Micellar Ru(II)–bipyridine photocatalysts for selective oxidation of thioethers to sulfoxides in water

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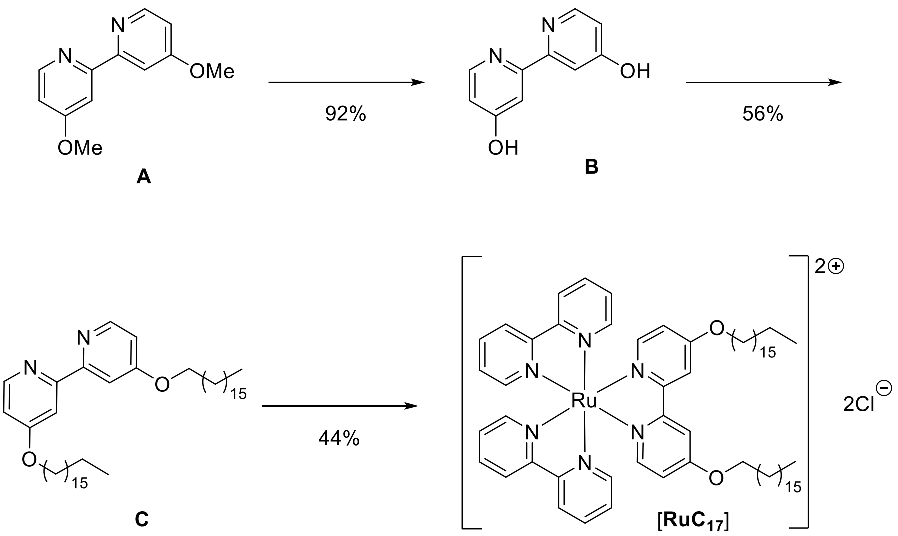
1) General

All reagents were purchased from Sigma-Aldrich and deuterated solvents from Eurisotop. NMR spectra were recorded on a Bruker Avance spectrometer at 400 MHz (^{1}H) and 100 MHz (^{13}C). Chemical shifts are given in ppm relative to the NMR solvent residual peak. Conversion and selectivity were determined directly from ^{1}H-NMR of crude products. Ultrasonic mixing was achieved using a Branson sonifier 550 equipped with a 3 mm tapered microtip (300 ms/s pulses, Output power 40%). Photopolymerization were carried out using a 40 W low-pressure mercury UV lamp (Heraeus) emitting at a wavelength of 254 nm. Photoredox reactions were run using KESSIL lamps PR160L 456 nm. Cyclic voltammetry (CV) experiments were performed at room temperature using a standard three-electrode cell configuration. A glassy carbon working electrode was used along with a titanium wire as the counter electrode, and a non-aqueous Ag/Ag+ electrode as the reference. All measurements were conducted in anhydrous acetonitrile (ACN) containing 0.1 M tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) as the supporting electrolyte. The working electrode was mechanically polished with alumina slurry, and the solution was thoroughly deaerated by bubbling with inert gas (N_2 or Ar) for 10 min. The voltammograms were recorded at a constant scan rate of 300 mV s^{-1}.

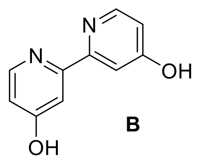
2) Catalyst preparation

a) Synthesis of ruthenium complex [**RuC₁₇**]



Scheme S1. Synthesis of complex [**RuC_{17}**].

- Demethylation of 4,4′-dimethoxy-2,2′-bipyridine

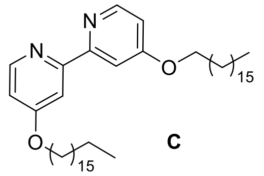


To a solution of 4,4′-dimethoxy-2,2′-bipyridine (**A**, 1 g, 4.6 mmol) in acetic acid (60 mL) was added hydrobromic acid 47% (16 mL, 92 mmol). The reaction mixture was stirred under reflux for 24 h, and the maximum of solvent was removed *in vacuo*. The concentrated solution was dissolved in water and neutralized with ammonium hydroxide. The precipitate formed was filtered and dried to yield [2,2'-bipyridine]-4,4'-diol (**B**) as a white solid (796 mg, 92%).

^{1}H NMR (400 MHz, CD_3CO_2D) δ 8.29 (d, *J* = 6.5 Hz, 2H), 7.65 (d, *J* = 2.0 Hz, 2H), 7.04 ppm (dd, *J* = 6.5, 2.0 Hz, 2H).

^{13}C NMR (101 MHz, CD_3CO_2D) δ 173.2, 147.3, 144. 7, 115.1, 111.8 ppm.

- Alkylation of [2,2'-bipyridine]-4,4'-diol

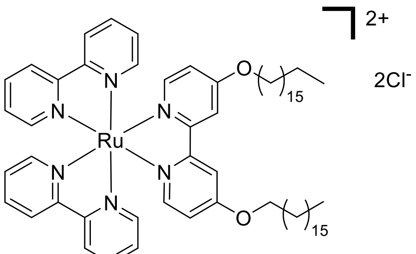


To a solution of [2,2'-bipyridine]-4,4'-diol (**B**, 0.1 g, 0.53 mmol, 1 equiv.) in DMF (5 mL) was added K_2CO_3 (0.37 g, 2.65 mmol, 5 equiv.) under an inert atmosphere. After 30 min, 1-bromoheptadecane (0.5 g, 1.59 mmol, 3 equiv.) was added to the mixture. The reaction mixture was heated at 80 °C for 24 h. The reaction medium was then diluted in water and extracted with DCM (3 × 30 mL). The organic phase was then washed with brine (3 × 30 mL), dried with $MgSO_4$, filtered and concentrated under reduced pressure. The crude residue was purified by silica gel column chromatography (*n*-hexane/ethyl acetate 95:5) to yield product **C** as a white solid (105 mg, 56%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (d, *J* = 6.0 Hz, 2H), 7.94 (d, *J* = 2.5 Hz, 2H), 6.82 (dd, *J* = 6.0, 2.5 Hz, 2H), 4.12 (t, *J* = 7.0 Hz, 4H), 1.80 (quint, *J* = 7.0 Hz, 4H), 1.45 (quint, *J* = 7.0 Hz, 4H), 1.39–1.15 (m, 52H), 0.87 ppm (t, *J* = 7.0 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.3, 157.7, 149.9, 111.5, 106.8, 68.2, 31.9, 29.7, 29.70, 29.7, 29.6, 29.7, 29.4, 29.3, 29.0, 25.9, 22.7, 14.2 ppm.

- Assembly of the ruthenium complex



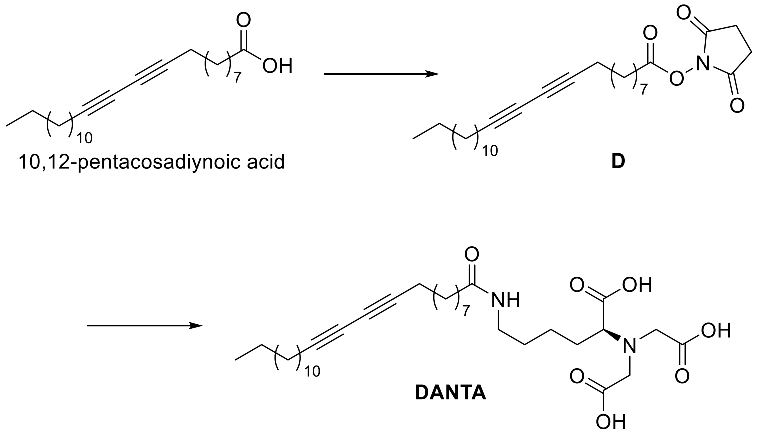
[**RuC$_{17}$**]

Compound **C** (49 mg, 0.073 mmol, 1 equiv.) and [Ru(bpy)$_2$Cl$_2$] (37 mg, 0.076 mmol, 1 equiv.) were dissolved in EtOH/H_2O 3:1 (*v*/*v*, 3 mL). The reaction mixture was stirred overnight at 80 °C the mixture was then concentrated under reduced pressure. The crude residue was then purified by silica gel column chromatography (DCM/MeOH 100:0 → 90:10) to yield [**RuC$_{17}$**] as an orange solid (34 mg, 44%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.05 (d, *J* = 7.0 Hz, 4H), 8.31 (d, *J* = 1.5 Hz, 2H), 8.08 (dd, *J* = 16.0, 8.0 Hz, 4H), 7.75 (d, *J* = 5.0 Hz, 2H), 7.63 (d, *J* = 5.0 Hz, 2H), 7.52–7.47 (m, 2H), 7.47–7.43 (m, 2H), 7.39 (d, *J* = 6.3 Hz, 2H), 6.98 (d, *J* = 5.0 Hz, 2H), 4.36 (t, *J* = 7.0 Hz, 4H), 1.78 (quint, *J* = 7.0 Hz, 4H), 1.41 (quint, *J* = 7.0 Hz, 4H), 1.34–1.14 (m, 52H), 0.84 ppm (t, *J* = 7.0 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.9, 157.7, 157.2, 157.1, 151.6, 151.0, 150.7, 138.1, 138.0, 127.9, 127.8, 125.5, 125.4, 115.0, 111.9, 70.7, 31.9, 29.7, 29.7, 29.7, 29.6, 29.5, 29.4, 29.3, 28.8, 25.9, 22.7, 14.1 ppm.

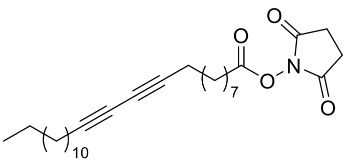
b) Synthesis of DANTA



Scheme S2. Synthesis of DANTA.

Micelles result from the self-assembly of a single amphiphilic monomer (DANTA) which was synthesized according to a previously reported protocol:[1]

- Activation of 10,12-pentacosadiynoic acid



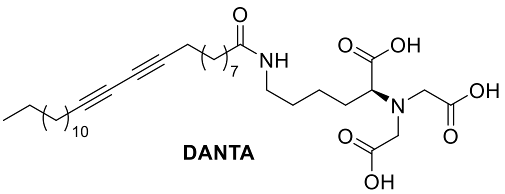
D

Pentacosa-10,12-diynoic acid (2 g, 5.4 mmol, 1 equiv.), EDCI (1.56 g, 1.5 equiv.) and *N*-hydroxysuccinimide (1 g, 1.8 equiv.) were solubilized in anhydrous DCM (80 mL). The solution was stirred at room temperature overnight under N_2, and quenched with H_2O. The aqueous phase was extracted twice with DCM. The organic phases were collected, dried with $MgSO_4$, filtered and concentrated under vacuum to yield compound **D** as a white solid (2.54 g, 99%).

^{1}H NMR (400 MHz, DMSO-d_6) δ 2.7–2.9 (m, 4H), 2.58 (t, J = 7.2 Hz, 2H), 2.22 (t, J = 7.2 Hz, 4H), 1.72 (q, J = 7.2 Hz, 2H), 1.49 (t, J = 7.2 Hz, 2H), 1.2–1.42 (m, 28H), 0.86 ppm (t, J = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 169.2 (2C), 168.5, 77.6, 77.3, 65.3, 65.2, 31.8, 28.1–30.7 (16C), 24.4, 22.5, 18.9 (2C), 13.9 ppm.

- Coupling with Lysine-NTA



DANTA

N^2,N^2-Bis(carboxymethyl)lysine (1 g, 1.2 equiv.) and NEt_3 (3.1 mL , 7 equiv.) were dispersed in DMF (80 mL). Compound **D** (1.44 g, 3.05 mmol, 1 equiv.) in DMF (50 mL) was then added. The solution was stirred at 60 °C for 1 h, and left at room temperature overnight. The solution was concentrated under vacuum, taken into H_2O, and acidified with HCl. The precipitate was filtered off, washed with water and dried under vacuum over P_2O_5. DANTA was obtained as a white solid (1.43 g, 76%).

