Electronic Supplementary Material (ESI) for ChemComm.

Pt(II) Coordination Complexes as Visible Light Photocatalysts for the Oxidation of Sulfides in Batch and Flow

Antonio Casado-Sánchez,[a] Rocío Gómez-Ballesteros,[b] Francisco Tato,[c] Francisco J. Soriano,[c] Gustavo Pascual-Coca,[c] Silvia Cabrera*[a] and José Alemán*[b]

[a] Departamento de Química Inorgánica (Módulo 7), Facultad de Ciencias, Universidad Autónoma de Madrid, 28049-Madrid, Spain. E-mail: silvia.cabrera@uam.es
[b] Departamento de Química Orgánica (Módulo 1), Facultad de Ciencias, Universidad Autónoma de Madrid, 28049-Madrid, Spain. E-mail: jose.aleman@uam.es; webpage: www.uam.es/jose.aleman
[c] Synthelia Organics Labs, C/Faraday 7. Labs 2.05 and 0.03, Parque Científico de Madrid, 28049-Madrid, Spain.

Contents

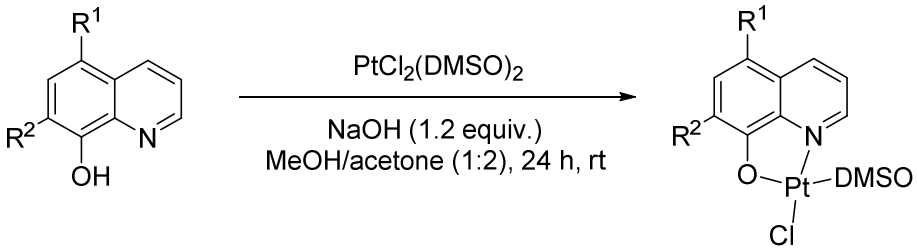
1. General methods and materials

NMR spectra were acquired on a Bruker 300 spectrometer, running at 300, 75 and 64.5 MHz for ^{1}H, ^{13}C and ^{195}Pt, respectively. Chemical shift (δ) are reported in ppm relative to residual solvent signals ($CDCl_3$: 7.26 ppm for ^{1}H-NMR, 77.0 ppm for ^{13}C-NMR; CD_2Cl_2: 5.32 ppm for ^{1}H-NMR, 53.84 ppm for ^{13}C-NMR; DMSO-d_6: 2.50 ppm for ^{1}H-NMR; D_2O: 4.79 ppm for ^{1}H-NMR). ^{13}C-NMR spectra were acquired on a broad band decoupled mode. ^{195}Pt-NMR spectra were obtained with chemical shifts reported in ppm downfield relative to the external reference 1.0 M Na_2PtCl_6 in D_2O. Melting points were measured using a Gallenkamp apparatus in open capillary tubes. Light irradiation was carried out using a 23 W compact fluorescent bulb (CFL) or 15 W blue light LED.

All reagents and materials were purchased from commercial sources and used without further purification. The *cis*-$PtCl_2(DMSO)_2$ complex[1] and 4-methoxy-3,5-dimethyl-2[(methylsulfide)methyl]pyridine[2] were prepared according to literature procedures.

2. Experimental procedures and characterization

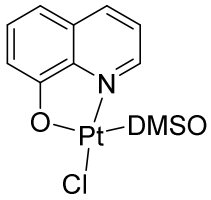
2.1. General procedure for the synthesis of complexes 1a-f.[3]



1a-f

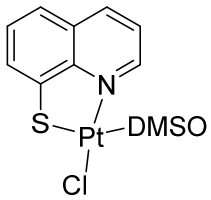
To a solution of NaOH (0.56 mmol) in 0.3 mL of MeOH was added the corresponding ligand (0.47 mmol) and the resulting suspension was stirred until the ligand was completely dissolved, obtaining a green-yellow solution. Then, a suspension of *cis*-$PtCl_2(DMSO)_2$ (0.45 mmol) in 0.6 ml of acetone was added. A yellow suspension was rapidly observed. The reaction was maintained for 24 h at rt and the solid product was then filtered, washed with cold water and ether, and dried under vacuum during 24-48 h.

[PtCl(quin)(dmso)] (1a)[3]



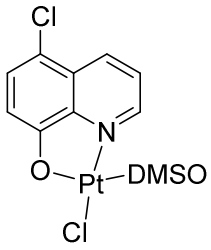
The product was obtained following the general procedure as a yellow-orange solid (78% yield) without further purification. **MP** (°C): 197.0-198.0 (decom.). **^{1}H-NMR (300 MHz, CD_2Cl_2)** δ: 9.41 (dd, *J* = 10.7, 1.2 Hz, 1H), 8.38 (dd, *J* = 8.4, 1.1 Hz, 1H), 7.58-7.40 (m, 2H), 7.06-7.02 (m, 2H), 3.61 (s, 6H). **^{13}C-NMR (75 MHz, $CDCl_3$)** δ: 148.6, 148.3, 140.3, 140.2, 131.5, 131.0, 121.7, 115.6, 114.6. 46.6. **^{195}Pt-NMR (64.5 MHz, $CDCl_3$)** δ: -2760.7. **HRMS (FAB$^+$):** calcd for $C_{11}H_{12}ClNO_2PtS$ (M^+): 452.9915; found: 452.9928. **FAB-MS**: *m/z* 453.0 $[M+H]^+$, 417.0 $[M-Cl]^+$. **Anal. calcd for** $C_{11}H_{12}ClNO_2PtS$: C, 29.18; H, 2.67; N, 3.09; found: C, 29.00; H, 2.67; N, 2.94.

[PtCl(dmso)(quinolin-8-thiolato)] (1b)



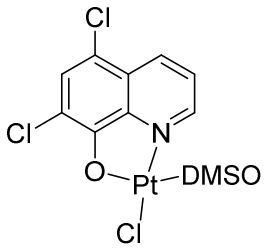
The product was obtained following the general procedure as a red solid (93% yield) without further purification. **MP** (°C): >289.3 (decom.). **^{1}H-NMR (300 MHz, $CDCl_3$)** δ: 9.89 (d, *J* = 5.4 Hz, 1H), 8.39 (d, *J* = 6.9 Hz, 1H), 7.81 (d, *J* = 6.5 Hz, 1H), 7.61-7.47 (m, 2H), 7.39 (d, *J* = 7.3 Hz, 1H), 3.64 (s, 6H). **^{13}C-NMR (75 MHz, $CDCl_3$)** δ: 152.0, 150.0, 142.3, 141.7, 130.6, 130.3, 128.7, 122.4, 121.1. 46.5. **^{195}Pt-NMR (64.5 MHz, $CDCl_3$)** δ: -3567.4. **FAB-MS**: *m/z* 468.9 $[M+H]^+$. **Anal. calcd for** $C_{11}H_{12}ClNOPtS_2$: C, 28.18; H, 2.58; N, 2.99; found: C, 27.88; H, 2.57; N, 3.01.

[PtCl(5-Cl-quin)(dmso)] (1c)[3]



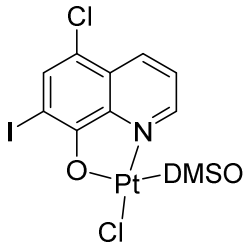
The product was obtained following the general procedure as a yellow-orange solid (77% yield) without further purification. **MP** (°C): 226.0-228.0 (decom.). **^{1}H-NMR (300 MHz, $CDCl_3$)** δ: 9.46 (d, *J* = 4.5 Hz, 1H), 8.70 (d, *J* = 8.5 Hz, 1H), 7.58 (d, *J* = 8.5 Hz, 1H), 7.53 (dd, *J* = 8.5, 5.4 Hz, 1H), 7.16 (d, *J* = 8.5 Hz, 1H), 3.64 (s, 6 H). Due to the low solubility of the complex ^{13}C-NMR spectrum was not possible to acquire. **^{195}Pt-NMR (64.5 MHz, $CDCl_3$)** δ: -2763.1. **HRMS (MALDI):** calcd for $C_{11}H_{11}Cl_2NO_2PtSNa$ $[M+Na]^+$: 509.9409; found: 509.9396. **FAB-MS**: *m/z* 486.9 $[M+H]^+$, 452.0 $[M-Cl]^+$. **Anal. calcd for** $C_{11}H_{11}Cl_2NO_2PtS$: C, 27.11; H, 2.28; N, 2.87; found: C, 26.80; H, 2.28; N, 2.70.

[PtCl(5,7-Cl_2-quin)(dmso)] (1d)[3]



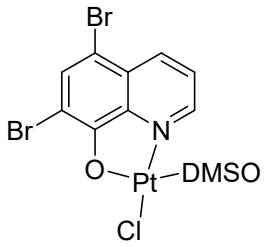
The product was obtained following the general procedure as a yellow solid (77% yield) without further purification. **MP** (°C): 236.5-238.5 (decom.). **^{1}H-NMR (300 MHz, $CDCl_3$)** δ: 9.11 (d, *J* = 4.6 Hz, 1H), 8.67 (d, *J* = 9.1 Hz, 1H), 7.67-7.61 (m, 2H), 3.66 (s, 6H). Due to the low solubility of the complex ^{13}C-NMR and ^{195}Pt-NMR spectra were not possible to acquire. **HRMS (MALDI)** calcd for $C_{11}H_{11}Cl_3NO_2PtS$ $[M+H]^+$: 521.9117; found: 521.9164. **FAB-MS**: *m/z* 521.9 $[M+H]^+$. **Anal. calcd for** $C_{11}H_{10}Cl_3NO_2PtS$: C, 25.32; H, 1.93; N, 2.68; found: C, 25.42; H, 2.04; N, 2.55.

