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Electronic Supplementary Information

Hydrogen Autotransfer and Related Dehydrogenative Coupling Reactions using a Rhenium(I) Pincer

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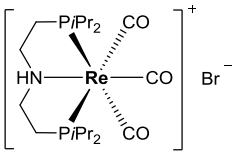
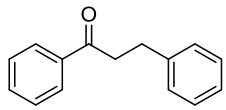
General information: Unless otherwise is stated, all reactions were conducted under an argon atmosphere with exclusion of moisture from reagents and glassware using standard techniques for manipulation air sensitive compounds. Reaction temperatures refer to external bath temperatures. TLC was effected on silica gel 60 F_{254} (layer thickness 0.2 mm) and components were located by observation under UV light and/or by treating the plates with a phosphomolybdic acid reagent followed by heating. Column chromatography was performed on silica gel (230–400 mesh) using ethyl acetate/heptane as eluent. NMR spectra were performed in a Bruker Avance 400 spectrometer using the residual solvent signal as internal standard [chloroform: 7.26 ppm (^{1}H), 77.0 ppm (^{13}C)]. All measurements were carried out at room temperature unless otherwise stated, and DEPT was used to assign carbon types. Mass spectra were in general recorded on a MAT 95XP or a HP 5973N mass selective detector. Gas chromatography was performed on a HP 6890N chromatograph with a HP5 column. Unless otherwise statement, commercial reagents were used as received without purification.



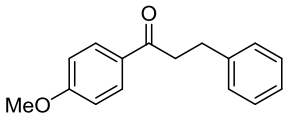
Synthesis of rhenium pincer complex 5: In a three-necked round-bottom flask (100 mL) under an argon atmosphere, $Re(CO)_5Br$ (1.5 mmol, 609.2 mg) was suspended in 25 mL toluene. Then, the PNP pincer ligand (1.6 mmol, 500mg, as 10 wt% solution in THF) was added dropwise via syringe at room temperature. After 10 min of stirring, the suspension was heated to 100 °C for 20 h. During that time the reaction mixture became a colourless solution. Cooling down to room temperature and removing the solvent at reduced pressure, led to a white solid. Washing this solid with toluene (3 x 10 mL) and drying under high vacuum provided the rhenium complex **5** (970.6 mg; 99%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.27 – 1.35 (m, 18H), 1.39 (dd, *J*=15.3, 7.0, 6H), 1.92 – 2.26 (m, 6H), 2.47 (ddt, *J*=14.3, 9.4, 7.1, 2H), 2.92 – 3.21 (m, 4H), 7.96 (b, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 18.3 (dd, *J*=3.9, 3.1), 19.6, 20.2, 22.0, 26.1 (dd, *J*=15.7, 14.4), 27.1 (dd, *J*=13.8, 10.1), 30.1 (dd, *J*=12.4, 10.4), 53.9, 189.6, 190.0, 195.1 ppm; ^{31}P NMR (121 MHz, $CDCl_3$): δ = 38.48 ppm; IR ATR (solid): $\tilde{\nu}$ [cm^{-1}] 2019 (s, $\tilde{\nu}$ CO), 1923 (s, $\tilde{\nu}$ CO); Elemental Anal. calcd. for $C_{19}H_{37}BrNO_3P_2Re$: C: 34.81, H: 5.69, N: 2.14; found: C: 34.74, H: 5.25, N: 1.84.

General procedure for the rhenium-catalysed *α*-alkylation of ketones with alcohols: In a glass pressure tube (25 mL) under an argon atmosphere, rhenium complex **5** (13.1 mg, 0.02 mmol), Cs_2CO_3 (6.5 mg, 0.02 mmol), ketone (**6**, 1.0 mmol) and alcohol (**7**, 1.2 mmol) were dissolved in *tert*-amyl alcohol (1 mL). Next the pressure tube was closed and the resulting mixture was stirred at 140 °C in an oil bath for 22 hours. After cooling down to room temperature, the crude was directly purified by flash chromatography on silica gel to afford, after concentration and high-vacuum drying, the corresponding products (**8**) in the reported yields.

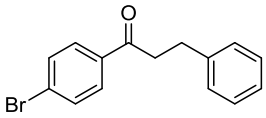
Analytical data of the synthesised ketones:



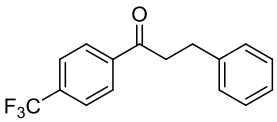
1,3-Diphenylpropan-1-one (8a):[1] Following the general procedure, 8**a** was obtained as a white solid (181.7 mg, 0.86 mmol, 86%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 3.07 (dd, *J* = 6.9, 8.5 Hz, 2H), 3.30 (dd, *J* = 6.8, 8.6 Hz, 2H), 7.07-7.35 (m, 5H), 7.44 (dd, *J* = 7.0, 8.4 Hz, 2H), 7.49-7.72 (m, 1H), 7.95 (dd, *J* = 1.4, 8.3 Hz, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 30.3 (CH_2), 40.6 (CH_2), 126.3 (CH), 128.2 (2 x CH), 128.6 (2 x CH), 128.7 (2 x CH), 128.8 (2 x CH), 133.2 (CH), 137.0 (C), 141.4 (C), 199.3 (C) ppm; GCMS (EI): *m/z* (%): 210 (60) [M^+], 105 (100), 91 (10), 77 (45); HRMS (ESI-TOF): *m/z*: calcd for $C_{15}H_{14}O$: 211.1117 $[M+H]^+$; found: 211.1118.



1-(4-Methoxyphenyl)-3-phenylpropan-1-one (8b):[1] Following the general procedure, **8b** was obtained as a white solid (217.4 mg, 0.91 mmol, 91%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 3.06 (dd, *J* = 6.8, 8.6 Hz, 2H), 3.17-3.41 (m, 2H), 3.87 (s, 3H), 6.93 (d, *J* = 8.9 Hz, 2H), 7.09-7.38 (m, 5H), 7.95 (d, *J* = 8.9 Hz, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 30.5 (CH_2), 40.3 (CH_2), 55.6 (CH_3), 113.9 (2 x CH), 126.2 (CH), 128.6 (2 x CH), 128.7 (2 x CH), 130.1 (C), 130.4 (2 x CH), 141.6 (C), 163.6 (C), 197.9 (C) ppm; GCMS (EI): *m/z* (%): 240 (100) [M^+], 209 (5), 165 (2); HRMS (ESI-TOF): *m/z*: calcd for $C_{16}H_{16}O_2$: 241.1223 $[M+H]^+$; found: 241.1224.



1-(4-Bromophenyl)-3-phenylpropan-1-one (8c):[1] Following the general procedure, **8c** was obtained as a white solid (172.8 mg, 0.60 mmol, 60%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 3.07 (t, *J* = 7.6 Hz, 2H), 3.27 (t, *J* = 7.6 Hz, 2H), 7.02-7.37 (m, 6H), 7.59 (d, *J* = 8.2 Hz, 2H), 7.82 (d, *J* = 8.2 Hz, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 30.1 (CH_2), 40.5 (CH_2), 126.3 (CH), 128.3 (C), 128.5 (2 x CH), 128.7 (2 x CH), 129.7 (2 x CH), 132.0 (2 x CH), 135.7 (C), 141.1 (C), 198.3 (C) ppm; GCMS (EI): *m/z* (%): 289 (43) [M^+], 288 (44), 209 (17), 184 (98), 183 (100); HRMS (ESI-TOF): *m/z*: calcd for $C_{15}H_{13}OBr$: 291.0203 $[M+H]^+$; found: 291.0203.



3-Phenyl-1-(4-(trifluoromethyl)phenyl)propan-1-one (8d):[1] Following the general procedure, **8d** was obtained as a white solid (146.7 mg, 0.53 mmol, 53%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 2.78-3.14 (m, 2H), 3.33 (dd, *J* = 7.0, 8.3 Hz, 2H), 7.15-7.36 (m, 5H), 7.72 (d, *J* = 8.2 Hz, 2H), 8.06 (d, *J* = 8.1 Hz, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 30.1 (CH_2), 40.9 (CH_2), 122.4 (C), 125.8 (q, *J* = 3.7 Hz, 2 x CH), 126.4 (CH), 128.5 (2 x CH), 128.6 (2 x CH), 128.7 (2 x CH), 134.5 (q, *J* = 32.8 Hz, C), 139.6 (C), 141.0 (C), 198.3 (C) ppm; GCMS (EI): *m/z* (%): 278 (49) [M^+], 209 (14), 173 (100), 145 (54), 105 (36); HRMS (ESI-TOF): *m/z*: calcd for $C_{16}H_{13}OF_3$: 279.0991 $[M+H]^+$; found: 279.0990.

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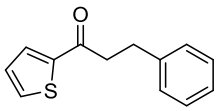
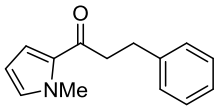
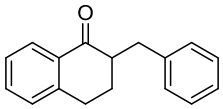
1 R. Wang, J. Ma, F. Li, *J. Org. Chem.* **2015**, *80*, 10769-10776.



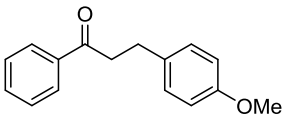
3-Phenyl-1-(thiophen-2-yl)propan-1-one (8e):[2] Following the general procedure, **8e** was obtained as a slightly yellow oil (190.5 mg, 0.88 mmol, 88%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 3.11 (dd, *J* = 6.8, 8.6 Hz, 2H), 3.23-3.37 (m, 2H), 7.14 (dd, *J* = 3.8, 4.9 Hz, 1H), 7.20-7.44 (m, 5H), 7.65 (dd, *J* = 1.2, 4.9 Hz, 1H), 7.72 (dd, *J* = 1.1, 3.8 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 30.5 (CH_2), 41.3 (CH_2), 126.3 (CH), 128.2 (CH), 128.5 (2 x CH), 128.7 (2 x CH), 131.9 (CH), 133.7 (CH), 141.1 (C), 144.3 (C), 192.3 (C) ppm; GCMS (EI): *m/z* (%): 216 (55) [M^+], 111 (100), 91 (14), 77 (10); HRMS (ESI-TOF): *m/z*: calcd for $C_{13}H_{12}OS$: 217.06826 $[M+H]^+$; found: 217.06821.



1-(1-Methyl-1H-pyrrol-2-yl)-3-phenylpropan-1-one (8f):[3] Following the general procedure, **8f** was obtained as a colourless oil (86.4 mg, 0.40 mmol, 40%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 3.07 (ddd, *J* = 1.9, 6.9, 8.7 Hz, 2H), 3.23-3.11 (m, 2H), 4.00 (s, 3H), 6.15 (dd, *J* = 2.5, 4.1 Hz, 1H), 6.84 (t, *J* = 2.1 Hz, 1H), 6.99 (dd, *J* = 1.7, 4.1 Hz, 1H), 7.17-7.40 (m, 5H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 31.0 (CH_2), 37.8 (CH_3), 40.8 (CH_2), 108.0 (CH), 119.1 (CH), 126.1 (CH), 128.5 (2 x CH), 128.6 (2 x CH), 130.7 (C), 131.1 (CH), 141.6 (C), 190.3 (C) ppm; GCMS (EI): *m/z* (%): 213 (50) [M^+], 108 (100), 81 (61), 53 (15); HRMS (ESI-TOF): *m/z*: calcd for $C_{14}H_{15}NO$: 214.1226 $[M+H]^+$; found: 214.1226.



2-Benzyl-3,4-dihydronaphthalen-1(2H)-one (8g):[1] Following the general procedure, **8g** was obtained as a white solid (90.5 mg, 0.38 mmol, 38%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.81 (dddd, *J* = 5.6, 9.9, 11.5, 13.4 Hz, 1H), 2.13 (dq, *J* = 4.5, 13.4 Hz, 1H), 2.67 (dd, *J* = 9.6, 13.6 Hz, 1H), 2.77 (ddt, *J* = 4.2, 9.6, 11.4 Hz, 1H), 2.86-3.00 (m, 2H), 3.52 (dd, *J* = 3.9, 13.6 Hz, 1H), 7.17-7.37 (m, 7H), 7.48 (td, *J* = 1.5, 7.5 Hz, 1H), 8.09 (dd, *J* = 1.4, 7.9 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 27.8 (CH_2), 28.8 (CH_2), 35.8 (CH_2), 49.6 (CH), 126.3 (CH), 126.8 (CH), 127.8 (CH), 128.5 (2 x CH), 128.8 (CH), 129.4 (2 x CH), 132.6 (CH), 133.4 (CH), 140.2 (C), 144.1 (C), 199.5 (C) ppm; GCMS (EI): *m/z* (%): 236 (100) [M^+], 208 (4), 158 (8); HRMS (ESI-TOF): *m/z*: calcd for $C_{17}H_{16}O$: 237.1274 $[M+H]^+$; found: 237.1274.



3-(4-Methoxyphenyl)-1-phenylpropan-1-one (9b):[1] Following the general procedure, **9b** was obtained as a white solid (191.6 mg, 0.80 mmol, 80%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 3.02 (dd, *J* = 7.0, 8.3 Hz, 2H), 3.27 (dd, *J* = 6.9, 8.4 Hz, 2H), 3.79 (s, 3H), 6.85 (d, *J* = 8.5 Hz, 2H), 7.18 (d, *J* = 8.6 Hz, 2H), 7.46 (dd, *J* = 6.9, 8.3 Hz, 2H), 7.50-7.65 (m, 1H), 7.96 (dd, *J* = 1.4, 8.4 Hz, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 29.4 (CH_2), 40.8 (CH_2), 55.4 (CH_3), 114.1 (2 x CH), 128.2 (2 x CH), 128.7 (2 x CH), 129.5 (2 x CH), 133.1 (CH), 133.4 (C), 137.0 (C), 158.1 (C), 199.5 (C) ppm; GCMS (EI): *m/z* (%): 240 (100) [M^+], 209 (3); HRMS (ESI-TOF): *m/z*: calcd for $C_{16}H_{16}O_2$: 263.1043 $[M+Na]^+$; found: 263.1043.

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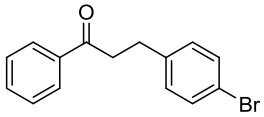
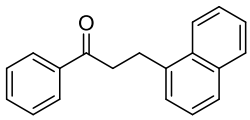
2 J. Liao, Z. Zhang, X. Tang, W. Wu, W. Guo and H. Jiang, *J. Org. Chem.*, **2015**, *8*, 8903-8909.

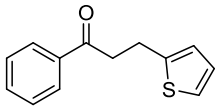
3 Q. Jiang, T. Guo, Q. Wang, P. Wu and Z. Yu, *Adv. Synth. Catal.*, **2013**, *355*, 1874-1880.



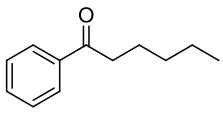
3-(4-Bromophenyl)-1-phenylpropan-1-one (9c):[4] Following the general procedure, **9c** was obtained as an orange solid (208.9 mg, 0.72 mmol, 72%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 3.03 (t, *J*=7.5, 2H), 3.28 (t, *J*=7.5, 2H), 7.09 – 7.18 (m, 2H), 7.38 – 7.51 (m, 4H), 7.53 – 7.59 (m, 1H), 7.86 – 8.01 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 29.55 (CH_2), 40.19 (CH_2), 120.00 (C), 128.12 (2 x CH), 128.76 (2 x CH), 130.36 (2 x CH), 131.66 (2 x CH), 133.29 (CH), 136.85 (C), 140.38 (C), 198.89 (C) ppm; GCMS (EI): *m/z* (%): 169 (22), 171 (22), 209 (16), 288 (100) [M+], 289 (21), 290 (99), 291 (16); HRMS (ESI-TOF): *m/z*: calcd for $C_{15}H_{13}BrO$: 289.02225 $[M+H]^+$; found: 289.02233.



3-(Naphthalen-1-yl)-1-phenylpropan-1-one (9d):[1] Following the general procedure, **9d** was obtained as a colourless oil (216.7 mg, 0.83 mmol, 83%). ^{1}H NMR (400 MHz, $CDCl_3$) *δ* = 3.24-3.49 (m, 2H), 3.51-3.67 (m, 2H), 7.37-7.63 (m, 7H), 7.75 (dd, *J* = 4.1, 5.4 Hz, 1H), 7.89 (dd, *J* = 1.5, 8.0 Hz, 1H), 7.97 (dd, *J* = 1.4, 8.4 Hz, 2H), 8.01-8.16 (m, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) *δ* = 27.3 (CH_2), 39.9 (CH_2), 123.6 (CH), 125.7 (CH), 125.8 (CH), 126.2 (CH), 126.3 (CH), 127.1 (CH), 128.2 (2 x CH), 128.8 (2 x CH), 129.1 (CH), 131.8 (C), 133.2 (CH), 134.1 (C), 137.0 (C), 137.5 (C), 199.4 (C) ppm; GCMS (EI): *m/z* (%): 260 (100) $[M^+]$, 241 (5), 155 (47); HRMS (ESI-TOF): *m/z*: calcd for $C_{19}H_{16}O$: 283.1093 $[M+Na]^+$; found: 283.1093.



1-Phenyl-3-(thiophen-2-yl)propan-1-one (9e):[5] Following the general procedure, **9e** was obtained as a white solid (148.1 mg, 0.68 mmol, 68%). ^{1}H NMR (400 MHz, $CDCl_3$) *δ* = 3.27-3.33 (m, 2H), 3.35-3.41 (m, 2H), 6.87 (dd, *J* = 1.1, 3.5 Hz, 1H), 6.93 (dd, *J* = 3.4, 5.2 Hz, 1H), 7.13 (dd, *J* = 1.1, 5.3 Hz, 1H), 7.47 (dd, *J* = 6.9, 8.3 Hz, 2H), 7.53-7.62 (m, 1H), 7.98 (dd, *J* = 1.3, 8.3 Hz, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) *δ* = 24.3 (CH_2), 40.7 (CH_2), 123.5 (CH), 124.8 (CH), 127.0 (CH), 128.1 (2 x CH), 128.8 (2 x CH), 133.3 (CH), 136.9 (C), 144.0 (C), 198.7 (C) ppm; GCMS (EI): *m/z* (%): 216 (73) $[M^+]$, 111 (56), 105 (100), 97 (54), 77 (64); HRMS (ESI-TOF): *m/z*: calcd for $C_{13}H_{12}OS$: 217.0682 $[M+H]^+$; found: 217.0682.



1-Phenylhexan-1-one (9f):[6] Following the general procedure, **9f** was obtained as a colourless oil (65.8 mg, 0.37 mmol, 37%). ^{1}H NMR (400 MHz, $CDCl_3$) *δ* = 0.88 -0.96 (m, 3H), 1.06-1.43 (m, 4H), 1.60-1.85 (m, 2H), 2.96 (t, *J* = 7.5 Hz, 2H), 7.46 (dd, *J* = 6.9, 8.3 Hz, 2H), 7.51-7.63 (m, 1H), 7.96 (dd, *J* = 1.7, 6.8 Hz, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) *δ* = 14.1 (CH_3), 22.7 (CH_2), 24.2 (CH_2), 31.7 (CH_2), 38.7 (CH_2), 128.2 (2 x CH), 128.7 (2 x CH), 132.9 (CH), 137.2 (C), 200.7 (C) ppm; GCMS (EI): *m/z* (%): 176 (8) $[M^+]$, 133

4 A. Stroba, F. Schaeffer, V. Hindie, L. Lopez-Garcia, I. Adrian, W. Fröhner, R. W. Hartmann, R. M. Biondi and M. Engel, *J. Med. Chem.*, **2009**, *52*, 4683-4693.

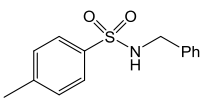
5 D. Weickmann and B. Plietker, *ChemCatChem*, **2013**, *5*, 2170-2173.

6 F. Li, J. Ma and N. Wang, *J. Org. Chem.*, **2014**, *79*, 10447-10455.

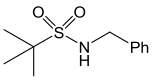
(6), 120 (61), 105 (100), 77 (38); HRMS (ESI-TOF): *m/z*: calcd for $C_{12}H_{16}O$: 177.1274 $[M+H]^+$; found: 177.1275.

General procedure for the rhenium-catalysed *N*-alkylation of sulfonamides with alcohols: In a glass pressure tube (25 mL) under an argon atmosphere, rhenium complex **5** (13.1 mg, 0.02 mmol), Cs_2CO_3 (6.5 mg, 0.02 mmol), sulfonamide (**9**, 1.0 mmol) and alcohol (**7**, 1.2 mmol) were dissolved in *tert*-amyl alcohol (1 mL). Next the pressure tube was closed and the resulting mixture was stirred at 150 °C in an oil bath for 22 hours. After cooling down to room temperature, the crude was directly purified by flash chromatography on silica gel to afford, after concentration and high-vacuum drying, the corresponding products (**10**) in the reported yields.

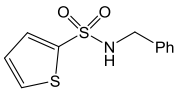
Analytical data of the synthesised sulfonamides:



N-Benzyltoloulsulfonamide (11a):[7] Following the general procedure, **11a** was obtained as a reddish sticky solid (220.0 mg, 0.84 mmol, 84%); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 2.44 (s, 3H), 4.11 (s, 2H), 4.82 (s, 1H), 7.20 (dd, *J*=7.2, 2.1, 2H), 7.23 – 7.34 (m, 5H), 7.69 – 7.82 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 21.7 (CH_3), 47.4 (CH_2), 127.3 (2 x CH), 128.0 (2 x CH), 128.0 (CH), 128.8 (2 x CH), 129.9 (2 x CH), 136.4 (C), 137.0 (C), 143.6 (C) ppm; GCMS (EI): *m/z* (%): 261 (9) $[M^+]$, 196 (31), 155 (100); HRMS (ESI-TOF): *m/z*: calcd for $C_{14}H_{15}NO_2S$: 284.07157 $[M+Na]^+$; found: 284.0717.



N-Benzyl-2-methylpropane-2-sulfonamide (11b):[8] Following the general procedure, **11b** was obtained as a white solid (179.7 mg, 0.79 mmol, 79%); ^{1}H NMR (300 MHz, $CDCl_3$) δ = 1.34 (s, 9H), 4.20 – 4.41 (m, 3H), 7.18 – 7.31 (m, 5H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ = 24.5 (3 x CH_3), 48.6 (CH_2), 60.1 (C), 127.8 (2 x CH), 127.9 (CH), 128.9 (2 x CH), 137.9 (C) ppm; GCMS (EI): *m/z* (%): 57 (44), 77 (9), 91 (19), 106 (100), 107 (17); HRMS (ESI-TOF): *m/z*: calcd for $C_{11}H_{17}NO_2S$: 250.08722 $[M+Na]^+$; found: 250.08746.

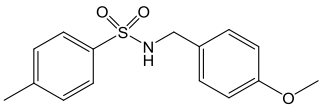


N-Benzylthiophene-2-sulfonamide (11c): Following the general procedure, **11c** was obtained as a yellow solid (72.6 mg, 0.29 mmol, 29%); ^{1}H NMR (300 MHz, $CDCl_3$) δ = 4.18 (d, *J*=5.4, 2H), 4.88 (s, 1H), 7.05 (dd, *J*=5.0, 3.7, 1H), 7.14 – 7.34 (m, 5H), 7.52 – 7.60 (m, 2H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ = 47.6 (CH_2), 127.6 (CH), 128.0 (2 x CH), 128.2 (CH), 128.9 (2 x CH), 132.1 (CH), 132.5 (CH), 136.0 (C), 141.0 (C) ppm; GCMS (EI): *m/z*

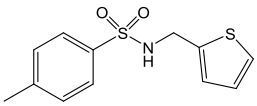
7 D. C. Johnson and T. S. Widlanski, *Tetrahedron Lett.*, **2004**, *45*, 8483-8487.

