Supporting information

Polysulfide Synthesis via Visible-Light-Induced Heteroarene-Migratory Dithiosulfonylation Reaction

Baoxu Wang, Zijing Hu, Lu Huang, Xiaorui Ren, Qianwen Gao,* and Xi Wang*

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.

Greater Bay Area Institute for Innovation, Hunan University, Guangzhou 511300, P. R. China.

E-mail: cccewangxi@hnu.edu.cn, gaoqw@hnu.edu.cn

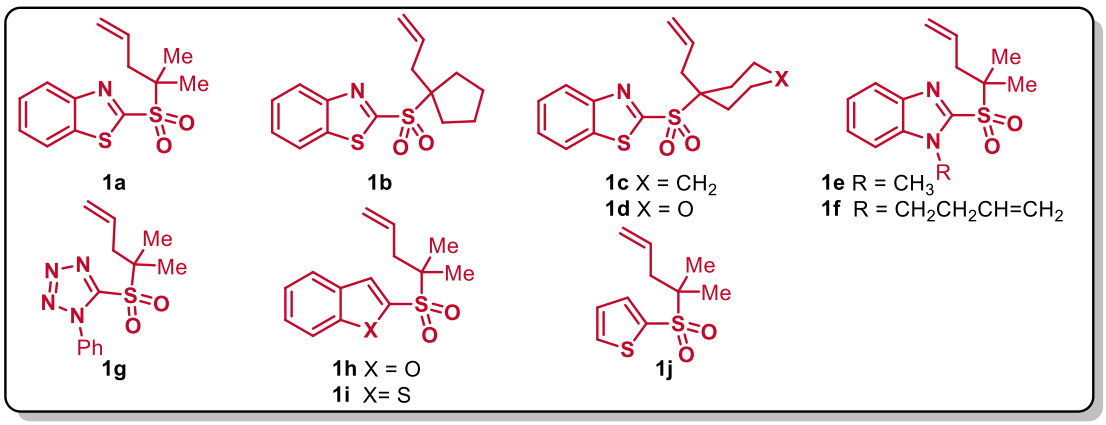
Table of Contents

1. General

All reactions involving air- or moisture-sensitive reagents or intermediates were carried out in flame-dried glassware under an argon 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. The reactions above room temperature were heated by oil bath. Commercially available reagents were used as received from Bide Pharmatech Ltd., Energy Chemical, Aladdin, Leyan, Alfa Aesar China, TCI China. For chromatography, 200-300 mesh silica gel (Qingdao, China) was employed. Analytical thin layer chromatography (TLC) was performed using silica gel plates. 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 Advance Neo 400 MHz and JEOL JNM-ECZ400S/L1 400MHz at 25 °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 77.00 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 and Thermo Finnigan MAT95XP. 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.

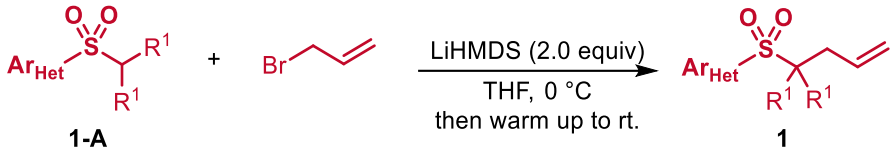
2. Preparation of starting materials

2.1 Preparation of substrates 1

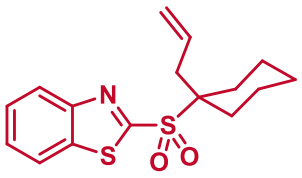


Substrates **1a-b**, **1h-j** prepared according to previously reported literature procedures.[1] Substrates **1c-g** was prepared according to the following procedure.

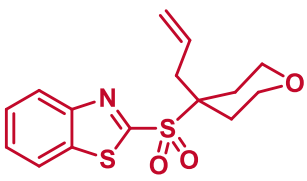
General procedure for the preparation of substrates 1 from allyl bromide (GP1)



A flame-dried Schlenk-flask equipped with a magnetic stir bar was charged with **1-A** (1.0 equiv) sealed with a septum, and degassed by alternating vacuum evacuation and nitrogen backfilling (three times) before allyl bromide (2.0 equiv) in THF was added. After that, the LiHMDS (1.0 M in THF, 2.0 equiv) was added dropwise over a period of 15 minutes at 0 °C subsequently. The reaction mixture was then stirred at room temperature for 5 h. After the reaction was complete, the reaction mixture was diluted with quenched by NH_4Cl (sat. aq.), which was followed by extraction with EtOAc. Then the organic phase was combined and dried over anhydrous Mg_2SO_4 and filtrated through a small pad of silica gel. The solvent was removed under reduced pressure with the aid of a rotary evaporator and the crude residue was purified by a silica gel column chromatography to give the corresponding pure substrates **1**.



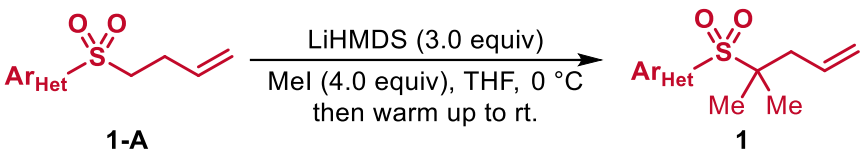
2-((1-Allylcyclohexyl)sulfonyl)benzo[*d*]thiazole (1c): The title compound was prepared according to general procedure (**GP1**) with **1c-A** (0.281 g, 1.00 mmol, 1.0 equiv), allyl bromide (0.242 g, 2.00 mmol, 2.0 equiv), and LiHMDS (1.0 M in THF, 2.0 mL, 2.00 mmol, 2.0 equiv) in THF (4.0 mL) at room temperature for 5 h. Purification via silica gel chromatography (PE:EtOAc = 10:1) gave the desired product **1c** as a white solid in 56% yield (0.180 g). **MP:** 99.2-100.6 °C; **TLC** $\mathbf{R_f}$ = 0.6 (PE:EtOAc = 5:1); **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 8.25 (d, J = 8.0 Hz, 1H), 8.01 (d, J = 7.9 Hz, 1H), 7.67-7.54 (m, 2H), 6.18-5.98 (m, 1H)., 5.19-5.05 (m, 2H), 2.75 (d, J = 7.0 Hz, 2H), 2.02 (dd, J^1 = 10.4 Hz, J^2 = 4.6 Hz, 4H), 1.76 (dt, J^1 = 13.6, J^2 = 3.9 Hz, 2H), 1.70-1.63 (m, 1H), 1.53-1.37 (m, 2H), 1.33-1.13 (m, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 164.5, 153.1, 137.3, 132.2, 127.8, 127.4, 125.7, 122.1, 118.9, 68.3, 34.7, 28.4, 24.5, 21.0; **HRMS** (EI) m/z = 321.0852, calcd. for $C_{16}H_{19}NO_2S_2$ $[M]^+$, found: 321.0850; **IR** (neat, cm^{-1}): 2935*m*, 2767*w*, 1468*m*, 1314*s*, 1142*m*, 1005*w*, 919*w*, 851*w*, 765*m*.



2-((4-Allyltetrahydro-2*H*-pyran-4-yl)sulfonyl)benzo[*d*]thiazole (1d): The title compound was prepared according to general procedure (**GP1**) with **1d-A** (0.198 g, 0.700 mmol, 1.0 equiv), allyl bromide (0.169 g, 1.400 mmol, 2.0 equiv),

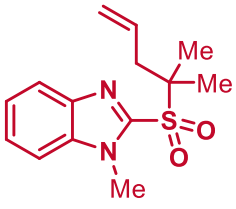
and LiHMDS (1.0 M in THF, 1.4 mL, 1.400 mmol, 2.0 equiv) in THF (2.5 mL) at room temperature for 5 h. Purification via silica gel chromatography (PE:EtOAc = 5:1) gave the desired product **1d** as a white solid in 75% yield (0.170 g). **MP:** 64.7-66.0 °C; **TLC** $\mathbf{R_f}$ = 0.6 (PE:EtOAc = 2:1); **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 8.21 (d, *J* = 7.9 Hz, 1H), 7.8 (d, *J* = 7.8 Hz, 1H), 7.64-7.52 (m, 2H), 6.06-5.92 (m, 1H), 5.16-5.08 (m, 2H), 3.93 (dt, J^1 = 12.0 Hz, J^2 = 4.1 Hz, 2H), 3.61-3.50 (m, 2H), 2.81 (d, *J* = 7.4 Hz, 2H), 2.37 (ddd, J^1 = 15.0 Hz, J^2 = 10.7 Hz, J^3 = 4.9 Hz, 2H), 1.88 (d, *J* = 14.5 Hz, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 163.4, 152.9, 137.0, 131.4, 128.0, 127.5, 125.5, 122.0, 119.8, 65.1, 62.7, 34.8, 28.4; **HRMS** (EI) *m*/*z* = 323.0644, calcd. for $C_{15}H_{17}NO_3S_2^+$ $[M]^+$, found: 323.0643; **IR** (neat, cm^{-1}): 2964*w*, 2861*w*, 1702*w*, 1468*m*, 1422*w*, 1319*s*, 1239*w*, 1159*m*, 1131*s*, 1097*m*, 1011*w*, 919*w*, 851*w*, 765*w*, 725*w*.

General procedure for the preparation of substrates 1 from methyl iodide (GP2)[2]



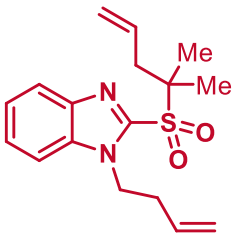
1-A **1**

A flame-dried Schlenk-flask equipped with a magnetic stir bar was charged with **1-A** (1.0 equiv) sealed with a septum, and degassed by alternating vacuum evacuation and nitrogen backfilling (three times) before THF was added. After that, the LiHMDS (1.0 M in THF, 3.0 equiv) was added dropwise over a period of 15 minutes at 0 °C subsequently at the same temperature for 30 min, MeI (4.0 equiv) was added, the reaction mixture was then stirred at room temperature for 5 h. After the reaction was complete, the reaction mixture was diluted with quenched by NH_4Cl (sat. aq.), which was followed by extraction with EtOAc. Then the organic phase was combined and dried over anhydrous Mg_2SO_4 and filtrated through a small pad of silica gel. The solvent was removed under reduced pressure with the aid of a rotary evaporator and the crude residue was purified by a silica gel column chromatography to give the corresponding pure substrates **1**.

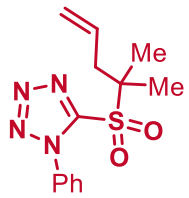


1-Methyl-2-((2-methylpent-4-en-2-yl)sulfonyl)-1*H*-benzo[*d*]imidazole (1e): The title compound was prepared according to general procedure (**GP2**) with **1e-A** (0.170 g, 0.850 mmol, 1.0 equiv), LiHMDS (1.0 M in THF, 2.25 mL, 2.25 mmol, 3.0 equiv), and MeI (3.40 mmol, 211 μL, 4.0 equiv) in THF (2.5 mL) at room temperature for 5 h. Purification via silica gel chromatography (PE:EtOAc = 20:1) gave the desired product **1e** as a white solid in 49% yield (0.117 g). **MP:** 65.4-66.7 °C **TLC** $\mathbf{R_f}$ = 0.3 (PE:EtOAc = 20:1); **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.93 (d, *J* = 8.1 Hz, 1H), 7.52-7.45 (m, 2H), 7.41 (ddd, J^1 = 8.3 Hz, J^2 = 6.1 Hz, J^3 = 2.2 Hz,

1H), 5.75 (ddt, J^1 = 17.4 Hz, J^2 = 9.7 Hz, J^3 = 7.5 Hz, 1H), 5.27-5.10 (m, 2H), 4.16 (s, 3H), 2.65 (d, J = 7.3 Hz, 2H), 1.44 (s, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 144.4, 141.3, 136.2, 130.9, 126.0, 124.1, 122.1, 120.5, 110.6, 65.1, 39.0, 32.2, 20.2; **HRMS** (EI) *m/z* = 278.1083, calcd. for $C_{14}H_{18}N_2O_2S^+$ $[M]^+$, found: 278.1083; **IR** (neat, cm^{-1}): 1456*m*, 1365*w*, 1314*s*, 1159*m*, 1119*m*, 1102*m*, 925*w*, 811*m*, 748*m*, 714*w*.

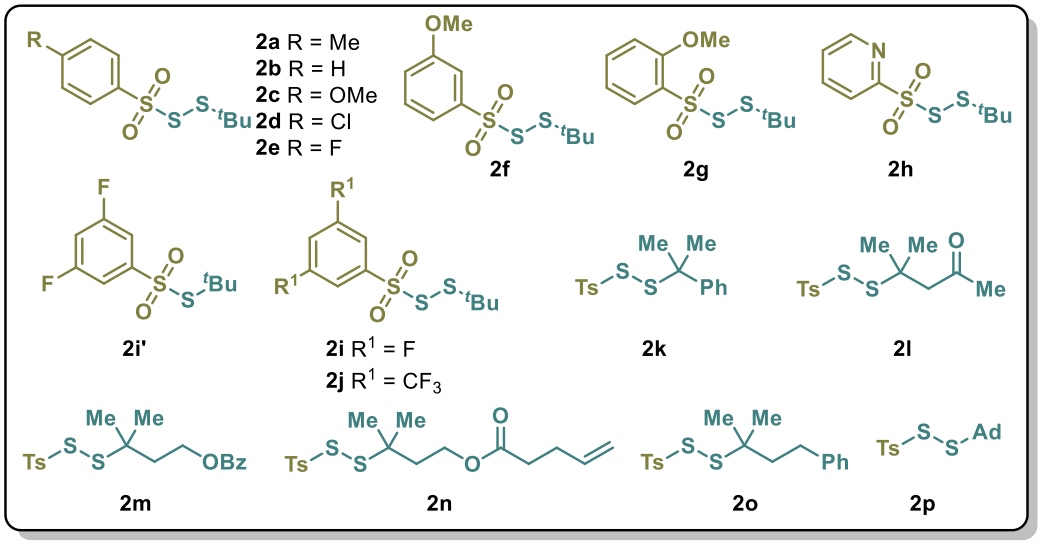


1-(But-3-en--yl)-2-((2-methylpent-4-en-2-yl)sulfonyl)-1*H*-benzo[*d*]imidazole (1f): The title compound was prepared according to general procedure (**GP2**) with **1f-A** (0.204 g, 0.700 mmol, 1.0 equiv), LiHMDS (1.0 M in THF, 2.1 mL, 2.10 mmol, 3.0 equiv), and MeI (3.40 mmol, 170 μL, 4.0 equiv) in THF (2.5 mL) at room temperature for 5 h. Purification via silica gel chromatography (PE:EtOAc = 20:1) gave the desired product **1f** as a colorless oil in 68% yield (0.152 g). **TLC R_f** = 0.4 (PE:EtOAc = 5:1); **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.93 (d, J = 8.4 Hz, 1H), 7.56-7.46 (m, 2H), 7.40 (ddd, J^1 = 8.2 Hz, J^2 = 5.2 Hz, J^3 = 3.1 Hz, 1H), 5.95-5.64 (m, 2H), 5.24-5.01 (m, 4H), 4.72-4.55 (m, 2H), 2.72-2.63 (m, 4H), 1.45 (s, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 144.4, 141.5, 135.3, 133.4, 131.0, 125.9, 124.0, 122.2, 120.4, 118.2, 111.1, 65.4, 45.3, 39.0, 34.8, 20.3; **HRMS** (EI) *m/z* =318.1397, calcd. for $C_{17}H_{22}N_2O_2S^+$ $[M]^+$, found: 318.1393; **IR** (neat, cm^{-1}): 2981*w*, 2935*w*, 1639*w*, 1462*w*, 1428*w*, 1345*w*, 1314*s*, 1159*w*, 1102*m*, 994*w*, 919*m*, 822*w*, 748*s*, 714*m*.



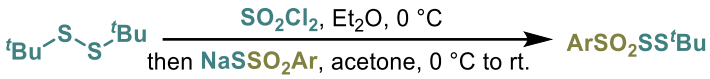
5-((2-Methylpent-4-en-2-yl)sulfonyl)-1-phenyl-1*H*-tetrazole (1g): The title compound was prepared according to general procedure (**GP2**) with **1g-A** (0.351 g, 1.33 mmol, 1.0 equiv), LiHMDS (1.0 M in THF, 4.0 mL, 4.00 mmol, 3.0 equiv), MeI (5.30 mmol, 330 μL, 4.0 equiv) in THF (5.0 mL) at room temperature for 5 h. Purification via silica gel chromatography (PE:EtOAc = 20:1) gave the desired product **1g** as a white solid in 83% yield (0.323 g). **MP:** 48.8-49.6 °C; **TLC R_f** = 0.3 (PE:EtOAc = 20:1); **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.87-7.44 (m, 5H), 5.72 (ddt, J^1 = 17.4 Hz, J^2 = 10.1 Hz, J^3 = 7.4 Hz, 1H), 5.30-5.10 (m, 2H), 2.66 (d, J = 7.4 Hz, 2H), 1.49 (s, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 151.9, 133.3, 131.4, 130.1, 129.3, 126.1, 121.2, 67.3, 38.9, 20.1; **HRMS** (EI) *m/z* = 292.0988, calcd. for $C_{13}H_{16}N_4O_2S^+$ $[M]^+$, found: 292.0989; **IR** (neat, cm^{-1}): 1496*w*, 1462*w*, 1336*s*, 1165*w*, 1114*m*, 925*w*, 765*m*, 731*w*.

2.2 Preparation of reagents 2

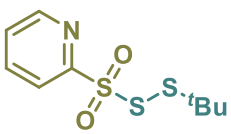


Reagents **2a-e**, **2k-l**, **2o-p**, prepared according to previously reported literature procedures.[3] Reagents **2f-j, 2m-n** was prepared according to the following procedure.

General procedure for the preparation of dithiosulfonate 2 from *tert*-butyldisulfide (GP3)[3]

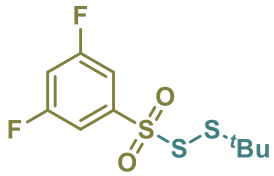


A flame-dried Schlenk-tube equipped with a magnetic stir bar was sealed with a septum, and degassed by alternating vacuum evacuation and argon backfilling (three times) before a solution of ^{t}BuSS^{t}Bu (1.0 equiv) in Et_2O was added. SO_2Cl_2 (1.0 equiv) was slowly added to the result solution at 0 ºC and the mixture was stirred at the same temperature for 1 h. Then a solution of $NaSSO_2Ar$ (2.0 equiv) in acetone was added slowly at 0 ºC and then the mixture was allowed to warm to room temperature stirred for 2 h. After the reaction was complete, the precipitate was filtered and the filtrate was evaporated under reduced pressure with the aid of a rotary evaporator the crude residue was purified by column chromatography to give the desired product.

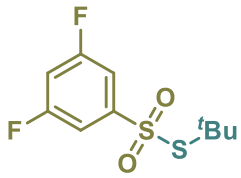


***SS*-(*tert*-Butyl) pyridine-2-sulfono(dithioperoxoate) (2h):** The title compound was prepared according to general procedure (**GP3**) with ^{t}BuSS^{t}Bu (0.446 g, 2.50 mmol, 1.0 equiv), SO_2Cl_2 (0.338 g, 2.50 mmol, 1.0 equiv), and sodium pyridine-2-sulfonothioate (1.000 g, 5.00 mmol, 2.0 equiv) in Et_2O and acetone (10 mL + 15 mL). Purification via silica gel chromatography (PE:EtOAc = 10:1) gave the desired product **2h** as a brown oil in 55% yield (0.723 g). **TLC R_f** = 0.2 (PE:EtOAc = 10:1); **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 8.79 (d, *J* = 4.5 Hz, 1H), 8.03 (d, *J* = 7.7 Hz, 1H), 7.97 (td,

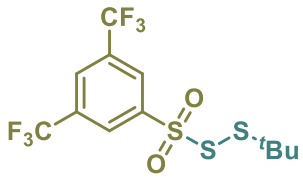
J^1 = 7.7 Hz, J^2 = 1.7 Hz, 1H), 7.57 (ddd, J^1 = 7.6 Hz, J^2 = 4.7 Hz, J^3 = 1.3 Hz, 1H), 1.37 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 159.3, 150.5, 138.1, 127.7, 122.8, 50.4, 30.0; **HRMS** (ESI) *m/z* = 286.0001, calcd. for $C_9H_{13}NO_2S_3Na^+$ $[M+Na]^+$, found: 286.0011; **IR** (neat, cm^{-1}): 2964*w*, 2924*w*, 1576*w*, 1451*w*, 1428*w*, 1365*w*, 1331*s*, 1154*s*, 1102*m*, 1079*w*, 988*w*, 777*w*, 731*w*.



***SS*-(*tert*-Butyl) 3,5-difluorobenzenesulfono(dithioperoxoate) (2i):** The title compound was prepared according to general procedure (**GP3**) with ^{t}BuSS^{t}Bu (0.892 g, 5.0 mmol, 1.0 equiv), SO_2Cl_2 (0.675 g, 5.00 mmol, 1.0 equiv), and sodium 3,5-difluorobenzenesulfonothioate (2.322 g, 10.00 mmol, 2.0 equiv) in Et_2O and acetone (20 mL + 30 mL), Purification via silica gel chromatography (PE:EtOAc = 200:1) gave the desired product **2i** as a colorless oil in 70% yield (1.045 g). **TLC R_f** = 0.6 (PE:EtOAc = 50:1); **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.46 (ddd, J^1 = 4.9 Hz, J^2 = 2.3 Hz, J^3 = 1.2 Hz, 2H), 7.10 (tt, J^1 = 8.4 Hz, J^2 = 2.3 Hz, 1H), 1.42 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 162.6 (dd, J^1 = 255.8 Hz, J^2 = 11.5 Hz), 145.7 (dd, J^1 = 8.4 Hz, J^2 = 8.4 Hz), 111.4 (dd, J^1 = 28.5 Hz, J^2 = 11.4 Hz), 109.5 (dd, J^1 = 25.0 Hz, J^2 = 25.0 Hz), 50.9, 30.2; **HRMS** (ESI) *m/z* =320.9860, calcd. for $C_{10}H_{12}O_2F_2S_3Na^+$ $[M+Na]^+$, found: 320.9865; **IR** (neat, cm^{-1}): 2965*w*, 2898*w*, 2864*w*, 1603*m*, 1441*m*, 1368*w*, 1336*m*, 1295*m*, 1127*s*, 1075*m*, 988*m*, 861*m*.



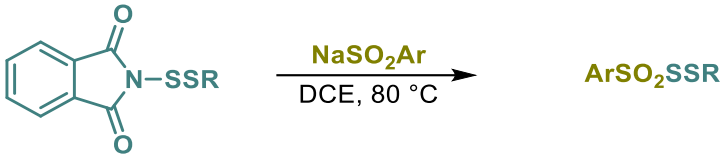
***S*-(*tert*-Butyl) 3,5-difluorobenzenesulfonothioate (2i'):** The title compound was isolated as a by-product from the 2i preparation process. **2i'** as a colorless oil in 25% yield (0.290 g). **TLC R_f** = 0.6 (PE:EtOAc = 50:1); **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.58-7.44 (m, 2H), 7.14-6.99 (m, 1H), 1.49 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 162.5 (dd, J^1 = 255.5 Hz, J^2 = 11.5 Hz), 149.7 (dd, J^1 = 8.2 Hz, J^2 = 8.2 Hz), 110.5 (dd, J^1 = 28.4 Hz, J^2 = 11.6 Hz), 108.9 (dd, J^1 = 25.1 Hz, J^2 = 25.1 Hz), 56.4, 30.8; **^{19}F NMR** (377 MHz, $CDCl_3$, 300 K): δ (ppm) = -105.0. **HRMS** (ESI) *m/z* =289.0139, calcd. for $C_{10}H_{12}O_2F_2S_2Na^+$ $[M+Na]^+$, found: 289.0144; **IR** (neat, cm^{-1}): 3090*w*, 2964*w*, 2924*w*, 1605*m*, 1439*m*, 1371*w*, 1331*m*, 1296*m*, 1131*s*, 1074*w*, 988*w*, 862*w*.



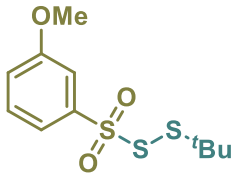
***SS*-(*tert*-Butyl) 3,5-bis(trifluoromethyl)benzenesulfono(dithioperoxoate) (2j)**: The title compound was prepared according to general procedure (**GP3**) with ^{t}BuSS^{t}Bu (0.892 g, 5.00 mmol, 1.0 equiv), SO_2Cl_2 (0.675 g, 5.00 mmol, 1.0 equiv), and sodium 3,5-difluorobenzenesulfonothioate (3.322 g, 10.00 mmol, 2.0 equiv) in Et_2O (20 mL) and acetone (30 mL). Purification via silica

gel chromatography (PE:EtOAc = 200:1) gave the desired product **2j** as a colorless oil in 47% yield (0.930 g). **TLC R_f** = 0.7 (PE:EtOAc = 50:1); **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 8.34 (s, 2H), 8.13 (s, 1H), 1.42 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 145.2, 133.0 (q, J = 34.8 Hz), 128.0 (q, J = 3.8 Hz), 127.3 (h, J = 3.6 Hz), 122.3 (q, J = 273.5 Hz), 51.2, 30.1; **HRMS** (ESI) m/z = 398.9976, calcd. for $C_{12}H_{13}O_2F_6S_3^+$ $[M+H]^+$, found: 398.9991; **IR** (neat, cm^{-1}): 2968*w*, 2927*w*, 2865*w*, 1356*m*, 1278*s*, 1137*m*, 1098*m*, 904*m*, 844*w*.

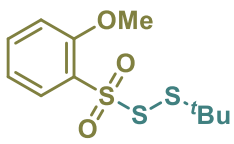
General procedure for the preparation of dithiosulfonate 2 from Harpp reagent (GP4)



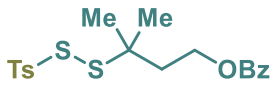
Dithiosulfonate **2k-2p** were prepared from from *N*-phthalimide disulfide[24]. A flame-dried Schlenk-flask equipped with a magnetic stir bar and a reflux condenser was charged with *N*-phthalimide disulfide (1.00 mmol, 1.0 equiv) and $NaSO_2Ar$ (1.00 mmol, 1.0 equiv) before DCE (10 mL) was added. The reaction mixture was stirred at 80 ºC for 8 h. After the reaction was complete, the reaction mixture was cooled to room temperature and filtered through a plug of Celite. Solvent was removed under reduced pressure with the aid of a rotary evaporator and the crude residue was purified by column chromatography to afford the desired product.



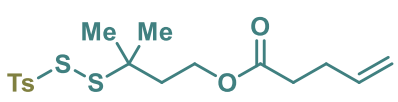
***SS*-(*tert*-Butyl) 3-methoxybenzenesulfono(dithioperoxoate) (2f):** The title compound was prepared according to general procedure (**GP4**) with 2-(*tert*-butyldisulfaneyl)isoindoline-1,3-dione (0.267 g, 1.00 mmol, 1.0 equiv) and sodium 3-methoxybenzenesulfinate (0.194 g, 1.00 mmol, 1.0 equiv) in DCE (10 mL) at 80 ºC for 8 h. Purification via silica gel chromatography (PE:EtOAc = 20:1) gave the desired product **2f** as a colorless oil in 66% yield (0.194 g). **TLC R_f** = 0.4 (PE:EtOAc = 20:1); **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.52 (ddd, J^1 = 7.8 Hz, J^2 = 1.7 Hz, J^3 = 1.1 Hz, 1H), 7.45 (t, J = 8.0 Hz, 1H), 7.40 (dd, J^1 = 2.6 Hz, J^2 = 1.7 Hz, 1H), 7.16 (ddd, J^1 = 8.2 Hz, J^2 = 2.6 Hz, J^3 = 1.1 Hz, 1H), 3.88 (s, 3H), 1.39 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 159.9, 144.1, 130.0, 120.6, 120.1, 112.1, 55.7, 50.4, 30.2; **HRMS** (ESI) m/z = 315.0154, calcd. for $C_{11}H_{16}O_3S_3Na^+$ $[M+Na]^+$, found: 315.0163; **IR** (neat, cm^{-1}): 2964*w*, 1593*w*, 1479*m*, 1433*w*, 1365*w*, 1319*m*, 1285*w*, 1245*m*, 1159*w*, 1137*s*, 1091*w*, 1068*w*, 1039*w*, 851*w*, 782*w*.



***SS*-(*tert*-Butyl) 2-methoxybenzenesulfono(dithioperoxoate) (2g):** The title compound was prepared according to general procedure (**GP4**) with 2-(*tert*-butyldisulfaneyl)isoindoline-1,3-dione (0.267 g, 1.00 mmol, 1.0 equiv) and sodium 2-methoxybenzenesulfinate (0.194 g, 1.00 mmol, 1.0 equiv) in DCE (10 mL) at 80 ºC for 8 h. Purification via silica gel chromatography (PE:EtOAc = 20:1) gave the desired product **2g** as a colorless oil in 65% yield (0.189 g). **TLC R_f** = 0.4 (PE:EtOAc = 5:1); **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.87 (dd, J^1 = 8.1 Hz, J^2 = 1.7 Hz, 1H), 7.58 (ddd, J^1 = 8.4 Hz, J^2 = 7.5 Hz, J^3 = 1.8 Hz, 1H), 7.10-7.01 (m, 2H), 4.03 (s, 3H), 1.33 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 157.1, 135.7, 131.2, 129.8, 120.1, 112.6, 56.4, 50.0, 30.0; **HRMS** (ESI) *m*/*z* = 315.0154, calcd. for $C_{11}H_{16}O_3S_3Na^+$ $[M+Na]^+$, found: 315.0159; **IR** (neat, cm^{-1}): 2964*w*, 1588*w*, 1479*m*, 1433*w*, 1365*w*, 1319*s*, 1279*m*, 1251*w*, 1142*s*, 1125*s*, 1062*w*, 1017*w*, 800*w*, 760*m*, 725*w*.

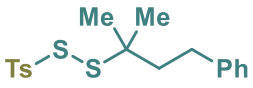


3-(3,3-Dioxo-3-(p-tolyl)-3λ^6-trisulfaneyl)-3-methylbutyl benzoate (2m): The title compound was prepared according to general procedure (**GP4**) with 3-((1,3-dioxoisoindolin-2-yl)disulfaneyl)-3-methylbutyl benzoate (0.402 g, 1.00 mmol, 1.0 equiv) and sodium sodium 4-methylbenzenesulfinate (0.178 g, 1.00 mmol, 1.0 equiv) in DCE (10 mL) at 80 ºC for 8 h. Purification via silica gel chromatography (PE:EtOAc = 10:1) gave the desired product **2m** as a colorless oil in 67% yield (0.275 g). **TLC R_f** = 0.5 (PE:EtOAc = 10:1); **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 8.06-7.99 (m, 2H), 7.80 (d, *J* = 8.3 Hz, 2H), 7.56 (t, *J* = 7.3 Hz, 1H), 7.44 (t, *J* = 7.7 Hz, 2H), 7.33 (d, *J* = 8.1 Hz, 2H), 4.47 (t, *J* = 6.6 Hz, 2H), 2.43 (s, 3H), 2.15 (t, *J* = 6.6 Hz, 2H), 1.45 (s, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 166.4, 145.2, 140.0, 133.0, 130.1, 129.8, 129.5, 128.4, 127.9, 61.7, 52.2, 40.1, 28.2, 21.7; **HRMS** (ESI) *m*/*z* = 411.0753, calcd. for $C_{19}H_{23}O_4S_3^+$ $[M+H]^+$, found: 411.0753; **IR** (neat, cm^{-1}): 2964*w*, 2924*w*, 1713*s*, 1593*w*, 1451*w*, 1325*m*, 1274*s*, 1137*s*, 1114*s*, 1074*s*, 1022*w*, 811*w*, 708*s*.



3-(3,3-Dioxo-3-(*p*-tolyl) -3λ^6-trisulfaneyl)-3-methylbutylpent-4-enoate (2n): The title compound was prepared according to general procedure (**GP4**) with 3-((1,3-dioxoisoindolin-2-yl)disulfaneyl)-3-methylbutyl pent-4-enoate (0.379 g, 1.00 mmol, 1.0 equiv) and sodium 4-methylbenzenesulfinate (0.178 g, 1.00 mmol, 1.0 equiv) in DCE (10 mL) at 80 ºC for 8 h. Purification via silica gel chromatography (PE:EtOAc = 10:1) gave the desired product **2n** as a colorless oil in 65% yield (0.253 g). **TLC R_f** = 0.3 (PE:EtOAc = 10:1); **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.80 (d, *J* = 8.3 Hz, 2H), 7.35 (d, *J* = 8.1 Hz, 2H), 6.08-5.66 (m, 1H), 5.23-4.92 (m, 2H), 4.22 (t, *J* = 6.8 Hz, 2H), 2.45 (s, 3H), 2.43-2.34 (m, 4H), 2.00 (t, *J* = 6.8 Hz, 2H), 1.39 (s, 6H);

^{13}C NMR (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 172.9, 145.2, 140.1, 136.6, 129.8, 127.9, 115.5, 61.1, 52.0, 40.0, 33.5, 28.7, 28.1, 21.7; **HRMS** (ESI) *m/z* = 411.0729, calcd. for $C_{17}H_{24}O_4S_3Na^+$ $[M+Na]^+$, found: 411.0737; **IR** (neat, cm^{-1}): 2965*w*, 2924*w*, 1735*s*, 1593*w*, 1453*w*, 1328*m*, 1166*w*, 1141*s*, 1078*m*, 917*w*, 812*w*, 702*w*.

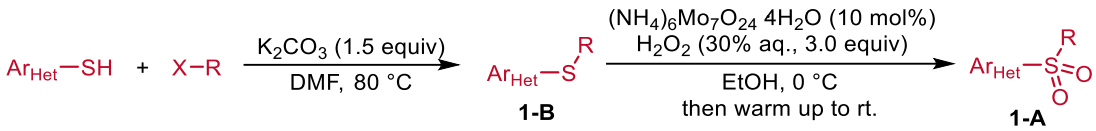


***SS*-(2-methyl-4-phenylbutan-2-yl) 4-methylbenzen-esulfono (dithioperoxoate) (2o):** The title compound was prepared according to general procedure (**GP4**) with 2-((2-methyl-4-phenylbutan-2-yl)disulfaneyl)isoindoline-1,3-dione (0.357 g, 1.00 mmol, 1.0 equiv) and sodium 4-methylbenzenesulfinate (0.178 g, 1.00 mmol, 1.0 equiv) in DCE (10 mL) at 80 ºC for 8 h. Purification via silica gel chromatography (PE:EtOAc = 10:1) gave the desired product **2o** as a colorless oil in 66% yield (0.242 g). **TLC R_f** = 0.4 (PE:EtOAc = 50:1); **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.80 (d, *J* = 8.4 Hz, 2H), 7.34-7.25 (m, 4H), 7.22-7.16 (m, 3H), 2.72-2.64 (m, 2H), 2.43 (s, 3H), 1.95-1.87 (m, 2H), 1.41 (s, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 145.1, 141.5, 140.1, 129.7, 128.4, 128.3, 127.9, 125.9, 53.5, 44.0, 31.2, 28.0, 21.7; **HRMS** (ESI) *m/z* = 389.0674, calcd. for $C_{18}H_{22}O_2S_3Na$ $[M+Na]^+$, found: 389.0684; **IR** (neat, cm^{-1}): 3027*w*, 2961*w*, 2925*w*, 2861*w*, 1593*w*, 1498*w*, 1453*w*, 1325*m*, 1138*s*, 1077*m*, 811*w*, 745*w*.

2.3 Preparation of other reagents

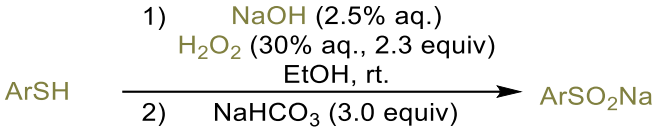
The **PC**, solvent, were commercially available from Energy Chemical, Aladdin, Leyan, Alfa Aesar China, TCI China.

Synthesis of 1-A and 1-B [4]



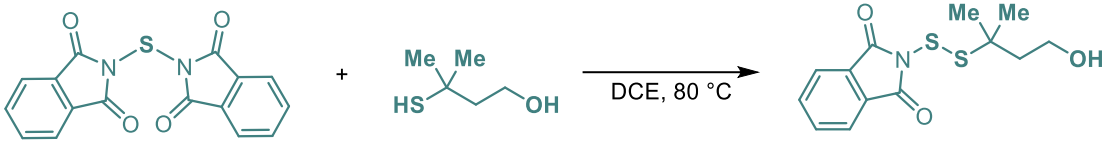
A flame-dried Schlenk-flask equipped with a magnetic stir bar was charged with $Ar_{Het}SH$ (1.0 equiv), compound alkyl halide (1.5 equiv), K_2CO_3 (1.5 equiv), and DMF was added, sealed with a septum. The reaction mixture was then stirred at 80 ºC for 6 h. The mixture was quenched with H_2O, extracted with EtOAc (15 mL × 3). The combined organic layer was washed with brine (15 mL × 3), dried over Na_2SO_4, and concentrated. The crude sulfide product **1-B** was used in the next step without further purification. The sulfide (1.0 equiv) was dissolved in EtOH, $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$ (10 mol%), and H_2O_2 (30% aq., 3.0 equiv) was added at 0 ºC. The resulting mixture was stirred at room temperature for 6 h, the mixture was quenched with $Na_2S_2O_3$ (sat. aq.), extracted with EtOAc (15 mL × 3). The combined organic layer was washed with brine (30 mL × 3), dried over Na_2SO_4, and concentrated. The crude compound **1-A** was used in the next step without further purification.

Synthesis of sulfonic acid sodium [5]

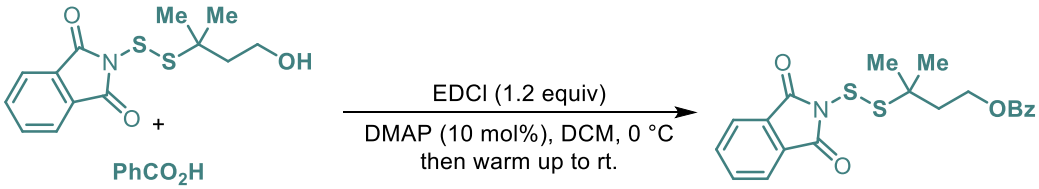


A Schlenk-flask equipped with a magnetic stir bar was charged with thiol (3.00 mmol, 1.0 equiv), NaOH (2.5% aq., 15 mL), and ethanol (15 mL). H_2O_2 (30% aq., 0.7 mL) was added to the solution with stirring at room temperature (exothermic) for 6 h. Then $NaHCO_3$ (9.00 mmol, 3.0 equiv) was added to the solution with stirring for 30 min, the solvent was evaporated off under reduced pressure. Wash the residue with ethyl alcohol (30 mL × 3). Evaporate the liquid phase to obtain sodium sulfonic acid salt.

Synthesis of *N*-dithiophthalimide reagents

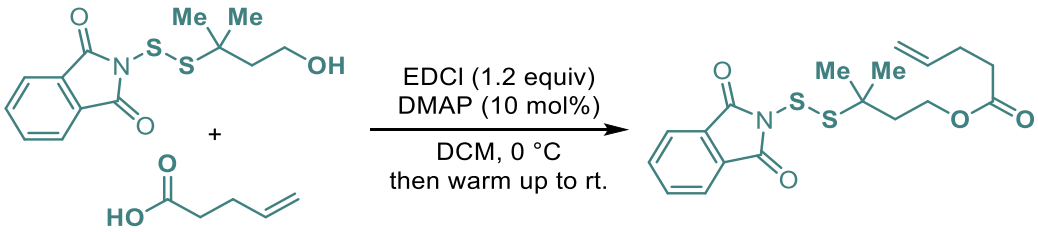


A flame-dried Schlenk-flask equipped with a magnetic stir bar was charged with *N*,*N*'-thiobisphthalimide (4.400 g, 13.50 mmol), 3-mercapto-3-methylbutan-1-ol (1.000 g, 9.000 mmol), and DCE (30 mL), sealed with a septum. The resulting mixture was stirred at 80 ºC for 6 h, and then cooled down to room temperature. The precipitate was removed by filtration, and the filtrate was concentrated and purification via silica gel chromatography (PE:EtOAc = 1:1) gave 2-((4-hydroxy-2-methylbutan-2-yl) disulfaneyl)isoindoline -1,3-dione as a yellow oil in 42% (1.259 g). **TLC R_f** = 0.2 (PE:EtOAc = 2:1); **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.92 (dd, J^1 = 5.5 Hz, J^2 = 3.1 Hz, 2H), 7.79 (dd, J^1 = 5.6 Hz, J^2 = 3.1 Hz, 2H), 3.70 (t, J = 6.9 Hz, 2H), 2.03 (t, J = 6.9 Hz, 2H), 1.63 (*br*, 1H), 1.41 (s, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 167.5, 134.7, 132.0, 124.0, 59.5, 51.1, 43.4, 28.1; **IR** (neat, cm^{-1}): 3498*br*, 2961*w*, 2918*w*,1785*w*, 1785*w*, 1736*s*, 1732*s*, 1702*m*, 1468*w*, 1366*w*, 1271*s*, 1124*w*, 1049*m*, 867*w*, 735*w*, 714*m*.



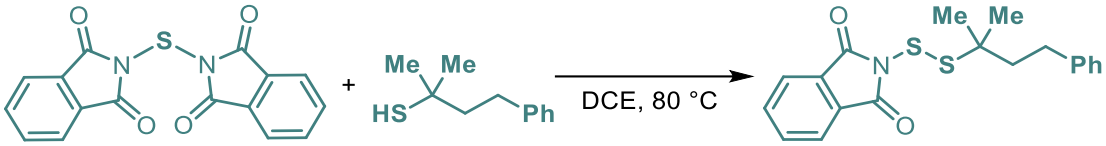
A flame-dried Schlenk-flask equipped with a magnetic stir bar was charged with 2-((4-hydroxy-2-methylbutan-2-yl)disulfaneyl)isoindoline-1,3-dione (0.489 g, 1.65 mmol, 1.0 equiv), EDCI (0.380 g, 1.98 mmol, 1.2 equiv), DMAP (20 mg, 0.165 mmol,

10 mol %), benzoic acid (0.212 g, 1.12 mmol, 1.2 equiv), and DCM (15 mL) were added. The reaction mixture was stirred at room temperature until the disappearance of 2-((4-hydroxy-2-methylbutan-2-yl) disulfaneyl)isoindoline-1,3-dione as monitored by TLC. The mixture was diluted with water, extracted with DCM (10 mL × 3), dried over anhydrous sodium sulfate, and filtered. The solvent was removed under reduced pressure. The residue was purified by flash column chromatography on silica gel (PE:EtOAc = 10:1 to 5:1) as an eluent to give 3-((1,3-dioxoisoindolin-2-yl)disulfaneyl)-3-methylbutyl benzoate as a colorless oil in 45% yield (0.300 g). **TLC** $\mathbf{R_f}$ = 0.2 (PE:EtOAc = 10:1); **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.99-7.90 (m, 2H), 7.87 (dd, J^1 = 5.5 Hz, J^2 = 3.1 Hz, 2H), 7.74 (dd, J^1 = 5.5 Hz, J^2 = 3.1 Hz, 2H), 7.55 (t, J = 7.4 Hz, 1H), 7.42 (t, J = 7.7 Hz, 2H), 4.36 (t, J = 6.9 Hz, 2H), 2.23 (t, J = 6.9 Hz, 2H), 1.48 (s, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 167.4, 166.3, 134.7, 132.9, 132.0, 130.0, 129.5, 128.3, 124.0, 61.8, 50.9, 39.4, 28.0; **HRMS** (ESI) m/z = 402.0828, calcd. for $C_{20}H_{20}NO_4S_2^+$ $[M+H]^+$, found: 402.0830; **IR** (neat, cm^{-1}): 2964*w*, 2924*w*, 1788*w*, 1736*s*, 1719*m*, 1468*w*, 1274*m*, 1114*w*, 1045*w*, 714*m*.



A flame-dried Schlenk-flask equipped with a magnetic stir bar was charged with 2-((4-hydroxy-2-methylbutan-2-yl)disulfaneyl)isoindoline-1,3-dione (0.528 g, 2.12 mmol, 1.0 equiv), EDCI (0.408 g, 2.12 mmol, 1.2 equiv), DMAP (22 mg, 0.18 mmol, 10 mol %), pent-4-enoic acid (0.212 g, 1.12 mmol, 1.2 equiv), and DCM (10 mL) were added. The reaction mixture was stirred at room temperature until the disappearance of 2-((4-hydroxy-2-methylbutan-2-yl) disulfaneyl)isoindoline-1,3-dione as monitored by TLC. The mixture was diluted with water, extracted with DCM (10 mL × 3), dried over anhydrous sodium sulfate, and filtered. The solvent was removed under reduced pressure. The residue was purified by flash column chromatography on silica gel (PE:EtOAc = 5:1) as an eluent to give 3-((1,3-dioxoisoindolin-2-yl) disulfaneyl)-3-methylbutyl pent-4-enoate as a colorless oil in 84% yield (0.568 g). **TLC** $\mathbf{R_f}$ = 0.3 (PE:EtOAc = 5:1); **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.92 (dd, J^1 = 5.5 Hz, J^2 = 3.1 Hz, 2H), 7.78 (dd, J^1 = 5.5 Hz, J^2 = 3.1 Hz, 2H), 5.85-5.71 (m, 1H), 5.09-4.94 (m, 2H), 4.12 (t, J = 7.0 Hz, 2H), 2.36-2.25 (m, 4H), 2.07 (t, J = 7.0 Hz, 2H), 1.41 (s, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 172.8, 167.4, 136.6, 134.7, 132.1, 124.0, 115.5, 61.2, 50.8, 39.3, 33.5, 28.7, 27.9; **HRMS** (ESI) m/z = 380.0985,

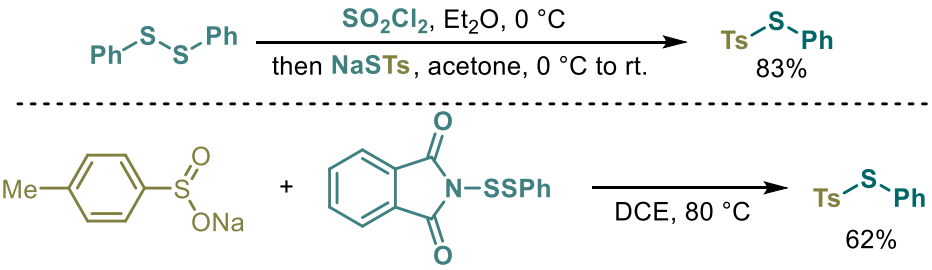
calcd. for $C_{18}H_{22}NO_4S_2^+$ $[M+H]^+$, found: 380.0999; **IR** (neat, cm^{-1}): 2965*w*, 2924*w*, 1735*s*, 1593*w*, 1453*w*, 1328*m*, 1166*m*, 1411*s*, 1078*m*, 917 *w*, 702*w*.



A flame-dried Schlenk-flask equipped with a magnetic stir bar was charged with *N*,*N*'-thiobisphthalimide (0.780 g, 2.400 mmol), 2-methyl-4-phenylbutane-2-thiol (0.300 g, 1.600 mmol), and DCE (10 mL) were added. The resulting mixture was stirred at 80 ºC for 6 h, and then cooled down to room temperature. The precipitate was removed by filtration, and the filtrate was concentrated and purified by chromatography to give 2-((2-methyl-4-phenylbutan-2-yl)disulfaneyl)isoindoline-1,3-dione as a white solid in 63% (0.363 g). **TLC R_f** = 0.3 (PE:EtOAc = 10:1); **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.88 (dd, J^1 = 5.5 Hz, J^2 = 3.1 Hz, 2H), 7.77 (dd, J^1 = 5.6 Hz, J^2 = 3.1 Hz, 2H), 7.17 (t, *J* = 7.3 Hz, 2H), 7.11 (t, *J* = 7.1 Hz, 1H), 7.05 (d, *J* = 7.3 Hz, 2H), 2.65-2.56 (m, 2H), 2.02-1.93 (m, 2H), 1.45 (s, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 167.5, 141.6, 134.7, 132.1, 128.3, 128.2, 125.8, 124.0, 52.5, 43.2, 31.2, 27.6; **IR** (neat, cm^{-1}): 2958*w*, 2930*w*,1782*w*, 1736*s*, 1611*w*, 1496*w*, 1468*w*, 1365*w*, 1342*w*, 1268*m*, 1165*w*, 1148*w*, 1119*w*, 1045*m*, 868*w*, 793*w*, 748*w*, 714*m*.

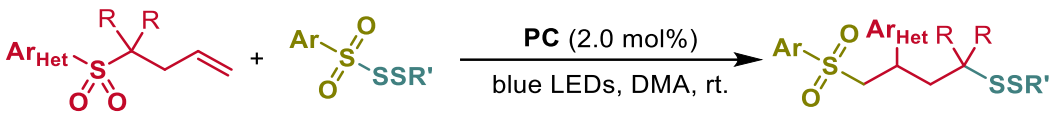
2.4 Limitations of the methods

We tried to synthesize some aryl dithiosulfonates according the following **GP3** and **GP4** but failed. Only *S*-phenyl 4-methylbenzenesulfonothioate was formed in 62% and 83% isolated yields respectively.



3. Convergent synthesis of polysulfide through sulfones 1 and reagent 2

3.1 General procedure for synthesis of polysulfides (GP5)

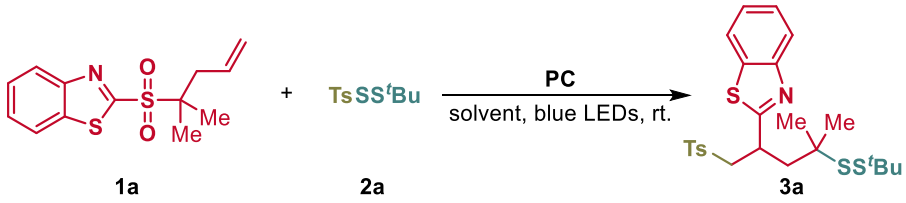


1 **2** **3**

A flame-dried Schlenk-tube equipped with a magnetic stir bar was charged with **1** (0.200 mmol, 1.0 equiv), **2** (0.300 mmol, 1.5 equiv), and **PC** (2.0 mol %), sealed with a septum, and degassed by alternating vacuum evacuation and argon backfilling (three times) before DMA (1 mL) was added. The reaction mixture was then stirred and irradiated using a 20 W blue LEDs lamp at room temperature for 12 h. After the reaction was completed, the mixture was diluted with EtOAc (2 mL), which was followed by extraction with EtOAc (5 mL × 3). The combined organic phase was washed with brine (10 mL), dried with Na_2SO_4 and the solvent was evaporated with the aid of a rotary evaporator. The crude product was purified by column chromatography to afford pure product **3**.

3.2 Screening of reaction conditions

Table S1 Reaction optimization.

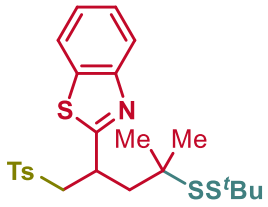


1a **2a** **3a**

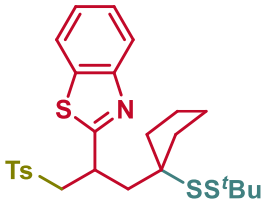
entry[a]	**2a**	**PC**	solvent	yield[b]
1	1.5 equiv	*fac*-Ir(ppy)$_3$	DMF	65%
2	1.5 equiv	eosin B	DMF	72%
3	1.5 equiv	eosin Y	DMF	62%
4	1.5 equiv	4CzIPN	DMF	65%
5	1.5 equiv	3DPAFIPN	DMF	66%
6	1.5 equiv	Fluorescein	DMF	70%
7	1.5 equiv	rhodamine B	DMF	trace
8	1.5 equiv	rhodamine 6G	DMF	45%
9	1.5 equiv	anthraquinone	DMF	67%
10	1.5 equiv	rose bengal	DMF	76%
11	1.5 equiv	solvent red 43	DMF	65%
12	1.5 equiv	methylene blue	DMF	34%
13	1.5 equiv	bromocresol green	DMF	nr.
14	1.5 equiv	disperse violet 28	DMF	trace
15	1.5 equiv	9,10-diphenylanthracene	DMF	75%
16	1.5 equiv	10-phenylphenothiazine	DMF	75%
17[c]	1.5 equiv	rose bengal	DMF	nr.
18	**1.5 equiv**	**rose bengal**	**DMA**	**79%**
19[d]	1.5 equiv	rose bengal	DMA	71%
20	1.5 equiv	rose bengal	DMSO	57%
21	1.5 equiv	rose bengal	NMP	74%
22	1.5 equiv	rose bengal	acetone	32%
23	1.5 equiv	rose bengal	EtOAc	47%
24	1.5 equiv	rose bengal	PhCF$_3$	nr.
25	1.5 equiv	rose bengal	DCE	nr.
26	1.5 equiv	rose bengal	^{i}PrOH	30%
27	1.5 equiv	rose bengal	MeCN	nr.
28	1.5 equiv	rose bengal	MeNO$_3$	nr.
29	1.2 equiv	rose bengal	DMA	59%
30	2.0 equiv	rose bengal	DMA	72%
31	2.5 equiv	rose bengal	DMA	74%
32[e]	1.5 equiv	rose bengal	DMA	71%
33[f]	1.5 equiv	rose bengal	DMA	69%

[a]Reaction condition: **1a** (0.100 mmol, 1.0 equiv), **2a**, **PC** (2.0 mol%), solvent (0.5 mL), room temperature, 12 h. [b]Isolated yield; "nr." stands for "no reaction". [c]The reaction was conducted in an open flask. [d]The amount of rose bengal reduced to 0.10 mol%. [e]White LEDs was used in place of blue LEDs. [f]Green LEDs was used in place of blue LEDs.

3.3 Spectral data of polysulfides



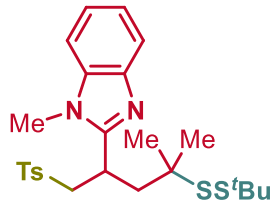
2-(4-(*tert*-Butyldisulfanyl)-4-methyl-1-tosylpentan-2-yl)benzo[*d*]thiazole (3a): The title compound was prepared according to general procedure (**GP5**) with rose bengal (4.1 mg, 4.0 μmol, 2.0 mol%), **1a** (56.3 mg, 0.200 mmol, 1.0 equiv), and **2a** (82.8 mg, 0.300 mmol, 1.5 equiv) in DMA (1 mL) at room temperature for 12 h. Purification via silica gel chromatography (PE:EtOAc = 10:1 to 5:1) gave the desired product **3a** as a white solid in 79% yield (77.9 mg). **MP:** 52.4-53.3 °C; **TLC** $\mathbf{R_f}$ = 0.4 (PE:EtOAc = 5:1); **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.77 (d, J = 8.1 Hz, 2H), 7.60 (d, J = 8.0 Hz, 2H), 7.40 (t, J = 7.7 Hz, 1H), 7.32 (t, J = 7.6 Hz, 1H), 7.02 (d, J = 8.0 Hz, 2H), 4.05-3.92 (m, 2H), 3.64-3.50 (m, 1H), 2.25 (dd, J^1 = 14.7 Hz, J^2 = 6.5 Hz, 1H), 2.18 (s, 4H), 1.28 (s, 9H), 1.24 (s, 3H), 1.21 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 171.9, 152.7, 144.4, 136.1, 134.7, 129.3, 127.9, 125.9, 125.0, 122.7, 121.5, 61.7, 49.1, 47.6, 46.7, 36.6, 30.5, 28.5, 27.9, 21.4; **HRMS** (ESI) m/z = 494.1310, calcd. for $C_{24}H_{32}NO_2S_4^+$ $[M+H]^+$, found: 494.1319; **IR** (neat, cm^{-1}): 2964*w*, 2924*w*, 1456*w*, 1319*m*, 1296*m*, 1142*s*, 1091*m*, 1017*w*, 811*w*, 760*m*, 731*w*.



2-(1-(1-(*tert*-Butyldisulfanyl)cyclopentyl)-3-tosylpropan-2-yl)benzo[*d*]thiazole (3b): The title compound was prepared according to general procedure (**GP5**) with rose bengal (4.1 mg, 4.0 μmol, 2.0 mol%), **1b** (61.5 mg, 0.200 mmol, 1.0 equiv), and **2a** (82.8 mg, 0.300 mmol, 1.5 equiv) in DMA (1 mL) at room temperature for 12 h. Purification via silica gel chromatography (PE:EtOAc = 10:1) gave the desired product **3b** as a tawny oil in 40% yield (41.0 mg). **TLC** $\mathbf{R_f}$ = 0.4 (PE:EtOAc = 5:1); **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.77 (t, J = 8.0 Hz, 2H), 7.59 (d, J = 8.2 Hz, 2H), 7.43-7.36 (m, 1H), 7.32 (td, J^1 = 7.6 Hz, J^2 = 1.3 Hz, 1H), 7.01 (d, J = 8.0 Hz, 2H), 4.10 (dddd, J^1 = 11.1 Hz, J^2 = 8.1 Hz, J^3 = 4.7 Hz, J^4 = 3.5 Hz, 1H), 4.01 (dd, J^1 = 14.1 Hz, J^2 = 9.4 Hz, 1H), 3.58 (dd, J^1 = 14.1 Hz, J^2 = 3.6 Hz, 1H), 2.31-2.21 (m, 2H), 2.18 (s, 3H), 2.03-1.94 (m, 1H), 1.79-1.66 (m, 2H), 1.64-1.49 (m, 3H), 1.48-1.44 (m, 1H), 1.30 (s, 10H); **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 171.7, 152.7, 144.2, 136.2, 134.8, 129.3, 127.8, 125.8, 124.9, 122.6, 121.5, 61.6, 61.6, 46.8, 46.2, 38.7, 37.2, 36.9, 30.7, 24.0, 23.2, 21.3; **HRMS** (ESI) m/z = 542.1286, calcd. for $C_{26}H_{33}NO_2S_4Na^+$ $[M+Na]^+$, found: 542.1294; **IR** (neat, cm^{-1}): 2958*w*, 2924*w*,1599*w*, 1451*w*, 1319*m*, 1142*s*, 1085*w*, 811*w*, 760*w*, 731*w*.

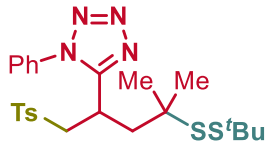
2-(1-(1-(*tert*-Butyldisulfaneyl)cyclohexyl)-3-tosylpropan-2-yl)benzo[*d*]thiazole (3c): The title compound was prepared according to general procedure (**GP5**) with rose bengal (4.1 mg, 4.0 μmol, 2.0 mol%), **1c** (64.3 mg, 0.200 mmol, 1.0 equiv), and **2a** (82.8 mg, 0.300 mmol, 1.5 equiv) in DMA (1 mL) at room temperature for 12 h. Purification via silica gel chromatography (PE:EtOAc = 10:1 to 5:1) gave the desired product **3c** as a white solid in 74% yield (79.5 mg). **MP:** 109.0-109.8 °C; **TLC** $\mathbf{R_f}$ = 0.4 (PE:EtOAc = 5:1); **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.82-7.71 (m, 2H), 7.57 (d, J = 8.1 Hz, 2H), 7.39 (t, J = 7.6 Hz, 1H), 7.32 (t, J = 7.7 Hz, 1H), 6.99 (d, J = 8.0 Hz, 2H), 4.12-3.97 (m, 2H), 3.74-3.60 (m, 1H), 2.27 (dd, J^1 = 15.2 Hz, J^2 = 6.1 Hz, 1H), 2.21-2.09 (m, 4H), 1.74-1.22 (m, 19H); **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 172.1, 152.7, 144.2, 136.2, 134.8, 129.2, 127.8, 125.8, 124.9, 122.6, 121.5, 61.8, 53.7, 46.8, 36.3, 35.7, 35.2, 30.8, 25.3, 22.4, 22.3, 21.3; **HRMS** (ESI) m/z = 556.1443, calcd. for $C_{27}H_{35}NO_2S_4Na^+$ $[M+Na]^+$, found: 556.1444; **IR** (neat, cm^{-1}): 2930*m*, 2855*w*, 1451*w*, 1439*w*, 1365*w*, 1319*m*, 1142*s*, 1085*w*, 811*w*, 760*m*, 731*w*.

2-(1-(4-(*tert*-Butyldisulfanyl)tetrahydro-2*H*-pyran-4-yl)-3-tosylpropan-2-yl)benzo[*d*]thiazole (3d): The title compound was prepared according to general procedure (**GP5**) with rose bengal (4.1 mg, 4.0 μmol, 2.0 mol%), **1d** (64.7 mg, 0.200 mmol, 1.0 equiv), and **2a** (82.8 mg, 0.300 mmol, 1.5 equiv) in DMA (1 mL) at room temperature for 12 h. Purification via silica gel chromatography (PE:EtOAc = 5:1 to 2:1) gave the desired product **3d** as a white solid in 73% yield (78.7 mg). **MP:** 105.4-106.8 °C; **TLC** $\mathbf{R_f}$ = 0.4 (PE:EtOAc = 2:1); **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.78 (d, J = 8.3 Hz, 2H), 7.59 (d, J = 8.2 Hz, 2H), 7.41 (t, J = 7.6 Hz, 1H), 7.33 (t, J = 7.6 Hz, 1H), 7.02 (d, J = 8.0 Hz, 2H), 4.10 (ddd, J^1 = 13.1 Hz, J^2 = 7.8 Hz, J^3 = 3.6 Hz, 1H), 3.98 (dd, J^1 = 14.3 Hz, J^2 = 9.1 Hz, 1H), 3.80 (ddd, J^1 = 11.9 Hz, J^2 = 8.9 Hz, J^3 = 3.1 Hz, 1H), 3.75-3.56 (m, 3H), 3.51 (dt, J^1 = 11.8 Hz, J^2 = 4.6 Hz, 1H), 2.39 (dd, J^1 = 15.0 Hz, J^2 = 7.7 Hz, 1H), 2.27-2.14 (m, 4H), 1.81 (dt, J^1 = 14.4 Hz, J^2 = 3.9 Hz, 1H), 1.67 (ddd, J^1 = 13.7 Hz, J^2 = 8.9 Hz, J^3 = 4.1 Hz, 1H), 1.60-1.47 (m, 2H), 1.29 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 171.5, 152.7, 144.3, 136.1, 134.7, 129.3, 127.8, 125.9, 125.1, 122.7, 121.5, 63.9, 63.7, 61.8, 51.0, 47.1, 45.6, 35.8, 35.6, 34.9, 30.8, 21.4; **HRMS** (ESI) m/z = 558.1235, calcd. for $C_{26}H_{33}NO_3S_4Na^+$ $[M+Na]^+$, found: 558.1245; **IR** (neat, cm^{-1}): 2958*w*, 2924*w*, 2861*w*, 1599*w*, 1513*w*, 1439*w*, 1319*m*, 1142*s*, 1108*m*, 1085*m*, 1017*w*, 914*w*, 811*w*, 765*m*, 731*w*.

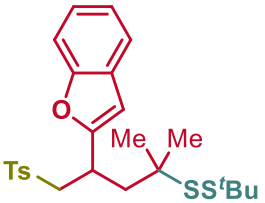


2-(4-(*tert*-Butyldisulfanyl)-4-methyl-1-tosylpentan-2-yl)-1-methyl-1*H*-benzo[*d*]imidazole (3e): The title compound was prepared according to general procedure (**GP5**) with rose bengal (4.1 mg, 4.0 μmol, 2.0 mol%), **1e** (55.7 mg, 0.200 mmol, 1.0 equiv), and **2a** (82.8 mg, 0.300 mmol, 1.5 equiv) in DMA (1 mL) at room temperature for 12 h. Purification via silica gel chromatography (PE:EtOAc = 10:1 to 5:1) gave the desired product **3e** as a colorless oil in 71% yield (69.8 mg). **TLC R$_f$** = 0.2 (PE:EtOAc = 5:1); **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.41 (d, J = 7.9 Hz, 1H), 7.35 (d, J = 8.3 Hz, 2H), 7.26-7.17 (m, 2H), 7.14 (ddd, J^1 = 8.3 Hz, J^2 = 6.7, J^3 = 1.7 Hz, 1H), 6.85 (d, J = 8.1 Hz, 2H), 4.05 (dd, J^1 = 14.1 Hz, J^2 = 10.4 Hz, 1H), 3.99-3.90 (m, 1H), 3.86 (s, 3H), 3.50 (dd, J^1 = 14.1 Hz, J^2 = 3.2 Hz, 1H), 2.33 (dd, J^1 = 14.5 Hz, J^2 = 8.7 Hz, 1H), 2.15-2.02 (m, 4H), 1.29 (s, 9H), 1.24 (s, 3H), 0.87 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 154.4, 144.0, 142.2, 135.7, 134.7, 129.0, 126.8, 122.2, 121.9, 118.9, 109.4, 62.0, 49.1, 47.1, 46.6, 30.5, 30.1, 29.7, 29.1, 27.4, 21.3; **HRMS** (ESI) m/z = 491.1855, calcd. for $C_{25}H_{35}N_2O_2S_3^+$ $[M+H]^+$, found: 491.1860; **IR** (neat, cm^{-1}): 2964*w*, 2924*w*, 1468*m*, 1451*m*, 1365*w*, 1319*m*, 1291*m*, 1137*s*, 1085*w*, 811*w*, 748*m*.

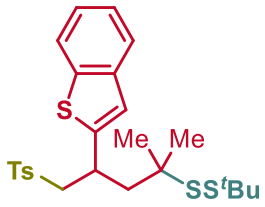
1-(But-3-en-1-yl)-2-(4-(*tert*-butyldisulfanyl)-4-methyl-1-tosylpentan-2-yl)-1*H*-benzo[*d*]imidazole (3f): The title compound was prepared according to general procedure (**GP5**) with rose bengal (4.1 mg, 4.0 μmol, 2.0 mol%), **1f** (63.7 mg, 0.200 mmol, 1.0 equiv), and **2a** (82.8 mg, 0.300 mmol, 1.5 equiv) in DMA (1 mL) at room temperature for 12 h. Purification via silica gel chromatography (PE:EtOAc = 10:1 to 5:1) gave the desired product **3f** as a colorless oil in 47% yield (50.0 mg). **TLC R$_f$** = 0.2 (PE:EtOAc = 5:1); **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.62-7.45 (m, 3H), 7.31-7.25 (m, 1H), 7.26-7.13 (m, 2H), 7.04 (d, J = 8.0 Hz, 2H), 5.87 (ddt, J^1 = 17.1 Hz, J^2 = 10.2 Hz, J^3 = 6.9 Hz, 1H), 5.23-5.07 (m, 2H), 4.40-4.17 (m, 2H), 3.95 (tt, J^1 = 7.7 Hz, J^2 = 5.0 Hz, 1H), 3.83 (dd, J^1 = 14.3 Hz, J^2 = 7.9 Hz, 1H), 3.63 (dd, J^1 = 14.3 Hz, J^2 = 5.1 Hz, 1H), 2.66 (td, J^1 = 10.3 Hz, J^2 = 3.2 Hz, 2H), 2.35 (dd, J^1 = 14.7 Hz, J^2 = 7.5 Hz, 1H), 2.30-2.15 (m, 4H), 1.35-1.24 (m, 12H), 1.02 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 154.6, 144.4, 142.3, 136.1, 134.2, 133.9, 129.3, 127.3, 122.3, 122.0, 119.1, 118.1, 109.9, 61.5, 49.0, 46.7, 46.6, 43.4, 33.9, 30.6, 29.7, 28.9, 27.9, 21.4; **HRMS** (ESI) m/z = 531.2168, calcd. for $C_{28}H_{39}N_2O_2S_3^+$ $[M+H]^+$, found: 531.2175; **IR** (neat, cm^{-1}): 2958*w*, 2924*w*, 1599*w*, 1502*w*, 1456*m*, 1365*w*, 1319*m*, 1291*m*, 1142*s*, 1085*w*, 1011*w*, 925*w*, 811*w*, 748*m*.



