Supporting information

Photocatalytic Selective Disulfuration of Aryl Aldehydes and Alkenyl Aldehydes with Dithiosulfonate as Bifunctional Disulfur Reagent and Hydrogen Atom Accepter

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Table of Contents

1. General

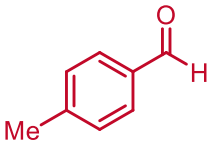
All reactions involving air- or moisture-sensitive reagents or intermediates were carried out in flame-dried glassware under an argon atmosphere using standard *Schlenk* techniques. All solvents were freshly distilled and degassed according to the handbook *Purification of Laboratory Chemicals* (4th 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 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 $CDCl_3$, DMSO-d_6 as solvent. Chemical shifts (ppm) are given relative to solvent: references for $CDCl_3$ were 7.26 ppm (^{1}H NMR) and 77.16 ppm (^{13}C NMR); references for DMSO-d_6 were 2.50 ppm (^{1}H NMR) and 39.52 ppm (^{13}C NMR); references for D_2O were 4.79 ppm (^{1}H 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.

2. Preparation of starting materials

2.1 Preparation of aryl aldehydes 1 and alkenyl aldehydes 4

Aldehydes **1a** – **1x**, **1z** – **1aa**, **1ac** – **1ag** are commercially available from Energy Chemical, Aladdin, Leyan. All commercially available aldehydes were used as received. Aldehydes **1y**,[1] **1ab**,[2] **1ai**,[3] **1al**,[4] **1ao**[5] were prepared according to previously reported literature procedures. Aldehydes **1ah**, **1aj**, **1ak**, **1am**, **1an** were prepared according to the following procedure.

Alkenyl aldehydes **4a** – **4v** were prepared according to previously reported literature procedures.[6]



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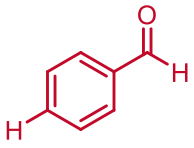

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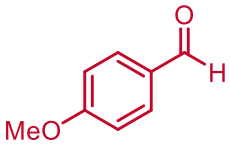

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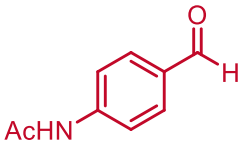

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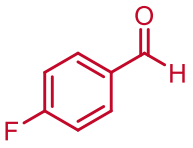

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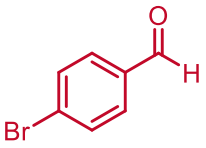

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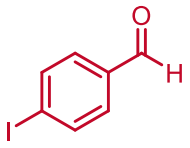

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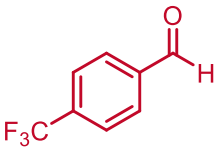

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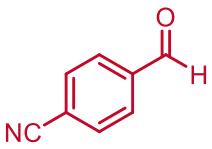

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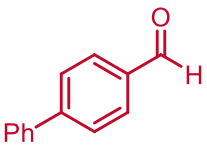

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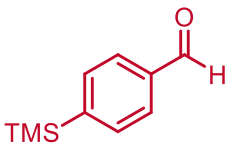

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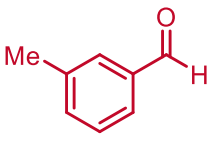

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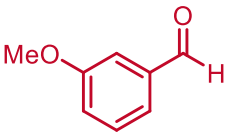

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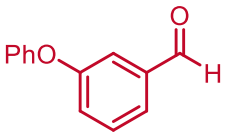

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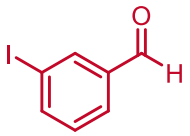

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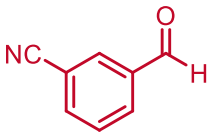

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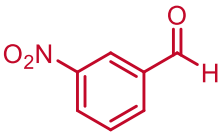

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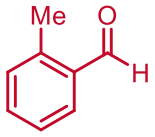

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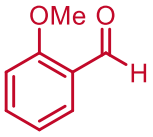

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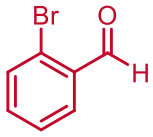

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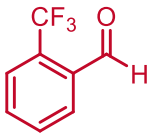

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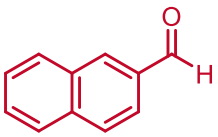

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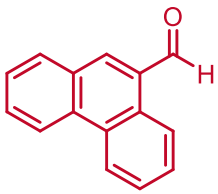

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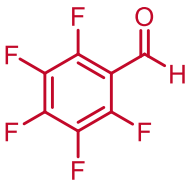

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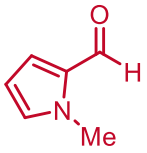

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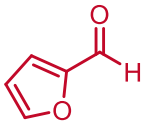

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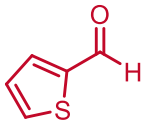

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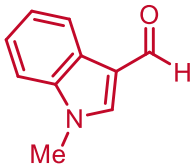

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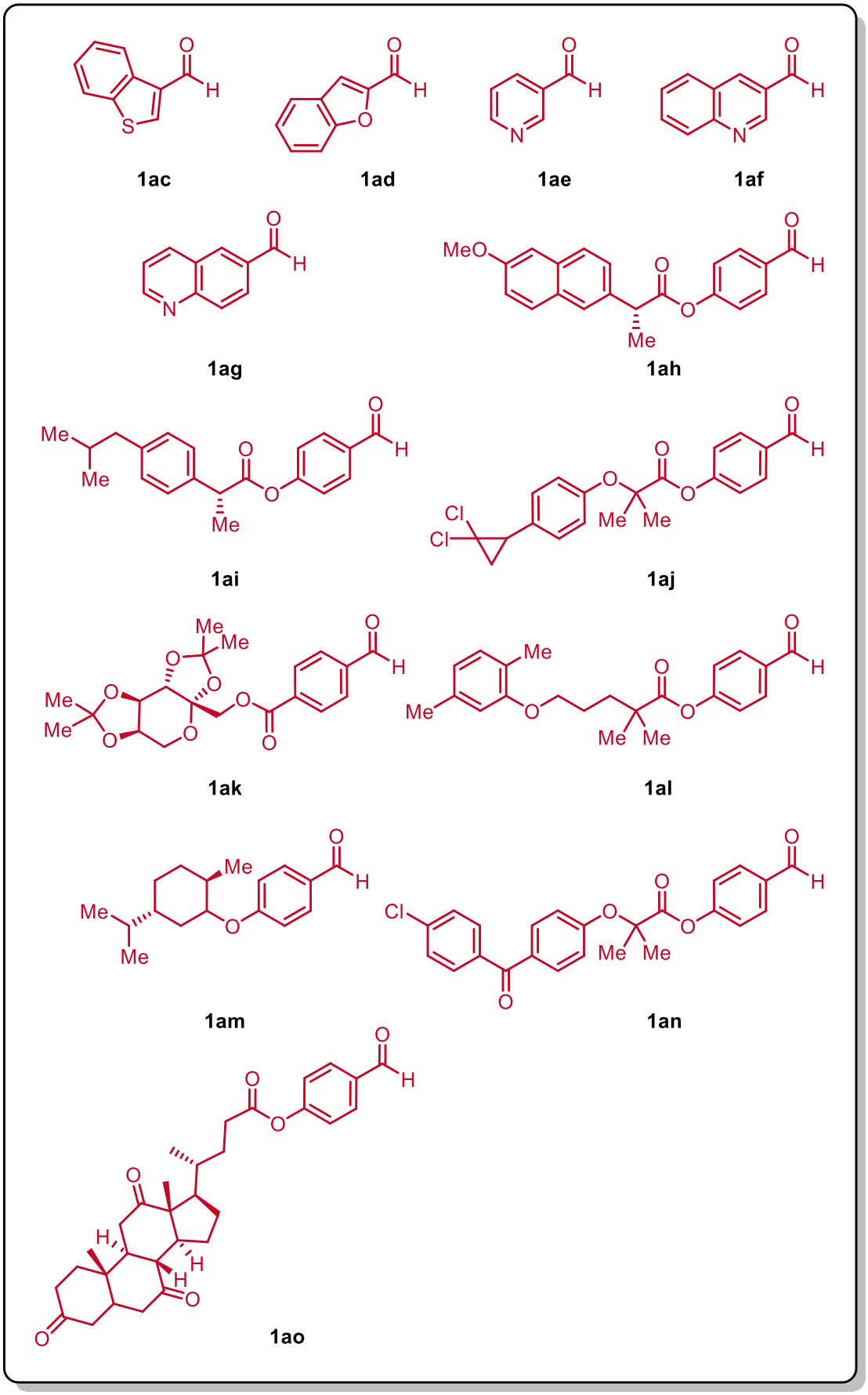
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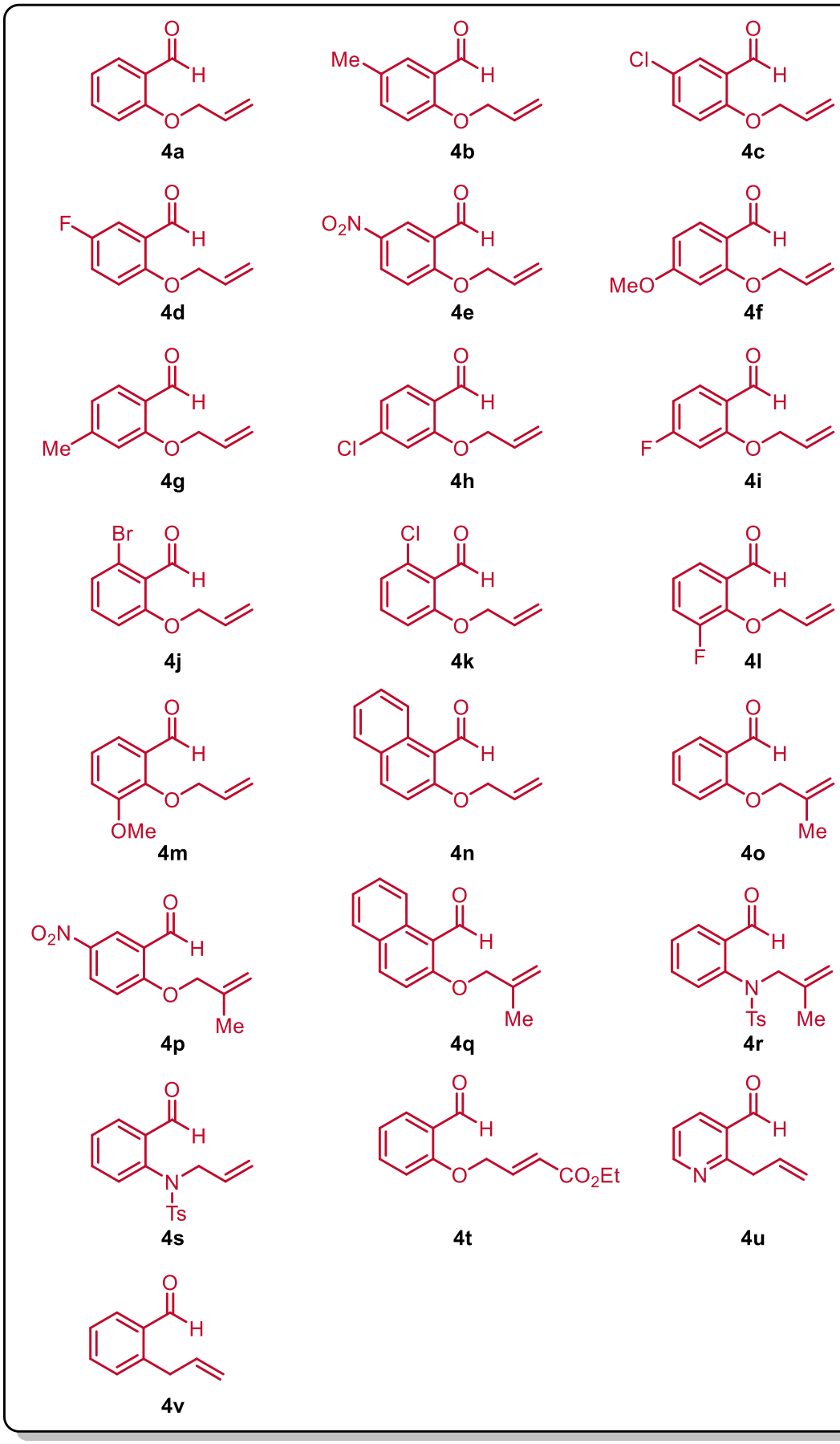
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4q
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4s
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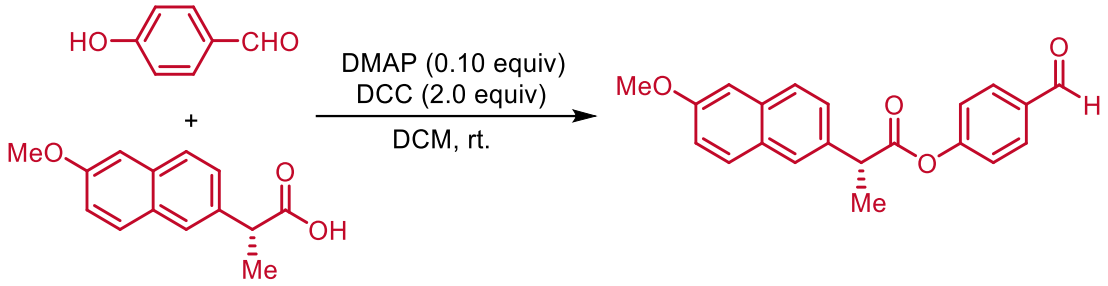
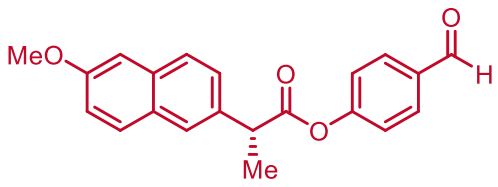
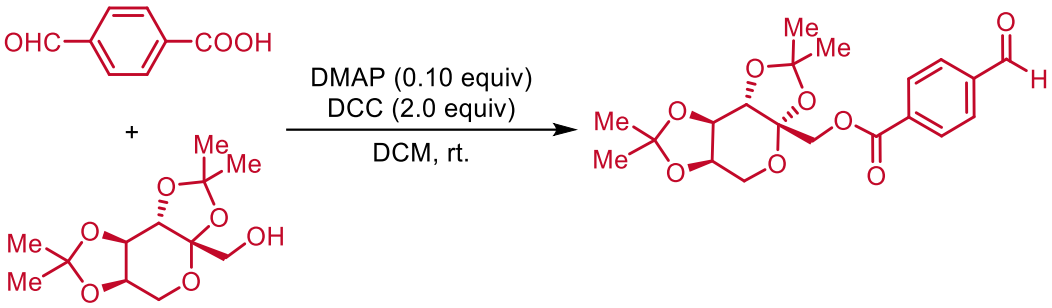
4u
4v

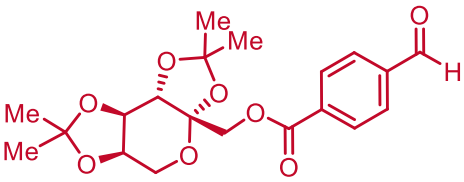
Preparation of aldehydes 1ah, 1aj, 1ak, 1am, and 1an



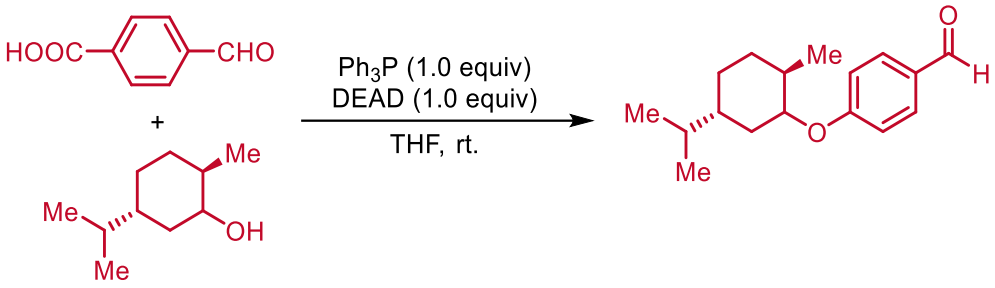


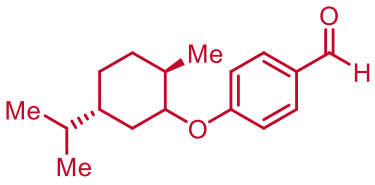
4-Formylphenyl (*R*)-2-(6-methoxynapht-h alen-2-yl)propanoate (1ah): A flame-dried Schlenk-flask equipped with a magnetic stir bar, was charged with 4-hydroxybenzaldehyde (1.221 g, 10.00 mmol, 1.0 equiv), (*R*)-2-(6-methoxynaphthalen-2-yl)propanoic acid (2.763 g, 12.00 mmol, 1.2 equiv), and DCC (4.127g, 20.00 mmol, 2.0 equiv), sealed with a septum, and degassed by alternating vacuum evacuation and nitrogen backfilling (three times) before DCM (25 mL) was added. Then DMAP (0.122 g, 1.00 mmol, 0.10 equiv) was added to the mixture under positive pressure. The reaction mixture was stirred at room temperature for 12 h. After the reaction was complete, the reaction mixture was diluted with DCM (30 mL) 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 (PE:EtOAc = 5:1) to give the corresponding pure aromatic aldehyde **1ah** as a white solid in 68% yield (2.2740 g). **TLC R_f** = 0.4 (PE:EtOAc = 3:1); **MP**: = 68 – 69 °C; **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 9.95 (s, 1H), 7.85 (d, *J* = 8.6 Hz, 2H), 7.81 – 7.70 (m, 3H), 7.50 (dd, J^1 = 8.6 Hz, J^2 = 1.7 Hz, 1H), 7.22 – 7.10 (m, 4H), 4.13 (q, *J* = 7.2 Hz, 1H), 3.92 (s, 3H), 1.72 (d, *J* = 7.2 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 190.8, 172.4, 157.8, 155.5, 134.6, 133.9, 133.8, 131.0, 129.2, 128.9, 127.5, 126.1, 125.9, 122.1, 119.2, 105.6, 55.2, 45.5, 18.3; **HRMS** (EI) *m*/*z* = 334.1205 calcd. for $C_{21}H_{18}O_4$ $[M]^+$, found: 334.1211; **IR** (neat, cm^{-1}): 2935*w*, 2848*w*, 1755*s*, 1698*s*, 1633*w*, 1599*s*, 1503*m*, 1462*w*, 1392*m*, 1264*m*, 1205*s*, 1155*s*, 1125*s*, 1067*s*, 1031*s*, 892*m*, 854*s*, 730*m*, 685*w*, 508*w*, 475*w*.



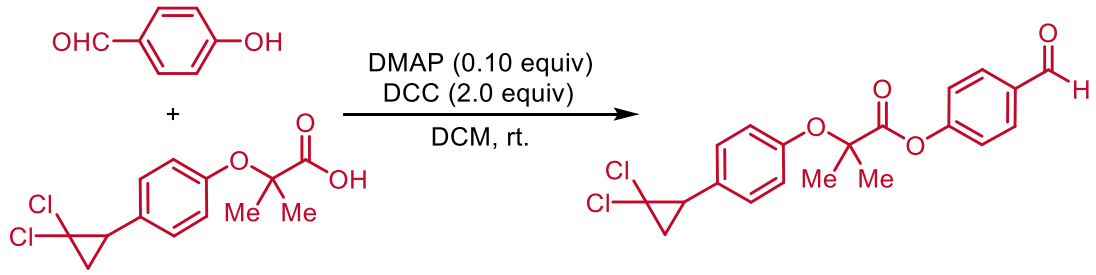


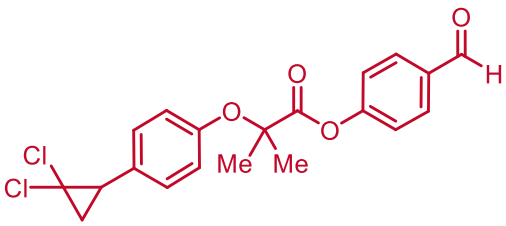
((3a*S*,5a*R*,8a*R*,8b*S*)-2,2,7,7-Tetramethyltetrahydro 3a*H*-bis([1,3]dioxolo)[4,5-*b*:4',5'-*d*]pyran-3a-yl)methyl 4-formylbenzoate (1aj): A flame-dried Schlenk-flask equipped with a magnetic stir bar, was charged with 4-formylbenzoic acid (1.802 g, 12.00 mmol, 1.2 equiv), ((3a*S*,5a*R*,8a*R*,8b*S*) -2,2,7,7-tetramethyltetrahydro-3a*H*-bis([1,3]dioxolo) [4,5-*b*:4',5'-*d*] pyran-3a-yl) methanol (2.207 g, 10.00 mmol, 1.0 equiv), and DCC (4.127g, 20.00 mmol, 2.0 equiv), sealed with a septum, and degassed by alternating vacuum evacuation and nitrogen backfilling (three times) before DCM (25 mL) was added. Then DMAP (0.122 g, 1.00 mmol, 0.10 equiv) was added to the mixture under positive pressure. The reaction mixture was stirred at room temperature for 12 h. After the reaction was complete, the reaction mixture was diluted with DCM (30 mL) 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 (PE:EtOAc = 15:1) to give the corresponding pure aromatic aldehyde **1aj** as a white solid in 26% yield (1.0195 g). **TLC R_f** = 0.4 (PE:EtOAc = 5:1); **MP**: = 84 – 86 °C; **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 10.10 (s, 1H), 8.23 (d, *J* = 8.3 Hz, 2H), 7.95 (d, *J* = 8.5 Hz, 2H), 4.71 (d, *J* = 11.8 Hz, 1H), 4.64 (dd, J^1 = 7.9 Hz, J^2 = 2.6 Hz, 1H), 4.44 (d, *J* = 2.6 Hz, 1H), 4.36 (d, *J* = 11.8 Hz, 1H), 4.26 (dd, J^1 = 7.9 Hz, J^2 = 1.1 Hz, 1H), 3.95 (dd, J^1 = 13.0 Hz, J^2 = 1.9 Hz, 1H), 3.80 (d, *J* = 13.2 Hz, 1H), 1.55 (s, 3H), 1.45 (s, 3H), 1.35 (d, *J* = 4.7 Hz, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 191.5, 165.0, 139.2, 134.9, 130.4, 129.5, 109.2, 108.9, 101.5, 70.7, 70.7, 70.1, 66.0, 61.4, 26.5, 25.9, 25.4, 24.0; **HRMS** (ESI) *m*/*z* = 415.1363 calcd. for $C_{20}H_{24}NaO_8$ $[M+Na]^+$, found: 415.1365; **IR** (neat, cm^{-1}): 2991*w*, 2935*w*, 1729*s*, 1706*s*, 1456*w*, 1375*s*, 1252*s*, 1165*m*, 1103*s*, 1089*s*, 1018*w*, 979*w*, 890*w*, 758*m*.



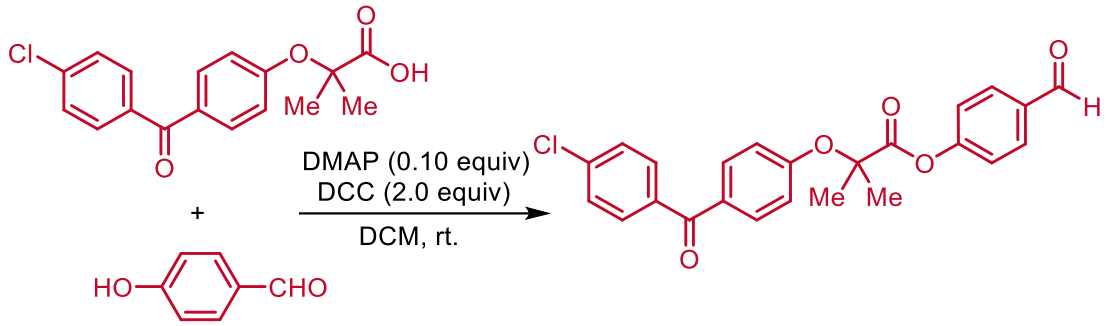


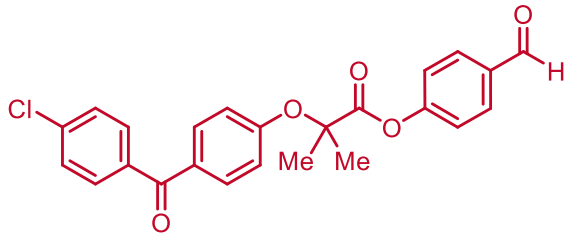
4(((2*R*,5*R*)-5-Isopropyl-2-methylcyclohexyl)oxy)benzaldehyde (1ak): A flame-dried Schlenk-flask equipped with a magnetic stir bar, was charged with 4-formylbenzoic acid (1.221 g, 10.00 mmol, 1.0 equiv), L-Menthol (1.563 g, 10.00 mmol, 1.0 equiv), and triphenylphosphine (2.623g, 10.00 mmol, 1.0 equiv), sealed with a septum, and degassed by alternating vacuum evacuation and nitrogen backfilling (three times) before THF (15 mL) was added. Then DEAD (1.742 g, 10.00 mmol, 1.0 equiv) in THF (10 mL) was added to the mixture under positive pressure. The reaction mixture was stirred at room temperature for 30 h. After the reaction was complete, the reaction mixture was diluted with DCM (30 mL) 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 (PE:EtOAc = 20:1) to give the corresponding pure aromatic aldehyde **1ak** as a colorless liquid in 63% yield (1.640 g). **TLC R_f** = 0.4 (PE:EtOAc = 20:1); **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 9.83 (s, 1H), 7.79 (d, *J* = 8.7 Hz, 2H), 6.96 (d, *J* = 8.7 Hz, 2H), 4.73 (s, 1H), 2.11 – 2.02 (m, 1H), 1.79 – 1.71 (m, 2H), 1.61 (dd, J^1 = 15.3 Hz, J^2 = 6.6 Hz, 2H), 1.53 (td, J^1 = 13.6 Hz, J^2 = 12.7 Hz, J^3 = 4.3 Hz, 1H), 1.09 – 0.93 (m, 3H), 0.90 (d, *J* = 6.7 Hz, 3H), 0.80 (m, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 190.6, 163.6, 132.1, 129.4, 115.5, 73.9, 47.5, 37.5, 34.8, 29.3, 26.2, 24.8, 22.2, 21.0, 20.7; **HRMS** (ESI) *m*/*z* = 283.1669 calcd. for $C_{17}H_{24}NaO_2$ $[M+Na]^+$, found: 283.1669; **IR** (neat, cm^{-1}): 2947*m*, 2924*m*, 2867*w*, 1690*s*, 1599*s*, 1576*m*, 1508*m*, 1456*w*, 1428*w*, 1308*m*, 1251*s*, 1216*m*, 1199*m*, 1154*s*, 1108*w*, 1022*m*, 959*m*, 937*m*, 891*w*, 874*w*, 828*s*.





4-Formylphenyl 2-(4-(2,2-dichlorocyclopopyl)phenoxy)-2-methylpropanoate (1am): A flame-dried Schlenk-flask equipped with a magnetic stir bar, was charged with 4-hydroxybenzaldehyde (1.221 g, 10.00 mmol, 1.0 equiv), 2-(4-(2,2-dichlorocyclopropyl)phenoxy)-2-methylpropanoic acid (3.470 g, 12.00 mmol, 1.2 equiv), and DCC (4.127g, 20.00 mmol, 2.0 equiv), sealed with a septum, and degassed by alternating vacuum evacuation and nitrogen backfilling (three times) before DCM (25 mL) was added. Then DMAP (0.122 g, 1.00 mmol, 0.10 equiv) was added to the mixture under positive pressure. The reaction mixture was stirred at room temperature for 12 h. After the reaction was complete, the reaction mixture was diluted with DCM (30 mL) 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 (PE:EtOAc = 20:1) to give the corresponding pure aromatic aldehyde **1am** as a colorless liquid in 74% yield (2.910 g). **TLC R_f** = 0.3 (PE:EtOAc = 10:1); **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 9.97 (s, 1H), 7.89 (d, *J* = 8.6 Hz, 2H), 7.17 (d, *J* = 8.7 Hz, 2H), 7.14 (d, *J* = 8.5 Hz, 2H), 6.93 (d, *J* = 8.6 Hz, 2H), 2.86 (t, *J* = 8.0 Hz, 1H), 1.96 (dd, J^1 = 10.7 Hz, J^2 = 7.4 Hz, 1H), 1.82 – 1.77 (m, 7H); **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 190.8, 172.2, 155.1, 154.8, 134.2, 131.2, 129.8, 128.6, 122.1, 118.5, 79.3, 60.8, 34.7, 25.8, 25.4; **HRMS** (ESI) *m*/*z* = 415.0474 calcd. for $C_{20}H_{18}Cl_2NaO_4$ $[M+Na]^+$, found: 415.0482; **IR** (neat, cm^{-1}): 1758*m*, 1700*m*, 1599*m*, 1510*s*, 1386*w*, 1242*w*, 1209*s*, 1156*s*, 1107*s*, 906*s*, 833*s*, 728*w*, 649*s*, 509*w*.

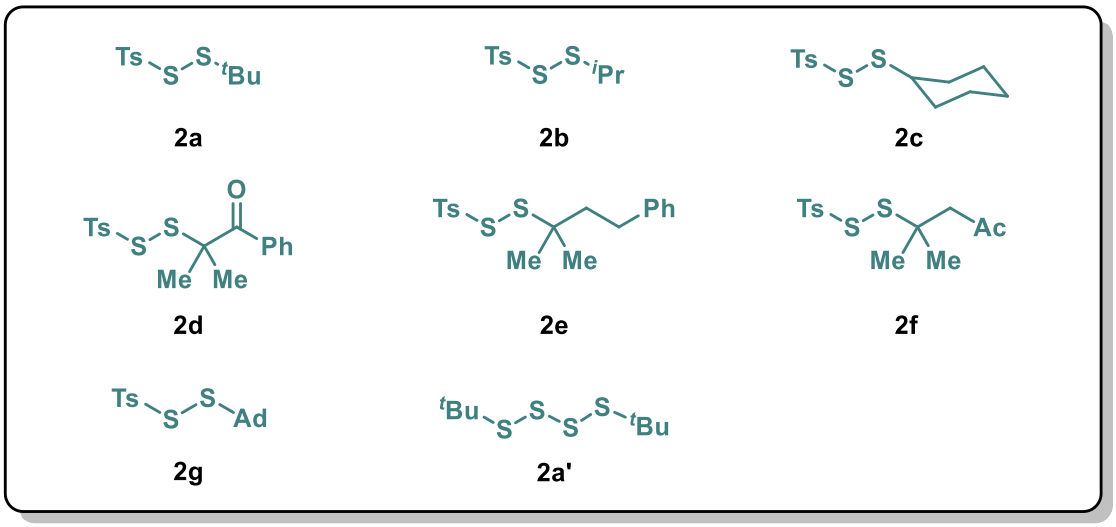




4-Formylphenyl 2-(4-(4-chloro-benzoyl)phenoxy)-2-methylpropanoate (1an): A flame-dried Schlenk-flask equipped with a magnetic stir bar, was charged with 4-hydroxybenzaldehyde (1.221 g, 10.00 mmol, 1.0 equiv), 2-(4-(4-chlorobenzoyl)phenoxy)-2-methylpropanoic acid (3.825 g, 12.00 mmol, 1.2 equiv), and DCC (4.127g, 20.00 mmol, 2.0 equiv), sealed with a septum, and degassed by alternating vacuum evacuation and nitrogen backfilling (three times) before DCM (25 mL) was added. Then DMAP (0.122 g, 1.00 mmol, 0.1 equiv) was added to the mixture under positive pressure. The reaction mixture was stirred at room temperature for 12 h. After the reaction was complete, the reaction mixture was diluted with DCM (30 mL) 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 (PE:EtOAc = 20:1) to give the corresponding pure aromatic aldehyde **1an** as a white solid in 76% yield (3.214 g); **MP**: = 103 – 105 °C;. **TLC** $\mathbf{R_f}$ = 0.3 (PE:EtOAc = 10:1); **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 9.94 (s, 1H), 7.87 (d, *J* = 8.6 Hz, 2H), 7.77 (d, *J* = 8.8 Hz, 2H), 7.68 (d, *J* = 8.5 Hz, 2H), 7.41 (d, *J* = 8.5 Hz, 2H), 7.16 (d, *J* = 8.6 Hz, 2H), 6.98 (d, *J* = 8.8 Hz, 2H), 1.82 (s, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 194.0, 190.6, 171.7, 159.2, 154.8, 138.4, 136.0, 134.2, 132.0, 131.1, 131.0, 130.7, 128.4, 121.9, 117.2, 79.3, 25.2; **HRMS** (EI) *m*/*z* = 422.0921 calcd. for $C_{24}H_{19}Cl_2ClO_5$ $[M]^+$, found: 422.0916; **IR** (neat, cm^{-1}): 1760*m*, 1700*m*, 1652*m*, 1596*s*, 1502*m*, 1386*w*, 1208*s*, 1155*s*, 1097*s*, 1013*s*, 852*s*, 763*m*, 649*m*, 478*w*.

2.2 Preparation of disulfur transfer reagents 2

The disulfur transfer reagents **2a** – **2g** and **2a'** were prepared according to the previously reported literature procedures.[7]



3. Photocatalytic selective disulfuration of aryl aldehydes and alkenyl aldehydes with dithiosulfonate as bifunctional disulfur reagent and hydrogen atom accepter

3.1 General procedure for disulfuration of aryl aldehydes (GP1)

GP1-1, for liquid aryl aldehydes and solid disulfuration reagent

A flame-dried Schlenk-tube equipped with a magnetic stir bar was charged with the dithiosulfonate reagent **2** (0.24 mmol, 1.2 equiv), phenanthrene-9,10-dione (4.2 mg, 0.020 mmol, 10 mol%), and Na_2CO_3 (25.4 mg, 0.240 mmol, 1.2 equiv), sealed with a septum, and degassed by alternating vacuum evacuation and argon backfilling (three times) before H_2O (2 mL) was added. The corresponding liquid aldehyde **1** (0.20 mmol, 1.0 equiv) was added to the mixture successively by micro-syringe. The reaction mixture was then stirred and irradiated using a 20 W blue LED lamp at room temperature for 12 h. After the reaction was completed, the mixture was diluted with EtOAc (4 mL), which was followed by extraction with EtOAc (10 mL x 3 times). 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 residue was purified by silica gel column chromatography to afford the desired product **3**.

GP1-2, for liquid aryl aldehydes and liquid disulfuration reagent

A flame-dried Schlenk-tube equipped with a magnetic stir bar was charged with phenanthrene-9,10-dione (4.2 mg, 0.020 mmol, 10 mol%) and Na_2CO_3 (25.4 mg, 0.240 mmol, 1.2 equiv), sealed with a septum, and degassed by alternating vacuum evacuation and argon backfilling (three times) before H_2O (2 mL) was added. The

liquid dithiosulfonate reagent **2** (0.24 mmol, 1.2 equiv) and the corresponding liquid aldehyde **1** (0.20 mmol, 1.0 equiv) were added to the mixture successively by micro-syringe. The reaction mixture was then stirred and irradiated using a 20 W blue LED lamp at room temperature for 12 h. After the reaction was completed, the mixture was diluted with EtOAc (4 mL), which was followed by extraction with EtOAc (10 mL x 3 times). 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 residue was purified by silica gel column chromatography to afford the desired desired product **3**.

GP1-3, for solid aryl aldehydes and solid disulfuration reagent

A flame-dried Schlenk-tube equipped with a magnetic stir bar was charged with the corresponding solid aldehyde **1** (0.20 mmol, 1.0 equiv), phenanthrene-9,10-dione (4.2 mg, 0.020 mmol, 10 mol%), Na_2CO_3 (25.4 mg, 0.240 mmol, 1.3 equiv), and the dithiosulfonate reagent **2** (0.24 mmol, 1.2 equiv), sealed with a septum, and degassed by alternating vacuum evacuation and argon backfilling (three times) before H_2O (2 mL) was added. The reaction mixture was then stirred and irradiated using a 20 W blue LED lamp at room temperature for 12 h. After the reaction was completed, the mixture was diluted with EtOAc (4 mL), which was followed by extraction with EtOAc (10 mL x 3 times). 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 residue was purified by silica gel column chromatography to afford the desired product **3**.

GP1-4, for solid aryl aldehydes and liquid disulfuration reagent

A flame-dried Schlenk-tube equipped with a magnetic stir bar was charged with the corresponding solid aldehyde **1** (0.20 mmol, 1.0 equiv), phenanthrene-9,10-dione (4.2 mg, 0.020 mmol, 10 mol%), and Na_2CO_3 (25.4 mg, 0.240 mmol, 1.2 equiv), sealed with a septum, and degassed by alternating vacuum evacuation and argon backfilling (three times) before H_2O (2 mL) was added. The liquid dithiosulfonate reagent **2** (0.24 mmol, 1.2 equiv) was added to the mixture successively by micro-syringe. The reaction mixture was then stirred and irradiated using a 20 W blue LED lamp at room temperature for 12 h. After the reaction was completed, the mixture was diluted with EtOAc (4 mL), which was followed by extraction with EtOAc (10 mL x 3 times). 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 residue was purified by silica gel column chromatography to afford the desired product **3**.

3.2 General procedure for disulfuration of alkenyl aldehydes (GP2)

GP2-1, for liquid alkenyl aldehydes and solid disulfuration reagent

A flame-dried Schlenk-tube equipped with a magnetic stir bar was charged with the dithiosulfonate reagent **2** (0.40 mmol, 2.0 equiv), phenanthrene-9,10-dione (4.2 mg, 0.020 mmol, 10 mol%), and Na_2CO_3 (27.3 mg, 0.260 mmol, 1.3 equiv), sealed with a septum, and degassed by alternating vacuum evacuation and argon backfilling (three times) before MeCN (2 mL) was added. The corresponding liquid alkenyl aldehyde **4** (0.20 mmol, 1.0 equiv) was added to the mixture successively by micro-syringe. The reaction mixture was then stirred and irradiated using a 20 W blue LED 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. The crude residue was purified by silica gel column chromatography to afford the desired product **5**.

GP2-2, for liquid alkenyl aldehydes and liquid disulfuration reagent

A flame-dried Schlenk-tube equipped with a magnetic stir bar was charged with phenanthrene-9,10-dione (4.2 mg, 0.020 mmol, 10 mol%), and Na_2CO_3 (27.3 mg, 0.260 mmol, 1.3 equiv), sealed with a septum, and degassed by alternating vacuum evacuation and argon backfilling (three times) before MeCN (2 mL) was added. The liquid dithiosulfonate reagent **2** (0.40 mmol, 2.0 equiv) and the corresponding liquid alkenyl aldehyde **4** (0.20 mmol, 1.0 equiv) were added to the mixture successively by micro-syringe. The reaction mixture was then stirred and irradiated using a 20 W blue LED 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. The crude residue was purified by silica gel column chromatography to afford the desired desired product **5**.

GP2-3, for solid alkenyl aldehydes and solid disulfuration reagent

A flame-dried Schlenk-tube equipped with a magnetic stir bar was charged with the corresponding solid alkenyl aldehyde **4** (0.20 mmol, 1.0 equiv), phenanthrene-9,10-dione (4.2 mg, 0.020 mmol, 10 mol%), Na_2CO_3 (27.3 mg, 0.260 mmol, 1.3 equiv), and the dithiosulfonate reagent **2** (0.40 mmol, 2.0 equiv), sealed with a septum, and degassed by alternating vacuum evacuation and argon backfilling (three times) before MeCN (2 mL) was added. The reaction mixture was then stirred and irradiated using a 20 W blue LED 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. The crude residue was purified by silica gel column chromatography to afford the desired product **5**.

GP2-4, for solid alkenyl aldehydes and liquid disulfuration reagent

A flame-dried Schlenk-tube equipped with a magnetic stir bar was charged with the corresponding solid alkenyl aldehyde **4** (0.20 mmol, 1.0 equiv), phenanthrene-9,10-dione (4.2 mg, 0.020 mmol, 10 mol%), and Na_2CO_3 (27.3 mg, 0.260 mmol, 1.3 equiv), sealed with a septum, and degassed by alternating vacuum evacuation and argon backfilling (three times) before MeCN (2 mL) was added. The liquid dithiosulfonate reagent **2** (0.40 mmol, 2.0 equiv) was added to the mixture successively by micro-syringe. The reaction mixture was then stirred and irradiated using a 20 W blue LED 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. The crude residue was purified by silica gel column chromatography to afford the desired product **5**.

3.3 Screening of reaction conditions

General procedure for optimization of reaction conditions of 3a (GP3)

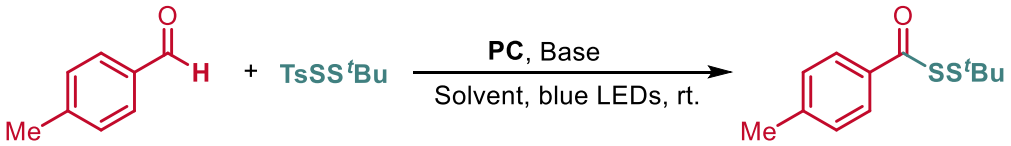
GP3-1, for solid base

A flame-dried Schlenk-tube equipped with a magnetic stir bar was charged with the dithiosulfonate reagent **2a**, **PC** (0.010 mmol, 10 mol%), and solid base, sealed with a septum, and degassed by alternating vacuum evacuation and argon backfilling (three times) before solvent (1 mL) was added. The liquid aldehyde **1a** (0.10 mmol, 1.0 equiv) was added to the mixture successively by micro-syringe. The reaction mixture was then stirred and irradiated using a 20 W blue LED lamp at room temperature for 12 h. After the reaction was completed, the mixture was diluted with EtOAc (4 mL), which was followed by extraction with EtOAc (10 mL x 3 times). 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 residue was purified by silica gel column chromatography to afford the desired product **3a**.

GP3-2, for liquid base

A flame-dried Schlenk-tube equipped with a magnetic stir bar was charged with the dithiosulfonate reagent **2a**, and **PC** (0.010 mmol, 10 mol%), sealed with a septum, and degassed by alternating vacuum evacuation and argon backfilling (three times) before solvent (1 mL) was added. The liquid base and aldehyde **1a** (0.10 mmol, 1.0 equiv) were added to the mixture successively by micro-syringe. The reaction mixture was then stirred and irradiated using a 20 W blue LED lamp at room temperature for 12 h. After the reaction was completed, the mixture was diluted with EtOAc (4 mL), which was followed by extraction with EtOAc (10 mL x 3 times). The combined

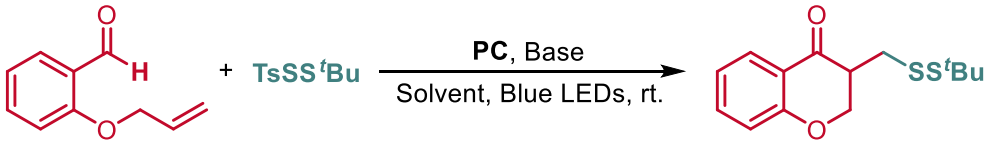
organic phase was washed with brine (10 mL), dried with Na_2SO_4 and the solvent was evaporated with the aid of a rotary evaporator. The crude residue was purified by silica gel column chromatography to afford the desired product **3a**.



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

Entry[a]	PC	2 (equiv)	Base (equiv)	Solvent	Yield (%)[b]
1	**PC 1**	**2a** (1.2 equiv)	Na_2CO_3 (1.2 equiv)	MeCN	trace
2	**PC 2**	**2a** (1.2 equiv)	Na_2CO_3 (1.2 equiv)	MeCN	trace
3	**PC 3**	**2a** (1.2 equiv)	Na_2CO_3 (1.2 equiv)	MeCN	39
4	**PC 4**	**2a** (1.2 equiv)	Na_2CO_3 (1.2 equiv)	MeCN	84
5	**PC 4**	**2a** (1.2 equiv)	Cs_2CO_3 (1.2 equiv)	MeCN	34
6	**PC 4**	**2a** (1.2 equiv)	K_2CO_3 (1.2 equiv	MeCN	60
7	**PC 4**	**2a** (1.2 equiv)	$NaHCO_3$ (1.2 equiv)	MeCN	62
8	**PC 4**	**2a** (1.2 equiv)	DIPEA (1.2 equiv)	MeCN	trace
9	**PC 4**	**2a** (1.2 equiv)	Et_3N (1.2 equiv)	MeCN	trace
10	**PC 4**	**2a** (1.2 equiv)	DBU (1.2 equiv)	MeCN	22
11	**PC 4**	**2a** (1.2 equiv)	DMAP (1.2 equiv)	MeCN	13
12	**PC 4**	**2a** (1.2 equiv)	DABCO(1.2 equiv)	MeCN	18
13	**PC 4**	**2a** (1.2 equiv)	Na_2CO_3 (1.2 equiv)	DCM	66
14	**PC 4**	**2a** (1.2 equiv)	Na_2CO_3 (1.2 equiv)	DMF	trace
15	**PC 4**	**2a** (1.2 equiv)	Na_2CO_3 (1.2 equiv)	Toluene	38
16	**PC 4**	**2a (1.2 equiv)**	**Na_2CO_3 (1.2 equiv)**	**H_2O**	**94**
17[c]	**PC 4**	**2a** (1.2 equiv)	Na_2CO_3 (1.2 equiv)	H_2O	55
18[d]	**PC 4**	**2a** (1.2 equiv)	Na_2CO_3 (1.2 equiv)	H_2O	59
19[e]	**PC 4**	**2a** (1.2 equiv)	Na_2CO_3 (1.2 equiv	H_2O	66
20	**PC 4**	**2a'** (1.2 equiv)	Na_2CO_3 (1.2 equiv)	H_2O	12
21	**PC 5**	**2a** (1.2 equiv)	Na_2CO_3 (1.2 equiv)	H_2O	nd.
22	**PC 4**	**2a** (1.5 equiv)	Na_2CO_3 (1.2 equiv)	H_2O	87
23	**PC 4**	**2a** (1.2 equiv)	Na_2CO_3 (1.5 equiv)	H_2O	84
24	**PC 4**	**2a** (1.2 equiv)	none	H_2O	35
25[f]	**PC 4**	**2a** (1.2 equiv)	Na_2CO_3 (1.2 equiv)	H_2O	nd.
26	none	**2a** (1.2 equiv)	Na_2CO_3 (1.2 equiv)	H_2O	nd.
27	**PC 5**	**2a** (1.2 equiv)	Na_2CO_3 (1.2 equiv)	H_2O	nd.
28	**PC4**	**2a'** (1.2 equiv)	Na_2CO_3 (1.2 equiv)	H_2O	12

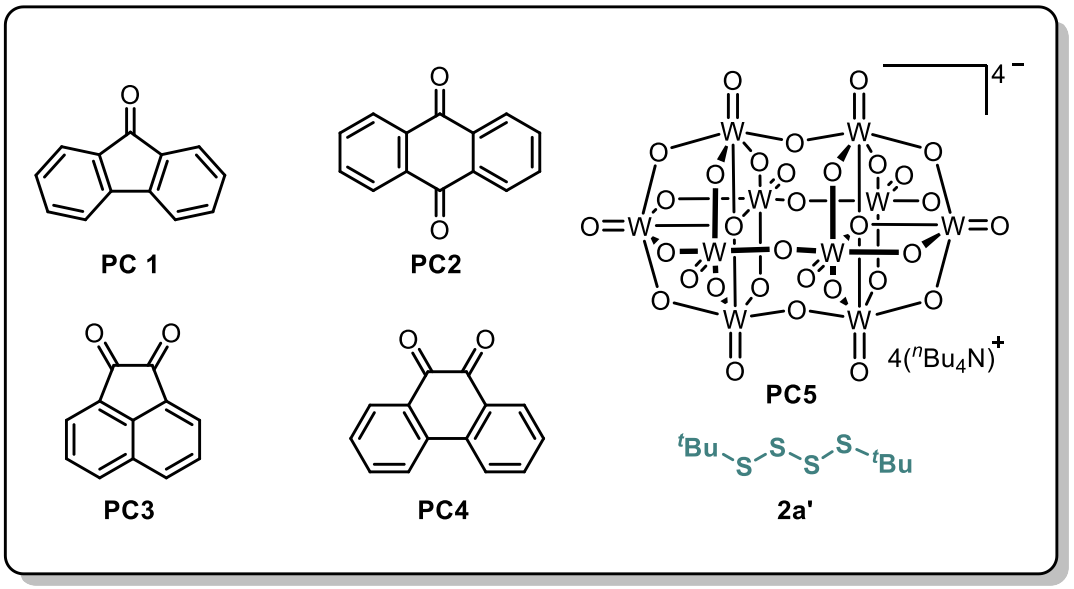
[a]Reaction condition: **1a** (0.10 mmol, 1.0 equiv), **2a**, **PC** (10 mol%), base, solvent (1 mL), blue LEDs, room temperature, 12 h. [b]Isolated yield. "nd." stands for "not detected". [c]The reaction was conducted with CFL as light souree. [d]The reaction was conducted with green LEDs as light source. [e]The reaction was conducted with white LEDs as light source. [f]The reaction was conducted in the dark.



4a **2a** **5a**

Entry[a]	PC	2 (equiv)	Base (equiv)	Solvent	Yield (%)[b]
1	**PC 1**	**2a** (1.2 equiv)	Na_2CO_3 (1.2 equiv)	MeCN	trace
2	**PC 2**	**2a** (1.2 equiv)	Na_2CO_3 (1.2 equiv)	MeCN	trace
3	**PC 3**	**2a** (1.2 equiv)	Na_2CO_3 (1.2 equiv)	MeCN	nd.
4	**PC 4**	**2a** (1.2 equiv)	Na_2CO_3 (1.2 equiv)	MeCN	39
5	**PC 5**	**2a** (1.2 equiv)	Na_2CO_3 (1.2 equiv)	MeCN	nd.
6	**PC 4**	**2a** (1.5 equiv)	Na_2CO_3 (1.2 equiv)	MeCN	61
7	**PC 4**	**2a** (1.8 equiv)	Na_2CO_3 (1.2 equiv)	MeCN	71
8	**PC 4**	**2a** (2.0 equiv)	Na_2CO_3 (1.2 equiv)	MeCN	80
9	**PC 4**	**2a** (2.0 equiv)	Na_2CO_3 (1.2 equiv)	Toluene	trace
10	**PC 4**	**2a** (2.0 equiv)	Na_2CO_3 (1.2 equiv)	Dioxane	nd.
11	**PC 4**	**2a** (2.0 equiv)	Na_2CO_3 (1.2 equiv)	CH_3Cl_3	21
12	**PC 4**	**2a** (2.0 equiv)	Na_2CO_3 (1.2 equiv)	H_2O	nd.
13	**PC 4**	**2a** (2.0 equiv)	Na_2CO_3 (1.2 equiv)	THF	24
14	**PC 4**	**2a** (2.0 equiv)	Na_2CO_3 (1.2 equiv)	EA	31
15	**PC 4**	**2a** (2.0 equiv)	Na_2CO_3 (1.2 equiv)	DMF	12
16	**PC 4**	**2a** (2.0 equiv)	Na_2CO_3 (1.2 equiv)	DMSO	trace
17	**PC 4**	**2a** (2.0 equiv)	Cs_2CO_3 (1.2 equiv)	MeCN	54
18	**PC 4**	**2a** (2.0 equiv)	K_2CO_3 (1.2 equiv)	MeCN	41
19	**PC 4**	**2a** (2.0 equiv)	$NaHCO_3$ (1.2 equiv)	MeCN	25
20	**PC 4**	**2a** (2.0 equiv)	NaOH (1.2 equiv)	MeCN	30
21	**PC 4**	**2a** (2.0 equiv)	DABCO (1.2 equiv)	MeCN	36
22	**PC 4**	**2a (2.0 equiv)**	**Na_2CO_3(1.3 equiv)**	**MeCN**	**84**
23	**PC 4**	**2a** (2.0 equiv)	Na_2CO_3 (1.4 equiv)	MeCN	83
24	**PC 4**	**2a** (2.0 equiv)	Na_2CO_3 (1.5 equiv)	MeCN	76
25[c]	**PC 4**	**2a** (2.0 equiv)	Na_2CO_3 (1.3 equiv)	MeCN	nd.
26	none	**2a** (2.0 equiv)	Na_2CO_3 (1.3 equiv)	MeCN	nd.

[a]Reaction condition: **4a** (0.10 mmol, 1.0 equiv), **2a**, PC (10.0 mol%), base, solvent (2 mL), blue LEDs, room temperature, 12 h. [b]Isolated yield. "nd." stands for "not detected". [c]The reaction was conducted in the dark.



General procedure for optimization of reaction conditions of 5a (GP4)

GP4-1, for solid base

A flame-dried Schlenk-tube equipped with a magnetic stir bar was charged with the dithiosulfonate reagent **2a**, **PC** (0.010 mmol, 10 mol%), and solid base, sealed with a septum, and degassed by alternating vacuum evacuation and argon backfilling (three times) before solvent (1 mL) was added. The alkenyl aldehyde **4a** (0.10 mmol, 1.0 equiv) was added to the mixture successively by micro-syringe. The reaction mixture was then stirred and irradiated using a 20 W blue LED 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. The crude residue was purified by silica gel column chromatography to afford the desired product **5a**.

GP4-2, for liquid base

A flame-dried Schlenk-tube equipped with a magnetic stir bar was charged with the dithiosulfonate reagent **2a**, and **PC** (0.010 mmol, 10 mol%), sealed with a septum, and degassed by alternating vacuum evacuation and argon backfilling (three times) before solvent (1 mL) was added. The liquid base and alkenyl aldehyde **4a** (0.10 mmol, 1.0 equiv) were added to the mixture successively by micro-syringe. The reaction mixture was then stirred and irradiated using a 20 W blue LED 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. The crude residue was purified by silica gel column chromatography to afford the desired product **5a**.

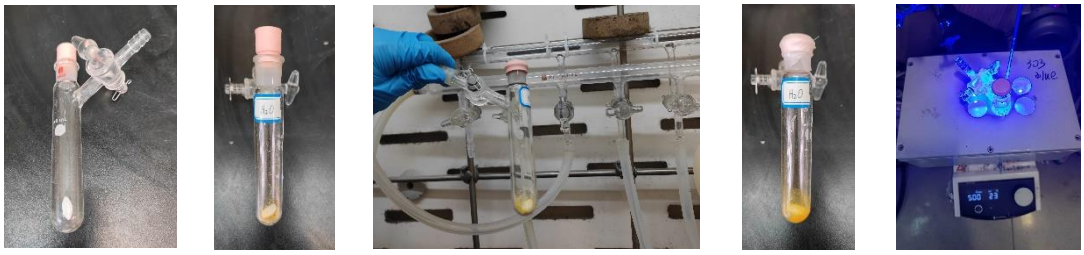


Figure S1 The reaction setup

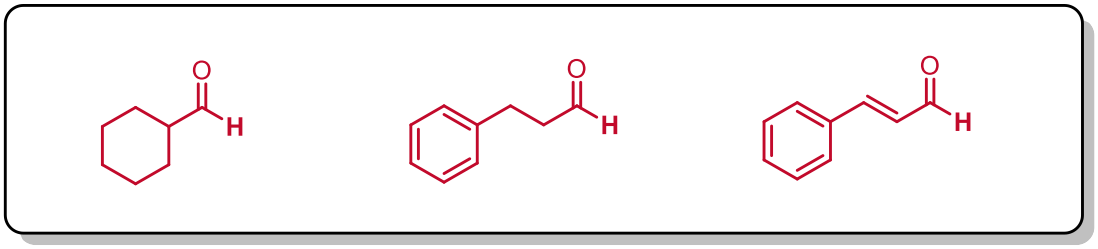


Figure S2 Inactive substrates

3.4 Gram-scale synthesis

The procedure for gram-scale synthesis of 3a

A flame-dried 250 mL Schlenk-flash equipped with a magnetic stir bar was charged with the dithiosulfonate reagent **2a** (2.650 g, 9.600 mmol, 1.2 equiv), phenanthrene-9,10-dione (166.5 mg, 0.8000 mmol, 10 mol%), and Na_2CO_3 (1.008 g, 9.600 mmol, 1.2 equiv), sealed with a septum, and degassed by alternating vacuum evacuation and argon backfilling (three times) before H_2O (80 mL) was added. The aldehyde **1a** (960.0 mg, 8.000 mmol, 1.0 equiv) was added to the mixture successively by syringe. The reaction mixture was circulated by the continuous flow platform with photoreactor and irradiated using a 20 W blue LED lamp at room temperature for 36 h. After the reaction was completed, the mixture was diluted with EtOAc (10 mL), which was followed by extraction with EtOAc (30 mL x 3 times). The combined organic phase was washed with brine (50 mL), dried with Na_2SO_4 and the solvent was evaporated with the aid of a rotary evaporator. The crude residue was purified by silica gel column chromatography to afford the desired product **3a** as a colorless liquid in 72% yield (1.3850 g).

The procedure for gram-scale synthesis of 5a

A flame-dried 250 mL Schlenk-flash equipped with a magnetic stir bar was charged with the dithiosulfonate reagent **2a** (4.420 g, 16.00 mmol, 2.0 equiv), phenanthrene-9,10-dione (166.5 mg, 0.8000 mmol, 10 mol%), and Na_2CO_3 (1.090 g, 10.40 mmol, 1.3 equiv), sealed with a septum, and degassed by alternating vacuum evacuation and argon backfilling (three times) before MeCN (80 mL) was added. The

alkenyl aldehyde **4a** (1.300 g, 8.000 mmol, 1.0 equiv) was added to the mixture successively by syringe. The reaction mixture was circulated by the continuous flow platform with photoreactor and irradiated using a 20 W blue LED lamp at room temperature for 36 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 the desired product **5a** as a colorless liquid in 70% yield (1.5815 g).

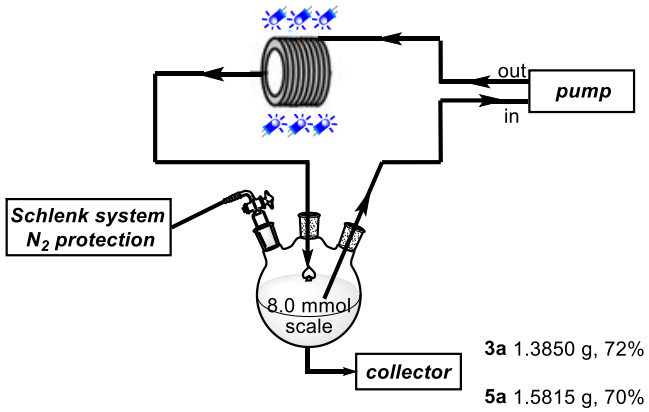
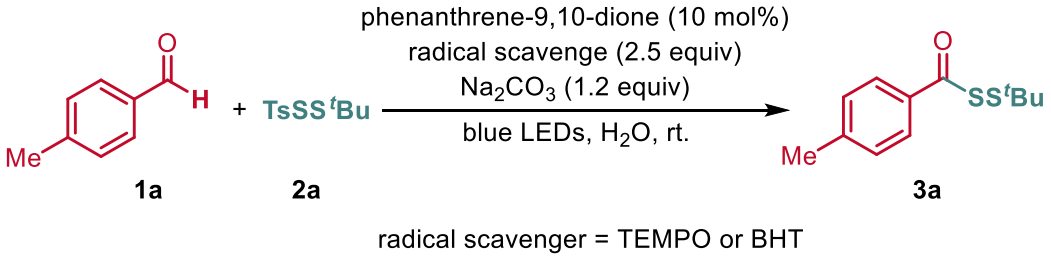


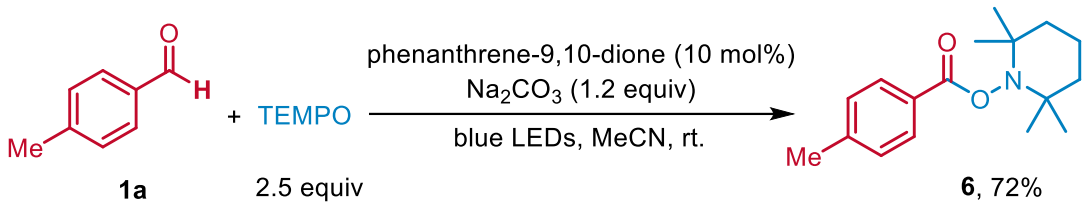
Figure S3. Schematic of the continuous flow platform with photoreactor

4. Mechanistic studies

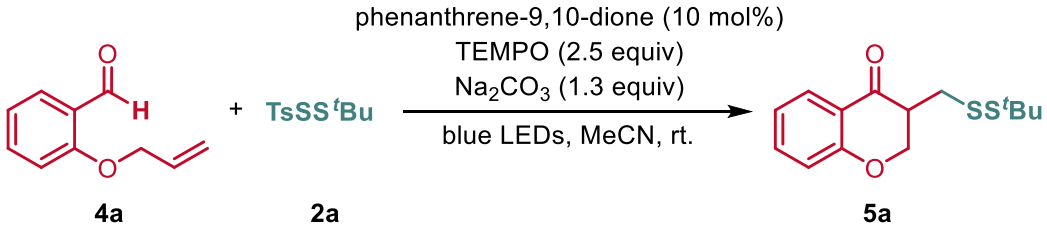


A flame-dried Schlenk-tube equipped with a magnetic stir bar was charged with the *SS*-(*tert*-butyl)4-methylbenzenesulfono(dithioperoxoate) **2a** (66.2 mg, 0.240 mmol, 1.2 equiv), phenanthrene-9,10-dione (4.2 mg, 0.020 mmol, 10 mol%), Na_2CO_3 (25.4 mg, 0.240 mmol, 1.2 equiv), and radical scavenger TEMPO (78.1 mg, 0.500 mmol, 2.5 equiv) or BHT (110.2 mg, 0.5000 mmol, 2.5 equiv), sealed with a septum, and degassed by alternating vacuum evacuation and argon backfilling (three times) before H_2O (2 mL) was added. The aldehyde **1a** (24.0 mg, 0.200 mmol, 1.0 equiv) was added to the mixture successively by micro-syringe. The reaction mixture was then stirred and irradiated using a 20 W blue LED lamp at room temperature for 12 h. After the reaction was completed, the mixture was diluted with EtOAc (4 mL), which was followed by extraction with EtOAc (10 mL x 3 times). 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. Trace amount of desired product **3a** was detected,

whereas TEMPO adduct and BHT adduct were not detected by TLC, GC-MS and ^{1}H NMR analysis.

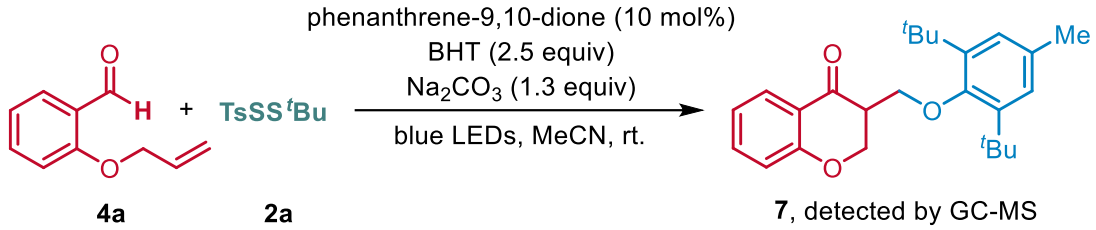


A flame-dried Schlenk-tube equipped with a magnetic stir bar was charged with the phenanthrene-9,10-dione (4.2 mg, 0.020 mmol, 10 mol%), Na_2CO_3 (25.4 mg, 0.240 mmol, 1.2 equiv), and radical scavenger TEMPO (78.1 mg, 0.500 mmol, 2.5 equiv), sealed with a septum, and degassed by alternating vacuum evacuation and argon backfilling (three times) before MeCN (2 mL) was added. The aldehyde **1a** (24.0 mg, 0.200 mmol, 1.0 equiv) was added to the mixture successively by micro-syringe. The reaction mixture was then stirred and irradiated using a 20 W blue LED 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. The crude residue was purified by silica gel column chromatography (PE:EtOAc = 50:1) to afford the TEMPO adduct **6** as a colorless liquid in 72% yield (37.6 mg). **TLC R_f** = 0.4 (PE:EtOAc = 20:1); **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.97 (d, *J* = 7.8 Hz, 2H), 7.25 (d, *J* = 8.0 Hz, 2H), 2.42 (s, 3H), 1.74 (t, *J* = 15.9 Hz, 3H), 1.58 (d, *J* = 12.7 Hz, 2H), 1.46 (d, *J* = 12.2 Hz, 1H), 1.27 (s, 6H), 1.11 (s, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 166.0, 143.0, 129.1, 128.7, 126.5, 59.9, 38.6, 31.5, 21.2, 20.4, 16.6; The spectral data are in accordance with previous reported literature.[8]



A flame-dried Schlenk-tube equipped with a magnetic stir bar was charged with the *SS*-(*tert*-butyl)4-methylbenzenesulfono(dithioperoxoate) **2a** (110.4 mg, 0.4000 mmol, 2.0 equiv), phenanthrene-9,10-dione (4.2 mg, 0.020 mmol, 10 mol%), sodium carbonate (26.8 mg, 0.260 mmol, 1.3 equiv), and radical scavenger TEMPO (78.2 mg, 0.500 mmol, 2.5 equiv), sealed with a septum, and degassed by alternating vacuum evacuation and argon backfilling (three times) before MeCN (2 mL) was added. The alkenyl aldehyde **1a** (32.4 mg, 0.200 mmol, 1.0 equiv) was added to the mixture

successively by micro-syringe. The reaction mixture was then stirred and irradiated using a 20 W blue LED 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. Trace amount of desired product **3a** was detected, whereas TEMPO adduct was not detected by TLC, GC-MS and ^{1}H NMR analysis.



4a **2a** **7**, detected by GC-MS

A flame-dried Schlenk-tube equipped with a magnetic stir bar was charged with the *SS*-(*tert*-butyl)4-methylbenzenesulfono(dithioperoxoate) **2a** (110.4 mg, 0.4000 mmol, 2.0 equiv), phenanthrene-9,10-dione (4.2 mg, 0.020 mmol, 10 mol%), sodium carbonate (26.8 mg, 0.260 mmol, 1.3 equiv), and radical scavenger BHT (110.2 mg, 0.5000 mmol, 2.5 equiv), sealed with a septum, and degassed by alternating vacuum evacuation and argon backfilling (three times) before MeCN (2 mL) was added. The alkenyl aldehyde **1a** (32.4 mg, 0.200 mmol, 1.0 equiv) was added to the mixture successively by micro-syringe. The reaction mixture was then stirred and irradiated using a 20 W blue LED 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. Trace amount of desired product **3a** was detected, and the BHT adduct **7** was detected by GC-MS.

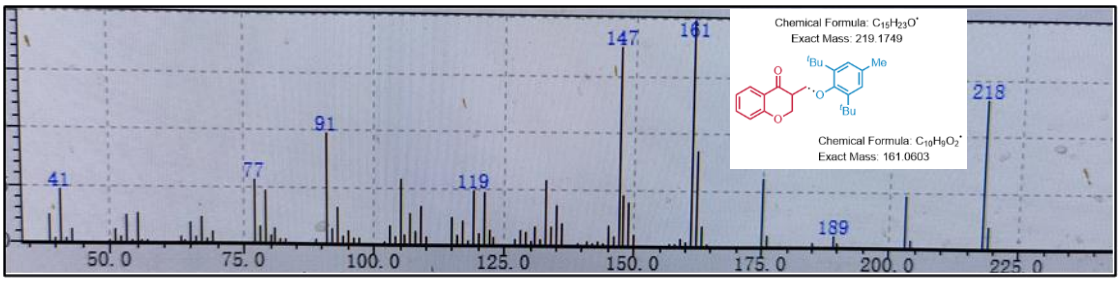
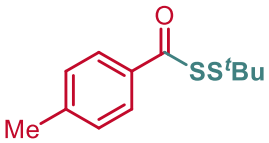


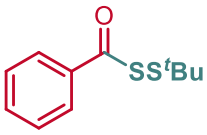
Figure S4 The GC-MS spectrum of BHT capture experiment

5. Spectral data of products

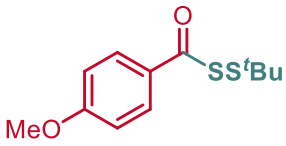


***SS*-(*tert*-Butyl) 4-methylbenzo(dithioperoxoate) (3a):** The title compound was prepared according to general procedure (**GP1-1**) with phenanthrene-9,10-dione (4.2 mg, 0.020 mmol, 10 mol%), Na_2CO_3 (25.4 mg, 0.240 mmol, 1.2 equiv), 4-methylbenzaldehyde **1a** (24.0 mg, 0.200 mmol, 1.0 equiv), and *SS*-(*tert*-butyl) 4-methylbenzenesulfono(dithioperoxoate) **2a** (66.2 mg, 0.240 mmol, 1.2 equiv) in

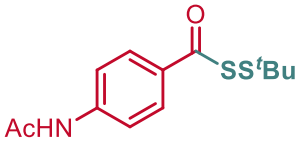
H_2O (2 mL) at room temperature for 12 h. Purification via silica gel chromatography (PE) gave the desired product **3a** as a colorless liquid in 94% yield (45.2 mg); **TLC R_f** = 0.6 (PE:EtOAc = 100:1); **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.94 (d, *J* = 8.2 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 2.43 (s, 3H), 1.35 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 189.8, 149.9, 133.3, 129.5, 127.8, 49.0, 29.8, 21.8; **HRMS** (ESI) *m*/*z* = 241.0715 calcd. for $C_{12}H_{16}OS_2$ $[M+H]^+$, found: 241.0715; **IR** (neat, cm^{-1}): 2960*w*, 2921*w*, 1698*s*, 1606*m*, 1454*m*, 1364*m*, 1202*s*, 1174*s*, 821*s*, 820*s*, 785*s*, 717*m*, 638*m*, 620*s*, 471*m*.



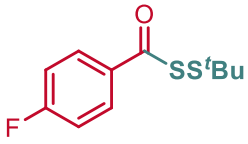
***SS*-(*tert*-Butyl) benzo(dithioperoxoate) (3b):** The title compound was prepared according to general procedure (**GP1-1**) with phenanthrene-9,10-dione (4.2 mg, 0.020 mmol, 10 mol%), Na_2CO_3 (25.4 mg, 0.240 mmol, 1.2 equiv), benzaldehyde **1b** (21.2 mg, 0.200 mmol, 1.0 equiv), and *SS*-(*tert*-butyl) 4-methylbenzenesulfono (dithioperoxoate) **2a** (66.2 mg, 0.240 mmol, 1.2 equiv) in H_2O (2 mL) at room temperature for 12 h. Purification via silica gel chromatography (PE) gave the desired product **3b** as a colorless liquid in 90% yield (40.7 mg); **TLC R_f** = 0.4 (PE:EtOAc = 100:1); **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 8.04 (d, *J* = 7.0 Hz, 2H), 7.62 (t, *J* = 7.5 Hz, 1H), 7.49 (t, *J* = 7.8 Hz, 2H), 1.36 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 190.4, 135.9, 133.9, 128.8, 127.8, 49.1, 29.8; The spectral data are in accordance with previous reported literature.[9]



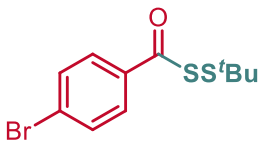
***SS*-(*tert*-Butyl) 4-methoxybenzo(dithioperoxoate) (3c):** The title compound was prepared according to general procedure (**GP1-1**) with phenanthrene-9,10-dione (4.2 mg, 0.020 mmol, 10 mol%), Na_2CO_3 (25.4 mg, 0.240 mmol, 1.2 equiv), 4-methoxybenzaldehyde **1c** (27.2 mg, 0.200 mmol, 1.0 equiv), and *SS*-(*tert*-butyl) 4-methylbenzenesulfono(dithioperoxoate) **2a** (66.2 mg, 0.240 mmol, 1.2 equiv) in H_2O (2 mL) at room temperature for 12 h. Purification via silica gel chromatography (PE) gave the desired product **3c** as a white solid in 96% yield (49.2 mg); **TLC R_f** = 0.4 (PE:EtOAc = 100:1); **MP**: = 91 – 93 °C; **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 8.02 (d, *J* = 8.9 Hz, 2H), 6.95 (d, *J* = 8.9 Hz, 2H), 3.87 (s, 3H), 1.35 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 188.5, 164.2, 130.0, 128.6, 114.0, 55.5, 48.8, 29.8; **HRMS** (ESI) *m*/*z* = 257.0664 calcd. for $C_{12}H_{17}O_2S_2$ $[M+H]^+$, found: 257.0672; **IR** (neat, cm^{-1}): 2961*w*, 2921*w*, 1693*m*, 1599*s*, 1576*w*, 1508*m*, 1456*w*, 1419*w*, 1308*w*, 1261*m*, 1209*s*, 1161*s*, 1208*w*, 887*s*, 837*m*, 788*w*.