[PtCl(5-Cl-7-I-quin)(dmso)] (1e)[3]



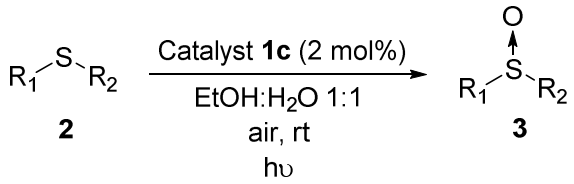
The product was obtained following the general procedure as a yellow solid (86% yield) without further purification. **MP** (°C): 195.5-196.5 (decom.). **^{1}H-NMR (300 MHz, CD_2Cl_2)** δ: 9.55 (dd, *J* = 5.5, 1.1 Hz, 1H), 8.71 (dd, *J* = 8.5, 1.1 Hz, 1H), 8.01 (s, 1H), 7.62 (dd, *J*= 8.5, 5.5, 1H), 3.63 (s, 6 H). **^{13}C-NMR (75 MHz, CD_2Cl_2)** δ: 166.4, 149.3, 138.4, 137.5, 137.4, 128.5, 122.6, 122.4 117.2, 46.7. **^{195}Pt-NMR (64.5 MHz, CD_2Cl_2)** δ: -2737.0. **HRMS (ESI$^+$)**: calcd for $C_{11}H_{11}Cl_2INO_2PtS$ $[M+H]^+$: 613.8582; found: 613.8505. **ESI-MS**: *m/z* 634.8 $[M+Na]^+$, 612.8 $[M]^+$. **Anal. calcd for** $C_{11}H_{10}Cl_2INO_2PtS$: C, 21.55; H, 1.64; N, 2.28; found: C, 22.04; H, 1.85; N, 2.39.

[PtCl(5,7-Br_2-quin)(dmso)] (1f)



The product was obtained following the general procedure as a yellow solid (76% yield) without further purification. **MP** (°C): >254.0 (decom.). **^{1}H-NMR (300 MHz, DMSO-d_6)** δ: 9.52 (d, *J* = 5.3 Hz, 1H), 8.73 (d, *J* = 8.5 Hz, 1H), 8.14 (s, 1H), 7.94 (dd, *J* = 8.5, 5.6 Hz, 1H), 2.55 (s, 6H). Due to the low solubility of the complex ^{13}C-NMR and ^{195}Pt-NMR spectra were not possible to acquire. **FAB-MS**: *m/z* 610.7 $[M+H]^+$. **Anal. calcd for** $C_{11}H_{10}Br_2ClNO_2PtS$: C, 21.64; H, 1.65; N, 2.29; found: C, 20.60; H, 1.77; N, 2.40.

2.2. General procedure for the photooxidation of sulfides in batch.



The corresponding sulfide (0.3 mmol) and photocatalyst **1c** (2.9 mg, 0.006 mmol) in 2 mL of EtOH/H_2O (v/v 1:1) were stirred at room temperature under 15 W blue LED light irradiation or a 23 W CFL in a vial open to the air. The reaction was monitored by TLC. After the total consumption of the sulfide, the crude was filtered through celite and purified by flash chromatography (the eluent is indicated in each case).

Methyl(4-methylphenyl)sulfoxide (3a)[4,5]

Chromatography: *n*-hexane/EtOAc 1:1; 98% yield; yellow oil. **^{1}H-NMR (300 MHz, $CDCl_3$)** δ: 7.52 (d, *J* = 8.1 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 2.70 (s, 3H), 2.41 (s, 3H).

(4-Methoxyphenyl)methylsulfoxide (3b)[5]

Chromatography: *n*-hexane/EtOAc 1:1; 91% yield; yellow oil. **^{1}H-NMR (300 MHz, $CDCl_3$)** δ: 7.57 (d, *J* = 8.8 Hz, 2H), 7.01 (d, *J* = 8.8 Hz, 2H), 3.83 (s, 3H), 2.67 (s, 3H).

(4-Cyanophenyl)methylsulfoxide (3c)[5,6]

This oxidation was carried out using a mixture of EtOH:H_2O:dioxane 90:5:5 as solvent. Chromatography: *n*-hexane/EtOAc 1:1; 62% yield; beige solid. **MP** (°C): 88.2-90.8 (Lit.[6] MP: 86-88 °C). **^{1}H-NMR (300 MHz, $CDCl_3$)** δ: 7.83 (d, *J* = 8.3 Hz, 2H), 7.76 (d, *J* = 8.4 Hz, 2H), 2.75 (s, 3H).

(2-Bromophenyl)methylsulfoxide (3d)[7]

Chromatography: *n*-hexane/EtOAc 1:1; 83% yield; yellow oil. **^{1}H-NMR (300 MHz, $CDCl_3$)** δ: 7.92 (d, *J* = 7.8 Hz, 1H), 7.59-7.53 (m, 2H), 7.38-7.32 (m, 1H), 2.80 (s, 3H).

Cyclopropylphenylsulfoxide (3e)[4,7]

Chromatography: *n*-hexane/EtOAc 1:1; 88% yield; colourless oil. **^{1}H-NMR (300 MHz, $CDCl_3$)** δ: 7.67-7.63 (m, 2H), 7.52-7.48 (m, 3H), 2.29-2.20 (m, 1H), 1.25-1.18 (m, 1H), 1.04-0.89 (m, 3H).

Benzylphenylsulfoxide (3f)[7,8]

This oxidation was carried out using a mixture of EtOH:H_2O:dioxane 90:5:5 as solvent. Chromatography: *n*-hexane/EtOAc 2:1; 83% yield; beige solid. **MP** (°C): 122.8-124.2 (Lit[8] MP: 124-126 °C). **^{1}H-NMR (300 MHz, $CDCl_3$)** δ: 7.39-7.29 (m, 5H), 7.22-7.15 (m, 3H), 6.92-6.89 (m, 2H), 4.02 (d, *J* = 12.6 Hz, 1H), 3.92 (d, *J* = 12.6 Hz, 1H).

Allylphenylsulfoxide (3g)[7]

Chromatography: *n*-hexane/EtOAc 1:1; 62% yield; colourless oil. **^{1}H-NMR (300 MHz, $CDCl_3$)** δ: 7.61-7.58 (m, 2H), 7.51-7.49 (m, 3H), 5.71-5.57 (m, 1H), 5.33 (d, *J* = 9.8 Hz, 1H), 5.19 (d, *J* = 16.0 Hz, 1H), 3.46-3.60 (m, 2H).

Dibutylsulfoxide (3h)[7]

Chromatography: *n*-hexane/EtOAc 6:1; 85% yield; colourless oil. **^{1}H-NMR (300 MHz, $CDCl_3$)** δ: 2.54-2.70 (m, 4H), 1.66-1.76 (m, 4H), 1.35-1.54 (m, 4H), 0.93 (t, *J* = 7.3 Hz, 6H).

(*tert*-Butyl)methylsulfoxide (3i)[9]

Chromatography: EtOAc; 79% yield; colourless oil. **^{1}H-NMR (300 MHz, $CDCl_3$)** δ: 2.35 (s, 3H), 1.22 (s, 9H).

4-Methoxy-3,5-dimethyl-2-[(methylsulfinyl)methyl]pyridine (3j)[2]

This oxidation was carried out using a mixture of EtOH:H_2O:dioxane 90:5:5 as solvent. Chromatography: CH_2Cl_2/MeOH 20:1; 87% yield; beige solid. **MP** (°C): 72.3-73.9 (Lit.[2] MP: 72-73 °C). **^{1}H-NMR (300 MHz, $CDCl_3$)** δ: 8.16 (s, 1H), 4.24 (d, *J* = 12.8 Hz, 1H), 4.11 (d, *J* = 12.8 Hz, 1H), 3.71 (s, 3H), 2.60 (s, 3H), 2.28 (s, 3H), 2.20 (s, 3H).

***L*-Methionine sulfoxide (3k)[10]**

This compound was obtained pure without flash chromatography as a mixture 1:1 of diastereoisomers, which are epimers at sulfur. 100% yield; beige solid. **MP** (°C): 214.8 (decom.). **^{1}H-NMR (300 MHz, $CDCl_3$)** δ: 3.90-3.96 (m, 1H), 3.22-2.95 (m, 2H), 2.78 (s, 3H), 2.39-2.32 (m, 2H).

4-[(Phenylmethyl)sulfinyl]-2-butanone (3l)[11]

This compound was prepared according to the following one-pot reaction: A mixture of benzylthiol (35 µL, 0.3 mmol) and 3-buten-2-one (24 µL, 0.3 mmol) in 1 mL of water was stirred at rt for 30 min.[12] Then, photocatalyst **1c** (2.9 mg, 0.006 mmol) and 1 mL of EtOH were added. The resulting mixture was stirred at room

temperature under 15 W blue LED light irradiation. Chromatography: *n*-hexane/EtOAc 4:1; 53% yield. **MP** (°C): 101-102. **^{1}H-NMR (300 MHz, $CDCl_3$)** δ: 7.32-7.36 (m, 5H), 4.04 (d, *J* = 12.8 Hz, 1H), 4.04 (d, *J* = 12.8 Hz, 1H), 3.96 (d, *J* = 12.8 Hz, 1H), 2.96-2.92 (m, 4H), 2.14 (s, 3H).

Diphenylsulfoxide (3m)[4,5]

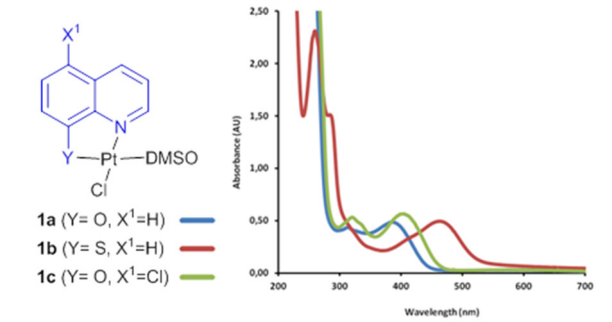
Chromatography: *n*-hexane/EtOAc 4:1; 6% yield; yellow oil. **^{1}H-NMR (300 MHz, $CDCl_3$)** δ: 7.66-7.64 (m, 2H), 7.46-7.45 (m, 3H).

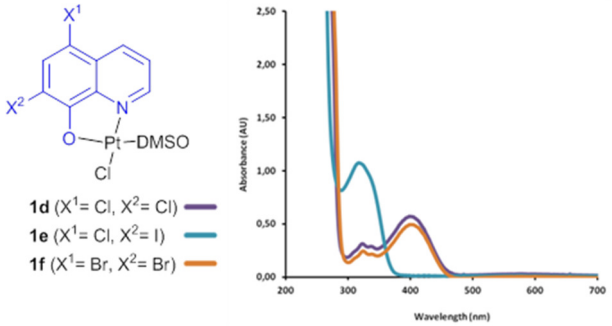
2.3. General Procedure for the photooxidation of sulfides under continuous-flow conditions.

