A sunlight-compatible photochemical thiol-ene reaction promoted by *para*cyclophane-derived photocatalyst.

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Contents

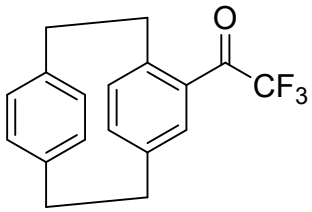
General remarks

Anhydrous solvents were purchased from Merck. All reagents were of commercial quality and were used without further purification. Analytical thin-layer chromatography (TLC) was performed on plates precoated with silica gel layers (Merck 60 F254). Visualization of the developed chromatogram was followed by UV absorbance. Flash column chromatography was performed using 40−63 mesh silica. Nuclear magnetic resonance spectra were recorded on a Bruker 400MHz NEO. Chemical shifts are reported in parts per million relative to an internal standard of residual chloroform (δ = 7.26ppm for ^{1}H NMR and 77.16 ppm for ^{13}C NMR). For the ^{1}H spectra, data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, and bs = broad singlet), coupling constant in Hz, and integration. High-resolution mass spectra (HRMS-ESI) were obtained on LCT Waters equipment. UV/vis Absorption spectra were measured in a 1 cm quartz cuvette using a Agilent Technologies Cary 60 spectrophotometer.
Optical rotations were recorded on a polarimeter with a sodium lamp of wavelength 589 nm and reported as follows; $[\alpha]^{T^{\circ}C}{}_{\lambda}$ (c, solvent).
All batch photoreactions were conducted in commercially-available EvoluChem™ PhotoRedOx TC. An EvoluChem 18 W LED lamp (405 nm) was used for the reactions.

Synthesis of photosensitizers

General procedure for the synthesis of photosensitizers:

In a two-neck round-bottom flask equipped with reflux condenser, septum and magnetic stirring bar, to a solution of aluminum trichloride (2 eq) in dry dichloromethane (0.25 M), under argon atmosphere and at 0°C was added anhydride or acyl chloride (2 eq) through septum. After 30 min stirring at 0°C, the septum was exchanged for a glass cap and the arene (1 eq) was rapidly added. The reaction mixture was stirred for 1h at 0°C then 3h at 40°C. The mixture was then cooled down to 0°C, quenched with concentrated chlorohydric acid (6 eq), then poured into a 1M sodium hydroxide solution (6 eq). Phases were separated and aqueous layer was extracted (3 times) with dichloromethane, dried over magnesium sulfate and condensed *in vacuo*. The residue was purified on silica gel column chromatography using a gradient of pentane and dichloromethane (10:0 to 9:1).



4-trifuoroacetyl[2.2]paracyclophane (PS1):

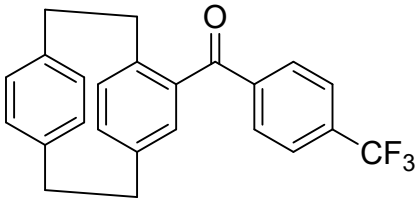
Synthesized according to general procedure using [2.2]paracyclophane (25 mmol, 5.2 g), trifluoroacetic anhydride (50 mmol, 7.0 mL) and aluminium trichloride (50 mmol, 6.7 g).

Product was obtained as a pale yellow solid (6.3 g, 82%)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14 (t, *J* = 2.1 Hz, 1H), 6.81 (dd, *J* = 7.8, 1.8 Hz, 1H), 6.65 (d, *J* = 7.8 Hz, 1H), 6.61 (dd, *J* = 7.8, 1.9 Hz, 1H), 6.54 (dd, *J* = 7.9, 1.9 Hz, 1H), 6.46 (dd, *J* = 7.9, 1.9 Hz, 1H),

6.40 (dd, *J* = 7.9, 1.9 Hz, 1H), 3.98 (ddd, *J* = 12.8, 6.9, 4.6 Hz, 1H), 3.30 – 3.15 (m, 4H), 3.12 – 3.01 (m, 2H), 3.00 – 2.90 (m, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -70.62.

According to previous description.[1]



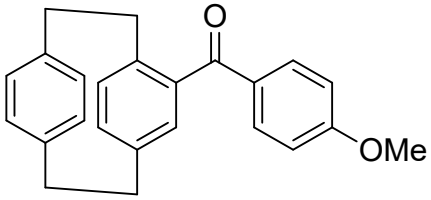
4-(*para*-trifluoromethylphenyl)[2.2]paracyclophane (PS2)

Synthesized according to general procedure using [2.2]paracyclophane (4.8 mmol, 1.0 g), 4-trifluoromethylbenzoyl chloride (9.6 mmol, 1.4 mL) and aluminum trichloride (8.4 mmol, 1.2 g).

Product was obtained as a white solid (0.91 g, 50%)

^{1}H NMR (400 MHz, Tol) δ 7.57 – 7.48 (m, 2H), 7.21 (d, *J* = 8.1 Hz, 2H), 6.86 (dd, *J* = 7.9, 1.8 Hz, 1H), 6.46 (d, *J* = 1.9 Hz, 1H), 6.39 – 6.30 (m, 3H), 6.26 (d, *J* = 7.8 Hz, 1H), 6.12 (dd, *J* = 7.9, 1.8 Hz, 1H), 3.44 – 3.27 (m, 2H), 2.96 – 2.86 (m, 1H), 2.85 – 2.73 (m, 2H), 2.71 – 2.57 (m, 2H), 2.51 (ddd, *J* = 12.9, 10.2, 5.0 Hz, 1H). ^{13}C NMR (101 MHz, Tol) δ 195.2, 142.5, 140.4, 140.0, 139.7, 136.9, 136.5, 136.4, 134.8, 133.5, 133.3, 133.1, 131.6, 130.8 (2C), 129.6, 125.70 (2C), 125.67, 125.63, 36.23, 35.83, 35.64, 35.44. ^{19}F NMR (376 MHz, Tol) δ -62.83.

HRMS (ESI-MS) for $C_{24}H_{19}F_3ONa$ $[M\text{-}Na]^+$ detected: m/z = 403.1278; calculated: m/z = 403.1280.

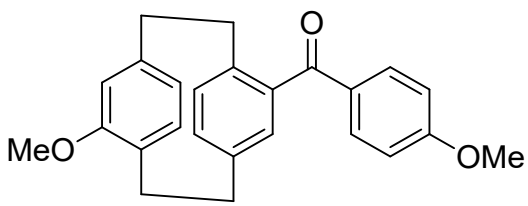


4-(*para*-methoxyphenyl)[2.2]paracyclophane (PS3):

Synthesized according to general procedure using [2.2]paracyclophane (4.8 mmol, 1.0 g), 4-methoxybenzoyl chloride (9.6 mmol, 1.6 g) and aluminum trichloride (8.4 mmol, 1.2 g).

Product was obtained as a white solid (0.61 g, 37%)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 – 7.65 (m, 2H), 6.92 – 6.84 (m, 2H), 6.78 (dt, *J* = 8.0, 1.1 Hz, 1H), 6.71 – 6.63 (m, 2H), 6.61 – 6.46 (m, 3H), 6.39 – 6.32 (m, 1H), 3.86 (s, 3H), 3.39 – 2.78 (m, 8H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.5, 163.3, 141.2, 140.0, 139.40, 139.38, 136.7, 135.8, 135.7, 134.0, 132.9, 132.8, 132.4 (3C), 131.7, 131.5, 113.6 (2C), 55.6, 35.7, 35.4, 35.3, 35.2.



HRMS (ESI-MS) for $C_{24}H_{22}O_2Na$ $[M\text{-}Na]^+$ detected: m/z = 365.1513; calculated: m/z = 365.1512.

4-(*para*-methoxyphenyl)-12-methoxy[2.2]paracyclophane (PS4):

To a solution of 4,12-dibromo*para*cyclophane (3 mmol, 1.1 g) in dry THF (25 mL), under Ar and at -78°C was added BuLi (2.5 M solution, 1.1 eq, 3.3 mmol, 1.35 mL) dropwise. After 30 min stirring, $B(OMe)_3$ (3 eq, 9 mmol, 1.0 mL) was added and the mixture was allowed to warm up

to RT upon stirring overnight. Then the mixture was cooled down to 0°C and NaOH (0.25 eq, 0.75 mmol, 30 mg in 0.1 mL H_2O) and H_2O_2 (30% w/v, 1.7 mL) were added and the mixture was stirred for 1 h. The mixture was quenched with NH_4Cl, extracted with DCM, dried and condensed *in vacuo*. The residue was purified on silica gel column chromatography using pentane/DCM/MeOH gradient (1:0:0 to 0:1:0 to 0:9:1).

4-hydroxy-12-bromo[2.2]*para*cyclophane was obtained as a white powder (353 mg, 39%)

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.98 (dd, *J* = 7.9, 1.8 Hz, 1H), 6.81 (dd, *J* = 7.8, 1.7 Hz, 1H), 6.47 (d, *J* = 1.8 Hz, 1H), 6.41 (d, *J* = 7.8 Hz, 1H), 6.36 (d, *J* = 7.7 Hz, 1H), 5.57 (d, *J* = 1.7 Hz, 1H), 4.49 (s, 1H), 3.49 (ddd, *J* = 12.9, 10.3, 2.2 Hz, 1H), 3.36 (ddd, *J* = 13.3, 10.1, 2.8 Hz, 1H), 3.10 (tdd, *J* = 12.6, 10.2, 5.4 Hz, 2H), 2.93 (dddd, *J* = 12.9, 11.0, 9.3, 2.5 Hz, 2H), 2.80 (ddd, *J* = 13.3, 10.7, 5.3 Hz, 1H), 2.68 (ddd, *J* = 13.5, 10.6, 5.3 Hz, 1H). According to literature data.[2]

To a RBF containing 4-hydroxy-12-bromo[2.2]*para*cyclophane (1.16 mmol, 353 mg) and K_2CO_3 (4 eq, 4.66 mmol, 644 mg) was added dry acetonitrile (15 mL). After 10 min stirring at RT, MeI (10 eq, 11.3 mmol, 725 µL) was added dropwise and the mixture was refluxed for 6 h. Then the mixture was partitioned between H_2O and DCM, aqueous layer was extracted with DCM and combined organic layers were dried and condensed *in vacuo*. The residue was purified on silica gel column chromatography using a gradient of pentane/Et_2O (1:0 to 4:1) to afford 4-methoxy-12-bromo[2.2]*para*cyclophane as a white solid (216 mg, 59%)

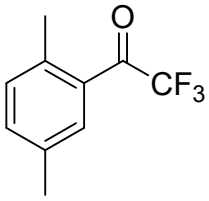
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.97 – 6.64 (m, 2H), 6.59 – 6.32 (m, 3H), 5.67 (s, 1H), 3.70 (s, 3H), 3.47 (m, 2H), 3.24 – 2.73 (m, 5H), 2.60 (m, 1H). According to literature data[2]

To a solution of 4-methoxy-12-bromo[2.2]*para*cyclophane (0.315 mmol, 100 mg) in dry THF (5 mL) at -78°C was added BuLi (2.5 M solution, 1.5 eq, 0.473 mmol, 190 µL). After 30 min stirring, the mixture was warmed up to 0°C before *para*-methoxybenzoyl chloride (4 eq, 1.26 mmol, 170 µL) was added all at once. The mixture was allowed to warm up to RT upon stirring overnight. Then it was quenched with H_2O and extracted with EtOAc. The combined organic layer was washed with NH_4Cl, H_2O and brine, dried and condensed *in vacuo*. The condensate was purified on silica gel column chromatography using pentane/Et_2O (4:1).

4-(*para*-methoxyphenyl)-12-methoxy[2.2]*para*cyclophane was obtained as a white powder (70 mg, 60%)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 – 7.63 (m, 2H), 6.94 (dd, *J* = 7.8, 1.9 Hz, 1H), 6.91 – 6.85 (m, 2H), 6.61 (d, *J* = 1.9 Hz, 1H), 6.52 – 6.44 (m, 2H), 6.28 (d, *J* = 7.6 Hz, 1H), 5.77 (d, *J* = 1.6 Hz, 1H), 3.85 (s, 3H), 3.74 (s, 3H), 3.43 (ddd, *J* = 13.0, 10.2, 2.8 Hz, 1H), 3.33 (ddd, *J* = 12.7, 10.5, 2.3 Hz, 1H), 3.24 – 3.06 (m, 2H), 2.98 (tdd, *J* = 12.9, 9.5, 2.6 Hz, 2H), 2.82 (ddd, *J* = 12.7, 10.4, 5.0 Hz, 1H), 2.58 (ddd, *J* = 13.0, 10.6, 5.2 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.2, 163.2, 157.6, 141.9, 140.7, 139.9, 137.1, 134.57, 134.55, 134.2, 132.3 (2C), 131.8, 131.5, 126.9, 123.7, 116.6, 113.6 (2C), 55.6, 54.6, 35.5, 35.1, 33.6, 30.4.

HRMS (ESI-MS) for $C_{25}H_{24}O_3Na$ [M-Na]+ detected: m/z = 395.1615; calculated: m/z = 395.1618.



1-(2,5-dimethylphenyl)-2,2,2-trifluoroethanone (PS5):

Synthesized according to general procedure using paraxylene (5 mmol, 0.62 mL), trifluoroacetic anhydride (10 mmol, 1.4 mL) and aluminium trichloride (10 mmol, 1.3 g).

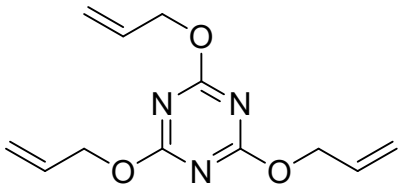
Product was obtained as a colorless oil (864 mg, 85%)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (t, *J* = 2.2 Hz, 1H), 7.34 (dd, *J* = 7.9, 1.8 Hz, 1H), 7.24 (d, *J* = 7.8 Hz, 1H), 2.53 (s, 3H), 2.40 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 182.7, 139.2, 135.7, 134.8, 132.5, 130.82, 130.78, 129.2, 21.3, 20.9. ^{19}F NMR (377 MHz, $CDCl_3$) δ -71.18.

According to previous description.[3]

Synthesis of substrates

Synthesis of triene substrate:



2,4,6-tris(allyloxy)-1,3,5-triazine (2u):

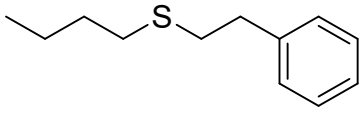
To a suspension of NaH (60% w, 3.5 eq, 19 mmol, 760 mg) in dry THF (10 mL) at 0°C was added dropwise allyl alcohol (3.5 eq, 19 mmol, 1.3 mL) solution in dry THF (4 mL). After 30 min stirring at RT, the mixture was cooled to 0°C before a solution of cyanuric acid (5.4 mmol, 1 g) in dry THF (4 mL) was added dropwise. The mixture was stirred at RT for 3 h before being poured into H_2O/ice and extracted with EtOAc. The organic layer was washed with NH_4Cl and brine, dried and condensed *in vacuo*. The residue was filtered on silica gel plug using pentane/EtOAC (10:1) as eluent.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.00 (ddt, *J* = 17.3, 10.5, 5.8 Hz, 3H), 5.36 (dq, *J* = 17.2, 1.5 Hz, 3H), 5.24 (dq, *J* = 10.4, 1.3 Hz, 3H), 4.86 (dt, *J* = 5.8, 1.4 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.9, 131.7, 118.9, 68.9. According to literature data.[4]

Optimization

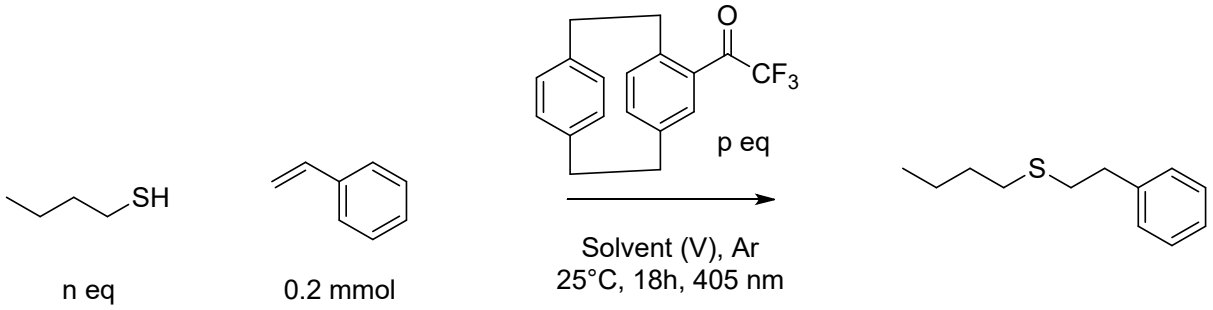
General procedure for optimization of photochemical thiol-ene reaction:

In a 2 mL screw-cap vial equipped with a septum cap and a magnetic stirring bar was added the photocatalyst (n mol%). The atmosphere was exchanged for argon, before previously degassed solvent (volume) was added through septum. Then styrene (0.2 mmol, 23 µL) and *n*-butanethiol (p eq) were successively added through septum before the vial was sealed with parafilm and irradiated at 405 nm for 18 h at 25 °C. The reaction mixture was then transferred to a round-bottom flask and concentrated *in vacuo*. Mesitylene (0.33 eq, 0.067 mmol) was added as an internal standard and the yield was estimated by ^{1}H NMR.



butyl(phenethyl)sulfane (3a):

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.28 (m, 2H), 7.25 – 7.19 (m, 3H), 2.94 – 2.86 (m, 2H), 2.83 – 2.74 (m, 2H), 2.55 (t, *J* = 7.3 Hz, 2H), 1.65 – 1.53 (m, 2H), 1.48 – 1.36 (m, 2H), 0.93 (t, *J* = 7.3 Hz, 3H). According to previous description.[5]

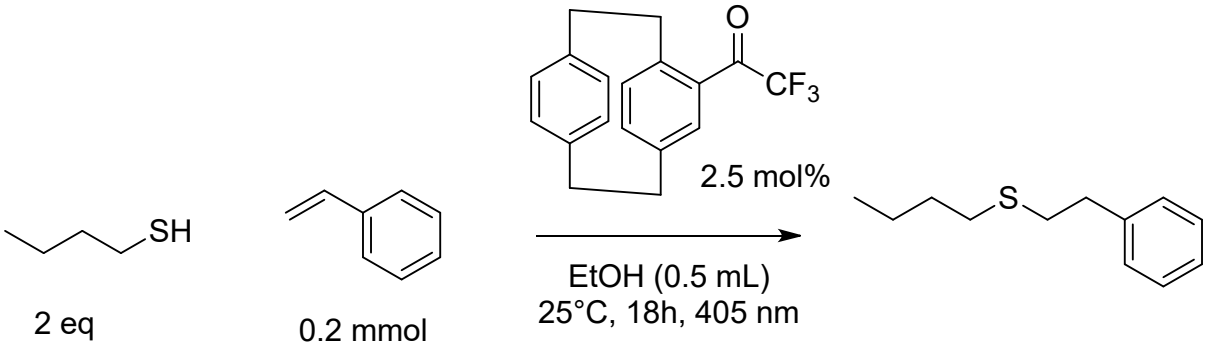


Eq Butanethiol	**Solvent (V)**	**Photocatalyst (eq)**	**^{1}H NMR Yield**
2 eq	MeOH (0.5 mL)	pCp-$COCF_3$ (5%)	Quant [88%]
2 eq	MeOH (0.5 mL)	pCp-$COCF_3$ (2.5%)	Quant
2 eq	ACN (0.5 mL)	pCp-$COCF_3$ (2.5%)	83%
2 eq	THF (0.5 mL)	pCp-$COCF_3$ (2.5%)	65%
2 eq	DMSO (0.5 mL)	pCp-$COCF_3$ (2.5%)	80%
2 eq	DCM (0.5 mL)	pCp-$COCF_3$ (2.5%)	55%
2 eq	neat	pCp-$COCF_3$ (2.5%)	90%
2 eq	**EtOH (0.5 mL)**	**pCp-$COCF_3$ (2.5%)**	**Quant [95%]**
2 eq	EtOH (0.5 mL)	pCp-$COCF_3$ (1%)	90%
1.5 eq	EtOH (0.5 mL)	pCp-$COCF_3$ (2.5%)	60%
1.2 eq	EtOH (0.5 mL)	pCp-$COCF_3$ (2.5%)	40%
2 eq	EtOH (0.5 mL)	pCp-CO-Ph-CF_3 (2.5%)	93%
2 eq	EtOH (0.5 mL)	pCp-CO-Ph-OMe (2.5%)	91%
2 eq	EtOH (0.5 mL)	MeO-pCp-CO-Ph-OMe (2.5%)	80%

Table S1: Optimization of photochemical thiol-ene reaction

Mechanistic investigation

Control experiments



Deviation from std	**^{1}H NMR Yield**
No photocat.	34%
No Light	5%
Me_2S_2 instead of BuSH	No conversion
p-Xyl-COCF3 as PC	72%

Table S2: Control experiments

Deuteration experiments

Deuterated thiophenol was synthesized as follows:

Figure S1: Synthesis of deuterated thiophenol

A solution of thiophenol (15 mmol, 1.5 mL) in heavy water (10 eq, 2.7 mL) was vigorously stirred at room temperature for 2h. The mixture was centrifugated and PhSD was pipetted out from D_2O. PhSD was obtained as a colorless liquid with 89% deuteration.

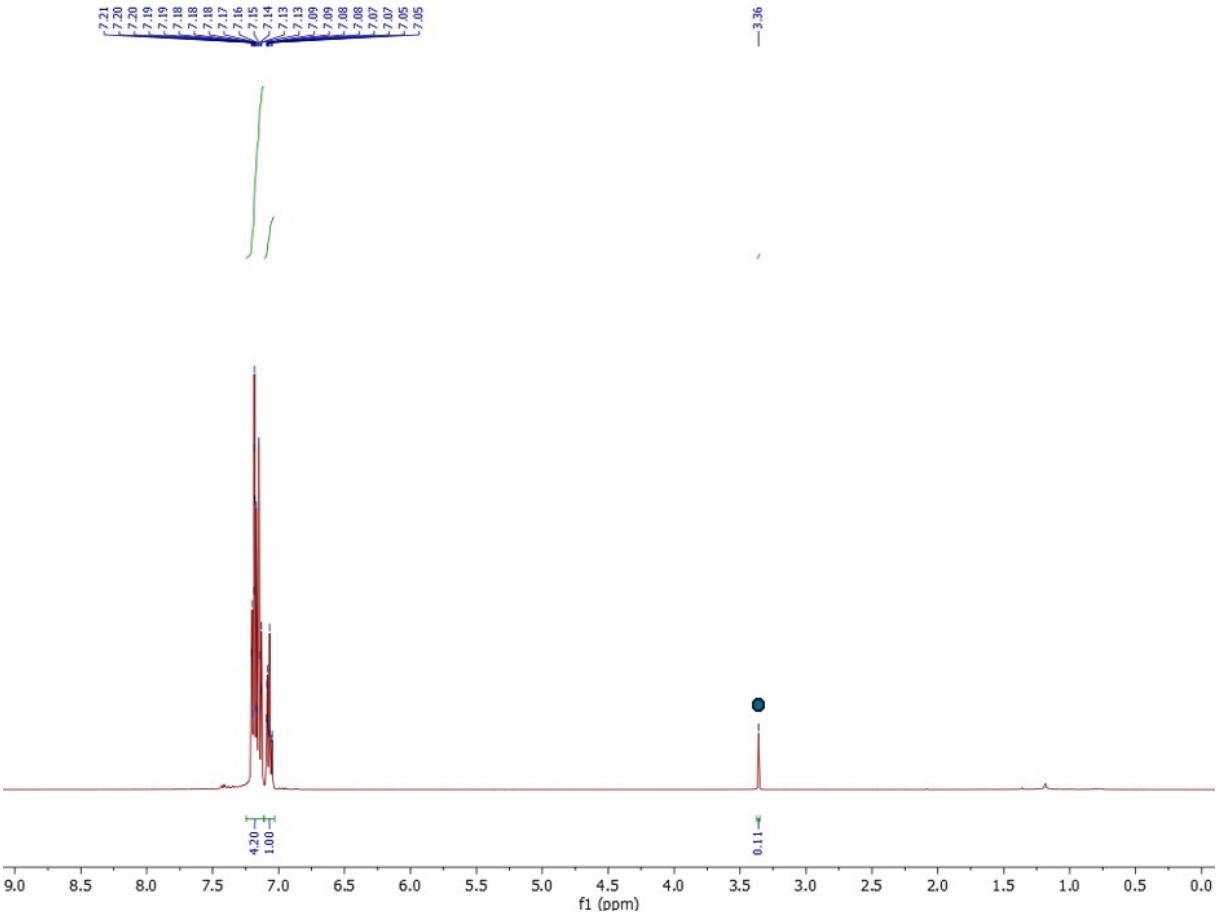


Figure S2: ^{1}H NMR ($CDCl_3$, 400 MHz) of deuterated thiophenol

Product deuteration:

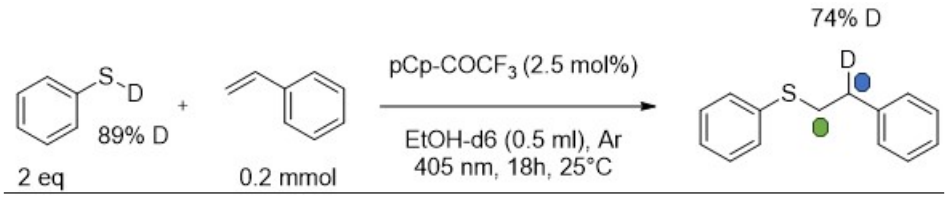


Figure S3: product deuteration

In a 2 mL screw-cap vial equipped with a septum cap and a magnetic stirring bar was added the pCp-$COCF_3$ (2.5 mol%, 1.5 mg). The atmosphere was exchanged for argon, before previously degassed d6-ethanol (0.5 mL) was added through septum. Then styrene (0.2 mmol, 23 µL) and PhSD (89% D, 2 eq, 41 µL) were successively added through septum before the vial was sealed with parafilm and irradiated at 405 nm for 18 h at 25 °C. The reaction mixture was then transferred to a round-bottom flask and concentrated *in vacuo*. Deuteration rate were estimated in ^{1}H NMR.

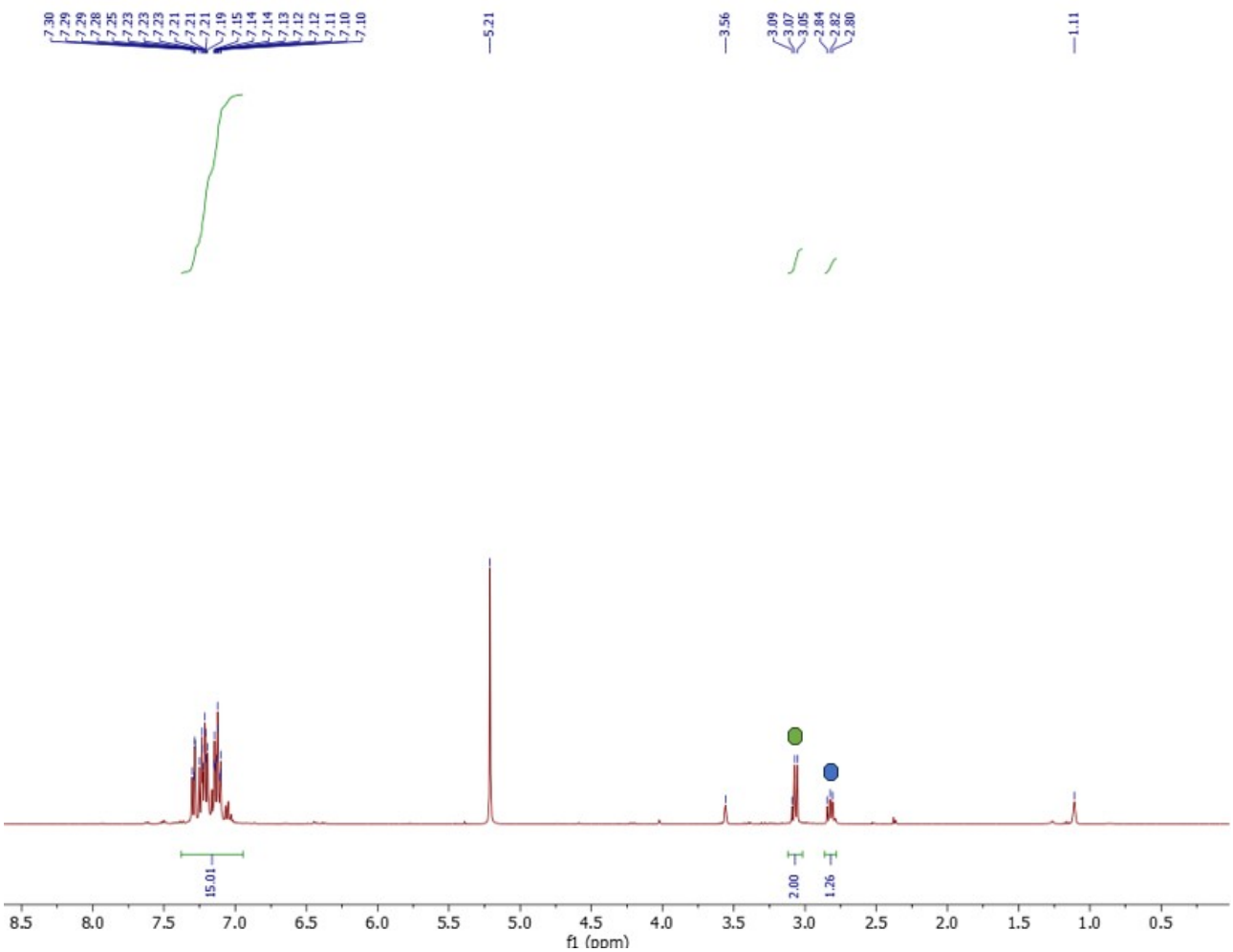


Figure S4: ^{1}H NMR (EtOH-d6, 400 MHz) of deuterated product

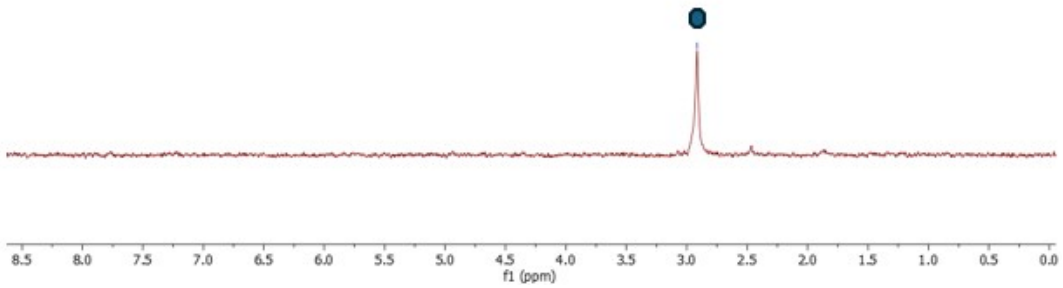


Figure S5: 2D NMR ($CHCl_3$, 76 MHz) of deuterated product

Catalyst deuteration:

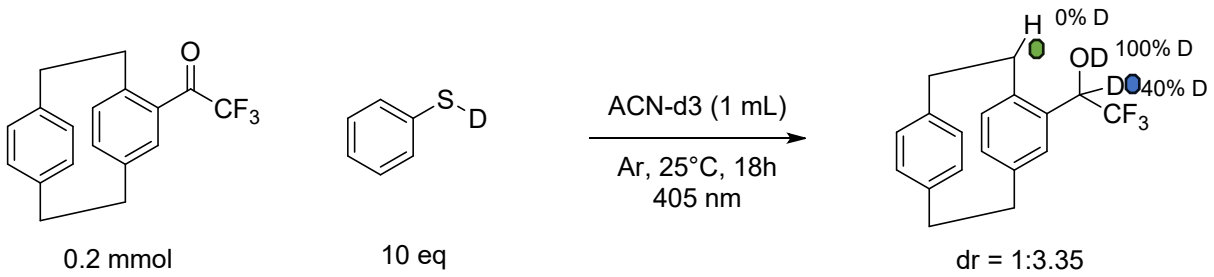


Figure S6: Catalyst deuteration

In a 2 mL screw-cap vial equipped with a septum cap and a magnetic stirring bar was added the pCp-$COCF_3$ (0.2 mmol, 66 mg). The atmosphere was exchanged for argon, before previously degassed d_3-acetonitrile (1 mL) was added through septum. Then PhSD (76% D, 10 eq, 205 µL) was added through septum before the vial was sealed with parafilm and irradiated at 405 nm for 18 h at 25 °C. The reaction mixture was then transferred to a round-bottom flask and concentrated *in vacuo*. Deuteration rate was estimated in ^{1}H NMR on the two diastereomers on the crude reaction mixture.

