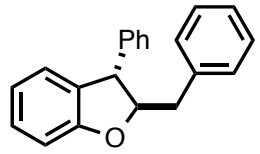
Relax. delay 1.000 sec
Acq. time 0.150 sec
Width 5896.2 Hz
2D Width 5896.2 Hz
2 repetitions
128 increments
OBSERVE H1, 699.7567747 MHz
DATA PROCESSING
Sq. sine bell 0.075 sec
F1 DATA PROCESSING
Sq. sine bell 0.022 sec
FT size 4096 x 4096
Total time 5 min 42 sec



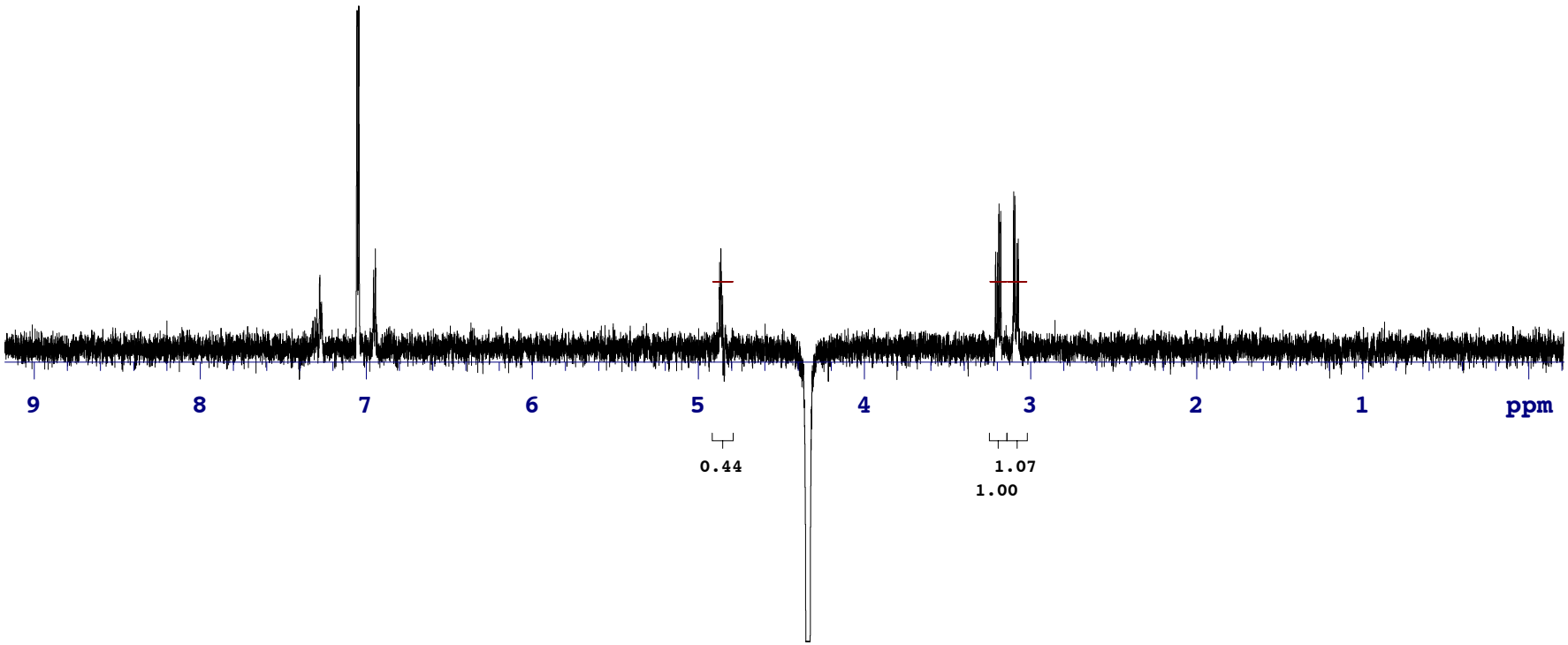
4o

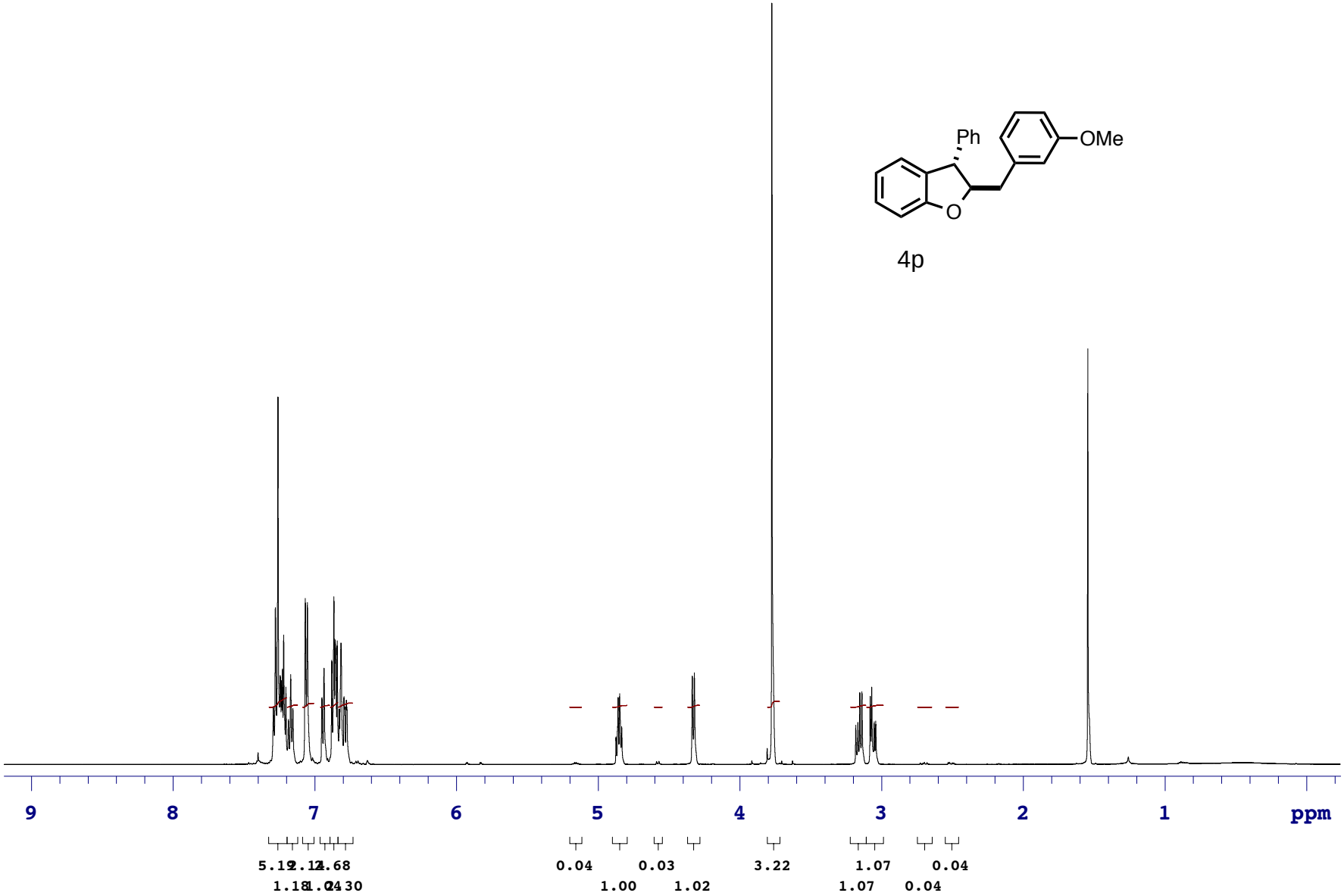




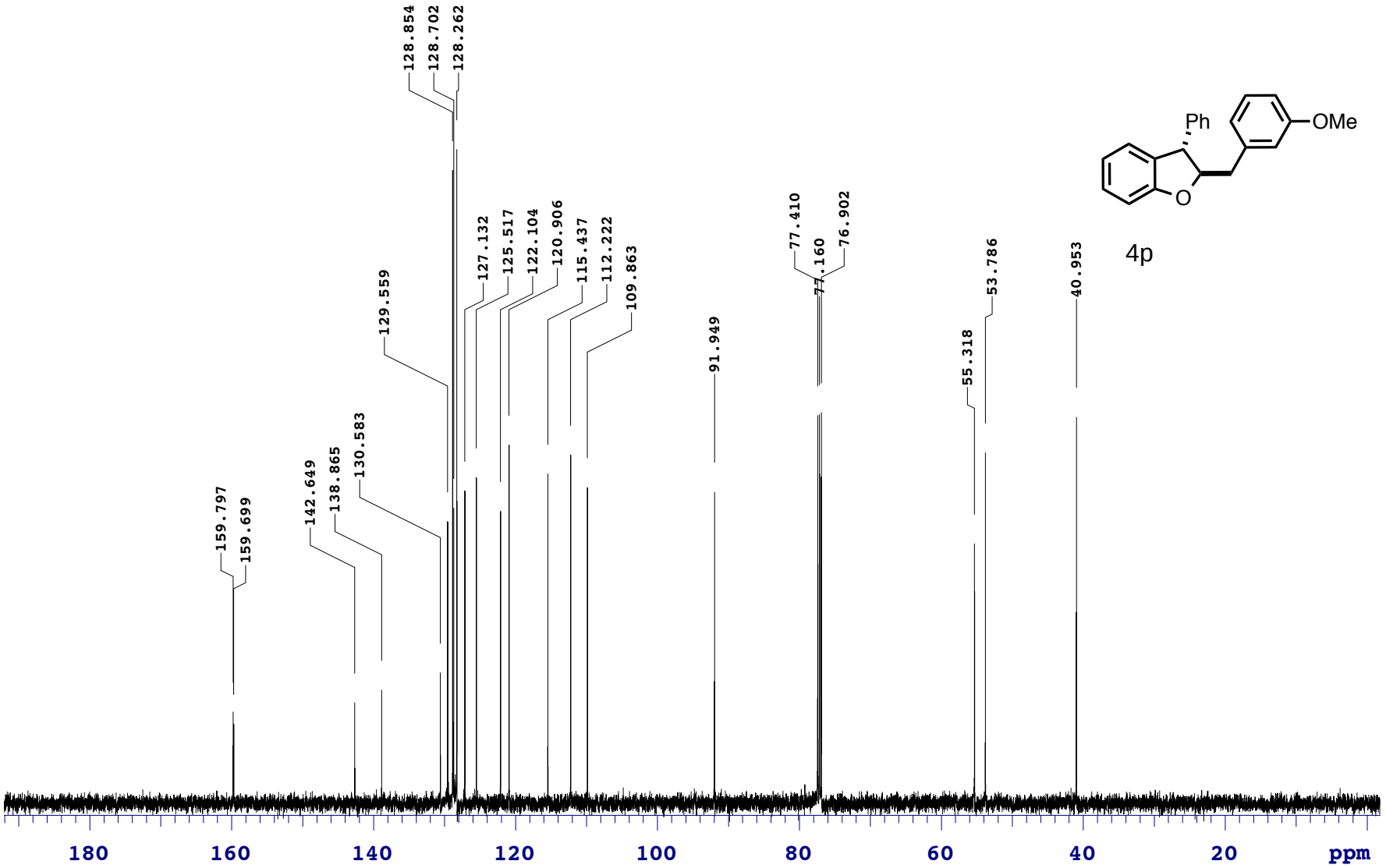


4o




Ph
OMe
O
9
8
7
6
5
4
3
2
1
ppm
5.19
2.12
4.68
1.18
1.02
4.30
0.04
1.00
0.03
1.02
3.22
1.07
1.07
0.04
0.04

4p


128.854
128.702
128.262
127.132
125.517
122.104
120.906
115.437
112.222
109.863
129.559
91.949
77.410
77.160
76.902
55.318
53.786
40.953
159.797
159.699
142.649
138.865
130.583
Ph
OMe
O
4p
180
160
140
120
100
80
60
40
20
ppm

JTH-II-66-1HCOSY

Sample Name:

Data Collected on:
yb.chem.lsa.umich.edu-vnmrs700
Archive directory:

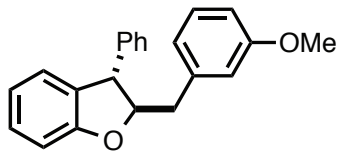
Sample directory:

FidFile: JTH-II-66-COSY

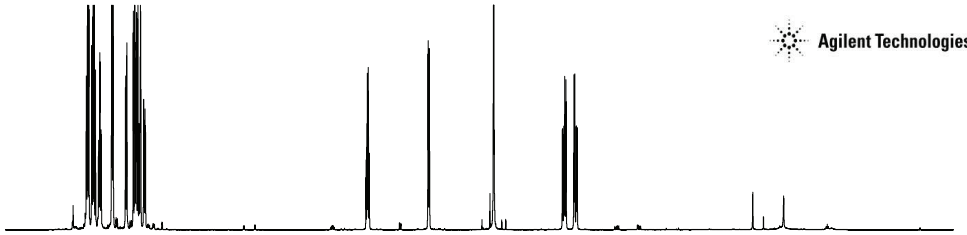
Pulse Sequence: gCOSY
Solvent: cdcl3
Data collected on: Jul 8 2014