8 D. M. Hodgson, P. G. Humphreys, S. M. Miles, C. A. J. Brierley and J. G. Ward, *J. Org. Chem.*, **2007**, *72,* 10009-10021.

(%): 151 (10), 187 (10), 188 (100), 189 (18), 252 (16), 253 (19) [M^+]; HRMS (ESI-TOF): *m/z*: calcd for $C_{11}H_{11}NO_2S_2$: 290.02799 $[M+Na]^+$; found: 290.02819.



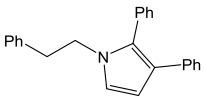
N-(4-Methoxybenzyl)-4-methylbenzenesulfonamide (11d):[9] Following the general procedure, **11a** was obtained as a reddish sticky solid (272.5 mg, 0.94 mmol, 94%); ^{1}H NMR (300 MHz, $CDCl_3$) δ = 2.44 (s, 3H), 3.77 (s, 3H), 3.94 – 4.15 (m, 2H), 4.69 (br. s, 1H), 6.72 – 6.86 (m, 2H), 7.03 – 7.18 (m, 2H), 7.30 (d, *J*=7.9, 2H), 7.66 – 7.84 (m, 2H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ = 21.7 (CH_3), 46.9 (CH_2), 55.4 (CH_3), 114.2 (2 x CH), 127.3 (2 x CH), 128.4 (C), 129.4 (2 x CH), 129.8 (2 x CH), 137.0 (C), 143.6 (C), 159.4 (C) ppm; GCMS (EI): *m/z* (%): 155 (52), 157 (10), 291 (100) [M^+], 292 (17); HRMS (ESI-TOF): *m/z*: calcd for $C_{15}H_{17}NO_3S$: 314.08214 $[M+Na]^+$; found: 314.08175.



4-Methyl-N-(thiophen-2-ylmethyl)benzenesulfonamide (11e):[10] Following the general procedure, **11e** was obtained as a slightly yellow solid (175.5 mg, 0.69 mmol, 69%); ^{1}H NMR (300 MHz, $CDCl_3$) δ = 2.43 (s, 3H), 4.32 (d, *J*=5.5, 2H), 4.95 (t, *J*=5.5, 1H), 6.78 – 6.91 (m, 2H), 7.18 (dd, *J*=4.9, 1.5, 1H), 7.27 – 7.33 (m, 2H), 7.63 – 7.86 (m, 2H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ = 21.7 (CH_3), 42.2 (CH_2), 125.9 (CH), 126.6 (CH), 127.0 (CH), 127.3 (2 x CH), 129.9 (2 x CH), 136.9 (C), 139.1 (C), 143.7 (C) ppm; GCMS (EI): *m/z* (%): 155 (56), 157 (100), 158 (10), 202 (18), 267 (35) [M^+]; HRMS (ESI-TOF): *m/z*: calcd for $C_{12}H_{13}NO_2S_2$: 276.01234 $[M+Na]^+$; found: 276.01253.

General procedure for the rhenium-catalysed synthesis of pyrroles: In a glass pressure tube (25 mL) under an argon atmosphere, rhenium complex **5** (6.5 mg, 0.01 mmol), Cs_2CO_3 (3.2 mg, 0.01 mmol), ketone (**6**, 0.75 mmol), diol (**11**, 5.0 mmol) and amine (**12**, 0.5 mmol) were dissolved in *tert*-amyl alcohol (1 mL). Next the pressure tube was closed and the resulting mixture was stirred at 150 °C in an oil bath for 22 hours. After cooling down to room temperature, the crude was directly purified by flash chromatography on silica gel to afford, after concentration and high-vacuum drying, the corresponding products (**13**) in the reported yields.

Analytical data of the synthesised pyrroles:



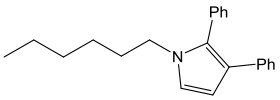
1-Phenethyl-2,3-diphenyl-1H-pyrrole (15a):[11] Following the general procedure, **15a** was obtained as a light grey solid (107.5 mg, 0.33 mmol, 66%); ^{1}H NMR (300 MHz, $CDCl_3$) δ = 2.71 – 2.83 (m, 2H), 3.88 – 3.97 (m, 2H), 6.36 (d, *J*=2.0, 1H), 6.67 (d, *J*=2.7, 1H), 6.79 – 6.89 (m, 2H), 6.94 – 7.04 (m, 1H), 7.03 – 7.20 (m, 9H), 7.24

9 A. Martínez-Asencio, D. J. Ramón and M. Yus, *Tetrahedron*, **2011**, *67*, 3140-3149.

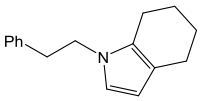
10 F. Shi, M. Tse, X. Cui, D. Gördes, D. Michalik, K. Thurow, Y. Deng and M. Beller, *Angew. Chem. Int. Ed.*, **2009**, *48*, 5912–5915.

11 M. Zhang, H. Neumann and M. Beller, *Angew. Chem. Int. Ed.*, **2013**, *52*, 597-601.

– 7.33 (m, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ = 38.2 (CH_2), 48.9 (CH_2), 108.0 (CH), 121.0 (CH), 122.8 (C), 125.1 (CH), 126.7 (CH), 127.7 (2 x CH), 127.8 (CH), 128.1 (2 x CH), 128.6 (2 x CH), 128.7 (2 x CH), 128.8 (2 x CH), 130.4 (C), 131.3 (2 x CH), 133.1 (C), 136.7 (C), 138.4 (C) ppm; GCMS (EI): *m/z* (%):217 (10), 219 (12), 230 (17), 231 (11), 232 (100), 233 (18), 323 (95) [M^+], 324 (24); HRMS (ESI-TOF): *m/z*: calcd for $C_{24}H_{21}N$: 324.17468 $[M+H]^+$; found: 324.17506.



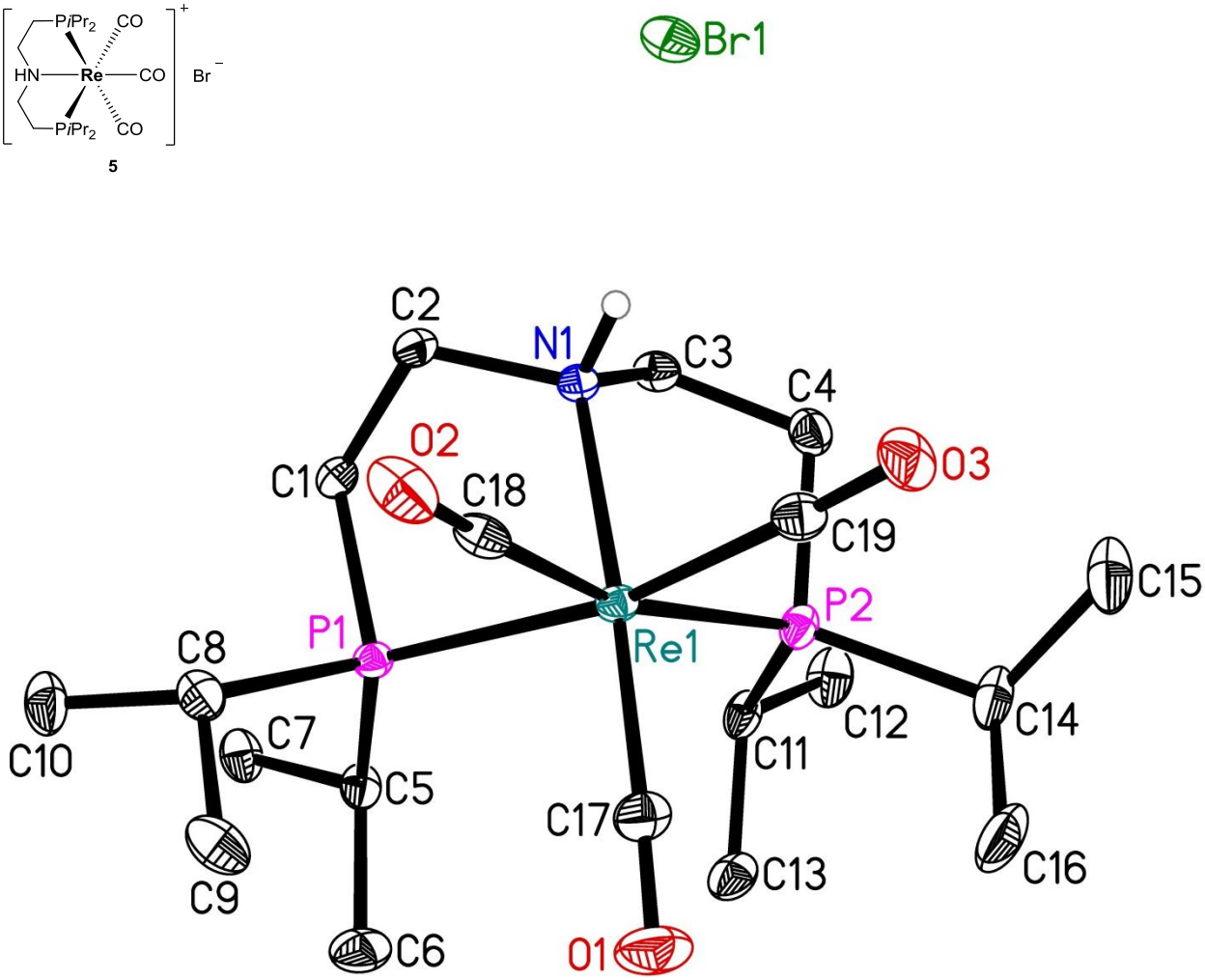
1-Hexyl-2,3-diphenyl-1H-pyrrole (15b): Following the general procedure, **15b** was obtained as a white solid (74.9 mg, 0.25 mmol, 49%); 1H NMR (300 MHz, $CDCl_3$) δ = 0.76 – 0.94 (m, 3H), 1.09 – 1.35 (m, 6H), 1.52 – 1.70 (m, 2H), 3.73 – 3.83 (m, 2H), 6.45 (d, J=1.9, 1H), 6.79 (d, J=2.8, 1H), 7.02 – 7.21 (m, 5H), 7.27 – 7.44 (m, 5H) ppm; 13C NMR (75 MHz, CDCl3) δ = 14.1 (CH3), 22.6 (CH2), 26.4 (CH2), 31.4 (CH2), 31.5 (CH2), 47.2 (CH2), 107.9 (CH), 120.9 (CH), 122.6 (C), 125.0 (CH), 127.7 (CH), 127.8 (2 x CH), 128.1 (2 x CH), 128.6 (2 x CH), 130.4 (C), 131.3 (2 x CH), 133.3 (C), 136.8 (CH) ppm; GCMS (EI): *m/z* (%):217 (18), 232 (100), 233 (26), 246 (15), 303 (82) [M^+], 304 (20); HRMS (ESI-TOF): *m/z*: calcd for $C_{22}H_{25}N$: 304.20598 $[M+H]^+$; found: 304.20605.



1-Phenethyl-4,5,6,7-tetrahydro-1H-indole (15c):[12] Following the general procedure, **15c** was obtained as a slightly yellow oil (33.8 mg, 0.15 mmol, 30%); ^{1}H NMR (400 MHz, DMSO-d6) δ = 1.50 – 1.75 (m, 4H), 2.34 (dt, *J*=28.9, 6.3, 4H), 2.82 – 2.92 (m, 2H), 3.90 (dd, *J*=8.2, 6.7, 2H), 5.71 (d, *J*=2.7, 1H), 6.53 (d, *J*=2.7, 1H), 7.09 – 7.15 (m, 2H), 7.15 – 7.32 (m, 3H) ppm; ^{13}C NMR (100 MHz, DMSO-d6) δ = 21.0 (CH_2), 23.0 (CH_2), 23.1 (CH_2), 23.3 (CH_2), 37.5 (CH_2), 46.9 (CH_2), 105.8 (CH), 115.7 (C), 118.4 (CH), 126.2 (CH), 126.6 (C), 128.2 (2 x CH), 128.8 (2 x CH), 138.8 (C) ppm; GCMS (EI): *m/z* (%): 197 (11), 224 (12), 225 (100) [M^+], 226 (18); HRMS (ESI-TOF): *m/z*: calcd for $C_{16}H_{19}N$: 226.15903 $[M+H]^+$; found: 226.15908.

12 M. Zhang, X. Fang, H. Neumann and M. Beller, *J. Am. Chem. Soc.*, **2013**, *135*, 11384-11388.

5



Molecular structure of rhenium complex 5 in the crystal. Displacement ellipsoids correspond to 30% probability. Hydrogen atoms except the NH-proton and solvent molecules are omitted for clarity. There are two molecules in the asymmetric unit of which one is shown.

Deposition number at the Cambridge Crystallographic Data Centre: CCDC 1522448.

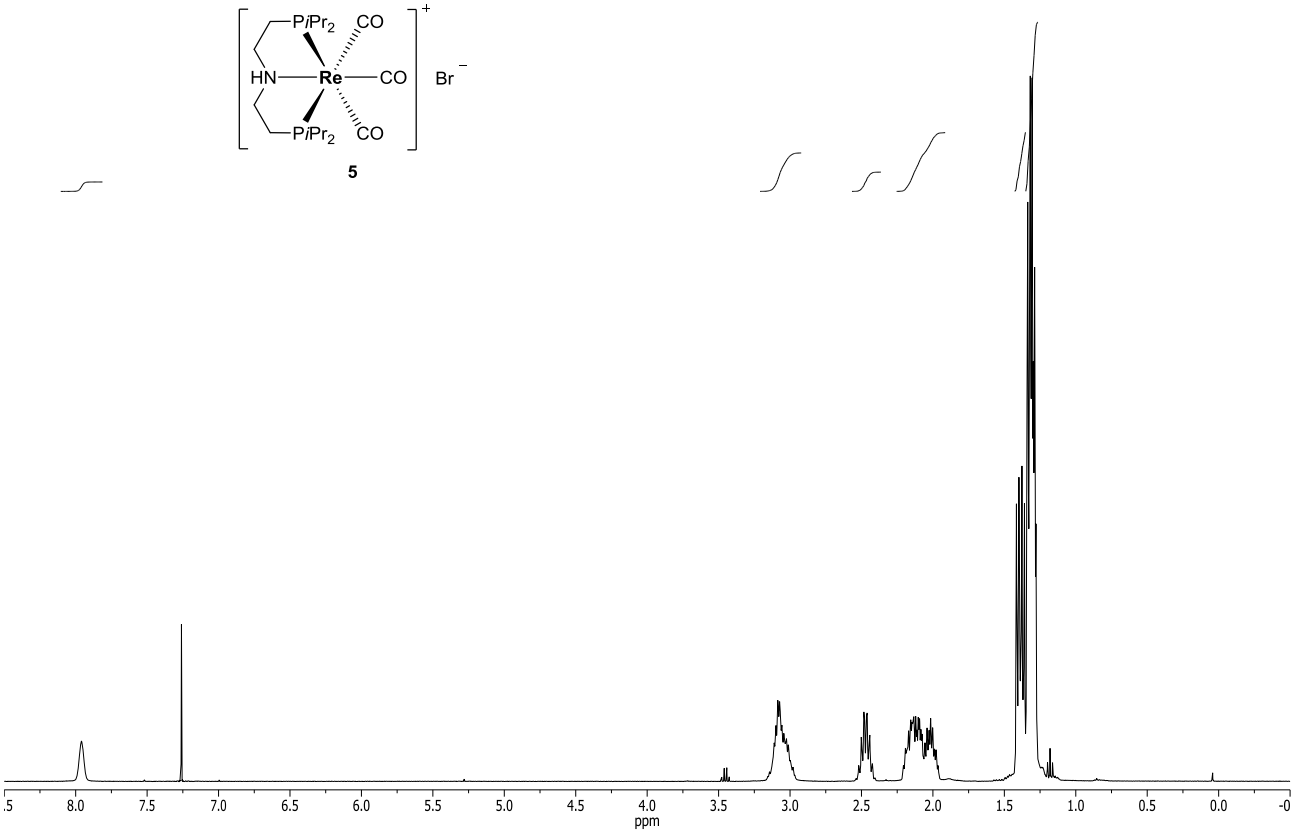
X-ray crystal structure analysis of rhenium complex 5:

Data were collected on a Bruker Kappa APEX II Duo diffractometer. The structure was solved by direct methods (SHELXS-97: Sheldrick, G. M. *Acta Crystallogr.* **2008**, *A64*, 112) and refined by full-matrix least-squares procedures on F^2 (SHELXL-2014: Sheldrick, G. M. *Acta Crystallogr.* **2015**, *C71*, 3). XP (Bruker AXS) was used for graphical representation.

Crystal data: $C_{21}H_{39}BrCl_6NO_3P_2Re$, M = 894.28, triclinic, space group P-1, a = 13.1267(4), b = 14.3240(4), c = 19.7297(6) Å, α = 73.2323(7)°, β = 86.4712(7)°, γ = 74.3165(7)°, V = 3419.20(18) Å^3, T = 150(2) K, Z = 4, 107219 reflections measured, 15704 independent reflections (R_{int} = 0.0380), final R values ($I > 2\sigma(I)$): R_1 = 0.0223, wR_2 = 0.0486, final R values (all data): R_1 = 0.0301, wR_2 = 0.0517, 683 parameters.

160610.440.12.fid
Piehl/ PP 194
Au1H CDCl3 /opt/topspin 1606 40

5



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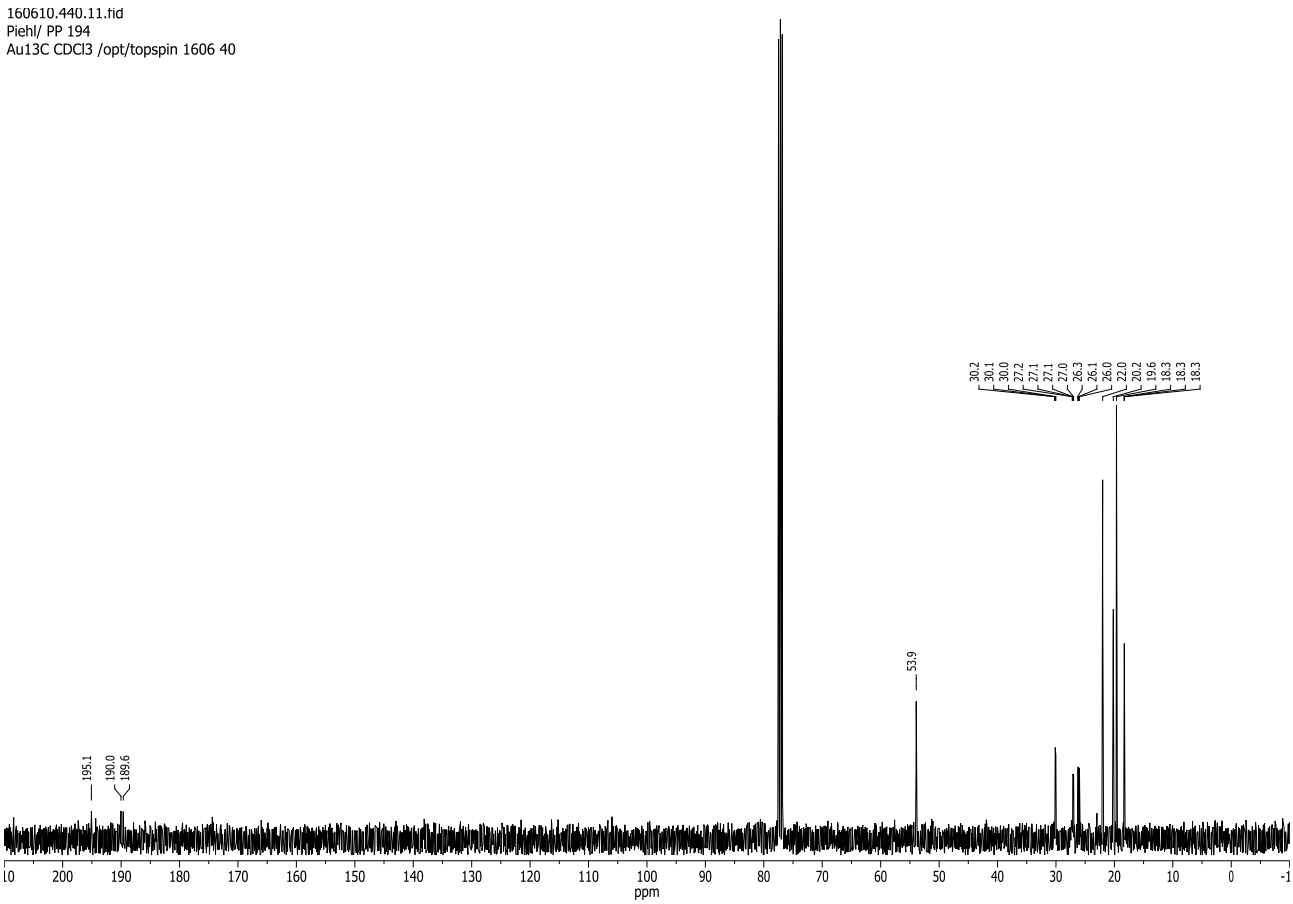

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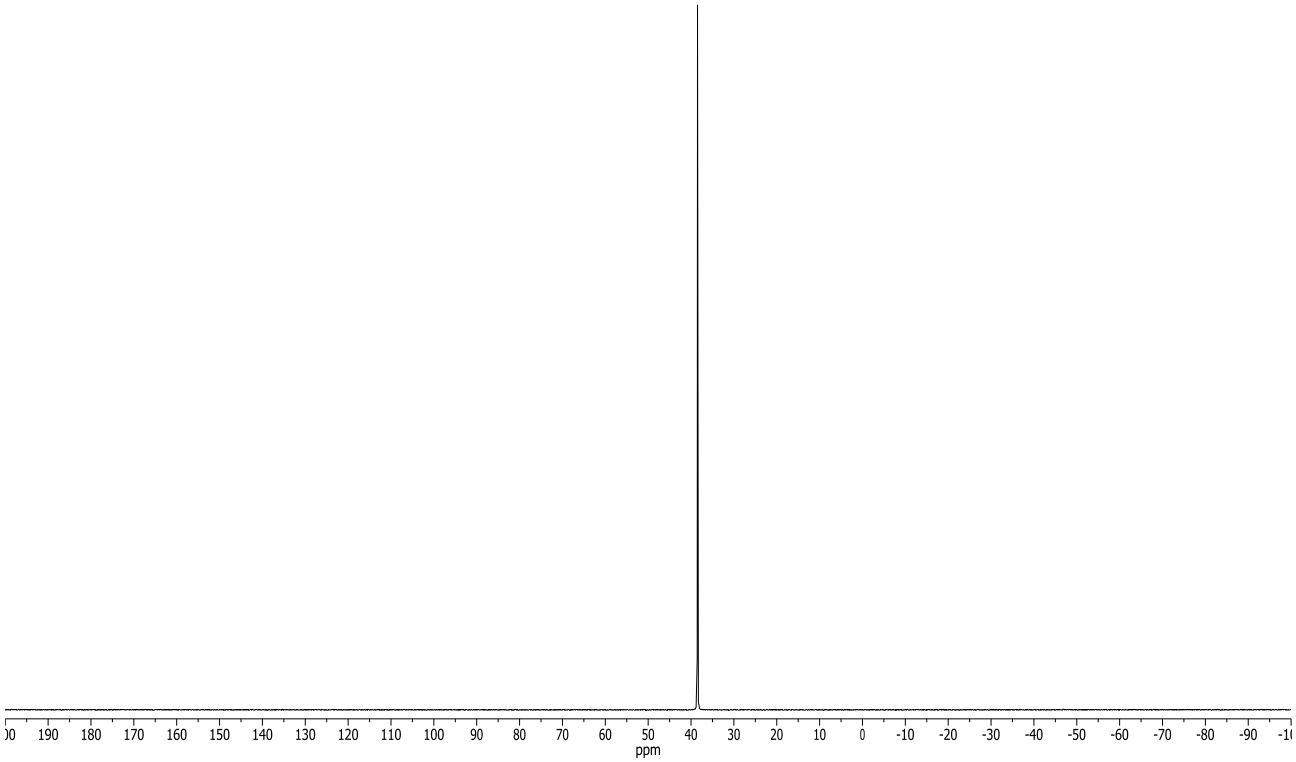