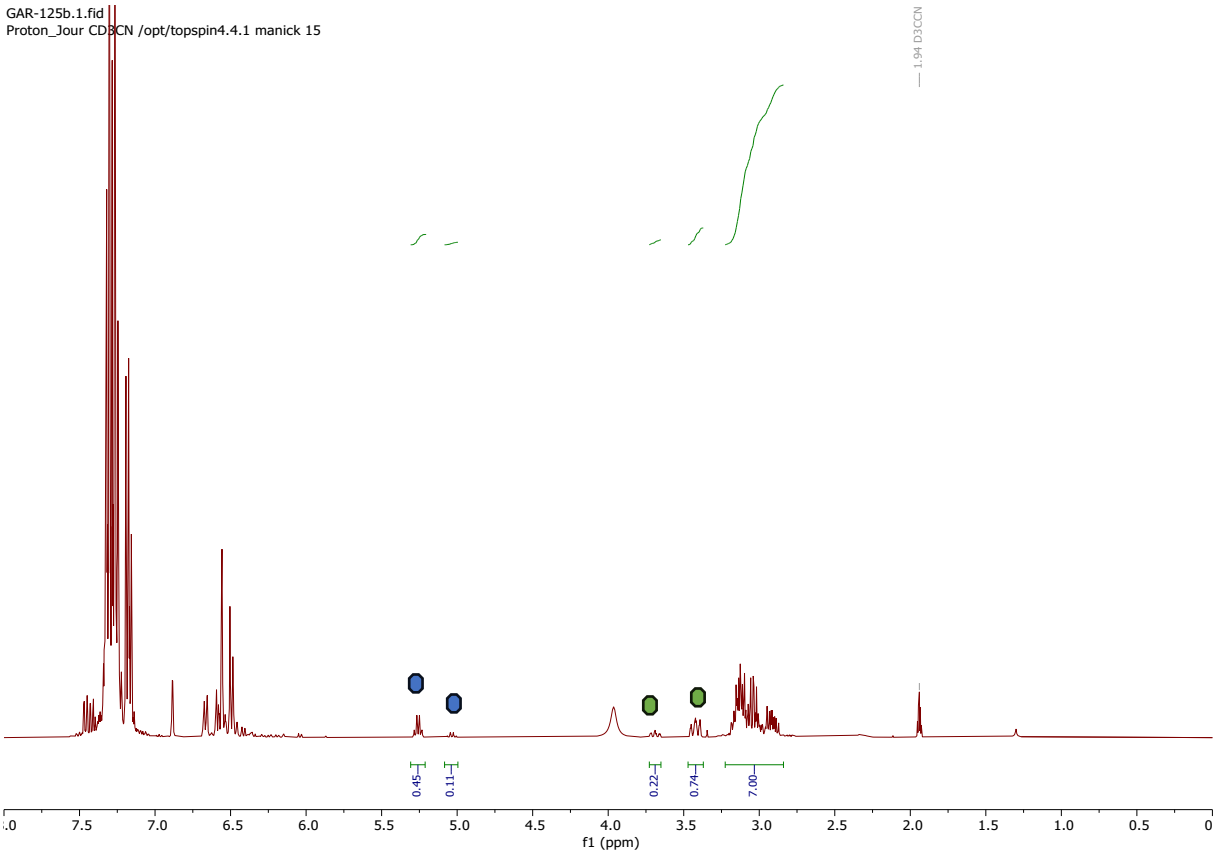


Figure S7: ^{1}H NMR (CD_3CN, 400 MHz) of deuterated catalyst

Reaction kinetics

In a 5 mL screw-cap vial equipped with a septum cap and a magnetic stirring bar was added PS1 or PS5 (2.5 mol%). The atmosphere was exchanged for argon, before previously degassed EtOH (2.5 mL) was added through septum. Then styrene (1.0 mmol) and *n*-butanethiol **1a** (2 eq, 2.0 mmol) were successively added through septum before the vial was sealed with parafilm and irradiated at 405 nm at 25 °C. A 100 µL aliquot was taken every 15 min and then one hour and then evaporated. In parallel, an internal standard solution of CH_2Br_2 was prepared by dissolving 0.1 mmol of CH_2Br_2 in 2.5 mL of $CDCl_3$. For each analysis, the evaporated aliquot was dissolved in 0.5 mL of $CDCl_3$ in an NMR tube, after which 100 µL of the internal-standard solution was added. The conversion was then determined by NMR.

PS1

Time (min.)	0	15	30	60	90	198	240	300	360
NMR yield (%)	0	4	5	11	14	21	26	34	36

PS5

Time (min.)	0	15	30	60	90	198	240	300	360
NMR yield (%)	0	2	3	6	9	12	15	18	23

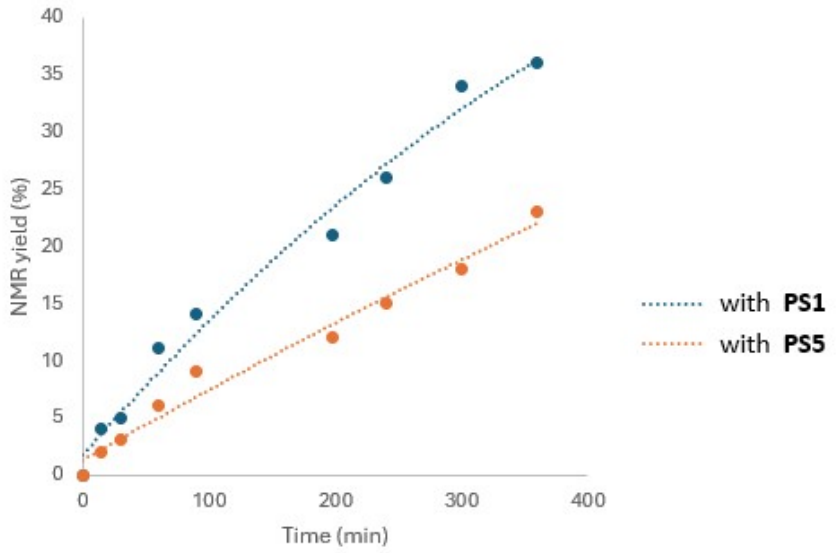


Figure S8: reaction kinetics

On/Off experiment

In an NMR tube were added pCp-$COCF_3$ (2.5 mol%, 1.5 mg), styrene (0.2 mmol, 23µL) and butanethiol (2 eq, 0.4 mmol, 43 µL). The atmosphere was switched for Ar before degassed D_3CCN (0.5 mL) was added. The tube was capped and sealed with parafilm before been irradiated and placed in the dark successively for the indicated time. Between each period, the tube was analyzed in ^1H NMR spectroscopy to evaluate conversion.

Time	Light	Remaining styrene	Product conversion
0 h	-	100%	0%
1 h	ON	61%	39%
1 h	OFF	61%	39%
2 h	ON	51%	49%
2 h	OFF	51%	49%
17 h	ON	22%	78%

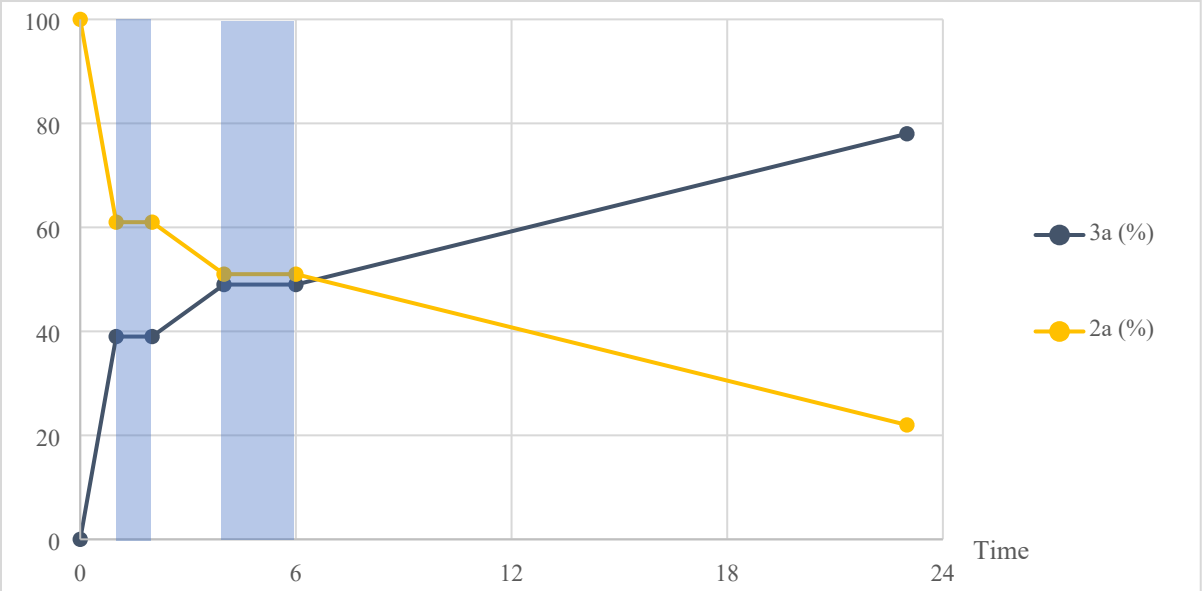


Figure S9: on/off experiments

Quantum yield

Photon flux measurement

The photon flux of a 18 W EvoluChem 405 PF lamp by standard ferrioxalate actinometry.[6] A 0.15 M potassium ferrioxalate solution was prepared by dissolving 1.81 g of potassium ferrioxalate hydrate in 0.05 M H_2SO_4 by using a 25.0 mL volumetric flask. A buffered solution of phenanthroline was prepared by dissolving 28.5 mg phenanthroline and 5.85 g of sodium acetate in 0.5 M H_2SO_4 by using a 25.0 mL volumetric flask. Both solutions were stored in the dark. To determine the photon flux of the spectrometer, 1.0 mL of the ferrioxalate solution was placed in a cuvette and irradiated for 90 seconds at λ = 405 nm in the EvoluChem™ PhotoRedOx TC. After irradiation, 1.0 mL of the buffer solution and 4 mL of distillated water were added to the cuvette. The mixture was stirred in the dark for 1h to allow complexation. The absorbance of the solution was measured at 510 nm. A non-irradiated sample was also prepared by mixing 1.0 mL of the ferrioxalate solution, 1.0 mL of the buffer solution and 4 mL of water. The absorbance of this solution was also measured at 510 nm.

To ensure reproducibility, the experiment was carried out three times.

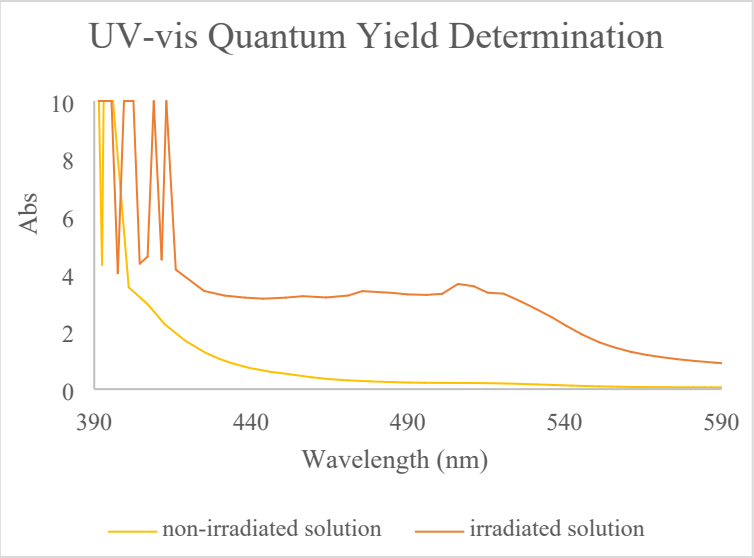


Figure S10: Absorbance curves of the irradiated solution and of the non-irradiated solution

$$\text{mol } (Fe^{2+}) = \frac{V \times \Delta A}{l \times \varepsilon} = \frac{0.006 \text{ L} \times 3.1904}{1 \text{ cm} \times 11100 \text{ L.mol}^{-1}.\text{cm}^{-1}} = 1.7 \times 10^{-6} \text{ mol}$$

V is the total volume of the solution, ΔA is the difference in absorbance at 510 nm between irradiated and non -irradiated solutions, l is the path length and Ɛ is the molar absorptivity at 510 nm.

$$\text{Photon flux} = \frac{\text{mol } (Fe^{2+})}{\phi \times t \times f} = \frac{1.7 \times 10^{-6} \text{ mol}}{1.15 \times 90 \text{ s} \times 0.999} = 1.6 \times 10^{-8} \text{ einstein.s}^{-1}$$

ϕ is the quantum yield of the ferrioxalate actinometer at 405 nm,[7] and f is the fraction of light absorbed at 405 nm ($f = 1\text{-}10^{-A}$).

Determination of the reaction quantum yield using PS1

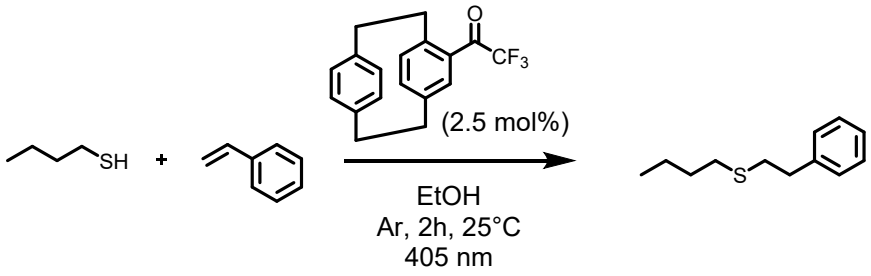


Figure S11: determination of the reaction quantum yield using PS1

In a 2 mL screw-cap vial equipped with a septum cap and a magnetic stirring bar was added the photocatalyst (2.5 mol%). The atmosphere was exchanged for argon, before previously degassed solvent (1.0 mL) was added through septum. Then styrene (0.4 mmol, 46 µL) and *n*-butanethiol (0.8 mmol, 84 µL) were successively added through septum before the vial was sealed with parafilm and irradiated at 405 nm for 2 h at 25 °C. The reaction mixture was then transferred to a round-bottom flask and concentrated *in vacuo*. Dibromomethane (0.1 eq,

0.04 mmol) was added as an internal standard and the yield was estimated in ^{1}H NMR. The absorbance of the reaction mixture is 0.7321, so f is calculated as the following:

$f = 1\text{-}10^{-A} = 0.81$

$$\phi = \frac{\text{mol product}}{\text{Photon flux x t x f}} = \frac{0.4 \times 10^{-3} \times 0.17 \text{ (yield)}}{1.6 \times 10^{-8} \text{ einstein.s}^{-1} \times 7200 \text{ s} \times 0.81} = 0.72$$

Determination of the reaction quantum yield using PS5

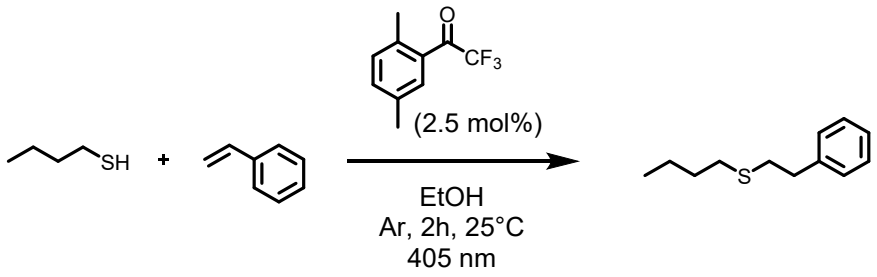


Figure S12: determination of the reaction quantum yield using PS5

In a 2 mL screw-cap vial equipped with a septum cap and a magnetic stirring bar was added the photocatalyst (2.5 mol%). The atmosphere was exchanged for argon, before previously degassed solvent (1.0 mL) was added through septum. Then styrene (0.4 mmol, 46 µL) and *n*-butanethiol (0.8 mmol, 84 µL) were successively added through septum before the vial was sealed with parafilm and irradiated at 405 nm for 4 h at 25 °C. The reaction mixture was then transferred to a round-bottom flask and concentrated *in vacuo*. Dibromomethane (0.1 eq, 0.04 mmol) was added as an internal standard and the yield was estimated in ^{1}H NMR. The absorbance of the reaction mixture is 0.0066, so f is calculated as the following:

$f = 1\text{-}10^{-A} = 0.015$

$$\phi = \frac{\text{mol product}}{\text{Photon flux x t x f}} = \frac{0.4 \times 10^{-3} \times 0.22 \text{ (yield)}}{1.6 \times 10^{-8} \text{ einstein.s}^{-1} \times 14\,400 \text{ s} \times 0.015} = 24$$

Stern-Volmer experiment

Fluorescence measurements were obtained using a spectrofluorometer JASCO FP-8600, with corrections applied for the detector's wavelength-dependent response. UV/vis Absorption spectra were measured in a 1 cm quartz cuvette using a Agilent Technologies Cary 60 spectrophotometer.

PS1 displays a maximum fluorescence at 345 nm in ACN ($l_{excitation}$ = 234 nm). Excitation of the samples was performed at 234 nm with entrance and exit slits positioned at 5 nm and 10 nm respectively. The fluorescence quenching constant of **PS1** by *n*-Butanethiol was determined

by following the fluorescence intensity of **PS1** with a gradual increase of *n*-Butanethiol concentration.

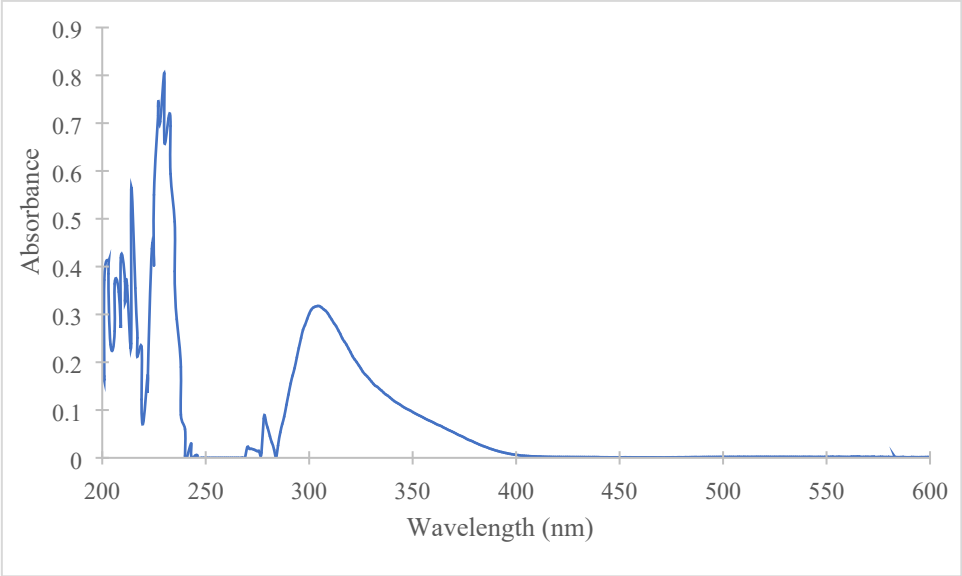


*Figure S 13: UV-vis absorbance spectra of **PS1** in ACN. [PS1] = 1.1 x 10^{-4} M*

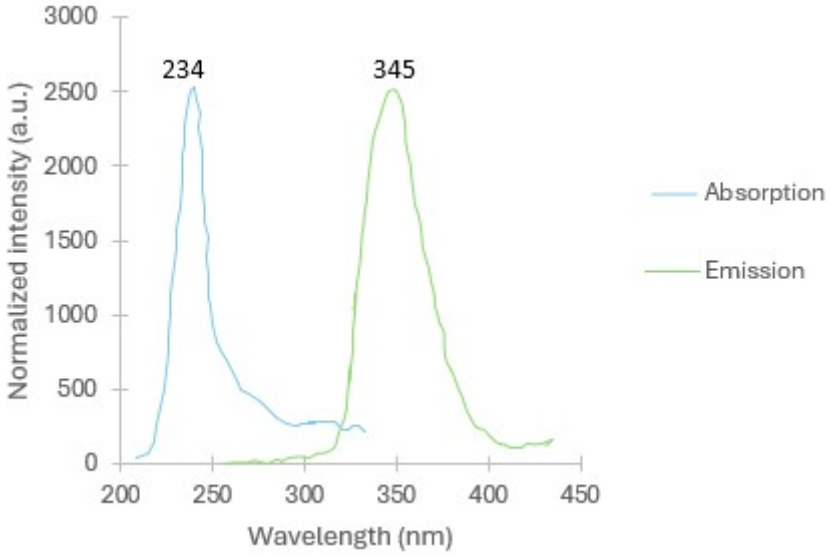


*Figure S 14: Normalized absorption and fluorescence spectra of **PS1** in ACN. [**PS1**] = 1.1 x 10^{-4} M. $l_{excitation}$ = 234 nm.*

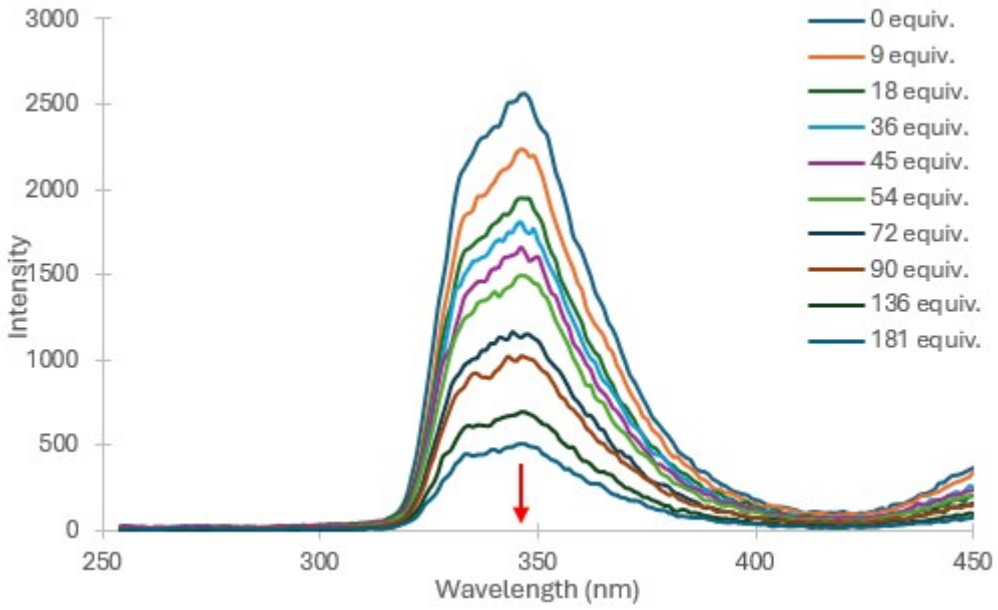


*Figure S 15 : Fluorescence intensity of **PS1** (C = 1.1 x 10^{-4} M) with a gradual increase of n-Butanethiol concentration (0 to 181 equivalents)*

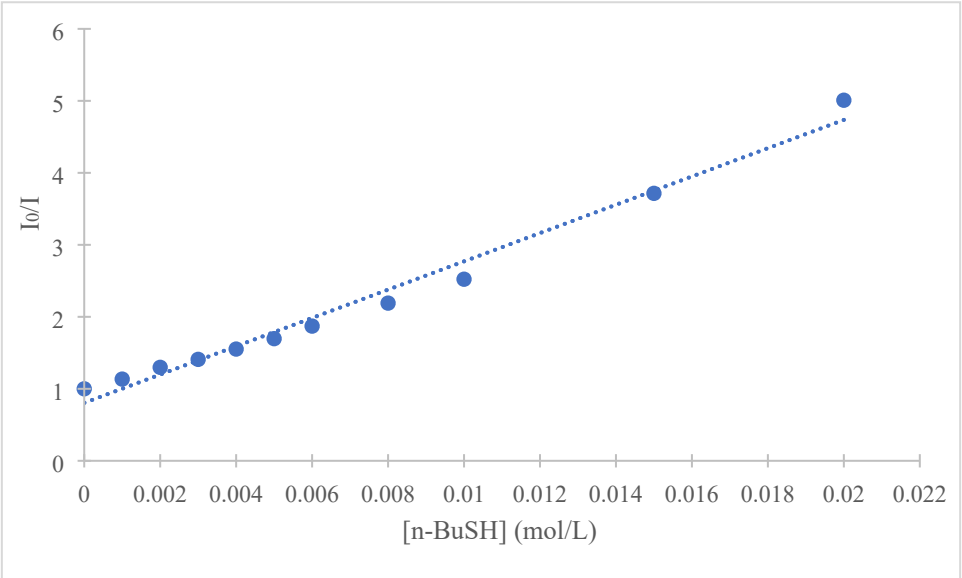


*Figure S 16: Stern-Volmer plot $I_0/I = f([n\text{-Butanethiol}])$ to evaluate the fluorescence quenching constant K_{SV} of **PS1** by n-Butanethiol (K_{SV} = 196.55 M^{-1}).*

EPR Spectroscopy

Degassing of solvent was done by freeze/taw cycle. Sample **A** was exposed under 405 nm (**Experiment A**). Sample **B** was exposed to sunlight in Marseille at the window lab, on the 1st of December 2025 at 3 pm (**Experiment B**). The samples are then deposited in the EPR cavity. Spectral simulations were carried out using PEST Winsin Public EPR Software tools, NIEHS.

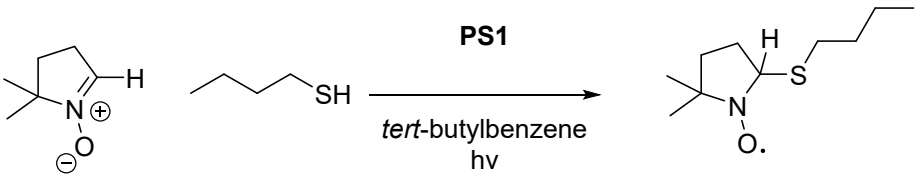


Figure S 17: Spin-trapping experiments in presence of DMPO

Experiment A:

EPR spectrum obtained when **PS1** is exposed to 405 nm light source in the presence of nBu-SH and DMPO in degassed *tert*-Butyl Benzene. Spectrum were recorded after 30 s of exposition. Initial concentrations : **PS1** 10 mM, *n*-Bu-SH 90 mM, DMPO 100 mM.

Settings : Bruker EMX (Cavity 4103TM), Freq. 9.797 GHz, MP 10 mW, Scan Time 41.9 s, Scan Range 8 mT, Mod. 0.02 mT, TC 20.48 ms, Gain 105.

Simulated coupling constants: A_N = 1.33 mT, A_H = 1.08 mT, $A_{H\gamma}$ = 0.1 mT, $A_{H\gamma}$ = 0.08 mT.

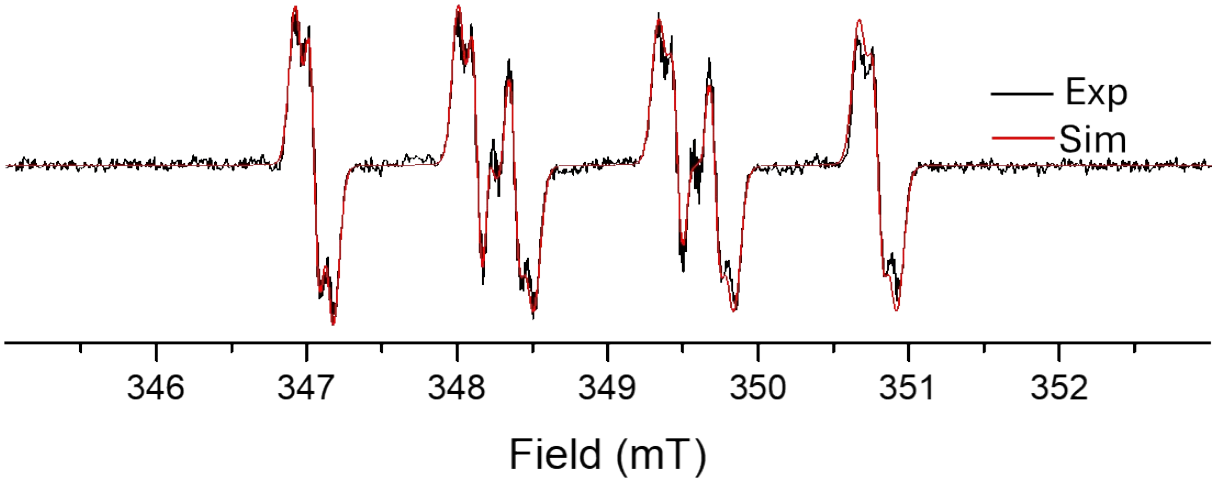


Figure S 18: Black curve: measured spectrum; Red curve: calculated for DMPO-1a adduct

Experiment B:

EPR spectrum obtained when **PS1** is exposed to sunlight in the presence of *n*Bu-SH and DMPO in degassed *tert*-Butyl Benzene. Spectrum recorded after 15 mins of exposition. Initial concentrations: **PS1** 10 mM, *n*Bu-SH 90 mM, DMPO 100 mM.