5-(4-(*tert*-Butyldisulfanyl)-4-methyl-1-tosylpentan-2-yl)-1-phenyl-1*H*-tetrazole (3g): The title compound was prepared according to general procedure (**GP5**) with 10-phenylphenothiazine (4.1 mg, 4.0 μmol, 2.0 mol%), **1g** (58.4 mg, 0.200 mmol, 1.0 equiv), and **2a** (82.8 mg, 0.300 mmol, 1.5 equiv) in DMA (1 mL) at room temperature for 12 h. Purification via silica gel chromatography (PE:EtOAc = 5:1 to 2:1) gave the desired product **3g** as a colorless oil in 50% yield (50.4 mg). **TLC** $\mathbf{R_f}$ = 0.1 (PE:EtOAc = 5:1); **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.72-7.66 (m, 2H), 7.65-7.58 (m, 5H), 7.30 (d, J = 8.0 Hz, 2H), 3.95-3.80 (m, 2H), 3.58 (dd, J^1 = 13.2 Hz, J^2 = 3.1 Hz, 1H), 2.44 (s, 3H), 2.13 (qd, J^1 = 14.8 Hz, J^2 = 5.7 Hz, 2H), 1.21 (s, 9H), 0.99 (s, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 156.9, 145.2, 135.9, 133.6, 130.5, 130.0, 129.9, 127.8, 125.8, 60.6, 48.0, 46.9, 46.7, 30.5, 28.1, 28.0, 26.3, 21.6; **HRMS** (EI) *m*/*z* = 504.1682, calcd. for $C_{24}H_{32}N_4O_2S_3^+$ $[M]^+$, found: 504.1681; **IR** (neat, cm^{-1}): 2964*w*, 2924*w*, 1599*w*, 1508*w*, 1496*w*, 1456*w*, 1365*w*, 1319*m*, 1302*w*, 1148*s*, 1114*w*, 1085*w*, 817*w*, 765*m*.



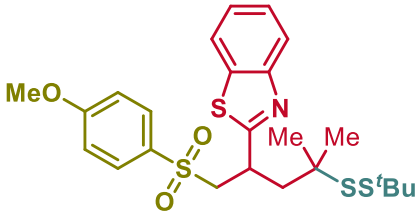
2-(4-(*tert*-Butyldisulfaneyl)-4-methyl-1-tosylpentan-2-yl)benzofuran (3h): The title compound was prepared according to general procedure (**GP5**) with rose bengal (4.1 mg, 4.0 μmol, 2.0 mol%), **1h** (52.9 mg, 0.200 mmol, 1.0 equiv), and **2a** (82.8 mg, 0.300 mmol, 1.5 equiv) in DMA (1 mL) at room temperature for 12 h. Purification via silica gel chromatography (PE:EtOAc = 10:1) gave the desired product **3h** as a colorless oil in 69% yield (65.9 mg). **TLC** $\mathbf{R_f}$ = 0.3 (PE:EtOAc = 10:1); **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.52 (d, J = 8.2 Hz, 2H), 7.38-7.33 (m, 1H), 7.18-7.10 (m, 3H), 6.94 (d, J = 8.0 Hz, 2H), 6.36 (s, 1H), 3.75-3.64 (m, 2H), 3.47-3.40 (m, 1H), 2.14 (s, 3H), 2.11-2.00 (m, 2H), 1.27 (s, 9H), 1.19 (s, 3H), 1.11 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 156.2, 154.1, 144.0, 135.9, 129.0, 128.0, 127.5, 123.6, 122.5, 120.6, 110.7, 104.7, 60.2, 49.0, 46.5, 45.3, 32.0, 30.5, 28.4, 27.1, 21.3; **HRMS** (ESI) *m*/*z* = 499.1406, calcd. for $C_{25}H_{32}O_3S_3Na^+$ $[M+Na]^+$, found: 499.1410; **IR** (neat, cm^{-1}): 2964*w*, 2924*w*, 1599*w*, 1456*m*, 1365*w*, 1319*m*, 1291*m*, 1251*w*, 1142*s*, 1085*m*, 811*m*, 748*m*.



2-(4-(*tert*-Butyldisulfanyl)-4-methyl-1-tosylpentan-2-yl)benzo[*b*]thiophene (3i): The title compound was prepared according to general procedure (**GP5**) with rose bengal (4.1 mg, 4.0 μmol, 2.0 mol%), **1i** (56.1 mg, 0.200 mmol, 1.0 equiv), and **2a** (82.8 mg, 0.300 mmol, 1.5 equiv) in DMA (1 mL) at room temperature for 12 h. Purification via silica gel chromatography (PE:EtOAc = 20:1 to 10:1) gave the desired product **3i** as a colorless oil in 28% yield (27.7 mg). **TLC**

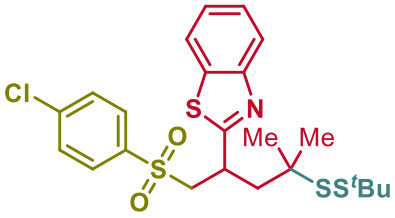
R_f = 0.3 (PE:EtOAc = 10:1); **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.64 (d, *J* = 7.9 Hz, 1H), 7.60-7.54 (m, 3H), 7.29 (dd, J^1 = 7.2 Hz, J^2 = 7.2 Hz,1H), 7.23 (dd, J^1 = 7.5 Hz, J^1 = 7.5 Hz,1H), 7.02 (d, *J* = 8.0 Hz, 2H), 6.94 (s, 1H), 3.88 (ddd, J^1 = 10.3 Hz, J^2 = 6.4 Hz, J^3 = 3.6 Hz, 1H), 3.50 (d, *J* = 6.6 Hz, 2H), 2.23 (s, 3H), 2.21-2.15 (m, 1H), 2.05 (dd, J^1 = 14.4 Hz, J^2 = 8.8 Hz, 1H), 1.29 (s, 9H), 1.25 (s, 3H), 1.16 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 147.4, 144.3, 139.3, 139.1, 136.4, 129.3, 127.9, 124.3, 124.0, 123.2, 122.4, 122.1, 63.6, 49.4, 48.7, 46.6, 34.4, 30.6, 28.9, 27.3, 21.4; **HRMS** (ESI) *m*/*z* = 515.1177, calcd. for $C_{25}H_{32}O_2S_4Na^+$ $[M+Na]^+$, found: 515.1188; **IR** (neat, cm^{-1}): 2958*w*, 2924*w*, 1456*w*, 1439*w*, 1365*w*, 1319*m*, 1296*m*, 1142*s*, 1086*m*, 817*w*, 748*m*, 725*w*.

2-(4-(*tert*-Butyldisulfanyl)-4-methyl-1-(phenylsulfonyl) pentan-2-yl)benzo[*d*]thiazole (3k): The title compound was prepared according to general procedure (**GP5**) with rose bengal (4.1 mg, 4.0 μmol, 2.0 mol%), **1a** (56.3 mg, 0.200 mmol, 1.0 equiv), and **2b** (78.7 mg, 0.300 mmol, 1.5 equiv) in DMA (1 mL) at room temperature for 12 h. Purification via silica gel chromatography (PE:EtOAc = 10:1 to 5:1) gave the desired product **3k** as a colorless oil in 74% yield (71.0 mg). **TLC R_f** = 0.4 (PE:EtOAc = 5:1); **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.89-7.66 (m, 4H), 7.48-7.15 (m, 5H), 4.06-3.88 (m, 2H), 3.68-3.50 (m, 1H), 2.27 (dd, J^1 = 14.8 Hz, J^2 = 6.5 Hz, 1H), 2.18 (dd, J^1 = 14.8 Hz, J^2 = 3.9 Hz, 1H), 1.28 (s, 9H), 1.23 (s, 3H), 1.21 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 171.9, 152.7, 139.1, 134.7, 133.2, 128.7, 127.9, 125.9, 125.1, 122.8, 121.5, 61.7, 49.1, 47.6, 46.7, 36.5, 30.6, 28.5, 27.9; **HRMS** (ESI) *m*/*z* = 502.0973, calcd. for $C_{23}H_{29}NO_2S_4Na^+$ $[M+Na]^+$, found: 502.0978; **IR** (neat, cm^{-1}): 2964*w*, 2924*w*, 1513*w*, 1445*w*, 1314*m*, 1148*s*, 1102*m*, 1085*m*, 1017*w*, 908*w*, 760*m*, 731*m*.

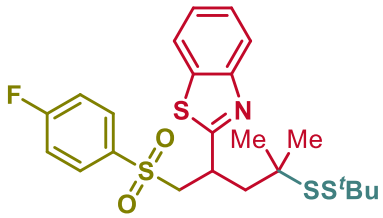


2-(4-(*tert*-Butyldisulfanyl)-1-((4-methoxyphen-yl)sulfonyl)-4-methylpentan-2-yl)benzo[*d*] thiazole (3l): The title compound was prepared according to general procedure (**GP5**) with rose bengal (4.1 mg, 4.0 μmol, 2.0 mol%), **1a** (56.3 mg, 0.200 mmol, 1.0 equiv), and **2c** (87.7 mg, 0.300 mmol, 1.5 equiv) in DMA (1 mL) at room temperature for 12 h. Purification via silica gel chromatography (PE:EtOAc = 10:1) gave the desired product **3l** as a white solid in 66% yield (66.8 mg). **MP:** 81.3-83.6 °C;**TLC R_f** = 0.2 (PE:EtOAc = 5:1); **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.78 (ddd, J^1 = 7.2 Hz, J^2 = 5.3 Hz, J^3 = 1.2 Hz, 2H), 7.69-7.56 (m, 2H), 7.44-7.37 (m, 1H), 7.33 (ddd, J^1 = 7.6 Hz, J^2 = 7.6 Hz, J^3 = 1.2 Hz, 1H), 6.73-6.58 (m, 2H), 4.06-

3.85 (m, 2H), 3.72-3.49 (m, 4H), 2.24 (dd, J^1 = 14.7 Hz, J^2 =6.5 Hz, 1H), 2.15 (dd, J^1 = 14.8 Hz, J^2 = 4.2 Hz, 1H), 1.28 (s, 9H), 1.24 (s, 3H), 1.22 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 172.0, 163.3, 152.7, 134.8, 130.6, 130.1, 125.9, 124.9, 122.7, 121.5, 113.9, 62.0, 55.4, 49.1, 47.7, 46.7, 36.7, 30.6, 28.5, 27.9; **HRMS** (ESI) *m/z* = 510.1260, calcd. for $C_{24}H_{32}NO_3S_4^+$ $[M+H]^+$, found: 510.1266; **IR** (neat, cm^{-1}): 2964*w*, 1593*w*, 1496*w*, 1456*w*, 1319*w*, 1262*m*, 1142*s*, 1091*m*, 1022*w*, 834*w*, 760*w*, 731*w*.

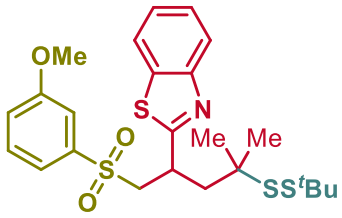


2-(4-(*tert*-Butyldisulfaneyl)-1-((4-chlorophenyl) sulfonyl)-4-methylpentan-2-yl)benzo[*d*]thiazole (3m): The title compound was prepared according to general procedure (**GP5**) with rose bengal (4.1 mg, 4.0 μmol, 2.0 mol%), **1a** (56.3 mg, 0.200 mmol, 1.0 equiv), and **2d** (89.1 mg, 0.300 mmol, 1.5 equiv) in DMA (1 mL) at room temperature for 12 h. Purification via silica gel chromatography (PE:EtOAc = 10:1) gave the desired product **3m** as a colorless oil in 72% yield (74.2 mg). **TLC R_f** = 0.4 (PE:EtOAc = 5:1); **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.77 (t, J = 8.4 Hz, 2H), 7.69-7.57 (m, 2H), 7.43 (t, J = 7.6 Hz, 1H), 7.35 (t, J = 7.6 Hz, 1H), 7.23-7.13 (m, 2H), 4.04 (dd, J^1 = 14.0 Hz, J^2 = 9.4 Hz, 1H), 4.00-3.92 (m, 1H), 3.61 (dd, J^1 = 14.0 Hz, J^2 = 3.4 Hz, 1H), 2.22 (dd, J^1 = 14.7 Hz, J^2 = 6.8 Hz, 1H), 2.13 (dd, J^1 = 14.8 Hz, J^2 = 4.6 Hz, 1H), 1.29 (s, 9H), 1.24 (s, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 171.4, 152.5, 140.0, 137.6, 134.5, 129.3, 128.9, 126.2, 125.3, 122.7, 121.5, 61.8, 49.1, 47.7, 46.8, 36.6, 30.6, 28.7, 27.8; **HRMS** (ESI) *m/z* = 514.0764, calcd. for $C_{23}H_{29}NO_2S_4Cl^+$ $[M+H]^+$, found: 514.0760; **IR** (neat, cm^{-1}): 2958*w*, 2924*w*, 2855*w*, 1582*w*, 1456*w*, 1393*w*, 1319*m*, 1148*s*, 1091*s*, 1011*w*, 828*w*, 765*m*, 731*w*.

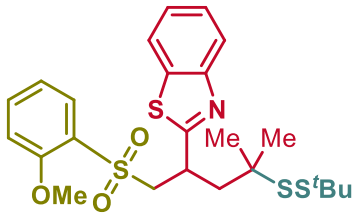


2-(4-(*tert*-Butyldisulfanyl)-1-((4-fluorophenyl)sulfonyl)-4-methylpentan-2-yl)benzo[*d*]thiazole (3n): The title compound was prepared according to general procedure (**GP5**) with rose bengal (4.1 mg, 4.0 μmol, 2.0 mol%), **1a** (56.3 mg, 0.200 mmol, 1.0 equiv), and **2e** (84.1 mg, 0.300 mmol, 1.5 equiv) in DMA (1 mL) at room temperature for 12 h. Purification via silica gel chromatography (PE:EtOAc = 10:1) gave the desired product **3n** as a white solid in 78% yield (77.8 mg). **MP:** 78.8-79.9 °C; **TLC R_f** = 0.2 (PE:EtOAc = 10:1); **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.78 (d, J = 8.2 Hz, 2H), 7.76-7.65 (m, 2H), 7.42 (ddd, J^1 = 8.4 Hz, J^2 = 7.2 Hz, J^3 = 1.3 Hz, 1H), 7.35 (ddd, J^1 = 8.3 Hz, J^2 = 7.3 Hz, J^3 = 1.3 Hz, 1H), 6.99-6.82 (m, 2H), 4.12-3.92 (m, 2H), 3.61 (dd, J^1 = 13.4 Hz, J^2 = 2.9 Hz, 1H), 2.24 (dd, J^1

= 14.7 Hz, J^2 = 6.6 Hz, 1H), 2.15 (dd, J^1 = 14.6 Hz, J^2 = 4.3 Hz, 1H), 1.28 (s, 9H), 1.24 (s, 3H), 1.23 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 171.6, 165.4 (d, J = 256.4 Hz), 152.6, 135.2 (d, J = 3.0 Hz), 134.6, 130.8 (d, J = 9.7 Hz), 126.1, 125.2, 122.7, 121.5, 115.9 (d, J = 22.8 Hz), 61.8, 49.0, 47.7, 46.7, 36.6, 30.5, 28.6, 27.8; **^{19}F NMR** (377 MHz, $CDCl_3$, 300 K): δ (ppm) = -103.8. **HRMS** (ESI) *m/z* = 498.1060, calcd. for $C_{23}H_{29}FNO_2S_4^+$ $[M+H]^+$, found: 498.1069; **IR** (neat, cm^{-1}): 2964*w*, 2924*w*, 1593*m*, 1491*m*, 1365*w*, 1319*m*, 1291*m*, 1234*m*, 1142*s*, 1085*m*, 840*m*, 760*m*, 731*w*.

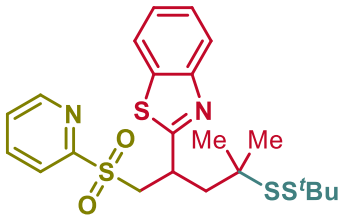


2-(4-(*tert*-Butyldisulfanyl)-1-((3-methoxyphenyl)sulfonyl)-4-methylpentan-2-yl)benzo[*d*]thiazole (3o): The title compound was prepared according to general procedure (**GP5**) with rose bengal (4.1 mg, 4.0 μmol, 2.0 mol%), **1a** (56.3 mg, 0.200 mmol, 1.0 equiv), and **2f** (82.8 mg, 0.300 mmol, 1.5 equiv) in DMA (1 mL) at room temperature for 12 h. Purification via silica gel chromatography (PE:EtOAc = 10:1) gave the desired product **3o** as a colorless oil in 73% yield (74.8 mg). **TLC R_f** = 0.3 (PE:EtOAc = 5:1); **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.79 (t, J = 7.8 Hz, 2H), 7.41 (td, J^1 = 7.6 Hz, J^2 = 1.4 Hz, 1H), 7.39-7.29 (m, 2H), 7.26-7.16 (m, 2H), 6.86 (ddd, J^1 = 8.3 Hz, J^2 = 2.7 Hz, J^3 = 0.9 Hz, 1H), 4.05-3.92 (m, 2H), 3.72 (s, 3H), 3.65-3.54 (m, 1H), 2.26 (dd, J^1 = 14.7 Hz, J^2 = 6.9 Hz, 1H), 2.17 (dd, J^1 = 14.7 Hz, J^2 =4.0 Hz, 1H), 1.28 (s, 9H), 1.23 (s, 3H), 1.22 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 171.9, 159.5, 152.6, 140.1, 134.7, 129.9, 125.9, 125.1, 122.7, 121.5, 120.1, 119.8, 112.3, 61.6, 55.5, 49.1, 47.6, 46.7, 36.4, 30.5, 28.5, 27.8; **HRMS** (ESI) *m/z* = 532.1079, calcd. for $C_{24}H_{31}NO_3S_4Na^+$ $[M+Na]^+$, found: 532.1075; **IR** (neat, cm^{-1}): 2964*w*, 2924*w*, 1599*w*, 1479*m*, 1456*m*, 1433*m*, 1365*w*, 1314*s*, 1291*m*, 1245*m*, 1137*s*, 1097*m*, 1039*w*, 862*w*, 760*m*, 731*w*.

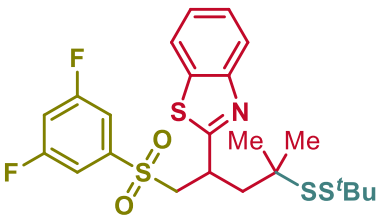


2-(4-(*tert*-Butyldisulfanyl)-1-((2-methoxyphenyl)sulfonyl)-4-methylpentan-2-yl)benzo[*d*]thiazole (3p): The title compound was prepared according to general procedure (**GP5**) with rose bengal (4.1 mg, 4.0 μmol, 2.0 mol%), **1a** (56.3 mg, 0.200 mmol, 1.0 equiv), and **2g** (82.8 mg, 0.300 mmol, 1.5 equiv) in DMA (1 mL) at room temperature for 12 h. Purification via silica gel chromatography (PE:EtOAc = 10:1) gave the desired product **3p** as a colorless oil in 55% yield (56.0 mg). **TLC R_f** = 0.2 (PE:EtOAc = 5:1); **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.79 (t, J = 7.8 Hz, 2H), 7.41 (td, J^1 = 7.6 Hz, J^2 = 1.4 Hz, 1H), 7.39-7.29 (m, 2H), 7.26-7.16 (m, 2H), 6.86 (dd, J^1 = 8.3 Hz, J^2 = 1.8 Hz, 1H), 4.05-3.92 (m, 2H), 3.72 (s, 3H), 3.65-3.54 (m, 1H), 2.26 (dd, J^1 = 14.7 Hz, J^2 = 6.9 Hz, 1H), 2.17 (dd, J^1 = 14.7 Hz, J^2 =4.0 Hz, 1H), 1.28 (s, 9H), 1.23 (s, 3H), 1.22 (s,

3H); **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 171.9, 159.5, 152.6, 140.1, 134.7, 129.9, 125.9, 125.1, 122.7, 121.5, 120.1, 119.8, 112.3, 61.6, 55.5, 49.1, 47.6, 46.7, 36.4, 30.5, 28.5, 27.8; **HRMS** (ESI) *m*/*z* = 532.1079, calcd. for $C_{24}H_{31}NO_3S_4Na^+$ $[M+Na]^+$, found: 532.1083; **IR** (neat, cm^{-1}): 2958*w*, 2924*w*, 1593*w*, 1479*m*, 1462*m*, 1433*m*, 1365*w*, 1314*m*, 1279*m*, 1245*w*, 1148*s*, 1131*m*, 1062*w*, 1017*w*, 805*w*, 760*s*, 731*w*.

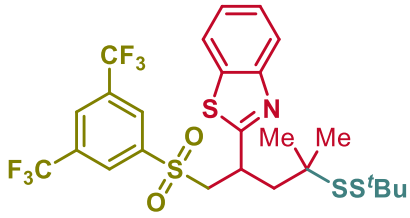


2-(4-(*tert*-Butyldisulfanyl)-4-methyl-1-(pyridin-2-yl-sulfonyl)pentan-2-yl)benzo[*d*]thiazole (3q): The title compound was prepared according to general procedure (**GP5**) with rose bengal (4.1 mg, 4.0 μmol, 2.0 mol%), **1a** (56.3 mg, 0.200 mmol, 1.0 equiv), and **2h** (79.0 mg, 0.300 mmol, 1.5 equiv) in DMA (1 mL) at room temperature for 12 h. Purification via silica gel chromatography (PE:EtOAc = 5:1 to 2:1) gave the desired product **3q** as a light yellow oil in 52% yield (50.2 mg). **TLC** R_f = 0.4 (PE:EtOAc = 2:1); **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 8.51 (d, J = 4.7 Hz, 1H), 7.81 (d, J = 7.8 Hz, 1H), 7.76 (d, J = 8.7 Hz, 2H), 7.55 (ddd, J^1 = 7.8 Hz, J^2 = 7.8 Hz, J^3 = 1.7 Hz, 1H), 7.39 (ddd, J^1 = 8.3 Hz, J^2 = 7.2 Hz, J^3 = 1.3 Hz, 1H), 7.32 (ddd, J^1 = 7.6 Hz, J^2 = 7.2 Hz, J^2 = 1.3 Hz, 1H), 7.19 (ddd, J^1 = 7.7 Hz, J^2 = 4.6 Hz, J^3 = 1.2 Hz, 1H), 4.33 (dd, J^1 = 14.6 Hz, J^2 = 9.2 Hz, 1H), 4.04 (tt, J^1 = 8.5 Hz, J^2 = 4.2 Hz, 1H), 3.76 (dd, J^1 = 14.7 Hz, J^2 = 4.5 Hz, 1H), 2.36 (dd, J^1 = 14.7 Hz, J^2 = 8.1 Hz, 1H), 2.20 (dd, J^1 = 14.7 Hz, J^2 = 4.0 Hz, 1H), 1.28 (s, 9H), 1.21 (s, 3H), 1.20 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 171.8, 156.9, 152.6, 149.8, 137.2, 134.7, 126.7, 125.9, 125.1, 122.8, 122.1, 121.5, 57.9, 49.1, 47.5, 46.7, 36.6, 30.6, 28.7, 27.8; **HRMS** (ESI) *m*/*z* = 503.0926, calcd. for $C_{22}H_{28}N_2O_2S_4Na^+$ $[M+Na]^+$, found: 503.0930; **IR** (neat, cm^{-1}): 2964*w*, 2924*w*, 1576*w*, 1513*w*, 1456*w*, 1433*w*, 1319*s*, 1159*s*, 1108*s*, 994*w*, 908*w*, 760*s*, 731*s*.

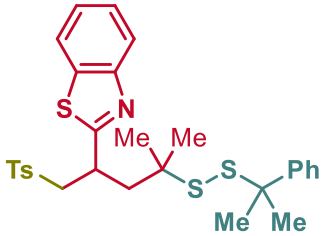


2-(4-(*tert*-Butyldisulfanyl)-1-((3,5-difluorophenyl) sulfonyl)-4-methylpentan-2-yl)benzo [*d*]thiazole (3r): The title compound was prepared according to general procedure (**GP5**) with rose bengal (4.1 mg, 4.0 μmol, 2.0 mol%), **1a** (56.3 mg, 0.200 mmol, 1.0 equiv), and **2i** (89.5 mg, 0.300 mmol, 1.5 equiv) in DMA (1 mL) at room temperature for 12 h. Purification via silica gel chromatography (PE:EtOAc = 20:1 to 10:1) gave the desired product **3r** as a white solid in 77% yield (79.4 mg). **MP:** 109.3-110.7 °C; **TLC** R_f = 0.2 (PE:EtOAc = 20:1); **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.78 (dd, J^1 = 8.0 Hz, J^2 = 8.0 Hz, 2H), 7.42 (ddd, J^1 = 8.1 Hz, J^2 = 7.7 Hz, J^3 = 1.4 Hz, 1H), 7.36 (ddd, J^1 = 7.5 Hz, J^2 = 7.5 Hz, 1.3 Hz, 1H), 7.26-7.20 (m, 2H), 6.67 (tt, J^1 = 8.4 Hz, J^2 = 2.4 Hz, 1H), 4.11 (dd, J^1 = 14.4 Hz, J^2 =

9.6 Hz, 1H), 4.03-3.92 (m, 1H), 3.65 (dd, J^1 = 14.4 Hz, J^2 = 3.6 Hz, 1H), 2.22 (dd, J^1 = 14.8 Hz, J^2 = 6.7 Hz, 1H), 2.12 (dd, J^1 = 14.8 Hz, J^2 = 4.8 Hz, 1H), 1.30 (s, 9H), 1.26 (s, 3H), 1.25 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 171.2, 162.3 (dd, J^1 = 255.3 Hz, J^2 = 11.5 Hz), 152.5, 142.3 (dd, J^1 = 8.2 Hz, J^2 = 8.2 Hz), 134.5, 126.1, 125.4, 122.7, 121.6, 111.6 (dd, J^1 = 28.3 Hz, J^2 = 11.3 Hz), 108.6 (dd, J^1 = 25.0 Hz, J^2 = 25.0 Hz), 61.6, 49.0, 47.7, 46.8, 36.5, 30.6, 28.8, 27.7; **^{19}F NMR** (377 MHz, $CDCl_3$, 300 K): δ (ppm) = -105.6. **HRMS** (EI) *m/z* = 515.0887, calcd. for $C_{23}H_{27}F_2NO_2S_4^+$ $[M]^+$, found: 515.0890; **IR** (neat, cm^{-1}): 2964*w*, 2924*w*, 1605*m*, 1513*w*, 1439*s*, 1331*m*, 1296*s*, 1131*s*, 988*w*, 862*w*, 760*m*.

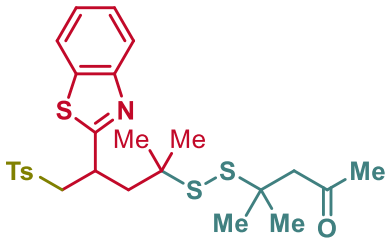


2-(1-((3,5-Bis(trifluoromethyl)phenyl)sulfonyl)-4-(*tert*-butyldisulfanyl)-4-methylpentan-2-yl)benzo[*d*]thiazole (3s): The title compound was prepared according to general procedure (**GP5**) with rose bengal (4.1 mg, 4.0 μmol, 2.0 mol%), **1a** (56.3 mg, 0.200 mmol, 1.0 equiv), and **2j** (119.5 mg, 0.3000 mmol, 1.5 equiv) in DMA (1 mL) at room temperature for 12 h. Purification via silica gel chromatography (PE:EtOAc = 25:1 to 15:1) gave the desired product **3s** as a colorless oil in 40% yield (49.0 mg). **TLC R_f** = 0.3 (PE:EtOAc = 20:1); **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 8.11 (s, 2H), 7.71 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.62-7.50 (m, 2H), 7.33 (dtd, J^1= 16.6 Hz, J^2= 7.3 Hz, J^3= 1.4 Hz, 2H), 4.35 (dd, J^1= 14.8 Hz, J^2= 10.5 Hz, 1H), 3.99 (dtd, J^1= 10.8 Hz, J^2= 5.6 Hz, J^3= 2.9 Hz, 1H), 3.75 (dd, J^1= 14.8 Hz, J^2= 3.0 Hz, 1H), 2.13 (dd, J^1 = 14.9 Hz, J^2 = 5.9 Hz, 1H), 2.08 (dd, J^1 = 14.9 Hz, J^2 = 5.4 Hz, 1H), 1.30 (s, 9H), 1.29 (s, 3H), 1.26 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 170.6, 152.1, 141.8, 134.1, 132.1 (q, *J* = 34.5 Hz), 128.2 (q, *J* = 3.6 Hz), 126.2 (q, *J* = 3.2 Hz), 126.1, 125.5, 122.5, 122.1(q, *J* = 273.6 Hz), 121.7, 61.2, 49.0, 47.8, 47.0, 36.6, 30.6, 28.8, 27.8; **^{19}F NMR** (377 MHz, $CDCl_3$, 300 K) δ (ppm) = -63.0; **HRMS** (ESI) *m/z* = 616.0902, calcd. for $C_{25}H_{28}NO_2S_4F_6^+$ $[M+H]^+$, found: 616.0902; **IR** (neat, cm^{-1}): 2964*w*, 2924*w*, 1456*w*, 1359*w*, 1279*s*, 1182*m*, 1142*s*, 1102*m*, 908*w*, 760*w*.

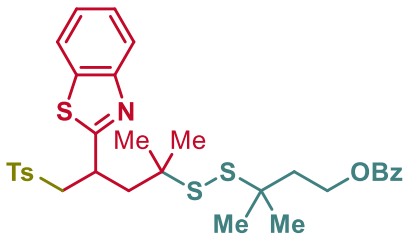


2-(4-Methyl-4-((2-phenylpropan-2-yl)disulfanyl)-1-tosylpentan-2-yl)benzo[*d*]thiazole (3t): The title compound was prepared according to general procedure (**GP5**) with rose bengal (4.1 mg, 4.0 μmol, 2.0 mol%), **1a** (56.3 mg, 0.200 mmol, 1.0 equiv), and **2k** (101.5 mg, 0.3000 mmol, 1.5 equiv) in DMA (1 mL) at room temperature for 12 h. Purification via silica gel chromatography (PE:EtOAc = 10:1 to 5:1) gave the desired product **3t** as a colorless oil in 71% yield (78.9 mg). **TLC R_f** = 0.2 (PE:EtOAc = 10:1); **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.76 (d, *J* = 8.1 Hz, 2H), 7.57 (d, *J* =

8.2 Hz, 2H), 7.52-7.44 (m, 2H), 7.39 (ddd, J^1 = 7.6 Hz, J^2 = 7.6 Hz, J^3 = 1.3 Hz, 1H), 7.36-7.27 (m, 3H), 7.19 (dd, J^1 = 7.3 Hz, J^2 = 7.3 Hz, 1H), 7.00 (d, J = 8.0 Hz, 2H), 3.95- 3.77 (m, 2H), 3.48-3.34 (m, 1H), 2.16 (s, 3H), 2.00 (dd, J^1 = 14.7 Hz, J^2 = 7.1 Hz, 1H), 1.88 (dd, J^1 = 14.7 Hz, J^2 = 4.2 Hz, 1H), 1.70 (s, 3H), 1.69 (s, 3H), 1.00 (s, 3H), 0.95 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 171.8, 152.6, 145.7, 144.3, 136.1, 134.7, 129.3, 128.1, 127.9, 127.0, 126.7, 125.8, 125.0, 122.7, 121.5, 61.7, 51.6, 49.7, 47.6, 36.6, 29.3, 29.2, 28.2, 27.4, 21.3; **HRMS** (ESI) *m/z* = 556.1467, calcd. for $C_{29}H_{34}NO_2S_4^+$ $[M+H]^+$, found: 556.1469; **IR** (neat, cm^{-1}): 2964*w*, 2924*w*, 1599*w*, 1456*w*, 1319*m*, 1142*s*, 1091*m*, 765*m*.

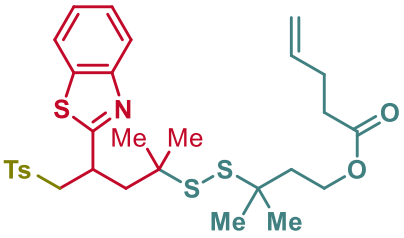


4-((4-(Benzo[*d*]thiazol-2-yl)-2-methyl-5-tosylpentan-2-yl)disulfaneyl)-4-methylpentan-2-one (3u): The title compound was prepared according to general procedure (**GP5**) with rose bengal (4.1 mg, 4.0 μmol, 2.0 mol%), **1a** (56.3 mg, 0.200 mmol, 1.0 equiv), and **2l** (95.5 mg, 0.300 mmol, 1.5 equiv) in DMA (1 mL) at room temperature for 12 h. Purification via silica gel chromatography (PE:EtOAc = 10:1) gave the desired product **3u** as a colorless oil in 66% yield (71.0 mg). **TLC R_f** = 0.2 (PE:EtOAc = 5:1); **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.78 (dd, J^1 = 8.0 Hz, J^2 = 3.0 Hz, 2H), 7.60 (d, J = 8.2 Hz, 2H), 7.44-7.37 (m, 1H), 7.32 (t, J = 7.6 Hz, 1H), 7.04 (d, J = 8.0 Hz, 2H), 4.03-3.88 (m, 2H), 3.55 (dd, J^1 = 13.4 Hz, J^2 = 3.6 Hz, 1H), 2.65 (s, 2H), 2.29 (dd, J^1 = 14.7 Hz, J^2 = 7.1 Hz, 1H), 2.24 – 2.16 (m, 4H), 2.10 (s, 3H), 1.38 (s, 3H), 1.37 (s, 3H), 1.25 (s, 3H), 1.23 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 206.4, 171.6, 152.6, 144.4, 136.1, 134.7, 129.3, 127.8, 125.9, 125.0, 122.7, 121.5, 61.7, 54.0, 49.5, 48.0, 47.6, 36.5, 32.0, 28.4, 28.1, 27.6, 27.5, 21.3; **HRMS** (ESI) *m/z* = 536.1416, calcd. for $C_{26}H_{34}NO_3S_4^+$ $[M+H]^+$, found: 536.1412; **IR** (neat, cm^{-1}): 2964*w*, 2924*w*, 1713*m*, 1599*w*, 1513*w*, 1439*m*, 1359*w*, 1319*m*, 1142*s*, 1114*m*, 1091*m*, 817*w*, 760*m*, 731*w*.

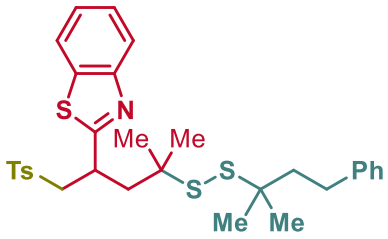


3-((4-(Benzo[*d*]thiazol-2-yl)-2-methyl-5-tosylpentan-2-yl)disulfanyl)-3-methylbutyl benzoate (3v): The title compound was prepared according to general procedure (**GP5**) with rose bengal (4.1 mg, 4.0 μmol, 2.0 mol%), **1a** (56.3 mg, 0.200 mmol, 1.0 equiv), and **2m** (123.2 mg, 0.3000 mmol, 1.5 equiv) in DMA (1 mL) at room temperature for 12 h. Purification via silica gel chromatography (PE:EtOAc = 10:1) gave the desired product **3v** as a colorless oil in 63% yield (79.0 mg). **TLC R_f** = 0.2 (PE:EtOAc = 5:1); **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 8.07-7.99 (m, 2H), 7.77 (dd, J^1 = 7.7 Hz, J^2 = 7.7 Hz, 2H), 7.61 (d,

J = 8.2 Hz, 2H), 7.59-7.51 (m, 1H), 7.47-7.35 (m, 3H), 7.31 (ddd, J^1 = 7.5 Hz, J^2 = 7.5 Hz, J^3 = 1.3 Hz, 1H), 7.04 (d, J = 8.0 Hz, 2H), 4.43 (t, J = 6.9 Hz, 2H), 4.02-3.88 (m, 2H), 3.61-3.50 (m, 1H), 2.28 (dd, J^1 = 14.7 Hz, J^2 = 7.2 Hz, 1H), 2.23-2.14 (m, 4H), 2.01 (t, J = 6.9 Hz, 2H), 1.34 (s, 6H), 1.25 (s, 3H), 1.23 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 171.8, 166.4, 152.7, 144.4, 136.1, 134.7, 132.9, 130.2, 129.5, 129.4, 128.3, 127.9, 125.9, 125.0, 122.7, 121.5, 62.0, 61.7, 49.4, 48.5, 47.7, 40.4, 36.6, 28.5, 28.0, 21.3; **HRMS** (ESI) *m/z* = 650.1498, calcd. for $C_{32}H_{37}NO_4S_4Na^+$ $[M+Na]^+$, found: 650.1506; **IR** (neat, cm^{-1}): 2964*w*, 2924*w*, 1719*s*, 1599*w*, 1456*w*, 1314*m*, 1274*s*, 1142*s*, 1114*s*, 811*w*, 760*w*, 714*m*.

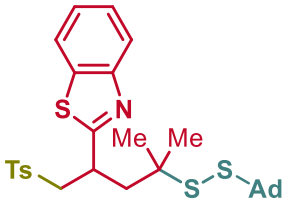


3-((4-(Benzo[*d*]thiazol-2-yl)-2-methyl-5-tosylpentan-2-yl)disulfaneyl)-3-methylbutyl pent-4-enoate (3w): The title compound was prepared according to general procedure (**GP5**) with rose bengal (4.1 mg, 4.0 μmol, 2.0 mol%), **1a** (56.3 mg, 0.200 mmol, 1.0 equiv), and **2n** (116.6 mg, 0.3000 mmol, 1.5 equiv) in DMA (1 mL) at room temperature for 12 h. Purification via silica gel chromatography (PE:EtOAc = 10:1 to 5:1) gave the desired product **3w** as a colorless oil in 56% yield (67.9 mg). **TLC R$_f$** = 0.2 (PE:EtOAc = 5:1); **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.82-7.72 (m, 2H), 7.61 (d, J = 8.0 Hz, 2H), 7.41 (t, J = 7.6 Hz, 1H), 7.32 (t, J = 7.6 Hz, 1H), 7.04 (d, J = 8.0 Hz, 2H), 5.89-5.70 (m, 1H), 5.03 (dd, J^1 = 21.2 Hz, J^2 = 13.7 Hz, 2H), 4.18 (t, J = 7.1 Hz, 2H), 4.02-3.86 (m, 2H), 3.55 (q, J = 8.3 Hz, 1H), 2.37 (q, J^1 = 5.4 Hz, J^2 = 4.6 Hz, 4H), 2.32-2.22 (m, 1H), 2.22-2.13 (m, 4H), 1.86 (t, J = 7.1 Hz, 2H), 1.28 (s, 6H), 1.24 (s, 3H), 1.21 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 172.9, 171.8, 152.7, 144.4, 136.6, 136.1, 134.7, 129.3, 127.9, 125.9, 125.0, 122.7, 121.5, 115.5, 61.7, 61.4, 49.4, 48.4, 47.6, 40.2, 36.5, 33.5, 28.8, 28.5, 28.4, 28.0, 21.3; **HRMS** (ESI) *m/z* = 606.1835, calcd. for $C_{30}H_{40}NO_4S_4^+$ $[M+H]^+$, found: 606.1832; **IR** (neat, cm^{-1}): 2958*w*, 2924*w*, 2855*w*, 1736*s*, 1456*w*, 1319*m*, 1142*s*, 1091*m*, 1017*w*, 919*w*, 817*w*, 760*m*.



2-(4-Methyl-4-((2-methyl-4-phenylbutan-2-yl)disulfanyl)-1-tosylpentan-2-yl)benzo[*d*]thiazole (3x): The title compound was prepared according to general procedure (**GP5**) with rose bengal (4.1 mg, 4.0 μmol, 2.0 mol%), **1a** (56.3 mg, 0.200 mmol, 1.0 equiv), and **2o** (110.0 mg, 0.3000 mmol, 1.5 equiv) in DMA (1 mL) at room temperature for 12 h. Purification via silica gel chromatography (PE:EtOAc = 10:1) gave the desired product **3x** as a colorless oil in 57% yield (66.4 mg). **TLC R$_f$** = 0.3 (PE:EtOAc = 5:1); **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) =

7.77 (dd, J^1 = 7.8 Hz, J^2 = 7.8 Hz, 2H), 7.60 (d, J = 8.1 Hz, 2H), 7.40 (dd, J^1 = 7. 6 Hz, J^2 = 7. 6 Hz, 1H), 7.35-7.13 (m, 6H), 7.02 (d, J = 8.1 Hz, 2H), 4.02-3.86 (m, 2H), 3.61-3.49 (m, 1H), 2.77-2.60 (m, 2H), 2.27 (dd, J^1 = 14.7 Hz, J^2 =7.0 Hz, 1H), 2.23-2.12 (m, 4H), 1.86-1.75 (m, 2H), 1.31 (s, 6H), 1.24 (s, 3H), 1.22 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 171.9, 152.7, 144.4, 142.1, 136.2, 134.7, 129.3, 128.4, 128.3, 127.9, 125.9, 125.8, 125.0, 122.7, 121.5, 61.7, 49.9, 49.2, 47.7, 44.3, 36.6, 31.3, 28.5, 28.3, 28.2, 28.0, 21.3; **HRMS** (ESI) *m/z* = 584.1780, calcd. for $C_{31}H_{38}NO_2S_4^+$ $[M+H]^+$, found: 584.1777; **IR** (neat, cm^{-1}): 2958*w*, 2924*w*, 1599*w*, 1456*w*, 1319*m*, 1296*m*, 1142*s*, 1085*m*, 908*w*, 811*w*, 760*m*, 731*m*, 702*w*.



2-(4-(((3s,5s,7s)-Adamantan-1-yl)disulfaneyl)-4-methyl-1-tosylpentan-2-yl)benzo[*d*]thiazole (3y): The title compound was prepared according to general procedure (**GP5**) with rose bengal (4.1 mg, 4.0 μmol, 2.0 mol%), **1a** (56.3 mg, 0.200 mmol, 1.0 equiv), and **2p** (106.4 mg, 0.3000 mmol, 1.5 equiv) in DMA (1 mL) at room temperature for 12 h. Purification via silica gel chromatography (PE:EtOAc = 10:1 to 5:1) gave the desired product **3y** as a white solid in 69% yield (79.2 mg). **MP:** 54.5-55.7 °C; **TLC R_f** = 0.4 (PE:EtOAc = 5:1); **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.77 (d, J = 8.4 Hz, 2H), 7.59 (d, J = 8.2 Hz, 2H), 7.44-7.36 (m, 1H), 7.36-7.28 (m, 1H), 7.02 (d, J = 8.0 Hz, 2H), 4.03-3.91 (m, 2H), 3.63-3.50 (m, 1H), 2.24 (dd, J^1 = 14.7 Hz, J^2 =6.5 Hz, 1H), 2.20 – 2.12 (m, 4H), 2.09-2.00 (m, 3H), 1.78 (d, J = 2.9 Hz, 6H), 1.71-1.59 (m, 6H), 1.23 (s, 3H), 1.20 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 171.9, 152.7, 144.3, 136.2, 134.7, 129.3, 127.9, 125.9, 125.0, 122.7, 121.5, 61.8, 48.7, 48.3, 47.6, 43.1, 36.6, 36.0, 30.0, 28.5, 27.9, 21.3; **HRMS** (ESI) *m/z* = 594.1599, calcd. for $C_{30}H_{37}NO_2S_4Na^+$ $[M+Na]^+$, found: 594.1603; **IR** (neat, cm^{-1}): 2953*w*, 2913*s*, 2850*w*, 1456*w*, 1319*m*, 1296*m*, 1142*s*, 1091*m*, 1039*w*, 811*w*, 760*m*, 731*w*.

3.4 Gram-scale reaction

A flame-dried flask equipped with a magnetic stir bar was charged with **1a** (0.844 g, 3.000 mmol, 1.0 equiv), **2a** (1.242 g, 4.500 mmol, 1.5 equiv), and rose bengal (61

mg, 0.060 mmol, 2.0 mol%), sealed with a septum, and degassed by alternating vacuum evacuation and argon backfilling (three times) before DMA (15 mL) was added. The reaction mixture was then stirred and irradiated using a 20 W blue LEDs lamp at room temperature for 24 h. After the reaction was completed, the mixture was diluted with EtOAc (10 mL), which was followed by extraction with EtOAc (15 mL × 3). The combined organic phase was washed with brine (20 mL × 3), dried with Na_2SO_4 and the solvent was evaporated with the aid of a rotary evaporator. The crude product was purified by column chromatography to afford pure product **3a** (1.080 g, 73%).

3.5 X-Ray crystallographic data compound 3r

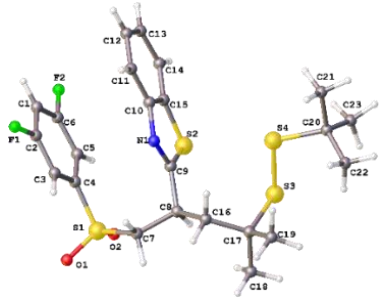
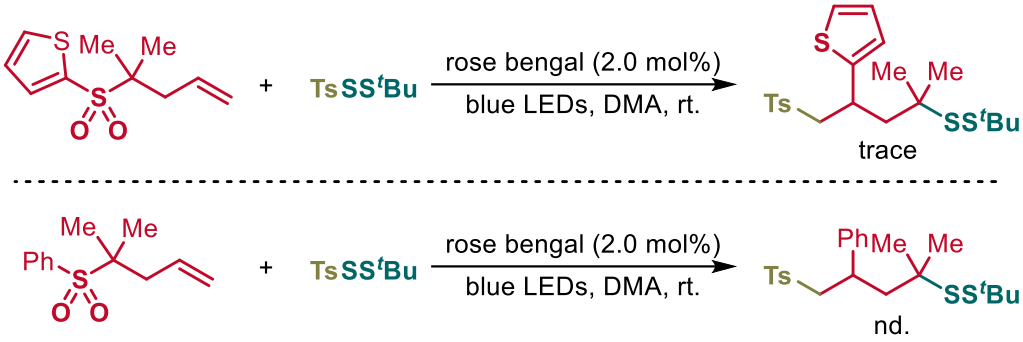


Table S2 Crystal data and structure refinement for 3r (CCDC 2224310).

Empirical formula	$C_{23}H_{27}F_2NO_2S_4$
Radiation	MoKα (λ = 0.71073)
Temperature/K	150
Bond precision	C-C = 0.0048 Å
Space group	P -1
Hall group	-P 1
a/Å	6.0073(2)
b/Å	11.3650(5)
c/Å	18.1482(7)
α/°	99.599(1)
β/°	90.858(1)
γ/°	94.491(1)
Volume/$Å^3$	1217.44(8)
Mr	516.70
Z	2
$\rho_{calc}g/cm^3$	1.410
μ/mm^{-1}	0.427
F(000)	542.0
h,k,lmax	7,13,21
Nref	4211
Tmin,Tmax	0.060,0.096
Data completeness	0.984
Theta(max)	24.998

R(reflections)	0.0522(3738)
wR_2(reflections)	0.1577(4211)
S	1.050
Npar	294

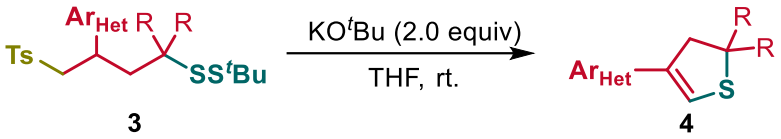
3.6 Limitations of the methods



When we attempted to convert the substrate bearing thiophene as a migratory group, only a trace amount of target product was observed. We have tested phenyl substituted sulfone under standard reaction conditions, unfortunately, the desired product was not detected.

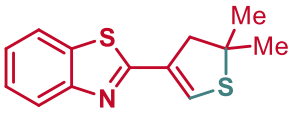
4. Follow-up transformations of polysulfides 3

4.1 General procedure for synthesis of dihydrothiophenes (GP6)



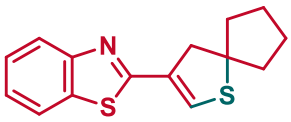
A flame-dried Schlenk tube equipped with a magnetic stir bar was charged with **3** (0.100 mmol, 1.0 equiv), KO^{t}Bu (22.4 mg, 0.200 mmol, 2.0 equiv), and THF (1 mL), sealed with a septum. The reaction was allowed to stir at room temperature for 2 h. After the reaction was complete, the solvent was removed under reduced pressure with the aid of a rotary evaporator. The crude residue was purified by silica gel column chromatography to afford pure product **4**.

4.2 Spectral data of dihydrothiophenes 4

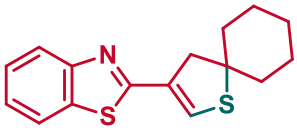


2-(5,5-dimethyl-4,5-dihydrothiophen-3-yl)benzo[*d*]thiazole (4a): The title compound was prepared according to general procedure (**GP6**) with **3a** (49.4 mg, 0.100 mmol, 1.0 equiv) and ^{t}BuOK (22.4 mg, 0.200 mmol, 2.0 equiv) in THF (1 mL) at room temperature for

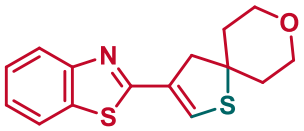
2 h. Purification via silica gel chromatography (PE:EtOAc = 50:1) gave the desired product **4a** as a white solid in >99% yield (24.8 mg). **MP:** 69.7-71.2 °C; **TLC R_f** = 0.5 (PE:EtOAc = 50:1); **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.93 (d, *J* = 8.2 Hz, 1H), 7.78 (d, *J* = 7.7 Hz, 1H), 7.42 (ddd, J^1 = 8.3 Hz, J^2 = 7.2 Hz, J^3 = 1.3 Hz, 1H), 7.31 (ddd, J^1 = 8.2 Hz, J^2 = 7.3 Hz, J^3 = 1.2 Hz, 1H), 7.15 (t, *J* = 1.8 Hz, 1H), 3.23 (d, *J* = 1.7 Hz, 2H), 1.61 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 163.5, 153.7, 134.2, 133.4, 129.2, 126.1, 124.8, 122.6, 121.3, 57.8, 50.4, 30.3; **HRMS** (ESI) *m*/*z* = 248.0562, calcd. for $C_{13}H_{14}NS_2^+$ $[M+H]^+$, found: 248.0573; **IR** (neat, cm^{-1}): 2958*w*, 2924*w*, 1565*s*, 1479*m*, 1456*w*, 1433*m*, 1274*w*, 1199*w*, 828*m*, 754*m*, 725*w*.



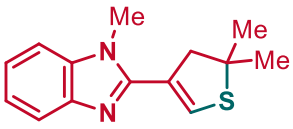
2-(1-thiaspiro[4.4]non-2-en-3-yl)benzo[*d*]thiazole(4b): The title compound was prepared according to general procedure (**GP6**) with **3b** (52.0 mg, 0.100 mmol, 1.0 equiv) and ^{t}BuOK (22.4 mg, 0.200 mmol, 2.0 equiv) in THF (1 mL) at room temperature for 2 h. Purification via silica gel chromatography (PE:EtOAc = 50:1) gave the desired product **4b** as a colorless oil in 82% yield (22.3 mg). **TLC R_f** = 0.4 (PE:EtOAc = 50:1); **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.93 (d, *J* = 8.1 Hz, 1H), 7.79 (dd, J^1 = 8.0, J^2 = 1.2 Hz, 1H), 7.42 (td, J^1 = 8.2, J^2 = 7.7, 1.3 Hz, 1H), 7.31 (td, J^1 = 7.6, J^2 = 1.2 Hz, 1H), 7.17 (t, *J* = 1.8 Hz, 1H), 3.35 (d, *J* = 1.8 Hz, 2H), 2.19-2.08 (m, 2H), 2.05-1.92 (m, 2H), 1.84-1.76 (m, 4H); **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 163.5, 153.6, 134.2, 133.6, 129.3, 126.1, 124.8, 122.5, 121.3, 67.7, 47.6, 41.3, 23.6; **HRMS** (ESI) *m*/*z* = 274.0719, calcd. for $C_{15}H_{16}NS_2^+$ $[M+H]^+$, found: 274.0714; **IR** (neat, cm^{-1}): 3061*w*, 2958*w*, 2873*w*, 1593*w*, 1565*s*, 1479*m*, 1456*w*, 1433*m*, 1314*w*, 1262*w*, 1245*w*, 1194*w*, 959*w*, 834*m*, 760*s*, 725*m*.



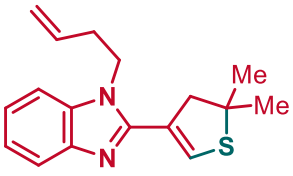
2-(1-thiaspiro[4.5]dec-2-en-3-yl)benzo[*d*]thiazole (4c): The title compound was prepared according to general procedure (**GP6**) with **3c** (53.4 mg, 0.100 mmol, 1.0 equiv) and ^{t}BuOK (22.4 mg, 0.200 mmol, 2.0 equiv) in THF (1 mL) at room temperature for 2 h. Purification via silica gel chromatography (PE:EtOAc = 50:1) gave the desired product **4c** as a colorless oil in >99% yield (28.7 mg). **TLC R_f** = 0.3 (PE:EtOAc = 50:1); **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.93 (d, *J* = 8.2 Hz, 1H), 7.77 (d, *J* = 7.9 Hz, 1H), 7.41 (t, *J* = 7.7 Hz, 1H), 7.30 (t, *J* = 7.6 Hz, 1H), 7.12 (s, 1H), 3.23 (s, 2H), 2.08 (dt, J^1 = 14.0, J^2 = 4.3 Hz, 2H), 1.72 (ddd, J^1 = 23.3, J^2 = 10.9, J^3 = 4.0 Hz, 4H), 1.65-1.51 (m, 3H), 1.39-1.28 (m, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 163.6, 153.6, 134.2, 133.1, 129.2, 126.1, 124.8, 122.5, 121.2, 64.3, 48.7, 39.5, 25.3, 24.1; **HRMS** (ESI) *m*/*z* = 288.0875, calcd. for $C_{16}H_{18}NS_2^+$ $[M+H]^+$, found: 288.0875; **IR** (neat, cm^{-1}): 3055*w*, 2924*s*, 2855*w*, 1593*w*, 1571*s*, 1479*m*, 1451*w*, 1433*m*, 1314*w*, 1274*w*, 1251*w*, 1188*w*, 948*w*, 834*w*, 754*s*, 725*m*.



2-(8-oxa-1-thiaspiro[4.5]dec-2-en-3-yl) benzo[*d*]thiazole (4d): The title compound was prepared according to general procedure (**GP6**) with **3d** (53.6 mg, 0.100 mmol, 1.0 equiv) and ^{t}BuOK (22.4 mg, 0.200 mmol, 2.0 equiv) in THF (1 mL) at room temperature for 2 h. Purification via silica gel chromatography (PE:EtOAc = 5:1) gave the desired product **4d** as a white solid in 88% yield (25.4 mg). **MP:** 115.3-116.1 °C; **TLC R_f** = 0.2 (PE:EtOAc = 20:1); **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.94 (d, J = 8.1 Hz, 1H), 7.79 (d, J = 8.1 Hz, 1H), 7.43 (ddd, J^1 = 8.3, J^2 = 7.3, J^3 = 1.3 Hz, 1H), 7.33 (ddd, J^1 = 8.3, J^2 = 7.2, J^2 = 1.2 Hz, 1H), 7.12 (d, J = 3.7 Hz, 1H), 3.92 (dt, J^1 = 12.2, J^2 = 4.0 Hz, 2H), 3.66 (ddd, J^1 = 12.3, J^2 = 9.6, J^3 = 2.9 Hz, 2H), 3.30 (d, J = 1.8 Hz, 2H), 2.12-1.94 (m, 4H); **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 163.2, 153.6, 134.2, 132.0, 129.3, 126.2, 125.0, 122.7, 121.3, 65.8, 60.8, 48.6, 39.3; **HRMS** (ESI) *m*/*z* = 290.0668, calcd. for $C_{15}H_{16}NOS_2^+$ $[M+H]^+$, found: 290.0662; **IR** (neat, cm^{-1}): 3055*w*, 2958*w*, 2935*w*, 2844*w*, 1593*w*, 1571*s*, 1479*m*, 1456*w*, 1433*s*, 1262*w*, 1239*w*, 1188*w*, 1125*w*, 1102*s*, 1017*w*, 948*w*, 834*w*, 760*s*, 731*w*.

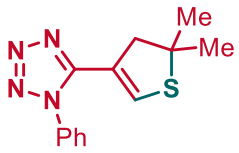


2-(5,5-dimethyl-4,5-dihydrothiophen-3-yl)-1-methyl-1*H*-benzo[*d*]imidazole (4e): The title compound was prepared according to general procedure (**GP6**) with **3e** (49.1 mg, 0.100 mmol, 1.0 equiv) and ^{t}BuOK (22.4 mg, 0.200 mmol, 2.0 equiv) in THF (1 mL) at room temperature for 2 h. Purification via silica gel chromatography (PE:EtOAc = 50:1) gave the desired product **4e** as a white solid in 79% yield (19.2 mg). **MP:** 113.2-113.7 °C; **TLC R_f** = 0.2 (PE:EtOAc = 10:1); **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.80-7.67 (m, 1H), 7.31-7.21 (m, 3H), 6.83 (d, J = 1.8 Hz, 1H), 3.85 (s, 3H), 3.33 (d, J = 1.8 Hz, 2H), 1.62 (s, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 149.4, 142.4, 136.3, 130.0, 124.1, 122.6, 122.2, 119.4, 108.9, 56.1, 52.4, 31.9, 30.0; **HRMS** (ESI) *m*/*z* = 245.1107, calcd. for $C_{14}H_{17}N_2S^+$ $[M+H]^+$, found: 245.1101; **IR** (neat, cm^{-1}): 3375*br*, 3061*w*, 2958*w*, 2924*w*, 2861*w*, 1611*w*, 1593*m*, 1576*m*, 1451*m*, 1393*w*, 1365*w*, 1325*w*, 1308*w*, 1285*w*, 1245*w*, 1148*w*, 1005*w*, 840*w*, 742*s*, 702*w*.

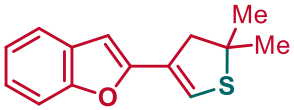


1-(but-3-en-1-yl)-2-(5,5-dimethyl-4,5-dihydrothiophen-3-yl)-1*H*-benzo[*d*] imidazole (4f): The title compound was prepared according to general procedure (**GP6**) with **3f** (49.1 mg, 0.100 mmol, 1.0 equiv) and ^{t}BuOK (22.4 mg, 0.200 mmol, 2.0 equiv) in THF (1 mL) at room temperature for 2 h. Purification via silica gel chromatography (PE:EtOAc = 50:1) gave the desired product **4f** as a colorless oil in 61% yield (17.3 mg). **TLC R_f** = 0.2 (PE:EtOAc = 10:1); **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.78-7.71 (m, 1H), 7.32 (ddt, J^1 = 7.2, J^2 = 3.3, J^3 = 1.7 Hz,

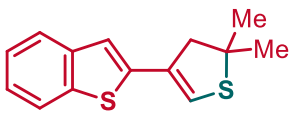
1H), 7.31-7.21 (m, 2H), 6.78 (t, J = 1.8 Hz, 1H), 5.82 (ddt, J^1 = 17.1, J^2 = 10.3, J^3 = 6.8 Hz, 1H), 5.18-5.11 (m, 1H), 5.14 – 5.08 (m, 1H), 4.38-4.27 (m, 2H), 3.33 (d, J = 1.8 Hz, 2H), 2.67-2.56 (m, 2H), 1.62 (s, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 148.9, 142.5, 135.6, 133.4, 129.4, 123.9, 122.7, 122.4, 119.5, 118.1, 109.3, 56.1, 52.9, 44.1, 33.9, 30.1; **HRMS** (ESI) *m/z* = 285.1420, calcd. for $C_{17}H_{21}N_2S^+$ $[M+H]^+$, found: 285.1415; **IR** (neat, cm^{-1}): 3381*br*, 3067*w*, 2970*w*, 2958*w*, 2924*w*, 1576*w*, 1451*m*, 1399*m*, 1365*w*, 1330*w*, 1285*m*, 1148*w*, 1005*w*, 919*w*, 840*w*, 822*w*, 742*s*.



5-(5,5-dimethyl-4,5-dihydrothiophen-3-yl)-1-phenyl-1*H*-tetrazole (4g): The title compound was prepared according to general procedure (**GP6**) with **3g** (50.5 mg, 0.100 mmol, 1.0 equiv) and ^{t}BuOK (22.4 mg, 0.200 mmol, 2.0 equiv) in THF (1 mL) at room temperature for 2 h. Purification via silica gel chromatography (PE:EtOAc = 50:1) gave the desired product **4g** as a white solid in 73% yield (18.8 mg). **MP:** 112.3-112.7 °C; **TLC R$_f$** = 0.2 (PE:EtOAc = 10:1); **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.63-7.57 (m, 3H), 7.46-7.41 (m, 2H), 6.46 (t, J = 1.8 Hz, 1H), 3.06 (d, J = 1.8 Hz, 2H), 1.52 (s, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 150.2, 135.6, 134.7, 130.9, 130.1, 126.1, 115.9, 57.1, 50.6, 30.0; **HRMS** (ESI) *m/z* = 259.1012, calcd. for $C_{13}H_{15}N_4S^+$ $[M+H]^+$, found: 259.1007; **IR** (neat, cm^{-1}): 3067*w*, 2964*w*, 2924*w*, 1588*s*, 1502*m*, 1473*w*,1456*w*, 1411*w*, 1365*w*, 1291*w*, 1268*w*, 1245*w*, 1148*w*, 1097*w*, 999*w*, 834*w*, 782*m*, 765*s*, 731*w*, 691*s*.



2-(5,5-dimethyl-4,5-dihydrothiophen-3-yl)benzofuran (4h): The title compound was prepared according to general procedure (**GP6**) with **3h** (47.7 mg, 0.100 mmol, 1.0 equiv) and ^{t}BuOK (22.4 mg, 0.200 mmol, 2.0 equiv) in THF (1 mL) at room temperature for 2 h. Purification via silica gel chromatography (PE:EtOAc = 50:1) gave the desired product **4h** as a white solid in 83% yield (19.1 mg). **MP:** 52.2-52.6 °C; **TLC R$_f$** = 0.6 (PE:EtOAc = 50:1); **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.53-7.46 (m, 1H), 7.41 (dd, J^1 = 8.1, J^2 = 1.0 Hz, 1H), 7.23 (td, J^1 = 7.8, J^2 = 1.6 Hz, 1H), 7.18 (td, J^1 = 7.4, J^2 = 1.2 Hz, 1H), 6.85 (t, J = 1.7 Hz, 1H), 6.36 (s, 1H), 2.92 (d, J = 1.8 Hz, 2H), 1.60 (s, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 154.5, 153.0, 129.1, 124.8, 124.0, 123.5, 122.7, 120.5, 110.6, 101.1, 56.9, 49.6, 30.2; **HRMS** (ESI) *m/z* = 231.0838, calcd. for $C_{14}H_{15}OS^+$ $[M+H]^+$, found: 231.0836; **IR** (neat, cm^{-1}): 3078*w*, 2970*w*, 2958*w*, 2924*w*, 2890*w*, 1605*m*, 1531*w*, 1451*s*, 1365*w*, 1302*w*, 1285*w*, 1256*m*, 1222*w*, 1199*w*, 1142*w*, 1108*w*, 1011*m*, 925*w*, 817*s*, 788*m*, 748*s*.



2-(5,5-dimethyl-4,5-dihydrothiophen-3-yl)benzo[*b*]thiophene (4i): The title compound was prepared according to general procedure (**GP6**) with **3i** (49.3 mg, 0.100 mmol, 1.0

equiv) and ^{t}BuOK (22.4 mg, 0.200 mmol, 2.0 equiv) in THF (1 mL) at room temperature for 2 h. Purification via silica gel chromatography (PE:EtOAc = 50:1) gave the desired product **4i** as a white solid in 64% yield (15.8 mg). **MP:** 119.6-120.2 °C; **TLC R_f** = 0.7 (PE:EtOAc = 20:1); **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.74-7.67 (m, 1H), 7.67-7.60 (m, 2H), 7.33-7.20 (m, 2H), 6.93 (s, 1H), 6.56 (t, *J* = 1.7 Hz, 1H), 3.00 (d, *J* = 1.7 Hz, 2H), 1.59 (s, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 140.3, 140.2, 138.5, 128.1, 124.4, 124.2, 123.1, 122.0, 118.9, 56.8, 51.2, 30.4; **HRMS** (ESI) *m*/*z* = 247.0610, calcd. for $C_{14}H_{15}S_2^+$ $[M+H]^+$, found: 247.0611; **IR** (neat, cm^{-1}): 3050*w*, 2970*w*, 2958*w*, 2924*w*, 1571*m*, 1456*m*, 1433*m*, 1365*w*, 1279*w*, 1228*w*, 1148*w*, 1102*w*, 937*w*, 822*m*, 805*s*, 742*s*, 725*m*.

4.3 X-Ray crystallographic data compound 4e

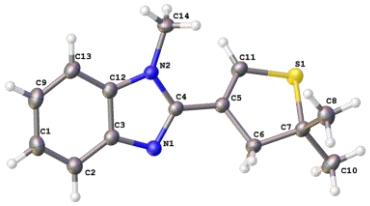
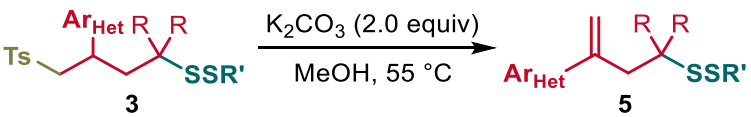


Table S3 Crystal data and structure refinement for 4e (CCDC 2251587).

Empirical formula	$C_{14}H_{16}N_2S$
Radiation	MoKα (λ = 0.71073)
Temperature/K	150
Bond precision	C-C = 0.0033 Å
Space group	P b c a
Hall group	-P 2ac 2ab
a/Å	11.807(4)
b/Å	10.063(3)
c/Å	21.134(7)
α/°	90
β/°	90
γ/°	90
Volume/$Å^3$	2511.1(14)
Mr	228.22
Z	8
$\rho_{calc}g/cm^3$	1.207
$M\mu/mm^{-1}$	0.233
F(000)	912.0
h,k,lmax	15,13,28
Nref	3108
Tmin,Tmax	0.528,0.746
Data completeness	0.995
Theta(max)	28.332
R(reflections)	0.0662(2810)
wR_2(reflections)	0.2379(3108)
S	1.083
Npar	154

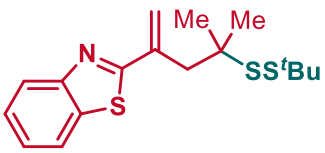
4.4 General procedure for synthesis of homoallyl disulfides (GP7)



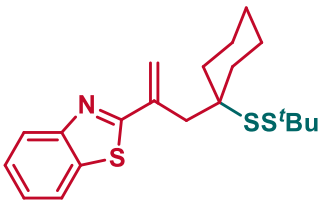
A flame-dried Schlenk tube equipped with a magnetic stir bar and a reflux condenser was charged with **3** (0.100 mmol, 1.0 equiv) and K_2CO_3 (27.6 mg, 0.200

mmol, 2.0 equiv), and MeOH (1 mL), sealed with a septum. The reaction was allowed to stir at 55 °C for 8 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 product **5**.