***SS*-(*tert*-Butyl) 4-acetamidobenzo(dithioperoxoate) (3d):** The title compound was prepared according to general procedure (**GP1-3**) with phenanthrene-9,10-dione (4.2 mg, 0.020 mmol, 10 mol%), Na_2CO_3 (25.4 mg, 0.240 mmol, 1.2 equiv), *N*-(4-formylphenyl)acetamide **1d** (32.6 mg, 0.200 mmol, 1.0 equiv), and *SS*-(*tert*-butyl) 4-methylbenzenesulfono(dithioperoxoate) **2a** (66.2 mg, 0.240 mmol, 1.2 equiv) in MeCN (2 mL) at room temperature for 12 h. Purification via silica gel chromatography (PE:EtOAc = 50:1) gave the desired product **3d** as a white solid in 71% yield (40.0 mg); **TLC R_f** = 0.3 (PE:EtOAc = 50:1); **MP**: = 141 – 144 °C; **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 8.00 – 7.98 (m, 3H), 7.66 (d, *J* = 8.4 Hz, 2H), 2.21 (s, 3H), 1.34 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 189.3, 168.9, 143.2, 131.1, 129.1, 119.0, 49.0, 29.8, 24.7; **HRMS** (ESI) *m*/*z* = 284.0773 calcd. for $C_{13}H_8NO_2S_2$ $[M+H]^+$, found: 284.0773; **IR** (neat, cm^{-1}): 2961*w*, 2923*w*, 1679*s*, 1590*s*, 1530*s*, 1406*m*, 1364*m*, 1317*m*, 1265*m*, 1209*s*, 1170*s*, 890*s*, 846*m*, 687*w*, 645*w*.

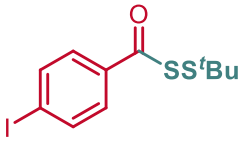


***SS*-(*tert*-Butyl) 4-fluorobenzo(dithioperoxoate) (3e):** The title compound was prepared according to general procedure (**GP1-1**) with phenanthrene-9,10-dione (4.2 mg, 0.020 mmol, 10 mol%), Na_2CO_3 (25.4 mg, 0.240 mmol, 1.2 equiv), 4-fluorobenzaldehyde **1e** (24.8 mg, 0.200 mmol, 1.0 equiv), and *SS*-(*tert*-butyl) 4-methylbenzenesulfono(dithioperoxoate) **2a** (66.2 mg, 0.240 mmol, 1.2 equiv) in H_2O (2 mL) at room temperature for 12 h. Purification via silica gel chromatography (PE) gave the desired product **3e** as a colorless liquid in 88% yield (42.8 mg); **TLC R_f** = 0.4 (PE:EtOAc = 100:1); **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 8.07 (dd, J^1 = 8.9 Hz, J^2 =5.3 Hz, 2H), 7.16 (t, *J* = 8.9 Hz, 2H), 1.35 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 189.0, 166.2 (d, *J* = 257.1 Hz, 1C), 132.2, (d, *J* = 3.2 Hz, 1C), 130.4 (d, *J* = 9.5 Hz, 2C), 116.0 (d, *J* = 22.1 Hz, 2C), 49.1, 29.8; **IR** (neat, cm^{-1}): 2962*w*, 1706*m*, 1683*s*, 1598*s*, 1503*s*, 1456*w*, 1408*w*, 1238*m*, 1196*m*, 1155*s*, 842*s*, 805*w*, 726*w*, 634*m*, 617*w*.

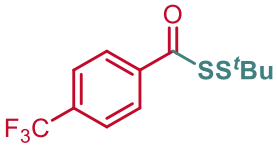


***SS*-(*tert*-Butyl) 4-bromobenzo(dithioperoxoate) (3f):** The title compound was prepared according to general procedure (**GP1-1**) with phenanthrene-9,10-dione (4.2 mg, 0.020 mmol, 10 mol%), Na_2CO_3 (25.4 mg, 0.240 mmol, 1.2 equiv), 4-bromobenzaldehyde **1f** (37.0 mg, 0.200 mmol, 1.0 equiv), and *SS*-(*tert*-butyl) 4-methylbenzenesulfono(dithioperoxoate) **2a** (66.2 mg, 0.240 mmol, 1.2 equiv) in H_2O (2 mL) at room temperature for 12 h. Purification via silica gel chromatography (PE) gave the desired product **3f** as a white solid in 82% yield (50.1 mg); **TLC R_f** =

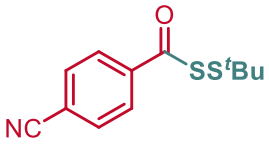
0.5 (PE:EtOAc = 100:1); **MP**: = 68 – 69 °C; **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.90 (d, *J* = 8.6 Hz, 2H), 7.63 (d, *J* = 8.6 Hz, 2H), 1.35 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 189.7, 134.6, 132.1, 129.1, 129.1, 49.3, 29.8; **HRMS** (APCI) *m*/*z* = 304.9664 calcd. for $C_{11}H_{14}OS_2Br$ $[M+H]^+$, found: 304.9667; **IR** (neat, cm^{-1}): 2961*w*, 2921*w*, 1689*s*, 1582*m*, 1395*m*, 1364*m*, 1198*s*, 1162*s*, 1168*s*, 1011*s*, 880*s*, 830*s*, 717*m*, 638*m*, 570*w*, 467*w*.



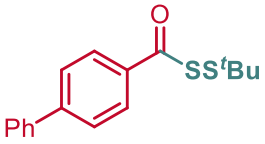
***SS*-(*tert*-Butyl) 4-iodobenzo(dithioperoxoate) (3g):** The title compound was prepared according to general procedure (**GP1-1**) with phenanthrene-9,10-dione (4.2 mg, 0.020 mmol, 10 mol%), Na_2CO_3 (25.4 mg, 0.240 mmol, 1.2 equiv), 4-iodobenzaldehyde **1g** (46.4 mg, 0.200 mmol, 1.0 equiv), and *SS*-(*tert*-butyl) 4-methylbenzenesulfono (dithioperoxoate) **2a** (66.2 mg, 0.240 mmol, 1.2 equiv) in H_2O (2 mL) at room temperature for 12 h. Purification via silica gel chromatography (PE) gave the desired product **3g** as a white solid in 44% yield (31.0 mg); **TLC R_f** = 0.4 (PE:EtOAc = 100:1); **MP**: = 54 – 56 °C; **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.85 (d, *J* = 8.6 Hz, 2H), 7.74 (d, *J* = 8.5 Hz, 2H), 1.35 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 190.0, 138.1, 135.1, 129.0, 101.9, 49.3, 29.8; **HRMS** (ESI) *m*/*z* = 352.9525 calcd. for $C_{11}H_{14}OS_2I$ $[M+H]^+$, found: 352.9526; **IR** (neat, cm^{-1}): 2960*w*, 2920*w*, 1689*s*, 1578*s*, 1478*w*, 1455*w*, 1389*m*, 1364*m*, 1193*s*, 1162*s*, 1057*s*, 881*s*, 821*m*, 715*m*, 700*m*, 638*m*.



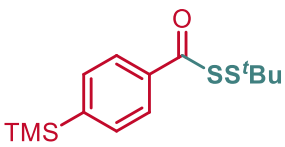
***SS*-(*tert*-Butyl) 4-(trifluoromethyl)benzo(dithioperoxoate) (3h):** The title compound was prepared according to general procedure (**GP1-1**) with phenanthrene-9,10-dione (4.2 mg, 0.020 mmol, 10 mol%), Na_2CO_3 (25.4 mg, 0.240 mmol, 1.2 equiv), 4-(trifluoromethyl)benzaldehyde **1h** (34.8 mg, 0.200 mmol, 1.0 equiv), and *SS*-(*tert*-butyl) 4-methylbenzenesulfono(dithioperoxoate) **2a** (66.2 mg, 0.240 mmol, 1.2 equiv) in H_2O (2 mL) at room temperature for 12 h. Purification via silica gel chromatography (PE) gave the desired product **3h** as a white solid in 57% yield (33.4 mg); **TLC R_f** = 0.5 (PE:EtOAc = 100:1); **MP**: = 49 – 52 °C; **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 8.13 (d, *J* = 7.8 Hz, 2H), 7.75 (d, *J* = 8.4 Hz, 2H), 1.37 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 190.0, 138.7, 135.1 (q, *J* = 32.3 Hz, 1C), 128.1, 125.9 (q, *J* = 3.0 Hz, 2C), 123.4 (q, *J* = 273.7 Hz, 1C), 49.5, 29.8; **HRMS** (ESI) *m*/*z* = 317.0252 calcd. for $C_{12}H_{13}F_3NaOS_2$ $[M+Na]^+$, found: 317.0263; **IR** (neat, cm^{-1}): 2964*w*, 2921*w*, 1698*m*, 1408*w*, 1366*w*, 1322*s*, 1202*m*, 1165*m*, 1132*s*, 1110*m*, 1066*s*, 1016*w*, 892*m*, 848*m*, 772*m*, 692*w*, 648*w*.



***SS*-(*tert*-Butyl) 4-cyanobenzo(dithioperoxoate) (3i):** The title compound was prepared according to general procedure (**GP1-3**) with phenanthrene-9,10-dione (4.2 mg, 0.020 mmol, 10 mol%), Na_2CO_3 (25.4 mg, 0.240 mmol, 1.2 equiv), 4-formylbenzonitrile **1i** (26.2 mg, 0.200 mmol, 1.0 equiv), and *SS*-(*tert*-butyl) 4-methylbenzenesulfono(dithioperoxoate) **2a** (66.2 mg, 0.240 mmol, 1.2 equiv) in H_2O (2 mL) at room temperature for 12 h. Purification via silica gel chromatography (PE) gave the desired product **3i** as a white solid in 48% yield (24.2 mg); **TLC R_f** = 0.4 (PE:EtOAc = 100:1); **MP**: = 63 – 65 °C; **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 8.12 (d, *J* = 8.5 Hz, 2H), 7.79 (d, *J* = 8.5 Hz, 2H), 1.37 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 189.9, 139.0, 132.7, 128.2, 117.7, 117.2, 49.7, 29.8; **IR** (neat, cm^{-1}): 2962*w*, 2923*w*, 2852*w*, 2233*w*, 1698*s*, 1470*w*, 1403*w*, 1365*w*, 1199*s*, 1163*m*, 894*s*, 845*w*, 764*w*, 637*w*, 541*w*.

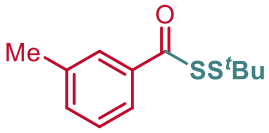


***SS*-(*tert*-Butyl) [1,1'-biphenyl]-4-carbo(dithioperoxoate) (3j):** The title compound was prepared according to general procedure (**GP1-3**) with phenanthrene-9,10-dione (4.2 mg, 0.020 mmol, 10 mol%), Na_2CO_3 (25.4 mg, 0.240 mmol, 1.2 equiv), 4-biphenylcarboxaldehyde **1j** (36.4 mg, 0.200 mmol, 1.0 equiv), and *SS*-(*tert*-butyl) 4-methylbenzenesulfono(dithioperoxoate) **2a** (66.2 mg, 0.240 mmol, 1.2 equiv) in H_2O (2 mL) at room temperature for 12 h. Purification via silica gel chromatography (PE) gave the desired product **3j** as a white solid in 68% yield (41.1 mg); **MP**: = 68 – 71 °C; **TLC R_f** = 0.4 (PE:EtOAc = 100:1); **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 8.12 (d, *J* = 8.6 Hz, 2H), 7.71 (d, *J* = 8.0 Hz, 2H), 7.63 (d, *J* = 6.9 Hz, 2H), 7.48 (t, *J* = 7.3 Hz, 2H), 7.42 (t, *J* = 7.3 Hz, 1H), 1.38 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 189.9, 146.7, 139.6, 134.5, 129.0, 128.4, 128.3, 127.4, 127.3, 49.1, 29.8; **HRMS** (ESI) *m*/*z* = 303.0872 calcd. for $C_{17}H_{19}OS_2$ $[M+H]^+$, found: 303.0877; **IR** (neat, cm^{-1}): 2961*w*, 2921*w*, 1690*s*, 1602*m*, 1364*m*, 1208*m*, 1175*s*, 1007*w*, 888*s*, 847*w*, 767*w*, 748*m*, 730*w*, 695*w*, 646*w*.

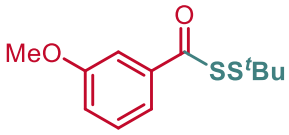


***SS*-(*tert*-Butyl) 4-(trimethylsilyl)benzo(dithioperoxoate) (3k):** The title compound was prepared according to general procedure (**GP1-1**) with phenanthrene-9,10-dione (4.2 mg, 0.020 mmol, 10 mol%), Na_2CO_3 (25.4 mg, 0.240 mmol, 1.2 equiv), 4-(trimethylsilyl)benzaldehyde **1k** (35.7 mg, 0.200 mmol, 1.0 equiv), and *SS*-(*tert*-butyl) 4-methylbenzenesulfono(dithioperoxoate) **2a** (66.2 mg, 0.240 mmol, 1.2 equiv) in H_2O (2 mL) at room temperature for 12 h. Purification via silica gel chromatography (PE) gave the desired product **3k** as a colorless liquid in 80% yield (47.5 mg); **TLC R_f** = 0.5 (PE:EtOAc = 100:1); **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ

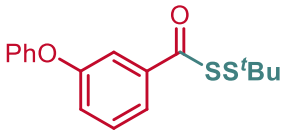
(ppm) = 7.99 (d, *J* = 8.1 Hz, 2H), 7.63 (d, *J* = 8.1 Hz, 2H), 1.35 (s, 9H), 0.30 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 190.5, 148.4, 135.9, 133.7, 126.6, 49.0, 29.8, -1.41; **IR** (neat, cm^{-1}): 2958*w*, 1695*s*, 1386*m*, 1365*m*, 1249*m*, 1209*s*, 1181*s*, 1164*m*, 1105*w*, 890*m*, 838*s*, 824*s*, 760*w*, 714*s*, 647*w*.



***SS*-(*tert*-Butyl) 3-methylbenzo(dithioperoxoate) (3l):** The title compound was prepared according to general procedure (**GP1-1**) with phenanthrene-9,10-dione (4.2 mg, 0.020 mmol, 10 mol%), Na_2CO_3 (25.4 mg, 0.240 mmol, 1.2 equiv), 3-methylbenzaldehyde **1l** (24.0 mg, 0.200 mmol, 1.0 equiv), and *SS*-(*tert*-butyl) 4-methylbenzenesulfono(dithioperoxoate) **2a** (66.2 mg, 0.240 mmol, 1.2 equiv) in H_2O (2 mL) at room temperature for 12 h. Purification via silica gel chromatography (PE) gave the desired product **3l** as a white solid in 96% yield (46.0 mg); **TLC R_f** = 0.5 (PE:EtOAc = 100:1); **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.84 – 7.82 (m, 2H), 7.41 (d, *J* = 7.5 Hz, 1H), 7.35 (t, *J* = 8.0 Hz, 1H), 2.41 (s, 3H), 1.35 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 190.4, 138.7, 135.8, 134.6, 128.7, 128.1, 125.0, 49.0, 29.8, 21.3; **HRMS** (APCI) *m*/*z* = 241.0715 calcd. for $C_{12}H_{17}OS_2$ $[M+H]^+$, found: 241.0718; **IR** (neat, cm^{-1}): 2961*w*, 2920*w*, 1696*s*, 1559*m*, 1456*w*, 1364*w*, 1186*s*, 1162*m*, 995*m*, 898*m*, 791*w*, 721*m*, 691*s*.

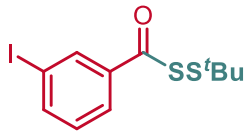


***SS*-(*tert*-Butyl) 3-methoxybenzo(dithioperoxoate) (3m):** The title compound was prepared according to general procedure (**GP1-1**) with phenanthrene-9,10-dione (4.2 mg, 0.020 mmol, 10 mol%), Na_2CO_3 (25.4 mg, 0.240 mmol, 1.2 equiv), 3-methoxybenzaldehyde **1m** (27.2 mg, 0.200 mmol, 1.0 equiv), and *SS*-(*tert*-butyl) 4-methylbenzenesulfono(dithioperoxoate) **2a** (66.2 mg, 0.240 mmol, 1.2 equiv) in H_2O (2 mL) at room temperature for 12 h. Purification via silica gel chromatography (PE) gave the desired product **3m** as a colorless liquid in 96% yield (49.2 mg); **TLC R_f** = 0.5 (PE:EtOAc = 100:1); **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.64 (d, *J* = 7.7 Hz, 1H), 7.49 (s, 1H), 7.38 (t, *J* = 8.0 Hz, 1H), 7.14 (d, *J* = 9.2 Hz, 1H), 3.85 (s, 3H), 1.35 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 190.3, 159.8, 137.1, 129.8, 120.3, 120.3, 111.9, 55.5, 49.0, 29.8; **HRMS** (ESI) *m*/*z* = 257.0664 calcd. for $C_{12}H_{17}OS_2$ $[M+H]^+$, found: 257.0672; **IR** (neat, cm^{-1}): 2923*w*, 1760*m*, 1685*w*, 1597*w*, 1512*s*, 1365*w*, 1242*w*, 1201*s*, 1112*s*, 1015*w*, 892*s*, 832*w*, 731*s*, 640*w*.

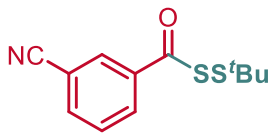


***SS*-(*tert*-Butyl) 3-phenoxybenzo(dithioperoxoate) (3n):** The title compound was prepared according to general procedure (**GP1-3**) with phenanthrene-9,10-dione (4.2 mg, 0.020 mmol,

10 mol%), Na_2CO_3 (25.4 mg, 0.240 mmol, 1.2 equiv), 3-phenoxybenzaldehyde **1n** (39.6 mg, 0.200 mmol, 1.0 equiv), and *SS*-(*tert*-butyl) 4-methylbenzenesulfono(dithioperoxoate) **2a** (66.2 mg, 0.240 mmol, 1.2 equiv) in H_2O (2 mL) at room temperature for 12 h. Purification via silica gel chromatography (PE) gave the desired product **3n** as a colorless liquid in 62% yield (39.8 mg); **TLC** $\mathbf{R_f}$ = 0.5 (PE:EtOAc = 100:1); **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.76 (d, *J* = 7.9 Hz, 1H), 7.63 (s, 1H), 7.43 (t, *J* = 8.0 Hz, 1H), 7.37 (t, *J* = 8.0 Hz, 2H), 7.23 (d, *J* = 8.2 Hz, 1H), 7.16 (t, *J* = 7.4 Hz, 1H), 7.03 (d, *J* = 7.6 Hz, 2H), 1.35 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 190.0, 157.9, 156.2, 137.5, 130.1, 130.0, 124.1, 123.7, 122.3, 119.3, 117.3, 49.1, 29.8; **HRMS** (ESI) *m*/*z* = 319.0821 calcd. for $C_{17}H_{18}O_2S_2$ $[M+H]^+$, found: 319.0828; **IR** (neat, cm^{-1}): 2961*w*, 2921*w*, 1694*m*, 1579*m*, 1489*m*, 1433*m*, 1365*m*, 1244*s*, 1211*m*, 1162*m*, 986*w*, 959*w*, 844*m*, 794*m*, 752*m*, 692*s*, 692*s*, 673*w*.

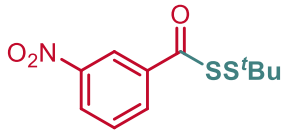


***SS*-(*tert*-Butyl) 3-iodobenzo(dithioperoxoate) (3o):** The title compound was prepared according to general procedure (**GP1-1**) with phenanthrene-9,10-dione (4.2 mg, 0.020 mmol, 10 mol%), Na_2CO_3 (25.4 mg, 0.240 mmol, 1.2 equiv), 3-iodobenzaldehyde **1o** (46.4 mg, 0.200 mmol, 1.0 equiv), and *SS*-(*tert*-butyl) 4-methylbenzenesulfono (dithioperoxoate) **2a** (66.2 mg, 0.240 mmol, 1.2 equiv) in H_2O (2 mL) at room temperature for 12 h. Purification via silica gel chromatography (PE) gave the desired product **3o** as a colorless liquid in 80% yield (56.4 mg); **TLC** $\mathbf{R_f}$ = 0.5 (PE:EtOAc = 100:1); **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 8.33 (s, 1H), 8.00 (d, *J* = 7.8 Hz, 1H), 7.94 (d, *J* = 7.9 Hz, 1H), 7.23 (t, *J* = 7.9 Hz, 1H), 1.36 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 189.3, 142.6, 137.5, 136.4, 130.4, 126.9, 94.4, 49.3, 29.8; **HRMS** (ESI) *m*/*z* = 352.9525 calcd. for $C_{11}H_{14}OS_2I$ $[M+H]^+$, found: 352.9526; **IR** (neat, cm^{-1}): 2961*w*, 2923*w*, 1756*m*, 1686*w*, 1598*w*, 1501*w*, 1472*w*, 1411*w*, 1365*w*, 1261*s*, 1204*s*, 1106*s*, 1046*m*, 895*s*, 801*s*, 730*m*, 664*w*, 640*m*.

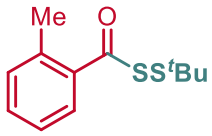


***SS*-(*tert*-Butyl) 3-cyanobenzo(dithioperoxoate) (3p):** The title compound was prepared according to general procedure (**GP1-1**) with phenanthrene-9,10-dione (4.2 mg, 0.020 mmol, 10 mol%), Na_2CO_3 (25.4 mg, 0.240 mmol, 1.2 equiv), 3-formylbenzonitrile **1p** (26.2 mg, 0.200 mmol, 1.0 equiv), and *SS*-(*tert*-butyl) 4-methylbenzenesulfono(dithioperoxoate) **2a** (66.2 mg, 0.240 mmol, 1.2 equiv) in H_2O (2 mL) at room temperature for 12 h. Purification via silica gel chromatography (PE) gave the desired product **3p** as a colorless liquid in 68% yield (34.1 mg); **TLC** $\mathbf{R_f}$ = 0.3 (PE:EtOAc = 100:1); **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 8.30 (s, 1H), 8.24 (d, *J* = 8.0 Hz, 1H), 7.89 (d, *J* = 7.8 Hz, 1H), 7.64 (t, *J* = 7.9 Hz, 1H), 1.36

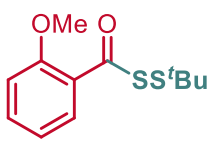
(s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 189.2, 136.8, 136.6, 131.6, 131.2, 129.9, 117.5, 113.5, 49.6, 29.8; **HRMS** (EI) *m*/*z* = 251.0439 calcd. for $C_{12}H_{13}NOS_2$ $[M]^+$, found: 251.0433; **IR** (neat, cm^{-1}): 2963*w*, 2923*w*, 2234*w*, 1692*s*, 1455*w*, 1422*w*, 1365*m*, 1232*s*, 1149*s*, 968*s*, 933*s*, 802*s*, 766*s*, 690*s*, 673*m*, 550*w*.



***SS*-(*tert*-Butyl) 3-nitrobenzo(dithioperoxoate) (3q):** The title compound was prepared according to general procedure (**GP1-1**) with phenanthrene-9,10-dione (4.2 mg, 0.020 mmol, 10 mol%), Na_2CO_3 (25.4 mg, 0.240 mmol, 1.2 equiv), 3-nitrobenzaldehyde **1q** (30.2 mg, 0.200 mmol, 1.0 equiv), and *SS*-(*tert*-butyl) 4-methylbenzenesulfono(dithioperoxoate) **2a** (66.2 mg, 0.240 mmol, 1.2 equiv) in H_2O (2 mL) at room temperature for 12 h. Purification via silica gel chromatography (PE) gave the desired product **3q** as a white solid in 34% yield (18.4 mg); **TLC R_f** = 0.5 (PE:EtOAc = 100:1); **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 8.86 (s, 1H), 8.47 (d, *J* = 8.3 Hz, 1H), 8.34 (d, *J* = 7.8 Hz, 1H), 7.72 (t, *J* = 8.0 Hz, 1H), 1.38 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 189.1, 148.4, 137.2, 133.2, 130.1, 128.0, 122.7, 49.7, 29.8; **HRMS** (EI) *m*/*z* = 271.0337 calcd. for $C_{11}H_{13}NO_3S_2$ $[M]^+$, found: 271.0326; **IR** (neat, cm^{-1}): 2963*w*, 2923*w*, 1698*m*, 1612*w*, 1533*s*, 1456*w*, 1346*s*, 1199*s*, 1162*m*, 1082*m*, 962*m*, 854*m*, 812*w*, 734*m*, 705*s*, 684*m*.

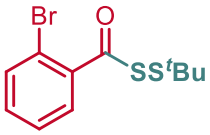


***SS*-(*tert*-Butyl) 2-methylbenzo(dithioperoxoate) (3r):** The title compound was prepared according to general procedure (**GP1-1**) with phenanthrene-9,10-dione (4.2 mg, 0.020 mmol, 10 mol%), Na_2CO_3 (25.4 mg, 0.240 mmol, 1.2 equiv), 2-methylbenzaldehyde **1r** (24.0 mg, 0.200 mmol, 1.0 equiv), and *SS*-(*tert*-butyl) 4-methylbenzenesulfono (dithioperoxoate) **2a** (66.2 mg, 0.240 mmol, 1.2 equiv) in H_2O (2 mL) at room temperature for 12 h. Purification via silica gel chromatography (PE) gave the desired product **3r** as a white solid in 57% yield (27.3 mg); **TLC R_f** = 0.5 (PE:EtOAc = 100:1); **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.86 (d, *J* = 7.6 Hz, 1H), 7.43 (t, *J* = 6.8 Hz, 1H), 7.34 – 7.26 (m, 2H), 2.47 (s, 3H), 1.37 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): 192.5, 137.1, 136.1, 132.2, 131.7, 128.6, 125.8, 49.0, 29.8, 20.5; **HRMS** (APCI) *m*/*z* = 241.0715 calcd. for $C_{12}H_{17}OS_2$ $[M+H]^+$, found: 241.0711; **IR** (neat, cm^{-1}): 2961*w*, 1702*s*, 1456*m*, 1364*m*, 1209*w*, 1188*s*, 1162*m*, 1162*s*, 882*s*, 780*w*, 761*s*, 721*m*, 675*m*, 647*s*.

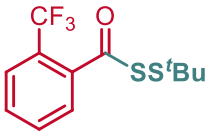


***SS*-(*tert*-Butyl) 2-methoxybenzo(dithioperoxoate) (3s):** The title compound was prepared according to general procedure (**GP1-1**) with phenanthrene-9,10-dione (4.2 mg, 0.020 mmol, 10 mol%), Na_2CO_3 (25.4 mg, 0.240 mmol, 1.2 equiv),

2-methoxybenzaldehyde **1s** (27.2 mg, 0.200 mmol, 1.0 equiv), and *SS*-(*tert*-butyl) 4-methylbenzenesulfono(dithioperoxoate) **2a** (66.2 mg, 0.240 mmol, 1.2 equiv) in H_2O (2 mL) at room temperature for 12 h. Purification via silica gel chromatography (PE) gave the desired product **3s** as a colorless liquid in 64% yield (33.0 mg); **TLC R_f** = 0.4 (PE:EtOAc = 100:1); **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.79 (d, *J* = 7.7 Hz, 1H), 7.50 (m, *J* = 8.0 Hz, 1H), 7.02 (m, 2H), 3.94 (s, 3H), 1.36 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 190.2, 158.1, 134.2, 129.9, 125.6, 120.6, 112.0, 55.8, 48.8, 29.9; **HRMS** (ESI) *m*/*z* = 257.0664 calcd. for $C_{12}H_{17}O_2S_2$ $[M+H]^+$, found: 257.0674; **IR** (neat, cm^{-1}): 3360*w*, 2921*w*, 2851*m*, 2359*w*, 1653*m*, 1635*w*, 1647*m*, 1285*w*, 1249*w*, 1162*w*, 1019*w*, 880*m*, 781*w*.

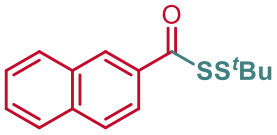


***SS*-(*tert*-Butyl) 2-bromobenzo(dithioperoxoate) (3t):** The title compound was prepared according to general procedure (**GP1-1**) with phenanthrene-9,10-dione (4.2 mg, 0.020 mmol, 10 mol%), Na_2CO_3 (25.4 mg, 0.240 mmol, 1.2 equiv), 2-bromobenzaldehyde **1t** (37.0 mg, 0.200 mmol, 1.0 equiv), and *SS*-(*tert*-butyl) 4-methylbenzenesulfono (dithioperoxoate) **2a** (66.2 mg, 0.240 mmol, 1.2 equiv) in H_2O (2 mL) at room temperature for 12 h. Purification via silica gel chromatography (PE) gave the desired product **3t** as a colorless liquid in 50% yield (30.3 mg); **TLC R_f** = 0.3 (PE:EtOAc = 100:1); **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.66 (d, *J* = 7.8 Hz, 1H), 7.60 (d, *J* = 7.4 Hz, 1H), 7.40 (t, *J* = 6.7 Hz, 1H), 7.35 (t, *J* = 8.0 Hz, 1H), 1.40 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 192.0, 138.6, 134.0, 132.6, 129.0, 127.3, 118.9, 49.6, 29.9; **HRMS** (ESI) *m*/*z* = 304.9664 calcd. for $C_{11}H_{14}OS_2Br$ $[M+H]^+$, found: 304.9662; **IR** (neat, cm^{-1}): 2961*w*, 2921*w*, 1706*s*, 1458*m*, 1365*m*, 1195*m*, 1162*m*, 1049*w*, 1029*w*, 889*s*, 862*w*, 760*s*, 727s, 691*m*, 642*m*.

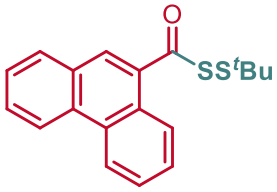


***SS*-(*tert*-Butyl) 2-(trifluoromethyl)benzo(dithioperoxoate) (3u):** The title compound was prepared according to general procedure (**GP1-1**) with phenanthrene-9,10-dione (4.2 mg, 0.020 mmol, 10 mol%), Na_2CO_3 (25.4 mg, 0.240 mmol, 1.2 equiv), 2-(trifluoromethyl)benzaldehyde **1u** (34.8 mg, 0.200 mmol, 1.0 equiv), and *SS*-(*tert*-butyl) 4-methylbenzenesulfono(dithioperoxoate) **2a** (66.2 mg, 0.240 mmol, 1.2 equiv) in H_2O (2 mL) at room temperature for 12 h. Purification via silica gel chromatography (PE) gave the desired product **3u** as a colorless liquid in 59% yield (34.7 mg); **TLC R_f** = 0.3 (PE:EtOAc = 100:1); **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.79 – 7.75 (m, 1H), 7.75 – 7.71 (m, 1H), 7.66 – 7.62 (m, 2H), 1.38 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 191.8, 136.4 (d, *J* = 1.8 Hz, 1C), 131.8, 131.5, 128.7, 127.6 (d, *J* = 32.8 Hz, 1C), 127.1 (q, *J* = 5.5 Hz, 1C), 123.0 (q, *J* = 274.1 Hz, 1C), 49.7, 29.8; **HRMS** (ESI) *m*/*z* = 317.0252 calcd. for $C_{12}H_{13}F_3NaOS_2$

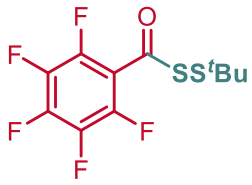
[M+Na]$^+$, found: 317.0263; **IR** (neat, cm^{-1}): 2963*w*, 2921*w*, 1698*m*, 1408*w*, 1366*w*, 1322*s*, 1202*m*, 1166*m*, 1134*s*, 1110*m*, 1056*s*, 1016*w*, 892*m*, 848*m*, 769*m*, 692*w*, 648*w*.



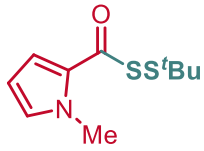
***SS*-(*tert*-Butyl) naphthalene-2-carbo(dithioperoxoate) (3v):** The title compound was prepared according to general procedure (**GP1-3**) with phenanthrene-9,10-dione (4.2 mg, 0.020 mmol, 10 mol%), Na_2CO_3 (25.4 mg, 0.240 mmol, 1.2 equiv), 2-naphthaldehyde **1v** (31.2 mg, 0.200 mmol, 1.0 equiv), and *SS*-(*tert*-butyl) 4-methylbenzenesulfono(dithioperoxoate) **2a** (66.2 mg, 0.240 mmol, 1.2 equiv) in H_2O (2 mL) at room temperature for 12 h. Purification via silica gel chromatography (PE) gave the desired product **3v** as a white solid in 86% yield (47.5 mg); **TLC R_f** = 0.5 (PE:EtOAc = 100:1); **MP**: = 53 – 55 ^{o}C; **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 8.63 (s, 1H), 8.03 (d, *J* = 8.6 Hz, 1H), 7.99 (d, *J* = 8.0 Hz, 1H), 7.93 – 7.87 (m, 2H), 7.65 – 7.55 (m, 2H), 1.39 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 190.3, 135.9, 133.1, 132.4, 129.6, 129.5, 128.8, 128.7, 127.8, 127.1, 123.4, 49.1, 29.8; **HRMS** (ESI) *m*/*z* = 277.0715 calcd. for $C_{15}H_{17}OS_2$ [M+H]$^+$, found: 277.0718; **IR** (neat, cm^{-1}): 2960*w*, 2921*w*, 1736*s*, 1455*m*, 1364*m*, 1159*s*, 1098*s*, 976*m*, 924*m*, 897*s*, 816*s*, 784*s*, 748*s*, 682*w*, 634*w*, 594*w*.



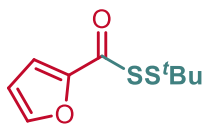
***SS*-(*tert*-Butyl) phenanthrene-9-carbo(dithioperoxoate) (3w):** The title compound was prepared according to general procedure (**GP1-3**) with phenanthrene-9,10-dione (4.2 mg, 0.020 mmol, 10 mol%), Na_2CO_3 (25.4 mg, 0.240 mmol, 1.2 equiv), phenanthrene-9-carbaldehyde **1w** (41.2 mg, 0.200 mmol, 1.0 equiv), and *SS*-(*tert*-butyl) 4-methylbenzenesulfono(dithioperoxoate) **2a** (66.2 mg, 0.240 mmol, 1.2 equiv) in H_2O (2 mL) at room temperature for 12 h. Purification via silica gel chromatography (PE) gave the desired product **3w** as a white solid in 80% yield (52.3 mg); **TLC R_f** = 0.5 (PE:EtOAc = 50:1); **MP**: = 121 – 123 ^{o}C; **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 8.72 – 8.66 (m, 2H), 8.43 (d, *J* = 9.6 Hz, 2H), 8.00 (d, *J* = 8.0 Hz, 1H), 7.79 – 7.64 (m, 4H), 1.46 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 192.7, 133.2, 132.1, 130.7, 130.3, 129.9, 129.7, 129.2, 127.8, 127.5, 127.3, 127.2, 125.9, 122.9, 122.7, 49.3, 29.9; **HRMS** (ESI) *m*/*z* = 327.0872 calcd. for $C_{19}H_{19}OS_2$ [M+H]$^+$, found: 327.0878; **IR** (neat, cm^{-1}): 2960*w*, 2921*w*, 1702*s*, 1528*w*, 1445*m*, 1364*m*, 1248*m*, 1204*m*, 1162*m*, 1065*s*, 1044*w*, 808*s*, 768*m*, 748*s*, 724*s*, 581*w*.



***SS*-(*tert*-Butyl) 2,3,4,5,6-pentafluorobenzo(dithioperoxoate) (3x):** The title compound was prepared according to general procedure (**GP1-1**) with phenanthrene-9,10-dione (4.2 mg, 0.020 mmol, 10 mol%), Na_2CO_3 (25.4 mg, 0.240 mmol, 1.2 equiv), 2,3,4,5,6-pentafluorobenzaldehyde **1x** (39.2 mg, 0.200 mmol, 1.0 equiv), and *SS*-(*tert*-butyl) 4-methylbenzenesulfono(dithioperoxoate) **2a** (66.2 mg, 0.240 mmol, 1.2 equiv) in H_2O (2 mL) at room temperature for 12 h. Purification via silica gel chromatography (PE) gave the desired product **3x** as a colorless liquid in 69% yield (43.6 mg); **TLC R_f** = 0.7 (PE:EtOAc = 100:1); **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 1.37 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 184.1, 144.4 – 144.4(m, 1C), 142.2 – 142.0(m, 1C), 141.9 – 141.7(m, 1C), 139.1 – 138.7(m, 1C), 136.5 – 136.2(m, 1C), 113.4 – 113.0(m, 1C), 50.2, 29.7; **HRMS** (EI) *m*/*z* = 316.0015 calcd. for $C_{11}H_9F_5OS_2$ $[M]^+$, found: 316.0006; **IR** (neat, cm^{-1}): 2965*w*, 2925*w*, 2360*w*, 1709*w*, 1649*w*, 1519*m*, 1498*s*, 1458*w*, 1415*w*, 1368*m*, 1314*m*, 1098*s*, 977*s*, 807*s*, 774*w*, 717*m*.

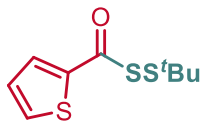


***SS*-(*tert*-Butyl) 1-methyl-1*H*-pyrrole-2-carbo(dithioperoxoate) (3y):** The title compound was prepared according to general procedure (**GP1-1**) with phenanthrene-9,10-dione (4.2 mg, 0.020 mmol, 10 mol%), Na_2CO_3 (25.4 mg, 0.240 mmol, 1.2 equiv), 1-methyl-1*H*-pyrrole-2-carbaldehyde **1y** (21.8 mg, 0.200 mmol, 1.0 equiv), and *SS*-(*tert*-butyl) 4-methylbenzenesulfono(dithioperoxoate) **2a** (66.2 mg, 0.240 mmol, 1.2 equiv) in H_2O (2 mL) at room temperature for 12 h. Purification via silica gel chromatography (PE) gave the desired product **3y** as a colorless liquid in 45% yield (20.7 mg); **TLC R_f** = 0.4 (PE:EtOAc = 100:1); **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.25 (d, J = 1.6 Hz, 1H), 6.89 (d, J = 1.9 Hz, 1H), 6.16 (dd, J^1 = 4.2 Hz, J^2 = 2.5 Hz, 1H), 3.91 (s, 3H), 1.34 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 179.5, 131.4, 127.4, 119.4, 108.9, 48.5, 37.2, 29.7; **HRMS** (ESI) *m*/*z* = 230.0668 calcd. for $C_{10}H_{16}NOS_2$ $[M+H]^+$, found: 230.0677; **IR** (neat, cm^{-1}): 2961*w*, 2921*w*, 1386*m*, 1364*m*, 1198*s*, 1152*s*, 1170*s*, 1011*s*, 890*s*, 822*s*, 716*m*, 636*m*, 470*w*, 457*w*.

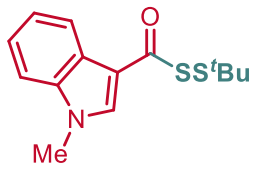


***SS*-(*tert*-Butyl) furan-2-carbo(dithioperoxoate) (3z):** The title compound was prepared according to general procedure (**GP1-1**) with phenanthrene-9,10-dione (4.2 mg, 0.020 mmol, 10 mol%), Na_2CO_3 (25.4 mg, 0.240 mmol, 1.2 equiv), furan-2-carbaldehyde **1z** (19.2 mg, 0.200 mmol, 1.0 equiv), and *SS*-(*tert*-butyl) 4-methylbenzenesulfono (dithioperoxoate) **2a** (66.2 mg, 0.240 mmol, 1.2 equiv) in H_2O (2 mL) at room temperature for 12 h. Purification via silica gel chromatography (PE) gave the desired product **3z** as a colorless liquid in 83% yield (36.0 mg); **TLC R_f** = 0.5 (PE:EtOAc = 100:1); **^{1}H NMR**

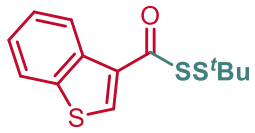
(400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.65 (d, *J* = 1.4 Hz, 1H), 7.32 (d, *J* = 3.6 Hz, 1H), 6.58 (dd, J^1 = 3.6 Hz, J^2 = 1.7 Hz, 1H), 1.34 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 179.0, 149.5, 147.1, 117.2, 112.5, 49.1, 29.7; **HRMS** (ESI) *m*/*z* = 217.0351 calcd. for $C_9H_{13}O_2S_2$ $[M+H]^+$, found: 217.0362; **IR** (neat, cm^{-1}): 2961*w*, 2922*w*, 1688*s*, 1563*m*, 1461*s*, 1384*m*, 1365*m*, 1248*s*, 1159*m*, 1078*w*, 1012*s*, 944*s*, 885*m*, 821*s*, 761*m*, 597*w*.



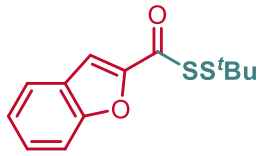
***SS*-(*tert*-Butyl) thiophene-2-carbo(dithioperoxoate) (3aa):** The title compound was prepared according to general procedure (**GP1-1**) with phenanthrene-9,10-dione (4.2 mg, 0.020 mmol, 10 mol%), Na_2CO_3 (25.4 mg, 0.240 mmol, 1.2 equiv), thiophene-2-carbaldehyde **1aa** (22.4 mg, 0.200 mmol, 1.0 equiv), and *SS*-(*tert*-butyl) 4-methylbenzenesulfono (dithioperoxoate) **2a** (66.2 mg, 0.240 mmol, 1.2 equiv) in H_2O (2 mL) at room temperature for 12 h. Purification via silica gel chromatography (PE) gave the desired product **3aa** as a white solid in 95% yield (50.7 mg); **TLC R_f** = 0.5 (PE:EtOAc = 100:1); **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.92 (d, *J* = 3.9 Hz, 1H), 7.69 (d, *J* = 4.9 Hz, 1H), 7.15 (t, *J* = 8.0 Hz, 1H), 1.34 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 182.2, 139.8, 133.9, 132.3, 128.1, 49.1, 29.7; **HRMS** (ESI) *m*/*z* = 233.0123 calcd. for $C_9H_{13}OS_3$ $[M+H]^+$, found: 233.0121; **IR** (neat, cm^{-1}): 2960*w*, 2920*w*, 1679*s*, 1512*w*, 1455*w*, 1408*s*, 1364*m*, 1349*m*, 1232*m*, 1192*s*, 1161*s*, 1079*w*, 1052*m*, 871*m*, 847*m*, 784*s*, 718*s*, 680*m*, 658*m*, 615*w*, 525*w*.



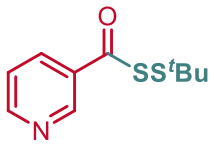
***SS*-(*tert*-Butyl) 1-methyl-1*H*-indole-3-carbo(dithioperoxoate) (3ab):** The title compound was prepared according to general procedure (**GP1-3**) with phenanthrene-9,10-dione (4.2 mg, 0.020 mmol, 10 mol%), Na_2CO_3 (25.4 mg, 0.240 mmol, 1.2 equiv), 1-methyl-1*H*-indole-3-carbaldehyde **1ab** (31.8 mg, 0.200 mmol, 1.0 equiv), and *SS*-(*tert*-butyl) 4-methylbenzenesulfono(dithioperoxoate) **2a** (66.2 mg, 0.240 mmol, 1.2 equiv) in H_2O (2 mL) at room temperature for 12 h. Purification via silica gel chromatography (PE:EtOAc = 100:1) gave the desired product **3ab** as a white solid in 82% yield (50.1 mg); **TLC R_f** = 0.5 (PE:EtOAc = 30:1); **MP**: = 108 – 110 °C; **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 8.28 (t, *J* = 4.0 Hz, 1H), 7.99 (s, 1H), 7.37 – 7.29 (m, 3H), 3.87 (s, 3H), 1.37 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 181.7, 137.2, 134.9, 125.7, 123.7, 122.9, 122.2, 113.8, 109.8, 48.4, 33.7, 29.8; **HRMS** (ESI) *m*/*z* = 280.0824 calcd. for $C_{14}H_{18}NOS_2$ $[M+H]^+$, found: 280.0833; **IR** (neat, cm^{-1}): 2961*w*, 2921*w*, 1679*s*, 1526*s*, 1461*s*, 1362*s*, 1202*m*, 1162*m*, 1127*m*, 1075*m*, 1033*m*, 816*s*, 750*s*.



***SS*-(*tert*-Butyl) benzo[*b*]thiophene-3-carbo(dithioperoxoate) (3ac):** The title compound was prepared according to general procedure (**GP1-1**) with phenanthrene-9,10-dione (4.2 mg, 0.020 mmol, 10 mol%), Na_2CO_3 (25.4 mg, 0.240 mmol, 1.2 equiv), benzo[*b*]thiophene-3-carbaldehyde **1ac** (32.4 mg, 0.200 mmol, 1.0 equiv), and *SS*-(*tert*-butyl) 4-methylbenzenesulfono(dithioperoxoate) **2a** (66.2 mg, 0.240 mmol, 1.2 equiv) in H_2O (2 mL) at room temperature for 12 h. Purification via silica gel chromatography (PE:EtOAc = 200:1) gave the desired product **3ac** as a white solid in 64% yield (36.4 mg); **TLC R_f** = 0.5 (PE:EtOAc = 50:1); **MP**: = 97 – 100 °C; **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 8.58 (s, 1H), 8.54 (d, *J* = 8.2 Hz, 1H), 7.87 (d, *J* = 8.0 Hz, 1H), 7.49 (t, *J* = 7.6 Hz, 1H), 7.43 (t, *J* = 7.6 Hz, 1H), 1.39 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 183.9, 139.6, 136.5, 135.7, 133.0, 126.0, 125.8, 124.8, 122.3, 49.0, 29.8; **HRMS** (ESI) *m*/*z* = 283.0280 calcd. for $C_{13}H_{15}OS_3$ $[M+H]^+$, found: 283.0285; **IR** (neat, cm^{-1}): 3070*w*, 2960*w*, 2920*w*, 1686*s*, 1489*m*, 1458*s*, 1423*m*, 1364*m*, 1258*m*, 1158*m*, 1138*m*, 1099*s*, 1051*s*, 1019*w*, 868*m*, 861*w*, 760*s*, 732*s*, 668*w*, 578*w*, 480*w*.

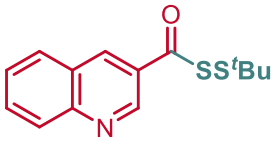


***SS*-(*tert*-Butyl) benzofuran-2-carbo(dithioperoxoate) (3ad):** The title compound was prepared according to general procedure (**GP1-1**) with phenanthrene-9,10-dione (4.2 mg, 0.020 mmol, 10 mol%), Na_2CO_3 (25.4 mg, 0.240 mmol, 1.2 equiv), benzofuran-2-carbaldehyde **1ad** (29.2 mg, 0.200 mmol, 1.0 equiv), and *SS*-(*tert*-butyl) 4-methylbenzenesulfono(dithioperoxoate) **2a** (66.2 mg, 0.240 mmol, 1.2 equiv) in H_2O (2 mL) at room temperature for 12 h. Purification via silica gel chromatography (PE) gave the desired product **3ad** as a colorless liquid in 42% yield (22.5 mg); **TLC R_f** = 0.5 (PE:EtOAc = 100:1); **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.72 (d, *J* = 8.1 Hz, 1H), 7.66 (s, 1H), 7.61 (d, *J* = 8.4 Hz, 1H), 7.50 (t, *J* = 7.8 Hz, 1H), 7.33 (t, *J* = 7.5 Hz, 1H), 1.38 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 181.1, 155.8, 149.8, 128.6, 126.7, 124.2, 123.3, 112.9, 112.5, 49.4, 29.8; **HRMS** (ESI) *m*/*z* = 267.0508 calcd. for $C_{13}H_{15}O_2S_2$ $[M+H]^+$, found: 267.0510; **IR** (neat, cm^{-1}): 2965*w*, 2921*w*, 1692*s*, 1678*s*, 1550*s*, 1364*w*, 1252*w*, 1155*m*, 1129*s*, 961*m*, 842*s*, 777*s*, 754*s*, 681*w*, 609*w*.

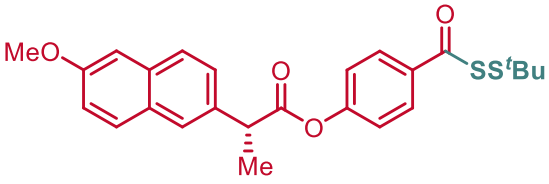


***SS*-(*tert*-Butyl) pyridine-3-carbo(dithioperoxoate) (3ae):** The title compound was prepared according to general procedure (**GP1-1**) with phenanthrene-9,10-dione (4.2 mg, 0.020 mmol, 10 mol%), Na_2CO_3 (25.4 mg, 0.240 mmol, 1.2 equiv), nicotinaldehyde **1ae** (21.4 mg, 0.200 mmol, 1.0 equiv), and *SS*-(*tert*-butyl) 4-methylbenzenesulfono (dithioperoxoate) **2a** (66.2 mg, 0.240 mmol, 1.2 equiv) in H_2O (2 mL) at room

temperature for 12 h. Purification via silica gel chromatography (PE:EtOAc = 100:1) gave the desired product **3ae** as a colorless liquid in 24% yield (11.0 mg); **TLC R_f** = 0.3 (PE:EtOAc = 50:1); **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 9.25 (s, 1H), 8.83 (d, *J* = 4.2 Hz, 1H), 8.27 (d, *J* = 8.0 Hz, 1H), 7.44 (dd, J^1 = 8.0 Hz, J^2 = 4.9 Hz, 1H), 1.37 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 189.5, 154.2, 148.7, 135.0, 131.7, 123.7, 49.5, 29.8; **HRMS** (ESI) *m*/*z* = 228.0511 calcd. for $C_{10}H_{14}NOS_2$ $[M+H]^+$, found: 228.0510; **IR** (neat, cm^{-1}): 2961*w*, 2921*w*, 1682*s*, 1482*m*, 1395*m*, 1364*m*, 1198*s*, 1062*s*, 1168*s*, 1011*s*, 880*s*, 830*s*, 717*m*, 638*m*, 487*w*.

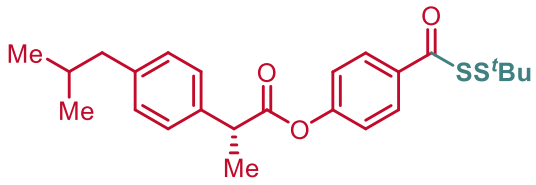


***SS*-(*tert*-Butyl) quinoline-3-carbo(dithioperoxoate) (3af):** The title compound was prepared according to general procedure (**GP1-3**) with phenanthrene-9,10-dione (4.2 mg, 0.020 mmol, 10 mol%), Na_2CO_3 (25.4 mg, 0.240 mmol, 1.2 equiv), quinoline-3-carbaldehyde **1af** (31.4 mg, 0.200 mmol, 1.0 equiv), and *SS*-(*tert*-butyl) 4-methylbenzenesulfono(dithioperoxoate) **2a** (66.2 mg, 0.240 mmol, 1.2 equiv) in H_2O (2 mL) at room temperature for 12 h. Purification via silica gel chromatography (PE:EtOAc = 50:1) gave the desired product **3af** as a white solid in 57% yield (31.7 mg); **TLC R_f** = 0.3 (PE:EtOAc = 20:1); **MP**: = 83 – 85 °C; **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 9.43 (s, 1H), 8.86 (s, 1H), 8.18 (d, *J* = 8.5 Hz, 1H), 7.98 (d, *J* = 8.2 Hz, 1H), 7.88 (t, *J* = 7.7 Hz, 1H), 7.67 (t, *J* = 7.5 Hz, 1H), 1.40 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 189.3, 150.2, 147.8, 136.8, 132.5, 129.6, 129.4, 128.6, 127.9, 126.7, 49.5, 29.9; **HRMS** (ESI) *m*/*z* = 278.0668 calcd. for $C_{14}H_{16}NOS_2$ $[M+H]^+$, found: 278.0674; **IR** (neat, cm^{-1}): 2961*w*, 2922*w*, 2853*s*, 1618*m*, 1569*w*, 1495*m*, 1456*w*, 1365*m*, 1274*w*, 1162*s*, 1124*s*, 921*w*, 897*m*, 825*s*, 781*m*, 754*m*.

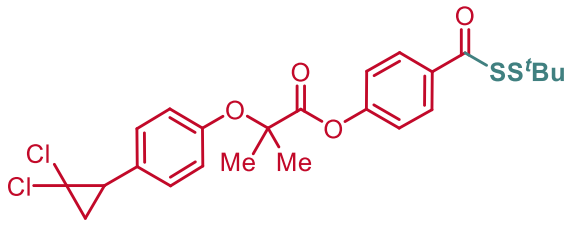


4-(*tert*-Butyldisulfannecarbonyl)phenyl (*R*)-2-(6-methoxynaphthalen-2-yl) propanoate (3ag): The title compound was prepared according to general procedure (**GP1-3**) with phenanthrene-9,10-dione (4.2 mg, 0.020 mmol, 10 mol%), Na_2CO_3 (25.4 mg, 0.240 mmol, 1.2 equiv), 4-formylphenyl (*R*)-2-(6-methoxynaphthalen-2-yl)propanoate **1ag** (66.9 mg, 0.200 mmol, 1.0 equiv), and *SS*-(*tert*-butyl) 4-methylbenzenesulfono (dithioperoxoate) **2a** (66.2 mg, 0.240 mmol, 1.2 equiv) in MeCN:H_2O (1 mL:1 mL) at room temperature for 12 h. Purification via silica gel chromatography (PE:EtOAc = 50:1) gave the desired product **3ag** as a white solid in 82% yield (50.1 mg); **TLC R_f** = 0.3 (PE:EtOAc = 10:1); **MP**: = 77 – 79 °C; **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 8.02 (d, *J* = 8.8 Hz, 2H), 7.79 – 7.73 (m, 3H), 7.49 (d, *J* = 9.2 Hz, 1H), 7.19 –

7.10 (m, 4H), 4.12 (q, *J* = 7.1 Hz, 1H), 3.92 (s, 3H), 1.71 (d, *J* = 7.2 Hz, 3H), 1.35 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 189.2, 172.5, 157.8, 155.2, 134.6, 133.9, 133.3, 129.3, 129.5, 128.9, 127.5, 126.2, 125.9, 121.9, 119.2, 105.6, 55.3, 49.1, 45.6, 29.7, 18.4; **HRMS** (ESI) *m*/*z* = 455.1345 calcd. for $C_{25}H_{27}O_4S_2$ $[M+H]^+$, found: 455.1347; **IR** (neat, cm^{-1}): 2961*w*, 1759*m*, 1686*m*, 1606*m*, 1501*w*, 1455*w*, 1392*w*, 1365*w*, 1265*w*, 1204*s*, 1161*s*, 1129*m*, 1068*w*, 1032*w*, 891*s*, 852*w*.

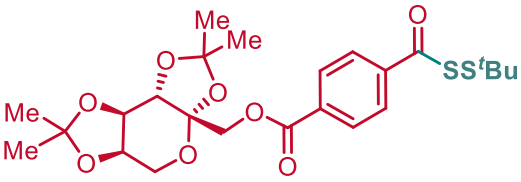


4-(*tert*-Butyldisulfannecarbonyl)phenyl (*R*)-2-(4-isobutylphenyl)propanoate (3ah): The title compound was prepared according to general procedure (**GP1-3**) with phenanthrene-9,10-dione (4.2 mg, 0.020 mmol, 10 mol%), Na_2CO_3 (25.4 mg, 0.240 mmol, 1.2 equiv), 4-formylphenyl (*R*)-2-(4-isobutylphenyl)propanoate **1ah** (74.5 mg, 0.240 mmol, 1.2 equiv), and *SS*-(*tert*-butyl) 4-methylbenzenesulfono(dithioperoxoate) **2a** (55.2 mg, 0.200 mmol, 1.0 equiv) in MeCN:H_2O (1 mL:1 mL) at room temperature for 12 h. Purification via silica gel chromatography (PE:EtOAc = 100:1) gave the desired product **3ah** as a colorless liquid in 78% yield (67.0 mg); **TLC R_f** = 0.3 (PE:EtOAc = 50:1); **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 8.04 (d, *J* = 8.7 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.16 (d, *J* = 8.0 Hz, 2H), 7.13 (d, *J* = 8.7 Hz, 2H), 3.96 (q, *J* = 7.1 Hz, 1H), 2.48 (d, *J* = 7.2 Hz, 2H), 1.91 – 1.84 (m, 1H), 1.62 (d, *J* = 7.1 Hz, 3H), 1.35 (s, 9H), 0.92 (d, *J* = 6.6 Hz, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 189.2, 172.5, 155.2, 141.0, 136.7, 133.2, 129. 6, 129.2, 127.1, 121.9, 49.1, 45.3, 45.0, 30.1, 29.7, 22.3, 18.4; **HRMS** (ESI) *m*/*z* = 431.1709 calcd. for $C_{24}H_{31}O_3S_2$ $[M+H]^+$, found: 431.1719; **IR** (neat, cm^{-1}): 2957*w*, 2923*w*, 1760*m*, 1686*m*, 1598*m*, 1501*m*, 1455*m*, 1365*m*, 1199*s*, 1060*s*, 1131*s*, 1066*m*, 890*s*, 847*w*, 801*w*, 640*m*.

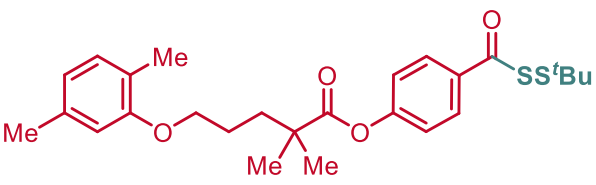


4-(*tert*-Butyldisulfannecarbonyl)phenyl2-(4-(2,2-dichlorocyclopropyl)phenoxy)-2-methyl propanoate (3ai): The title compound was prepared according to general procedure (**GP1-3**) with phenanthrene-9,10-dione (4.2 mg, 0.020 mmol, 10 mol%), Na_2CO_3 (25.4 mg, 0.240 mmol, 1.2 equiv), 4-formylphenyl 2-(4-(2,2-dichlorocyclopropyl)phenoxy)-2-methylpropanoate **1ai** (78.7 mg, 0.200 mmol, 1.0 equiv), and *SS*-(*tert*-butyl) 4-methylbenzenesulfono(dithioperoxoate) **2a** (66.2 mg, 0.240 mmol, 1.2 equiv) in MeCN:H_2O (1 mL:1 mL) at room temperature for 12 h. Purification via silica gel chromatography (PE:EtOAc = 50:1) gave the desired product **3ai** as a colorless liquid in 70% yield (71.1 mg); **TLC R_f** = 0.4

(PE:EtOAc = 20:1); **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 8.05 (d, *J* = 8.7 Hz, 2H), 7.17 (d, *J* = 8.7 Hz, 2H), 7.09 (d, *J* = 8.6 Hz, 2H), 6.93 (d, *J* = 8.6 Hz, 2H), 2.86 (t, *J* = 8.7 Hz, 1H), 1.96 (dd, J^1 = 10.7 Hz, J^2 = 7.4 Hz, 1H), 1.81 (d, *J* = 7.9 Hz, 1H), 1.77 (s, 6H), 1.35 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 189.2, 172.3, 154.8, 154.8, 133.7, 129.9, 129.4, 128.7, 121.9, 118.6, 79.3, 60.8, 49.2, 34.8, 29.8, 25.8, 25.4, 25.4; **HRMS** (ESI) *m*/*z* = 535.0342 calcd. for $C_{24}H_{26}O_4NaS_2Cl_2$ $[M+Na]^+$, found: 535.0549; **IR** (neat, cm^{-1}): 2923*w*, 1760*m*, 1658*m*, 1598*m*, 1512*s*, 1365*w*, 1242*w*, 1201*s*, 1166*s*, 1112*s*, 1015*w*, 892*s*, 832*w*, 731*s*, 640*s*.

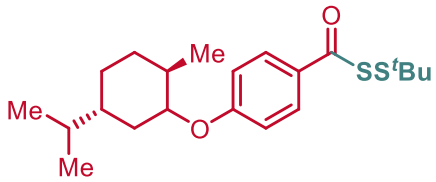


((3a*S*,5a*R*,8a*R*,8b*S*)-2,2,7,7-Tetramethyltetrahydro-3a*H*-bis([1,3]dioxolo)[4,5-*b*:4',5'-*d*]pyran-3a-yl)methyl4-(*tert*-butyldisulfannecarbonyl)benzoate (3aj): The title compound was prepared (**GP1-1**) according to general procedure with phenanthrene-9,10-dione (4.2 mg, 0.020 mmol, 10 mol%), Na_2CO_3 (25.4 mg, 0.240 mmol, 1.2 equiv), ((3a*S*,5a*R*,8a*R*,8b*S*)-2,2,7,7-tetramethyltetrahydro-3a*H*-bis([1,3]dioxolo)[4,5-*b*:4',5'-*d*]pyran-3a-yl)methyl 4-formylbenzoate **1aj** (78.5 mg, 0.200 mmol, 1.0 equiv), and *SS*-(*tert*-butyl) 4-methylbenzenesulfono(dithioperoxoate) **2a** (66.2 mg, 0.240 mmol, 1.2 equiv) in MeCN (2 mL) at room temperature for 12 h. Purification via silica gel chromatography (PE:EtOAc = 20:1) gave the desired product **3aj** as a white solid in 53% yield (54.7 mg); **TLC R_f** = 0.5 (PE:EtOAc = 5:1); **MP**: = 79 – 82 °C; **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 8.17 (d, *J* = 8.5 Hz, 2H), 8.07 (d, *J* = 8.2 Hz, 2H), 4.70 (d, *J* = 11.8 Hz, 1H), 4.64 (dd, J^1 = 7.8 Hz, J^2 = 2.6 Hz, 1H), 4.44 (d, *J* = 2.7 Hz, 1H), 4.35 (d, *J* = 11.8 Hz, 1H), 4.26 (d, *J* = 7.8 Hz, 1H), 3.95 (d, *J* = 13.0 Hz, 1H), 3.80 (d, *J* = 13.0 Hz, 1H), 1.54 (s, 3H), 1.45 (s, 3H), 1.36 (s, 9H), 1.35 (s, 3H), 1.32 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 190.2, 164.8, 139.3, 134.4, 130.2, 127.6, 109.2, 108.9, 101.5, 70.7, 70.6, 70.0, 65.8, 61.4, 49.4, 29.8, 26.5, 25.9, 25.5, 24.0; **HRMS** (ESI) *m*/*z* = 535.1431 calcd. for $C_{24}H_{32}O_8NaS_2$ $[M+Na]^+$, found: 535.1436; **IR** (neat, cm^{-1}): 2977*w*, 294*w*, 1730*s*, 1695*m*, 1456*w*, 1382*m*, 1274*s*, 1252*s*, 1198*s*, 1163*s*, 1108*s*, 1072*s*, 1018*w*, 890*s*, 774*w*, 698*w*.

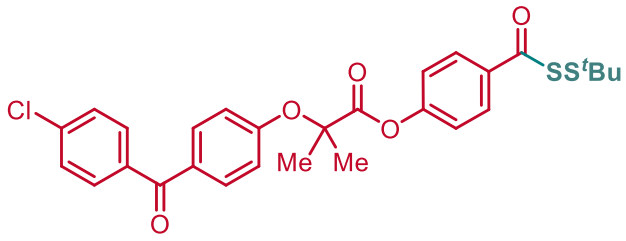


4-(*tert*-Butyldisulfannecarbonyl)phenyl 5-(2,5-dimethylphenoxy)-2,2-dimethylpentanoate (3ak): The title compound was prepared according to general procedure (**GP1-3**) with phenanthrene-9,10-dione (4.2 mg, 0.020 mmol, 10 mol%), Na_2CO_3 (25.4 mg, 0.240 mmol, 1.2 equiv), 4-formylphenyl 5-(2,5-dimethylphenoxy)-2,2-dimethylpentanoate

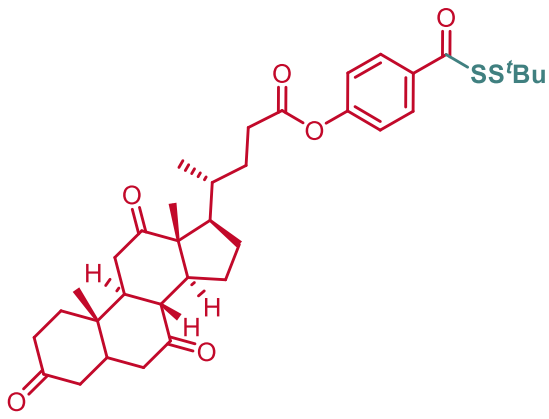
1ak (70.9 mg, 0.200 mmol, 1.0 equiv), and *SS*-(*tert*-butyl) 4-methylbenzenesulfono(dithioperoxoate) **2a** (66.2 mg, 0.240 mmol, 1.2 equiv) in MeCN:H_2O (1 mL:2 mL) at room temperature for 12 h. Purification via silica gel chromatography (PE:EtOAc = 50:1) gave the desired product **3ak** as a colorless liquid in 76% yield (72.0 mg); **TLC R_f** = 0.5 (PE:EtOAc = 20:1); **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 8.06 (d, *J* = 8.7 Hz, 2H), 7.15 (d, *J* = 8.7 Hz, 2H), 7.00 (d, *J* = 7.4 Hz, 1H), 6.67 (d, *J* = 7.5 Hz, 1H), 6.62 (s, 1H), 3.99 (t, *J* = 5.4 Hz, 2H), 2.30 (s, 3H), 2.17 (s, 3H), 1.93 – 1.84 (m, 4H), 1.39 (s, 6H), 1.36 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 189.3, 175.7, 156.8, 155.5, 136.5, 133.3, 130.4, 129.3, 123.6, 122.1, 120.8, 112.0, 67.6, 49.2, 42.6, 37.1, 29.8, 25.2, 25.1, 21.4, 15.8; **HRMS** (ESI) *m*/*z* = 497.1791 calcd. for $C_{26}H_{34}O_4NaS_2$ $[M+Na]^+$, found: 497.1797; **IR** (neat, cm^{-1}): 2961*w*, 2923*w*, 1756*m*, 1686*w*, 1598*w*, 1501*w*, 1472*w*, 1411*w*, 1365*w*, 1261*m*, 1204*s*, 1159*s*, 1045*m*, 889*s*, 800*s*, 730*m*.



***SS*-(*tert*-Butyl)4-(((2*R*,5*R*)-5-isopropyl-2-methyl -cyclohexyl)oxy)benzo(dithioperoxoate) (3al):** The title compound was prepared according to general procedure (**GP1-1**) with phenanthrene-9,10-dione (4.2 mg, 0.020 mmol, 10 mol%), Na_2CO_3 (25.4 mg, 0.240 mmol, 1.2 equiv), 4-(((2*R*,5*R*) -5-isopropyl-2-methylcyclohexyl)oxy)benzaldehyde **1al** (52.1 mg, 0.200 mmol, 1.0 equiv), and *SS*-(*tert*-butyl) 4-methylbenzenesulfono(dithioperoxoate) **2a** (66.2 mg, 0.240 mmol, 1.2 equiv) in MeCN:H_2O (1 mL:1 mL) at room temperature for 12 h. Purification via silica gel chromatography (PE:EtOAc = 100:1) gave the desired product **3al** as a colorless liquid in 80% yield (61.0 mg); **TLC R_f** = 0.5 (PE:EtOAc = 20:1); **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 8.01 (d, *J* = 8.9 Hz, 2H), 6.93 (d, *J* = 8.9 Hz, 2H), 4.73 (s, 1H), 2.08 (dd, J^1 = 15.9 Hz, J^2 = 1.9 Hz, 1H), 1.82 – 1.74 (m, 2H), 1.70 – 1.62 (m, 2H), 1.56 (dd, J^1 = 12.7 Hz, J^2 = 3.5 Hz, 1H), 1.34 (s, 9H), 1.27 (d, *J* = 12.3 Hz, 1H), 1.06 (dt, J^1 = 11.9 Hz, J^2 = 2.1 Hz, 2H), 0.92 (d, *J* = 6.7 Hz, 3H), 0.85 – 0.79 (m, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 188.3, 163.1, 130.2, 127.9, 115.1, 73.9, 48.8, 47.5, 37.5, 34.8, 29.7, 29.2, 26.2, 24.8, 22.2, 21.0 20.7; **HRMS** (ESI) *m*/*z* = 403.1736 calcd. for $C_{21}H_{33}O_2S_2$ $[M+H]^+$, found: 403.1741; **IR** (neat, cm^{-1}): 2955*w*, 2922*w*, 1692*m*, 1599*s*, 1572*w*, 1505*w*, 1456*w*, 1365*w*, 1306*w*, 1258*s*, 1198*s*, 1162*s*, 1025*w*, 890*s*, 837*m*, 643*w*.

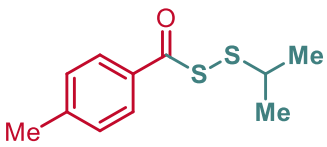


4-(*tert*-Butyldisulfannecarbonyl) phenyl 2-(4-(4-chlorobenzoyl) phenoxy)-2-methylpropanoate (3am): The title compound was prepared according to general procedure (**GP1-3**) with phenanthrene-9,10-dione (4.2 mg, 0.020 mmol, 10 mol%), Na_2CO_3 (25.4 mg, 0.240 mmol, 1.2 equiv), 4-formylphenyl 2-(4-(4-chlorobenzoyl)phenoxy) -2-methylpropanoate **1am** (84.6 mg, 0.200 mmol, 1.0 equiv), and *SS*-(*tert*-butyl) 4-methylbenzenesulfono(dithioperoxoate) **2a** (66.2 mg, 0.240 mmol, 1.2 equiv) in MeCN:H_2O (1 mL: 1mL) at room temperature for 12 h. Purification via silica gel chromatography (PE:EtOAc = 50:1) gave the desired product **3am** as a colorless liquid in 46% yield (50.5 mg); **TLC R_f** = 0.5 (PE:EtOAc = 10:1); **MP**: = 68 – 71 °C; **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 8.06 (d, *J* = 8.7 Hz, 2H), 7.79 (d, *J* = 8.8 Hz, 2H), 7.71 (d, *J* = 8.5 Hz, 2H), 7.45 (d, *J* = 8.5 Hz, 2H), 7.12 (d, *J* = 8.7 Hz, 2H), 6.99 (d, *J* = 8.8 Hz, 2H), 1.83 (s, 6H), 1.34 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 194.1, 189.2, 171.8, 159.3, 154.6, 138.5, 136.2, 133.8, 132.1, 131.1, 130.9, 129.4, 128.6, 121.7, 117.3, 79.4, 49.2, 29.8, 25.4; **HRMS** (ESI) *m*/*z* = 565.0881 calcd. for $C_{28}H_{27}O_5NaS_2Cl$ $[M+Na]^+$, found: 565.0883; **IR** (neat, cm^{-1}): 2961*w*, 2923*w*, 1762*m*, 1685*m*, 1653*m*, 1598*s*, 1506*m*, 1456*w*, 1365*w*, 1249*w*, 1201*s*, 1161*s*, 1111*s*, 1015*w*, 928*m*, 892*s*, 854*w*, 764*m*, 731*m*, 640*w*.