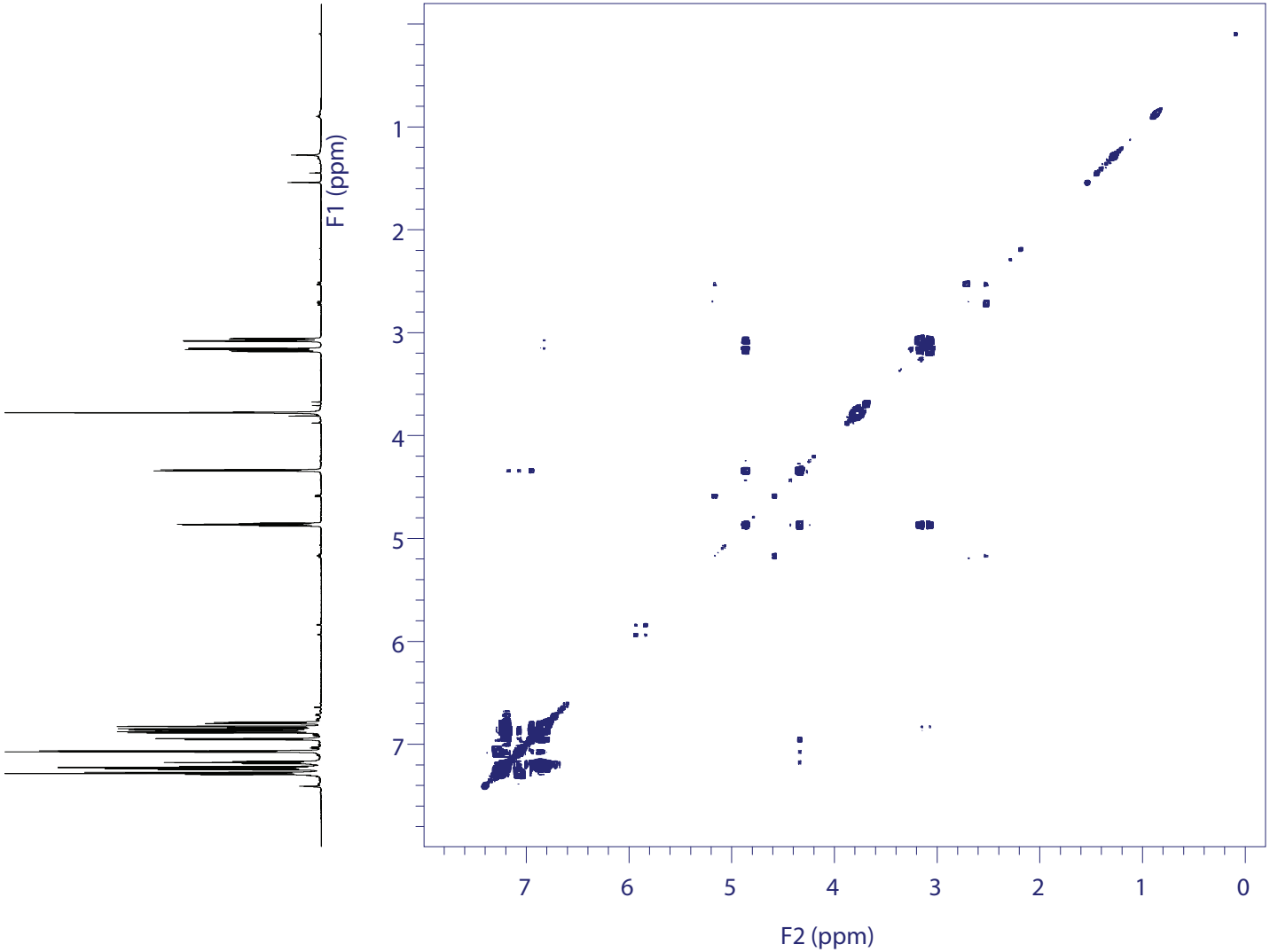
Temp. 25.0 C / 298.1 K
Operator: jhutt

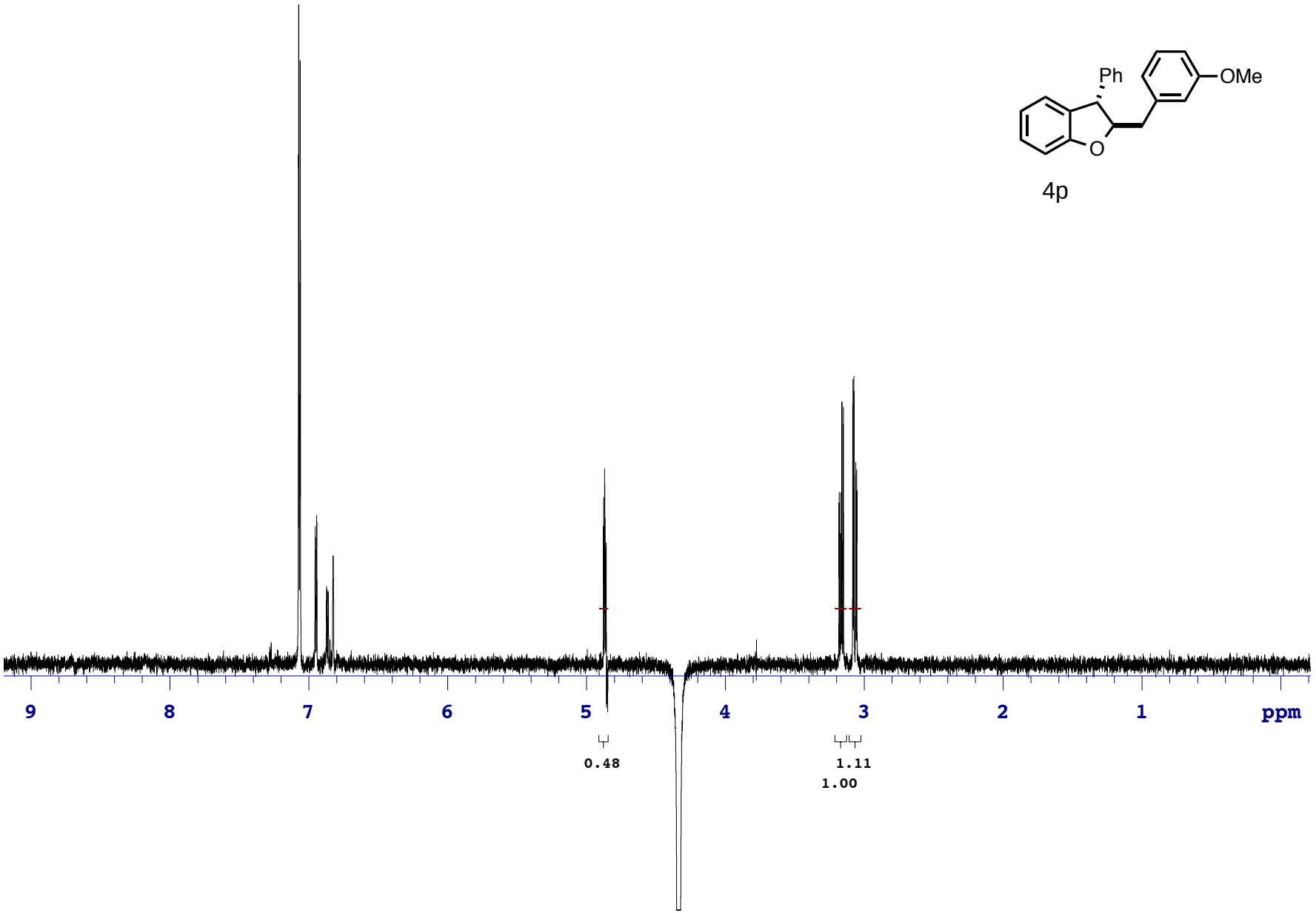
Relax. delay 1.000 sec
Acq. time 0.150 sec
Width 5733.9 Hz
2D Width 5733.9 Hz
2 repetitions
128 increments
OBSERVE H1, 699.7567747 MHz
DATA PROCESSING
Sq. sine bell 0.075 sec
F1 DATA PROCESSING
Sq. sine bell 0.022 sec
FT size 4096 x 4096
Total time 5 min 42 sec