Settings: Bruker Elexsys (Cavity SHQ), Freq. 9.828 GHz, MP 10 mW, Scan Time 9 s, Scan Range 8 mT, Mod. 0.1 mT, TC 0, Gain 60 db.

Coupling constants: A_N = 1.32 mT, A_H = 1.08 mT, 2x$A_{H\gamma}$ = 0.09 mT; * DMPO overoxidation species.

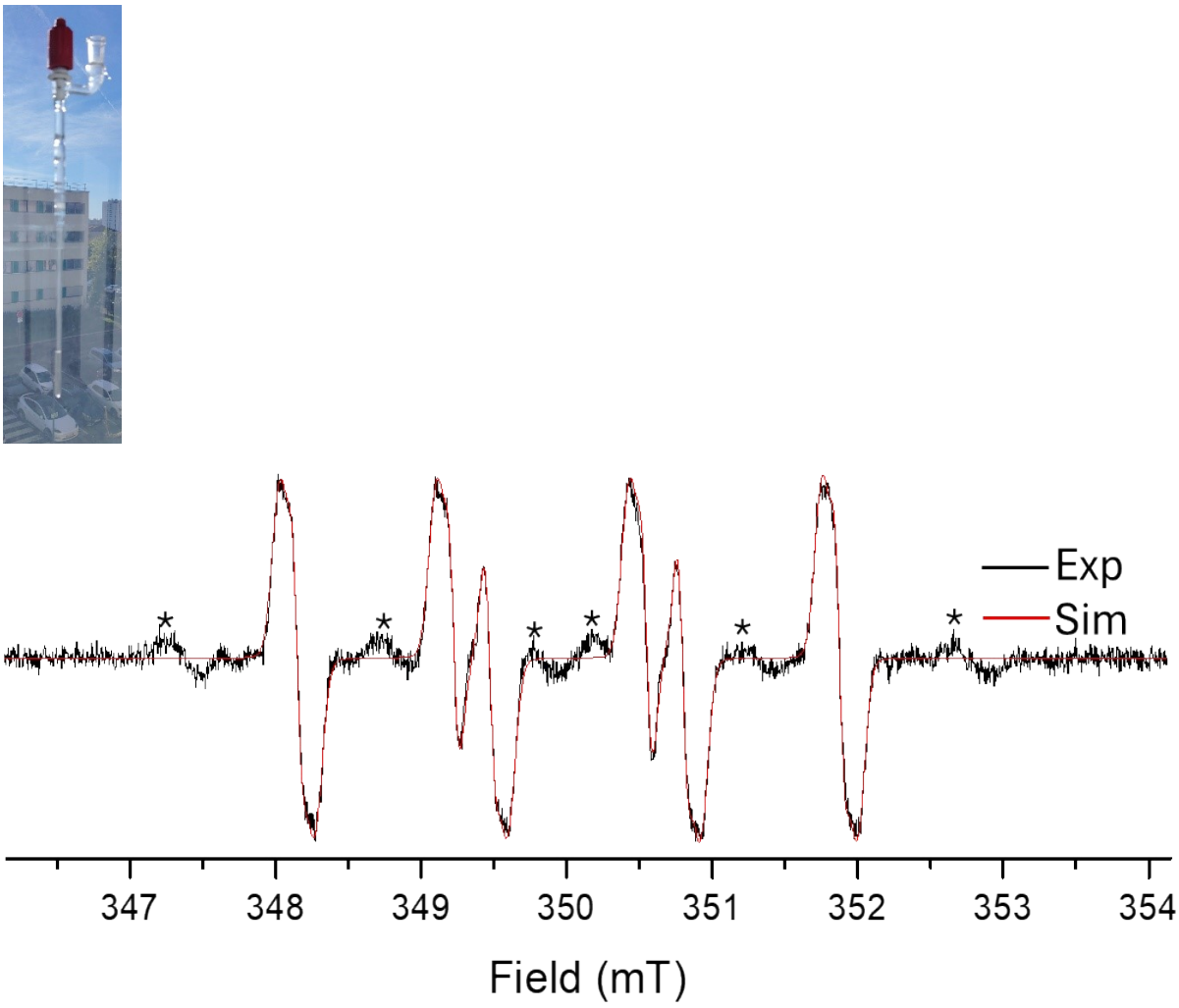


Figure S 19: Black curve: measured spectrum; Red curve: calculated for DMPO-1a adduct

Toxicity assay

Impact of PS1, and PS2 on the viability of human HepG2 cells. Human cells originating from liver (HepG2) were exposed for 48 hours to increasing concentrations of **PS1** (yellow triangles) or **PS2** (green squares). At the end of the incubation, the cell viability was measured using resazurin, cell viability of treated cells was expressed as percentage of viability of control cells treated with the vehicle alone (DMSO). data were fitted and analyzed using GrapPad Prism. Values are expressed as means +/- SD, n=3.

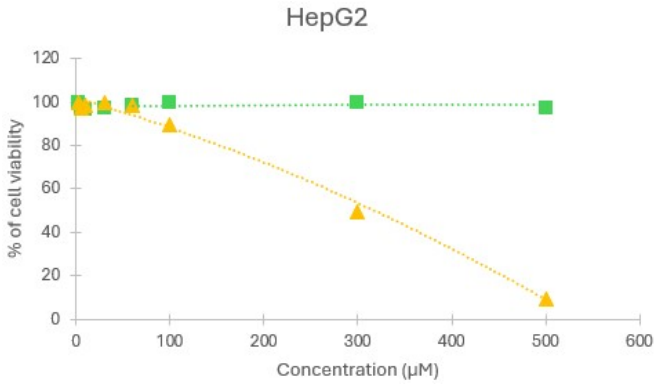


*Figure S20: Impact of **PS1**, and **PS2** on the viability of human HepG2 cells*

Cytotoxic Concentration 50% (CC_{50}) of PS1, and PS2 on human HepG2 cells:

CC_{50} (expressed in µM) on human HepG2 cells exposed for 48 hours to molecules were determined from graph above using GraphPad Prism.

PS1	221.3+/-9.8
PS2	>500

Synthesis of products via thiol-ene reaction

Photobox version

General procedure for scope of photochemical thiol-ene reaction in photobox:

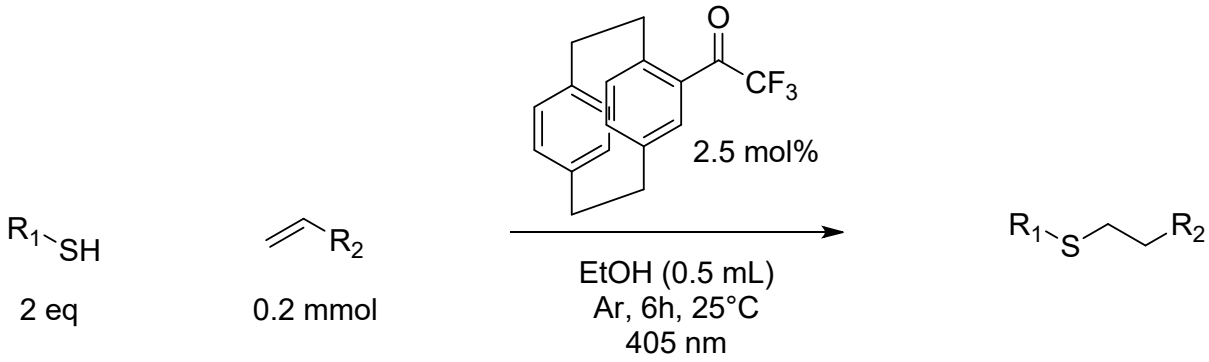
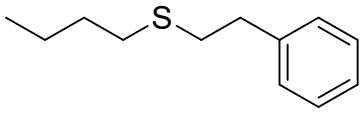


Figure S21: Photochemical thiol-ene reaction in photobox

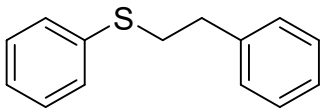
In a 2 mL screw-cap vial equipped with a septum cap and a magnetic stirring bar was added the **PS1** (2.5 mol%, 1.5 mg). The atmosphere was exchanged for argon, before previously degassed EtOH (0.5 mL) was added through septum. Then alkene (0.2 mmol) and thiol (2 eq, 0.4 mmol) were successively added through septum before the vial was sealed with parafilm and irradiated at 405 nm for 18 h at 25 °C. The reaction mixture was then transferred to a round-bottom flask and concentrated *in vacuo*. The condensate was purified on silica gel column chromatography.



butyl(phenethyl)sulfane (3a):

According to general procedure using styrene (23 µL) and butanethiol (43 µL). Colorless oil (29 mg, 75%).

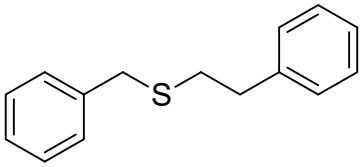
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.28 (m, 2H), 7.25 – 7.19 (m, 3H), 2.94 – 2.86 (m, 2H), 2.83 – 2.74 (m, 2H), 2.55 (t, *J* = 7.3 Hz, 2H), 1.65 – 1.53 (m, 2H), 1.48 – 1.36 (m, 2H), 0.93 (t, *J* = 7.3 Hz, 3H). According to previous description.[5]



phenethyl(phenyl)sulfane (3b):

According to general procedure using styrene (23 µL) and thiophenol (41 µL). Colorless oil (42 mg, 98%).

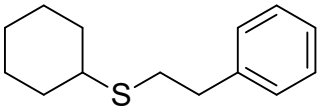
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.25 (m, 2H), 7.20 (ddd, *J* = 7.9, 6.5, 3.1 Hz, 4H), 7.15 – 7.07 (m, 4H), 3.14 – 3.02 (m, 2H), 2.84 (dd, *J* = 9.3, 6.5 Hz, 2H). According to literature data[8]



benzyl(phenethyl)sulfane (3c):

According to general procedure using styrene (23 µL) and benzylthiol (47 µL). Colorless oil (40 mg, 88%)

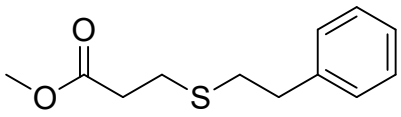
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 – 7.20 (m, 4H), 7.20 – 7.09 (m, 4H), 7.08 – 7.02 (m, 2H), 3.62 (s, 2H), 2.75 (dd, *J* = 9.3, 6.4 Hz, 2H), 2.62 – 2.53 (m, 2H). According to literature data.[8]



cyclohexyl(phenethyl)sulfane (3d):

According to general procedure using styrene (23 µL) and cyclohexylthiol (49 µL). Colorless oil (24 mg, 55%)

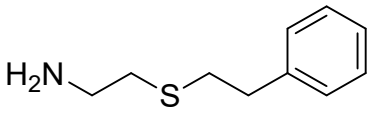
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.27 (m, 2H), 7.22 (dq, *J* = 8.8, 2.4 Hz, 3H), 2.91 – 2.85 (m, 2H), 2.83 – 2.76 (m, 2H), 2.66 (tt, *J* = 10.6, 3.8 Hz, 1H), 2.06 – 1.91 (m, 2H), 1.85 – 1.72 (m, 2H), 1.67 – 1.58 (m, 1H), 1.42 – 1.18 (m, 5H). According to literature data.[9]



Methyl (3-phenethylthio)propionate (3f):

According to general procedure using styrene (23 µL) and methyl 3-thiopropionate (44 µL). Colorless oil (35 mg, 78%)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.27 (m, 2H), 7.25 – 7.18 (m, 3H), 3.70 (s, 3H), 2.93 – 2.86 (m, 2H), 2.84 – 2.77 (m, 4H), 2.61 (t, *J* = 7.4 Hz, 2H). According to literature data.[10]

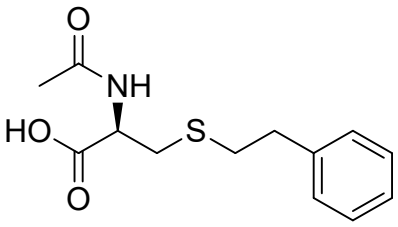


2-(phenethylthiol)ethanamine (3g):

According to general procedure using (styrene (23 µL) and cysteamine (30.9 mg). Colorless oil (33 mg, 91%)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.27 (m, 2H), 7.24 – 7.17 (m, 3H), 2.93 – 2.85 (m, 4H), 2.77 (ddd, *J* = 8.3, 6.7, 1.2 Hz, 2H), 2.64 (t, *J* = 6.4 Hz, 2H), 2.10 (d, *J* = 8.6 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.5, 128.6 (4C), 126.5, 41.0, 36.5, 36.1, 33.4.

HRMS (ESI-MS) for $C_{10}H_{15}NS$ [M+H$^+$] detected: m/z = 182.0997; calculated: m/z = 182.0998.

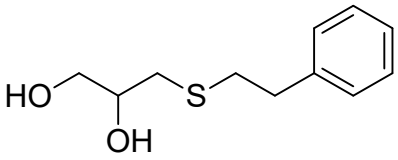


(*R*)-2-acetamido-3-(phenethylthio)propionic acid (3h):
According to general procedure using (styrene (23 µL) and N-acetylcysteine (65.3 mg). Colorless oil (48 mg, 90%)

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.55 (s, 1H), 7.20 (t, *J* = 7.5 Hz, 2H), 7.16 – 7.06 (m, 3H), 6.60 (d, *J* = 7.4 Hz, 1H), 4.70 (dt, *J* = 7.5, 5.1 Hz, 1H), 3.04 – 2.88 (m, 2H), 2.83 – 2.66 (m, 4H), 1.96 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.3, 171.8, 140.1, 128.62 (2C), 128.61 (2C), 126.6, 52.2, 36.2, 34.2, 33.9, 22.9.

HRMS (ESI-MS) for $C_{13}H_{17}NO_3SNa$ [M+Na]$^+$ detected: m/z = 190.0818; calculated: m/z = 190.0821.

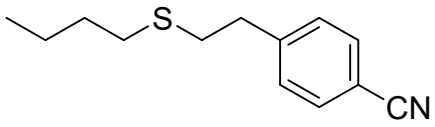
$[\alpha]^{24}_{589}$ +13 (c 1.498 g/100mL, CH_2Cl_2).



3-(phenethylthio)propane-1,2-diol (3i):
According to general procedure using (styrene (23 µL) and 1-thiolglycerol (35 µL). Colorless oil (34 mg, 80%)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.27 (m, 2H), 7.25 – 7.17 (m, 3H), 3.78 (dddd, *J* = 8.1, 6.0, 4.7, 3.3 Hz, 1H), 3.72 (dd, *J* = 11.3, 3.3 Hz, 1H), 3.53 (dd, *J* = 11.3, 6.0 Hz, 1H), 2.93 – 2.86 (m, 4H), 2.85 – 2.78 (m, 2H), 2.68 (dd, *J* = 13.7, 4.7 Hz, 1H), 2.60 (dd, *J* = 13.7, 8.0 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.2, 128.63 (2C), 128.59 (2C), 126.6, 70.2, 65.5, 36.3, 35.9, 34.0.

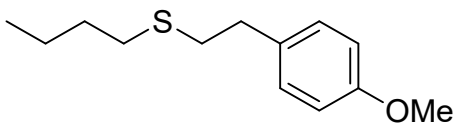
HRMS (ESI-MS): for $C_{13}H_{17}NO_3SNa$ [M+Na]$^+$ detected m/z = 235.0763; calculated m/z = 235.0763.



4-(2-(butylthio)ethyl)benzonitrile (3j):
According to general procedure using 4-cyanostyrene (26 mg) and *n*BuSH (43 µL). Colorless oil (30 mg, 70%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 – 7.54 (m, 2H), 7.35 – 7.28 (m, 2H), 2.94 (t, *J* = 7.9 Hz, 2H), 2.77 (t, *J* = 7.4 Hz, 2H), 2.51 (t, *J* = 7.5 Hz, 2H), 1.55 (quint., *J* = 6.9 Hz, 2H), 1.39 (sex, *J* = 7.3 Hz, 2H), 0.91 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.3, 132.4, 129.5, 119.1, 110.4, 36.4, 33.1, 32.2, 31.8, 22.1, 13.8.

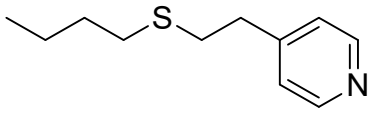
HRMS (ESI-MS): for $C_{13}H_{18}NS$ [M+H]$^+$ detected m/z = 220.1158; calculated m/z = 220.1154.



butyl(4-methoxyphenethyl)sulfane (3k):
According to general procedure using 4-vinylanisole (27 µL) and *n*BuSH (43 µL). Colorless oil (40 mg, 91%).

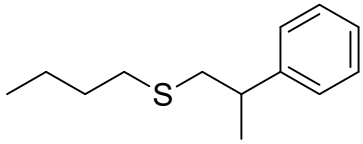
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15 – 7.09 (m, 2H), 6.87 – 6.81 (m, 2H), 3.79 (s, 3H), 2.87 – 2.79 (m, 2H), 2.78 – 2.70 (m, 2H), 2.53 (t, *J* = 7.3 Hz, 2H), 1.63 – 1.52 (m, 2H), 1.47 – 1.35 (m, 2H), 0.92 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ158.2, 132.9, 129.5, 113.9, 55.3, 35.6, 34.1, 32.1, 31.9, 22.1, 13.8.

HRMS (ESI-MS): for $C_{13}H_{21}OS$ $[M+H]^+$ detected m/z = 225.1302; calculated m/z = 225.1308.



4-(2-(butylthio)ethyl)pyridine (3l):
According to general procedure using 4-vinyl pyridine (26 µL) and *n*BuSH (43 µL). Colorless oil (38 mg, 97%). According to literature data.[11]

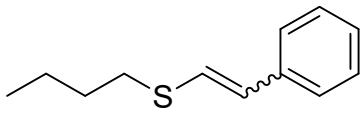
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 – 8.45 (m, 2H), 7.18 – 7.13 (m, 2H), 2.92-2.84 (m, 2H), 2.81-2.73 (m, 2H), 2.52 (t, *J* = 7.3 Hz, 2H), 1.61-1.51 (m, 2H), 1.39 (sex, *J* = 7.3 Hz, 2H), 0.90 (t, *J* = 7.3 Hz, 3H).



butyl(2-phenylpropyl)sulfane (3m):
According to general procedure using α-methylstyrene (52 µL) and *n*BuSH (84 µL). Colorless oil (34 mg, 41%).

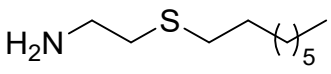
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.28 (m, 2H), 7.26 – 7.18 (m, 3H), 2.99-2.88 (m, 1H), 2.84-2.75 (m, 1H), 2.74-2.64 (m, 1H), 2.44 (t, *J* = 6.9 Hz, 2H), 1.63-1.46 (m, 2H), 1.42-1.32 (m, 2H), 1.37 (d., *J* = 6.8 Hz, 3H), 0.89 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.0, 128.5, 126.9, 126.4, 40.8, 40.3, 32.5, 31.8, 22.0, 21.0, 13.7.

HRMS (ESI-MS): for $C_{13}H_{20}SAg$ $[M+Ag]^+$ detected m/z = 315.0332; calculated m/z = 315.0331.



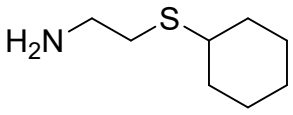
butyl(styryl)sulfane (3n):
According to general procedure using phenylacetylene (22 µL) and *n*BuSH (43 µL). Colorless oil (39 mg, 100%). Mixture of diastereomers (dr 85/15). According to literature data.[12]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53-7.46 (m, 0.3H), 7.40-7.27 (m, 3.7H), 7.23-7.14 (m, 1H), 6.74 (d, *J* = 15.6 Hz, 0.85H), 6.47 (d, *J* = 15.6 Hz, 0.85H), 6.44 (d, *J* = 10.7 Hz, 0.15H), 6.26 (d, *J* = 10.8 Hz, 0.15H), 2.81 (t, *J* = 7.2 Hz, 2H), 1.75-1.63 (m, 2H), 1.55-1.39 (m, 2H), 0.96 (t, *J* = 7.3 Hz, 3H).



2-(octylthio)ethan-1-amine (3o):
According to general procedure using 4-vinyl 1-octene (22 mg) and cysteamine (31 mg). Yellow paste (24 mg, 62%). According to literature data.[13]

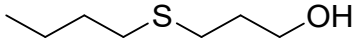
^{1}H NMR (400 MHz, $CDCl_3$) δ 3.09-3.00 (brs, 2H), 2.93 (t, *J* = 6.4 Hz, 2H), 2.66 (t, *J* = 6.4 Hz, 2H), 2.45 (t, *J* = 7.3 Hz, 2H), 1.62-1.51 (m, 2H), 1.42-1.17 (m, 10H), 0.87 (t, *J* = 7.0 Hz, 3H).



2-(cyclohexylthio)ethan-1-amine (3p):

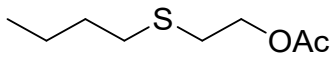
According to general procedure using cyclohexene (20 µL) and cysteamine (31 mg). Orange paste (24 mg, 77%). According to literature data.[13]

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.34-4.20 (brs, 2H), 3.09-2.98 (m, 2H), 2.79 (t, *J* = 6.6 Hz, 2H), 2.72-2.63 (m, 1H), 2.01-1.92 (m, 2H), 1.81-1.72 (m, 2H), 1.65-1.57 (m, 1H), 1.39-1.17 (m, 5H).



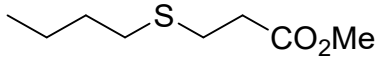
3-(butylthio)propan-1-ol (3q):
According to general procedure using allyl alcohol (14 µL) and *n*BuSH (43 µL). Colorless oil (25 mg, 84%)

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.74 (t, *J* = 6.1 Hz, 2H), 2.61 (t, *J* = 7.1 Hz, 2H), 2.51 (t, *J* = 7.3 Hz, 2H), 2.00 (s, 1H), 1.89 – 1.79 (m, 2H), 1.61 – 1.51 (m, 2H), 1.47 – 1.33 (m, 2H), 0.90 (t, *J* = 7.3 Hz, 3H). According to literature data[12]



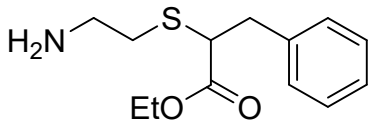
2-(butylthio)ethyl acetate (3r):
According to general procedure using vinyl acetate (19 µL) and *n*BuSH (43 µL). Pale yellow oil (29 mg, 82%)

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.20 (t, *J* = 7.0 Hz, 1H), 2.72 (t, *J* = 7.0 Hz, 1H), 2.55 (t, *J* = 7.4 Hz, 1H), 2.05 (s, 2H), 1.56 (tdd, *J* = 8.2, 7.1, 6.0 Hz, 1H), 1.46 – 1.32 (m, 1H), 0.90 (t, *J* = 7.3 Hz, 2H). According to literature data.[15]



methyl 3-(butylthio)propionate (3s):
According to general procedure using methyl acrylate (18 µL) and *n*BuSH (43 µL). Colorless oil (13 mg, 37%)

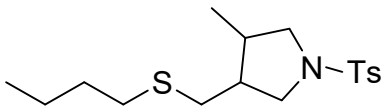
^{1}H NMR (400 MHz, $CDCl_3$) δ 3.69 (s, 3H), 2.77 (t, *J* = 7.4 Hz, 2H), 2.60 (t, *J* = 7.2 Hz, 2H), 2.52 (t, *J* = 7.4 Hz, 2H), 1.61 – 1.51 (m, 2H), 1.40 (h, *J* = 7.3 Hz, 2H), 0.91 (t, *J* = 7.3 Hz, 3H). According to literature data.[16]



ethyl 2-((2-aminoethyl)thio)-3-phenylpropanoate (3t):
According to general procedure using ethyl cinnamate (67 µL) and cysteamine (62 mg). Yellow oil (86 mg, 85%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35-7.24 (m, 4H), 7.24-7.17 (m, 1H), 4.25 (t, *J* = 7.7 Hz, 1H), 4.04 (qd, *J* = 2.3 Hz, 7.1 Hz, 2H), 2.90-2.79 (m, 2H), 2.78-2.67 (m, 2H), 2.49-2.35 (m, 2H), 1.81-1.69 (br s, 2H), 1.13 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.7, 141.4, 128.6, 127.7, 127.6, 60.7, 45.1, 41.7, 40.8, 35.2, 14.1.

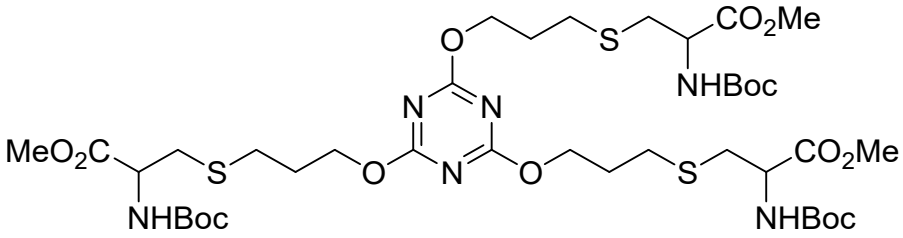
HRMS (ESI-MS) for $C_{13}H_{20}NO_2S$ $[M+H]^+$ detected m/z = 254.1211; calculated m/z = 254.1209.



3-((butylthio)methyl)-4-methyl-1-tosylpyrrolidine (3u) :
According to general procedure using *N*,*N*-diallyl-4-methylbenzenesulfonamide (51 mg) and *n*BuSH (43 µL). Yellow oil (63 mg, 90%). Mixture of diastereomers (dr 65/35).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74-7.66 (m, 2H), 7.30 (d, *J* = 8.2 Hz, 2H), 3.52 (dd, *J* = 7.2 Hz, 10.1 Hz, 0.3H, min), 3.47 (dd, *J* = 7.1 Hz, 9.7 Hz, 0.3H, min), 3.42 (dd, *J* = 6.7 Hz, 10.1 Hz, 0.7H, Maj), 3.36 (dd, *J* = 6.4 Hz, 9.7 Hz, 0.7H, Maj), 3.12 (dd, *J* = 7.0 Hz, 10.0 Hz, 0.7H, Maj), 3.01 (dd, *J* = 7.6 Hz, 10.1 Hz, 0.3H, min), 2.98 (dd, *J* = 4.4 Hz, 7.7 Hz, 0.7H, Maj), 2.79 (dd, *J* = 7.9 Hz, 9.7 Hz, 0.3H, min), 2.56 (dd, *J* = 4.8 Hz, 12.7 Hz, 0.3H, min), 2.46-2.38 (m, 5.3H), 2.28-2.06 (m, 2H), 1.88-1.68 (m, 1H), 1.55-1.43 (m, 2H), 1.41-1.28 (m, 2H), 0.92 (d, *J* = 6.4 Hz, 1H, min), 0.87 (t, *J* = 7.2 Hz, 3H), 0.76 (d, *J* = 6.9 Hz, 2H, Maj). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.4, 143.4, 134.1, 133.8, 129.7, 129.7, 127.6, 127.5, 54.8, 54.6, 52.9, 51.1, 45.7, 41.8, 38.4, 35.3, 34.3, 32.5, 32.3, 31.7, 31.7, 30.7, 22.0, 21.9, 21.6, 16.8, 13.7, 12.9.

HRMS (ESI-MS) for $C_{17}H_{28}NO_2S_2$ $[M+H]^+$ detected m/z = 342.1559; calculated m/z = 342.1556.



trimethyl 3,3',3''-((((1,3,5-triazine-2,4,6-triyl)tris(oxy))tris(propane-3,1-diyl))tris(sulfanediyl))tris(2-((tert-butoxycarbonyl)amino)propanoate) (3v):

According to general procedure using 2,4,6-tris(allyloxy)-1,3,5-triazine (50 mg) and *N*-(*tert*-Butoxycarbonyl)-L-cysteine methyl ester (6 eq, 282 mg). Colorless oil (150 mg, 79%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.45-5.24 (br d, 3H), 4.55-4.44 (br m, 3H), 4.45 (t, *J* = 6.19 Hz, 6H), 3.76 (s, 9H), 3.00-2.83 (m, 6H), 2.68 (t, *J* = 7.1 Hz, 6H), 2.06-1.95 (m, 6H), 1.43 (s, 27H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.1, 171.2, 155.2, 80.3, 66.7, 53.4, 52.7, 34.7, 29.1, 28.6, 28.4.

HRMS (ESI-MS) for $C_{39}H_{66}N_6O_{15}S_3Na$ $[M+Na]^+$ detected m/z = 977.3632; calculated m/z = 977.3641.

Procedure for the preparation of 3a on a 1 mmol scale.

In a screw-cap vial equipped with a septum cap and a magnetic stirring bar was added the pCp-$COCF_3$ (2.5 mol%, 7.6 mg). The atmosphere was exchanged for argon, before previously degassed EtOH (2.5 mL) was added through septum. Then styrene (1 mmol) and Butanethiol (2 eq, 2 mmol) were successively added through septum before the vial was sealed with parafilm and irradiated at 405 nm for 18 h at 25 °C. The reaction mixture was then transferred to a round-bottom flask and concentrated *in vacuo*. The condensate was purified on silica gel column chromatography using a gradient of pentane/DCM (1:0 to 4:1) unless otherwise mentioned to afford the product **3a** (76%, 138 mg).

