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SUPPORTING INFORMATION

Evaluation of Fullerene Soot and Fullerene Nanodispersion as Recyclable Heterogeneous Off-the-Shelf Photocatalysts

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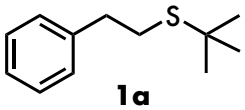
Materials and Methods

All chemicals were used as received from commercial suppliers. Fullerene C_{60} was purchased from Acros, fullerene soot was purchased from Aldrich. All moisture sensitive reactions were carried out under an atmosphere of argon using oven-dried glassware. Anhydrous tetrahydrofuran was distilled from benzophenone-sodium, dichloromethane and dimethylformamide was distilled from calcium hydride and toluene was distilled from sodium. Yields refer to chromatographically and spectroscopically homogeneous materials. Reactions were monitored by thin-layer chromatography (TLC) carried out on 0.25 mm Merck silica gel plates (60F-254) using UV light (general), aq. $KMnO_4$ solution (for unsaturated compounds), phosphomolybdic acid and vanillin solutions (general). Flash column chromatography was performed on Merck silica gel (60, particle size 0.0430-0.663 mm). Melting points were recorded with a Gallenkamp apparatus and are not corrected. ^1H and ^{13}C spectra were recorded on Bruker 400 MHz spectrometer. Chemicals shifts are given in parts per million, relative to TMS using the residual solvent peaks at δ = 7.26 (^1H NMR) and 77.16 (^{13}C NMR) ppm in $CDCl_3$. The following abbreviations (or combinations thereof) were used to describe ^1H NMR multiplicities: s – singlet, d – doublet, t – triplet, q – quartet, m – multiplet, br – broad, app.– apparent. High resolution mass spectra (HRMS) were recorded on Bruker Daltonics microTOF-II or Waters QTOF XEVO-G2 spectrometer equipped with ESI ion source. IR spectra recorded on Perkin Elmer Spectrum BX FT-IR System. Scanning electron microscopy (SEM) images were taken for the morphology characterization with Hitachi SU-70 SEM. Samples for SEM characterization were prepared by dispersing particles on a carbon plate. Raman spectra were recorded with a WITec Confocal Raman Microscope (WITec alpha300 R, Ulm, Germany), using a frequency doubled YAG:Nd laser (532 nm) for sample excitation.

Abbreviations of chemicals: DCM - dichloromethane, EA - ethylacetate, MeOH - methanol, PE - petrol ether (b.p. 40-60^{o}C fraction), TEA - triethylamine, THF – tetrahydrofuran, DMF – dimethylformamide, DIPEA – *N*,*N*-diisopropylethylamine.

S1. Synthesis

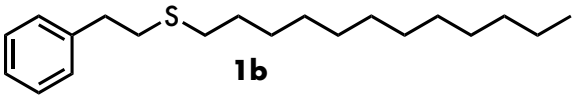
Synthesis of starting materials



1a

***tert*-Butyl(2-phenylethyl)sulfide 1a.** A mixture of 2-methyl-2-propanethiol (0.4 mL, 3.51 mmol, 1.3 equiv), 2-phenylethylbromide (0.37 mL, 2.70 mmol, 1.0 equiv) and K_2CO_3 (0.49 g, 3.51 mmol, 1.3 equiv) in DMF (7 mL) was stirred at room temperature for 24 hours. The reaction mixture was diluted with 1.0 M HCl solution and extracted with EA. The organic phase was washed with 1.0 M HCl solution and brine, dried over anhydrous Na_2SO_4 and evaporated to dryness. The crude was purified by column chromatography on silica gel (PE:EA 100:1, R_f = 0.29) to afford 503 mg (96 %) of **1a** as a colorless oil.

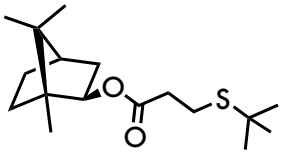
Spectral data were in accordance with a literature [S1].



1b

***n*-dodecyl(2-phenylethyl)sulfide 1b.** A mixture of 1-dodecanethiol (0.84 mL, 3.51 mmol, 1.3 equiv), 2-phenylethylbromide (0.37 mL, 2.70 mmol, 1.0 equiv) and K_2CO_3 (0.49 g, 3.51 mmol, 1.3 equiv) in DMF (7 mL) was stirred at room temperature for 24 hours. The reaction mixture was diluted with 1.0 M HCl solution and extracted with EA. The organic phase was washed with 1.0 M HCl solution and brine, dried over anhydrous Na_2SO_4 and evaporated to dryness. The crude was purified by column chromatography on silica gel (PE:EA 100:1, R_f = 0.30) to afford 760 mg (92 %) of **1b** as a colorless oil.

Spectral data were in accordance with a literature [S2].



1c

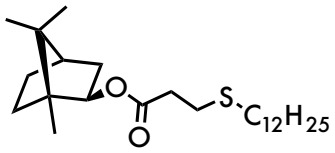
Isobornyl-3-(*tert*-butylthio)propionate 1c. Under inert atmosphere tert-butylthiol (1.1 mL, 9.60 mmol, 2.0 equiv) and catalytic amount of NaOMe (78 mg, 1.44 mmol, 0.3 equiv) were dissolved in anh. MeOH (20 mL). The reaction mixture was cooled down to 0 °C and isobornyl acrylate (1 mL, 4.80 mmol, 1 equiv) was added dropwise over a period of 10 min. The reaction mixture was

allowed to warm up to room temperature overnight. The solvent was removed under reduced pressure. The crude was dissolved in $CHCl_3$ and washed with H_2O and brine, dried over anhydrous Na_2SO_4 and evaporated to dryness. The crude was purified by column chromatography on silica gel (PE:EA 100:1, R_f = 0.33) to afford 1.23 g (86 %) of **1c** as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 4.76 – 4.62 (m, 1H), 2.78 (dd, J = 8.2, 7.3 Hz, 2H), 2.55 (dd, J = 8.2, 7.1 Hz, 2H), 1.90 – 1.62 (m, 4H), 1.62 – 1.49 (m, 1H), 1.32 (s, 9H), 1.21 – 1.02 (m, 2H), 1.02 (s, 3H), 0.83 (s, 3H), 0.82 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 171.58, 81.37, 48.79, 47.03, 45.14, 42.42, 38.90, 35.51, 33.83, 31.02, 27.14, 23.63, 20.22, 20.03, 11.60.

HRMS-ESI$^+$: m/z $[M+Na]^+$ calcd. for $C_{17}H_{31}O_3SNa$ 337.4732; found 337.1809 (only sulfoxide formed during the measurements can be detected with ESI).



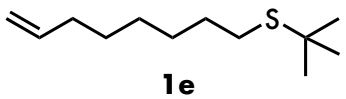
1d

Isobornyl-3-(*n*-dodecylthio)propionate 1d. Under inert atmosphere a mixture of 1-dodecanethiol (0.83 mL, 2.88 mmol, 2.2 equiv), isobornyl acrylate (0.3 mL, 1.44 mmol, 1.0 equiv) and triethylamine (0.48 mL, 2.88 mmol, 2.2 equiv) in dry THF (5 mL) was heated at 70 °C for 48 hours. The reaction mixture was cooled down to room temperature and solvent was removed under reduced pressure. The crude was purified by column chromatography on silica gel (PE:EA 100:1, R_f = 0.33) to afford 413 mg (58 %) of **1d** as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 4.74 – 4.64 (m, 1H), 2.76 (t, J = 7.5 Hz, 2H), 2.57 (t, J = 7.5 Hz, 2H), 2.51 (t, J = 7.4 Hz, 2H), 1.85 – 1.65 (m, 4H), 1.62 – 1.51 (m, 3H), 1.36 (t, J = 7.5 Hz, 2H), 1.32 (s, 16H), 1.19 – 1.03 (m, 2H), 0.97 (s, 3H), 0.88 (t, J = 6.9 Hz, 3H), 0.84 (s, 3H), 0.83 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 171.59, 81.48, 48.82, 47.08, 45.18, 38.95, 35.48, 33.87, 32.26, 32.06, 29.80, 29.78, 29.75, 29.70, 29.68, 29.50, 29.38, 29.03, 27.29, 27.17, 22.84, 20.25, 20.06, 14.27, 11.63.

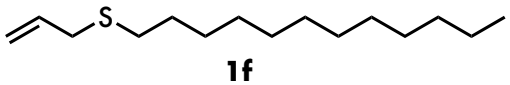
HRMS-ESI$^+$: m/z $[M+Na]^+$ calcd. for $C_{25}H_{47}O_3SNa$ 449.6892; found 449.3056 (only sulfoxide formed during the measurements can be detected with ESI).



1e

***tert*-butyl(oct-7-en-1-yl)sulfane 1e**. A mixture of 8-bromo-1-octene (0.5 g, 2.62 mmol, 1.0 equiv), 2-methyl-2-propanethiol (0.38 mL, 3.40 mmol, 1.3 equiv) and K_2CO_3 (0.47 g, 3.40 mmol, 1.3 equiv) in DMF (7 mL) was stirred at room temperature for 24 hours. The reaction mixture was diluted with 1.0 M HCl solution and extracted with EA. The organic phase was washed with 1.0 M HCl solution, water and brine, dried over anhydrous Na_2SO_4 and evaporated to dryness. The crude was purified by column chromatography on silica gel (PE:EA 100:1, R_f = 0.47) to afford 523 mg (99 %) of **1e** as a colorless oil.

Spectral data were in accordance with a literature [S3].



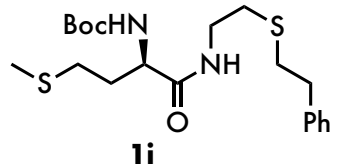
1f

Allyl-*n*-dodecylsulfide 1f. A mixture of allylbromide (0.36 mL, 4.13 mmol, 1.0 equiv), *n*-dodecanethiol (1.29 mL, 5.37 mmol, 1.3 equiv) and K_2CO_3 (0.742 g, 5.37 mmol, 1.3 equiv) in DMF (7 mL) was stirred at room temperature for 24 hours. The reaction mixture was diluted with 1.0 M HCl solution and extracted with EA. The organic phase was washed with 1.0 M HCl solution, water and brine, dried over anhydrous Na_2SO_4 and evaporated to dryness. The crude was purified by column chromatography on silica gel (PE, R_f = 0.54) to afford 994 mg (99 %) of **1f** as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 5.89 – 5.73 (m, 1H), 5.18 – 5.02 (m, 2H), 3.12 (d, J = 7.2 Hz, 2H), 2.44 (t, J = 7.5 Hz, 2H), 1.54 (q, J = 7.6 Hz, 2H), 1.41 – 1.33 (m, 2H), 1.26 (m, 16H), 0.88 (t, J = 6.7 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 134.76, 116.80, 34.92, 32.07, 30.88, 29.80, 29.78, 29.75, 29.68, 29.49, 29.49, 29.41, 29.06, 22.84, 14.26.

HRMS-ESI$^+$: m/z $[M+H]^+$ calcd. for $C_{15}H_{31}S$ 243.2141; found 243.2131.



1i

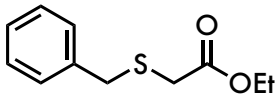
(R)-*tert*-Butyl (1-(methylthio)-4-oxo-6-(phenethylthio)hexan-3-yl)carbamate 1i. A mixture of N-((*tert*-butyloxy)carbonyl)-L-methionine p-nitrophenyl ester (600 mg, 1.622 mmol, 1.0 equiv), 2-(2-phenylethylsulfanyl)ethanamine (300 mg, 1.655 mmol, 1.02 equiv) and TEA (0.24 mL, 1.72

mmol, 1.04 equiv) in DMF (5 mL) was stirred at room temperature for 24 hours. The reaction mixture was diluted with water and extracted with EA. The organic phase was washed with water and brine, dried over anhydrous Na_2SO_4 and evaporated to dryness. The crude was purified by column chromatography on silica gel (DCM, R_f = 0.19) to afford 530 mg (79 %) of **1i** as a yellow solid. M.p. 48 – 50 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33 – 7.27 (m, 2H), 7.24 – 7.18 (m, 3H), 6.51 (s, 1H), 5.17 (s, 1H), 4.35 – 4.16 (m, 1H), 3.59 – 3.27 (m, 2H), 2.92 – 2.84 (m, 2H), 2.83 – 2.74 (m, 2H), 2.65 (t, J = 6.5 Hz, 2H), 2.62 – 2.47 (m, 2H), 2.10 (s, 3H), 2.09 – 2.03 (m, 1H), 1.97 – 1.85 (m, 1H), 1.44 (s, 9H)

^{13}C NMR (101 MHz, $CDCl_3$): δ 171.61, 155.67, 140.33, 128.65, 126.59, 80.32, 53.62, 38.48, 36.33, 33.32, 31.95, 31.80, 30.37, 28.46, 15.43.

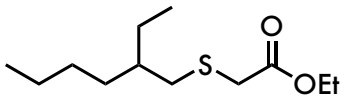
HRMS-ESI$^+$: m/z $[M+Na]^+$ calcd. for $C_{20}H_{32}N_2O_3S_2Na$ 435.5962; found 435.1741.



1j

Ethyl(benzylthio)acetate 1j. Under inert atmosphere a mixture of ethyl mercaptoacetate (0.46 mL, 4.16 mmol, 1.0 equiv), benzylbromide (0.49 mL, 4.16 mmol, 1.0 equiv) and K_2CO_3 (0.63 g, 4.16 mmol, 1.0 equiv) in DMF (7 mL) was stirred at room temperature for 24 hours. The reaction mixture was diluted with water and extracted with EA. The organic phase was washed with water and brine, dried over anhydrous Na_2SO_4 and evaporated to dryness. The crude was purified by column chromatography on silica gel (PE:EA 50:1, R_f = 0.29) to afford 727 mg (83 %) of **1j** as a bluish oil.

Spectral data were in accordance with a literature [S4].



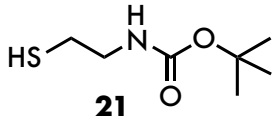
1k

Ethyl(2-ethylhexylthio)acetate 1k. Under inert atmosphere a mixture of ethyl mercaptoacetate (0.46 mL, 4.16 mmol, 1.0 equiv), 2-ethylhexylbromide (0.74 mL, 4.16 mmol, 1.0 equiv) and K_2CO_3 (633 mg, 4.16 mmol, 1.1 equiv) in DMF (7 mL) was stirred at room temperature for 24 hours. The reaction mixture was diluted with water and extracted with EA. The organic phase was washed with water and brine, dried over anhydrous Na_2SO_4 and evaporated to dryness. The crude was purified by column chromatography on silica gel (PE:EA 100:1, R_f = 0.2) to afford 938 mg (91 %) of **1k** as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 4.19 (q, J = 7.2 Hz, 2H), 3.18 (s, 2H), 2.62 (d, J = 6.3 Hz, 2H), 1.58 – 1.46 (m, 1H), 1.45 – 1.17 (m, 11H), 0.99 – 0.82 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 170.81, 61.39, 39.01, 37.34, 34.42, 32.47, 28.94, 25.63, 23.10, 14.33, 14.22, 10.87.

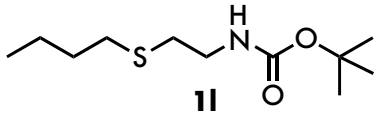
HRMS-ESI$^+$: m/z $[M+H]^+$ calcd. for $C_{12}H_{25}O_2S$ 233,1570; found 233.1556.



21

2-[(*tert*-Butoxycarbonyl)amino]-1-ethanethiol 21. Under inert atmosphere to a stirred solution of 2-aminoethanethiol hydrochloride (1 g, 8.80 mmol, 1.0 equiv) in dry THF (20 mL) was added NaH 60% (528 mg, 13.203 mmol, 1.5 equiv) at 0 ºC in an ice bath. After 5 min, the ice bath was removed, and the reaction mixture was stirred for 10 min in room temperature. The reaction mixture was cooled to 0 °C again and neat di-tert-butyl decarbonate (2 g, 9.242 mmol, 1.05 equiv) was added. After 20 min, the ice bath was removed, the reaction mixture was stirred for 2 hours in room temperature and quenched with an aqueous solution of $NaHCO_3$. The reaction mixture was poured into water and the resulting solution extracted with EA. The organic phase was dried over anhydrous Na_2SO_4 and evaporated to dryness. The crude was purified by column chromatography on silica gel ($CHCl_3$, R_f = 0.42) to afford 907 mg (58 %) as a colorless oil.

Spectral data were in accordance with a literature [S5].



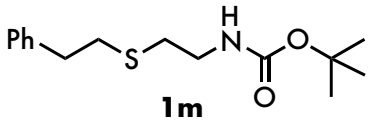
1l

***tert*-Butyl-(2-(butylthio)ethyl)carbamate 1l**. A mixture of 2-[(tert-Butoxycarbonyl)amino]-1-ethanethiol **21** (300 mg, 1.70 mmol, 1.0 equiv), *n*-butylbromide (0.22 mL, 2.03 mmol, 1.2 equiv) and K_2CO_3 (280 mg, 2.03 mmol, 1.2 equiv) in DMF (5 mL) was heated at 70 °C for 48 hours. The reaction mixture was cooled down to room temperature and it was diluted with water and extracted with EA. The organic phase was washed with water and brine, dried over anhydrous Na_2SO_4 and evaporated to dryness. The crude was purified by column chromatography on silica gel (PE:EA 30:1, R_f = 0.45) to afford 113 mg (29 %) of **1l** as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 4.92 (s, 1H), 3.31 (q, J = 6.3 Hz, 2H), 2.63 (t, J = 6.5 Hz, 2H), 2.52 (t, J = 7.3 Hz, 2H), 1.61 – 1.50 (m, 2H), 1.45 (s, 9H), 1.44 – 1.34 (m, 2H), 0.91 (t, J = 7.3 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 155.92, 79.53, 39.86, 32.44, 31.91, 31.65, 28.54, 22.09, 13.80.

HRMS-ESI$^+$: m/z $[M+H]^+$ calcd. for $C_{11}H_{24}NO_2S$ 234.1522; found 234.1524.



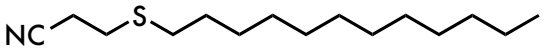
1m

***tert*-Butyl-N-[2-(2-phenylethylthio)ethyl]carbamate 1m**. A mixture of 2-[(tert-Butoxycarbonyl)amino]-1-ethanethiol (237 mg, 1.33 mmol, 1.0 equiv), 2-phenylethylbromide (0.24 mL, 1.74 mmol, 1.3 equiv) and K_2CO_3 (240 mg, 1.74 mmol, 1.3 equiv) in DMF (5 mL) was heated at 70 °C for 48 hours. The reaction mixture was cooled down to room temperature and it was diluted with water and extracted with EA. The organic phase was washed with water and brine, dried over anhydrous Na_2SO_4 and evaporated to dryness. The crude was purified by column chromatography on silica gel (PE:EA 30:1, R_f = 0.12) to afford 165 mg (44 %) of **1m** as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34 – 7.27 (m, 2H), 7.25 – 7.18 (m, 3H), 4.88 (s, 1H), 3.31 (q, J = 8.1, 6.3 Hz, 2H), 2.99 – 2.84 (m, 2H), 2.84 – 2.75 (m, 2H), 2.65 (t, J = 6.5 Hz, 2H), 1.44 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 155.85, 140.38, 128.60, 128.59, 126.52, 36.38, 33.42, 32.55, 28.50, 28.48, 28.29.

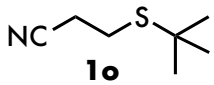
HRMS-ESI$^+$: m/z $[M+H]^+$ calcd. for $C_{15}H_{24}NO_2S$ 282.1522; found 282.1522.



1n

3-(*n*-Dodecylthio)propanenitrile 1n. 1-dodecanethiol (4.5 mL, 18.86 mmol, 2.0 equiv) and NaOMe (146 mg, 2.70 mmol, 0.05 equiv) were dissolved in MeOH (20 mL) and the solution was cooled down to 0 °C in an ice bath. Acrylonitrile (0.61 mL, 9.43 mmol, 1.0 equiv) was added dropwise over a period of approx. 10 min. The reaction was allowed to reach room temperature overnight. The reaction mixture was evaporated to dryness. Then the crude was dissolved in $CHCl_3$ and washed with washed with water and brine. The crude was purified by column chromatography on silica gel (PE:EA 40:1, R_f = 0.33) to afford 2.31 g (96 %) of **1n** as a white solid.

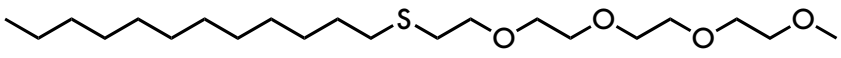
Spectral data were in accordance with a literature [S6].



1o

3-(*tert*-Butylthio)propanenitrile 1o. 2-methyl-2-propanethiol (2.1 mL, 18.86 mmol, 2.0 equiv) and NaOMe (146 mg, 2.70 mmol, 0.05 equiv) were dissolved in MeOH (20 mL) and the solution was cooled down to 0 °C in an ice bath. Acrylonitrile (0.61 mL, 9.43 mmol, 1.0 equiv) was added dropwise over a period of approx. 10 min. The reaction was allowed to reach room temperature overnight. The reaction mixture was evaporated to dryness. Then the crude was dissolved in $CHCl_3$ and washed with water and brine. The crude was purified by column chromatography on silica gel (PE:EA 40:1, R_f = 0.33) to afford 1.05 g (78 %) of **1o** as a white solid.

Spectral data were in accordance with a literature [S7].



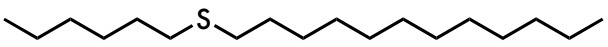
1p

***n*-Dodecylmethyl-2,5,8,11-tetraoxatridecane-13-sulfide 1p.** A mixture of 1-dodecanethiol (0.13 mL, 0.538 mmol, 1.0 equiv), 1-bromo-tetraethyleneglycol monomethyl ether (146 mg, 0.538 mmol, 1.0 equiv) and K_2CO_3 (82 mg, 0.592 mmol, 1.1 equiv) in DMF (4 mL) was stirred at room temperature for 24 hours. The reaction mixture was diluted with water and extracted with EA. The organic phase was washed with water and brine, dried over anhydrous Na_2SO_4 and evaporated to dryness. The crude was purified by column chromatography on silica gel (PE:EA 1:1, R_f = 0.25) to afford 166 mg (78 %) of **1p** as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 3.71 – 3.60 (m, 12H), 3.58 – 3.51 (m, 2H), 3.38 (s, 3H), 2.70 (t, J = 7.1 Hz, 2H), 2.53 (t, J = 7.24 Hz, 2H), 1.61 – 1.52 (m, 2H), 1.41 – 1.19 (m, 18H), 0.87 (t, J = 6.64 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 72.11, 71.19, 70.79, 70.76, 70.70, 70.46, 59.20, 32.76, 32.07, 31.53, 29.98, 29.81, 29.78, 29.76, 29.69, 29.50, 29.41, 29.04, 22.84, 14.27.

HRMS-ESI$^+$: m/z $[M+H]^+$ calcd. for $C_{21}H_{45}O_4S$ 393.3033; found 393.3037.



1q

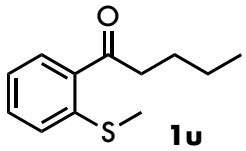
***n*-dodecylhexylsulfide 1q.** A mixture of 1-dodecanethiol (0.59 mL, 2.47 mmol, 1.0 equiv), 1-bromohexane (0.35 mL, 2.47 mmol, 1.0 equiv) and K_2CO_3 (0.44 g, 3.21 mmol, 1.3 equiv) in DMF (7 mL) was stirred at room temperature for 24 hours. The reaction mixture was diluted with water and extracted with EA. The organic phase was washed with water and brine, dried over

anhydrous Na_2SO_4 and evaporated to dryness. The crude was purified by column chromatography on silica gel (PE, R_f = 0.34) to afford 635 mg (90 %) of **1q** as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 2.50 (t, J = 7.4 Hz, 4H), 1.63 – 1.52 (m, 4H), 1.43 – 1.33 (m, 4H), 1.33 – 1.21 (m, 20H), 0.94 – 0.83 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 32.36, 32.07, 31.63, 29.91, 29.87, 29.81, 29.79, 29.76, 29.69, 29.50, 29.42, 29.12, 28.80, 22.84, 22.72, 14.27, 14.19.

HRMS-ESI$^+$: m/z $[M+H]^+$ calcd. for $C_{18}H_{39}SO$ 303.2716; found 303.2718 (only sulfoxide formed during the measurements can be detected with ESI).



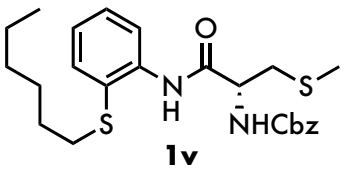
1u

1-(2-(methylthio)phenyl)pentan-1-one 1u. Under inert atmosphere 1-(2-mercaptophenyl)pentan-1-one (300 mg, 1.54 mmol, 1.0 equiv) was added to a suspension of NaH 60 % (62 mg, 1.54 mmol, 1.0 equiv) in dry THF (5 mL) and the mixture was stirred for 10 min. Then MeI (0.12 mL, 1.85 mmol, 1.2 equiv) was added and the reaction mixture was stirred at room temperature for 24 hours. The reaction mixture was quenched with H_2O and extracted with DCM. The organic phase was dried over anhydrous Na_2SO_4 and evaporated to dryness. The crude was purified by column chromatography on silica gel (PE:EA 100:1, R_f = 0.22) to afford 267 mg (83 %) of **1u** as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82 (dd, J = 7.8, 1.5 Hz, 1H), 7.46 (td, J = 7.5 Hz, 1.5 Hz, 1H), 7.33 (d, J = 8.0 Hz, 1H), 7.19 (td, J = 7.5, 1.2 Hz, 1H), 2.95 (t, J = 7.4 Hz, 2H), 2.43 (s, 3H), 1.72 (p, J = 7.5 Hz, 2H), 1.46 – 1.35 (m, 2H), 0.94 (t, J = 7.3 Hz, 3H) .

^{13}C NMR (101 MHz, $CDCl_3$): δ 202.01, 142.20, 135.06, 132.06, 130.12, 125.37, 123.63, 40.00, 26.70, 22.62, 16.20, 14.09.

HRMS-ESI$^+$: m/z $[M+H]^+$ calcd. for $C_{12}H_{17}OS$ 209.0995; found 209.0994.



1v

(S)-benzyl (1-((2-(hexylthio)phenyl)amino)-4-(methylthio)-1-oxobutan-2-yl)carbamate 1v. Under inert atmosphere a mixture of 2-(hexylthio)aniline (300 mg, 1.43 mmol, 1.5 equiv), N-Carbobenzyloxy-L-methionine (270 mg, 0.96 mmol, 1.0 equiv), DIPEA (0.18 mL, 1.05 mmol, 1.1 equiv) and HATU (400 mg, 1.05 mmol, 1.1 equiv) in anhyd. DCM (5 mL) was stirred at room

temperature for 24 hours. The reaction mixture was diluted with water and extracted with DCM. The organic phase was washed with water and brine, dried over anhydrous Na_2SO_4 and evaporated to dryness. The crude was purified by column chromatography on silica gel ($CHCl_3$:MeOH 100:1, R_f = 0.44) to afford 380 mg (56 %) of **1v** as a yellow solid. M.p. 59 – 61 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.12 (s, 1H), 8.36 (dd, J = 8.0, 1.0 Hz, 1H), 7.50 (dd, J = 7.6, 1.5 Hz, 1H), 7.42 – 7.28 (m, 6H), 7.07 (td, J = 7.6, 1.4 Hz, 1H), 5.63 (d, J = 8.1 Hz, 1H), 5.15 (s, 2H), 4.59 (d, J = 7.2 Hz, 1H), 2.81 – 2.47 (m, 4H), 2.33 – 2.18 (m, 1H), 2.12 (s, 3H), 2.10 – 2.01 (m, 1H), 1.51 (p, J = 7.4 Hz, 2H), 1.34 (p, J = 9.2, 8.3 Hz, 2H), 1.29 – 1.17 (m, 4H), 0.86 (t, J = 6.9 Hz, 3H).

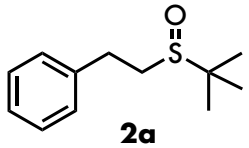
^{13}C NMR (101 MHz, $CDCl_3$): δ 169.44, 156.17, 138.86, 136.18, 135.14, 129.53, 128.70, 128.40, 128.24, 124.57, 123.95, 120.33, 67.40, 55.22, 36.35, 31.73, 31.43, 30.27, 29.61, 28.46, 22.64, 15.44, 14.13.

HRMS-ESI$^+$: m/z $[M+H]^+$ calcd. for $C_{25}H_{35}N_2O_3S_2$ 475.2084; found 475.2086.

Photocatalytic oxidation of sulfides

General procedure for photocatalytic oxidation of sulfides

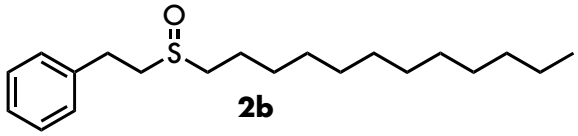
a) **Using C_{60} solution in toluene (5.0 mg in 2.0 mL) as a catalyst.** The substrate (0.05 – 0.2 mmol) was dissolved in 2.0 mL of the solvent (EtOH or CH_3CN) and the solution of C_{60} was added (50 µL). Then the reaction mixture was irradiated with a Blue LED (450 ± 10 nm, 100 W) with continuous stirring at room temperature. The progress of the reaction was monitored by TLC. After the complete conversion was achieved, the solvent was removed under reduced pressure. The crude was purified by column chromatography on silica gel (eluent $CHCl_3$ or $CHCl_3$:MeOH 100:1).
b) **Using C_{60} soot powder as a catalyst.** The substrate (0.05 – 0.2 mmol) was dissolved in 2.0 mL of the solvent (EtOH or CH_3CN) and 1.0 mg of C_{60} soot was added. Then the reaction mixture was purged with O_2 for 15 minutes and was irradiated with a Blue LED (450 ± 10 nm, 100 W) with continuous stirring at room temperature. The progress of the reaction was monitored by TLC. After the complete conversion was achieved, the solvent was removed under reduced pressure. The crude was purified by column chromatography on silica gel (eluent $CHCl_3$ or $CHCl_3$:MeOH 100:1).
c) **Using C_{60} soot suspension in toluene (2.0 mg in 4.0 mL) as a catalyst.** The substrate (0.05 – 0.2 mmol) was dissolved in 2.0 mL of the solvent (EtOH or CH_3CN) and the solution of C_{60} soot was added (100 µL). Then the reaction mixture was purged with O_2 for 15 minutes and was irradiated with a Blue LED (450 ± 10 nm, 100 W) with continuous stirring at room temperature. The progress of the reaction was monitored by TLC. After the complete conversion was achieved, the solvent was removed under reduced pressure. The crude was purified by column chromatography on silica gel (eluent $CHCl_3$ or $CHCl_3$:MeOH 100:1).



2a

(2-(*tert*-Butylsulfinyl)ethyl)benzene 2a. The product was obtained as a colorless oil following the general procedures: a) in EtOH irradiated with a Blue LED for 24 hours (yield 78 %) or in CH_3CN irradiated with a Blue LED or 48 hours (yield 48 %); b) in EtOH irradiated with a Blue LED for 96 hours (yield 93 %); c) in EtOH irradiated with a Blue LED for 24 hours (yield 97 %) or in CH_3CN irradiated with a Blue LED for 96 hours (yield 81 %).

Spectral data were in accordance with a literature [S8].



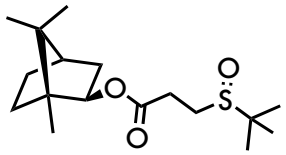
2b

(2-(*n*-Dodecylsulfinyl)ethyl)benzene 2b. The product was obtained as a white solid following the general procedures: a) in EtOH irradiated with a Blue LED for 24 hours (yield 99 %) or in CH_3CN irradiated with a Blue LED for 48 hours (yield 60 %); b) in EtOH irradiated with a Blue Led for 5 days (yield 99 %); c) in EtOH irradiated with a Blue LED for 24 hours (yield 93 %) or in CH_3CN irradiated with a Blue LED for 48 hours (yield 82 %). M.p. 66 – 68 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35 – 7.29 (m, 2H), 7.27 – 7.22 (m, 3H), 3.20 – 3.03 (m, 2H), 3.01 – 2.84 (m, 2H), 2.78 – 2.68 (m, 1H), 2.67 – 2.56 (m, 1H), 1.83 – 1.69 (m, 2H), 1.52 – 1.37 (m, 2H), 1.25 (s, 16H), 0.88 (t, J = 6.7 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 139.17, 128.93, 128.71, 126.90, 53.93, 52.75, 32.05, 29.75, 29.67, 29.49, 29.47, 29.33, 29.02, 22.83, 22.77, 14.26.

HRMS-ESI$^+$: m/z $[M+H]^+$ calcd. for $C_{20}H_{35}OS$ 323.2403; found 323.2403.



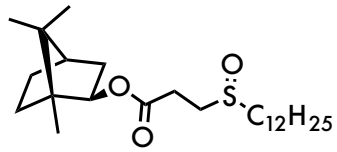
2c

Isobornyl 3-(*tert*-butylsulfinyl)propionate 2c. The product was obtained as a colorless oil following the general procedures: a) in EtOH irradiated with a Blue LED for 48 hours (yield 84 %) or in CH_3CN irradiated with a Blue LED for 48 hours (yield 35 %); b) in EtOH irradiated with a Blue LED for 48 hours (yield 74 %); c) in EtOH irradiated with a Blue LED for 48 hours (yield 74 %) or in CH_3CN irradiated with a Blue LED for 48 hours (yield 55 %).