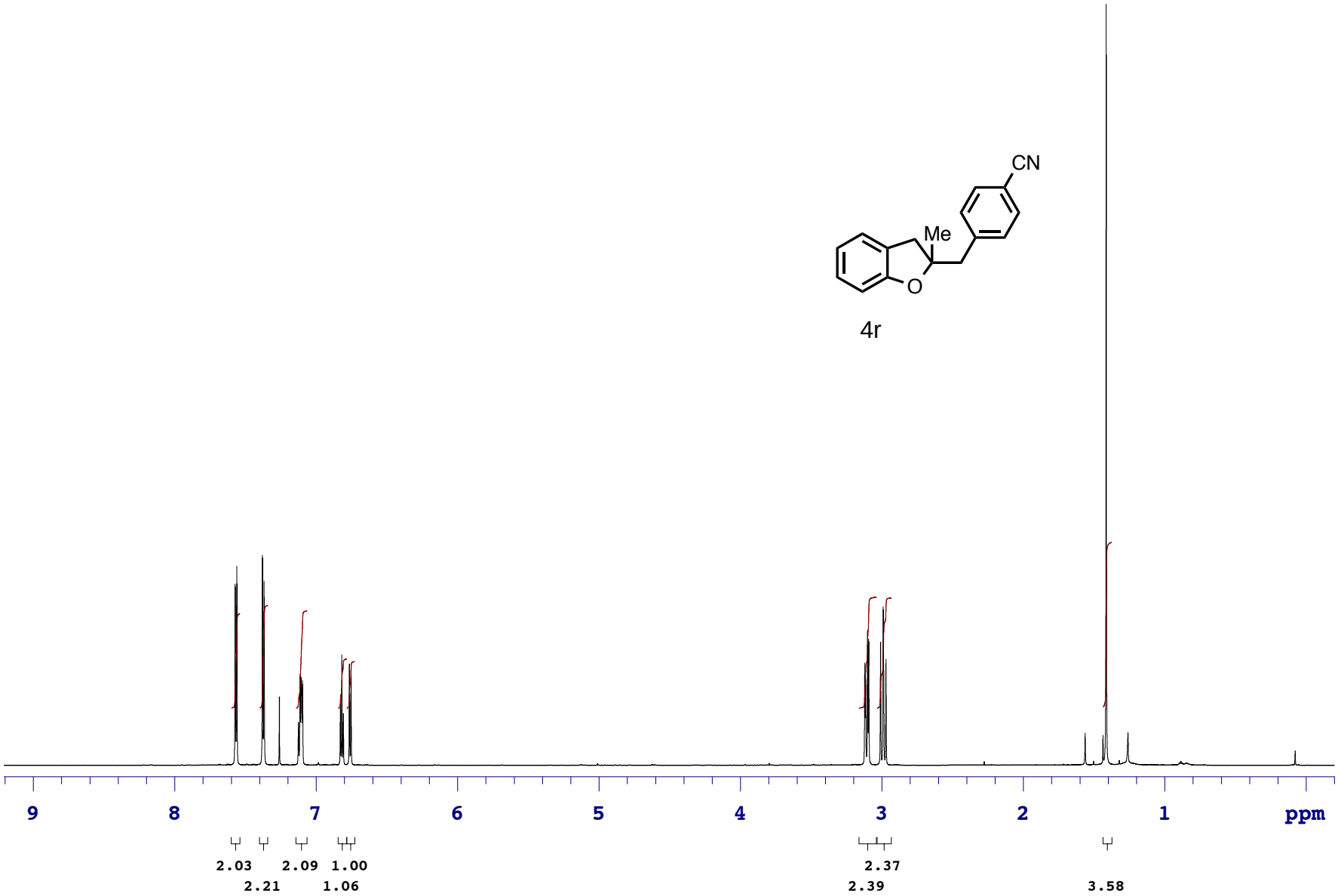


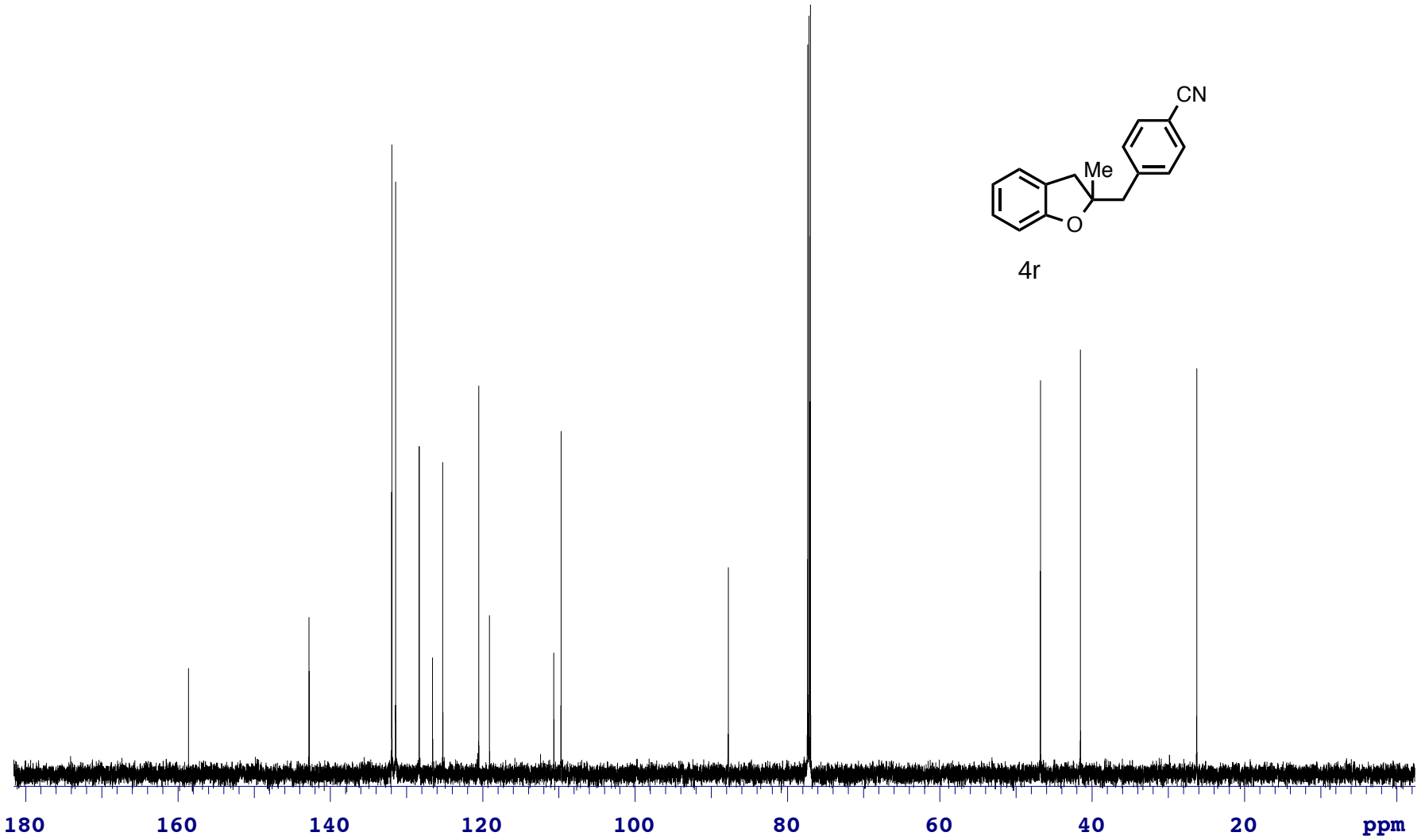
4p



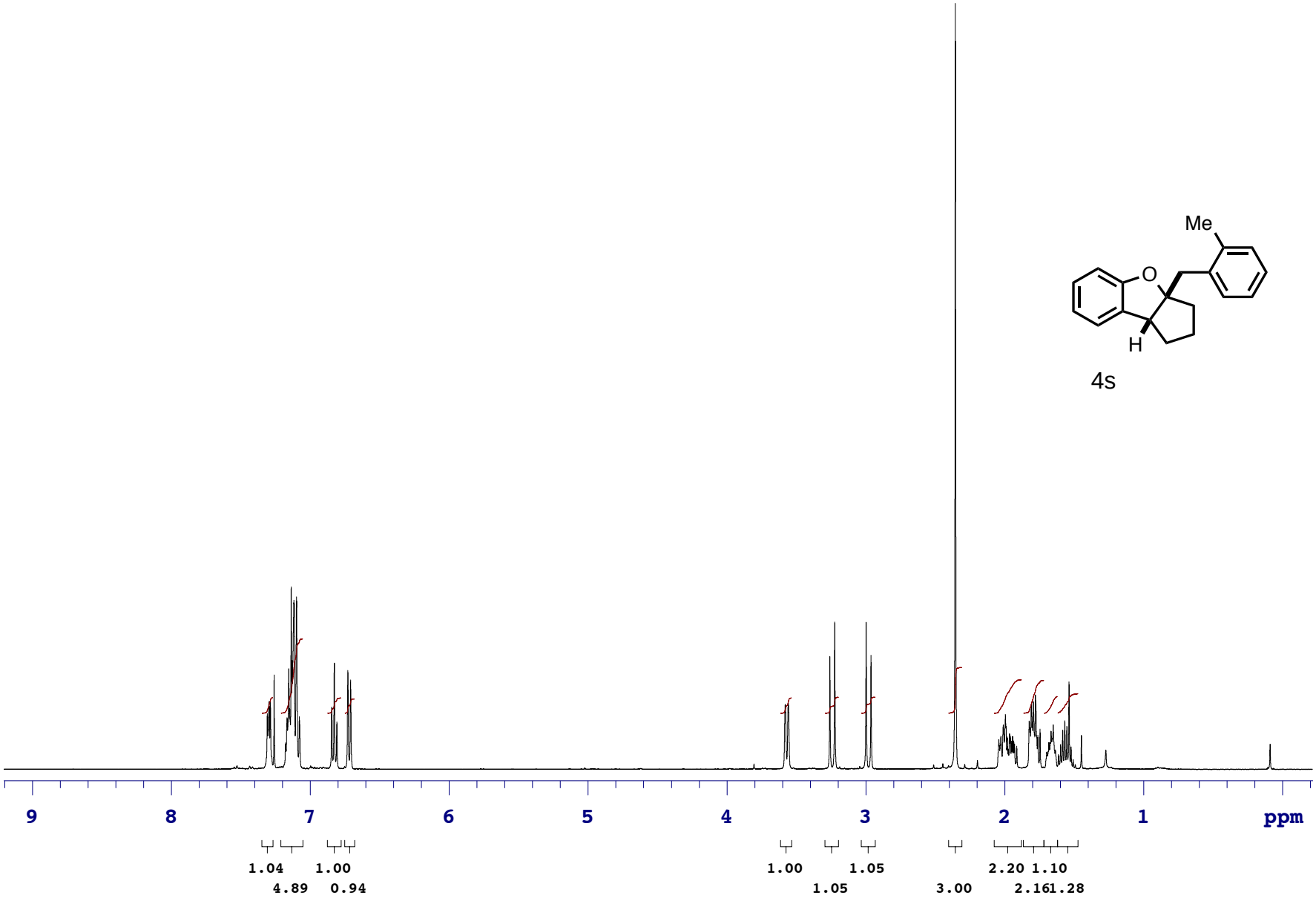



Ph
OMe
O
4p
9
8
7
6
5
4
3
2
1
ppm
0.48
1.11
1.00

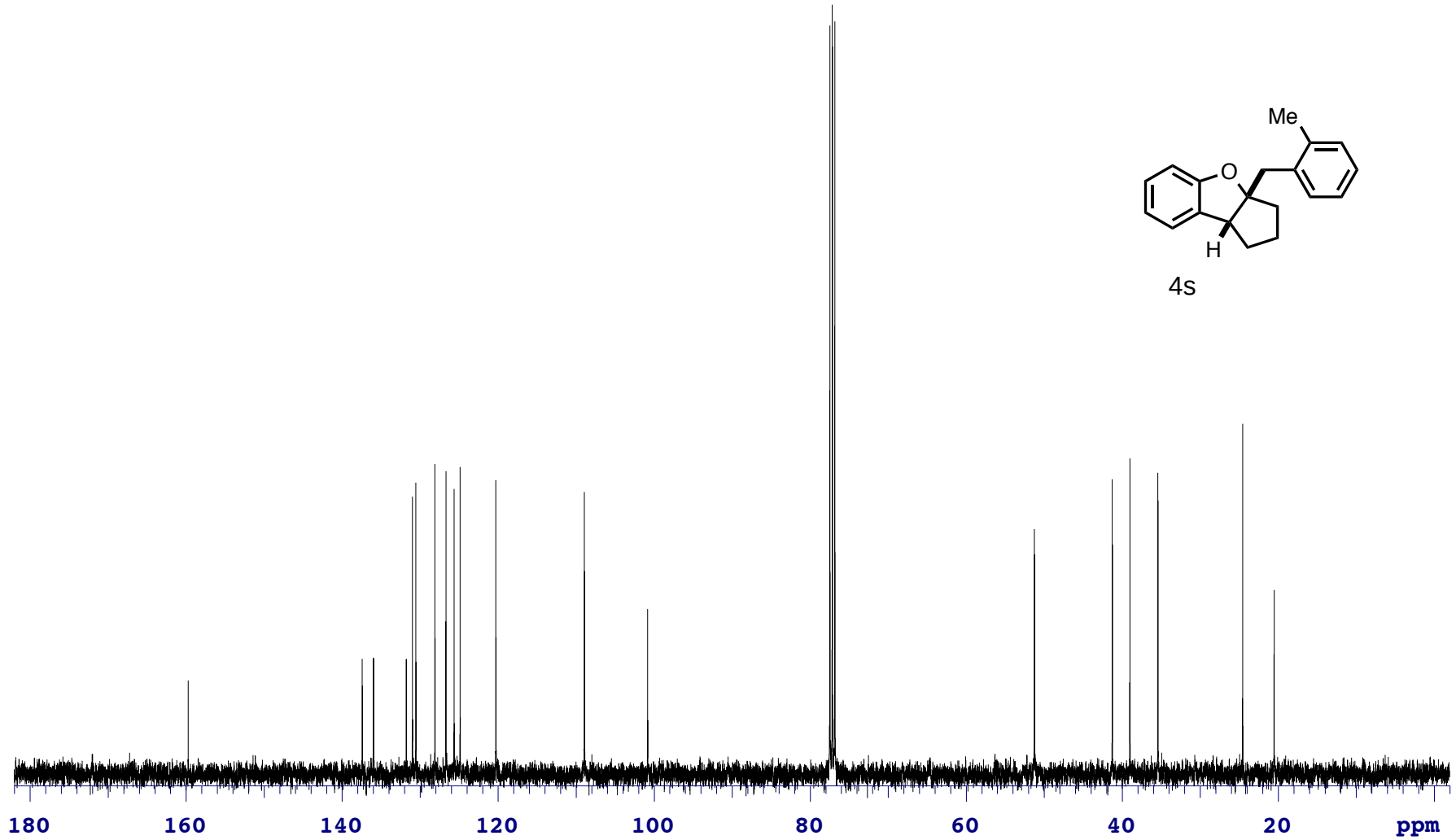

CN
Me
O
4r
9
8
7
6
5
4
3
2
1
ppm
2.03
2.21
2.09
1.00
1.06
2.37
2.39
3.58



4r


Me
O
H
9
8
7
6
5
4
3
2
1
ppm
1.04
4.89
1.00
0.94
1.00
1.05
1.05
3.00
2.20
1.10
2.16
1.28

4s



4s

JTH-II-77-1HCOSY

Sample Name:

Data Collected on:
yb.chem.lsa.umich.edu-vnmrs700
Archive directory:

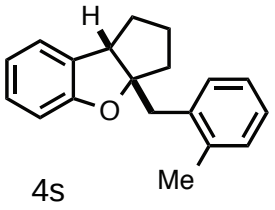
Sample directory:

FidFile: JTH-II-77-COSY

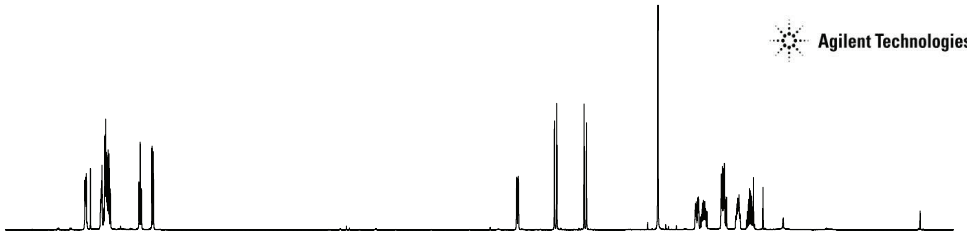
Pulse Sequence: gCOSY
Solvent: cdcl3
Data collected on: Jul 7 2014

