ELECTRONIC SUPPORTING INFORMATION

For

Highly Chemoselective Homologative Assembly of the α-Substituted Methylsulfinamide Motif from *N*-Sulfinylamines

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TABLE OF CONTENTS

Instrumentation and General Analytical Methods

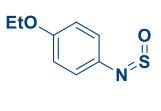
Melting points were determined on a Reichert–Kofler hot-stage microscope and are uncorrected. Mass spectra were obtained on a Shimadzu QP 1000 instrument (EI, 70 eV) and on a Bruker maXis 4G instrument (ESI-TOF, HRMS). ^{1}H and ^{13}C NMR spectra were additionally recorded with a Bruker 200 spectrometer (200 MHz for ^{1}H, 50 MHz for ^{13}C), with a JEOL 600 spectrometer (600 MHz for ^{1}H, 150 MHz for ^{13}C) and with a Bruker Advance III 500 spectrometer (500 MHz for ^{1}H, 125 MHz for ^{13}C. The center of the (residual) solvent signal was used as an internal standard which was related to TMS with δ 7.26 ppm (^{1}H in $CDCl_3$), 7.16 ppm (^{1}H in C_6D_6), 2.05 ppm (^{1}H in acetone-d_6) and δ 77.0 ppm (^{13}C in $CDCl_3$), 128.06 (^{13}C in C_6D_6), 202.26 – 29.84 ppm (^{13}C in acetone-d_6).[1] When recording ^{1}H spectra in acetone-d_6, occasionally it could be observed the water signal in this deuterated solvent at δ 2.84 ppm; in case of recording ^{13}C spectra in acetone-d_6 it could be noticed overlapping of alkyl-type signals at *ca.* δ 29.8 ppm. Spin-spin coupling constants (*J*) are given in Hz. In nearly all cases, full and unambiguous assignment of all resonances was performed by combined application of standard NMR techniques, such as APT, HSQC, HMBC, HSQCTOCSY, COSY and NOESY experiments.

Starting materials were prepared as detailed below; those ones not reported in the manuscript are indicated with the descriptor **nn-*sm***, being **nn** the corresponding final compound in the manuscript.

All reactions were performed under an inert atmosphere of argon using standard schlenk techniques. THF and 2-MeTHF were distilled over Na/benzophenone. Chemicals were purchased from SigmaAldrich, Acros, Alfa Aesar, Fluorochem and TCI Europe. Solutions were evaporated under reduced pressure with a rotary evaporator. For column chromathography, silica Gel 60 (0.04-0.063 mm) was used. TLC was carried out on aluminium sheets precoated with silica gel 60F254 (Merchery-Nagel, Merk); the spots were visualised under UV light (λ = 254 nm) and/or $KMnO_4$ (aq.) was used as revealing system.

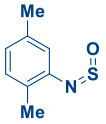
Synthesis of Starting Materials

Most of *N*-sulfinylamines employed as starting materials are known substrates and were prepared as previously reported (see Table below).



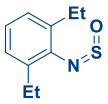
Ling, L. *et al.*
ACS Catal. 2022, **12**, 15334

1



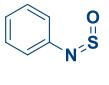
Hanson, P. *et al*.
J. Chem. Soc., Perkin Trans. I 1984**,** 2429

5-*sm*



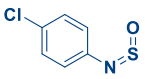
Davis, M. *et al.*
J. Chem. Soc., Perkin Trans. I 1973, 2057

6-*sm*



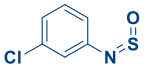
Ling, L. *et al.*
ACS Catal. 2022, **12**, 15334

7-*sm*



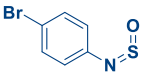
Ling, L. *et al.*
ACS Catal. 2022, **12**, 15334

10-*sm*



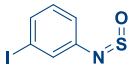
Ling, L. *et al.*
ACS Catal. 2022, **12**, 15334

11-*sm*



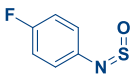
Ling, L. *et al.*
ACS Catal. 2022, **12**, 15334

12-*sm*



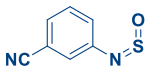
Makarov, A. Y. *et al.*
Heteroat. Chem, 2001,**12**, 563

13-*sm*



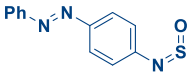
Ling, L. *et al.*
ACS Catal. 2022, **12**, 15334

14-*sm*



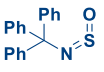
Meller, A. *et al.*
Chem. Ber. 1980, **113**, 1950

16-*sm*



Zibarev, A.V. *et al.*
Russ. J. Gen. Chem. 1988, **58**, 404

19-*sm*



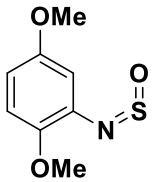
Ling, L. et al.
ACS Catal. 2022, **12**, 15334

27-*sm*

Unknown analogues were obtained adapting reported procedures,[2] according to the general protocol:

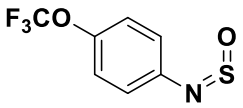
Under Ar atmosphere, to a solution of the competent amine (1.0 equiv) in dry diethyl ether, was added triethylamine (2.0 equiv) and, the mixture is cooled down to 0 °C. Then $SOCl_2$ (1.0 equiv) was added dropwise and the resulting mixture was stirred for 2 hours at 0 °C before it was filtered over celite. Upon removal of the solvent under reduced pressure, the final product was obtained in sufficiently pure form (as judged by ^{1}H-NMR spectra) without needing of further operations. Due to the well known instability of most of *N*-sulfinylamines,[3] they were used in the homologative sequence immediately after their preparation and proof of purity *via* ^{1}H-NMR analysis.

2,5-dimethoxy-*N*-sulfinylaniline (3-*sm*)



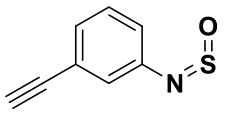
By following the general protocol, starting from 2,5-dimethoxyaniline (0.153 g, 1.0 mmol, 1.0 equiv), triethylamine (0.202 g, 0.28 mL, 2.0 mmol, 2.0 equiv) and $SOCl_2$ (0.119 g, 0.07 mL, 1.0 mmol, 1.0 equiv) in dry diethyl ether (5 mL), compound **3-*sm*** was obtained quantitatively (0.199 g) as a brown solid. **^{1}H NMR** (200 MHz, Acetone-d_6) δ: 6.69 (d, 1H, Ph H-3), 6.32 (d, 1H, Ph H-6), 6.12 (dd, 1H, Ph H-4), 3.74 (s, 3H, OMe C-2), 3.65 (s, 3H, OMe C4).

4-trifluoromethoxy-*N*-sulfinylaniline (4-*sm*)



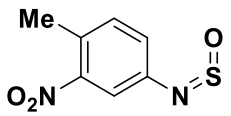
By following the general protocol, starting from 4-trifluoromethoxyaniline (0.177 g, 0.13 mL, 1.0 mmol, 1.0 equiv), triethylamine (0.202 g, 0.28 mL, 2.0 mmol, 2.0 equiv) and $SOCl_2$ (0.119 g, 0.07 mL, 1.0 mmol, 1.0 equiv) in dry diethyl ether (5 mL), compound **4-*sm*** was obtained quantitatively (0.223 g) as a brown solid. **^{1}H NMR** (200 MHz, $CDCl_3$) δ: 7.93 (m, 2H, Ph H-2,6), 7.25 (m, 2H, Ph H-3,5).

3-ethynyl-*N*-sulfinylaniline (8-*sm*)



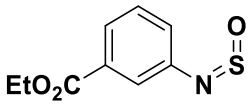
By following the general protocol, starting from 3-ethynylaniline (0.117 g, 0.11 mL, 1.0 mmol, 1.0 equiv), triethylamine (0.202 g, 0.28 mL, 2.0 mmol, 2.0 equiv) and $SOCl_2$ (0.119 g, 0.07 mL, 1.0 mmol, 1.0 equiv) in dry diethyl ether (5 mL), compound **8-*sm*** was obtained quantitatively (0.163 g) as a dark brown solid. **^{1}H NMR** (200 MHz, Acetone-d6) δ: 7.92 (brs, 1H), 7.80 (m, 1H), 7.54 (m, 2H), 3.77 (s, 1H, CCH).

4-methyl-3-nitro-*N*-sulfinylaniline (15-*sm*)



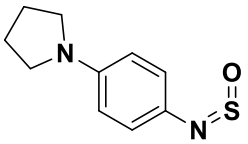
By following the general protocol, starting from 4-methyl-3-nitrolaniline (0.152 g, 1.0 mmol, 1.0 equiv), triethylamine (0.202 g, 0.28 mL, 2.0 mmol, 2.0 equiv) and $SOCl_2$ (0.119 g, 0.07 mL, 1.0 mmol, 1.0 equiv) in dry diethyl ether (5 mL), compound **15-*sm*** was obtained quantitatively (0.198 g) as a dark yellow solid. **^{1}H NMR** (200 MHz, Acetone-d6) δ: 8.39 (d, 1H, Ph H-2), 7.96 (dd, 1H, Ph H-6), 7.62 (d, 1H, Ph H-5), 2.61 (s, 3H, Me).

Ethyl 3-(*N*-sulfinylamino)benzoate (17-*sm*)



By following the general protocol, starting from ethyl 3-aminobenzoate (0.165 g, 1.0 mmol, 1.0 equiv), triethylamine (0.202 g, 0.28 mL, 2.0 mmol, 2.0 equiv) and $SOCl_2$ (0.119 g, 0.07 mL, 1.0 mmol, 1.0 equiv) in dry diethyl ether (5 mL), compound **17-*sm*** was obtained quantitatively (0.211 g) as a brown solid. **^{1}H NMR** (200 MHz, Acetone-d6) δ: 8.41 (t, 1H, Ph H-2), 8.13-7.96 (m, 2H, Ph H-4,6), 7.66 (t, 1H, Ph H-5), 4.39 (q, 2H, CH_2), 1.38 (t, 3H, Me).

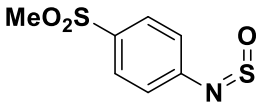
4-(pyrrolidine-1-yl)-*N*-sulfinylaniline (18-*sm*)



By following the general protocol, starting from 4-(pyrrolidine-1-yl)-aniline (0.162 g, 1.0 mmol, 1.0 equiv), triethylamine (0.202 g, 0.28 mL, 2.0 mmol, 2.0 equiv) and $SOCl_2$ (0.119 g, 0.07 mL, 1.0 mmol, 1.0 equiv) in dry

diethyl ether (5 mL), compound **18-*sm*** was obtained quantitatively (0.208 g) as a black solid. **^{1}H NMR** (200 MHz, Acetone-d6) δ: 7.89 (d, 2H, Ph H-3), 6.48 (d, 2H, Ph H-2), 3.37 (m, 4H, N-CH_2), 2.05 (m, 4H, N-CH_2-$\underline{CH_2}$).

Methyl 4-(*N*-sulfinylamino)benzenesulfonate (20-*sm*)



By following the general protocol, starting from methyl 4-aminobenzenesulfonate (0.187 g, 1.0 mmol, 1.0 equiv), triethylamine (0.202 g, 0.28 mL, 2.0 mmol, 2.0 equiv) and $SOCl_2$ (0.119 g, 0.07 mL, 1.0 mmol, 1.0 equiv) in dry diethyl ether (5 mL), compound **20-*sm*** was obtained quantitatively (0.233 g) as a brown solid. **^{1}H NMR** (200 MHz, Acetone-d6) δ: 8.06 (m, 2H, Ph H-3), 7.91 (m, 2H, Ph H-2), 3.18 (s, 3H, Me).

General procedures for the synthesis of α-(halo)substituted methylsulfinamides

α-Halomethylsulfinamides (GP1)

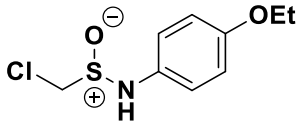
Under Ar atmosphere, to the solution of *N*-sulfinylamine (1.0 equiv) in dry THF, the competent dihalomethane (3 equiv) was added and the resulting solution was cooled down to -78 °C. Then MeLi-LiBr (2.2 M in Et_2O, 2.8 equiv) was added dropwise and, the mixture was stirred for 1 hour at -78 °C; subsequently, a saturated solution of NH_4Cl (aq.) was added. The organic phase was extracted with EtOAc (3 x 10mL) and was washed with brine then, was dried over anhydrous Na_2SO_4 and the solvent was removed under reduced pressure. The final product was obtained after purification by column chromatography on silica gel.

α, α -dihalomethylsulfinamides (GP2)

Under Ar atmosphere, a solution of *n*-BuLi (2.5 M solution in hexanes, 2.2 equiv) was added *via* a syringe pump (rate 0.2 mL/min) to a stirred solution (0 °C) of 2,2,6,6-tetramethylpiperidine (TMP, 2.4 equiv) in dry THF (10 mL) and the mixture was stirred for 15 min. In a separate round-bottomed flask, to the solution of *N*-sulfinylamine (1.0 equiv) in dry THF, the competent dihalomethane (3 equiv) was added and the reaction mixture was cooled down to -78 °C. Then, the freshly prepared LiTMP was added dropwise and the reaction was stirred for 1 hour at -78 °C; subsequently, a saturated solution of NH_4Cl (aq.) was added. The organic phase was extracted with EtOAc (3 x 10mL) and was washed with brine then, was dried over anhydrous Na_2SO_4 and the solvent was removed under reduced pressure. The final product was obtained after purification by column chromatography on silica gel.

Characterization and Spectral Data of the Compounds

1-chloro-*N*-(4-ethoxyphenyl)methanesulfinamide (2)



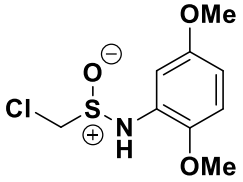
By following GP1, starting from 4-ethoxy-*N*-sulfinylaniline (0.183 g, 1.0 mmol, 1.0 equiv), chloroiodomethane (0.662 g, 0.36 mL, 3.0 mmol, 3.0 equiv) and MeLi-LiBr (2.2 M in Et_2O, 1.2 mL, 2.8 mmol, 2.8 equiv) in dry THF (2 mL), compound **2** was obtained in 85% yield (0.199 g) as a yellow oil after purification by column chromatography on silica gel (Hex:EtOAc 6:4).

^{1}H NMR (500 MHz, Acetone-d_6) δ: 7.78 (brs, 1H, NH), 7.11 (m, 2H, Ph H-2,6), 6.89 (m, 2H, Ph H-3,5), 4.56 (A-part of an AB system, $^2J_{AB}$ = 10.7 Hz, 1H diast, CH_2), 4.53 (B-part of an AB system, $^2J_{AB}$ = 10.7 Hz, 1H diast, CH_2), 4.01 (q, ^3J = 7.0 Hz, 2H, OCH_2), 1.34 (t, ^3J = 7.0 Hz, 3H, CH_3).

^{13}C NMR (125 MHz, Acetone-d_6) δ: 157.0 (Ph C-4), 133.7 (Ph C-1), 123.6 (Ph C-2,6), 115.9 (Ph C-3,5), 64.2 (OCH_2), 58.0 (CH_2), 15.1 (CH_3).

HRMS (ESI), *m/z*: calcd. for $C_9H_{12}ClNNaO_2S^+$: 256.0169 $[M + Na]^+$; found: 256.0173.

1-chloro-*N*-(2,5-dimethoxyphenyl)methanesulfinamide (3)



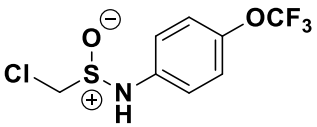
By following GP1, starting from 2,5-dimethoxy-*N*-sulfinylaniline (0.199 g, 1.0 mmol, 1.0 equiv), chloroiodomethane (0.662 g, 0.36 mL, 3.0 mmol, 3.0 equiv) and MeLi-LiBr (2.2 M in Et_2O, 1.2 mL, 2.8 mmol, 2.8 equiv) in dry THF (2 mL), compound **3** was obtained in 78% yield (0.195 g) as a yellow oil after purification by column chromatography on silica gel (DCM:EtOAc 9:1).

^{1}H NMR (500 MHz, Acetone-d_6) δ: 7.57 (brs, 1H, NH), 6.94 (d, ^3J = 8.9 Hz, 1H, Ph H-3), 6.87 (d, ^4J = 2.9 Hz, 1H, Ph H-6), 6.57 (dd, ^3J = 8.9 Hz, ^4J = 2.9 Hz, 1H, Ph H-4), 4.86 (A-part of an AB system, $^2J_{AB}$ = 10.7 Hz, 1H diast, CH_2), 4.73 (B-part of an AB system, $^2J_{AB}$ = 10.7 Hz, 1H diast, CH_2), 3.79 (s, 3H, OCH_3 at C-5), 3.74 (s, 3H, OCH_3 at C-2).

^{13}C NMR (125 MHz, Acetone-d_6) δ: 155.1 (Ph C-2), 144.5 (Ph C-5), 132.2 (Ph C-1), 113.5 (Ph C-3), 107.9 (Ph C-4), 105.3 (Ph C-6), 58.9 (CH_2), 56.9 (OCH_3 at C-5), 55.8 (OCH_3 at C-2).

HRMS (ESI), *m/z*: calcd. for $C_9H_{12}ClNNaO_3S^+$: 272.0119 $[M + Na]^+$; found: 272.0114.

1-chloro-*N*-(4-trifluoromethoxyphenyl)methanesulfinamide (4)



By following GP1, starting from 4-trifluoromethoxy-*N*-sulfinylaniline (0.223 g, 1.0 mmol, 1.0 equiv), chloroiodomethane (0.662 g, 0.36 mL, 3.0 mmol, 3.0 equiv) and MeLi-LiBr (2.2 M in Et_2O, 1.2 mL, 2.8 mmol, 2.8 equiv) in dry THF (2 mL), compound **4** was obtained in 80% yield (0.219 g) as a yellow solid after purification by column chromatography on silica gel (DCM:EtOAc 95:5).

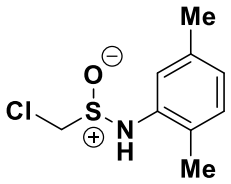
mp = 64-66 °C

^{1}H NMR (500 MHz, Acetone-d_6) δ: 8.38 (brs, 1H), 7.31-7.26 (m, 4H), 4.73 (A-part of an AB system, $^2J_{AB}$ = 10.7 Hz, 1H diast, CH_2), 4.69 (B-part of an AB system, $^2J_{AB}$ = 10.7 Hz, 1H diast, CH_2).

^{13}C NMR (125 MHz, Acetone-d_6) δ: 145.2, 141.4, 123.3, 120.6, 58.6.

HRMS (ESI), *m/z*: calcd. for $C_8H_7ClF_3NNaO_2S^+$: 295.9730 [M + Na]$^+$; found: 295.9730.

1-chloro-*N*-(2,5-dimethylphenyl)methanesulfinamide (5)



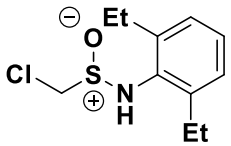
By following GP1, starting from 2,5-dimethyl-*N*-sulfinylaniline (0.167 g, 1.0 mmol, 1.0 equiv), chloroiodomethane (0.662 g, 0.36 mL, 3.0 mmol, 3.0 equiv) and MeLi-LiBr (2.2 M in Et_2O, 1.2 mL, 2.8 mmol, 2.8 equiv) in dry THF (2 mL), compound **5** was obtained in 81% yield (0.176 g) as a yellow oil after purification by column chromatography on silica gel (DCM:EtOAc 95:5).

^{1}H NMR (500 MHz, Acetone-d_6) δ: 7.51 (brs, 1H, NH), 7.13 (s, 1H, Ph H-6), 7.08 (d, ^3J = 7.7 Hz, 1H, Ph H-3), 6.86 (d, ^3J = 7.7 Hz, 1H, Ph H-4), 4.75 (A-part of an AB system, $^2J_{AB}$ = 10.6 Hz, 1H diast, CH_2), 4.65 (B-part of an AB system, $^2J_{AB}$ = 10.6 Hz, 1H diast, CH_2), 2.28 (s, 3H, CH_3 Ph-C5), 2.25 (3H, CH_3 Ph C-2).

^{13}C NMR (125 MHz, Acetone-d_6) δ: 139.8 (Ph C-1), 137.3 (Ph C-5), 131.6 (Ph C-3), 127.5 (Ph C-2), 125.9 (Ph C-4), 122.5 (Ph C-6), 58.3 (CH_2), 21.0 (CH_3 Ph-C5), 18.29 (CH_3 Ph-C2).

HRMS (ESI), *m/z*: calcd. for $C_9H_{12}ClNNaOS^+$: 240.0220 [M + Na]$^+$; found: 240.0221.

1-chloro-*N*-(2,6-diethylphenyl)methanesulfinamide (6)



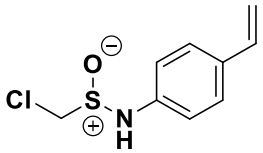
By following GP1, starting from 2,6-diethylsulfinylaniline (0.195 g, 1.0 mmol, 1.0 equiv), chloroiodomethane (0.662 g, 0.36 mL, 3.0 mmol, 3.0 equiv) and MeLi-LiBr (2.2 M in Et_2O, 1.2 mL, 2.8 mmol, 2.8 equiv) in dry THF (2 mL), compound **6** was obtained in 85% yield (0.209 g) as a yellow oil after purification by column chromatography on silica gel (DCM:EtOAc 9:1).

^{1}H NMR (500 MHz, Acetone-d_6) δ: 7.14 (m, 3H, Ph H-3,4,5), 7.09 (brs, 1H, NH), 4.88 (A-part of an AB system, $^2J_{AB}$ = 10.7 Hz, 1H diast, CH_2), 4.72 (B-part of an AB system, $^2J_{AB}$ = 10.7 Hz, 1H diast, CH_2), 2.87-2.73 (m, 4H, $C\underline{H}_2CH_3$), 1.18 (t, ^3J = 7.6 Hz, 6H, $CH_2C\underline{H}_3$).

^{13}C NMR (125 MHz, Acetone-d_6) δ: 142.0 (Ph C-2,6), 136.5 (Ph C-1), 127.7 (Ph C-4), 127.7 (Ph C-3,5), 60.0 (CH_2), 25.3 ($\underline{C}H_2CH_3$), 15.3 ($CH_2\underline{C}H_3$).

HRMS (ESI), *m/z*: calcd. for $C_{11}H_{16}ClNNaOS^+$: 268.0533 [M + Na]$^+$; found: 268.0534.

1-chloro-*N*-(4-vinylphenyl)methanesulfinamide (7)



By following GP1, starting from 4-vinyl-*N*-sulfinylaniline (0.165 g, 1.0 mmol, 1.0 equiv), chloroiodomethane (0.662 g, 0.36 mL, 3.0 mmol, 3.0 equiv) and MeLi-LiBr (2.2 M in Et_2O, 1.2 mL, 2.8 mmol, 2.8 equiv) in dry THF (2 mL), compound **7** was obtained in 79% yield (0.170 g) as a yellow solid after purification by column chromatography on silica gel (DCM:EtOAc 95:5).

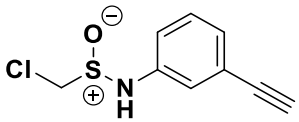
mp = 69-71 °C

^{1}H NMR (500 MHz, Acetone-d_6) δ: 8.17 (s, 1H, NH), 7.43 (m, 2H, Ph), 7.14 (m, 2H, Ph), 6.70 (dd, ^3J = 17.7 Hz, 11.0 Hz, 1H, $C\underline{H}$=CH_2), 5.71 (dd, ^3J = 17.7 Hz, ^2J = 1.0 Hz, 1H, CH$C\underline{H_2}$ trans), 5.15 (dd, ^3J = 11.0 Hz, ^2J = 1.0 Hz, 1H, CH$C\underline{H_2}$ cis), 4.70 (A-part of an AB system, $^2J_{AB}$ = 10.7 Hz, 1H diast, CH_2), 4.65 (B-part of an AB system, $^2J_{AB}$ = 10.7 Hz, 1H diast, CH_2).

^{13}C NMR (125 MHz, Acetone-d_6) δ: 141.8, 137.1, 133.6, 128.2, 119.5, 112.8, 58.5.

HRMS (ESI), *m/z*: calcd. for $C_9H_{10}ClNNaOS^+$: 238.0064 [M + Na]$^+$; found: 238.0061.

1-chloro-*N*-(3-ethynylphenyl)methanesulfinamide (8)



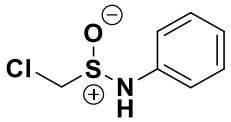
By following GP1, starting from 3-ethynyl-*N*-sulfinylaniline (0.163 g, 1.0 mmol, 1.0 equiv), chloroiodomethane (0.662 g, 0.36 mL, 3.0 mmol, 3.0 equiv) and MeLi-LiBr (2.2 M in Et_2O, 1.2 mL, 2.8 mmol, 2.8 equiv) in dry THF (2 mL), compound **8** was obtained in 82% yield (0.175 g) as a yellow oil after purification by column chromatography on silica gel (DCM:EtOAc 9:1).

^{1}H NMR (500 MHz, Acetone-d_6) δ: 8.23 (brs, 1H), 7.34 (t, ^3J = 8.0 Hz, 1H, Ph H-5), 7.27 (t, ^4J = 1.7 Hz, 1H, Ph H-2), 7.19 (m, 2H, Ph H-4,6), 4.71 (A-part of an AB system, $^2J_{AB}$ = 10.7 Hz, 1H diast, CH_2), 4.67 (B-part of an AB system, $^2J_{AB}$ = 10.7 Hz, 1H diast, CH_2), 3.69 (s, 1H, CCH).

^{13}C NMR (125 MHz, Acetone-d_6) δ: 142.6 (Ph C-1), 130.7 (Ph C-5), 127.4 (Ph C-4), 124.3 (Ph C-3), 122.4 (Ph C-2), 120.1 (Ph C-6), 83.9 ($\underline{C}CH$), 79.6 ($C\underline{C}H$), 58.7 (CH_2).

HRMS (ESI), *m/z*: calcd. for $C_9H_8ClNNaOS^+$: 235.9907 [M + Na]$^+$; found: 235.9905.

1-chloro-*N*-phenylmethanesulfinamide (9)



By following GP1, starting from *N*-sulfinylaniline (0.139 g, 1.0 mmol, 1.0 equiv), chloroiodomethane (0.662 g, 0.36 mL, 3.0 mmol, 3.0 equiv) and MeLi-LiBr (2.2 M in Et_2O, 1.2 mL, 2.8 mmol, 2.8 equiv) in dry THF (2 mL), compound **9** was obtained in 84% yield (0.159 g) as a yellow solid after purification by column chromatography on silica gel (*n*-hexane:EtOAc 6:4).

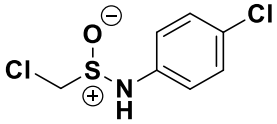
mp = 68-70 °C

^{1}H NMR (500 MHz, Acetone-d_6) δ: 8.10 (brs, 1H, NH), 7.32 (m, 2H, Ph H-3,5), 7.16 (m, 2H, Ph H-2,6), 7.06 (m, 1H, Ph H-4), 4.69 (A-part of an AB system, $^2J_{AB}$ = 10.7 Hz, 1H diast, CH_2), 4.64 (B-part of an AB system, $^2J_{AB}$ = 10.7 Hz, 1H diast, CH_2).

^{13}C NMR (125 MHz, Acetone-d_6) δ: 142.2 (Ph C-1), 130.3 (Ph C-3,5), 123.9 (Ph C-4), 119.6 (Ph C-2,6), 58.6 (CH_2).

HRMS (ESI), *m/z*: calcd. for $C_7H_{10}ClNNaOS^+$: 211.9907 $[M + Na]^+$; found: 211.9904.

1-chloro-*N*-(4-chlorophenyl)methanesulfinamide (10)



By following GP1, starting from 4-chloro-*N*-sulfinylaniline (0.173 g, 1.0 mmol, 1.0 equiv), chloroiodomethane (0.662 g, 0.36 mL, 3.0 mmol, 3.0 equiv) and MeLi-LiBr (2.2 M in Et_2O, 1.2 mL, 2.8 mmol, 2.8 equiv) in dry THF (2 mL), compound **10** was obtained in 89% yield (0.199 g) as a yellow solid after purification by column chromatography on silica gel (DCM:EtOAc 9:1).

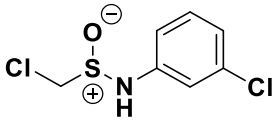
mp = 86-90 °C

^{1}H NMR (500 MHz, Acetone-d_6) δ: 8.24 (brs, 1H, NH), 7.34 (m, 2H, Ph H-3,5), 7.18 (m, 2H, Ph H-4,6), 4.70 (A-part of an AB system, $^2J_{AB}$ = 10.7 Hz, 1H diast, CH_2), 4.66 (B-part of an AB system, $^2J_{AB}$ = 10.7 Hz, 1H diast, CH_2).

^{13}C NMR (125 MHz, Acetone-d_6) δ: 141.1 (Ph C-1), 130.2 (Ph C-3,5), 128.5 (Ph C-4), 121.1 (Ph C-2,6), 58.5 (CH_2).

HRMS (ESI), *m/z*: calcd. for $C_7H_7Cl_2NNaOS^+$: 245.9518 $[M + Na]^+$; found: 245.9519.

1-chloro-*N*-(3-chlorophenyl)methanesulfinamide (11)



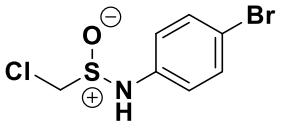
By following GP1, starting from 3-chlorosulfinylaniline (0.173 g, 1.0 mmol, 1.0 equiv), chloroiodomethane (0.662 g, 0.36 mL, 3.0 mmol, 3.0 equiv) and MeLi-LiBr (2.2 M in Et_2O, 1.2 mL, 2.8 mmol, 2.8 equiv) in dry THF (2 mL), compound **11** was obtained in 87% yield (0.195 g) as a yellow oil after purification by column chromatography on silica gel (DCM:EtOAc 9:1).

^{1}H NMR (500 MHz, Acetone-d_6) δ: 7.33 (t, ^3J = 8.1 Hz, 1H, Ph H-5), 7.19 (t, ^4J = 2.1 Hz, 1H, Ph H-2), 7.12 (ddd, ^3J = 8.1 Hz, ^4J = 2.1 Hz, ^4J = 0.9 Hz, 1H, Ph H-6), 7.07 (ddd, ^3J = 8.1 Hz, ^4J = 2.1 Hz, ^4J = 0.9 Hz, 1H, Ph H-4), 4.74 (A-part of an AB system, $^2J_{AB}$ = 10.7 Hz, 1H diast, CH_2), 4.70 (B-part of an AB system, $^2J_{AB}$ = 10.7 Hz, 1H diast, CH_2).

^{13}C NMR (125 MHz, Acetone-d_6) δ: 143.8 (Ph C-1), 135.3 (Ph C-3), 131.8 (Ph C-5), 123.6 (Ph C-4), 118.9 (Ph C-2), 117.6 (Ph C-6), 58.7 (CH_2).

HRMS (ESI), *m/z*: calcd. for $C_7H_7Cl_2NNaOS^+$: 245.9518 $[M + Na]^+$; found: 245.9516.

1-bromo-*N*-(4-chlorophenyl)methanesulfinamide (12)



By following GP1, starting from 4-bromo-*N*-sulfinylaniline (0.216 g, 1.0 mmol, 1.0 equiv), chloroiodomethane (0.662 g, 0.36 mL, 3.0 mmol, 3.0 equiv) and MeLi-LiBr (2.2 M in Et_2O, 1.2 mL, 2.8 mmol, 2.8 equiv) in dry THF (2 mL), compound **12** was obtained in 86% yield (0.231 g) as a yellow solid after purification by column chromatography on silica gel (DCM:EtOAc 9:1).

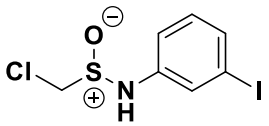
mp= 78-80 °C

^{1}H NMR (500 MHz, Acetone-d_6) δ: 8.26 (brs, 1H, NH), 7.48 (m, 2H, Ph H-3,5), 7.13 (m, 2H, Ph H-4,6), 4.70 (A-part of an AB system, $^2J_{AB}$ = 10.7 Hz, 1H diast, CH_2), 4.66 (B-part of an AB system, $^2J_{AB}$ = 10.7 Hz, 1H diast, CH_2).

^{13}C NMR (125 MHz, Acetone-d_6) δ: 141.7 (Ph C-1), 133.2 (Ph C-3,5), 121.4 (Ph C-4), 115.9 (Ph C-2,6), 58.5 (CH_2).

