Angewandte Chemie
Eine Zeitschrift der Gesellschaft Deutscher Chemiker

Supporting Information

69451 Weinheim, Germany

Alkylation of *N*-(2-pyridyl)sulfonyl aryl aldimines with organozinc halides: conciliation of reactivity and chemoselectivity

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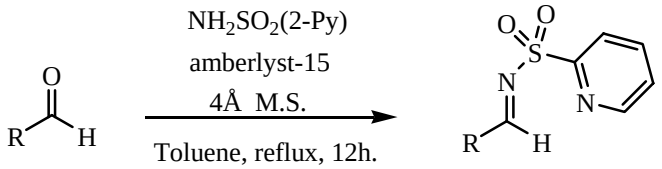
EXPERIMENTAL SECTION

General methods.

Melting points were taken in open-end capillary tubes. NMR spectra were recorded [300 MHz (^{1}H), 75 MHz (^{13}C)] at room temperature in $CDCl_3$ calibrated at 7.26 ppm (^{1}H) or 77.0 ppm (^{13}C). Mass spectra (MS) were determined at an ionizing voltage of 70 eV. All the reactions were carried out in anhydrous solvents and under nitrogen atmosphere. CH_2Cl_2 was dried and stored over microwave-activated 4Å molecular sieves. Flash column chromatography was performed using silica gel (230-400 mesh). Alkylzinc bromides were purchased to Aldrich or prepared following the literature procedure.[1]

Synthesis of 2-pyridylsulfonyl imines

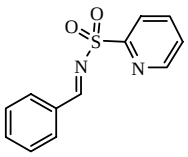
The starting sulfonylimines were prepared in good yields by direct condensation between the corresponding aldehyde and 2-pyridylsulfonamide[2] following the procedure described by Davis[3] (see Scheme below).



1f,	R= Ph,	80%
4f,	R= 4-MeOC$_6$H$_4$,	68%
5f,	R= 4-FC$_6$H$_4$,	78%
6f,	R= 2-BrC$_6$H$_4$,	72%
7f,	R= 3-MeC$_6$H$_4$,	82%
8f,	R= 2-Naph,	78%
9f,	R= 2-Furyl,	83%
10f,	R= 2-Thienyl,	71%
11f	R= N-Bn-2-pyrrol,	79%
12f,	R= 4-AcC$_6$H$_4$,	67%

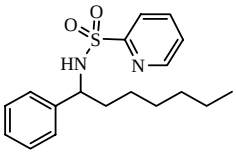
[1] S. Hou, *Org. Lett*. **2003**, *5*, 423
[2] S. Diltz, G. Aguirre, F. Ortega, P. J. Walsh, *Tet. Asymm.* **1997**, *8*, 3559.
[3] L. C. Vishwakarma,O. D. Stringer, F. A. Davis, *Org. Synth.* **1987**, *66*, 203.

Representative procedure for the synthesis of (*E*)-phenyl-*N*-(2-pyridylsulfonyl)methanimine (1f)[4]



A mixture of benzaldehyde (712 µL, 7.0 mmol), *N*-2-pyridylsulfonamide (1.10 g, 7.0 mmol), Amberlyst-15 (100 mg) and 4Å molecular sieves in dry toluene (10 mL) was heated to reflux in a sealed tube overnight. The mixture was cooled to room temperature before it was filtered through celite. The filtrate was concentrated and the resulting yellow solid was triturated with diethyl ether to afford pure imine **1f** as a white solid; yield: 1.30 g (80%); m.p.: 118-120 ºC. ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.28 (s, 1H), 8.75 (ddd, *J*= 0.8, 1.6 and 4.7 Hz, 1H), 8.26 (m, 1H), 8.11-7.90 (m, 3H), 7.66 (m, 1H), 7.58-7.48 (m, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): 174.3, 155.9, 150.4, 138.1, 135.4, 132.4, 131.7, 129.2, 127.2, 123.4.

Representative procedure for the addition of alkylzinc bromides to imines: Synthesis of 1-phenyl-*N*-(2-pyridylsulfonyl)heptan-1-amine (2f).



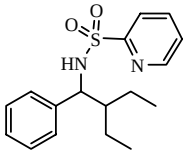
To a solution of $Cu(OTf)_2$ (3.6 mg, 5.0 mol%) and **1f** (49.2 mg, 0.2 mmol.) in CH_2Cl_2 (2 mL, 0.1 M) under nitrogen atmosphere, was added commercially available 0.5 M solution of hexylzinc bromide solution in THF (800 µL, 0.4 mmol.).[5] The mixture was stirred 10 min at rt before it was quenched with water (2 mL) and extracted with CH_2Cl_2 (3x 2 mL). The combined organic phase was dried (Na_2SO_4) and evaporated. The residue was purified by flash chromatography using Et_3N neutralized silica gel (*n*-Hexane-EtOAc 2:1) to afford pure amine **2f** as a white solid; yield: 123.6 mg (93%); m.p.: 58-60 ºC; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.54 (d, *J*= 4.4 Hz, 1H), 7.61-7.50 (m, 2H), 7.23 (m, 1H), 7.05-6.90 (m, 5H), 5.81 (d, *J*= 7.7 Hz, 1H), 4.32 (q, *J*= 7.6 Hz, 1H), 1.76 (m, 1H), 1.61

[4] a) J. Esquivias, R. Gómez Arrayás, J. C. Carretero, *J. Org. Chem.* **2005**, *70*, 7451. b) J. Esquivias, R. Gómez Arrayás, J. C. Carretero, *Angew. Chem. Int. Ed.* **2006**, *45*, 629.

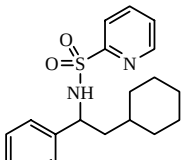
[5] When hexylzinc bromide is prepared according to the literature procedure (ref. 1), a 1 M solution of this reagent in DMA (400 µL, 0.4 mmol) is added to the reaction mixture containing $Cu(OTf)_2$ and **1f** in CH_2Cl_2.

(m, 1H), 1.30-0.98 (m, 8H), 0.75 (t, *J*= 6.7 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): 157.8, 149.7, 140.6, 137.4, 128.2, 127.2, 126.7, 126.0, 122.0, 58.9, 37.3, 31.6, 28.8, 25.9, 22.5, 14.0. MS (FAB+) m/z 333.2 ($M+H^+$, 100), FAB+ HRMS for $C_{18}H_{25}O_2N_2S$ ($M+H^+$): Calcd: 333.1636. Found: 333.1650. Anal. Calcd for $C_{18}H_{24}O_2N_2S$: C 65.03, H 7.28, N 8.43, S 9.65; found: C 64.67, H 7.13, N 8.31, S 9.55.

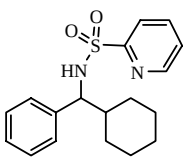
2-Ethyl-1-phenyl-*N*-(2-pyridylsulfonyl)butan-1-amine (3f). yield 92%, yellow solid; m.p.: 70-71 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.36 (d, *J*= 4.4 Hz, 1H), 7.60-7.47 (m, 2H), 7.17 (m, 1H), 6.98-6.82 (m, 5H), 5.53 (d, *J*= 9.1 Hz, 1H), 4.30 (dd, *J*= 7.6 and 9.0 Hz, 1H), 1.62-1.30 (m, 3H), 1.15-0.95 (m, 2H), 0.79 (t, *J*= 7.1 Hz, 3H), 0.68 (t, *J*= 7.3 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): 157.6, 149.6, 139.8, 137.3, 128.0, 127.1, 126.8, 125.9, 122.0, 60.5, 46.6, 21.5, 20.8, 10.7, 10.5. Anal. Calcd for $C_{17}H_{22}O_2N_2S$: C 65.03, H 7.28, N 8.43, S 9.64; found: C 64.51, H 7.03, N 8.88, S 9.93.



2-Cyclohexyl-1-phenyl-*N*-(2-pyridylsulfonyl)ethanamine (13f). yield 88%, white solid; m.p.: 122-124 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.41 (d, *J*= 4.4 Hz, 1H), 7.60-7.50 (m, 2H), 7.21 (m, 1H), 7.10-6.90 (m, 5H), 5.43 (d, *J*= 8.1 Hz, 1H), 4.42 (q, *J*= 8.1 Hz, 1H), 1.70-1.41 (m, 7H), 1.22-1.01 (m, 4H) 0.91-0.72 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): 157.8, 149.7, 141.0, 137.4, 128.2, 127.2, 126.6, 126.0, 122.0, 56.3, 45.3, 33.8, 33.2, 32.8, 26.4, 26.0, 25.9. Anal. Calcd for $C_{19}H_{24}O_2N_2S$: C 66.25, H 7.02, N 8.13, S 9.29; found: C 65.91, H 7.07, N 8.10, S 9.00.

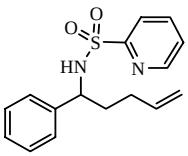


1-Cyclohexyl-1-phenyl-*N*-(2-pyridylsulfonyl)methanamine (14f). yield 81%, white solid; m.p.: 150-151 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.34 (d, *J*= 4.4 Hz, 1H), 7.58-7.48 (m, 2H), 7.17 (m, 1H), 6.98-6.92 (m, 3H), 6.84-6.80 (m, 2H), 5.40 (d, *J*= 8.9 Hz, 1H), 4.06 (t, *J*= 8.7 Hz, 1H), 1.99 (m, 1H), 1.70 (m, 1H), 1.60-1.46 (m, 3H) 1.24-0.72 (m,



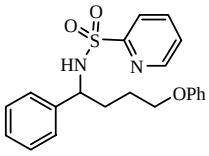
6H). ^{13}C NMR (75 MHz, $CDCl_3$): 157.7, 149.6, 139.5, 137.3, 128.0, 127.1, 127.0, 125.9, 122.0, 63.9, 43.5, 29.8, 29.6, 26.2, 25.9. Anal. Calcd for $C_{18}H_{22}O_2N_2S$: C 65.42, H 6.71, N 8.48, S 9.70; found: C 64.97, H 6.76, N 8.38, S 9.32. MS (FAB+) m/z 331.1 ($M+H^+$, 64.5), FAB+ HRMS for $C_{18}H_{22}O_2N_2S$ ($M+H^+$): Calcd: 331.1480. Found: 331.1488.

1-Phenyl-*N*-(2-pyridylsulfonyl)pent-4-en-1-amine (15f). yield 90%, white



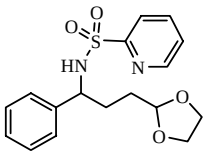
solid; m.p.: 75-76 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.41 (d, *J*= 4.4 Hz, 1H), 7.62-7.53 (m, 2H), 7.23 (m, 1H), 7.02-6.97 (m, 3H), 6.95-6.90 (m, 2H), 5.72-5.58 (m, 2H), 4.90 (m, 1H), 4.86 (m. 1H), 4.35 (q, *J*= 7.4 Hz, 1H), 2.00-1.60 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): 157.7, 149.7, 140.2, 137.5, 137.1, 128.3, 127.3, 126.7, 126.1, 122.0, 115.6, 58.3, 41.2, 48.6. MS (FAB+) m/z 303.1 ($M+H^+$, 100), FAB+ HRMS for $C_{16}H_{19}O_2N_2S$ ($M+H^+$): Calcd: 303.1167. Found: 303.1178. Anal. Calcd for $C_{16}H_{18}O_2N_2S$: C 63.55, H 6.00, N 9.26, S 10.60; found: C 63.07, H 6.02, N 9.17, S 10.36.

4-Phenoxy-1-phenyl-*N*-(2-pyridylsulfonyl)butan-1-amine (16f). yield 84%,



white solid; m.p.: 58-60 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.38 (d, *J*= 4.4 Hz, 1H), 7.62-7.50 (m, 2H), 7.25-7.10 (m, 4H), 7.02-6.93 (m, 4H), 6.88-6.80 (m, 2H), 6.78-6.72 (m, 1H), 5.85 (d, *J*= 8.2 Hz, 1H), 4.40 (q, *J*= 7.3 Hz, 1H), 4.05 (t, *J*= 6.0 Hz, 1H), 3.81 (t, *J*= 6.0 Hz, 1H), 2.02-1.50 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): 158.8, 157.7, 149.7, 140.3, 137.5, 129.5, 129.4, 128.3, 127.4, 126.7, 126.1, 122.0, 120.8, 120.7, 114.5, 114.4, 67.0, 65.6, 60.4, 58.6. MS (FAB+) m/z 383.1 ($M+H^+$, 100), FAB+ HRMS for $C_{21}H_{23}O_3N_2S$ ($M+H^+$): Calcd: 383.1429. Found: 383.1432.

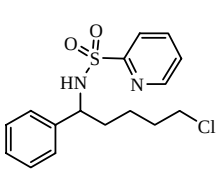
3-(1,3-Dioxolan-2-yl)-1-phenyl-*N*-(2-pyridylsulfonyl)propan-1-amine (17f).



yield 92%, white solid; m.p.: 112-113 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.87 (d, *J*= 4.4 Hz, 1H), 7.63-7.48 (m, 2H), 7.37 (m, 1H), 7.04 (s, 5H), 6.71 (d, *J*= 7.1 Hz, 1H), 4.83 (t, *J*= 4.3 Hz, 1H), 4.47 (q, *J*= 7.5 Hz, 1H), 4.00-3.61 (m, 4H), 2.00-1.55 (m, 4H).

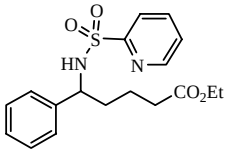
^{13}C NMR (75 MHz, $CDCl_3$): 149.9, 140.2, 138.4, 128.3, 127.3, 126.7, 126.5, 122.6, 103.6, 64.9, 58.8, 31.4, 30.0. MS (FAB+) m/z 349.1 ($M+H^+$, 20), FAB+ HRMS for $C_{17}H_{21}O_4N_2S$ ($M+H^+$): Calcd: 349.1222. Found: 349.1237.

5-Chloro-1-phenyl-*N*-(2-pyridylsulfonyl)pentan-1-amine (18f). yield 95%,



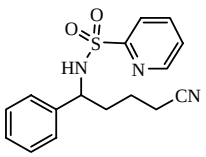
white solid; m.p.: 79-80 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.42 (d, *J*= 4.4 Hz, 1H), 7.65-7.55 (m, 2H), 7.23 (m, 1H), 7.03-6.90 (m, 5H), 5.77 (d, *J*= 8.2 Hz, 1H), 4.33 (q, *J*= 7.6 Hz, 1H), 3.37 (t, *J*= 6.6 Hz, 2H), 1.83 (m, 1H), 1.72-1.59 (m, 3H), 1,40 (m, 1H), 1.23 (m 1H). ^{13}C NMR (75 MHz, $CDCl_3$): 157.7, 149.7, 140.2, 137.5, 128.4, 127.4, 126.7, 126.1, 122.0, 58.7, 44.6, 36.5, 32.0, 23.4. MS (FAB+) m/z 339.1 ($M+H^+$, 100), FAB+ HRMS for $C_{16}H_{19}O_2N_2SCl$ ($M+H^+$): Calcd: 339.0934. Found: 339.0942, Anal. Calcd for $C_{16}H_{19}O_2N_2SCl$: C 56.71, H 5.65, N 8.27, S 9.46; found: C 56.27, H 5.64, N 8.19, S 9.30.

Ethyl 5-phenyl-5-*N*-(2-pyridylsulfonylamino)pentanoate (19f). yield 88%,



white solid; m.p.: 71-72 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.50 (d, *J*= 4.4 Hz, 1H), 7.73-7.62 (m, 2H), 7.32 (m, 1H), 7.12-7.00 (m, 5H), 5.81 (d, *J*= 8.1 Hz, 1H), 4.45 (q, *J*= 7.3 Hz, 1H), 4.11 (q, *J*= 7.1 Hz, 2H), 2.26 (t, *J*= 7.2 Hz, 2H), 1.92 (m, 1H), 1.85-1.65 (m, 2H), 1.54 (m, 1H), 1.25 (t, *J*= 7.1 Hz, 3H) . ^{13}C NMR (75 MHz, $CDCl_3$): 173.1, 157.8, 149.7, 140.2, 137.5, 128.3, 127.4, 126.7, 126.1, 122.0, 60.3, 58.6, 36.5, 33.6, 21.4, 14.2. MS (FAB+) m/z 363.1 ($M+H^+$, 90), FAB+ HRMS for $C_{18}H_{23}O_4N_2S$ ($M+H^+$): Calcd: 363.1378. Found: 363.1396, Anal. Calcd for $C_{18}H_{22}O_4N_2S$: C 59.65, H 6.12, N 7.73, S 8.85; found: C 59.30, H 6.14, N 7.70, S 8.61.

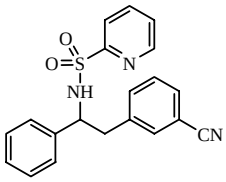
5-Phenyl-5-*N*-(2-pyridylsulfonylamino)pentanenitrile (20f).



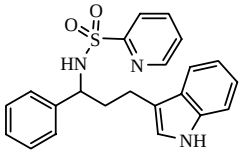
yield 90%, yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.39 (d, *J*= 4.4 Hz, 1H), 7.68-7.57 (m, 2H), 7.24 (ddd, *J*= 1.4, 4.7 and 7.2 Hz, 1H), 7.06-7.00 (m, 3H), 6.95-6.90 (m, 2H), 5.68 (d, *J*= 8.5 Hz, 1H), 4.36 (q, *J*= 7.9 Hz, 1H), 2.37-2.28 (t, *J*= 7.0 Hz, 2H), 2.00-1.45 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): 157.5, 149.7, 139.6, 137.6,

128.5, 127.7, 126.5, 126.3, 122.0, 119.2, 58.1, 35.9, 22.1, 16.7. MS (FAB+) m/z 316.1 ($M+H^+$, 10), FAB+ HRMS for $C_{16}H_{18}O_2N_3S$ ($M+H^+$): Calcd: 316.1119. Found: 316.1109.

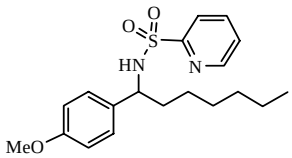
3-[2-Phenyl-*N*-(2-pyridylsulfonylamino)ethyl]benzonitrile (21f). yield 90%, white solid; m.p.: 85-86 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.34 (d, *J*= 4.4 Hz, 1H), 7.61-7.57 (m, 2H), 7.34 (m, 1H), 7.25-7.10 (m, 4H), 7.05-6.98 (m, 3H), 6.94-6.90 (m, 2H), 6.20 (d, *J*= 7.9 Hz, 1H), 4.63 (q, *J*= 7.4 Hz, 1H), 3.16 (dd, *J*= 7.1 and 13.8 Hz, 1H), 2.98 (dd, *J*= 7.6 and 13.8 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): 157.5, 149.7, 139.2, 138.4, 137.7, 134.1, 132.9, 130.4, 129.1, 128.4, 127.8, 126.8, 126.3, 121.9, 118.7, 112.3, 59.8, 43.1.



3-(1H-Indol-3-yl)-1-phenyl-*N*-(2-pyridylsulfonyl)propan-1-amine (22f). yield 82%, yellow solid; m.p.: 107-109 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.99 (d, *J*= 4.4 Hz, 1H), 7.30-6.90 (m, 12H), 6.76 (d, *J*= 8.3 Hz, 1H), 6.58 (s, 1H), 4.05 (q, *J*= 7.4 Hz, 1H), 2.45-2.35 (m, 2H), 1.09 (t, *J*= 7.4 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): 156.1, 149.0, 136.7, 128.9, 128.8, 126.5, 125.8, 122.0, 121.1 119.4, 118.7, 110.1, 67.2, 18.0, 13.9. MS (FAB+) m/z 392.1 ($M+H^+$, 8.4), FAB+ HRMS for $C_{22}H_{22}O_2N_3S$ ($M+H^+$): Calcd: 392.1433. Found: 392. 1380.



1-(4-Methoxyphenyl)-*N*-(2-pyridylsulfonyl)heptan-1-amine (23f). yield 80%, yellow solid; m.p.: 58-60 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.45 (d, *J*= 4.4 Hz, 1H), 7.63-7.56 (m, 2H), 7.25 (m, 1H), 6.84 (d, *J*= 8.6 Hz, 2H), 6.52 (d, *J*= 8.6 Hz, 2H), 5.33 (d, *J*= 7.7 Hz, 1H), 4.26 (q, *J*= 7.6 Hz, 1H), 3.64 (s, 3H), 1.75 (m, 1H), 1.60 (m, 1H), 1.24-1.02 (m, 8H), 0.76 (t, *J*= 6.7 Hz, 3H) . ^{13}C NMR (75 MHz, $CDCl_3$): 158.6, 157.9, 149.7, 137.4, 132.7, 132.0, 127.9, 126.0, 122.6, 114.3, 113.6, 58.3, 55.4, 37.3, 31.6, 28.8, 25.9, 22.5, 14.0. MS (FAB+) m/z 363.2 ($M+H^+$, 15), FAB+ HRMS for $C_{19}H_{27}O_3N_2S$ ($M+H^+$): Calcd: 363.1742. Found: 363.1744.



1-(4-Methoxyphenyl)-*N*-(2-pyridylsulfonyl)pent-4-en-1-amine (24f). yield 83%, yellow solid; m.p.: 73-75 ºC; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.43 (d, *J*= 4.4 Hz, 1H), 7.62-7.57 (m, 2H), 7.24 (m, 1H), 6.85 (d, *J*= 8.7 Hz, 2H), 6.53 (d, *J*= 8.7 Hz, 2H), 5.65 (m, 1H), 4.90 (m, 1H), 4.85 (m. 1H), 4.30 (q, *J*= 7.4 Hz, 1H), 3.65 (s, 3H), 1.96-1.83 (m, 3H), 1.71 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): 158.7, 157.9, 149.7, 137.4, 137.2, 128.0, 126.0, 122.1, 115.6, 113.6, 57.8, 55.2, 36.2, 30.0. MS (FAB+) m/z 333.1 ($M+H^+$, 20), FAB+ HRMS for $C_{17}H_{21}O_3N_2S$ ($M+H^+$): Calcd: 333.1272. Found: 333.1276.

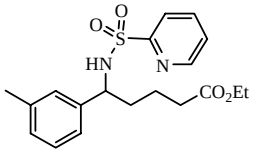
5-Chloro-1-(4-fluorophenyl)-*N*-(2-pyridylsulfonyl)pentan-1-amine (25f). yield 88%, white solid; m.p.: 87-89 ºC; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.44 (d, *J*= 4.4 Hz, 1H), 7.65-7.60 (m, 2H), 7.27 (m, 1H), 6.93 (m, 2H), 6.70 (m, 2H), 5.61 (d, *J*= 8.0 Hz, 1H), 4.32 (q, *J*= 7.6 Hz, 1H), 3.37 (t, *J*= 6.6 Hz, 2H), 1.80 (m, 1H), 1.71-1.58 (m, 3H), 1,39 (m, 1H), 1.21 (m 1H). ^{13}C NMR (75 MHz, $CDCl_3$): 157.8, 149.8, 137.6, 136.2, 128.4, 128.3, 126.2, 122.0, 115.3, 115.0, 58.0, 44.5, 36.4, 31.9, 23.4. MS (FAB+) m/z 357.1 ($M+H^+$, 70), FAB+ HRMS for $C_{16}H_{19}O_2N_2SFCl$ ($M+H^+$): Calcd: 357.0839. Found: 357.0836.

3-(1,3-Dioxolan-2-yl)-1-(4-fluorophenyl)-*N*-(2-pyridylsulfonyl) propan-1-amine (26f). yield 85%, colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.46 (d, *J*= 4.4 Hz, 1H), 7.63-7.59 (m, 2H), 7.27 (m, 1H), 6.95 (m, 2H), 6.69 (m, 2H), 5.76 (d, *J*= 7.4 Hz, 1H), 4.77 (t, *J*= 4.3 Hz, 1H), 4.39 (q, *J*= 7.4 Hz, 1H), 3.90-3.70 (m, 4H), 1.95-1.44 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): 157.7, 149.8, 137.5, 136.3, 136.2, 128.4, 128.3, 126.2, 122.1, 115.2, 114.9, 103.5, 65.0, 64.9, 57.8, 31.0, 29.8. MS (FAB+) m/z 367.1 ($M+H^+$, 25), FAB+ HRMS for $C_{17}H_{20}O_2N_2SF$ ($M+H^+$): Calcd: 367.1127. Found: 367.1132

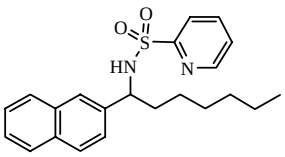
Ethyl 5-(2-bromophenyl)-5-*N*-(2-pyridylsulfonylamino)pentanoate (27f). yield 87%, white solid; m.p.: 100-102 ºC; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.43 (d, *J*=

4.4 Hz, 1H), 7.73 (m, 1H), 7.61 (dt, *J*= 1.7 and 7.7 Hz, 1H), 7.29-7.20 (m, 2H), 7.11 (dd, *J*= 1.7 and 7.8 Hz, 1H), 7.01 (dt, *J*= 1.1 and 7.4 Hz, 1H), 6.87 (dt, *J*= 1.7 and 7.9 Hz, 1H), 5.94 (d, *J*= 8.2 Hz, 1H), 4.79 (q, *J*= 7.9 Hz, 1H), 4.03 (q, *J*= 7.2 Hz, 2H), 2.23 (t, *J*= 6.3 Hz, 2H), 1.81-1.60 (m, 3H), 1.51 (m, 1H), 1.16 (t, *J*= 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): 173.1, 157.2, 149.8, 139.6, 137.5, 132.7, 128.7, 128.3, 127.6, 126.3, 122.5, 122.2, 60.4, 57.2, 36.5, 33.4, 21.1, 14.2. MS (FAB+) m/z 443.1 ($M+H^+$, 100), FAB+ HRMS for $C_{18}H_{22}O_4N_2SBr$ ($M+H^+$): Calcd: 441.0483. Found: 441.0492.

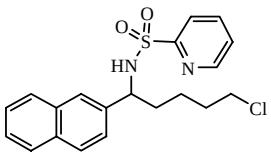
Ethyl *N*-(2-pyridylsulfonylamino)-5-(3-tolyl)pentanoate (28f). yield 84%, white solid; m.p.: 70-71 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.41 (d, *J*= 4.4 Hz, 1H), 7.63-7.54 (m, 2H), 7.22 (m, 1H), 6.90 (m, 1H), 6.81 (m, 1H), 6.73 (m, 1H), 6.68 (m, 1H), 6.49 (d, *J*= 8.1 Hz, 1H), 4.29 (q, *J*= 7.2 Hz, 1H), 4.02 (q, *J*= 7.2 Hz, 2H), 2.19 (t, *J*= 7.2 Hz, 2H), 2.09 (s, 3H), 1.85-1.55 (m, 3H), 1.45 (m, 1H), 1.16 (t, *J*= 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): 173.1, 149.8, 140.0, 137.9, 137.3, 128.3, 128.2, 127.3, 126.0, 123.8, 122.0, 60.4, 56.4, 36.5, 33.6, 21.2, 14.2. MS (FAB+) m/z 377.2 ($M+H^+$, 65), FAB+ HRMS for $C_{19}H_{25}O_4N_2S$ ($M+H^+$): Calcd: 377.1535. Found: 377.1553.



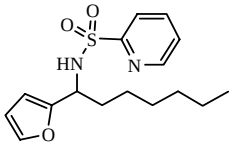
1-(Naphthalen-2-yl)-*N*-(2-pyridylsulfonyl)heptan-1-amine (29f). yield 91%, yellow solid; m.p.: 71-73 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.29 (d, *J*= 4.4 Hz, 1H), 7.65-7.55 (m, 2H), 7.48-7.41 (m, 2H), 7.38-7.32 (m, 3H), 7.06 (dd, *J*= 1.7 and 8.5 Hz, 1H), 7.23 (m, 1H), 6.93 (ddd, *J*= 1.0, 4.7 and 7.6 Hz, 1H), 5.85 (m, 1H), 4.49 (q, *J*= 7.6 Hz, 1H), 1.85 (m, 1H), 1.74 (m, 1H), 1.29-1.00 (m, 8H), 0.75 (t, *J*= 6.7 Hz, 3H) . ^{13}C NMR (75 MHz, $CDCl_3$): 157.7, 149.5, 137.7, 137.1, 132.8, 132.5, 128.1, 127.1, 127.4, 126.2, 126.0, 125.9, 125.7, 124.3, 122.0, 59.1, 37.0, 31.5, 28.8, 25.9, 22.5, 14.0. MS (FAB+) m/z 383.2 ($M+H^+$, 25), FAB+ HRMS for $C_{22}H_{27}O_2N_2S$ ($M+H^+$): Calcd: 383.1793. Found: 383.1802.



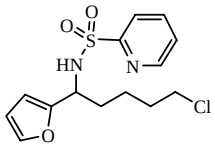
5-Chloro-1-(naphthalen-2-yl)-*N*-(2-pyridylsulfonyl)pentan-1-amine (30f). yield 89%, yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.29 (d, *J*= 4.4 Hz, 1H), 7.65-7.46 (m, 4H), 7.4-7.29 (m, 4H), 7.06 (dd, *J*= 1.8 and 8.5 Hz, 1H), 6.97 (ddd, *J*= 1.1, 4.7 and 7.7 Hz, 1H), 5.45 (m, 1H), 4.50 (q, *J*= 7.5 Hz, 1H), 3.37 (t, *J*= 6.7 Hz, 2H), 1.62-1.20 (m, 4H), 1.45 (m, 1H), 1.26 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): 157.6, 149.5, 137.2, 137.1, 132.8, 132.6, 128.3, 127.7, 127.4, 126.2, 126.0, 125.8, 122.0, 58.9, 44.6, 36.2, 32.0, 23.4. MS (FAB+) m/z 389.1 ($M+H^+$, 15), FAB+ HRMS for $C_{20}H_{22}O_2N_2SCl$ ($M+H^+$): Calcd: 389.1090. Found: 389.1093.



1-(Furan-2-yl)-*N*-(2-pyridylsulfonyl)heptan-1-amine (31f). yield 92%, white solid; m.p.: 58-60 ºC; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.46 (d, *J*= 4.4 Hz, 1H), 7.82-7.70 (m, 2H), 7.32 (ddd, *J*= 1.4, 4.7 and 7.2 Hz, 1H), 6.96 (dd, *J*= 0.7 and 1.7 Hz, 1H), 5.94 (dd, *J*= 1.9 and 3.3 Hz, 1H), 5.78 (d, *J*= 3.2 Hz, 1H), 5.45 (d, *J*= 9.2 Hz, 1H), 4.40 (q, *J*= 7.5 Hz, 1H), 1.80-1.65 (m, 2H), 1.30-1.05 (m, 8H), 0.78 (t, *J*= 7.0 Hz, 3H) . ^{13}C NMR (75 MHz, $CDCl_3$): 157.6, 152.8, 149.7, 141.8, 137.8, 126.2, 122.0, 109.8, 106.9, 127.4, 126.2, 126.0, 125.9, 125.7, 124.3, 122.0, 52.1, 34.6, 31.5, 28.6, 25.6, 22.5, 14.0. MS (FAB+) m/z 323.2 ($M+H^+$, 27), FAB+ HRMS for $C_{16}H_{23}O_3N_2S$ ($M+H^+$): Calcd: 323.1429. Found: 323.1441.



5-Chloro-1-(furan-2-yl)-*N*-(2-pyridylsulfonyl)pentan-1-amine (32f). yield 90%, yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.47 (d, *J*= 4.4 Hz, 1H), 7.83-7.70 (m, 2H), 7.31 (ddd, *J*= 1.4, 4.7 and 7.2 Hz, 1H), 7.01 (dd, *J*= 0.8 and 1.7 Hz, 1H), 5.97 (dd, *J*= 1.8 and 3.3 Hz, 1H), 5.79 (d, *J*= 3.2 Hz, 1H), 5.25 (d, *J*= 8.9 Hz, 1H), 4.43 (q, *J*= 7.5 Hz, 1H), 3.41 (t, *J*= 6.7 Hz, 2H), 1.82-1.20 (m, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): 157.6, 152.4, 149.9, 141.9, 137.7, 126.3, 121.8, 110.0, 107.0, 51.9, 44.6, 33.9, 31.9, 23.1. MS (FAB+) m/z 329.0 ($M+H^+$, 20), FAB+ HRMS for $C_{14}H_{18}O_3N_2SCl$ ($M+H^+$): Calcd: 329.0726. Found: 329.0712.



5-*N*-(2-Pyridylsulfonylamino)-5-(thiophen-2-yl)pentanenitrile (33f). yield 80%, colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.47 (d, *J*= 4.4 Hz, 1H), 7.82-7.75 (m, 2H), 7.34 (ddd, *J*= 1.4, 4.7 and 7.2 Hz, 1H), 6.99 (dd, *J*= 1.4 and 4.9 Hz, 1H), 6.68-6.62 (m, 2H), 5.66 (d, *J*= 8.5 Hz, 1H), 4.69 (q, *J*= 7.9 Hz, 1H), 2.31 (t, *J*= 7.0 Hz, 2H), 2.00-1.55 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): 157.4, 149.7, 138.1, 126.7, 125.3, 125.0, 122.1, 119.2, 53.4, 36.6, 22.1, 16.7. MS (FAB+) m/z 322.0 ($M+H^+$, 37), FAB+ HRMS for $C_{14}H_{16}O_2N_3S_2$ ($M+H^+$): Calcd: 322.0684. Found: 322.0688.