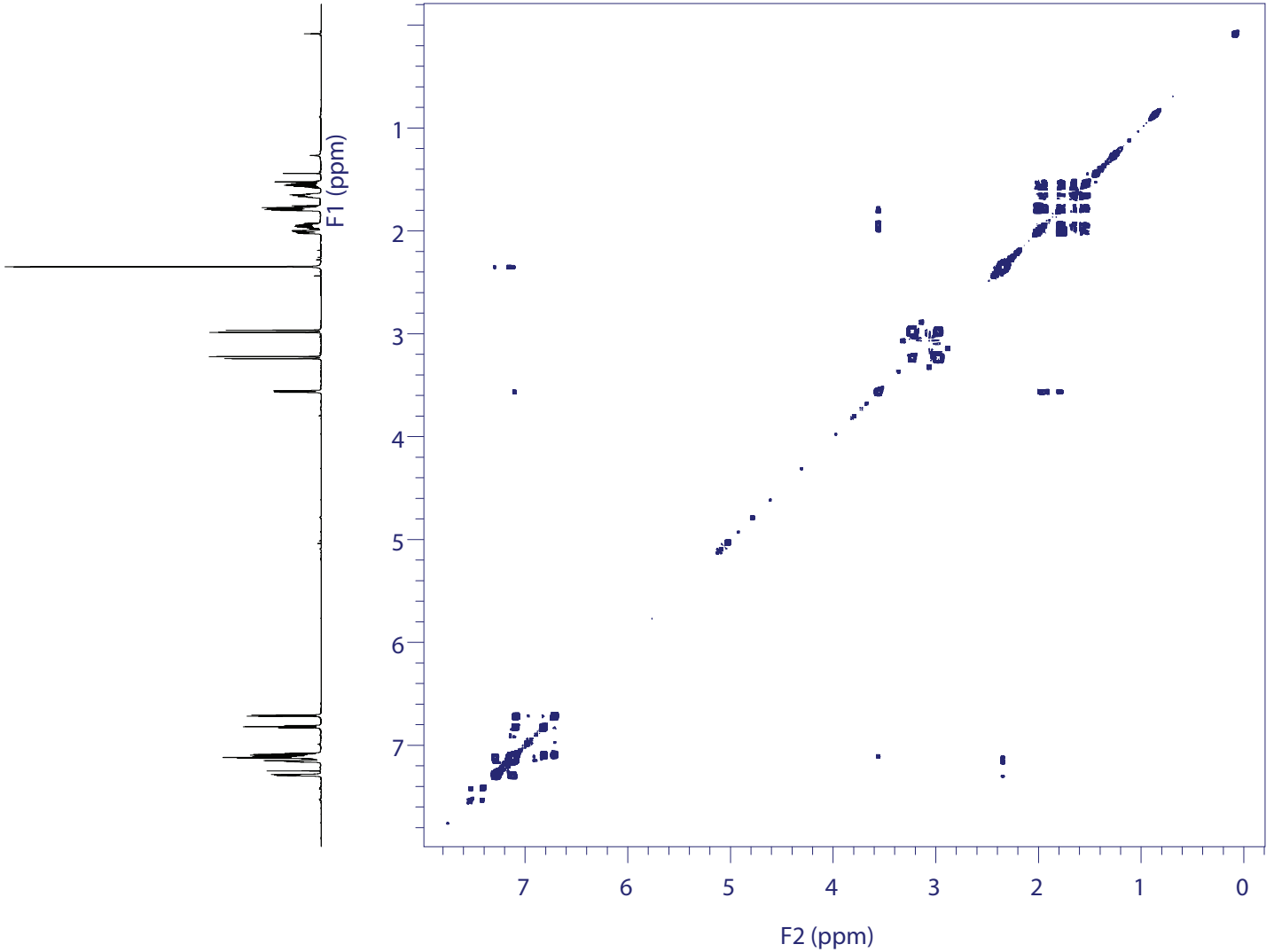
Temp. 25.0 C / 298.1 K
Operator: jhutt

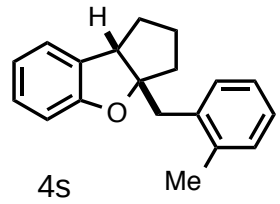
Relax. delay 1.000 sec
Acq. time 0.150 sec
Width 5733.9 Hz
2D Width 5733.9 Hz
2 repetitions
128 increments
OBSERVE H1, 699.7567747 MHz
DATA PROCESSING
Sq. sine bell 0.075 sec
F1 DATA PROCESSING
Sq. sine bell 0.022 sec
FT size 4096 x 4096
Total time 5 min 42 sec



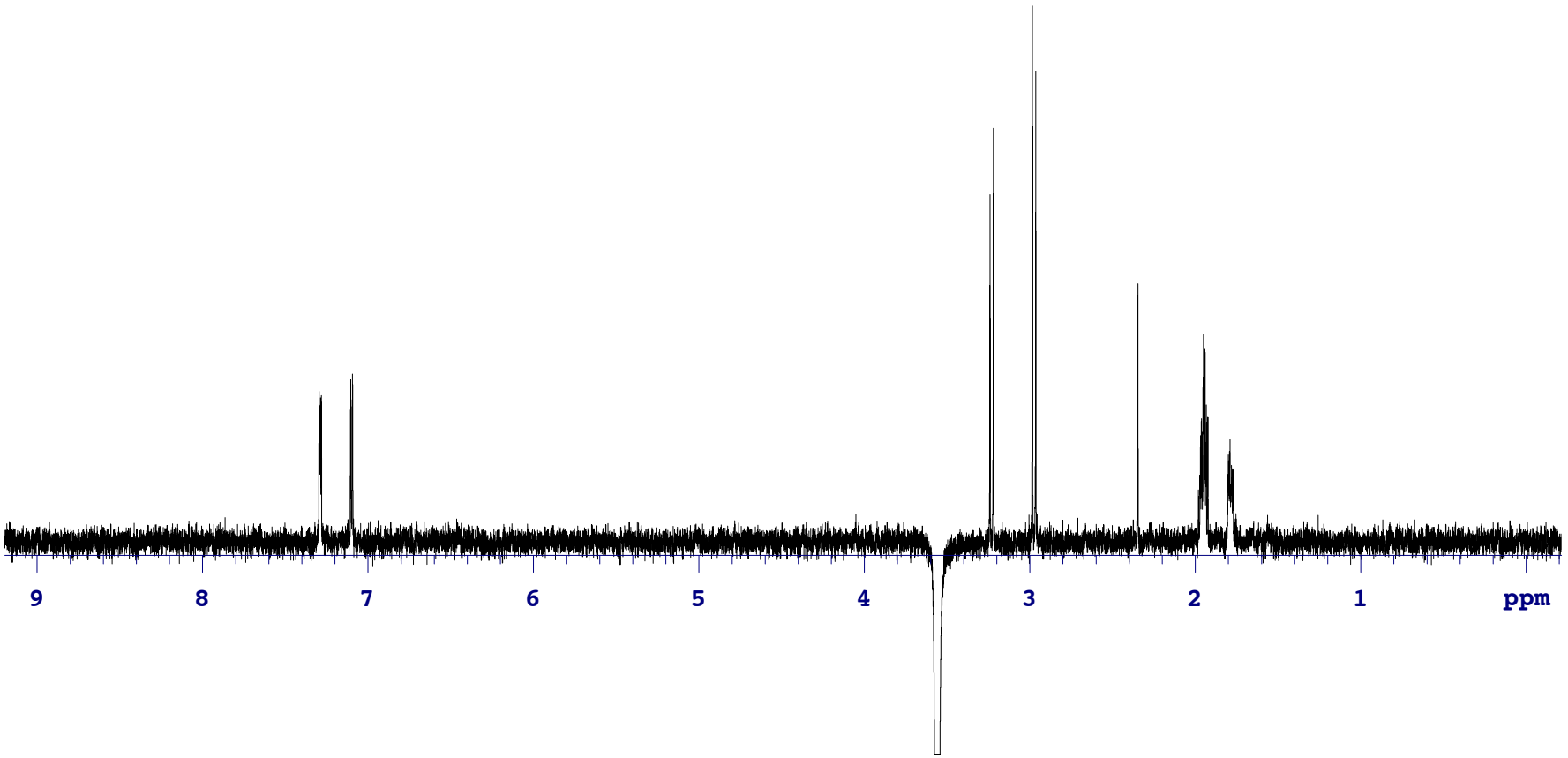
4s

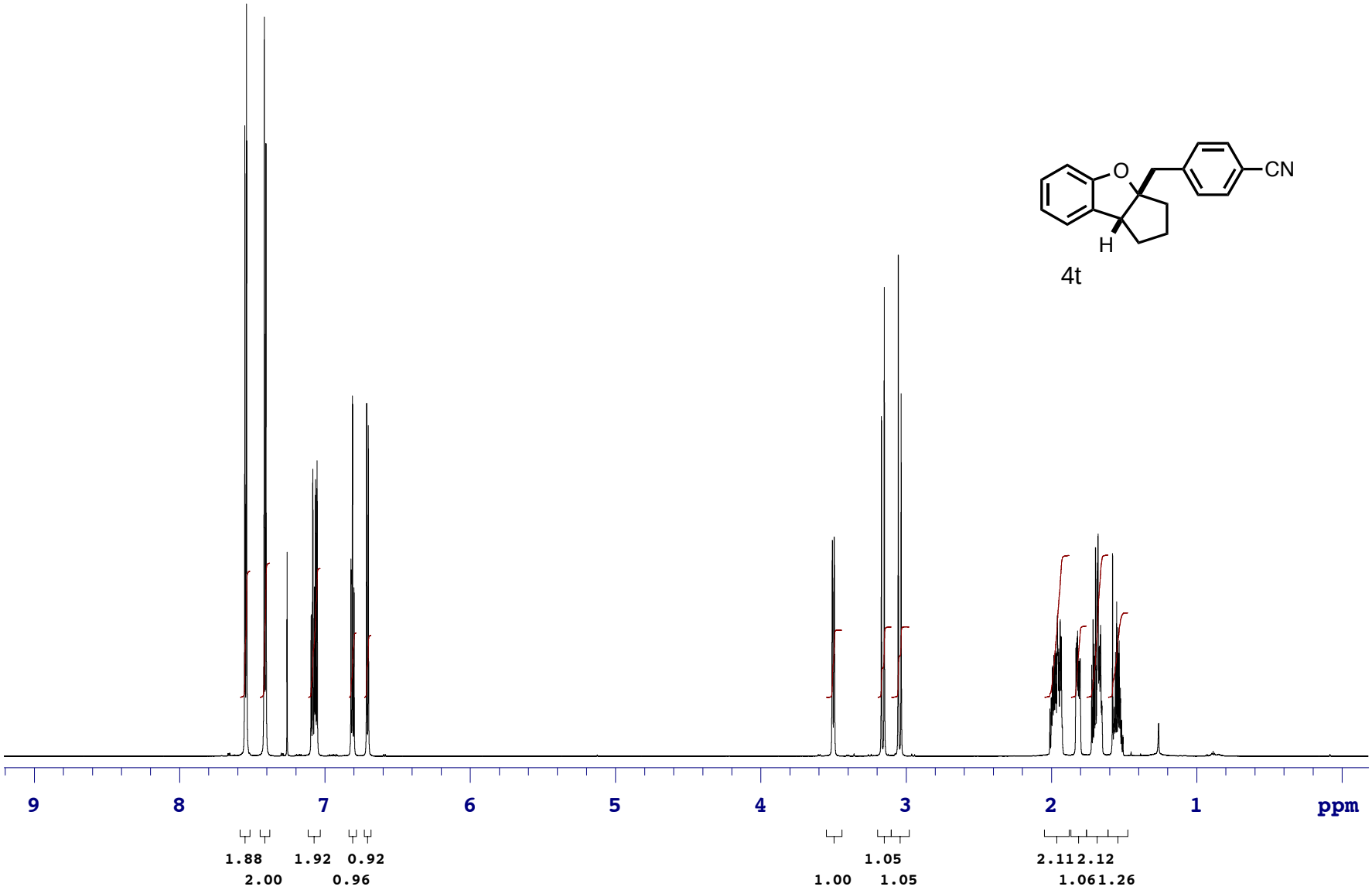




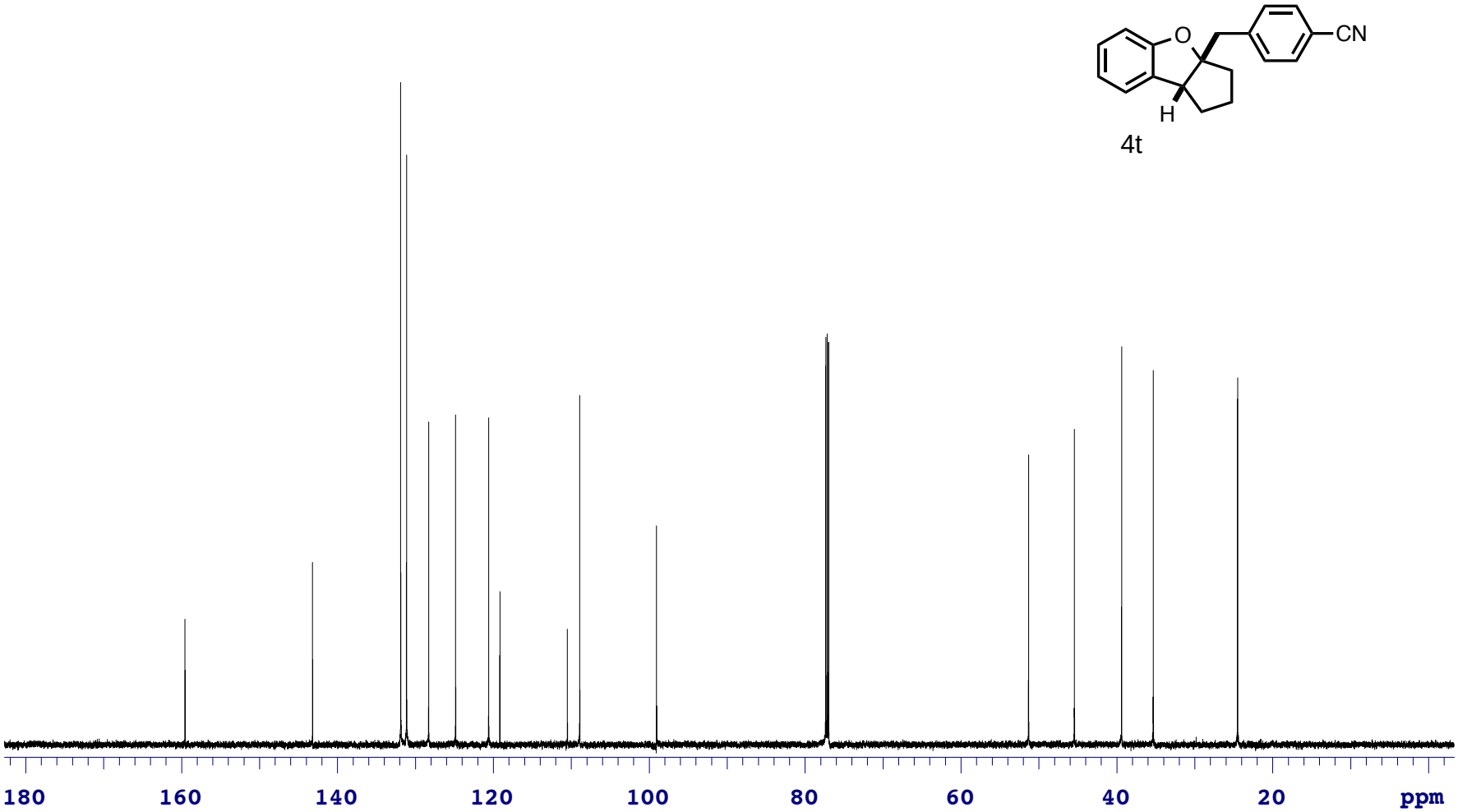


4s




O
CN
H
9
8
7
6
5
4
3
2
1
ppm
1.88
2.00
1.92
0.92
0.96
1.00
1.05
1.05
2.11
2.12
1.06
1.26