^{1}H NMR (400 MHz, DMSO-d_6) δ 7.68 (t, 1H, J = 5.6 Hz), 3.39–3.50 (AB, J_{AB} = 17.6 Hz, 4H), 3.35 (t, J = 7.3 Hz, 1H), 2.97 (m, 2H), 2.24 (t, J = 6.8 Hz, 4H), 2.00 (t, J = 7.2 Hz, 2H), 1.1–1.6 (m, 38H), 0.82 ppm (t, J = 6.8 Hz, 3H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 174.3, 173.6 (2C), 172.2, 78.0 (2C), 65.7, 64.7 (2C), 53.7 (2C), 38.6, 35.8, 28.0–31.7 (16C), 25.7, 23.5, 22.5, 18.7 (2C), 14.3 ppm.

c) Preparation of *p*DANTA micelles

A solution of DANTA (50 mg) in 0.01 M aqueous sodium hydroxide (5 mL) was sonicated with an ultrasonic probe (300 ms pulses per second, 25 W output power) for 10 min. The solution was then subjected to UV light (254 nm, low pressure mercury UV lamp, Heraeus) irradiation for 5 h to yield *p*DANTA micelles. The suspension was then passed through a size exclusion chromatography column (Sephadex) eluted with deionized water, affording a neutral colloid.

d) Preparation of [**RuC_{17}**]@*p*DANTA micelle

A stock solution of [**RuC_{17}**] was prepared in $CHCl_3$ at a concentration of 1 mg/mL. In parallel, pDANTA micelles (10 mg) were dispersed in Milli-Q water (1 mL) in a glass vial. The chloroform solution of [**RuC_{17}**] (100 µL, 0.1 mg of PS) was added to the aqueous micellar suspension. Encapsulation of [**RuC_{17}**] into the micelles was achieved by ultrasonic mixing using a Branson Sonifier 550 equipped with a 3 mm tapered microtip (300 ms/s pulses, Output power 40% for 10 min). During sonication, the chloroform phase gradually evaporated, leading to the formation of a fully aqueous and stable colloid. The obtained aqueous suspension of [**RuC_{17}**]@*p*DANTA (10 mg micelles loaded with 0.1 mg of [**RuC_{17}**]) was used directly in the photocatalytic experiments.

3) Characterization of the catalyst

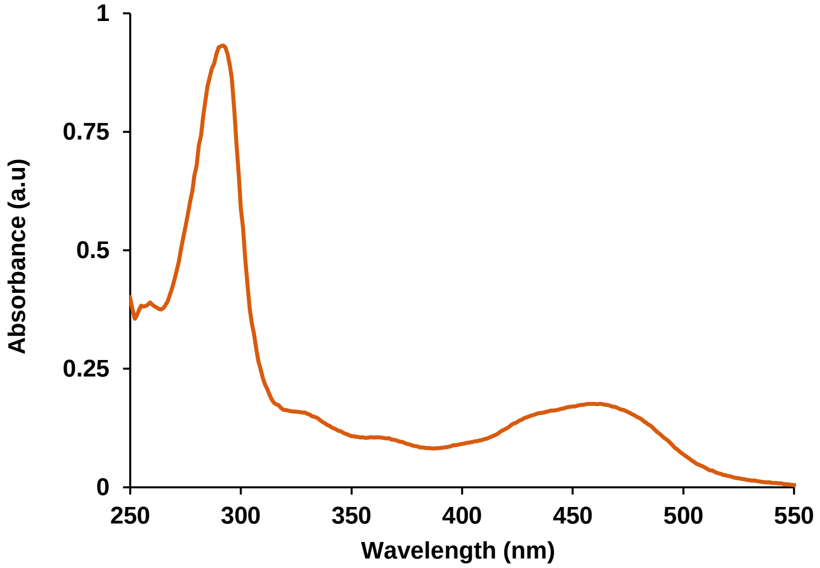


Figure S1. Absorption spectrum of [**RuC_{17}**] in chloroform.

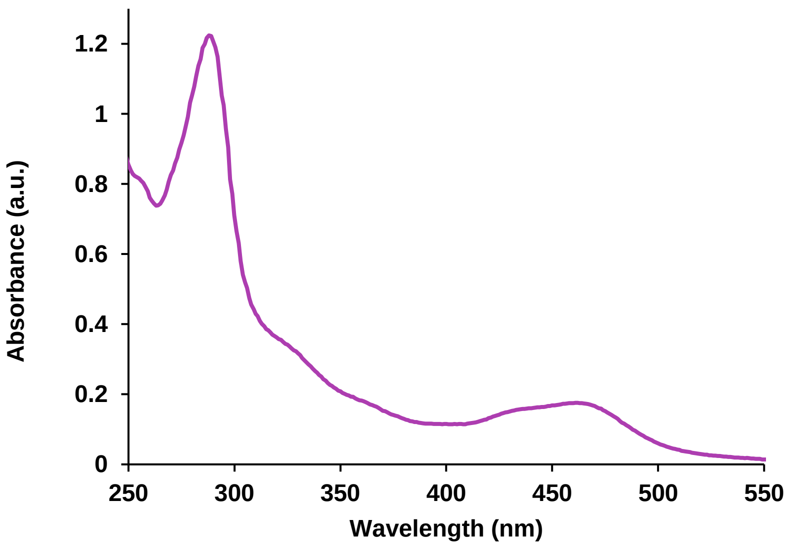


Figure S2. Absorption spectrum of [**RuC_{17}**]@*p*DANTA in water.

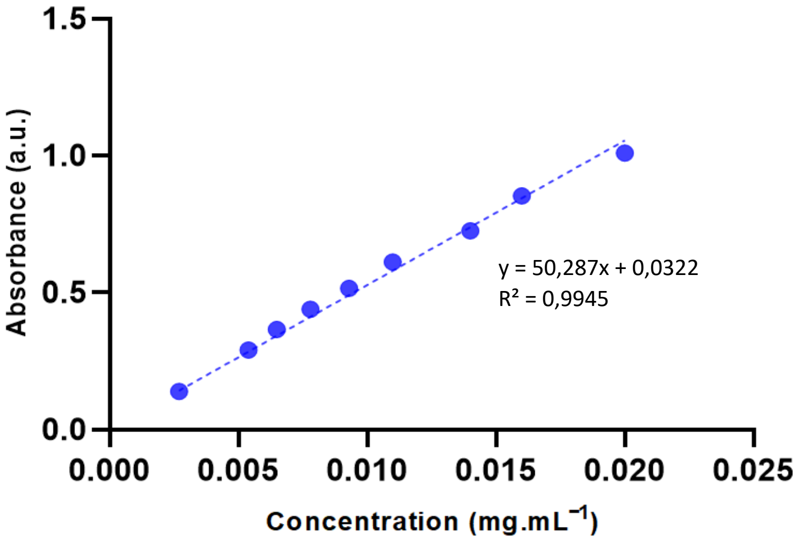


Figure S3. Calibration curve of [**RuC_{17}**] in chloroform (292 nm).

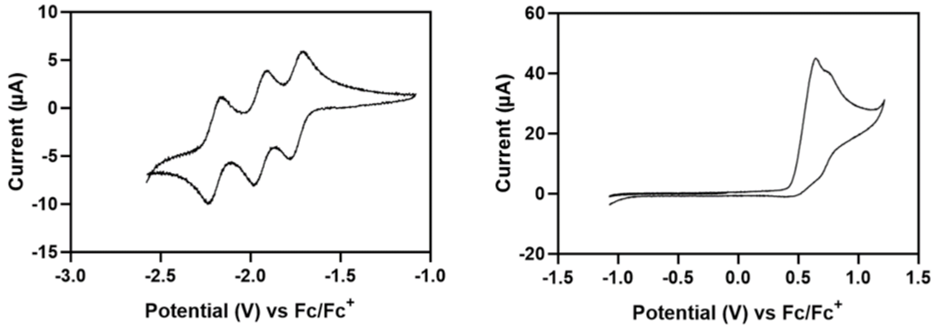


Figure S4. Cyclic voltammograms of complex [**RuC_{17}**] recorded in CH_3CN (0.1 M Bu_4NPF_6) at a glassy carbon working electrode with scan rate 300 mV s^{-1}.

4) Mechanistic investigations

- Control experiments

Table S1. Additional experiments carried out for mechanistic investigations.[a]

Entry	Solvent	Additive	Time (h)	Conv. (%)
1	H_2O	DABCO	3	45
2	H_2O	benzoquinone	3	72
3	D_2O	none	2	100

[a] Conditions: **1a** (0.1 mmol), [**RuC_{17}**]@*p*DANTA (0.1 mol%), additive (1 equiv.), room temperature, blue light (456 nm), air atmosphere.

- Singlet oxygen production

To evaluate singlet oxygen generation, a 3:1 (*v*/*v*) DMSO/water mixture containing DPBF at a final concentration of approximately 0.74 mM was prepared, to achieve an initial absorbance of 1.0 at 417 nm. For the photosensitizer, the concentration of [**RuC_{17}**]@pDANTA was adjusted to approximately 0.01 mg/mL to ensure an absorbance of 0.1 at the irradiation wavelength (456 nm). The samples were illuminated using a 456 nm blue light source and UV-vis absorption spectra were recorded at cumulative intervals of illumination of 0, 5, 10, 15, and 20 seconds.

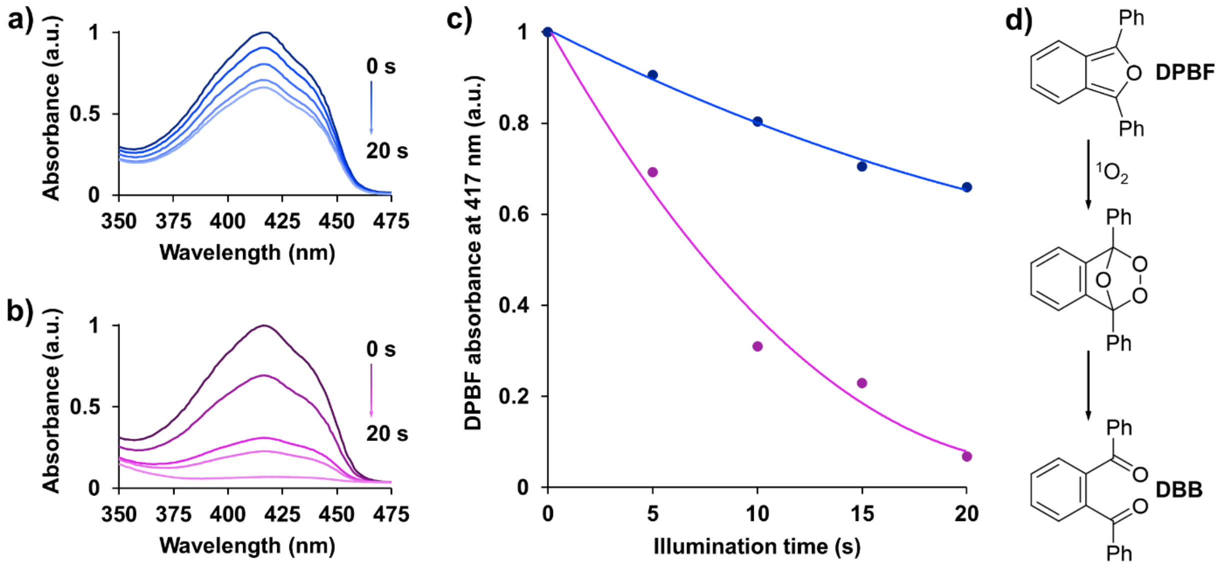
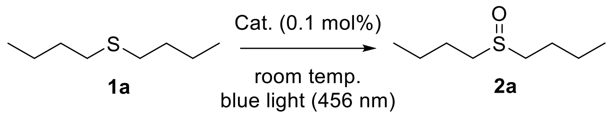


Figure S5. a) UV-vis spectra of a DPBF (0.74 mM) solution in DMSO/water 1:1 after 0, 5, 10, 15, or 20 s of blue light (456 nm) illumination; b) UV-vis spectra of a DPBF (0.74 mM) and [**RuC_{17}**]@*p*DANTA (0.01 mg mL^{-1}) mixture in DMSO/water 1:1 after 0, 5, 10, 15, or 20 s of blue light (456 nm) illumination; c) Evolution of DPBF absorbance at 417 nm in the absence (blue) or in the presence (purple) of [**RuC_{17}**]@*p*DANTA, as a function of illumination time; d) Conversion of 1,3-diphenylisobenzofuran (**DPBF**, strong 417 nm absorbance) into dibenzoylbenzene (**DBB**, no 417 nm absorbance) in the presence of $^1O_2$.

5) General procedure for photocatalytic oxidation



Scheme S3. General procedure for photocatalytic oxidation.

