Practical Catalytic Asymmetric Synthesis of Diaryl-, and Diheteroarylmethanols

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Supporting Information

Table of Contents **page**

General Methods. All reactions were performed under a nitrogen atmosphere with oven-dried glassware using standard Schlenk or vacuum line techniques. The progress of reactions was monitored by thin-layer chromatography (TLC) performed on Whatman precoated silica gel 60 Å K6F plates and visualized by ultra-violet light or by staining with cerium-ammonium-molybdate. *t*-BuOMe was distilled from Na/benzophenone and toluene was dried through alumina columns. TEEDA was distilled and stored under nitrogen. The ^{1}H NMR and $^{13}C\{^{1}H\}$ NMR spectra were obtained on a Brüker Fourier transform NMR spectrometer at either 300 or 500 and 75 or 125 MHz, respectively. ^{1}H NMR spectra were referenced to tetramethylsilane in $CDCl_3$ or residual protonated solvent; $^{13}C\{^{1}H\}$ NMR spectra were referenced to residual solvent. Analysis of enantiomeric excess was performed using a Hewlett-Packard 1100 Series HPLC and a chiral column. Alternatively, a Berger SFC PioNTo ™ ® was employed when the compounds could not be resolved by HPLC. The optical rotations were recorded using a JASCO DIP-370. Infrared spectra were obtained using a Perkin-Elmer Spectrum 100 Series spectrometer. All reagents were purchased from Aldrich or Acros unless otherwise described. 3-Benzofurancarboxaldehyde was synthesized according to known procedure starting from

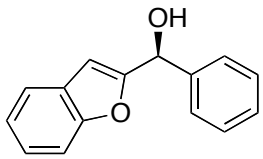
commercially available 3-methylbenzofuran.[1] Binaphthyl amino alcohol ligand **L2** was synthesized according to Chan's procedure.[2,3] EtZnCl was synthesized following Guerrero's method.[4,5] All the commercially available aldehyde substrates were distilled prior to use. Silica gel (Silicaflash P60 40-63 μm, Silicycle) was used for air-flashed chromatography. Silica gel treated with triethylamine (deactivated silica gel) was prepared by mixing 20 mL of triethyl amine with 800 mL of silica. All the compounds characterized in the present Supporting Information have been purified using deactivated silica gel. Compounds in Scheme 2 and Table 3 were characterized in our initial communication,[6] except for compound **7**, which is characterized herein.

Caution. Dialkylzinc and alkyl lithium reagents are pyrophoric. Care and appropriate laboratory equipment must be used when handling these reagents.

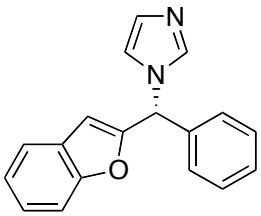
Synthesis and characterization of Aryl, Heteroaryl- and Diheteroarylmethanols

General Procedure A. A nitrogen purged Schlenk flask was charged with 3-bromofuran (67.0 μL 0.75 mmol) and *t*-BuOMe (1 mL) and cooled to –78 °C. *n*-BuLi (0.3 mL, 2.5 M in hexanes, 0.75 mmol) was then added dropwise and the solution was stirred for 1 h at this temperature. During this time a white precipitate formed. EtZnCl (97.0 mg, 0.75 mmol) was added to the reaction flask as a solid at –78 °C followed by toluene (3 mL). The heterogeneous solution was stirred at –78 °C for 30 min and then warmed at 0 °C. TEEDA (64 μL, 0.30 mmol) was added and the solution stirred for an additional 30 min. (–)-MIB (190 μL, 0.1 M solution in hexanes, 0.019 mmol) was added to the reaction flask and the solution was stirred for 5 min before 2-thiophenecarboxaldehyde (35 μL, 0.37 mmol, dissolved in 1.5 mL of toluene) was added over 1.5 h by syringe pump. The reaction mixture was stirred at 0 °C and monitored by TLC until completion (approximately 10 h). The reaction mixture was diluted with 3 mL EtOAc and quenched with water (5 mL). The organic layer was separated and the aqueous solution extracted with EtOAc (3 × 10 mL). The combined organic layer was washed with brine (5 mL), dried over $MgSO_4$, filtered, and the solvent was removed under reduced pressure. The crude product was purified by column chromatography on deactivated silica gel.

General Procedure B. This procedure is exactly the same as General Procedure A except that the catalyst loading was 10% mol.

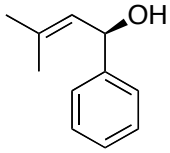


Benzofuran-2-yl(phenyl)methanol (1). General Procedure A was applied to 2-benzofurancarboxaldehyde (36.5 mg, 0.25 mmol) and bromobenzene (53 μL, 0.50 mmol). The crude product was purified by column chromatography on silica gel (hexanes/EtOAc : 95/5) to give **1** (51.7 mg, 92% yield) as a yellow solid. The enantiomeric excess was determined by HPLC with a Chiralcel AS-H column (hexanes:2-propanol = 98:2, flow rate = 0.5 mL/min), t_r (1) = 44.6 min, t_r (2) = 48.4 min, $[\alpha]_D^{20}$ = +3.5 (*c* = 0.041, $CHCl_3$, 90% ee); ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.49 (d, *J* = 4.5 Hz, 1H), 5.97 (d, *J* = 4.5 Hz, 1H), 6.54 (s, 1H), 7.18-7.24 (m, 3H), 7.33-7.44 (m, 3H), 7.49-7.53 (m, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz): δ 70.9, 104.3, 111.6, 121.4, 123.1, 124.5, 127.0, 128.3, 128.6, 128.9, 140.0, 155.3, 158.0; IR (neat): 3389, 3019, 2960, 2925, 2873, 1706, 1597, 1496, 1452, 1264, 1200, 1124 cm^{-1}; HRMS calcd for $C_{15}H_{11}O$ $(M\text{-}OH)^+$: 207.0810, found 207.0802. The data collected are in agreement with previously published results.[7,8]

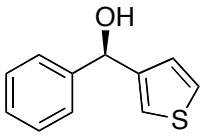


1-(benzofuran-2-yl(phenyl)methyl)-1*H*-imidazole (2). A 10 mL Schlenk flask was charged with benzofuran-2-yl(phenyl)methanol (43.5 mg, 0.19 mmol) and THF (1 mL). PPh_3 (66.0 mg, 0.25 mmol) and imidazole (17.2 mg, 0.25 mmol) where quickly weighted into the flask and stirred at 0 °C for 5 min. Finally DIAD (diisopropyl azodicarboxylate) (50 μL, 0.25 mmol) was added and the reaction stirred at room temperature for 12 h. The volatile materials were removed *in vacuo* and the oil thus obtained was dissolved in DCM (5 mL) and washed with water (3 mL). The water layer was then exctracted with DCM (3 × 10 mL). The combined organic layer was washed with brine (5 mL) dried over $MgSO_4$, filtered, and the volatile material were removed under reduced pressure. The crude product was purified by column chromatography on deactivated silica gel (hexanes/2-propanol : 95/5) to give **2** (22 mg, 41% yield) as a yellow solid. 18 mg of **1** (0.08 mmol) were recovered unreacted but with no loss of ee. Thus the yield based on recovered starting material was 84%. The enantiomeric excess was determined by HPLC with a Chiralcel AS-H column (hexanes:2-propanol = 90:10, flow rate = 0.5 mL/min), t_r (1) = 24.6 min, t_r (2) = 32.6 min, = –2.7 (*c* = 0.027, $CHCl_3$, 90% ee); ^{1}H NMR ($CDCl_3$, 300 MHz): δ 6.51 (t, *J* = 0.9 Hz, 1H), 6.62 (s, 1H), 6.99 (t, *J* = 1.2 Hz, 1H), 7.14 (t, *J* = 1.2 Hz, 1H), 7.20-7.28 (m, 4H), 7.30-7.35 (m, 1H), 7.39-7.42 (m, 3H) 7.45-7.49 (m, 1H) 7.53-7.57 (m, 2H); ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz): δ 59.5, 107.4, 111.7, 119.1, 121.5, 123.4, 125.3, 127.6, 129.1, 129.2, 129.7, 136.8, 137.2, 154.1, 155.4; IR (neat): 3442, 3191, 3146, 3056,

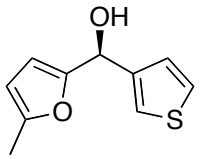
2980, 2930, 1968, 1899, 1821, 1721, 1590, 1483, 1453, 1437, 1373, 1310, 1279, 1254, 1226, 1196, 1120, 1072, 1028, 997 cm^{-1}; HRMS calcd for $C_{18}H_{15}N_2O$ $(MH)^+$: 275.1184, found 275.1184. The data collected are in agreement with previously published results.[9]



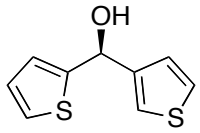
3-Methyl-1-phenylbut-2-en-1-ol (7). General Procedure A was applied to 3-methyl-2-butenal (24.2 μL, 0.25 mmol) and bromobenzene (53.0 μL, 0.5 mmol). The crude product was purified by column chromatography on silica gel (hexanes/EtOAc : 95/5) to give **7** (35.1 mg, 85.9% yield) as an oil. The enantiomeric excess was determined by HPLC with a Chiralcel AD-H column (hexanes:2-propanol = 99:1, flow rate = 0.5 mL/min), t_r (1) = 55.1 min, t_r (2) = 60.9 min, = –118.3 (*c* = 0.106, $CHCl_3$, 90% ee); ^1H NMR ($CDCl_3$, 500 MHz): δ 1.74 (d, *J* = 1.1 Hz, 3H), 1.80 (d, *J* = 1.1 Hz, 3H), 1.86 (d, *J* = 2.9 Hz, 1H), 5.40 (dt, *J* = 1.1, 8.8 Hz, 1H), 5.45 (dd, *J* = 3.0, 8.8 Hz, 1H), 7.22-7.27 (m, 1H), 7.31-7.39 (m, 4H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz): δ 18.2, 25.8, 70.7, 125.8, 127.2, 127.7, 128.4, 135.2, 144.2; IR (neat): 3335, 3085, 3062, 3029, 2972, 2913, 2792, 1948, 1880, 1806, 1674, 1602, 1492, 1450, 1375, 1332, 1281, 1249, 1195, 1109, 1075 cm^{-1}; HRMS calcd for $C_{11}H_{14}ONa$ $(M+Na)^+$: 185.0966, found 185.0948. The data collected are in agreement with previously published results.[10]



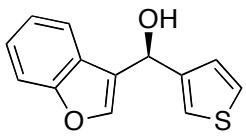
Phenyl(thiophen-3-yl)methanol (25). General Procedure A was applied to benzaldehyde (38 μL, 0.38 mmol) and 3-bromothiophene (70 μL, 0.75 mmol). The crude product was purified by column chromatography on silica gel (hexanes/EtOAc : 95/5) to give **25** (44.0 mg, 68% yield) as an oil. The enantiomeric excess was determined by HPLC with a Chiralcel AS-H column (hexanes:2-propanol = 99:1, flow rate = 0.5 mL/min), t_r (1) = 65.5 min, t_r (2) = 69.0 min, = –19.5 (*c* = 0.026, $CHCl_3$, 90% ee); ^1H NMR ($CDCl_3$, 500 MHz): δ 2.18 (d, *J* = 4.3 Hz, 1H), 5.88 (d, *J* = 4.3 Hz, 1H), 6.98 (dd, *J* = 1.5, 4.3 Hz, 1H), 7.16 (m, 1H), 7.24-7.29 (m, 2H), 7.32-7.39 (m, 5H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz): δ 72.8, 121.6, 126.1, 126.3, 126.4, 127.7, 128.5, 143.3, 145.2; IR (neat): 3944, 3756, 3691, 3595, 3054, 2987, 2685, 2522, 2411, 2372, 2305, 2126, 2055, 1603, 1551, 1493, 1421, 1265, 1149, 1080, 1020 cm^{-1}; HRMS calcd for $C_{11}H_9S$ $(M-OH)^+$: 173.0425, found 173.0430. The data collected are in agreement with previously published results.[11,12]



(5-methylfuran-2-yl)(thiophen-3-yl)methanol (26). General Procedure B was applied to 5-methyl-2-furancarboxaldehyde (37 μL, 0.37 mmol) and 3-bromothiophene (70 μL, 0.75 mmol). The crude product was purified by column chromatography on silica gel (hexanes/EtOAc : 95/5) to give **26** (52.0 mg, 72% yield) as a yellow oil. The enantiomeric excess was determined by HPLC with a Chiralcel OD-H column (hexanes:2-propanol = 98:2, flow rate = 0.5 mL/min), t_r (1) = 57.8 min, t_r (2) = 62.8 min, = +11.5 (*c* = 0.024, $CHCl_3$, 92% ee); ^1H NMR ($CDCl_3$, 300 MHz): δ 2.30 (m, 4H), 5.85 (d, *J* = 5.1 Hz, 1H), 5.91 (m 1H), 6.04 (d, *J* = 3.7 Hz, 1H), 7.12 (m, 1H), 7.31 (m, 2H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): δ 13.8, 66.8, 106.4, 108.5, 122.4, 126.2, 126.7, 142.4, 152.6, 154.0; IR (neat): 3370, 3105, 2920, 1560, 1420, 1262, 1218, 1148, 1018 cm^{-1}; HRMS calcd for $C_{10}H_{10}O_2Na$ $(M+Na)^+$: 217.0299, found 217.0302.

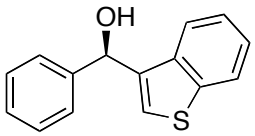


Thiophen-2-yl(thiophen-3-yl)methanol (27). General Procedure A was applied to 2-thiophenecarboxaldehyde (470 μL, 0.37 mmol) and 3-bromothiophene (940 μL, 0.75 mmol). The crude product was purified by column chromatography on silica gel (hexanes/EtOAc : 95/5) to give **27** (820 mg, 83% yield) as a solid. The enantiomeric excess was determined by HPLC with a Chiralcel OD-H column (hexanes:2-propanol = 97:3, flow rate = 0.5 mL/min), t_r (1) = 43.6 min, t_r (2) = 48.9 min, = +5.0 (*c* = 0.015, $CHCl_3$, 93% ee); ^1H NMR ($CDCl_3$, 300 MHz): δ 2.35 (d, *J* = 4.5 Hz, 1H), 6.15 (d, *J* = 4.5 Hz, 1H), 6.96-6.98 (m 2H), 7.10-7.12 (m, 1H), 7.28-7.29 (m, 1H), 7.31-7.33 (m, 2H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): δ 69.1, 122.1, 125.1, 125.6, 126.4, 126.6, 126.9, 144.8, 147.7; IR (neat): 3234, 3108, 2957, 2923, 1438, 1417, 1362, 1291, 1274,1227, 1215, 1177, 1134, 1075, 1024 cm^{-1}; HRMS calcd for $C_9H_9OS_2$ $(MH)^+$: 197.0095, found 197.0095. The title compound was observed as a byproduct but not fully characterized in the work of Ravikanth, thus a full characterization is herein reported.[11]



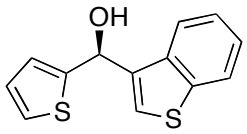
Benzofuran-3-yl(thiophen-3-yl)methanol (28). General Procedure A was applied to 3-benzofurancarboxaldehyde (36.5 mg, 0.25 mmol) and 3-bromothiophene (47 μL, 0.5 mmol). The crude product was purified by column chromatography on silica gel (hexanes/EtOAc : 95/5) to give **28** (18.0 mg, 60% yield) as a thick oil. The enantiomeric excess was determined by HPLC with a Chiralcel OD-H column (hexanes:2-propanol = 97.5:2.5, flow rate = 0.5 mL/min), t_r (1) = 76.2 min, t_r (2) = 83.9 min,

= +29.5 (*c* = 0.010, $CHCl_3$, 94% ee); ^1H NMR ($CDCl_3$, 500 MHz): δ 2.26 (d, *J* = 5.0 Hz, 1H), 6.16 (d, *J* = 4.0 Hz, 1H), 7.13-7.15 (m, 1H), 7.20-7.24 (m, 1H), 7.29-7.38 (m, 3H), 7.49-7.52 (m, 2H), 7.58 (s, 1H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz): δ 65.7, 111.6, 120.6, 122.2, 122.8, 123.4, 124.6, 126.0, 126.3, 126.4, 142.3, 143.7, 155.8; IR (DCM): 3944, 3756, 3691, 3594, 3054, 2987, 2831, 2685, 2521, 2410, 2305, 2126, 2054, 1579, 1551, 1421, 1265, 1135, 1105, 1075, 1010 cm^{-1}; HRMS calcd for $C_{13}H_{10}O_2S$ $(M)^+$: 230.0402, found 230.0406.



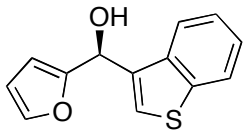
Benzo[*b*]thiophen-3-yl(phenyl)methanol (29). General Procedure B was applied to benzaldehyde (37.8 μL, 0.37 mmol) and 3-bromobenzothiophene (98 μL, 0.75 mmol). The crude product was purified by column chromatography on silica gel (hexanes/EtOAc : 95/5) to give **29** (57 mg, 65% yield) as a white solid. The enantiomeric excess was determined by HPLC with a Chiralcel AS-H column (hexanes:2-propanol = 98:2, flow rate = 0.5 mL/min), t_r (1) = 50.7 min, t_r (2) = 54.0 min,

= +7.0 (*c* = 0.020, $CHCl_3$, 88% ee); ^1H NMR ($CDCl_3$, 300 MHz): δ 2.26 (d, *J* = 4.2 Hz, 1H), 6.18 (d, *J* = 4.2 Hz, 1H), 7.27-7.39 (m, 6H), 7.45-7.48 (m, 2H), 7.71-7.75 (m, 1H), 7.83-7.86 (m, 1H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): δ 72.5, 122.9, 123.1, 124.1, 124.3, 124.7, 127.1, 128.3, 128.9, 137.5, 138.8, 141.2, 142.4; IR (neat): 3351, 3061, 3028, 2955, 2880, 1949, 1903, 1732, 1602, 1562, 1524, 1493, 1455, 1428, 1366, 1334, 1288, 1256, 1196, 1174, 1156, 1110, 1089, 1055, 1018, 1004 cm^{-1}; HRMS calcd for $C_{15}H_{11}S$ $(M\text{-}OH)^+$: 223.0581, found 223.0565. The data collected are in agreement with previously published results.[8]

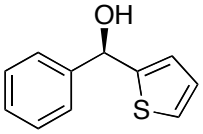


Benzo[*b*]thiophen-3-yl(thiophen-2-yl)methanol (30). General Procedure B was applied to 2-thiophenecarboxaldehyde (35 μL, 0.37 mmol) and 3-bromobenzothiophene (98 μL, 0.75 mmol). The crude product was purified by column chromatography on silica gel (hexanes/EtOAc : 90/10) to give **30** (64.5 mg, 70% yield) as an oil. The enantiomeric excess was determined by SFC with a Chiralcel AS-H column (2-propanol:CO_2:MeOH 30-80%, flow rate 2% min; oven temperature: 40 ºC, detection: 220 nm), t_r (1) = 5.87 min, t_r (2) = 6.39 min, = +9.8 (*c* = 0.017, $CHCl_3$, 81% ee); ^1H NMR ($CDCl_3$, 300 MHz): δ 2.47 (d, *J* = 4.2 Hz, 1H), 6.42 (dt, *J* = 0.9, 4.2 Hz, 1H), 6.97 (dd, *J* = 3.3, 4.8 Hz, 1H), 7.02 (ddd, *J* = 0.6, 1.2, 3.6 Hz, 1H), 7.30 (dd, *J* = 1.2, 4.8 Hz, 1H), 7.32-7.36 (m, 2H), 7.53 (d, *J* = 0.9 Hz, 1H), 7.74-7.77 (m, 1H), 7.86-7.89 (m, 1H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): δ 68.4, IR (neat): 3931, 3819, 3360, 3104, 3072, 2956, 2923, 2867, 2299, 1944, 1908, 1791, 1667,

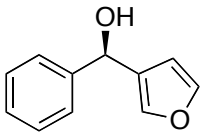
1609, 1562, 1524, 1459, 1428, 1366, 1290, 1263, 1228, 1174, 1137, 1120, 1088, 1053, 1036, 1020 cm^{-1}; HRMS calcd for $C_{13}H_9S_2$ $(M\text{-}OH)^+$: 229.0137, found 229.0146.