^{31}P-NMR

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Miguel/ MPL PP 011
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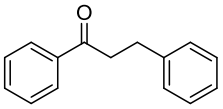

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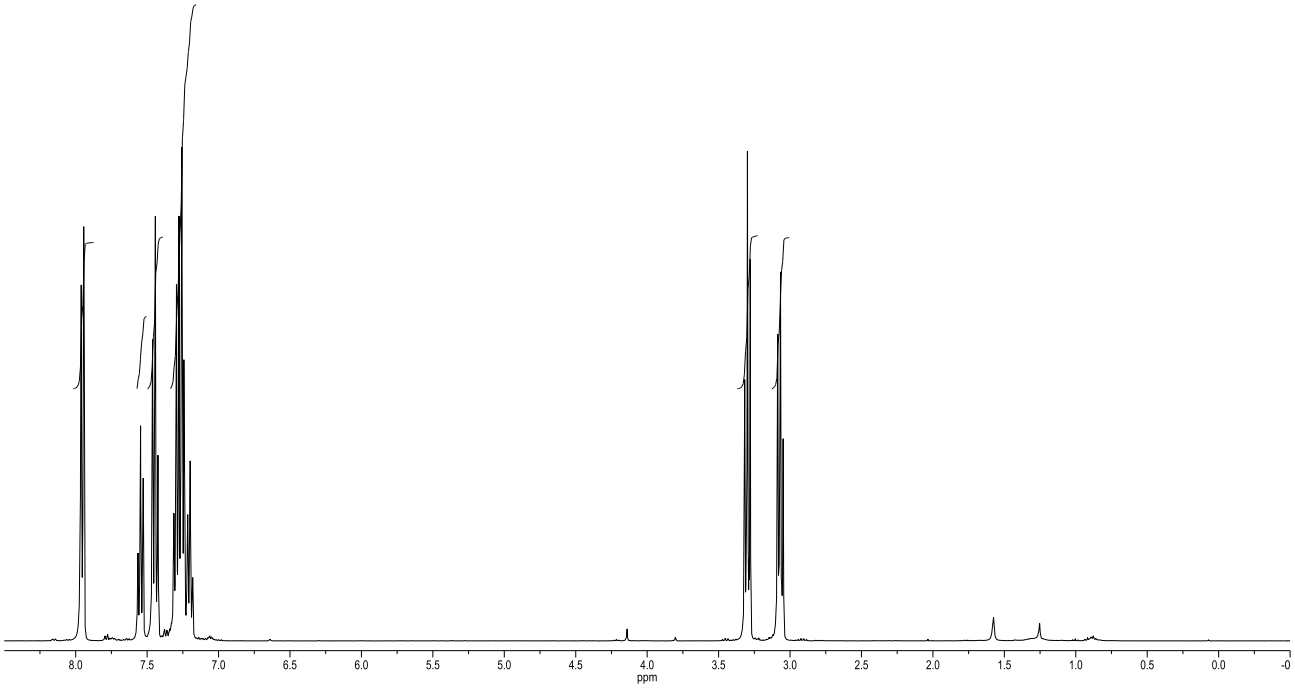

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Miguel/ MPL PP 011
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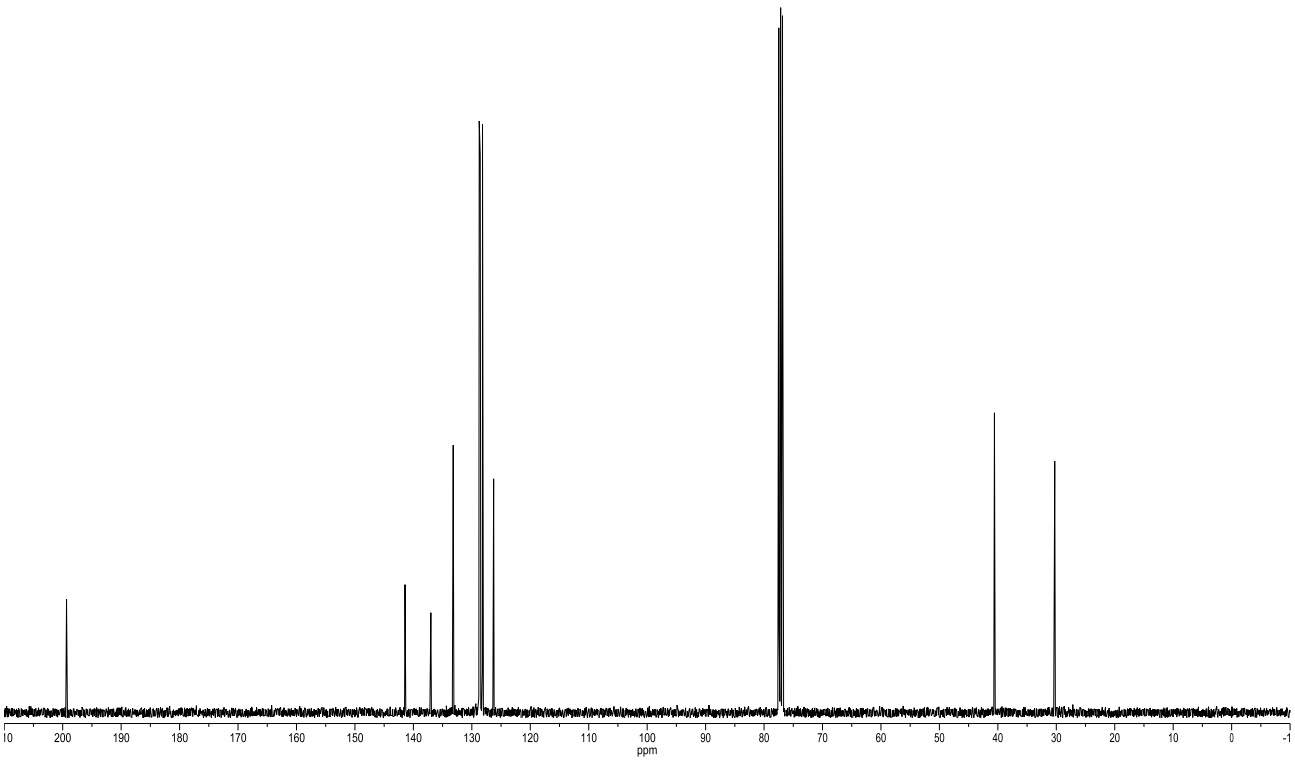

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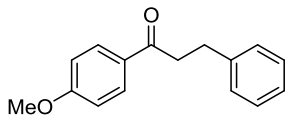
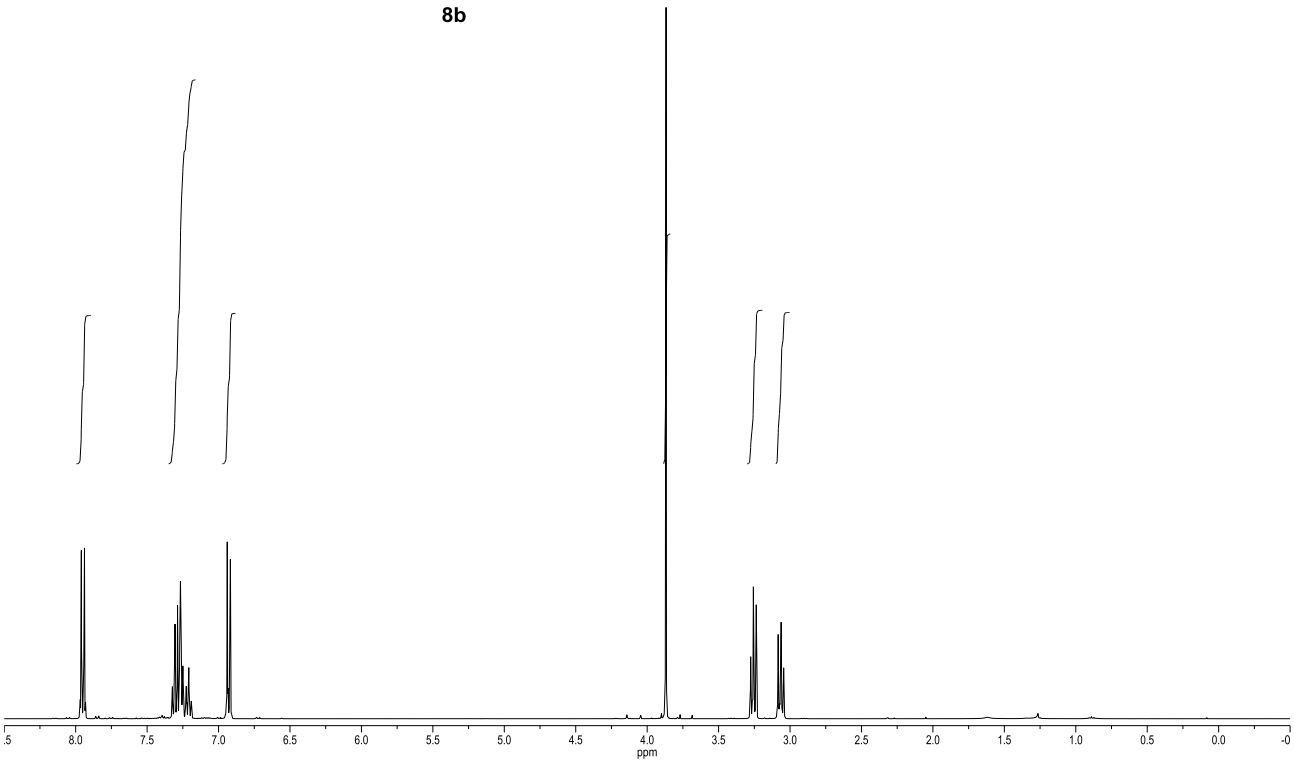


8b



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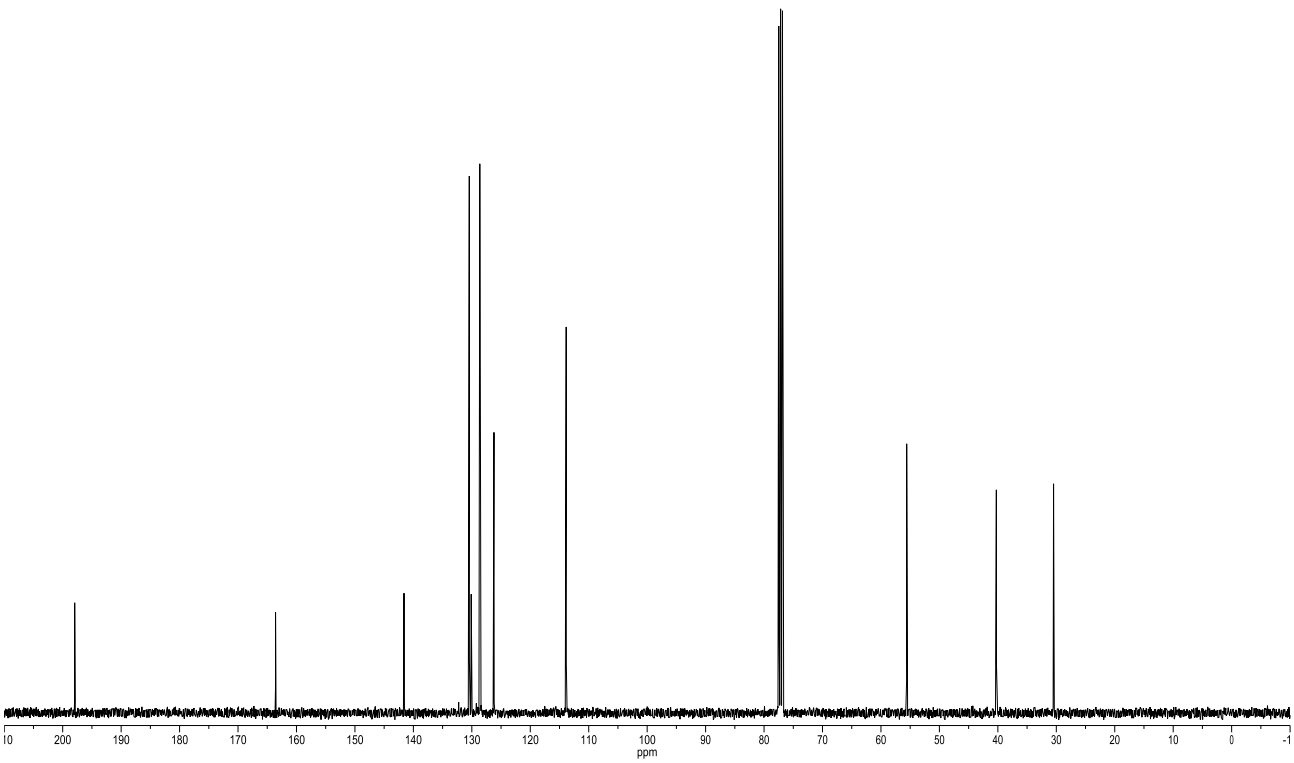
Au13C CDCl3 /opt/topspin 1602 17



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Miguel/ MPL PP 079
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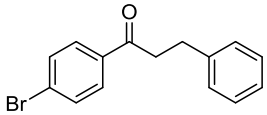

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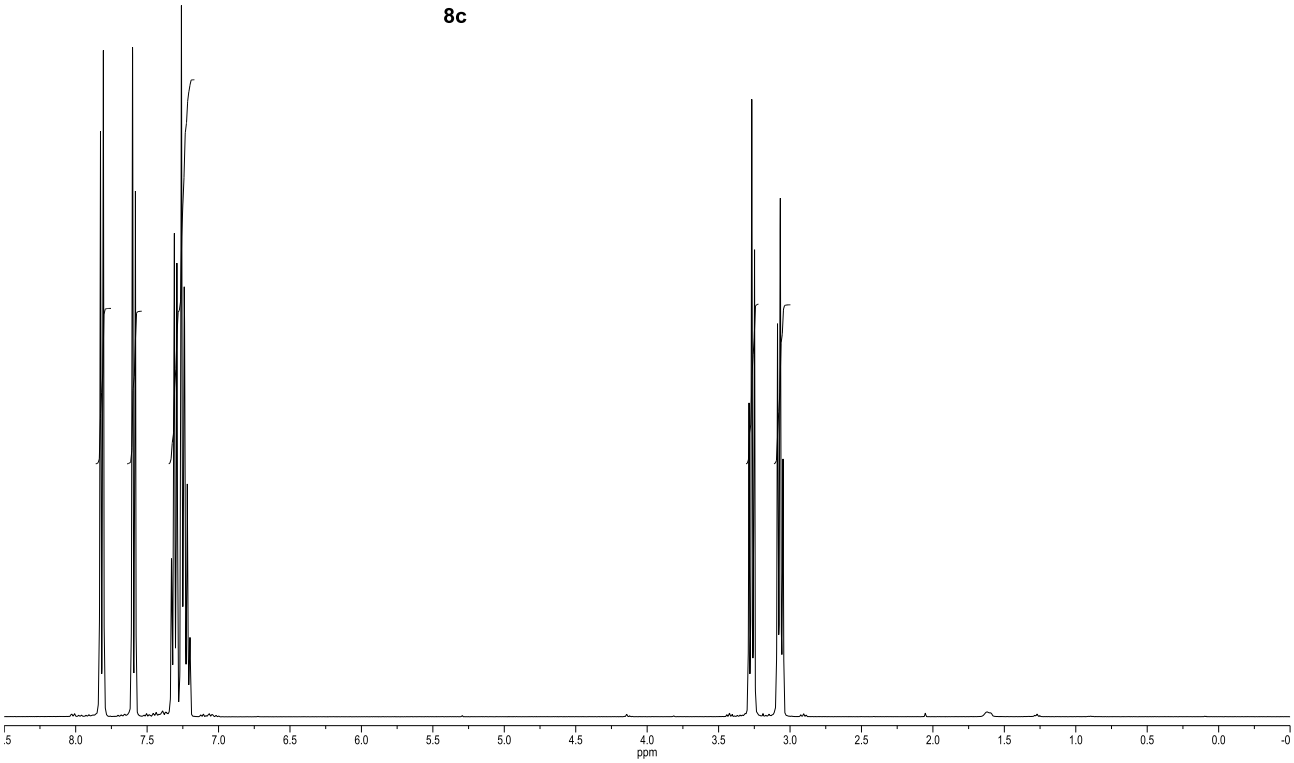

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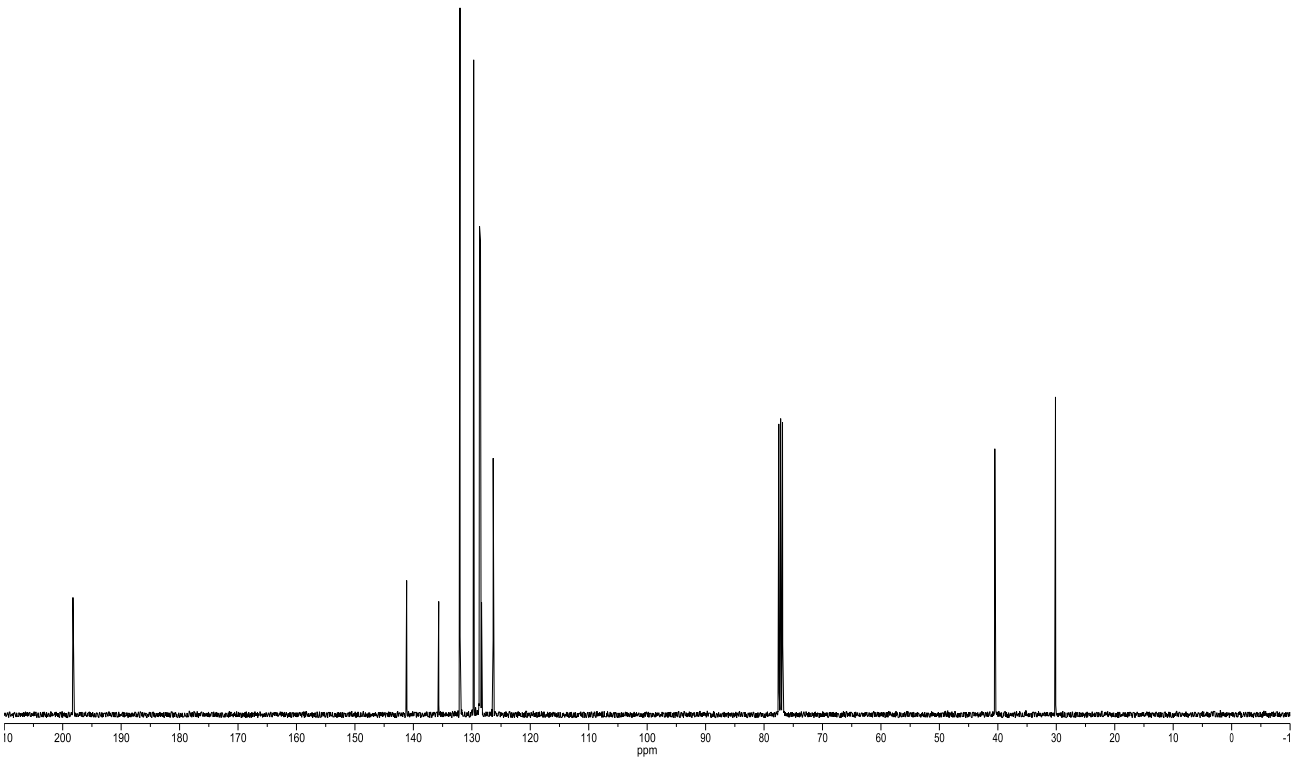

