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Supporting Information

Metal-Free C–H Sulfonamidation of Pyrroles by Visible Light Photoredox Catalysis

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1. General information

All NMR spectra were measured at room temperature using a Bruker Avance 300 (300 MHz for ^{1}H, 75 MHz for ^{13}C, 282 MHz for ^{19}F) or a Bruker Avance 400 (400 MHz for ^{1}H, 101 MHz for ^{13}C, 376 MHz for ^{19}F)[1] NMR spectrometer. All chemical shifts are reported in δ-scale as parts per million [ppm] (multiplicity, coupling constant *J*, number of protons) relative to the solvent residual peaks as the internal standard.[2] Coupling constants *J* are given in Hertz [Hz]. Abbreviations used for signal multiplicity: ^{1}H-NMR: b = broad, s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, dt = doublet of triplets, dq = doublet of quartets, and m = multiplet; ^{13}C-NMR: (+) = primary/tertiary, (–) = secondary, (C_q) = quaternary carbon). The mass spectrometrical measurements were performed at the Central Analytical Laboratory of the University of Regensburg. All mass spectra were recorded on a Finnigan MAT 95, ThermoQuest Finnigan TSQ 7000, Finnigan MAT SSQ 710 A or an Agilent Q-TOF 6540 UHD instrument. GC measurements were performed on a GC 7890 from Agilent Technologies. Data acquisition and evaluation was done with Agilent ChemStation Rev.C.01.04. [35]. GC/MS measurements were performed on a 7890A GC system from Agilent Technologies with an Agilent 5975 MSD Detector. Data acquisition and evaluation was done with MSD ChemStation E.02.02.1431.A capillary column HP-5MS/30 m x 0.25 mm/0.25 µM film and helium as carrier gas (flow rate of 1 mL/min) were used. The injector temperature (split injection: 40:1 split) was 280 °C, detection temperature 300 °C (FID). GC measurements were made and investigated via integration of the signal obtained. The GC oven temperature program was adjusted as follows: initial temperature 40 °C was kept for 3 minutes, the temperature was increased at a rate of 15 °C/min over a period of 16 minutes until 280 °C was reached and kept for 5 minutes, the temperature was again increased at a rate of 25 °C/min over a period of 48 seconds until the final temperature (300 °C) was reached and kept for 5 minutes. The internal standard was chosen suitable for the molecule. Analytical TLC was performed on silica gel coated alumina plates (MN TLC sheets ALUGRAM® Xtra SIL G/UV$_{254}$). Visualization was done by UV light (254 or 366 nm). If necessary, potassium permanganate or vanillin was used for chemical staining. Purification by column chromatography was performed with silica gel 60 M (40–63 µm, 230–440 mesh, Merck) on a Biotage® Isolera™ Spektra One device. For irradiation with blue light OSRAM Oslon SSL 80 LDCQ7P-1U3U (blue, λ_{max} = 455 nm, I_{max} = 1000 mA, 1.12

W) was used. For irradiation with green light Cree XPEGRN L1 G4 Q4 (green, λ_{max} = 535 nm, I_{max} = 1000 mA, 1.12 W) was used. For irradiation with UV light Edison Edixeon EDEV-SLC1-03 (UV, λ_{max} = 395–410 nm, I_{max} = 700 mA, 3.00 W) was used. The X-ray structure analysis measurements were run at the X-Ray Structure Analysis Department of the University of Regensburg. All measurements were performed on an Agilent Technologies SuperNova, Agilent Technologies Gemini R Ultra or an Agilent Technologies GV 1000 instrument.

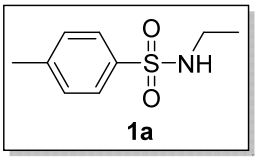
2. General procedures

2.1 General procedure for the preparation of sulfonamides

These compounds were prepared according to a published procedure.[3]

A 0.3 M solution of sulfonylchloride (1 equiv.) in EtOAc was prepared. At 0 °C the corresponding primary amine (2 equiv.) was added dropwise. The reaction mixture was stirred at room temperature for 1 h. Distilled water (20 ml) was added and the reaction mixture was extracted with EtOAc (3 x 20 ml). The combined organic layers were dried over $MgSO_4$ and the solvent was removed under reduced pressure. If necessary, the crude product was purified by automated flash column chromatography (PE/EtOAc, 0-25% EtOAc) yielding the corresponding sulfonamide **1**.

***N*-Ethyl-4-methylbenzene-1-sulfonamide (1a)[3]**



1a

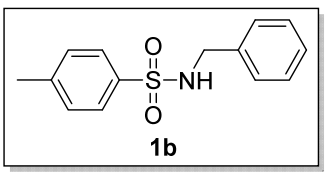
^{1}H NMR (400 MHz, $CDCl_3$, δ_H): 7.74 (d, *J* = 8.2 Hz, 2H), 7.27 (d, *J* = 8.2 Hz, 2H), 5.08 (t, *J* = 6.0 Hz, 1H), 2.94 (dq, *J* = 7.2, 6.0 Hz, 2H), 2.39 (s, 3H), 1.05 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$, δ_C): 143.4 (C_q), 137.0 (C_q), 129.8 (+), 127.2 (+), 38.3 (–), 21.6 (+), 15.1 (+).

HRMS (ESI) (m/z): $[M + H]^+$ ($C_9H_{14}NO_2S$) calc.: 200.0740, found: 200.0744.

Yield: 95%.

***N*-Benzyl-4-methylbenzene-1-sulfonamide (1b)[4]**



1b

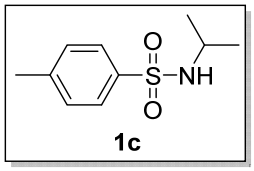
^{1}H NMR (400 MHz, $CDCl_3$, δ_H): 7.79 – 7.74 (m, 2H), 7.33 – 7.25 (m, 5H), 7.23 – 7.16 (m, 2H), 4.62 (t, *J* = 6.2 Hz, 1H), 4.13 (d, *J* = 6.1 Hz, 2H), 2.44 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$, δ_C): 143.7 (C_q), 137.0 (C_q), 136.4 (C_q), 129.9 (+), 128.9 (+), 128.1 (+), 128.0 (+), 127.4 (+), 47.5 (–), 21.7 (+).

HRMS (APCI) (m/z): $[M + H]^+$ ($C_{14}H_{16}NO_2S$) calc.: 262.0896, found: 262.0903.

Yield: 32%.

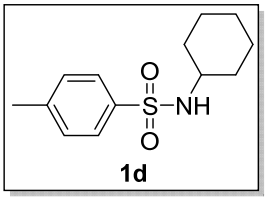
4-Methyl-*N*-(propan-2-yl)benzene-1-sulfonamide (1c)[5]



1c

^{1}H NMR (400 MHz, $CDCl_3$, δ_H): 7.79 – 7.74 (m, 2H), 7.31 – 7.26 (m, 2H), 5.20 (d, *J* = 7.4 Hz, 1H), 3.38 (dq, *J* = 7.4, 6.6 Hz, 1H), 2.37 (s, 3H), 1.02 (d, *J* = 6.5 Hz, 6H).
^{13}C NMR (101 MHz, $CDCl_3$, δ_C): 143.1 (C_q), 138.2 (C_q), 129.6 (+), 127.0 (+), 46.0 (+), 23.6 (+), 21.5 (+).
HRMS (APCI) (m/z): $[M + H]^+$ ($C_{10}H_{16}NO_2S$) calc.: 214.0896, found: 214.0901.
Yield: 87%.

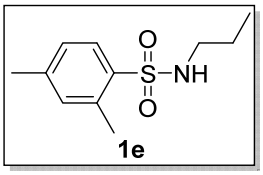
***N*-Cyclohexyl-4-methylbenzene-1-sulfonamide (1d)[5]**



1d

^{1}H NMR (400 MHz, $CDCl_3$, δ_H): 7.77 (d, *J* = 8.2 Hz, 2H), 7.27 (d, *J* = 8.2 Hz, 2H), 5.16 (d, *J* = 7.5 Hz, 1H), 3.09 (s, 1H), 2.40 (s, 3H), 1.75 – 1.67 (m, 2H), 1.65 – 1.55 (m, 2H), 1.51 - 1.41 (m, 1H), 1.32 – 0.97 (m, 5H).
^{13}C NMR (101 MHz, $CDCl_3$, δ_C): 143.1 (C_q), 138.6 (C_q), 129.6 (+), 127.0 (+), 52.6 (+), 33.8 (–), 25.2 (–), 24.7 (–), 21.5 (+).
HRMS (APCI) (m/z): $[M + H]^+$ ($C_{13}H_{20}NO_2S$) calc.: 254.1209, found: 254.1214.
Yield: 51%.

2,4-Dimethyl-*N*-propylbenzene-1-sulfonamide (1e)



1e

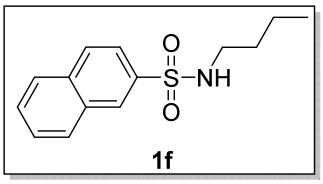
^{1}H NMR (400 MHz, $CDCl_3$, δ_H): 7.88 – 7.81 (m, 1H), 7.13 – 7.05 (m, 2H), 5.03 (t, *J* = 6.1 Hz, 1H), 2.84 (dt, *J* = 7.2, 6.1 Hz, 2H), 2.58 (s, 3H), 2.33 (s, 3H), 1.47 (hept, *J* = 7.3 Hz, 2H), 0.81 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$, δ_C): 143.4 (C_q), 136.9 (C_q), 135.1 (C_q), 133.4 (+), 129.9 (+), 126.8 (+), 44.9 (–), 23.2 (–), 21.4 (+), 20.3 (+), 11.3 (+).

HRMS (ESI) (m/z): $[M + H]^+$ ($C_{11}H_{18}NO_2S$) calc.: 228.1053, found: 228.1055.

Yield: 99%.

***N*-Butylnaphthalene-2-sulfonamide (1f)[6]**



1f

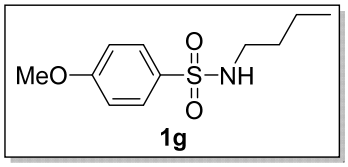
^{1}H NMR (300 MHz, $CDCl_3$, δ_H): 8.52 – 8.46 (m, 1H), 7.97 – 7.80 (m, 4H), 7.64 – 7.51 (m, 2H), 5.56 (t, *J* = 6.1 Hz, 1H), 2.96 (dt, *J* = 7.1, 6.1 Hz, 2H), 1.51 – 1.35 (m, 2H), 1.33 – 1.15 (m, 2H), 0.77 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$, δ_C): 136.7 (C_q), 134.7 (C_q), 132.1 (C_q), 129.4 (+), 129.1 (+), 128.7 (+), 128.3 (+), 127.8 (+), 127.4 (+), 122.3 (+), 43.0 (–), 31.5 (–), 19.6 (–), 13.5 (+).

HRMS (ESI) (m/z): $[M + H]^+$ ($C_{14}H_{18}NO_2S_2$) calc.: 264.1053, found: 264.1052.

Yield: 88%.

***N*-Butyl-4-methoxybenzene-1-sulfonamide (1g)[7]**



1g

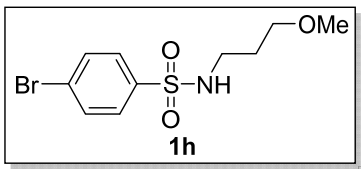
^{1}H NMR (300 MHz, $CDCl_3$, δ_H): 7.81 – 7.73 (m, 2H), 6.95 – 6.87 (m, 2H), 5.30 (t, *J* = 6.1 Hz, 1H), 3.79 (s, 3H), 2.82 (q, *J* = 6.6 Hz, 2H), 1.42 – 1.31 (m, 2H), 1.27 – 1.14 (m, 2H), 0.76 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$, δ_C): 162.7 (C_q), 131.4 (C_q), 129.1 (+), 114.1 (+), 55.5 (+), 42.8 (–), 31.4 (–), 19.6 (–), 13.4 (+).

HRMS (ESI) (m/z): $[M + H]^+$ ($C_{11}H_{18}NO_3S$) calc.: 244.1002, found: 244.1006.

Yield: 96%.

4-Bromo-*N*-(3-methoxypropyl)benzene-1-sulfonamide (1h)



1h

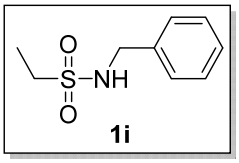
^{1}H NMR (400 MHz, $CDCl_3$, δ_H): 7.75 – 7.69 (m, 2H), 7.68 – 7.62 (m, 2H), 5.22 (t, *J* = 5.7 Hz, 1H), 3.41 (t, *J* = 5.6 Hz, 2H), 3.28 (s, 3H), 3.08 (q, *J* = 5.9 Hz, 2H), 1.75 – 1.67 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$, δ_C): 139.3 (C_q), 132.5 (+), 128.8 (+), 127.5 (C_q), 71.8 (–), 59.0 (+), 42.5 (–), 28.9 (–).

HRMS (ESI) (m/z): $[M + H]^+$ ($C_{10}H_{15}BrNO_3S$) calc.: 307.9951, found: 307.9956.

Yield: 90%.

***N*-Benzylethane-1-sulfonamide (1i)[8]**



1i

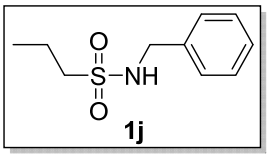
^{1}H NMR (300 MHz, $CDCl_3$, δ_H): 7.44 – 7.27 (m, 5H), 4.53 (s, 1H), 4.30 (d, *J* = 6.0 Hz, 2H), 2.96 (q, *J* = 7.4 Hz, 2H), 1.32 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$, δ_C): 137.0 (C_q), 129.0 (+), 128.2 (+), 128.0 (+), 47.7 (–), 47.4 (–), 8.4 (+).

HRMS (APCI) (m/z): $[M + H]^+$ ($C_9H_{14}NO_2S$) calc.: 200.0740, found: 200.0740.

Yield: 25%.

***N*-Benzylpropane-1-sulfonamide (1j)[8]**



1j

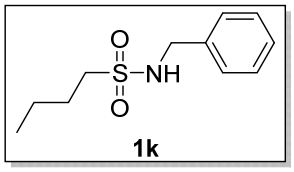
^{1}H NMR (400 MHz, $CDCl_3$, δ_H): 7.38 – 7.23 (m, 5H), 5.20 (s, 1H), 4.24 (s, 2H), 2.84 – 2.79 (m, 2H), 1.76 – 1.67 (m, 2H), 0.92 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$, δ_C): 137.2 (C_q), 128.7 (+), 127.9 (+), 127.9 (+), 54.9 (–), 47.0 (–), 17.2 (–), 12.9 (+).

HRMS (ESI) (m/z): $[M + H]^+$ ($C_{10}H_{16}NO_2S$) calc.: 214.0896, found: 214.0898.

Yield: 96%.

***N*-Benzylbutane-1-sulfonamide (1k)[9]**



1k

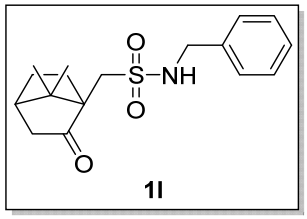
^{1}H NMR (400 MHz, $CDCl_3$, δ_H): 7.41 – 7.26 (m, 5H), 4.72 (t, *J* = 5.5 Hz, 1H), 4.29 (d, *J* = 5.9 Hz, 2H), 2.97 – 2.81 (m, 2H), 1.77 – 1.67 (m, 2H), 1.36 (hept, *J* = 7.4 Hz, 2H), 0.88 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$, δ_C): 137.1 (C_q), 129.0 (+), 128.2 (+), 128.1 (+), 53.2 (–), 47.3 (–), 25.7 (–), 21.6 (–), 13.6 (+).

HRMS (ESI) (m/z): $[M + H]^+$ ($C_{11}H_{18}NO_2S_2$) calc.: 228.1053, found: 228.1059.

Yield: 83%.

***N*-Benzyl-1-[7,7-dimethyl-2-oxobicyclo[2.2.1]heptan-1-yl]methanesulfonamide (1l)**



1l

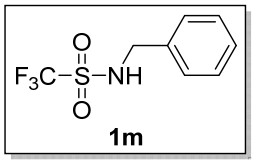
^{1}H NMR (300 MHz, $CDCl_3$, δ_H): 7.41 – 7.21 (m, 5H), 5.87 (t, *J* = 6.4 Hz, 1H), 4.31 (d, *J* = 6.4 Hz, 2H), 3.13 (d, *J* = 15.1 Hz, 1H), 2.81 (d, *J* = 15.1 Hz, 1H), 2.36 – 2.26 (m, 1H), 2.18 – 2.03 (m, 2H), 2.00 – 1.82 (m, 3H), 1.42 – 1.31 (m, 1H), 0.91 (s, 3H), 0.70 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$, δ_C): 216.9 (C_q), 137.0 (C_q), 128.7 (+), 128.3 (+), 127.8 (+), 59.2 (C_q), 50.5 (–), 48.7 (C_q), 47.7 (–), 42.9 (–), 42.6 (+), 27.0 (–), 26.7 (–), 19.7 (+), 19.4 (+).

HRMS (ESI) (m/z): $[M + H]^+$ ($C_{17}H_{24}NO_3S$) calc.: 322.1471, found: 322.1478.

Yield: 78%.

***N*-Benzyl-1,1,1-trifluoromethanesulfonamide (1m)[10]**



1m

^{1}H NMR (300 MHz, $CDCl_3$, δ_H): 7.46 – 7.28 (m, 5H), 4.85 (s, 1H), 4.44 (s, 2H).

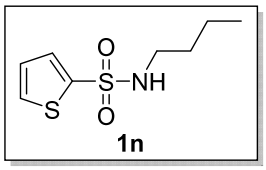
^{13}C NMR (75 MHz, $CDCl_3$, δ_C): 135.2 (C_q), 129.3 (+), 128.9 (+), 128.0 (+), 119.8 (d, $^{1}J_{CF}$ = 320.9 Hz, C_q), 48.4 (–).

^{19}F NMR (282 MHz, $CDCl_3$, δ_F): -77.6 (s).

HRMS (EI+) (m/z): [$M^{+\cdot}$] ($C_8H_8F_3NO_2S$) calc.: 239.0222, found: 239.0222.

Yield: 88%.

***N*-Butylthiophene-2-sulfonamide (1n)[7]**



1n

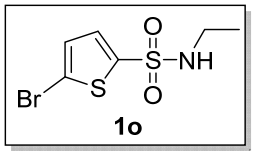
^{1}H NMR (400 MHz, $CDCl_3$, δ_H): 7.60 (ddd, *J* = 10.1, 5.0, 1.4 Hz, 2H), 7.09 (dd, *J* = 5.0, 3.7 Hz, 1H), 4.61 (t, *J* = 6.1 Hz, 1H), 3.04 (dt, *J* = 7.1, 6.1 Hz, 2H), 1.53 – 1.41 (m, 2H), 1.38 – 1.26 (m, 2H), 0.87 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$, δ_C): 141.1 (C_q), 132.2 (+), 131.8 (+), 127.5 (+), 43.3 (–), 31.6 (–), 19.8 (–), 13.7 (+).

HRMS (ESI) (m/z): [M + H]$^{+}$ ($C_8H_{14}NO_2S_2$) calc.: 220.0460, found: 220.0464.

Yield: 95%.

5-Bromo-*N*-ethylthiophene-2-sulfonamide (1o)



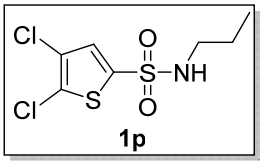
1o

^{1}H NMR (400 MHz, $CDCl_3$, δ_H): 7.36 (d, *J* = 4.0 Hz, 1H), 7.06 (d, *J* = 4.0 Hz, 1H), 4.60 (t, *J* = 5.9 Hz, 1H), 3.10 (dq, *J* = 7.2, 5.6 Hz, 2H), 1.17 (t, *J* = 7.2 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$, δ_C): 142.0 (C_q), 132.3 (+), 130.5 (+), 119.9 (C_q), 38.7 (–), 15.1 (+).

HRMS (EI+) (m/z): [$M^{+\cdot}$] ($C_6H_8BrNO_2S_2$) calc.: 268.9174, found: 268.9168.

Yield: 98%.

4,5-Dichloro-*N*-propylthiophene-2-sulfonamide (1p)



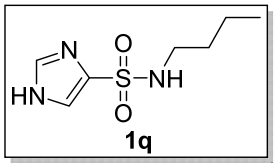
1p

^{1}H NMR (300 MHz, $CDCl_3$, δ_H): 7.38 (s, 1H), 5.01 (t, *J* = 6.0 Hz, 1H), 3.01 (dt, *J* = 7.1, 5.9 Hz, 2H), 1.56 (hept, *J* = 7.3 Hz, 2H), 0.92 (t, *J* = 7.4 Hz, 3H).
^{13}C NMR (75 MHz, $CDCl_3$, δ_C): 137.6 (C_q), 131.2 (C_q), 130.9 (+), 124.9 (C_q), 45.4 (–), 23.0 (–), 11.2 (+).

HRMS (ESI) (m/z): [M + H]$^+$ ($C_7H_{10}Cl_2NO_2S_2$) calc.: 273.9525, found: 273.9523.

Yield: 93%.

***N*-Butyl-1*H*-imidazole-4-sulfonamide (1q)**



1q

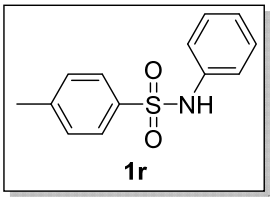
^{1}H NMR (400 MHz, Acetone-*d*$_6$, δ_H): 12.33 (s, 1H), 7.90 (d, *J* = 1.3 Hz, 1H), 7.70 (d, *J* = 1.2 Hz, 1H), 6.50 (t, *J* = 6.1 Hz, 1H), 2.97 – 2.92 (m, 2H), 1.49 – 1.44 (m, 2H), 1.34 – 1.28 (m, 2H), 0.83 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (101 MHz, Acetone-*d*$_6$, δ_C): 140.5 (C_q), 137.7 (+), 121.0 (+), 43.3 (–), 32.1 (–), 20.1 (–), 13.6 (+).

HRMS (ESI) (m/z): $[M + H]^+$ ($C_7H_{14}N_3O_2S$) calc.: 204.0801, found: 204.0805.

Yield: 94%.

4-Methyl-*N*-phenylbenzene-1-sulfonamide (1r)[11]



1r

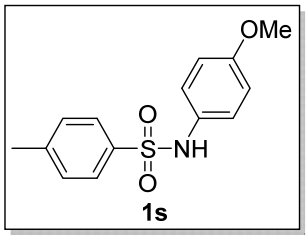
^{1}H NMR (400 MHz, $CDCl_3$, δ_H): 7.71 – 7.63 (m, 2H), 7.25 – 7.19 (m, 4H), 7.14 – 7.03 (m, 3H), 6.90 (s, 1H), 2.37 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$, δ_C): 144.1 (C_q), 136.7 (C_q), 136.2 (C_q), 129.8 (+), 129.4 (+), 127.4 (+), 125.4 (+), 121.7 (+), 21.7 (+).

HRMS (APCI) (m/z): $[M + H]^+$ ($C_{13}H_{14}NO_2S$) calc.: 248.0740, found: 248.0750.

Yield: 93%.

***N*-(4-Methoxyphenyl)-4-methylbenzene-1-sulfonamide (1s)[11]**



1s

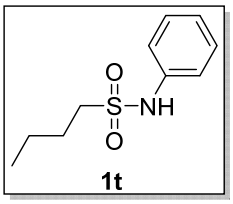
^{1}H NMR (300 MHz, $CDCl_3$, δ_H): 7.61 – 7.53 (m, 2H), 7.24 – 7.18 (m, 2H), 7.00 – 6.93 (m, 2H), 6.79 – 6.71 (m, 2H), 6.45 (s, 1H), 3.75 (s, 3H), 2.38 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$, δ_C): 158.1 (C_q), 143.8 (C_q), 136.1 (C_q), 129.7 (+), 128.9 (C_q), 127.5 (+), 125.7 (+), 114.5 (+), 55.6 (+), 21.7 (+).

HRMS (APCI) (m/z): $[M + H]^+$ ($C_{14}H_{16}NO_3S$) calc.: 278.0845, found: 278.0852.

Yield: 32%.

***N*-Phenylbutane-1-sulfonamide (1t)[12]**



1t

^{1}H NMR (400 MHz, $CDCl_3$, δ_H): 7.62 (s, 1H), 7.34 – 7.26 (m, 4H), 7.16 – 7.09 (m, 1H), 6.98 (s, 1H), 3.15 – 3.07 (m, 2H), 1.84 – 1.74 (m, 2H), 1.37 (hept, *J* = 7.4 Hz, 2H), 0.85 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$, δ_C): 137.1 (C_q), 129.5 (+), 124.8 (+), 120.3 (+), 51.1 (–), 25.2 (–), 21.3 (–), 13.4 (+).

HRMS (ESI) (m/z): $[M + H]^+$ ($C_{10}H_{16}NO_2S$) calc.: 214.0896, found: 214.0900.

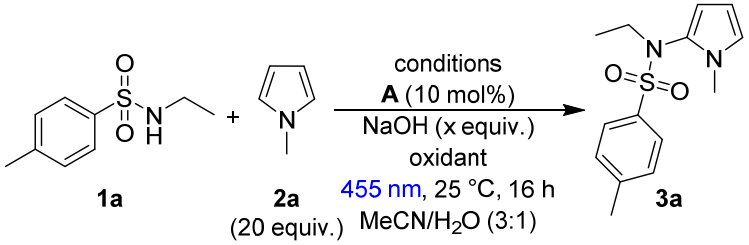
Yield: 84%.

2.2 General reaction conditions for the photocatalytic sulfonamidation

A 5 mL crimp cap vial was equipped with the sulfonamide **1** (0.2 mmol, 1 equiv.), the trapping reagent **2** (5-20 equiv.), sodium hydroxide (16.0 mg, 0.4 mmol, 2 equiv.), 9-mesityl-10-methylacridinium perchlorate (8.2 mg, 10 mol%) and a stirring bar. The solvent mixture MeCN/H_2O (3:1, 2.0 mL) was added *via* syringe and the vessel was capped to prevent evaporation. Oxygen atmosphere was introduced *via* needle and a balloon filled with oxygen. The reaction mixture was stirred and irradiated using a blue LED (455 nm) for 3-16 h at 25 °C. The progress could be monitored by TLC, GC analysis and GC/MS analysis.

The reaction mixture was diluted with water (50 mL) and extracted with EtOAc (3 x 50 mL). The combined organic layers were dried over $MgSO_4$, and the solvents were removed under reduced pressure. Evaporation of volatiles led to the crude product. Purification of the crude product was performed by automated flash column chromatography (PE/EtOAc, 0-25% EtOAc) yielding the corresponding product **3**.

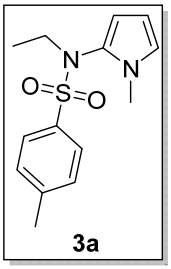
Table S-1. Optimization of the reaction conditions: screening of oxidants and bases.



entry	conditions	yield [%][a]
1	**A** (10 mol%), x = 2, Ph-NO_2 (1 equiv.)	18
2	**A** (10 mol%), x = 2, $(NH_4)_2S_2O_8$ (1 equiv.)	-
3	**A** (10 mol%), KOH (2 equiv.), O_2-balloon	45
4	**A** (10 mol%), K_3PO_4 (2 equiv.), O_2-balloon	36
5	**A** (10 mol%), KO^{t}Bu (2 equiv.), O_2-balloon	31
6	**A** (10 mol%), K_2CO_3 (2 equiv.), O_2-balloon	13
7	**A** (10 mol%), Cs_2CO_3 (2 equiv.), O_2-balloon	6
8	**A** (10 mol%), CsF (2 equiv.), O_2-balloon	-

[a] Determined by GC analysis with naphthalene as internal standard.

***N*-Ethyl-4-methyl-*N*-(1-methyl-1*H*-pyrrol-2-yl)benzene-1-sulfonamide (3a)**



3a

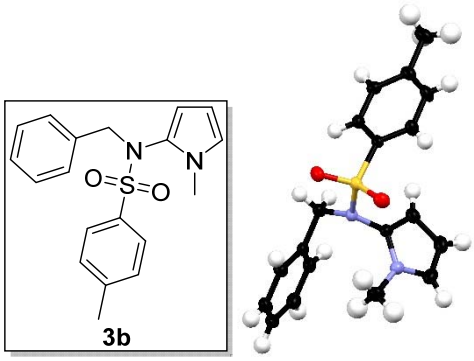
^{1}H-NMR (300 MHz, $CDCl_3$, δ_H): 7.65 – 7.57 (m, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 6.58 (dd, *J* = 3.1, 1.8 Hz, 1H), 5.99 (dd, *J* = 3.8, 3.0 Hz, 1H), 5.42 (dd, *J* = 3.8, 1.8 Hz, 1H), 3.83 (s, 1H), 3.62 (s, 3H), 3.07 (s, 1H), 2.43 (s, 3H), 1.03 (t, *J* = 7.1 Hz, 3H).

^{13}C-NMR (75 MHz, $CDCl_3$, δ_C): 143.6 (C_q), 134.7 (C_q), 129.3 (+), 128.3 (+), 127.1 (C_q), 120.8 (+), 106.3 (+), 104.7 (+), 47.8 (–), 33.0 (+), 21.6 (+), 13.7 (+).

HRMS (ESI) (m/z): $[M + H]^+$ ($C_{14}H_{19}N_2O_2S$) calc.: 279.1162, found: 279.1162.

Yield: 84%.

***N*-Benzyl-4-methyl-*N*-(1-methyl-1*H*-pyrrol-2-yl)benzene-1-sulfonamide (3b)**



^{1}H-NMR (400 MHz, $CDCl_3$, δ_H): 7.70 – 7.65 (m, 2H), 7.36 – 7.29 (m, 2H), 7.24 – 7.18 (m, 3H), 7.19 – 7.13 (m, 2H), 6.38 (dd, *J* = 3.0, 1.8 Hz, 1H), 5.94 (dd, *J* = 3.8, 3.0 Hz, 1H), 5.49 (dd, *J* = 3.8, 1.8 Hz, 1H), 5.06 (s, 1H), 3.94 (s, 1H), 3.12 (s, 3H), 2.47 (s, 3H).

^{13}C-NMR (101 MHz, $CDCl_3$, δ_C): 143.8 (C_q), 135.8 (C_q), 135.1 (C_q), 129.5 (+), 129.5 (+), 128.4 (+), 128.3 (+), 128.1 (+), 127.3 (C_q), 120.7 (+), 106.3 (+), 104.9 (+), 57.5 (–), 32.7 (+), 21.7 (+).

HRMS (ESI) (m/z): $[M + H]^+$ ($C_{19}H_{21}N_2O_2S$) calc.: 341.1318, found: 341.1325.

X-ray crystallography: The mono-crystals suitable for X-ray-measurement were obtained by slow evaporation of a solvent mixture ($CDCl_3$/heptane).

(λ = 1.54184 Å, at 123 K)

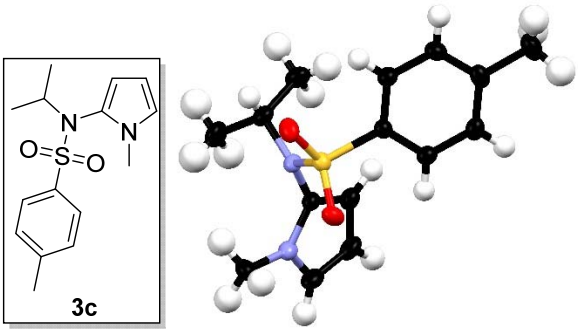
Yield: 97%.

Table S-2. Crystallographic data for **3b**.[a]

Molecular formula	$C_{19}H_{20}N_2O_2S$
M_r	340.43
Space group	P 1 21/c 1
a [Å]	15.7933(3)
b [Å]	8.92836(18)
c [Å]	12.9799(3)
α [°]	90
β [°]	110.209(3)
γ [°]	90
V [Å^3]	1717.60(7)
Z	4

[a] Reported data in accordance with the calculated data.

4-Methyl-*N*-(propan-2-yl)-*N*-(1-methyl-1*H*-pyrrol-2-yl)benzene-1-sulfonamide (3c)



^{1}H-NMR (400 MHz, $CDCl_3$, δ_H): 7.66 – 7.61 (m, 2H), 7.30 – 7.23 (m, 3H), 6.65 (dd, *J* = 3.0, 1.8 Hz, 1H), 6.03 (dd, *J* = 3.8, 3.0 Hz, 1H), 5.60 (dd, *J* = 3.8, 1.8 Hz, 1H), 4.50 (hept, *J* = 6.7 Hz, 1H), 3.59 (s, 3H), 2.43 (s, 3H), 1.03 (d, *J* = 6.7 Hz, 3H), 0.84 (d, *J* = 6.6 Hz, 3H).

^{13}C-NMR (101 MHz, $CDCl_3$, δ_C): 143.4 (C_q), 137.4 (C_q), 129.4 (+), 128.1 (+), 122.9 (C_q), 121.7 (+), 108.6 (+), 106.2 (+), 52.0 (+), 33.2 (+), 22.2 (+), 21.7 (+), 20.7 (+).

HRMS (ESI) (m/z): $[M + H]^+$ ($C_{15}H_{21}N_2O_2S$) calc.: 293.1318, found: 293.1323.

X-ray crystallography: The mono-crystals suitable for X-ray-measurement were obtained by slow evaporation of a solvent mixture ($CDCl_3$/heptane).

(λ = 1.54184 Å, at 123 K)

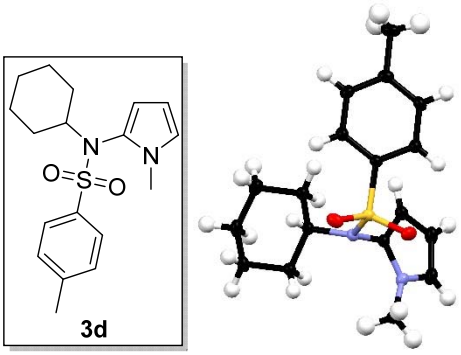
Yield: 49%.

Table S-3. Crystallographic data for **3c**.[a]

Molecular formula	2 x $C_{15}H_{20}N_2O_2S$
M_r	584.78
Space group	P 1 21/n 1
a [Å]	18.0343(3)
b [Å]	7.5810(1)
c [Å]	23.5816(3)
α [°]	90
β [°]	109.174(2)
γ [°]	90
V [Å^3]	3045.18(8)
Z	4

[a] Reported data in accordance with the calculated data.

***N*-Cyclohexyl-4-methyl-*N*-(1-methyl-1*H*-pyrrol-2-yl)benzene-1-sulfonamide (3d)**



^{1}H-NMR (400 MHz, $CDCl_3$, δ_H): 7.63 (d, *J* = 8.3 Hz, 2H), 7.26 (d, *J* = 8.0 Hz, 2H), 6.63 (dd, *J* = 3.0, 1.8 Hz, 1H), 6.02 (dd, *J* = 3.8, 3.0 Hz, 1H), 5.57 (dd, *J* = 3.8, 1.8 Hz, 1H), 4.06 (tt, *J* = 11.7, 3.8 Hz, 1H), 3.58 (s, 3H), 2.42 (s, 3H), 2.00 – 1.92 (m, 1H), 1.76 – 1.67 (m, 1H), 1.66 – 1.58 (m, 1H), 1.55 – 1.47 (m, 1H), 1.44 – 1.32 (m, 2H), 1.26 – 1.05 (m, 2H), 0.99 – 0.81 (m, 2H).

^{13}C-NMR (101 MHz, $CDCl_3$, δ_C): 143.3 (C_q), 137.7 (C_q), 129.6 (+), 127.9 (+), 123.7 (C_q), 121.5 (+), 108.7 (+), 106.1 (+), 59.9 (+), 33.3 (+), 32.7 (–), 31.3 (–), 26.0 (–), 25.7 (–), 25.1 (–), 21.7 (+).

HRMS (ESI) (m/z): $[M + H]^+$ ($C_{18}H_{25}N_2O_2S$) calc.: 333.1631, found: 333.1636.

X-ray crystallography: The mono-crystals suitable for X-ray-measurement were obtained by slow evaporation of a solvent mixture ($CDCl_3$/heptane).

(λ = 1.54184 Å, at 123 K)

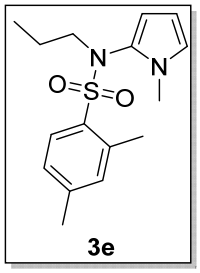
Yield: 30%.

Table S-4. Crystallographic data for **3d**.[a]

Molecular formula	$C_{18}H_{24}N_2O_2S$
M_r	332.45
Space group	P 1 21/n 1
a [Å]	10.79743(16)
b [Å]	13.3813(2)
c [Å]	11.85342(17)
α [°]	90
β [°]	96.5156(12)
γ [°]	90
V [Å^3]	1701.56(4)
Z	4

[a] Reported data in accordance with the calculated data.

2,4-Dimethyl-*N*-(1-methyl-1H-pyrrol-2-yl)-N-propylbenzene-1-sulfonamide (3e)



3e

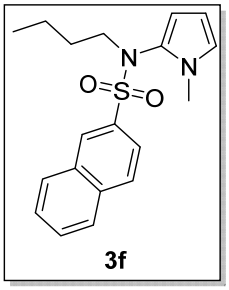
^{1}H-NMR (400 MHz, $CDCl_3$, δ_H): 7.70 (d, *J* = 8.1 Hz, 1H), 7.09 (d, *J* = 8.6 Hz, 1H), 7.05 (s, 1H), 6.54 (dd, *J* = 3.0, 1.9 Hz, 1H), 5.97 (dd, *J* = 3.8, 3.0 Hz, 1H), 5.50 (dd, *J* = 3.8, 1.9 Hz, 1H), 3.72 (d, *J* = 24.7 Hz, 1H), 3.58 (s, 3H), 3.13 (s, 1H), 2.36 (s, 3H), 2.27 (s, 3H), 1.45 (d, *J* = 24.6 Hz, 2H), 0.87 (t, *J* = 7.4 Hz, 3H).

^{13}C-NMR (101 MHz, $CDCl_3$, δ_C): 143.4 (C_q), 138.6 (C_q), 133.6 (C_q), 133.2 (+), 130.4 (+), 127.2 (C_q), 126.8 (+), 120.8 (+), 106.5 (+), 105.8 (+), 54.8 (–), 33.2 (+), 21.8 (–), 21.4 (+), 21.2 (+), 11.2 (+).

HRMS (ESI) (m/z): $[M + H]^+$ ($C_{16}H_{23}N_2O_2S$) calc.: 307.1475, found: 307.1482.

Yield: 57%.

***N*-Butyl-*N*-(1-methyl-*1H*-pyrrol-2-yl)naphthalene-2-sulfonamide (3f)**



3f

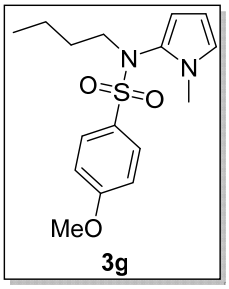
^{1}H-NMR (400 MHz, $CDCl_3$, δ_H): 8.33 – 8.28 (m, 1H), 7.97 – 7.91 (m, 3H), 7.75 (dd, *J* = 8.6, 1.9 Hz, 1H), 7.68 – 7.57 (m, 2H), 6.61 (dd, *J* = 3.0, 1.9 Hz, 1H), 6.00 (dd, *J* = 3.8, 3.0 Hz, 1H), 5.41 (dd, *J* = 3.8, 1.9 Hz, 1H), 3.85 (s, 1H), 3.68 (s, 3H), 3.06 (s, 1H), 1.57 – 1.27 (m, 4H), 0.88 (t, *J* = 7.0 Hz, 3H).

^{13}C-NMR (101 MHz, $CDCl_3$, δ_C): 134.9 (C_q), 134.7 (C_q), 132.0 (C_q), 129.6 (+), 129.4 (+), 128.8 (+), 128.7 (+), 127.9 (+), 127.6 (C_q), 127.4 (+), 123.7 (+), 120.8 (+), 106.5 (+), 104.8 (+), 53.0 (–), 33.1 (+), 30.5 (–), 19.8 (–), 13.8 (+).

HRMS (ESI) (m/z): $[M + H]^+$ ($C_{19}H_{23}N_2O_2S$) calc.: 343.1475, found: 343.1486.

Yield: 79%.

***N*-Butyl-4-methoxy-*N*-(1-methyl-1*H*-pyrrol-2-yl)benzene-1-sulfonamide (3g)**



3g

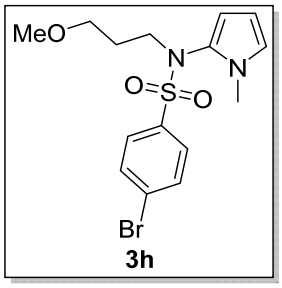
^{1}H-NMR (400 MHz, $CDCl_3$, δ_H): 7.67 – 7.60 (m, 2H), 6.99 – 6.91 (m, 2H), 6.56 (dd, *J* = 3.0, 1.8 Hz, 1H), 5.99 (dd, *J* = 3.8, 3.0 Hz, 1H), 5.42 (dd, *J* = 3.8, 1.8 Hz, 1H), 3.87 (s, 3H), 3.71 (s, 1H), 3.62 (s, 3H), 2.96 (s, 1H), 1.48 – 1.21 (m, 4H), 0.86 (t, *J* = 7.0 Hz, 3H).

^{13}C-NMR (101 MHz, $CDCl_3$, δ_C): 163.1 (C_q), 130.4 (+), 129.2 (C_q), 128.0 (C_q), 120.7 (+), 113.8 (+), 106.3 (+), 104.4 (+), 55.7 (+), 52.8 (–), 33.1 (+), 30.5 (–), 19.9 (–), 13.8 (+).

HRMS (ESI) (m/z): $[M + H]^+$ ($C_{16}H_{23}N_2O_3S$) calc.: 323.1424, found: 323.1434.

Yield: 59%.

4-Bromo-*N*-(3-methoxypropyl)-*N*-(1-methyl-1*H*-pyrrol-2-yl)benzene-1-sulfonamide (3h)



3h

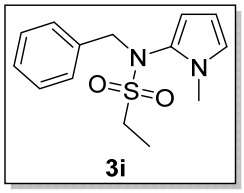
^{1}H-NMR (300 MHz, $CDCl_3$, δ_H): 7.66 – 7.53 (m, 4H), 6.56 (dd, *J* = 3.0, 1.8 Hz, 1H), 5.97 (dd, *J* = 3.8, 3.0 Hz, 1H), 5.41 (dd, *J* = 3.8, 1.8 Hz, 1H), 3.92 – 3.76 (m, 1H), 3.61 (s, 3H), 3.37 – 3.29 (m, 2H), 3.26 (s, 3H), 3.16 – 2.99 (m, 1H), 1.79 – 1.51 (m, 2H).