4t


O
CN
H
4t
180
160
140
120
100
80
60
40
20
ppm

Proton Spectrum

Sample Name:

Data Collected on:
yb.chem.lsa.umich.edu-vnmrs700
Archive directory:

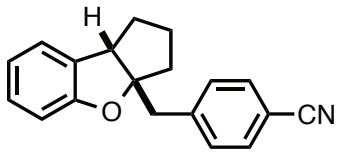
Sample directory:

FidFile: JTH-II-78-COSY

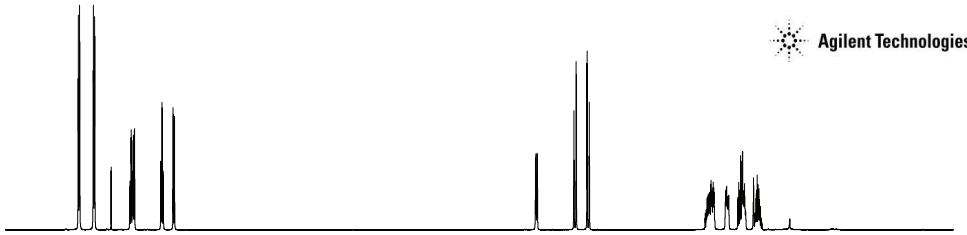
Pulse Sequence: gCOSY
Solvent: cdcl3
Data collected on: Jul 4 2014

Temp. 25.0 C / 298.1 K
Operator: jhutt

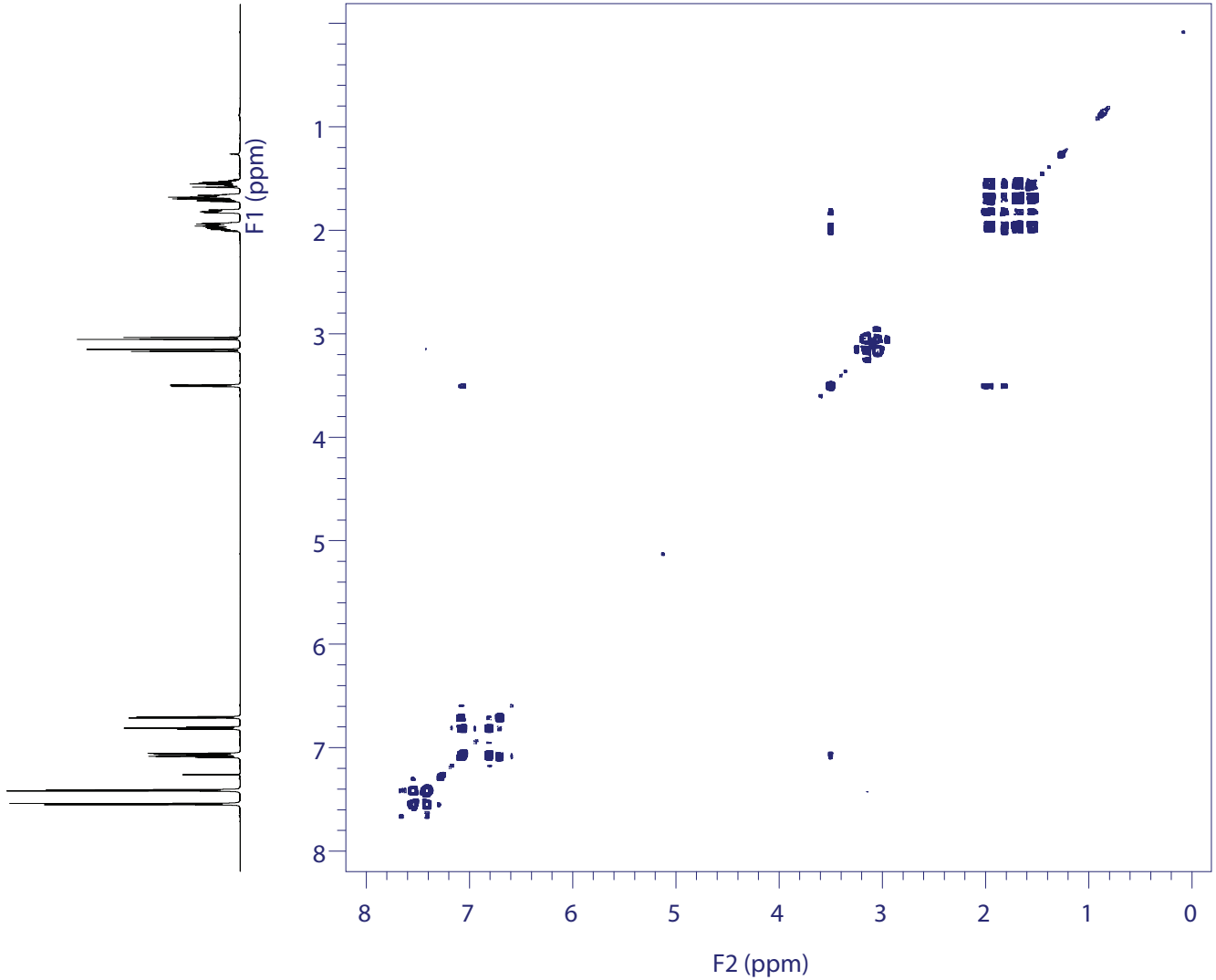
Relax. delay 1.000 sec
Acq. time 0.150 sec
Width 5868.5 Hz
2D Width 5868.5 Hz
2 repetitions
128 increments
OBSERVE H1, 699.7567663 MHz
DATA PROCESSING
Sq. sine bell 0.075 sec
F1 DATA PROCESSING
Sq. sine bell 0.022 sec
FT size 4096 x 4096
Total time 5 min 42 sec