1-(1-Benzyl-1H-pyrrol-2-yl)-2-cyclohexyl-*N*-(2-pyridylsulfonyl) ethanamine (34f). yield 68%, white solid; m.p.: 110-112 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.53 (d, *J*= 4.4 Hz, 1H), 7.73-7.68 (m, 2H), 7.33 (m, 1H), 7.25-7.10 (m, 3H), 6.92-6.87 (m, 2H), 6.45 (dd, *J*= 1.8 and 2.5 Hz, 1H), 5.90-5.85 (m, 2H), 5.21 (d, *J*= 16.3 Hz, 1H), 5.05 (d, *J*= 8.4 Hz, 1H), 4.88 (d, *J*= 16.3 Hz, 1H), 4.42 (q, *J*= 8.1 Hz, 1H), 1.50-1.13 (m, 6H), 1.05-1.65 (m, 5H) 0.51-0.32 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): 158.3, 149.9, 138.4, 137.7, 131.6, 128.7, 127.5, 126.4, 126.2, 122.4, 121.5, 107.3, 50.4, 48.0, 43.5, 34.0, 32.9, 32.5, 26.3, 25.9. MS (FAB+) m/z 424.2 ($M+H^+$, 5), FAB+ HRMS for $C_{24}H_{30}O_2N_3S$ ($M+H^+$): Calcd: 424.2059. Found: 424.2050.

1-[[4-[5-Chloro-1-*N*-(2-pyridylsulfonylamino)pentyl]phenyl]] ethanone (35f). yield 77%, yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.45 (d, *J*= 4.4 Hz, 1H), 7.75-7.55 (m, 4H), 7.27 (m, 1H), 7.11 (d, *J*= 8.3 Hz, 2H), 6.00 (d, *J*= 7.9 Hz, 1H), 4.43 (q, *J*= 7.6 Hz, 1H), 3.36 (t, *J*= 6.5 Hz, 2H), 2.47 (s, 3H), 1.93-1.60 (m, 4H), 1.52-1.20 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): 197.5, 157.7, 149.7, 145.9, 137.7, 136.2, 128.4, 127.1, 126.9, 126.3, 122.0, 58.3, 44.5, 36.3, 31.8, 23.3. MS (FAB+) m/z 381.1 ($M+H^+$, 65), FAB+ HRMS for $C_{18}H_{22}O_3N_2SCl$ ($M+H^+$): Calcd: 381.0961. Found: 381.0953.

Ethyl 5-(4-acetylphenyl)-5-(2-pyridylsulfonylamino)pentanoate (36f). yield 83%, yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.43 (d, *J*= 4.4 Hz, 1H), 7.75-7.55 (m, 4H), 7.25 (m, 1H), 7.12 (d, *J*= 8.3 Hz, 2H), 6.16 (d, *J*= 7.7 Hz, 1H), 4.44 (q, *J*= 7.5 Hz, 1H), 4.01 (q, *J*= 7.1 Hz, 2H), 2.46 (s, 3H), 2.16 (t, *J*= 7.2 Hz, 2H), 1.90-1.55 (m, 3H), 1.42 (m, 1H), 1.14 (t, *J*= 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): 197.5, 173.0, 157.7, 149.7, 145.9, 137.6, 128.9, 128.4, 126.9, 126.3, 122.0, 60.4, 58.2, 36.3, 33.4, 26.6, 21.3, 14.2. MS (FAB+) m/z 405.2 ($M+H^+$, 100), FAB+ HRMS for $C_{20}H_{25}O_5N_2S$ ($M+H^+$): Calcd: 405.1484. Found: 405.1484.

1-[[4-[2-Ethyl-1-*N*-(2-pyridylsulfonylamino)butyl]phenyl]] ethanone (37f). yield 85%, yellow solid; m.p.: 87-88 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.28 (d, *J*= 4.4 Hz, 1H), 7.52-7.40 (m, 4H), 7.09 (m, 1H), 6.92 (d, *J*= 8.2 Hz, 2H), 5.42 (d, *J*= 8.8 Hz, 1H), 4.29 (dd, *J*= 7.4 and 8.5 Hz, 1H), 2.34 (s, 3H), 1.42-1.15 (m, 3H), 1.15-0.95 (m, 2H), 0.65 (t, *J*= 7.3 Hz, 3H), 0.58 (t, *J*= 7.3 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): 197.5, 157.6, 149.7, 145.7, 137.4, 135.8, 128.0, 127.3, 126.2, 122.0, 60.0, 46.9, 30.9, 26.6, 21.6, 20.8, 10.8, 10.6. MS (FAB+) m/z 361.1.0 ($M+H^+$, 100), FAB+ HRMS for $C_{19}H_{25}O_3N_2S$ ($M+H^+$): Calcd: 361.1586. Found: 361.1591.

(*Z*)-1,3-Diphenyl-*N*-(2-pyridylsulfonyl)non-1-en-1-amine (39). yield 97%, white solid; m.p.: 68-70 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.56 (d, *J*= 4.4 Hz, 1H), 7.59-7.50 (m, 2H), 7.30-7.05 (m, 11H), 6.91 (s, 1H), 5.66 (d, *J*= 9.7 Hz, 1H), 3.52 (m, 1H), 1.60-1.35 (m, 2H), 1.30-1.09 (m, 8H), 0.77 (t, *J*= 6.7 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): 157.3, 150.0, 143.7, 137.7, 137.4, 133.6, 130.8, 128.7, 128.1, 127.9, 127.4, 127.1, 126.7, 126.5, 122.8, 63.1, 43.5, 37.6, 31.7, 29.3, 27.4, 22.6, 14.1. MS (FAB+) m/z 435.2 ($M+H^+$, 80), FAB+ HRMS for $C_{26}H_{31}O_2N_2S$ ($M+H^+$): Calcd: 435.2106. Found: 435.2100.

(*Z*)-8-Chloro-1,3-diphenyl-*N*-(2-pyridylsulfonyl)-1-octen-1-amine (40). yield 94%, white gummy solid; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.56 (d, *J*= 4.4 Hz, 1H), 7.62-7.50 (m, 2H) 7.28 (m, 1H), 7.24-7.15 (m, 4H), 7.12-7.02 (m, 6H), 6.93 (m, 1H), 5.68 (d, *J*= 9.3 Hz, 1H), 3.58 (q, *J*= 7.1, 1H), 3.38 (t, *J*= 6.7 Hz, 2H), 1.70-1.40 (m, 4H), 1.32-0.90 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): 157.3, 150.0, 143.3, 137.7, 137.5, 133.9, 130.6, 128.9, 128.8, 128.1, 127.4, 127.2, 126.8, 126.7, 122.7, 44.8, 43.3, 36.5, 32.4, 24.6.

Ethyl (*Z*)-5,7-diphenyl-7-*N*-(2-pyridylsulfonyl)hept-6-enoate (41). yield 88%, white oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.69 (d, *J*= 4.4 Hz, 1H), 7.75-7.60 (m, 2H), 7.41 (m, 1H), 7.35-7.15 (m, 10H), 7.04 (s, 1H), 5.79 (d, *J*= 9.5 Hz, 1H), 4.16 (q, *J*= 7.1 Hz, 2H), 3.71 (q, *J*= 7.2 Hz, 1H), 2.29 (t, *J*= 7.2 Hz, 2H), 1.80-1.40 (m, 4H), 1.29 (t, *J*= 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): 173.5, 157.3, 150.0, 143.2, 137.6, 137.5, 134.0, 130.4, 128.8, 128.1, 127.9, 127.4, 127.1, 126.7, 126.6, 122.7, 60.3, 43.1, 36.5, 34.0, 22.7, 14.3.

Representative procedure for the deprotection of *N*-(2-pyridyl) sulfonyl amines: Synthesis of 3-(1,3-dioxolan-2-yl)-1-phenylpropan-1-amine (43).

To a suspension of magnesium turnings (303 mg, 12.4 mmol) in dry MeOH (10 mL) cooled to 0ºC, was added a solution of sulfonamide **17f** in dry MeOH (2 mL). The resulting mixture was stirred at room temperature for 3 h. Then it was filtered over Celite and the filtrated was washed with $NaHCO_3$. The organic phase was dried (Na_2SO_4) and concentrated to afford the pure amine **43** as a brown oil, yield: 239 mg (92%); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.18-7.12 (m,4H), 7.08 (m, 1H), 4.68 (t, *J*= 4.6 Hz, 1H), 3.80-3.61 (m, 5H), 1.91 (bs, 2H), 1.70-1.35 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): 145.8, 128.5, 127.1, 126.4, 104.3, 64.9, 56.1, 33.4, 30.1. MS (FAB+) m/z 208.1 ($M+H^+$, 90), FAB+ HRMS for $C_{12}H_{18}NO_2$ ($M+H^+$): Calcd: 208.1337. Found: 208.1348.

5-Chloro-1-phenylpentan-1-amine (44). yield 90%, brown oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.32-7.10 (m, 5H), 3.83 (t, *J*= 7.1 Hz, 1H), 3.42 (t, *J*= 6.7 Hz, 2H), 2.80 (bs, 2H), 1.70-1.65 (m, 4H), 1,50-1.15 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): 145.4, 128.6, 127.2, 126.4, 56.1, 44.8, 38.3, 32.4, 23.9. MS (FAB+) m/z 162.1 ($M\text{-}Cl^+$, 100) 198.1 ($M+H^+$, 10), FAB+ HRMS for $C_{11}H_{17}N_1Cl$ ($M+H^+$): Calcd: 198.1049. Found: 198.1043.

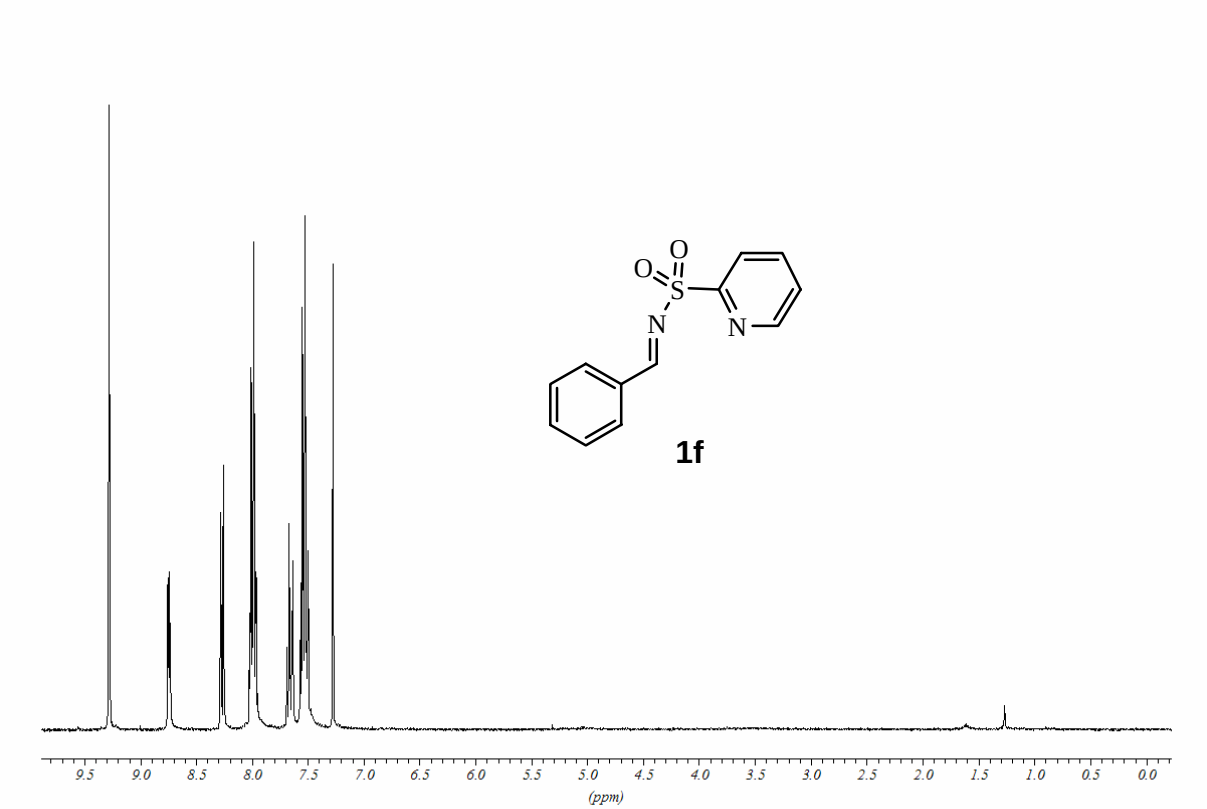
2-Phenylpiperidine[6] **(45).**yield 78%, yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.50-7.02 (m,5H), 3.70 (dd, *J*= 2.6 and 11.2 Hz, 1H), 3.20 (m, 1H), 2.90 (m, 1H), 2.00-1.51 (m, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): 145.8, 128.8, 127.7, 127.0, 62.8, 48.2, 35.4, 26.3, 25.8.

6-Phenylpiperidin-2-one[7] **(46).** yield 94%, brown solid; m.p.: 115-116; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.40-7.12 (m,5H), 5.90 (bs, 1H), 4.47 (dd, *J*= 4.6 and 8.8 Hz, 1H), 2.45-2.31 (m, 2H), 2.04 (m, 1H), 1.90-1.51 (m, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): 172.5, 142.7, 128.7, 126.1, 57.5, 32.1, 31.3, 19.5.

6-(4-Acetylphenyl)piperidin-2-one (47).yield 90%, brown oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.60 (d, *J*= 8.2 Hz, 2H), 7.08 (d, *J*= 8.2 Hz, 2H), 5.96 (bs, 1H), 4.45 (dd, *J*= 4.9 and 9.1 Hz, 1H), 2.44 (s, 3H), 2.42-2.34 (m, 2H), 2.01 (m, 1H), 1.90-1.50 (m, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): 197.5, 172.3, 142.7, 134.0, 128.1, 126.7, 57.1, 32.1, 31.3, 29.3, 19.4.

[6] C. A. Willoughby; S. L. Buchwald *J.Am.Chem.Soc.*, **1994**, *116*, 8952
[7] F. A. Davis; J. M. Szewcsyk *Tetrahedron Lett.* **1998**, *39*, 5951