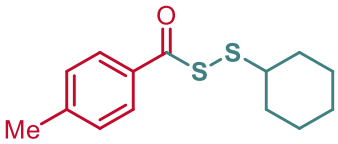


4-(*tert*-Butyldisulfannecarbonyl)phenyl(4*R*)-4-((8*R*,9*S*,10*S*,13*R*,14*S*,17*R*)-10,13-dimethyl-3,7,12-trioxohexadecahydro-1*H*-cyclopenta[*a*]phenanthrene -17-yl)pentanoate (3an): The title compound was prepared according to general procedure (**GP1-3**) with phenanthrene-9,10-dione (4.2 mg, 0.020 mmol, 10 mol%), Na_2CO_3 (25.4 mg, 0.240 mmol, 1.2 equiv), 4-formylphenyl (4*R*)-4-((8*R*,9*S*,10*S*,13*R*,14*S*,17*R*)-10,13-dimethyl-3,7,12-trioxohexadecahydro-1*H*-cyclopenta[*a*]phenanthren-17-yl)pentanoate **1an** (101.3 mg, 0.2000 mmol, 1.0 equiv), and *SS*-(*tert*-butyl) 4-methylbenzenesulfono(dithioperoxoate) **2a** (66.2 mg, 0.240 mmol, 1.2 equiv) in MeCN (2 mL) at room temperature for 12 h. Purification via silica gel chromatography (PE:EtOAc = 5:1) gave the desired product **3an** as a white solid in 60% yield (75.2 mg); **TLC R_f** = 0.3 (PE:EtOAc = 2:1); **MP**: = 192 – 194 °C;

^{1}H NMR (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 8.07 (d, *J* = 8.8 Hz, 2H), 7.21 (d, *J* = 8.7 Hz, 2H), 2.94 – 2.85 (m, 3H), 2.72 – 2.64 (m, 1H), 2.59 – 2.50 (m, 1H), 2.37 – 2.32 (m, 4H), 2.27 – 2.15 (m, 4H), 2.06 (d, *J* = 11.6 Hz, 3H), 1.98 – 1.95 (m, 2H), 1.90 – 1.83 (m, 1H), 1.63 (s, 3H), 1.40 (s, 4H), 1.35 (s, 9H), 1.09 (s, 3H), 0.92 (d, *J* = 6.6 Hz, 3H), 0.88 – 0.83 (m, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 211.9, 209.0, 208.6, 189.3, 171.8, 155.1, 133.3, 129.3, 122.0, 56.9, 51.7, 49.2, 49.0, 46.8, 45.6, 45.5, 44.9, 42.8, 38.6, 36.5, 36.0, 35.4, 35.2, 31.5, 30.2, 29.8, 27.6, 25.1, 21.9, 18.7, 11.8; **HRMS** (ESI) *m*/*z* = 649.2628 calcd. for $C_{35}H_{46}O_6NaS_2$ $[M+Na]^+$, found: 649.2627; **IR** (neat, cm^{-1}): 2963*w*, 2940*w*, 1760*m*, 1709*s*, 1598*w*, 1463*w*, 1382*w*, 1205*m*, 1161*s*, 1121*m*, 1014*w*, 910*m*, 892*s*, 731*s*, 570*w*, 643*w*.

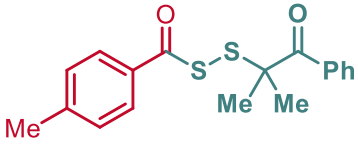


***SS*-Isopropyl 4-methylbenzo(dithioperoxoate) (3ao):** The title compound was prepared according to general procedure (**GP1-2**) with phenanthrene-9,10-dione (4.2 mg, 0.020 mmol, 10 mol%), Na_2CO_3 (25.4 mg, 0.240 mmol, 1.2 equiv), 4-methylbenzaldehyde **1a** (24.0 mg, 0.200 mmol, 1.0 equiv), and *SS*-isopropyl 4-methylbenzenesulfono(dithioperoxoate) **2b** (63.0 mg, 0.240 mmol, 1.2 equiv) in H_2O (2 mL) at room temperature for 12 h. Purification via silica gel chromatography (PE) gave the desired product **3ao** as a colorless liquid in 47% yield (21.1 mg); **TLC R_f** = 0.4 (PE:EtOAc = 100:1); **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.92 (d, *J* = 7.8 Hz, 2H), 7.28 (d, *J* = 9.1 Hz, 2H), 3.18 – 3.08 (m, 1H), 2.43 (s, 3H), 1.34 (s, 3H), 1.32 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 190.1, 145.0, 133.3, 129.5, 127.8, 41.5, 22.5, 21.8; **HRMS** (ESI) *m*/*z* = 227.0599 calcd. for $C_{11}H_{15}OS_2$ $[M+H]^+$, found: 227.0563; **IR** (neat, cm^{-1}): 2961*w*, 2922*m*, 2853*w*, 1698*s*, 1606*m*, 1203*s*, 1175*s*, 888*s*, 821*m*, 787*m*, 716*w*, 640*w*, 620*w*.

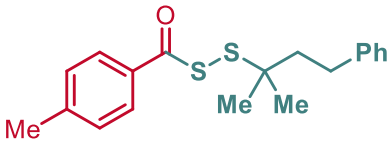


***SS*-Cyclohexyl 4-methylbenzo(dithioperoxoate) (3ap):** The title compound was prepared according to general procedure (**GP1-3**) with phenanthrene-9,10-dione (4.2 mg, 0.020 mmol, 10 mol%), Na_2CO_3 (25.4 mg, 0.240 mmol, 1.2 equiv), 4-methylbenzaldehyde **1a** (24.0 mg, 0.200 mmol, 1.0 equiv), and *SS*-cyclohexyl 4-methylbenzenesulfono(dithioperoxoate) **2c** (72.6 mg, 0.240 mmol, 1.2 equiv) in H_2O (2 mL) at room temperature for 12 h. Purification via silica gel chromatography (PE) gave the desired product **3ap** as a colorless liquid in 53% yield (28.0 mg); **TLC R_f** = 0.4 (PE:EtOAc = 100:1); **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.91 (d, *J* = 7.7 Hz, 2H), 7.27 (d, *J* = 8.2 Hz, 2H), 2.88 – 2.83 (m, 1H), 2.42 (s, 3H), 2.06 – 2.04 (m, 2H), 1.81 – 1.77 (m, 2H), 1.62 – 1.59 (m, 1H), 1.41 – 1.25 (m, 5H); **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 190.3, 144.9, 133.3, 129.5, 127.8, 49.6, 32.6, 26.0, 25.5, 21.7; **HRMS** (ESI) *m*/*z* = 266.0872 calcd. for $C_{14}H_{19}OS_2$

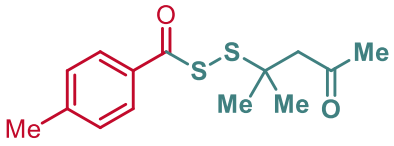
$[M+H]^+$, found: 267.0879; **IR** (neat, cm^{-1}): 2928*s*, 2853*m*, 1695*s*, 1606*m*, 1448*m*, 1204*s*, 1174*s*, 1154*s*, 888*s*, 821*m*, 787*m*, 753*w*, 717*w*, 798*s*, 638*w*, 621*w*, 471*w*.



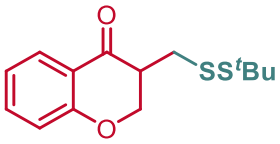
***SS*-(2-Methyl-1-oxo-1-phenylpropan-2-yl)4-methylbenzo(dithioperoxoate) (3aq):** The title compound was prepared according to general procedure (**GP1-2**) with phenanthrene-9,10-dione (4.2 mg, 0.020 mmol, 10 mol%), Na_2CO_3 (25.4 mg, 0.240 mmol, 1.2 equiv), 4-methylbenzaldehyde **1a** (24.0 mg, 0.200 mmol, 1.0 equiv), and *SS*-(2-methyl-1-oxo-1-phenylpropan-2-yl) 4-methylbenzenesulfono(dithioperoxoate) **2d** (72.6 mg, 0.240 mmol, 1.2 equiv) in H_2O (2 mL) at room temperature for 12 h. Purification via silica gel chromatography (PE:EtOAc = 150:1) gave the desired product **3aq** as a colorless liquid in 56% yield (37.2 mg); **TLC R_f** = 0.4 (PE:EtOAc = 50:1); **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 8.13 (d, *J* = 7.1 Hz, 2H), 7.86 (d, *J* = 8.3 Hz, 2H), 7.51 (t, *J* = 7.3 Hz, 1H), 7.44 (t, *J* = 7.5 Hz, 2H), 7.25 (d, *J* = 9.4 Hz, 2H), 2.41 (s, 3H), 1.65 (s, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 199.3, 188.4, 145.3, 136.7, 132.8, 131.7, 129.5, 129.3, 128.0, 128.0, 56.7, 25.8, 21.7; **HRMS** (ESI) *m*/*z* = 353.0640 calcd. for $C_{18}H_{18}NaO_2S_2$ $[M+Na]^+$, found: 353.0636; **IR** (neat, cm^{-1}): 2923*w*, 1702*m*, 1670*s*, 1605*m*, 1445*w*, 1262*w*, 1205*s*, 1174*s*, 1115*w*, 977*m*, 888*m*, 821*w*, 785*m*, 705*m*, 640*w*, 620*m*.



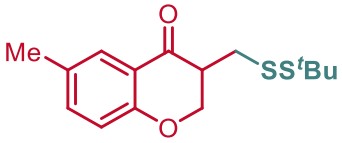
***SS*-(2-Methyl-4-phenylbutan-2-yl) 4-methylbenzo (dithioperoxoate) (3ar):** The title compound was prepared according to general procedure (**GP1-2**) with phenanthrene-9,10-dione (4.2 mg, 0.020 mmol, 10 mol%), Na_2CO_3 (25.4 mg, 0.240 mmol, 1.2 equiv), 4-methylbenzaldehyde **1a** (24.0 mg, 0.200 mmol, 1.0 equiv), and *SS*-(2-methyl-4-phenylbutan-2-yl) 4-methylbenzenesulfono(dithioperoxoate) **2e** (88.0 mg, 0.240 mmol, 1.2 equiv) in H_2O (2 mL) at room temperature for 12 h. Purification via silica gel chromatography (PE) gave the desired product **3ar** as a colorless liquid in 83% yield (54.7 mg); **TLC R_f** = 0.3 (PE:EtOAc = 100:1); **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.94 (d, *J* = 8.2 Hz, 2H), 7.32 – 7.26 (m, 4H), 7.22 – 7.16 (m, 3H), 2.84 – 2.78 (m, 2H), 2.43 (s, 3H), 1.90 – 1.84 (m, 2H), 1.39 (s, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 189.8, 145.0, 142.1, 133.3, 129.5, 128.4, 128.4, 127.9, 125.8, 52.2, 43.6, 31.3, 27.6, 21.7; **HRMS** (ESI) *m*/*z* = 353.1004 calcd. for $C_{19}H_{22}ONaS_2$ $[M+Na]^+$, found: 353.1007; **IR** (neat, cm^{-1}): 2958*w*, 2923*w*, 1698*s*, 1605*m*, 1698*w*, 1453*w*, 1365*w*, 1203*s*, 1174*s*, 1117*w*, 887*s*, 821*w*, 717*m*, 638*m*, 570*w*, 467*w*.



***SS*-(2-Methyl-4-oxopentan-2-yl) 4-methylbenzo (dithioperoxoate) (3as):** The title compound was prepared according to general procedure (**GP1-2**) with phenanthrene-9,10-dione (4.2 mg, 0.020 mmol, 10 mol%), Na_2CO_3 (25.4 mg, 0.240 mmol, 1.2 equiv), 4-methylbenzaldehyde **1a** (24.0 mg, 0.200 mmol, 1.0 equiv), and *SS*-(2-methyl-4-oxopentan-2-yl) 4-methylbenzenesulfono(dithioperoxoate) **2f** (76.4 mg, 0.240 mmol, 1.2 equiv) in H_2O (2 mL) at room temperature for 12 h. Purification via silica gel chromatography (PE:EtOAc = 100:1) gave the desired product **3as** as a white solid in 64% yield (36.6 mg); **TLC R_f** = 0.3 (PE:EtOAc = 20:1); **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.93 (d, *J* = 8.3 Hz, 2H), 7.29 (d, *J* = 8.1 Hz, 2H), 2.76 (s, 2H), 2.43 (s, 3H), 2.16 (s, 3H), 1.47 (s, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 206.2, 189.5, 145.2, 133.0, 129.6, 127.9, 53.3, 50.0, 31.9, 26.9, 21.8; **IR** (neat, cm^{-1}): 2963*w*, 2923*w*, 1695*s*, 1605*m*, 1458*w*, 1369*m*, 1204*s*, 1172*s*, 1116*m*, 884*s*, 821*m*, 785*s*, 717*w*, 620*s*, 547*w*, 471*w*.

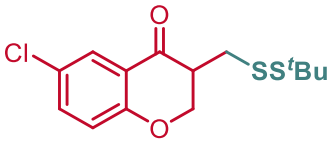


3-((*tert*-Butyldisulfaneyl)methyl)chroman-4-one (5a): The title compound was prepared according to general procedure (**GP2-1)** with phenanthrene-9,10-dione (4.2 mg, 0.020 mmol, 10 mol%), Na_2CO_3 (27.3 mg, 0.260 mmol, 1.3 equiv), 2-(allyloxy)benzaldehyde **4a** (32.4 mg, 0.200 mmol, 1.0 equiv), and *SS*-(*tert*-butyl) 4-methylbenzenesulfono(dithioperoxoate) **2a** (110.4 mg, 0.4000 mmol, 2.0 equiv) in MeCN (2 mL) at 30 ºC for 12 h. Purification via silica gel chromatography (PE:EtOAc = 100:1) gave the desired product **5a** as a colorlrss liquid in 82% yield (46.3 mg); **TLC R_f** = 0.5 (PE:EtOAc = 50:1); **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.88 (d, *J* = 8.2 Hz, 1H), 7.48 (t, *J* = 7.9 Hz, 1H), 7.02 (t, *J* = 7.5 Hz, 1H), 6.98 (d, *J* = 8.4 Hz, 1H), 4.69 (dd, J^1 = 11.5 Hz, J^2 = 4.6 Hz, 1H), 4.43 (dd, J^1 = 11.3 Hz, J^2 = 9.6 Hz, 1H), 3.31 (dd, J^1 = 13.6 Hz, J^2 = 3.9 Hz, 1H), 3.19 – 3.10 (m, 1H), 2.72 (dd, J^1 = 13.6 Hz, J^2 = 10.0 Hz, 1H), 1.35 (m, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 192.8, 161.6, 136.1, 127.4, 121.5, 120.5, 117.9, 69.1, 48.4, 45.4, 36.4, 29.9; **HRMS** (ESI) *m*/*z* = 283.0821 calcd. for $C_{14}H_{19}O_2S_2$ $[M+H]^+$, found: 283.0830; **IR** (neat, cm^{-1}): 2960*w*, 2924*w*, 2857*w*, 1690*s*, 1606*s*, 1479*s*, 1466*m*, 1364*m*, 1326*m*, 1215*m*, 1165*m*, 1035*w*, 761*s*, 674*w*.

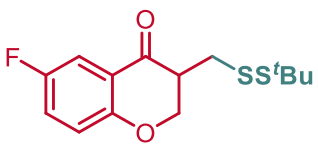


3-((*tert*-Butyldisulfaneyl)methyl)-6-methylchroman-4-one (5b): The title compound was prepared according to general procedure (**GP2-1)** phenanthrene-9,10-dione with (4.2 mg, 0.020 mmol, 10 mol%), Na_2CO_3 (27.3 mg, 0.260 mmol, 1.3 equiv), 2-(allyloxy)-5- methylbenzaldehyde **4b** (35.2 mg, 0.200

mmol, 1.0 equiv), and *SS*-(*tert*-butyl) 4-methylbenzenesulfono(dithioperoxoate) **2a** (110.4 mg, 0.4000 mmol, 2.0 equiv) in MeCN (2 mL) at 30 °C for 12 h. Purification via silica gel chromatography (PE:EtOAc = 200:1) gave the desired product **5b** as a colorless liquid in 43% yield (25.5 mg); **TLC R_f** = 0.5 (PE:EtOAc = 50:1); **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.66 (s, 1H), 7.29 (d, *J* = 8.2 Hz, 1H), 6.88 (d, *J* = 8.4 Hz, 1H), 4.65 (dd, J^1 = 11.4 Hz, J^2 = 4.5 Hz, 1H), 4.40 (dd, J^1 = 11.4 Hz, J^2 = 9.1 Hz, 1H), 3.29 (dd, J^1 = 13.5 Hz, J^2 = 3.9 Hz, 1H), 3.15 – 3.08 (m, 1H), 2.71 (dd, J^1 = 13.5 Hz, J^2 = 10.0 Hz, 1H), 2.30 (s, 3H), 1.35 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 193.0, 159.6, 137.2, 131.0, 120.1, 117.6, 69.1, 48.4, 45.5, 36.5, 29.9, 20.4; **HRMS** (ESI) *m*/*z* = 319.0797 calcd. for $C_{15}H_{20}O_2NaS_2$ $[M+Na]^+$, found: 319.0712; **IR** (neat, cm^{-1}): 2964*w*, 2924*w*, 2861*w*, 1685*s*, 1616*s*, 1491*s*, 1456*w*, 1422*m*, 1365*w*, 1291*s*, 1256*w*, 1222*m*, 1159*w*, 1137*w*, 1028*w*, 822*m*, 754*w*, 537*w*.

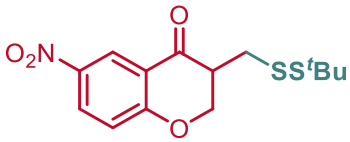


3-((*tert*-Butyldisulfaneyl)methyl)-6-chlorochroman-4-one (5c): The title compound was prepared according to general procedure (**GP2-1)** with phenanthrene-9,10-dione (4.2 mg, 0.020 mmol, 10 mol%), Na_2CO_3 (27.3 mg, 0.260 mmol, 1.3 equiv), 2-(allyloxy)-5-chlorobenzaldehyde **4c** (39.3 mg, 0.200 mmol, 1.0 equiv), and *SS*-(*tert*-butyl)4-methylbenzenesulfono (dithioperoxoate) **2a** (110.4 mg, 0.4000 mmol, 2.0 equiv) in MeCN (2 mL) at 30 °C for 12 h. Purification via silica gel chromatography (PE:EtOAc = 100:1) gave the desired product **5c** as a colorlrss liquid in 75% yield (47.6 mg); **TLC R_f** = 0.4 (PE:EtOAc = 50:1); **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.83 (d, *J* = 2.7 Hz, 1H), 7.41 (dd, J^1 = 8.9 Hz, J^2 = 2.7 Hz, 1H), 6.94 (d, *J* = 8.9 Hz, 1H), 4.69 (dd, J^1 = 11.6 Hz, J^2 = 4.6 Hz, 1H), 4.42 (dd, J^1 = 11.6 Hz, J^2 = 9.4 Hz, 1H), 3.29 (dd, J^1 = 13.6 Hz, J^2 = 3.9 Hz, 1H), 3.19 – 3.12 (m, 1H), 2.70 (dd, J^1 = 13.6 Hz, J^2 = 10.0 Hz, 1H), 1.35 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 191.7, 160.0, 135.9, 127.1, 126.6, 121.3, 119.6, 69.3, 48.5, 45.2, 36.2, 29.9; **HRMS** (ESI) *m*/*z* = 317.0431 calcd. for $C_{14}H_{18}O_2S_2Cl$ $[M+H]^+$, found: 317.0438; **IR** (neat, cm^{-1}): 2961*w*, 2921*w*, 2853*w*, 1692*m*, 1605*m*, 1476*s*, 1456*w*, 1421*m*, 1362*w*, 1296*w*, 1271*s*, 1209*w*, 1165*w*, 824*w*.

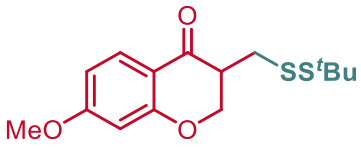


3-((*tert*-Butyldisulfaneyl)methyl)-6-fluorochroman-4-one (5d): The title compound was prepared according to general procedure (**GP2-1)** with phenanthrene-9,10-dione (4.2 mg, 0.020 mmol, 10 mol%), Na_2CO_3 (27.3 mg, 0.260 mmol, 1.3 equiv), 2-(allyloxy)-5-fluorobenzaldehyde **4d** (36.0 mg, 0.200 mmol, 1.0 equiv), and *SS*-(*tert*-butyl)4-methylbenzenesulfono(dithioperoxoate) **2a** (110.4 mg, 0.4000 mmol, 2.0 equiv) in MeCN (2 mL) at 30 °C for 12 h. Purification via silica gel chromatography (PE:EtOAc = 50:1) gave the desired product **5d** as a white solid in

63% yield (38.1 mg); **TLC R_f** = 0.4 (PE:EtOAc = 20:1); **MP**: = 43 – 45 °C; **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.55 (dd, J^1 = 8.2 Hz, J^2 = 3.2 Hz, 1H), 7.25 – 7.20 (m, 1H), 6.99 (dd, J^1 = 9.1 Hz, J^2 = 4.2 Hz, 1H), 4.70 (dd, J^1 = 11.5 Hz, J^2 = 4.6 Hz, 1H), 4.43 (dd, J^1 = 11.5 Hz, J^2 = 9.4 Hz, 1H), 3.32 (dd, J^1 = 13.6 Hz, J^2 = 3.9 Hz, 1H), 3.21 – 3.13 (m, 1H), 2.73 (dd, J^1 = 13.6 Hz, J^2 = 10.0 Hz, 1H), 1.38 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 192.1, 157.9 (d, J = 1.7 Hz, 1C), 157.3 (d, J = 243.0 Hz, 1C), 123.7 (d, J = 24.7 Hz, 1C), 120.9 (d, J = 6.3 Hz, 1C), 119.6 (d, J = 7.4 Hz, 1C), 112.2 (d, J = 23.5 Hz, 1C), 69.3, 48.4, 45.2, 36.3, 29.9; **HRMS** (ESI) *m*/*z* = 323.0546 calcd. for $C_{14}H_{17}FNaO_2S_2$ $[M+Na]^+$, found: 323.0554; **IR** (neat, cm^{-1}): 2963*w*, 2923*w*, 1692*m*, 1622*w*, 1486*s*, 1456*w*, 1435*m*, 1364*w*, 1269*s*, 1166*w*, 1148*w*, 1121*w*, 1018*w*, 887*w*, 825*w*, 752*w*.

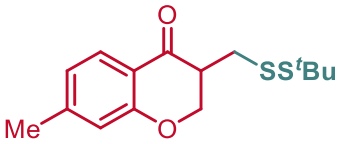


3-((*tert*-Butyldisulfaneyl)methyl)-6-nitrochroman-4-one (5e): The title compound was prepared according to general procedure (**GP2-3**) with phenanthrene-9,10-dione (4.2 mg, 0.020 mmol, 10 mol%), Na_2CO_3 (27.3 mg, 0.260 mmol, 1.3 equiv), 2-(allyloxy)-5-nitrobenzaldehyde **4e** (41.4 mg, 0.200 mmol, 2.0 equiv), and *SS*-(*tert*-butyl)4-methylbenzenesulfono (dithioperoxoate) **2a** (110.4 mg, 0.4000 mmol, 2.0 equiv) in MeCN (2 mL) at 30 °C for 12 h. Purification via silica gel chromatography (PE:EtOAc = 50:1) gave the desired product **5e** as a white solid in 40% yield (26.0 mg); **TLC R_f** = 0.4 (PE:EtOAc = 20:1); **MP**: = 57 – 59 °C; **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 8.77 (d, J = 2.8 Hz, 1H), 8.33 (dd, J^1 = 9.2 Hz, J^2 = 2.9 Hz, 1H), 7.12 (d, J = 9.1 Hz, 1H), 4.84 (dd, J^1 = 11.7 Hz, J^2 = 4.8 Hz, 1H), 4.53 (dd, J^1 = 11.7 Hz, J^2 = 9.8 Hz, 1H), 3.33 (dd, J^1 = 13.6 Hz, J^2 = 3.9 Hz, 1H), 3.30 – 3.23 (m, 1H), 2.71 (dd, J^1 = 13.6 Hz, J^2 = 9.6 Hz, 1H), 1.36 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 190.8, 165.5, 142.2, 130.4, 123.9, 120.1, 119.3, 69.8, 48.6, 45.0, 35.8, 29.9; **HRMS** (ESI) *m*/*z* = 328.0672 calcd. for $C_{14}H_{18}N8O_4S_2$ $[M+H]^+$, found: 328.0677; **IR** (neat, cm^{-1}): 2961*w*, 2923*w*, 1700*s*, 1618*s*, 1585*m*, 1525*m*, 1481*m*, 1436*m*, 1329*s*, 1299*w*, 1271*s*, 1219*w*, 1165*w*, 911*w*, 840*w*, 734*m*.

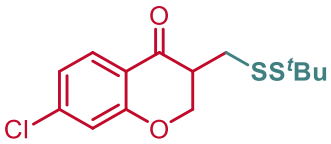


3-((*tert*-Butyldisulfaneyl)methyl)-7-methoxychroman-4-one (5f): The title compound was prepared according to general procedure (**GP2-3**) with phenanthrene-9,10-dione (4.2 mg, 0.020 mmol, 10 mol%), Na_2CO_3 (27.3 mg, 0.260 mmol, 1.3 equiv), 2-(allyloxy) -4-methoxybenzaldehyde **4f** (39.2 mg, 0.200 mmol, 1.0 equiv), and *SS*-(*tert*-butyl) 4-methylbenzenesulfono(dithioperoxoate) **2a** (110.4 mg, 0.4000 mmol, 2.0 equiv) in MeCN (2 mL) at 30 °C for 12 h. Purification via silica gel chromatography

(PE:EtOAc = 100:1) gave the desired product **5f** as a white solid in 68% yield (42.5 mg); **TLC R_f** = 0.3 (PE:EtOAc = 20:1); **MP**: = 60 – 62 °C; **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.81 (d, *J* = 8.8 Hz, 1H), 6.58 (dd, J^1 = 8.8 Hz, J^2 = 2.4 Hz, 1H), 6.41 (d, *J* = 2.4 Hz, 1H), 4.65 (dd, J^1 = 11.4 Hz, J^2 = 4.5 Hz, 1H), 4.42 (dd, J^1 = 11.4 Hz, J^2 = 8.9 Hz, 1H), 3.83 (s, 3H), 3.30 (dd, J^1 = 13.6 Hz, J^2 = 3.8 Hz, 1H), 3.11 – 3.04 (m, 1H), 2.70 (dd, J^1 = 13.6 Hz, J^2 = 10.2 Hz, 1H), 1.35 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 191.4, 166.1, 163.6, 129.1, 114.4, 110.2, 100.6, 69.4, 55.6, 48.3, 45.1, 36.7, 29.9; **HRMS** (ESI) *m*/*z* = 31.0927 calcd. for $C_{15}H_{21}O_3S_2$ $[M+H]^+$, found: 313.0940; **IR** (neat, cm^{-1}): 2961*w*, 2923*w*, 2858*w*, 1679*m*, 1609*s*, 1578*w*, 1469*w*, 1385*w*, 1362*w*, 1258*s*, 1162*s*, 1125*w*, 1029*w*, 837*w*.

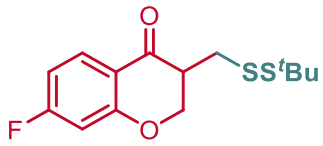


3-((*tert*-Butyldisulfaneyl)methyl)-7-methylchromn-4-one (5g): The title compound was prepared according to general procedure (**GP2-1**) with phenanthrene-9,10-dione (4.2 mg, 0.020 mmol, 10 mol%), Na_2CO_3 (27.3 mg, 0.260 mmol, 1.3 equiv), 2-(allyloxy)-4-methylbenzaldehyde **4g** (35.2 mg, 0.200 mmol, 1.0 equiv), and *SS*-(*tert*-butyl) 4-methylbenzenesulfono(dithioperoxoate) **2a** (110.4 mg, 0.4000 mmol, 2.0 equiv) in MeCN (2 mL) at 30 °C for 12 h. Purification via silica gel chromatography (PE:EtOAc = 100:1) gave the desired product **5g** as a colorlrss liquid in 36% yield (21.3 mg); **TLC R_f** = 0.4 (PE:EtOAc = 50:1); **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.77 (d, *J* = 8.1 Hz, 1H), 6.84 (d, *J* = 6.5 Hz, 1H), 6.78 (s, 1H), 4.66 (dd, J^1 = 11.4 Hz, J^2 = 4.6 Hz, 1H), 4.40 (dd, J^1 = 11.4 Hz, J^2 = 9.1 Hz, 1H), 3.30 (dd, J^1 = 13.5 Hz, J^2 = 3.9 Hz, 1H), 3.11 (m, 1H), 2.36 (s, 3H), 1.35 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 192.5, 161.6, 147.7, 127.2, 122.9, 118.3, 117.8, 69.1, 48.3, 45.4, 36.6, 30.0, 21.9; **HRMS** (ESI) *m*/*z* = 319.0797 calcd. for $C_{15}H_{20}O_2NaS_2$ $[M+Na]^+$, found: 319.0791; **IR** (neat, cm^{-1}): 2960*w*, 2901*w*, 2854*w*, 1683*m*, 1618*s*, 1469*w*, 1422*w*, 1364*w*, 1331*w*, 1232*w*, 1154*w*, 1042*w*, 907*s*, 825*s*, 650*w*.

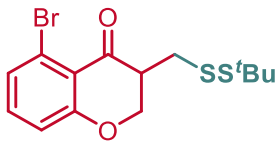


3-((*tert*-Butyldisulfaneyl)methyl)-7-methylchromn-4-one (5h): The title compound was prepared according to general procedure (**GP2-1**) with phenanthrene-9,10-dione (4.2 mg, 0.020 mmol, 10 mol%), Na_2CO_3 (27.3 mg, 0.260 mmol, 1.3 equiv), 2-(allyloxy)-4-chlorobenzaldehyde **4h** (39.3 mg, 0.200 mmol, 1.0 equiv), and *SS*-(*tert*-butyl) 4-methylbenzenesulfono (dithioperoxoate) **2a** (110.4 mg, 0.4000 mmol, 2.0 equiv) in MeCN (2 mL) at 30 °C for 12 h. Purification via silica gel chromatography (PE:EtOAc = 100:1) gave the desired product **5h** as a colorlrss liquid in 65% yield (41.2 mg); **TLC R_f** = 0.5 (PE:EtOAc = 50:1); **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.81 (d, *J* = 8.9 Hz, 1H), 7.00 (d, *J* = 7.2 Hz, 2H), 4.70 (dd,

J^1 = 11.5 Hz, J^2 = 4.6 Hz, 1H), 4.43 (dd, J^1 = 11.3 Hz, J^2 = 9.6 Hz, 1H), 3.29 (dd, J^1 = 13.6 Hz, J^2 = 3.9 Hz, 1H), 3.18 – 3.11 (m, 1H), 2.70 (dd, J^1 = 13.6 Hz, J^2 = 9.9 Hz, 1H), 1.35 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 191.8, 161.9, 142.0, 128.6, 122.4, 119.1, 118.0, 69.5, 48.4, 45.3, 36.3, 29.9; **HRMS** (ESI) *m*/*z* = 317.0431 calcd. for $C_{14}H_{18}O_2S_2Cl$ $[M+H]^+$, found: 317.0443; **IR** (neat, cm^{-1}): 2961*w*, 2923*w*, 2854*w*, 1690*m*, 1600*s*, 1568*w*, 1720*w*, 1425*m*, 1379*w*, 1364*w*, 1321*w*, 1258*w*, 1029*w*, 908*s*, 725*w*.

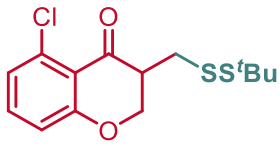


3-((*tert*-Butyldisulfaneyl)methyl)-7-fluorochroman-4-one (5i): The title compound was prepared according to general procedure (**GP2-1)** with phenanthrene-9,10-dione (4.2 mg, 0.020 mmol, 10 mol%), Na_2CO_3 (27.3 mg, 0.260 mmol, 1.3 equiv), 2-(allyloxy)-4-fluorobenzaldehyde **4i** (36.0 mg, 0.200 mmol, 1.0 equiv), and *SS*-(*tert*-butyl) 4-methylbenzenesulfono(dithioperoxoate) **2a** (110.4 mg, 0.4000 mmol, 2.0 equiv) in MeCN (2 mL) at 30 °C for 12 h. Purification via silica gel chromatography (PE:EtOAc = 100:1) gave the desired product **5i** as a colorlrss liquid in 68% yield (40.7 mg); **TLC R_f** = 0.5 (PE:EtOAc = 20:1); **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.90 (dd, J^1 = 8.8 Hz, J^2 = 6.6 Hz, 1H), 6.76 – 6.72 (m, 1H), 6.66 (dd, J^1 = 9.8 Hz, J^2 = 2.4 Hz, 1H), 4.70 (dd, J^1 = 11.5 Hz, J^2 = 4.7 Hz, 1H), 4.44 (dd, J^1 = 11.5 Hz, J^2 = 9.4 Hz, 1H), 3.30 (dd, J^1 = 13.6 Hz, J^2 = 3.9 Hz, 1H), 3.18 – 3.11 (m, 1H), 2.70 (dd, J^1 = 13.6 Hz, J^2 = 10.0 Hz, 1H), 1.35 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 191.4, 167.5 (d, *J* = 256.5 Hz, 1C), 163.3 (d, *J* = 13.7 Hz, 1C), 129.9 (d, *J* = 11.4 Hz, 1C), 117.5 (d, *J* = 2.5 Hz, 1C), 110.0 (d, *J* = 22.8 Hz, 1C), 104.6 (d, *J* = 24.5 Hz, 1C), 69.6, 48.4, 45.2, 36.3, 29.9; **HRMS** (ESI) *m*/*z* = 301.0727 calcd. for $C_{14}H_{18}O_2S_2F$ $[M+H]^+$, found: 301.0734; **IR** (neat, cm^{-1}): 2963*w*, 2923*w*, 2861*w*, 1689*s*, 1616*s*, 1588*m*, 1469*w*, 1438*m*, 1382*w*, 1364*w*, 132*w*, 1244*s*, 1145*s*, 1119*w*, 1029*w*, 910*w*, 854*m*, 732*m*.

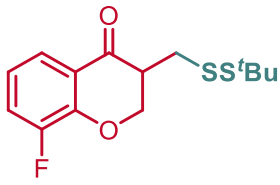


5-Bromo-3-((*tert*-butyldisulfaneyl)methyl)chroman-4-one (5j): The title compound was prepared according to general procedure (**GP2-3)** with phenanthrene-9,10-dione (4.2 mg, 0.020 mmol, 10 mol%), Na_2CO_3 (27.3 mg, 0.260 mmol, 1.3 equiv), 2-(allyloxy)-6-bromobenzaldehyde **4j** (48.2 mg, 0.200 mmol, 1.0 equiv), and *SS*-(*tert*-butyl) 4-methylbenzenesulfono(dithioperoxoate) **2a** (110.4 mg, 0.4000 mmol, 2.0 equiv) in MeCN (2 mL) at 30 °C for 12 h. Purification via silica gel chromatography (PE:EtOAc = 100:1) gave the desired product **5j** as a colorlrss liquid in 62% yield (44.6 mg); **TLC R_f** = 0.6 (PE:EtOAc = 20:1); **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.27 (d, *J* = 7.7 Hz, 1H), 7.21 (d, *J* = 7.9 Hz, 1H), 6.94 (d, *J* = 8.2 Hz, 1H), 4.67 (dd, J^1 = 11.5 Hz, J^2 = 4.7 Hz, 1H), 4.38 (dd, J^1 = 11.4 Hz, J^2 =

9.6 Hz, 1H), 3.30 (dd, J^1 = 13.7 Hz, J^2 = 4.0 Hz, 1H), 3.21 – 3.14 (m, 1H), 2.67 (dd, J^1 =13.7 Hz, J^2 = 10.0 Hz, 1H), 1.33 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 191.2, 163.1, 135.1, 128.5, 121.8, 118.7, 117.7, 68.6, 48.5, 45.7, 36.3, 29.9; **HRMS** (ESI) *m*/*z* = 360.9926 calcd. for $C_{14}H_{18}O_2S_2Br$ $[M+H]^+$, found: 360.9933; **IR** (neat, cm^{-1}): 2964*w*, 2924*w*, 1696*s*, 1593*s*, 1559*w*, 1468*m*, 1445*s*, 1365*w*, 1314*s*, 1251*m*, 1165*m*, 1028*w*, 948*w*, 862*m*, 788*m*.

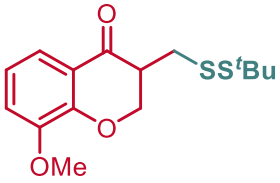


3-((*tert*-Butyldisulfaneyl)methyl)-5-chlorochroman-4-one (5k): The title compound was prepared according to general procedure (**GP2-3)** with phenanthrenequinone (4.2 mg, 0.020 mmol, 10 mol%), Na_2CO_3 (27.3 mg, 0.260 mmol, 1.3 equiv), 2-(allyloxy)-6-chlorobenzaldehyde **4k** (39.3 mg, 0.200 mmol, 1.0 equiv), and *SS*-(*tert*-butyl) 4-methylbenzenesulfono(dithioperoxoate) **2a** (110.4 mg, 0.4000 mmol, 2.0 equiv) in MeCN (2 mL) at 30 °C for 12 h. Purification via silica gel chromatography (PE:EtOAc = 100:1) gave the desired product **5k** as a colorlrss liquid in 92% yield (58.0 mg); **TLC R_f** = 0.6 (PE:EtOAc = 20:1); **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.32 (t, *J* = 8.1 Hz, 1H), 7.04 (d, *J* = 8.0 Hz, 1H), 6.91 (d, *J* = 8.4 Hz, 1H), 4.68 (dd, J^1 = 11.4 Hz, J^2 = 4.6 Hz, 1H), 4.40 (dd, J^1 = 11.5 Hz, J^2 = 9.5 Hz, 1H), 3.31 (dd, J^1 = 13.6 Hz, J^2 = 4.0 Hz, 1H), 3.22 – 3.15 (m, 1H), 2.69 (dd, J^1 = 13.6 Hz, J^2 = 9.9 Hz, 1H), 1.35 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 191.0, 163.0, 134.8, 134.6, 124.8, 117.9, 116.9, 68.7, 48.4, 46.1, 36.3, 29.9; **HRMS** (ESI) *m*/*z* = 339.0521 calcd. for $C_{14}H_{17}O_2S_2ClNa$ $[M+Na]^+$, found: 339.0266; **IR** (neat, cm^{-1}): 2961*w*, 2923*w*, 2861*w*, 1690*s*, 1595*s*, 1565*m*, 1468*m*, 1448*s*, 1362*m*, 1311*s*, 1256*s*, 1164*m*, 1088*w*, 1061*w*, 1029*s*, 955*m*, 878*s*, 791*s*, 765*s*, 702*w*, 645*w*, 530*w*.

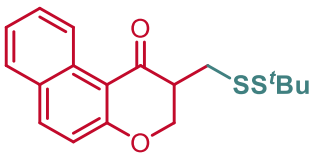


3-((*tert*-Butyldisulfaneyl)methyl)-8-fluorochroman-4-one (5l): The title compound was prepared according to general procedure (**GP2-1)** with phenanthrene-9,10-dione (4.2 mg, 0.020 mmol, 10 mol%), Na_2CO_3 (27.3 mg, 0.260 mmol, 1.3 equiv), 2-(allyloxy)-3-fluorobenzaldehyde **4l** (36.0 mg, 0.200 mmol, 1.0 equiv), and *SS*-(*tert*-butyl) 4-methylbenzenesulfono(dithioperoxoate) **2a** (110.4 mg, 0.4000 mmol, 2.0 equiv) in MeCN (2 mL) at 30 °C for 12 h. Purification via silica gel chromatography (PE:EtOAc = 50:1) gave the desired product **5l** as a white solid in 78% yield (47.1 mg); **TLC R_f** = 0.4 (PE:EtOAc = 20:1); **MP**: = 44 °C; **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.66 (d, *J* = 8.0 Hz, 1H), 7.33 – 7.26 (m, 1H), 6.98 – 6.93 (m, 1H), 4.79 (dd, J^1 = 11.5 Hz, J^2 = 4.6 Hz, 1H), 4.51 (dd, J^1 = 11.5 Hz, J^2 = 9.4 Hz, 1H), 3.30 (dd, J^1 = 13.5 Hz, J^2 = 4.0 Hz, 1H), 3.26 – 3.17 (m, 1H), 2.73 (dd, J^1 = 13.6 Hz, J^2 = 9.7 Hz, 1H), 1.35 (s, 9H); **^{13}C NMR** (101 MHz,

$CDCl_3$, 300 K): δ (ppm) = 191.8, 151.5 (d, *J* = 248.9 Hz, 1C), 149.9 (d, *J* = 11.5 Hz, 1C), 122.6, 122.4 (d, *J* = 3.9 Hz, 1C), 121.9 (d, *J* = 17.5 Hz, 1C), 121.9 (d, *J* = 17.5 Hz, 1C), 69.8, 48.4, 45.5, 36.2, 29.9; **HRMS** (ESI) *m*/*z* = 323.0546 calcd. for $C_{14}H_{17}FNaO_2S_2$ $[M+Na]^+$, found: 323.0559; **IR** (neat, cm^{-1}): 2961*w*, 2941*w*, 1695*s*, 1618*m*, 1587*w*, 1499*s*, 1453*w*, 1364*w*, 1298*m*, 1262*m*, 1219*w*, 1165*w*, 1064*w*, 1018*w*, 910*w*, 802*w*, 764*w*, 730*w*, 587*w*.

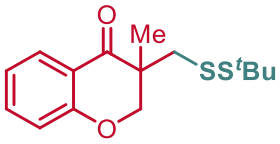


3-((*tert*-Butyldisulfaneyl)methyl)-8-methoxychroman-4-one (5m): The title compound was prepared according to general procedure (**GP2-1)** with phenanthrene-9,10-dione (4.2 mg, 0.020 mmol, 10 mol%), Na_2CO_3 (27.3 mg, 0.260 mmol, 1.3 equiv), 2-(allyloxy)-3-methoxybenzaldehyde **4m** (38.4 mg, 0.200 mmol, 1.0 equiv), and *SS*-(*tert*-butyl) 4-methylbenzenesulfono(dithioperoxoate) **2a** (110.4 mg, 0.4000 mmol, 2.0 equiv) in MeCN (2 mL) at 30 °C for 12 h. Purification via silica gel chromatography (PE:EtOAc = 100:1) gave the desired product **5m** as a white solid in 78% yield (48.7 mg); **TLC R_f** = 0.5 (PE:EtOAc = 20:1); **MP**: = 58 °C; **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.48 (d, *J* = 7.9 Hz, 1H), 7.05 (d, *J* = 8.1 Hz, 1H), 6.96 (t, *J* = 7.9 Hz, 1H), 4.76 (dd, J^1 = 11.5 Hz, J^2 = 4.5 Hz, 1H), 4.52 (dd, J^1 = 11.5 Hz, J^2 = 9.0 Hz, 1H), 3.91 (s, 3H), 3.27 (dd, J^1 = 13.5 Hz, J^2 = 4.0 Hz, 1H), 3.20 – 3.13 (m, 1H), 2.74 (dd, J^1 = 13.5 Hz, J^2 = 9.9 Hz, 1H), 1.34 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 192.7, 151.5, 148.8, 121.1, 121.0, 118.5, 116.7, 69.6, 56.2, 48.3, 45.3, 36.3, 29.9; **HRMS** (ESI) *m*/*z* = 355.0746 calcd. for $C_{15}H_{20}O_3NaS_2$ $[M+Na]^+$, found: 355.0746; **IR** (neat, cm^{-1}): 2960*w*, 2923*w*, 1688*s*, 1605*m*, 1583*m*, 1491*s*, 1441*m*, 1362*w*, 1301*m*, 1268*s*, 1251*m*, 1215*m*, 1188*m*, 1166*m*, 1062*w*, 1029*w*, 958*w*, 735*w*.

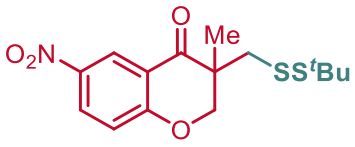


2-((*tert*-Butyldisulfaneyl)methyl)-2,3-dihydro-1*H*-benzo[*f*]chromen-1-one (5n): The title compound was prepared according to general procedure (**GP2-3)** with phenanthrene-9,10-dione (4.2 mg, 0.020 mmol, 10 mol%), Na_2CO_3 (27.3 mg, 0.260 mmol, 1.3 equiv), 2-(allyloxy)-1-naphthaldehyde **4n** (42.4 mg, 0.200 mmol, 1.0 equiv), and *SS*-(*tert*-butyl) 4-methylbenzenesulfono (dithioperoxoate) **2a** (110.4 mg, 0.4000 mmol, 2.0 equiv) in MeCN (2 mL) at 30 °C for 12 h. Purification via silica gel chromatography (PE:EtOAc = 100:1) gave the desired product **5n** as a white solid in 72% yield (47.6 mg); **TLC R_f** = 0.6 (PE:EtOAc = 20:1); **MP**: = 88 – 90 °C; **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) =9.43 (d, *J* = 8.6 Hz, 1H), 7.93 (d, *J* = 9.0 Hz, 1H), 7.75 (d, *J* = 8.9 Hz, 1H), 7.63 (t, *J* = 7.8 Hz, 1H), 7.43 (t, *J* = 7.5 Hz, 1H), 7.11 (d, *J* = 9.0 Hz, 1H), 4.75 (dd, J^1 = 11.4 Hz, J^2 = 4.6 Hz, 1H), 4.58 (dd, J^1 = 11.4 Hz, J^2 = 8.6 Hz, 1H), 3.34 (dd, J^1 = 13.5 Hz, J^2 = 4.0 Hz,

1H), 3.25 – 3.17 (m, 1H), 2.80 (dd, J^1 = 13.5 Hz, J^2 = 10.1 Hz, 1H), 1.37 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 193.8, 163.6, 137.6, 131.6, 129.7, 129.2, 128.4, 125.8, 124.9, 118.6, 112.1, 68.9, 48.4, 46.2, 37.1, 30.0; **HRMS** (ESI) *m*/*z* = 333.0977 calcd. for $C_{18}H_{21}O_2S_2$ $[M+H]^+$, found: 333.0993; **IR** (neat, cm^{-1}): 2961*w*, 2923*w*, 2858*w*, 1666*m*, 1618*w*, 1598*m*, 1569*w*, 1613*m*, 1471*m*, 1435*s*, 1376*m*, 1364*m*, 1345*w*, 1236*s*, 1208*w*, 1164*w*, 1142*w*, 1127*w*, 908*s*, 825*m*, 754*s*, 650*m*, 580*w*.

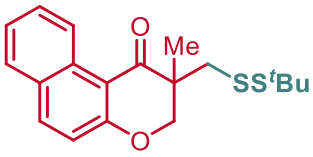


3-((*tert*-Butyldisulfaneyl)methyl)-3-methylchroman-4-one (5o): The title compound was prepared according to general procedure (**GP2-1**) with phenanthrene-9,10-dione (4.2 mg, 0.020 mmol, 10 mol%), Na_2CO_3 (27.3 mg, 0.260 mmol, 1.3 equiv), 2-((2-methylallyl)oxy)benzaldehyde **4o** (35.2 mg, 0.200 mmol, 1.0 equiv), and *SS*-(*tert*-butyl) 4-methylbenzenesulfono(dithioperoxoate) **2a** (110.4 mg, 0.4000 mmol, 2.0 equiv) in MeCN (2 mL) at 30 °C for 12 h. Purification via silica gel chromatography (PE:EtOAc = 100:1) gave the desired product **5o** as a colorlrss liquid in 85% yield (50.2 mg); **TLC R_f** = 0.5 (PE:EtOAc = 20:1); **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.90 (d, *J* = 7.9 Hz, 1H), 7.48 (t, *J* = 6.9 Hz, 1H), 7.03 (t, *J* = 7.5 Hz, 1H), 6.98 (d, *J* = 8.4 Hz, 1H), 4.55 (d, *J* = 11.6 Hz, 1H), 4.21 (d, *J* = 11.6 Hz, 1H), 3.21 (d, *J* = 13.5 Hz, 1H), 2.96 (d, *J* = 13.5 Hz, 1H), 1.31 (s, 9H), 1.28 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 195.2, 161.1, 135.9, 127.9, 121.6, 119.5, 117.7, 73.6, 48.2, 46.6, 46.5, 29.7, 17.6; **HRMS** (ESI) *m*/*z* = 317.0797 calcd. for $C_{15}H_{20}O_2NaS_2$ $[M+Na]^+$, found: 317.0791; **IR** (neat, cm^{-1}): 2961*w*, 2923*w*, 2860*w*, 1685*s*, 1606*s*, 1581*w*, 1491*s*, 1364*m*, 1465*s*, 1384*w*, 1362*m*, 1311*s*, 1282*s*, 1212*s*, 1165*m*, 1146*m*, 1104*w*, 1037*m*, 1021*m*, 948*m*, 822*s*, 694*w*, 527*w*.

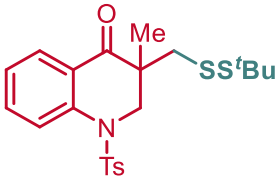


3-((*tert*-Butyldisulfaneyl)methyl)-3-methyl-6-nitrochroman-4-one (5p): The title compound was prepared according to general procedure (**GP2-3**) with phenanthrene-9,10-dione (4.2 mg, 0.020 mmol, 10 mol%), Na_2CO_3 (27.3 mg, 0.260 mmol, 1.3 equiv), 2-((2-methylallyl)oxy)-5-nitrobenzaldehyde **4p** (44.2 mg, 0.200 mmol, 1.0 equiv), and *SS*-(*tert*-butyl) 4-methylbenzenesulfono(dithioperoxoate) **2a** (110.4 mg, 0.4000 mmol, 2.0 equiv) in MeCN (2 mL) at 30 °C for 12 h. Purification via silica gel chromatography (PE:EtOAc = 100:1) gave the desired product **5p** as a colorlrss liquid in 46% yield (31.4 mg); **TLC R_f** = 0.4 (PE:EtOAc = 50:1); **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 8.79 (s, 1H), 8.33 (d, *J* = 9.2 Hz, 1H), 7.26 (s, 1H), 4.69 (d, *J* = 13.9 Hz, 1H), 4.35 (d, *J* = 11.9 Hz, 1H), 3.20 (d, *J* = 13.7 Hz, 1H), 2.96 (d, *J* = 13.7 Hz, 1H), 1.31 – 1.30 (m, 12H); **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 193.2, 165.0, 142.4, 130.2, 124.5, 119.1, 74.2, 48.4, 46.6, 46.2, 29.7, 17.7; **HRMS** (ESI) *m*/*z* = 342.0828

calcd. for $C_{15}H_{20}NO_4S_2$ $[M+H]^+$, found: 342.0833; **IR** (neat, cm^{-1}): 2964*w*, 2924*w*, 2861*w*, 1702*m*, 1616*s*, 1588*m*, 1525*m*, 1479*m*, 1433*m*, 1336*s*, 1279*s*, 1216*w*, 1165*w*, 1079*w*, 1017*m*, 931*w*, 840*w*, 748*w*, 687*w*.

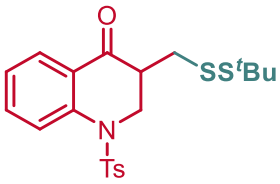


2-((*tert*-Butyldisulfaneyl)methyl)-2-methyl-2,3-dihydro-1*H*-benzo[*f*]chromen-1-one (5q): The title compound was prepared according to general procedure (**GP2-3)** with phenanthrene-9,10-dione (4.2 mg, 0.020 mmol, 10 mol%), Na_2CO_3 (27.3 mg, 0.260 mmol, 1.3 equiv), 2-((2-methylallyl)oxy)-1-naphthaldehyde **4q** (45.3 mg, 0.200 mmol, 1.0 equiv), and *SS*-(*tert*-butyl) 4-methylbenzenesulfono (dithioperoxoate) **2a** (110.4 mg, 0.4000 mmol, 2.0 equiv) in MeCN (2 mL) at 30 °C for 12 h. Purification via silica gel chromatography (PE:EtOAc = 100:1) gave the desired product **5q** as a colorlrss liquid in 74% yield (51.2 mg); **TLC R_f** = 0.5 (PE:EtOAc = 50:1); **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 9.44 (d, *J* = 8.7 Hz, 1H), 7.93 (d, *J* = 8.9 Hz, 1H), 7.75 (d, *J* = 8.1 Hz, 1H), 7.63 (t, *J* = 7.4 Hz, 1H), 7.43 (t, *J* = 7.4 Hz,1H), 7.10 (d, *J* = 9.1 Hz, 1H), 4.67 (d, *J* = 11.5 Hz, 1H), 4.32 (d, *J* = 11.6 Hz, 1H), 3.27 (d, *J* = 13.6 Hz, 1H), 3.03 (d, *J* = 13.4 Hz, 1H), 1.34 (s, 3H), 1.29 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 196.4, 163.1, 137.5, 131.9, 129.6, 129.4, 128.4, 125.9, 124.9, 118.5, 111.1, 73.4, 48.2, 47.2, 46.9, 29.7, 18.0; **HRMS** (ESI) *m*/*z* = 347.1134 calcd. for $C_{19}H_{23}O_2S_2$ $[M+H]^+$, found: 347.1145; **IR** (neat, cm^{-1}): 2964*m*, 2924*w*, 2857*w*, 1668*s*, 1616*w*, 1599*w*, 1565*w*, 1513*s*, 1468*m*, 1433*s*, 1365*s*, 1279*w*, 1234*w*, 1205*w*, 1165*w*, 1142w, 1028w, 994w, 828s, 754m, 503w.

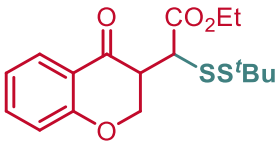


3-((*tert*-Butyldisulfaneyl)methyl)-3-methyl-1-tosyl-2,3-dihydroquinolin-4(1*H*)-one (5r): The title compound was prepared according to general procedure (**GP2-3)** with phenanthrene-9,10-dione (4.2 mg, 0.020 mmol, 10 mol%), Na_2CO_3 (27.3 mg, 0.260 mmol, 1.3 equiv), *N*-(2-formylphenyl)-4-methyl-*N*-(2-methylallyl)benzenesulfonamide **4r** (65.9 mg, 0.200 mmol, 1.0 equiv), and *SS*-(*tert*-butyl) 4-methylbenzenesulfono(dithioperoxoate) **2a** (110.4 mg, 0.4000 mmol, 2.0 equiv) in MeCN (2 mL) at 30 °C for 12 h. Purification via silica gel chromatography (PE:EtOAc = 50:1) gave the desired product **5r** as a colorlrss liquid in 40% yield (35.8 mg); **TLC R_f** = 0.2 (PE:EtOAc = 20:1); **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 8.00 (d, *J* = 7.9 Hz, 1H), 7.83 (d, *J* = 8.0 Hz, 2H), 7.63 (d, *J* = 8.5 Hz, 1H), 7.43 (t, *J* = 7.9 Hz, 1H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.10 (t, *J* = 7.6 Hz, 1H), 4.20 (s, 2H), 3.39 (d, *J* = 13.6 Hz, 1H), 2.97 (d, *J* = 13.6 Hz, 1H), 2.43 (s, 3H), 1.34 – 1.32 (m, 12H); **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 195.7, 144.5, 142.3, 136.8, 134.6, 130.1, 129.2, 126.9, 123.5, 122.0,

118.6, 54.5, 48.3, 47.8, 47.7, 29.8, 21.6, 19.8; **HRMS** (ESI) *m*/*z* = 450.1126 calcd. for $C_{22}H_{28}NO_3S_3$ $[M+H]^+$, found: 450.1125; **IR** (neat, cm^{-1}): 2964*m*, 2924*w*, 2861*w*, 1685*m*, 1599*m*, 1479*m*, 1456*m*, 1369*s*, 1296*w*, 1222*w*, 1165*s*, 1085*w*, 1039*w*, 965*w*, 1165*w*, 920*w*, 811w, 742w, 663m, 571m, 543w.

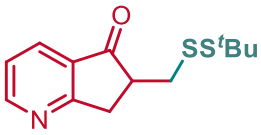


3-((*tert*-Butyldisulfaneyl)methyl)-1-tosyl-2,3-dihydroquinolin-4(1*H*)-one (5s): The title compound was prepared according to general procedure (**GP2-3)** with phenanthrene-9,10-dione (4.2 mg, 0.020 mmol, 10 mol%), Na_2CO_3 (27.3 mg, 0.260 mmol, 1.3 equiv), *N*-allyl-*N*-(2-formylphenyl)-4-methylbenzenesulfonamide **4s** (63.1 mg, 0.200 mmol, 1.0 equiv), and *SS*-(*tert*-butyl) 4-methylbenzenesulfono(dithioperoxoate) **2a** (110.4 mg, 0.4000 mmol, 2.0 equiv) in MeCN (2 mL) at 30 °C for 12 h. Purification via silica gel chromatography (PE:EtOAc = 50:1) gave the desired product **5s** as a white solid in 46% yield (39.7 mg); **TLC** R_f = 0.5 (PE:EtOAc = 5:1); **MP**: = 71 – 74 °C; **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.94 – 7.91 (m, 2H), 7.63 (d, *J* = 8.1 Hz, 2H), 7.57 (t, *J* = 6.8 Hz, 1H), 7.26 – 7.22 (m, 4H), 4.76 (dd, J^1 = 14.2 Hz, J^2 = 5.0 Hz, 1H), 3.75 (dd, J^1 = 14.3 Hz, J^2 = 12.5 Hz, 1H), 3.29 (dd, J^1 = 13.7 Hz, J^2 = 3.4 Hz, 1H), 2.69 – 2.62 (m, 1H), 2.51 (dd, J^1 = 13.7 Hz, J^2 = 9.3 Hz, 1H), 2.40 (s, 3H), 1.34 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 193.7, 144.5, 142.4, 136.6, 134.8, 130.2, 128.0, 127.0, 125.2, 124.7, 123.8, 49.6, 48.3, 44.9, 37.8, 29.9, 21.6; **HRMS** (ESI) *m*/*z* = 458.0889 calcd. for $C_{21}H_{25}NO_3NaS_2$ $[M+Na]^+$, found: 458.0888; **IR** (neat, cm^{-1}): 2961*w*, 2924*w*, 2857*w*, 1688*m*, 1598*m*, 1475*m*, 1458*m*, 1355*s*, 1296*w*, 1262*w*, 1224*w*, 1162*s*, 1089*s*, 1038*w*, 952*w*, 885*w*, 812*m*, 764*m*, 734*m*, 660*s*, 623*s*, 546*m*.

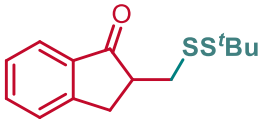


Ethyl 2-(*tert*-butyldisulfaneyl)-2-(4-oxochroman-3-yl) acetate (5t): The title compound was prepared according to general procedure (**GP2-3)** with phenanthrene-9,10-dione (4.2 mg, 0.020 mmol, 10 mol%), Na_2CO_3 (27.3 mg, 0.260 mmol, 1.3 equiv), ethyl (*E*)-4-(2-formylphenoxy)but-2-enoate **4t** (46.9 mg, 0.200 mmol, 1.0 equiv), and *SS*-(*tert*-butyl) 4-methylbenzenesulfono(dithioperoxoate) **2a** (110.4 mg, 0.4000 mmol, 2.0 equiv) in MeCN (2 mL) at 30 °C for 12 h. Purification via silica gel chromatography (PE:EtOAc = 50:1) gave the desired product **5t** as a colorlrss liquid in 44% yield (31.3 mg); **TLC** R_f = 0.2 (PE:EtOAc = 20:1); **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.84 (d, *J* = 7.8 Hz, 1H), 7.49 (t, *J* = 6.9 Hz, 1H), 7.05 – 6.96 (m, 2H), 4.94 (dd, J^1 = 11.4 Hz, J^2 = 5.0 Hz, 1H), 4.43 (t, *J* = 11.8 Hz, 1H), 4.28 (q, *J* = 7.1 Hz, 2H), 3.69 (d, *J* = 9.4 Hz, 1H), 3.53 – 3.47 (m, 1H), 1.40 – 1.31 (m, 12H); **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 191.4, 170.3, 161.6, 136.2,

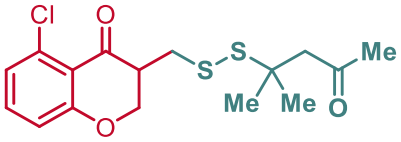
127.4, 121.6, 120.3, 117.8, 68.9, 61.6, 53.6, 48.8, 47.8, 29.8, 14.1; **HRMS** (ESI) *m/z* = 377.0852 calcd. for $C_{17}H_{22}O_4NaS_2$ $[M+Na]^+$, found: 377.0843; **IR** (neat, cm^{-1}): 2961*w*, 2923*w*, 1731*s*, 1690*s*, 1608*s*, 1479*s*, 1365*w*, 1292*m*, 1244*m*, 1215*m*, 1149*m*, 1037*w*, 1012*w*, 948*w*, 768*w*, 755*w*.



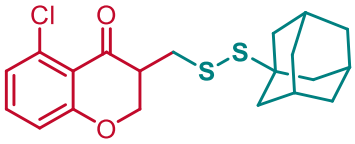
6-((*tert*-Butyldisulfaneyl)methyl)-6,7-dihydro-5*H*-cyclopenta[*b*]pyridin-5-one (5u): The title compound was prepared according to general procedure (**GP2-1)** with phenanthrene-9,10-dione (4.2 mg, 0.020 mmol, 10 mol%), Na_2CO_3 (27.3 mg, 0.260 mmol, 1.3 equiv), 2-(allyloxy)benzaldehyde **4u** (29.4 mg, 0.200 mmol, 1.0 equiv), and *SS*-(*tert*-butyl) 4-methylbenzenesulfono(dithioperoxoate) **2a** (110.4 mg, 0.4000 mmol, 2.0 equiv) in MeCN (2 mL) at 30 °C for 12 h. Purification via silica gel chromatography (PE:EtOAc = 10:1) gave the desired product **5u** as a colorlrss liquid in 66% yield (32.7 mg); **TLC R_f** = 0.3 (PE:EtOAc = 3:1); **MP**: = 62 °C; **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 8.83 (d, *J* = 4.9 Hz, 1H), 8.02 (d, *J* = 7.2 Hz, 1H), 7.33 (dd, J^1 = 7.8 Hz, J^2 = 4.8 Hz, 1H), 3.53 (dd, J^1 = 18.9 Hz, J^2 = 8.8 Hz, 1H), 3.38 (dd, J^1 = 12.9 Hz, J^2 = 3.7 Hz, 1H), 3.31 – 3.15 (m, 2H), 2.83 (dd, J^1 = 13.0 Hz, J^2 = 9.5 Hz, 1H), 1.35 (s, 10H); **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 205.0, 173.0, 156.1, 132.2, 129.9, 122.7, 48.3, 46.9, 41.6, 34.9, 29.9; **HRMS** (ESI) *m/z* = 268.0824 calcd. for $C_{13}H_{18}NOS_2$ $[M+H]^+$, found: 268.0824; **IR** (neat, cm^{-1}): 2964*w*, 2924*w*, 1713*s*, 1576*m*, 1468*w*, 1416*w*, 1365*w*, 1285*w*, 1165*w*, 1097*w*, 782*w*, 725*w*.



2-((*tert*-Butyldisulfaneyl)methyl)-2,3-dihydro-1*H*-inden-1-one (5v): The title compound was prepared according to general procedure (**GP2-1)** with phenanthrene-9,10-dione (4.2 mg, 0.020 mmol, 10 mol%), Na_2CO_3 (27.3 mg, 0.260 mmol, 1.3 equiv), 2-allylbenzaldehyde **4v** (29.2 mg, 0.200 mmol, 1.0 equiv), and *SS*-(*tert*-butyl) 4-methylbenzenesulfono(dithioperoxoate) **2a** (110.4 mg, 0.4000 mmol, 2.0 equiv) in MeCN (2 mL) at 30 °C for 12 h. Purification via silica gel chromatography (PE:EtOAc = 100:1) gave the desired product **5v** as a colorlrss liquid in 81% yield (43.0 mg); **TLC R_f** = 0.5 (PE:EtOAc = 50:1); **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.75 (d, *J* = 7.7 Hz, 1H), 7.60 (t, *J* = 7.5 Hz, 1H), 7.48 (d, *J* = 7.7 Hz, 1H), 7.37 (t, *J* = 7.4 Hz, 1H), 3.40 (d, *J* = 16.8 Hz, 2H), 3.08 (d, *J* = 15.6 Hz, 2H), 2.73 (t, *J* = 12.8 Hz 1H), 1.36 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 206.5, 153.5, 136.5, 135.0, 127.5, 126.6, 124.0, 48.2, 47.1, 42.0, 32.4, 30.0; **HRMS** (ESI) *m/z* = 289.0691 calcd. for $C_{14}H_{18}ONaS_2$ $[M+Na]^+$, found: 289.0696; **IR** (neat, cm^{-1}): 2960*w*, 2921*w*, 1709*s*, 1609*w*, 1463*m*, 1362*m*, 1329*w*, 1295*w*, 1276*m*, 1206*w*, 1166*m*, 1094*w*, 1029*w*, 754*s*, 591*w*, 470*w*.



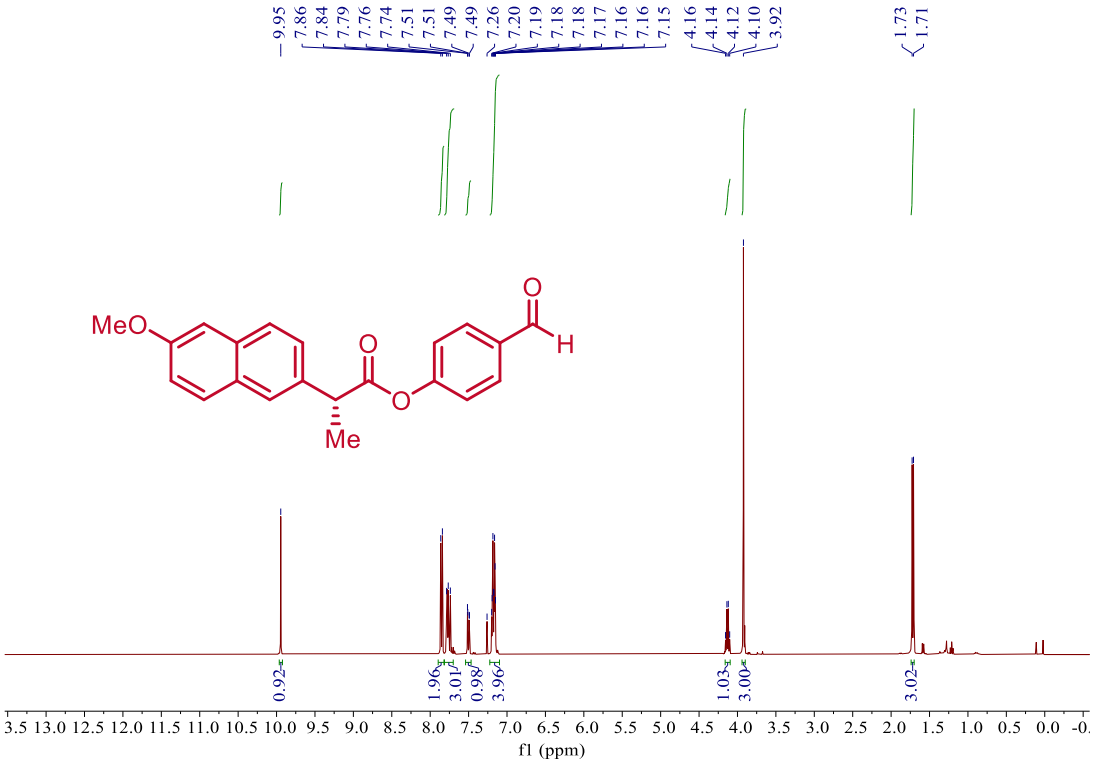
5-Chloro-3-(((2-methyl-4-oxopentan-2-yl)disulfaneyl)methyl)chroman-4-one (5w): The title compound was prepared according to general procedure (**GP2-2)** with phenanthrene-9,10-dione (4.2 mg, 0.020 mmol, 10 mol%), Na_2CO_3 (27.3 mg, 0.260 mmol, 1.3 equiv), 2-(allyloxy)-6-chlorobenzaldehyde **4w** (39.3 mg, 0.200 mmol, 1.0 equiv), and *SS*-(2-methyl-4-oxopentan-2-yl) 4-methylbenzenesulfono(dithioperoxoate) **2f** (146.6 mg, 0.4000 mmol, 2.0 equiv) in MeCN (2 mL) at 30 °C for 12 h. Purification via silica gel chromatography (PE:EtOAc = 100:1) gave the desired product **5w** as a colorlrss liquid in 53% yield (38.0 mg); **TLC R_f** = 0.6 (PE:EtOAc = 20:1); **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.33 (t, *J* = 8.1 Hz, 1H), 7.04 (d, *J* = 7.9 Hz, 1H), 6.91 (d, *J* = 8.4 Hz, 1H), 4.67 (dd, J^1 = 11.5 Hz, J^2 = 4.7 Hz, 1H), 4.38 (dd, J^1 = 11.5 Hz, J^2 = 9.6 Hz, 1H), 3.30 (dd, J^1 = 13.6 Hz, J^2 = 4.2 Hz, 1H), 3.17 (m, 1H), 2.76 (m, 3H), 2.16 (s, 3H), 1.45 (s, 3H), 1.44 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 206.3, 190.8, 163.0, 134.9, 134.5, 124.8, 117.8, 116.9, 68.6, 53.2, 49.7, 46.1, 36.4, 32.1, 27.2, 27.0; **HRMS** (ESI) *m*/*z* = 381.0356 calcd. for $C_{16}H_{19}O_3S_2ClNa$ $[M+Na]^+$, found: 381.0364; **IR** (neat, cm^{-1}): 2964*w*, 2924*w*, 2867*w*, 1690*s*, 1593*s*, 1468*m*, 1448*s*, 1251*m*, 1176*w*, 1028*m*, 954*s*, 880*s*, 793*s*, 742*w*, 525*w*.