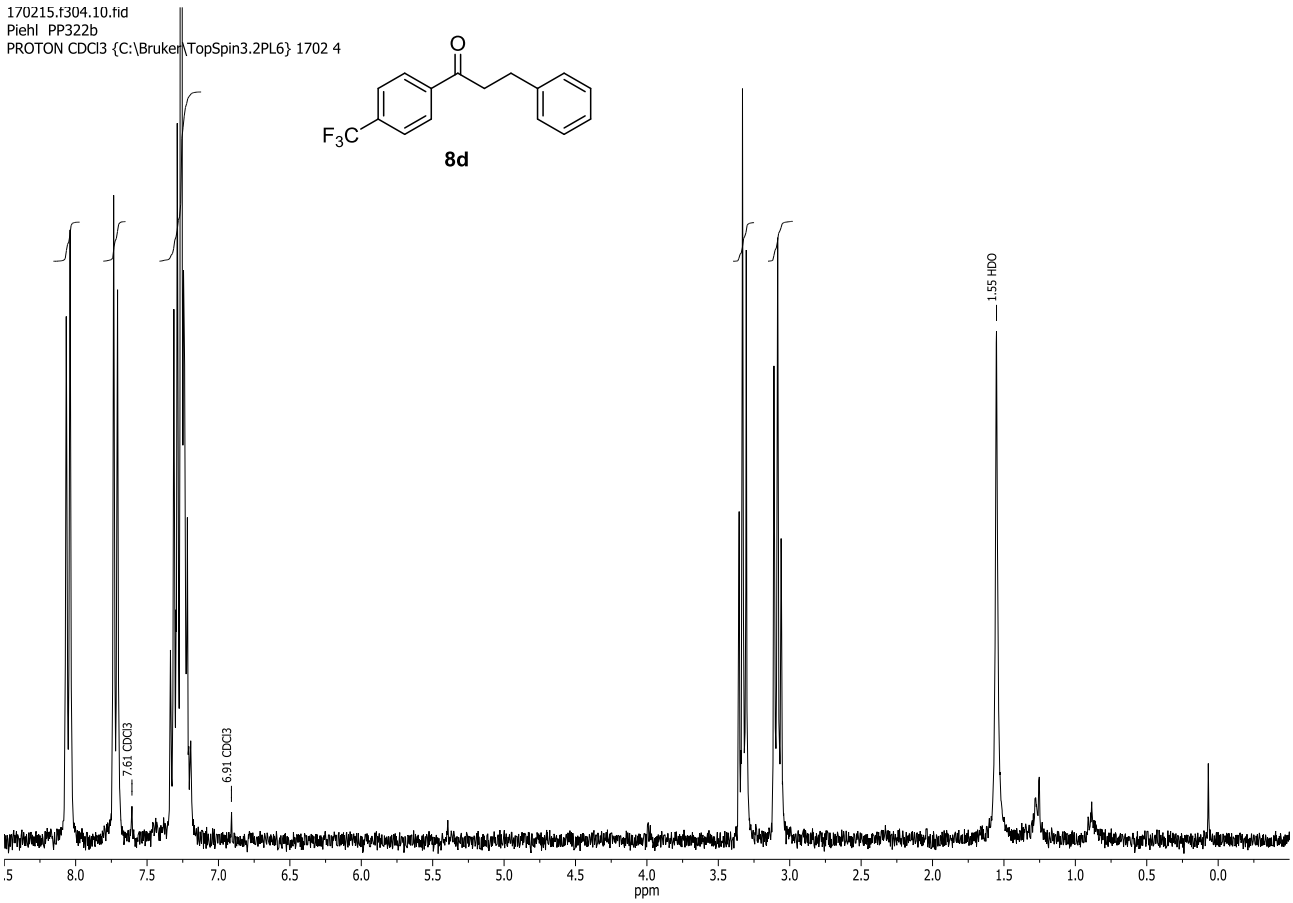
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Piehl PP322b
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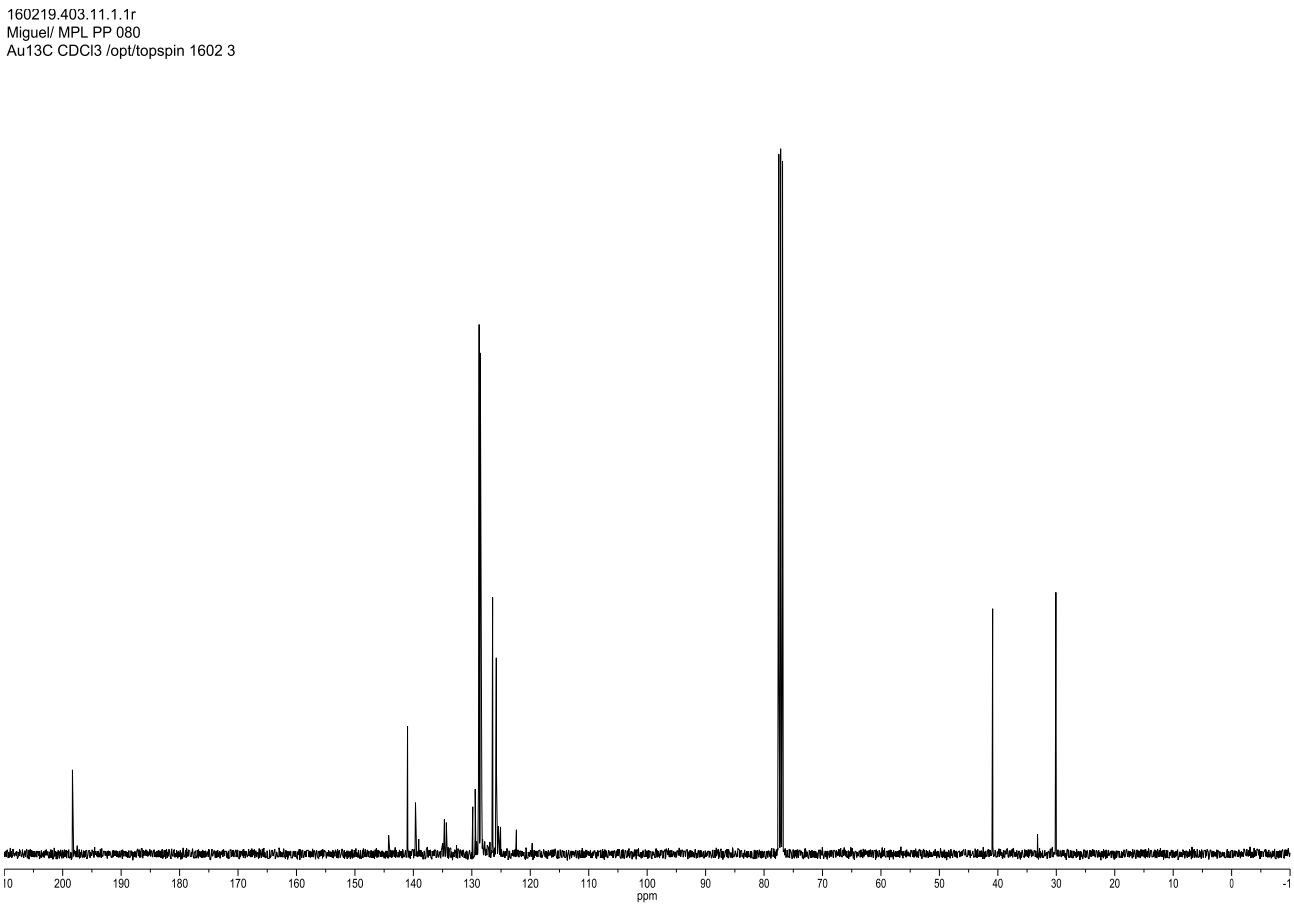
ppm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Miguel/ MPL PP 080
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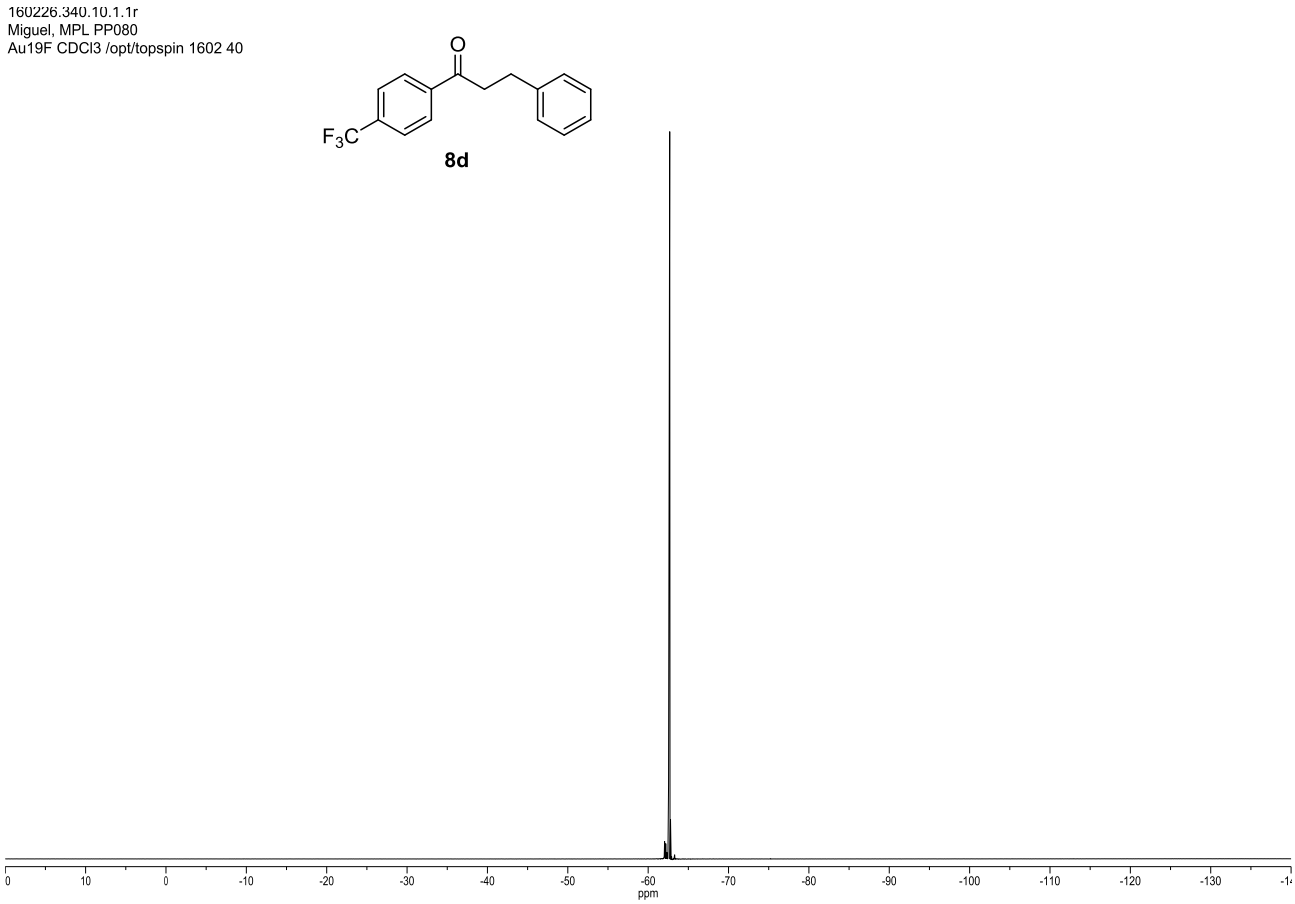
ppm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Miguel, MPL PP080
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O
F3C
8d
0
10
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ppm

^{19}F-NMR

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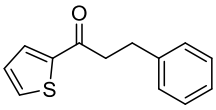

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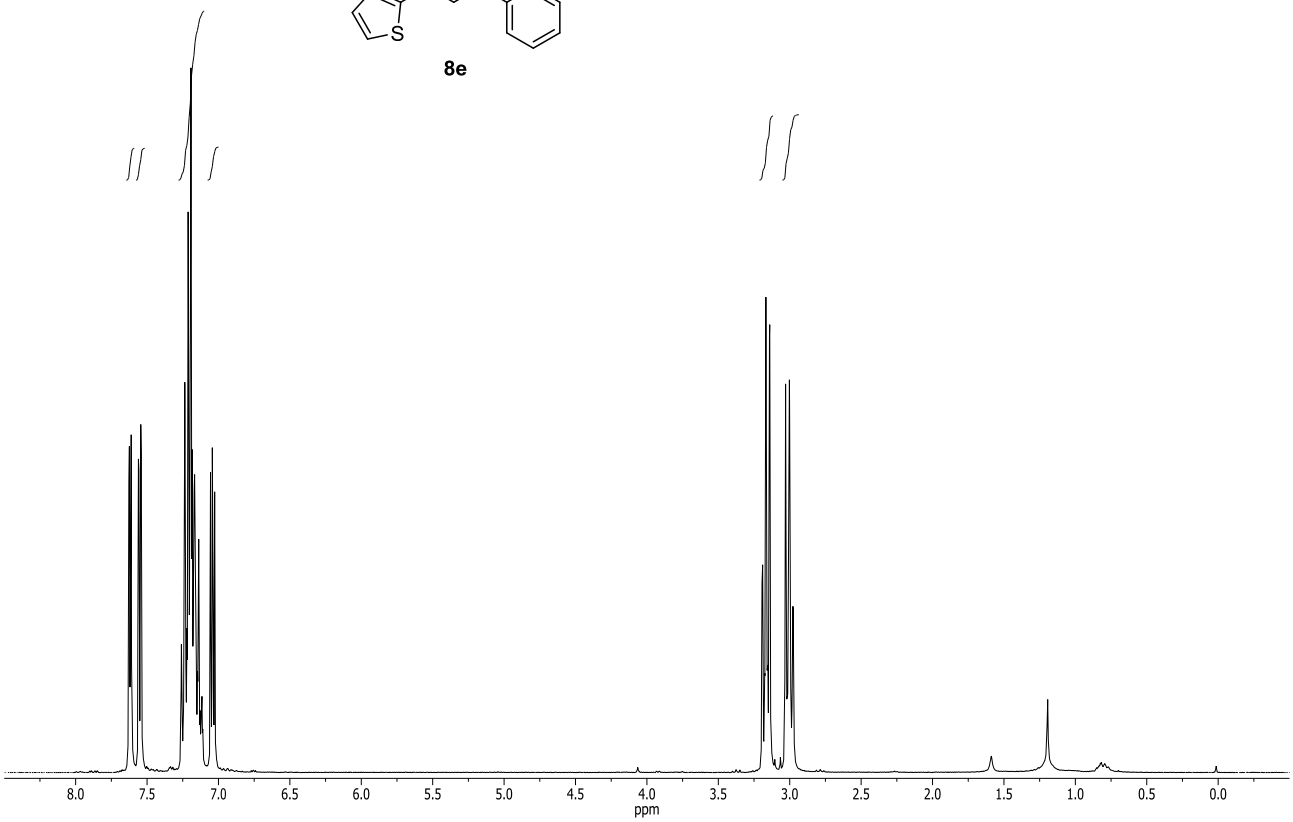

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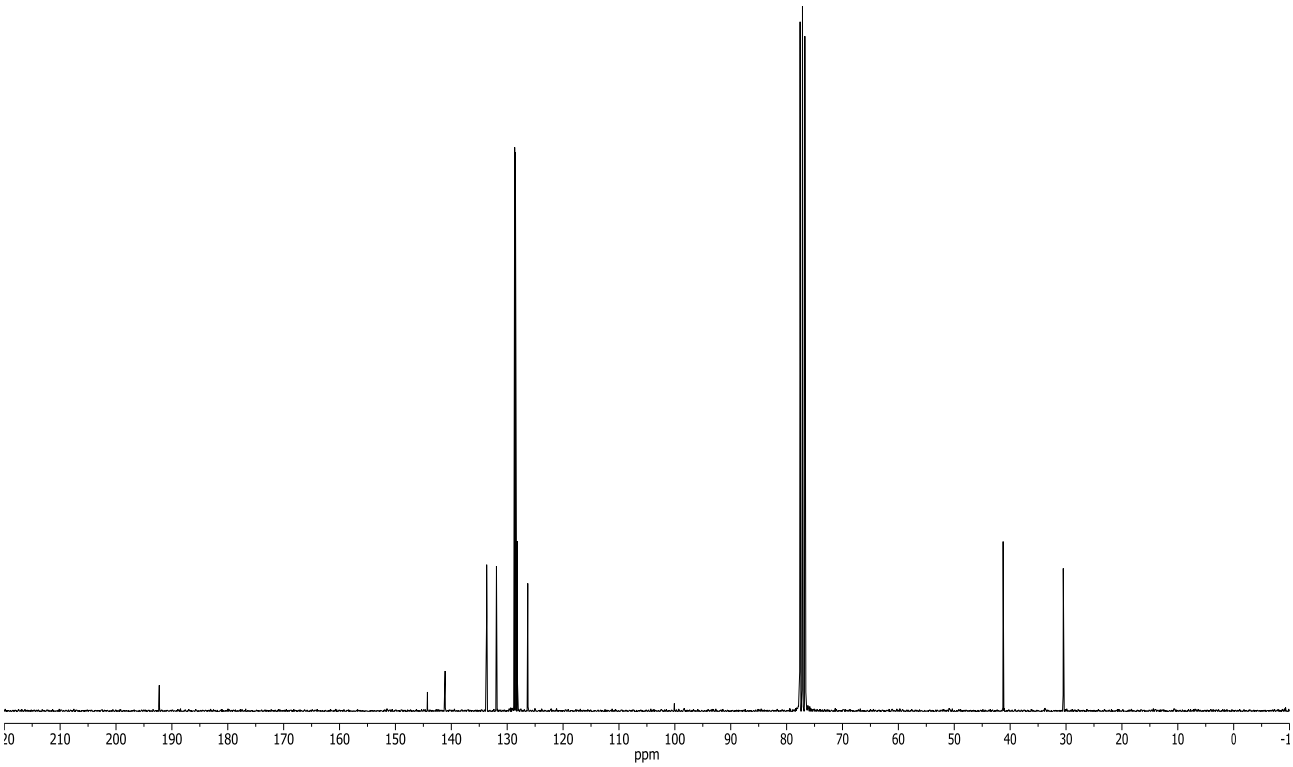

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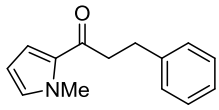
Au1H CDCl3 /opt/topspin 1602 24



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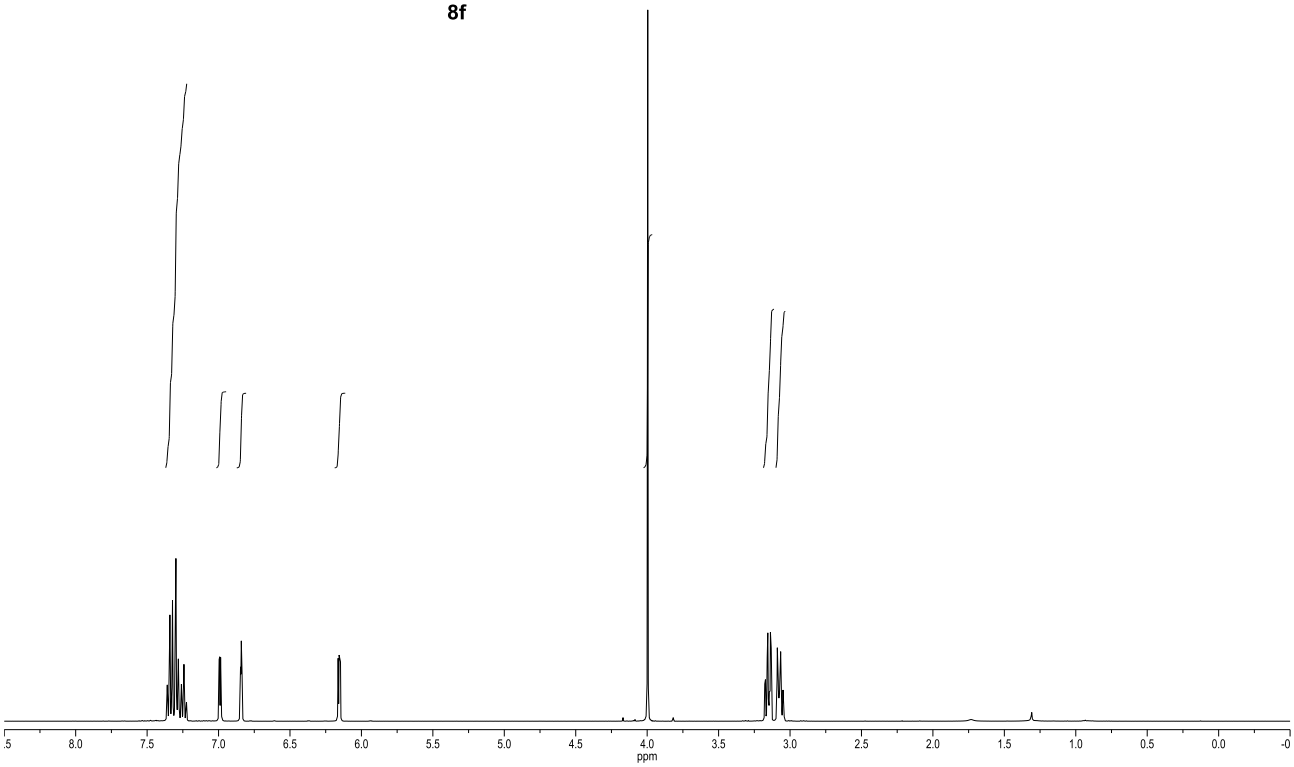

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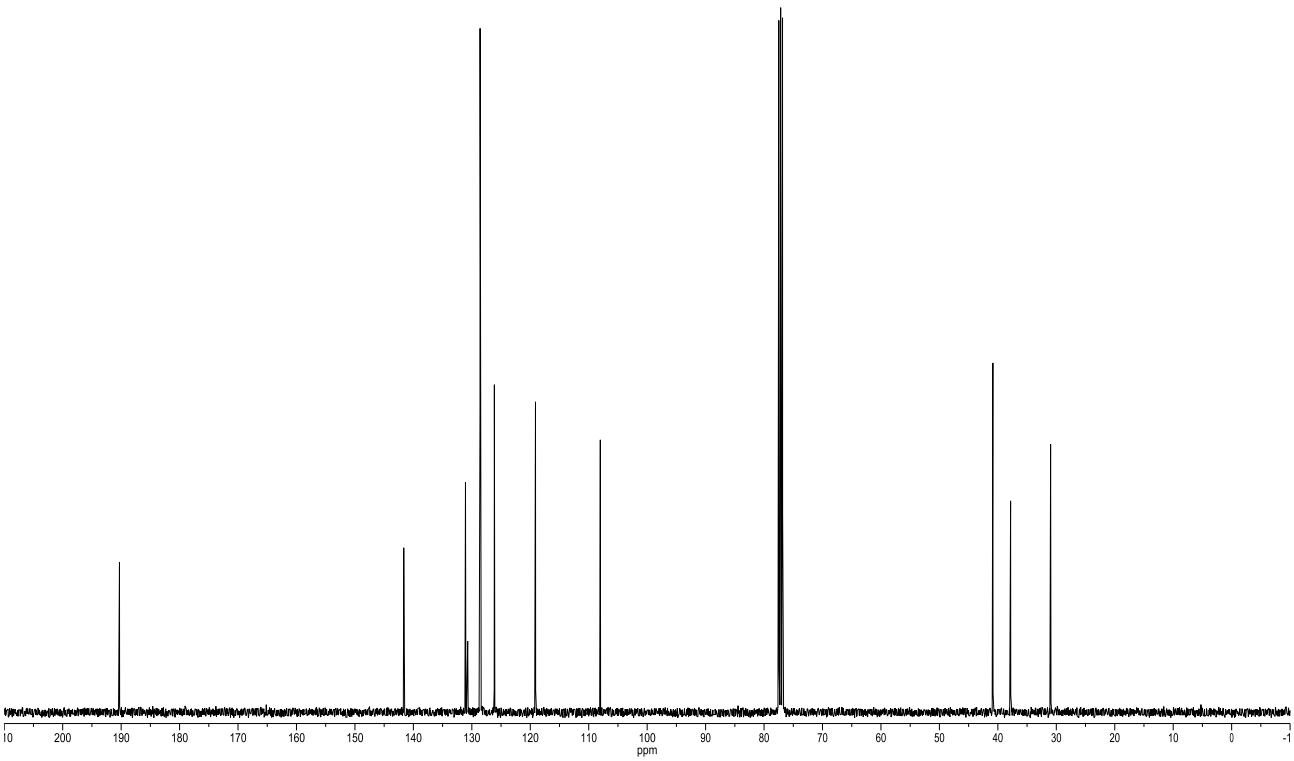

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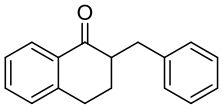

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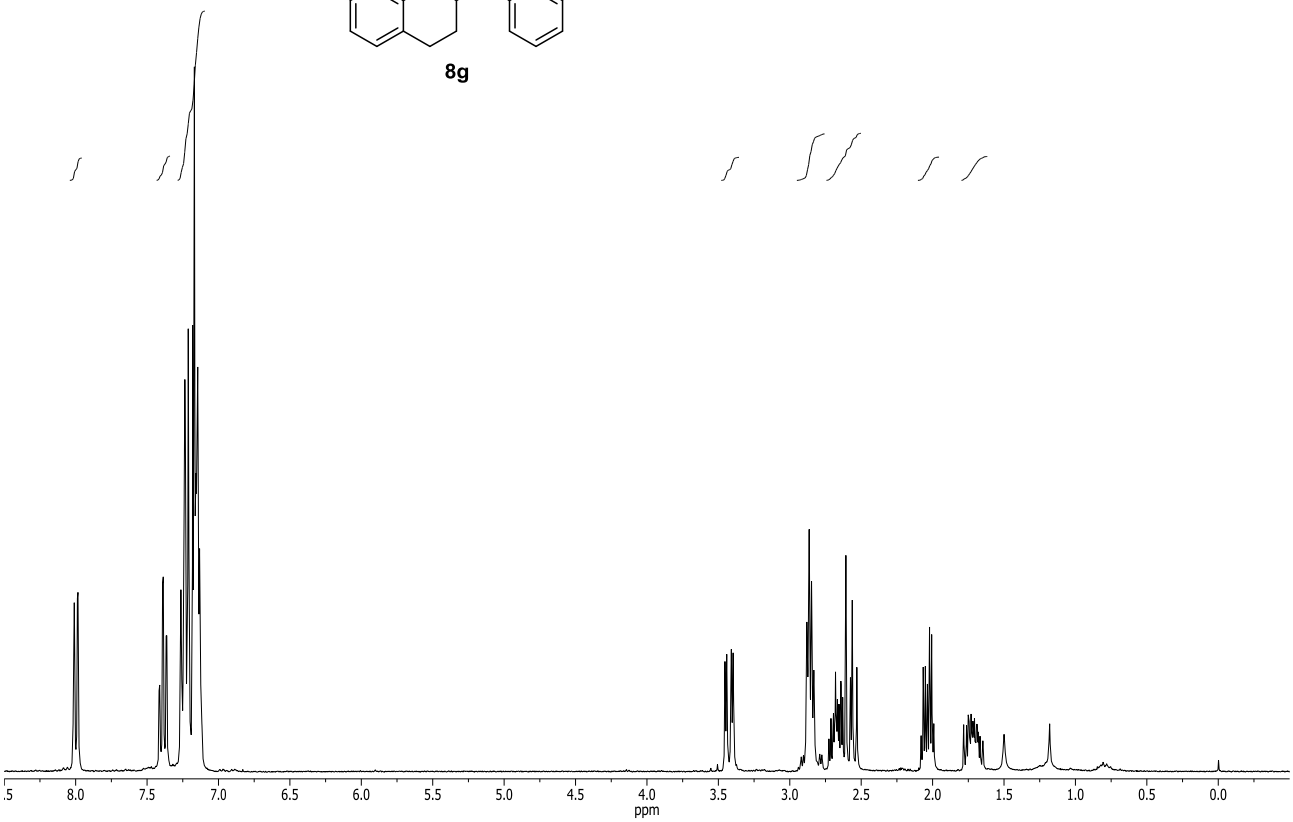