Sunlight version:

General procedure for scope of photochemical thiol-ene reaction at sunlight:

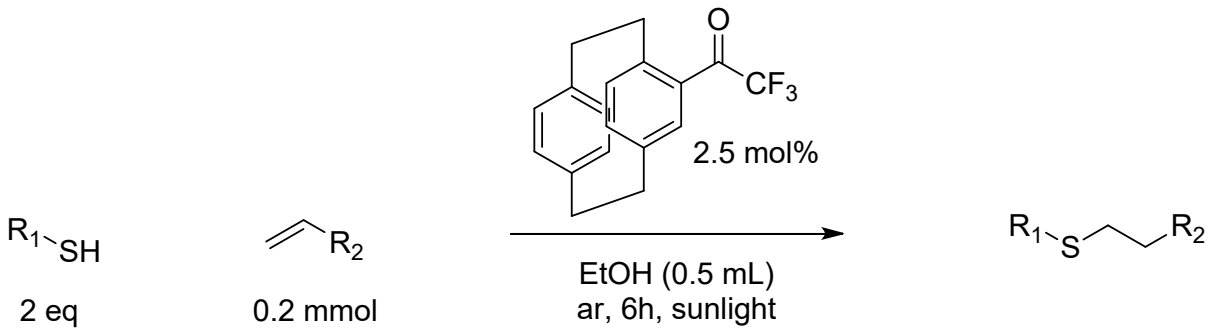
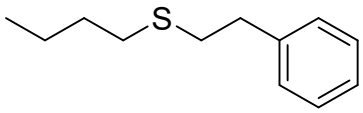
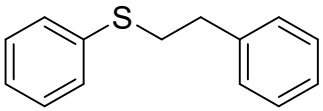


Figure S22: photochemical thiol-ene reaction at sunlight

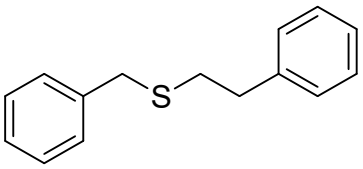
In a 2 mL screw-cap vial equipped with a septum cap and a magnetic stirring bar was added the **PS1** (2.5 mol%, 1.5 mg), alkene (0.2 mmol) and thiol (2 eq). The atmosphere was exchanged for argon, before previously degassed EtOH (0.5 mL) was added through septum, the vial was sealed with parafilm and irradiated at sunlight for 6h. The reaction mixture was then transferred to a round-bottom flask and concentrated *in vacuo*. Mesitylene (0.33 eq, 0.067 mmol) was added as an internal standard and the yield was estimated in ^{1}H NMR



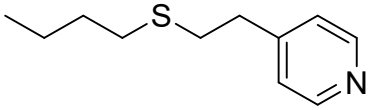
butyl(phenethyl)sulfane (3a):
Using styrene (23 µL) and *n*BuSH (43 µL). 75% yield. 16/09/2025. [43.3358663°, 5.4125640°]. 9am-3pm. 20-25°C.



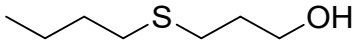
phenethyl(phenyl)sulfane (3b):
Using styrene (23 µL) and thiophenol (41 µL). +99% yield. 19/09/2025. [43.3358663°, 5.4125640°]. 10am-4pm. 22-28°C.



benzyl(phenethyl)sulfane (3c):
Using styrene (23 µL) and benzylthiol (47 µL). 91% yield. 19/09/2025. [43.3358663°, 5.4125640°]. 10am-4pm. 22-28°C.



4-(2-(butylthio)ethyl)pyridine (3l):
Using 4-vinylpyridine (22 µL) and *n*BuSH (43 µL). 72% yield. 19/09/2025. [43.3358663°, 5.4125640°]. 10am-4pm. 22-28°C.



3-(butylthio)propan-1-ol (3q):
Using allyl alcohol (14 µL) and *n*BuSH (43 µL). +99% yield. 19/09/2025. [43.3358663°, 5.4125640°]. 10am-4pm. 22-28°C.

TON determination:

In a 2 mL screw-cap vial equipped with a septum cap and a magnetic stirring bar was added the **PS1** (2.5 mol%, 3 mg). The atmosphere was exchanged for argon, before previously degassed EtOH (1 mL) was added through septum. Then styrene (0.4 mmol) and n-Butanethiol (2 eq, 0.8 mmol) were successively added through septum before the vial was sealed with parafilm and irradiated at 405 nm for 18 h at 25 °C. The reaction mixture was then transferred

to a round-bottom flask and concentrated *in vacuo*. NMR yield was determined using CH_2Br_2 as internal standard. Internal standard was evaporated. Then styrene (0.4 mmol), 1-Butanethiol (2 eq, 0.8 mmol) and EtOH (1 ml) were successively added through septum before the vial was sealed with parafilm and irradiated at 405 nm for 18 h at 25 °C. The second NMR yield was determined and the third turn was performed.

Cumulative turnover number (TON) refers to the total number of moles of product formed per mole of catalyst over multiple catalytic cycles, without replenishing the catalyst.

References

[1] J. Lahann, I. S. Choi, J. Lee, K. F. Jensen, R. Langer *Angew. Chem. Int Ed.* **2001**, *40*, 3166.

[2] T. Focken, J. Rudolph, C. Bolm *Synthesis* **2005**, *3*, 429.

[3] G. Simchen, A. Schmidt *Synthesis* **1996**, *9*, 1093.

[4] M. Yamaura; Nippon Kasei Chem; WO2010137517A1

[5] M. Jean, J. Renault, P. van de Weghe, N. Asao, *Tetrahedron Lett.* **2010**, *51*, 378–381.

[6] M. A. Cismesia, T. P. Yoon, *Chem. Sci.* **2015**, *6*, 5426-5434.

[7] C.G. Hatchard, C.A. Parker, *Mathematical and PhysicalSciences* **1956**, *235*, 518-536.

[8] M. Van Hoof, R. J. Mayer, J. Moran, D. Lebœuf *Angew. Chem. Int. Ed.* **2025**, *64*, e202417089.

[9] H. Wu, S. Chen, C. Liu, Q. Zhao, Z. Wang, Q. Jin, S. Sun, J. Guo, X. He, P. J. Walsh, Y. Shang *Angew. Chem. Int. Ed.* **2024**, *63*, e202314790

[10] S. Shen, F. Zhang, S. Zeng, Y. Tian, X. Chai, S. Gee, B. D. Hammock, J. Zheng *Anal. Chem.* **2009**, *81*, 2668.

[11] A.R. Katritzky, I. Takahashi, C.M. Marson, *J. Org. Chem.* **1986**, *25*, 4914.

[12] C. G. Bates, P. Saejueng, M. Q. Doherty, D. Venkataraman *Org. Lett.* **2004**, *26*, 5005.

[13] H. Ishibashi, M. Uegaki, M. Sakai, Y. Takeda *Tetrahedron* **2001**, *57*, 2115.

[14] J. V. Comasseto, R. A. Gariani, J. L. Princival, A. A. Dos Santos, F. K. Zinn *J. Organomet. Chem.* **2008**, *693*, 2929.

[15] F.-W. Lu, B.-K. Liu, Q. Wu, D.-S. Lv, X.-F. Lin *Adv. Synth. Catal.* **2008**, *350*, 1959.

[16] H.-Y. Huang, C.-F. Liang *Asian J. Org. Chem.* **2018**, *7*, 955.