NMR SPECTRA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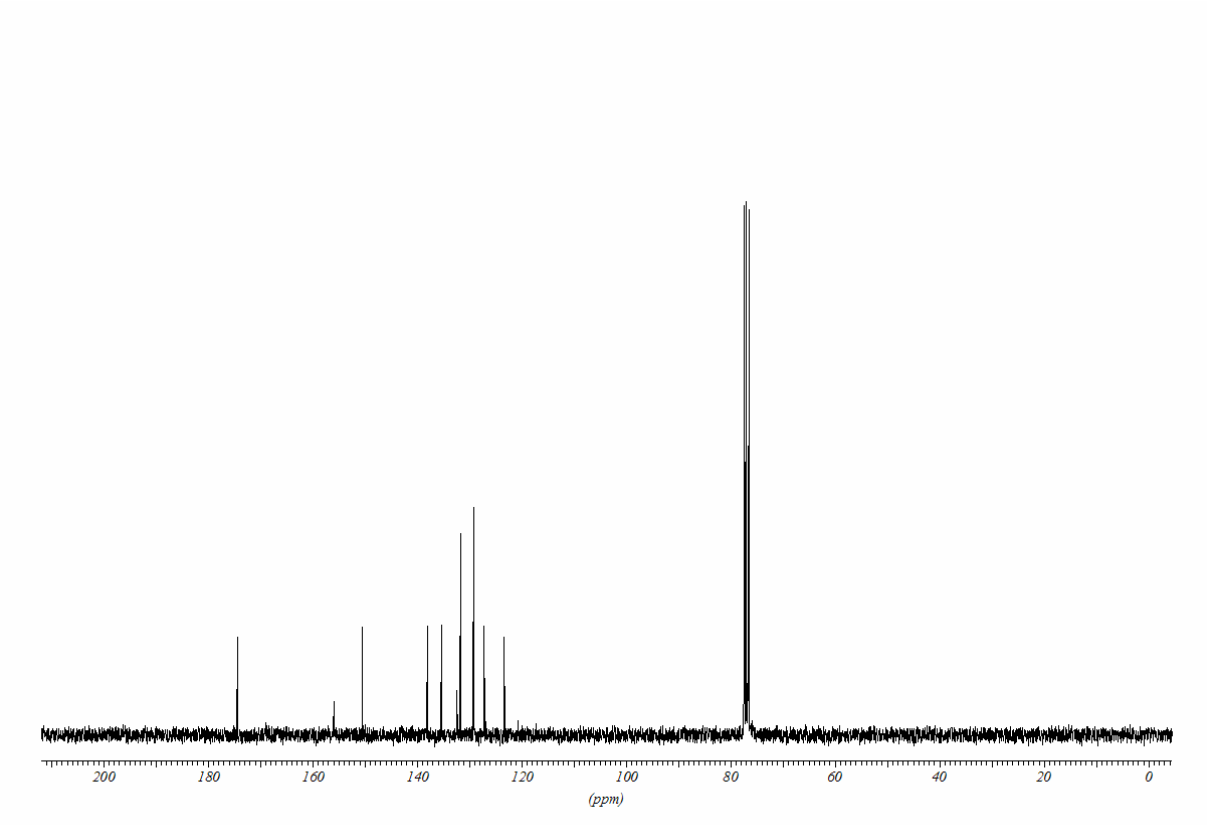
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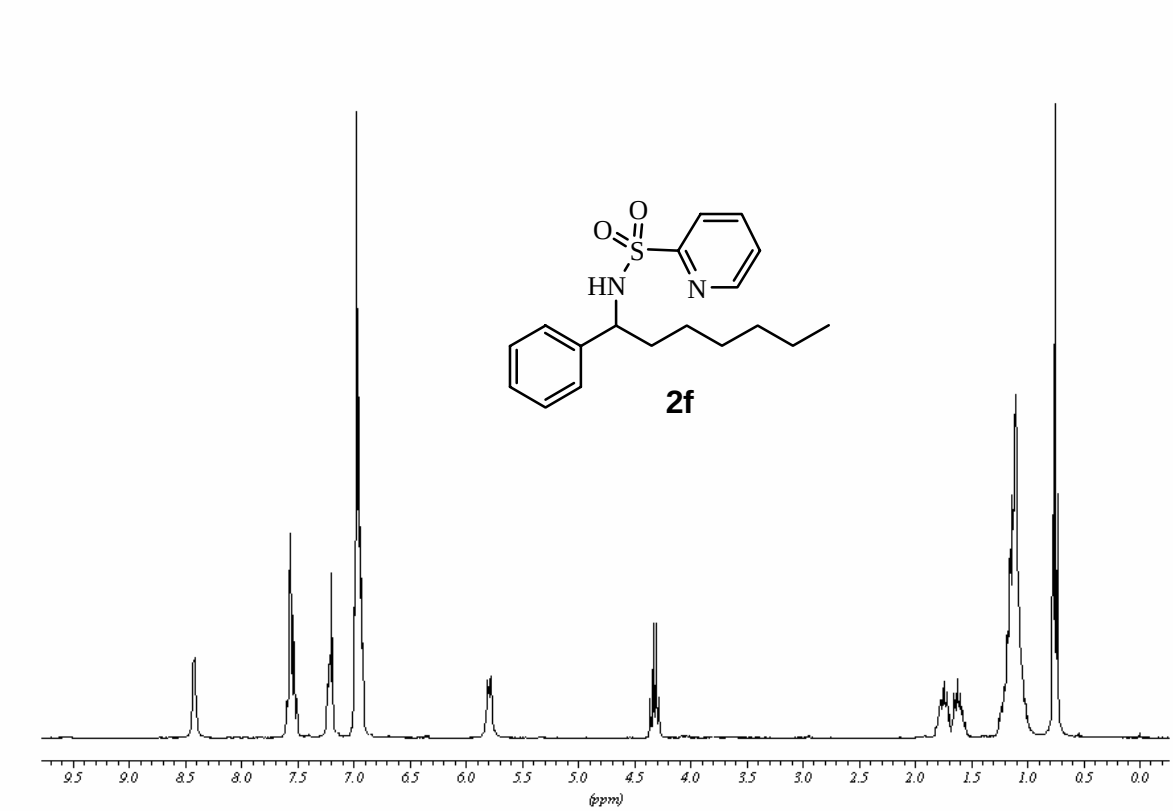
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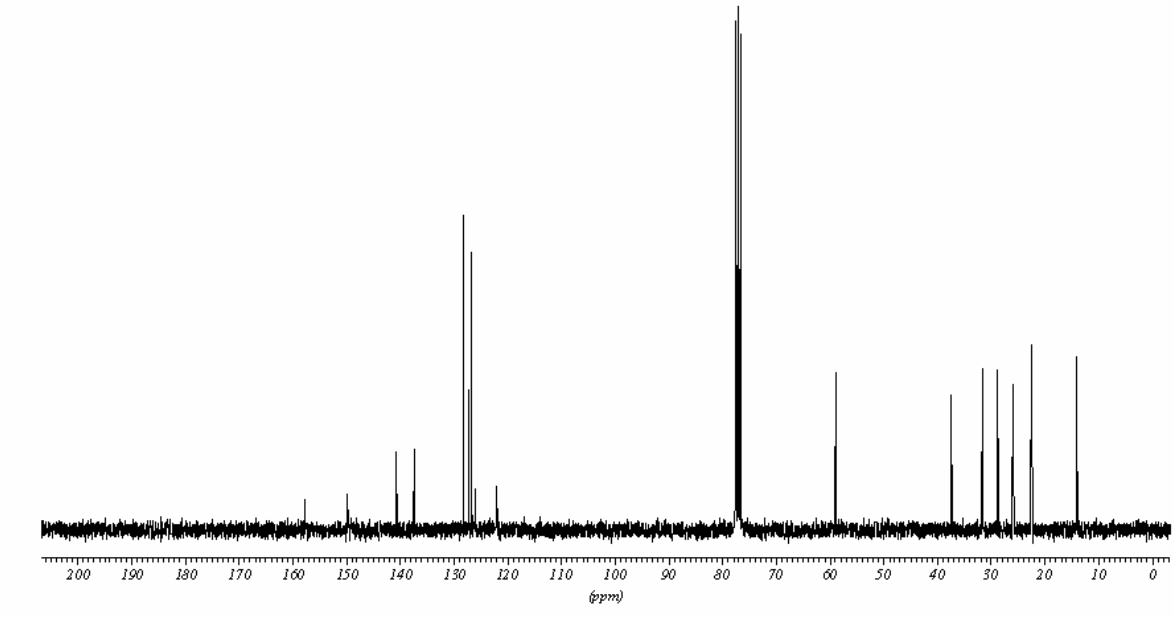
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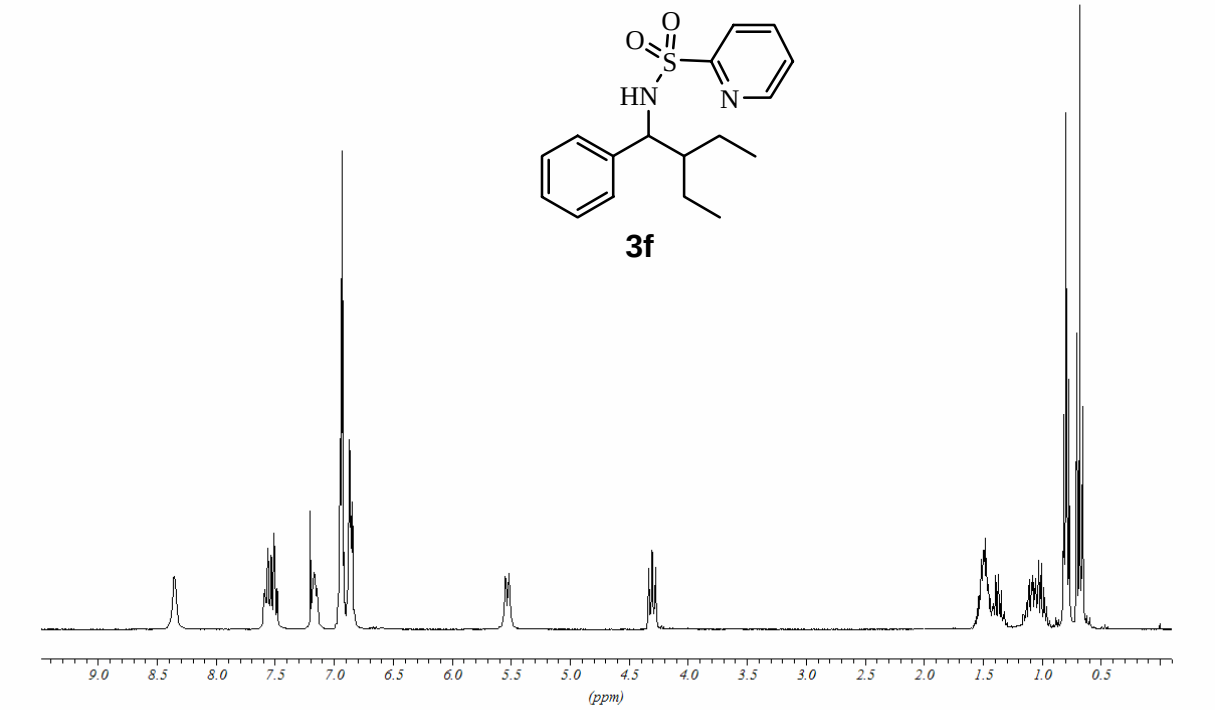
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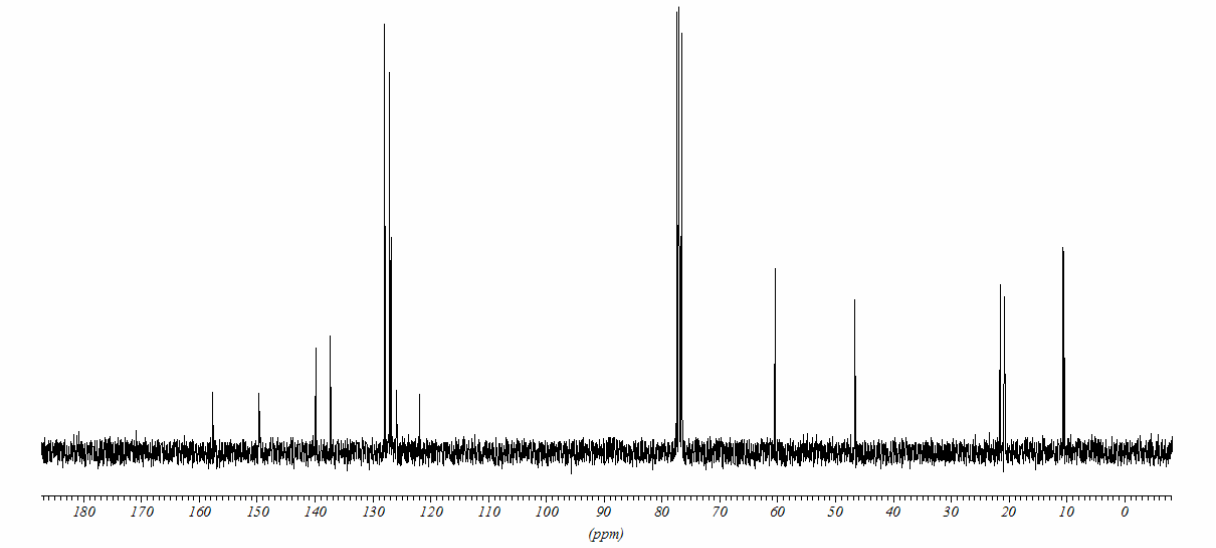
3f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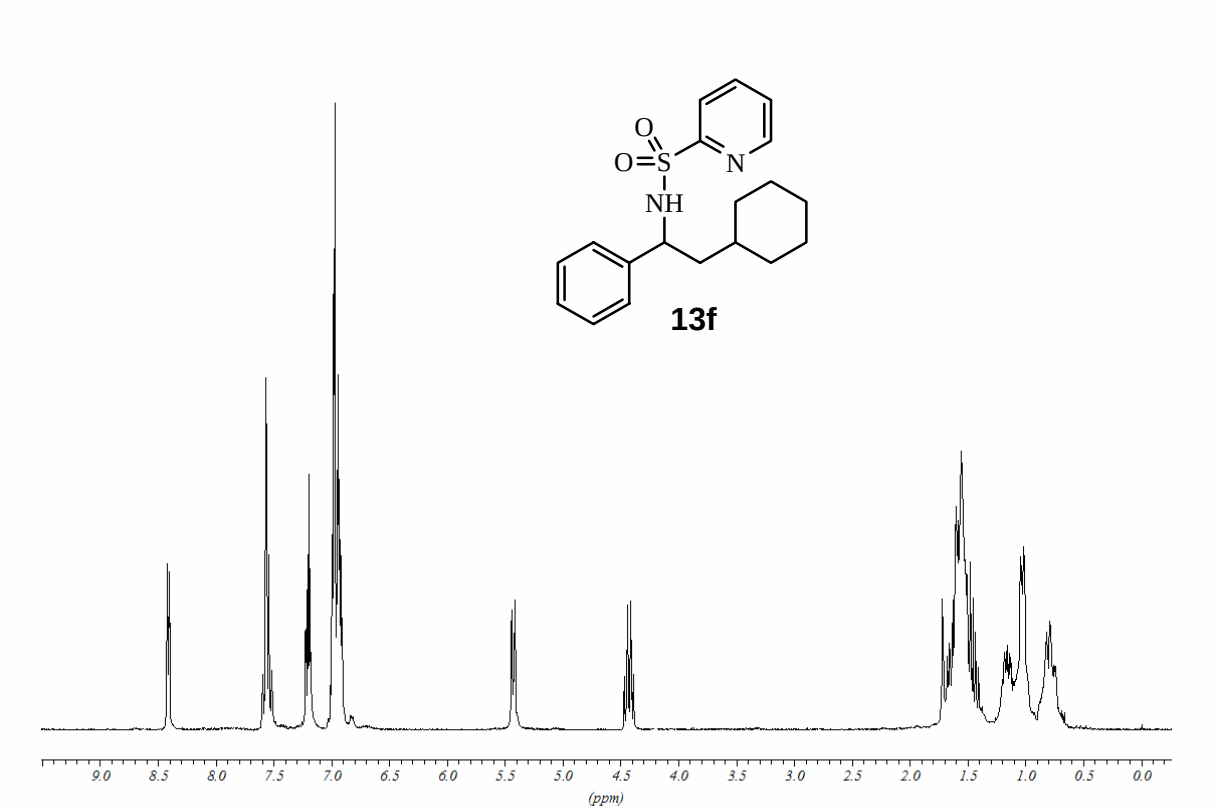
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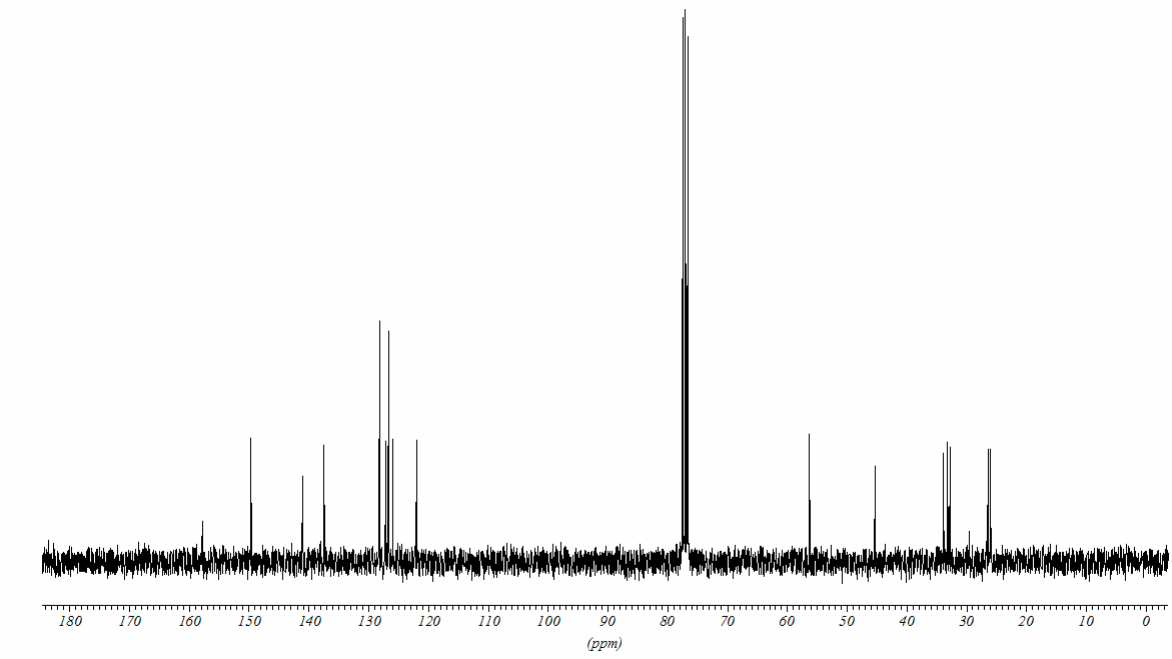
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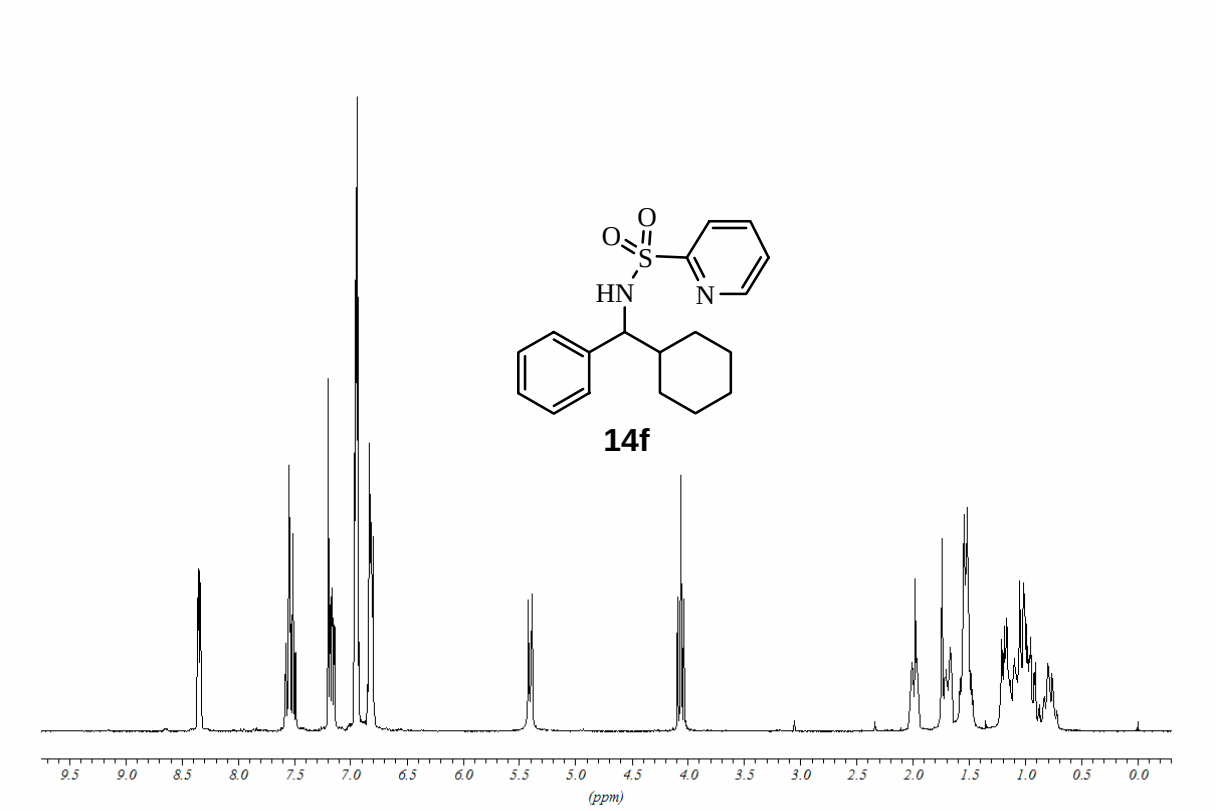
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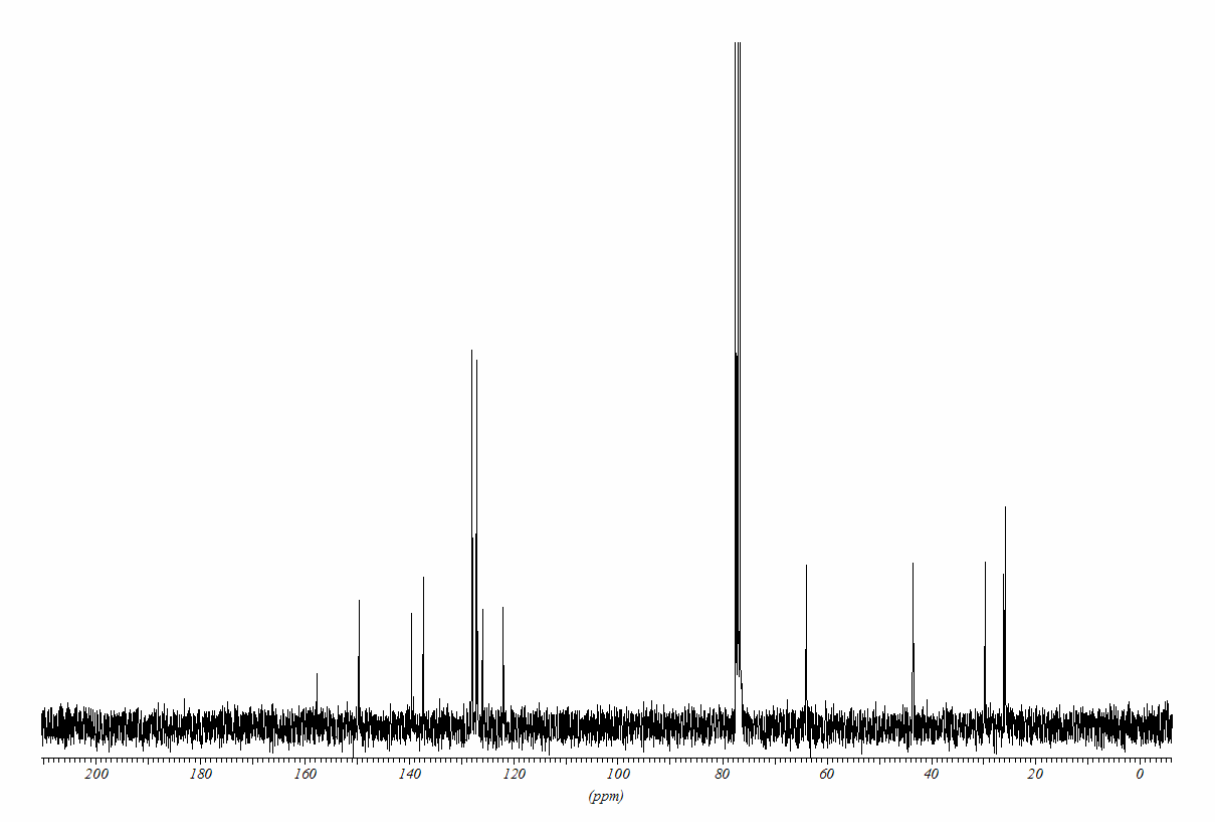
14f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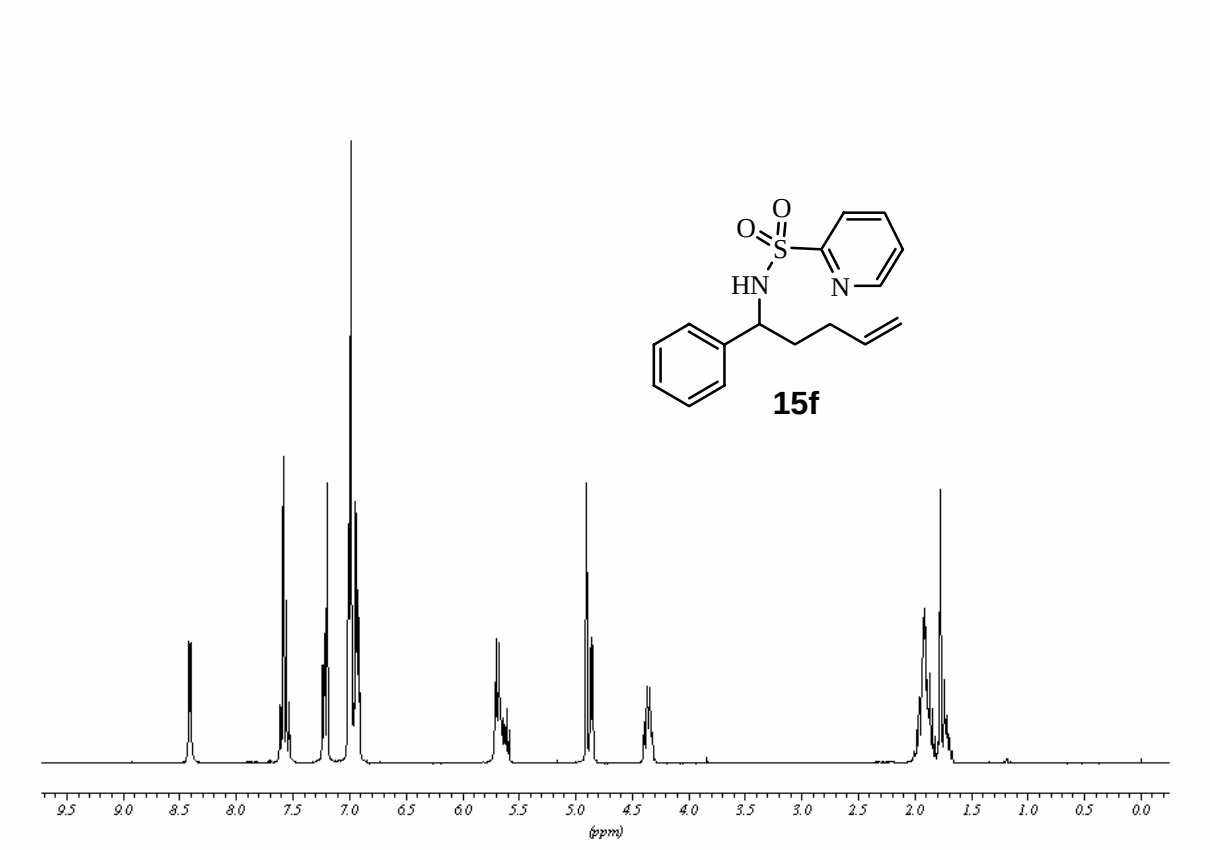
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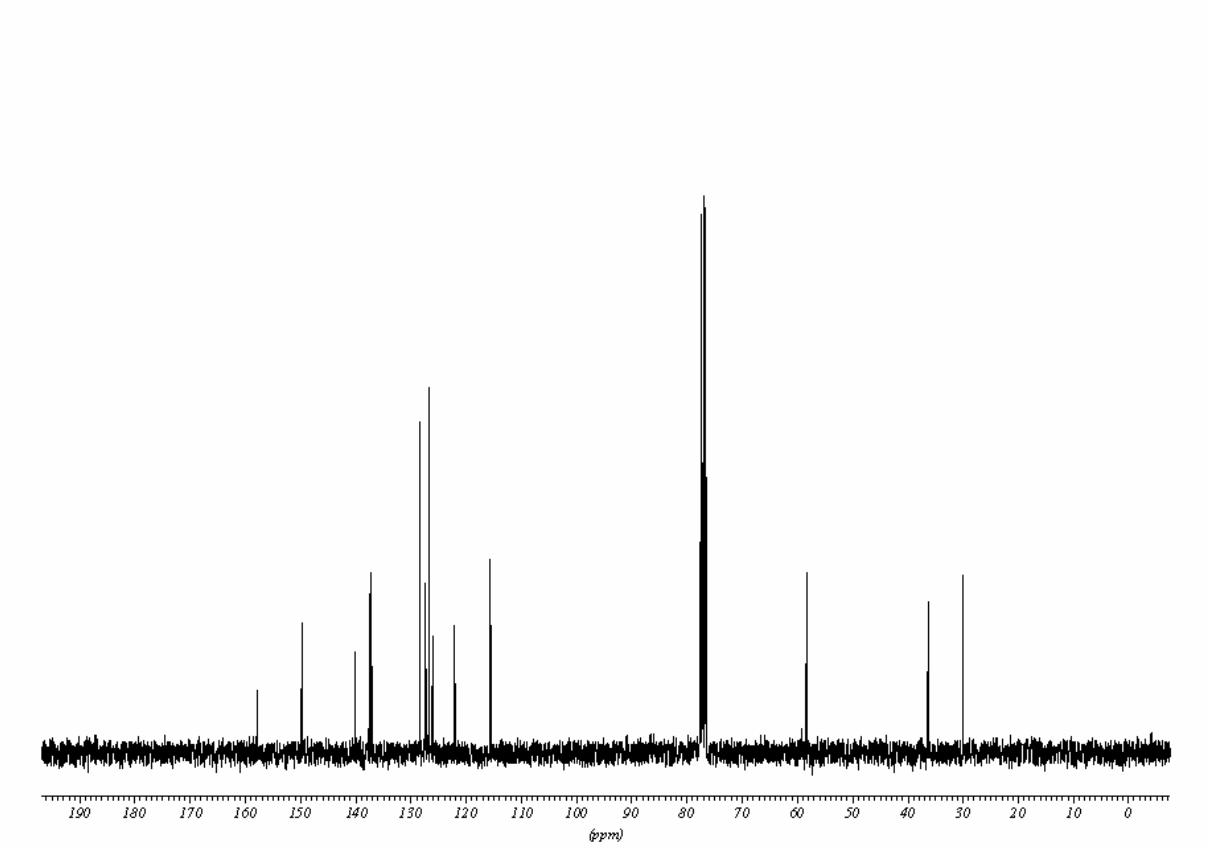
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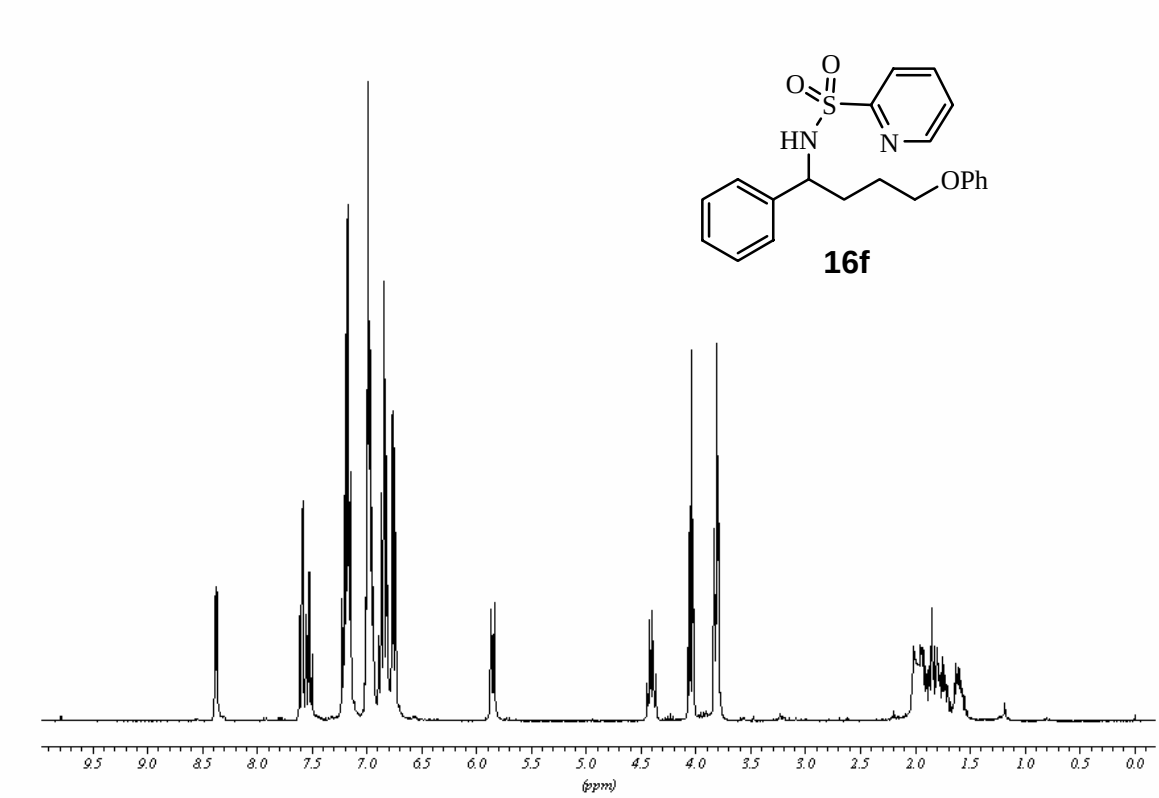
