Supporting information

Visible light photoredox-catalyzed deoxydisulfuration of alcohols

Chaoyang Liu,[1] Xiaoman Lin,[1] Delie An,[*1] Xi Wang[*1,2] and Qianwen Gao[*1,2]

[1]*College of Chemistry and Chemical Engineering, State Key Laboratory of Chemo/Biosensing and Chemometrics, Advanced Catalytic Engineering Research Center of the Ministry of Education, Hunan University, Changsha 410082, P. R. China.*

[2]*Greater Bay Area Institute for Innovation, Hunan University, Guangzhou 511300, P. R. China. Changsha 410082, P. R. China.*

E-mail: gaoqw@hnu.edu.cn

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1. General

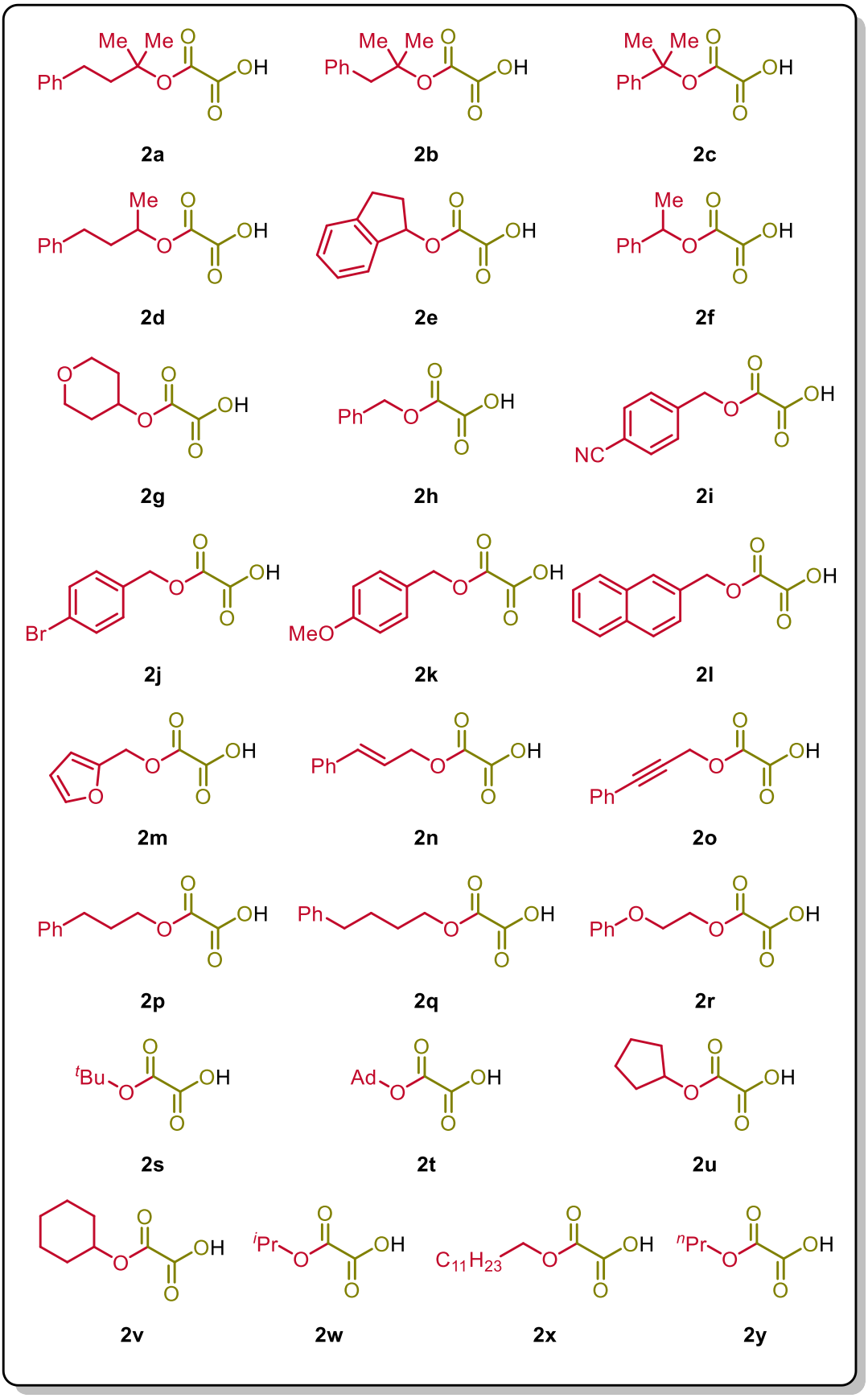
All reactions involving air- or moisture-sensitive reagents or intermediates were carried out in flame-dried glassware under a nitrogen atmosphere using standard *Schlenk* techniques. All solvents were freshly distilled and degassed according to the handbook *Purification of Laboratory Chemicals* (4th Edition, Butterworth Heinemann, W. L. F. Armarego and Douglas Dalzell Perrin). The boiling point of petroleum ether (PE) was between 60 and 90 ºC. Commercially available reagents were used as received from Energy Chemical, Aladdin, Leyan, Alfa Aesar China, TCI China. For chromatography, 300-400 mesh silica gel (Qingdao, China) was employed. Analytical thin layer chromatography (TLC) was performed using silica gel plates (Qingdao, China). Visualisation was by ultraviolet fluorescence, and/or phosphomolybdic acid, and/or $KMnO_4$ (1.5 g in 400 mL H_2O, 5.0 g $NaHCO_3$). ^{1}H-Nuclear Magnetic Resonance (^{1}H-NMR), ^{13}C Nuclear Magnetic Resonance (^{13}C-NMR) spectra and ^{19}F-Nuclear Magnetic Resonance (^{19}F-NMR) were recorded on Bruker 400 MHz and JEOL JNM-ECZ400S/L1 400 MHz at 20 °C with $CDCl_3$ as solvent. Chemical shifts (ppm) are given relative to solvent: references for $CDCl_3$ were 7.26 ppm (^{1}H NMR) and 77.16 ppm (^{13}C NMR). The data are reported as follows: chemical shift (ppm), multiplicity (s = singlet, d = doublet, t = triplet, q= quartet, m = multiplet, br = broad), coupling constant *J*(Hz), and integration. High resolution mass spectra were recorded on Thermo Oribtrap Exploris 120, Thermo Finnigan MAT95XP, JEOL AccuTOF LC-plus 4G, Agilent 7250 Accurate-Mass Q-TOF GC/MS. IR spectra were recorded on SHIMADZU IRSpirit-T and reported in unit of cm^{-1}. GC and GCMS data were recorded on SHIMADZU Nexis GC-2030 and SHIMADZU GCMS-QP2020NX respectively. The data of Stern-Volmer analysis were recorded on JASCO FP-8500 Fluorescence Spectrometer. The data of cyclic voltammetry was measured using BAS Epsilon electrochemical analyzer.

2. Preparation of starting materials

2.1 Preparation of oxalate 2

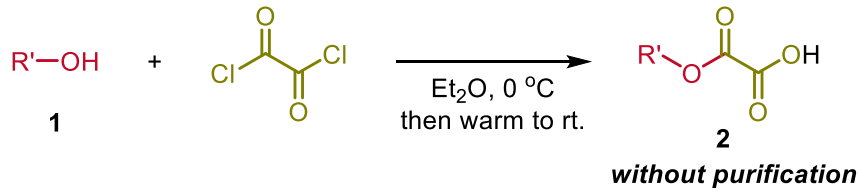
The oxalate was prepared according to the previously reported literature procedures.[1] The spectral data was consistent with the literature data: **2a**,[1a] **2b**,[1b] **2c**,[1c] **2d**,[1a] **2e**,[1d] **2f**,[1e] **2g**,[1d] **2h**,[1d] **2i**,[1d] **2j**,[1f] **2k**,[1g] **2l**,[1d] **2m**,[1h] **2n**,[1a] **2o**,[1a] **2p**,[1b] **2q**,[1d] **2r**,[1i] **2s**,[1d] **2t**,[1d] **2u**,[1d] **2v**,[1d] **2w**,[1b] **2x**,[1a] **2y**[1b].

Table S1 Oxalate substrates.



Procedure for the preparation of oxalate.

General procedure for the preparation of oxalate 2 from the corresponding alcohol (GP1)

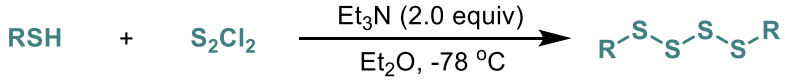


A flame-dried Schlenk-tube equipped with a magnetic stir bar was sealed with a septum, and degassed by alternating vacuum evacuation and nitrogen backfilling (three times) before alcohol (10.0 mmol 1.0 equiv) in Et_2O (50 mL) was added. The solution was cooled to 0 °C. To the resulting solution, oxalyl chloride (20.0 mmol, 2.0 equiv) was added dropwise. After the addition was completed, and homogeneous reaction mixture was allowed to warm to ambient temperature and stir for 18 h. The reaction was cooled to 0 °C and quenched by the slow addition of H_2O (10 mL). After stirring for 1 h at an ambient temperature, the resulting mixture was transferred to a separatory funnel, and the aqueous layer mixture was extracted with three portions of Et_2O. The combined organic layers were washed with brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure, affording the title compound. All of the oxalates were used without further purification.

2.2 Preparation of disulfur transfer reagents 3.

The disulfur transfer reagents were prepared according to the previously reported literature procedures[2]. The spectral data was consistent with the literature data: **3a**,[2a] **3b**,[2b] **3c**,[2c] **3d**,[2d] **3e**,[2c] **3f**,[2e] **3g**,[2c] **3h**,[2c] **3i**,[2c] **3j**,[2f] **3k**,[2f] **3l**,[2g] **3m**,[2h] **3n**,[2h] **3o**,[2g] **3p**,[2h] **3q**,[2i] **3r**,[2i] **3s**.[2i]

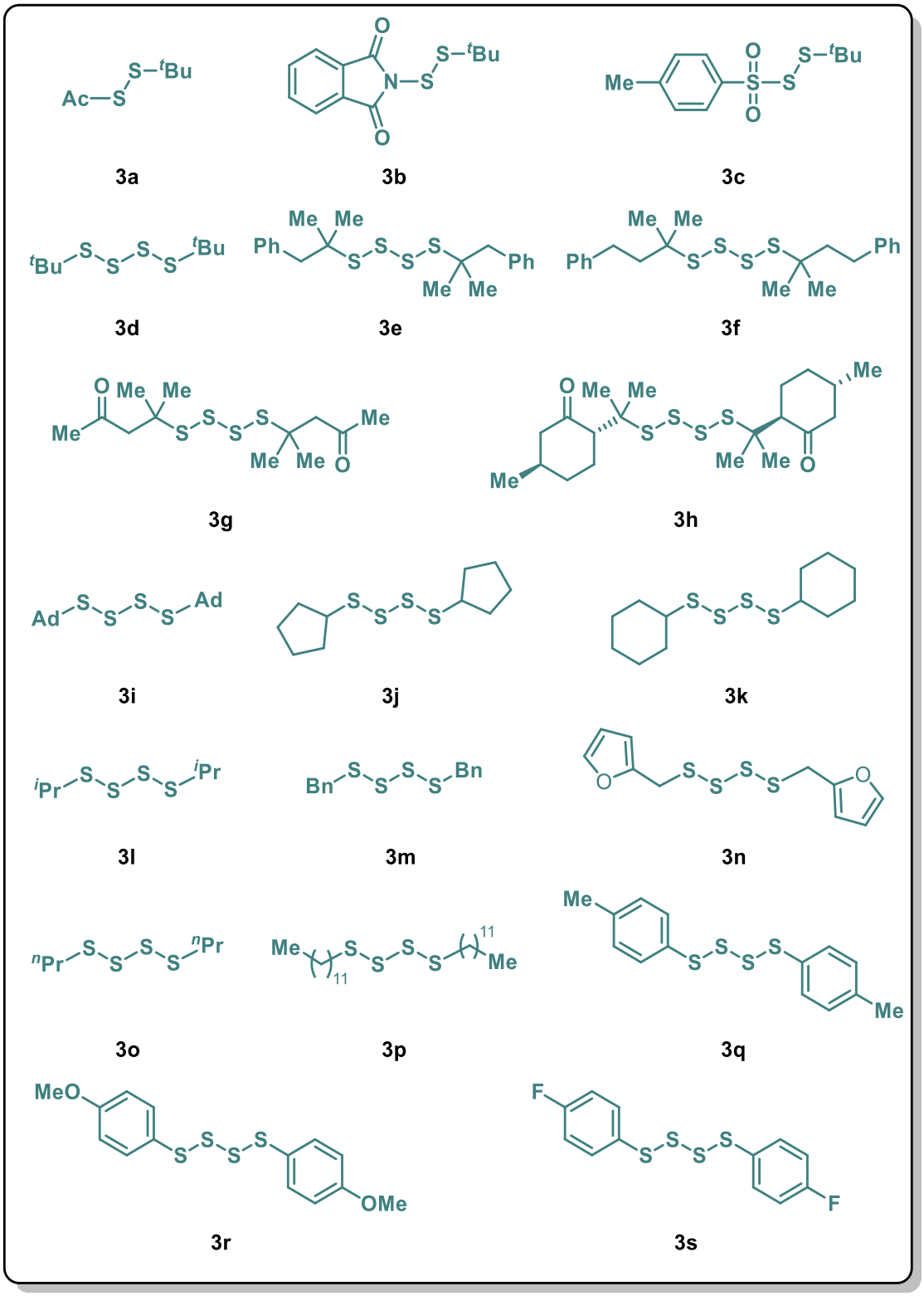
General procedure for synthesis of tetrasulfide (GP2)



A flame-dried Schlenk-tube equipped with a magnetic stir bar was sealed with a septum, and degassed by alternating vacuum evacuation and nitrogen backfilling (three times) before a solution of disulphur dichloride (0.48 mL, 6.0 mmol, 1.0 equiv) in Et_2O (20 mL) was added. The solution was cooled to -78 °C. To the resulting solution, thiol (12.00 mmol, 2.0 equiv) in Et_2O (20 mL) solution mixed with Et_3N (1.70 mL, 12.0 mmol, 2.0 equiv) was added dropwise over 1 h. After the addition was completed, the solution was continued stirring for additional 30 min and then allowed to warm to the room temperature. After the reaction was complete, the reaction was quenched with

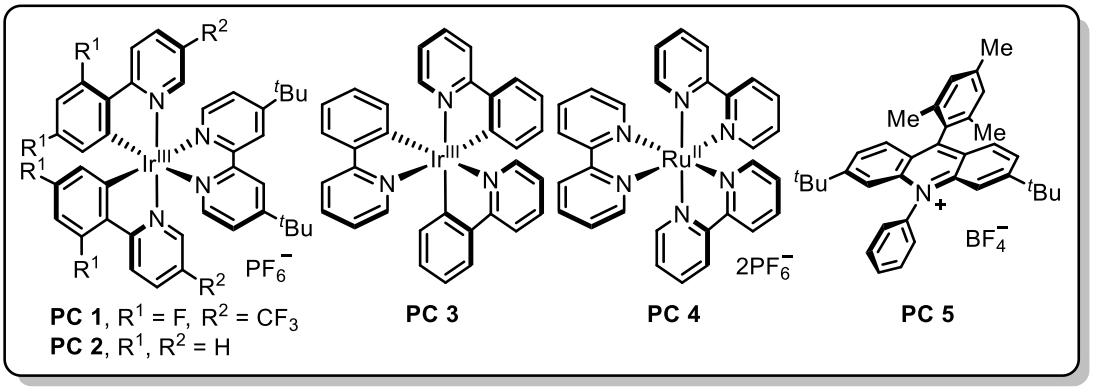
H_2O. The organic layer was separated and washed with H_2O (40 mL), Na_2CO_3 (sat. soln., 40 mL) and brine (40 mL), dried over $MgSO_4$, filtered, and concentrated with the aid of a rotary evaporator. The crude residue was purification via silica gel chromatography gave the desired tetrasulfide.

Table S2 Disulfur transfer reagents.



2.3 Preparation of Photocatalyst.

Table S3 Photocatalysts.



The photocatalyst were prepared according to the previously reported literature procedures.[3] The spectral data is consistent with the literature data: **PC 1**,[3a] **PC 2**,[3b] **PC 3**,[3c] **PC 4**,[3d] **PC 5**.[3e]

3. Photoredox-catalyzed deoxydisulfuration of activated alcohols with tetrasulfide

3.1 General procedure for synthesis of unsymmetrical alkyl disulfides (GP3)

GP3-1, **for liquid oxalate and liquid tetrasulfide reagent.**

A flame-dried Schlenk-tube equipped with a magnetic stir bar was charged with **PC 1** (0.006 mmol, 3 mol%), Cs_2CO_3 (0.60 mmol, 3.0 equiv), sealed with a septum, and degassed by alternating vacuum evacuation and nitrogen backfilling (three times) before DCE (2 mL) was added. The corresponding liquid oxalate **2** (0.40 mmol, 2.0 equiv) and the liquid tetrasulfide reagent **3** (0.20 mmol, 1.0 equiv) were added successively by micro-syringe. The reaction mixture was then stirred and irradiated using a 20 W blue LED lamp at room temperature for 24 h. After the reaction was complete, the solvent was removed under reduced pressure with the aid of a rotary evaporator. The crude residue was purified by silica gel column chromatography to afford pure unsymmetric disulfide product **4**.

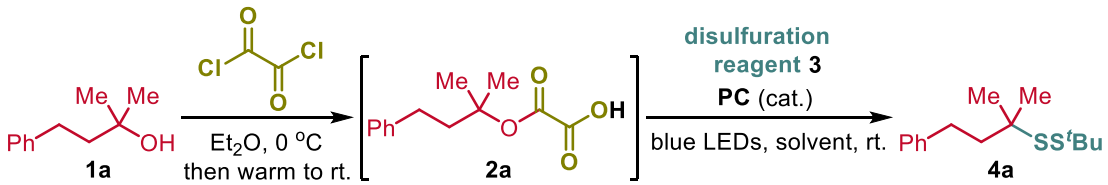
GP3-2, **for liquid oxalate and solid tetrasulfide reagent**

A flame-dried Schlenk-tube equipped with a magnetic stir bar was charged with **PC 1** (0.006 mmol, 3 mol%), Cs_2CO_3 (0.60 mmol, 3.0 equiv), and the corresponding solid tetrasulfide reagent **3** (0.20 mmol, 1.0 equiv), sealed with a septum, and degassed by alternating vacuum evacuation and nitrogen backfilling (three times) before DCE (2 mL) was added. The liquid oxalate **2** (0.40 mmol, 2.0 equiv) were added successively by micro-syringe. The reaction mixture was then stirred and irradiated using a 20 W blue LED lamp at room temperature for 24 h. After the reaction was complete, the

solvent was removed under reduced pressure with the aid of a rotary evaporator. The crude residue was purified by silica gel column chromatography to afford pure unsymmetric disulfide product **4**.

3.2 Screening of reaction conditions.

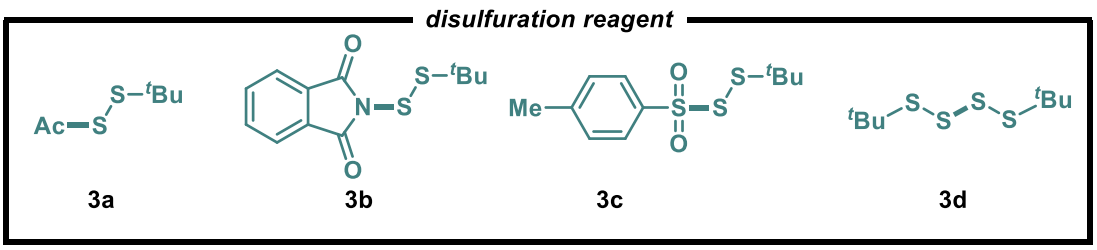
Table S4 Reaction optimization.

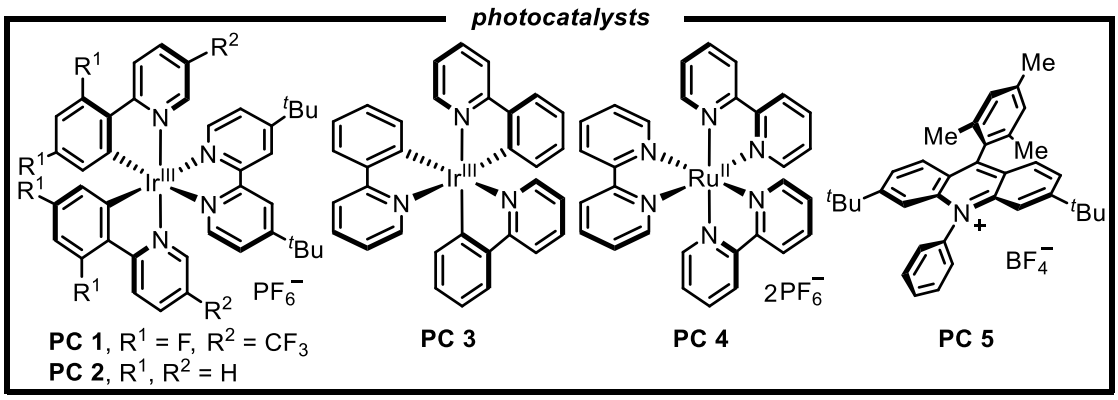


entry[a]	3	PC	base	solvent	yield (%)[b]
1	**3a**	**PC 1**	CsOAc	DCM	nd.
2	**3b**	**PC 1**	CsOAc	DCM	nd.
3	**3c**	**PC 1**	CsOAc	DCM	12
4	**3c**	**PC 2**	CsOAc	DCM	8
5	**3c**	**PC 3**	CsOAc	DCM	nd.
6	**3c**	**PC 4**	CsOAc	DCM	trace
7	**3c**	**PC 5**	CsOAc	DCM	trace
8	**3d**	**PC 1**	CsOAc	DCM	23
9	**3d**	**PC 1**	CsOAc	DCE	33
10	**3d**	**PC 1**	CsOAc	$CHCl_3$	17
11	**3d**	**PC 1**	Cs_2CO_3	DCE	40
12	**3d**	**PC 1**	CsOH	DCE	25
13[c]	**3d**	**PC 1**	**Cs_2CO_3**	**DCE**	**85(82)**
14[d]	**3d**	**PC 1**	Cs_2CO_3	DCE	nd.
15[e]	**3d**	**none**	Cs_2CO_3	DCE	nd.

[a]Reaction conditions: **2a** (0.24 mmol, 1.2 equiv), **3** (0.20 mmol, 1.0 equiv), **PC** (3.0 mol%), base (0.24 mmol, 1.2 equiv) solvent (2 mL), blue LEDs, rt., 24 h; [b]Yield determined by GC analysis using *n*-dodecane as an internal standard; The value in parentheses refers to isolated yield; "nd." stands for "not detected"; [c]The amount of **2a** increased to 2.0 equivalent and Cs_2CO_3 increased to 3.0 equivalent; [d]The reaction was conducted in the dark; [e]The reaction proceeded in the absence of photocatalyst.

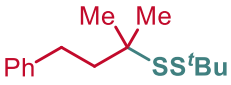
Table S5 Disulfuration reagents and photocatalysts tested.



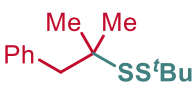


A flame-dried Schlenk-tube equipped with a magnetic stir bar was charged with **PC** (0.006 mmol, 3mol%), base (0.240 mmol, 1.2 equiv), sealed with a septum, and degassed by alternating vacuum evacuation and nitrogen backfilling (three times) before solvent (2 mL) was added. The corresponding 2-((2-methyl-4-phenylbutan-2-yl)oxy)-2-oxoacetic acid **2a** (0.22 mmol, 1.2 equiv) and disulfuration reagent **3** (0.20 mmol, 1.0 equiv) were added successively by micro-syringe. The reaction mixture was then stirred and irradiated using a 20 W blue LED lamp at room temperature for 24 h. After the reaction was complete, the solvent was removed under reduced pressure with the aid of a rotary evaporator. The crude residue was analyzed by GC, GC-MS and ^{1}H NMR.

3.3 Spectral data of unsymmetrical disulfides.

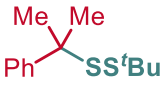


(3-(*tert*-Butylsulfinothioyl)-3-methylbutyl)benzene (4a and 4s): The title compound prepared according to the general procedure (**GP3-1**) with **PC 1** (6.6 mg, 6.0 μmol, 3 mol%), 2-((2-methyl-4-phenylbutan-2-yl)oxy)-2-oxoacetic acid **2a** (94.5 mg, 0.400 mmol, 2.0 equiv), Cs_2CO_3 (195.5 mg, 0.6000 mmol, 3.0 equiv) and 1,4-di-*tert*-butyl-tetrasulfane **3d** (48.5 mg, 0.200 mmol, 1.0 equiv) in DCE (2 mL) at room temperature for 24 h. Purification via silica gel chromatography (PE:DCM = 20:1) gave the desired unsymmetric disulfide product **4a** as a light yellow oil in 82% yield (44.0 mg). **TLC** $\mathbf{R_f}$ = 0.6 (PE:DCM = 10:1); **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.31 – 7.27 (m, 2H), 7.21 – 7.19 (m, 3H), 2.74 – 2.70 (m, 2H), 1.88 – 1.84 (m, 2H), 1.36 (s, 6H), 1.34 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 142.5, 128.5, 125.9, 49.5, 46.4, 44.5, 31.5, 30.8, 28.4; **HRMS** (EI) *m/z* = 268.1319, calcd. for $C_{15}H_{24}S_2$ $[M]^+$, found: 268.1314; **IR** (neat, cm^{-1}): 2964*w*, 2895*w*, 2838*w*, 1593*m*, 1576*w*, 1439*w*, 1371*m*, 1245*m*, 885*w*, 834*s*, 760*m*, 737 *m*, 685*w*, 657*w*, 640*w*.

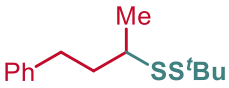


(2-(*tert*-Butylsulfinothioyl)-2-methylpropyl)benzene (4b): The title compound prepared according to the general procedure (**GP3-1**) with **PC 1** (6.6 mg, 6.0 μmol, 3 mol%), 2-((2-methyl-1-phenyl-

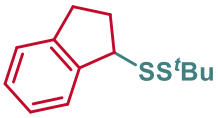
propan-2-yl)oxy)-2-oxoacetic acid **2b** (88.9 mg, 0.400 mmol, 2.0 equiv), Cs_2CO_3 (195.5 mg, 0.6000 mmol, 3.0 equiv) and 1,4-di-*tert*-butyl-tetrasulfane **3d** (48.5 mg, 0.200 mmol, 1.0 equiv) in DCE (2 mL) at room temperature for 24 h. Purification via silica gel chromatography (PE:DCM = 20:1) gave the desired unsymmetric disulfide product **4b** as a light yellow oil in 70% yield (35.6 mg). **TLC R_f** = 0.6 (PE:DCM = 10:1); **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.35 – 7.28 (m, 3H), 7.23 (d, *J* = 7.4 Hz, 2H), 2.91 (s, 2H), 1.39 (s, 9H), 1.30 (s, 6H).; **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 137.9, 130.9, 128.0, 126.5, 49.9, 48.6, 46.6, 30.8, 27.7; **HRMS** (EI) *m*/*z* = 254.1163, calcd. for $C_{14}H_{22}S_2$ $[M]^+$, found: 254.1164; **IR** (neat, cm^{-1}): 2935*w*, 2821*w*, 1611*m*, 1491*w*, 1451*m*, 1057*s*, 1011*w*, 788*m*, 765*m*, 731*w*, 628*w*, 531*w*.



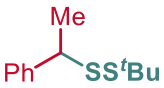
(2-(*tert*-Butylsulfinothioyl)propan-2-yl)benzene (4c): The title compound prepared according to the general procedure (**GP3-1**) with **PC 1** (6.6 mg, 6.0 μmol, 3 mol%), 2-oxo-2-((2-phenylpropan-2-yl)oxy) acetic acid **2c** (83.3 mg, 0.400 mmol, 2.0 equiv), Cs_2CO_3 (195.5 mg, 0.6000 mmol, 3.0 equiv) and 1,4-di-*tert*-butyl-tetrasulfane **3d** (48.5 mg, 0.200 mmol, 1.0 equiv) in DCE (2 mL) at room temperature for 24 h. Purification via silica gel chromatography (PE:DCM = 20:1) gave the desired unsymmetric disulfide product **4c** as a light yellow oil in 43% yield (20.7 mg). **TLC R_f** = 0.6 (PE:DCM = 10:1); **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.53 (d, *J* = 7.1 Hz, 2H), 7.33 (t, *J* = 7.7 Hz, 2H), 7.24 – 7.20 (m, 1H), 1.73 (s, 6H), 1.13 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 146.0, 128.2, 127.1, 126.8, 51.4, 46.9, 30.6, 29.4; **HRMS** (EI) *m*/*z* = 240.1006, calcd. for $C_{13}H_{20}S_2$ $[M]^+$, found: 240.1003; **IR** (neat, cm^{-1}): 2961*w*, 2921*w*, 1453*m*, 1362*m*, 1165*m*, 747*m*, 701*s*.



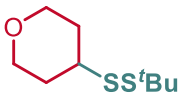
(3-(*tert*-Butylsulfinothioyl)butyl)benzene (4d): The title compound prepared according to the general procedure (**GP3-1**) with **PC 1** (6.6 mg, 6.0 μmol, 3 mol%), 2-oxo-2-((4-phenylbutan-2-yl)oxy)acetic acid **2d** (88.9 mg, 0.400 mmol, 2.0 equiv), Cs_2CO_3 (195.5 mg, 0.6000 mmol, 3.0 equiv) and 1,4-di-*tert*-butyl-tetrasulfane **3d** (48.5 mg, 0.200 mmol, 1.0 equiv) in DCE (2 mL) at room temperature for 24 h. Purification via silica gel chromatography (PE:DCM = 20:1) gave the desired unsymmetric disulfide product **4d** as a light yellow oil in 43% yield (21.9 mg). **TLC R_f** = 0.7 (PE:DCM = 10:1); **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.32 – 7.28 (m, 2H), 7.23 – 7.18 (m, 3H), 2.88 – 2.72 (m, 3H), 2.09 – 2.00 (m, 1H), 1.87 – 1.78 (m, 1H), 1.36 (d, *J* = 6.8 Hz, 3H), 1.32 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 141.8, 128.54, 128.48, 126.0, 47.6, 46.4, 38.1, 33.2, 30.2, 20.6. The spectral data are in accordance with previous reported literature.[4]



1-(*tert*-Butylsulfinothioyl)-2,3-dihydro-1*H*-indene (4e): The title compound prepared according to the general procedure (**GP3-1**) with **PC 1** (6.6 mg, 6.0 μmol, 3 mol%), 2-((2,3-dihydro-1*H*-inden-1-yl)oxy)-2-oxoacetic acid **2e** (82.5 mg, 0.400 mmol, 2.0 equiv), Cs_2CO_3 (195.5 mg, 0.6000 mmol, 3.0 equiv) and 1,4-di-*tert*-butyl-tetrasulfane **3d** (48.5 mg, 0.200 mmol, 1.0 equiv) in DCE (2 mL) at room temperature for 24 h. Purification via silica gel chromatography (PE:DCM = 20:1) gave the desired unsymmetric disulfide product **4e** as a light yellow oil in 42% yield (20.2 mg). **TLC R_f** = 0.6 (PE:DCM = 10:1); **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.45 – 7.43 (m, 1H), 7.23 – 7.19 (m, 3H), 4.42 (dd, J^1 = 7.4 Hz, J^2 = 5.2 Hz, 1H), 3.16 – 3.08 (m, 1H), 2.85 – 2.81 (m, 1H), 2.52 – 2.45 (m, 1H), 2.41 – 2.43 (m, 1H), 1.37 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 144.2, 142.7, 128.2, 126.5, 125.3, 125.0, 56.5, 48.0, 33.3, 30.5, 30.2; **HRMS** (EI) *m*/*z* = 238.0850, calcd. for $C_{13}H_{18}S_2$ $[M]^+$, found: 238.0852; **IR** (neat, cm^{-1}): 2961*w*, 2921*w*, 1453*m*, 1362*m*, 1165*m*, 747*m*, 701*s*.