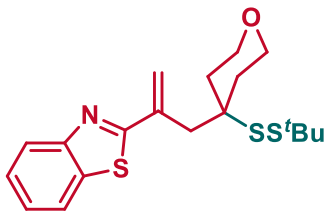
4.5 Spectral data of homoallyl disulfides 5



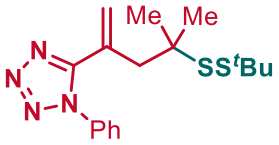
2-(4-(*tert*-butyldisulfaneyl)-4-methylpent-1-en-2-yl)benzo[*d*]thiazole (5a): The title compound was prepared according to general procedure (**GP7**) with **3a** (49.4 mg, 0.100 mmol, 1.0 equiv) and K_2CO_3 (27.6 mg, 0.200 mmol, 2.0 equiv) in methanol (1 mL) at 55 ºC for 8 h. Purification via silica gel chromatography (PE:EtOAc = 50:1) gave the desired product **5a** as a colorless oil in 91% yield (30.9 mg). **TLC R_f** = 0.4 (PE:EtOAc = 50:1); **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.99 (d, J = 8.1 Hz, 1H), 7.82 (d, J = 7.9 Hz, 1H), 7.44 (ddd, J^1 = 8.3 Hz, J^2 = 7.2 Hz, J^3 = 1.3 Hz, 1H), 7.35 (ddd, J = 8.4, J^2 = 7.2, J^3 = 1.2 Hz, 1H), 6.07 (s, 1H), 5.58 (s, 1H), 3.07 (s, 2H), 1.33 (s, 9H), 1.27 (s, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 169.9, 153.6, 139.8, 134.9, 126.0, 125.3, 123.9, 123.3, 121.4, 49.8, 46.5, 44.8, 30.6, 28.1; **HRMS** (ESI) m/z = 360.0885, calcd. for $C_{17}H_{23}NS_3Na^+$ $[M+Na]^+$, found: 360.0884; **IR** (neat, cm^{-1}): 3061*w*, 2958*s*, 2924*m*, 2861*w*, 1622*w*, 1491*w*, 1456*m*, 1439*w*, 1382*w*, 1365*m*, 1314*w*, 1239*w*, 1165*w*, 1114*m*, 1079*w*, 1034*w*, 914*w*, 760*s*, 731*m*.



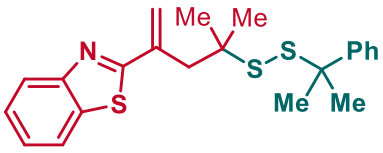
2-(3-(1-(*tert*-butyldisulfaneyl)cyclohexyl)prop-1-en-2-yl)benzo[*d*]thiazole (5b): The title compound was prepared according to general procedure (**GP7**) with **3c** (53.4 mg, 0.100 mmol, 1.0 equiv) and K_2CO_3 (27.6 mg, 0.200 mmol, 2.0 equiv) in methanol (1 mL) at 55 ºC for 8 h. Purification via silica gel chromatography (PE:EtOAc = 50:1) gave the desired product **5b** as a colorless oil in 86% yield (32.4 mg). **TLC R_f** = 0.4 (PE:EtOAc = 50:1); **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.99 (d, J = 8.1 Hz, 1H), 7.84 (d, J = 7.9 Hz, 1H), 7.45 (t, J = 7.7 Hz, 1H), 7.36 (t, J = 7.6 Hz, 1H), 6.10 (s, 1H), 5.62 (s, 1H), 3.13 (s, 2H), 1.73-1.61 (m, 5H), 1.59-1.45 (m, 5H), 1.36 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 170.5, 153.6, 139.4, 135.0, 126.0, 125.2, 124.4, 123.2, 121.4, 54.9, 46.7, 43.4, 35.0, 30.9, 25.5, 22.4; **HRMS** (ESI) m/z = 378.1378, calcd. for $C_{20}H_{28}NS_3^+$ $[M+H]^+$, found: 378.1369; **IR** (neat, cm^{-1}): 2930*s*, 2855*m*, 1491*w*, 1461*m*, 1439*m*, 1358*w*, 1314*w*, 1245*w*, 1159*m*, 1125*w*, 1079*w*, 1028*w*, 1011*w*, 937*w*, 914*w*, 760*s*, 725*m*.



4-(2-(benzo[*b*]thiophen-2-yl)allyl)-4-(*tert*-butyldisulfaneyl)tetrahydro-2*H*-pyran (5c): The title compound was prepared according to general procedure (**GP7**) with **3d** (53.6 mg, 0.100 mmol, 1.0 equiv) and K_2CO_3 (27.6 mg, 0.200 mmol, 2.0 equiv) in methanol (1 mL) at 55 °C for 8 h. Purification via silica gel chromatography (PE:EtOAc = 30:1) gave the desired product **5c** as a colorless oil in 64% yield (24.1 mg). **TLC R_f** = 0.4 (PE:EtOAc = 30:1); **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.98 (d, *J* = 8.3 Hz, 1H), 7.83 (d, *J* = 8.0 Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 1H), 7.37 (t, *J* = 7.6 Hz, 1H), 6.12 (s, 1H), 5.66 (s, 1H), 3.82-3.68 (m, 4H), 3.20 (s, 2H), 1.84 (ddd, J^1 = 14.1, J^2 = 9.4, J^3 = 4.5 Hz, 2H), 1.73-1.66 (m, 2H), 1.36 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 170.0, 153.5, 138.8, 135.0, 126.1, 125.4, 125.0, 123.3, 121.4, 64.1, 51.9, 46.9, 43.0, 34.7, 30.9; **HRMS** (ESI) *m*/*z* = 380.1171, calcd. for $C_{19}H_{26}NOS_3^+$ $[M+H]^+$, found: 380.1160; Chemical Formula: **IR** (neat, cm^{-1}): 2958*w*, 2855*w*, 1491*w*, 1456*w*, 1433*w*, 1359*w*, 1314*w*, 1239*w*, 1159*w*, 1125*w*, 1102*w*, 1028*w*, 1011*w*, 914*w*, 851*w*, 760*m*, 731*w*.

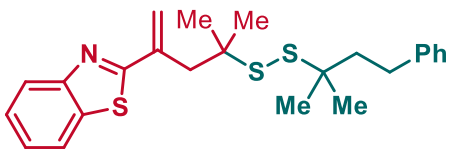


5-(4-(*tert*-butyldisulfaneyl)-4-methylpent-1-en-2-yl)-1-phenyl-1*H*-tetrazole (5d): The title compound was prepared according to general procedure (**GP7**) with **3g** (50.5 mg, 0.100 mmol, 1.0 equiv) and K_2CO_3 (27.6 mg, 0.200 mmol, 2.0 equiv) in methanol (1 mL) at 55 °C for 8 h. Purification via silica gel chromatography (PE:EtOAc = 5:1) gave the desired product **5d** as a colorless oil in 55% yield (19.0 mg). **TLC R_f** = 0.3 (PE:EtOAc = 5:1); **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.55 (s, 5H), 5.55 (s, 1H), 5.53 (s, 1H), 2.73 (s, 2H), 1.23 (s, 9H), 1.18 (s, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 154.4, 134.6, 130.3, 129.9, 129.8, 127.8, 125.0, 49.1, 46.5, 46.5, 30.5, 28.0; **HRMS** (ESI) *m*/*z* = 349.1515, calcd. for $C_{17}H_{25}N_4S_2^+$ $[M+H]^+$, found: 349.1506; **IR** (neat, cm^{-1}): 2964*m*, 2895*w*, 2861*w*, 1593*w*, 1508*m*, 1491*m*, 1456*s*, 1416*w*, 1382*w*, 1365*m*, 1268*w*, 1156*m*, 1108*m*, 1017*w*, 931*w*, 765*s*, 691*s*.

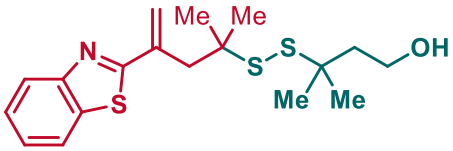


2-(4-methyl-4-((2-phenylpropan-2-yl)disulfaneyl)pent-1-en-2-yl)benzo[*d*]thiazole (5e): The title compound was prepared according to general procedure (**GP7**) with **3t** (55.6 mg, 0.100 mmol, 1.0 equiv) and K_2CO_3 (27.6 mg, 0.200 mmol, 2.0 equiv) in methanol (1 mL) at 55 °C for 8 h. Purification via silica gel chromatography (PE:EtOAc = 50:1) gave the desired product **5e** as a colorless oil in 74% yield (29.6 mg). **TLC R_f** = 0.5 (PE:EtOAc = 20:1); **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.99 (d, *J* = 8.1 Hz, 1H), 7.83 (d, *J* = 7.9 Hz, 1H), 7.54 (d, *J* = 7.8 Hz, 2H), 7.45 (t, *J* = 7.7 Hz, 1H), 7.40-7.29 (m, 3H), 7.21

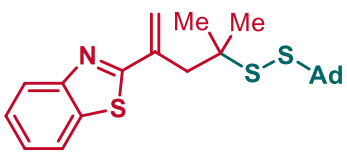
(t, J = 7.3 Hz, 1H), 6.03 (s, 1H), 5.49 (s, 1H), 2.89 (s, 2H), 1.75 (s, 6H), 1.07 (s, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 169.9, 153.6, 145.7, 139.8, 135.0, 128.1, 127.0, 126.7, 126.0, 125.3, 123.9, 123.3, 121.4, 51.6, 50.5, 44.8, 29.3, 27.9; **HRMS** (ESI) m/z = 422.1041, calcd. for $C_{22}H_{25}NS_3Na^+$ $[M+Na]^+$, found: 422.1032; **IR** (neat, cm^{-1}): 3061*w*, 2964*m*, 2924*w*, 2861*w*, 1491*m*, 1456*m*, 1433*m*, 1382*w*, 1365*w*, 1314*w*, 1239*w*, 1114*m*, 1097*m*, 1079*w*, 1034*m*, 1011*w*, 914*w*, 760*s*, 731*m*, 697*s*.



2-(4-methyl-4-((2-methyl-4-phenylbutan-2-yl)disulfaneyl)pent-1-en-2-yl) benzo[*d*]thiazole (5f): The title compound was prepared according to general procedure (**GP7**) with **3y** (58.4 mg, 0.100 mmol, 1.0 equiv) and K_2CO_3 (27.6 mg, 0.200 mmol, 2.0 equiv) in methanol (1 mL) at 55 °C for 8 h. Purification via silica gel chromatography (PE:EtOAc = 50:1) gave the desired product **5f** as a colorless oil in 85% yield (36.2 mg). **TLC R_f** = 0.4 (PE:EtOAc = 50:1); **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.98 (d, J = 8.1 Hz, 1H), 7.83 (d, J = 7.9 Hz, 1H), 7.44 (t, J = 7.6 Hz, 1H), 7.36 (t, J = 7.6 Hz, 1H), 7.27 (t, J = 7.0 Hz, 2H), 7.18 (d, J = 7.6 Hz, 2H), 6.08 (s, 1H), 5.59 (s, 1H), 3.09 (s, 2H), 2.78-2.66 (m, 2H), 1.93-1.82 (m, 2H), 1.36 (s, 6H), 1.28 (s, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 169.9, 153.7, 142.3, 139.8, 135.0, 128.4, 126.0, 125.7, 125.3, 124.0, 123.3, 121.4, 50.0, 49.7, 44.9, 44.4, 31.3, 28.4, 28.2; **HRMS** (ESI) m/z = 450.1354, calcd. for $C_{24}H_{29}NS_3Na^+$ $[M+Na]^+$, found: 450.1344; **IR** (neat, cm^{-1}): 2958*w*, 2924*w*, 2861*w*, 1496*w*, 1456*w*, 1433*w*, 1365*w*, 1194*w*, 1114*w*, 1034*w*, 914*w*, 760*m*, 731*w*, 697*m*.

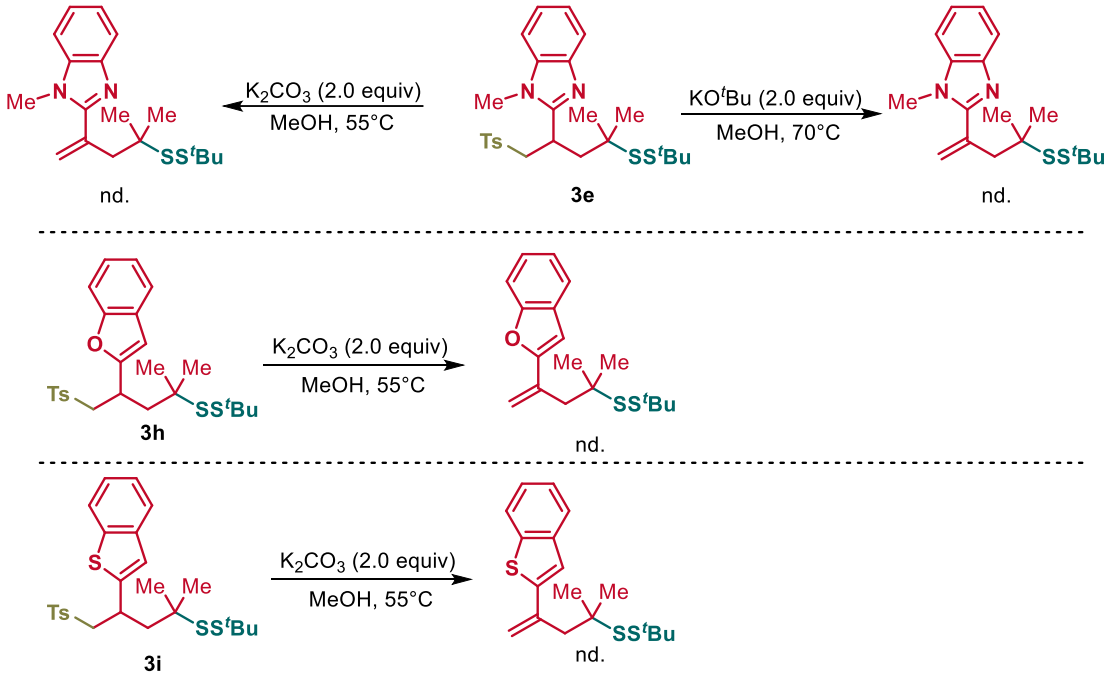


3-((4-(benzo[*d*]thiazol-2-yl)-2-methylpent-4-en-2-yl)disulfaneyl)-3-methylbutan-1-ol (5g): The title compound was prepared according to general procedure (**GP7**) with **3v** (62.8 mg, 0.100 mmol, 1.0 equiv) and K_2CO_3 (27.6 mg, 0.200 mmol, 2.0 equiv) in methanol (1 mL) at 55 °C for 8 h. Purification via silica gel chromatography (PE:EtOAc = 5:1) gave the desired product **5g** as a colorless oil in 69% yield (25.3 mg). **TLC R_f** = 0.2 (PE:EtOAc = 5:1); **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 8.01 (d, J = 8.1 Hz, 1H), 7.83 (d, J = 8.0 Hz, 1H), 7.45 (t, J = 7.7 Hz, 1H), 7.37 (t, J = 7.6 Hz, 1H), 6.06 (s, 1H), 5.58 (s, 1H), 3.85 (t, J = 7.1 Hz, 2H), 3.08 (s, 2H), 2.11 (s, 1H), 1.89 (t, J = 7.1 Hz, 2H), 1.33 (s, 6H), 1.27 (s, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 170.1, 153.5, 139.8, 134.9, 126.1, 125.4, 124.1, 123.3, 121.4, 59.7, 50.0, 48.5, 45.1, 44.5, 28.7, 28.0; **HRMS** (ESI) m/z = 368.1171, calcd. for $C_{18}H_{26}NOS_3^+$ $[M+H]^+$, found: 368.1161; **IR** (neat, cm^{-1}): 3358*br*, 2958*w*, 2924*w*, 1491*w*, 1456*w*, 1439*w*, 1382*w*, 1365*w*, 1314*w*, 1114*w*, 1034*w*, 914*w*, 760*m*, 731*w*.



2-(4-(((3*s*,5*s*,7*s*)-adamantan-1-yl)disulfaneyl)-4-methy-lpent-1-en-2-yl)benzo[*d*]thiazole (5h): The title compound was prepared according to general procedure (**GP7**) with **3y** (57.2 mg, 0.100 mmol, 1.0 equiv) and K_2CO_3 (27.6 mg, 0.200 mmol, 2.0 equiv) in methanol (1 mL). The reaction was allowed to stir at 55 °C for 8 h. Purification via silica gel chromatography (PE:EtOAc = 50:1) gave the desired product **5h** as a colorless oil in 97% yield (40.2 mg). **TLC** R_f = 0.4 (PE:EtOAc = 50:1); **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 8.00 (d, *J* = 8.1 Hz, 1H), 7.84 (d, *J* = 7.9 Hz, 1H), 7.45 (t, *J* = 7.7 Hz, 1H), 7.36 (t, *J* = 7.6 Hz, 1H), 6.08 (s, 1H), 5.59 (s, 1H), 3.07 (s, 2H), 2.07 (s, 3H), 1.85 (d, *J* = 2.9 Hz, 6H), 1.67 (s, 6H), 1.27 (s, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 170.0, 153.7, 139.9, 135.0, 126.0, 125.3, 123.9, 123.3, 121.4, 49.4, 48.1, 44.8, 43.2, 36.1, 30.0, 28.1; **HRMS** (ESI) *m*/*z* = 416.1535, calcd. for $C_{23}H_{30}NS_3^+$ $[M+H]^+$, found: 416.1526; **IR** (neat, cm^{-1}): 2958*w*, 2907*m*, 2850*w*, 1491*w*, 1456*w*, 1433*w*, 1382*w*, 1365*w*, 1342*w*, 1314*w*, 1296*w*, 1245*w*, 1119*w*, 1034*w*, 914*w*, 760*m*, 725*w*.

4.6 Limitations of the methods

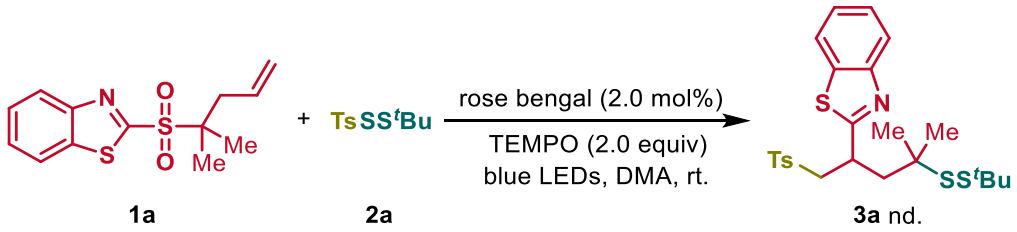


We have conducted experiments with polysulfide compounds containing various heteroarenes such as benzimidazole, benzofuran, and benzothiophene to explore their potential for follow-up transformations. Regrettably, we did not detect any desired products, even when we employed a stronger base, KO^{t}Bu, at elevated temperatures instead of K_2CO_3. This failure in conversion is likely due to the insufficient acidity of the *α*-H in the heteroaryl unit under the current KO^{t}Bu/MeOH or K_2CO_3/MeOH systems. It is possible that the reactivities are influenced by the coordination effect of

the *N* donor on the heteroarene. We are actively working on resolving this limitation as part of our ongoing efforts.

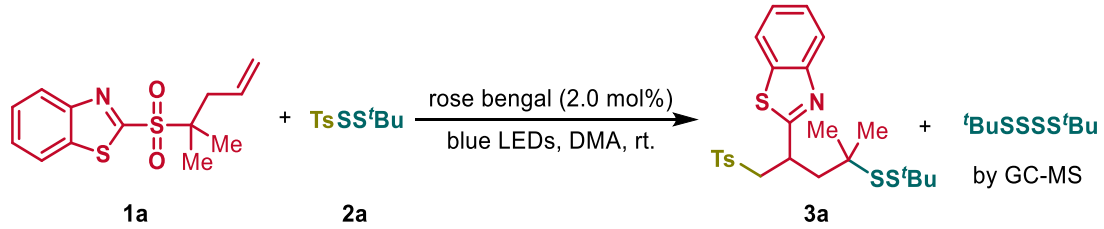
5. Mechanistic study

5.1 Radical trapping experiment



A flame-dried Schlenk tube equipped with a magnetic stir bar was charged with rose bengal (2.0 mg, 0.0020 mmol, 2.0 mol%), **1a** (28.1 mg, 0.100 mmol, 1.0 equiv), and **2a** (41.4 mg, 0.150 mmol, 1.5 equiv), sealed with a septum, and degassed by alternating vacuum evacuation and nitrogen backfilling (three times) before DMA (0.5 mL) was added, which was irradiated by blue LEDs and stirred at room temperature for 12 h. Compound **3a** was not detected based on TLC analysis.

5.2 ^{t}BuSSSS^{t}Bu capture experiment



A flame-dried Schlenk tube equipped with a magnetic stir bar was charged with rose bengal (2.0 mg, 0.0020 mmol, 2.0 mol%), **1a** (28.1 mg, 0.100 mmol, 1.0 equiv), and **2a** (41.4 mg, 0.150 mmol, 1.5 equiv), sealed with a septum, and degassed by alternating vacuum evacuation and nitrogen backfilling (three times) before DMA (0.5 mL) was added, which was irradiated by blue LEDs and stirred at room temperature for 12 h. Appropriate amount of reaction liquid was collected for analysis. Compound ^{t}BuSSSS^{t}Bu was observed by GC-MS analysis. A set of molecular ion peak [M^{+} = 242] was observed at the position with a retention time of 9.665 minutes in **Figure S1**, which was confirmed as the chromatographic peak of ^{t}BuSSSS^{t}Bu by comparison with the standard ^{t}BuSSSS^{t}Bu spectrum in **Figure S2**, which indicates that ^{t}BuSSSS^{t}Bu is produced during the reaction.

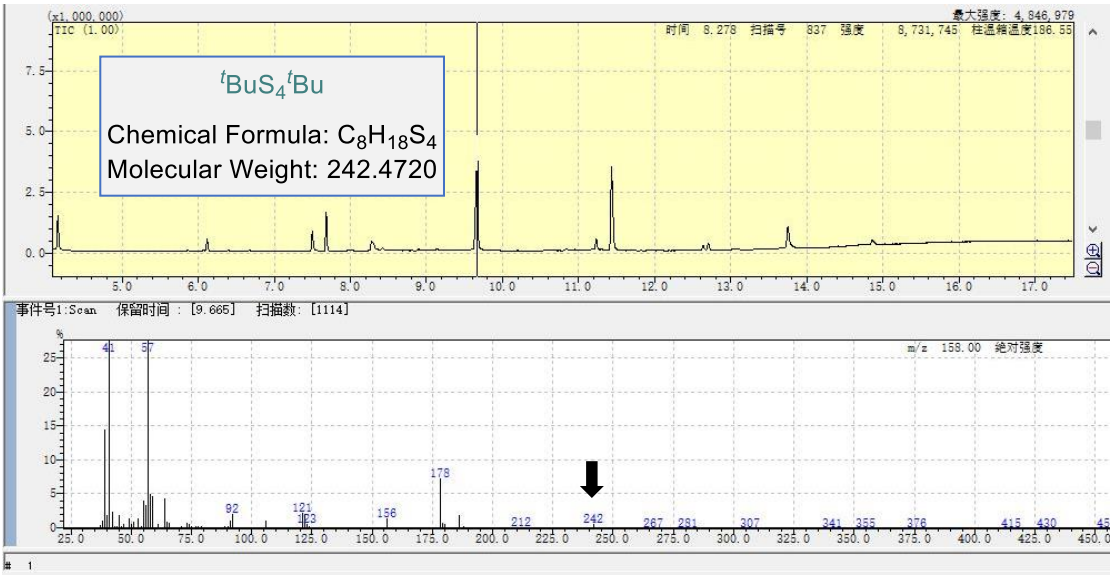


Figure S1 The ᵗBuSSSSᵗBu capture experiment spectrum.

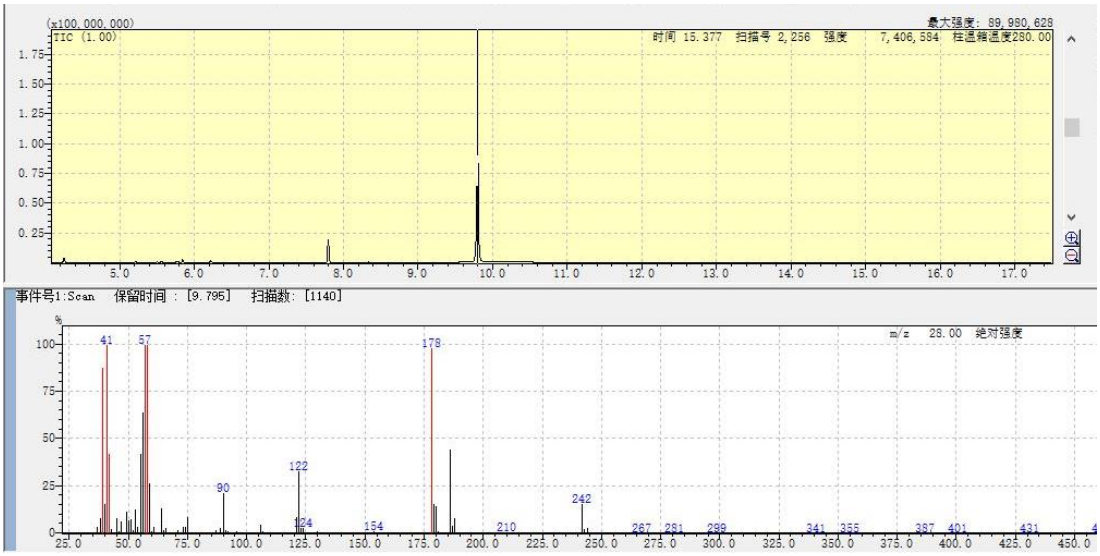
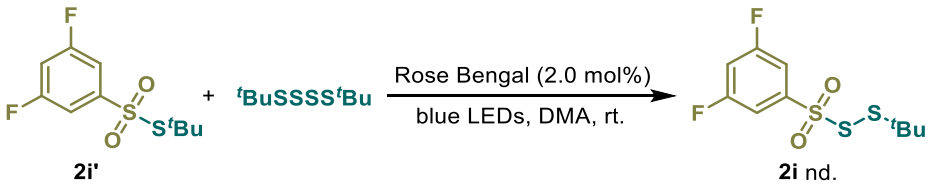


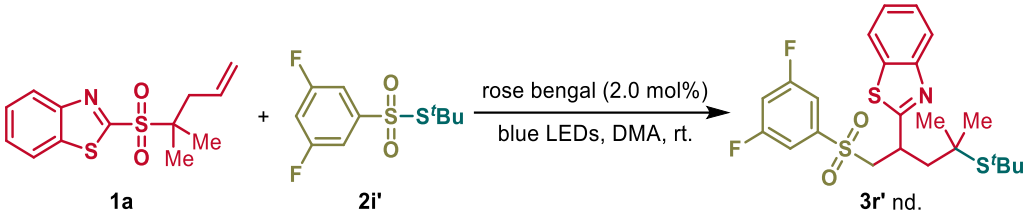
Figure S2 The standard ᵗBuSSSSᵗBu spectrum.

5.3 Control experiments

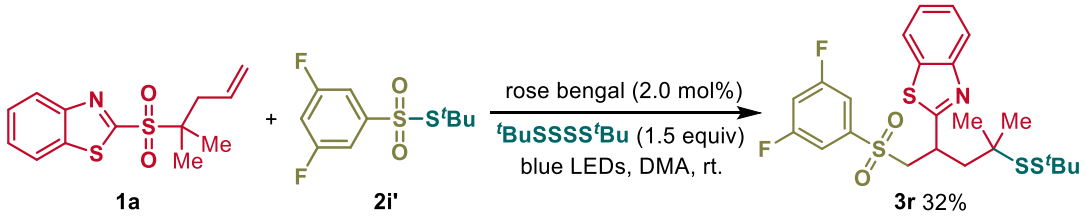


A flame-dried Schlenk tube equipped with a magnetic stir bar was charged with rose bengal (2.0 mg, 0.0020 mmol, 2.0 mol%), **2i'** (26.6 mg, 0.100 mmol, 1.0 equiv), and ᵗBuSSSSᵗBu (36.3 mg, 0.150 mmol, 1.5 equiv), sealed with a septum, and degassed by alternating vacuum evacuation and nitrogen backfilling (three times) before DMA

(0.5 mL) was added. The reaction mixture was then stirred and irradiated using a 20 W blue LEDs lamp at room temperature for 12 h. After the reaction was complete, the solvent was removed under reduced pressure with the aid of a rotary evaporator. **2i** was not detected based on GC-MS analysis.



A flame-dried Schlenk tube equipped with a magnetic stir bar was charged with rose bengal (2.0 mg, 0.0020 mmol, 2.0 mol%), **1a** (28.1 mg, 0.100 mmol, 1.0 equiv), and **2i'** (39.9 mg, 0.150 mmol, 1.5 equiv), sealed with a septum, and degassed by alternating vacuum evacuation and nitrogen backfilling (three times) before DMA (0.5 mL) was added. The reaction mixture was then stirred and irradiated using a 20 W blue LEDs lamp at room temperature for 12 h. **3r'** was not detected based on TLC analysis.



A flame-dried Schlenk tube equipped with a magnetic stir bar was charged with rose bengal (2.0 mg, 0.0020 mmol, 2.0 mol%), **1a** (28.1 mg, 0.100 mmol, 1.0 equiv), **2i'** (39.9 mg, 0.150 mmol, 1.5 equiv), and ^{t}BuSSSS^{t}Bu (36.3 mg, 0.150 mmol, 1.5 equiv), sealed with a septum, and degassed by alternating vacuum evacuation and nitrogen backfilling (three times) before DMA (0.5 mL) was added. The reaction mixture was then stirred and irradiated using a 20 W blue LEDs lamp at room temperature for 12 h. After the reaction was completed, the mixture was diluted with EtOAc (2 mL), which was followed by extraction with EtOAc (5 mL × 3). The combined organic phase was washed with brine (10 mL), dried with Na_2SO_4 and the solvent was evaporated with the aid of a rotary evaporator. The crude product was purified by column chromatography to afford product **3r** in 32% yield.

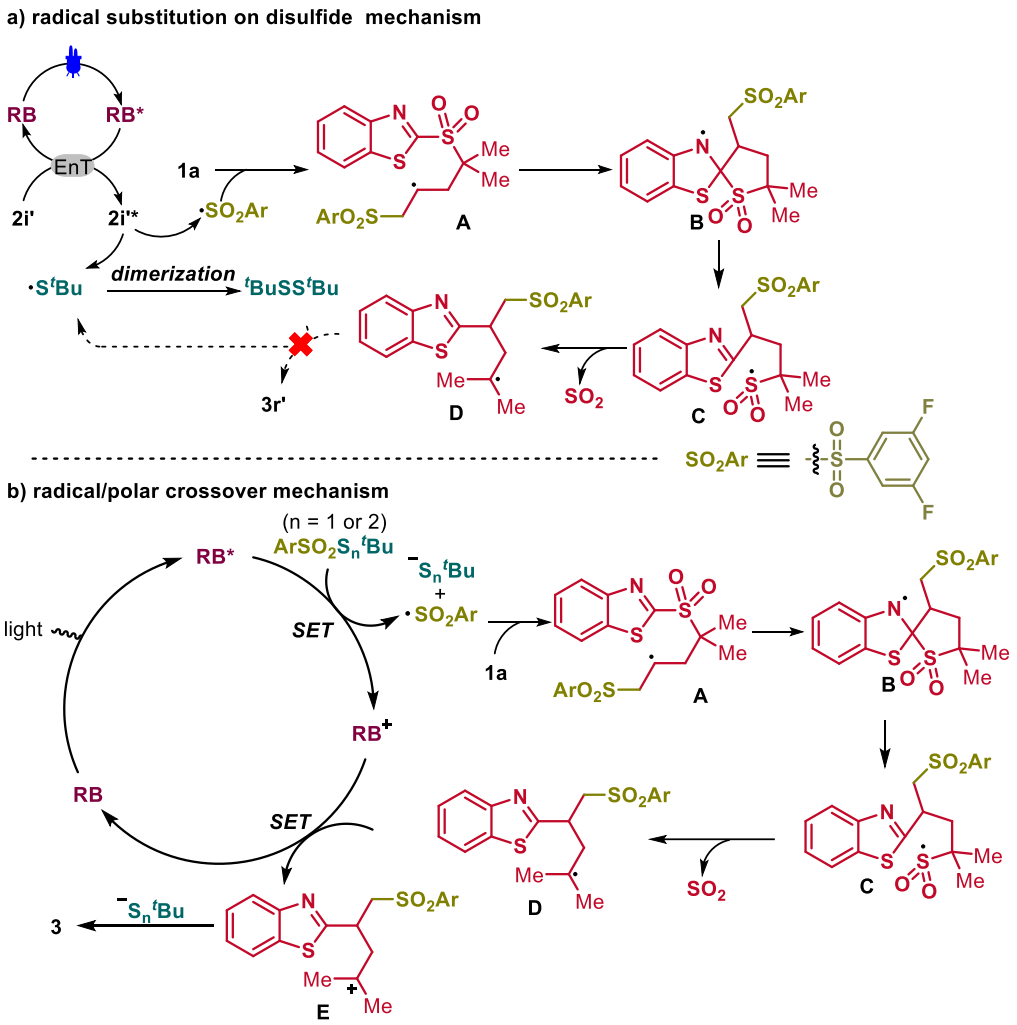
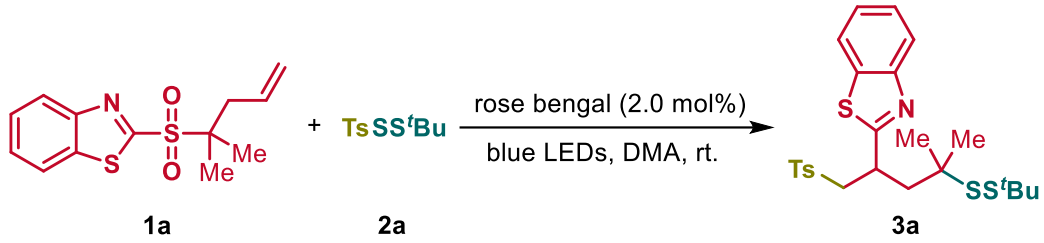


Figure S3 Unlikely mechanism.

5.4 Light on/off experiment



A flame-dried Schlenk tube equipped with a magnetic stir bar was charged with rose bengal (8.1 mg, 0.0080 mol, 2.0 mol%), **1a** (112.6 mg, 0.4000 mmol, 1.0 equiv), **2a** (165.9 mg, 0.6000 mmol, 1.5 equiv), and 1,3,5-trimethoxybenzene (33.6 mg, 0.200 mmol, 0.50 equiv), sealed with a septum, and degassed by alternating vacuum evacuation and nitrogen backfilling (three times) before DMA (2.0 mL) was added, which was irradiated by blue LEDs and stirred at room temperature, and the light was turned on and off every 20 minutes. During each on/off shift, approximate 100 μL reaction mixture was taken by a syringe, which was directly transferred into an NMR tube, additional 0.50 mL $CDCl_3$ was added. Comparison of the integration of the internal standard 1,3,5-trimethoxybenzene (6.08 ppm, s, 3H) with that of **1a** (5.78 ppm, ddt, J^1 = 17.4 Hz, J^2 = 10.1 Hz, J^3 = 7.4 Hz,1H) revealed conversion of **1a**.

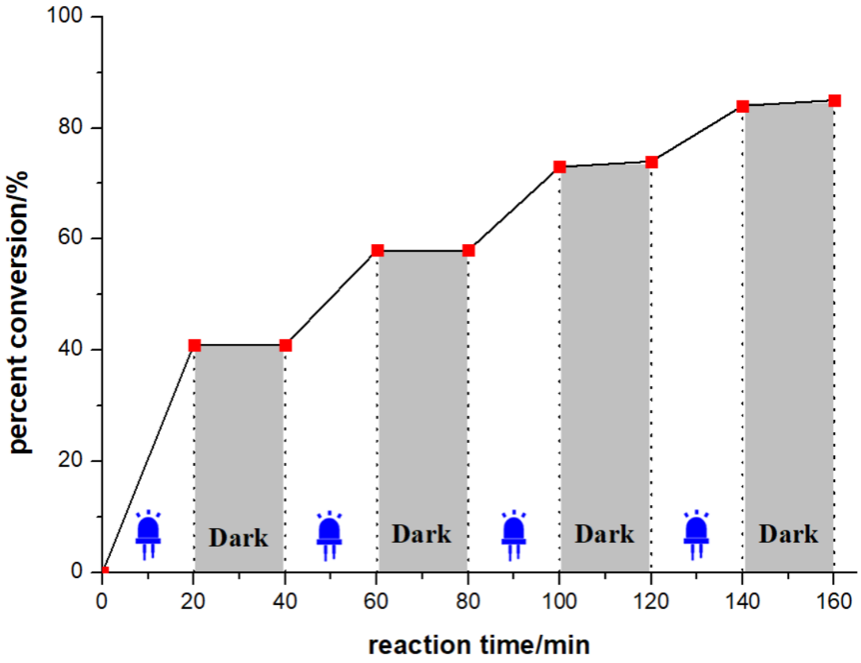


Figure S4 Time profile of the reaction with and without light.

The light on/off experiment verified the necessity of continuous irradiation of visible light, which suggested that chain propagation might not be involved in the mechanistic pathway.

5.5 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, $K_3[FeC_2O_4]_3 \cdot 3H_2O$ (0.737 g, 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 LEDs 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 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 S5**). The absorbances (510 nm) of the samples irradiated for 0 s, 10 s, 20 s and 30 s were also measured according to the similar procedure.

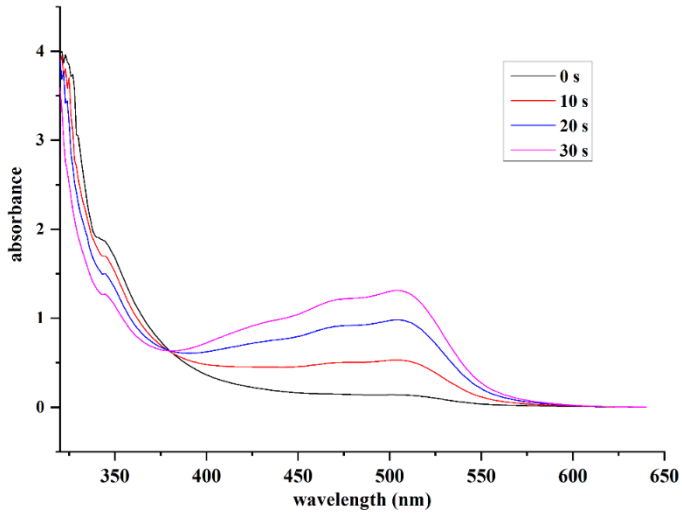


Figure S5 Actinometry: UV/Vis spectra of ferrioxalate and 1,10-phenanthroline solutions.

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

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

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 S6**):

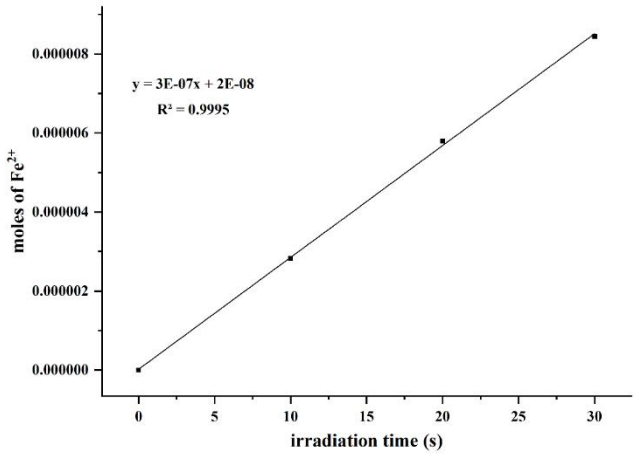


Figure S6 Actinometry: Moles of Fe^{2+} formed vs. irradiation time.

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

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

Φ is the quantum yield of the ferrioxalate actinometer (approximated as 1.11, reported for a 0.006 M solution at $\lambda = 436$ nm).[7] t is the irradiation time. f is the fraction of light absorbed at 440 nm (0.3821).

The fraction of light absorbed was determined according to the following equation: $f = 1 - 10^{-A}$

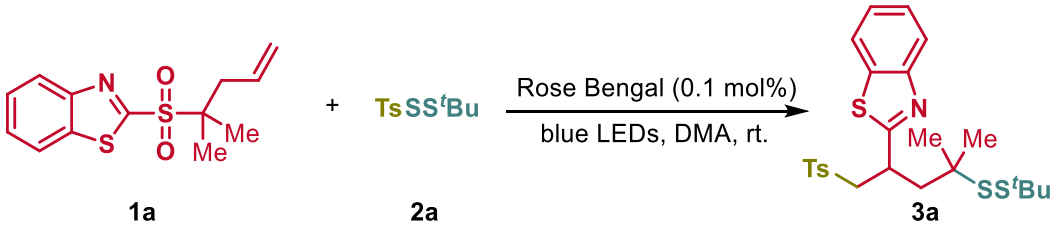
A is the measured absorbance (0.2091, 440 nm) of the 0.006 M solution of $K_3[FeC_2O_4]_3 \cdot 3H_2O$.

Table S4 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.

Determination of the quantum yield



1a **2a** **3a**

A flame-dried Schlenk tube equipped with a magnetic stir bar was charged with **1a** (28.1 mg, 0.1 mmol, 1.0 equiv) and **2a** (41.4 mg, 0.3 mmol, 1.5 equiv), sealed with a septum, and degassed by alternating vacuum evacuation and nitrogen backfilling (three times) before a solution of rose bengal in DMA (0.2 mmol/L, 0.5 mL) was added in a flask. The reaction mixture was then stirred and irradiated using a 20 W blue LEDs lamp at room temperature. The reaction was stopped at 15 min and 30 min, respectively, and the yield was determined by separation. The quantum yield (Φ) was then calculated according to the following equation:

$$\Phi = \frac{\textit{moles of product}}{\textit{photo flux} \bullet t \bullet f}$$

The average radiant flux was tested as 6.72×10^{-7} Einstein/s, where t is the time, and f is the fraction of light absorbed by rose bengal at 440 nm. A solution of rose bengal in DMA (0.2 mmol/L) was prepared, and the absorbance of the solution at 440 nm was 0.2213. The fraction of light absorbed at 440 nm was calculated according to the following equation:

$$f = 1 - 10^{-A} = 0.3992$$

Table S5 Calculation of quantum yield.

	reaction time (s)	yield (%)	moles of product (mol)	quantum yield Φ
1	900	14%	1.36×10^{-5}	0.0563
2	1800	27%	2.67×10^{-5}	0.0553

The average quantum yield Φ is 0.0558.

5.6 Stern-Volmer fluorescence quenching studies

Fluorescence quenching experiments were performed on JASCO FP-8500 Fluorescence Spectrometer. The measurements were carried out mixing a 0.05 mM solution of rose bengal in DMA (2 mL) with the appropriate amount of quencher in a quartz cuvette equipped with a septum.

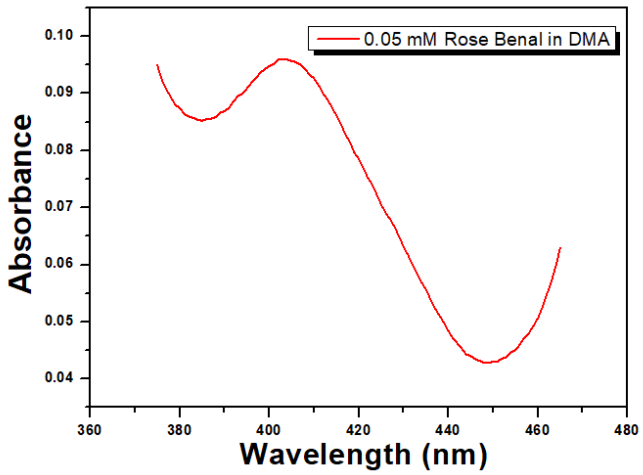


Figure S7 UV/Vis spectra of 0.05 mM solution of rose bengal.

All solutions were irradiated at λ = 402 nm (absorption maximum of rose bengal) and the emission intensity at 498 nm was observed. Plots were constructed according to the Stern-Volmer equation and K_{sv} was calculated[6].

Stern-Volmer equation: $I_0/I = 1 + K_{sv}[Q]$

Increasing amounts of reagent **2a** were added to a solution of rose bengal in DMA (0.05 mM). After each addition, an emission spectrum of the solution was recorded. The results in **Figure S8** indicate that **2a** quenches emission of rose bengal*.

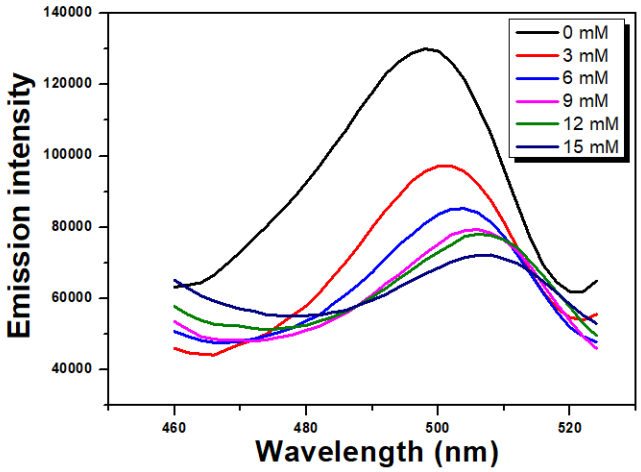


Figure S8 Emission spectrum of rose bengal * varying concentration of 1a.

[quencher]/M	I	I_0/I
0	130000	1
0.003	95600	1.3598
0.006	81100	1.6030
0.009	72700	1.7882
0.012	70800	1.8362
0.015	66900	1.9432

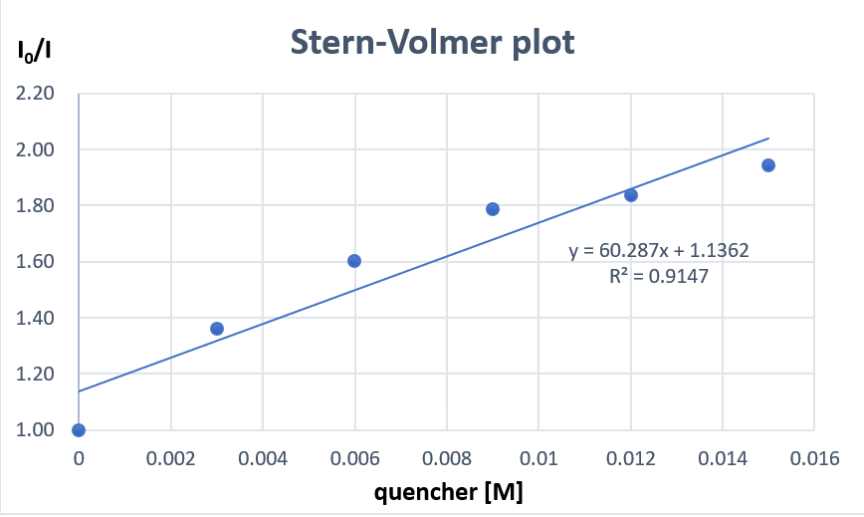


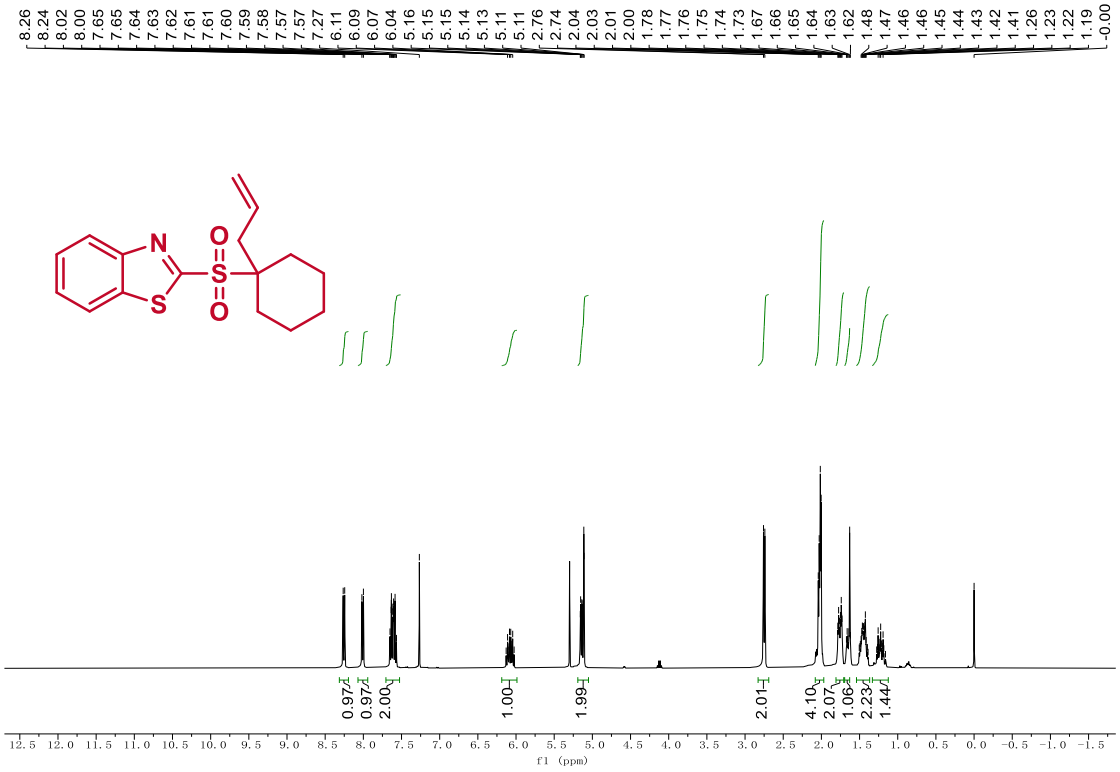
Figure S9 Stern-Volmer plot of rose bengal quenching with varying [2a].

The Stern-Volmer plot reported in **Figure S9** shows a linear correlation between the amounts of **2a** and the ratio I_0/I with a constant K_{sv} of 60.3 M^{-1}.

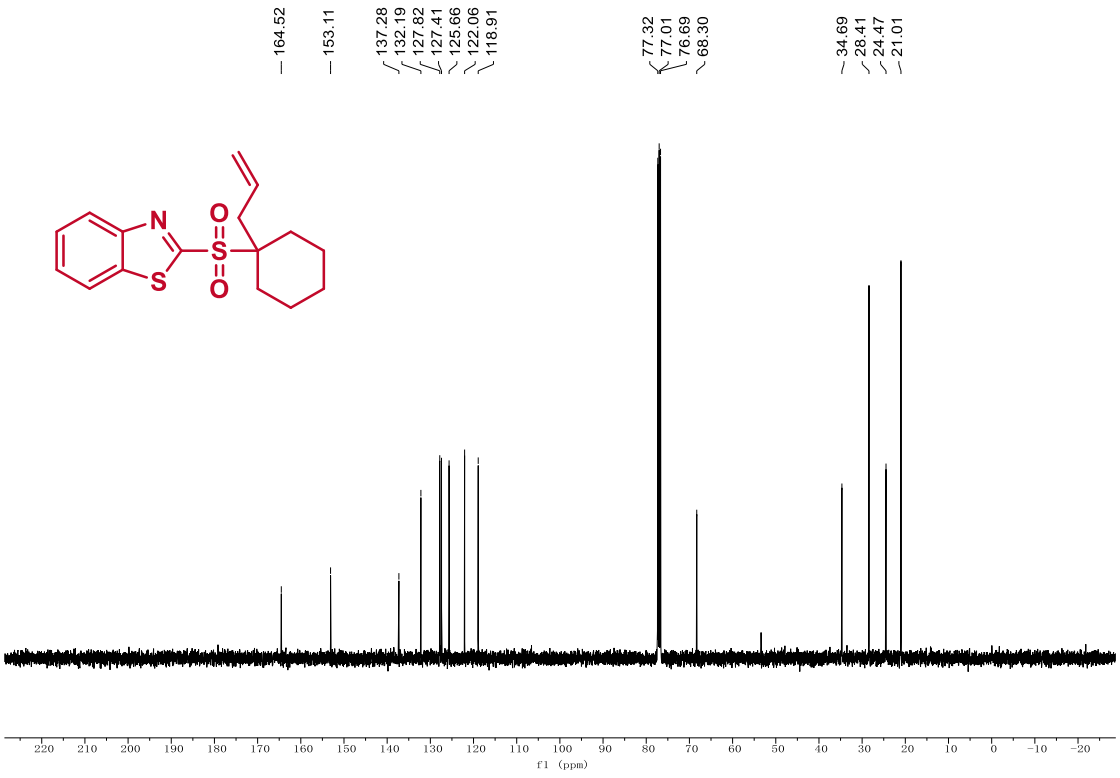
6. Spectra

6.1 Spectra of substrates 1

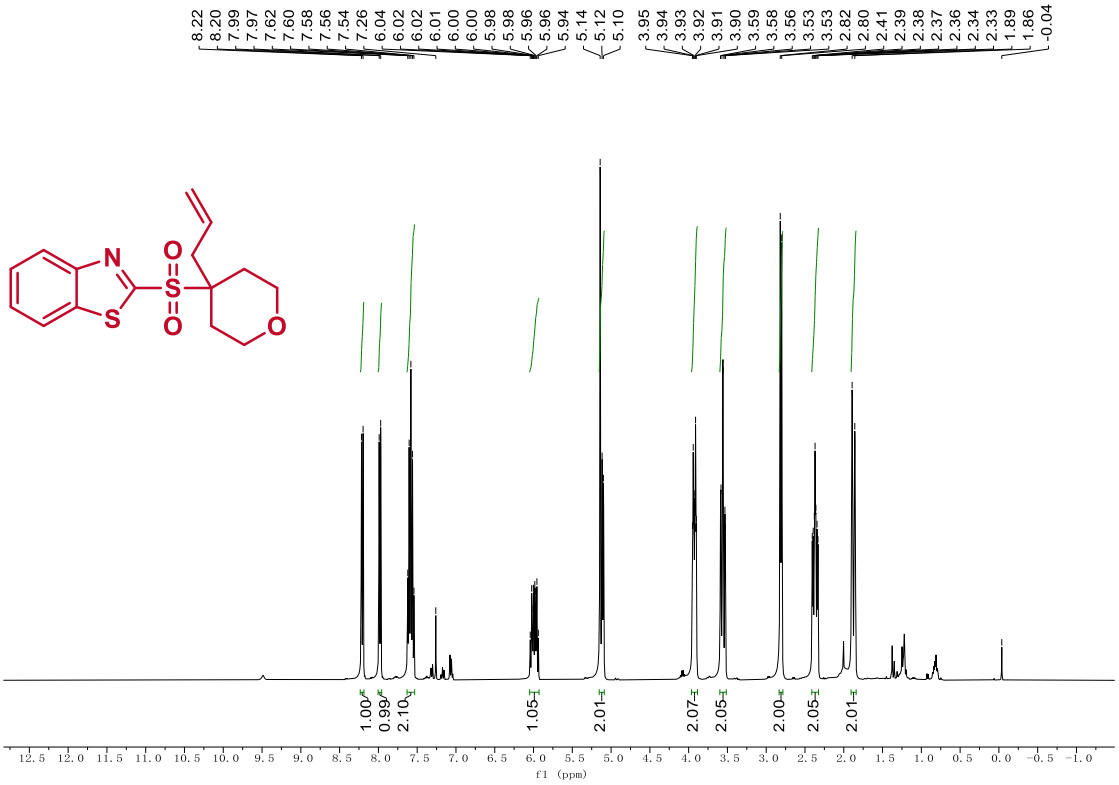
^{1}H NMR Spectrum of 2-((1-allylcyclohexyl)sulfonyl)benzo[*d*]thiazole (1c):



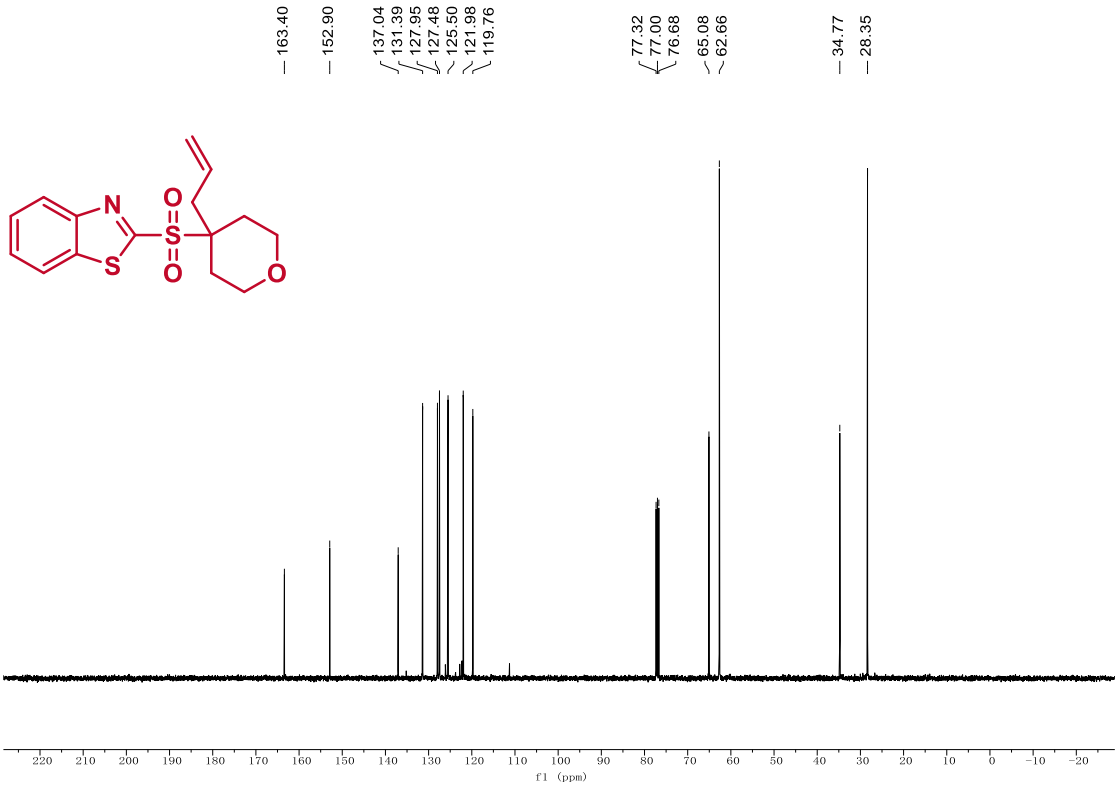
^{13}C NMR Spectrum of 2-((1-allylcyclohexyl)sulfonyl)benzo[*d*]thiazole (1c):



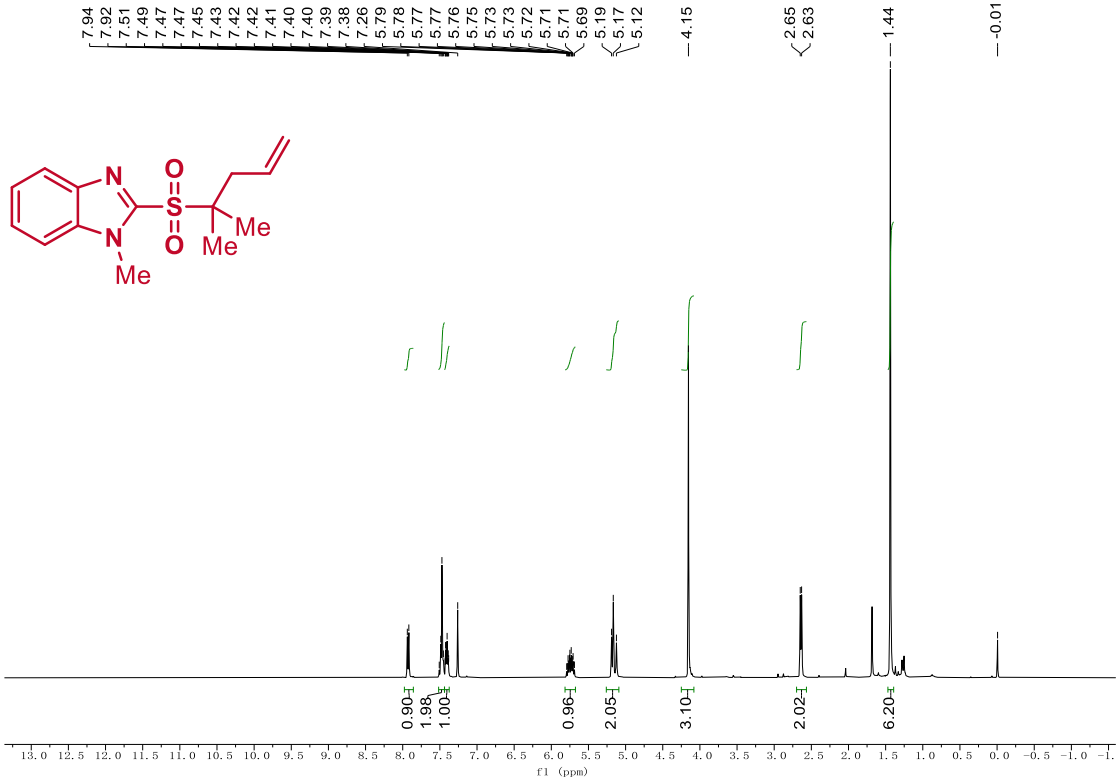
^{1}H NMR Spectrum of 2-((4-allyltetrahydro-2H-pyran-4-yl)sulfonyl)benzo[*d*] thiazole (1d):



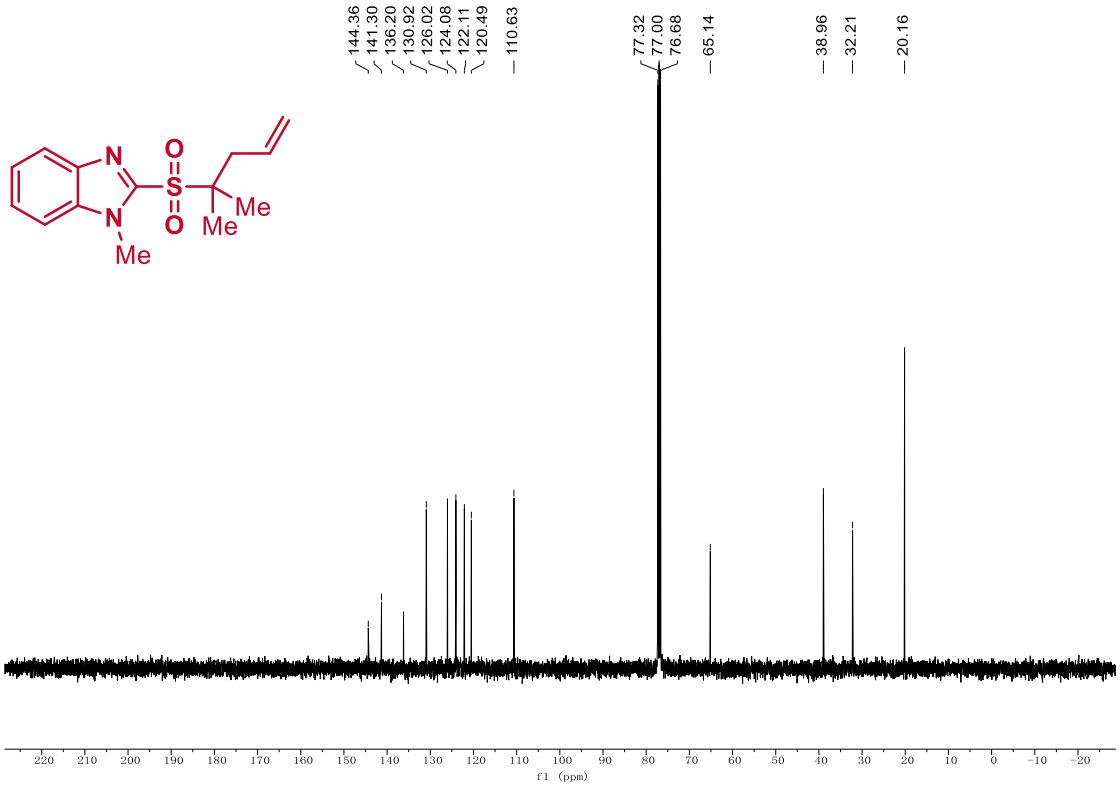
^{13}C NMR Spectrum of 2-((4-allyltetrahydro-2H-pyran-4-yl)sulfonyl)benzo[*d*] thiazole (1d):



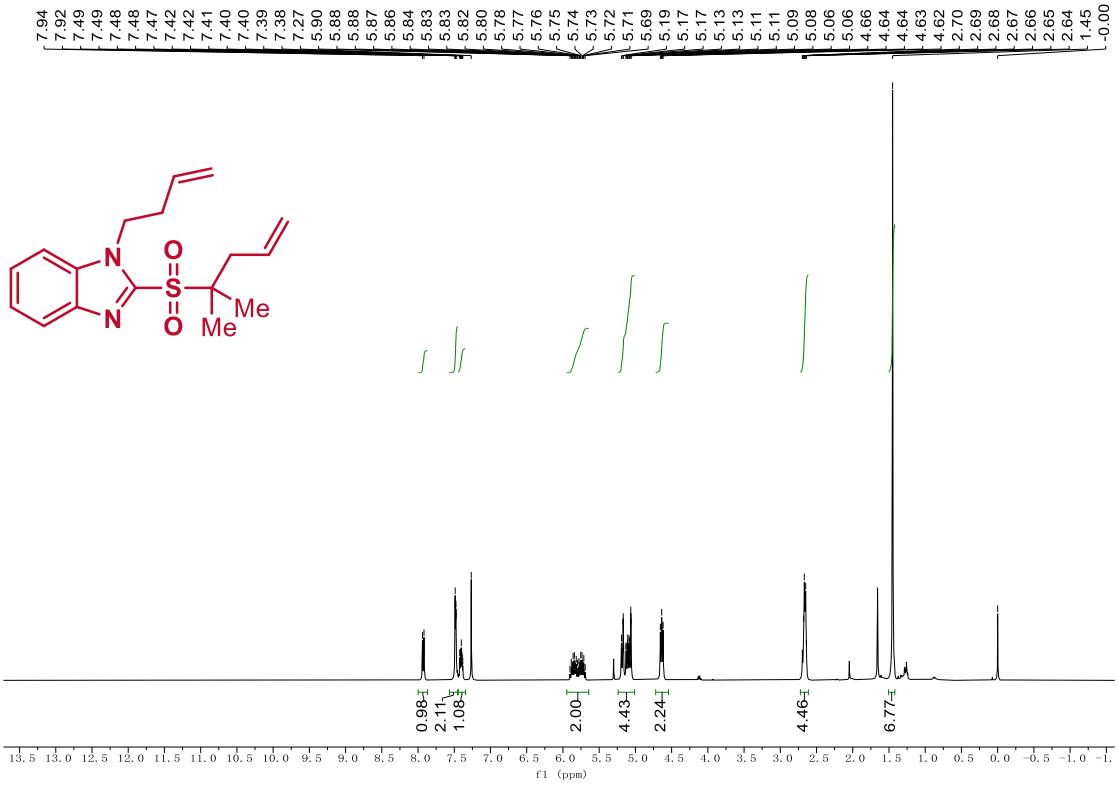
^{1}H NMR Spectrum of 1-methyl-2-((2-methylpent-4-en-2-yl)sulfonyl)-1*H*-benzo[*d*]imidazole (1e):