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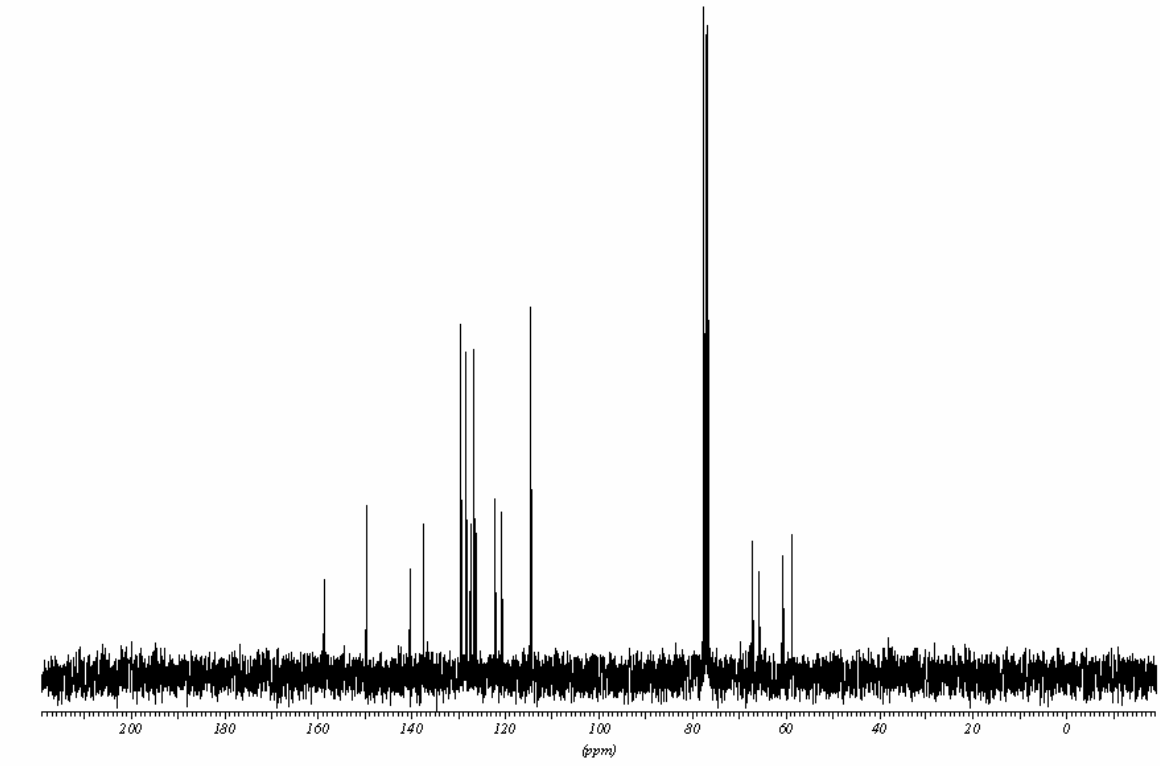
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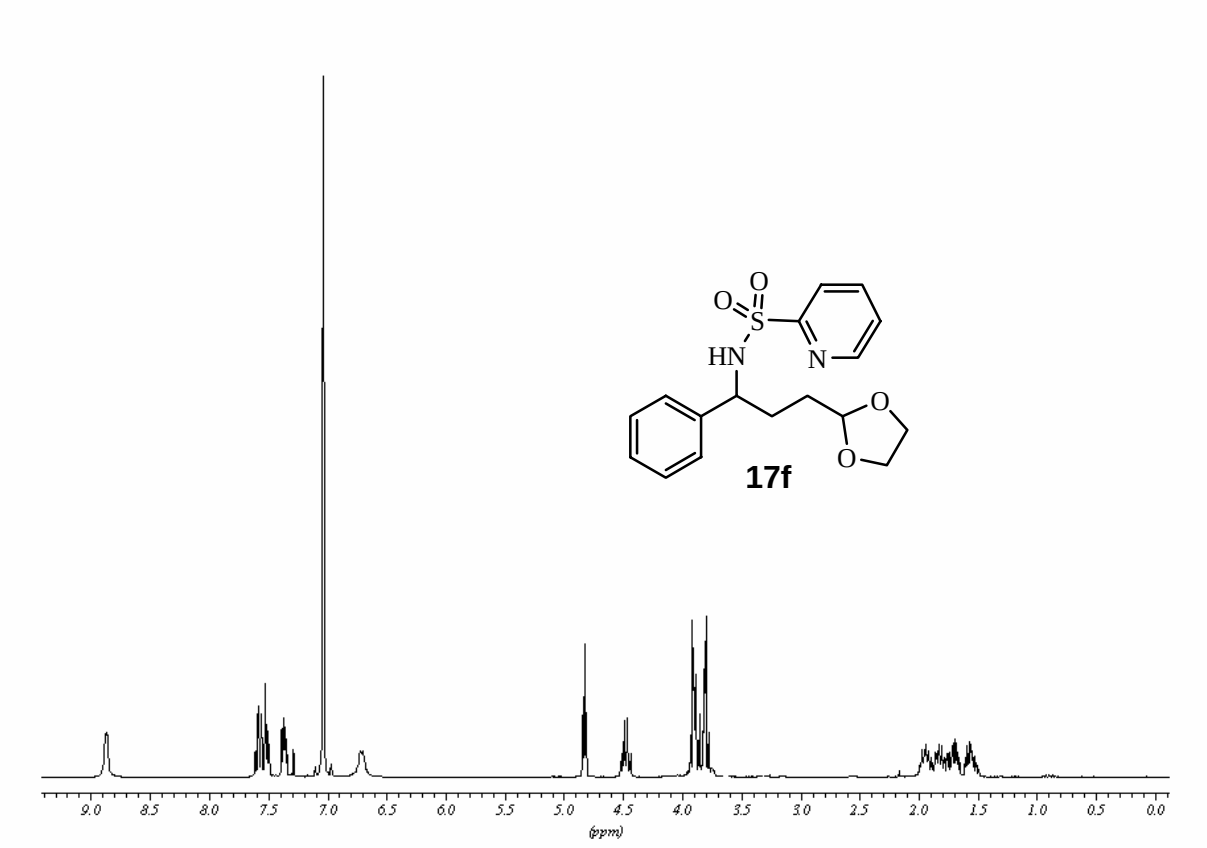
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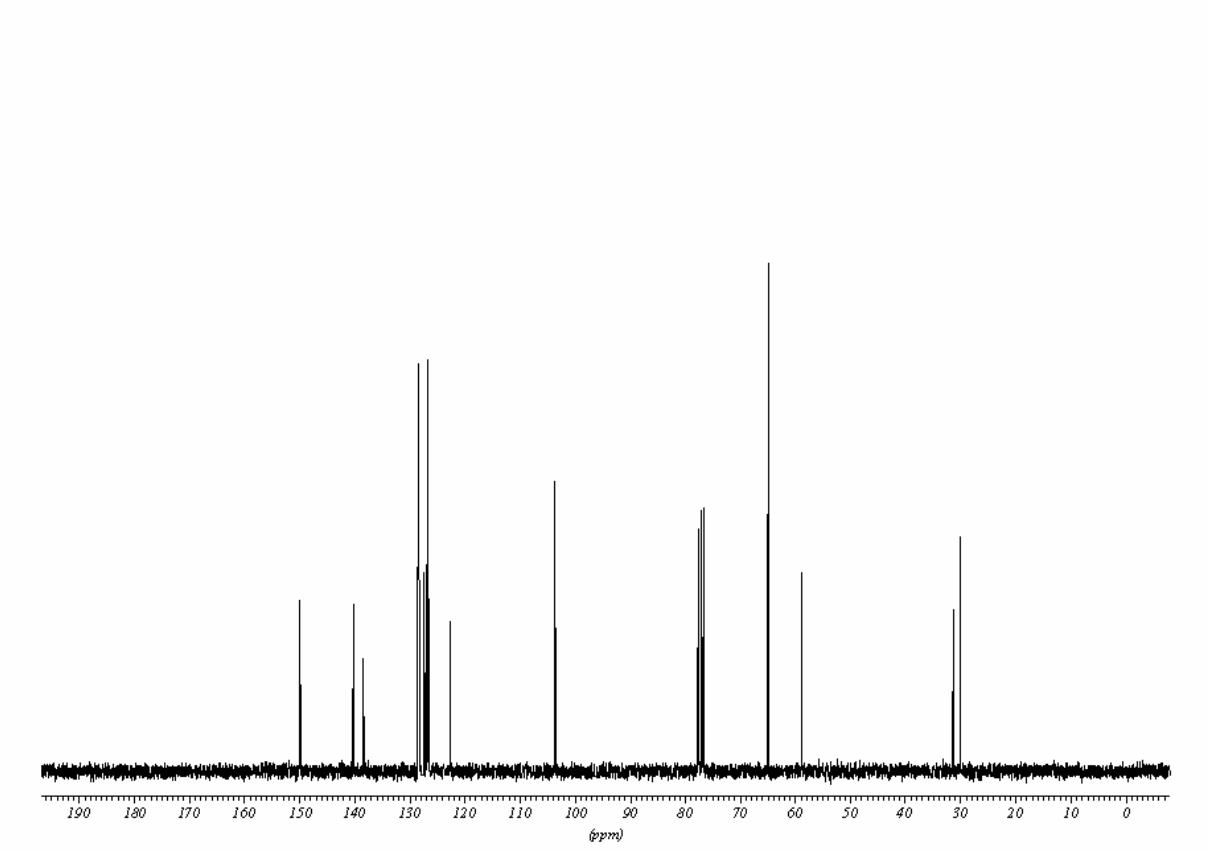
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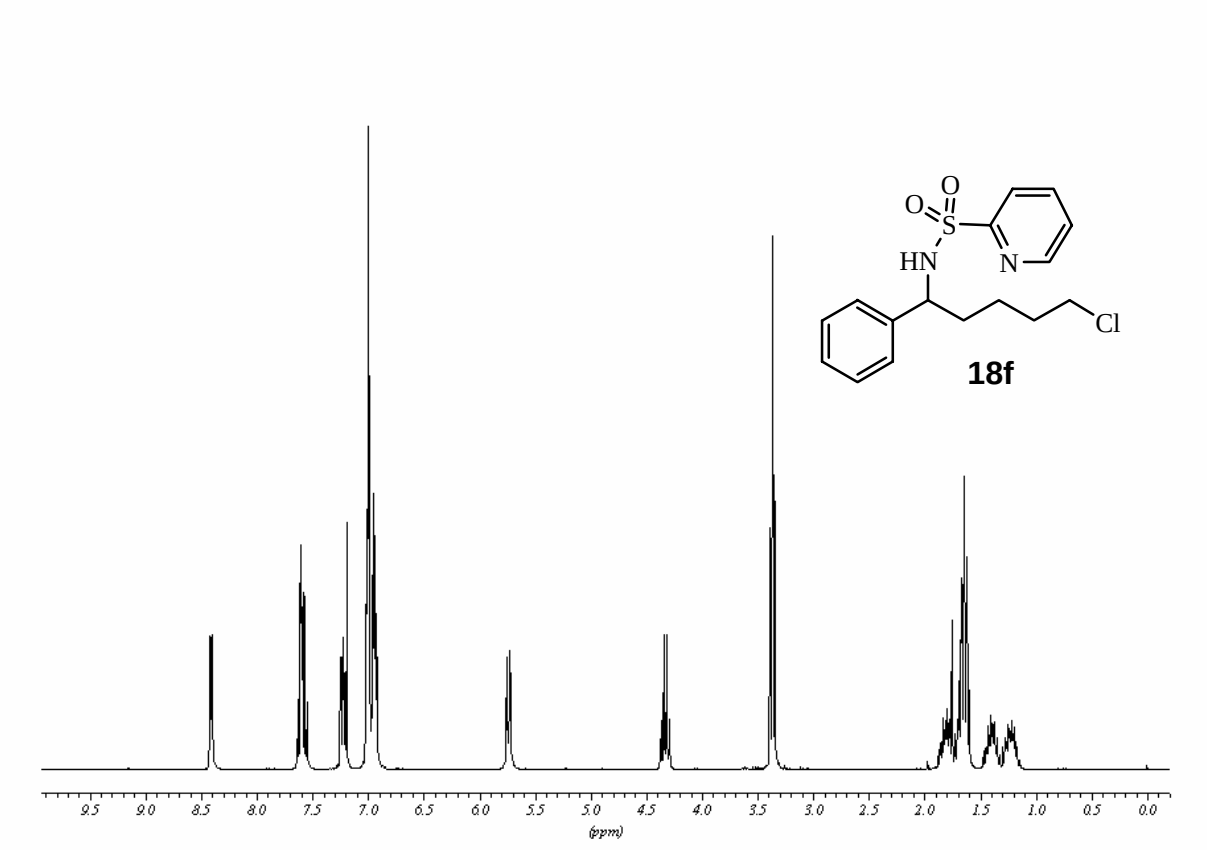
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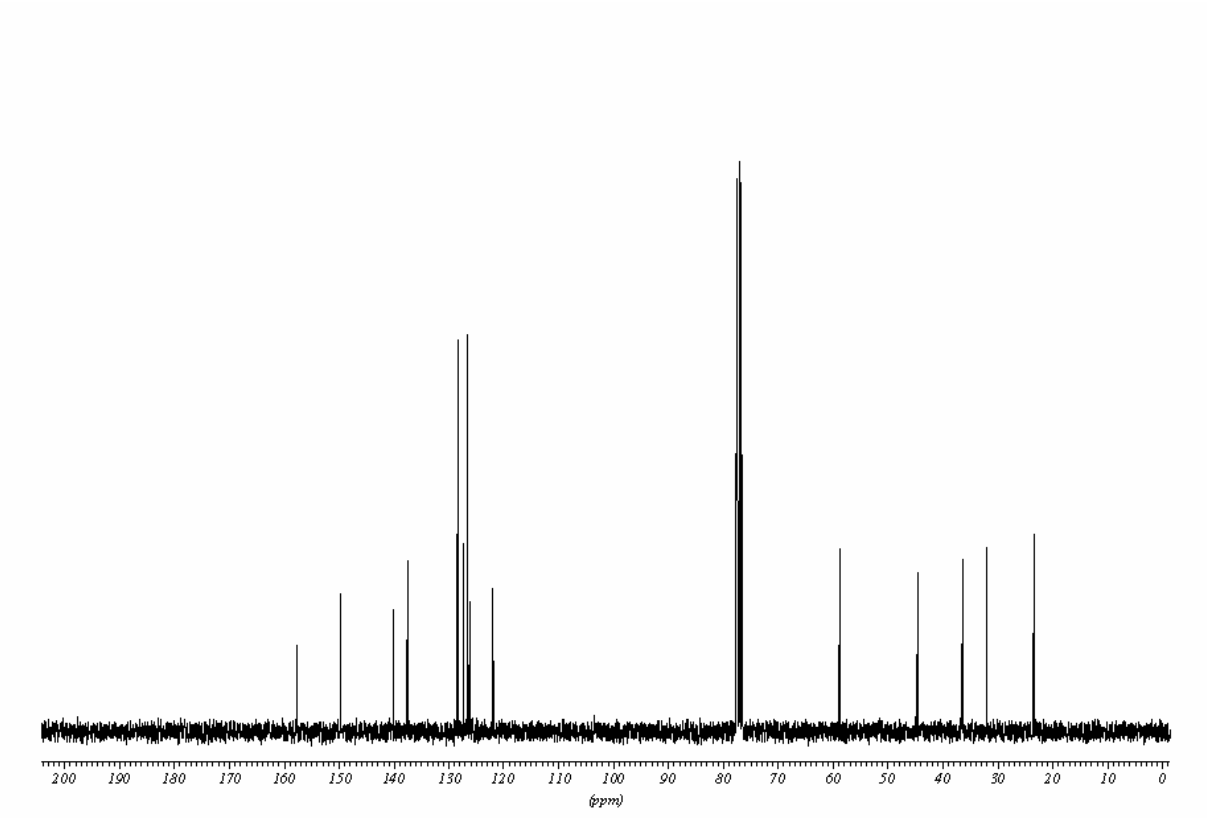
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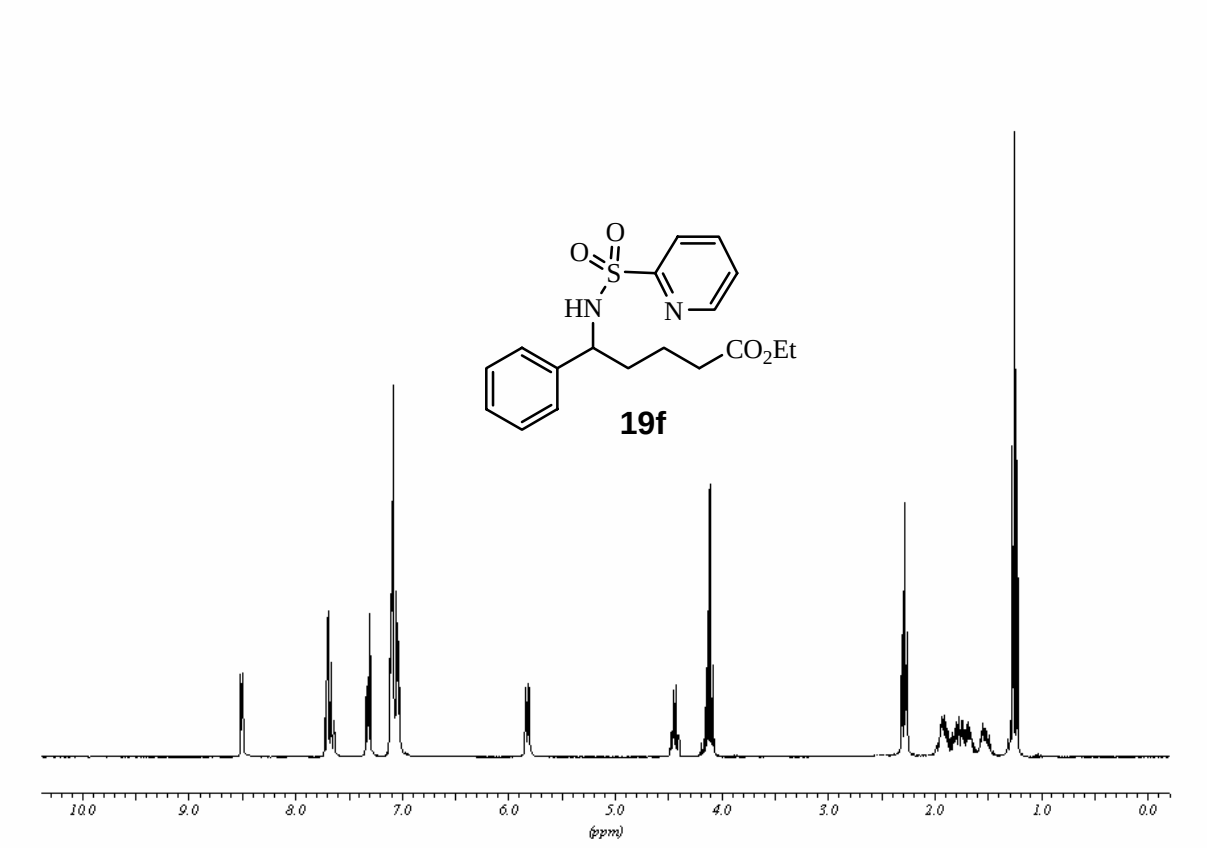
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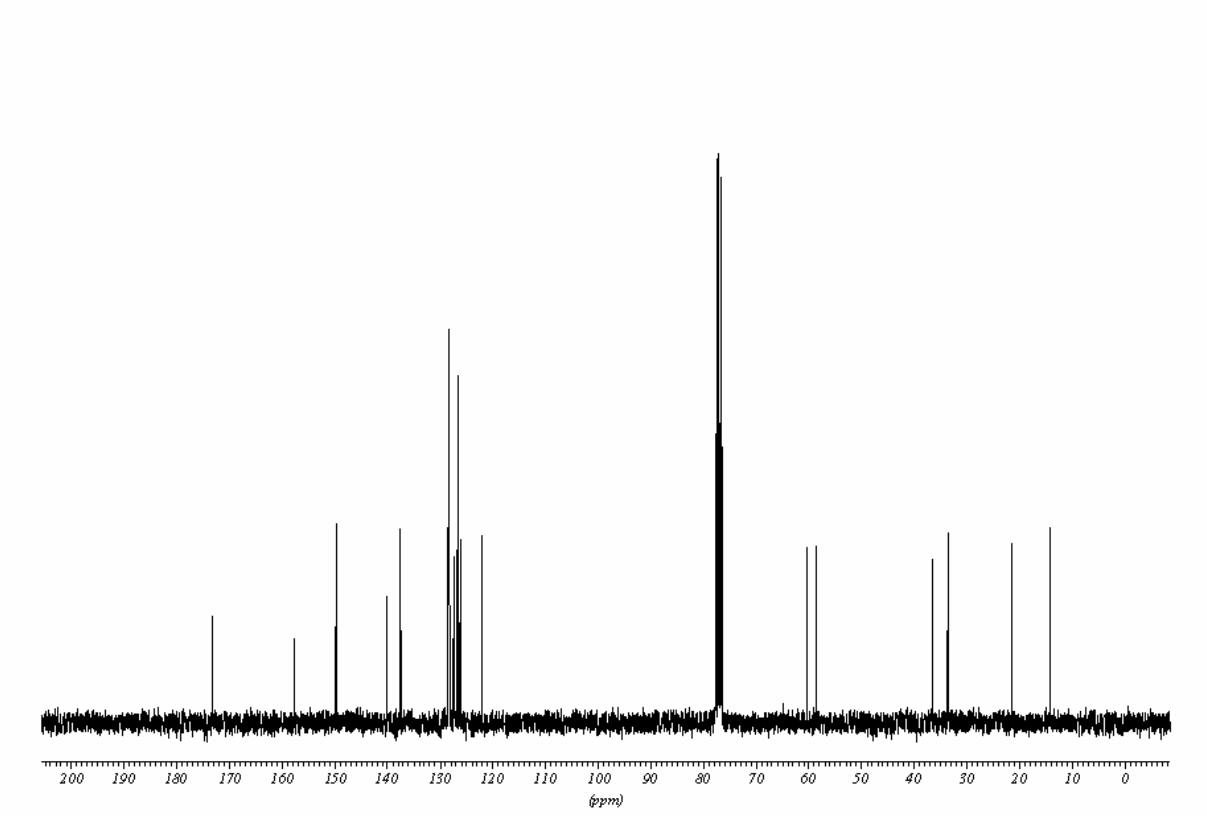
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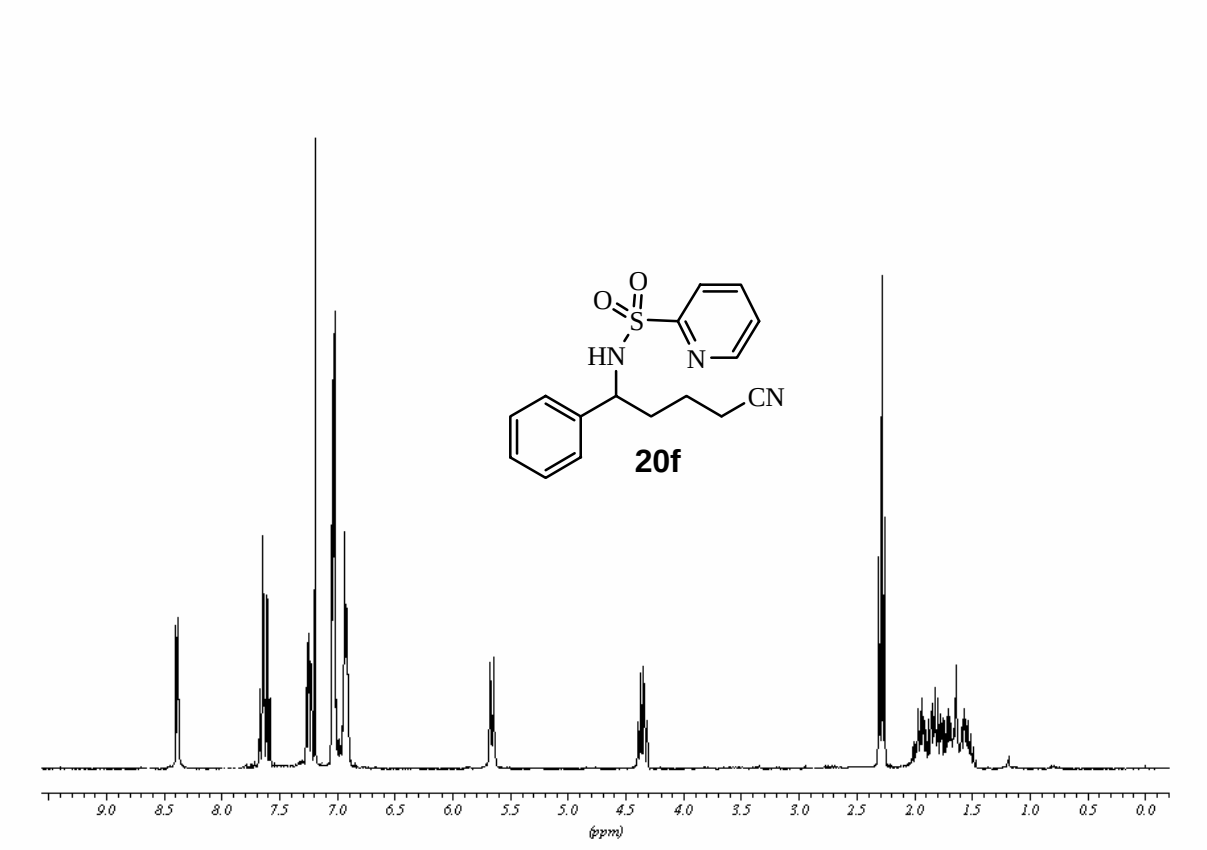
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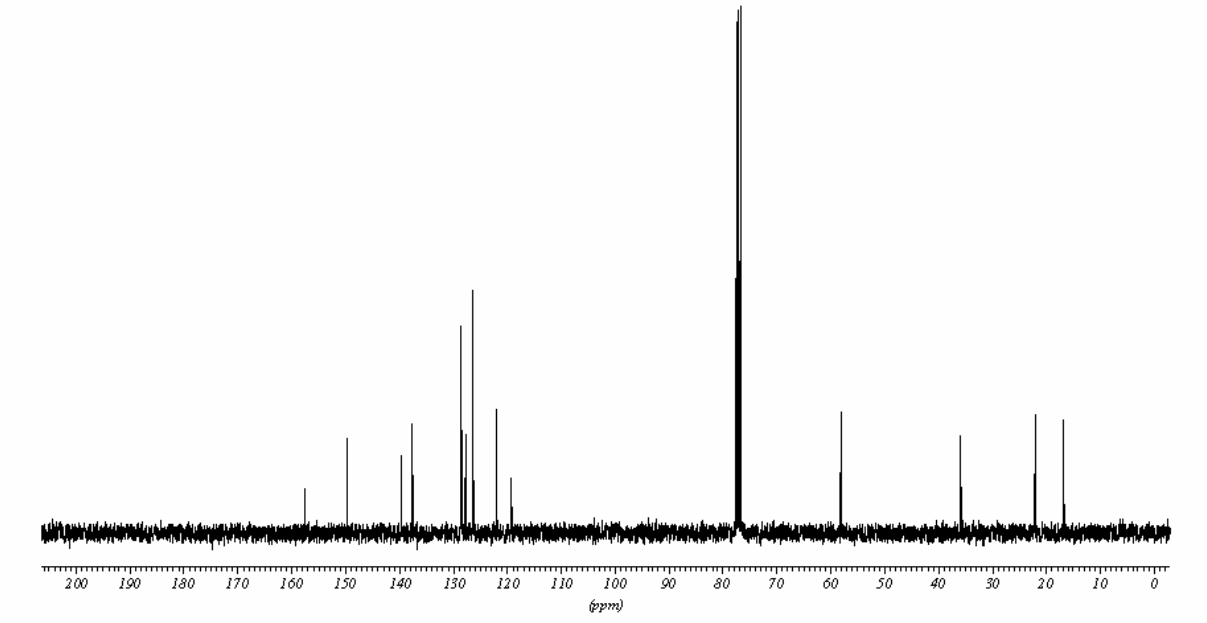
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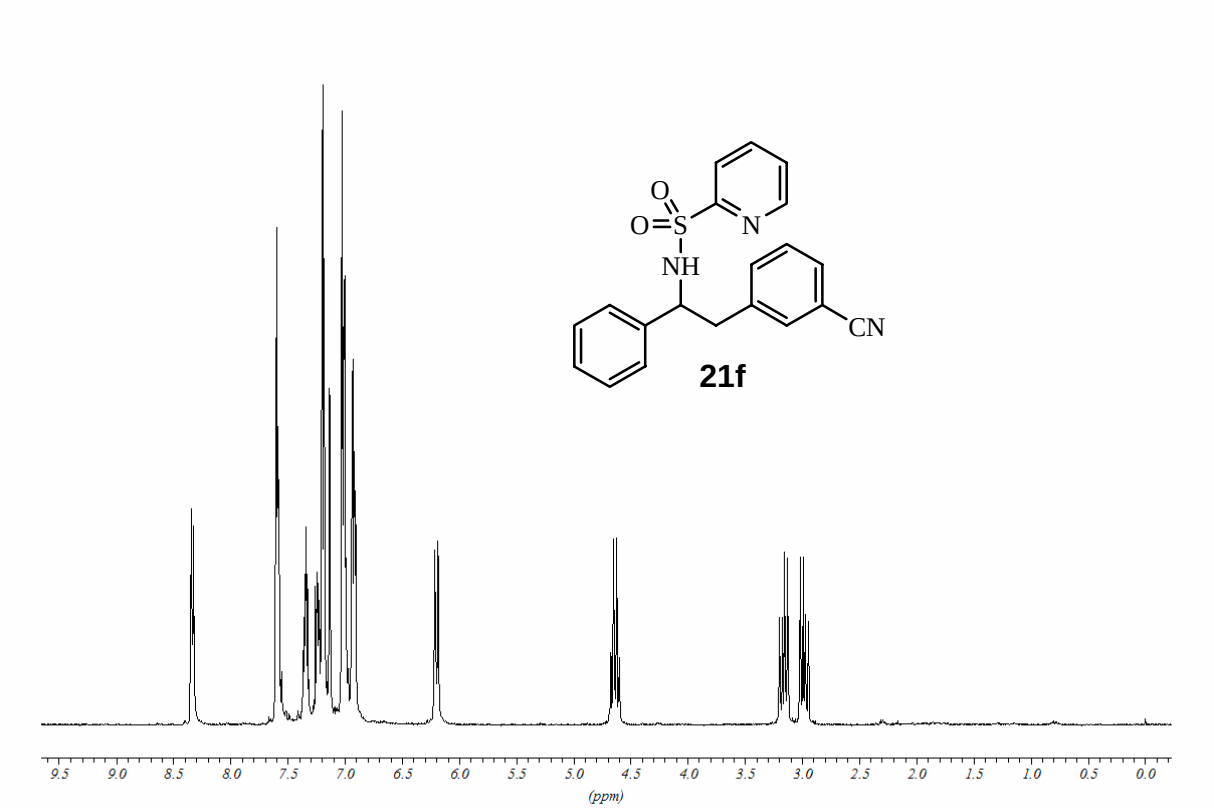
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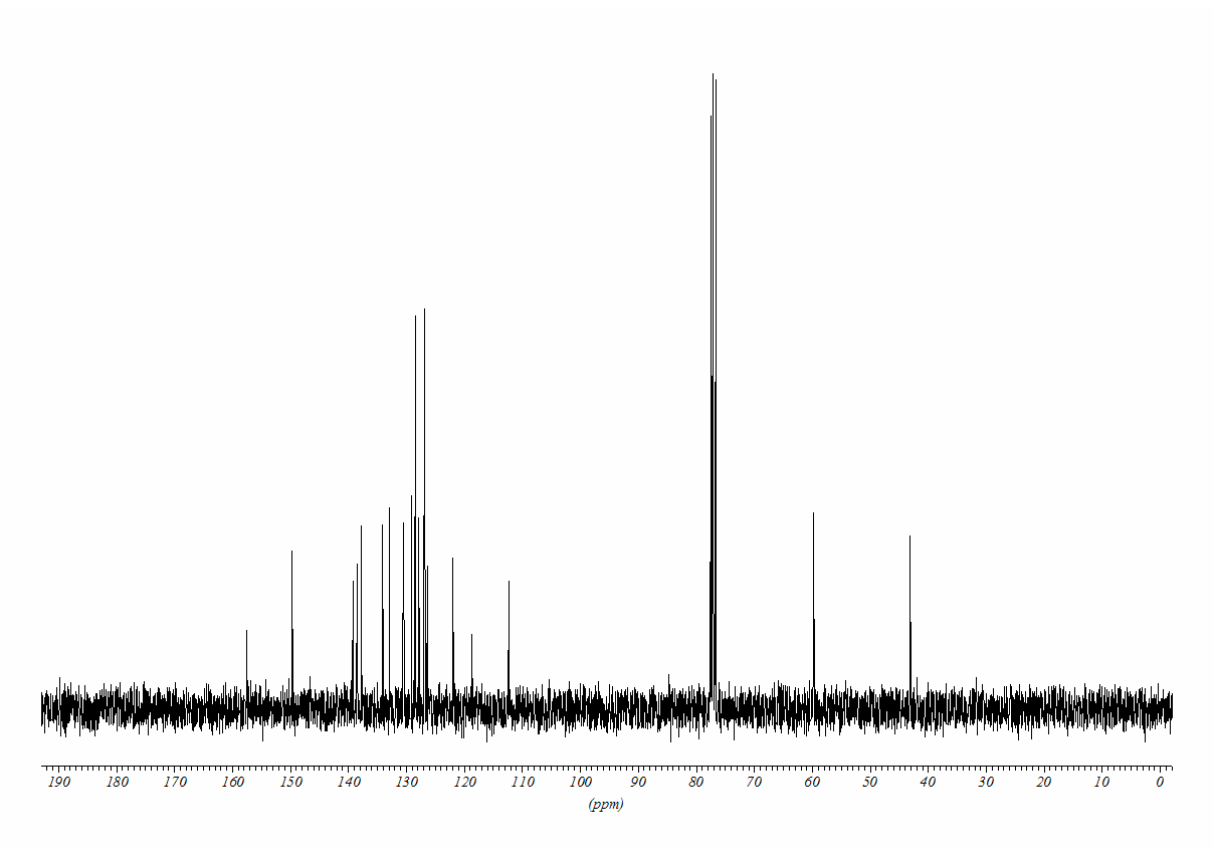
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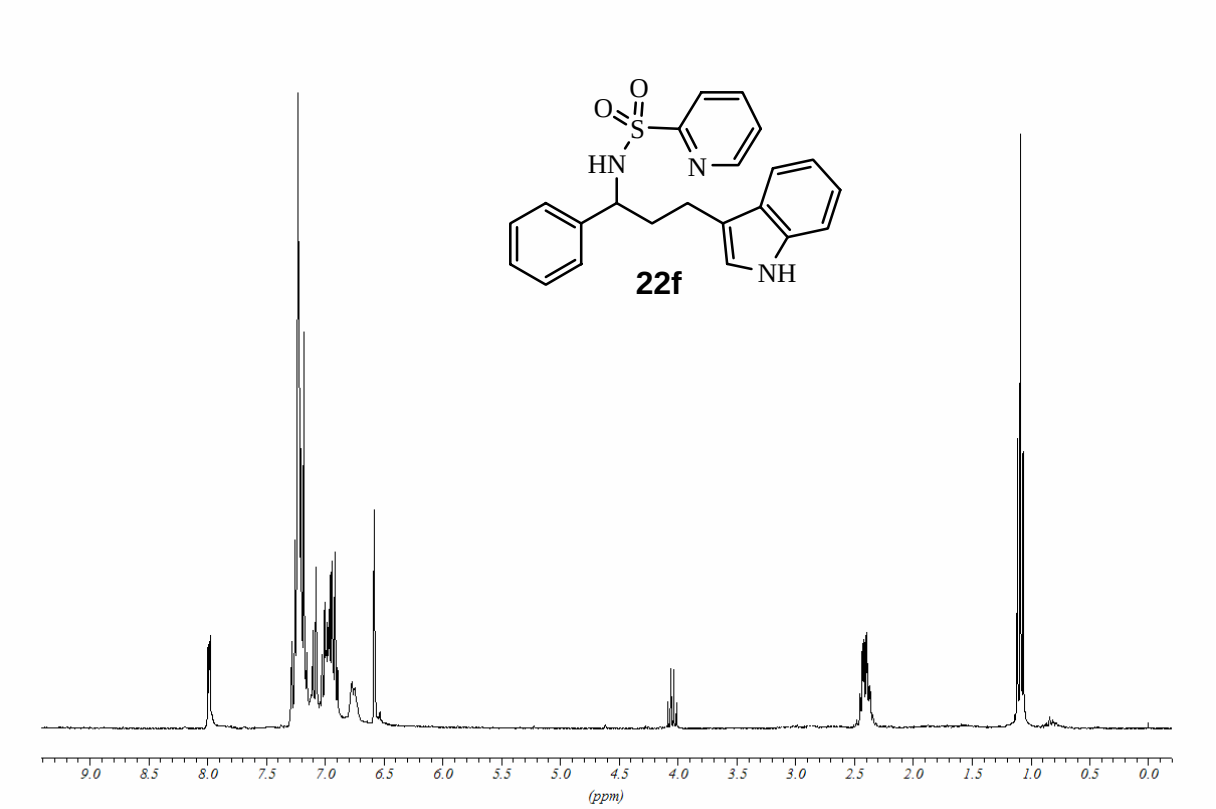
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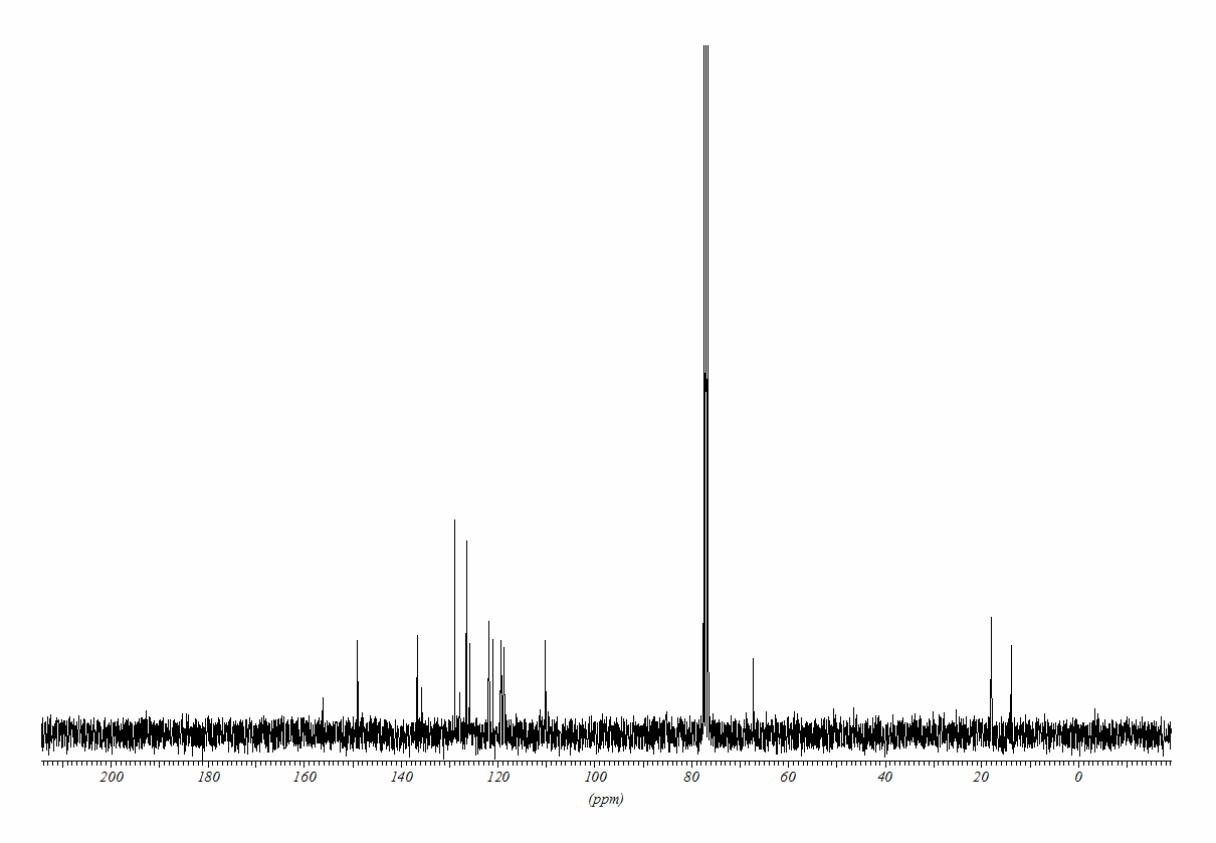