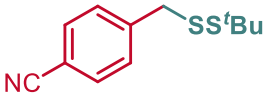
(1-(*tert*-Butylsulfinothioyl)ethyl)benzene (4f): The title compound prepared according to the general procedure (**GP3-1**) with **PC 1** (6.6 mg, 6.0 μmol, 3 mol%), 2-oxo-2-(1-phenylethoxy)acetic acid **2f** (77.7 mg, 0.400 mmol, 2.0 equiv), Cs_2CO_3 (195.5 mg, 0.6000 mmol, 3.0 equiv) and 1,4-di-*tert*-butyl-tetrasulfane **3d** (48.5 mg, 0.200 mmol, 1.0 equiv) in DCE (2 mL) at room temperature for 24 h. Purification via silica gel chromatography (PE:DCM = 20:1) gave the desired unsymmetric disulfide product **4f** as a light yellow oil in 53% yield (24.0 mg). **TLC R_f** = 0.7 (PE:DCM = 10:1); **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.31 (d, *J* = 4.4 Hz, 4H), 7.24 (s, 1H), 3.99 (q, *J* = 7.0 Hz, 1H), 1.66 (d, *J* = 7.0 Hz, 3H), 1.30 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 142.5, 128.6, 127.8, 127.6, 51.3, 48.0, 30.2, 21.3. The spectral data are in accordance with previous reported literature.[2f]



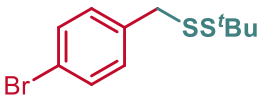
4-(*tert*-Butyldisulfanyl)tetrahydro-2*H*-pyran (4g): The title compound prepared according to the general procedure (**GP3-1**) with **PC 1** (6.6 mg, 6.0 μmol, 3 mol%), 2-oxo-2-((tetrahydro-2*H*-pyran-4-yl)oxy)acetic acid **2g** (69.7 mg, 0.400 mmol, 2.0 equiv), Cs_2CO_3 (195.5 mg, 0.6000 mmol, 3.0 equiv) and 1,4-di-*tert*-butyl-tetrasulfane **3d** (48.5 mg, 0.200 mmol, 1.0 equiv) in DCE (2 mL) at room temperature for 24 h. Purification via silica gel chromatography (PE:DCM = 20:1) gave the desired unsymmetric disulfide product **4g** as a light yellow oil in 50% yield (20.6 mg). **TLC R_f** = 0.6 (PE:DCM = 10:1); **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 3.98 (dt, J^1 = 11.8 Hz, J^2 = 3.8 Hz, 2H), 3.40 (td, J^1= 11.2 Hz, J^2= 2.4 Hz, 2H), 2.93 – 2.85 (m, 1H), 2.01 (d, *J* = 12.3 Hz, 2H), 1.65 – 1.61 (m, 2H), 1.32 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 67.5, 47.6, 46.9,

32.9, 30.2. The spectral data are in accordance with previous reported literature.[5]

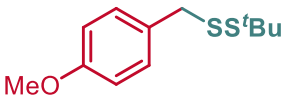
((*tert*-Butylsulfinothioyl)methyl)benzene (4h): The title compound prepared according to the general procedure (**GP3-1**) with **PC 1** (6.6 mg, 6.0 μmol, 3 mol%), 2-(benzyloxy)-2-oxoacetic acid **2h** (72.1 mg, 0.400 mmol, 2.0 equiv), Cs_2CO_3 (195.5 mg, 0.6000 mmol, 3.0 equiv) and 1,4-di-*tert*-butyl-tetrasulfane **3d** (48.5 mg, 0.200 mmol, 1.0 equiv) in DCE (2 mL) at room temperature for 24 h. Purification via silica gel chromatography (PE:DCM = 20:1) gave the desired unsymmetric disulfide product **4h** as a light yellow oil in 68% yield (28.9 mg). **TLC R_f** = 0.5 (PE:DCM = 10:1); **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.33 – 7.26 (m, 5H), 3.94 (s, 2H), 3.80 (s, 3H), 1.34 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 137.5, 129.4, 128.7, 127.5, 48.2, 45.9, 30.2. The spectral data are in accordance with previous reported literature.[2f]



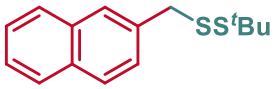
4-((*tert*-Butylsulfinothioyl)methyl)benzonitrile (4i): The title compound prepared according to the general procedure (**GP3-1**) with **PC 1** (6.6 mg, 6.0 μmol, 3 mol%), 2-((4-cyanobenzyl) oxy)-2-oxoacetic acid **2i** (82.1 mg, 0.400 mmol, 2.0 equiv), Cs_2CO_3 (195.5 mg, 0.6000 mmol, 3.0 equiv) and 1,4-di-*tert*-butyl-tetrasulfane **3d** (48.5 mg, 0.200 mmol, 1.0 equiv) in DCE (2 mL) at room temperature for 24 h. Purification via silica gel chromatography (PE:DCM = 20:1) gave the desired unsymmetric disulfide product **4i** as a light yellow oil in 65% yield (30.9 mg). **TLC R_f** = 0.5 (PE:DCM = 10:1); **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.61 (d, *J* = 8.4 Hz, 2H), 7.40 (d, *J* = 8.3 Hz, 2H), 3.91 (s, 2H), 1.33 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 143.3, 132.4, 130.1, 118.9, 111.3, 48.5, 44.9, 30.1. The spectral data are in accordance with previous reported literature.[2f]



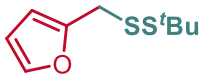
1-Bromo-4-((*tert*-Butylsulfinothioyl)methyl)benzene (4j): The title compound prepared according to the general procedure (**GP3-1**) with **PC 1** (6.6 mg, 6.0 μmol, 3 mol%), 2-((4-bromo-benzyl)oxy)-2-oxoacetic acid **2j** (103.6 mg, 0.4000 mmol, 2.0 equiv), Cs_2CO_3 (195.5 mg, 0.6000 mmol, 3.0 equiv) and 1,4-di-*tert*-butyl-tetrasulfane **3d** (48.5 mg, 0.200 mmol, 1.0 equiv) in DCE (2 mL) at room temperature for 24 h. Purification via silica gel chromatography (PE:DCM = 20:1) gave the desired unsymmetric disulfide product **4j** as a light yellow oil in 63% yield (36.7 mg). **TLC R_f** = 0.5 (PE:DCM = 10:1); **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.46 – 7.42 (m, 2H), 7.19 – 7.16 (m, 2H), 3.86 (s, 2H), 1.34 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 136.6, 131.8, 131.0, 121.5, 48.3, 44.9, 30.1. The spectral data are in accordance with previous reported literature.[6]



1-((*tert*-Butylsulfinothioyl)methyl)-4-methoxybenzene(4k): The title compound prepared according to the general procedure (**GP3-1**) with **PC 1** (6.6 mg, 6.0 μmol, 3 mol%), 2-((4-methoxybenzyl)oxy)-2-oxoacetic acid **2k** (84.1 mg, 0.400 mmol, 2.0 equiv), Cs_2CO_3 (195.5 mg, 0.6000 mmol, 3.0 equiv) and 1,4-di-*tert*-butyl-tetrasulfane **3d** (48.5 mg, 0.200 mmol, 1.0 equiv) in DCE (2 mL) at room temperature for 24 h. Purification via silica gel chromatography (PE:DCM = 10:1) gave the desired unsymmetric disulfide product **4k** as a light yellow oil in 54% yield (26.2 mg). **TLC R_f** = 0.3 (PE:DCM = 10:1); **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.24 (d, J = 8.6 Hz, 2H), 6.86 (d, J = 8.6 Hz, 2H), 3.92 (s, 2H), 3.80 (s, 3H), 1.36 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 159.0, 130.5, 129.4, 114.0, 55.3, 48.1, 45.3, 30.1. The spectral data are in accordance with previous reported literature.[2f]



2-((*tert*-Butylsulfinothioyl)methyl)naphthalene (4l): The title compound prepared according to the general procedure (**GP3-1**) with **PC 1** (6.6 mg, 6.0 μmol, 3 mol%), 2-(naphthalen-2-ylmethoxy)-2-oxoacetic acid **2l** (92.1 mg, 0.400 mmol, 2.0 equiv), Cs_2CO_3 (195.5 mg, 0.6000 mmol, 3.0 equiv) and 1,4-di-*tert*-butyl-tetrasulfane **3d** (48.5 mg, 0.200 mmol, 1.0 equiv) in DCE (2 mL) at room temperature for 24 h. Purification via silica gel chromatography (PE:DCM = 20:1) gave the desired unsymmetric disulfide product **4l** as a light yellow oil in 72% yield (37.8 mg). **TLC R_f** = 0.6 (PE:DCM = 10:1); **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.84 – 7.82 (m, 3H), 7.74 (s, 1H), 7.52 – 7.45 (m, 3H), 4.12 (s, 2H), 1.38 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 134.9, 133.4, 132.8, 128.5, 128.0, 127.9, 127.8, 127.4, 126.3, 126.0, 48.3, 46.1, 30.2. The spectral data are in accordance with previous reported literature.[2f]



2-((*tert*-Butylsulfinothioyl)methyl)furan (4m): The title compound prepared according to the general procedure (**GP3-1**) with **PC 1** (6.6 mg, 6.0 μmol, 3 mol%), 2-(furan-2-ylmethoxy)-2-oxoacetic acid **2m** (68.0 mg, 0.400 mmol, 2.0 equiv), Cs_2CO_3 (195.5 mg, 0.6000 mmol, 3.0 equiv) and 1,4-di-*tert*-butyl-tetrasulfane **3d** (48.5 mg, 0.200 mmol, 1.0 equiv) in DCE (2 mL) at room temperature for 24 h. Purification via silica gel chromatography (PE:DCM = 20:1) gave the desired unsymmetric disulfide product **4m** as a light yellow oil in 42% yield (17.0 mg). **TLC R_f** = 0.6 (PE:DCM = 10:1); **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.37 (dd, J^1 = 1.9 Hz, J^2 = 0.9 Hz, 1H), 6.32 – 6.31 (m, 1H), 6.24 (d, J = 3.2 Hz, 1H), 3.94 (s, 2H), 1.32 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 150.8, 142.5, 110.7, 108.7, 48.2, 37.9, 30.0. The spectral data are in accordance with previous reported literature.[6]

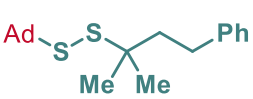
(*E*)-(3-(*tert*-Butylsulfinothioyl)prop-1-en-1-yl)benzene (4n): The title compound prepared according to the general procedure (**GP3-1**) with **PC 1** (6.6 mg, 6.0 μmol, 3 mol%), 2-(cinnamyloxy)-2-oxoacetic acid **2n** (82.5 mg, 0.400 mmol, 2.0 equiv), Cs_2CO_3 (195.5 mg, 0.6000 mmol, 3.0 equiv) and 1,4-di-*tert*-butyl-tetrasulfane **3d** (48.5 mg, 0.200 mmol, 1.0 equiv) in DCE (2 mL) at room temperature for 24 h. Purification via silica gel chromatography (PE:DCM = 20:1) gave the desired unsymmetric disulfide product product **4n** as a light yellow oil in 46% yield (21.9 mg). **TLC R_f** = 0.6 (PE:DCM = 10:1); **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.41 (d, *J* = 7.4 Hz, 2H), 7.34 (t, *J* = 7.5 Hz, 2H), 7.29 (s, 1H), 6.51 (d, *J* = 15.7 Hz, 1H), 6.26 (dt, J^1 = 15.5 Hz, J^2 =7.6 Hz, 1H), 3.56 (d, *J* = 8.3 Hz, 2H), 1.38 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 136.8, 133.6, 128.7, 127.8, 126.6, 124.9, 48.0, 43.9, 30.2. The spectral data are in accordance with previous reported literature.[2f]

1-(*tert*-Butyl)-2-(3-phenylprop-2-yn-1-yl)disulfane (4o): The title compound prepared according to the general procedure (**GP3-1**) with **PC 1** (6.6 mg, 6.0 μmol, 3 mol%), 2-oxo-2-((3-phenyl-prop-2-yn-1-yl)oxy)acetic acid **2o** (81.7 mg, 0.400 mmol, 2.0 equiv), Cs_2CO_3 (195.5 mg, 0.6000 mmol, 3.0 equiv) and 1,4-di-*tert*-butyl-tetrasulfane **3d** (48.5 mg, 0.200 mmol, 1.0 equiv) in DCE (2 mL) at room temperature for 24 h. Purification via silica gel chromatography (PE:DCM = 20:1) gave the desired unsymmetric disulfide product **4o** as a light yellow oil in 48% yield (22.7 mg). **TLC R_f** = 0.7 (PE:DCM = 10:1); **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.45 – 7.42 (m, 2H), 7.31 – 7.29 (m, 2H), 3.71 (s, 2H), 1.38 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 131.9, 128.41, 128.39, 123.1, 85.1, 85.0, 48.4, 30.6, 30.2. The spectral data are in accordance with previous reported literature.[4]

(3-(*tert*-Butylsulfinothioyl)propyl)benzene (4p): The title compound prepared according to the general procedure (**GP3-1**) with **PC 1** (6.6 mg, 6.0 μmol, 3 mol%), 2-oxo-2-(3-phenylpropoxy)acetic acid **2p** (83.3 mg, 0.400 mmol, 2.0 equiv), Cs_2CO_3 (195.5 mg, 0.6000 mmol, 3.0 equiv) and 1,4-di-*tert*-butyl-tetrasulfane **3d** (48.5 mg, 0.200 mmol, 1.0 equiv) in DCE (2 mL) at room temperature for 24 h. Purification via silica gel chromatography (PE:DCM = 20:1) gave the desired unsymmetric disulfide product **4p** as a light yellow oil in 32% yield (15.4 mg). **TLC R_f** = 0.7 (PE:DCM = 10:1); **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.32 – 7.28 (m, 2H), 7.22 – 7.19 (m, 3H), 2.76 – 2.71 (m, 4H), 2.06 – 1.99 (m, 2H), 1.34 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 141.5, 128.6, 128.5, 126.0, 47.8, 40.0, 34.5, 30.8, 30.1. The spectral data are in accordance with previous reported literature.[2j]

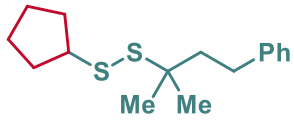
(4-(*tert*-Butylsulfinothioyl)butyl)benzene (4q): The title compound prepared according to the general procedure (**GP3-1**) with **PC 1** (6.6 mg, 6.0 μmol, 3 mol%), 2-oxo-2-(4-phenylbutoxy)acetic acid **2q** (88.9 mg, 0.400 mmol, 2.0 equiv), Cs_2CO_3 (195.5 mg, 0.6000 mmol, 3.0 equiv) and 1,4-di-*tert*-butyl-tetrasulfane **3d** (48.5 mg, 0.200 mmol, 1.0 equiv) in DCE (2 mL) at room temperature for 24 h. Purification via silica gel chromatography (PE:DCM = 20:1) gave the desired unsymmetric disulfide product **4q** as a light yellow oil in 32% yield (16.3 mg). **TLC R_f** = 0.7 (PE:DCM = 10:1); **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.23 (d, *J* = 7.8 Hz, 2H), 7.16 – 7.13 (m, 3H), 2.71 – 2.68 (m, 2H), 2.61 – 2.58 (m, 2H), 1.67 (s, 4H), 1.29 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 142.3, 128.5, 128.5, 125.9, 47.9, 40.9, 35.6, 30.4, 30.1, 29.1. The spectral data are in accordance with previous reported literature.[2j]

(2-(*tert*-Butylsulfinothioyl)ethoxy)benzene (4r): The title compound prepared according to the general procedure (**GP3-1**) with **PC 1** (6.6 mg, 6.0 μmol, 3 mol%), 2-oxo-2-(2-phenoxyethoxy)acetic acid **2r** (84.1 mg, 0.400 mmol, 2.0 equiv), Cs_2CO_3 (195.5 mg, 0.6000 mmol, 3.0 equiv) and 1,4-di-*tert*-butyl-tetrasulfane **3d** (48.5 mg, 0.200 mmol, 1.0 equiv) in DCE (2 mL) at room temperature for 24 h. Purification via silica gel chromatography (PE:DCM = 20:1) gave the desired unsymmetric disulfide product **4r** as a light yellow oil in 34% yield (16.5 mg). **TLC R_f** = 0.6 (PE:DCM = 10:1); **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) =7.33 – 7.29 (m, 2H), 7.00 – 6.94 (m, 3H), 4.24 (t, *J* = 7.0 Hz, 2H), 3.07 (t, *J* = 7.0 Hz, 2H), 1.38 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 158.5, 129.6, 121.1, 114.7, 66.6, 48.1, 39.1, 30.0. The spectral data are in accordance with previous reported literature.[2j]

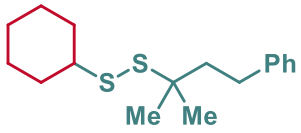


(3s,5s,7s)-1-((2-Methyl-4-phenylbutan-2-yl)-sulfinothioyl) adamantane (4t and 4ae): The title compound prepared according to the general procedure (**GP3-1**) with **PC 1** (6.6 mg, 6.0 μmol, 3 mol%), 2-(((3s,5s,7s)-adamantan-1-yl)oxy)-2-oxoacetic acid **2t** (89.7 mg, 0.400 mmol, 2.0 equiv), Cs_2CO_3 (195.5 mg, 0.6000 mmol, 3.0 equiv) and 1,4-bis(2-methyl-4-phenylbutan-2-yl)tetrasulfane **3f** (84.5 mg, 0.200 mmol, 1.0 equiv) in DCE (2 mL) at room temperature for 24 h. Purification via silica gel chromatography (PE:DCM = 20:1) gave the desired unsymmetric disulfide product **4t** as a light yellow oil in 72% yield (49.9 mg). **TLC R_f** = 0.5 (PE:DCM = 10:1); **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.30 – 7.28 (m, 2H), 7.20 – 7.16 (m, 3H), 2.74 – 2.69 (m, 2H), 2.06 (s, 3H), 1.86 – 1.82 (m, 8H), 1.67 (d, *J* = 3.4 Hz, 6H), 1.34 (s, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 142.5, 128.51, 128.49, 125.9, 49.2, 48.0, 44.4, 43.3, 36.2, 31.5, 30.2, 28.4; **HRMS** (EI) *m/z* = 346.1789, calcd. for $C_{21}H_{30}S_2$ $[M]^+$,

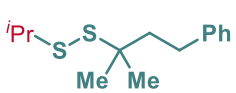
found: 346.1793; **IR** (neat, cm^{-1}): 2899*m*, 2847*m*, 1451*m*, 1341*m*, 1296*m*, 1039*m*, 1101*w*, 977*w*,734*w*, 685*w*.



1-Cyclopentyl-2-(2-methyl-4-phenylbutan-2-yl)disulfane (4u and 4af): The title compound prepared according to the general procedure (**GP3-1**) with **PC 1** (6.6 mg, 6.0 μmol, 3 mol%), 2-(cyclopentyloxy)-2-oxoacetic acid **2u** (63.3 mg, 0.400 mmol, 2.0 equiv), Cs_2CO_3 (195.5 mg, 0.6000 mmol, 3.0 equiv) and 1,4-bis(2-methyl-4-phenylbutan-2-yl)tetrasulfane **3f** (84.5 mg, 0.200 mmol, 1.0 equiv) in DCE (2 mL) at room temperature for 24 h. Purification via silica gel chromatography (PE:DCM = 20:1) gave the desired unsymmetric disulfide product **4u** as a light yellow oil in 56% yield (31.4 mg). **TLC** $\mathbf{R_f}$ = 0.6 (PE:DCM = 10:1); **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.31 – 7.27 (m, 2H), 7.21 – 7.17 (m, 3H), 3.32 – 3.28 (m, 1H), 2.73 – 2.68 (m, 2H), 2.00 – 1.95 (m, 2H), 1.92 – 1.87 (m, 2H), 1.78 – 1.67 (m, 4H), 1.62 – 1.56 (m, 2H), 1.37 (s, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 142.5, 128.52, 128.46, 125.9, 51.0, 50.8, 43.6, 33.2, 31.5, 28.0, 24.7; **HRMS** (EI) *m*/*z* = 280.1319, calcd. for $C_{16}H_{24}S_2$ $[M]^+$, found: 280.1325; **IR** (neat, cm^{-1}): 2360*m*, 2331*m*, 1394*m*, 1215*m*, 1083*w*, 986*w*, 848*m*, 696*s*, 668*s*, 485*w*.

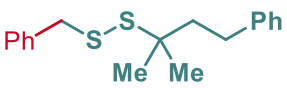


1-Cyclohexyl-2-(2-methyl-4-phenylbutan-2-yl)disulfane (4v and 4ag): The title compound prepared according to the general procedure (**GP3-1**) with **PC 1** (6.6 mg, 6.0 μmol, 3 mol%), 2-(cyclohexyloxy)-2-oxoacetic acid **2v** (68.9 mg, 0.400 mmol, 2.0 equiv), Cs_2CO_3 (195.5 mg, 0.6000 mmol, 3.0 equiv) and 1,4-bis(2-methyl-4-phenylbutan-2-yl)tetrasulfane **3f** (84.5 mg, 0.200 mmol, 1.0 equiv) in DCE (2 mL) at room temperature for 24 h. Purification via silica gel chromatography (PE:DCM = 20:1) gave the desired unsymmetric disulfide product **4v** as a light yellow oil in 50% yield (29.5 mg). **TLC** $\mathbf{R_f}$ = 0.6 (PE:DCM = 10:1); **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.30 – 7.27 (m, 2H), 7.20 – 7.17 (m, 3H), 2.72 – 2.68 (m, 3H), 2.11 – 2.03 (m, 3H), 1.89 – 1.85 (m, 2H), 1.78 (d, *J* = 4.3 Hz, 3H), 1.61 (s, 4H), 1.35 (s, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 142.5, 128.51, 128.47, 125.9, 50.6, 50.2, 43.5, 33.1, 31.4, 28.0, 26.1, 25.9; **HRMS** (EI) *m*/*z* = 294.1476, calcd. for $C_{17}H_{26}S_2$ $[M]^+$, found: 294.1474; **IR** (neat, cm^{-1}): 2964*w*, 2838*w*, 1765*s*, 1611*m*, 1571*m*, 1502*s*, 1371*s*, 1205*s*, 1017*s*, 919*m*, 834*w*, 754*m*, 685*m*, 531*w*.

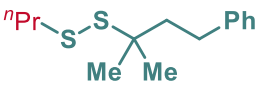


(3-(Isopropylsulfinothioyl)-3-methylbutyl)benzene (4w and 4ah): The title compound prepared according to the general procedure (**GP3-1**) with **PC 1** (6.6 mg, 6.0 μmol, 3 mol%),2-isopropoxy-2-oxoacetic acid **2w** (52.8 mg, 0.400 mmol, 2.0 equiv), Cs_2CO_3 (195.5 mg, 0.6000 mmol, 3.0 equiv) and 1,4-bis(2-methyl-4-phenylbutan-2-yl)tetrasulfane **3f** (84.5

mg, 0.200 mmol, 1.0 equiv) in DCE (2 mL) at room temperature for 24 h. Purification via silica gel chromatography (PE:DCM = 20:1) gave the desired unsymmetric disulfide product **4w** as a light yellow oil in 52% yield (26.5 mg). **TLC R_f** = 0.7 (PE:DCM = 10:1); **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.32 – 7.28 (m, 2H), 7.21 – 7.18 (m, 3H), 3.01 – 2.94 (m, 1H), 2.73 – 2.69 (m, 2H), 1.91 – 1.87 (m, 2H), 1.37 (s, 6H), 1.32 (d, *J* = 6.8 Hz, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 142.5, 128.53, 128.46, 125.9, 50.7, 43.7, 41.7, 31.5, 28.0, 22.7; **HRMS** (EI) *m*/*z* = 254.1163, calcd. for $C_{14}H_{22}S_2$ $[M]^+$, found: 254.1164; **IR** (neat, cm^{-1}): 2964*w*, 2838*w*, 1765*s*, 1611*m*, 1571*m*, 1502*s*, 1371*s*, 1154*s*, 919*m*, 834*w*, 754*m*, 685*m*, 531*w*.

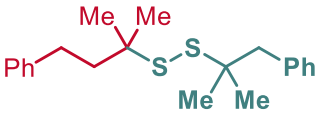


1-Benzyl-2-(2-methyl-4-phenylbutan-2-yl)disulfane (4x and 4ai): The title compound prepared according to the general procedure (**GP3-1**) with **PC 1** (6.6 mg, 6.0 μmol, 3 mol%), 2-(benzyloxy)-2-oxoacetic acid **2h** (72.1 mg, 0.400 mmol, 2.0 equiv), Cs_2CO_3 (195.5 mg, 0.6000 mmol, 3.0 equiv) and 1,4-bis(2-methyl-4-phenylbutan-2-yl)tetrasulfane **3f** (84.5 mg, 0.200 mmol, 1.0 equiv) in DCE (2 mL) at room temperature for 24 h. Purification via silica gel chromatography (PE:DCM = 15:1) gave the desired unsymmetric disulfide product **4x** as a light yellow oil in 66% yield (39.9 mg). **TLC R_f** = 0.4 (PE:DCM = 10:1); **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.33 – 7.29 (m, 7H), 7.21 – 7.17 (m, 3H), 3.95 (s, 2H), 2.73 – 2.68 (m, 2H), 1.94 – 1.89 (m, 2H), 1.38 (s, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 142.4, 137.4, 129.3, 128.7, 128.6, 128.5, 127.6, 126.0, 51.3, 45.7, 43.6, 31.4, 29.8, 28.0; **HRMS** (EI) *m*/*z* = 302.1163, calcd. for $C_{18}H_{22}S_2$ $[M]^+$, found: 302.1160; **IR** (neat, cm^{-1}): 2935*w*, 2821*w*, 2364*w*, 1508*s*, 1491*w*, 1245*s*, 1188*w*, 1057*s*, 1011*w*, 788*m*, 765*m*, 731*w*, 628*w*, 531*w*.

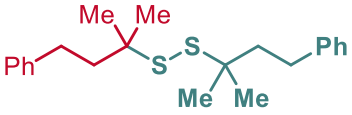


(3-Methyl-3-(propylsulfinothioyl)butyl)benzene(4z and 4ak): The title compound prepared according to the general procedure (**GP3-1**) with **PC 1** (6.6 mg, 6.0 μmol, 3 mol%), 2-oxo-2-propoxyacetic acid **2y** (52.8 mg, 0.400 mmol, 2.0 equiv), Cs_2CO_3 (195.5 mg, 0.6000 mmol, 3.0 equiv) and 1,4-bis(2-methyl-4-phenylbutan-2-yl)tetrasulfane **3f** (84.5 mg, 0.200 mmol, 1.0 equiv) in DCE (2 mL) at room temperature for 24 h. Purification via silica gel chromatography (PE:DCM = 20:1) gave the desired unsymmetric disulfide product **4z** as a light yellow oil in 32% yield (16.3 mg). **TLC R_f** = 0.7 (PE:DCM = 10:1); **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.31 – 7.27 (m, 2H), 7.19 (d, *J* = 7.3 Hz, 3H), 2.72 – 2.67 (m, 4H), 1.91 – 1.87 (m, 2H), 1.74 – 1.65 (m, 2H), 1.36 (s, 6H), 0.99 (t, *J* = 7.4 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 142.5, 128.54, 128.48, 125.9, 50.9, 43.5, 42.8, 31.4, 27.9, 22.8, 13.3; **HRMS** (EI) *m*/*z* = 254.1163, calcd. for $C_{14}H_{22}S_2$ $[M]^+$, found: 254.1166; **IR** (neat, cm^{-1}): 2965*m*, 2925*w*, 2866*w*, 2360*w*, 2344*w*, 1494*m*, 1446*m*, 1366*w*, 1135*w*, 1100*w*, 1029*w*, 766*m*, 749*m*,

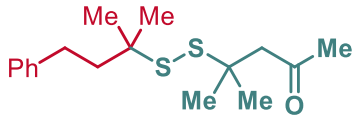
695*s*, 536*m*.



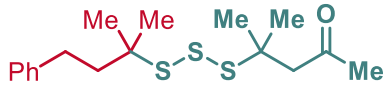
1-(2-Methyl-1-phenylpropan-2-yl)-2-(2-methyl-4-phenylbutan-2-yl)disulfane (4aa): The title compound prepared according to the general procedure (**GP3-1**) with **PC 1** (6.6 mg, 6.0 μmol, 3 mol%), 2-((2-methyl-4-phenylbutan-2-yl)oxy)-2-oxoacetic acid **2a** (94.5 mg, 0.400 mmol, 2.0 equiv), Cs_2CO_3 (195.5 mg, 0.6000 mmol, 3.0 equiv) and 1,4-bis(2-methyl-1-phenylpropan-2-yl)tetrasulfane **3e** (78.8 mg, 0.200 mmol, 1.0 equiv) in DCE (2 mL) at room temperature for 24 h. Purification via silica gel chromatography (PE:DCM = 20:1) gave the desired unsymmetric disulfide product **4aa** as a light yellow oil in 42% yield (28.9 mg). **TLC R_f** = 0.5 (PE：DCM = 10:1); **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.32 – 7.27 (m, 5H), 7.23 – 7.19 (m, 5H), 2.89 (s, 2H), 2.77 – 2.72 (m, 2H), 1.91 – 1.87 (m, 2H), 1.39 (s, 6H), 1.27 (s, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 142.4, 137.8, 130.9, 128.5, 128.0, 126.5, 125.9, 50.0, 49.8, 48.6, 44.6, 31.5, 28.5, 27.8; **HRMS** (EI) *m*/*z* = 344.1632, calcd. for $C_{21}H_{28}S_2$ $[M]^+$, found: 344.1636; **IR** (neat, cm^{-1}): 2924*w*, 2855*w*, 2804*w*, 1582*s*, 1456*s*, 1336*w*, 1308*m*, 1137*m*, 1091*w*, 937*w*, 874*w*, 765*s*, 714*s*.



1,2-Bis(2-methyl-4-phenylbutan-2-yl)disulfane (4ab): The title compound prepared according to the general procedure (**GP3-1**) with **PC 1** (6.6 mg, 6.0 μmol, 3 mol%), 2-((2-methyl-4-phenylbutan-2-yl)oxy)-2-oxoacetic acid **2a** (94.5 mg, 0.400 mmol, 2.0 equiv), Cs_2CO_3 (195.5 mg, 0.6000 mmol, 3.0 equiv) and 1,4-bis(2-methyl-4-phenylbutan-2-yl)tetrasulfane **3f** (84.5 mg, 0.200 mmol, 1.0 equiv) in DCE (2 mL) at room temperature for 24 h. Purification via silica gel chromatography (PE:DCM = 15:1) gave the desired symmetric disulfide product **4ab** as a light yellow oil in 42% yield (30.1 mg). **TLC R_f** = 0.4 (PE:DCM = 10:1); **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.32 – 7.28 (m, 2H), 7.22 – 7.18 (m, 3H), 2.76 – 2.71 (m, 2H), 1.91 – 1.86 (m, 2H), 1.38 (s, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 142.4, 128.51, 128.50, 125.9, 49.7, 44.5, 31.5, 28.5; **HRMS** (EI) *m*/*z* = 358.1789, calcd. for $C_{22}H_{30}S_2$ $[M]^+$, found: 358.1788; **IR** (neat, cm^{-1}): 2963*w*, 2919*w*, 2854*w*, 2360*w*, 1494*w*, 1446*w*, 1363*w*, 1125*w*, 1095*m*, 1073*w*, 1029*w*, 763*s*, 692*s*, 609*m*, 545*m*.

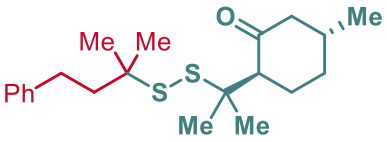


4ac



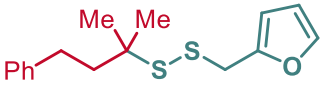
4ac'

The title compound prepared according to the general procedure (**GP3-1**) with **PC 1** (6.6 mg, 6.0 μmol, 3 mol%), 2-((2-methyl-4-phenylbutan-2-yl)oxy)-2-oxo-acetic acid **2a** (94.5 mg, 0.400 mmol, 2.0 equiv), Cs_2CO_3 (195.5 mg, 0.6000 mmol, 3.0 equiv) and 4,4'-tetrasulfanediylbis(4-methylpentan-2-one) **3g** (65.3 mg, 0.200 mmol, 1.0 equiv) in DCE (2 mL) at room temperature for 24 h. Purification via silica gel chromatography (PE:DCM = 5:1) gave the desired unsymmetric disulfide product **4ac** and **4ac'** as a light yellow oil in 76% yield (49.6 mg). **4-methyl-4-((2-methyl-4-phenylbutan-2-yl)disulfaneyl)pentan-2-one (4ac)** and **4-methyl-4-((2-methyl-4-phenylbutan-2-yl)trisulfaneyl)pentan-2-one (4ac')**: **TLC** R_f = 0.3 (PE:DCM = 2:1); **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) =7.33 – 7.29 (m, 2H), 7.26 – 7.19 (m, 3H), 2.89 (s, 1H), 2.75 – 2.71 (m, 3H), 2.19 (d, *J* = 14.6 Hz, 3H), 1.98 – 1.94 (m, 1H), 1.91 – 1.86 (m, 1H), 1.52 (s, 3H), 1.46 (s, 3H), 1.43 (s, 3H), 1.39 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 206.9, 206.6, 142.32, 142.27, 128.6, 128.58, 128.55, 128.53, 126.0, 54.4, 53.2, 52.6, 50.2, 50.1, 47.9, 44.5, 43.4, 32.27, 32.26, 31.5, 31.3, 28.4, 28.0, 27.8, 27.4. **HRMS** (EI) *m/z* = 310.1425, calcd. for $C_{17}H_{26}OS_2$ $[M]^+$, found: 310.1427 (**4ac**) and **HRMS** (EI) *m/z* = 342.1146, calcd. for $C_{17}H_{26}OS_3$ $[M]^+$, found: 342.1145 (**4ac'**); **IR** (neat, cm^{-1}): 2958*m*, 2924*m*, 2861*m*, 1719*s*, 1456*s*, 1382*w*, 1359*s*, 1336*w*, 1194*w*, 1114*s*, 748*m*, 697*s*.

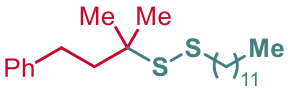


5-Methyl-2-(2-((2-methyl-4-phenylbutan-2-yl)di-sulfaneyl)propan-2-yl)cyclohexan-1-one (4ad): The title compound prepared according to the general procedure (**GP3-1**) with **PC 1** (6.6 mg, 6.0 μmol, 3 mol%), 2-((2-methyl-4-phenylbutan-2-yl)oxy)-2-oxoacetic acid **2a** (94.5 mg, 0.400 mmol, 2.0 equiv), Cs_2CO_3 (195.5 mg, 0.6000 mmol, 3.0 equiv) and 6,6'-(tetrasulfane-diylbis(propane-2,2-diyl))bis(3-methylcyclohexan-1-one) **3h** (86.8 mg, 0.200 mmol, 1.0 equiv) in DCE (2 mL) at room temperature for 24 h. Purification via silica gel chromatography (PE:DCM = 3:1) gave the desired unsymmetric disulfide product **4ad** as a light yellow oil in 71% yield (51.7 mg). **TLC** R_f = 0.3 (PE:DCM = 2:1); **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.30 – 7.26 (m, 2H), 7.20 – 7.16 (m, 3H), 2.73 – 2.68 (m, 2H), 2.57 – 2.47 (m, 2H), 2.30 – 2.25 (m, 1H), 2.05 – 1.98 (m, 1H), 1.91 – 1.82 (m, 4H), 1.51 (s, 3H), 1.37 (s, 3H), 1.35 (s, 6H), 1.00 (d, *J* = 6.2 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 211.1, 142.3, 128.52, 128.47, 125.9, 58.0, 52.4, 51.4, 49.8, 44.5, 36.9, 34.5, 31.5, 29.9, 28.7, 28.2, 27.7, 23.7, 22.4; **HRMS** (EI) *m/z* = 364.1895, calcd. for $C_{21}H_{32}OS_2$ $[M]^+$, found: 364.1891; **IR** (neat, cm^{-1}): 2964*w*,

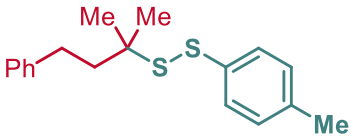
2827*w*, 1680*s*, 1599*s*, 1576*s*, 1496*s*, 1451*s*, 1359*s*, 1319*w*, 1171*m*, 1005*s*, 902*w*, 834*w*, 811*w*, 765*s*, 691*s*.



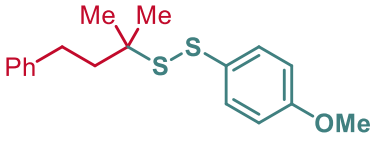
2-(((2-Methyl-4-phenylbutan-2-yl)disulfaneyl)methyl) furan (4aj): The title compound prepared according to the general procedure (**GP3-1**) with **PC 1** (6.6 mg, 6.0 μmol, 3 mol%), 2-((2-methyl-4-phenylbutan-2-yl)oxy)-2-oxoacetic acid **2a** (94.5 mg, 0.400 mmol, 2.0 equiv), Cs_2CO_3 (195.5 mg, 0.6000 mmol, 3.0 equiv) and 1,4-bis (furan-2-ylmethyl)tetrasulfane **3n** (58.1 mg, 0.200 mmol, 1.0 equiv) in DCE (2 mL) at room temperature for 24 h. Purification via silica gel chromatography (PE:DCM = 20:1) gave the desired unsymmetric disulfide product **4aj** as a light yellow oil in 36% yield (21.1mg). **TLC R$_f$** = 0.4 (PE:DCM = 10:1); **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.38 (dd, J^1 = 2.0 Hz, J^2 = 0.8 Hz, 1H), 7.33 – 7.30 (m, 2H), 7.22 (d, J = 6.2 Hz, 3H), 6.33 (dd, J^1 = 3.3 Hz, J^2 = 1.9 Hz, 1H), 6.26 (d, J = 3.2 Hz, 1H), 3.97 (s, 2H), 2.74 – 2.70 (m, 2H), 1.94 – 1.90 (m, 2H), 1.38 (s, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 150.7, 142.6, 142.3, 128.6, 128.5, 126.0, 110.7, 108.8, 51.4, 43.6, 37.8, 31.4, 27.8; **HRMS** (EI) *m*/*z* = 292.0956, calcd. for $C_{16}H_{20}OS_2$ $[M]^+$, found: 292.0952; **IR** (neat, cm^{-1}): 2958*w*, 2924*w*, 2861*w*, 1496*s*, 1456*s*, 1382*m*, 1365*m*, 1239*w*, 1199*w*, 1148*s*, 1114*m*, 1068*m*, 1011*s*, 937*s*, 805*w*, 737*s*, 697*s*.