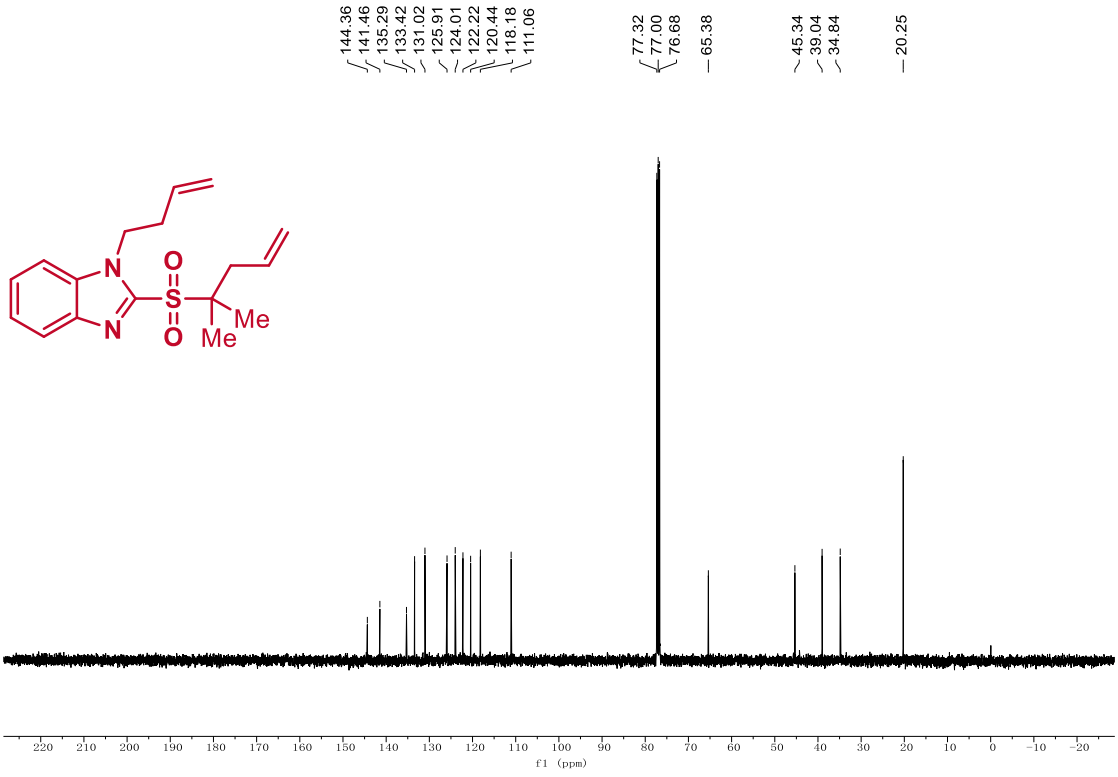
^{13}C NMR Spectrum of 1-methyl-2-((2-methylpent-4-en-2-yl)sulfonyl)-1*H*-benzo[*d*]imidazole (1e):



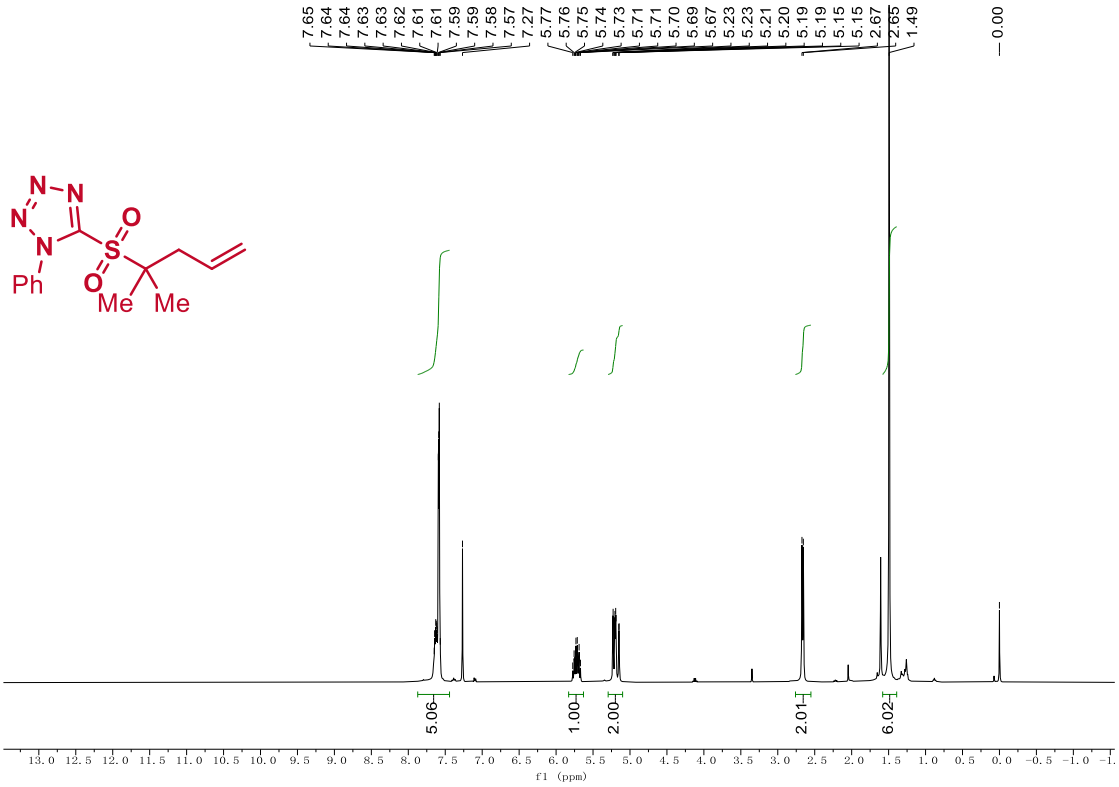
^{1}H NMR Spectrum of 1-(but-3-en-1-yl)-2-((2-methylpent-4-en-2-yl)sulfonyl)-1*H*-benzo[*d*] imidazole (1f):



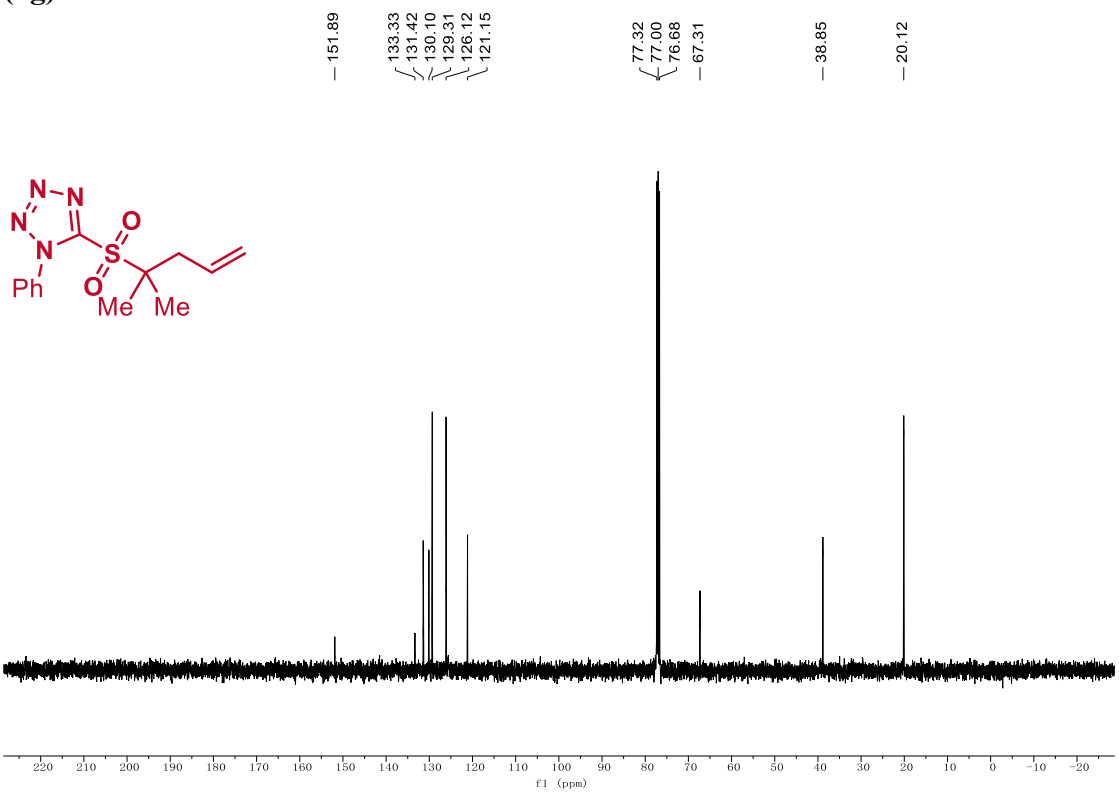
^{13}C NMR Spectrum of 1-(but-3-en-1-yl)-2-((2-methylpent-4-en-2-yl)sulfonyl)-1*H*-benzo[*d*] imidazole (1f):



^{1}H NMR Spectrum of 5-((2-methylpent-4-en-2-yl)sulfonyl)-1-phenyl-1*H*-tetrazole (1g):

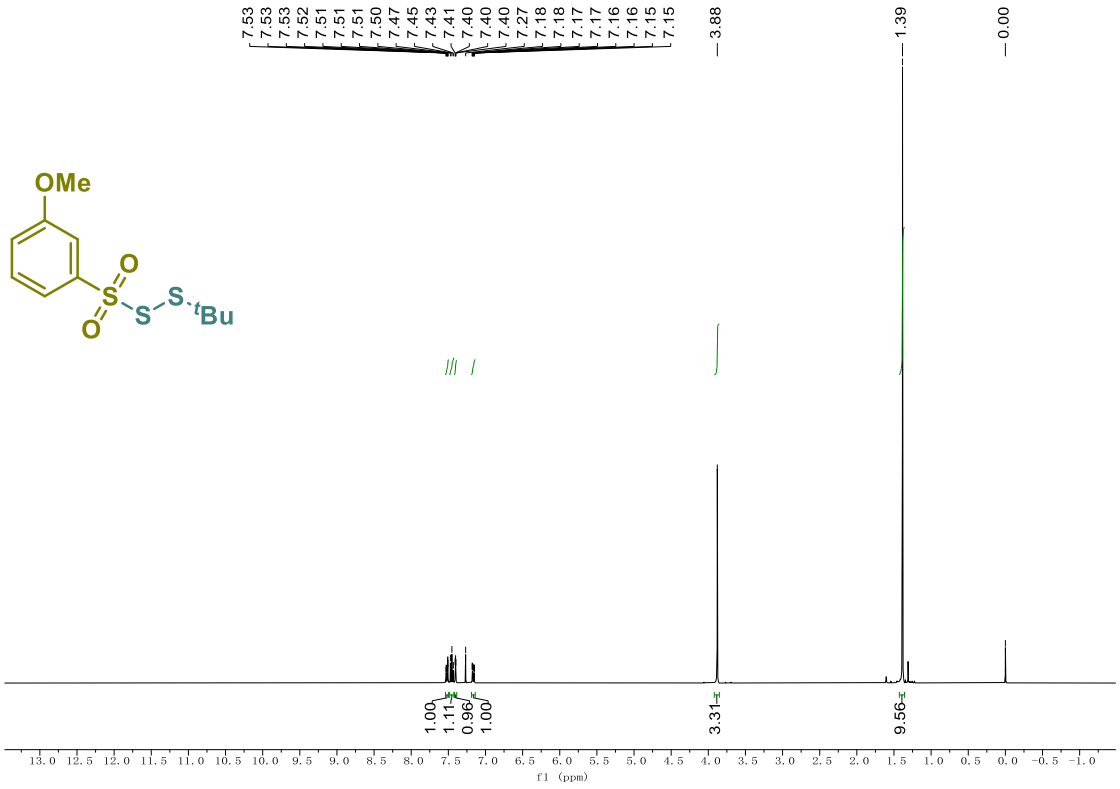


^{13}C NMR Spectrum of 5-((2-methylpent-4-en-2-yl)sulfonyl)-1-phenyl-1*H*-tetrazole (1g):

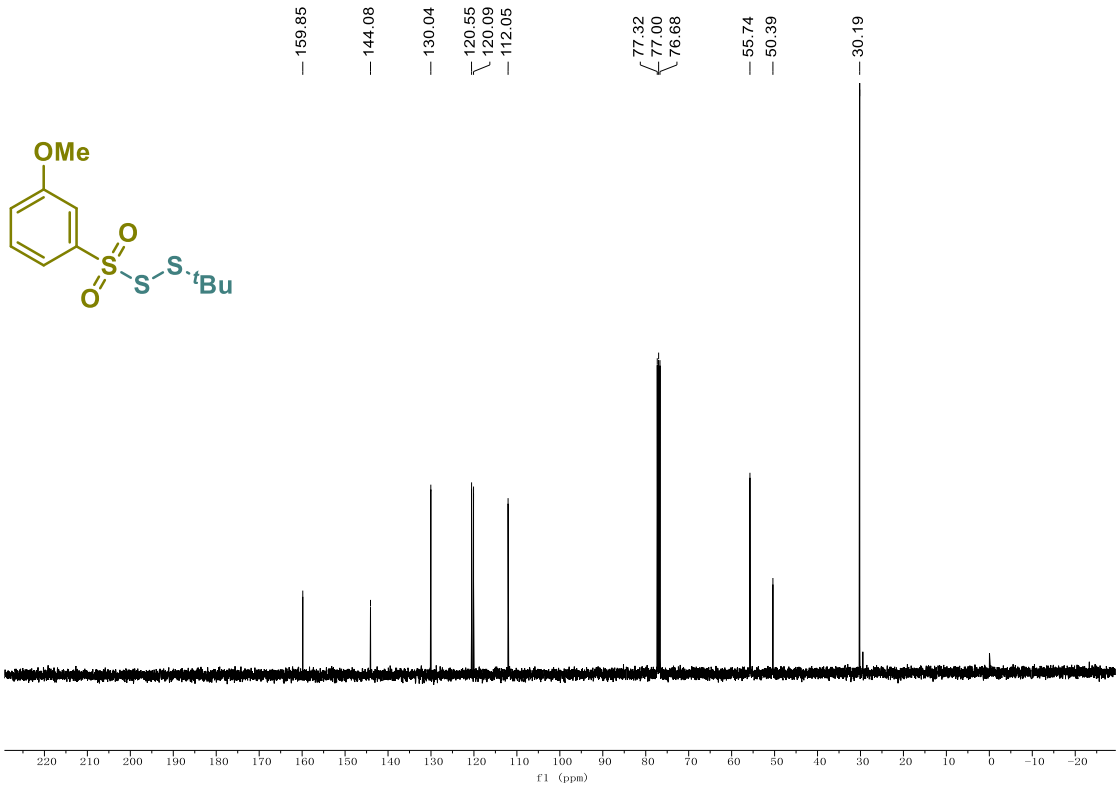


6.2 Spectra of dithiosulfonate 2

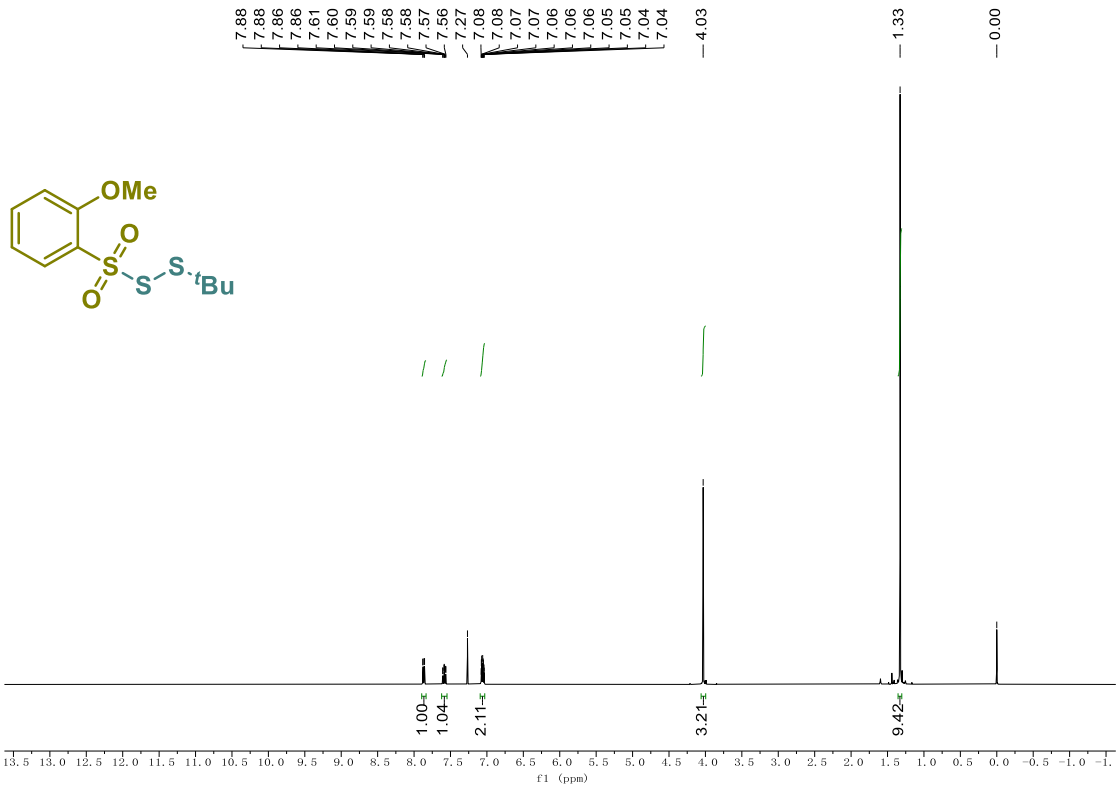
^{1}H NMR Spectrum of *SS*-(*tert*-butyl) 3-methoxybenzenesulfono(dithioperoxoate) (2f):



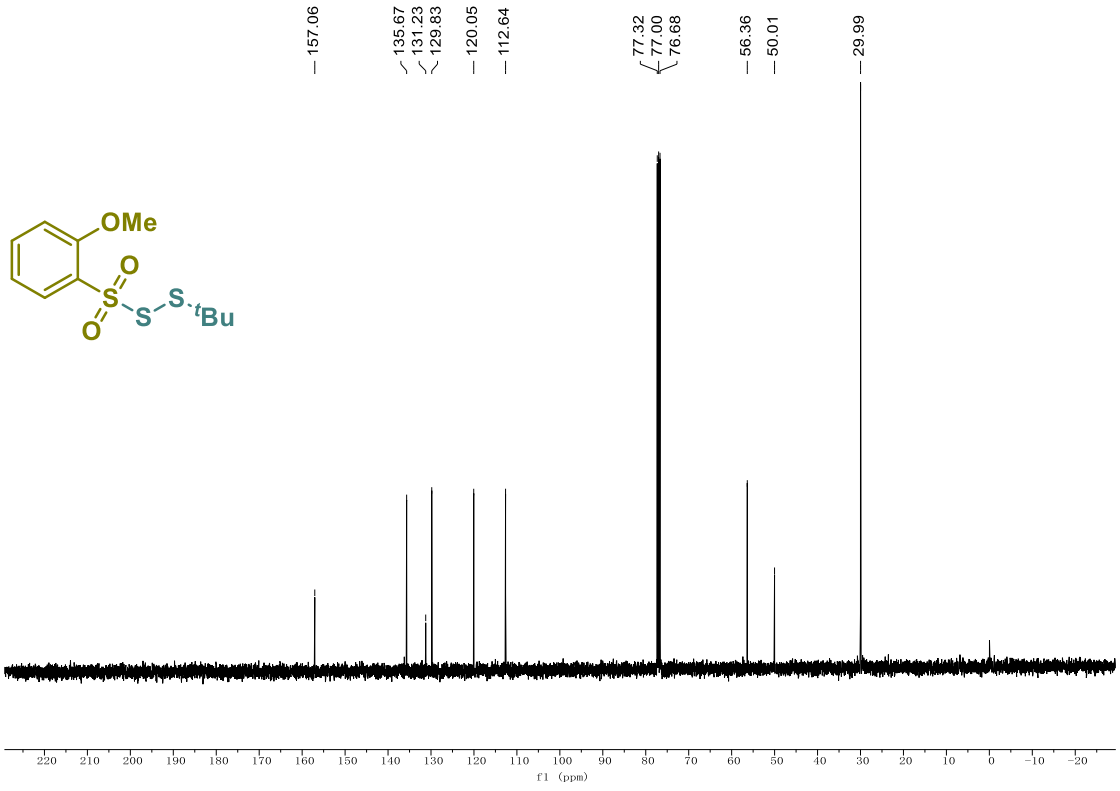
^{13}C NMR Spectrum of *SS*-(*tert*-butyl) 3-methoxybenzenesulfono(dithioperoxoate) (2f):



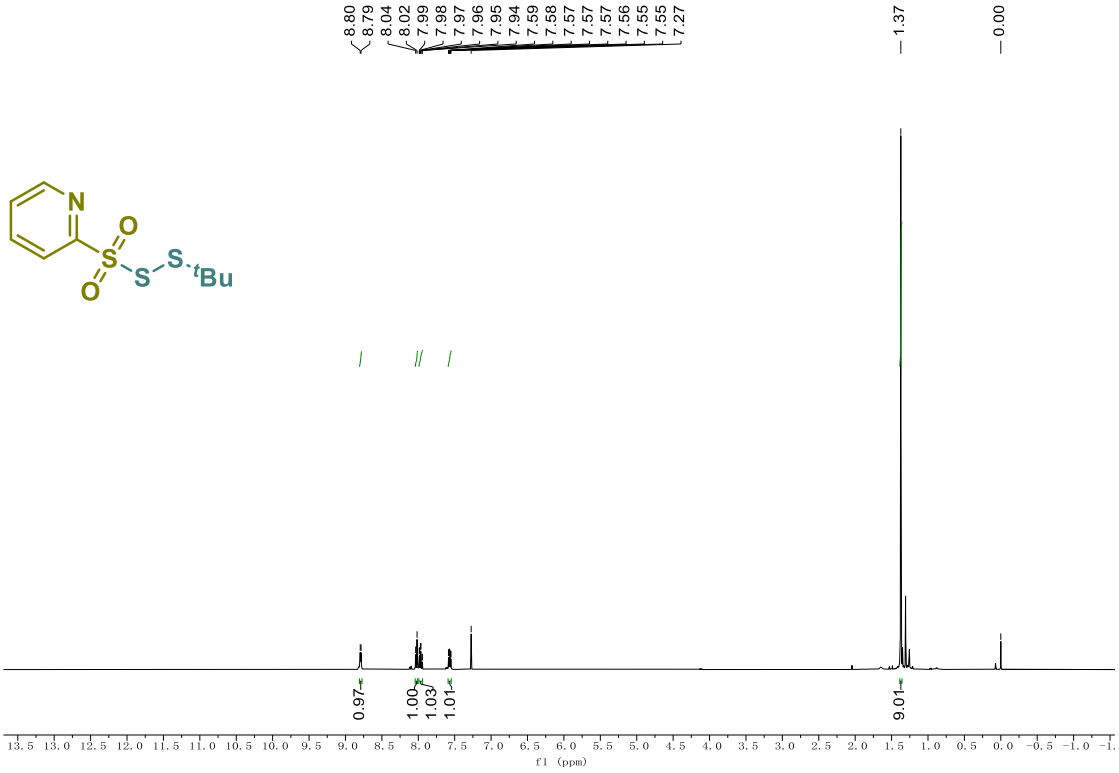
^{1}H NMR Spectrum of *SS*-(*tert*-butyl) 2-methoxybenzenesulfono(dithioperoxoate) (2g):



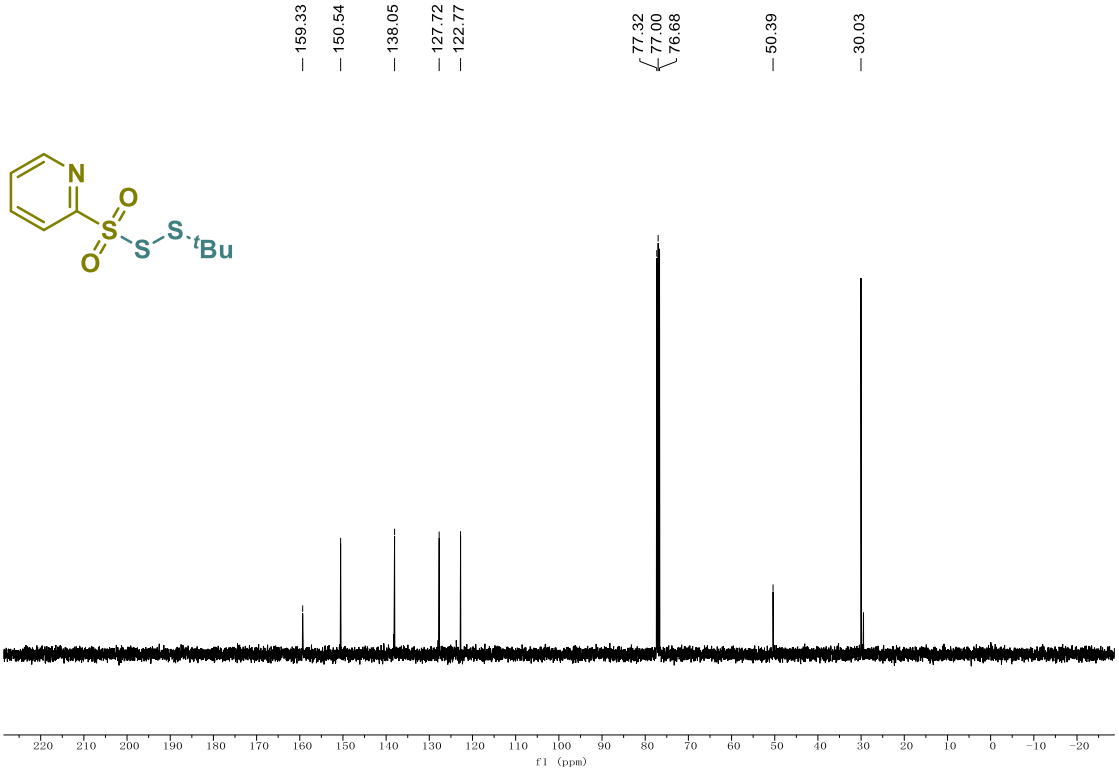
^{13}C NMR Spectrum of *SS*-(*tert*-butyl) 2-methoxybenzenesulfono(dithioperoxoate) (2g):



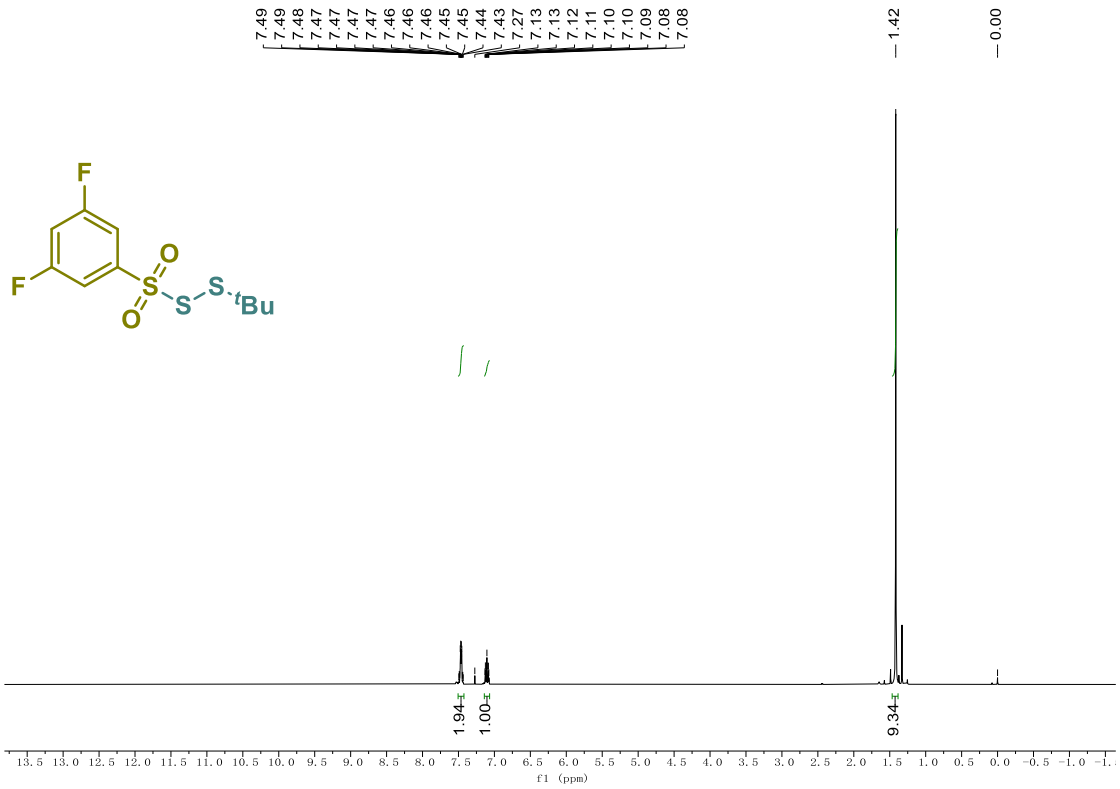
^{1}H NMR Spectrum of *SS*-(*tert*-butyl) pyridine-2-sulfono(dithioperoxoate) (2h):



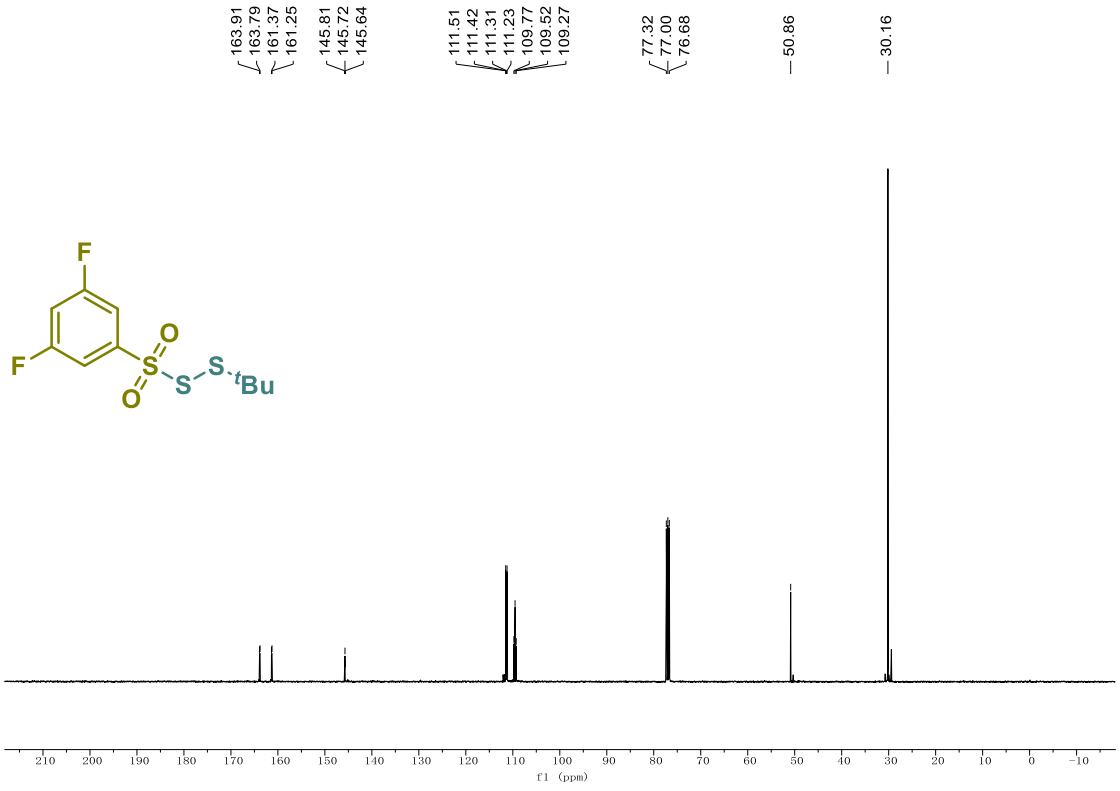
^{13}C NMR Spectrum of *SS*-(*tert*-butyl) pyridine-2-sulfono(dithioperoxoate) (2h):



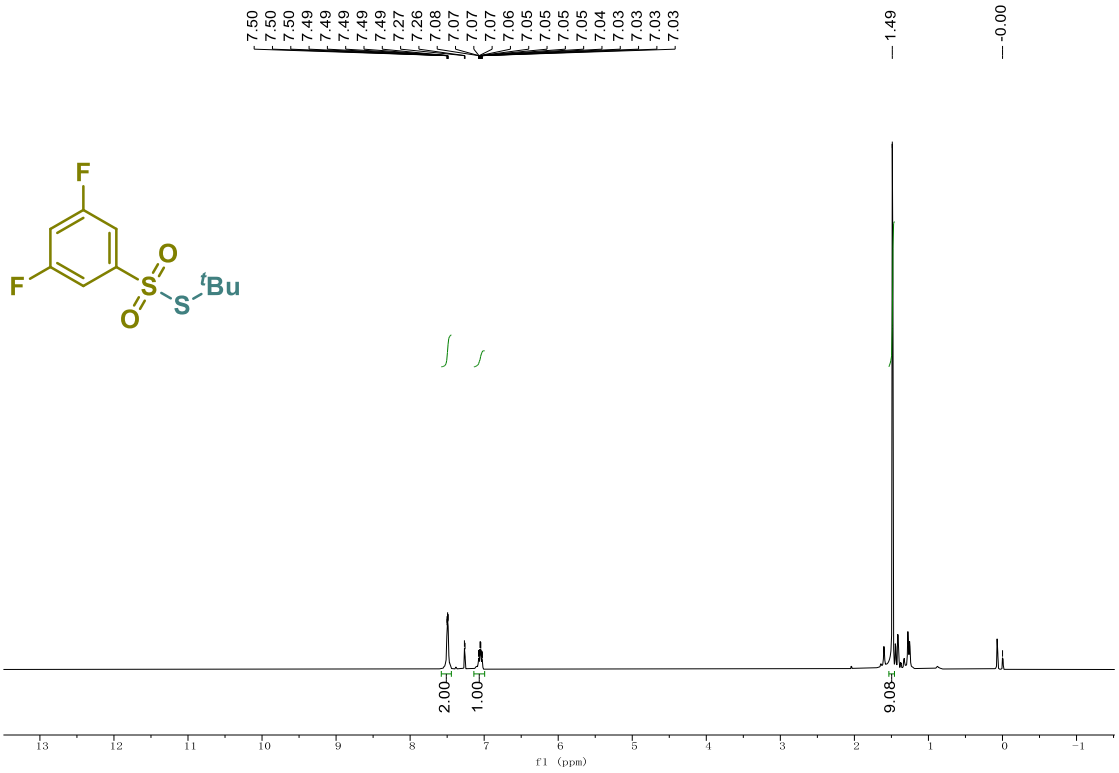
^{1}H NMR Spectrum of *SS*-(*tert*-butyl) 3,5-difluorobenzenesulfono(dithioperoxoate) (2i):



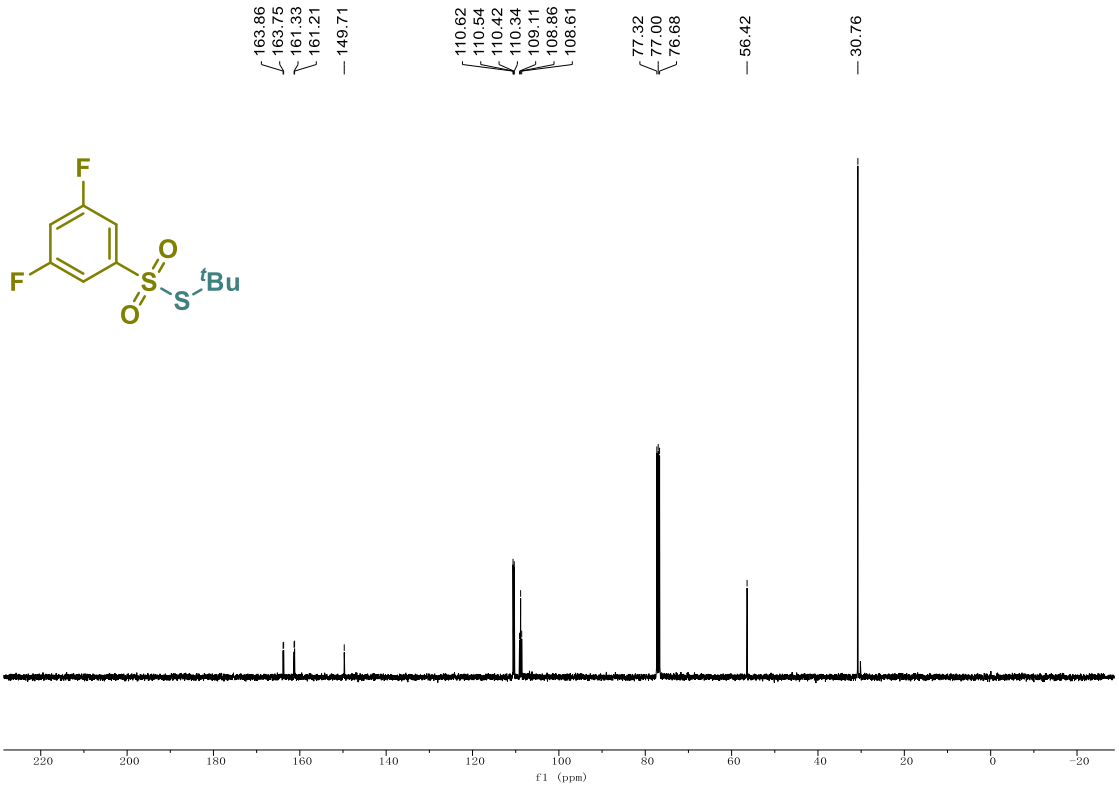
^{13}C NMR Spectrum of *SS*-(*tert*-butyl) 3,5-difluorobenzenesulfono(dithioperoxoate) (2i):



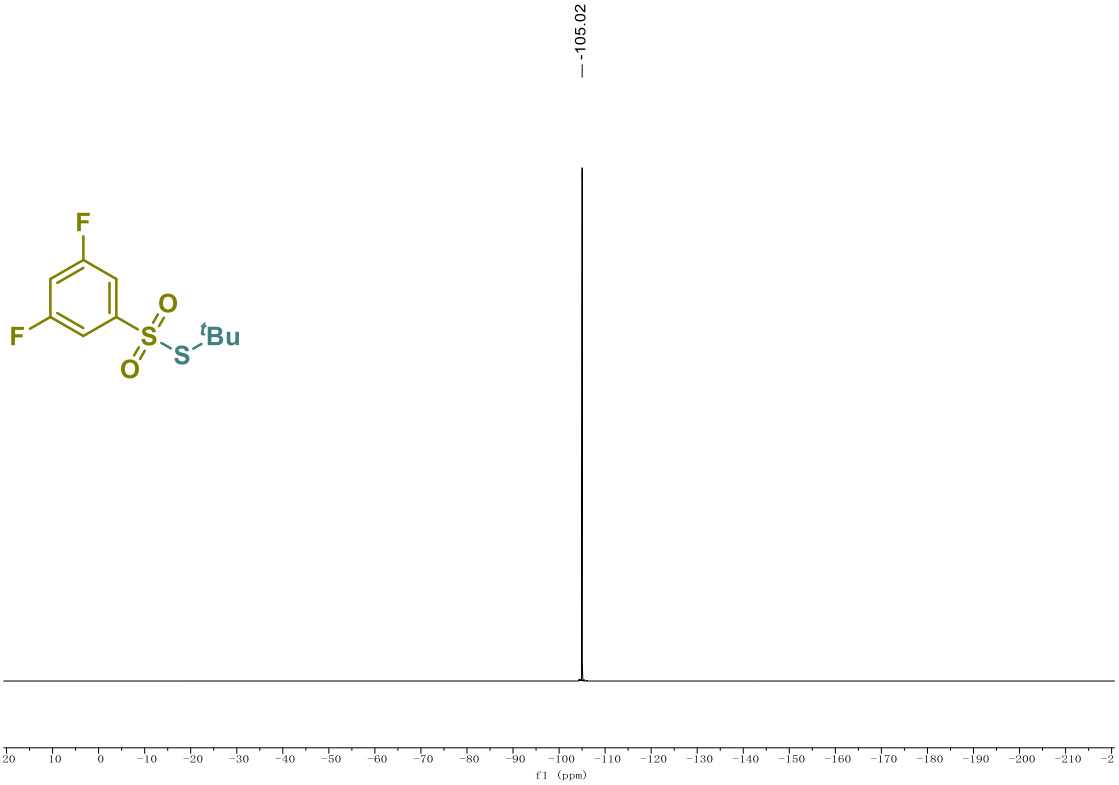
^{1}H NMR Spectrum of *S*-(*tert*-butyl) 3,5-difluorobenzenesulfonothioate (2i'):



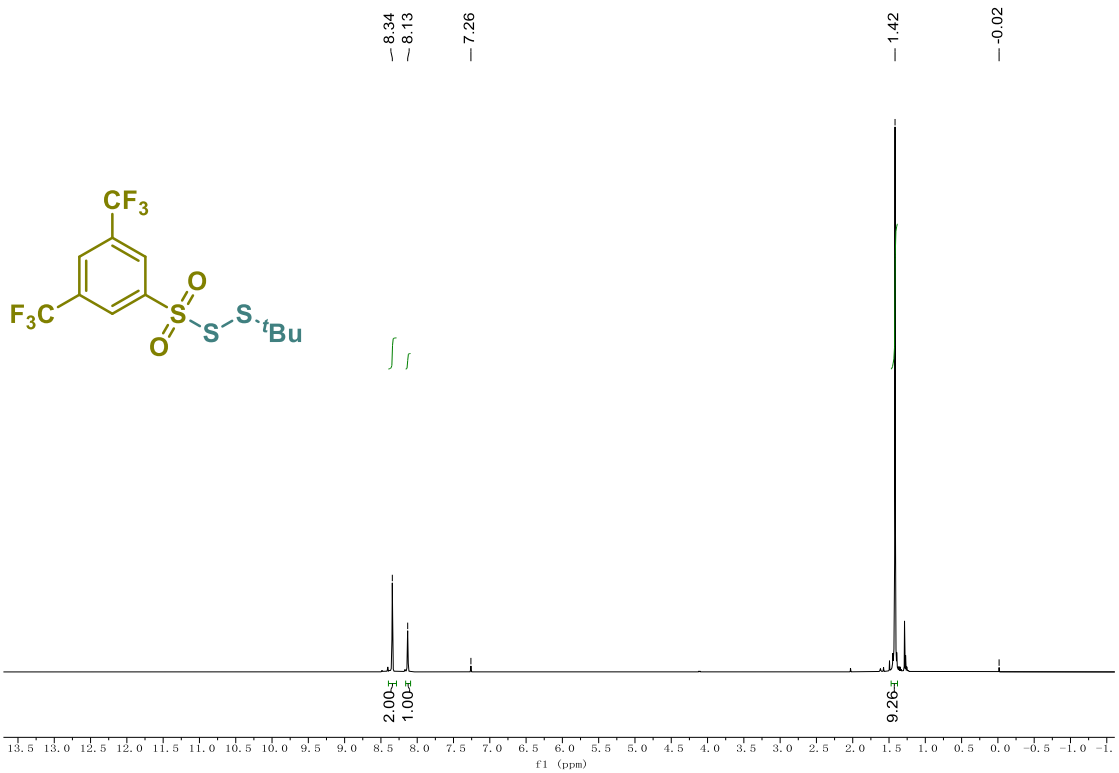
^{13}C NMR Spectrum of *S*-(*tert*-butyl) 3,5-difluorobenzenesulfonothioate (2i'):



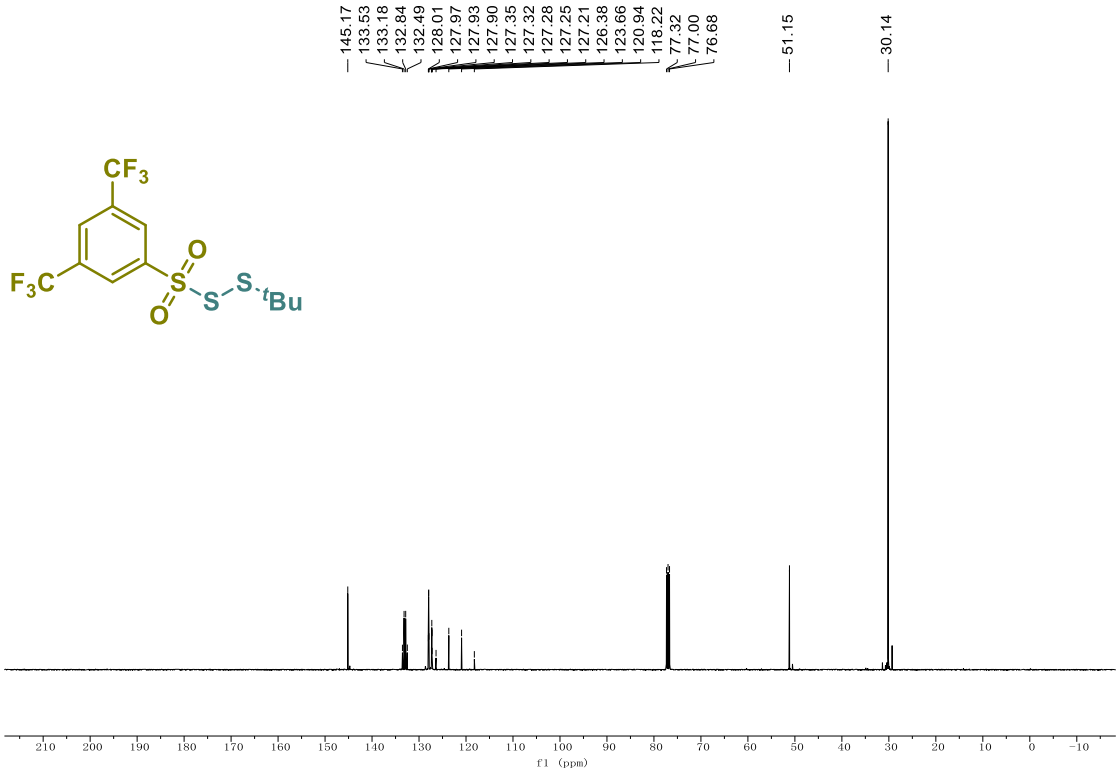
^{19}F NMR Spectrum of *S*-(*tert*-butyl) 3,5-difluorobenzenesulfonothioate (2i'):



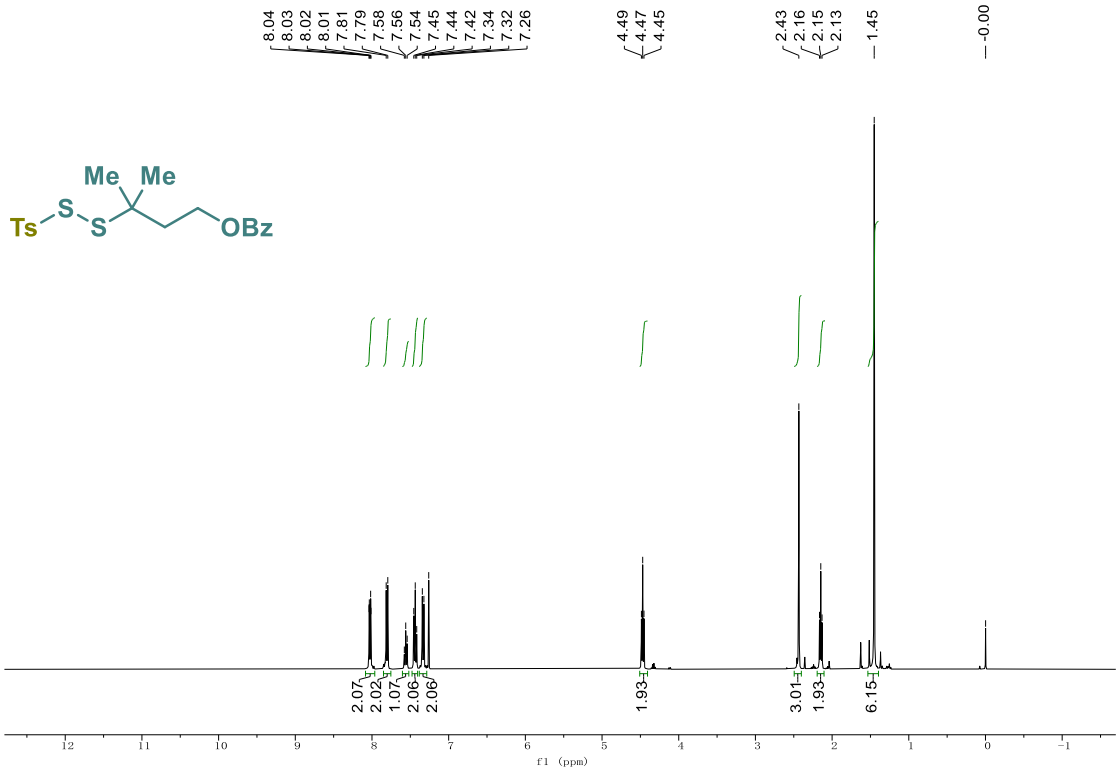
^{1}H NMR Spectrum of *SS*-(*tert*-butyl) 3,5-bis(trifluoromethyl)benzenesulfono (dithioperoxoate) (2j):



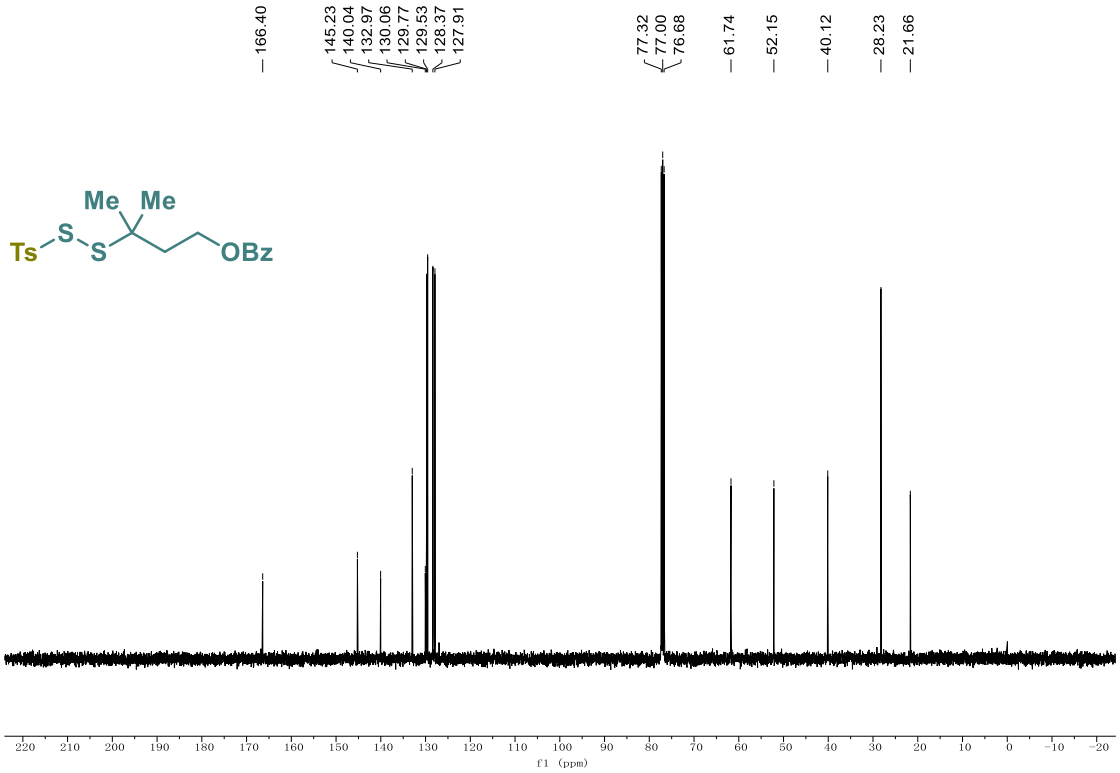
^{13}C NMR Spectrum of *SS*-(*tert*-butyl) 3,5-bis(trifluoromethyl)benzenesulfono (dithioperoxoate) (2j)：



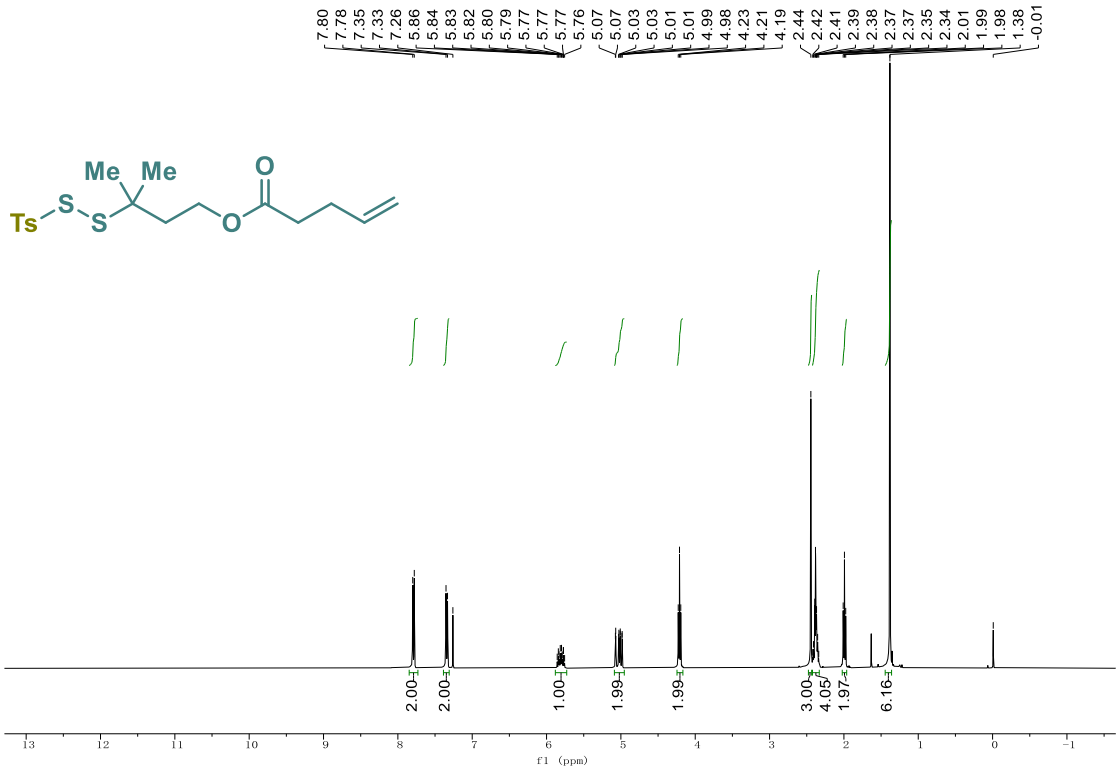
^{1}H NMR Spectrum of 3-(3,3-dioxo-3-(*p*-tolyl)-3λ^{6}-trisulfaneyl)-3-methylbutyl benzoate (2m):



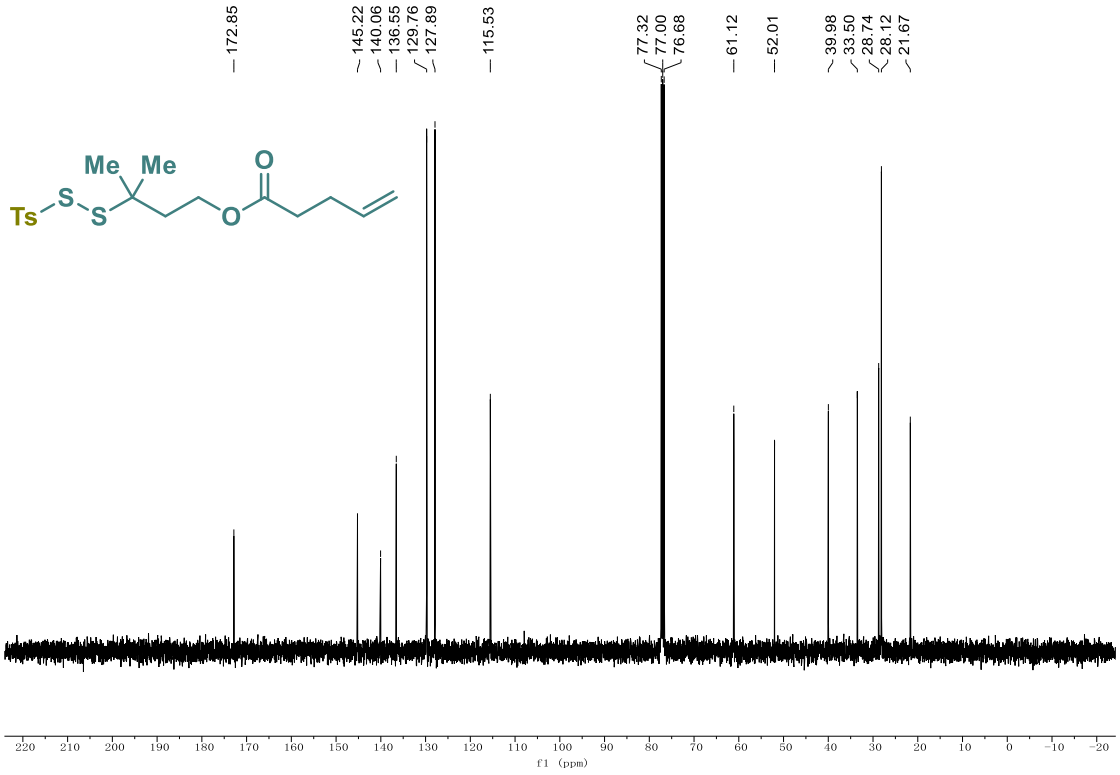
^{13}C NMR Spectrum of 3-(3,3-dioxo-3-(*p*-tolyl)-3λ^{6}-trisulfaneyl)-3-methylbutyl benzoate (2m):



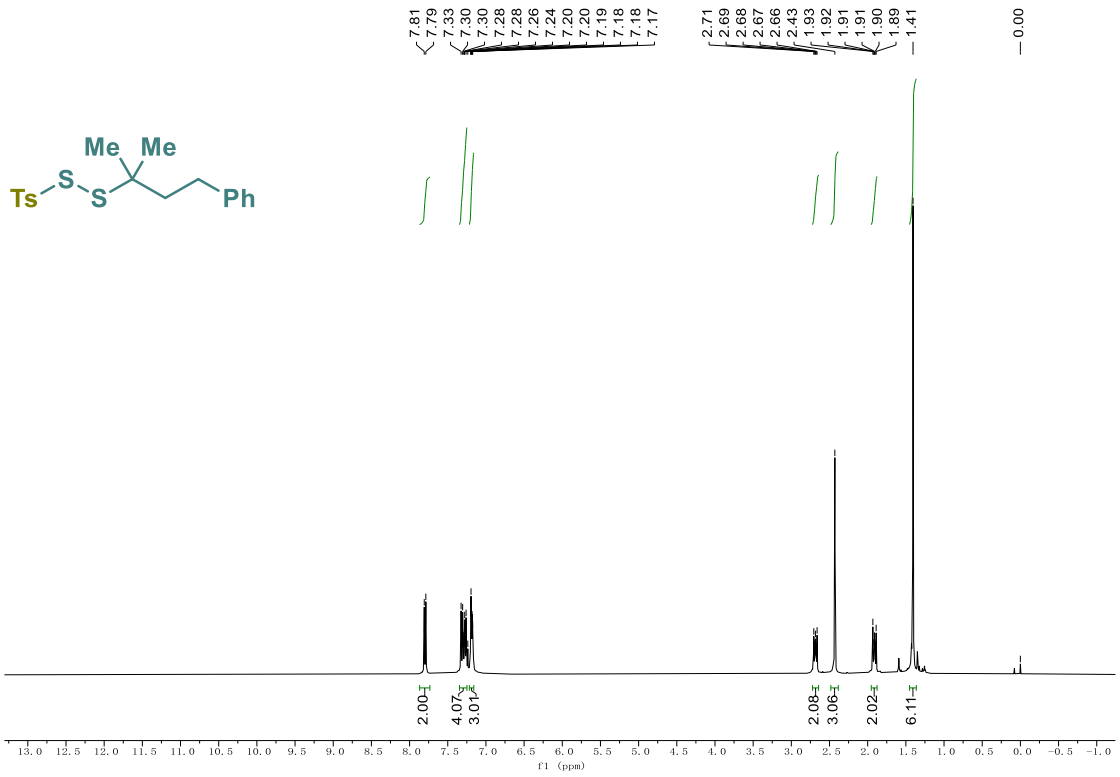
^{1}H NMR Spectrum of 3-(3,3-dioxo-3-(*p*-tolyl)-3λ^{6}-trisulfaneyl)-3-methylbutyl pent-4-enoate (2n):



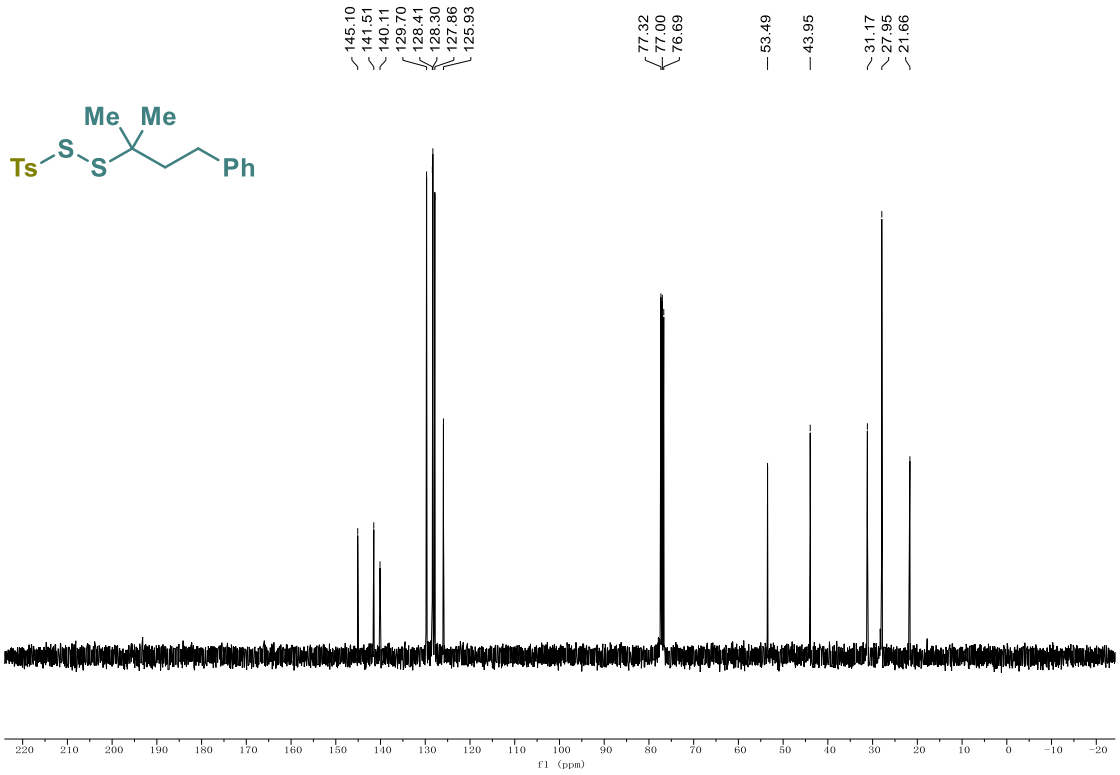
^{13}C NMR Spectrum of 3-(3,3-dioxo-3-(*p*-tolyl)-3λ^{6}-trisulfaneyl)-3-methylbutyl pent-4-enoate (2n):



^{1}H NMR Spectrum of *SS*-(2-methyl-4-phenylbutan-2-yl) 4-methylbenzenesulfono (dithioperoxoate) (2o):

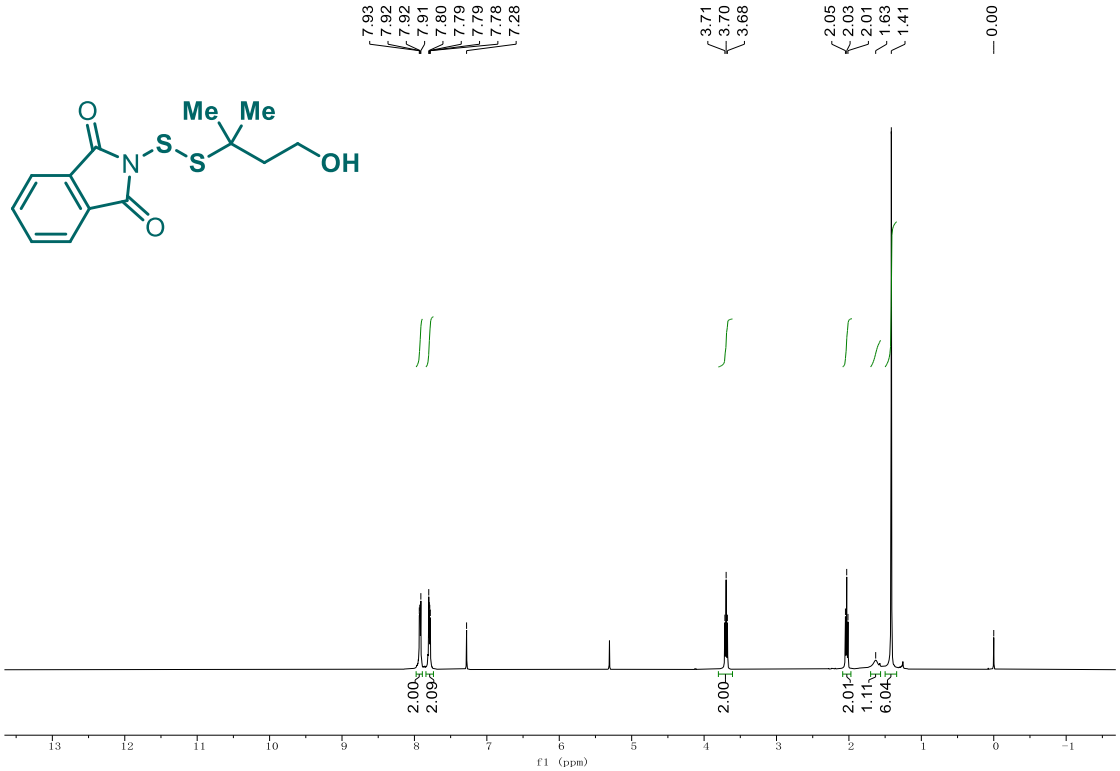


^{13}C NMR Spectrum of *SS*-(2-methyl-4-phenylbutan-2-yl) 4-methylbenzenesulfono(dithioperoxoate) (2o):