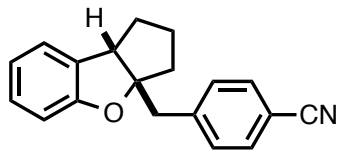


4t

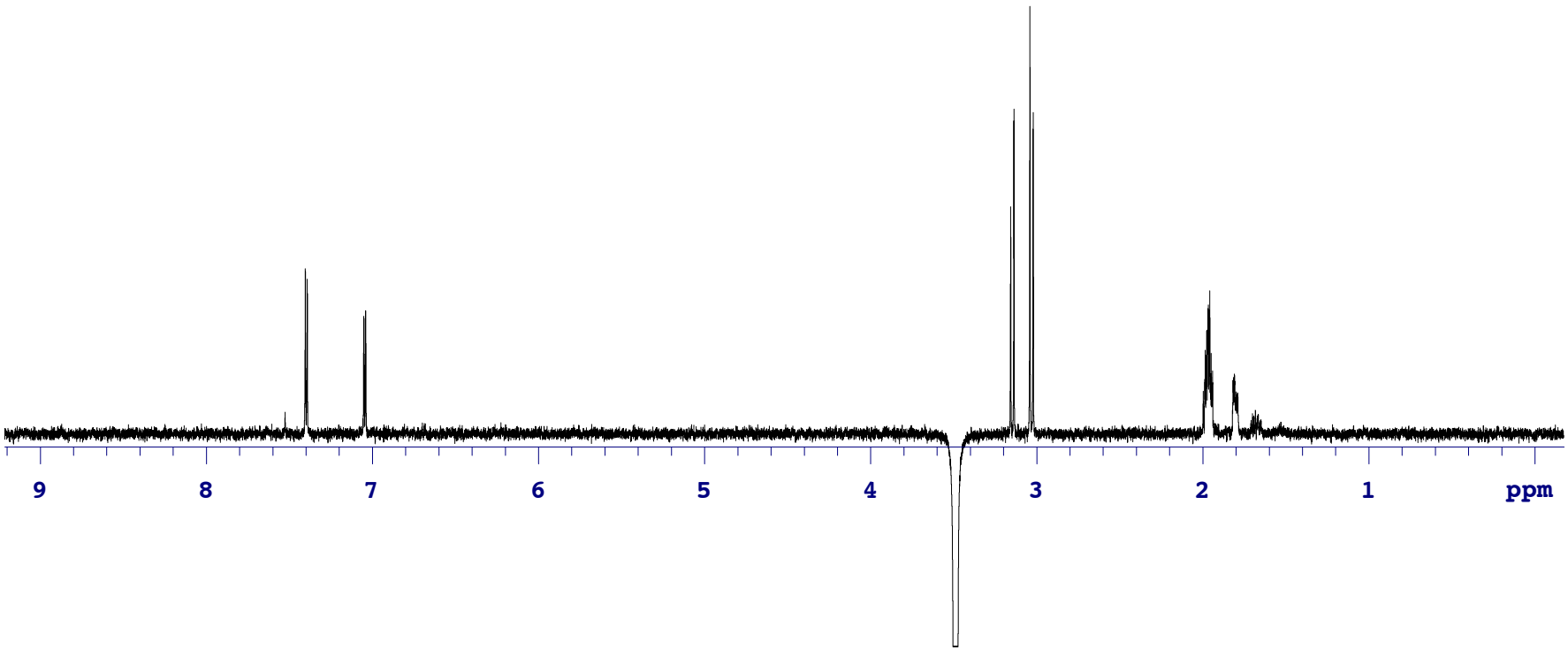


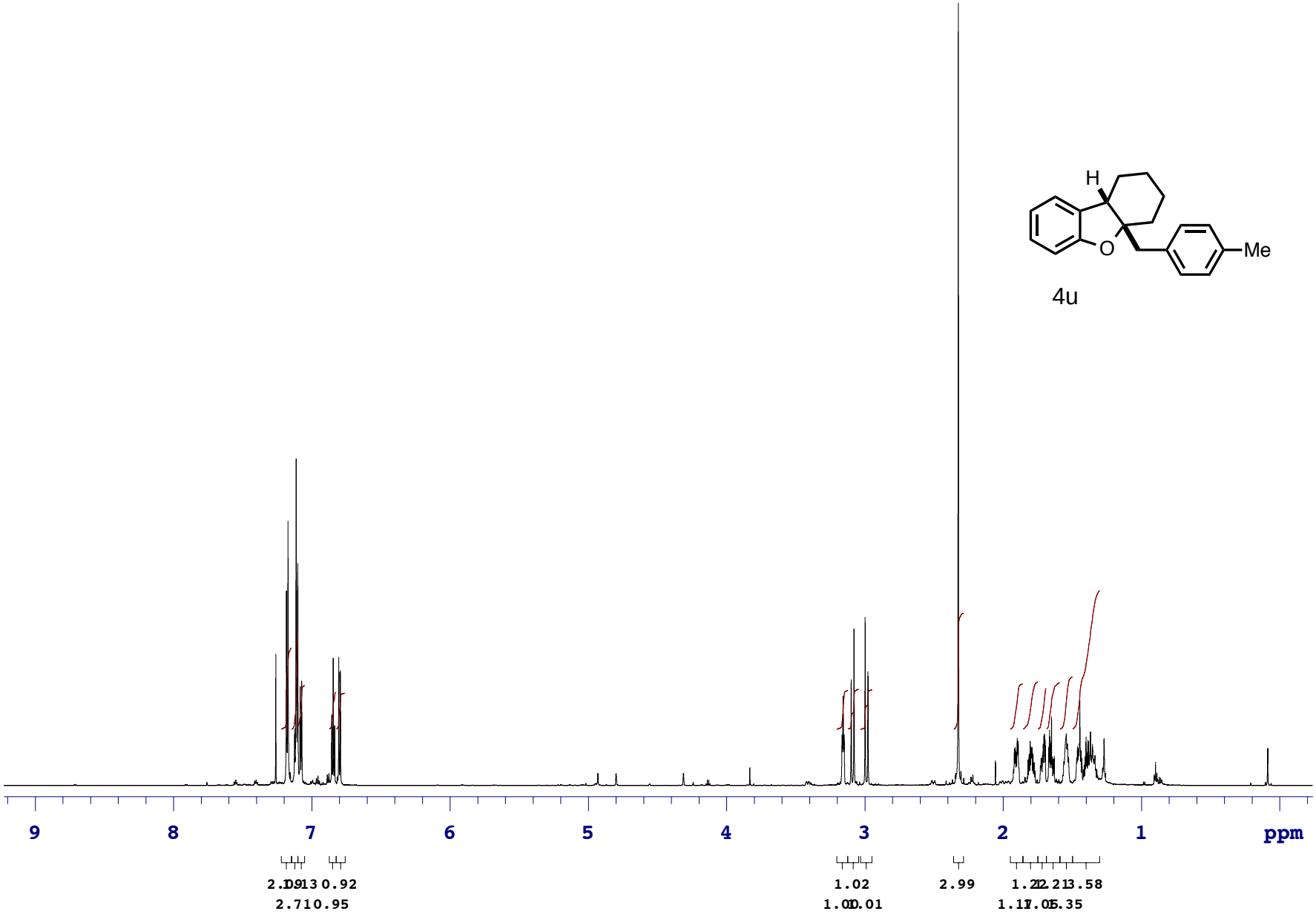
Agilent Technologies

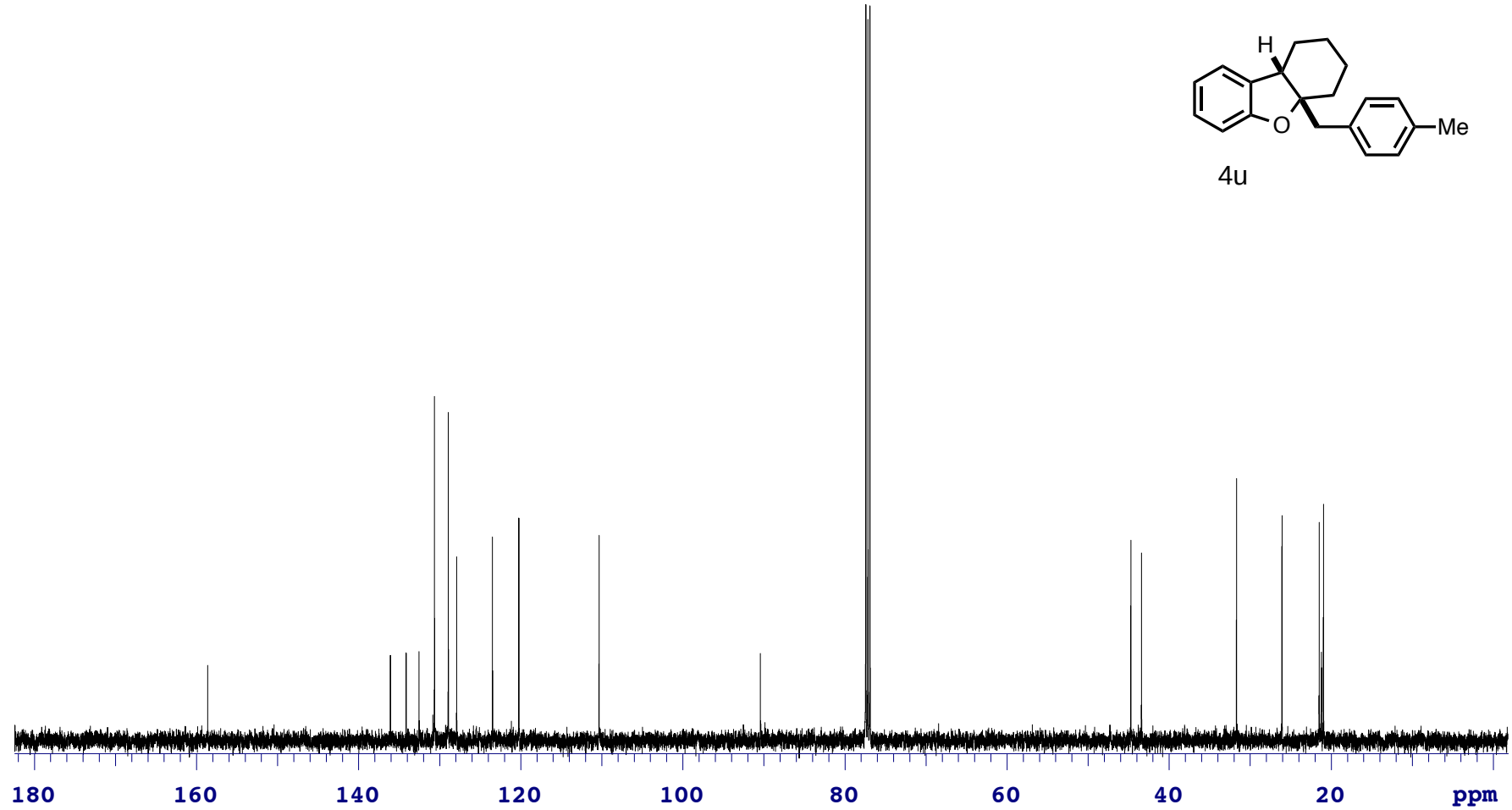




4t




H
O
Me
4u
9
8
7
6
5
4
3
2
1
ppm
2.10
0.91
3
0.92
2.71
0.95
1.02
1.00
0.01
2.99
1.22
2.21
3.58
1.11
7.00
5.35


H
O
Me
4u
180
160
140
120
100
80
60
40
20
ppm

JTH-II-75-HF-1HCOSY

Sample Name:

Data Collected on:
yb.chem.lsa.umich.edu-vnmrs700
Archive directory:

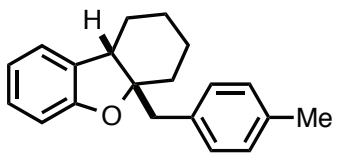
Sample directory:

FidFile: JTH-II-75-HF-COSY

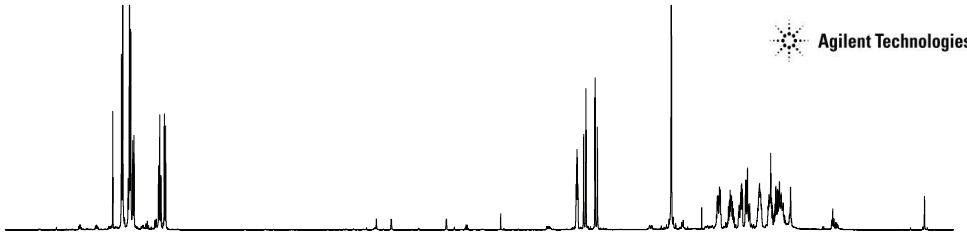
Pulse Sequence: gCOSY
Solvent: cdcl3
Data collected on: Jul 7 2014

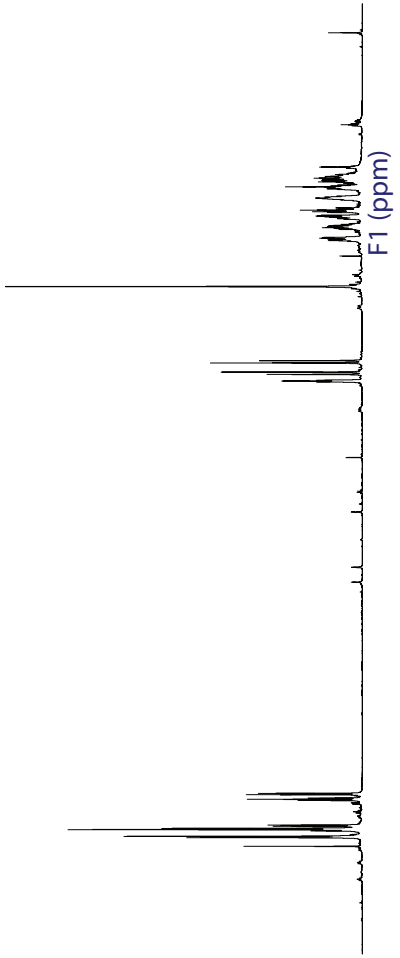
Temp. 25.0 C / 298.1 K
Operator: jhutt

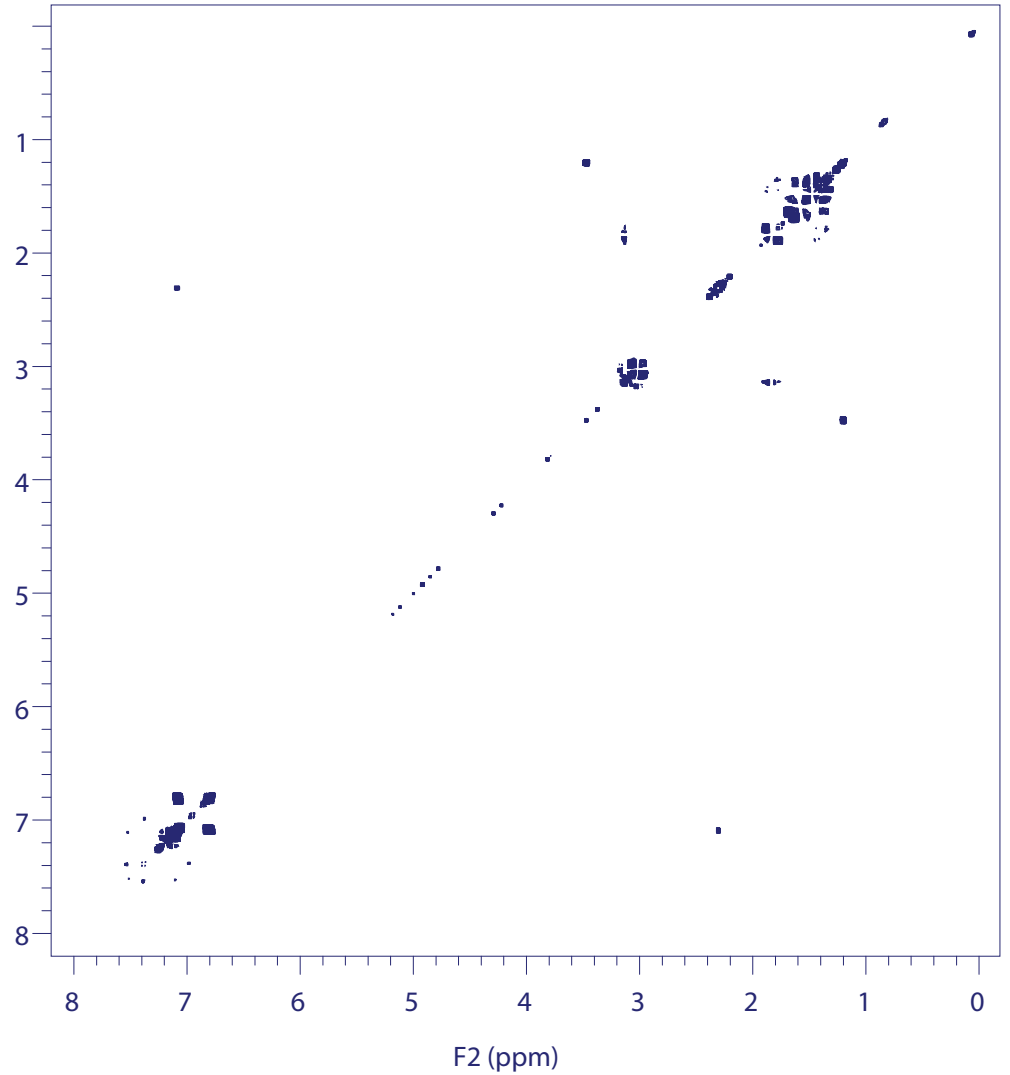
Relax. delay 1.000 sec
Acq. time 0.150 sec
Width 5868.5 Hz
2D Width 5868.5 Hz
2 repetitions
128 increments
OBSERVE H1, 699.7567747 MHz
DATA PROCESSING
Sq. sine bell 0.075 sec
F1 DATA PROCESSING
Sq. sine bell 0.022 sec
FT size 4096 x 4096
Total time 5 min 42 sec