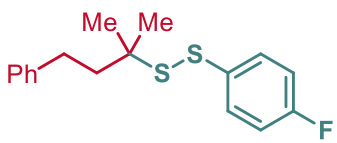
1-Dodecyl-2-(2-methyl-4-phenylbutan-2-yl)disulfane (4ak and 4y): The title compound prepared according to the general procedure (**GP3-1**) with **PC 1** (6.6 mg, 6.0 μmol, 3 mol%), 2-((2-methyl-4-phenylbutan-2-yl)oxy)-2-oxoacetic acid **2a** (94.5 mg, 0.400 mmol, 2.0 equiv), Cs_2CO_3 (195.5 mg, 0.6000 mmol, 3.0 equiv) and 1,4-didodecyltetrasulfane **3p** (93.2 mg, 0.200 mmol, 1.0 equiv) in DCE (2 mL) at room temperature for 24 h. Purification via silica gel chromatography (PE:DCM = 20:1) gave the desired unsymmetric disulfide product **4ak** as a light yellow oil in 60% yield (45.7 mg). **TLC R$_f$** = 0.6 (PE:DCM = 10:1); **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.30 – 7.27 (m, 3H), 7.20 – 7.16 (m, 2H), 2.72 – 2.68 (m, 4H), 1.91 – 1.87 (m, 2H), 1.66 – 1.64 (m, 2H), 1.36 (s, 6H), 1.27 (s, 18H), 0.89 (t, J = 7.0 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 142.5, 128.53, 128.47, 125.9, 50.9, 43.5, 40.9, 32.1, 31.4, 29.80, 29.78, 29.75, 29.73, 29.6, 29.50, 29.48, 29.4, 28.7, 27.9, 22.8, 14.3; **HRMS** (EI) *m*/*z* = 381.2571, calcd. for $C_{23}H_{40}S_2$ $[M]^+$, found: 381.2576; **IR** (neat, cm^{-1}): 2964*w*, 2873*w*, 1502*s*, 1485*s*, 1451*m*, 1371*s*, 1354*m*, 1228*w*, 1176*m*, 1154*m*, 1011*m*, 982*w*, 942*w*, 800*s*, 742*s*, 685*s*, 520*s*.



1-(2-Methyl-4-phenylbutan-2-yl)-2-(*p*-tolyl)disulfane (4am): The title compound prepared according to the general procedure (**GP3-2**) with **PC 1** (6.6 mg, 6.0 μmol, 3 mol%), 2-((2-methyl-4-phenylbutan-2-yl)oxy)-2-oxo-acetic acid **2a** (94.5 mg, 0.400 mmol, 2.0 equiv), Cs_2CO_3 (195.5 mg, 0.6000 mmol, 3.0 equiv) and 1,4-di-*p*-tolyltetrasulfane **3q** (62.1 mg, 0.200 mmol, 1.0 equiv) in DCE (2 mL) at room temperature for 24 h. Purification via silica gel chromatography (PE:DCM = 20:1) gave the desired unsymmetric disulfide product **4am** as a light yellow oil in 36% yield (21.8 mg). **TLC** $\mathbf{R_f}$ = 0.6 (PE:DCM = 10:1); ^{1}**H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.60 (d, *J* = 8.2 Hz, 2H), 7.34 (t, *J* = 7.3 Hz, 2H), 7.28 – 7.25 (m, 1H), 7.22 (d, *J* = 8.0 Hz, 2H), 7.08 (d, *J* = 7.1 Hz, 2H), 2.74 – 2.70 (m, 2H), 2.44 (s, 3H), 1.97 – 1.92 (m, 2H), 1.44 (s, 6H); ^{13}**C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 142.2, 136.8, 135.3, 129.7, 128.5, 128.43, 128.36, 125.8, 52.3, 43.4, 31.4, 27.9, 21.1; **HRMS** (EI) *m/z* = 302.1163, calcd. for $C_{18}H_{22}S_2$ $[M]^+$, found: 302.1169; **IR** (neat, cm^{-1}): 2958*w*, 2924*w*, 2855*w*, 1491*s*, 1456*s*, 1382*w*, 1365*w*, 1194*w*, 1114*w*, 1074*w*, 1017*w*, 805*s*, 742*s*, 697*s*.



1-(4-Methoxyphenyl)-2-(2-methyl-4-phenylbutan- 2-yl)disulfane (4an): The title compound prepared according to the general procedure (**GP3-2**) with **PC 1** (6.6 mg, 6.0 μmol, 3 mol%), 2-((2-methyl-4-phenyl-butan-2-yl)oxy)-2-oxoacetic acid **2a** (94.5 mg, 0.400 mmol, 2.0 equiv), Cs_2CO_3 (195.5 mg, 0.6000 mmol, 3.0 equiv) and 1,4-bis(4-methoxyphenyl)tetrasulfane **3r** (68.5 mg, 0.200 mmol, 1.0 equiv) in DCE (2 mL) at room temperature for 24 h. Purification via silica gel chromatography (PE:DCM = 10:1) gave the desired unsymmetric disulfide product **4an** as a light yellow oil in 45% yield (28.7 mg). **TLC** $\mathbf{R_f}$ = 0.2 (PE:DCM = 10:1); ^{1}**H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.59 – 7.55 (m, 2H), 7.30 – 7.26 (m, 2H), 7.22 – 7.19 (m, 1H), 7.03 (d, *J* = 6.9 Hz, 1H), 6.90 – 6.87 (m, 2H), 3.83 (s, 3H), 2.66 – 2.62 (m, 2H), 1.91 – 1.86 (m, 2H), 1.38 (s, 6H); ^{13}**C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 159.3, 142.2, 131.2, 129.6, 128.4, 128.3, 125.8, 114.6, 55.4, 52.2, 43.3, 31.3, 27.9; **HRMS** (EI) *m/z* = 318.1112, calcd. for $C_{18}H_{22}OS_2$ $[M]^+$, found: 318.1108; **IR** (neat, cm^{-1}): 2958*w*, 2924*w*, 1593*m*, 1491*s*, 1456*m*, 1285*m*, 1245*s*, 1171*m*, 1028*m*, 822*s*, 748*m*, 697*s*.



1-(4-Fluorophenyl)-2-(2-methyl-4-phenylbutan-2-yl) disulfane (4ao): The title compound prepared according to the general procedure (**GP3-2**) with **PC 1** (6.6 mg, 6.0 μmol, 3 mol%), 2-((2-methyl-4-phenyl- butan-2-yl)oxy)-2-oxoacetic acid **2a** (94.5 mg, 0.400 mmol, 2.0 equiv), Cs_2CO_3 (195.5 mg, 0.6000 mmol,

3.0 equiv) and 1,4-bis(4-fluorophenyl)tetrasulfane **3s** (63.7 mg, 0.200 mmol, 1.0 equiv) in DCE (2 mL) at room temperature for 24 h. Purification via silica gel chromatography (PE:DCM = 20:1) gave the desired unsymmetric disulfide product **4ao** as a light yellow oil in 31% yield (19.0 mg). **TLC R_f** = 0.5 (PE:DCM = 10:1); **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.60 – 7.55 (m, 2H), 7.29 – 7.26 (m, 2H), 7.21 – 7.18 (m, 1H), 7.04 – 7.00 (m, 4H), 2.67 – 2.62 (m, 2H), 1.90 – 1.85 (m, 2H), 1.35 (s, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 162.1 (*J* = 245.1 Hz), 142.1, 134.0 (*J* = 3.2 Hz), 130.2, (*J* = 8.1 Hz) 128.5, 128.4, 125.9, 116.0 (*J* = 22.0 Hz), 52.6, 43.3, 31.3, 27.9; **HRMS** (EI) *m*/*z* = 306.0912, calcd. for $C_{17}H_{19}FS_2$ $[M]^+$, found: 306.0910; **IR** (neat, cm^{-1}): 2958*w*, 2924*w*, 2861*w*, 1588*m*, 1485*s*, 1451*m*, 1222*s*, 1154*m*, 1119*w*, 1074*w*, 1011*w*, 828*s*, 742*m*, 697*s*, 623*m*.

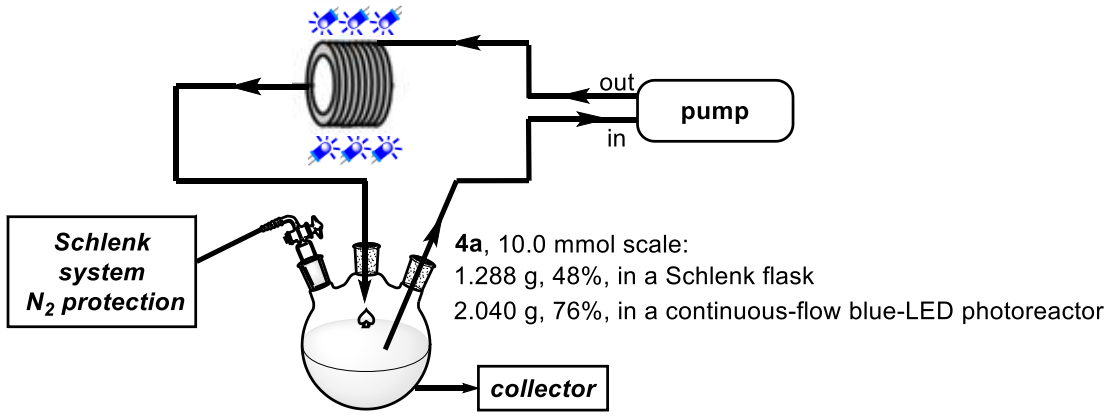
3.4 Gram-scale synthesis of 4a

3.4.1 Schlenk bottle with photoreactor.

A flame-dried 250 mL Schlenk-bottle equipped with a magnetic stir bar was charged with **PC 1** (336.6 mg, 0.3000 mmol, 3.0 mol%), Cs_2CO_3 (9.774 g, 30.00 mmol, 3.0 equiv), sealed with a septum, and degassed by alternating vacuum evacuation and nitrogen backfilling (three times) before DCE (100 mL) was added. 2-((2-methyl-4-phenyl- butan-2-yl)oxy)-2-oxoacetic acid **2a** (4.725 g, 20.00 mmol, 2.0 equiv), 1,4-di-*tert*-butyltetrasulfane **3d** (2.425 g, 10.00 mmol, 1.0 equiv) were added successively. The reaction mixture was irradiated using a 20 W blue LED lamp at room temperature for 48 h. After the reaction was complete, the solvent was removed under reduced pressure with the aid of a rotary evaporator. Purification via silica gel chromatography (PE:DCM = 20:1) gave the unsymmetric disulfide product **4a** as a light yellow oil in 48% yield (1.288 g).

3.4.2 Schematic of the continuous flow platform with photoreactor.

Figure S1 Schematic of the continuous flow platform with photoreactor.

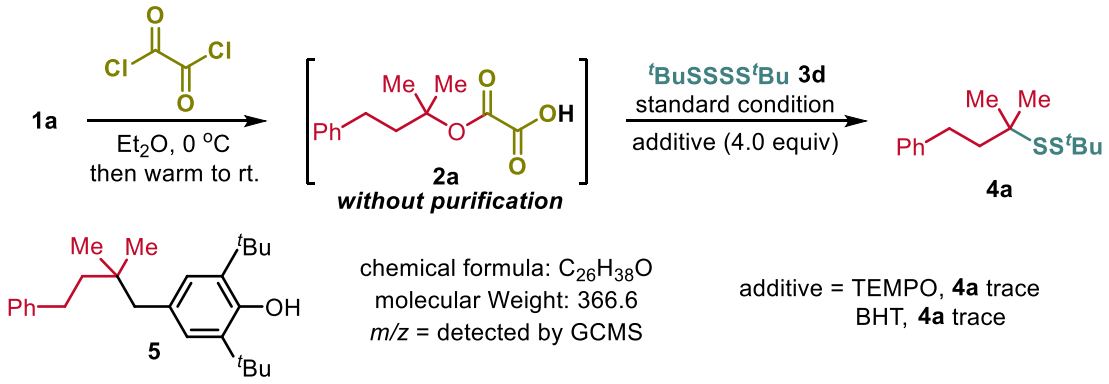


A flame-dried 250 mL three-necked glass bottle equipped with a magnetic stir bar

was charged with **PC 1** (336.6 mg, 0.3000 mmol, 3.0 mol%), Cs_2CO_3 (9.774 g, 30.00 mmol, 3.0 equiv) sealed with septums and degassed by alternating vacuum evacuation and nitrogen backfilling (three times) before DCE (100 mL) was added. 2-((2-methyl-4-phenyl- butan-2-yl)oxy)-2-oxoacetic acid **2a** (4.725 g, 20.00 mmol, 2.0 equiv), 1,4-di-*tert*-butyltetrasulfane **3d** (2.425 g, 10.00 mmol, 1.0 equiv) were added successively. The reaction mixture was circulated by the continuous flow platform with photoreactor and irradiated using a 20 W blue LED lamp at room temperature for 48 h. After the reaction was complete, the solvent was removed under reduced pressure with the aid of a rotary evaporator. Purification via silica gel chromatography (PE:DCM = 20:1) gave the unsymmetric disulfide product **4a** as a light yellow oil in 76% yield (2.040 g).

4. Mechanistic study.

4.1 Radical trapping experiment.



A flame-dried Schlenk-tube equipped with a magnetic stir bar was charged with **PC 1** (6.6 mg, 6.0 μmol, 3 mol%), Cs_2CO_3 (195.5 mg, 0.6000 mmol, 3.0 equiv), radical scavenger (for TEMPO 125.0 mg, 0.8000 mmol, 4.0 equiv; for BHT 176.3 mg, 0.8000 mmol, 4.0 equiv), sealed with a septum, and degassed by alternating vacuum evacuation and nitrogen backfilling (three times) before DCE (2 mL) was added. Then 2-((2-methyl-4-phenylbutan-2-yl)oxy)-2-oxoacetic acid **2a** (94.5 mg, 0.400 mmol, 2.0 equiv), 1,4-di-*tert*-butyltetrasulfane **3d** (48.5 mg, 0.200 mmol, 1.0 equiv), and *n*-dodecane (34.1 mg, 0.200 mmol, 1.0 equiv) were added successively by micro-syringe. The reaction mixture was then stirred and irradiated using a 20 W blue LED lamp at room temperature for 24 h. After the reaction was complete, the solvent was removed under reduced pressure with the aid of a rotary evaporator. unsymmetric disulfide product **4a** and radical adducts **5** were detected based on GC-MS, GC, TLC, and analysis of crude residue.

4.2 Light on/off experiment

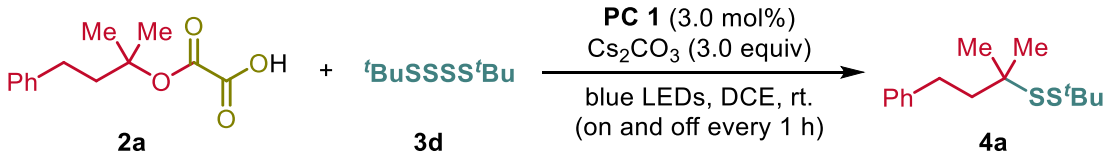
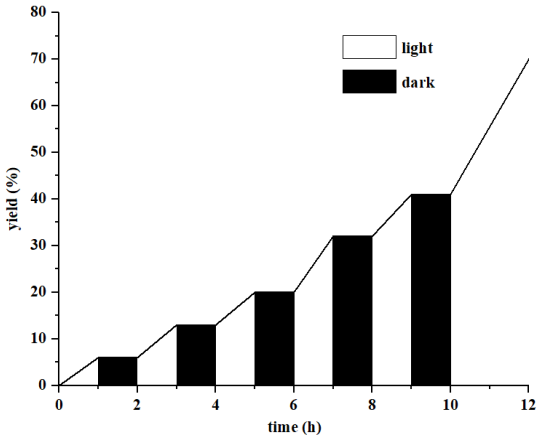


Figure S2. The yield of 4a in on-off-control experiment.



A flame-dried Schlenk-tube equipped with a magnetic stir bar was charged with **PC 1** (6.6 mg, 6.0 μmol, 3 mol%), Cs_2CO_3 (195.5 mg, 0.6000 mmol, 3.0 equiv), sealed with a septum, and degassed by alternating vacuum evacuation and nitrogen backfilling (three times) before DCE (2 mL) was added. Then 2-((2-methyl-4-phenylbutan-2-yl)oxy)-2-oxoacetic acid **2a** (94.5 mg, 0.400 mmol, 2.0 equiv), 1,4-di-*tert*-butyltetrasulfane **3d** (48.5 mg, 0.200 mmol, 1.0 equiv), and *n*-dodecane (34.1 mg, 0.200 mmol, 1.0 equiv) were added successively by micro-syringe. The reaction mixture was then stirred and irradiated using a 20 W blue LED lamp at room temperature. As the reaction proceeded, the light was turned on and off every 1 h. During each on/off shift, reaction mixture (100 μL) was taken out by a micro-syringe. The yield of **4a** was calculated based on GC analysis using *n*-dodecane as an internal standard.

4.3 Quantum yield measurement

Determination of the photon flux

The photon flux of the LED setup was determined by using standard ferrioxalate actinometry[7] following a modified literature procedure.[8]

Preparation of 0.05 M H_2SO_4 aqueous solution:

In a 1 L volumetric flask, of conc. H_2SO_4 (98% w/w, 18.4 M, 2.72 mL, 50.0 mmol) was added to 400 mL of deionized water. Then, deionized water was added to dilute the resulting solution until the level reached 1 L graduation mark.

Preparation of 0.006 M ferrioxalate solution:

In a dark room, $K_3[FeC_2O_4]_3{\cdot}3H_2O$ (737 mg, 1.95 mmol) was added to a 250 mL

volumetric flask. Then, the prepared H_2SO_4 (0.05 M aq.) was added to volumetric flask until the level reached 250 mL graduation mark. The mixture was shaken and mixed well. The resulting solution was sealed and stored in the dark before used.

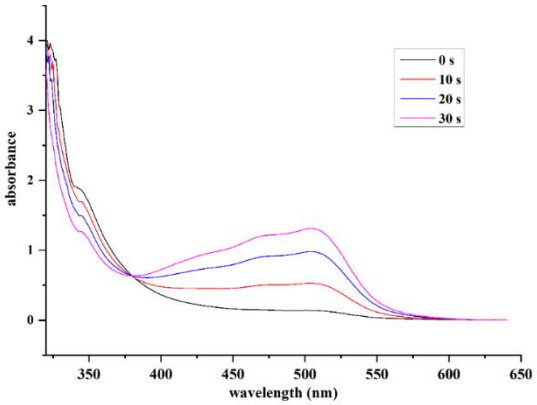
Preparation of Buffer solution:

To a 100 mL volumetric flask was added NaOAc (7.30 g, 89.0 mmol) and 50 mL deionized water. To the resulting solution, conc. H_2SO_4 (98% w/w, 18.4 M, 0.967 mL, 17.8 mmol) was added dropwise. Deionized water was added subsequently until the level reached 100 mL graduation mark. The mixture was evenly spread out and thoroughly mixed in solution by using ultrasonic for 5 min.

Measurements of photo flux:

While being careful to minimize exposure to background light, the ferrioxalate solution (0.006 M, 4.0 mL) was added to a 10 mL Schlenk tube. The Schlenk tube was positioned 5 cm from a 20 W blue LED lamp at room temperature and irradiated for 10 sec. After 10 sec. of irradiation, the solution (0.50 mL) was immediately transferred to a foil-covered 10 mL volumetric flask containing 1,10-phenanthroline (10 mg, 0.050 mmol) and the buffer solution (0.50 mL). Deionized water was then added to the flask to make a total volume of 10 mL. The mixture in the flask was shaken and mixed well. The resulting solution was stored in the dark for approximately 1 h. Then the solution (1.0 mL) was transferred to a quartz cuvette (1.0 cm path length) and the corresponding UV/Vis spectra (510 nm) were measured and recorded on JASCO V-650 spectrophotometer (Figure S3). The absorbances (510 nm) of the samples irradiated for 0 s, 20 s and 30 s were also measured according to the similar procedure.

Figure S3. Actinometry: **UV/Vis spectra of ferrioxalate and 1,10-phenanthroline solutions.**

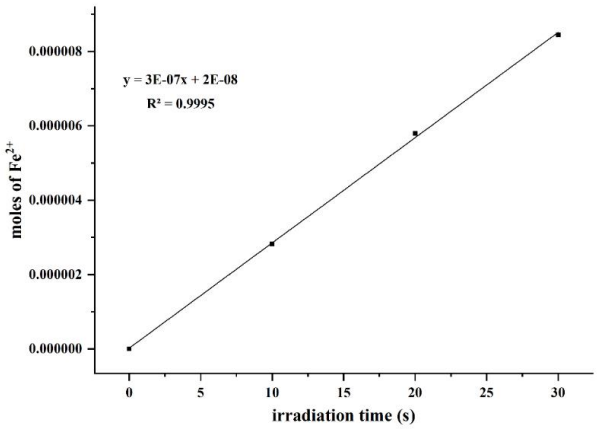


The moles of ferrous ions formed in the irradiated volume are given by moles.

$$\text{moles } Fe^{2+} = V_1 \cdot V_3 \cdot \Delta A\,(510\text{ nm}) / V_2 \cdot l \cdot \varepsilon\,(510\text{ nm})$$

V_1 is the irradiated volume (4 mL), V_2 is the aliquot of the irradiated solution taken for the determination of the ferrous ions (0.5 mL), V_3 is the final volume after complexation with phenanthroline (10 mL), *l* is the optical pathlength of the irradiation cell (1.0 cm), ΔA (510 nm) is the difference in absorbance at λ = 510 nm between the irradiated and non-irradiated ferrioxalate and 1,10-phenanthroline solutions, and ε (510 nm) is the molar absorptivity of the $Fe(phen)_3^{2+}$ complex at λ = 510 nm (11100 $L \cdot mol^{-1} \cdot cm^{-1}$). The moles of Fe^{2+} were plotted as a function of time (Figure S4).

Figure S4. Actinometry: **Moles of Fe^{2+} formed vs. irradiation time.**



The photon flux was then calculated according to the following equation:

$$\text{photo flux} = \text{moles } Fe^{2+} / \Phi \cdot t \cdot f$$

Φ is the quantum yield of the ferrioxalate actinometer (approximated as 1.11, reported for a 0.006 M solution at λ = 436 nm).[8] *t* is the irradiation time *f* is the fraction of light absorbed at 455nm (0.3821).

The fraction of light absorbed was determined according to the following equation:

$$f = 1 - 10^{-A}$$

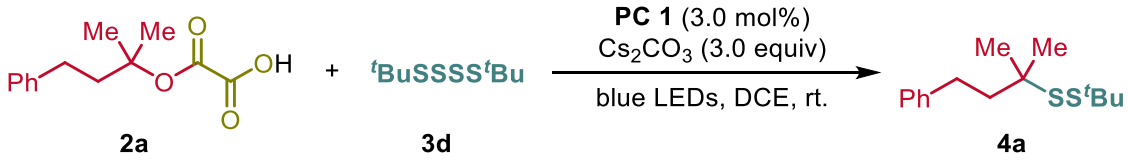
A is the measured absorbance (0.2091, 440 nm) of the 0.006 M solution of $K_3[FeC_2O_4]_3 \cdot 3H_2O$.

Table S6. Calculation of radiant flux.

irradiation time (s)	absorbance (A)	ΔA	moles Fe^{2+} (mol)	radiant flux (Einstein/s)
non-irradiation	0.138	-	-	-
10	0.53	0.392	2.8252×10^{-6}	6.666×10^{-7}
20	0.981	0.804	5.7946×10^{-6}	6.851×10^{-7}
30	1.311	1.172	8.4468×10^{-6}	6.639×10^{-7}

The average radiant flux is 6.72×10^{-7} Einstein/s.

4.4 Determination of the quantum yield



A flame-dried Schlenk-tube equipped with a magnetic stir bar was charged with **PC 1** (6.6 mg, 6.0 μmol, 3 mol%), Cs_2CO_3 (195.5 mg, 0.6000 mmol, 3.0 equiv), sealed with a septum, and degassed by alternating vacuum evacuation and nitrogen backfilling (three times) before DCE (2 mL) was added. Then 2-((2-methyl-4-phenylbutan-2-yl)oxy)-2-oxoacetic acid **2a** (94.5 mg, 0.400 mmol, 2.0 equiv), 1,4-di-*tert*-butyltetrasulfane **3d** (48.5 mg, 0.200 mmol, 1.0 equiv), and *n*-dodecane (34.1 mg, 0.200 mmol, 1.0 equiv) were added successively by micro-syringe. The reaction mixture was then stirred and irradiated using a 20 W blue LED lamp at room temperature for 24 h. Periodic aliquots (every 1h, 100 μL) were removed by a syringe and directly analyzed by GC using *n*-dodecane as the internal standard. The quantum yield (Φ) was then calculated according to the following equation:

$$\Phi = \text{moles of product} / (\text{photo flux} \cdot t \cdot f)$$

The photon flux of the blue LEDs photoreactor device was determined by using standard ferrioxalate actinometry according to the following a modified literature procedure. [7] The average radiant flux was reported as 6.72×10^{-7} Einstein/s, where t is the time, and f is the fraction of light absorbed by **PC 1** at 455 nm. A solution of **PC 1** in DCE (4.0×10^{-4} M) was prepared, and the absorbance of the solution at 455 nm was 1.0236. The fraction of light absorbed at 455 nm was calculated according to the following equation:

$$f = 1 - 10^{-A} = 0.9053$$

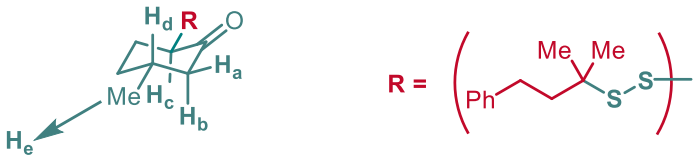
Table S7. Calculation of quantum yield.

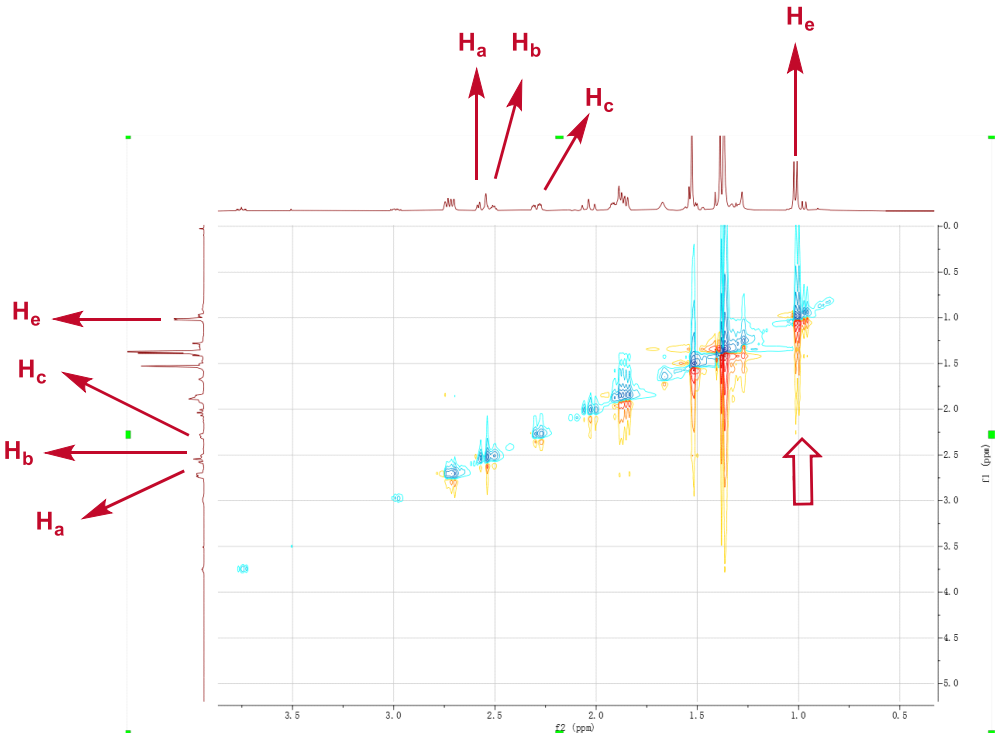
	reaction time (s)	yield (%)	moles of product (mol)	quantum yield (Φ)
1	3600	6%	1.20×10^{-5}	0.0055
2	7200	14%	2.80×10^{-5}	0.0064
3	10800	21%	4.20×10^{-5}	0.0064
4	14400	30%	6.00×10^{-5}	0.0068
5	18000	43%	8.60×10^{-5}	0.0079

The average quantum yield Φ is 0.0066.

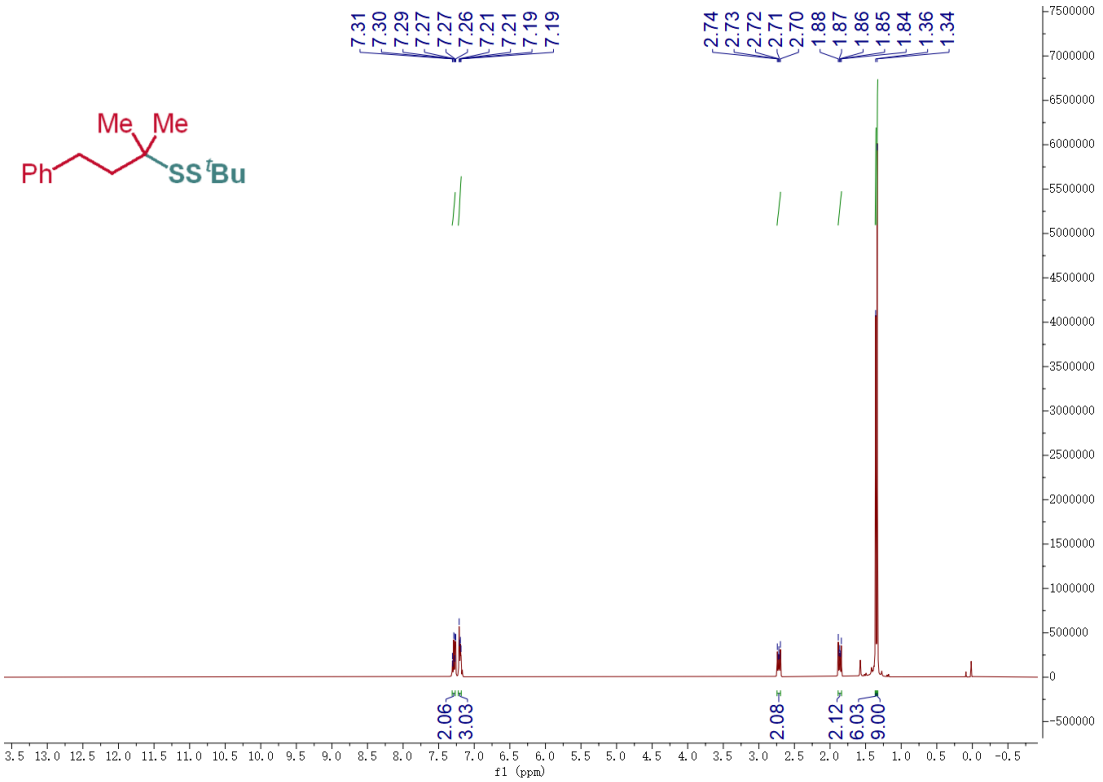
5. Spectra of disulfide product 4

NOESY Spectrum of 4ad

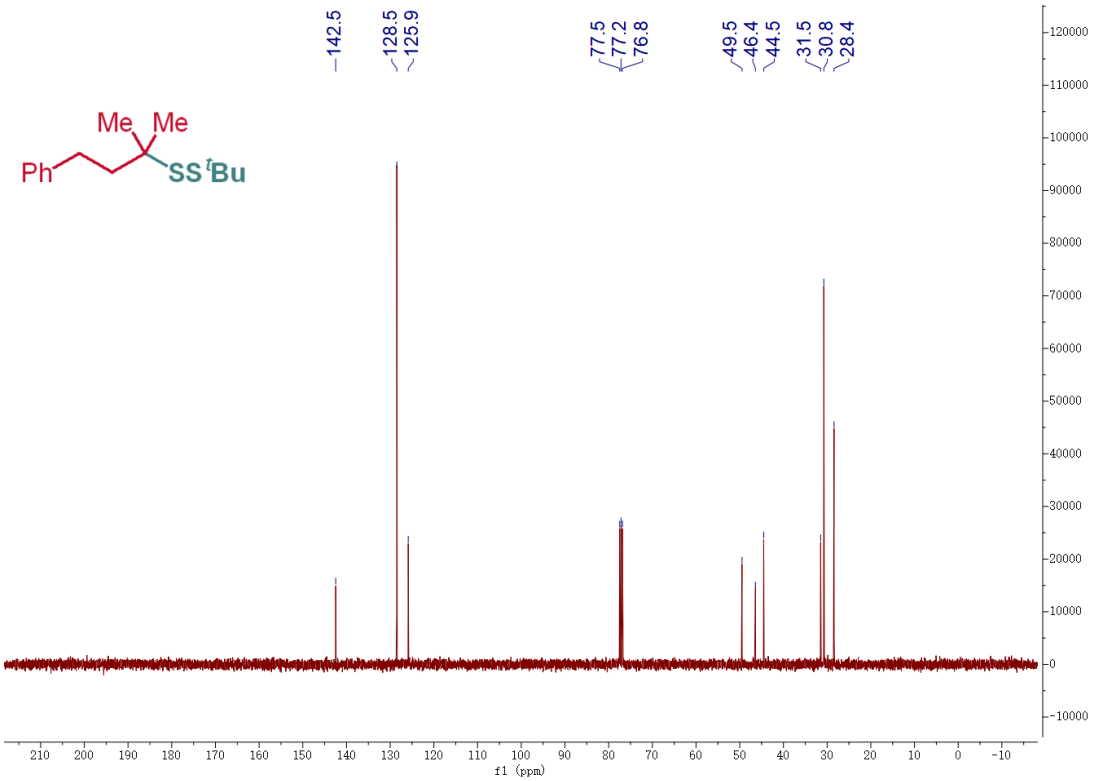




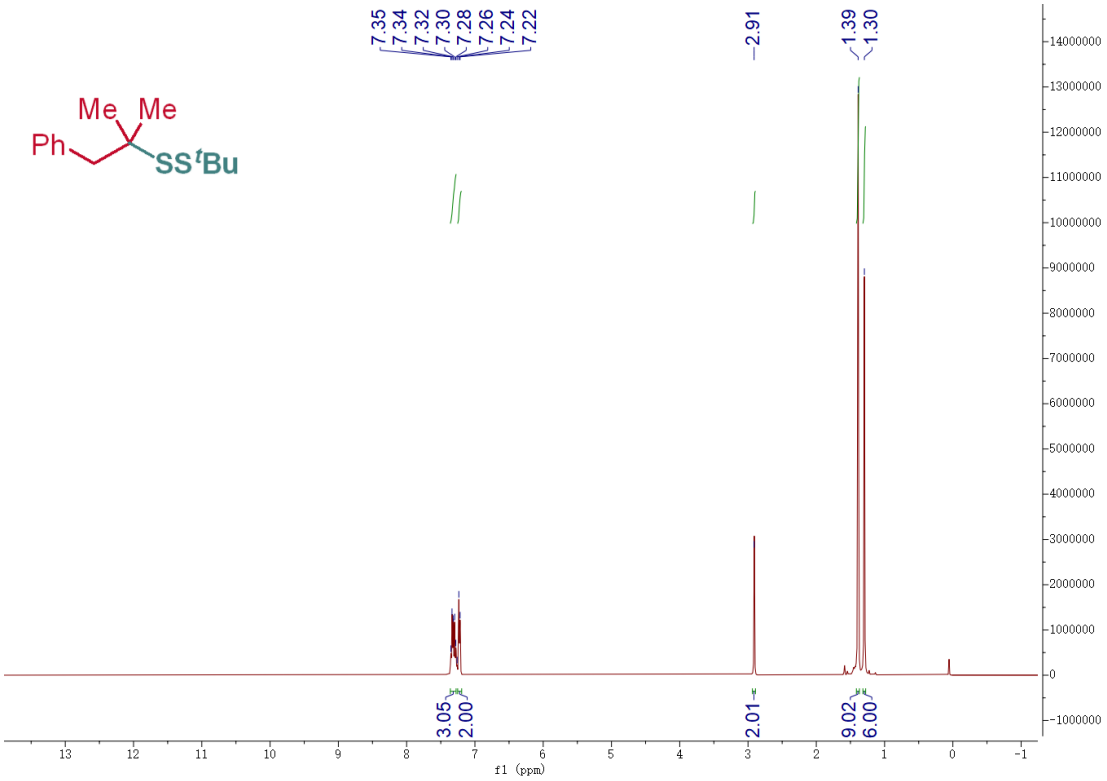
^{1}H NMR Spectrum of (3-(*tert*-Butylsulfinothioyl)-3-methylbutyl)benzene 4a and 4s