^{1}H NMR (400 MHz, $CDCl_3$): δ 4.77 – 4.64 (m, 1H), 2.95 – 2.77 (m, 3H), 2.75 – 2.55 (m, 1H), 1.90 – 1.66 (m, 4H), 1.58 – 1.48 (m, 1H), 1.27 (s, 9H), 1.21 – 1.03 (m, 2H), 0.96 (s, 3H), 0.84 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 171.24, 82.06, 82.01, 53.42, 48.91, 48.89, 47.08, 45.15, 45.14, 40.88, 38.88, 38.86, 33.83, 28.77, 28.75, 27.14, 22.93, 20.21, 20.07, 11.63, 11.62.

HRMS-ESI$^+$: m/z $[M+Na]^+$ calcd. for $C_{17}H_{31}O_3SNa$ 337.1808; found 337.1812.



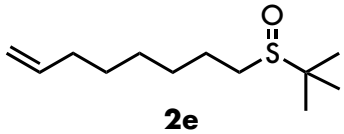
2d

Isobornyl 3-(*n*-dodecylsulfinyl)propionate 2d. The product was obtained as a white solid following the general procedures: a) in EtOH irradiated with a Blue LED for 24 hours (yield 69 %) or in CH_3CN irradiated with a Blue LED for 48 hours (yield 86 %); b) in EtOH irradiated with a Blue LED for 48 hours (yield 88 %); c) in EtOH irradiated with a Blue LED for 48 hours (yield 92 %) or in CH_3CN irradiated with a Blue LED for 48 hours (yield 78 %). M.p. 70 – 74 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 4.70 (dt, J = 7.1 Hz, 3.1 Hz, 1H), 3.11 – 2.93 (m, 1H), 2.93 – 2.77 (m, 3H), 2.77 – 2.59 (m, 2H), 1.88 – 1.61 (m, 6H), 1.61 – 1.50 (m, 1H), 1.50 – 1.39 (m, 2H), 1.25 (s, 16H), 1.19 – 1.04 (m, 2H), 0.96 (s, 3H), 0.92 – 0.77 (m, 9H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 170.98, 82.13, 82.10, 52.92, 48.91, 48.89, 47.08, 47.04, 45.13, 38.84, 33.82, 32.04, 29.74, 29.66, 29.48, 29.47, 29.32, 28.98, 27.57, 27.12, 22.82, 22.76, 20.20, 20.06, 14.25, 11.61.

HRMS-ESI$^+$: m/z $[M+Na]^+$ calcd. for $C_{25}H_{47}O_3SNa$ 449.3060; found 449.3049.



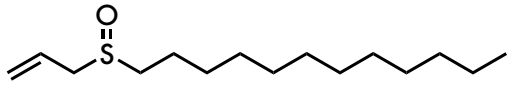
2e

8-(*tert*-Butylsulfinyl)oct-1-ene 2e. The product was obtained as a yellow oil following the general procedures: a) in EtOH irradiated with a Blue LED for 24 hours (yield 92 %) or in CH_3CN irradiated with a Blue LED for 24 hours (yield 59 %); b) in EtOH irradiated with a Blue LED for 72 hours (yield 77 %); c) in EtOH irradiated with a Blue LED for 24 hours (yield 85 %) or in CH_3CN irradiated with a Blue Led for 24 hours (yield 94 %).

^{1}H NMR (400 MHz, $CDCl_3$): δ 5.79 (ddt, J = 16.9, 10.1, 6.7 Hz, 1H), 5.06 – 4.89 (m, 2H), 2.44 (t, J = 7.7 Hz, 2H), 2.04 (q, J = 6.8 Hz, 2H), 1.95 – 1.72 (m, 2H), 1.57 – 1.32 (m, 6H), 1.23 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 138.99, 114.51, 52.81, 45.76, 33.74, 29.01, 28.82, 28.75, 23.85, 23.02.

HRMS-ESI$^+$: m/z $[M+H]^+$ calcd. for $C_{12}H_{25}OS$ 217.1621; found 217.1621.



2f

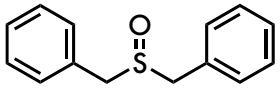
Allyl(*n*-dodecyl)sulfoxide 2f. The product was obtained as a yellow solid following the general procedures: a) in EtOH irradiated with a Blue LED for 24 hours (yield 68 %) or in CH_3CN irradiated with a Blue LED for 72 hours (yield 71 %); c) in EtOH irradiated with a Blue LED for 72 hours (yield 90 %) or in CH_3CN irradiated with a Blue Led for 72 hours (yield 70 %). M.p. 56 – 60 °C.

Using C_{60}/C_{70} nanodispersion: The substrate (35.4 mg, 0.146 mmol) was dissolved EtOH (2mL) and the solution of $C_{60/}C_{70}$ (1.0 mg/1.0 mg in 0.8 mL toluene) was added (50 µL). Then the reaction mixture was irradiated with a Blue LED (450 ± 10 nm, 100 W) with continuous stirring at room temperature for 24 hours. The reaction course was monitored by TLC. After the complete conversion was achieved, the solvent was removed under reduced pressure. The crude waas purified by column chromatography on silica gel ($CHCl_3$:MeOH 100:1) to afford 28.3 mg (75 %) of **2f**.

^{1}H NMR (400 MHz, $CDCl_3$): δ 5.88 (ddt, J = 17.6, 10.2, 7.5 Hz, 1H), 5.47 – 5.32 (m, 2H), 3.55 – 3.34 (m, 2H), 2.75 – 2.60 (m, 2H), 1.82 – 1.68 (m, 2H), 1.52 – 1.37 (m, 2H), 1.25 (s, 16H), 0.86 (t, J = 6.7 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 126.05, 123.42, 55.94, 51.16, 32.02, 29.71, 29.64, 29.47, 29.44, 29.32, 28.98, 22.79, 22.58, 14.23.

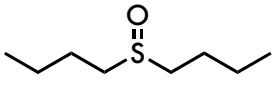
HRMS-ESI$^+$: m/z $[M+H]^+$ calcd. for $C_{15}H_{31}OS$ 259.2090; found 259.2090.



2g

Dibenzylsulfoxide 2g. The product was obtained as a white solid following the general procedures: a) in EtOH irradiated with a Blue Led for 24 hours (yield 98 %) or in CH_3CN irradiated with a Blue LED for 4 days (yield 69 %); b) in EtOH irradiated with a Blue LED for 6 days (yield 81 %); c) in EtOH irradiated with a Blue LED for 24 hours (yield 94 %).

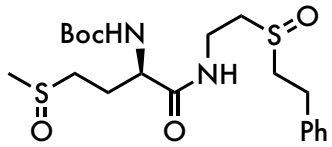
Spectral data were in accordance with a literature [S9].



2h

Dibutylsulfoxide 2h. The product was obtained as a colorless crystals following the general procedures: a) in EtOH irradiated with a Blue LED for 24 hours (yield 79 %) or in CH_3CN irradiated with a Blue Led for 24 hours (yield 80 %); b) in EtOH irradiated with a Blue LED for 7 days (yield 82 %); c) in EtOH irradiated with a Blue LED for 24 hours (yield 57 %) or in CH_3CN irradiated with a Blue LED for 72 hours (yield 90 %).

Spectral data were in accordance with a literature [S10].



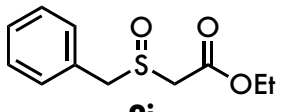
2i

***tert*-Butyl((3R)-1-(methylsulfinyl)-4-oxo-6-(phenethylsulfinyl)hexan-3-yl)carbamate 2i.** The product was obtained as a white solid following the general procedures: a) in EtOH irradiated with a Blue LED for 24 hours (yield 73 %) or in CH_3CN irradiated with a Blue LED for 24 hours (yield 51 %); b) in EtOH irradiated with a Blue LED for 24 hours (yield 35 %); c) in EtOH irradiated with a Blue Led for 24 hours (yield 92 %) or in CH_3CN irradiated with a Blue LED for 24 hours (yield 36 %). M.p. 78 – 86 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77 (d, J = 36.4 Hz, 1H), 7.30 (t, J = 7.5 Hz, 2H), 7.25 – 7.20 (m, 3H), 5.82 (d, J = 39.8 Hz, 1H), 4.33 (s, 1H), 3.83 – 3.59 (m, 2H), 3.17 – 2.90 (m, 5H), 2.91 – 2.71 (m, 3H), 2.58 (s, 3H), 2.35 – 2.07 (m, 2H), 1.42 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 171.77, 155.76, 138.65, 128.94, 128.68, 126.98, 80.25, 53.99, 52.99, 51.57, 34.29, 34.20, 28.85, 28.46, 27.18, 26.21.

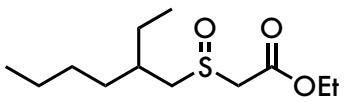
HRMS-ESI$^+$: m/z $[M+H]^+$ calcd. for $C_{25}H_{35}N_2O_5S_2$ 507.1982; found 507.1982.



2j

Ethylbenzylsulfinylacetate 2j. The product was obtained as a white solid following the general procedures: a) in EtOH irradiated with a Blue LED for 24 hours (yield 59 %) or in CH_3CN irradiated with a Blue LED for 24 hours (yield 21 %); b) in EtOH irradiated with a Blue LED for 48 hours (yield 58 %); c) in EtOH irradiated with a Blue LED for 48 hours (yield 44 %) or in CH_3CN irradiated with a Blue LED for 48 hours (yield 18 %).

Spectral data were in accordance with a literature [S4].



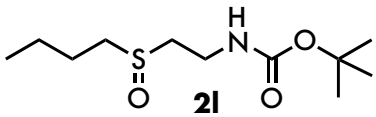
2k

2-Ethylhexylethoxycarbonylmethylsulfoxide 2k. The product was obtained as a colorless oil following the general procedures: a) in EtOH irradiated with a Blue LED for 24 hours (yield 56 %) or in CH_3CN irradiated with a Blue LED for 72 hours (yield 36 %); b) in EtOH irradiated with a Blue LED for 72 hours (yield 47 %); c) in EtOH irradiated with a Blue LED for 24 hours (yield 53 %) or in CH_3CN irradiated with a Blue LED for 72 hours (yield 16 %).

^{1}H NMR (400 MHz, $CDCl_3$): δ 4.25 (q, J = 7.1 Hz, 2H), 3.68 (d, J = 1.2 Hz, 2H), 2.86 (dt, J = 13.0, 4.3 Hz, 1H), 2.73 (ddd, J = 13.0, 9.1, 6.9 Hz, 1H), 2.02 – 1.90 (m, 1H), 1.57 – 1.37 (m, 4H), 1.31 (t, J = 7.1 Hz, 7H), 0.97 – 0.87 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 165.34, 62.25, 58.87, 58.73, 56.87, 56.84, 34.55, 34.29, 32.85, 32.20, 28.64, 28.37, 26.32, 25.32, 23.01, 22.94, 14.28, 14.15, 10.71, 10.27.

HRMS-ESI$^+$: m/z $[M+H]^+$ calcd. for $C_{12}H_{25}O_3S$ 249.1519; found 249.1519.



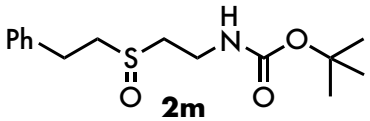
2l

***tert*-Butyl(2-(butylsulfinyl)ethyl)carbamate 2l.** The product was obtained as a white solid following the general procedures: a) in EtOH irradiated with a Blue LED for 24 hours (yield 96 %) or in CH_3CN irradiated with a Blue LED for 24 hours (yield 97 %); b) in EtOH irradiated with a Blue LED for 5 days (yield 72 %); c) in EtOH irradiated with a Blue LED for 24 hours (yield 98 %) or in CH_3CN irradiated with a Blue LED for 24 hours (yield 65 %). M.p. 48 – 52 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 5.29 (s, 1H), 3.62 (q, J = 6.0 Hz, 2H), 2.96 (dt, J = 12.9 Hz, 1H), 2.85 – 2.73 (m, 2H), 2.73 – 2.60 (m, 1H), 1.83 – 1.67 (m, 2H), 1.57 – 1.36 (m, 11H), 0.95 (t, J = 7.3 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 156.04, 79.83, 52.55, 51.77, 35.41, 28.47, 24.71, 22.13, 13.78.

HRMS-ESI$^+$: m/z $[M+H]^+$ calcd. for $C_{11}H_{24}NO_3S$ 250.1471; found 250.1465.



2m

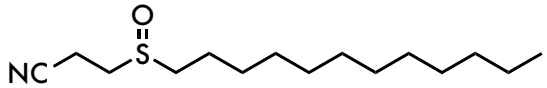
***tert*-Butyl(2-(phenethylsulfinyl)ethyl)carbamate 2m.** The product was obtained as a white solid following the general procedures: a) in EtOH irradiated with a Blue LED for 24 hours (yield 82 %) or in CH_3CN irradiated with a Blue LED for 24 hours (yield 60 %); b) in EtOH irradiated with a Blue

LED for 24 hours (yield 98 %); c) in EtOH irradiated with a Blue LED for 48 hours (yield 42 %) or in CH_3CN irradiated with a Blue LED for 24 hours (yield 78 %). M.p. 58 – 60 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36 – 7.29 (m, 2H), 7.25 (dd, J = 7.5 Hz, 5.7 Hz, 3H), 5.23 (s, 1H), 3.64 (q, J = 6.1 Hz, 2H), 3.17 – 3.02 (m, 3H), 3.02 – 2.91 (m, 2H), 2.80 (dt, J = 13.1 Hz, 5.4 Hz, 1H), 1.43 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 156.01, 138.75, 128.97, 128.70, 127.01, 79.94, 54.21, 51.96, 35.45, 28.97, 28.49.

HRMS-ESI$^+$: m/z $[M+H]^+$ calcd. for $C_{15}H_{24}NO_3S$ 298.1471; found 298.1469.



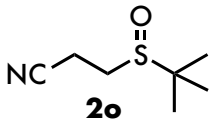
2n

(*n*-Dodecylsulfinyl)propanenitrile 2n. The product was obtained as a white solid following the general procedures: a) in EtOH irradiated with a Blue LED for 48 hours (yield 92 %) or in CH_3CN irradiated with a Blue LED for 24 hours (yield 61 %); b) in EtOH irradiated with a Blue LED for 48 hours (yield 67 %); c) in EtOH irradiated with a Blue LED for 24 hours (yield 96 %) or in CH_3CN irradiated with a Blue LED for 48 hours (yield 80 %). M.p. 72 – 74 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 3.04 – 2.93 (m, 1H), 2.93 – 2.84 (m, 3H), 2.84 – 2.75 (m, 1H), 2.74 – 2.62 (m, 1H), 1.87 – 1.68 (m, 2H), 1.56 – 1.38 (m, 2H), 1.25 (s, 16H), 0.86 (t, J = 6.7 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 117.60, 52.76, 46.56, 31.98, 29.67, 29.58, 29.40, 29.23, 28.82, 22.76, 22.67, 14.20, 11.10.

HRMS-ESI$^+$: m/z $[M+H]^+$ calcd. for $C_{15}H_{30}NOS$ 272.2043; found 272.2043.



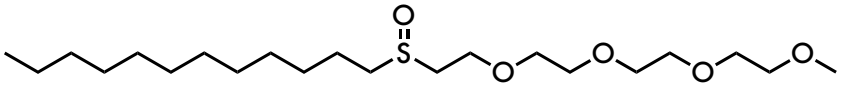
2o

(*tert*-Butylsulfinyl)propanenitrile 2o. The product was obtained as a yellow oil following the general procedures: a) in EtOH irradiated with a Blue LED for 48 hours (yield 72 %) or in CH_3CN irradiated with a Blue LED for 48 hours (yield 89 %); b) in EtOH irradiated with a Blue LED for 72 hours (yield 70 %); c) in EtOH irradiated with a Blue LED for 48 hours (yield 53 %) or in CH_3CN irradiated with a Blue LED for 72 hours (yield 59 %).

^{1}H NMR (400 MHz, $CDCl_3$): δ 2.96 – 2.61 (m, 4H), 1.25 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 117.67, 54.00, 40.97, 22.73, 12.56.

HRMS-ESI$^+$: m/z $[M+H]^+$ calcd. for $C_7H_{14}NOS$ 160.0791; found 160.0783.



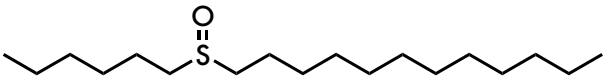
2p

***n*-Dodecyl-2,5,8,11-tetraoxatridecane-13-sulfoxide 2p.** The product was obtained as a yellow solid following the general procedures: a) in EtOH irradiated with a Blue LED for 24 hours (yield 99 %) or in CH_3CN irradiated with a Blue LED for 24 hours (yield 80 %); b) in EtOH irradiated with a Blue LED for 72 hours (yield 88 %) or in CH_3CN irradiated with a Blue LED for 9 days (yield 79 %); c) in EtOH irradiated with a Blue LED for 72 hours (yield 97 %) or in CH_3CN irradiated with a Blue LED for 72 hours (yield 82 %). M.p. 38 – 40 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 3.90 (dd, J = 7.0, 4.3 Hz, 2H), 3.73 – 3.59 (m, 10H), 3.57 – 3.51 (m, 2H), 3.36 (s, 3H), 2.97 (dt, J = 13.7, 7.0 Hz, 1H), 2.83 (dt, J = 13.3, 4.3 Hz, 1H), 2.78 – 2.63 (m, 2H), 1.85 – 1.67 (m, 2H), 1.53 – 1.37 (m, 2H), 1.25 (s, 16H), 0.86 (t, J = 6.7 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ δ 72.07, 70.80, 70.75, 70.73, 70.66, 70.57, 63.85, 59.15, 53.09, 52.79, 32.01, 29.72, 29.66, 29.48, 29.44, 29.34, 28.97, 22.79, 22.78, 14.22.

HRMS-ESI$^+$: m/z $[M+H]^+$ calcd. for $C_{21}H_{45}O_5S$ 409.2982; found 409.2983.



2q

***n*-Dodecylhexylsulfoxide 2q.** The product was obtained as a white solid following the general procedures: a) in EtOH irradiated with a Blue LED for 24 hours (yield 95 %) or in CH_3CN irradiated with a Blue LED for 48 hours (yield 93 %); b) in EtOH irradiated with a Blue LED for 96 hours (yield 98 %) or in CH_3CN irradiated with a Blue LED for 72 hours (yield 85 %); c) in EtOH irradiated with a Blue LED for 48 hours (yield 91.8 %) or in CH_3CN irradiated with a Blue LED for 48 hours (yield 82 %). M.p. 63 – 64 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 2.81 – 2.70 (m, 2H), 2.70 – 2.59 (m, 2H), 1.85 – 1.68 (m, 4H), 1.55 – 1.38 (m, 4H), 1.37 – 1.20 (m, 20H), 0.95 – 0.83 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 52.38, 32.05, 31.51, 29.75, 29.68, 29.51, 29.48, 29.35, 29.02, 28.69, 22.83, 22.78, 22.74, 22.55, 14.26, 14.11.

HRMS-ESI$^+$: m/z $[M+H]^+$ calcd. for $C_{18}H_{39}OS$ 303.2716; found 303.2716.

Photocatalytic oxidation of bissulfide 1v

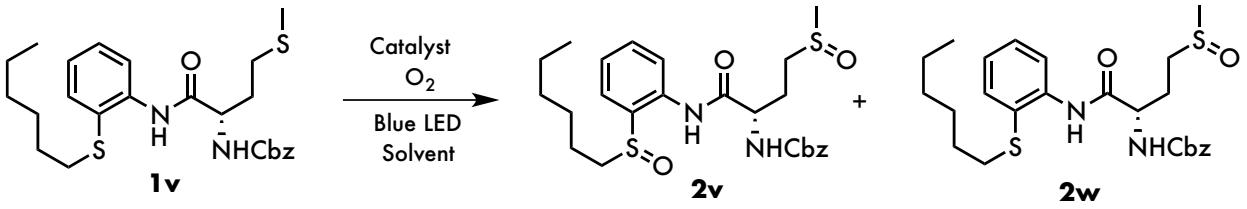


Table S1. Catalyst screening.

Entry	Catalyst	Solvent	Time	Yield of 2w (%)	Yield of 2v (%)
1	C_{60} solution in toluene	EtOH	1 day	14	81
2	C_{60} soot powder	EtOH	5 days	28	72
3	C_{60} soot dispersion in toluene	EtOH	3 days	15	68
4	C_{60} solution in toluene	CH_3CN	1 day	28	46
5	C_{60} soot powder	CH_3CN	9 days	22	31
6	C_{60} soot dispersion in toluene	CH_3CN	3 days	39	61

General procedures for bisulfoxide 2w and 2v

a) **Using C_{60} solution in toluene (5.0 mg in 2.0 mL) as a catalyst.** The substrate **1v** (0.08 mmol) was dissolved in 2.0 mL of the solvent (EtOH or CH_3CN) and solution of C_{60} was added (50 µL). Then the reaction mixture was irradiated with a Blue LED (450 ± 10 nm, 100 W) with continuous stirring at room temperature. The progress of the reaction was monitored by TLC. After the complete conversion was achieved, the solvent was removed under reduced pressure. The crudes were purified by column chromatography on silica gel ($CHCl_3$:MeOH 50:1 to 40:1, R_f = 0.13 and 0.2) to afford **2v** and **2w** as yellow oils.

b) **Using C_{60} soot powder as a catalyst.** The substrate **1v** (0.08 mmol) was dissolved in 2.0 mL of the solvent (EtOH or CH_3CN) and 1.0 mg of C_{60} soot was added. Then the reaction mixture was purged with O_2 for 15 minutes and was irradiated with a Blue LED (450 ± 10 nm, 100 W) with continuous stirring at room temperature. The progress of the reaction was monitored by TLC. After the complete conversion was achieved, the solvent was removed under reduced pressure. The crudes were purified by column chromatography on silica gel ($CHCl_3$:MeOH 50:1 to 40:1, R_f = 0.13 and 0.2) to afford **2v** and **2w** as yellow oils.

c) **Using C_{60} soot suspension in toluene (2.0 mg in 4.0 mL) as a catalyst**. The substrate **1v** (0.08 mmol) was dissolved in 2.0 mL of the solvent (EtOH or CH_3CN) and the suspension of C_{60} soot was added (100 µL). Then the reaction mixture was purged with O_2 for 15 minutes and was irradiated with a Blue LED (450 ± 10 nm, 100 W) with continuous stirring at room temperature. The progress of the reaction was monitored by TLC. After the complete conversion was achieved, the solvent was removed under reduced pressure. The crudes were

purified by column chromatography on silica gel ($CHCl_3$:MeOH 50:1 to 40:1, R_f = 0.13 and 0.2) to afford **2v** and **2w** as yellow oils.

^{1}H NMR of **2w** (400 MHz, $CDCl_3$): δ 10.33 (d, J = 17.1 Hz, 1H), 8.44 (t, J = 8.6 Hz, 1H), 7.87 (d, J = 7.9 Hz, 1H), 7.63 (t, J = 7.9 Hz, 1H), 7.44 – 7.27 (m, 6H), 6.53 (dd, J = 29.0, 7.3 Hz, 1H), 5.36 – 5.01 (m, 2H), 4.61 – 4.36 (m, 1H), 3.05 (q, J = 9.7, 9.2 Hz, 2H), 2.98 – 2.71 (m, 2H), 2.56 (s, 3H), 2.51 – 2.33 (m, 2H), 1.70 – 1.53 (m, 2H), 1.38 – 1.13 (m, 6H), 0.83 (t, J = 6.8 Hz, 3H).

^{13}C NMR of **2w**(101 MHz, $CDCl_3$): δ 169.98, 169.90, 169.07, 156.77, 136.70, 136.68, 136.19, 136.17, 135.24, 130.46, 130.45, 129.34, 128.87, 128.85, 128.68, 128.66, 128.40, 128.38, 128.35, 128.24, 128.23, 126.62, 124.81, 124.76, 124.62, 124.61, 122.91, 122.82, 120.72, 120.61, 67.62, 67.59, 67.39, 55.99, 55.32, 55.22, 50.12, 38.44, 38.32, 36.06, 31.44, 31.27, 29.83, 29.58, 28.47, 27.91, 26.00, 25.48, 25.28, 22.64, 22.44, 22.40, 14.14, 14.03.

HRMS-ESI$^+$ of **2w**: m/z $[M+H]^+$ calcd. for $C_{25}H_{35}N_2O_4S_2$ 491.2033; found 491.2033.

^{1}H NMR of **2v** (400 MHz, $CDCl_3$): δ 11.17 (d, J = 51.6 Hz, 1H), 8.53 – 8.29 (m, 1H), 7.47 (t, J = 7.9 Hz, 1H), 7.43 – 7.23 (m, 6H), 7.20 – 7.12 (m, 1H), 6.56 – 6.18 (m, 1H), 5.33 – 5.00 (m, 2H), 4.46 (s, 1H), 3.30 – 3.01 (m, 1H), 2.99 – 2.69 (m, 3H), 2.55 (s, 3H), 2.48 – 2.22 (m, 2H), 2.06 (s, 2H), 1.39 (q, J = 7.5 Hz, 2H), 1.34 – 1.10 (m, 4H), 0.97 – 0.80 (m, 3H).

^{13}C NMR of **2v** (101 MHz, $CDCl_3$): δ 170.03, 169.88, 169.70, 169.67, 156.52, 156.31, 139.75, 139.69, 136.35, 132.44, 128.62, 128.60, 128.29, 128.26, 128.24, 128.22, 127.44, 126.54, 126.41, 124.22, 124.17, 124.08, 124.06, 123.02, 122.93, 67.31, 67.29, 55.20, 55.00, 54.80, 50.11, 38.69, 38.60, 38.45, 38.36, 31.44, 31.42, 28.27, 28.24, 26.19, 25.79, 25.48, 23.21, 23.14, 22.49, 22.47, 14.06.

HRMS-ESI$^+$ of **2v**: m/z $[M+H]^+$ calcd. for $C_{25}H_{35}N_2O_5S_2$ 507.1982; found 507.1982.

Photocatalytic oxidation of thioanisole

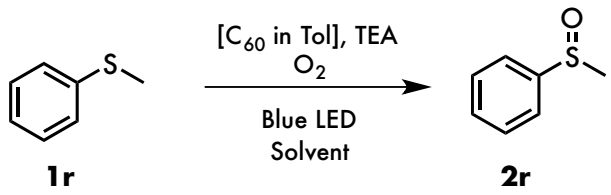
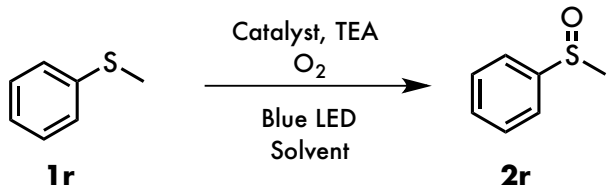


Table S2. Optimization of amine-mediated thioanisole sulfoxidation.

Entry	TEA	Solvent	O_2 (air)	Time	Yield (%)

1	0.10 equiv	MeOH	+	3 days	63
2	0.05 equiv	EtOH	+	5 days	96
3	0.10 equiv	EtOH	+	3 days	71
4	0.15 equiv	EtOH	+	3 days	77
5	0.20 equiv	EtOH	+	5 days	95
6	0.50 equiv	EtOH	+	4 days	89
7	1.0 equiv	EtOH	+	7 days	76
8	0.20 equiv	CH_3CN	+	5 days	6



1r **2r**

Table S3. Catalyst screening.

Entry	Catalyst	Solvent	Time	Yield (%)
1	C_{60} solution in toluene	EtOH	5 days	95
2	C_{60} soot powder	EtOH	7 days	22
3	C_{60} soot dispersion in toluene	EtOH	6 days	42
4	C_{60} solution in toluene	CH_3CN	5 days	6
5	C_{60} soot powder	CH_3CN	10 days	0
6	C_{60} soot dispersion in toluene	CH_3CN	6 days	5

General procedures for methyl phenyl sulfoxide 2r

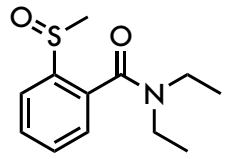
d) Using C_{60} solution in toluene (5.0 mg in 2.0 mL) as a catalyst. Solvent in the reaction vial was purged with O_2 for 15 minutes. Thioanisole (0.3 mmol, 1.0 equiv) and TEA (0.2 equiv) was dissolved in 2.0 mL of the solvent. Then solution of C_{60} was added (50 µL) and the reaction mixture was irradiated with a Blue LED (450 ± 10 nm, 100 W) with continuous stirring at room temperature. The progress of the reaction was monitored by TLC. After the complete conversion was achieved, the solvent was removed under reduced pressure. The crudes were purified by column chromatography on silica gel ($CHCl_3$:MeOH 100:1, R_f = 0.1) to afford **2r** as a yellow oil.

e) Using C_{60} soot powder as a catalyst. Solvent in the reaction vial was purged with O_2 for 15 minutes. Thioanisole (0.3 mmol, 1.0 equiv) and TEA (0.2 equiv) was dissolved in 2.0 mL of the

solvent. Then 1.0 mg of C_{60} soot was added and the reaction mixture was irradiated with a Blue LED (450 ± 10 nm, 100 W) with continuous stirring at room temperature. The progress of the reaction was monitored by TLC. After the complete conversion was achieved, the solvent was removed under reduced pressure. The crudes were purified by column chromatography on silica gel ($CHCl_3$:MeOH 100:1, R_f = 0.1) to afford **2r** as a yellow oil.

f) Using C_{60} soot suspension in toluene (2.0 mg in 4.0 mL) as a catalyst. Solvent in the reaction vial was purged with O_2 for 15 minutes. Thioanisole (0.3 mmol, 1.0 equiv) and TEA (0.2 equiv) was dissolved in 2.0 mL of the solvent. Then suspension of C_{60} soot was added (100 µL) and the reaction mixture was irradiated with a Blue LED (450 ± 10 nm, 100 W) with continuous stirring at room temperature. The progress of the reaction was monitored by TLC. After the complete conversion was achieved, the solvent was removed under reduced pressure. The crudes were purified by column chromatography on silica gel ($CHCl_3$:MeOH 100:1, R_f = 0.1) to afford **2r** as a yellow oil.

Spectral data were in accordance with a literature [S11].



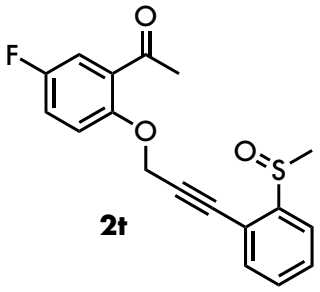
2s

***N*,*N*-diethyl-2-(methylsulfinyl)benzamide 2s.** The product was obtained following the general procedures: a) solvent in the reaction vial was purged with O_2 for 15 minutes. N,N-diethyl-2-(methylthio)benzamide **1s** (36 mg, 0.16 mmol, 1.0 equiv) and TEA (3.2 mg, 0.032 mmol, 0.2 equiv) was dissolved in EtOH (2mL). Then solution of C_{60} in toluene was added (50 µL) and the reaction mixture was irradiated with a Blue LED (450 ± 10nm, 100W) with continuous stirring at room temperature for 7 days. The reaction course was monitored by TLC. After the complete conversion was achieved, the solvent was removed under reduced pressure. The crudes were purified by column chromatography on silica gel ($CHCl_3$:MeOH 100:1, R_f = 0.1) to afford 34 mg (89 %) of **2s** as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.12 (dd, J = 7.9, 1.3 Hz, 1H), 7.64 (td, J = 7.7, 1.3 Hz, 1H), 7.51 (td, J = 7.5, 1.3 Hz, 1H), 7.29 (dd, J = 7.5, 1.3 Hz, 1H), 3.64 (dq, J = 14.2, 7.1 Hz, 1H), 3.44 (dq, J = 14.0, 7.1 Hz, 1H), 3.21 (qd, J = 7.2, 4.5 Hz, 2H), 2.85 (s, 3H), 1.25 (t, J = 7.1 Hz, 3H), 1.11 (t, J = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 167.63, 144.09, 134.07, 130.81, 130.43, 125.79, 123.84, 44.37, 43.38, 39.37, 14.14, 12.63.

HRMS-ESI$^+$: m/z $[M+H]^+$ calcd. for $C_{12}H_{18}NO_2S$ 240.1053; found 240.1053.



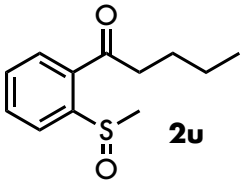
2t

1-(5-fluoro-2-((3-(2-(methylsulfinyl)phenyl)prop-2-yn-1-yl)oxy)phenyl)ethenone 2t. The product was obtained following the general procedures: a) solvent in the reaction vial was purged with O_2 for 15 minutes. Sulfide **1t** (37 mg, 0.12 mmol, 1.0 equiv) and TEA (2.4 mg, 0.024 mmol, 0.2 equiv) was dissolved in EtOH (2.0 mL). Then solution of C_{60} in toluene was added (50 µL) and the reaction mixture was irradiated with a Blue LED (450 ± 10 nm, 100 W) with continuous stirring at room temperature for 8 days. The progress of the reaction was monitored by TLC. After the complete conversion was achieved, the solvent was removed under reduced pressure. The crudes were purified by column chromatography on silica gel ($CHCl_3$:MeOH 100:1, R_f = 0.1) to afford 33 mg (85 %) of **2t** as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94 (d, J = 7.7 Hz, 1H), 7.66 – 7.54 (m, 1H), 7.52 – 7.40 (m, 3H), 7.25 – 7.16 (m, 1H), 7.09 (dd, J = 9.1, 4.1 Hz, 1H), 5.05 (s, 2H), 2.65 (s, 3H), 2.62 (s7, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 198.01, 198.00, 158.73, 156.32, 152.81, 152.79, 147.91, 133.07, 130.63, 130.50, 123.51, 120.12, 119.89, 117.85, 117.11, 116.87, 115.10, 115.02, 91.51, 82.98, 57.48, 42.32, 31.88.

HRMS-ESI$^+$: m/z $[M+H]^+$ calcd. for $C_{18}H_{16}FO_3S$ 331.0799; found 331.0798.