A general procedure for photocatalytic oxidation is given for the oxidation of dibutyl sulfide **1a**: 1 mL of the aqueous colloidal suspension of [$\mathbf{RuC_{17}}$]@*p*DANTA containing 10 mg of micelles and 0.1 mg (0.1 mol%) of the photocatalyst was introduced into a 8 mL reaction vial. Dibutyl sulfide (14.6 mg, 0.1 mmol, 1 equiv.) was then added. The reaction mixture vigorously stirred and was irradiated with a LED lamp (456 nm, Kessil PR160L-456, 100% intensity, placed 1 cm from the reaction vial, see Figure S6) at room temperature until full conversion, as monitored by TLC. After completion of the reaction, the mixture was extracted with diethyl ether (5 × 3 mL). The combined organic layers were dried over anhydrous $MgSO_4$, filtered, and the solvent was removed under reduced pressure. The crude product was analyzed by ^{1}H-NMR spectroscopy without further purification.

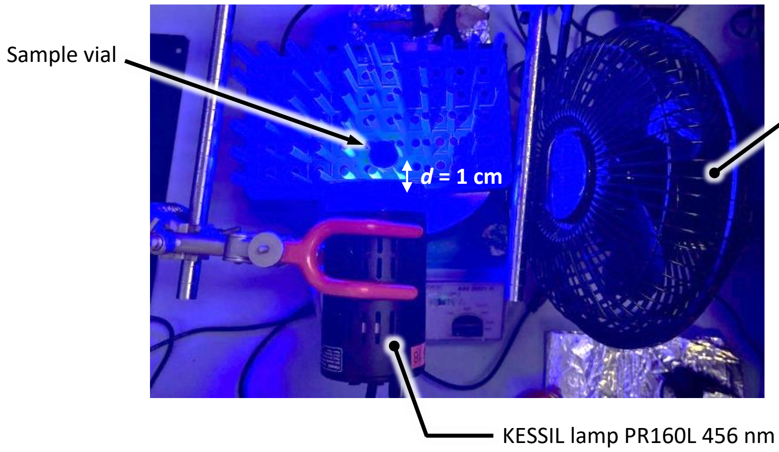
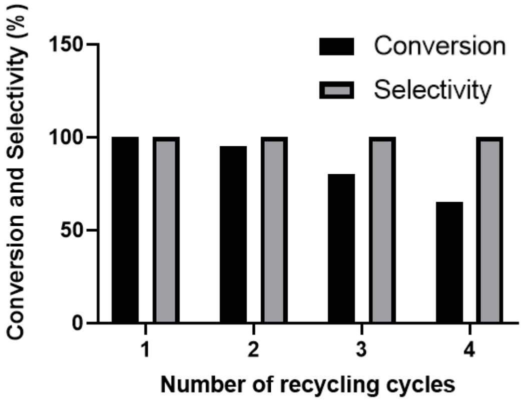


Figure S6. Pictures of the photocatalytic set up (*d* is the distance between the lamp and the sample vial).

6) Study of recyclability

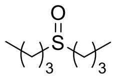
The sustainability of the process was evaluated by recycling the nanohybrid catalyst over multiple cycles. After each run, the organic product was extracted using diethyl ether, leaving the catalyst in the aqueous phase. This phase was successfully engaged in the next catalytic run by adding fresh substrate without the need for further purification or regeneration steps.



Cycle	Conversion (%)	Selectivity (%)
1	100	100
2	95	100
3	80	100
4	65	100

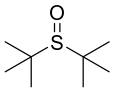
Figure S7. Evolution of conversion and selectivity as a function of the number of catalyst recycling cycles.

7) Spectroscopic data

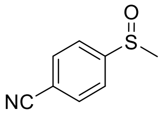


1H NMR (400 MHz, $CDCl_3$) δ 2.73–2.61 (m, 4H), 1.80–1.72 (m, 4H), 1.60–1.40 (m, 4H), 0.98 ppm (t, J = 7.3 Hz, 6H).

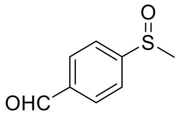
13C NMR (101 MHz, $CDCl_3$) δ 52.1, 24.5, 22.0, 13.6 ppm.



1H NMR (400 MHz, CDCl3): δ 1.34 (s, 18H).

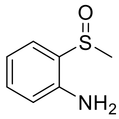


1H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, J = 8.8 Hz, 2H), 7.76 (d, J = 8.8 Hz, 2H), 2.75 ppm (s, 3H).



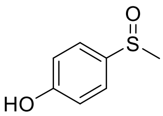
1H NMR (400 MHz, $CDCl_3$) δ 10.07 (s, 1H), 8.03 (d, J = 8.8 Hz, 2H), 7.80 (d, J = 8.8 Hz, 2H), 2.77 ppm (s, 3H).

13C NMR (101 MHz, $CDCl_3$) δ 191.3, 152.5, 138.1, 130.4, 124.2, 43.8 ppm.



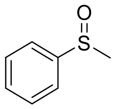
1H NMR (400 MHz, $CDCl_3$) δ 7.25–7.18 (m, 2H), 6.82–6.62 (m, 2H), 2.93 ppm (s, 3H).

13C NMR (101 MHz, $CDCl_3$) δ 147.5, 132.5, 126.4, 123.5, 117.7, 117.6, 38.1 ppm.



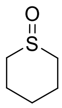
1H NMR (400 MHz, $CDCl_3$) δ 9.06 (s, 1H), 7.50 (d, J = 8.8 Hz, 2H), 6.96 (d, J = 8.8 Hz, 2H), 2.75 ppm (s, 3H).

13C NMR (101 MHz, $CDCl_3$) δ 160.7, 133.4, 126.2, 116.9, 43.2 ppm.

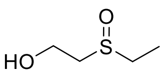


1H NMR (400 MHz, $CDCl_3$) δ 7.68–7.55 (m, 2H), 7.55–7.43 (m, 3H), 2.69 ppm (s, 3H).

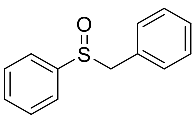
13C NMR (101 MHz, $CDCl_3$) δ 145.8, 131.0, 129.4, 123.5, 44.0 ppm.



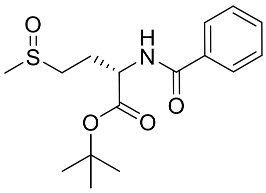
1H NMR (400 MHz, $CDCl_3$) δ 2.91 (ddd, J = 12.0, 8.5, 3.0 Hz, 2H), 2.78 (ddd, J = 12.0, 8.5, 3.0 Hz, 2H), 2.34–2.19 (m, 2H), 1.78–1.51 ppm (m, 4H).



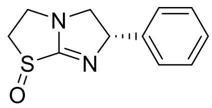
1H NMR (400 MHz, $CDCl_3$) δ 3.72 (t, J = 5.9 Hz, 2H), 2.74 (t, J = 5.9 Hz, 2H), 2.55 (q, J = 7.4 Hz, 2H), 1.28 ppm (t, J = 7.4 Hz, 3H).



1H NMR (400 MHz, $CDCl_3$) δ 7.53–6.93 (m, 10H), 4.08 (d, J = 12.6 Hz, 1H), 3.98 ppm (d, J = 12.6 Hz, 1H).



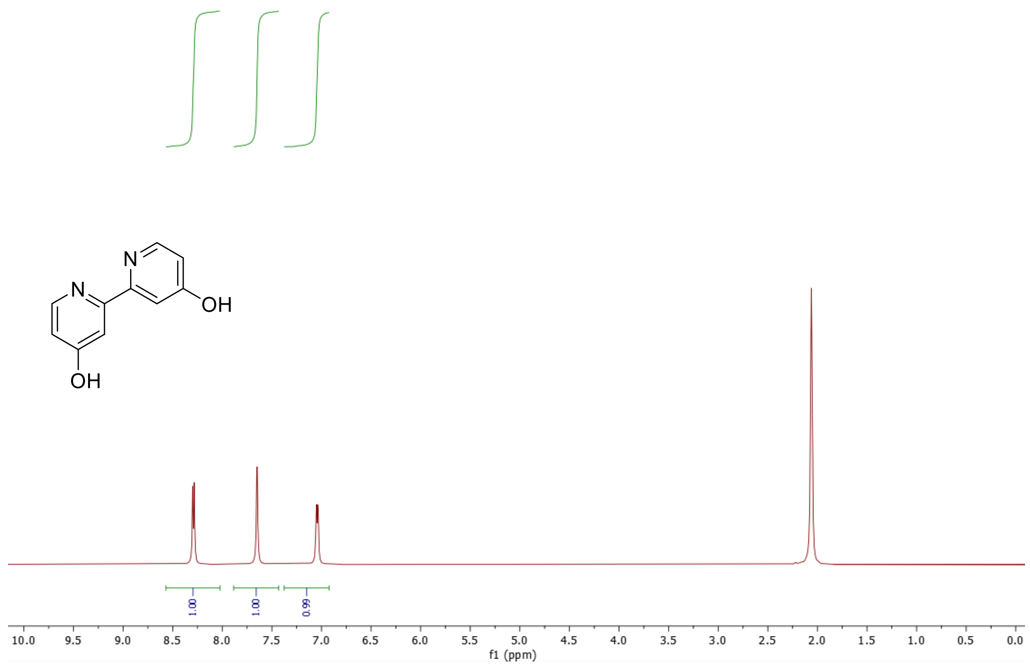
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94–7.68 (m, 2H), 7.59–7.38 (m, 3H), 4.93–4.59 (m, 1H), 2.96–2.78 (m, 2H), 2.58 (s, 3H), 2.56–2.39 (m, 1H), 2.34–2.19 (m, 1H), 1.50 (t, *J* = 1.8 Hz, 9H).