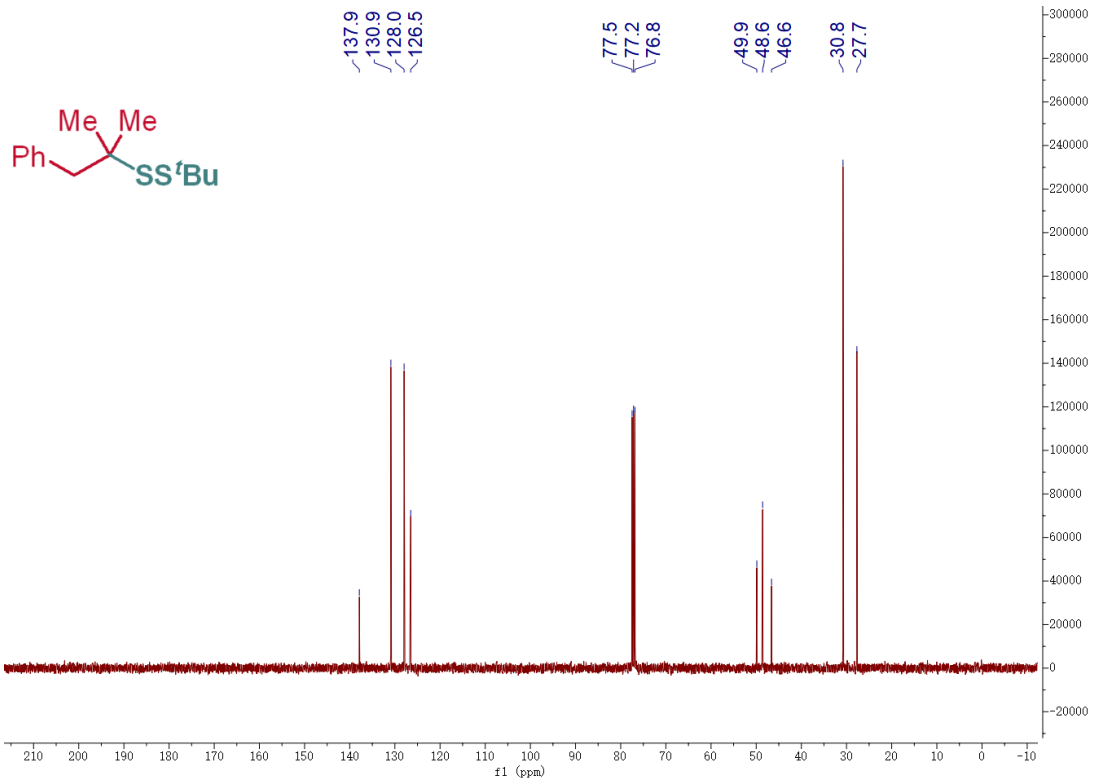
^{13}C NMR Spectrum of (3-(*tert*-Butylsulfinothioyl)-3-methylbutyl)benzene 4a and 4s



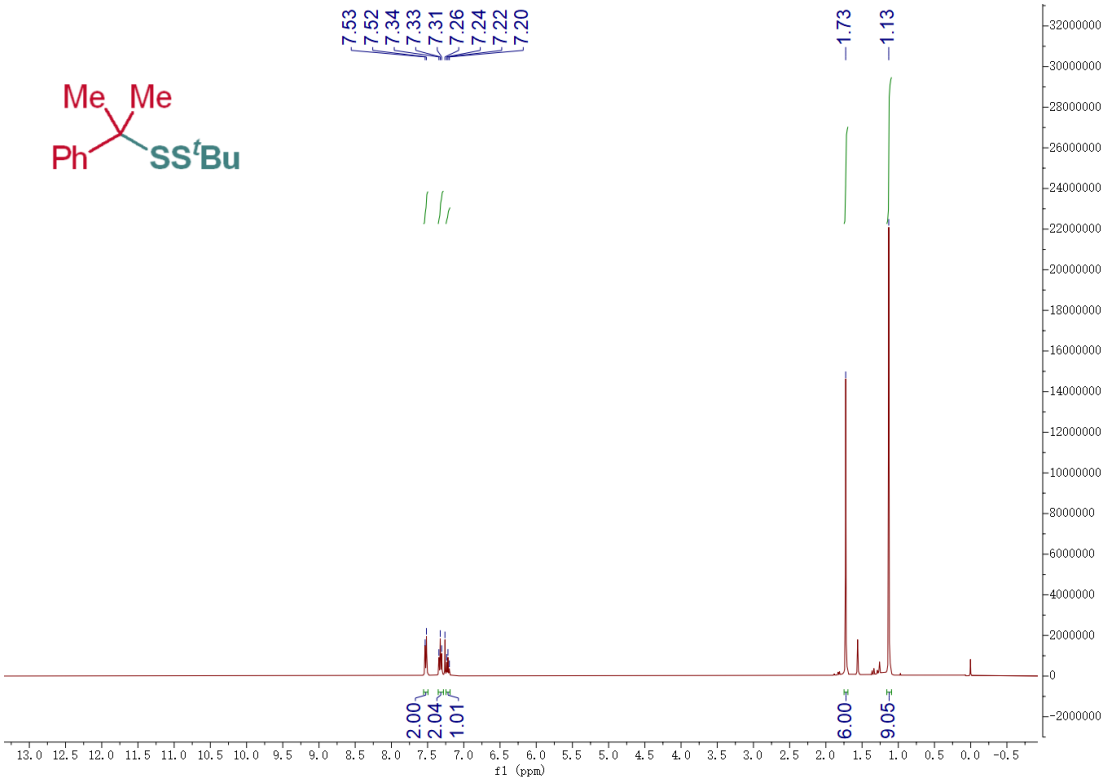
^{1}H NMR Spectrum of (2-(tert-Butylsulfinothioyl)-2-methylpropyl)benzene 4b



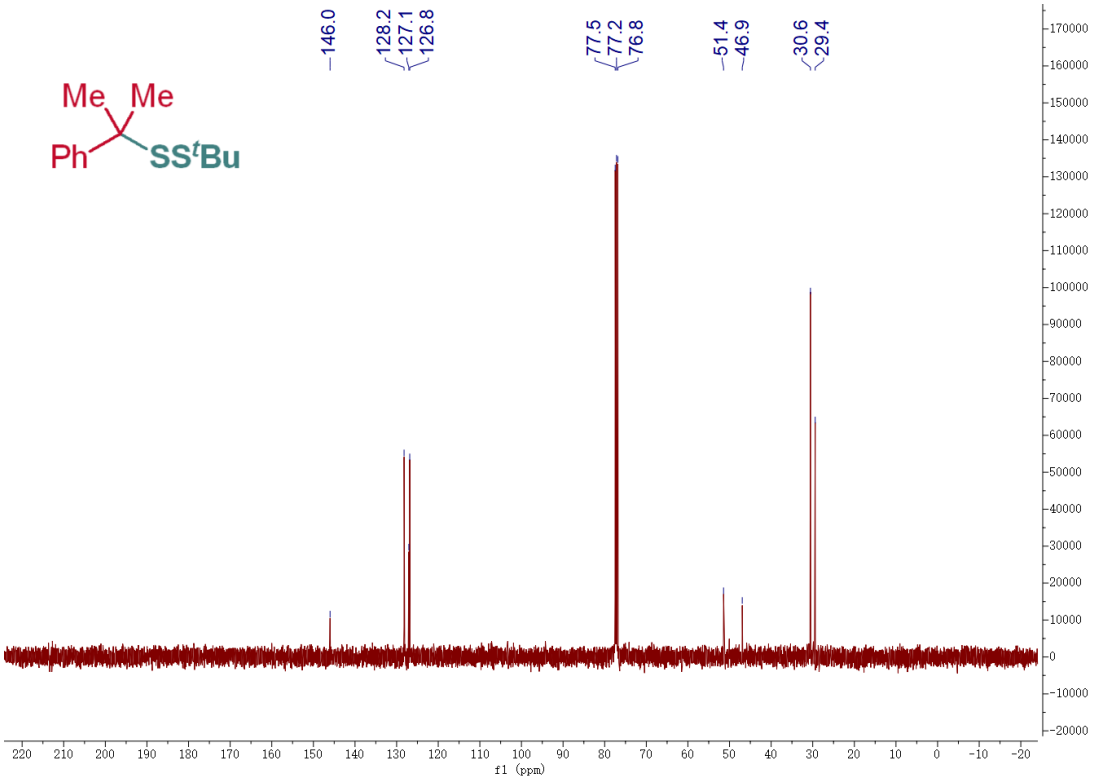
^{13}C NMR Spectrum of (2-(*tert*-Butylsulfinothioyl)-2-methylpropyl)benzene 4b



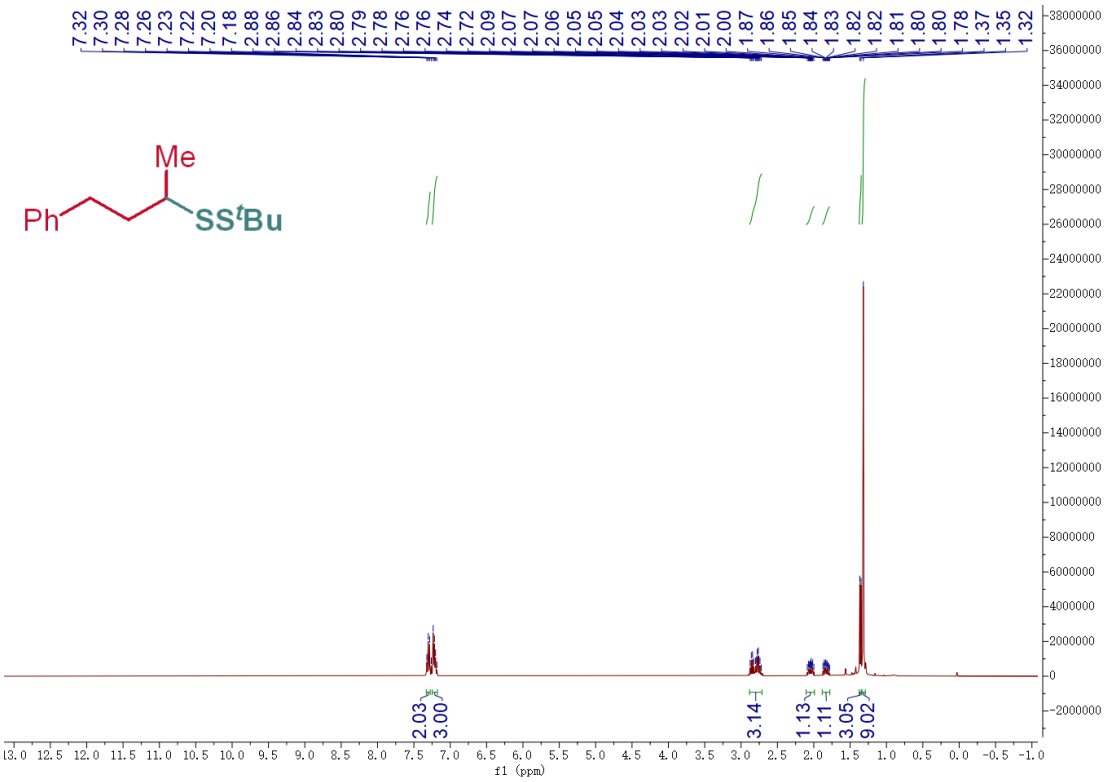
^{1}H NMR Spectrum of (2-(*tert*-Butylsulfinothioyl)propan-2-yl)benzene 4c



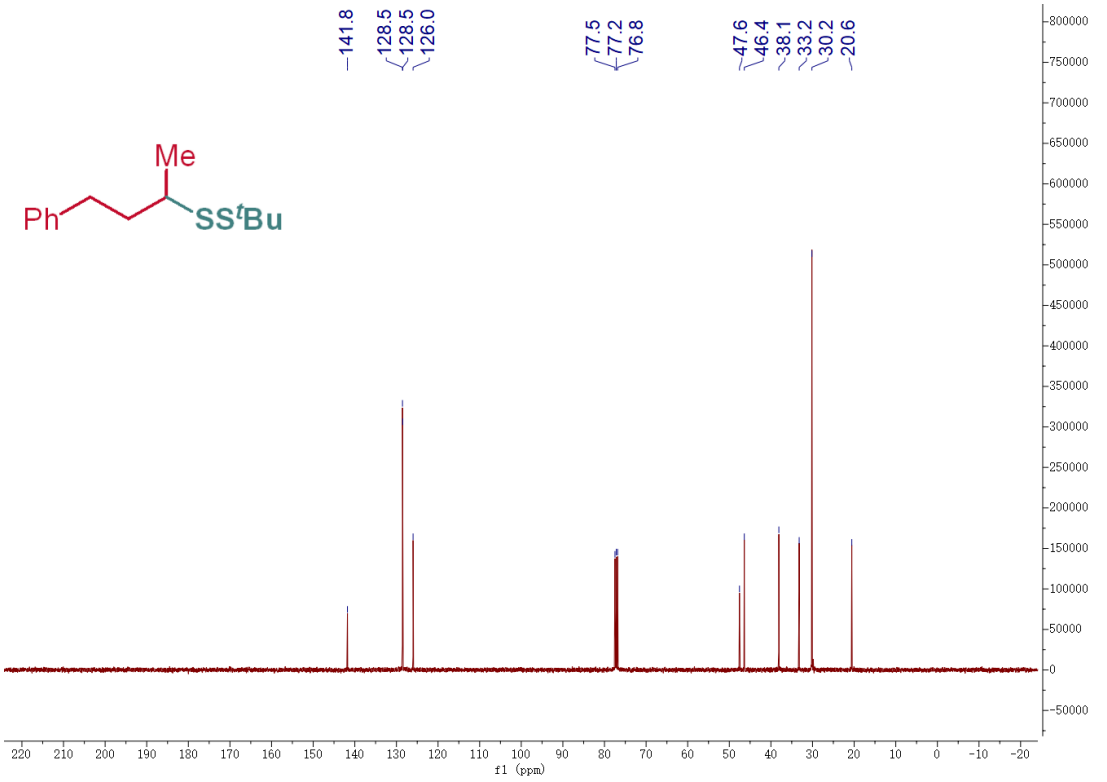
^{13}C NMR Spectrum of (2-(*tert*-Butylsulfinothioyl)propan-2-yl)benzene 4c



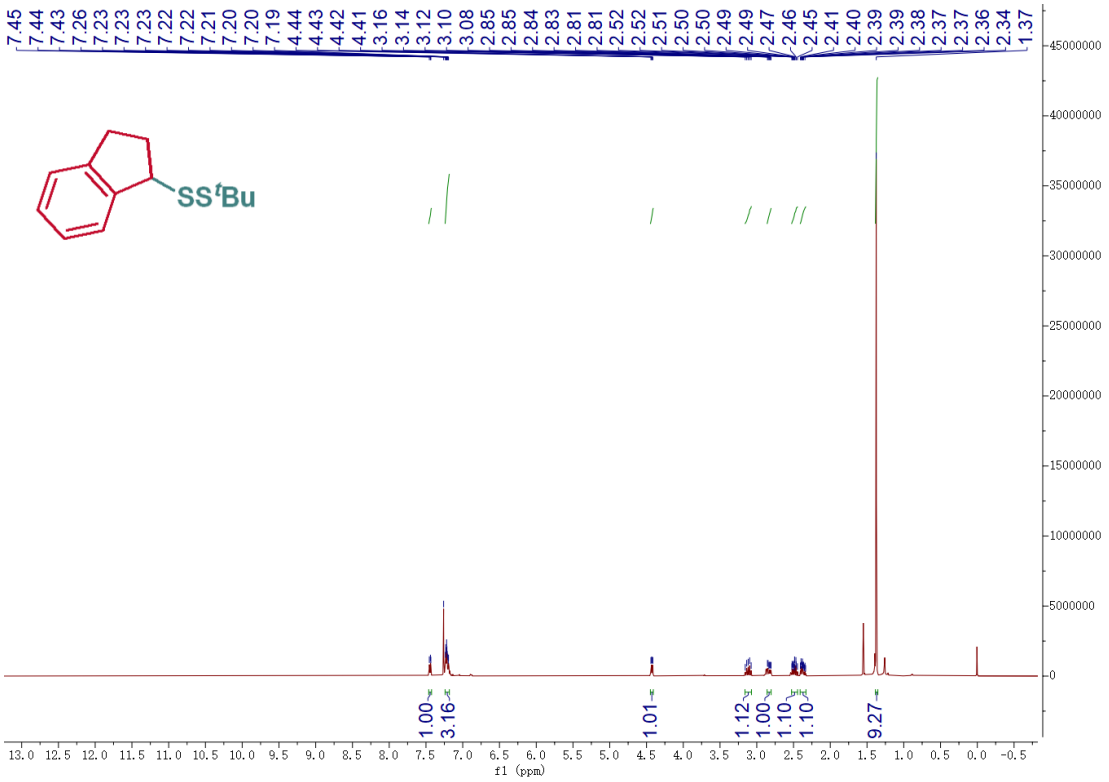
^{1}H NMR Spectrum of (3-(*tert*-Butylsulfinothioyl)butyl)benzene 4d



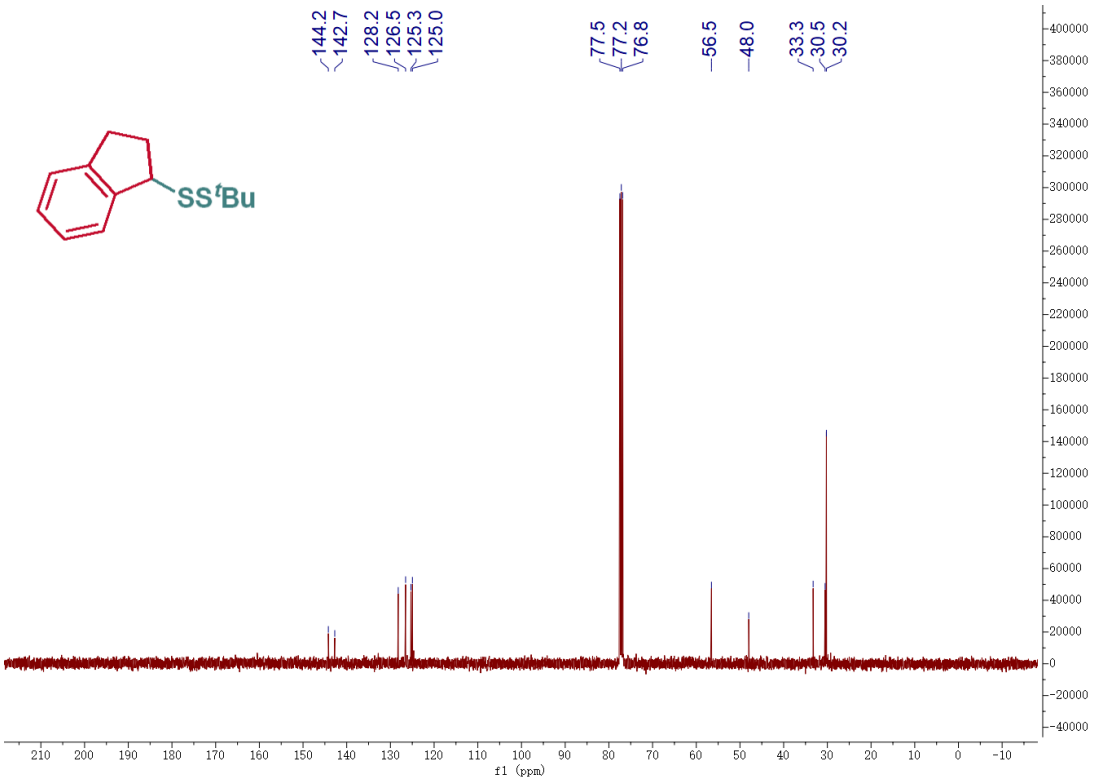
^{13}C NMR Spectrum of (3-(*tert*-Butylsulfinothioyl)butyl)benzene 4d



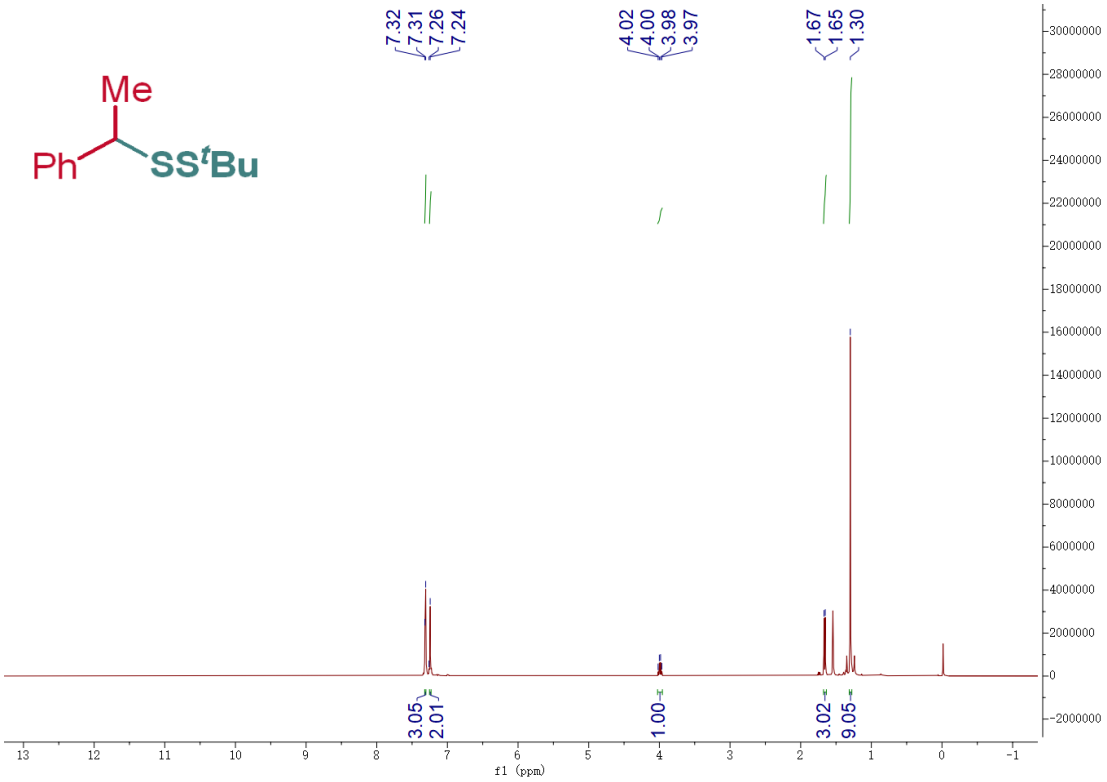
^{1}H NMR Spectrum of 1-(*tert*-Butylsulfinothioyl)-2,3-dihydro-1*H*-indene 4e



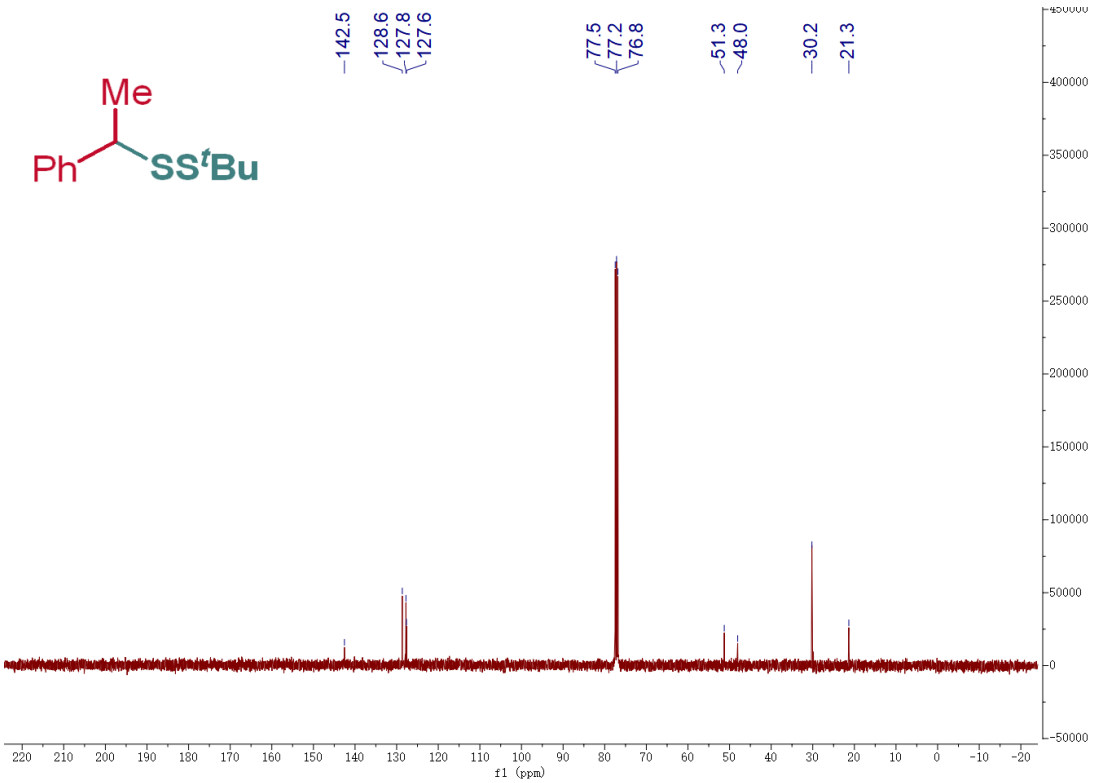
^{13}C NMR Spectrum of 1-(*tert*-Butylsulfinothioyl)-2,3-dihydro-1*H*-indene 4e



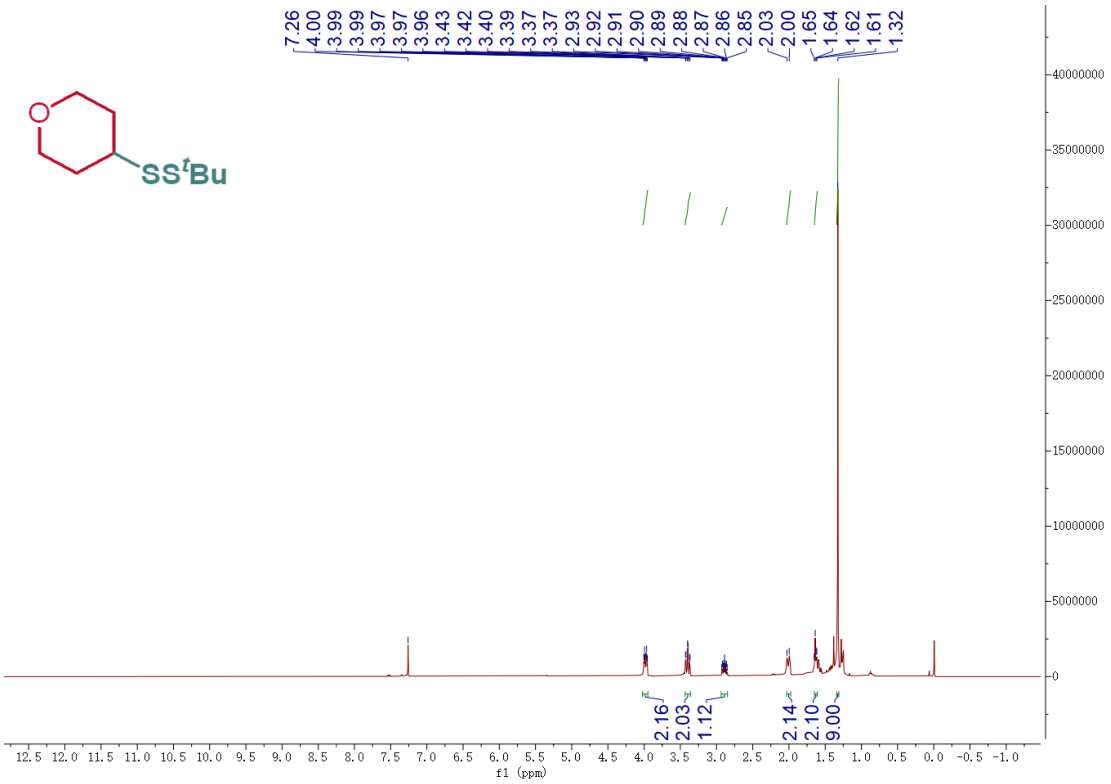
^{1}H NMR Spectrum of (1-(*tert*-Butylsulfinothioyl)ethyl)benzene 4f



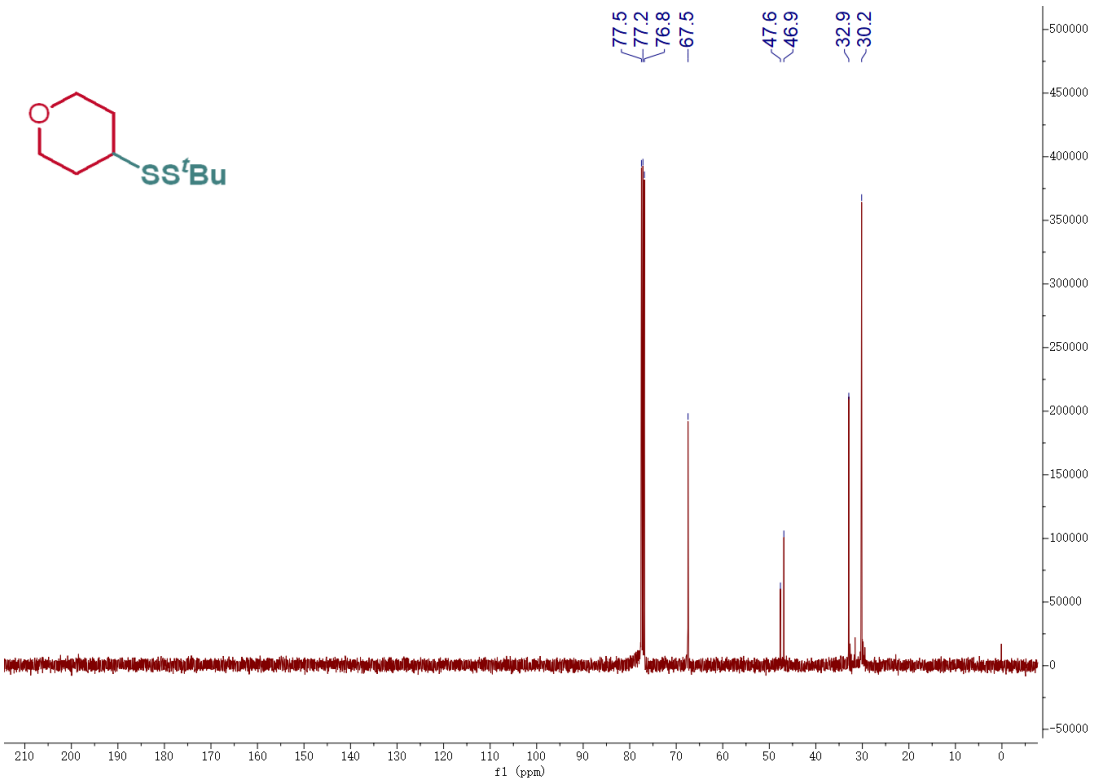
^{13}C NMR Spectrum of (1-(*tert*-Butylsulfinothioyl)ethyl)benzene 4f



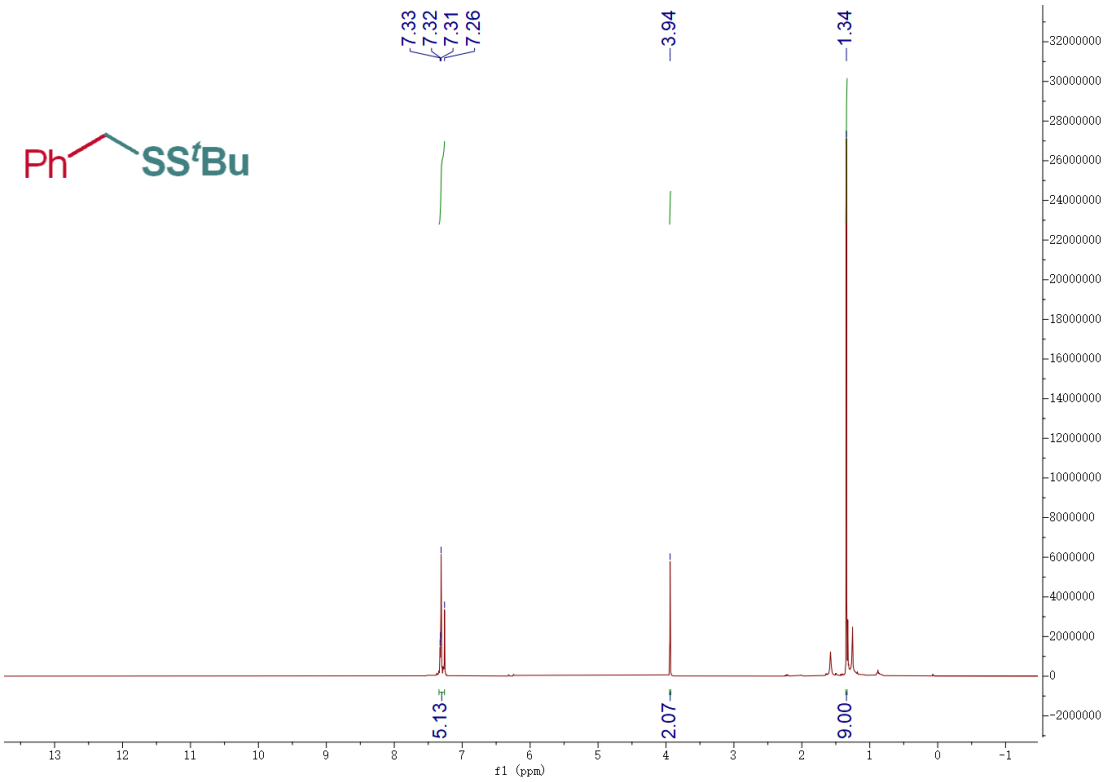
^{1}H NMR Spectrum of 4-(*tert*-Butyldisulfanyl)tetrahydro-2*H*-pyran 4g