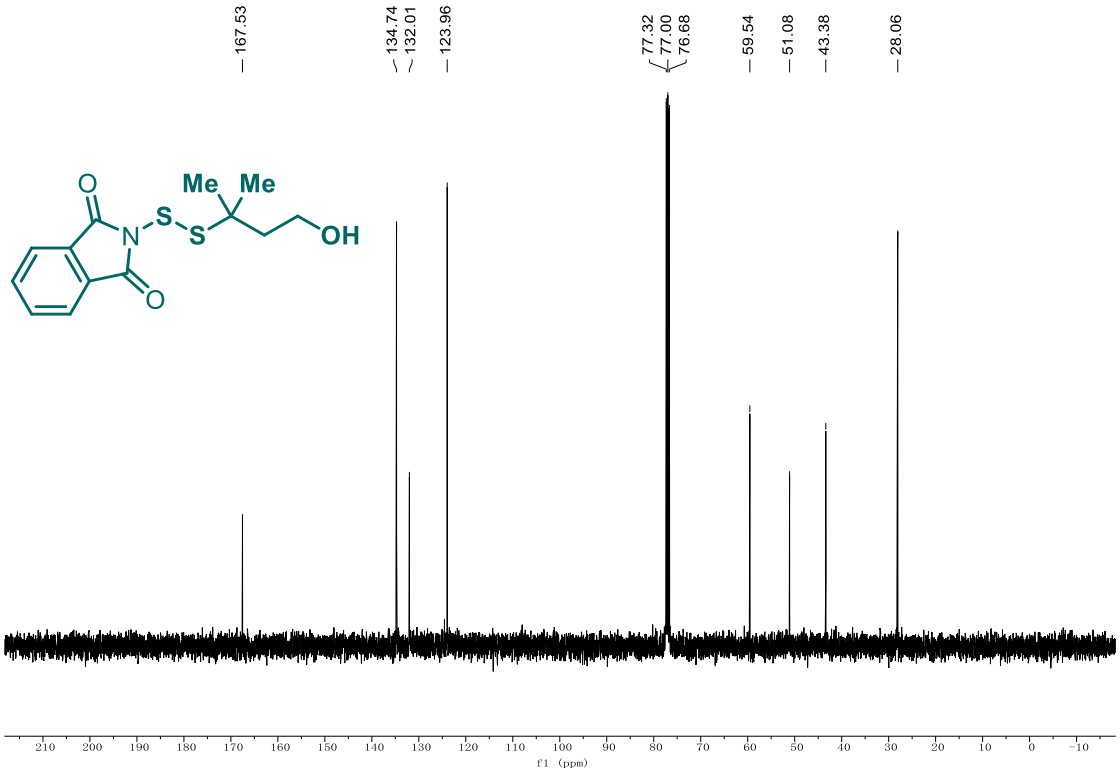


6.3 Spectra of other reagents

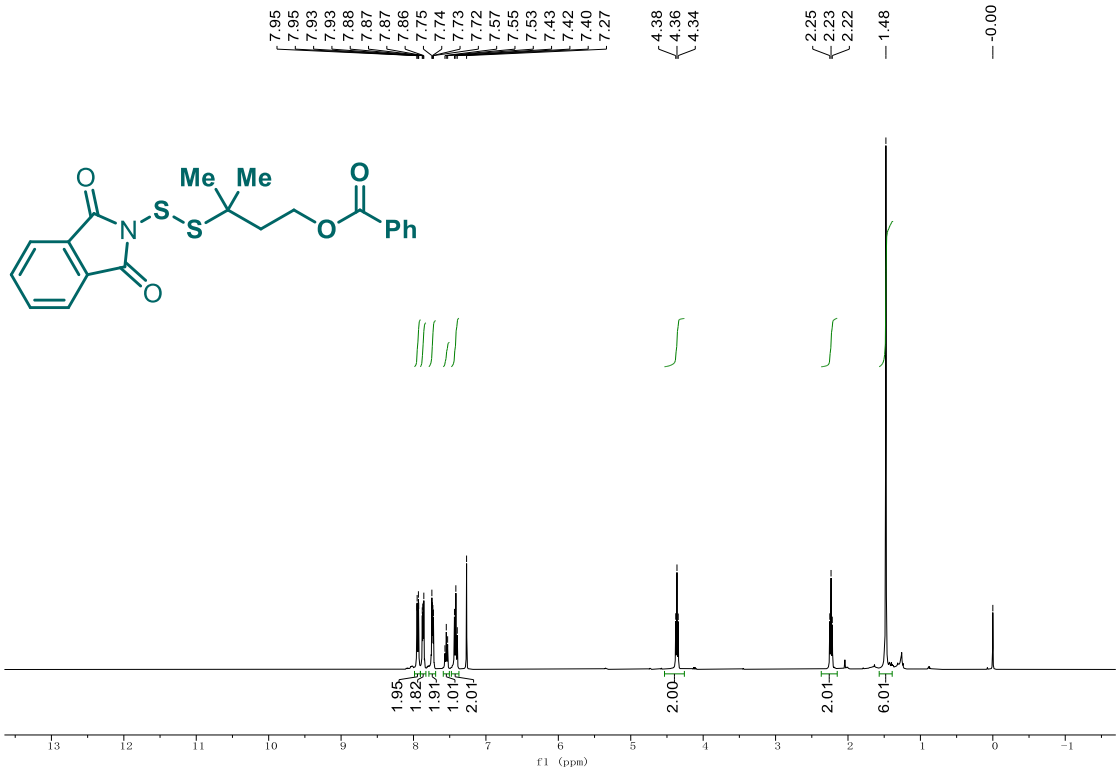
^{1}H NMR Spectrum of 2-((4-hydroxy-2-methylbutan-2-yl)disulfanyl)isoindoline-1,3-dione:



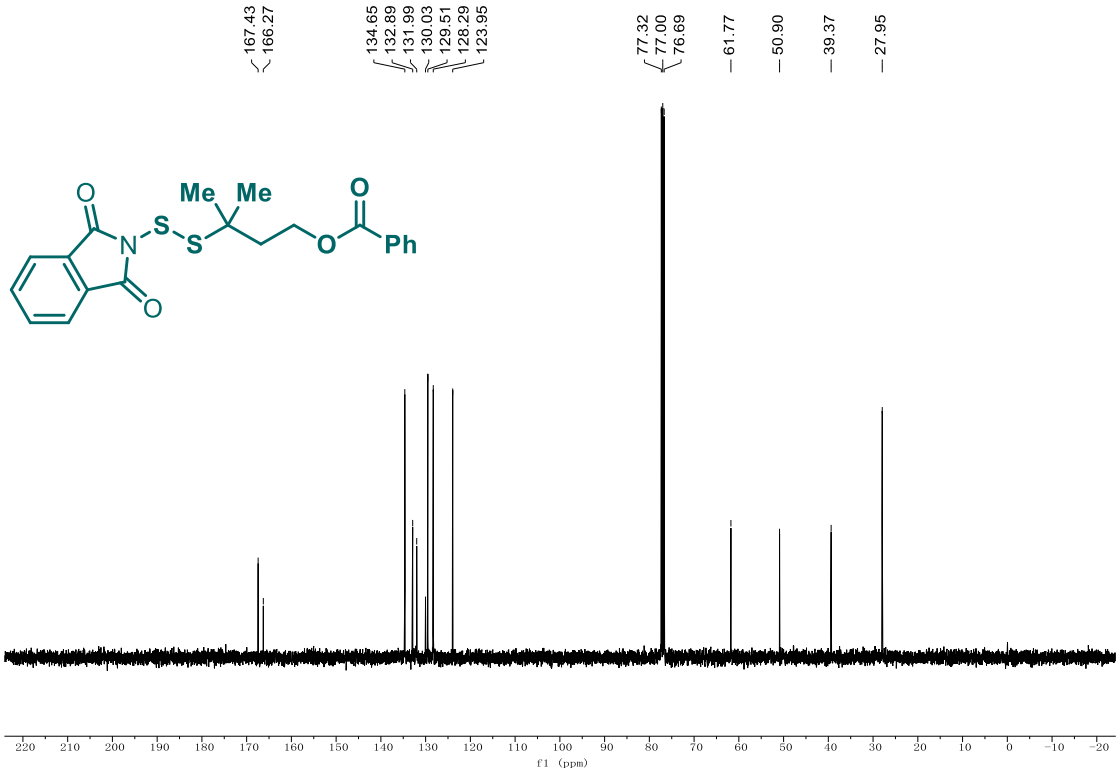
^{13}C NMR Spectrum of 2-((4-hydroxy-2-methylbutan-2-yl)disulfanyl)isoindoline-1,3-dione:



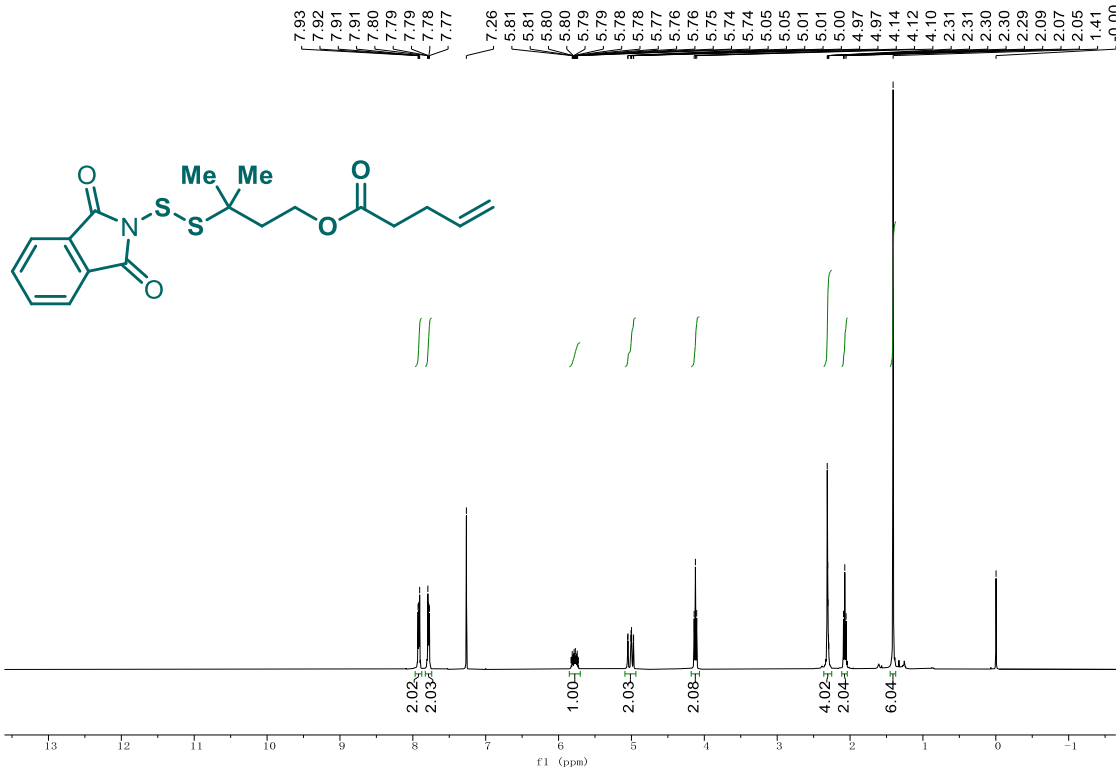
^{1}H NMR Spectrum of 3-((1,3-dioxoisoindolin-2-yl)disulfanyl)-3-methylbutyl benzoate:



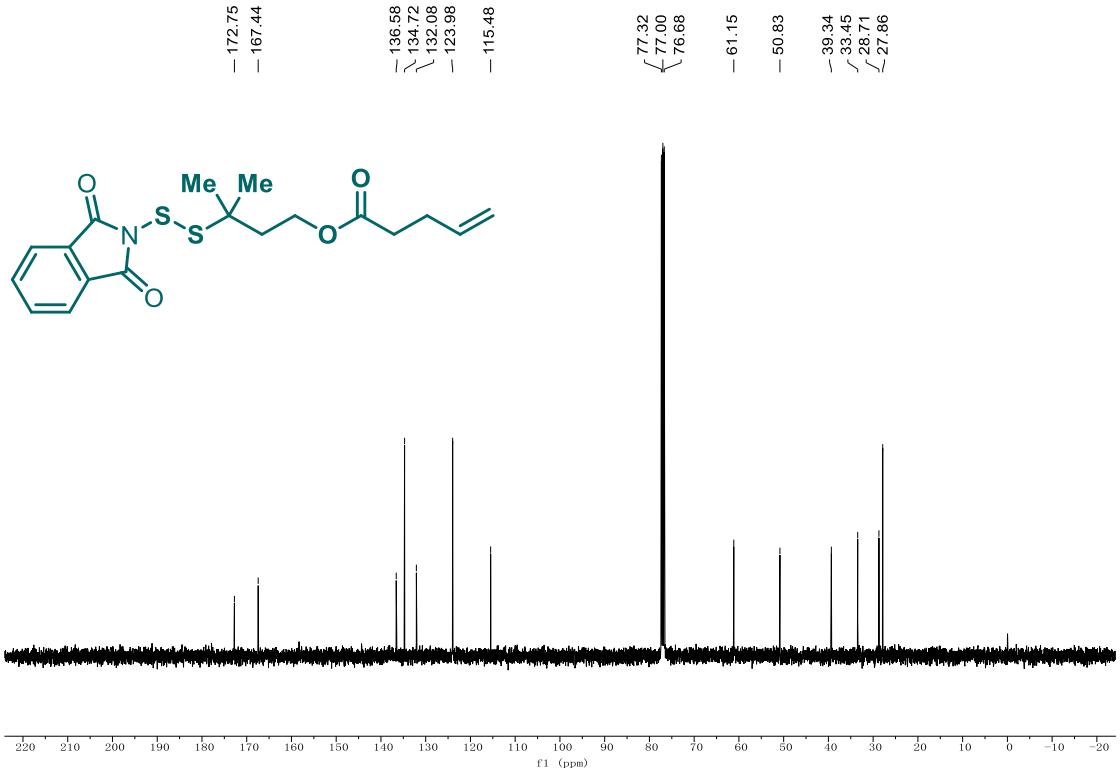
^{13}C NMR Spectrum of 3-((1,3-dioxoisoindolin-2-yl)disulfanyl)-3-methylbutyl pent-4-enoate:



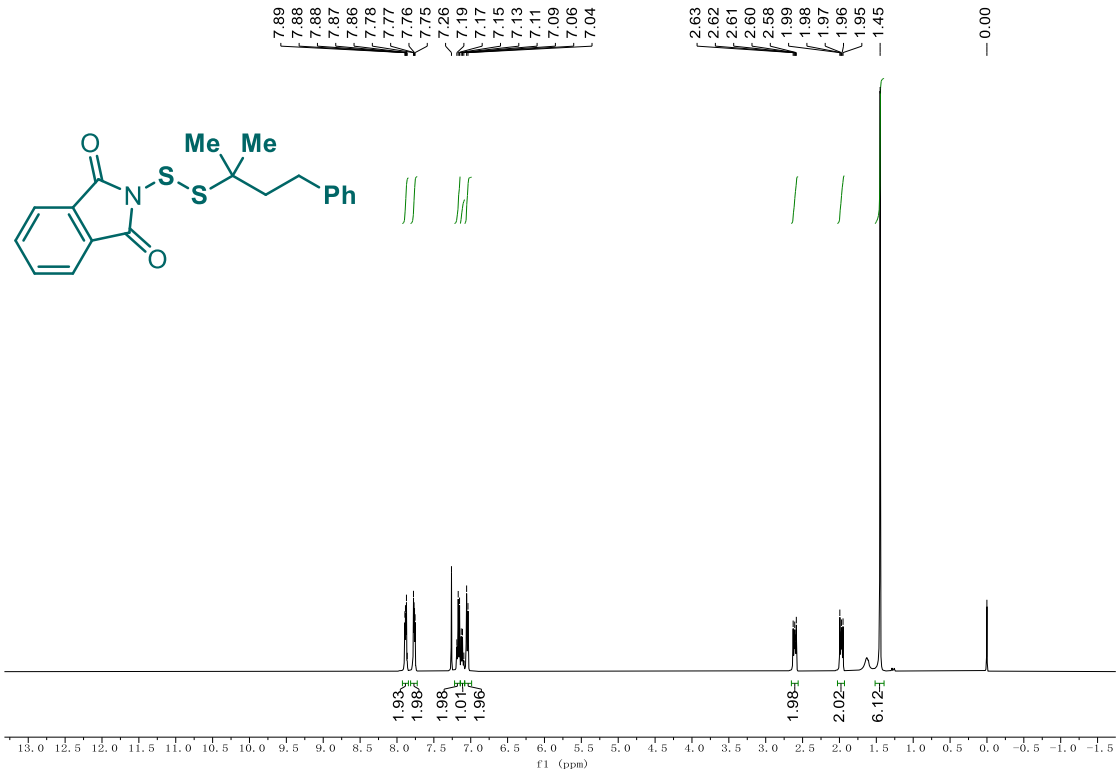
^{1}H NMR Spectrum of 3-((1,3-dioxoisoindolin-2-yl)disulfanyl)-3-methylbutyl pent-4-enoate:



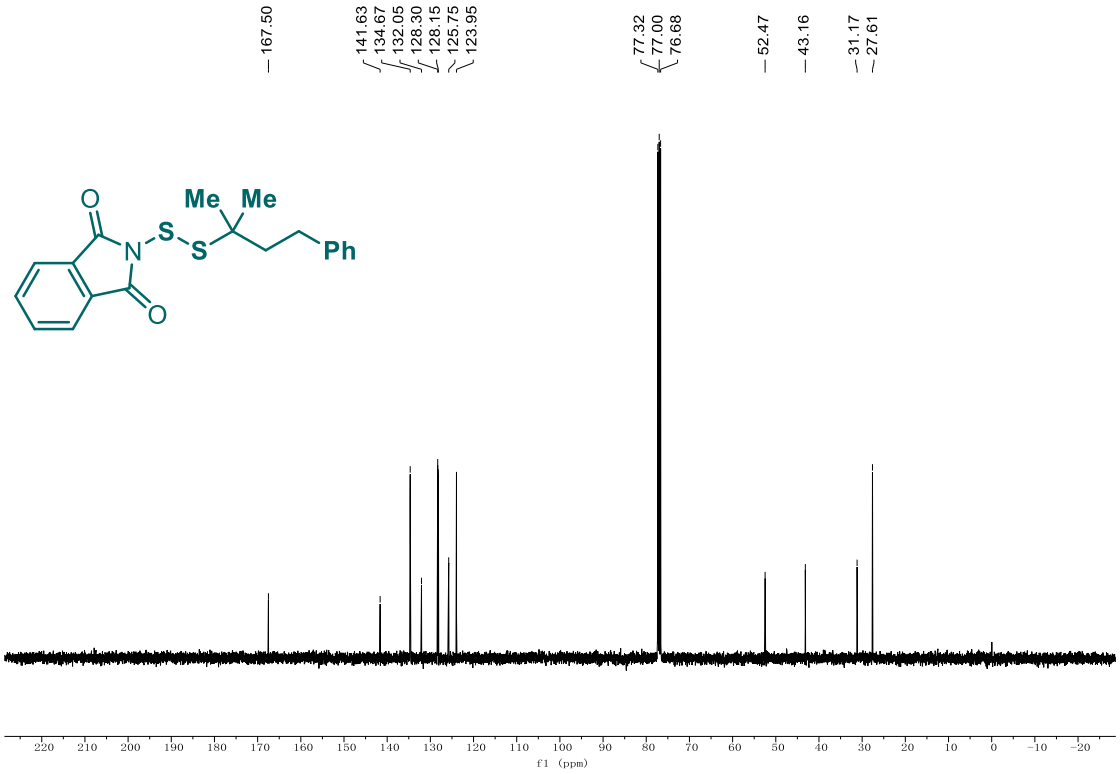
^{13}C NMR Spectrum of 3-((1,3-dioxoisoindolin-2-yl)disulfanyl)-3-methylbutyl pent-4-enoate:



^{1}H NMR Spectrum of 2-((2-methyl-4-phenylbutan-2-yl)disulfaneyl)isoindoline-1,3-dione:

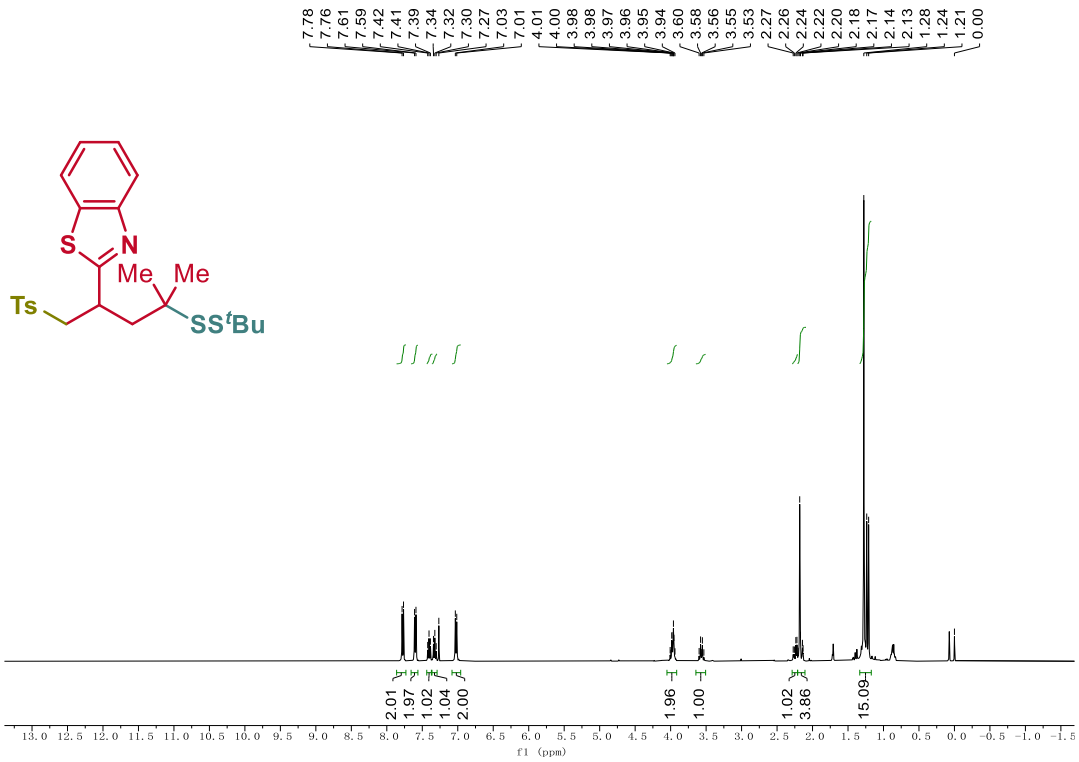


^{13}C NMR Spectrum of 2-((2-methyl-4-phenylbutan-2-yl)disulfaneyl)isoindoline-1,3-dione:

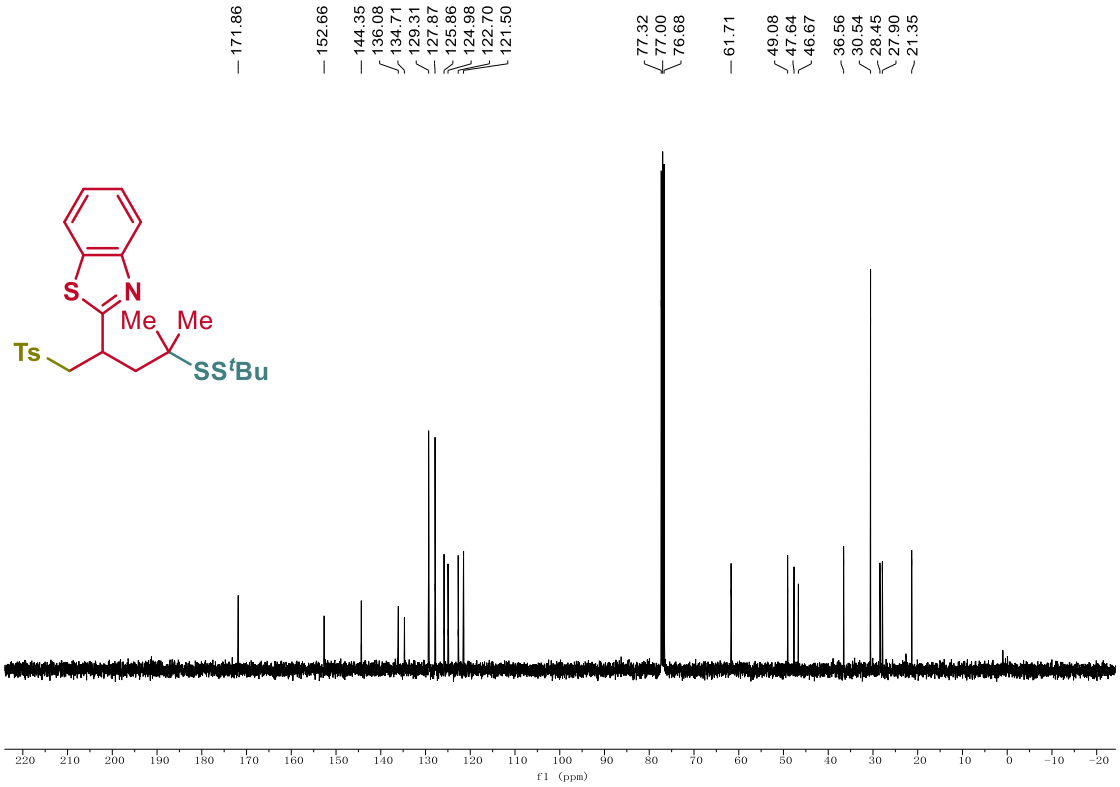


6.4 Spectra of polysulfides

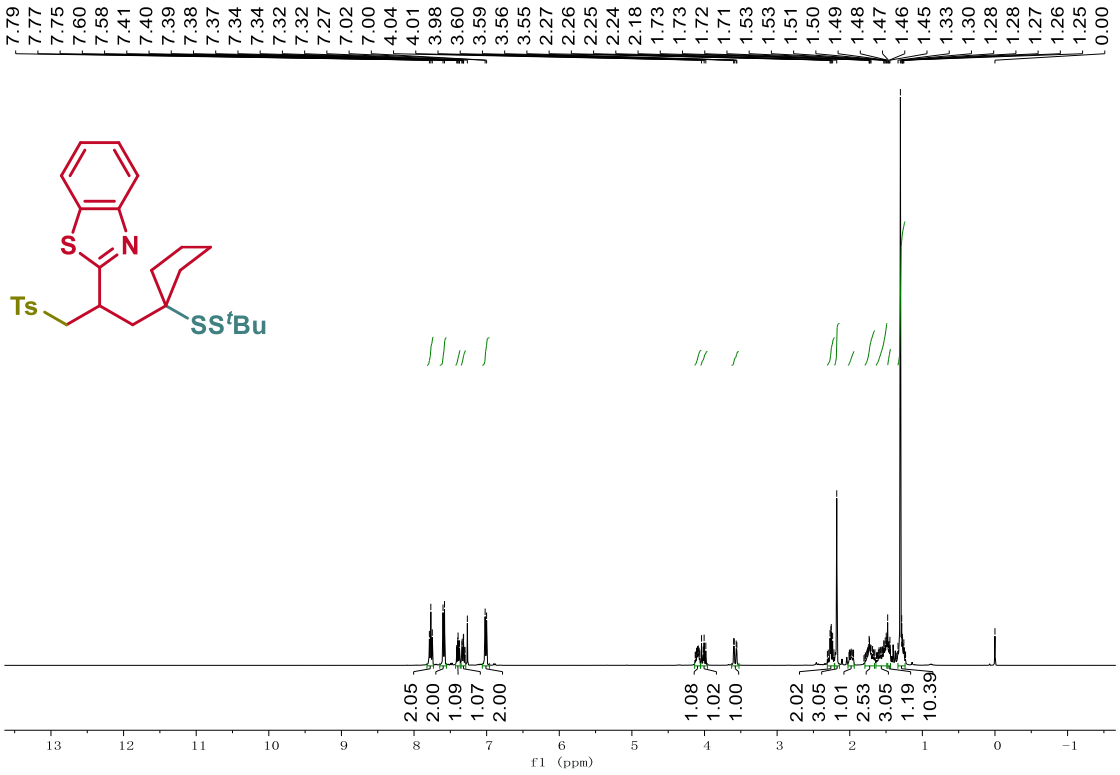
^{1}H NMR Spectrum of 2-(4-(*tert*-butyldisulfanyl)-4-methyl-1-tosylpentan-2-yl)benzo[*d*]thiazole (3a):



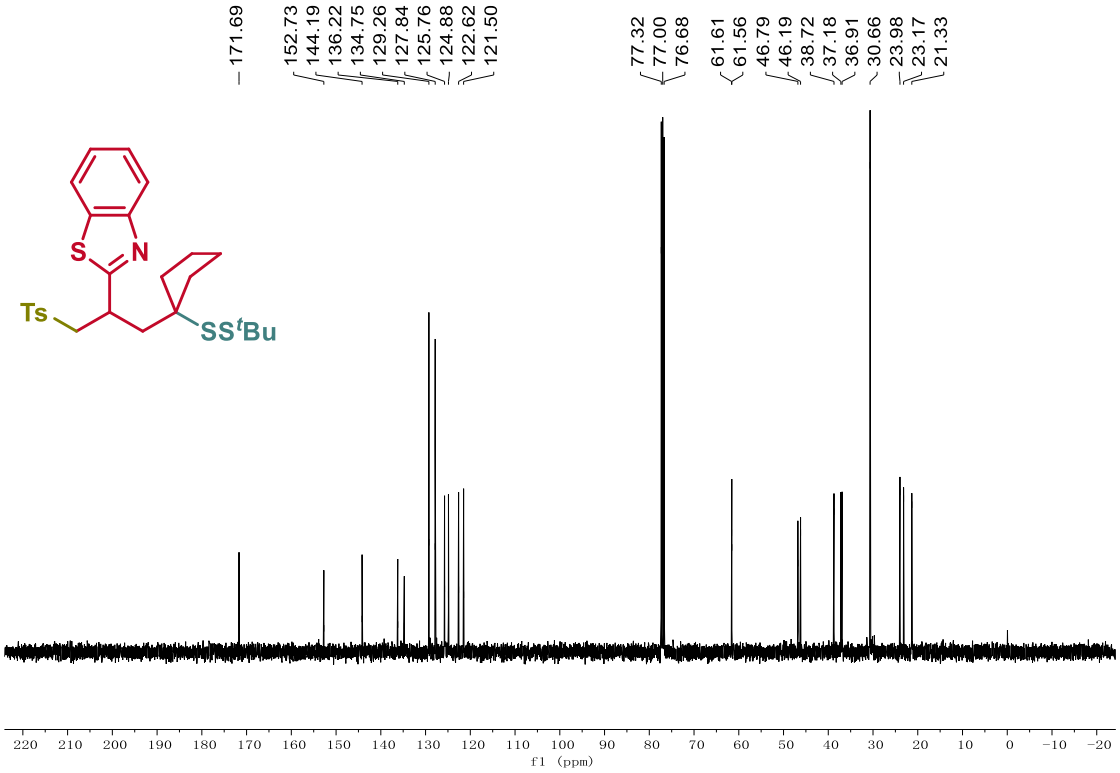
^{13}C NMR Spectrum of 2-(4-(*tert*-butyldisulfanyl)-4-methyl-1-tosylpentan-2-yl)benzo[*d*]thiazole (3a):



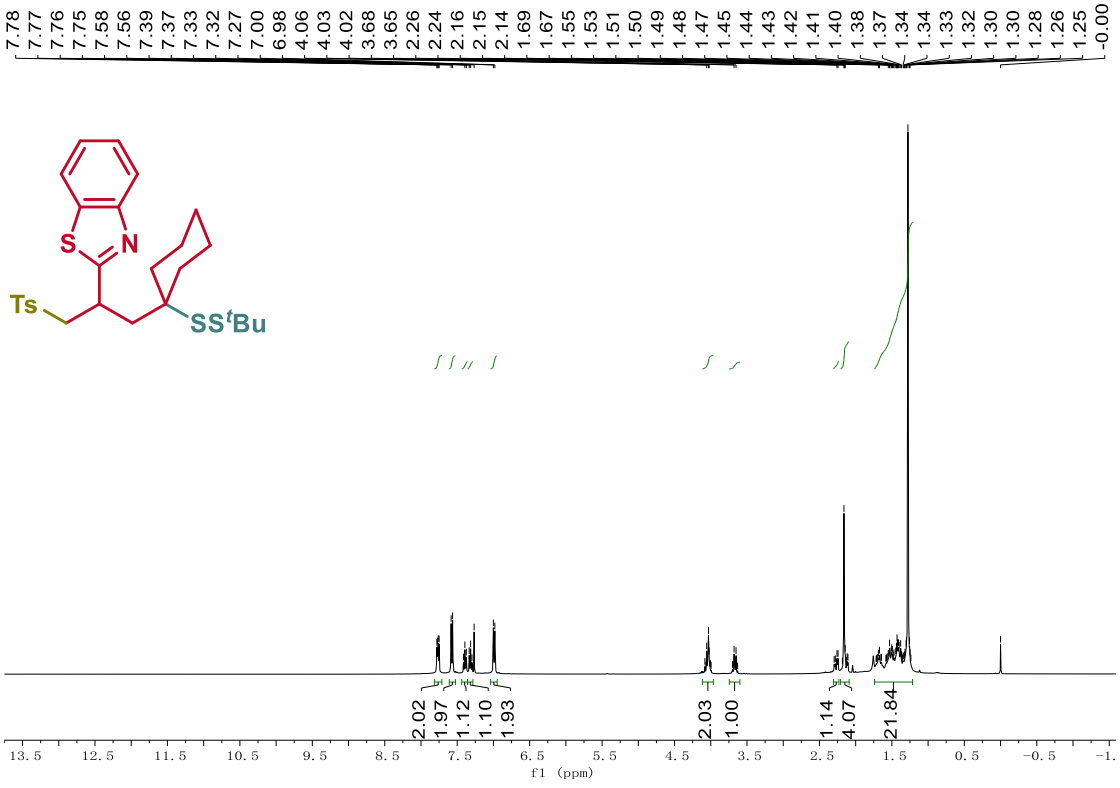
^{1}H NMR Spectrum of 2-(1-(1-(*tert*-butyldisulfanyl)cyclopentyl)- 3-tosylpropan-2-yl)benzo[*d*]thiazole (3b):



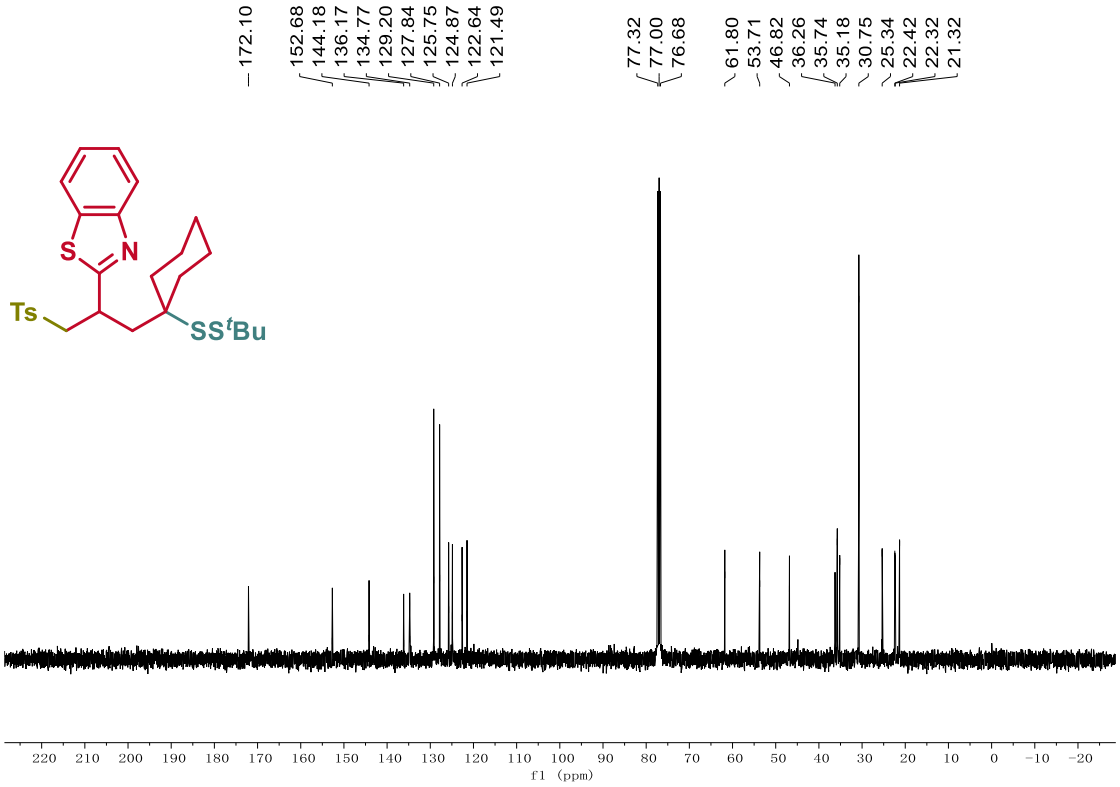
^{13}C NMR Spectrum of 2-(1-(1-(*tert*-butyldisulfanyl)cyclopentyl)- 3-tosylpropan-2-yl)benzo[*d*]thiazole (3b):



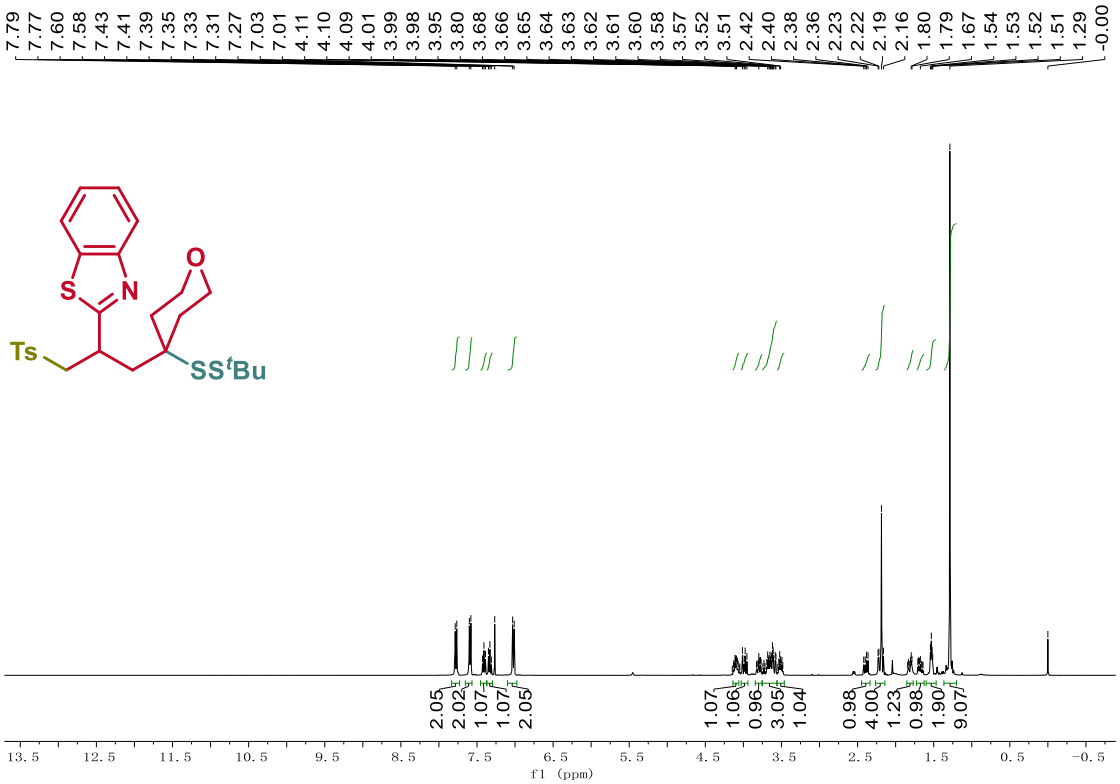
^{1}H NMR Spectrum of 2-(4-(*tert*-butyldisulfanyl)-4-methyl-1-tosylpentan-2-yl)benzo[*d*]thiazole (3c):



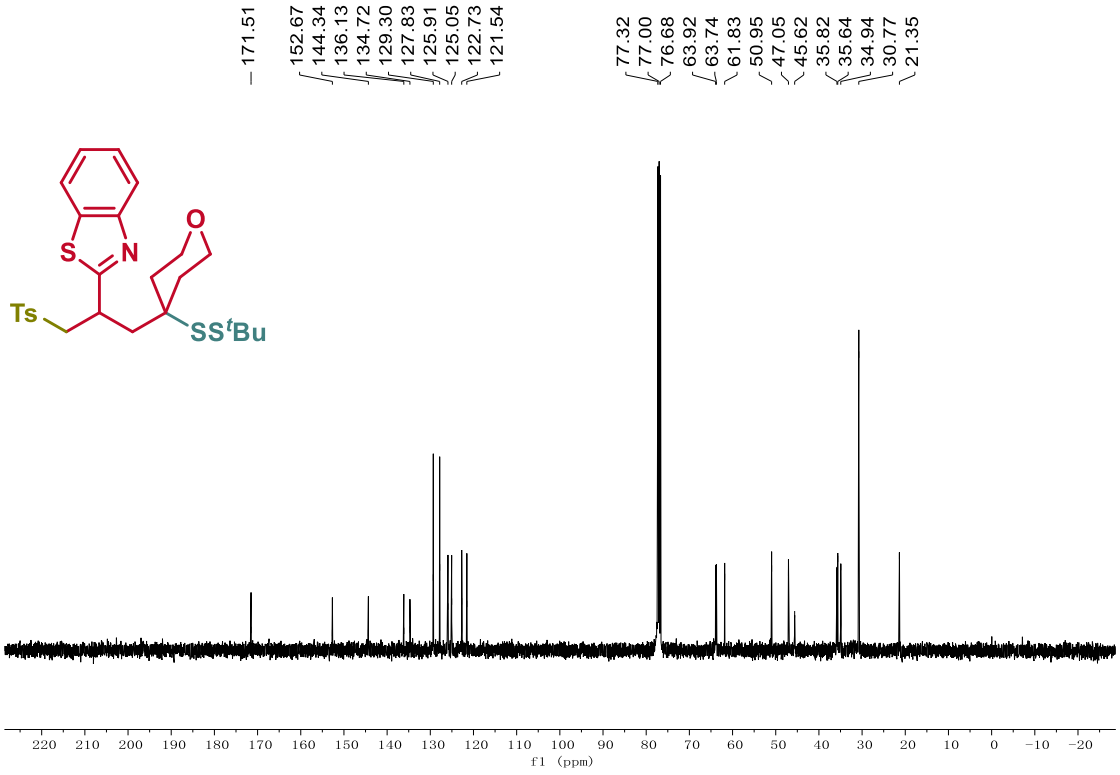
^{13}C NMR Spectrum of 2-(4-(*tert*-butyldisulfanyl)-4-methyl-1-tosylpentan-2-yl)benzo[*d*]thiazole (3c):



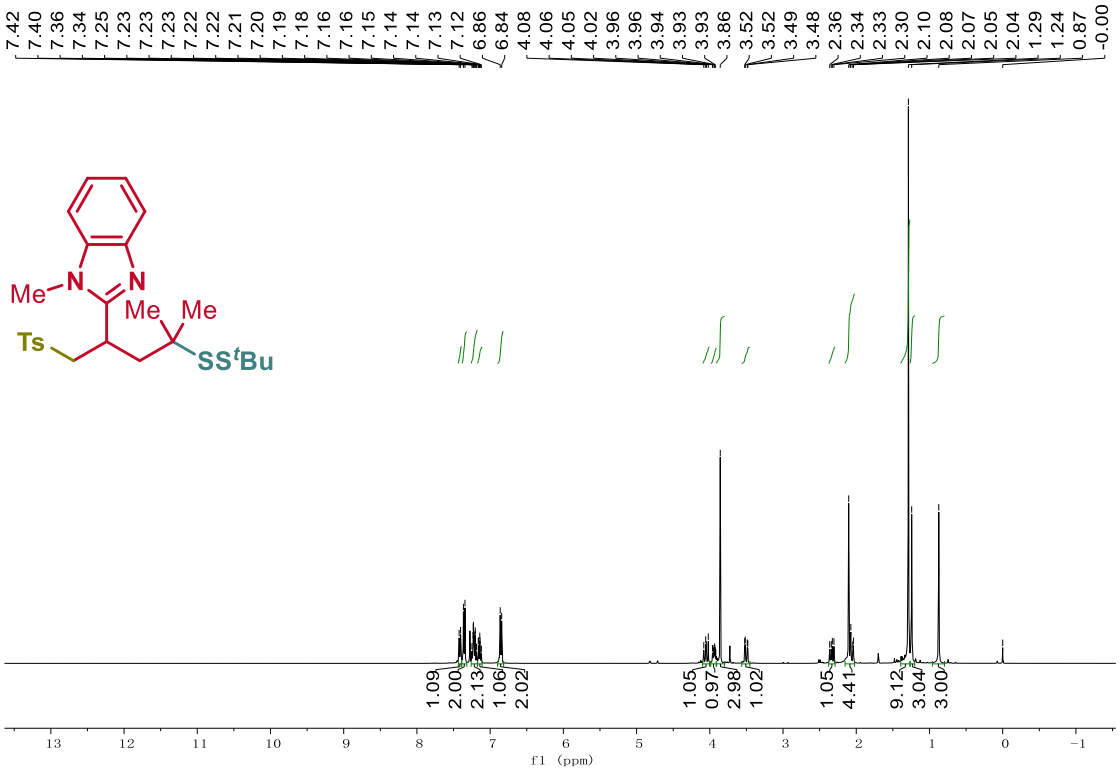
^{1}H NMR Spectrum of 2-(1-(4-(*tert*-butyldisulfanyl)tetrahydro-2*H*-pyran-4-yl)- 3-tosylpropan-2-yl)benzo[*d*]thiazole (3d):



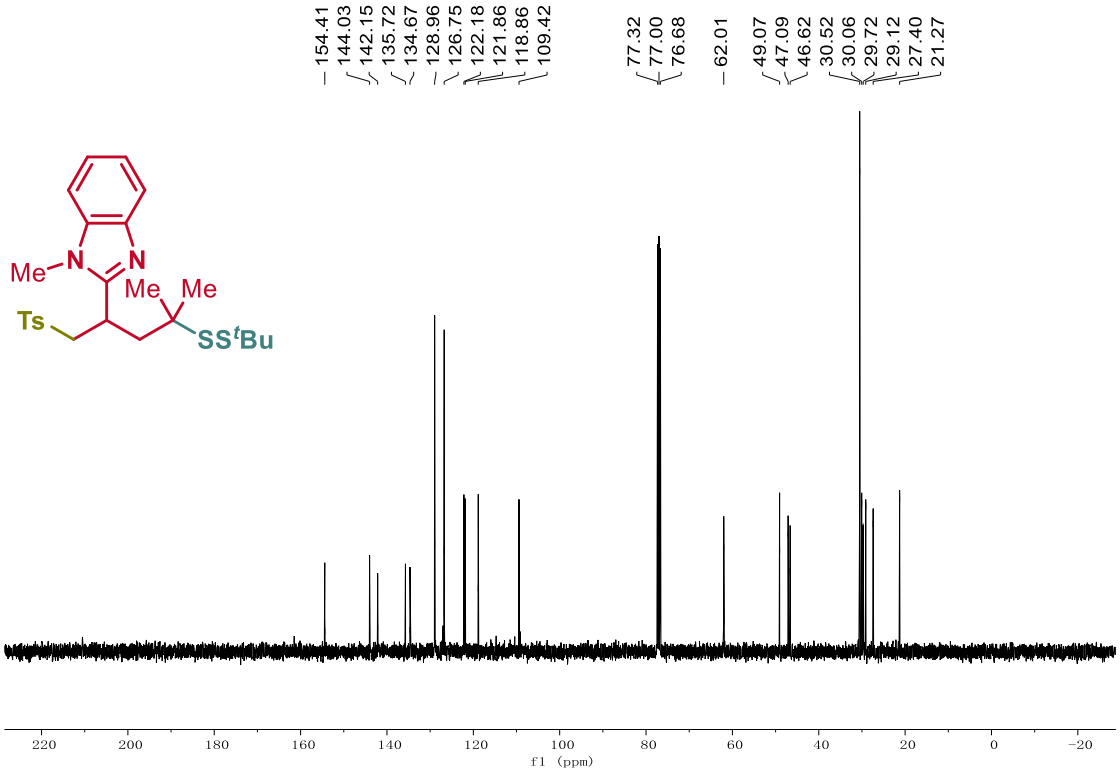
^{13}C NMR Spectrum of 2-(1-(4-(*tert*-butyldisulfanyl)tetrahydro-2*H*-pyran-4-yl)- 3-tosylpropan-2-yl)benzo[*d*]thiazole (3d):



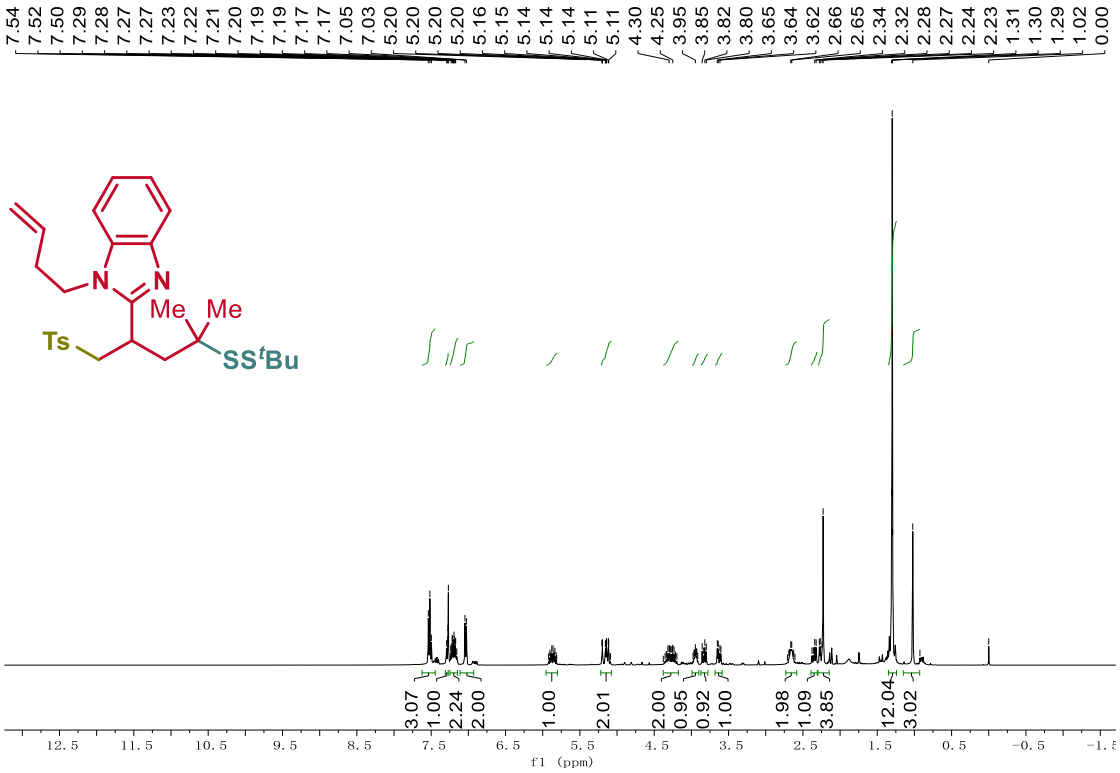
^{1}H NMR Spectrum of 2-(4-(*tert*-butyldisulfanyl)-4-methyl-1-tosylpentan-2-yl)- 1-methyl-1*H*-benzo[*d*]imidazole (3e):



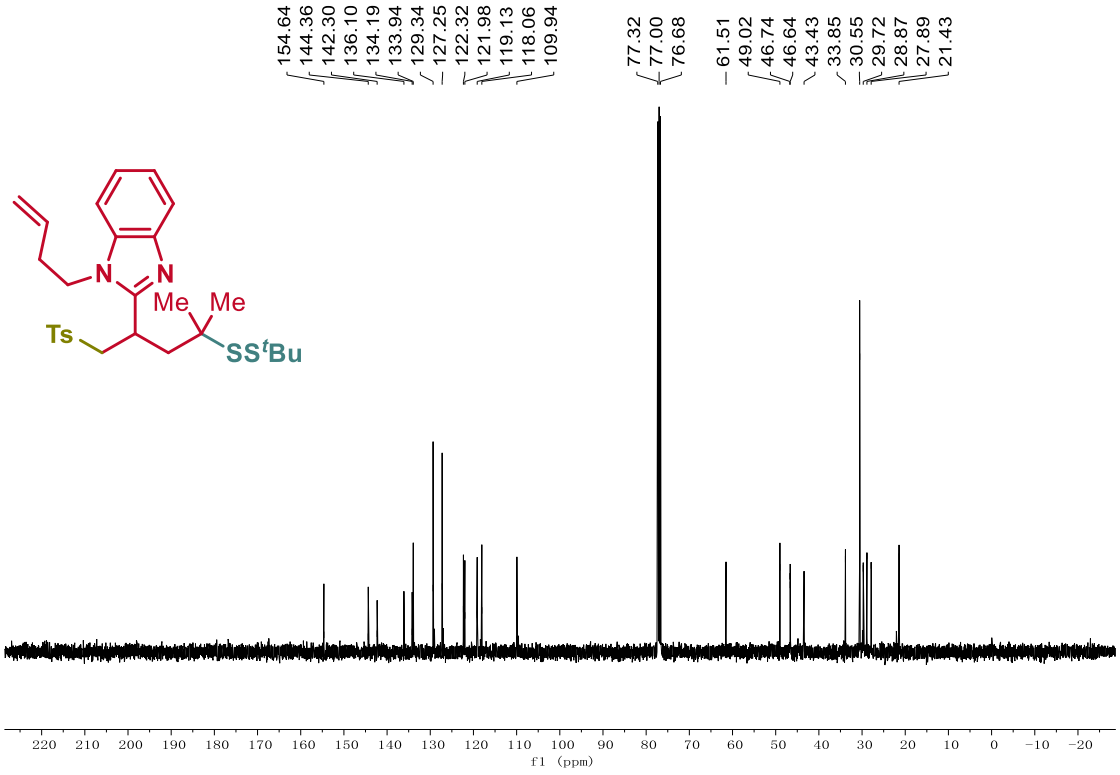
^{13}C NMR Spectrum of 2-(4-(*tert*-butyldisulfanyl)-4-methyl-1-tosylpentan-2-yl)- 1-methyl-1*H*-benzo[*d*]imidazole (3e):



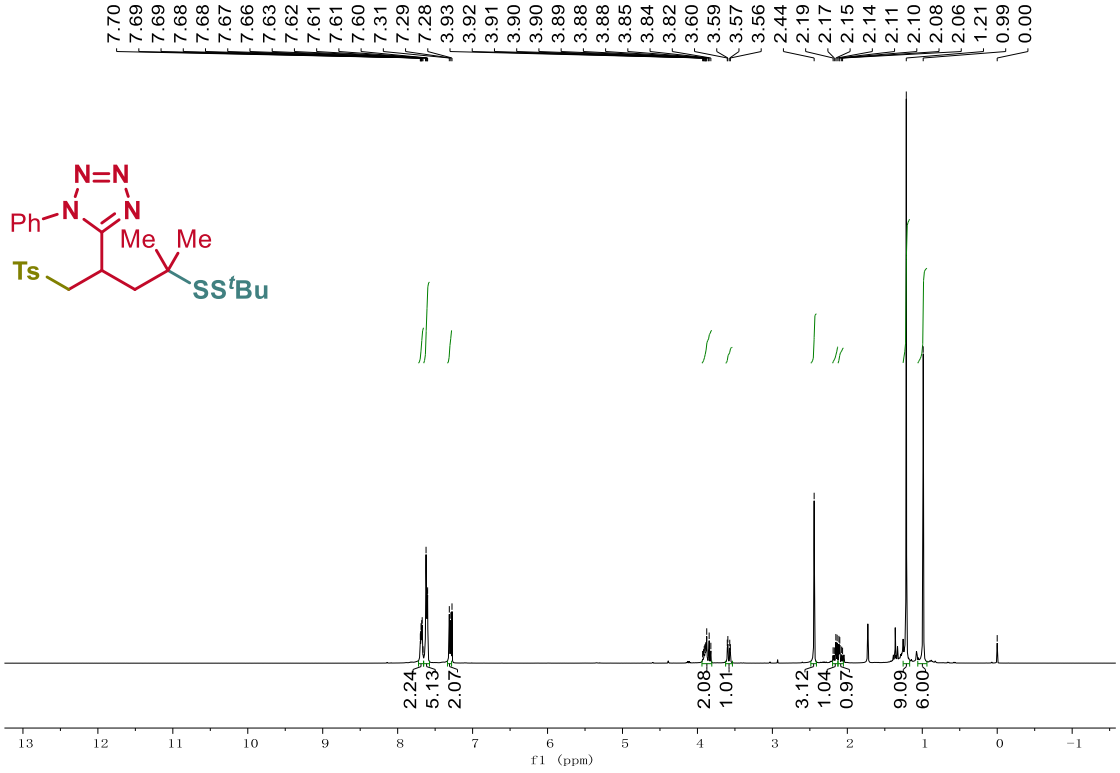
^{1}H NMR Spectrum of 1-(but-3-en-1-yl)-2-(4-(*tert*-butyldisulfanyl)- 4-methyl-1-tosylpentan-2-yl)-1*H*-benzo[*d*]imidazole (3f):



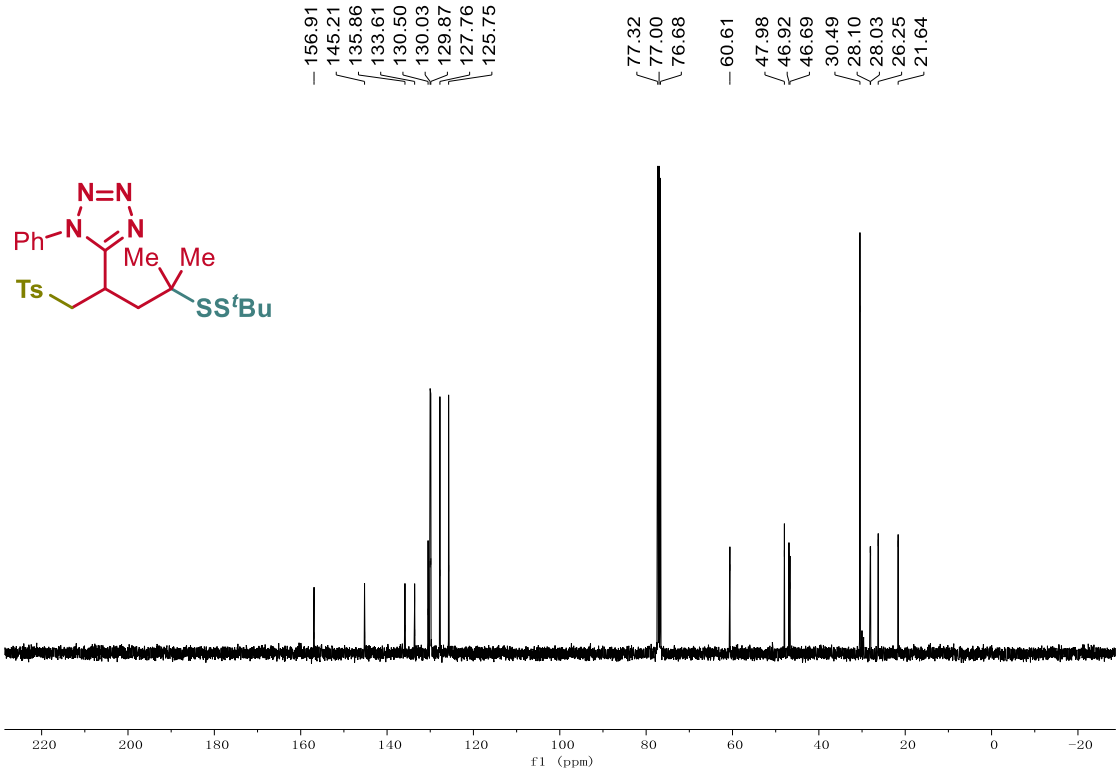
^{13}C NMR Spectrum of 1-(but-3-en-1-yl)-2-(4-(*tert*-butyldisulfanyl)- 4-methyl-1-tosylpentan-2-yl)-1*H*-benzo[*d*]imidazole (3f):



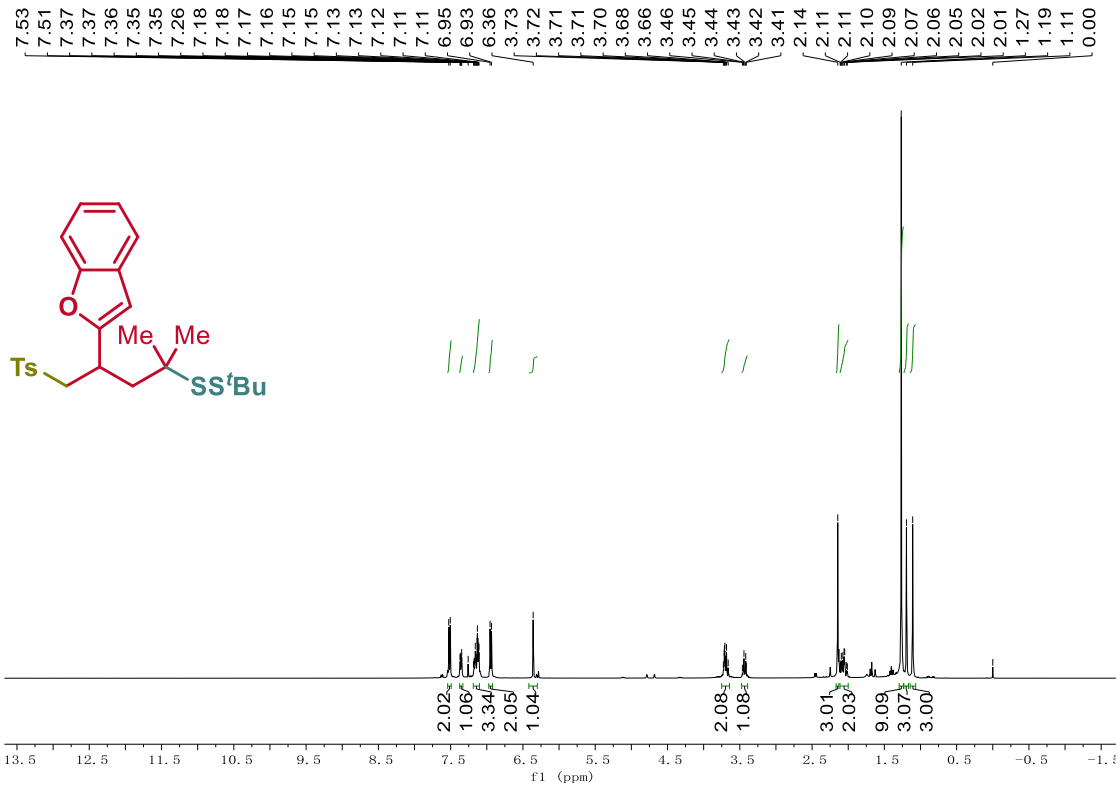
^{1}H NMR Spectrum of 5-(4-(*tert*-butyldisulfanyl)-4-methyl-1-tosylpentan-2-yl)- 1-phenyl-1*H*-tetrazole (3g):



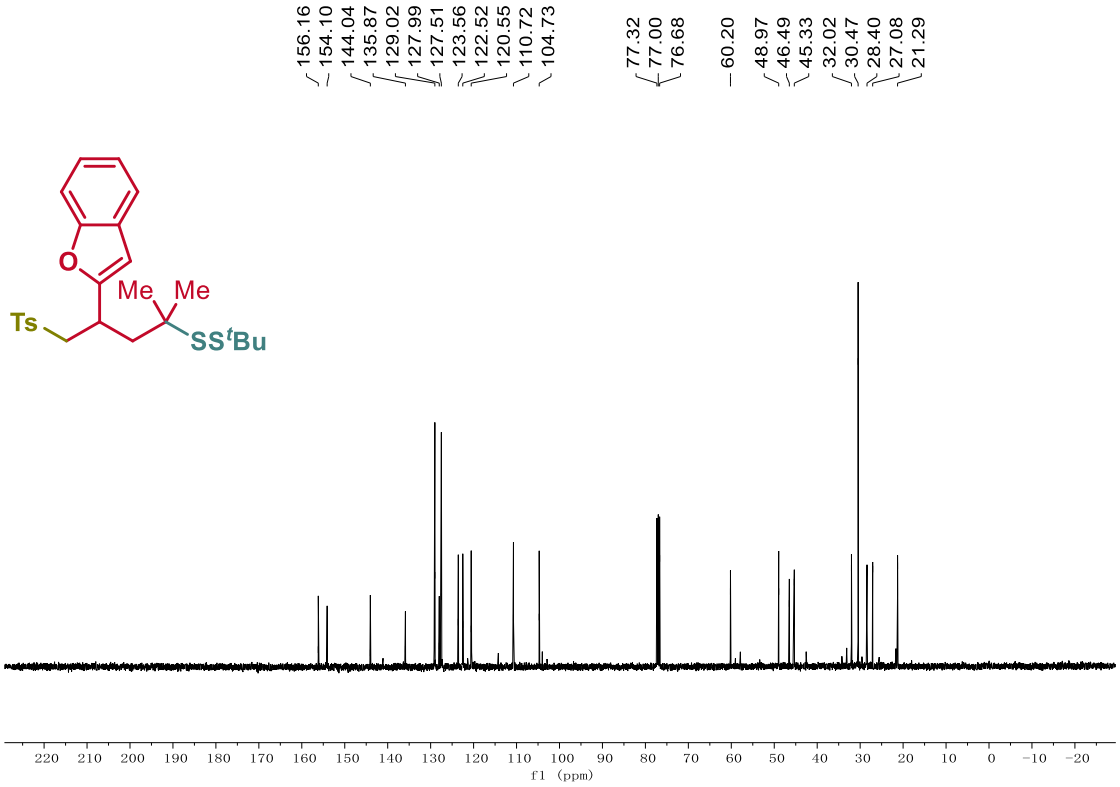
^{13}C NMR Spectrum of 5-(4-(*tert*-butyldisulfanyl)-4-methyl-1-tosylpentan-2-yl)- 1-phenyl-1*H*-tetrazole (3g):



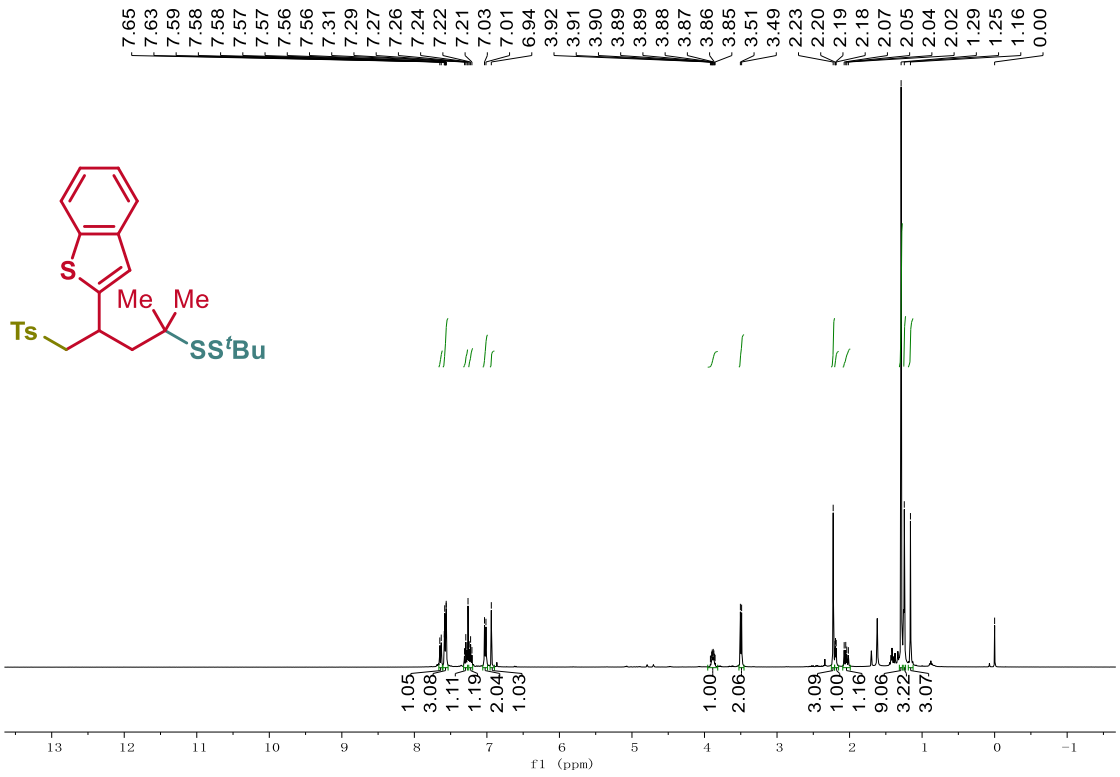
^{1}H NMR Spectrum of 2-(4-(*tert*-butyldisulfaneyl)-4-methyl-1-tosylpentan-2-yl)benzofuran (3h):