2u

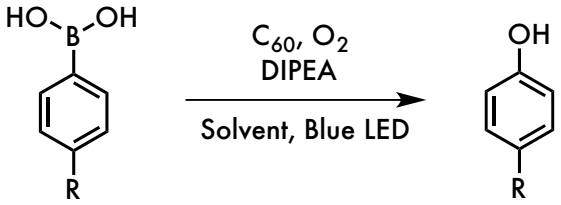
1-(2-(methylsulfinyl)phenyl)pentan-1-one 2u. The product was obtained following the general procedures: a) solvent in the reaction vial was purged with O_2 for 15 minutes. **1u** (33 mg, 0.16 mmol, 1.0 equiv) and TEA (3.2 mg, 0.032 mmol, 0.2 equiv) was dissolved in EtOH (2mL). Then solution of C_{60} in toluene was added (50 µL) and the reaction mixture was irradiated with a Blue LED (450 ± 10 nm, 100 W) with continuous stirring at room temperature for 4 days. The progress of the reaction was monitored by TLC. After the complete conversion was achieved, the solvent was removed under reduced pressure. The crudes were purified by column chromatography on silica gel ($CHCl_3$:MeOH 100:1, R_f = 0.1) to afford 32 mg (90 %) of **2u** as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.36 (d, *J* = 7.8 Hz, 1H), 7.97 (dd, *J* = 7.8, 1.3 Hz, 1H), 7.80 (td, *J* = 7.6, 1.3 Hz, 1H), 7.59 (td, *J* = 7.6, 1.3 Hz, 1H), 2.99 (td, *J* = 7.3, 4.0 Hz, 2H), 2.81 (s, 3H), 1.73 – 1.62 (m, 2H), 1.38 (h, *J* = 7.4 Hz, 2H), 0.92 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 201.14, 150.29, 134.00, 133.76, 130.29, 129.73, 124.65, 44.46, 38.77, 26.28, 22.41, 13.96.

HRMS-ESI^{+}: m/z $[M+H]^+$ calcd. for $C_{12}H_{17}O_2S$ 225.0944; found 225.0944.

Photocatalytic hydroxylation of arylboronic acids to phenols

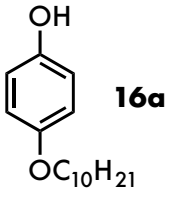


General procedure for photoinduced hydroxylation of arylboronic acids:

a) **Using C_{60} solution in toluene (5.0 mg in 2.0 mL) as a catalyst.** The substrate (0.1 – 0.25 mmol) was dissolved in 2.0 mL of the solvent (EtOH or $CHCl_3$), then DIPEA (2 equiv) and the solution of C_{60} was added (50 µL). The reaction mixture was purged with O_2 for 15 minutes and was irradiated with a Blue LED (450 ± 10 nm, 100 W) with continuous stirring at room temperature. The progress of the reaction was monitored by TLC. After the complete conversion was achieved, the solvent was removed under reduced pressure. The crude was purified by column chromatography on silica gel.

b) **Using C_{60} soot powder as a catalyst.** The substrate (0.1 – 0.25 mmol) was dissolved in 2mL of the solvent (EtOH or $CHCl_3$), then DIPEA (2 equiv) and 1.0 mg of C_{60} soot was added. The reaction mixture was purged with O_2 for 15 minutes and was irradiated with a Blue LED (450 ± 10 nm, 100 W) with continuous stirring at room temperature. The progress of the reaction was monitored by TLC. After the complete conversion was achieved, the solvent was removed under reduced pressure. The crude was purified by column chromatography on silica gel.

c) **Using C_{60} soot suspension in toluene (2.0 mg in 4.0 mL) as a catalyst.** The substrate (0.1 – 0.25 mmol) was dissolved in 2mL of the solvent (EtOH or $CHCl_3$)), then DIPEA (2 equiv) and the suspension of C_{60} soot was added (100 µL). The reaction mixture was purged with O_2 for 15 minutes and was irradiated with a Blue LED (450 ± 10nm, 100W) with continuous stirring at room temperature. The progress of the reaction was monitored by TLC. After the complete conversion was achieved, the solvent was removed under reduced pressure. The crude was purified by column chromatography on silica gel.

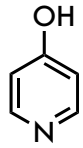


16a

4-Decyloxyphenol 16a. The product was obtained following the general procedures photoinduced hydroxylation of arylboronic acids: a) in EtOH irradiated with a Blue LED for 4 days (yield 96 %) or in $CHCl_3$ irradiated with a Blue Led for 48 hours (yield 48 %); b) in EtOH irradiated

with a Blue Led for 13 days (yield 99 %) or in $CHCl_3$ irradiated with a Blue Led for 48 hours (yield 93 %); c) in EtOH irradiated with a Blue LED for 10 days (yield 89 %) or in $CHCl_3$ irradiated with a Blue LED for 24 hours (yield 59 %). The crudes were purified by column chromatography on silica gel ($CHCl_3$ to $CHCl_3$:MeOH 100:1, R_f = 0.45) to afford **15a** as a white solid.

Spectral data were in accordance with a literature [S12].



16b

Pyridin-4-ol 16b. The product was obtained following the general procedures photoinduced hydroxylation of arylboronic acids: a) in EtOH irradiated with a Blue LED for 48 hours (yield 100 %); b) in EtOH irradiated with a Blue LED for 9 days (yield 63 %); c) in EtOH irradiated with a Blue LED for 9 days (yield 67 %). The crudes were purified by column chromatography on silica gel ($CHCl_3$:MeOH 5:1, R_f = 0.09) to afford **16b** as a white solid.

Spectral data were in accordance with a literature [S13].

Photoinduced oxidative cyclization of *N*,*N*-dimethylaniline with maleimide

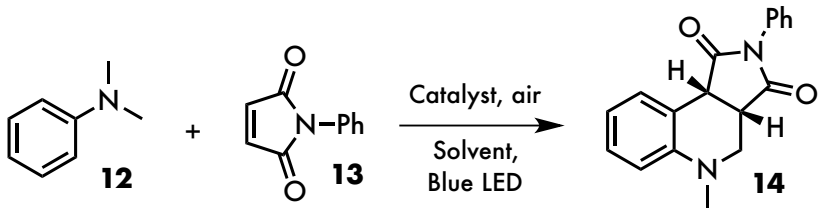


Table S4. Screening of reaction conditions.

Entry	Catalyst	Solvent	Time	Yield (%)
1	C_{60} solution in toluene	EtOH	5 days	75
2	C_{60} soot powder	EtOH	5 days	71
3	C_{60} soot dispersion in toluene	EtOH	4 days	68
4	C_{60} solution in toluene	CH_3CN	2 days	56
5	C_{60} soot powder	CH_3CN	15 days	68
6	C_{60} soot dispersion in toluene	CH_3CN	3 days	51
7	C_{60} solution in toluene	$CHCl_3$	12 days	73
8	C_{60} soot powder	$CHCl_3$	12 days	45
9	C_{60} soot dispersion in toluene	$CHCl_3$	12 days	46

General procedures for (3aS*,9bR*)-5-Methyl-2-phenyl-3a,4,5,9b-tetrahydro-1H-pyrrolo[3,4-c]quinoline-1,3(2H)-dione 14.

a) **Using C_{60} solution in toluene (5.0 mg in 2.0 mL) as a catalyst.** N-Phenylmaleimide (0.2 mmol, 1.0 equiv) and *N*,*N*-dimethylaniline (2.0 equiv) was dissolved in 3mL of the solvent. Then solution of C_{60} was added (50 µL) and the reaction mixture was irradiated with a Blue LED (450 ± 10 nm, 100 W) with continuous stirring at room temperature. The progress of the reaction was monitored by TLC. After the complete conversion was achieved, the solvent was removed under reduced pressure. The crudes were purified by column chromatography on silica gel ($CHCl_3$, R_f = 0.22) to afford **14** as a yellow solid.

b) **Using C_{60} soot powder as a catalyst.** *N*-Phenylmaleimide (0.2 mmol, 1.0 equiv) and N,N-dimethylaniline (2.0 equiv) was dissolved in 3.0 mL of the solvent. Then 1.0 mg of C_{60} soot was added and the reaction mixture was irradiated with a Blue LED (450 ± 10 nm, 100 W) with continuous stirring at room temperature. The progress of the reaction was monitored by TLC. After the complete conversion was achieved, the solvent was removed under reduced pressure. The crudes were purified by column chromatography on silica gel ($CHCl_3$, R_f = 0.22) to afford **14** as a yellow solid.

c) Using C_{60} soot suspension in toluene (2.0 mg in 4.0 mL) as a catalyst N-Phenylmaleimide (0.2 mmol, 1.0 equiv) and *N,N*-dimethylaniline (2.0 equiv) was dissolved in 3.0 mL of the solvent. Then suspension of C_{60} soot was added (100 µL) and the reaction mixture was irradiated with a Blue LED (450 ± 10 nm, 100 W) with continuous stirring at room temperature. The progress of the reaction was monitored by TLC. After the complete conversion was achieved, the solvent was removed under reduced pressure. The crudes were purified by column chromatography on silica gel ($CHCl_3$, R_f = 0.22) to afford **14** as a yellow solid.

Spectral data were in accordance with a literature [S14].

Oxidative cyanation of *N*-phenyltetrahydroisoquinoline

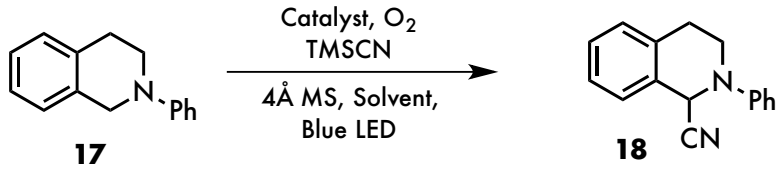


Table S5. Screening of reaction conditions.

Entry	Catalyst	Solvent	Time	Yield (%)
1	C_{60} solution in toluene	EtOH	1 day	70
2	C_{60} soot powder	EtOH	17 days	86
3	C_{60} soot dispersion in toluene	EtOH	17 days	74
4	C_{60} solution in toluene	CH_3CN	2 days	63
5	C_{60} soot powder	CH_3CN	-	0
6	C_{60} soot dispersion in toluene	CH_3CN	6 days	52
7	C_{60} solution in toluene	$CHCl_3$	-	0
8	C_{60} soot powder	$CHCl_3$	7 days	84
9	C_{60} soot dispersion in toluene	$CHCl_3$	2 days	65

General procedures for 2-phenyl-1,2,3,4-tetrahydroisoquinoline-1-carbonitrile 18.

a) Using C_{60} solution in toluene (5.0 mg in 2.0 mL) as a catalyst. 2-phenyl-1,2,3,4-tetrahydroisoquinoline (0.16 mmol, 1.0 equiv) and TMSCN (2.5 equiv) was dissolved in 3mL of the solvent. Then activated molecular sieves 4 Å and the solution of C_{60} (50 µL) was added. The reaction mixture was purged with O_2 for 15 minutes and was irradiated with a Blue LED (450 ± 10 nm, 100 W) with continuous stirring at room temperature. The progress of the reaction was monitored by TLC. After the complete conversion was achieved, the solvent

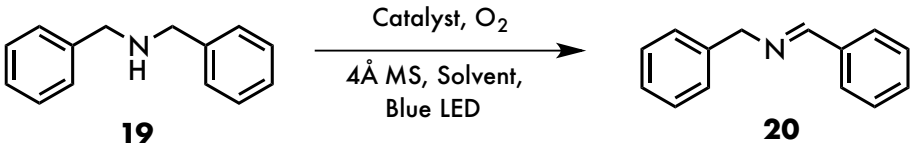
was removed under reduced pressure. The crudes were purified by column chromatography on silica gel (PE:EA 40:1, R_f = 0.17) to afford **18** as a yellow oil.

b) Using C_{60} soot powder as a catalyst. 2-phenyl-1,2,3,4-tetrahydroisoquinoline (0.16 mmol, 1.0 equiv) and TMSCN (2.5 equiv) was dissolved in 3.0 mL of the solvent. Then activated molecular sieves 4 Å and the C_{60} soot (1 mg) was added. The reaction mixture was purged with O_2 for 15 minutes and was irradiated with a Blue LED (450 ± 10 nm, 100 W) with continuous stirring at room temperature. The progress of the reaction was monitored by TLC. After the complete conversion was achieved, the solvent was removed under reduced pressure. The crudes were purified by column chromatography on silica gel (PE:EA 40:1, R_f =0.17) to afford **18** as a yellow oil.

c) Using C_{60} soot suspension in toluene (2.0 mg in 4.0 mL) as a catalyst 2-phenyl-1,2,3,4-tetrahydroisoquinoline (0.16 mmol, 1.0 equiv) and TMSCN (2.5 equiv) was dissolved in 3.0 mL of the solvent. Then activated molecular sieves 4 Å and the suspension of C_{60} soot (100 µL) was added. The reaction mixture was purged with O_2 for 15 minutes and was irradiated with a Blue LED (450 ± 10 nm, 100 W) with continuous stirring at room temperature. The progress of the reaction was monitored by TLC. After the complete conversion was achieved, the solvent was removed under reduced pressure. The crudes were purified by column chromatography on silica gel (PE:EA 40:1, R_f = 0.17) to afford **18** as a yellow oil.

Spectral data were in accordance with a literature [S15].

Oxidation of secondary benzylamines to imines



19 **20**

Table S6. Screening of reaction conditions.

Entry	Catalyst	Solvent	Time	Yield (%)
1	C_{60} solution in toluene	EtOH	3 day	88
2	C_{60} soot powder	EtOH	-	0
3	C_{60} soot dispersion in toluene	EtOH	-	0
4	C_{60} solution in toluene	CH_3CN	3 days	86
5	C_{60} soot powder	CH_3CN	-	0
6	C_{60} soot dispersion in toluene	CH_3CN	17 days	85
7	C_{60} solution in toluene	$CHCl_3$	1 day	100
8	C_{60} soot powder	$CHCl_3$	4 days	78

9	C_{60} soot dispersion in toluene	$CHCl_3$	8 days	91

General procedures for oxidation of dibenzylamine 20.

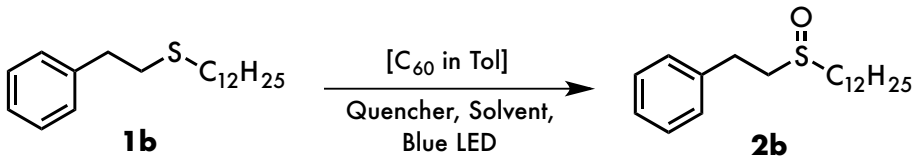
a) **Using C_{60} solution in toluene (5.0 mg in 2.0 mL) as a catalyst.** Dibenzylamine (0.16 mmol) was dissolved in 3.0 mL of the solvent. Then activated molecular sieves 4 Å and the solution of C_{60} (50 µL) was added. The reaction mixture was purged with O_2 for 15 minutes and was irradiated with a Blue LED (450 ± 10 nm, 100 W) with continuous stirring at room temperature. The progress of the reaction was monitored by TLC. After the complete conversion was achieved, the solvent was removed under reduced pressure to afford **20** as a yellow oil.

b) **Using C_{60} soot powder as a catalyst.** Dibenzylamine (0.16 mmol) dissolved in 3mL of the solvent. Then activated molecular sieves 4 Å and the C_{60} soot (1.0 mg) was added. The reaction mixture was purged with O_2 for 15 minutes and was irradiated with a Blue LED (450 ± 10 nm, 100 W) with continuous stirring at room temperature. The progress of the reaction was monitored by TLC. After the complete conversion was achieved, the solvent was removed under reduced pressure to afford **20** as a yellow oil.

c) **Using C_{60} soot suspension in toluene (2.0 mg in 4.0 mL) as a catalyst** Dibenzylamine (0.16 mmol) was dissolved in 3.0 mL of the solvent. Then activated molecular sieves 4 Å and the suspension of C_{60} soot (100 µL) was added. The reaction mixture was purged with O_2 for 15 minutes and was irradiated with a Blue LED (450 ± 10 nm, 100 W) with continuous stirring at room temperature. The progress of the reaction was monitored by TLC. After the complete conversion was achieved, the solvent was removed under reduced pressure to afford **20** as a yellow oil.

Spectral data were in accordance with a literature [S16].

S2. Control and mechanistic experiments



1b **2b**

Table S7. Control experiments of sulfoxidation.

Entry	Catalyst	Solvent	O_2	Quencher	Yield (%)
1	+	EtOH	+	none	99
2	-	EtOH	+	-	0

3	+	anhyd. EtOH	+ (air)	-	67
4	+	anhyd. EtOH	- (Ar)	-	19
5	+	CH_3CN	+	-	60
6	+	anhyd. CH_3CN	-	-	0
7	+	Toluene	+	-	31
8	+	EtOH	+	2 equiv. TEMPO	29
9	+	EtOH	+	2 equiv. DABCO	41
10	+	EtOH	+	2 equiv. 1,4-benzoquinone	31
11	+	EtOH	+	2 equiv hydroquinone	50
12	+	EtOH	+	6mol% $Co(acac)_3$	41
13	+(FS)	CH_3CN	+	1 equiv. 1,4-dimethoxybenzene	35
14	+(FS)	CH_3CN	+	6mol% $Co(acac)_3$	60

S3. SEM and Raman spectroscopy

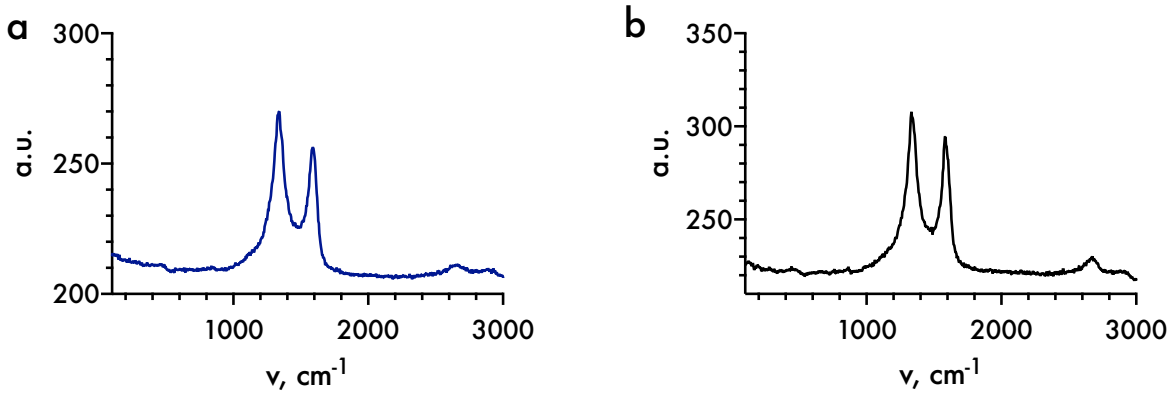


Figure S1. Raman spectra of fullerene soot (a) before use and (b) after 10 cycles.

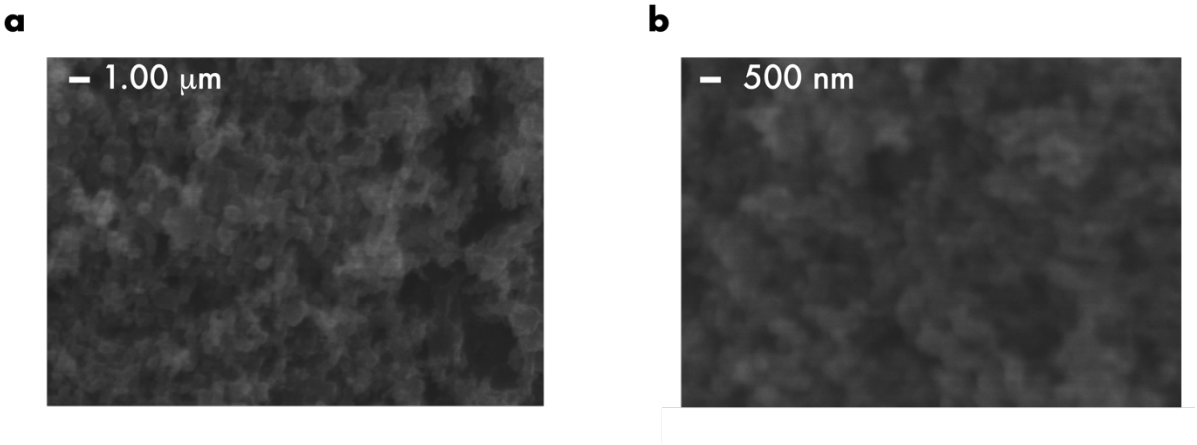


Figure S2. SEM image of fullerene soot: (a) commercial material and (b) from toluene suspension. Significant particle size reduction is observed after stirring fullerene soot in toluene.

Copies of NMR spectra

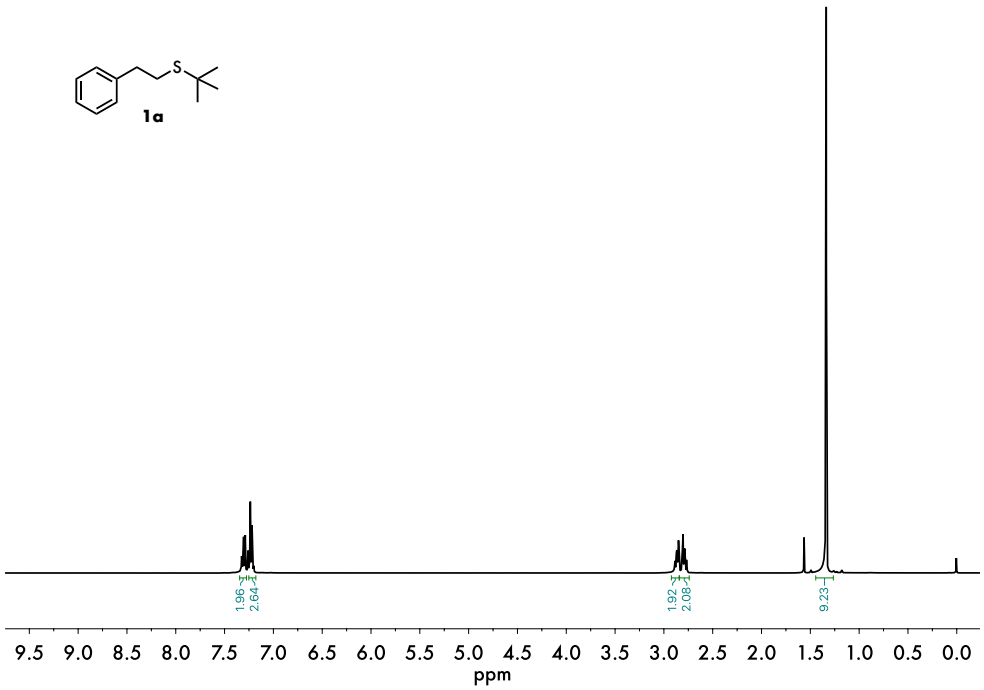


Figure S3. ^{1}H NMR spectrum of **1a**.

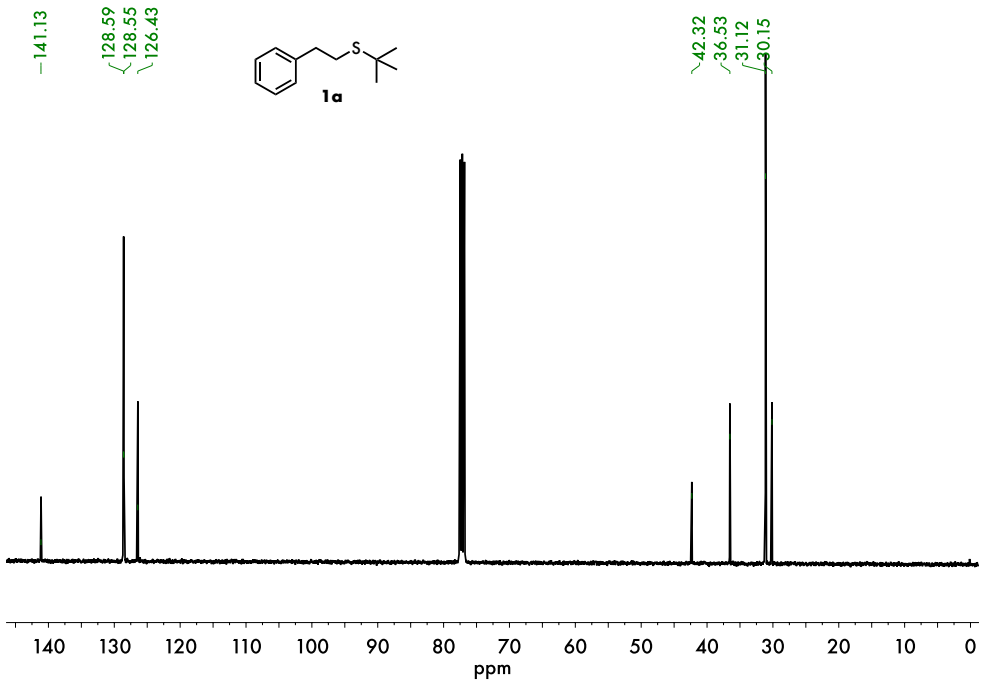


Figure S4. ^{13}C NMR spectrum of **1a**.

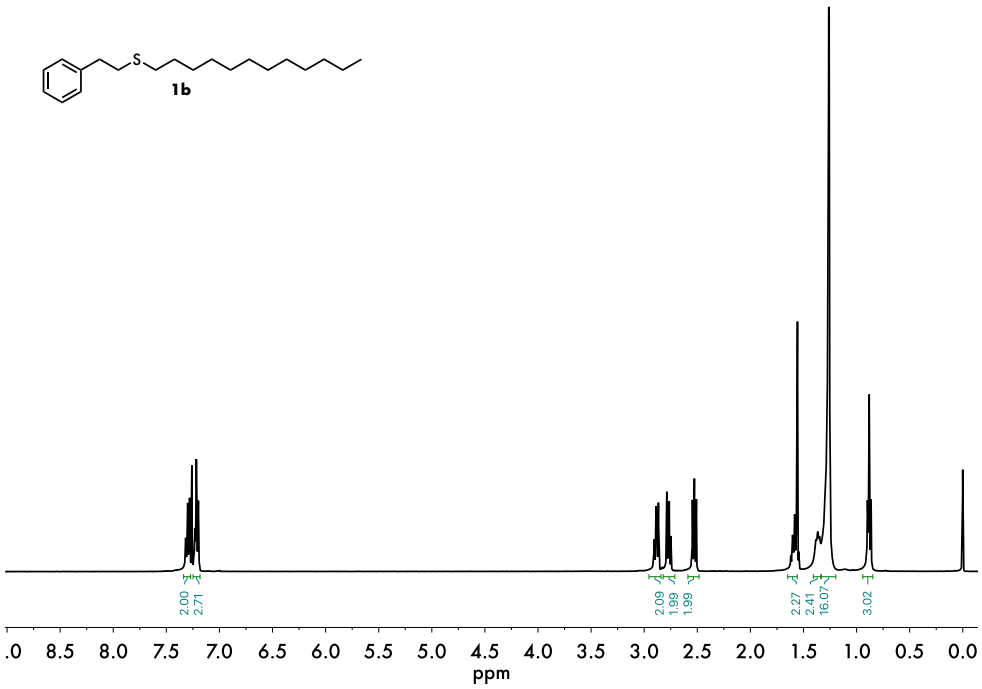


Figure S5. ^{1}H NMR spectrum of **1b**.

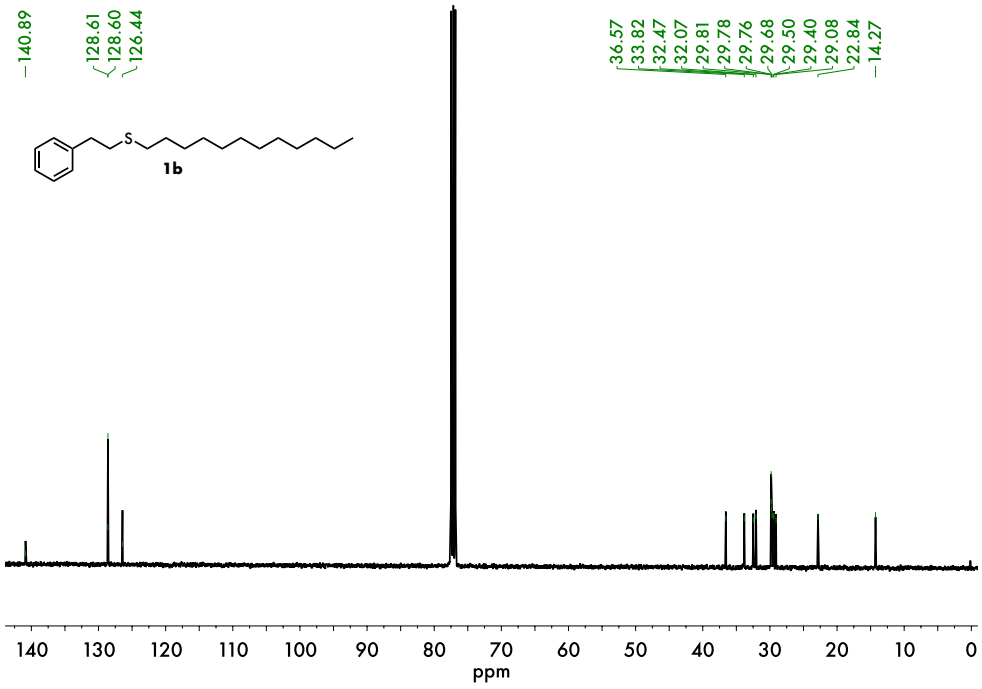


Figure S6. ^{13}C NMR spectrum of **1b**.

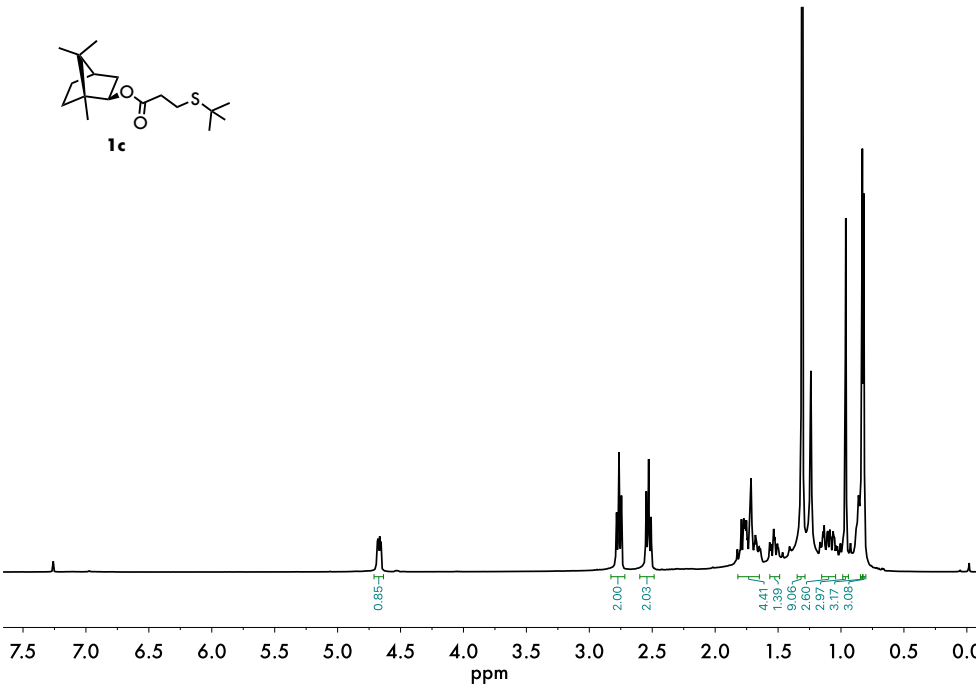


Figure S7. ^{1}H NMR spectrum of **1c**.

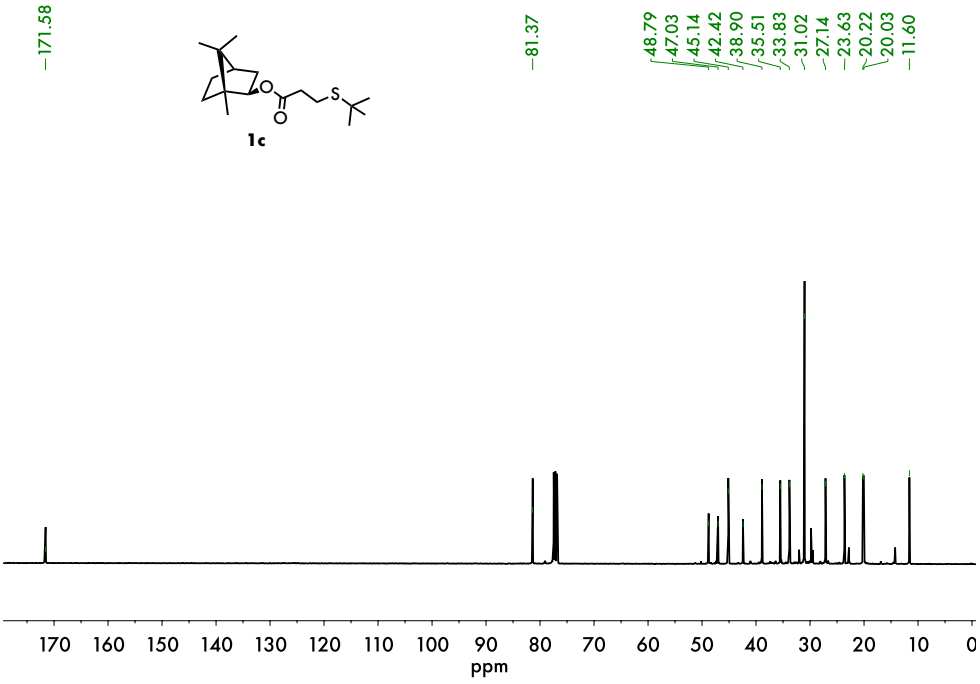


Figure S8. ^{13}C NMR spectrum of **1c**.