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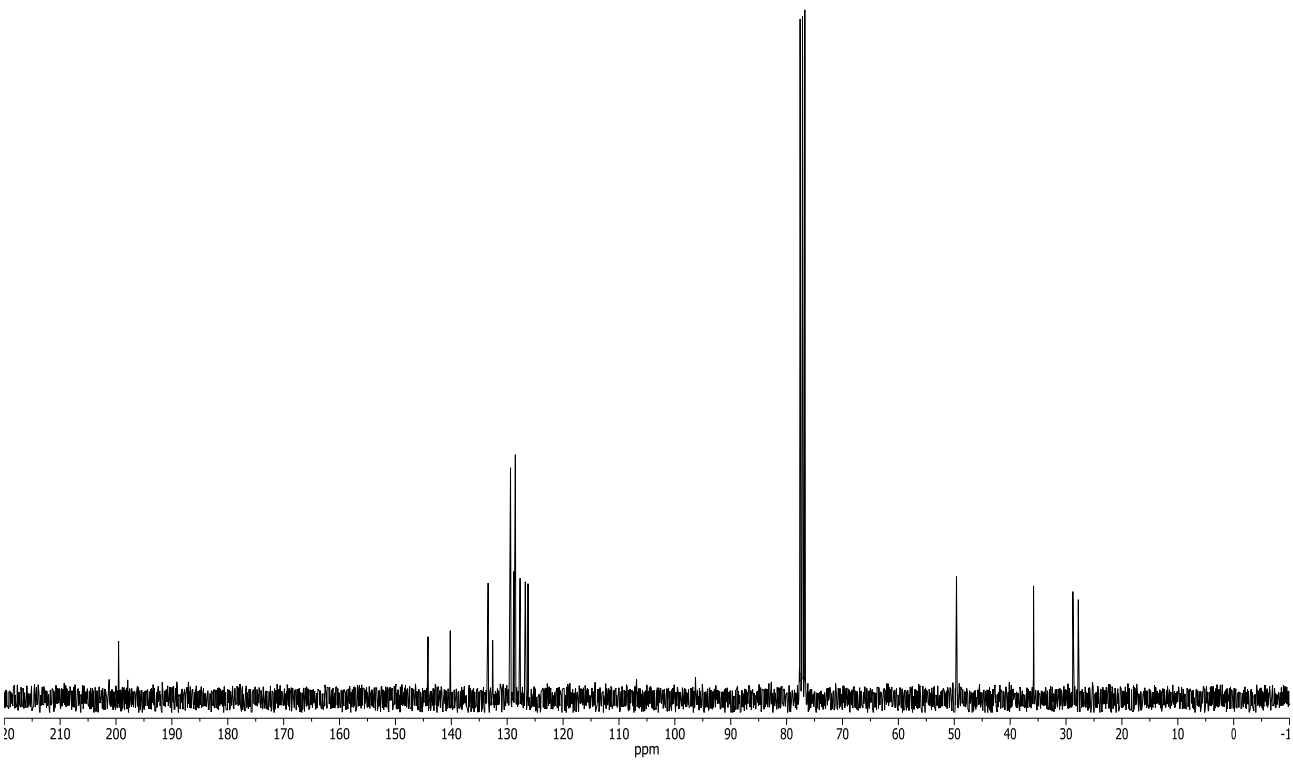

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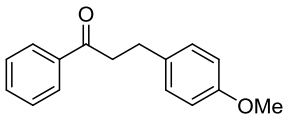

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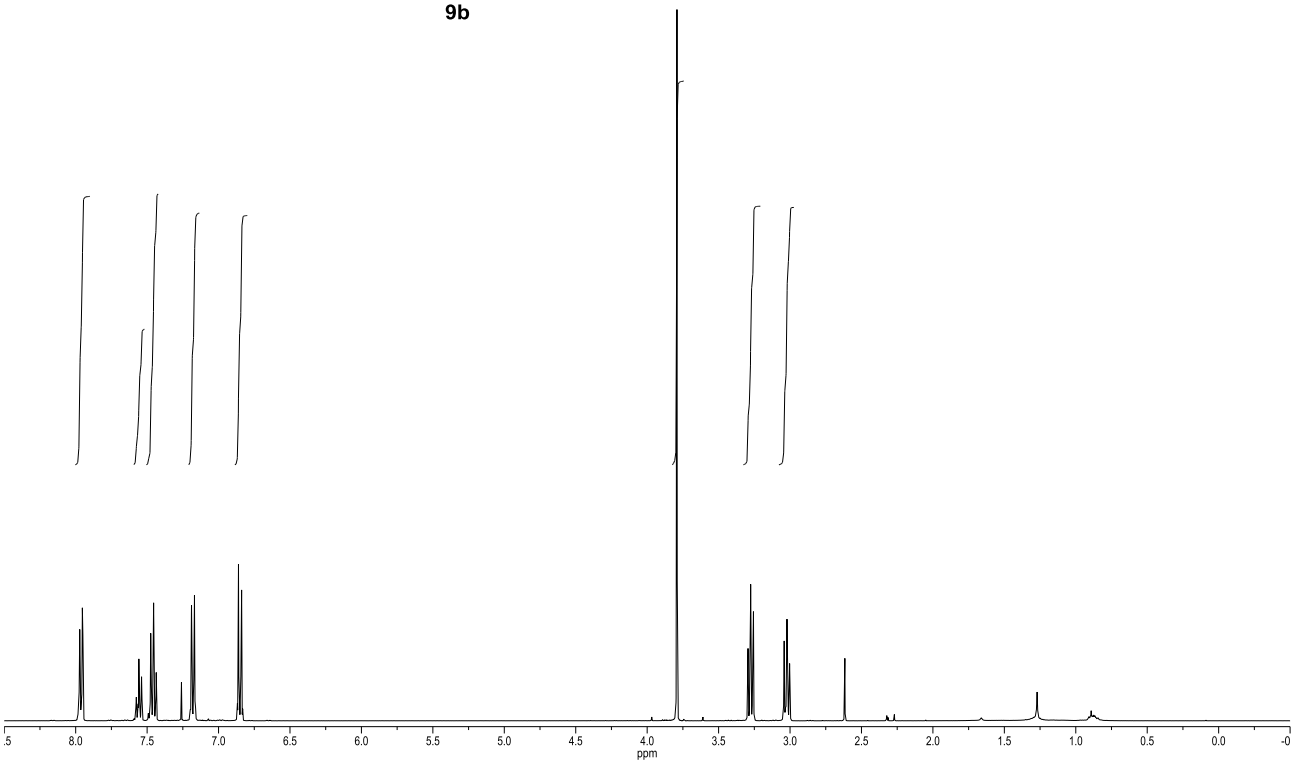

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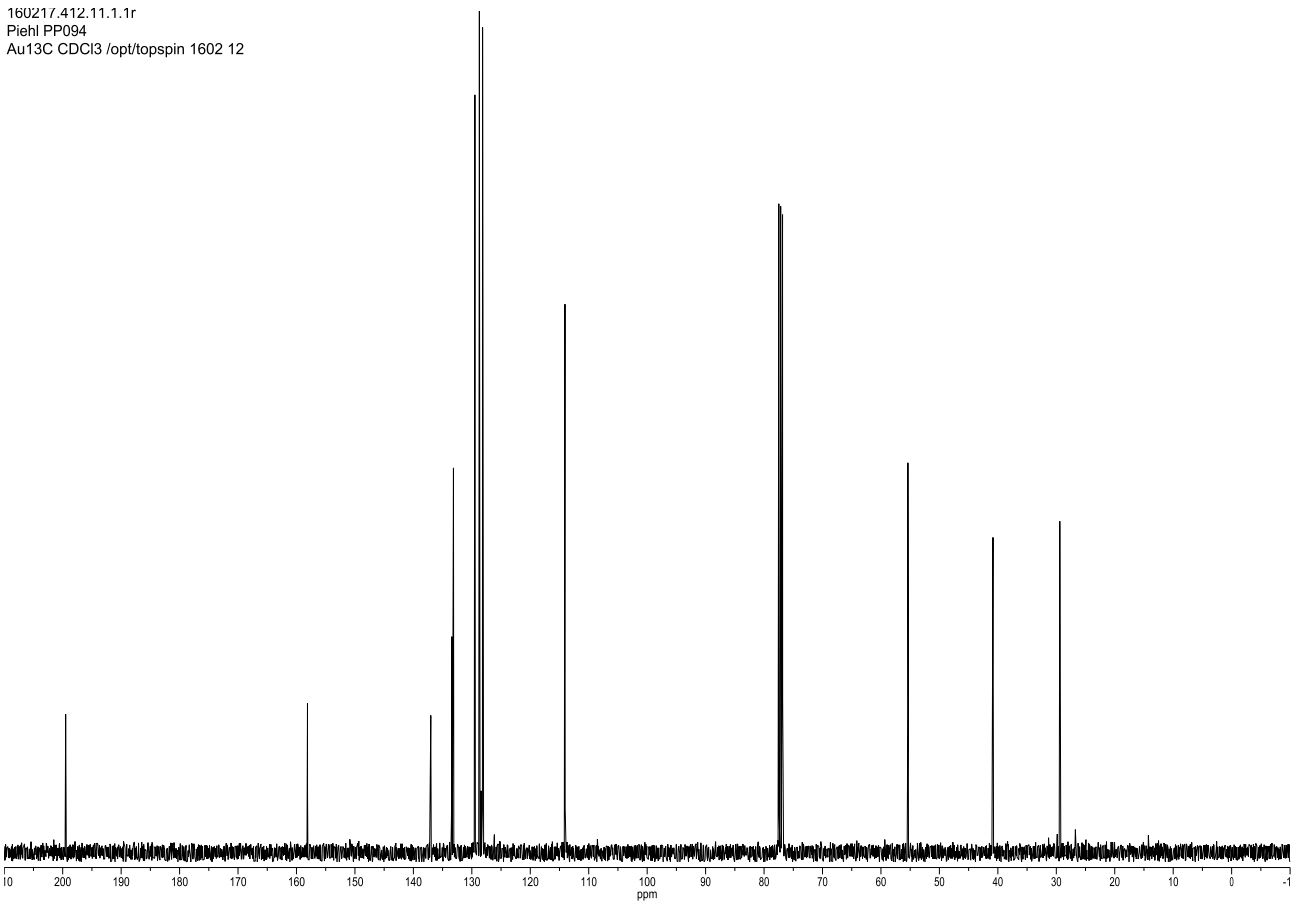

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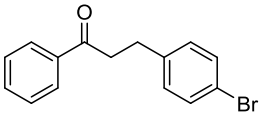

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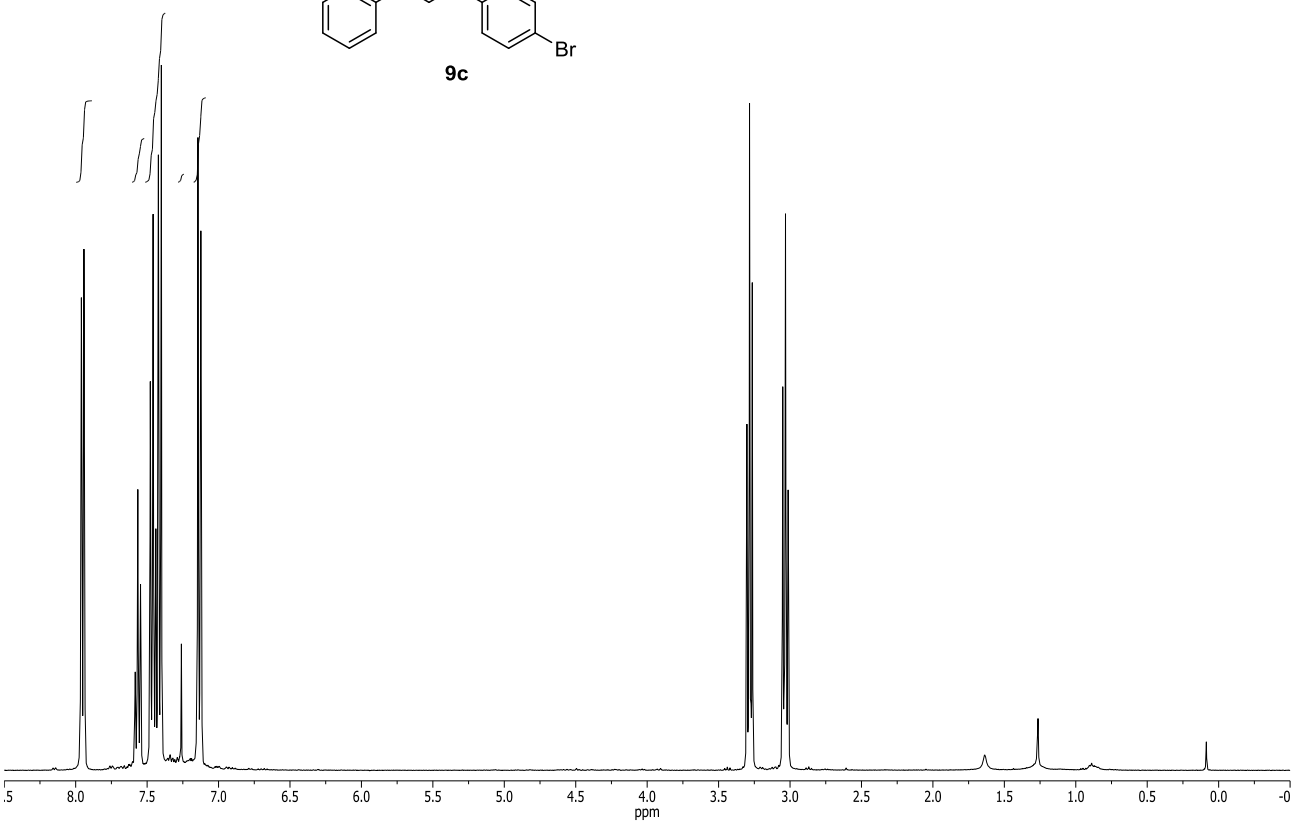

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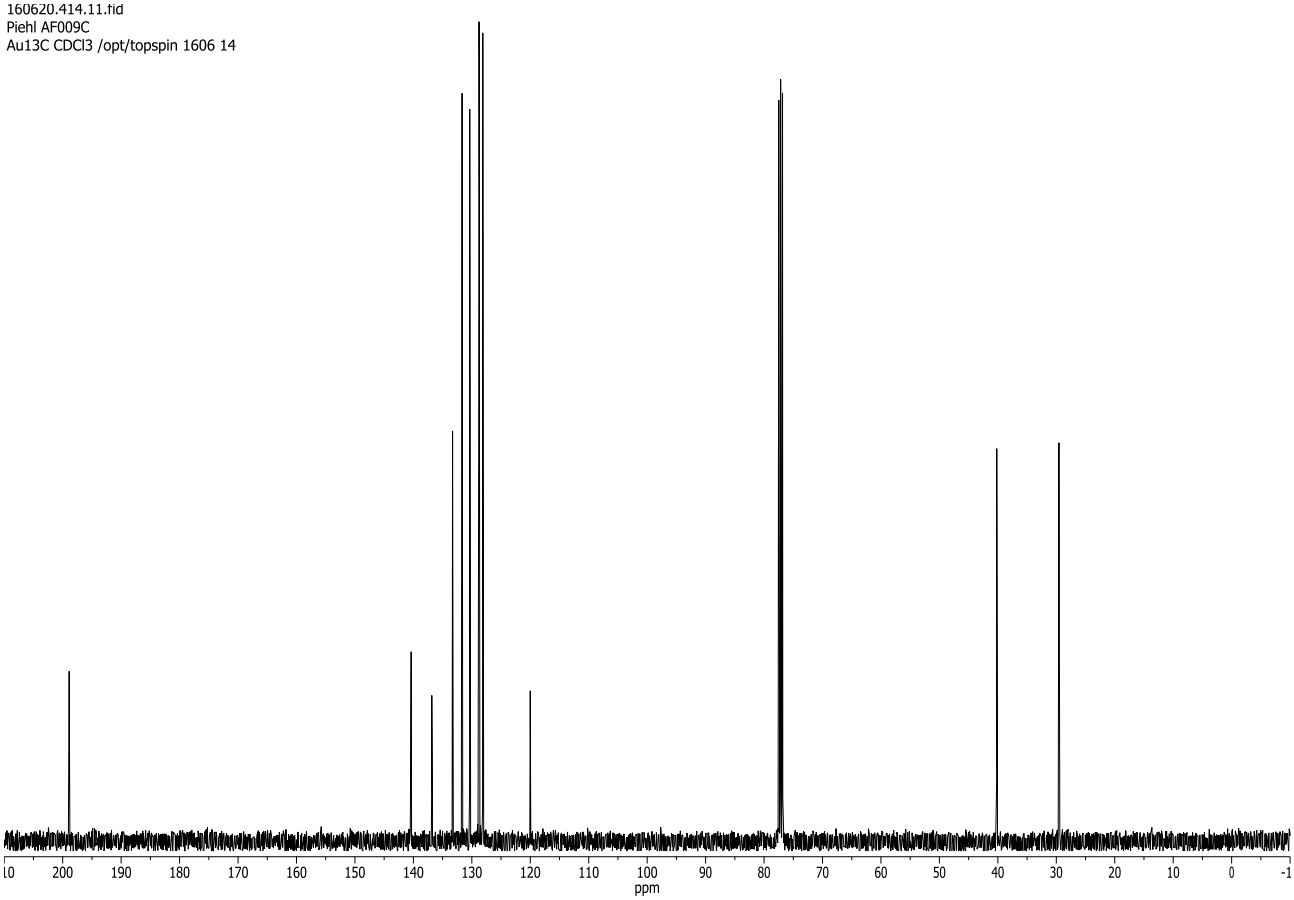

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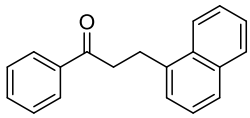
Au1H CDCl3 /opt/topspin 1701 10



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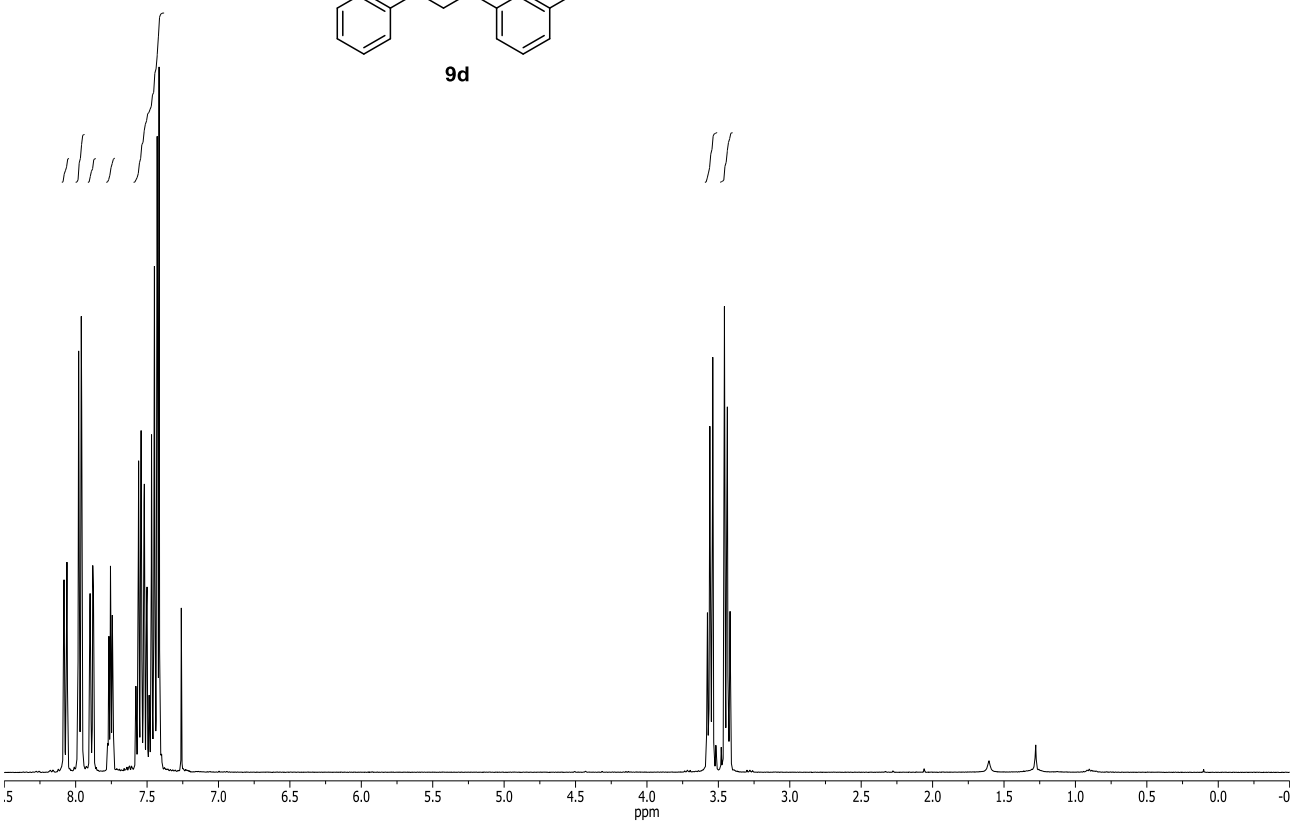