The corresponding sulfide (0.3 mmol), catalyst **1c** (1 mol%), and 1,4-dioxane (1 mmol; 3.23 eq.) were dissolved in EtOH-H_2O (v/v 9:1) to a total volume of 2 mL and stirred under sonication at 50-70 °C in order to get a homogeneous solution. The mixture was reserved as a stock solution and injected into the system by a sample loop (100, 500, or 800 µL) which was connected to the solvent channel via a six-way valve. The flow system consisted of a HPLC pump and an O_2 gas cylinder connected both through a T-mixer to the coil reactor which was made from FEP capillary tube (1/16″ OD; 0,75 mm ID; 9,27 m length) with a reactor volume of 4.1 mL. To irradiate the system a blue LED device (15 W) was assembled around the coil reactor. Once the sample loop was charged with the stock solution, the six-way valve was switched to the "run" position to connect the sample loop to the reactor. Then the liquid stream and the gaseous stream were mixed together in a T-mixer (0.8 mm channel size), and the resulting segmented flow stream was passed through the PEF coil reactor at 37 °C. The outflow was collected in a fraction collector, and the crude mixture was analyzed by HPLC and GC. For the residence time scan, pump flow rates were varied to adjust the lowest residence time that led to the highest yield.

3. UV-Vis spectra of the complexes.

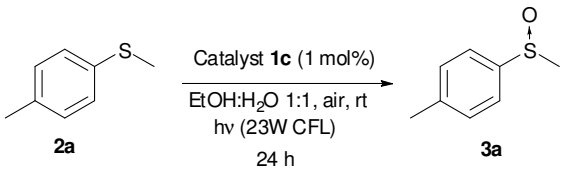
The electronic spectra of 1.0 mM solutions of the corresponding complexes in CH_3CN were recorder using an Agilent 8453 UV-vis spectrophotometer.





4. Control and mechanistic experiments.

Table S1. Control experiments in the presence (+) or absence (-) of catalyst, oxygen or light.

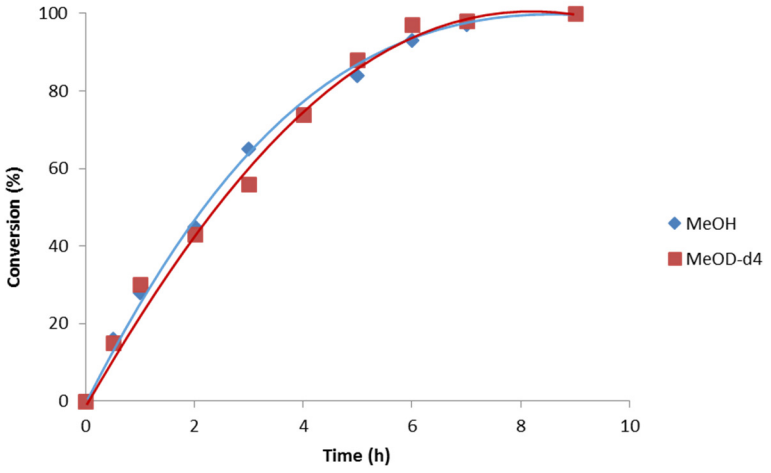


2a 3a

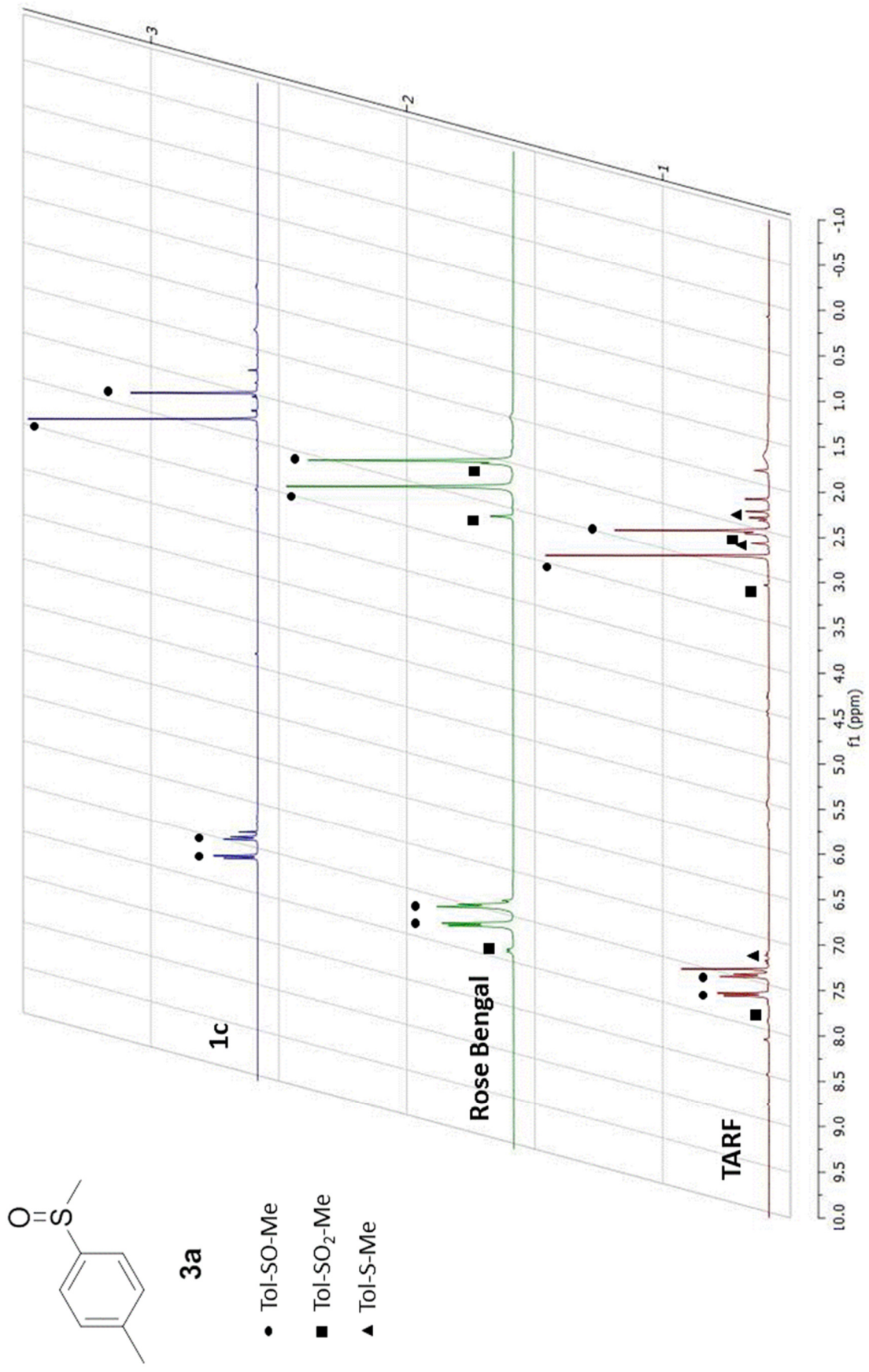
Entry	Catalyst	O_2 (air)	Light	Conversion (%)[a]
1	+	+	+	100
2	-	+	+	<5
3	+	+	-	<5
4	+	-	+	<5

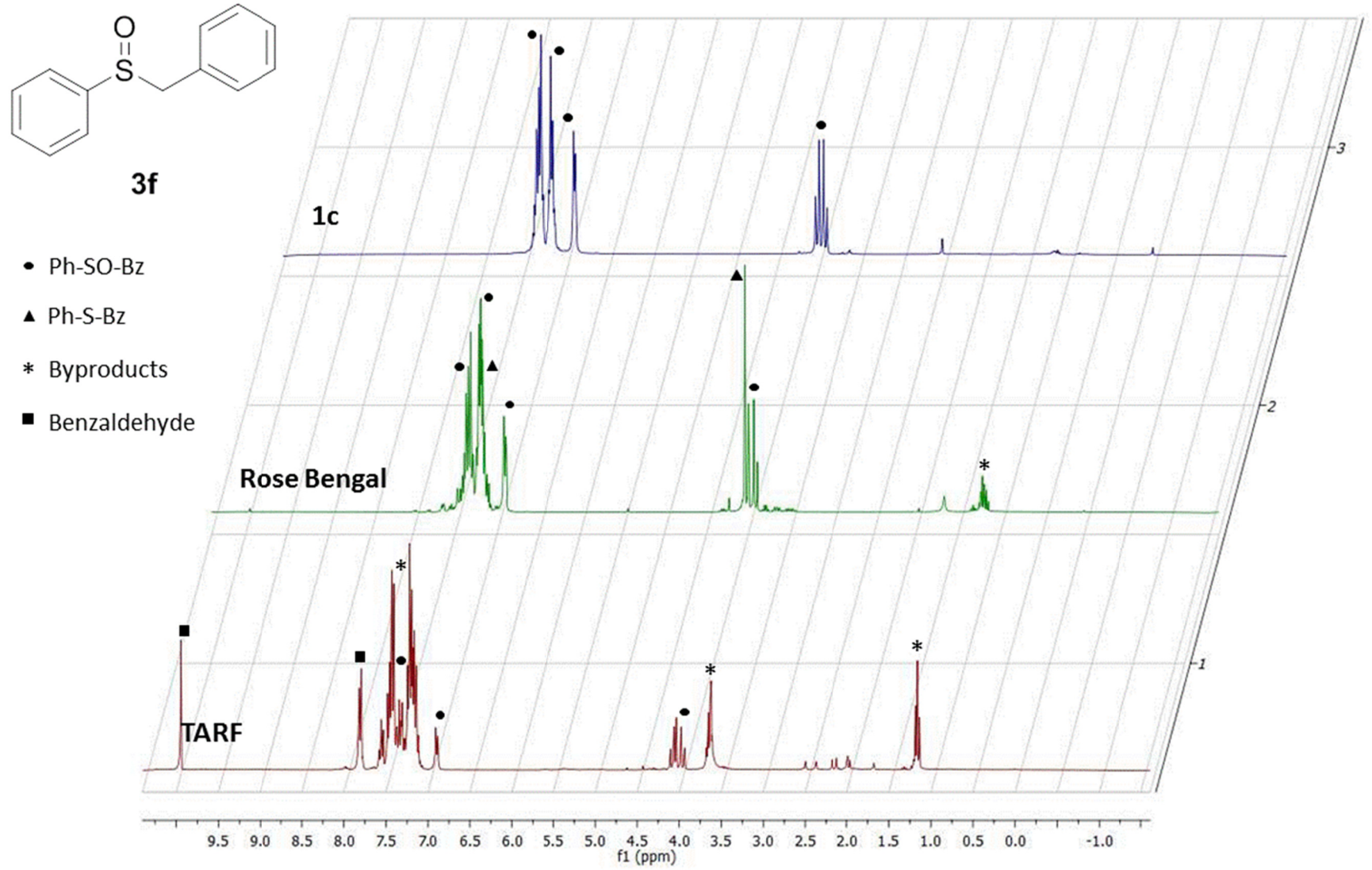
[a] Conversion determined by ^{1}H NMR analysis of the crude mixture.