^{13}C-NMR (75 MHz, $CDCl_3$, δ_C): 136.3 (C_q), 132.0 (+), 129.8 (+), 128.0 (C_q), 127.0 (C_q), 121.1 (+), 106.6 (+), 104.7 (+), 69.5 (–), 58.7 (+), 50.5 (–), 33.1 (+), 28.6 (–).

HRMS (ESI) (m/z): $[M + H]^+$ ($C_{15}H_{20}BrN_2O_3S$) calc.: 387.0373, found: 387.0376.

Yield: 99%.

***N*-Benzyl-*N*-(1-methyl-1*H*-pyrrol-2-yl)ethane-1-sulfonamide (3i)**



3i

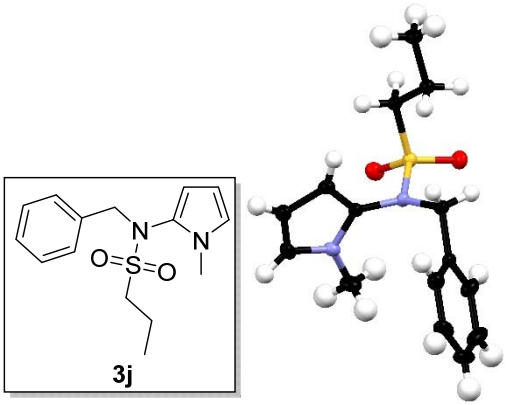
^{1}H-NMR (400 MHz, $CDCl_3$, δ_H): 7.31 – 7.26 (m, 3H), 7.24 – 7.19 (m, 2H), 6.43 (t, *J* = 2.4 Hz, 1H), 6.06 (d, *J* = 2.4 Hz, 2H), 4.93 (s, 1H), 4.41 (s, 1H), 3.17 (q, *J* = 7.4 Hz, 2H), 3.08 (s, 3H), 1.44 (t, *J* = 7.4 Hz, 3H).

^{13}C-NMR (101 MHz, $CDCl_3$, δ_C): 136.3 (C_q), 129.6 (+), 128.6 (+), 128.3 (+), 127.1 (C_q), 121.3 (+), 106.7 (+), 105.6 (+), 57.9 (–), 44.8 (–), 32.8 (+), 7.9 (+).

HRMS (ESI) (m/z): $[M + H]^+$ ($C_{14}H_{19}N_2O_2S$) calc.: 279.1162, found: 279.1169.

Yield: 83%.

***N*-Benzyl-*N*-(1-methyl-1*H*-pyrrol-2-yl)propane-1-sulfonamide (3j)**



^{1}H-NMR (400 MHz, $CDCl_3$, δ_H): 7.30 – 7.26 (m, 3H), 7.24 – 7.20 (m, 2H), 6.43 (t, *J* = 2.4 Hz, 1H), 6.08 – 6.04 (m, 2H), 4.93 (s, 1H), 4.39 (s, 1H), 3.15 – 3.10 (m, 2H), 3.08 (s, 3H), 1.99 – 1.87 (m, 2H), 1.08 (t, *J* = 7.4 Hz, 3H).

^{13}C-NMR (101 MHz, $CDCl_3$, δ_C): 136.3 (C_q), 129.6 (+), 128.6 (+), 128.3 (+), 127.1 (C_q), 121.2 (+), 106.7 (+), 105.5 (+), 57.7 (–), 52.0 (–), 32.8 (+), 17.0 (–), 13.2 (+).

HRMS (ESI) (m/z): $[M + H]^+$ ($C_{15}H_{21}N_2O_2S$) calc.: 293.1318, found: 293.1323.

X-ray crystallography: The mono-crystals suitable for X-ray-measurement were obtained by slow evaporation of a solvent mixture ($CDCl_3$/heptane).

(λ = 1.54184 Å, at 123 K)

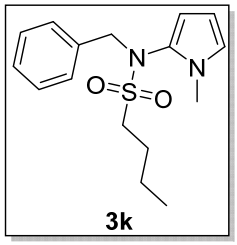
Yield: 75%.

Table S-5. Crystallographic data for **3j**.[a]

Molecular formula	$C_{15}H_{20}N_2O_2S$
M_r	292.39
Space group	P -1
a [Å]	6.2192(2)
b [Å]	9.1506(2)
c [Å]	13.4968(3)
α [°]	98.630(2)
β [°]	96.960(3)
γ [°]	92.679(3)
V [Å^3]	752.15(4)
Z	2

[a] Reported data in accordance with the calculated data.

***N*-Benzyl-*N*-(1-methyl-*1H*-pyrrol-2-yl)butane-1-sulfonamide (3k)**



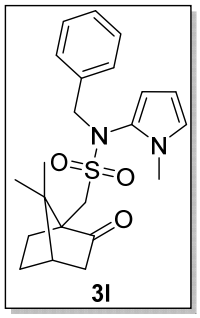
^{1}H-NMR (400 MHz, $CDCl_3$, δ_H): 7.26 (m, 5H), 6.43 (t, *J* = 2.4 Hz, 1H), 6.07 (d, *J* = 2.4 Hz, 2H), 4.93 (s, 1H), 4.40 (s, 1H) 3.20 – 3.11 (m, 2H), 3.09 (s, 3H), 1.92 – 1.82 (m, 2H), 1.48 (hept, *J* = 7.4 Hz, 2H), 0.97 (t, *J* = 7.4 Hz, 3H).

^{13}C-NMR (101 MHz, $CDCl_3$, δ_C): 136.2 (C_q), 129.5 (+), 128.5 (+), 128.2 (+), 127.1 (C_q), 121.2 (+), 106.6 (+), 105.5 (+), 57.7 (–), 50.0 (–), 32.7 (+), 25.1 (–), 21.7 (–), 13.7 (+).

HRMS (ESI) (m/z): $[M + H]^+$ ($C_{16}H_{23}N_2O_2S$) calc.: 307.1475, found: 307.1485.

Yield: 84%.

***N*-Benzyl-1-[(1R,4S)-7,7-dimethyl-2-oxobicyclo[2.2.1]heptan-1-yl]-*N*-(1-methyl-1*H*-pyrrol-2-yl)methanesulfonamide (3l)**



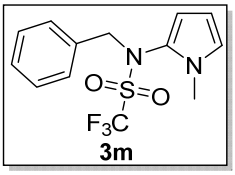
^{1}H-NMR (400 MHz, $CDCl_3$, δ_H): 7.25 (m, 5H), 6.44 – 6.39 (m, 1H), 6.14 (dd, *J* = 3.8, 1.8 Hz, 1H), 6.06 (t, *J* = 3.4 Hz, 1H), 4.95 (s, 1H), 4.41 (s, 1H) 3.62 (s, 1H), 3.08 (s, 3H), 2.50 (m, 1H), 2.39 (ddd, *J* = 18.4, 4.8, 3.2 Hz, 1H), 2.08 (t, *J* = 4.5 Hz, 1H), 1.93 (d, *J* = 18.4 Hz, 1H), 1.81 – 1.54 (m, 1H), 1.42 (d, *J* = 11.1 Hz, 1H), 1.16 (s, 3H), 0.87 (s, 3H).

^{13}C-NMR (101 MHz, $CDCl_3$, δ_C): 215.2 (C_q), 136.0 (C_q), 129.6 (+), 128.5 (+), 128.2 (+), 127.3 (C_q), 121.1 (+), 106.7 (+), 106.3 (+), 58.5 (C_q), 57.4 (–), 47.8 (C_q), 46.5 (–), 43.0 (+), 42.6 (–), 32.7 (+), 26.9 (–), 25.5 (–), 20.2 (+), 19.8 (+).

HRMS (ESI) (m/z): $[M + H]^+$ ($C_{22}H_{29}N_2O_3S$) calc.: 401.1893, found: 401.1905.

Yield: 77%.

***N*-Benzyl-1,1,1-trifluoro-*N*-(1-methyl-1*H*-pyrrol-2-yl)methanesulfonamide (3m)**



3m

^{1}H-NMR (400 MHz, $CDCl_3$, δ_H): 7.32 (m, 3H), 7.18 – 7.12 (m, 2H), 6.41 (dd, *J* = 3.1, 1.9 Hz, 1H), 6.20 (ddq, *J* = 3.9, 1.9, 1.0 Hz, 1H), 6.09 (dd, *J* = 3.9, 3.0 Hz, 1H), 5.13 (d, *J* = 13.4 Hz, 1H), 4.41 (d, *J* = 13.4 Hz, 1H), 2.87 (s, 3H).

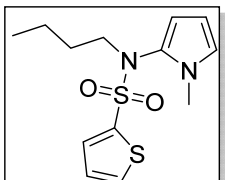
^{13}C-NMR (101 MHz, $CDCl_3$, δ_C): 134.3 (C_q), 129.9 (+), 129.1 (+), 128.9 (+), 123.8 (C_q), 121.9 (+), 120.6 (d, $^{1}J_{CF}$ = 325.0 Hz, C_q), 107.4 (+), 107.2 (+), 59.6 (–), 32.5 (+).

^{19}F NMR (376 MHz, $CDCl_3$, δ_F): -73.0 (s).

HRMS (ESI) (m/z): $[M + H]^+$ ($C_{13}H_{14}F_3N_2O_2S$) calc.: 319.0723, found: 319.0730.

Yield: 55%.

***N*-Butyl-*N*-(1-methyl-1*H*-pyrrol-2-yl)thiophene-2-sulfonamide (3n)**



3n

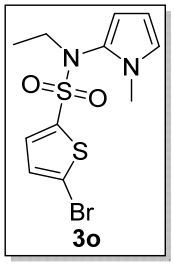
^{1}H-NMR (400 MHz, DMSO-d_6, δ_H): 8.04 (dd, *J* = 5.0, 1.3 Hz, 1H), 7.58 (dd, *J* = 3.7, 1.3 Hz, 1H), 7.25 (dd, *J* = 5.0, 3.8 Hz, 1H), 6.73 (dd, *J* = 2.8, 2.0 Hz, 1H), 5.94 (dd, *J* = 3.6, 3.1 Hz, 1H), 5.50 (dd, *J* = 3.8, 1.8 Hz, 1H), 3.68 (s, 1H), 3.51 (s, 3H), 3.06 (s, 1H), 1.26 (s, 4H), 0.82 (t, *J* = 7.0 Hz, 3H).

^{13}C-NMR (101 MHz, DMSO-d_6, δ_C): 136.9 (C_q), 134.0 (+), 133.5 (+), 127.8 (+), 126.6 (C_q), 121.2 (+), 106.1 (+), 104.1 (+), 52.2 (–), 32.5 (+), 29.8 (–), 19.1 (–), 13.5 (+).

HRMS (ESI) (m/z): $[M + H]^+$ ($C_{13}H_{19}N_2O_2S_2$) calc.: 299.0882, found: 299.0889.

Yield: 99%.

5-Bromo-*N*-ethyl-*N*-(1-methyl-*1H*-pyrrol-2-yl)thiophene-2-sulfonamide (3o)



3o

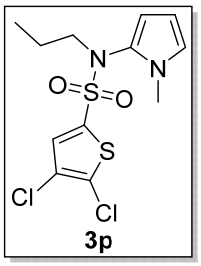
^{1}H-NMR (400 MHz, $CDCl_3$, δ_H): 7.23 (d, *J* = 4.0 Hz, 1H), 7.09 (d, *J* = 4.0 Hz, 1H), 6.60 (dd, *J* = 3.0, 1.8 Hz, 1H), 6.04 (dd, *J* = 3.8, 3.0 Hz, 1H), 5.64 (dd, *J* = 3.8, 1.8 Hz, 1H), 3.81 (s, 1H), 3.61 (s, 3H), 3.20 (s, 1H), 1.08 (t, *J* = 7.1 Hz, 3H).

^{13}C-NMR (101 MHz, $CDCl_3$, δ_C): 138.7 (C_q), 133.5 (+), 130.4 (+), 126.3 (C_q), 121.3 (+), 120.2 (C_q), 106.6 (+), 104.7 (+), 48.1 (–), 33.0 (+), 13.8 (+).

HRMS (ESI) (m/z): $[M + H]^+$ ($C_{11}H_{14}BrN_2O_2S$) calc.: 348.9675, found: 348.9685.

Yield: 84%.

4,5-Dichloro-*N*-(1-methyl-*1H*-pyrrol-2-yl)-*N*-propylthiophene-2-sulfonamide (3p)



3p

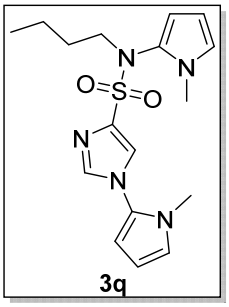
^{1}H-NMR (400 MHz, $CDCl_3$, δ_H): 7.28 (s, 1H), 6.60 (dd, *J* = 3.0, 1.8 Hz, 1H), 6.06 (dd, *J* = 3.9, 3.0 Hz, 1H), 5.69 (dd, *J* = 3.8, 1.8 Hz, 1H), 3.74 (s, 1H), 3.61 (s, 3H), 3.11 (s, 1H), 1.67 – 1.35 (m, 2H), 0.90 (t, *J* = 7.4 Hz, 3H).

^{13}C-NMR (101 MHz, $CDCl_3$, δ_C): 134.3 (C_q), 132.0 (+), 131.8 (C_q), 126.6 (C_q), 124.9 (C_q), 121.5 (+), 106.8 (+), 104.6 (+), 55.2 (–), 33.2 (+), 21.7 (–), 11.1 (+).

HRMS (ESI) (m/z): $[M + H]^+$ ($C_{12}H_{15}Cl_2N_2O_2S_2$) calc.: 352.9947, found: 352.9949.

Yield: 95%.

***N*-Butyl-*N*,1-bis(1-methyl-*1H*-pyrrol-2-yl)-*1H*-imidazole-4-sulfonamide (3q)**



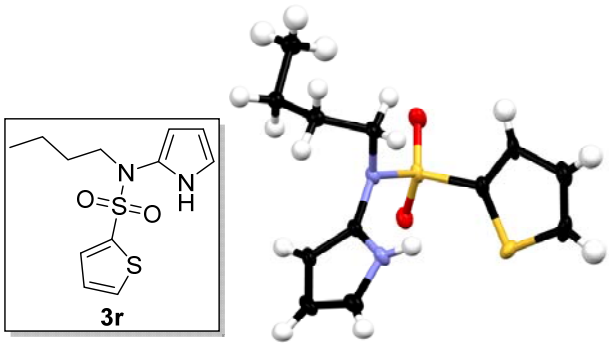
^{1}H-NMR (400 MHz, $CDCl_3$, δ_H): 7.65 (d, *J* = 1.4 Hz, 1H), 7.35 (d, *J* = 1.4 Hz, 1H), 6.64 (dd, *J* = 3.0, 1.9 Hz, 1H), 6.54 (dd, *J* = 3.0, 1.8 Hz, 1H), 6.20 (dd, *J* = 3.8, 1.9 Hz, 1H), 6.15 (dd, *J* = 3.8, 3.0 Hz, 1H), 5.96 (dd, *J* = 3.8, 3.0 Hz, 1H), 5.52 (dd, *J* = 3.8, 1.8 Hz, 1H), 4.07 (s, 1H), 3.63 (s, 3H), 3.38 (s, 4H), 1.57 – 1.30 (m, 4H), 0.89 (t, *J* = 7.2 Hz, 3H).

^{13}C-NMR (101 MHz, $CDCl_3$, δ_C): 140.0 (+), 139.1 (C_q), 127.9 (C_q), 126.5 (+), 123.8 (C_q), 122.1 (+), 120.8 (+), 107.4 (+), 106.4 (+), 105.9 (+), 104.4 (+), 54.2 (–), 33.1 (+), 32.9 (+), 31.1 (–), 19.9 (–), 13.9 (+).

HRMS (ESI) (m/z): $[M + H]^+$ ($C_{17}H_{24}N_5O_2S$) calc.: 362.1645, found: 362.1652.

Yield: 37%.

***N*-Butyl-*N*-(1*H*-pyrrol-2-yl)thiophene-2-sulfonamide (3r)**



^{1}H-NMR (400 MHz, $CDCl_3$, δ_H): 8.46 (s, 1H), 7.58 (dd, *J* = 5.0, 1.3 Hz, 1H), 7.38 (dd, *J* = 3.8, 1.3 Hz, 1H), 7.08 (dd, *J* = 5.0, 3.8 Hz, 1H), 6.66 (dt, *J* = 2.9, 1.6 Hz, 1H), 6.09 (dd, *J* = 6.4, 3.1 Hz, 1H), 5.61 (ddd, *J* = 3.9, 2.6, 1.6 Hz, 1H), 3.48 – 3.44 (m, 2H), 1.54 – 1.45 (m, 2H), 1.40 – 1.29 (m, 2H), 0.88 (t, *J* = 7.3 Hz, 3H).

^{13}C-NMR (101 MHz, $CDCl_3$, δ_C): 137.1 (C_q), 133.0 (+), 132.3 (+), 127.4 (+), 126.7 (C_q), 116.3 (+), 108.2 (+), 102.7 (+), 51.3 (–), 30.4 (–), 19.8 (–), 13.7 (+).

HRMS (ESI) (m/z): $[M + H]^+$ ($C_{12}H_{17}N_2O_2S_2$) calc.: 285.0726, found: 285.0731.

X-ray crystallography: The mono-crystals suitable for X-ray-measurement were obtained by slow evaporation of a solvent mixture ($CDCl_3$/heptane).

(λ = 1.54184 Å, at 123 K)

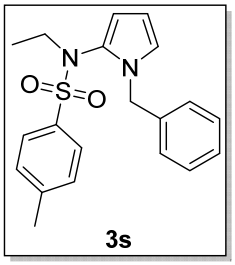
Yield: 79%.

Table S-6. Crystallographic data for **3r**.[a]

Molecular formula	$C_{12}H_{16}N_2O_2S_2$
M_r	284.39
Space group	P 1 21/c 1
a [Å]	14.6626(5)
b [Å]	5.39440(16)
c [Å]	18.2386(6)
α [°]	90
β [°]	113.435(4)
γ [°]	90
V [Å^3]	1323.60(8)
Z	4

[a] Reported data in accordance with the calculated data.

***N*-(1-Benzyl-*1H*-pyrrol-2-yl)-*N*-ethyl-4-methylbenzene-1-sulfonamide (3s)**



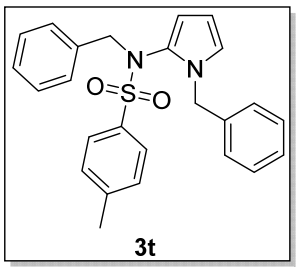
^{1}H-NMR (300 MHz, $CDCl_3$, δ_H): 7.66 – 7.60 (m, 2H), 7.40 – 7.19 (m, 7H), 6.57 (dd, *J* = 3.1, 1.8 Hz, 1H), 6.05 (dd, *J* = 3.8, 3.1 Hz, 1H), 5.49 (dd, *J* = 3.8, 1.8 Hz, 1H), 5.31 (d, *J* = 15.4 Hz, 1H), 5.09 (d, *J* = 15.4 Hz, 1H), 3.65 – 3.51 (m, 1H), 3.18 – 3.02 (m, 1H), 2.45 (s, 3H), 0.84 (t, *J* = 7.2 Hz, 3H).

^{13}C-NMR (75 MHz, $CDCl_3$, δ_C): 143.8 (C_q), 138.0 (C_q), 134.6 (C_q), 129.4 (+), 128.7 (+), 128.5 (+), 128.1 (+), 127.6 (+), 127.3 (C_q), 120.4 (+), 106.7 (+), 105.2 (+), 49.5 (–), 47.6 (–), 21.7 (+), 13.5 (+).

HRMS (ESI) (m/z): $[M + H]^+$ ($C_{20}H_{23}N_2O_2S$) calc.: 355.1475, found: 355.1475.

Yield: 48%.

***N*-Benzyl-*N*-(1-benzyl-*1H*-pyrrol-2-yl)-4-methylbenzene-1-sulfonamide (3t)**



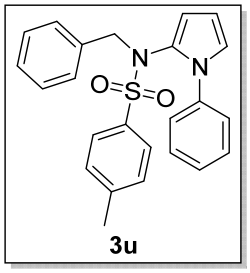
^{1}H-NMR (300 MHz, $CDCl_3$, δ_H): 7.81 – 7.65 (m, 2H), 7.36 (d, *J* = 8.1 Hz, 2H), 7.30 – 7.15 (m, 8H), 6.83 – 6.66 (m, 2H), 6.24 (dd, *J* = 3.1, 1.8 Hz, 1H), 5.99 (dd, *J* = 3.8, 3.2 Hz, 1H), 5.58 (dd, *J* = 3.8, 1.8 Hz, 1H), 5.03 (d, *J* = 12.8 Hz, 1H), 4.89 – 4.60 (m, 2H), 4.02 (d, *J* = 12.8 Hz, 1H), 2.49 (s, 3H).

^{13}C-NMR (75 MHz, $CDCl_3$, δ_C): 143.9 (C_q), 137.3 (C_q), 135.5 (C_q), 134.6 (C_q), 129.7 (+), 129.5 (+), 128.6 (+), 128.5 (+), 128.4 (+), 128.3 (+), 128.1 (+), 127.5 (C_q), 127.4 (+), 119.6 (+), 106.8 (+), 104.8 (+), 57.2 (–), 49.0 (–), 21.7 (+).

HRMS (ESI) (m/z): $[M + H]^+$ ($C_{25}H_{25}N_2O_2S$) calc.: 417.1631, found: 417.1638.

Yield: 64%.

***N*-Benzyl-4-methyl-*N*-(1-phenyl-*1H*-pyrrol-2-yl)benzene-1-sulfonamide (3u)**



3u

^{1}H-NMR (300 MHz, $CDCl_3$, δ_H): 7.73 – 7.65 (m, 2H), 7.38 – 7.30 (m, 2H), 7.26 – 7.19 (m, 3H), 7.18 – 7.10 (m, 1H), 7.10 – 7.00 (m, 2H), 7.00 – 6.92 (m, 2H), 6.85 – 6.78 (m, 2H), 6.60 (dd, *J* = 3.1, 1.9 Hz, 1H), 6.11 (dd, *J* = 3.8, 3.1 Hz, 1H), 5.71 (dd, *J* = 3.8, 1.9 Hz, 1H), 4.75 (s, 1H), 3.98 (s, 1H), 2.48 (s, 3H).

^{13}C-NMR (75 MHz, $CDCl_3$, δ_C): 144.0 (C_q), 138.6 (C_q), 135.2 (C_q), 134.6 (C_q), 129.7 (+), 129.6 (+), 128.7 (+), 128.6 (+), 128.2 (+), 127.9 (+), 127.8 (C_q), 127.0 (+), 126.5 (+), 121.5 (+), 107.5 (+), 106.7 (+), 57.7 (–), 21.8 (+).

HRMS (ESI) (m/z): $[M + H]^+$ ($C_{24}H_{23}N_2O_2S$) calc.: 403.1475, found: 403.1481.

Yield: 10%.

3. Cyclic voltammetry measurement

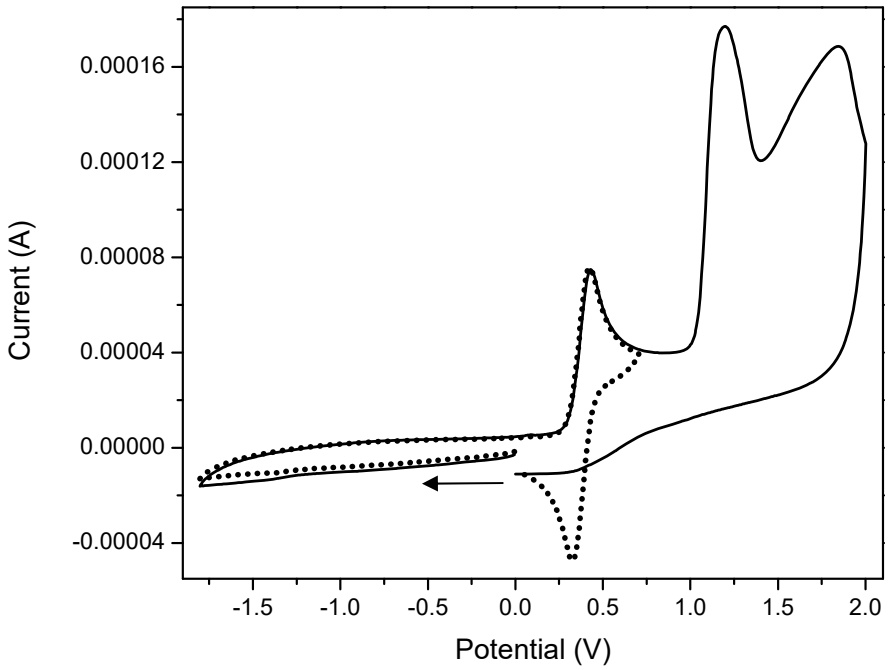
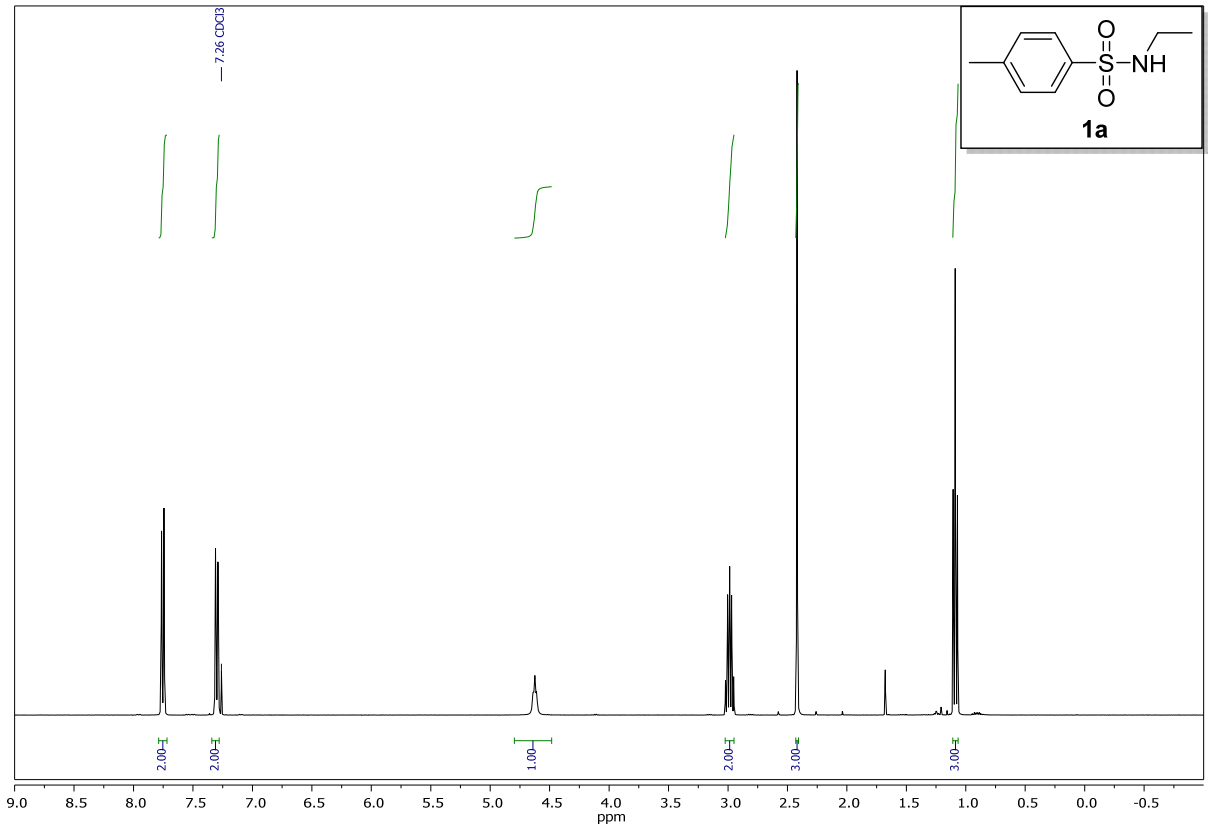


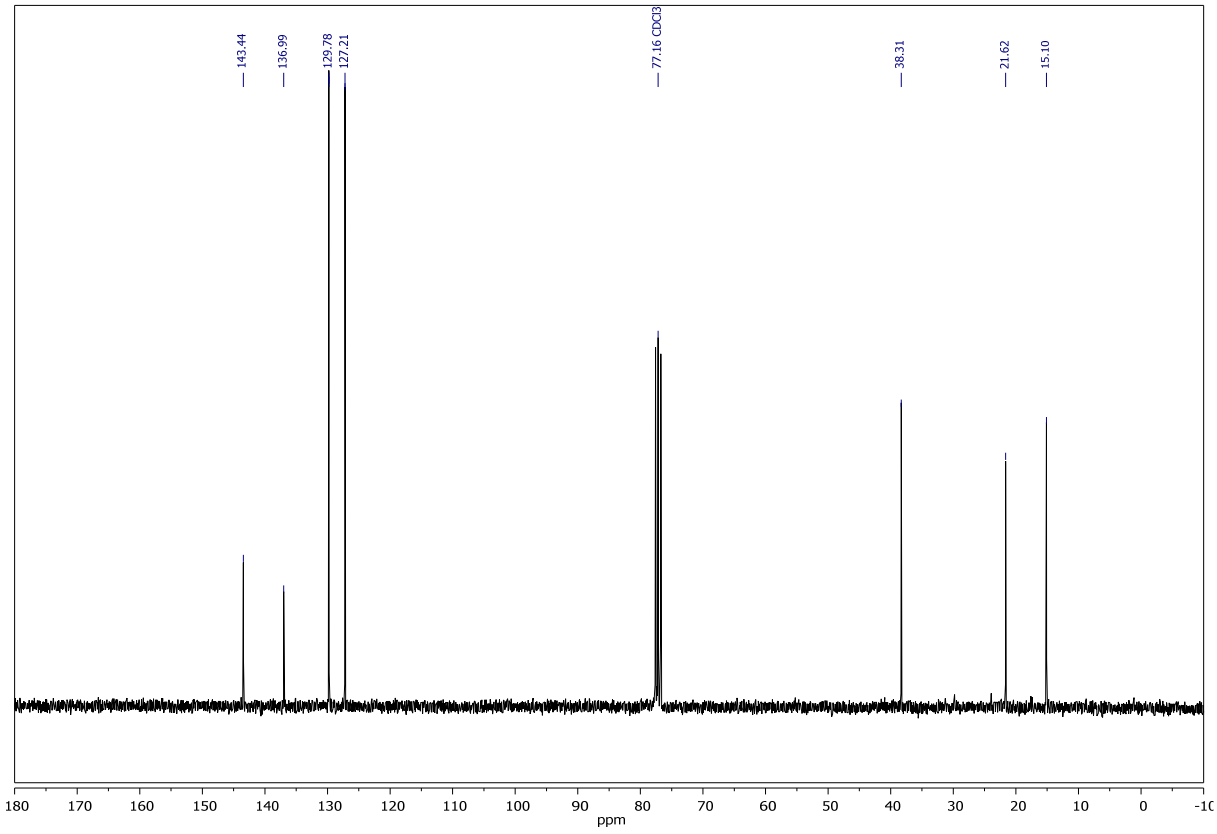
Figure S-2. Cyclic voltammogram of *N*-Me-Pyrrole (**2a**) in CH_3CN under argon (scan direction indicated by black arrow). The irreversible peaks at 1.19 V and 1.86 V correspond to the oxidation potentials of **2a** (oxidation potential of 1.20 V and 1.86 V vs SCE – the dotted line shows the addition of ferrocene).

CV measurements were performed with the three-electrode potentiostat galvanostat PGSTAT302N from Metrohm Autolab using a glassy carbon working electrode, a platinum wire counter electrode, a silver wire as a reference electrode and TBATFB 0.1 M as supporting electrolyte. The potentials are given relative to the Fc/Fc^+ redox couple with ferrocene as internal standard. The control of the measurement instrument, the acquisition and processing of the cyclic voltammetric data were performed with the software Metrohm Autolab NOVA 1.10.4. The measurements were carried out as follows: a 0.1 M solution of TBATFB in acetonitrile was added to the measuring cell and the solution was degassed by argon purge for 5 min. After recording the baseline the electroactive compound was added (0.01 M) and the solution was again degassed a stream of argon for 5 min. The cyclic voltammogram was recorded with one to three scans. Afterwards ferrocene (2.20 mg, 12.0 µmol) was added to the solution which was again degassed by argon purge for 5 min and the final measurement was performed with three scans.

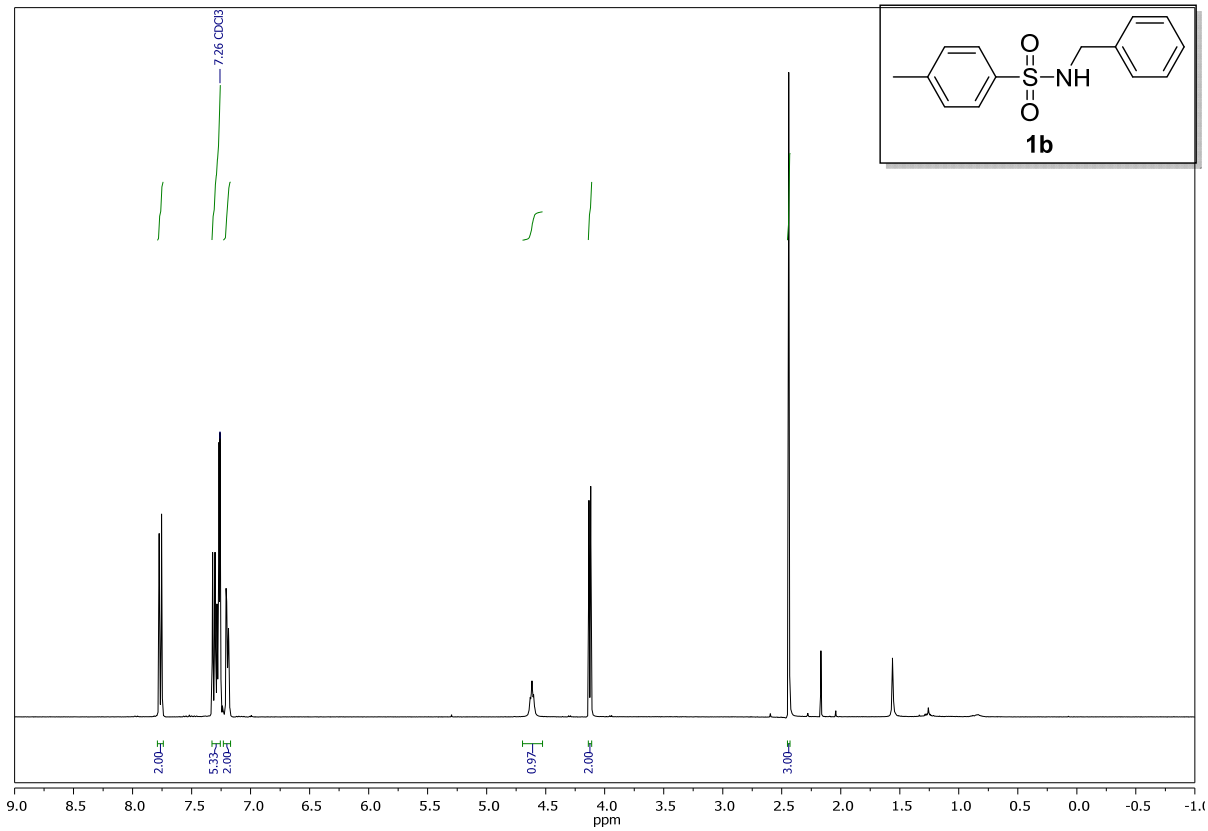
4. ^{1}H-, ^{13}C- and ^{19}F-spectra

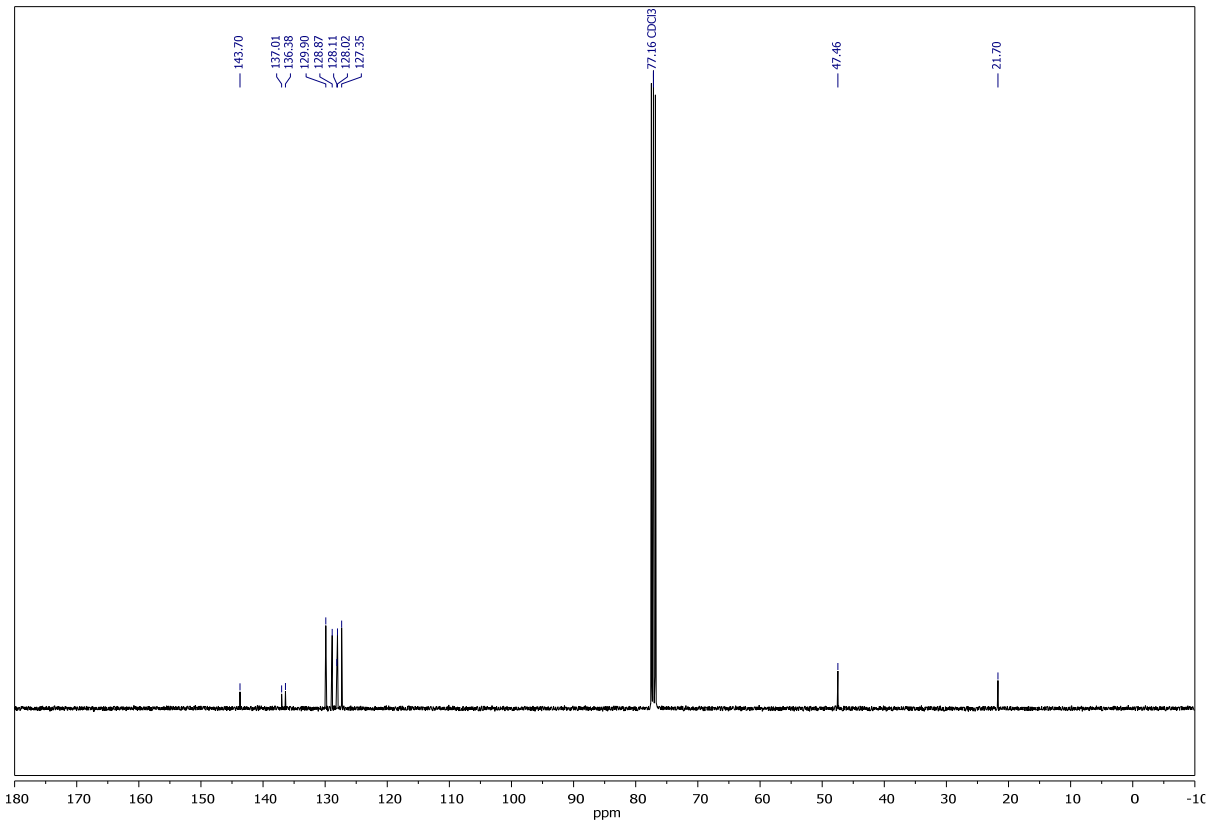
Compound **1a**, ^{1}H-, and ^{13}C-NMR ($CDCl_3$):



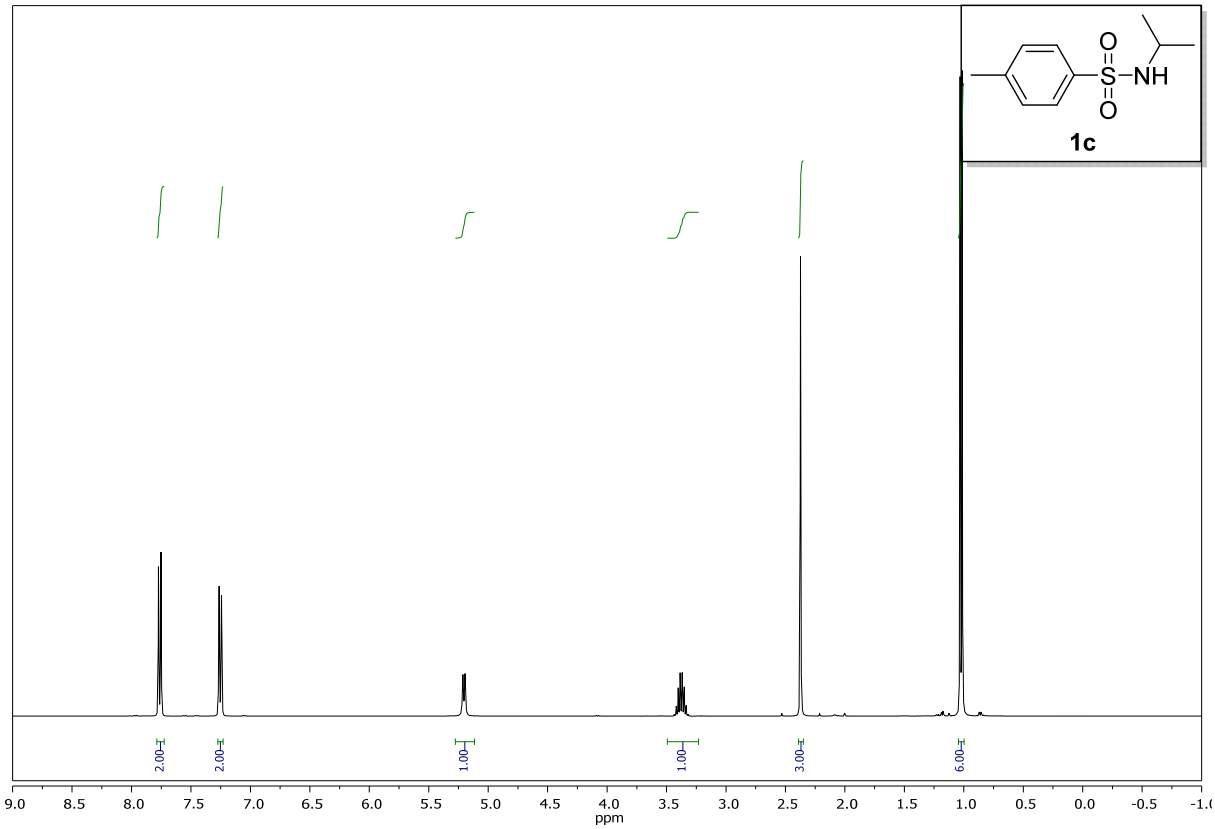


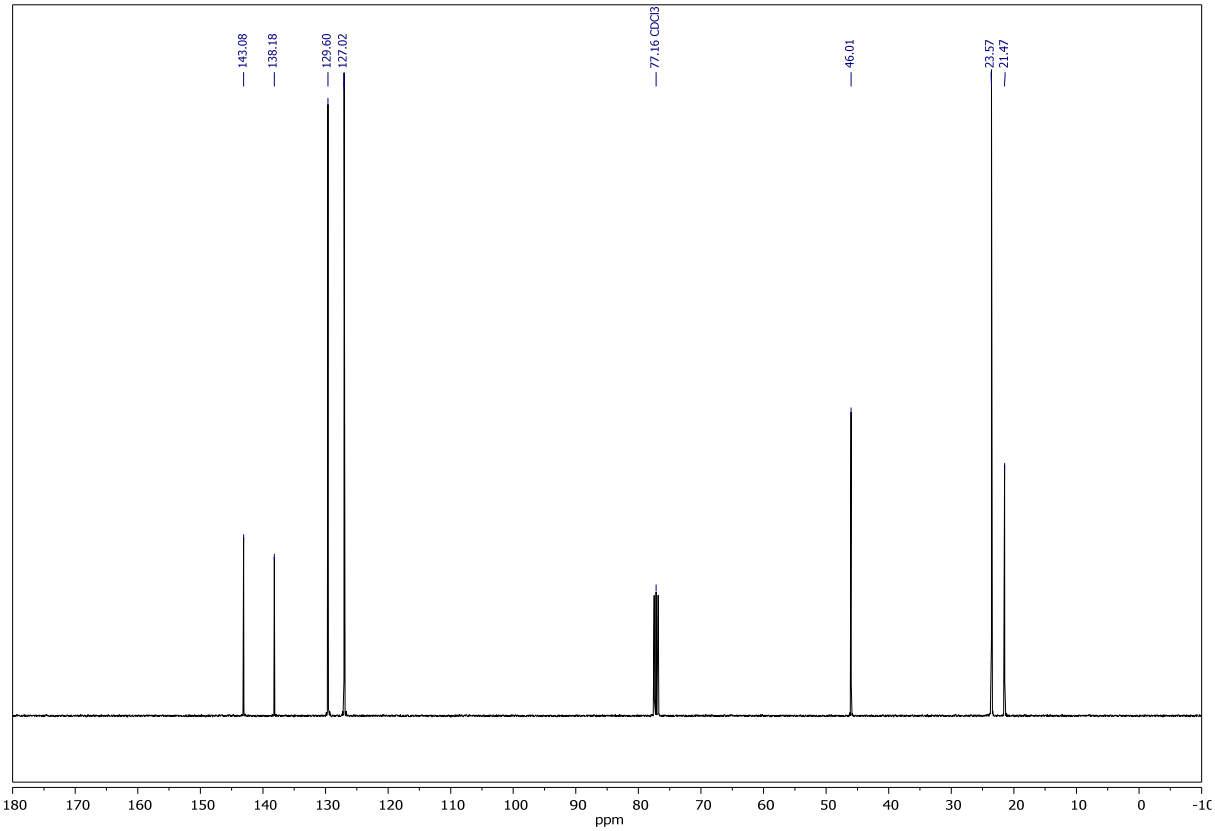
Compound **1b**, ^{1}H-, and ^{13}C-NMR ($CDCl_3$):