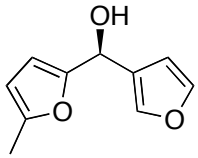
Benzo[*b*]thiophen-3-yl(furan-2-yl)methanol (31). General Procedure B was applied to furfural (31 μL, 0.37 mmol) and 3-bromobenzothiophene (98 μL, 0.75 mmol). The crude product was purified by column chromatography on silica gel (hexanes/EtOAc : 90/10) to give **31** (60.2 mg, 70% yield) as an oil. The enantiomeric excess was determined by HPLC with a Chiralcel AD-H column (hexanes:2-propanol = 97.5:2.5, flow rate = 0.5 mL/min), t_r (1) = 60.2 min, t_r (2) = 71.1 min, = +17.6 (*c* = 0.017, $CHCl_3$, 82% ee); ^1H NMR ($CDCl_3$, 300 MHz): δ 2.46 (d, *J* = 4.8 Hz, 1H), 6.20 (d, *J* = 4.8 Hz, 1H), 6.23 (dt, *J* = 0.6, 3.3 Hz, 1H), 6.35 (dd, *J* = 1.8, 3.3 Hz, 1H), 7.34-7.37 (m, 2H), 7.43 (dd, *J* = 0.6, 1.2 Hz, 1H), 7.50 (d, *J* = 0.9 Hz, 1H), 7.75-7.79 (m, 1H), 7.86-7.89 (m, 1H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): δ 66.2, 108.0, 110.6, 122.7, 123.1, 124.3, 124.4, 124.7, 136.0, 137.3, 141.1, 142.8, 154.9; IR (neat): 3937, 3418, 3115, 3060, 2924, 2634, 2303, 2082, 1945, 1910, 1713, 1562, 1523, 1501, 1426, 1428, 1346, 1264, 1151, 1095 cm^{-1}; HRMS calcd for $C_{13}H_9OS$ $(M\text{-}OH)^+$: 213.0374, found 213.0371.



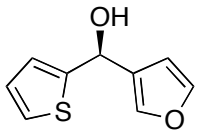
Phenyl(thiophen-2-yl)methanol (32). General Procedure B was applied to benzaldehyde (37.8 μL, 0.37 mmol) and 2-bromothiophene (72.5 μL, 0.75 mmol). The crude product was purified by column chromatography on silica gel (hexanes/EtOAc : 95/5) to give **32** (39.4 mg, 57% yield) as a white solid. The enantiomeric excess was determined by HPLC with a Chiralcel AS-H column (hexanes:2-propanol = 99:1, flow rate = 0.5 mL/min), t_r (1) = 65.0 min, t_r (2) = 71.9 min, = –9.0 (*c* = 0.030, $CHCl_3$, 90% ee); ^1H NMR ($CDCl_3$, 300 MHz): δ 2.41 (d, *J* = 4.2 Hz, 1H), 6.11 (d, *J* = 4.2 Hz, 1H), 6.93-6.95 (m, 1H), 6.98-7.01 (m, 1H), 7.31-7.33 (m, 1H), 7.36-7.45 (m, 3H), 7.49-7.52 (m, 2H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): δ 72.7, 125.2, 125.7, 126.6, 126.9, 128.3, 128.8, 143.2, 148.0; IR (DCM): 3944, 3757, 3691, 3589, 3054, 2987, 2831, 2685, 2521, 2410, 2305, 2126, 2054, 1602, 1551, 1421, 1265, 1156, 1016 cm^{-1}; HRMS calcd for $C_{13}H_{10}O_2S$ $(M\text{-}OH)^+$: 173.0425, found 173.0430. The data collected are in agreement with previously published results.[12]



Furan-3-yl(phenyl)methanol (33). General Procedure A was applied to benzaldehyde (37.8 μL, 0.37 mmol) and 3-bromofuran (67 μL, 0.75 mmol). The crude product was purified by column chromatography on silica gel (hexanes/EtOAc : 95/5) to give **33** (56.6 mg, 86% yield) as an oil. The enantiomeric excess was determined by HPLC with a Chiralcel AS-H column (hexanes:2-propanol = 99:1, flow rate = 0.5 mL/min), t_r (1) = 61.6 min, t_r (2) = 67.2 min, = –2.7 (*c* = 0.033, $CHCl_3$, 93% ee); ^1H NMR ($CDCl_3$, 500 MHz): δ 2.10 (d, *J* = 4.0 Hz, 1H), 5.80 (d, *J* = 4.0 Hz, 1H), 6.34-6.35 (m, 1H), 7.31-7.33 (m, 2H), 7.36-7.39 (m, 3H), 7.41-7.43 (m, 2H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz): δ 69.8, 109.4, 126.6, 128.1, 128.8, 129.2, 140.0, 143.2, 143.7; IR (neat): 3944, 3756, 3691, 3595, 3054, 2987, 2685, 2521, 2410, 2305, 2126, 2054, 1601, 1551, 1492, 1421, 1265, 1157, 1024 cm^{-1}; HRMS calcd for $C_{11}H_{10}O_2Na$ $(M+Na)^+$: 197.0578, found 197.0577. The data collected are in agreement with previously published results.[13]

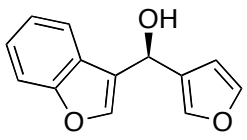


Furan-3-yl(5-methylfuran-2-yl)methanol (34). General Procedure B was applied to 5-methyl-2-furalaldehyde (37 μL, 0.37 mmol) and 3-bromofuran (67 μL, 0.75 mmol). The crude product was purified by column chromatography on silica gel (hexanes/EtOAc : 90/10) to give **34** (44.4 mg, 67% yield) as an oil. The enantiomeric excess was determined by HPLC with a Chiralcel OD-H column (hexanes:2-propanol = 99:1, flow rate = 0.5 mL/min), t_r (1) = 46.8 min, t_r (2) = 51.5 min, = +4.0 (*c* = 0.024, $CHCl_3$, 80% ee); ^1H NMR ($CDCl_3$, 300 MHz): δ 2.21 (d, *J* = 5.1 Hz, 1H), 2.30 (s, 3H), 5.73 (d, *J* = 5.1 Hz, 1H), 5.91-5.93 (m, 1H), 6.10-6.11 (m, 1H), 6.47-6.48 (m, 1H), 7.41-7.42 (m, 1H), 7.47-7.48 (m, 1H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): δ 13.8, 63.5, 106.4, 108.3, 109.6, 126.3, 140.3, 143.5, 152.6, 153.7; IR (neat): 3401, 3132, 2923, 1714, 1622, 1562, 1505, 1383, 1218, 1156, 1021 cm^{-1}; HRMS calcd for $C_{10}H_{10}O_3Na$ $(M+Na)^+$: 201.0528, found 201.0531.

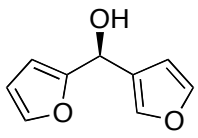


Furan-3-yl(thiophen-2-yl)methanol (35). General Procedure A was applied to 2-thiophenecarboxaldehyde (35 μL, 0.37 mmol) and 3-bromofuran (67 μL, 0.75 mmol). The crude product was purified by column chromatography on silica gel (hexanes/EtOAc : 95/5) to give **35** (44.4 mg, 60% yield) as an oil. The enantiomeric excess was determined by HPLC with a Chiralcel OD-H column (hexanes:2-propanol = 97:3, flow rate = 0.5 mL/min), t_r (1) = 40.4 min, t_r (2) = 47.1 min, = +18.2 (*c* = 0.032, $CHCl_3$, 99% ee); ^1H NMR ($CDCl_3$, 500 MHz): δ 2.27 (d, *J* = 5.0 Hz, 1H), 6.04 (d, *J* = 5.0 Hz, 1H), 6.44-6.45 (m, 1H),

6.97-6.99 (m, 1H), 7.01-7.02 (m, 1H), 7.30 (dd, J = 1.5, 5.0 Hz, 1H) 7.41 (t, J = 1.5 Hz, 1H), 7.45-7.46 (m, 1H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz): δ 65.8, 109.3, 125.0, 125.6, 126.9, 128.6, 140.1, 143,7, 147.4; IR (neat): 3410, 3108, 2924, 2855, 1759, 1672, 1614, 1507, 1416, 1264, 1230, 1156, 1022 cm^{-1}; HRMS calcd for $C_9H_7O_2S$ $(M-H)^+$: 179.0167, found 179.0169.

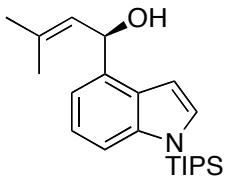


Benzofuran-3-yl(furan-3-yl)methanol (36). General Procedure A was applied to 3-benzofuranecarboxaldehyde (19 mg, 0.13 mmol) and 3-bromofuran (23.5 μL, 0.26 mmol). The crude product was purified by column chromatography on silica gel (hexanes/EtOAc : 95/5) to give **36** (21.9 mg, 79% yield) as an oil. The enantiomeric excess was determined by HPLC with a Chiralcel OD-H column (hexanes:2-propanol = 97.5:2.5, flow rate = 0.5 mL/min), t_r (1) = 54.6 min, t_r (2) = 69.5 min, = +12.9 (c = 0.010, $CHCl_3$, 94% ee); ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.11 (d, J = 4.5 Hz, 1H), 6.05 (d, J = 4.5 Hz, 1H), 6.44-6.45 (m, 1H), 7.21-7.34 (m, 2H), 7.42-7.43 (m, 1H), 7.48-7.52 (m, 2H), 7.54-7.57 (m, 1H), 7.59-7.60 (m, 1H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 75 MHz): δ 62.6, 109.4, 111.8, 120.8, 122.9, 123.3, 124.8, 126.2, 127.6, 140.2, 142.4, 143.9; IR (neat): 3367, 3148, 3060, 2962, 2923, 2874, 1901, 1783, 1702, 1596, 1579, 1502, 1477, 1452, 1333, 1276, 1216, 1184, 1158, 1103, 1075, 1024, 1009, 959 cm^{-1}; HRMS calcd for $C_{13}H_{10}O_3$ $(M)^+$: 214.0630, found 214.0622.

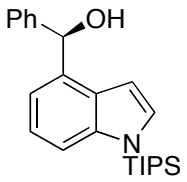


Furan-2-yl(furan-3-yl)methanol (37). General Procedure A was applied to furfural (31 mg, 0.37 mmol) and 3-bromofuran (67 μL, 0.75 mmol). The crude product was purified by column chromatography on silica gel (hexanes/EtOAc : 95/5) to give **37** (37.5 mg, 61% yield) as an oil. The enantiomeric excess was determined by HPLC with a Chiralcel OD-H column (hexanes:2-propanol = 97:3, flow rate = 0.5 mL/min), t_r (1) = 35.6 min, t_r (2) = 38.6 min, = –1.2 (c = 0.023, $CHCl_3$, 89% ee); ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.21 (d, J = 5.1 Hz, 1H), 5.80 (d, J = 5.0 Hz, 1H), 6.25 (dt, J = 0.9, 3.3 Hz, 1H), 6.35 (dd, J = 0.3, 3.3 Hz, 1H), 6.47 (dd, J = 0.3, 0.9 Hz, 1H), 7.42-7.43 (m, 2H), 7.47-7.48 (m, 1H), 7.48-7.52 (m, 2H), 7.54-7.57 (m, 1H), 7.59-7.60 (m, 1H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 75 MHz): δ 63.5, 107.3, 109.5, 110.5, 126.2, 140.3, 142.7, 143.6, 155.5; IR (neat): 3401, 3148, 2924, 1722, 1626, 1568, 1504, 1466, 1391, 1315, 1222, 1158, 1072, 1014 cm^{-1}; HRMS calcd for $C_9H_9O_3$ $(M-OH)^+$: 165.0538, found 165.0546.

General Procedure C. A nitrogen purged Schlenk flask was charged with 4-bromo-1-TIPS indole (106.5 mg, 0.3 mmol) and *t*-BuOMe (1 mL) and cooled to –78 °C. *t*-BuLi (0.18 mL, 1.7 M in pentane, 0.3 mmol) was then added dropwise and the solution was stirred for 1 h at this temperature. During this time a white precipitate formed. EtZnCl (39.6 mg, 0.3 mmol) was added to the reaction flask as a solid at –78 °C followed by toluene (3 mL). The heterogeneous solution was stirred at –78 °C for 30 min and then warmed at 0 °C. TEEDA (26 μL, 0.12 mmol) was added and the solution stirred for an additional 30 min. (–)-MIB (150 μL, 0.1 M solution in hexanes, 0.015 mmol) was added to the reaction flask and the solution was stirred for 5 min before 3-methyl-2-butenal (14.7 μL, 0.15 mmol, dissolved in 1.5 mL of toluene) was added over 1.5 h by syringe pump. The reaction mixture was stirred at 0 °C and monitored by TLC until completion (approximately 10 h). The reaction mixture was diluted with 3 mL EtOAc and quenched with water (5 mL). The organic layer was separated and the aqueous solution extracted with EtOAc (3 × 10 mL). The combined organic layer was washed with brine (5 mL), dried over $MgSO_4$, filtered, and the solvent was removed under reduced pressure. The crude product was purified by column chromatography on deactivated silica gel.



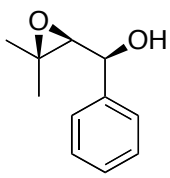
3-Methyl-1-(1-(triisopropylsilyl)-1*H*-indol-4-yl)but-2-en-1-ol (38). General Procedure C was applied to 3-methyl-2-butenal (14.5 μL, 0.15 mmol) and 4-bromo-1-TIPS indole (106.5 mg, 0.3 mmol). The crude product was purified by column chromatography on silica gel (hexanes/EtOAc : 95/5) to give **38** (37.1 mg, 65% yield) as an oil. The enantiomeric excess was determined by HPLC with a Chiralcel OD-H column (hexanes:2-propanol = 99:1, flow rate = 0.5 mL/min), t_r (1) = 44.2 min, t_r (2) = 47.3 min, = –61.5 (*c* = 0.049, $CHCl_3$, 90% ee); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 1.13 (d, *J* = 7.33 Hz, 18H), 1.69 (sept, *J* = 7.3 Hz, 1H), 1.75 (d, *J* = 1.3 Hz, 3H), 1.86 (d, *J* = 1.3 Hz, 3H), 1.88 (d, *J* = 3.0 Hz, 1H), 5.66 (d apparent quintet, 1.3 Hz, 8.8 Hz, 1H), 5.81 (d, *J* = 8.8 Hz, 1H) 6.76 (m, 1H), 7.12 (d, *J* = 8.0 Hz, 1H), 7.16 (m, 1H), 7.25 (m, 1H), 7.42 (d, *J* = 8.0 Hz, 1H); ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz): δ 12.8, 18.1, 18.2, 25.8, 70.2, 103.2, 113.2, 116.5, 121.2, 127.2, 128.8, 130.9, 135.1, 135.7, 141.2; IR (neat): 3392, 2948, 2868, 1669, 1599, 1514, 1464, 1426, 1384, 1279, 1204, 1148, 1123, 1071 cm^{-1}; HRMS calcd for $C_{22}H_{34}NSi$ $(M\text{-}OH)^+$: 340.2451, found 340.2461.



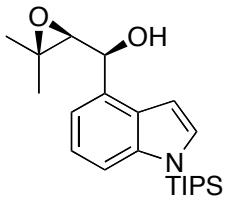
Phenyl(1-(triisopropylsilyl)-1*H*-indol-4-yl)methanol (39). General Procedure C was applied to benzaldehyde (15 μL, 0.15 mmol) and 4-bromo-1-TIPS indole (106.5 mg, 0.3 mmol). The crude product was purified by column chromatography on silica gel (hexanes/EtOAc : 95/5) to give **39** (34.1 mg, 60% yield) as an oil. The enantiomeric excess was determined by HPLC with a Chiralcel OD-H column (hexanes:2-propanol = 99:1, flow rate = 0.5 mL/min), t_r (1) = 79.9 min, t_r (2) = 89.9 min, = +24.4 (*c* = 0.047, $CHCl_3$, 90% ee); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 1.12 (d, *J* = 7.1 Hz, 18H), 1.68 (sept, *J* = 7.1 Hz, 3H), 2.30 (d, *J* = 3.6 Hz, 1H), 6.24 (d, *J* = 3.0 Hz, 1H), 6.68 (d, *J* = 3.0 Hz, 1H), 7.10 (m, 2H), 7.23 (m, 2H), 7.32 (t, *J* = 7.1 Hz, 2H), 7.44 (d, *J* = 7.1 Hz, 1H), 7.48 (d, *J* = 7.9 Hz, 2H); ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz): δ 12.7, 18.1, 74.9, 103.0, 113.5, 117.5, 121.2, 126.6, 127.1, 128.2, 129.3, 131.2, 135.3, 141.1, 143.5; IR (neat): 3402, 3060, 3028, 2948, 2868, 2728, 1946, 1892, 1807, 1715, 1601, 1582, 1514, 1493, 1478, 1463, 1453, 1427, 1391, 1368, 1279, 1203, 1148, 1123, 1071 cm^{-1}; HRMS calcd for $C_{24}H_{32}NSi$ $(M\text{-}OH)^+$: 362.2304, found 362.2305.

General Procedure D. A nitrogen purged Schlenk flask was charged with 4-bromo-1-TIPS indole (106.5 mg, 0.3 mmol) and *t*-BuOMe (1 mL) and cooled to –78 °C. Alkyl lithium (*n*-BuLi or *t*-BuLi, see below, 0.3 mmol) was added dropwise and the solution was stirred for 1 h. EtZnCl (39.6 mg, 0.3 mmol) was delivered to the reaction flask as a solid at –78 °C. Toluene (3 mL) was next added giving a heterogenous mixture. The solution was warmed to –10 °C and stirred at that temperature for 3 h. Then TEEDA (26 μL, 0.12 mmol) was added and the solution was stirred for an additional 30 min. (–)-MIB (150 μL, 0.1 M solution in hexanes, 0.015 mmol) was added to the reaction flask and the solution was stirred for 5 min before 3-methyl-2-butenal (14.7 μL, 0.15 mmol, dissolved in 1.5 mL of toluene) was delivered over 1.5 h by syringe pump. The reaction mixture was stirred at –10 °C and monitored by TLC until completion. Upon completion of the reaction the solution was warmed to 0 ºC. $ZnEt_2$ (0.15 mL, 1 M in hexanes, 0.15 mmol) was added followed by TBHP (0.14 mL, 5.5 M in decane, 0.77 mmol). After stirring for 5 min $Ti(O\text{-}i\text{Pr})_4$ (30 μL, 1 M in hexanes, 0.03 mmol) was added and the reaction stirred until the epoxidation reached completion (approximately 3 h). After the reaction was complete by TLC analysis, it was diluted with 3 mL EtOAc and quenched with water (5 mL). The organic layer was separated and the aqueous solution extracted with EtOAc (3 × 10 mL). The combined organic layer was washed with brine (5 mL), dried over $MgSO_4$, filtered, and the volatile

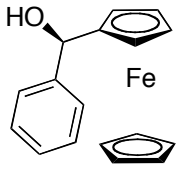
materials were removed under reduced pressure. The crude product was purified by column chromatography on deactivated silica gel.



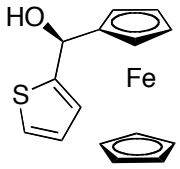
(3,3-Dimethyloxiran-2-yl)(phenyl)methanol (40). General Procedure D was applied to 3-methyl-2-butenal (24.2 μL, 0.25 mmol), bromobenzene (53.0 μL, 0.5 mmol) and *n*-BuLi (0.2 mL, 2.5 M in hexanes, 0.5 mmol). The crude product was purified by column chromatography on silica gel (hexanes/EtOAc : 90/10) to give **40** (30.3 mg, 67.8% yield) as an oil. The diastereomeric ratio was determined by ^{1}H NMR of the crude product (dr > 20:1); = –23.1 (*c* = 0.043, $CHCl_3$, 90% ee); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 1.29 (s, 3H), 1.43 (s, 3H), 2.60 (d, *J* = 2.9 Hz, 1H), 2.97 (d, *J* = 8.1 Hz, 1H), 4.55 (dd, *J* = 2.9, 8.1 Hz, 1H), 7.29-7.34 (m, 1H), 7.36-7.39 (m, 4H); ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz): δ 19.6, 24.8, 60.0, 68.0, 72.6, 125.9, 128.0, 128.6, 140.1; IR (neat): 3417, 3063, 3032, 2964, 2927, 2741, 1955, 1888, 1812, 1764, 1634, 1604, 1586, 1494, 1455, 1427, 1380, 1323, 1282, 1248, 1193, 1130, 1075 cm^{-1}; HRMS calcd for $C_{11}H_{14}ONa$ $(M+Na)^+$: 201.0891, found 201.0885.