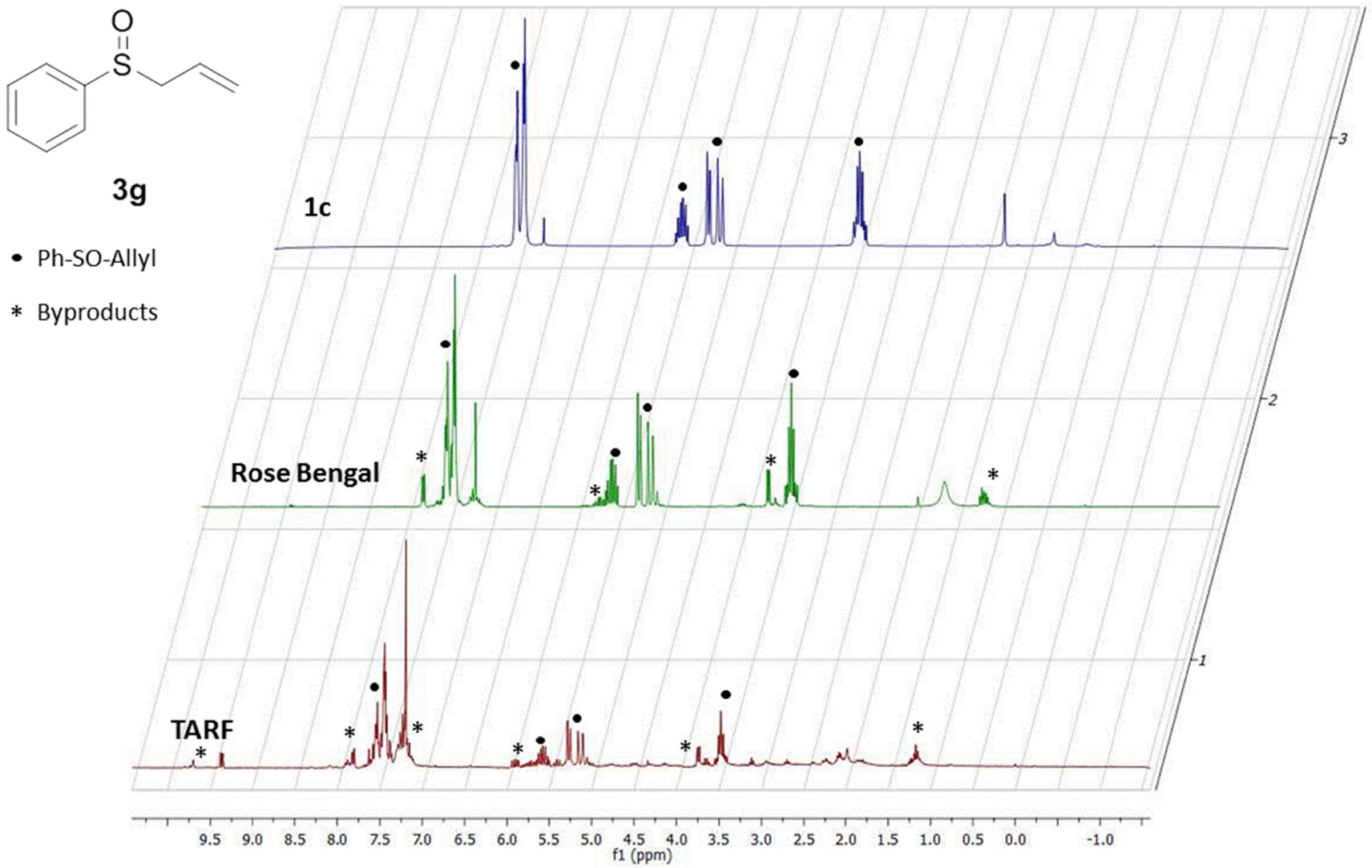
Figure S1. Kinetic experiments using MeOH or deuterated MeOH.