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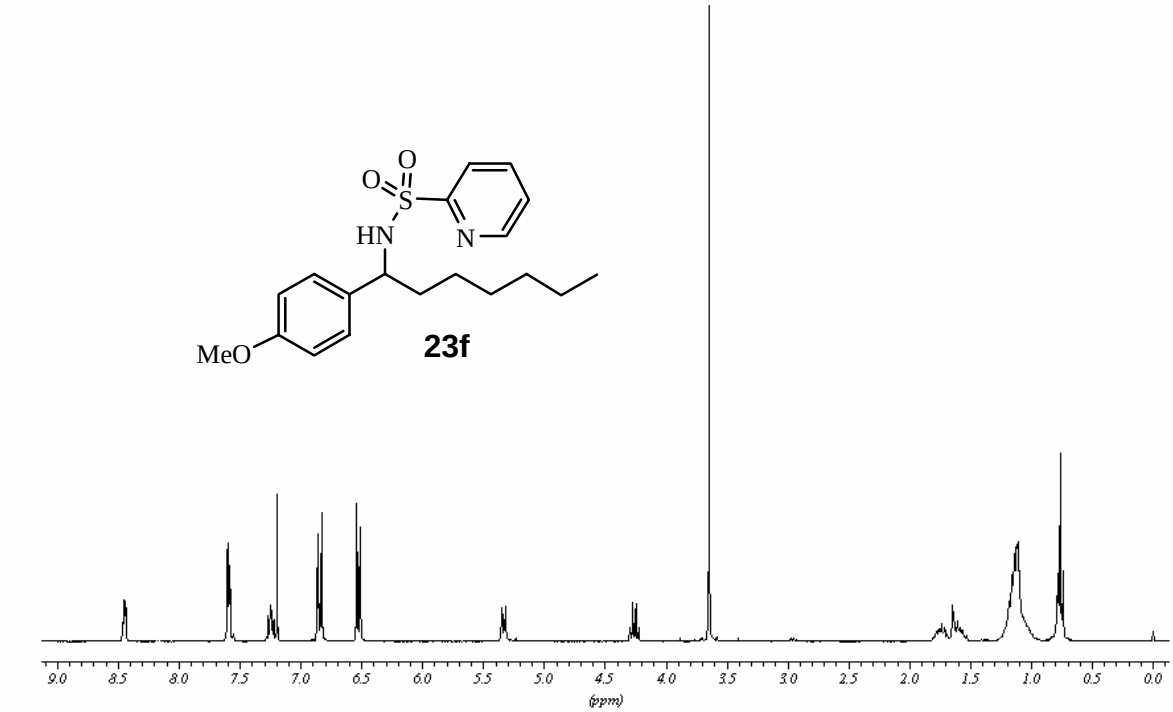
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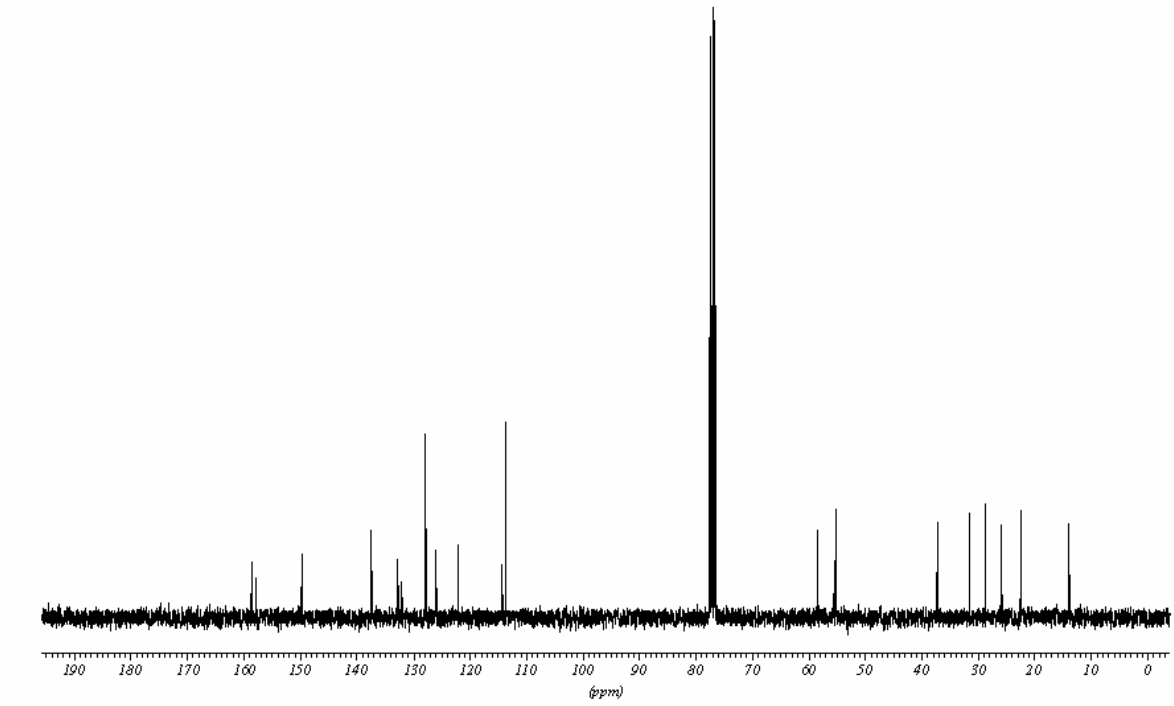
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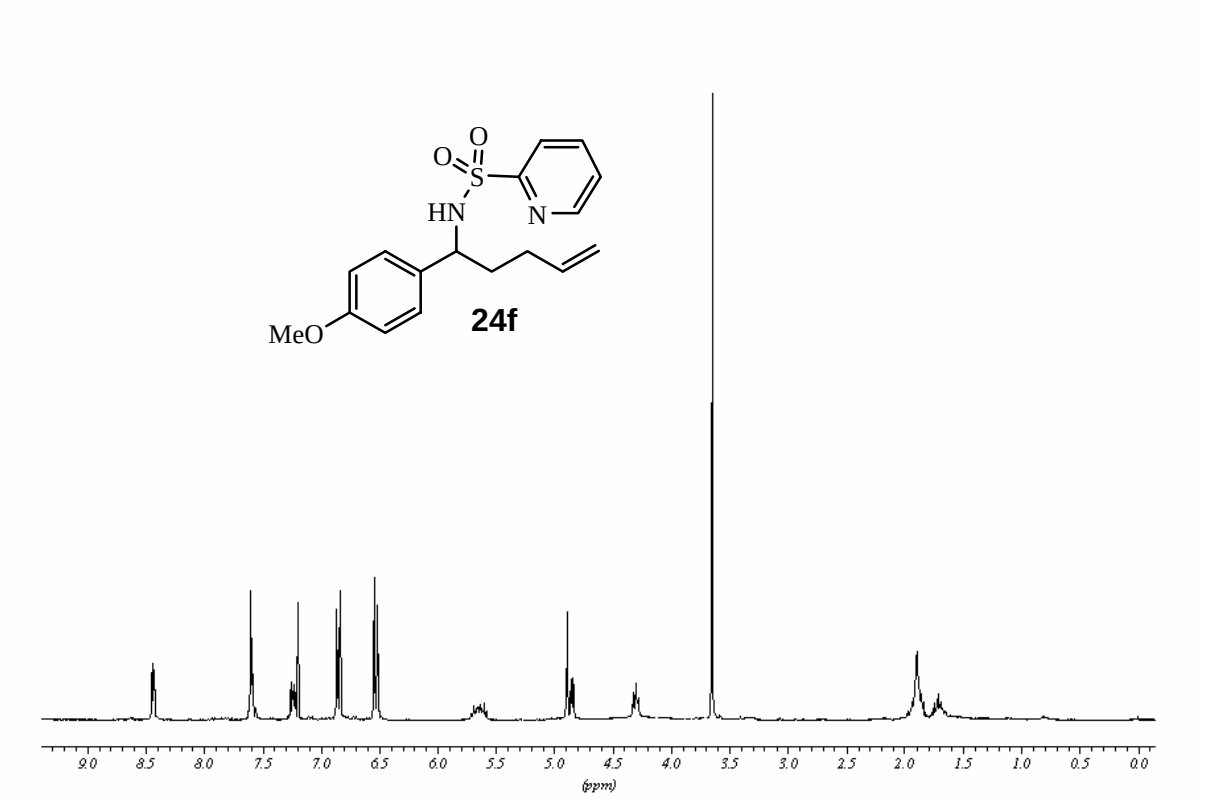
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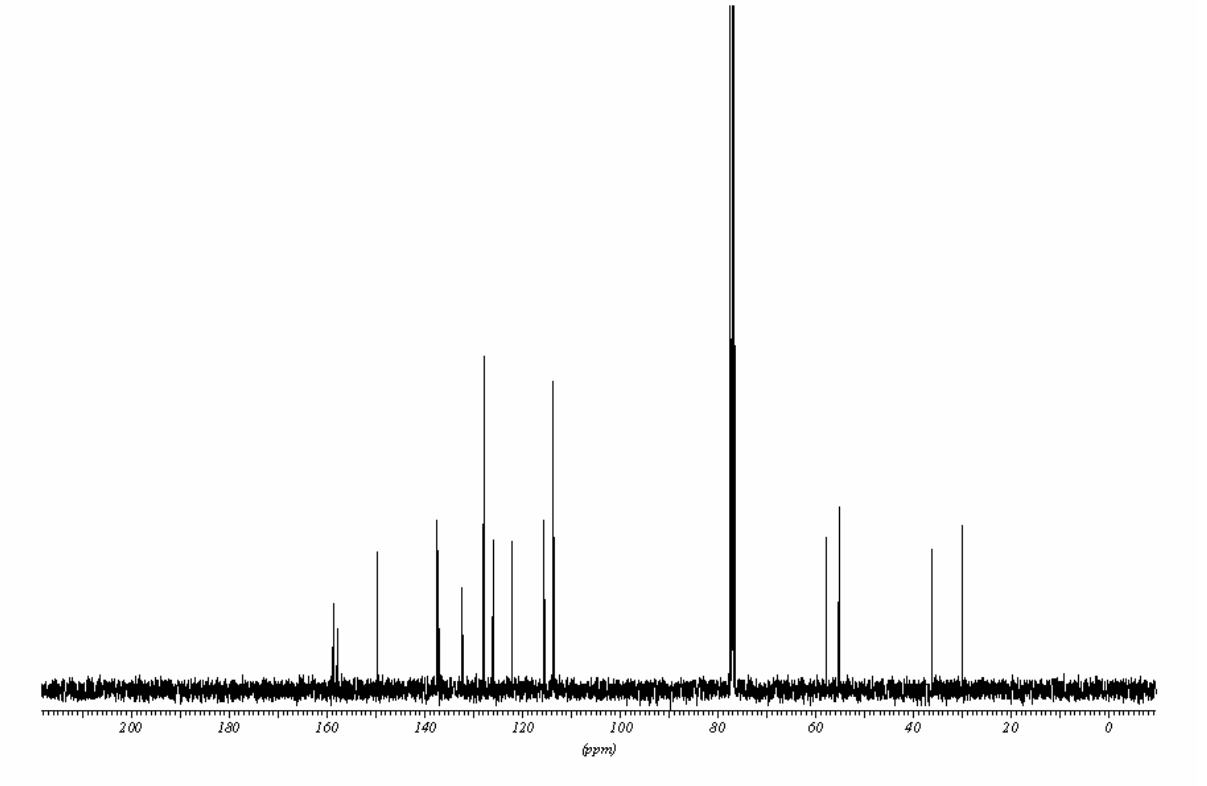
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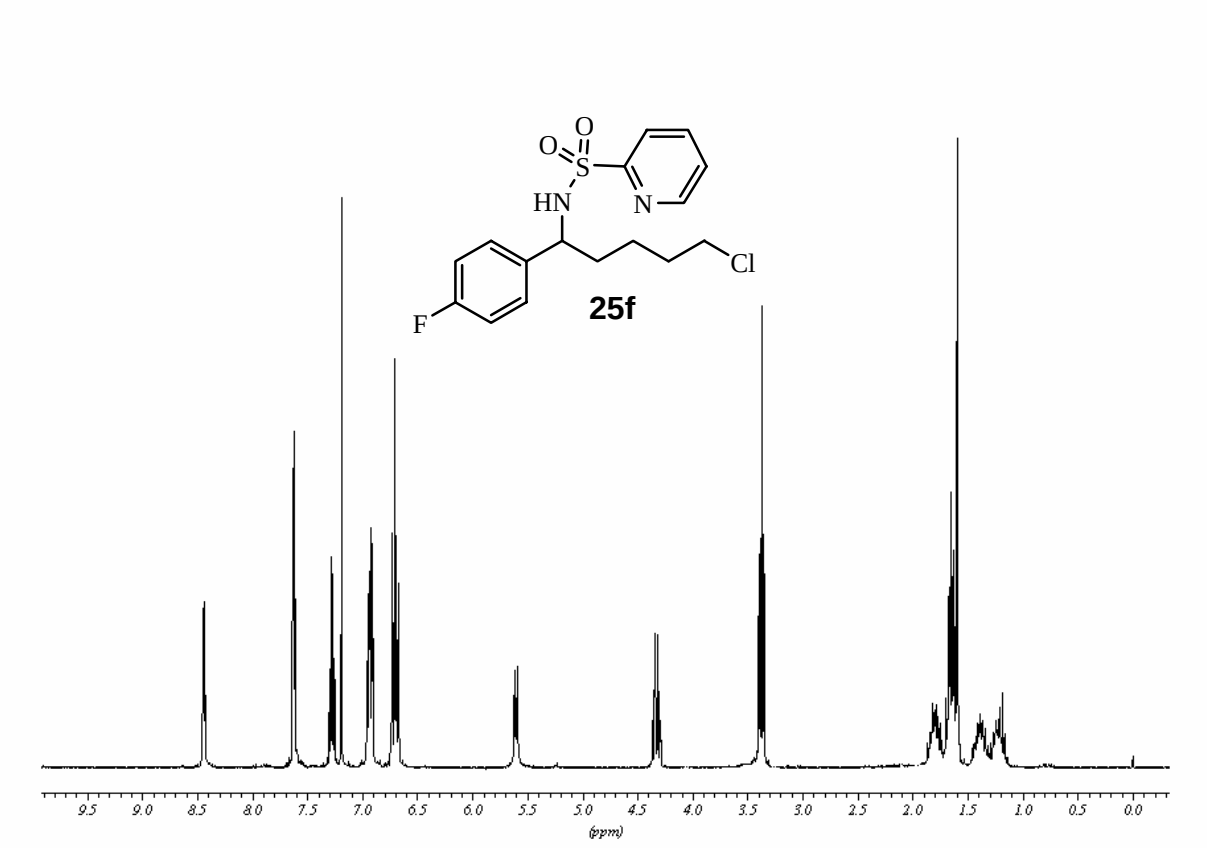
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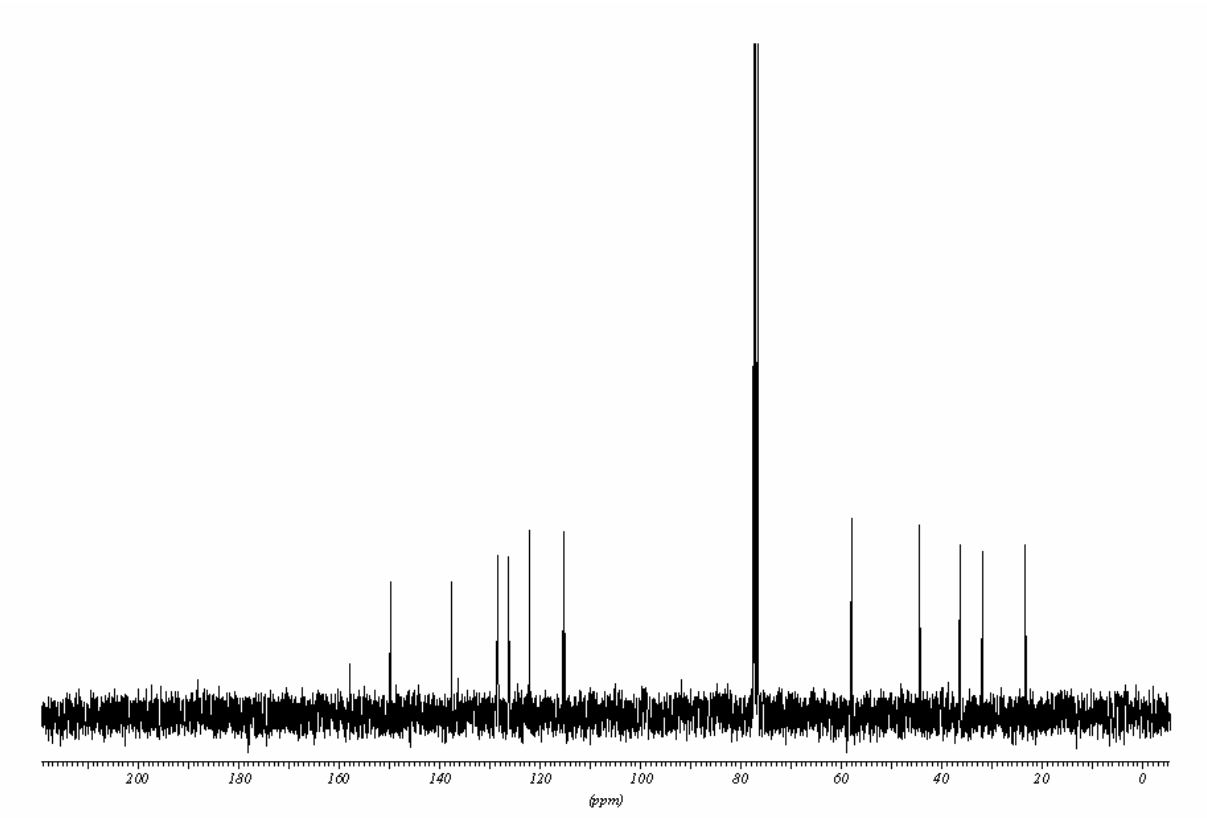
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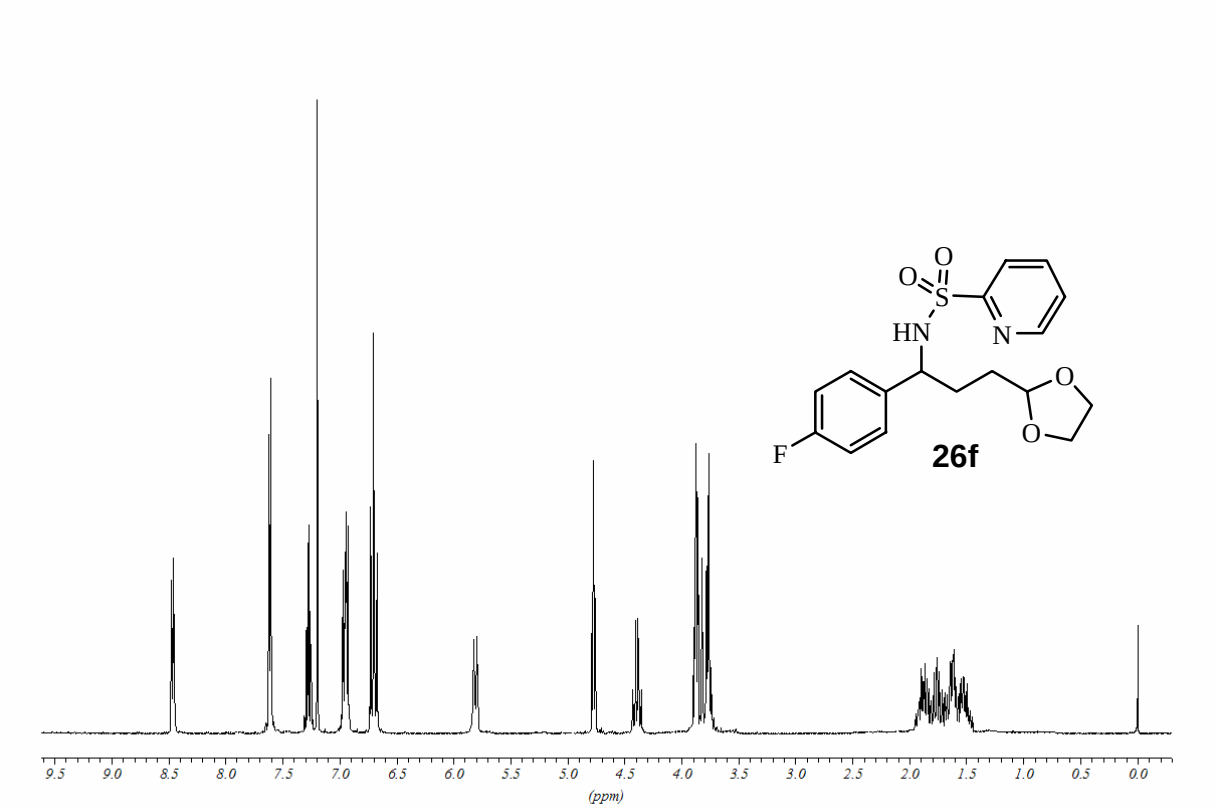
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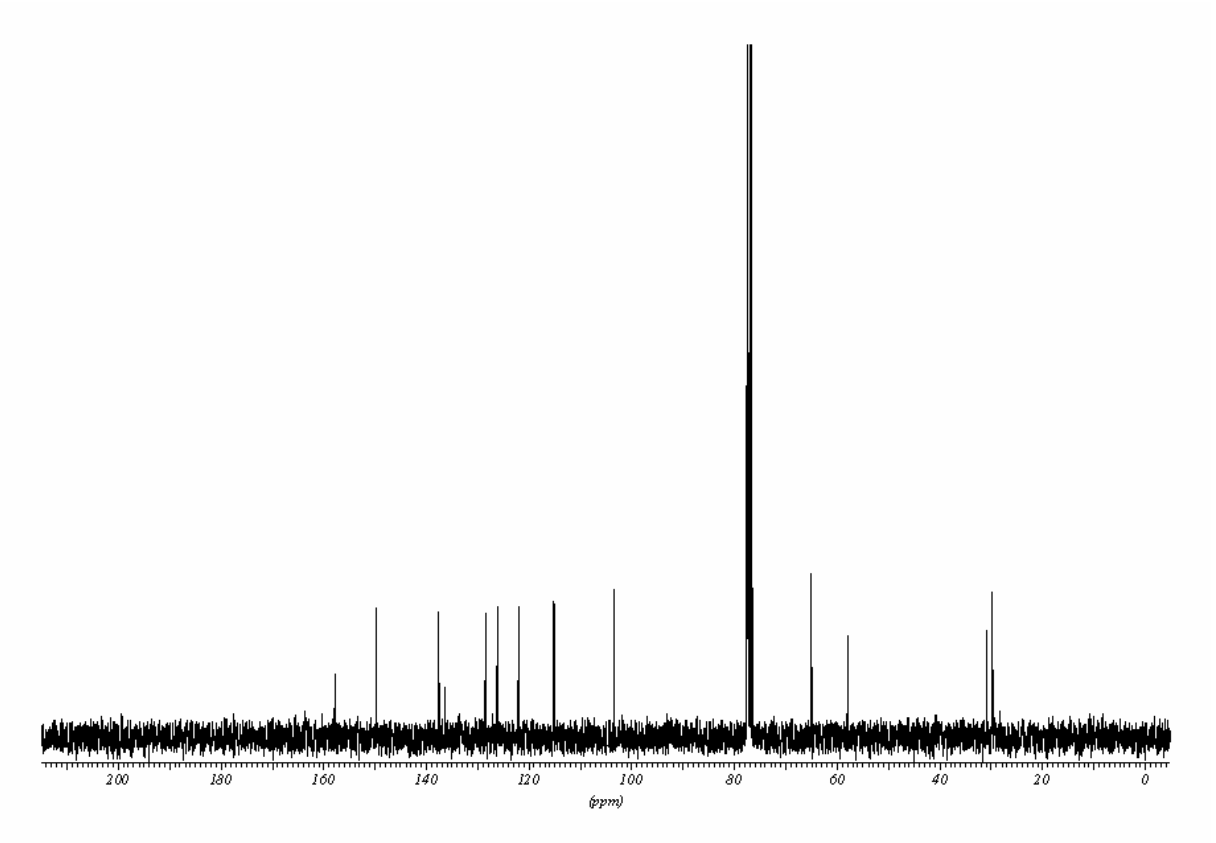
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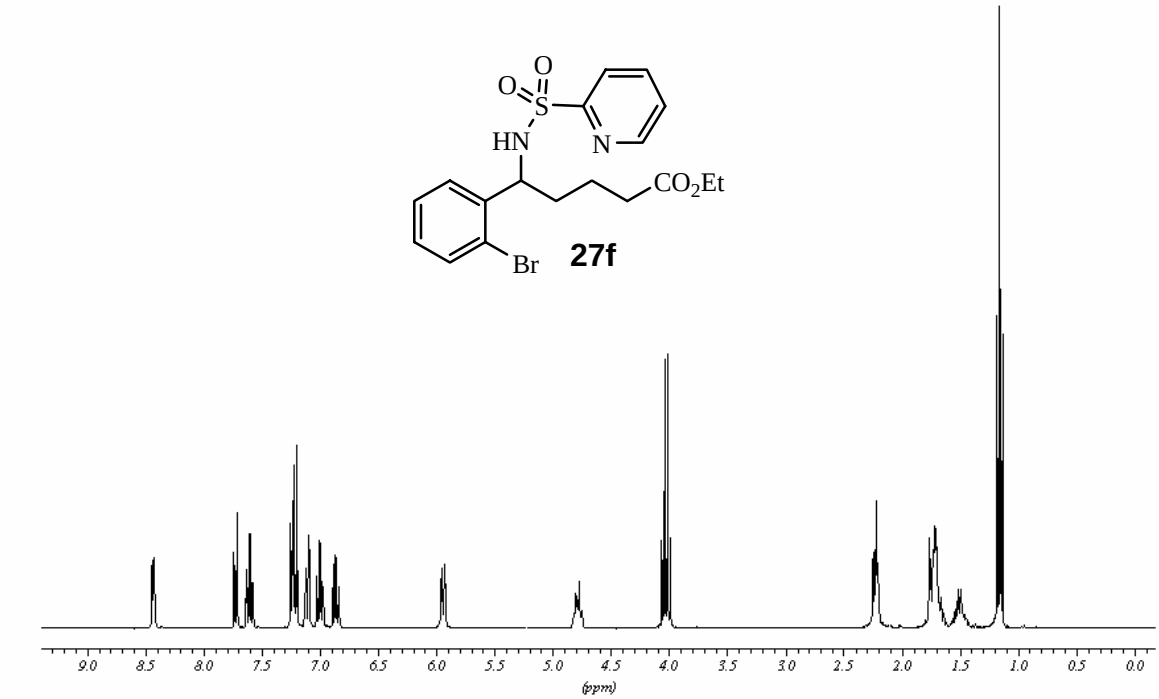
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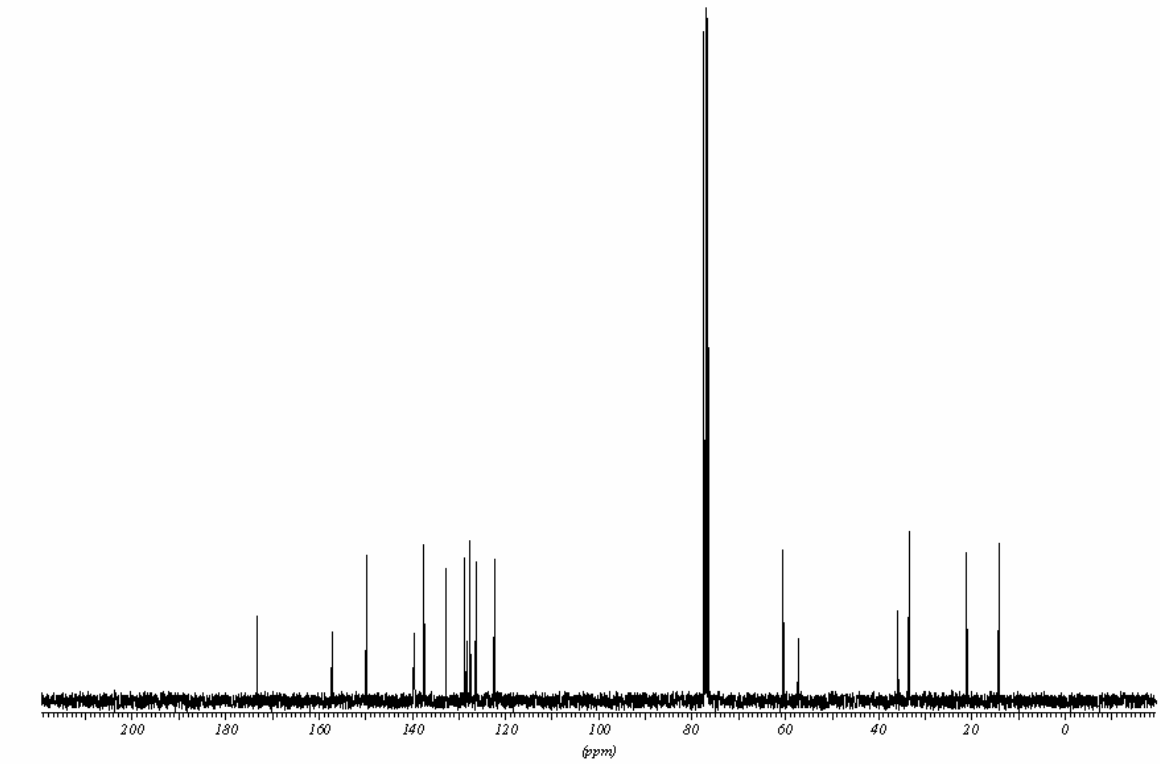
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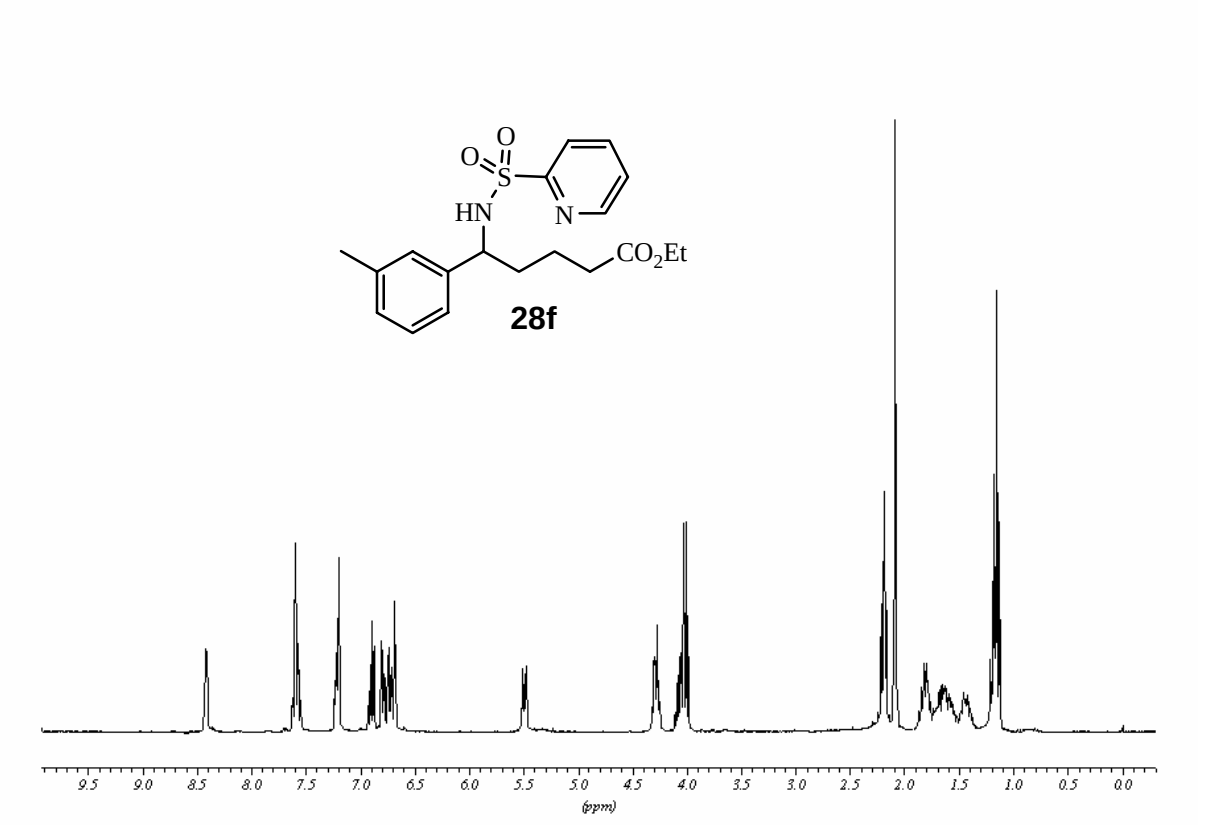
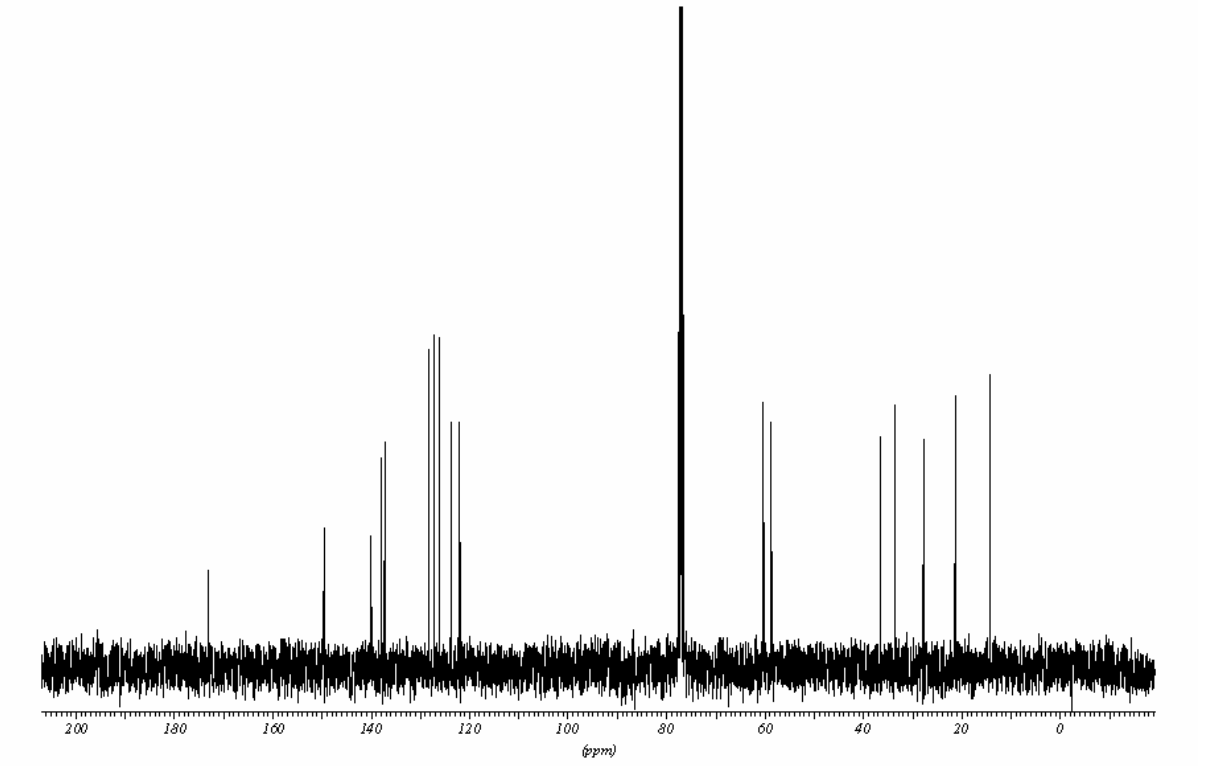
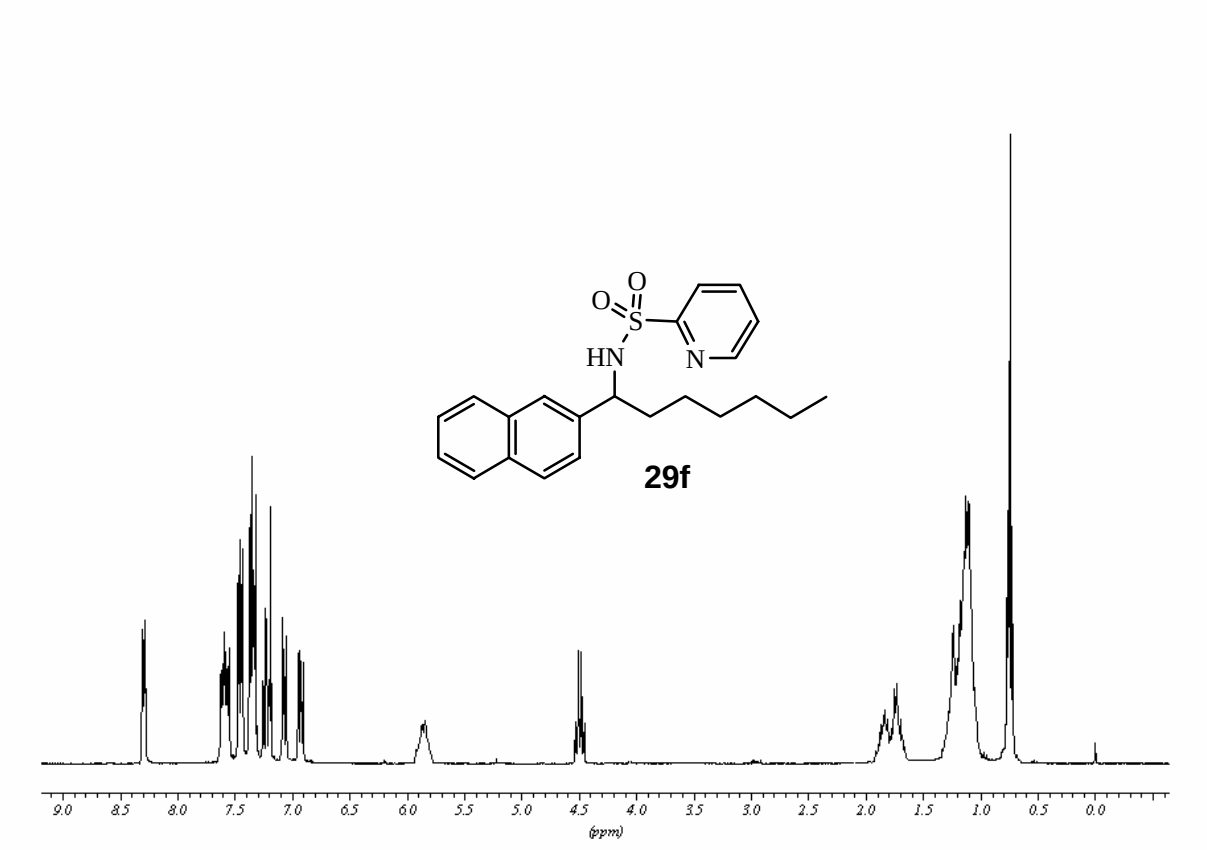
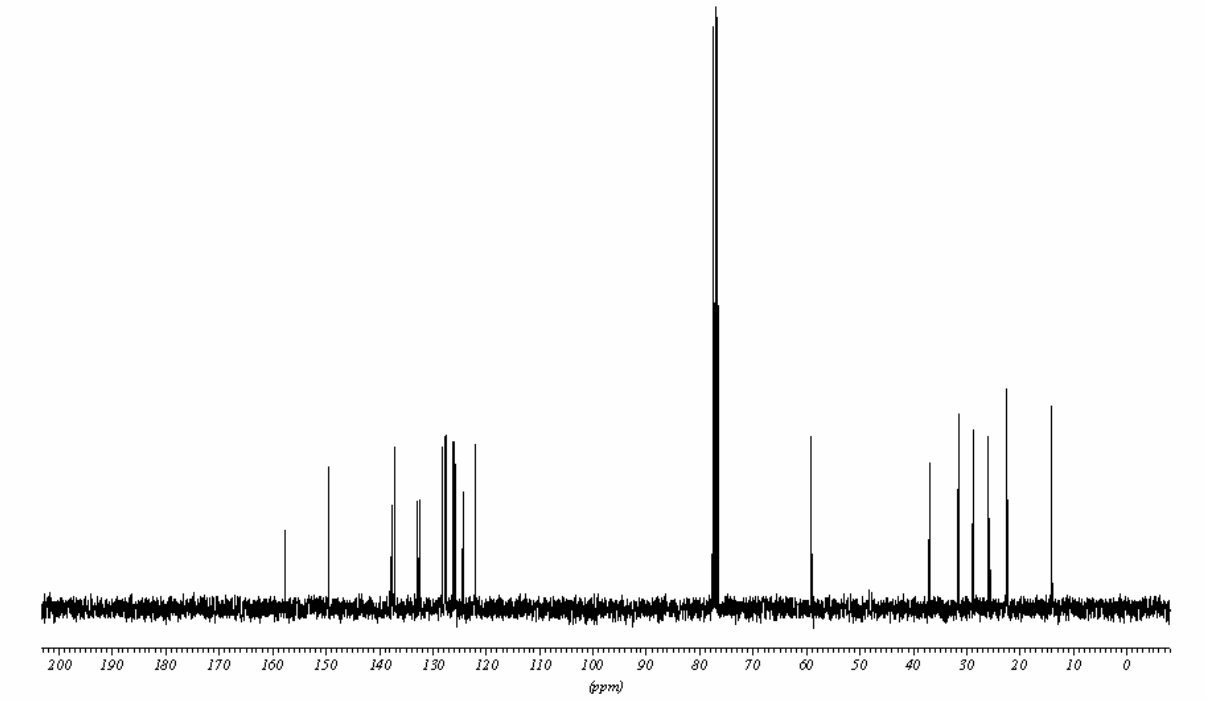
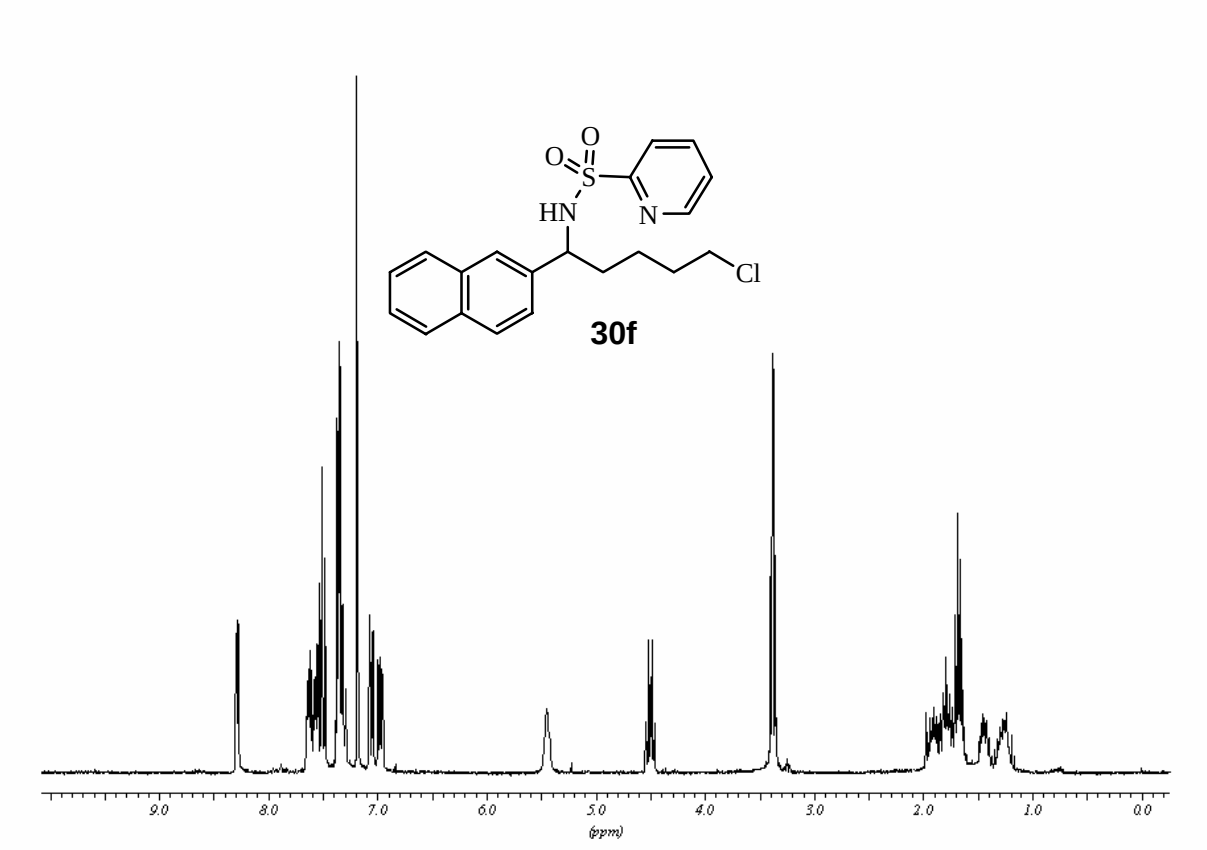
(ppm)