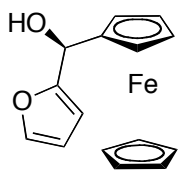
(3,3-Dimethyloxiran-2-yl)(1-(triisopropylsilyl)-1*H*-indol-4-yl)methanol (41). General Procedure D was applied to 3-methyl-2-butenal (14.5 μL, 0.15 mmol), 4-bromo-1-TIPS indole (106.5 mg, 0.3 mmol) and *t*-BuLi (0.18 mL, 1.7 M in pentane, 0.3 mmol). The crude product was purified by column chromatography on silica gel (hexanes/EtOAc : 90/10) to give **41** (36.6 mg, 64.9% yield) as an oil. The diastereomeric ratio was determined by ^{1}H NMR of the crude product (dr > 20:1); = –6.1 (*c* = 0.041, $CHCl_3$, 90% ee); 1.13 (d, *J* = 7.6 Hz, 18H), 1.29 (s, 3H), 1.43 (s, 3H), 1.69 (sept, *J* = 7.6 Hz, 3H), 2.48 (d, *J* = 3.0 Hz, 1H), 3.31 (d, *J* = 8.1 Hz, 1H), 4.89 (dd, *J* = 3.0, 8.1 Hz, 1H), 6.80 (d, *J* = 3.3 Hz, 1H), 7.10-7.14 (m, 1H), 7.30 (d, *J* = 3.3 Hz, 1H), 7.47 (dd, *J* = 2.8, 6.9 Hz, 1H); ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz): δ 12.8, 18.0, 19.5, 24.8, 60.1, 67.3, 72.2, 103.3, 113.9, 117.6, 121.1, 129.2, 131.5, 141.3; IR (neat): 3445, 3135, 3081, 3048, 2948, 2892, 2868, 2760, 2729, 2625, 2559, 2361, 2343, 2246, 2150, 2074, 1892, 1824, 1740, 1675, 1599, 1514, 1463, 1428, 1378, 1345, 1323, 1280, 1248, 1209, 1150, 1124, 1096, 1073 cm^{-1}; HRMS calcd for $C_{22}H_{35}NO_2NaSi$ $(M+Na)^+$: 396.2335, found 396.2321.



Phenyl(ferrocenyl)methanol (44). General Procedure A was applied to benzaldehyde (19 μL, 0.188 mmol), bromoferrocene (99 mg, 0.37 mmol) and Chan's ligand **L2** (94 μL, 0.1 M in toluene, 0.0094 mmol). The crude product was purified by column chromatography on silica gel (hexanes/EtOAc : 95/5) to give **44** (47 mg, 86% yield) as a red solid. The enantiomeric excess was determined by HPLC with a Chiralcel AD-H column (hexanes:2-propanol = 93:7, flow rate = 0.5 mL/min), t_r (1) = 26.7 min, t_r (2) = 45.2 min, = –94.4 (*c* = 0.016, $CHCl_3$, 98% ee); ^1H NMR ($CDCl_3$, 360 MHz): δ 2.42 (d, *J* = 3.24 Hz, 1H), 4.22 (s, 9H), 5.46 (d, *J* = 3.24 Hz, 1H), 7.30-7.40 (m, 5H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz): δ 66.2, 67.7, 68.3, 68.4, 68.7, 72.3, 94.5, 126.4, 127.7, 128.4, 143.5; IR (DCM): 3944, 3757, 3691, 3584, 3054, 2987, 2685, 2521, 2410, 2305, 2126, 2054, 1602, 1550, 1493, 1421, 1383, 1265, 1172, 1105, 1079, 1045, 1016, 1002, 896 cm^{-1}; HRMS calcd for $C_{17}H_{16}O_1Fe$ $(M)^+$: 292.0550, found 292.0559. The data collected are in agreement with previously published results.[3,14,15]



Thienyl(ferrocenyl)methanol (43). General Procedure A was applied to 2-thiophenecarboxaldehyde (17.5 μL, 0.188 mmol), bromoferrocene (99 mg, 0.37 mmol) and Chan's ligand **L2** (94 μL, 0.1 M in toluene, 0.0094 mmol). The crude product was purified by column chromatography on silica gel (hexanes/EtOAc : 95/5) to give **43** (52.9 mg, 95% yield) as a red solid. The enantiomeric excess was determined by HPLC with a Chiralcel AD-H column (hexanes:2-propanol = 95:5, flow rate = 0.5 mL/min), t_r (1) = 42.7 min, t_r (2) = 51.0 min, = –73.3 (*c* = 0.023, $CHCl_3$, 98% ee); ^1H NMR ($CDCl_3$, 500 MHz): δ 2.55 (d, *J* = 3.5 Hz, 1H), 4.25 (s, 9H), 5.73 (d, *J* = 3.5 Hz, 1H), 6.94-6.95 (m, 2H), 7.24-7.25 (m, 1H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz): δ 66.5, 67.5, 68.4, 68.5, 68.6, 68.9, 93.6, 124.6, 124.9, 126.5 147.5; IR (neat): 3928, 3542, 3435, 3096, 2972, 2927, 2867, 2253, 2054, 1666, 1532, 1437, 1411, 1393, 1292, 1260, 1231, 1191, 1158, 1106, 1041, 1002 cm^{-1}; HRMS calcd for $C_{15}H_{14}O_1SFe$ $(M)^+$: 298.0115, found 298.0104. The data collected are in agreement with previously published results.[15]



Furanyl(ferrocenyl)methanol (42). General Procedure A was applied to furfural (15.5 μL, 0.188 mmol), bromoferrocene (99 mg, 0.37 mmol) and Chan's ligand **L2** (94 μL, 0.1 M in toluene, 0.0094 mmol). The crude product was purified by column chromatography on silica gel (hexanes/EtOAc : 95/5) to give **42** (50 mg, 95% yield) as a yellow oil. The enantiomeric excess was determined by HPLC with a Chiralcel OD-H column (hexanes:2-propanol = 95:5, flow rate = 0.5 mL/min), t_r (1) = 37.6 min, t_r (2) = 45.2 min, = –30.0 (*c* = 0.022, $CHCl_3$, 96% ee); ^1H NMR ($CDCl_3$, 500 MHz): δ 2.36 (d, *J* = 5.1 Hz, 1H), 4.18 (s, 7H), 4.26-4.29 (m, 2H), 5.48 (d, *J* = 5.1 Hz, 1H), 6.23-6.24 (m, 1H), 6.33-6.35 (m, 1H), 6.40-6.41 (m, 1H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): δ 66.3, 67.2, 67.5, 68.4, 68.5, 68.9, 90.7, 106.7, 110.3, 142.1, 155.8; IR (neat): 3928, 3401, 3095, 2920, 1637, 1504, 1467, 1411, 1301, 1211, 1170, 1147, 1105, 1043, 1002 cm^{-1}; HRMS calcd for $C_{15}H_{14}O_2NaFe$ $(M+Na)^+$: 305.0241, found 305.0244. The data collected are in agreement with previously published results.[15,16]