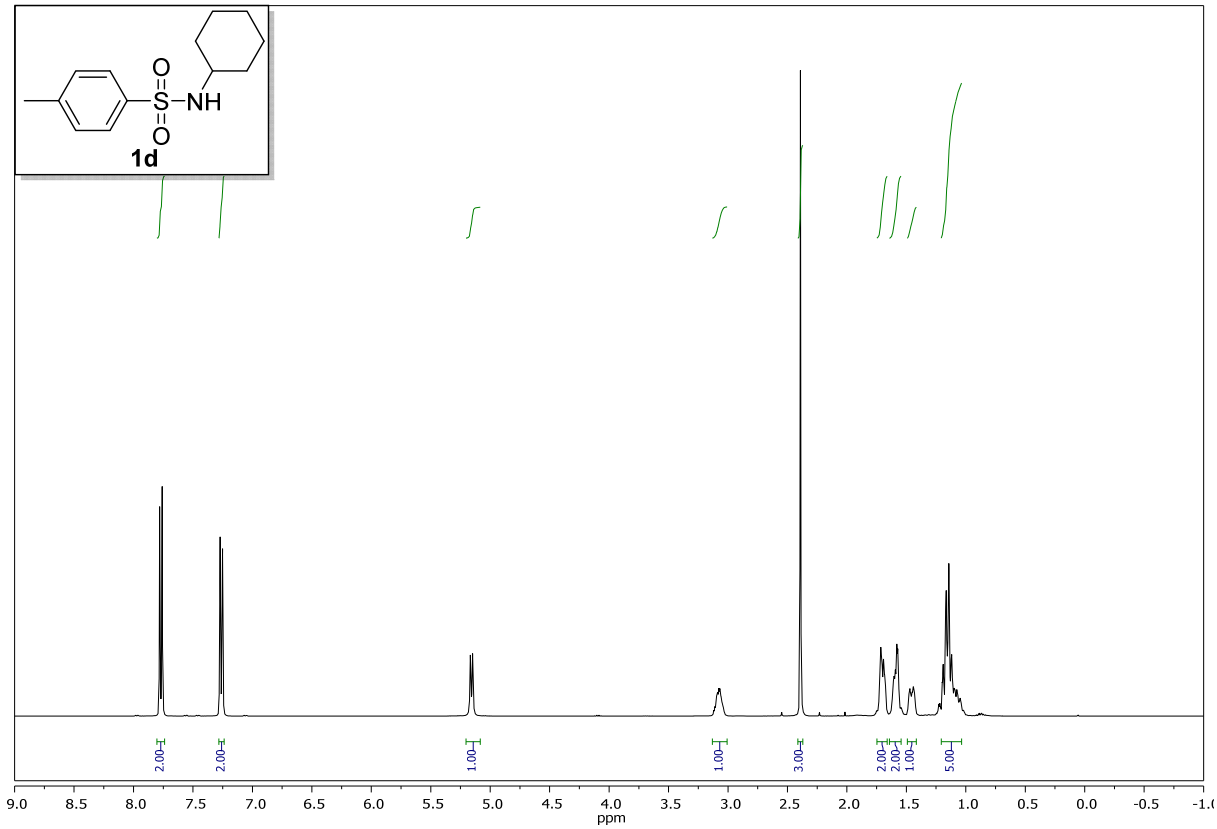


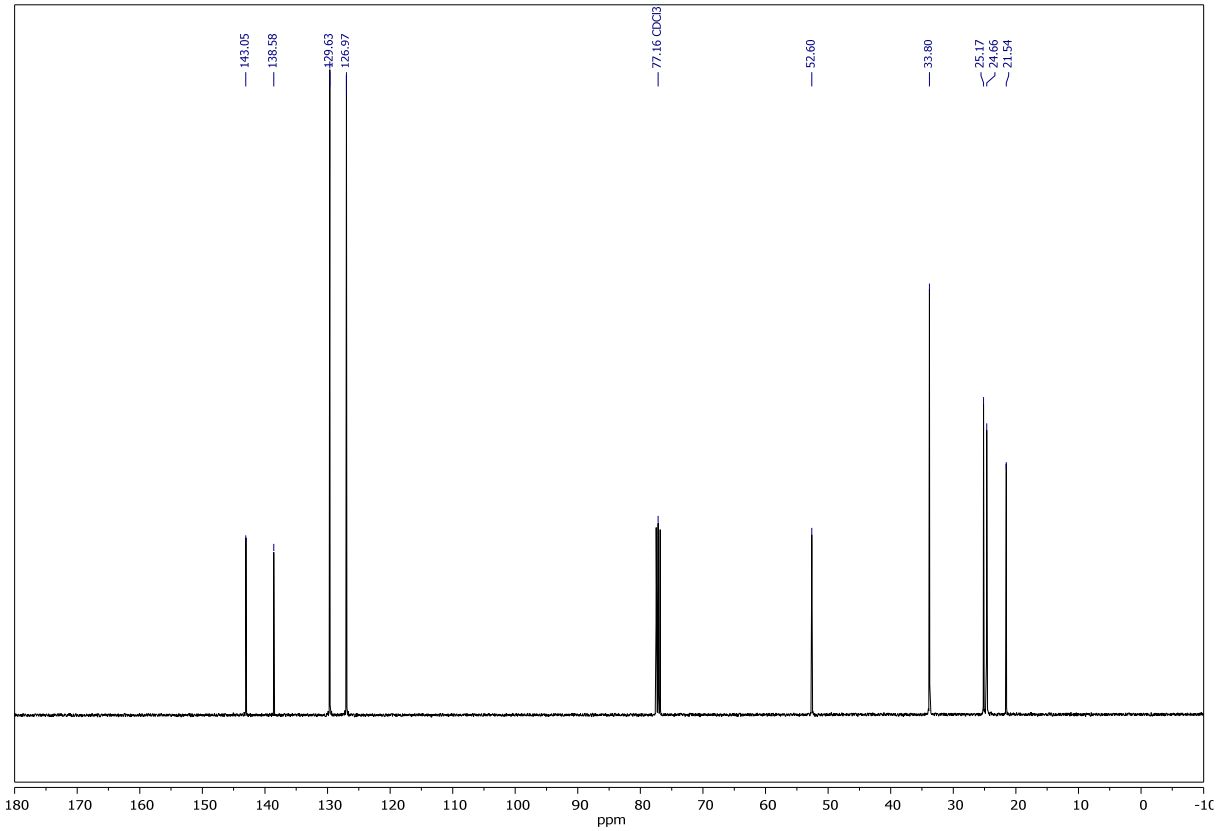
Compound **1c**, ^{1}H-, and ^{13}C-NMR ($CDCl_3$):



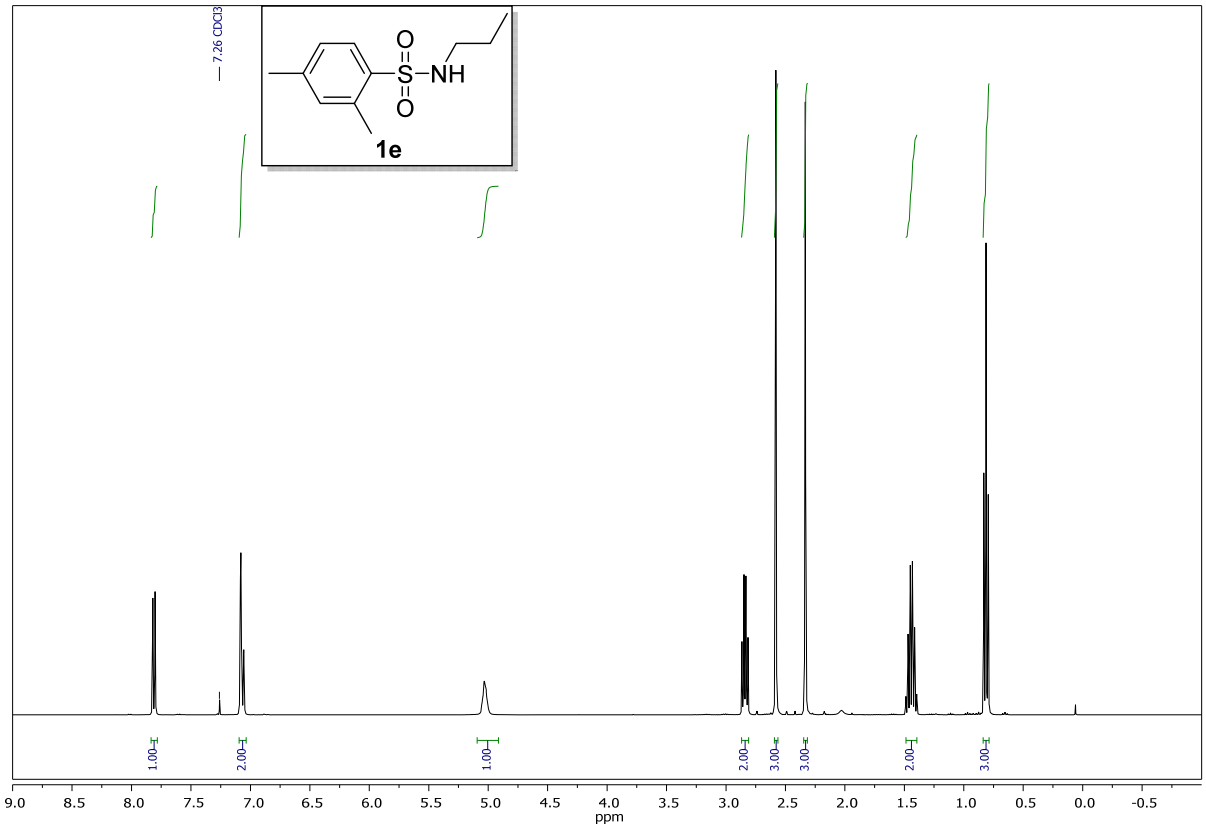


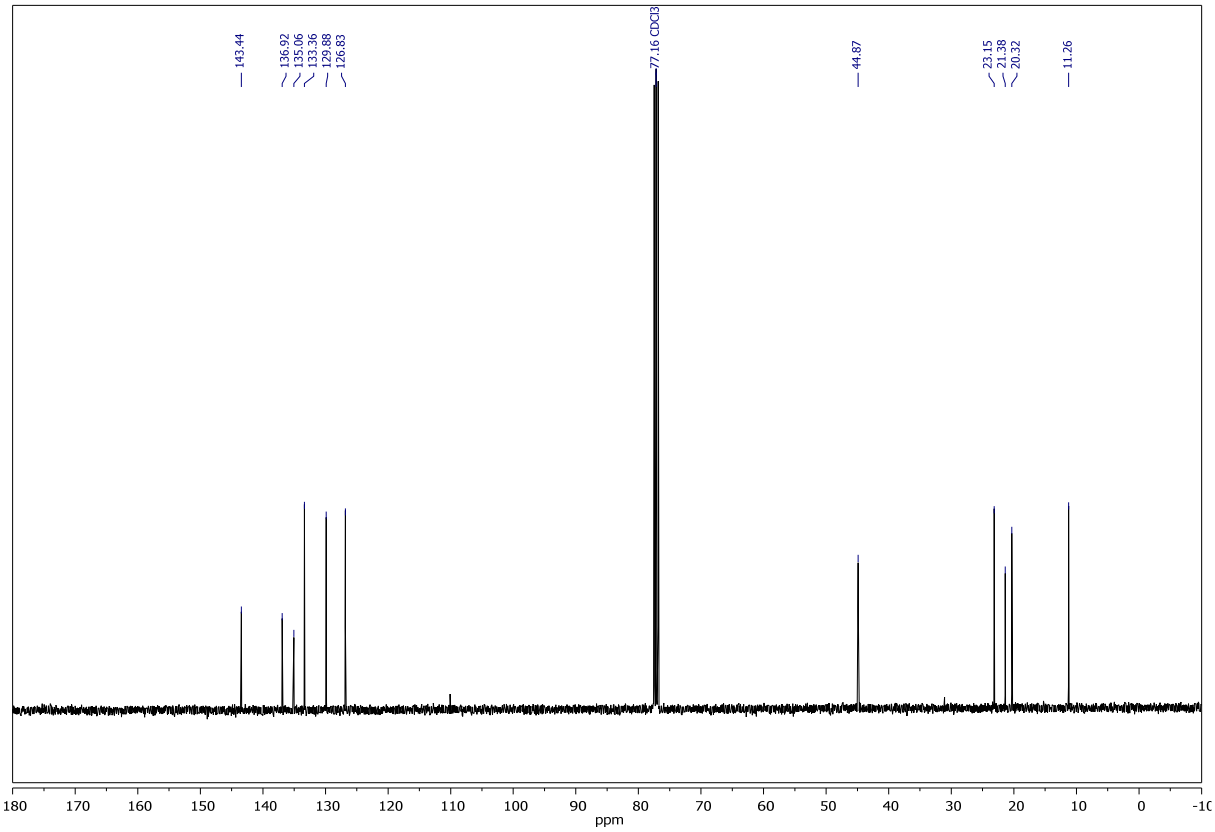
Compound **1d**, ^{1}H-, and ^{13}C-NMR ($CDCl_3$):



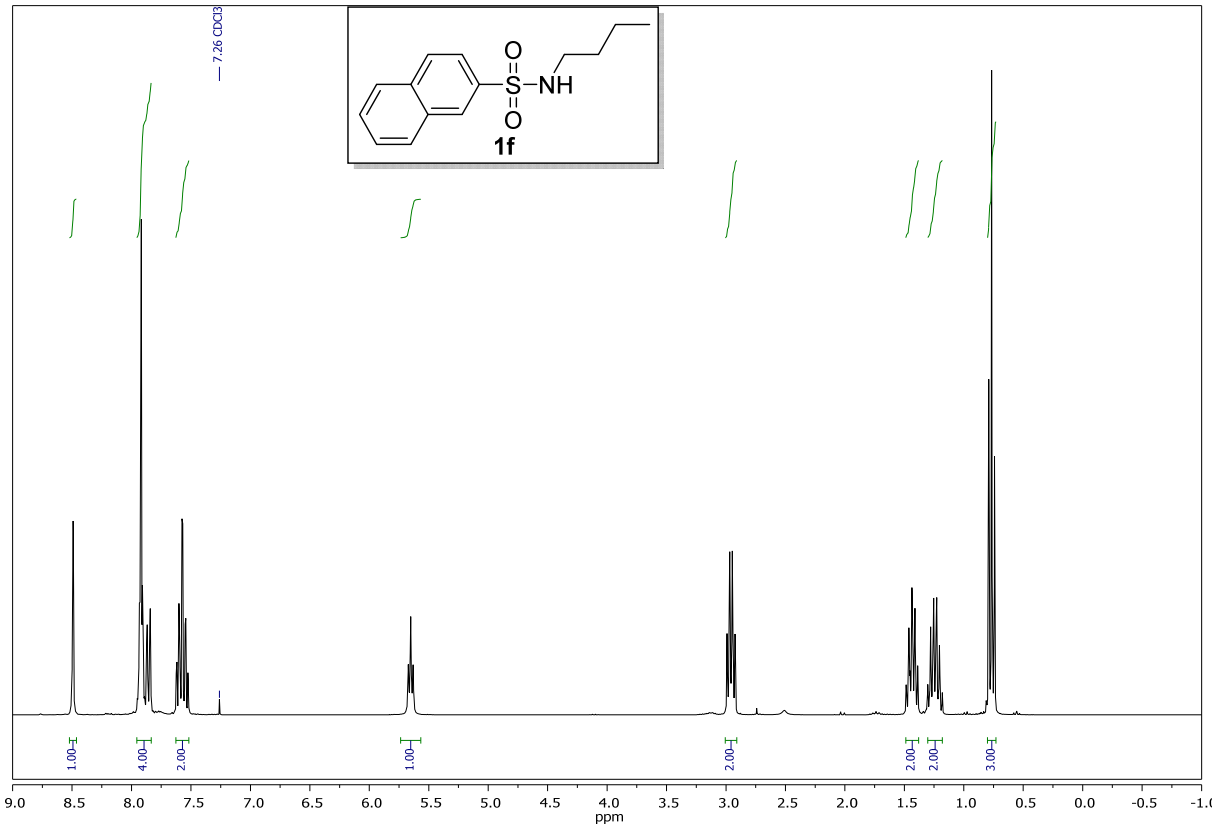


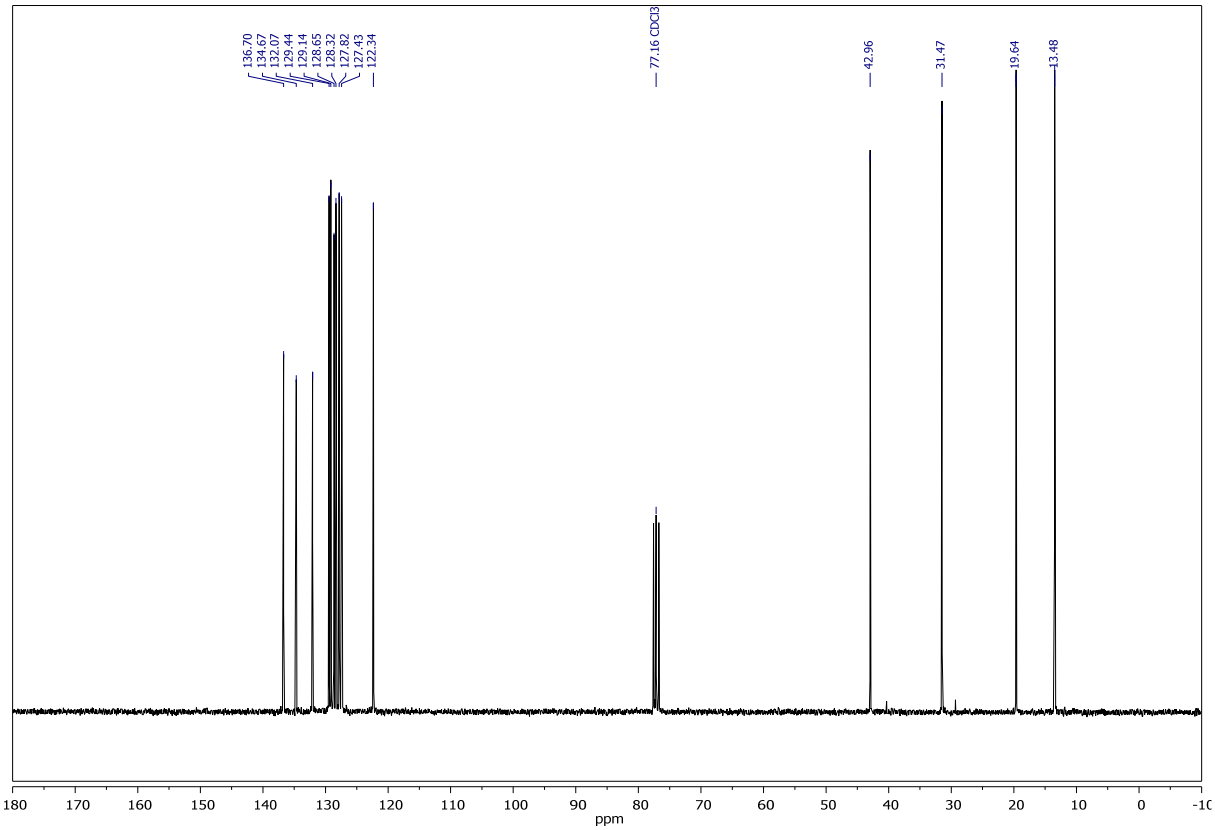
Compound **1e**, ^{1}H-, and ^{13}C-NMR ($CDCl_3$):



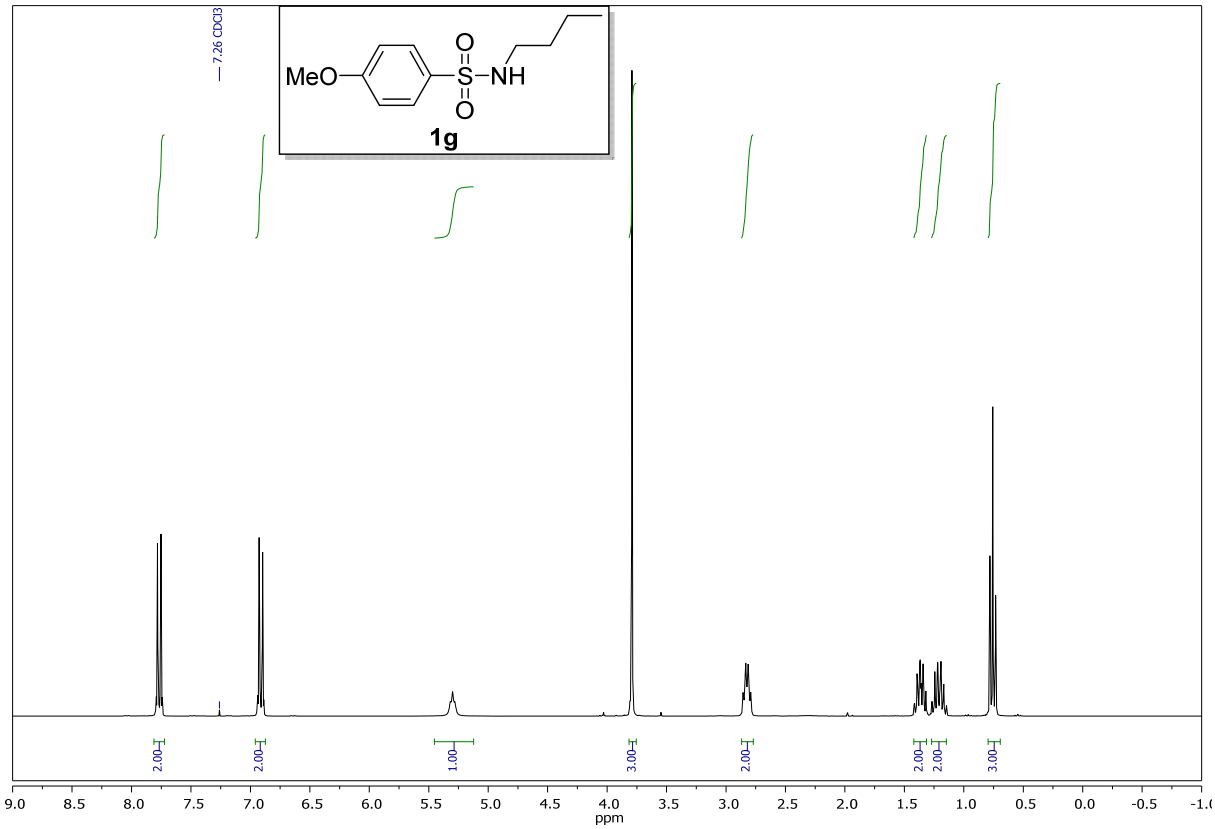


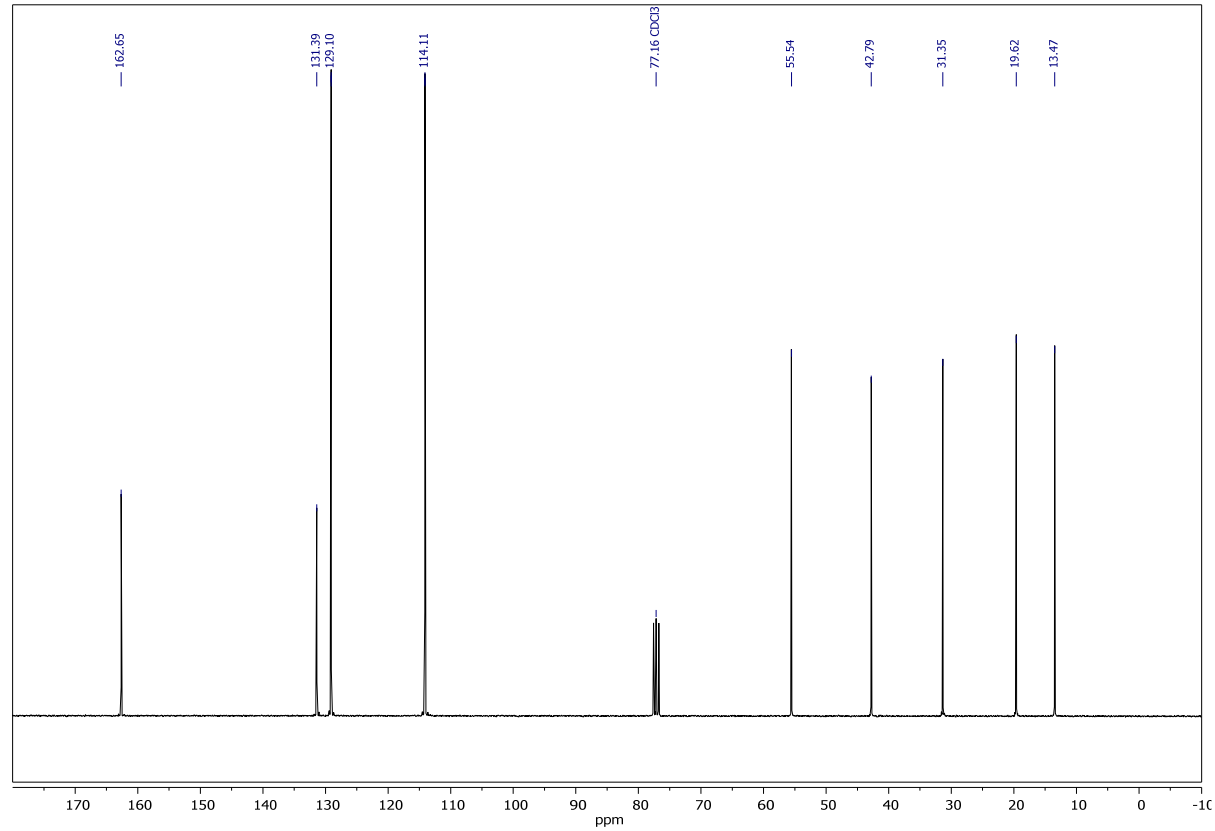
Compound **1f**, ^{1}H-, and ^{13}C-NMR ($CDCl_3$):



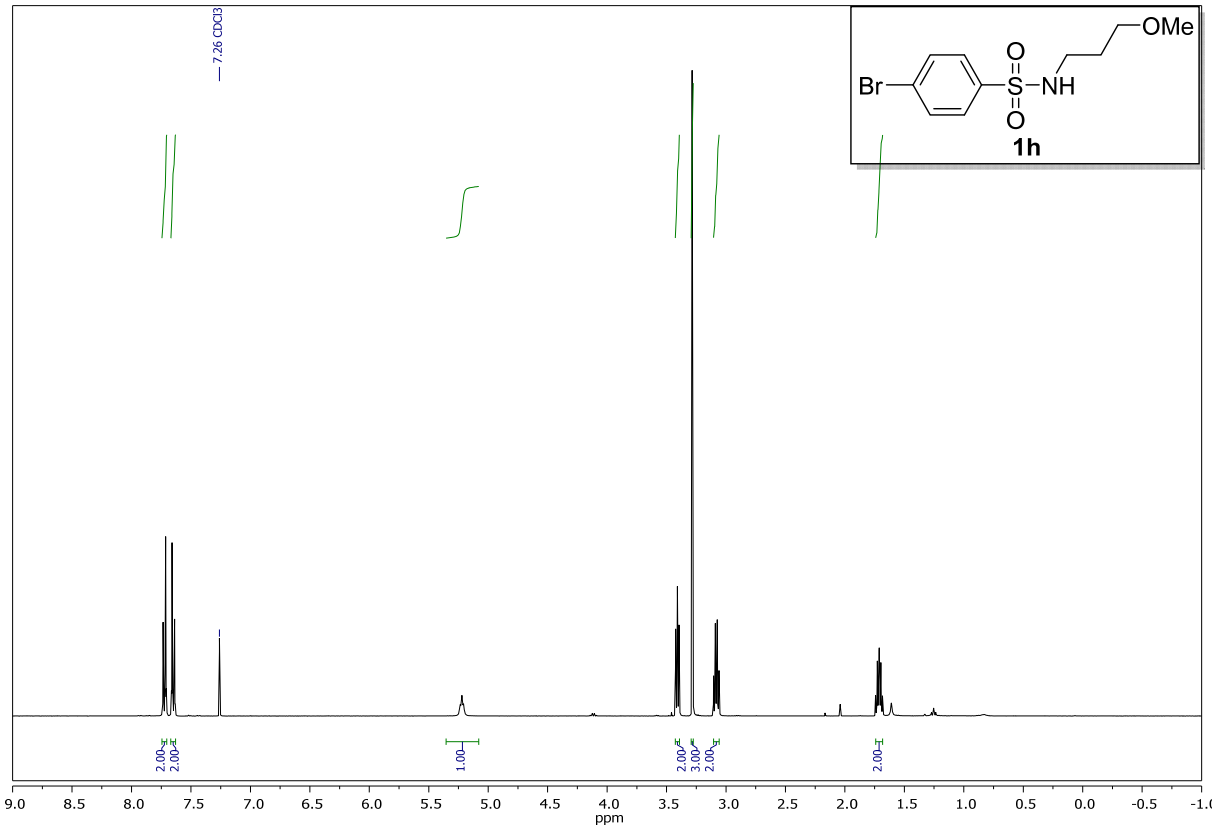


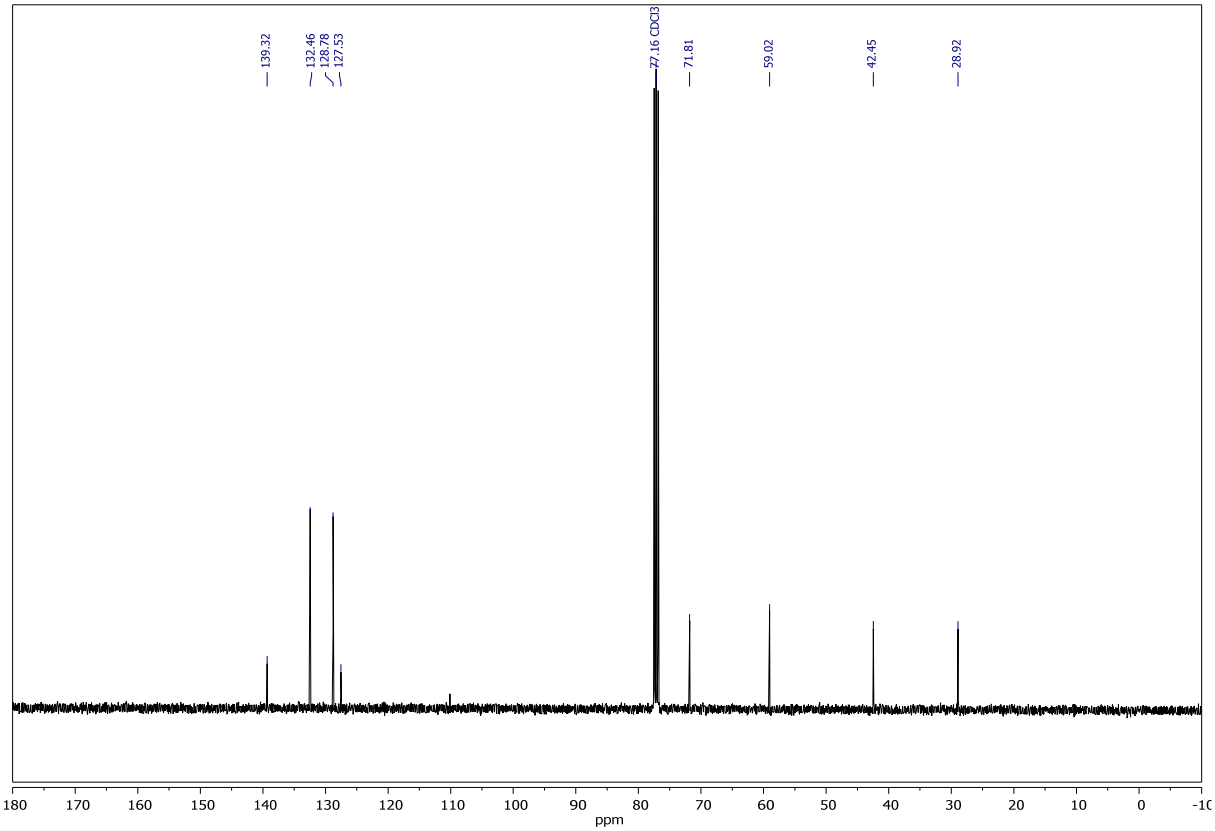
Compound **1g**, ^{1}H-, and ^{13}C-NMR ($CDCl_3$):



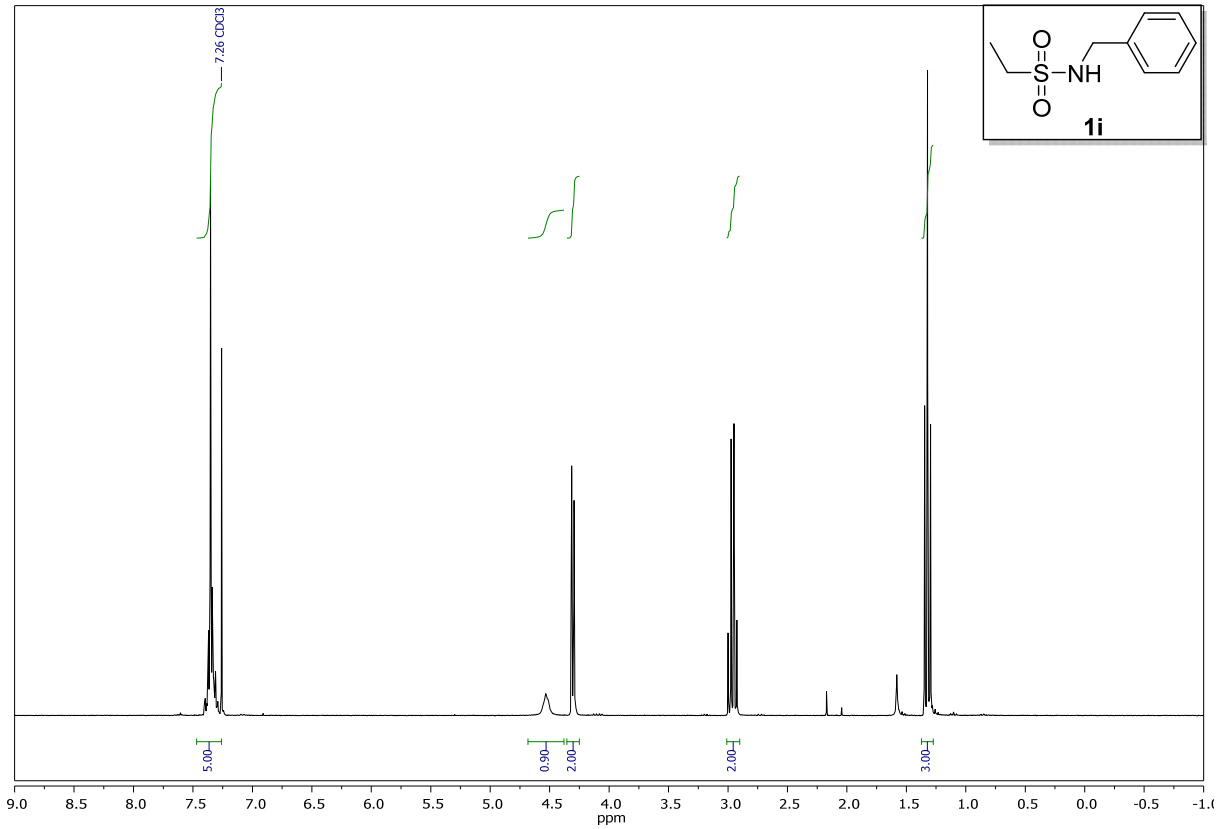


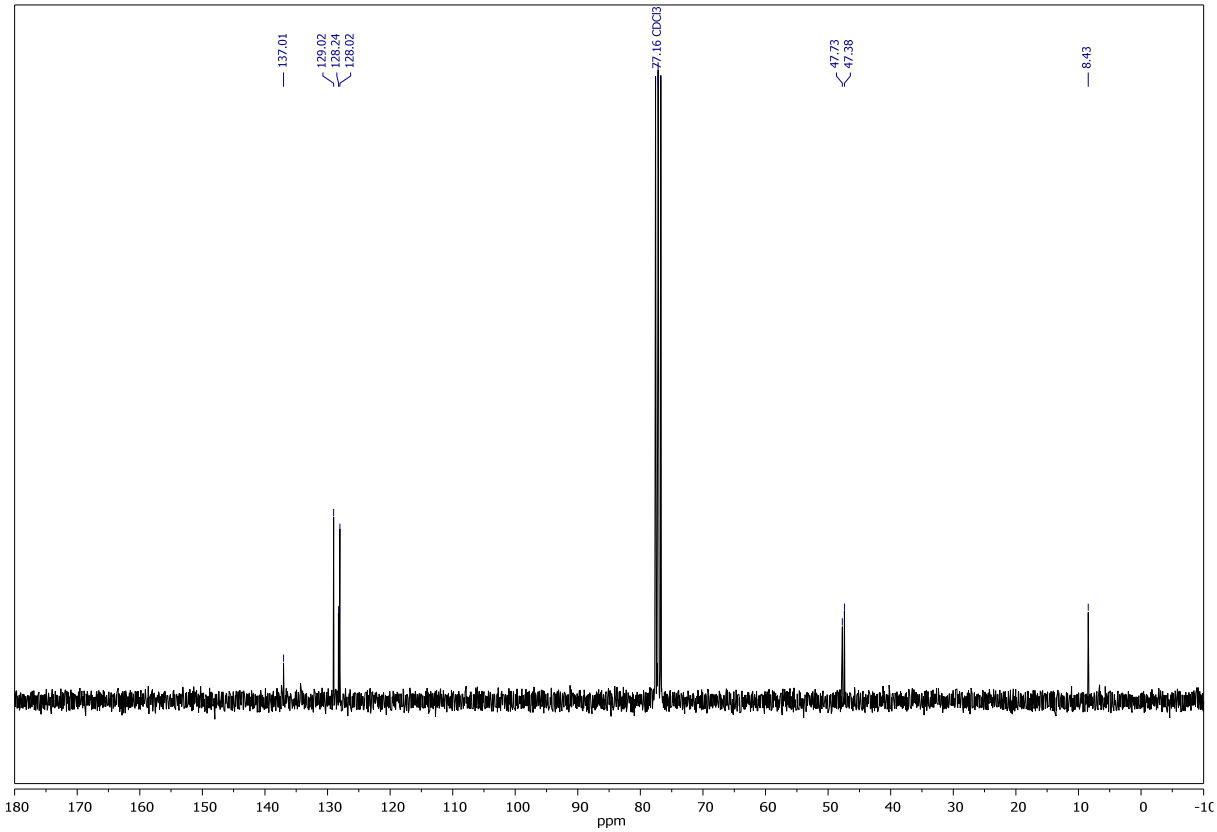
Compound **1h**, ^{1}H-, and ^{13}C-NMR ($CDCl_3$):