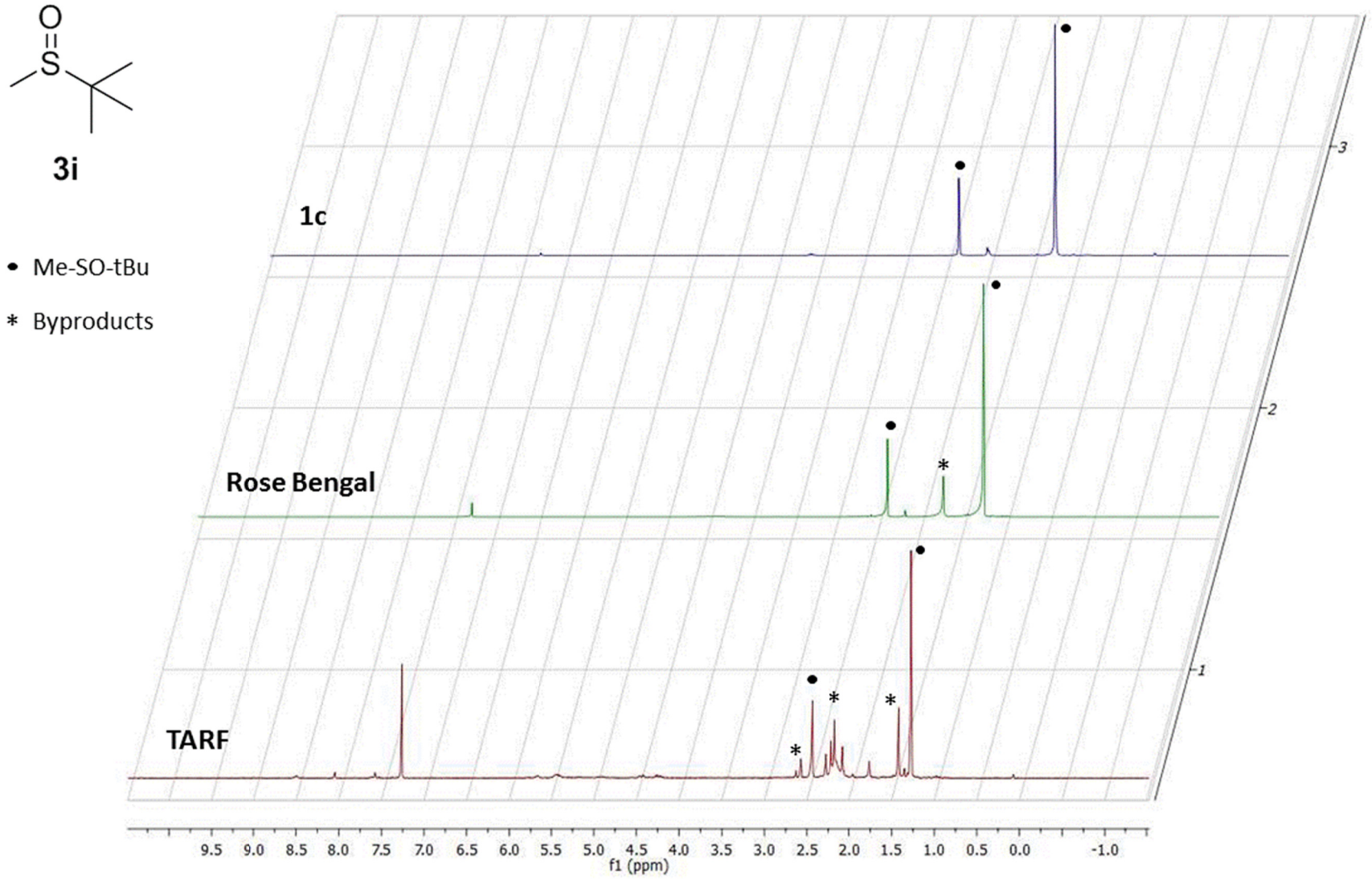


5. Comparative studies: NMR of the crude reactions.

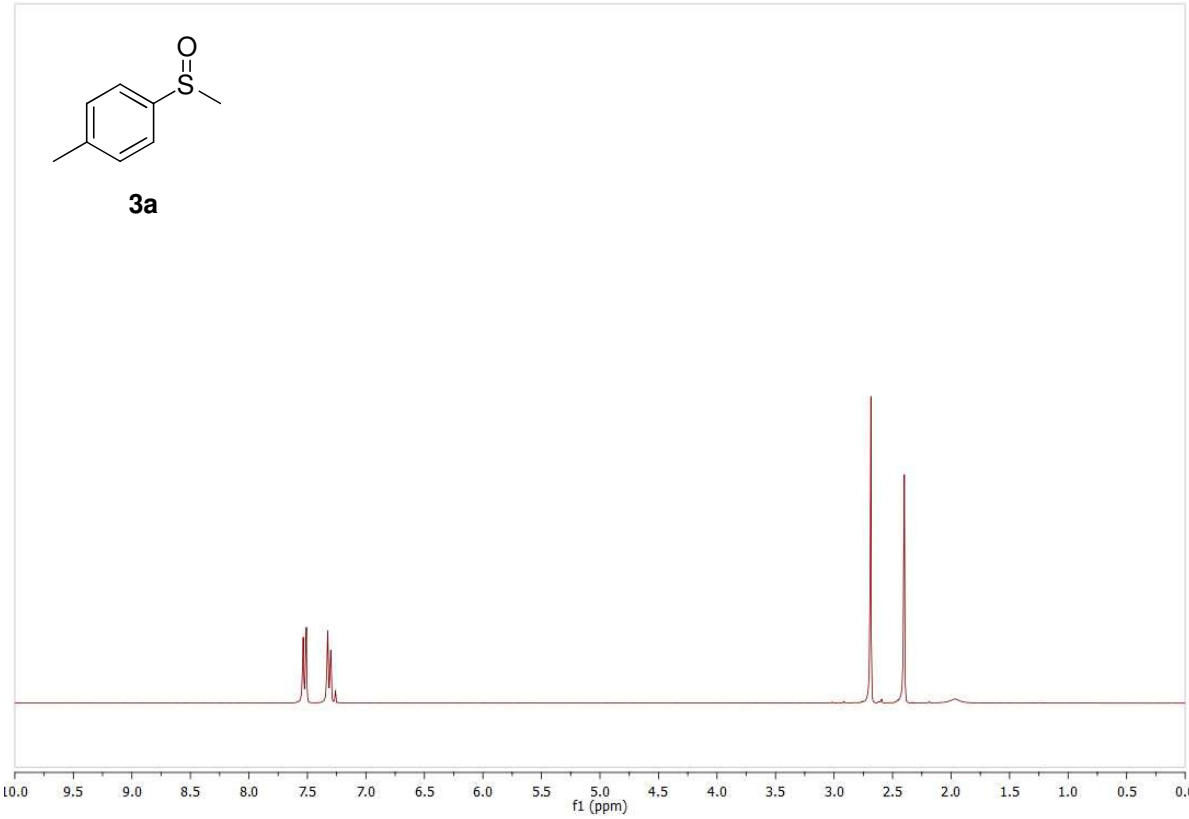


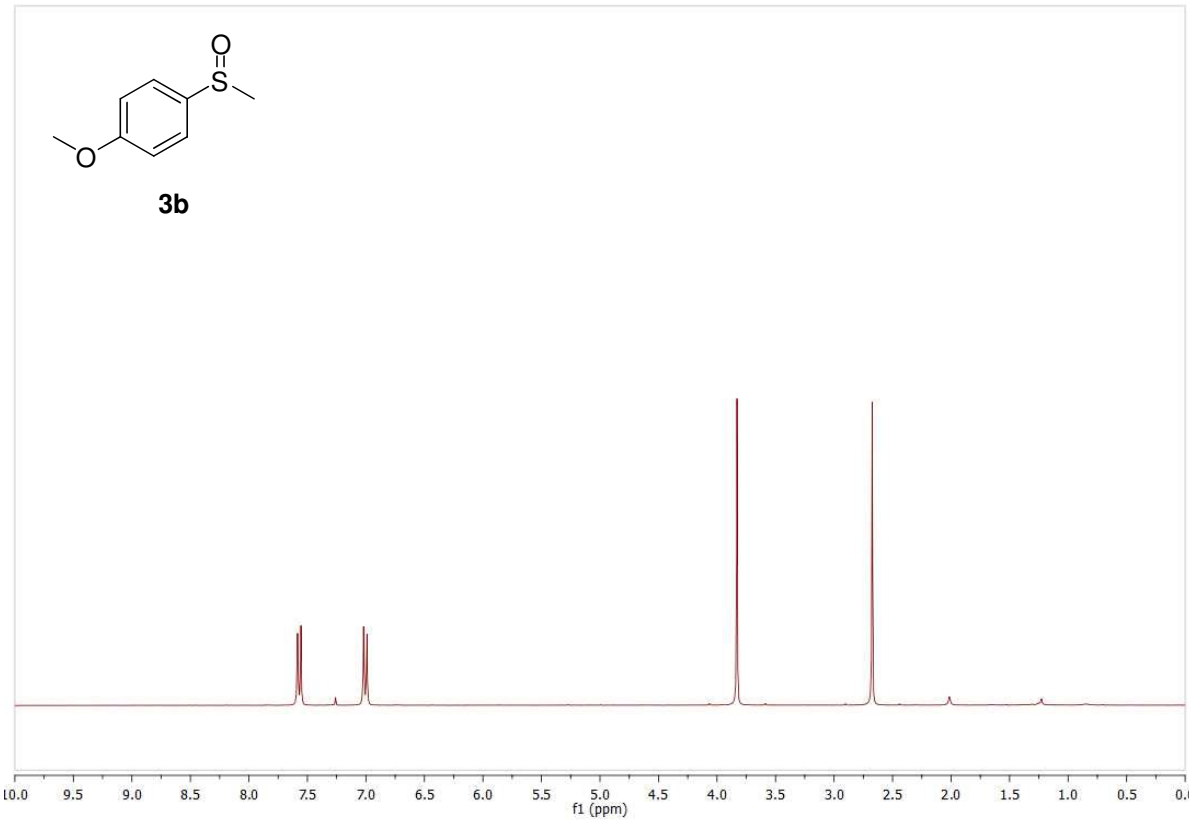

3f
1c
Rose Bengal
TARF
Ph-SO-Bz
Ph-S-Bz
Byproducts
Benzaldehyde
f1 (ppm)

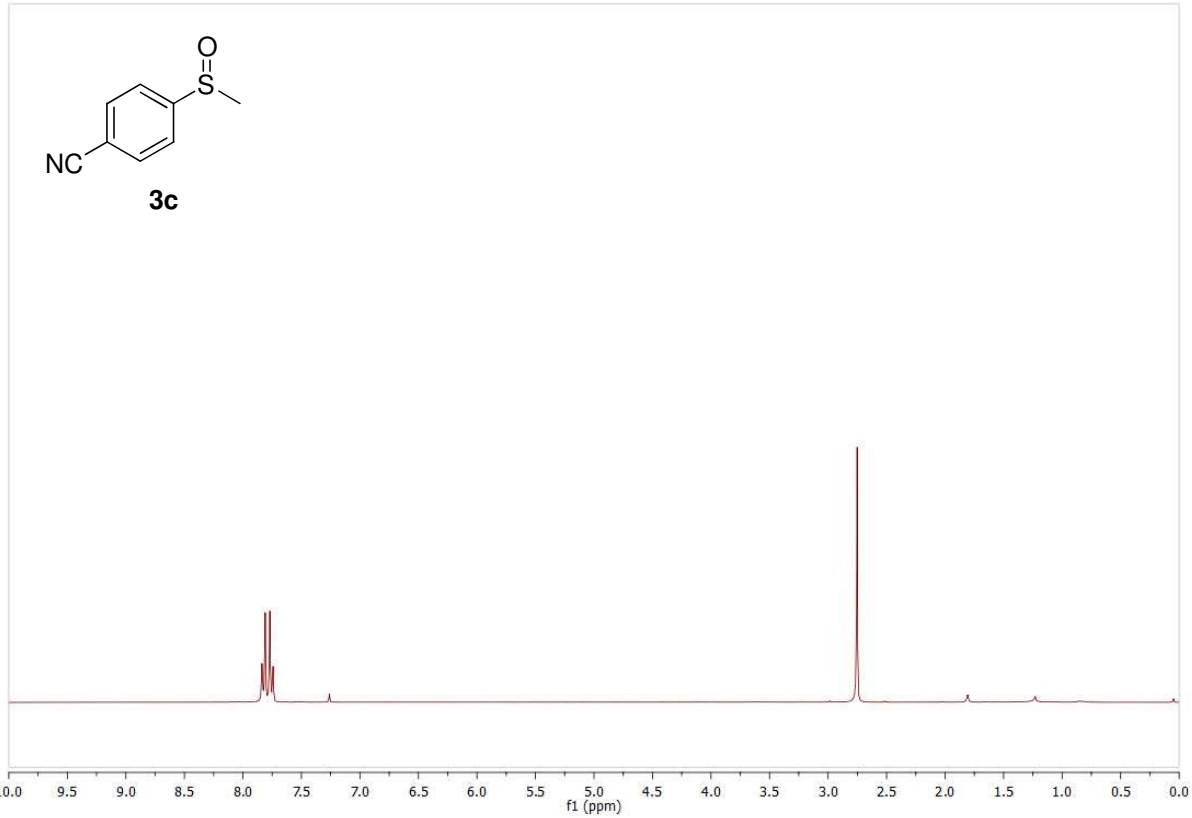

3g
• Ph-SO-Allyl
* Byproducts
1c
Rose Bengal
TARF
f1 (ppm)


3i
• Me-SO-tBu
* Byproducts
1c
Rose Bengal
TARF
3
2
1
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -1.0
f1 (ppm)