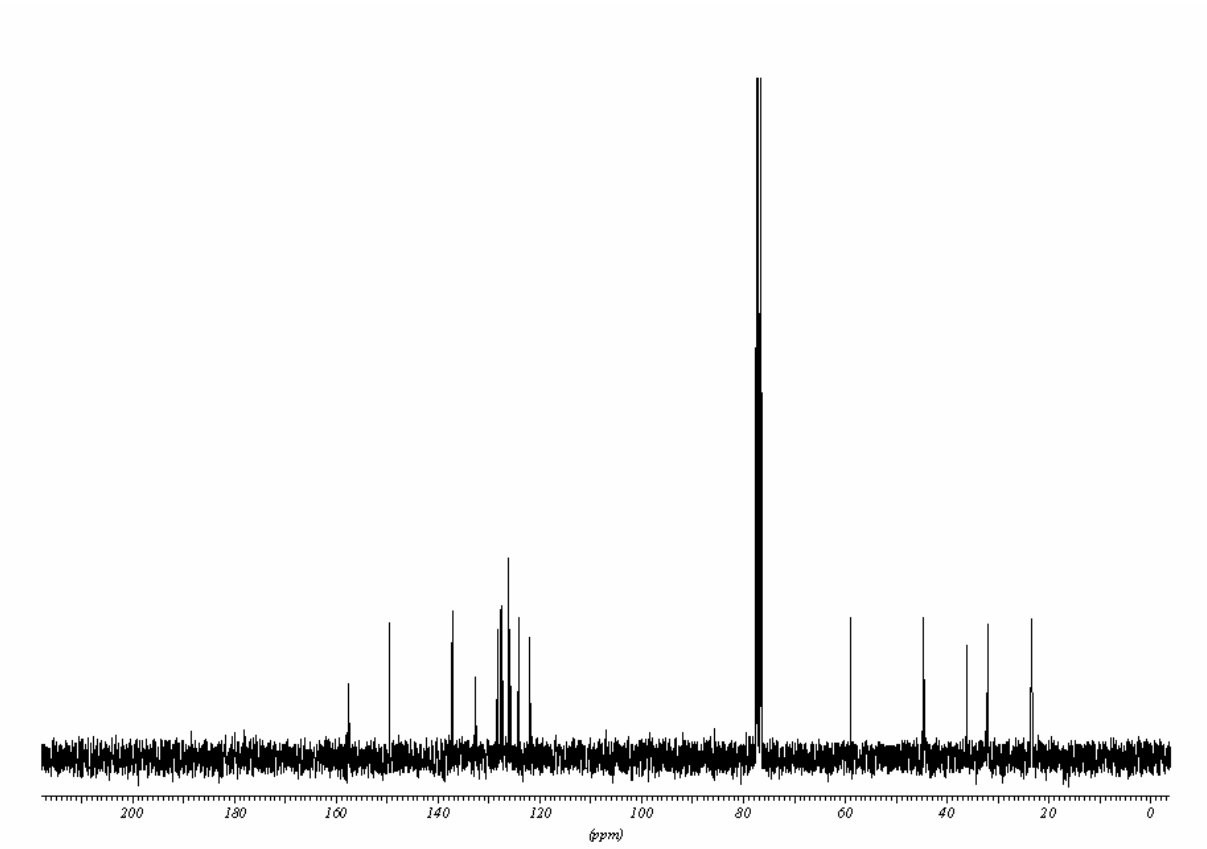

O
O
S
HN
N
CO2Et
28f
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
(ppm)

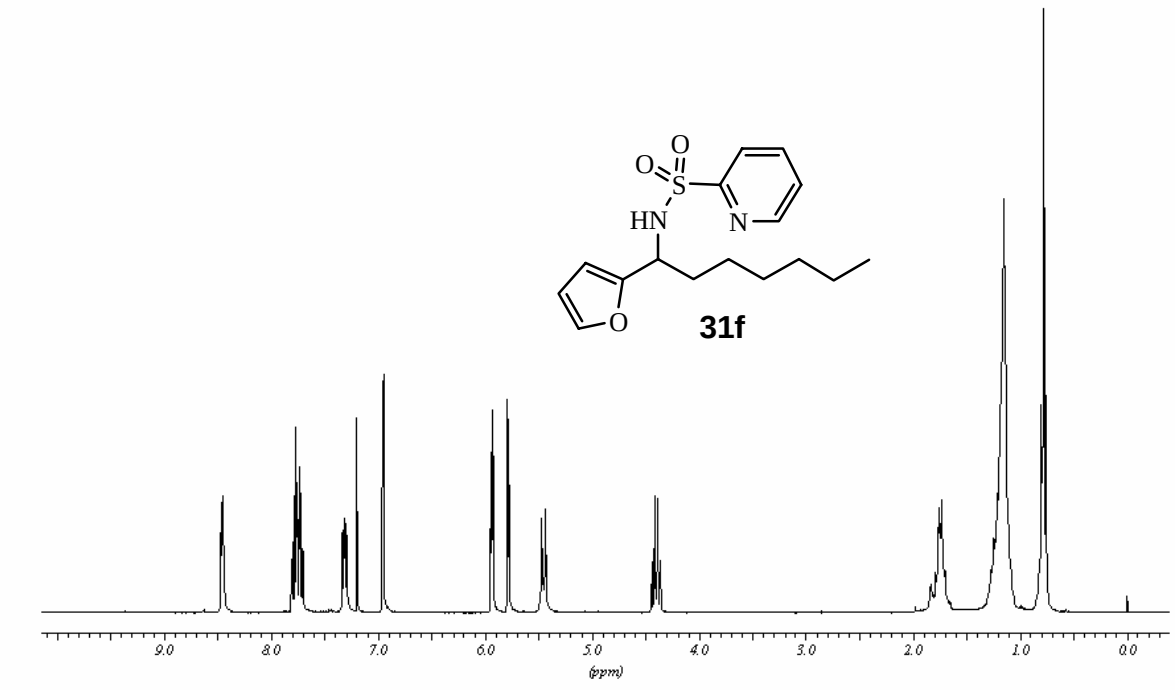

200 180 160 140 120 100 80 60 40 20 0
(ppm)


O
O
S
HN
N
29f
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
(ppm)

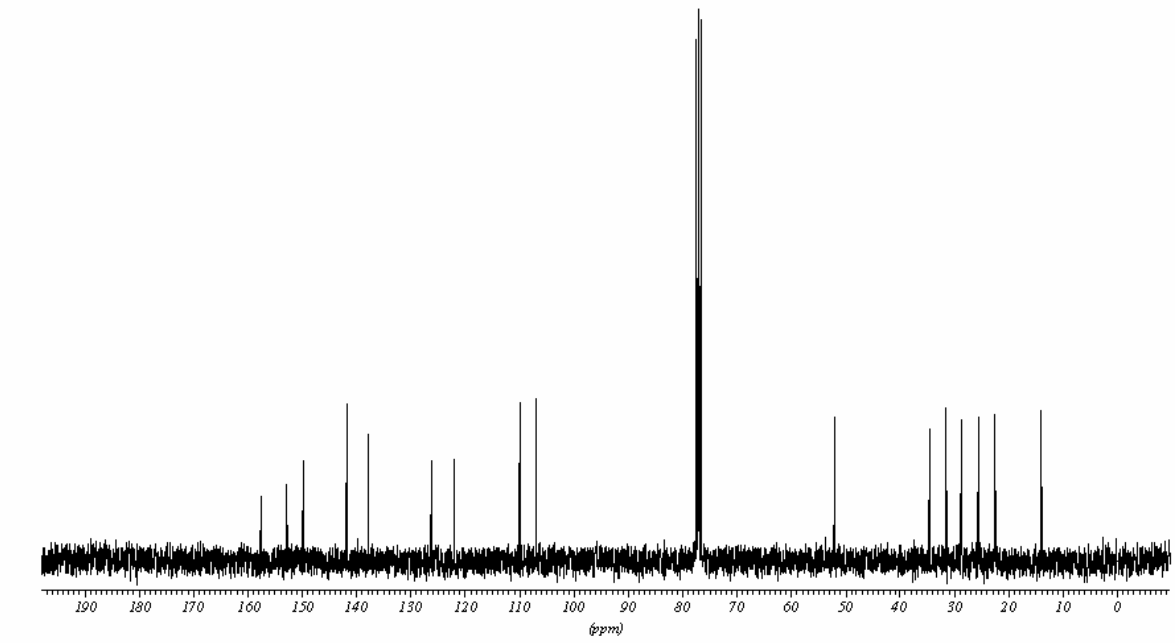

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
(ppm)

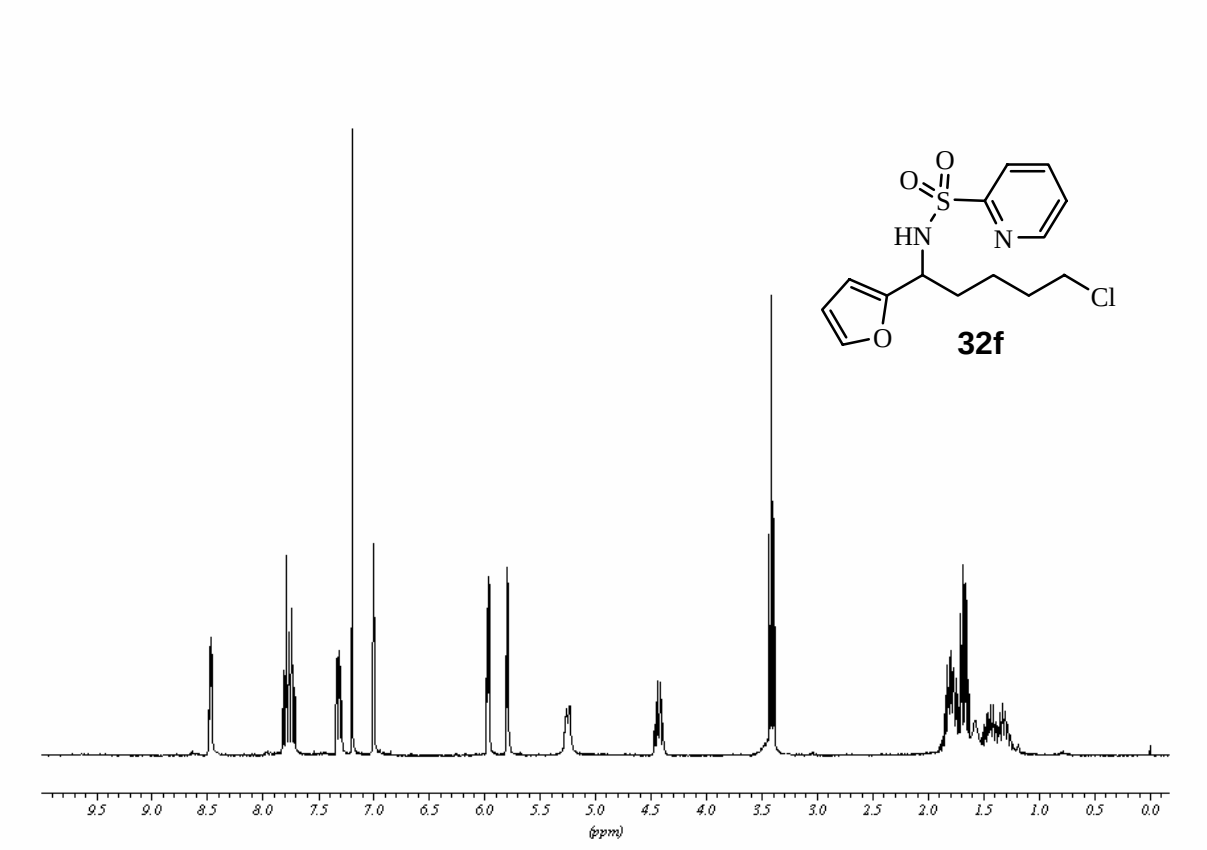

O
O
S
HN
N
Cl
30f
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
(ppm)

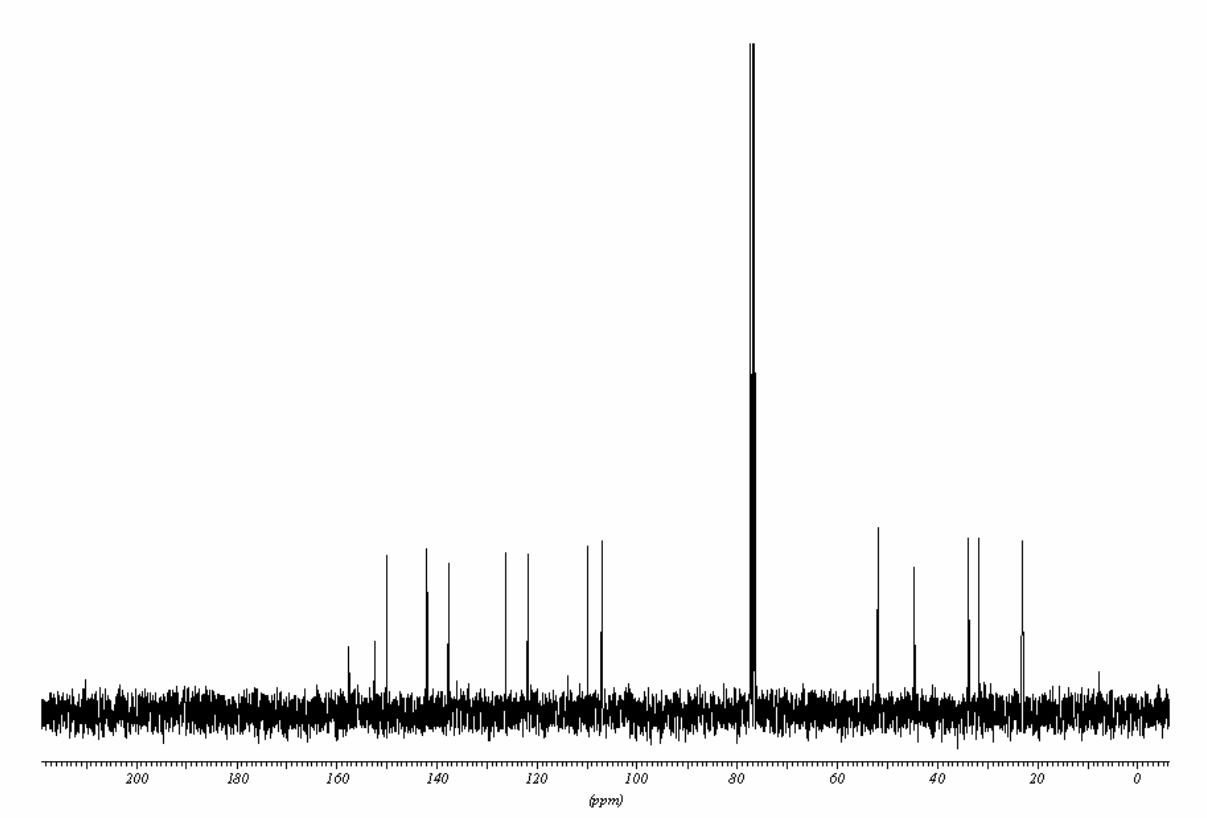

200
180
160
140
120
100
80
60
40
20
0
(ppm)

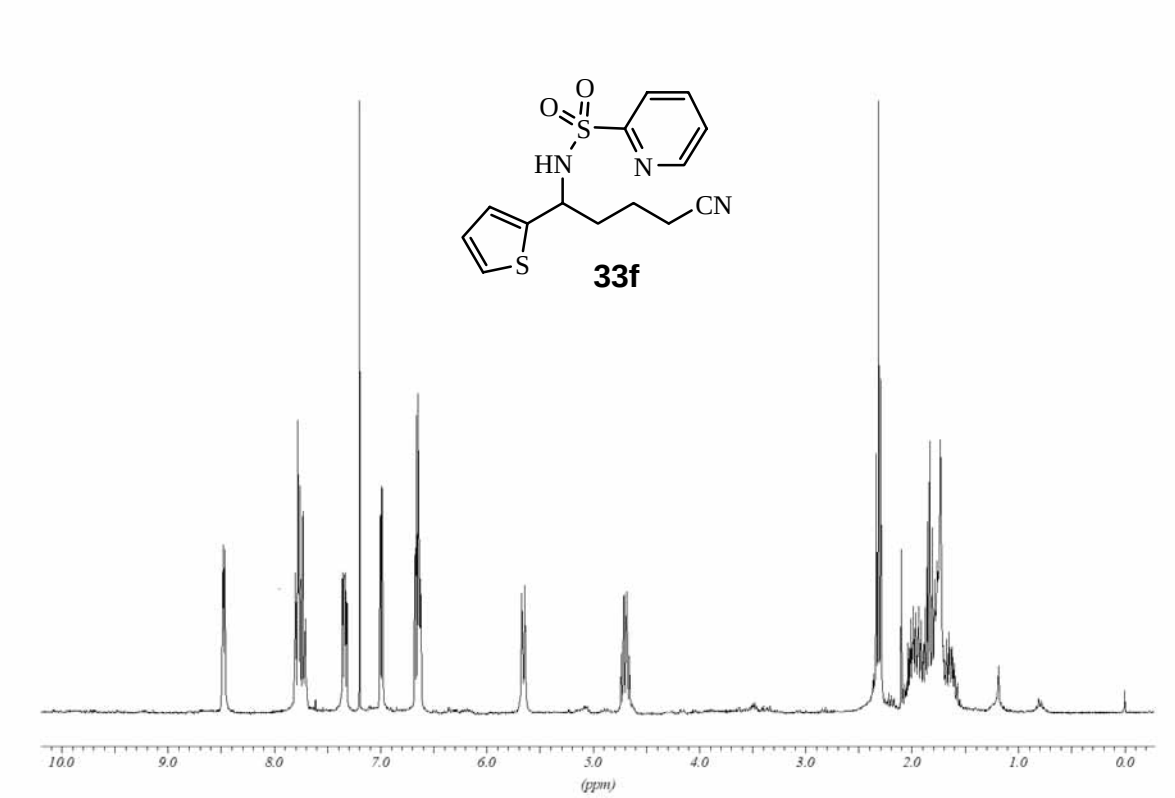

O
O
S
HN
N
O
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
(ppm)

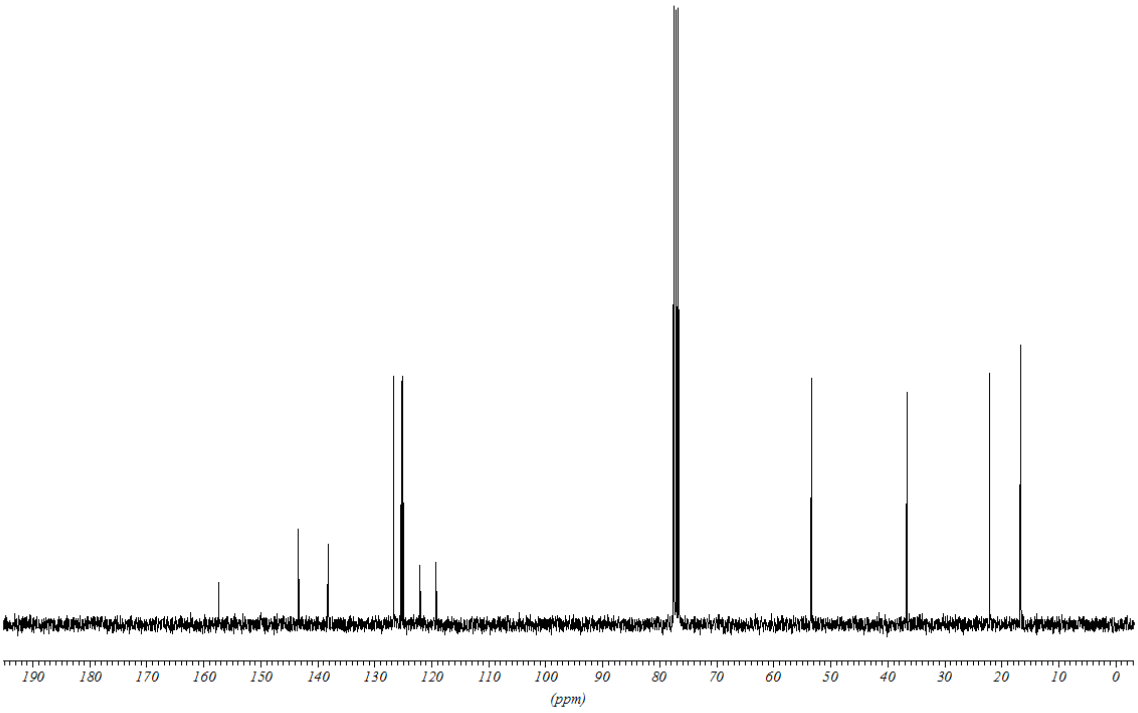
31f

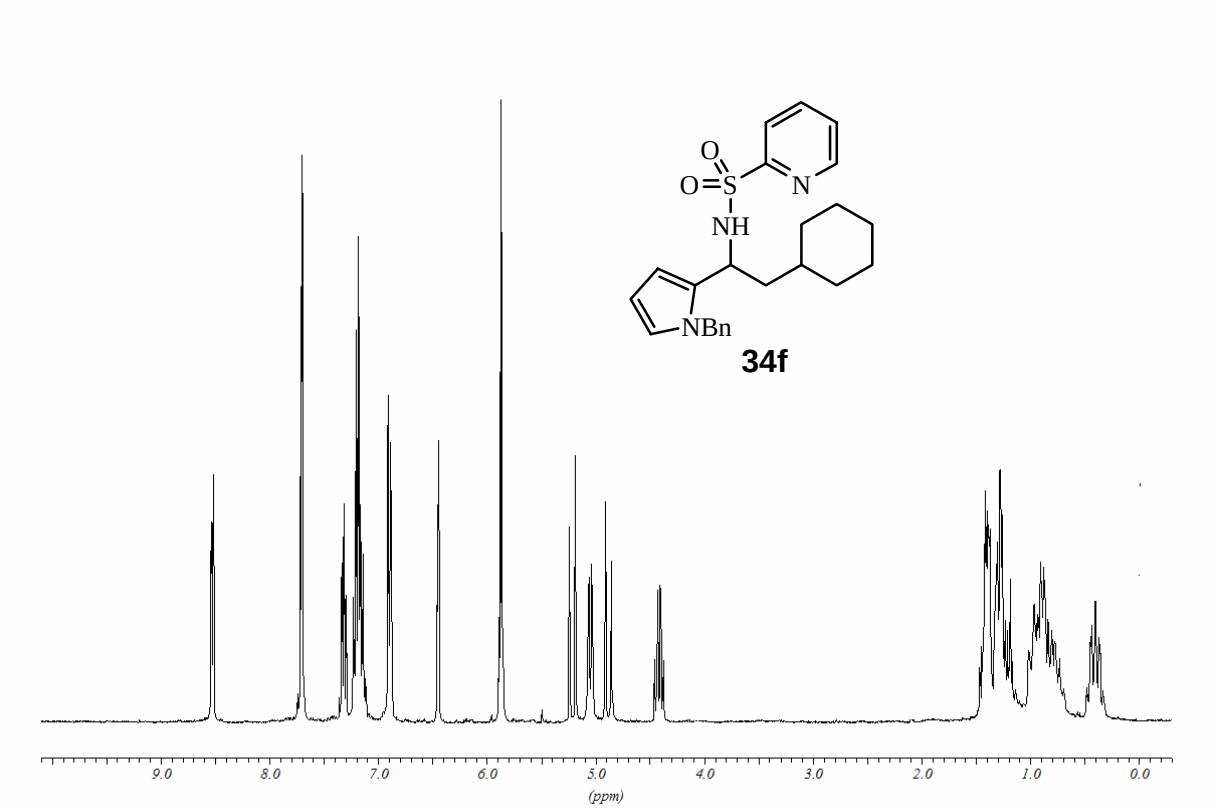

190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
(ppm)


O
O
S
HN
N
Cl
O
32f
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
(ppm)

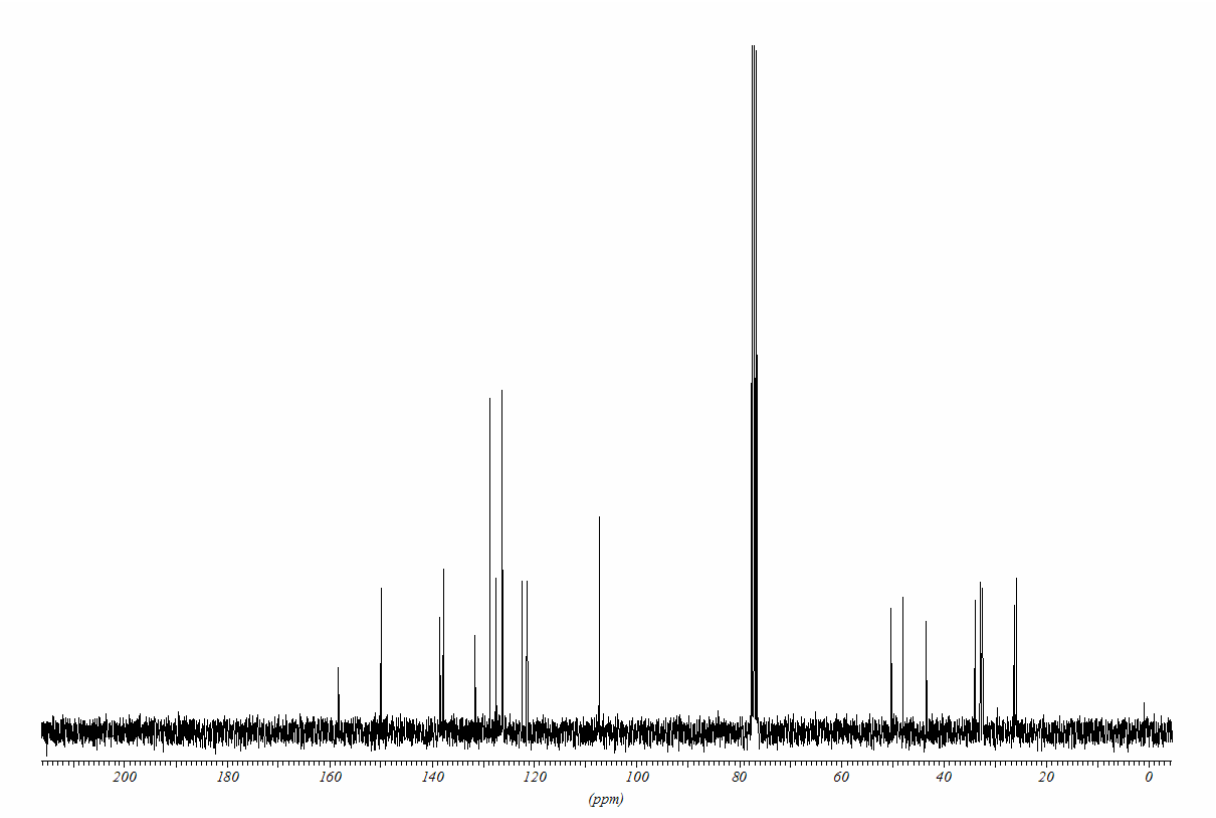

200 180 160 140 120 100 80 60 40 20 0
(ppm)

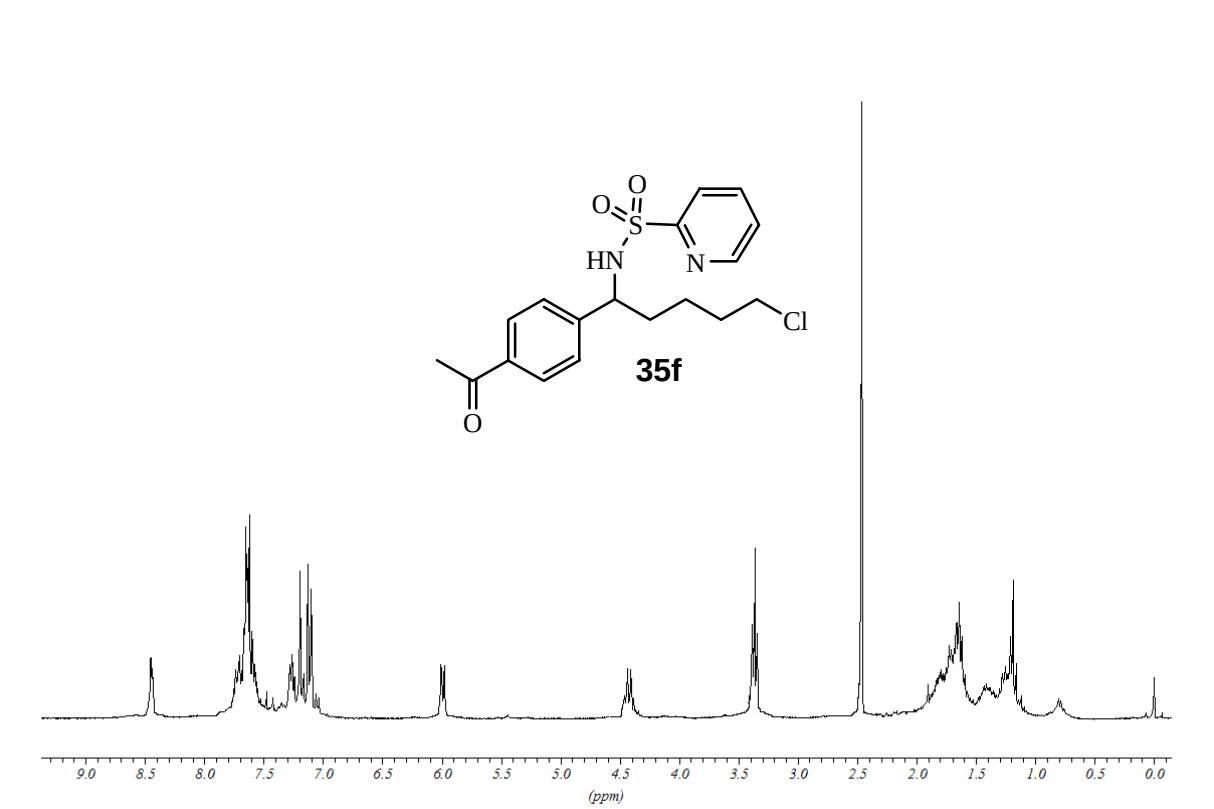

O
O
S
HN
N
CN
S
33f
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
(ppm)