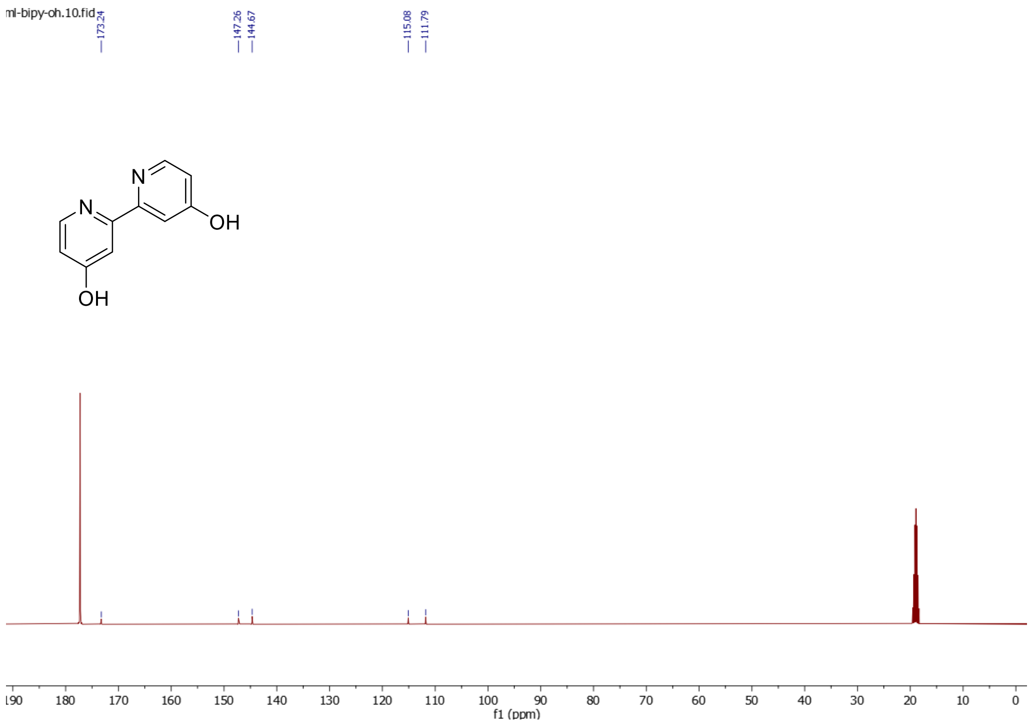


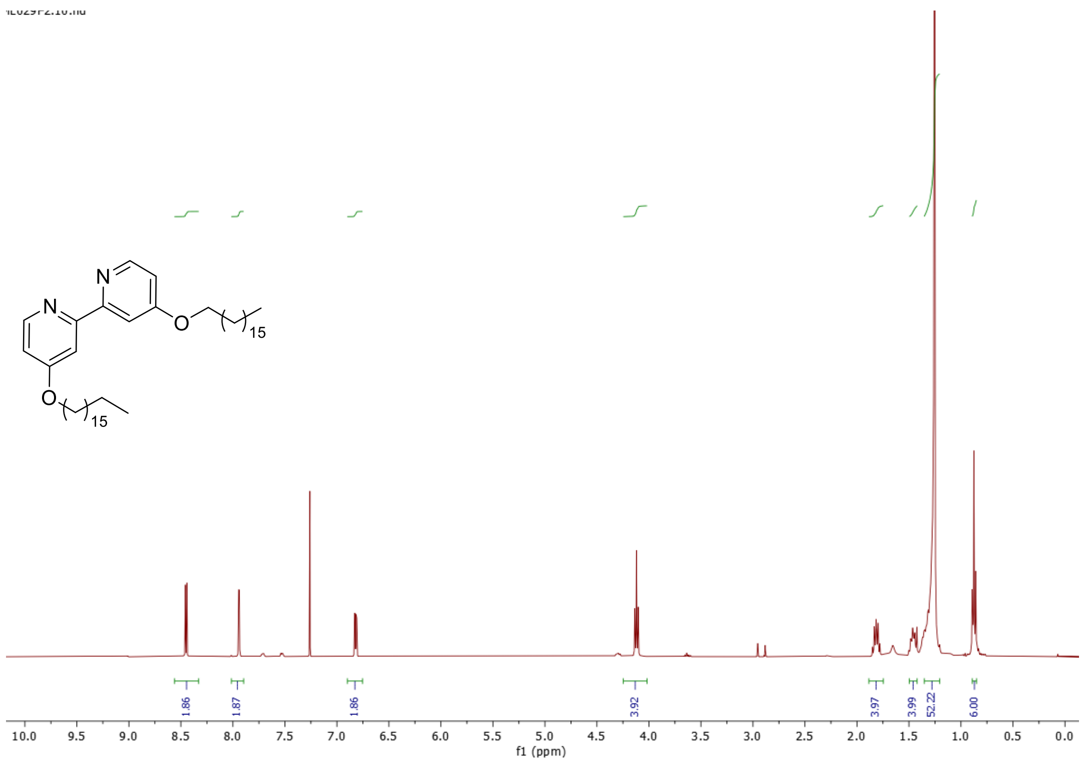
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41–7.22 (m, 5H), 5.47 (t, *J* = 9.0 Hz, 1H), 3.73–3.61 (m, 2H), 3.54 (ddd, *J* = 11, 6.5, 4.5 Hz, 1H), 3.37 (ddd, *J* = 8.5, 6.5, 4.5 Hz, 1H), 3.14 (td, *J* = 8.5, 6.5 Hz, 1H), 3.01 ppm (t, *J* = 9.0 Hz, 1H).

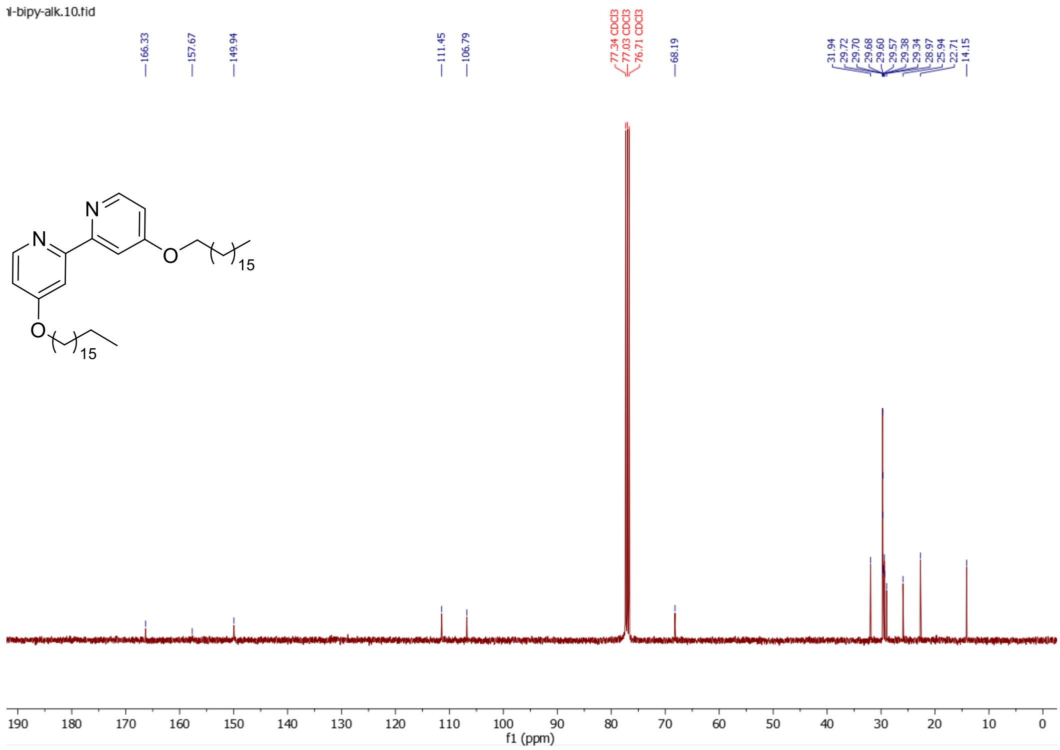
^{13}C NMR (101 MHz, $CDCl_3$) δ 170.2, 143.0, 128.6, 127.4, 126.7, 49.3, 34.2 ppm.