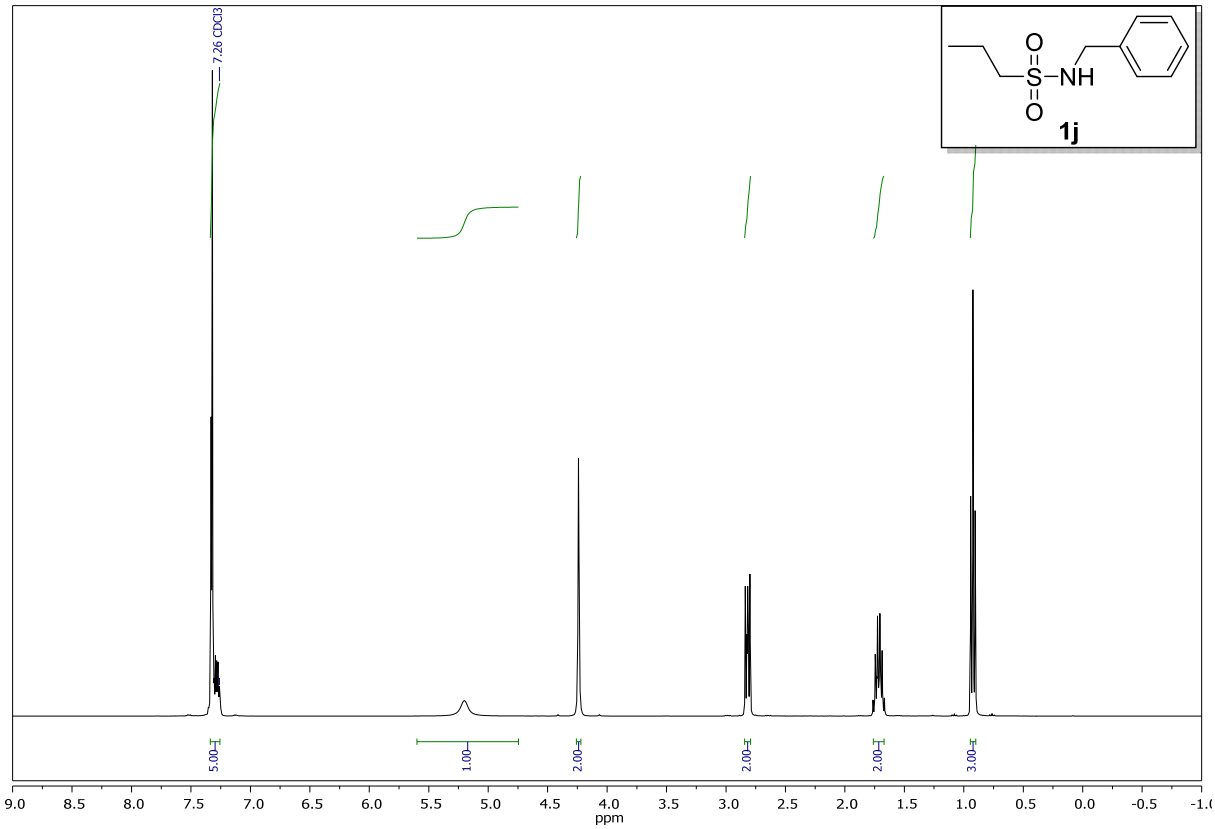


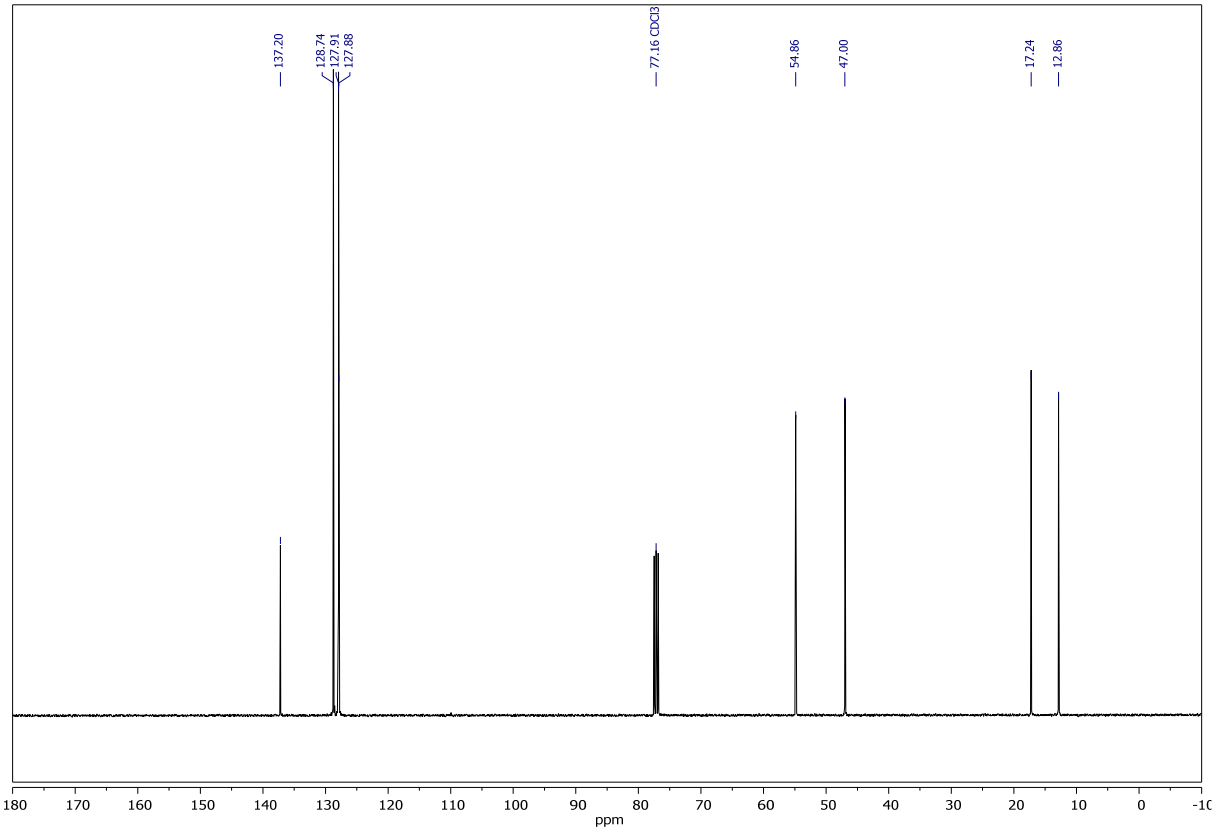
Compound **1i**, ^{1}H-, and ^{13}C-NMR ($CDCl_3$):



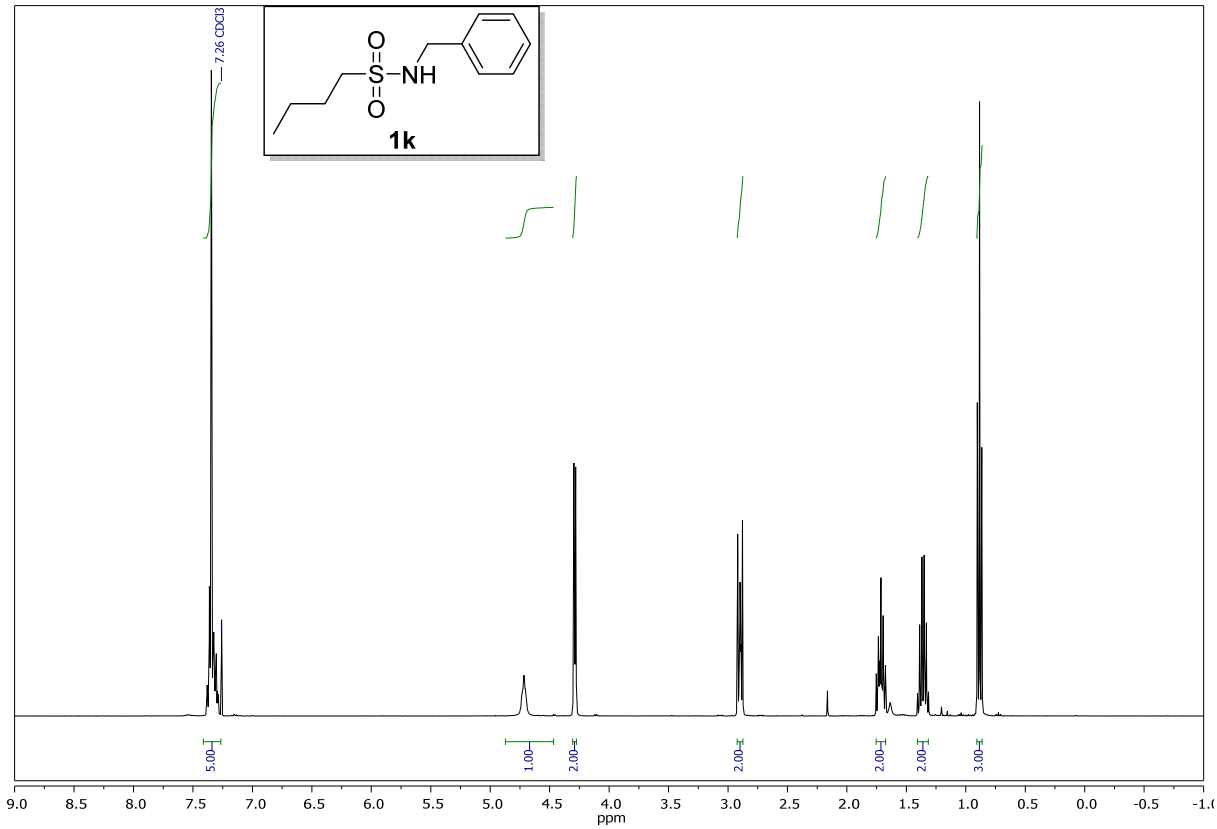


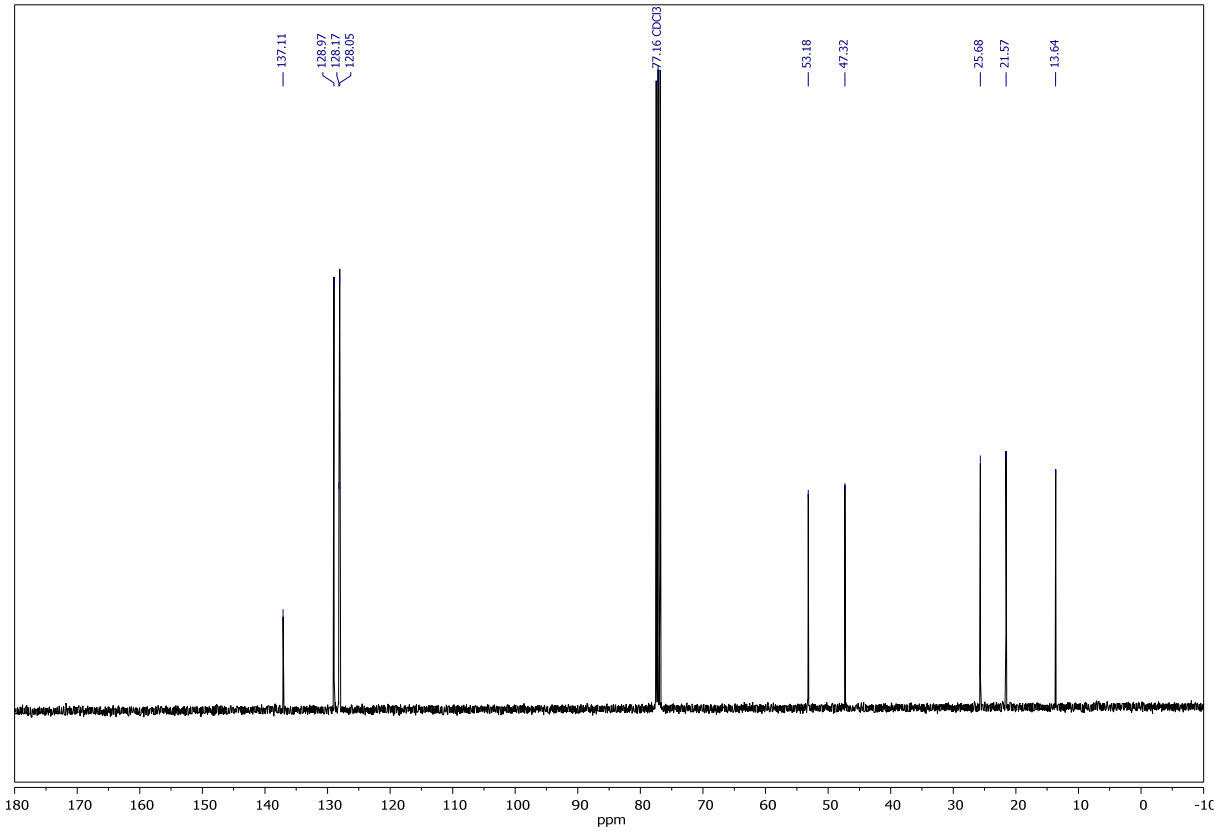
Compound **1j**, ^{1}H-, and ^{13}C-NMR ($CDCl_3$):



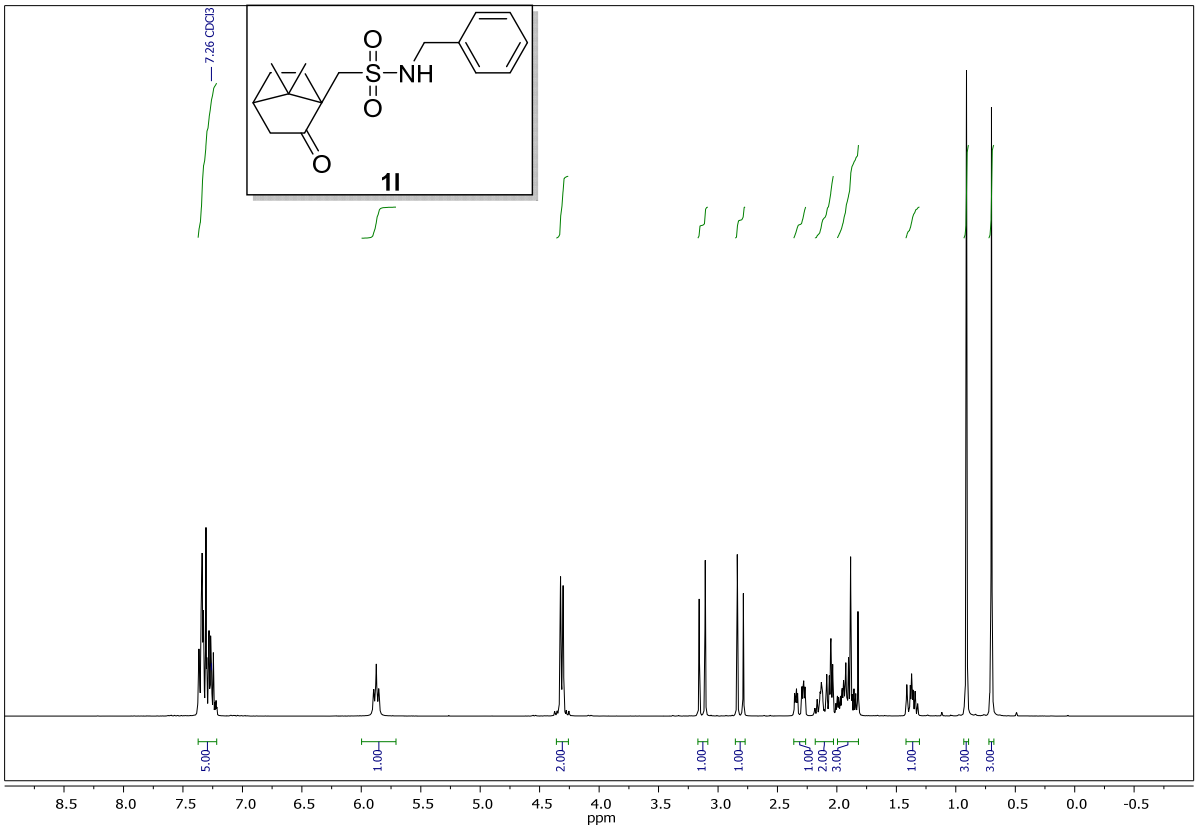


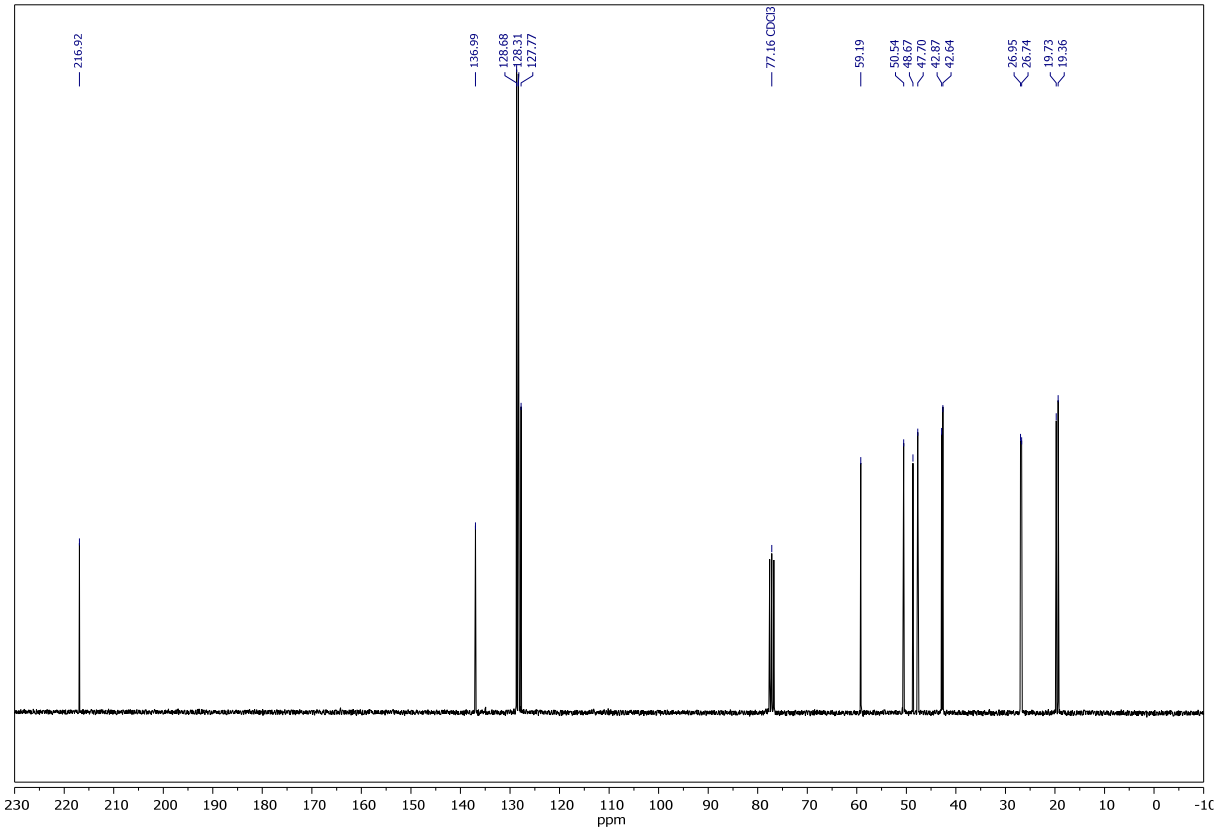
Compound **1k**, ^{1}H-, and ^{13}C-NMR ($CDCl_3$):



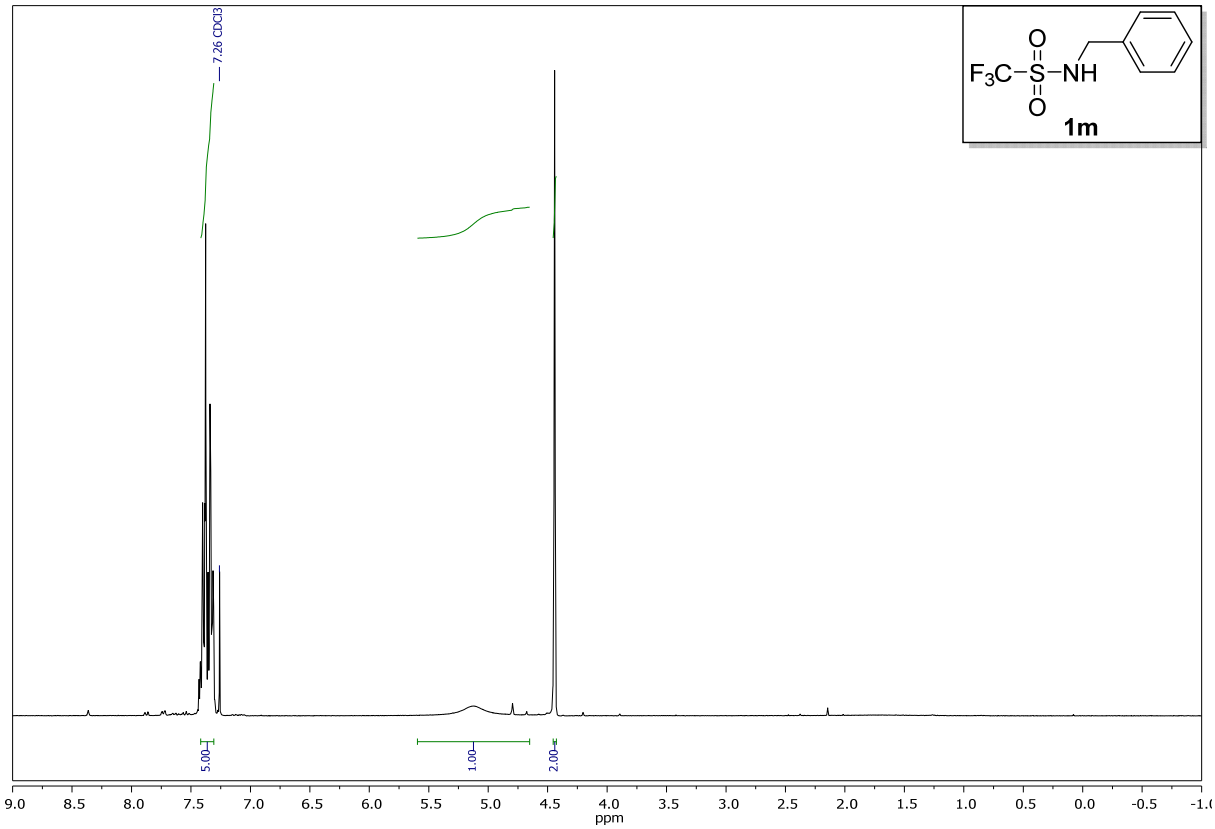


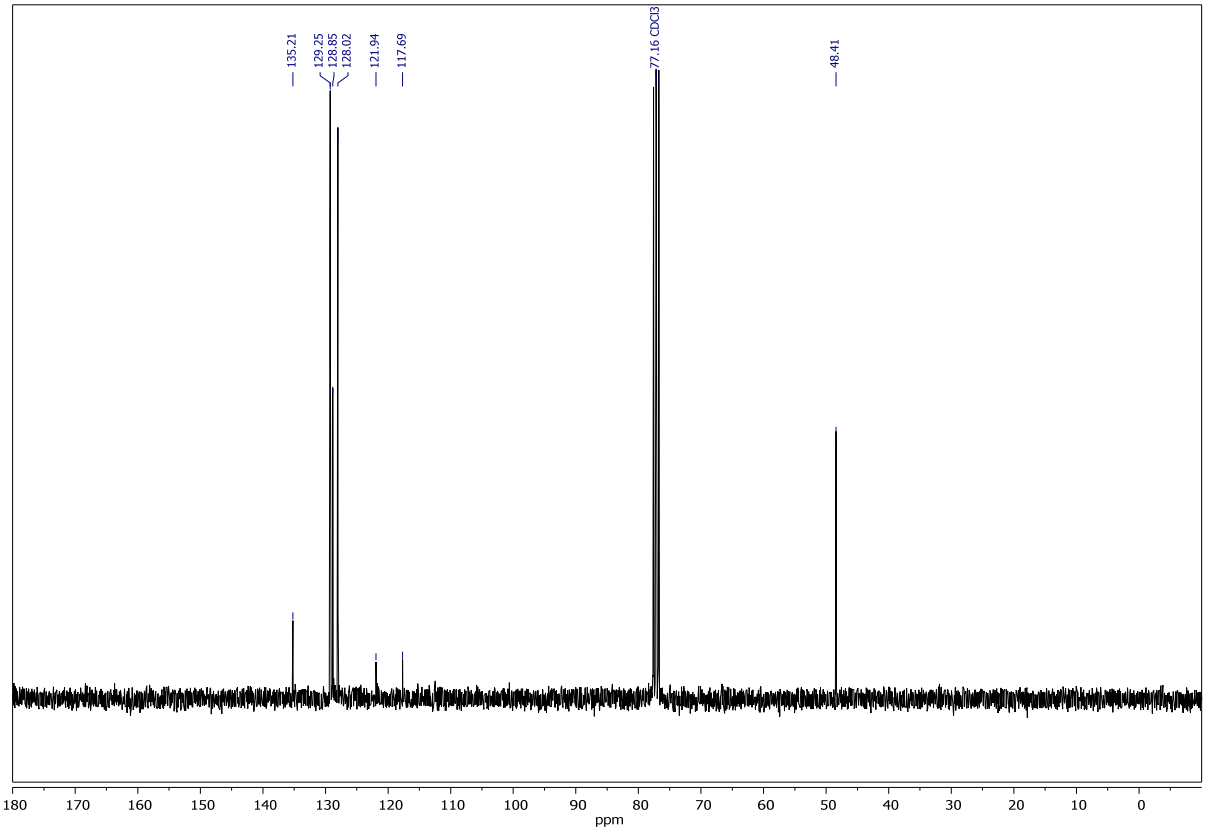
Compound **1l**, ^{1}H-, and ^{13}C-NMR ($CDCl_3$):

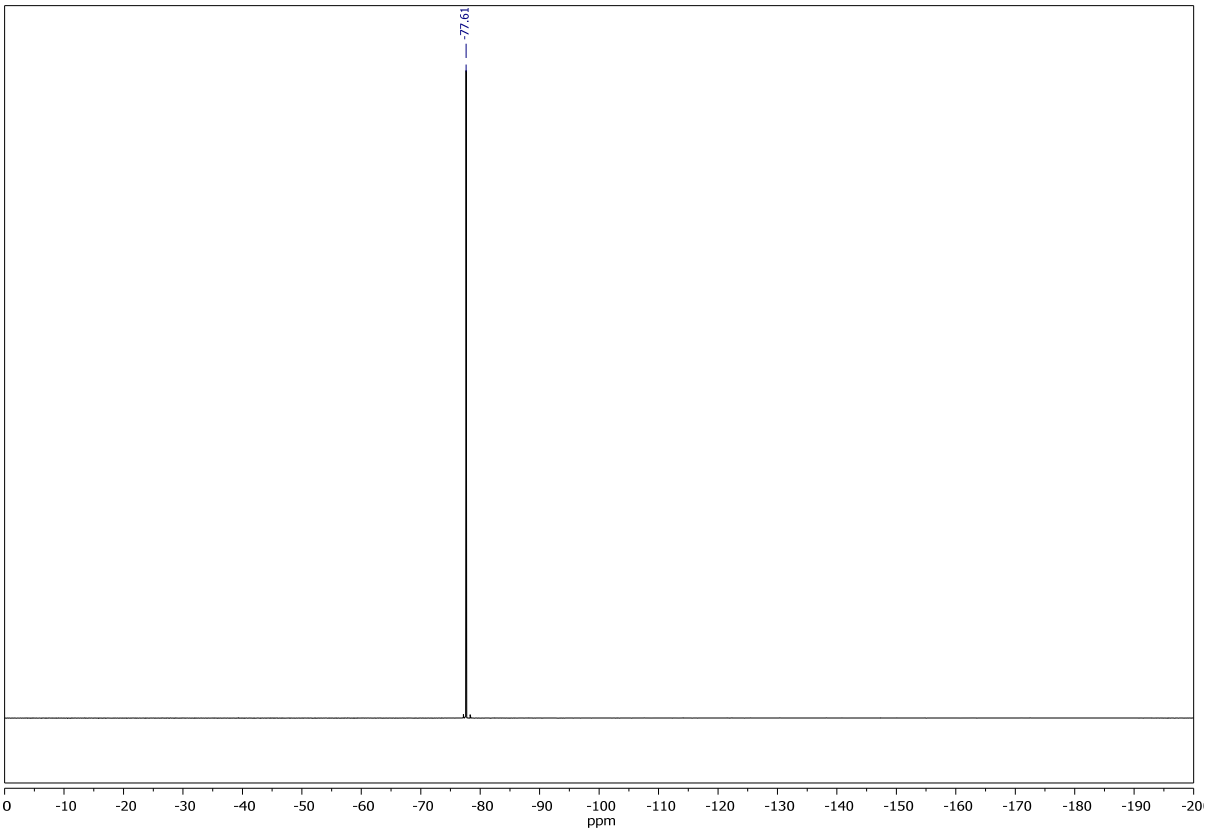




Compound **1m**, ^{1}H-, ^{13}C and ^{19}F-NMR ($CDCl_3$):






-77.61
0
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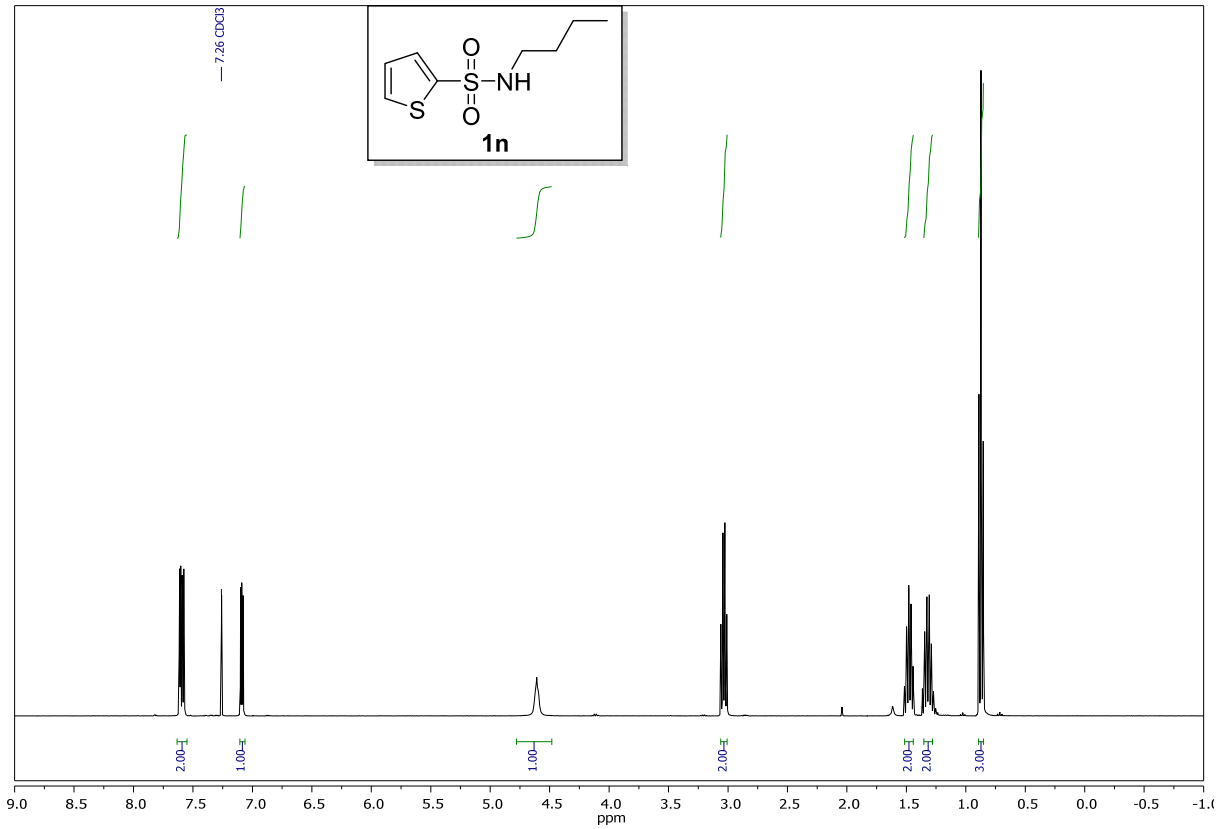
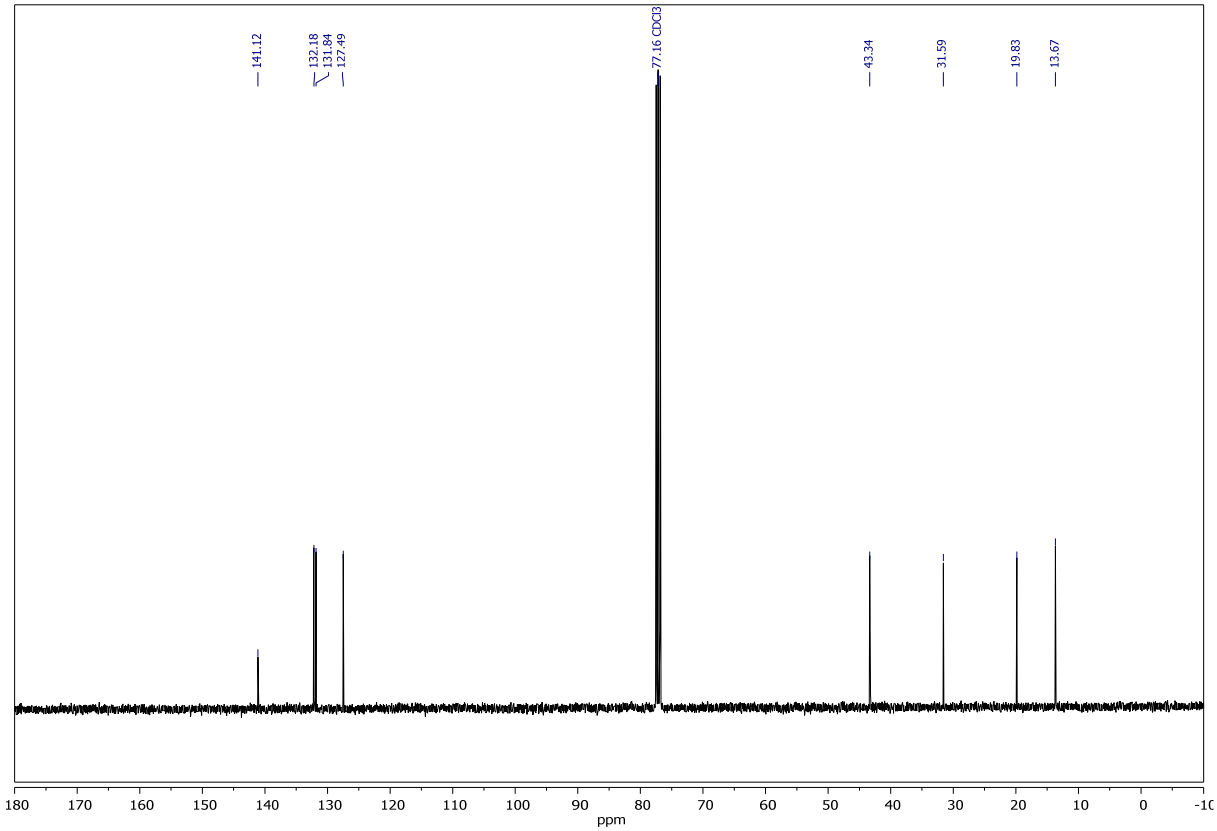
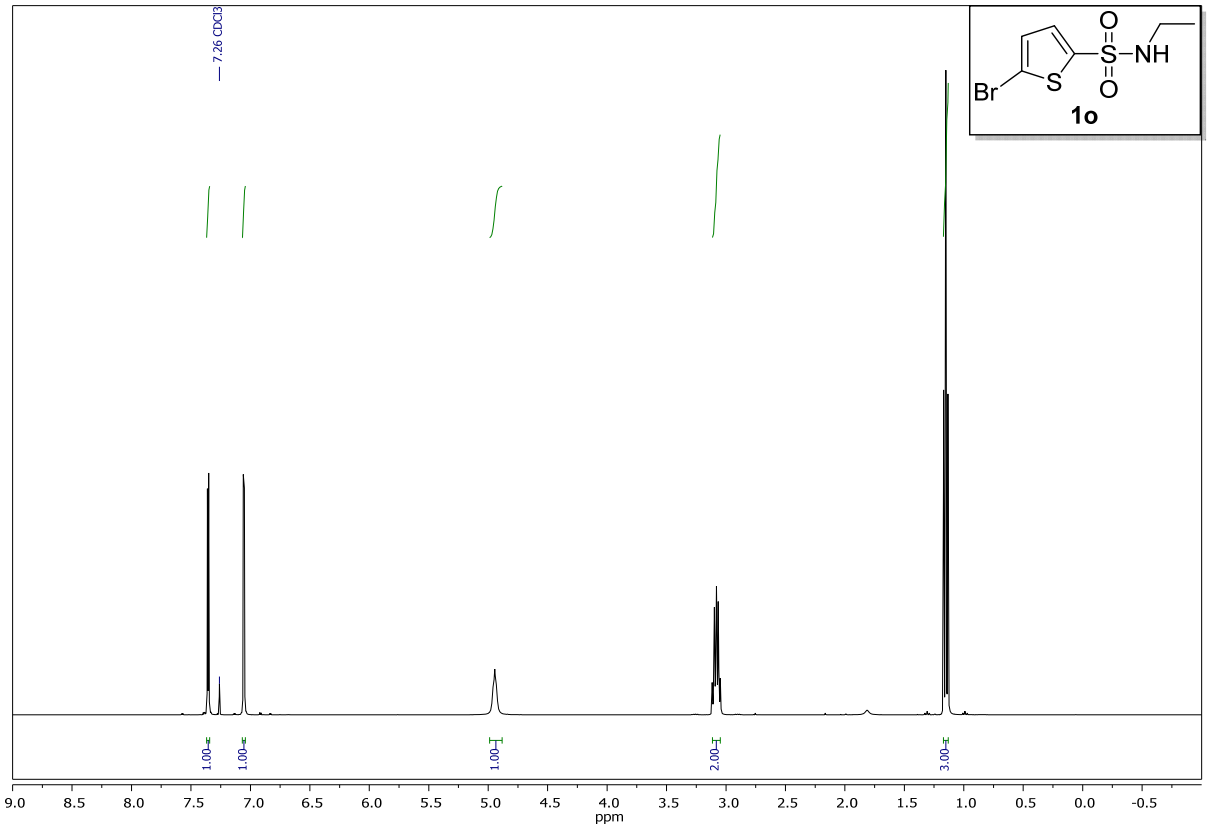
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
ppm

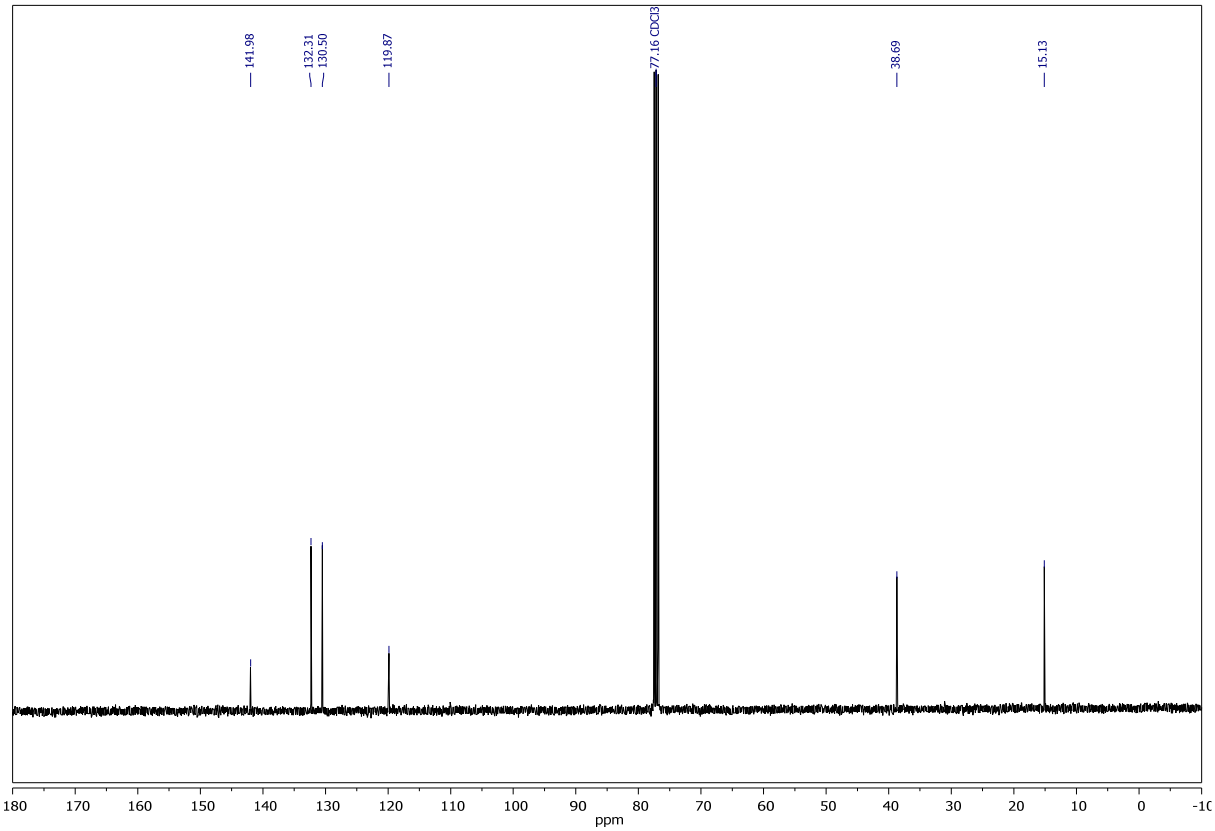
Compound **1n**, ^{1}H-, and ^{13}C-NMR ($CDCl_3$):