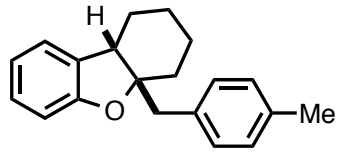


4u

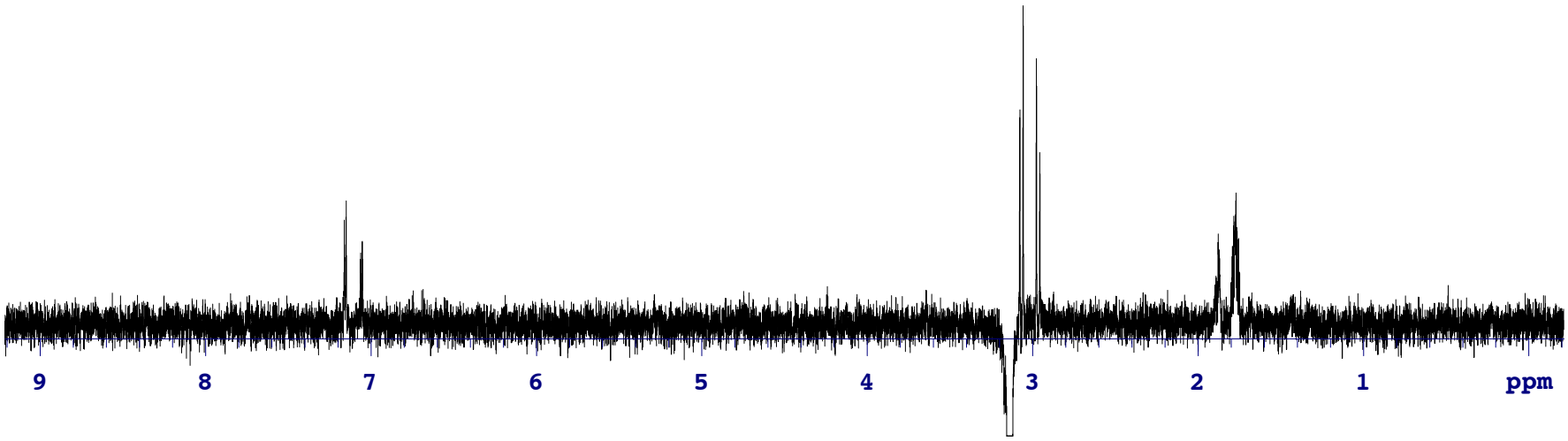


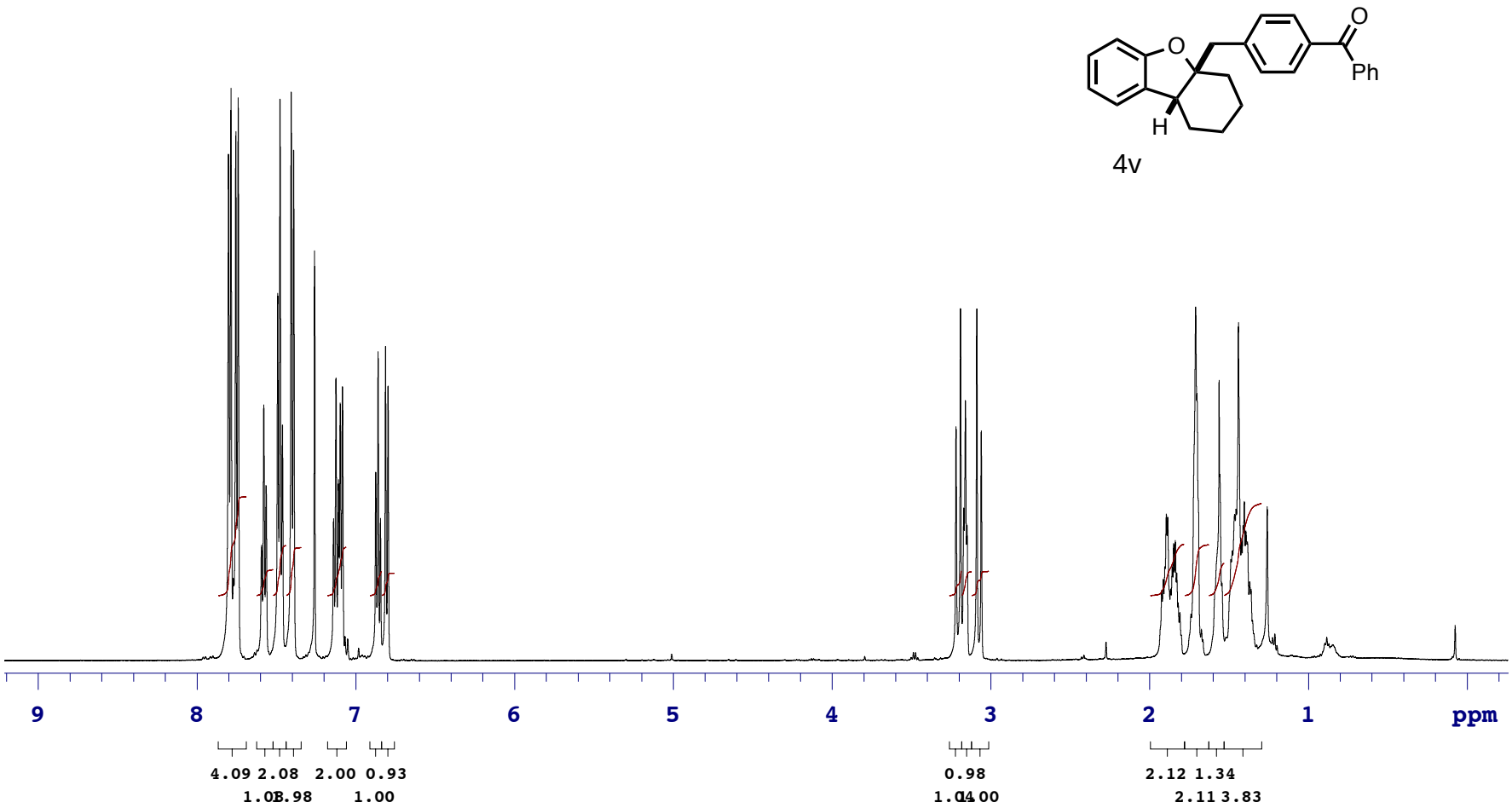




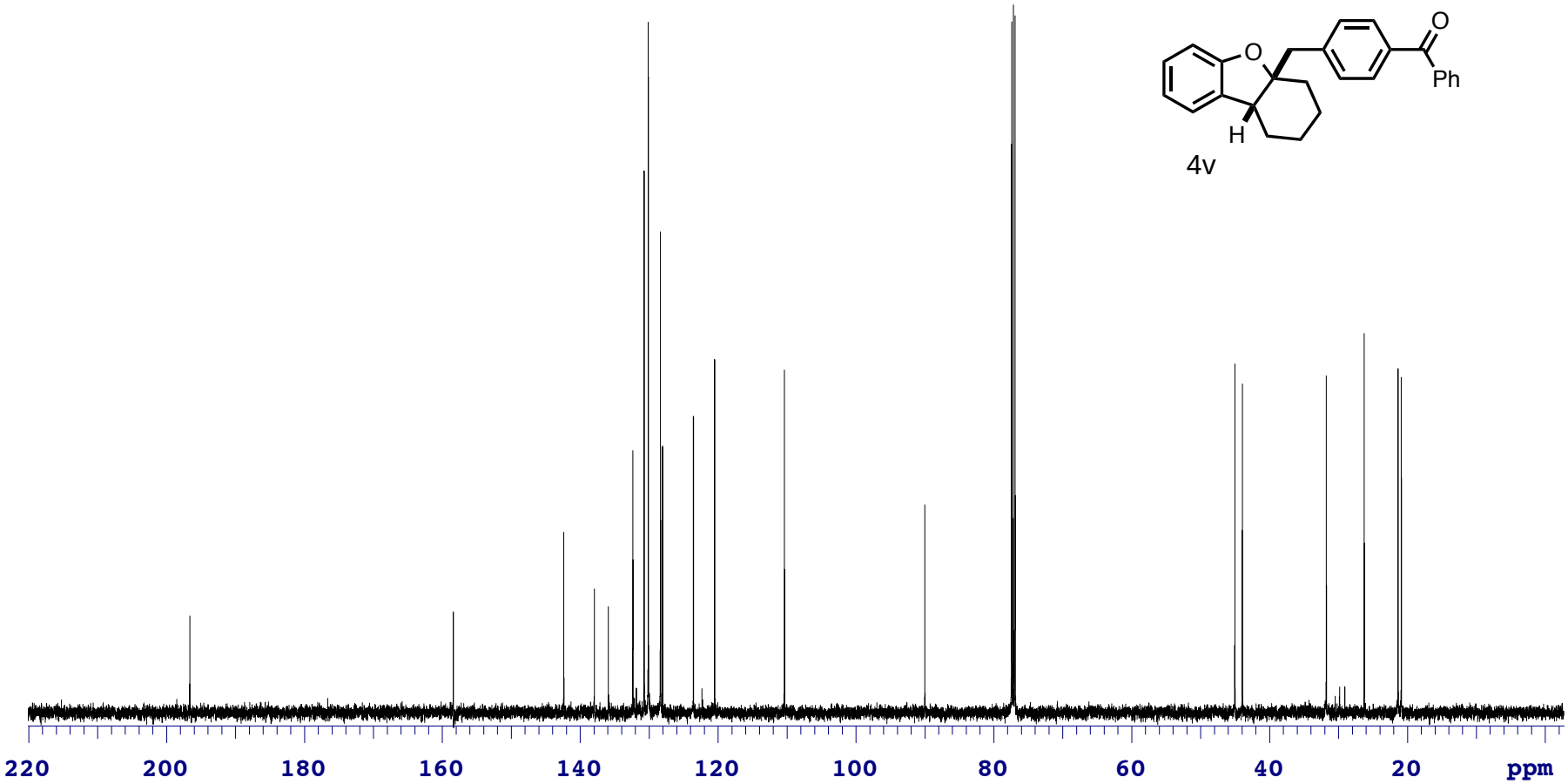


4u





4v


O
O
Ph
H
4v
220
200
180
160
140
120
100
80
60
40
20
ppm

Proton Spectrum

Sample Name:

Data Collected on:
yb.chem.lsa.umich.edu-vnmrs700
Archive directory:

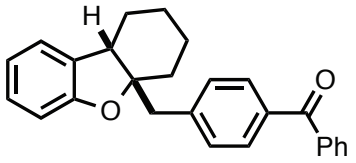
Sample directory:

FidFile: JTH-II-76-HF-COSY

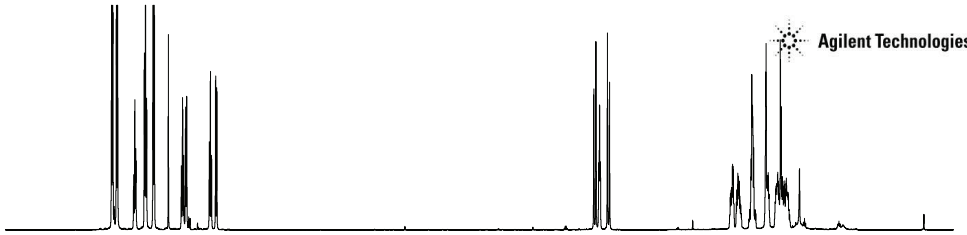
Pulse Sequence: gCOSY
Solvent: cdcl3
Data collected on: Jul 4 2014

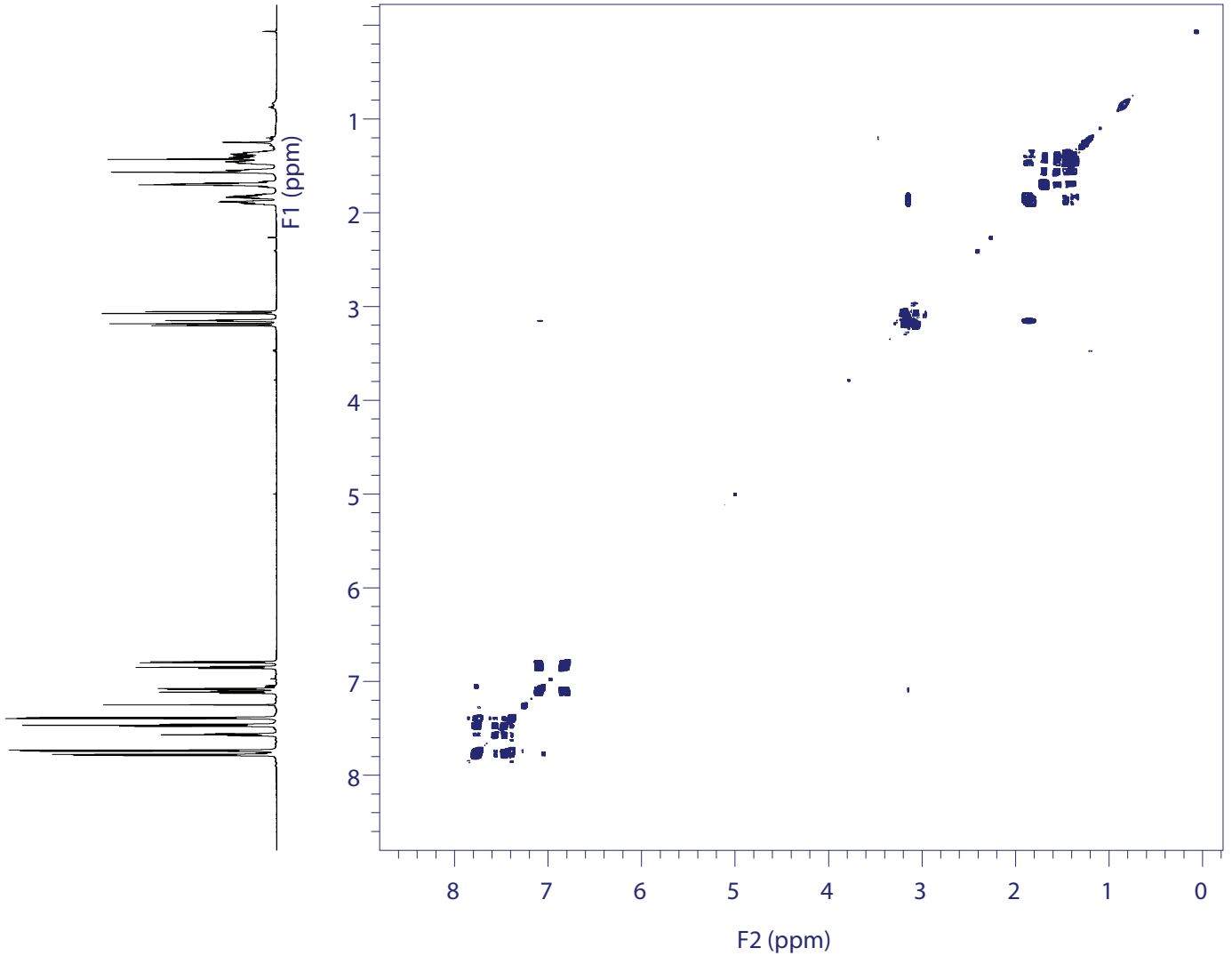
Temp. 25.0 C / 298.1 K
Operator: jhutt

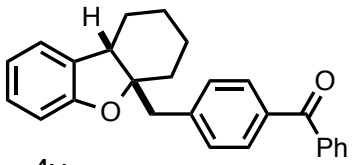
Relax. delay 1.000 sec
Acq. time 0.150 sec
Width 6313.1 Hz
2D Width 6313.1 Hz
2 repetitions
128 increments
OBSERVE H1, 699.7567747 MHz
DATA PROCESSING
Sq. sine bell 0.075 sec
F1 DATA PROCESSING
Sq. sine bell 0.020 sec
FT size 4096 x 4096
Total time 5 min 42 sec