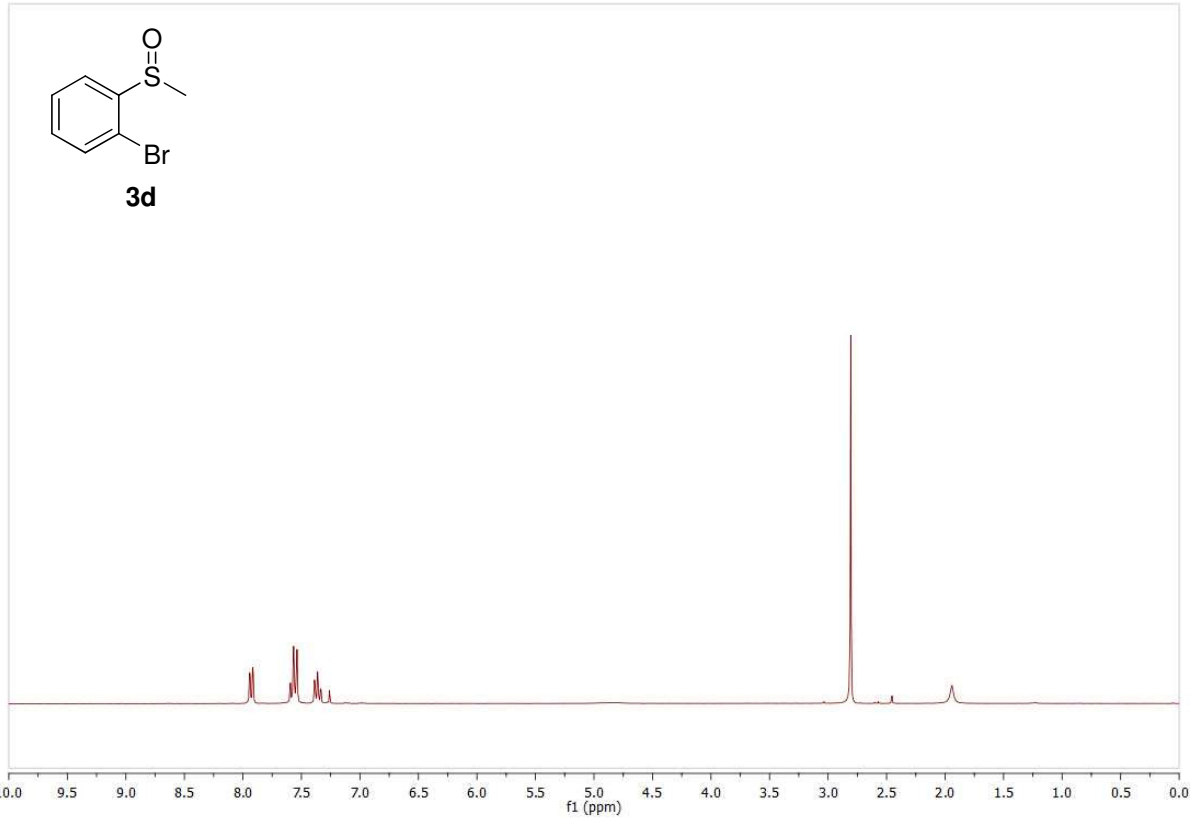
6. ^{1}H NMR spectra of sulfoxides 3.