HRMS (ESI), *m/z*: calcd. for $C_7H_7BrClNNaOS^+$: 289.9012 $[M + Na]^+$; found: 289.9008.

1-chloro-*N*-(3-iodophenyl)methanesulfinamide (13)



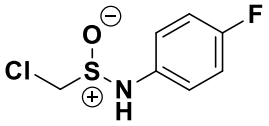
By following GP1, starting from 3-iodo-*N*-sulfinylaniline (0.265 g, 1.0 mmol, 1.0 equiv), chloroiodomethane (0.662 g, 0.36 mL, 3.0 mmol, 3.0 equiv) and MeLi-LiBr (2.2 M in Et_2O, 1.2 mL, 2.8 mmol, 2.8 equiv) in dry THF (2 mL), compound **13** was obtained in 84% yield (0.265 g) as a yellow oil after purification by column chromatography on silica gel (DCM:EtOAc 9:1).

^{1}H NMR (500 MHz, Acetone-d_6) δ: 8.24 (brs, 1H, NH), 7.54 (t, ^4J = 1.9 Hz, 1H, Ph H-2), 7.43 (dt, ^3J = 7.9 Hz, ^4J = 1.0 Hz, 1H, Ph H-4), 7.20 (ddd, ^3J = 7.9 Hz, ^4J = 1.9 Hz, ^4J = 0.8 Hz, 1H, Ph H-6), 7.11 (t, ^3J = 7.9 Hz, 1H, Ph H-5), 4.72 (A-part of an AB system, $^2J_{AB}$ = 10.7 Hz, 1H diast, CH_2), 4.68 (B-part of an AB system, $^2J_{AB}$ = 10.7 Hz, 1H diast, CH_2).

^{13}C NMR (125 MHz, Acetone-d_6) δ: 143.9 (Ph C-1), 132.8 (Ph C-4), 132.1 (Ph C-5), 127.9 (Ph C-2), 118.7 (Ph C-6), 95.0 (Ph C-3), 58.8 (CH_2).

HRMS (ESI), *m/z*: calcd. for $C_7H_7ClINNaOS^+$: 337.8874 $[M + Na]^+$; found: 337.8872.

1-chloro-*N*-(4-fluorophenyl)methanesulfinamide (14)



By following GP1, starting from 4-fluoro-*N*-sulfinylaniline (0.157 g, 1.0 mmol, 1.0 equiv), chloroiodomethane (0.662 g, 0.36 mL, 3.0 mmol, 3.0 equiv) and MeLi-LiBr (2.2 M in Et_2O, 1.2 mL, 2.8 mmol, 2.8 equiv) in dry THF (2 mL), compound **14** was obtained in 85% yield (0.177 g) as a yellow solid after purification by column chromatography on silica gel (DCM:EtOAc 95:5).

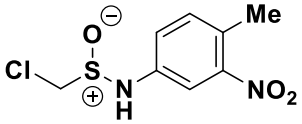
mp = 86-90 °C

^{1}H NMR (500 MHz, Acetone-d_6) δ: 8.09 (brs, 1H, NH), 7.21 (m, 2H, Ph H-3,5), 7.11 (m, 2H, Ph H-4,6), 4.65 (A-part of an AB system, $^2J_{AB}$ = 10.7 Hz, 1H diast, CH_2), 4.62 (B-part of an AB system, $^2J_{AB}$ = 10.7 Hz, 1H diast, CH_2).

^{13}C NMR (125 MHz, Acetone-d_6) δ: 161.0, 159.1, 137.9, 122.4, 122.4, 116.9, 116.7, 58.3.

HRMS (ESI), *m/z*: calcd. for $C_7H_7ClFNNaOS^+$: 229.9813 $[M + Na]^+$; found: 229.9814.

1-chloro-*N*-(4-methyl-3-nitrophenyl)methanesulfinamide (15)



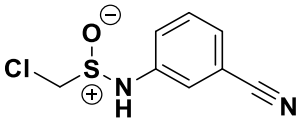
By following GP1, starting from 4-methyl-3-nitro-*N*-sulfinylaniline (0.198 g, 1.0 mmol, 1.0 equiv), chloroiodomethane (0.662 g, 0.36 mL, 3.0 mmol, 3.0 equiv) and MeLi-LiBr (2.2 M in Et_2O, 1.2 mL, 2.8 mmol, 2.8 equiv) in dry THF (2 mL), compound **15** was obtained in 79% yield (0.196 g) as a yellow oil after purification by column chromatography on silica gel (DCM:EtOAc 9:1).

^{1}H NMR (500 MHz, Acetone-d_6) δ: 8.52 (brs, 1H, NH), 7.77 (d, ^4J = 2.2 Hz, 1H, Ph H-2), 7.42 (m, 2H, Ph H-5,6), 4.76 (A-part of an AB system, $^2J_{AB}$ = 10.8 Hz, 1H diast, CH_2), 4.72 (B-part of an AB system, $^2J_{AB}$ = 10.8 Hz, 1H diast, CH_2), 2.50 (s, 3H, CH_3).

^{13}C NMR (125 MHz, Acetone-d_6) δ: 141.4, 141.2, 134.7, 128.1, 124.0, 114.9, 58.7, 19.4.

HRMS (ESI), *m/z*: calcd. for $C_8H_9ClN_2NaO_3S^+$: 270.9915 $[M + Na]^+$; found: 270.9913.

1-chloro-*N*-(3-cyanophenyl)methanesulfinamide (16)



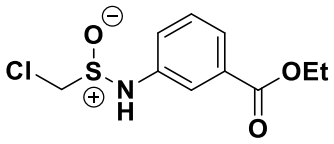
By following GP1, starting from ethyl 3-cyano-*N*-sulfinylaniline (0.164 g, 1.0 mmol, 1.0 equiv), chloroiodomethane (0.662 g, 0.36 mL, 3.0 mmol, 3.0 equiv) and MeLi-LiBr (2.2 M in Et_2O, 1.2 mL, 2.8 mmol, 2.8 equiv) in dry THF (2 mL), compound **16** was obtained in 80% yield (0.172 g) as a yellow oil after purification by column chromatography on silica gel (DCM:EtOAc 9:1).

^{1}H NMR (500 MHz, Acetone-d_6) δ: 8.52 (brs, 1H, NH), 7.54 (m, 1H, Ph H-5), 7.51 (m, 1H, Ph H-2), 7.49 (m, 1H, Ph H-6), 7.44 (m, 1H, Ph H-4), 4.77 (A-part of an AB system, $^2J_{AB}$ = 10.8 Hz, 1H diast, CH_2), 4.74 (B-part of an AB system, $^2J_{AB}$ = 10.8 Hz, 1H diast, CH_2).

^{13}C NMR (125 MHz, Acetone-d_6) δ: 143.5 (Ph C-1), 131.7 (Ph C-5), 127.3 (Ph H-4), 123.6 (Ph C-6), 121.9 (Ph C-2), 119.0 (CN), 114.2 (Ph C-3), 58.9 (CH_2).

HRMS (ESI), *m/z*: calcd. for $C_8H_7ClN_2NaOS^+$: 236.9860 [M + Na]$^+$; found: 236.9862.

Ethyl 3-(((chloromethyl)sulfinyl)amino)benzoate (17)



By following GP1, starting from ethyl 3-((oxo-λ^4-sulfaneylidene)amino)benzoate (0.211 g, 1.0 mmol, 1.0 equiv), chloroiodomethane (0.662 g, 0.36 mL, 3.0 mmol, 3.0 equiv) and MeLi-LiBr (2.2 M in Et_2O, 1.2 mL, 2.8 mmol, 2.8 equiv) in dry THF (2 mL), compound **17** was obtained in 83% yield (0.217 g) as a yellow solid after purification by column chromatography on silica gel (DCM:EtOAc 9:1).

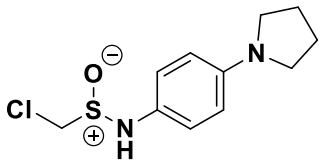
mp = 65-68 °C

^{1}H NMR (500 MHz, Acetone-d_6) δ: 8.34 (brs, 1H, NH), 7.79 (t, ^4J = 1.9 Hz, 1H, Ph H-2), 7.70 (dt, ^3J = 7.6 Hz, ^4J = 1.4 Hz, 1H, Ph H-4), 7.46 (t, ^3J = 7.6 Hz, 1H, Ph H-5), 7.41 (ddd, ^3J = 8.1 Hz, ^4J = 2.3 Hz, ^4J = 1.2 Hz, 1H, Ph H-6), 4.74 (A-part of an AB system, $^2J_{AB}$ = 10.7 Hz, 1H diast, CH_2), 4.70 (B-part of an AB system, $^2J_{AB}$ = 10.7 Hz, 1H diast, CH_2), 4.35 (q, ^3J = 7.1 Hz, 2H, OCH_2), 1.36 (t, ^3J = 7.1 Hz, 3H, CH3).

^{13}C NMR (125 MHz, Acetone-d_6) δ: 166.3 (C=O), 142.7 (Ph C-1), 132.7 (Ph C-3), 130.6 (Ph C-5), 124.6 (Ph C-4), 123.6 (Ph C-6), 119.8 (Ph C-2), 61.7 (OCH_2), 58.8 (CH_2), 14.5 (CH_3).

HRMS (ESI), *m/z*: calcd. for $C_{10}H_{12}ClNNaO_3S^+$: 284.0119 [M + Na]$^+$; found: 284.0122.

1-chloro-*N*-(4-(pyrrolidin-1-yl)phenyl)methanesulfinamide (18)



By following GP1, starting from 4-(pyrrolidin-1-yl)-*N*-sulfinylaniline (0.208 g, 1.0 mmol, 1.0 equiv), chloroiodomethane (0.662 g, 0.36 mL, 3.0 mmol, 3.0 equiv) and MeLi-LiBr (2.2 M in Et_2O, 1.2 mL, 2.8 mmol, 2.8 equiv) in dry THF (2 mL), compound **18** was obtained in 81% yield (0.210 g) as a yellow solid after purification by column chromatography on silica gel (DCM:EtOAc 1:1).

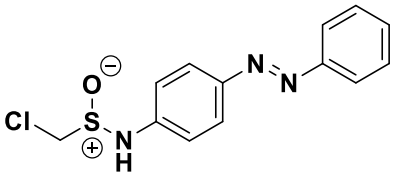
mp = 190 °C

^{1}H NMR (500 MHz, Acetone-d_6) δ: 7.52 (brs, 1H, NH), 7.05 (m, 2H, Ph), 6.52 (m, 2H, Ph), 4.45 (A-part of an AB system, $^2J_{AB}$ = 10.6 Hz, 1H diast, CH_2), 4.42 (B-part of an AB system, $^2J_{AB}$ = 10.6 Hz, 1H diast, CH_2), 3.24 (m, 4H, pyrrolidin H-1,4), 1.99 (m, 4H, pyrrolidin H-2,3).

^{13}C NMR (125 MHz, Acetone-d_6) δ: 147.0, 127.9, 125.7, 112.8, 57.4, 48.4, 26.0.

HRMS (ESI), *m/z*: calcd. for $C_{11}H_{16}ClN_2OS^+$: 259.0666 [M + H]$^+$; found: 259.0669.

1-chloro-*N*-(4-(phenyldiazenyl)phenyl)methanesulfinamide (19)



By following GP1, starting from ((4-(phenyldiazenyl)phenyl)imino)-λ^4-sulfanone (0.243 g, 1.0 mmol, 1.0 equiv), chloroiodomethane (0.662 g, 0.36 mL, 3.0 mmol, 3.0 equiv) and MeLi-LiBr (2.2 M in Et_2O, 1.2 mL, 2.8 mmol, 2.8 equiv) in dry THF (2 mL), compound **19** was obtained in 84% yield (0.247) as a yellow solid after purification by column chromatography on silica gel (DCM:EtOAc 95:5).

mp = 131-134 °C

^{1}H NMR (500 MHz, Acetone-d_6) δ: 8.60 (brs, 1H, NH), 7.94 (m, 2H, Ph2 H-2,6), 7.90 (m, 2H, Ph1 H-2,6), 7.57 (m, 2H, Ph2 H-3,5), 7.52 (m, 1H, Ph2 H-4), 7.34 (m, 2H, Ph1 H-3,5), 4.81 (A-part of an AB system, $^2J_{AB}$ = 10.7 Hz, 1H diast, CH_2), 4.75 (B-part of an AB system, $^2J_{AB}$ = 10.7 Hz, 1H diast, CH_2).

^{13}C NMR (125 MHz, Acetone-d_6) δ: 153.3 (Ph2 C-1), 148.9 (Ph1 C-4), 145.7 (Ph1 C-1), 131.7 (Ph2 C-4), 130.1 (Ph2 C-3,5), 125.4 (Ph1 C-3,5), 123.4 (Ph2 C-4,6), 118.7 (Ph1 C-2,6), 58.9 (CH_2).

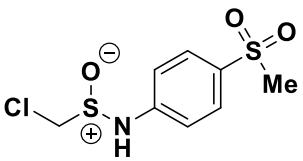
HRMS (ESI), *m/z*: calcd. for $C_{13}H_{13}ClN_3OS^+$: 294.0462 [M + H]$^+$; found: 294.0455.

Scale up of the reaction using 20 mmol of starting material

By following GP1, starting from ((4-(phenyldiazenyl)phenyl)imino)-λ^4-sulfanone (4.860 g, 20.0 mmol, 1.0 equiv), chloroiodomethane (13.240 g, 7.20 mL, 60.0 mmol, 3.0 equiv) and MeLi-LiBr (2.2 M in Et_2O, 24 mL, 56.0 mmol, 2.8 equiv) in dry THF (40 mL), compound **19** was obtained in 86% yield (5.058 g) as a yellow solid after purification by column chromatography on silica gel (DCM:EtOAc 95:5).

Spectroscopic and spectrometric data match with those ones reported for running the reaction at 1 mmol scale.

1-chloro-*N*-(4-(methylsulfonyl)phenyl)methanesulfinamide (20)



By following GP1, starting from 4-methylsulfonyl-*N*-sulfinylaniline (0.217 g, 1.0 mmol, 1.0 equiv), chloroiodomethane (0.662 g, 0.36 mL, 3.0 mmol, 3.0 equiv) and MeLi-LiBr (2.2 M in Et_2O, 1.2 mL, 2.8 mmol, 2.8 equiv) in dry THF (2 mL), compound **20** was obtained in 82% yield (0.220 g) as a yellow solid after purification by column chromatography on silica gel (DCM:EtOAc 6:4).

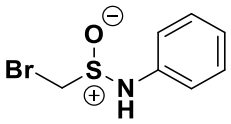
mp = 135-138 °C

^{1}H NMR (500 MHz, Acetone-d_6) δ: 8.75 (brs, 1H, NH), 7.88 (m, 2H, Ph H-3,5), 7.35 (m, 2H, Ph H-2,6), 4.81 (A-part of an AB system, $^2J_{AB}$ = 10.8 Hz, 1H diast, CH_2), 4.77 (B-part of an AB system, $^2J_{AB}$ = 10.8 Hz, 1H diast, CH_2), 3.08 (s, 3H, CH_3).

^{13}C NMR (125 MHz, Acetone-d_6) δ: 147.5 (Ph C-1), 135.7 (Ph C-4), 130.2 (Ph C-3,5), 117.9 (Ph C-2,6), 59.0 (CH_2), 44.6 (CH_3).

HRMS (ESI), *m/z*: calcd. for $C_8H_{10}ClNNaO_3S_2^+$: 289.9683 $[M + H]^+$; found: 289.9676.

1-bromo-*N*-phenylmethanesulfinamide (21)



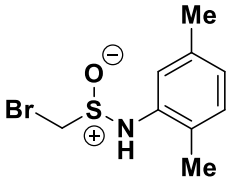
By following GP1, starting from *N*-sulfinylaniline (0.139 g, 1.0 mmol, 1.0 equiv), bromoiodomethane (0.662 g, 0.36 mL, 3.0 mmol, 3.0 equiv) and MeLi-LiBr (2.2 M in Et_2O, 1.2 mL, 2.8 mmol, 2.8 equiv) in dry THF (2 mL), compound **21** was obtained in 84% yield (0.197 g) as a yellow oil after purification by column chromatography on silica gel (*n*-hexane:EtOAc 6:4).

^{1}H NMR (500 MHz, C_6D_6) δ: 6.97 (m, 2H, Ph H-3,5), 6.83 (m, 2H, Ph H-2,6), 6.81 (m, 1H, Ph H-4), 5.98 (brs, 1H, NH), 3.61 (A-part of an AB system, $^2J_{AB}$ = 10.2 Hz, 1H diast, CH_2), 3.51 (B-part of an AB system, $^2J_{AB}$ = 10.2 Hz, 1H diast, CH_2).

^{13}C NMR (125 MHz, C_6D_6) δ: 140.2 (Ph C-1), 129.7 (Ph C-3,5), 124.1 (Ph C-4), 120.1 (Ph C-2,6), 46.5 (CH_2).

HRMS (ESI), *m/z*: calcd. for $C_7H_{11}NOS^+$: 235.9744 $[M + H]^+$; found: 235.9741.

1-bromo-*N*-(2,5-dimethylphenyl)methanesulfinamide (22)



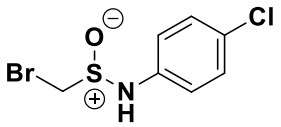
By following GP1, starting from 2,5-dimethyl-*N*-sulfinylaniline (0.167 g, 1.0 mmol, 1.0 equiv), bromooiodomethane (0.662 g, 0.36 mL, 3.0 mmol, 3.0 equiv) and MeLi-LiBr (2.2 M in Et_2O, 1.2 mL, 2.8 mmol, 2.8 equiv) in dry THF (2 mL), compound **22** was obtained in 79% yield (0.207 g) as a yellow oil after purification by column chromatography on silica gel (DCM:EtOAc 95:5).

^{1}H NMR (500 MHz, Acetone-d_6) δ: 7.41 (brs, 1H, NH), 7.13 (s, 1H, Ph H-6), 7.08 (d, ^3J = 7.7 Hz, 1H, Ph H-3), 6.86 (d, ^3J = 7.7 Hz, 1H, Ph H-4), 4.68 (A-part of an AB system, $^2J_{AB}$ = 10.1 Hz, 1H diast, CH_2), 4.54 (B-part of an AB system, $^2J_{AB}$ = 10.1 Hz, 1H diast, CH_2), 2.28 (s, 3H, CH_3 Ph-5), 2.26 (3H, CH_3 Ph-2).

^{13}C NMR (125 MHz, Acetone-d_6) δ: 139.8 (Ph C-1), 137.3 (Ph C-5), 131.6 (Ph C-3), 127.4 (Ph C-2), 125.8 (Ph C-4), 122.4 (Ph C-6), 46.0 (CH_2), 21.0 (CH_3 Ph-C5), 17.6 (CH_3 Ph-C2).

HRMS (ESI), *m/z*: calcd. for $C_9H_{12}BrNNaOS^+$: 283.9715 $[M + Na]^+$; found: 283.9711.

1-bromo-*N*-(4-chlorophenyl)methanesulfinamide (23)



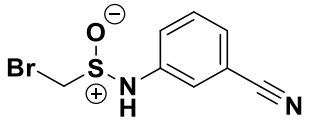
By following GP1, starting from 4-chloro-*N*-sulfinylaniline (0.173 g, 1.0 mmol, 1.0 equiv), bromooiodomethane (0.662 g, 0.36 mL, 3.0 mmol, 3.0 equiv) and MeLi-LiBr (2.2 M in Et_2O, 1.2 mL, 2.8 mmol, 2.8 equiv) in dry THF (2 mL), compound **23** was obtained in 86% yield (0.230 g) as a yellow oil after purification by column chromatography on silica gel (DCM:EtOAc 9:1).

^{1}H NMR (500 MHz, Acetone-d_6) δ: 8.19 (brs, 1H, NH), 7.34 (m, 2H, Ph H-3,5), 7.18 (m, 2H, Ph H-4,6), 4.61 (A-part of an AB system, $^2J_{AB}$ = 10.1 Hz, 1H diast, CH_2), 4.55 (B-part of an AB system, $^2J_{AB}$ = 10.1 Hz, 1H diast, CH_2).

^{13}C NMR (125 MHz, Acetone-d_6) δ: 141.1 (Ph C-1), 130.2 (Ph C-3,5), 128.5 (Ph C-4), 121.1 (Ph C-2,6), 46.0 (CH_2).

HRMS (ESI), *m/z*: calcd. for $C_7H_7BrClNNaOS^+$: 289.9012 $[M + Na]^+$; found: 289.9011.

1-bromo-*N*-(3-cyanophenyl)methanesulfinamide (24)



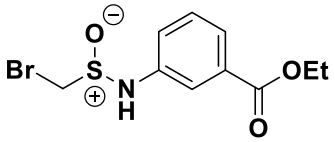
By following GP1, starting from 3-cyano-*N*-sulfinylaniline (0.164 g, 1.0 mmol, 1.0 equiv), bromooiodomethane (0.662 g, 0.36 mL, 3.0 mmol, 3.0 equiv) and MeLi-LiBr (2.2 M in Et_2O, 1.2 mL, 2.8 mmol, 2.8 equiv) in dry THF (2 mL), compound **24** was obtained in 83% yield (0.215 g) as a yellow oil after purification by column chromatography on silica gel (DCM:EtOAc 9:1).

^{1}H NMR (500 MHz, Acetone-d_6) δ: 8.44 (brs, 1H, NH), 7.54 (m, 1H, Ph H-5), 7.51 (m, 1H, Ph H-2), 7.49 (m, 1H, Ph H-6), 7.44 (m, 1H, Ph H-4), 4.68 (A-part of an AB system, $^2J_{AB}$ = 10.2 Hz, 1H diast, CH_2), 4.62 (B-part of an AB system, $^2J_{AB}$ = 10.2 Hz, 1H diast, CH_2).

^{13}C NMR (125 MHz, Acetone-d_6) δ: 143.5 (Ph C-1), 131.7 (Ph C-5), 127.1 (Ph H-4), 123.5 (Ph C-6), 121.8 (Ph C-2), 118.9 (CN), 114.2 (Ph C-3), 46.3 (CH_2).

HRMS (ESI), *m/z*: calcd. for $C_8H_7BrN_2NaOS^+$: 280.9355 $[M + Na]^+$; found: 280.9350.

Ethyl 3-(((bromomethyl)sulfinyl)amino)benzoate (25)



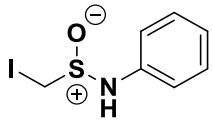
By following GP1, starting from ethyl 3-((oxo-λ^4-sulfaneylidene)amino)benzoate (0.211 g, 1.0 mmol, 1.0 equiv), bromoiodomethane (0.662 g, 0.36 mL, 3.0 mmol, 3.0 equiv) and MeLi-LiBr (2.2 M in Et_2O, 1.2 mL, 2.8 mmol, 2.8 equiv) in dry THF (2 mL), compound **25** was obtained in 84% yield (0.257 g) as a yellow oil after purification by column chromatography on silica gel (DCM:EtOAc 9:1).

^{1}H NMR (500 MHz, Acetone-d_6) δ: 8.27 (s, 1H, NH), 7.79 (t, ^4J = 2.0 Hz, 1H, Ph H-2), 7.70 (dt, ^3J = 7.6 Hz , ^4J = 1.3 Hz , 1H, Ph H-4), 7.46 (t, ^3J = 8.0 Hz, 1H, Ph H-5), 7.42 (ddd, ^3J = 8.0 Hz, ^4J = 2.3 Hz, ^4J = 1.3 Hz, 1H, Ph H-6), 4.65 (A-part of an AB system, $^2J_{AB}$ = 10.1 Hz, 1H diast, CH_2), 4.59 (B-part of an AB system, $^2J_{AB}$ = 10.1 Hz, 1H diast, CH_2), 4.35 (q, ^3J = 7.1 Hz, 2H, OCH_2), 1.36 (t, ^3J = 7.1 Hz, 3H, CH_3).

^{13}C NMR (125 MHz, Acetone-d_6) δ: 166.3 (C=O), 142.7 (Ph C-1), 132.7 (Ph C-3), 130.6 (Ph C-5), 124.6 (Ph C-4), 123.6 (Ph C-6), 119.8 (Ph C-2), 61.7 (OCH_3), 46.2 (CH_2), 14.5 (CH_3).

HRMS (ESI), *m/z*: calcd. for $C_{10}H_{12}BrNNaO_3S^+$: 327.9613 [M + Na]$^+$; found: 327.9611.

1-iodo-*N*-phenylmethanesulfinamide (26)



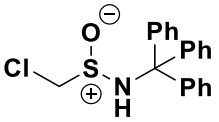
By following GP1, starting from *N*-sulfinylaniline (0.139 g, 1.0 mmol, 1.0 equiv), diiodomethane (0.804 g, 0.24 mL, 3.0 mmol, 3.0 equiv) and MeLi-LiBr (2.2 M in Et_2O, 1.2 mL, 2.8 mmol, 2.8 equiv) in dry THF (2 mL), compound **26** was obtained in 82% yield (0.231 g) as a yellow oil after purification by column chromatography on silica gel (*n*-hexane:EtOAc 6:4).

^{1}H NMR (200 MHz, Acetone-d_6) δ: 7.75 (brs, 1H), 7.31 (m, 2H), 7.15 (m, 2H), 7.04 (m, 1H), 4.54 (A-part of an AB system, $^2J_{AB}$ = 10.1 Hz, 1H diast, CH_2), 4.42 (B-part of an AB system, $^2J_{AB}$ = 10.1 Hz, 1H diast, CH_2).

^{13}C NMR (50 MHz, Acetone-d_6) δ: 142.3, 130.3, 123.8, 119.6, 20.5.

HRMS (ESI), *m/z*: calcd. for $C_7H_8INNaOS^+$: 303.9264 [M + Na]$^+$; found: 303.9268.

1-chloro-*N*-tritylmethanesulfinamide (27)



By following GP1, starting from *N*-tritylsulfinylamine (0.305 g, 1.0 mmol, 1.0 equiv), chloroiodomethane (0.662 g, 0.36 mL, 3.0 mmol, 3.0 equiv) and MeLi-LiBr (2.2 M in Et_2O, 1.2 mL, 2.8 mmol, 2.8 equiv) in dry THF (2 mL), compound **(27)** was obtained in 91% yield (0.391 g) as a white solid after purification by column chromatography on silica gel (petroleum ether/EtOAc 75:25).

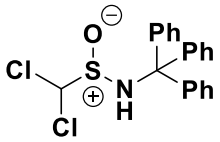
mp= 169-170 °C

^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.37-7.27 (m, 15H, Ph), 5.57 (brs, 1H, NH), 4.29 (A-part of an AB system, $^2J_{AB}$ = 10.7 Hz, d, 1H diast, CH_2), 3.99 (B-part of an AB system, $^2J_{AB}$ = 10.7 Hz, d, 1H diast, CH_2).

^{13}C NMR (150 MHz, $CDCl_3$) δ: 144.3, 129.0, 128.2, 127.6, 72.5, 61.2.

HRMS (ESI), *m/z*: calcd. for $C_{20}H_{18}ClNNaOS^+$: 378.0695 [M + Na]$^+$; found: 378.0699.

1,1-dichloro-*N*-tritylmethanesulfinamide (28)



By following GP2, starting from TMP (0.396 g, 0.47 mL, 2.8 mmol, 2.8 equiv) and *n*-BuLi (1.12 mL of 2.5 M in hexane, 2.8 mmol, 2.8 equiv) in dry THF (3 mL) and, *N*-tritylsulfinylamine (0.305 g, 1.0 mmol, 1.0 equiv), dichloromethane (0.255 g, 0.19 mL, 3.0 mmol, 3.0 equiv) in dry THF (2 mL), compound **34** was obtained in 85% yield (0.332 g) as a white solid after purification by column chromatography on silica gel (petroleum ether:EtOAc 85:15).

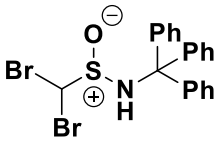
mp= 173-174 °C

^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.37-7.30 (m, 15H, Ph), 5.92 (s, 1H, CH), 5.41 (brs, 1H, NH).

^{13}C NMR (150 MHz, $CDCl_3$) δ: 144.0, 129.2, 128.2, 127.8, 84.0, 72.7.

HRMS (ESI), *m/z*: calcd. for $C_{20}H_{17}Cl_2NNaOS^+$: 412.0306 [M + Na]$^+$; found: 412.0311.

1,1-dibromo-*N*-tritylmethanesulfinamide (29)



By following GP2, starting from TMP (0.396 g, 0.47 mL, 2.8 mmol, 2.8 equiv) and n-BuLi (1.12 mL of 2.5 M in hexane, 2.8 mmol, 2.8 equiv) in dry THF (3 mL) and, *N*-tritylsulfinylamine (0.305 g, 1.0 mmol, 1.0 equiv), dibromomethane (0.522 g, 0.21 mL, 3.0 mmol, 3.0 equiv) in dry THF (2 mL), compound **35** was obtained in 81% yield (0.381 g) as a white solid after purification by column chromatography on silica gel (petroleum ether:EtOAc 85:15).

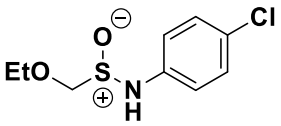
Mp = 175-176 °C

^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.37-7.31 (m, 15H, Ph), 5.83 (brs, 1H, NH), 5.39 (s, 1H, CH).

^{13}C NMR (150 MHz, $CDCl_3$) δ: 144.0, 129.1, 128.2, 127.8, 75.2, 60.4.

HRMS (ESI), *m/z*: calcd. for $C_{20}H_{17}Br_2NNaOS^+$: 499.9293 [M + Na]$^+$; found: 499.9297.

***N*-(4-chlorophenyl)-1-ethoxymethanesulfinamide (30)**



Lithium metal (0.069 g, 10.0 mmol, 10.0 equiv) and 4,4'-di-*tert*-butylbiphenyl (DTBB, 0.013 g, 0.05 mmol, 0.05 equiv) were dissolved in dry THF (3mL) and the mixture was stirred until the appearance of a dark green color. Then, chloromethyl ethyl ether (0.189 g, 2 mmol, 2 equiv)) was added dropwise at -78 °C and the solution was stirred for 10 min. Afterwards, 4-chloro-*N*-sulfinylaniline (0.173 g, 1.0 mmol, 1.0 equiv) was added and the reaction mixture was stirred at -78 °C for additional 1.5 h before quenching with NH_4Cl (aq.). The mixture was allowed to reach room temperature and was extracted with Et_2O (3 x 10 mL). The combined organic

phases were dried over anhydrous Na_2SO_4 and the solvents were removed under reduced pressure. The final product **30** was obtained in 85% yield (0.199 g) as a yellow solid after purification by column chromatography on silica gel (DCM:EtOAc 9:1).

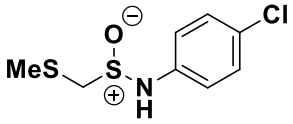
mp = 83 °C

^{1}H NMR (500 MHz, Acetone-d_6) δ: 8.01 (brs, 1H, NH), 7.31 (m, 2H, Ph), 7.13 (m, 2H, Ph), 4.60 (A-part of an AB system, $^2J_{AB}$ = 10.6 Hz, 1H diast, CH_2), 4.52 (B-part of an AB system, $^2J_{AB}$ = 10.6 Hz, 1H diast, CH_2), 3.85 (q, ^3J = 7.1 Hz, 2H, OCH_2), 1.19 (t, ^3J = 7.1 Hz, 3H, CH_3).

^{13}C NMR (125 MHz, Acetone-d_6) δ: 142.3, 130.1, 127.6, 120.2, 88.4, 69.2, 15.4.

HRMS (ESI), *m/z*: calcd. for $C_9H_{12}ClNNaO_2S^+$: 256.0169 [M + Na]$^+$; found: 256.0173.

***N*-(4-chlorophenyl)-1-(methylthio)methanesulfinamide (31)**



Lithium metal (0.069 g, 10.0 mmol, 10.0 equiv) and 4,4'-di-*tert*-butylbiphenyl (DTBB, 0.013 g, 0.05 mmol, 0.05 equiv) were dissolved in dry THF (3mL) and stirred until the appearance of a dark green color. Then chloromethyl methyl sulfide (0.353 g, 2 mmol, 2 equiv)) was added dropwise at -78 °C and the solution was stirred for 10 min. Afterwards, 4-chloro-*N*-sulfinylaniline (0.173 g, 1.0 mmol, 1.0 equiv) was added and the reaction mixture was stirred at -78 °C for additional 1.5 h before quenching with NH_4Cl (aq.). The mixture was allowed to reach room temperature and was extracted with Et_2O (3 x 10 ml). The combined organic phases were dried over anhydrous Na_2SO_4 and the solvents were removed under reduced pressure. The final product **31** was obtained in 82% yield (0.193 g) as a yellow solid after purification by column chromatography on silica gel (DCM:EtOAc 8:2).