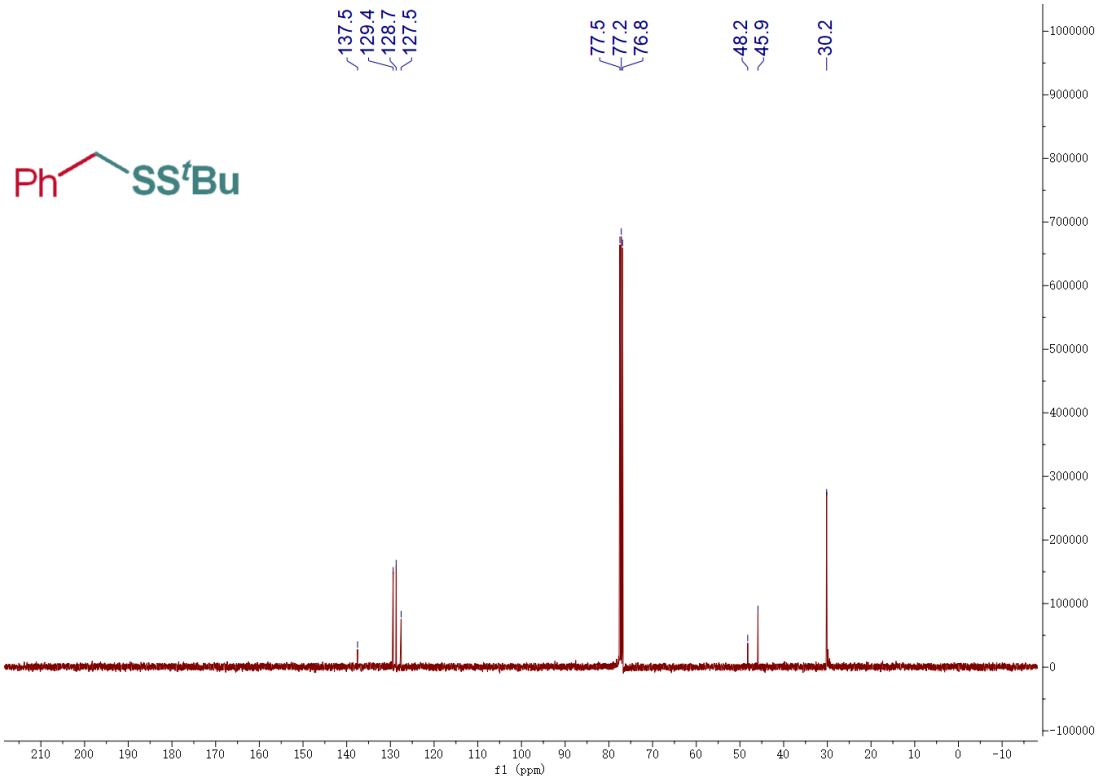
^{13}C NMR Spectrum of 4-(*tert*-Butyldisulfanyl)tetrahydro-2*H*-pyran 4g



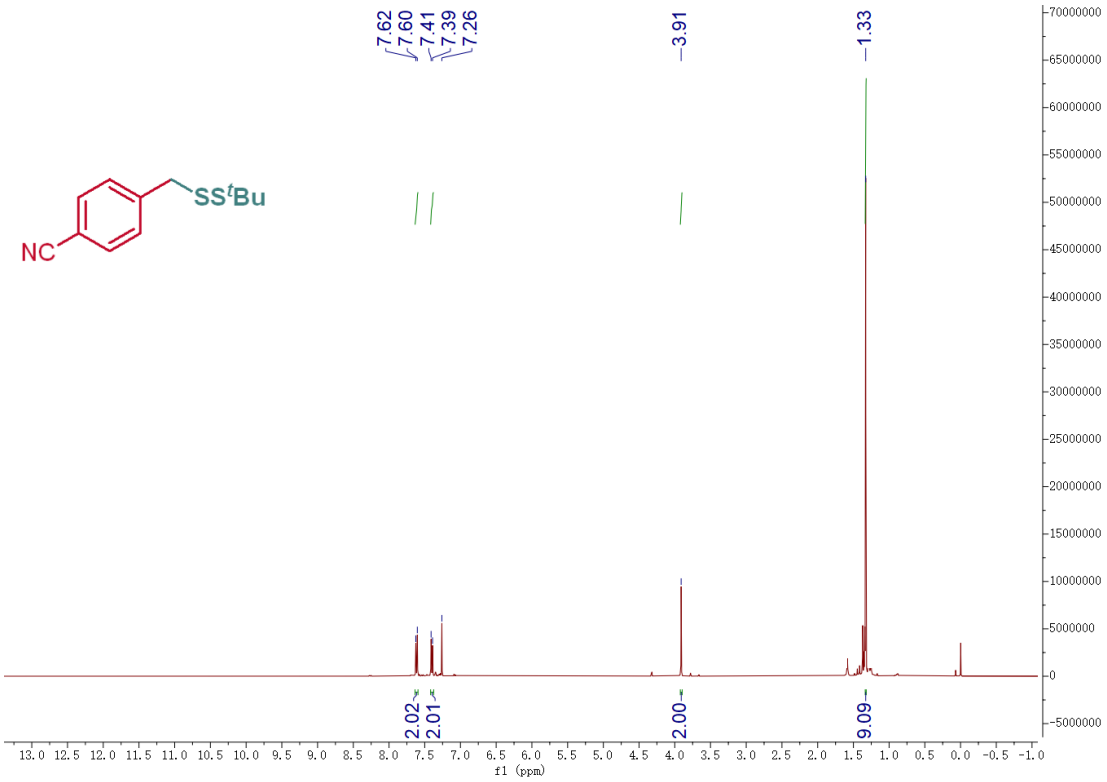
^{1}H NMR Spectrum of ((*tert*-Butylsulfinothioyl)methyl)benzene 4h



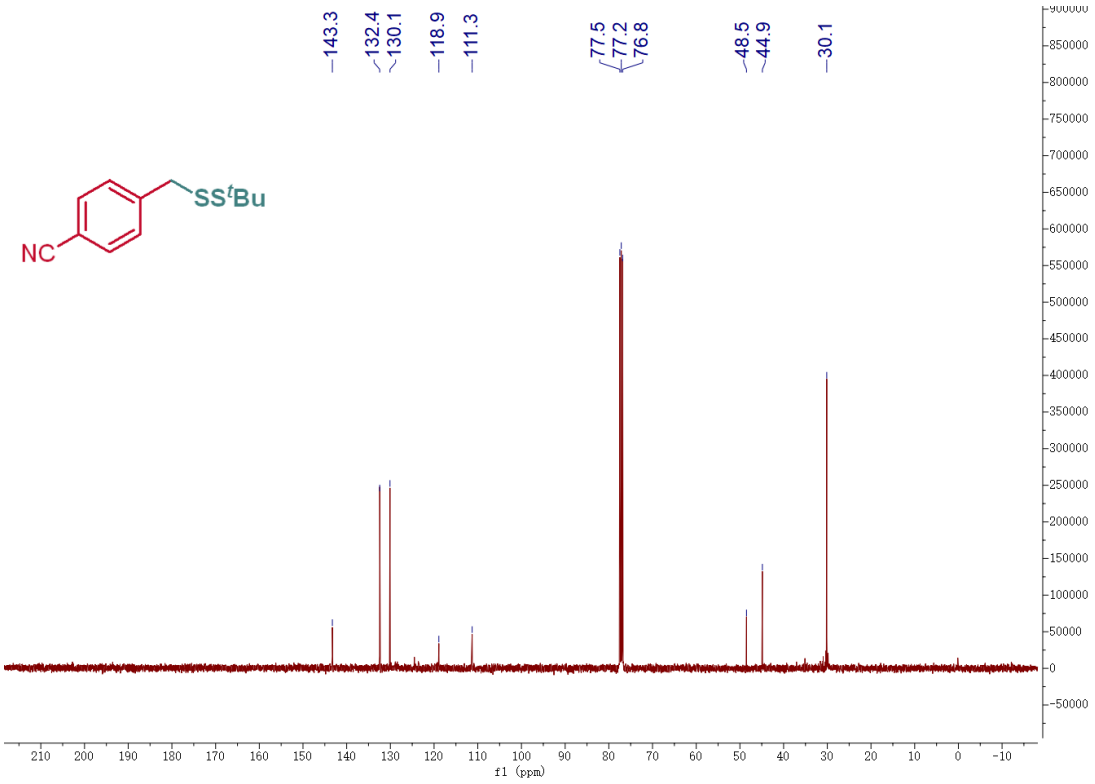
^{13}C NMR Spectrum of ((*tert*-Butylsulfinothioyl)methyl)benzene 4h



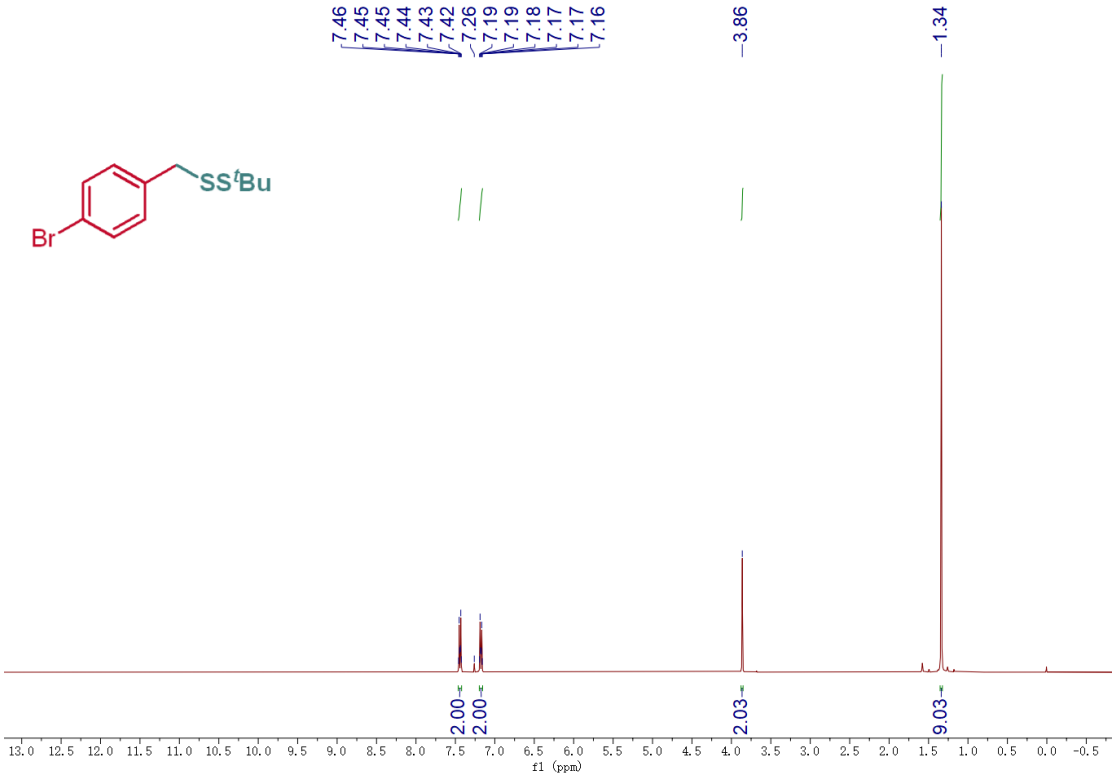
^{1}H NMR Spectrum of 4-((*tert*-Butylsulfinothioyl)methyl)benzonitrile 4i



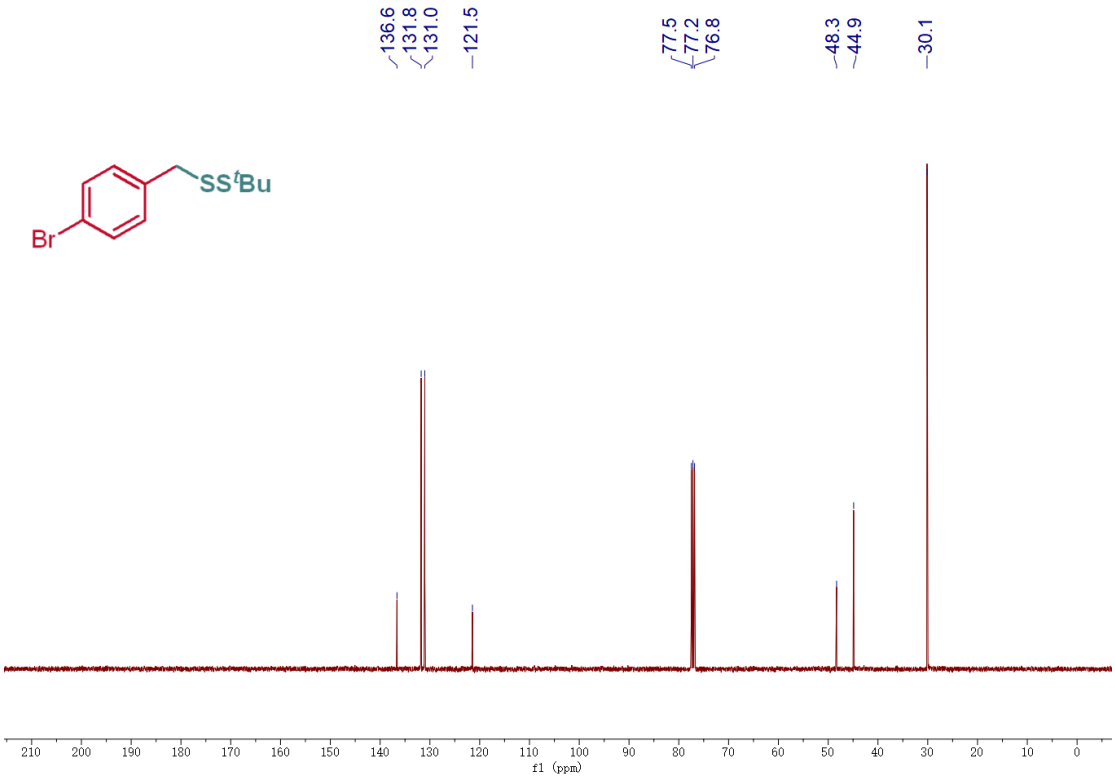
^{13}C NMR Spectrum of 4-((*tert*-Butylsulfinothioyl)methyl)benzonitrile 4i



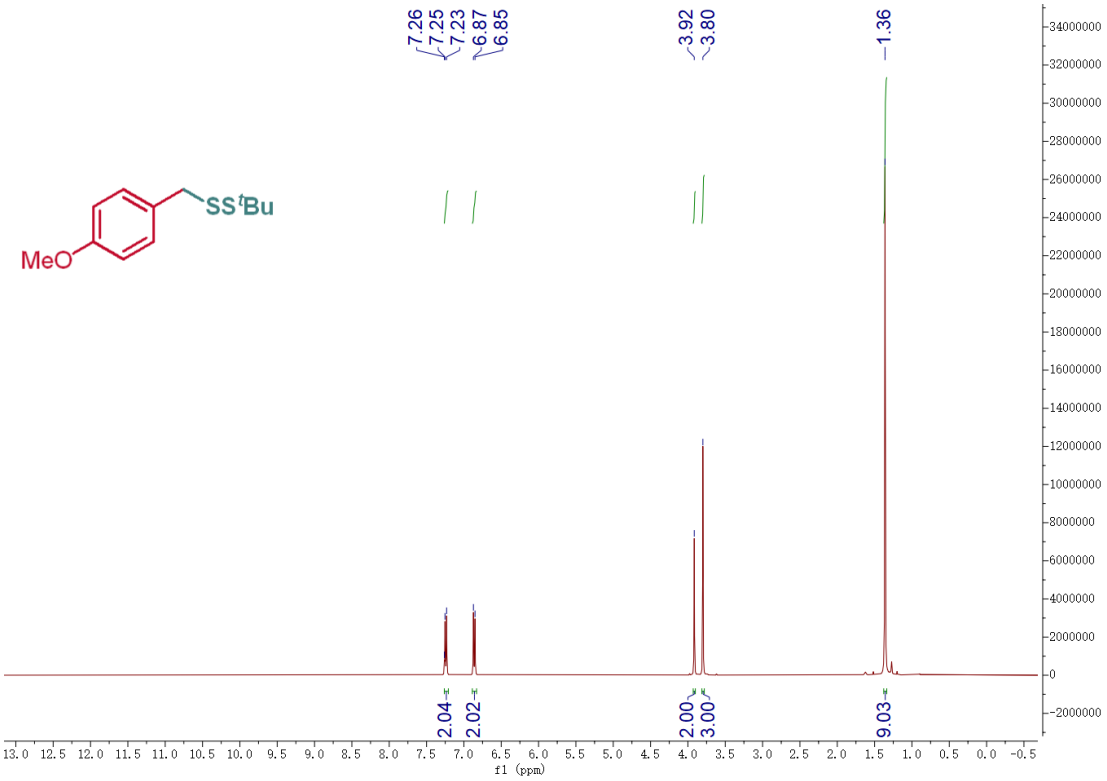
^{1}H NMR Spectrum of 1-Bromo-4-((*tert*-butylsulfinothioyl)methyl)benzene 4j



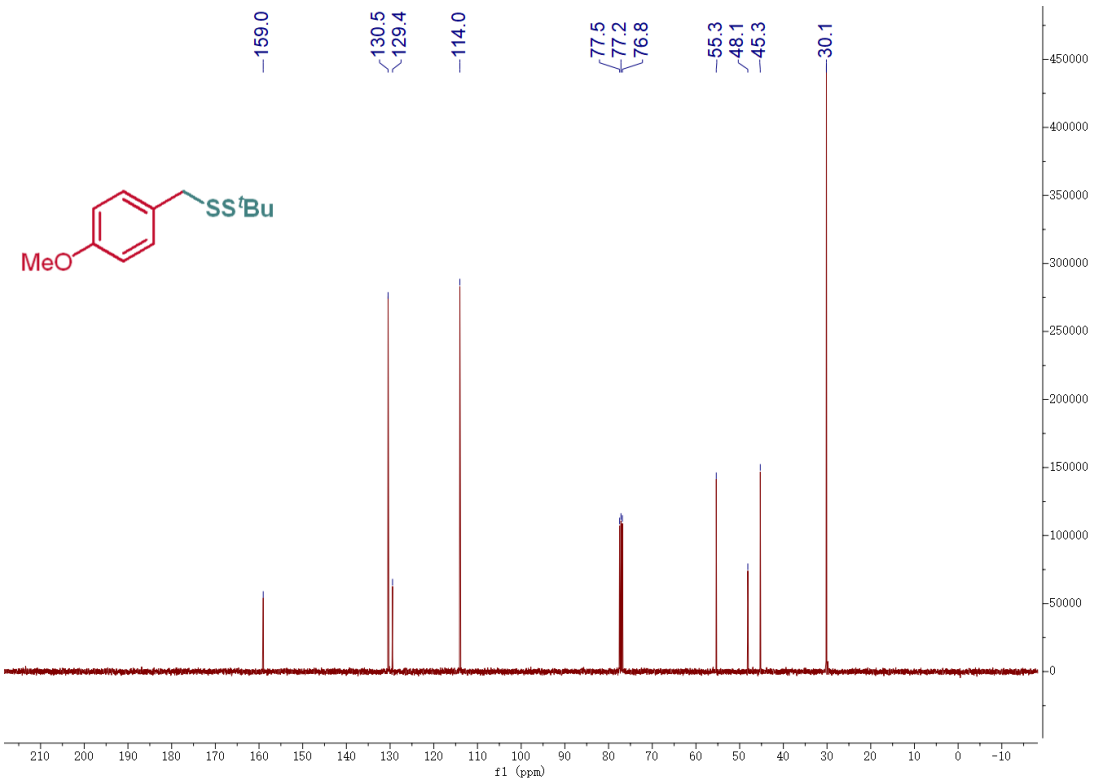
^{13}C NMR Spectrum of 1-Bromo-4-((*tert*-butylsulfinothioyl)methyl)benzene 4j



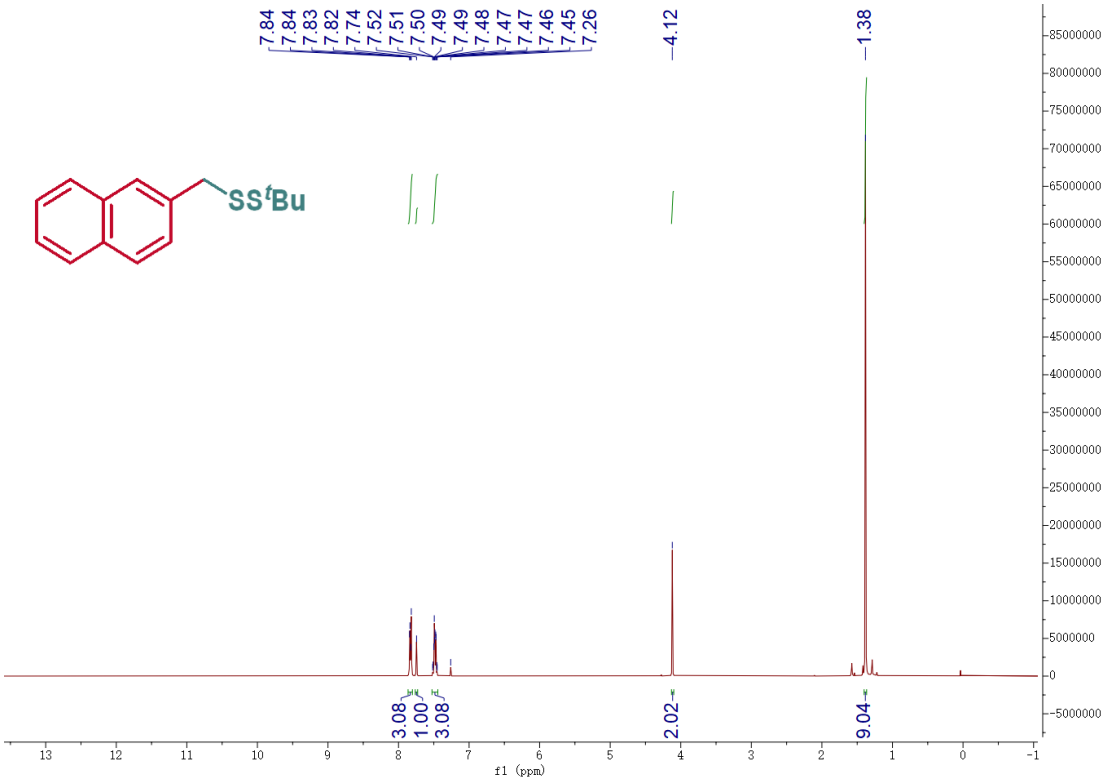
^{1}H NMR Spectrum of 1-((*tert*-Butylsulfinothioyl)methyl)-4-methoxybenzene 4k



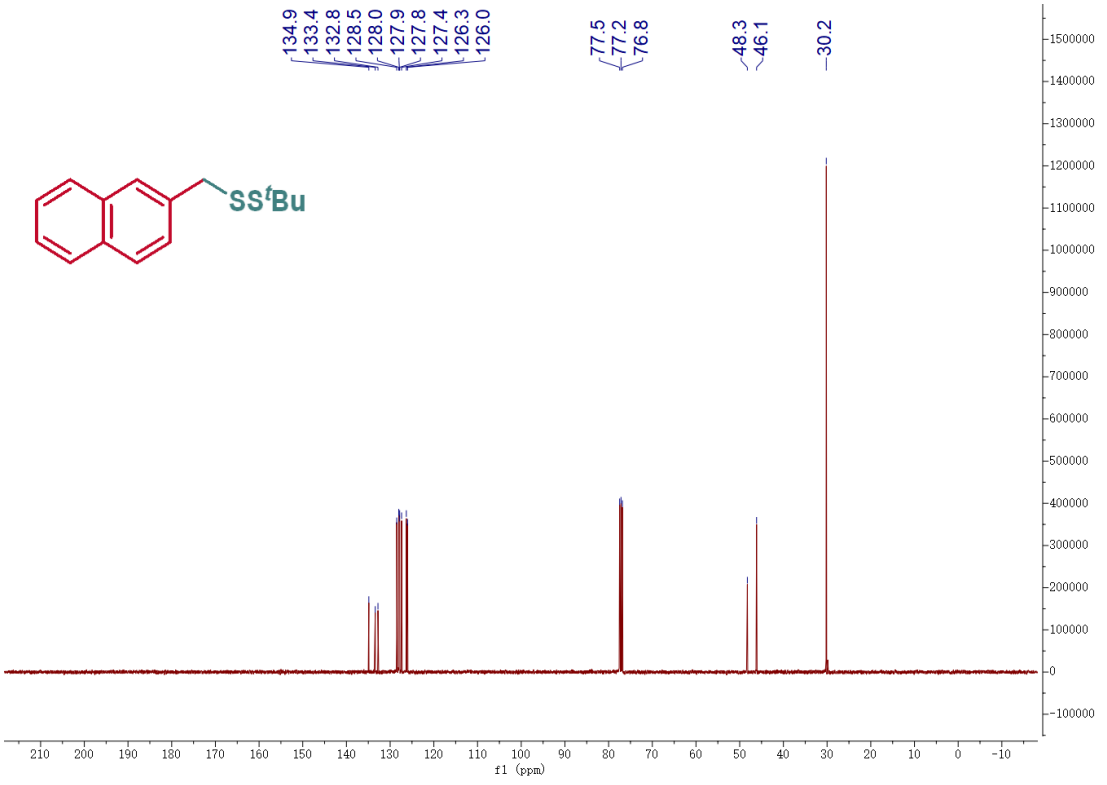
^{13}C NMR Spectrum of 1-((*tert*-Butylsulfinothioyl)methyl)-4-methoxybenzene 4k



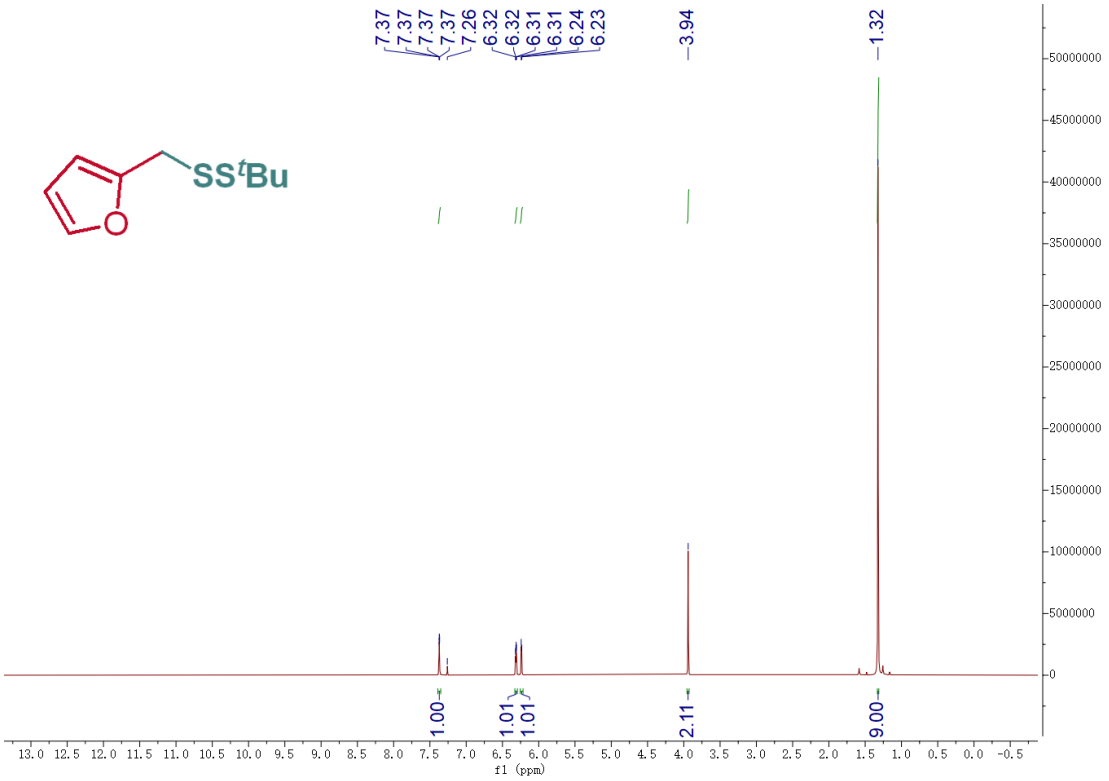
^{1}H NMR Spectrum of 2-((*tert*-Butylsulfinothioyl)methyl)naphthalene 4l



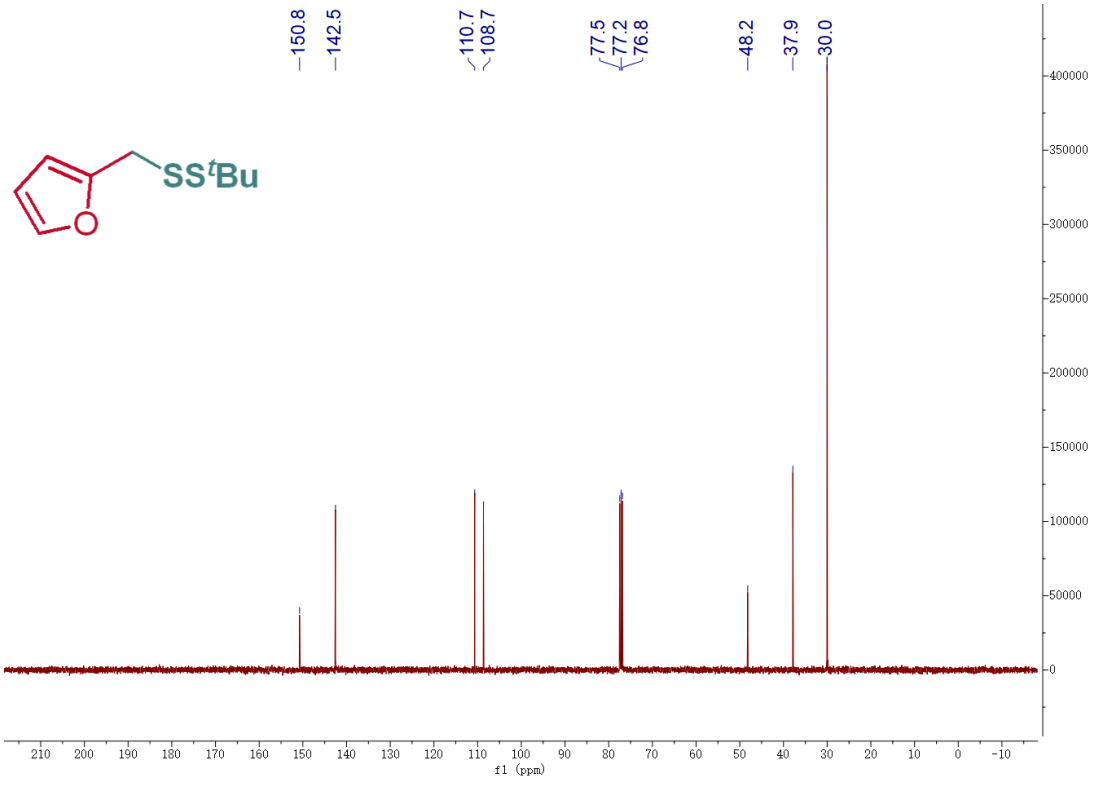
^{13}C NMR Spectrum of 2-((*tert*-Butylsulfinothioyl)methyl)naphthalene 4l



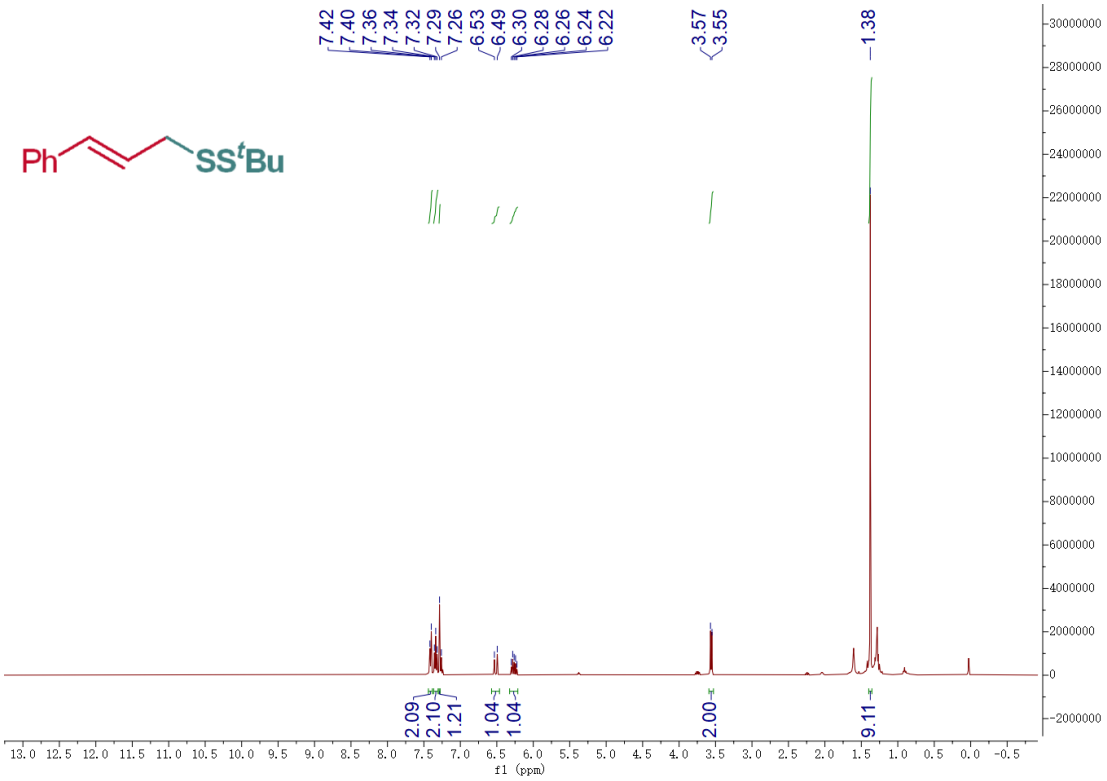
^{1}H NMR Spectrum of 2-((*tert*-Butylsulfinothioyl)methyl)furan 4m



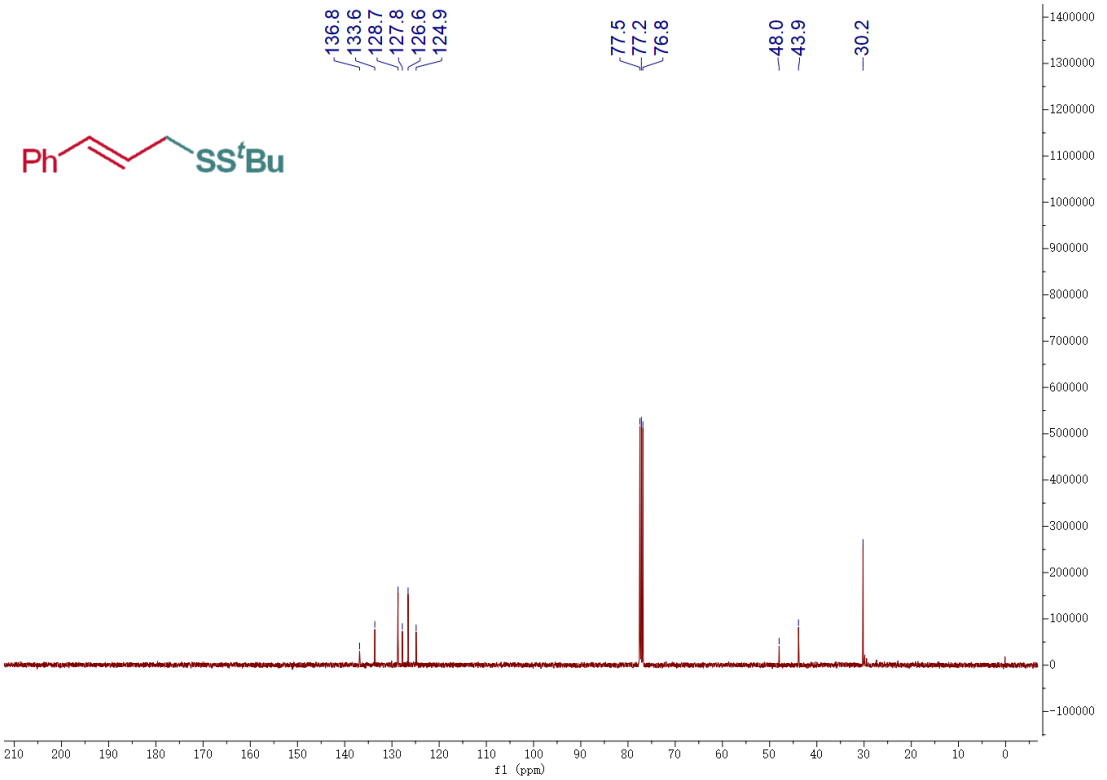
^{13}C NMR Spectrum of 2-((*tert*-Butylsulfinothioyl)methyl)furan 4m