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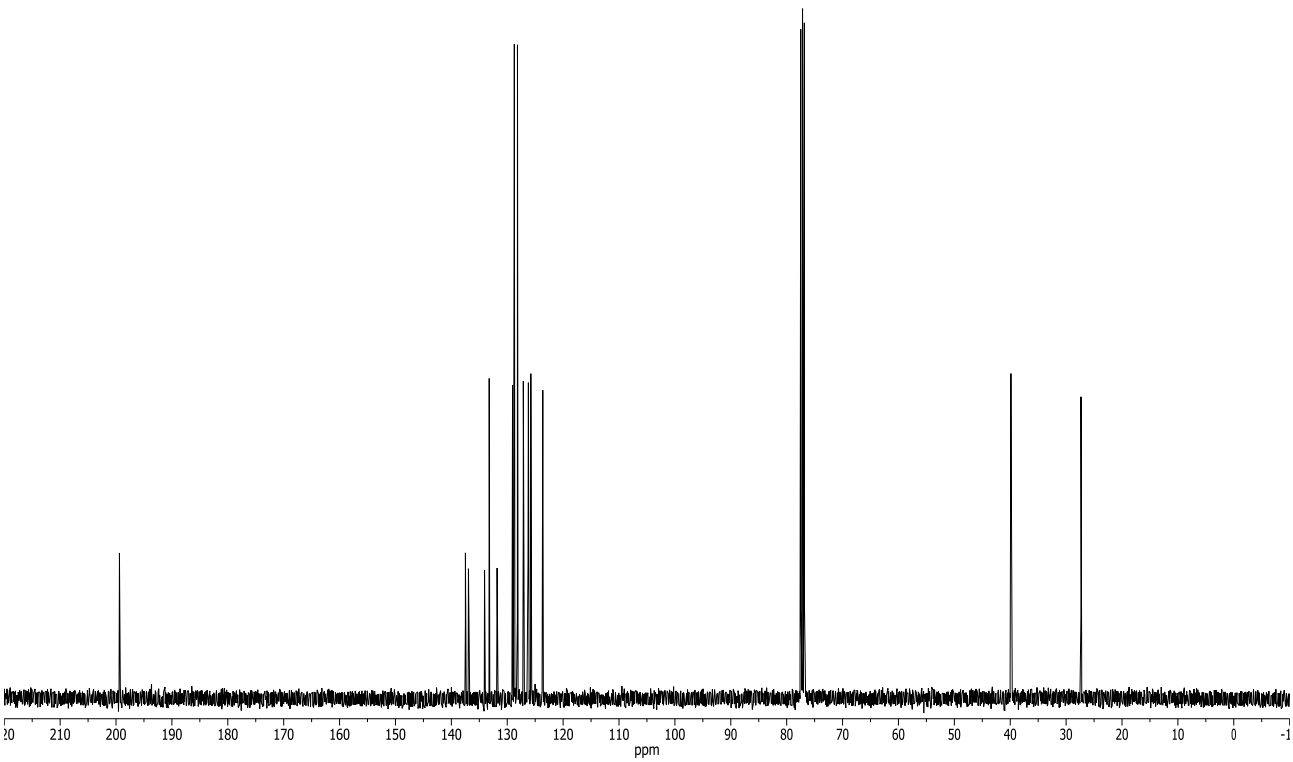

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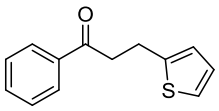

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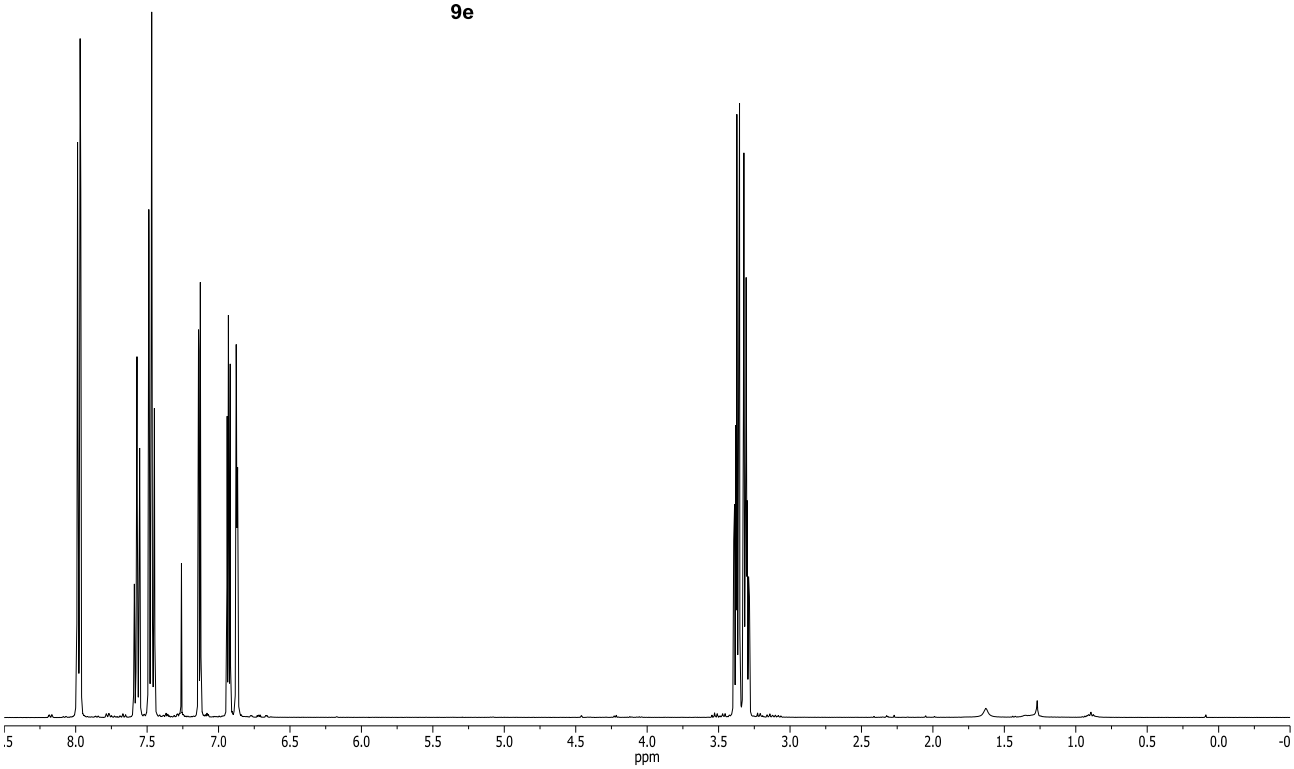

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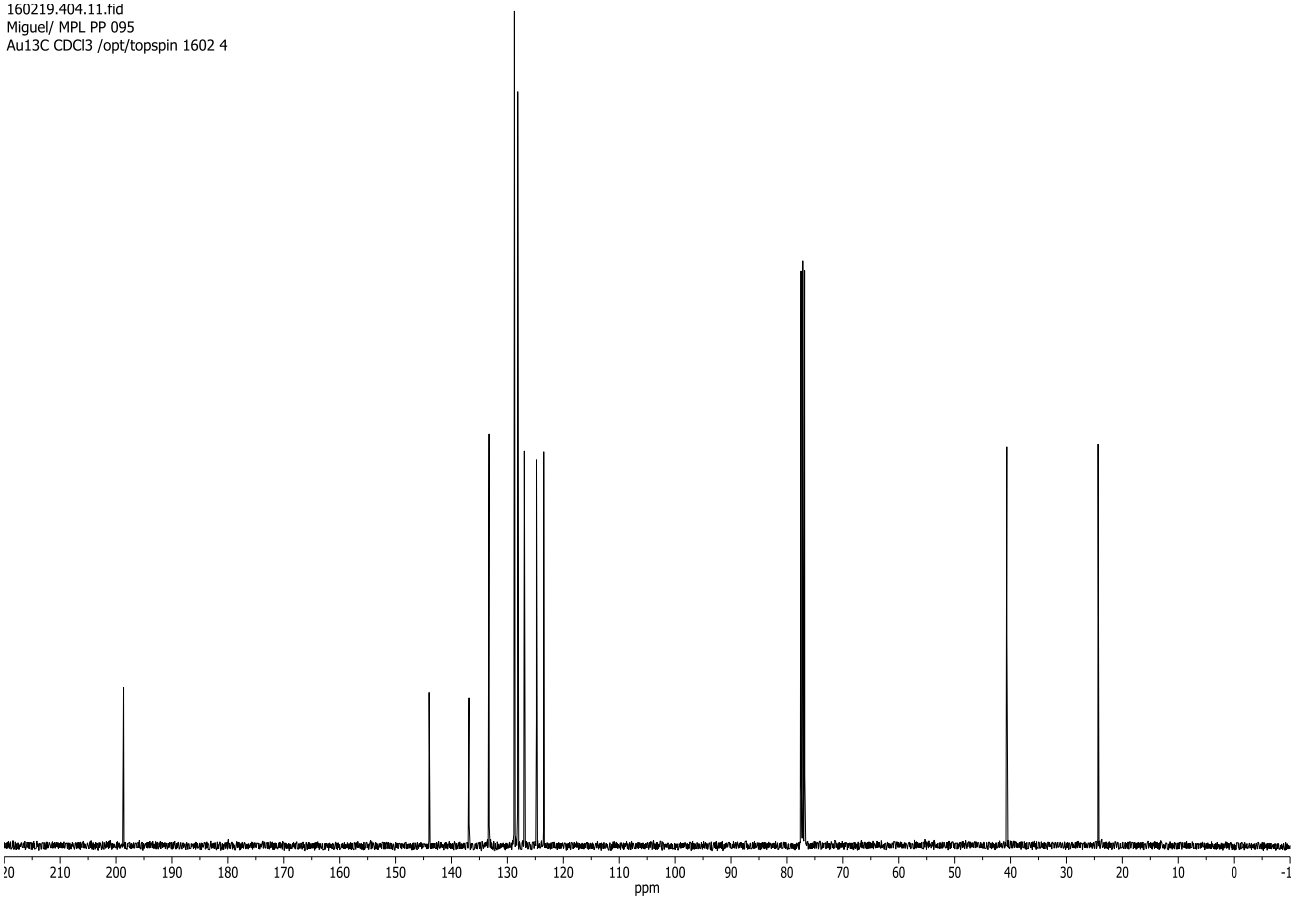

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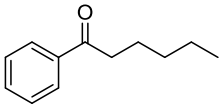

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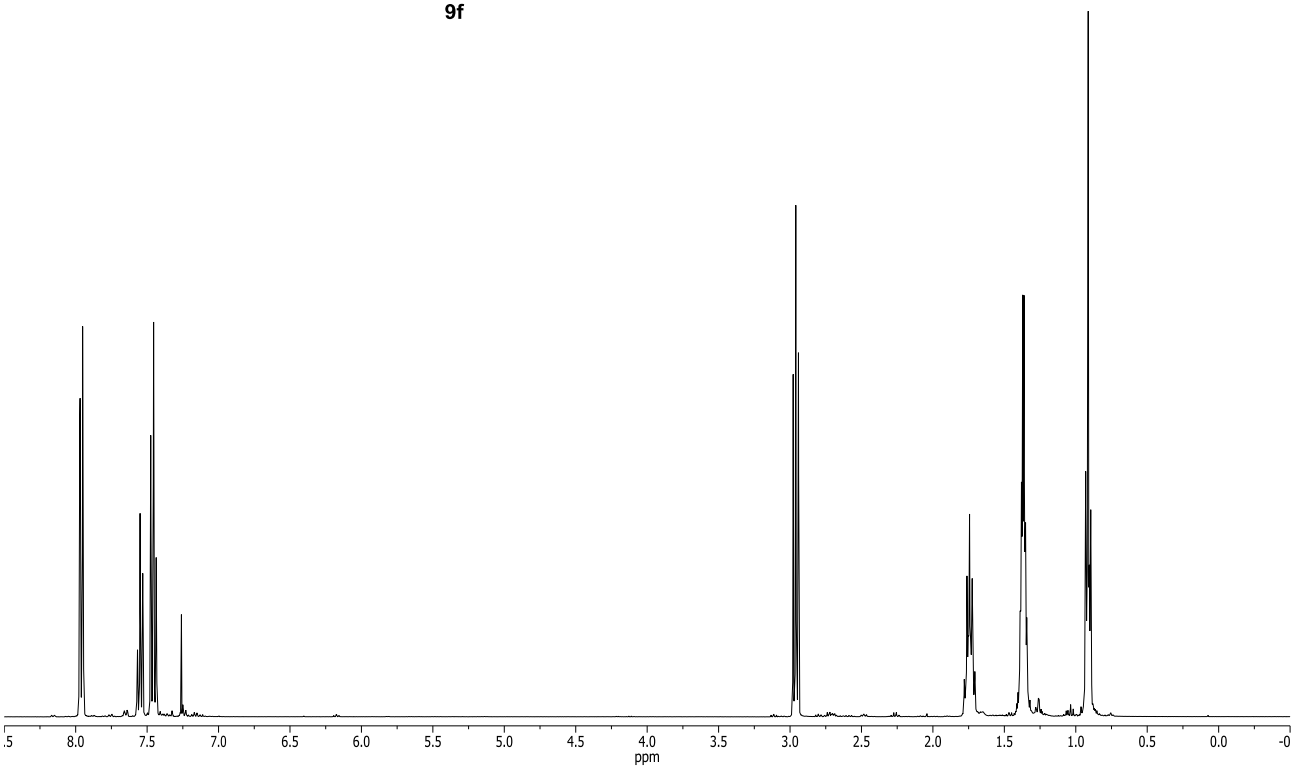

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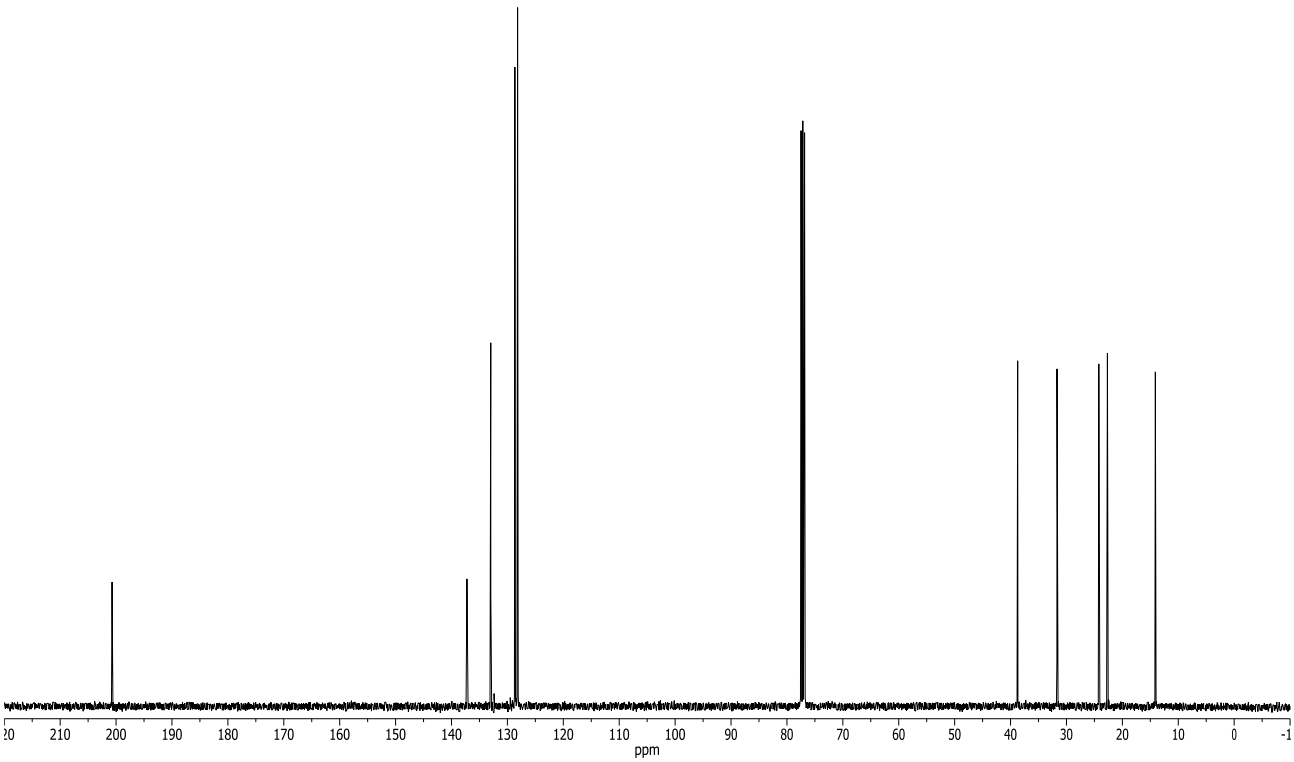

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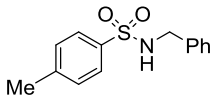

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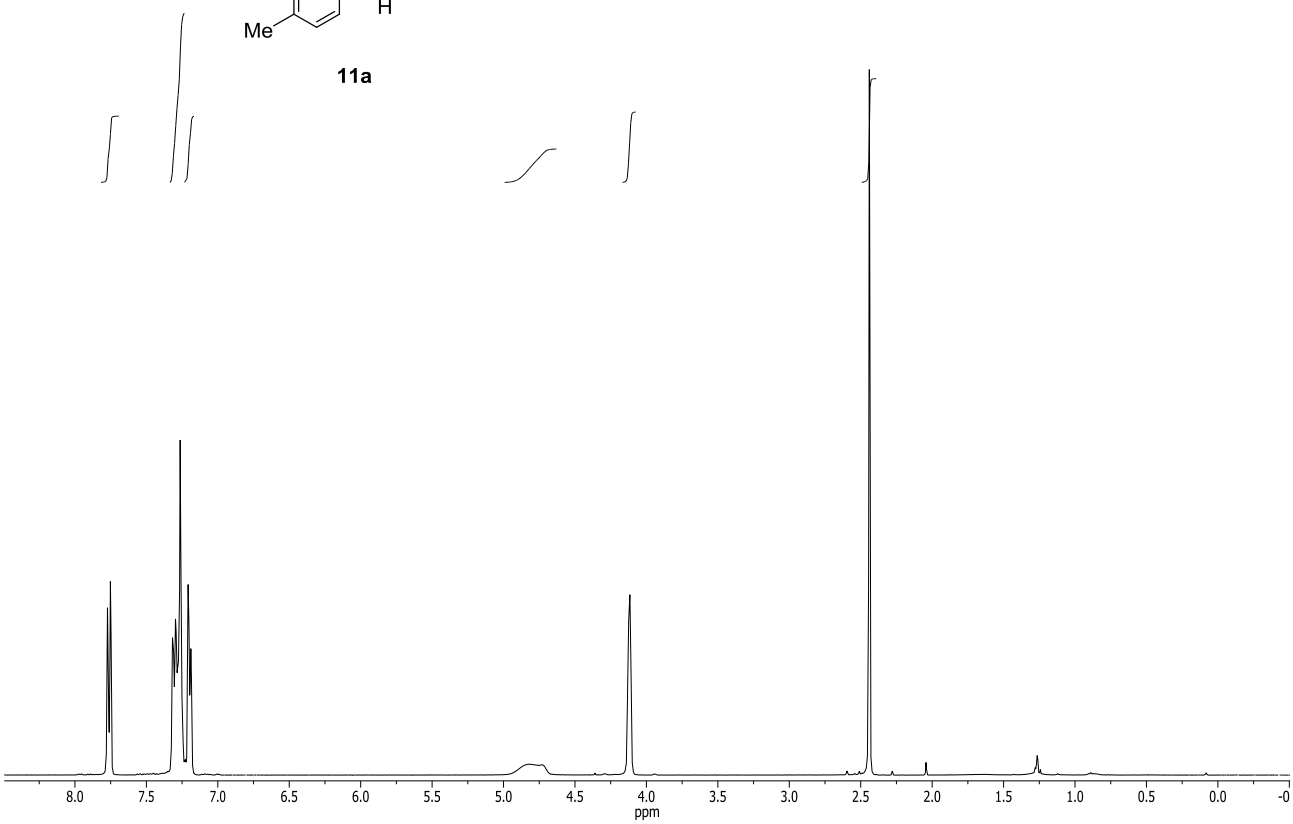

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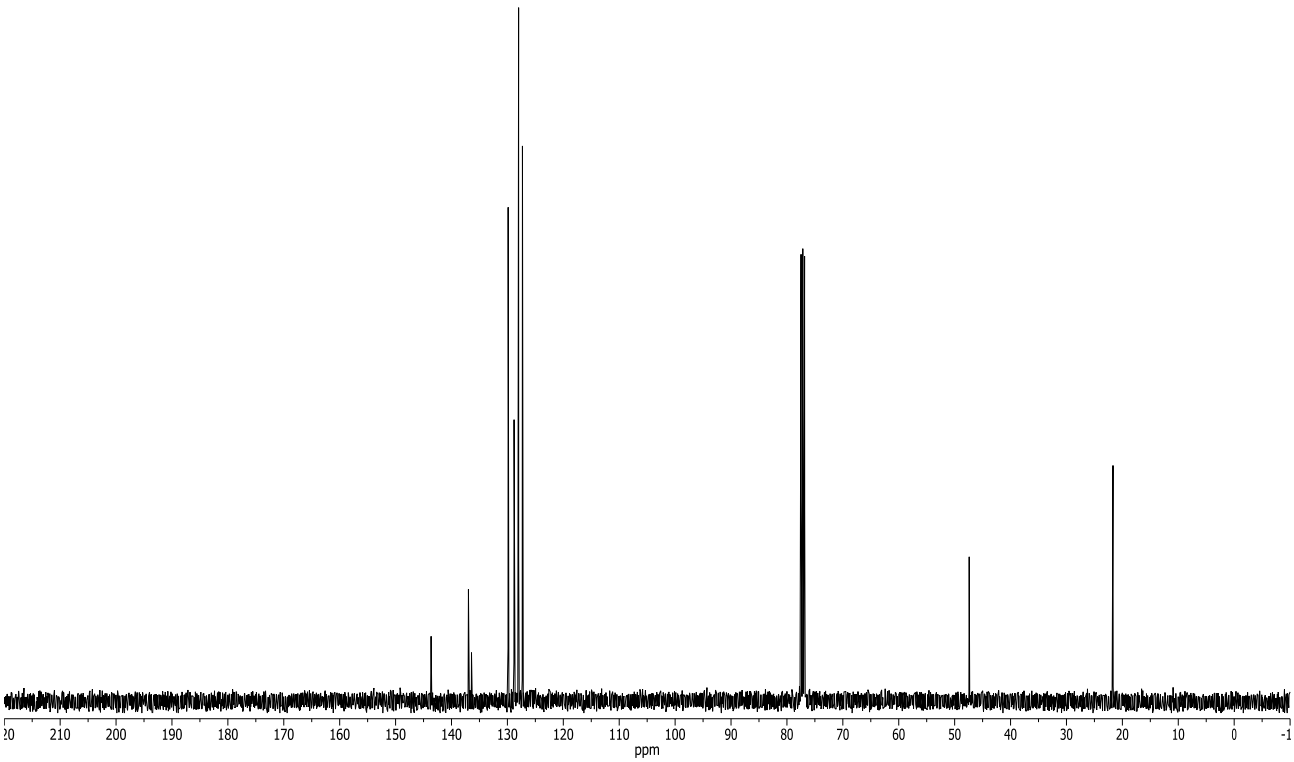

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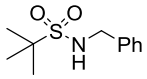