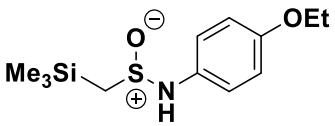
mp = 108-110 °C

^{1}H NMR (500 MHz, Acetone-d_6) δ: 8.01 (brs, 1H, NH), 7.31 (m, 2H, Ph H-3,5), 7.14 (m, 2H, Ph H-4,6), 4.07 (A-part of an AB system, $^2J_{AB}$ = 13.8 Hz, 1H diast, CH_2), 3.87 (B-part of an AB system, $^2J_{AB}$ = 13.8 Hz, 1H diast, CH_2), 2.33 (s, 3H, CH_3).

^{13}C NMR (125 MHz, Acetone-d_6) δ: 142.2 (Ph C-1), 130.1 (Ph C-3,5), 127.7 (Ph C-4), 120.5 (Ph C-2,6), 57.9 (CH_2), 16.7 (SCH_3).

HRMS (ESI), *m/z*: calcd. for $C_8H_{10}ClNNaOS^+$: 257.9785 [M + Na]$^+$; found: 257.9787.

***N*-(4-ethoxyphenyl)-1-(trimethylsilyl)methanesulfinamide (32)**



To the solution of 4-ethoxy-*N*-sulfinylaniline (0.183 g, 1.0 mmol, 1.0 equiv) in dry THF at -78 °C under argon, commercially available trimethylsilyl-methyllithium (0.7 M in *n*-hexane, 2.9 mL, 2.0 mmol, 2.0 equiv) was added dropwise and the solution was stirred for 1.5 h before quenching with NH_4Cl (aq.). The solution was allowed to reach room temperature and was extracted with Et_2O (3 x 10 ml). The combined organic phases

were dried over anhydrous Na_2SO_4 and the solvents were removed under reduced pressure. The final product **32** was obtained in 86% yield (0.233 g) as a white solid after purification by column chromatography on silica gel (DCM:EtOAc 9:1).

mp = 112-113 °C

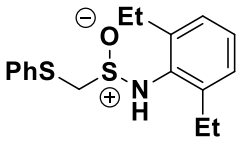
^{1}H NMR (500 MHz, Acetone-d_6) δ: 7.35 (brs, 1H, NH), 7.02 (m, 2H, Ph H-2,6), 6.85 (m, 2H, Ph H-3,5), 3.99 (q, ^3J = 7.0 Hz, 2H, C$\underline{H}_2$CH$_3$), 2.68 (A-part of an AB system, $^2J_{AB}$ = 13.8 Hz, 1H diast, CH_2), 2.51 (B-part of an AB system, $^2J_{AB}$ = 13.8 Hz, 1H diast, CH_2), 1.33 (t, ^3J = 7.0 Hz, 3H, CH$_2$C$\underline{H}_3$), 0.18 (s, 9H, Si(CH$_3$)$_3$).

^{13}C NMR (125 MHz, Acetone-d_6) δ: 156.0 (Ph C-4), 136.4 (Ph C-1), 121.8 (Ph C-2,6), 115.9 (Ph C-3,5), 64.2 (C$\underline{H}_2$CH$_3$), 46.8 (CH_2), 15.2 (CH$_2$C$\underline{H}_3$), -1.0 (Si(CH$_3$)$_3$).

HRMS (ESI), *m/z*: calcd. for $C_{12}H_{21}NNaO_2SSi^+$: 294.0954 [M + Na]$^+$; found: 294.0951.

Synthetic manipulation of products

N-(2,6-diethylphenyl)-1-(phenylthio)methanesulfinamide (33)



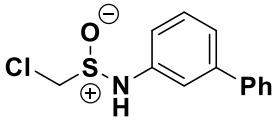
To a solution of 1-chloro-*N*-(2,6-diethylphenyl)methanesulfinamide **(6)** (0.100 g, 0.407 mmol, 1 equiv) in MeCN (3 mL), potassium carbonate (0.06 g, 0.407 mmol, 1 equiv) and thiophenol (0.04 mL, 0.407 mmol, 1 equiv) were added and the reaction mixture was stirred for 1 h at 85 °C under microwave irradiation. Upon quenching with NH_4Cl (aq.), the organic phase was extracted with Et_2O (3 x 10 mL), dried over anhydrous Na_2SO_4 and the solvents were removed under reduced pressure. The final product **33** was obtained in 87% yield (0.113 g) as a yellow oil after purification by column chromatography on silica gel (DCM 100%).

^{1}H NMR (500 MHz, Acetone-d_6) δ: 7.61 (m, 2H, Ph), 7.38 (m, 2H, Ph), 7.29 (m, 1H, Ph), 7.10 (m, 3H, Ph), 6.97 (brs, 1H, NH), 4.66 (A-part of an AB system, $^2J_{AB}$ = 14.0 Hz, 1H diast, CH_2), 4.41 (B-part of an AB system, $^2J_{AB}$ = 14.0 Hz, 1H diast, CH_2), 2.85-2.71 (m, 4H, C$\underline{H}_2$CH$_3$), 1.15 (t, ^3J = 7.6 Hz, 6H, CH$_2$C$\underline{H}_3$).

^{13}C NMR (125 MHz, Acetone-d_6) δ: 141.5, 137.1, 135.7, 130.5, 130.1, 127.9, 127.6, 127.3, 58.7, 25.3, 15.3.

HRMS (ESI), *m/z*: calcd. for $C_{17}H_{21}NNaOS_2^+$: 342.0957 [M + Na]$^+$; found: 342.0963.

N-([1,1'-biphenyl]-3-yl)-1-chloromethanesulfinamide (34)



In a dry Schlenk flask $Pd_2(dba)_3$ (4.6 mg, 0.005 mmol, 0.025 equiv) and P(*t*-Bu)$_3$ (0.4 mg, 0.002 mmol, 0.10 equiv) were added to anhydrous toluene. Then, 1-chloro-*N*-(3-iodophenyl)methanesulfinamide **(13)** (60.0 mg, 0.19 mmol, 1 equiv) was included to the mixture at -10 °C. Phenyllithium (1.9 M in *n*-dibutyl ether, 0.57 mmol, 0.3 mL, 3.0 equiv) was diluted with toluene (3.15 mL) to reach a concentration of 0.6 M and TMEDA

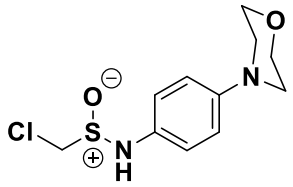
(0.23 mmol, 0.034 mL, 1.2 equiv) was added to form a combined (PhLi-TMEDA) solution was slowly added over 2 h *via* a syringe pump to the mixture of **13** – Pd catalyst and phosphine. After the addition was completed, $NaHCO_3$ (aq. 5%) was added and the mixture was extracted with diethyl ether (3 x 5 mL). The organic phases were collected, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. Compound **34** was obtained in 71% yield (36.0 mg) as a yellow oil after chromatography on silica gel (DCM:EtOAc 9:1).

^{1}H NMR (500 MHz, Acetone-d_6) δ: 8.25 (brs, 1H, NH), 7.63 (m, 2H, Ph), 7.33-7.47 (m, 7H, Ph), 7.17 (m, 1H, Ph), 4.75 (A-part of an AB system, $^2J_{AB}$ = 10.7 Hz, 1H diast, CH_2), 4.69 (B-part of an AB system, $^2J_{AB}$ = 10.7 Hz, 1H diast, CH_2).

^{13}C NMR (125 MHz, Acetone-d_6) δ: 143.3, 142.7, 141.3, 130.9, 129.7, 128.5, 127.7, 122.6, 118.5, 118.0, 58.7.

HRMS (ESI), *m/z*: calcd. for $C_{13}H_{12}ClNNaOS^+$: 288.0220 [M + Na]$^+$; found: 288.0218.

1-chloro-*N*-(4-morpholinophenyl)methanesulfinamide (35)



1-bromo-*N*-(4-chlorophenyl)methanesulfinamide **12** (1.0 mmol, 0.271 g, 1.0 equiv) was dissolved in anhydrous toluene (5 mL) and consecutively were added $PdCl_2$[P(*o*-Tol)$_3$] (0.05 mmol, 0.04 g, 0.05 equiv), LiHDMS (1.0 M in THF, 1.2 mL, 1.2 equiv) and morpholine (1.0 mmol, 0.087 g, 0.09 mL, 1.0 equiv). After degassing with Ar (x 3) the resulting mixture was gently stirred at 110 °C for 18 h and then cooled at rt and diluted with diethyl ether (10 mL). The mixture was flushed upon a plug of Celite and washed with water (3 mL). The extracted organic phase was dried over anhydrous sodium sulfate and the solvent was removed under reduced pressure. The obtained crude was purified on silica gel (*n*-hexane: EtOAc 1:1) as the mobile phase, giving compound **35** in 72% yield (0.198g) as a yellow solid.

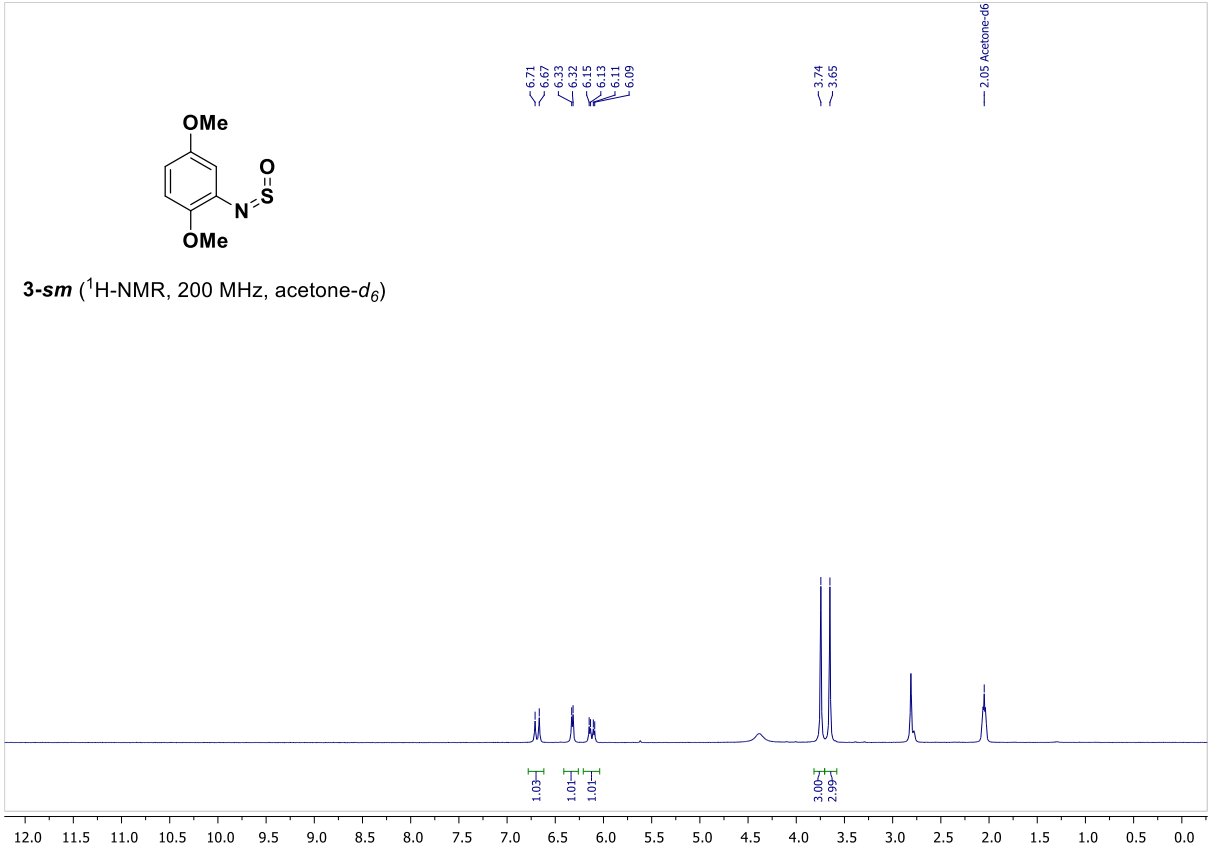
mp = 112-115 °C

^{1}H NMR (500 MHz, Acetone-d_6) δ: 7.74 (brs, 1H, NH), 7.09 (m, 2H, Ph H-2,6), 6.94 (m, 2H, Ph H-3,5), 4.55 (A-part of an AB system, $^2J_{AB}$ = 10.7 Hz, 1H diast, CH_2), 4.52 (B-part of an AB system, $^2J_{AB}$ = 10.7 Hz, 1H diast, CH_2), 3.76 (m, 4H, OCH_2), 3.08 (m, 4H, NCH_2).

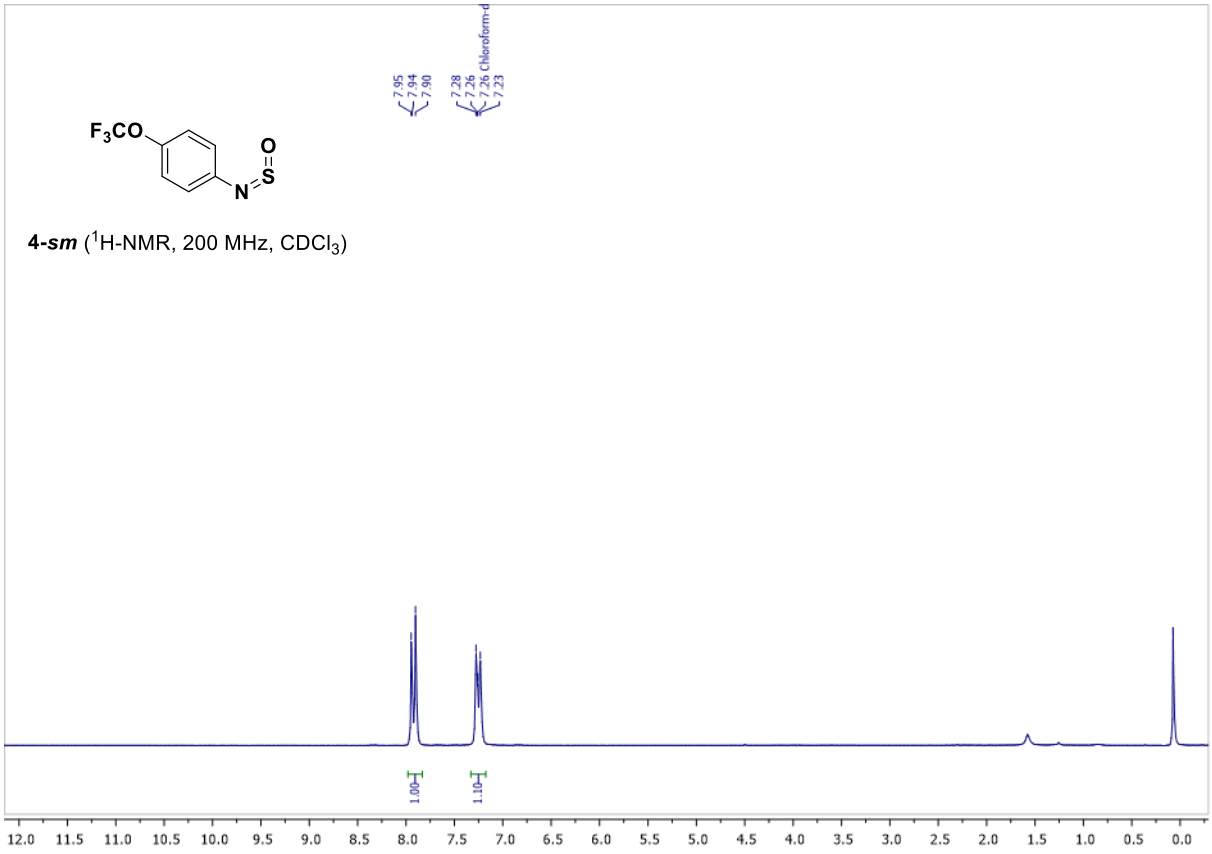
^{13}C NMR (125 MHz, Acetone-d_6) δ: 149.6 (Ph C-4), 133.0 (Ph C-1), 123.3 (Ph C-2,6), 117.3 (Ph C-3,5), 67.4 (OCH_2), 58.0 (CH_2), 50.4 (NCH_2).

HRMS (ESI), *m/z*: calcd. for $C_{11}H_{16}ClN_2O_2S^+$: 275.0616 [M + H]$^+$; found: 275.0615.

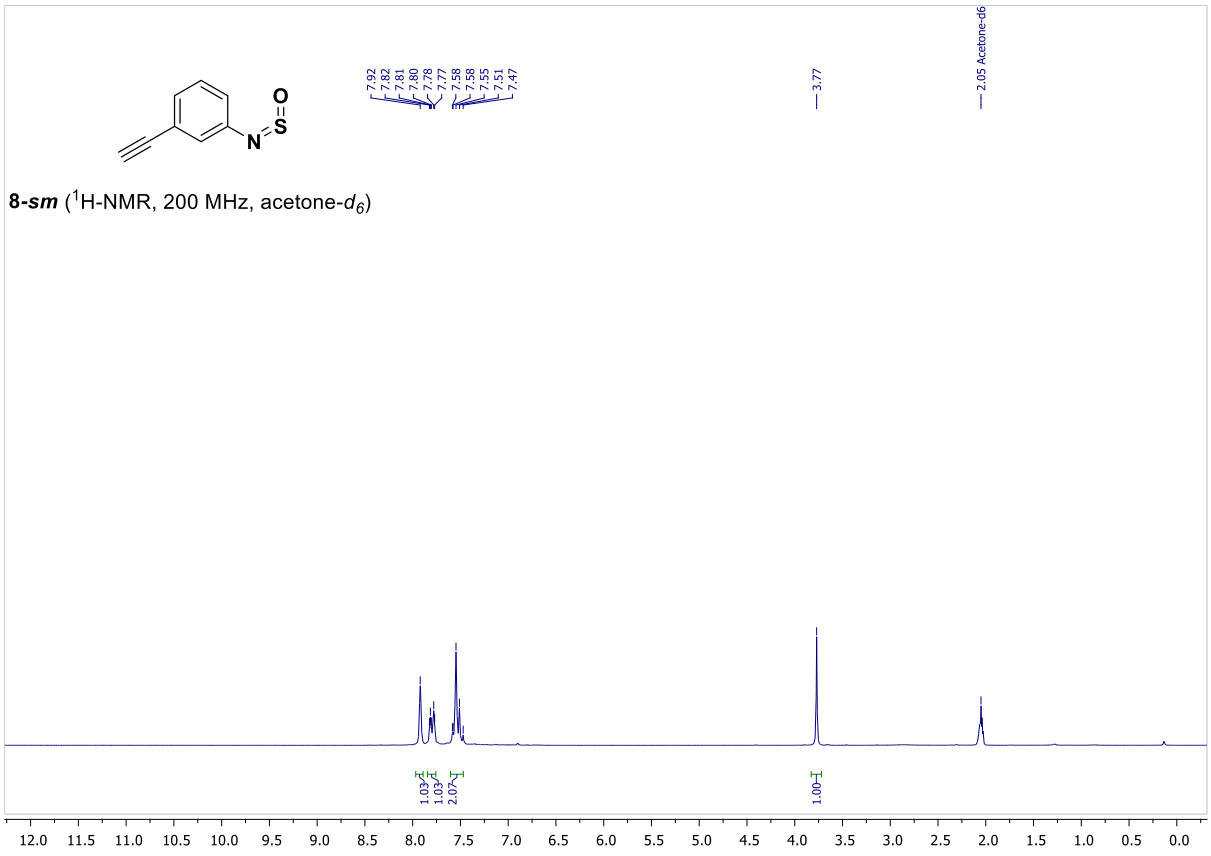
Copies of NMR Spectra of Compounds



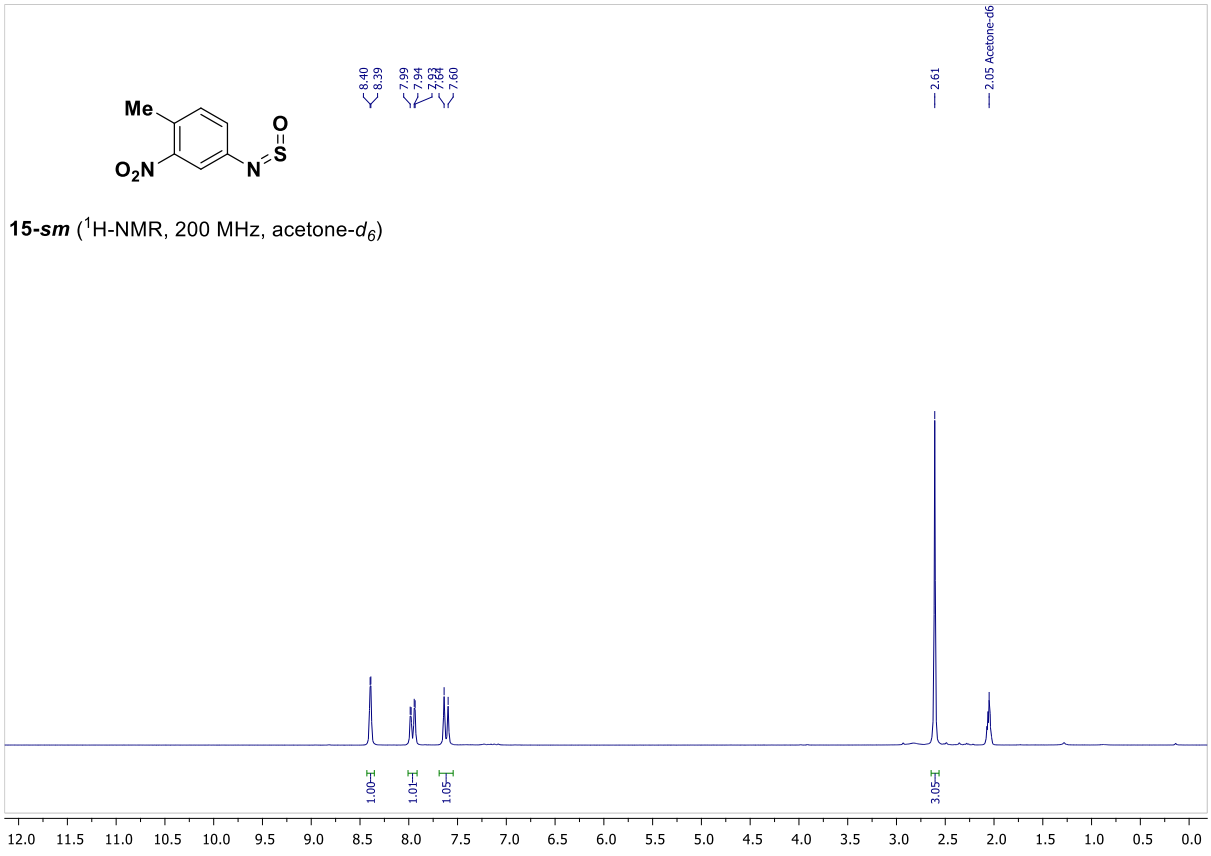
3-*sm* (^{1}H-NMR, 200 MHz, acetone-d_6)



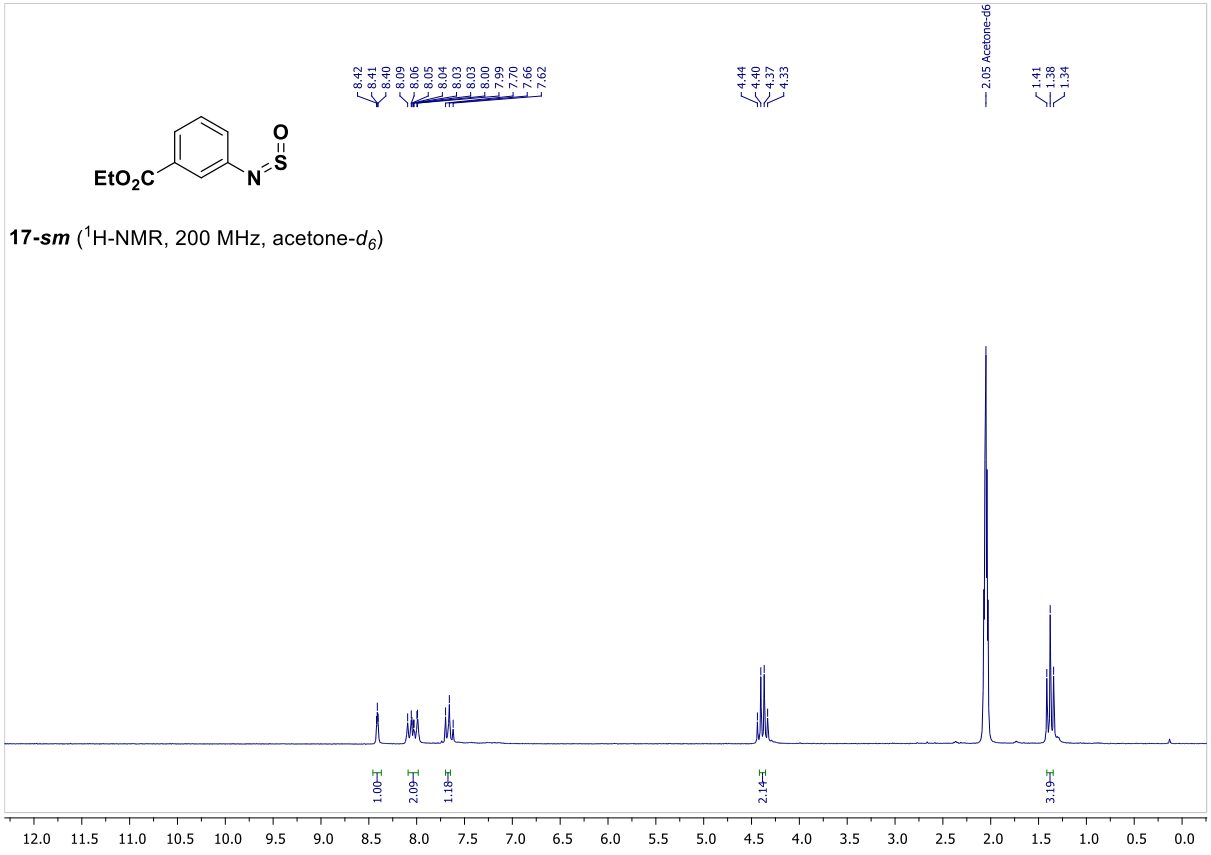
4-*sm* (^{1}H-NMR, 200 MHz, $CDCl_3$)



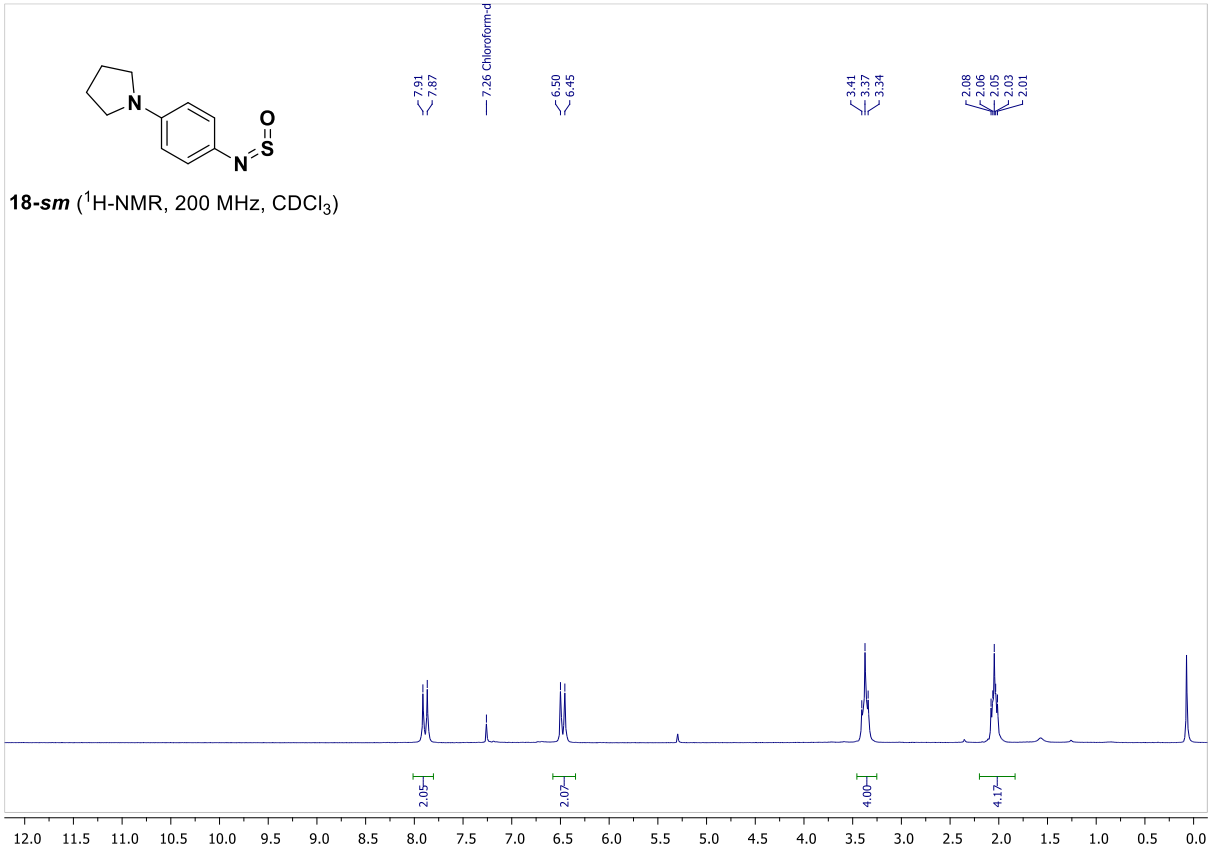
8-*sm* (^{1}H-NMR, 200 MHz, acetone-d_6)



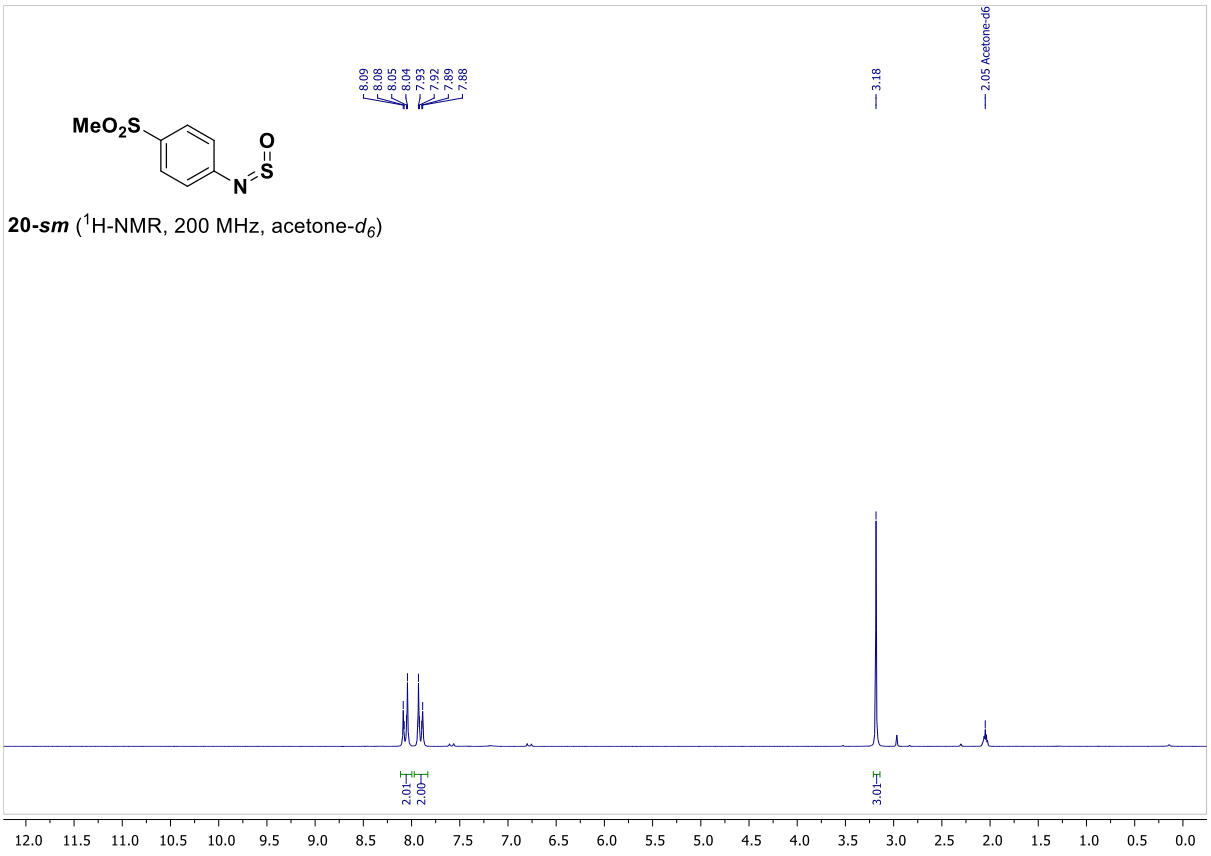
15-*sm* (^{1}H-NMR, 200 MHz, acetone-d_6)