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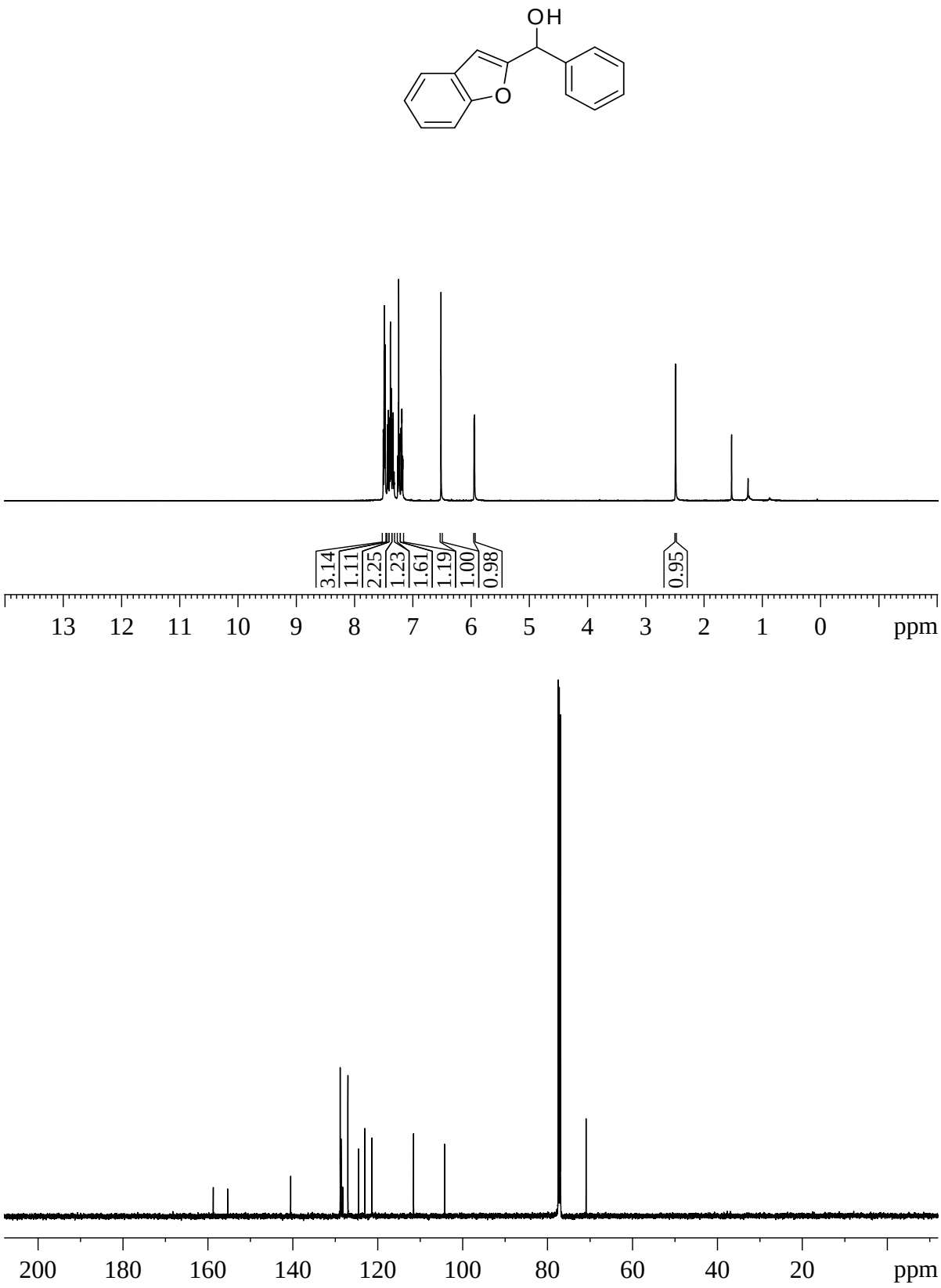
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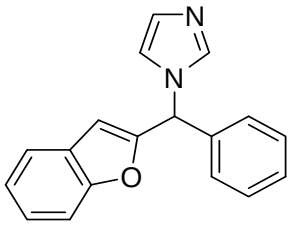
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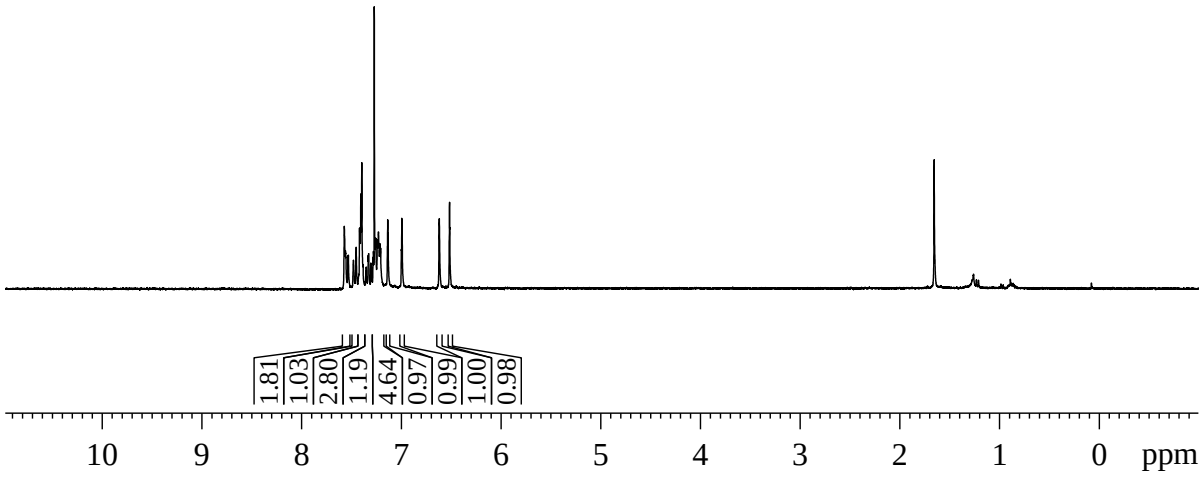
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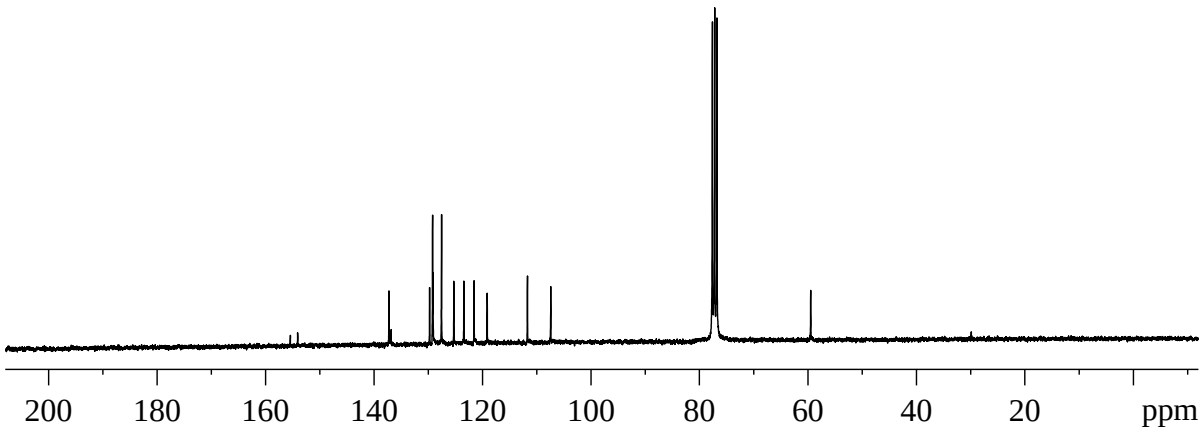
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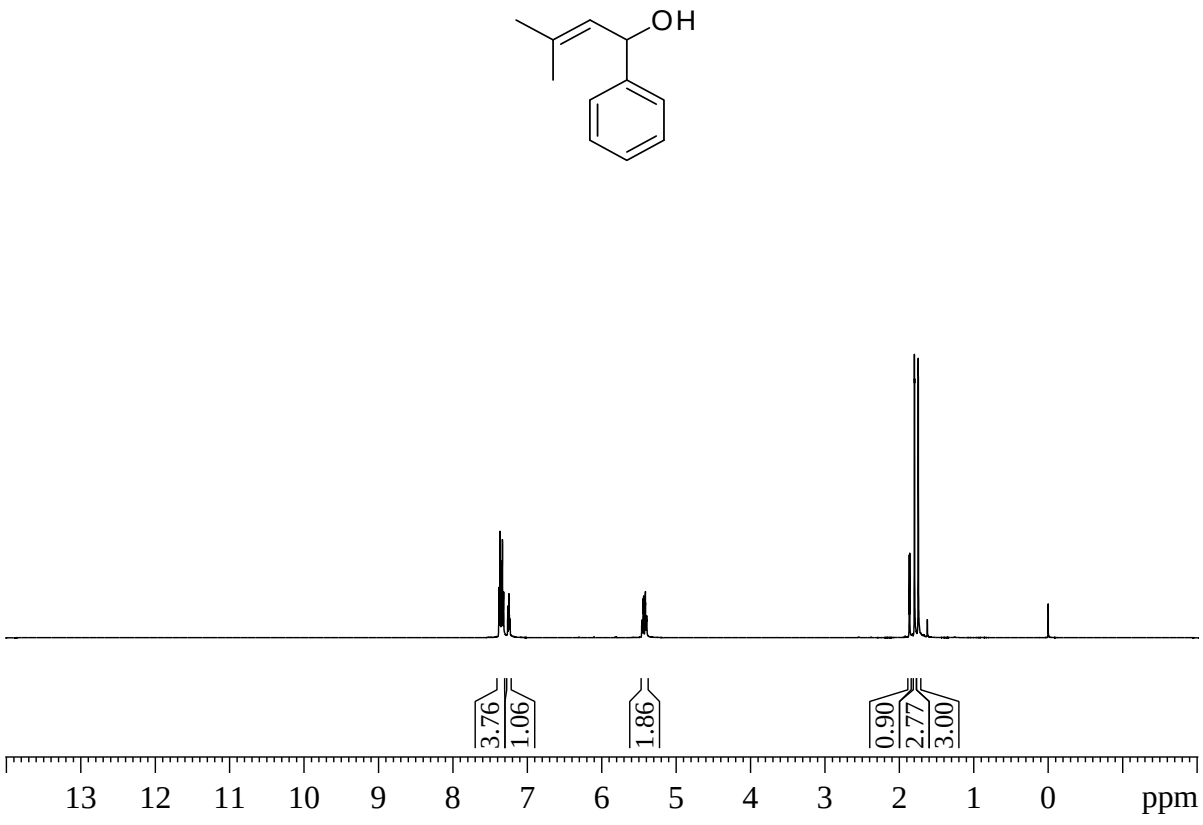
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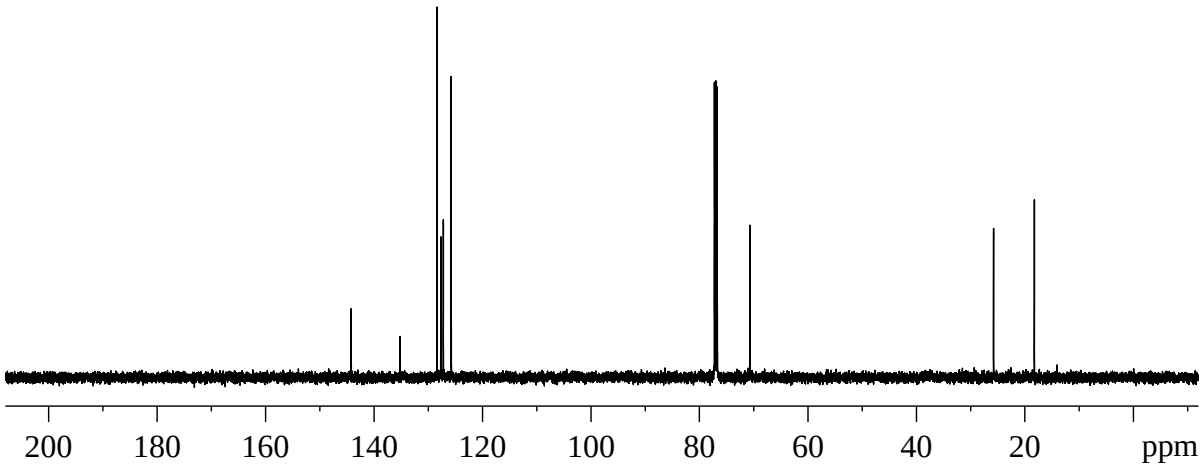
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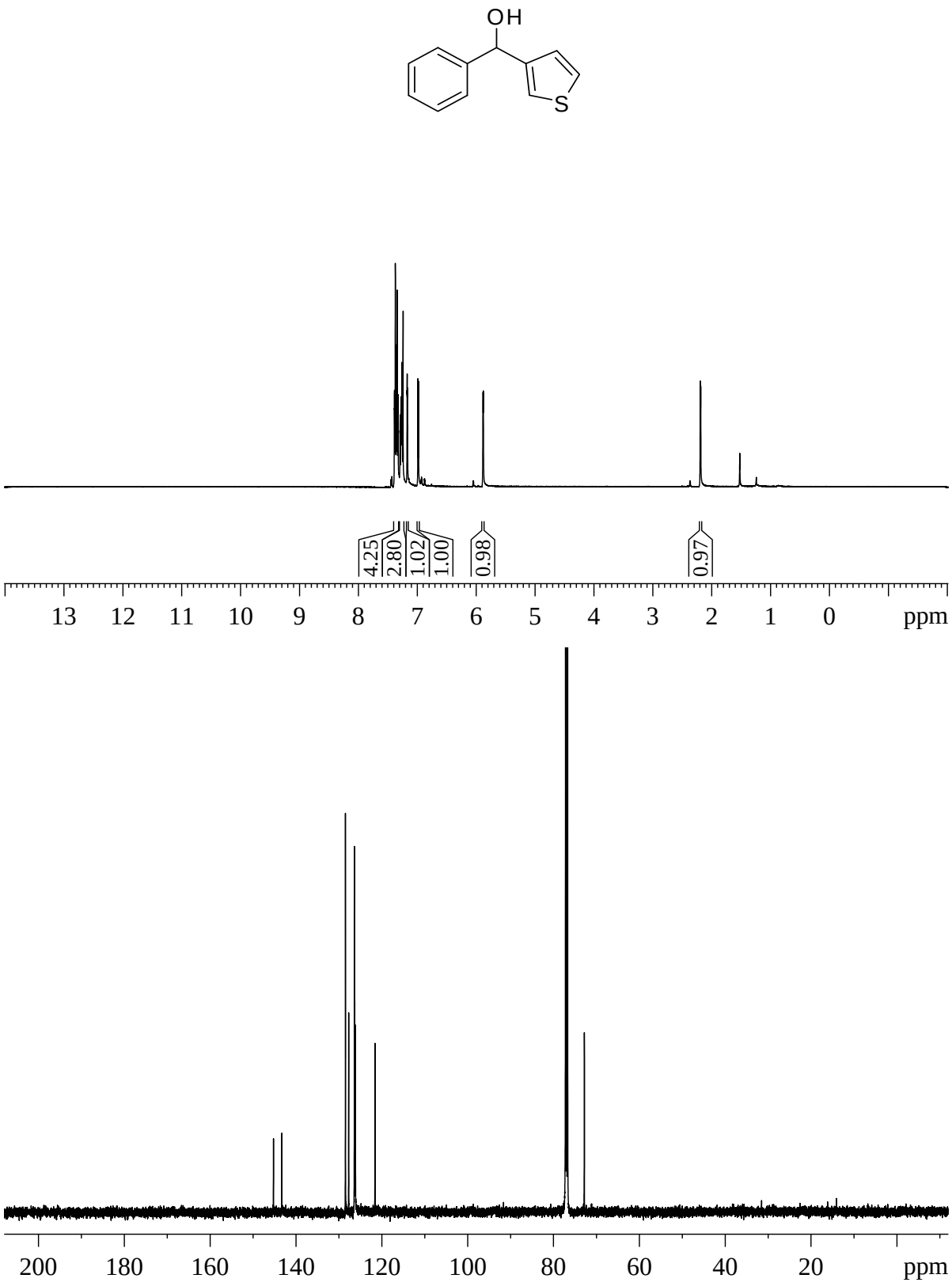
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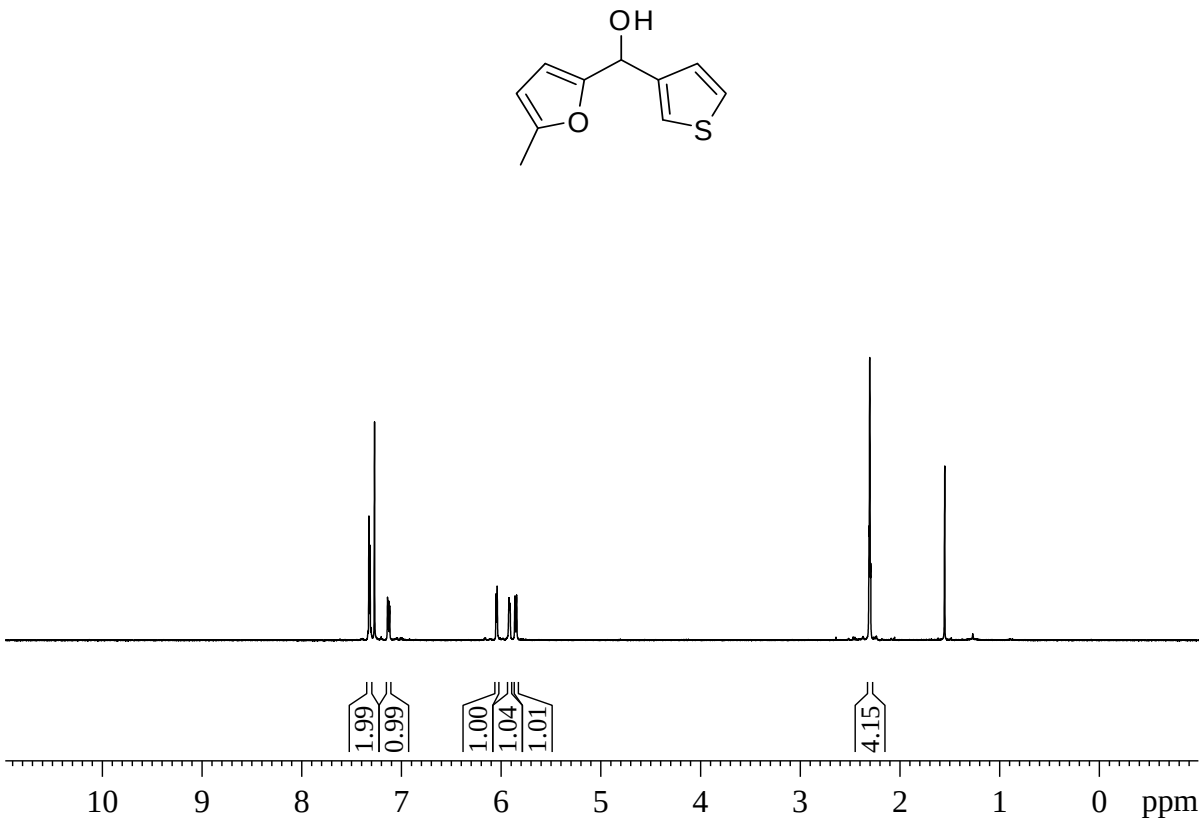
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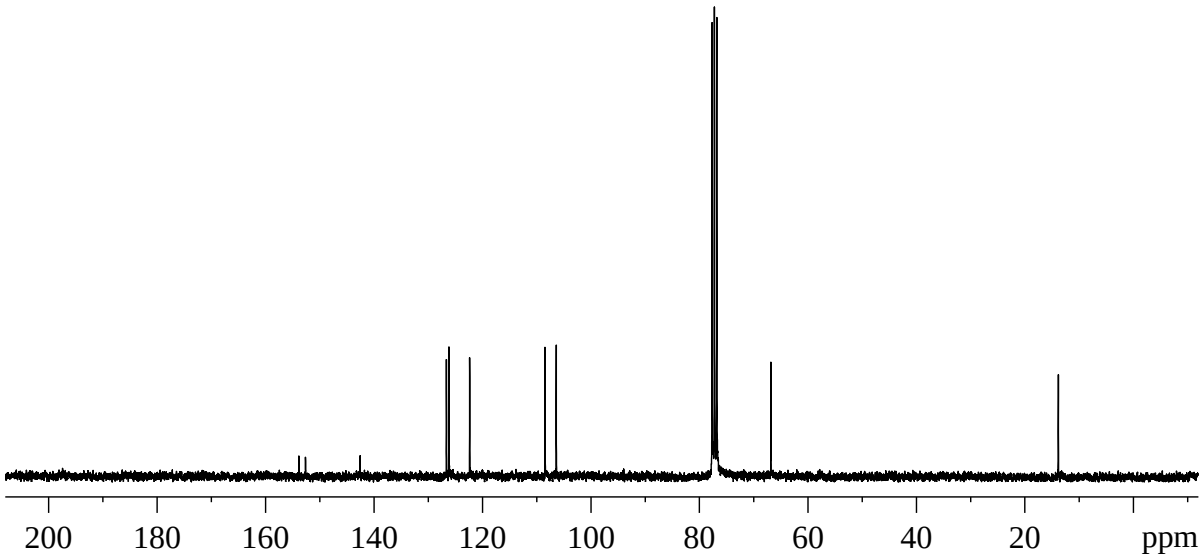
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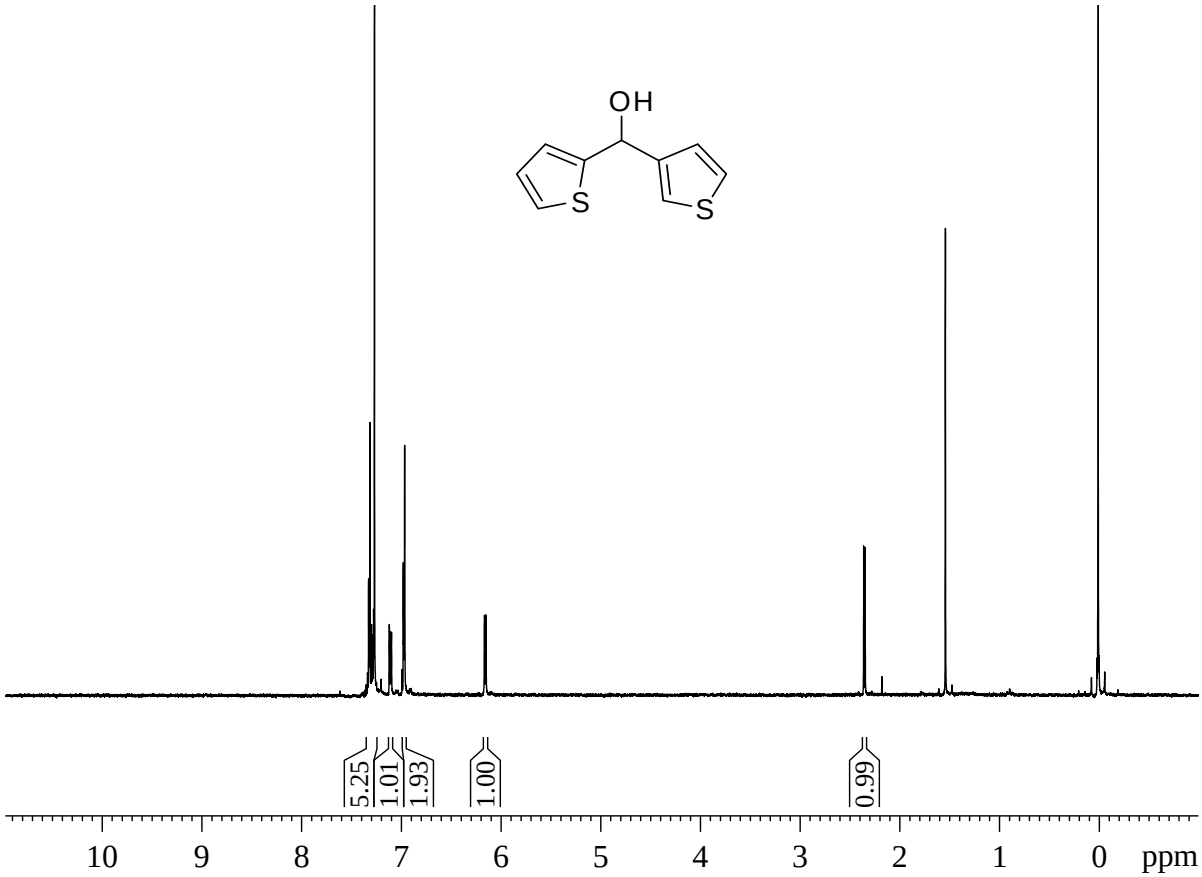
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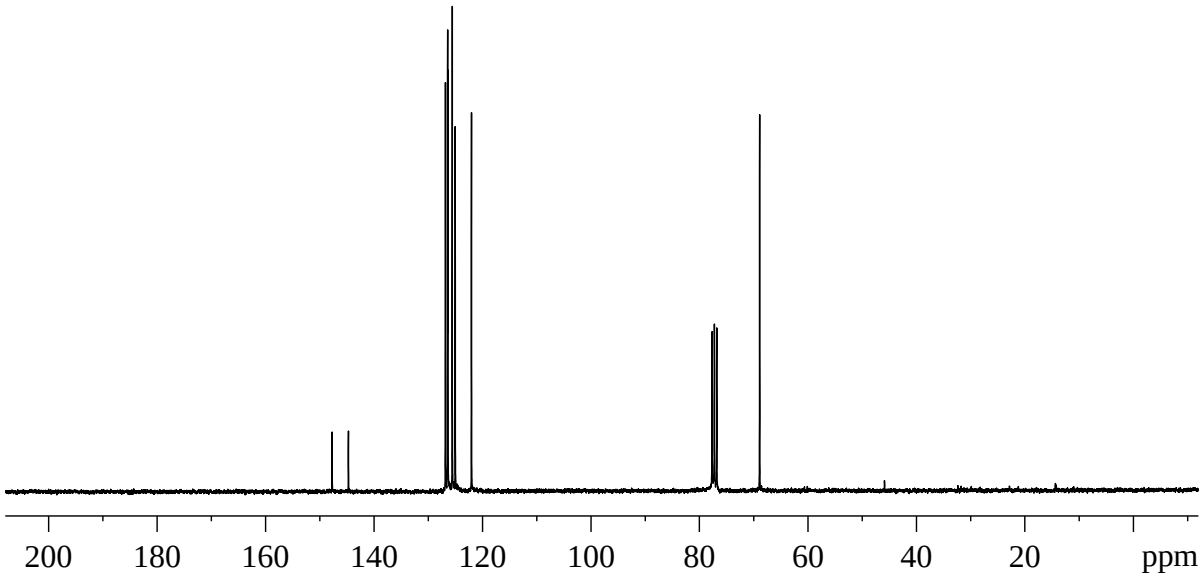
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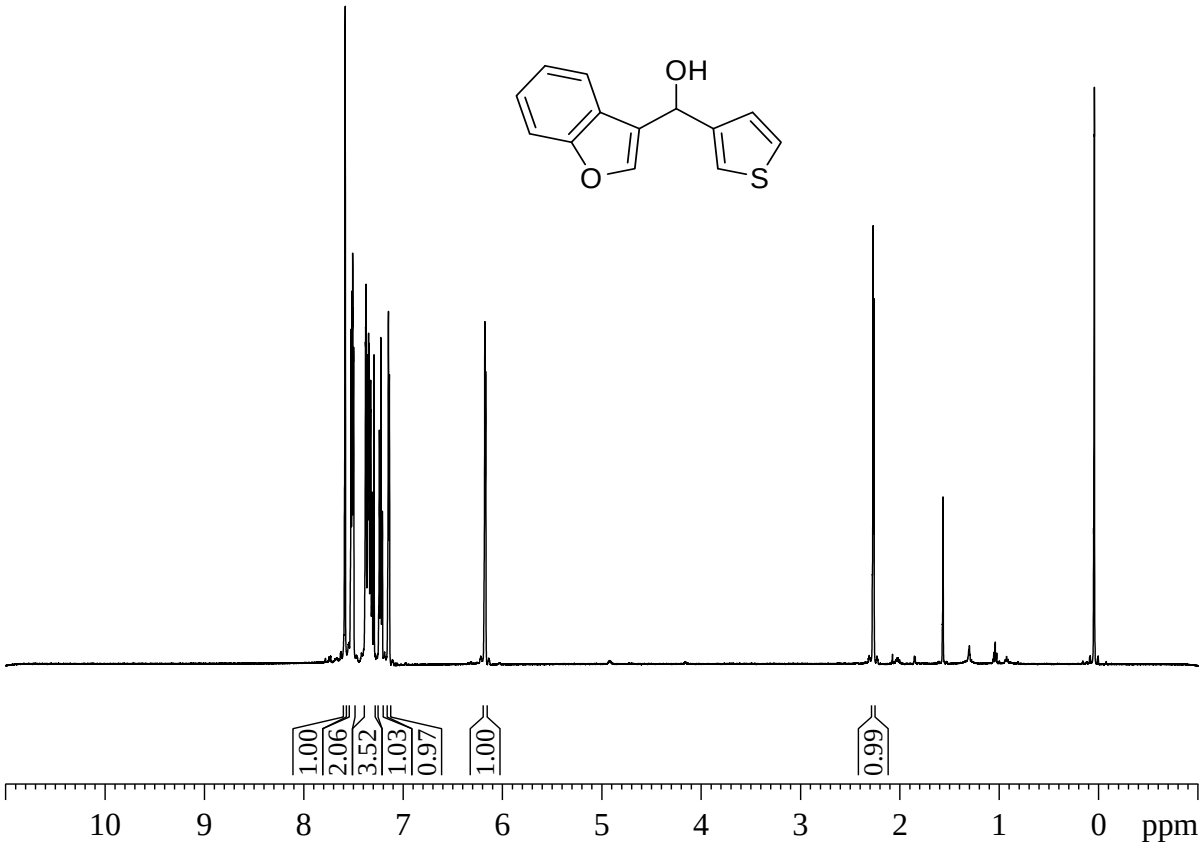
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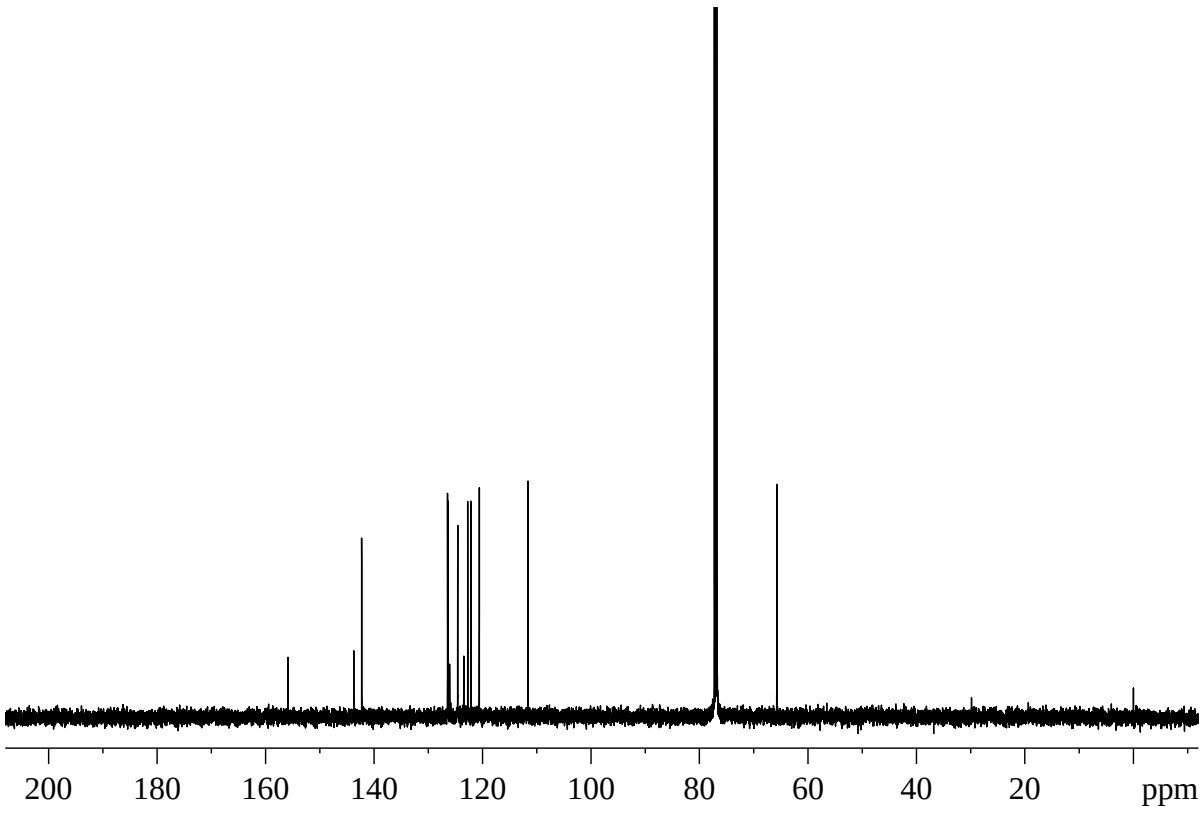
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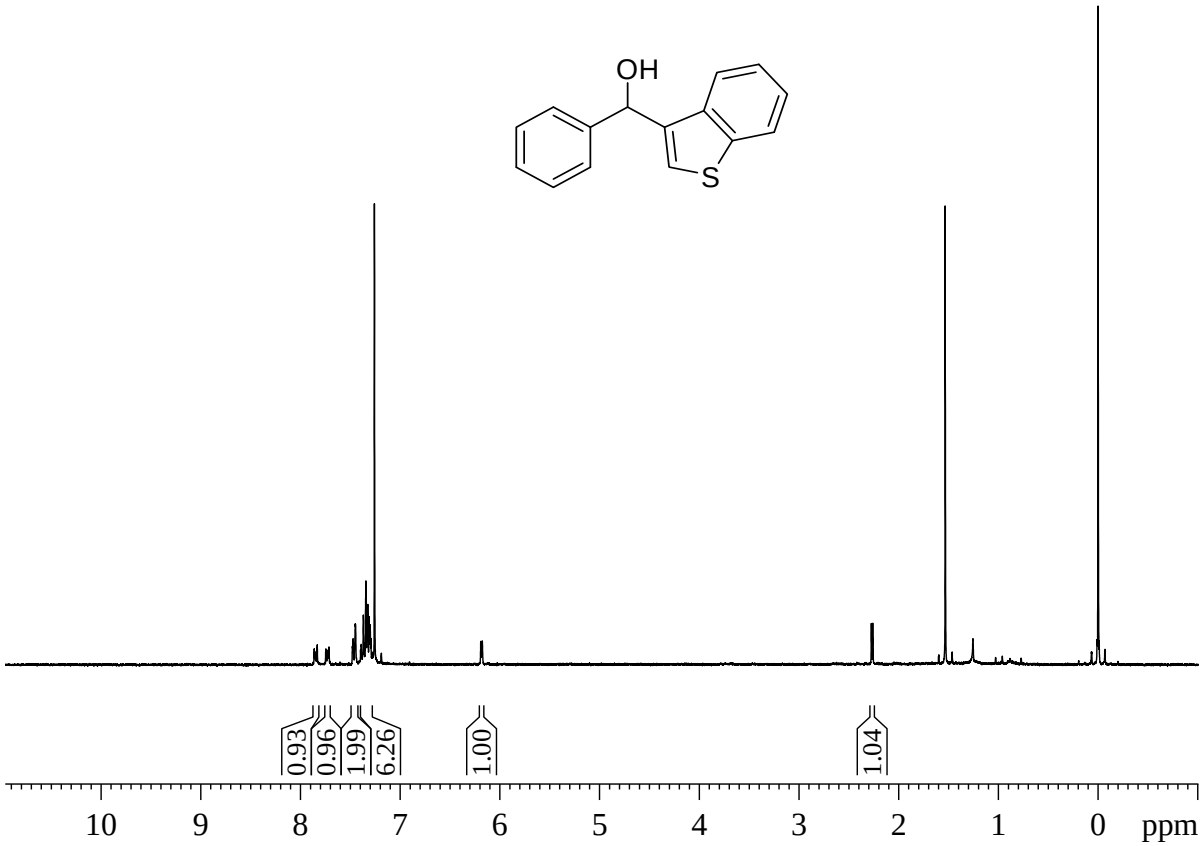
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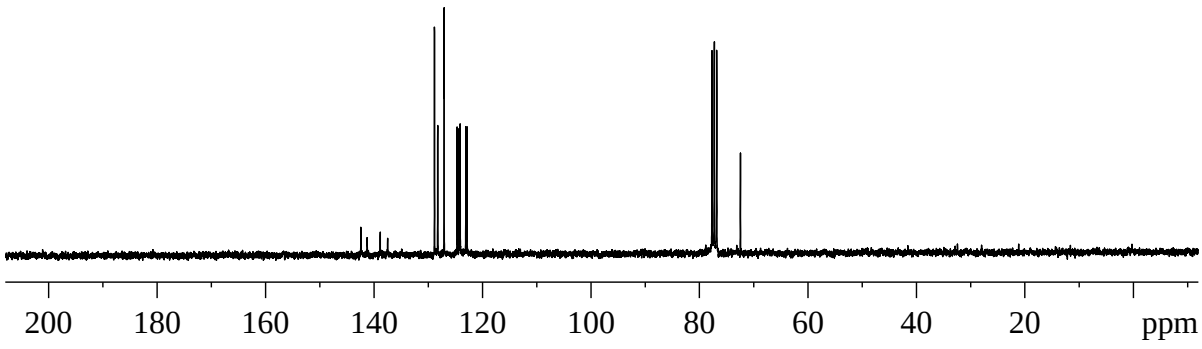
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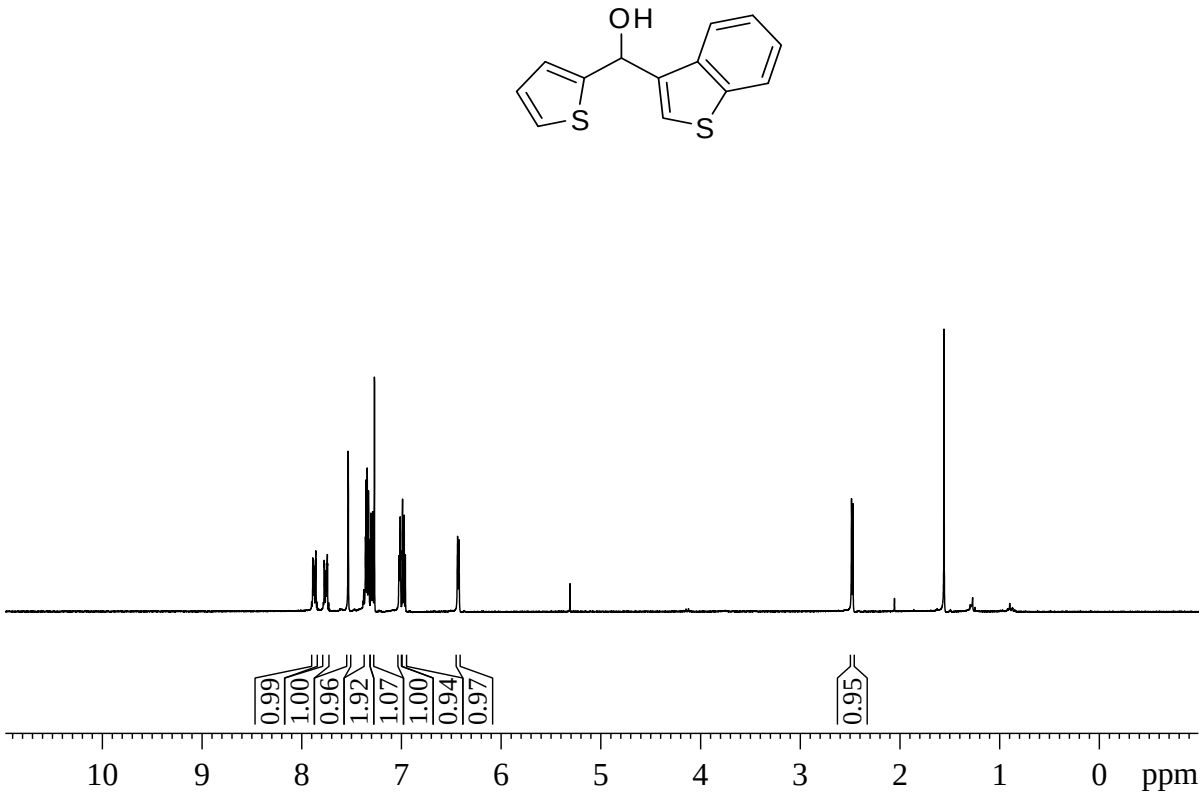
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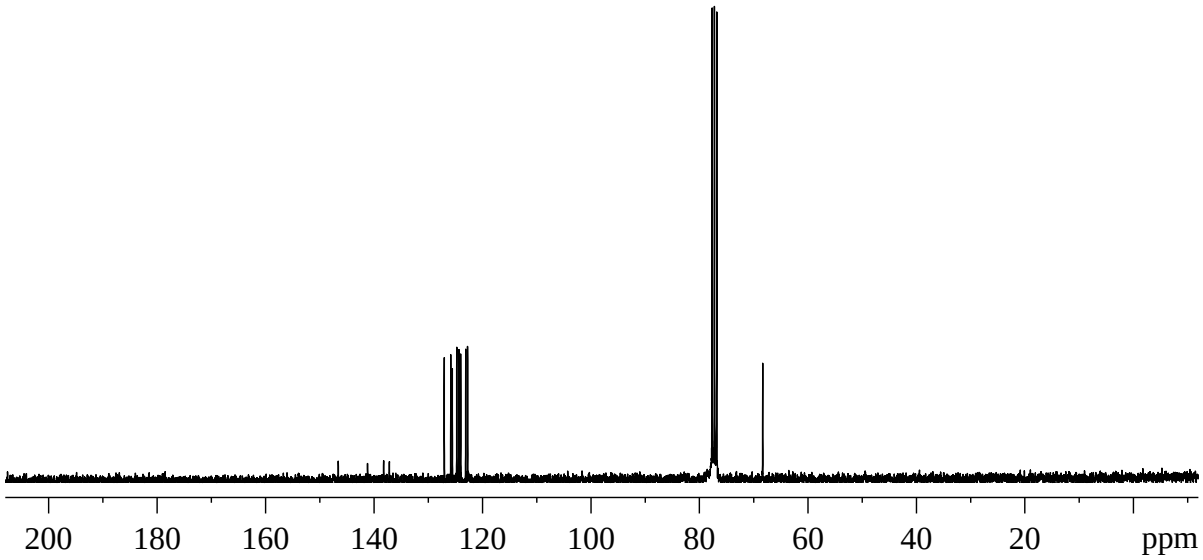
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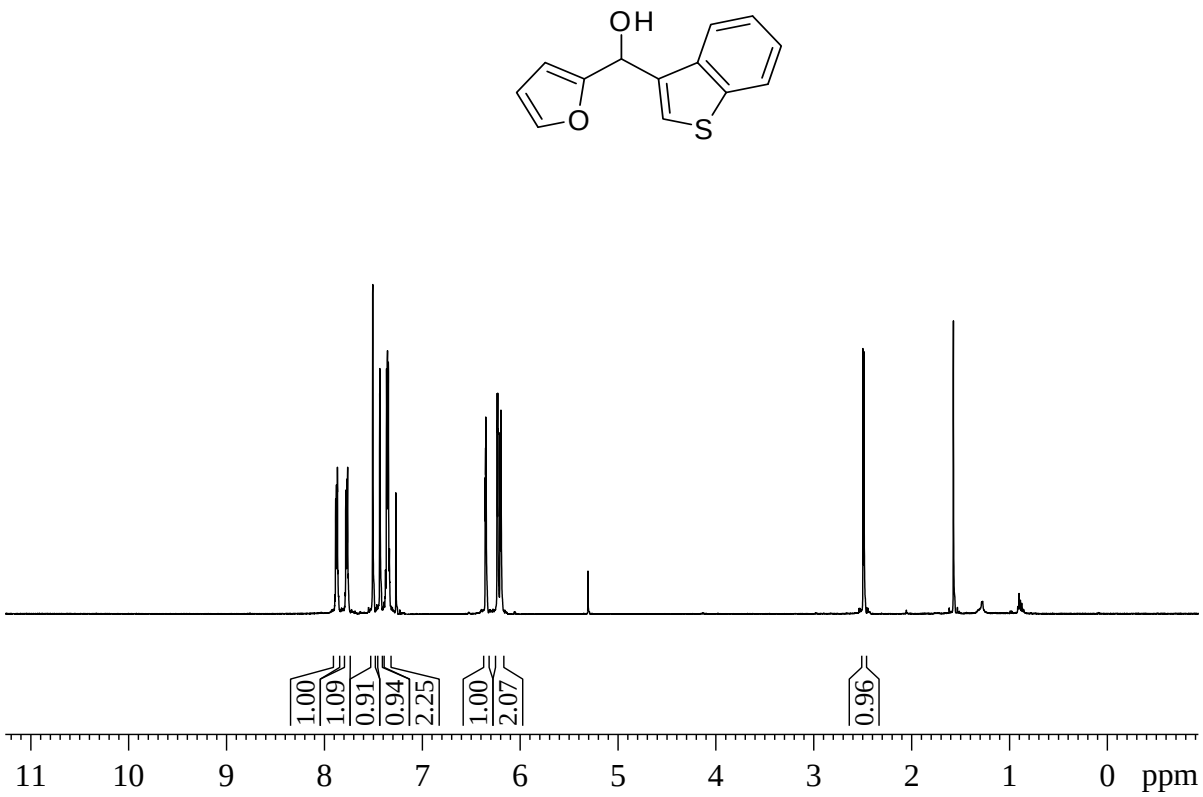
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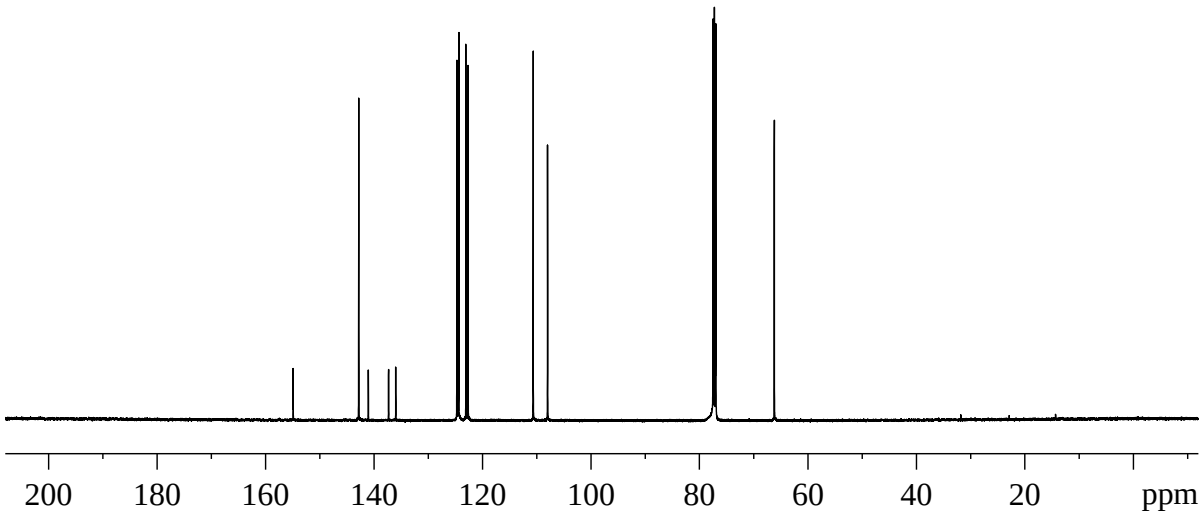
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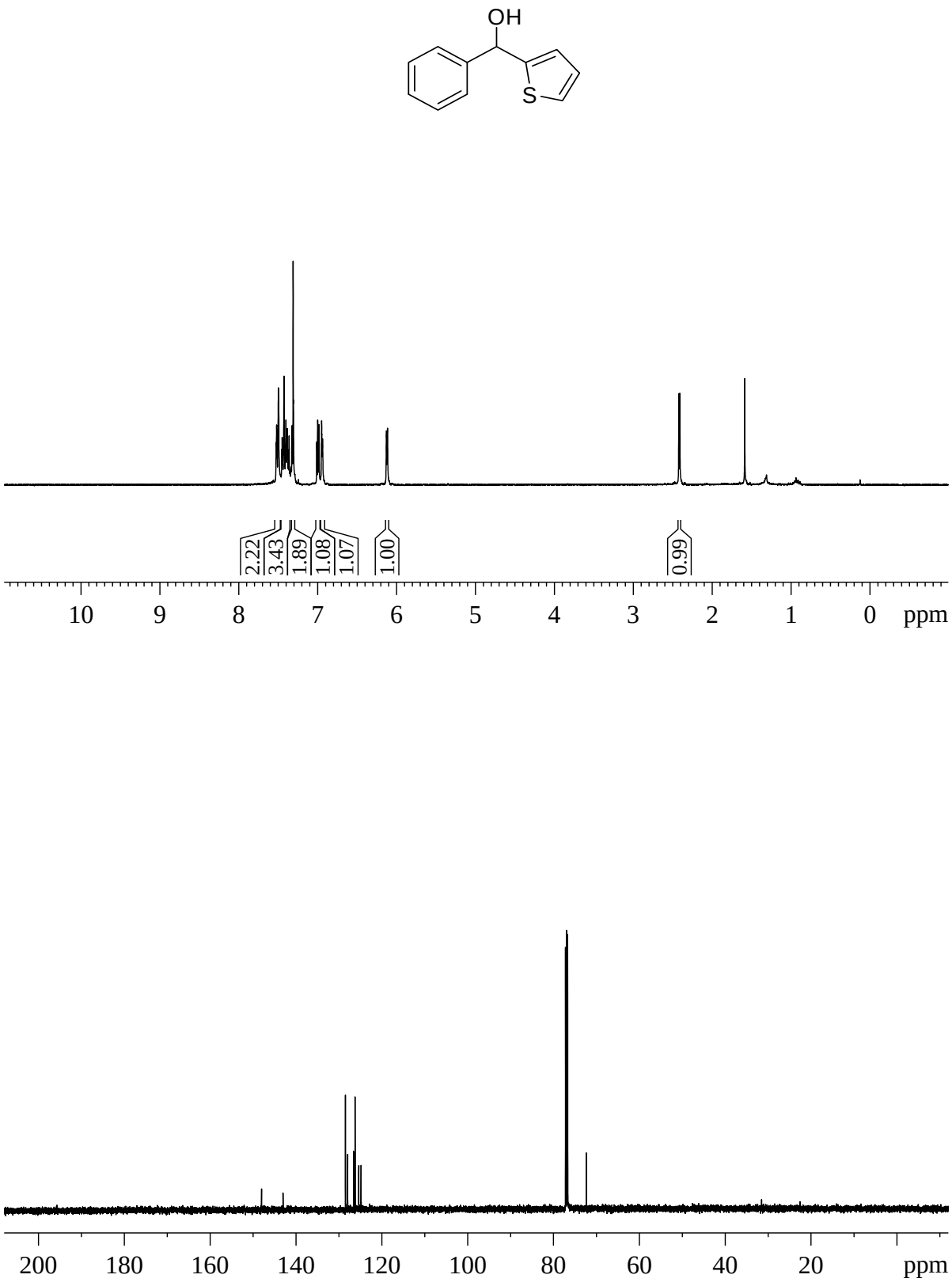
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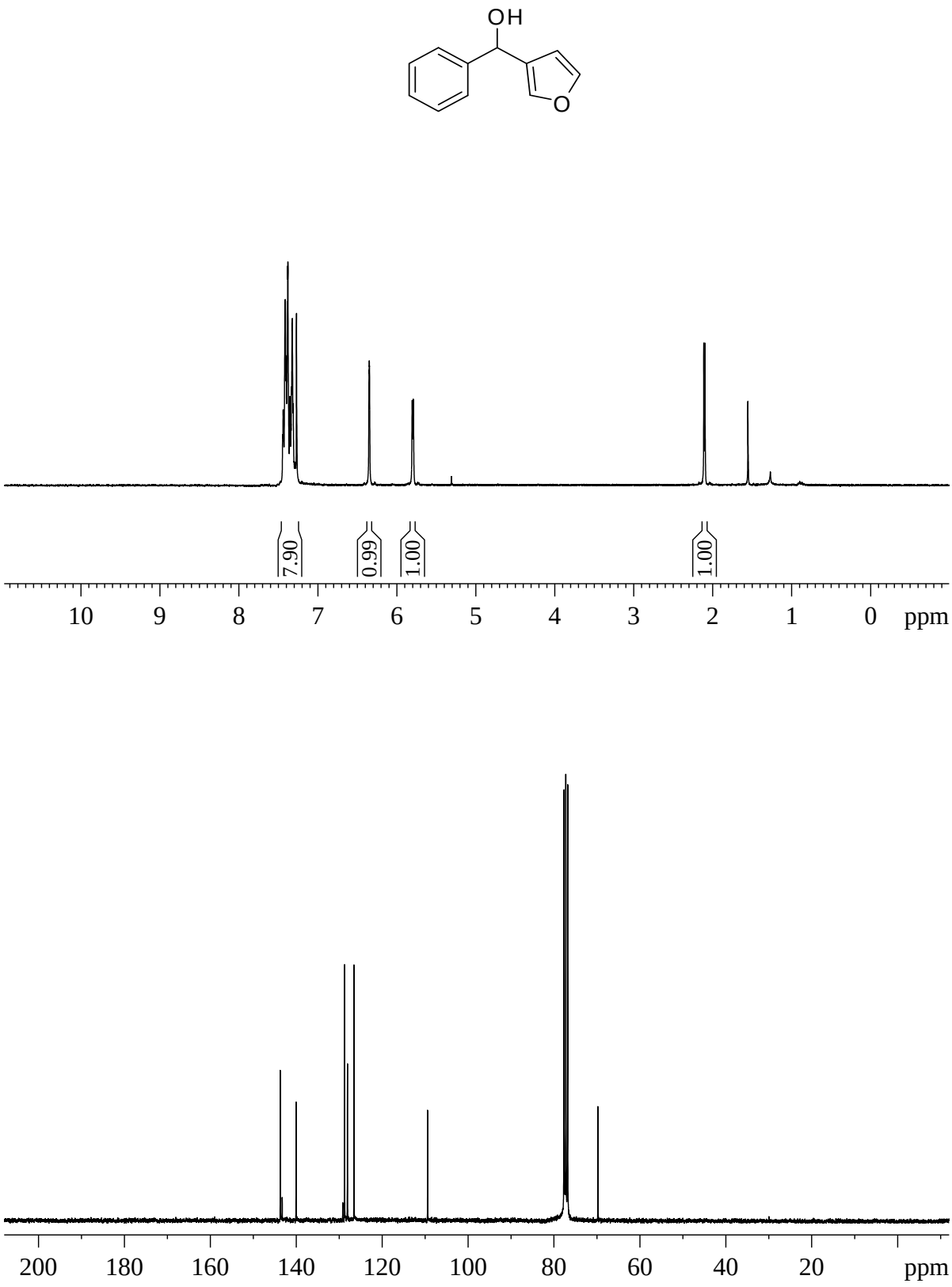
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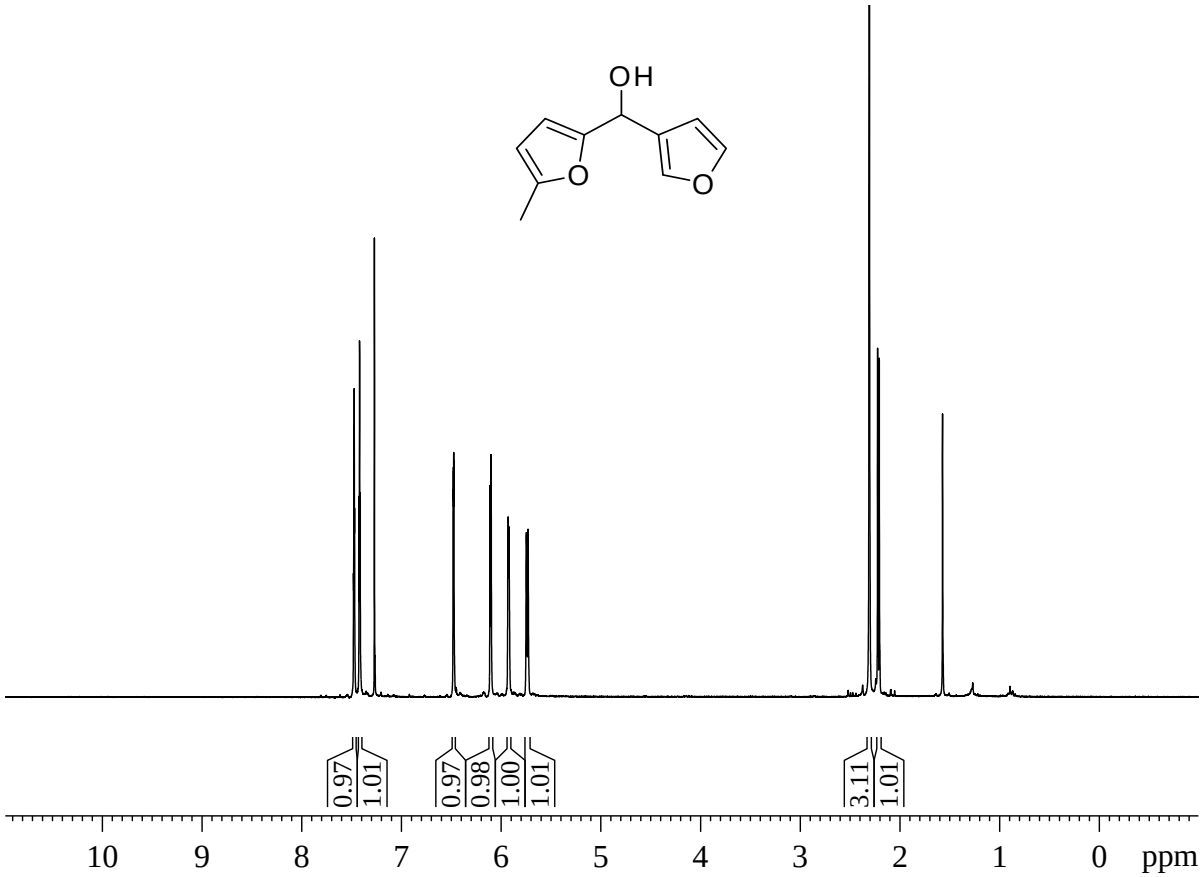
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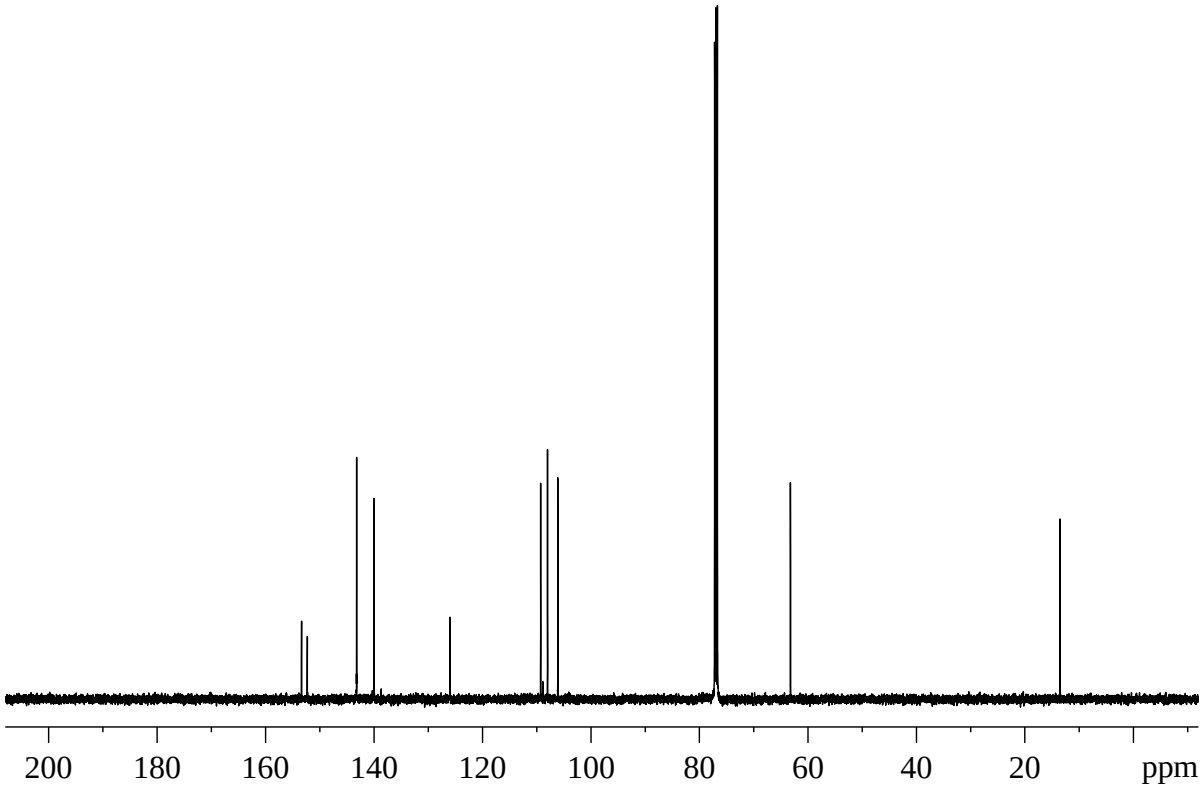
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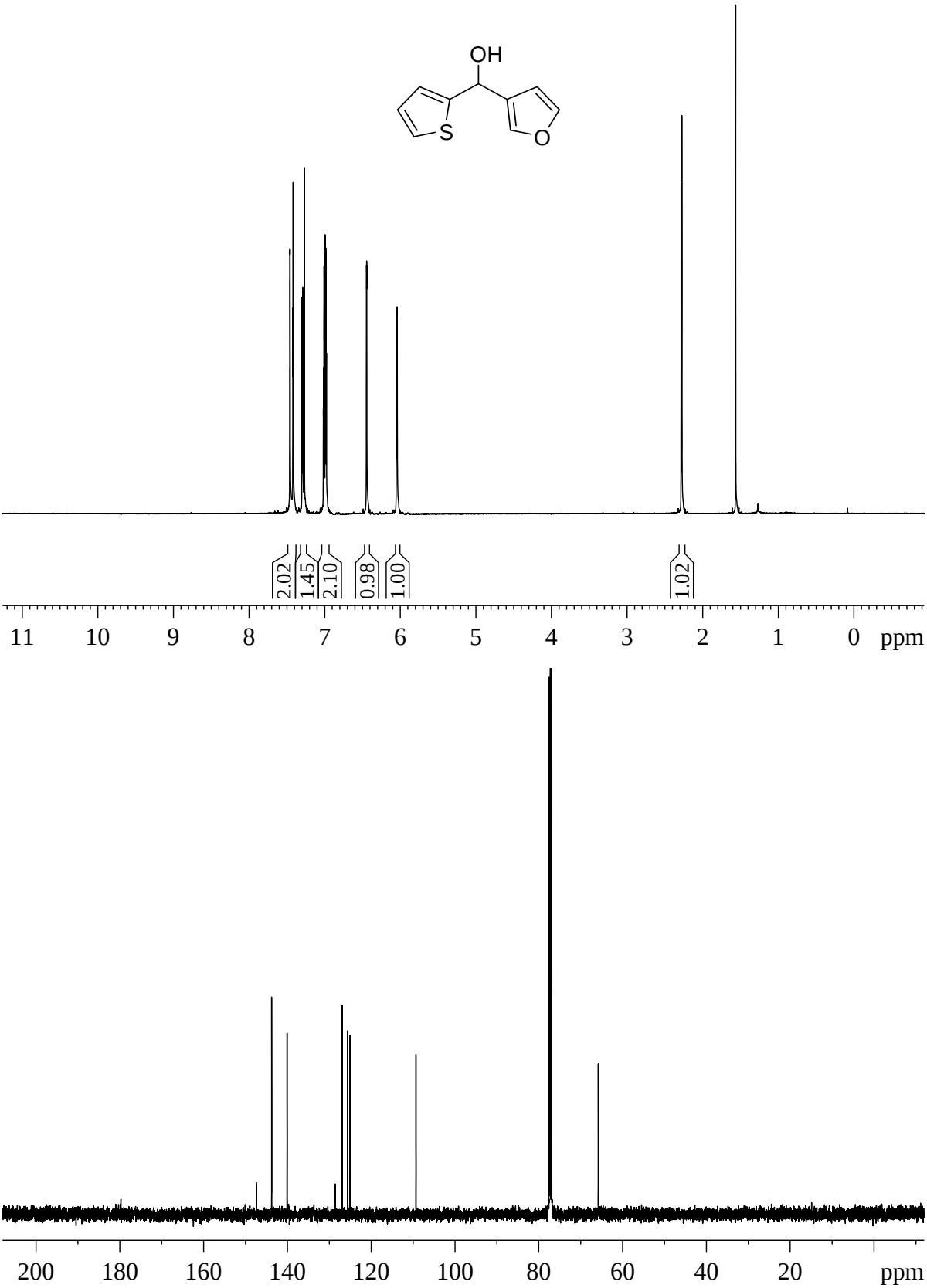
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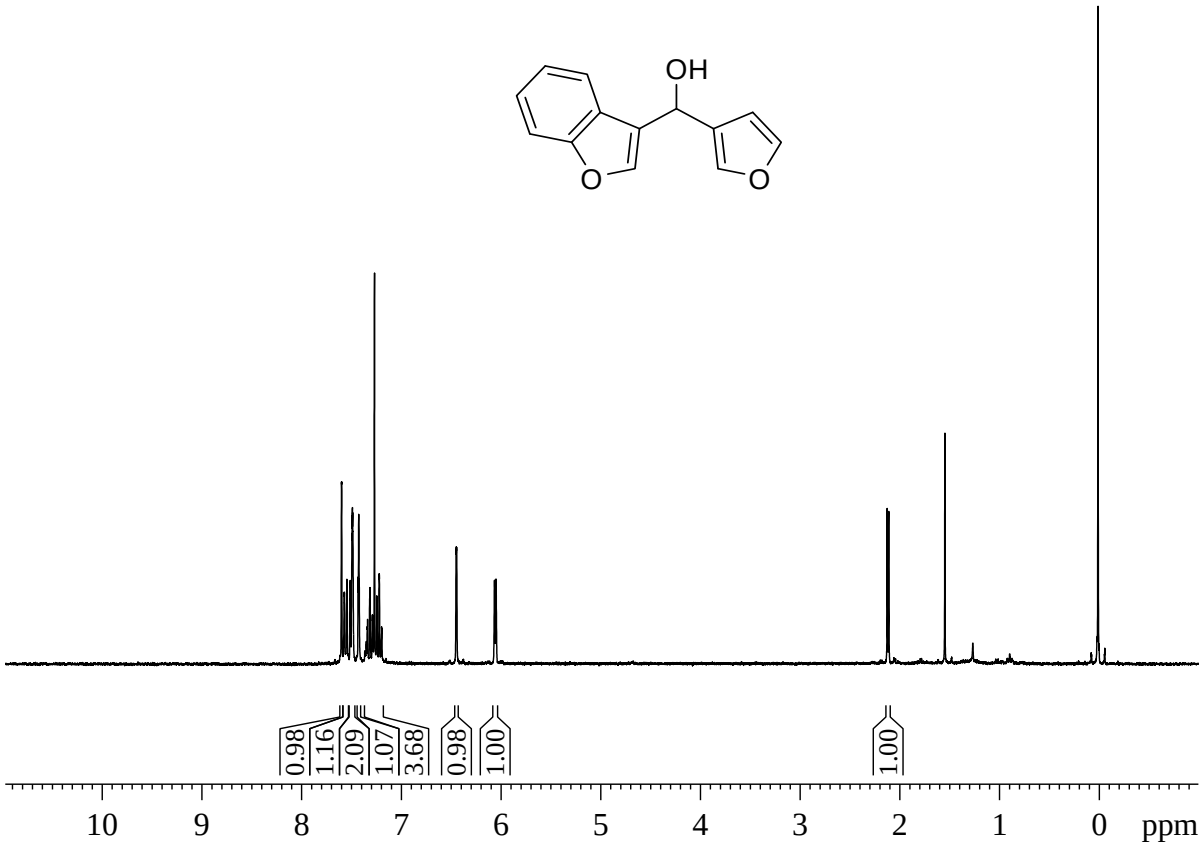
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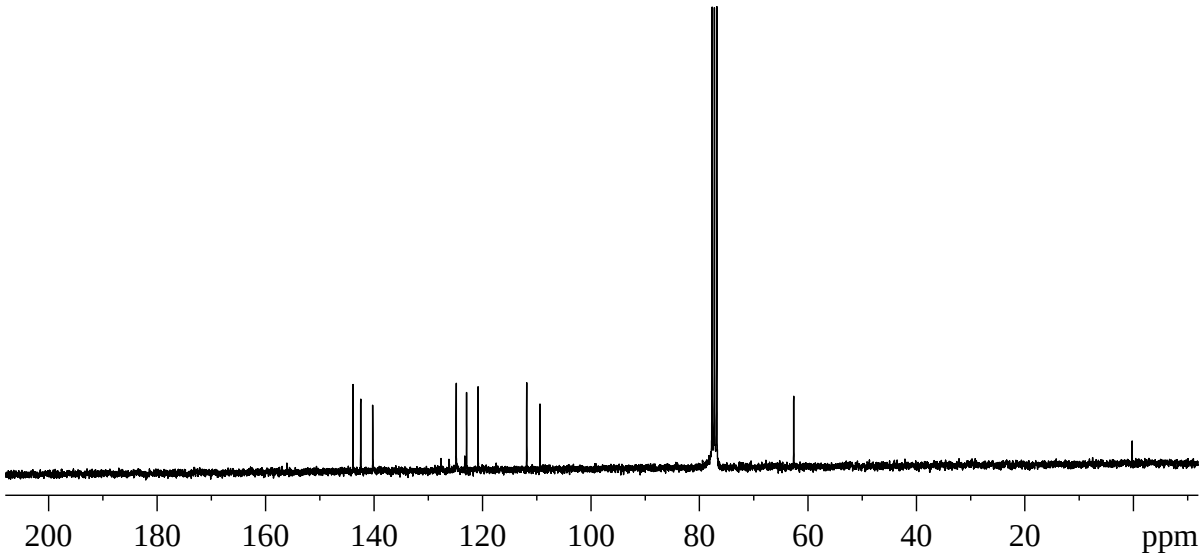
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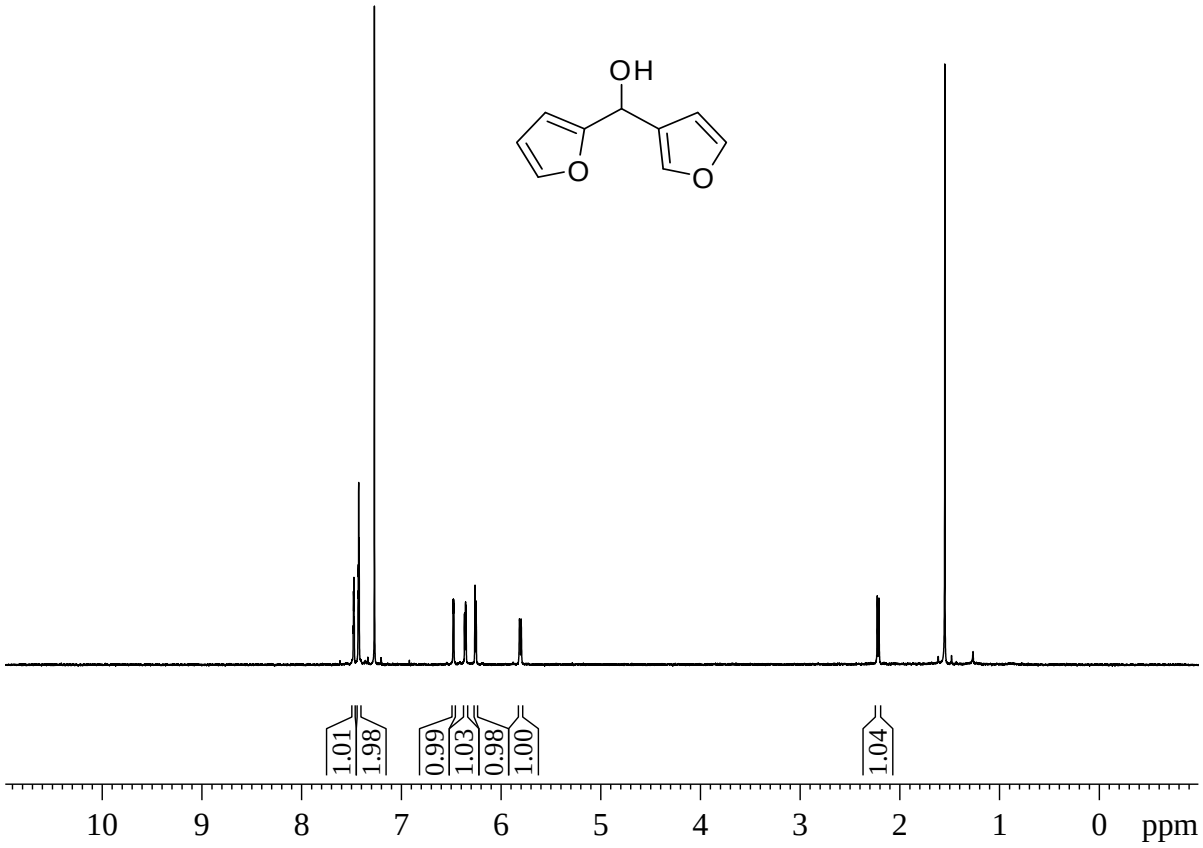
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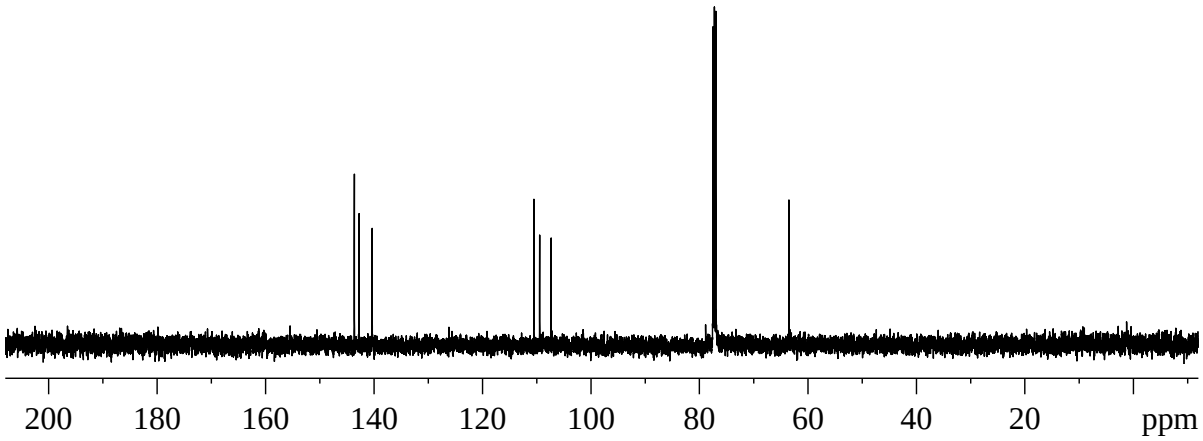
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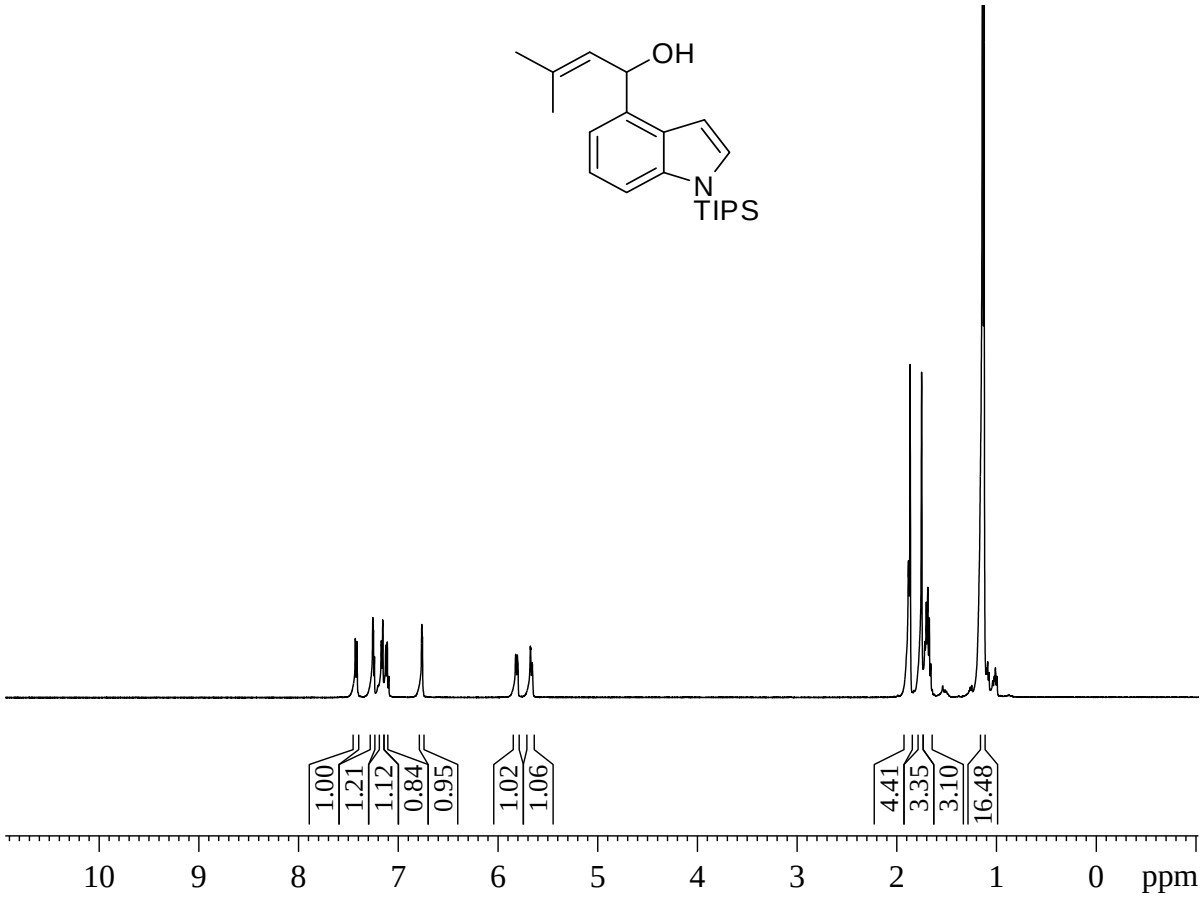
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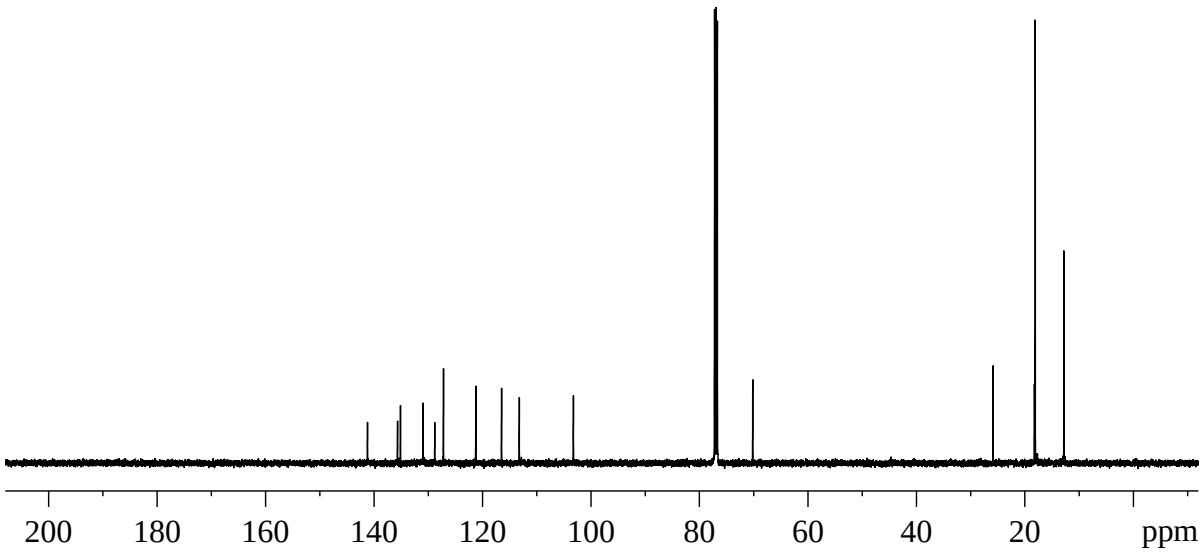
16.48
10
9
8
7
6
5
4
3
2
1
0
ppm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180
160
140
120
100
80
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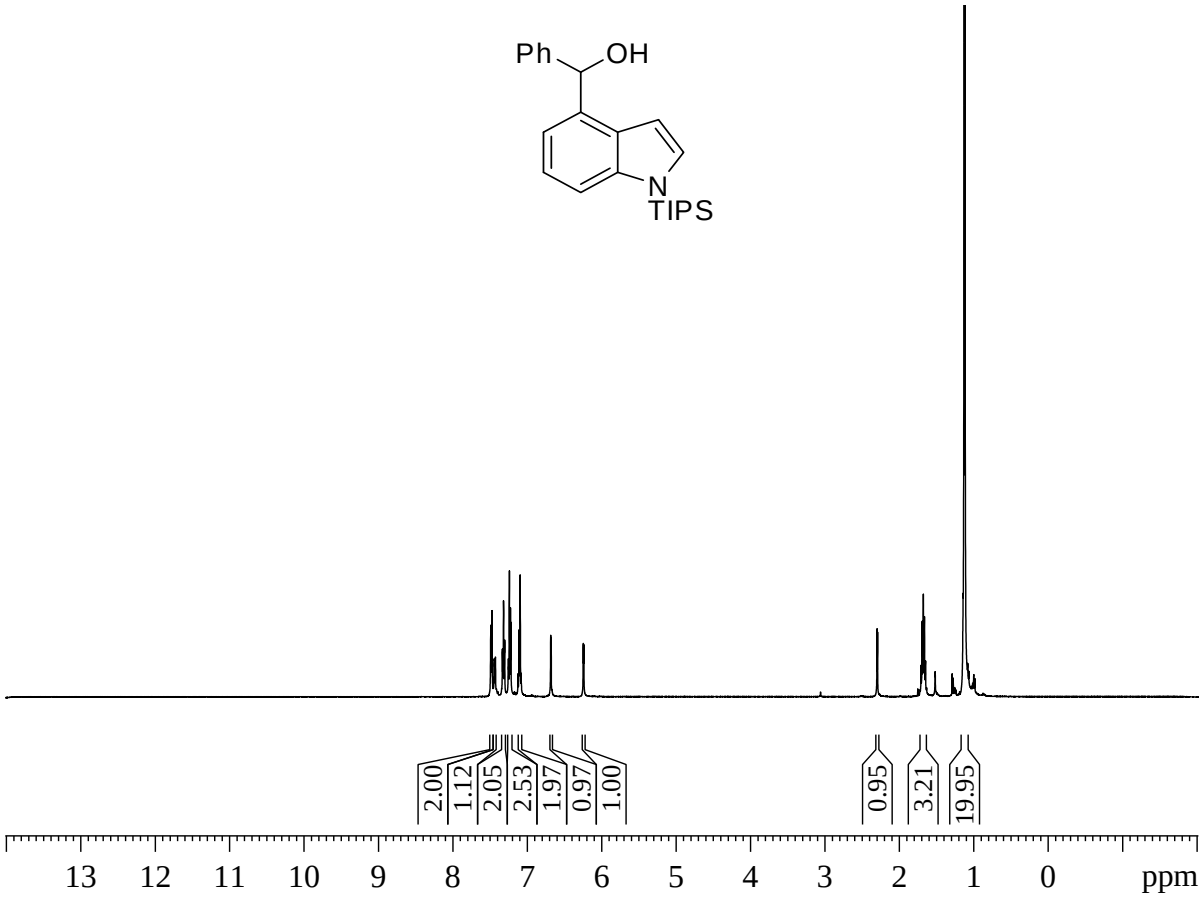
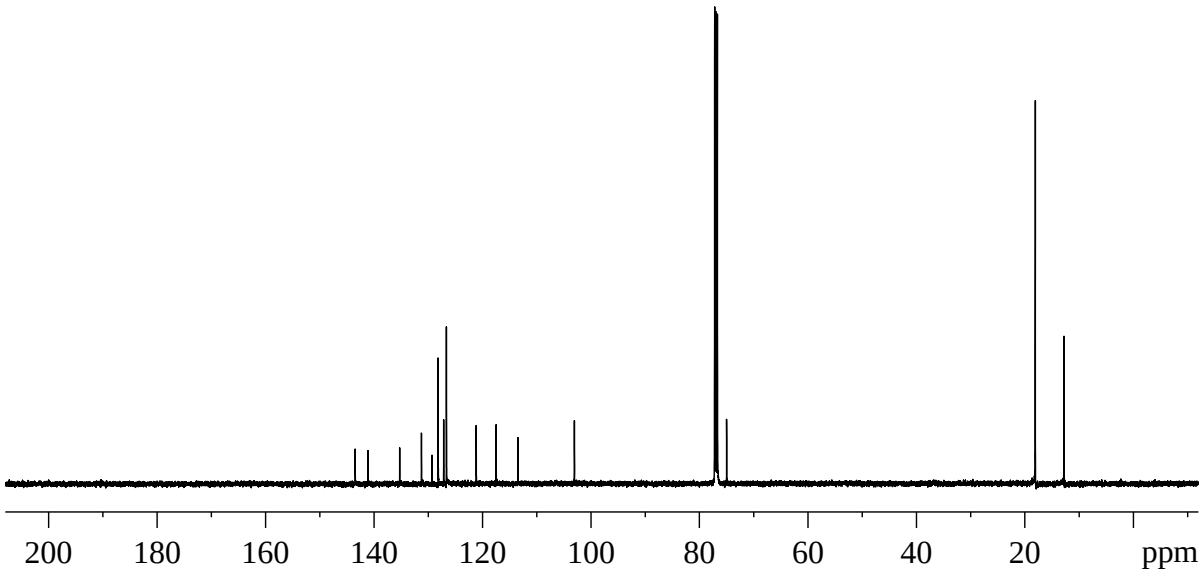
20
ppm