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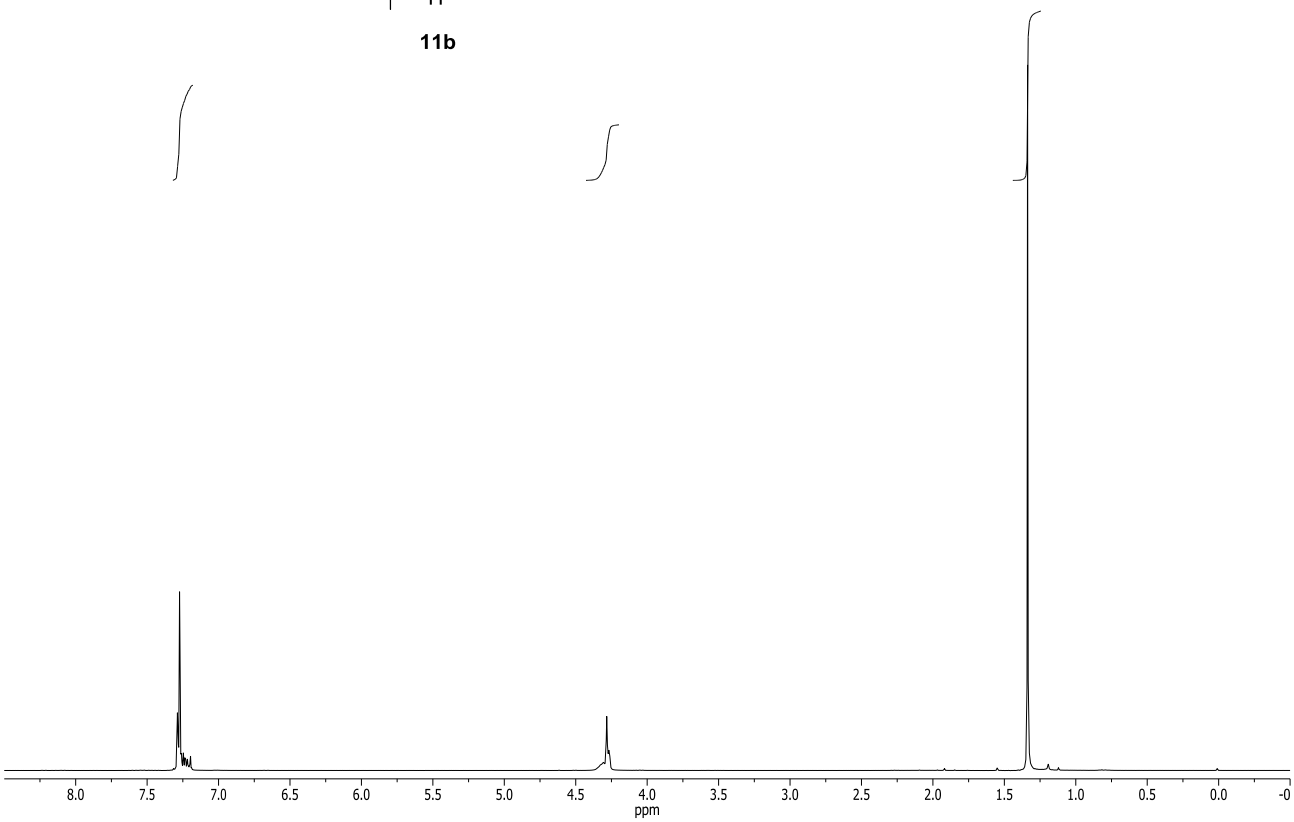

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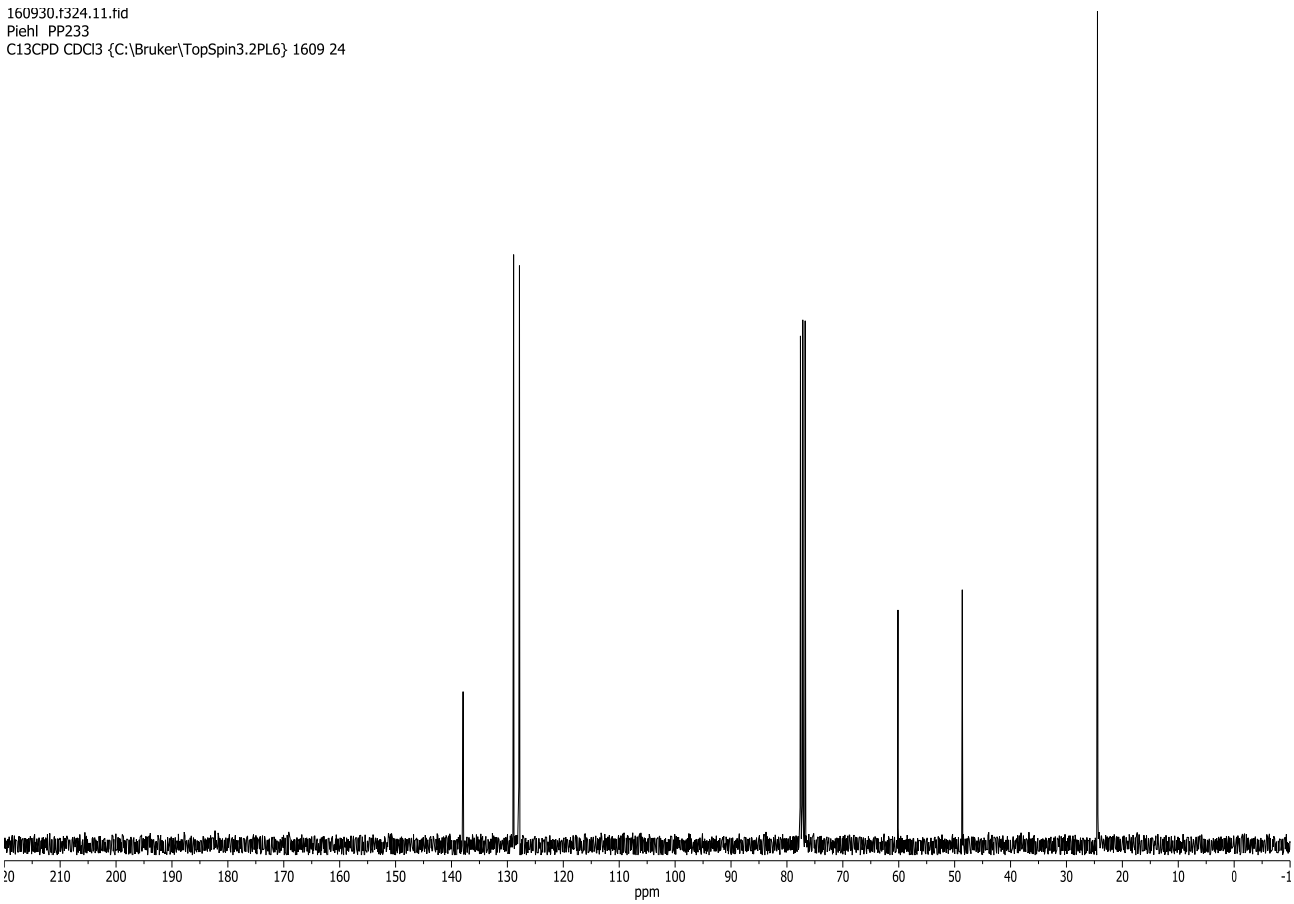

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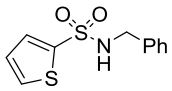

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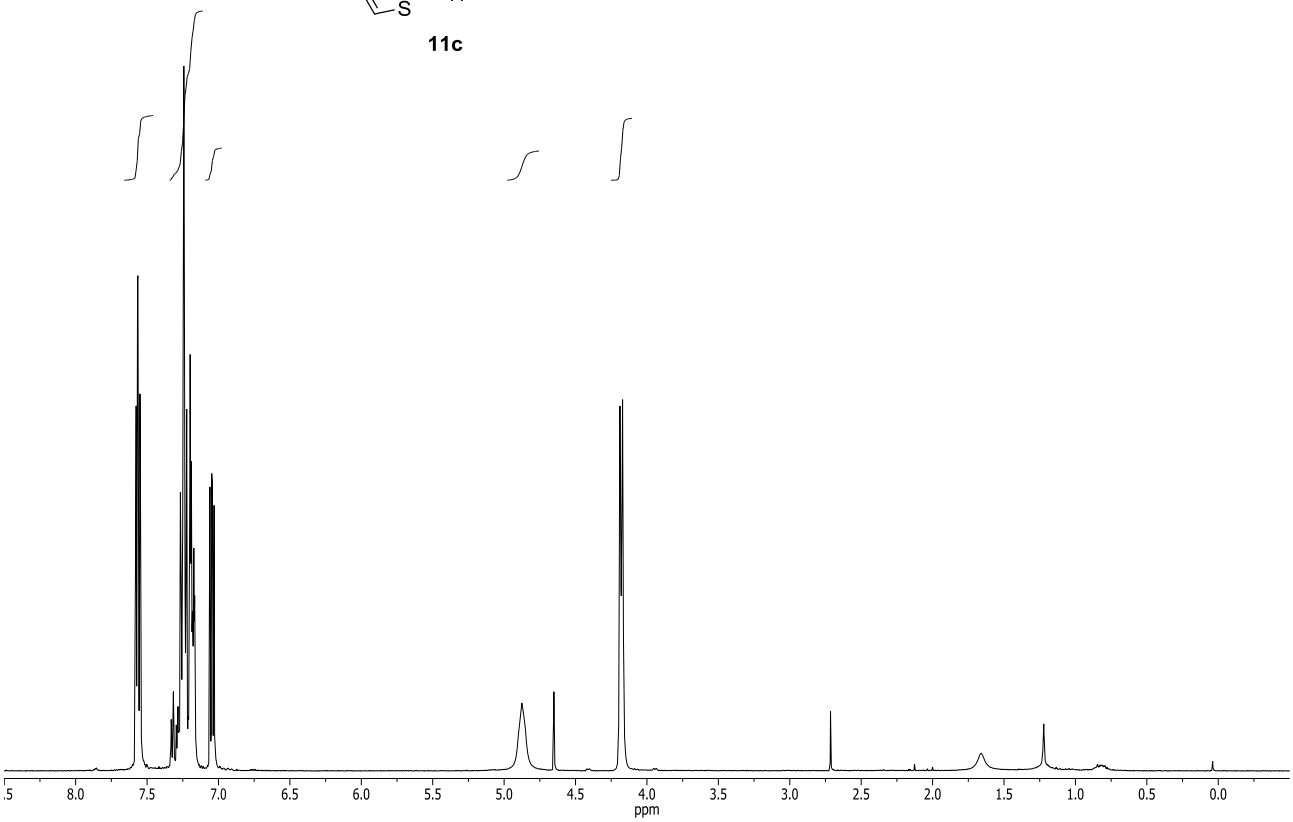

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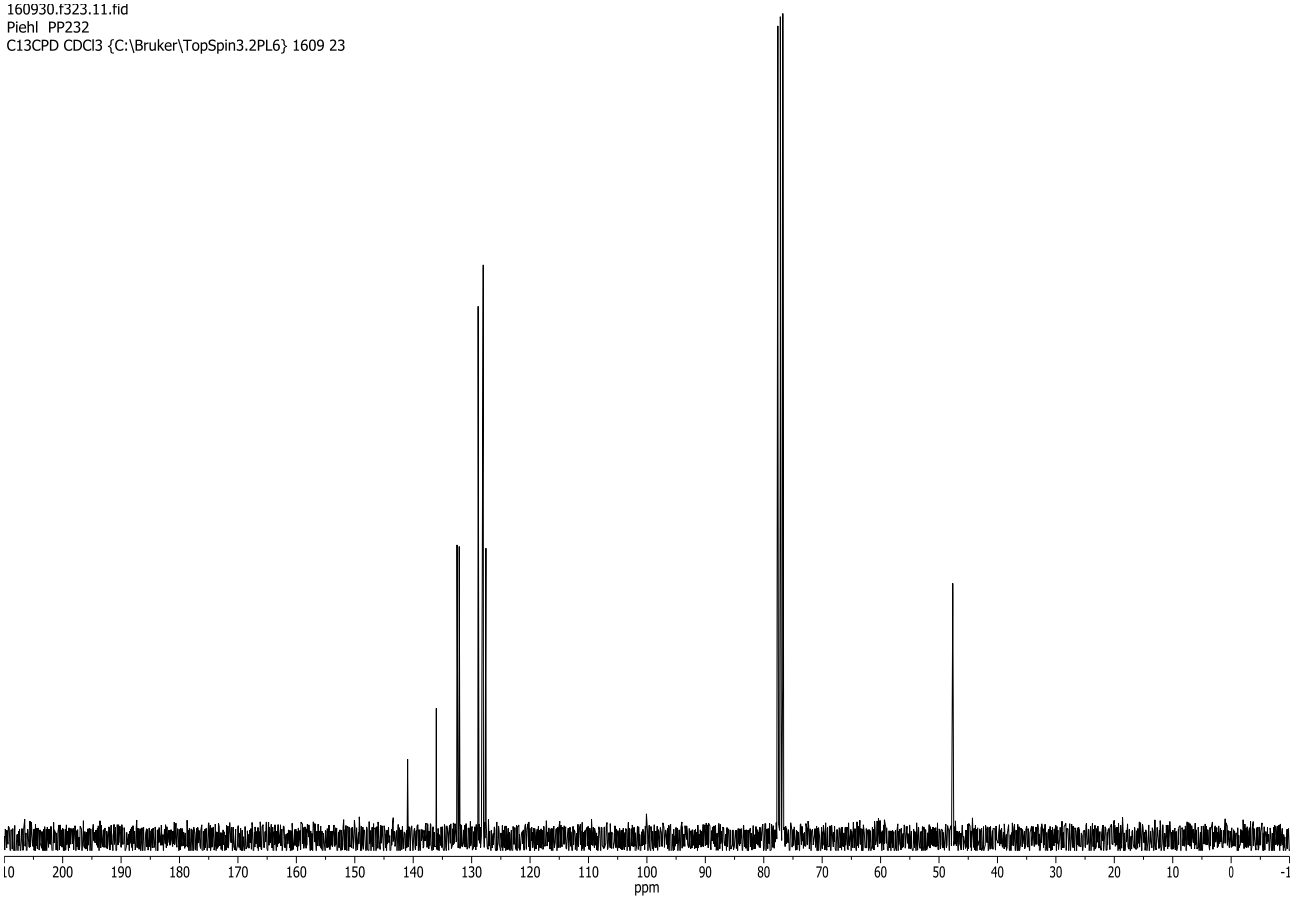

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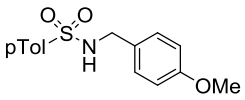

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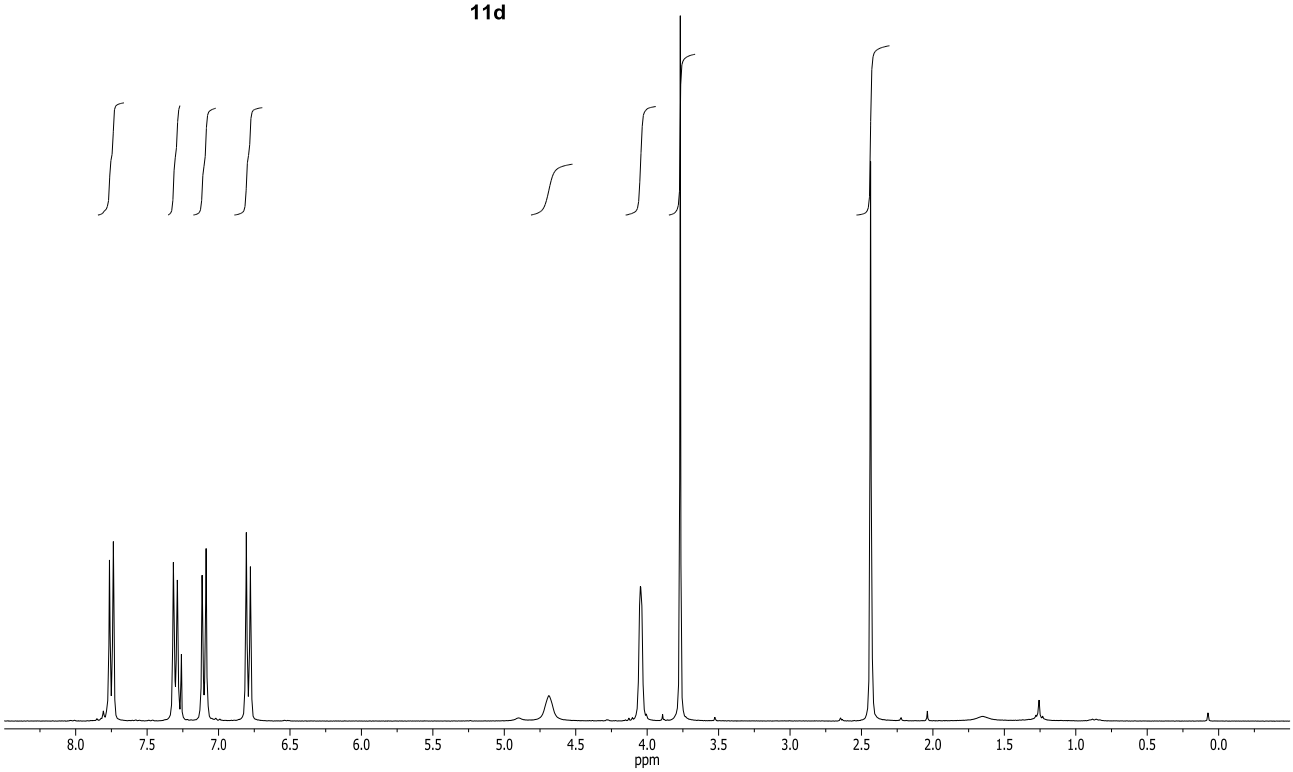

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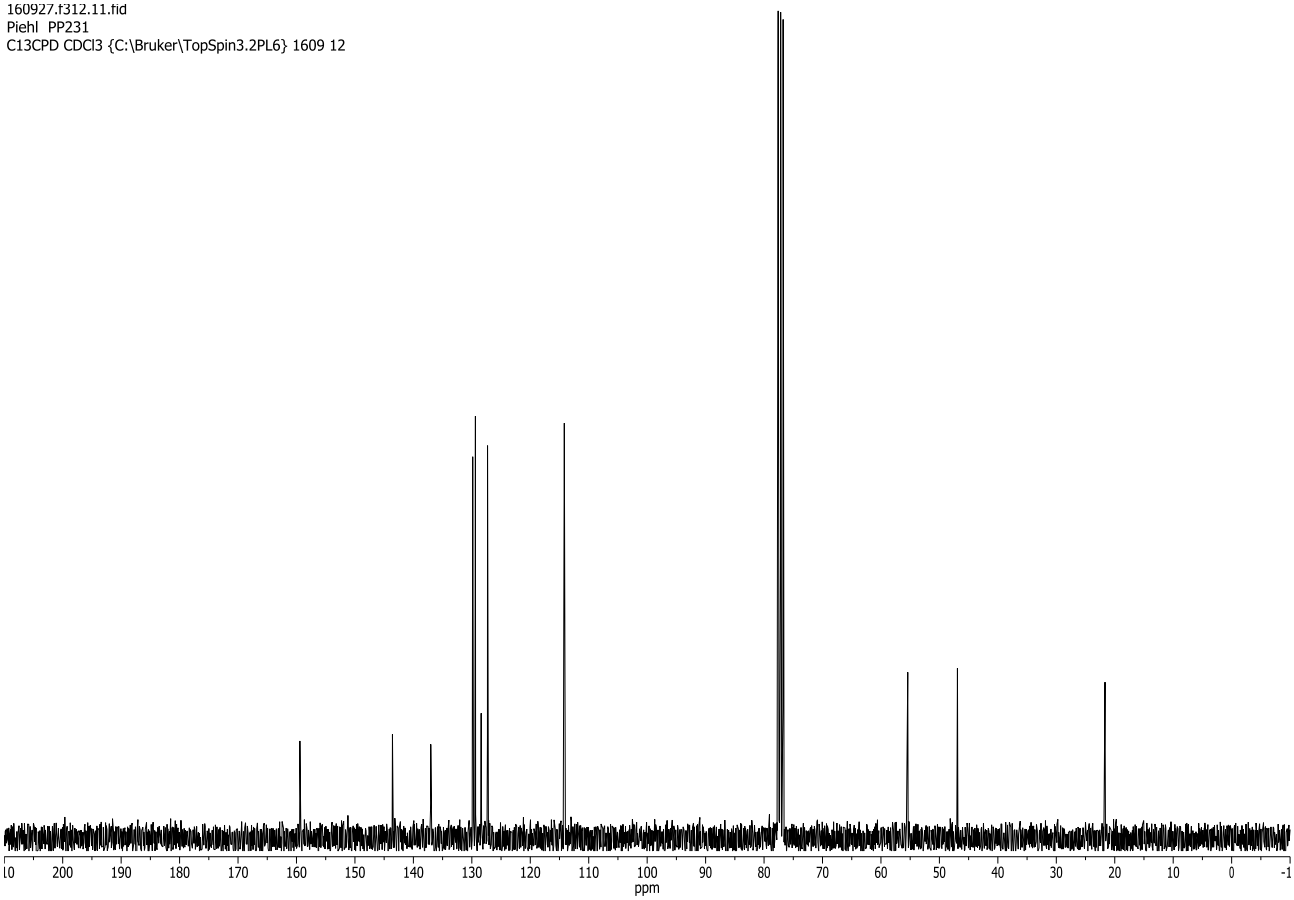

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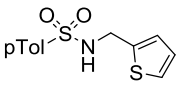

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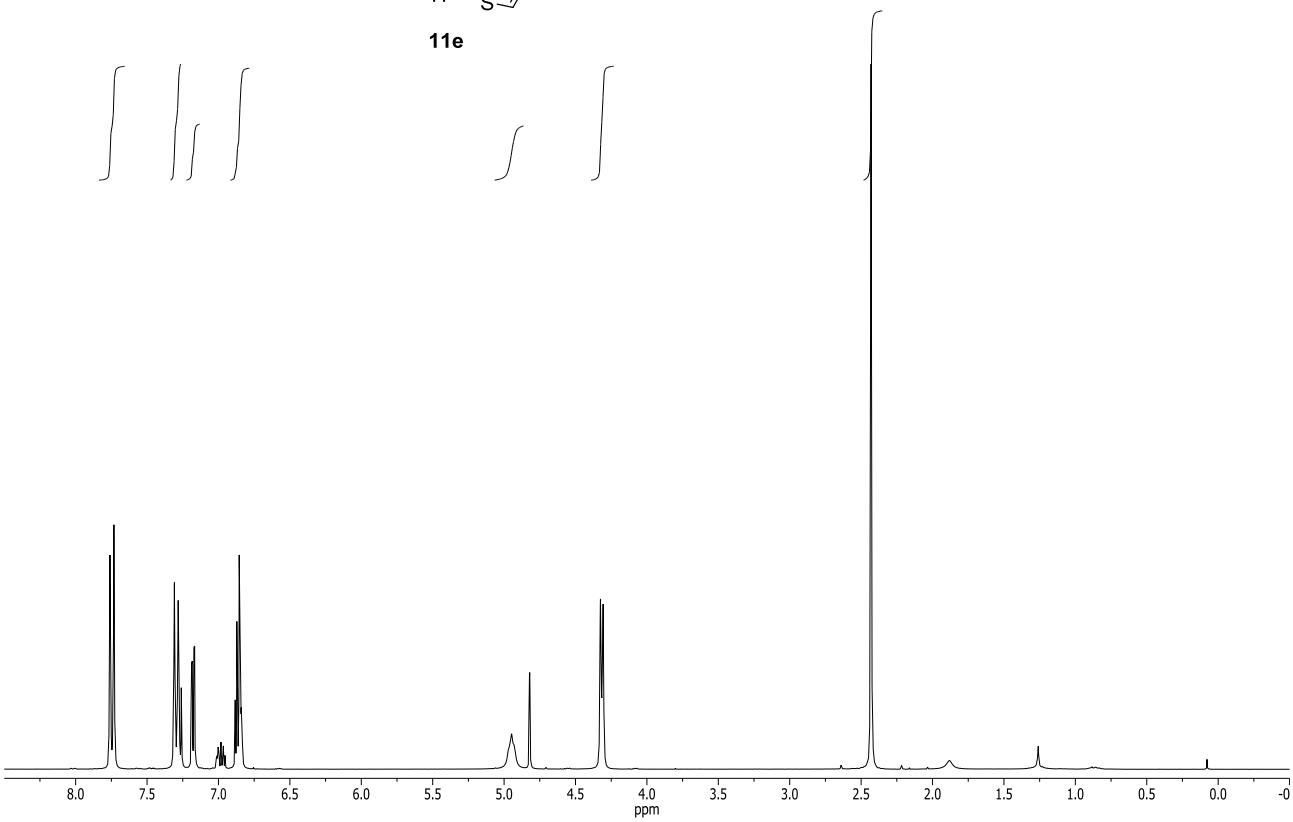