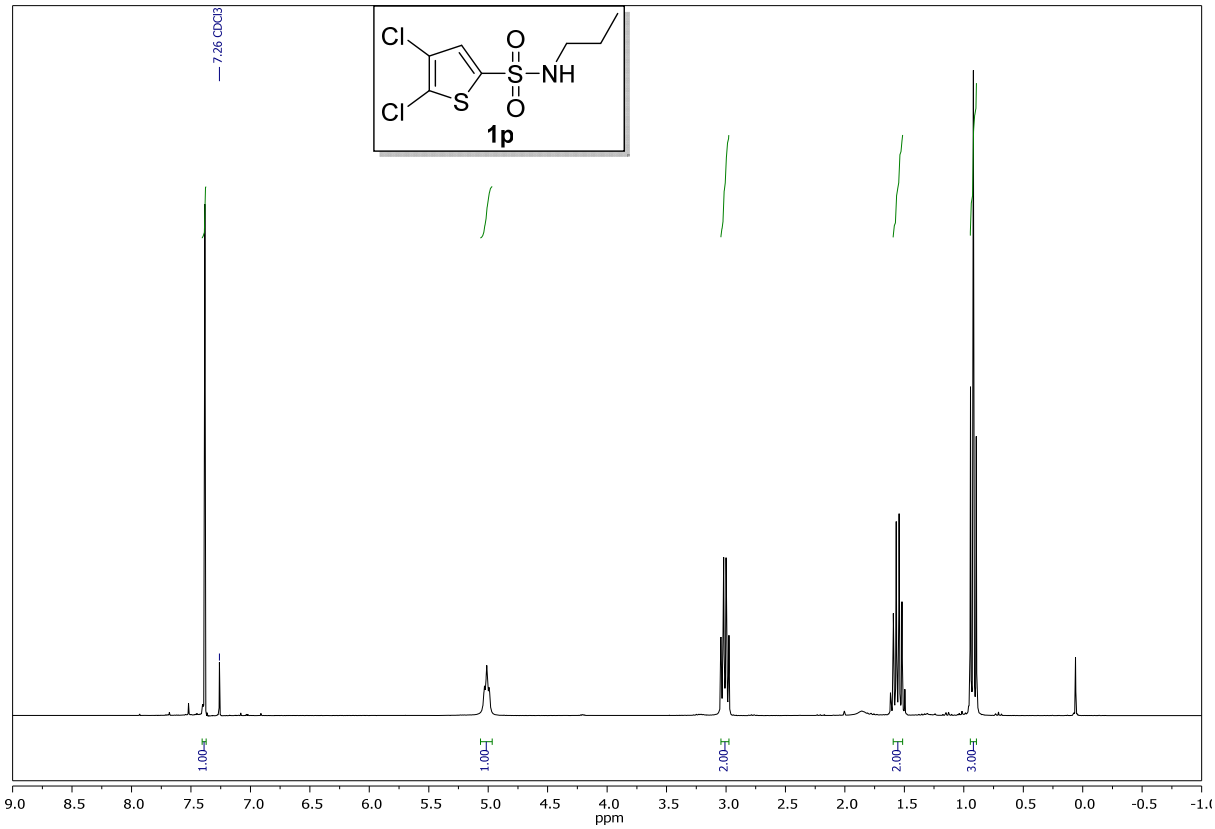


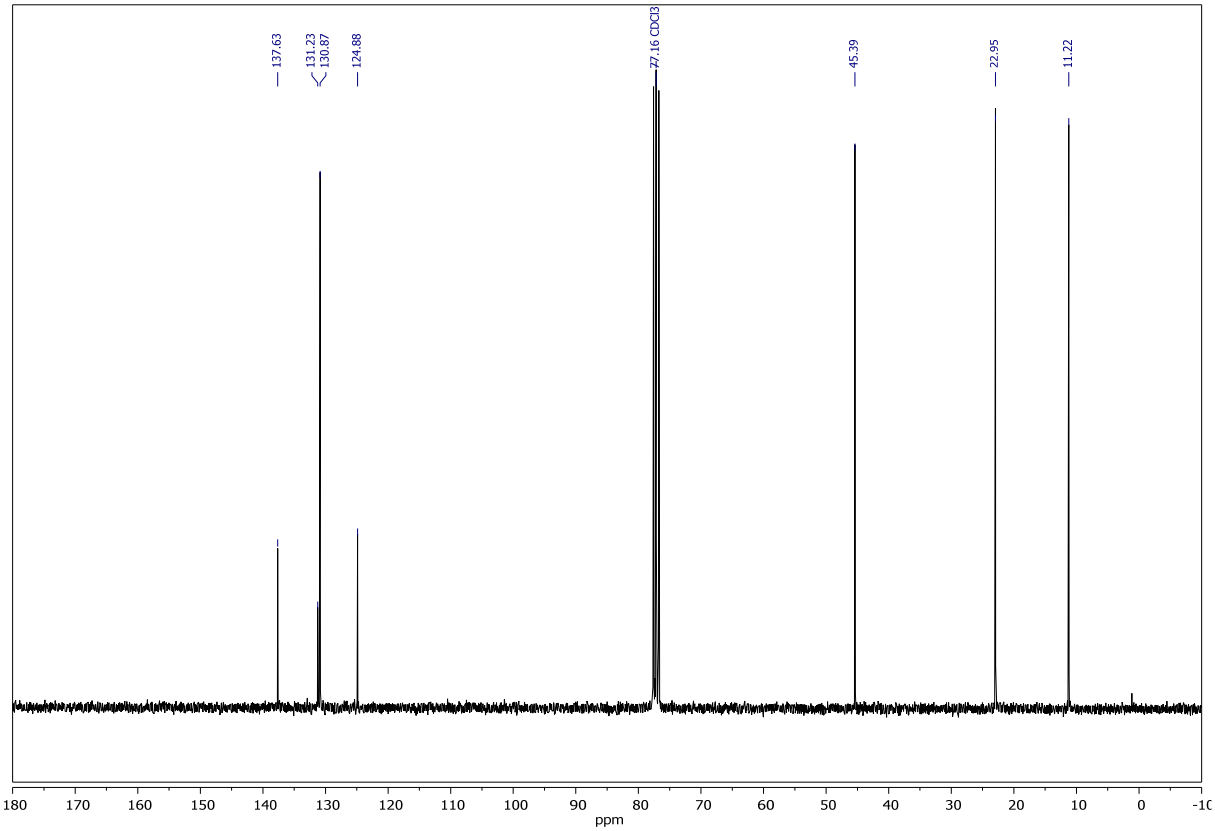
Compound **1o**, ^{1}H-, and ^{13}C-NMR ($CDCl_3$):



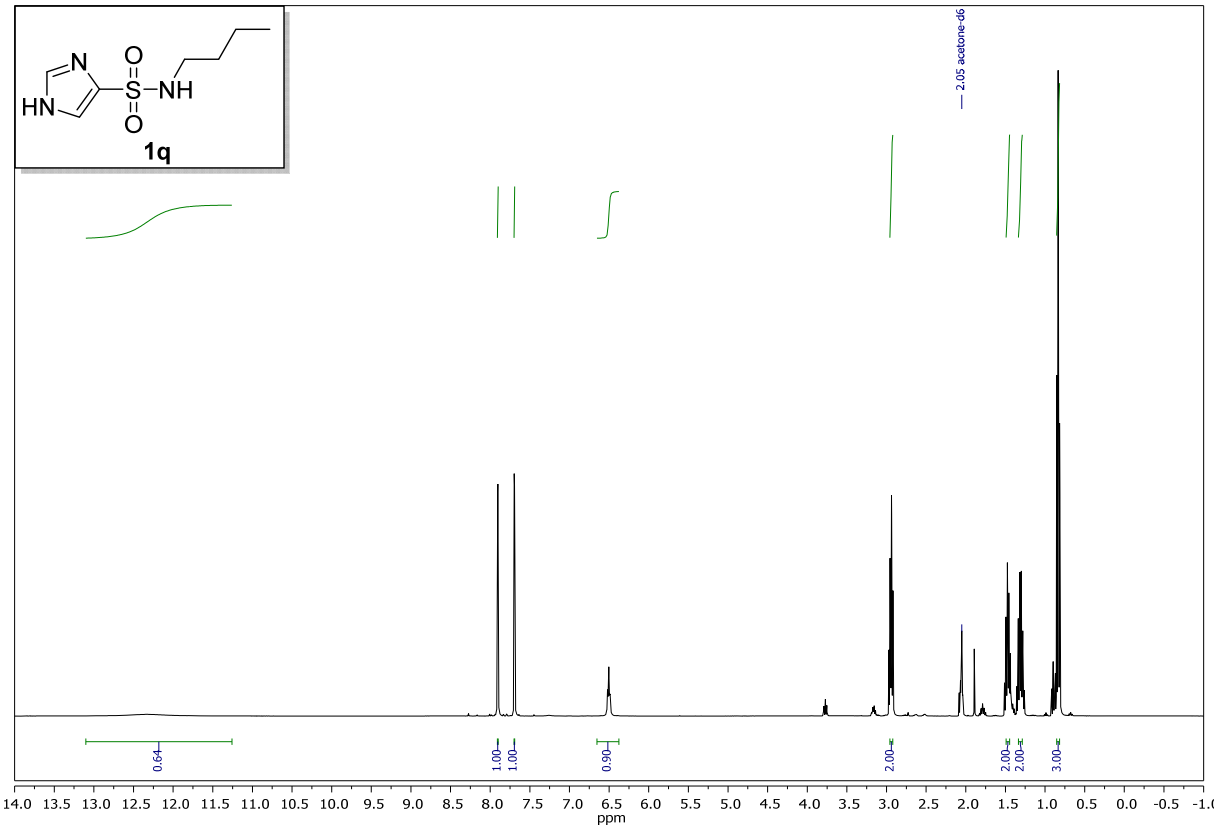


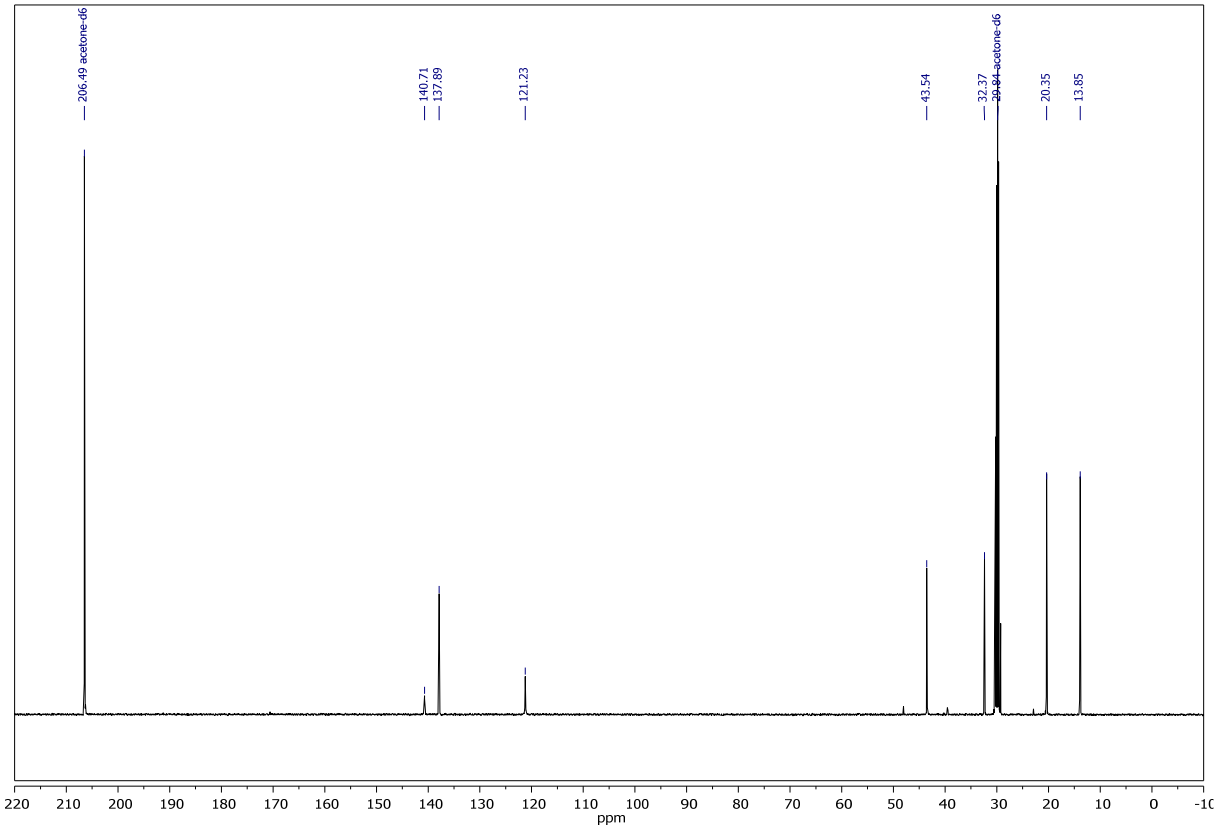
Compound **1p**, ^{1}H-, and ^{13}C-NMR ($CDCl_3$):



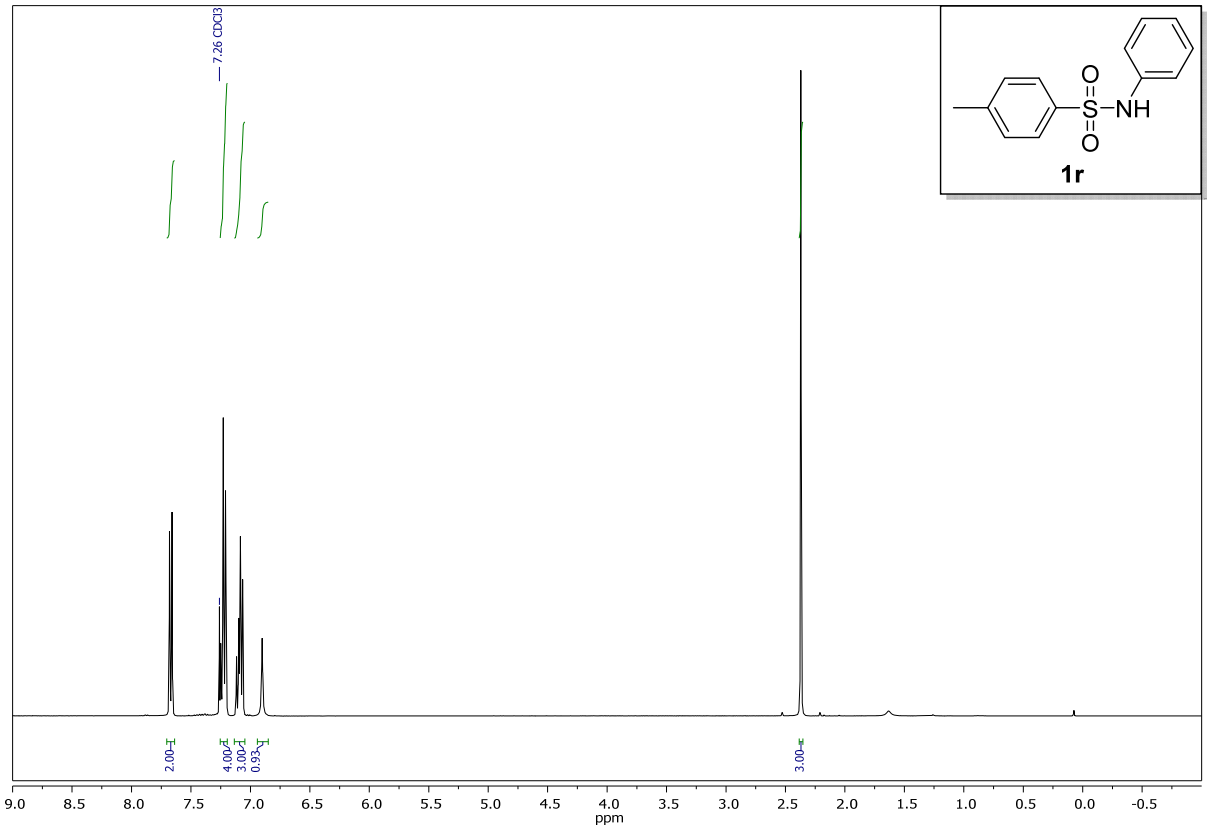


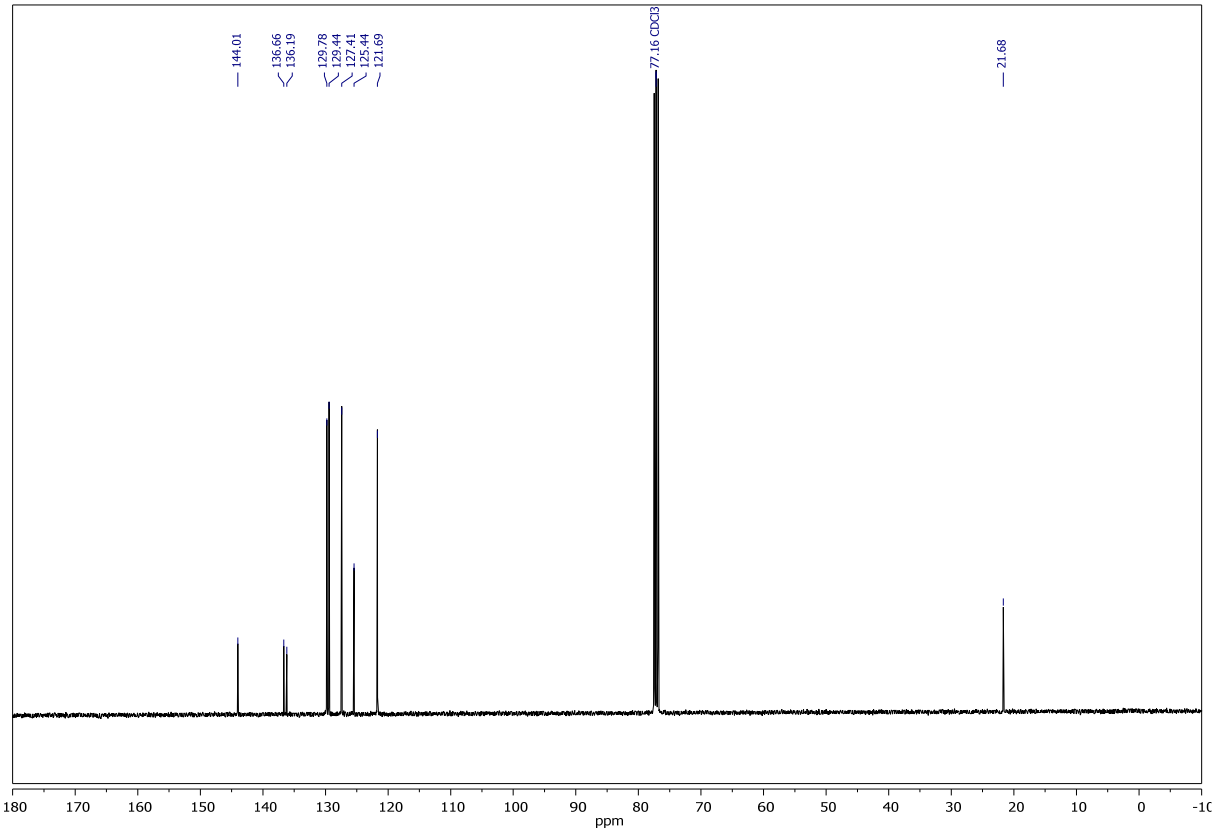
Compound **1q**, ^{1}H-, and ^{13}C-NMR (acetone-d_6):



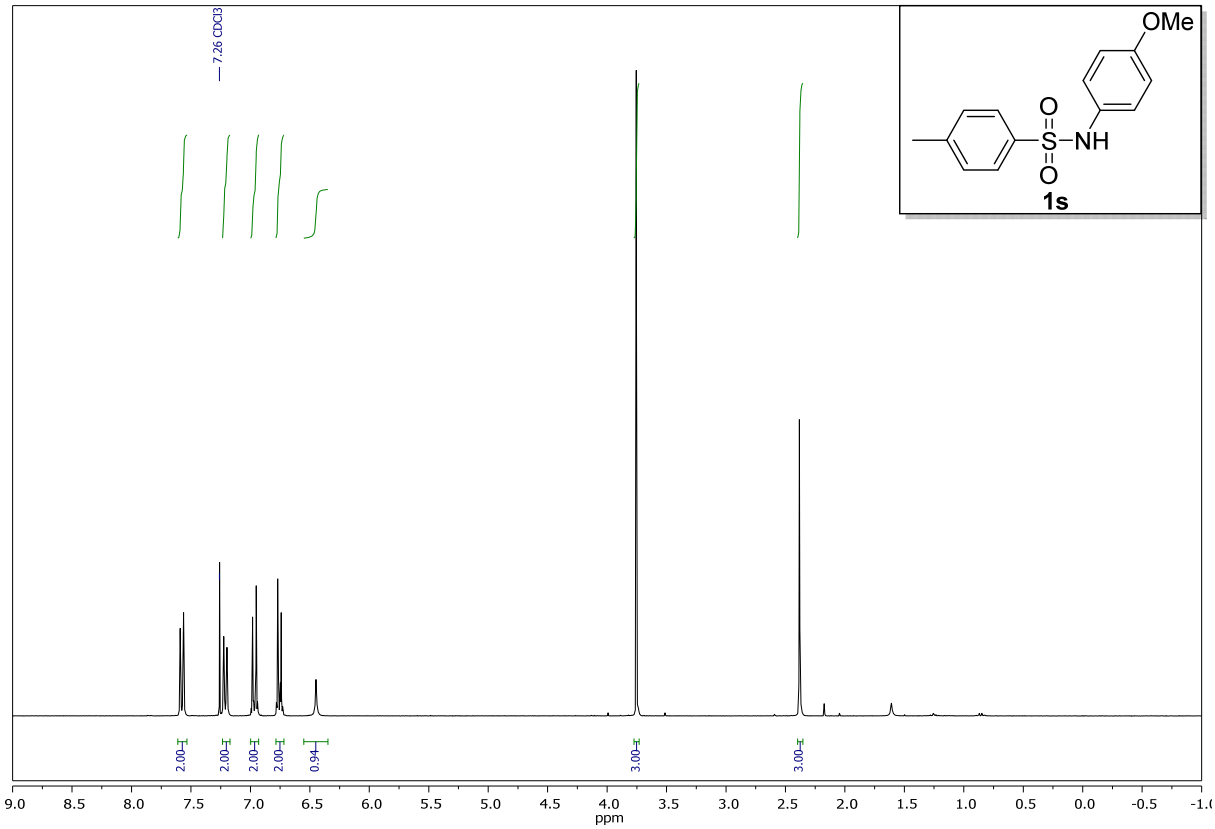


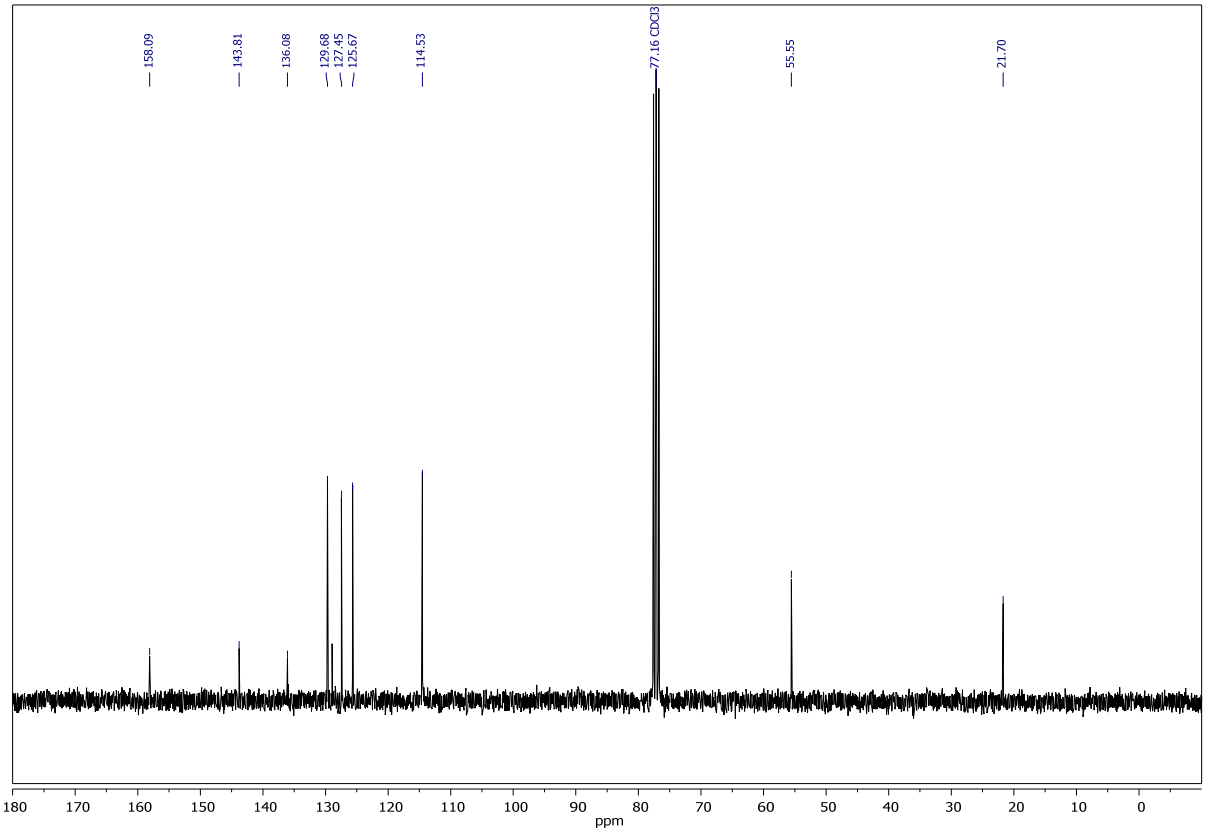
Compound **1r**, ^{1}H-, and ^{13}C-NMR ($CDCl_3$):



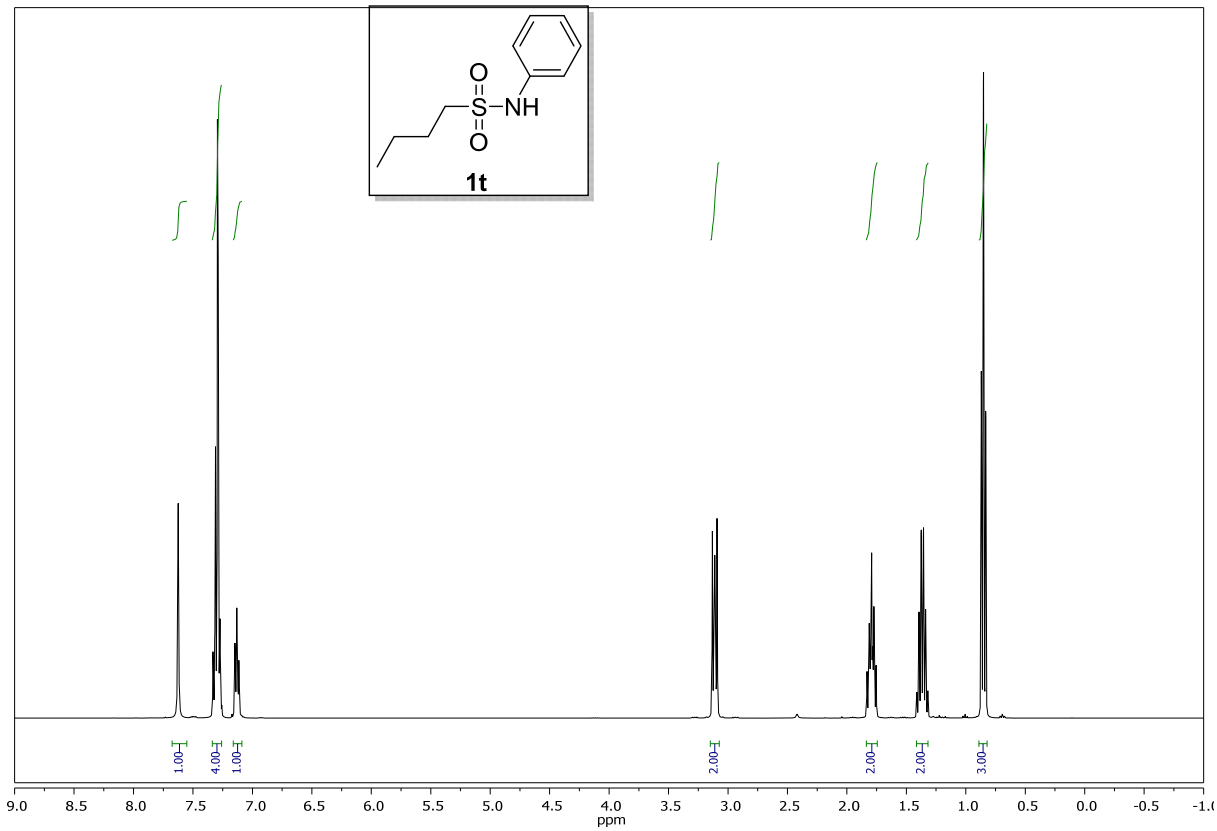


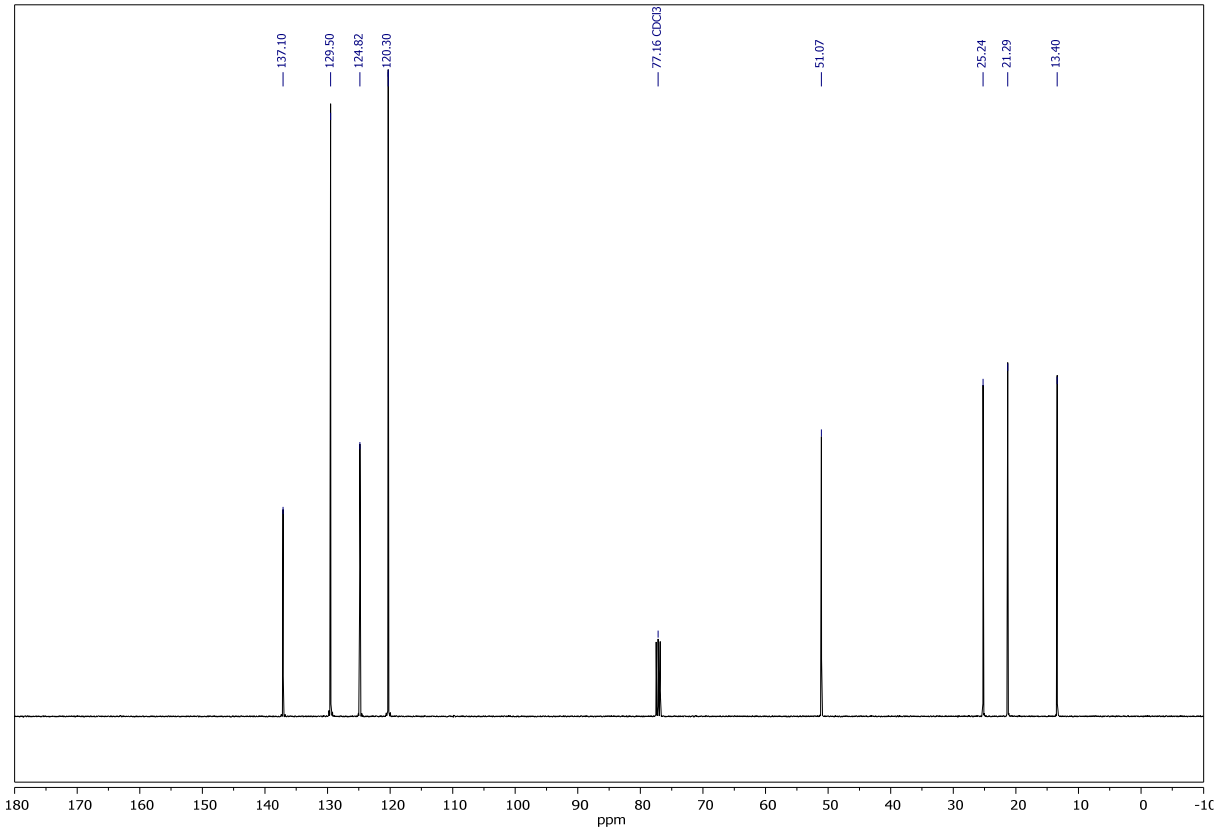
Compound **1s**, ^{1}H-, and ^{13}C-NMR ($CDCl_3$):



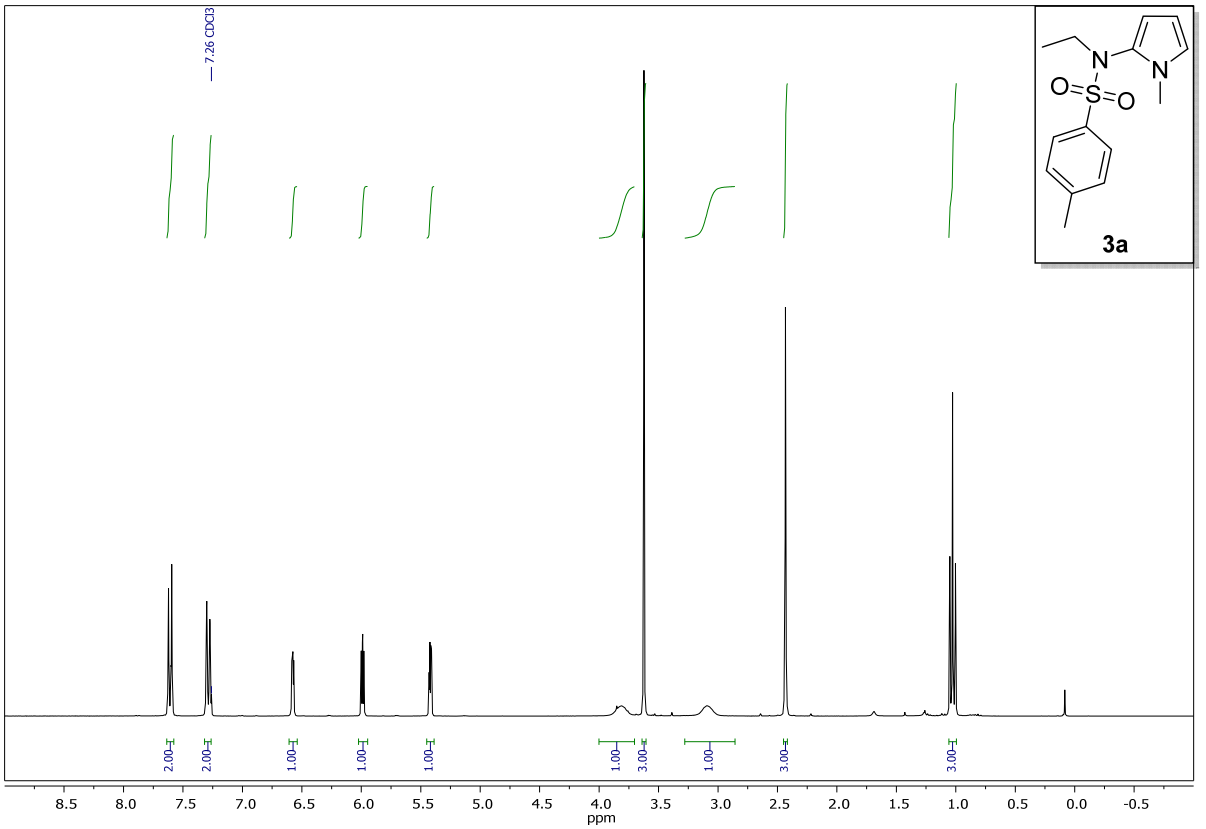


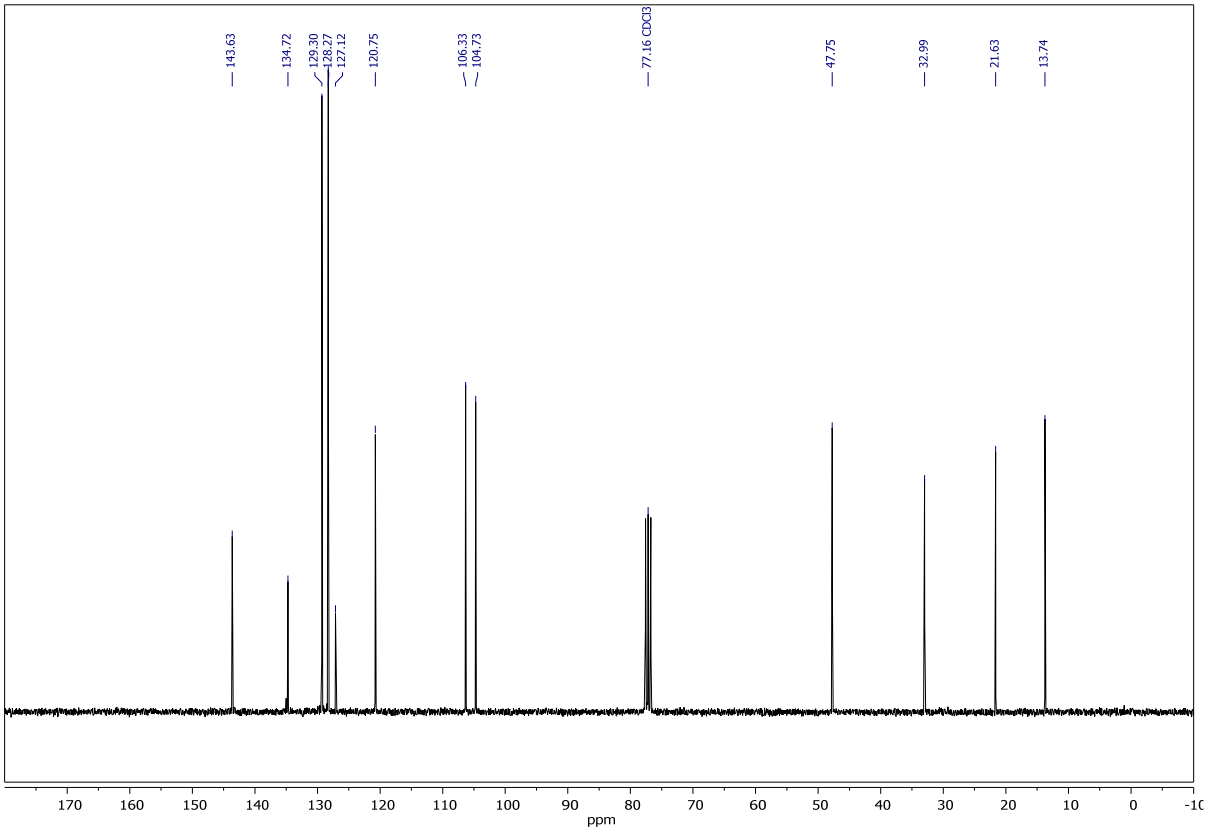
Compound **1t**, ^{1}H-, and ^{13}C-NMR ($CDCl_3$):



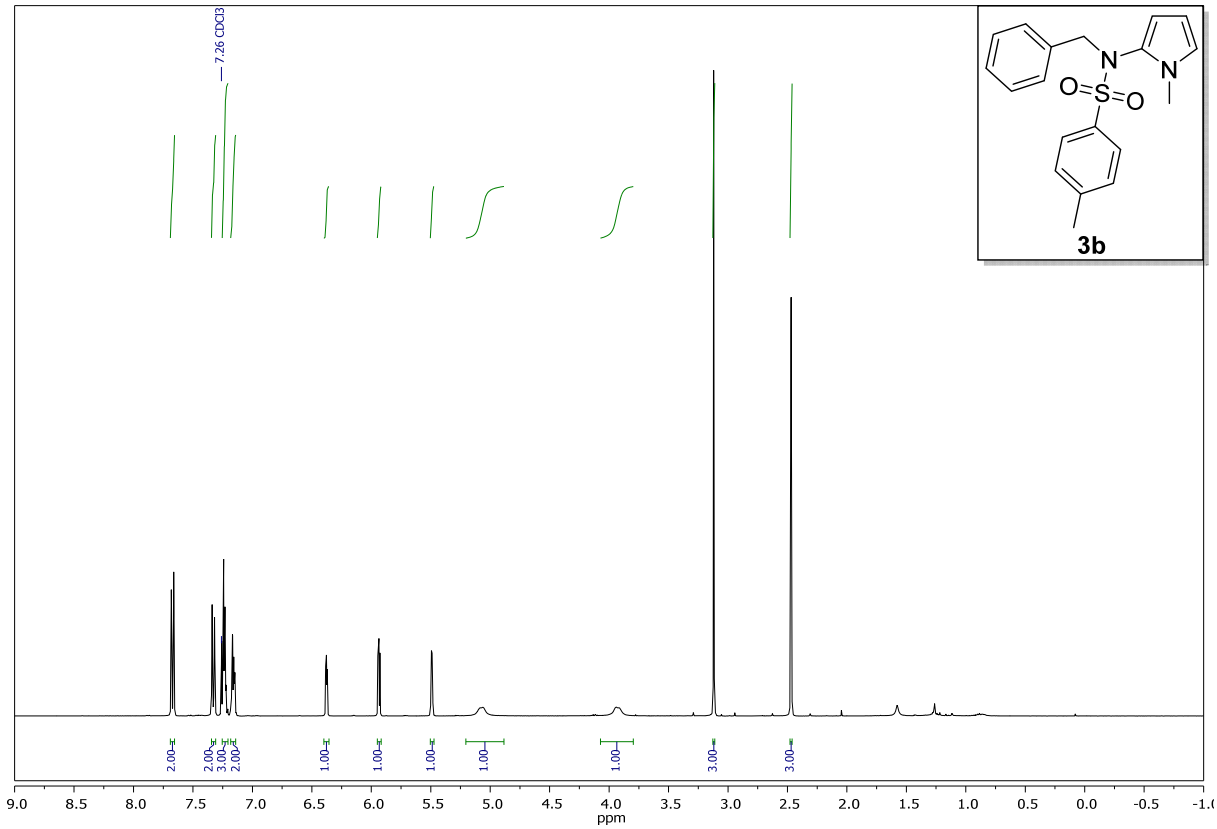


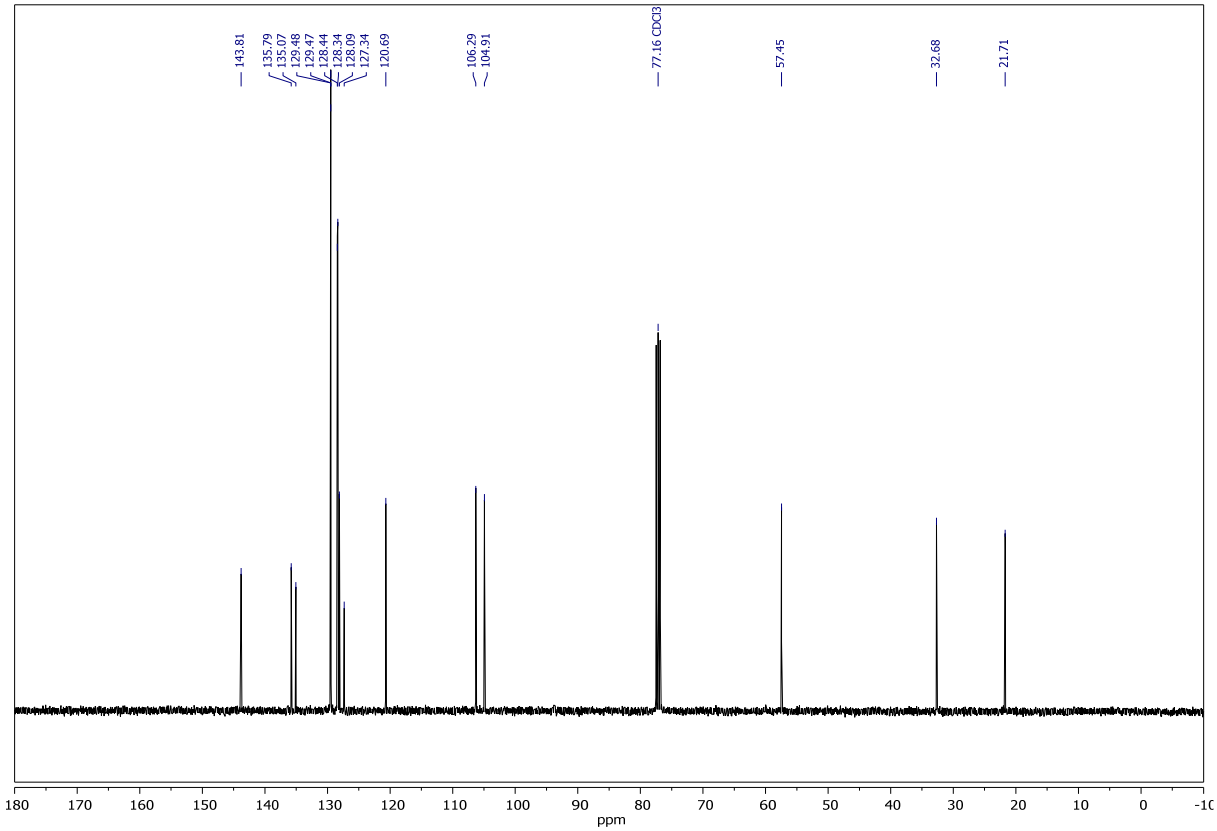
Compound **3a**, ^{1}H-, and ^{13}C-NMR ($CDCl_3$):