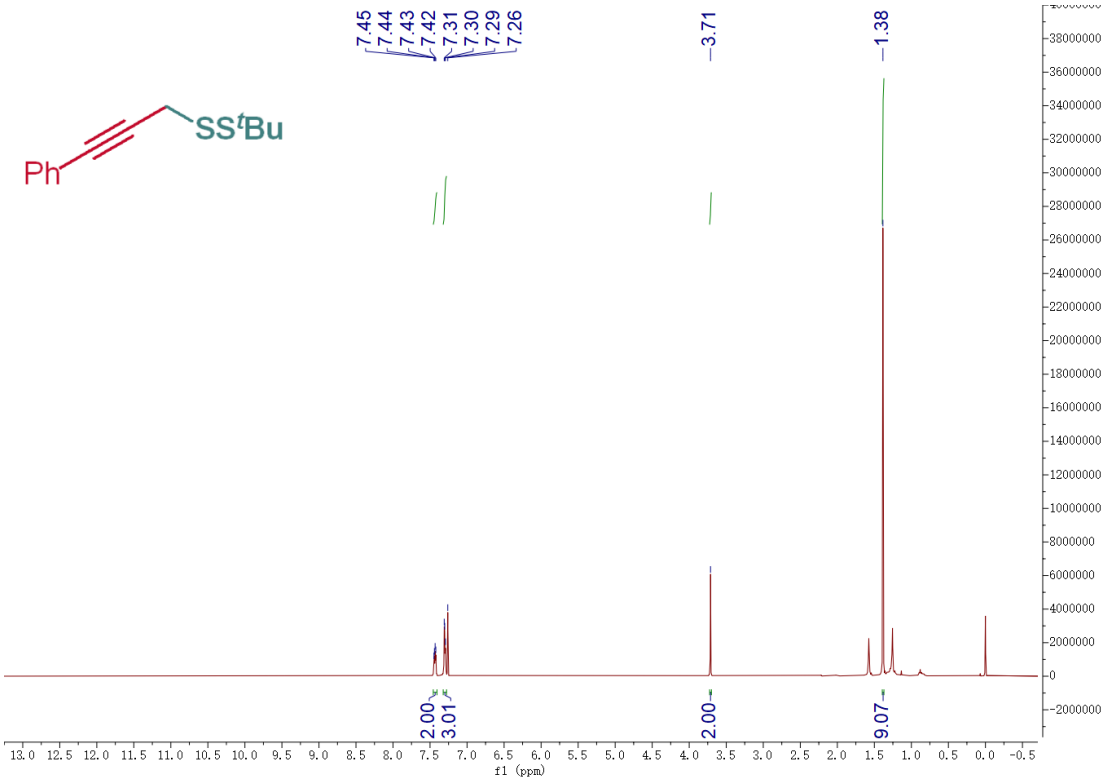
^{1}H NMR Spectrum of (*E*)-(3-(*tert*-Butylsulfinothioyl)prop-1-en-1-yl)benzene 4n



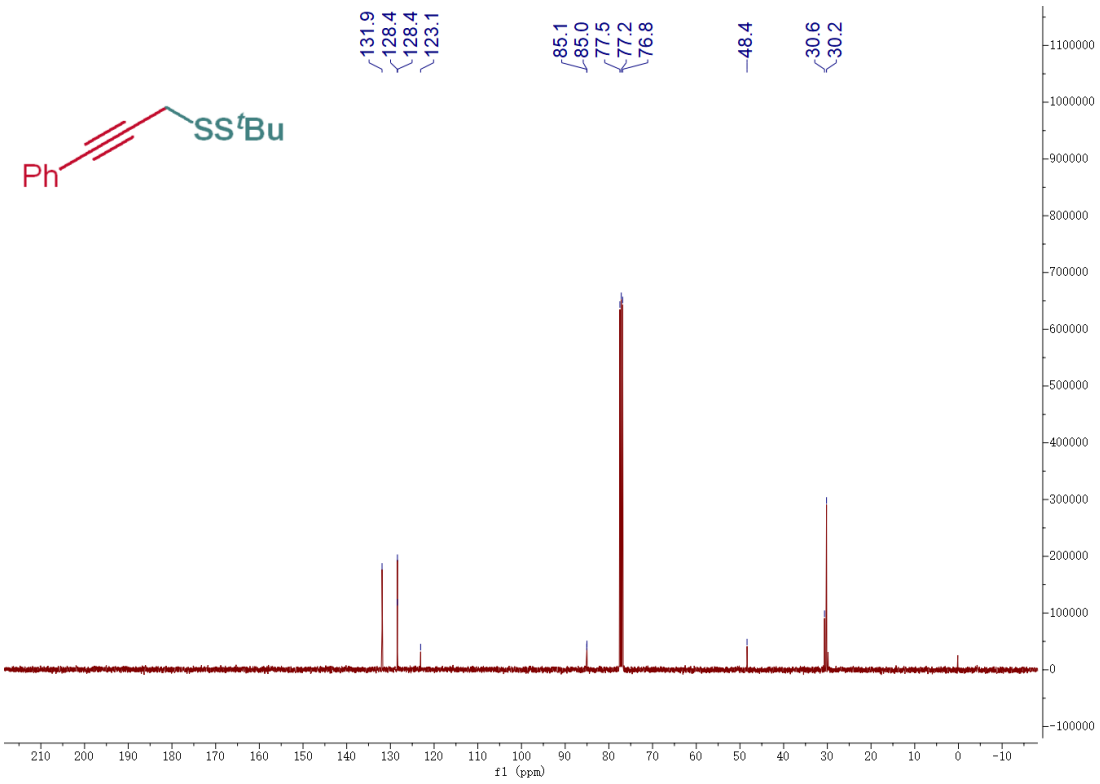
^{13}C NMR Spectrum of (*E*)-(3-(*tert*-Butylsulfinothioyl)prop-1-en-1-yl)benzene 4n



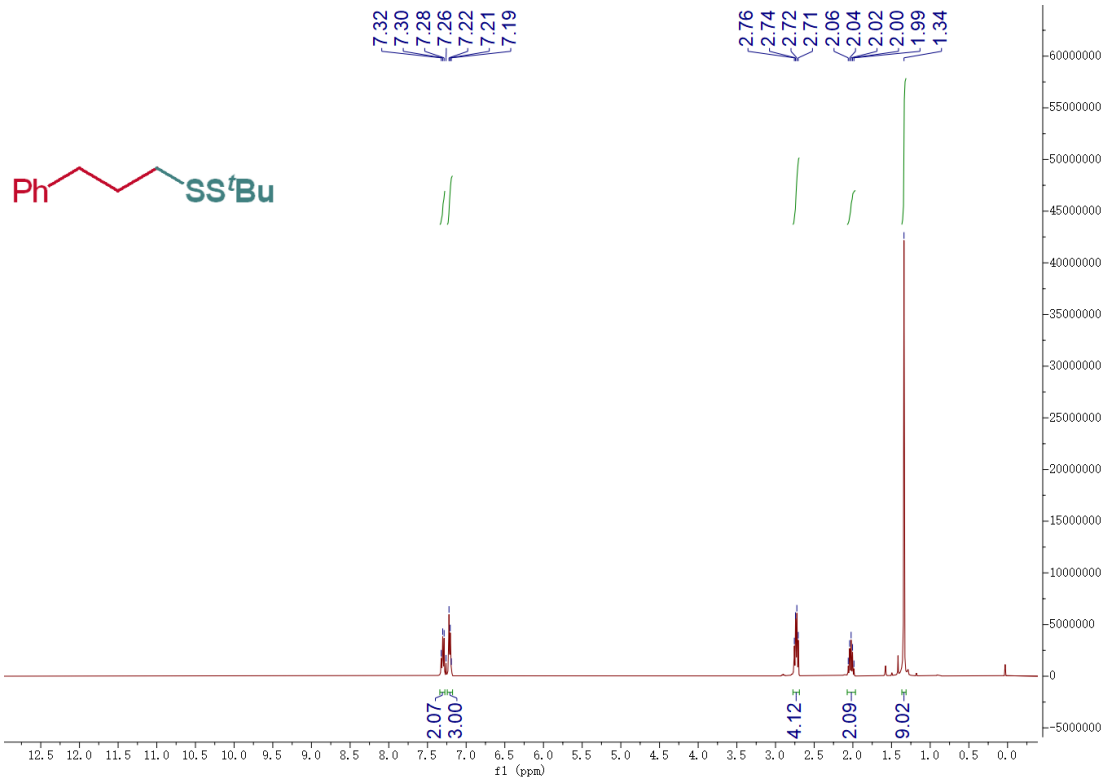
^{1}H NMR Spectrum of 1-(*tert*-Butyl)-2-(3-phenylprop-2-yn-1-yl)disulfane 4o



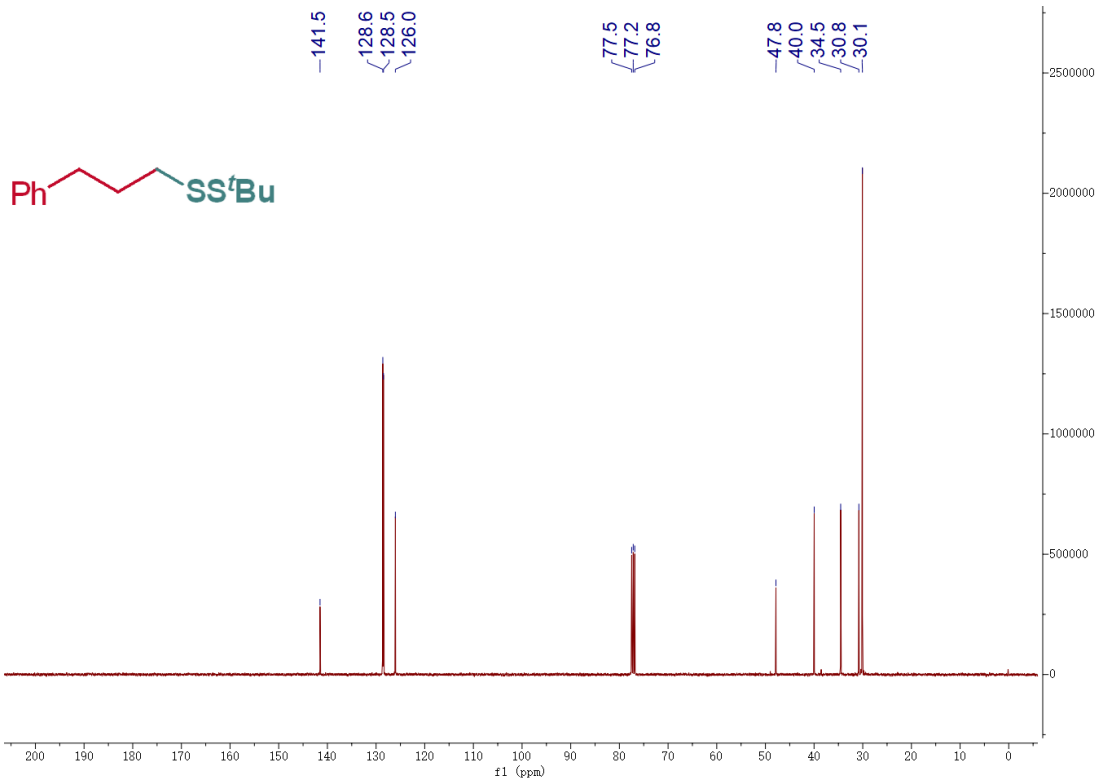
^{13}C NMR Spectrum of 1-(*tert*-Butyl)-2-(3-phenylprop-2-yn-1-yl)disulfane 4o



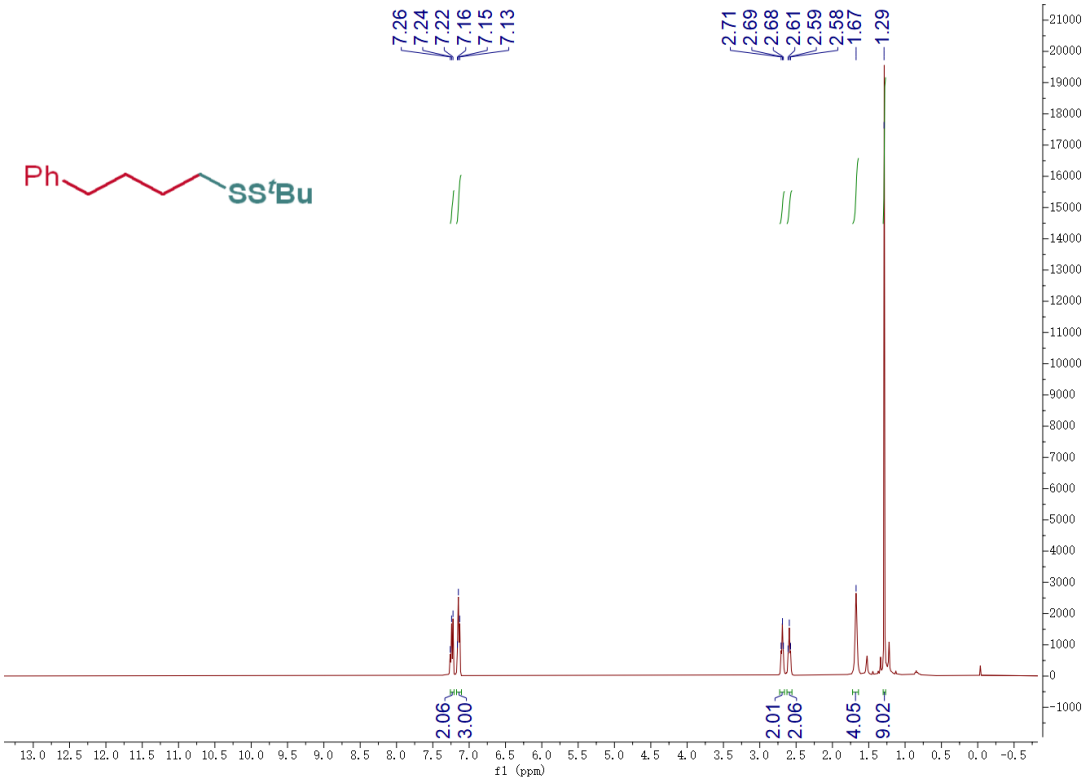
^{1}H NMR Spectrum of (3-(*tert*-Butylsulfinothioyl)propyl)benzene 4p



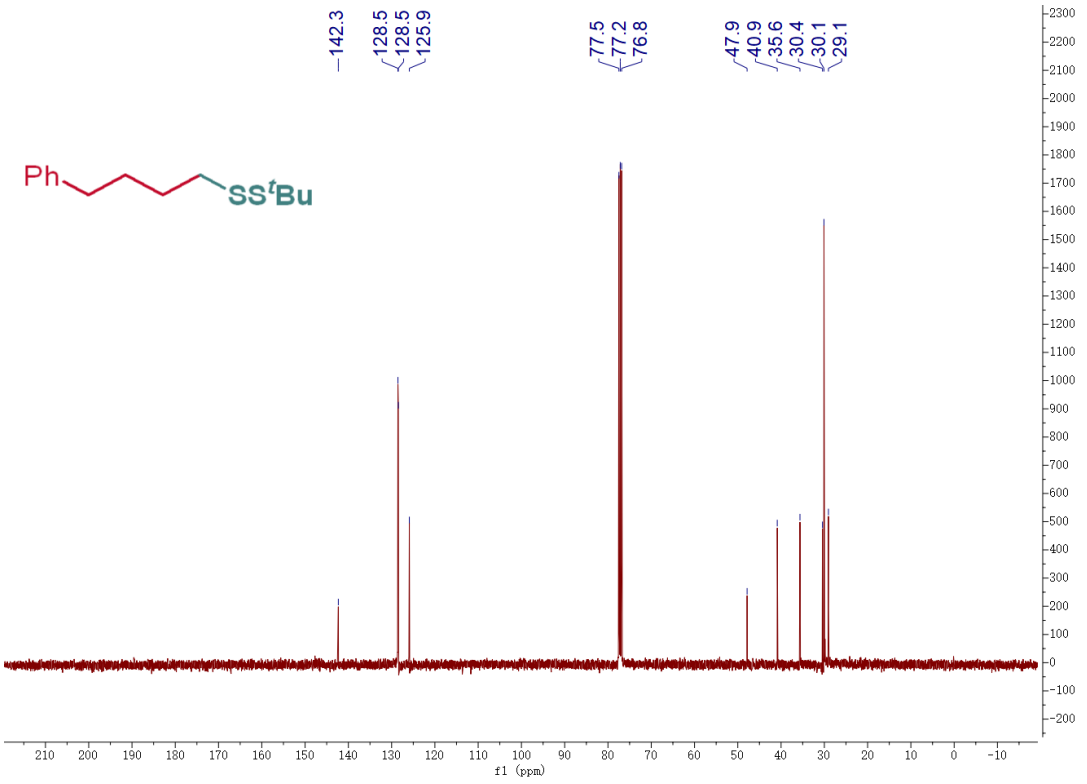
^{13}C NMR Spectrum of (3-(*tert*-Butylsulfinothioyl)propyl)benzene 4p



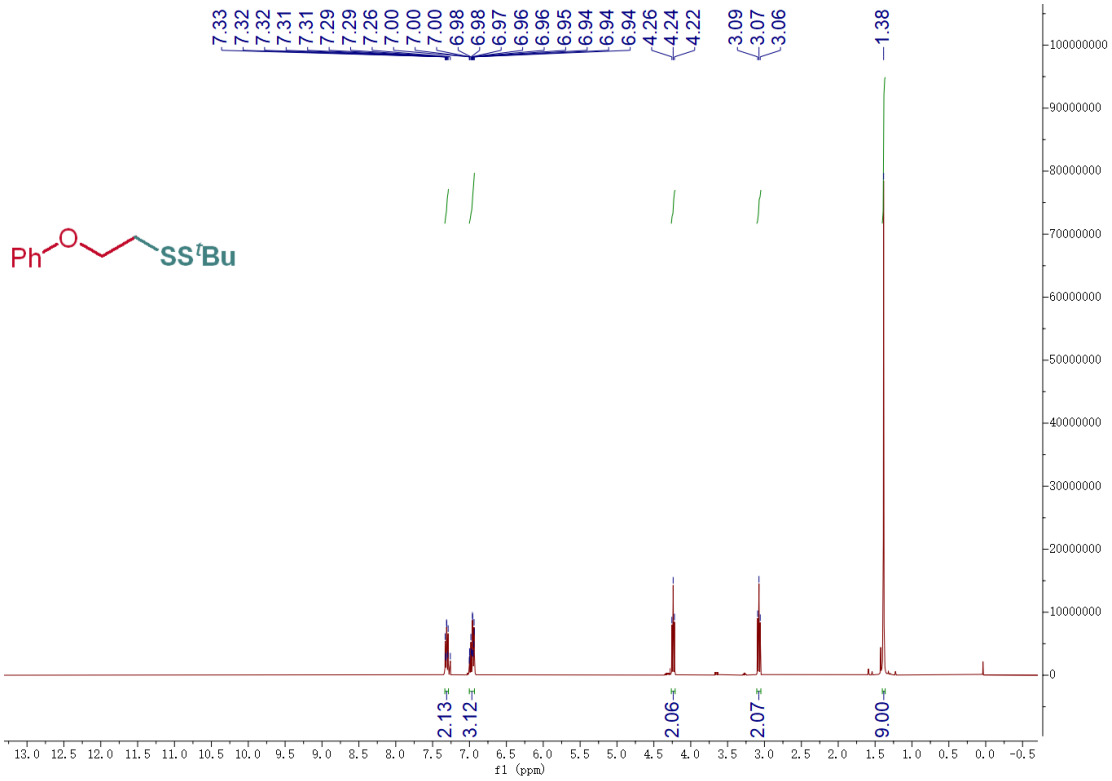
^{1}H NMR Spectrum of (4-(*tert*-Butylsulfinothioyl)butyl)benzene 4q



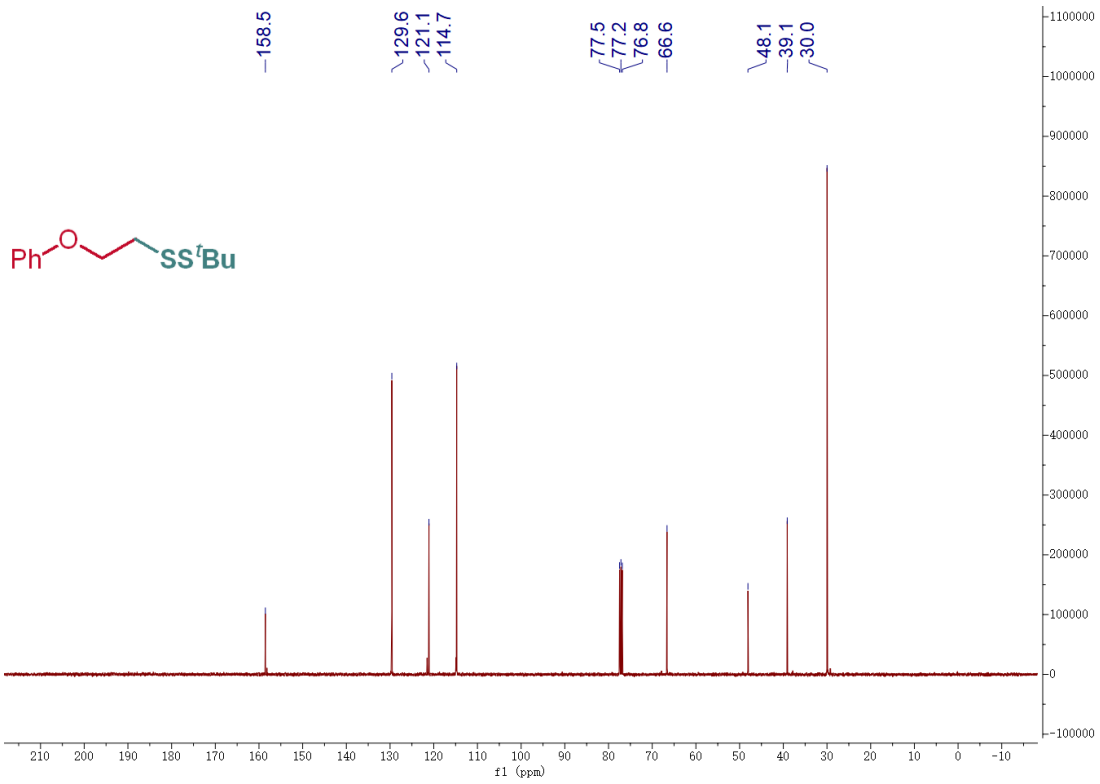
^{13}C NMR Spectrum of (4-(*tert*-Butylsulfinothioyl)butyl)benzene 4q



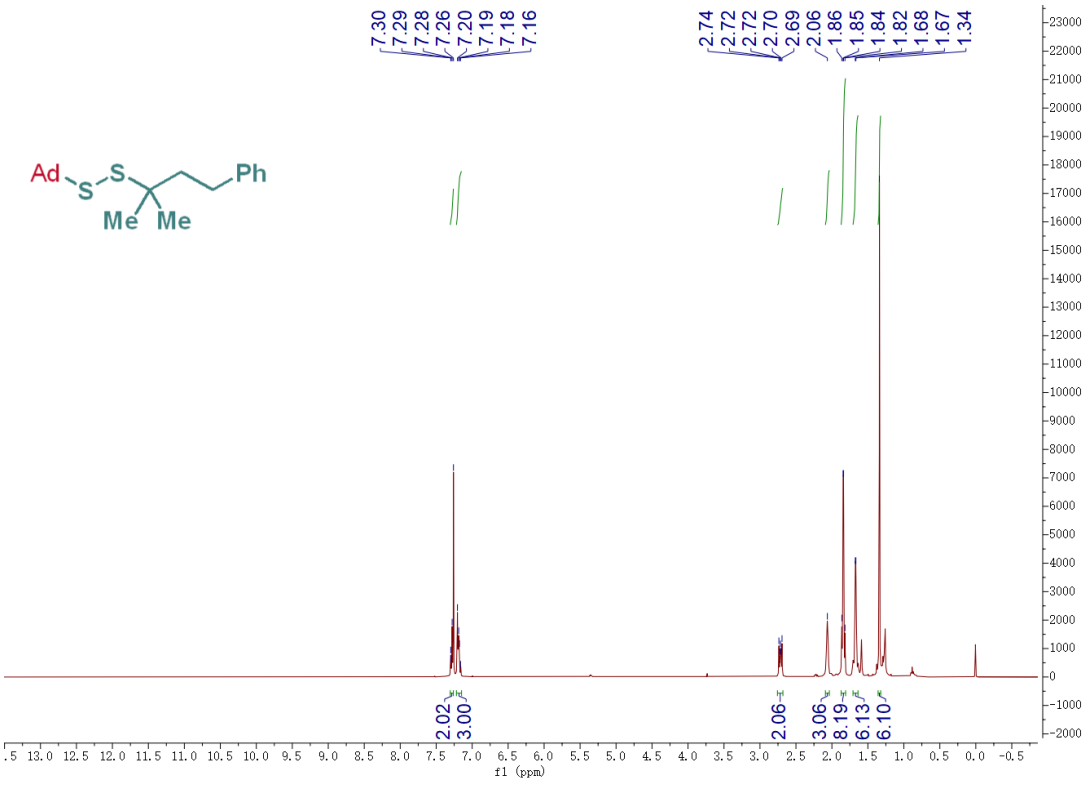
^{1}H NMR Spectrum of (2-(*tert*-Butylsulfinothioyl)ethoxy)benzene 4r



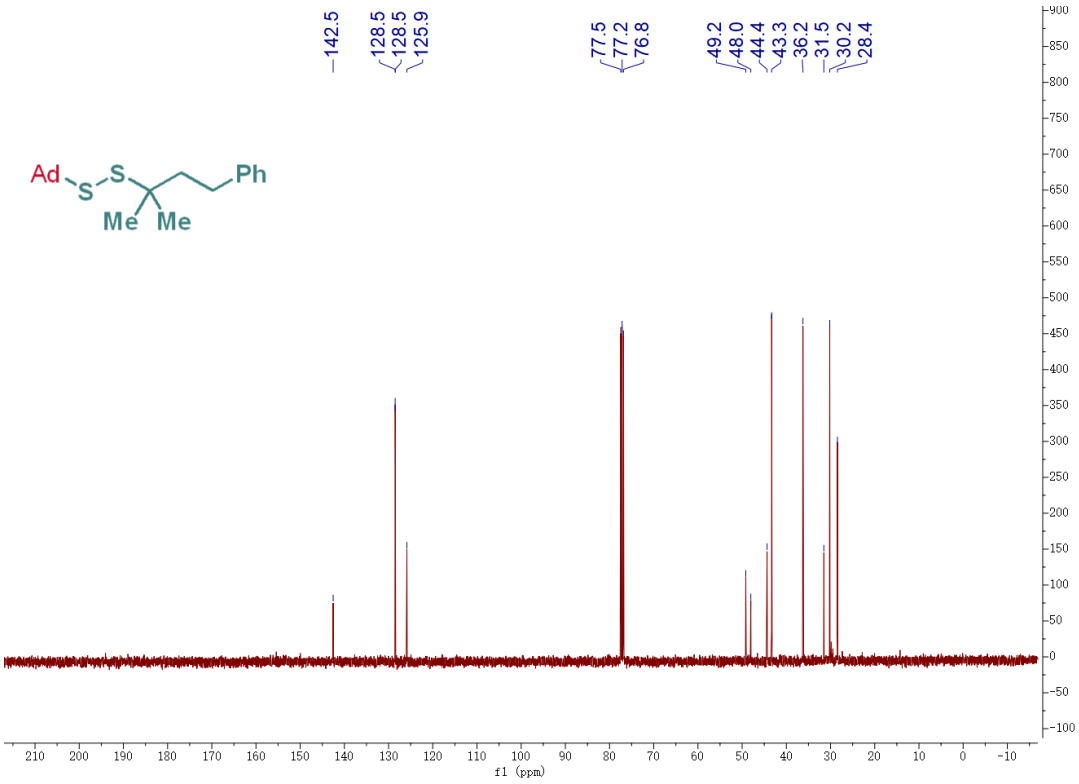
^{13}C NMR Spectrum of (2-(*tert*-Butylsulfinothioyl)ethoxy)benzene 4r



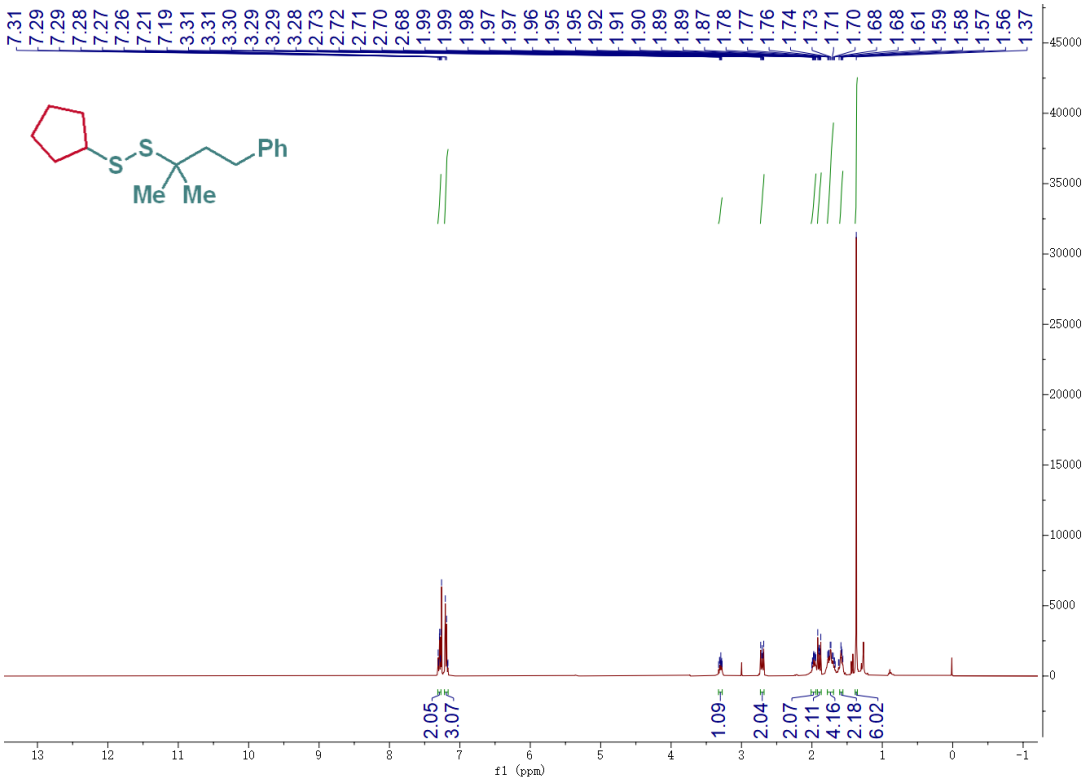
^{1}H NMR Spectrum of (3s,5s,7s)-1-((2-Methyl-4-phenylbutan-2-yl)-sulfinothioyl) adamantane 4t and 4ae



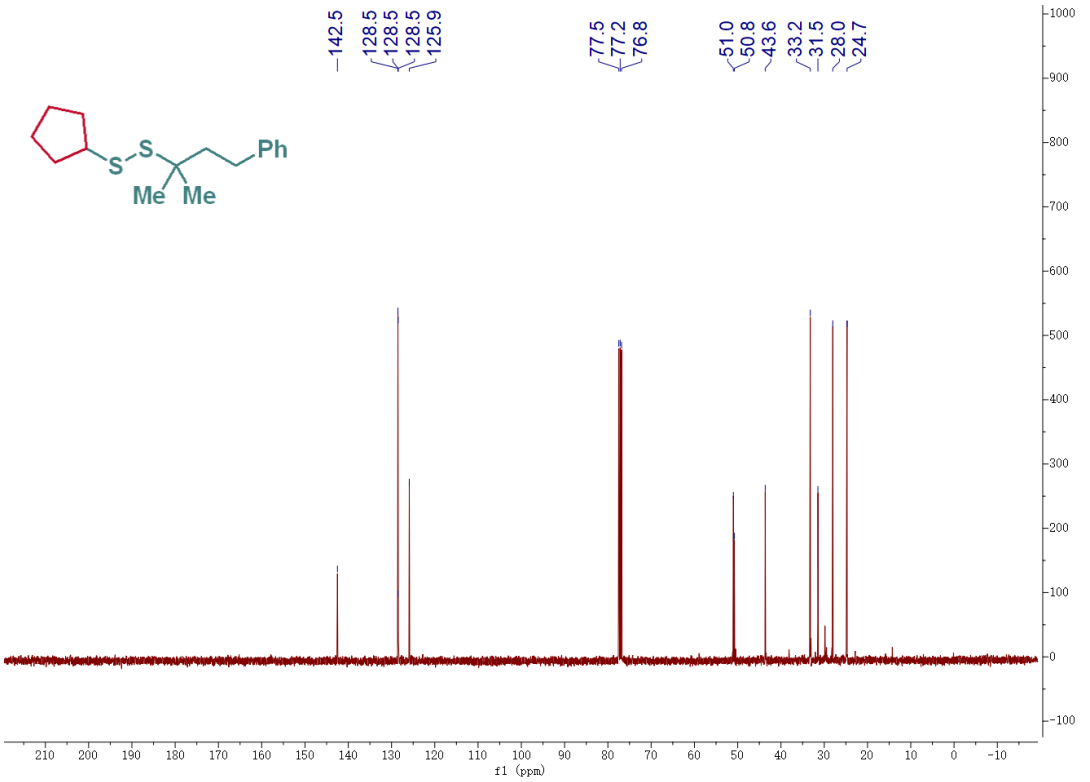
^{13}C NMR Spectrum of (3s,5s,7s)-1-((2-Methyl-4-phenylbutan-2-yl)-sulfinothioyl) adamantane 4t and 4ae



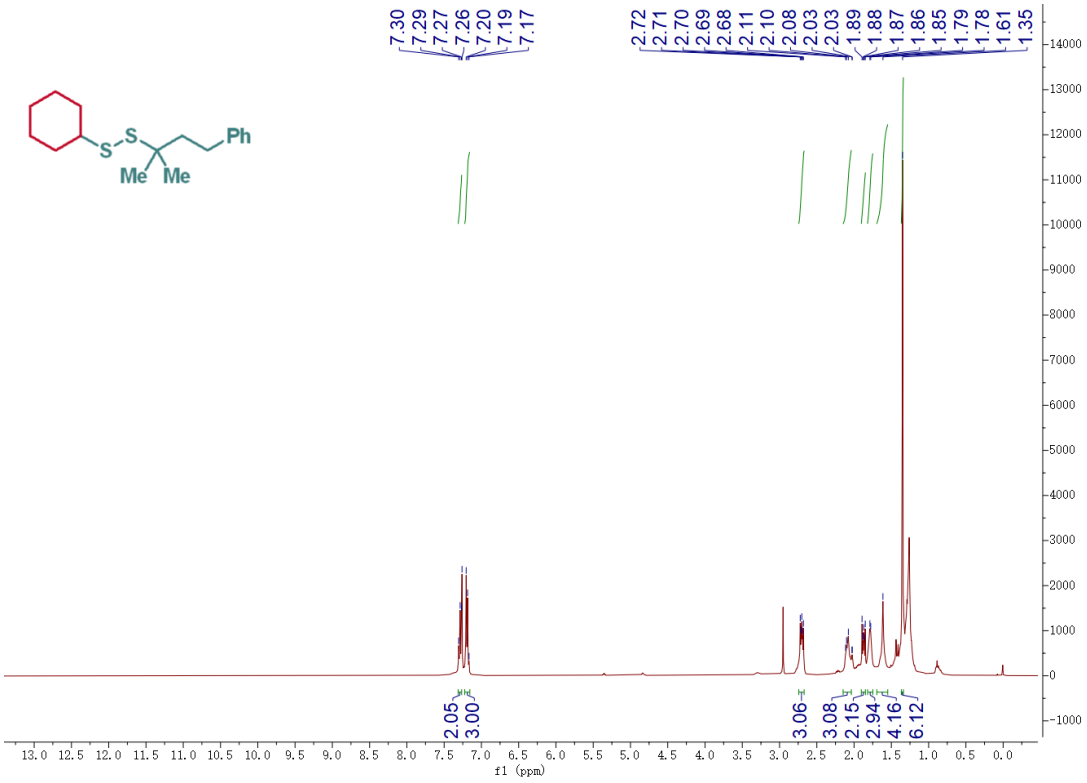
^{1}H NMR Spectrum of 1-Cyclopentyl-2-(2-methyl-4-phenyl-butan-2-yl)disulfane 4u and 4af