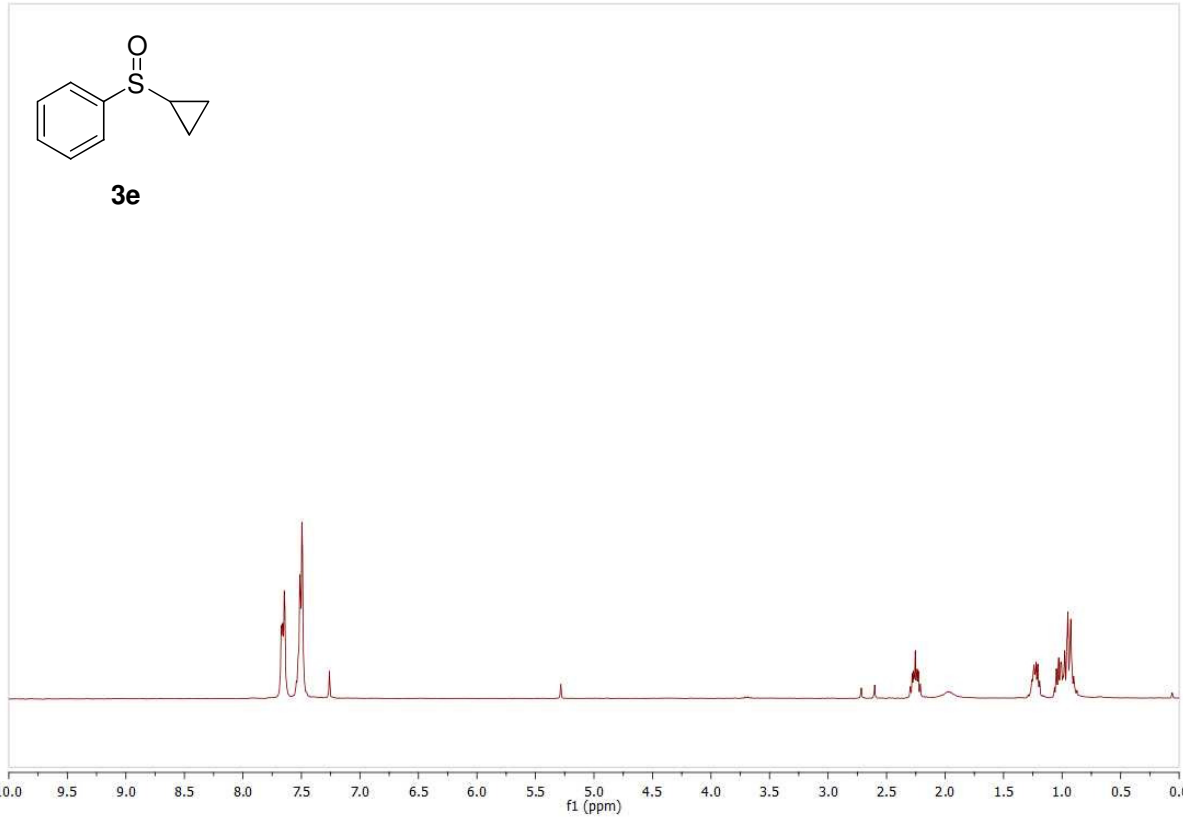


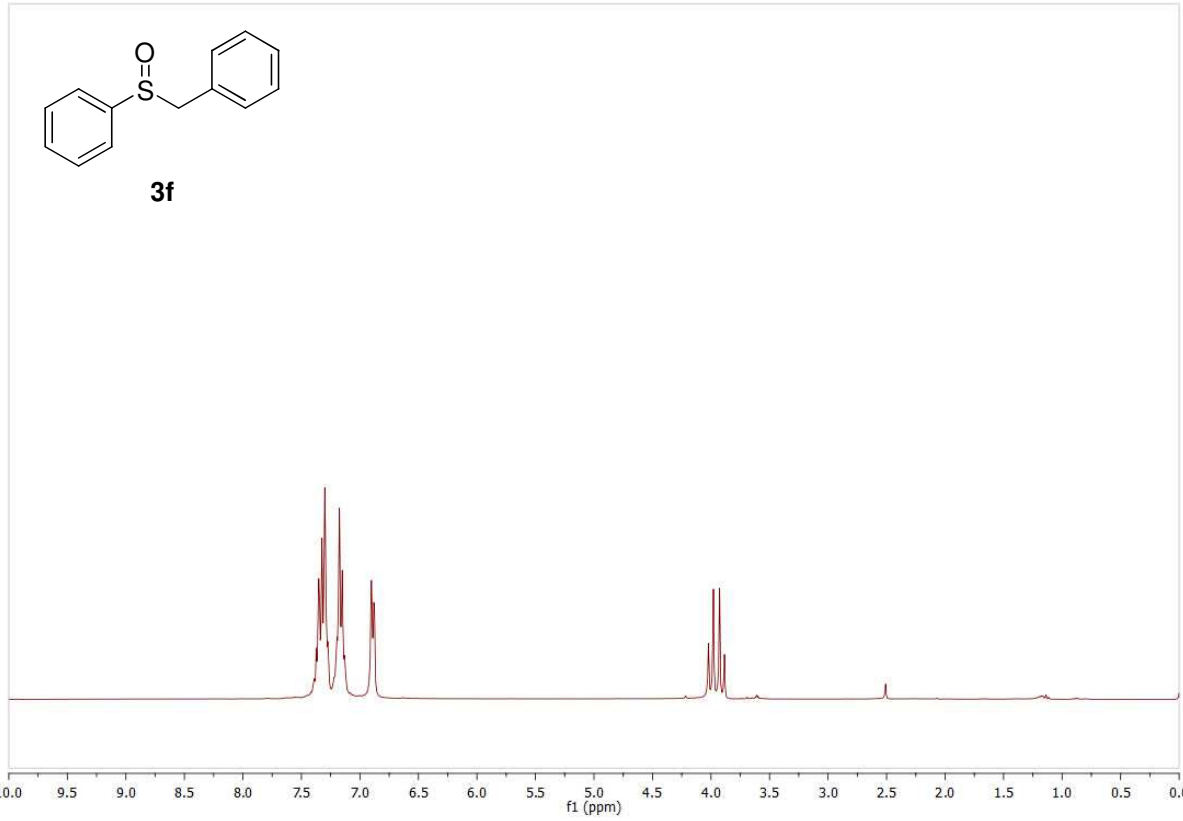

O
S
NC
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

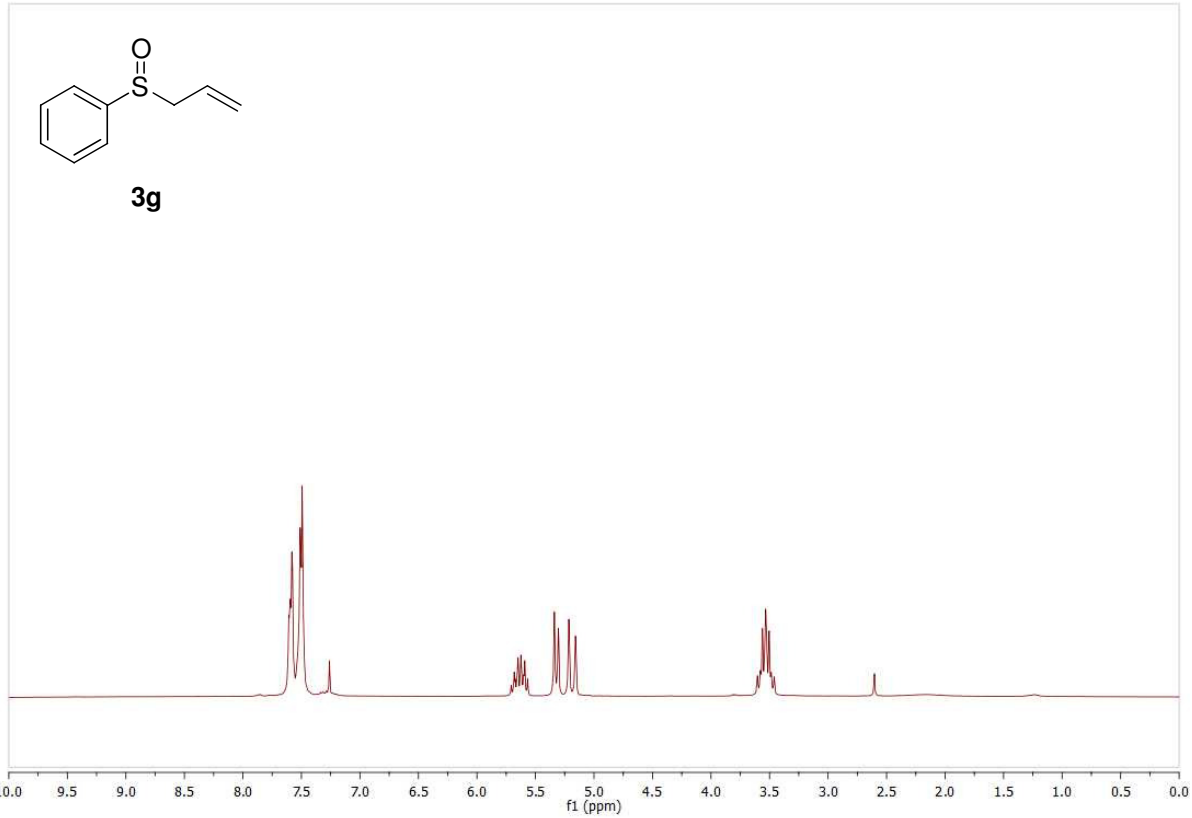
3c

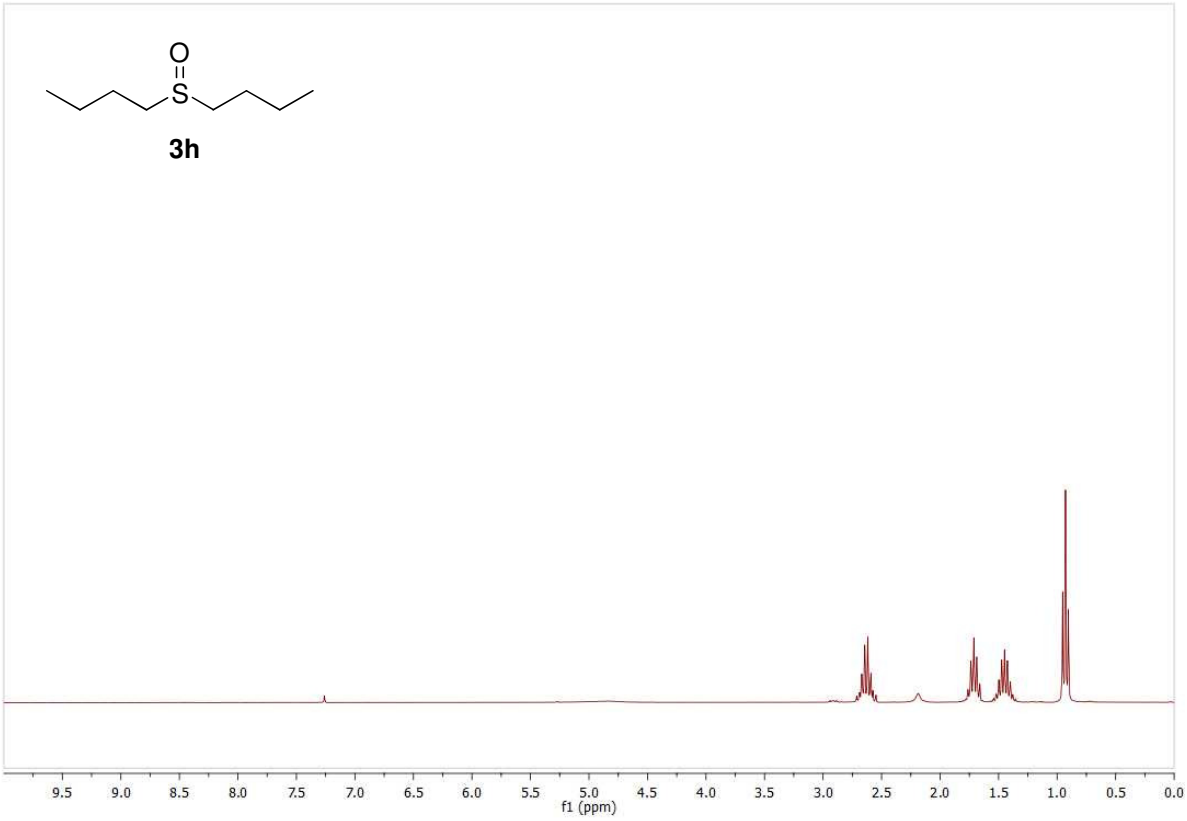

O
S
Br
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

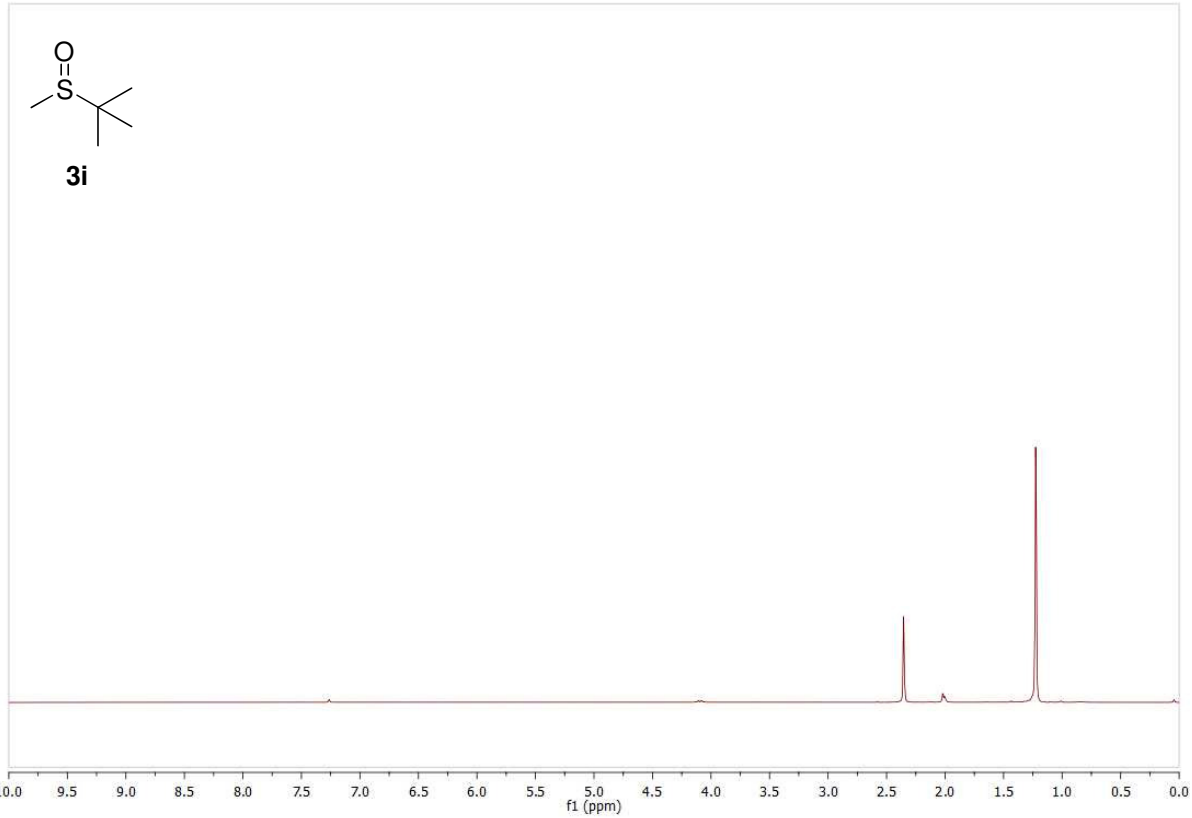
3d

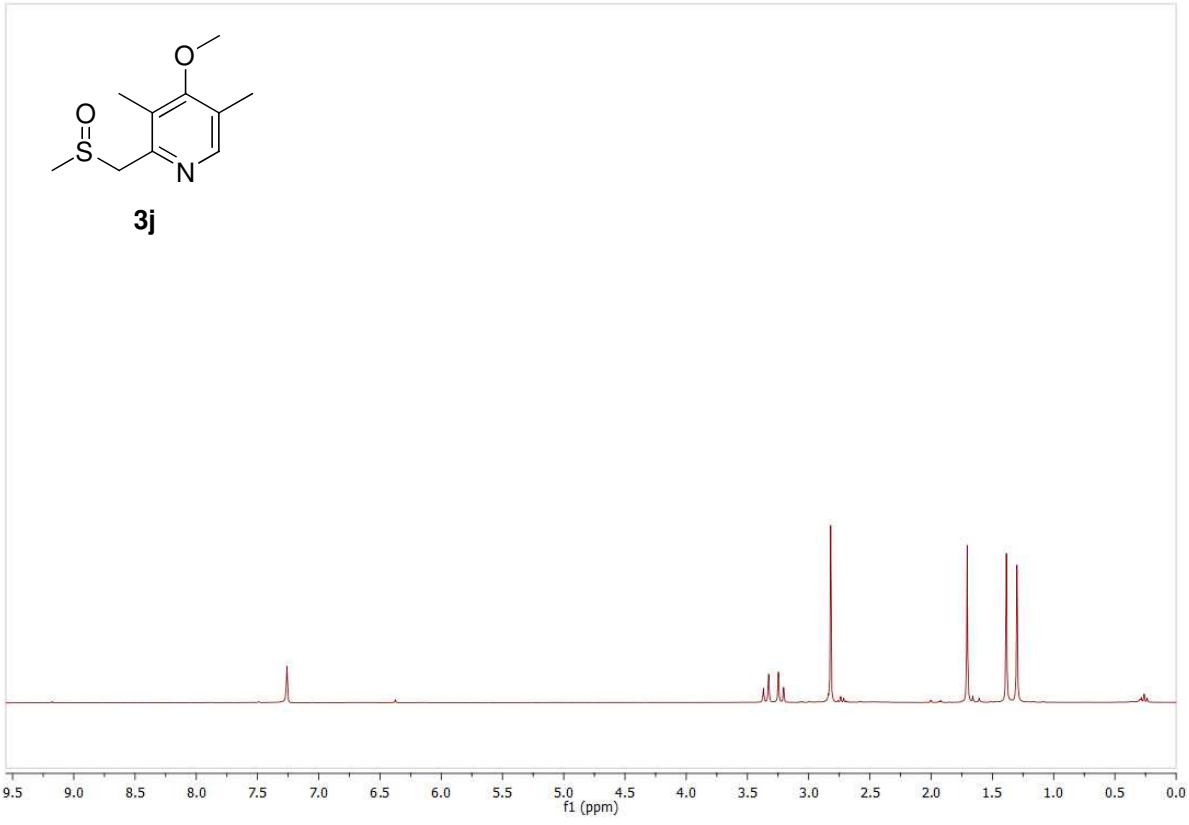

O
S
3e
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

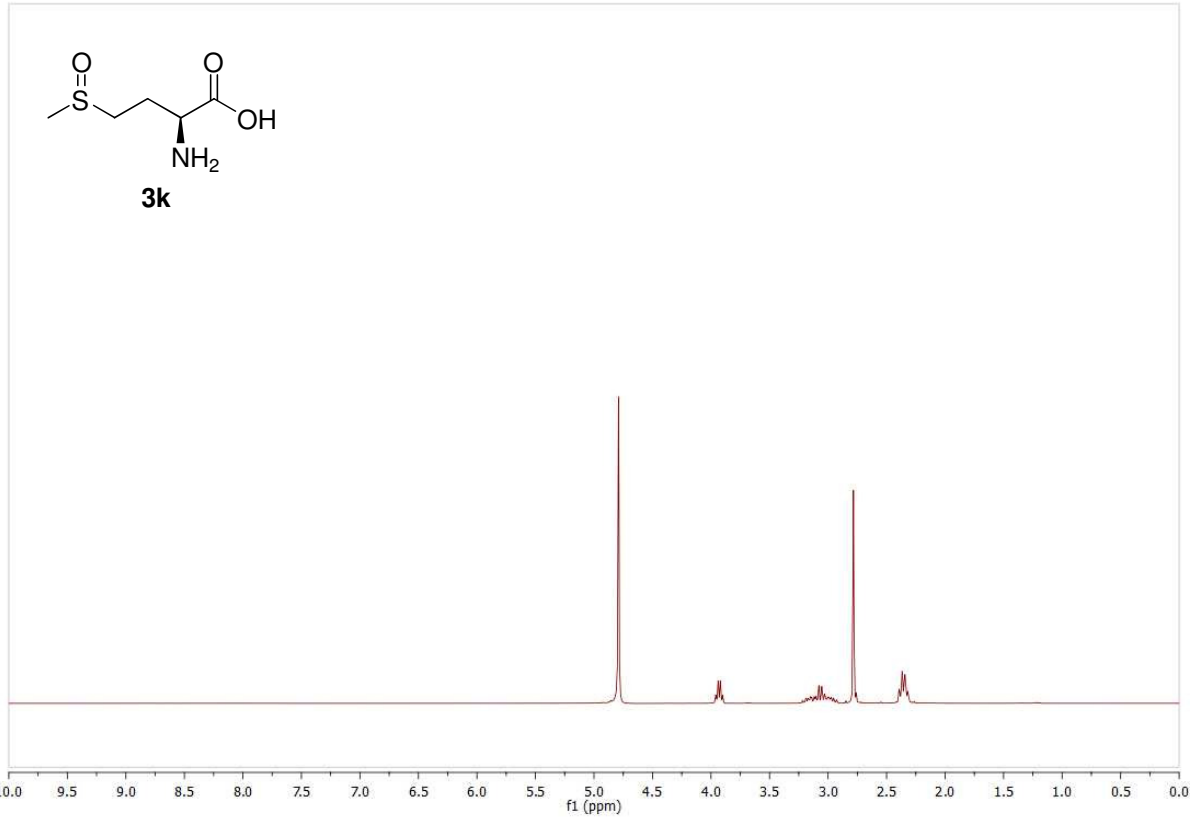

O
S
3f
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


O
S
3g