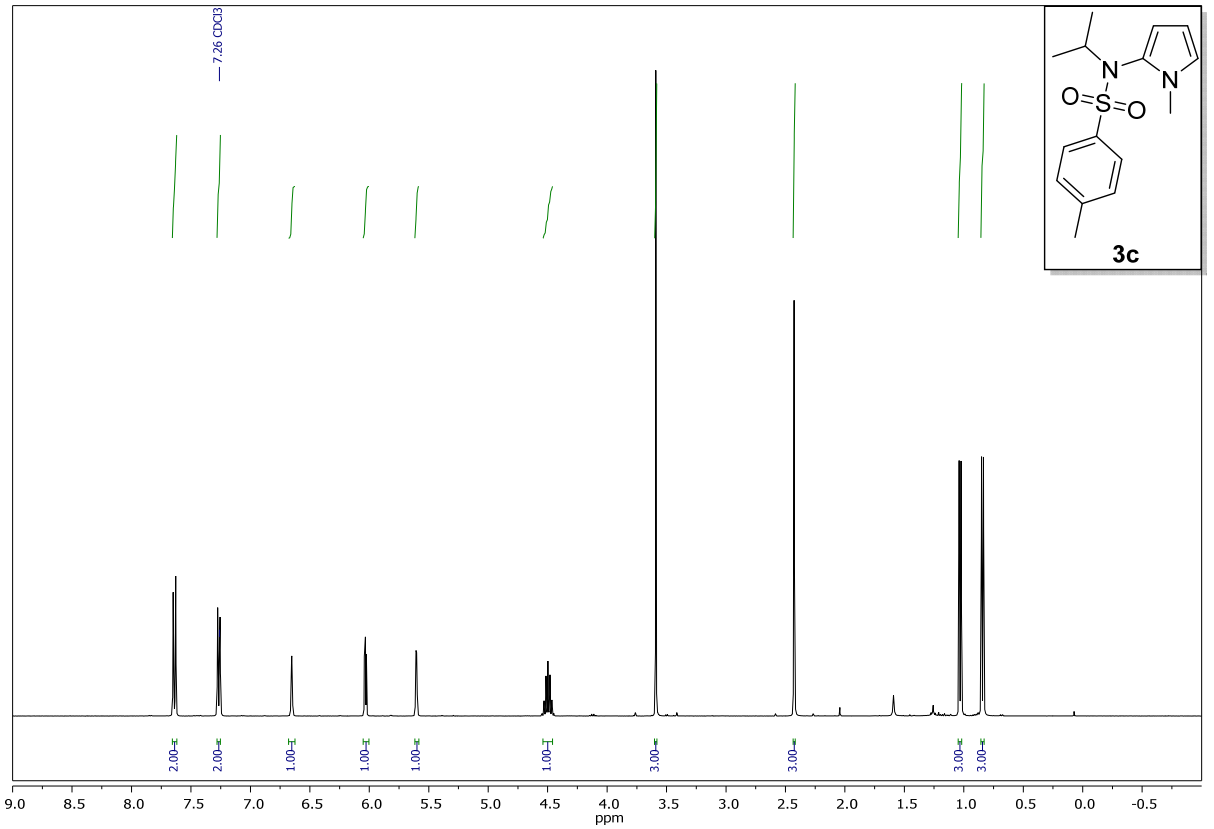


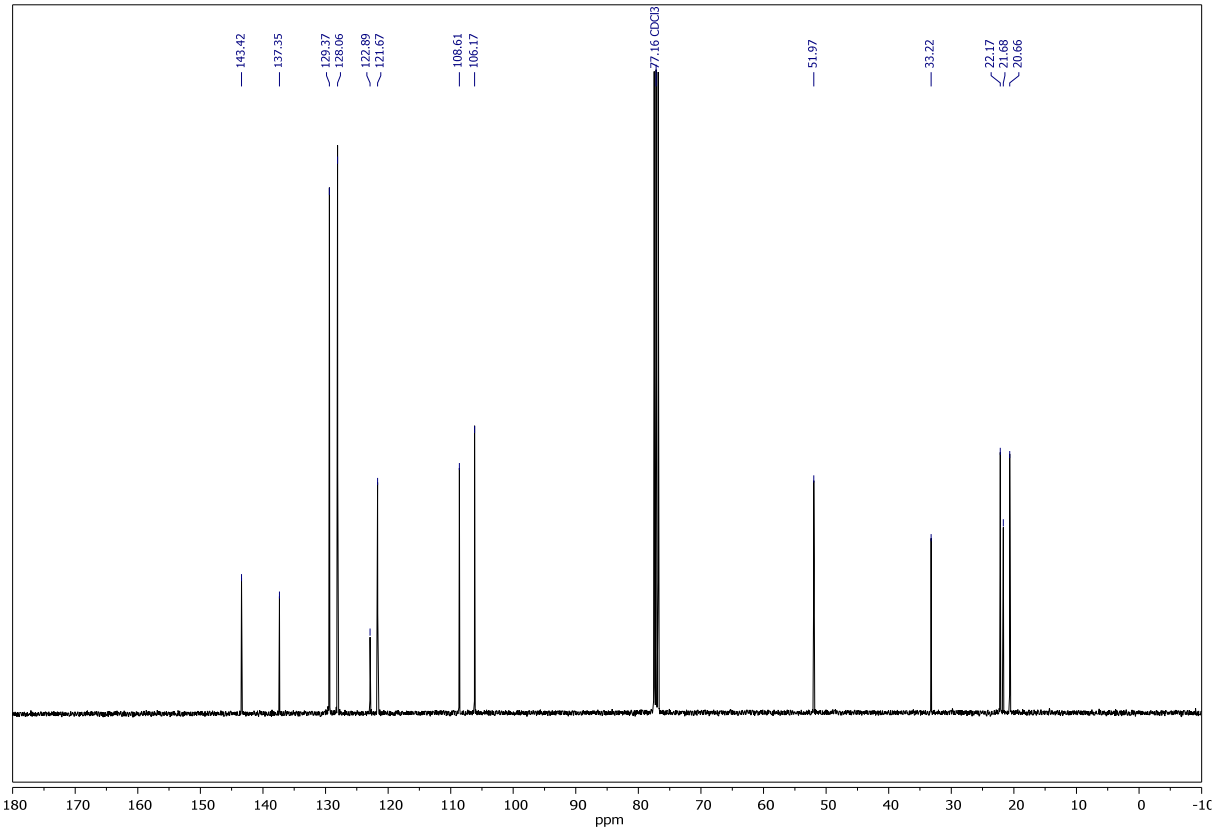
Compound **3b**, ^{1}H-, and ^{13}C-NMR ($CDCl_3$):



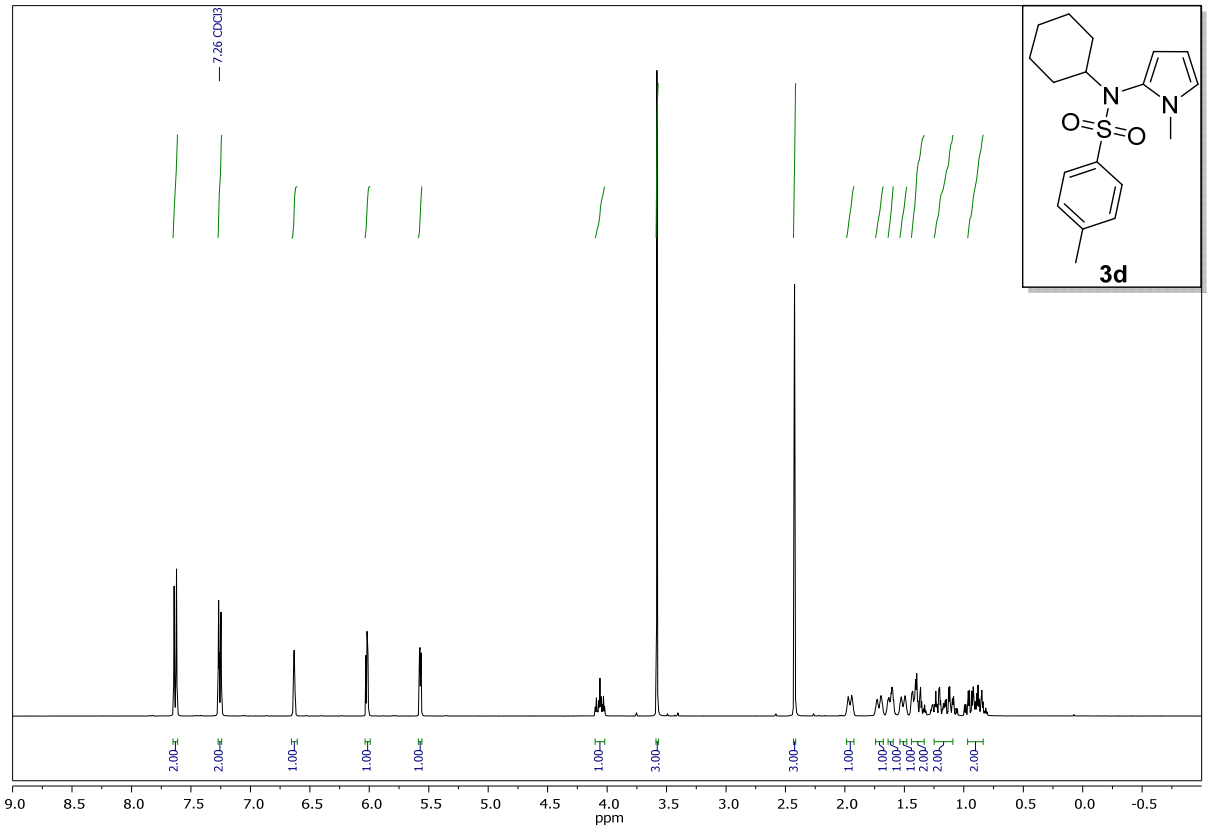


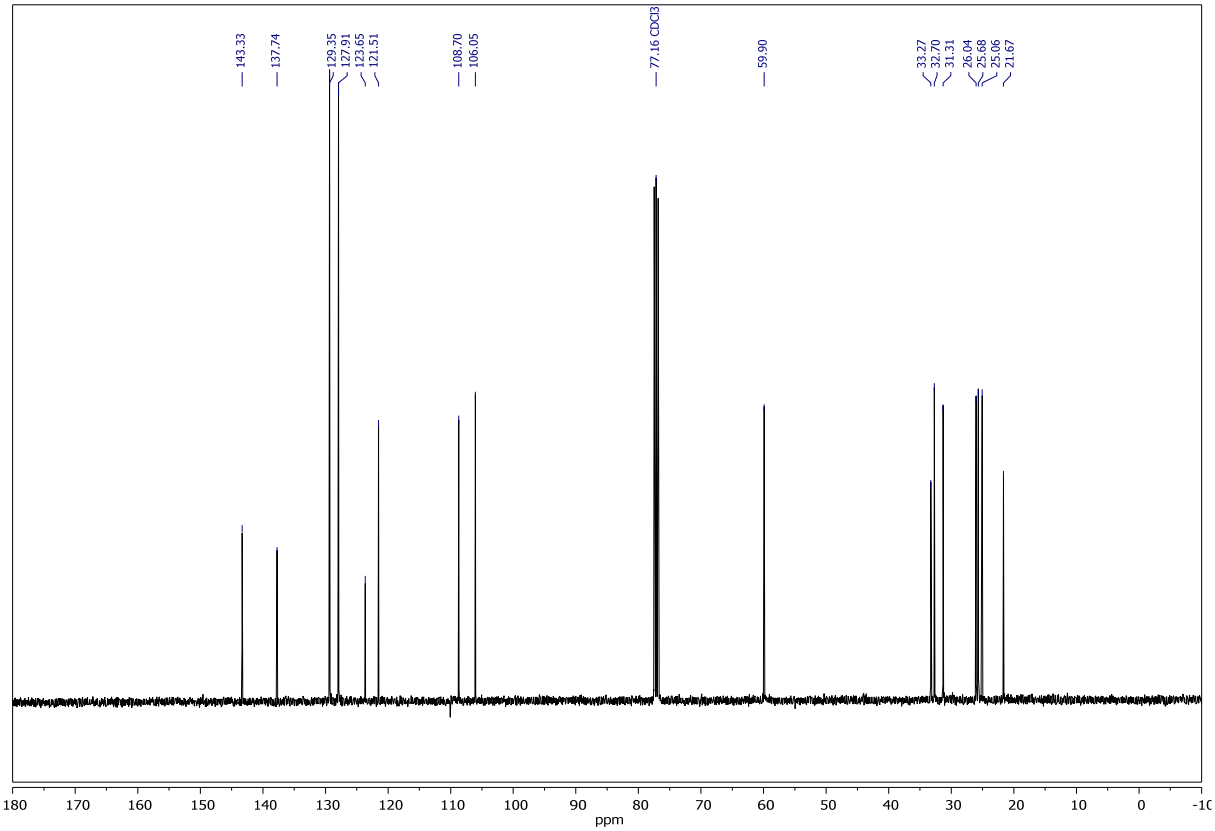
Compound **3c**, ^{1}H-, and ^{13}C-NMR ($CDCl_3$):



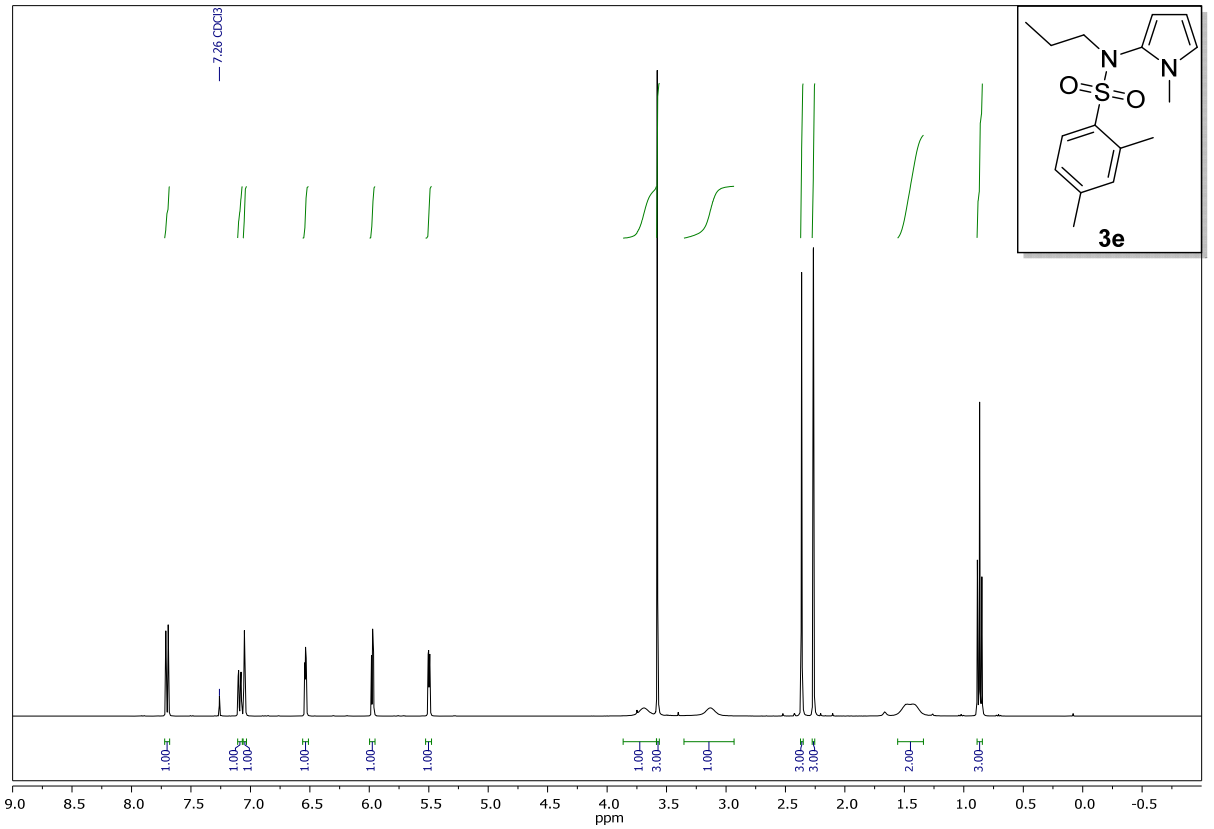


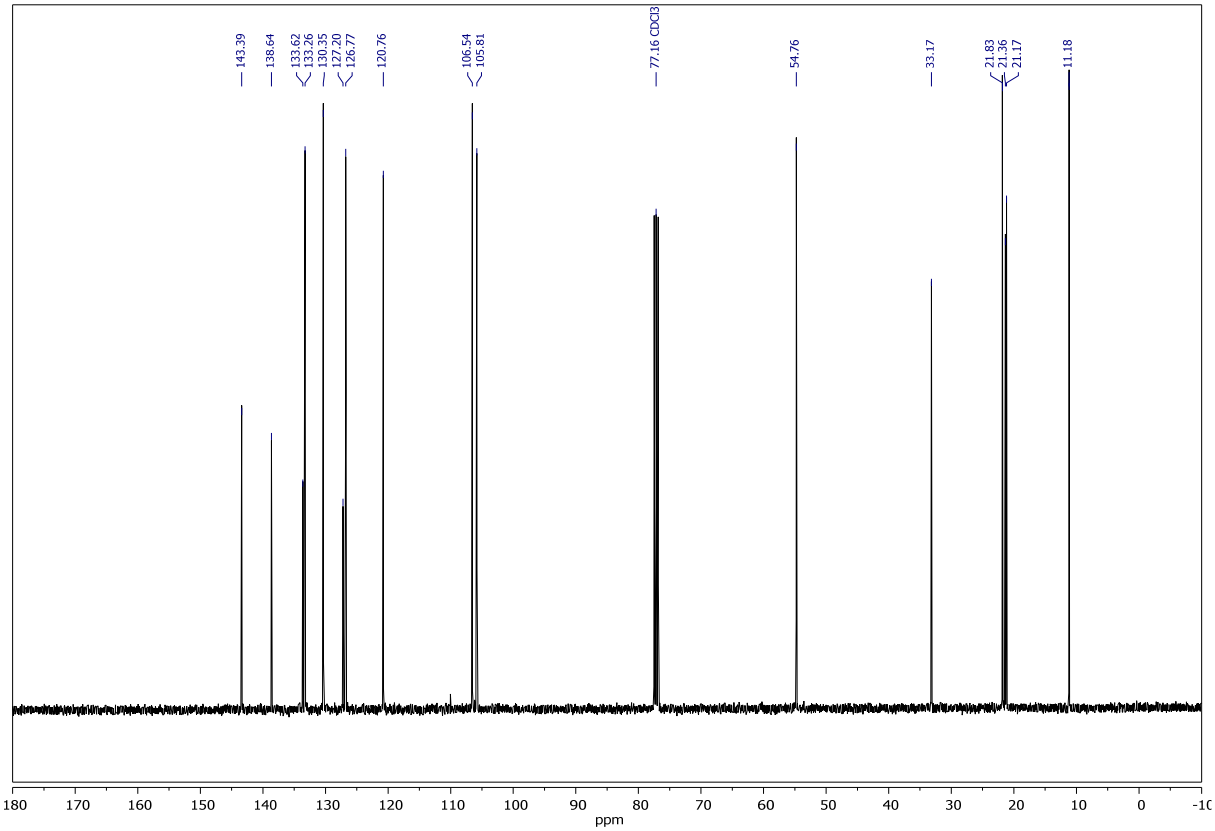
Compound **3d**, ^{1}H-, and ^{13}C-NMR ($CDCl_3$):



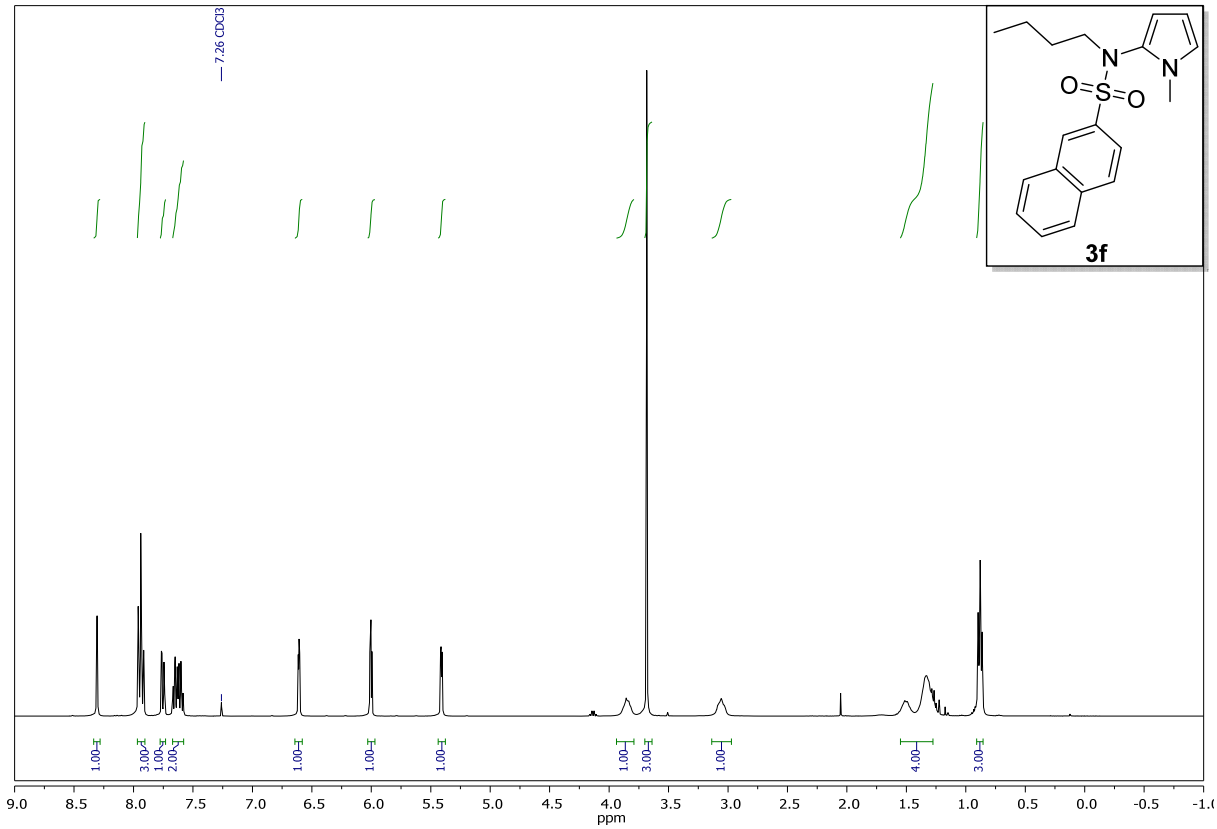


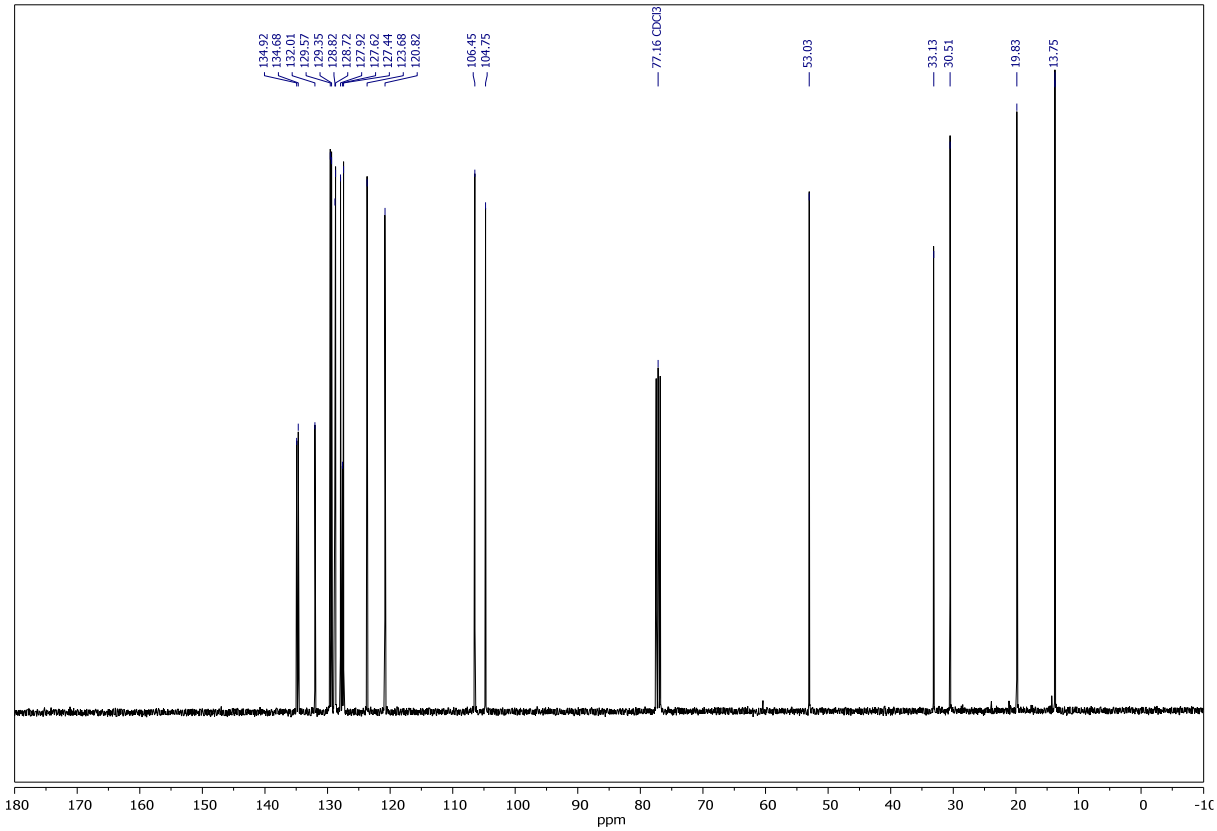
Compound **3e**, ^{1}H-, and ^{13}C-NMR ($CDCl_3$):



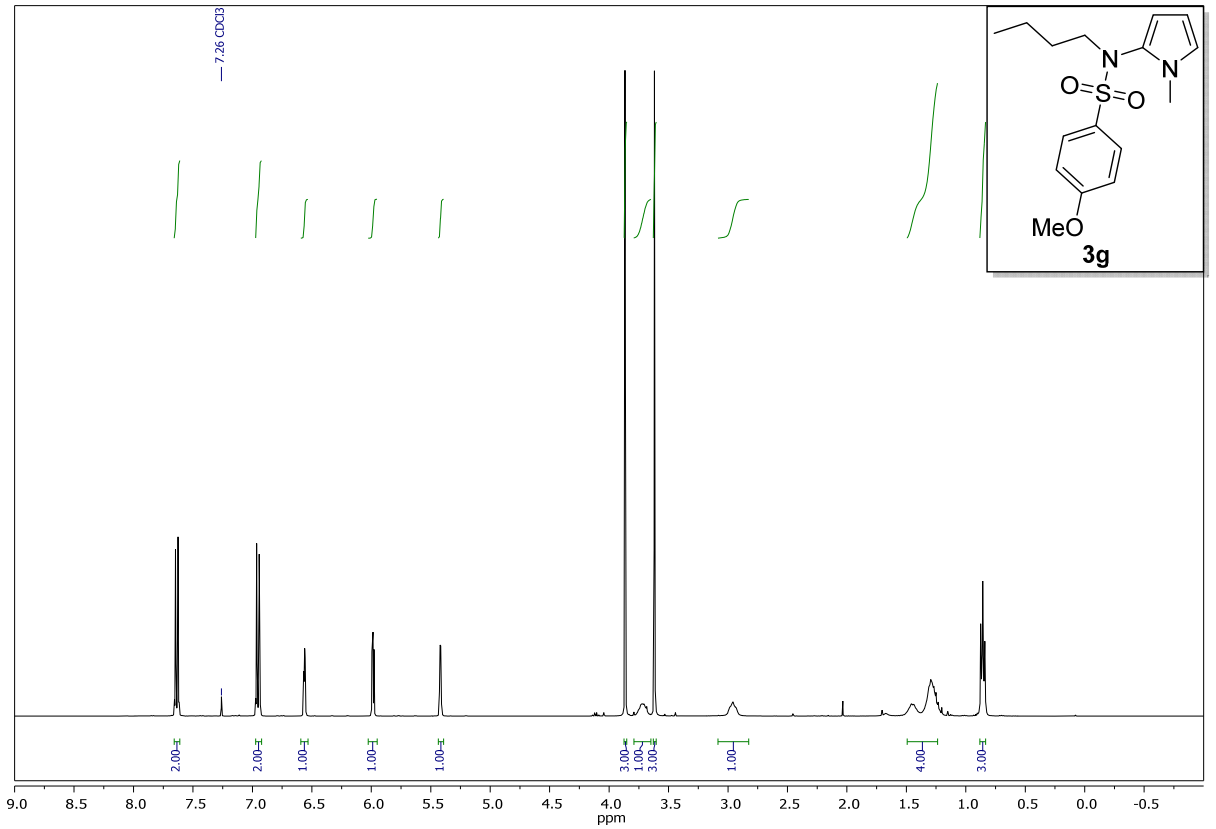


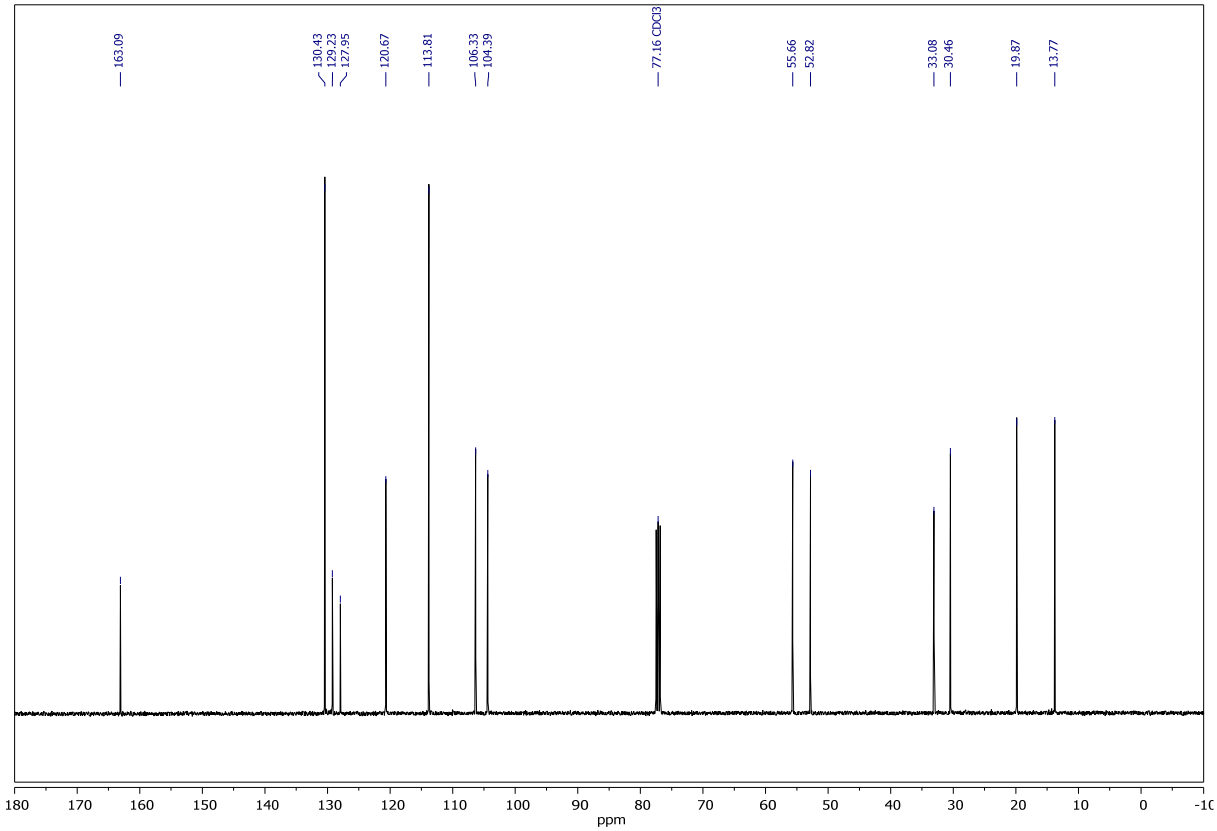
Compound **3f**, ^{1}H-, and ^{13}C-NMR ($CDCl_3$):



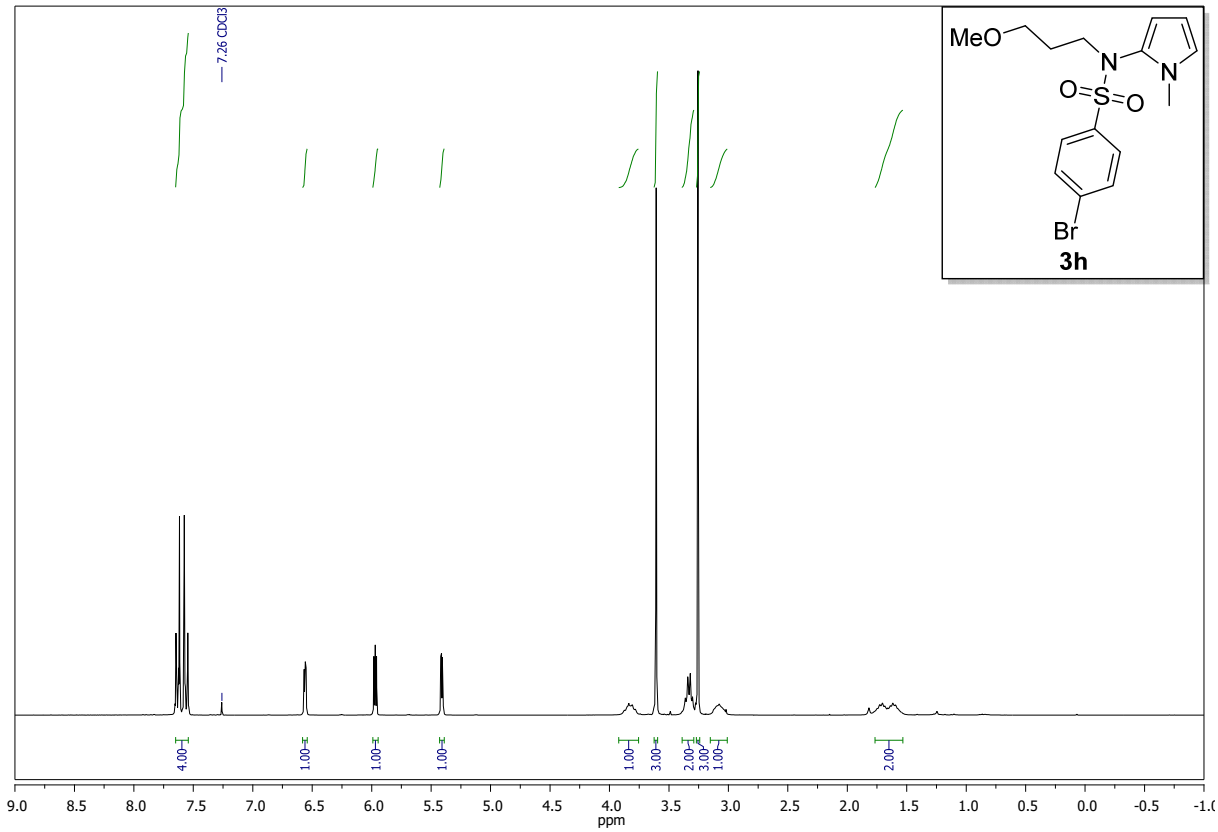


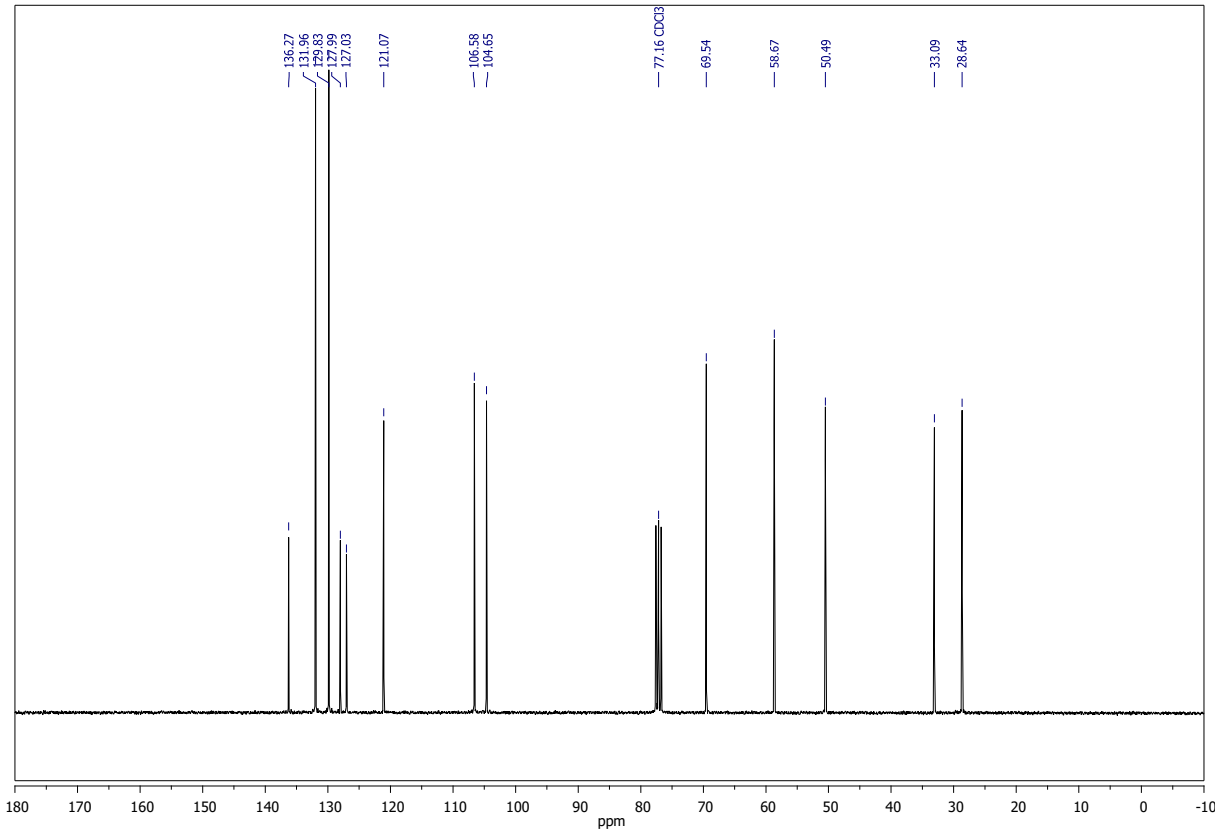
Compound **3g**, ^{1}H-, and ^{13}C-NMR ($CDCl_3$):



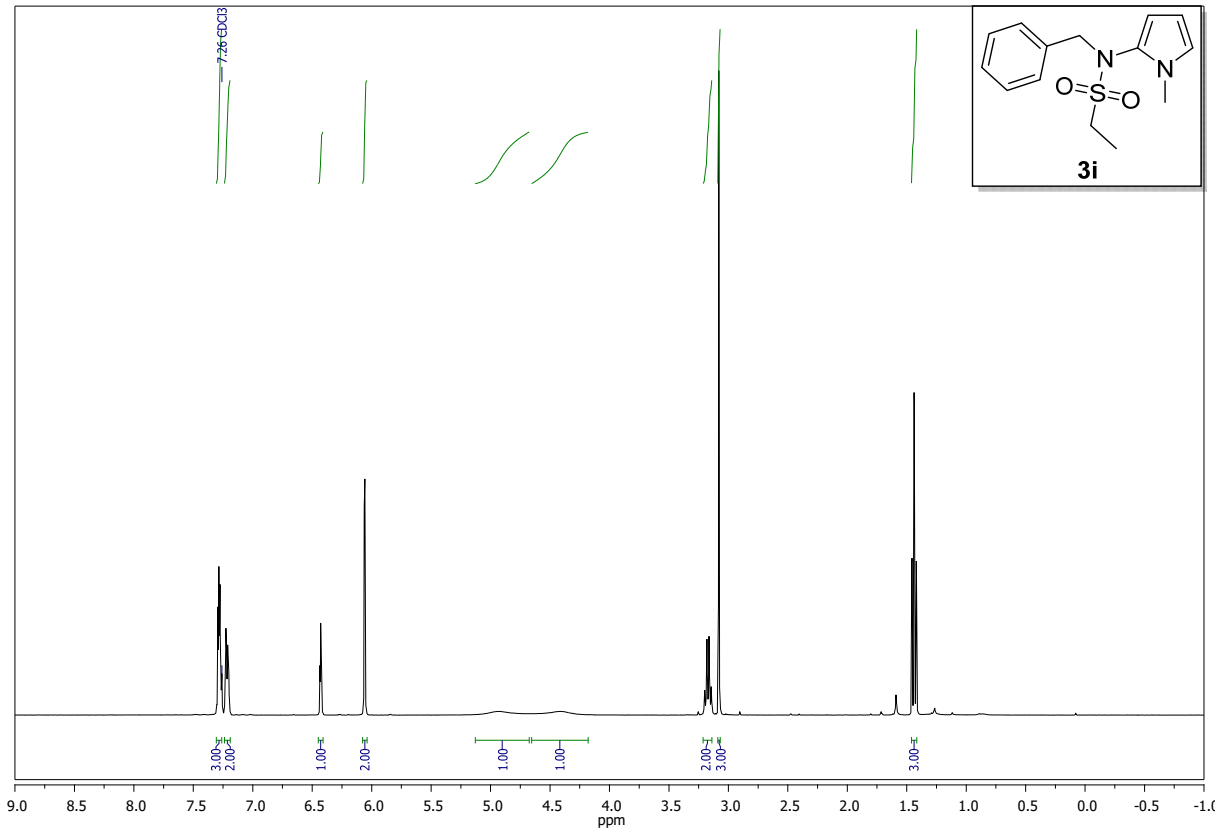


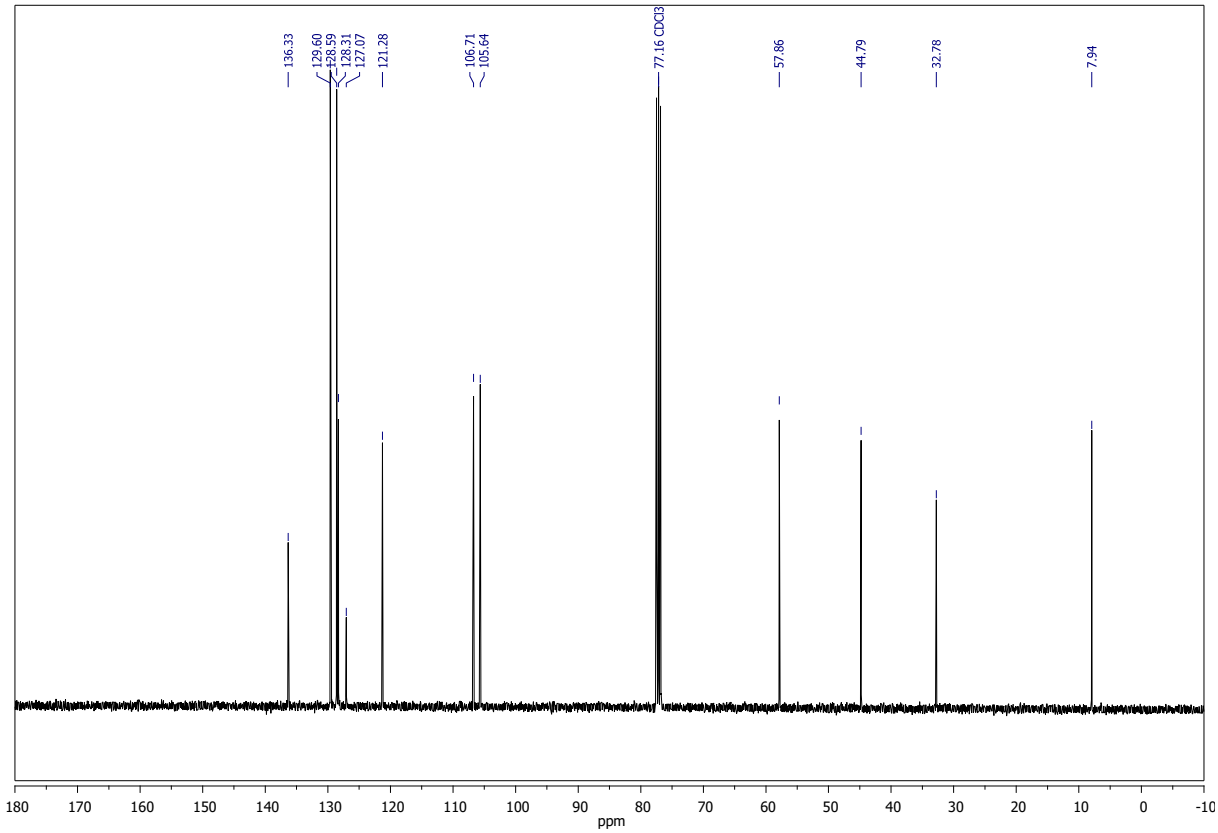
Compound **3h**, ^{1}H-, and ^{13}C-NMR ($CDCl_3$):