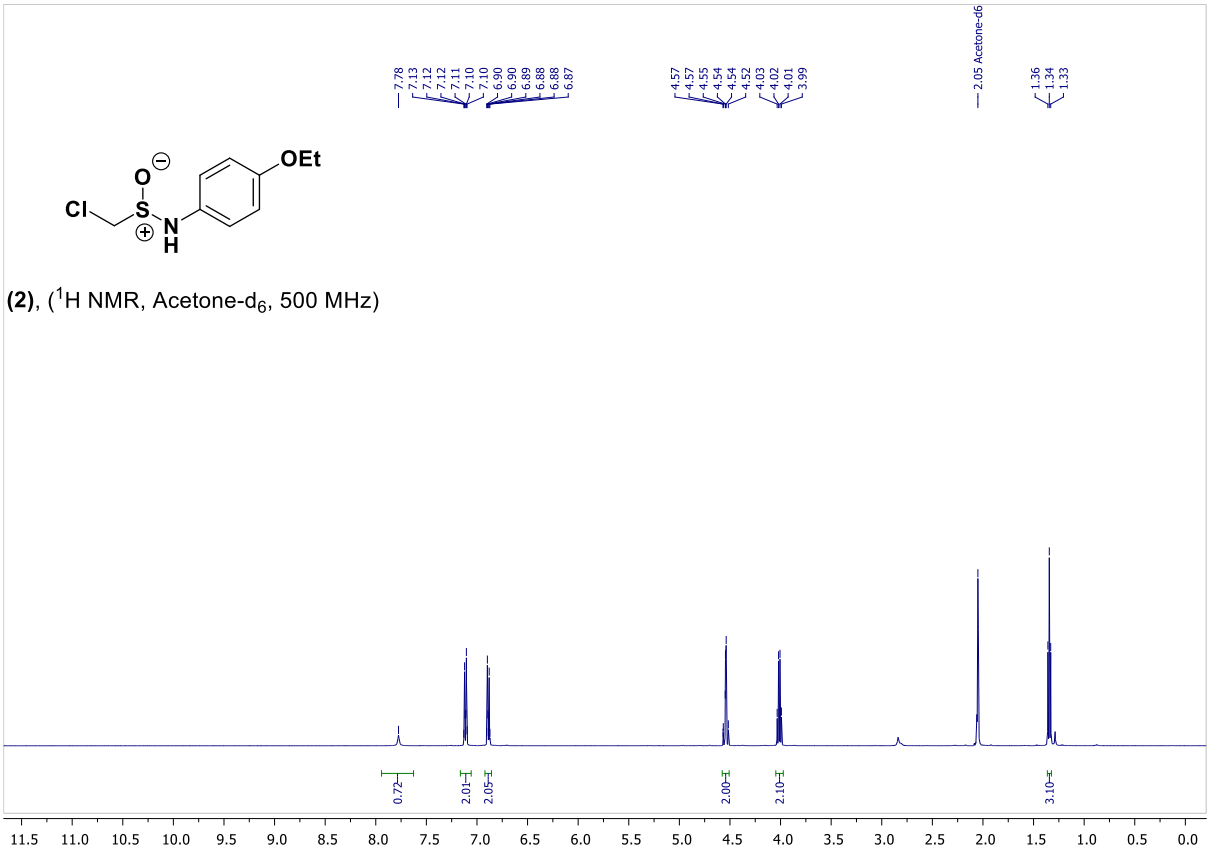
17-*sm* (^{1}H-NMR, 200 MHz, acetone-d_6)



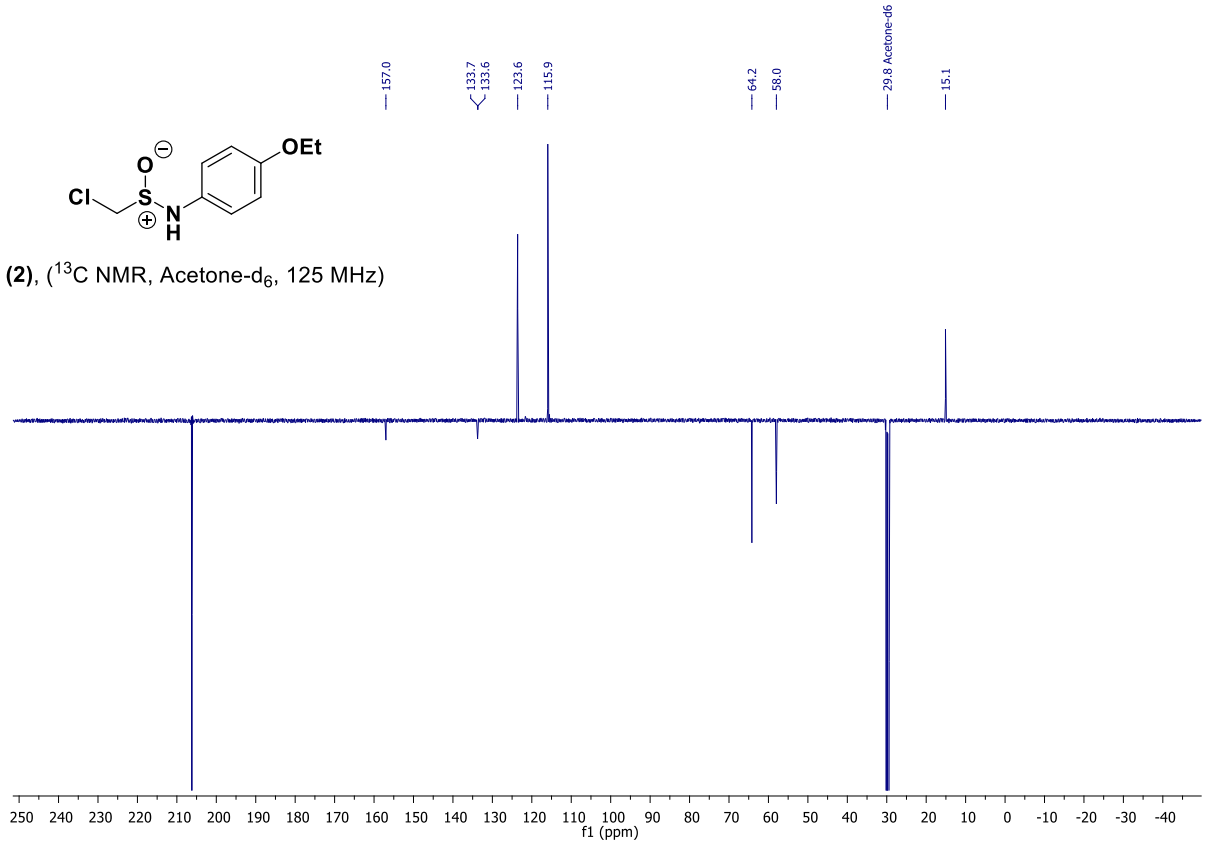
18-*sm* (^{1}H-NMR, 200 MHz, $CDCl_3$)



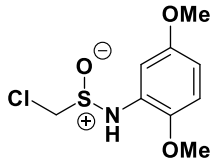
20-*sm* (^{1}H-NMR, 200 MHz, acetone-d_6)



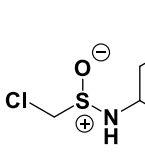
(2), (^{1}H NMR, Acetone-d_6, 500 MHz)



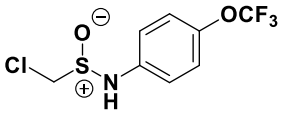
(2), (^{13}C NMR, Acetone-d_6, 125 MHz)



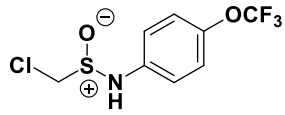
(3), (^{1}H NMR, Acetone-d$_6$, 500 MHz)



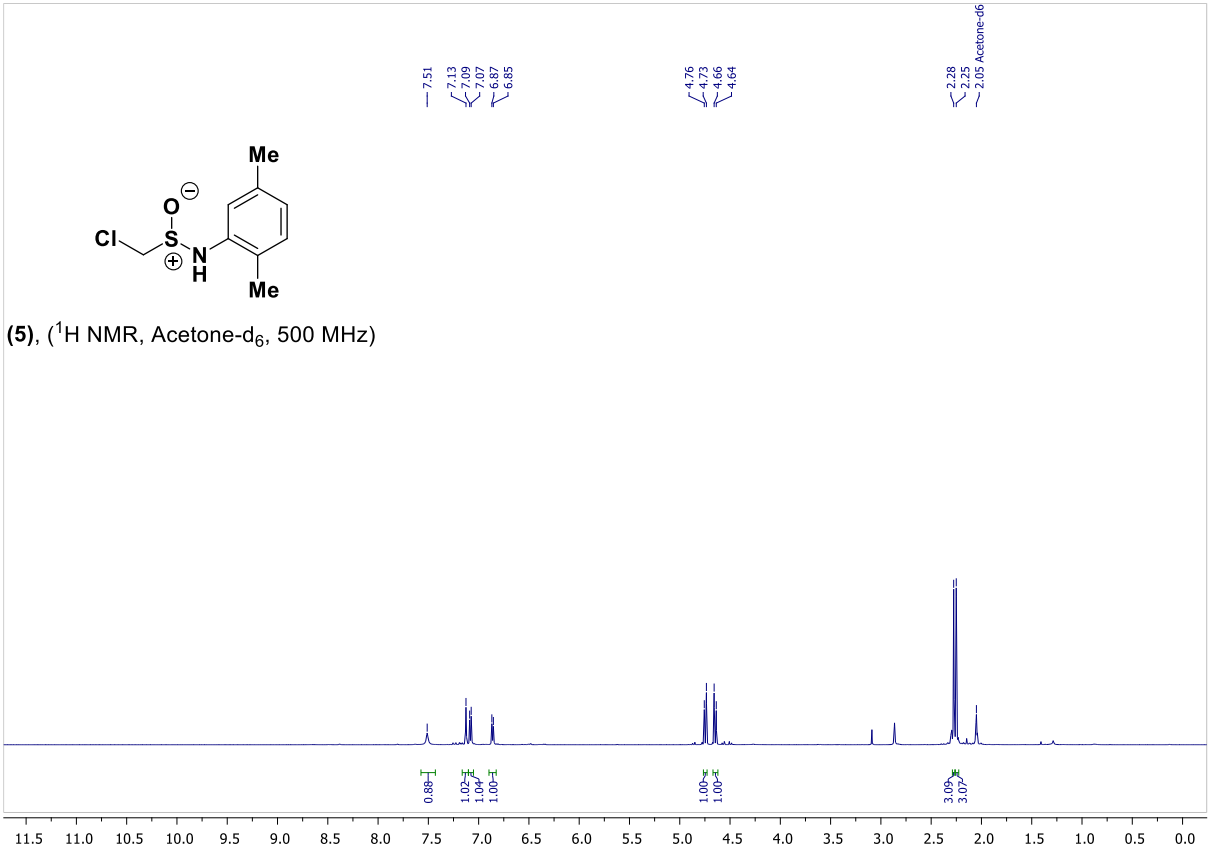
(3), (^{13}C NMR, Acetone-d$_6$, 125 MHz)



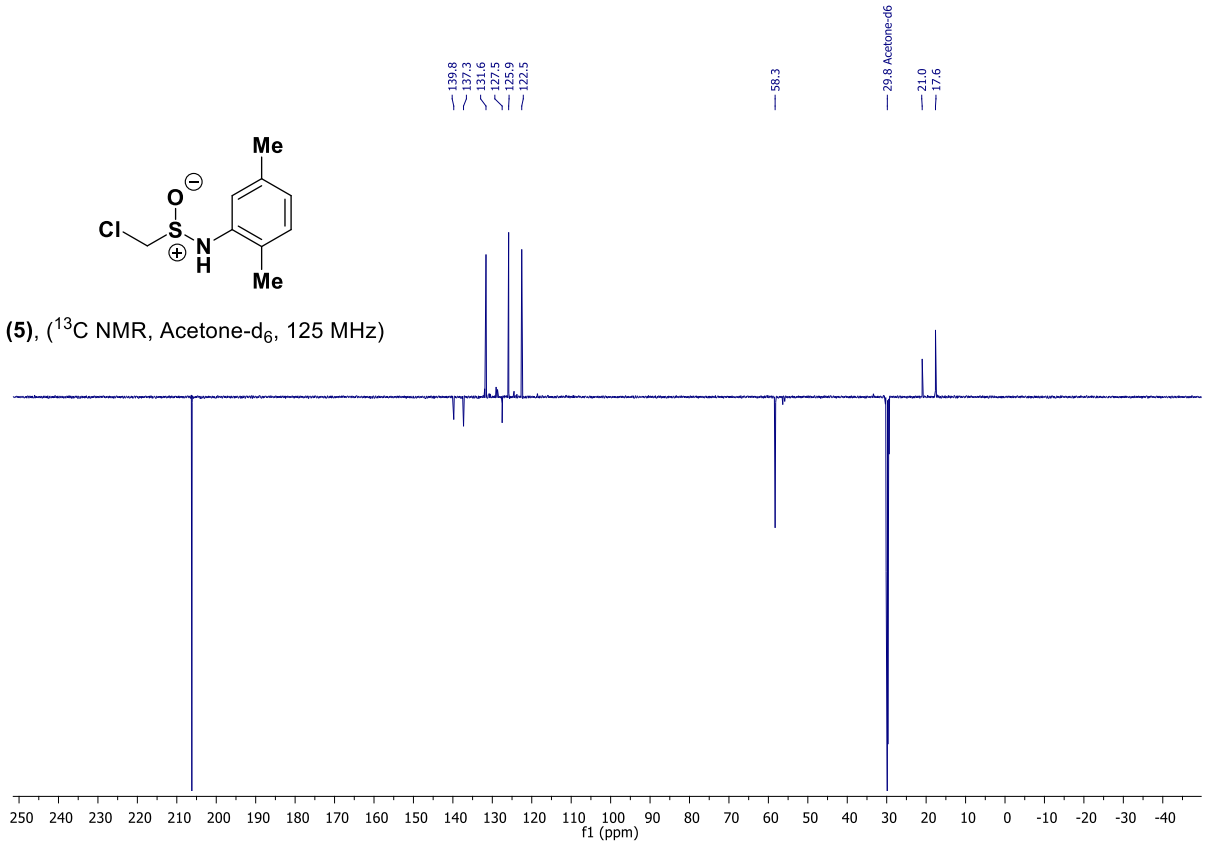
(4), (^{1}H NMR, Acetone-d_6, 500 MHz)



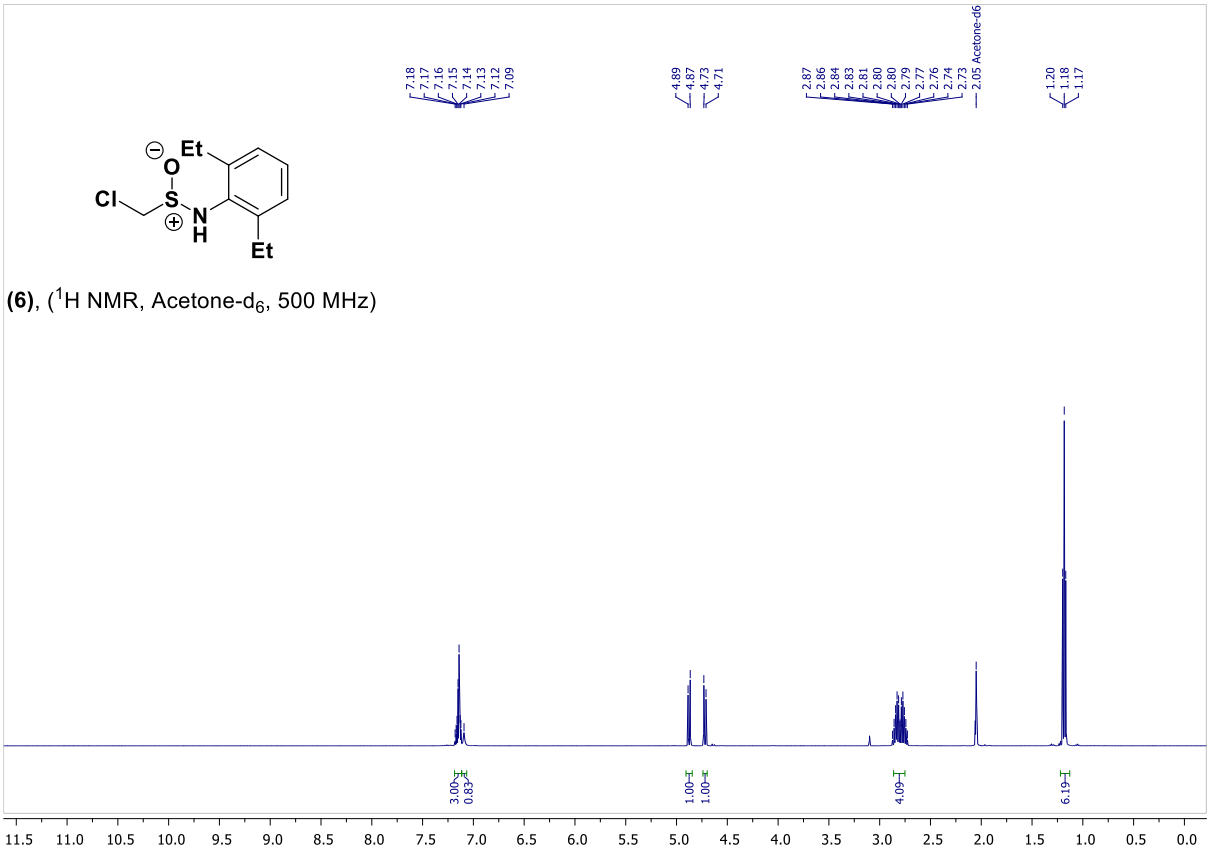
(4), (^{13}C NMR, Acetone-d_6, 125 MHz)



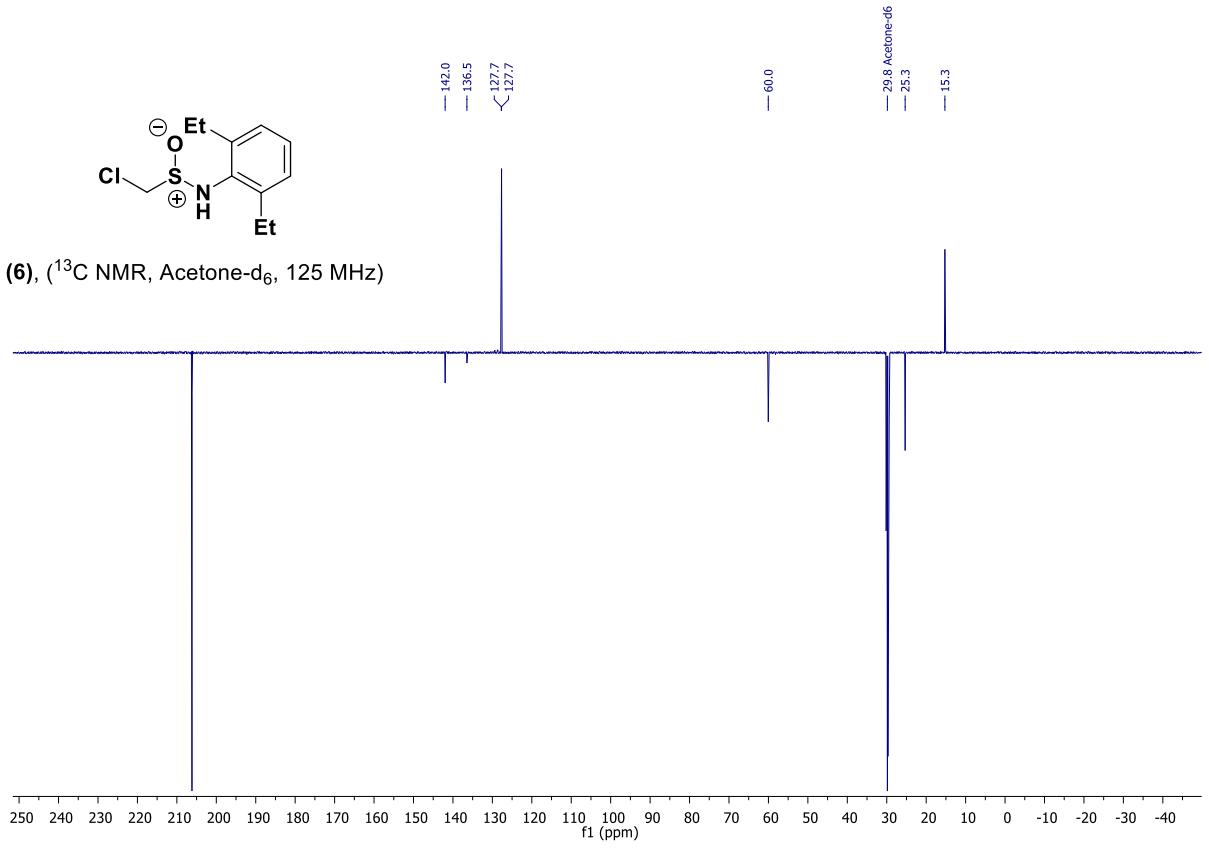
(5), (^{1}H NMR, Acetone-d_6, 500 MHz)



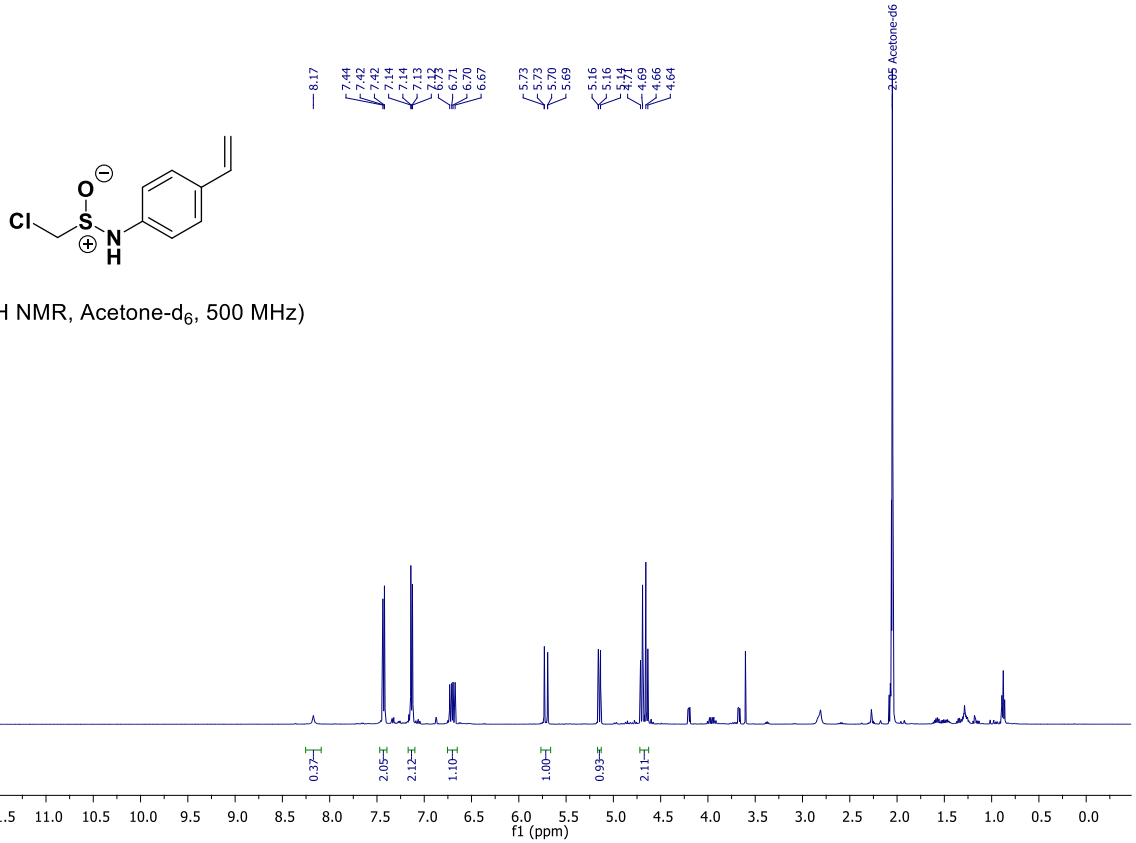
(5), (^{13}C NMR, Acetone-d_6, 125 MHz)



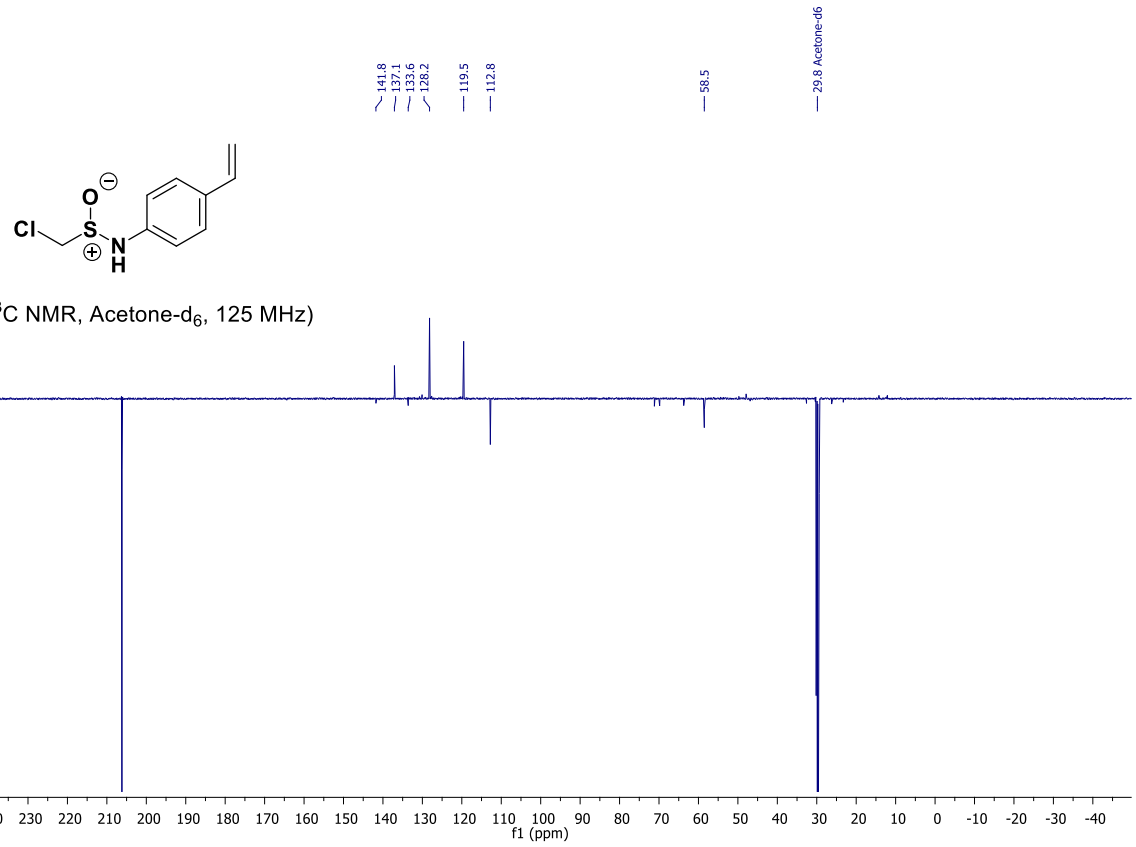
(6), (^{1}H NMR, Acetone-d_6, 500 MHz)



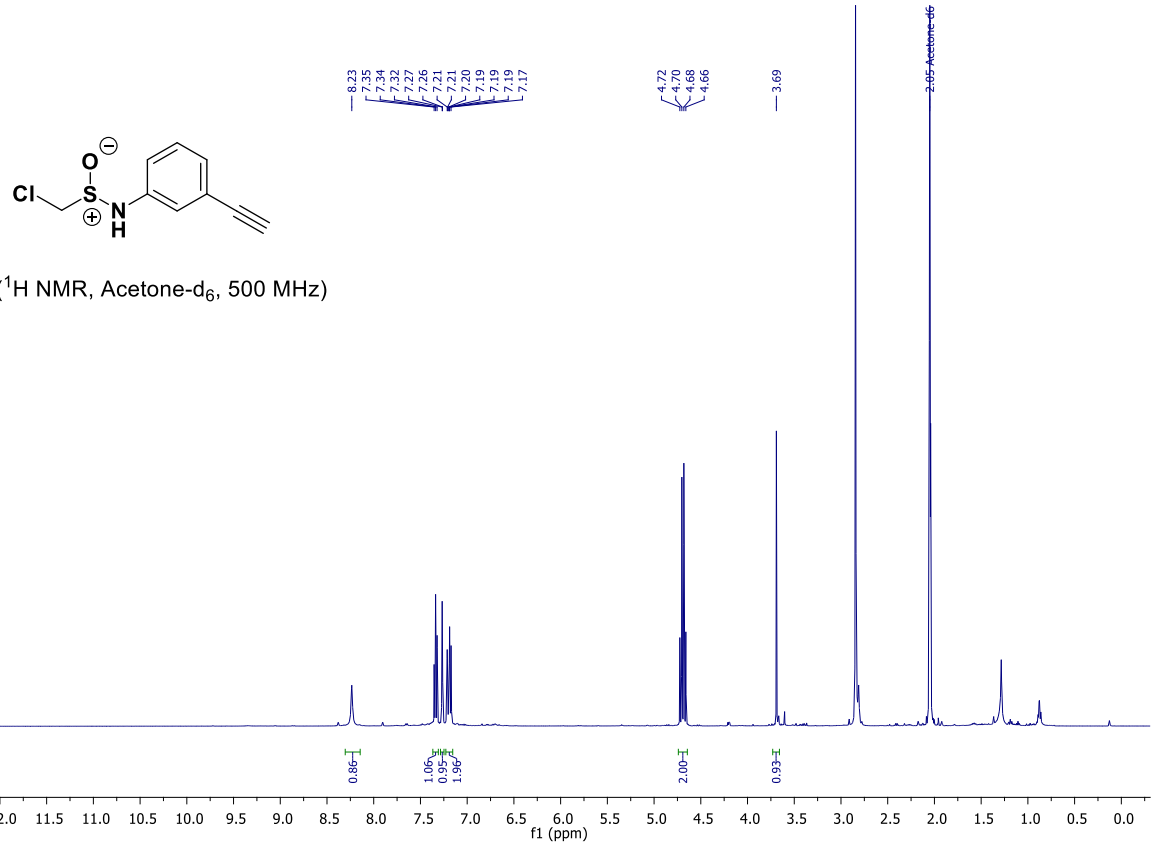
(6), (^{13}C NMR, Acetone-d_6, 125 MHz)