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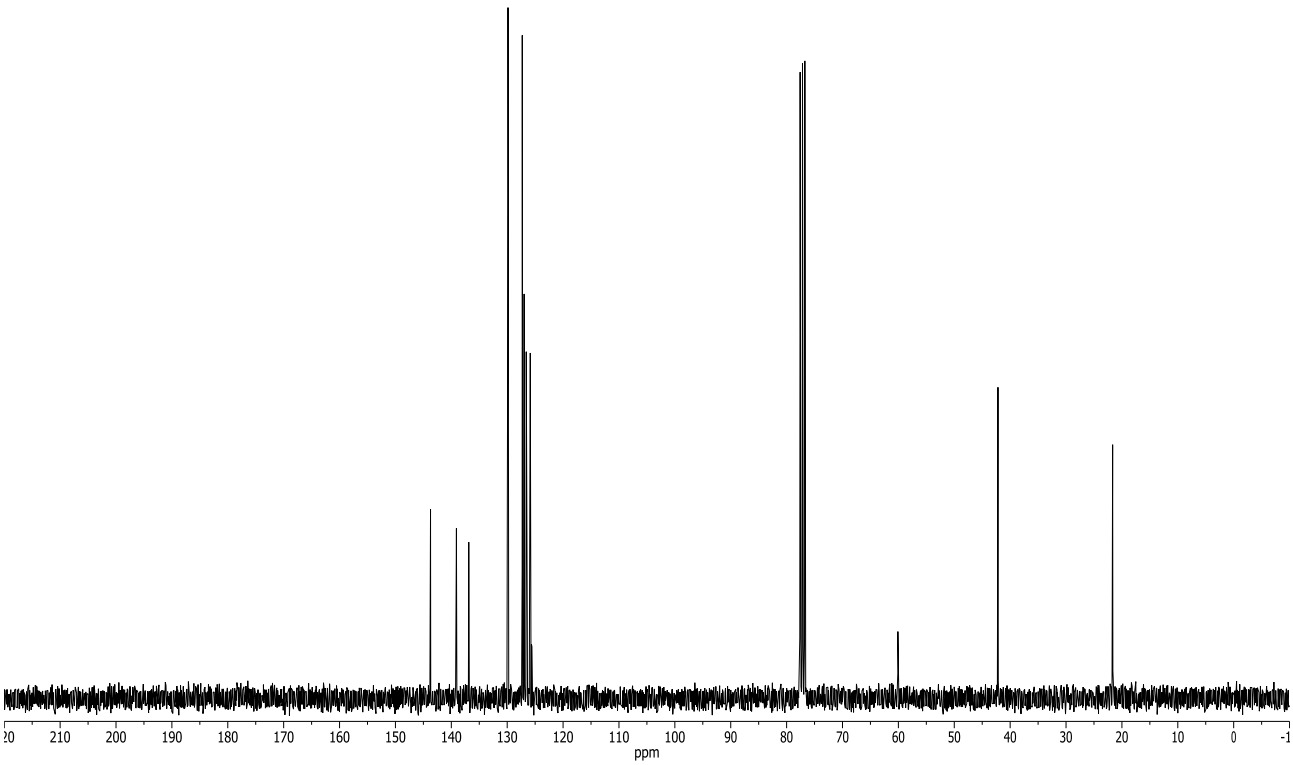

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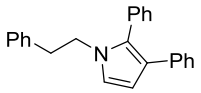

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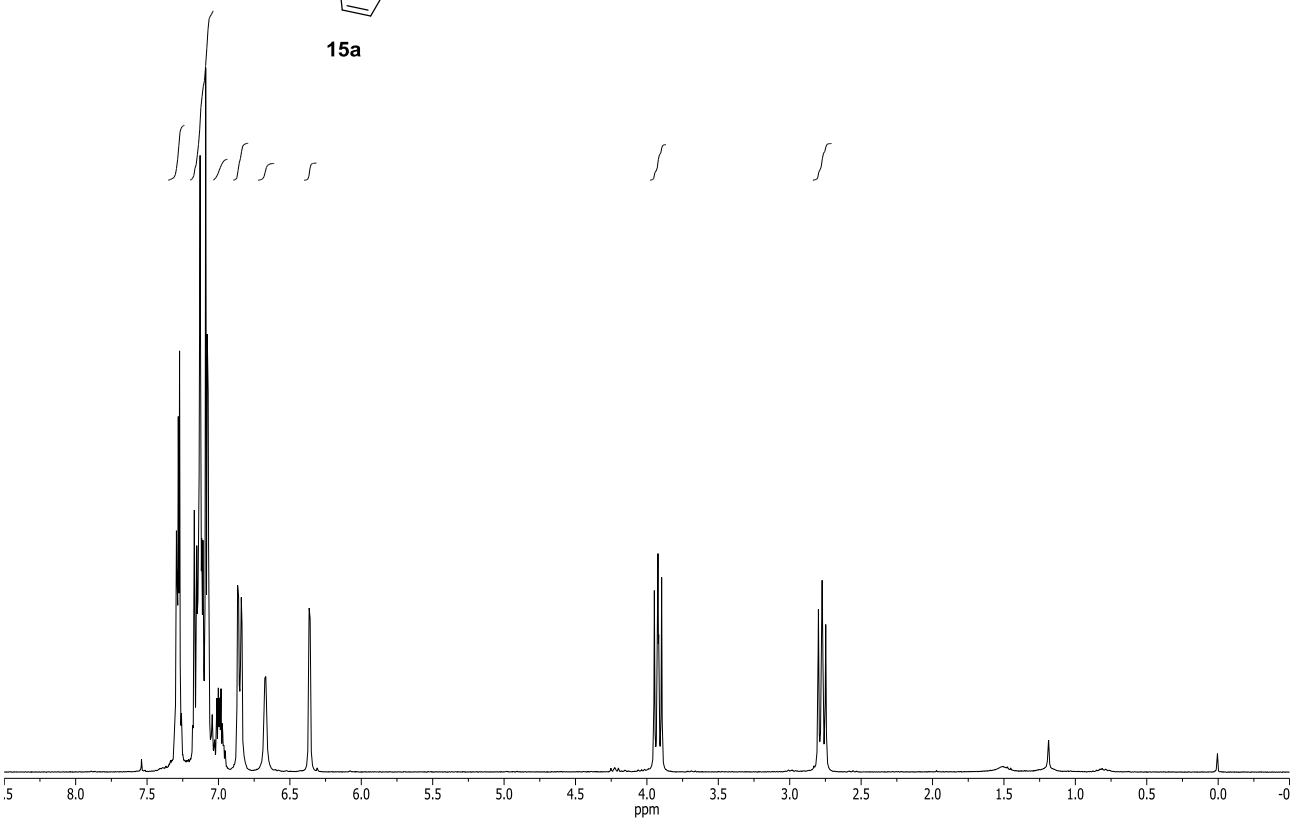

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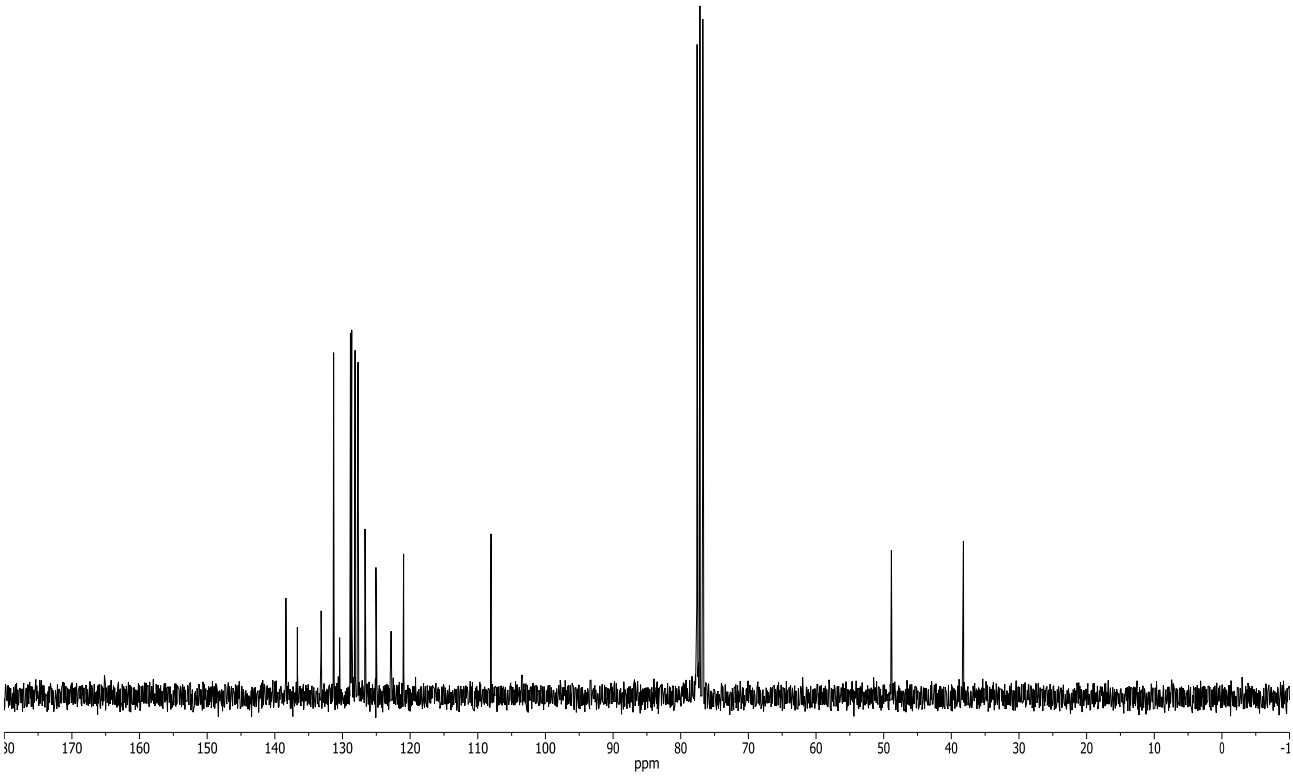

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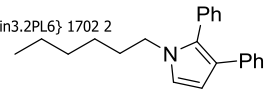

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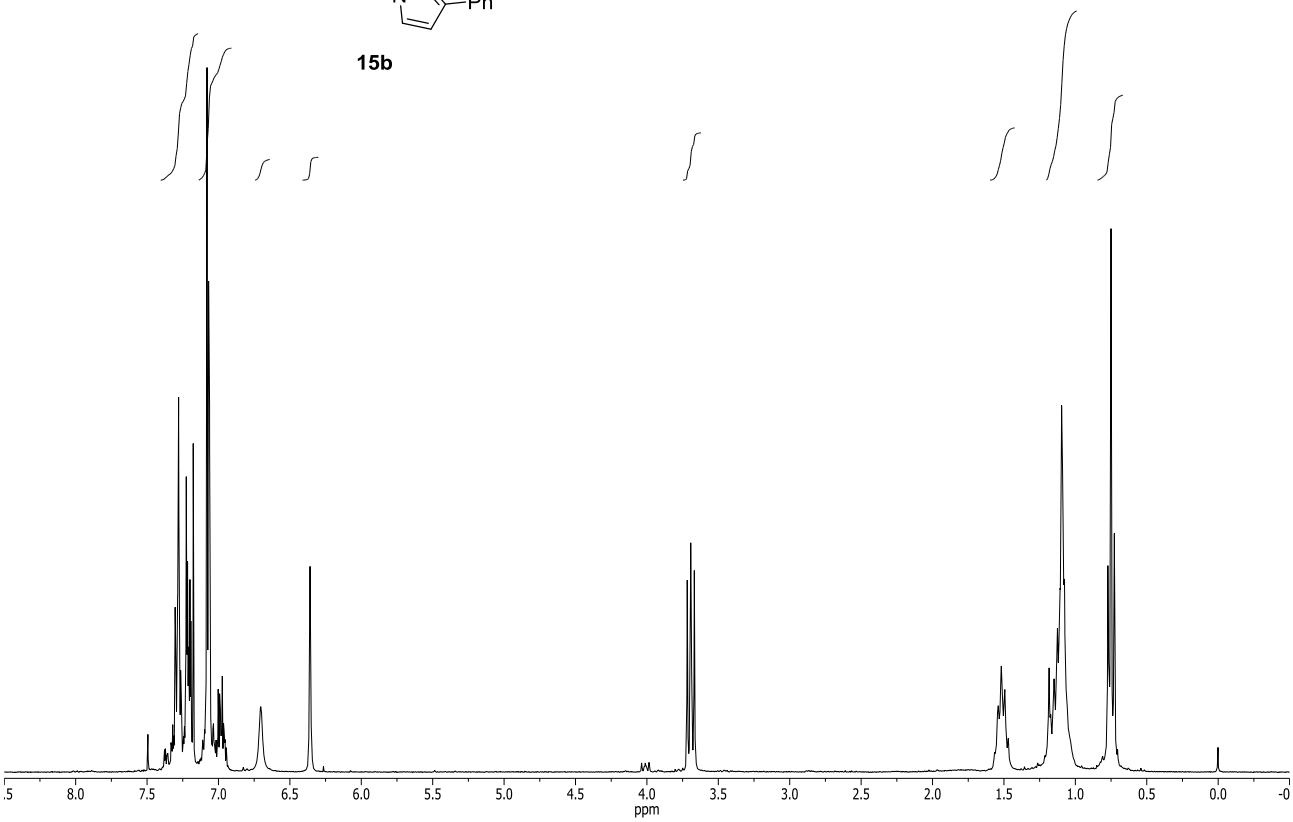

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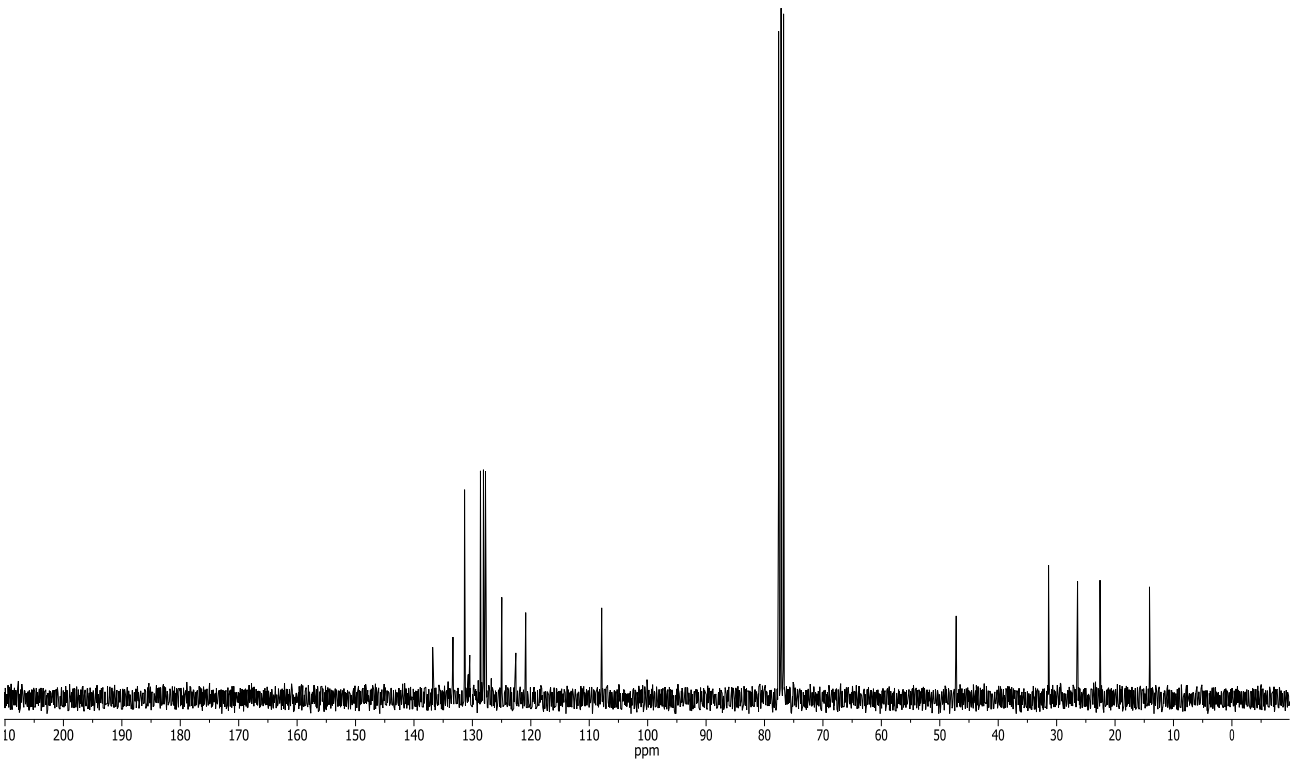

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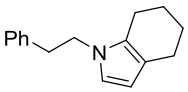

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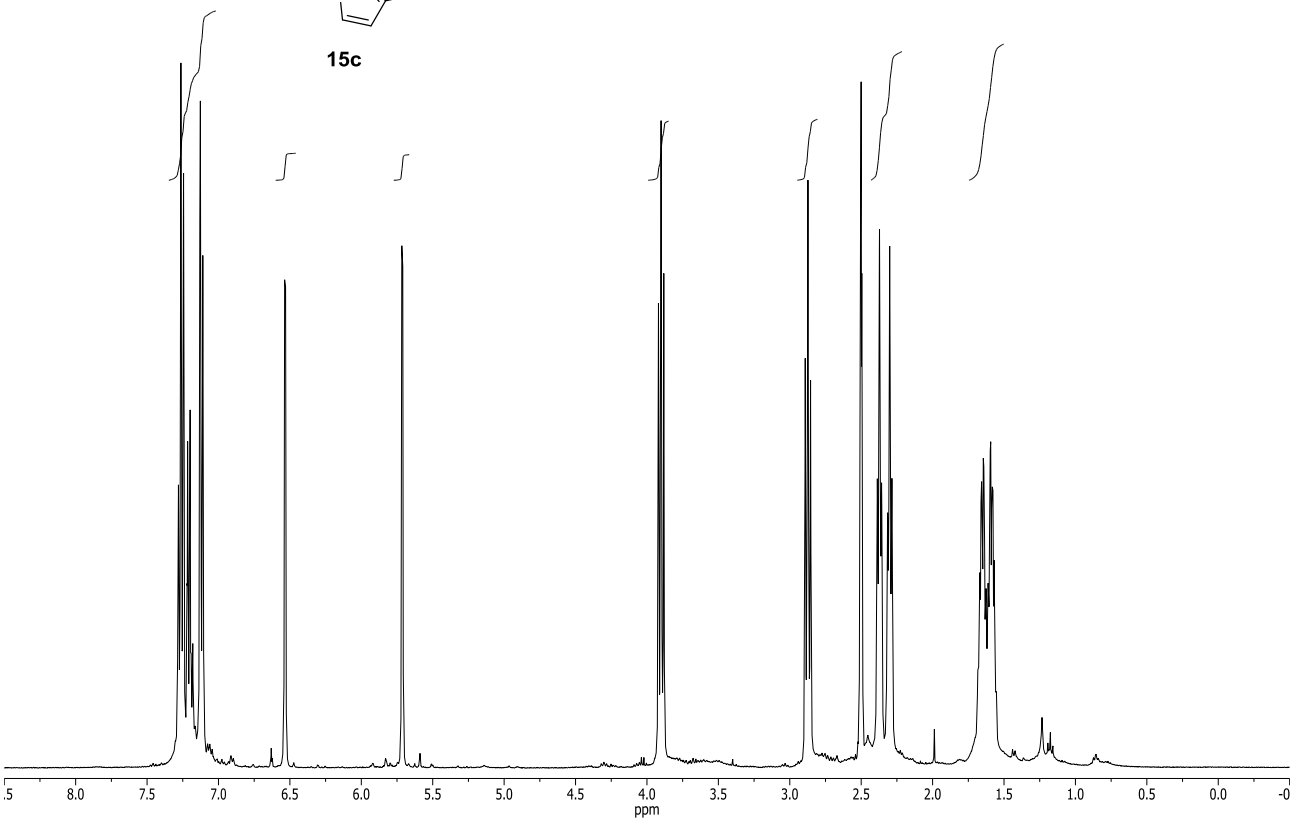
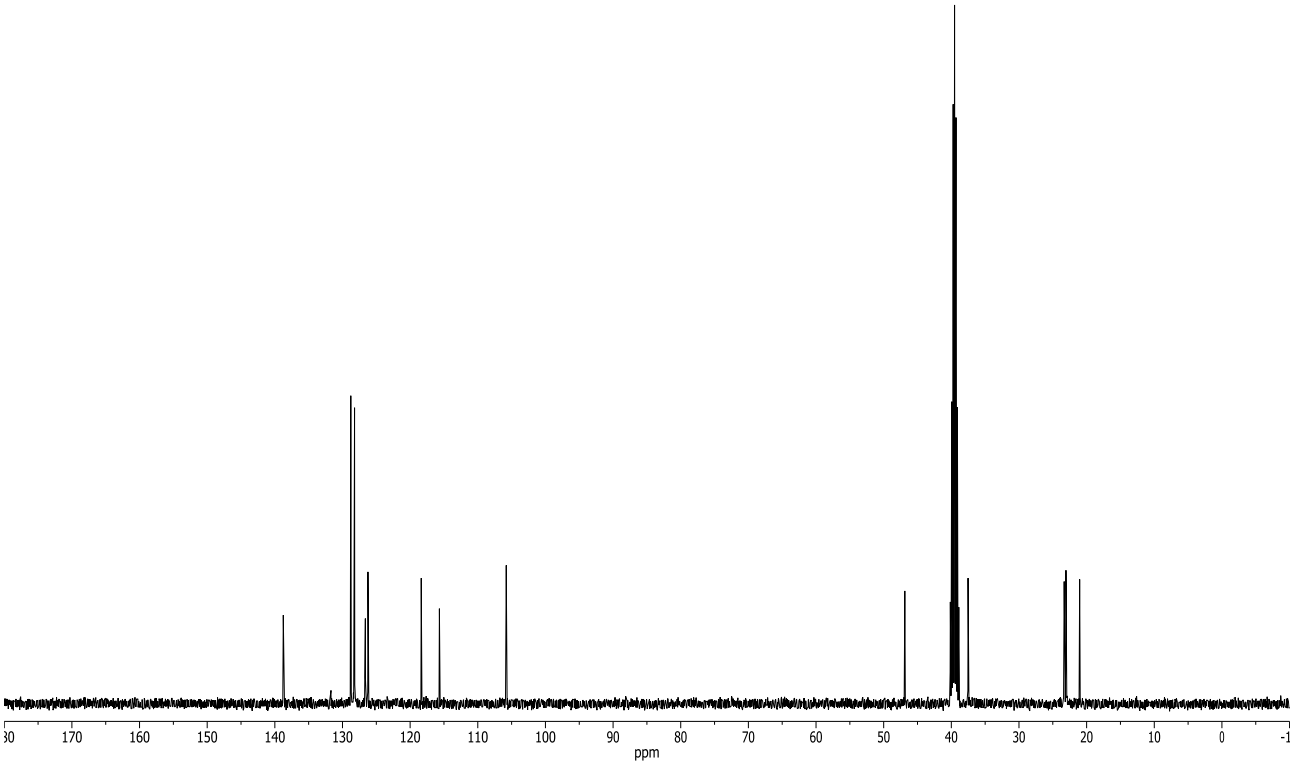
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