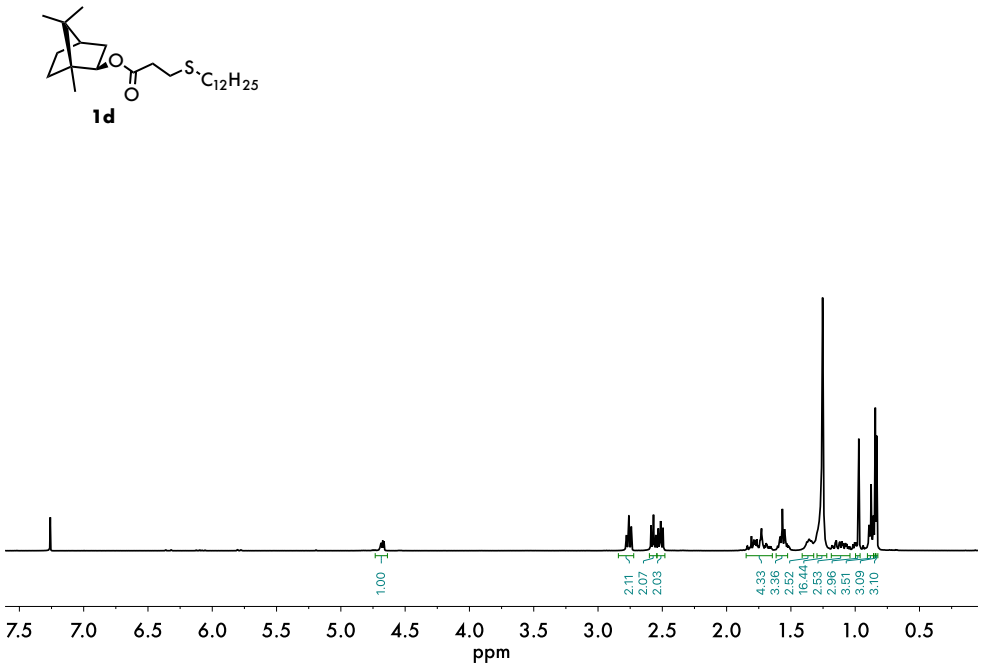


Figure S9. ^{1}H NMR spectrum of **1d**.

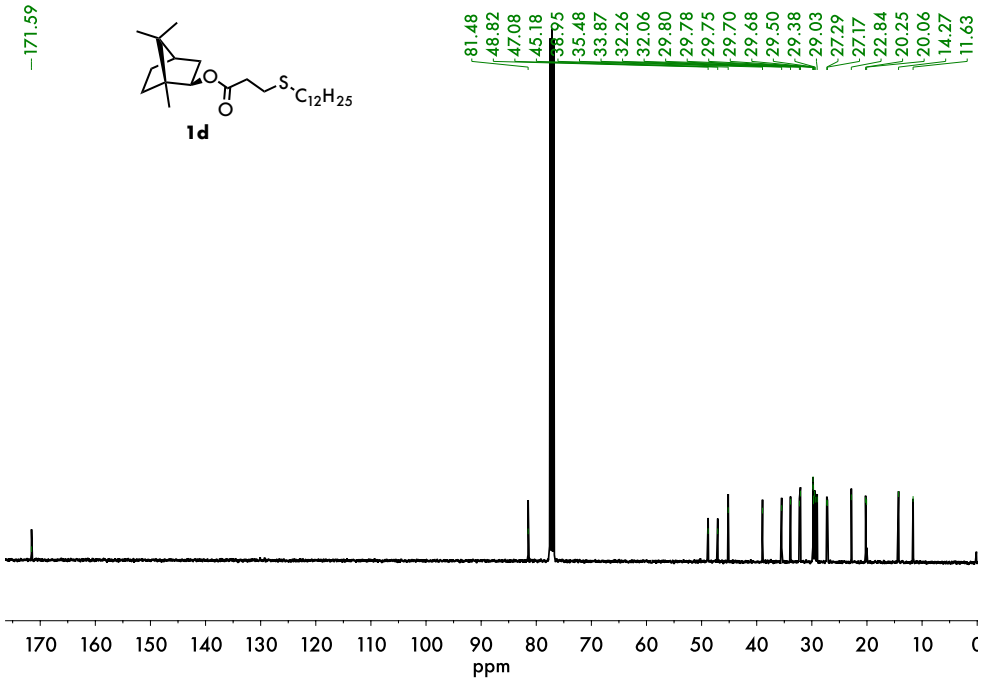


Figure S10. ^{13}C NMR spectrum of **1d**.

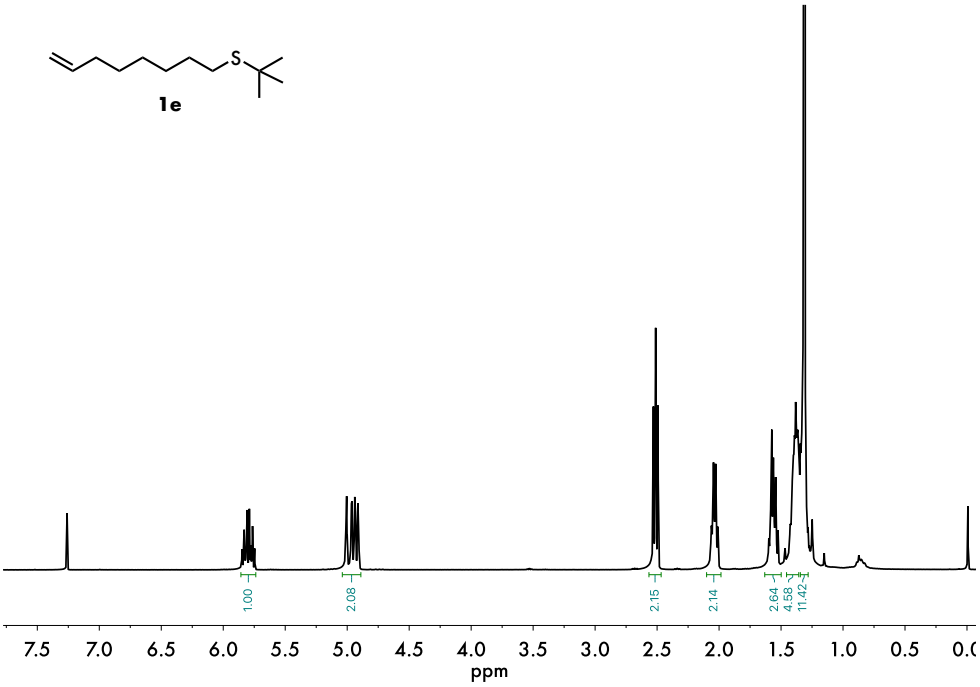


Figure S11. ^{1}H NMR spectrum of **1e**.

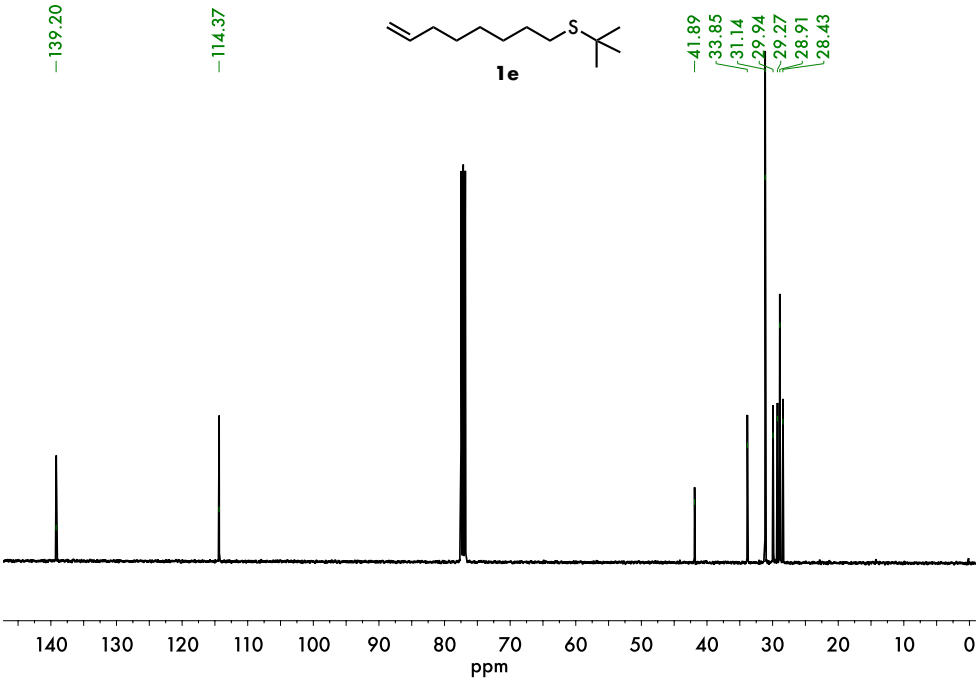


Figure S12. ^{13}C NMR spectrum of **1e**.

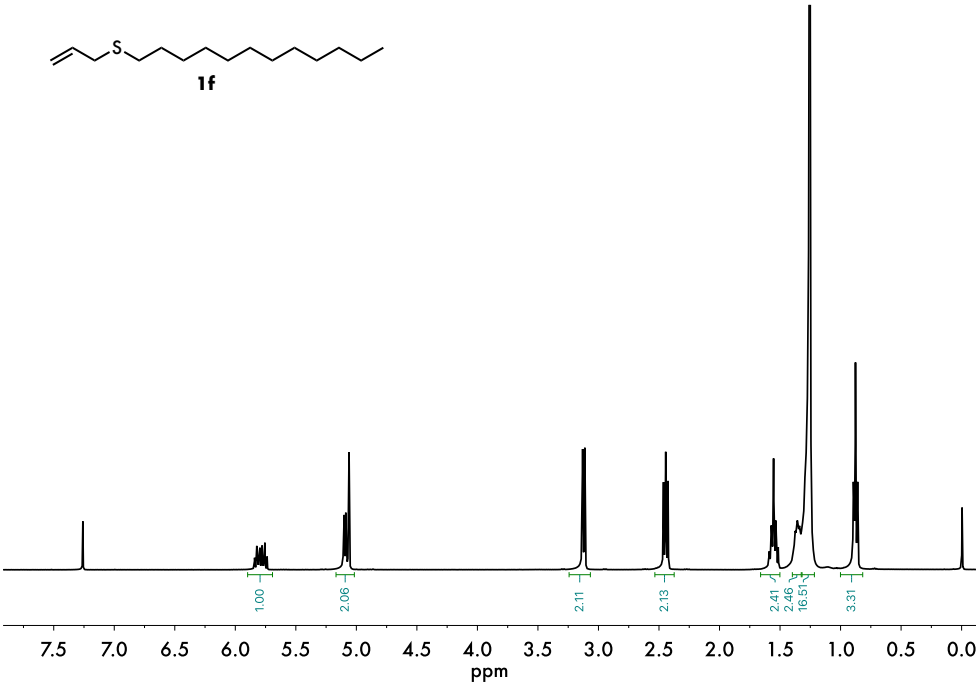


Figure S13. ^{1}H NMR spectrum of **1f**.

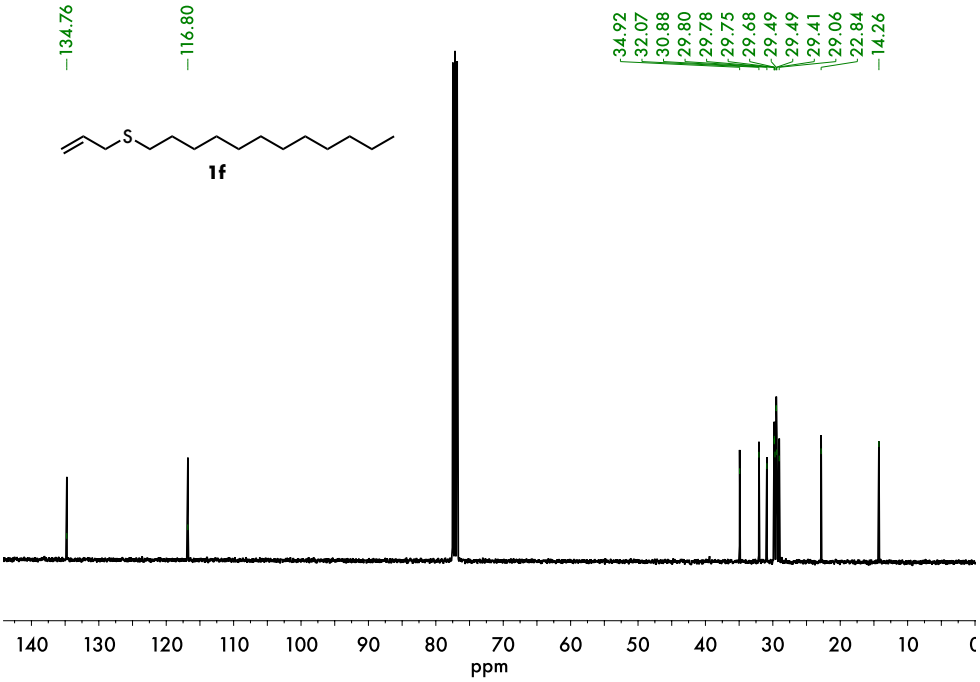


Figure S14. ^{13}C NMR spectrum of **1f**.

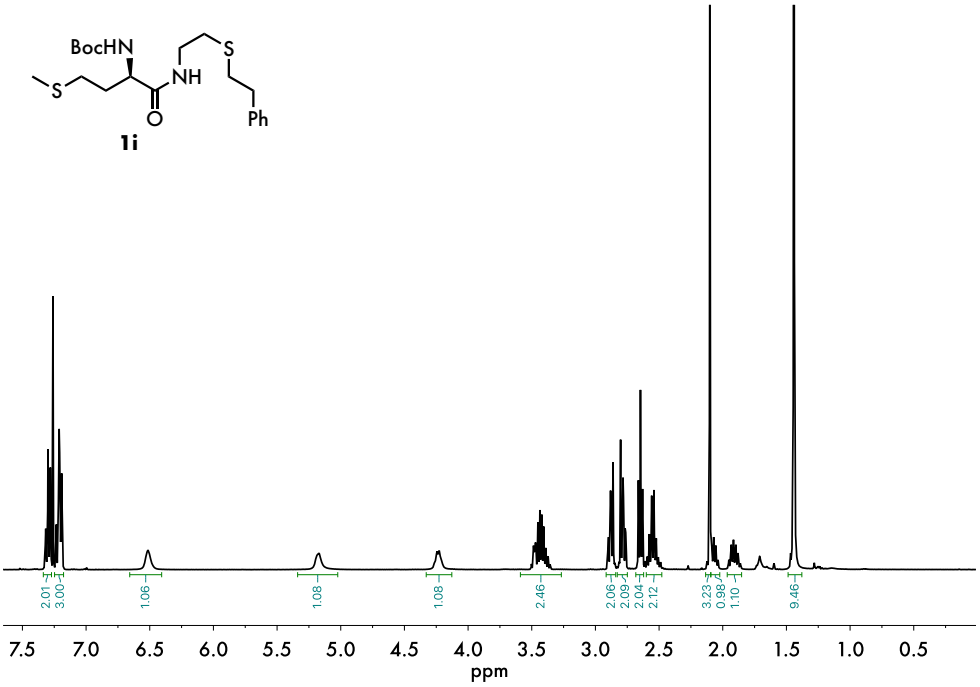


Figure S15. ^{1}H NMR spectrum of **1i**.

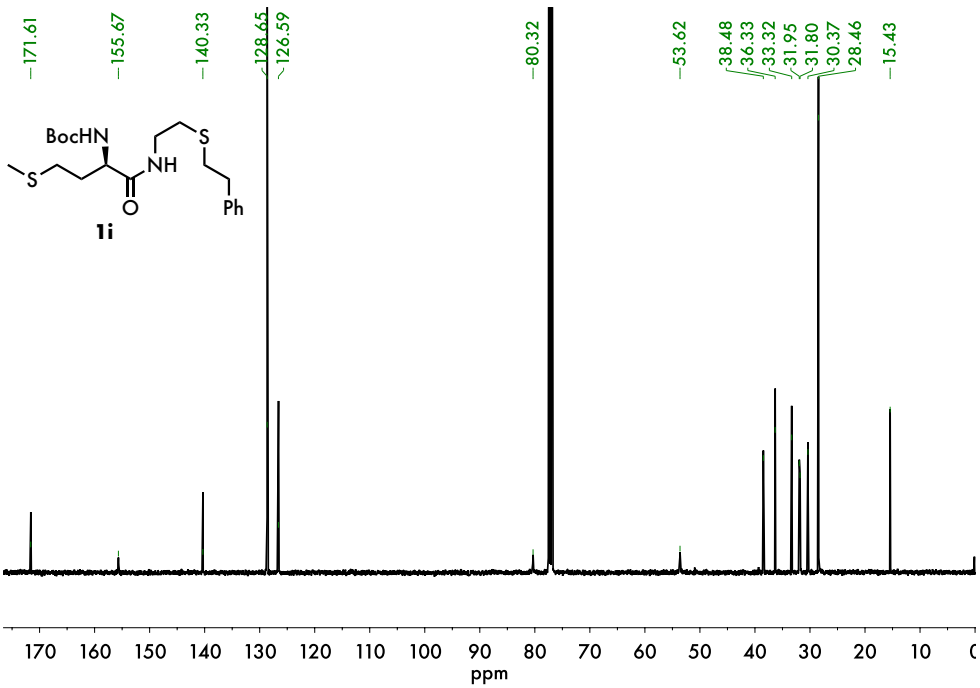


Figure S16. ^{13}C NMR spectrum of **1i**.

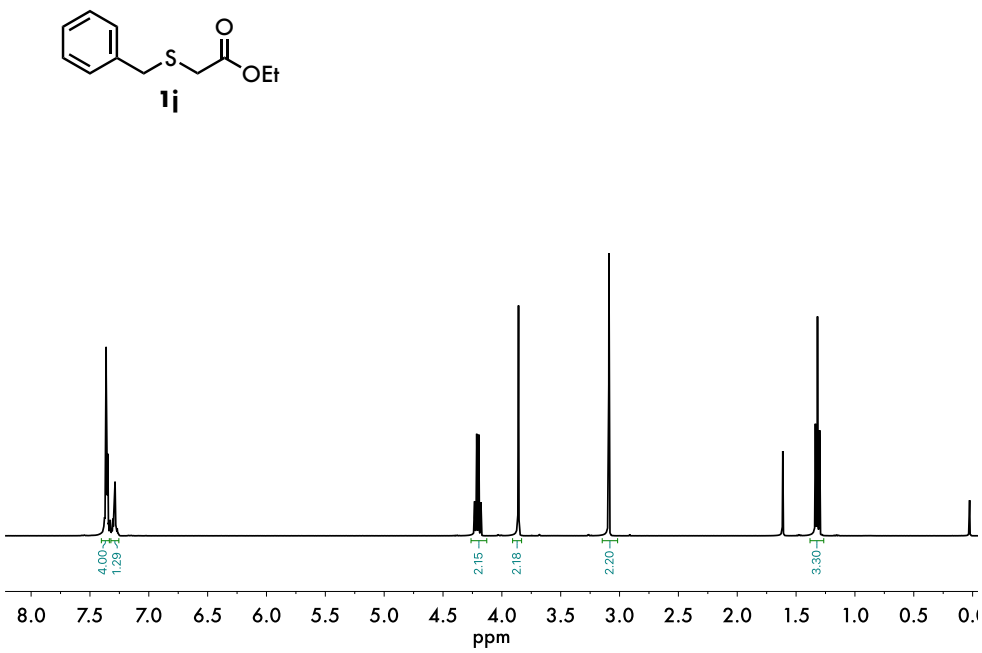


Figure S17. ^{1}H NMR spectrum of **1j**.

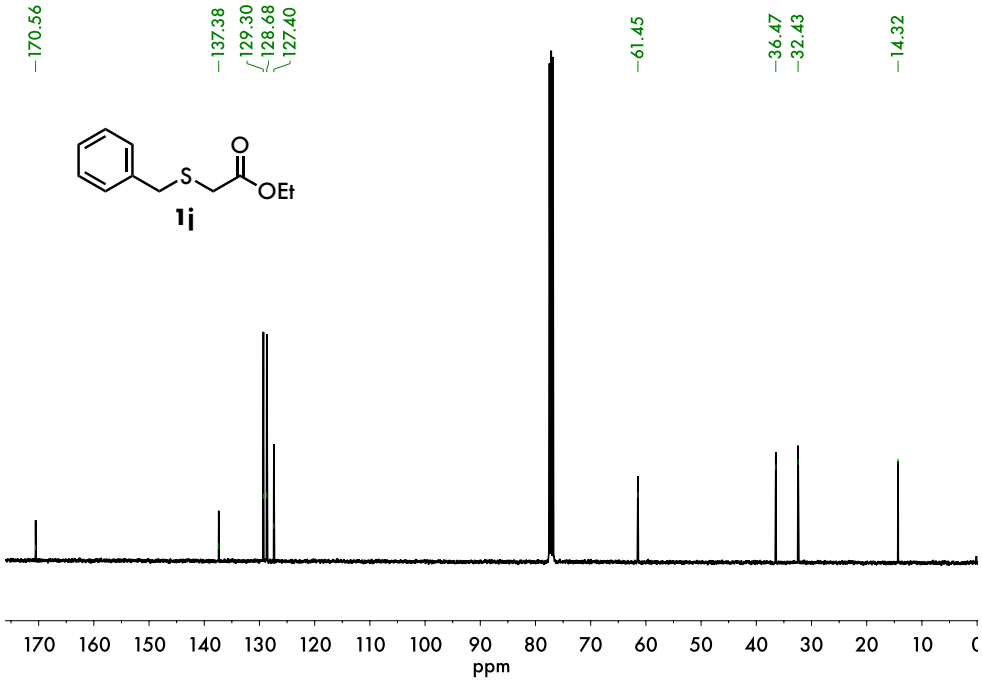


Figure S18. ^{13}C NMR spectrum of **1j**.

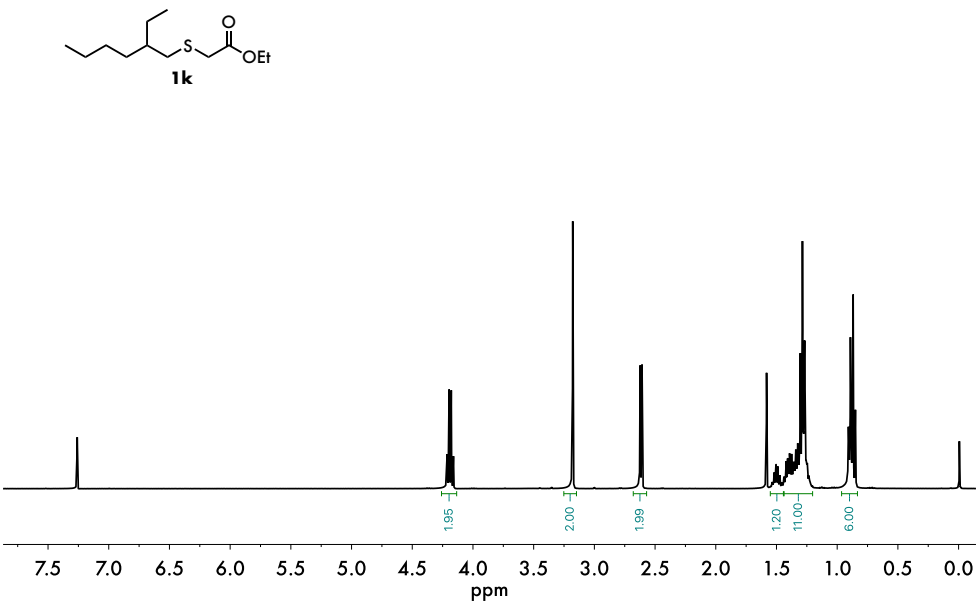


Figure S19. ^{1}H NMR spectrum of **1k**.

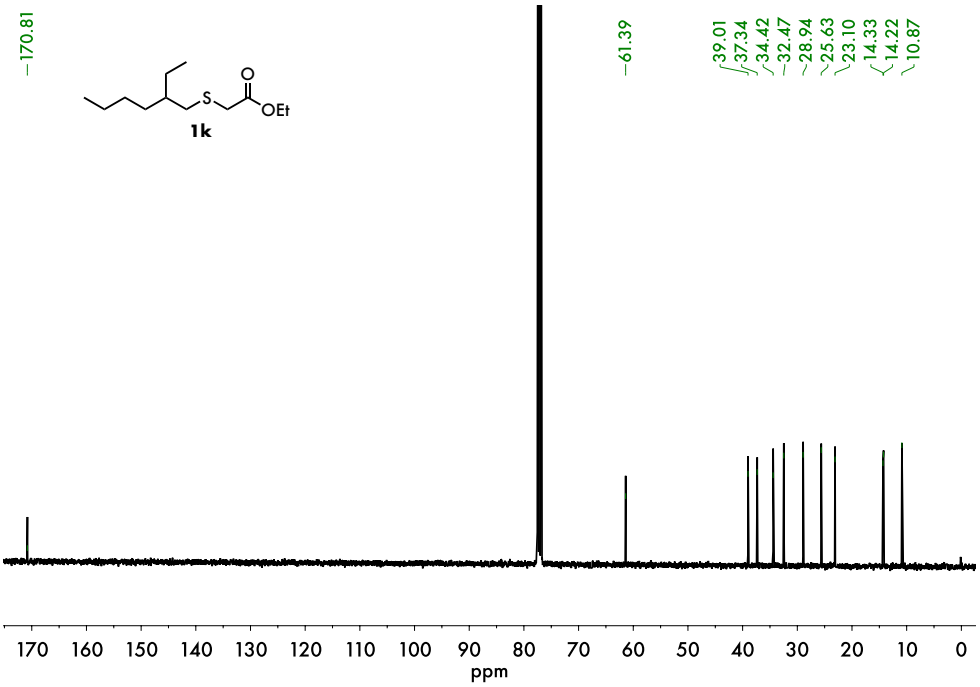


Figure S20. ^{13}C NMR spectrum of **1k**.

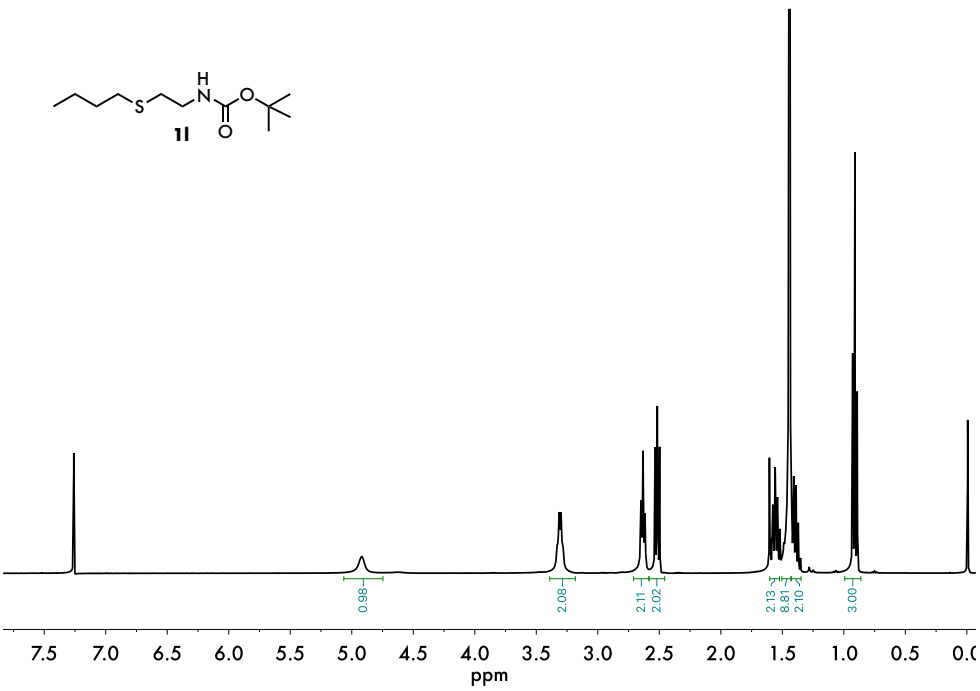


Figure S21. ^{1}H NMR spectrum of **1l**.

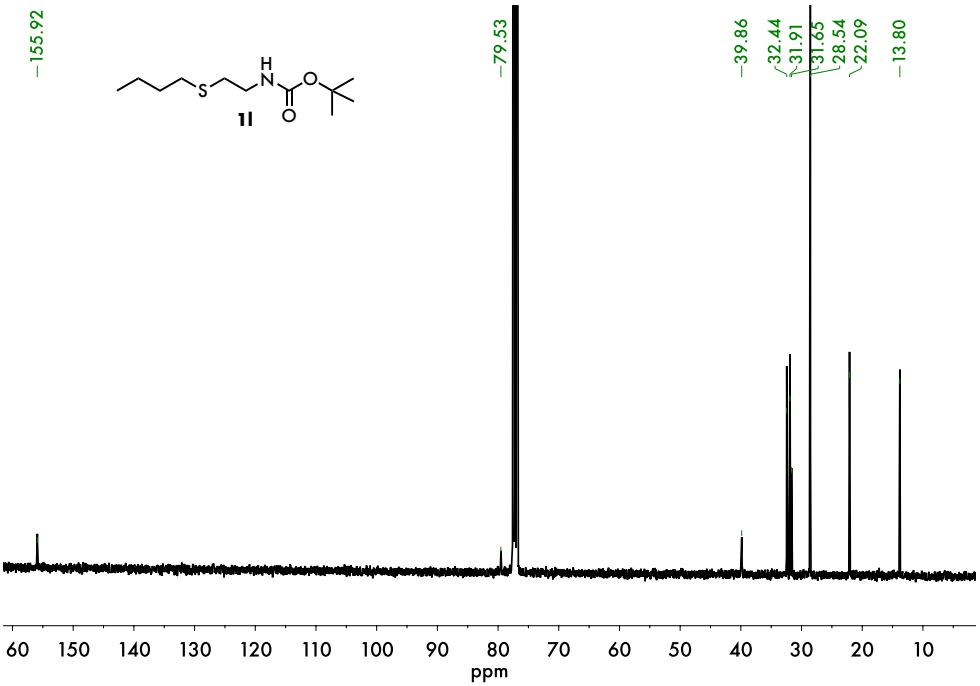


Figure S22. ^{13}C NMR spectrum of **1l**.

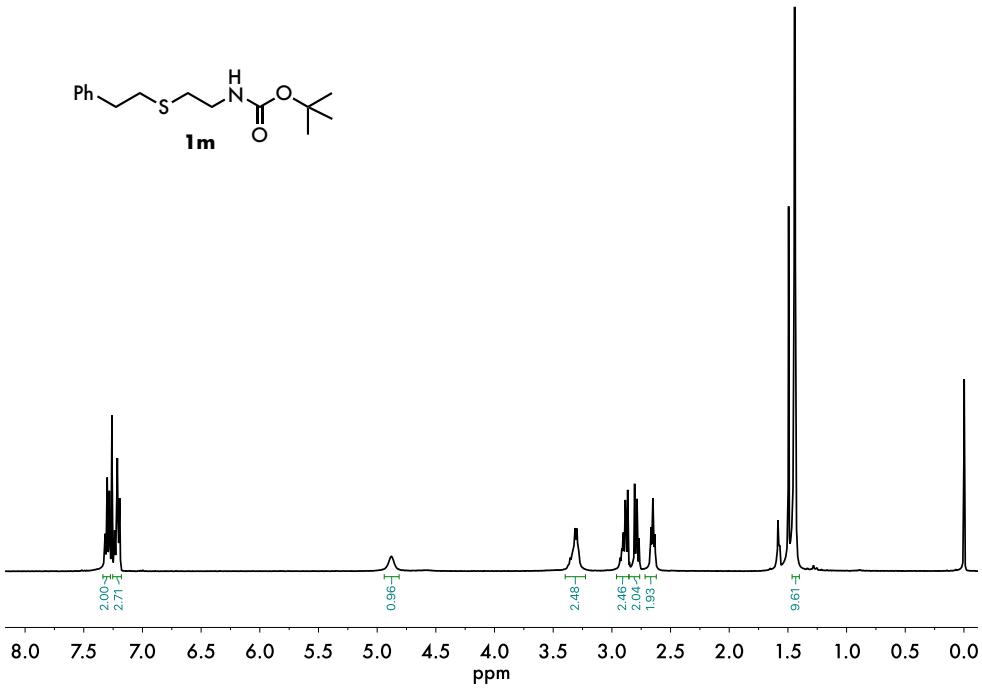


Figure S23. ^{1}H NMR spectrum of **1m**.

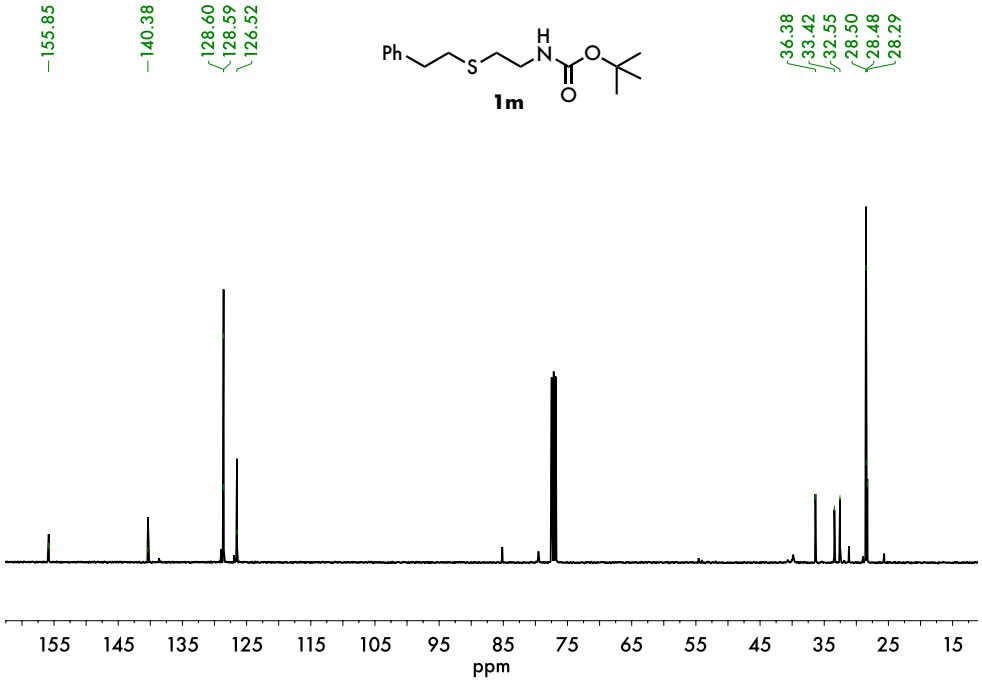


Figure S24. ^{13}C NMR spectrum of **1m**.