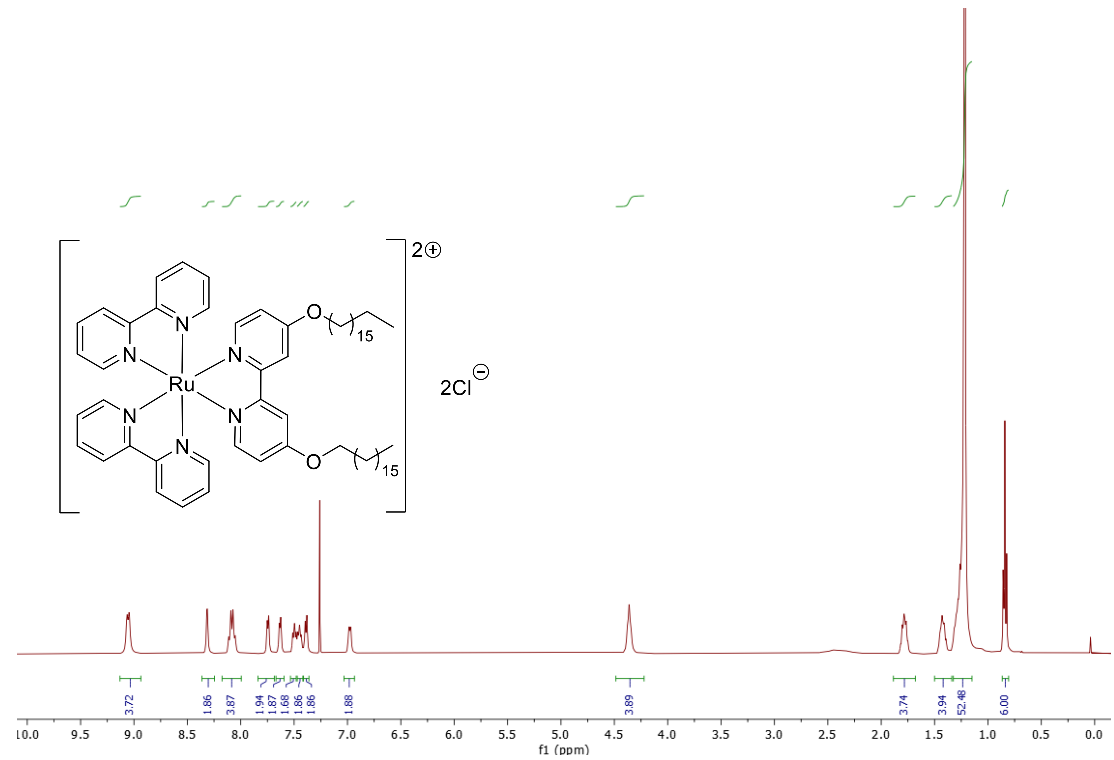
8) Copies of NMR Spectra

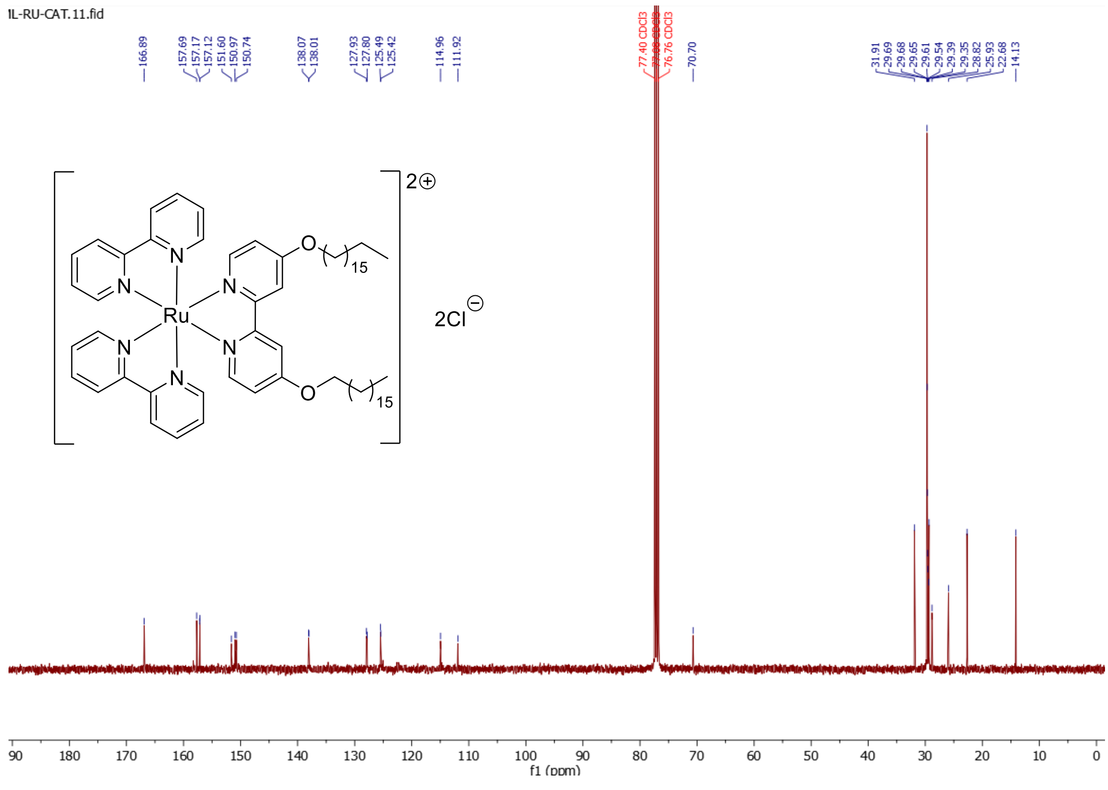


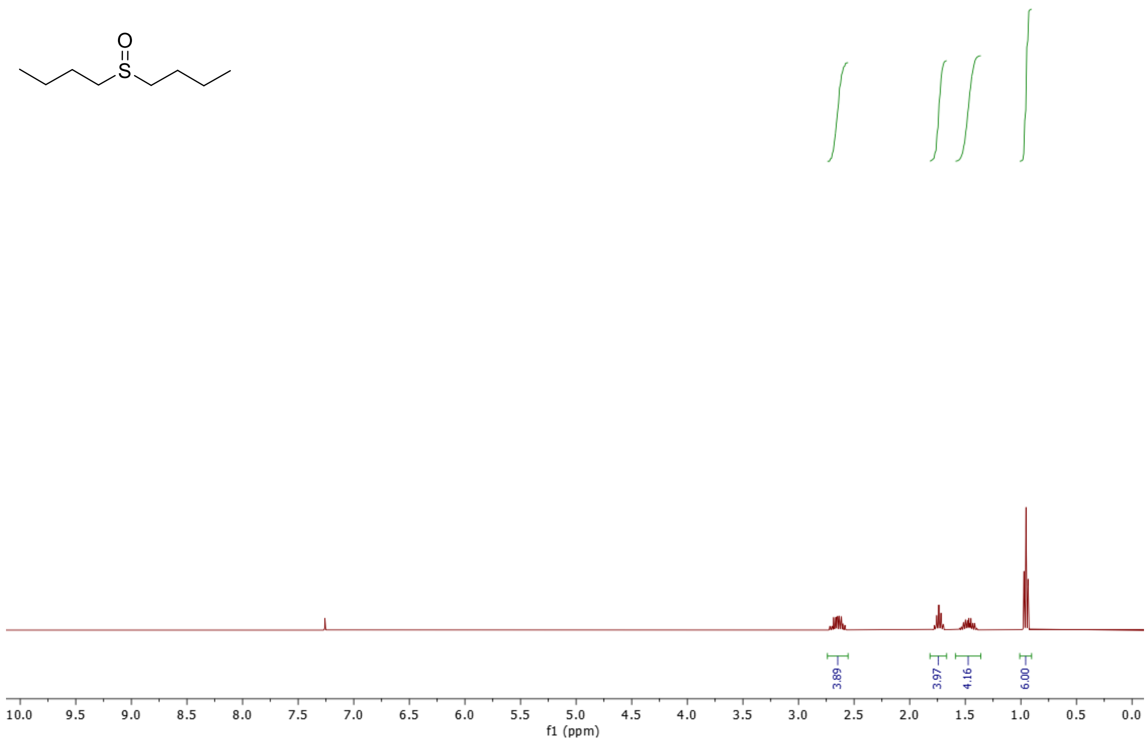


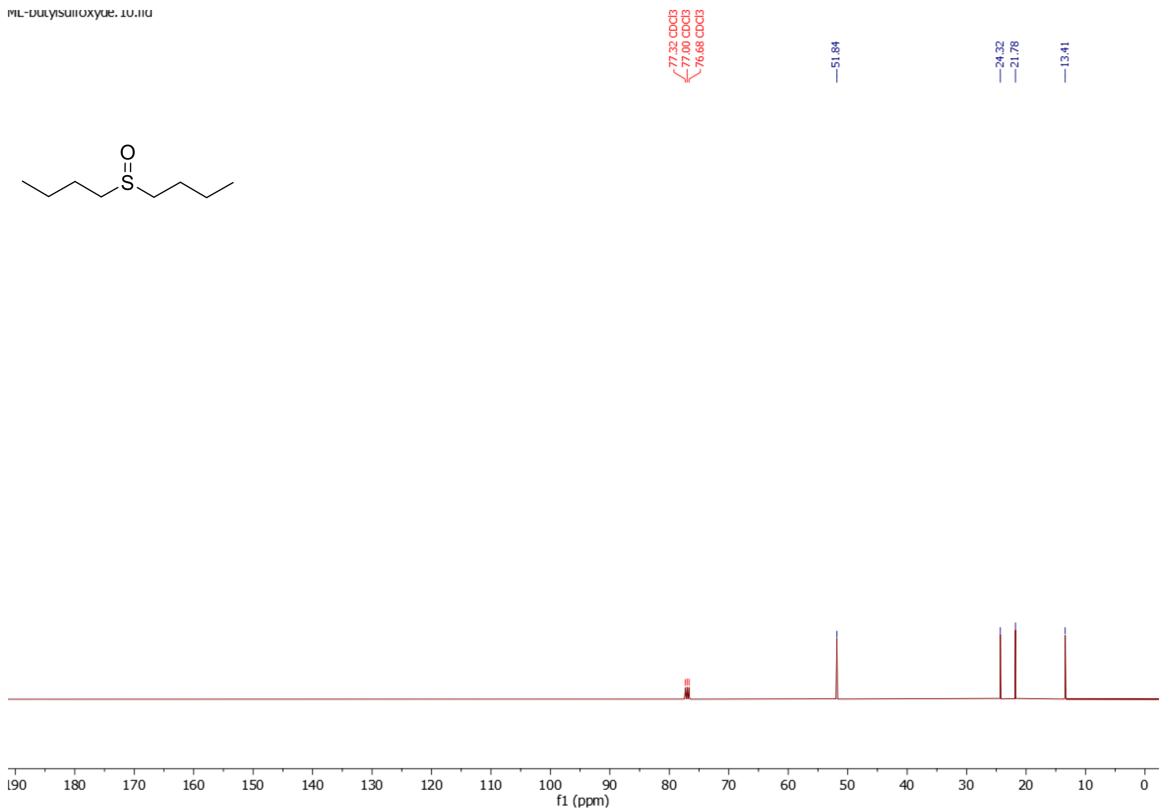

N
N
O
O
15
15
1.86
1.87
1.86
3.92
3.97
3.99
52.22
6.00
f1 (ppm)

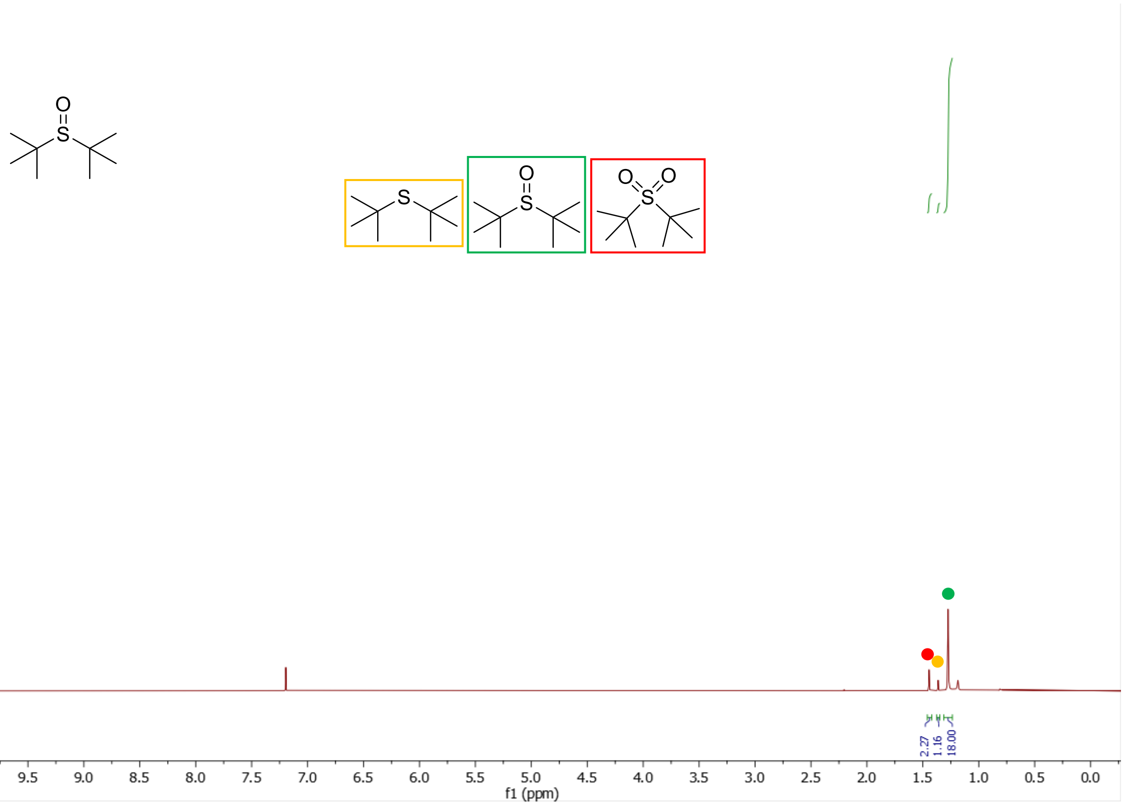

l-bipy-alk.10.fid
166.33
157.67
149.94
111.45
106.79
77.34 CDCl3
77.03 CDCl3
76.71 CDCl3
68.19
31.94
29.72
29.70
29.68
29.60
29.57
29.38
29.34
28.97
25.94
22.71
14.15
N
N
O
O
15
15
f1 (ppm)

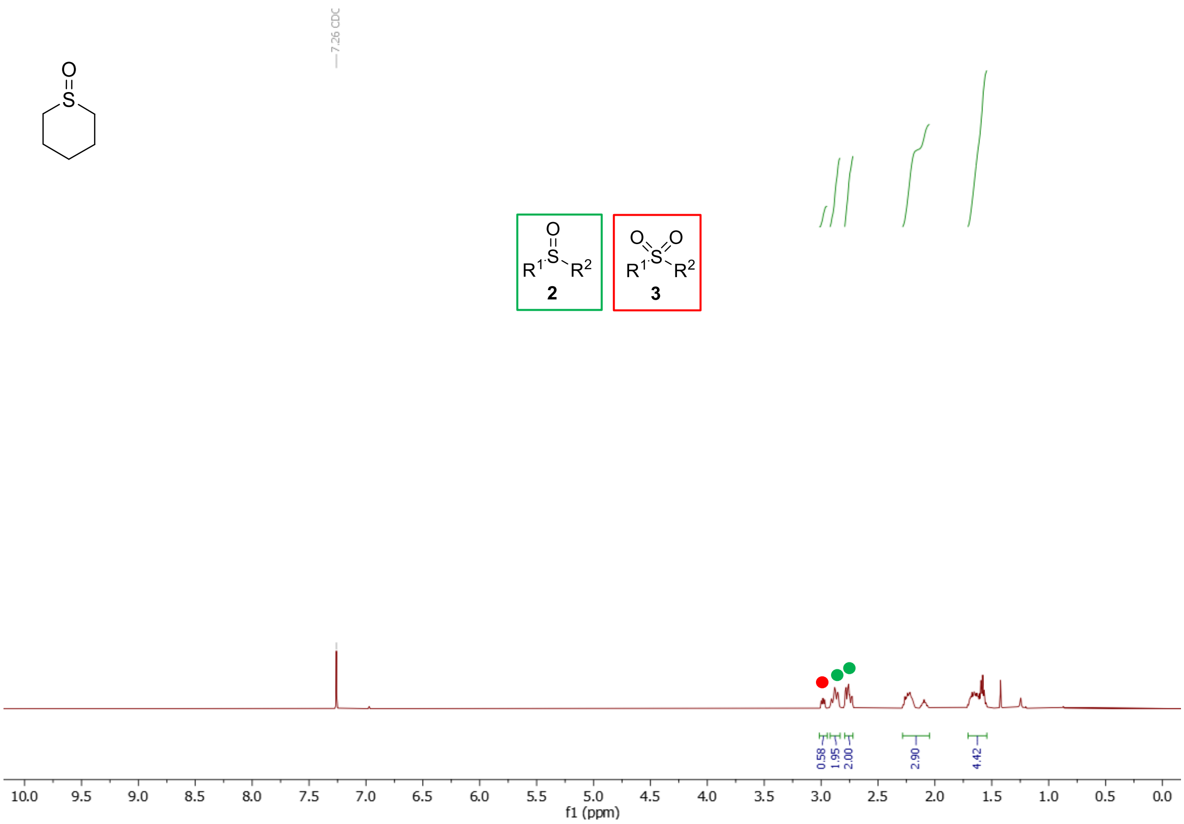




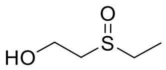

O
S
3.89
3.97
4.16
6.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

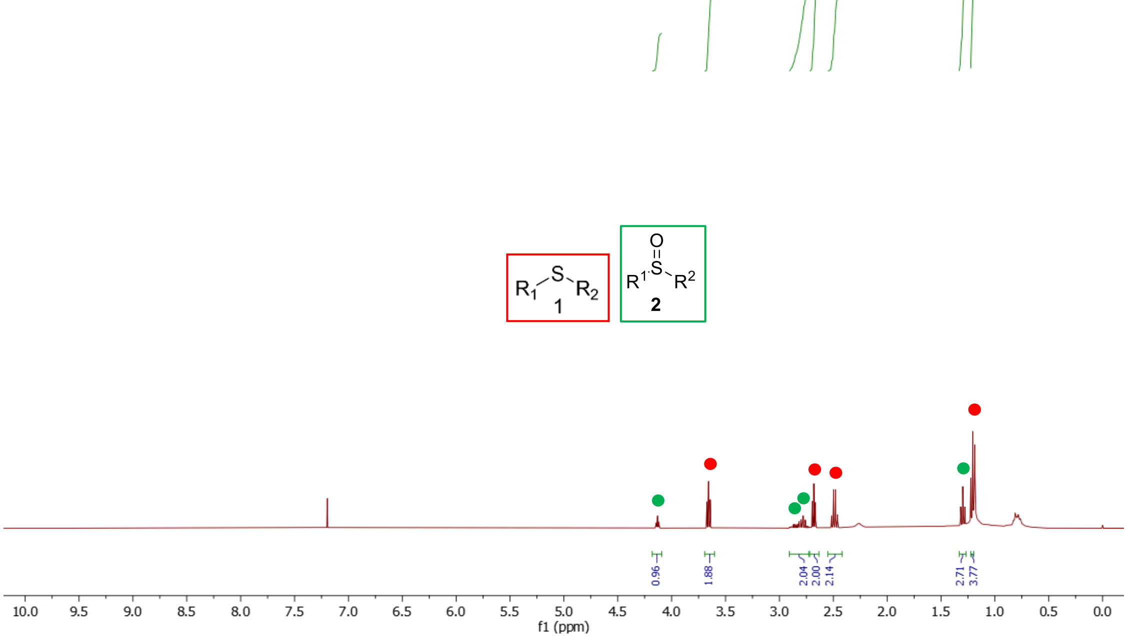

77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
51.84
24.32
21.78
13.41
O
S
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