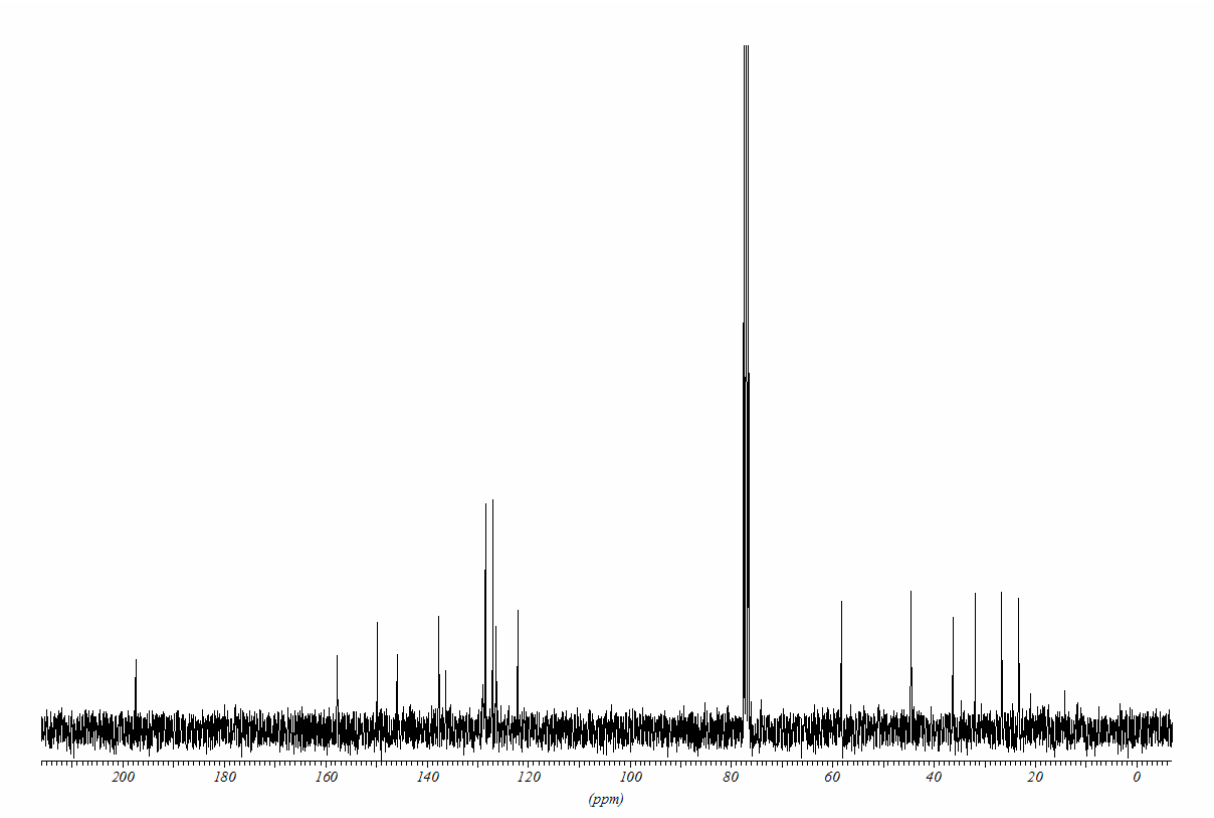

190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
(ppm)

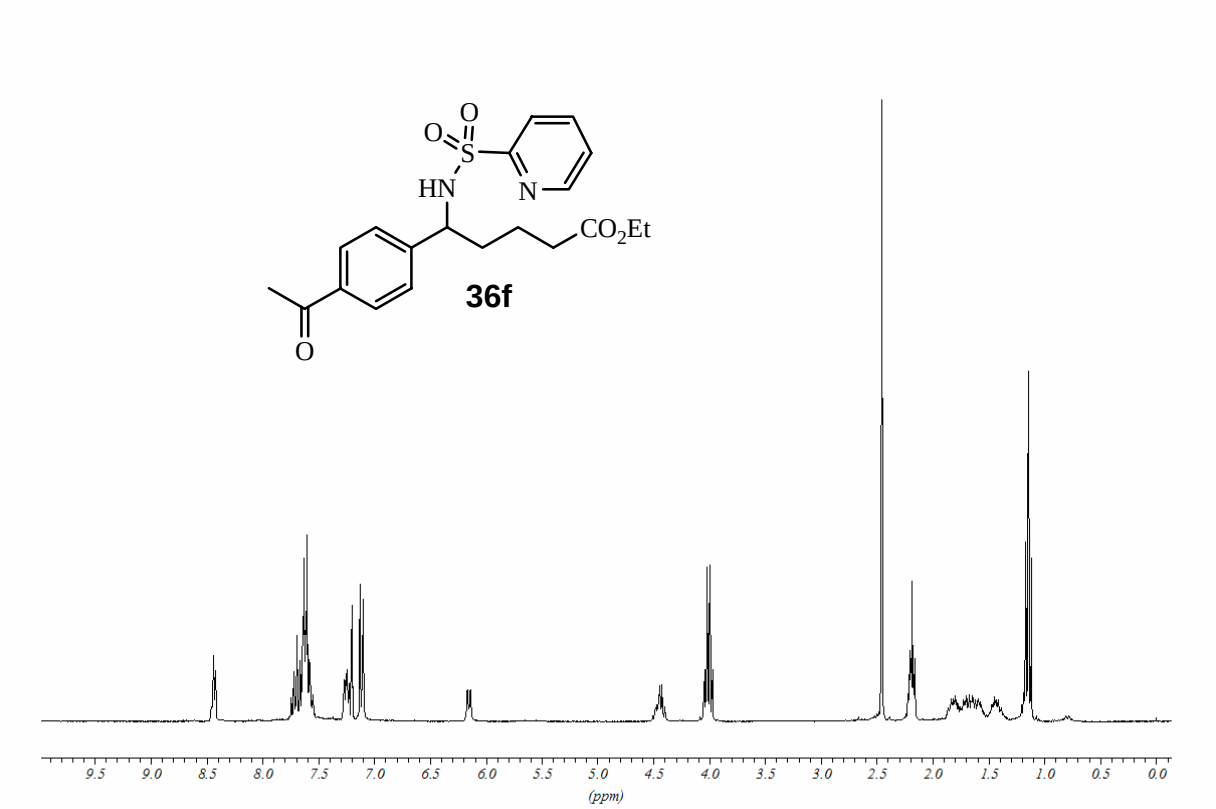

O
O
S
N
NH
NBn
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
(ppm)

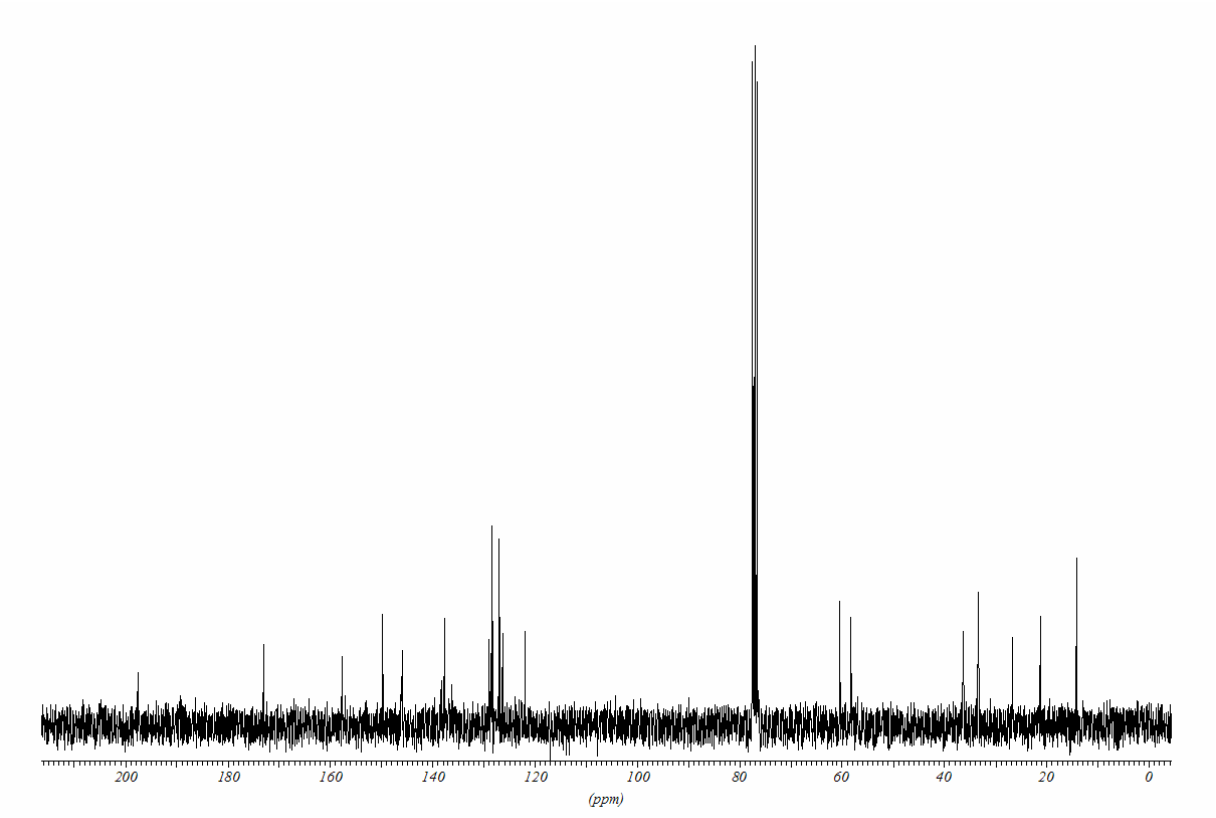
34f

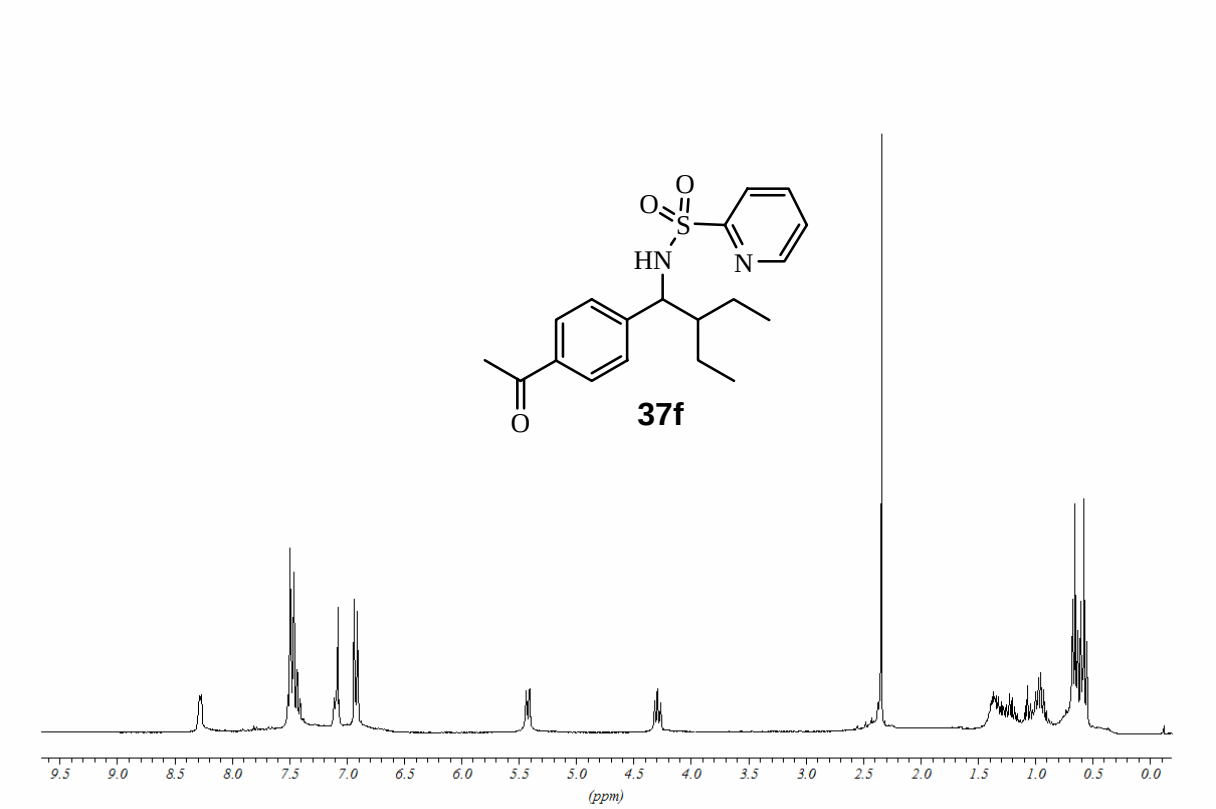

200
180
160
140
120
100
80
60
40
20
0
(ppm)

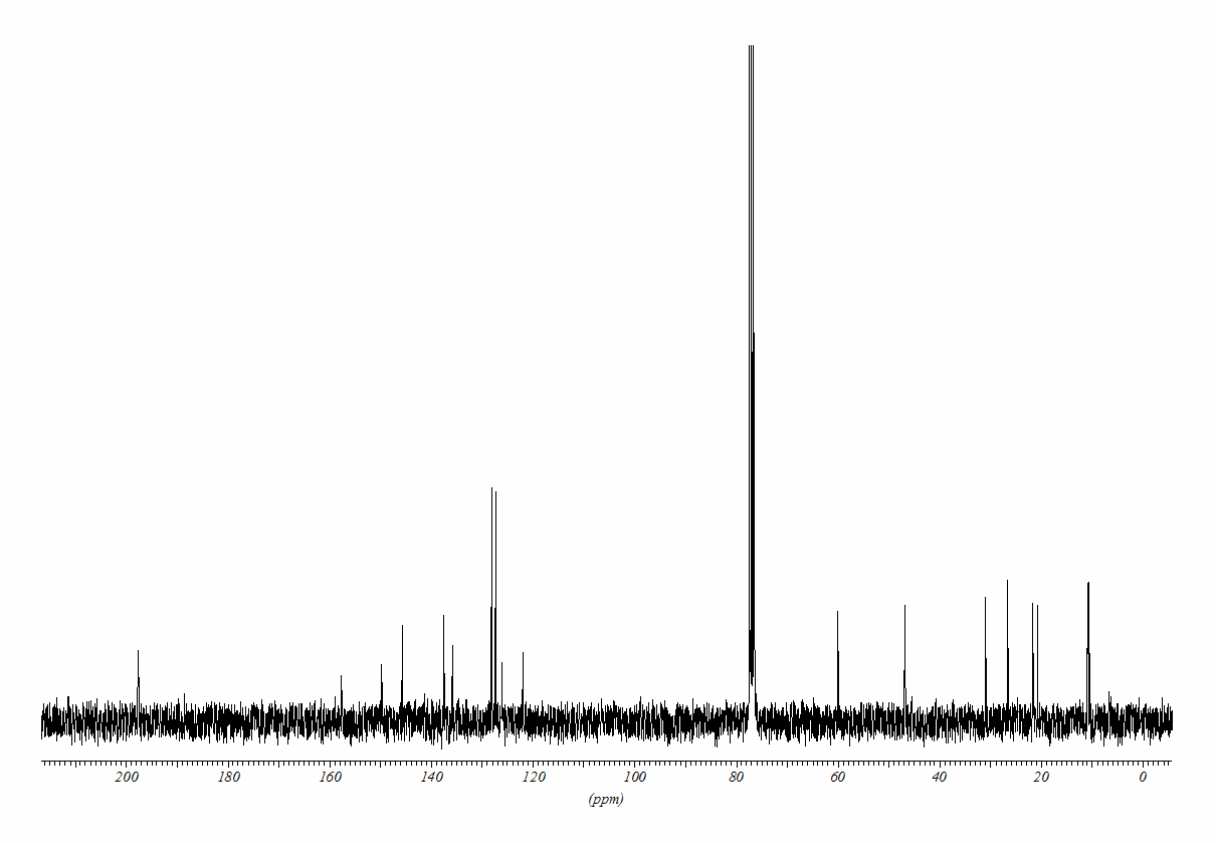

O
O
S
HN
N
Cl
O
35f
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
(ppm)

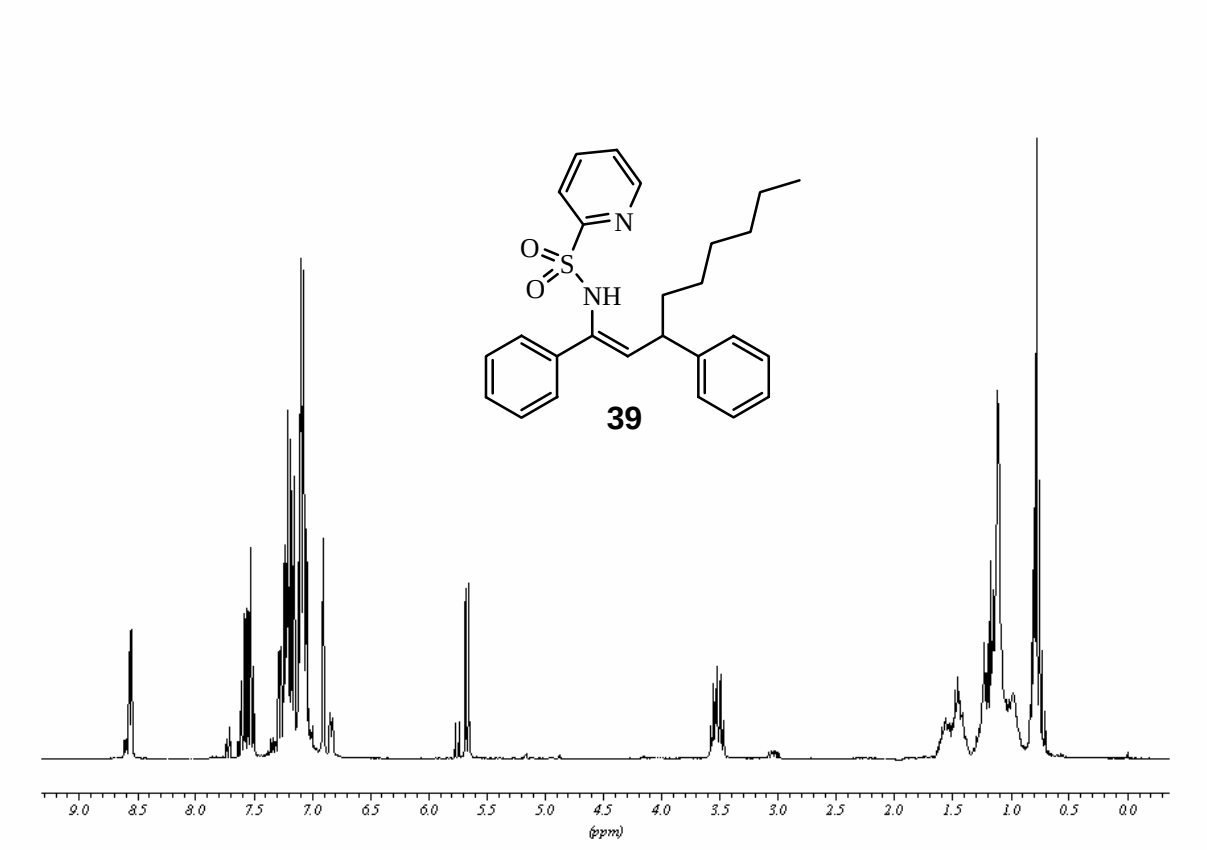

200 180 160 140 120 100 80 60 40 20 0
(ppm)

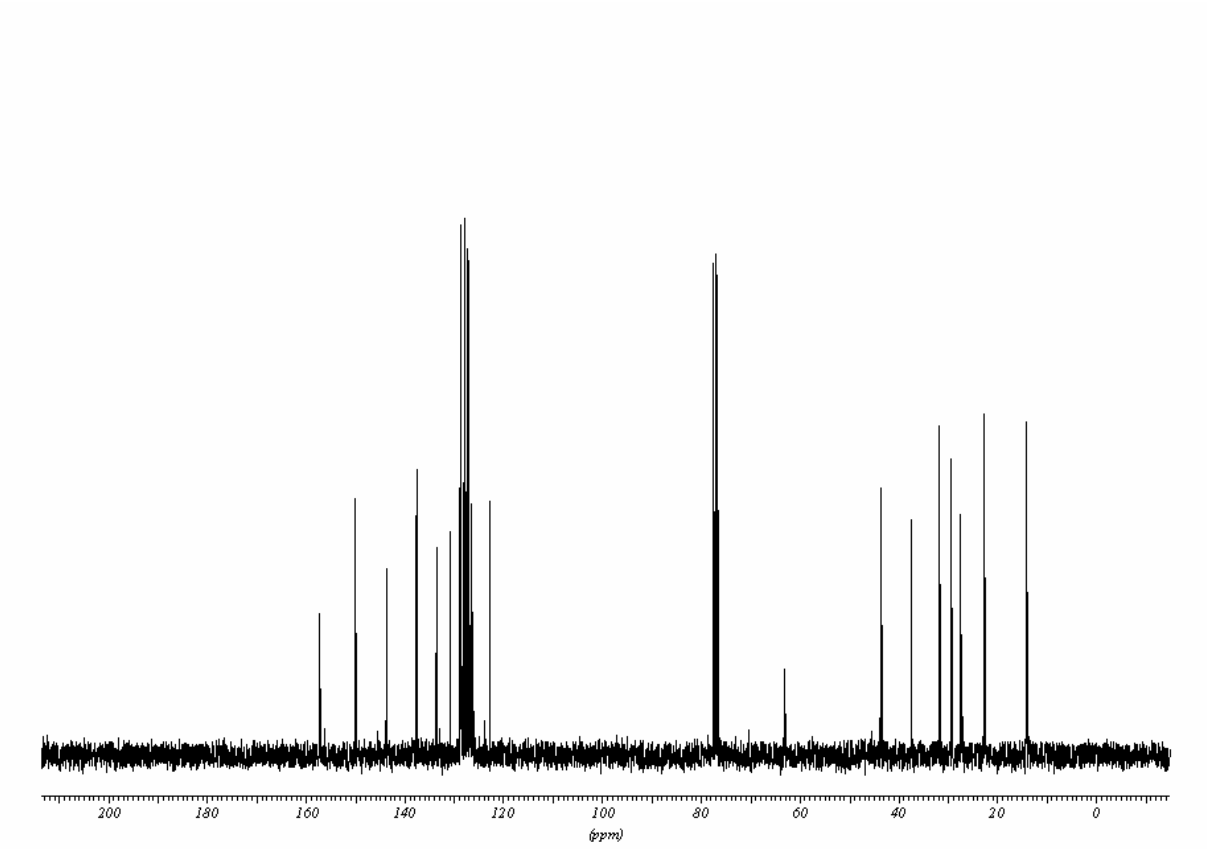

O
O
S
HN
N
CO2Et
36f
O
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
(ppm)

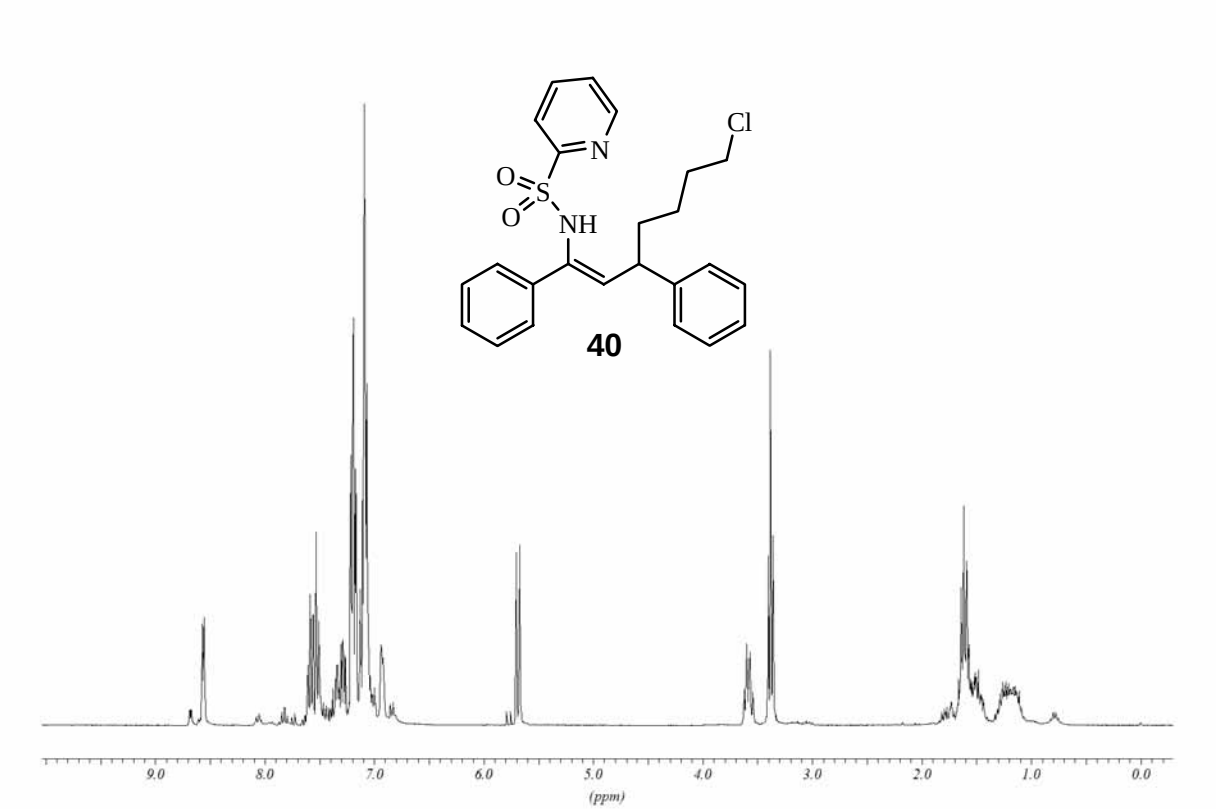

200 180 160 140 120 100 80 60 40 20 0
(ppm)


O
O
S
HN
N
O
37f
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
(ppm)

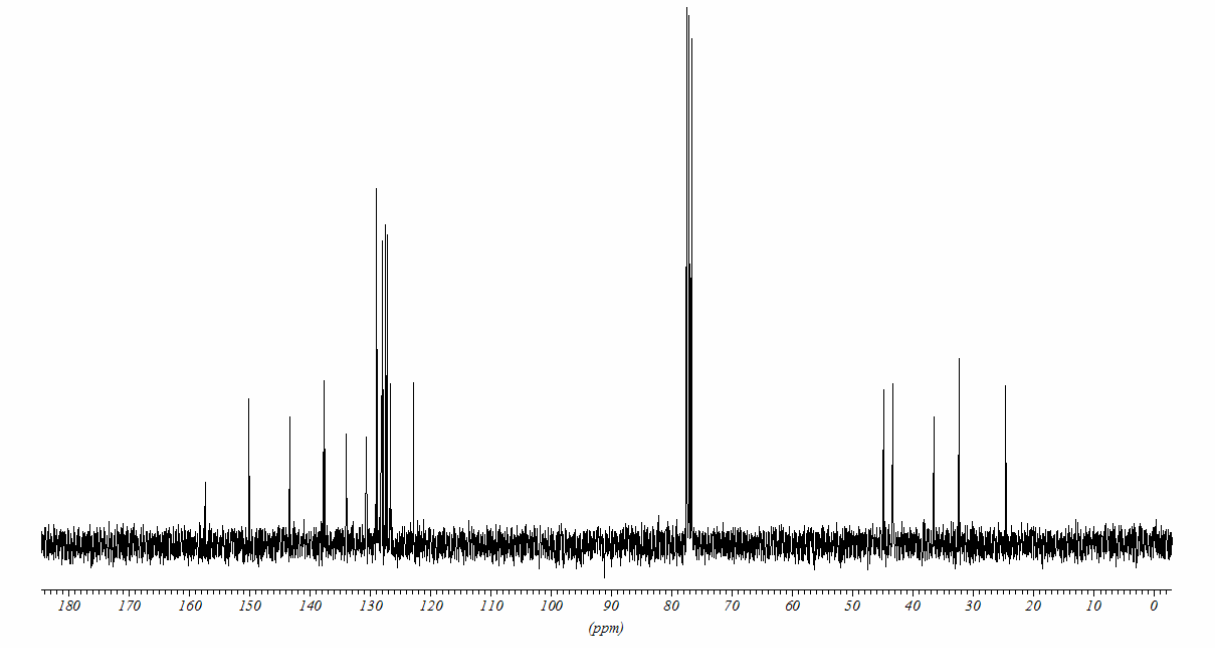

200 180 160 140 120 100 80 60 40 20 0
(ppm)

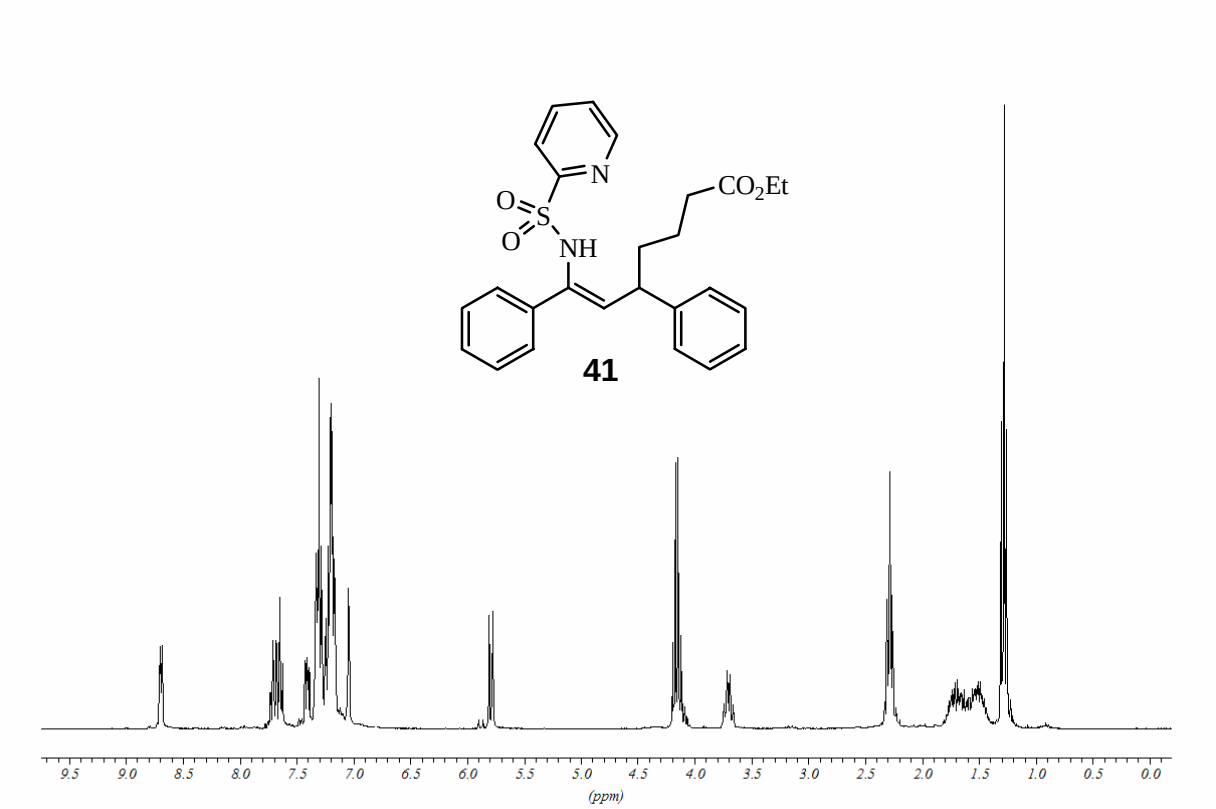

N
O
S
O
NH
39
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
(ppm)

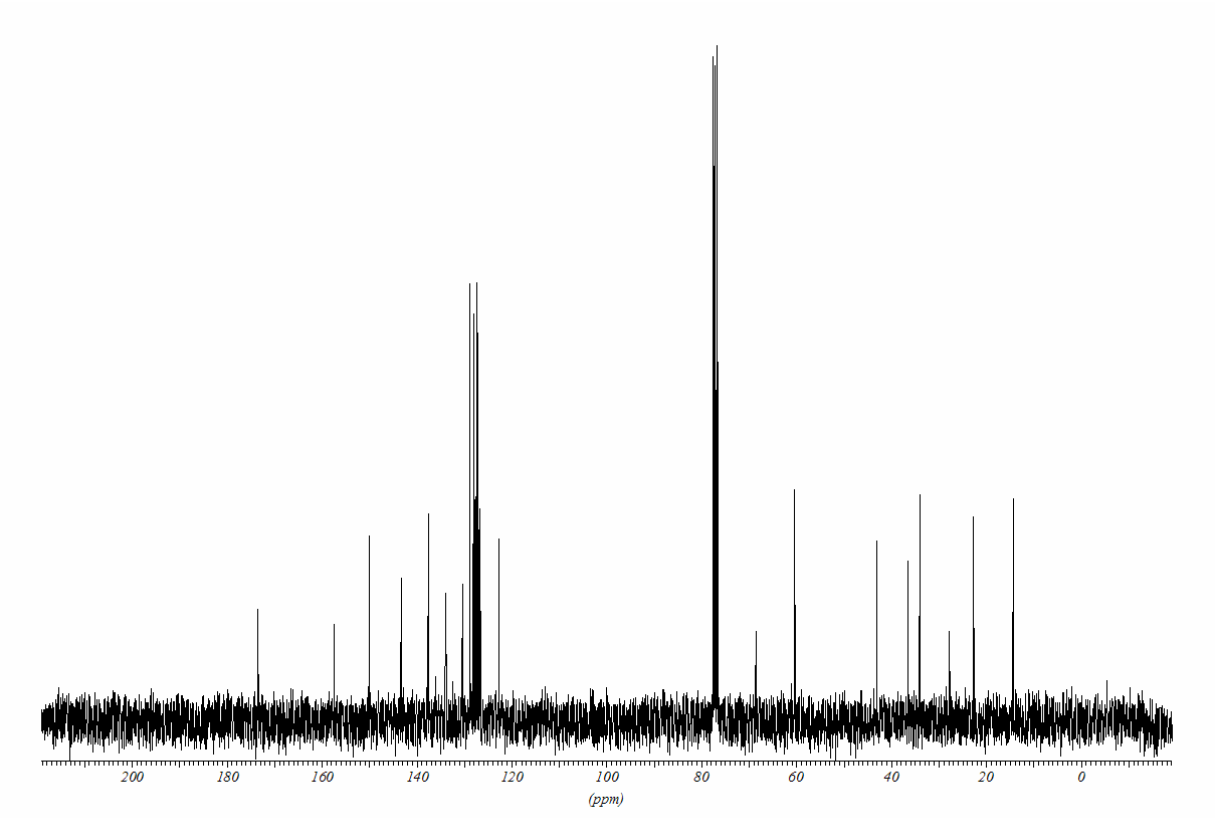

200
180
160
140
120
100
80
60
40
20
0
(ppm)