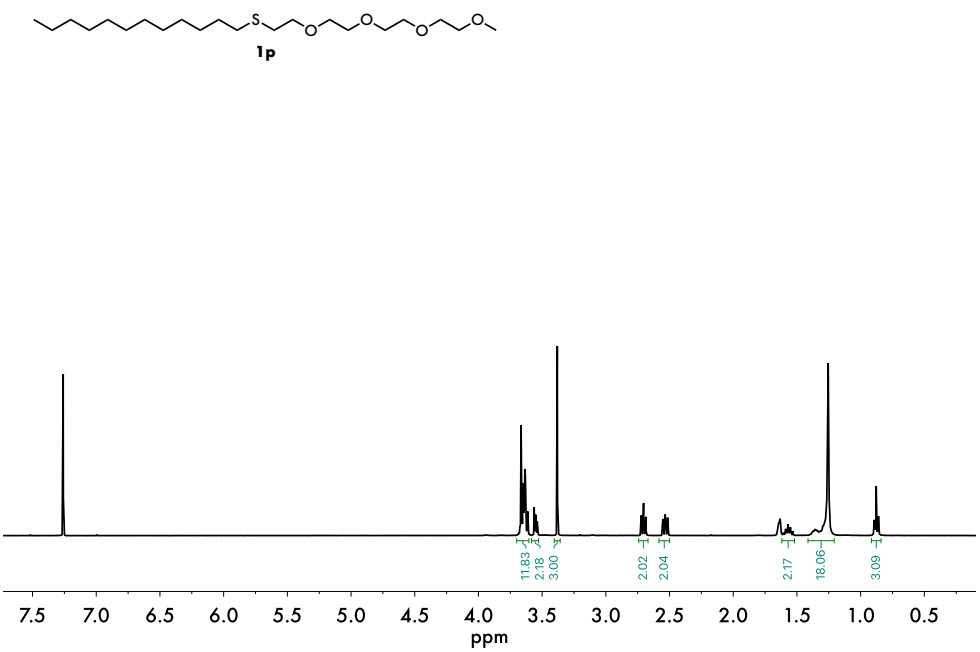


Figure S25. ^{1}H NMR spectrum of **1p**.

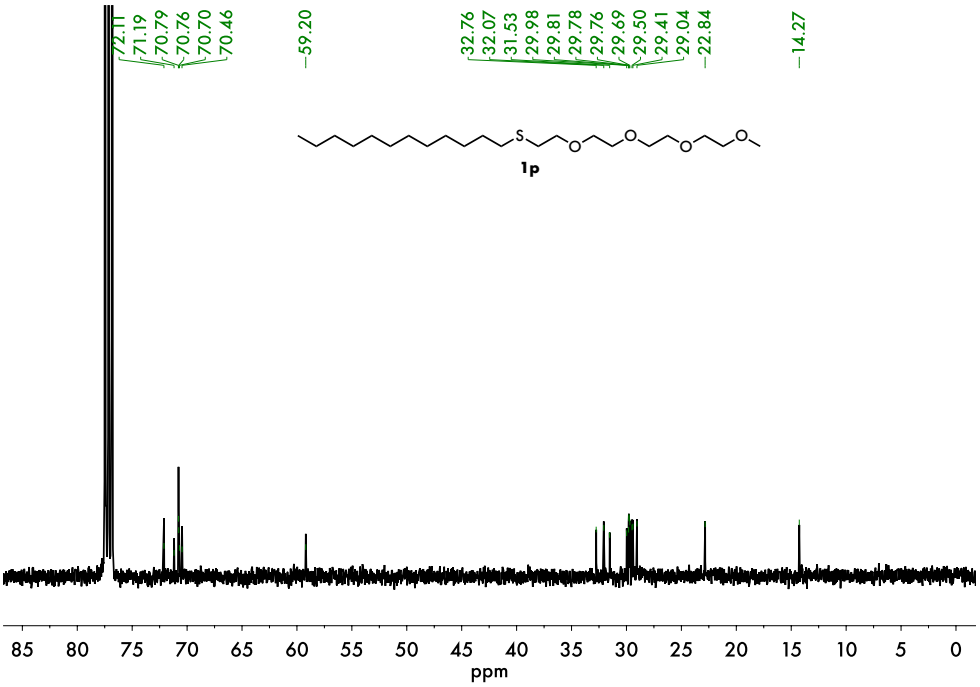


Figure S26. ^{13}C NMR spectrum of **1p**.

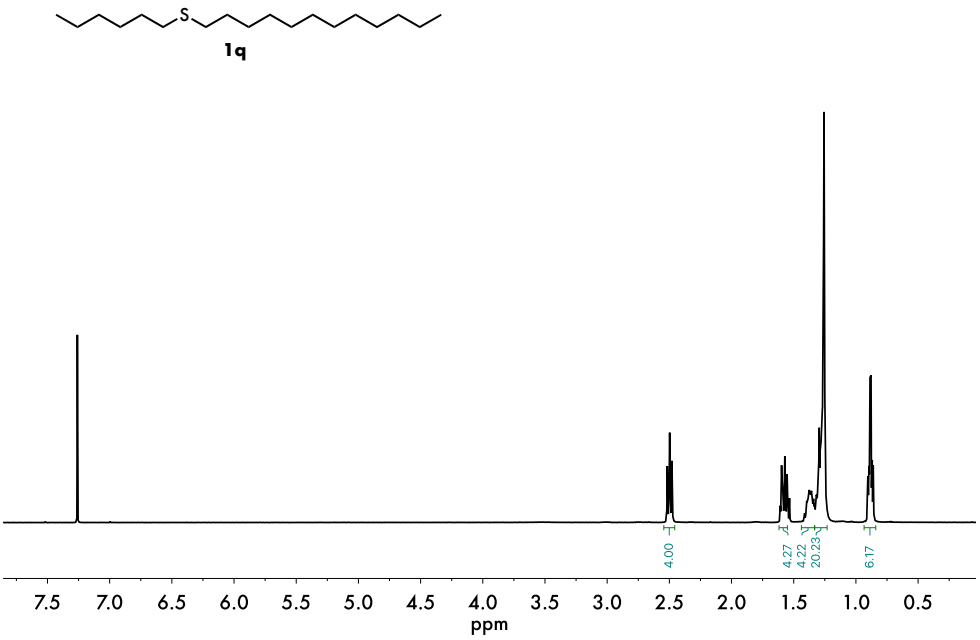


Figure S27. ^{1}H NMR spectrum of **1q**.

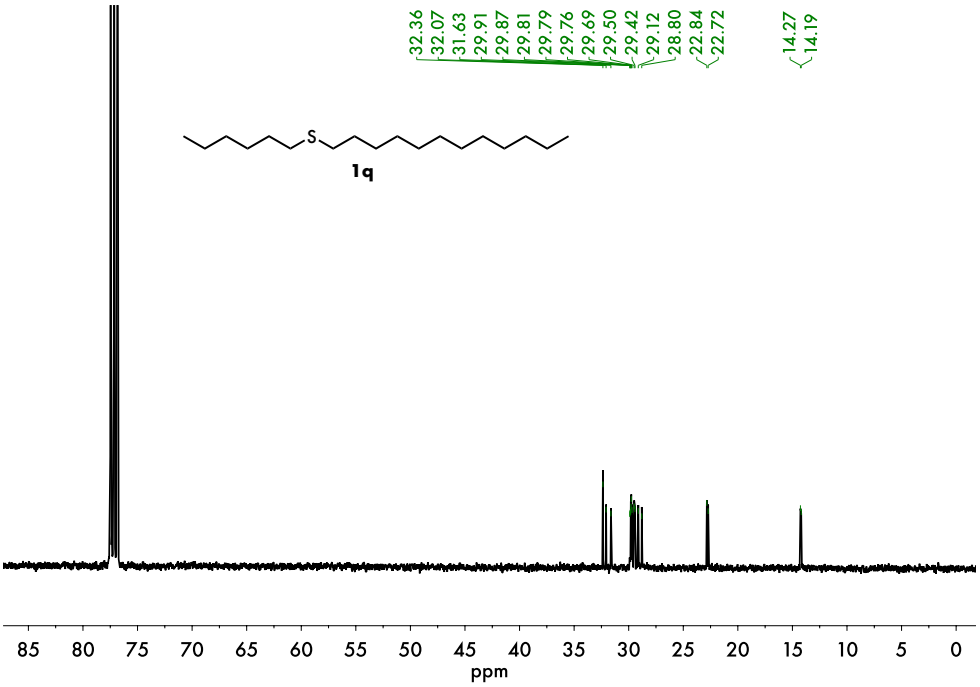


Figure S28. ^{13}C NMR spectrum of **1q**.

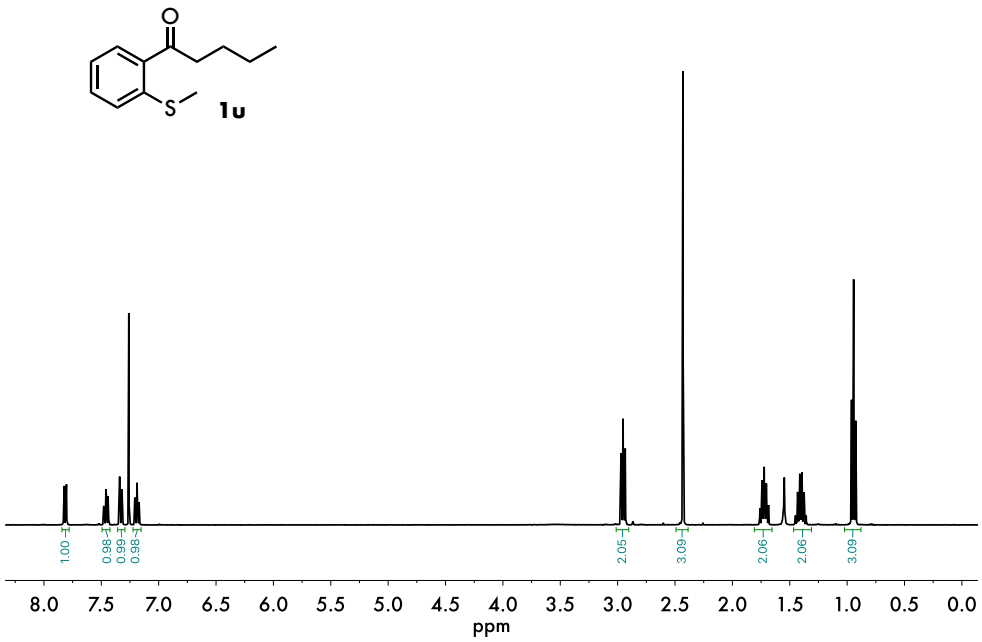


Figure S29. ^{1}H NMR spectrum of **1u**.

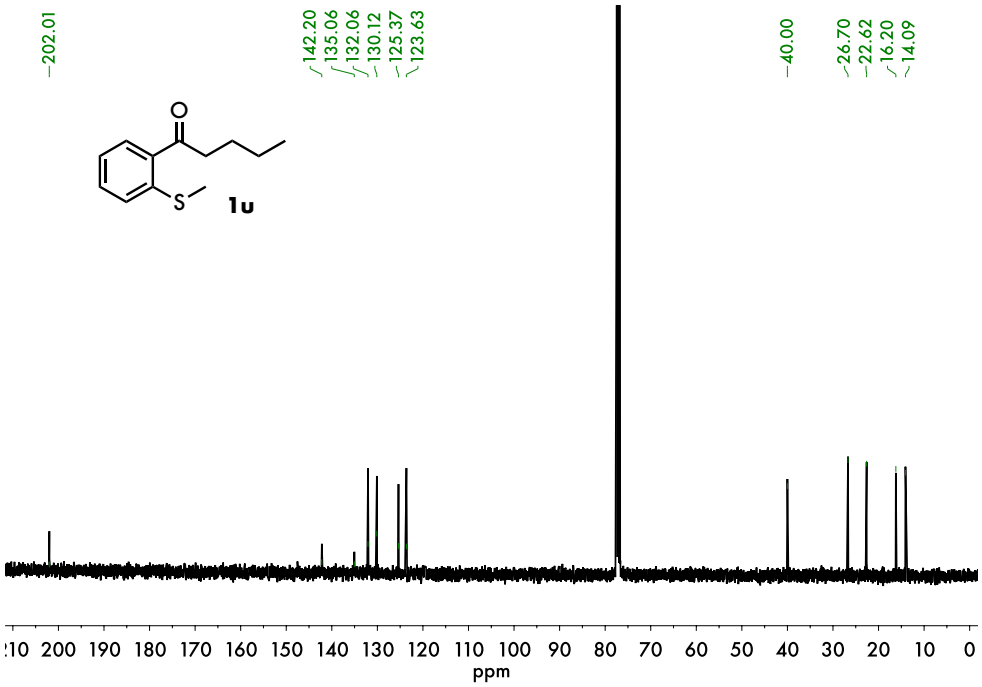


Figure S30. ^{13}C NMR spectrum of **1u**.

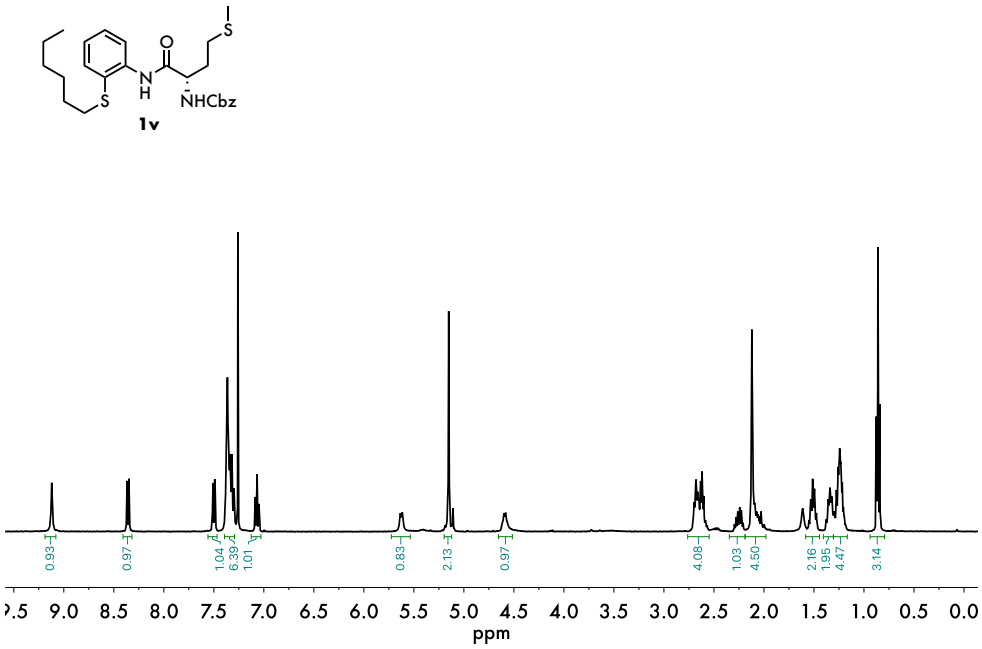


Figure S31. ^{1}H NMR spectrum of **1v**.

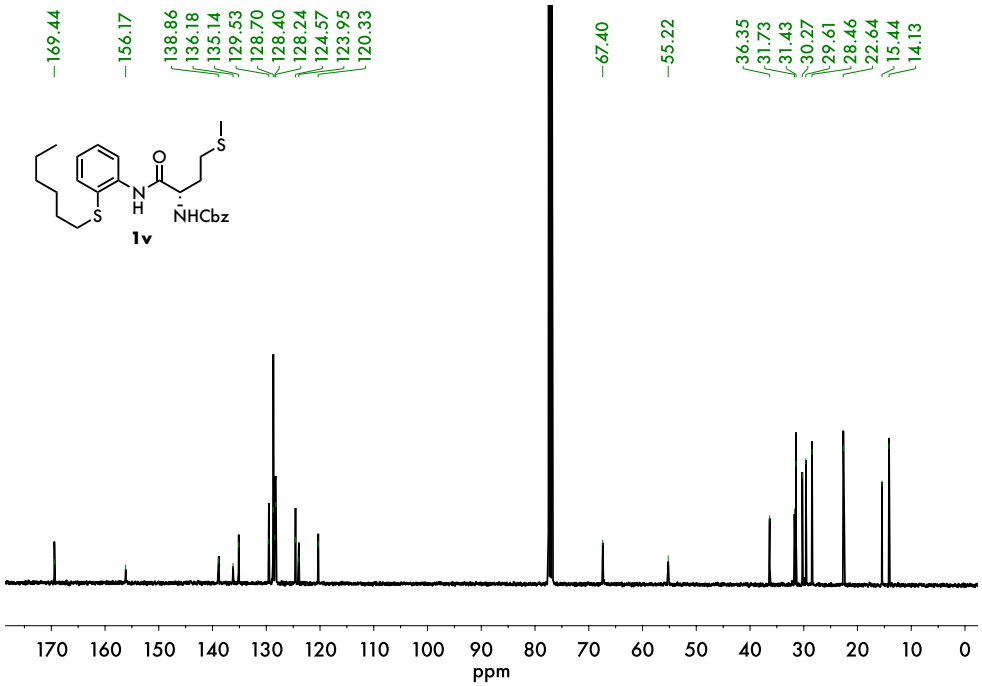


Figure S32. ^{13}C NMR spectrum of **1v**.

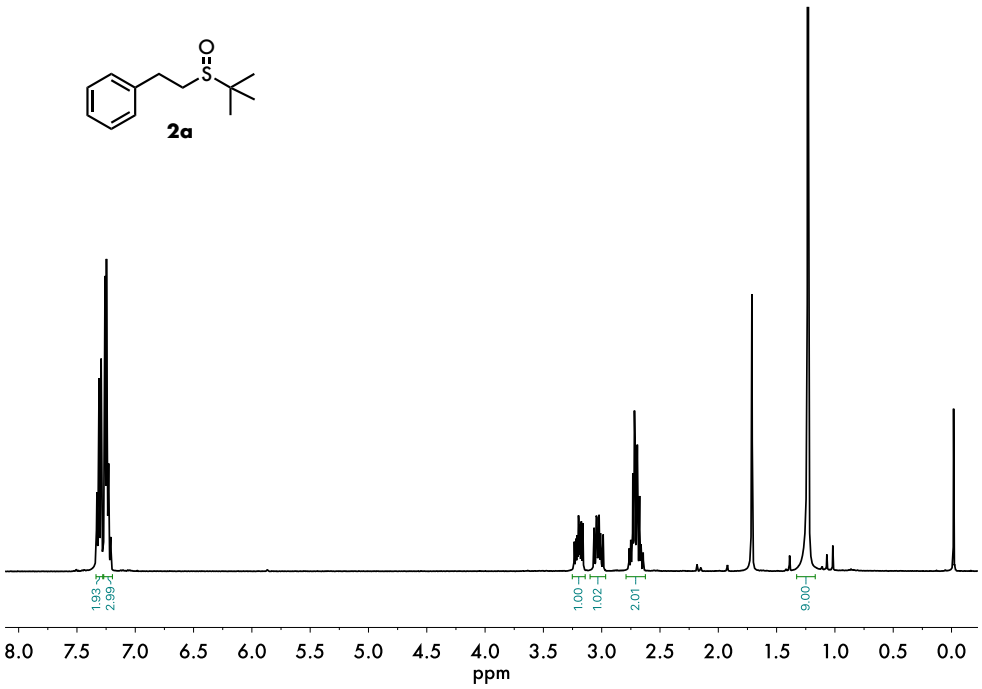


Figure S33. ^{1}H NMR spectrum of **2a**.

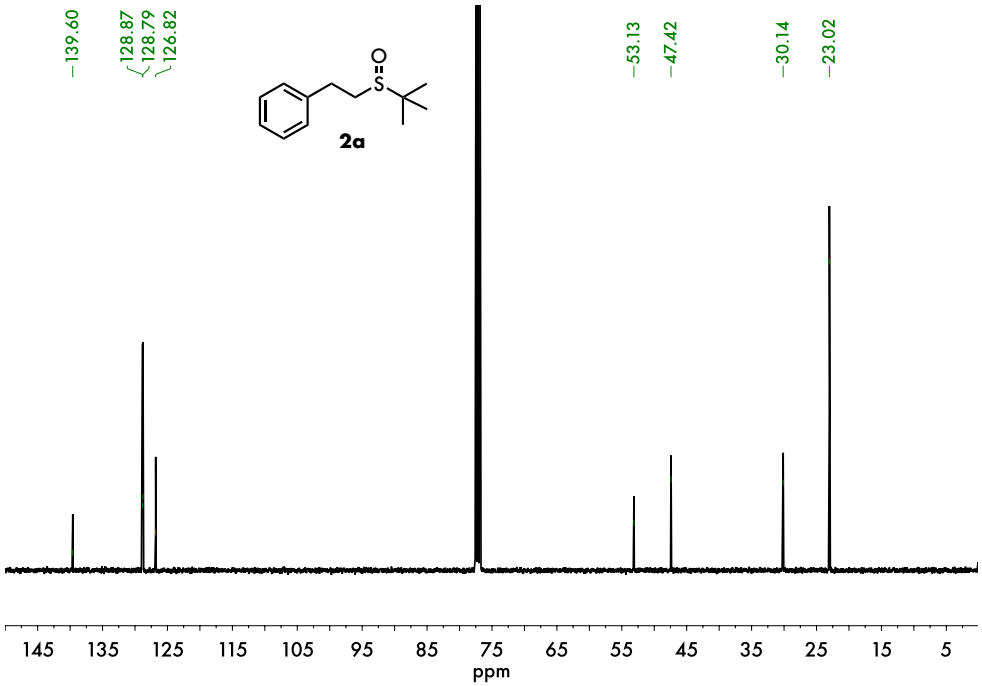


Figure S34. ^{13}C NMR spectrum of **2a**.

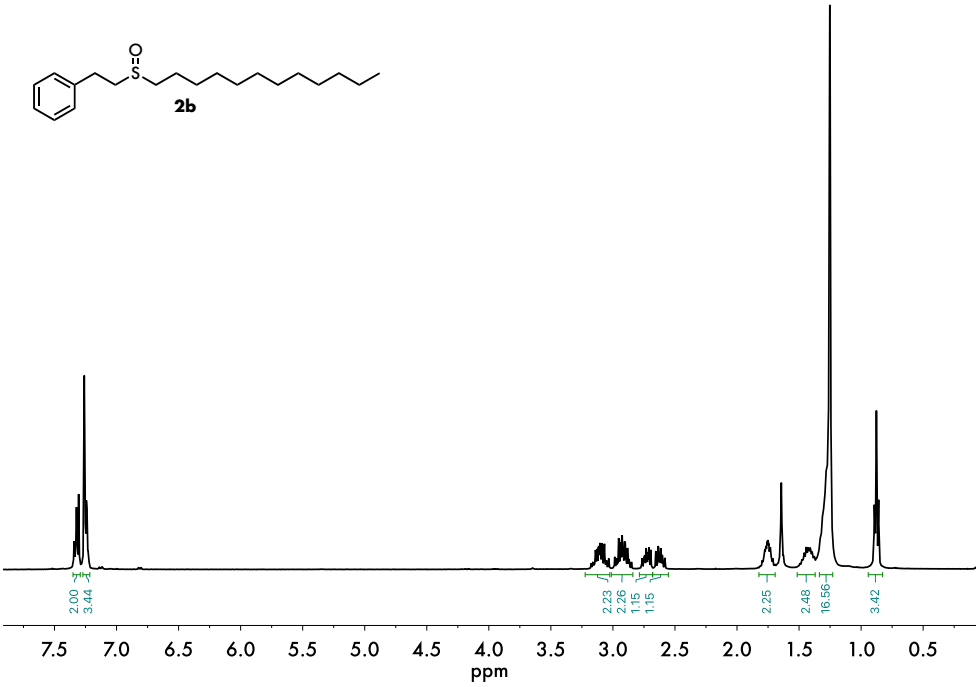


Figure S35. ^{1}H NMR spectrum of **2b**.

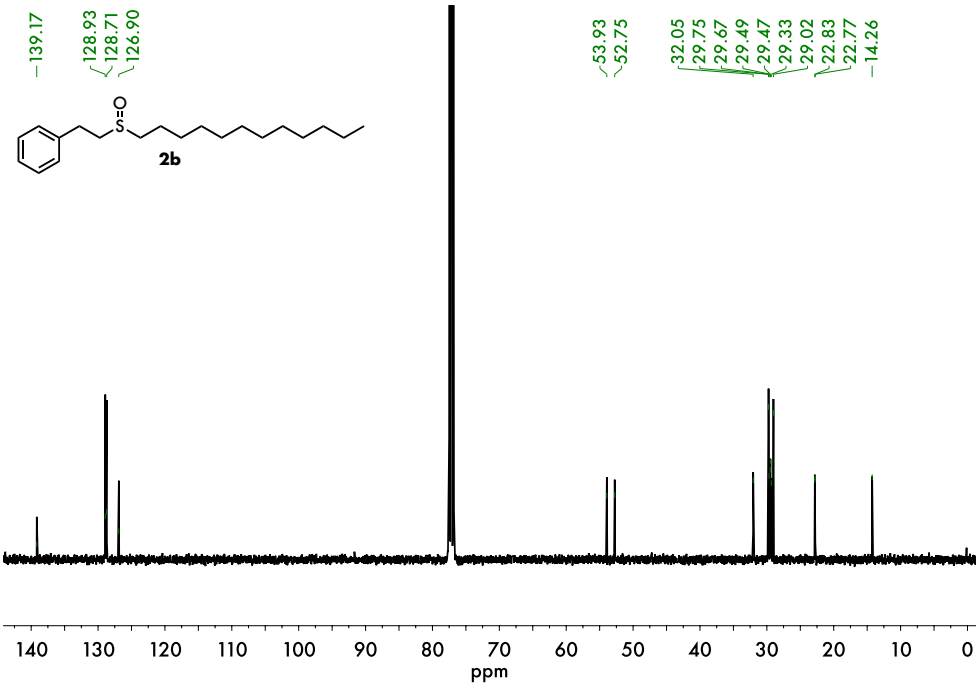


Figure S36. ^{13}C NMR spectrum of **2b**.

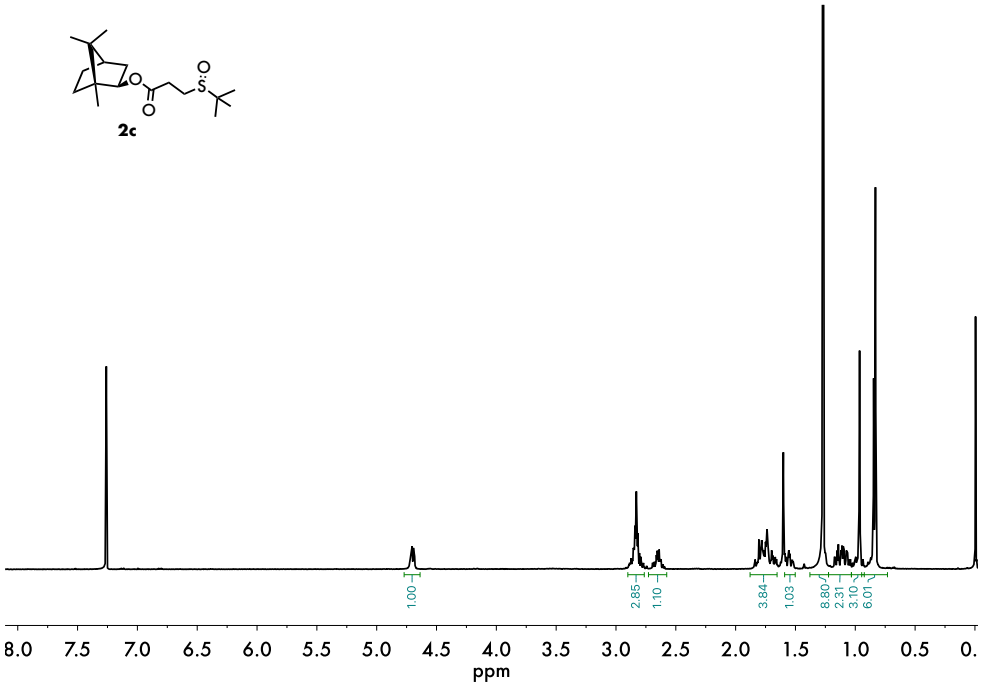


Figure S37. ^{1}H NMR spectrum of **2c**.

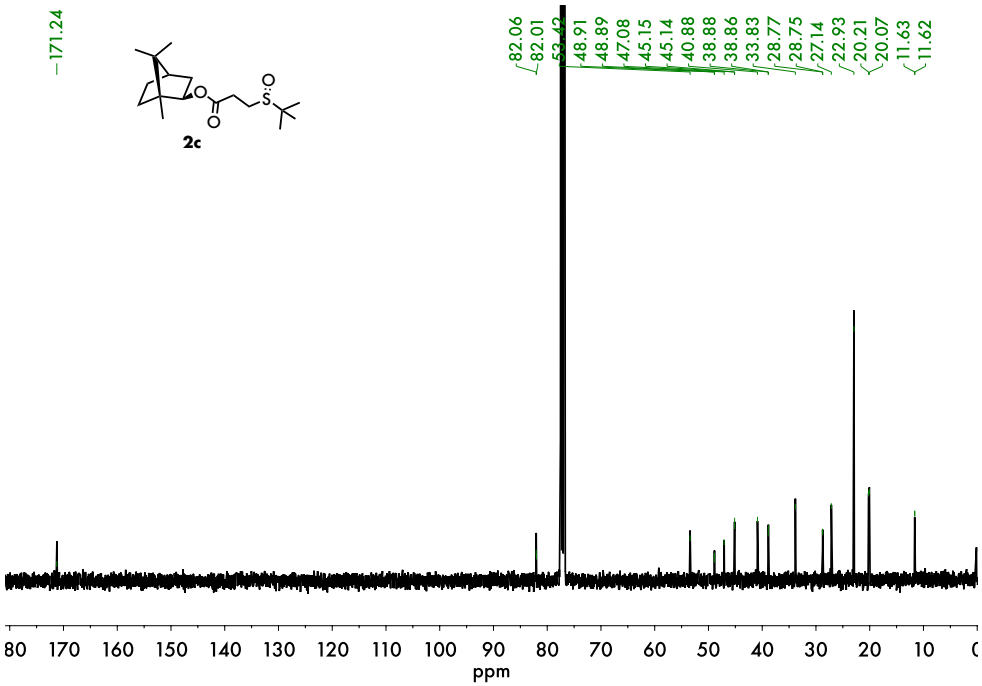


Figure S38. ^{13}C NMR spectrum of **2c**.

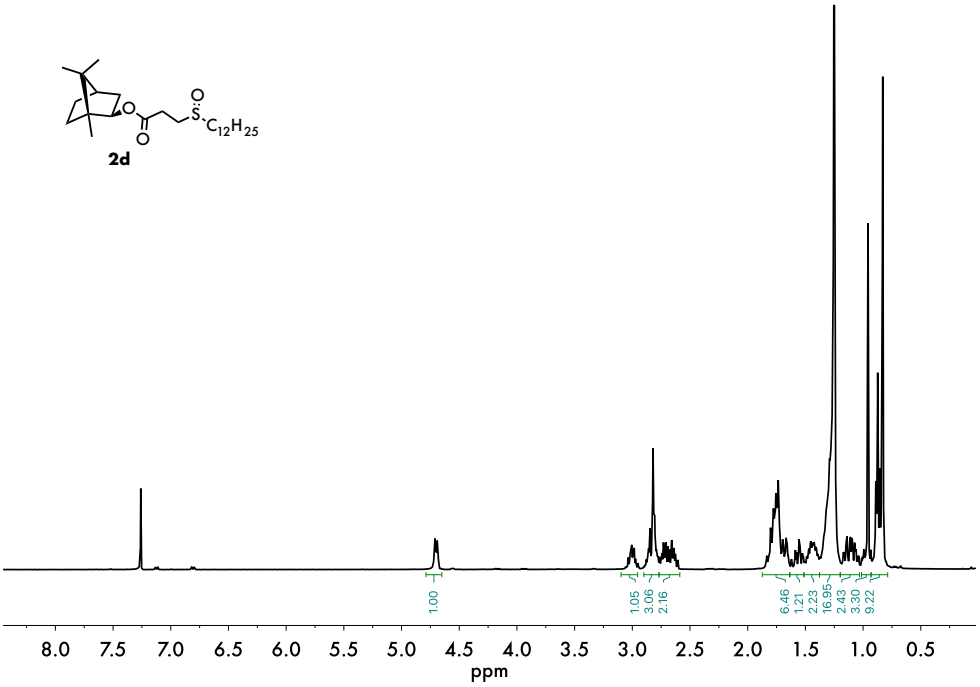


Figure S39. ^{1}H NMR spectrum of **2d**.