Spectra

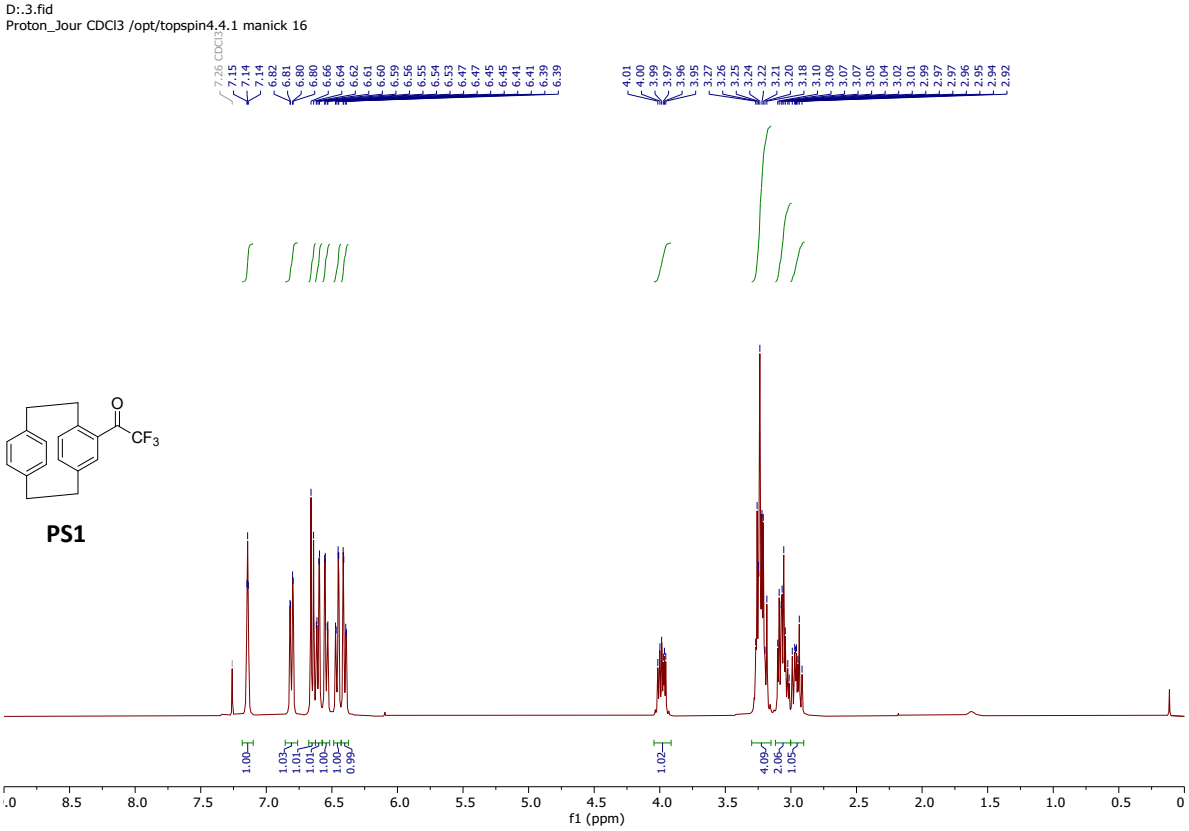


Figure S23: ^{1}H NMR ($CDCl_3$, 400 MHz) of PS1

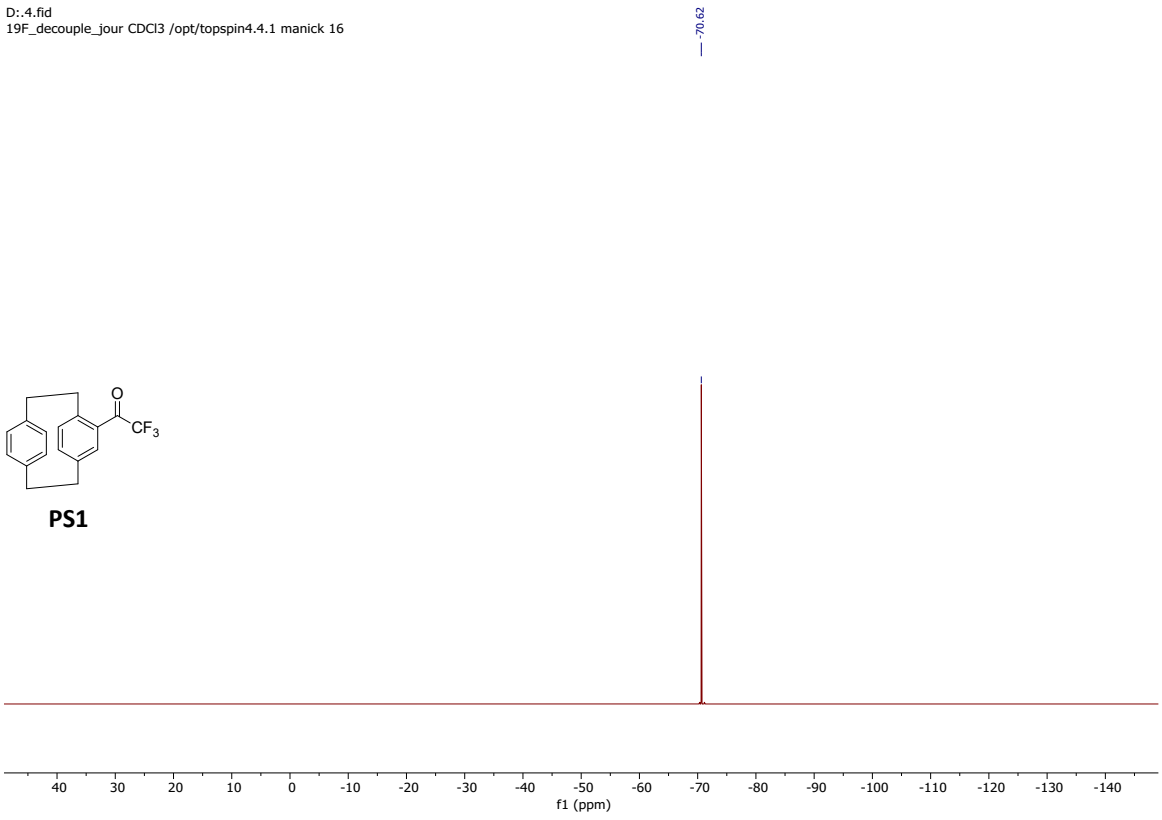


Figure S24: ^{19}F NMR ($CDCl_3$, 376 MHz) of PS1

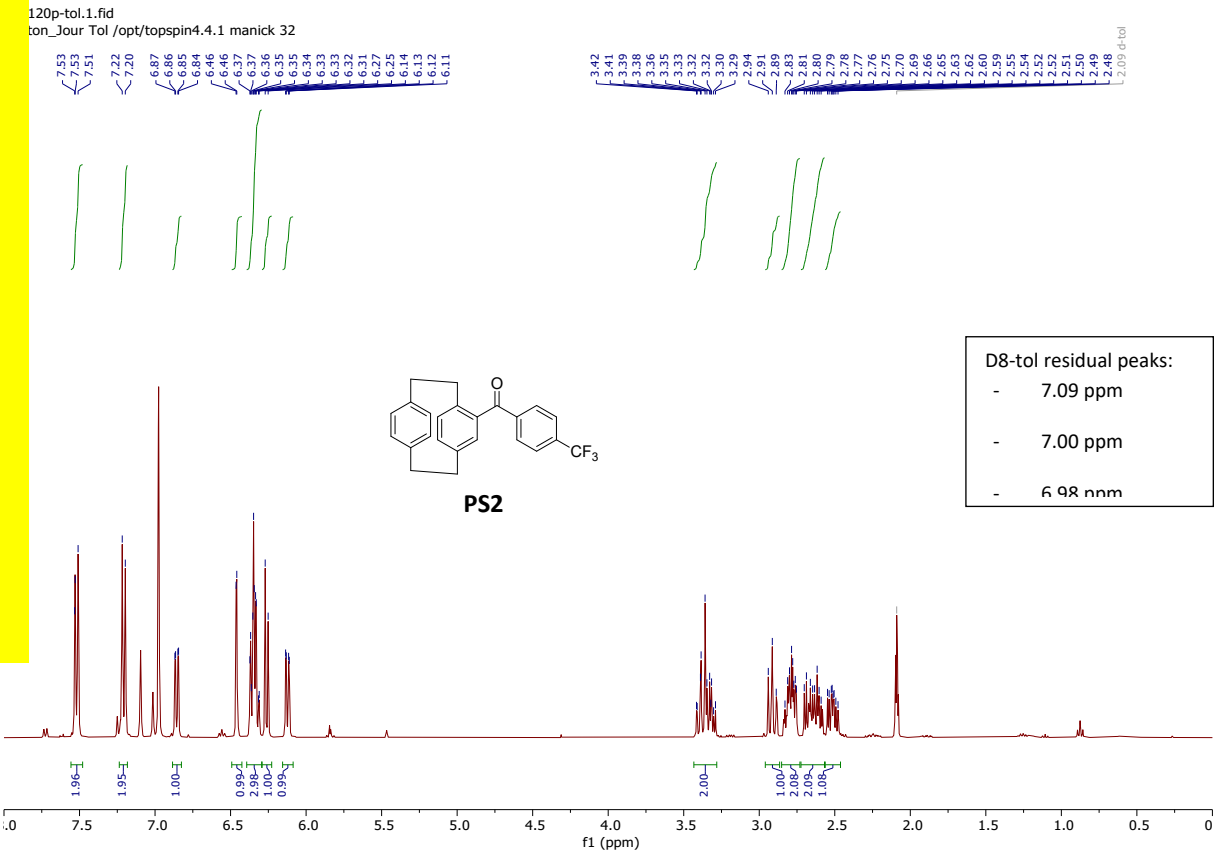


Figure S25: ^{1}H NMR (toluene, 400 MHz) of PS2

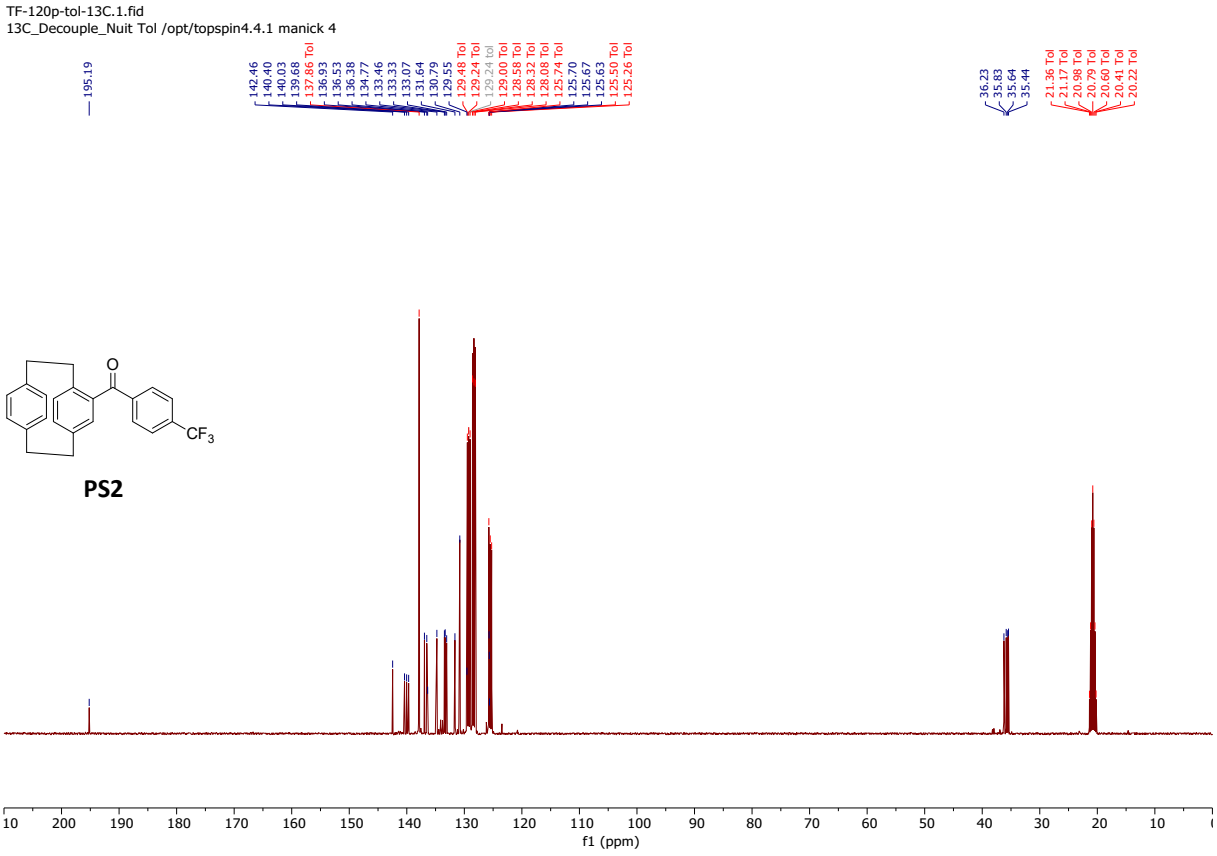


Figure S26: $^{13}C\{1H\}$ NMR (toluene, 101 MHz) of PS2

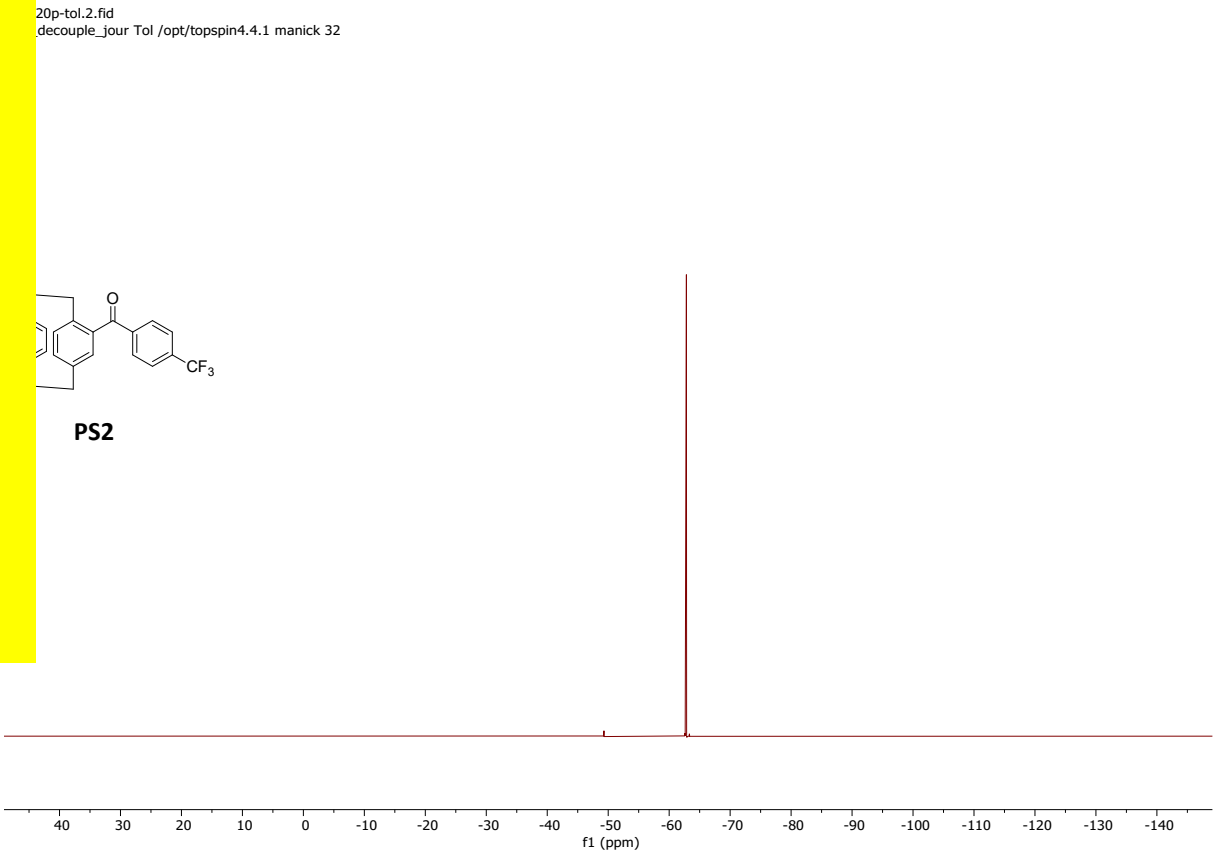


Figure S27: ^{19}F NMR (toluene, 376 MHz) of PS2

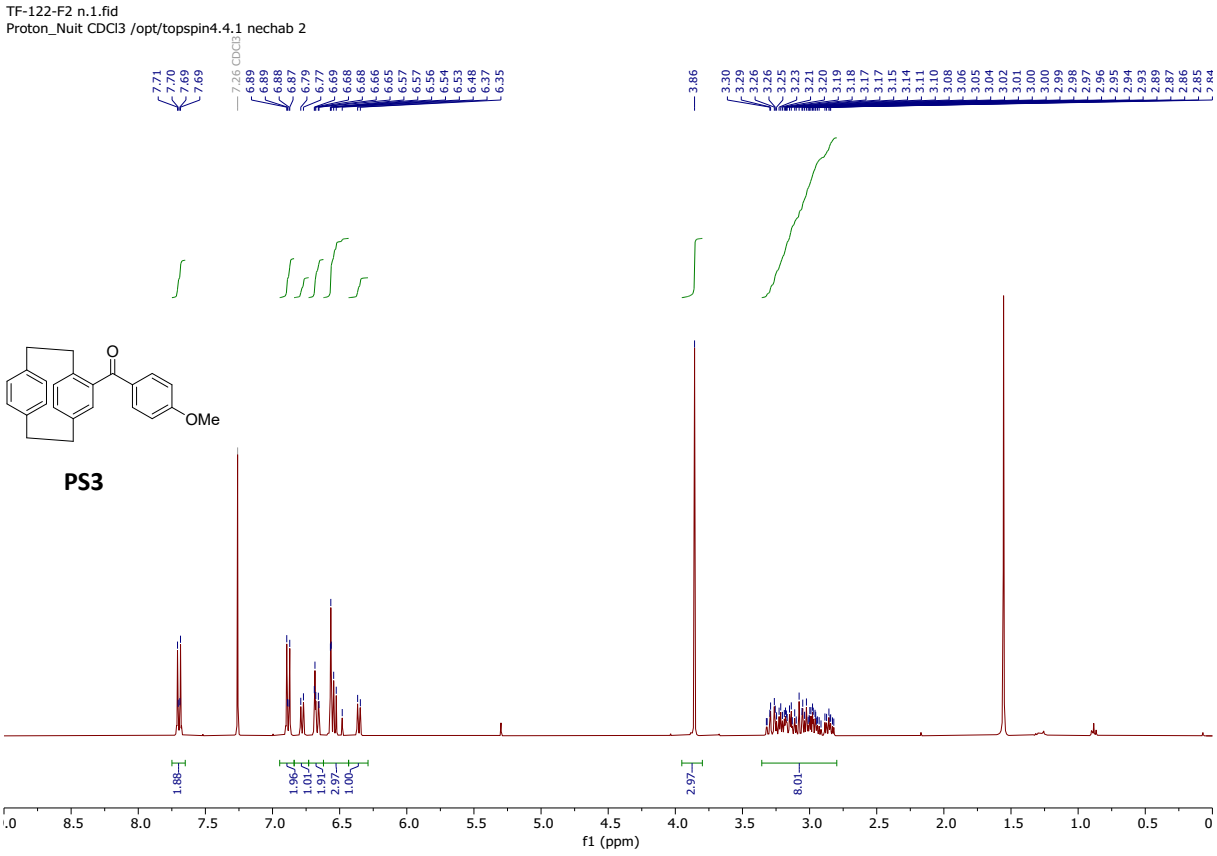


Figure S28: ^{1}H NMR ($CDCl_3$, 400 MHz) of PS3

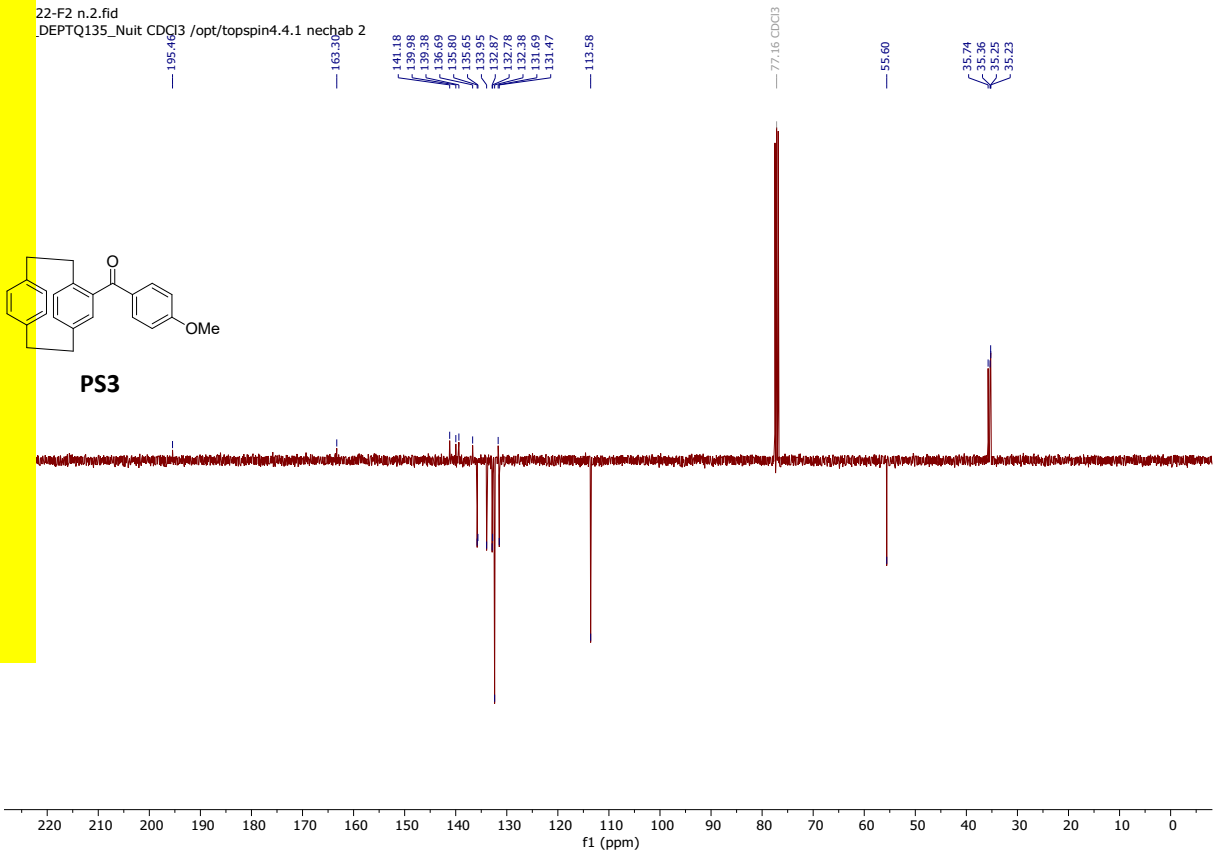


Figure S29: DEPT NMR ($CDCl_3$, 101 MHz) of PS3

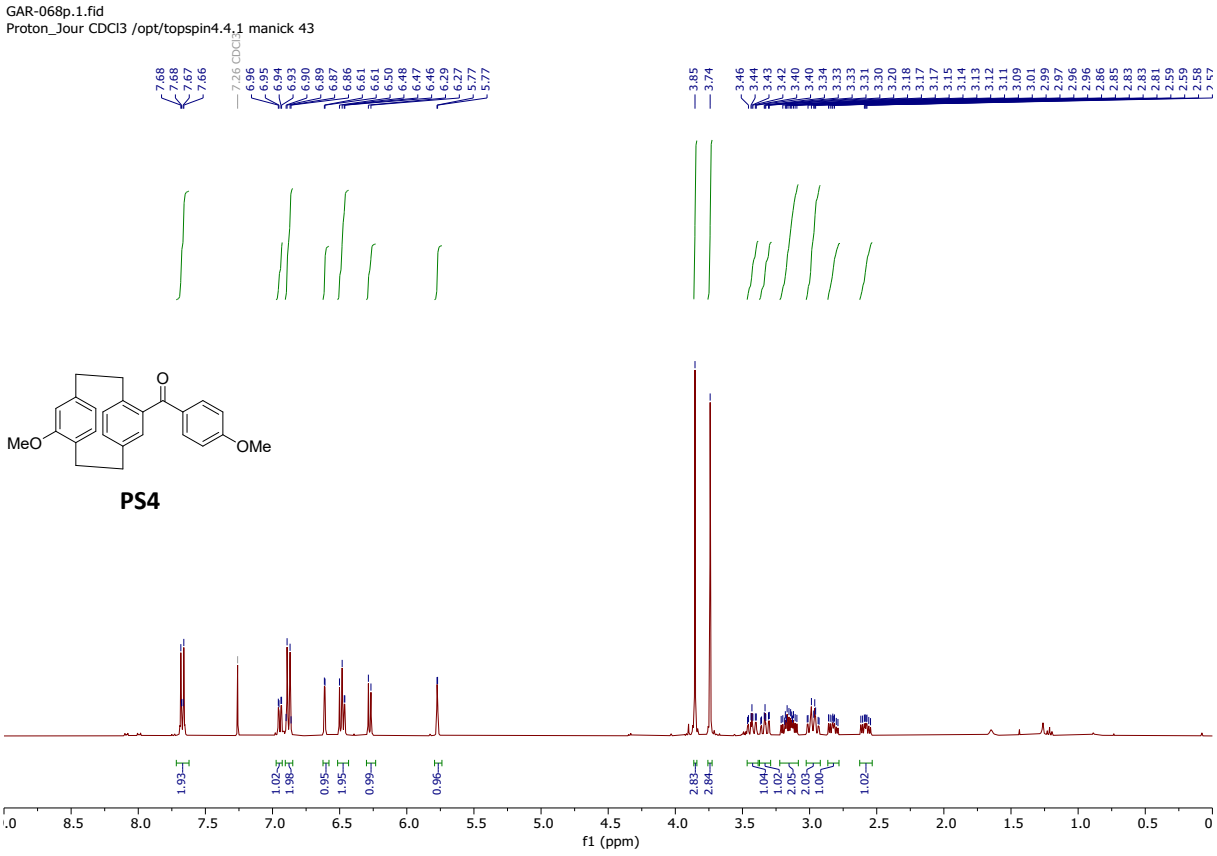


Figure S30: ^1H NMR ($CDCl_3$, 400 MHz) of PS4

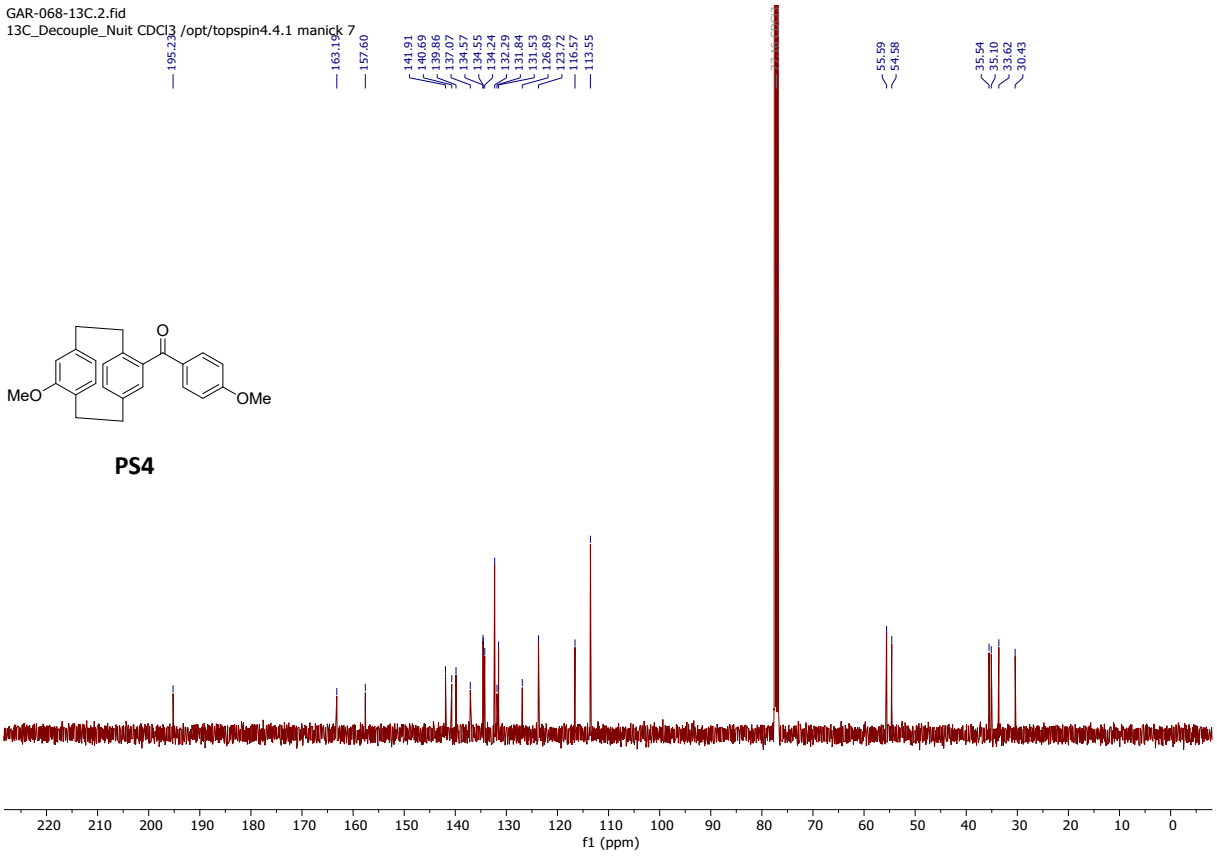


Figure S31: $^{13}C\{1H\}$ NMR ($CDCl_3$, 101 MHz) of PS4

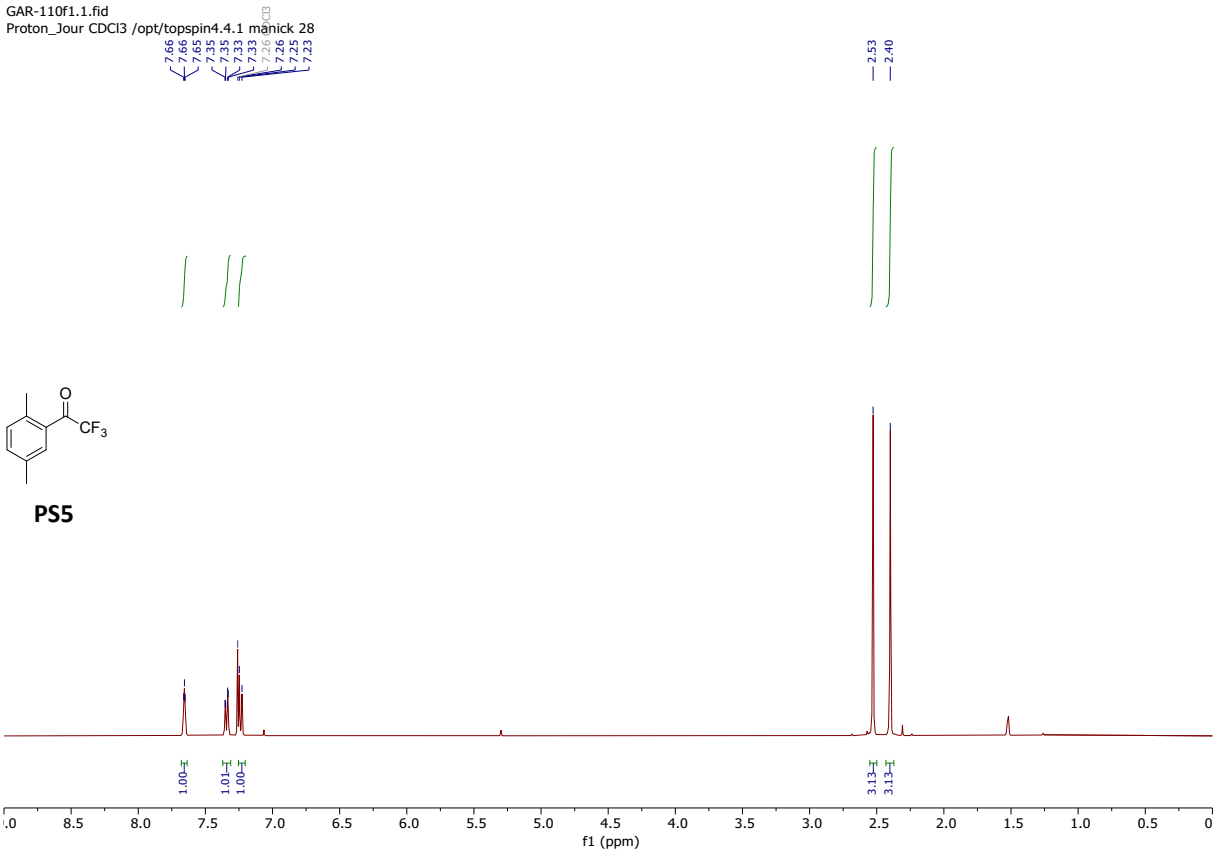


Figure S32: ^{1}H NMR ($CDCl_3$, 400 MHz) of PS5

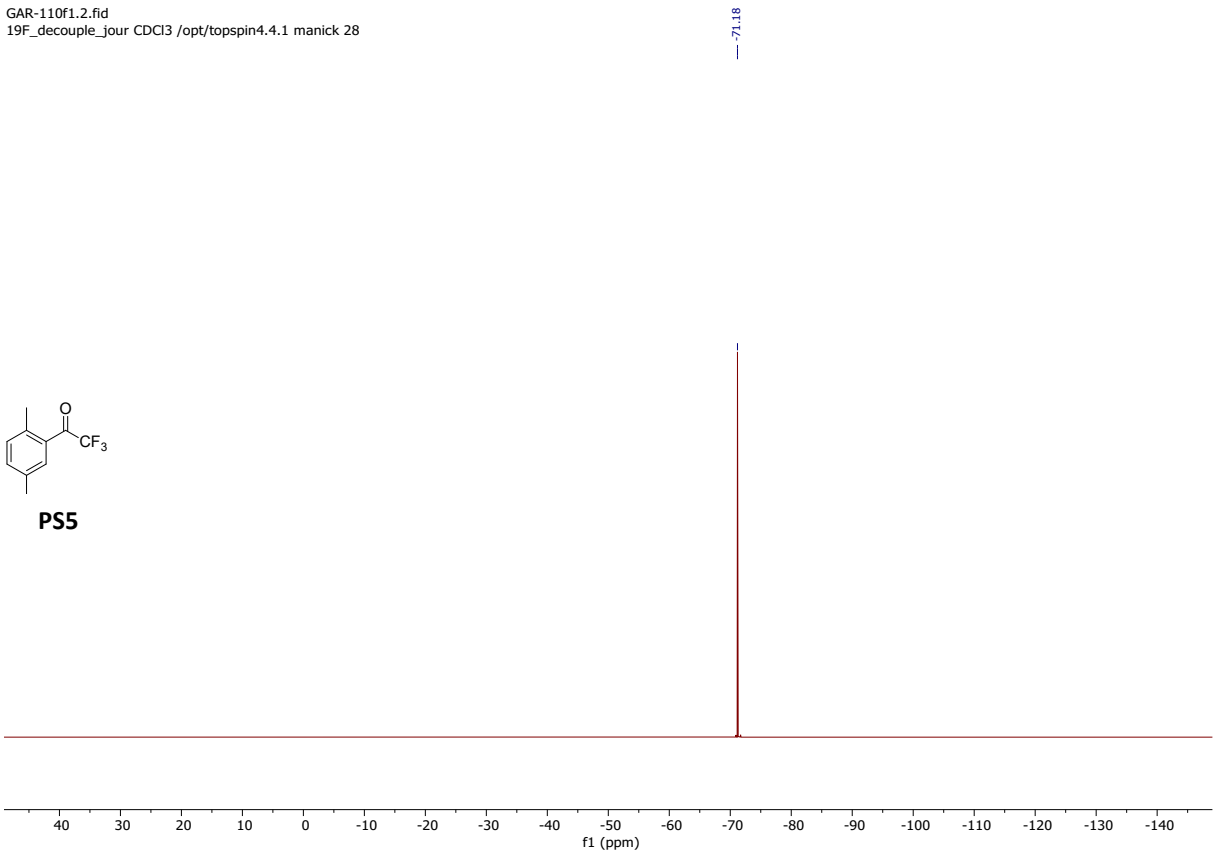


Figure S33: ^{19}F NMR ($CDCl_3$, 162 MHz) of PS5

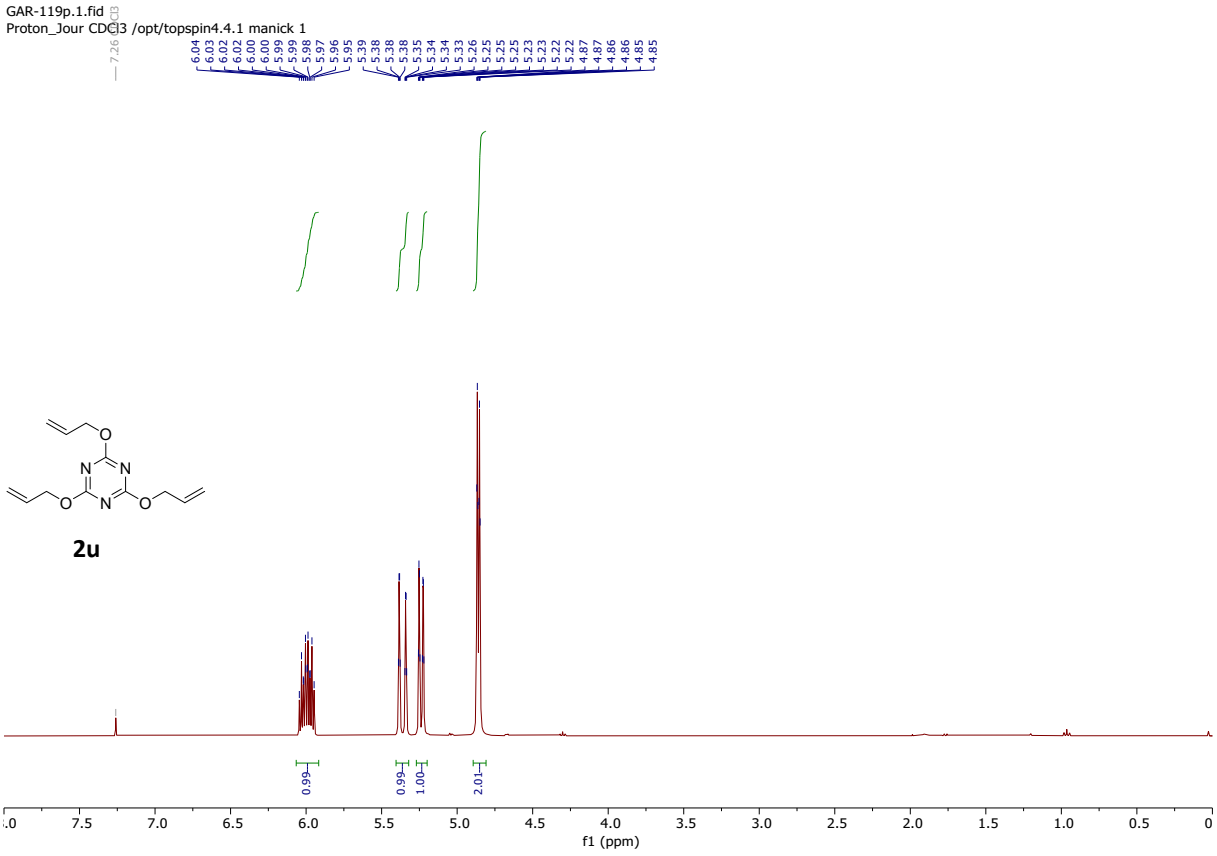


Figure S34: ^{1}H NMR ($CDCl_3$, 400 MHz) of 2u

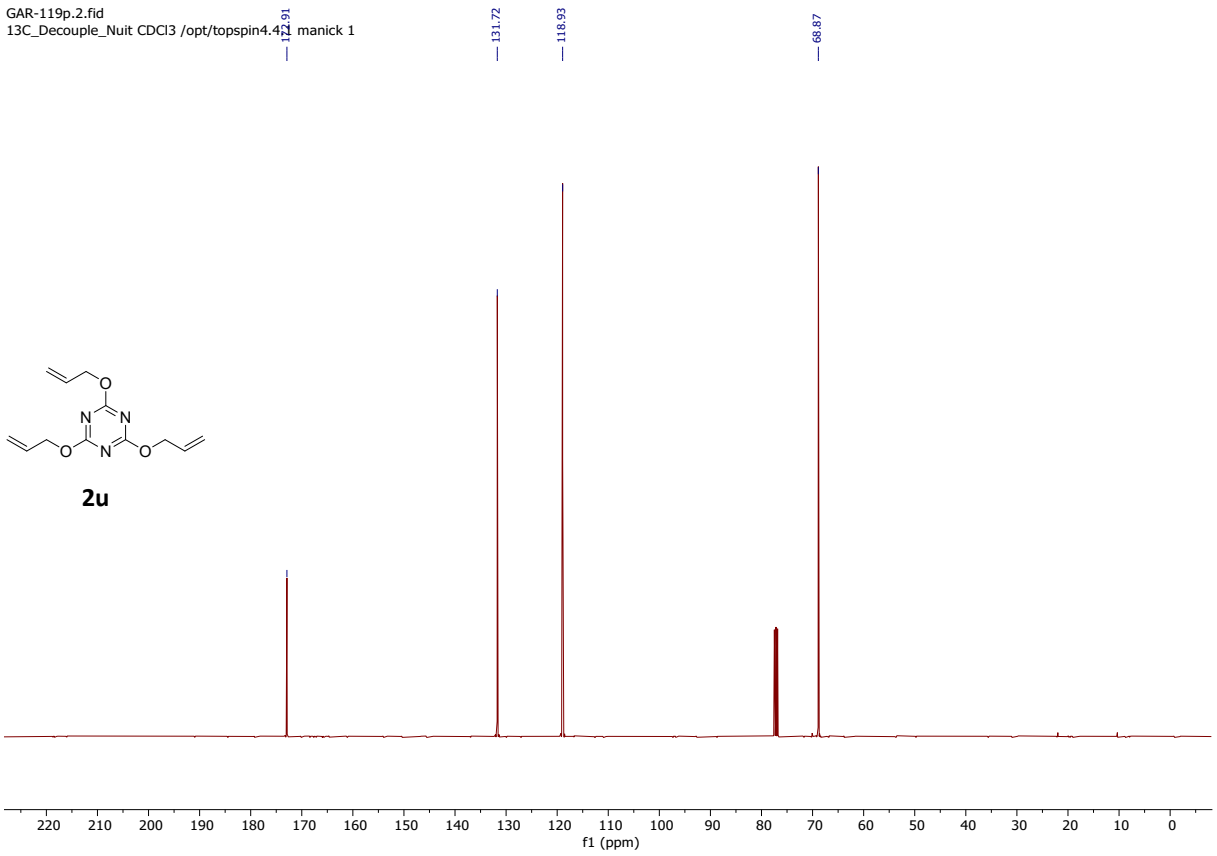