Ph
OH
N
TIPS
2.00
1.12
2.05
2.53
1.97
0.97
1.00
0.95
3.21
19.95
13 12 11 10 9 8 7 6 5 4 3 2 1 0
ppm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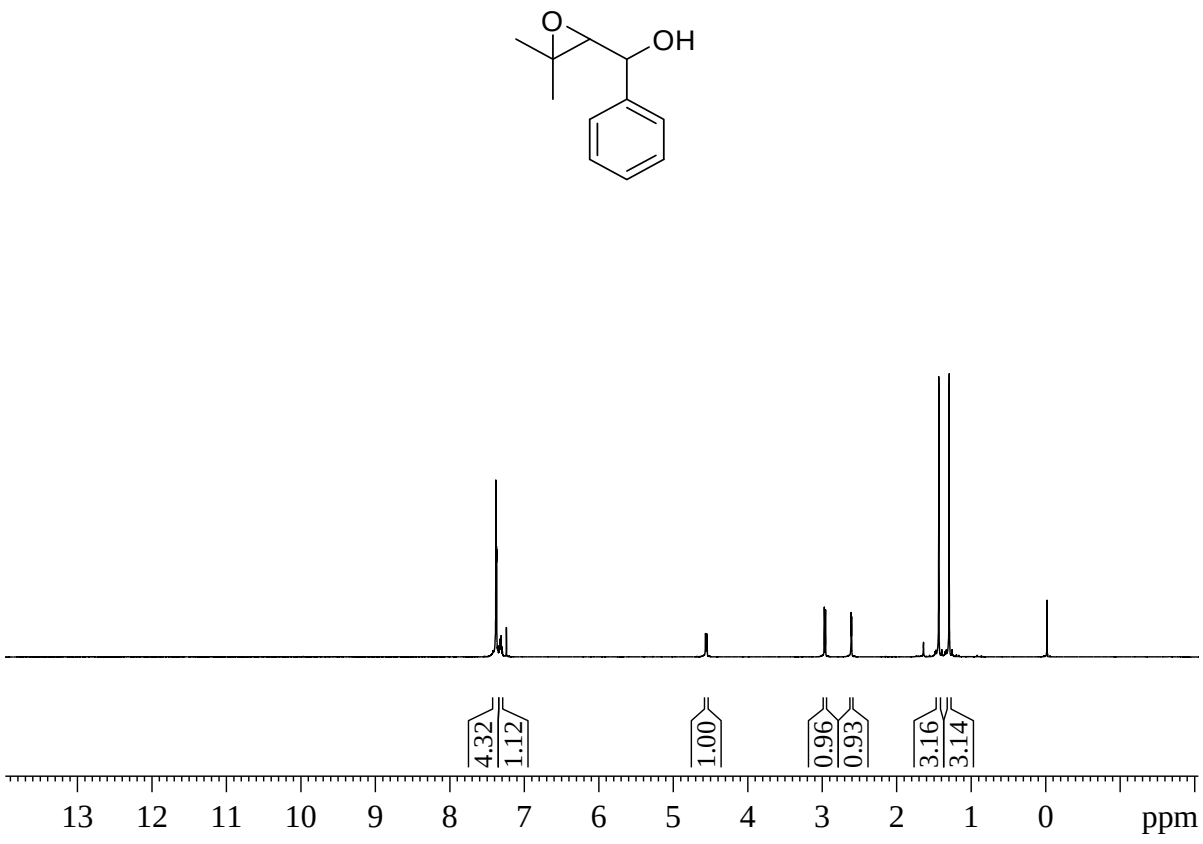
ppm