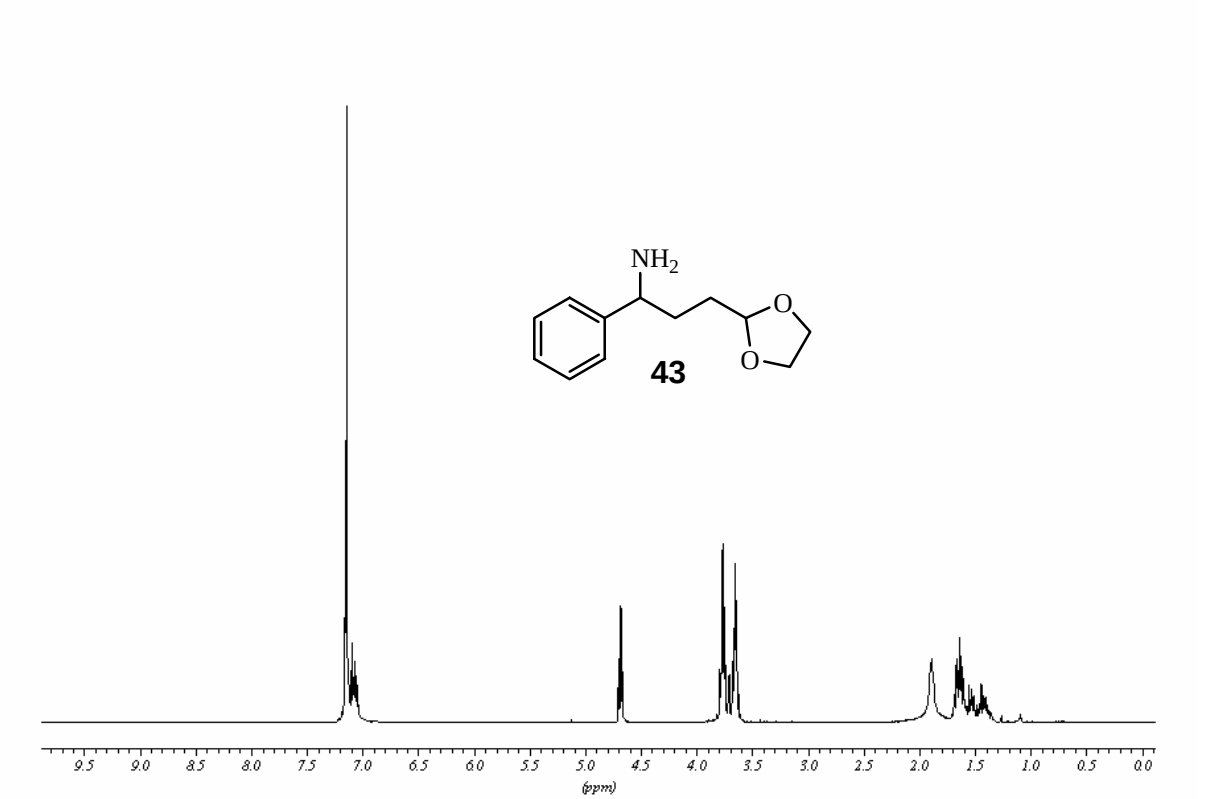

Cl
N
O
S
O
NH
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
(ppm)

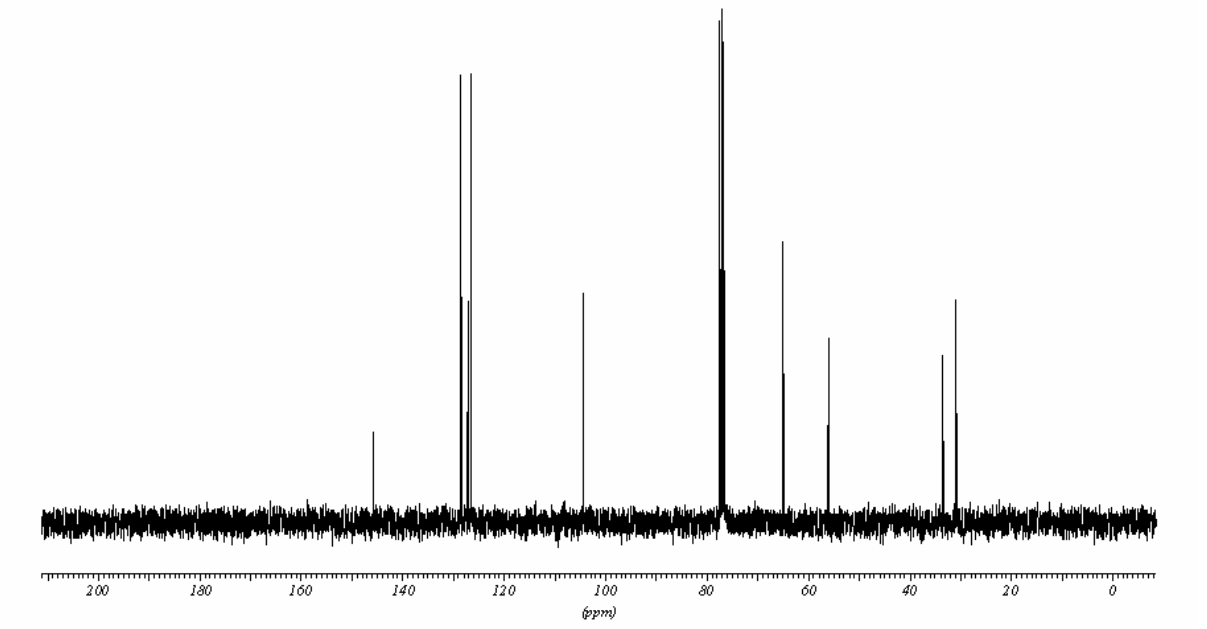
40

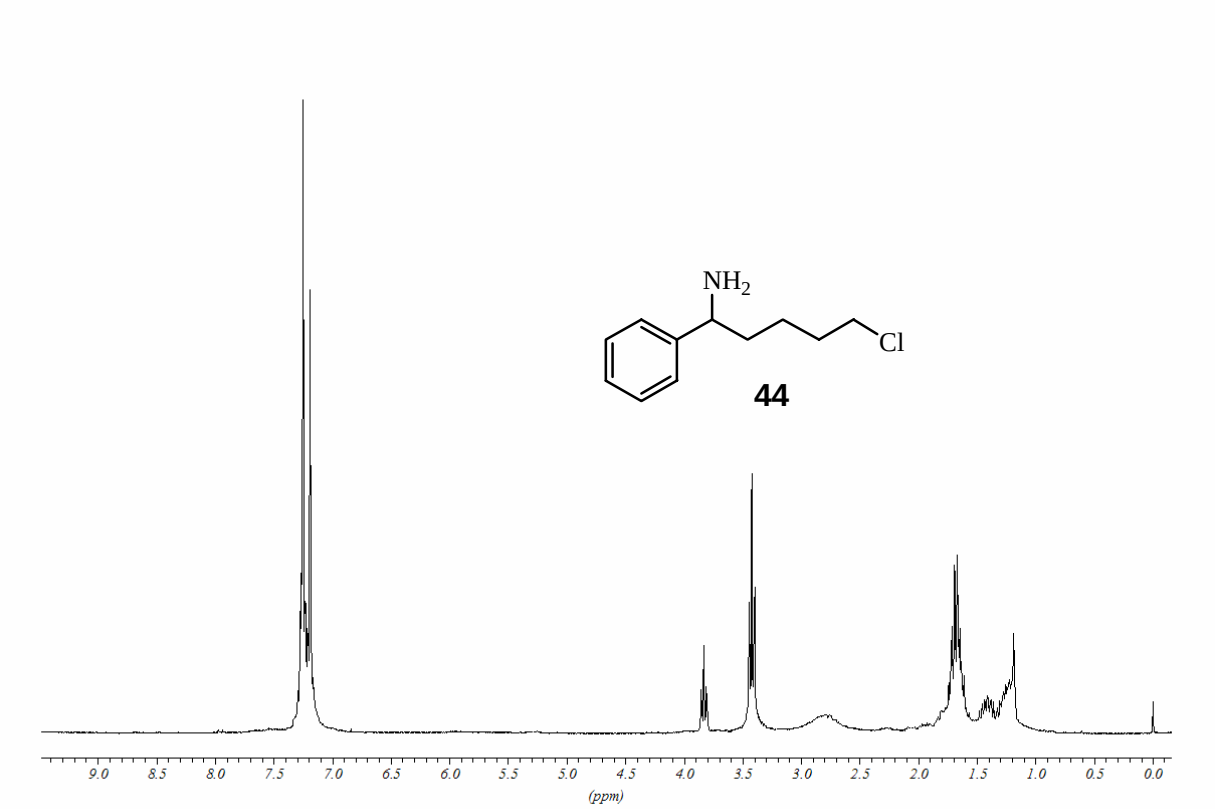

180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
(ppm)

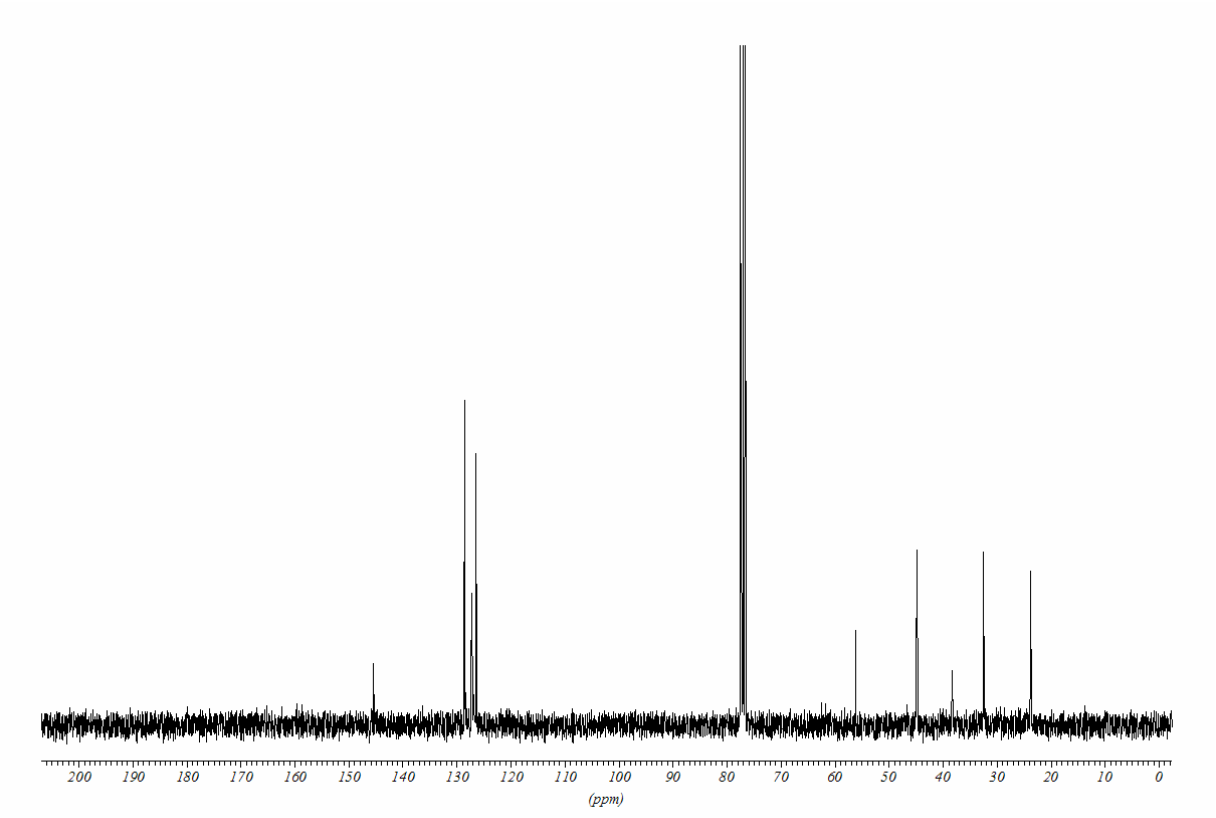

N
O
S
O
NH
CO2Et
41
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
(ppm)

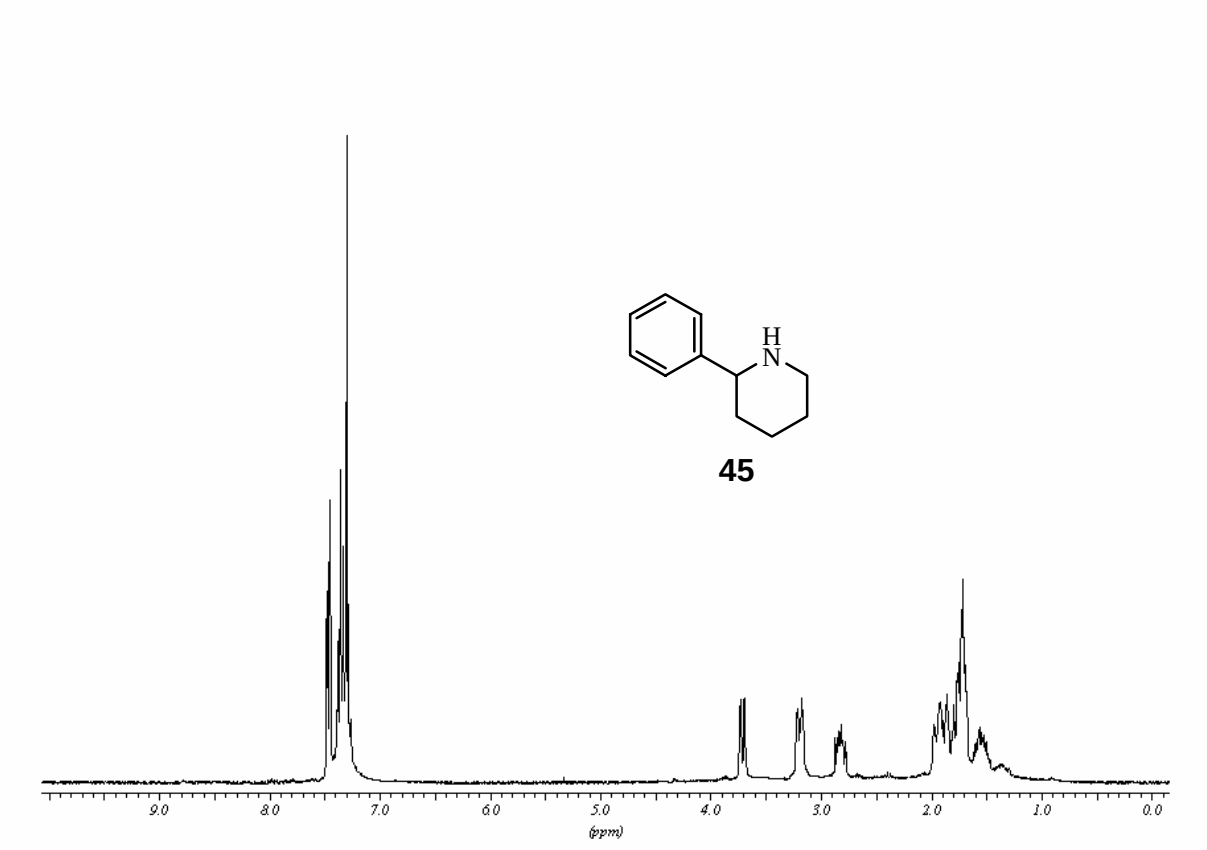

200 180 160 140 120 100 80 60 40 20 0
(ppm)


NH2
O
O
43
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
(ppm)

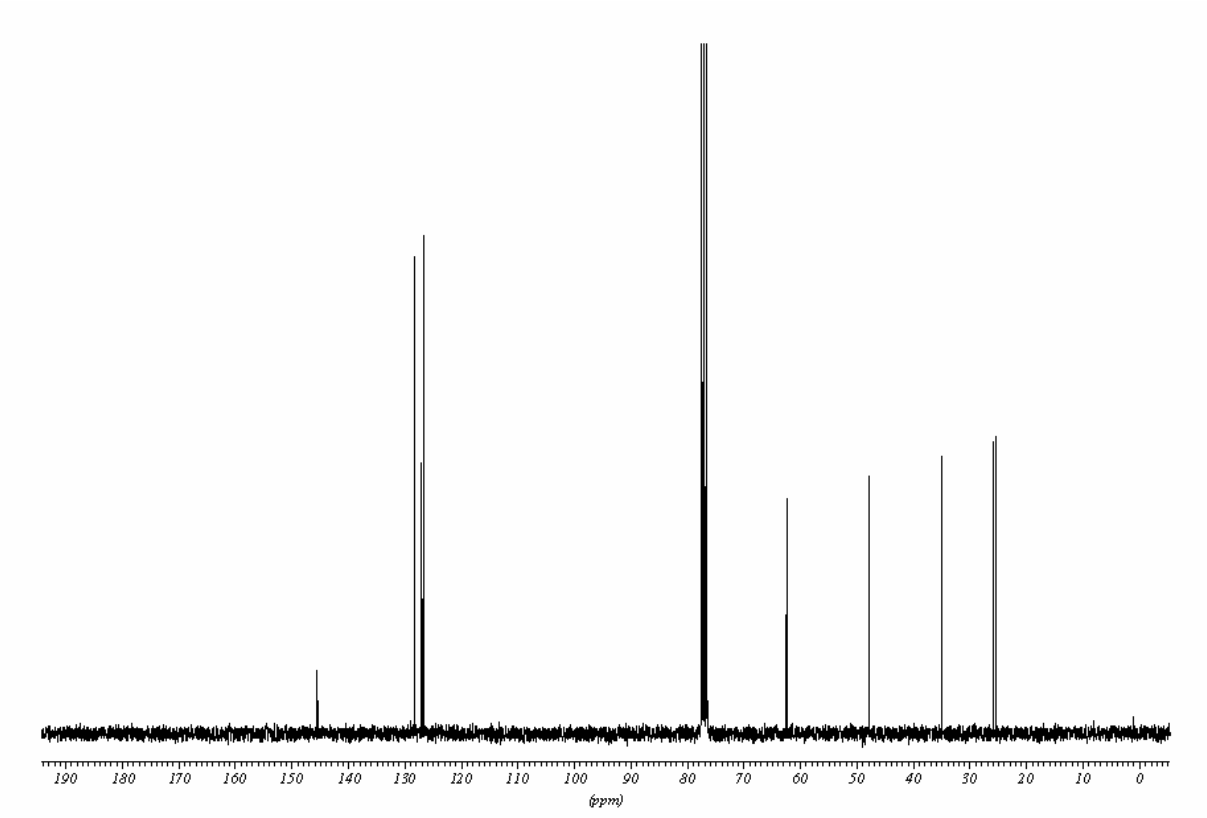

200 180 160 140 120 100 80 60 40 20 0
(ppm)

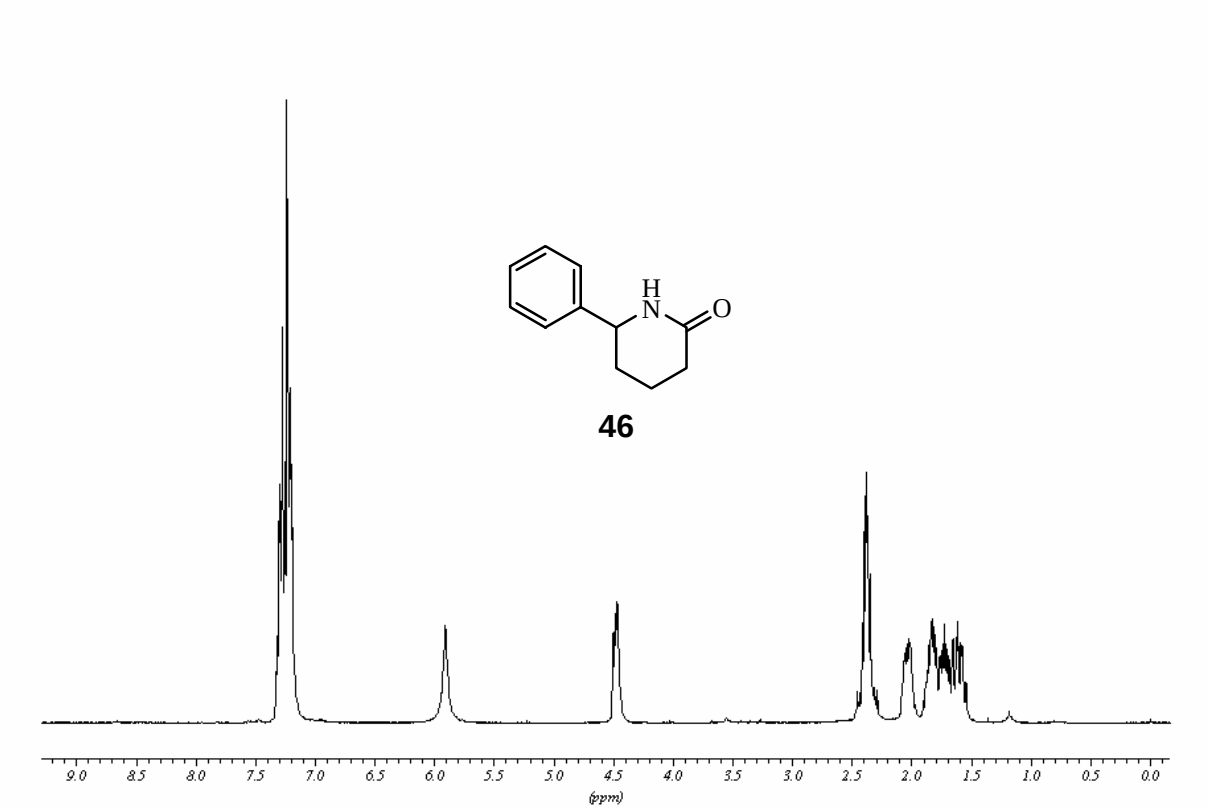

NH2
Cl
44
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
(ppm)


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

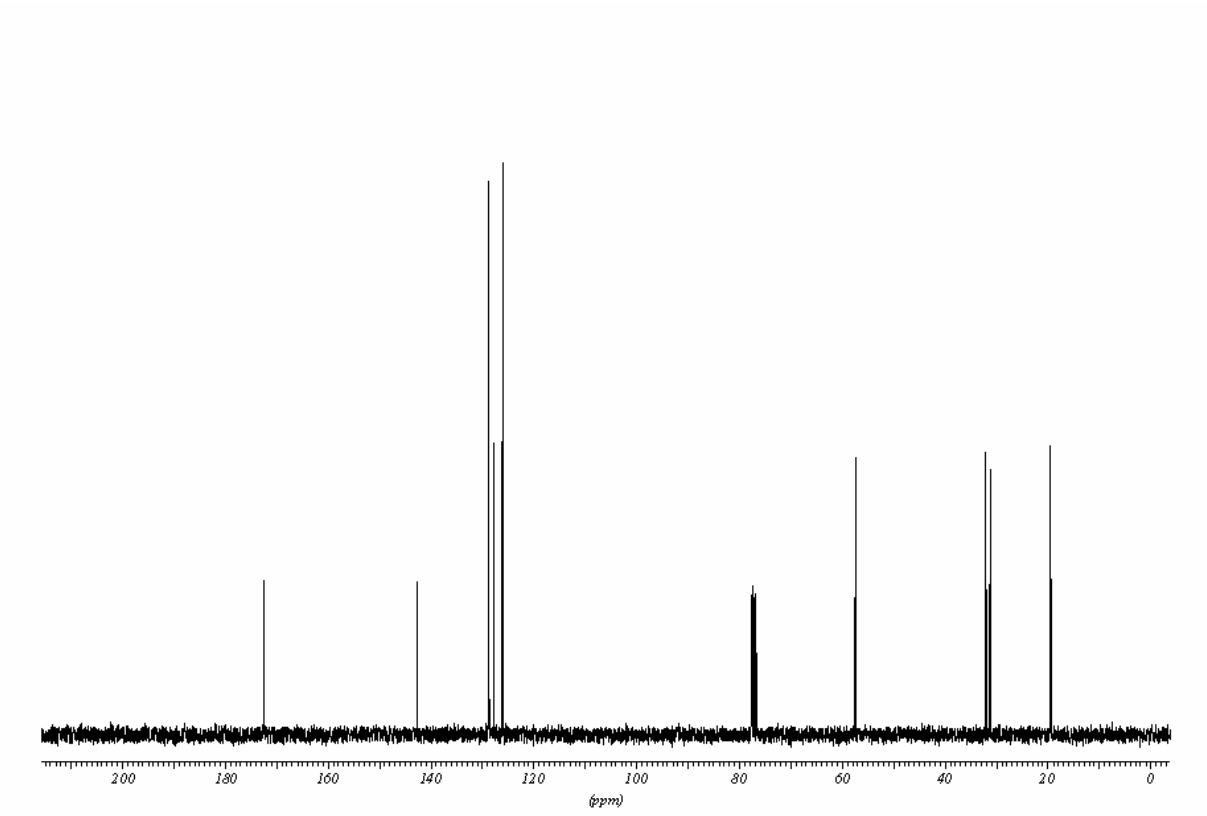

H
N
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
(ppm)

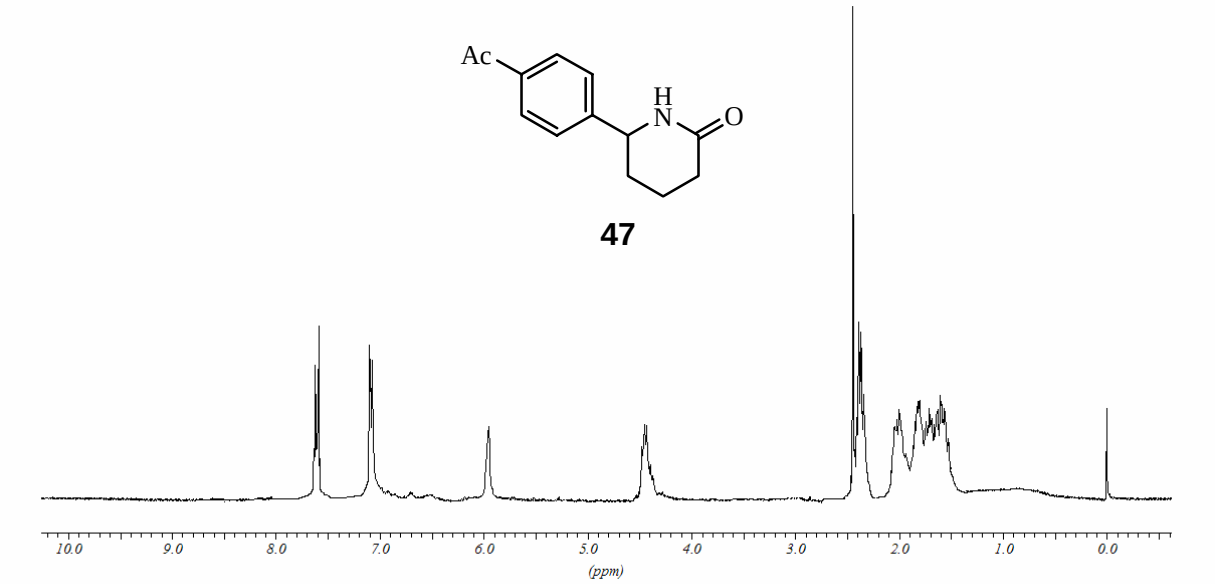
45


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

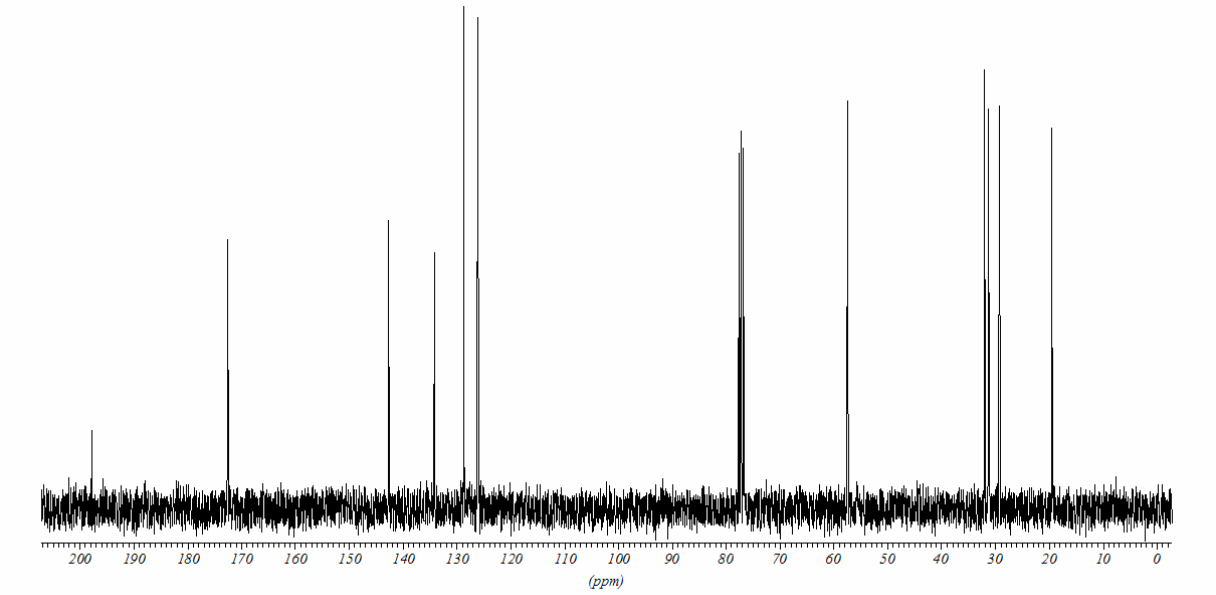

H
N
O
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
(ppm)

46

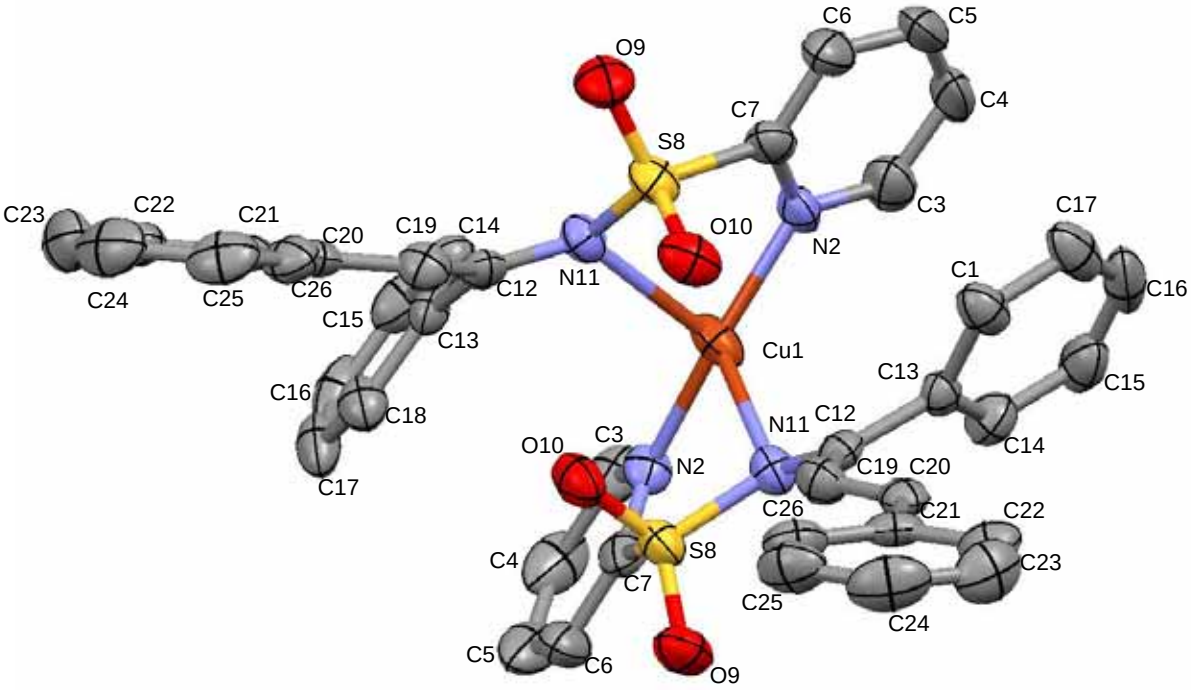

200
180
160
140
120
100
80
60
40
20
0
(ppm)


Ac
H
N
O
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
(ppm)

47


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

X-ray structure of complex **42**



Suitable crystals of complex **42** for X-ray diffraction analysis were grown by slow diffusion of a mixture of diethyl ether/n-hexane into a solution of **42** in CH_2Cl_2 at 4 ºC.