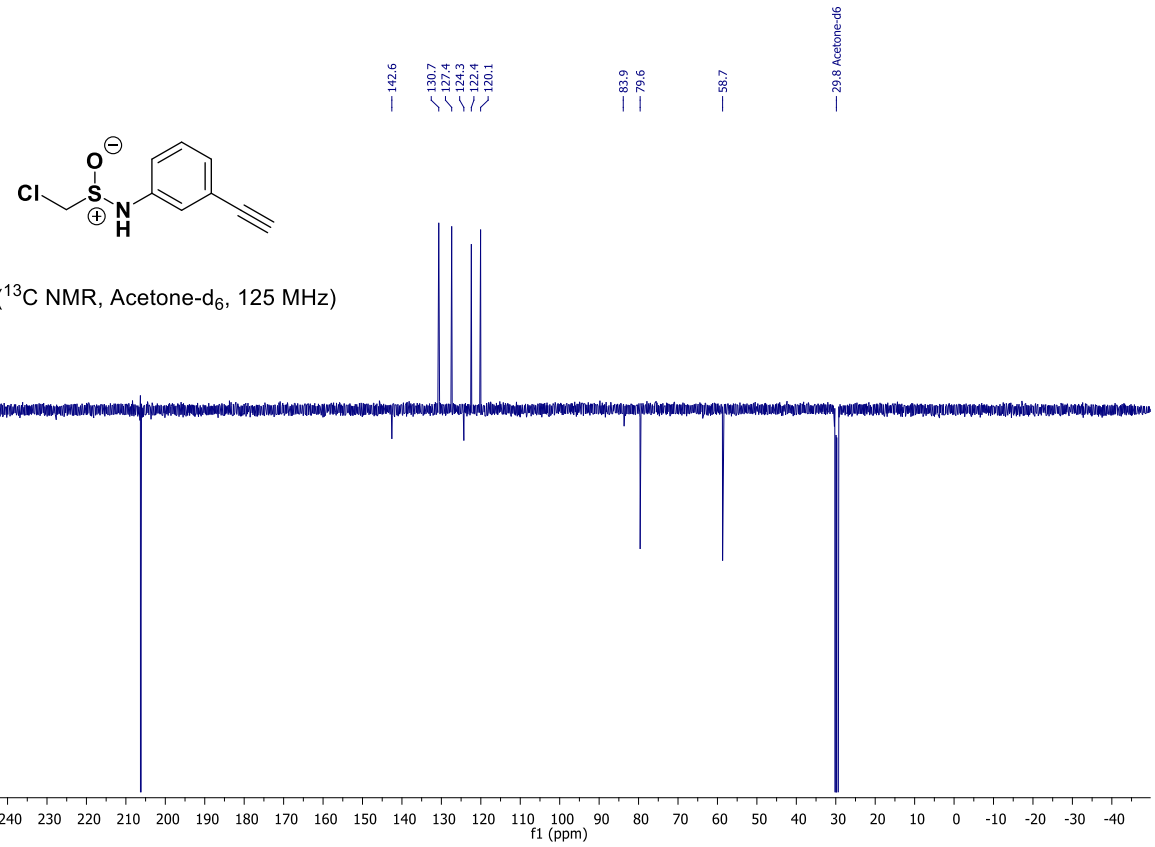
(7), (^{1}H NMR, Acetone-d_6, 500 MHz)



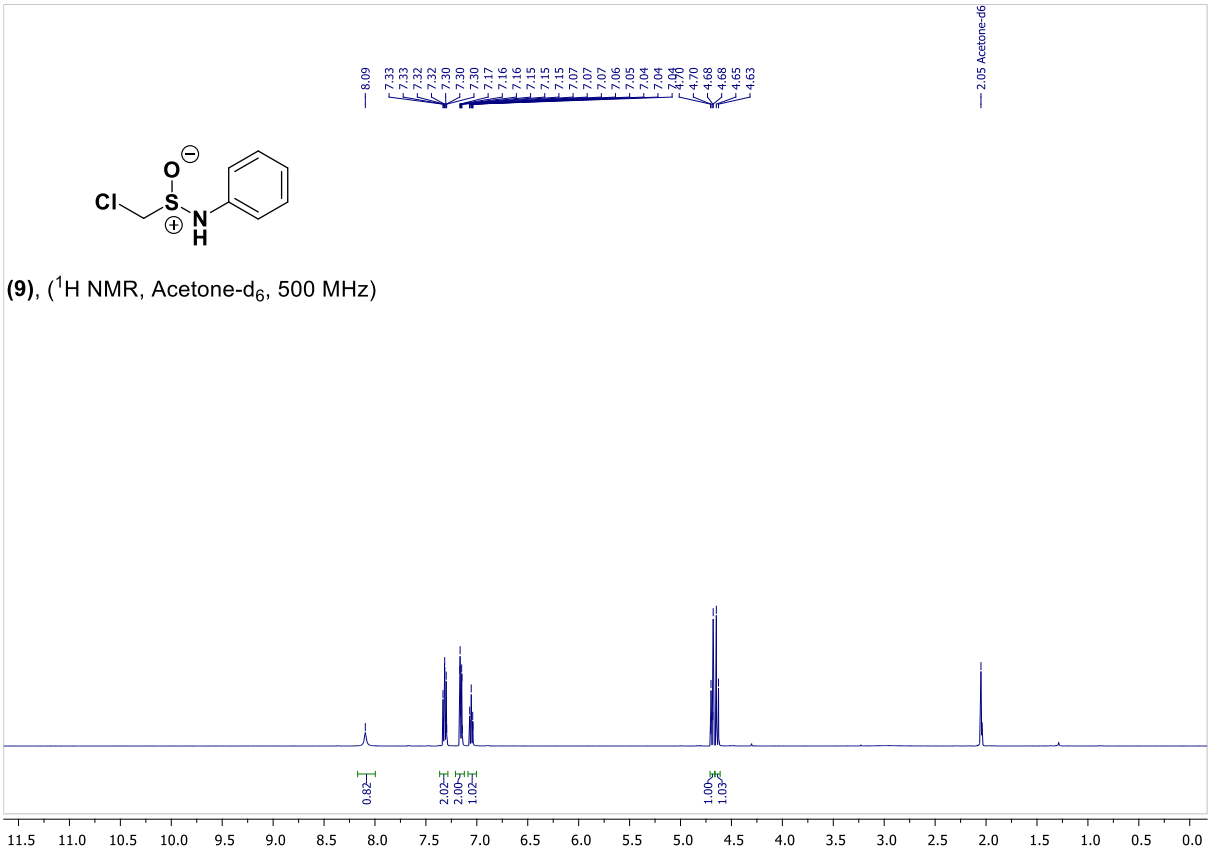
(7), (^{13}C NMR, Acetone-d_6, 125 MHz)



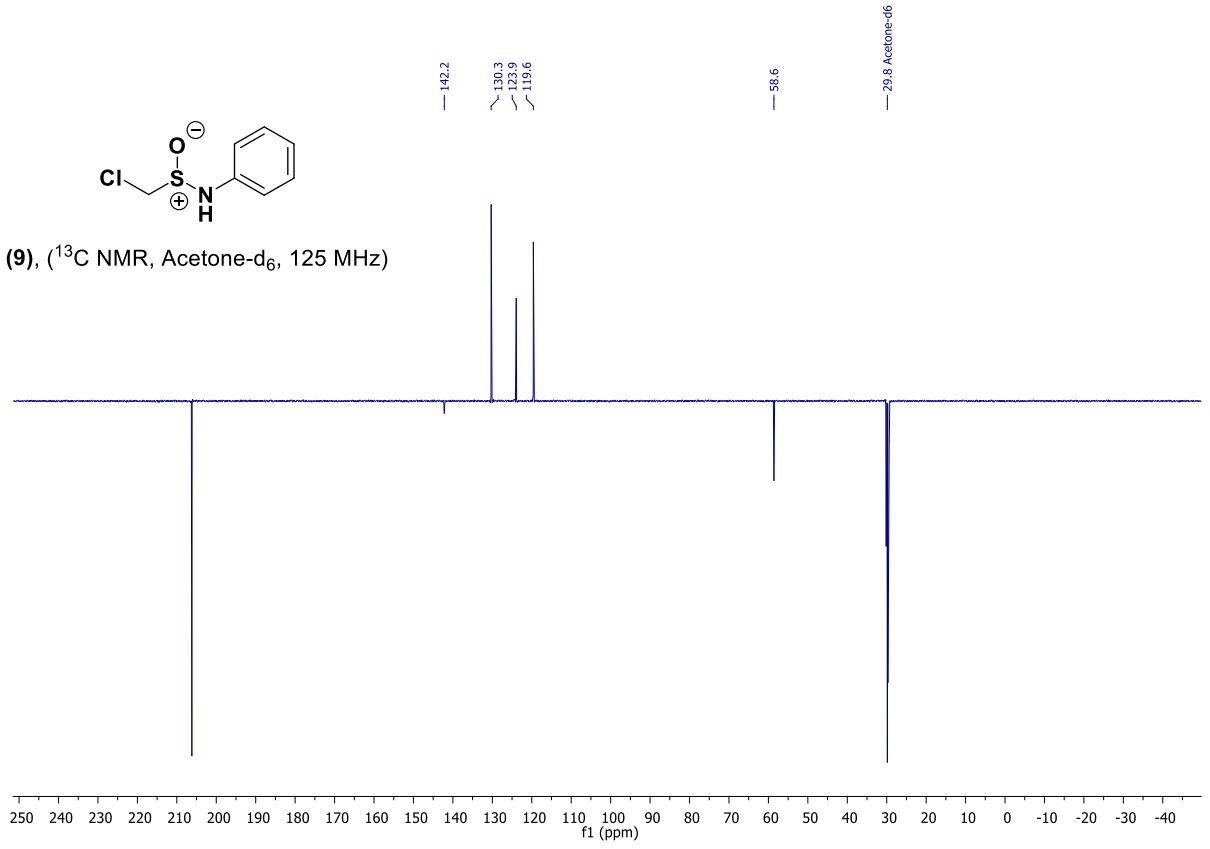
(8), (^{1}H NMR, Acetone-d_6, 500 MHz)



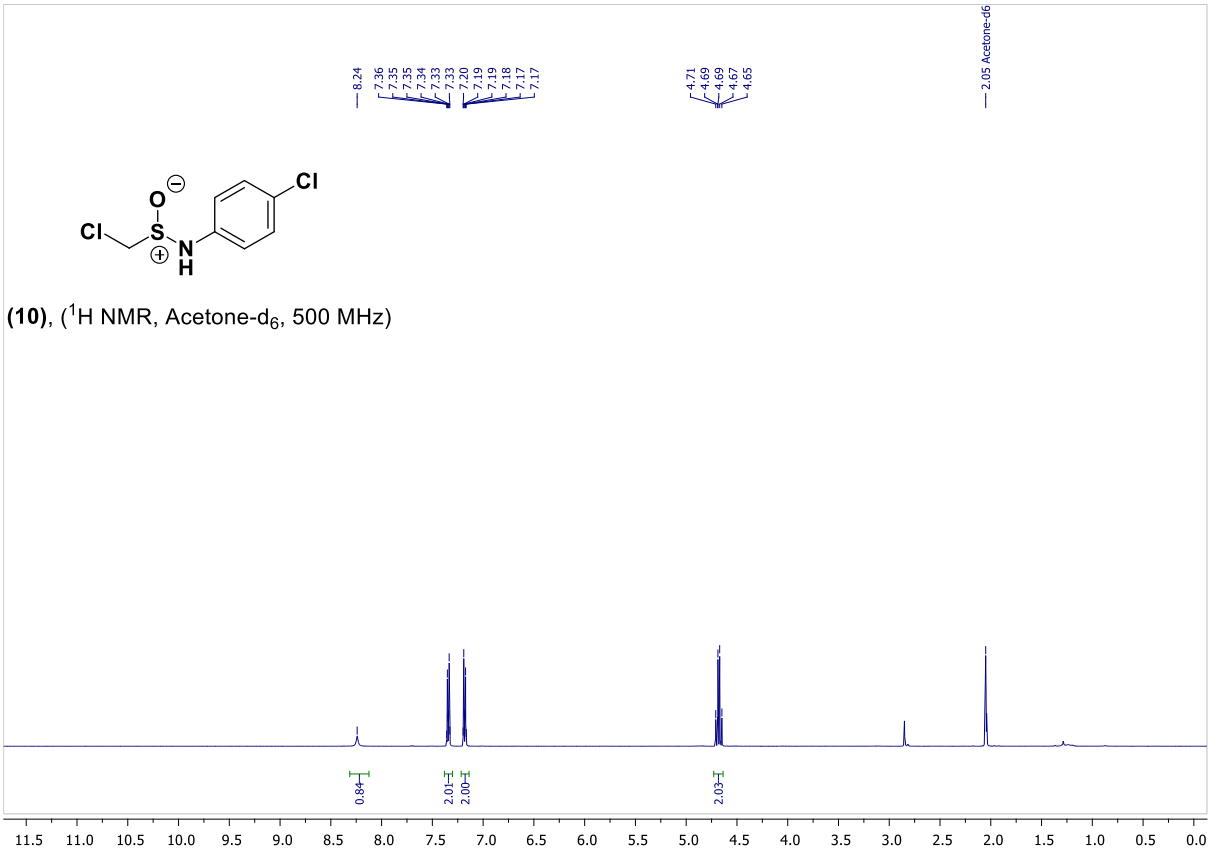
(8), (^{13}C NMR, Acetone-d_6, 125 MHz)



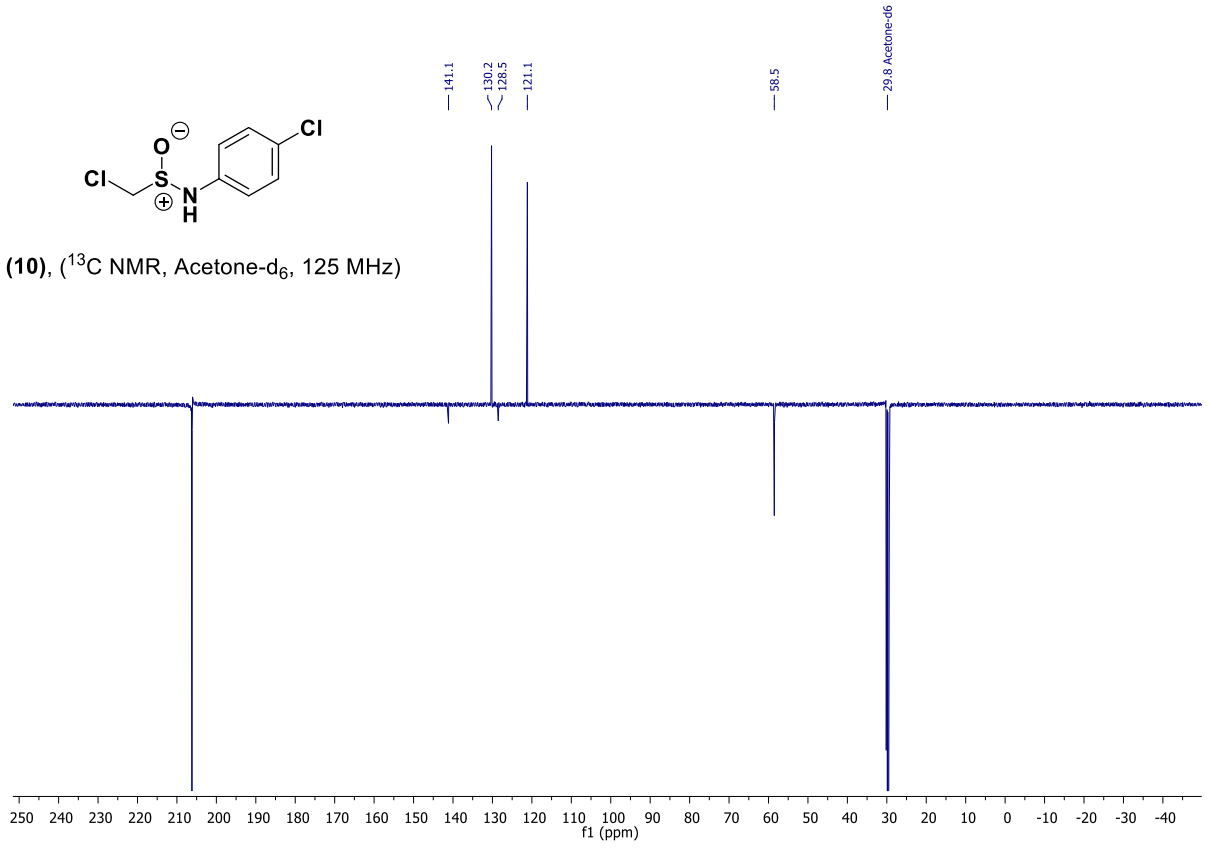
(9), (^{1}H NMR, Acetone-d$_6$, 500 MHz)



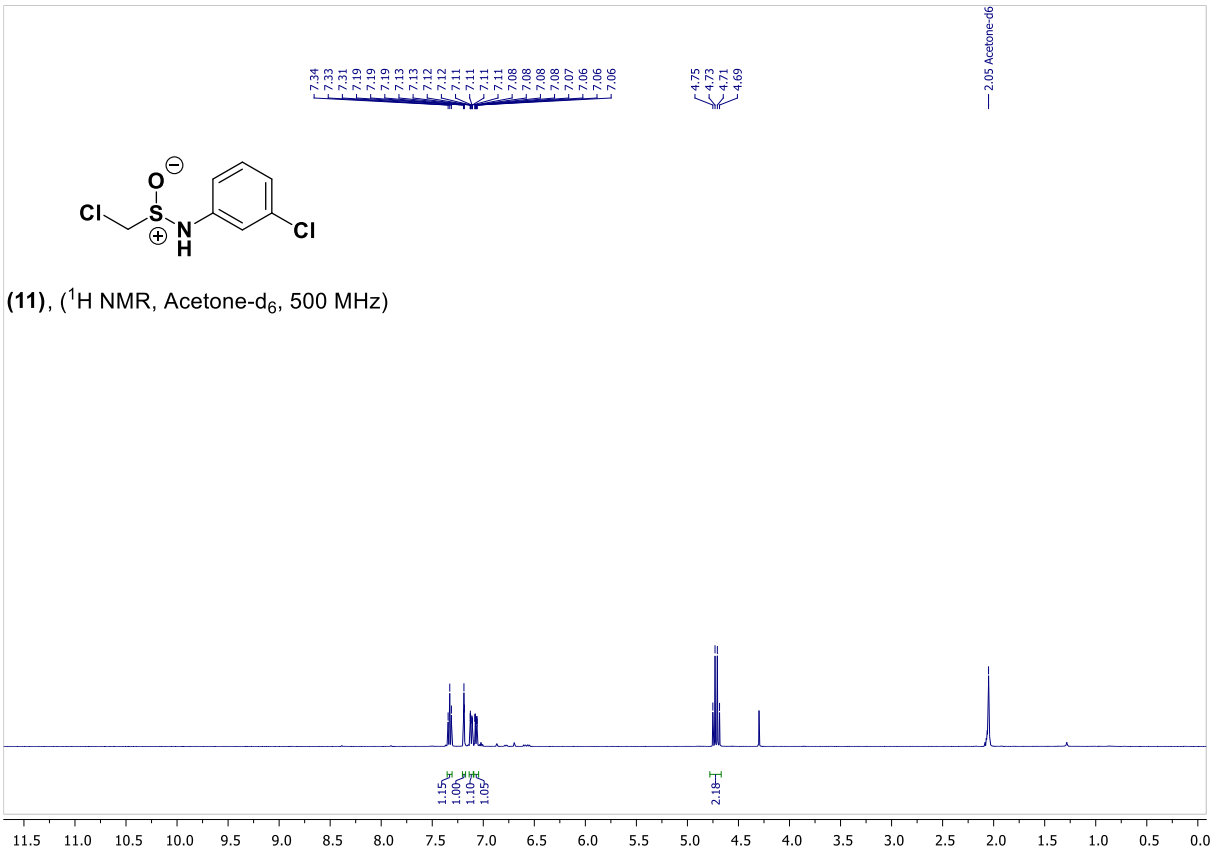
(9), (^{13}C NMR, Acetone-d$_6$, 125 MHz)



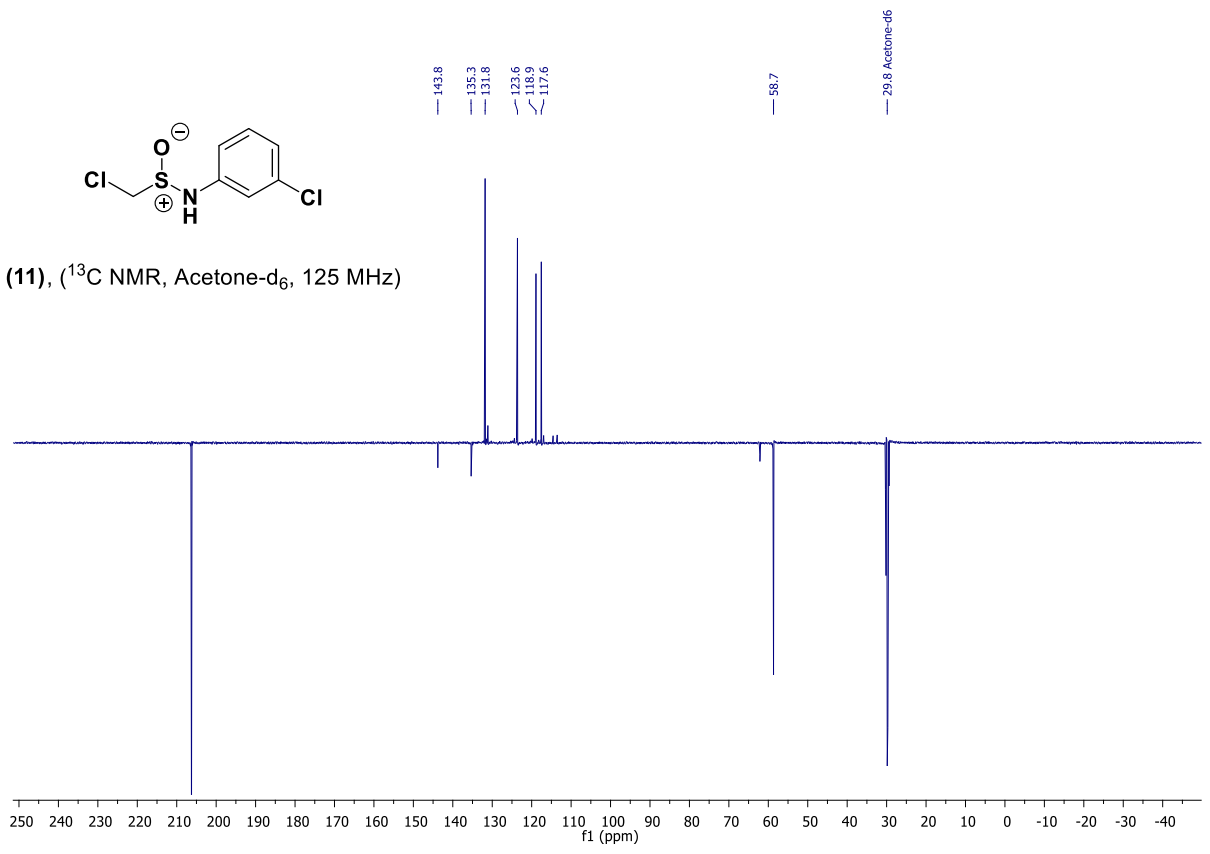
(10), (^{1}H NMR, Acetone-d_6, 500 MHz)



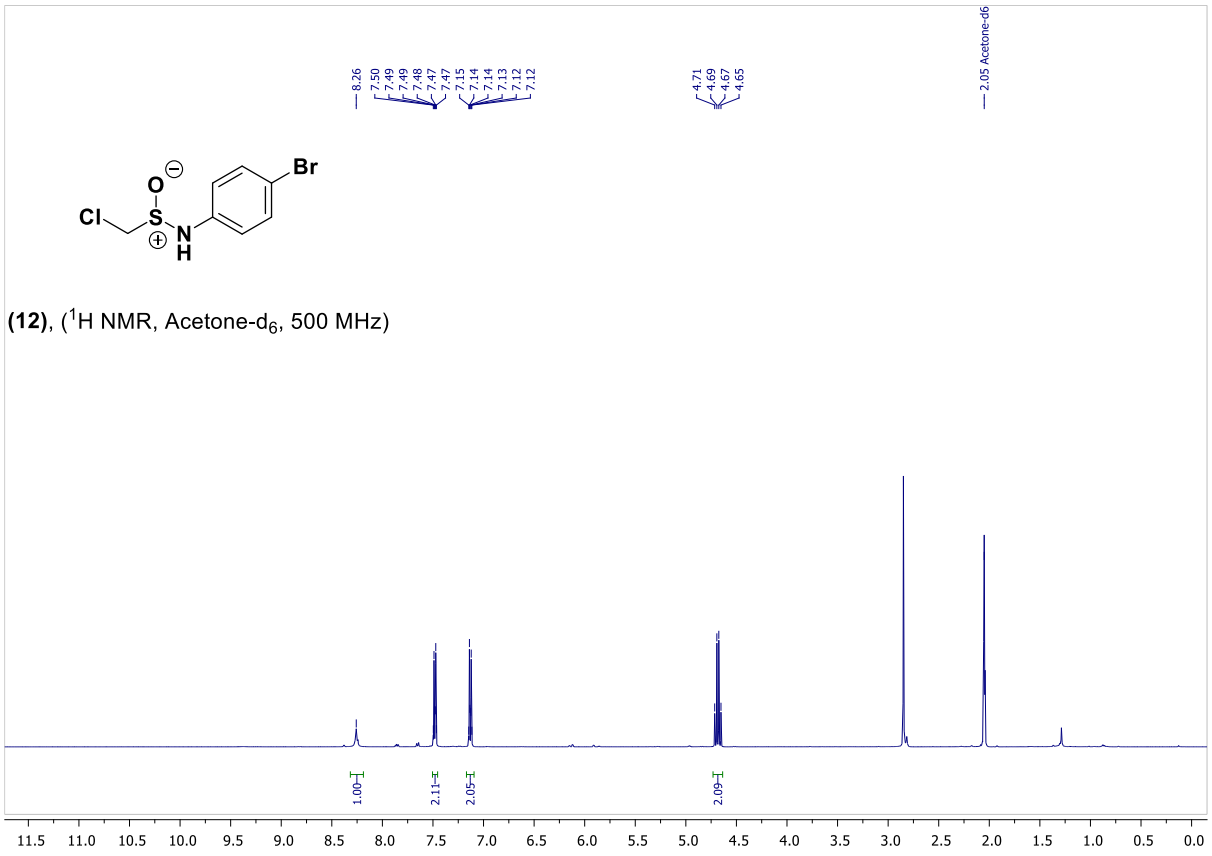
(10), (^{13}C NMR, Acetone-d_6, 125 MHz)



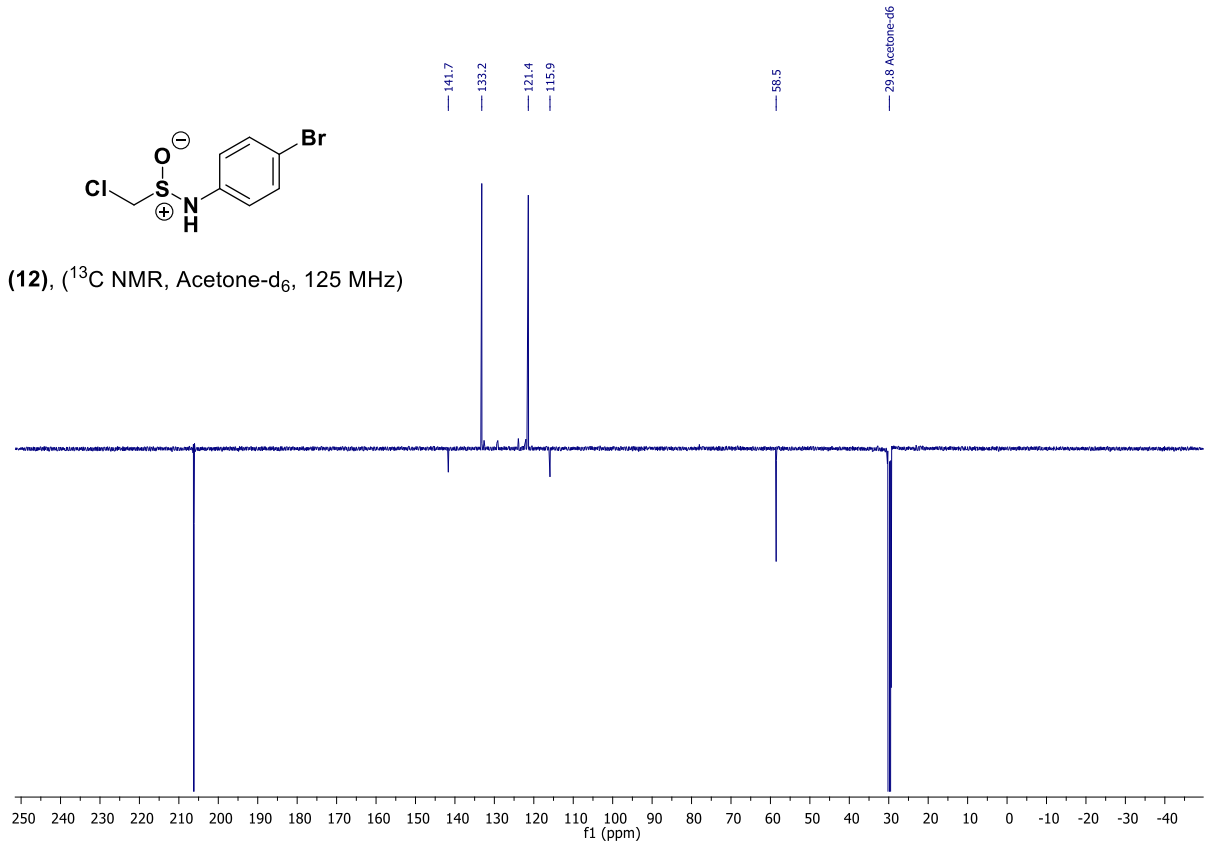
(11), (^{1}H NMR, Acetone-d_6, 500 MHz)



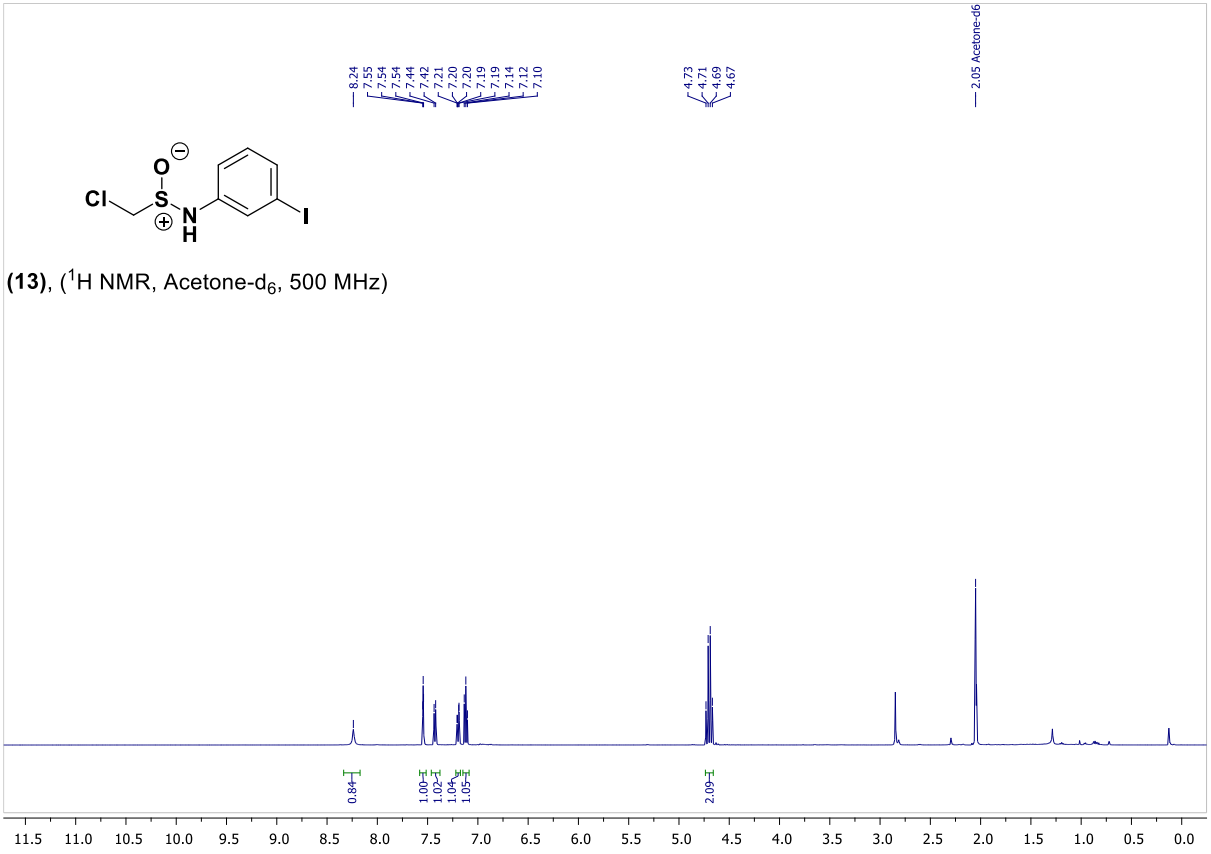
(11), (^{13}C NMR, Acetone-d_6, 125 MHz)