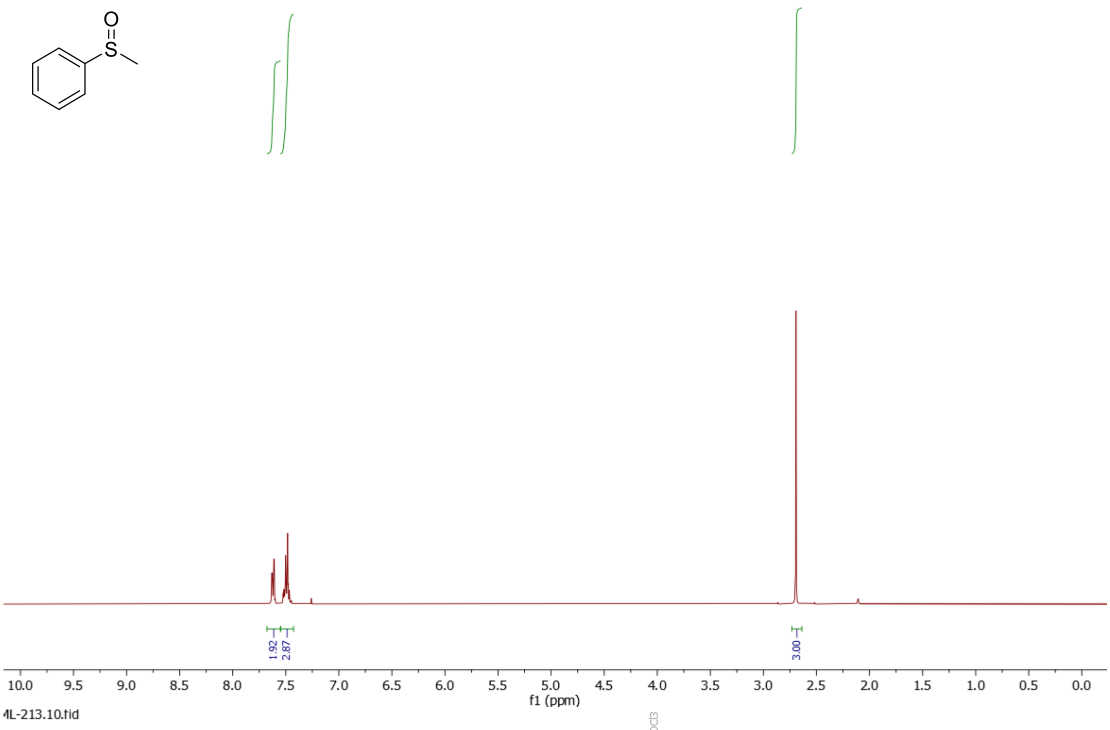

2.27
1.16
18.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)



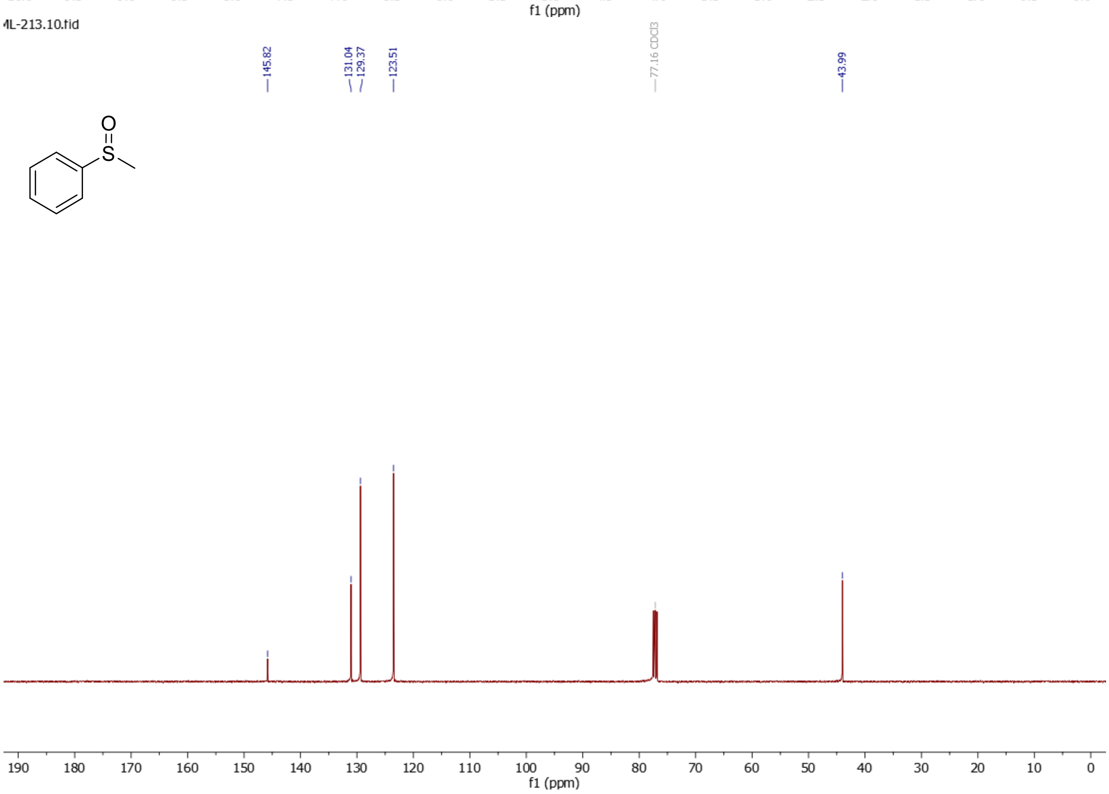
7.26 CDC
R1 S R2
2
R1 S R2
3
0.58
1.95
2.00
2.90
4.42
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


HO
S
O

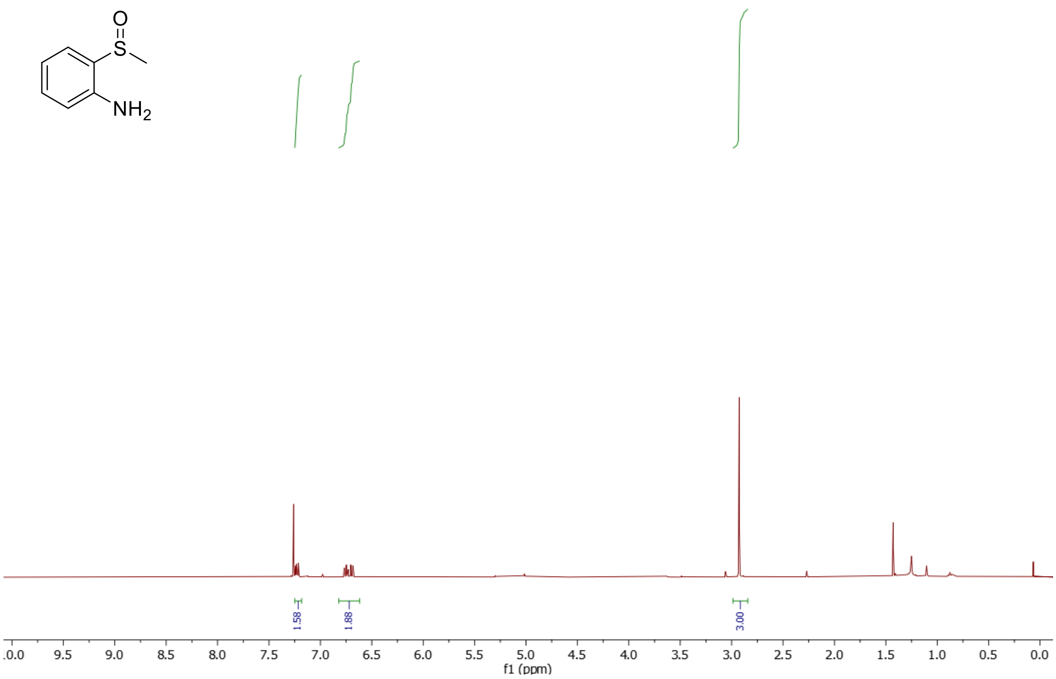

R1 S R2
1
O
S
R1 R2
2
0.96
1.88
2.04
2.00
2.14
2.71
3.77
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)