Compound **3i**, ^{1}H-, and ^{13}C-NMR ($CDCl_3$):





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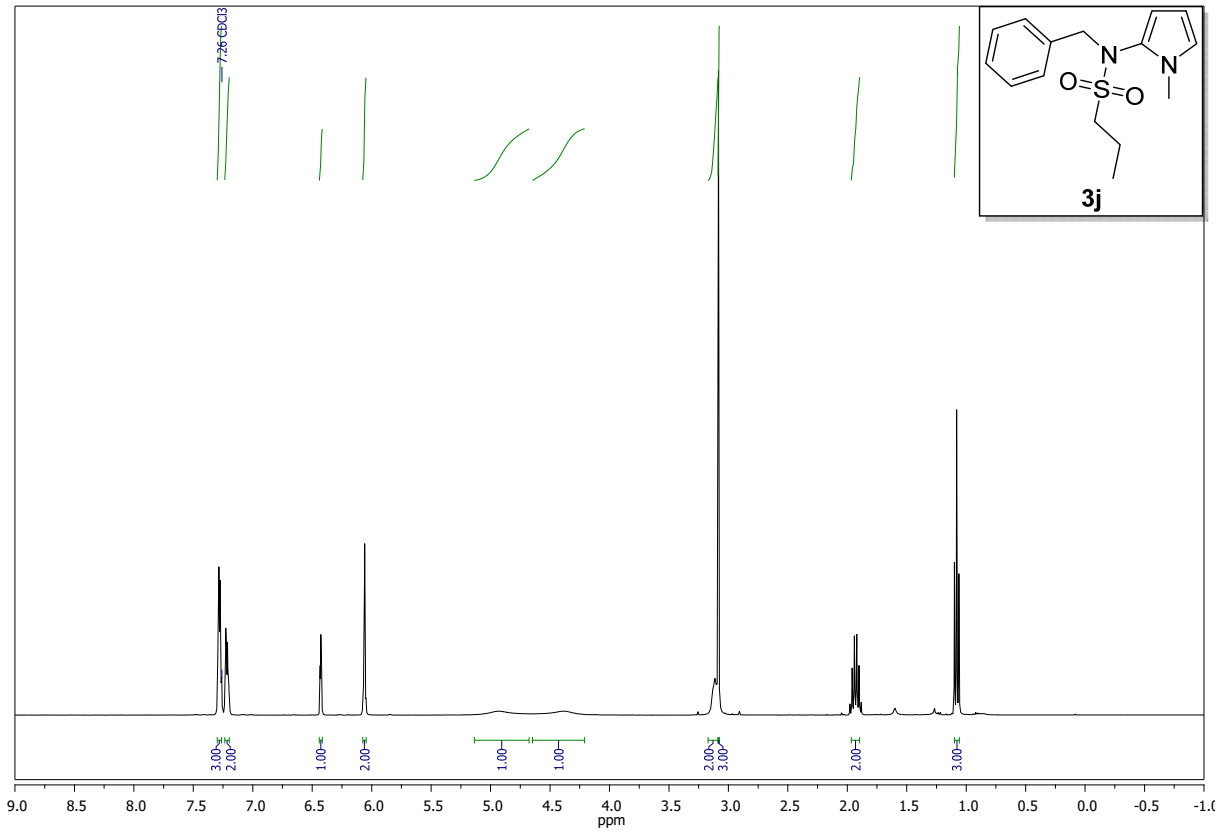
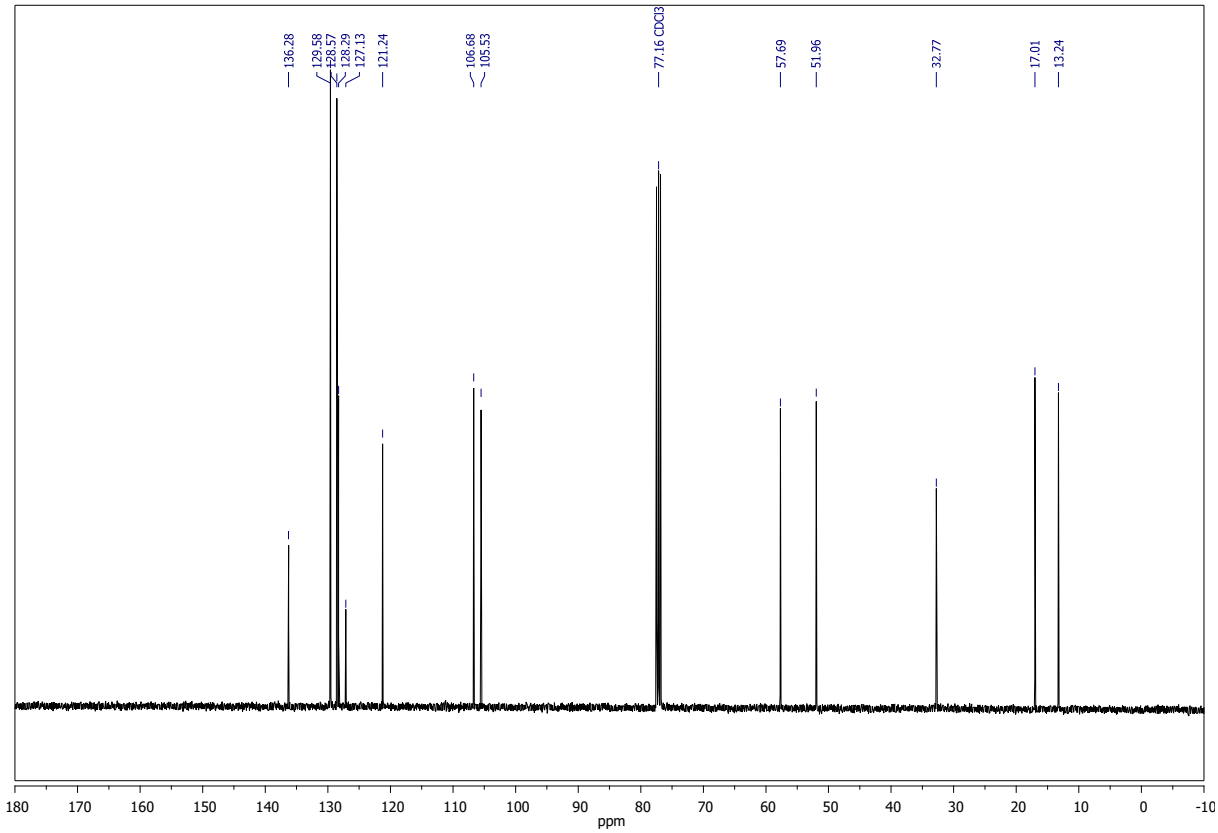
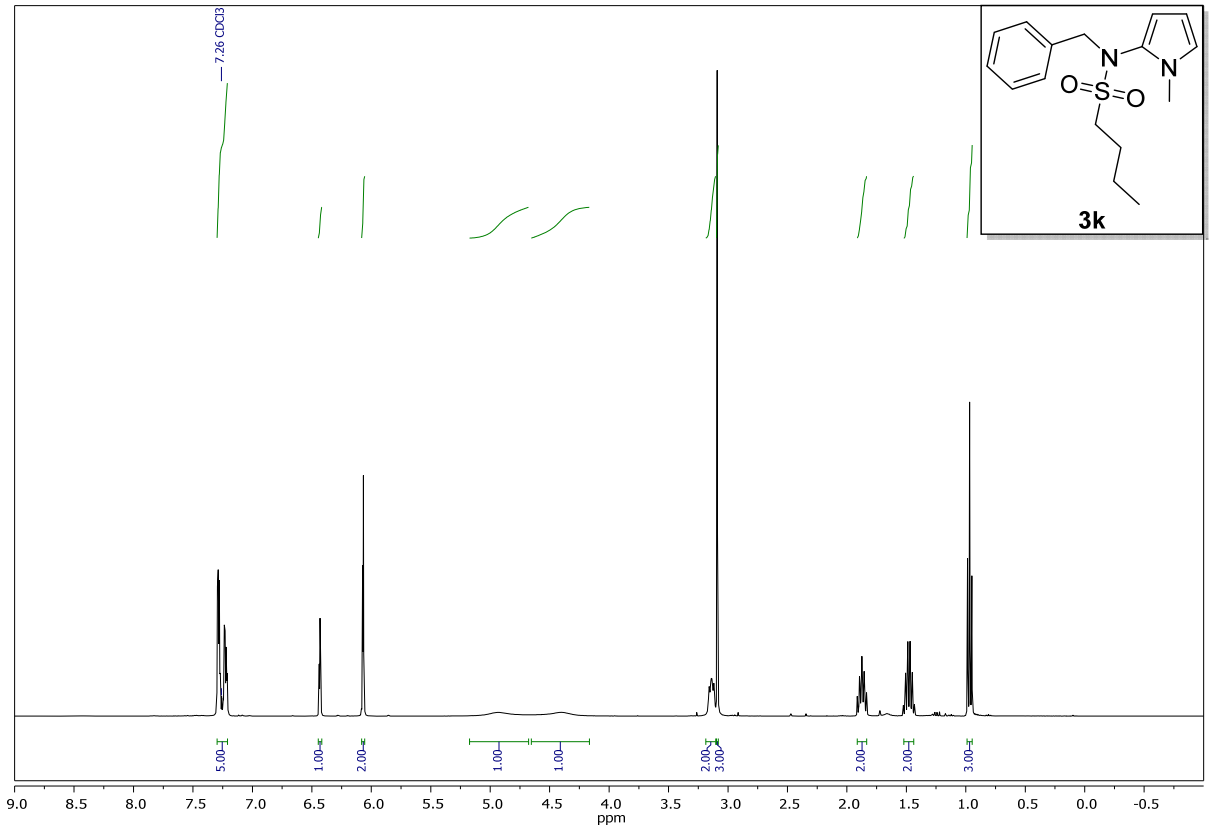
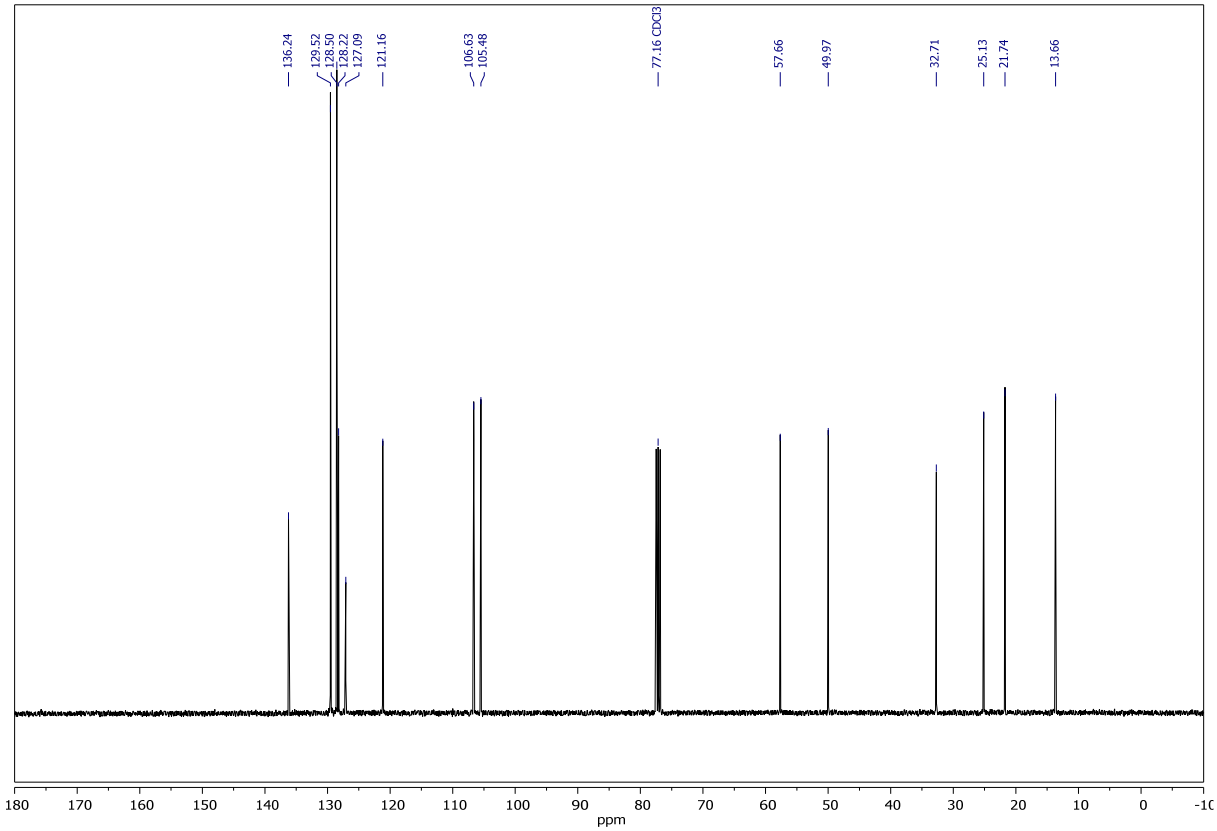


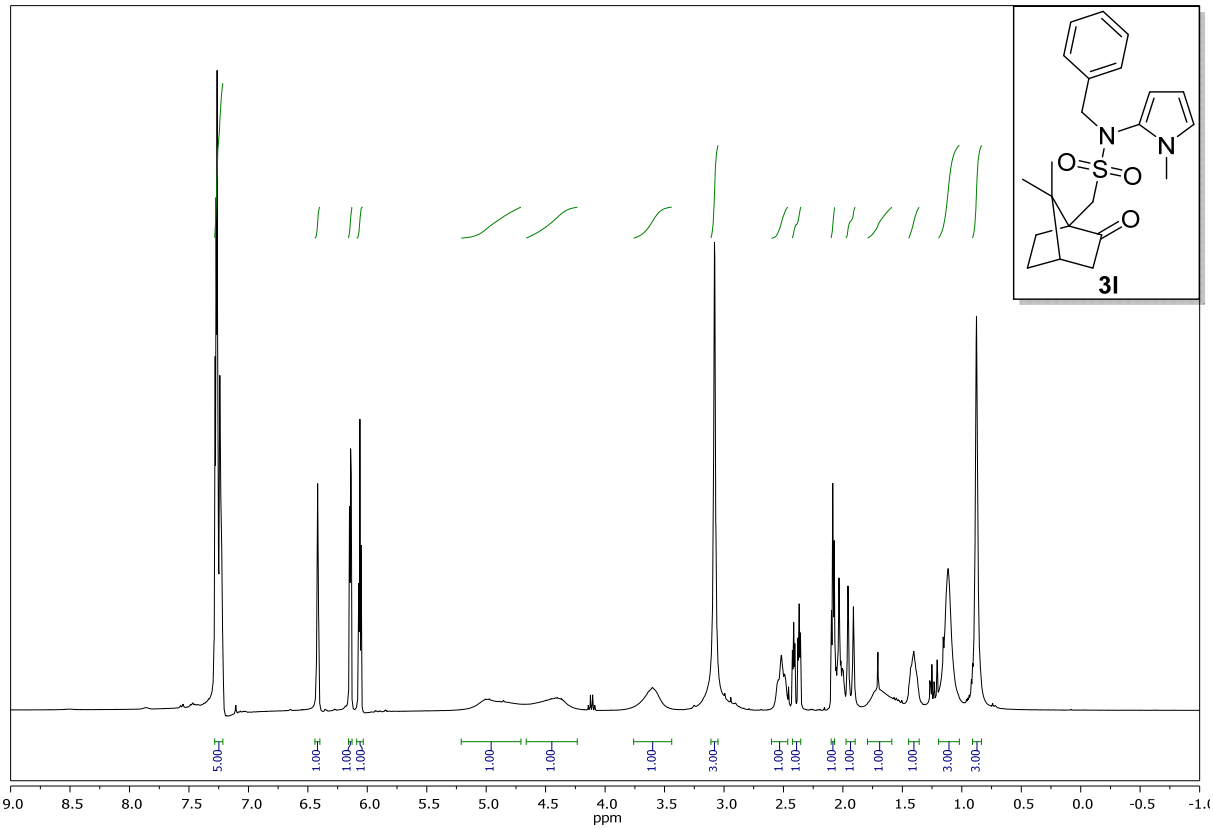


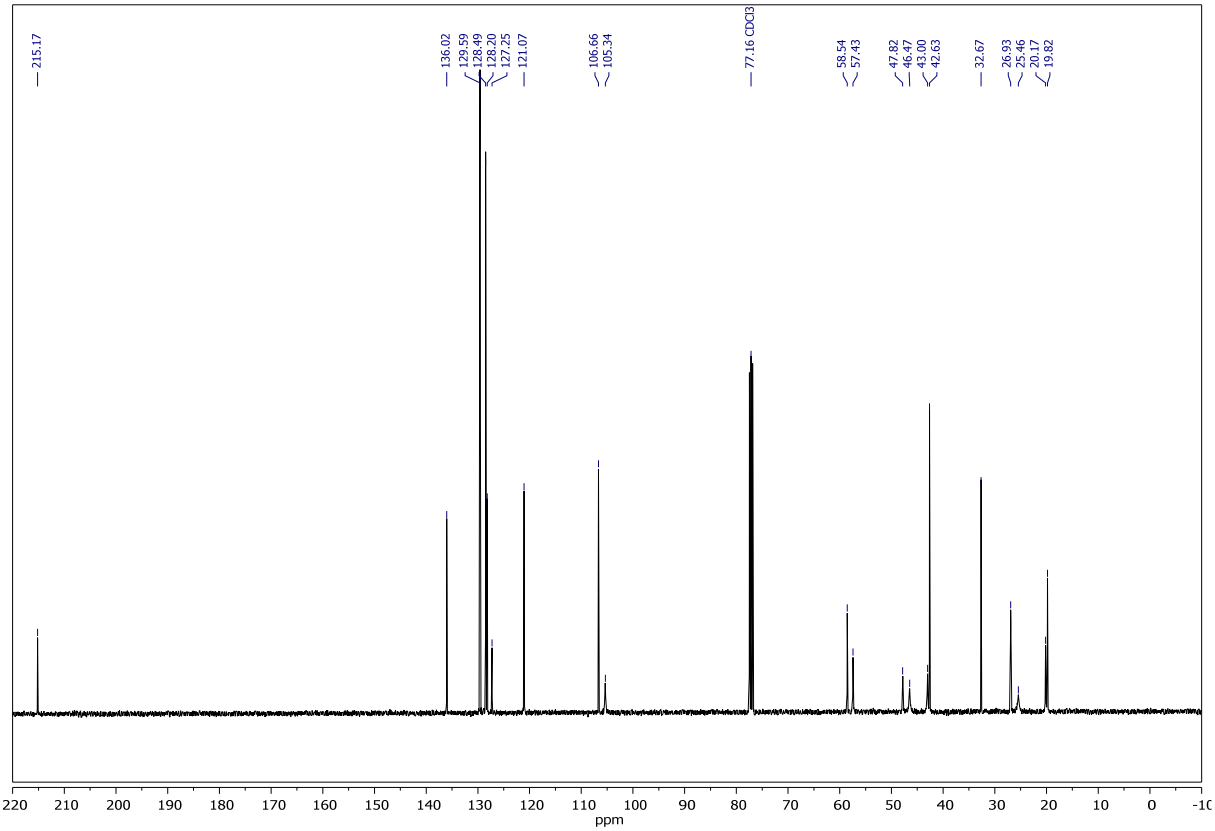
Compound **3k**, ^{1}H-, and ^{13}C-NMR ($CDCl_3$):



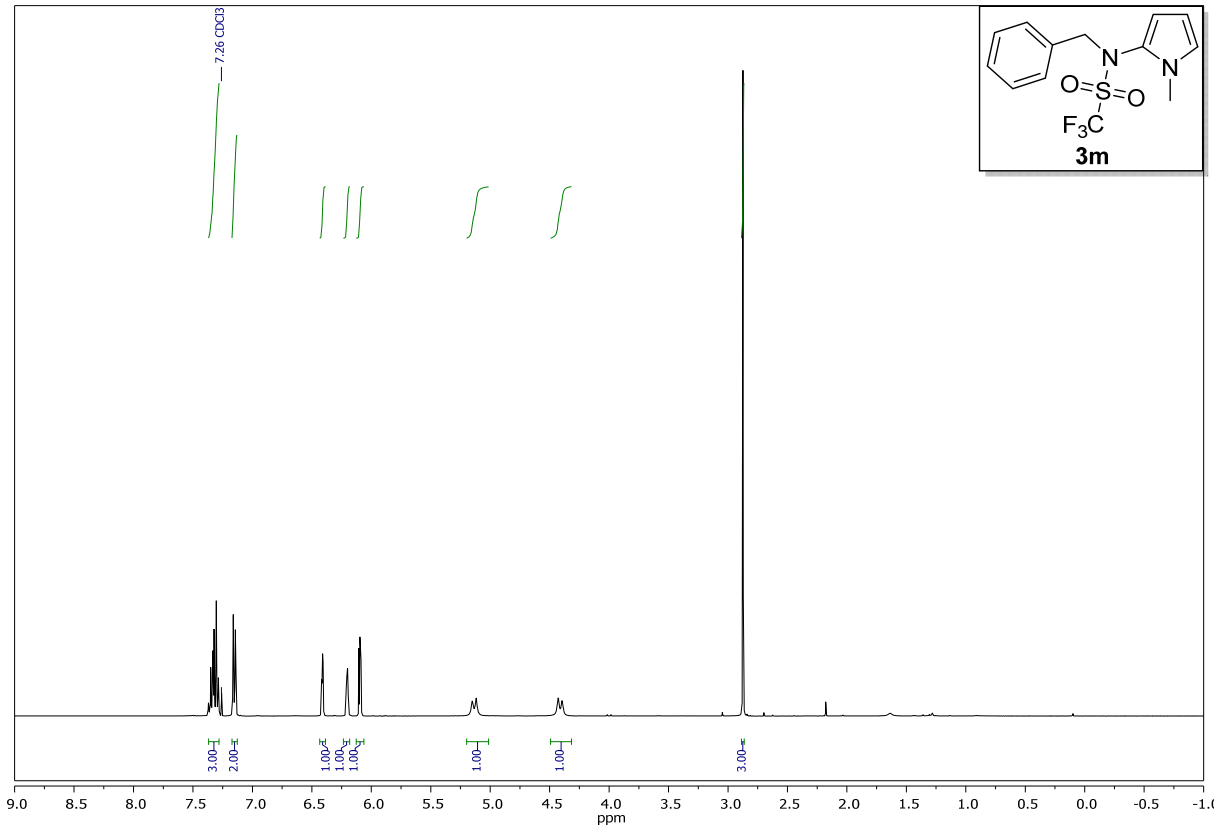


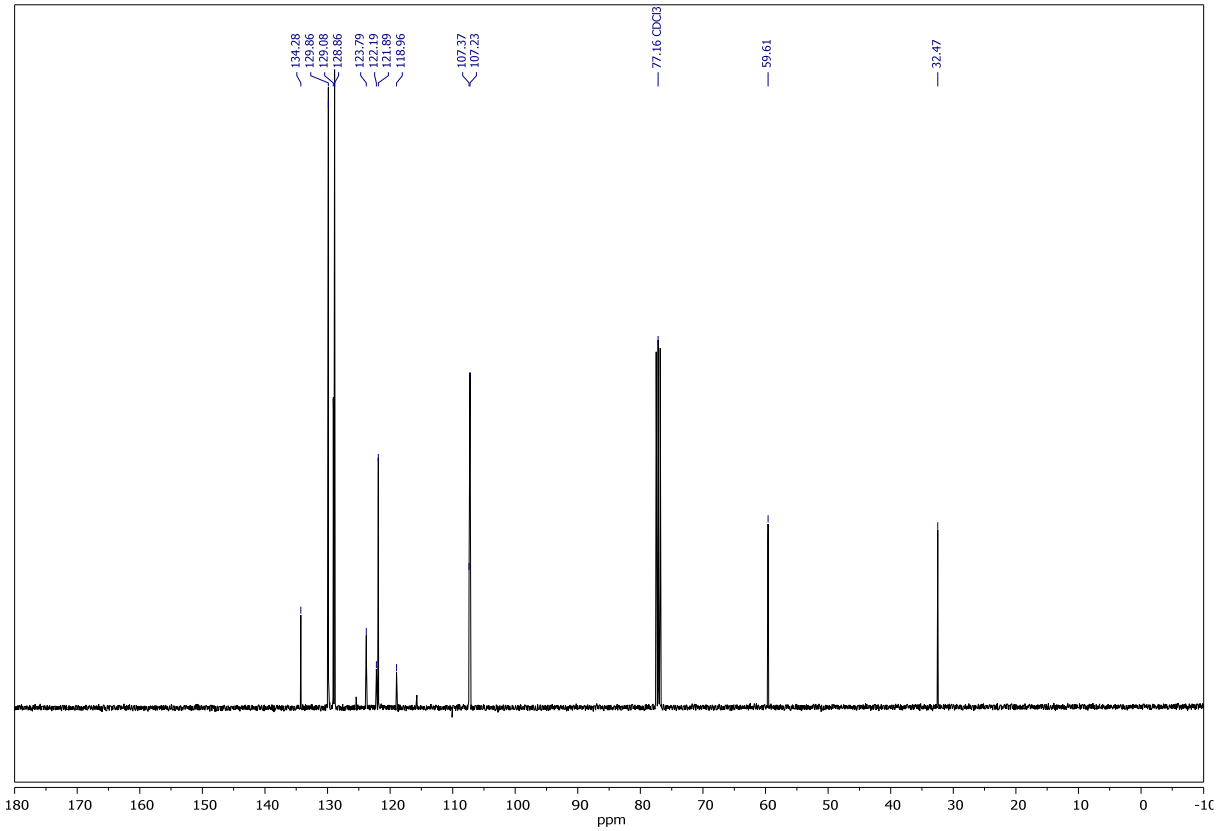
Compound **3l**, ^{1}H-, and ^{13}C-NMR ($CDCl_3$):

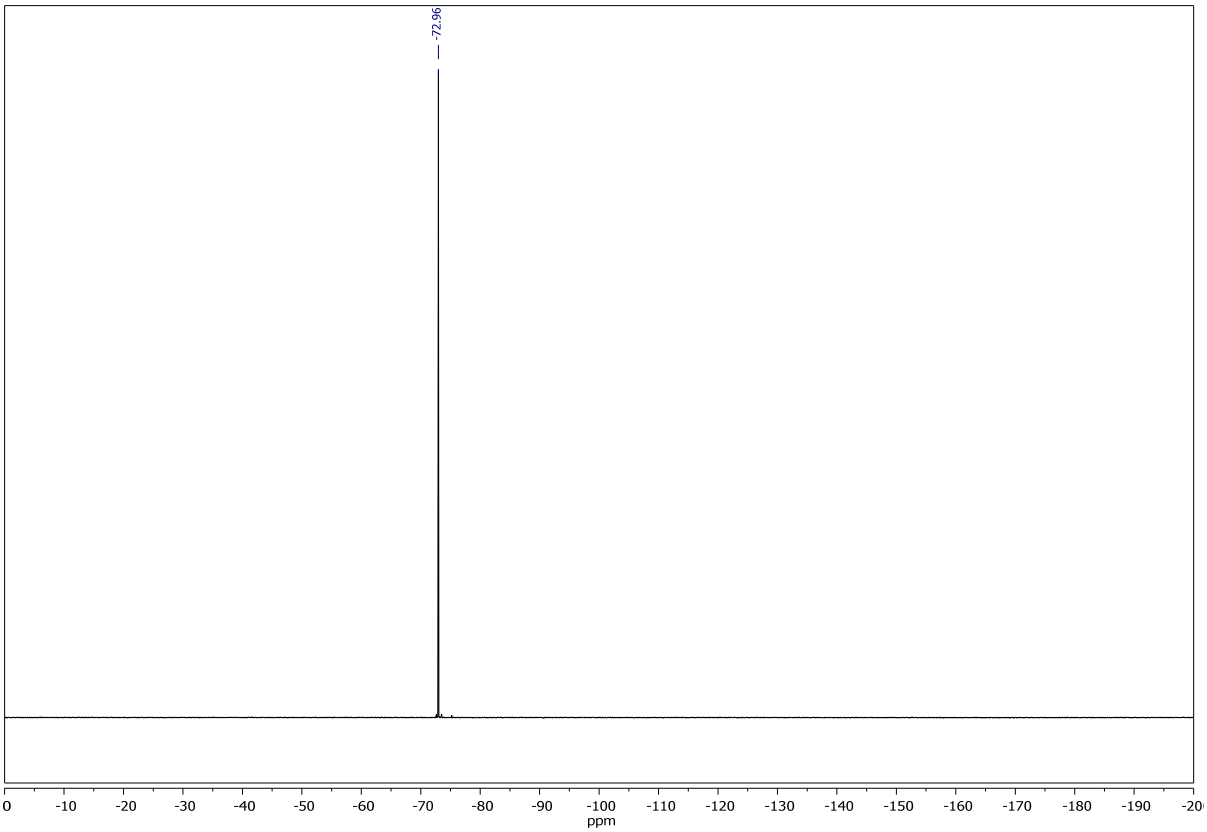




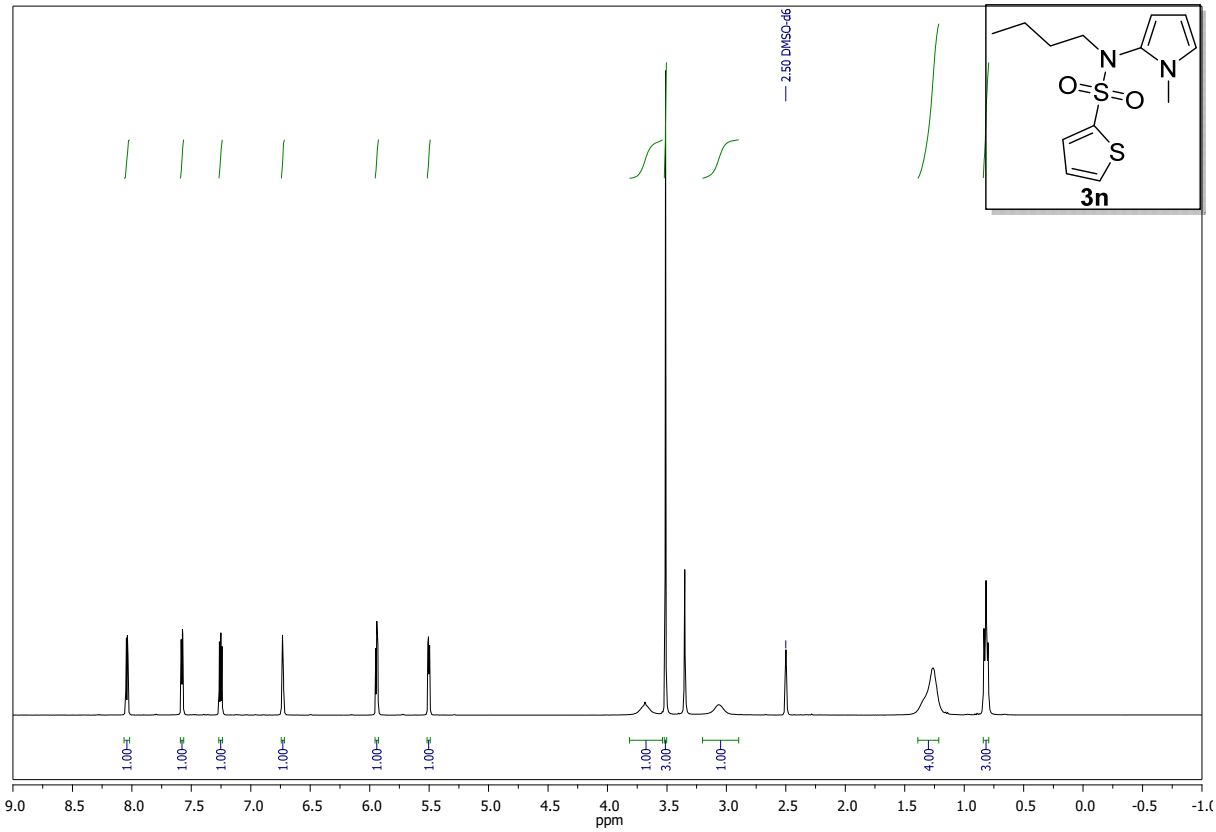
Compound **3m**, ^{1}H-, ^{13}C and ^{19}F-NMR ($CDCl_3$):

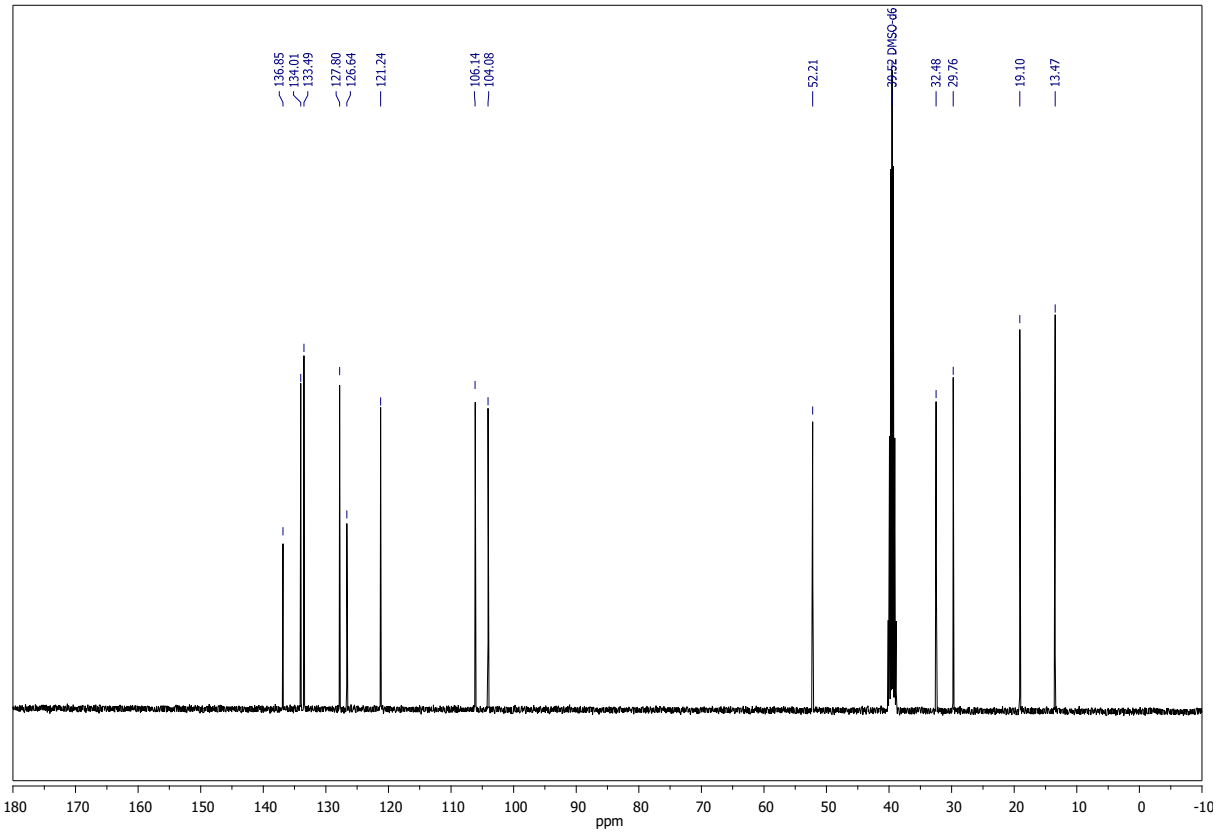




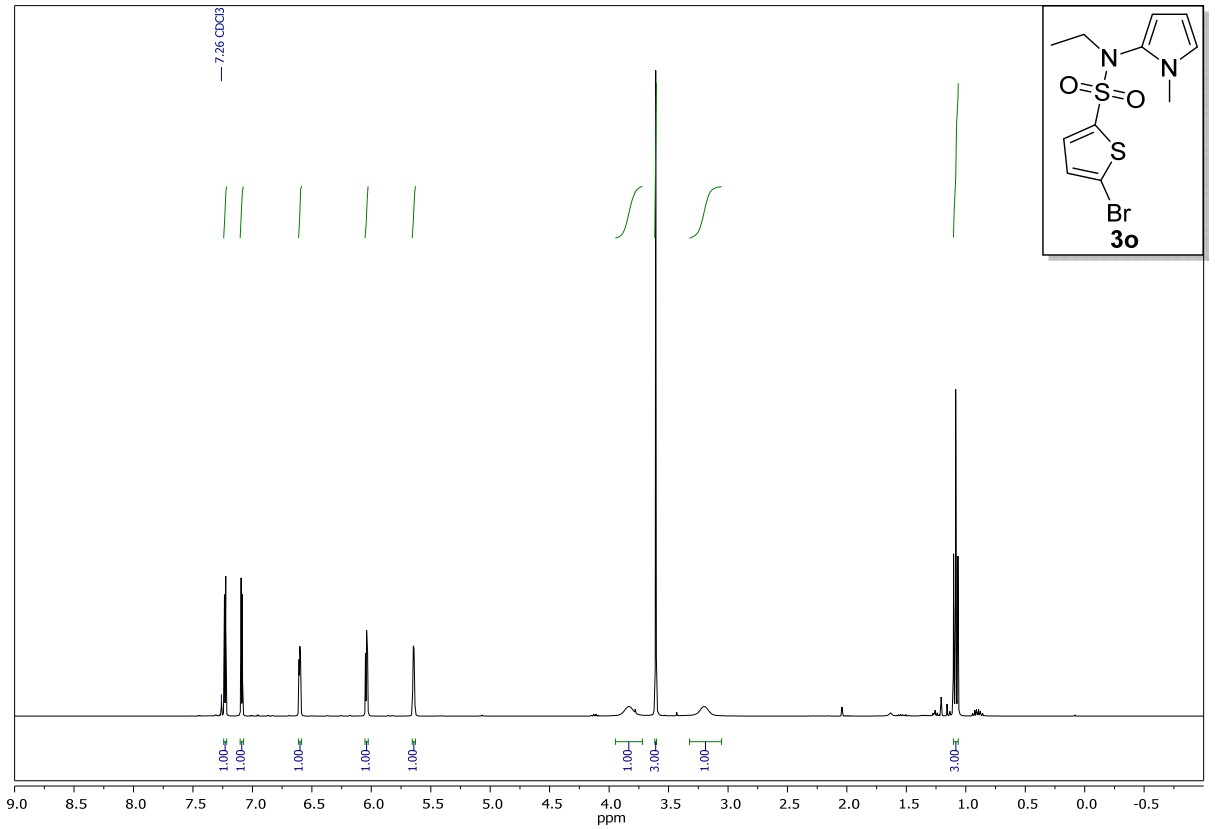

-72.96
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
ppm

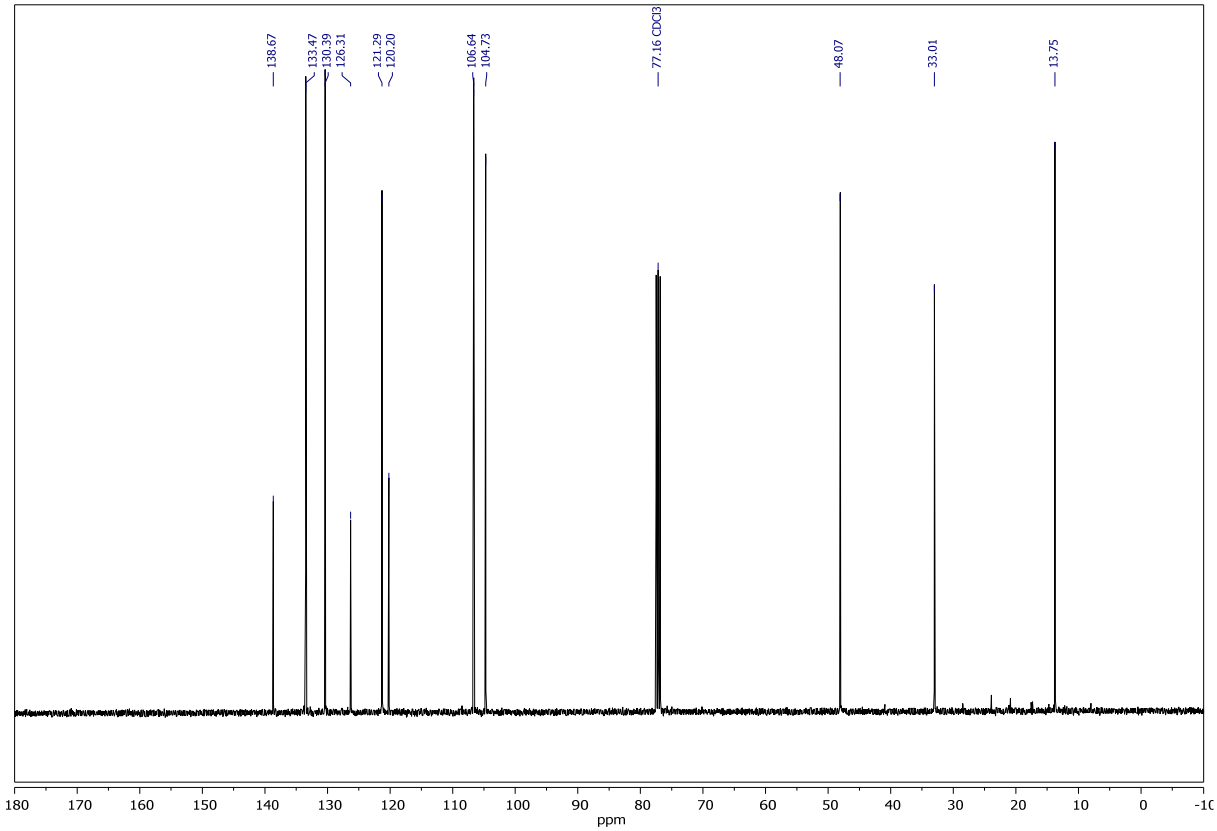
Compound **3n**, ^{1}H-, and ^{13}C-NMR (DMSO-d_6):