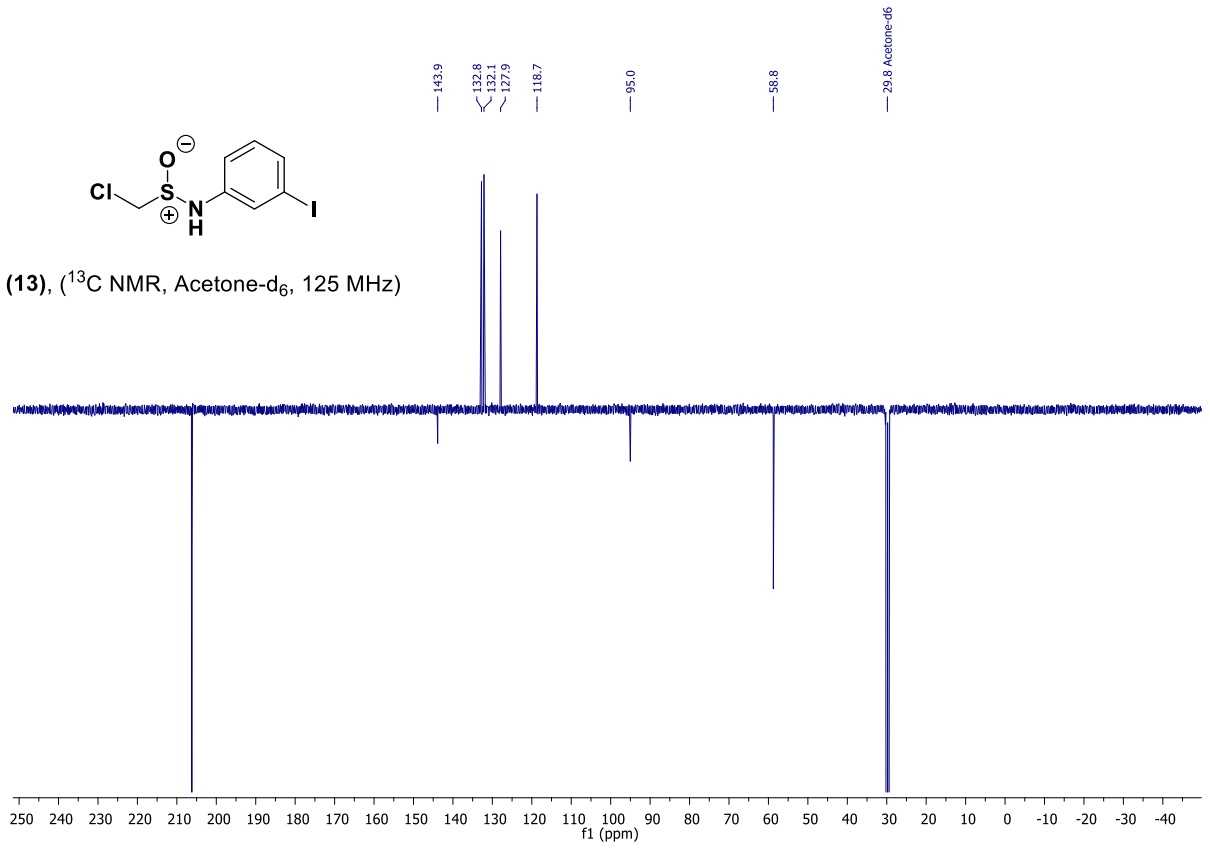
(12), (^{1}H NMR, Acetone-d_6, 500 MHz)



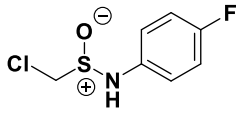
(12), (^{13}C NMR, Acetone-d_6, 125 MHz)



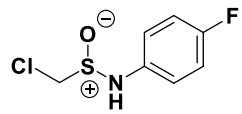
(13), (^{1}H NMR, Acetone-d_6, 500 MHz)



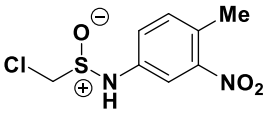
(13), (^{13}C NMR, Acetone-d_6, 125 MHz)



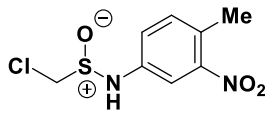
(14), (^{1}H NMR, Acetone-d$_6$, 500 MHz)



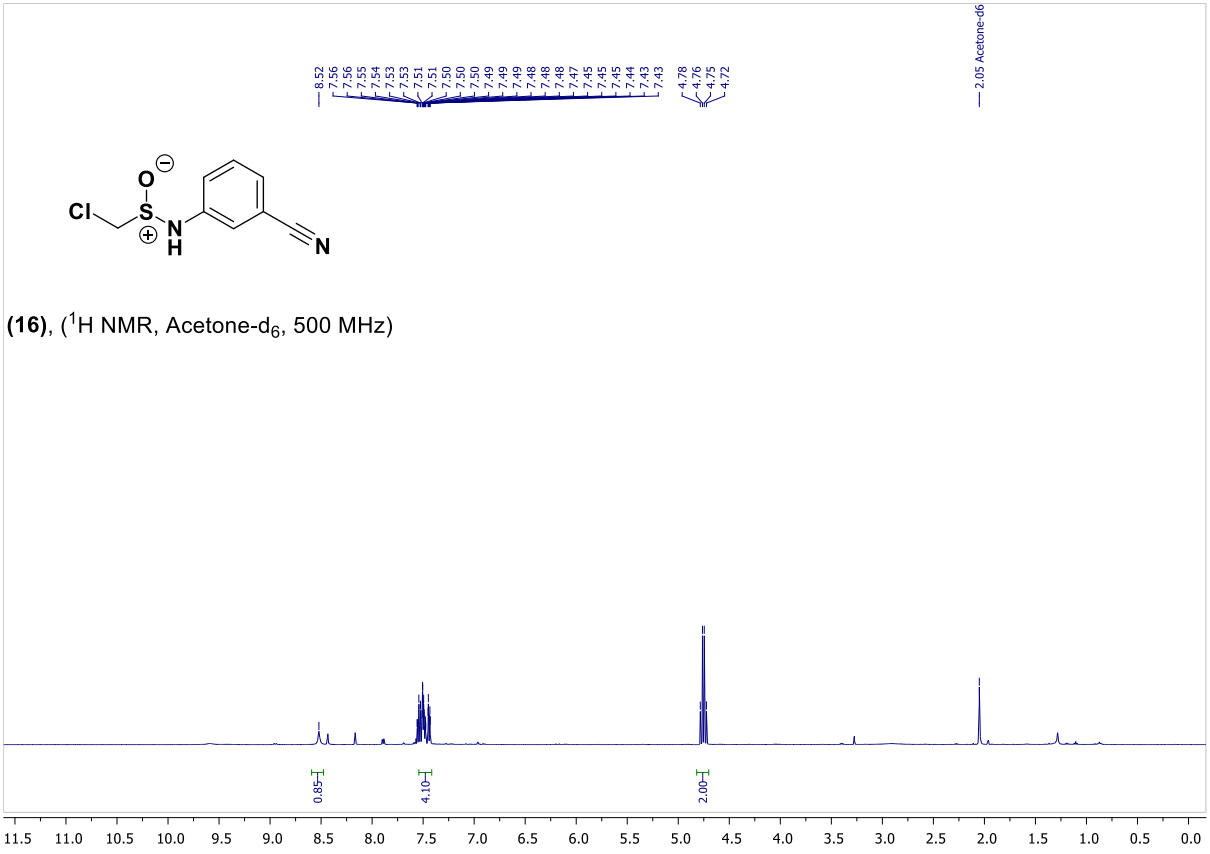
(14), (^{13}C NMR, Acetone-d$_6$, 125 MHz)



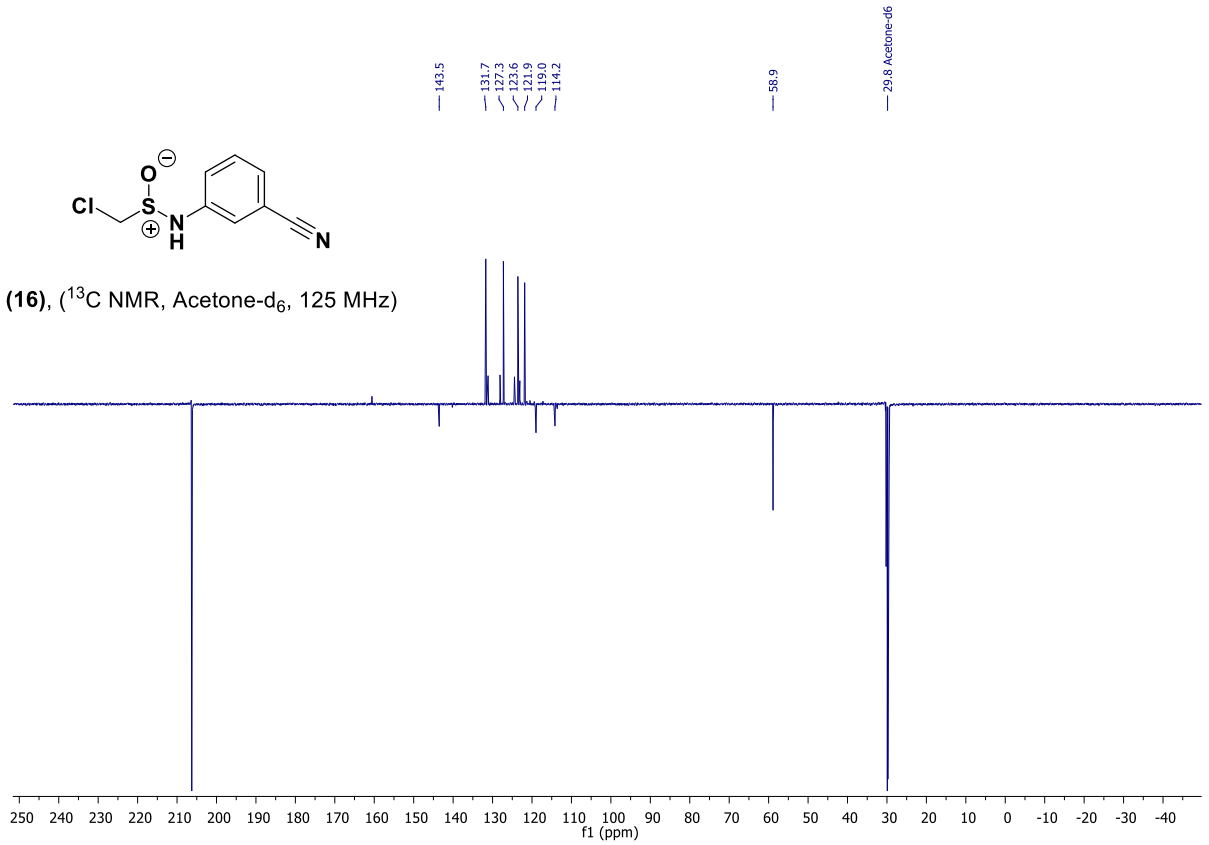
(15), (^{1}H NMR, Acetone-d_6, 500 MHz)



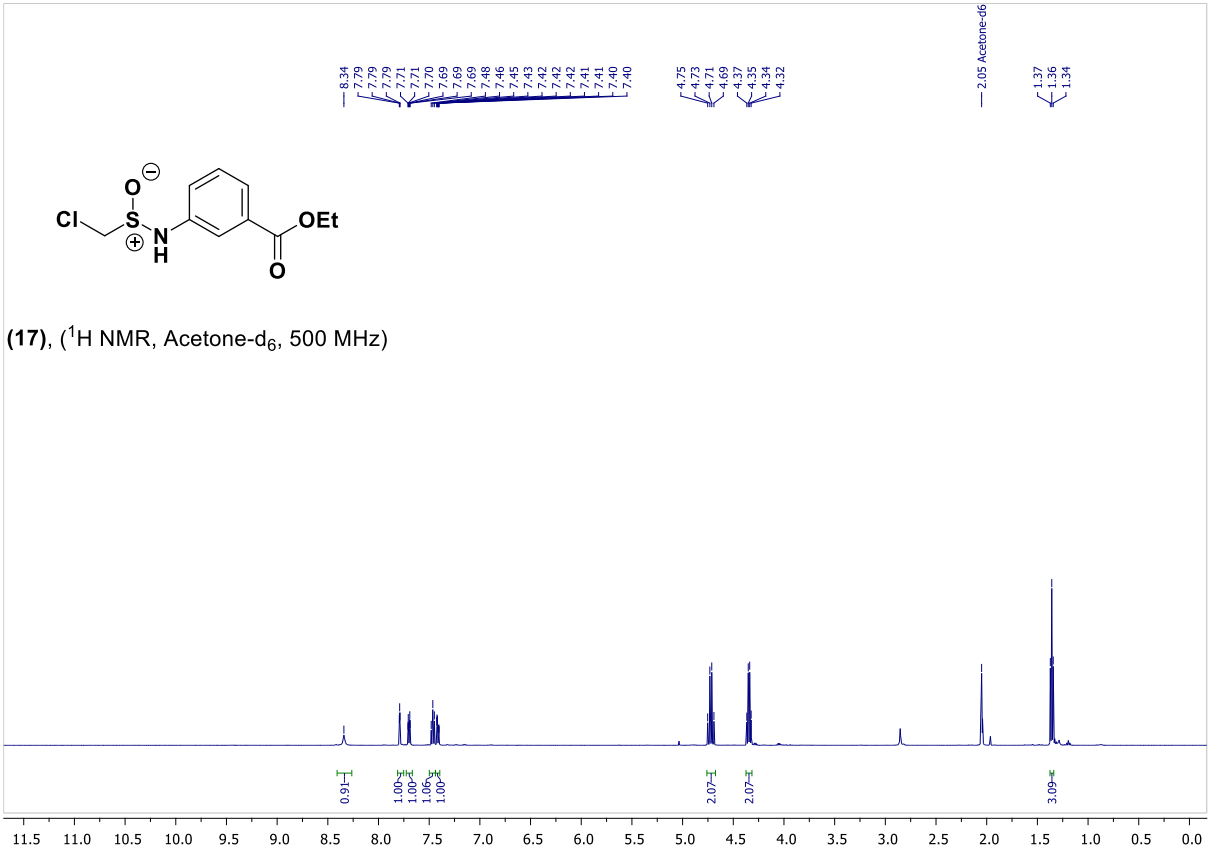
(15), (^{13}C NMR, Acetone-d_6, 125 MHz)



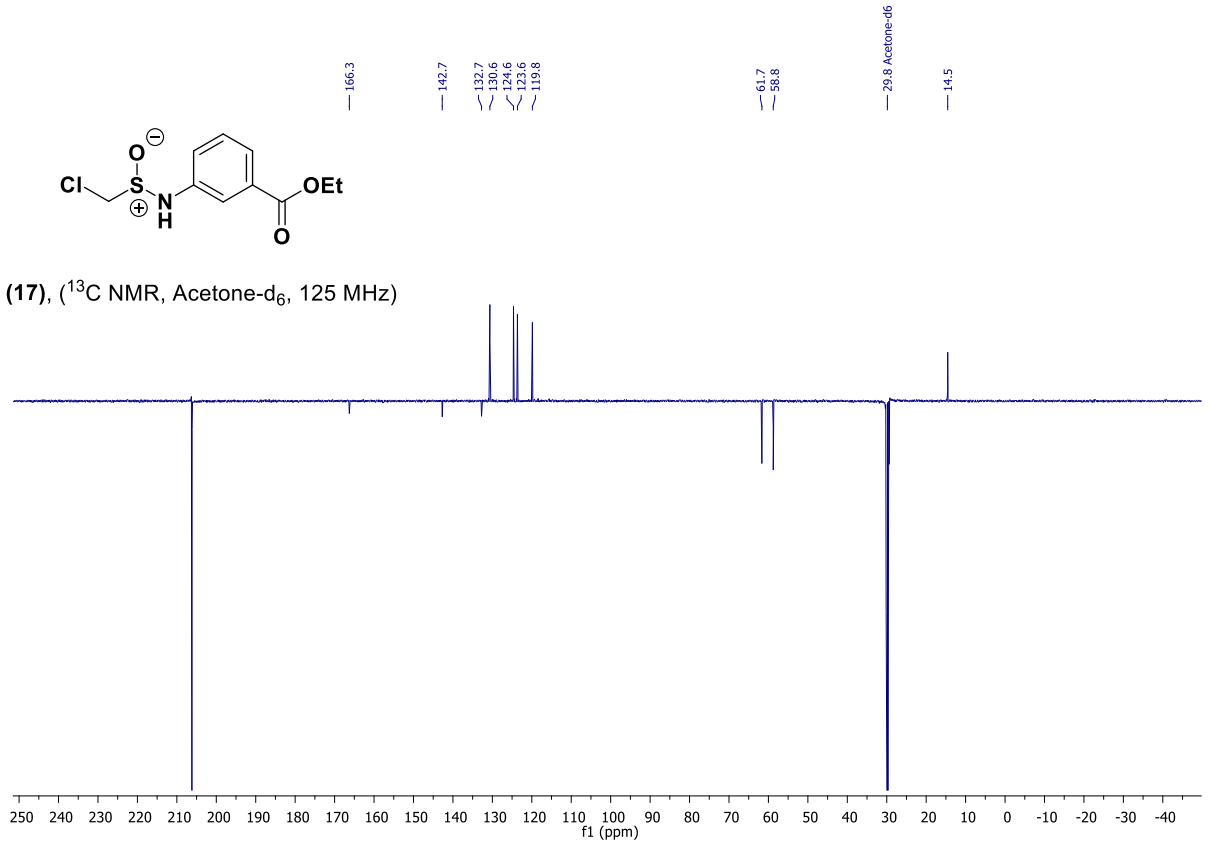
(16), (^{1}H NMR, Acetone-d_6, 500 MHz)



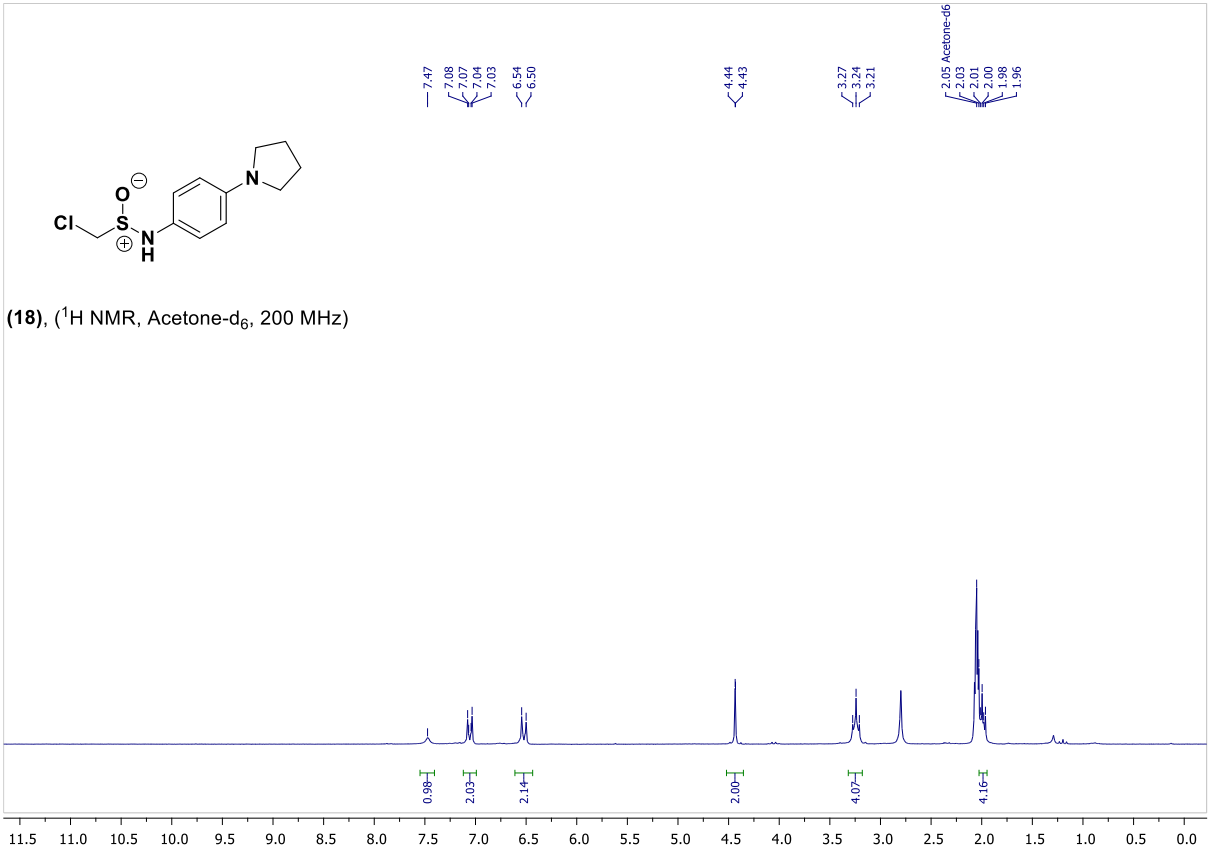
(16), (^{13}C NMR, Acetone-d_6, 125 MHz)



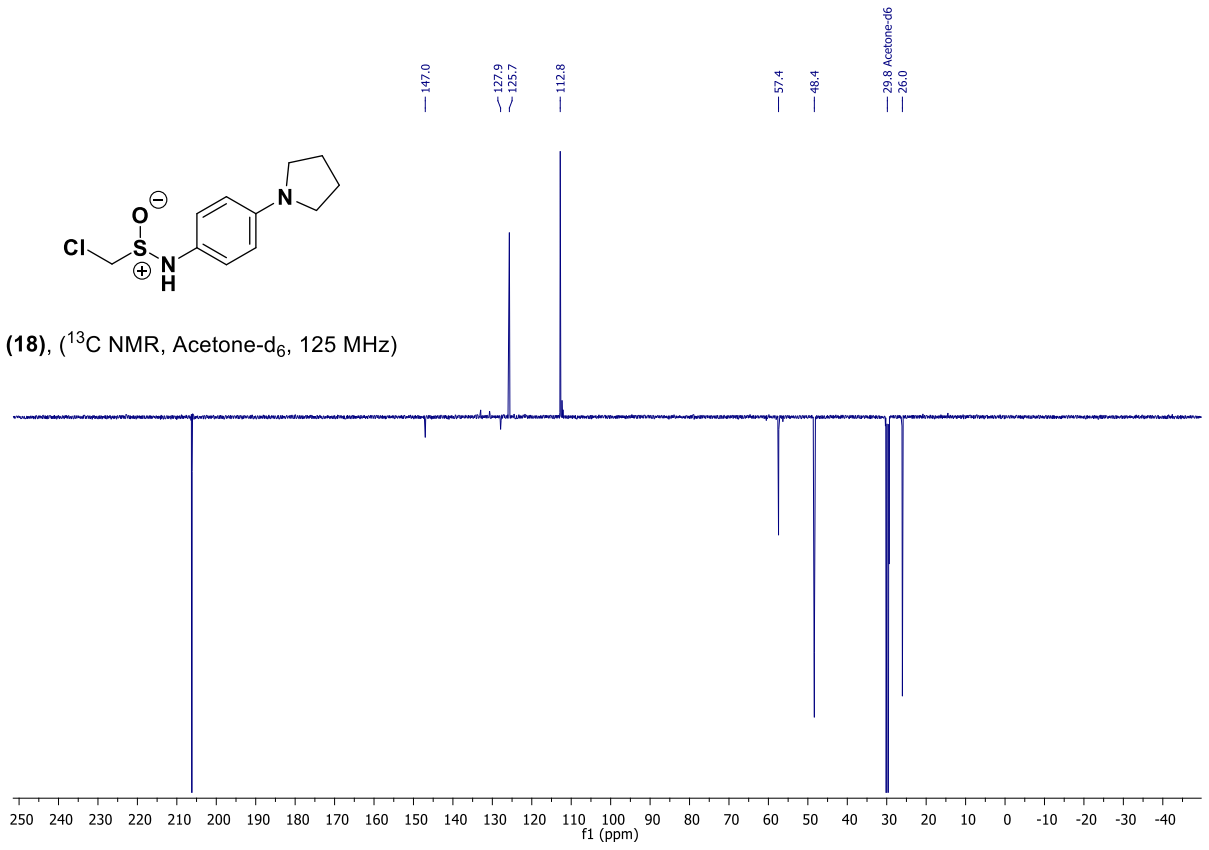
(17), (^{1}H NMR, Acetone-d_6, 500 MHz)



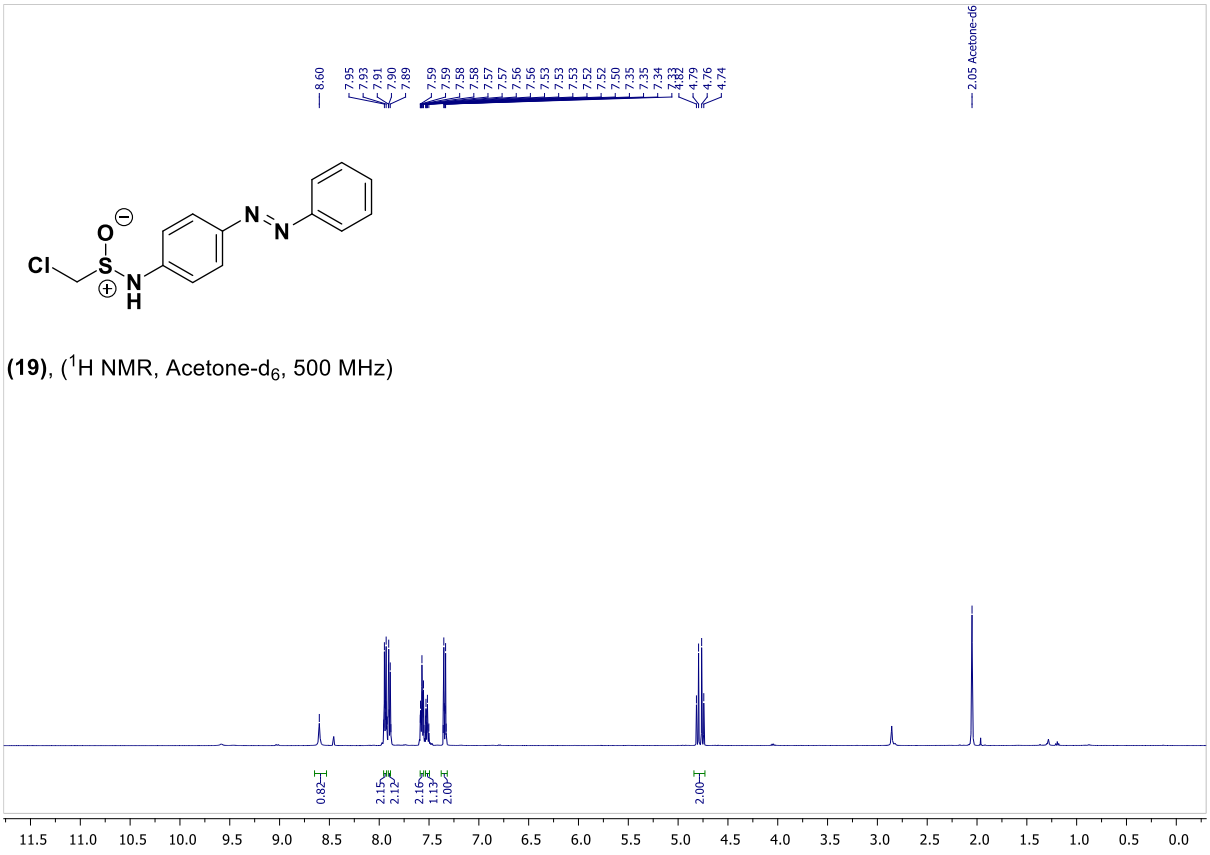
(17), (^{13}C NMR, Acetone-d_6, 125 MHz)



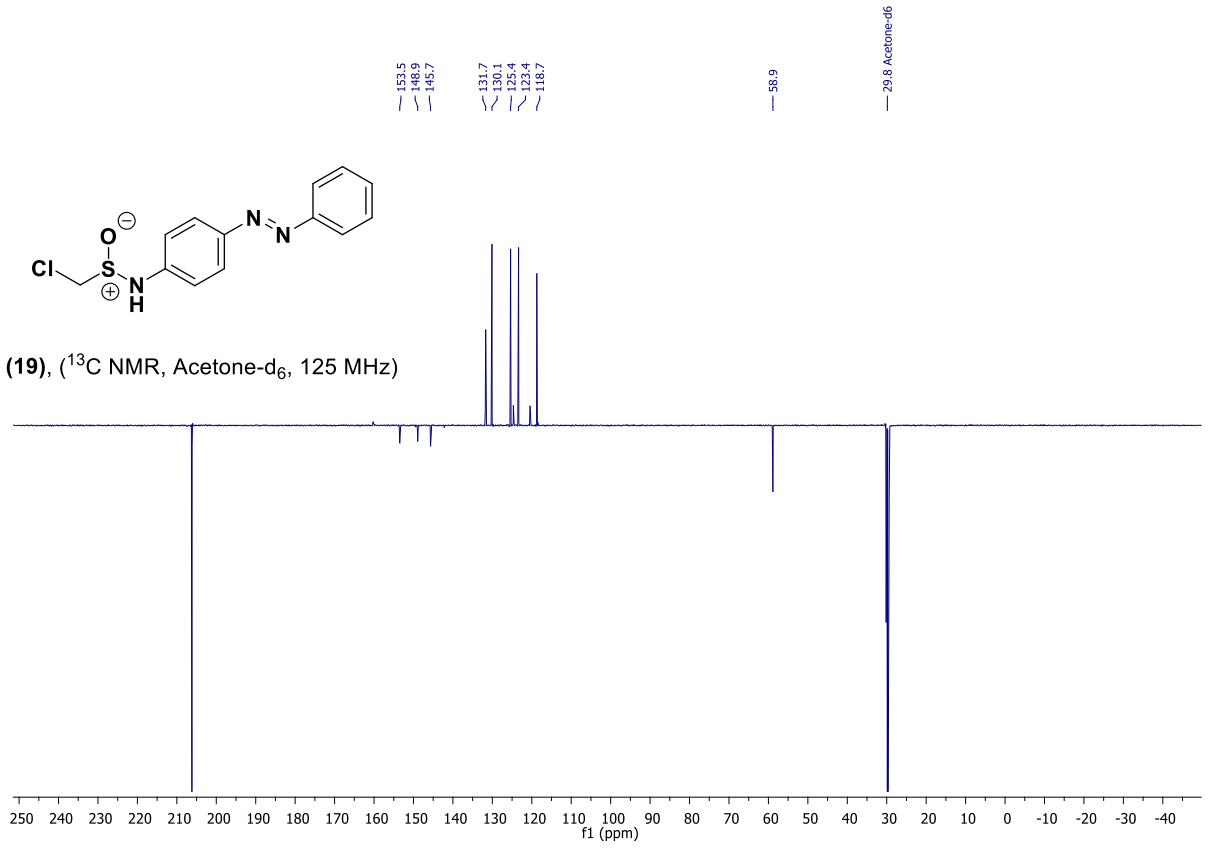
(18), (^{1}H NMR, Acetone-d_6, 200 MHz)



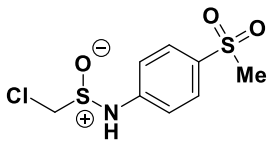
(18), (^{13}C NMR, Acetone-d_6, 125 MHz)



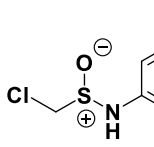
(19), (^{1}H NMR, Acetone-d_6, 500 MHz)



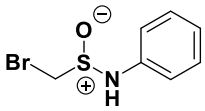
(19), (^{13}C NMR, Acetone-d_6, 125 MHz)



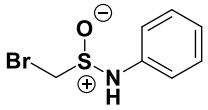
(20), (^{1}H NMR, Acetone-d_6, 500 MHz)



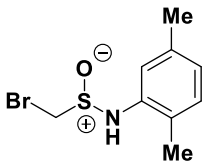
(20), (^{13}C NMR, Acetone-d_6, 125 MHz)



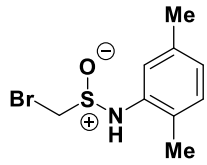
(21), (^{1}H NMR, Acetone-d_6, 500 MHz)



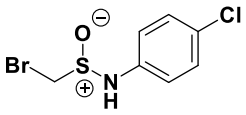
(21), (^{13}C NMR, Acetone-d_6, 125 MHz)