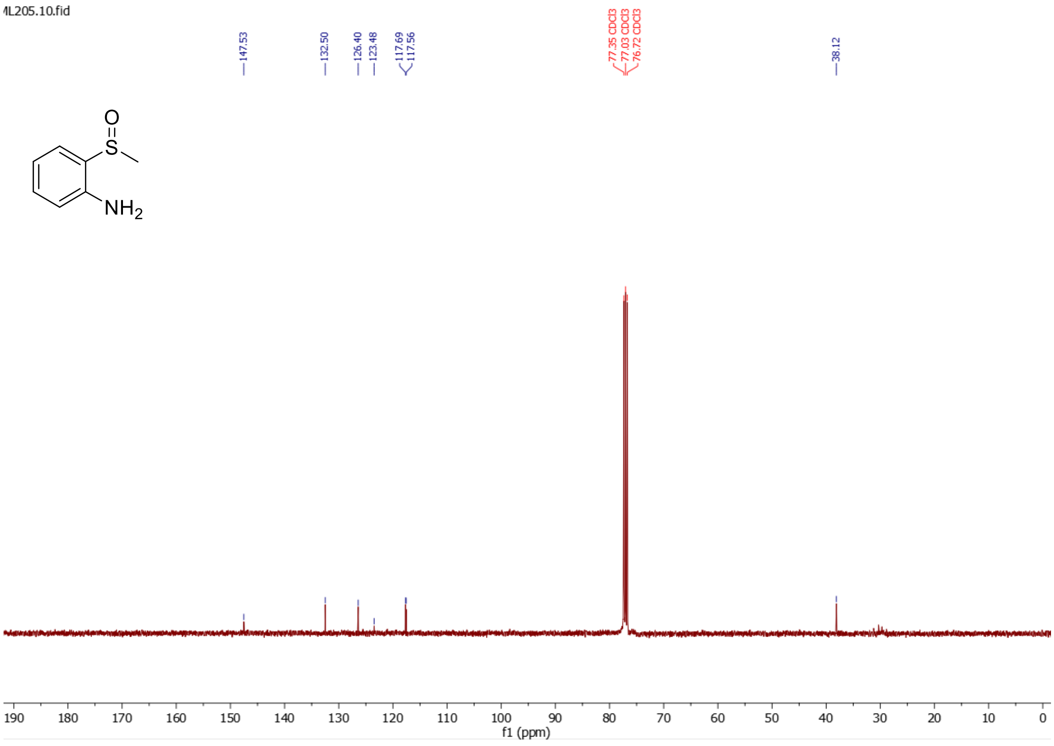
1.92
2.87
3.00
f1 (ppm)
ML-213.10.fid



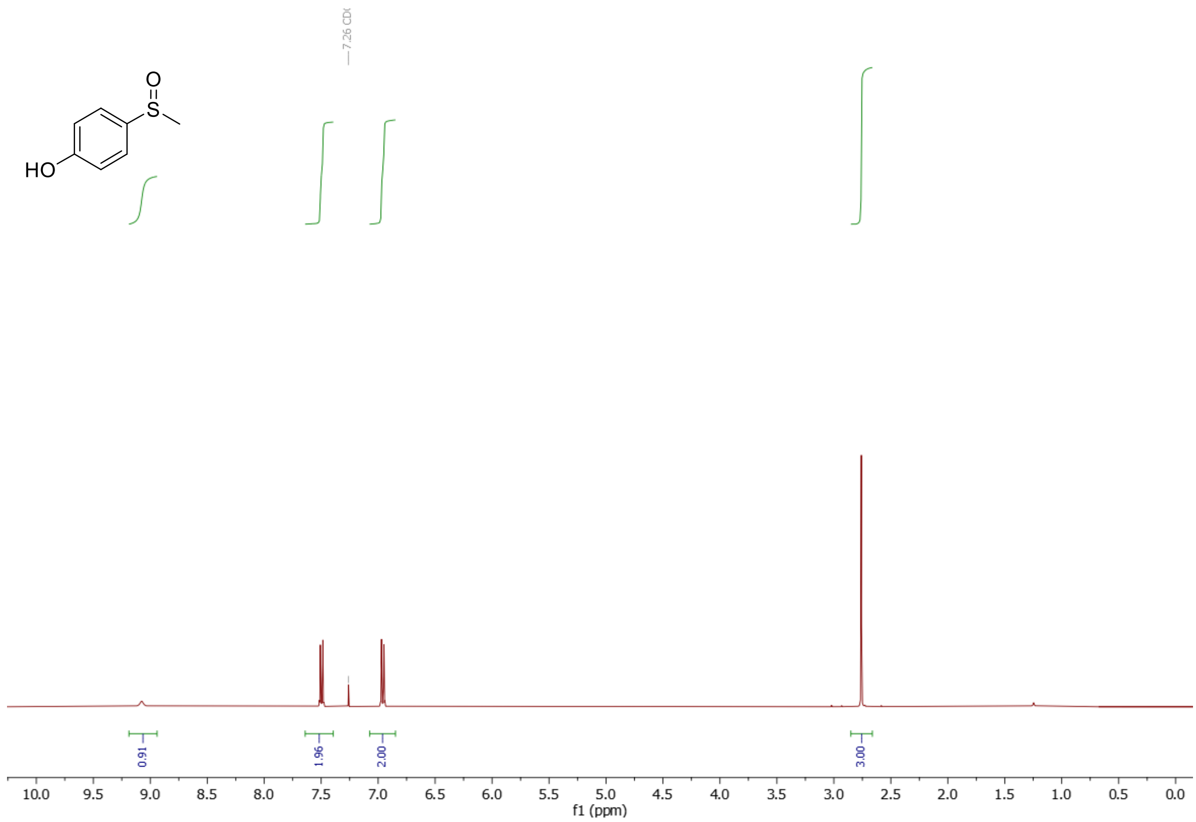
145.82
131.04
129.37
123.51
77.16 CDCl3
43.99
f1 (ppm)

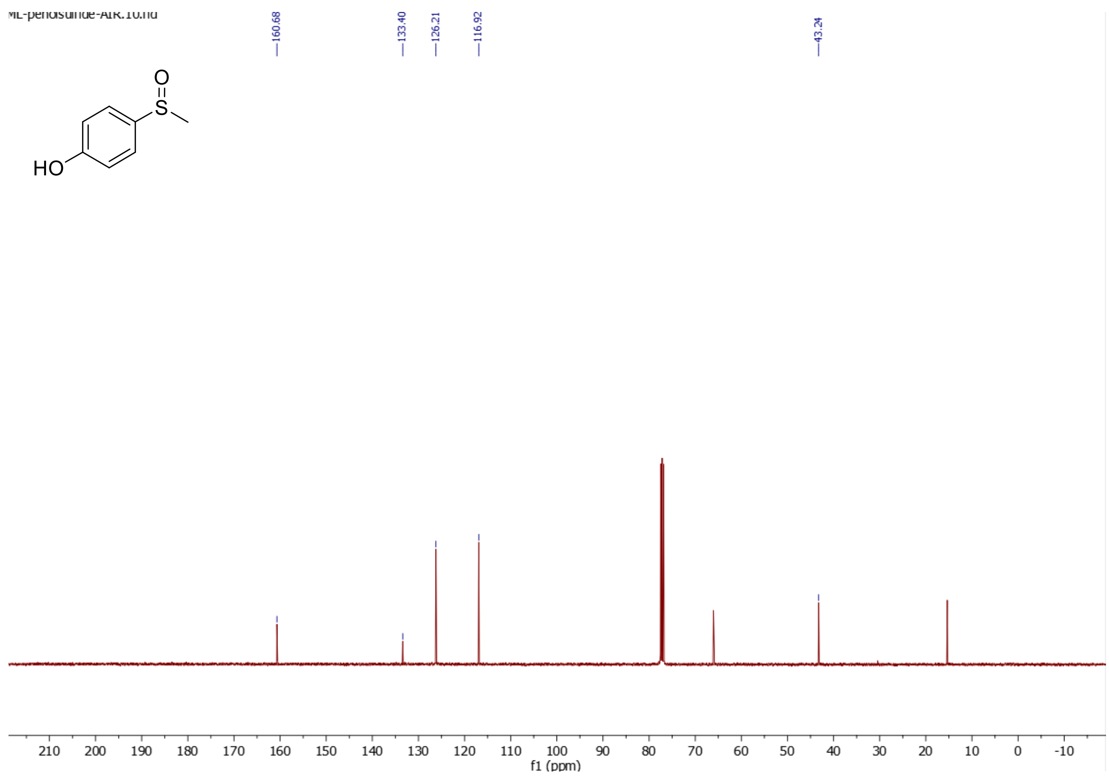


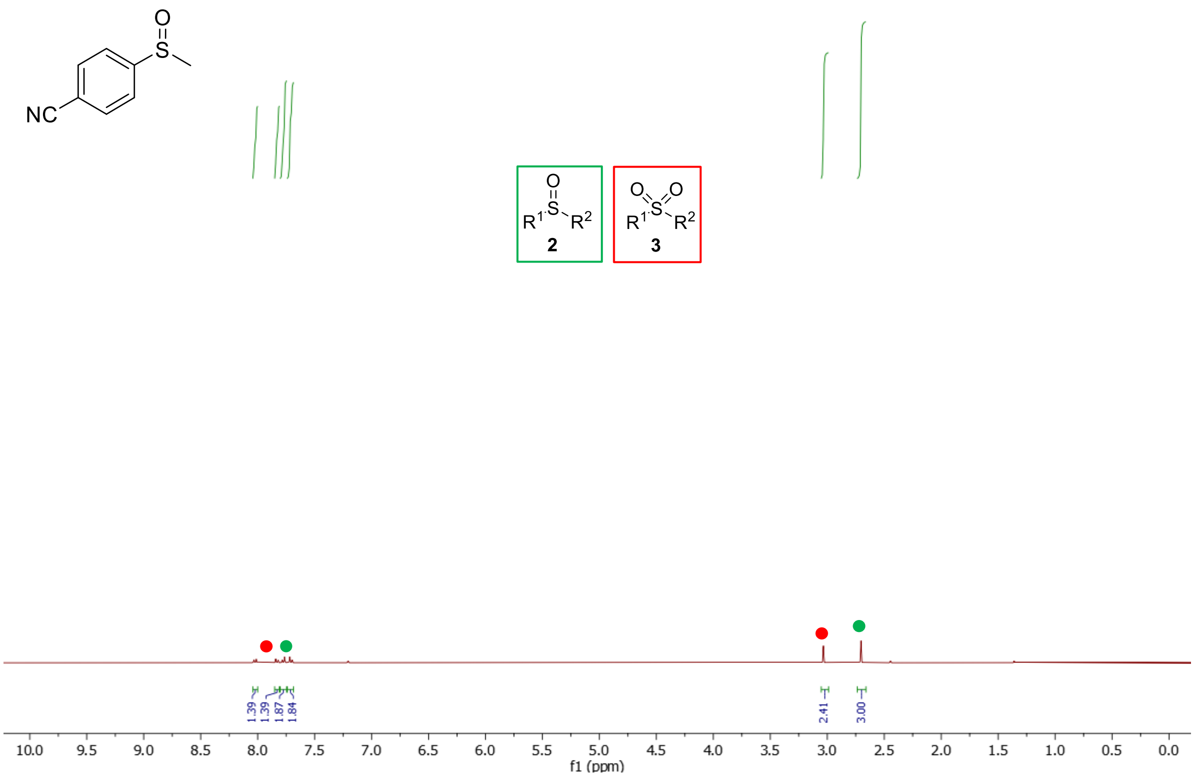
O
S
NH2
1.58
1.88
3.00
.0.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

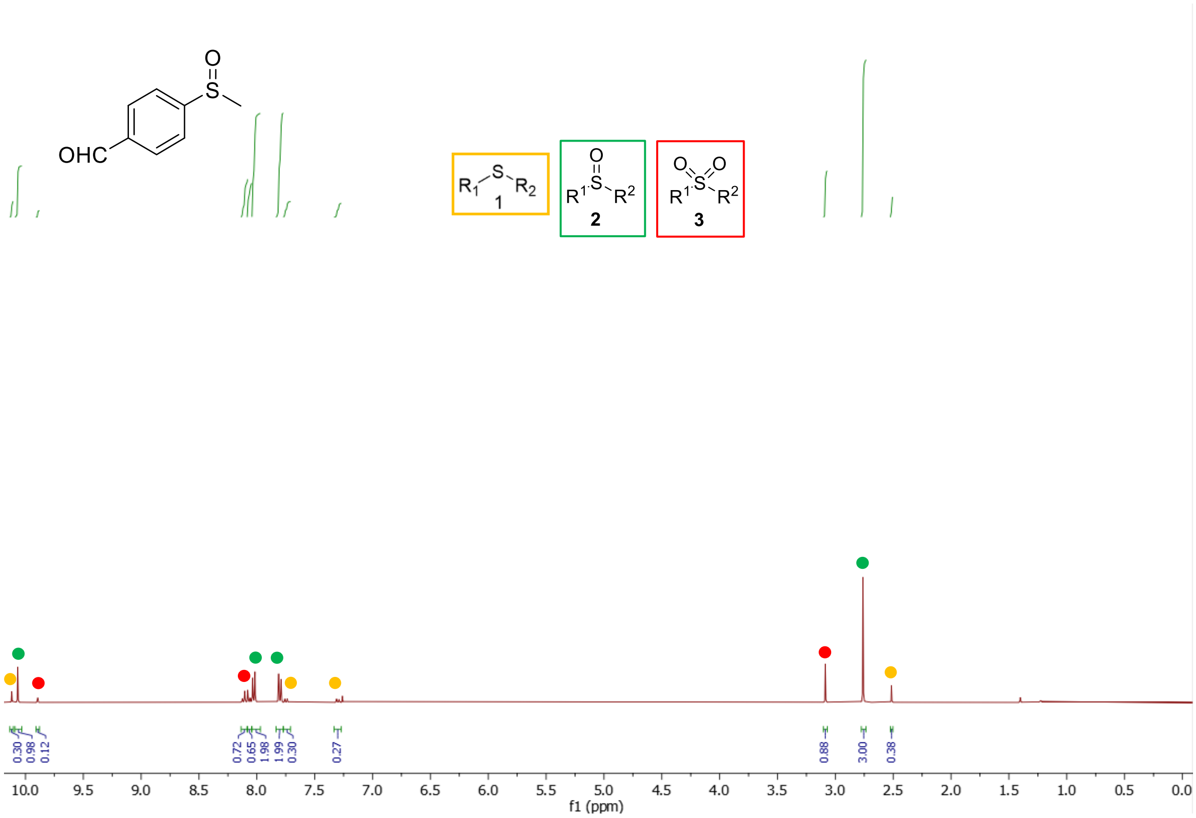


ML205.10.fid
147.53
132.50
126.40
123.48
117.69
117.56
77.35 CDCl3
77.03 CDCl3
76.72 CDCl3
38.12
O
S
NH2
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