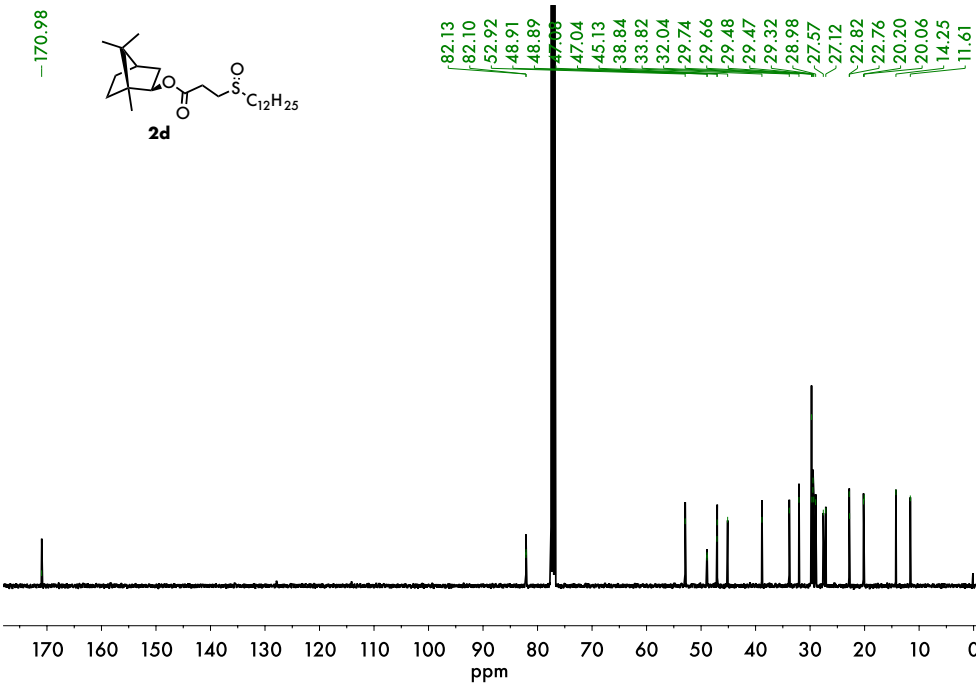


Figure S40. ^{13}C NMR spectrum of **2d**.

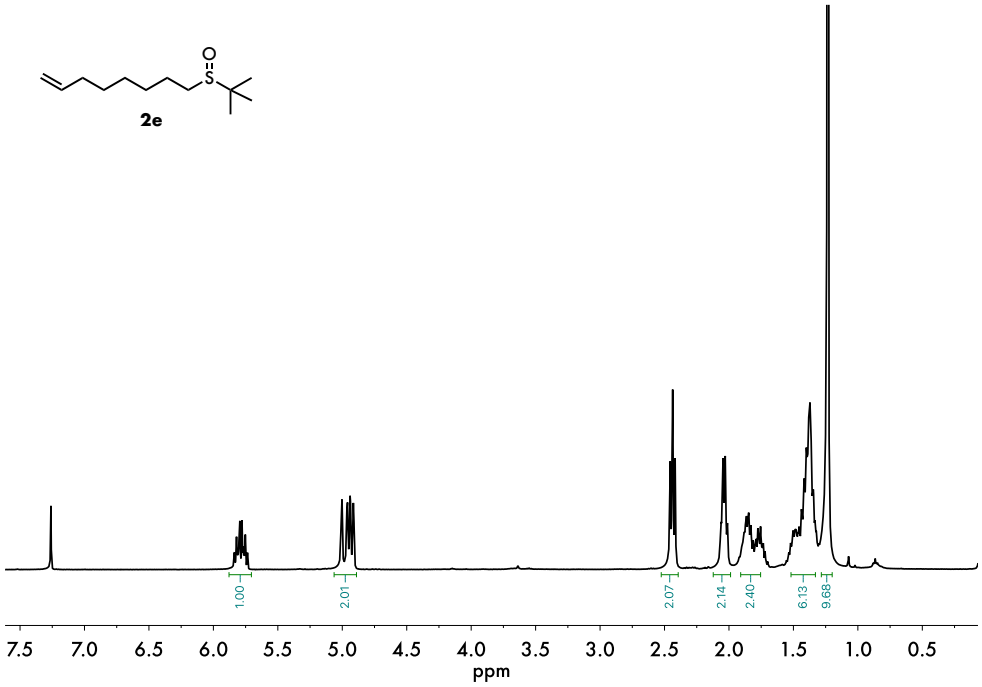


Figure S41. ^{1}H NMR spectrum of **2e**.

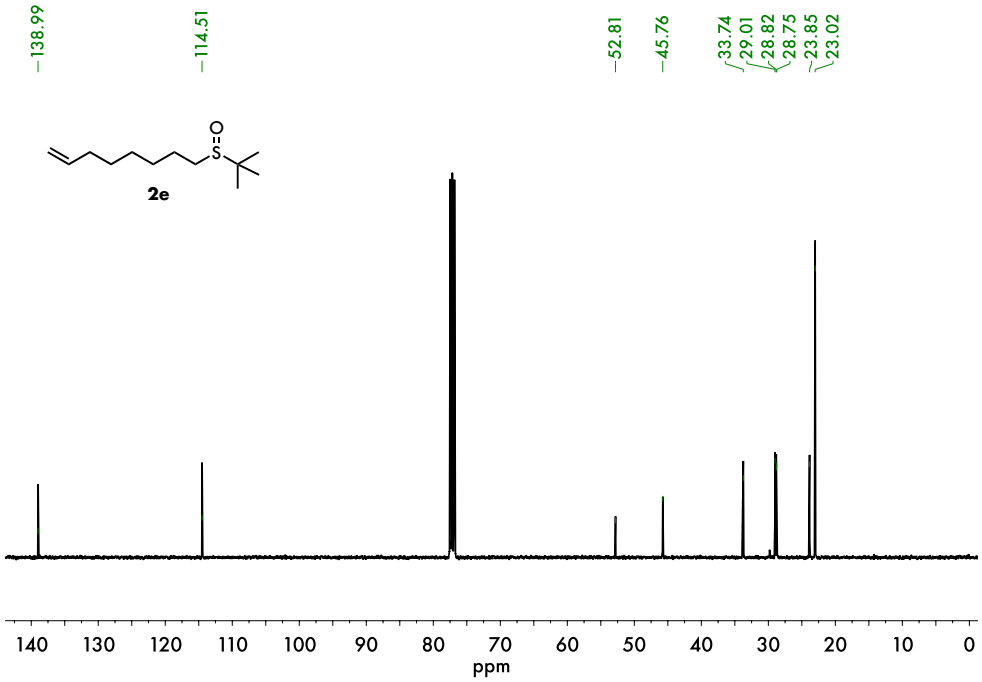


Figure S42. ^{13}C NMR spectrum of **2e**.

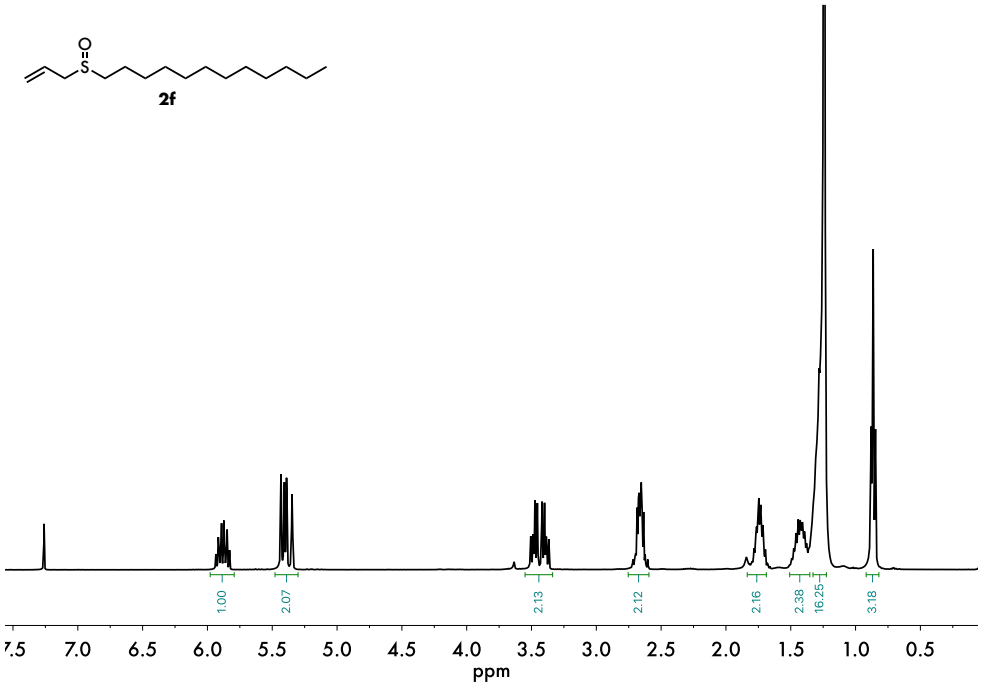


Figure S43. ^{1}H NMR spectrum of **2f**.

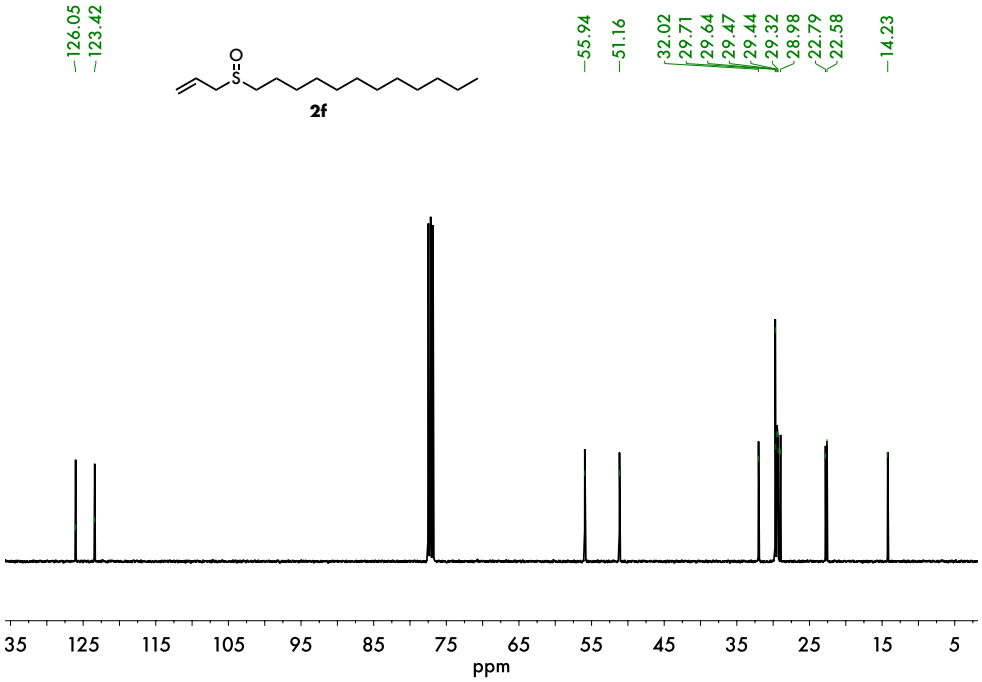
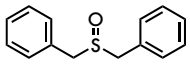


Figure S44. ^{13}C NMR spectrum of **2f**.



2g

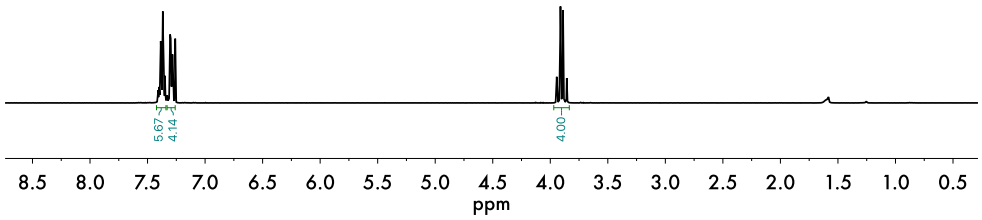


Figure S45. ^{1}H NMR spectrum of **2g**.

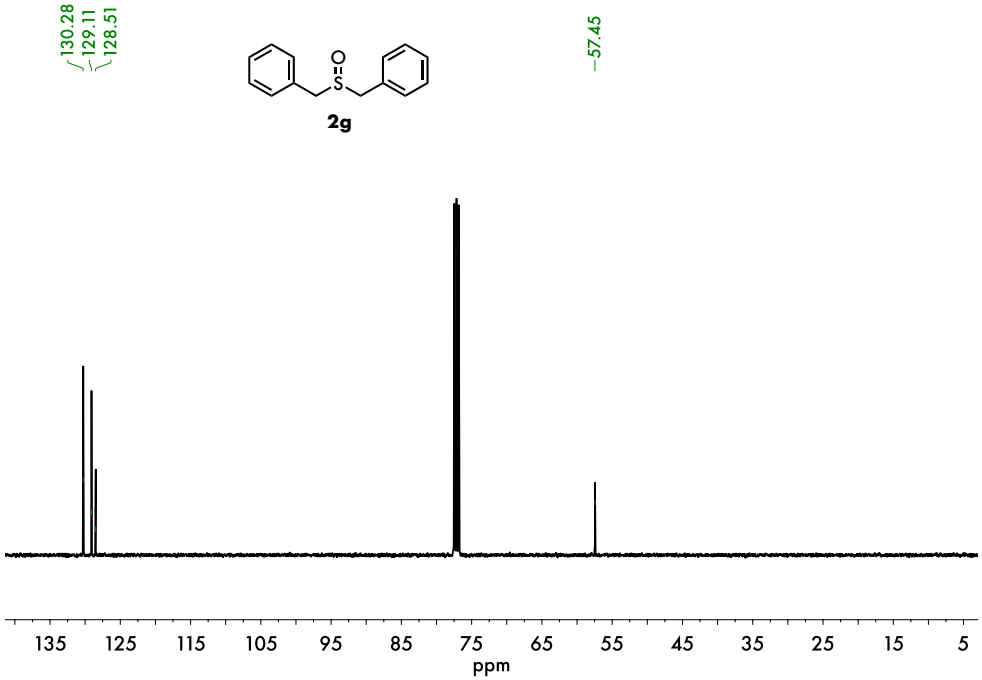


Figure S46. ^{13}C NMR spectrum of **2g**.

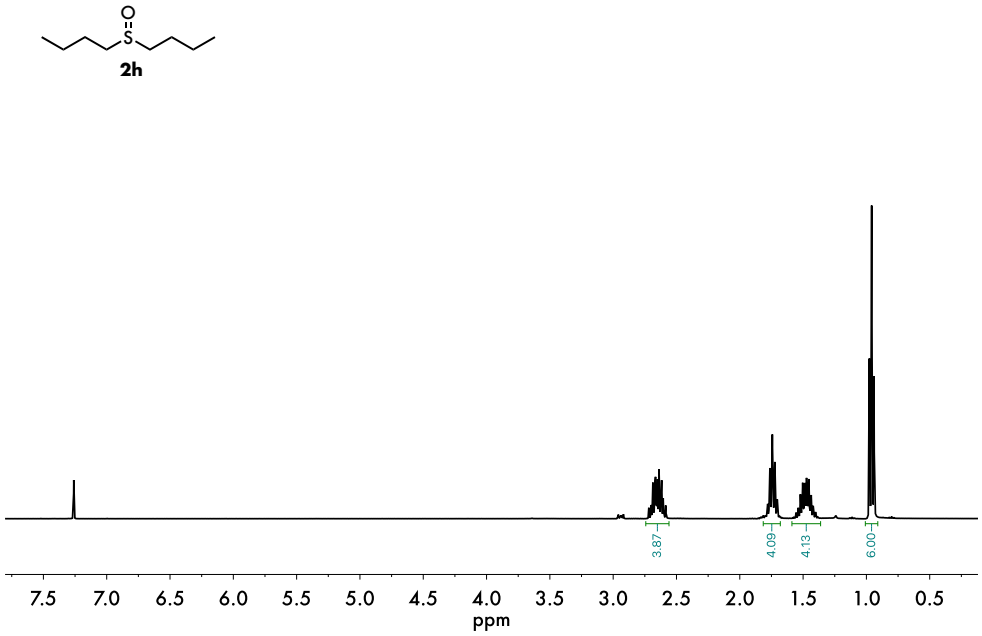


Figure S47. ^{1}H NMR spectrum of **2h**.

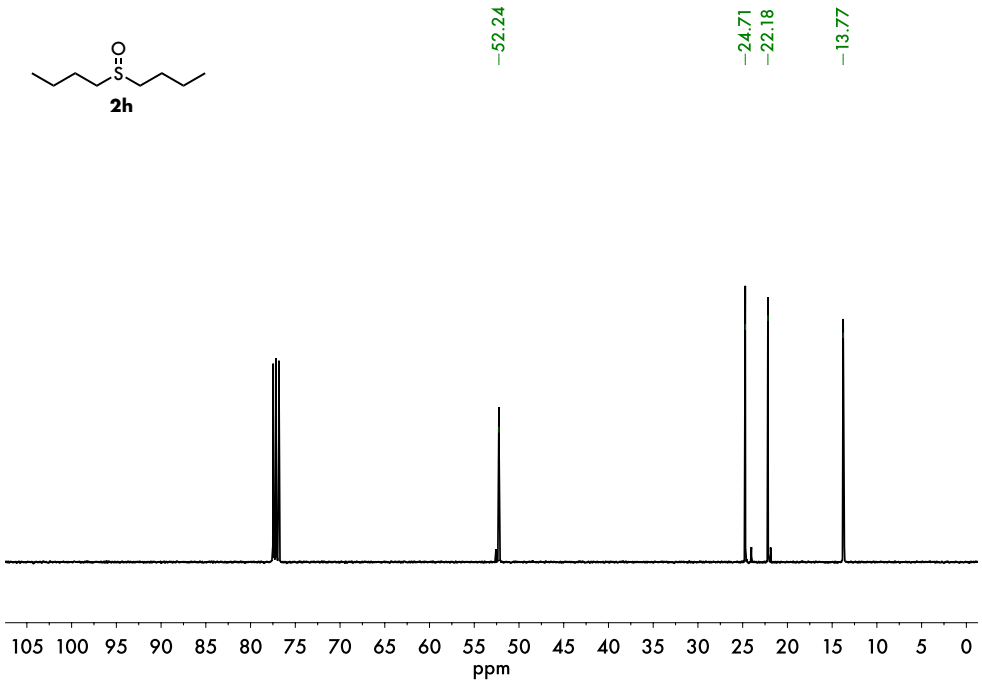


Figure S48. ^{13}C NMR spectrum of **2h**.

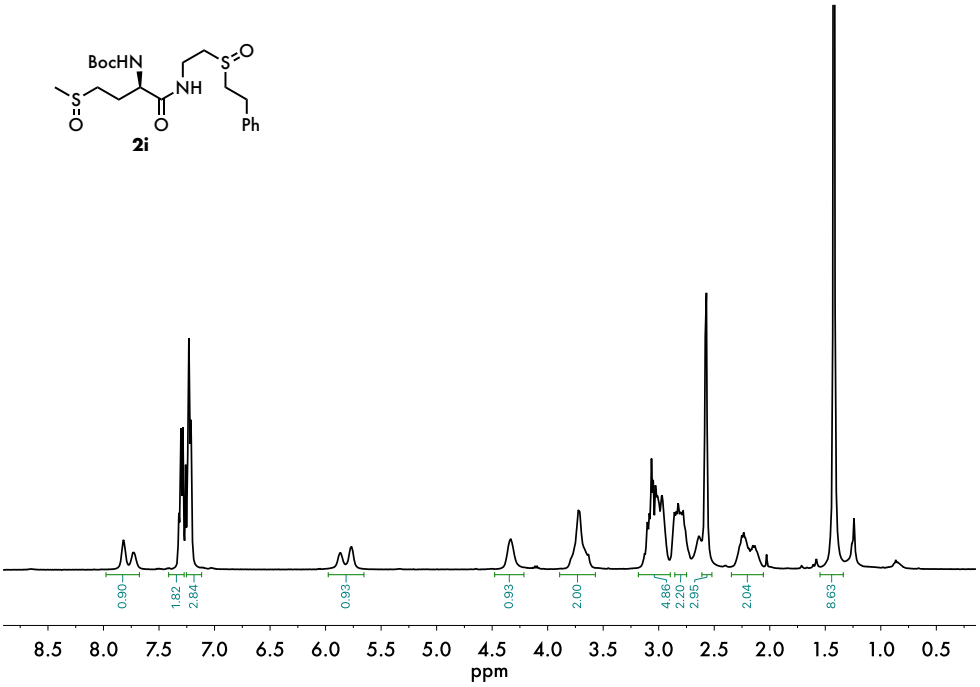


Figure S49. ^{1}H NMR spectrum of **2i**.

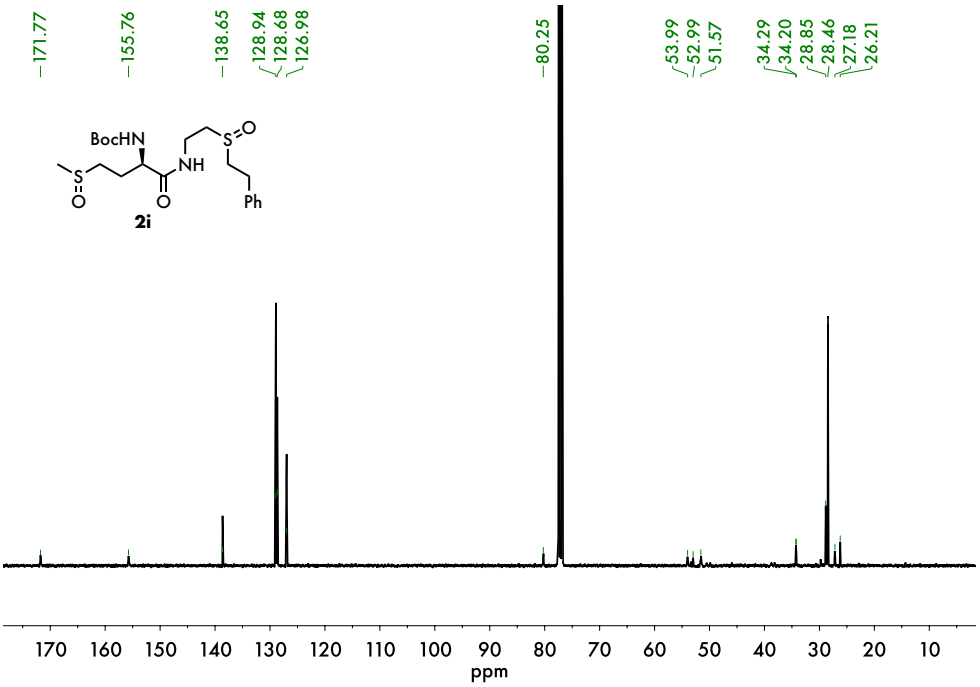


Figure S50. ^{13}C NMR spectrum of **2i**.

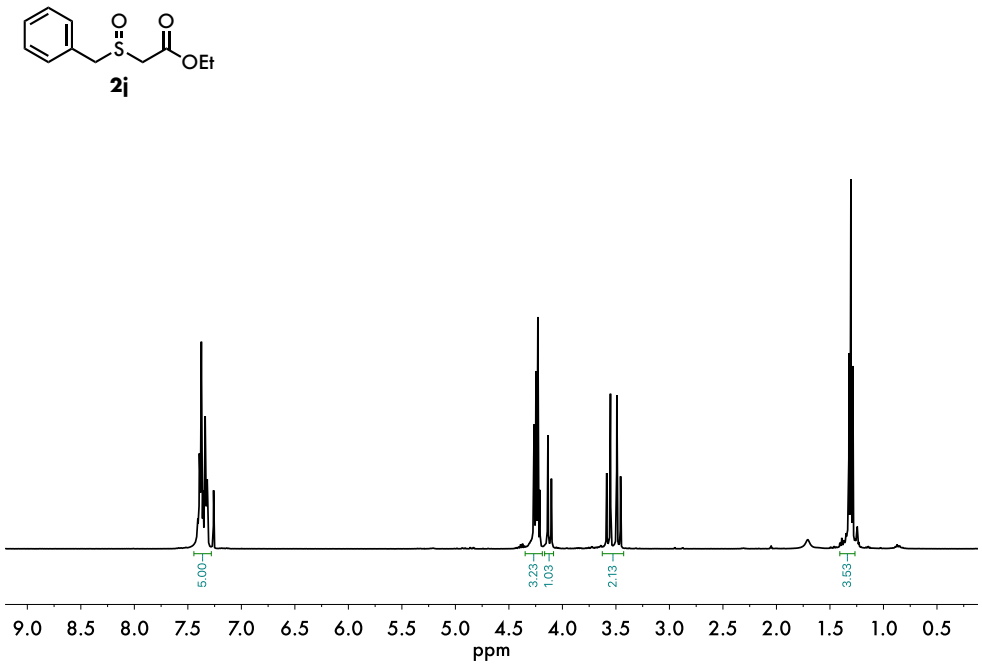


Figure S51. ^{1}H NMR spectrum of **2j**.

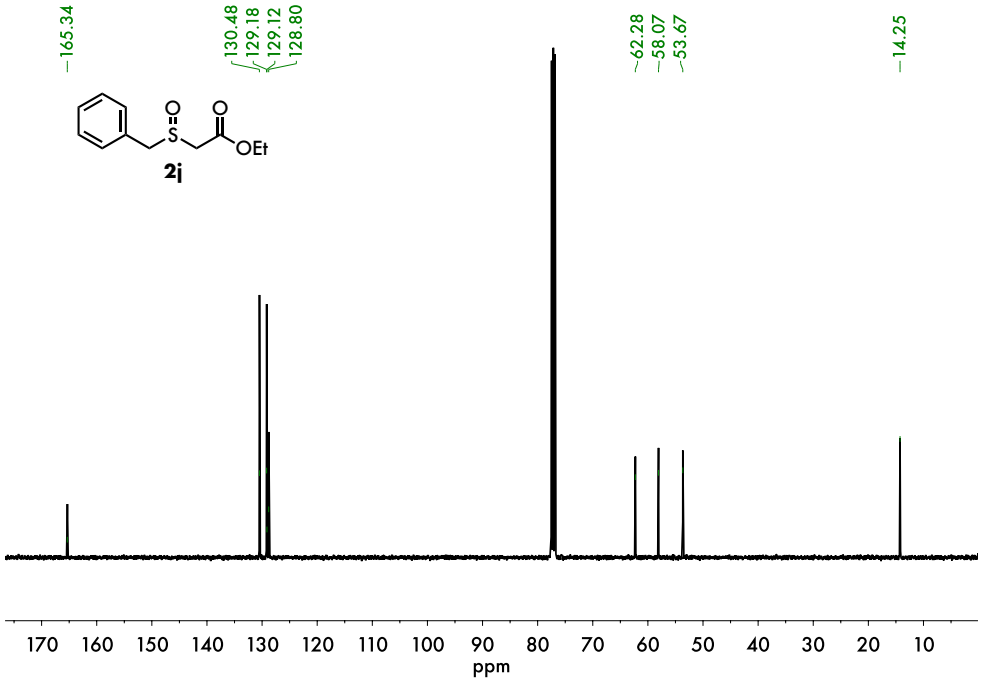


Figure S52. ^{13}C NMR spectrum of **2j**.

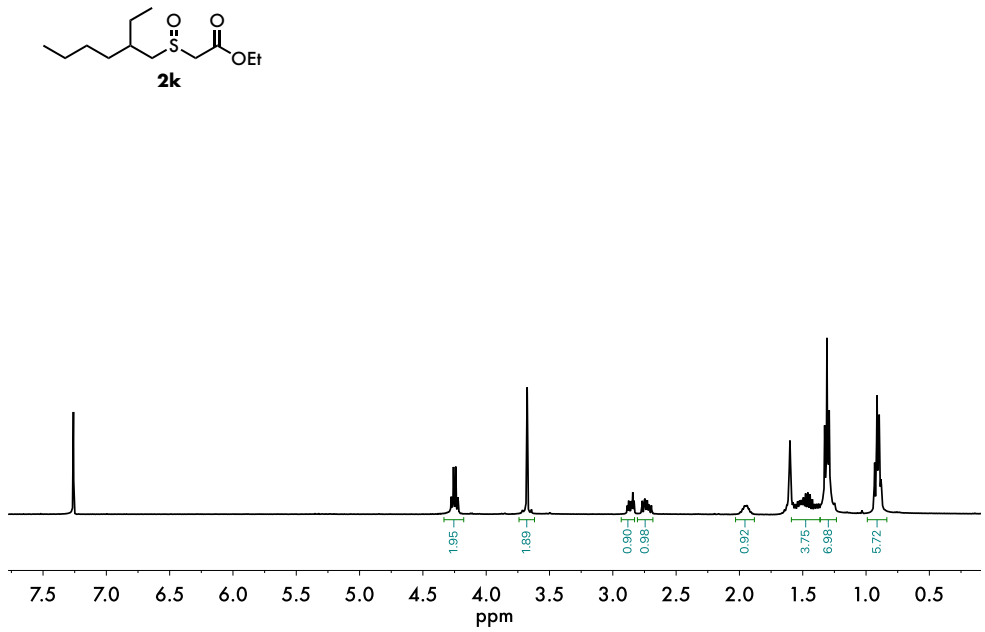


Figure S53. ^{1}H NMR spectrum of **2k**.

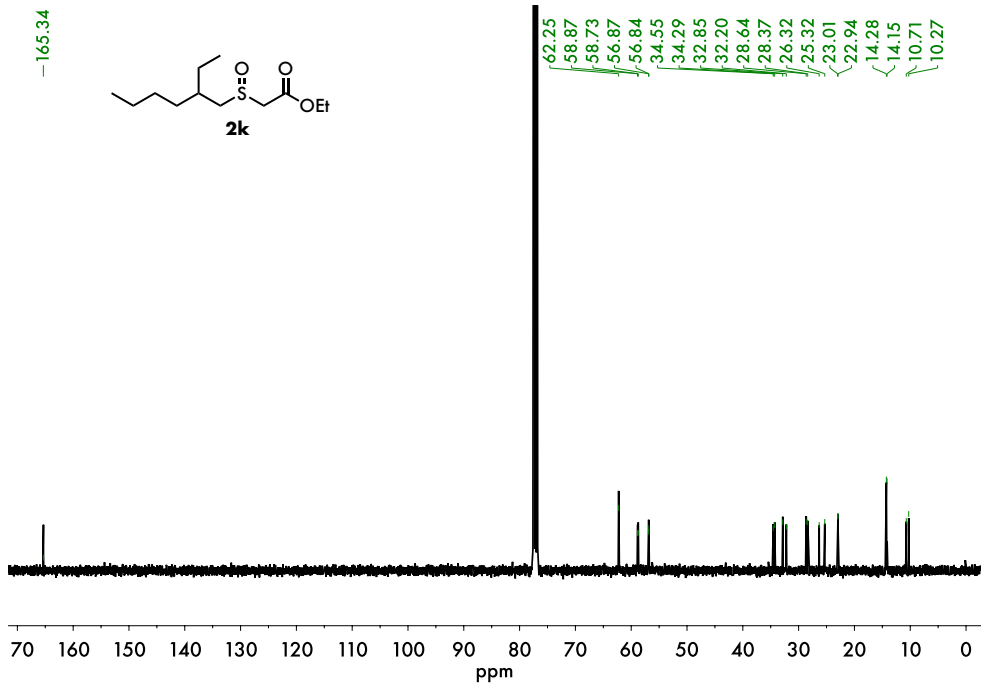


Figure S54. ^{13}C NMR spectrum of **2k**.

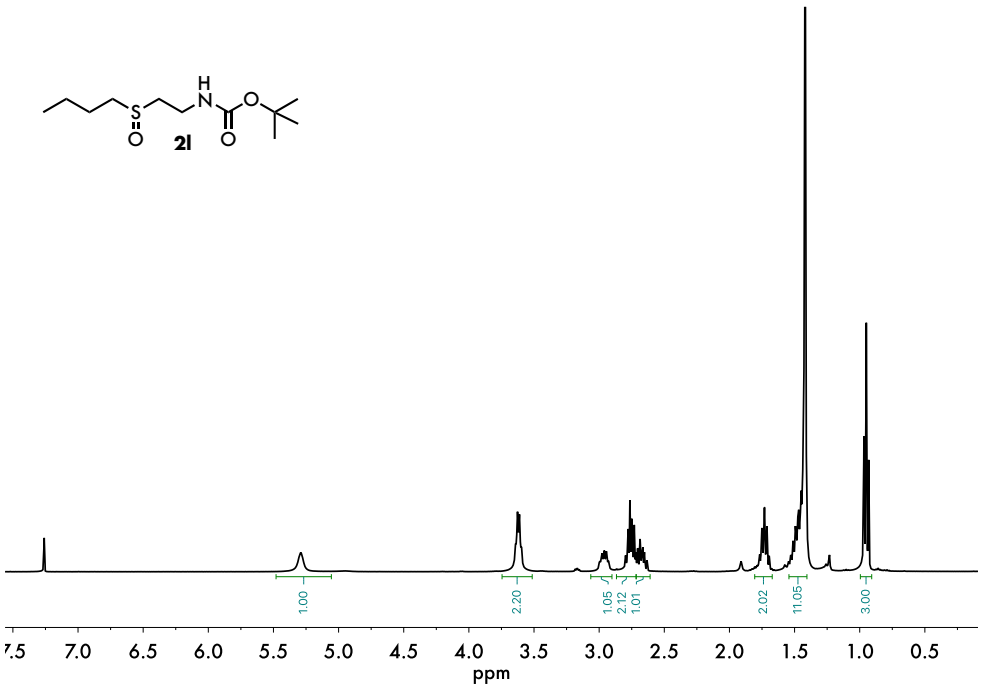


Figure S55. ^{1}H NMR spectrum of **2l**.