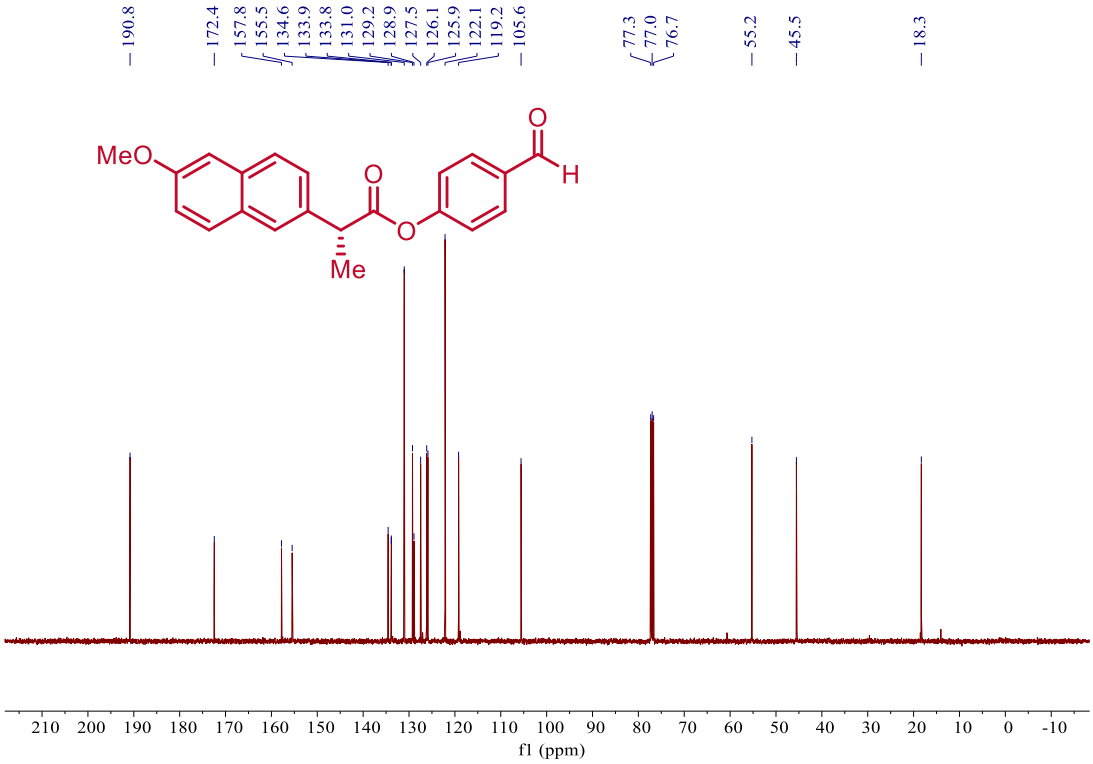
3-((((3*R*,5*R*,7*R*)-Adamantan-1-yl)disulfaneyl)methyl)-5-chlorochroman-4-one (5x): The title compound was prepared according to general procedure (**GP2-3)** with phenanthrene-9,10-dione (4.2 mg, 0.020 mmol, 10 mol%), Na_2CO_3 (27.3 mg, 0.260 mmol, 1.3 equiv), 2-(allyloxy)-6-chlorobenzaldehyde **4x** (39.3 mg, 0.200 mmol, 1.0 equiv), and *SS*-((3*s*,5*s*,7*s*)-adamantan-1-yl) 4-methylbenzenesulfono(dithioperoxoate) **2g** (141.8 mg, 0.4000 mmol, 2.0 equiv) in MeCN (2 mL) at 30 °C for 12 h. Purification via silica gel chromatography (PE:EtOAc = 100:1) gave the desired product **5x** as a colorlrss liquid in 67% yield (52.9 mg); **TLC R_f** = 0.6 (PE:EtOAc = 20:1); **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.32 (t, *J* = 8.1 Hz, 1H), 7.03 (d, *J* = 7.9 Hz, 1H), 6.91 (d, *J* = 8.4 Hz, 1H), 4.68 (dd, J^1 = 11.5 Hz, J^2 = 4.6 Hz, 1H), 4.39 (dd, J^1 = 11.5 Hz, J^2 = 9.3 Hz, 1H), 3.27 (dd, J^1 = 13.5 Hz, J^2 = 4.0 Hz, 1H), 3.19 (m, 4.3 Hz, 1H), 2.65 (dd, J^1 = 13.5 Hz, J^2 = 9.9 Hz, 1H), 2.07 (s, 3H), 1.86 (s, 6H), 1.67 (s, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 191.2, 163.0, 134.8, 134.5, 124.8, 117.9, 116.9, 68.7, 50.1, 45.9, 42.6, 36.8, 36.0, 29.8; **HRMS** (ESI) *m*/*z* = 417.0720 calcd. for $C_{20}H_{23}O_2S_2ClNa$ $[M+Na]^+$, found: 417.0723; **IR** (neat, cm^{-1}): 2907*s*, 2950*m*, 1690*s*, 1690*s*, 1593*s*, 1565*w*, 1468m, 1445*s*, 1314*s*, 1251*s*, 1121*w*, 1102*w*, 1038*m*, 954*w*, 880*m*, 794*m*.

6. Spectra

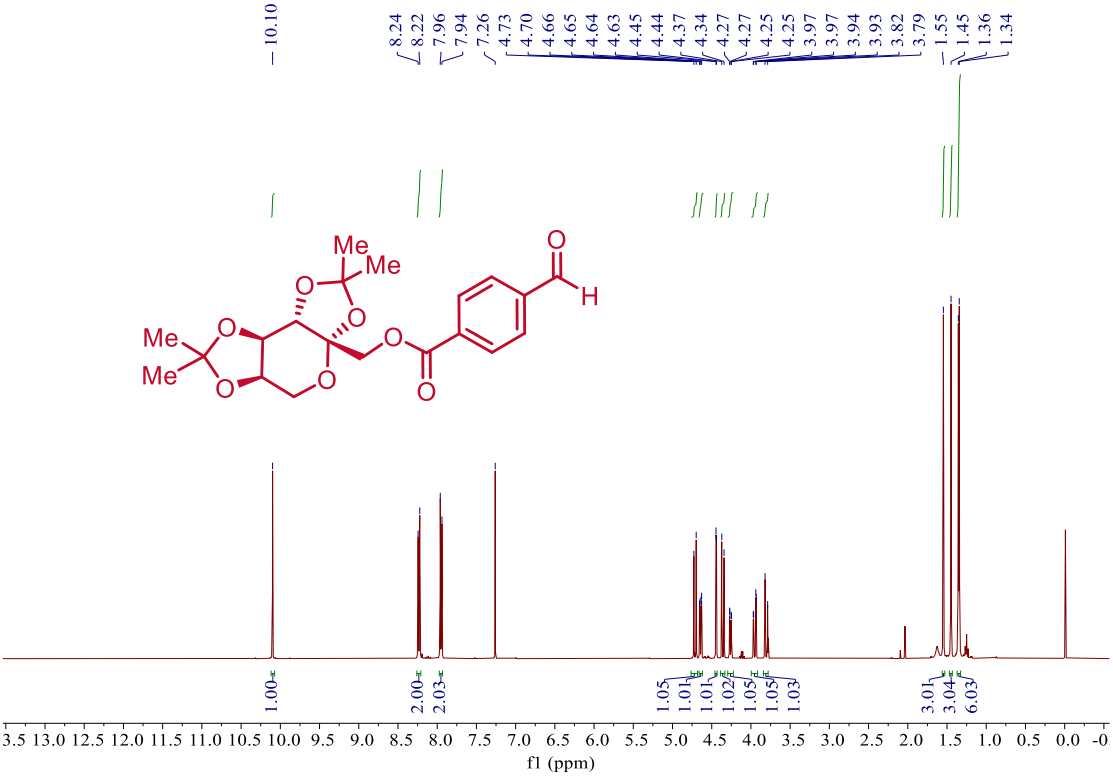
^{1}H NMR Spectrum of 4-Formylphenyl (*R*)-2-(6-methoxynaphthalen-2-yl) propanoate 1aj



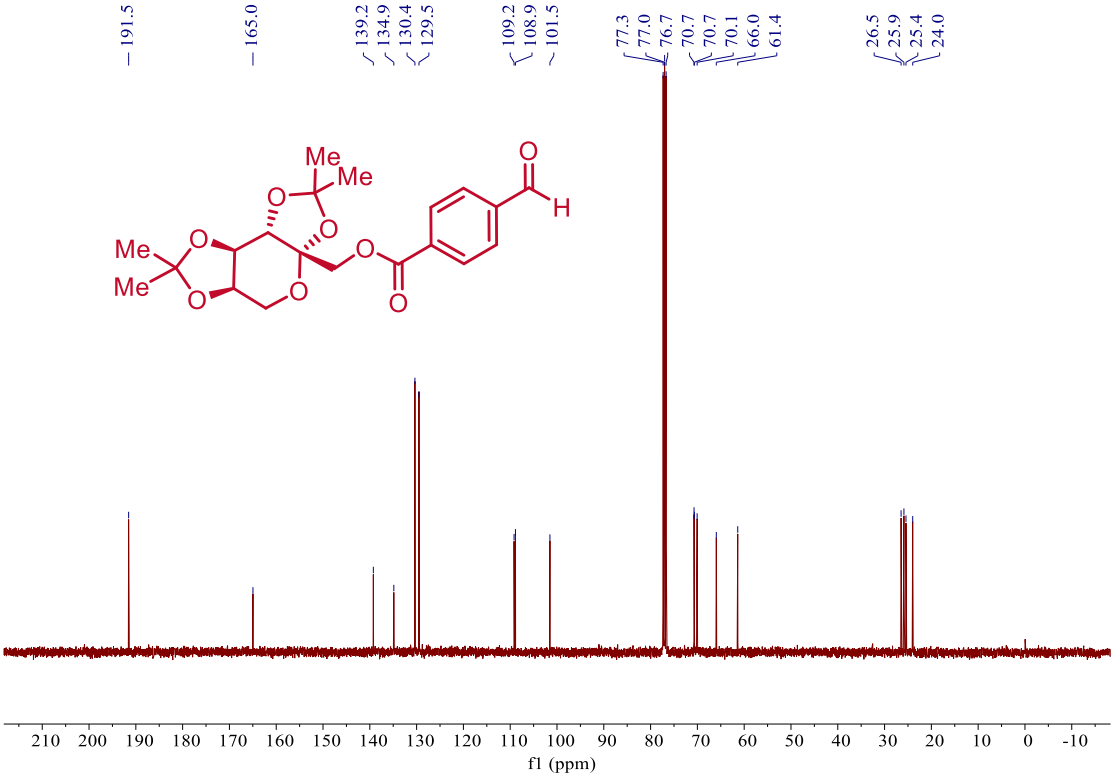
^{13}C NMR Spectrum of 4-Formylphenyl (*R*)-2-(6-methoxynaphthalen-2-yl) propanoate 1aj



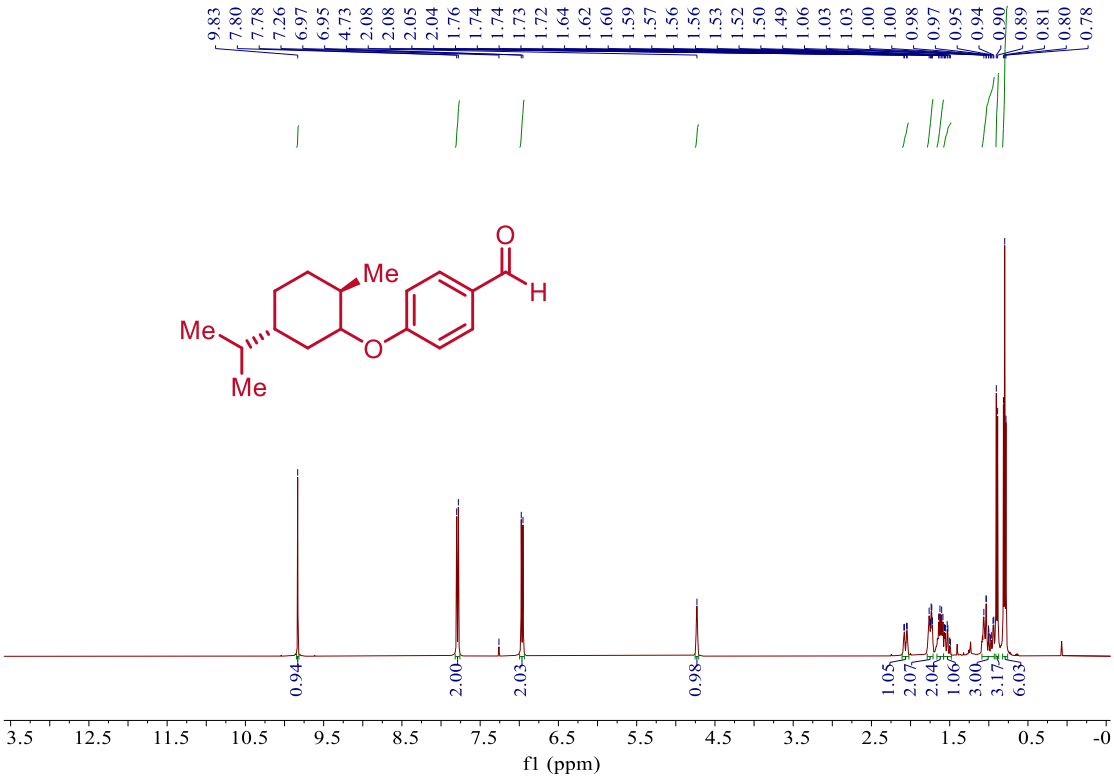
^{1}H NMR Spectrum of (3a*S*,5a*R*,8a*R*,8b*S*)-2,2,7,7-Tetramethyltetrahydro-3a*H*-bis([1,3]dioxolo)[4,5-*b*:4',5'-*d*]pyran-3a-yl)methyl 4-formylbenzoate 1aj



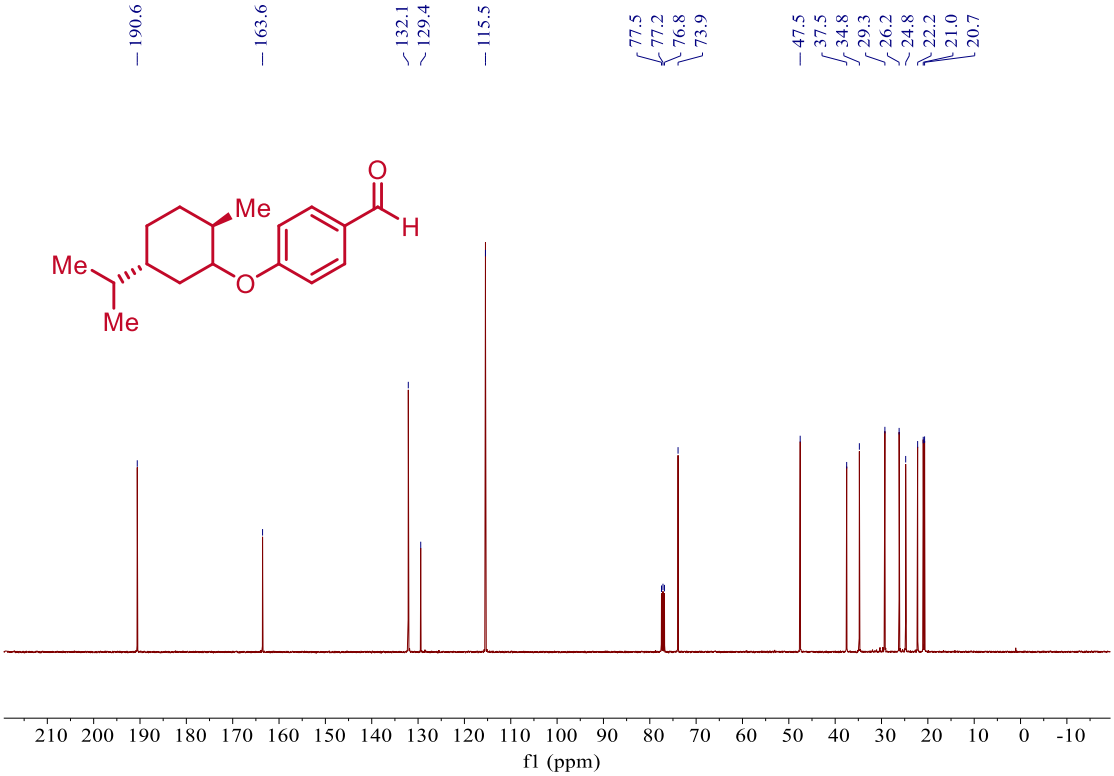
^{13}C NMR Spectrum of (3a*S*,5a*R*,8a*R*,8b*S*)-2,2,7,7-Tetramethyltetrahydro-3a*H*-bis([1,3]dioxolo)[4,5-*b*:4',5'-*d*]pyran-3a-yl)methyl 4-formylbenzoate 1aj



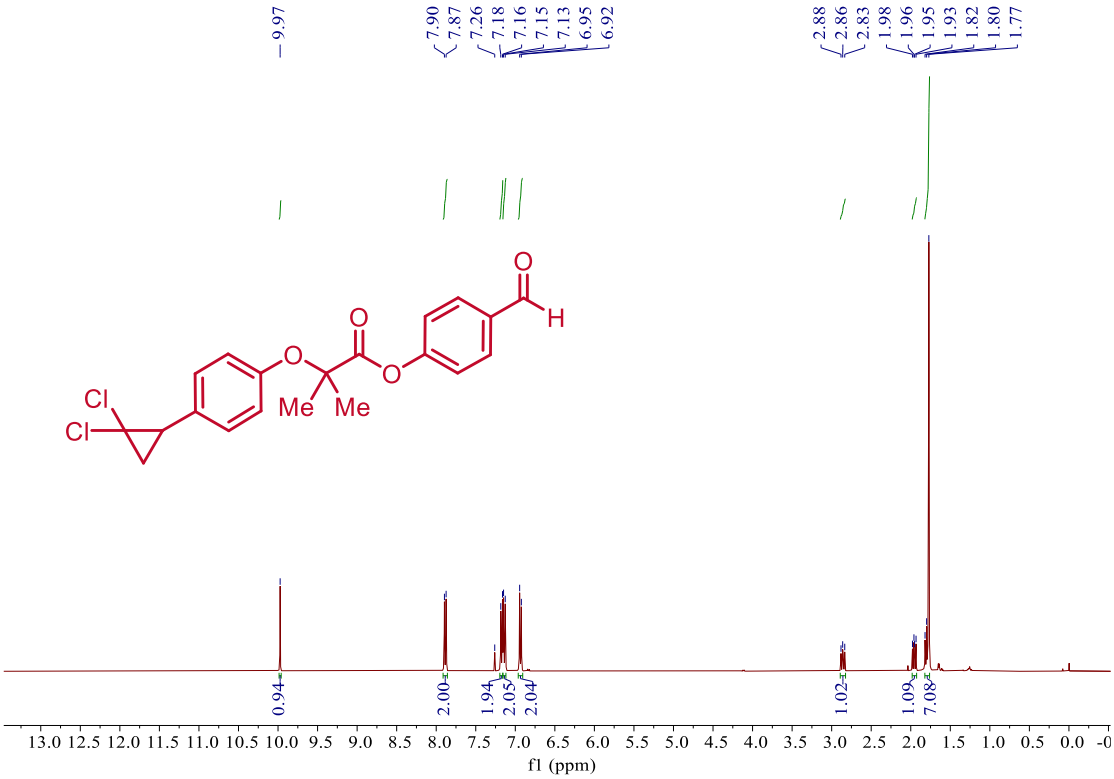
^{1}H NMR Spectrum of 4-(((2*R*,5*R*)-5-Isopropyl-2-methylcyclohexyl)oxy)benz aldehyde 1ak



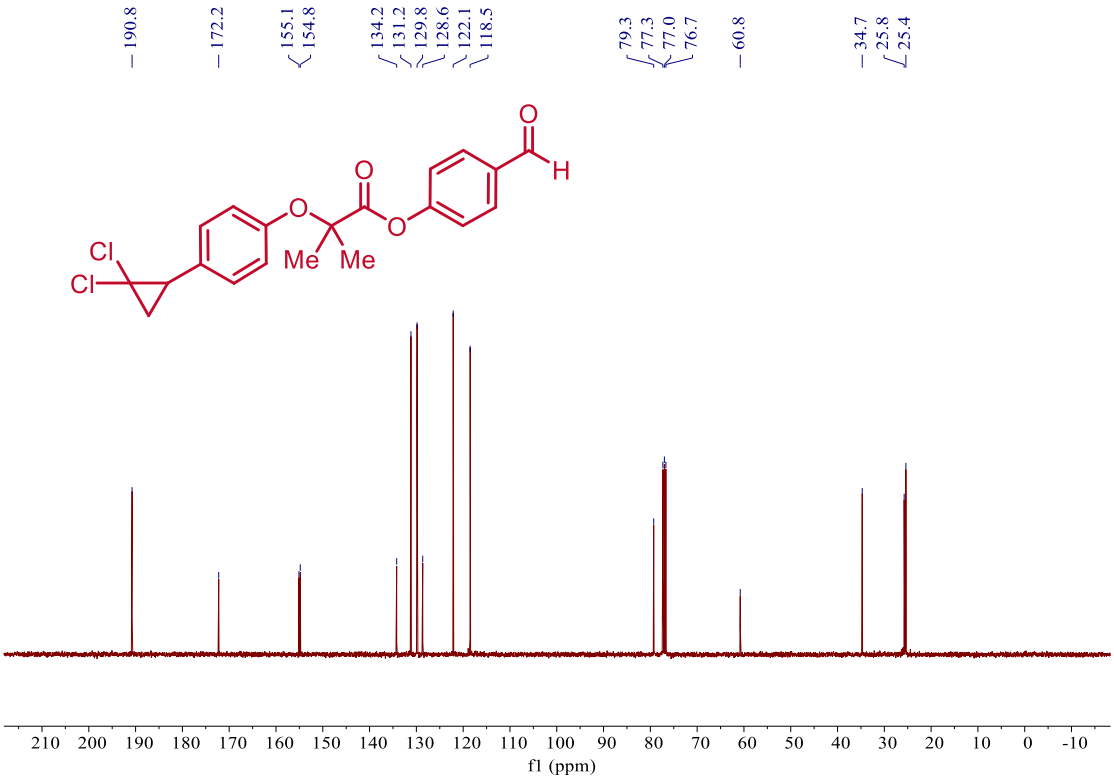
^{13}C NMR Spectrum of 4-(((2*R*,5*R*)-5-Isopropyl-2-methylcyclohexyl)oxy)benz aldehyde 1ak



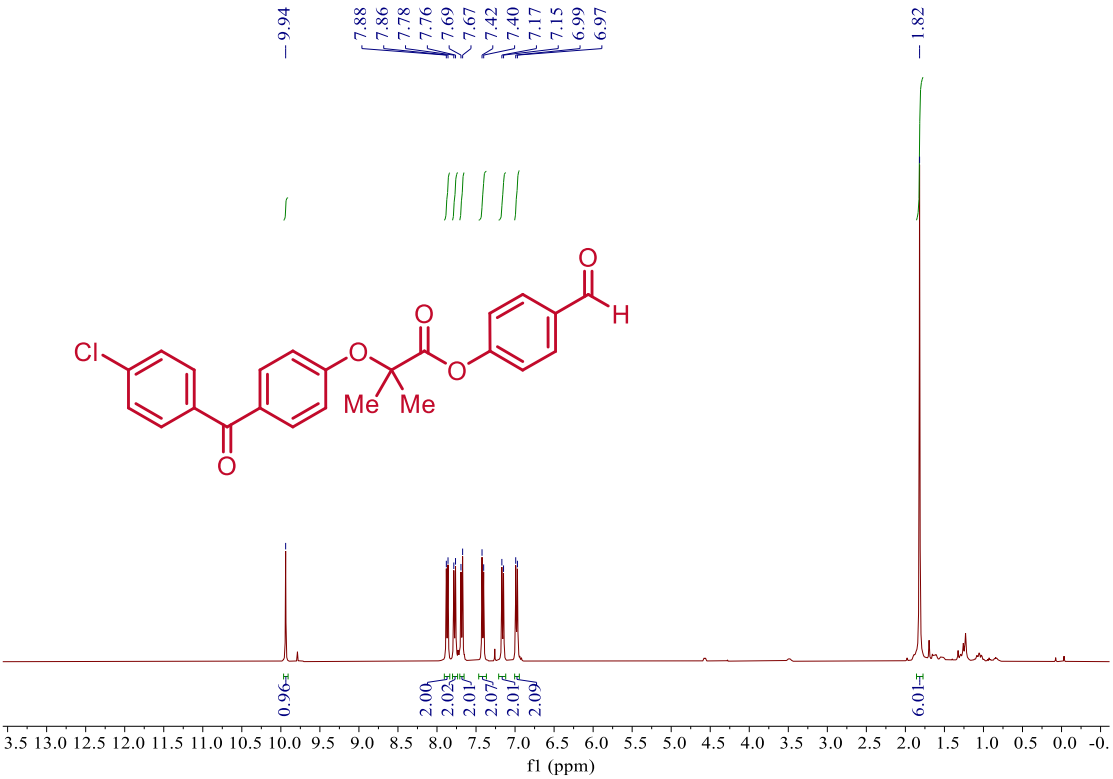
^{1}H NMR Spectrum of 4-Formylphenyl 2-(4-(2,2-dichlorocyclopropyl) phenoxy) -2-methylpropanoate 1am



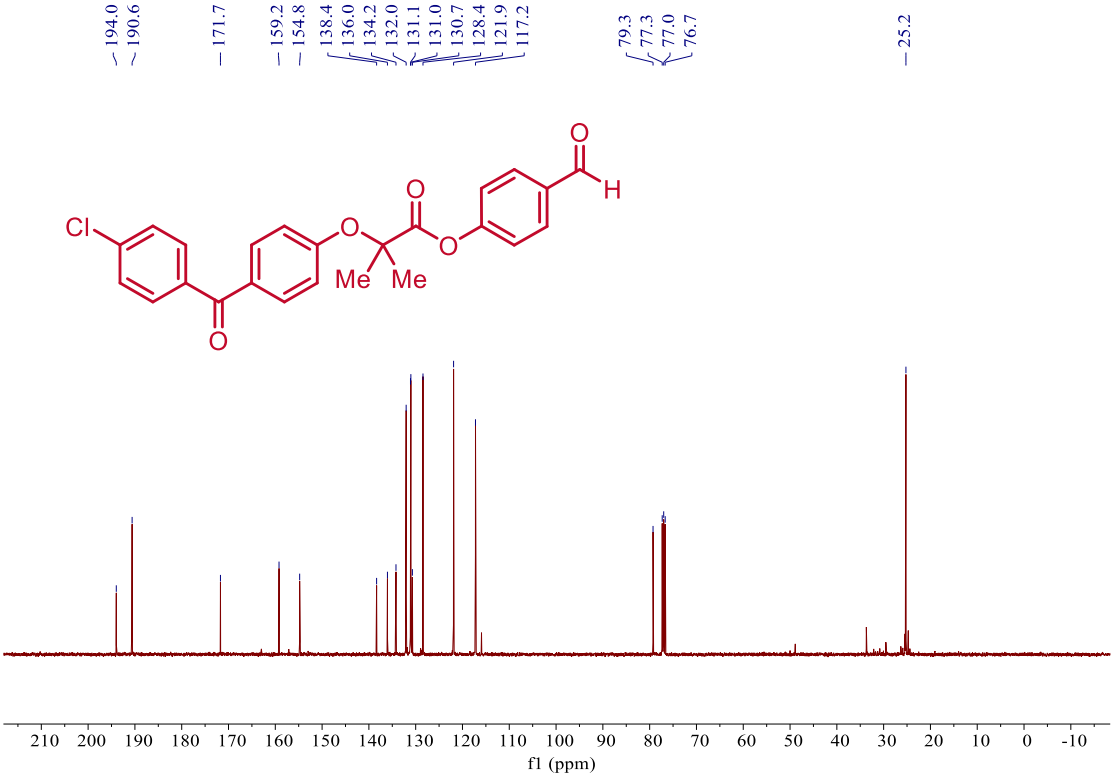
^{13}C NMR Spectrum of 4-Formylphenyl 2-(4-(2,2-dichlorocyclopropyl) phenoxy) -2-methylpropanoate 1am



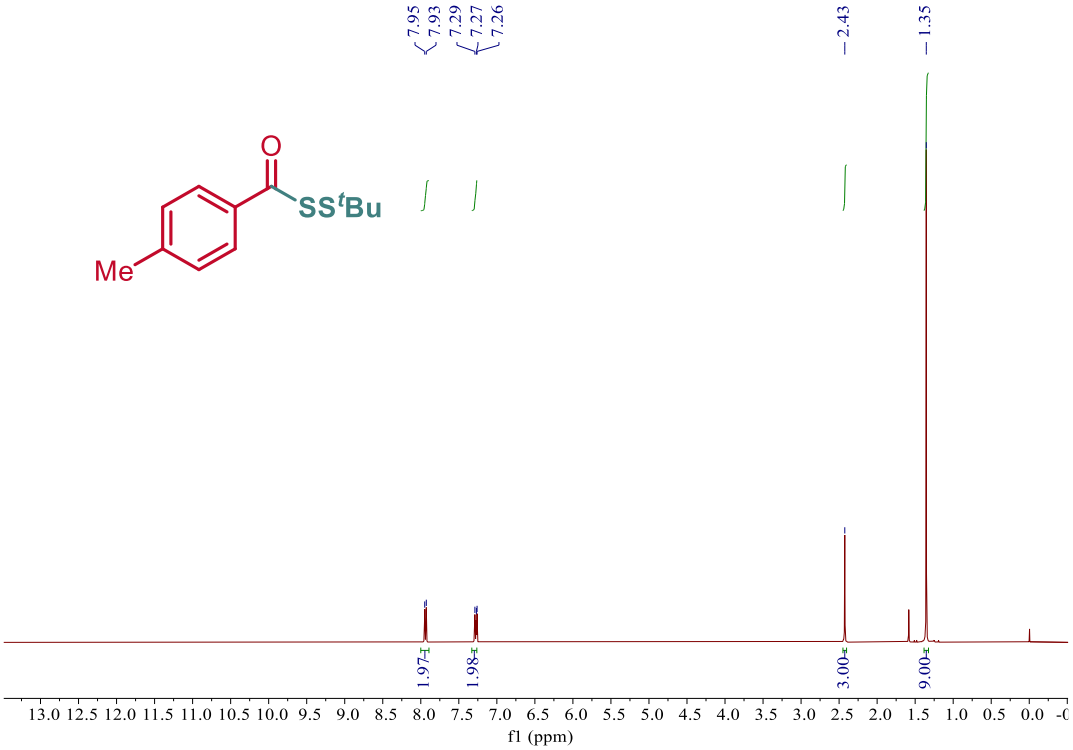
^{1}H NMR Spectrum of 4-Formylphenyl 2-(4-(4-chlorobenzoyl)phenoxy)-2-methylpropanoate 1an



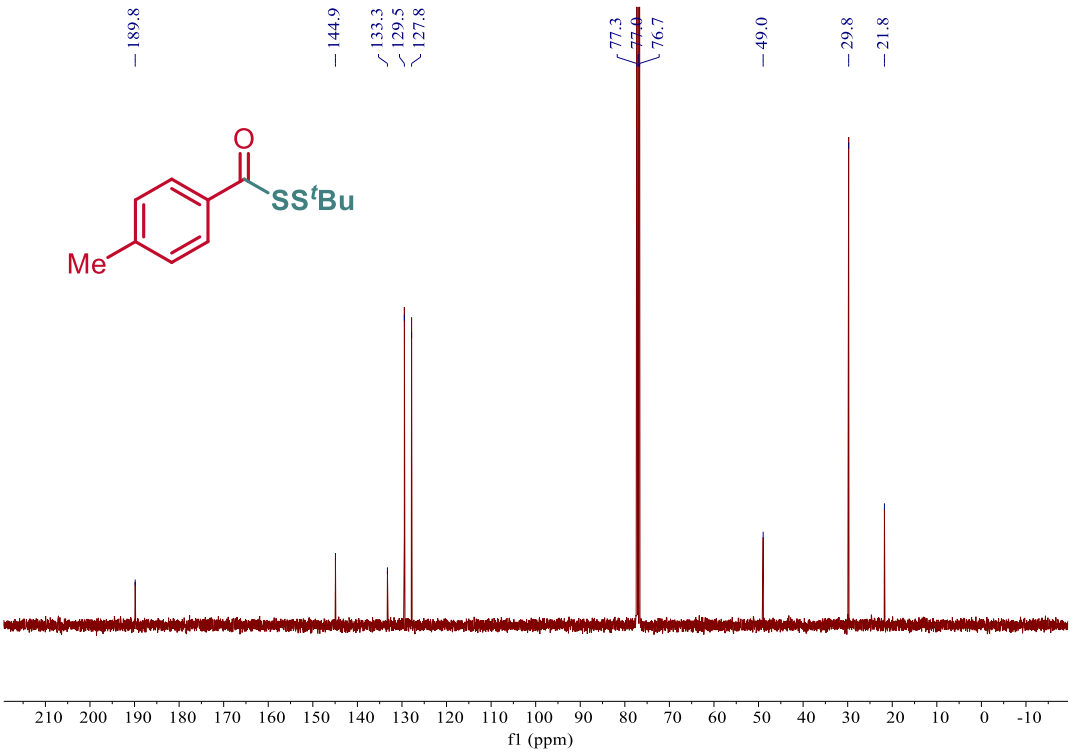
^{13}C NMR Spectrum of 4-Formylphenyl 2-(4-(4-chlorobenzoyl)phenoxy)-2-methylpropanoate 1an



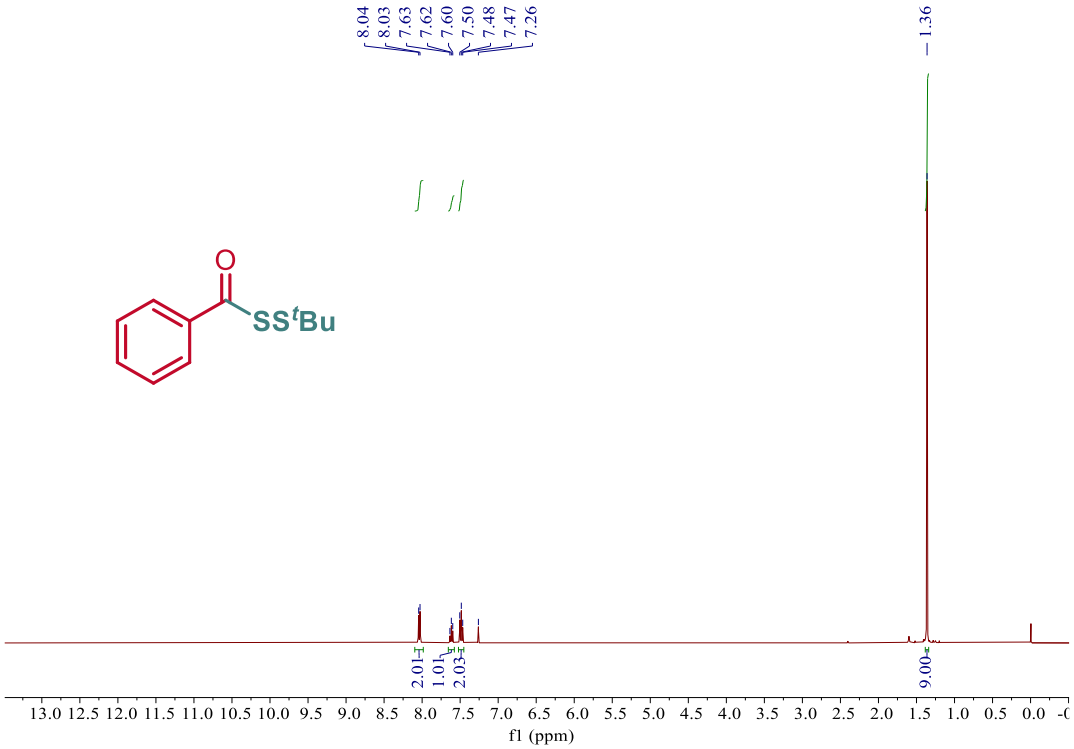
^{1}H NMR Spectrum of *SS*-(*tert*-Butyl) 4-methylbenzo(dithioperoxoate) 3a



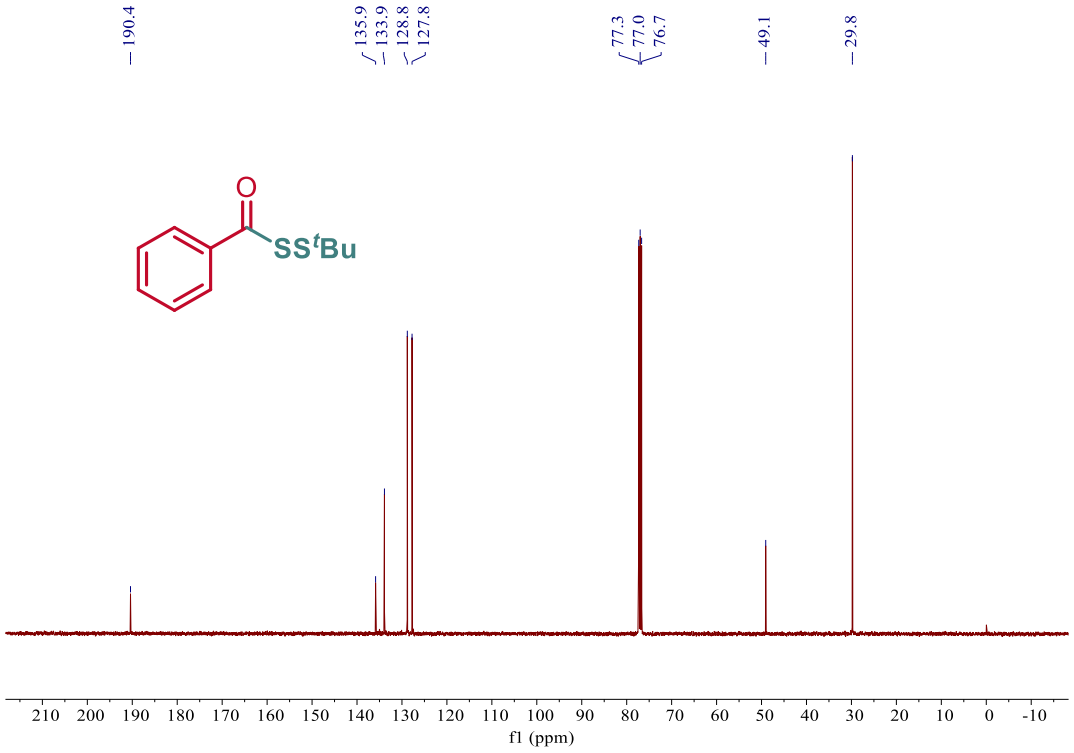
^{13}C NMR Spectrum of *SS*-(*tert*-Butyl) 4-methylbenzo(dithioperoxoate) 3a



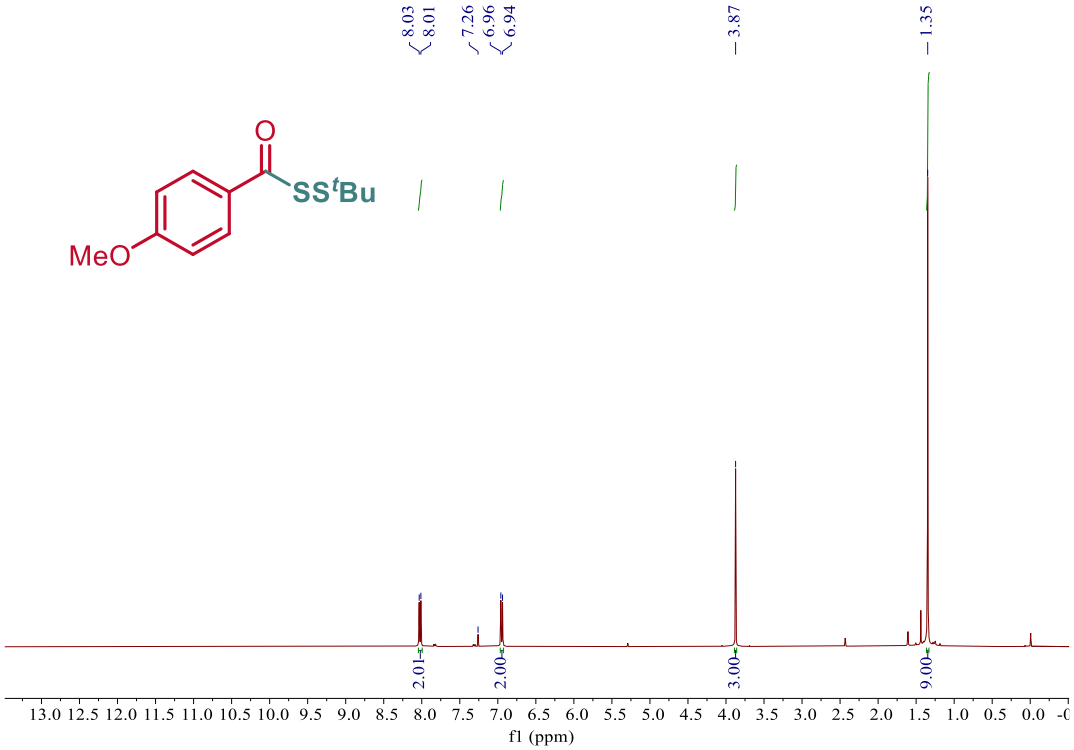
^{1}H NMR Spectrum of *SS*-(*tert*-Butyl) benzo(dithioperoxoate) 3b



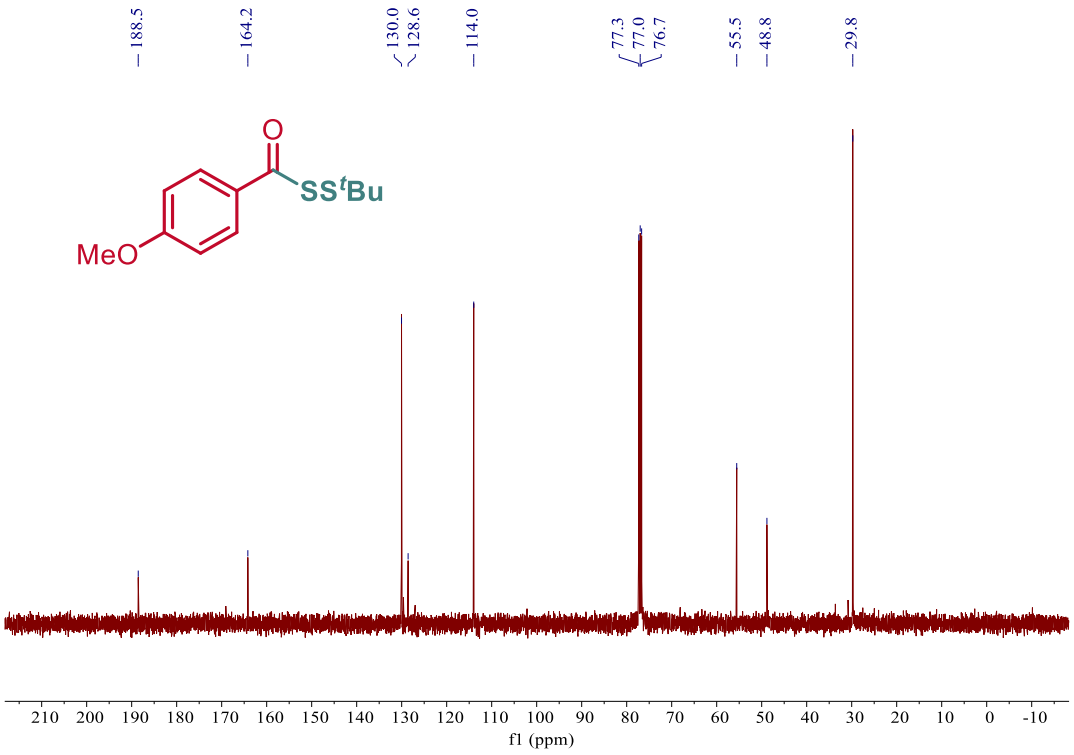
^{13}C NMR Spectrum of *SS*-(*tert*-Butyl) benzo(dithioperoxoate) 3b



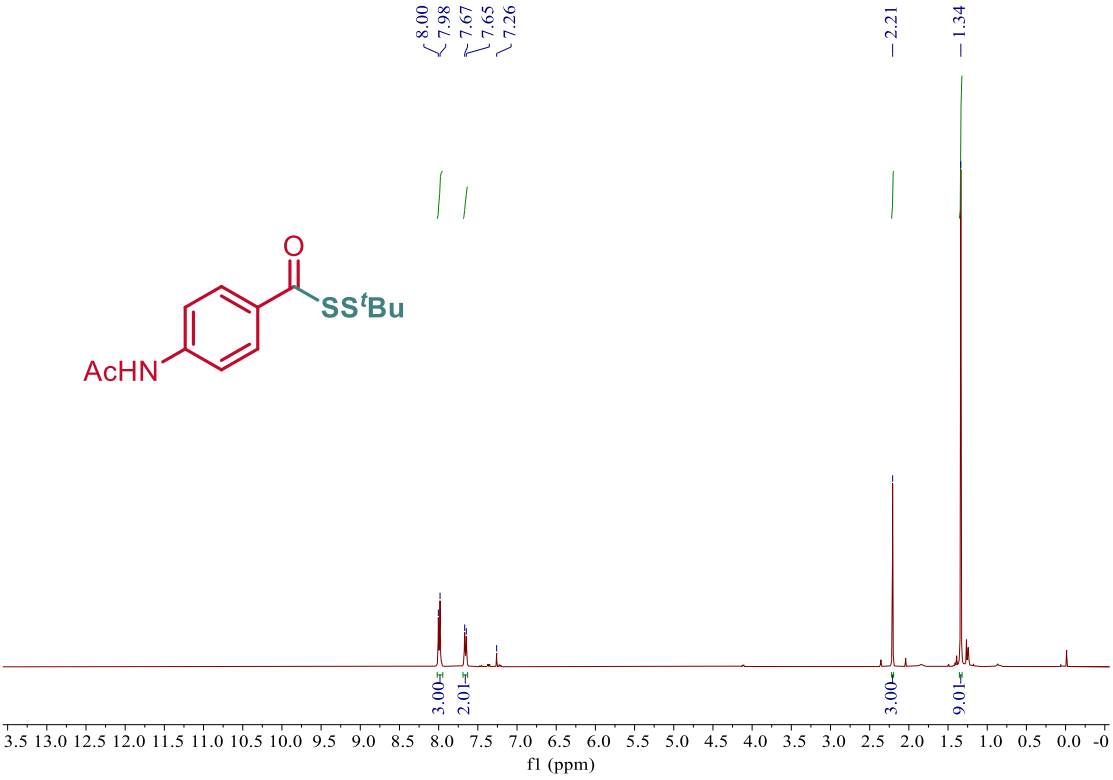
^{1}H NMR Spectrum of *SS*-(*tert*-Butyl) 4-methoxybenzo(dithioperoxoate) 3c



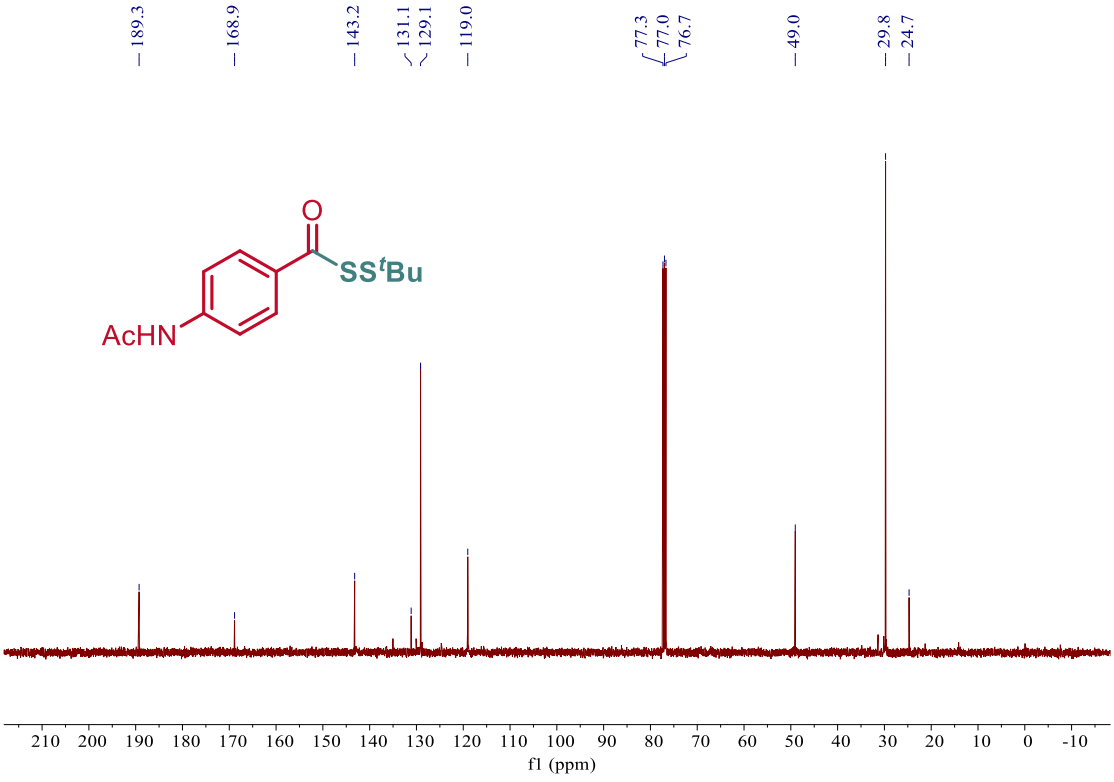
^{13}C NMR Spectrum of *SS*-(*tert*-Butyl) 4-methoxybenzo(dithioperoxoate) 3c



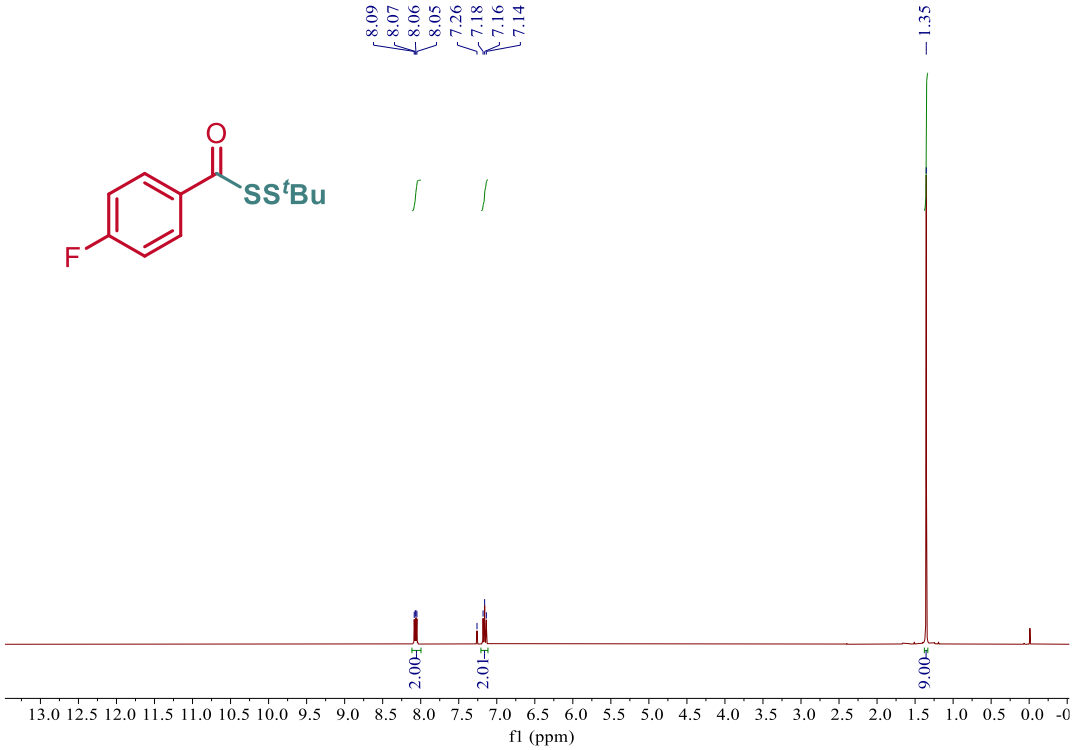
^{1}H NMR Spectrum of *SS*-(*tert*-Butyl) 4-acetamidobenzo(dithioperoxoate) 3d



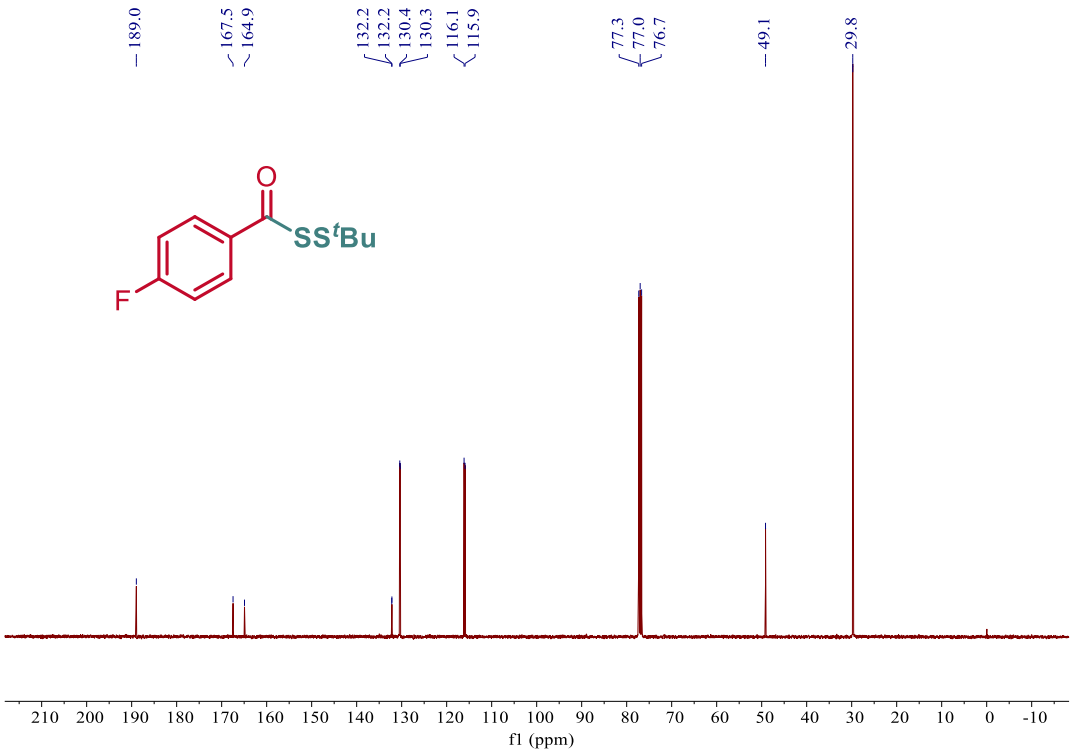
^{13}C NMR Spectrum of *SS*-(*tert*-Butyl) 4-acetamidobenzo(dithioperoxoate) 3d



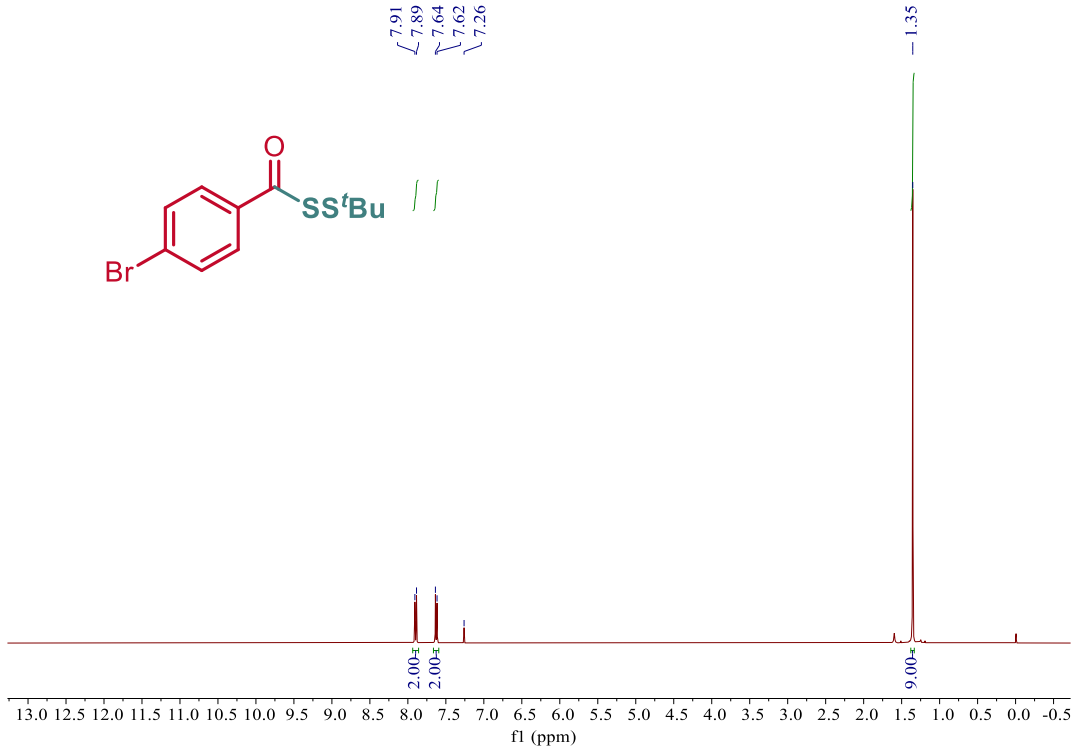
^{1}H NMR Spectrum of *SS*-(*tert*-Butyl) 4-fluorobenzo(dithioperoxoate) 3e



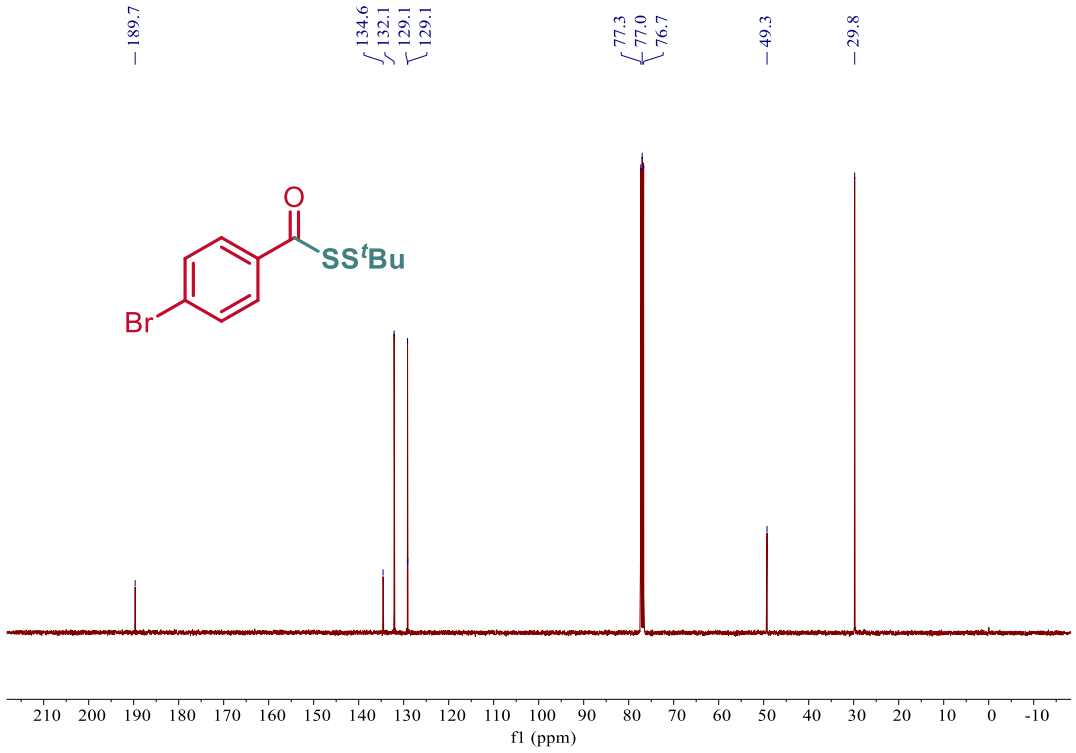
^{13}C NMR Spectrum of *SS*-(*tert*-Butyl) 4-fluorobenzo(dithioperoxoate) 3e



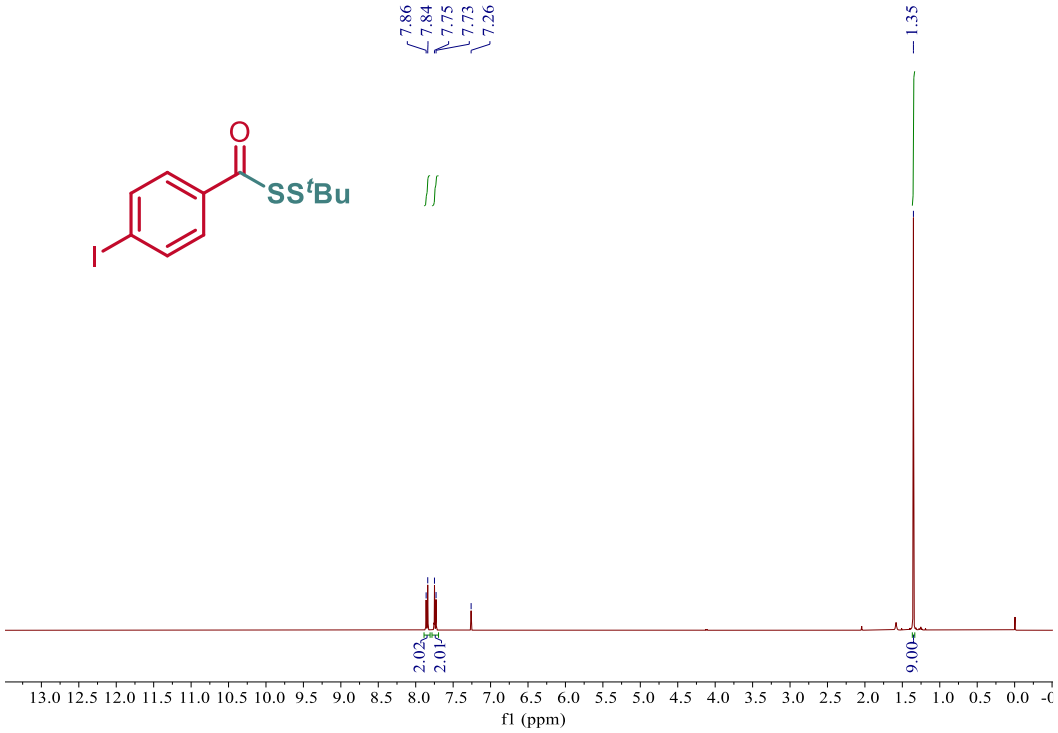
^{1}H NMR Spectrum of *SS*-(*tert*-Butyl) 4-bromobenzo(dithioperoxoate) 3f



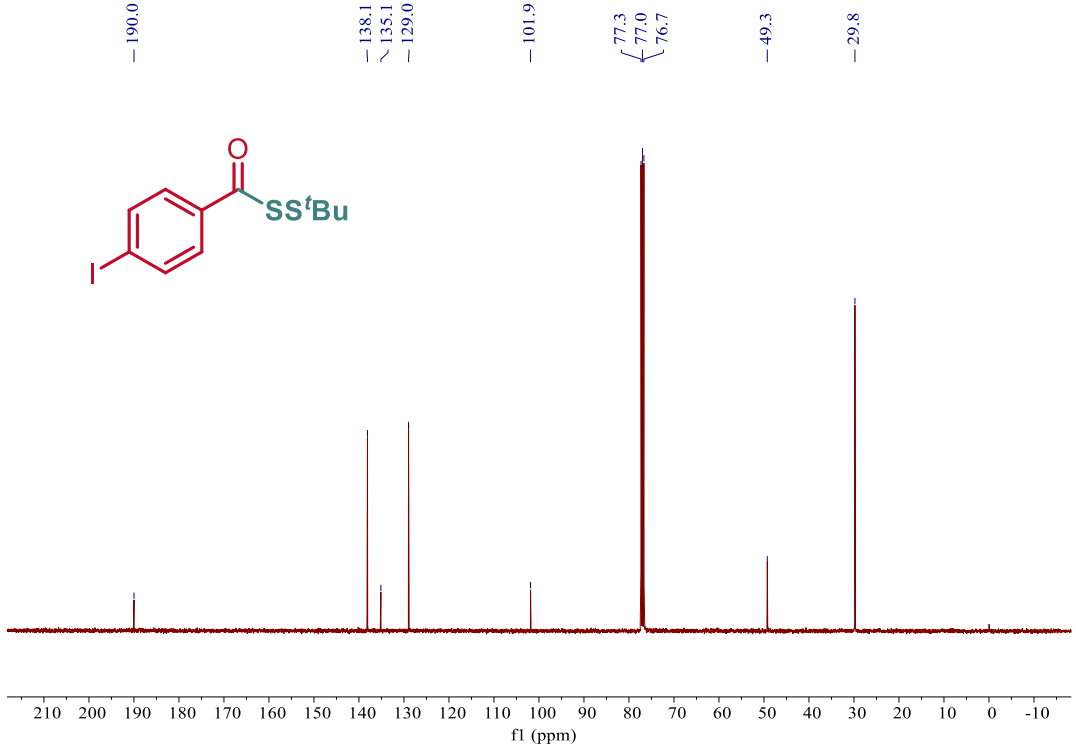
^{13}C NMR Spectrum of *SS*-(*tert*-Butyl) 4-bromobenzo(dithioperoxoate) 3f



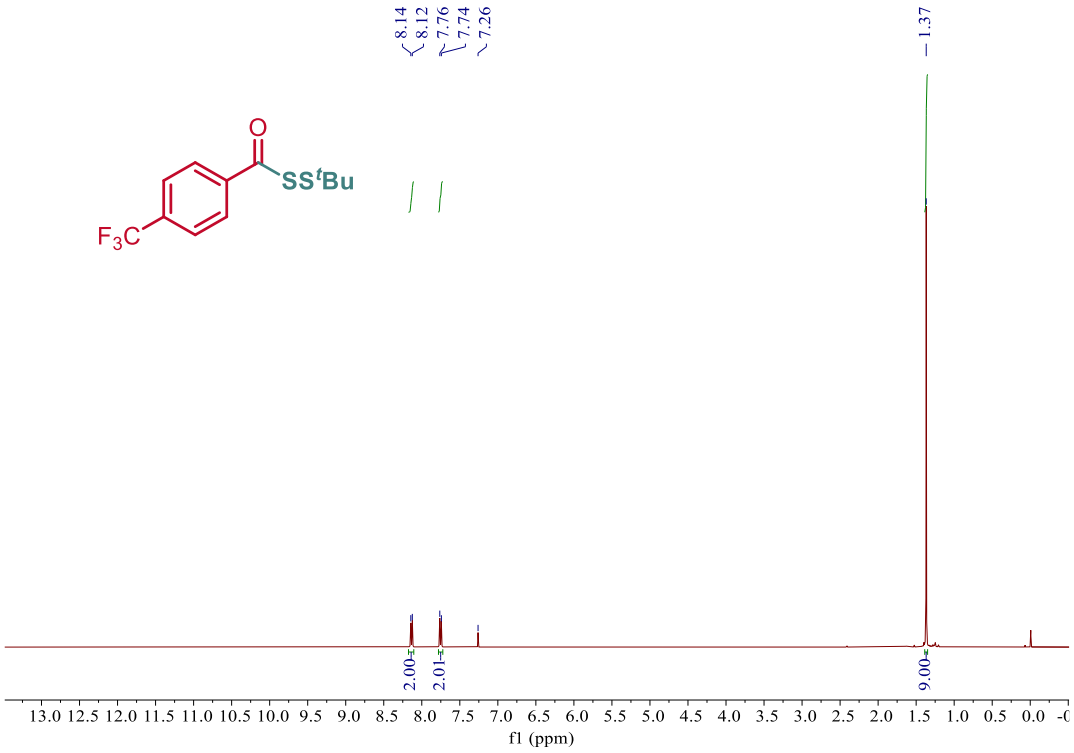
^{1}H NMR Spectrum of *SS*-(*tert*-Butyl) 4-iodobenzo(dithioperoxoate) 3g



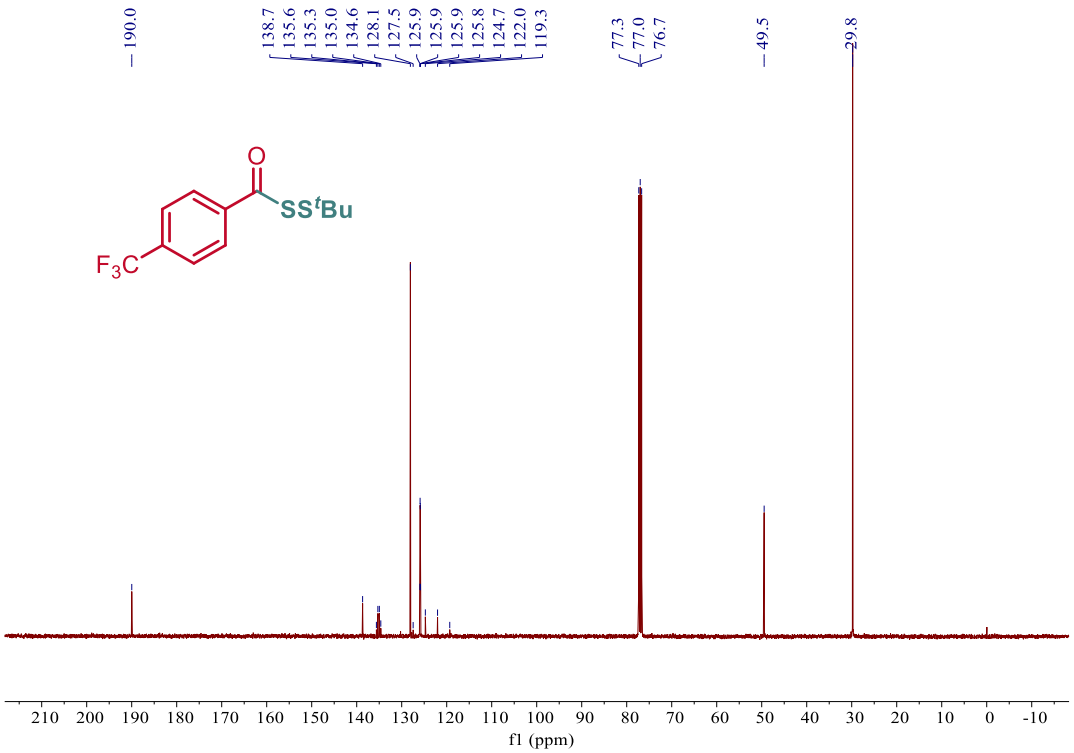
^{13}C NMR Spectrum of *SS*-(*tert*-Butyl) 4-iodobenzo(dithioperoxoate) 3g



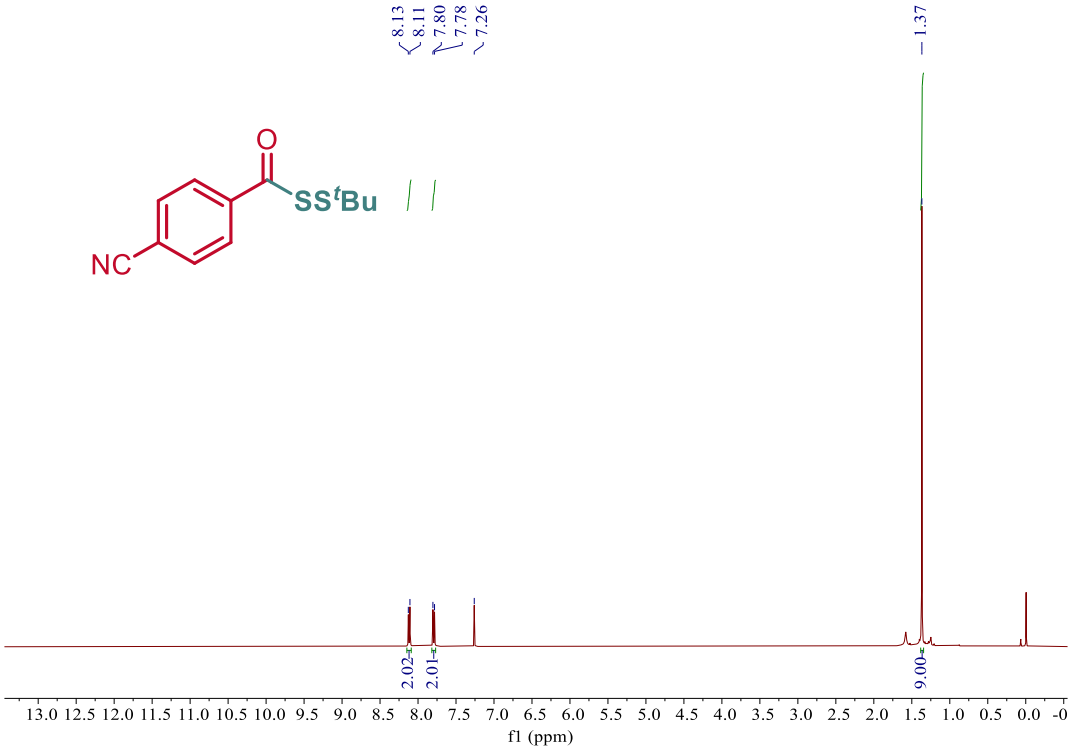
^{1}H NMR Spectrum of *SS*-(*tert*-Butyl) 4-(trifluoromethyl)benzo(dithioperoxoate) 3h