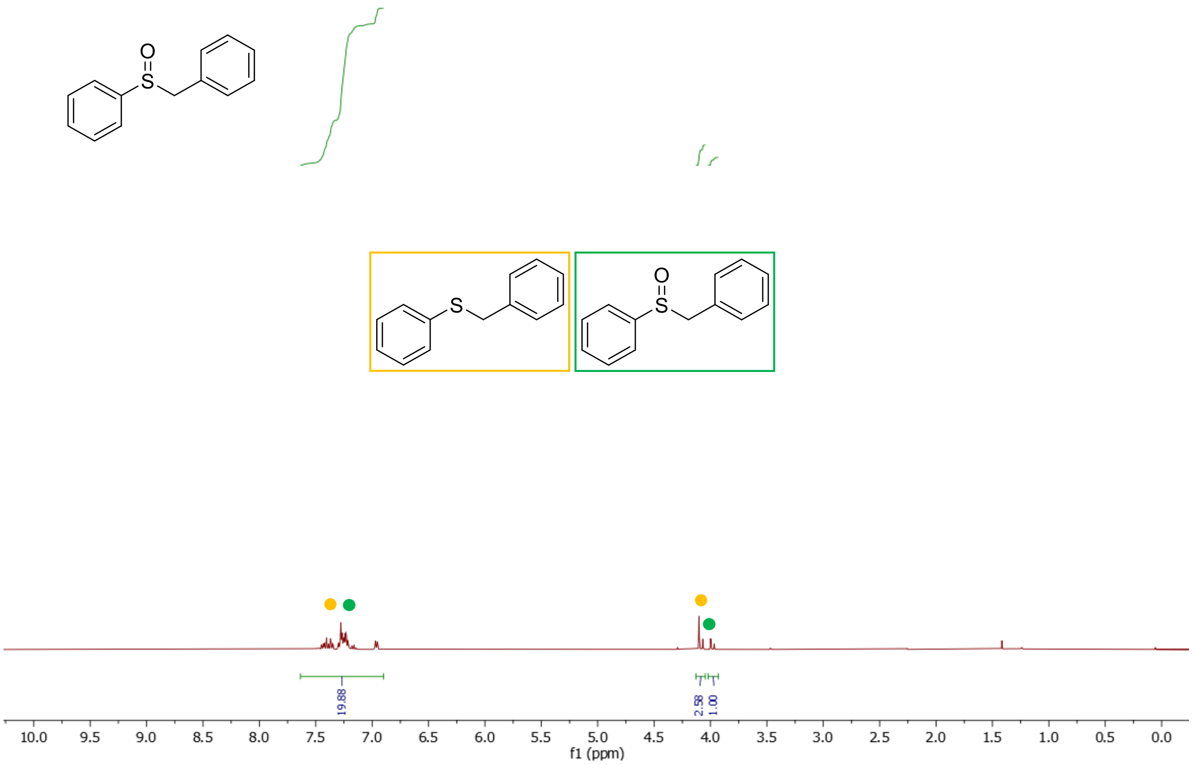


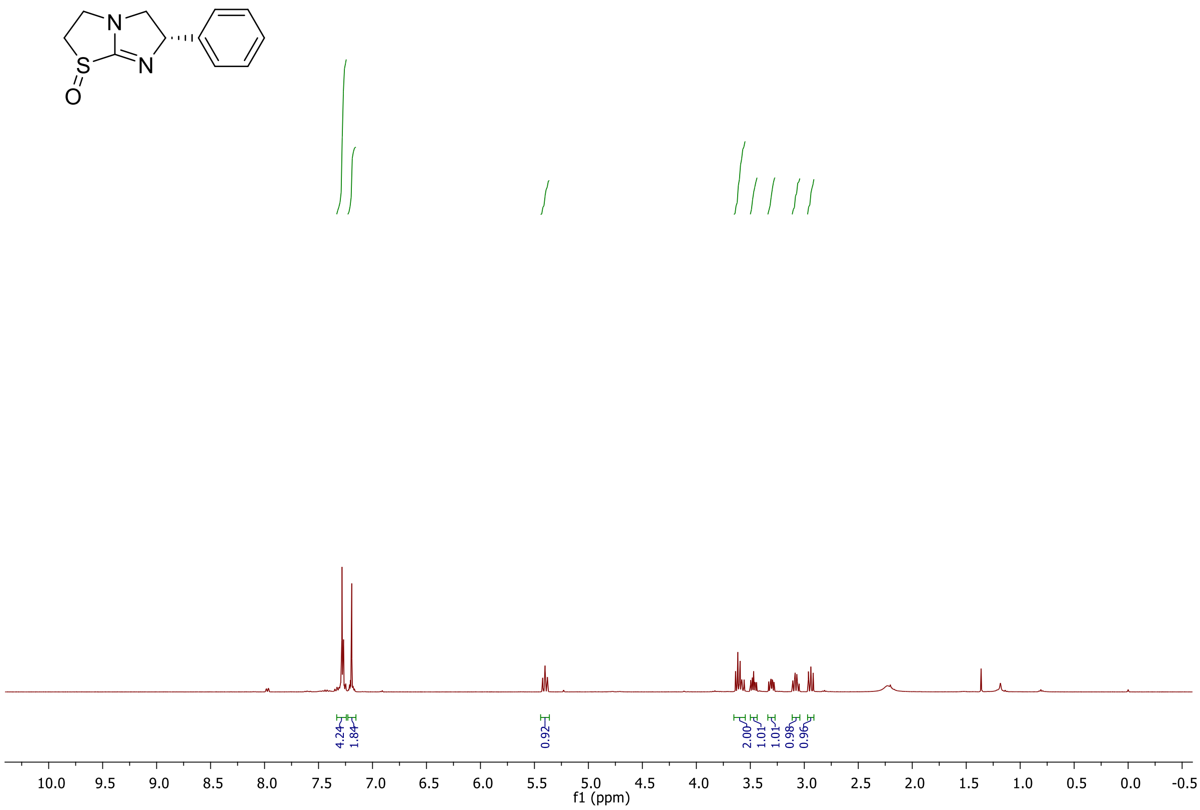


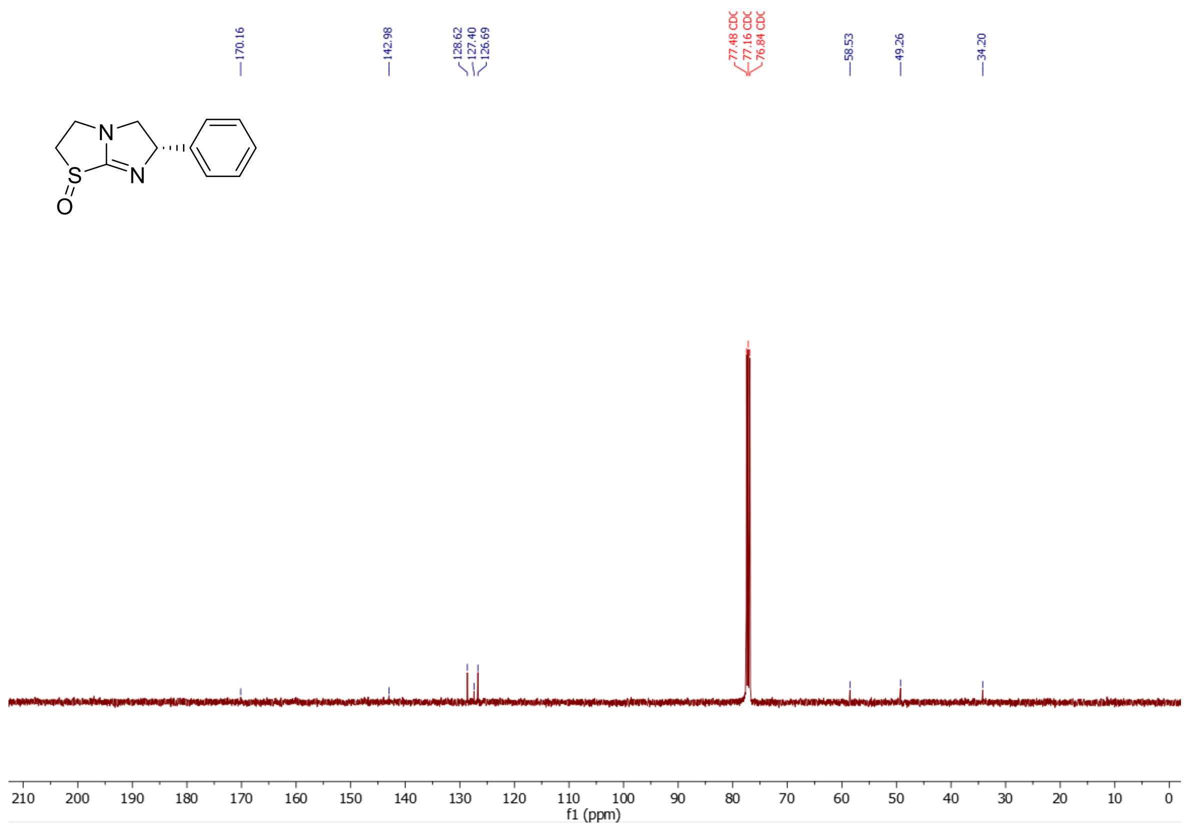

NC
2
3
1.39
1.39
1.87
1.84
2.41
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

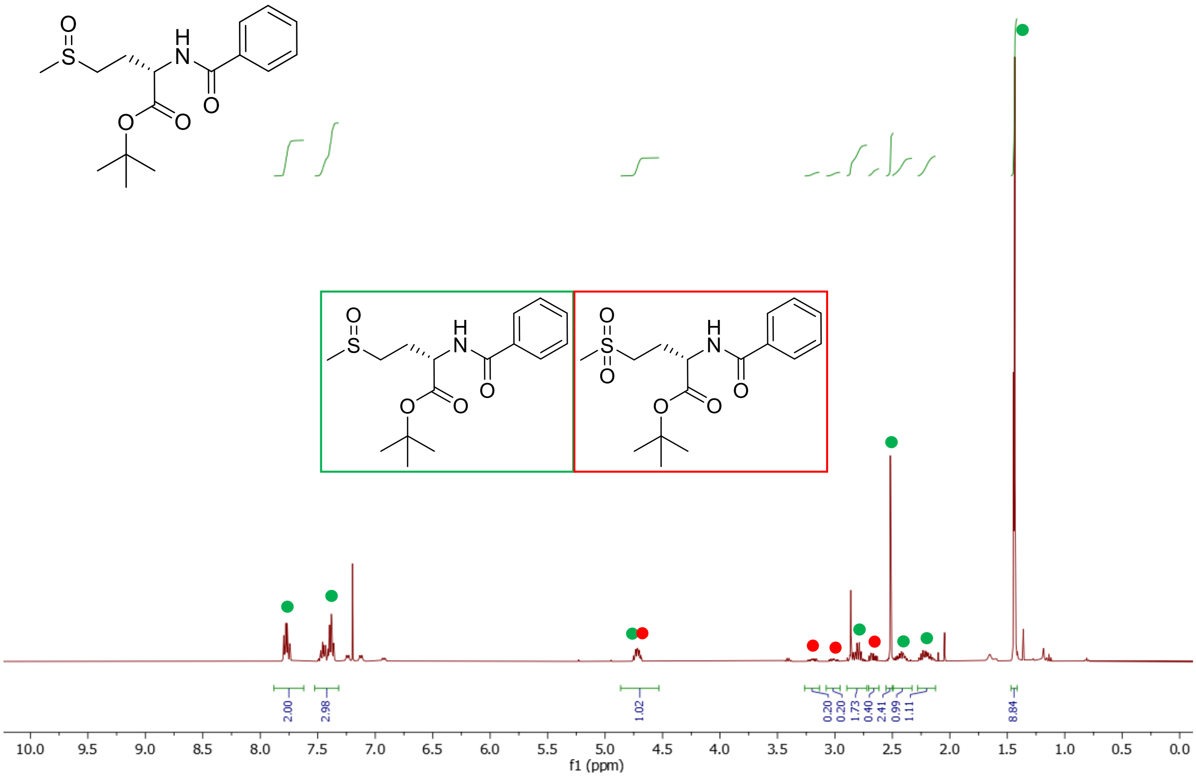


OHC
1
2
3
f1 (ppm)


19.88
2.58
1.00
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)


4.24
1.84
0.92
2.00
1.01
1.01
0.98
0.96
f1 (ppm)


170.16
142.98
128.62
127.40
126.69
77.48 CDC
77.16 CDC
76.84 CDC
58.53
49.26
34.20
f1 (ppm)



[1] J. Ogier, T. Arnauld, G. Carrot, A. Lhumeau, J.-M. Delbos, C. Boursier, O. Loreau, F. Lefoulon and E. Doris, *Org. Biomol. Chem.*, **2010**, *8*, 3902–3907.