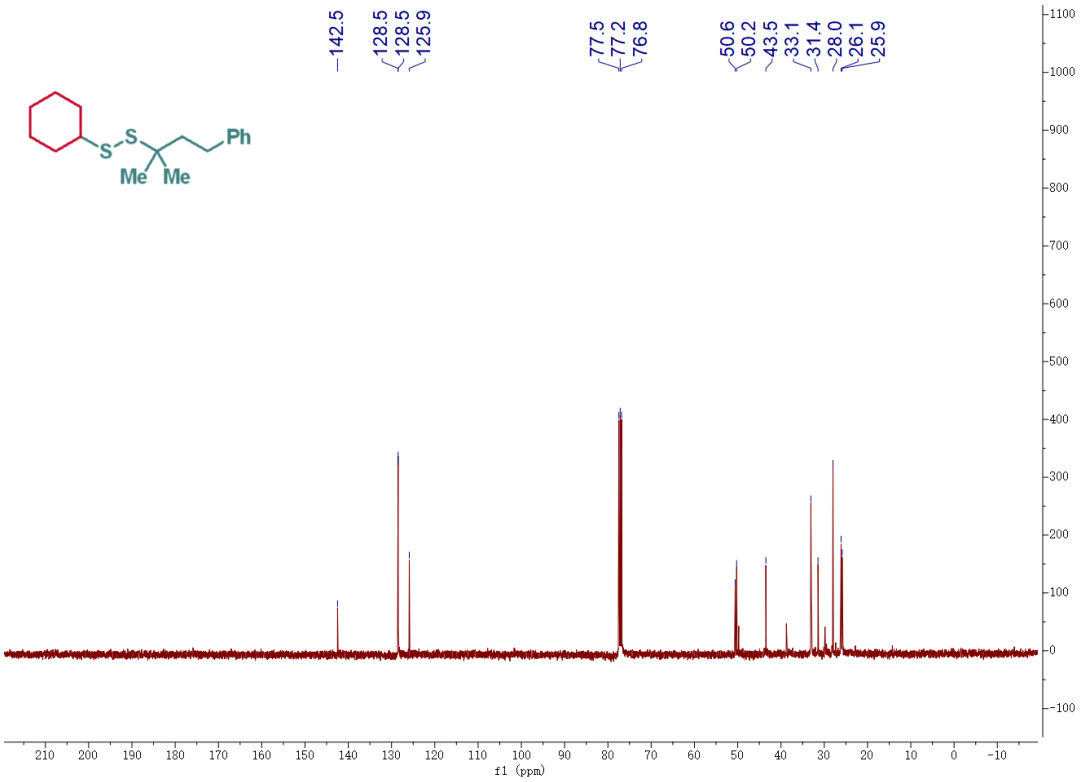
^{13}C NMR Spectrum of 1-Cyclopentyl-2-(2-methyl-4-phenyl-butan-2-yl)disulfane 4u and 4af



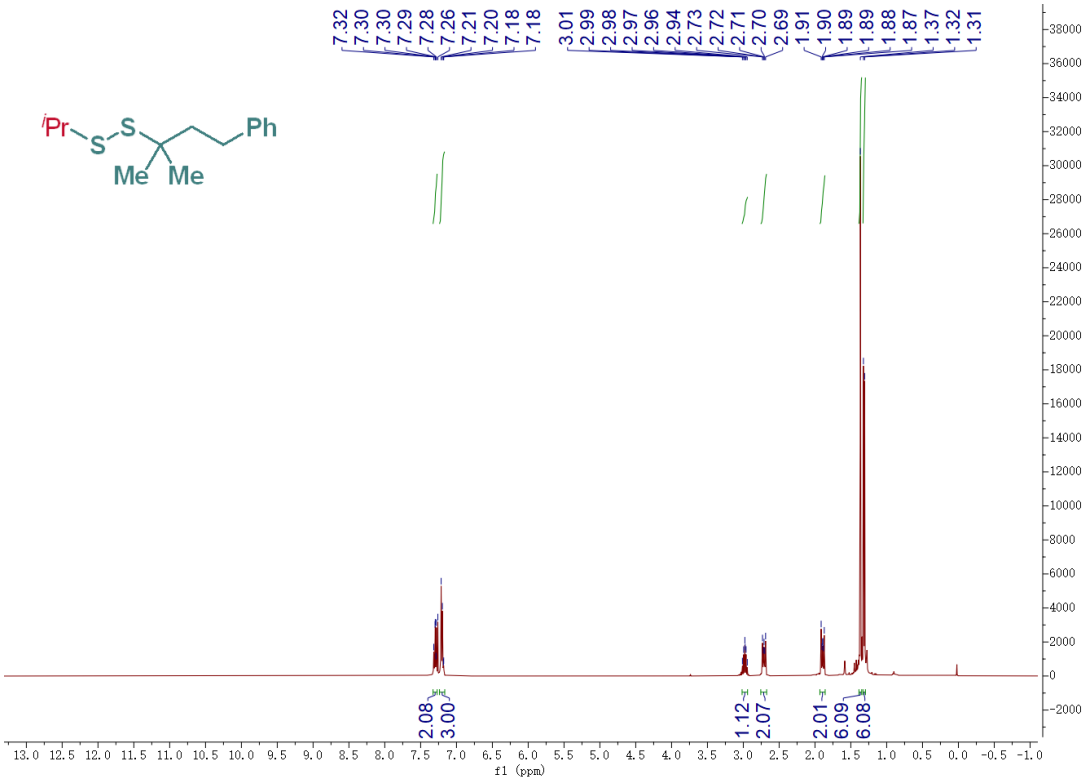
^{1}H NMR Spectrum of 1-Cyclohexyl-2-(2-methyl-4-phenyl- butan-2-yl)disulfane 4v and 4ag



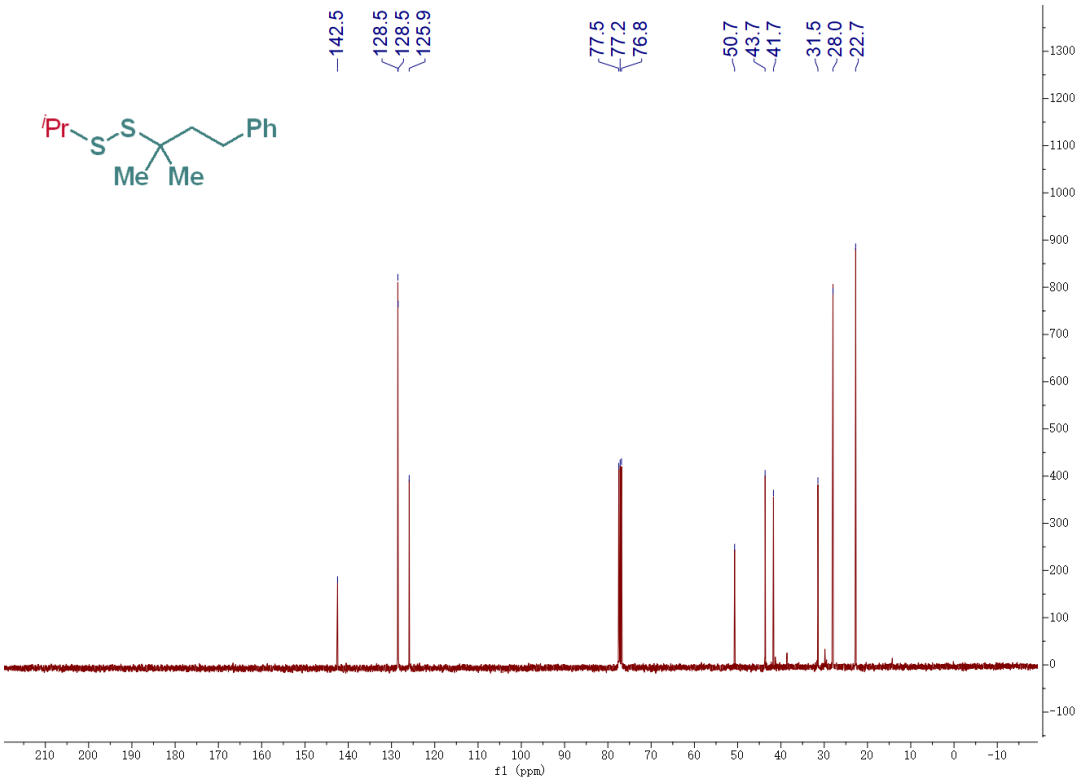
^{13}C NMR Spectrum of 1-Cyclohexyl-2-(2-methyl-4-phenyl- butan-2-yl)disulfane 4v and 4ag



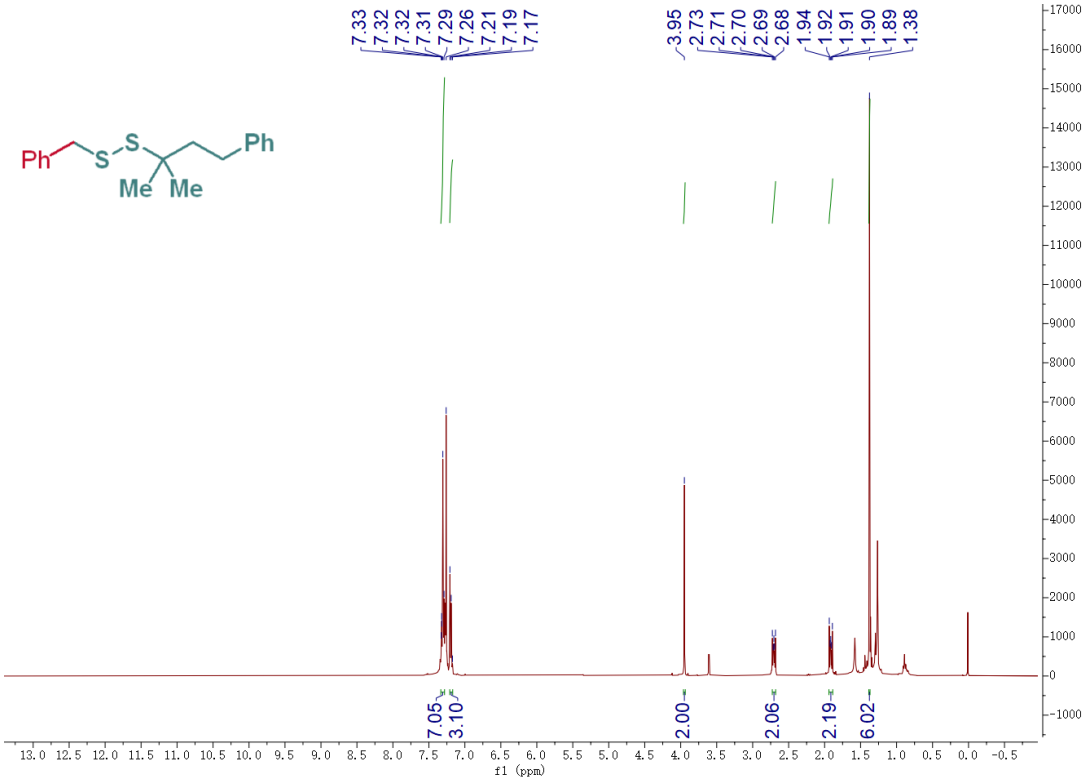
^{1}H NMR Spectrum of (3-(Isopropylsulfinothioyl)-3-methylbutyl)benzene 4w and 4ah



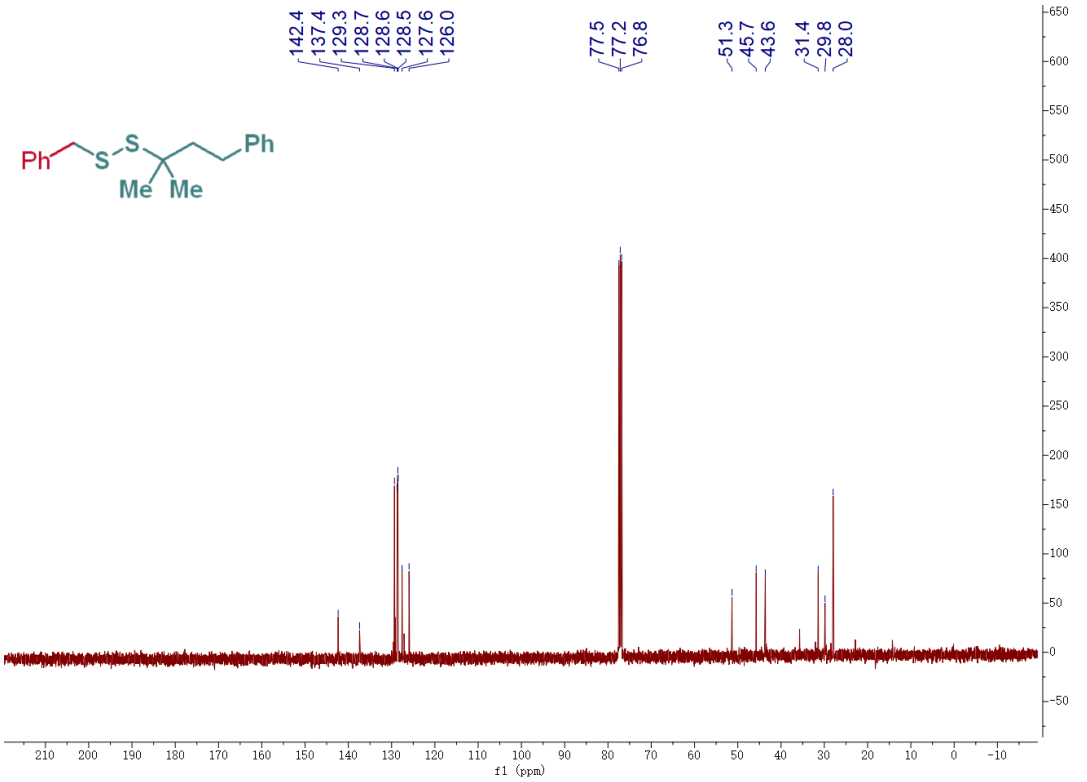
^{13}C NMR Spectrum of (3-(Isopropylsulfinothioyl)-3-methylbutyl)benzene 4w and 4ah



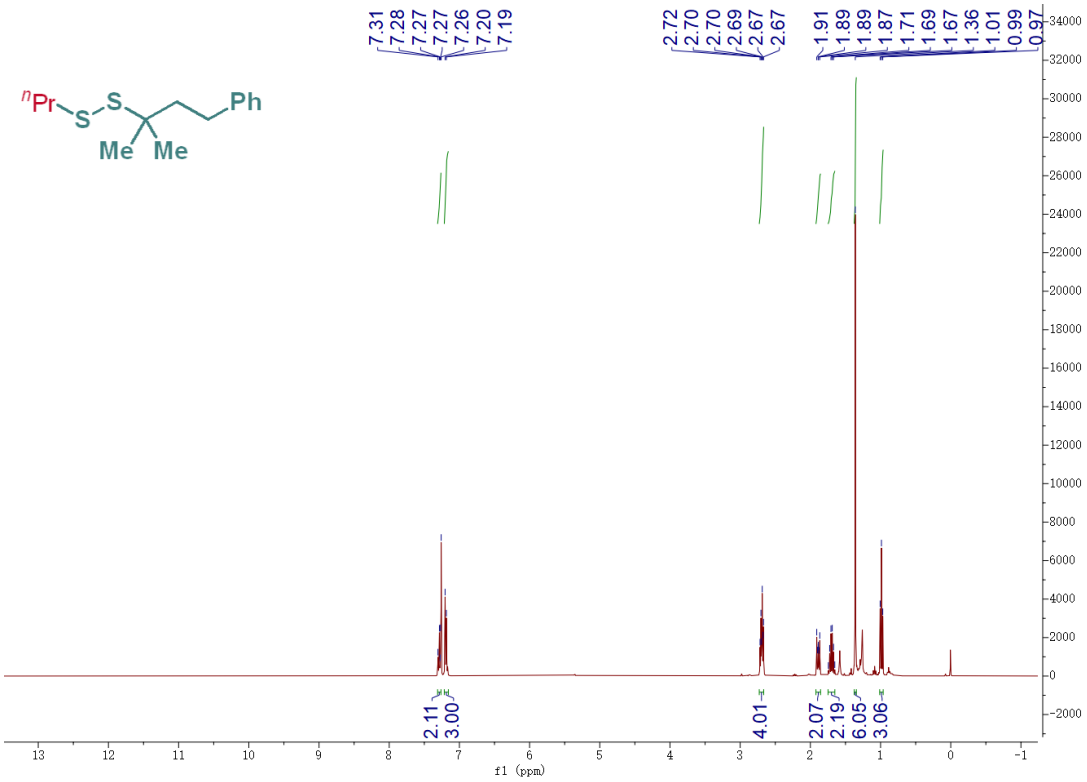
^{1}H NMR Spectrum of 1-Benzyl-2-(2-methyl-4-phenylbutan-2-yl)disulfane 4x and 4ai



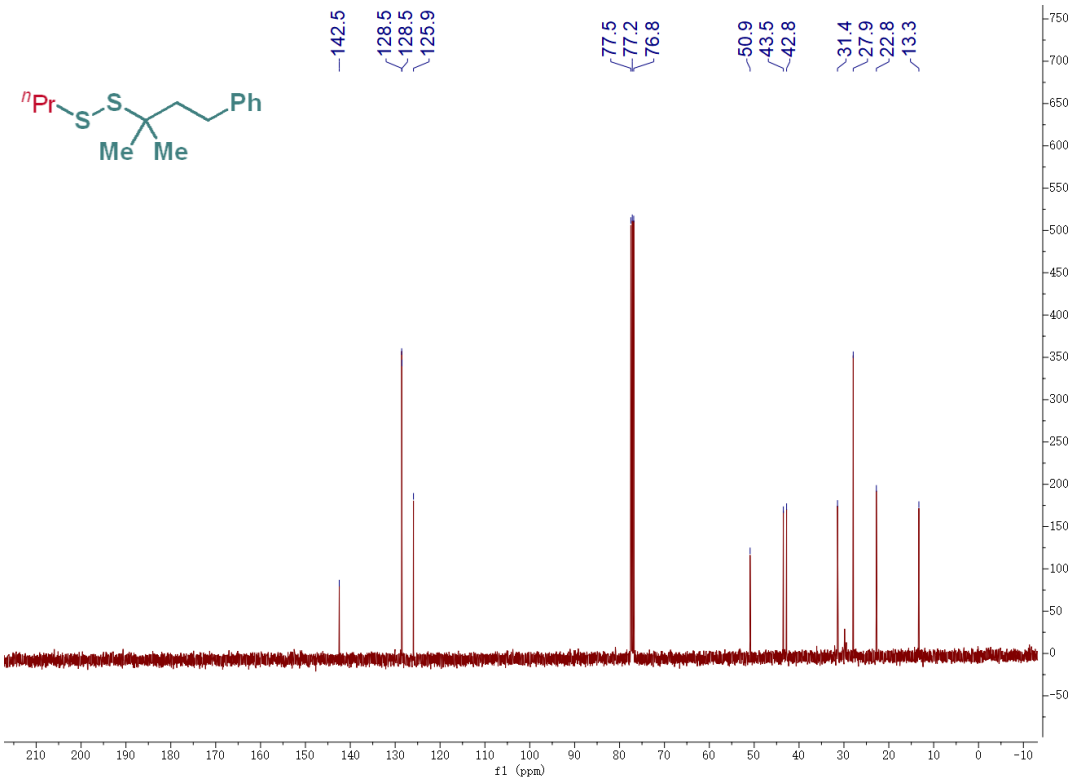
^{13}C NMR Spectrum of 1-Benzyl-2-(2-methyl-4-phenylbutan-2-yl)disulfane 4x and 4ai



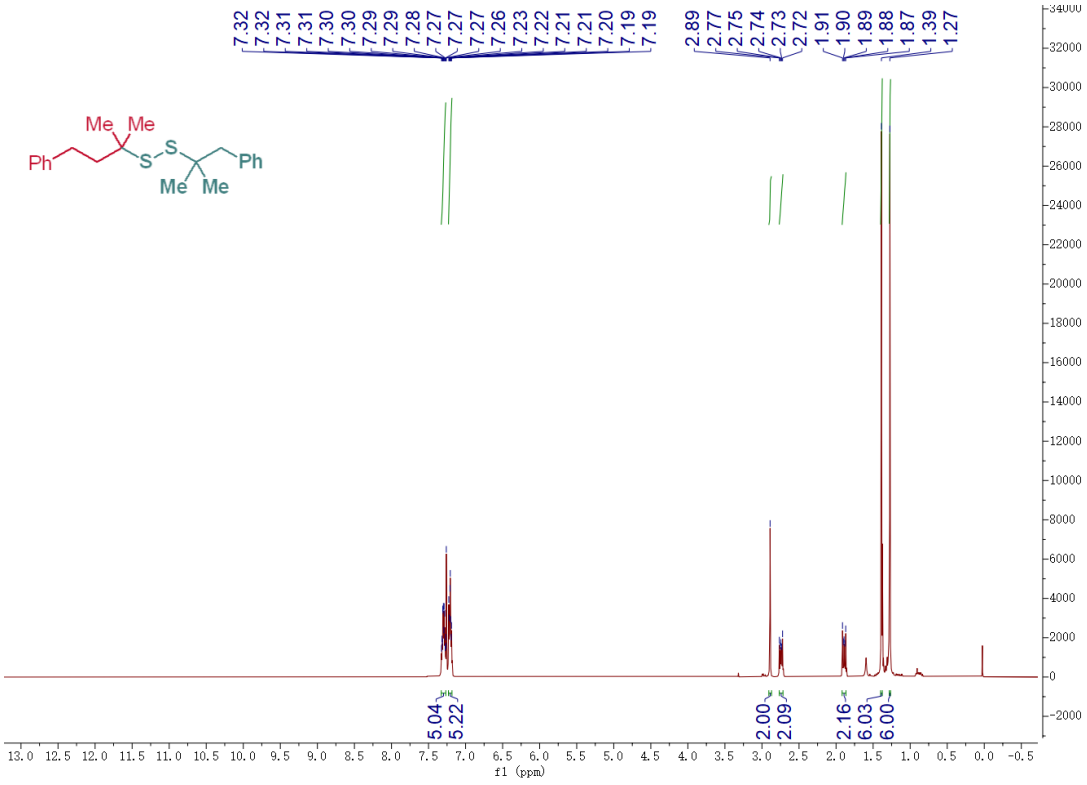
^{1}H NMR Spectrum of (3-Methyl-3-(propylsulfinothioyl)butyl)benzene 4z and 4ak



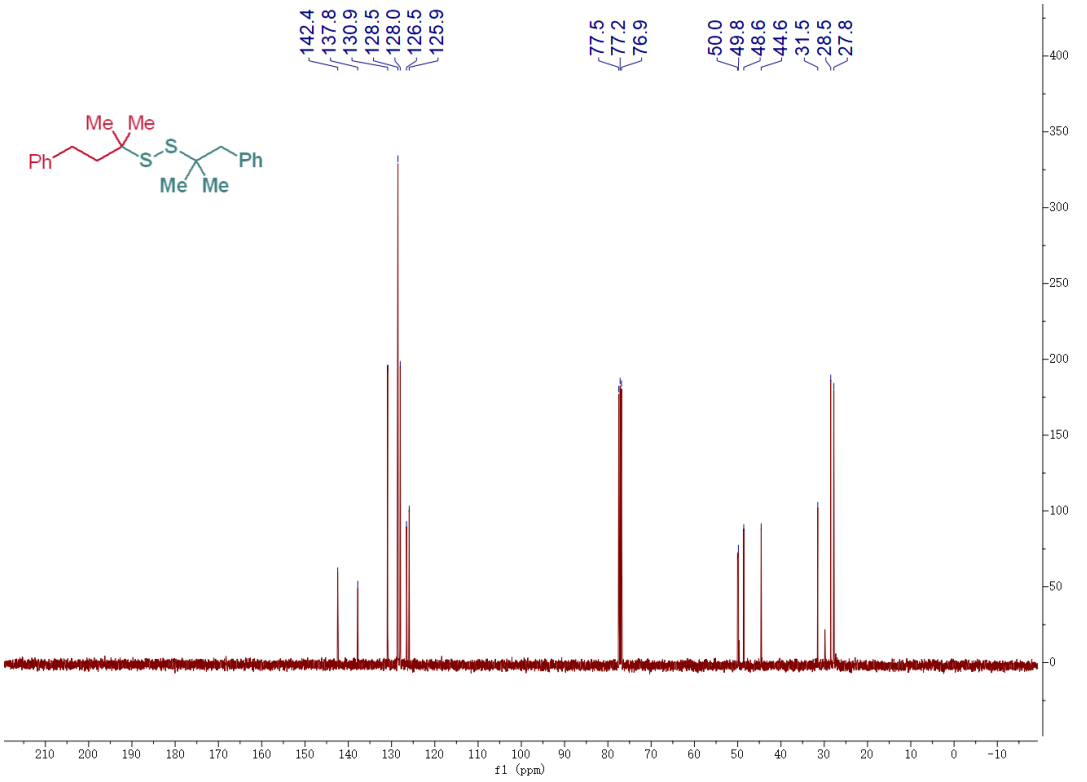
^{13}C NMR Spectrum of (3-Methyl-3-(propylsulfinothioyl)butyl)benzene 4z and 4ak



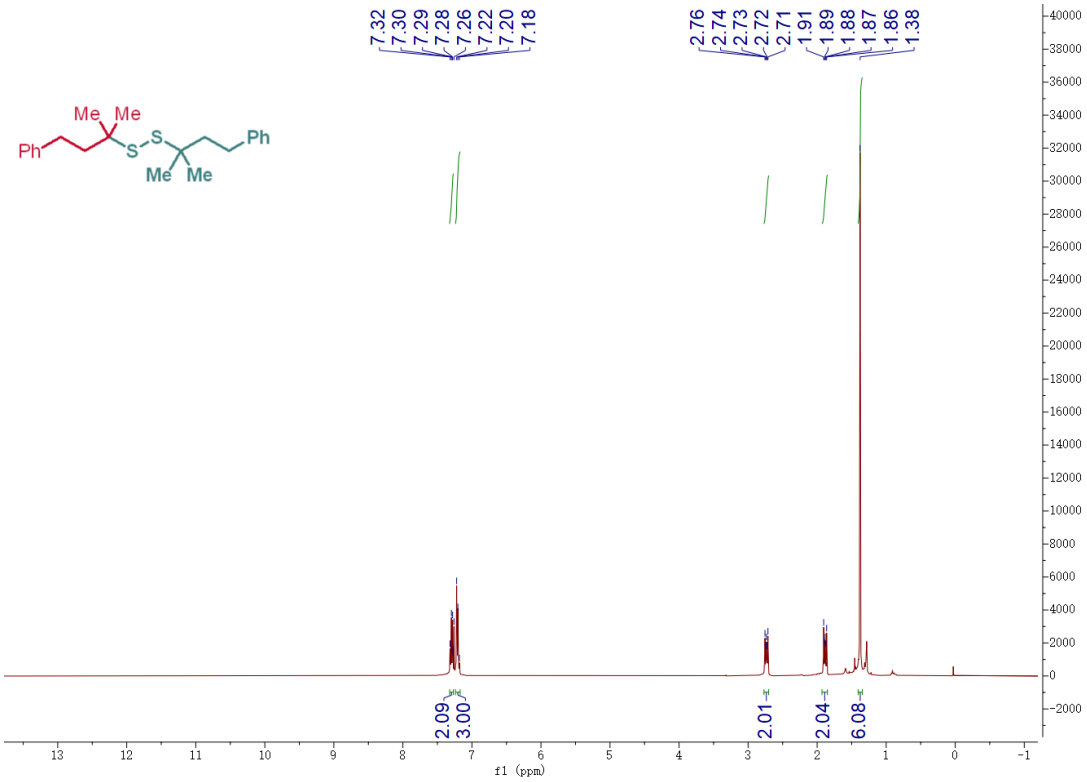
^{1}H NMR Spectrum of 1-(2-Methyl-1-phenylpropan-2-yl)-2-(2-methyl-4-phenyl-butan-2-yl)disulfane 4aa



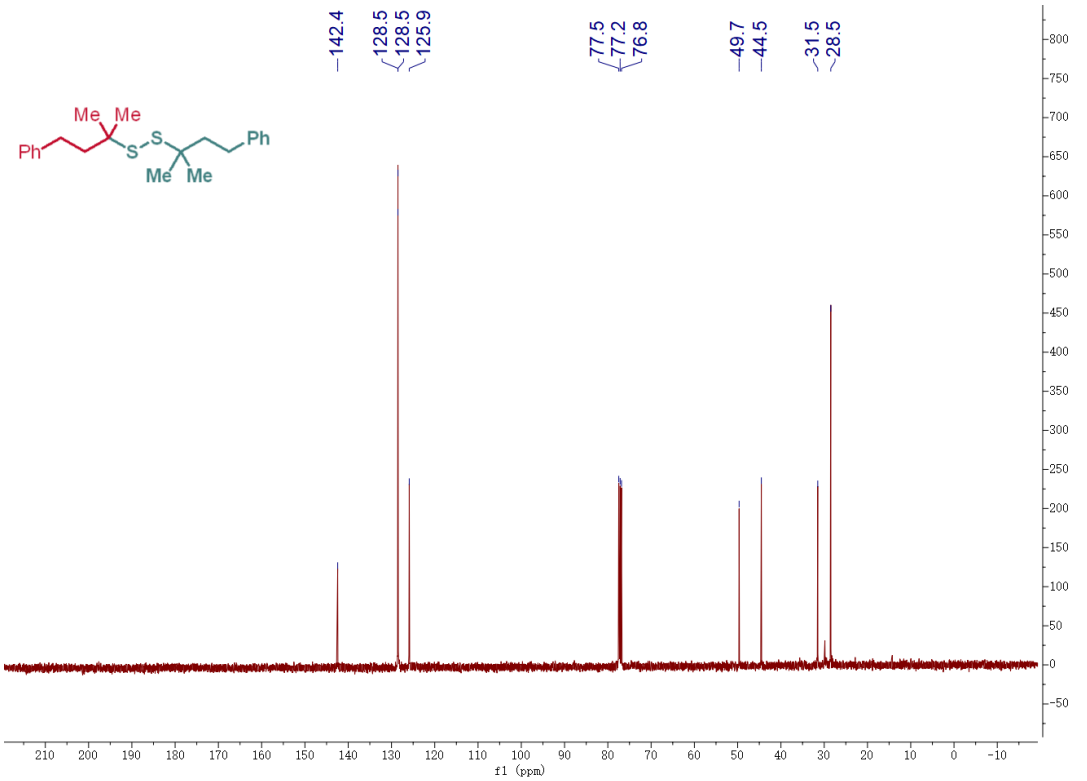
^{13}C NMR Spectrum of 1-(2-Methyl-1-phenylpropan-2-yl)-2-(2-methyl-4-phenyl-butan-2-yl)disulfane 4aa



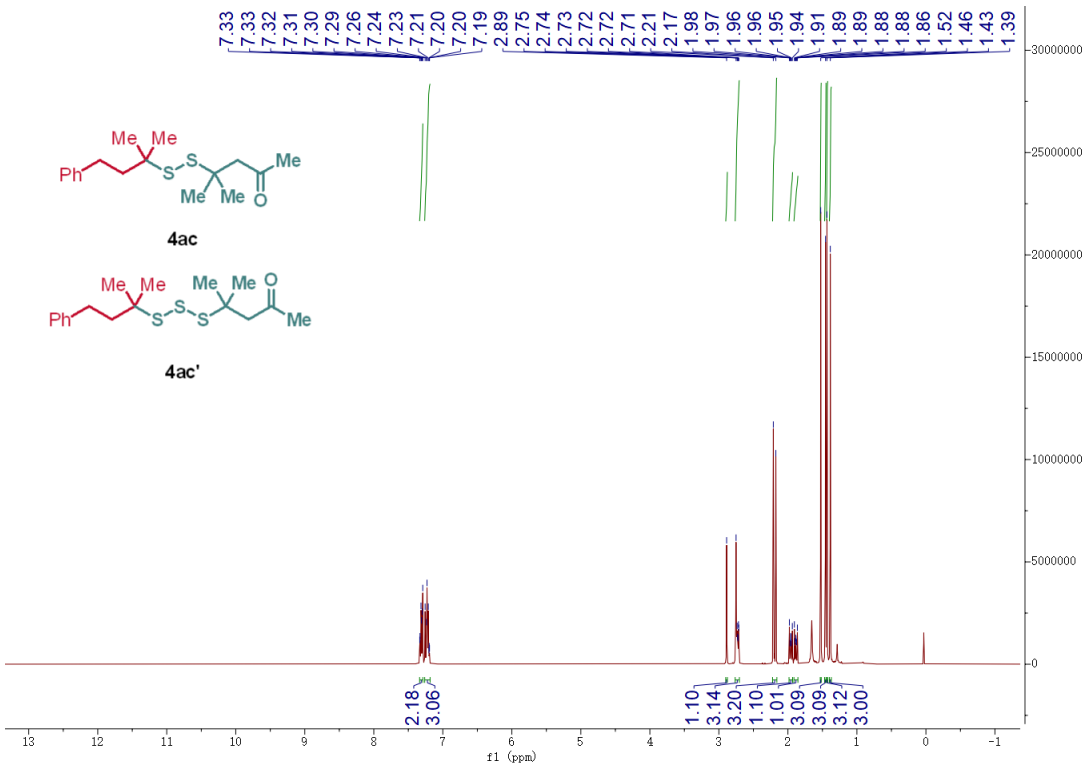
^{1}H NMR Spectrum of 1,2-Bis(2-methyl-4-phenylbutan-2-yl)disulfane 4ab



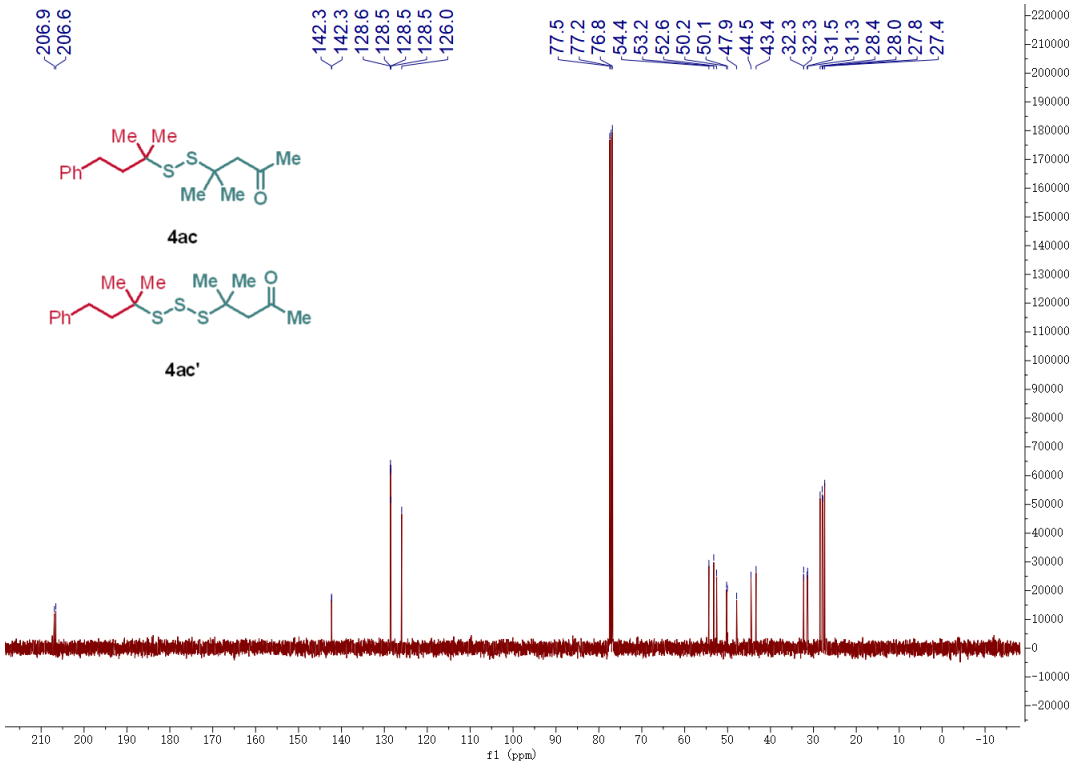
^{13}C NMR Spectrum of 1,2-Bis(2-methyl-4-phenylbutan-2-yl)disulfane 4ab