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

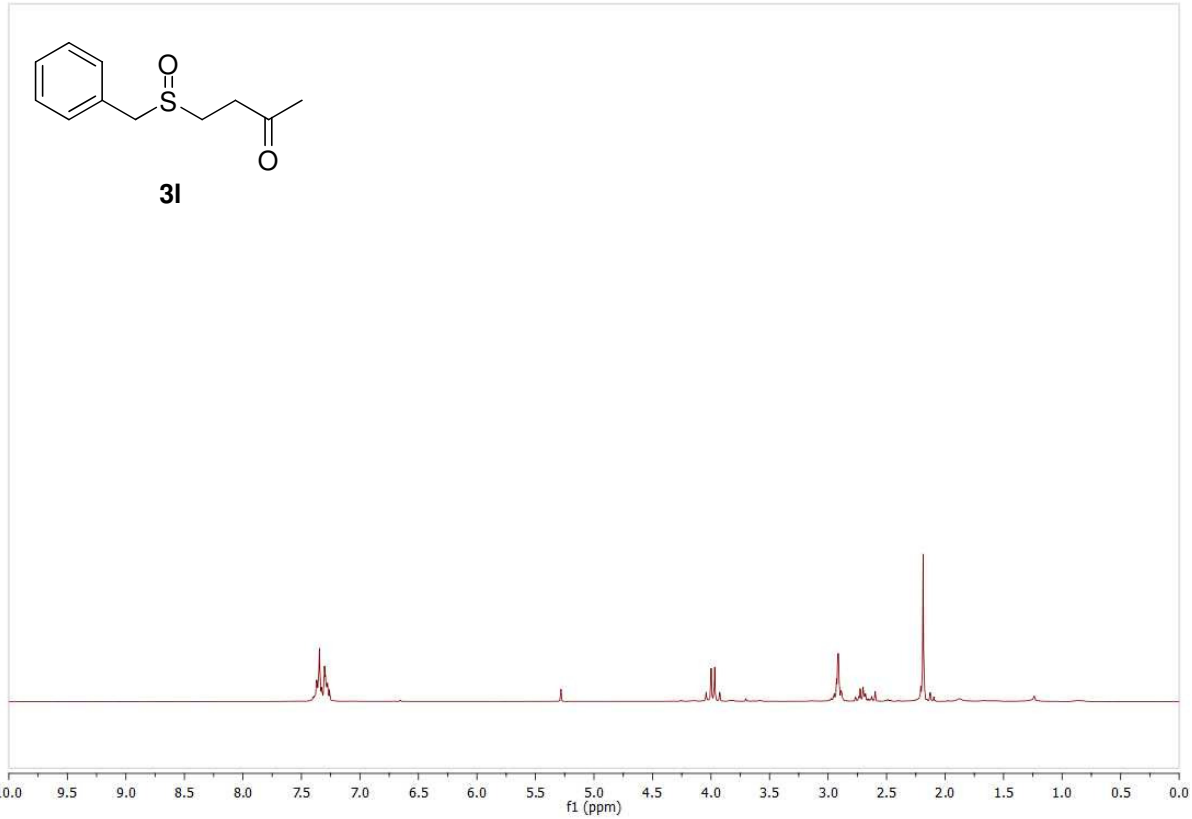

O
S
3h
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


O
S
3i
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

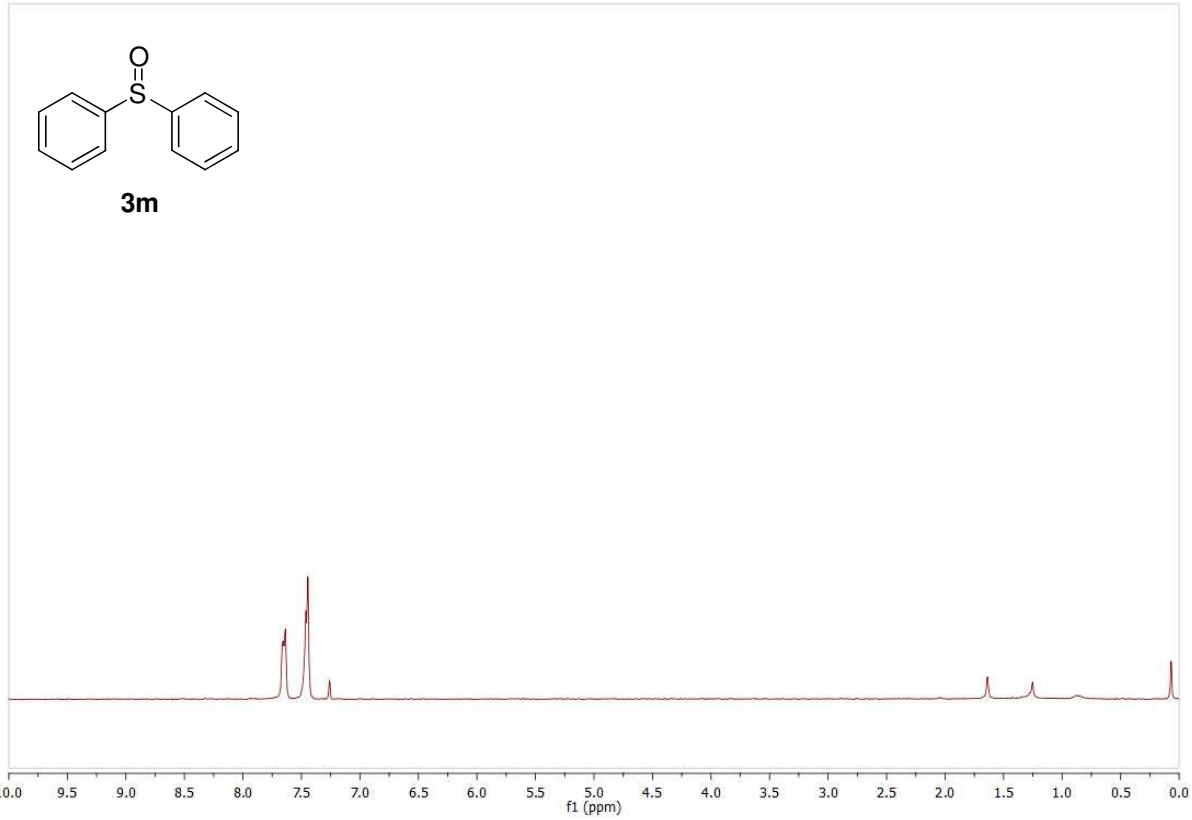

O
O
S
N
3j
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


O
O
S
OH
NH2
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

3k


O
S
O
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

3l


O
S
3m
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

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