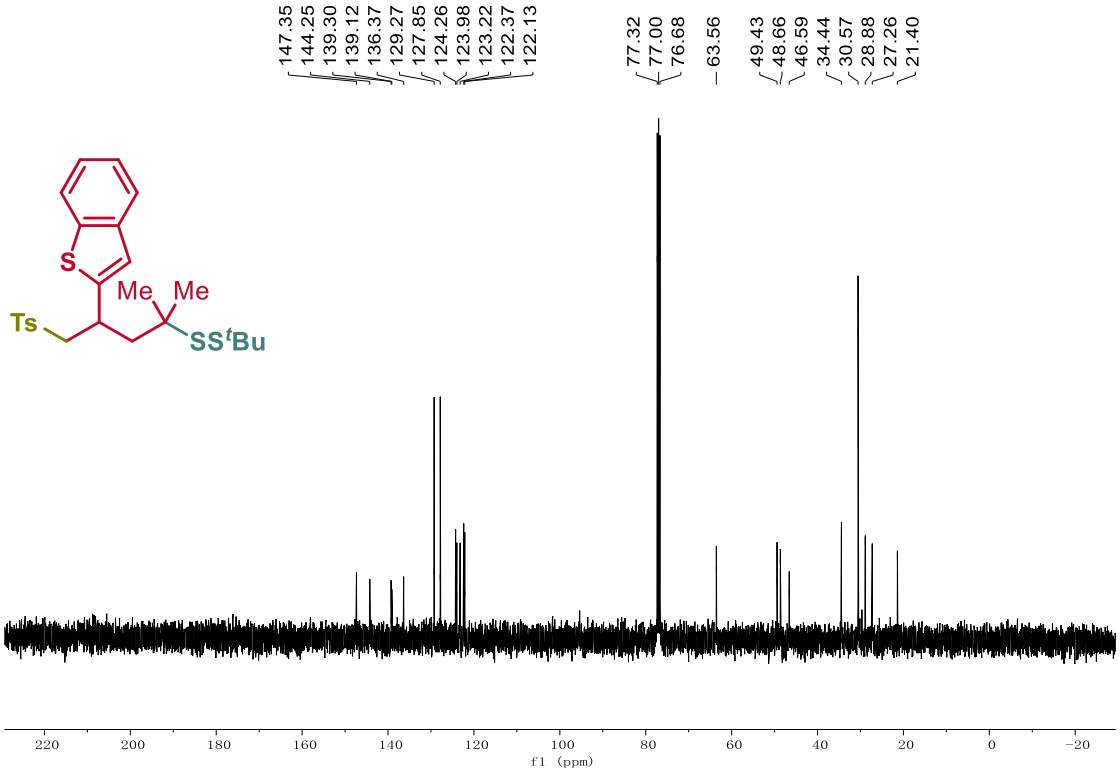
^{13}C NMR Spectrum of 2-(4-(*tert*-butyldisulfaneyl)-4-methyl-1-tosylpentan-2-yl)benzofuran(3h):



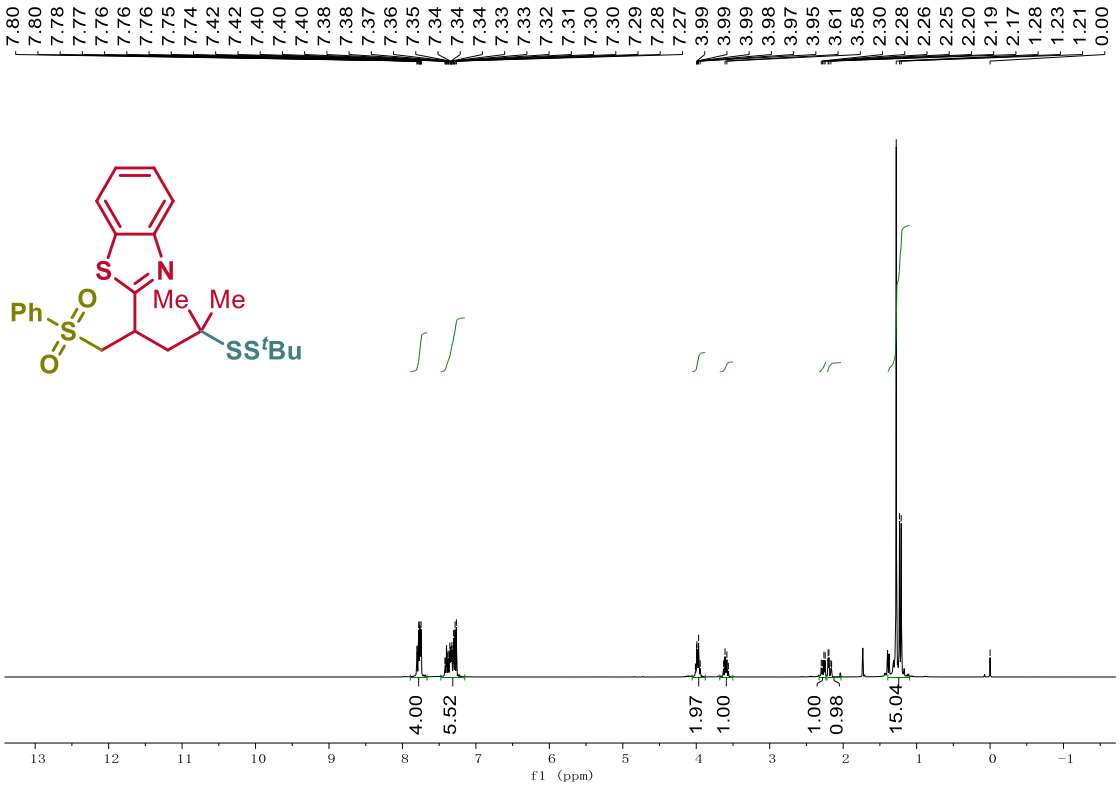
^{1}H NMR Spectrum of 2-(4-(*tert*-butyldisulfanyl)-4-methyl-1-tosylpentan-2-yl)benzo[*b*]thiophene (3i):



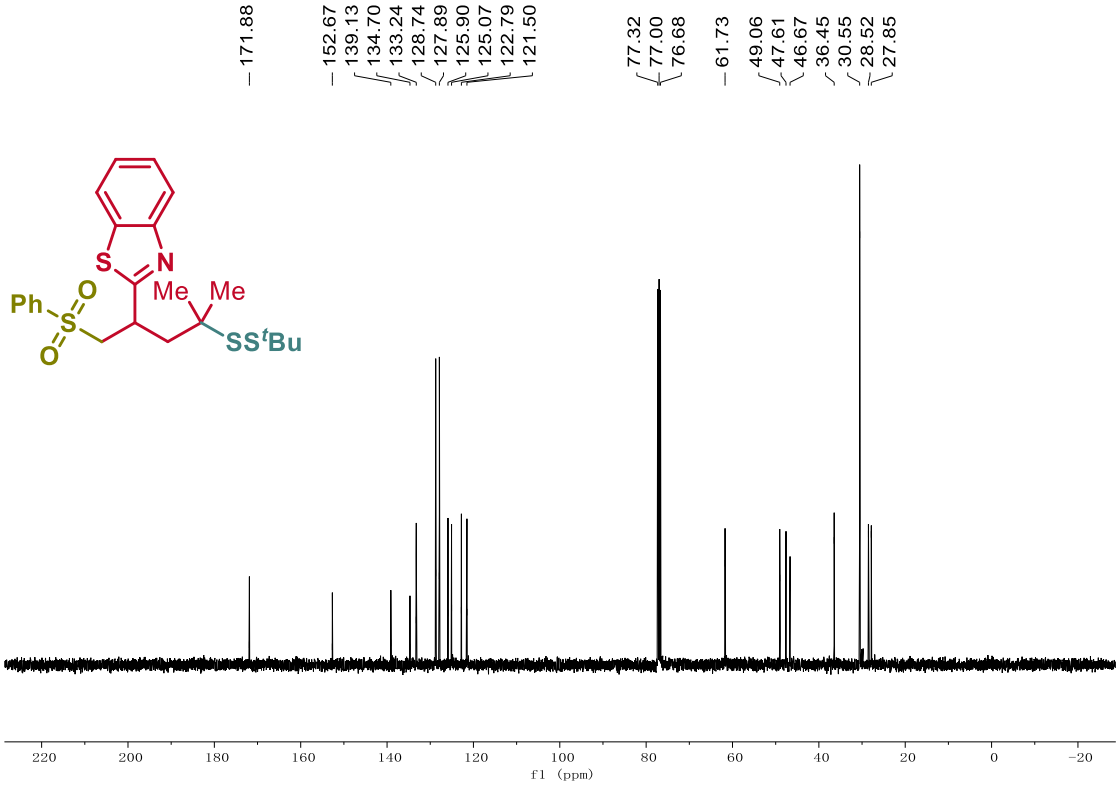
^{13}C NMR Spectrum of 2-(4-(*tert*-butyldisulfanyl)-4-methyl-1-tosylpentan-2-yl)benzo[*b*]thiophene (3i):



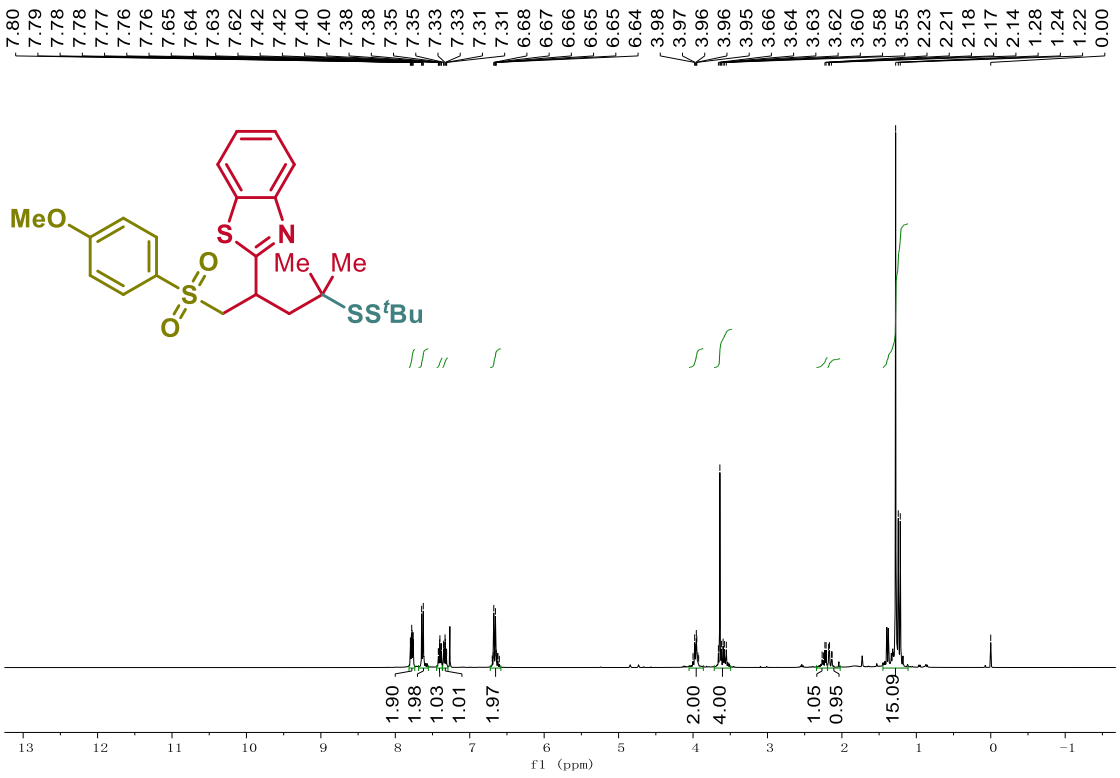
^{1}H NMR Spectrum of 2-(4-(*tert*-butyldisulfanyl)-4-methyl-1-(phenylsulfonyl) pentan-2-yl)benzo[*d*]thiazole (3k):



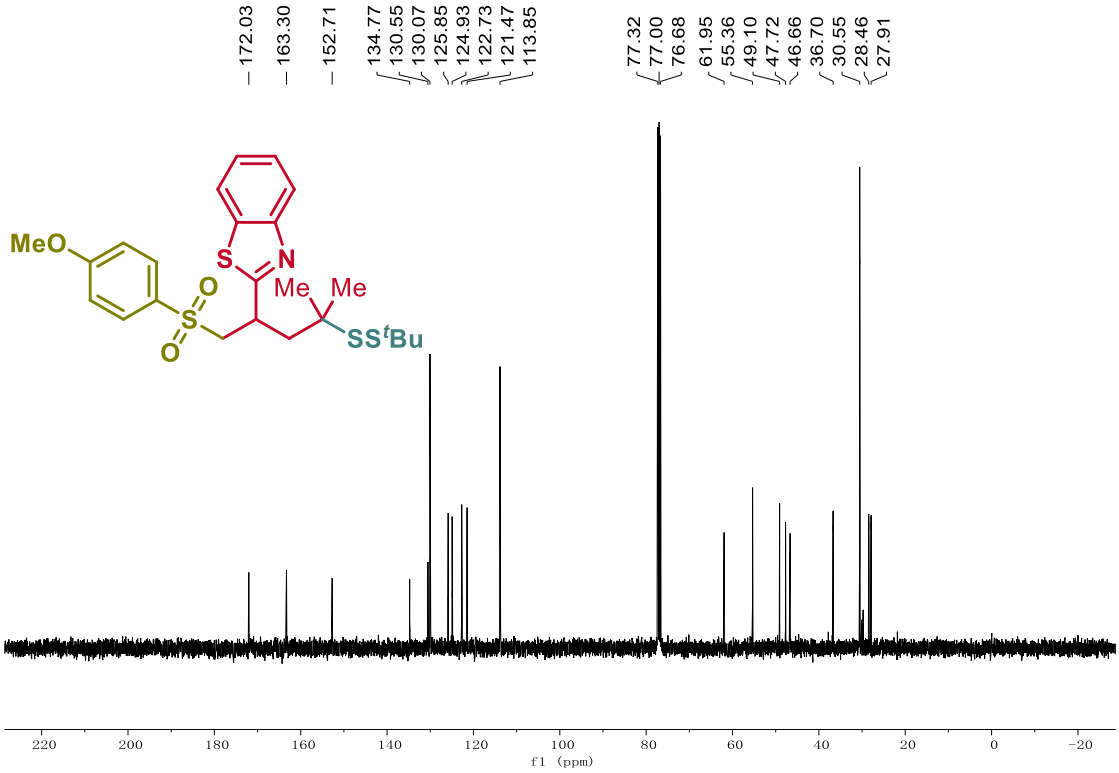
^{13}C NMR Spectrum of 2-(4-(*tert*-butyldisulfanyl)-4-methyl-1-(phenylsulfonyl) pentan-2-yl)benzo[*d*]thiazole (3k):



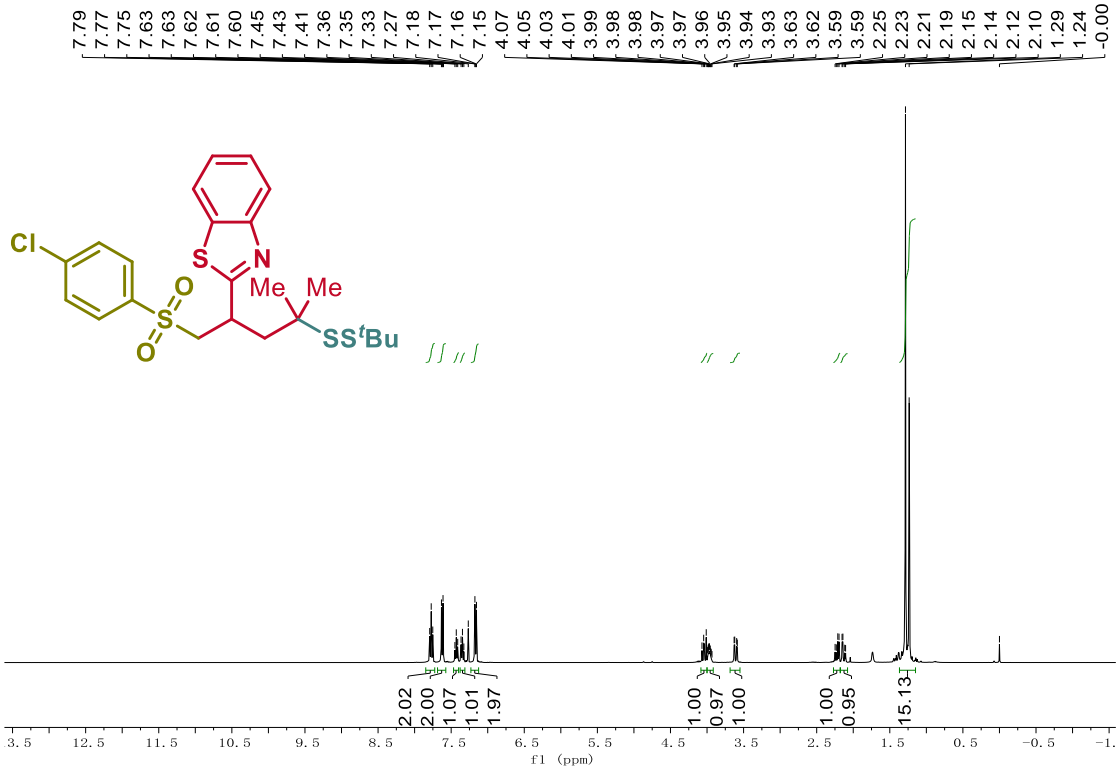
^{1}H NMR Spectrum of 2-(4-(*tert*-butyldisulfanyl)- 1-((4-methoxyphenyl)sulfonyl)-4-methylpentan-2-yl)benzo[*d*]thiazole (3l):



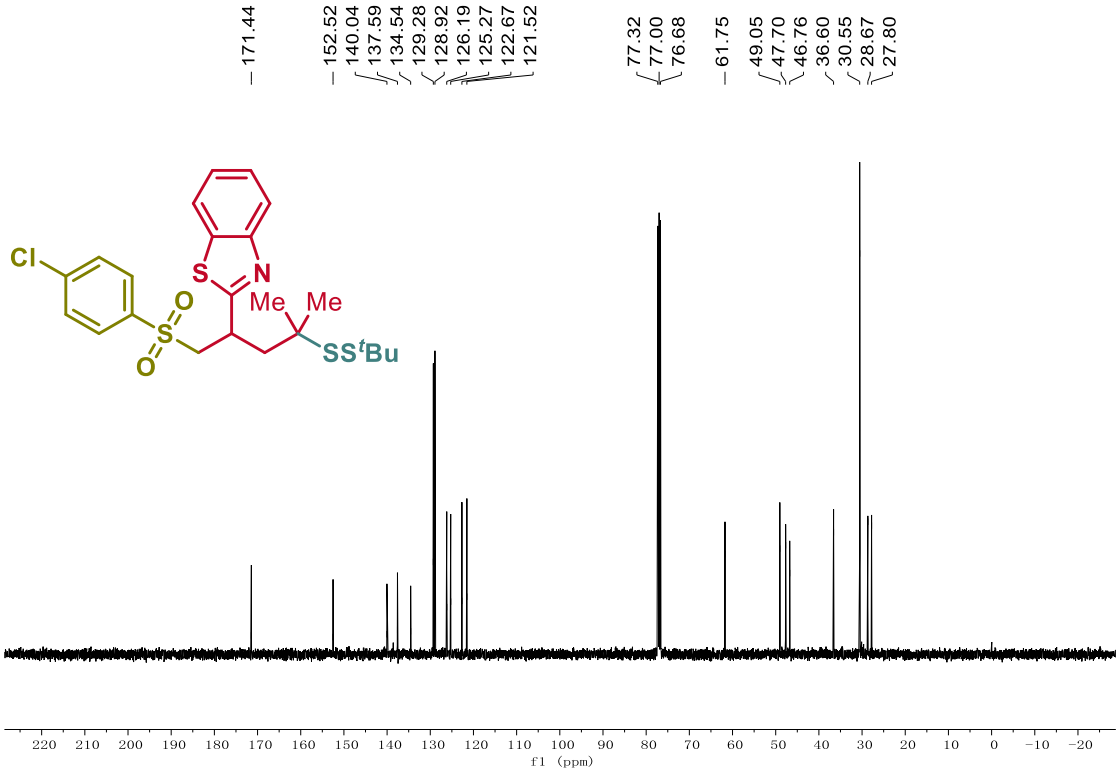
^{13}C NMR Spectrum of 2-(4-(*tert*-butyldisulfanyl)- 1-((4-methoxyphenyl)sulfonyl)-4-methylpentan-2-yl)benzo[*d*]thiazole (3l):



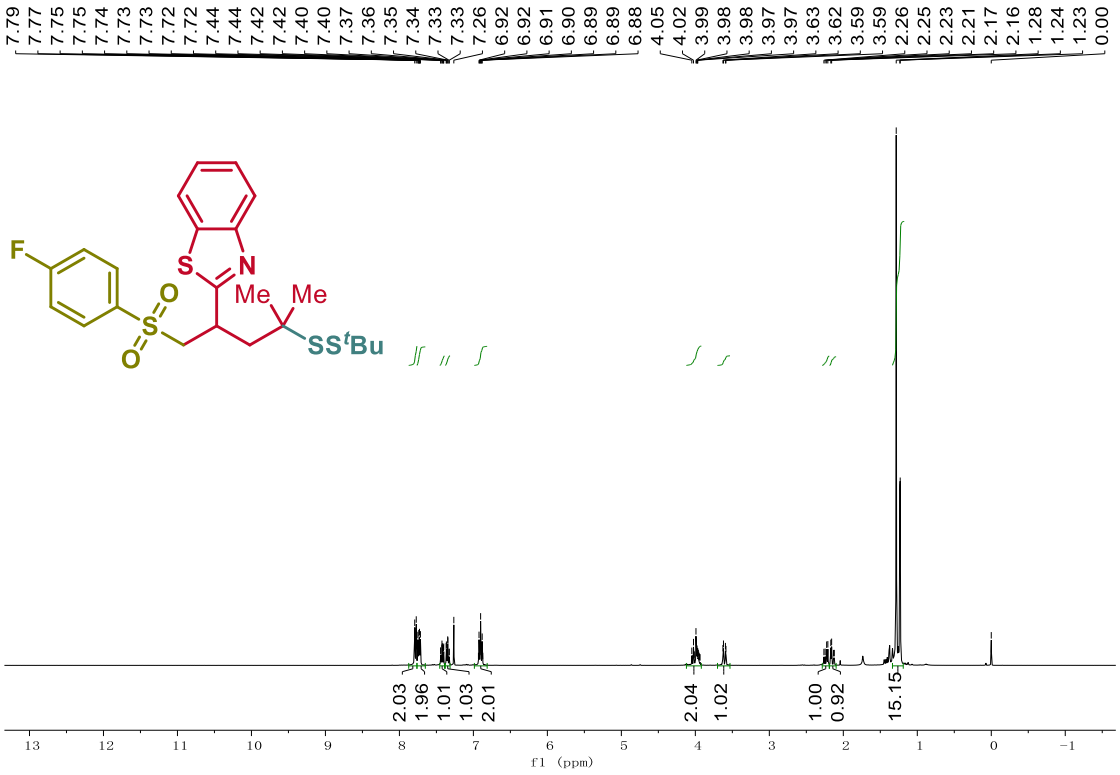
^{1}H NMR Spectrum of 2-(4-(*tert*-butyldisulfaneyl)-1-((4-chlorophenyl) sulfonyl)-4-methylpentan-2-yl)benzo[*d*]thiazole (3m):



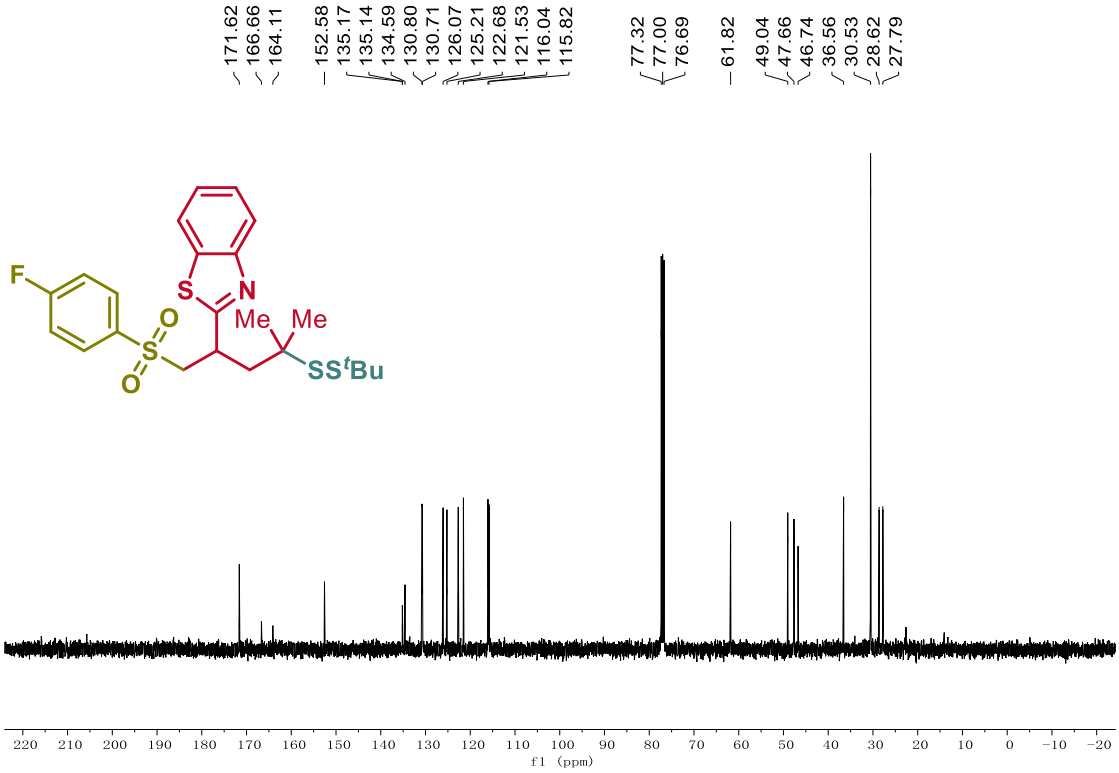
^{13}C NMR Spectrum of 2-(4-(*tert*-butyldisulfaneyl)-1-((4-chlorophenyl) sulfonyl)-4-methylpentan-2-yl)benzo[*d*]thiazole (3m):



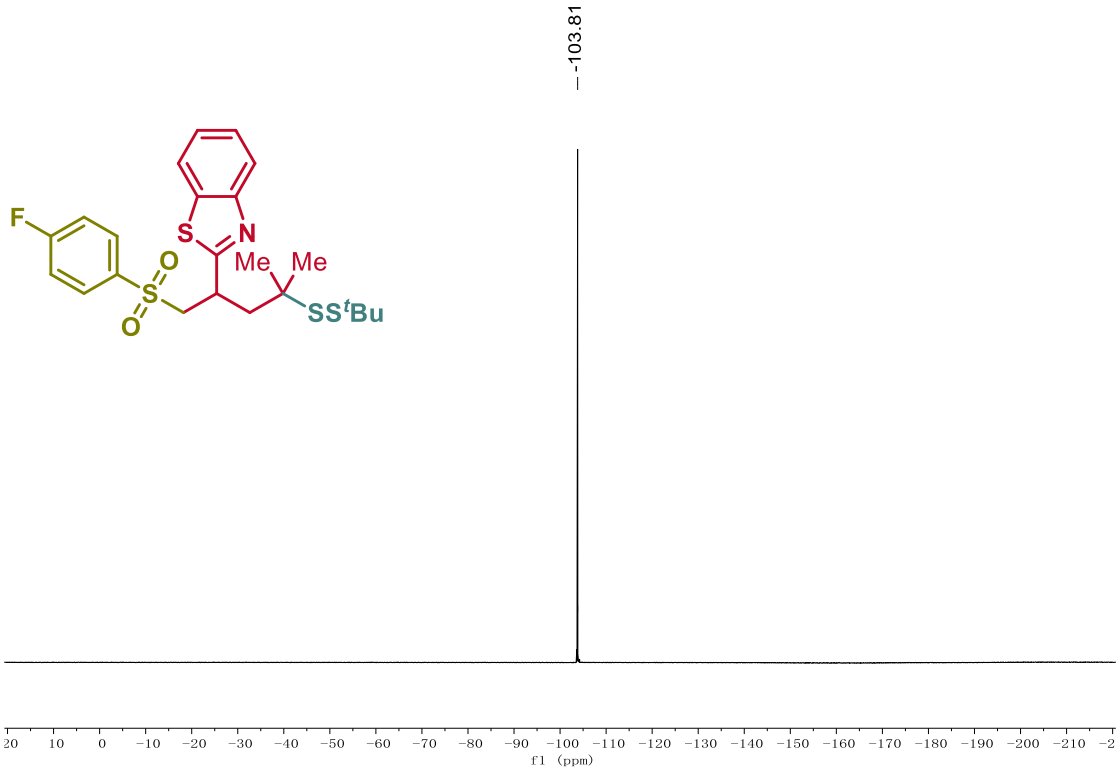
^{1}H NMR Spectrum of 2-(4-(*tert*-butyldisulfanyl)-1-((4-fluorophenyl)sulfonyl)- 4-methylpentan-2-yl)benzo[*d*]thiazole (3n):



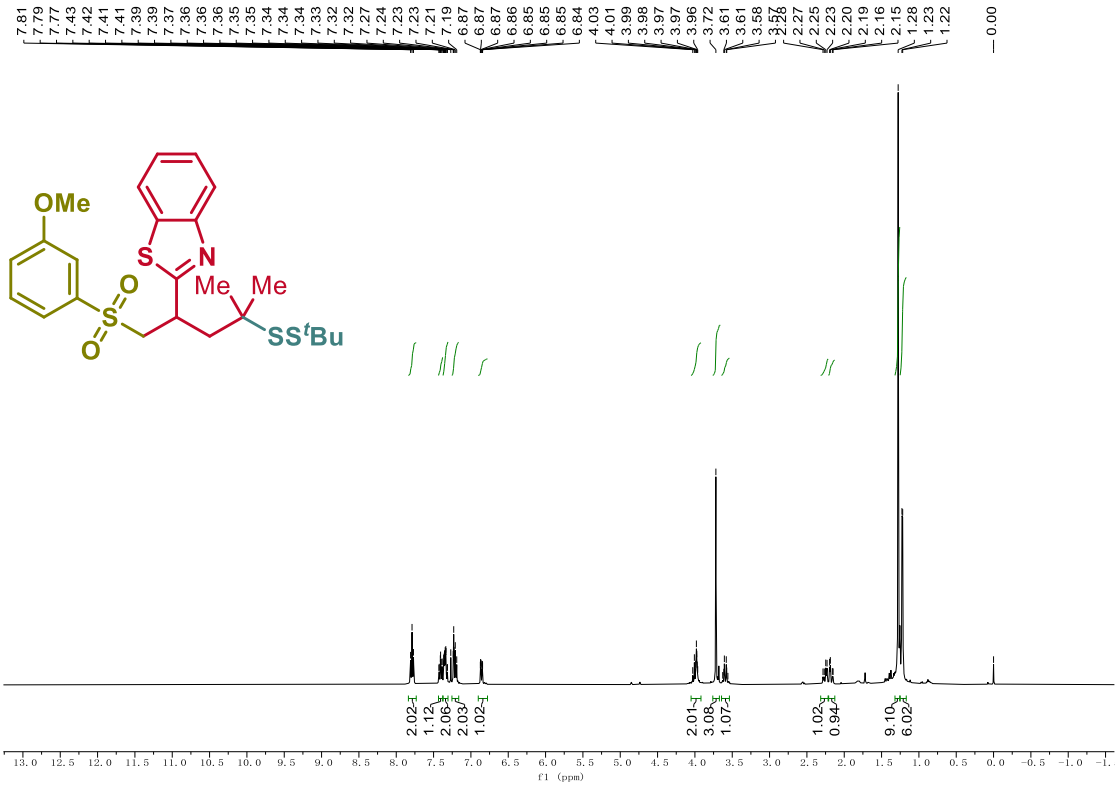
^{13}C NMR Spectrum of 2-(4-(*tert*-butyldisulfanyl)- 1-((4-fluorophenyl)sulfonyl)-4-methylpentan-2-yl)benzo[*d*]thiazole (3n):



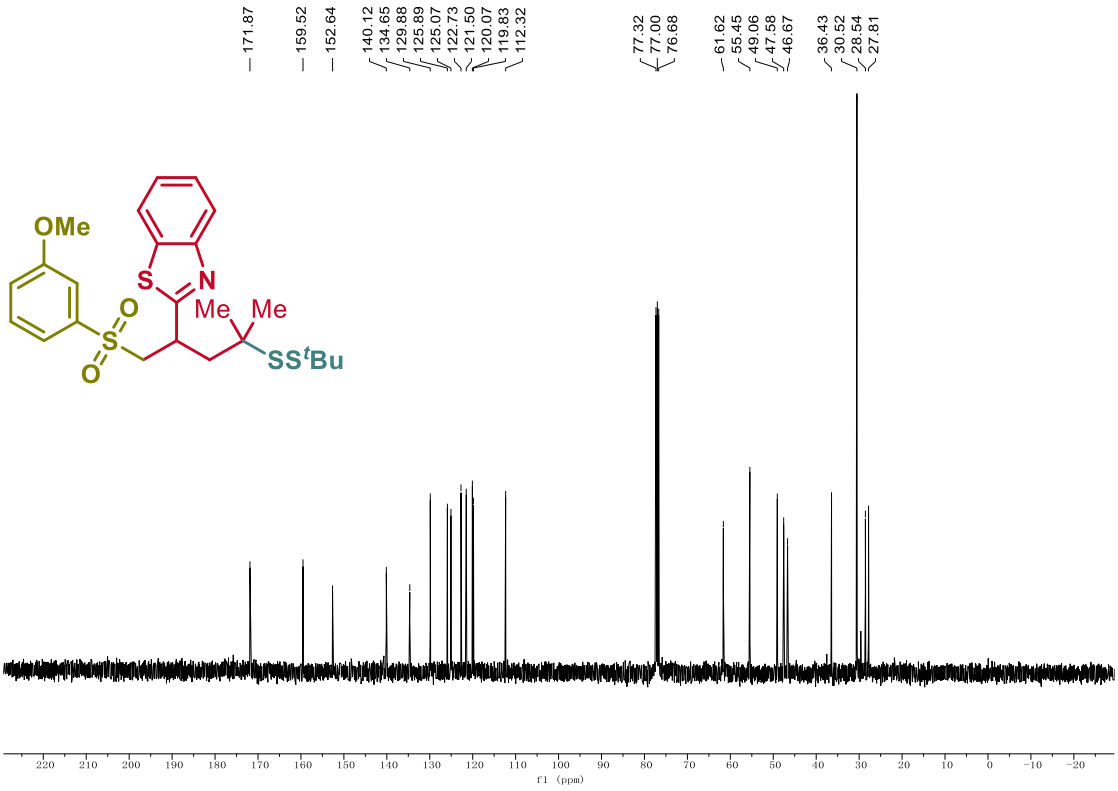
^{19}F NMR Spectrum of 2-(4-(*tert*-butyldisulfanyl)- 1-((4-fluorophenyl)sulfonyl)-4-methylpentan-2-yl)benzo[*d*]thiazole (3n):



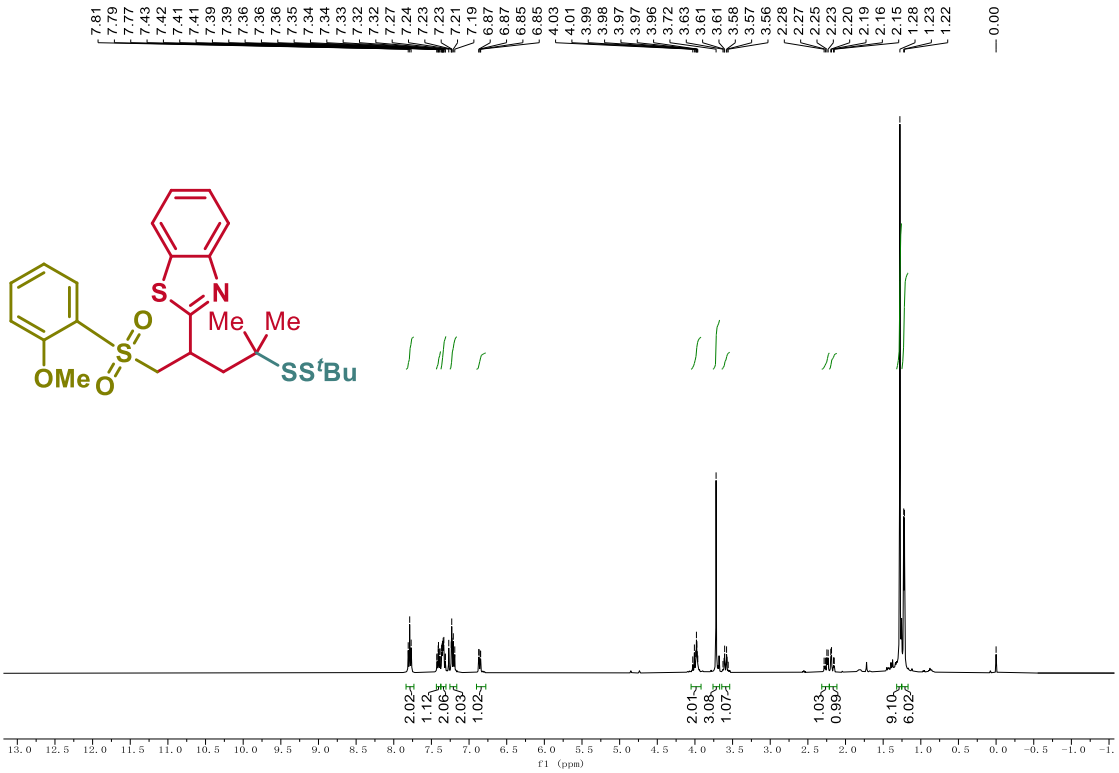
^{1}H NMR Spectrum of 2-(4-(*tert*-butyldisulfanyl)- 1-((3-methoxyphenyl)sulfonyl)-4-methylpentan-2-yl)benzo[*d*]thiazole (3o):



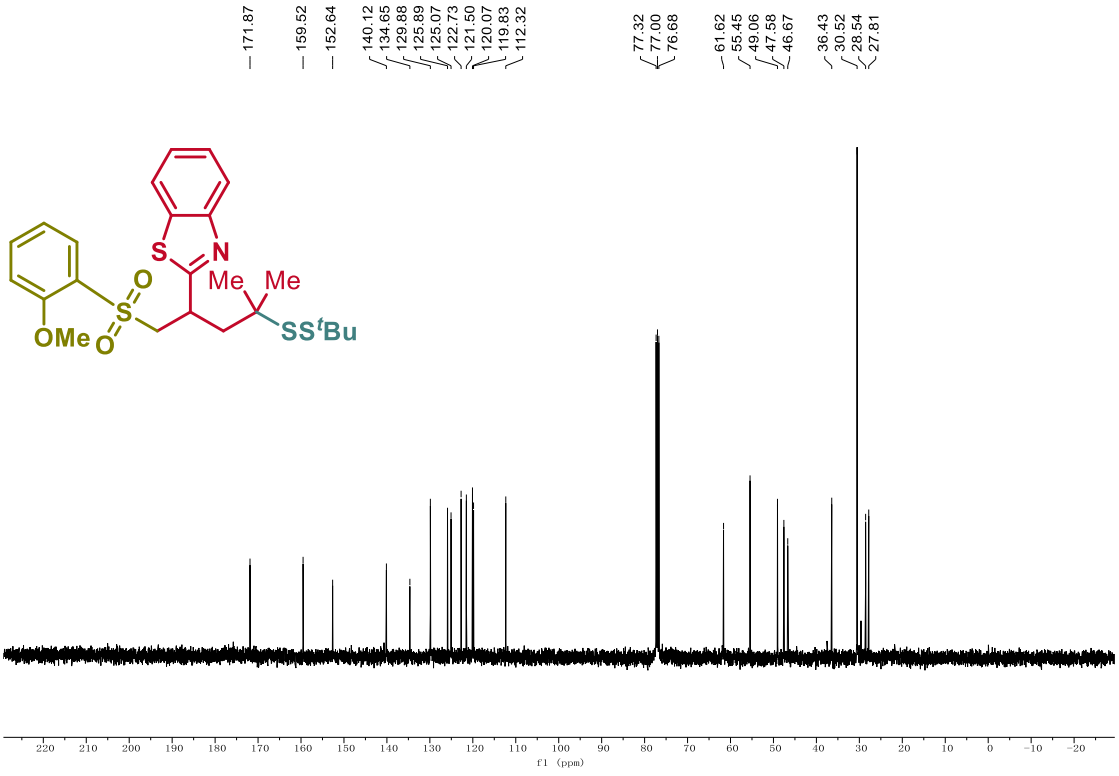
^{13}C NMR Spectrum of 2-(4-(*tert*-butyldisulfanyl)- 1-((3-methoxyphenyl)sulfonyl)-4-methylpentan-2-yl)benzo[*d*]thiazole (3o):



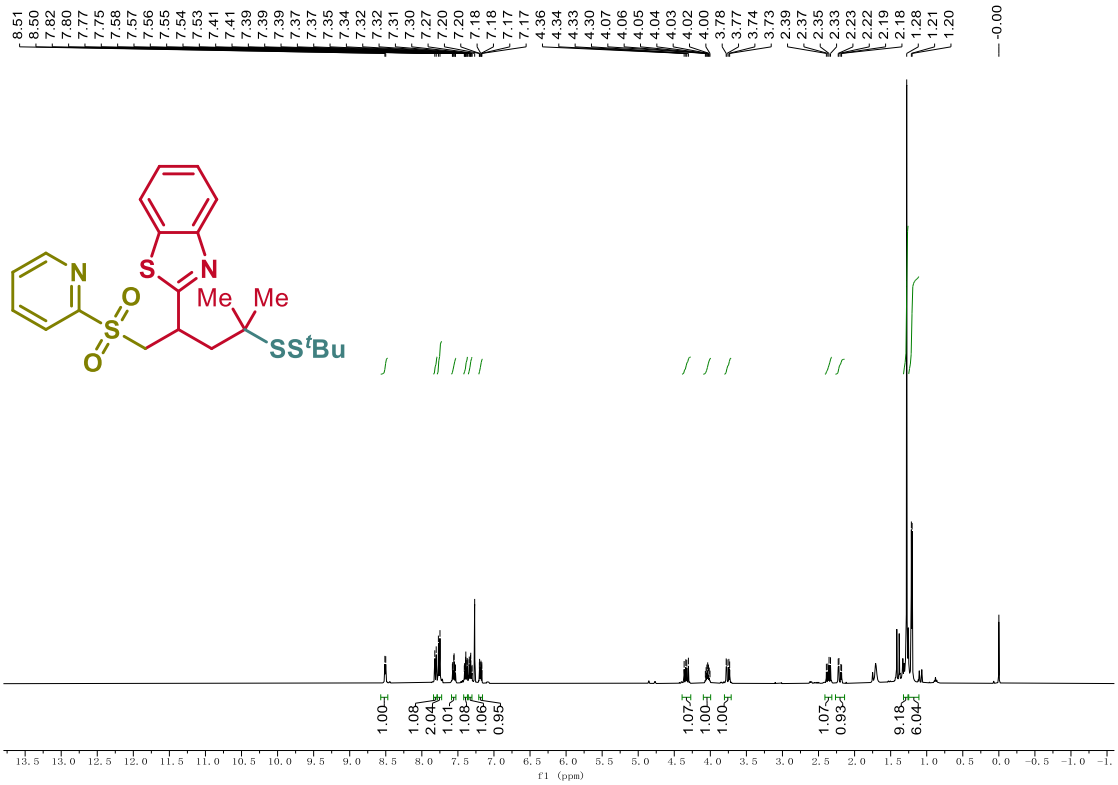
^{1}H NMR Spectrum of 2- (4-(*tert*-butyldisulfanyl)- 1-((2-methoxyphenyl)sulfonyl)-4-methylpentan-2-yl)benzo[*d*]thiazole (3p):



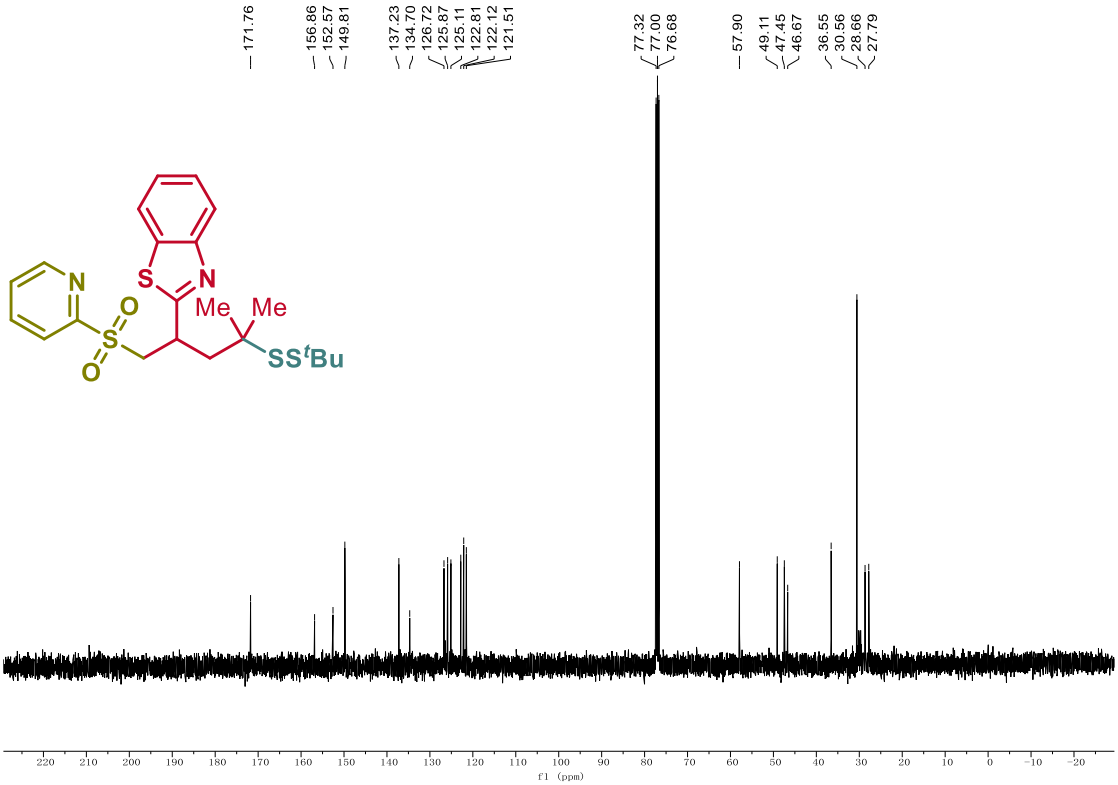
^{13}C NMR Spectrum of 2-(4-(*tert*-butyldisulfanyl)- 1-((2-methoxyphenyl)sulfonyl)-4-methylpentan-2-yl)benzo[*d*]thiazole (3p):



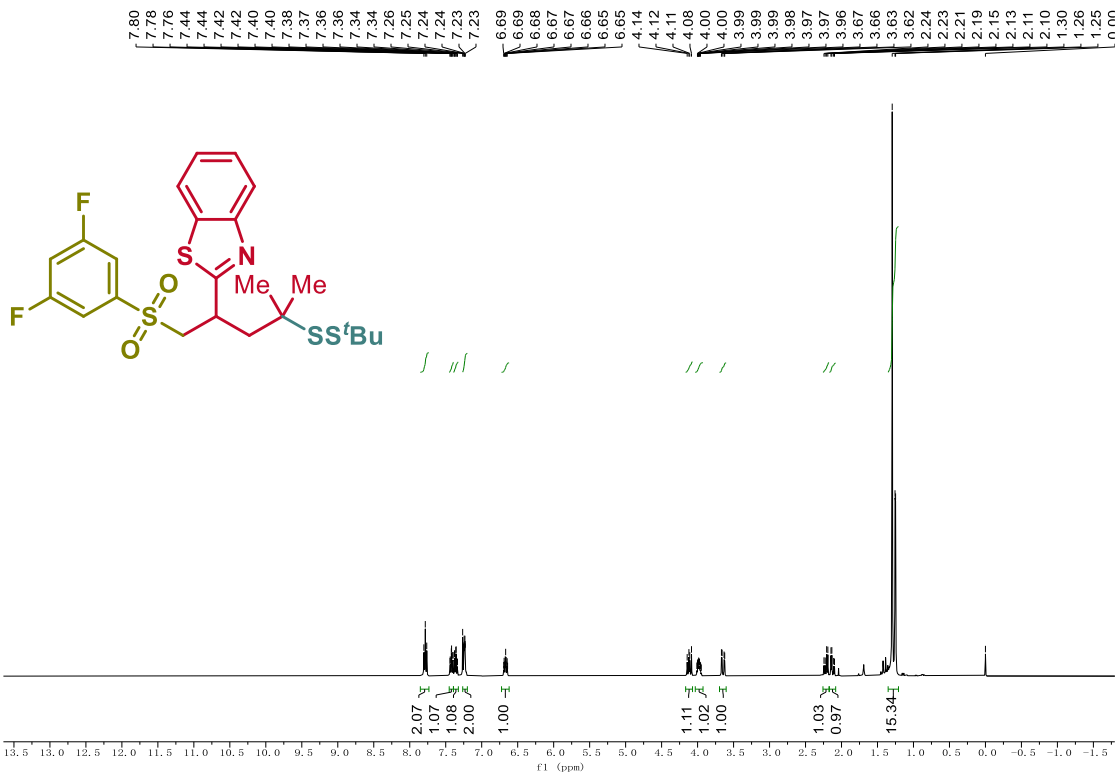
^{1}H NMR Spectrum of 2-(4-(*tert*-butyldisulfanyl)-4-methyl-1-(pyridin-2-ylsulfonyl)pentan-2-yl)benzo[*d*]thiazole (3q):



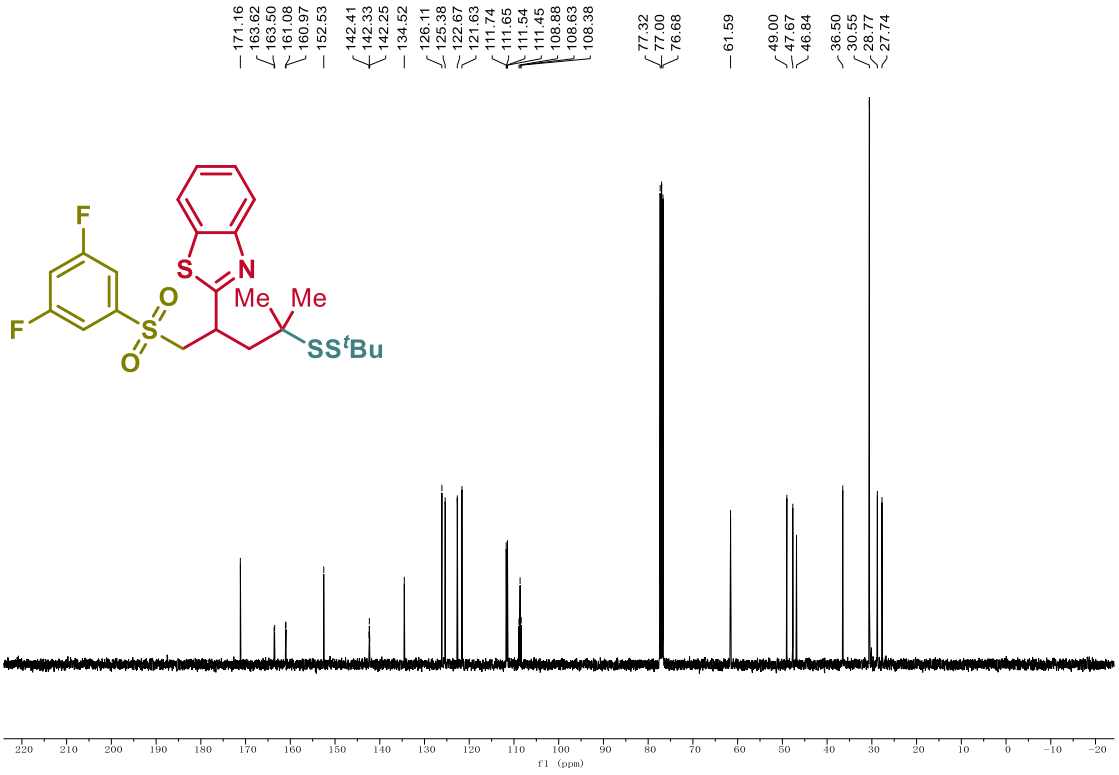
^{13}C NMR Spectrum of 2-(4-(*tert*-butyldisulfanyl)-4-methyl-1-(pyridin-2-ylsulfonyl)pentan-2-yl)benzo[*d*]thiazole (3q):



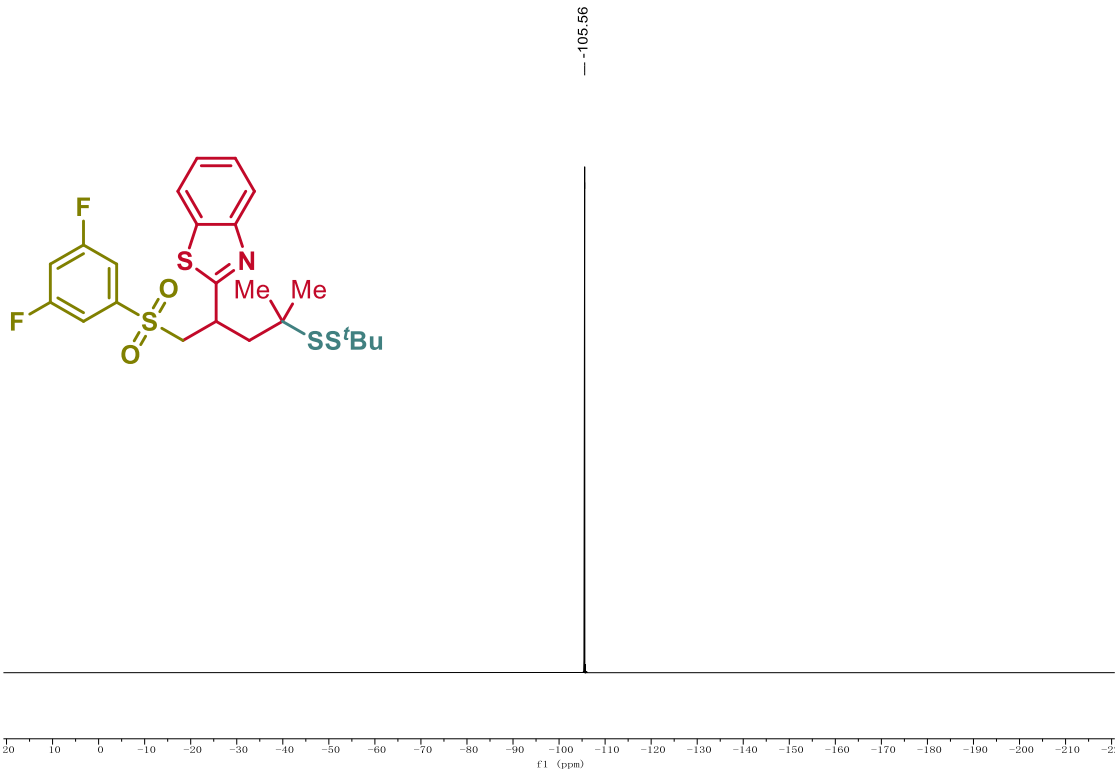
^{1}H NMR Spectrum of 2-(4-(*tert*-butyldisulfanyl)-1-((3,5-difluorophenyl)sulfonyl)-4-methylpentan-2-yl)benzo[*d*]thiazole (3r):



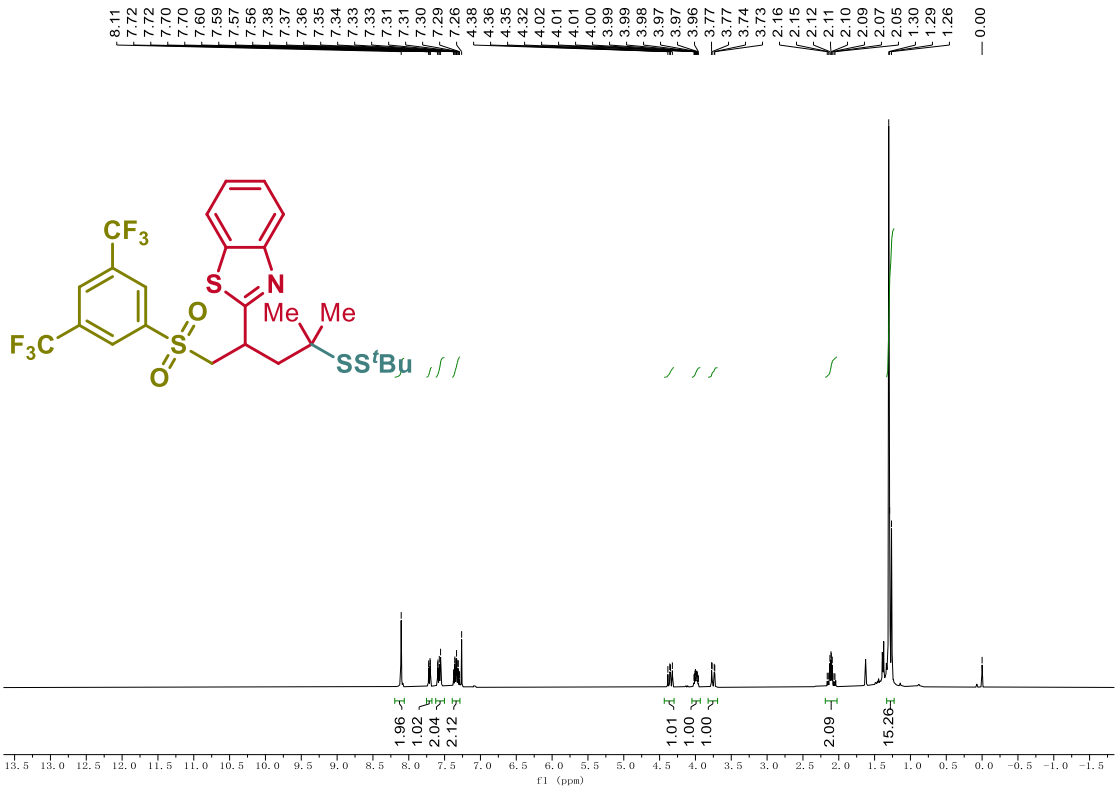
^{13}C NMR Spectrum of 2-(4-(*tert*-butyldisulfanyl)-1-((3,5-difluorophenyl)sulfonyl)-4-methylpentan-2-yl)benzo[*d*]thiazole (3r):



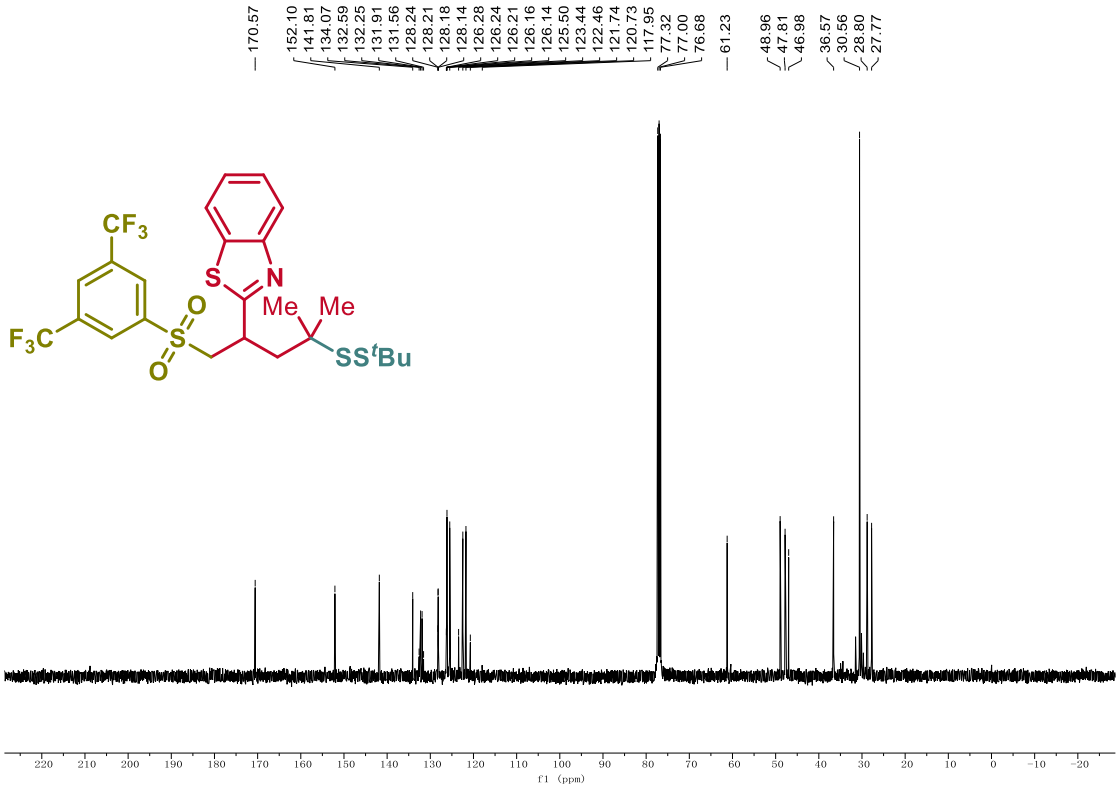
^{19}F NMR Spectrum of 2-(4-(*tert*-butyldisulfanyl)- 1-((3,5-difluorophenyl)sulfonyl)-4-methylpentan-2-yl)benzo[*d*]thiazole (3r):



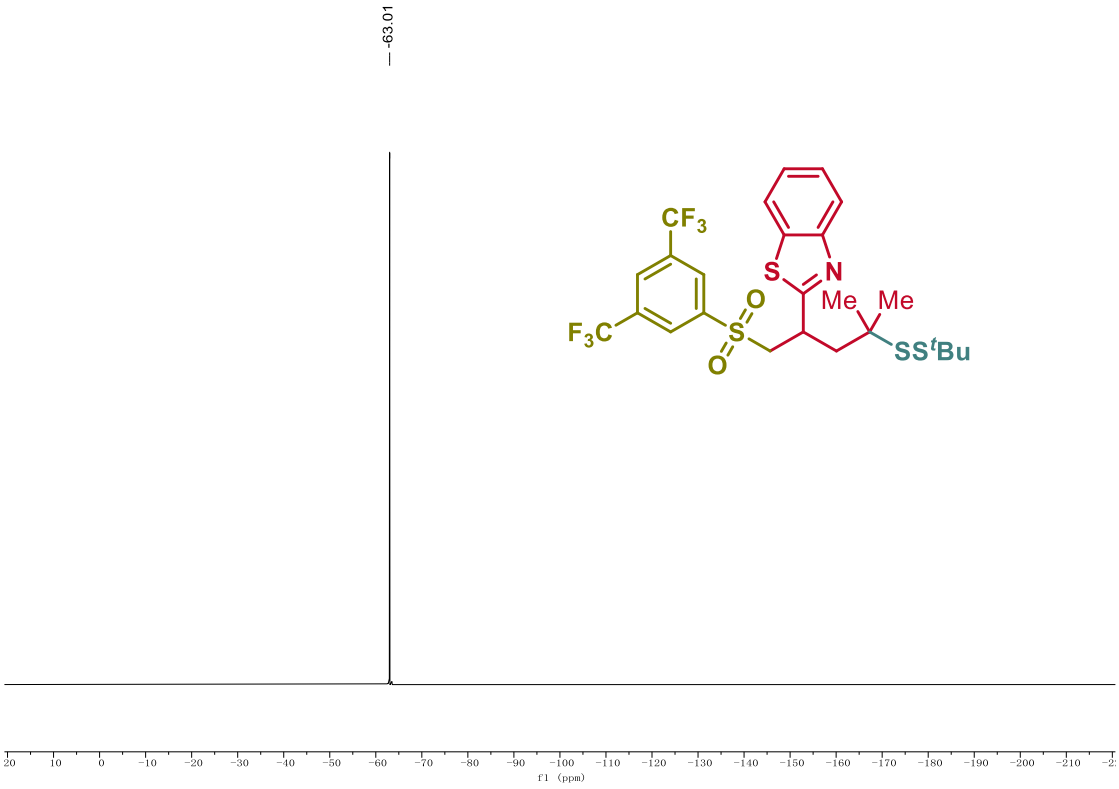
^{1}H NMR Spectrum of 2-(1-((3,5-bis(trifluoromethyl)phenyl)sulfonyl)-4-(*tert*-butyldisulfanyl)-4-methylpentan-2-yl) benzo[*d*]thiazole (3s):



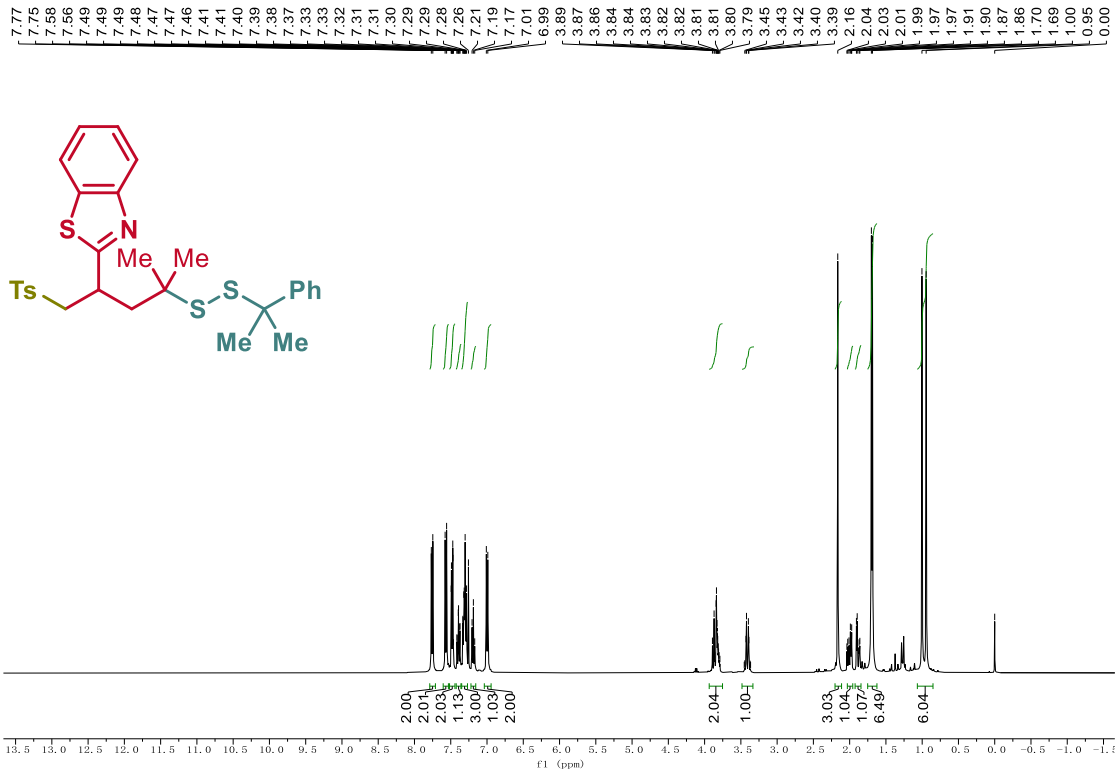
^{13}C NMR Spectrum of 2-(1-((3,5-bis(trifluoromethyl)phenyl)sulfonyl)-4-(*tert*-butyldisulfanyl)-4-methylpentan-2-yl) benzo[*d*]thiazole (3s):