Figure S35: $^{13}C\{1H\}$ NMR ($CDCl_3$, 101 MHz) of 2u

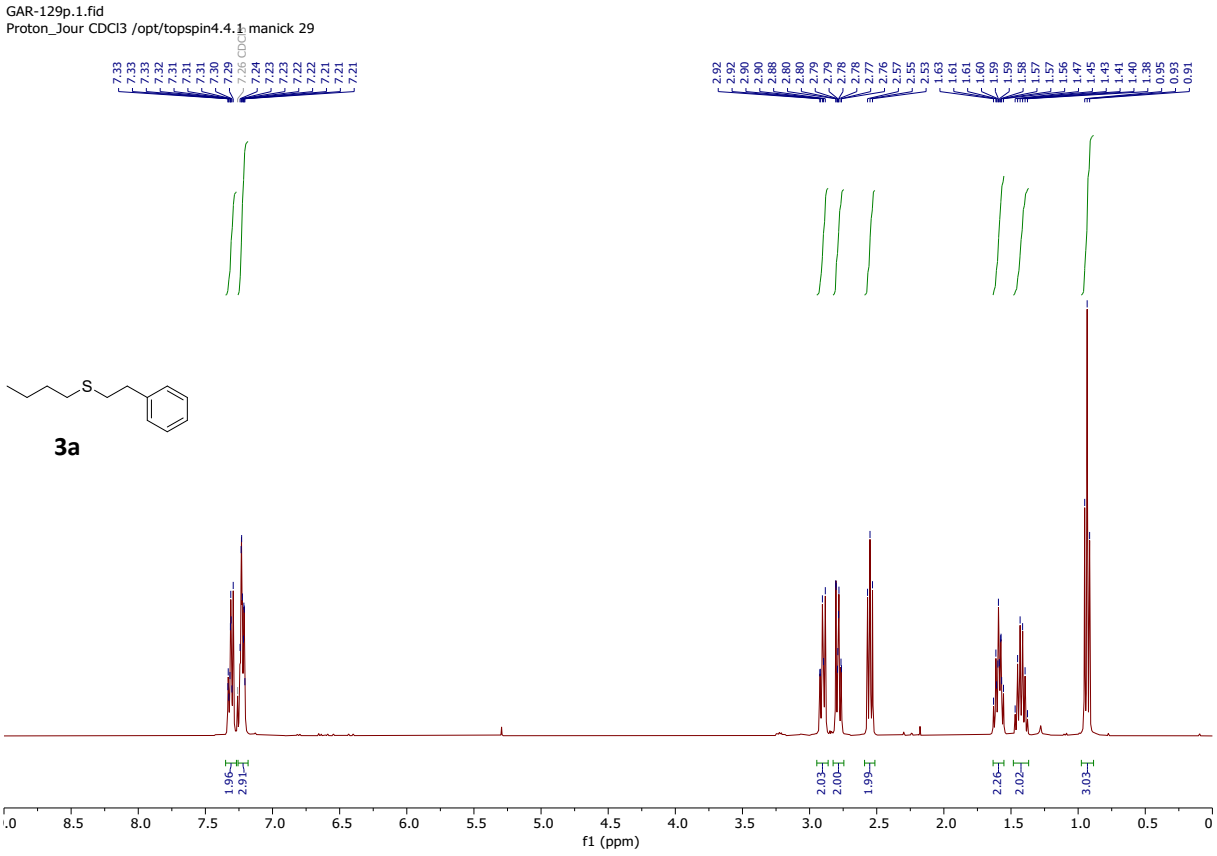


Figure S36: ^{1}H NMR ($CDCl_3$, 400 MHz) of 3a

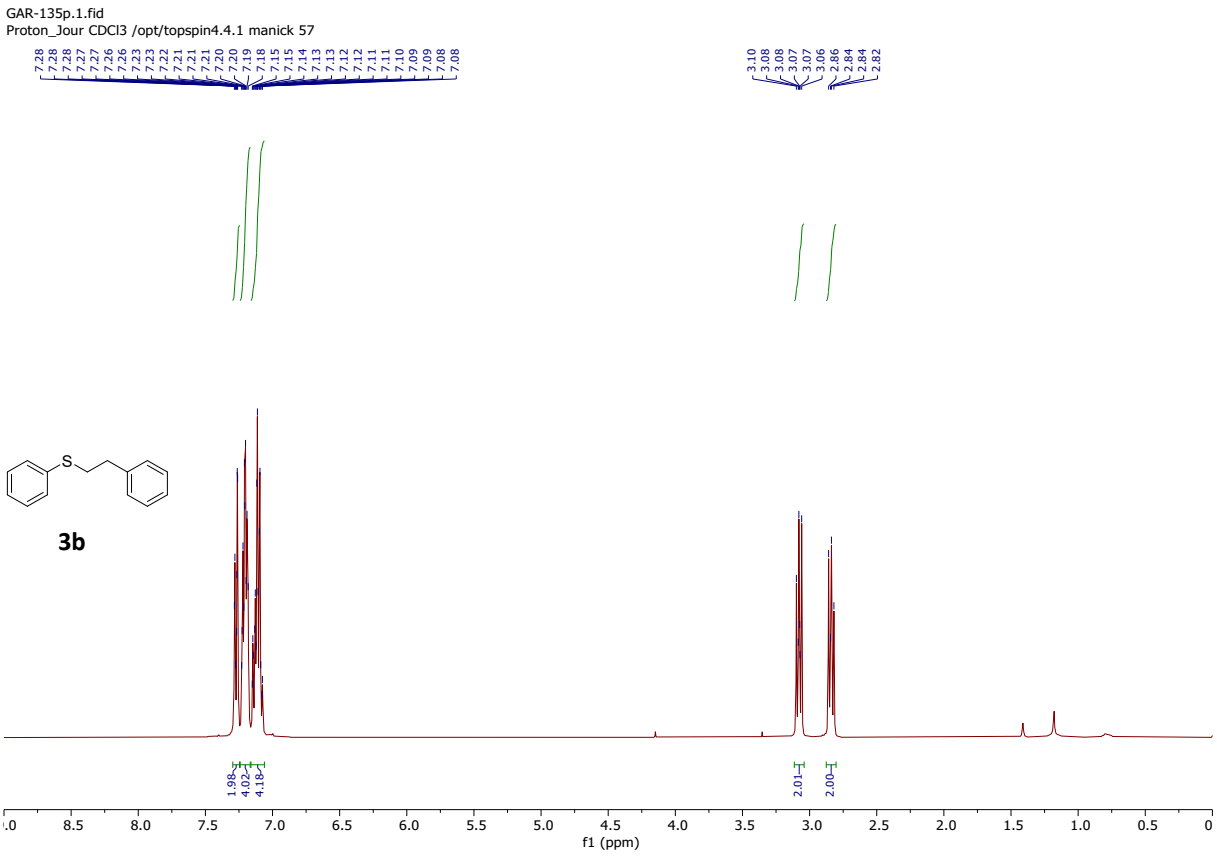


Figure S37: ^1H NMR ($CDCl_3$, 400 MHz) of 3b

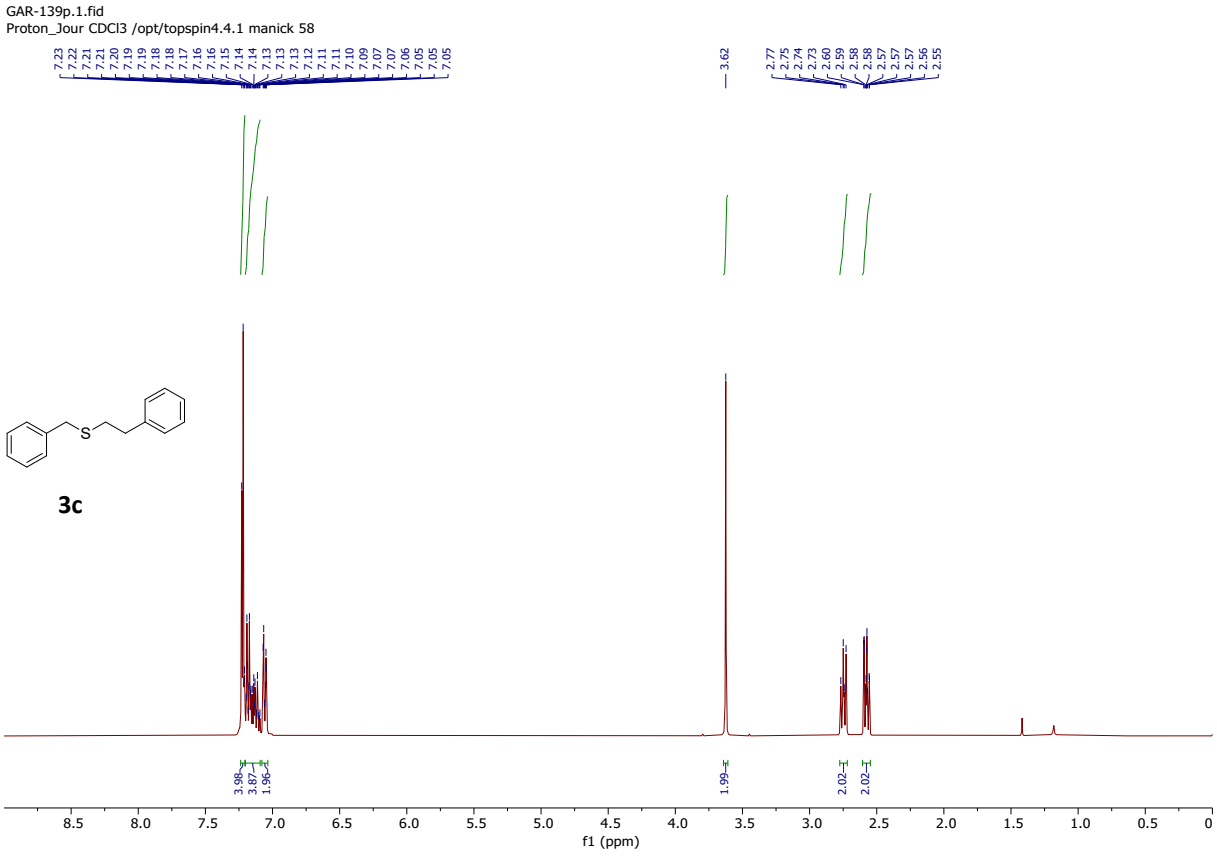


Figure S38: ^1H NMR ($CDCl_3$, 400 MHz) of 3c

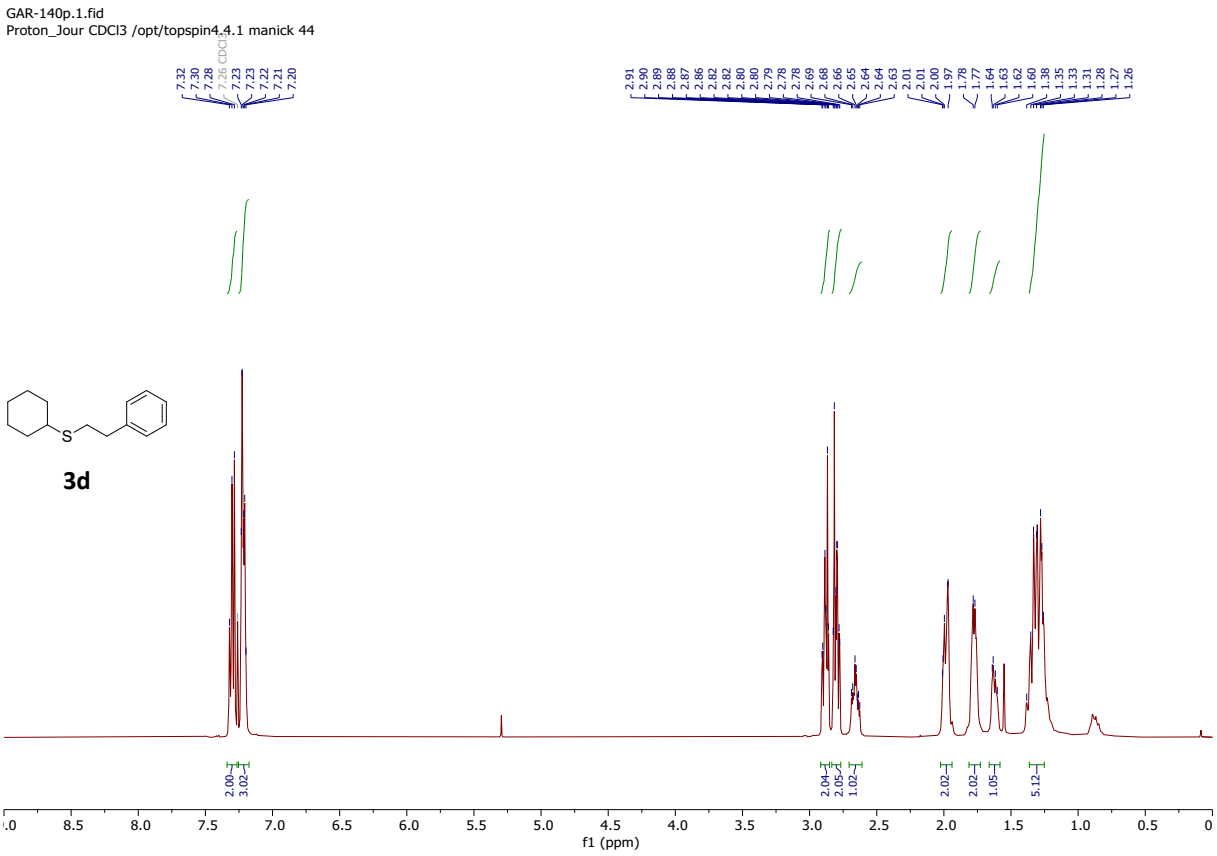


Figure S39: ^1H NMR ($CDCl_3$, 400 MHz) of 3d

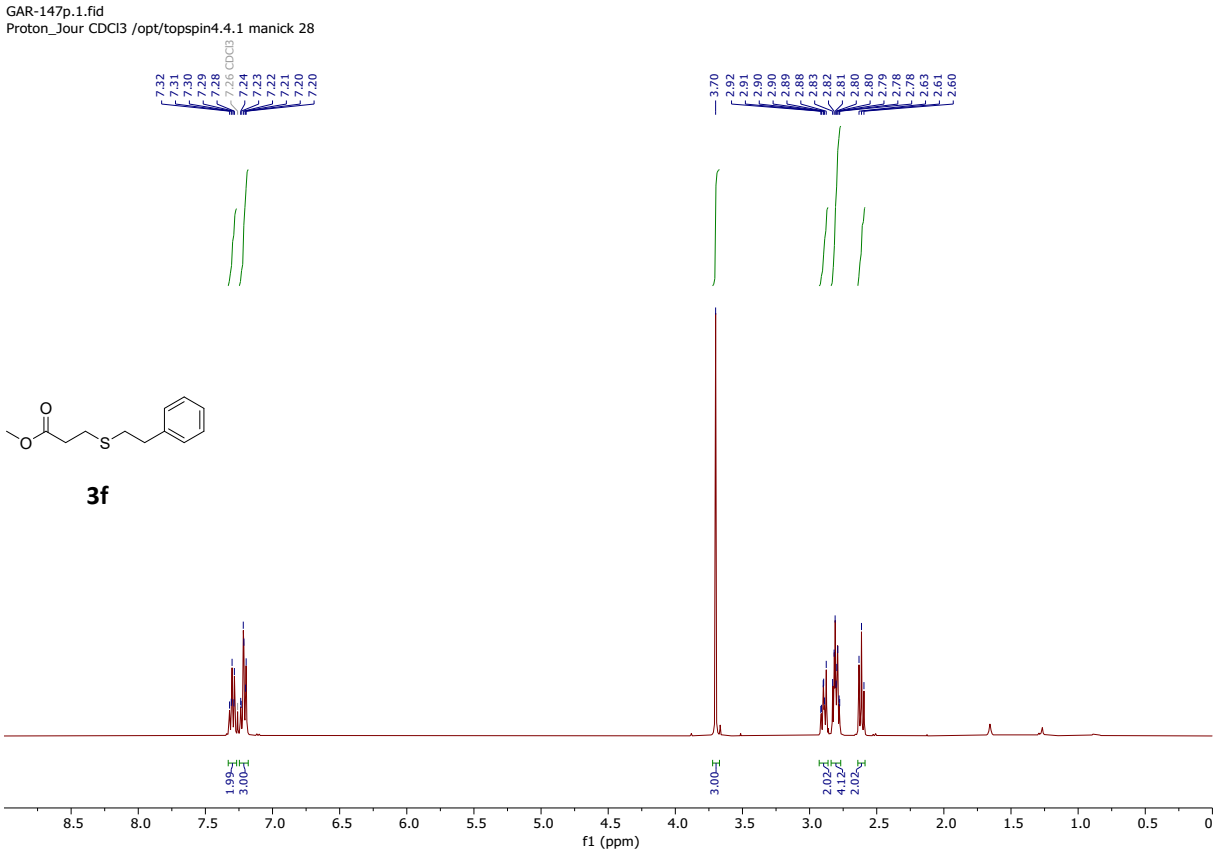


Figure S40: ^1H NMR ($CDCl_3$, 400 MHz) of 3f

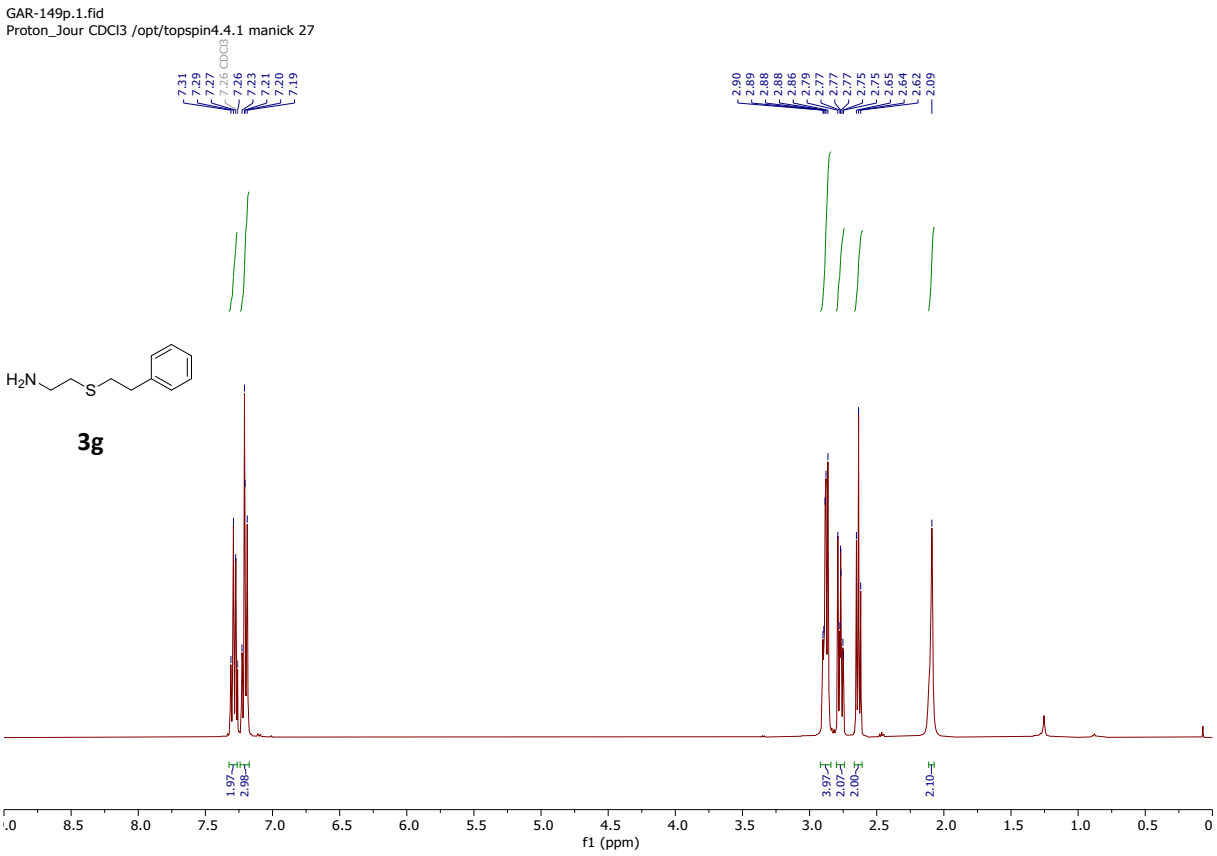
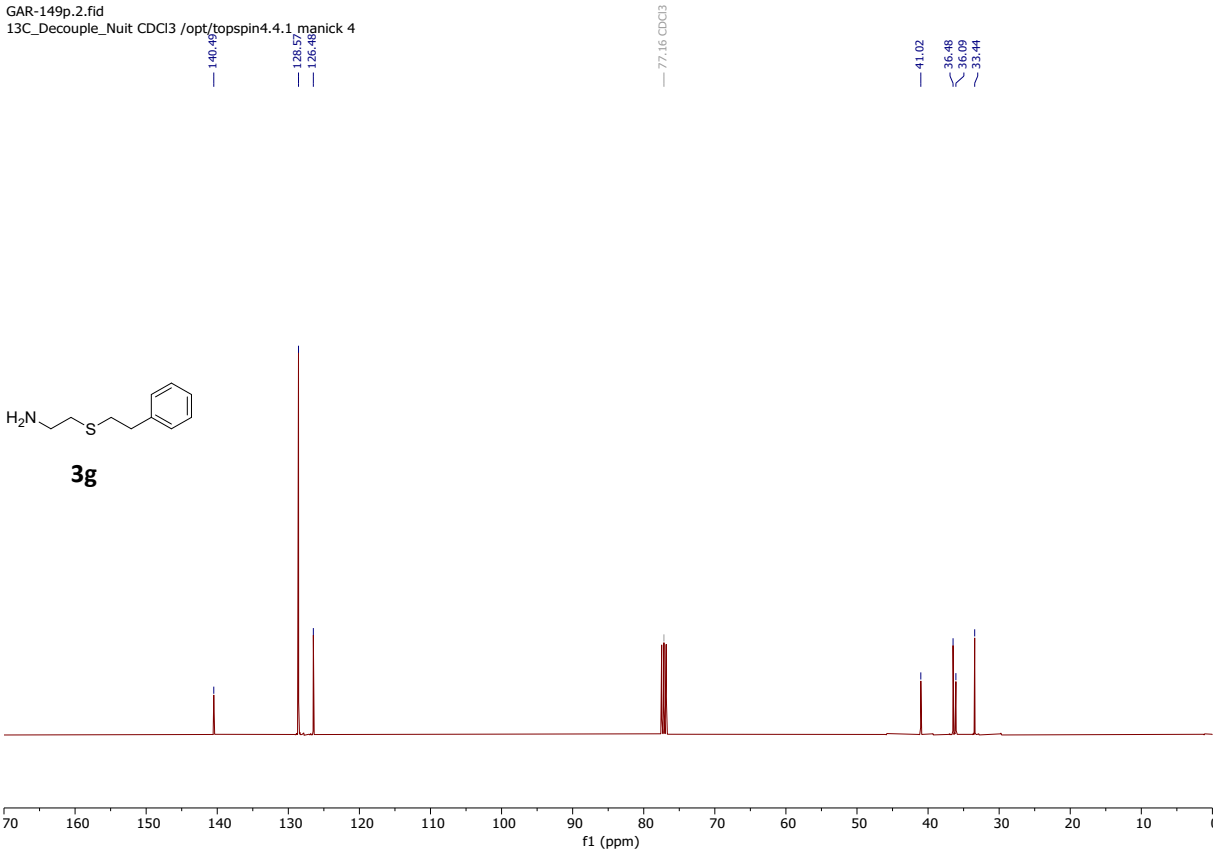


Figure S41: ^{1}H NMR ($CDCl_3$, 400 MHz) of 3g



FigureS42: $^{13}C\{1H\}$ NMR ($CDCl_3$, 101 MHz) of 3g

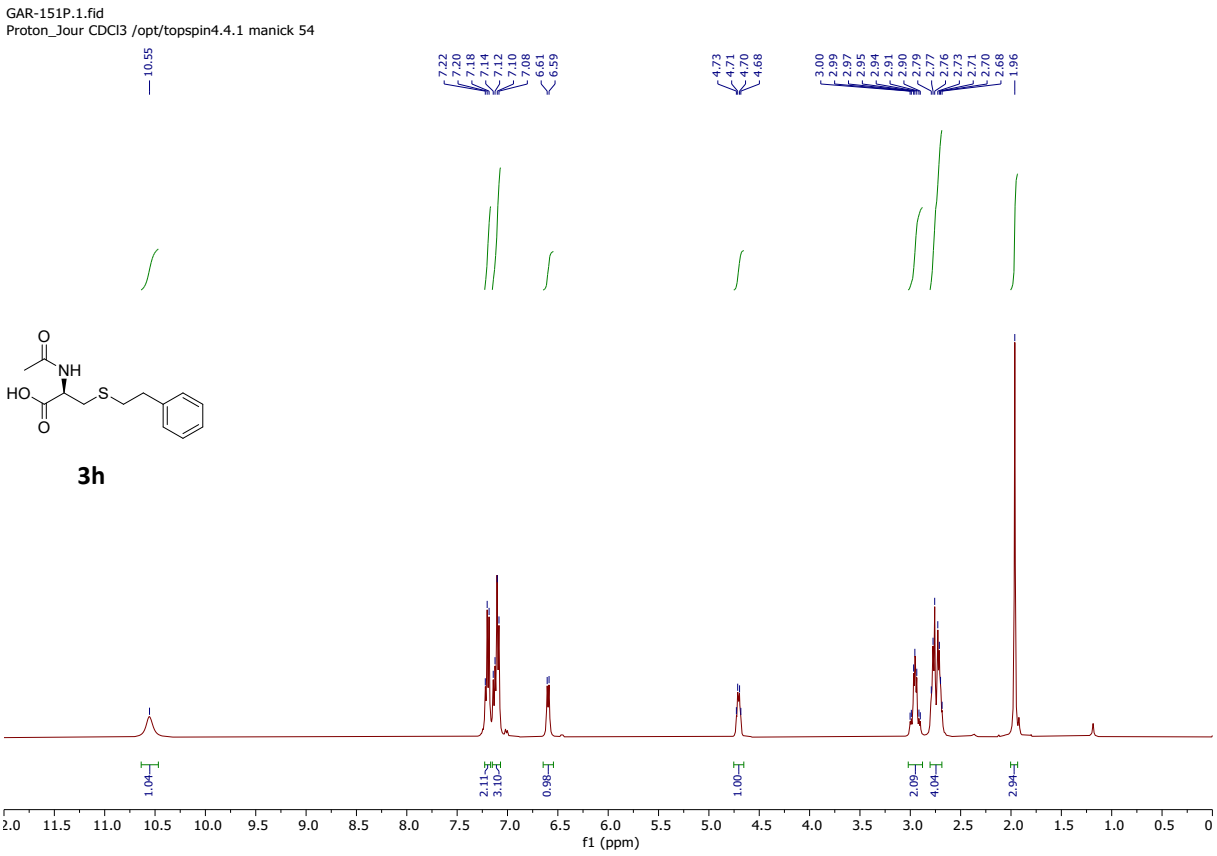


Figure S43: ^{1}H NMR ($CDCl_3$, 400 MHz) of 3h

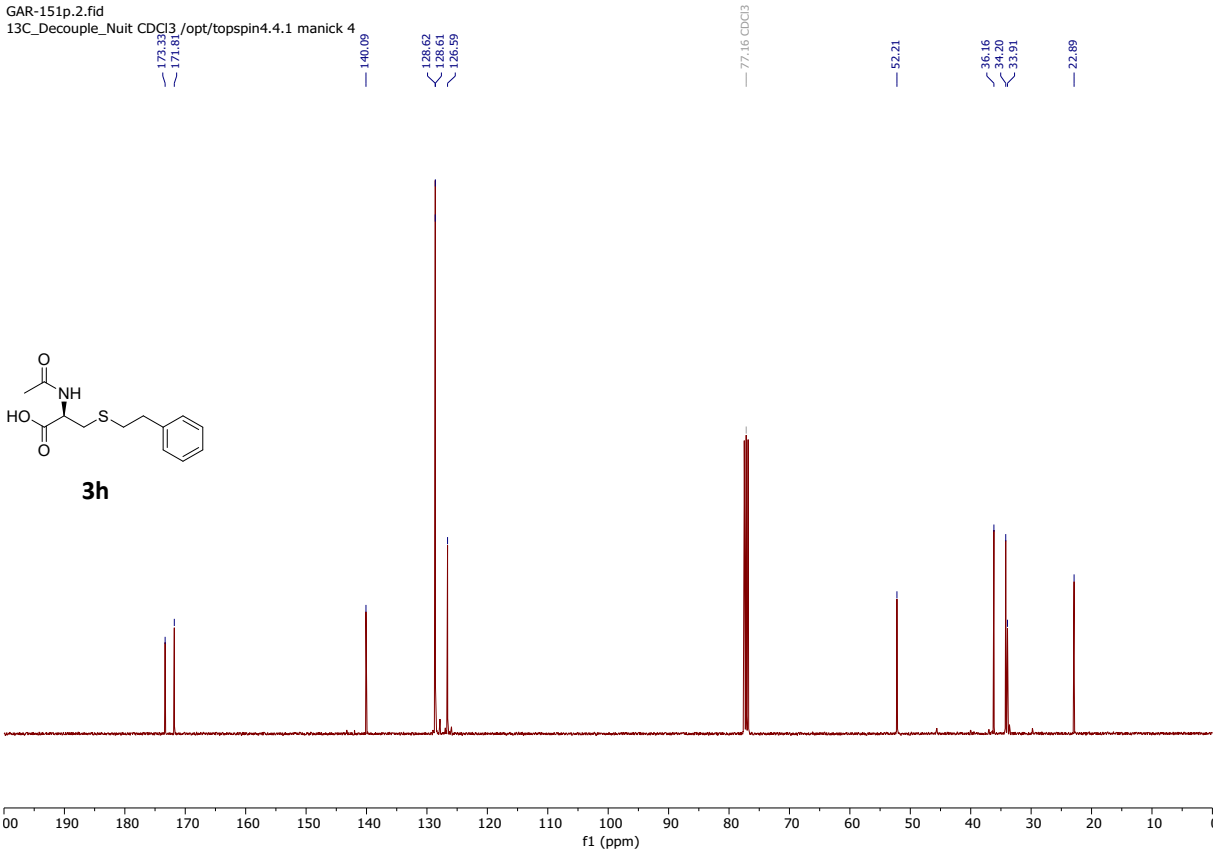


Figure S44: $^{13}C\{1H\}$ NMR ($CDCl_3$, 101 MHz) of 3h

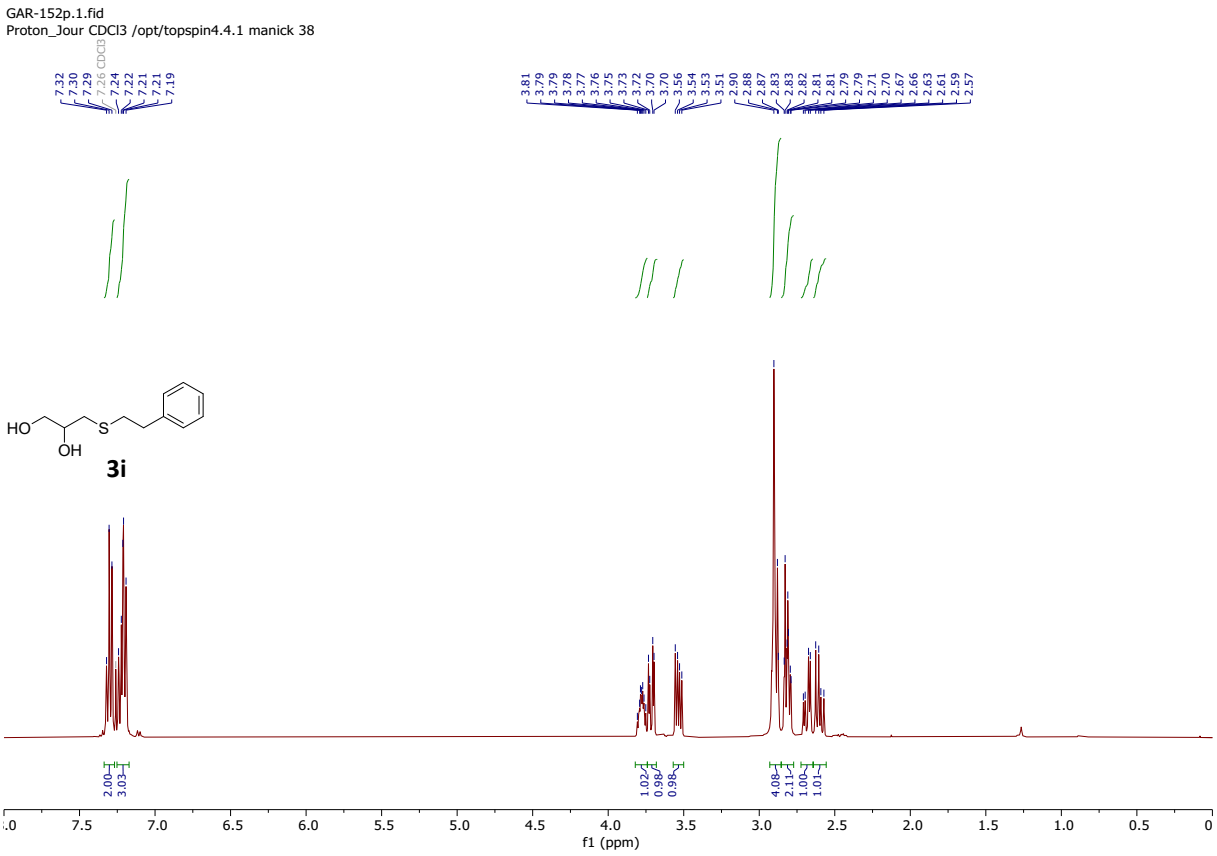


Figure S45: ^{1}H NMR ($CDCl_3$, 400 MHz) of 3i

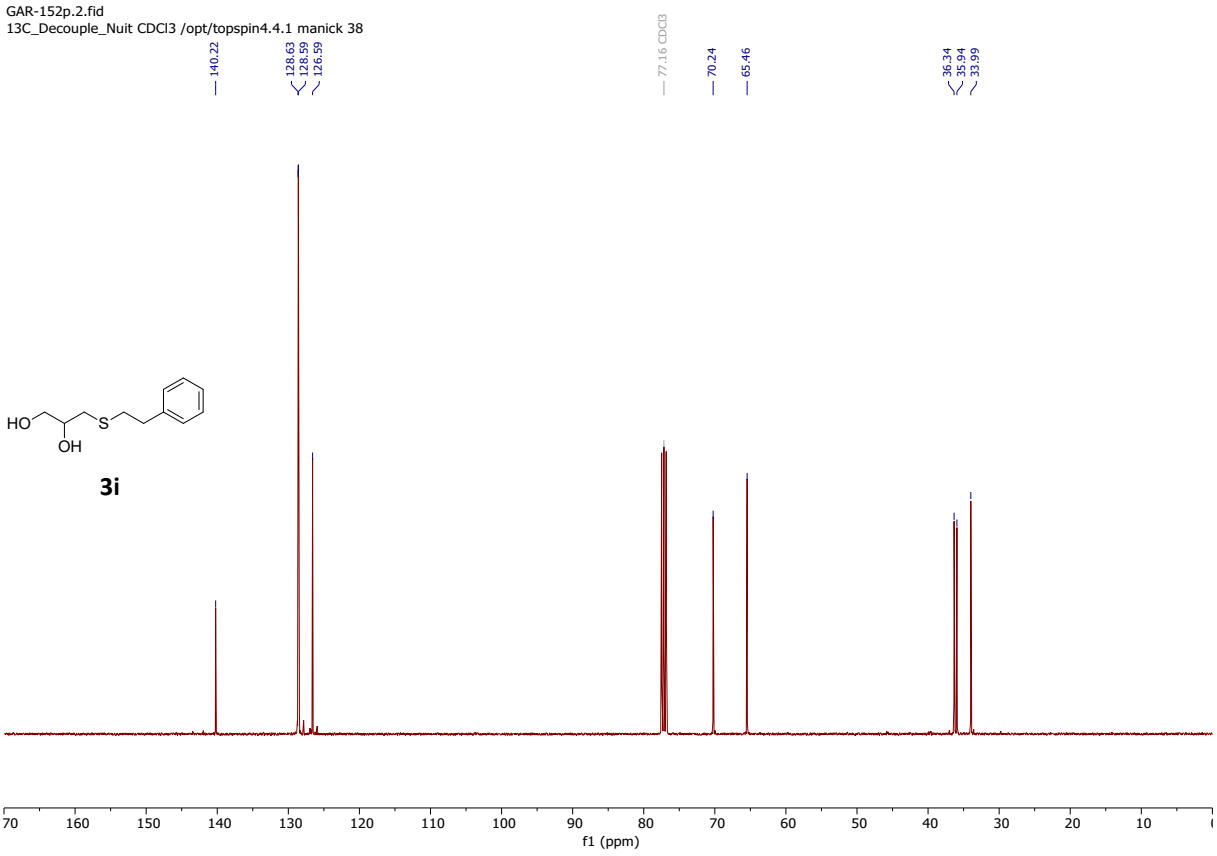


Figure S46: $^{13}C\{1H\}$ NMR ($CDCl_3$, 101 MHz) of 3i

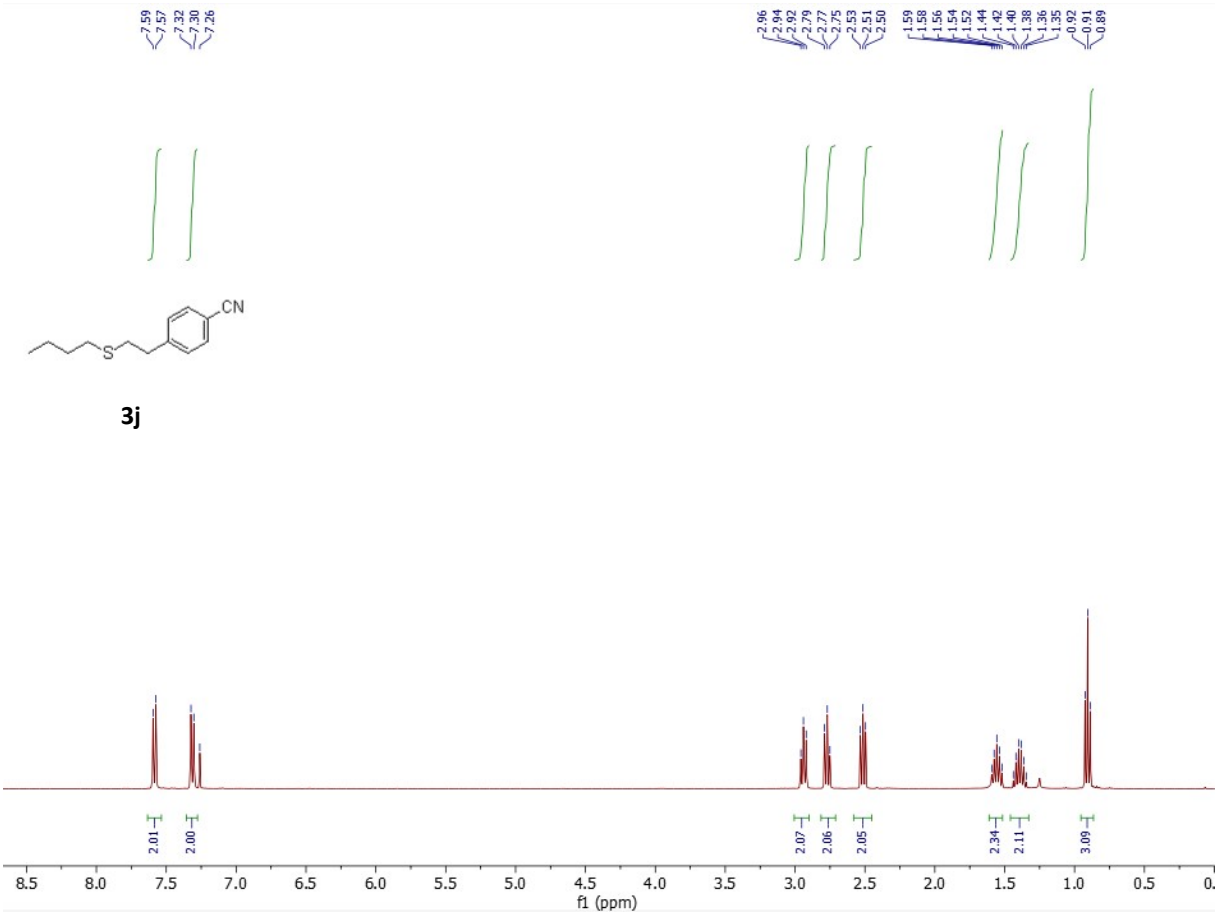
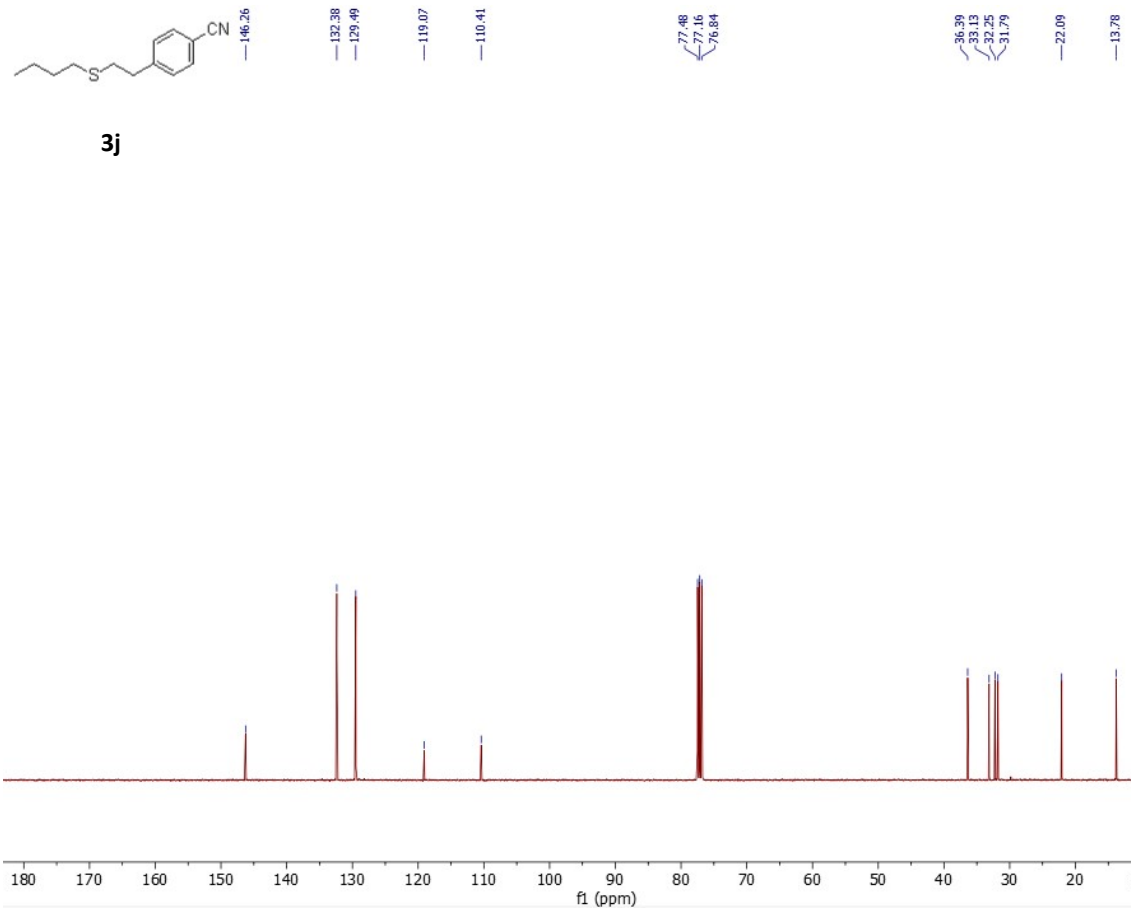