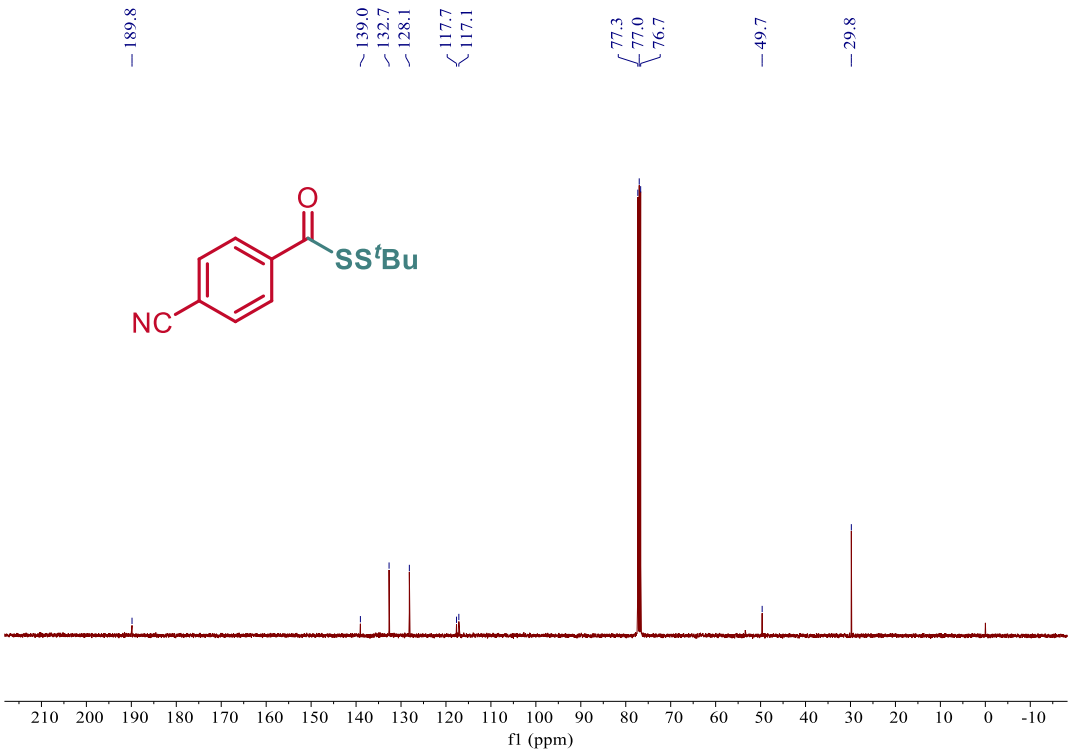
^{13}C NMR Spectrum of *SS*-(*tert*-Butyl) 4-(trifluoromethyl)benzo(dithioperoxoate) 3h



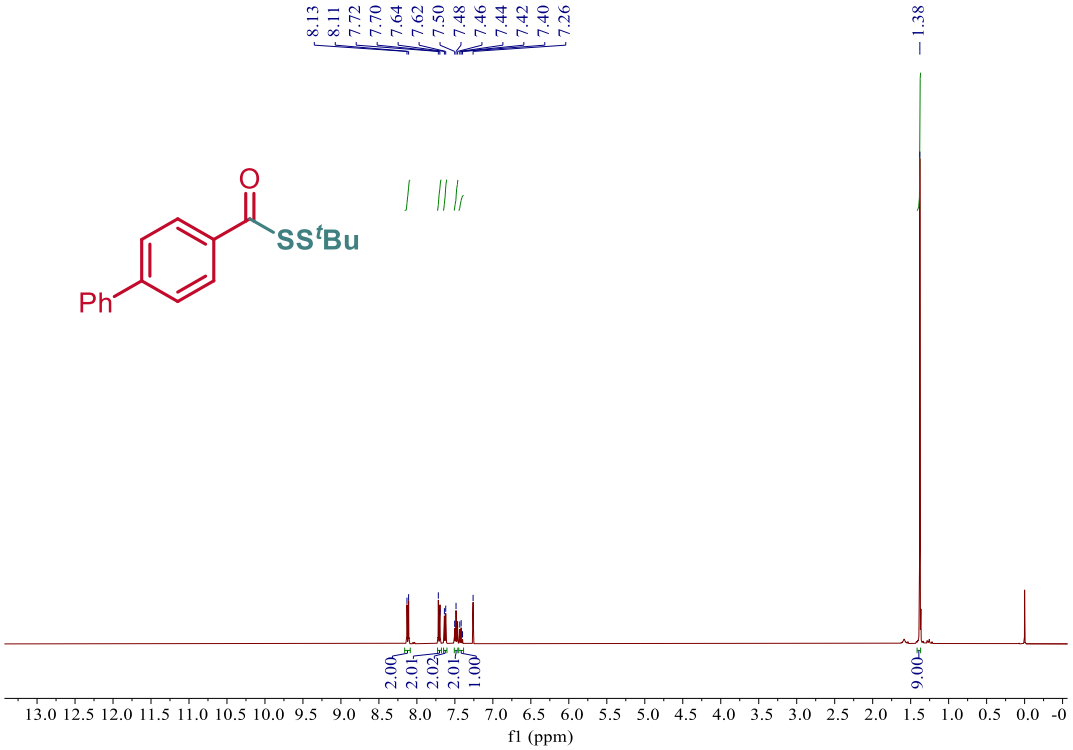
^{1}H NMR Spectrum of *SS*-(*tert*-Butyl) 4-cyanobenzo(dithioperoxoate) 3i



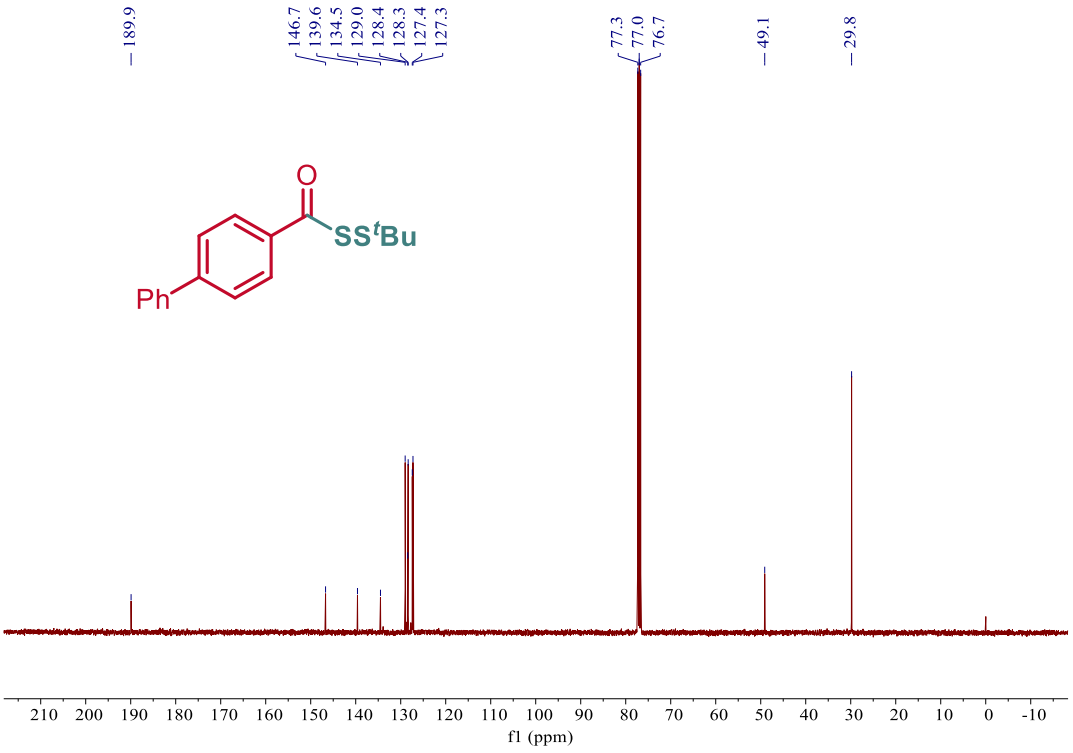
^{13}C NMR Spectrum of *SS*-(*tert*-Butyl) 4-cyanobenzo(dithioperoxoate) 3i



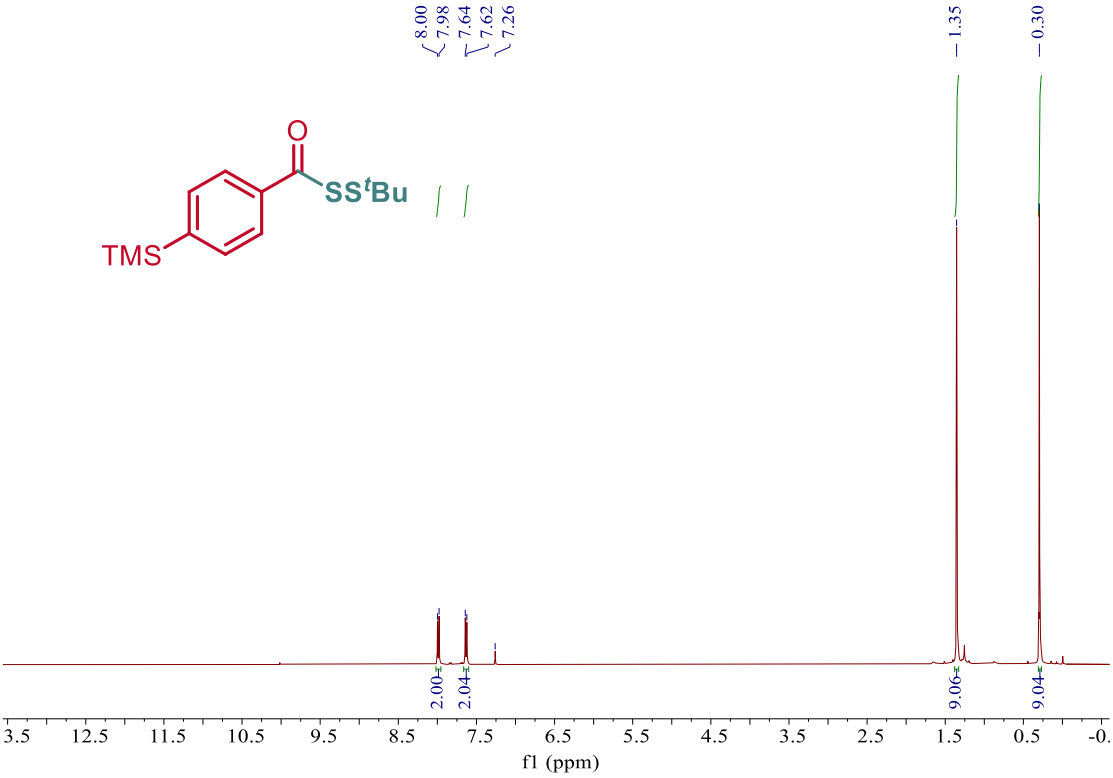
^{1}H NMR Spectrum of *SS*-(*tert*-Butyl) [1,1'-biphenyl]-4-carbo(dithioperoxoate) 3j



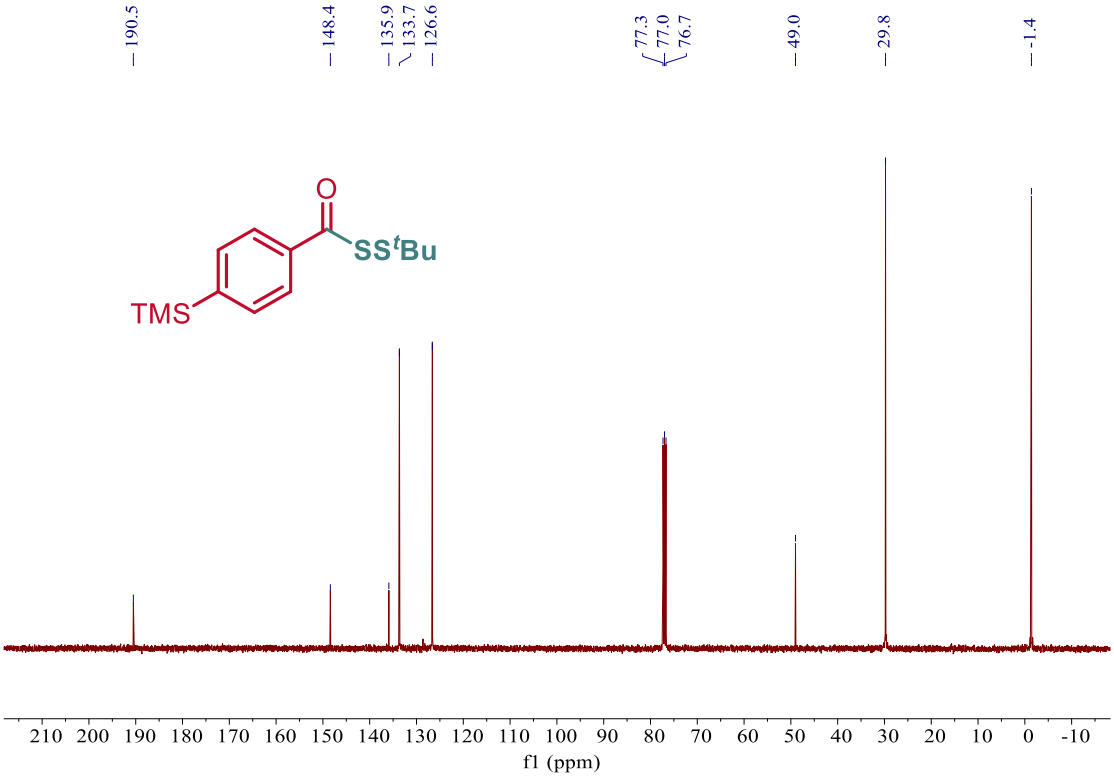
^{13}C NMR Spectrum of *SS*-(*tert*-Butyl) [1,1'-biphenyl]-4-carbo(dithioperoxoate) 3j



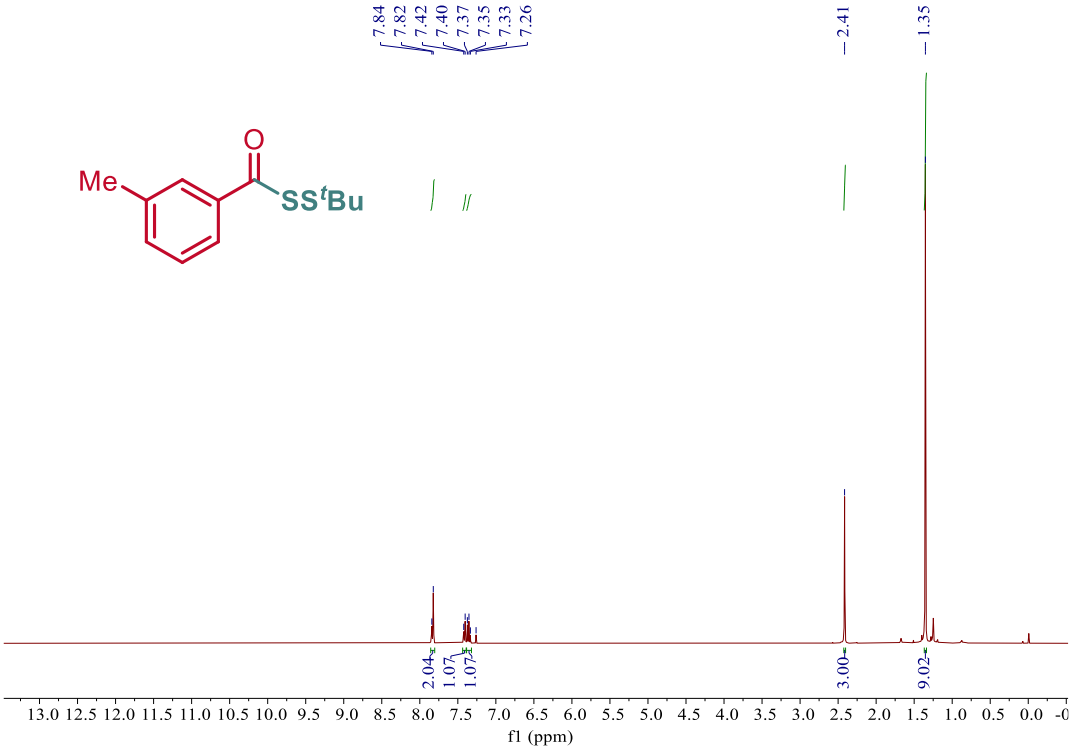
^{1}H NMR Spectrum of *SS*-(*tert*-Butyl) 4-(trimethylsilyl)benzo(dithioperoxoate) 3k



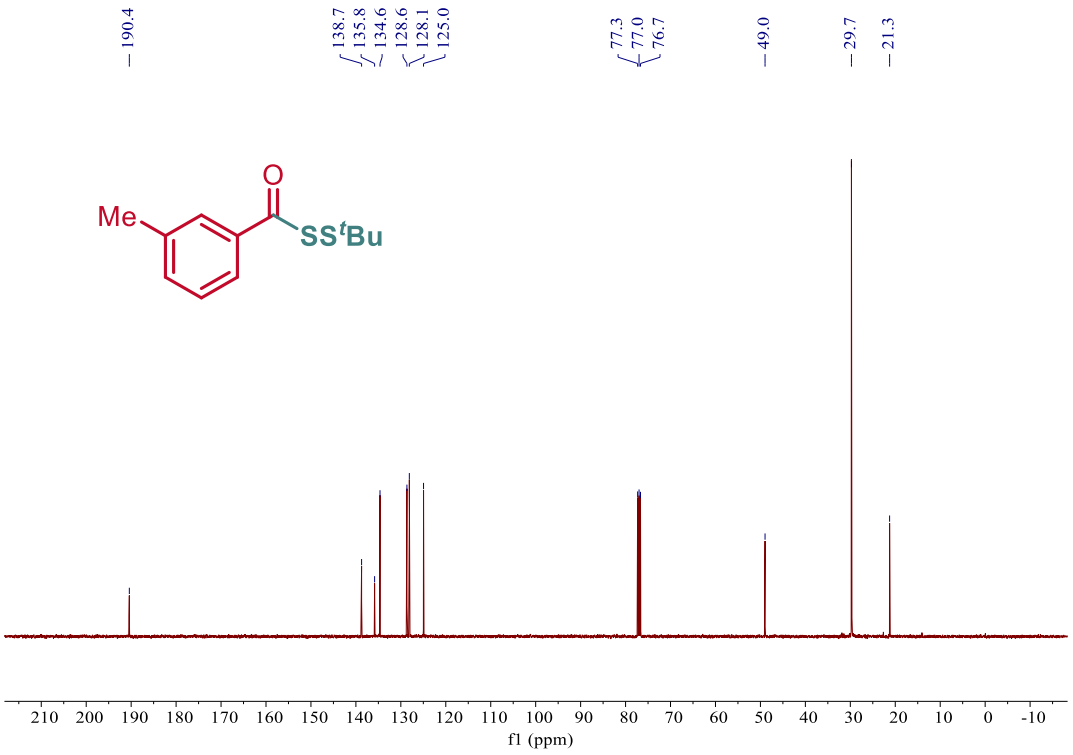
^{13}C NMR Spectrum of *SS*-(*tert*-Butyl) 4-(trimethylsilyl)benzo(dithioperoxoate) 3k



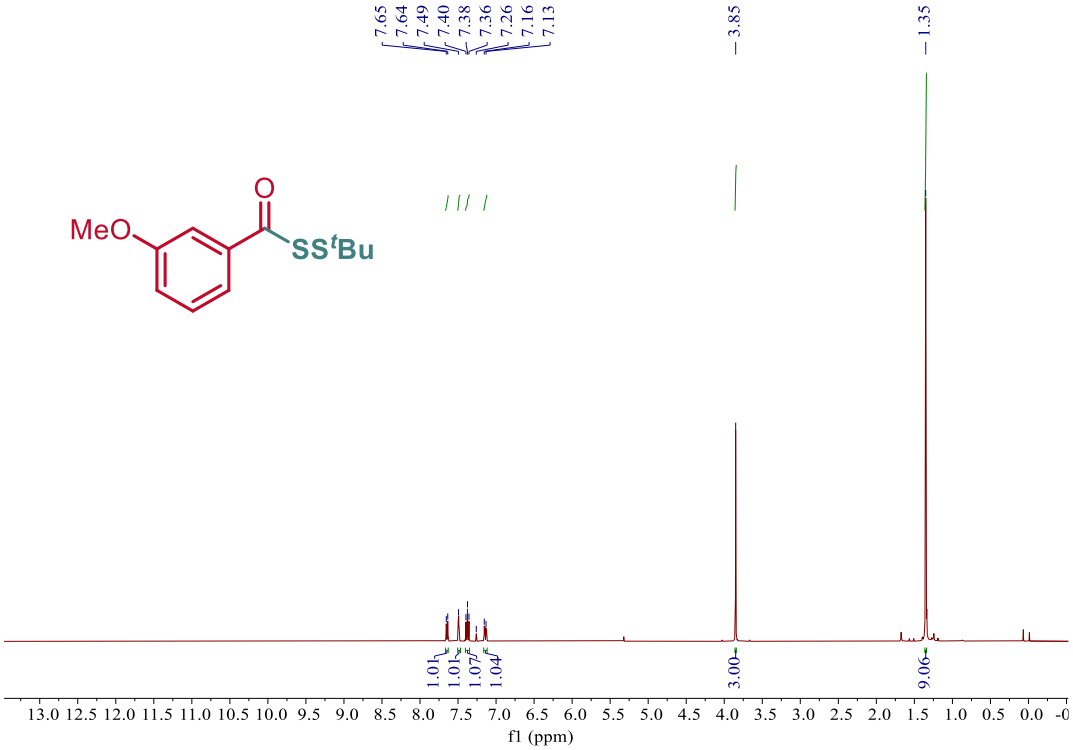
^{1}H NMR Spectrum of *SS*-(*tert*-Butyl) 3-methylbenzo(dithioperoxoate) 3l



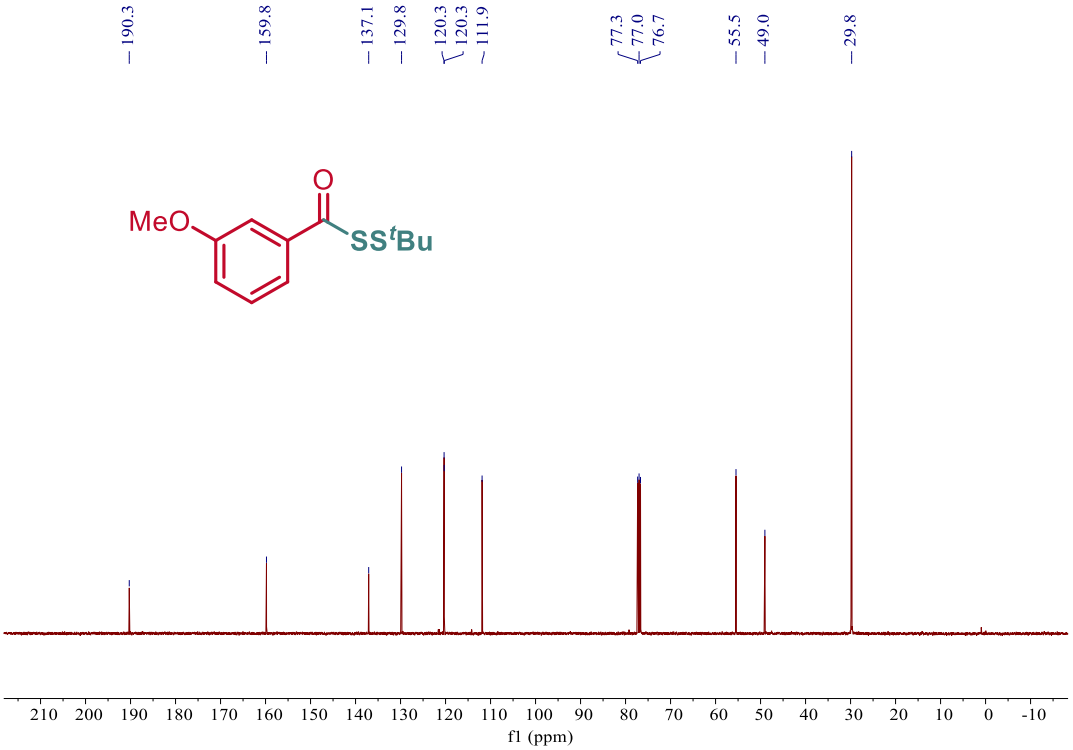
^{13}C NMR Spectrum of *SS*-(*tert*-Butyl) 3-methylbenzo(dithioperoxoate) 3l



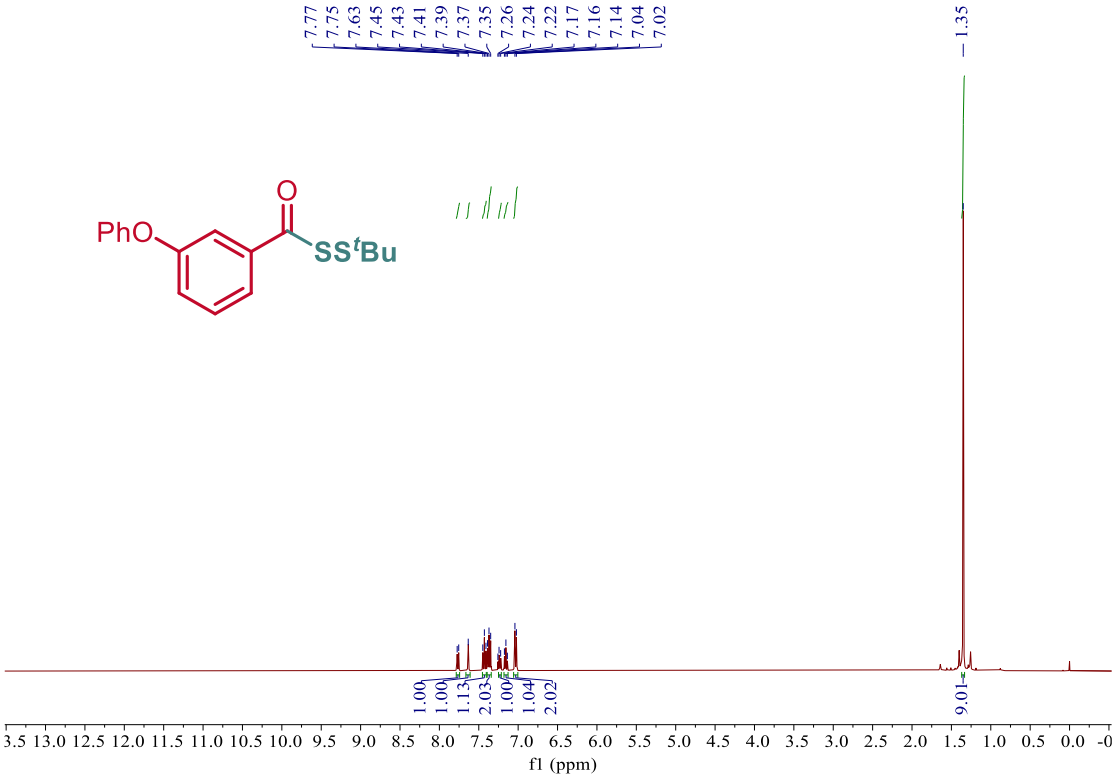
^{1}H NMR Spectrum of *SS*-(*tert*-Butyl) 3-methoxybenzo(dithioperoxoate) 3m



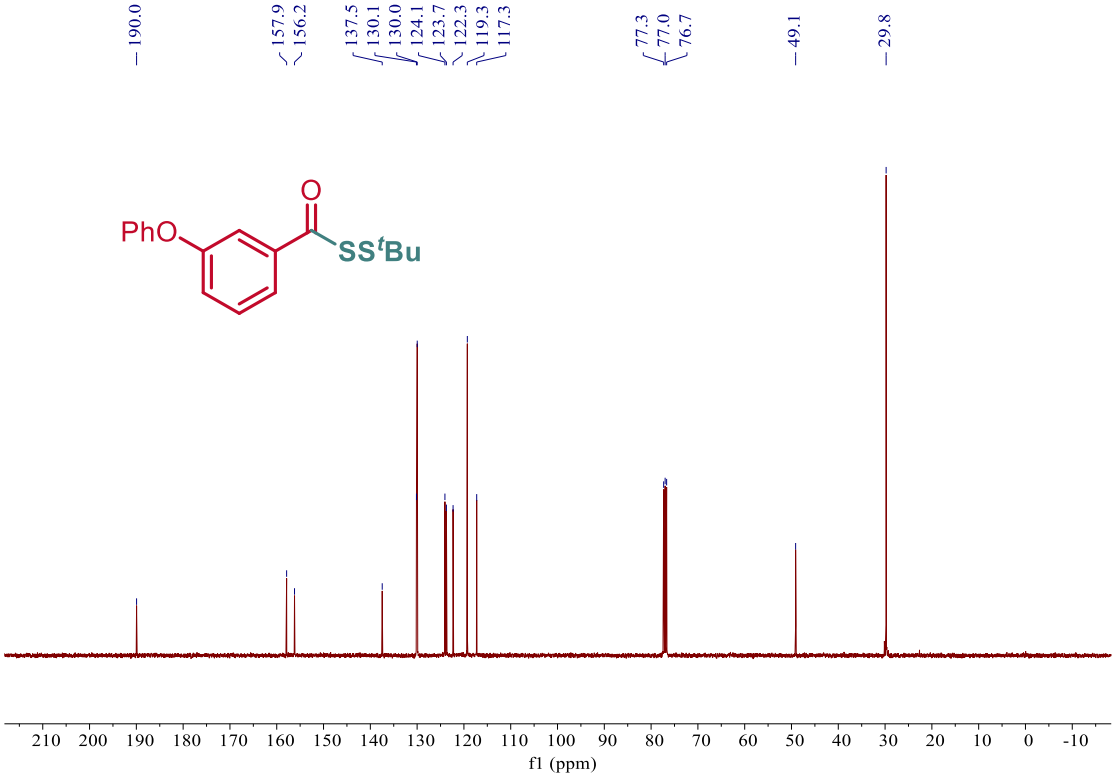
^{13}C NMR Spectrum of *SS*-(*tert*-Butyl) 3-methoxybenzo(dithioperoxoate) 3m



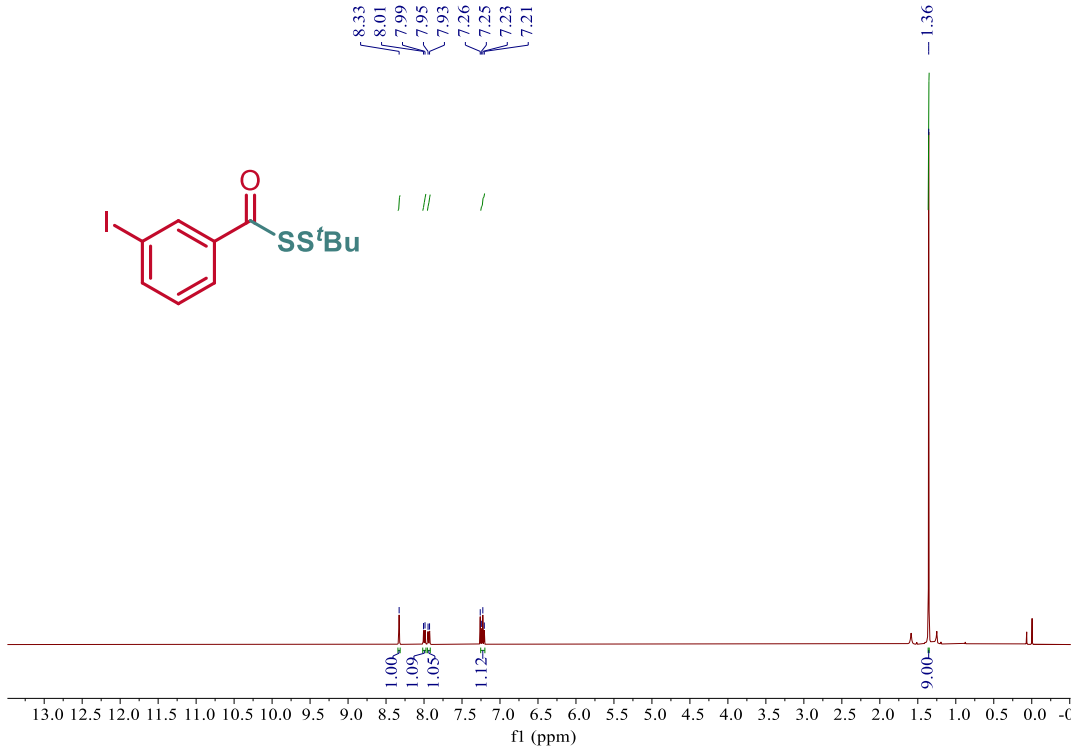
^{1}H NMR Spectrum of *SS*-(*tert*-Butyl) 3-phenoxybenzo(dithioperoxoate) 3n



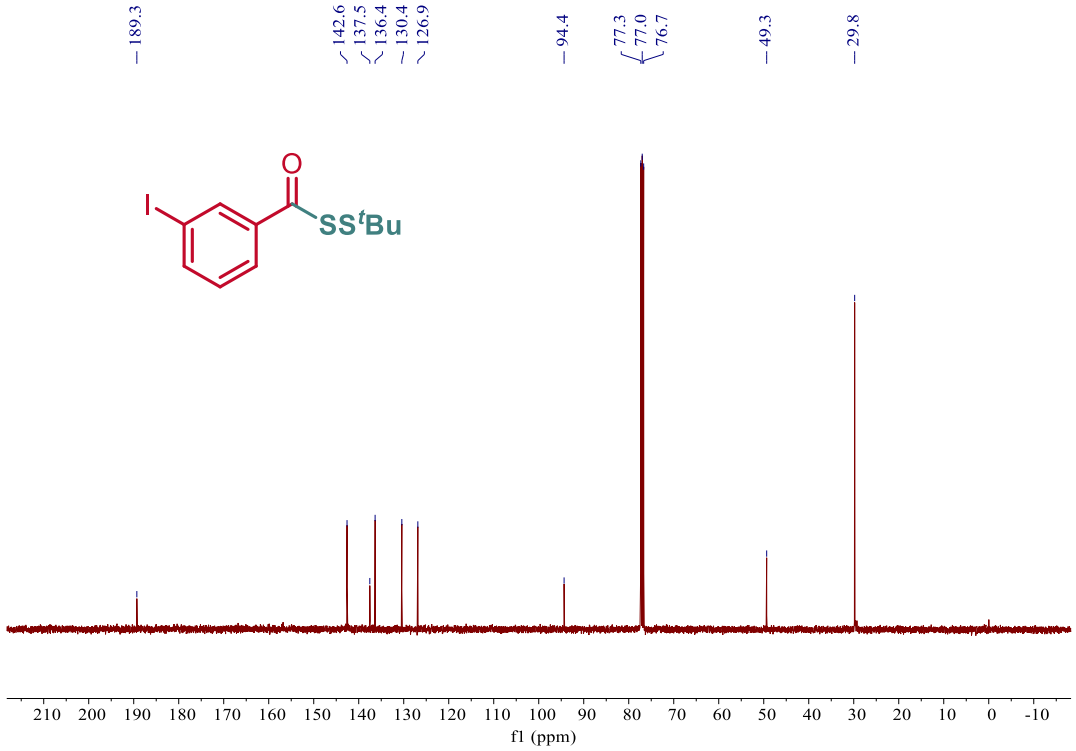
^{13}C NMR Spectrum of *SS*-(*tert*-Butyl) 3-phenoxybenzo(dithioperoxoate) 3n



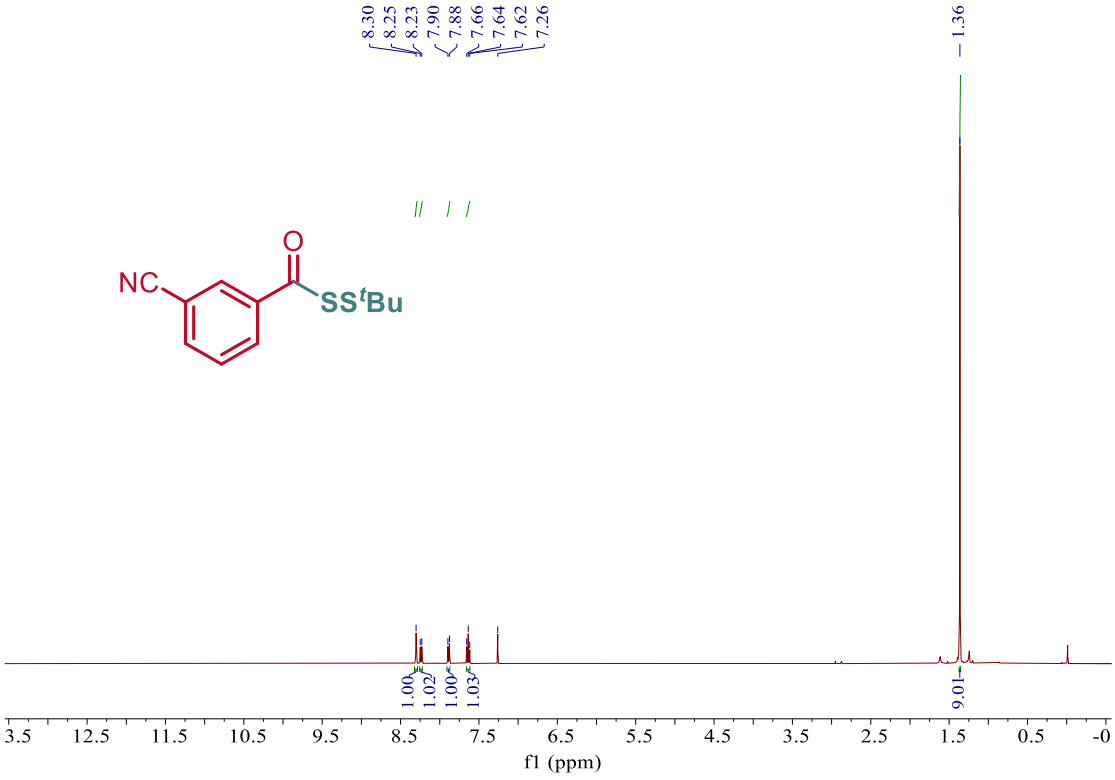
^{1}H NMR Spectrum of *SS*-(*tert*-Butyl) 3-iodobenzo(dithioperoxoate) 3o



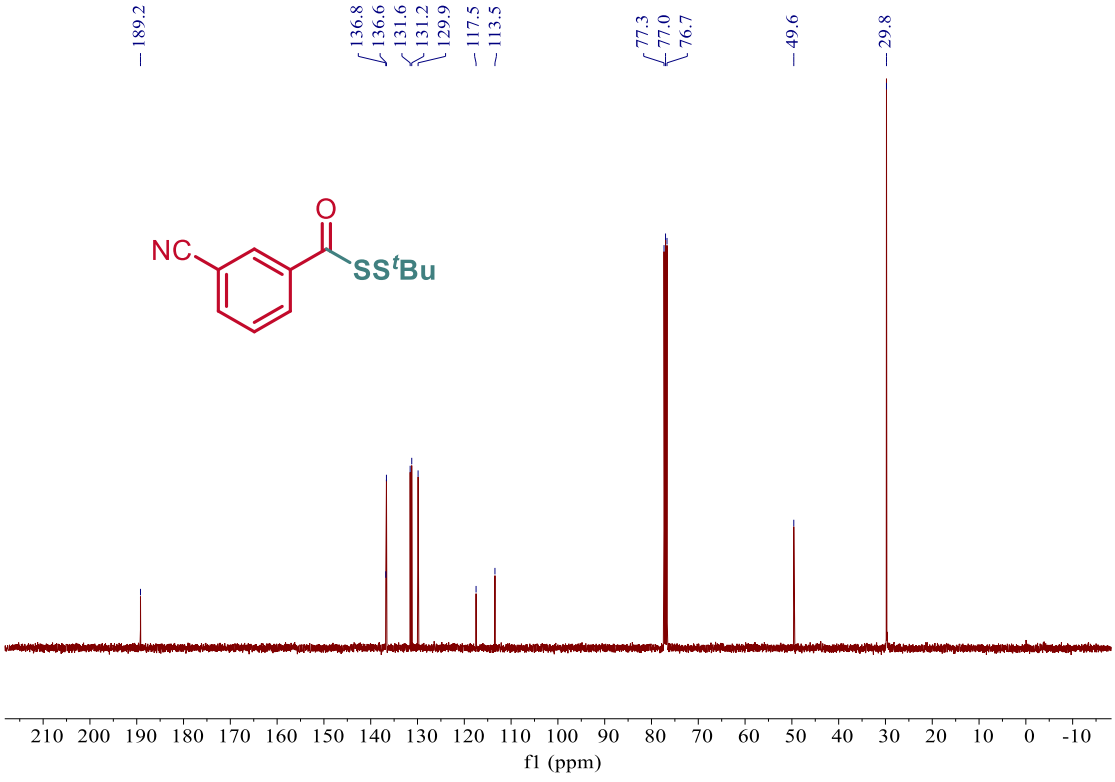
^{13}C NMR Spectrum of *SS*-(*tert*-Butyl) 3-iodobenzo(dithioperoxoate) 3o



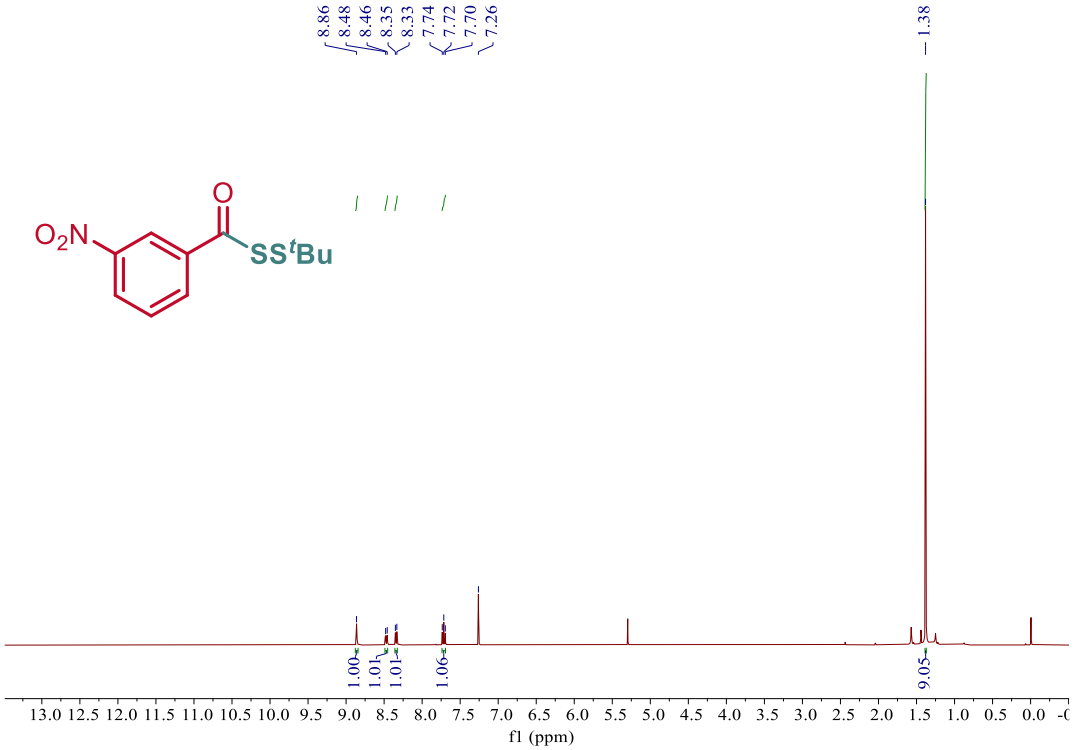
^{1}H NMR Spectrum of *SS*-(*tert*-Butyl) 3-cyanobenzo(dithioperoxoate) 3p



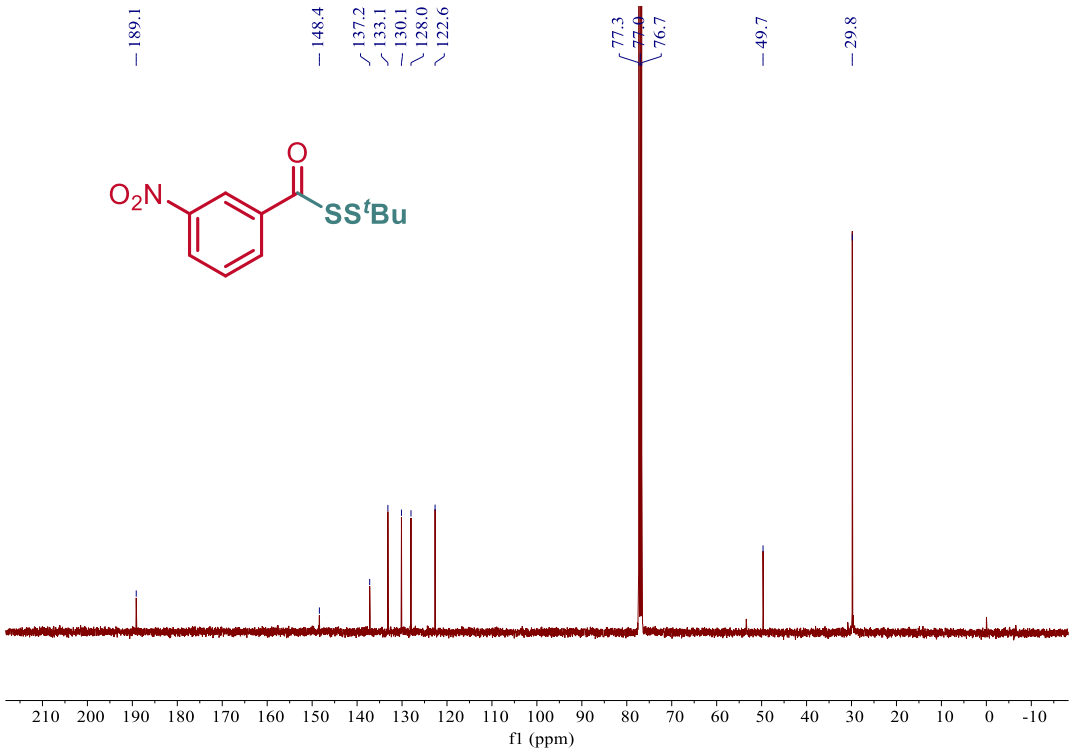
^{13}C NMR Spectrum of *SS*-(*tert*-Butyl) 3-cyanobenzo(dithioperoxoate) 3p



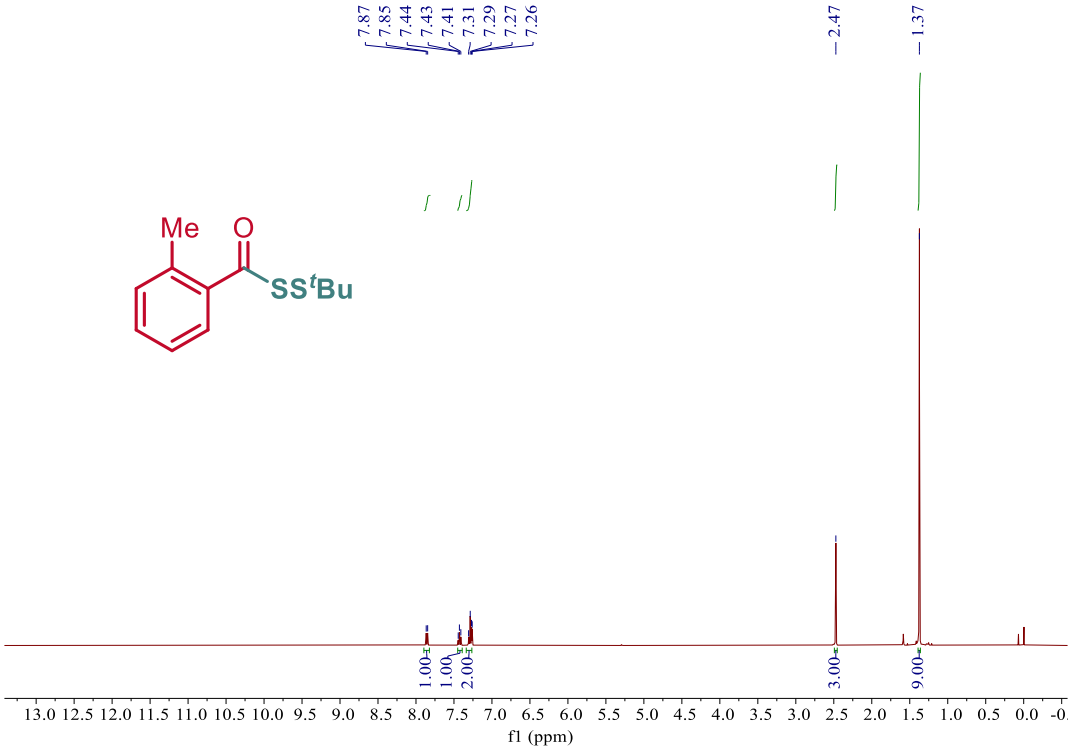
^{1}H NMR Spectrum of *SS*-(*tert*-Butyl) 3-nitrobenzo(dithioperoxoate) 3q



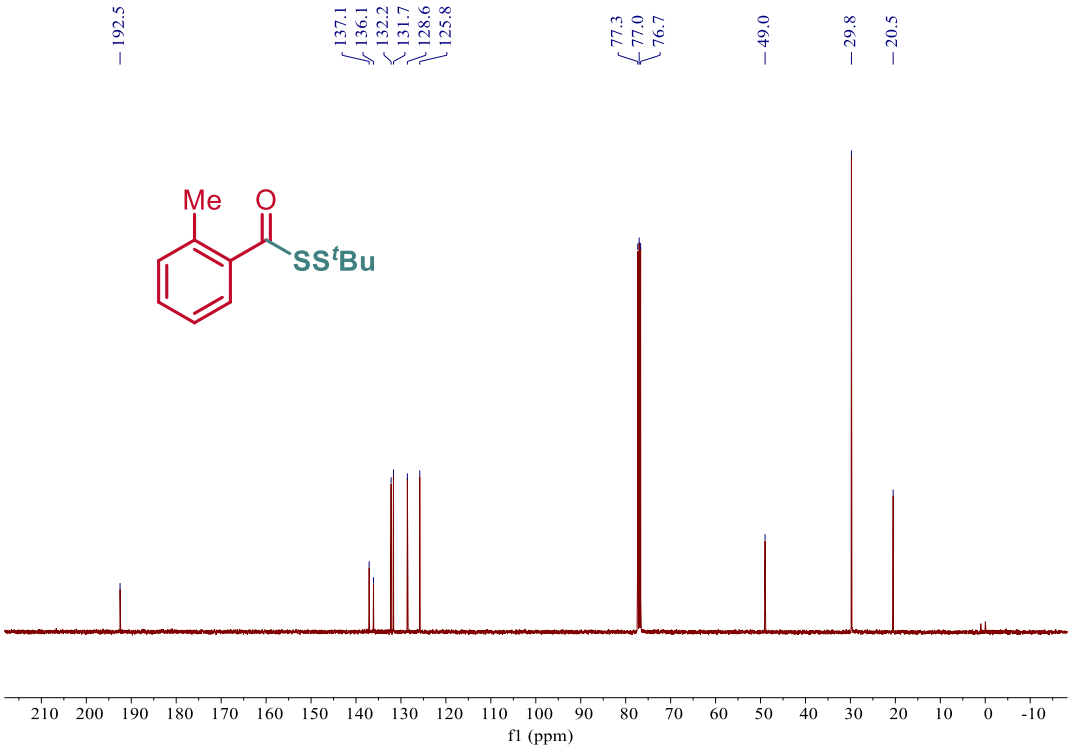
^{13}C NMR Spectrum of *SS*-(*tert*-Butyl) 3-nitrobenzo(dithioperoxoate) 3q



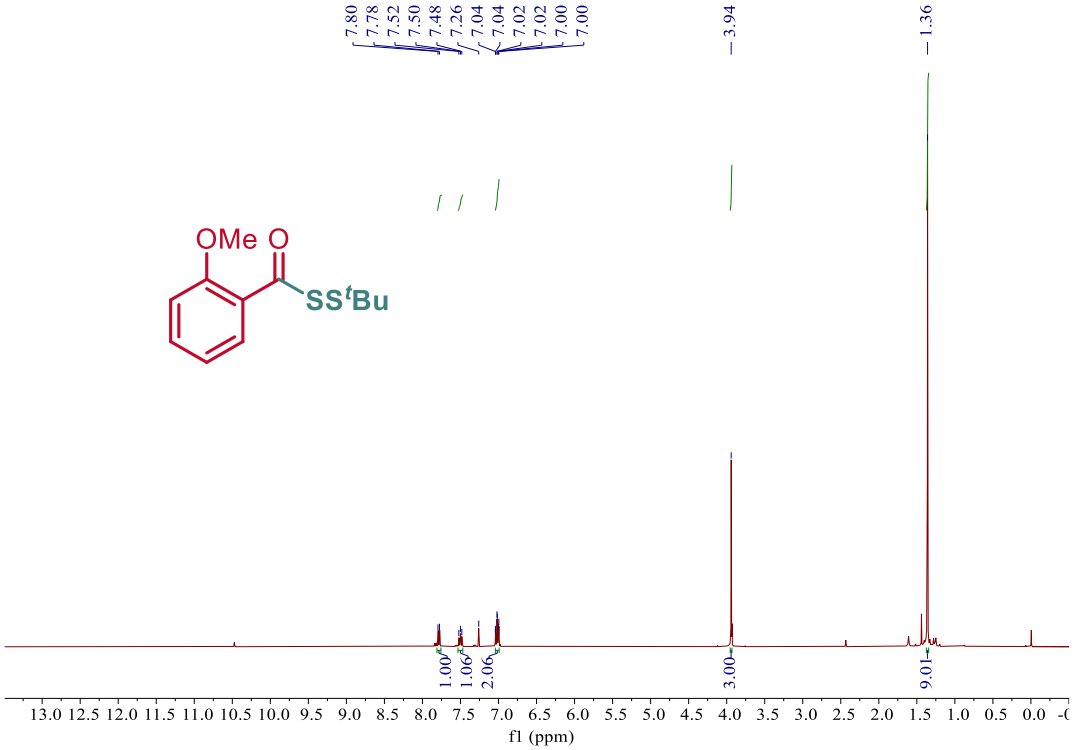
^{1}H NMR Spectrum of *SS*-(*tert*-Butyl) 2-methylbenzo(dithioperoxoate) 3r



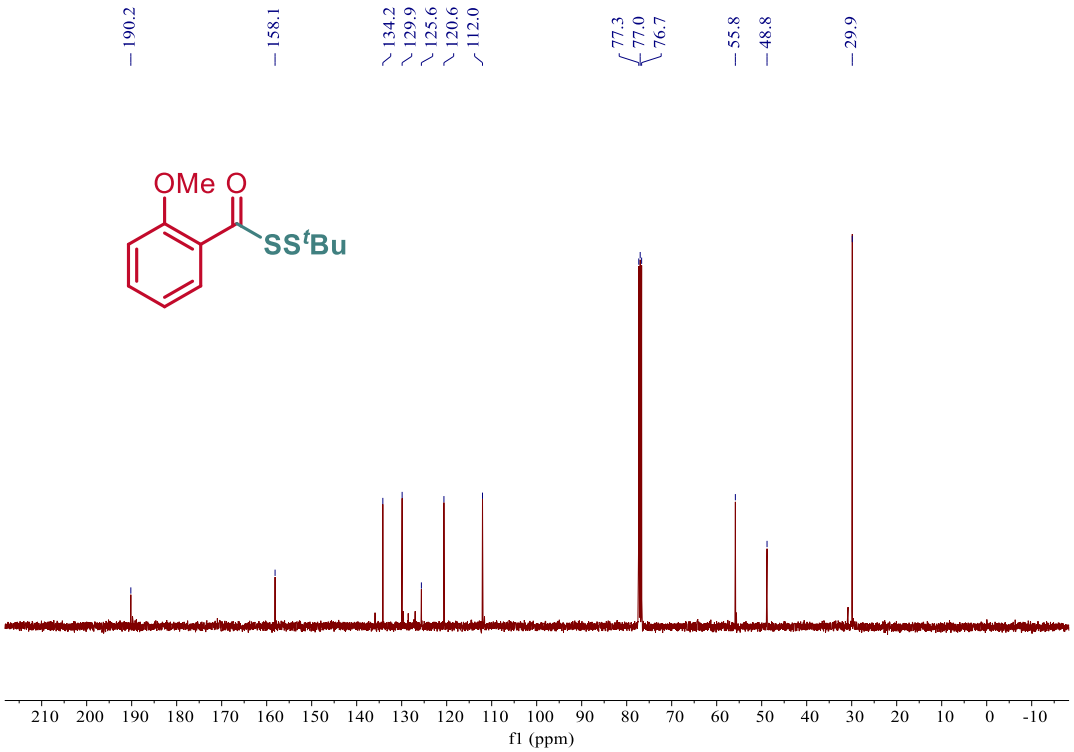
^{13}C NMR Spectrum of *SS*-(*tert*-Butyl) 2-methylbenzo(dithioperoxoate) 3r



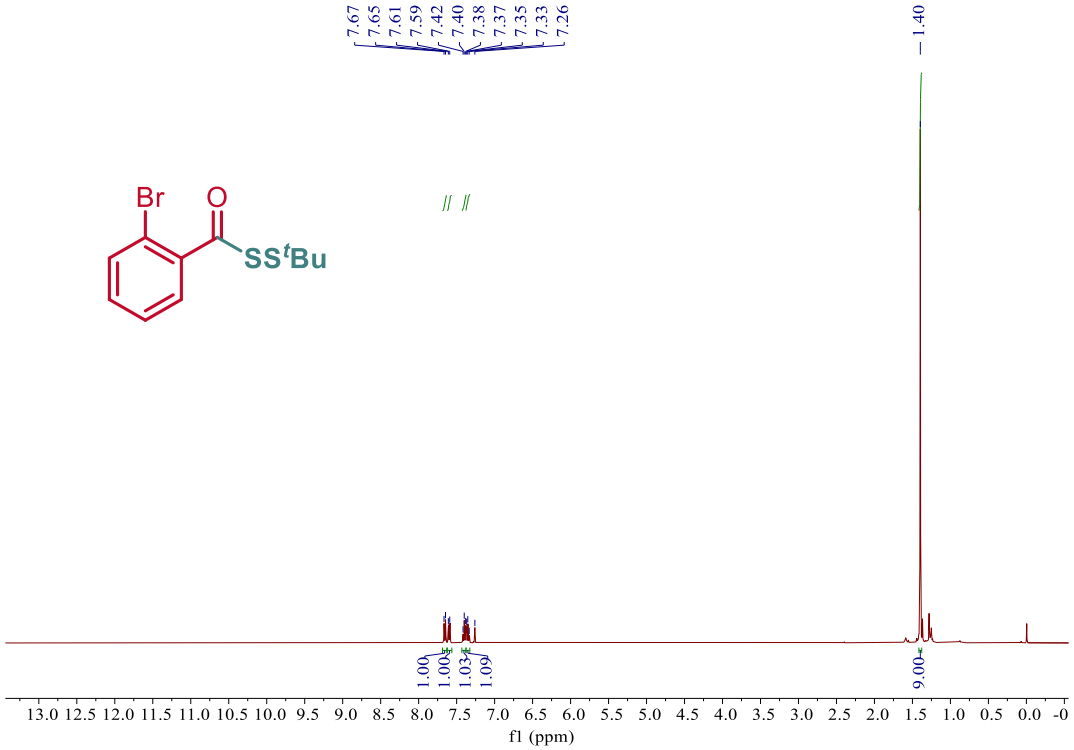
^{1}H NMR Spectrum of *SS*-(*tert*-Butyl) 2-methoxybenzo(dithioperoxoate) 3s



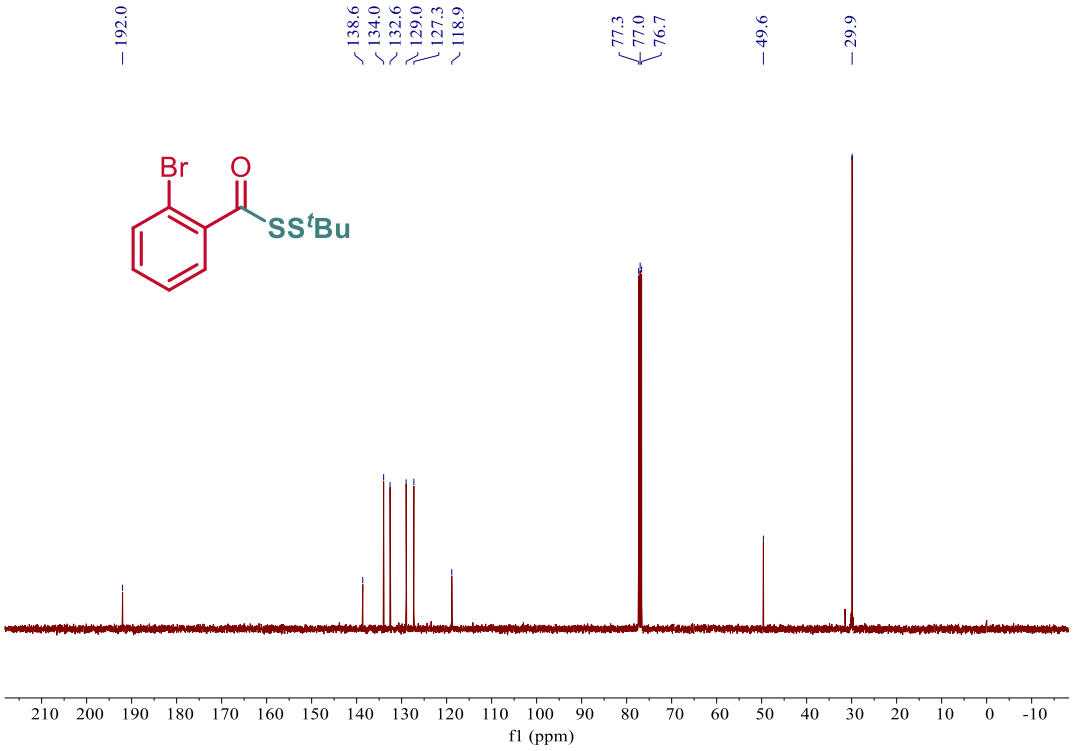
^{13}C NMR Spectrum of *SS*-(*tert*-Butyl) 2-methoxybenzo(dithioperoxoate) 3s



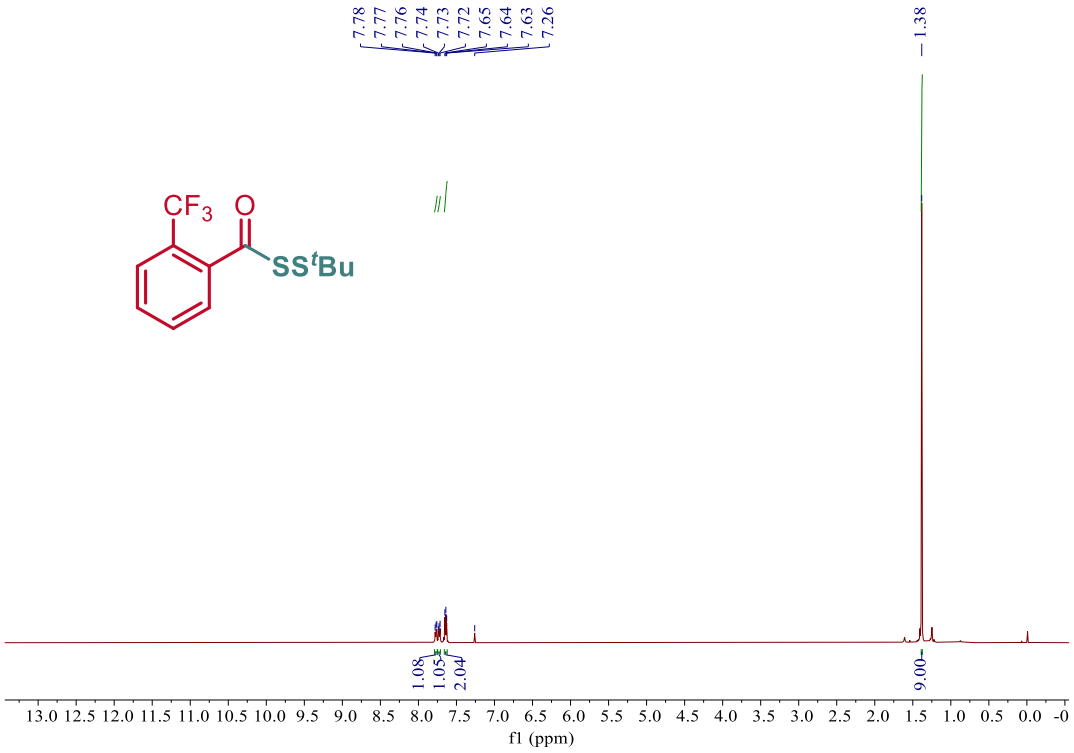
^{1}H NMR Spectrum of *SS*-(*tert*-Butyl) 2-bromobenzo(dithioperoxoate) 3t



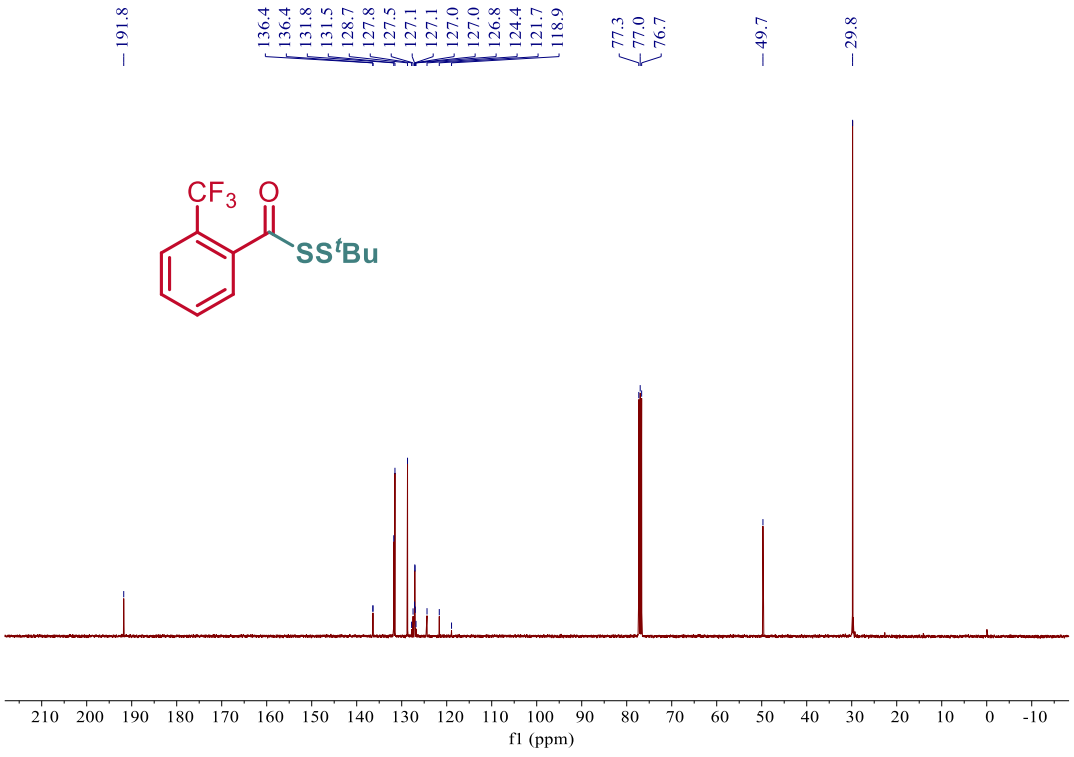
^{13}C NMR Spectrum of *SS*-(*tert*-Butyl) 2-bromobenzo(dithioperoxoate) 3t



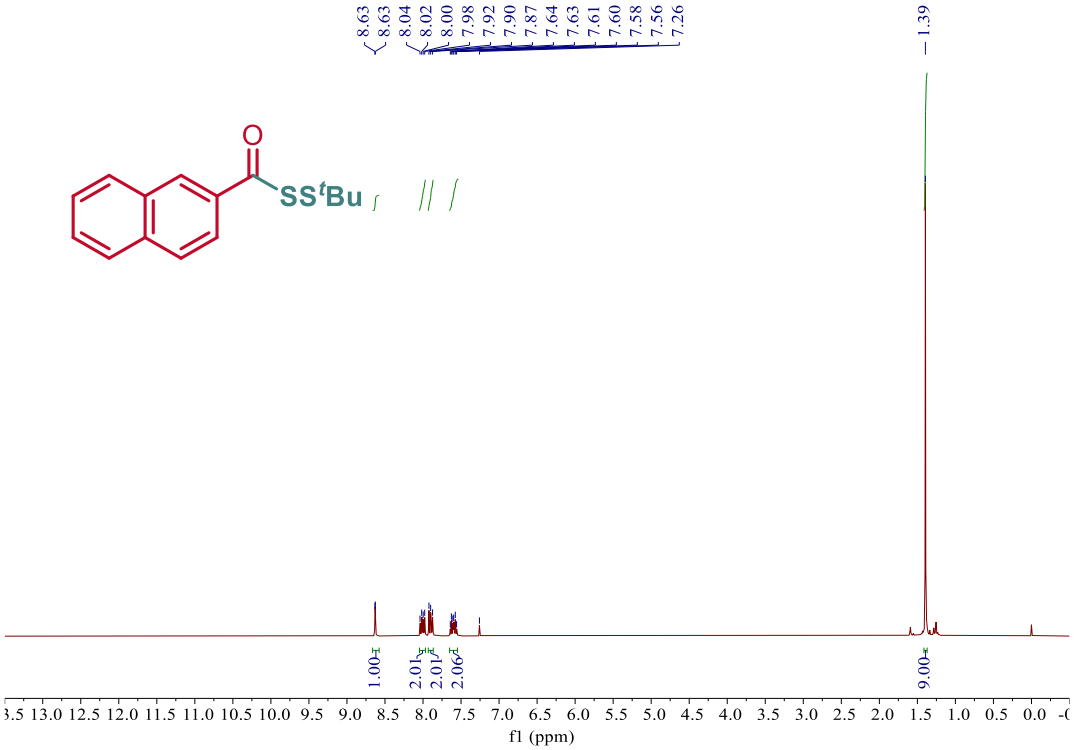
^{1}H NMR Spectrum of *SS*-(*tert*-Butyl) 2-(trifluoromethyl)benzo(dithioperoxoate) 3u