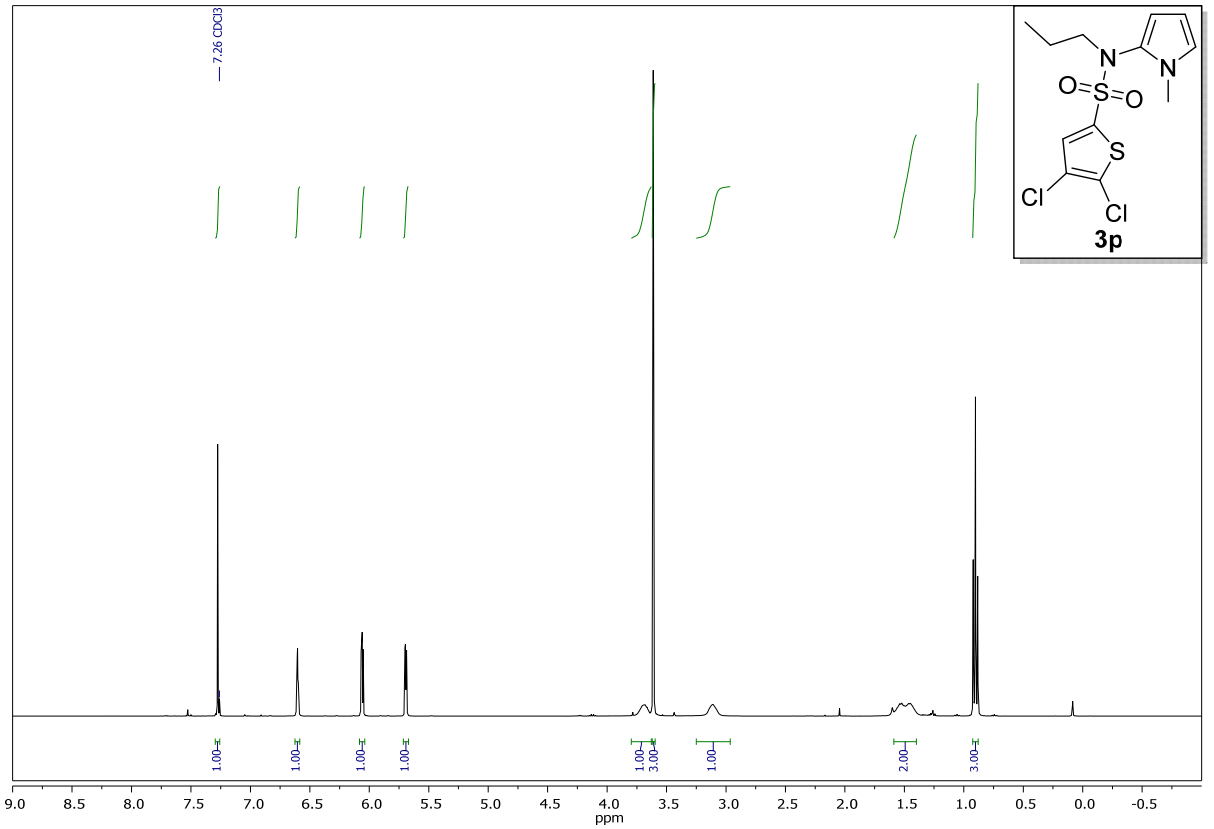


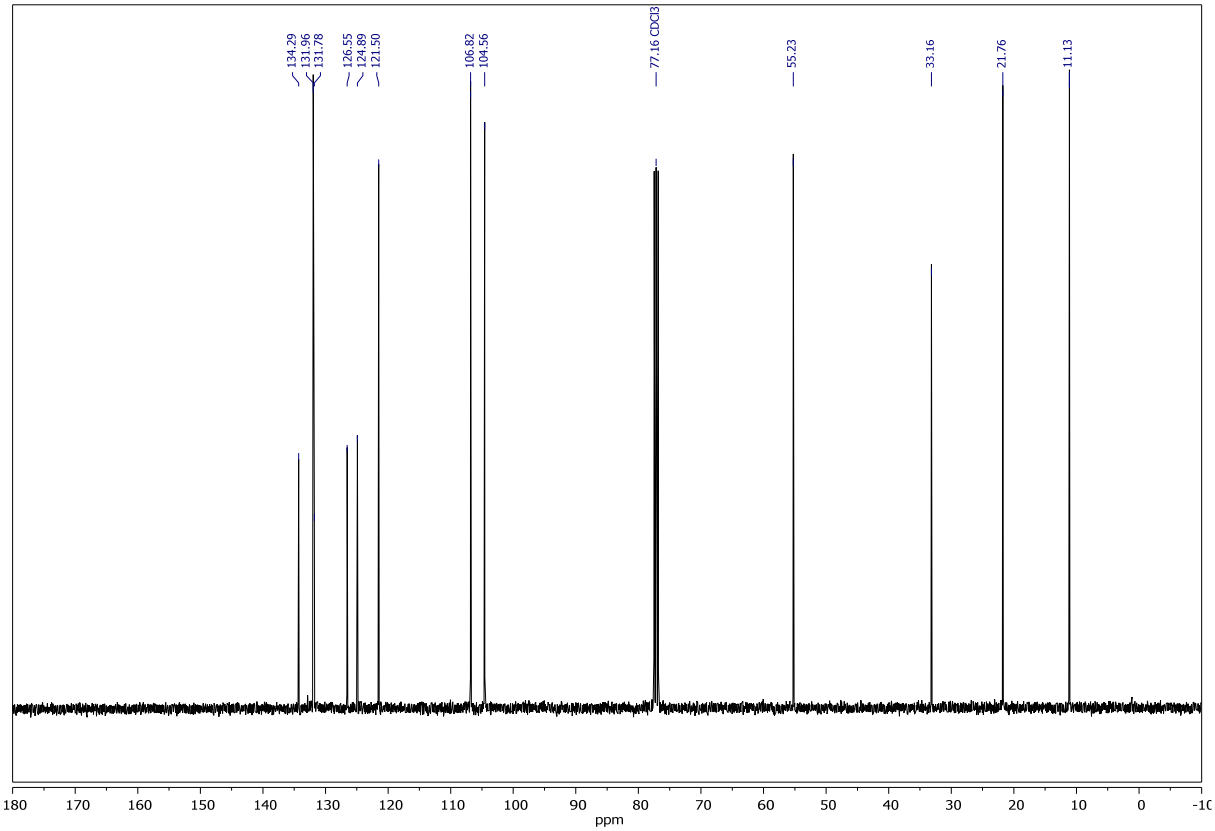
Compound **3o**, ^{1}H-, and ^{13}C-NMR ($CDCl_3$):



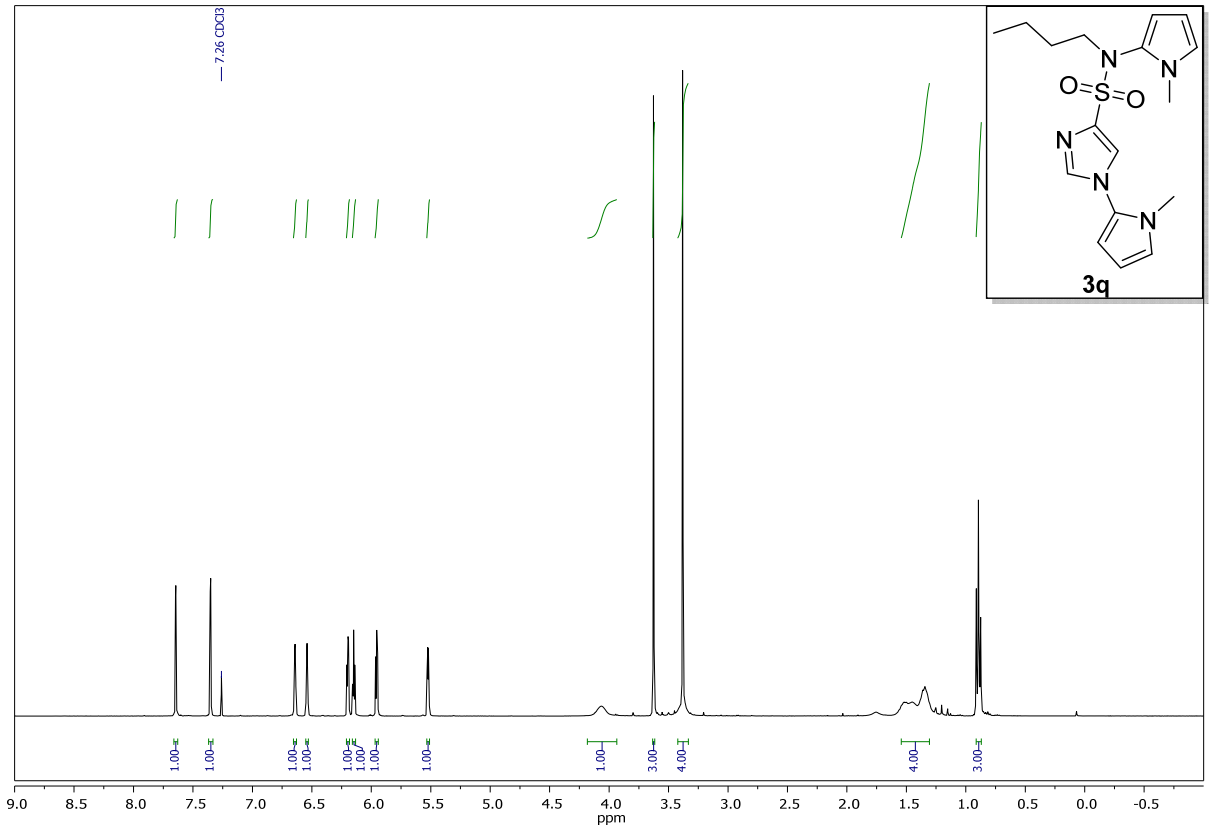


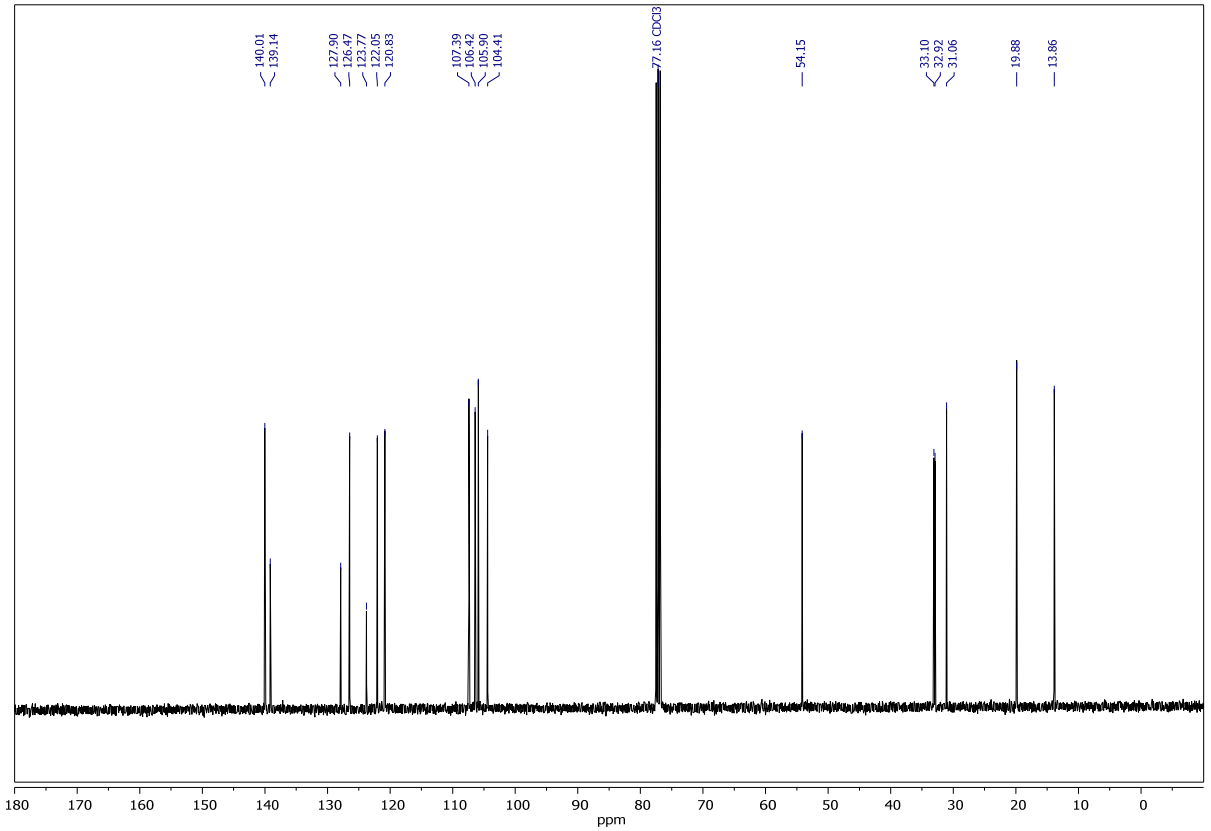
Compound **3p**, ^{1}H-, and ^{13}C-NMR ($CDCl_3$):



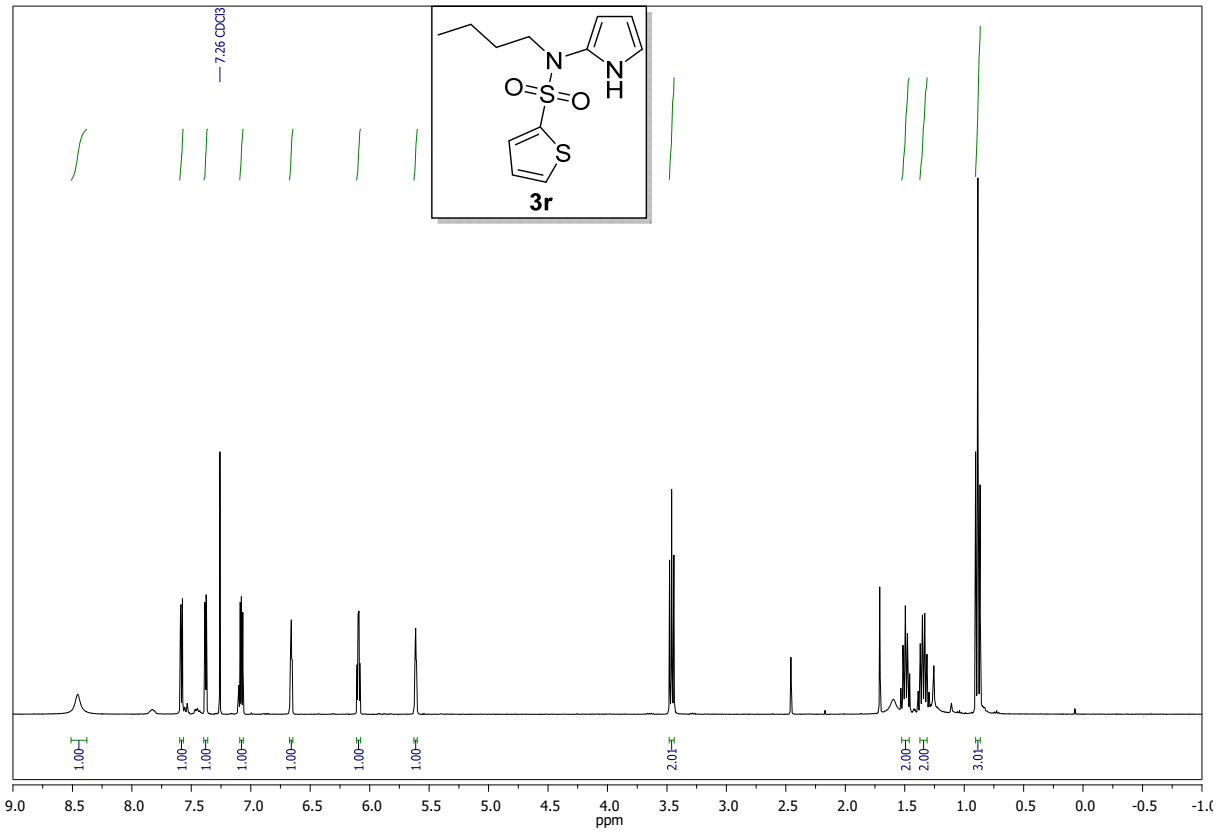


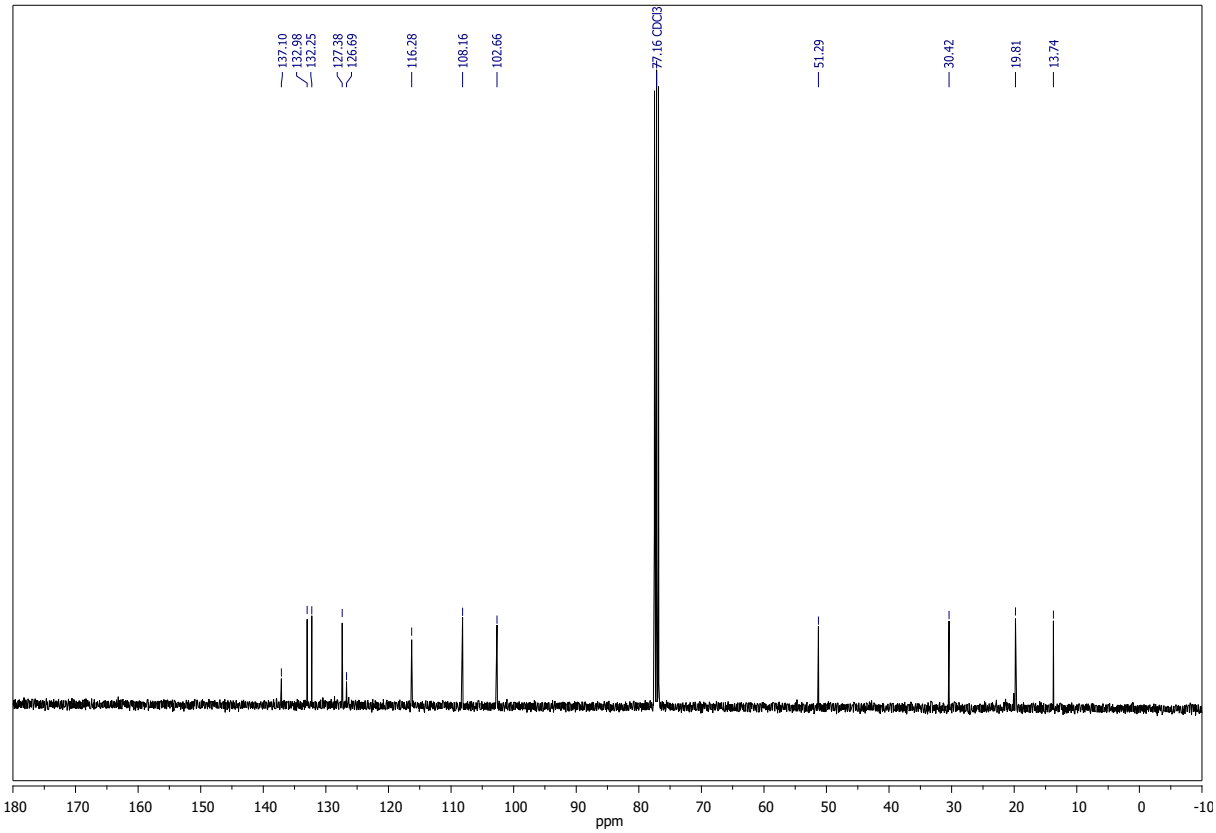
Compound **3q**, ^{1}H-, and ^{13}C-NMR ($CDCl_3$):



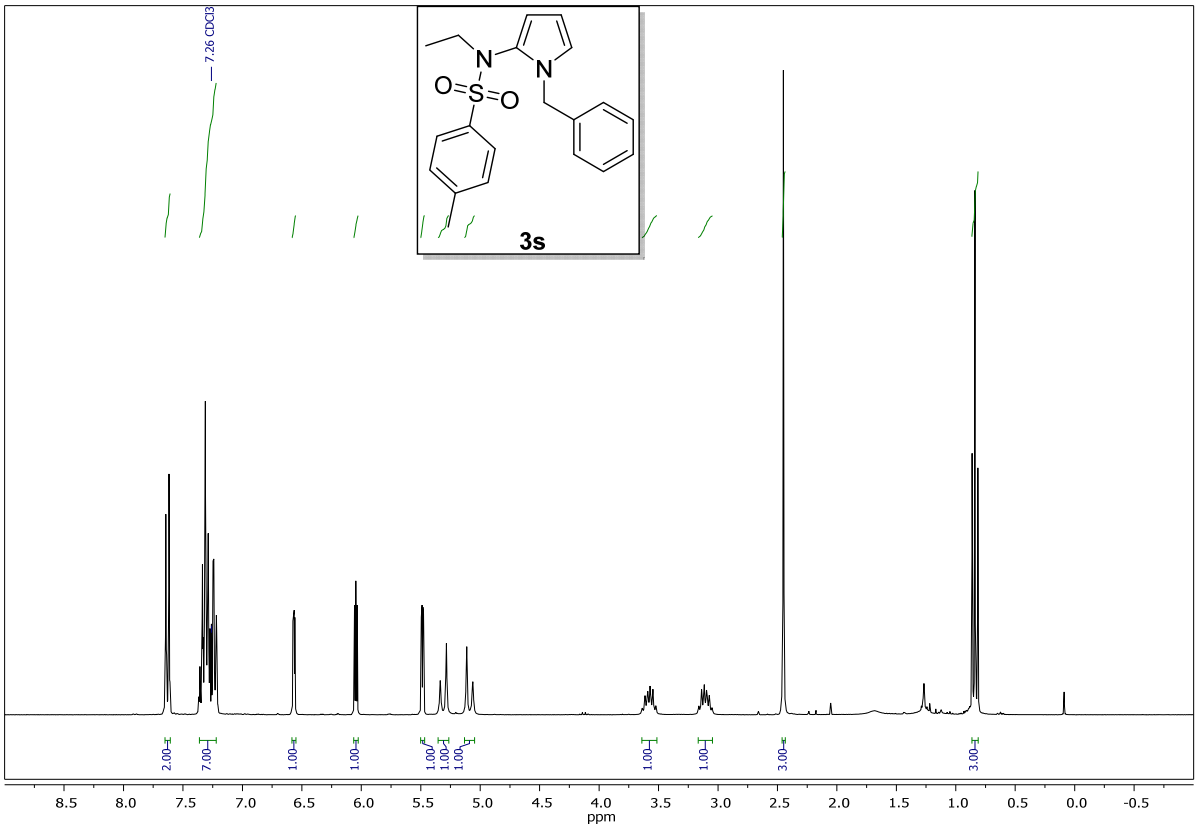


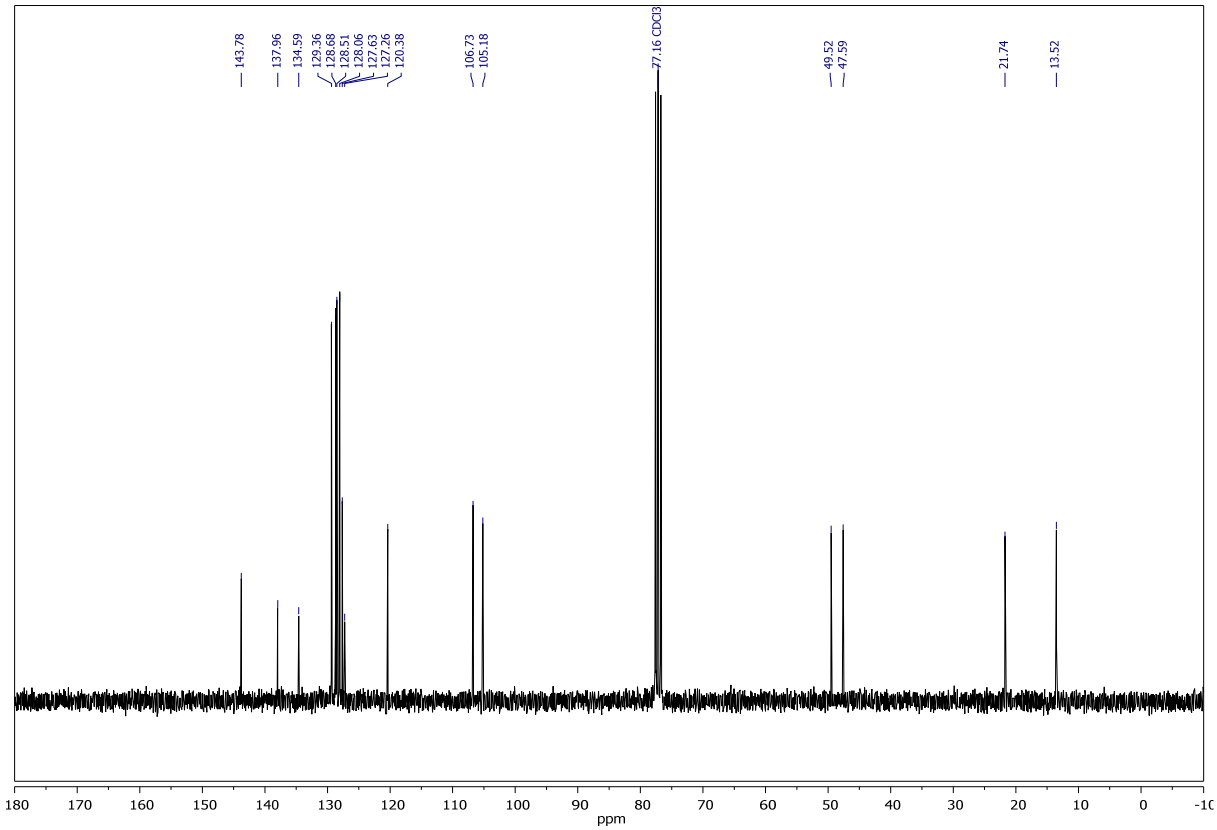
Compound **3r**, ^{1}H-, and ^{13}C-NMR ($CDCl_3$):



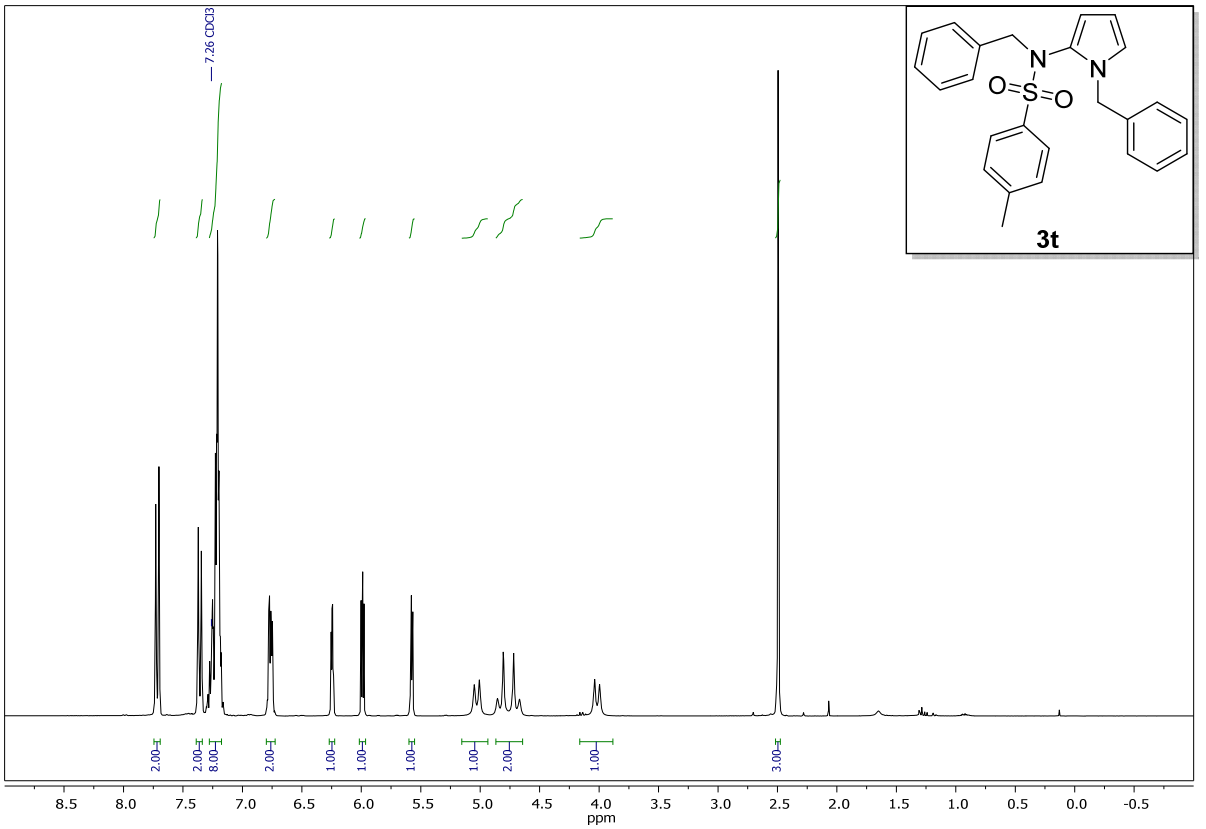


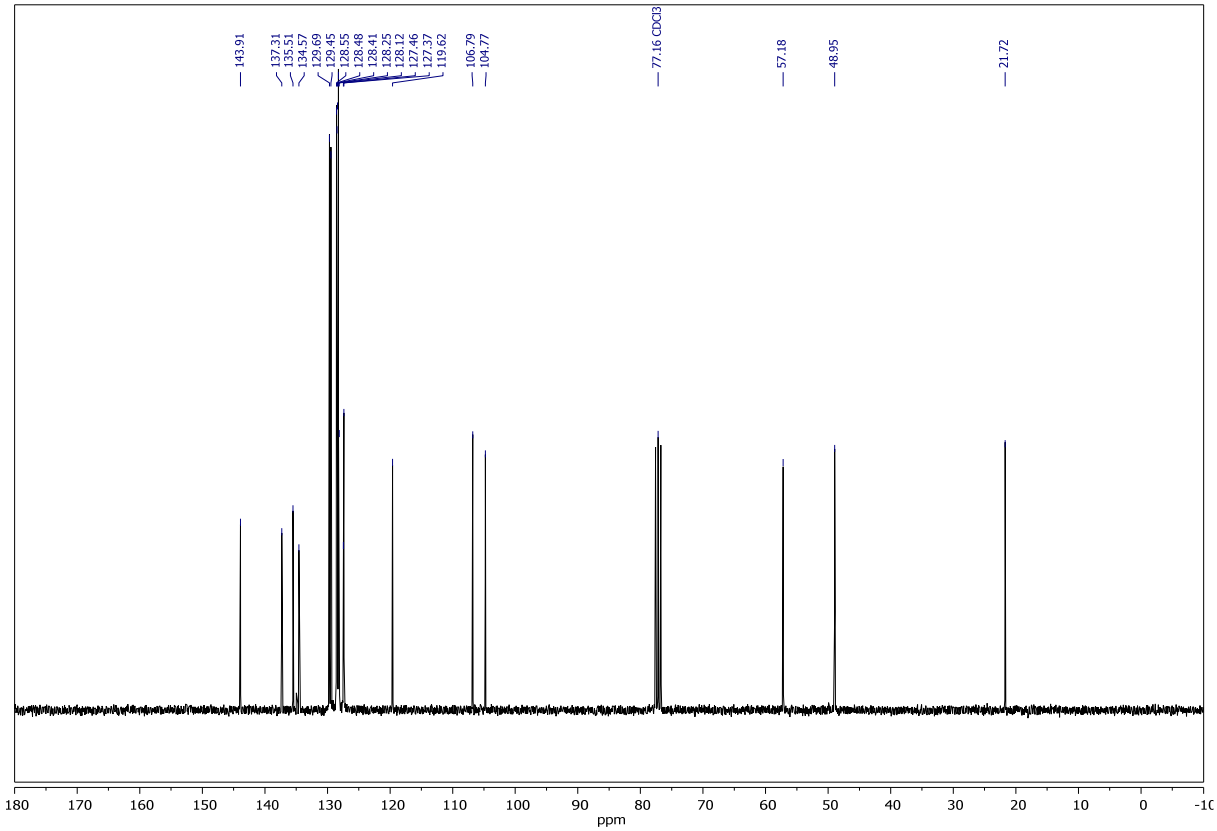
Compound **3s**, ^{1}H-, and ^{13}C-NMR ($CDCl_3$):



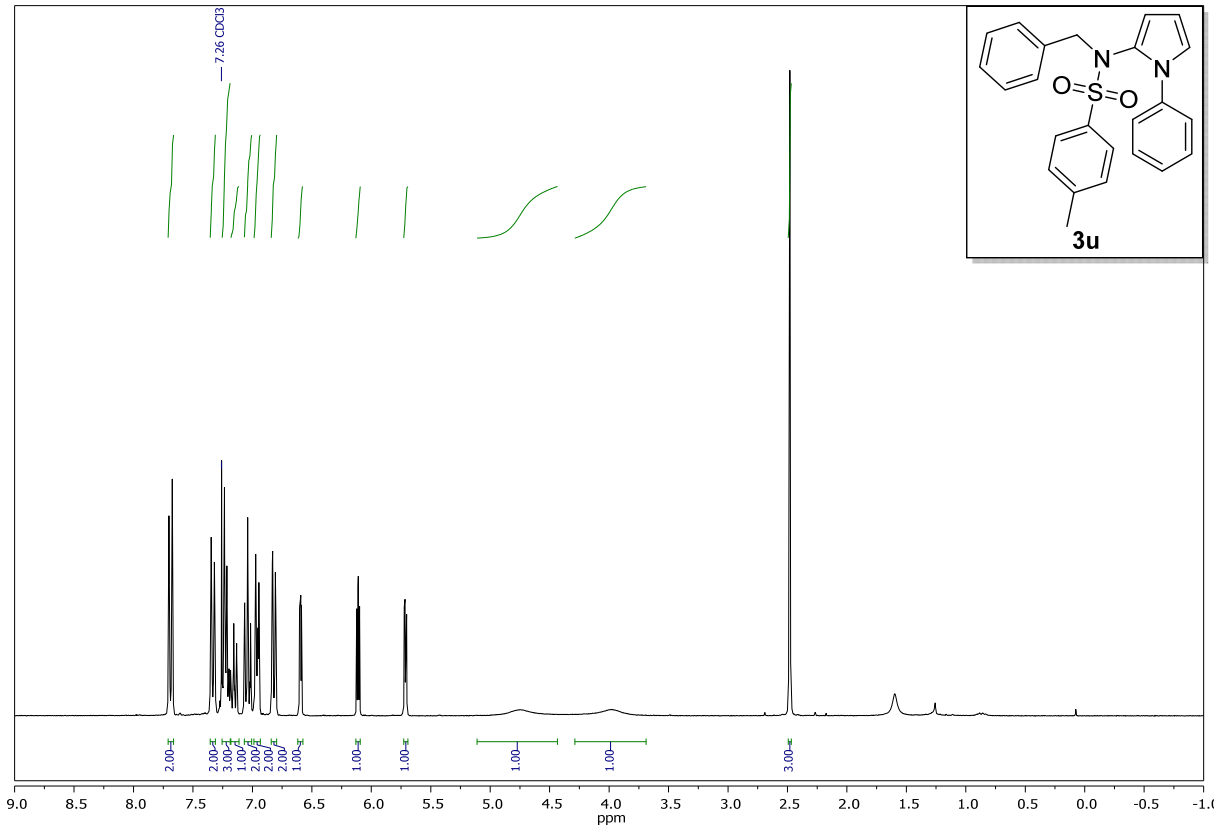


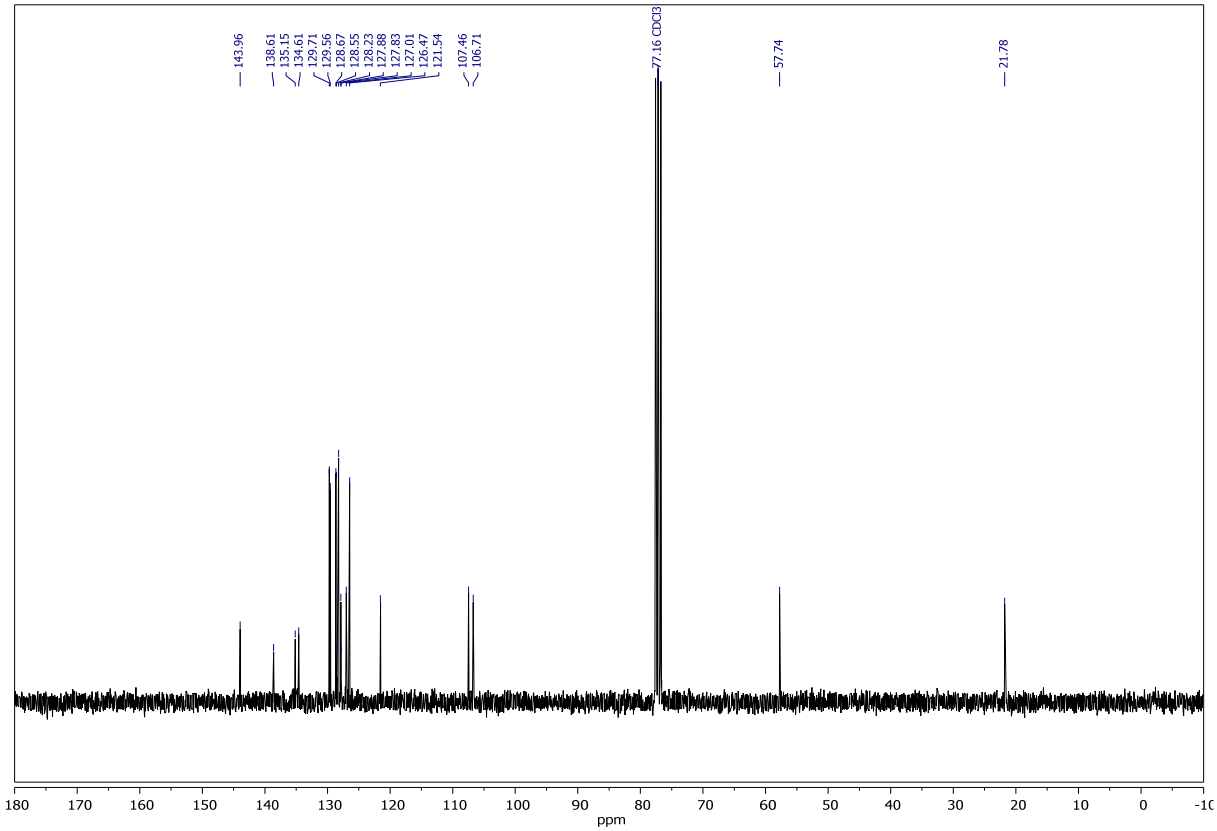
Compound **3t**, ^{1}H-, and ^{13}C-NMR ($CDCl_3$):





Compound **3u**, ^{1}H-, and ^{13}C-NMR ($CDCl_3$):





5. References

[1] R. K. Harris, E. D. Becker, S. M. Cabral de Menezes, R. Goodfellow, P. Granger, *Magn. Reson. Chem.* **2002**, *40*, 489-505.

[2] a) H. E. Gottlieb, V. Kotlyar, A. Nudelman, *J. Org. Chem.* **1997**, *62*, 7512-7515; b) G. R. Fulmer, A. J. M. Miller, N. H. Sherden, H. E. Gottlieb, A. Nudelman, B. M. Stoltz, J. E. Bercaw, K. I. Goldberg, *Organometallics* **2010**, *29*, 2176-2179.

[3] C. Schneider, E. Broda, V. Snieckus, *Org. Lett.* **2011**, *13*, 3588-3591.

[4] X. Pan, J. Gao, J. Liu, J. Lai, H. Jiang, G. Yuan, *Green Chem.* **2015**, *17*, 1400-1403.

[5] C. Buathongjan, D. Beukeaw, S. Yotphan, *Eur. J. Org. Chem.* **2015**, *2015*, 1575-1582.

[6] J. E. Banning, J. Gentillon, P. G. Ryabchuk, A. R. Prosser, A. Rogers, A. Edwards, A. Holtzen, I. A. Babkov, M. Rubina, M. Rubin, *J. Org. Chem.* **2013**, *78*, 7601-7616.

[7] S. Y. Chow, M. Y. Stevens, L. R. Odell, *J. Org. Chem.* **2016**, *81*, 2681-2691.

[8] B. T. Burlingham, T. S. Widlanski, *J. Am. Chem. Soc.* **2001**, *123*, 2937-2945.

[9] Y. Joyard, C. Papamicael, P. Bohn, L. Bischoff, *Org. Lett.* **2013**, *15*, 2294-2297.

[10] N. W. Barnett, R. Bos, S. W. Lewis, R. A. Russell, *Analyst* **1998**, *123*, 1239-1245.

[11] F. Zhao, B. Li, H. Huang, G.-J. Deng, *RSC Adv.* **2016**, *6*, 13010-13013.

[12] A. Alba, A. Schopp, A.-P. De Sousa Delgado, R. Cherif-Cheikh, B. Martín-Vaca, D. Bourissou, *J. Polym. Sci., Part A: Polym. Chem.* **2010**, *48*, 959-965.