Figure S47: ^{1}H NMR ($CDCl_3$*, 400 MHz) of* 3j



3j

Figure S 48: $^{13}C\{1H\}$ NMR ($CDCl_3$, 101 MHz) of 3j

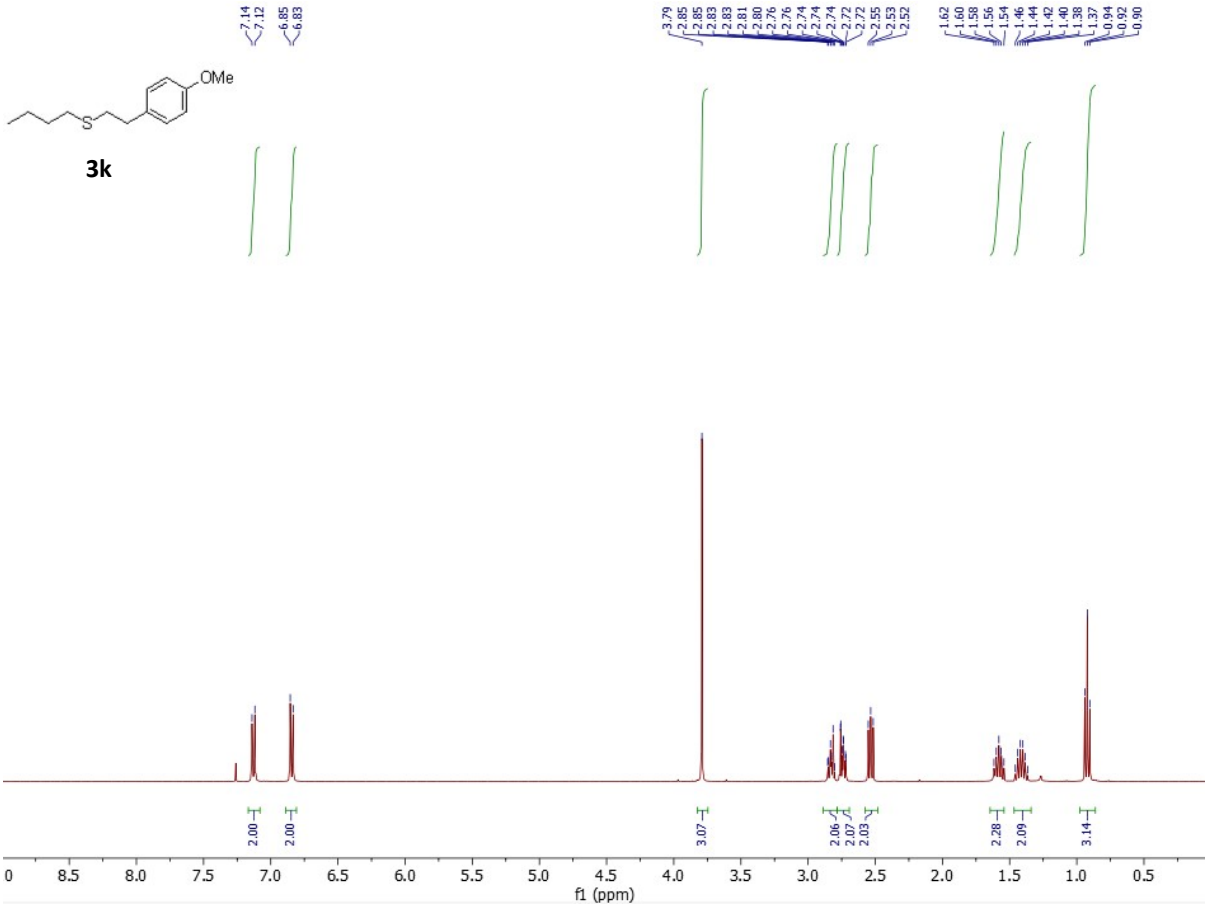


Figure S49: ^{1}H NMR ($CDCl_3$*, 400 MHz) of* 3k

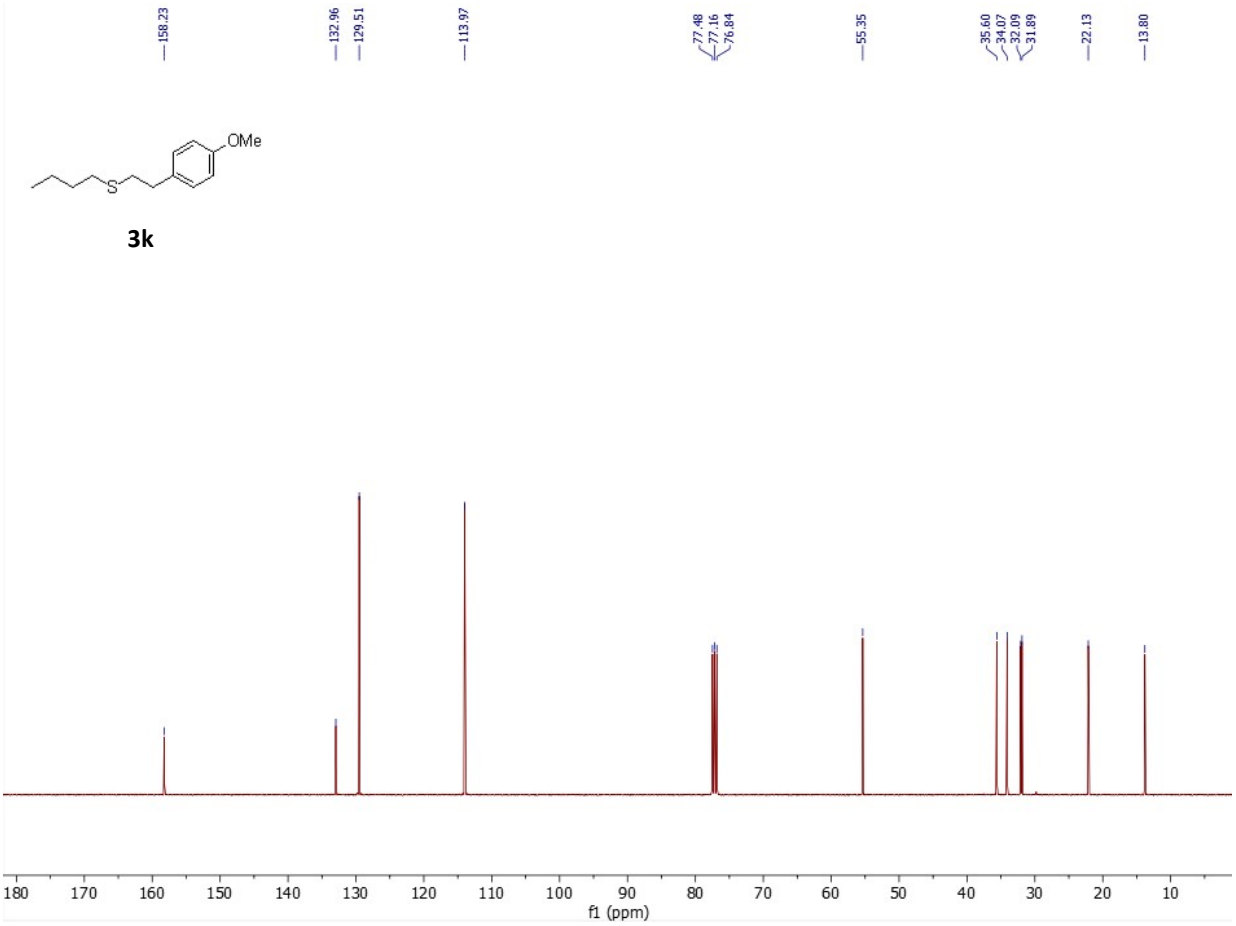


Figure S 50: $^{13}C\{1H\}$ NMR ($CDCl_3$, 101 MHz) of 3k

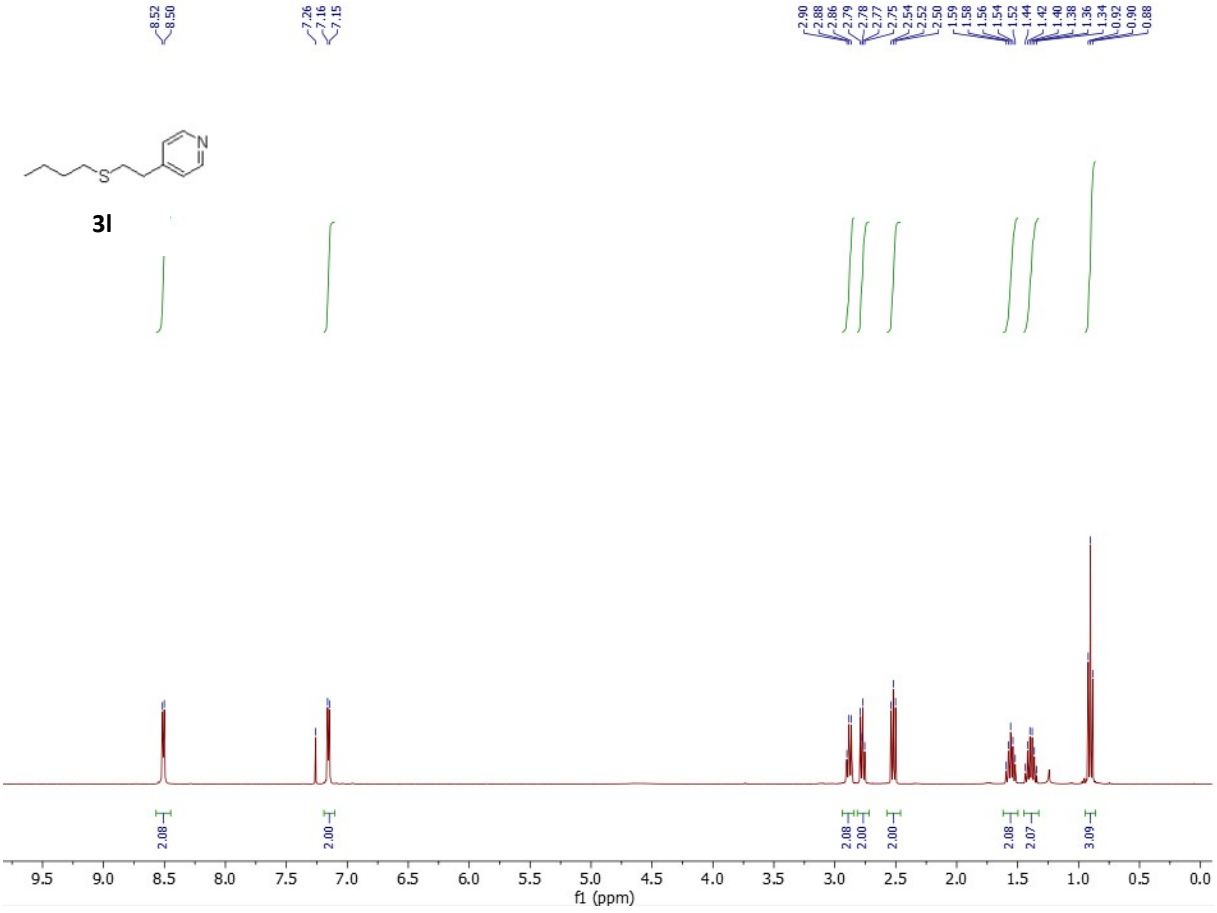


Figure S51: ^{1}H NMR ($CDCl_3$*, 400 MHz) of* 3l

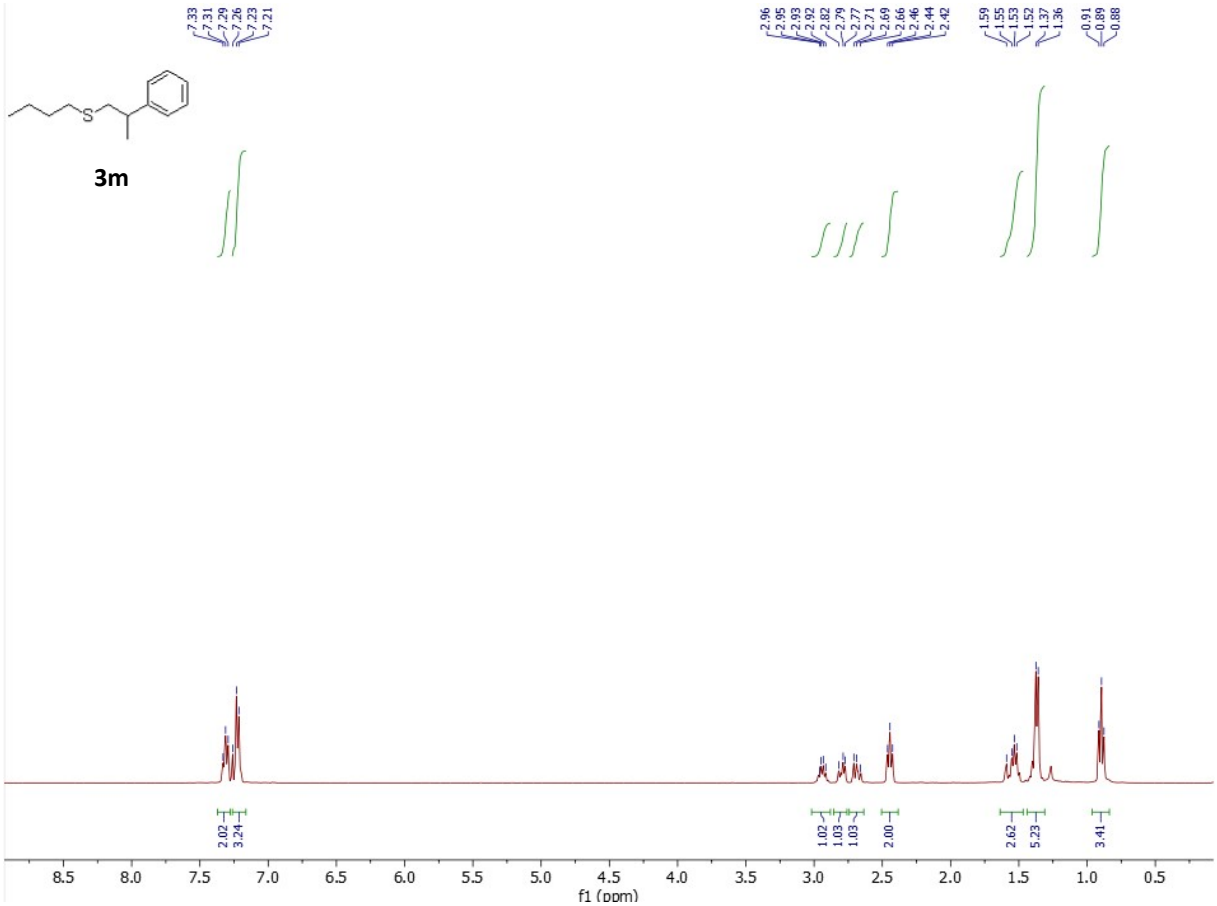
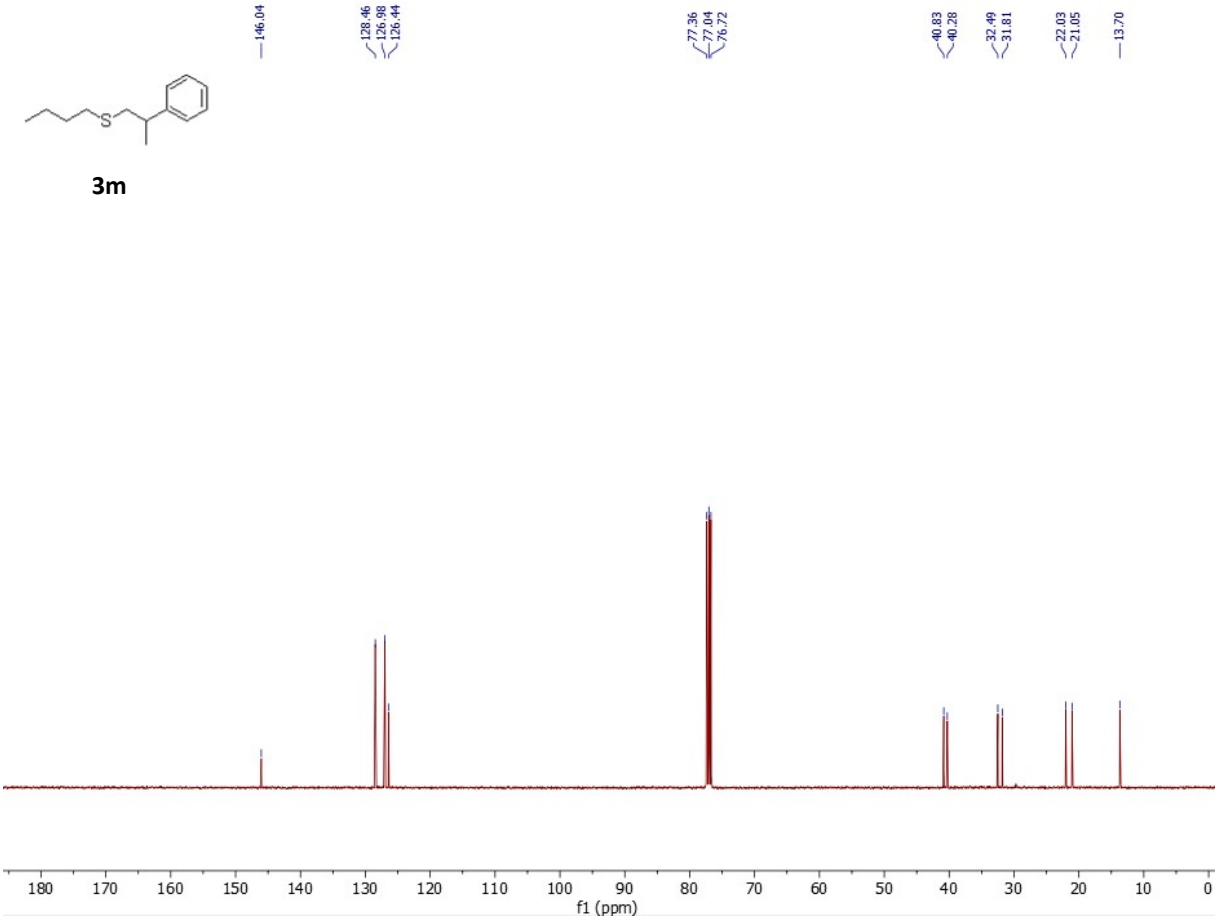


Figure S52: ^{1}H NMR ($CDCl_3$*, 400 MHz) of* 3m



3m

Figure S 53: $^{13}C\{1H\}$ NMR ($CDCl_3$, 101 MHz) of 3m

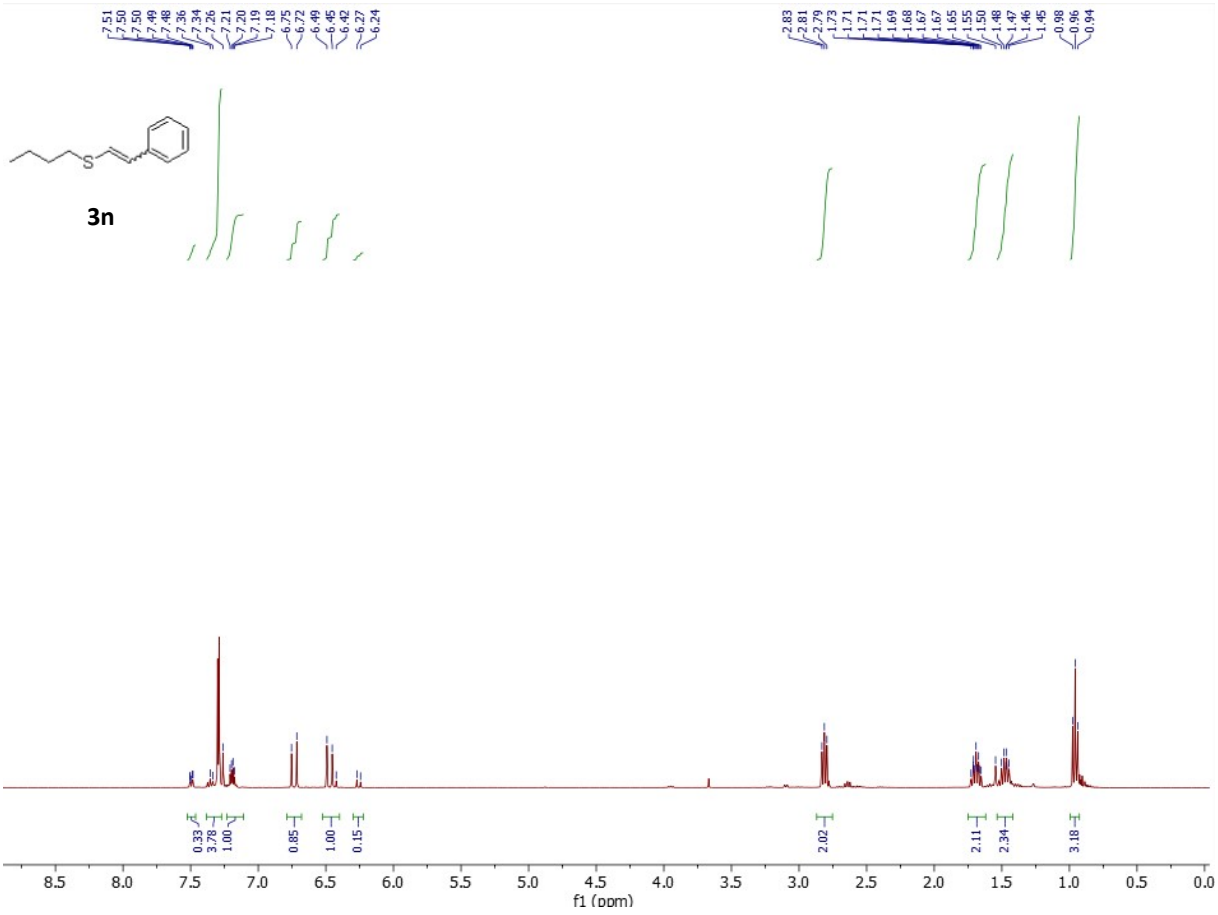
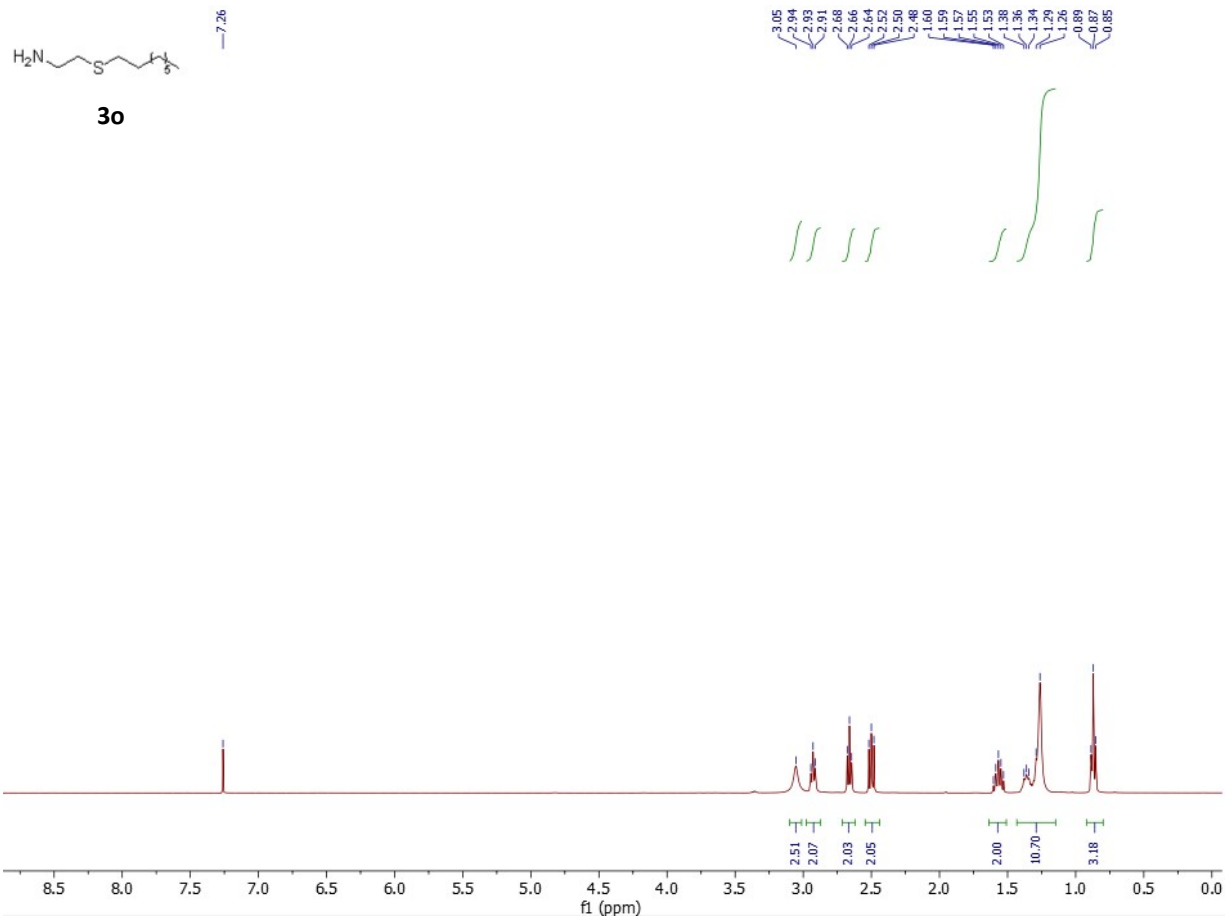