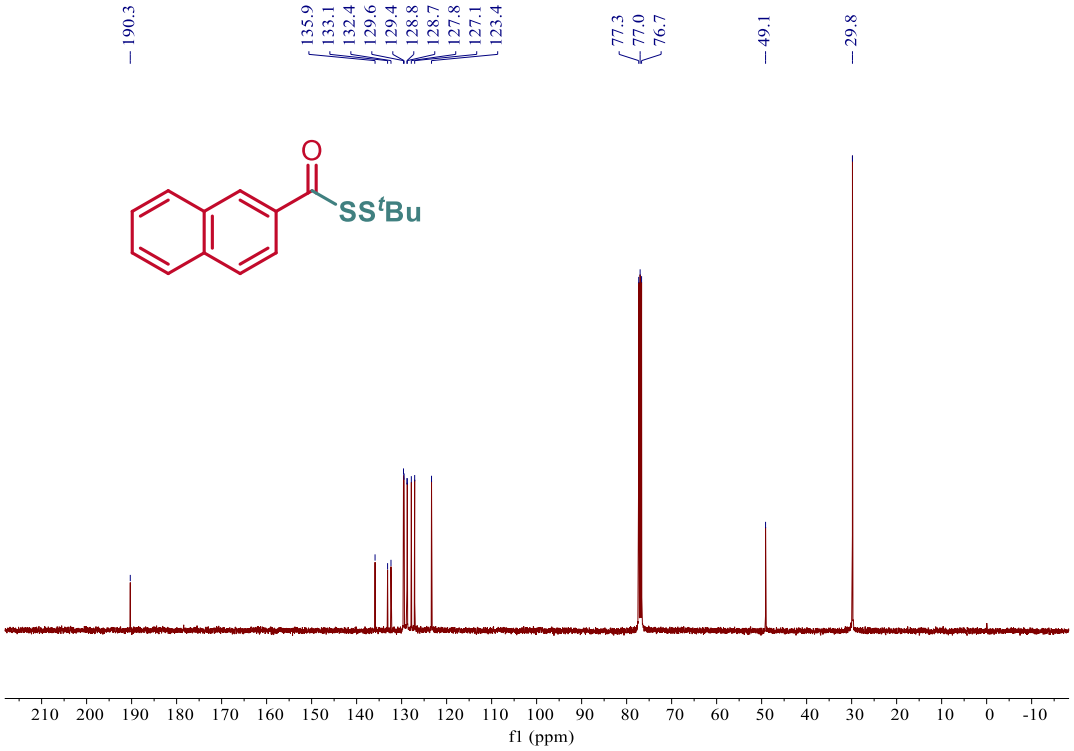
^{13}C NMR Spectrum of *SS*-(*tert*-Butyl) 2-(trifluoromethyl)benzo(dithioperoxoate) 3u



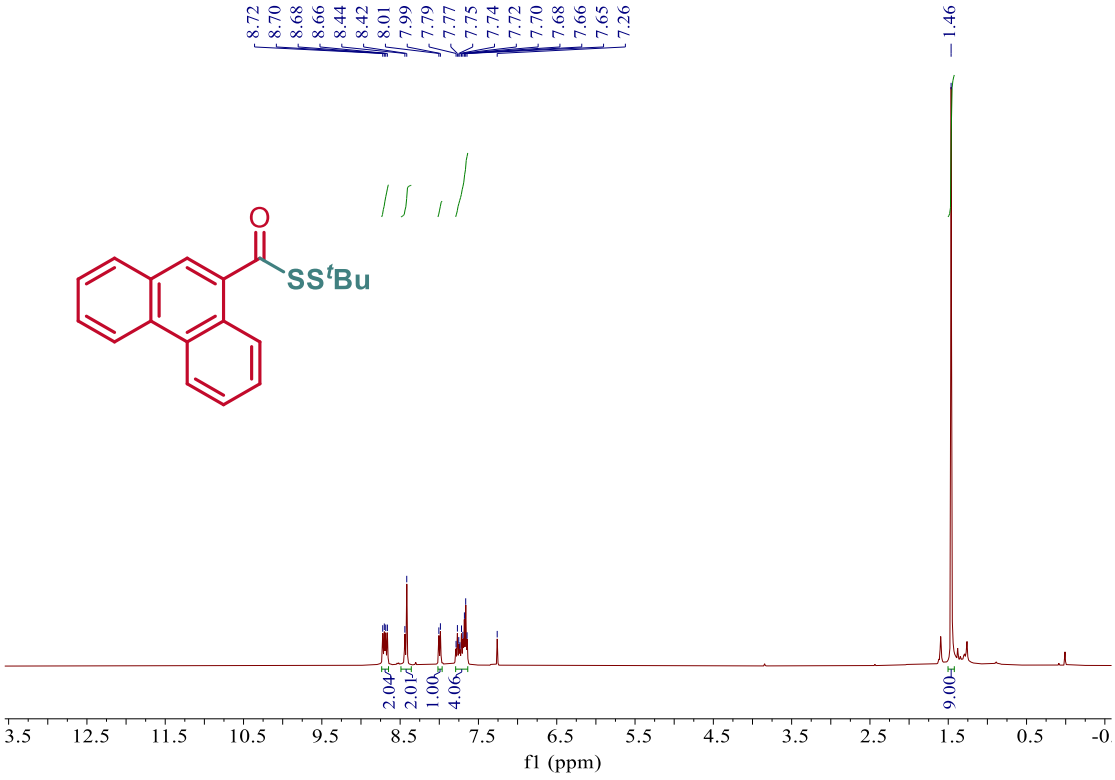
^{1}H NMR Spectrum of *SS*-(*tert*-Butyl) naphthalene-2-carbo(dithioperoxoate) 3v



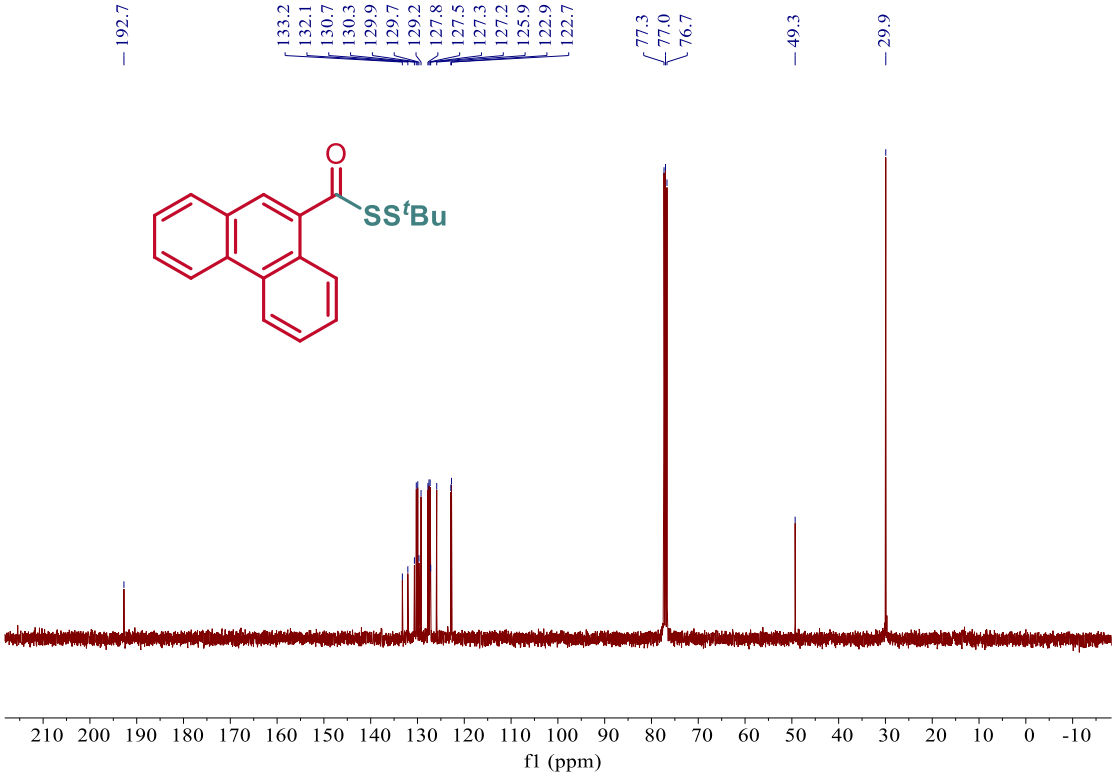
^{13}C NMR Spectrum of *SS*-(*tert*-Butyl) naphthalene-2-carbo(dithioperoxoate) 3v



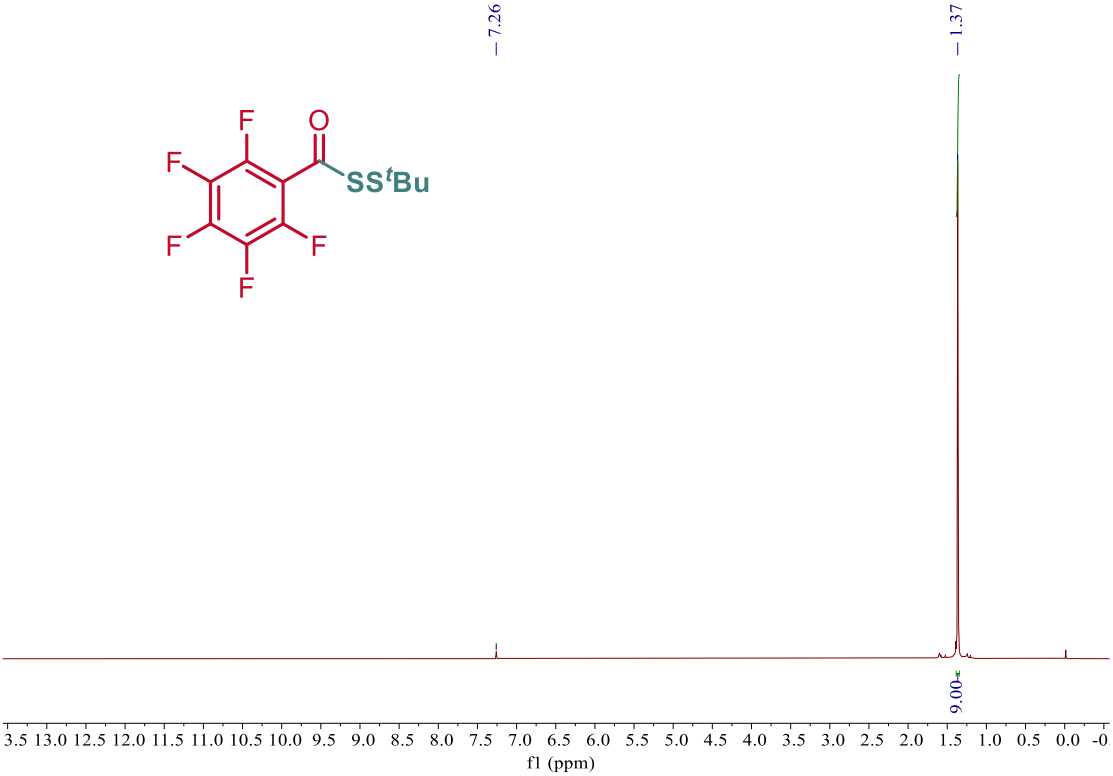
^{1}H NMR Spectrum of *SS*-(*tert*-Butyl) phenanthrene-9-carbo(dithioperoxoate) 3w



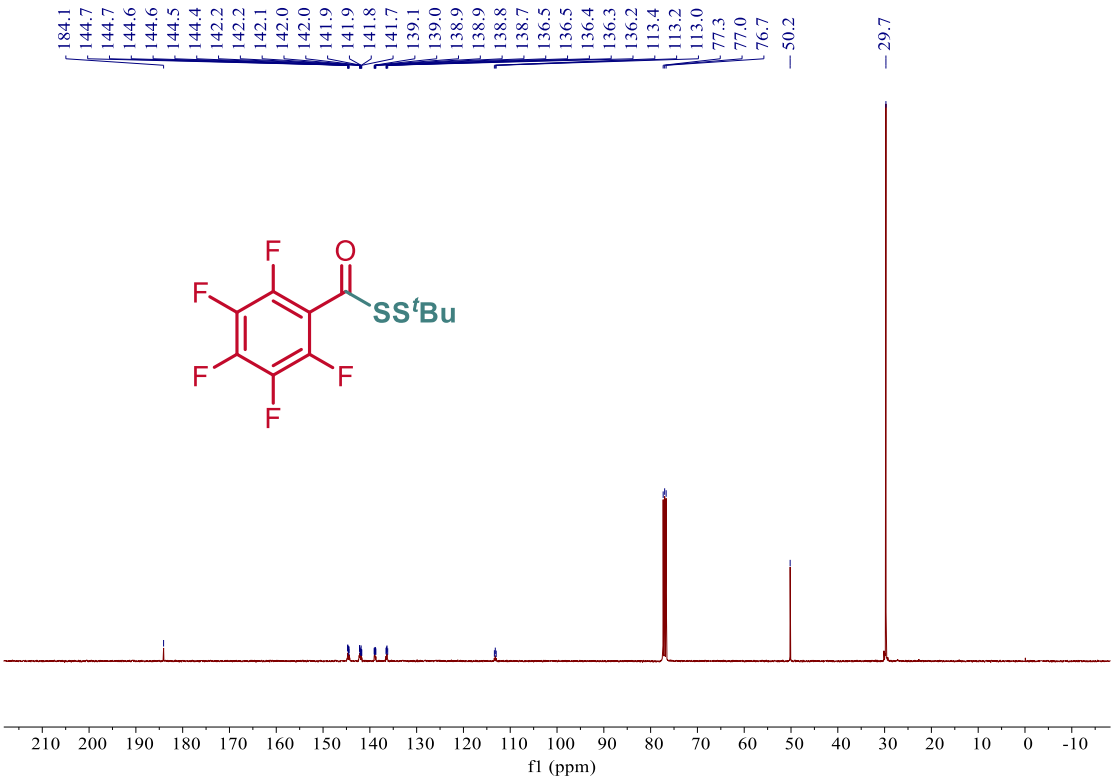
^{13}C NMR Spectrum of *SS*-(*tert*-Butyl) phenanthrene-9-carbo(dithioperoxoate) 3w



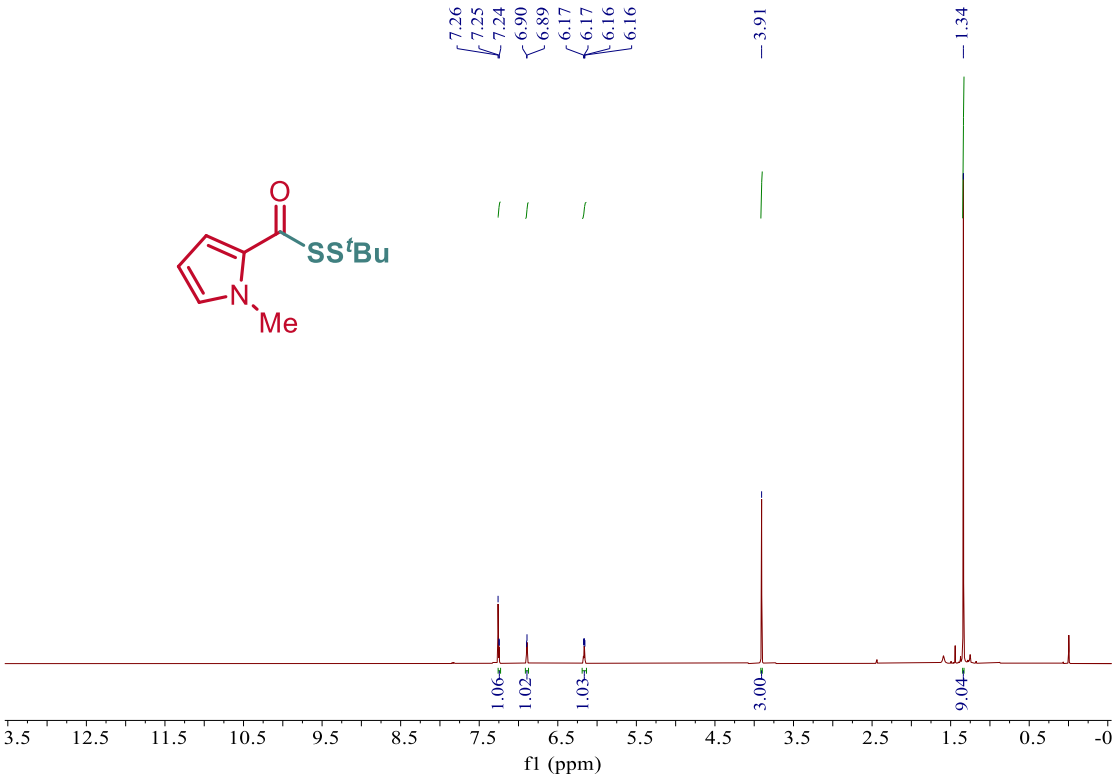
^{1}H NMR Spectrum of *SS*-(*tert*-Butyl) 2,3,4,5,6-pentafluorobenzo(dithioperoxoate) 3x



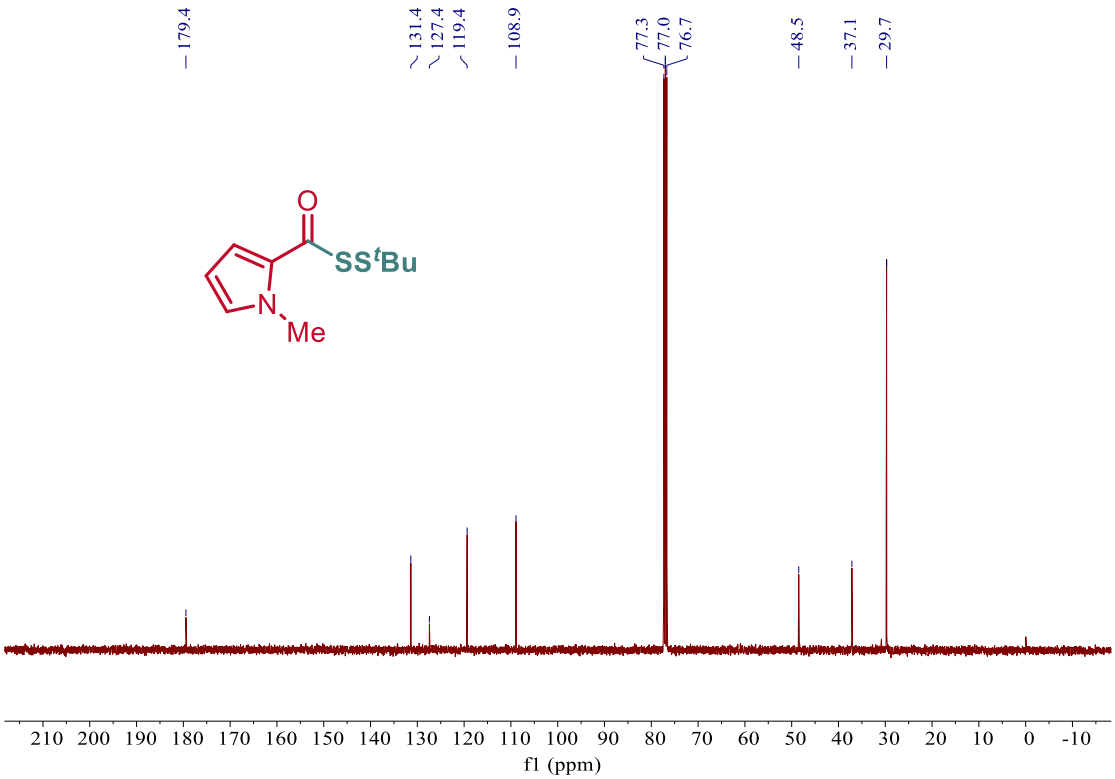
^{13}C NMR Spectrum of *SS*-(*tert*-Butyl) 2,3,4,5,6-pentafluorobenzo(dithioperoxoate) 3x



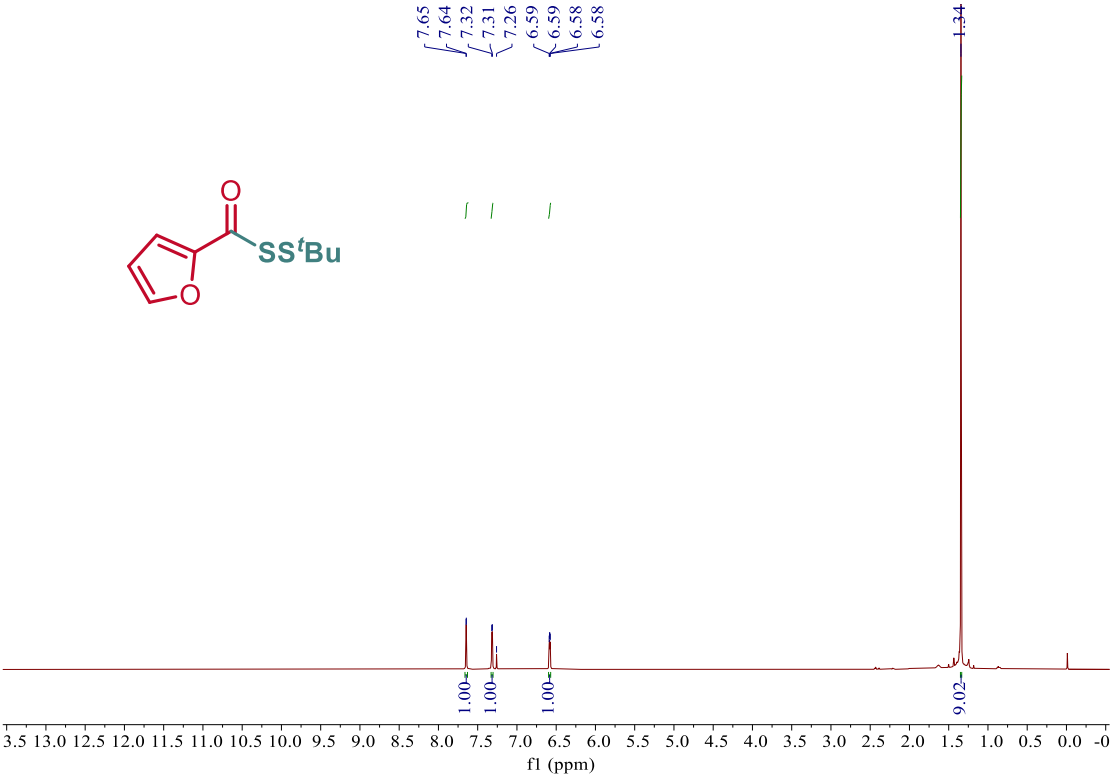
^{1}H NMR Spectrum of *SS*-(*tert*-Butyl) 1-methyl-1*H*-pyrrole-2-carbo(dithioperoxoate) 3y



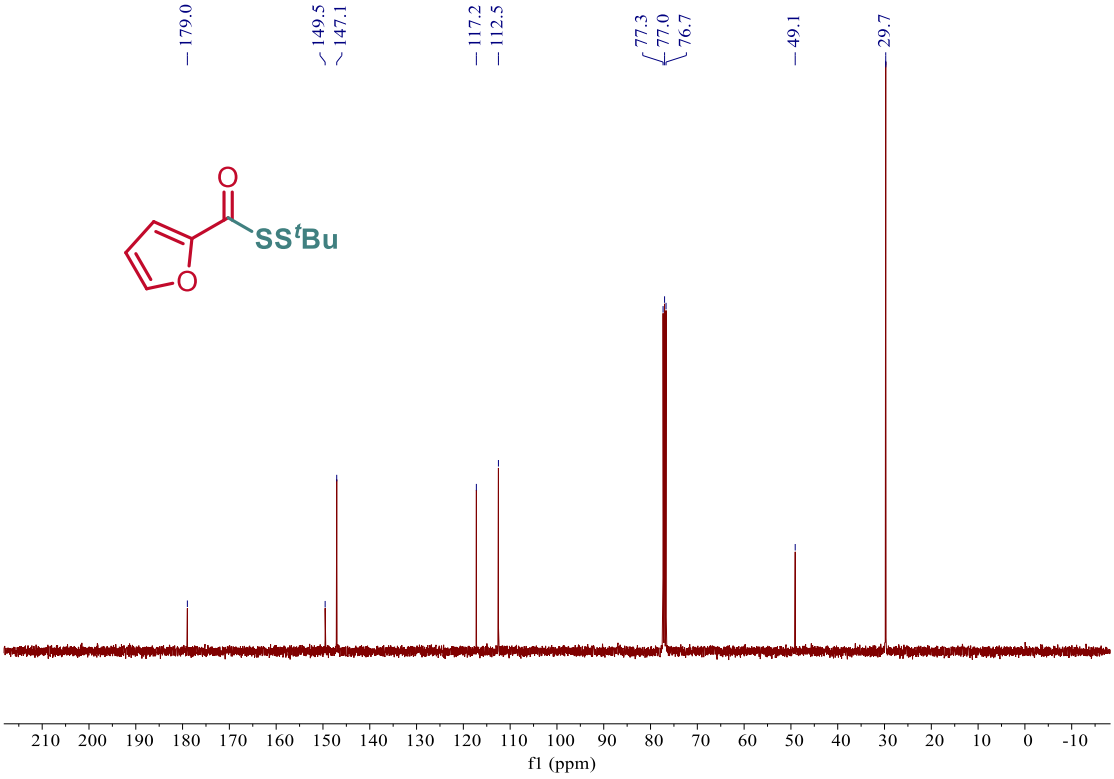
^{13}C NMR Spectrum of *SS*-(*tert*-Butyl) 1-methyl-1*H*-pyrrole-2-carbo(dithioperoxoate) 3y



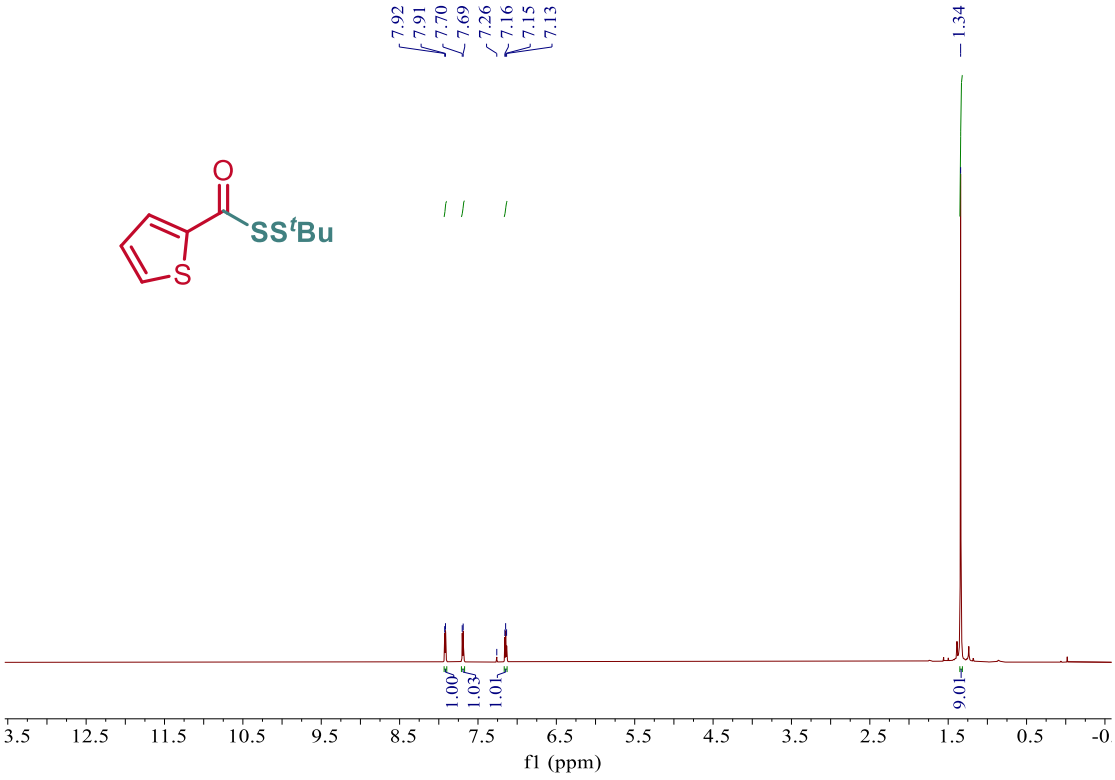
^{1}H NMR Spectrum of *SS*-(*tert*-Butyl) furan-2-carbo(dithioperoxoate) 3z



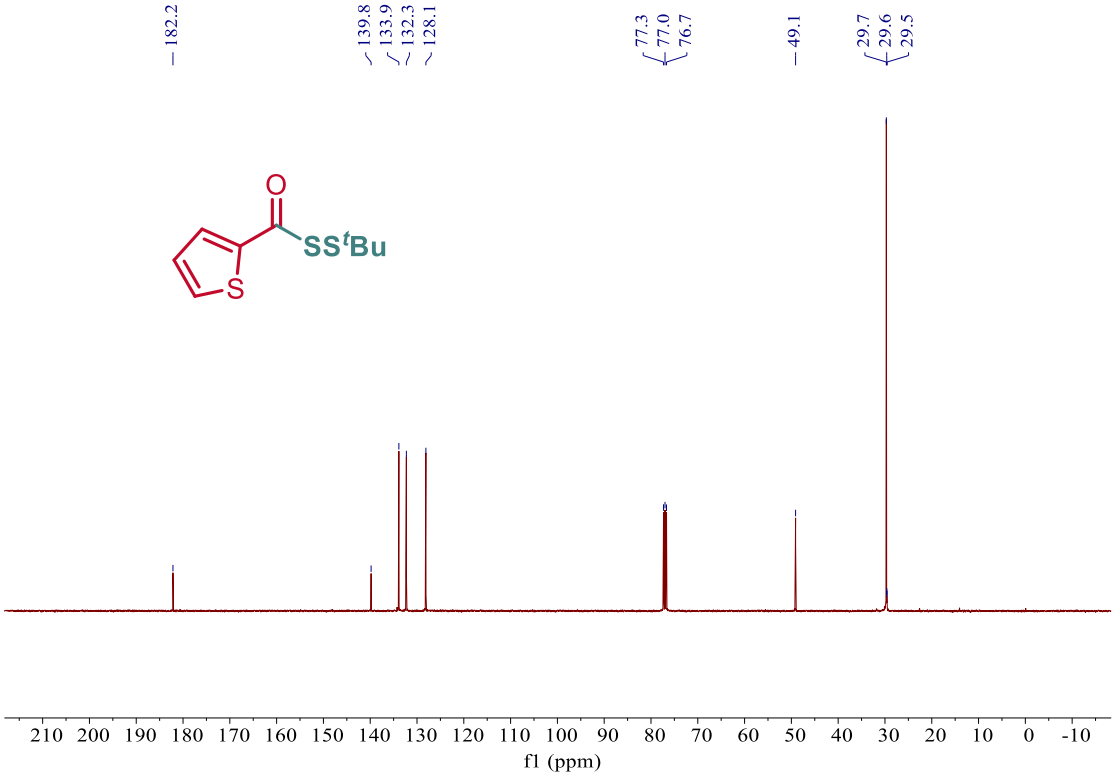
^{13}C NMR Spectrum of *SS*-(*tert*-Butyl) furan-2-carbo(dithioperoxoate) 3z



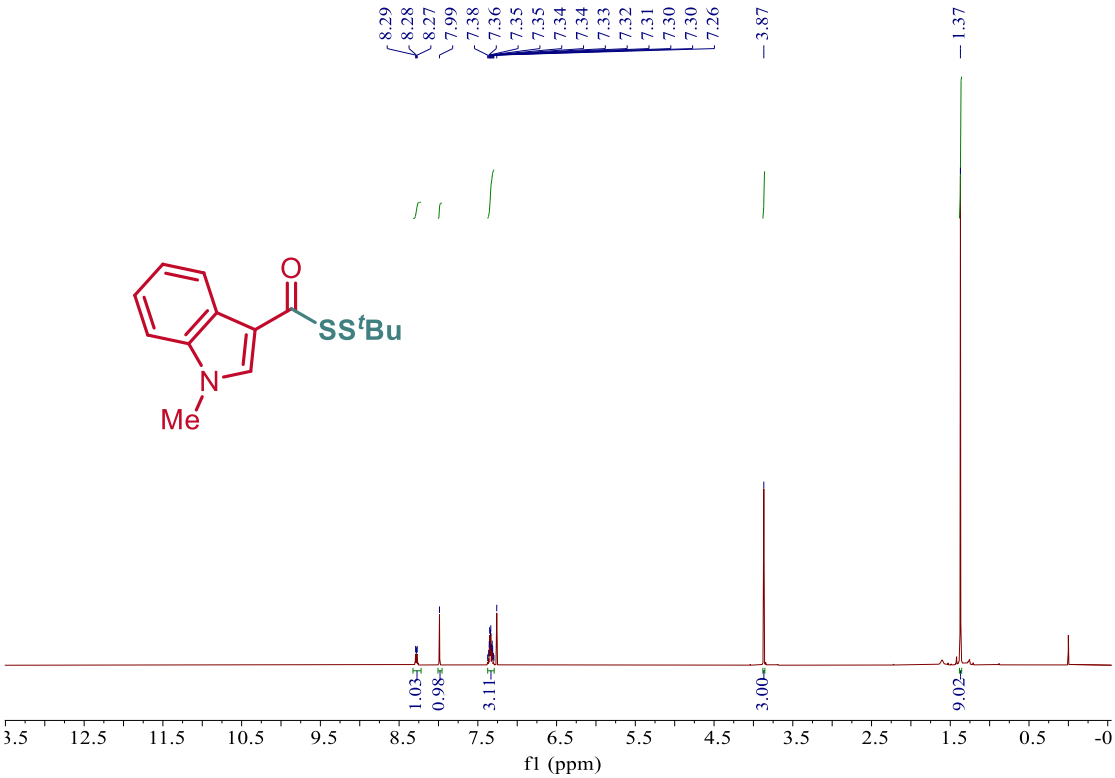
^{1}H NMR Spectrum of *SS*-(*tert*-Butyl) thiophene-2-carbo(dithioperoxoate) 3aa



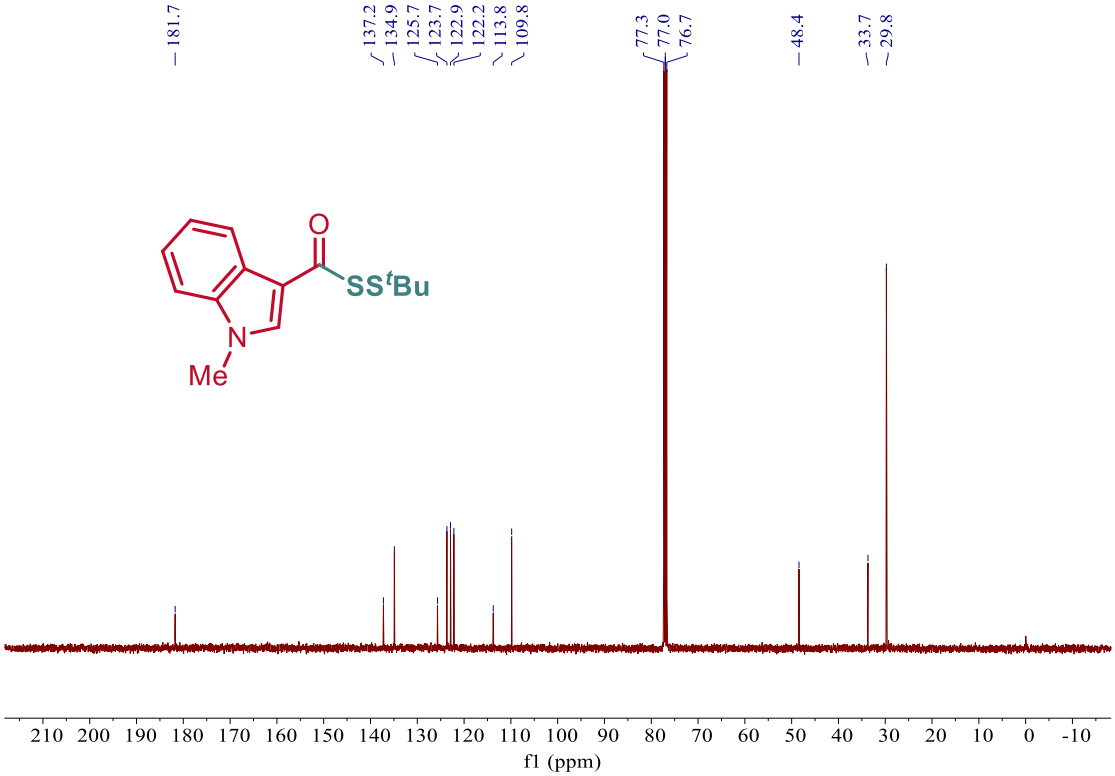
^{13}C NMR Spectrum of *SS*-(*tert*-Butyl) thiophene-2-carbo(dithioperoxoate) 3aa



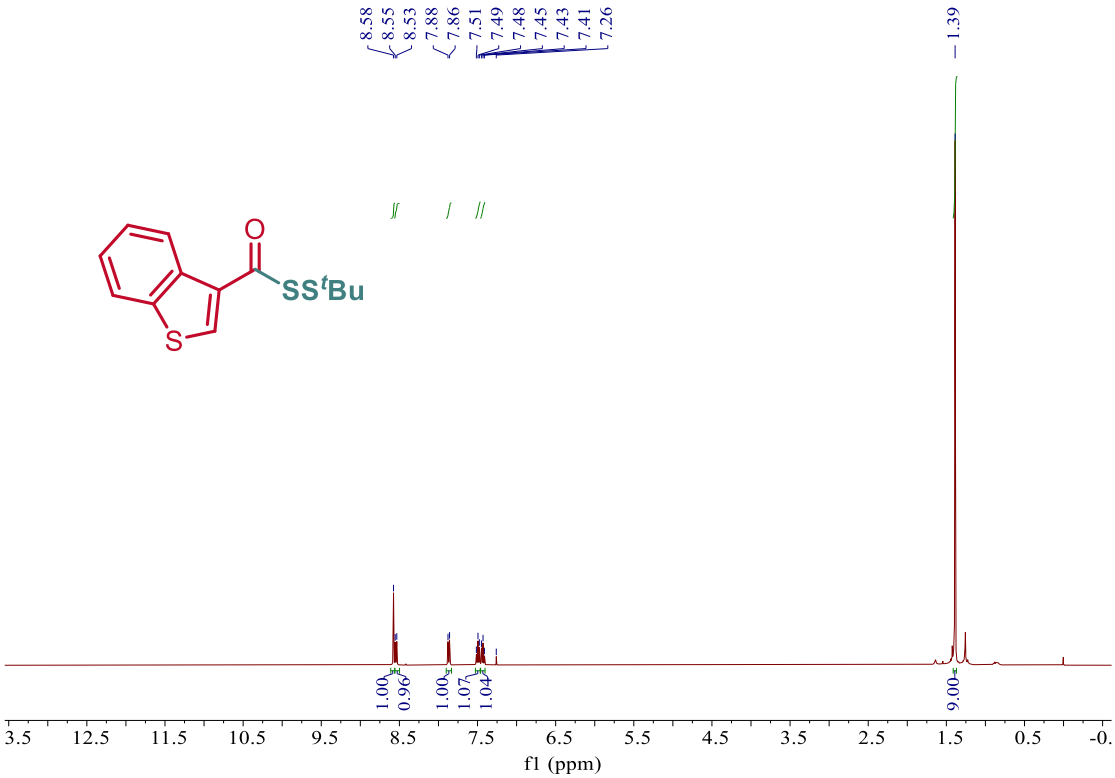
^{1}H NMR Spectrum of *SS*-(*tert*-Butyl) 1-methyl-1*H*-indole-3-carbo(dithioperoxo ate) 3ab



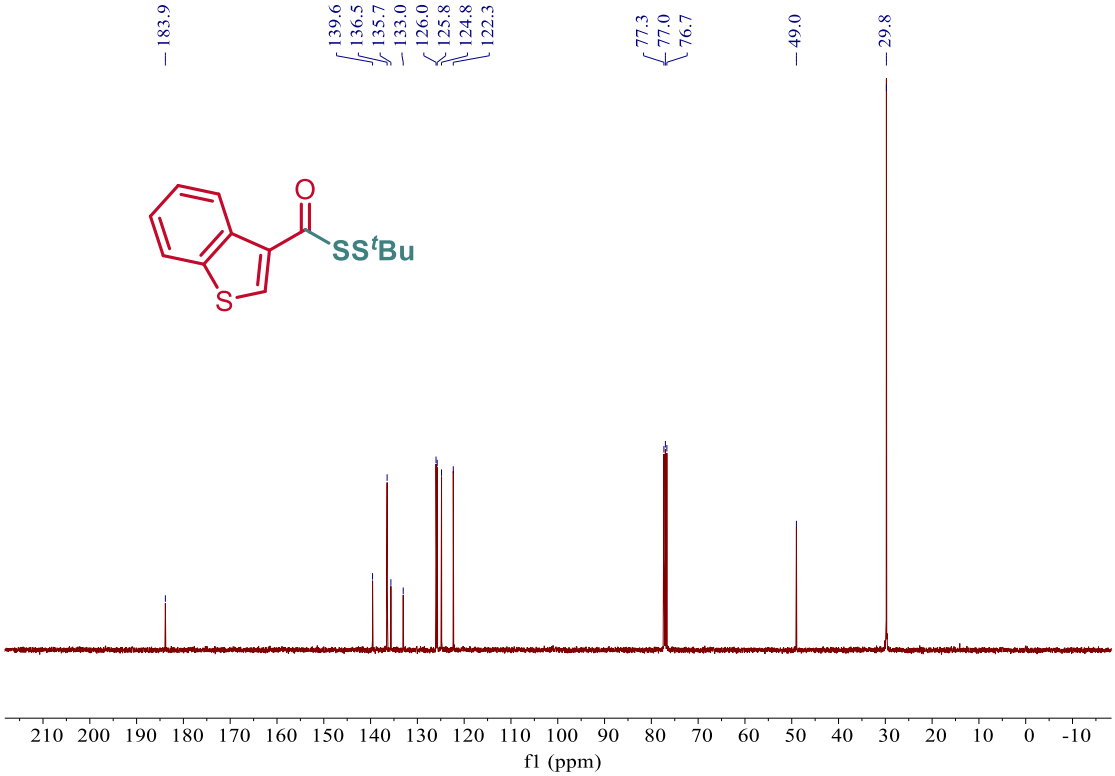
^{13}C NMR Spectrum of *SS*-(*tert*-Butyl) 1-methyl-1*H*-indole-3-carbo (dithioperoxo ate) 3ab



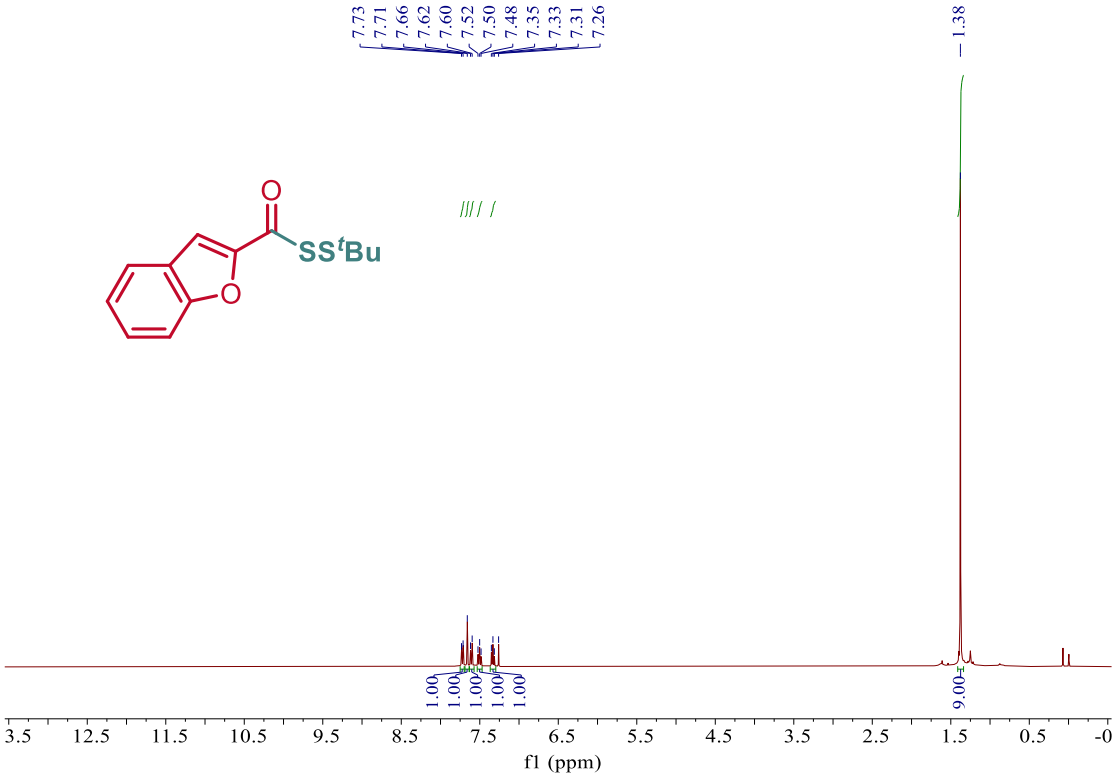
^{1}H NMR Spectrum of *SS*-(*tert*-Butyl) benzo[*b*]thiophene-3-carbo(dithioperoxoate) 3ac



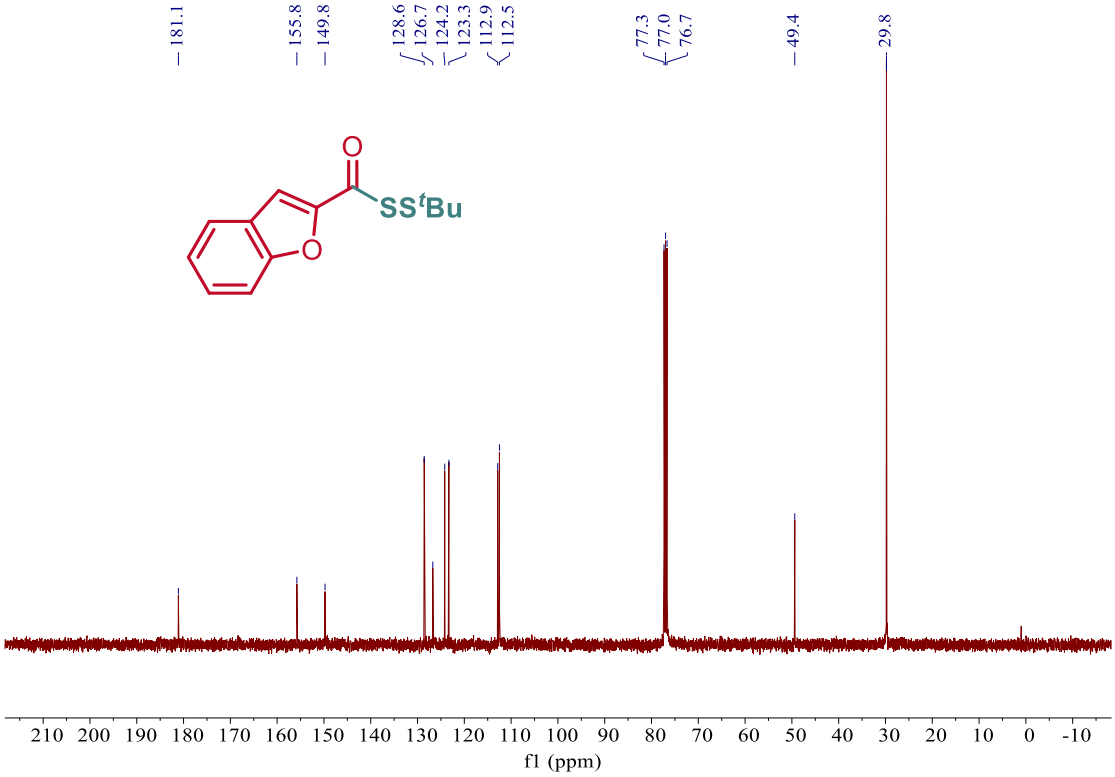
^{13}C NMR Spectrum of *SS*-(*tert*-Butyl) benzo[*b*]thiophene-3-carbo(dithioperoxoate) 3ac



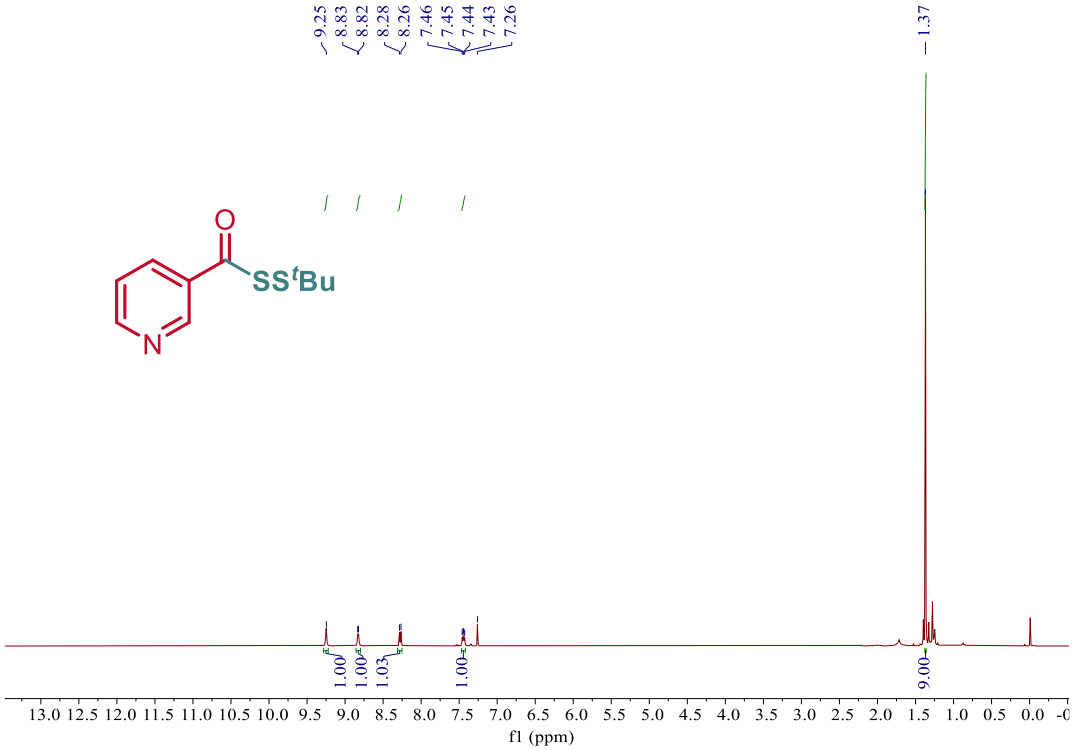
^{1}H NMR Spectrum of *SS*-(*tert*-Butyl) benzofuran-2-carbo(dithioperoxoate) 3ad



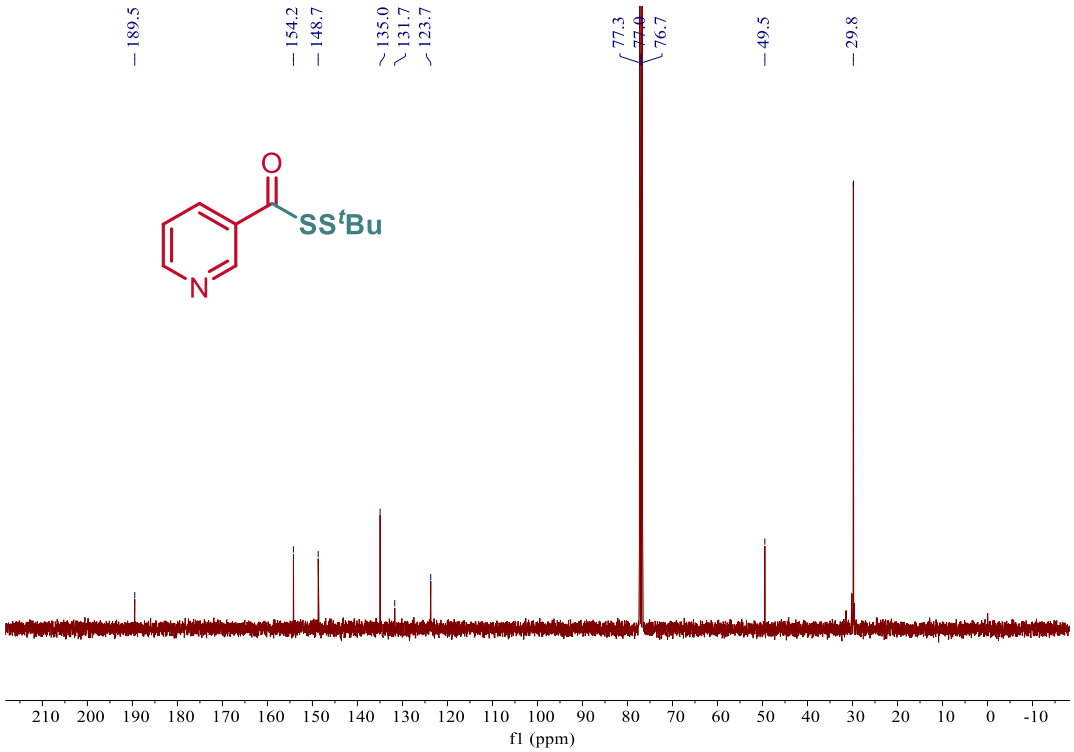
^{13}C NMR Spectrum of *SS*-(*tert*-Butyl) benzofuran-2-carbo(dithioperoxoate) 3ad



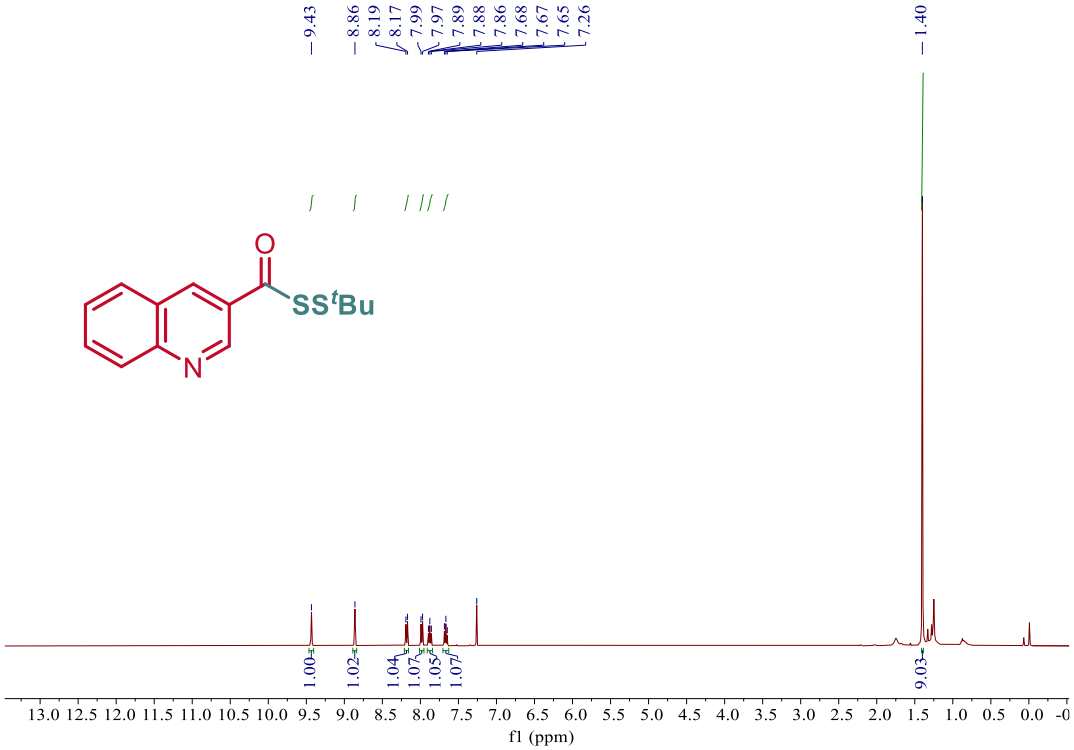
^{1}H NMR Spectrum of *SS*-(*tert*-Butyl) pyridine-3-carbo(dithioperoxoate) 3ae



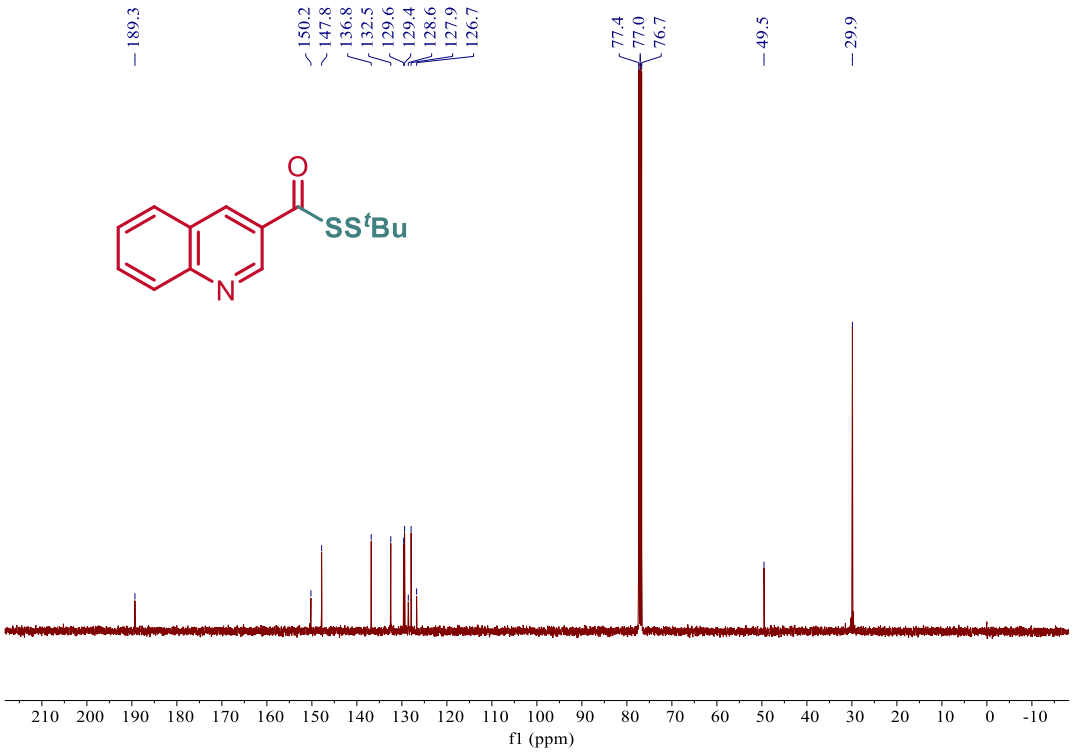
^{13}C NMR Spectrum of *SS*-(*tert*-Butyl) pyridine-3-carbo(dithioperoxoate) 3ae



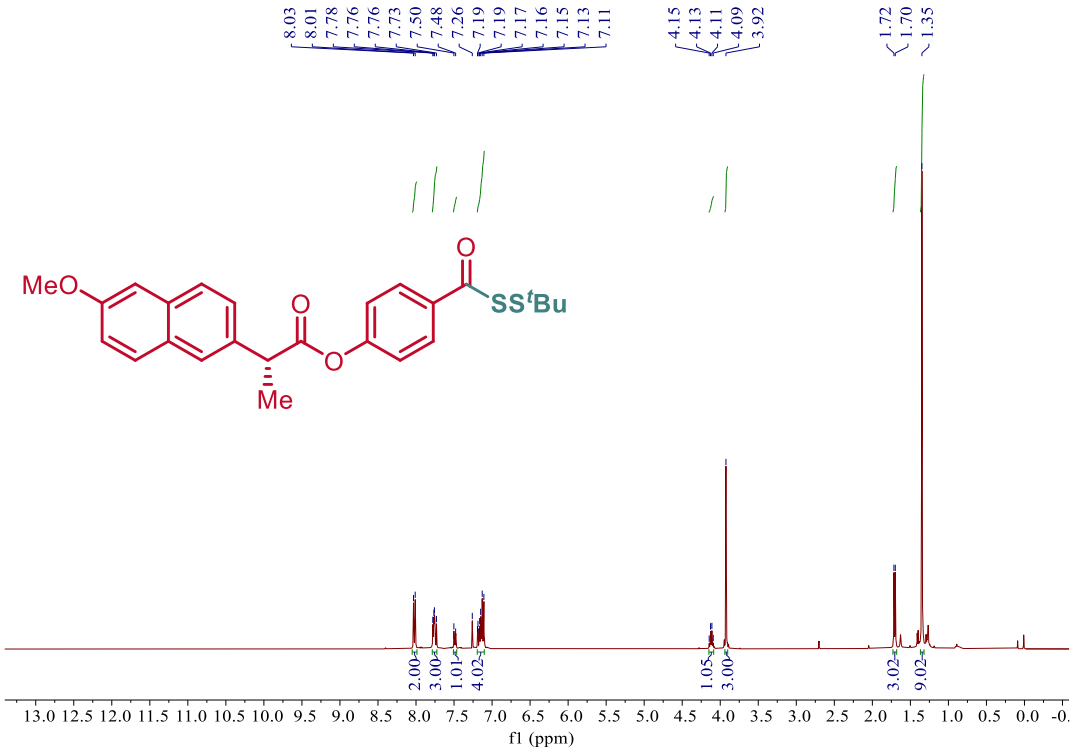
^{1}H NMR Spectrum of *SS*-(*tert*-Butyl) quinoline-3-carbo(dithioperoxoate) 3af



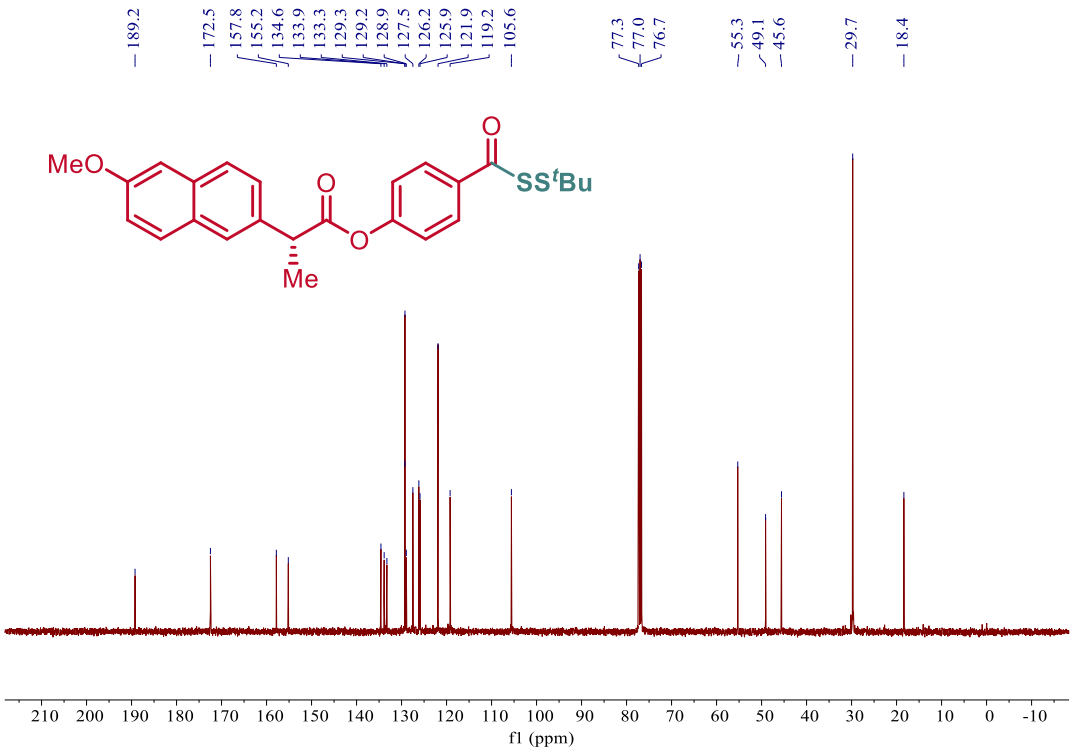
^{13}C NMR Spectrum of *SS*-(*tert*-Butyl) quinoline-3-carbo(dithioperoxoate) 3af



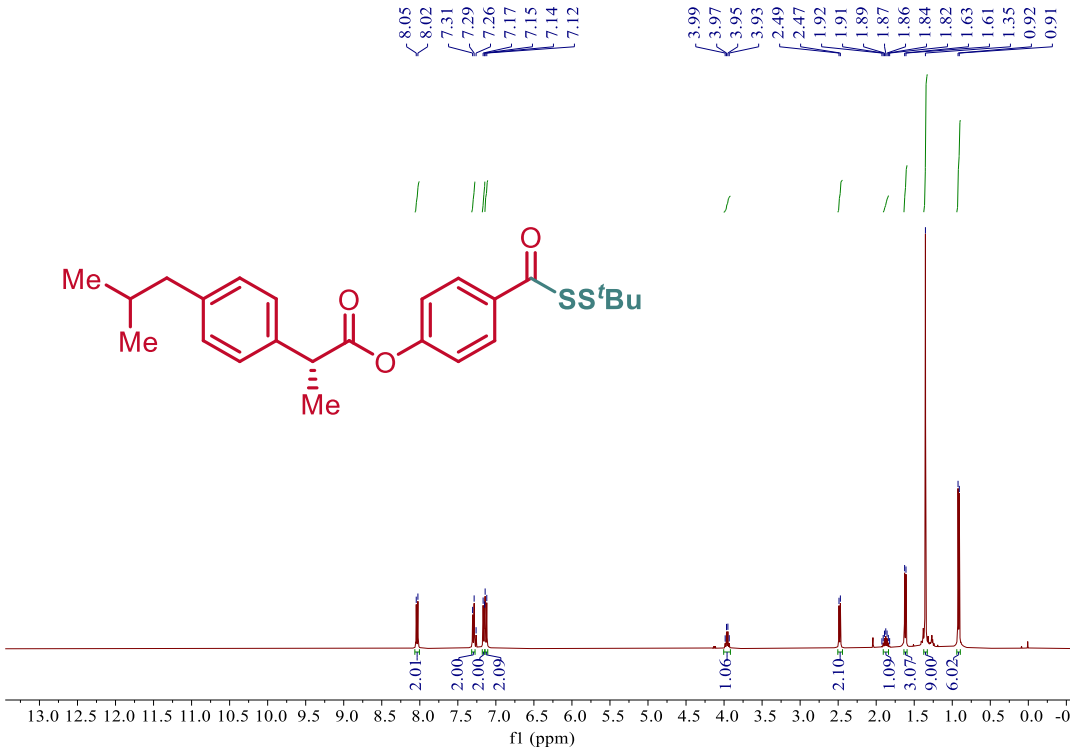
^{1}H NMR Spectrum of 4-(*tert*-Butyldisulfannecarbonyl)phenyl (*R*)-2-(6-methoxy-naphthalen-2-yl)propanoate 3ag



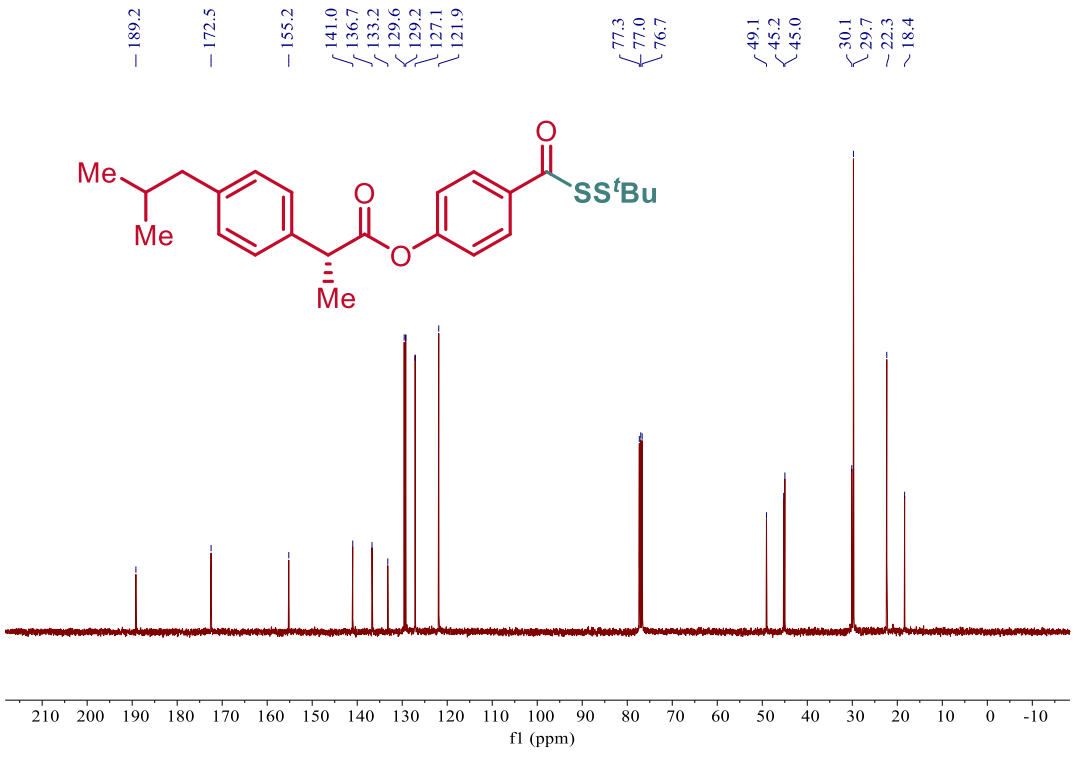
^{13}C NMR Spectrum of 4-(*tert*-Butyldisulfannecarbonyl)phenyl (*R*)-2-(6-methoxy-naphthalen-2-yl)propanoate 3ag



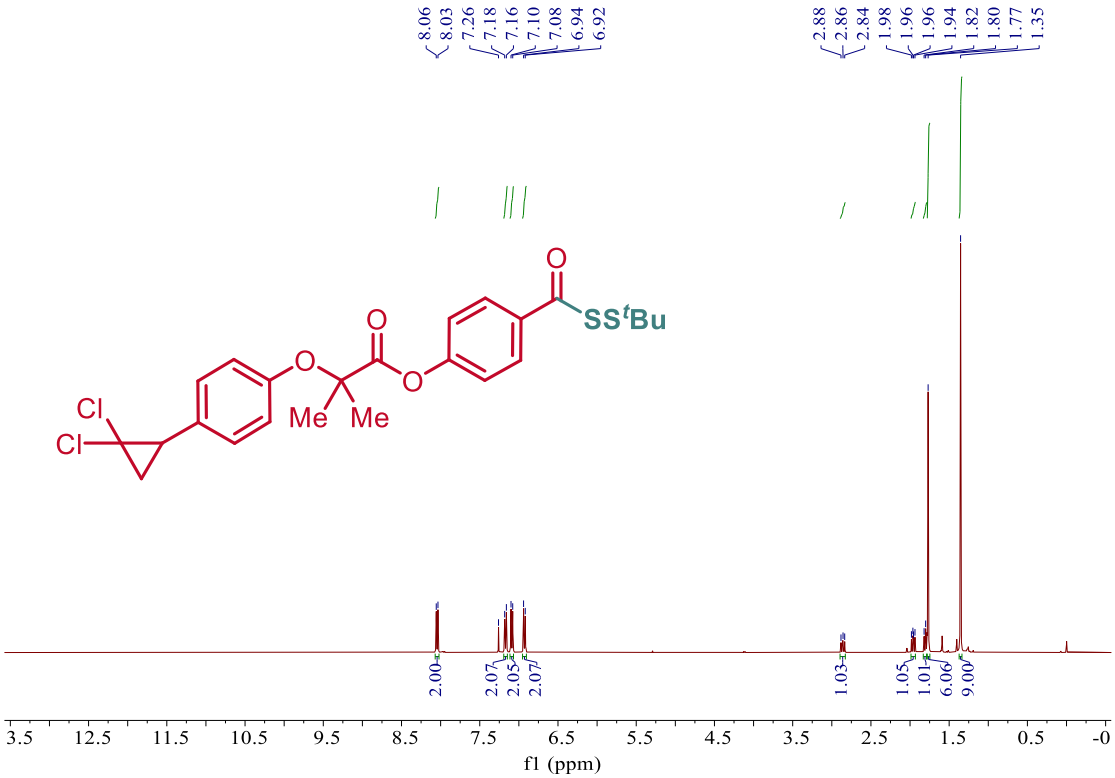
^{1}H NMR Spectrum of 4-(*tert*-Butyldisulfannecarbonyl)phenyl (*R*)-2-(4-isobutyl-phenyl)propanoate 3ah