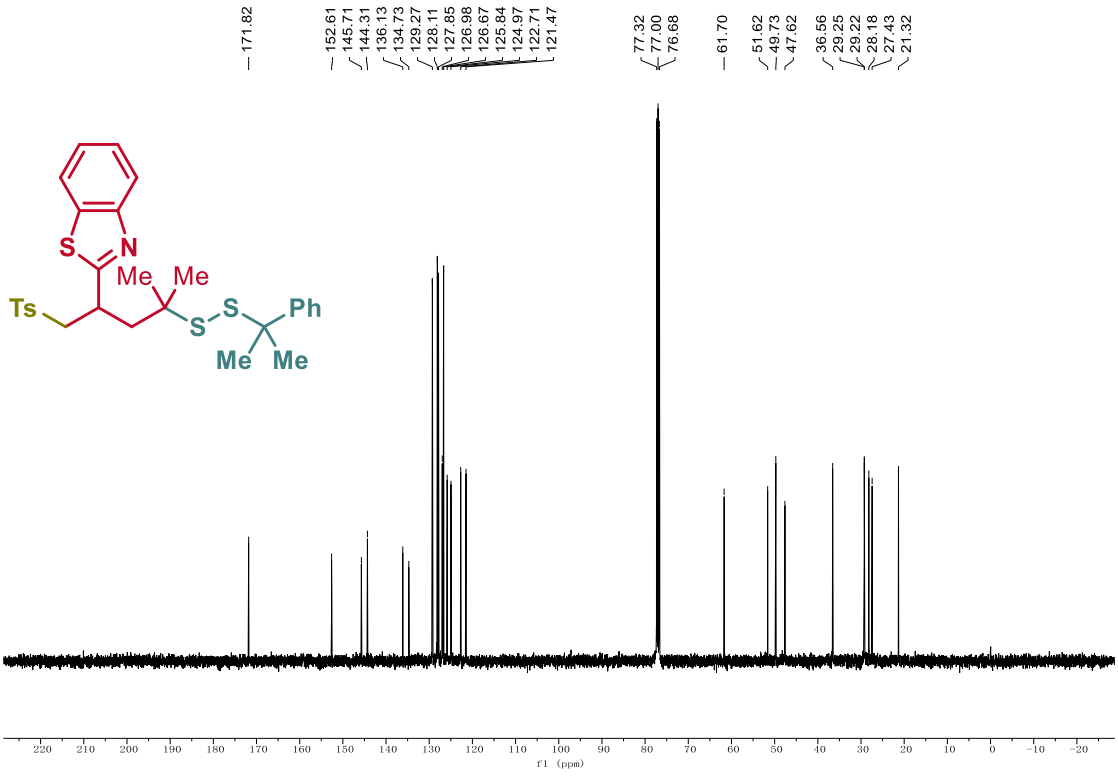
^{19}F NMR Spectrum of 2-(1-((3,5-bis(trifluoromethyl)phenyl)sulfonyl)-4-(*tert*-butyldisulfanyl)-4-methylpentan-2-yl) benzo[*d*]thiazole (3s):



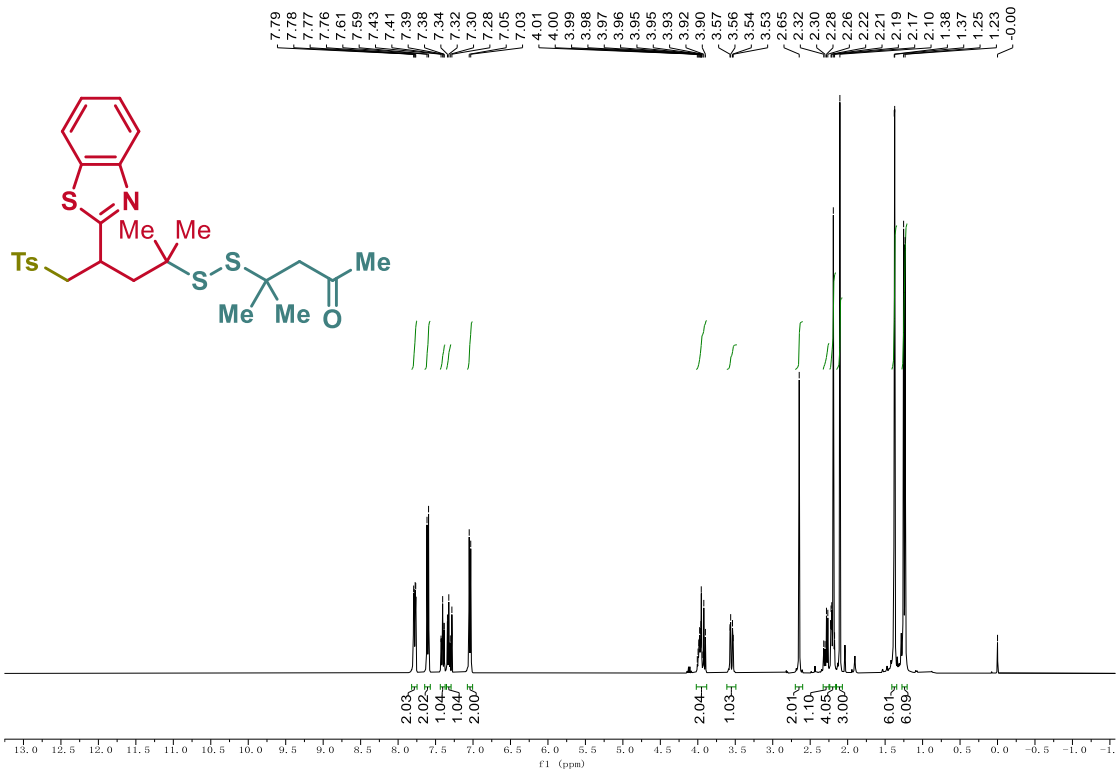
^{1}H NMR Spectrum of 2-(4-methyl-4-((2-phenylpropan-2-yl)disulfanyl)-1-tosylpentan-2-yl)benzo[*d*]thiazole (3t):



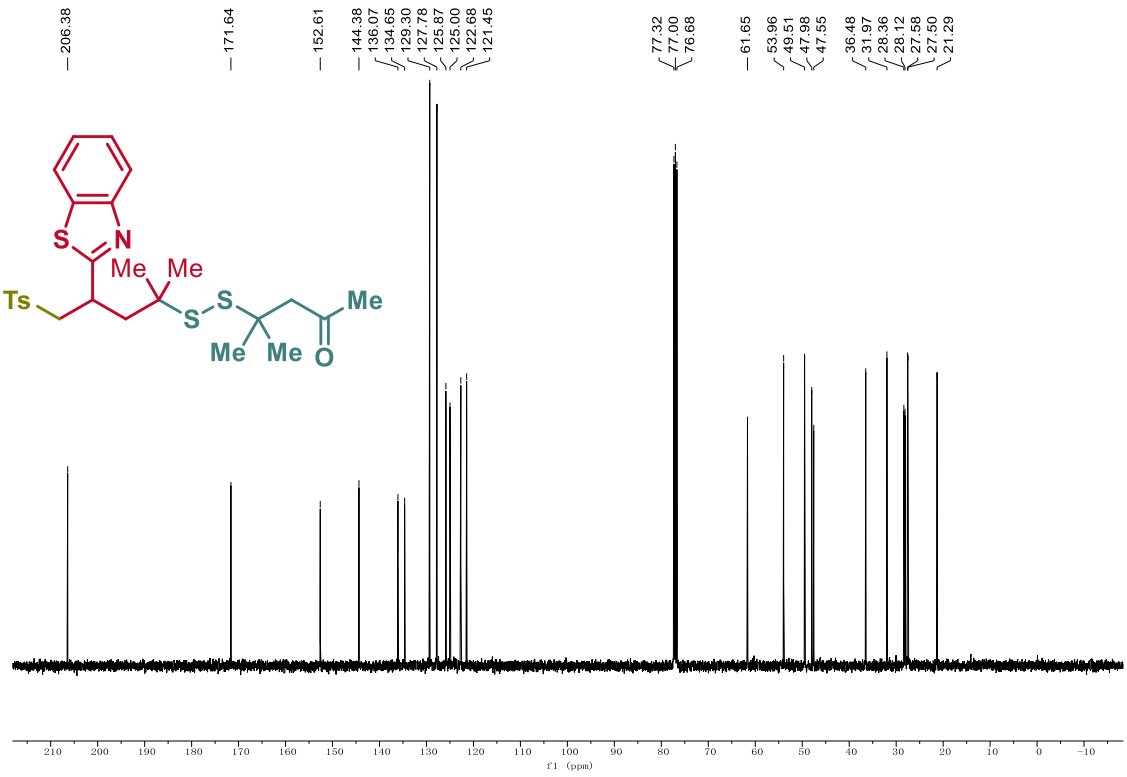
^{13}C NMR Spectrum of 2-(4-methyl-4-((2-phenylpropan-2-yl)disulfanyl)-1-tosylpentan-2-yl)benzo[*d*]thiazole (3t):



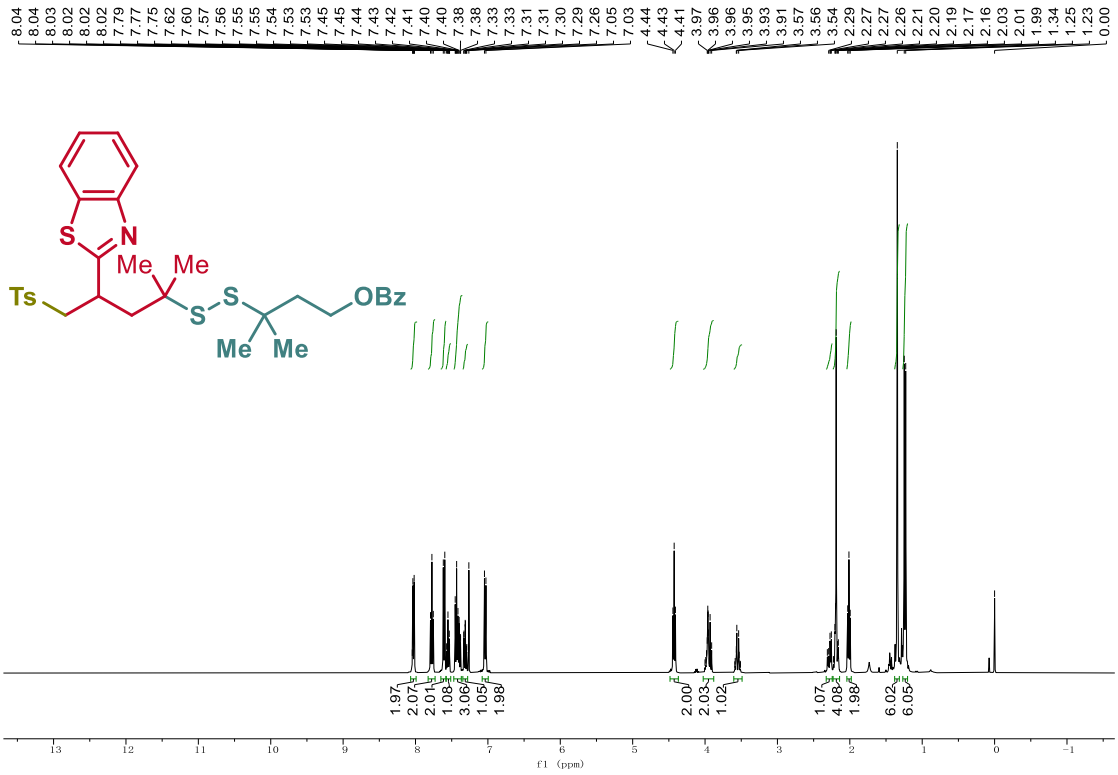
^{1}H NMR Spectrum of 4-((4-(benzo[*d*]thiazol-2-yl)-2-methyl-5-tosylpentan-2-yl)disulfaneyl)-4-methylpentan-2-one (3u):



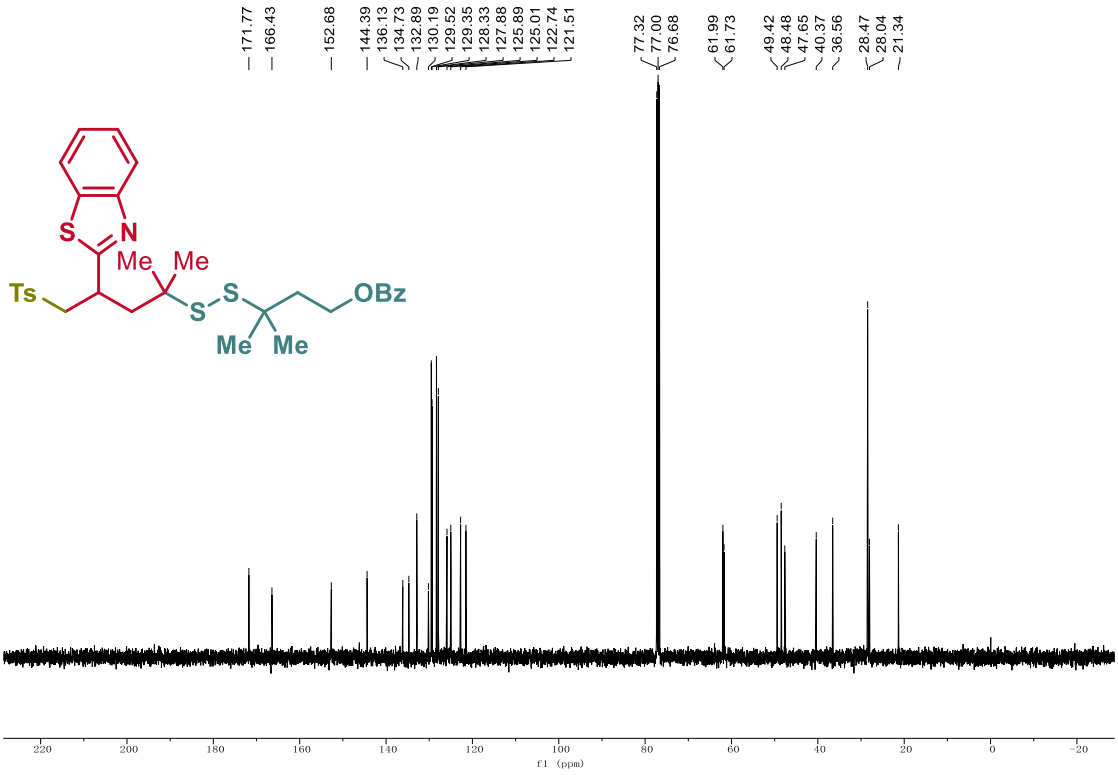
^{13}C NMR Spectrum of 4-((4-(benzo[*d*]thiazol-2-yl)-2-methyl-5-tosylpentan-2-yl)disulfaneyl)-4-methylpentan-2-one (3u):



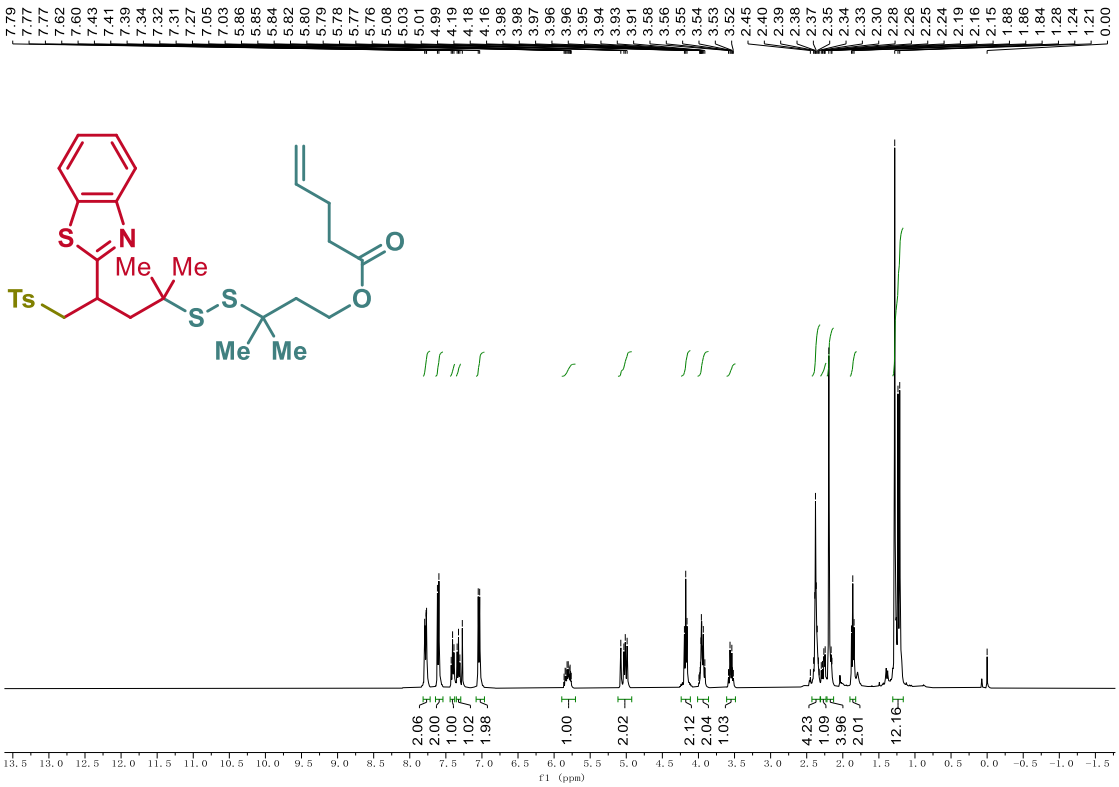
^{1}H NMR Spectrum of 3-((4-(benzo[*d*]thiazol-2-yl)-2-methyl-5-tosylpentan-2-yl)disulfanyl)-3-methylbutyl benzoate (3v):



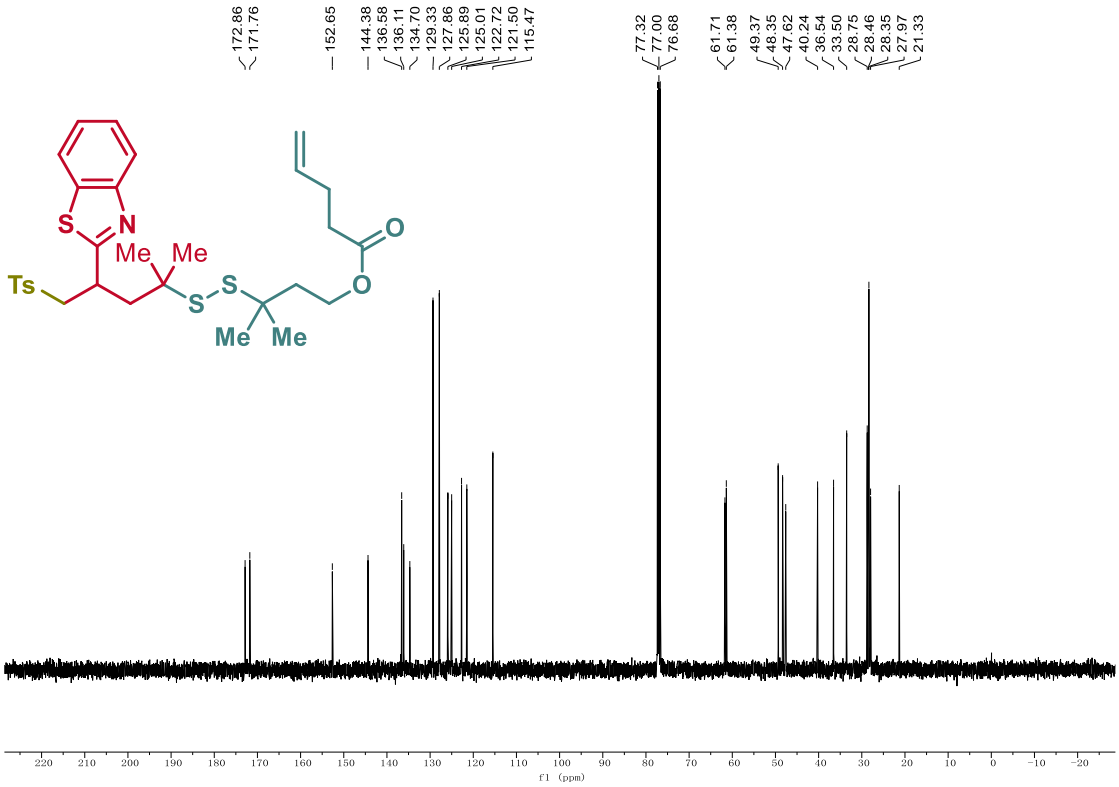
^{13}C NMR Spectrum of 3-((4-(benzo[*d*]thiazol-2-yl)-2-methyl-5-tosylpentan-2-yl)disulfanyl)-3-methylbutyl benzoate (3v):



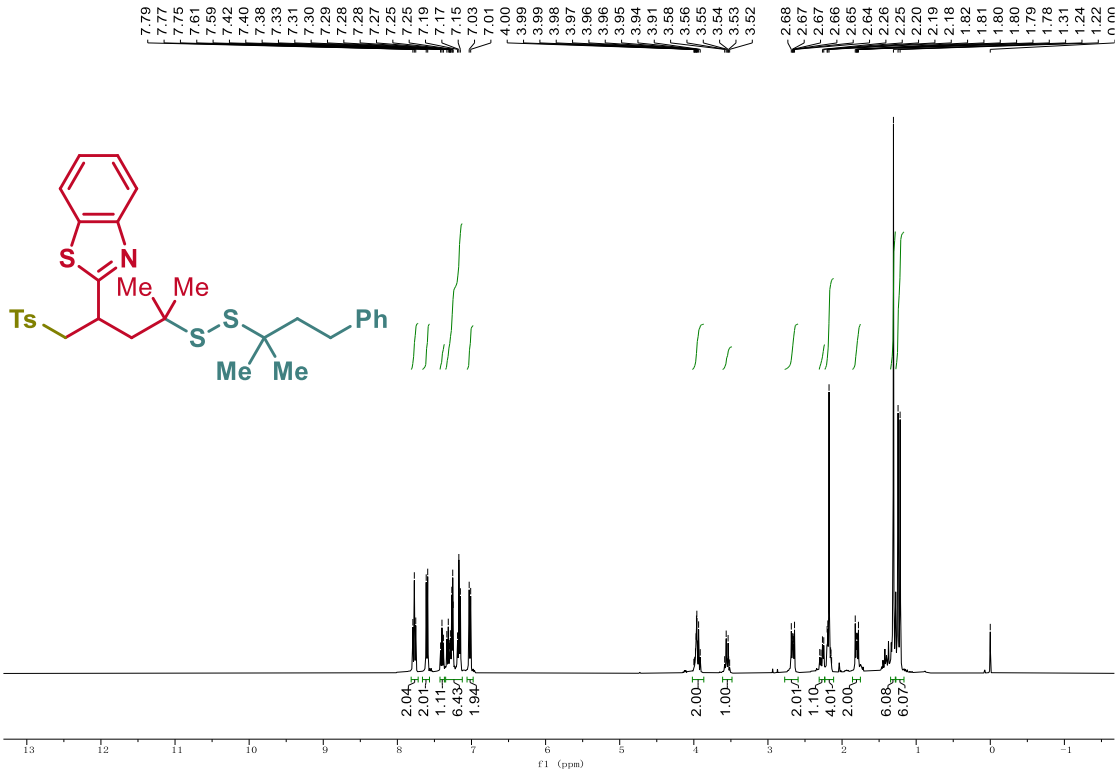
^{1}H NMR Spectrum of 3-((4-(benzo[*d*]thiazol-2-yl)-2-methyl-5-tosylpentan-2-yl)disulfaneyl)-3-methylbutyl pent-4-enoate (3w):



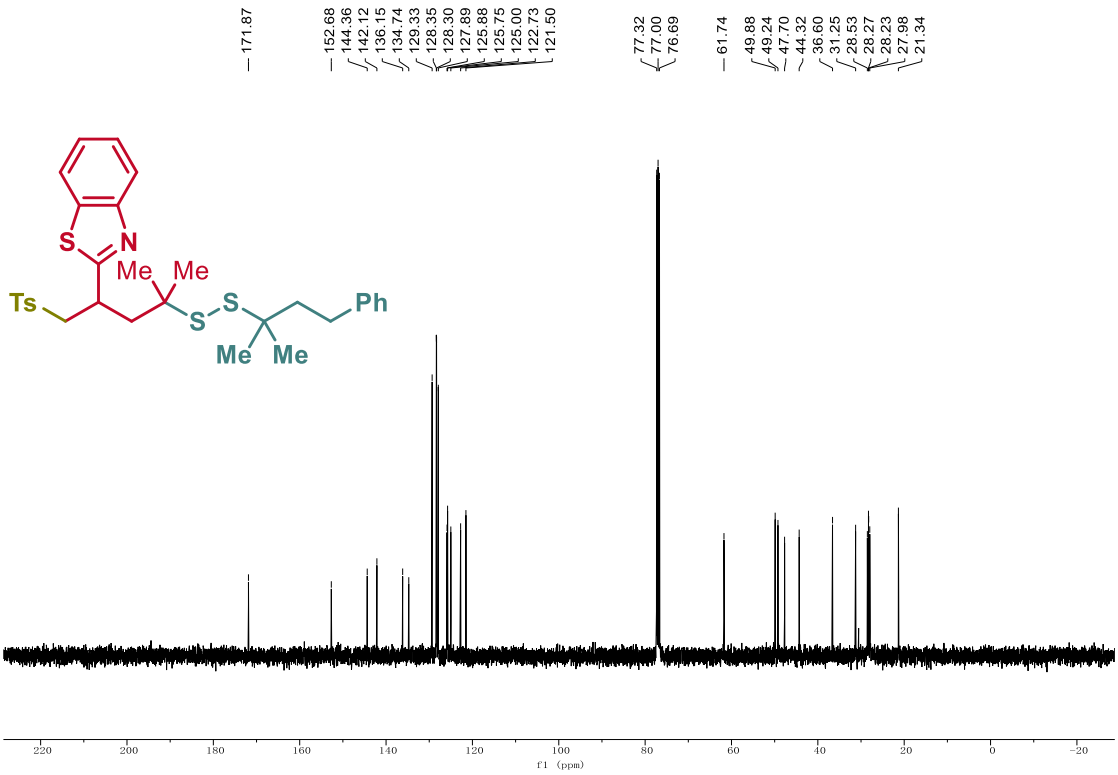
^{13}C NMR Spectrum of 3-((4-(benzo[*d*]thiazol-2-yl)-2-methyl-5-tosylpentan-2-yl)disulfaneyl)-3-methylbutyl pent-4-enoate (3w):



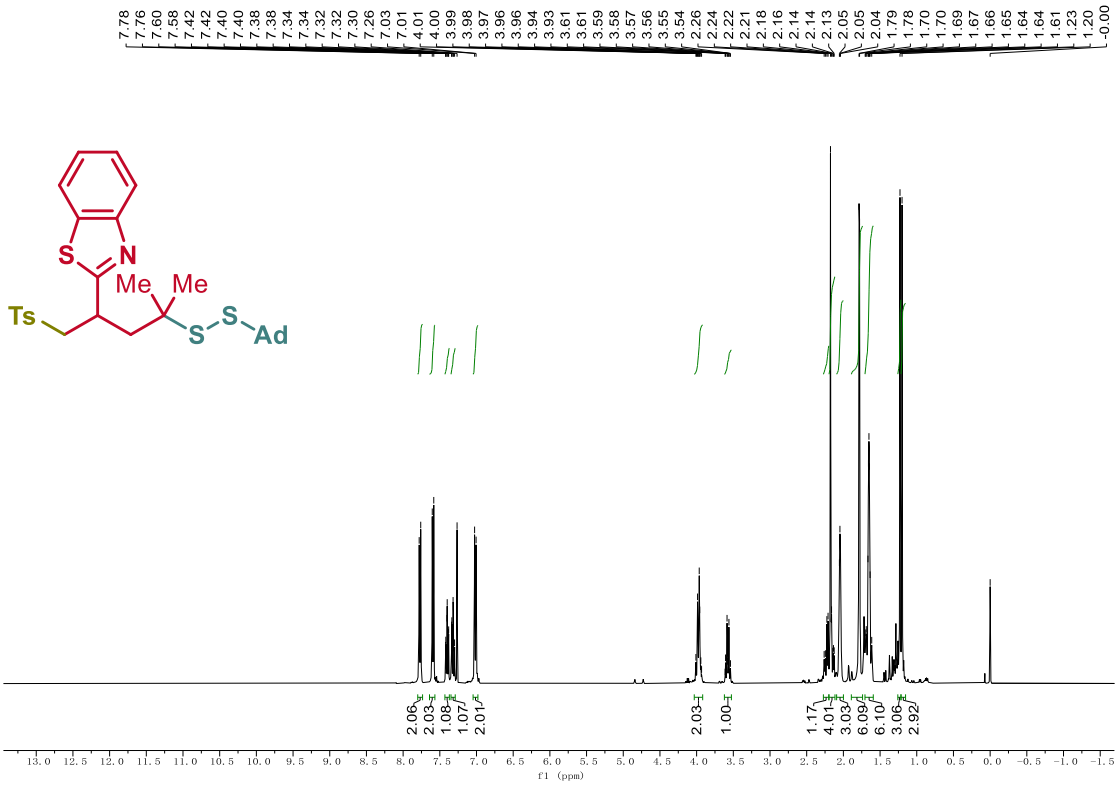
^{1}H NMR Spectrum of 2-(4-methyl-4-((2-methyl-4-phenylbutan-2-yl)disulfanyl)-1-tosylpentan-2-yl)benzo[*d*]thiazole (3x):



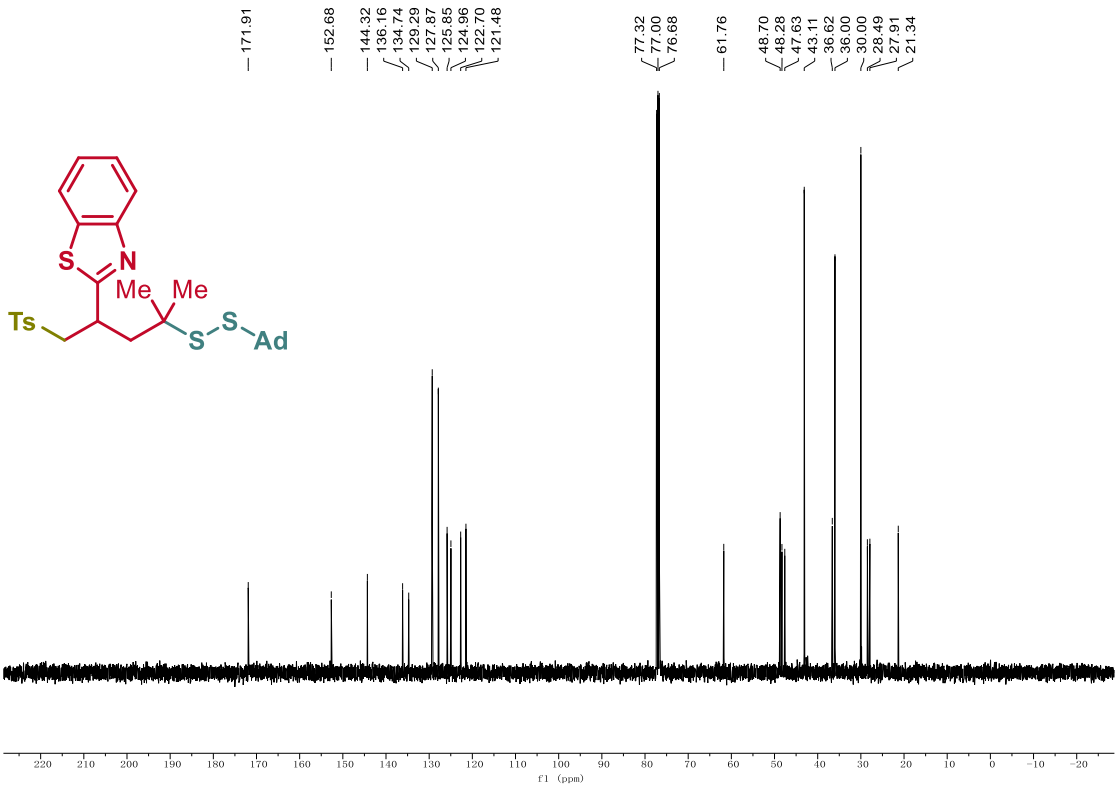
^{13}C NMR Spectrum of 2-(4-methyl-4-((2-methyl-4-phenylbutan-2-yl)disulfanyl)-1- tosylpentan-2-yl)benzo[*d*]thiazole (3x):



^{1}H NMR Spectrum of 2-(4-(((3s,5s,7s)-adamantan-1-yl)disulfaneyl)-4-methyl-1-tosylpentan-2-yl)benzo[*d*]thiazole (3y):

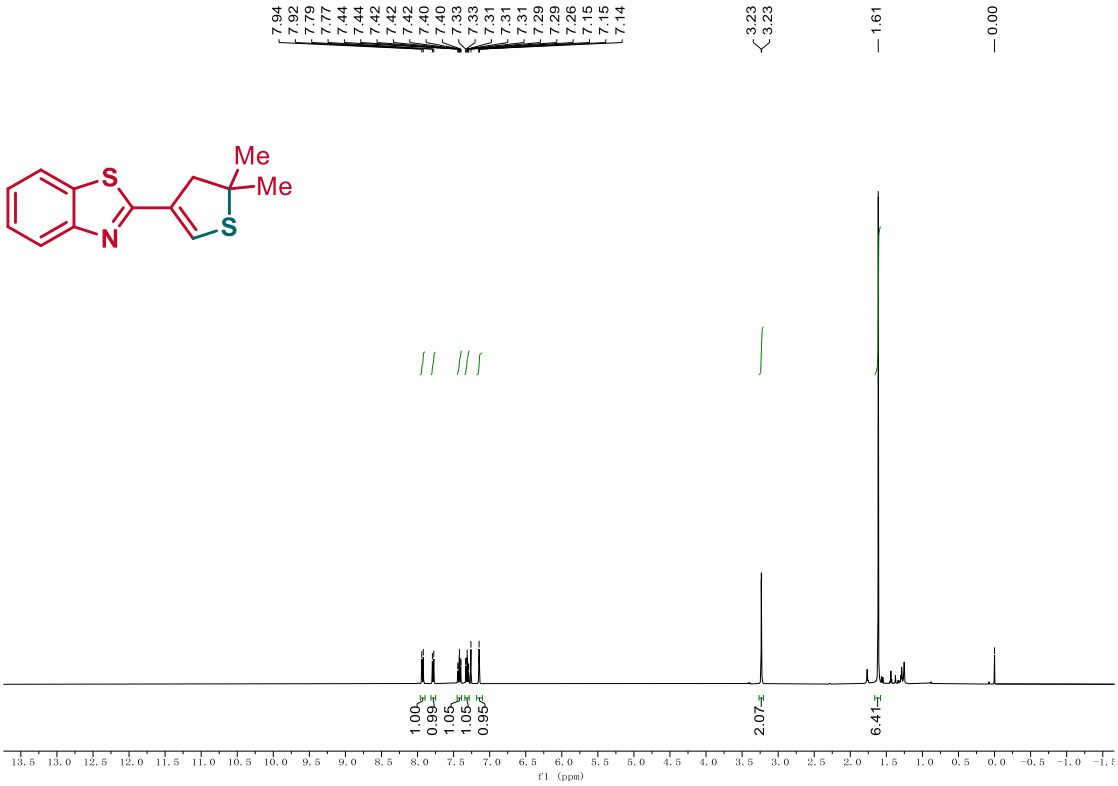


^{13}C NMR Spectrum of 2-(4-(((3s,5s,7s)-adamantan-1-yl)disulfaneyl)-4-methyl-1-tosylpentan-2-yl)benzo[*d*]thiazole (3y):

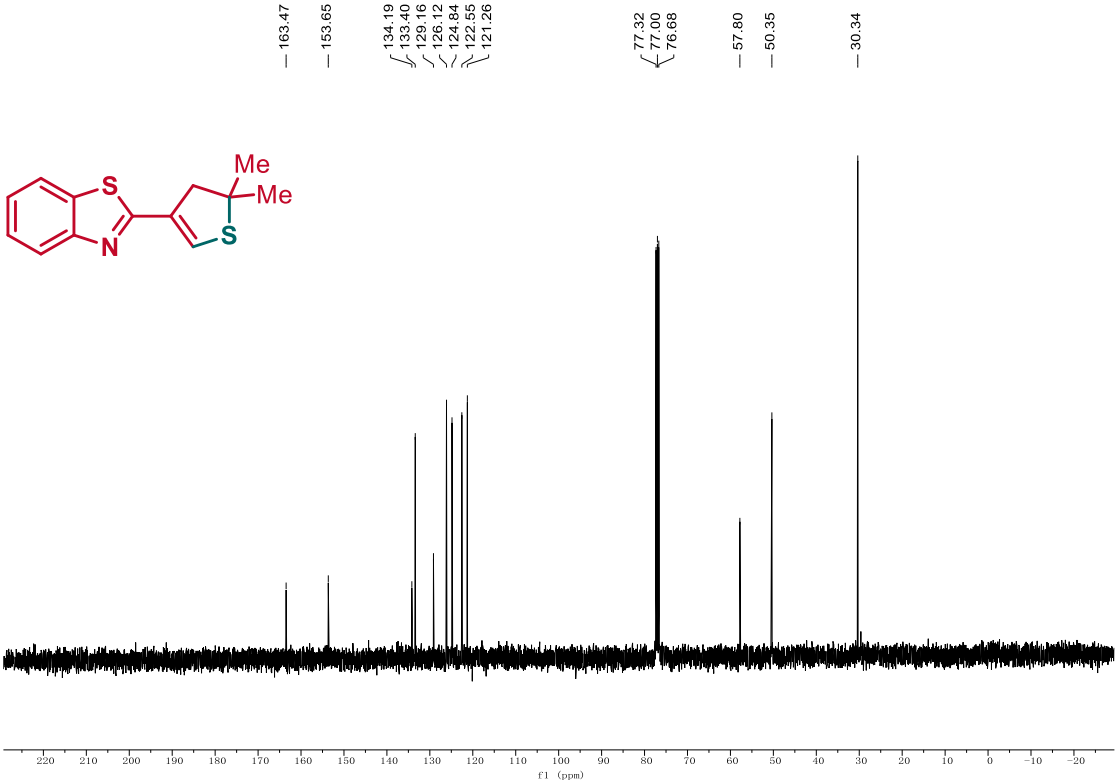


6.5 Spectra of dihydrothiophenes

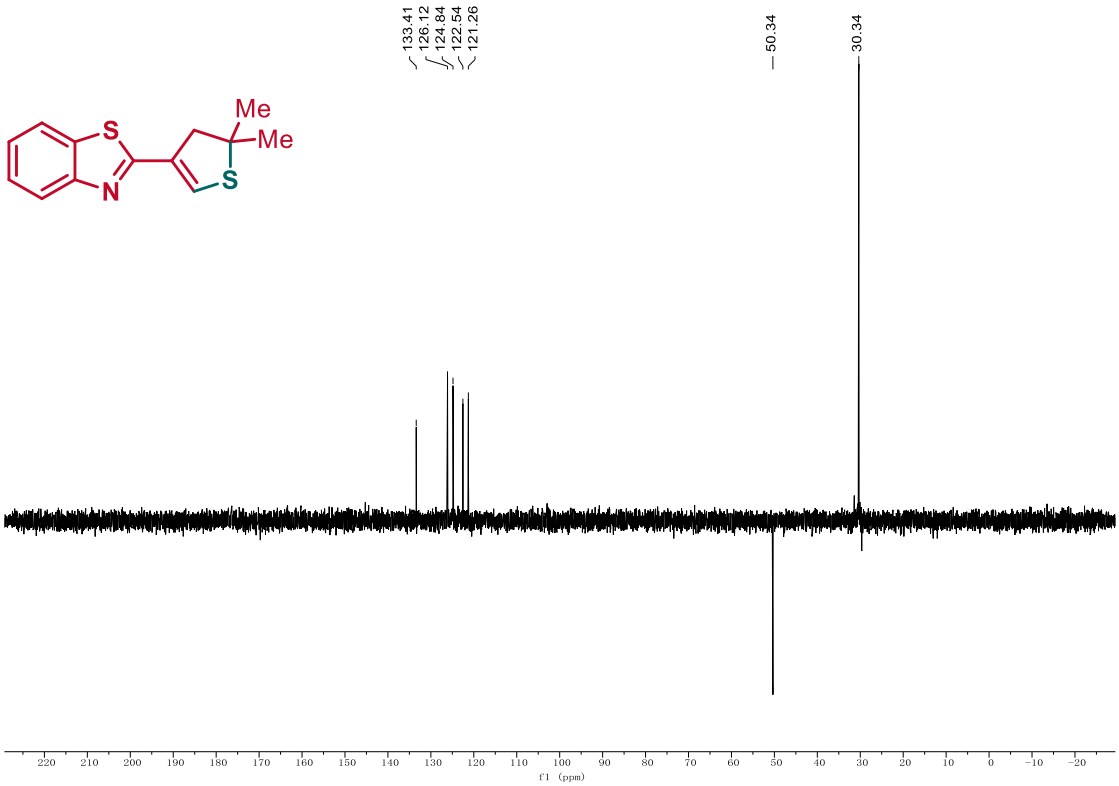
^{1}H NMR Spectrum of 2-(5,5-dimethyl-4,5-dihydrothiophen-3-yl)benzo[*d*]thiazole (4a):



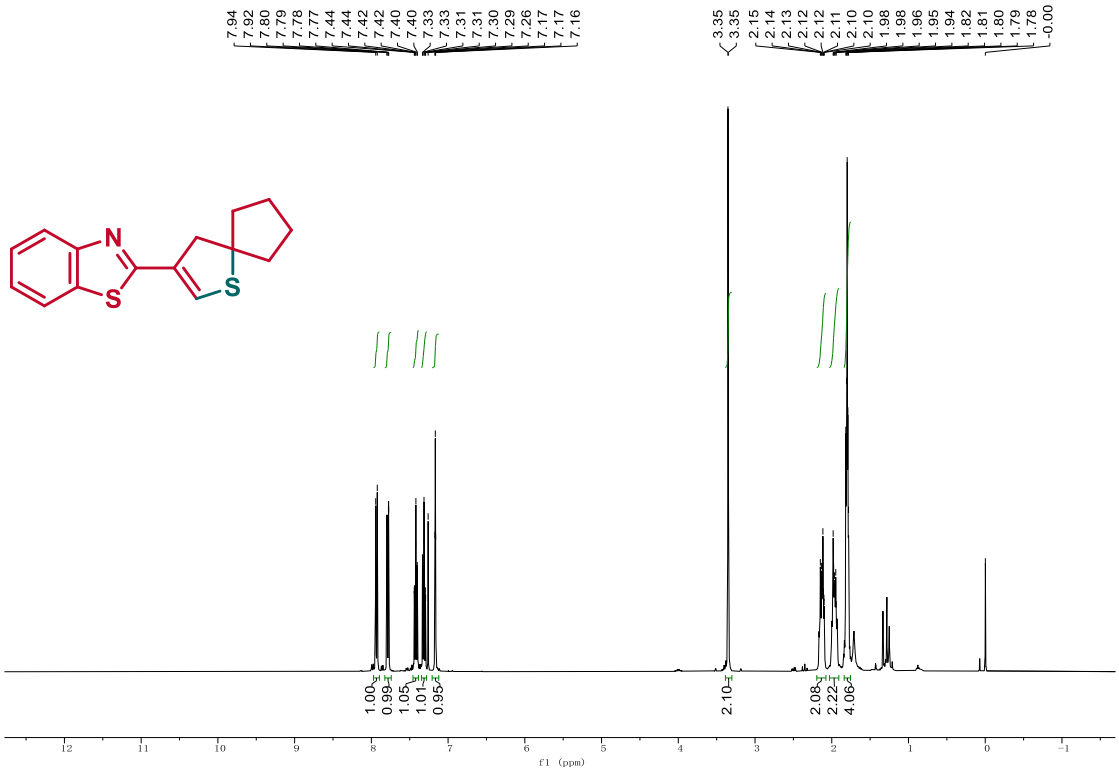
^{13}C NMR Spectrum of 2-(5,5-dimethyl-4,5-dihydrothiophen-3-yl)benzo[*d*]thiazole (4a):



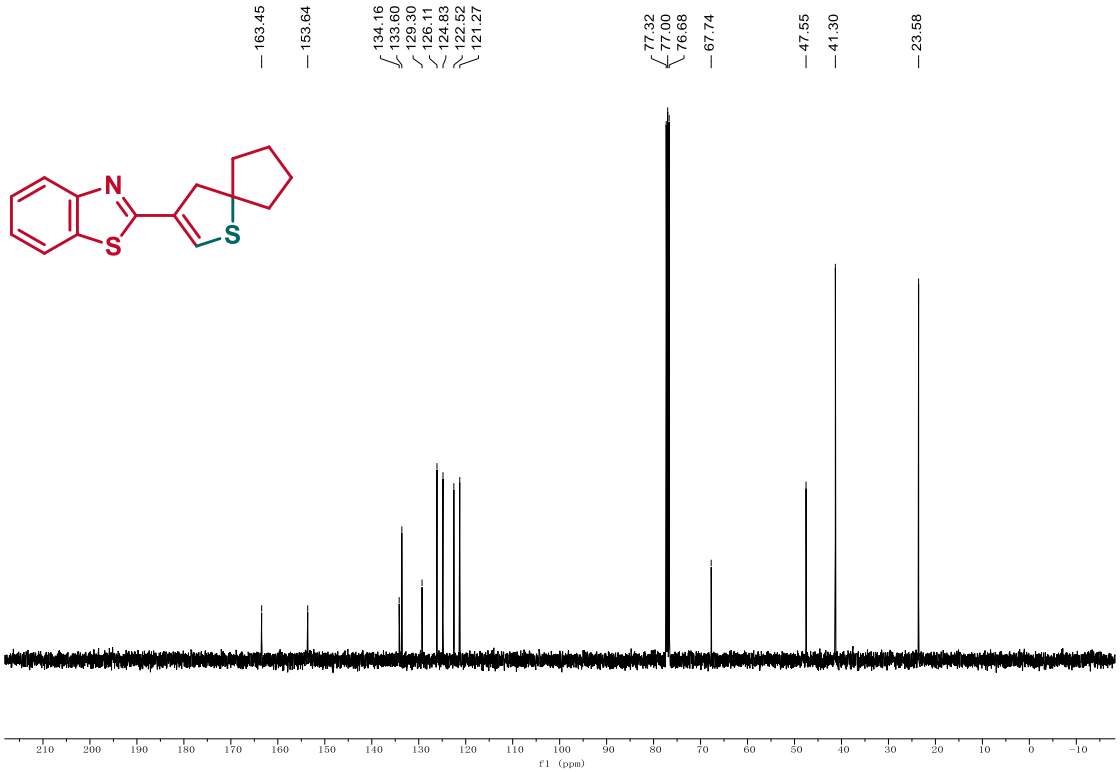
DEPT 135 Spectrum of 2-(5,5-dimethyl-4,5-dihydrothiophen-3-yl)benzo[*d*] thiazole (4a):



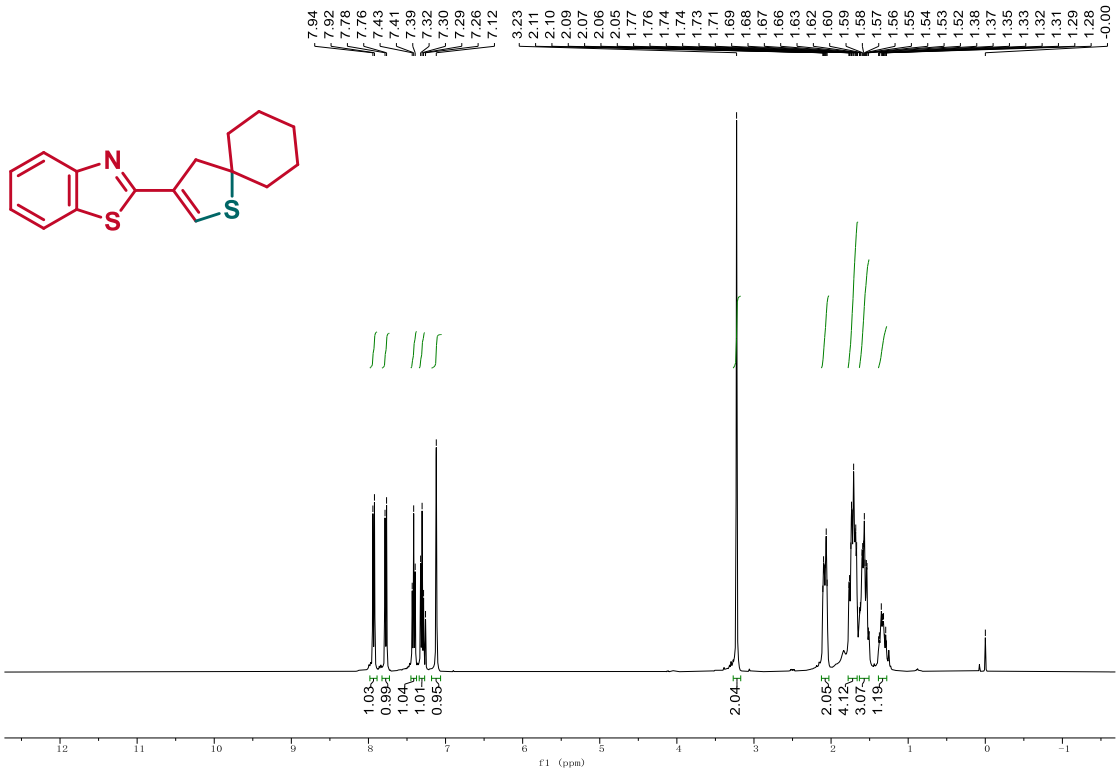
^{1}H NMR Spectrum of 2-(1-thiaspiro[4.4]non-2-en-3-yl)benzo[*d*]thiazole (4b):



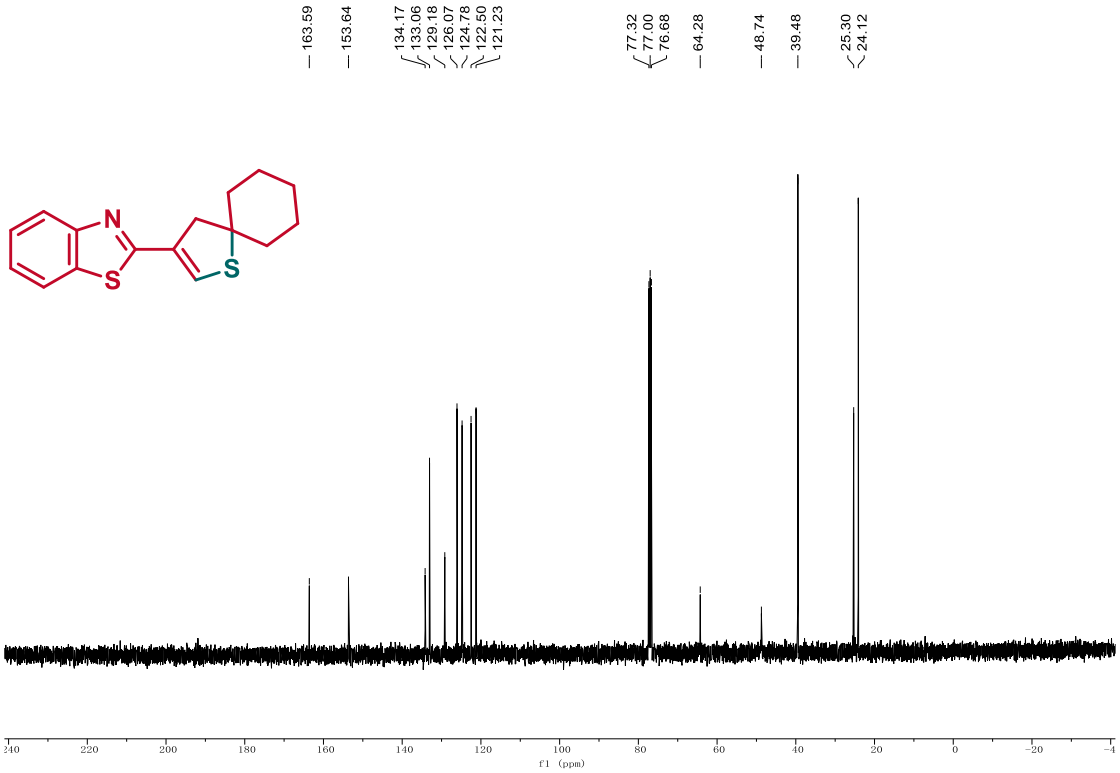
^{13}C NMR Spectrum of 2-(1-thiaspiro[4.4]non-2-en-3-yl)benzo[*d*]thiazole (4b):



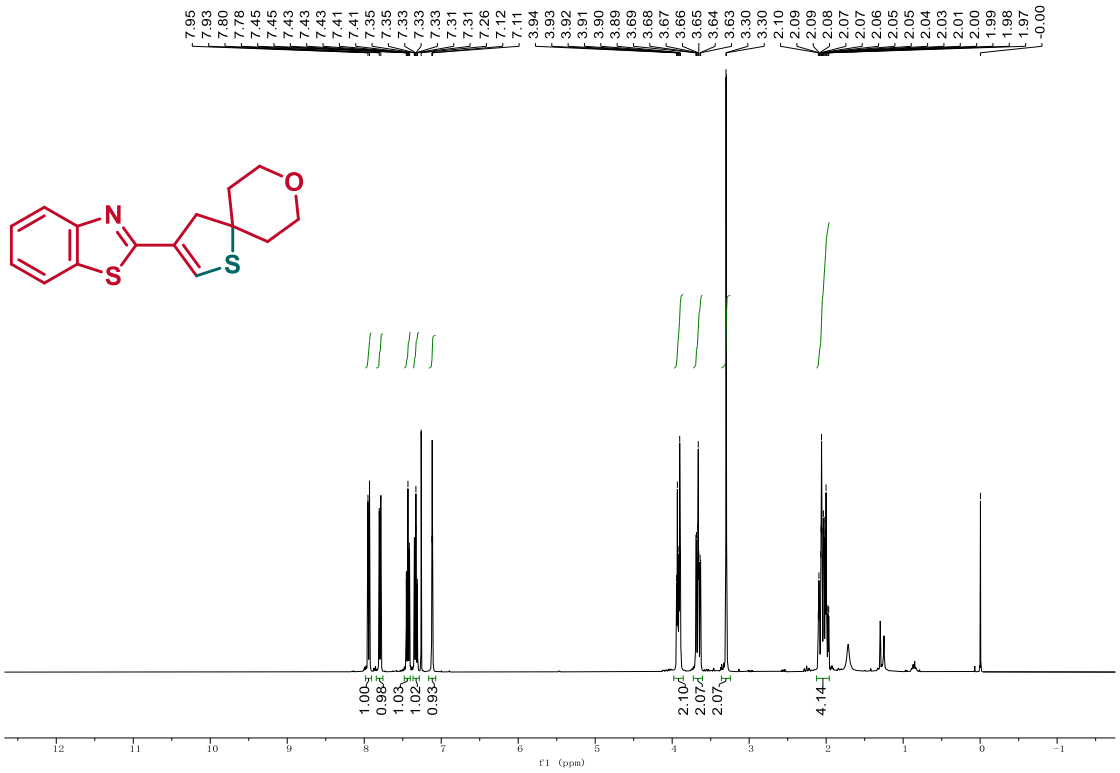
^{1}H NMR Spectrum of 2-(1-thiaspiro[4.5]dec-2-en-3-yl)benzo[*d*]thiazole (4c):



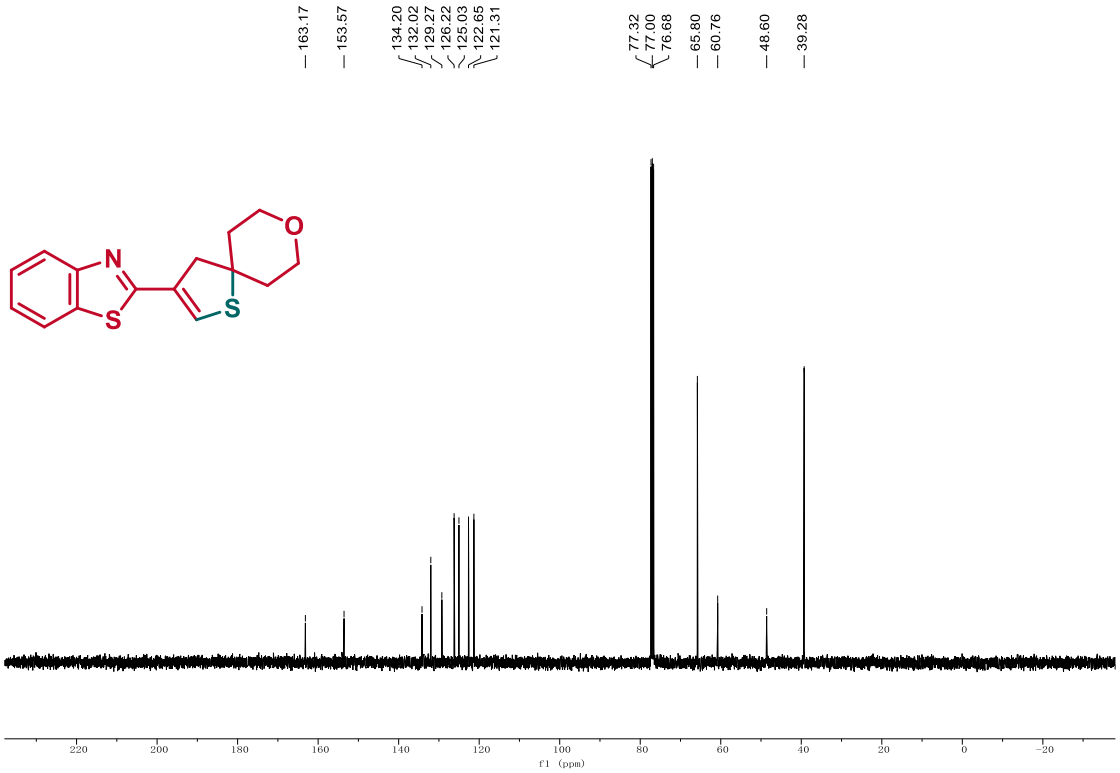
^{13}C NMR Spectrum of 2-(1-thiaspiro[4.5]dec-2-en-3-yl)benzo[*d*]thiazole (4c):



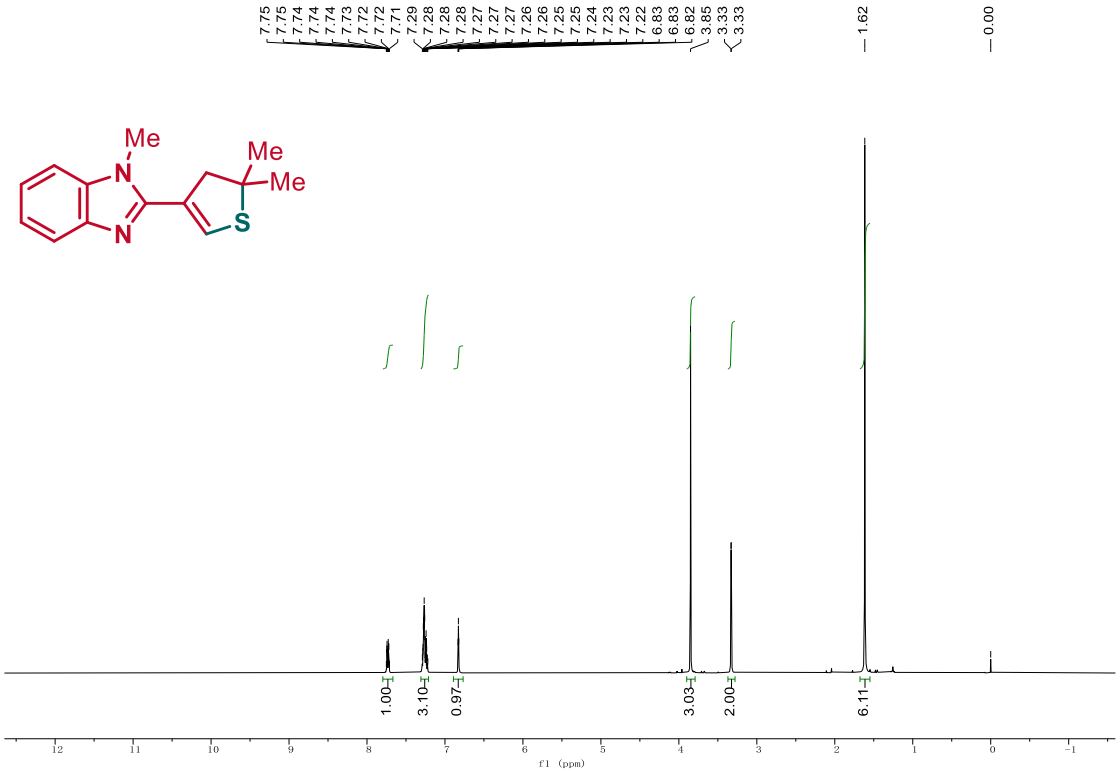
^{1}H NMR Spectrum of 2-(8-oxa-1-thiaspiro[4.5]dec-2-en-3-yl)benzo[*d*]thiazole (4d):



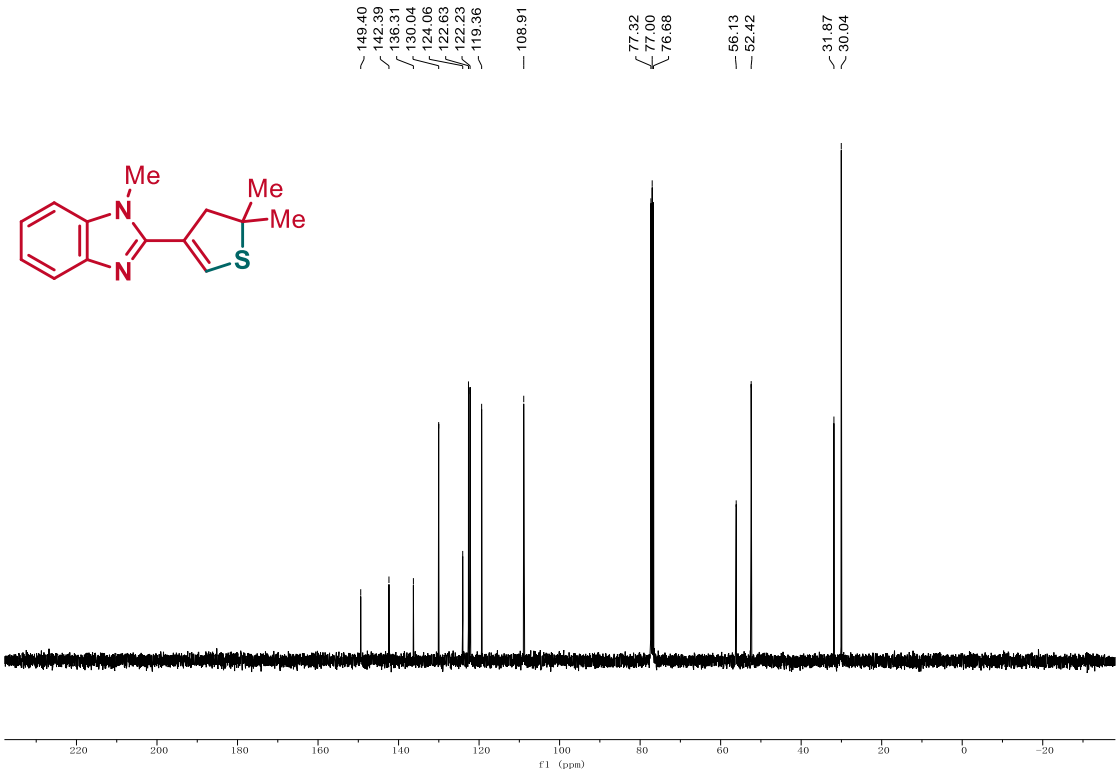
^{13}C NMR Spectrum of 2-(8-oxa-1-thiaspiro[4.5]dec-2-en-3-yl)benzo[*d*]thiazole(4d):



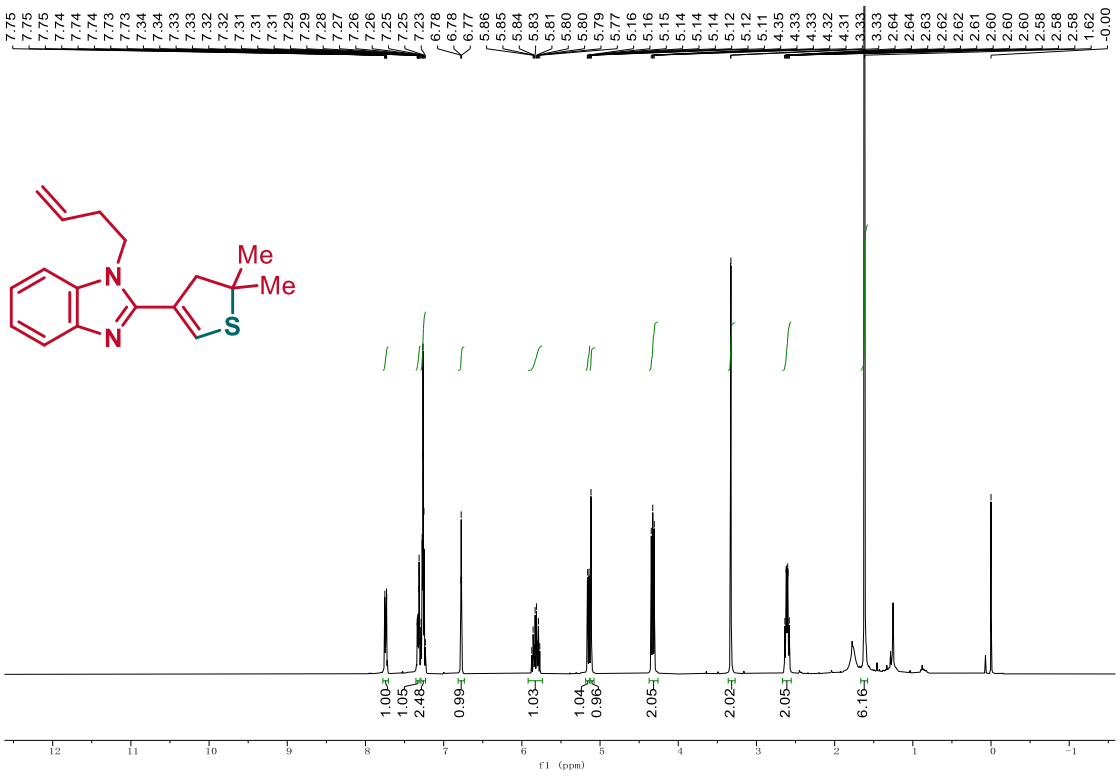
^{1}H NMR Spectrum of 2-(5,5-dimethyl-4,5-dihydrothiophen-3-yl)-1-methyl-1*H*-benzo[*d*]imidazole (4e):



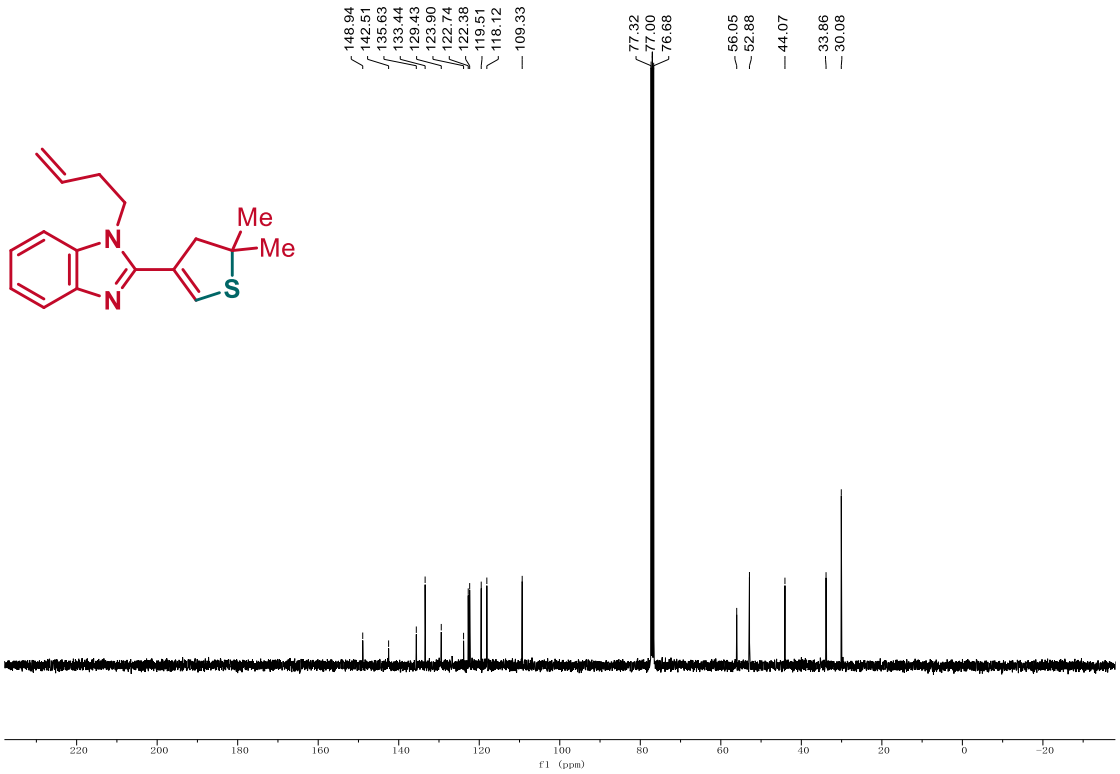
^{13}C NMR Spectrum of 2-(5,5-dimethyl-4,5-dihydrothiophen-3-yl)-1-methyl-1*H*-benzo[*d*]imidazole (4e):