Figure S54: ^{1}H NMR ($CDCl_3$*, 400 MHz) of* 3n



3o

Figure S55: ^{1}H NMR ($CDCl_3$*, 400 MHz) of* 3o

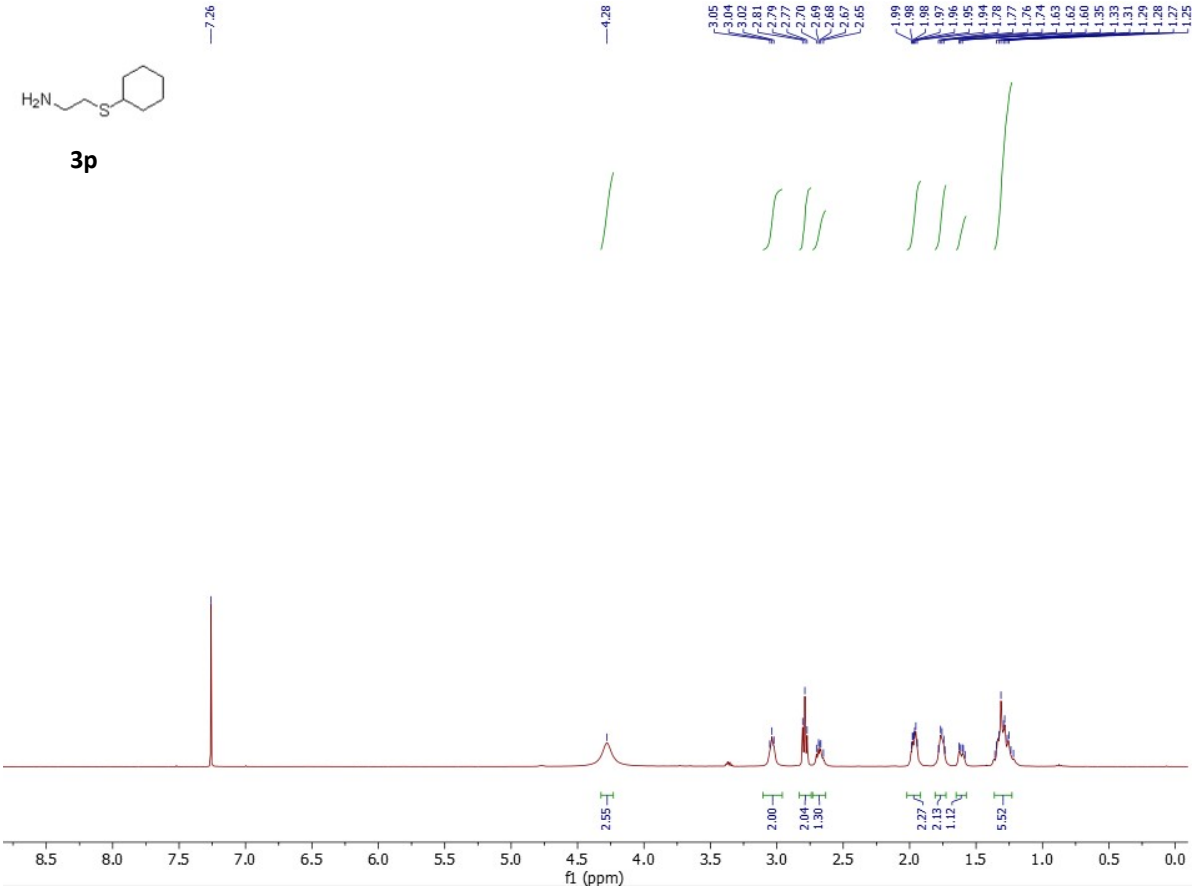


Figure S 56: ^{1}H NMR ($CDCl_3$*, 400 MHz) of* 3p

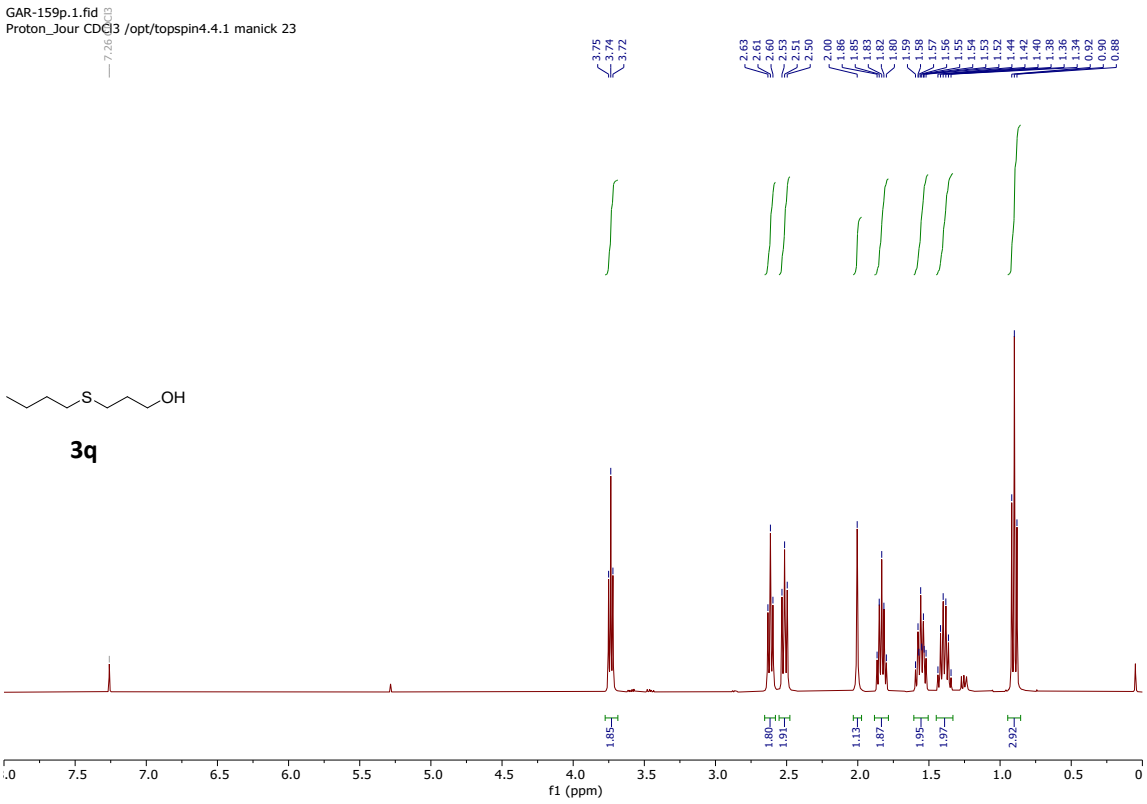


Figure S 57: ^{1}H NMR ($CDCl_3$, 400 MHz) of 3q

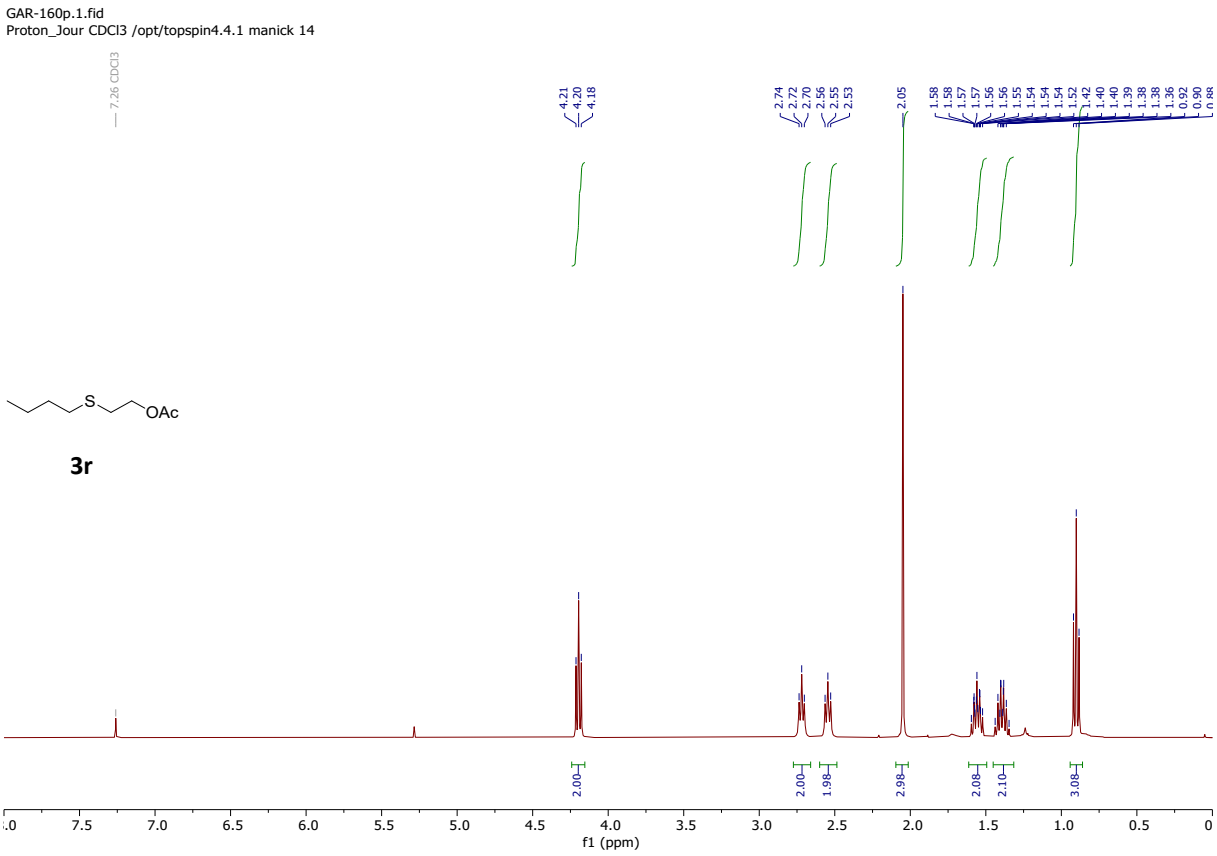


Figure S 58: ^{1}H NMR ($CDCl_3$, 400 MHz) of 3r

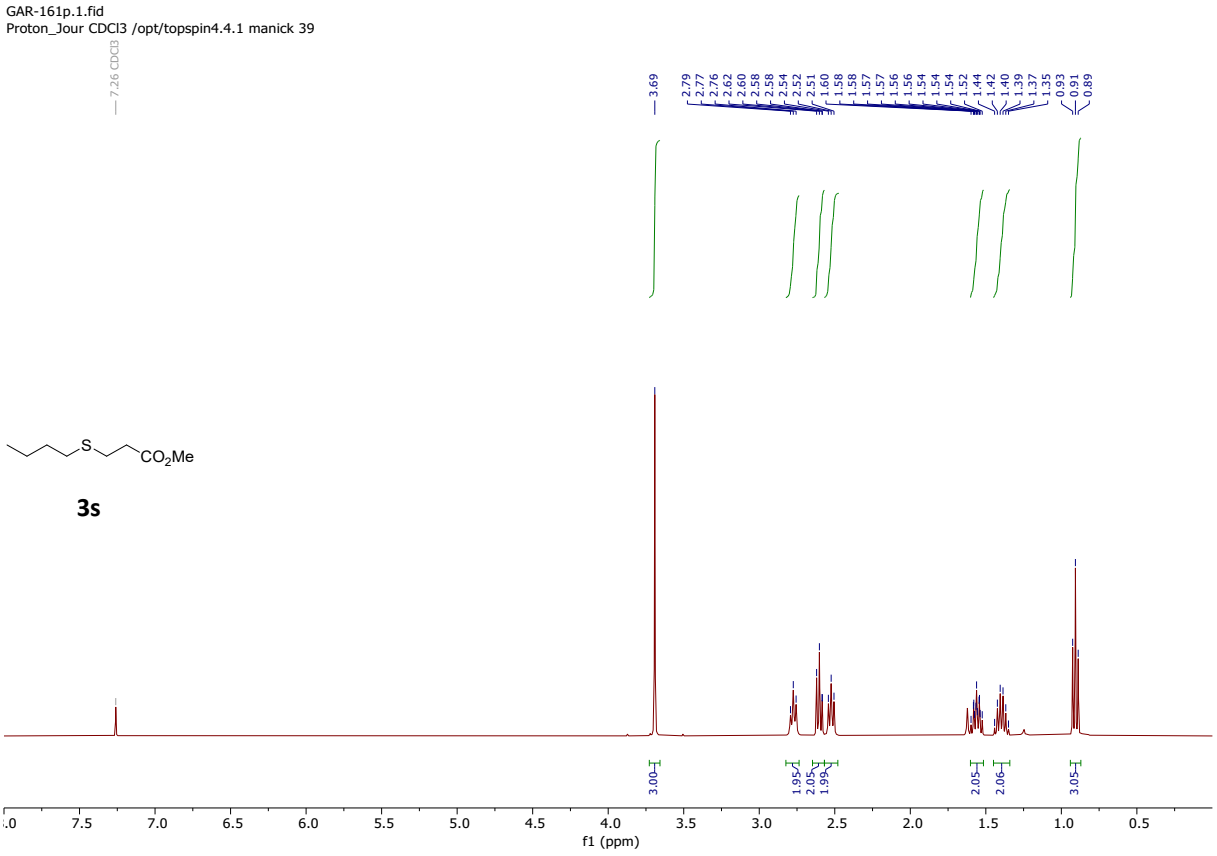


Figure S 59: ^{1}H NMR ($CDCl_3$, 400 MHz) of 3s

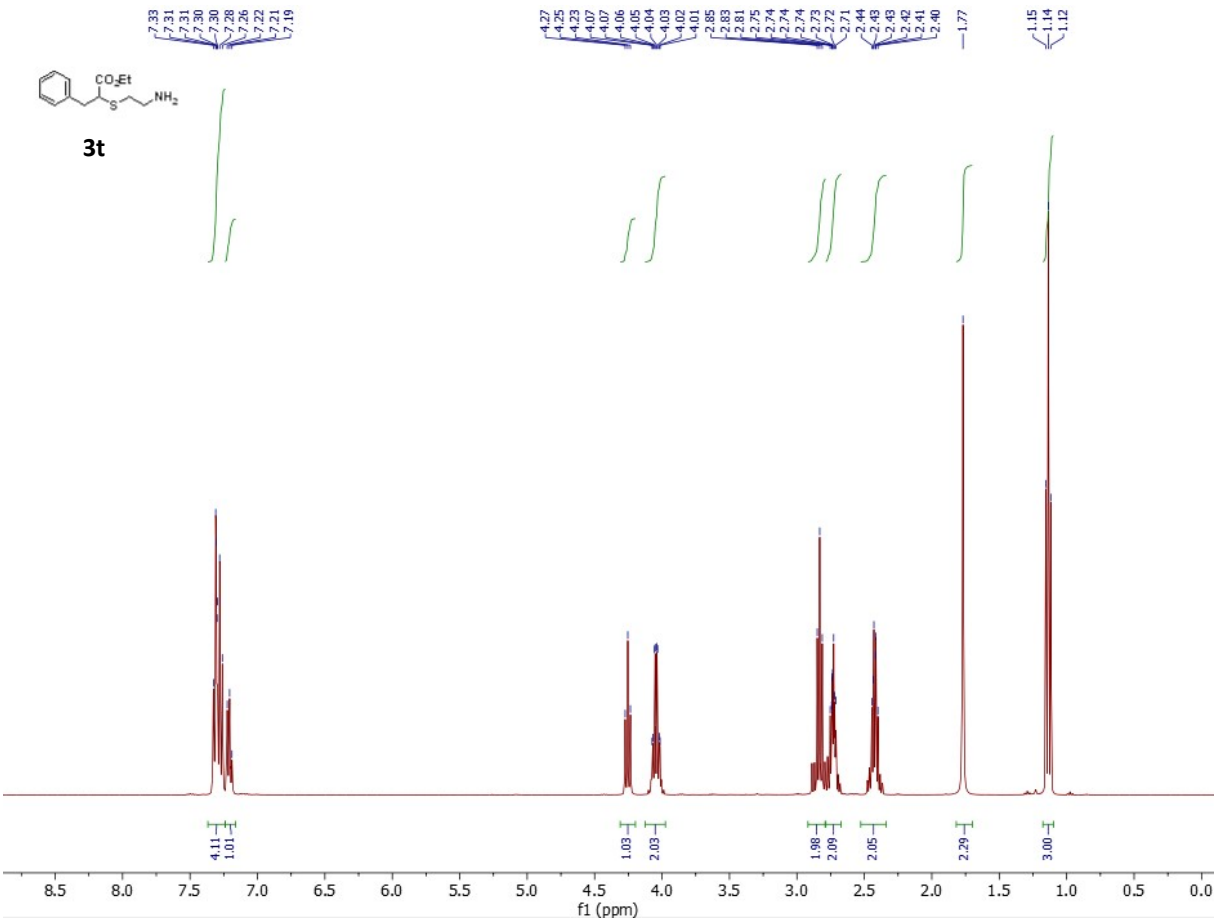


Figure S 60: ^{1}H NMR ($CDCl_3$*, 400 MHz) of* 3t

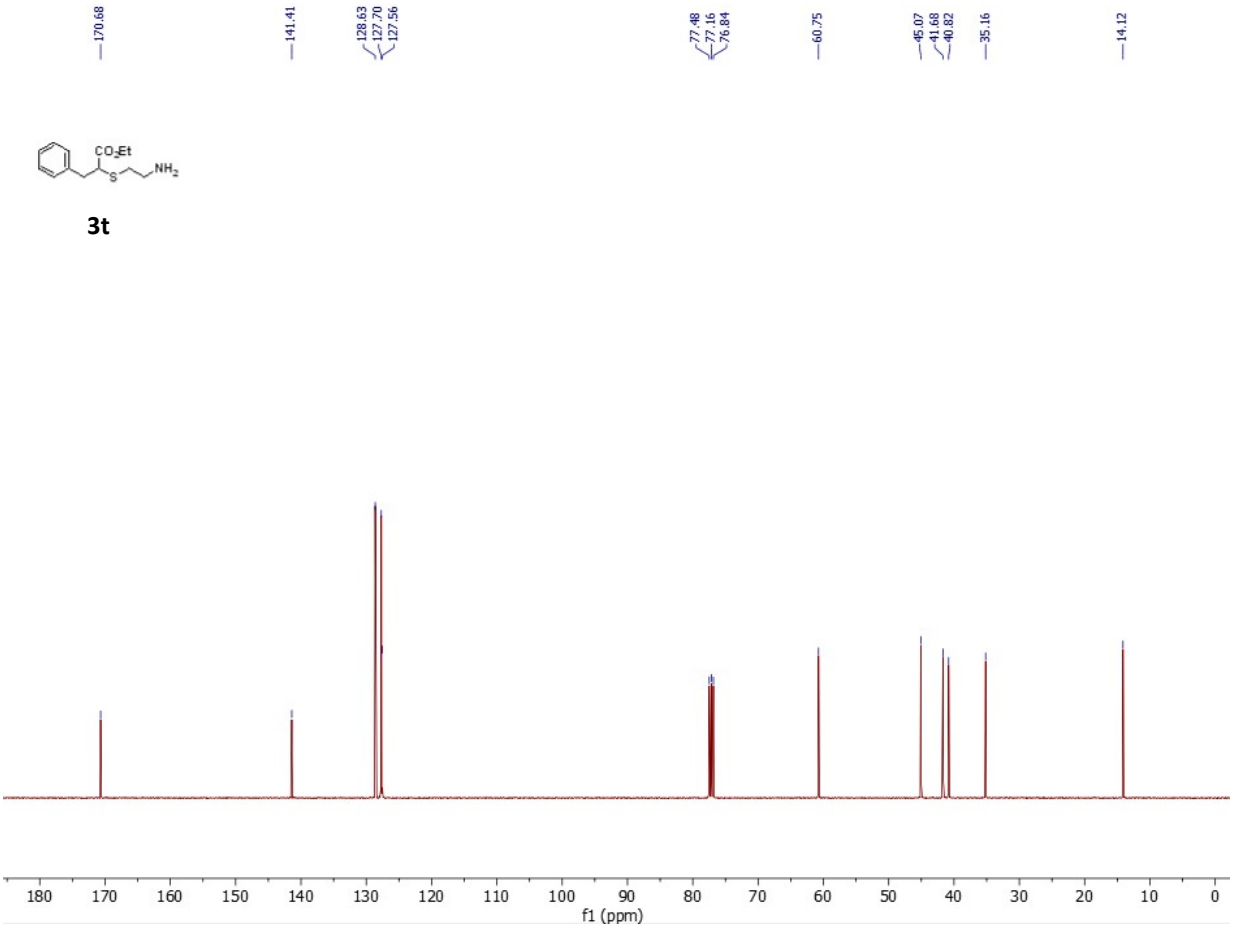


Figure S 61: $^{13}C\{1H\}$ NMR ($CDCl_3$, 101 MHz) of 3t

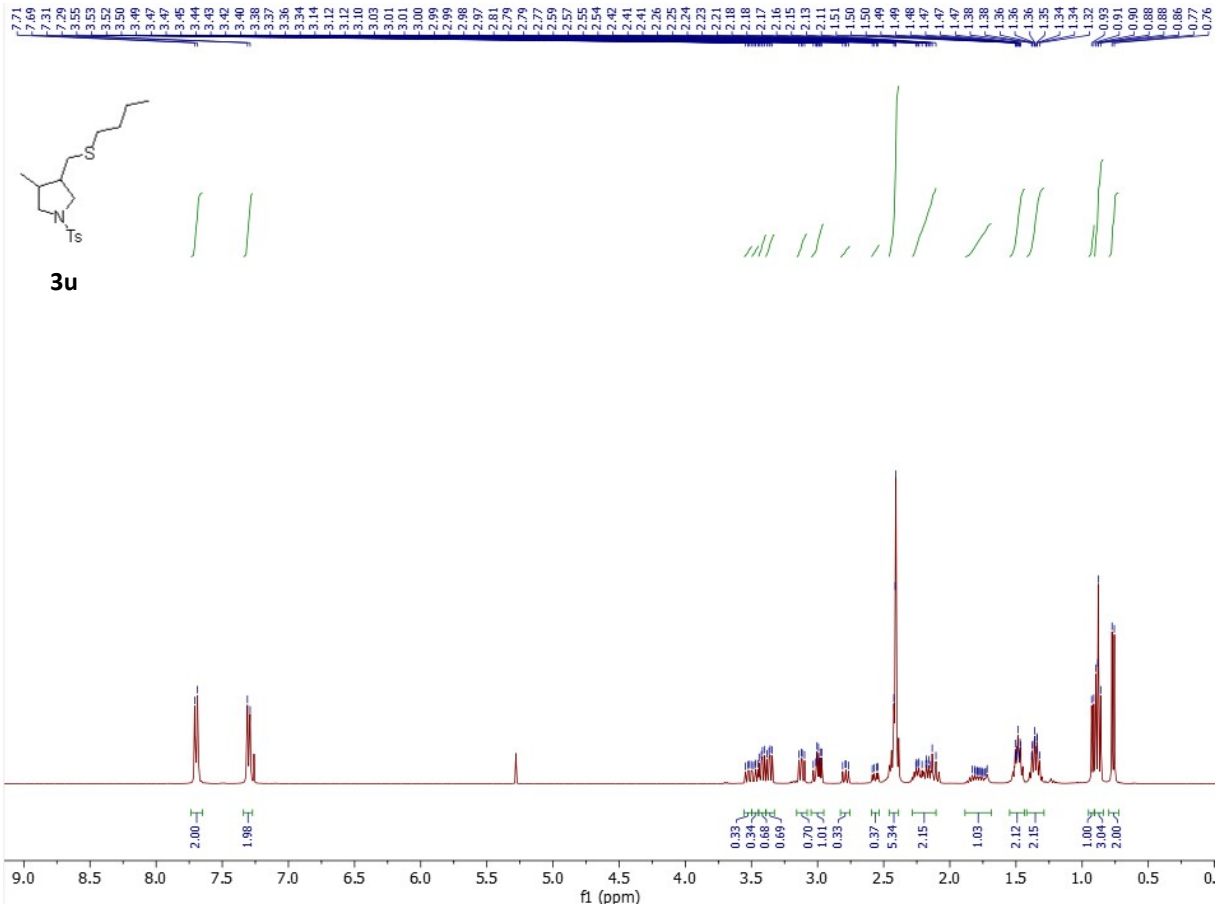
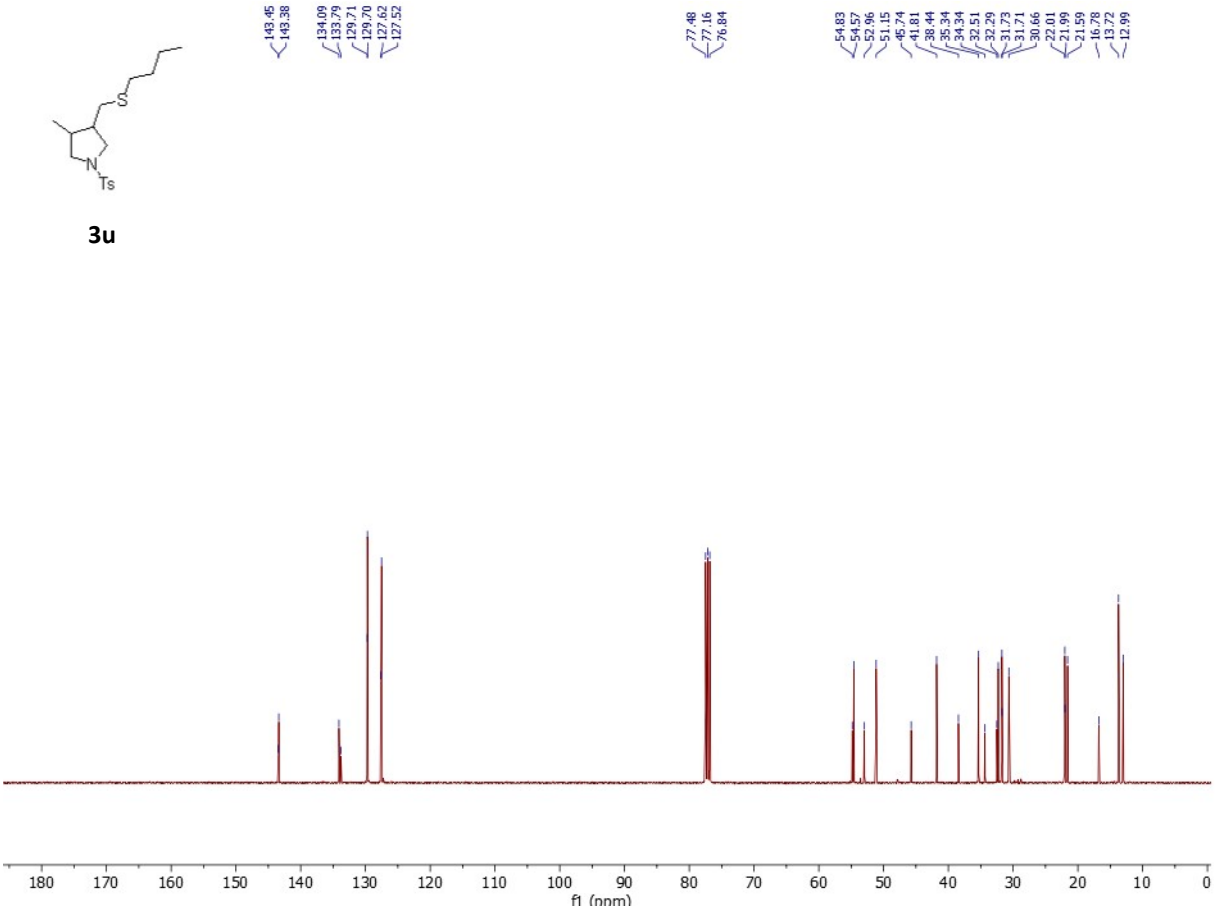


Figure S 62: ^{1}H NMR ($CDCl_3$*, 400 MHz) of* 3u



3u

Figure S 63: $^{13}C\{1H\}$ NMR ($CDCl_3$, 101 MHz) of 3u

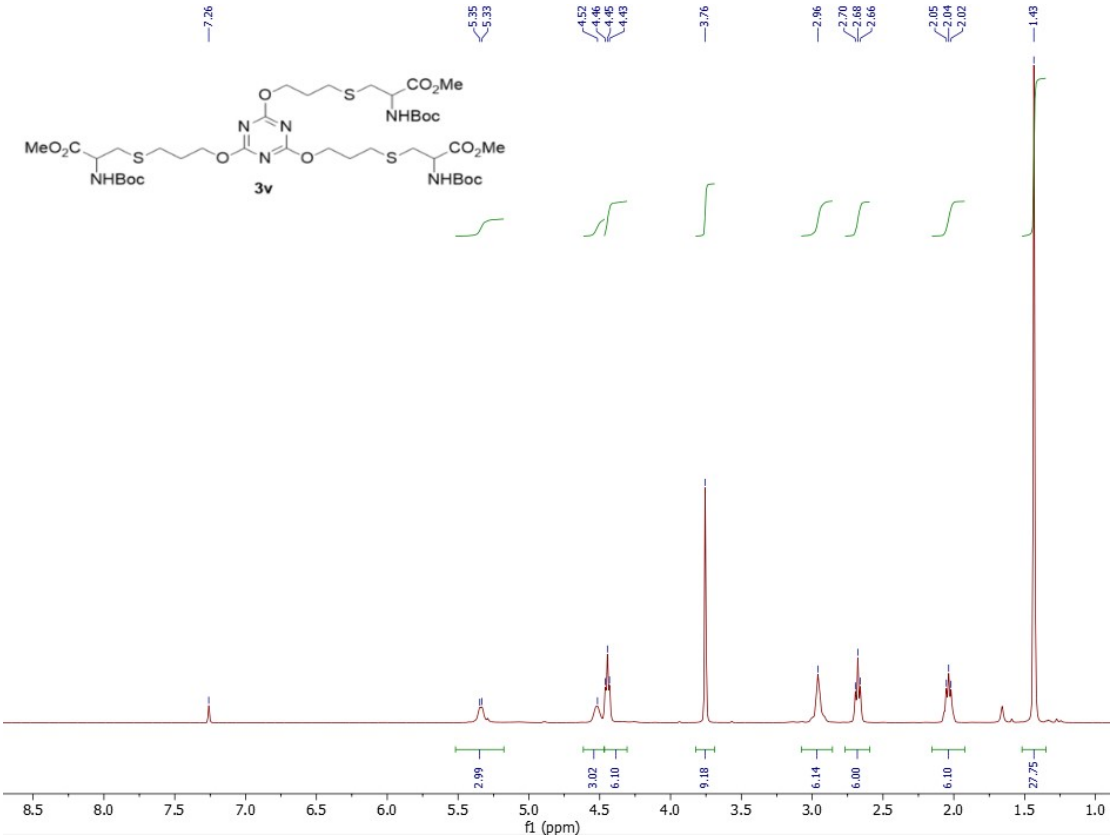


Figure S 64: ^{1}H NMR ($CDCl_3$*, 400 MHz) of* 3v

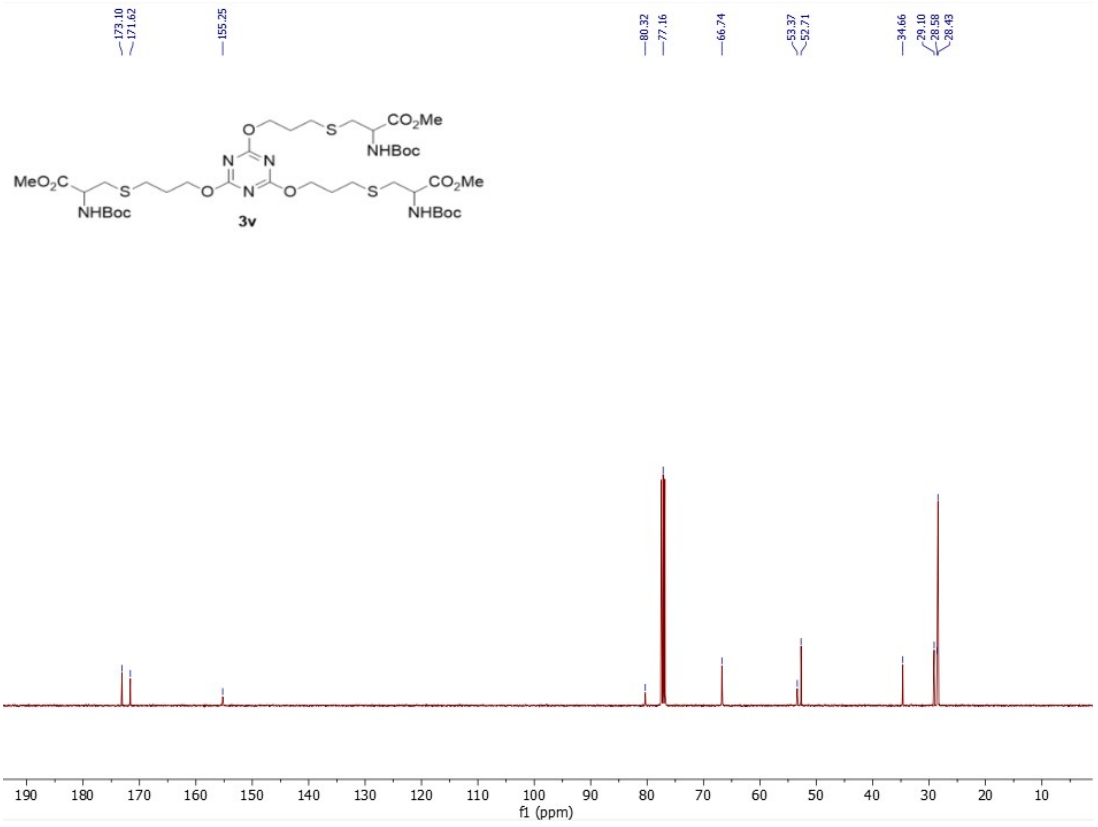


Figure S 65: $^{13}C\{1H\}$ NMR ($CDCl_3$, 101 MHz) of 3v