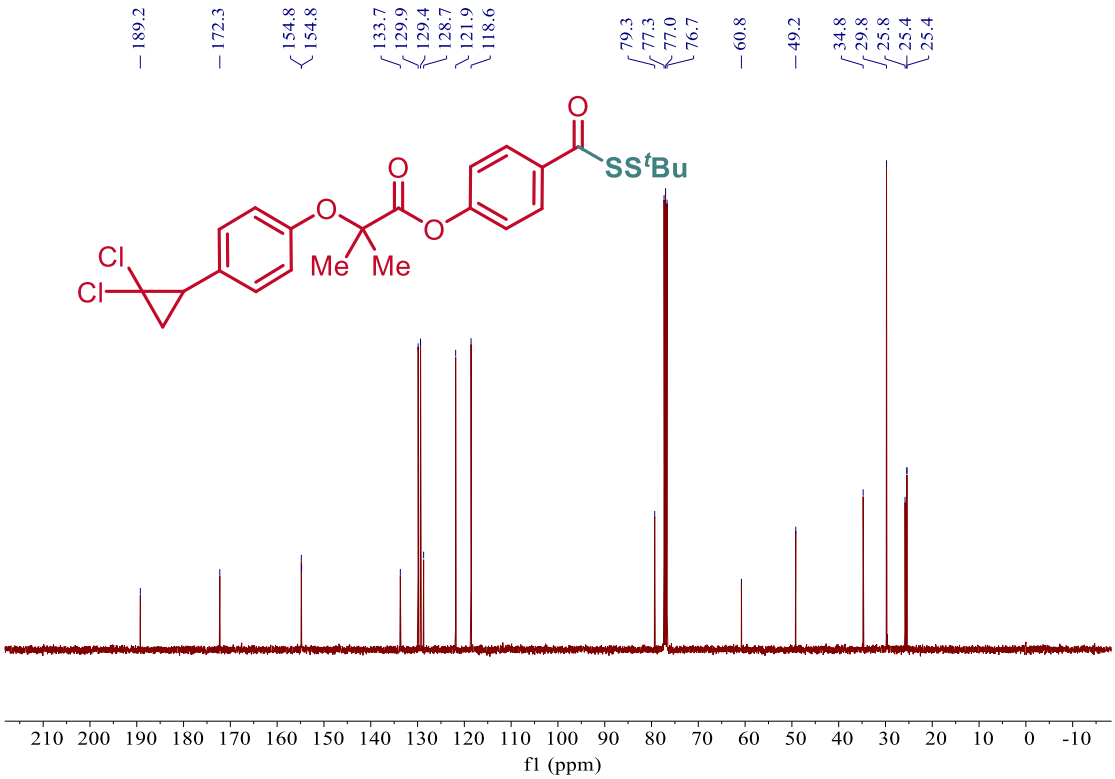
^{13}C NMR Spectrum of 4-(*tert*-Butyldisulfannecarbonyl)phenyl (*R*)-2-(4-isobutyl-phenyl)propanoate 3ah



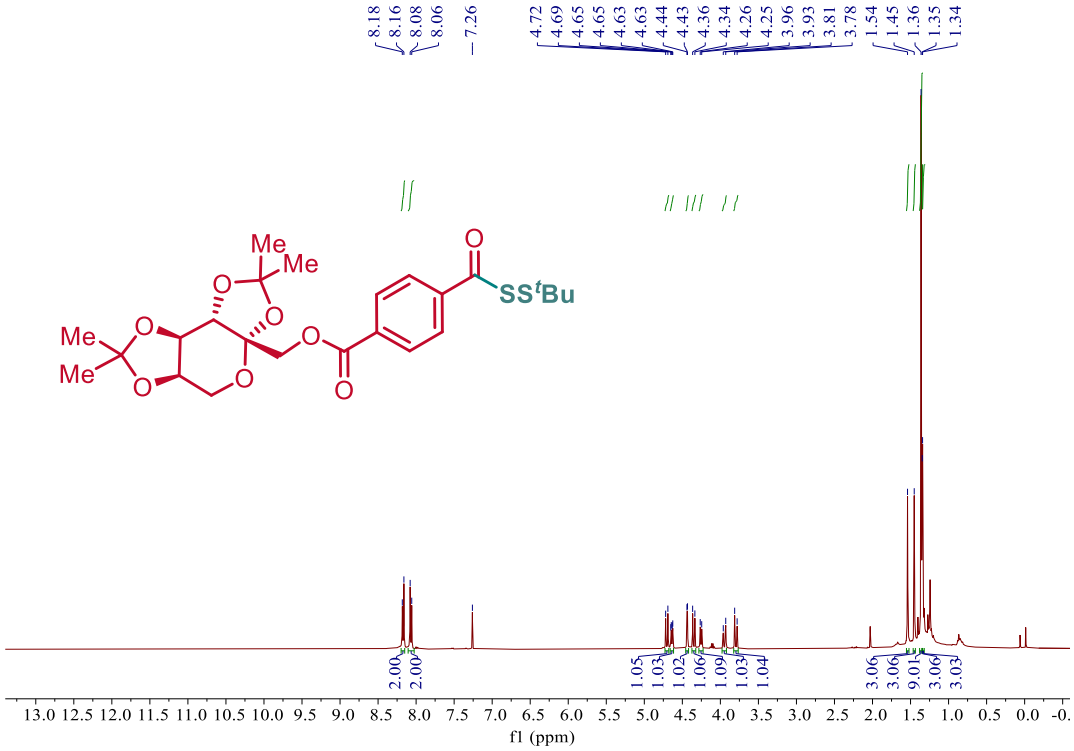
^{1}H NMR Spectrum of 4-(*tert*-Butyldisulfannecarbonyl)phenyl 2-(4-(2,2-dichloro cyclopropyl)phenoxy)-2-methylpropanoate 3ai



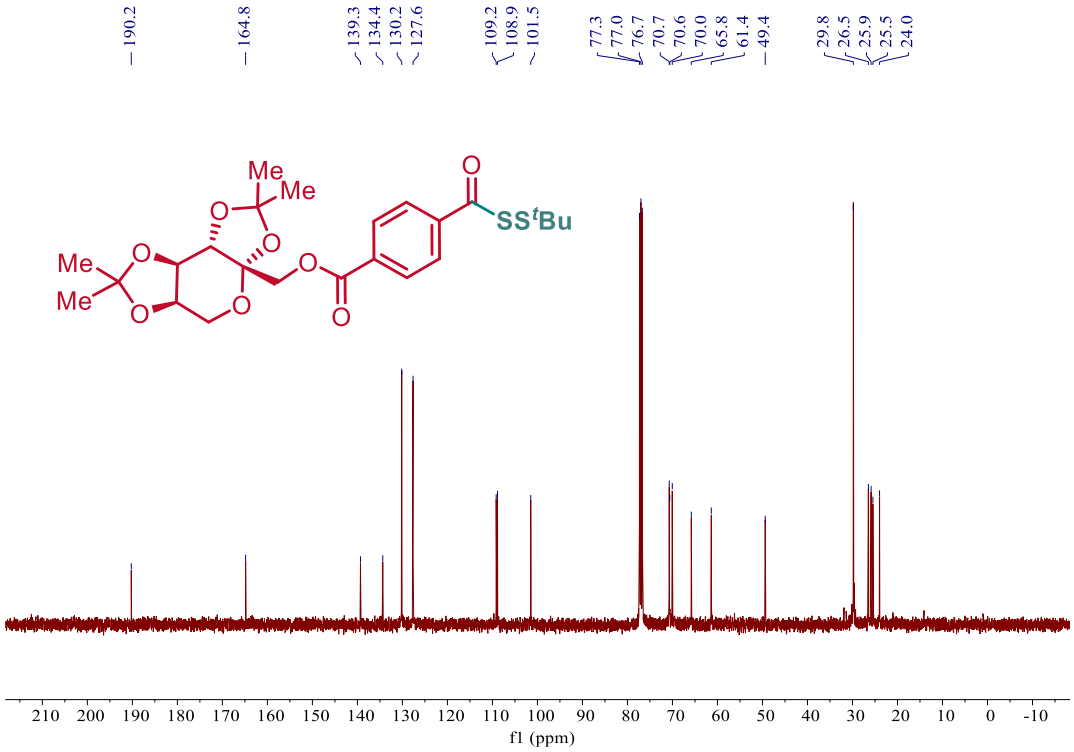
^{13}C NMR Spectrum of 4-(*tert*-Butyldisulfannecarbonyl)phenyl 2-(4-(2,2-dichloro cyclopropyl)phenoxy)-2-methylprop anoate 3ai



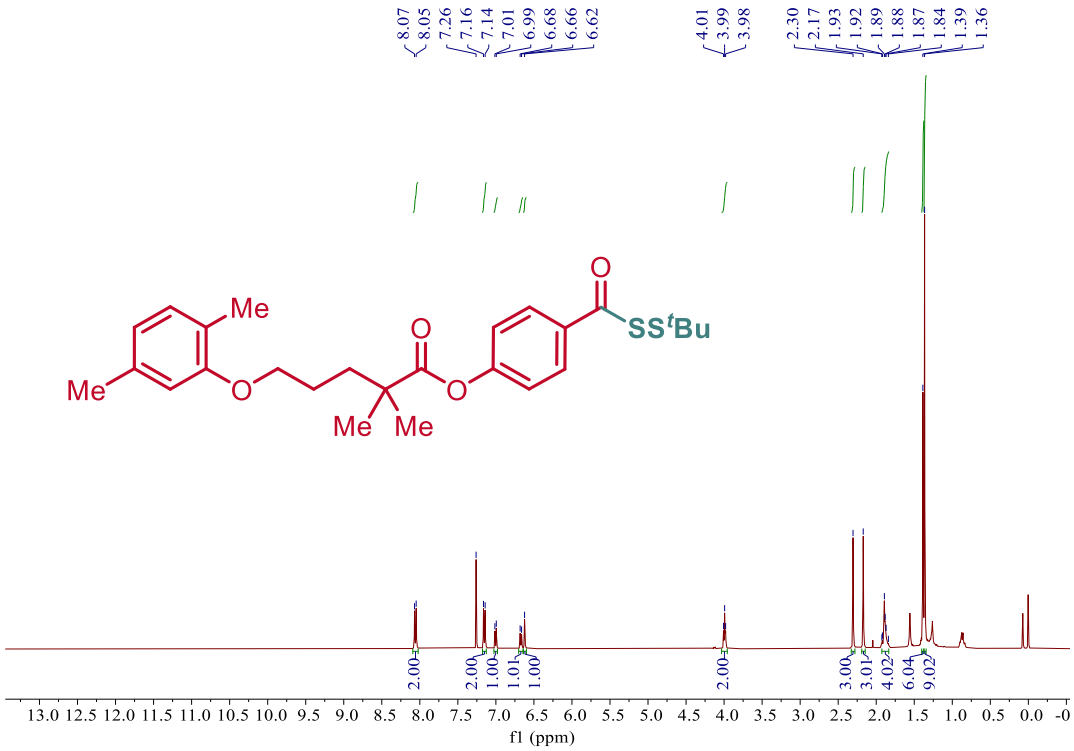
^{1}H NMR Spectrum of ((3a*S*,5a*R*,8a*R*,8*bS*)-2,2,7,7-Tetramethyltetrahydro-3a*H*-bis([1,3]dioxolo)[4,5-*b*:4',5'-*d*]pyran-3a-yl)methyl 4-(*tert*-butyldisulfannecarbonyl) benzoate 3aj



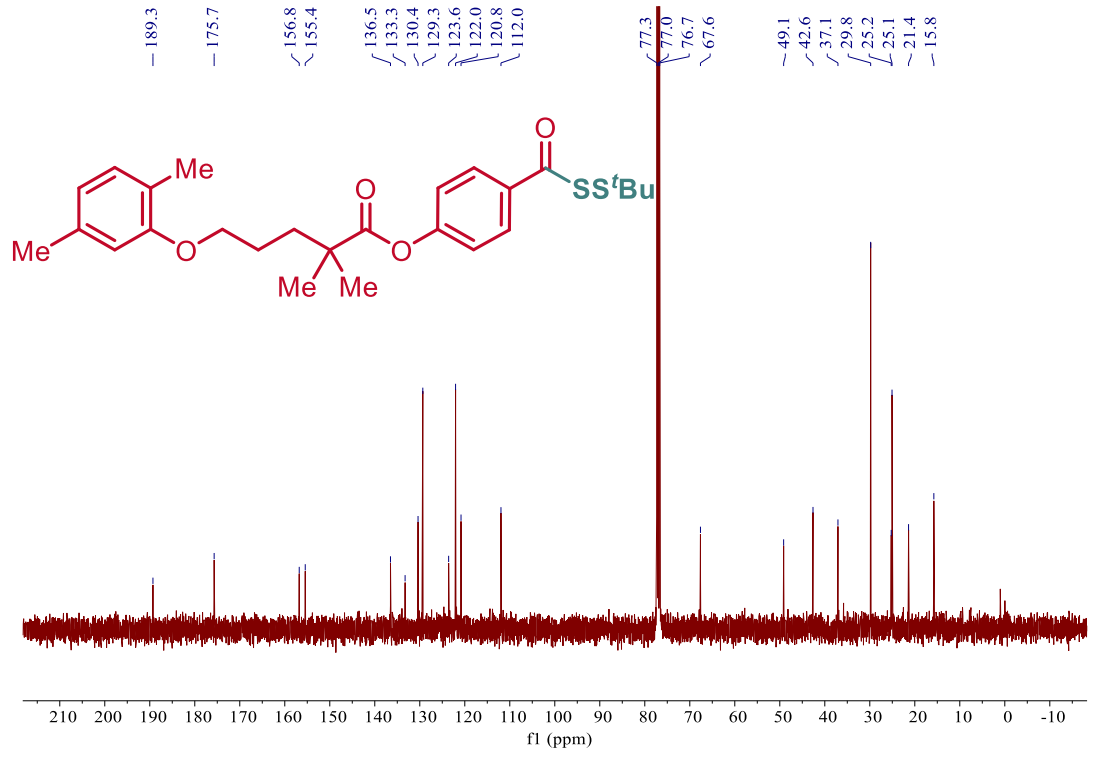
^{13}C NMR Spectrum of ((3a*S*,5a*R*,8a*R*,8*bS*)-2,2,7,7-Tetramethyltetrahydro-3a*H*-bis([1,3]dioxolo)[4,5-*b*:4',5'-*d*]pyran-3a-yl)methyl 4-(*tert*-butyldisulfannecarbonyl) benzoate 3aj



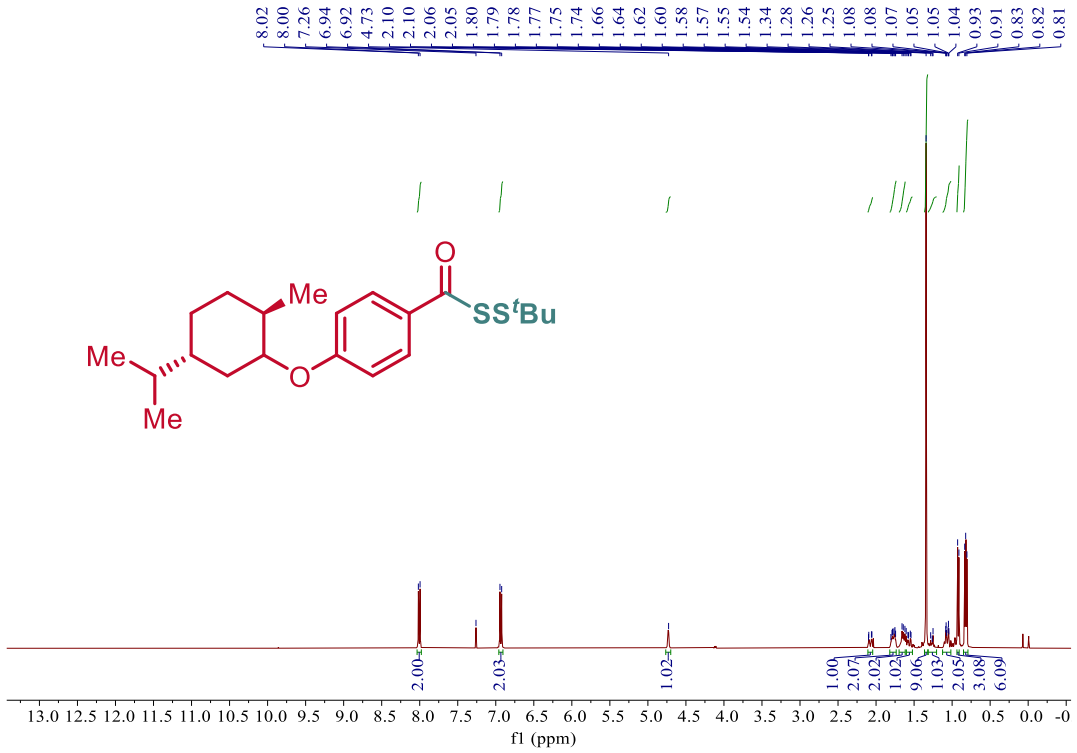
^{1}H NMR Spectrum of 4-(*tert*-Butyldisulfannecarbonyl)phenyl 5-(2,5-dimethyl phenoxy)-2,2-dimethylpentanoate 3ak



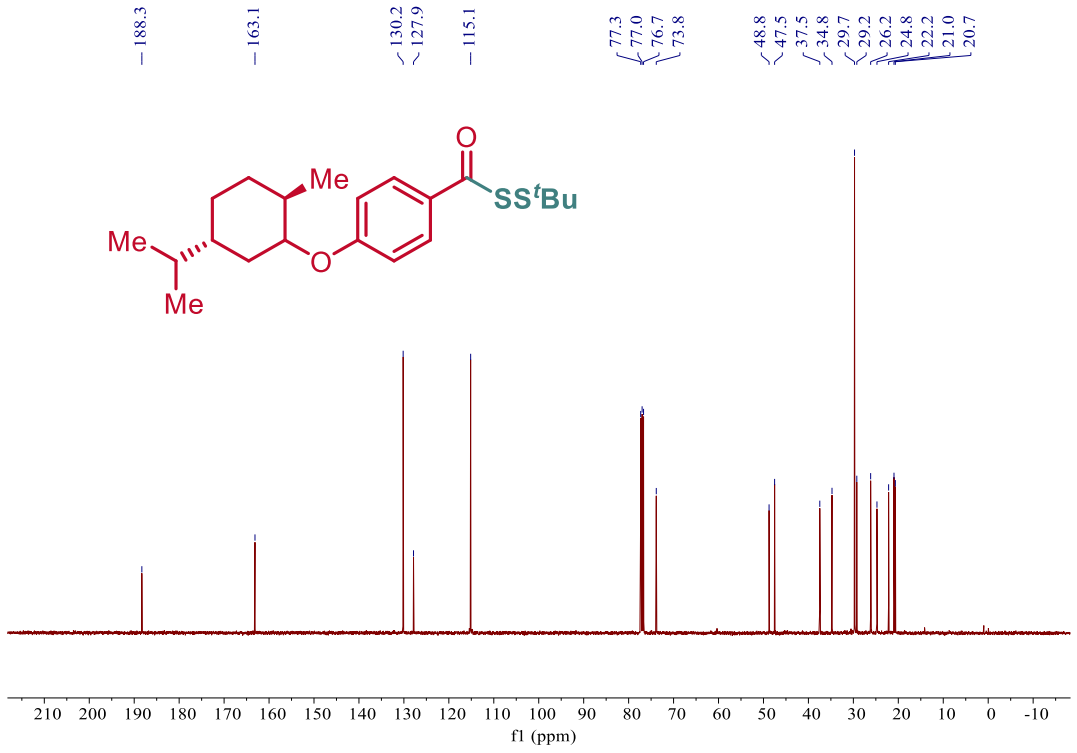
^{13}C NMR Spectrum of 4-(*tert*-Butyldisulfannecarbonyl)phenyl 5-(2,5-dimethyl phenoxy)-2,2-dimethylpentanoate 3ak



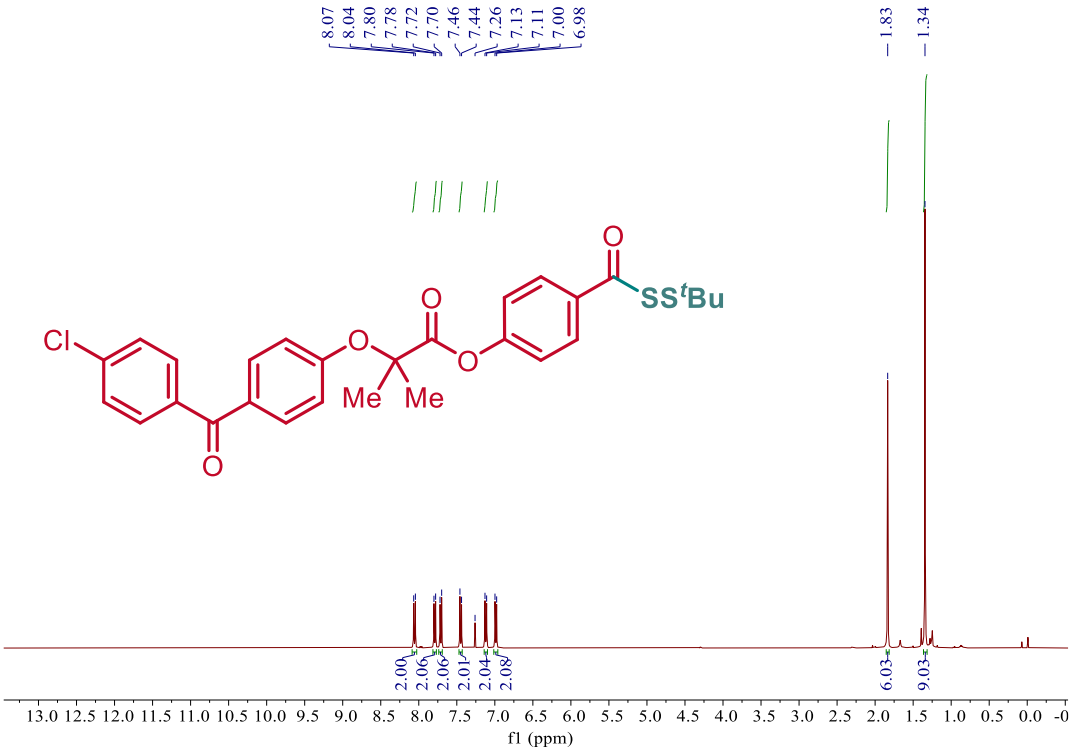
^{1}H NMR Spectrum of *SS*-(*tert*-Butyl) 4-(((2*R*,5*R*)-5-isopropyl-2-methylcyclohexyl) oxy)benzo(dithioperoxoate) 3al



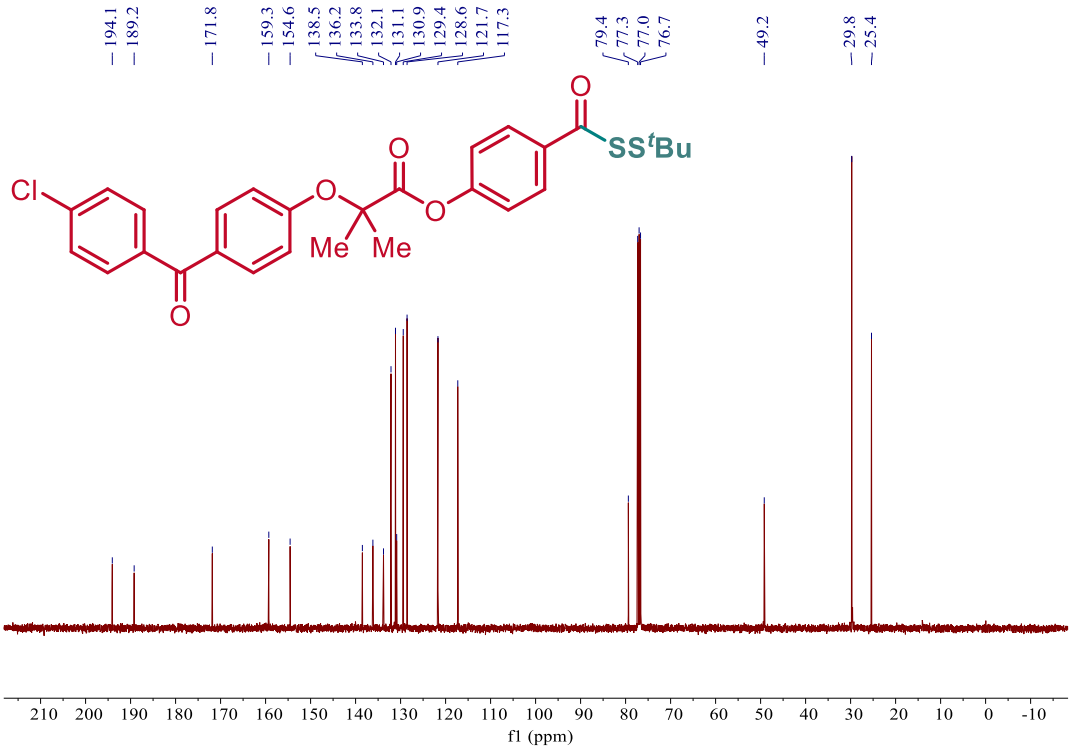
^{13}C NMR Spectrum of *SS*-(*tert*-Butyl) 4-(((2*R*,5*R*)-5-isopropyl-2-methylcyclohex yl)oxy)benzo(dithioperoxoate) 3al



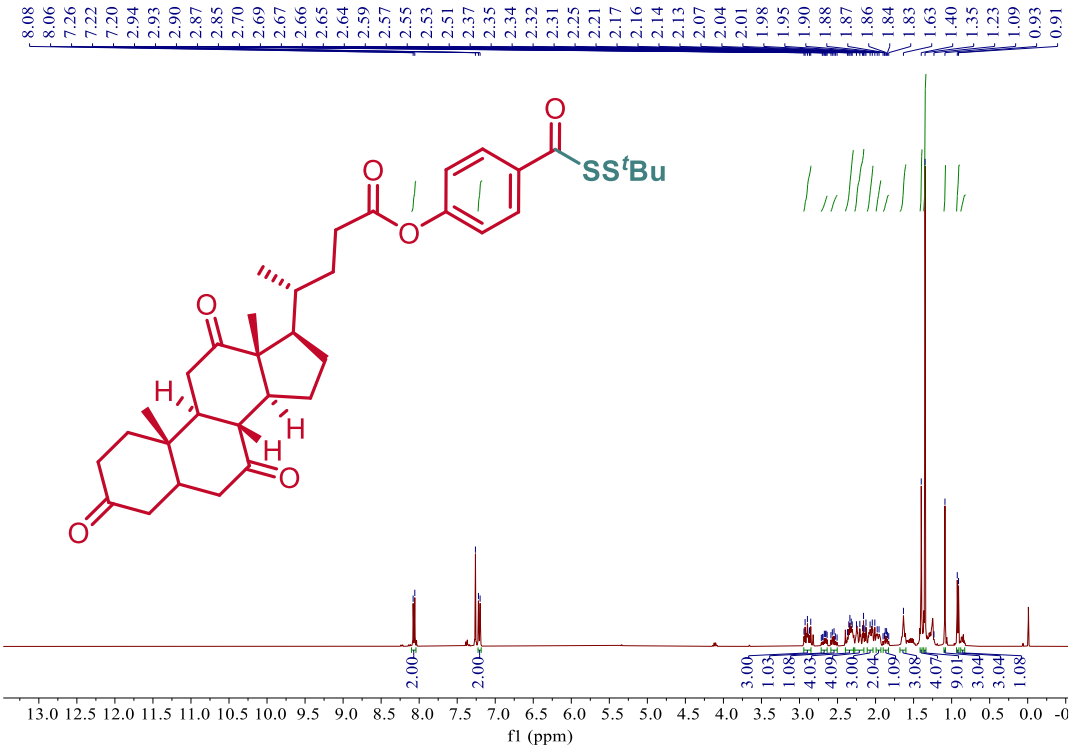
^{1}H NMR Spectrum of 4-(*tert*-Butyldisulfannecarbonyl)phenyl 2-(4-(4-chloroben zoyl)phenoxy)-2-methylpropanoate 3am



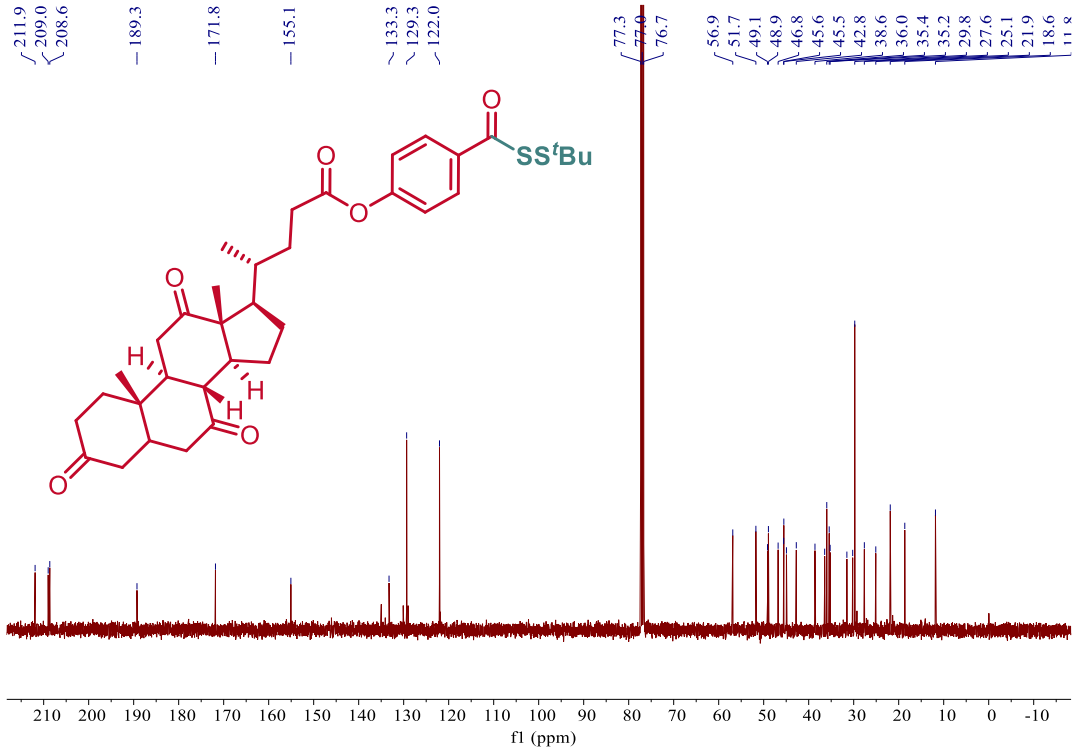
^{13}C NMR Spectrum of 4-(*tert*-Butyldisulfannecarbonyl)phenyl 2-(4-(4-chloroben zoyl)phenoxy)-2-methylpropanoate 3am



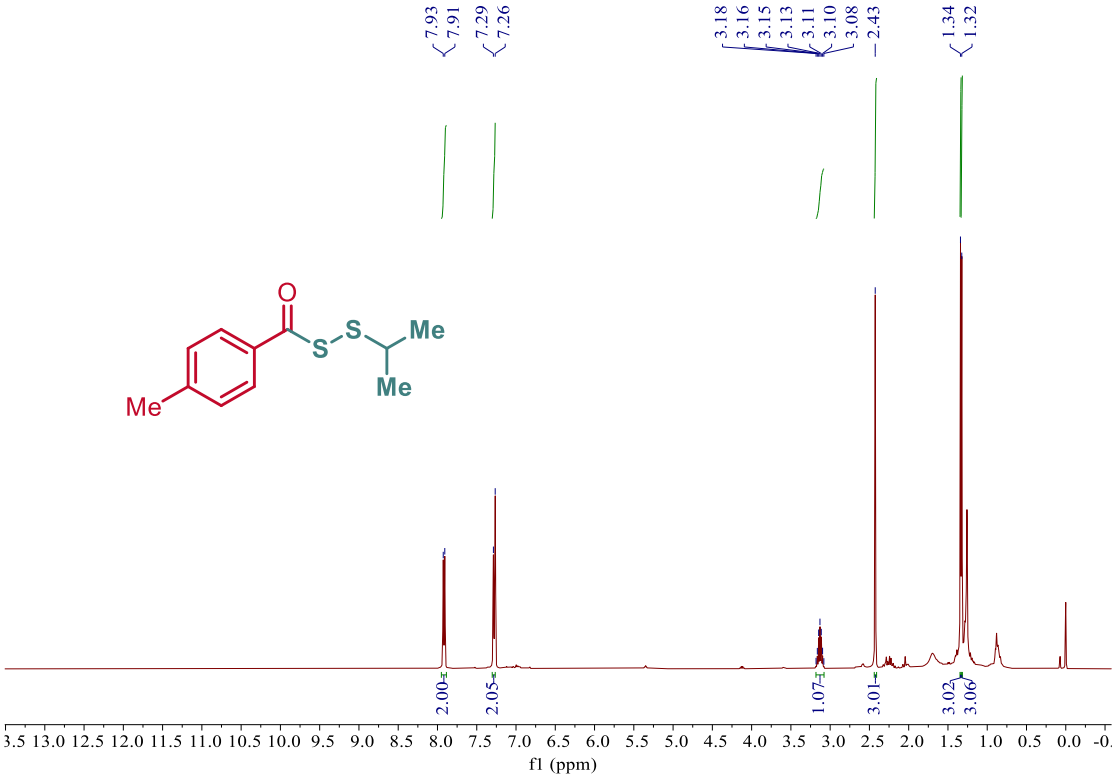
^{1}H NMR Spectrum of 4-(*tert*-Butyldisulfannecarbonyl)phenyl (4*R*)-4-((8*R*,9*S*,10*S*,13*R*,14*S*,17*R*)-10,13-dimethyl-3,7,12-trioxohexadecahydro-1*H*-cyclopenta[*a*]phenanthren-17-yl)pentanoate 3an



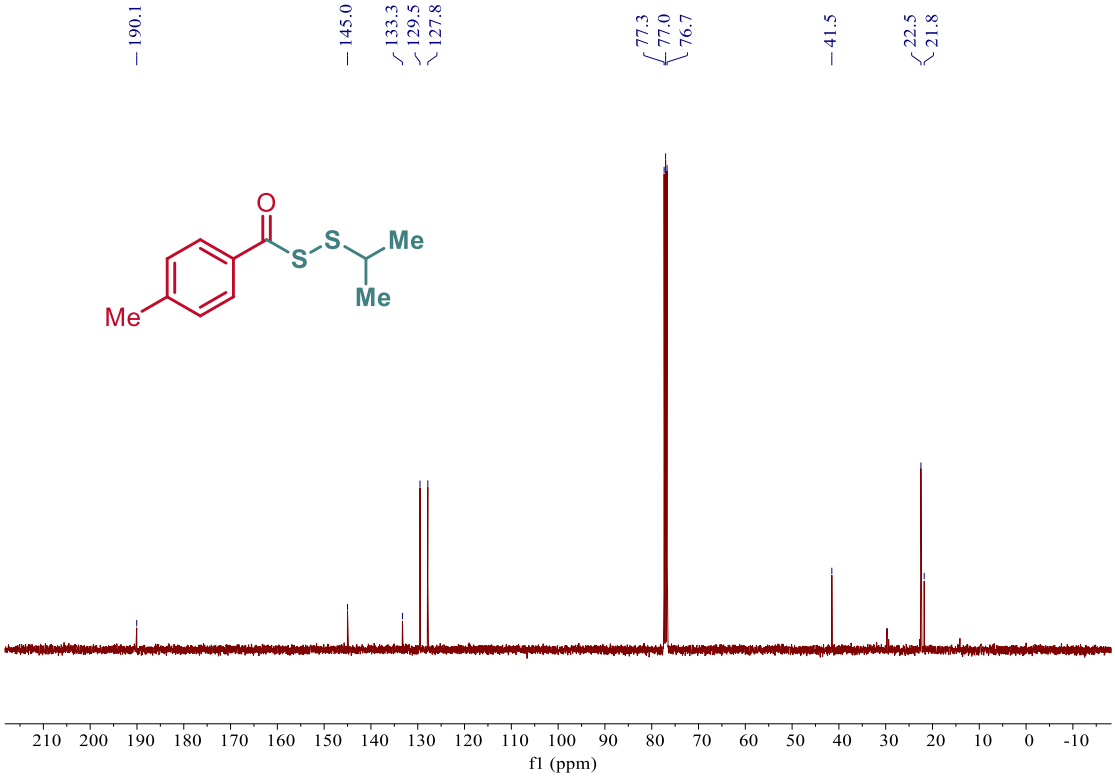
^{13}C NMR Spectrum of 4-(*tert*-Butyldisulfannecarbonyl)phenyl (4*R*)-4-((8*R*,9*S*,10*S*,13*R*,14*S*,17*R*)-10,13-dimethyl-3,7,12-trioxohexadecahydro-1*H*-cyclopenta[*a*]phenanthren-17-yl)pentanoate 3an



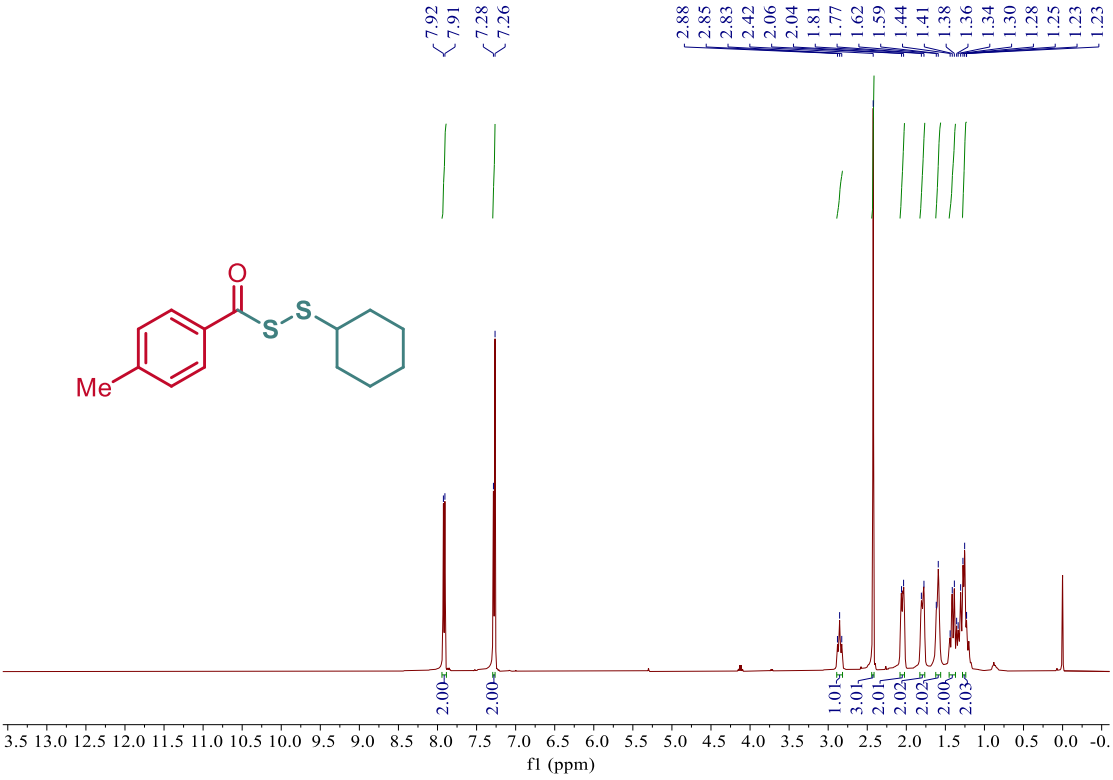
^{1}H NMR Spectrum of *SS*-Isopropyl 4-methylbenzo(dithioperoxoate) 3ao



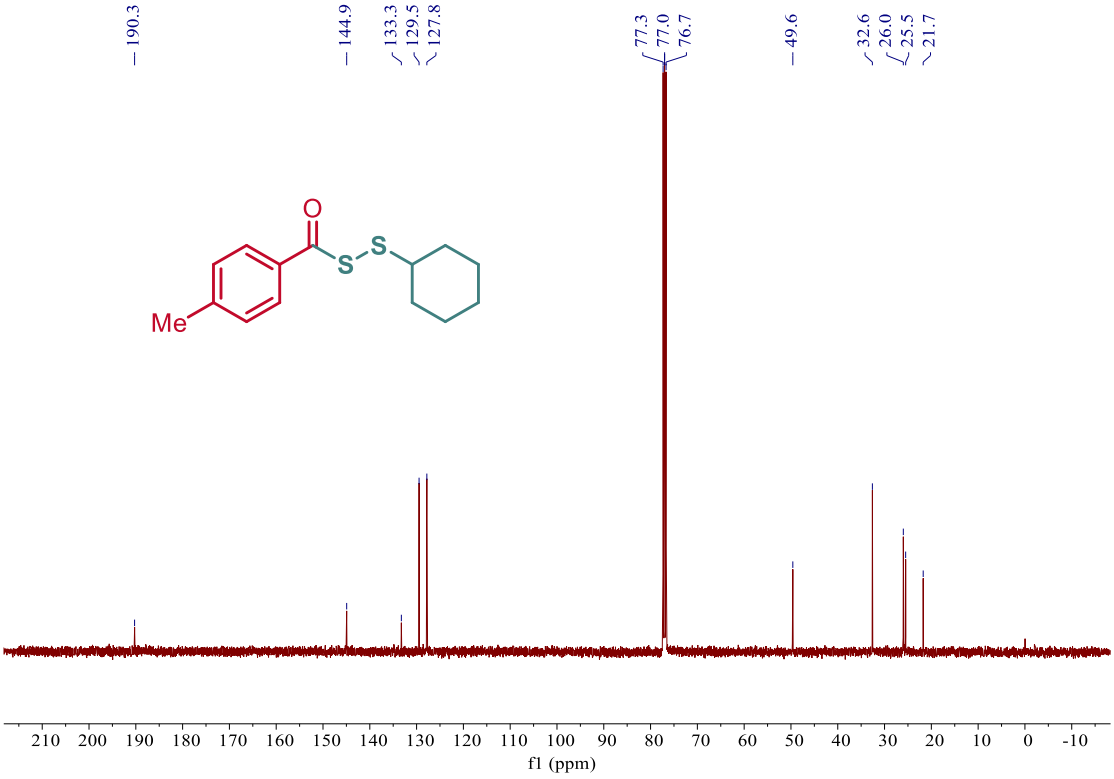
^{13}C NMR Spectrum of *SS*-Isopropyl 4-methylbenzo(dithioperoxoate) 3ao



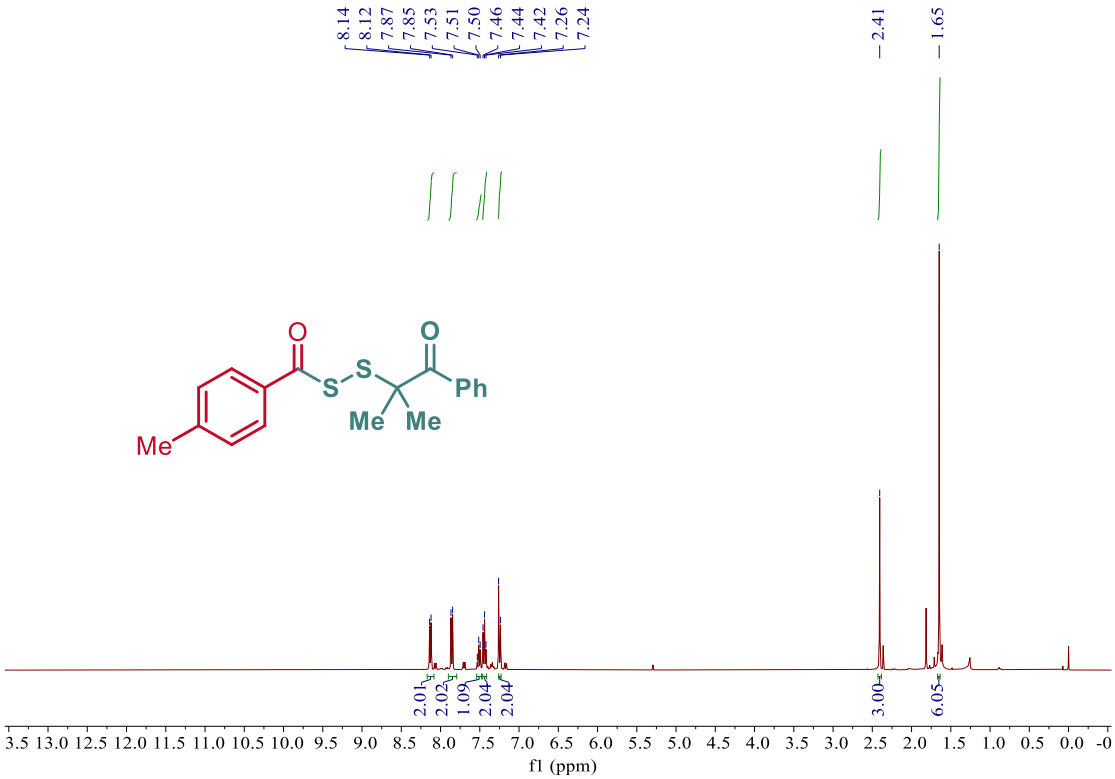
^{1}H NMR Spectrum of *SS*-Cyclohexyl 4-methylbenzo(dithioperoxoate) 3ap



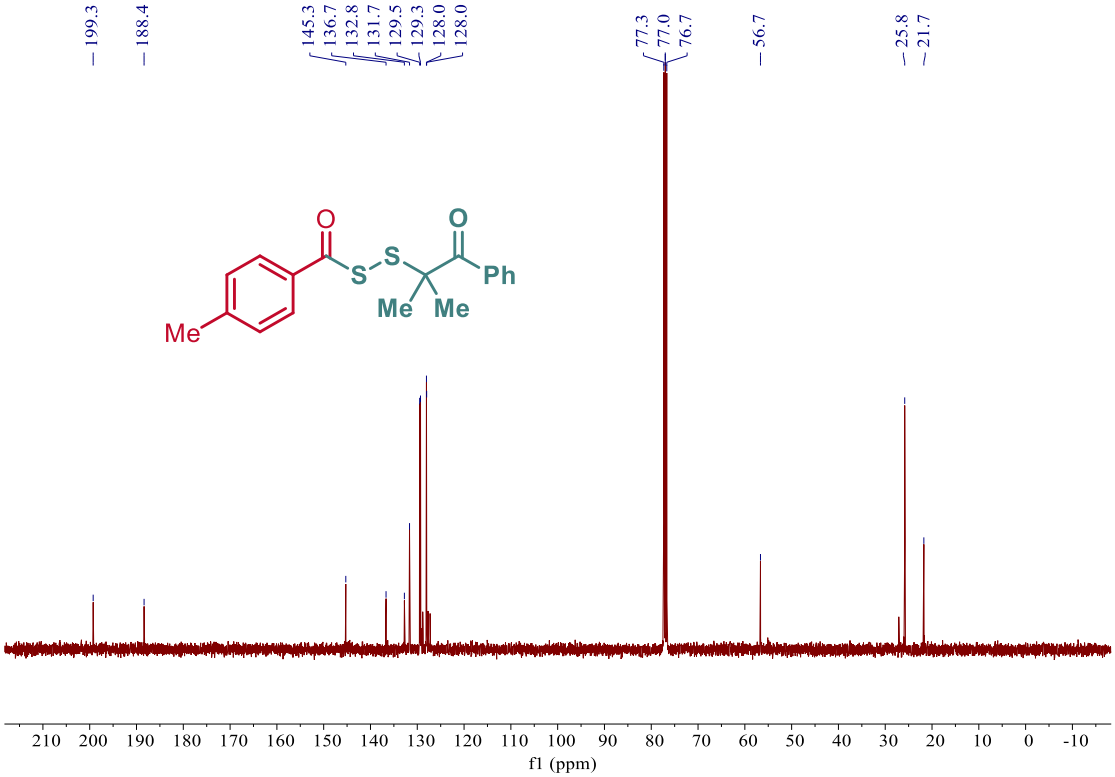
^{13}C NMR Spectrum of *SS*-Cyclohexyl 4-methylbenzo(dithioperoxoate) 3ap



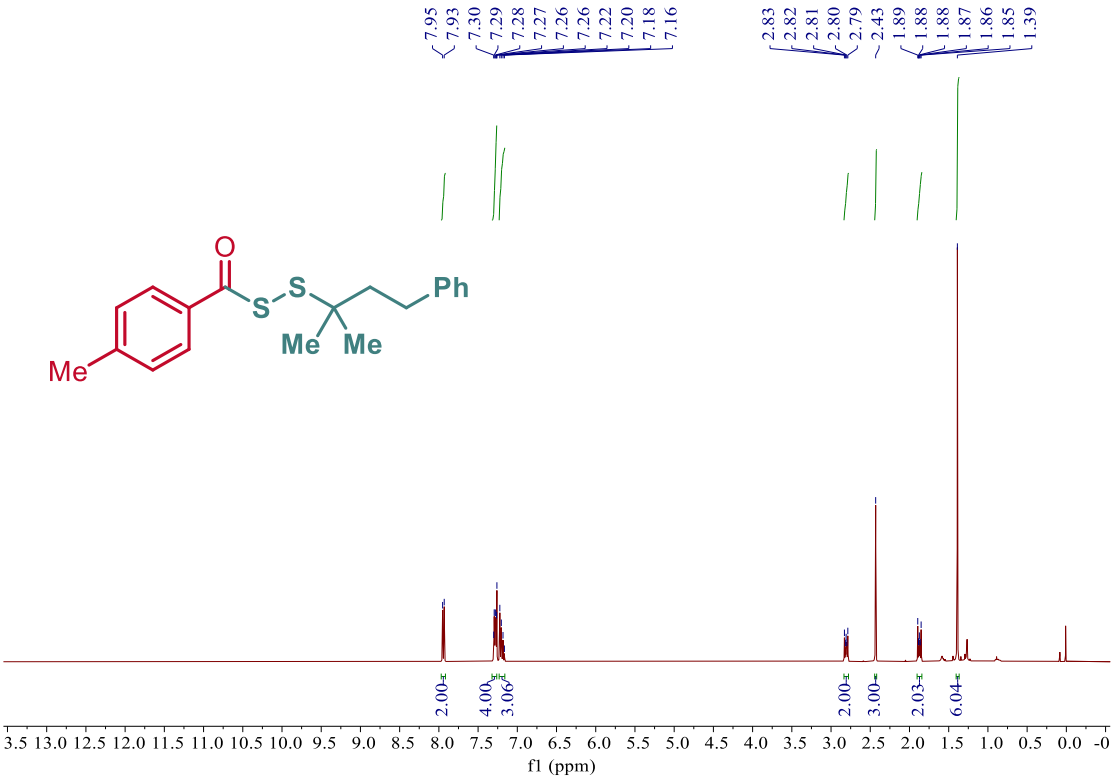
^{1}H NMR Spectrum of *SS*-(2-Methyl-1-oxo-1-phenylpropan-2-yl) 4-methylbenzo (dithioperoxoate) 3aq



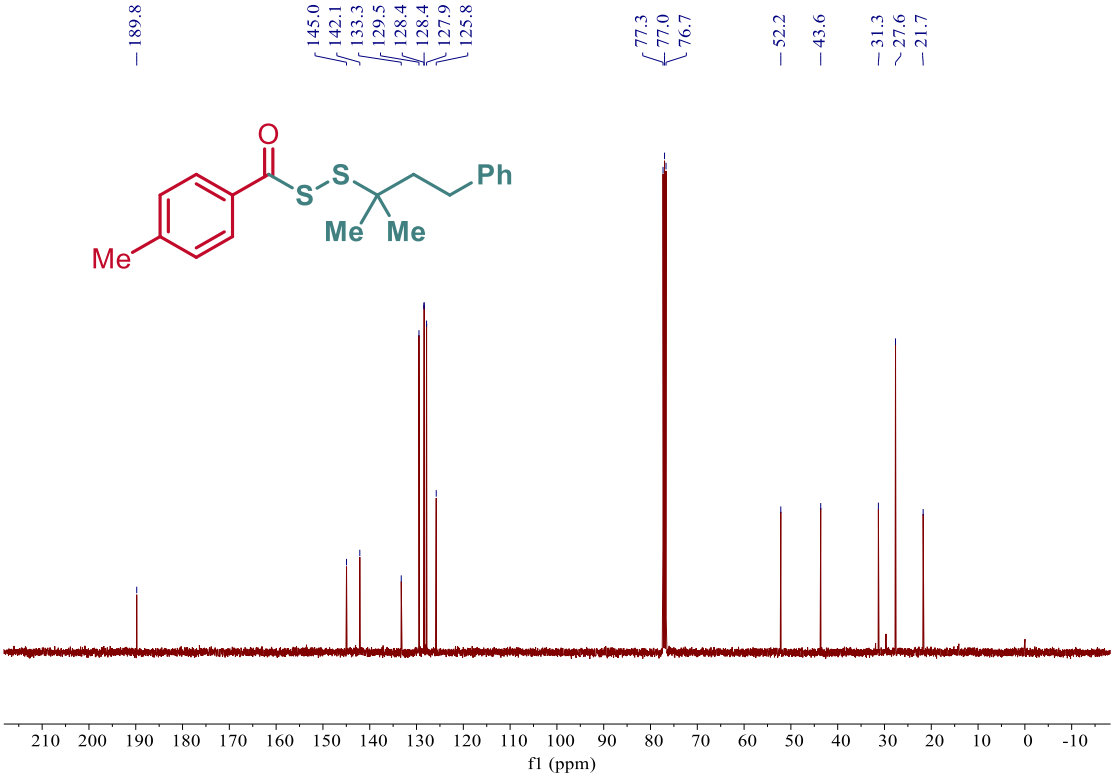
^{13}C NMR Spectrum of *SS*-(2-Methyl-1-oxo-1-phenylpropan-2-yl) 4-methylbenzo (dithioperoxoate) 3aq



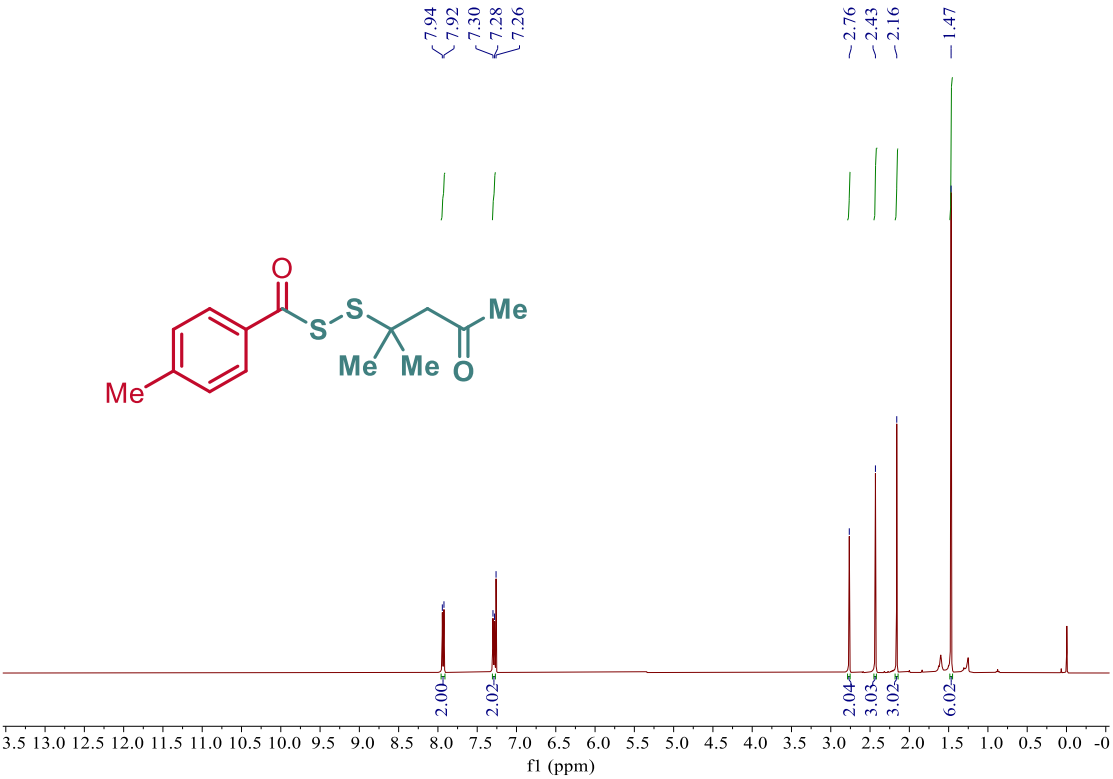
^{1}H NMR Spectrum of *SS*-(2-Methyl-4-phenylbutan-2-yl) 4-methylbenzo(dithioperoxoate) 3ar



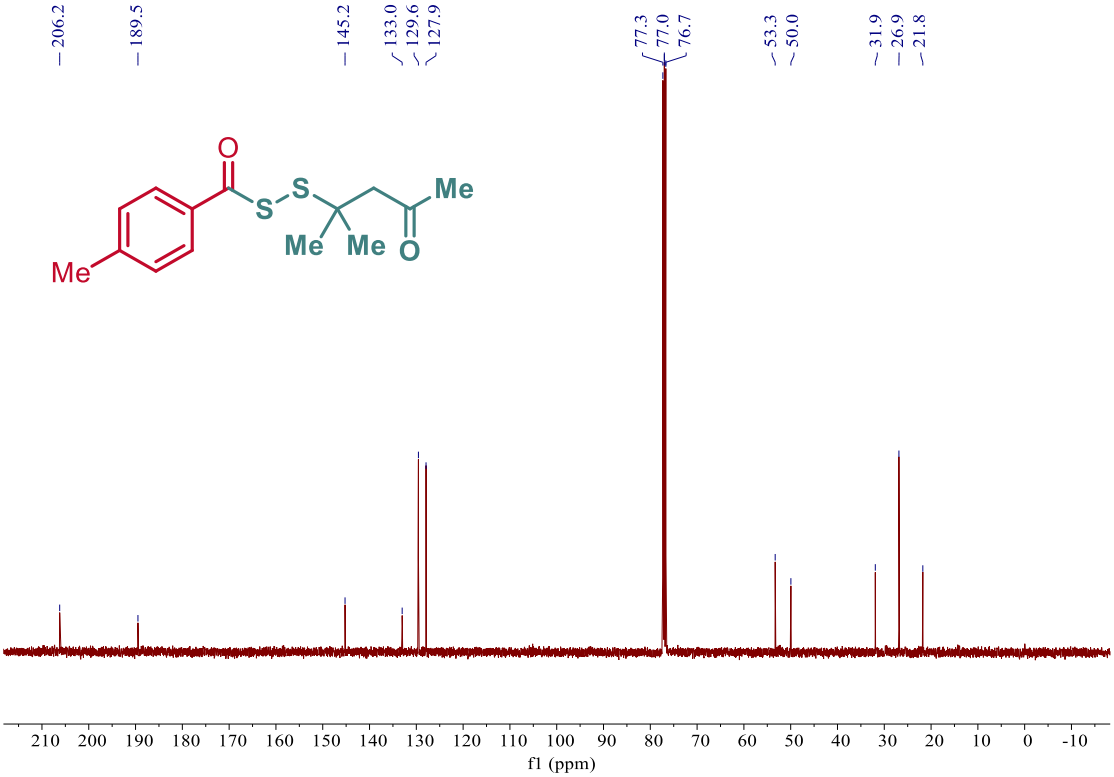
^{13}C NMR Spectrum of *SS*-(2-Methyl-4-phenylbutan-2-yl) 4-methylbenzo(dithioperoxoate) 3ar



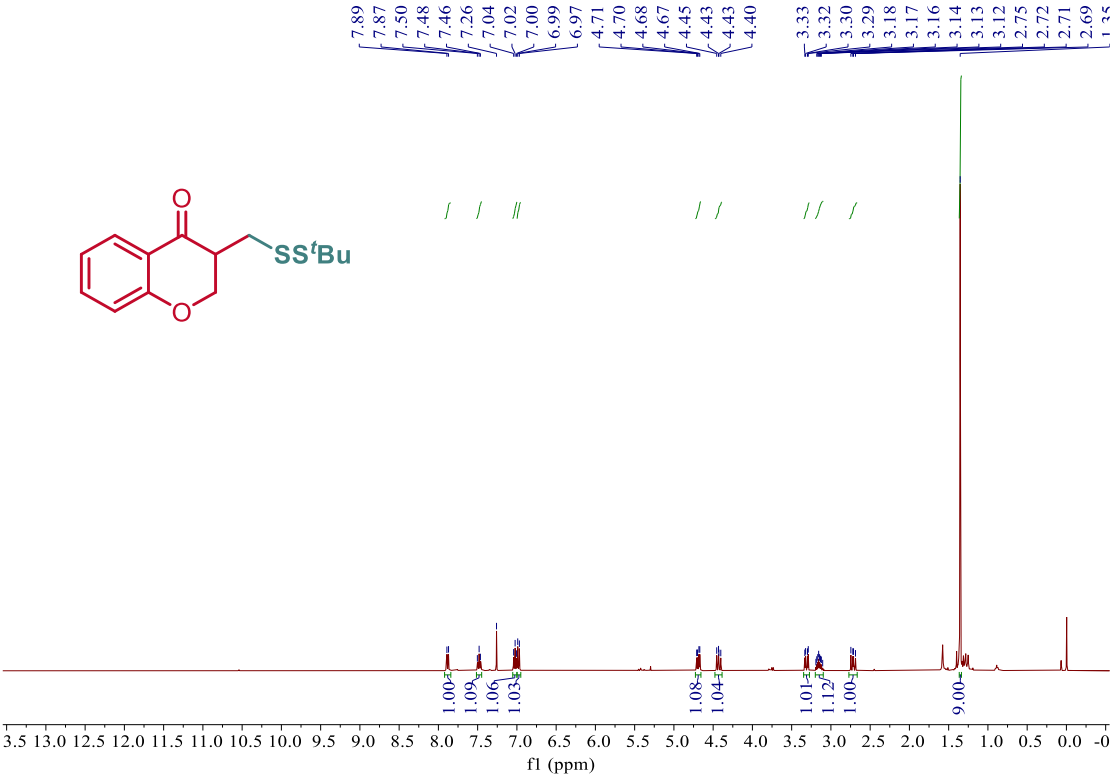
^{1}H NMR Spectrum of *SS*-(2-Methyl-4-oxopentan-2-yl) 4-methylbenzo(dithioperoxoate) 3as



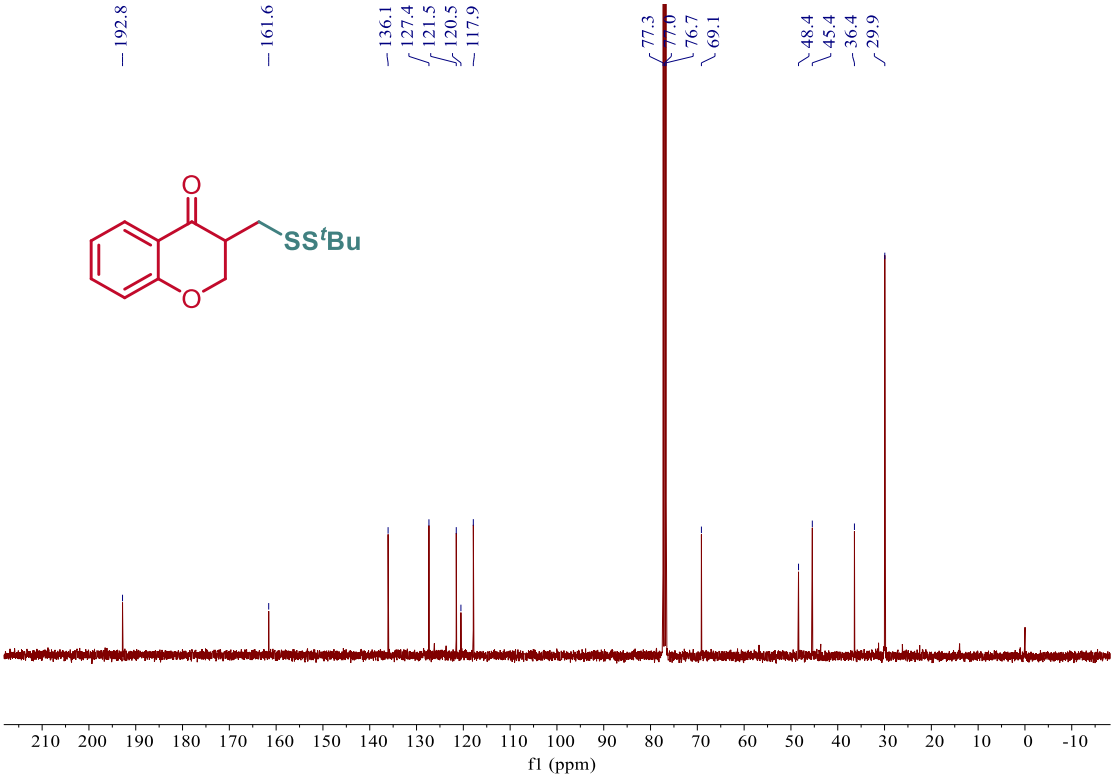
^{13}C NMR Spectrum of *SS*-(2-Methyl-4-oxopentan-2-yl) 4-methylbenzo(dithioperoxoate) 3as



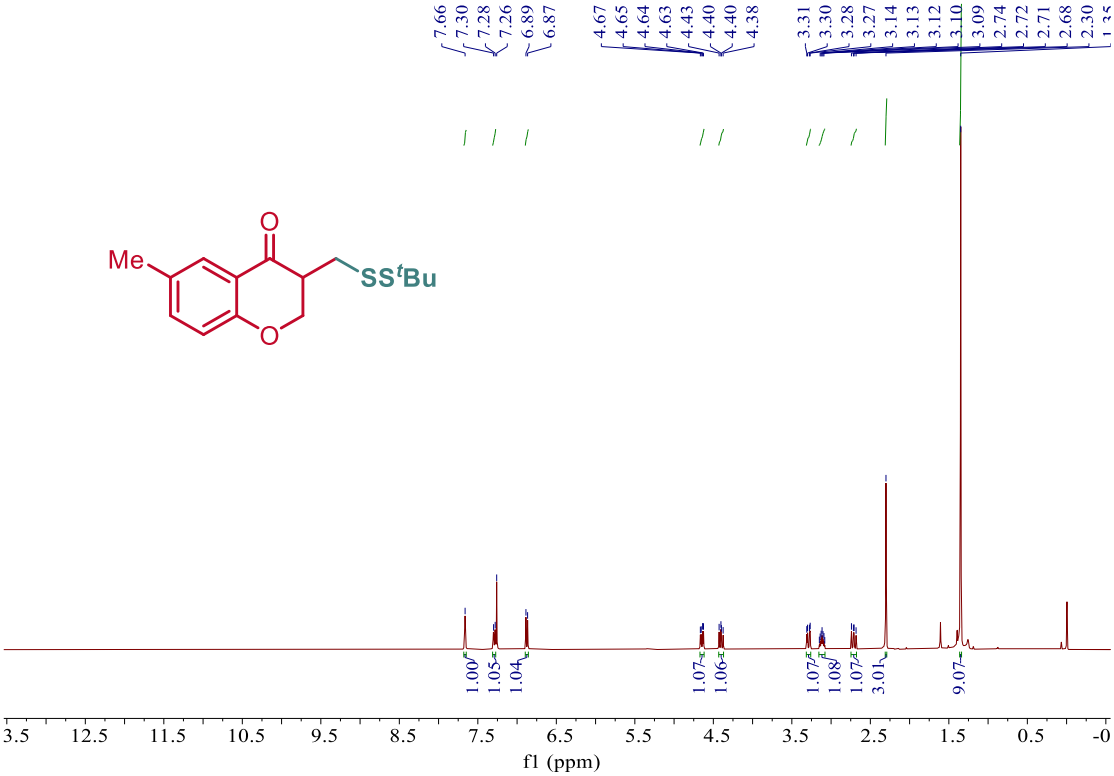
^{1}H NMR Spectrum of 3-((*tert*-Butyldisulfaneyl)methyl)chroman-4-one 5a



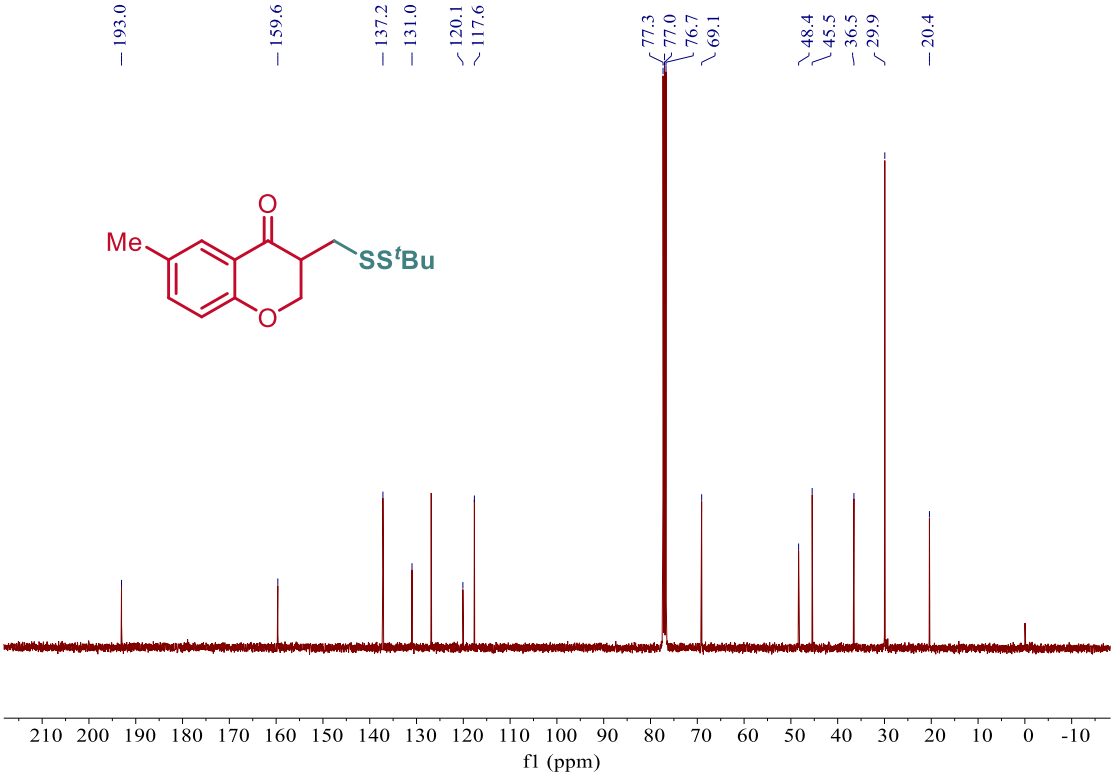
^{13}C NMR Spectrum of 3-((*tert*-Butyldisulfaneyl)methyl)chroman-4-one 5a