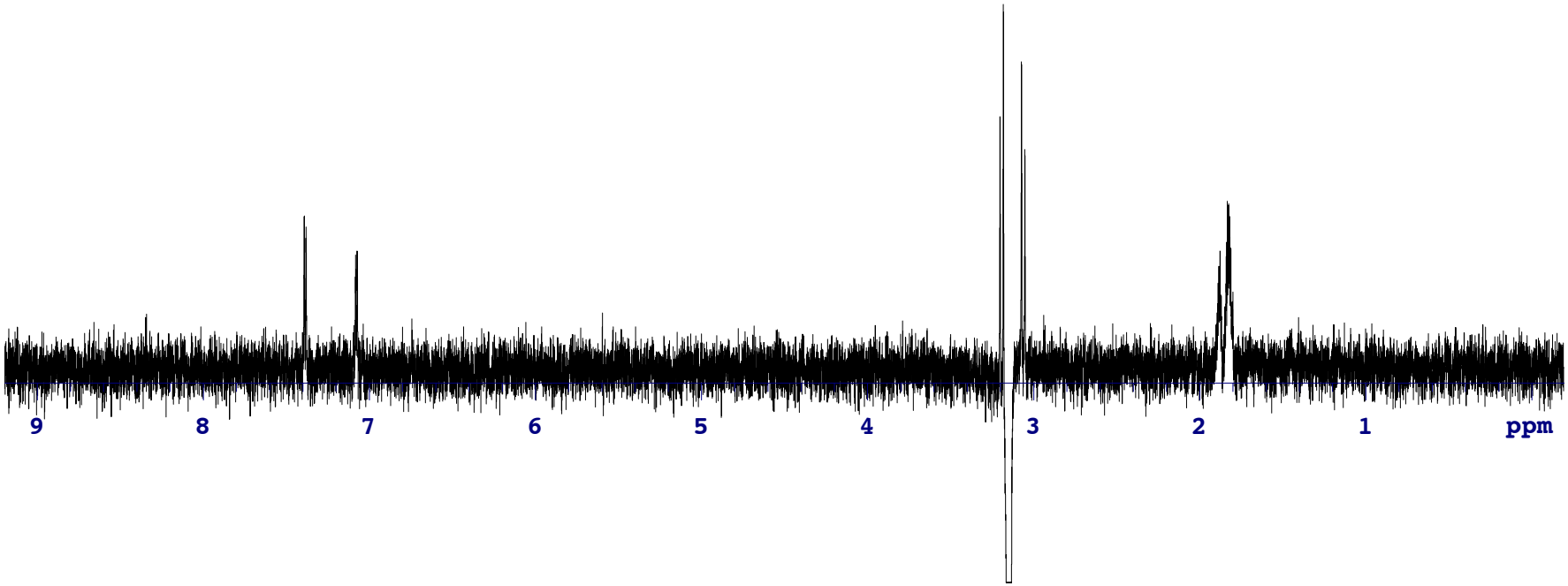
4v

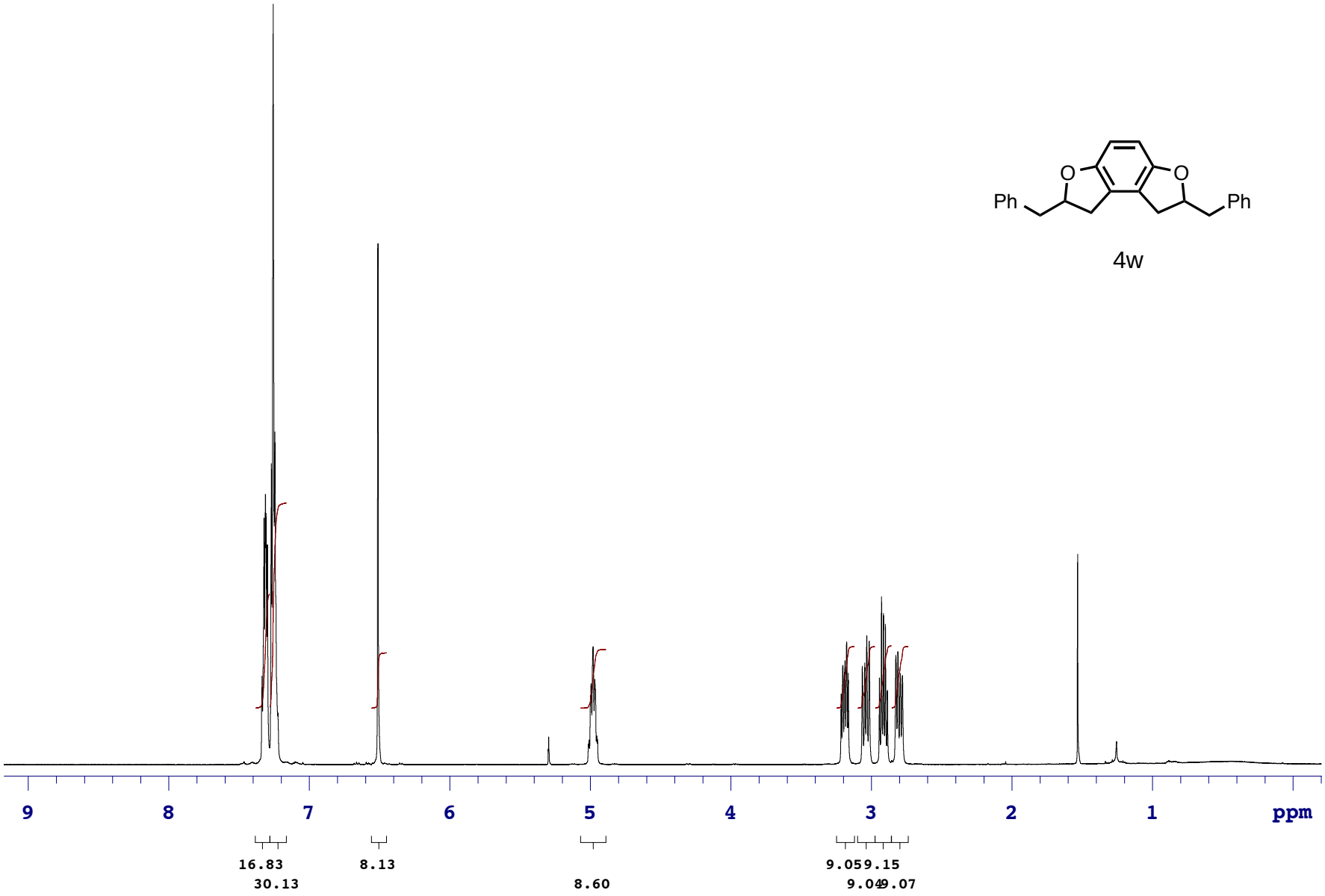


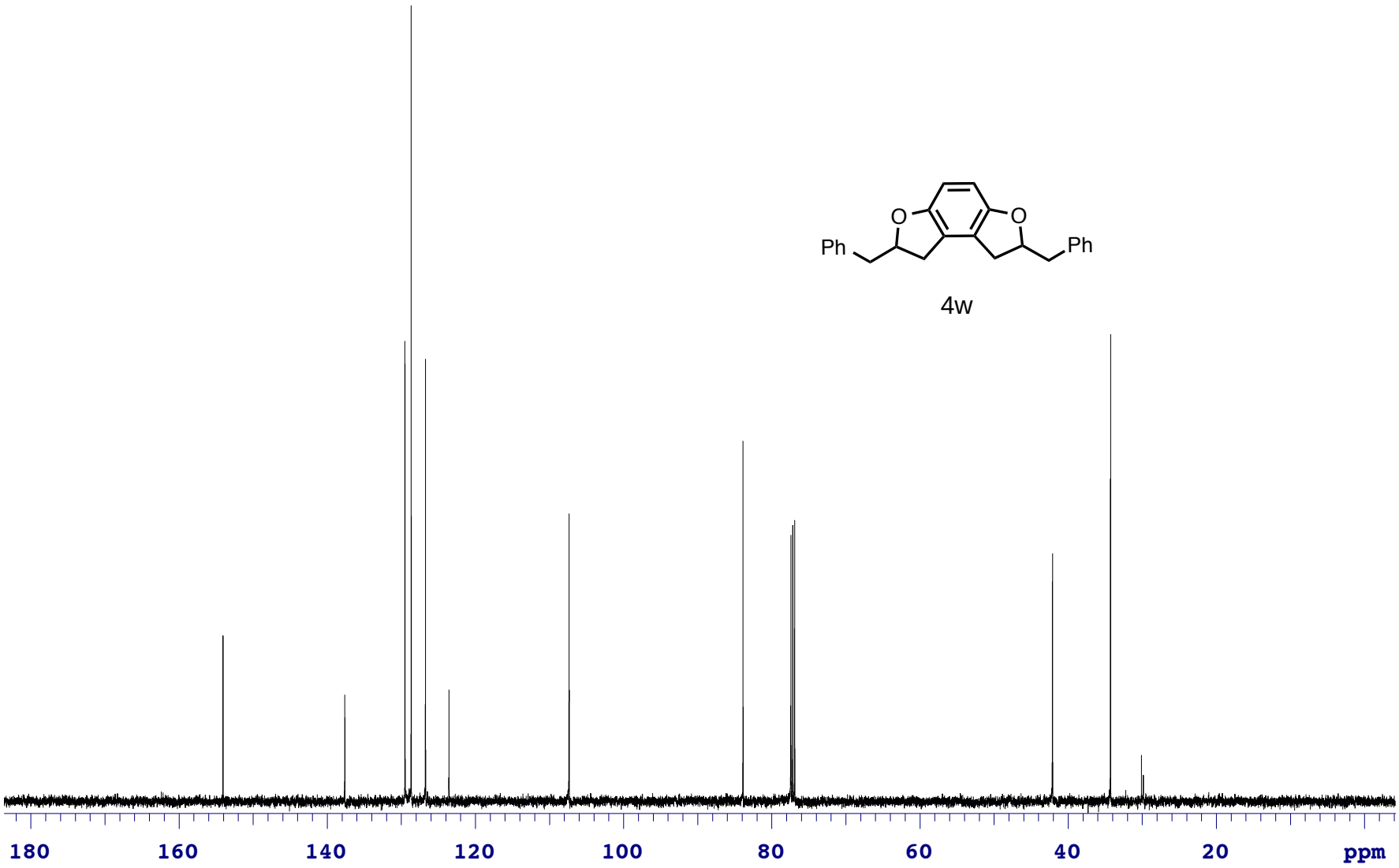




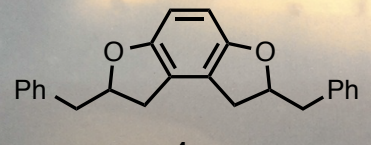
4v



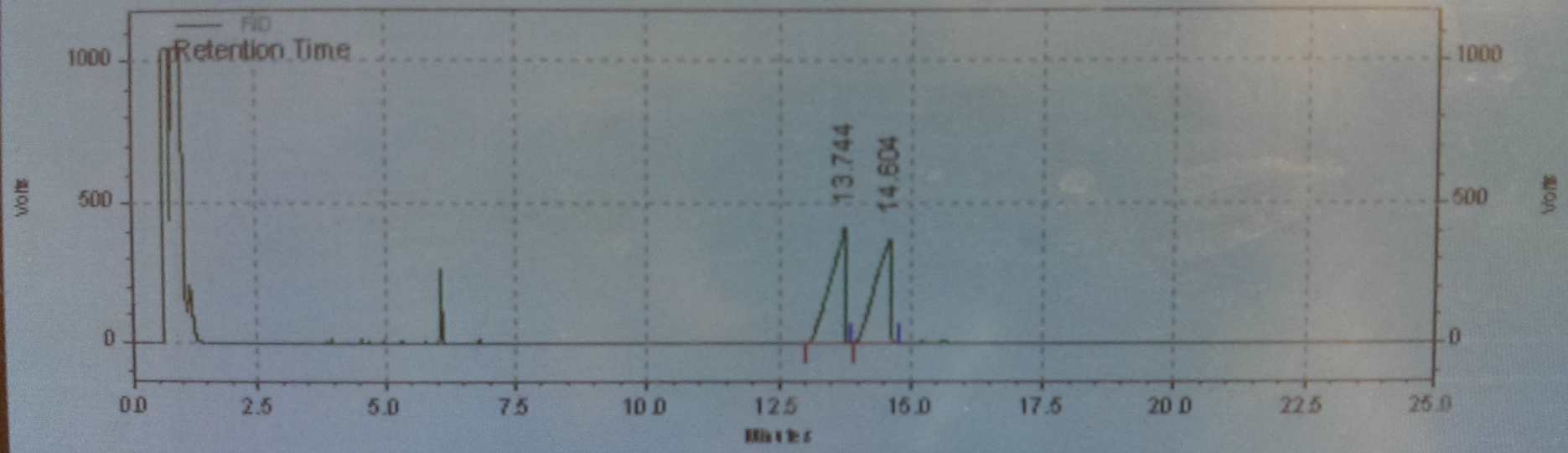

O
O
Ph
Ph
4w
9
8
7
6
5
4
3
2
1
ppm
16.83
30.13
8.13
8.60
9.05
9.15
9.04
9.07


O
O
Ph
Ph
4w
180
160
140
120
100
80
60
40
20
ppm

Acquired: 7/3/2014 12:03:03 PM
Printed: 07/03/2014 01:11:41 PM



4w



FID Results

Retention Time	Area	Area %	Height	Height %
13.744	8177471	52.13	412144	52.58
14.604	7508606	47.87	371674	47.42

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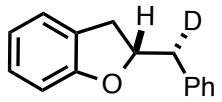
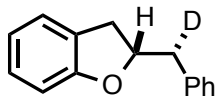


Independently Prepared
Standard

d-4a

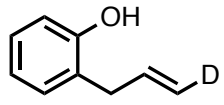
Agilent Technologies



Independently Prepared Standard

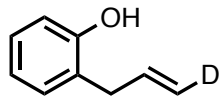
d-4a

Agilent Technologies



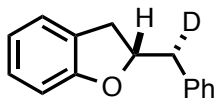
d-2a

Agilent Technologies



d-2a

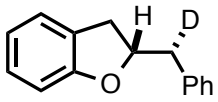
Agilent Technologies



Prepared Via Caboetherification
Anti-Conditions

d-4a

Agilent Technologies



Prepared Via Caboetherification
Anti-Conditions

d-4a