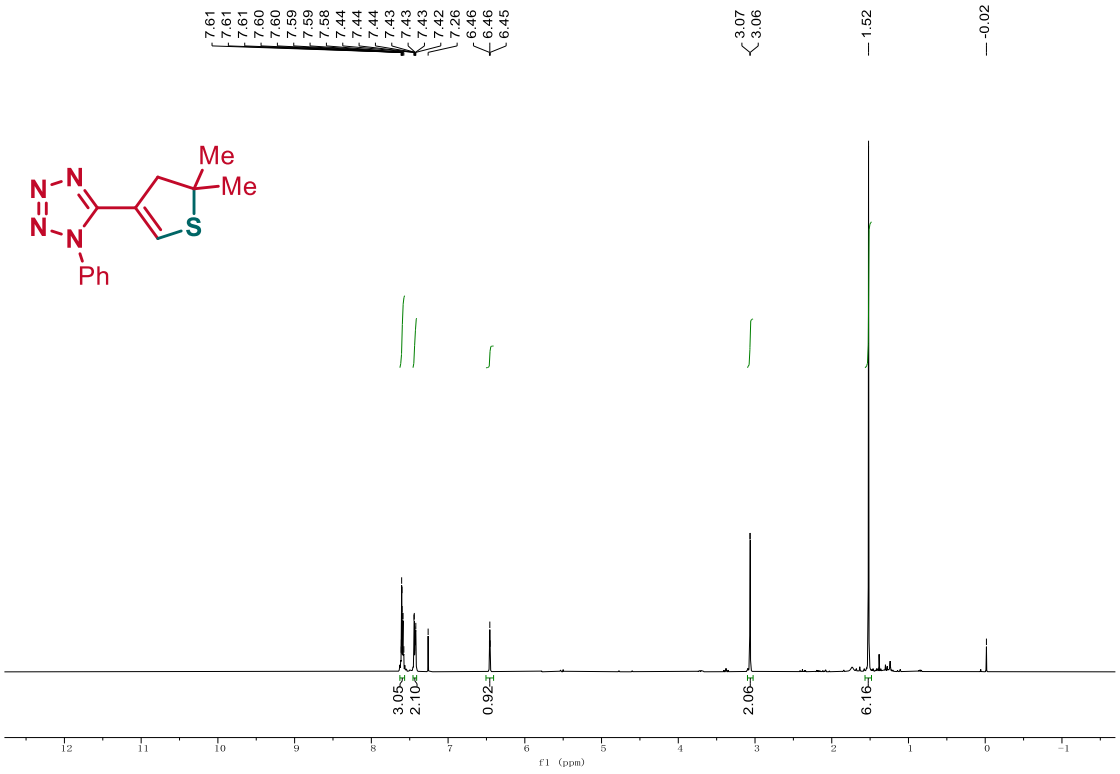
^{1}H NMR Spectrum of 1-(but-3-en-1-yl)-2-(5,5-dimethyl-4,5-dihydrothiophen-3-yl)-1*H*-benzo[*d*]imidazole (4f):



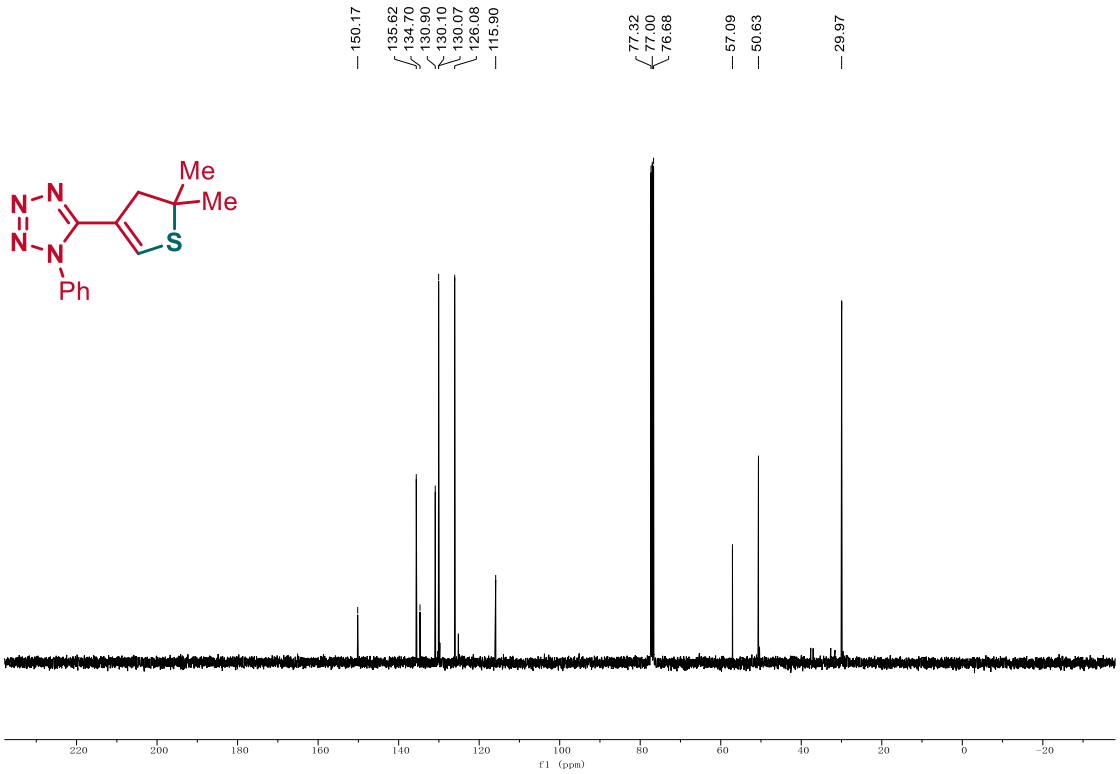
^{13}C NMR Spectrum of 1-(but-3-en-1-yl)-2-(5,5-dimethyl-4,5-dihydrothiophen-3-yl)-1*H*-benzo[*d*]imidazole (4f):



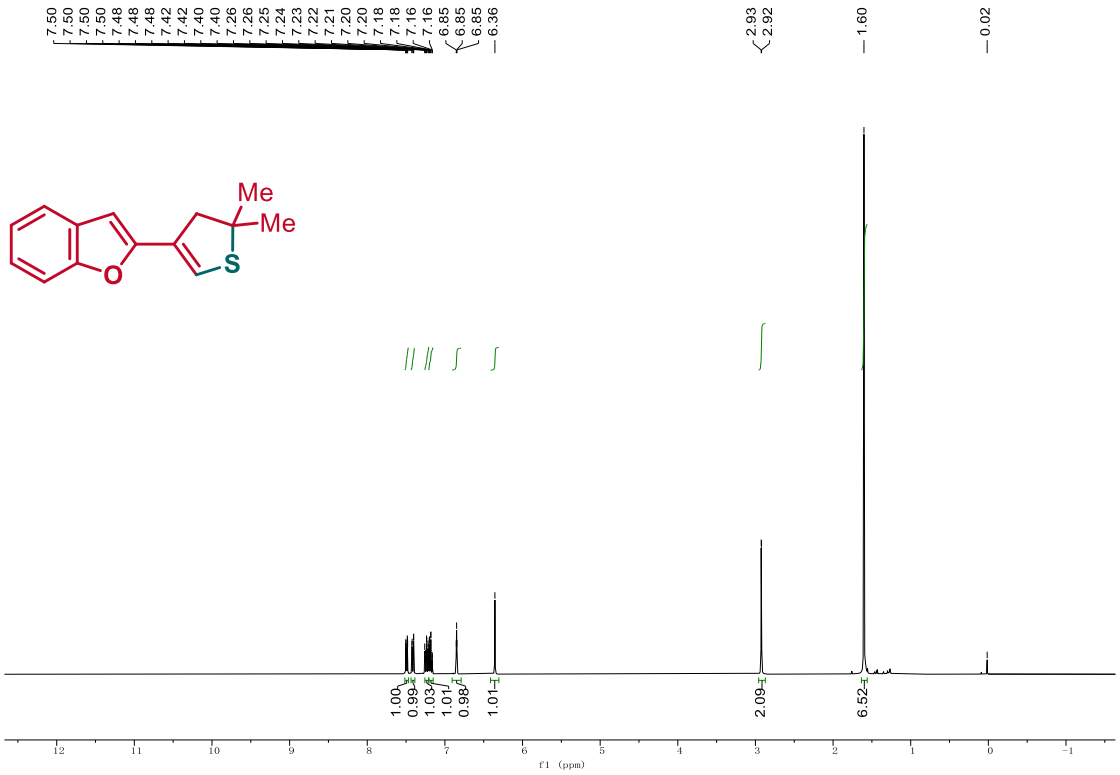
^{1}H NMR Spectrum of 5-(5,5-dimethyl-4,5-dihydrothiophen-3-yl)-1-phenyl-1*H*-tetrazole (4g):



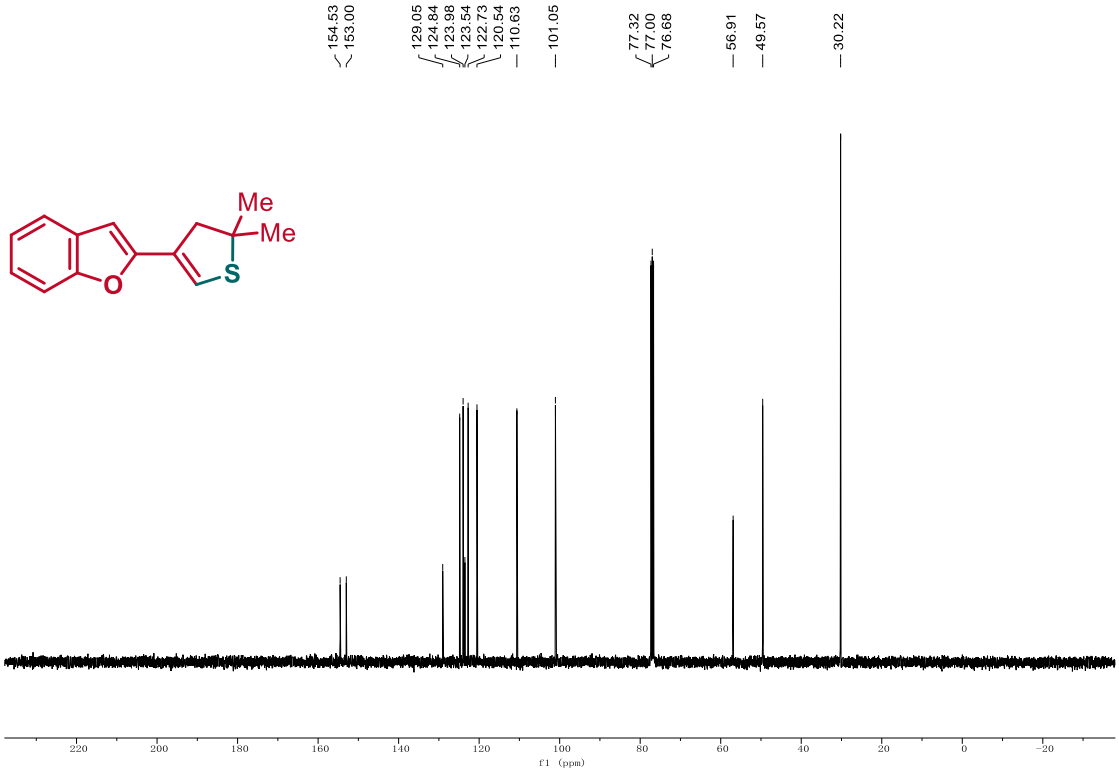
^{13}C NMR Spectrum of 5-(5,5-dimethyl-4,5-dihydrothiophen-3-yl)-1-phenyl-1H-tetrazole (4g):



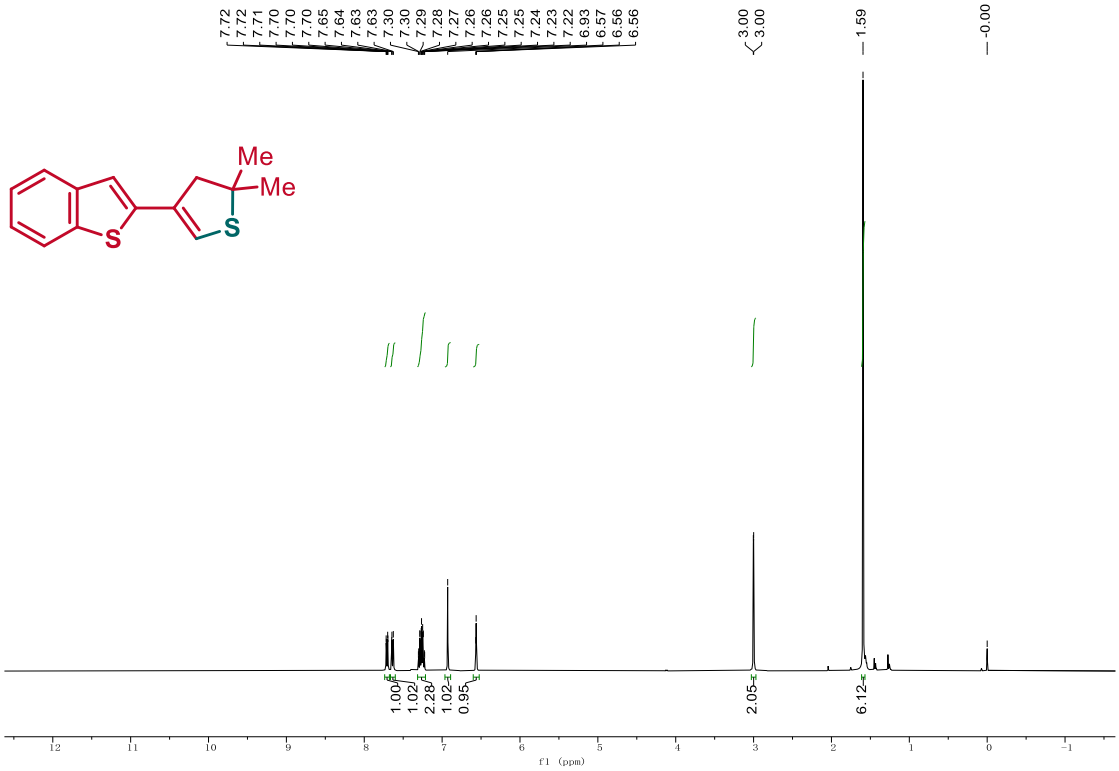
^{1}H NMR Spectrum of 2-(5,5-dimethyl-4,5-dihydrothiophen-3-yl)benzofuran (4h):



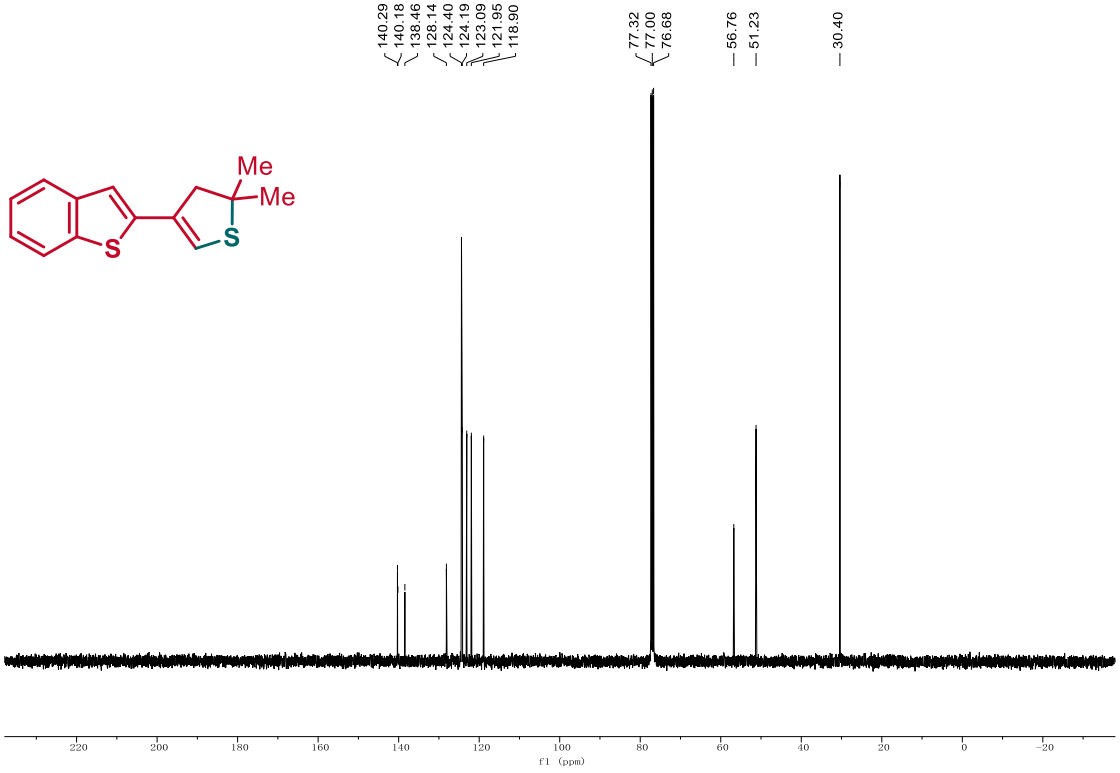
^{13}C NMR Spectrum of 2-(5,5-dimethyl-4,5-dihydrothiophen-3-yl)benzofuran (4h):



^{1}H NMR Spectrum of 2-(5,5-dimethyl-4,5-dihydrothiophen-3-yl)benzo[*b*]thiophene (4i):

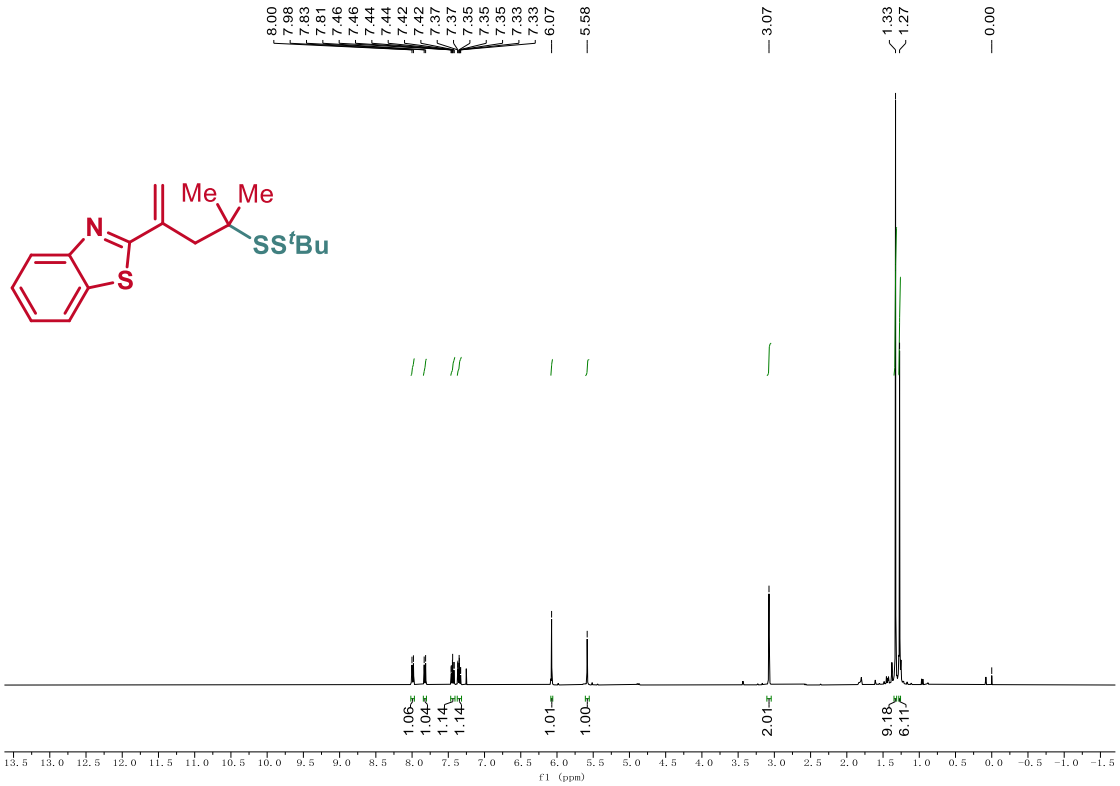


^{13}C NMR Spectrum of 2-(5,5-dimethyl-4,5-dihydrothiophen-3-yl)benzo[*b*]thiophene (4i):

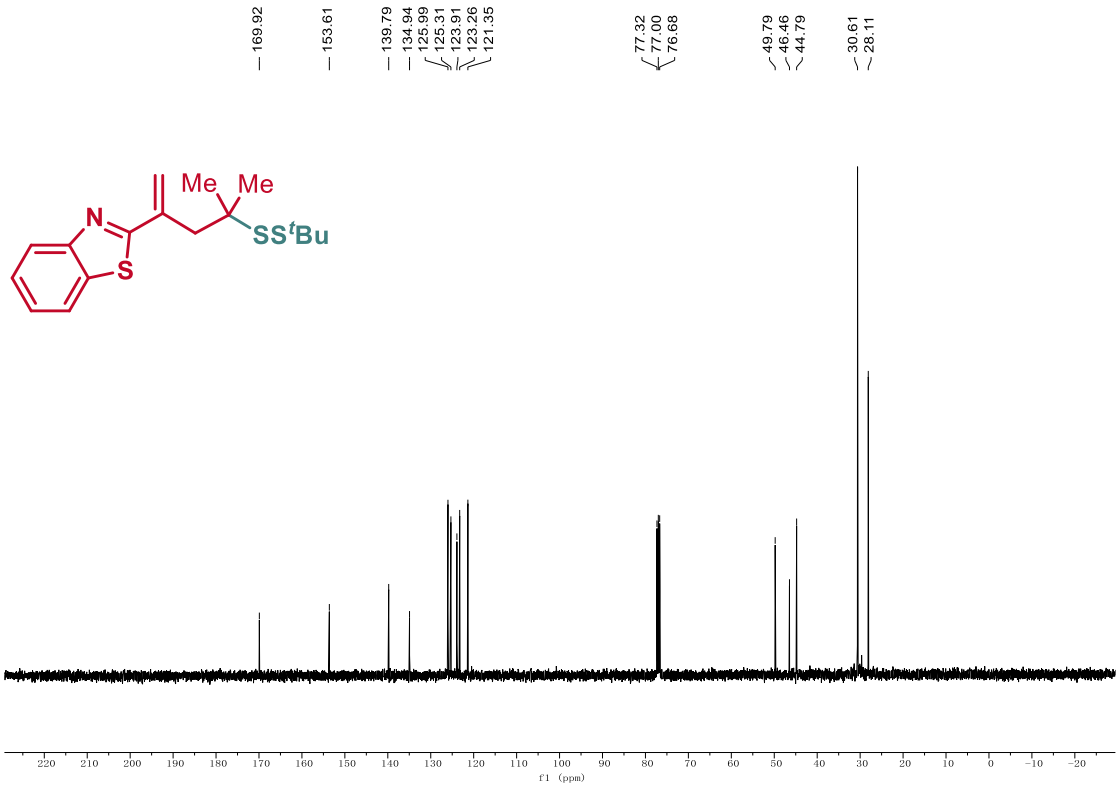


6.6 Spectra of homoallyl disulfides

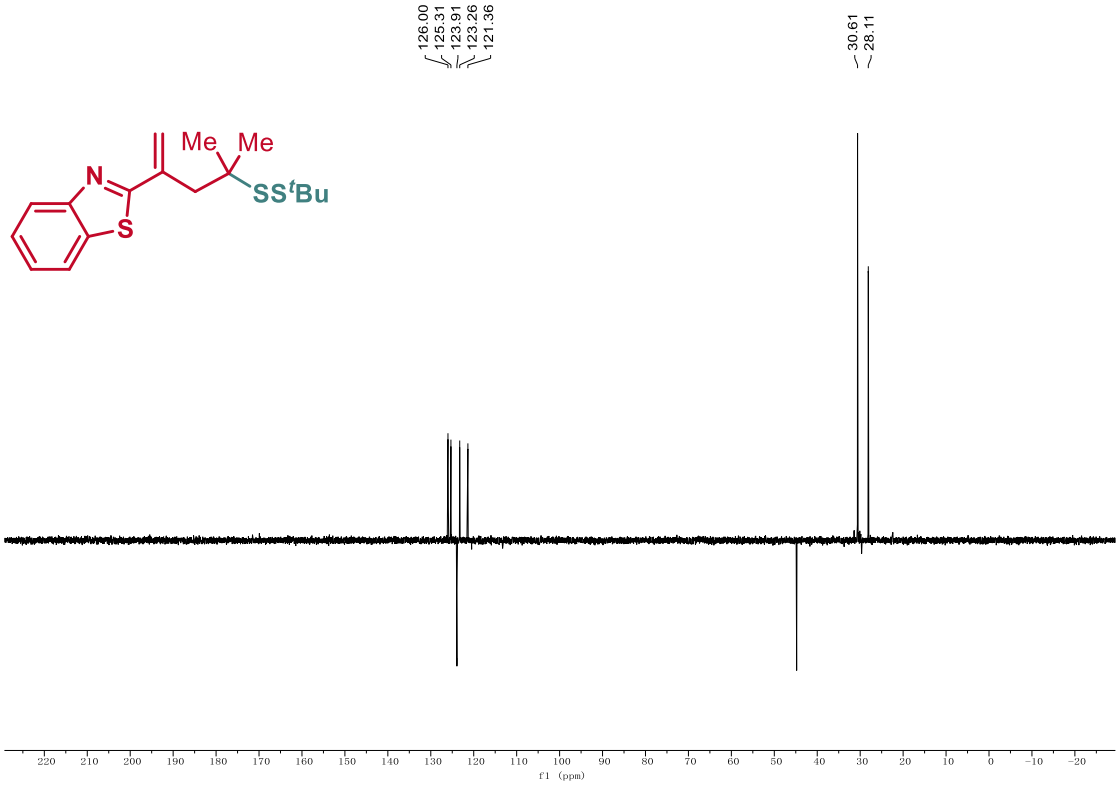
^{1}H NMR Spectrum of 2-(4-(*tert*-butyldisulfaneyl)-4-methylpent-1-en-2-yl)benzo[*d*]thiazole (5a):



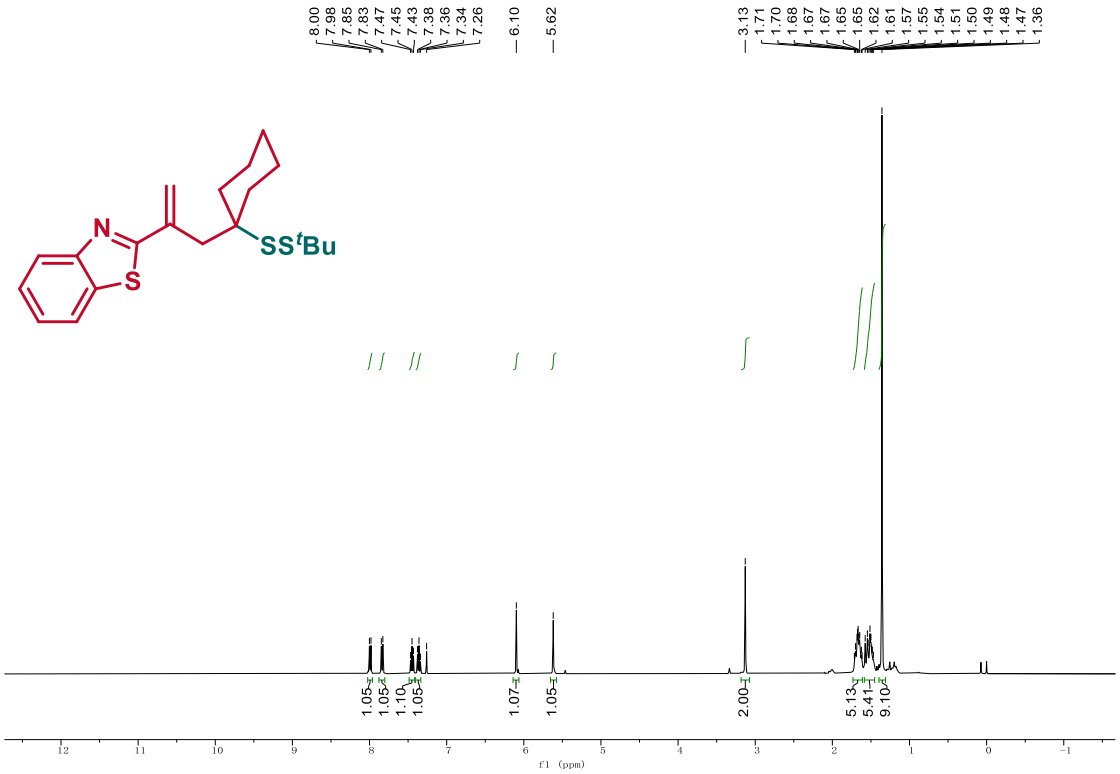
^{13}C NMR Spectrum of 2-(4-(*tert*-butyldisulfaneyl)-4-methylpent-1-en-2-yl)benzo[*d*]thiazole (5a):



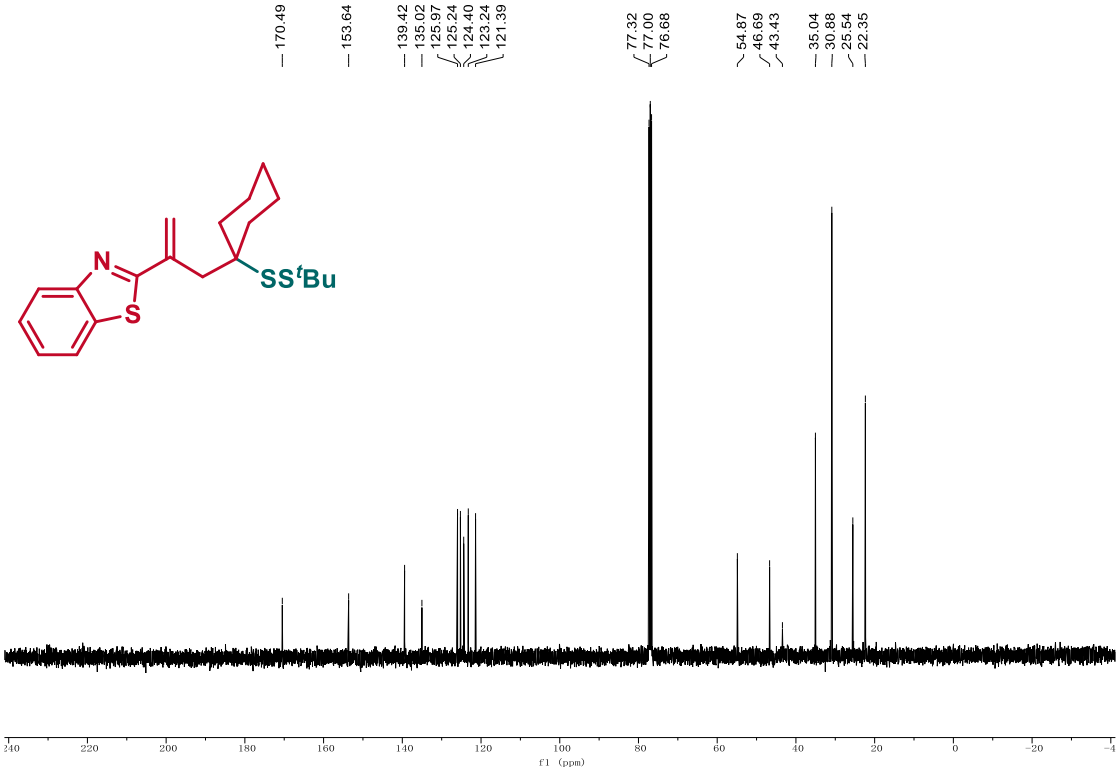
DEPT 135 Spectrum of 2-(4-(*tert*-butyldisulfaneyl)-4-methylpent-1-en-2-yl)benzo[*d*]thiazole (5):



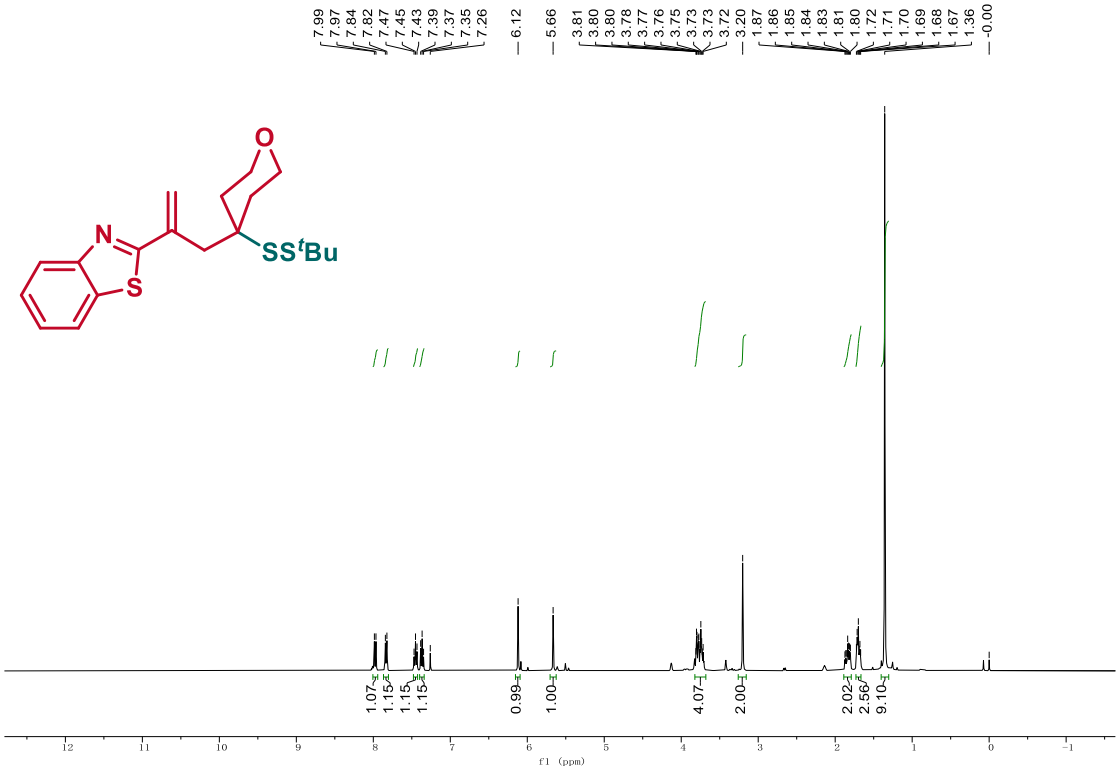
^{1}H NMR Spectrum of 2-(3-(1-(*tert*-butyldisulfaneyl)cyclohexyl)prop-1-en-2-yl)benzo[*d*]thiazole (5b):



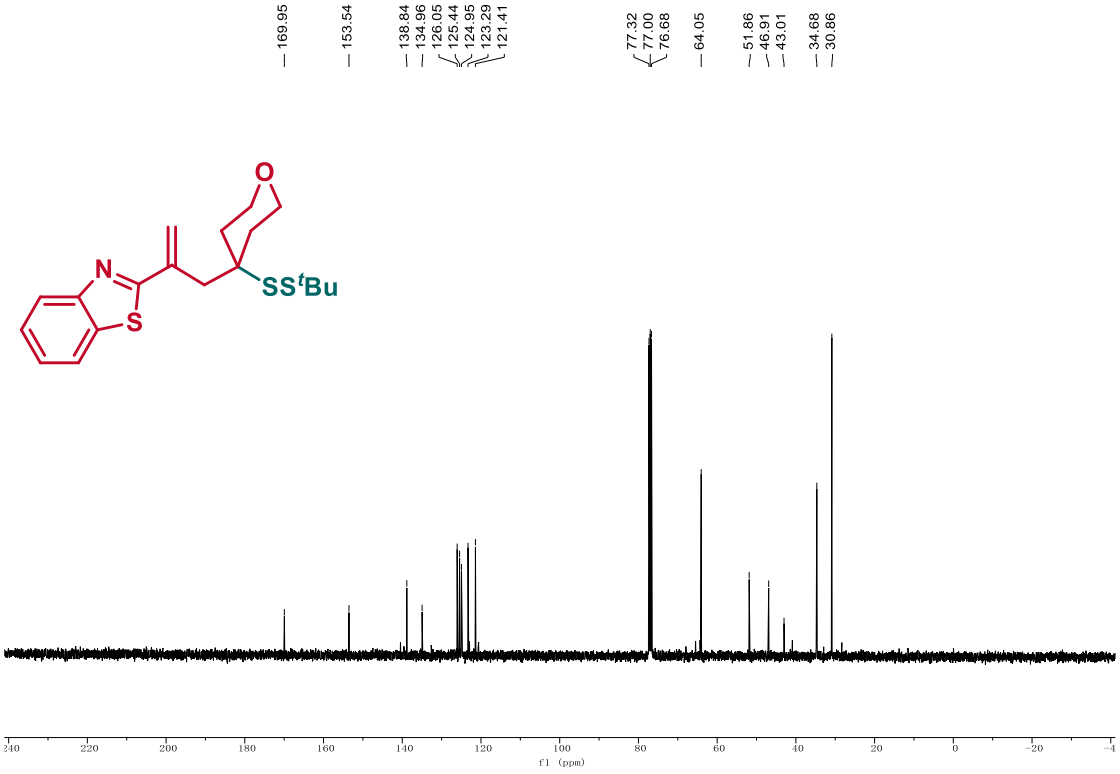
^{13}C NMR Spectrum of 2-(3-(1-(*tert*-butyldisulfaneyl)cyclohexyl)prop-1-en-2-yl)benzo[*d*]thiazole (5b):



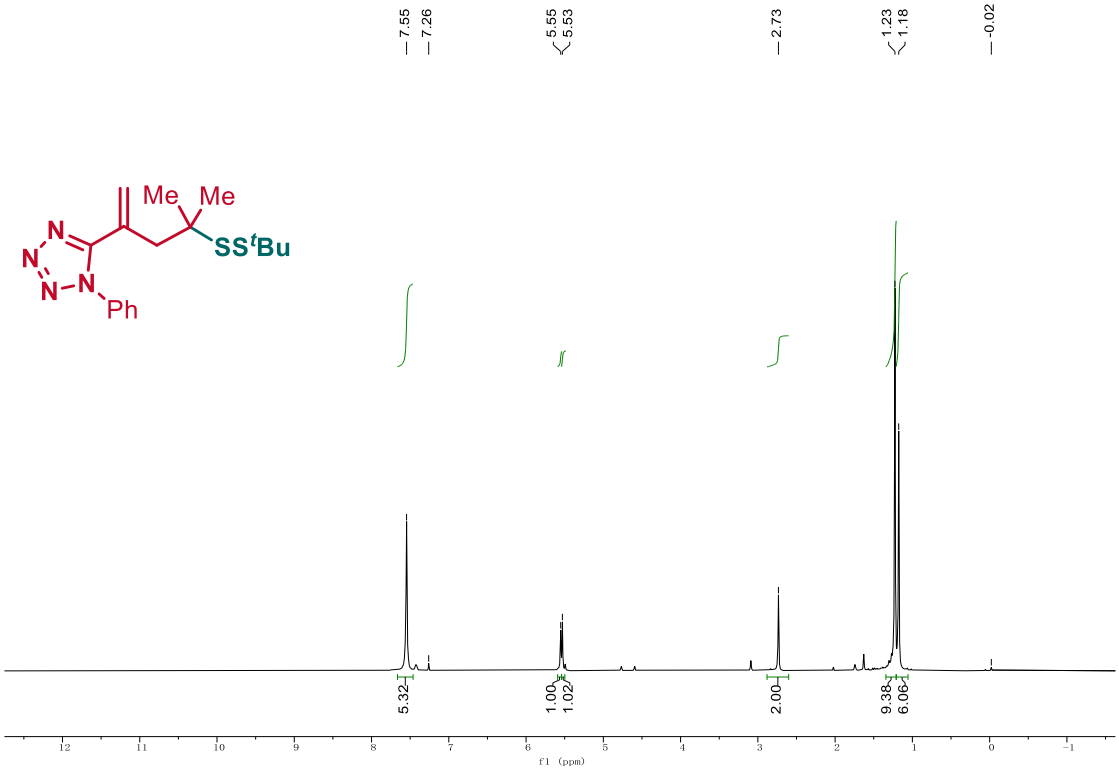
^{1}H NMR Spectrum of 4-(2-(benzo[*b*]thiophen-2-yl)allyl)-4-(*tert*-butyldisulfaneyl)tetrahydro-2*H*- pyran (5c):



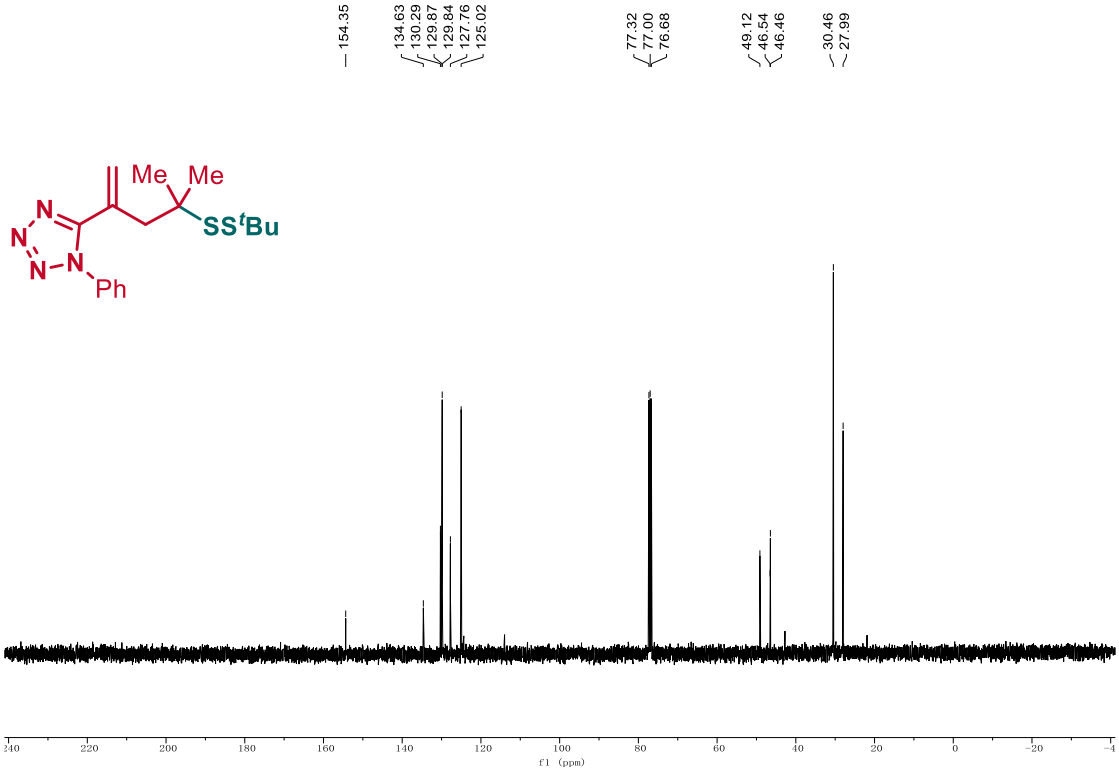
^{13}C NMR Spectrum of 4-(2-(benzo[*b*]thiophen-2-yl)allyl)-4-(*tert*-butyldisulfaneyl)tetrahydro-2*H*- pyran (5c):



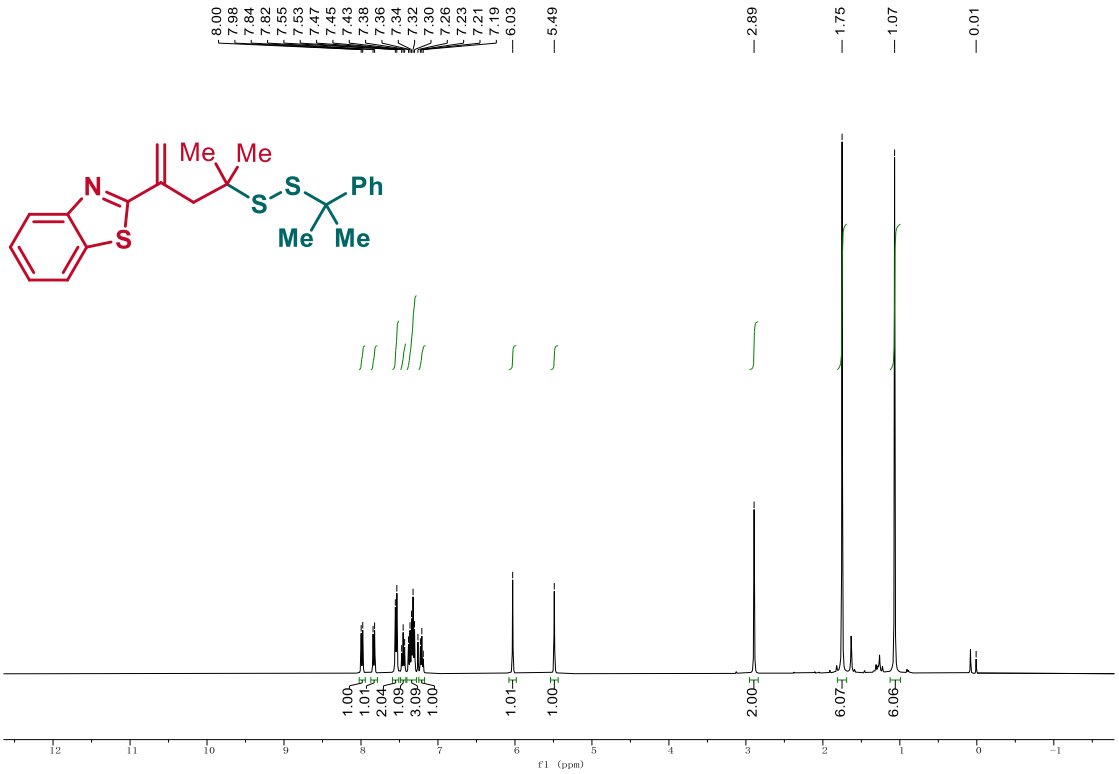
^{1}H NMR Spectrum of 5-(4-(*tert*-butyldisulfaneyl)-4-methylpent-1-en-2-yl)-1-phenyl-1*H*-tetrazole (5d):



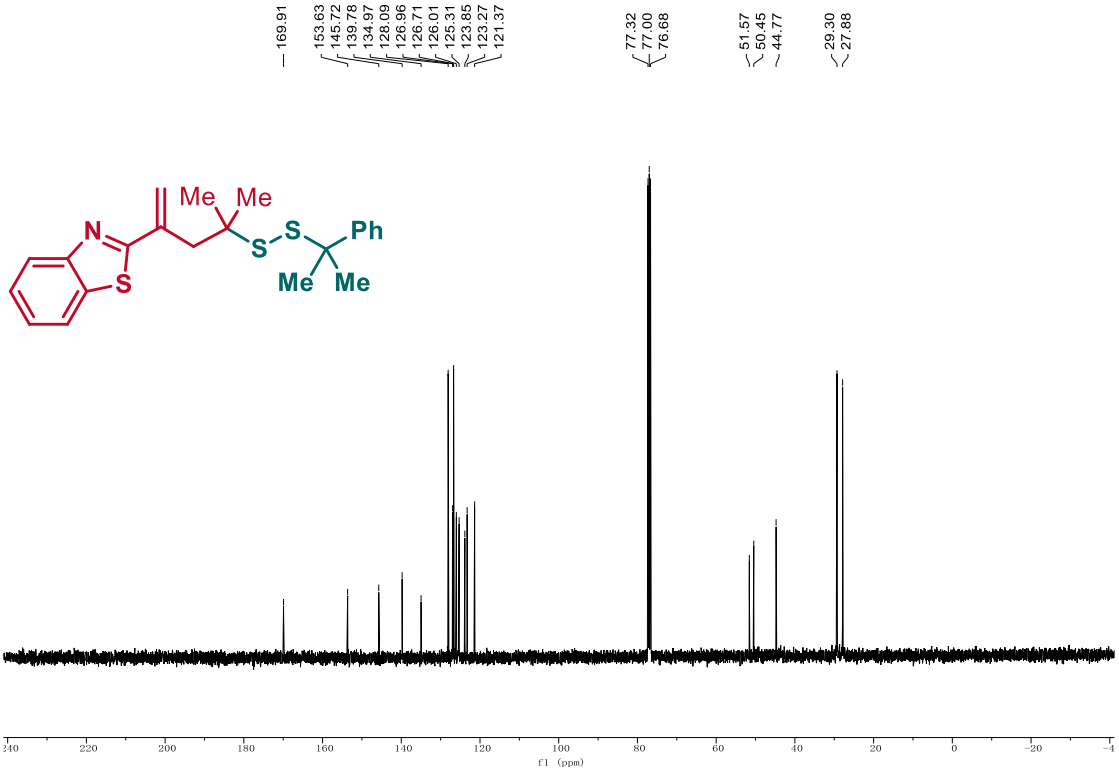
^{13}C NMR Spectrum of 5-(4-(*tert*-butyldisulfaneyl)-4-methylpent-1-en-2-yl)-1-phenyl-1*H*-tetrazole (5d):



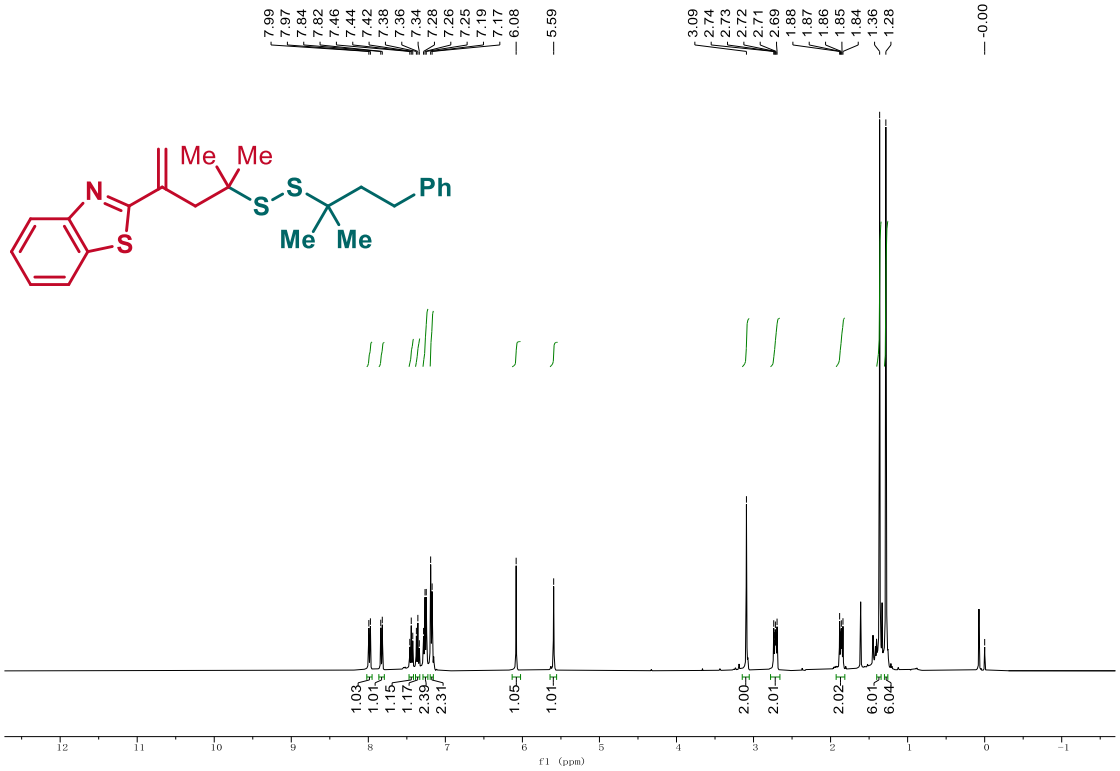
^{1}H NMR Spectrum of 2-(4-methyl-4-((2-phenylpropan-2-yl)disulfaneyl)pent-1-en-2-yl)benzo[*d*] thiazole (5e):



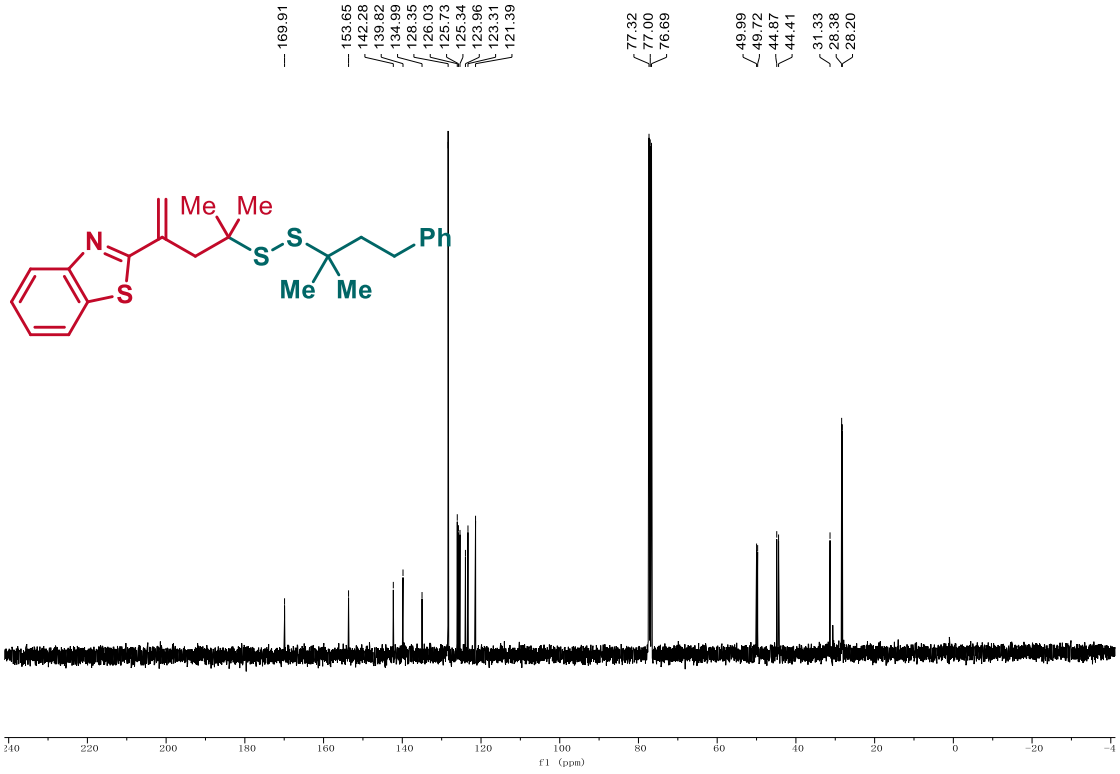
^{13}C NMR Spectrum of 2-(4-methyl-4-((2-phenylpropan-2-yl)disulfaneyl)pent-1-en-2-yl)benzo[*d*] thiazole (5e):



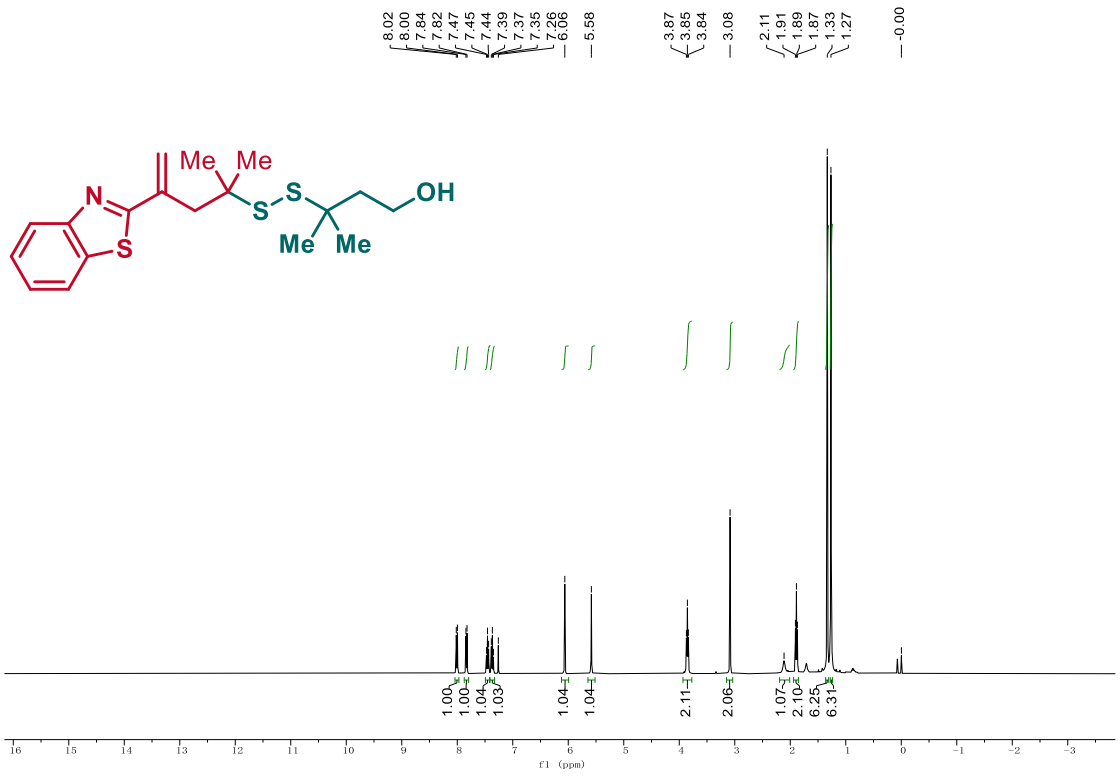
^{1}H NMR Spectrum of 2-(4-methyl-4-((2-methyl-4-phenylbutan-2-yl)disulfaneyl)pent-1-en-2-yl) benzo[*d*]thiazole (5f):



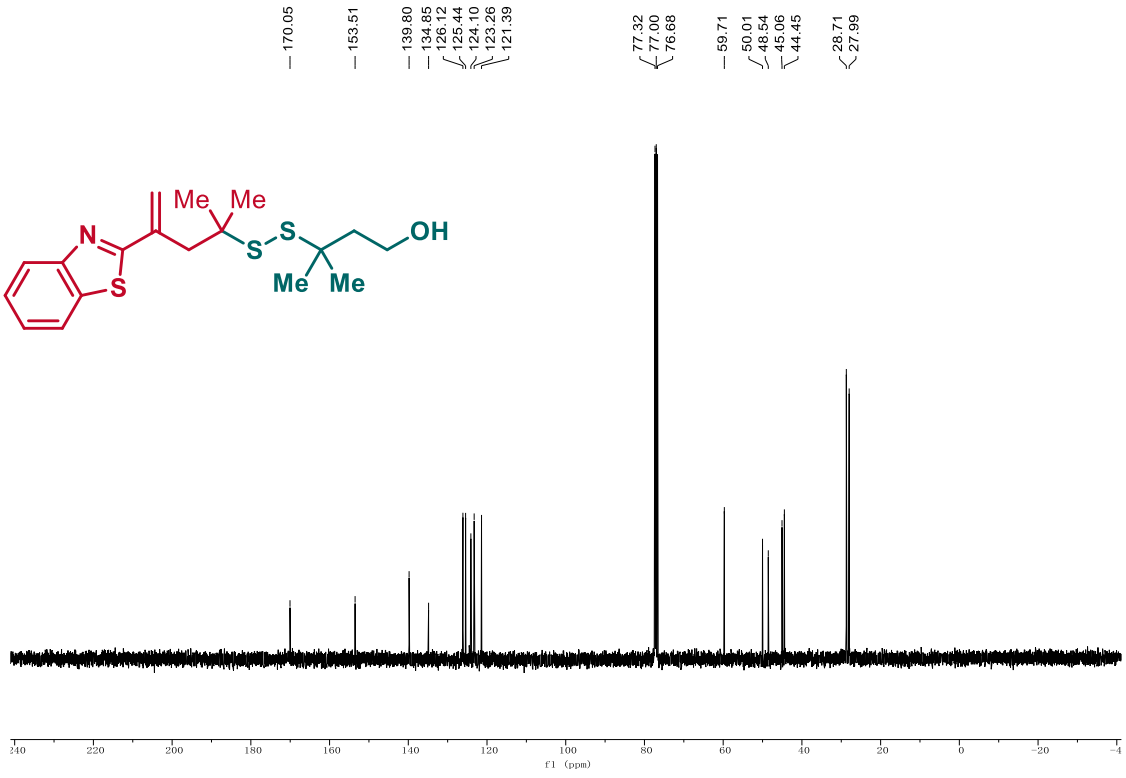
^{13}C NMR Spectrum of 2-(4-methyl-4-((2-methyl-4-phenylbutan-2-yl)disulfaneyl)pent-1-en-2-yl) benzo[*d*]thiazole (5f):



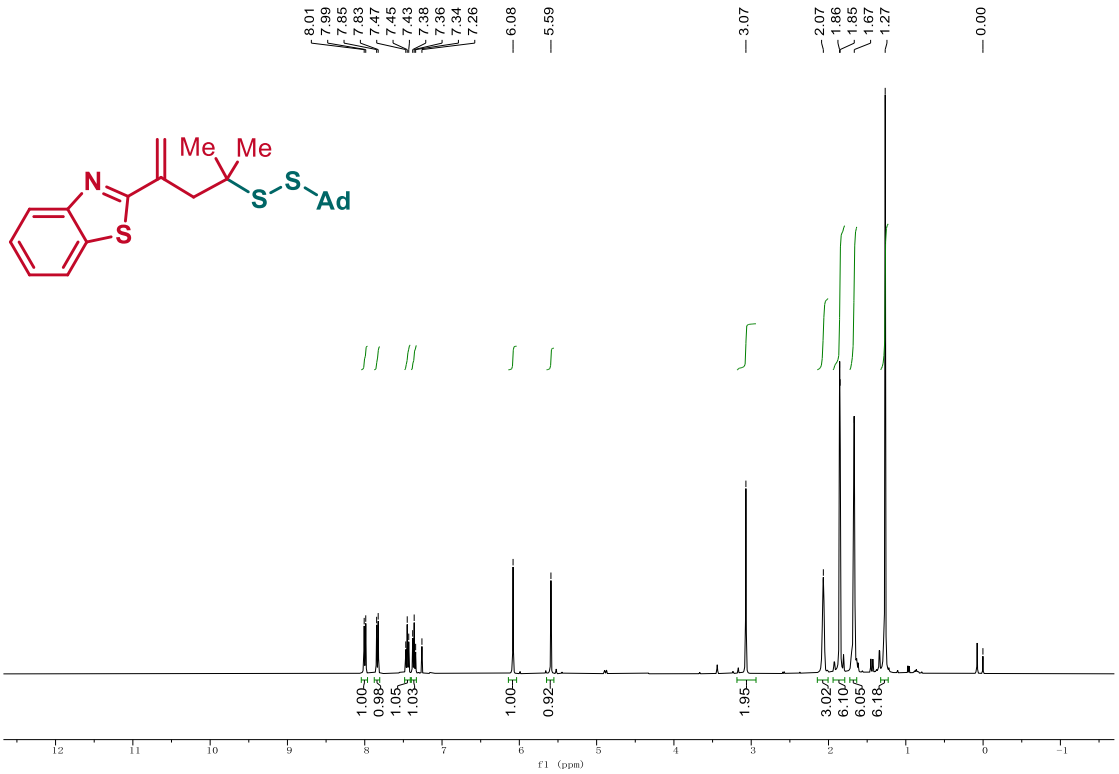
^{1}H NMR Spectrum of 3-((4-(benzo[*d*]thiazol-2-yl)-2-methylpent-4-en-2-yl) disulfaneyl)-3-methylbutan-1-ol (5g):



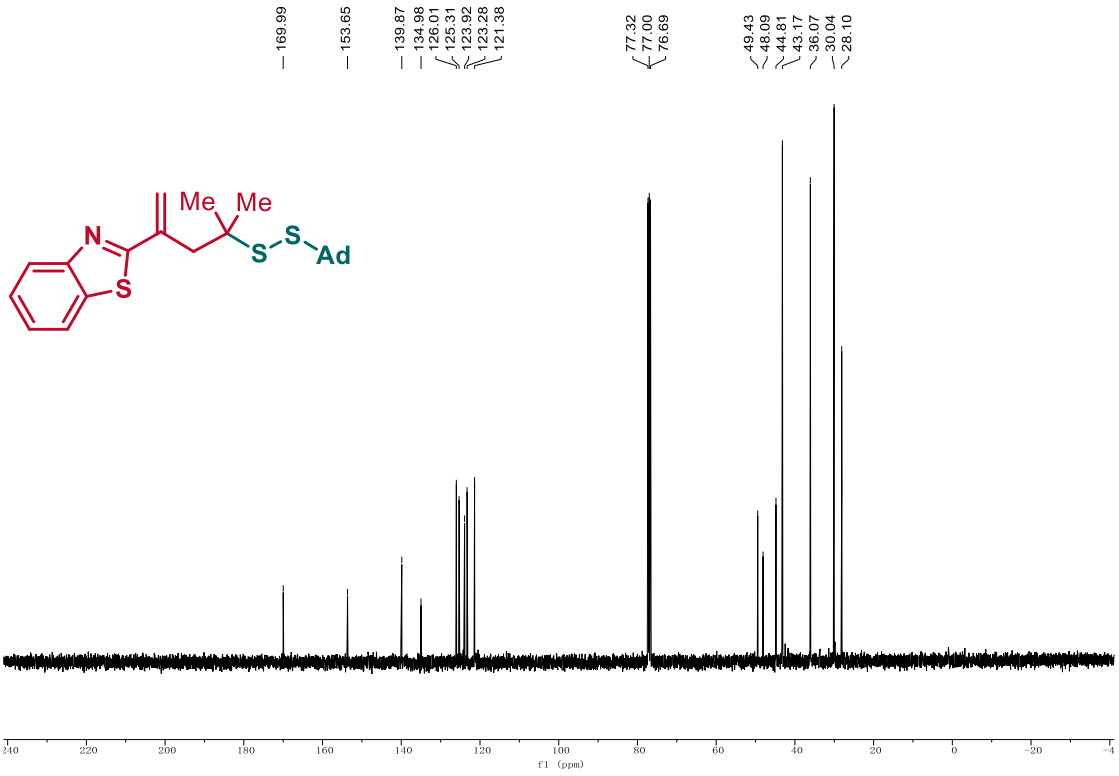
^{13}C NMR Spectrum of 3-((4-(benzo[*d*]thiazol-2-yl)-2-methylpent-4-en-2-yl) disulfaneyl)-3-methylbutan-1-ol (5g):



^{1}H NMR Spectrum of 2-(4-(((3*s*,5*s*,7*s*)-adamantan-1-yl)disulfaneyl)-4-methylpent-1-en-2-yl) benzo[*d*]thiazole (5f):



^{13}C NMR Spectrum of 2-(4-(((3*s*,5*s*,7*s*)-adamantan-1-yl)disulfaneyl)-4-methylpent-1-en-2-yl) benzo[*d*]thiazole (5f):



7. References

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