O
OH
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1.12
1.00
0.96
0.93
3.16
3.14
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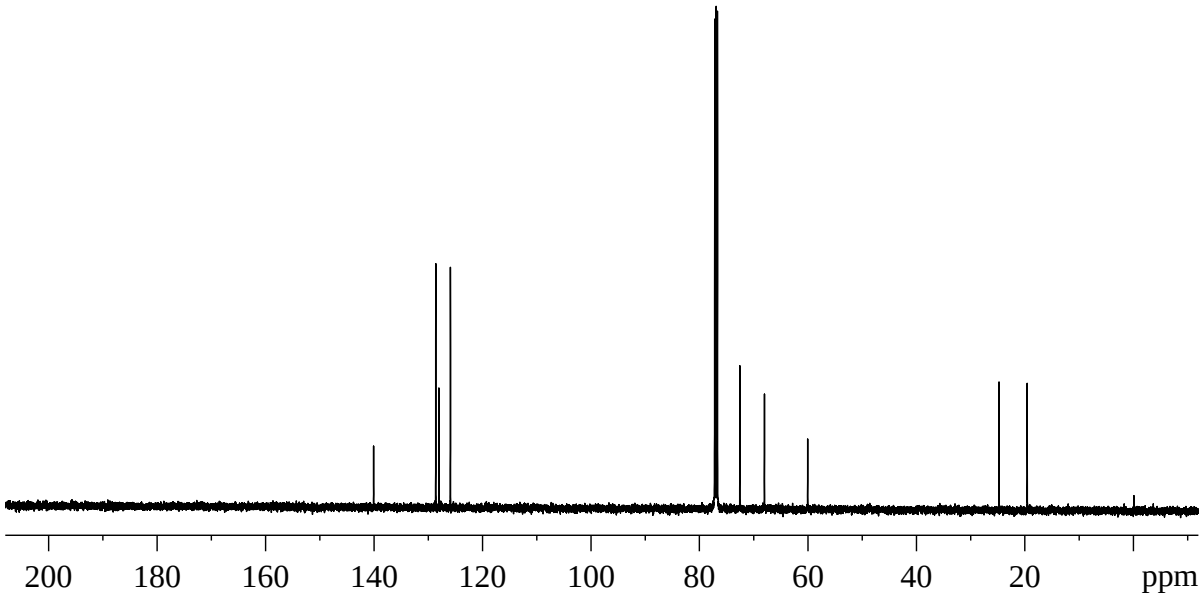
ppm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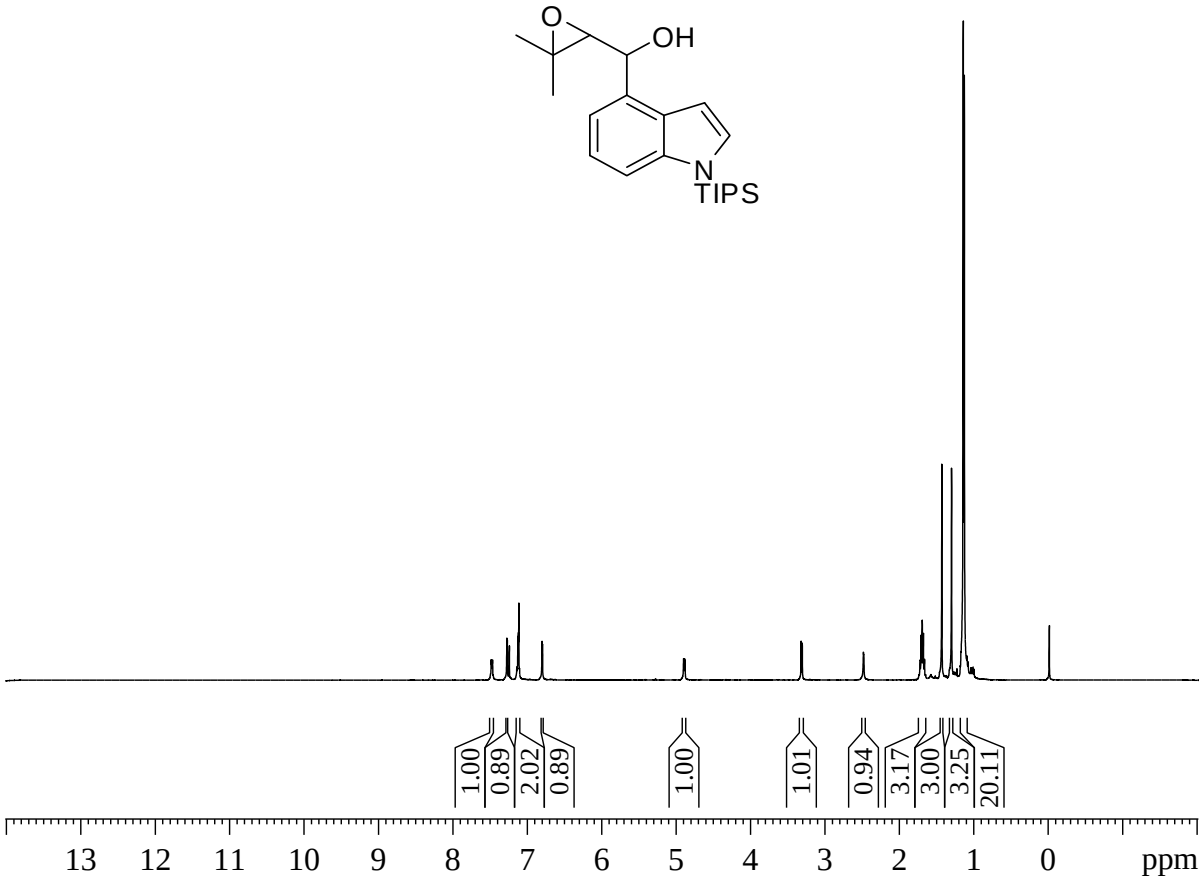
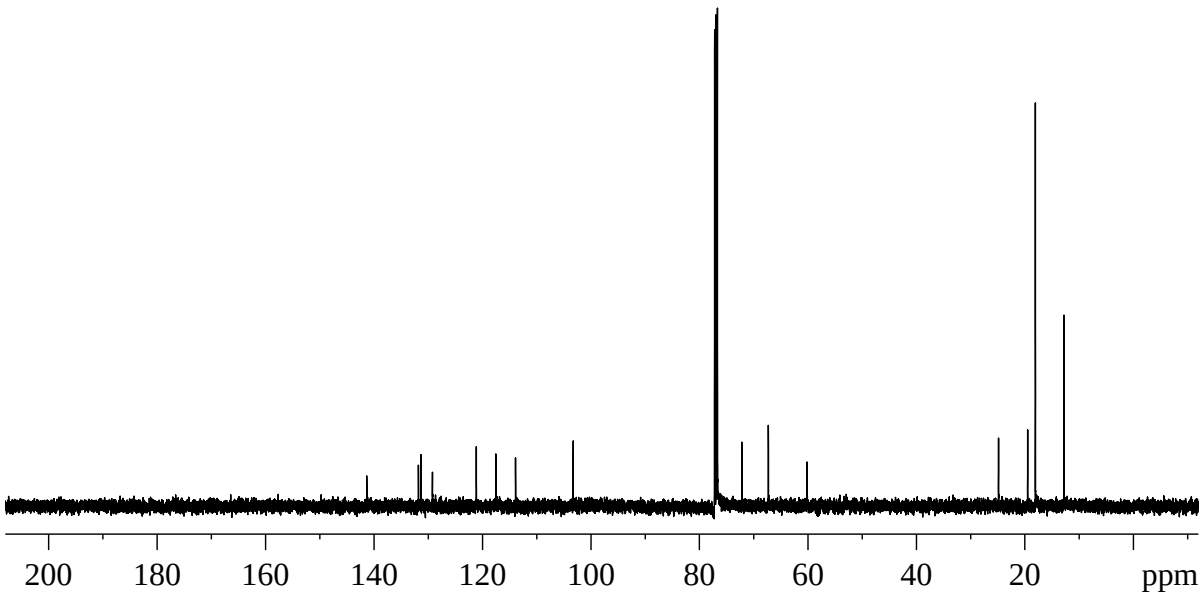
ppm