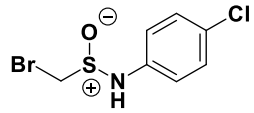
(22), (^{1}H NMR, Acetone-d_6, 500 MHz)



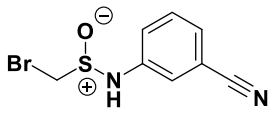
(22), (^{13}C NMR, Acetone-d_6, 125 MHz)



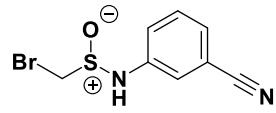
(23), (^{1}H NMR, Acetone-d_6, 500 MHz)



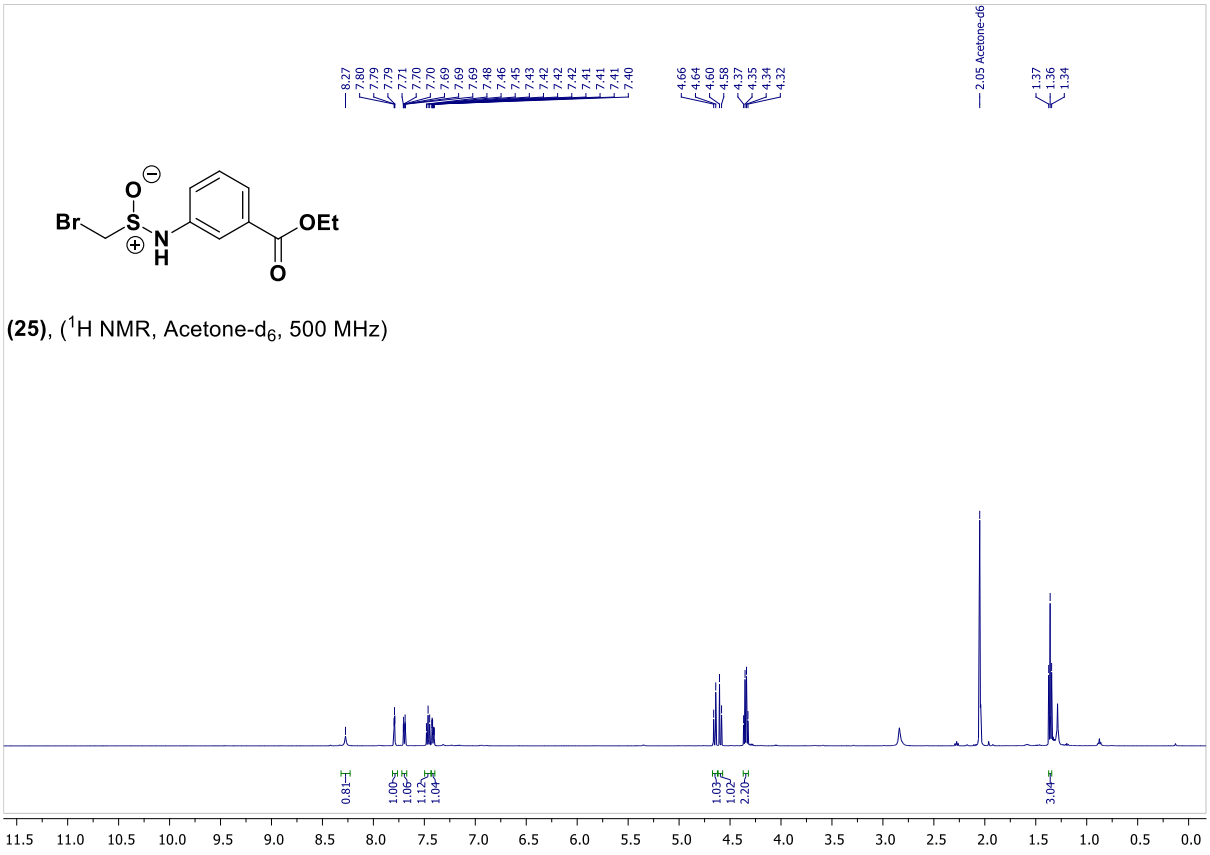
(23), (^{13}C NMR, Acetone-d_6, 125 MHz)



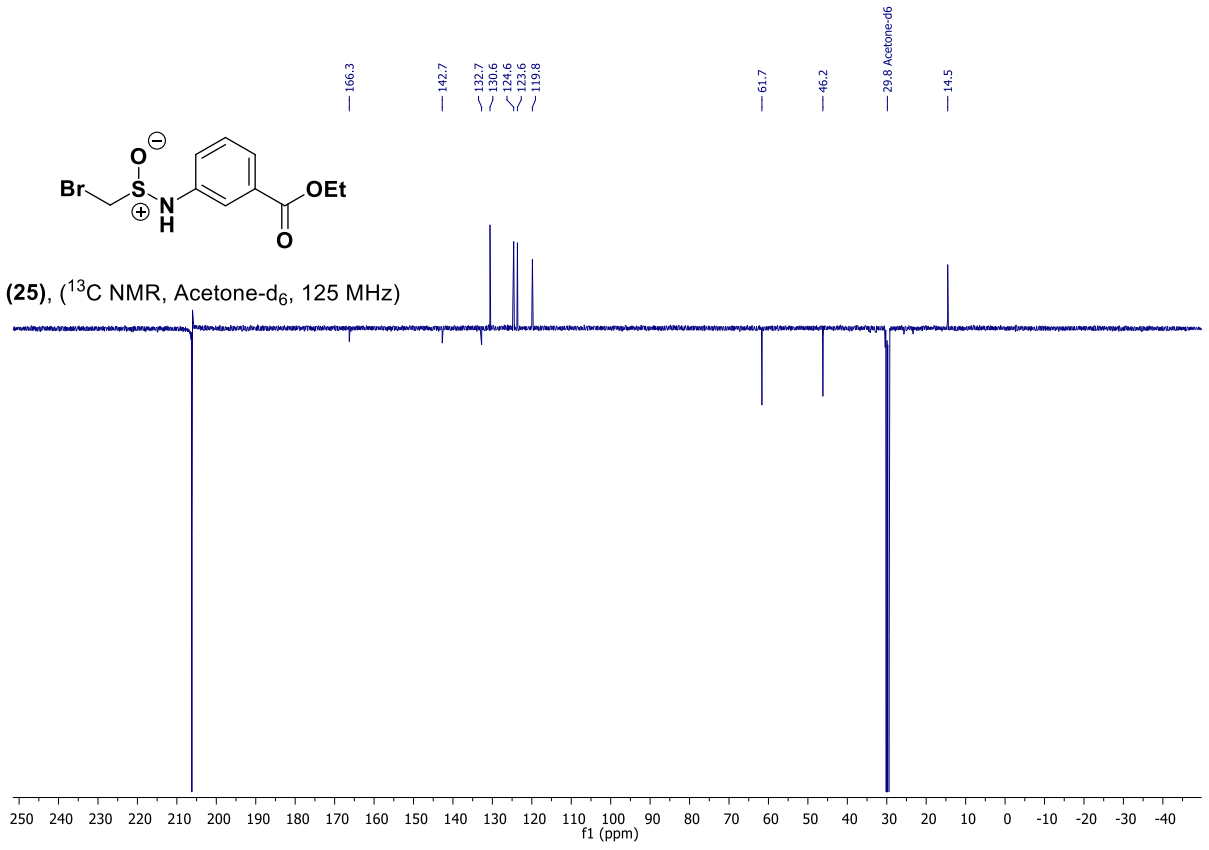
(24), (^{1}H NMR, Acetone-d_6, 500 MHz)



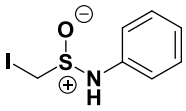
(24), (^{13}C NMR, Acetone-d_6, 125 MHz)



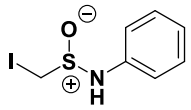
(25), (^{1}H NMR, Acetone-d_6, 500 MHz)



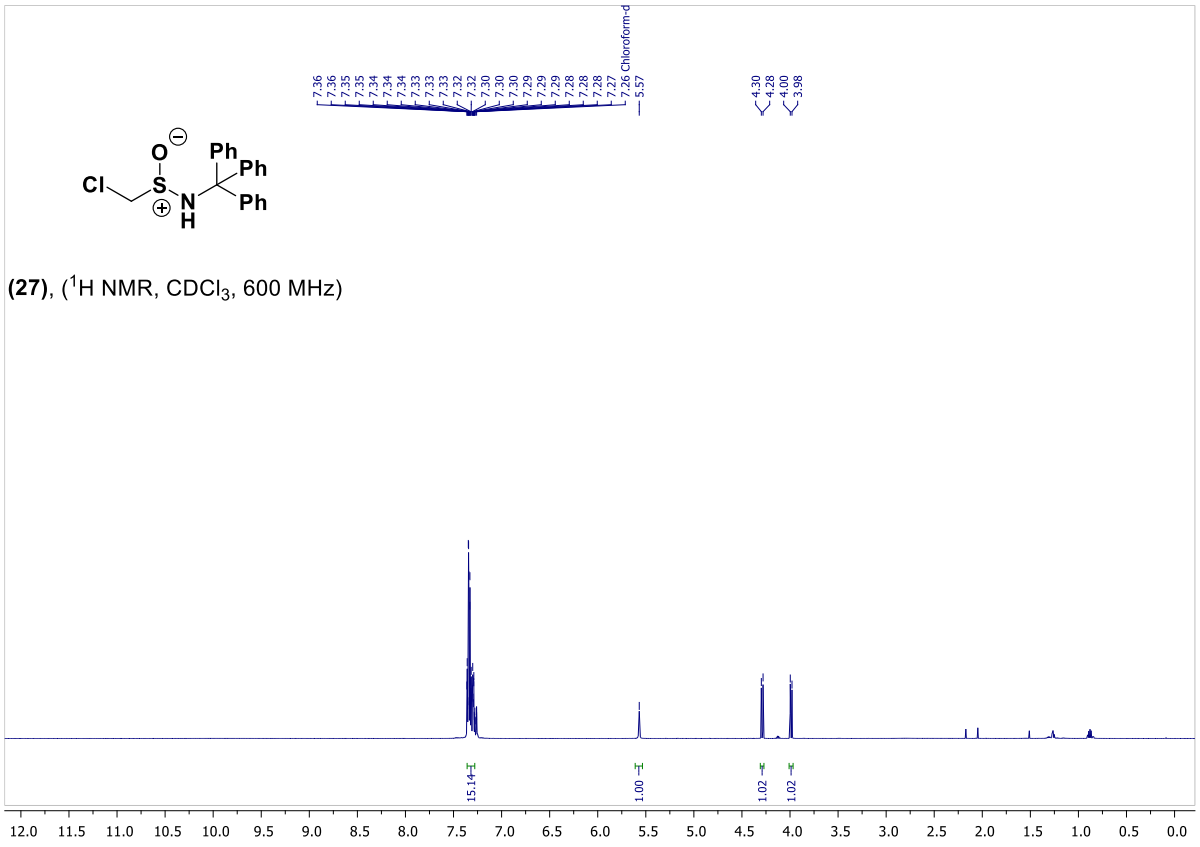
(25), (^{13}C NMR, Acetone-d_6, 125 MHz)



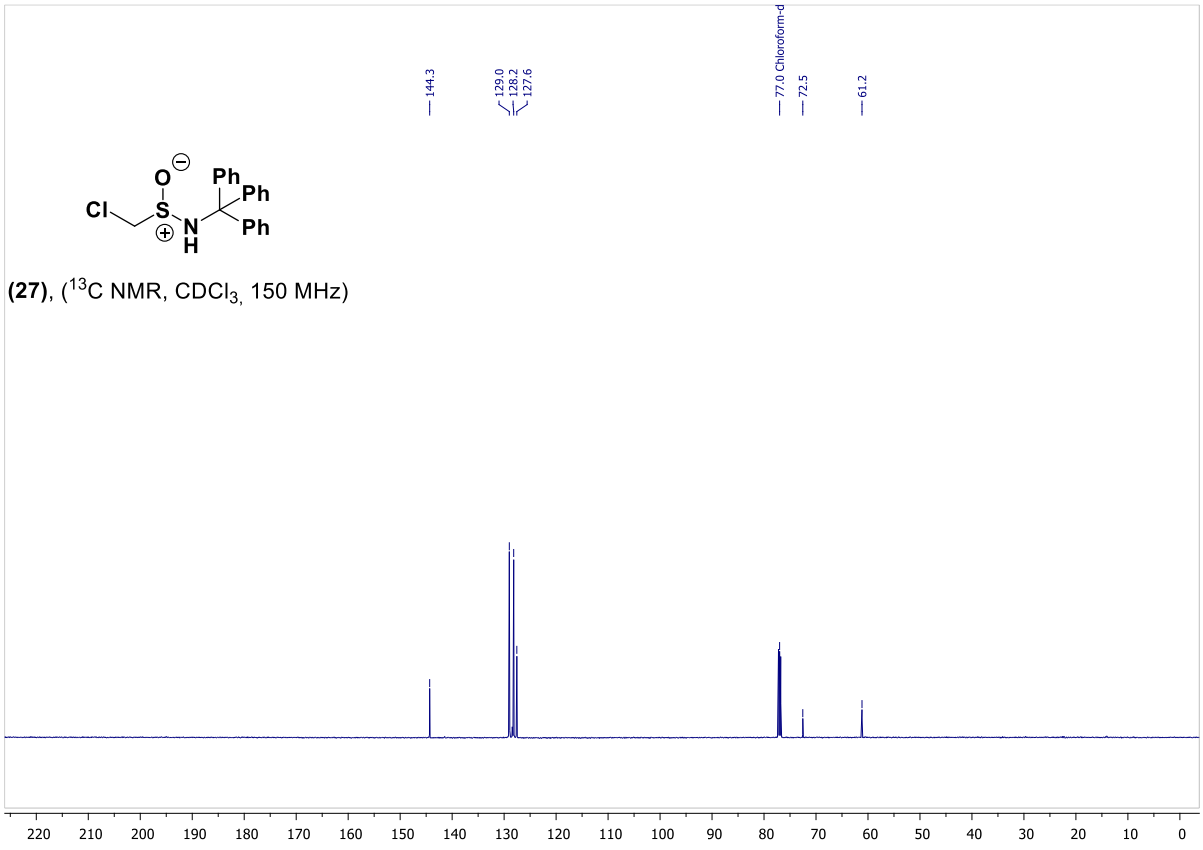
(26), (^{1}H NMR, Acetone-d_6, 200 MHz)



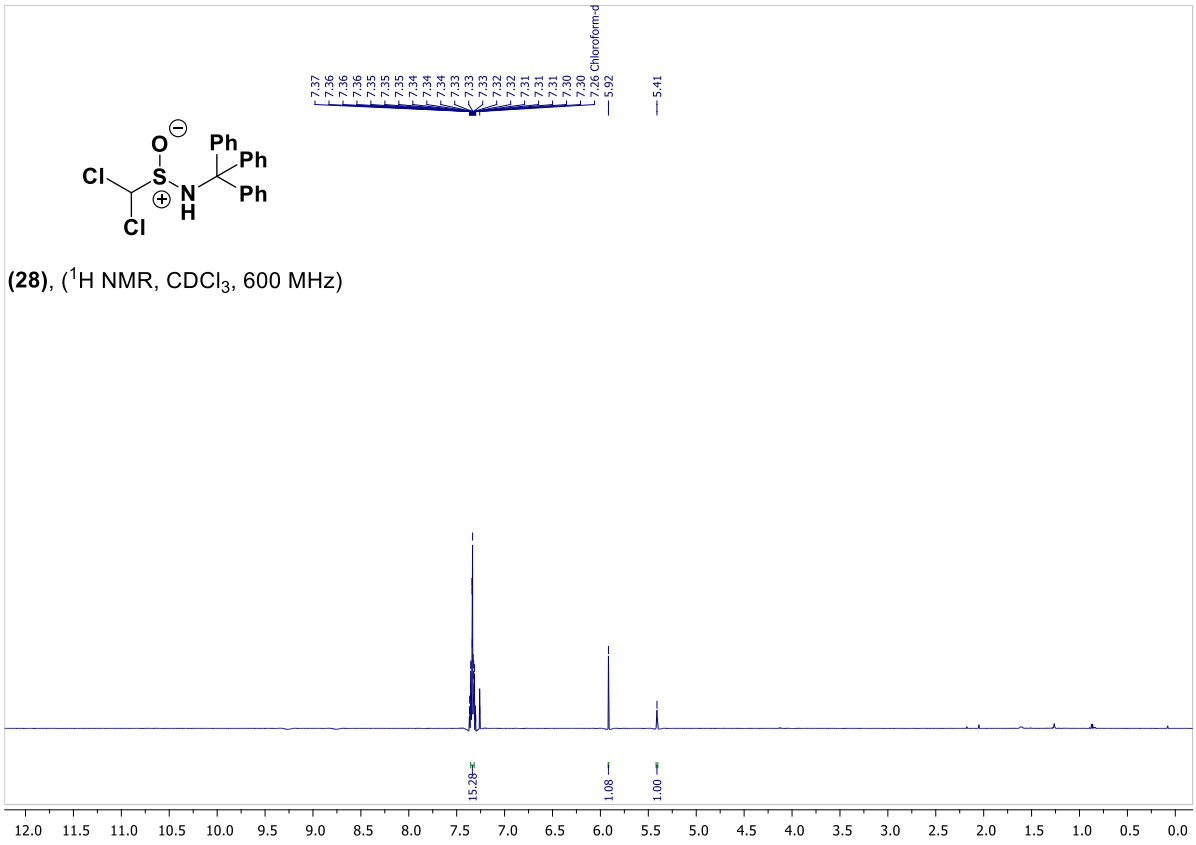
(26), (^{13}C NMR, Acetone-d_6, 50 MHz)



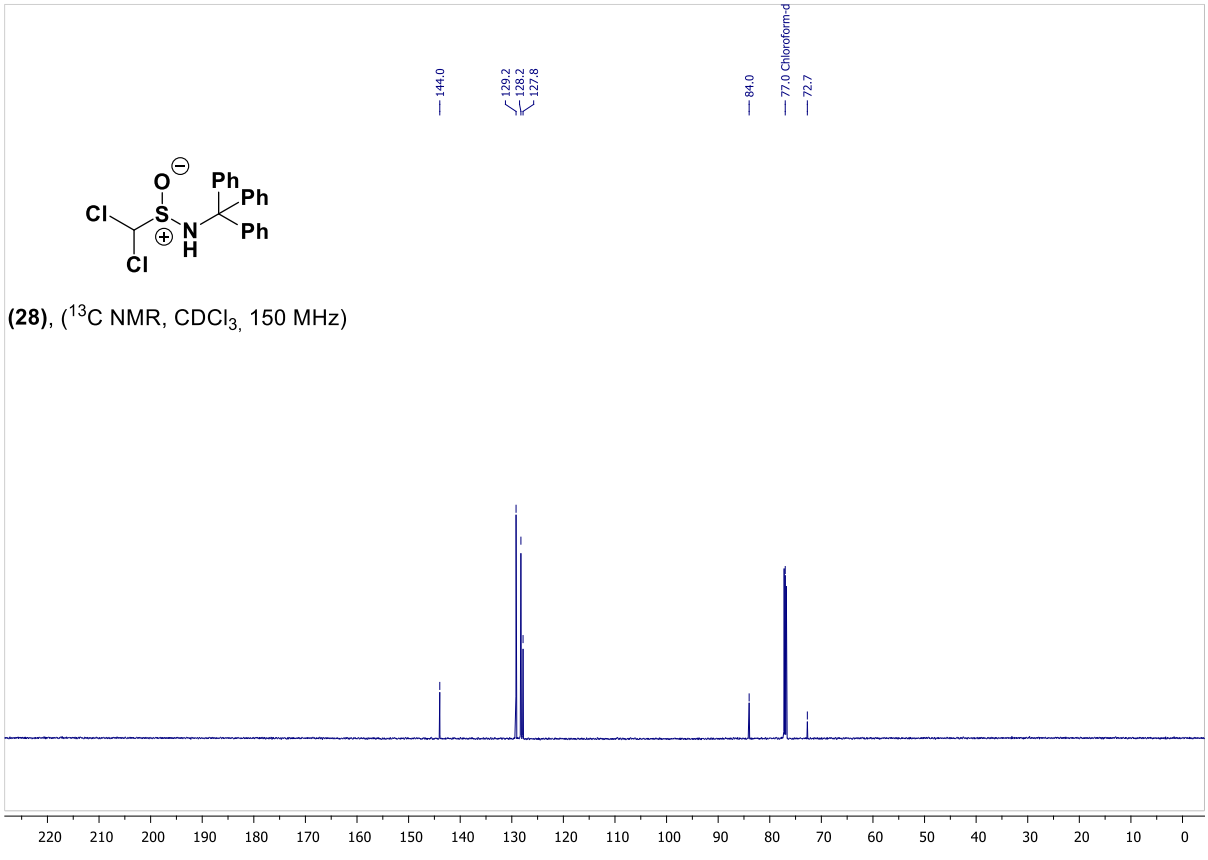
(27), (^{1}H NMR, $CDCl_3$, 600 MHz)



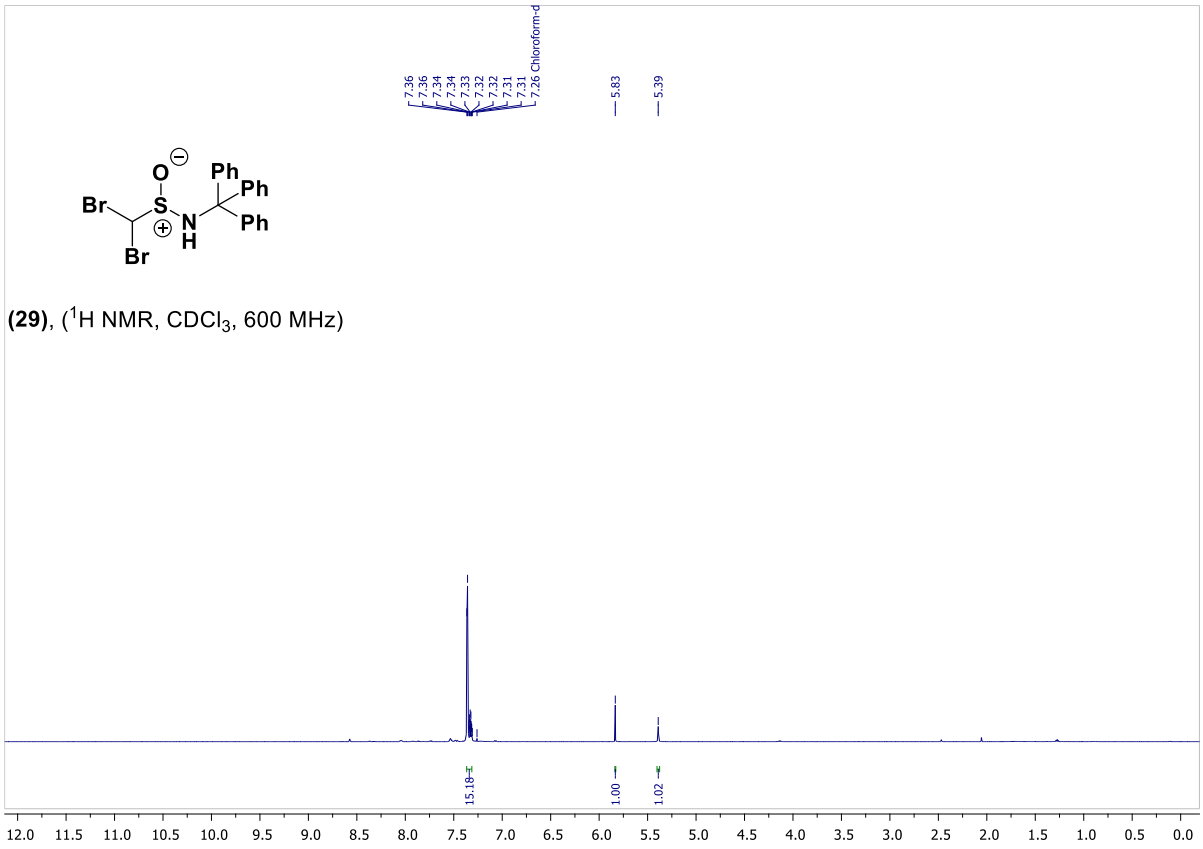
(27), (^{13}C NMR, $CDCl_3$, 150 MHz)



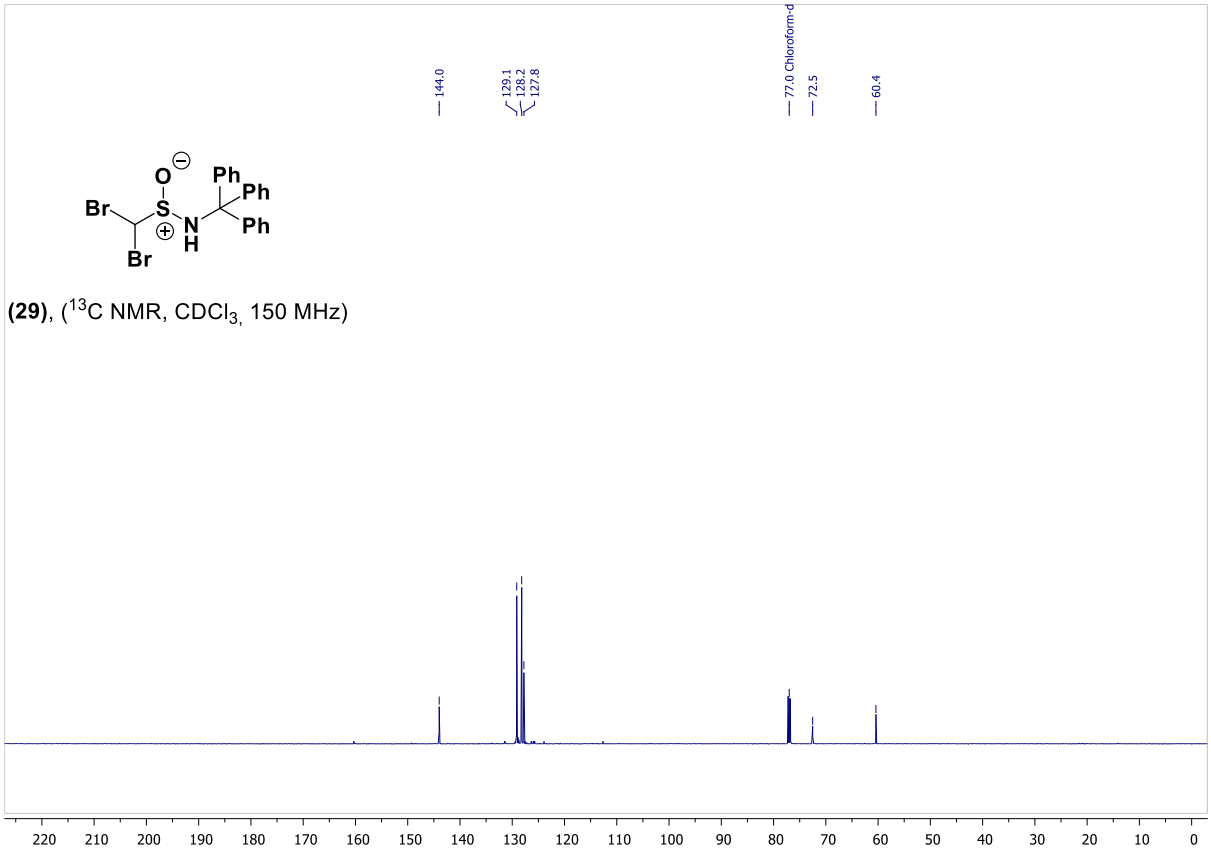
(28), (^{1}H NMR, $CDCl_3$, 600 MHz)



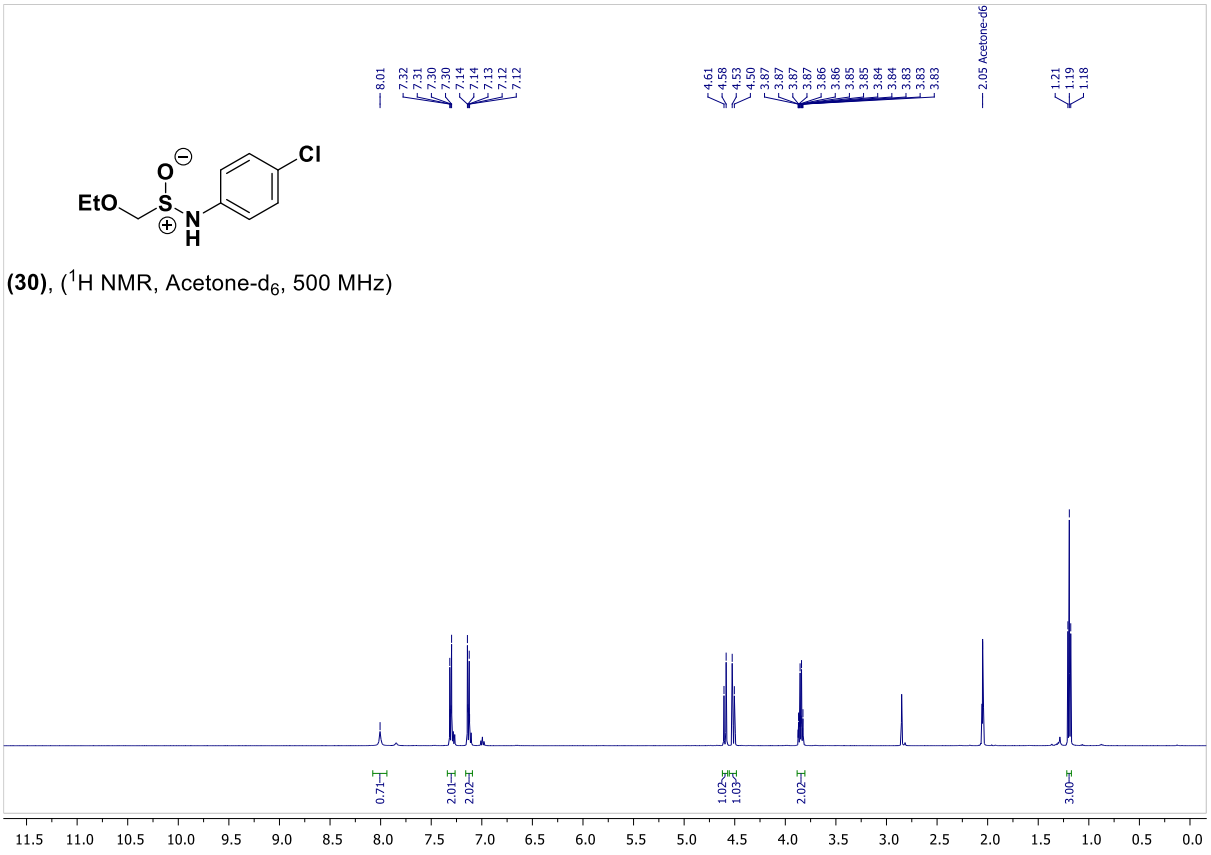
(28), (^{13}C NMR, $CDCl_3$, 150 MHz)