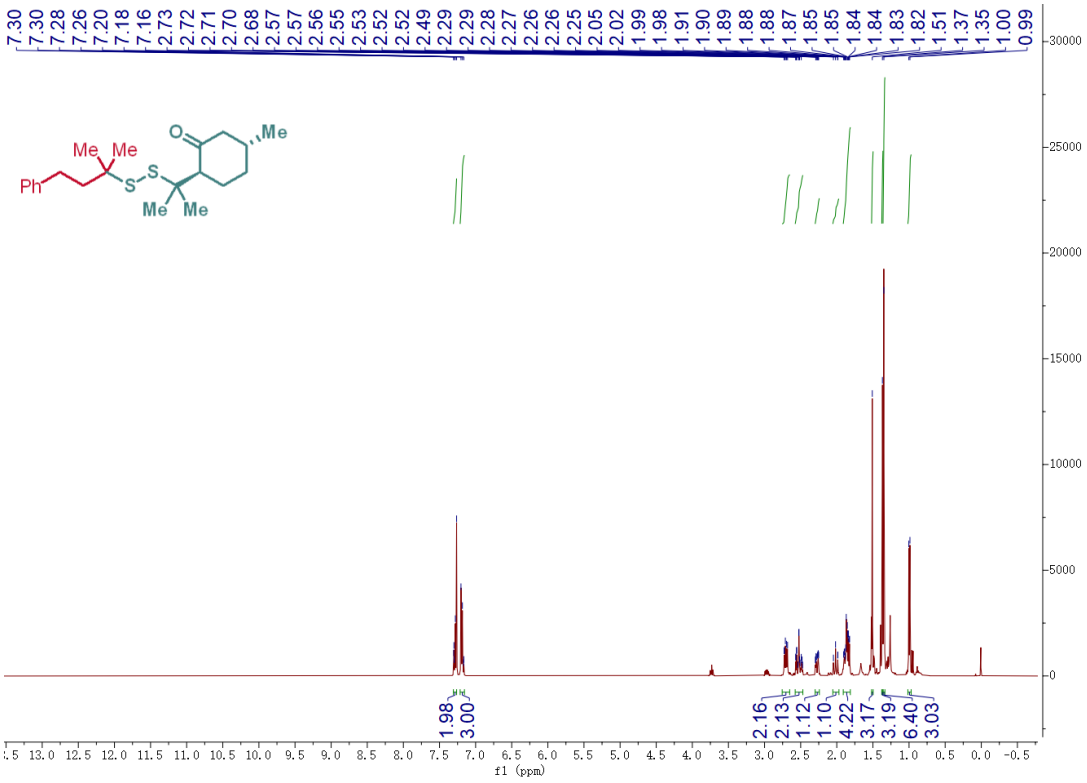
^{1}H NMR Spectrum of 4-methyl-4-((2-methyl-4-phenylbutan-2-yl)disulfaneyl) pentan-2-one (4ac) and 4-methyl-4-((2-methyl-4-phenylbutan-2-yl)trisulfaneyl) pentan-2-one (4ac')



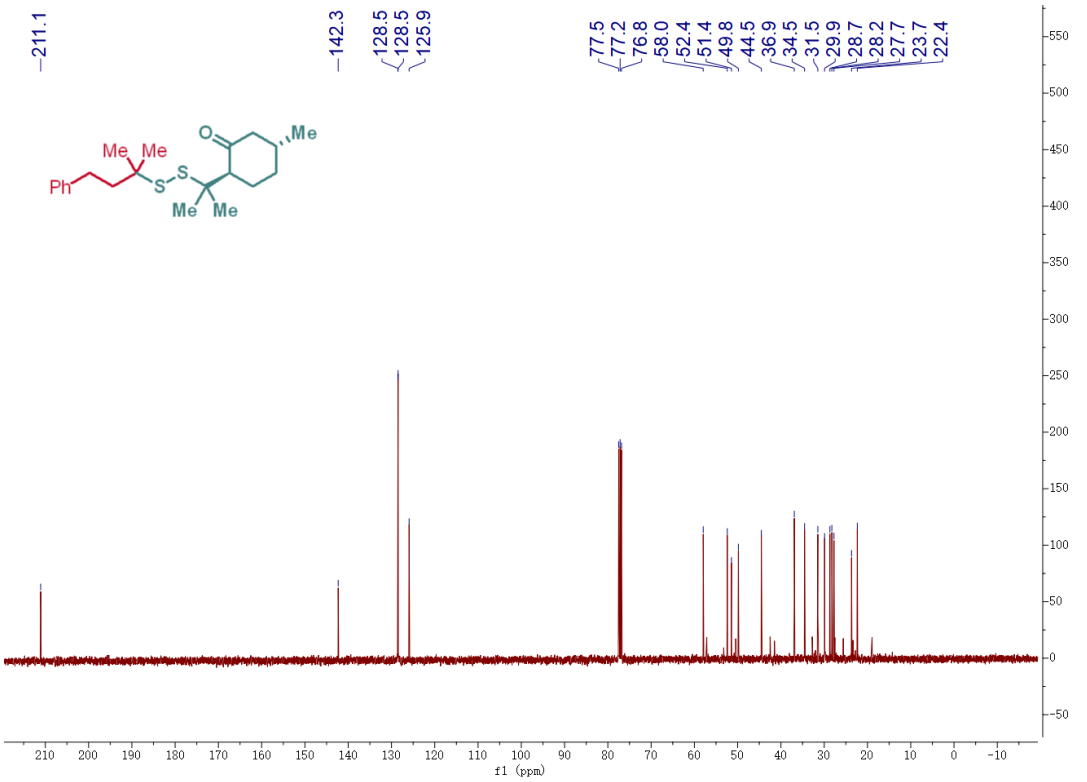
^{13}C NMR Spectrum of 4-methyl-4-((2-methyl-4-phenylbutan-2-yl)disulfaneyl) pentan-2-one (4ac) and 4-methyl-4-((2-methyl-4-phenylbutan-2-yl)trisulfaneyl) pentan-2-one (4ac')



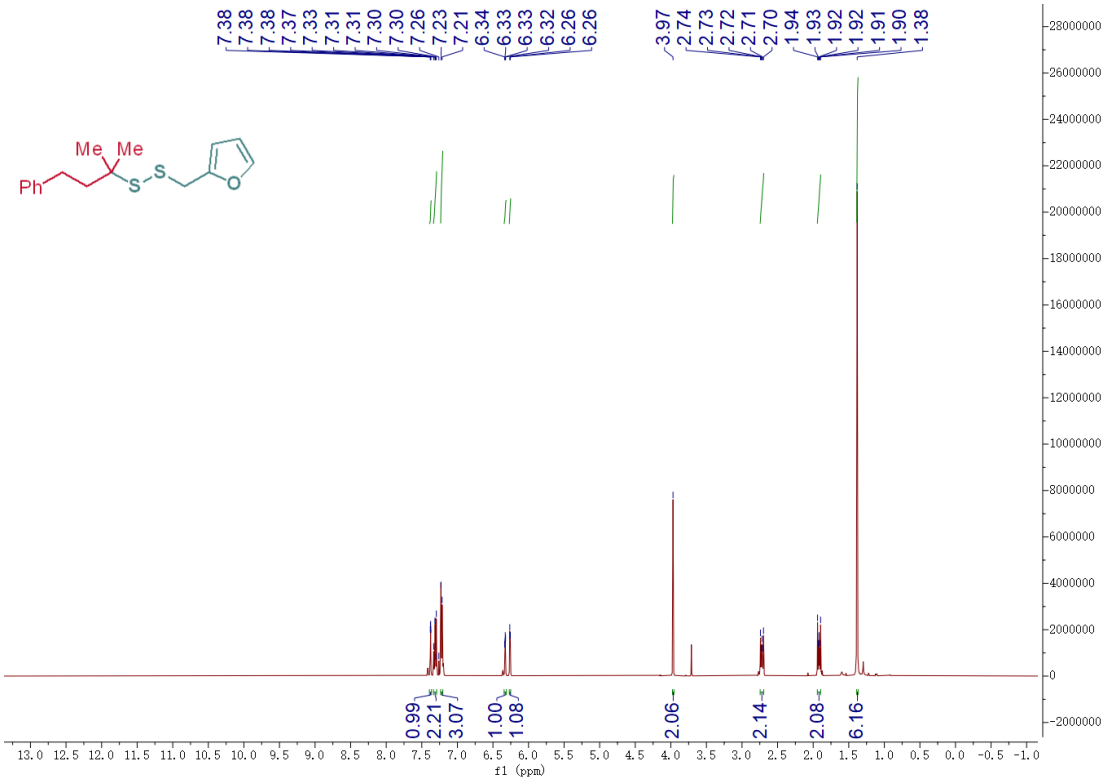
^{1}H NMR Spectrum of 5-Methyl-2-(2-((2-methyl-4-phenylbutan-2-yl)disulfaneyl) propan-2-yl)cyclohexan-1-one 4ad



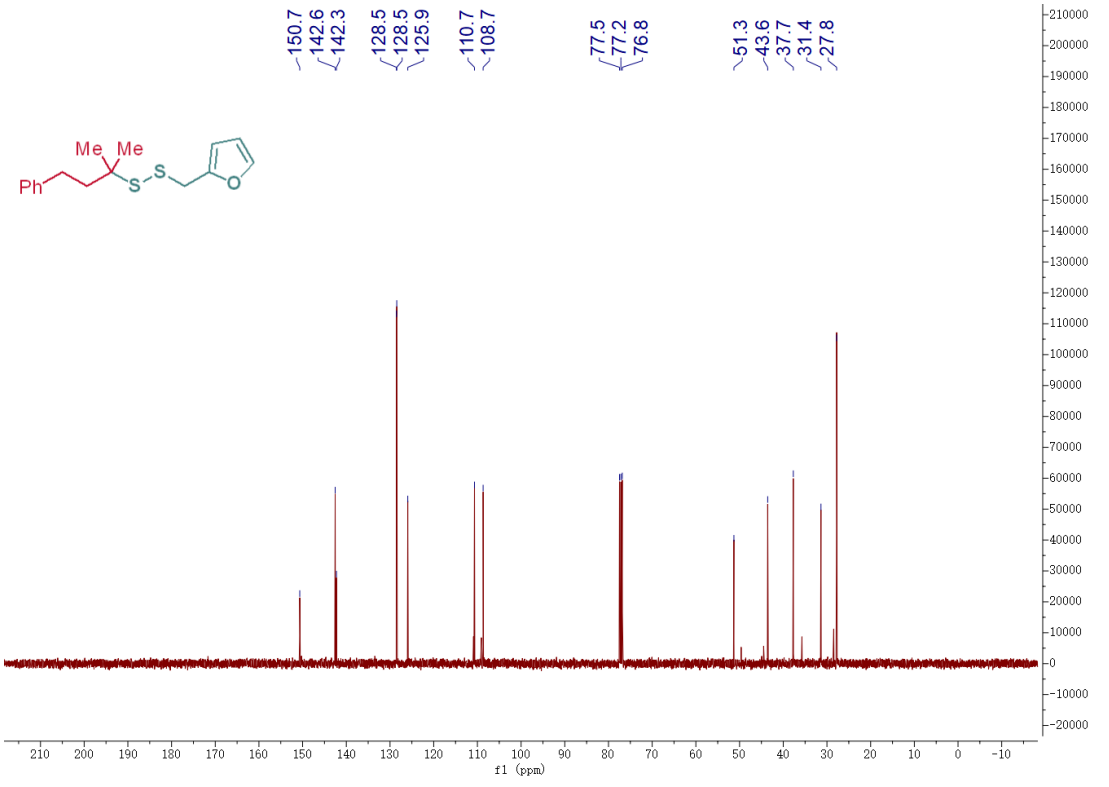
^{13}C NMR Spectrum of 5-Methyl-2-(2-((2-methyl-4-phenylbutan-2-yl)disulfaneyl) propan-2-yl)cyclohexan-1-one 4ad



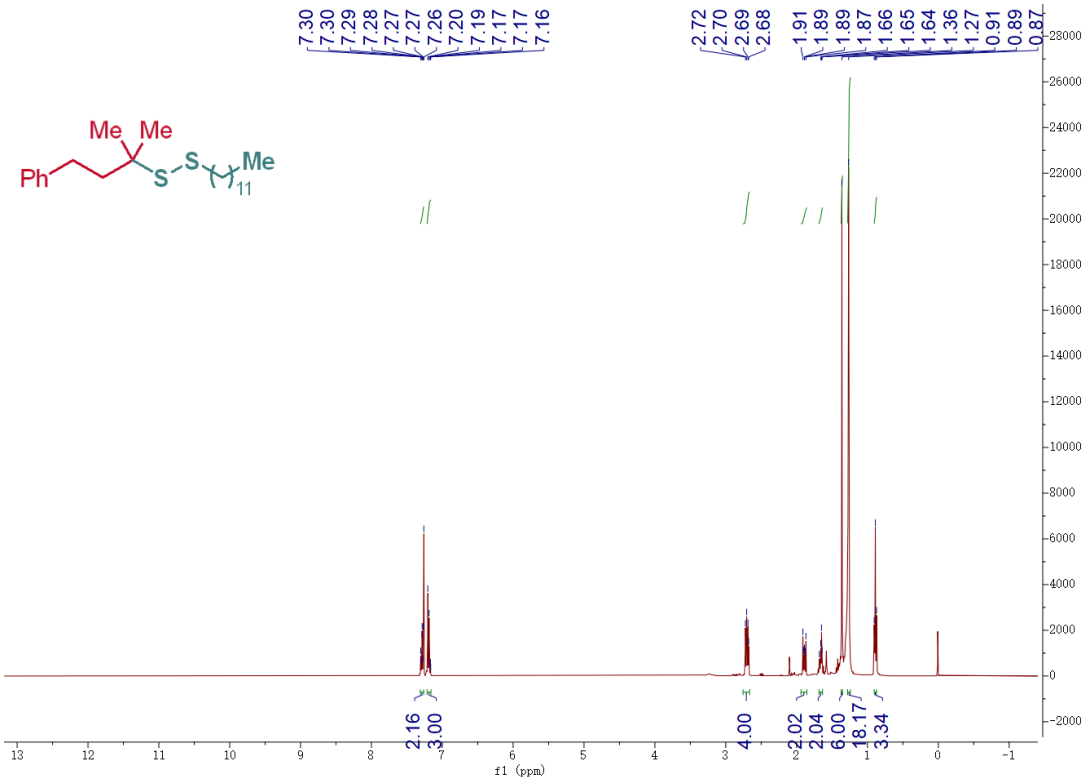
^{1}H NMR Spectrum of 2-(((2-Methyl-4-phenylbutan-2-yl)disulfaneyl)methyl) furan 4aj



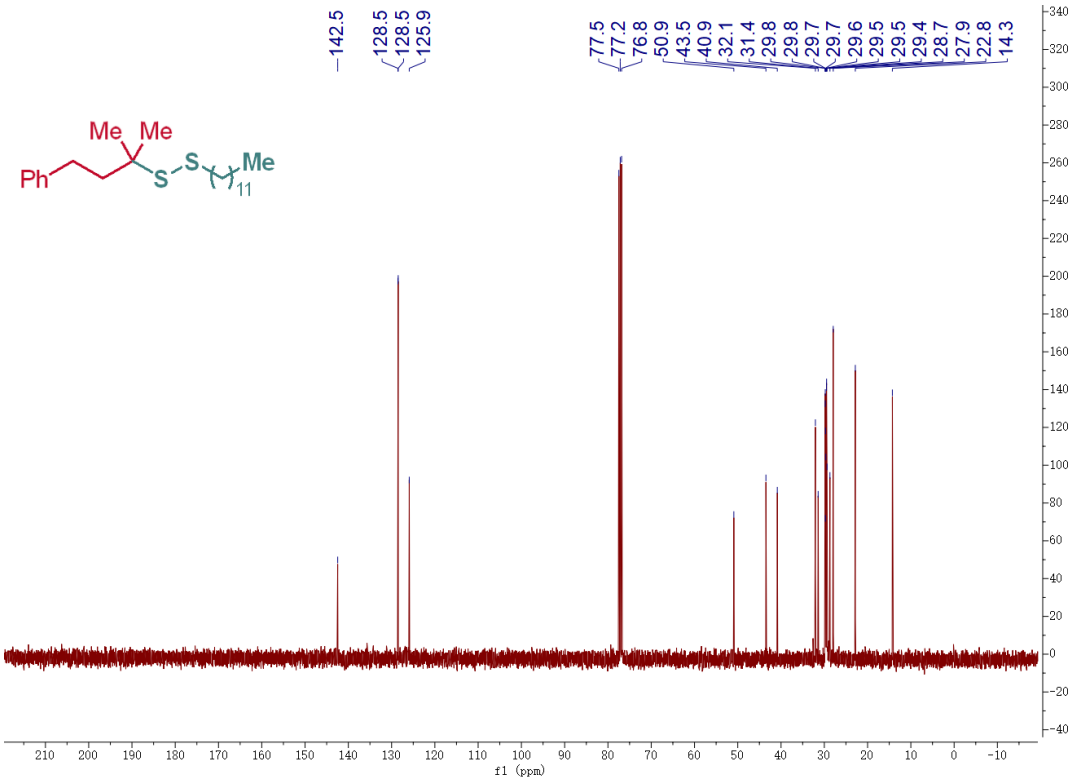
^{13}C NMR Spectrum of 2-(((2-Methyl-4-phenylbutan-2-yl)disulfaneyl)methyl) furan 4aj



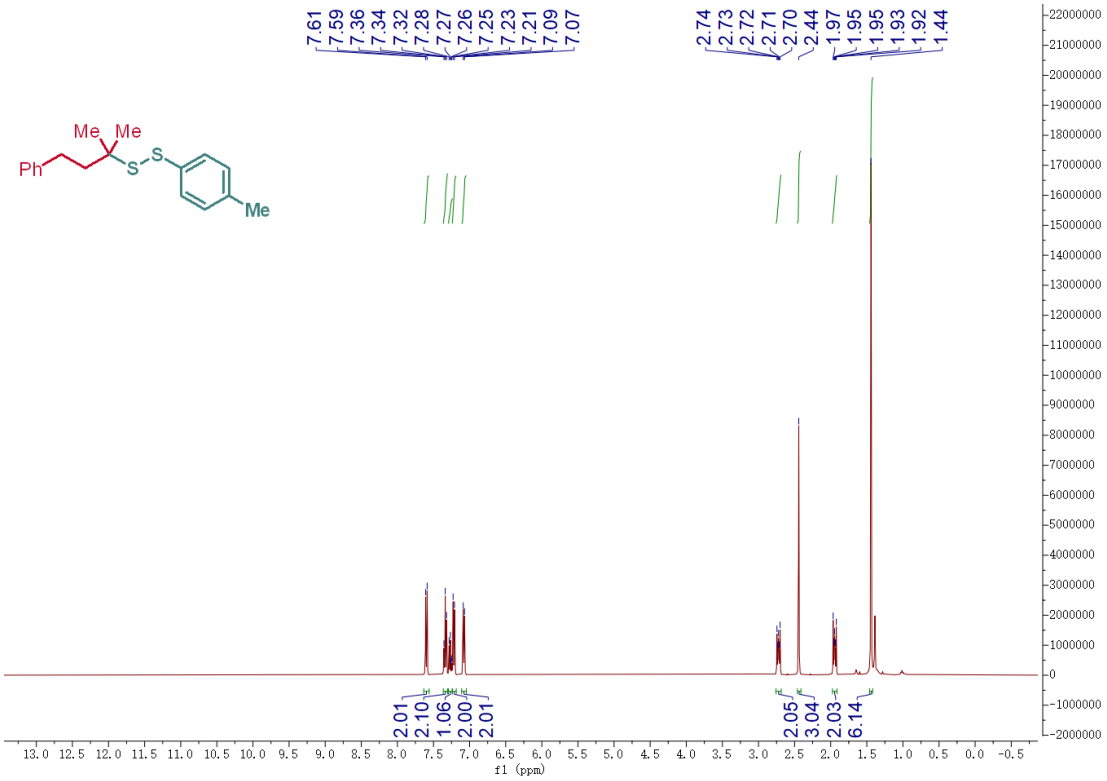
^{1}H NMR Spectrum of 1-Dodecyl-2-(2-methyl-4-phenylbutan-2-yl)disulfane 4y and 4al



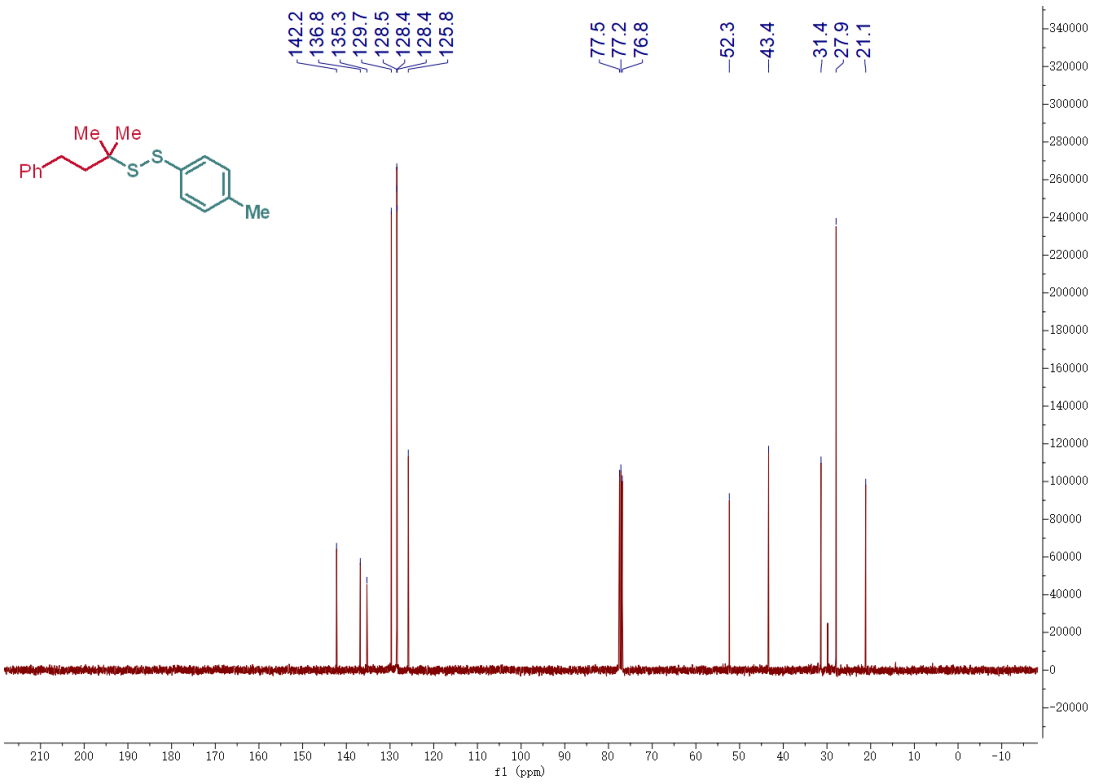
^{13}C NMR Spectrum of 1-Dodecyl-2-(2-methyl-4-phenylbutan-2-yl)disulfane 4y and 4al



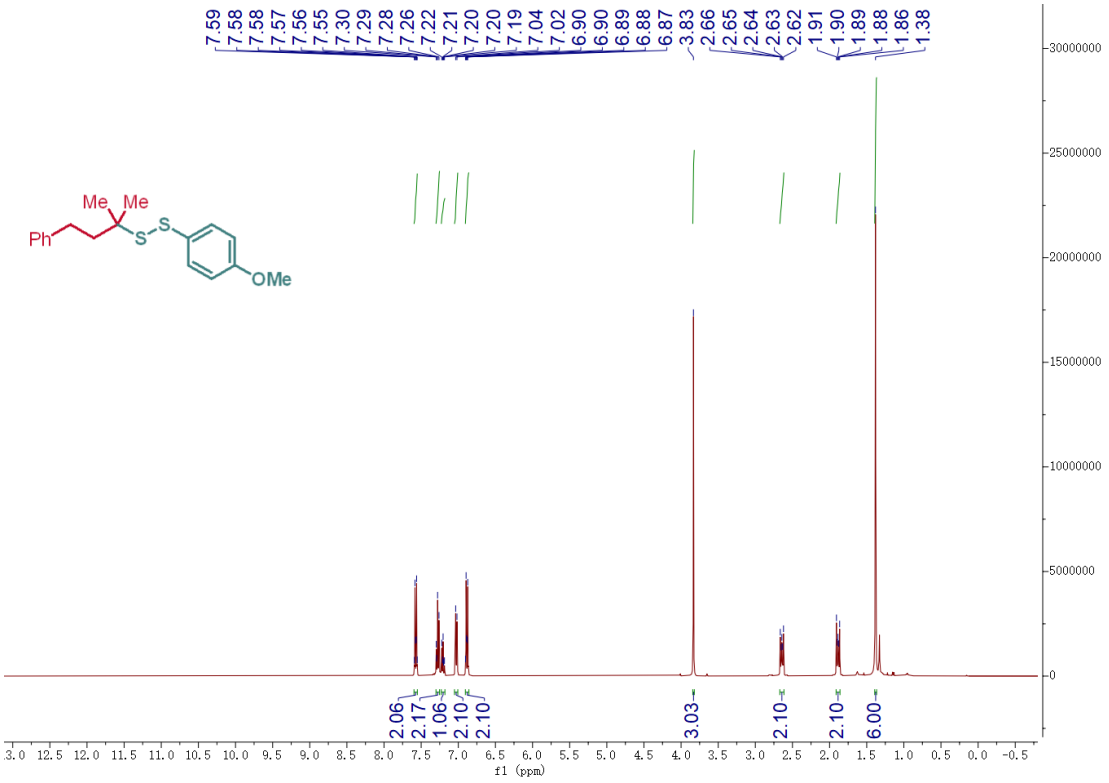
^{1}H NMR Spectrum of 1-(2-Methyl-4-phenylbutan-2-yl)-2-(*p*-tolyl)disulfane 4am



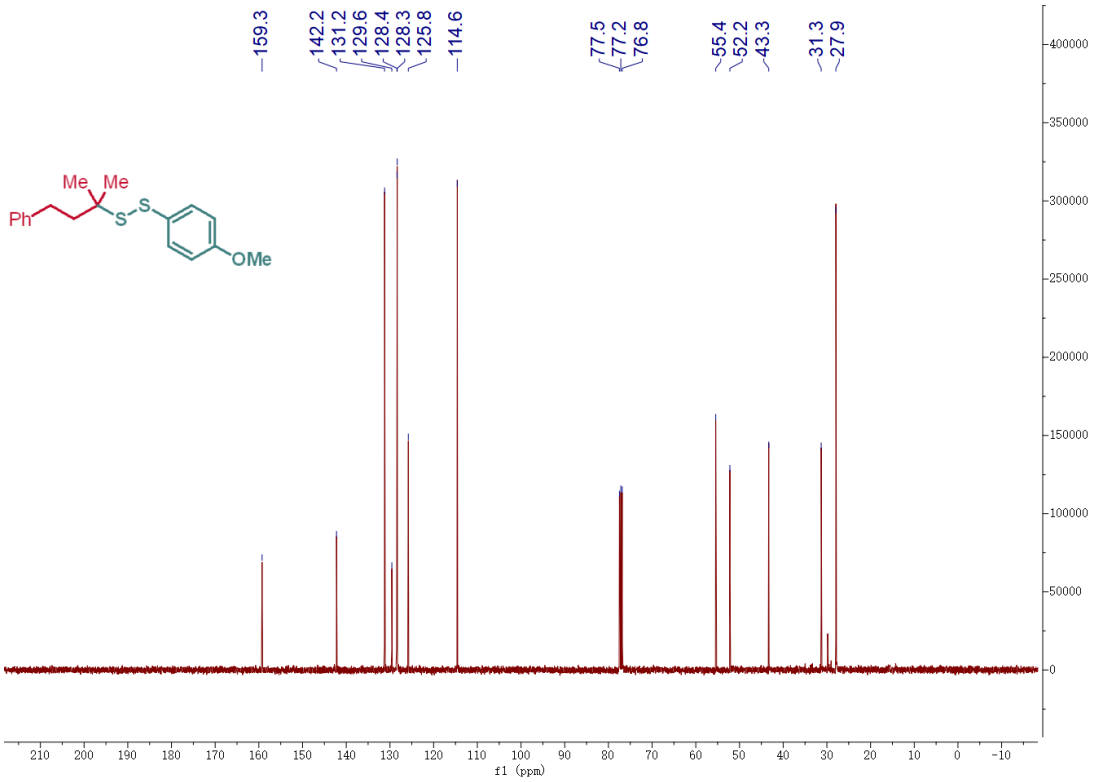
^{13}C NMR Spectrum of 1-(2-Methyl-4-phenylbutan-2-yl)-2-(*p*-tolyl)disulfane 4am



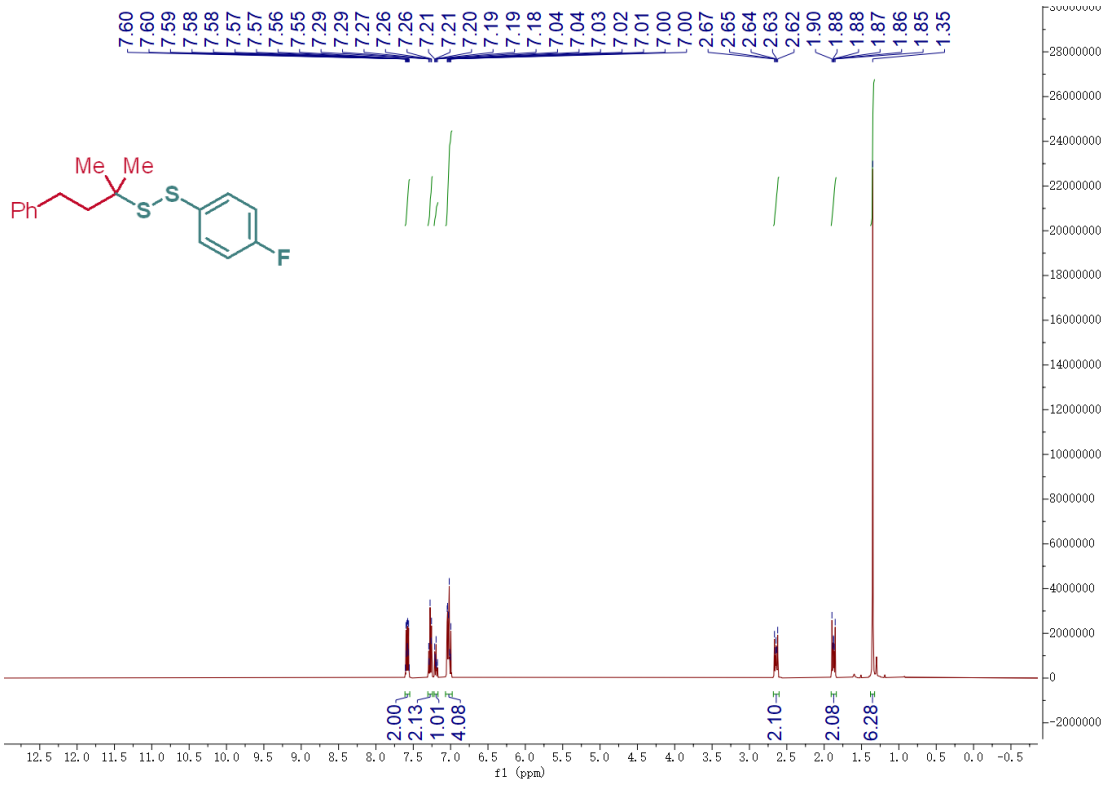
^{1}H NMR Spectrum of 1-(4-Methoxyphenyl)-2-(2-methyl-4-phenylbutan-2-yl)disulfane 4an



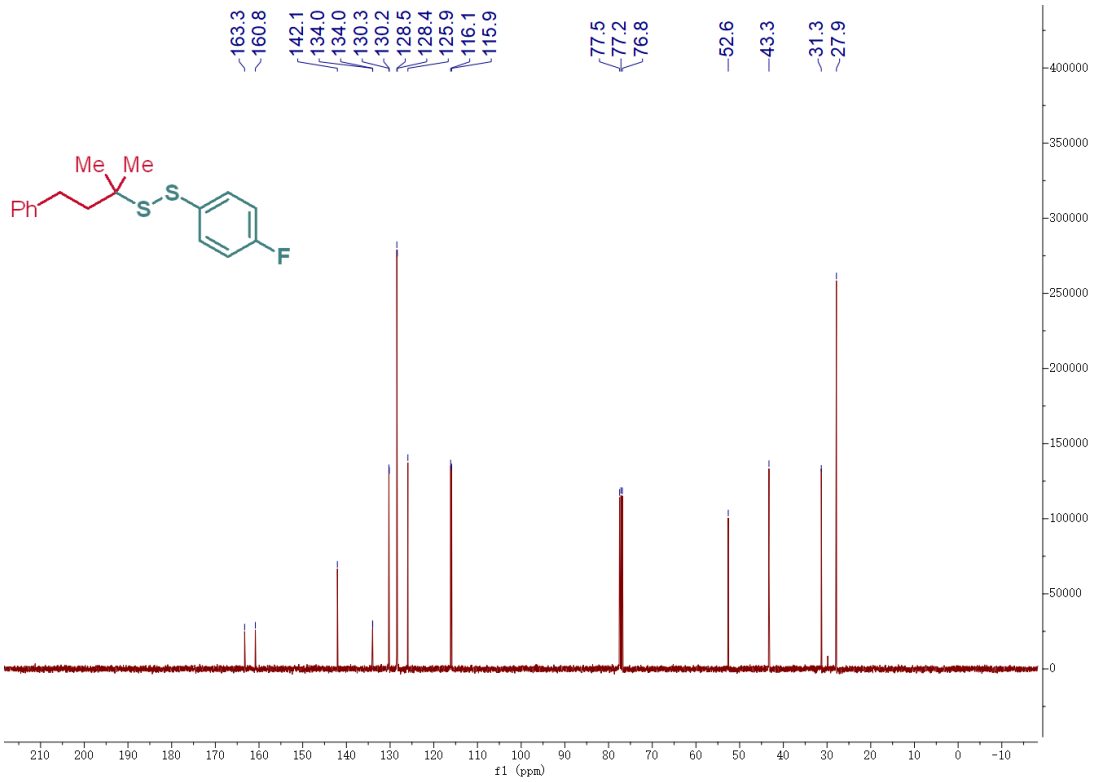
^{13}C NMR Spectrum of 1-(4-Methoxyphenyl)-2-(2-methyl-4-phenylbutan-2-yl)disulfane 4an



^{1}H NMR Spectrum of 1-(4-Fluorophenyl)-2-(2-methyl-4-phenylbutan-2-yl)disulfane 4ao



^{13}C NMR Spectrum of 1-(4-Fluorophenyl)-2-(2-methyl-4-phenylbutan-2-yl)disulfane 4ao



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