O
OH
N
TIPS
1.00
0.89
2.02
0.89
1.00
1.01
0.94
3.17
3.00
3.25
20.11
13 12 11 10 9 8 7 6 5 4 3 2 1 0 ppm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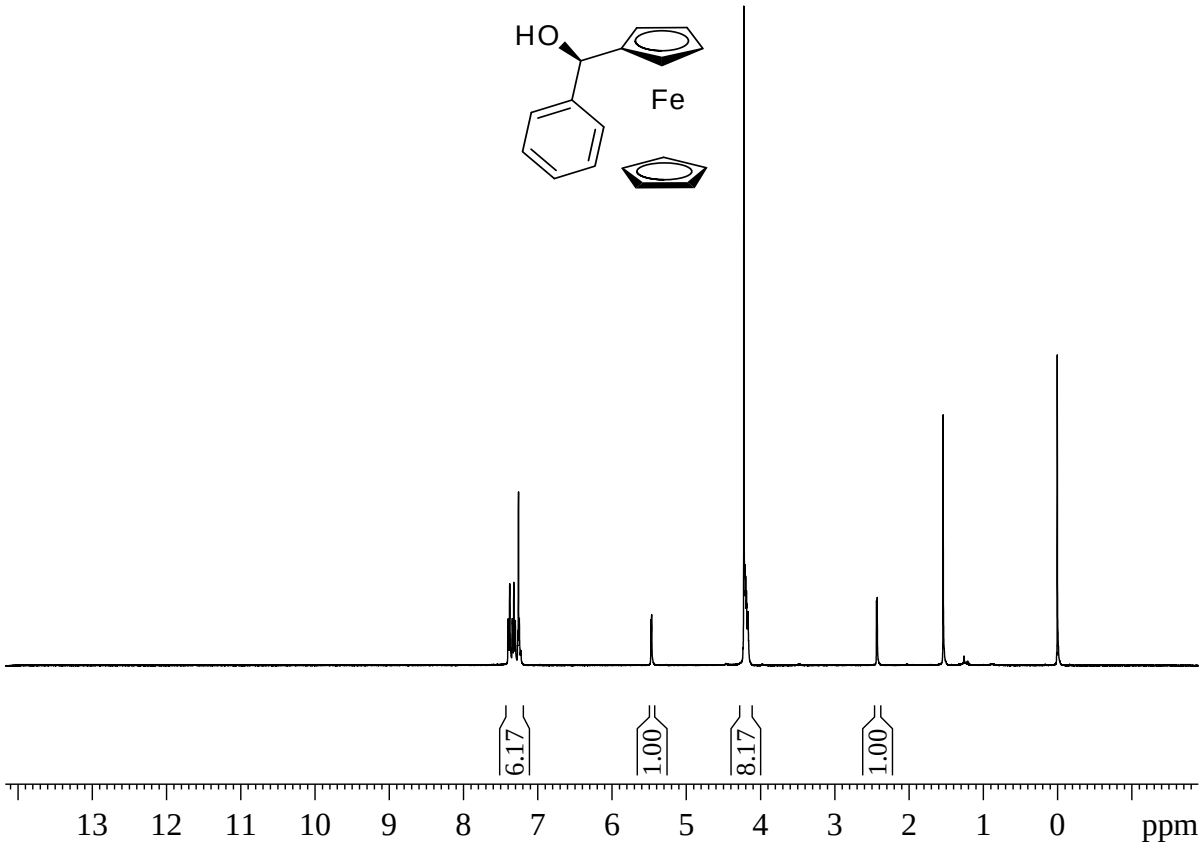
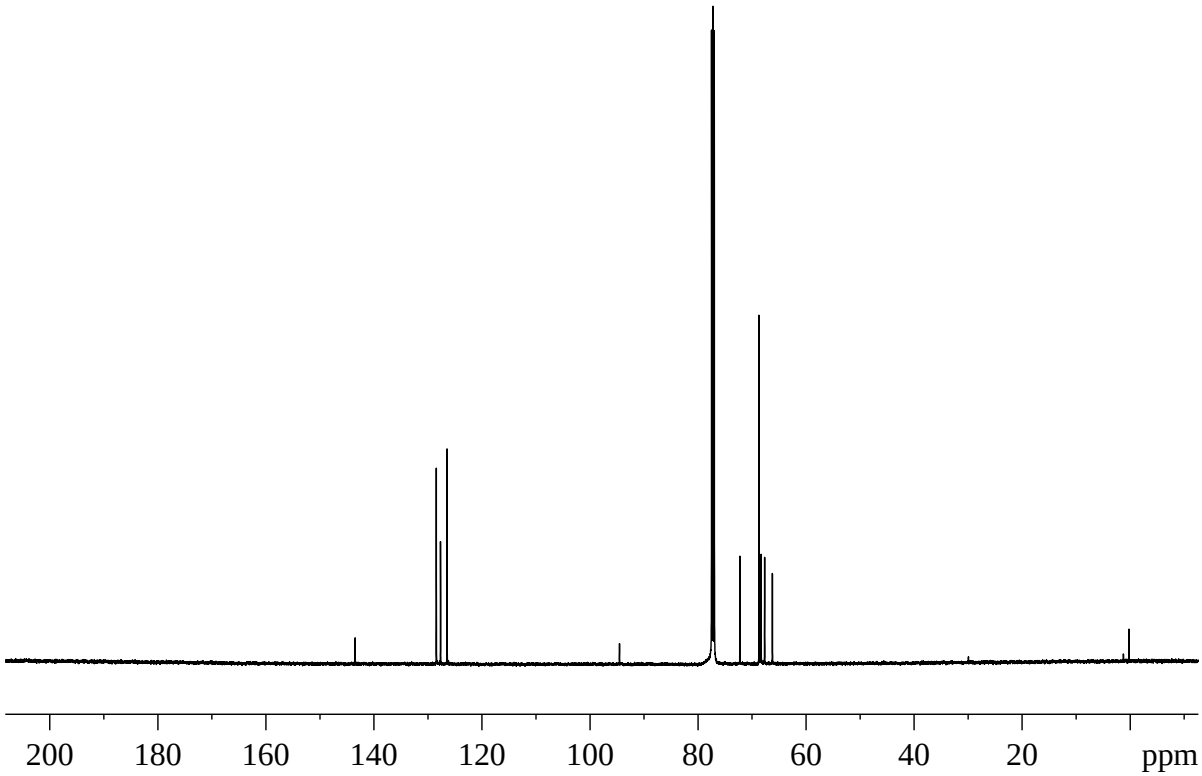
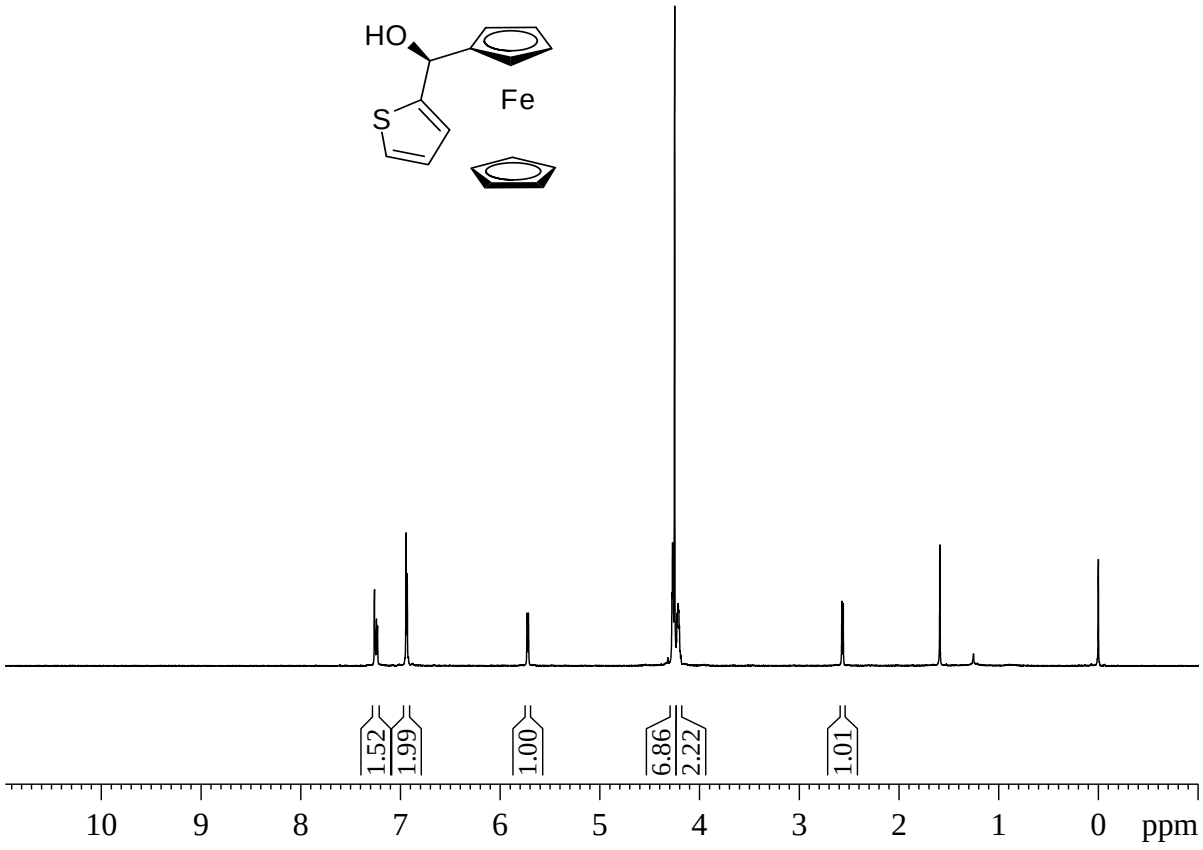