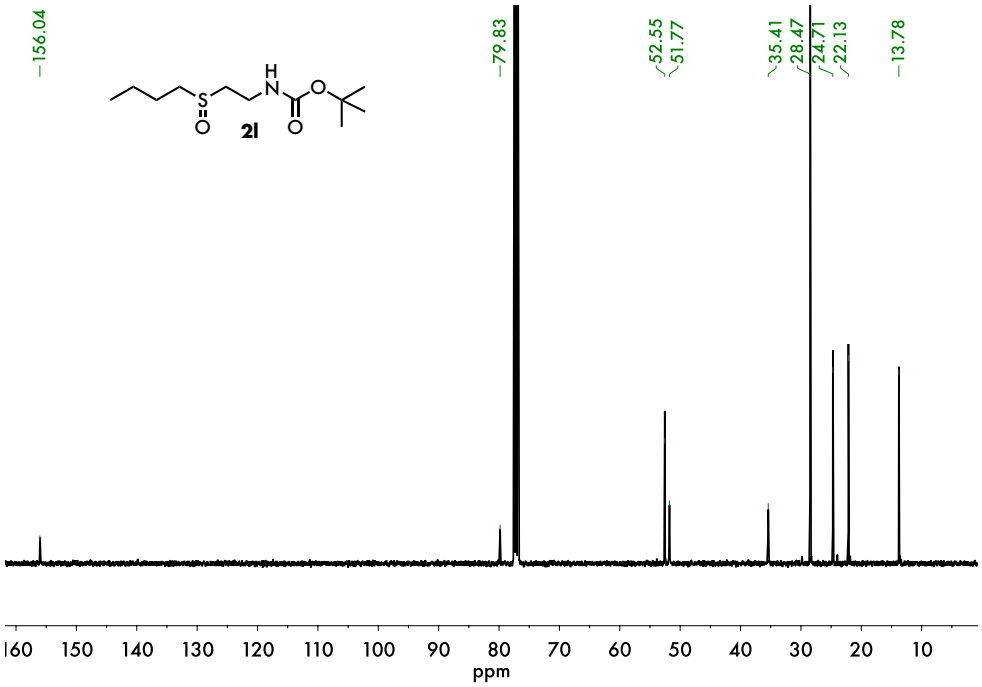


Figure S56. ^{13}C NMR spectrum of **2l**.

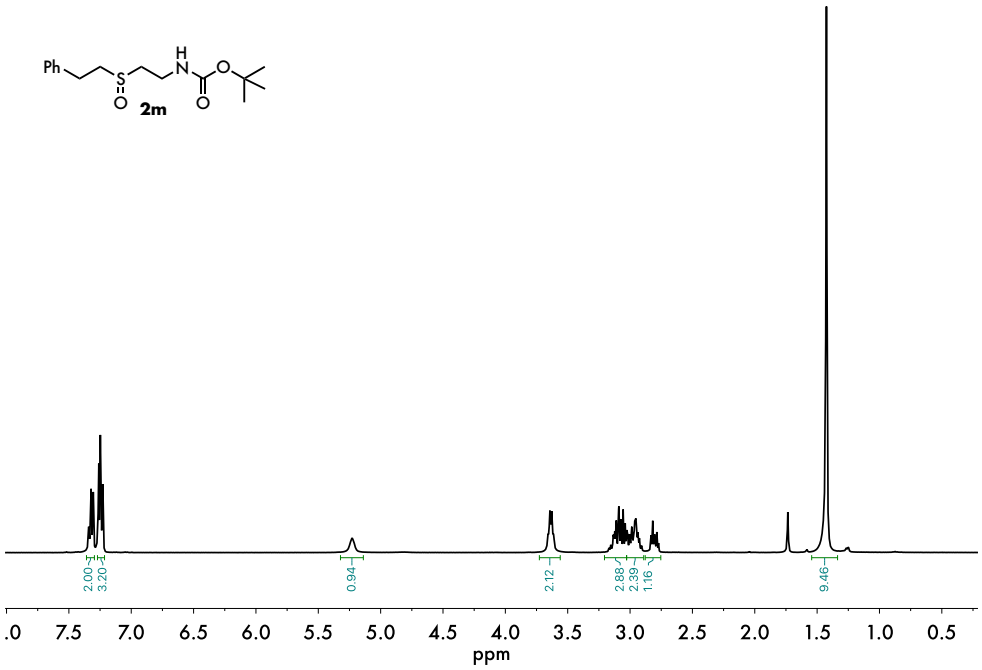


Figure S57. ^{1}H NMR spectrum of **2m**.

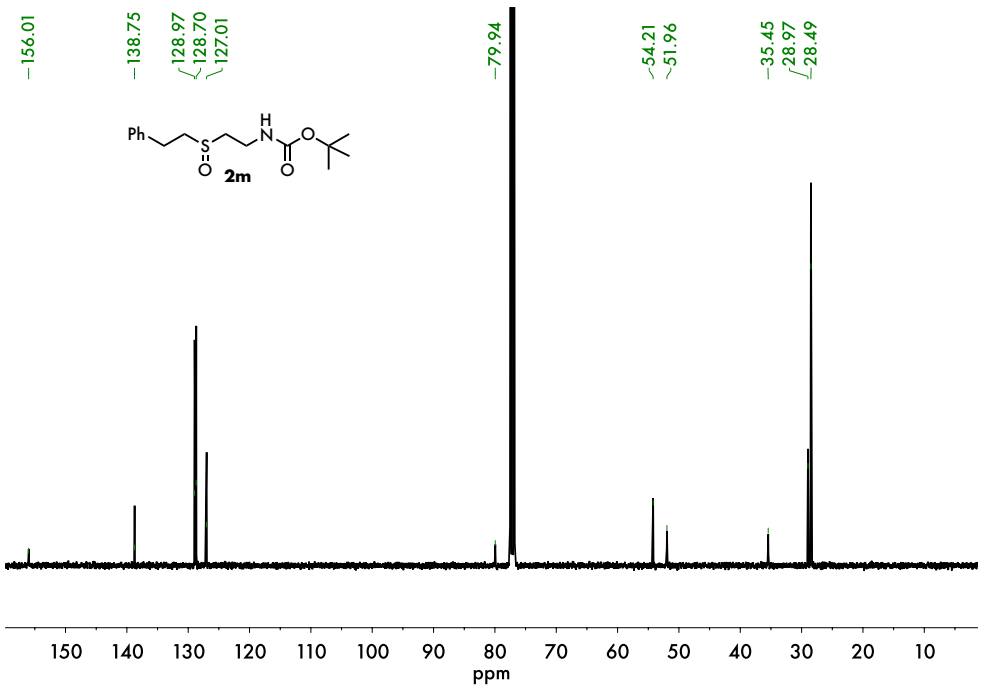


Figure S58. ^{13}C NMR spectrum of **2m**.

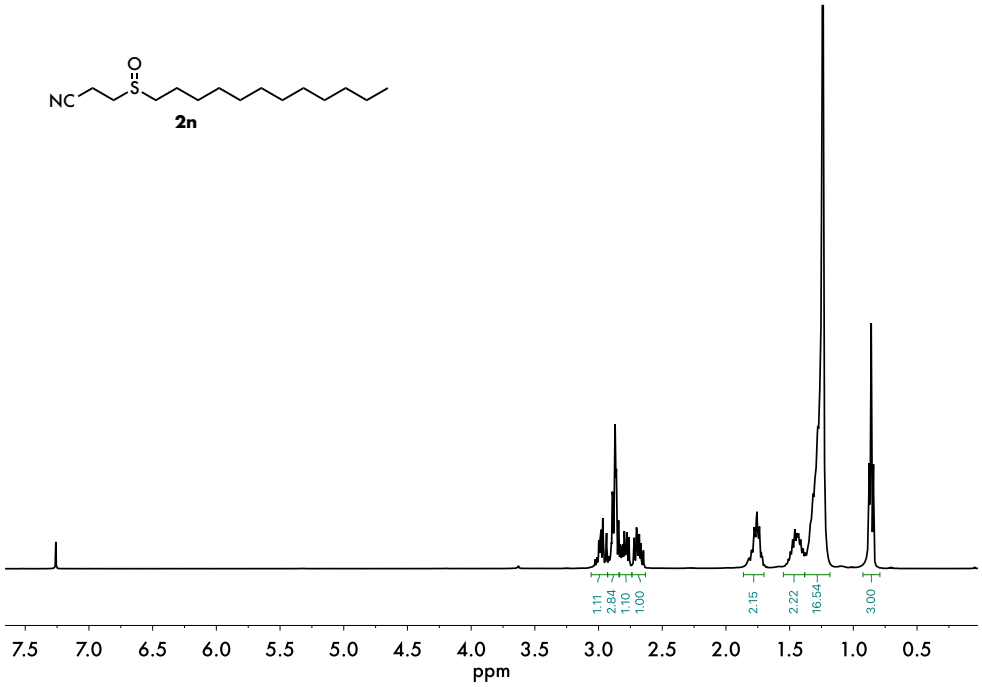


Figure S59. ^{1}H NMR spectrum of **2n**.

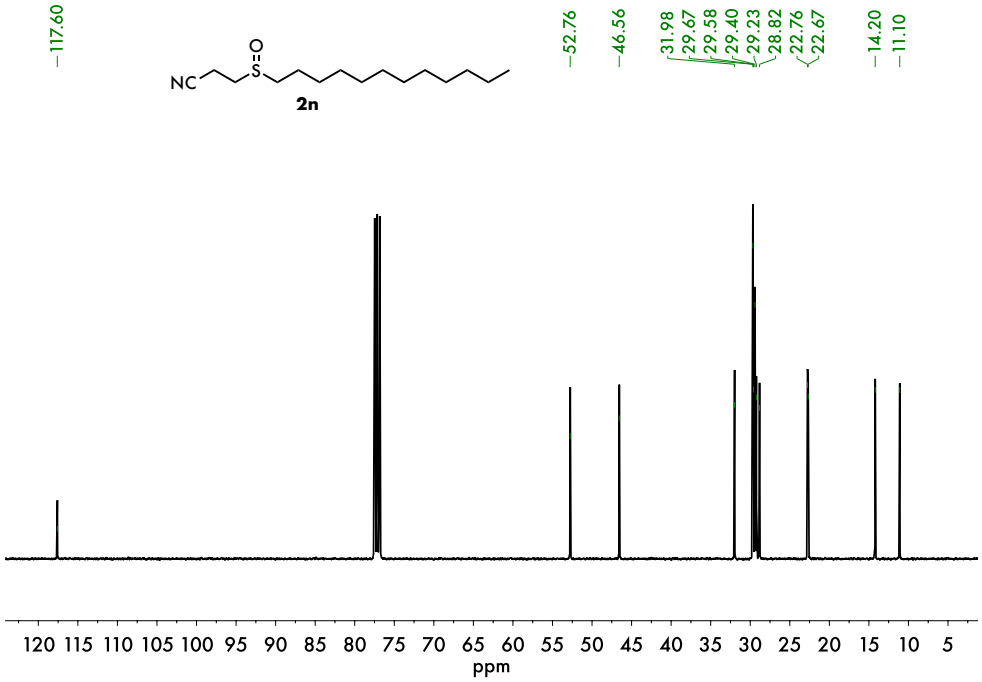


Figure S60. ^{13}C NMR spectrum of **2n**.

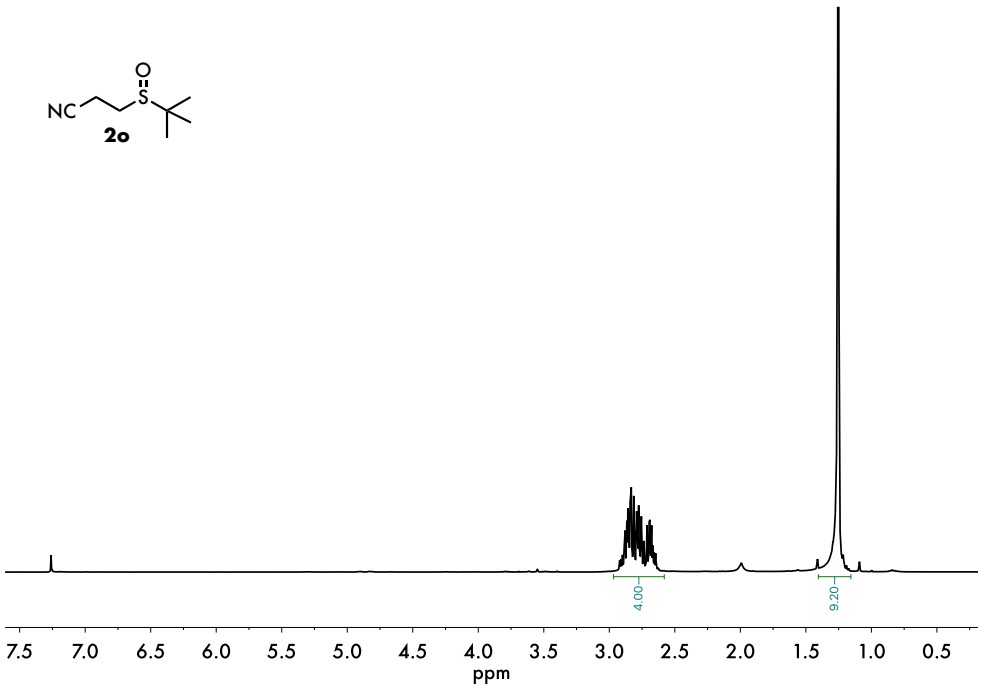


Figure S61. ^{1}H NMR spectrum of **2o**.

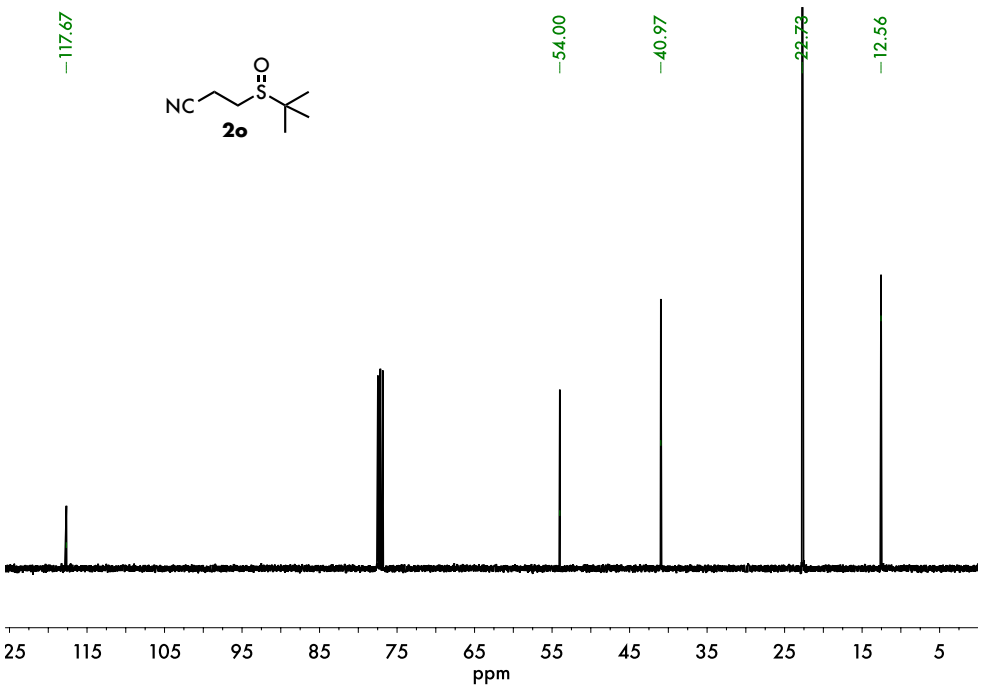


Figure S62. ^{13}C NMR spectrum of **2o**.

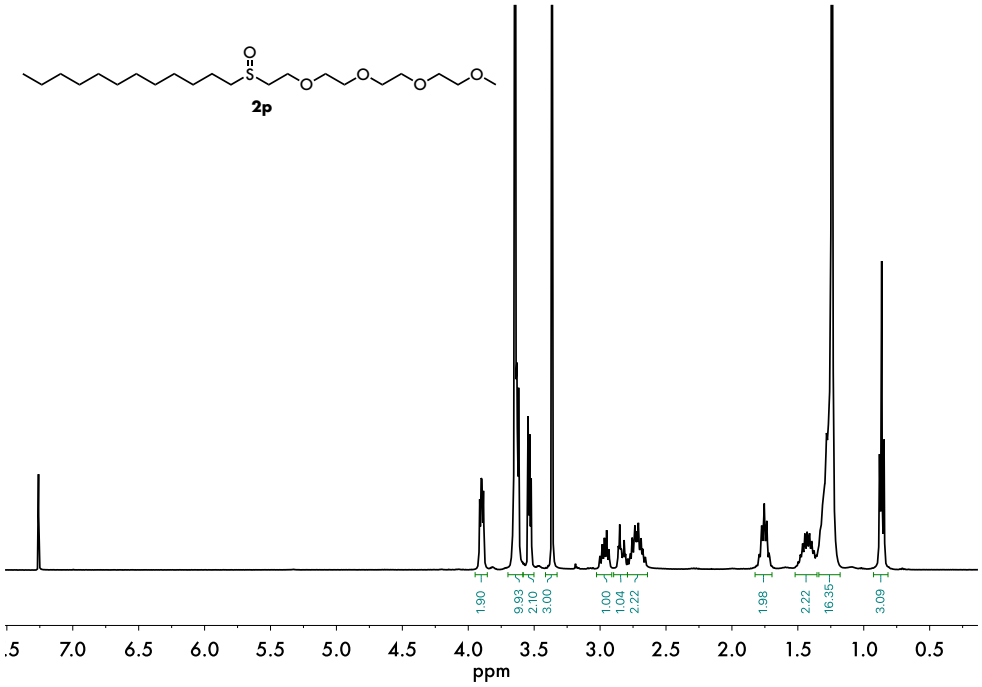


Figure S63. ^{1}H NMR spectrum of **2p**.

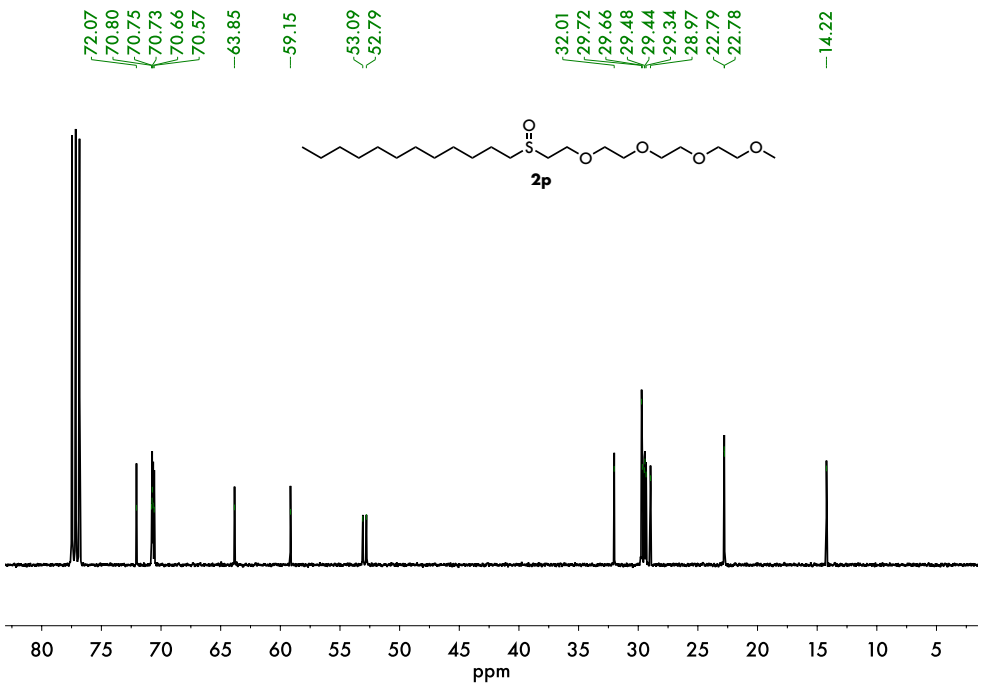


Figure S64. ^{13}C NMR spectrum of **2p**.

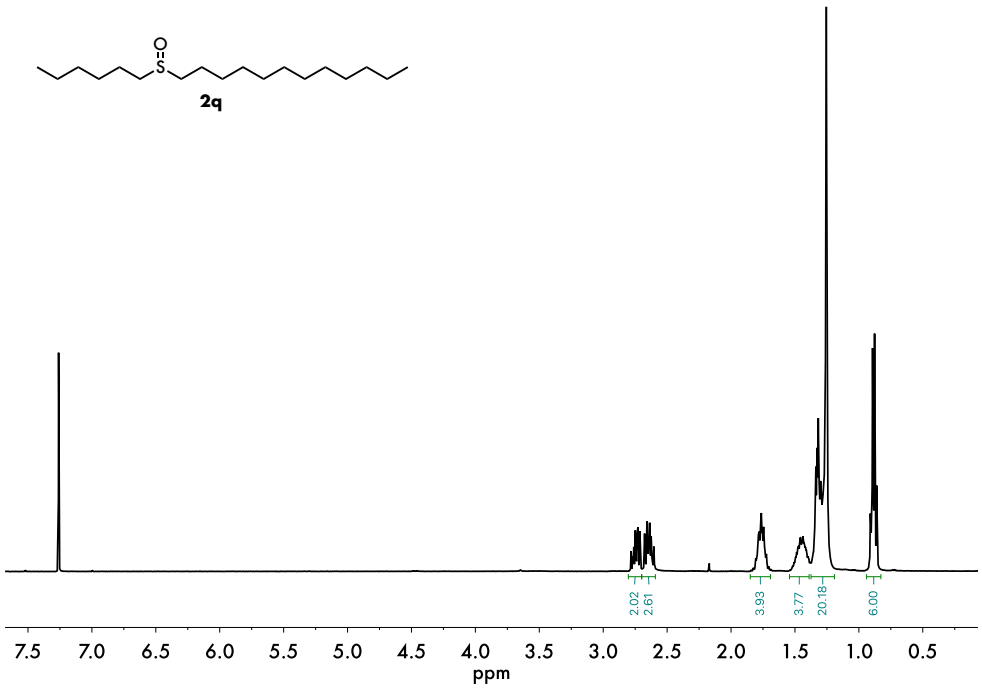


Figure S65. ^{1}H NMR spectrum of **2q**.

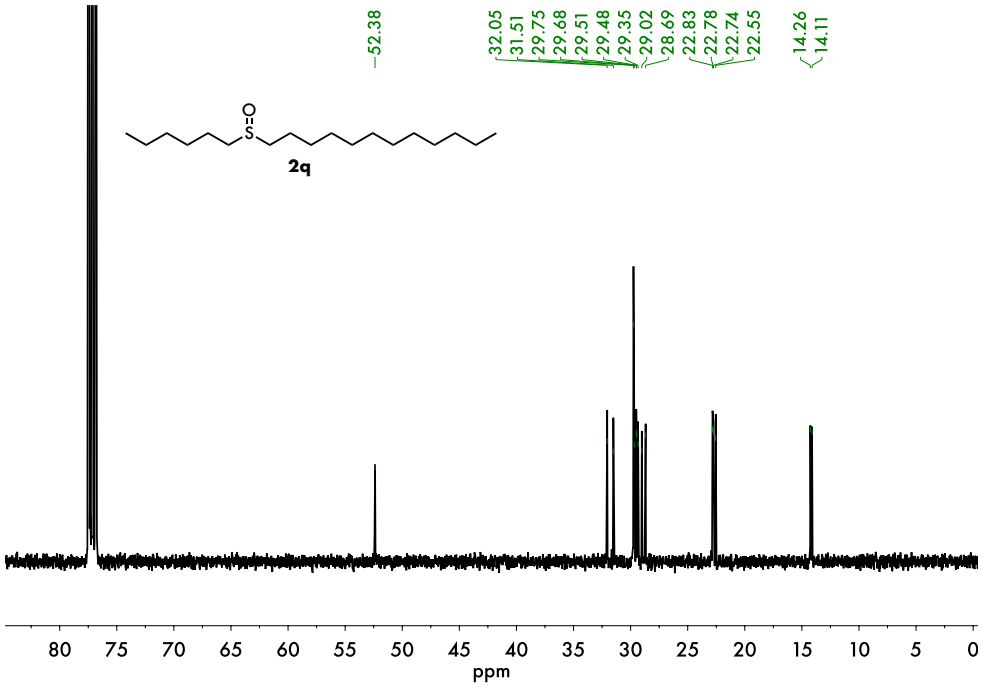


Figure S66. ^{13}C NMR spectrum of **2q**.

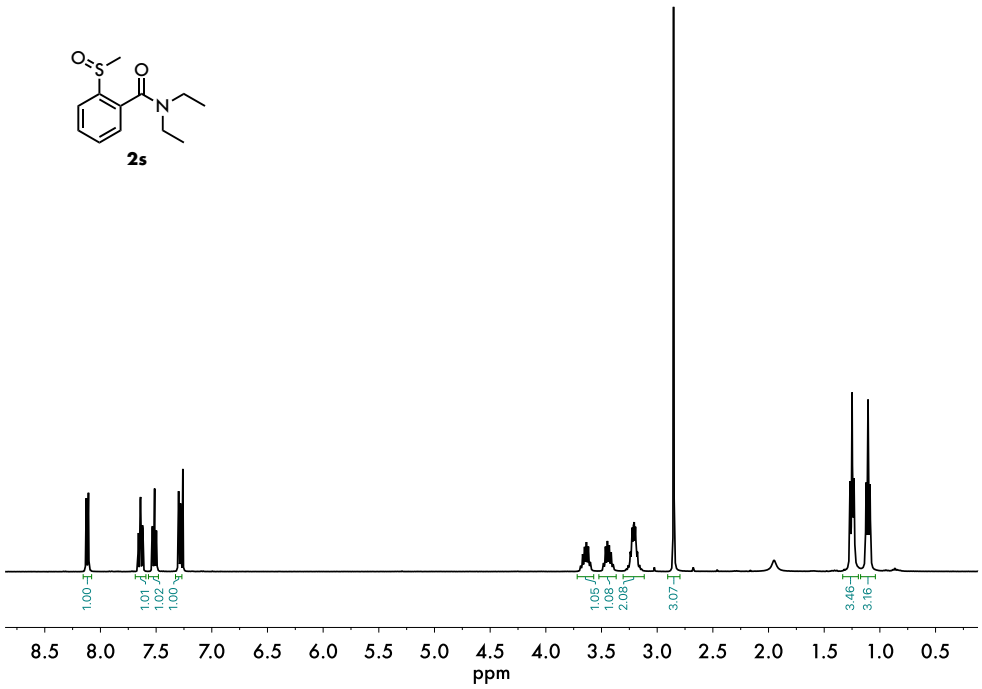


Figure S67. ^{1}H NMR spectrum of **2s**.

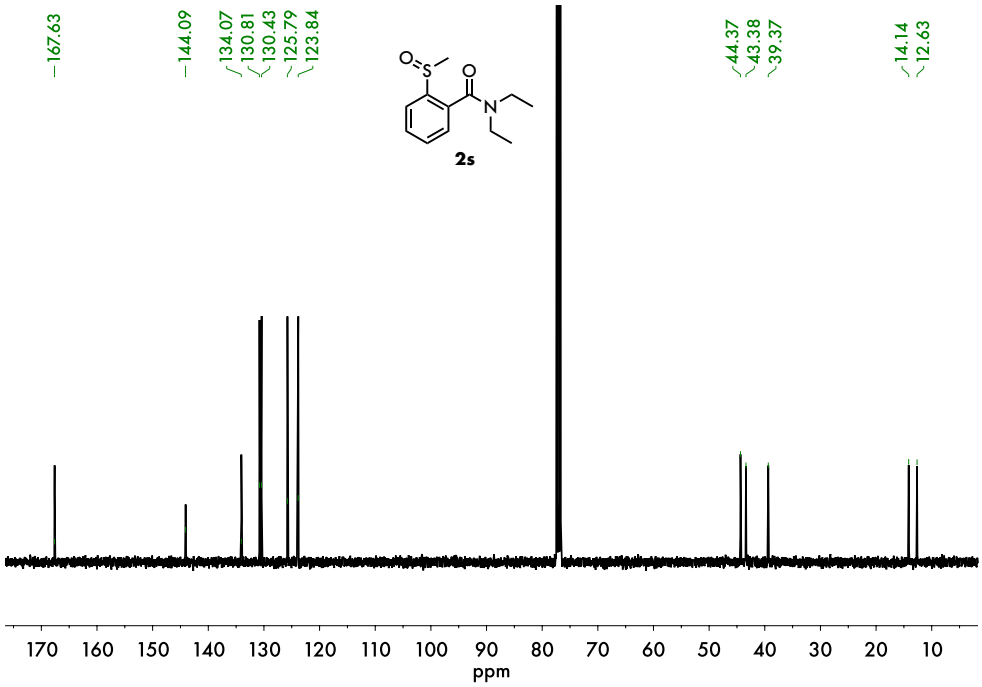


Figure S68. ^{13}C NMR spectrum of **2s**.

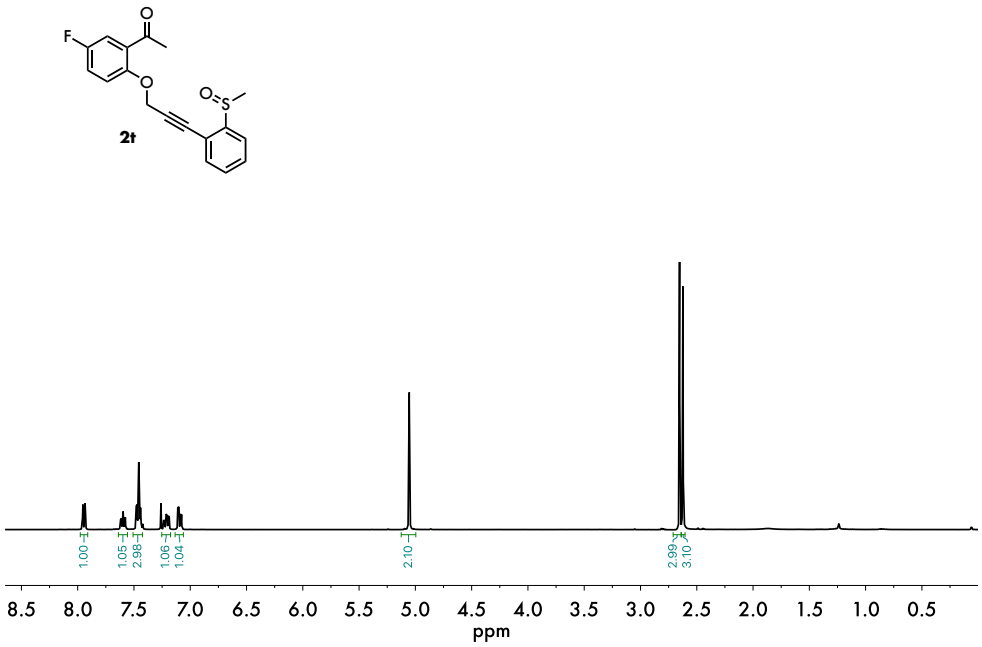


Figure S69. ^{1}H NMR spectrum of **2t**.

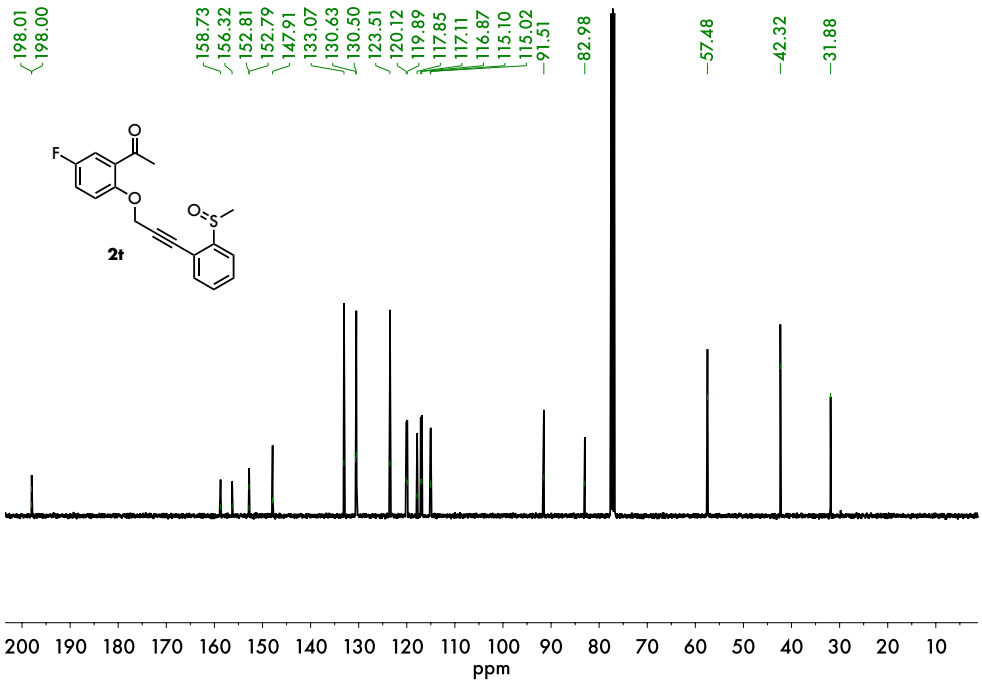


Figure S70. ^{13}C NMR spectrum of **2t**.