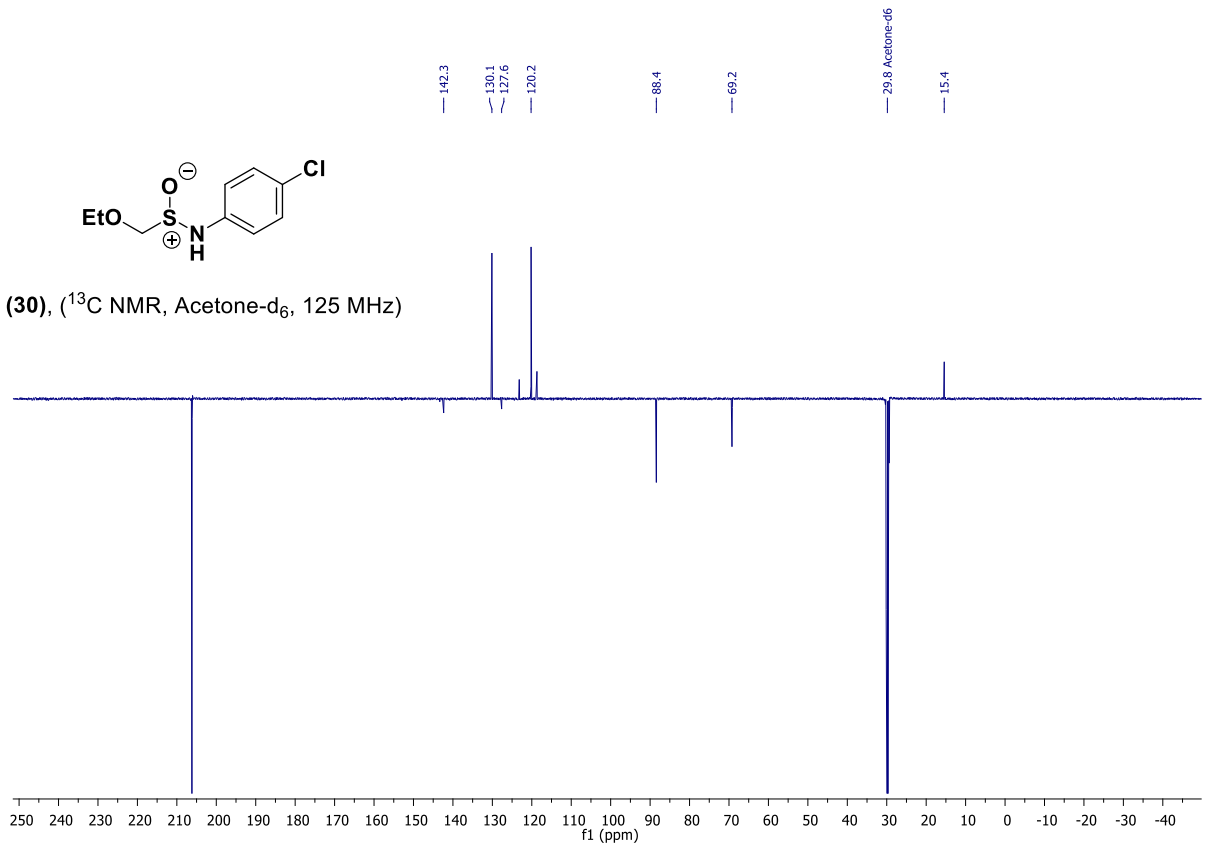
(29), (^{1}H NMR, $CDCl_3$, 600 MHz)



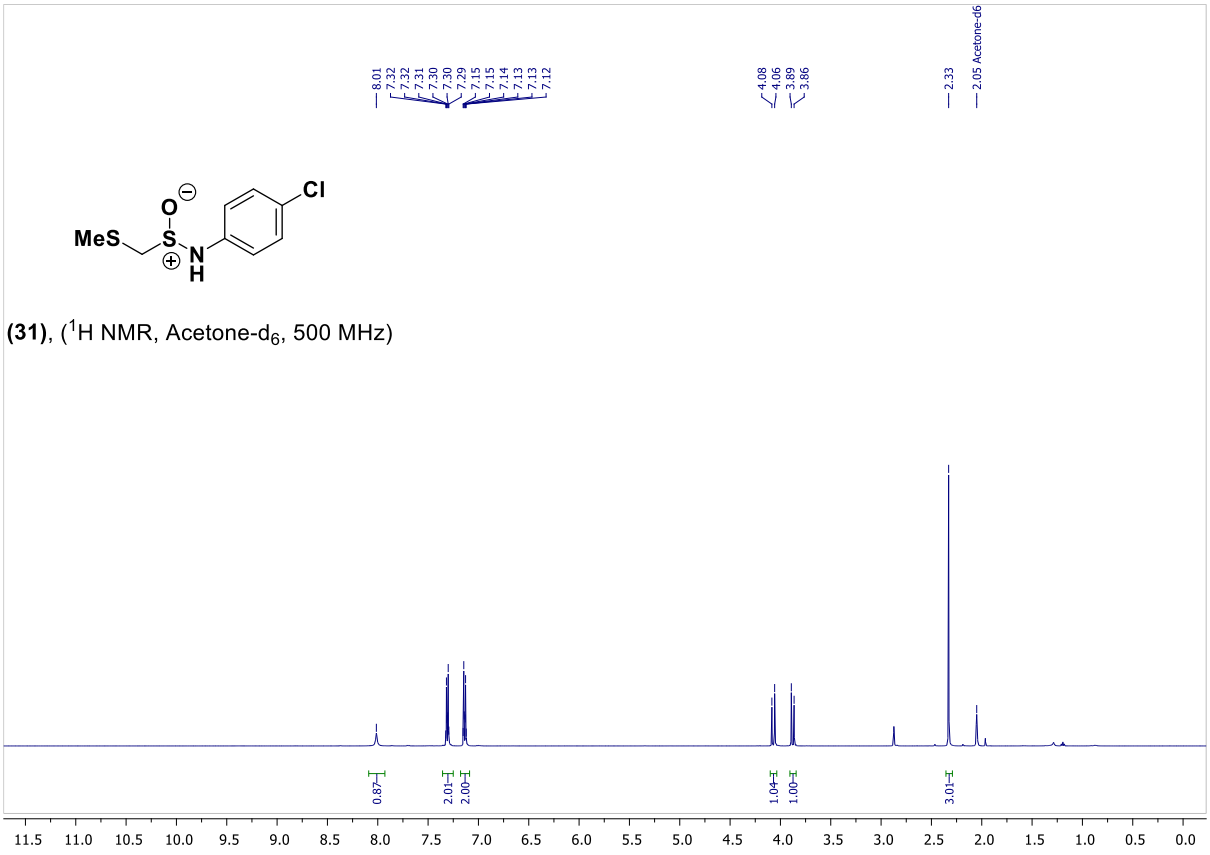
(29), (^{13}C NMR, $CDCl_3$, 150 MHz)

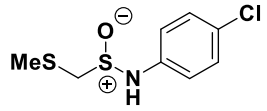


(30), (^{1}H NMR, Acetone-d_6, 500 MHz)



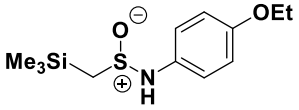
(30), (^{13}C NMR, Acetone-d_6, 125 MHz)



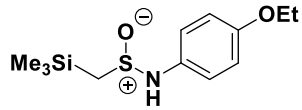


(31), (^{1}H NMR, Acetone-d_6, 500 MHz)

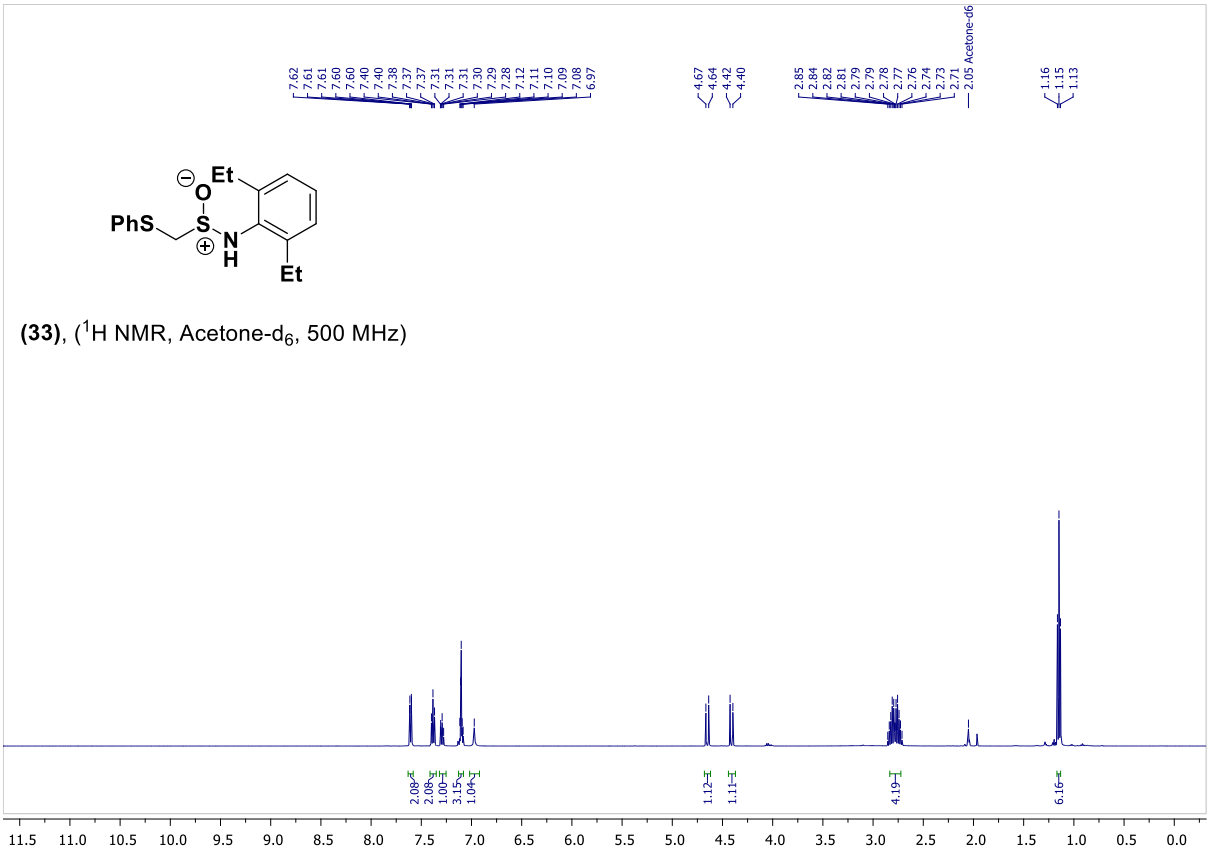
(31), (^{13}C NMR, Acetone-d_6, 125 MHz)



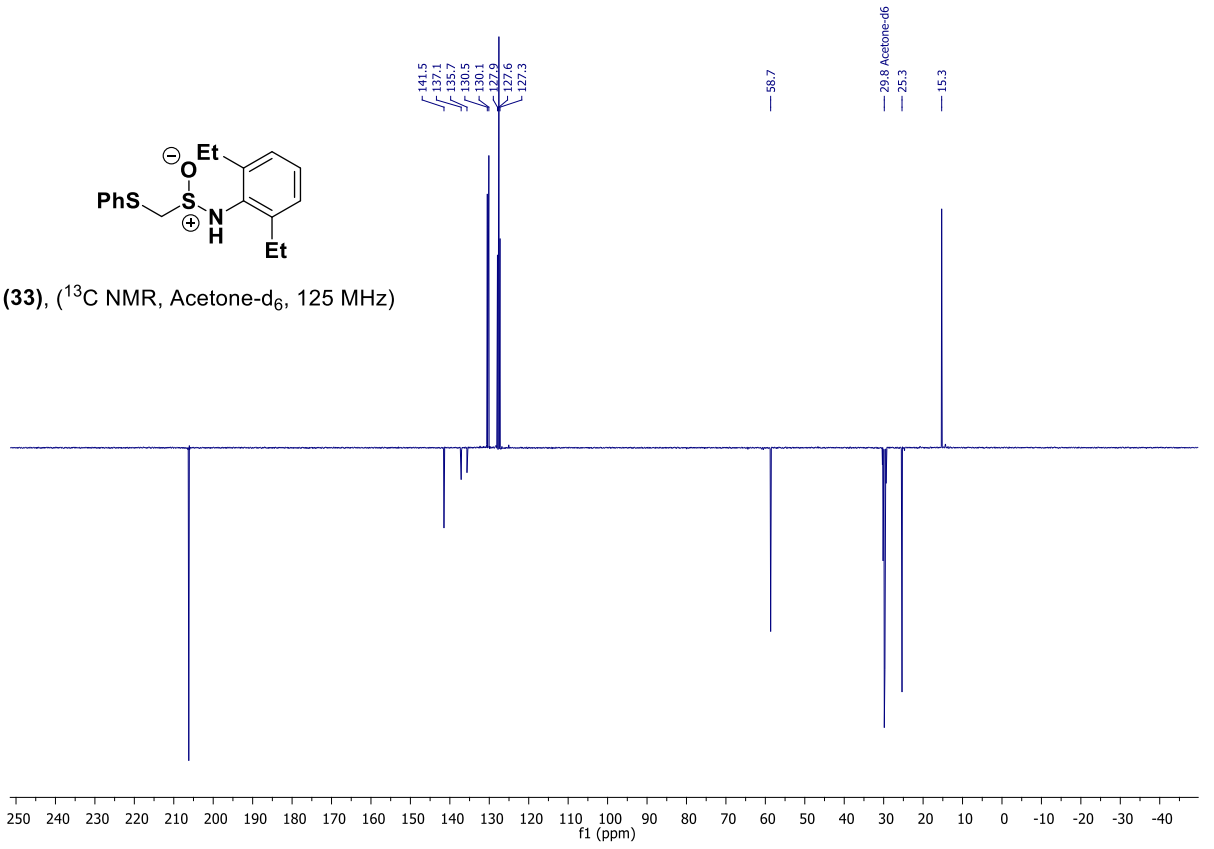
(32), (^{1}H NMR, Acetone-d_6, 500 MHz)



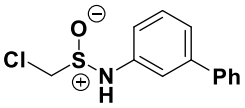
(32), (^{13}C NMR, Acetone-d_6, 125 MHz)



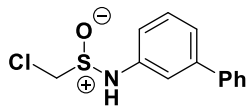
(33), (^{1}H NMR, Acetone-d_6, 500 MHz)



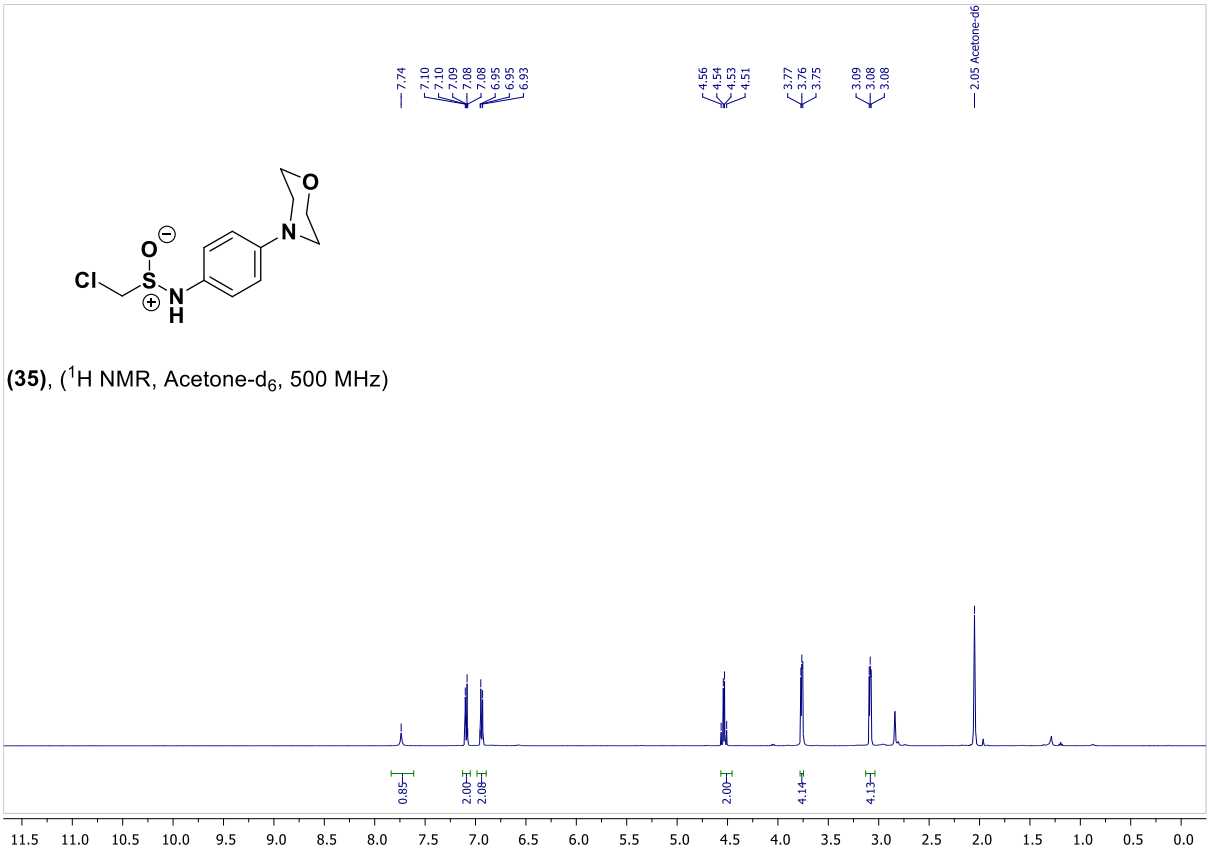
(33), (^{13}C NMR, Acetone-d_6, 125 MHz)



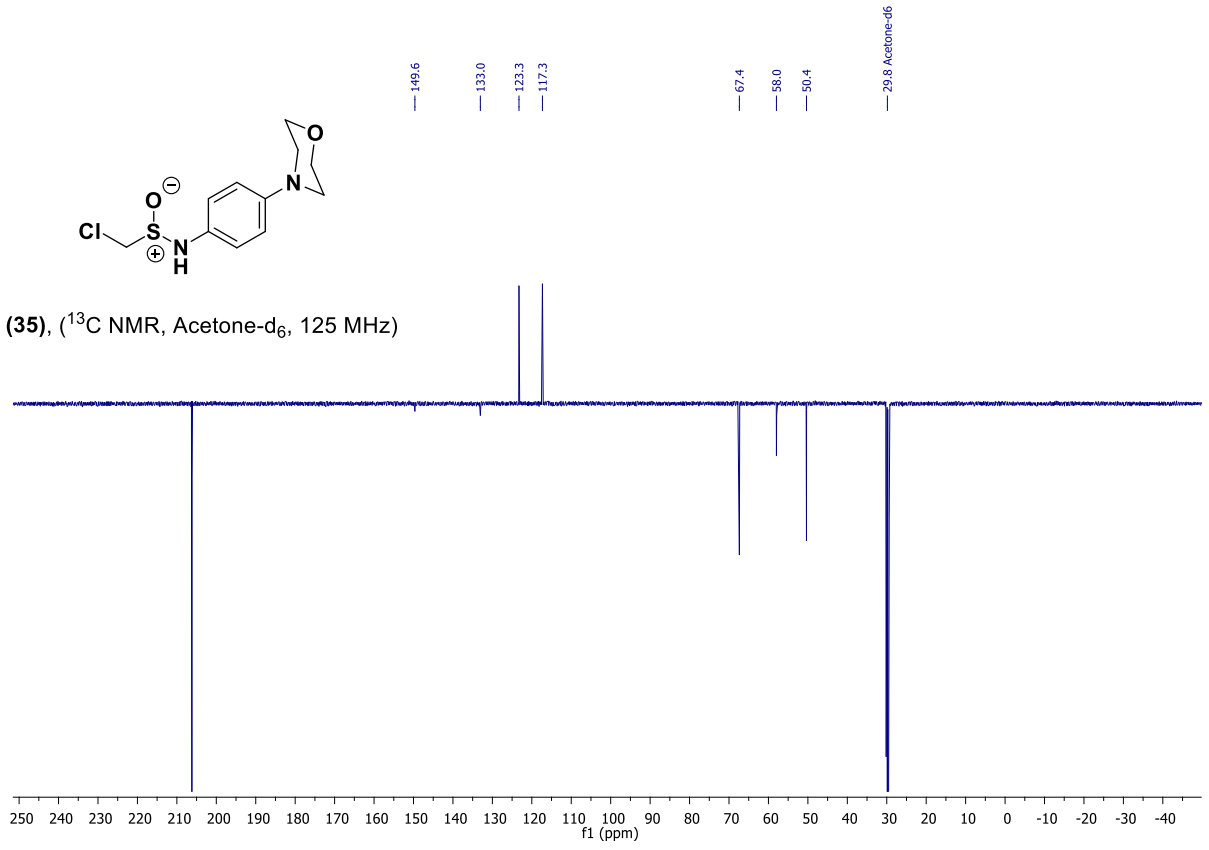
(34), (^{1}H NMR, Acetone-d$_6$, 500 MHz)



(34), (^{13}C NMR, Acetone-d$_6$, 125 MHz)



(35), (^{1}H NMR, Acetone-d_6, 500 MHz)



(35), (^{13}C NMR, Acetone-d_6, 125 MHz)

X-Ray Analysis for Compound 19

The X-ray intensity data was measured on Bruker D8 Venture diffractometer equipped with multilayer monochromator, Mo K/α INCOATEC micro focus sealed tube and Oxford cooling system. The structure was solved by *Direct Methods*. Non-hydrogen atoms were refined with *anisotropic displacement parameters*. Hydrogen atoms were inserted at calculated positions and refined with riding model. The following software were used: *Bruker SAINT software package* using a narrow-frame algorithm for frame integration, SADABS[4] for absorption correction, *OLEX2*[5] for structure solution, refinement, molecular diagrams and graphical user-interface, *Shelxle*[6] for refinement and graphical user-interface *SHELXS-2015*[7] for structure solution, *SHELXL-2015*[7] for refinement, *Platon*[8] for symmetry check. Experimental data and CCDC-Codes Experimental data (Available online: http://www.ccdc.cam.ac.uk/conts/retrieving.html) can be found in Table 1. Crystal data, data collection parameters, and structure refinement details are given in Table 2. Asymmetric Unit visualized in Figure 1. Data quality overview is visualized in Figures 2 and 3.

Table 1

Sample	Machine	Source	Temp.	Detector Distance	Time/ Frame	#Frames	Frame width	CCDC
			[K]	[mm]	[s]		[°]	
Compound 19	D8-Bruker	Mo	120	35	16	2472	0.5	2191935

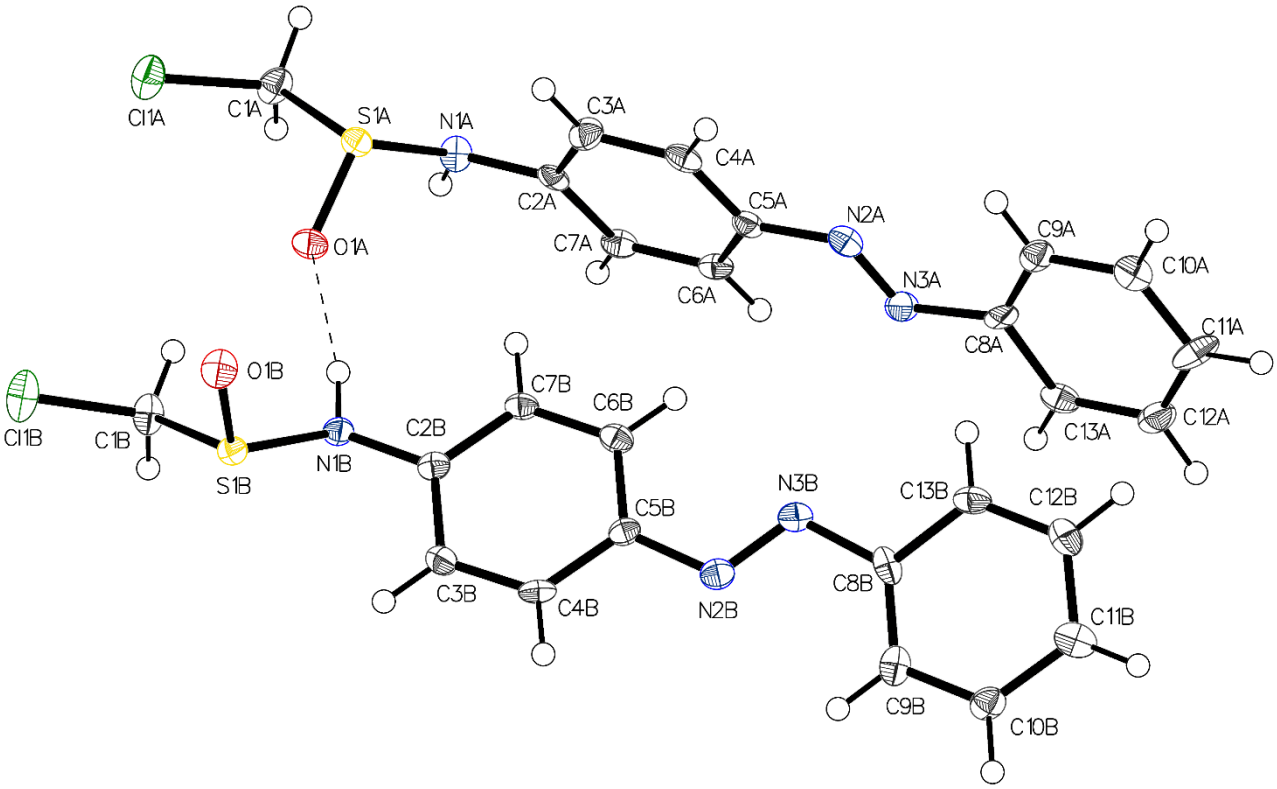


Figure 1 Asymmetric Unit drawn with 50% displacement ellipsoid. The bond precision for C-C single bonds is 0.0042Å. In the asymmetric unit both chiral species exist at the S1 positions (S1A in R, S1B in S). Never the less the centrosymmetric space group P-1 produces both species for all S positions. Two Hydrogen bond interactions in the packing can be mentioned, one visible in the Asymmetric Unit N1B – H – O1A and on in the expanded packing N1A – H – O1B.

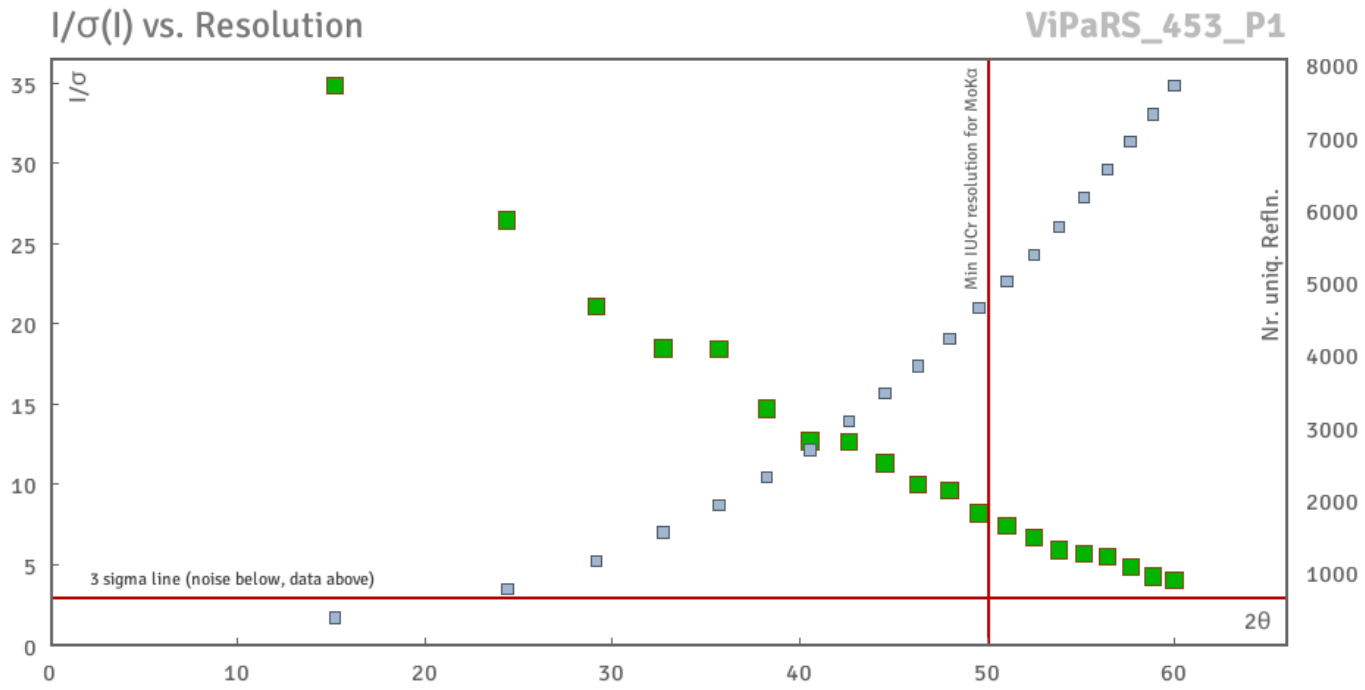


Figure 2 Data Quality – I/Sigma (I) level view

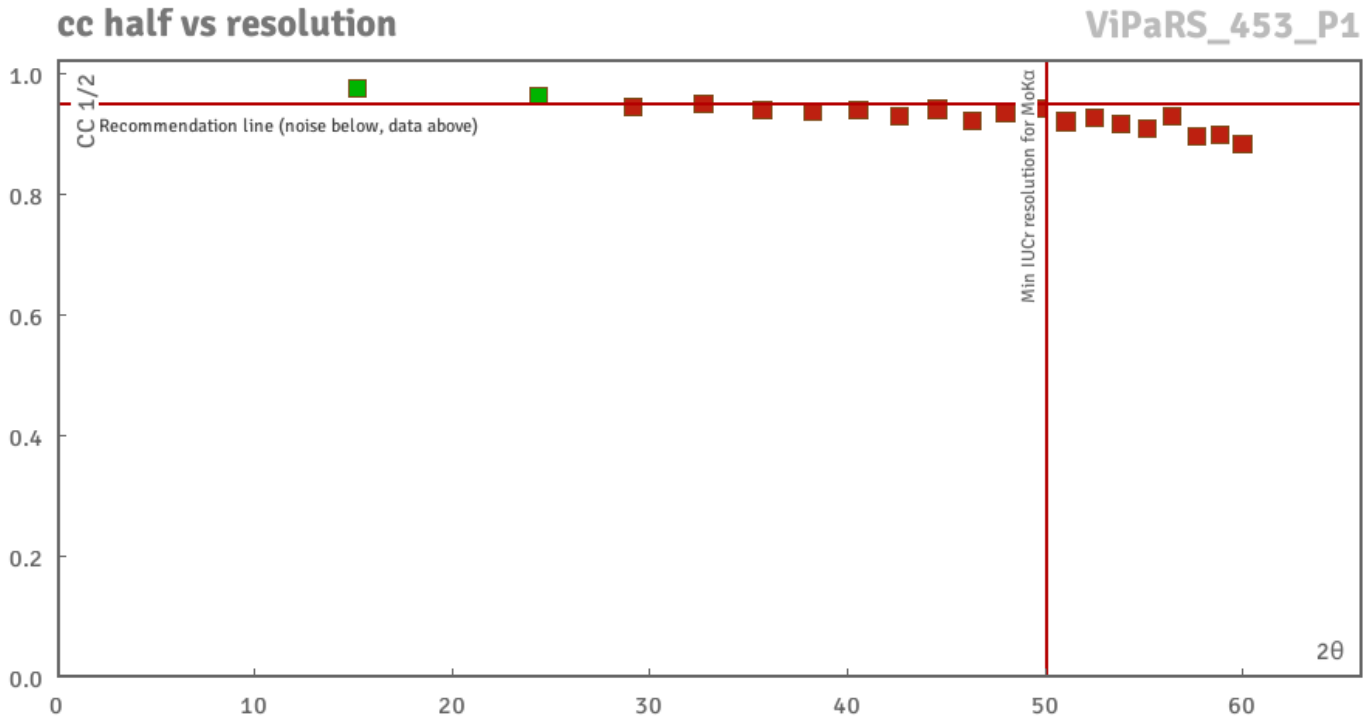


Figure 3 Data Quality – CC 1/2 level view. The recommendation level should be interpreted softly. As long as the I/sigma(I) is of high quality and the cc half is close to the recommendation line the data quality is reliable.

Table 2 Sample and crystal data, data collection and structure refinement. Detailed information can found in the Cif Code of CCDC: **2191935**

Identification code	ViPaRS_453_P1
Empirical formula	$C_{13}H_{12}ClN_3OS$
Formula weight	293.77
Temperature/K	120,0
Crystal system	triclinic
Space group	P-1
a/Å	7.7841(8)
b/Å	10.3422(10)
c/Å	17.0738(17)
α/°	81.082(3)
β/°	85.679(3)

γ/°	89.945(3)
Volume/Å^3	1354.0(2)
Z	4
ρ_{calc}g/cm^3	1.441
μ/mm^{-1}	0.431
F(000)	608.0
Crystal size/mm^3	0.18 × 0.11 × 0.03
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	2.422 to 50.694
Index ranges	-9 ≤ h ≤ 9, -12 ≤ k ≤ 12, -20 ≤ l ≤ 20
Reflections collected	28319
Independent reflections	4975 [R_{int} = 0.0605, R_{sigma} = 0.0371]
Data/restraints/parameters	4975/0/351
Goodness-of-fit on F^2	1.074
Final R indexes [I>=2σ (I)]	R_1 = 0.0561, wR_2 = 0.1385
Final R indexes [all data]	R_1 = 0.0641, wR_2 = 0.1453
Largest diff. peak/hole / e Å^{-3}	1.19/-0.36

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