HO
Fe
6.17
1.00
8.17
1.00
13 12 11 10 9 8 7 6 5 4 3 2 1 0
ppm


200 180 160 140 120 100 80 60 40 20
ppm


HO
Fe
S
1.52
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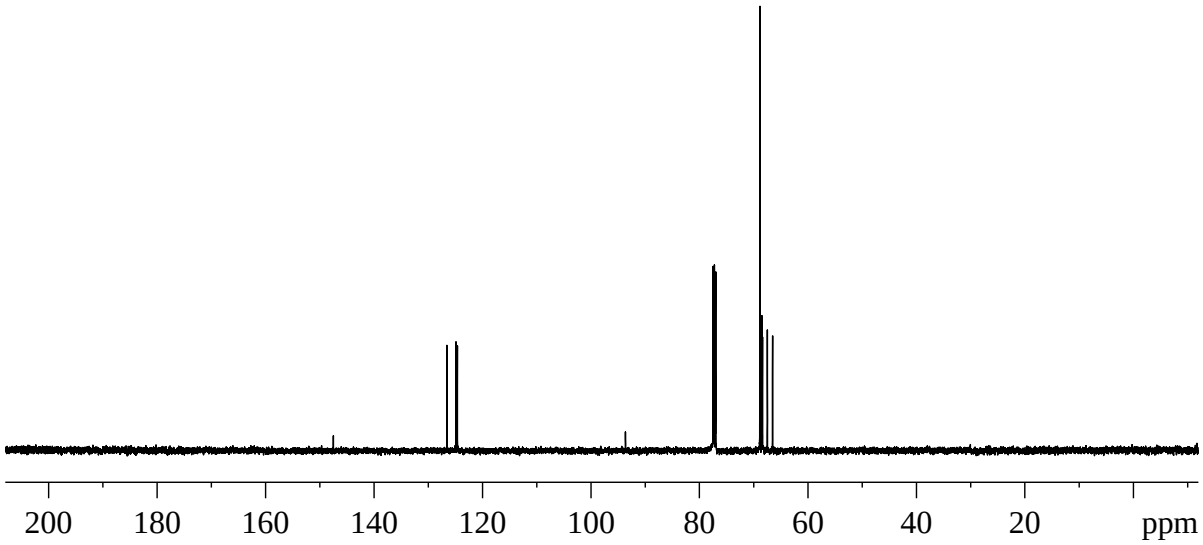
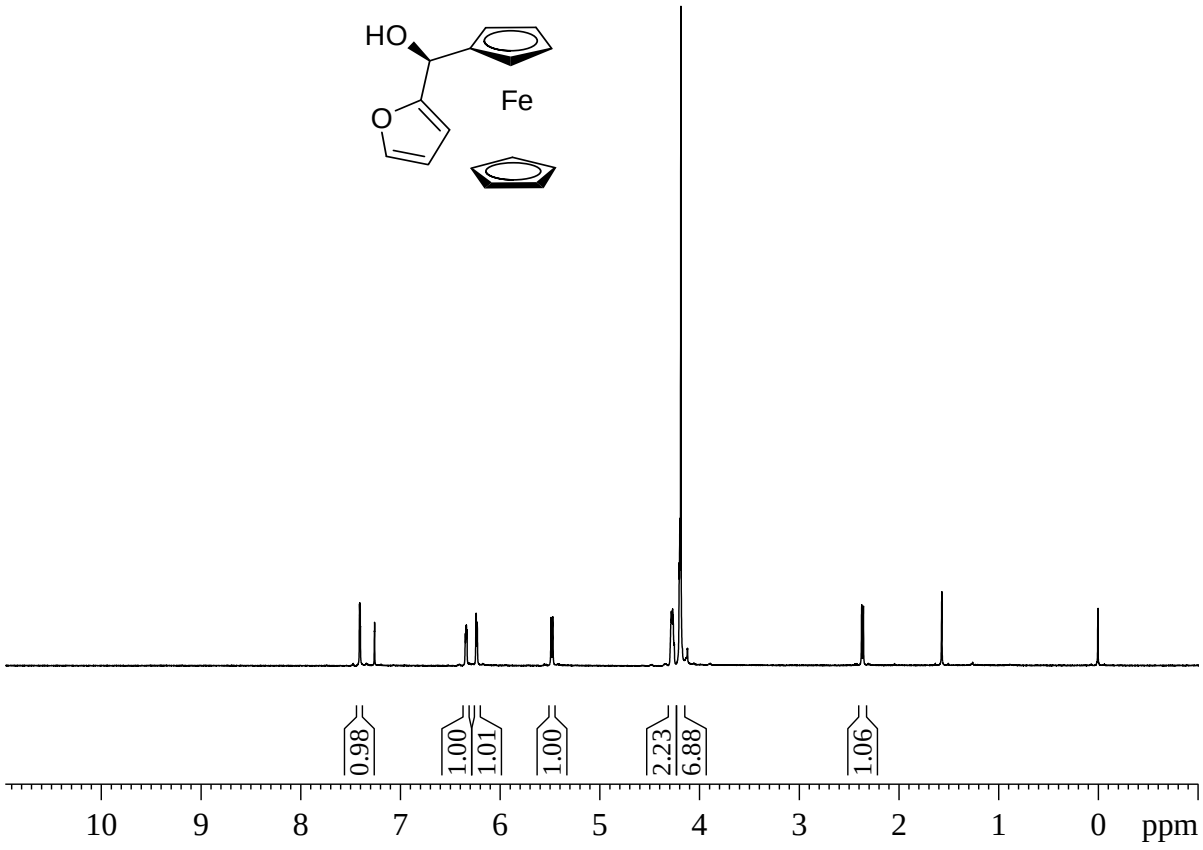
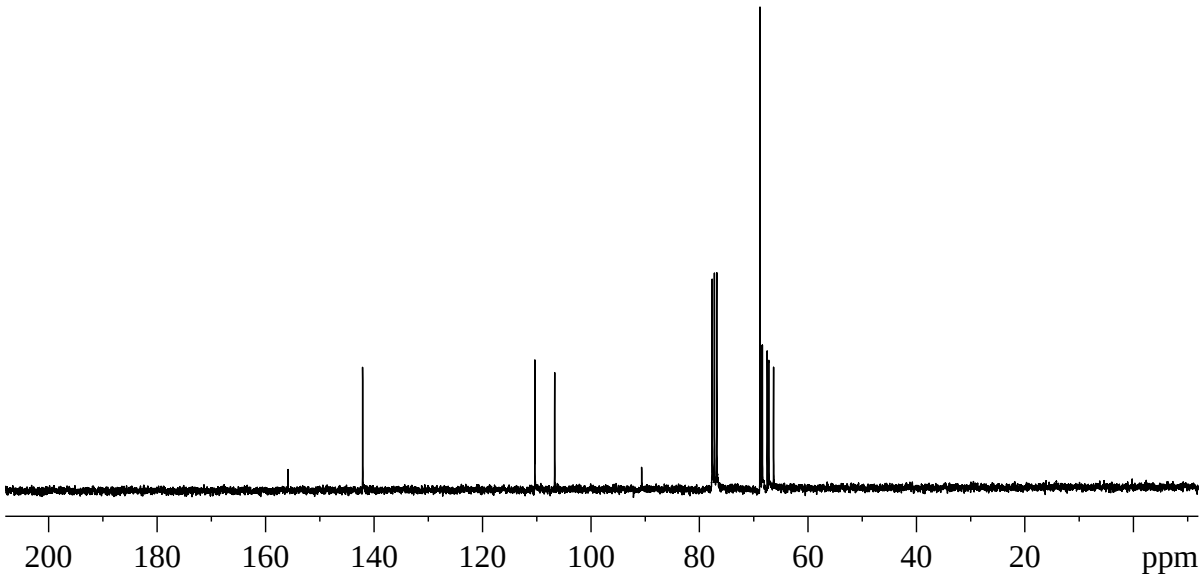
1.00
6.86
2.22
1.01
10
9
8
7
6
5
4
3
2
1
0
ppm


200
180
160
140
120
100
80
60
40
20
ppm


HO
Fe
O
0.98
1.00
1.01
1.00
2.23
6.88
1.06
10
9
8
7
6
5
4
3
2
1
0
ppm


200
180
160
140
120
100
80
60
40
20
ppm