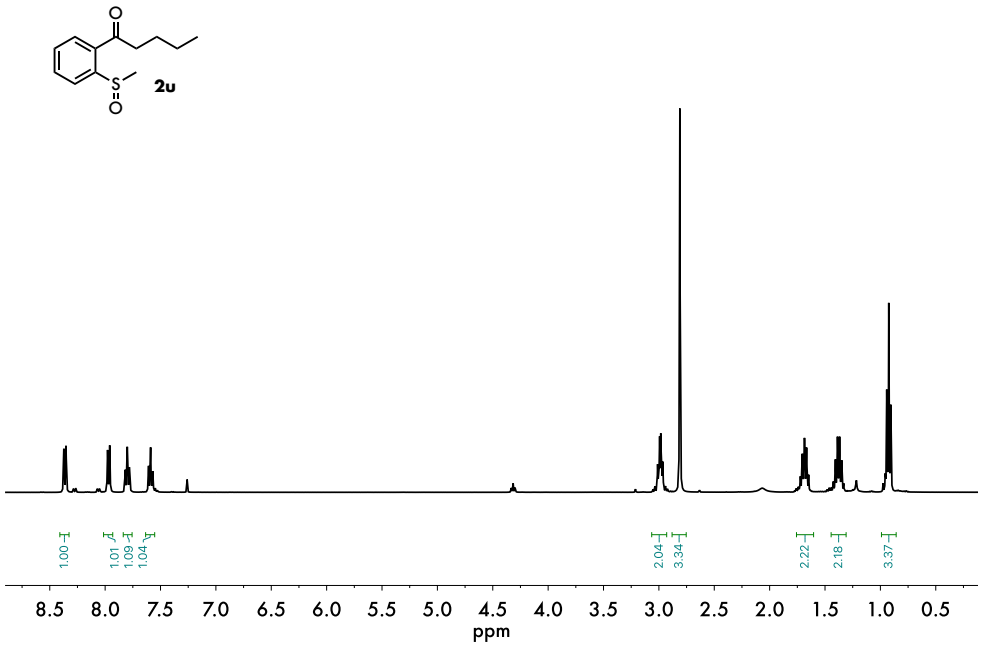


Figure S71. ^{1}H NMR spectrum of **2u**.

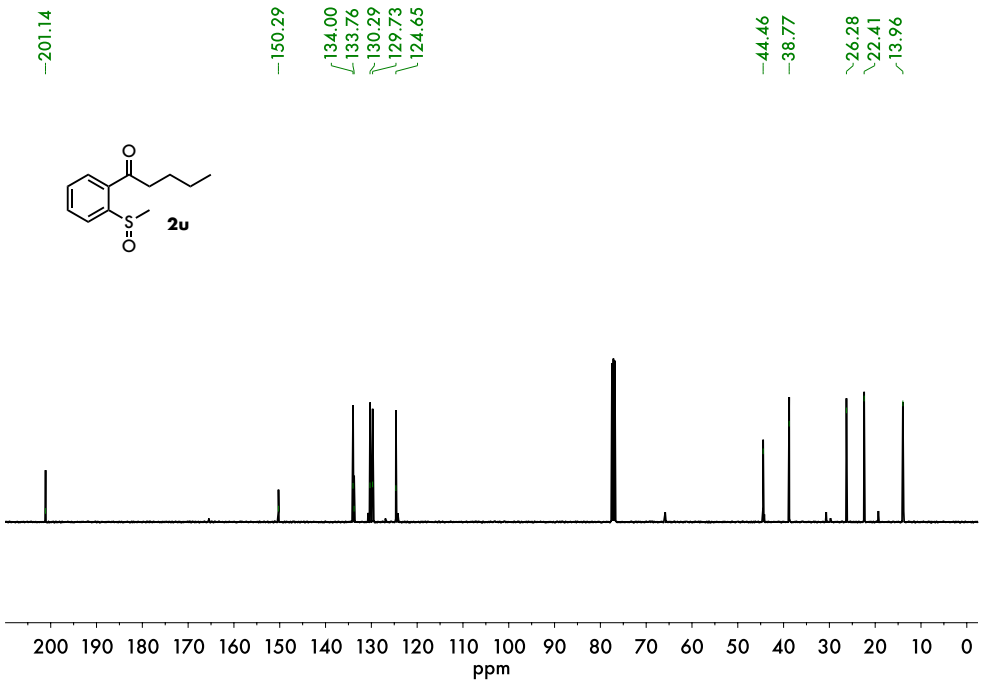


Figure S72. ^{13}C NMR spectrum of **2u**.

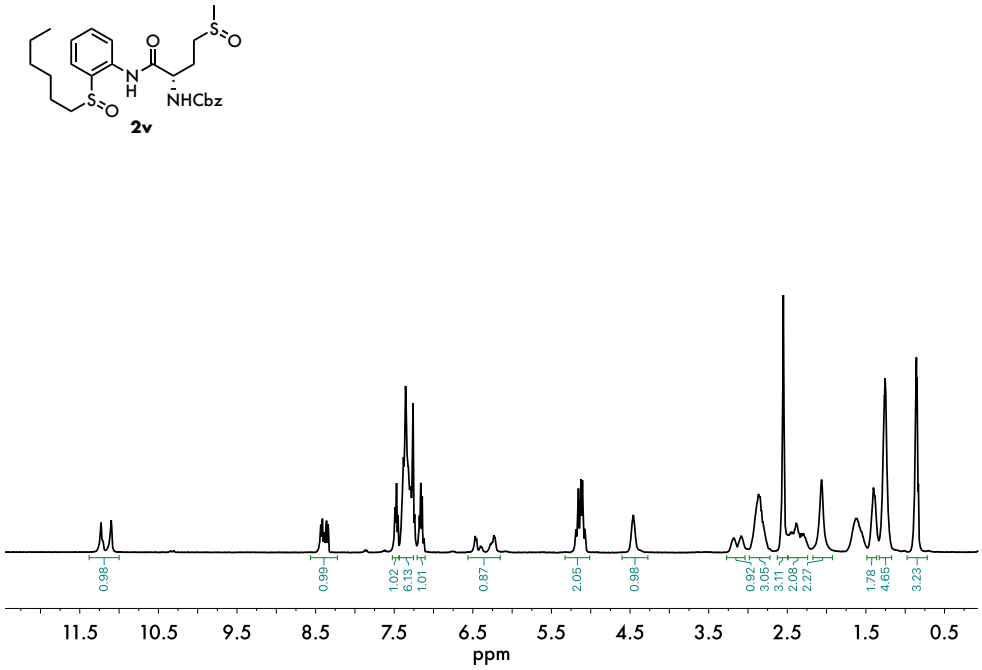


Figure S73. ^{1}H NMR spectrum of **2v**.

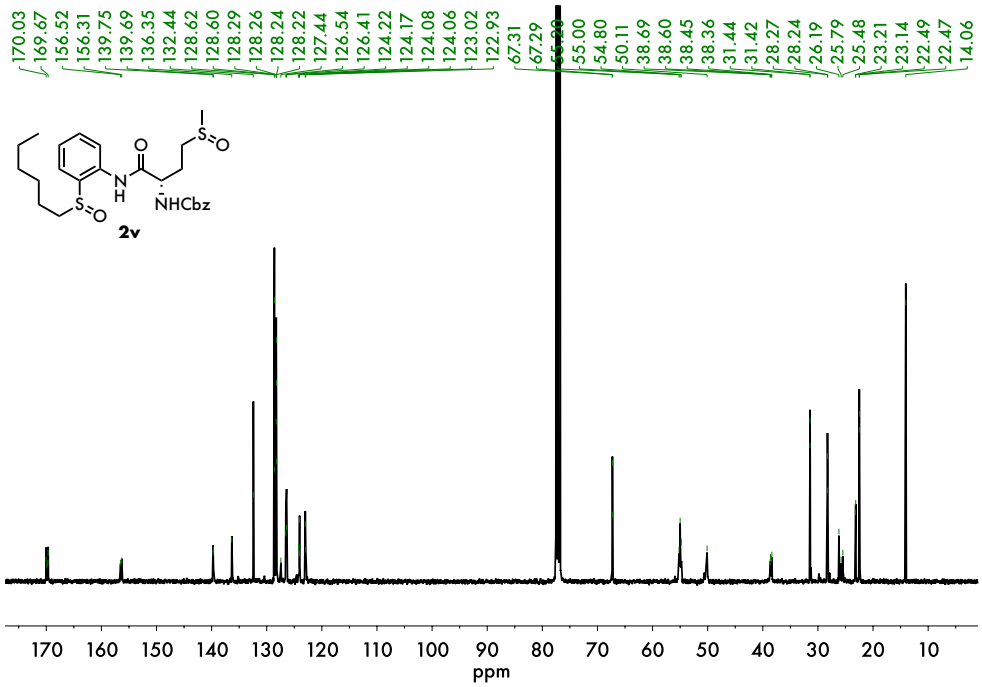


Figure S74. ^{13}C NMR spectrum of **2u**.

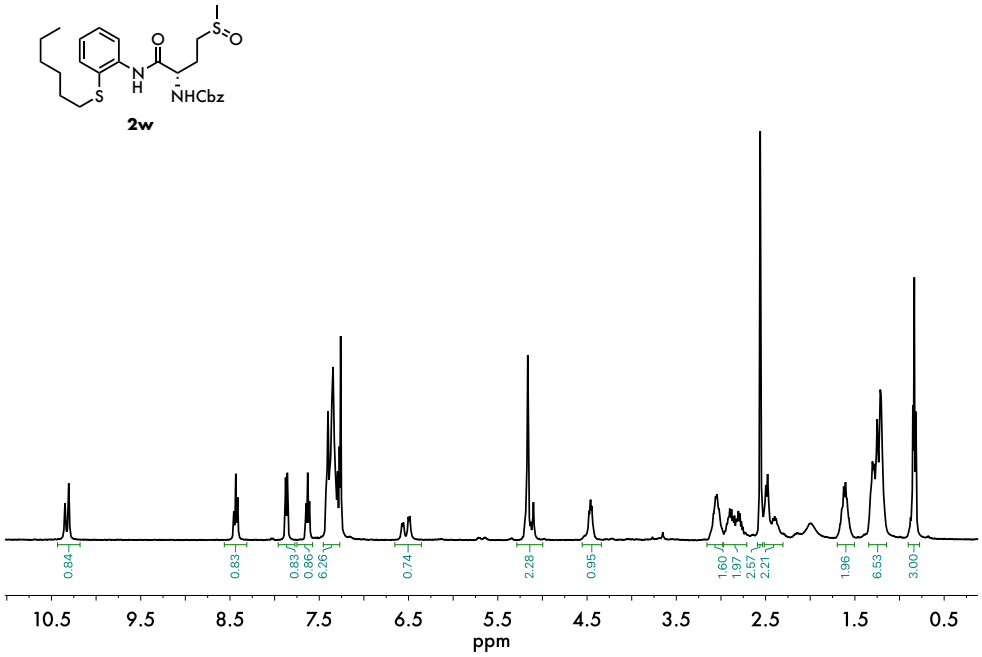


Figure S75. ^{1}H NMR spectrum of **2w**.

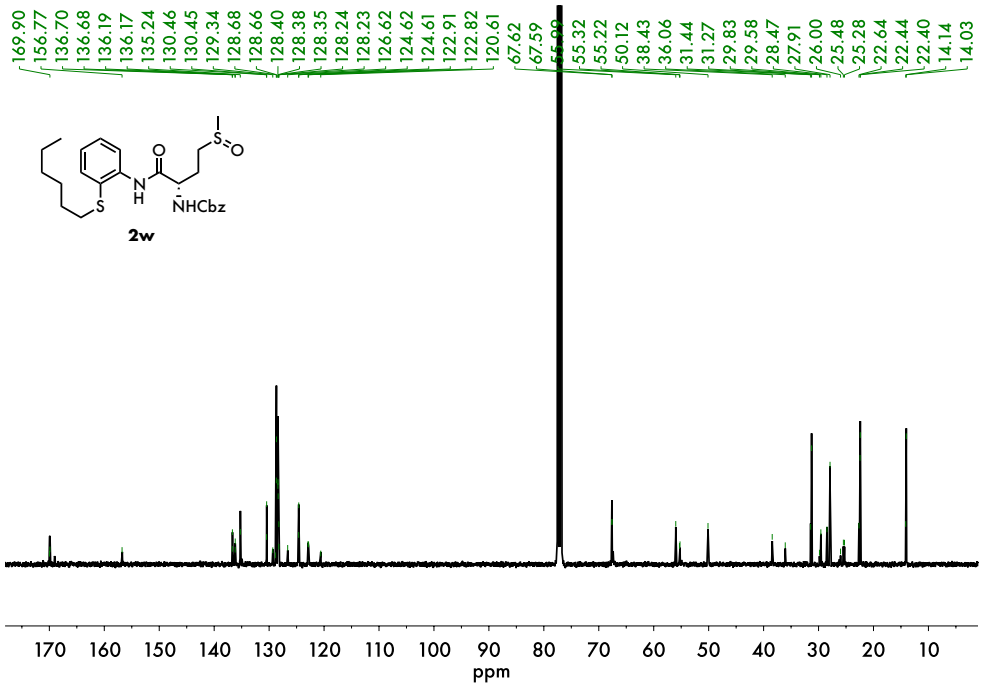


Figure S76. ^{13}C NMR spectrum of **2u**.

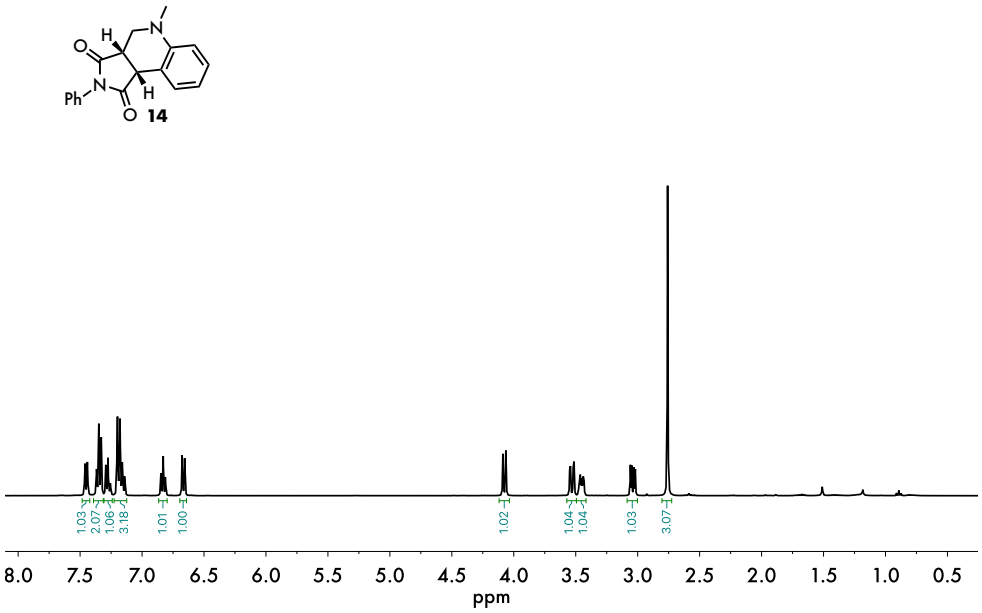


Figure S77. ^{1}H NMR spectrum of **14**.

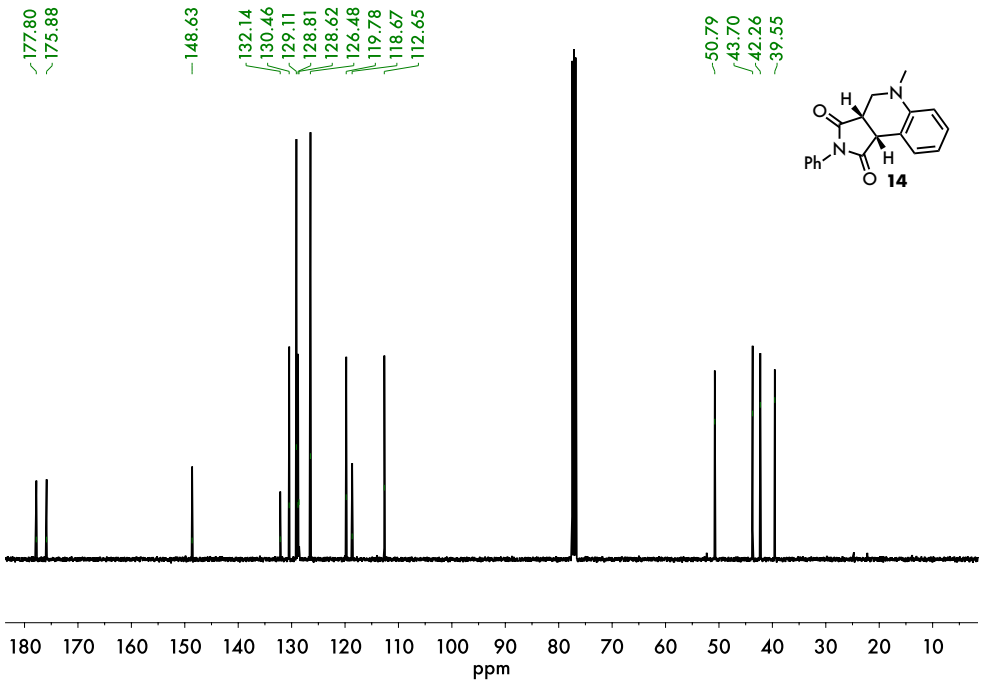


Figure S78. ^{13}C NMR spectrum of **14**.

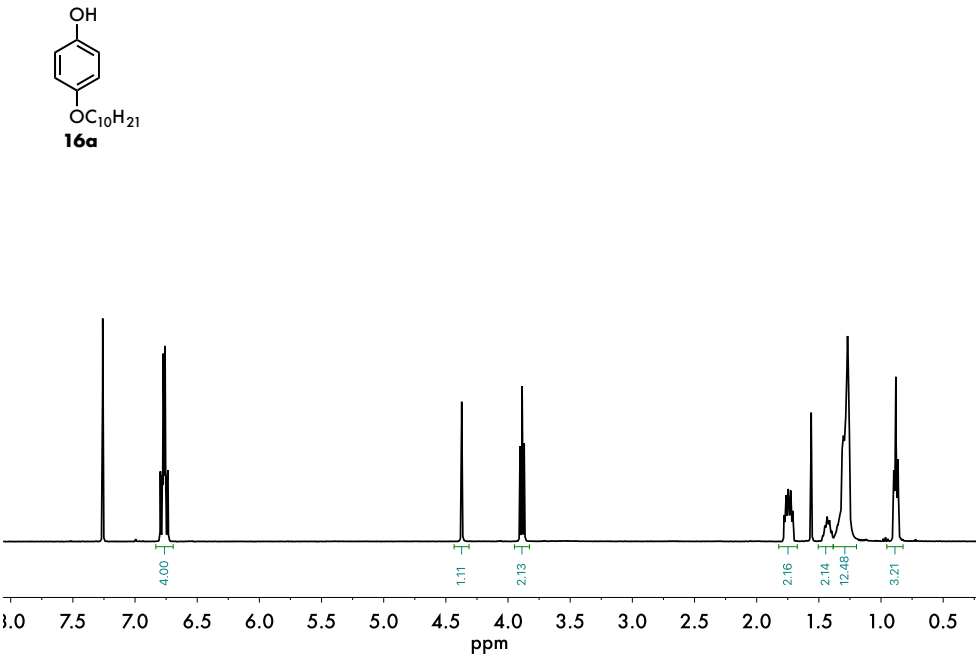


Figure S79. ^{1}H NMR spectrum of **16a**.

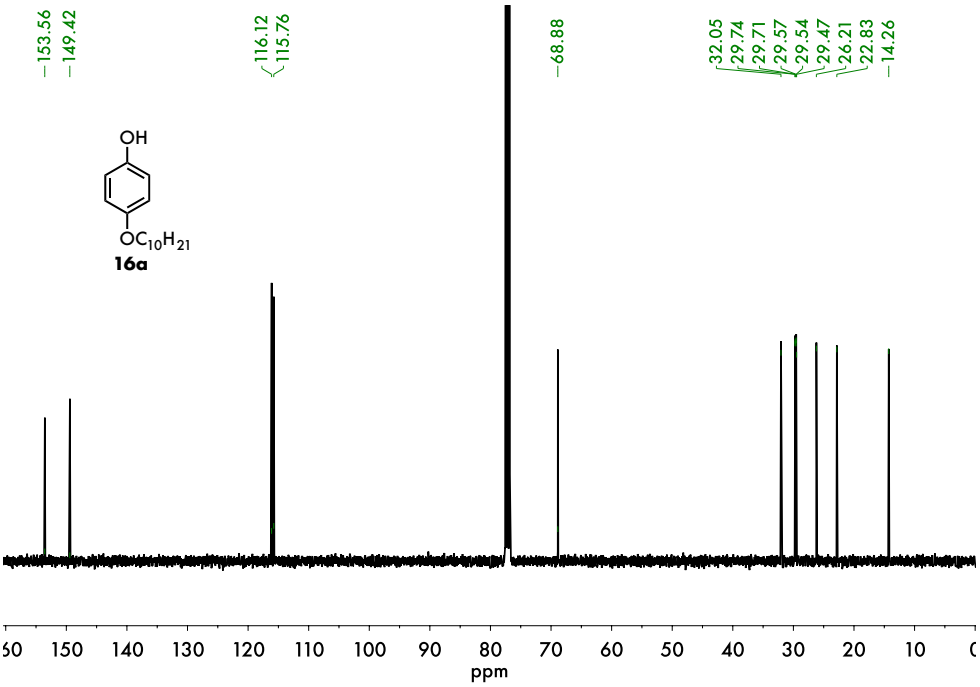


Figure S80. ^{13}C NMR spectrum of **16a**.

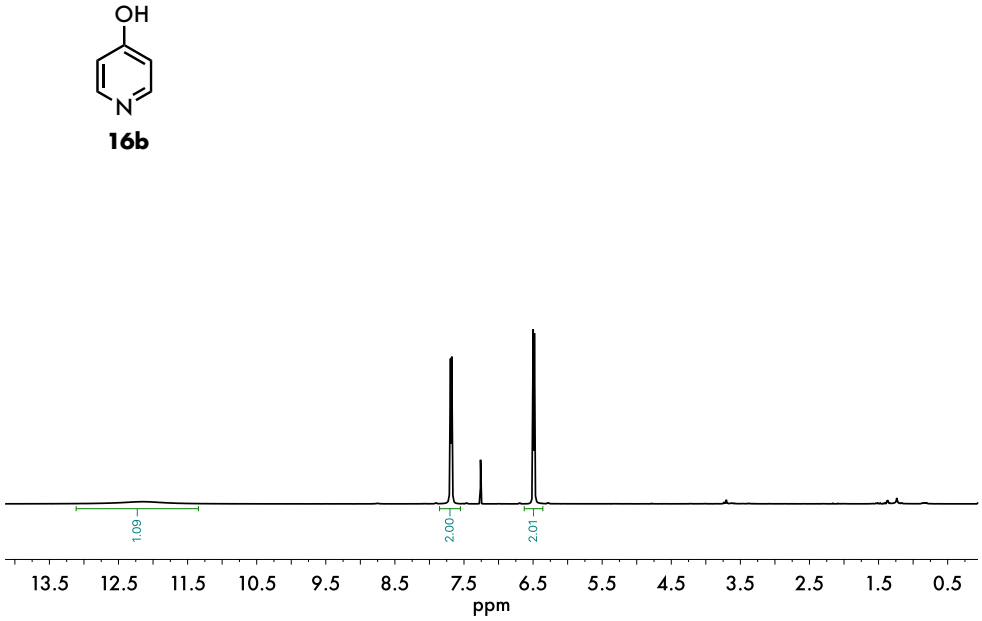


Figure S81. ^{1}H NMR spectrum of **16b**.

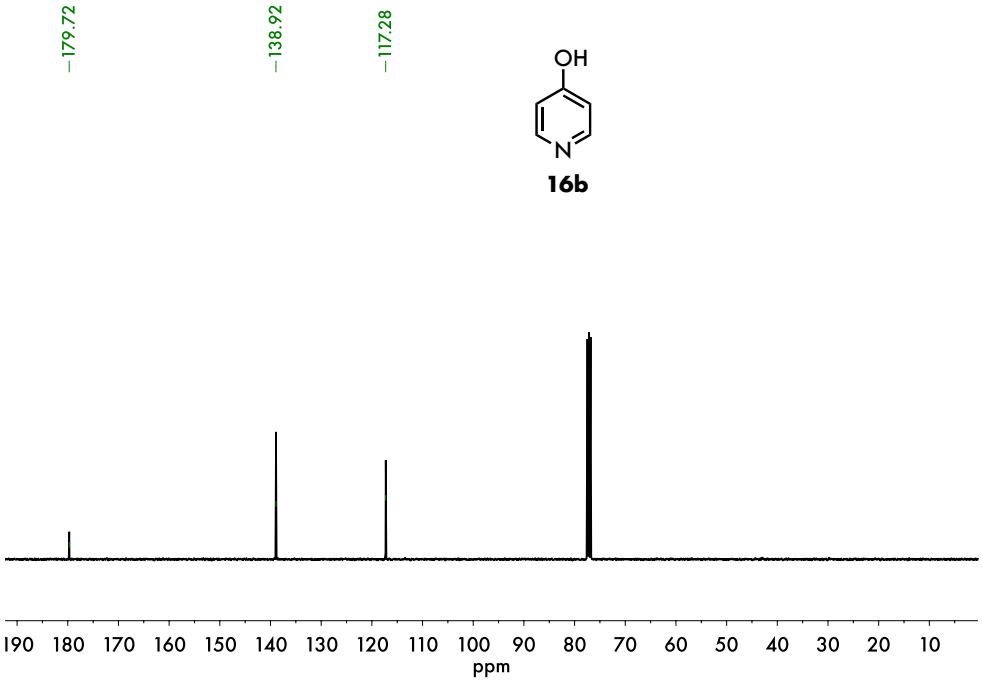


Figure S82. ^{13}C NMR spectrum of **16b**.

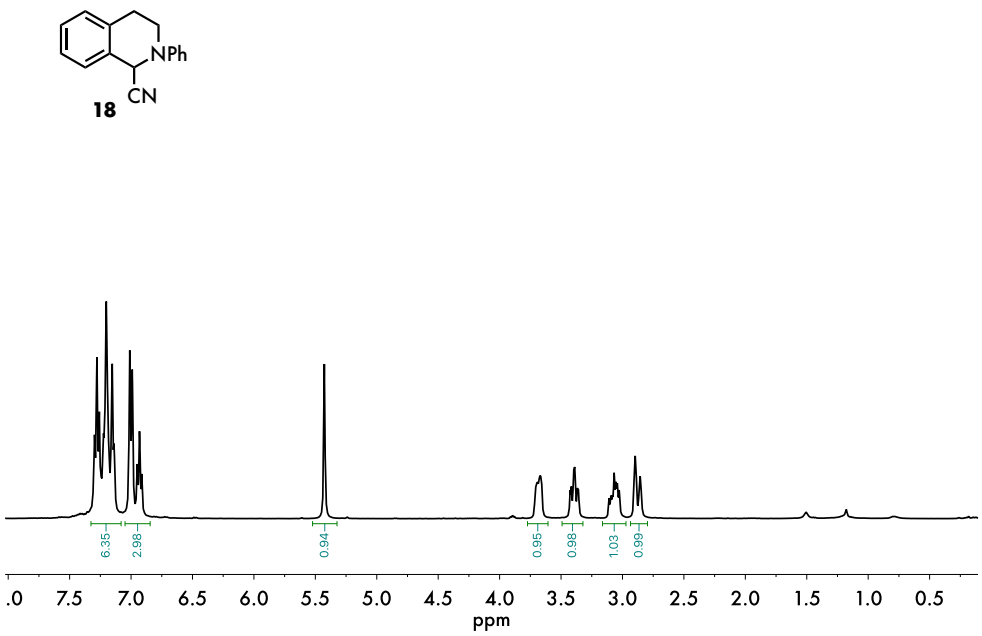


Figure S83. ^{1}H NMR spectrum of **18**.

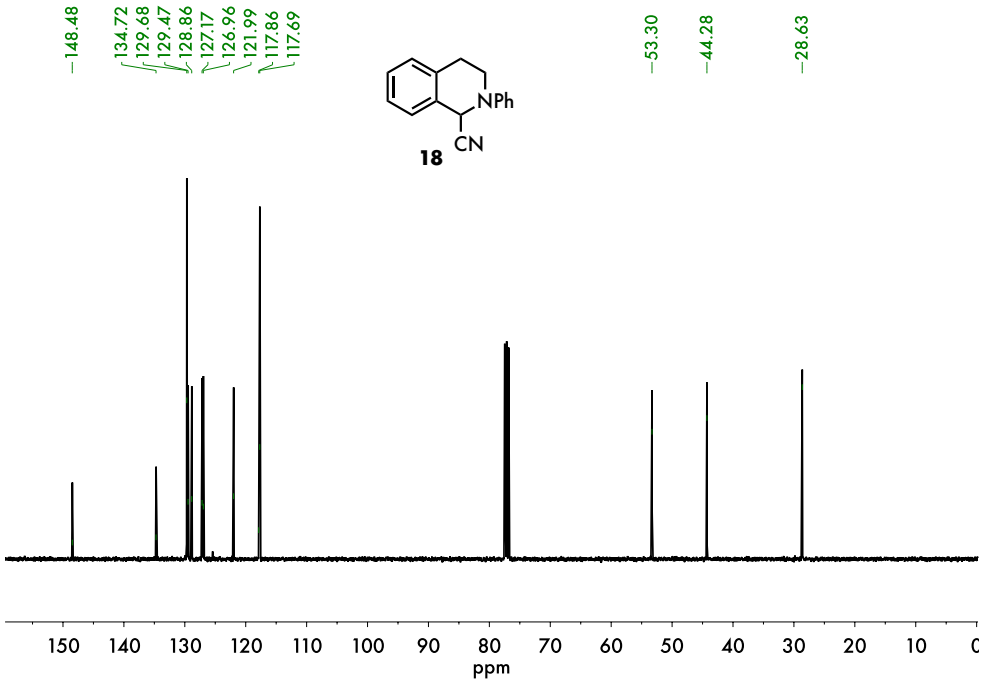


Figure S84. ^{13}C NMR spectrum of **18**.

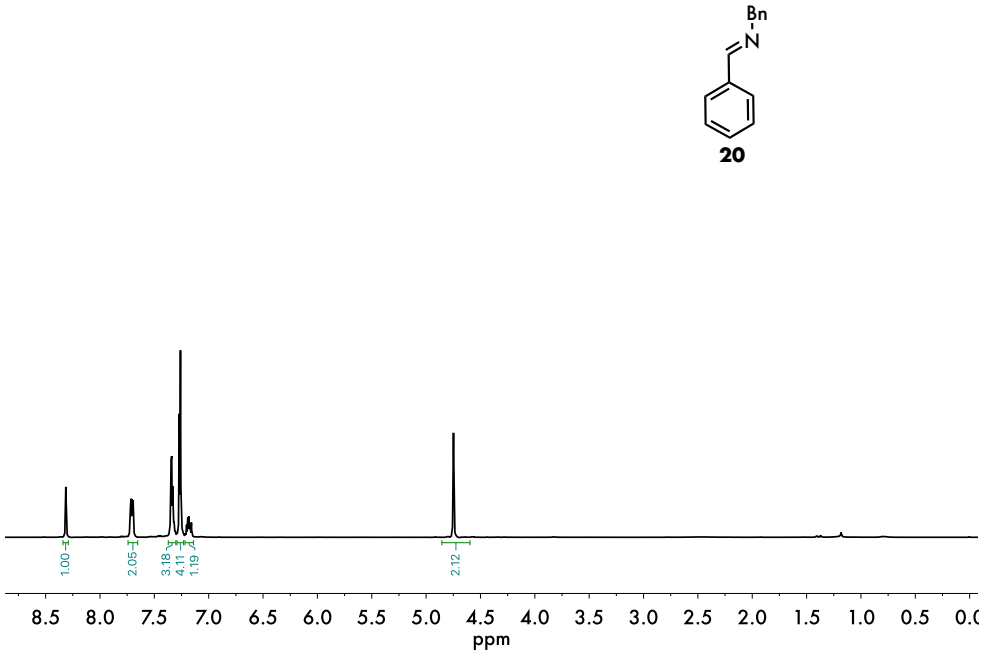


Figure S85. ^{1}H NMR spectrum of **20**.

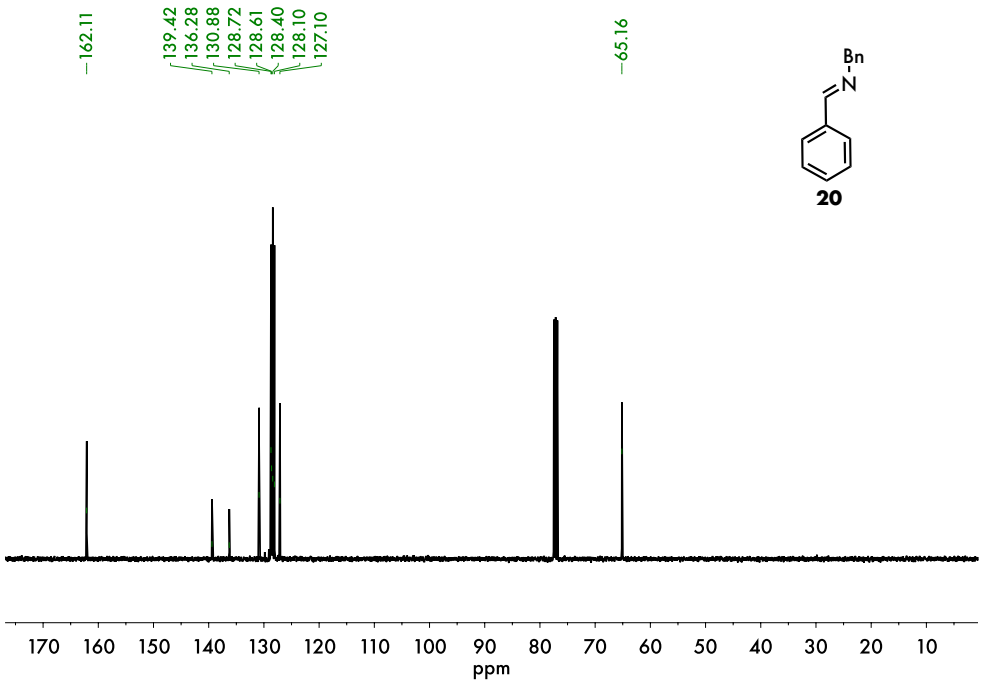


Figure S85. ^{13}C NMR spectrum of **20**.

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