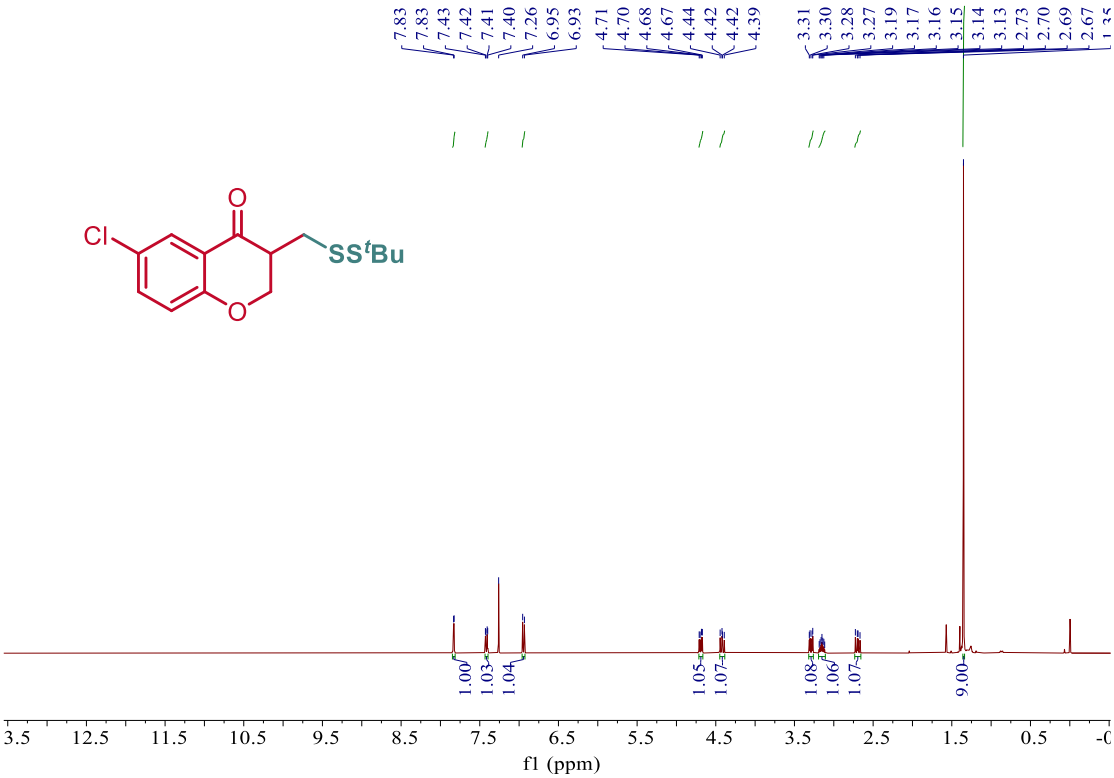
^{1}H NMR Spectrum of 2-((*tert*-Butyldisulfaneyl)methyl)-2,3-dihydro-1*H*-benzo [*f*]chromen-1-one 5b



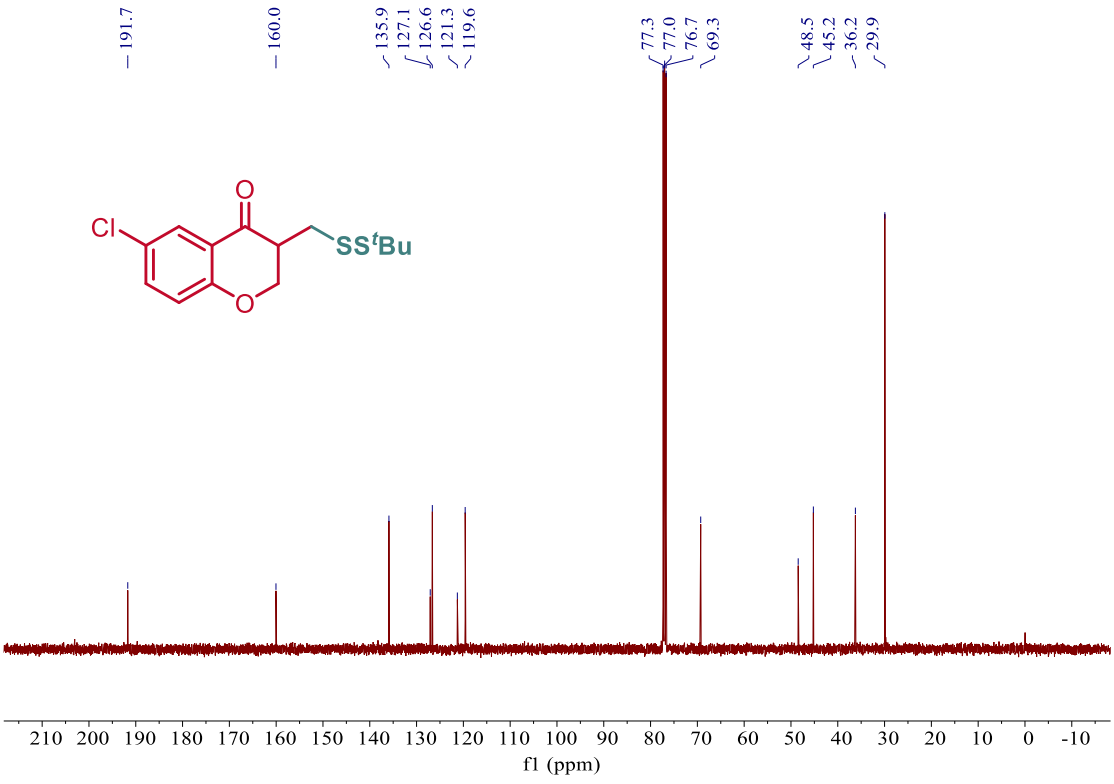
^{13}C NMR Spectrum of 2-((*tert*-Butyldisulfaneyl)methyl)-2,3-dihydro-1*H*-benzo [*f*]chromen-1-one 5b



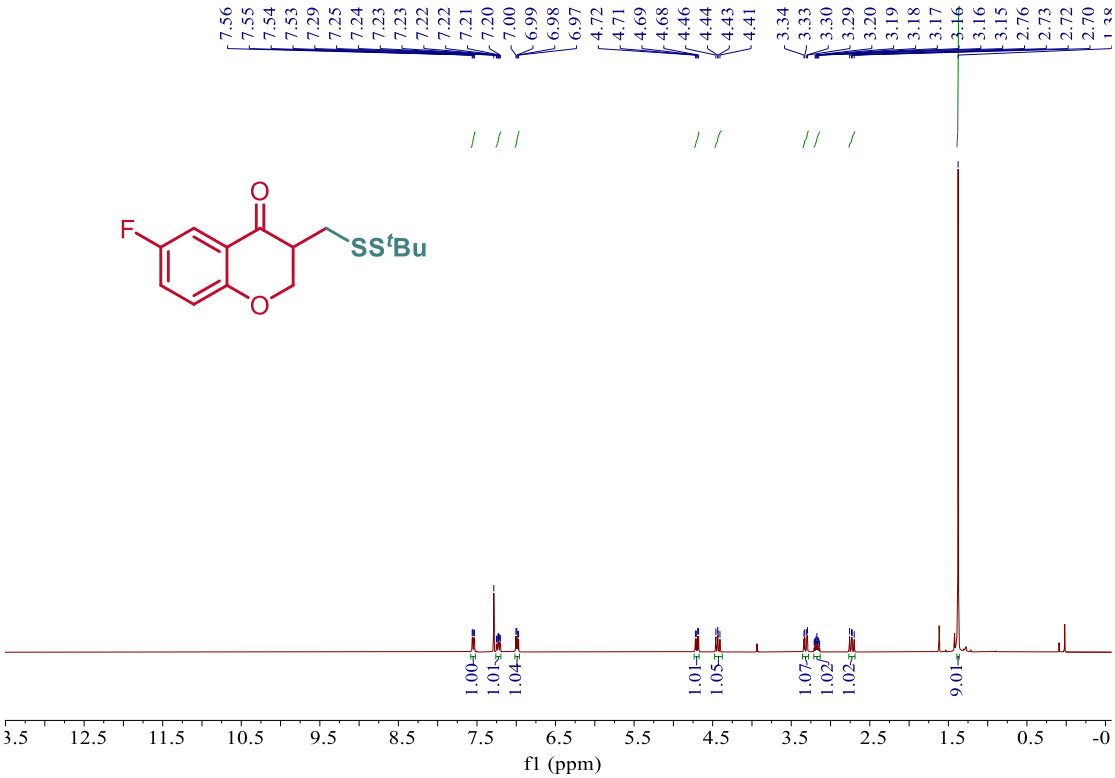
^{1}H NMR Spectrum of 3-((*tert*-Butyldisulfaneyl)methyl)-6-chlorochroman-4-one 5c



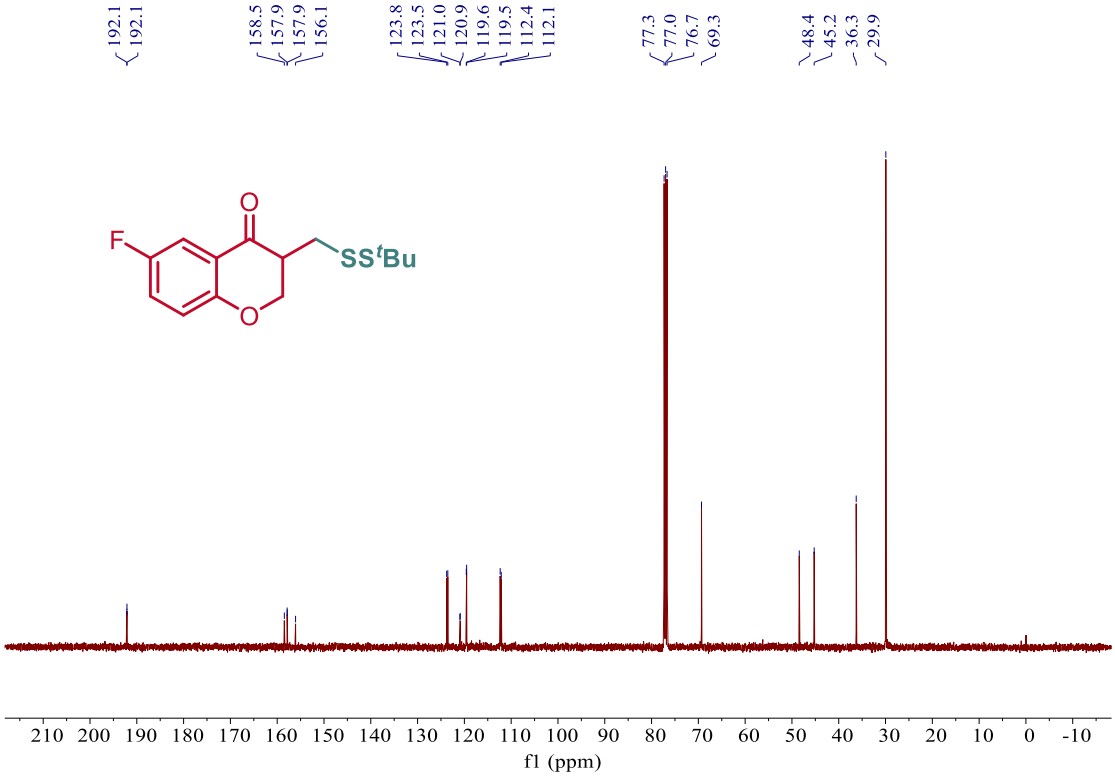
^{13}C NMR Spectrum of 3-((*tert*-Butyldisulfaneyl)methyl)-6-chlorochroman-4-one 5c



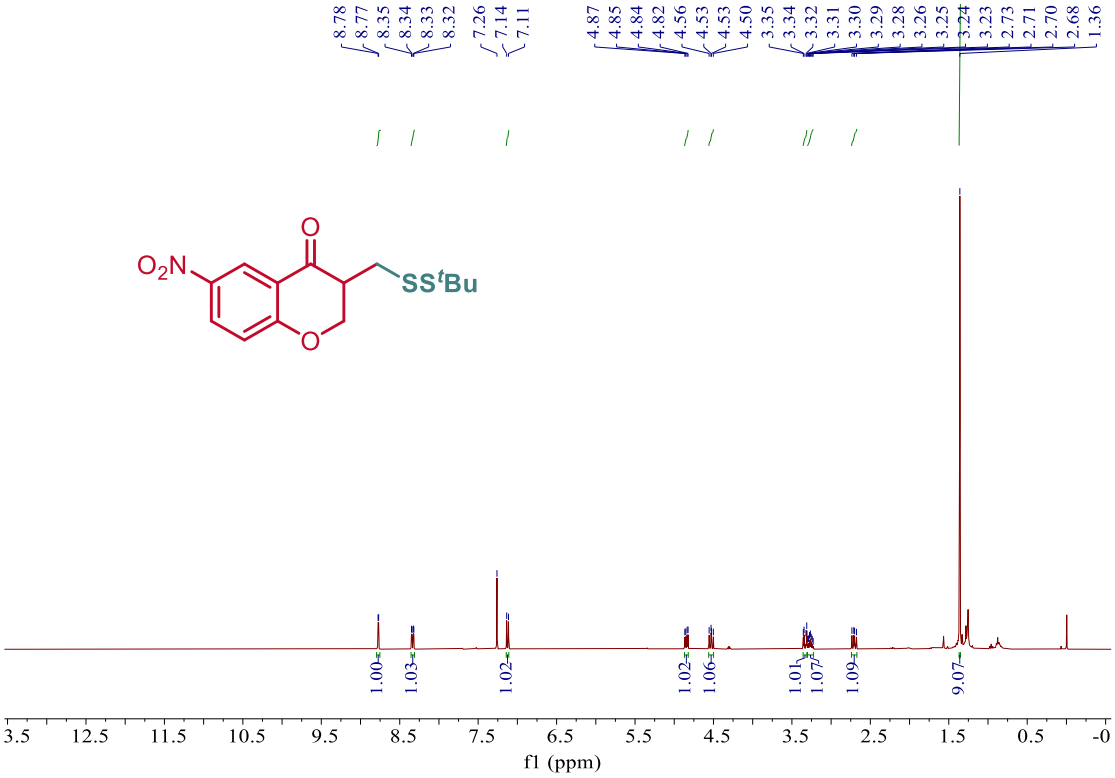
^{1}H NMR Spectrum of 3-((*tert*-Butyldisulfaneyl)methyl)-6-fluorochroman-4-one 5d



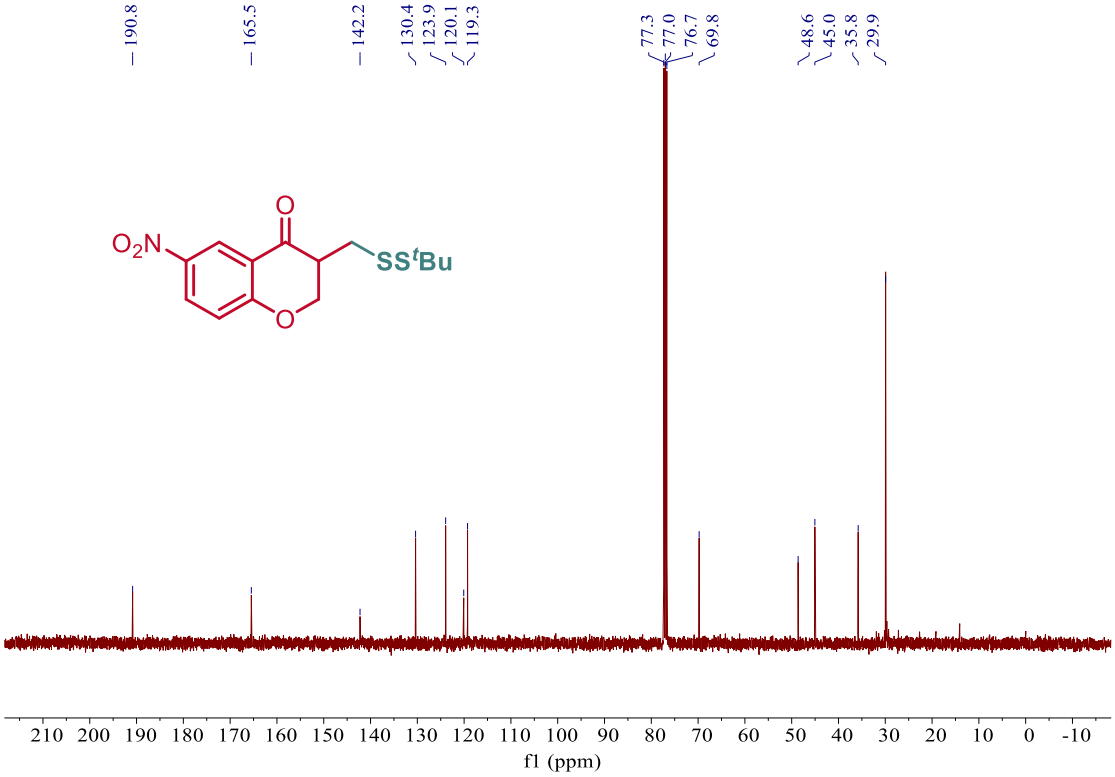
^{13}C NMR Spectrum of 3-((*tert*-Butyldisulfaneyl)methyl)-6-fluorochroman-4-one 5d



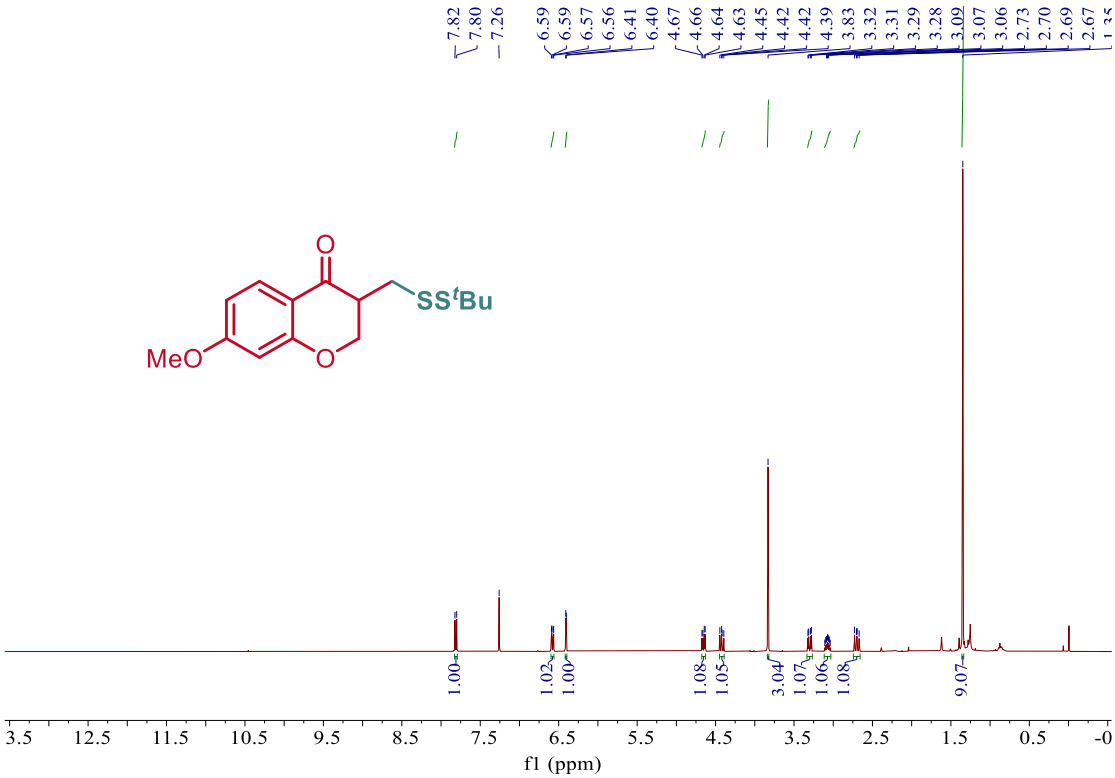
^{1}H NMR Spectrum of 3-((*tert*-Butyldisulfaneyl)methyl)-6-nitrochroman-4-one 5e



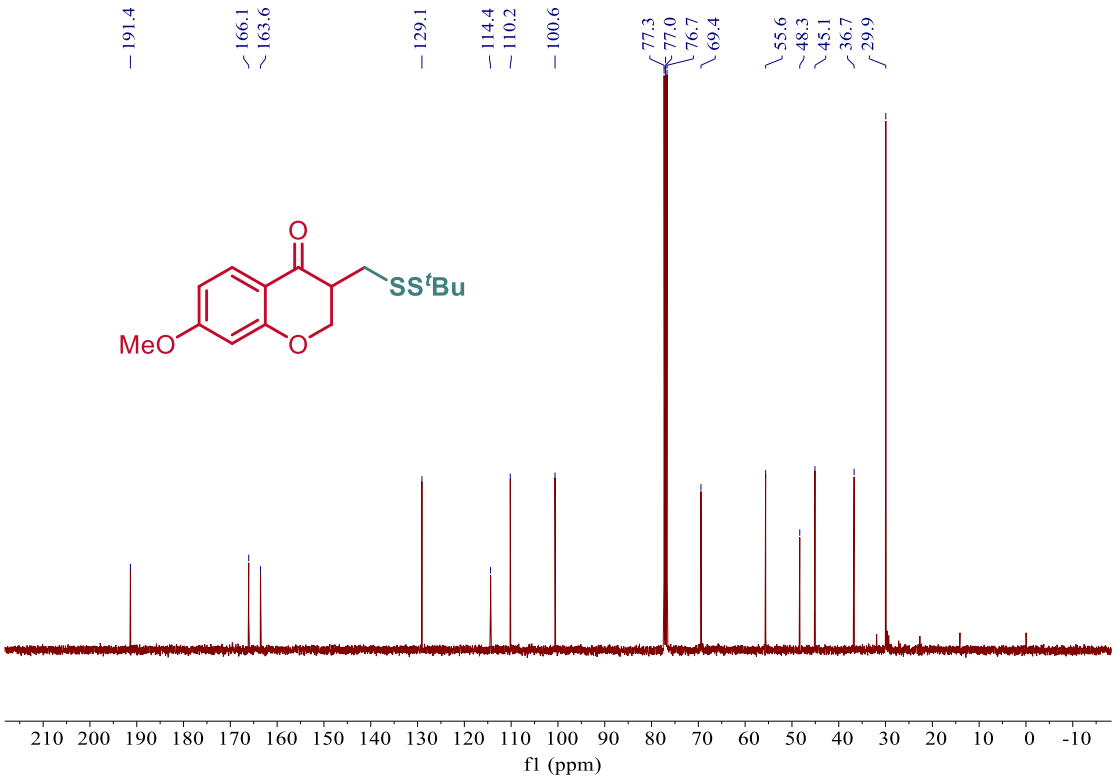
^{13}C NMR Spectrum of 3-((*tert*-Butyldisulfaneyl)methyl)-6-nitrochroman-4-one 5e



^{1}H NMR Spectrum of 3-((*tert*-Butyldisulfaneyl)methyl)-7-methoxychroman-4-one 5f



^{13}C NMR Spectrum of 3-((*tert*-Butyldisulfaneyl)methyl)-7-methoxychroman-4-one 5f



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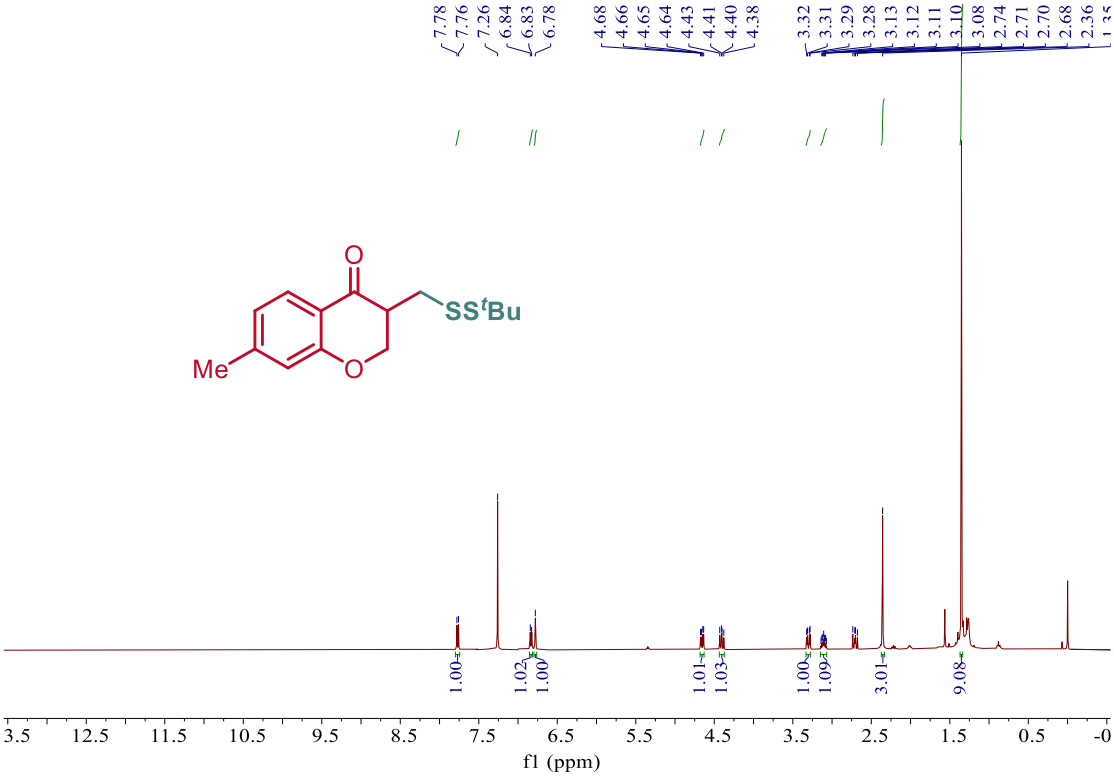
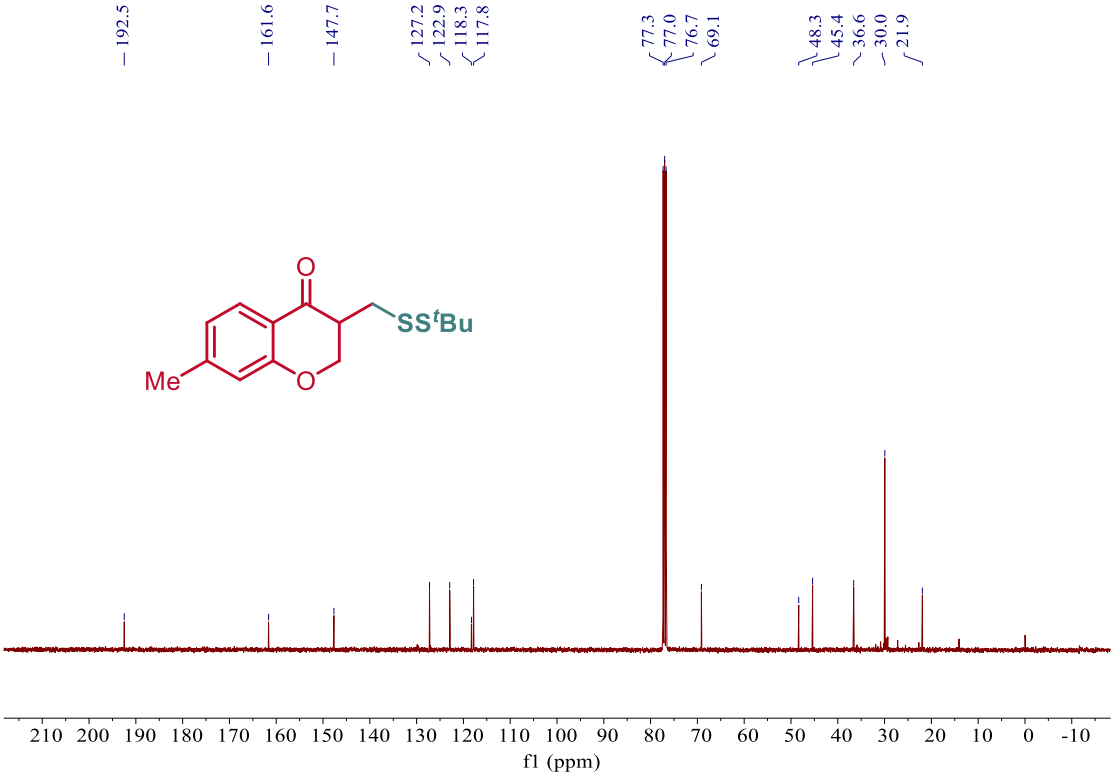
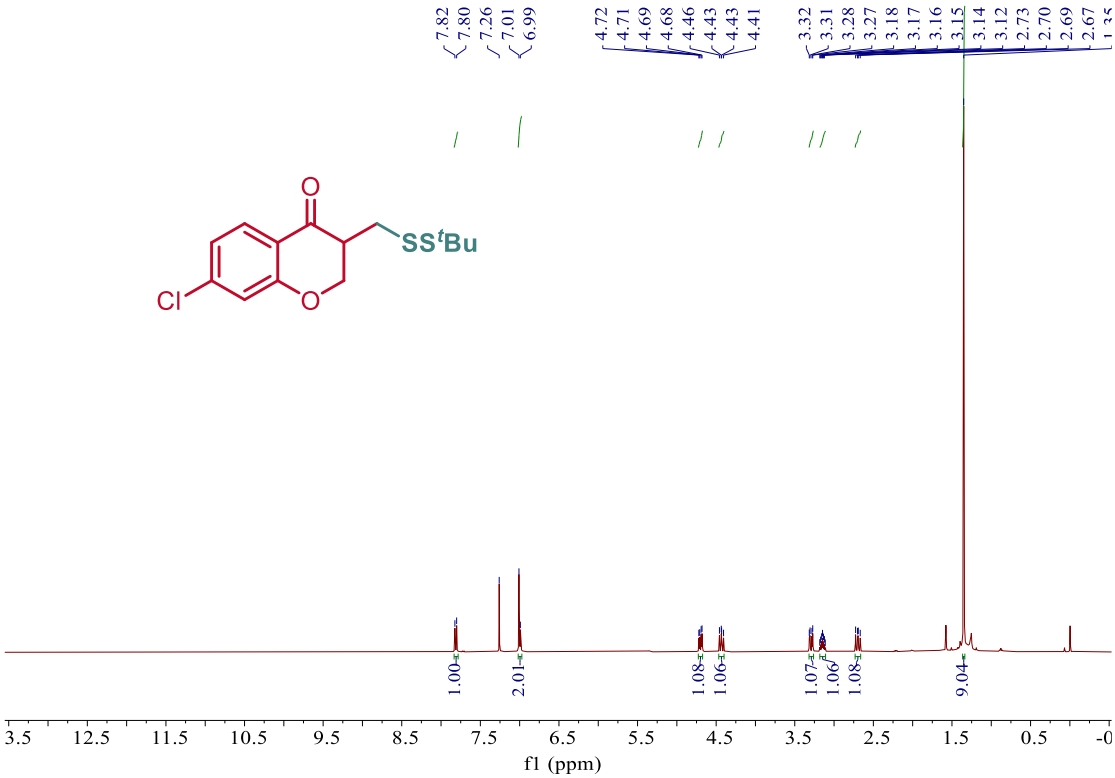


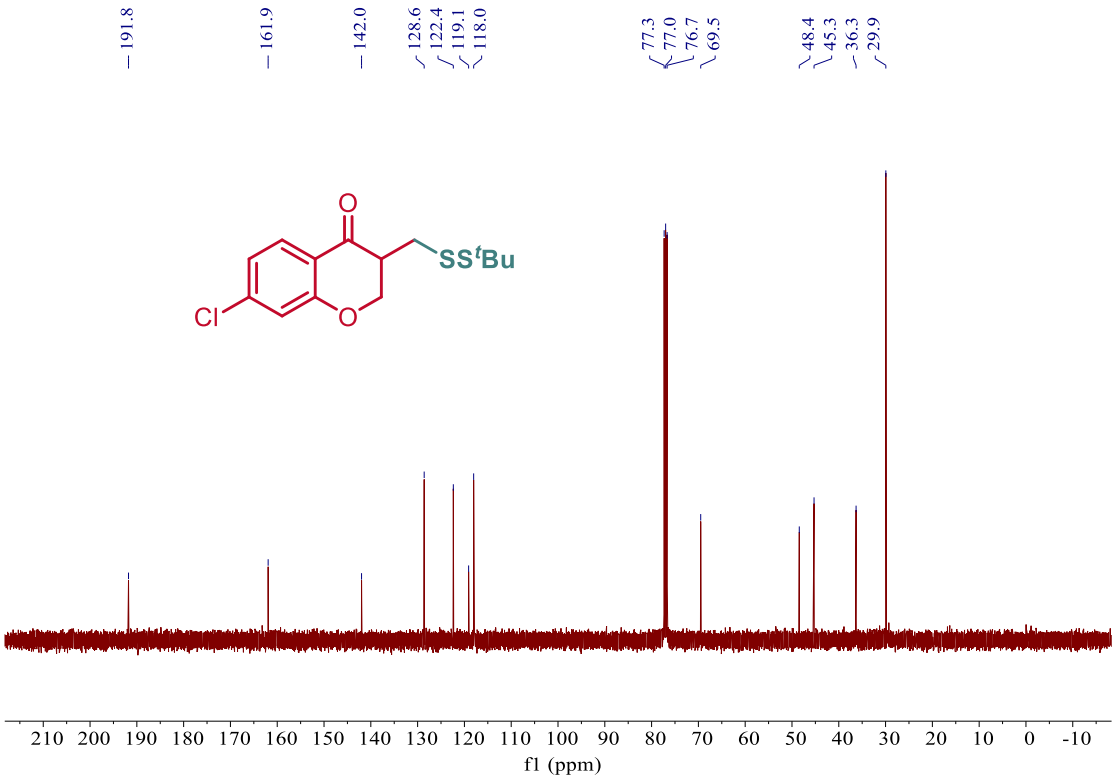
^{13}C NMR Spectrum of 3-((*tert*-Butyldisulfaneyl)methyl)-7-methylchroman-4-one 5g



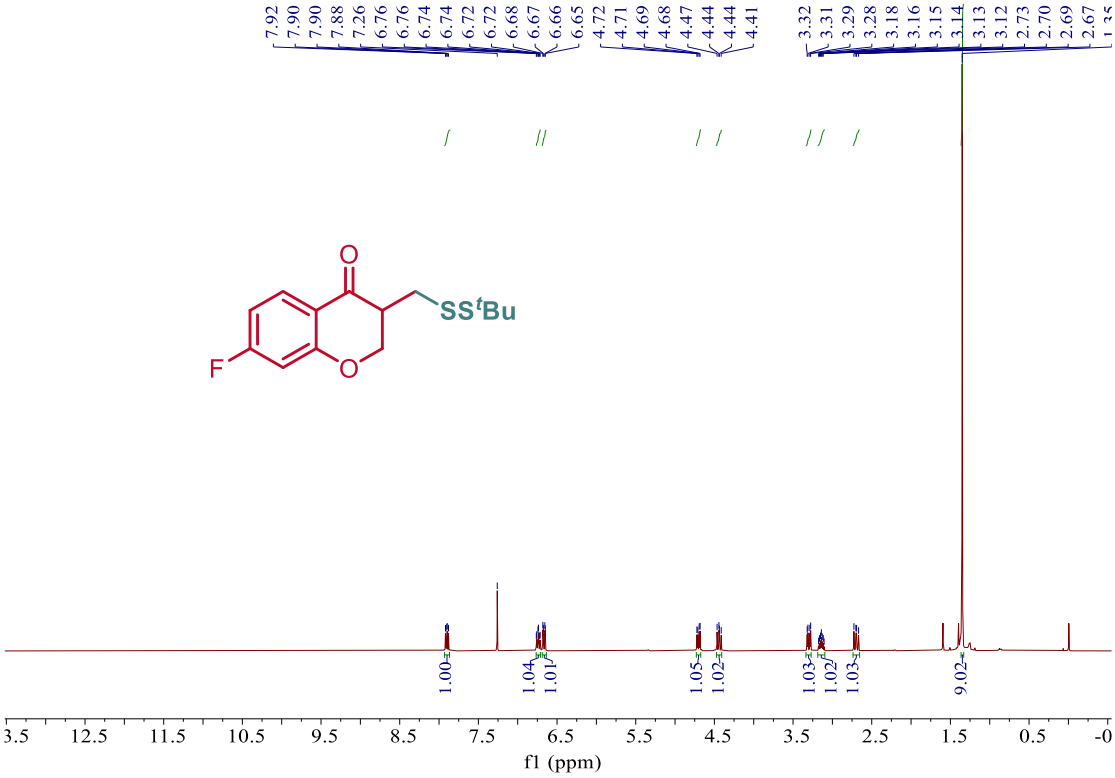
^{1}H NMR Spectrum of 3-((*tert*-Butyldisulfaneyl)methyl)-7-chlorochroman-4-one 5h



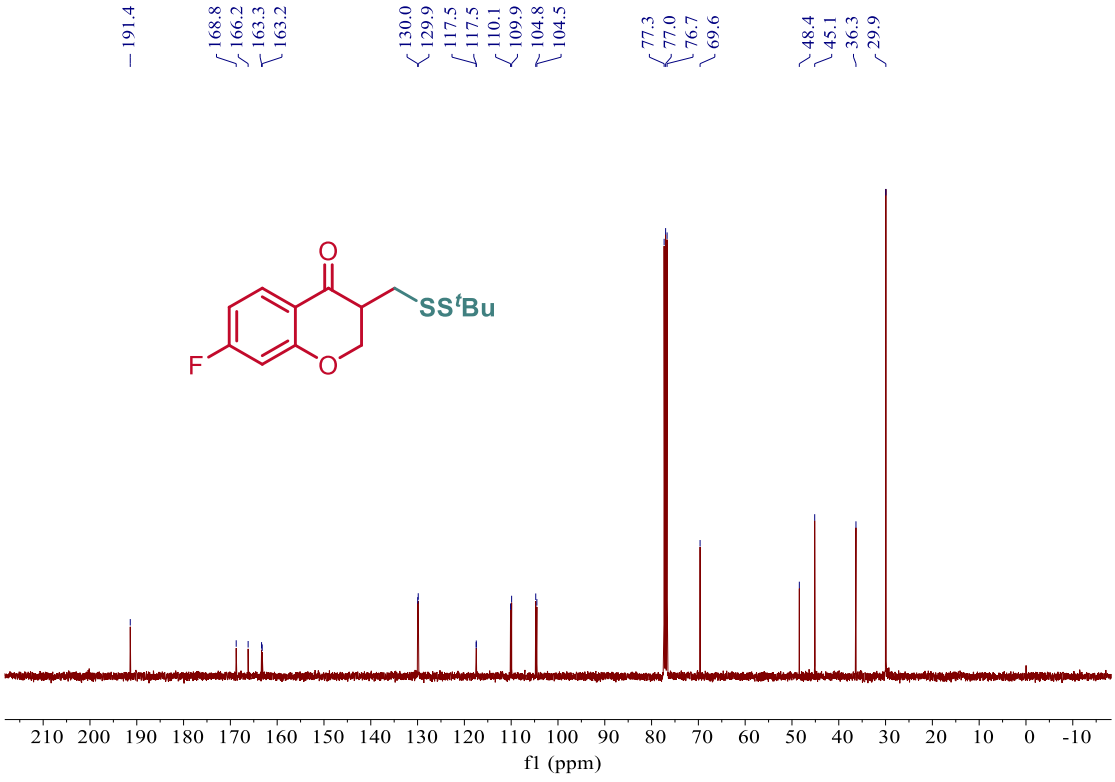
^{13}C NMR Spectrum of 3-((*tert*-Butyldisulfaneyl)methyl)-7-chlorochroman-4-one 5h



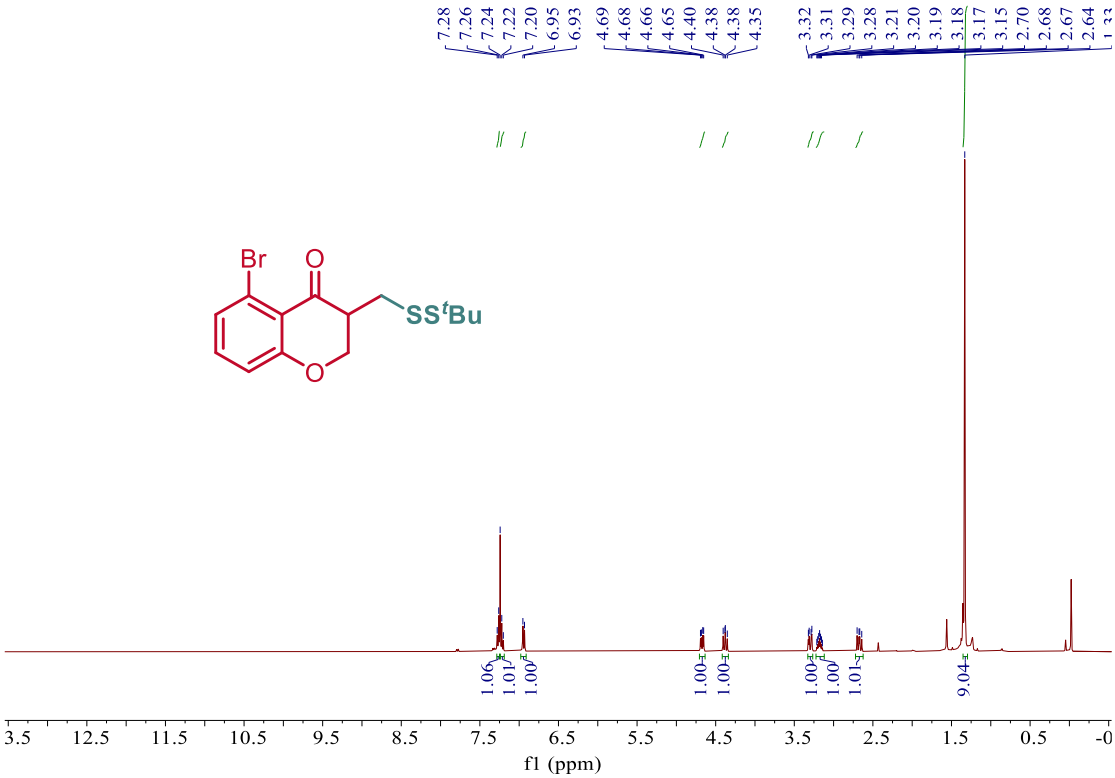
^{1}H NMR Spectrum of 3-((*tert*-Butyldisulfaneyl)methyl)-7-fluorochroman-4-one 5i



^{13}C NMR Spectrum of 3-((*tert*-Butyldisulfaneyl)methyl)-7-fluorochroman-4-one 5i



^{1}H NMR Spectrum of 5-Bromo-3-((*tert*-butyldisulfaneyl)methyl)chroman-4-one 5j



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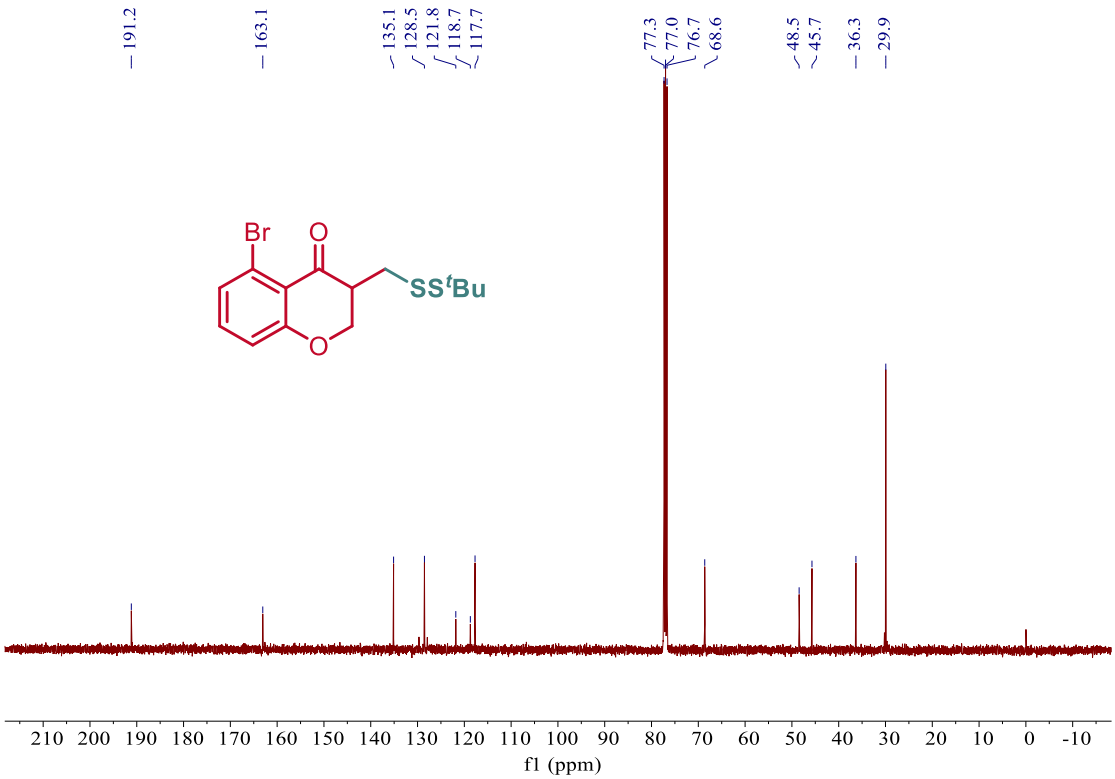

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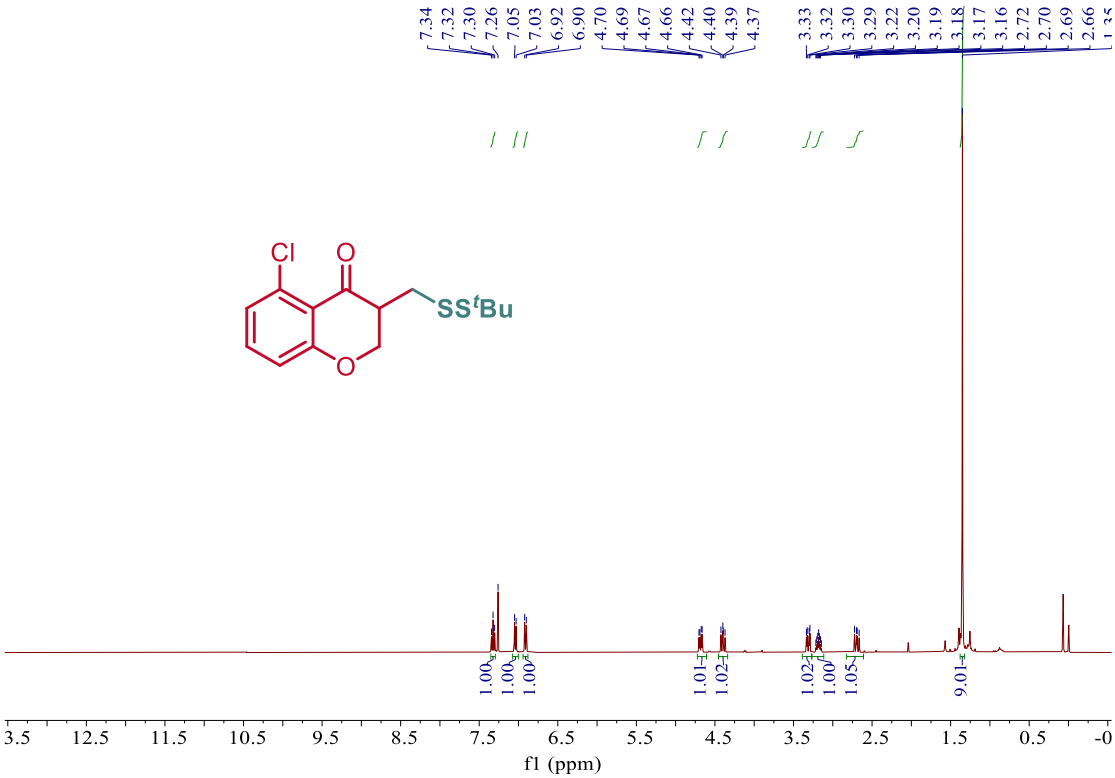

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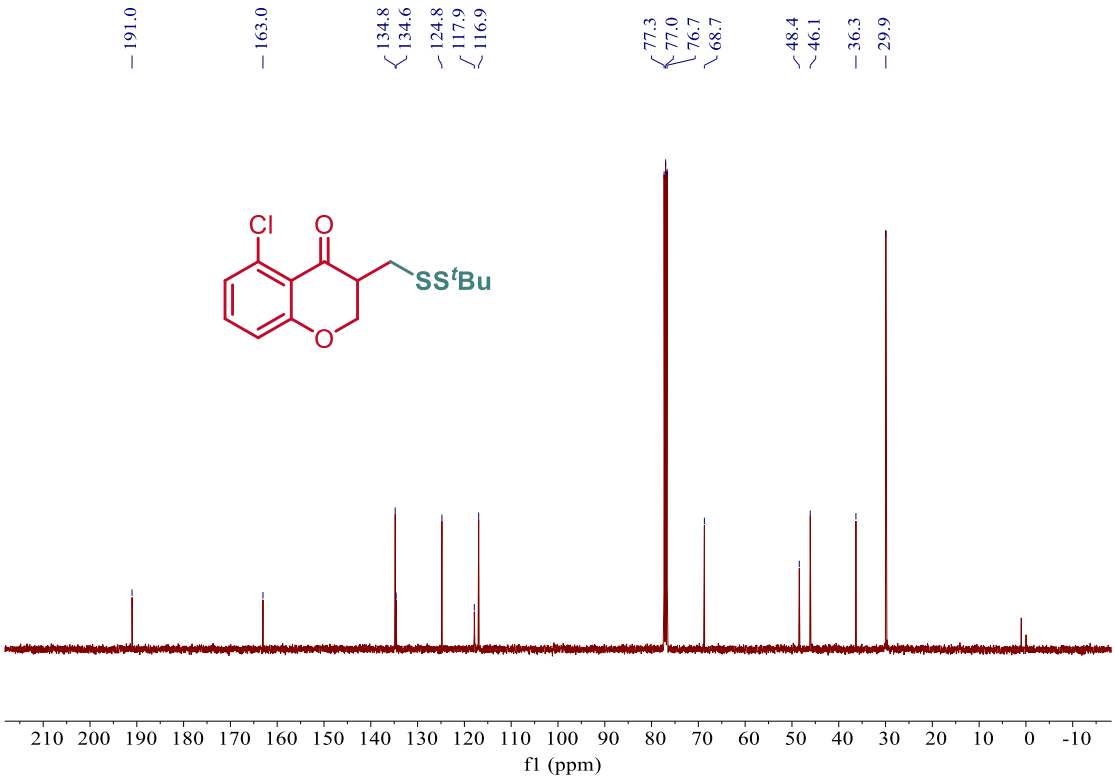
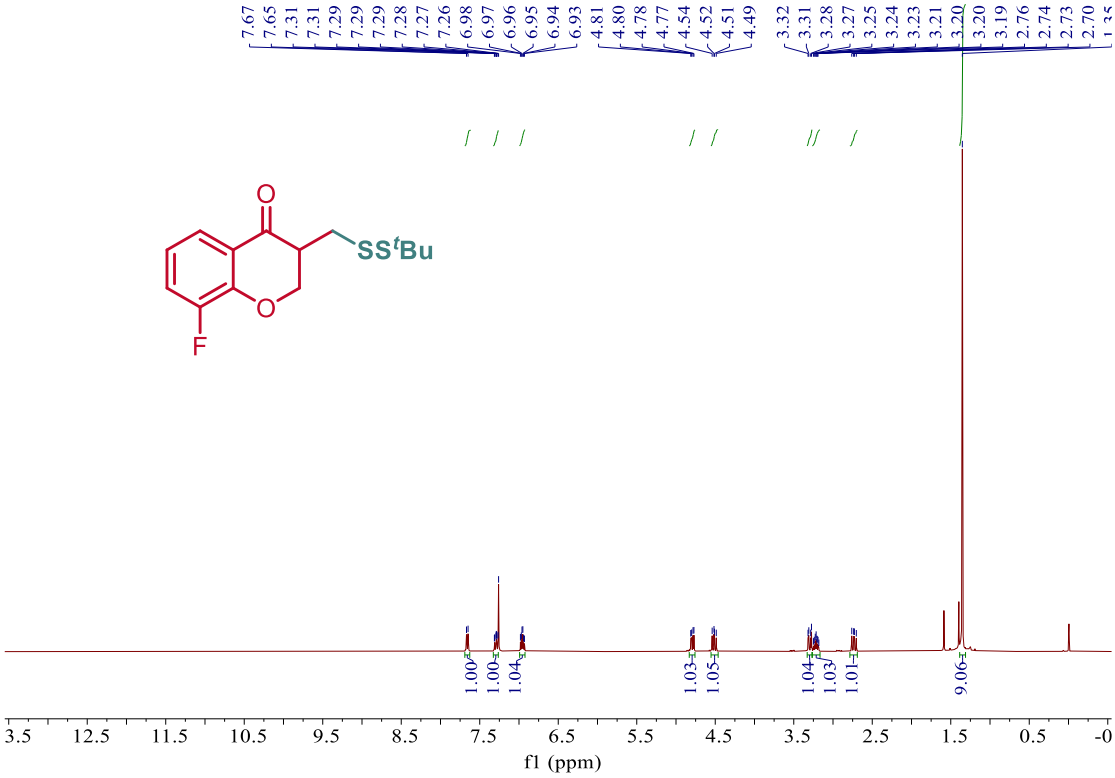
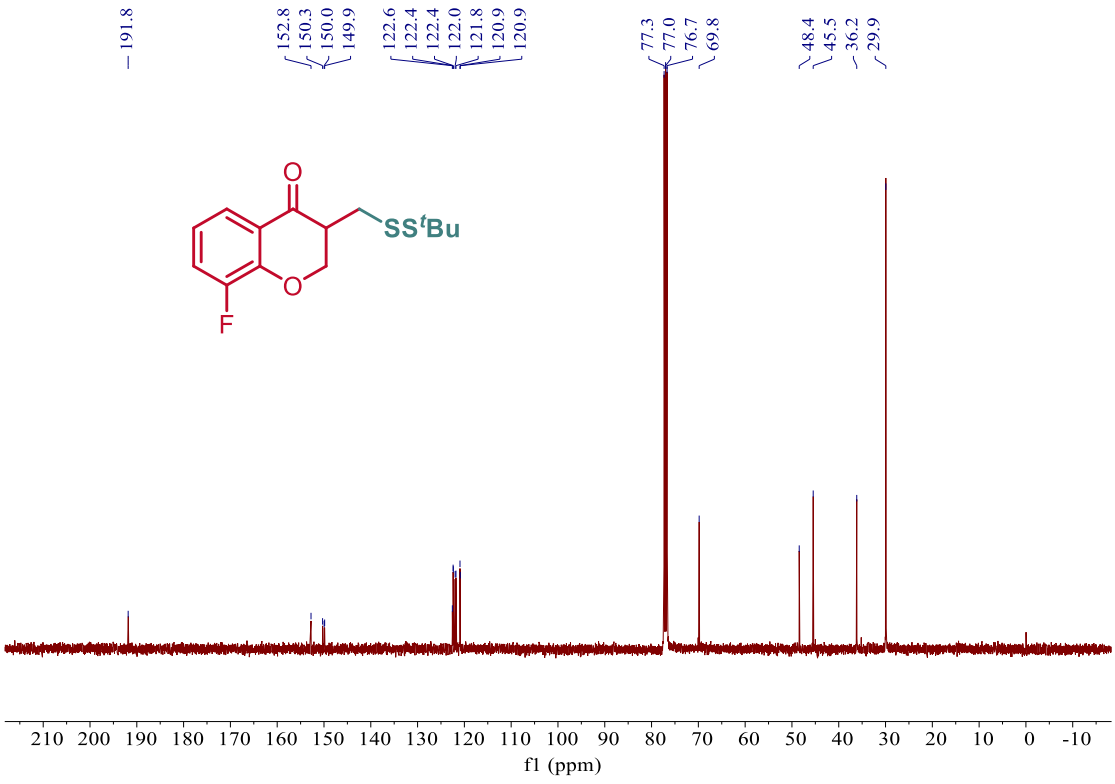


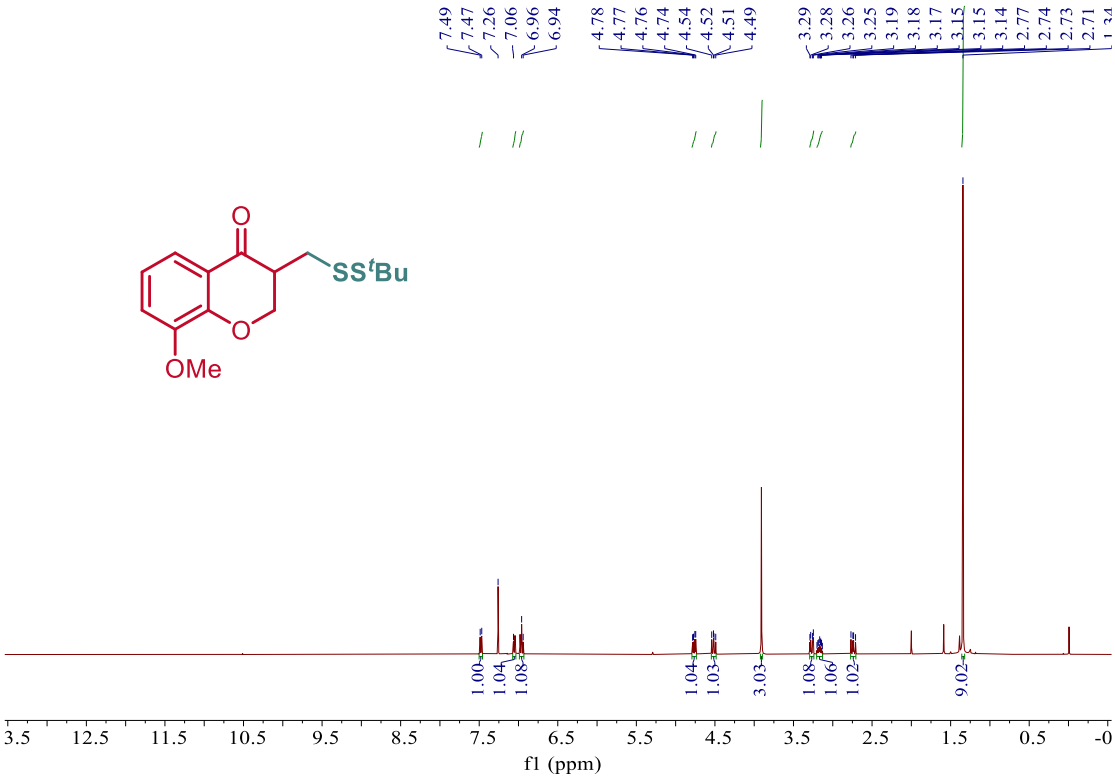
^{1}H NMR Spectrum of 3-((*tert*-Butyldisulfaneyl)methyl)-8-fluorochroman-4-one 5l



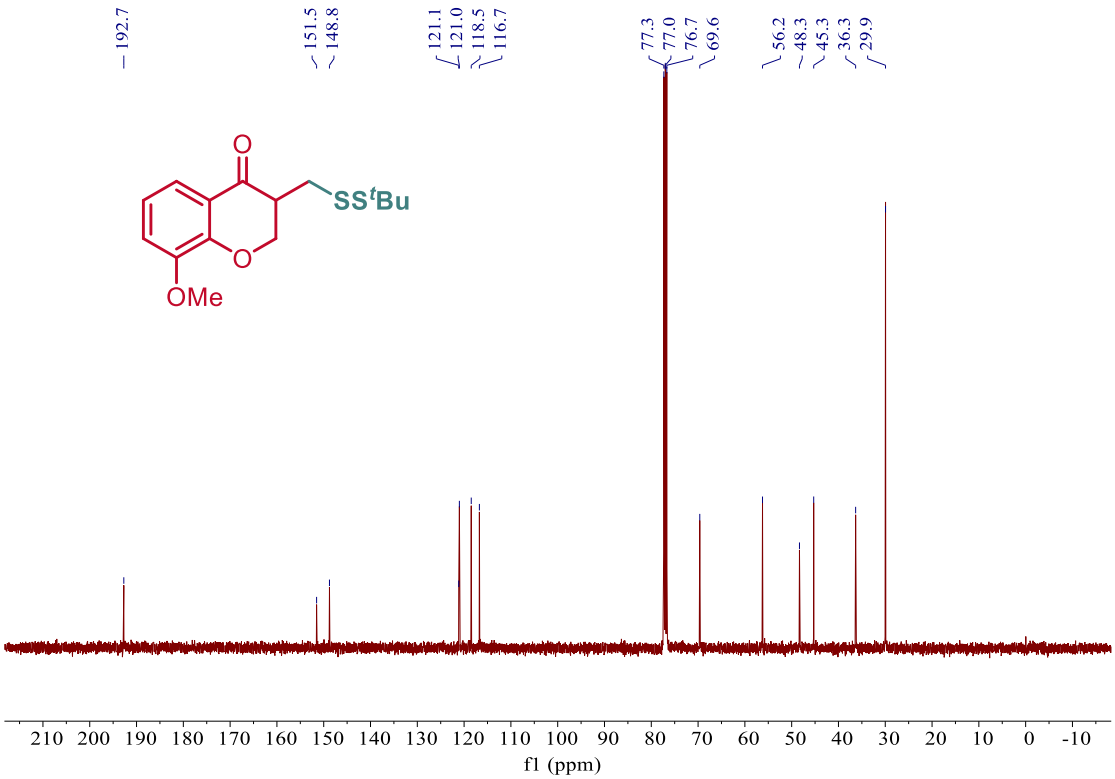
^{13}C NMR Spectrum of 3-((*tert*-Butyldisulfaneyl)methyl)-8-fluorochroman-4-one 5l



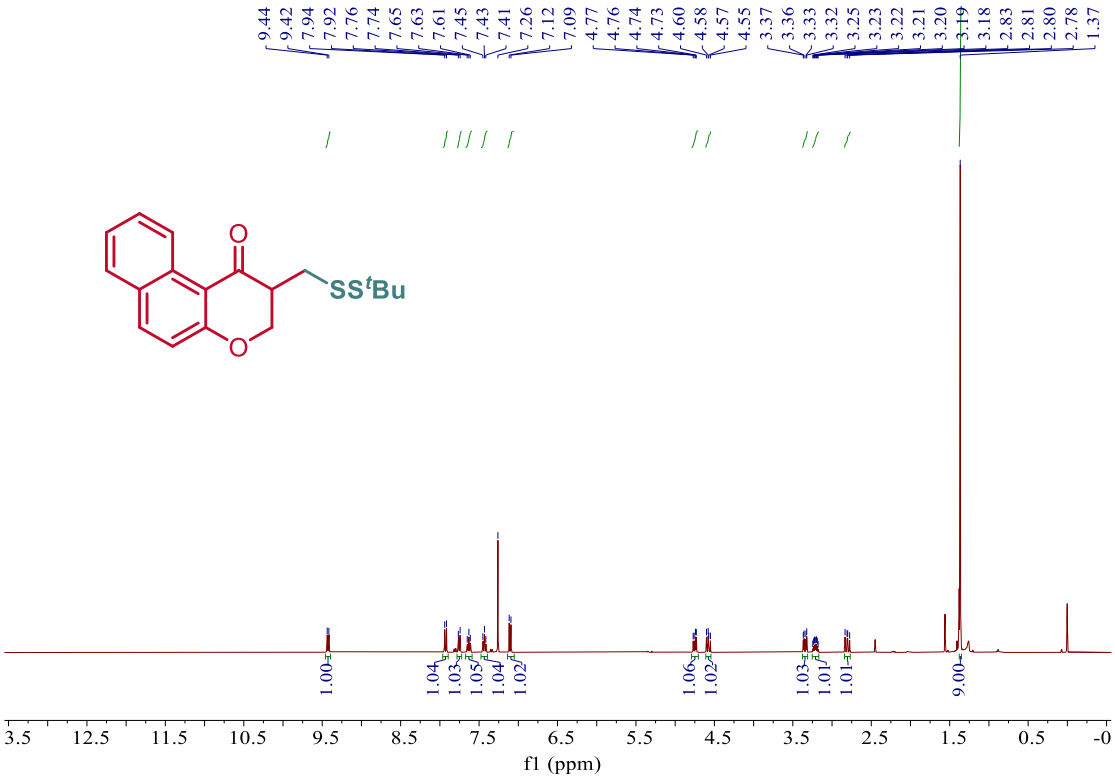
^{1}H NMR Spectrum of 3-((*tert*-Butyldisulfaneyl)methyl)-8-methoxychroman-4-one 5m



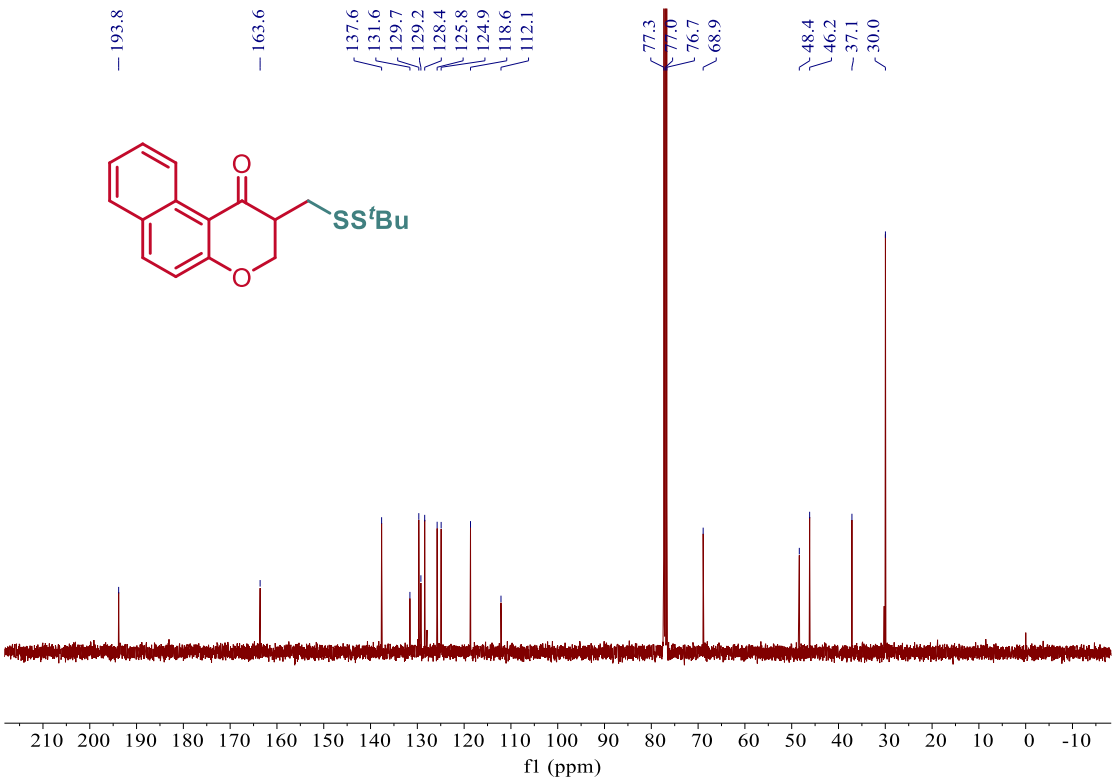
^{13}C NMR Spectrum of 3-((*tert*-Butyldisulfaneyl)methyl)-8-methoxychroman-4-one 5m



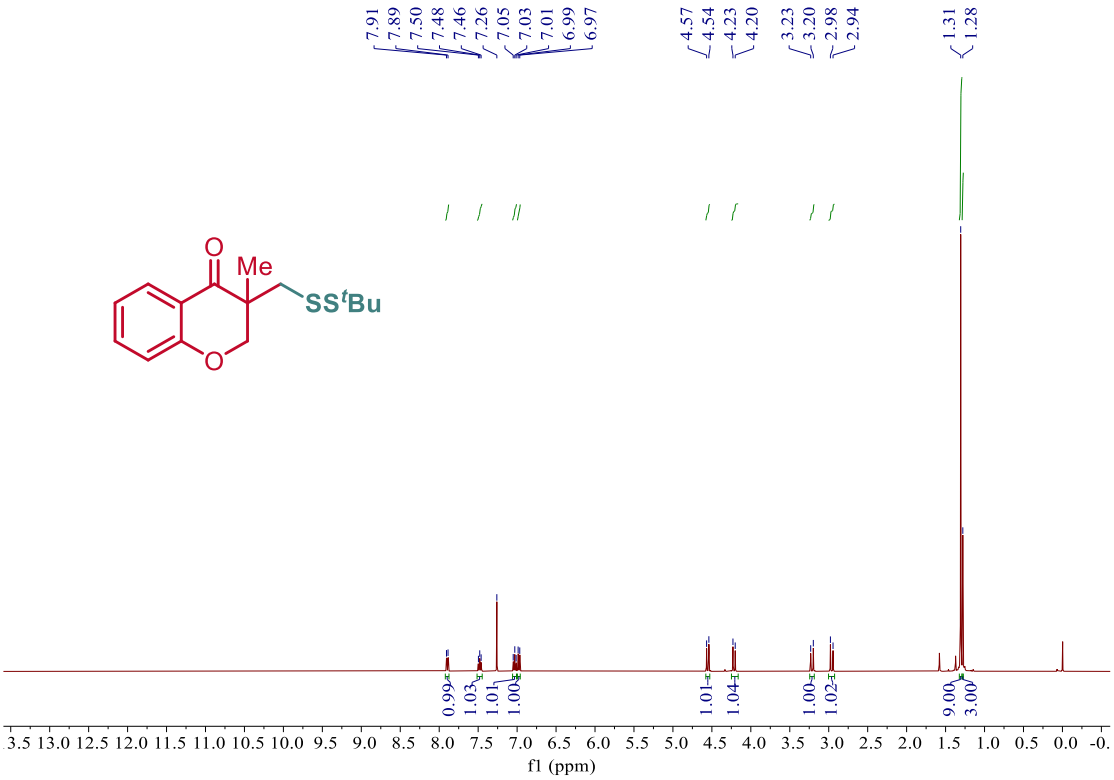
^{1}H NMR Spectrum of 2-((*tert*-Butyldisulfaneyl)methyl)-2,3-dihydro-1*H*-benzo[*f*] chromen-1-one 5n



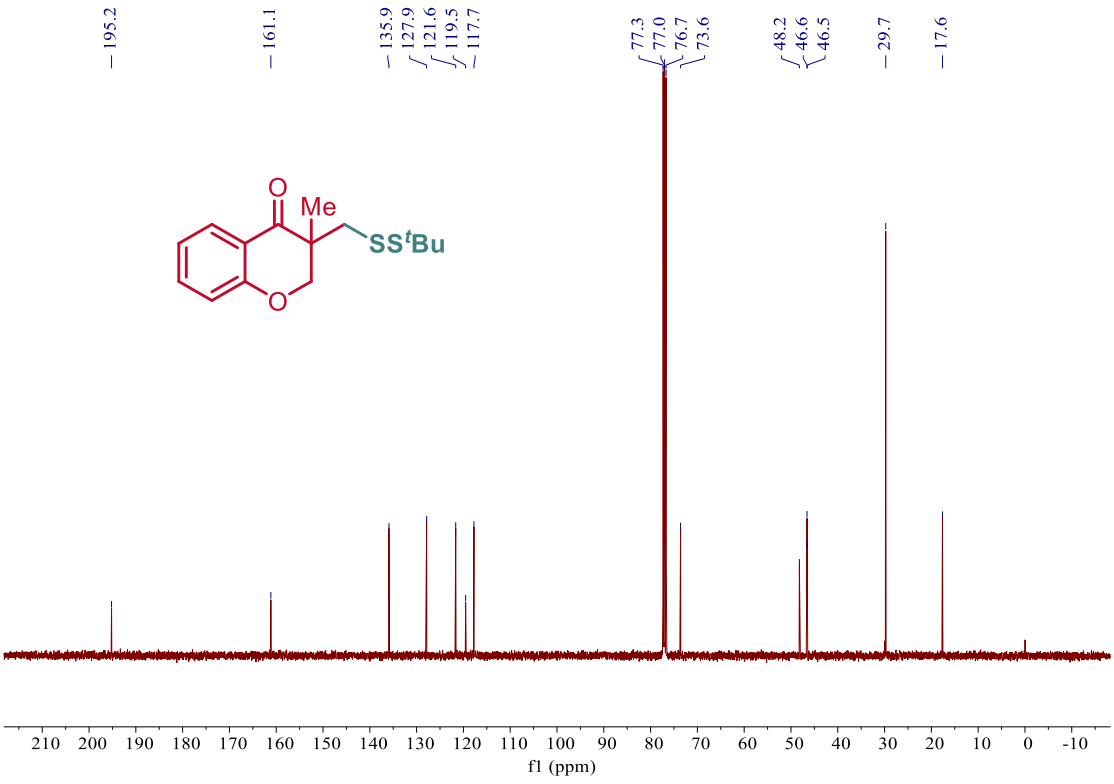
^{13}C NMR Spectrum of 2-((*tert*-Butyldisulfaneyl)methyl)-2,3-dihydro-1*H*-benzo[*f*] chromen-1-one 5n



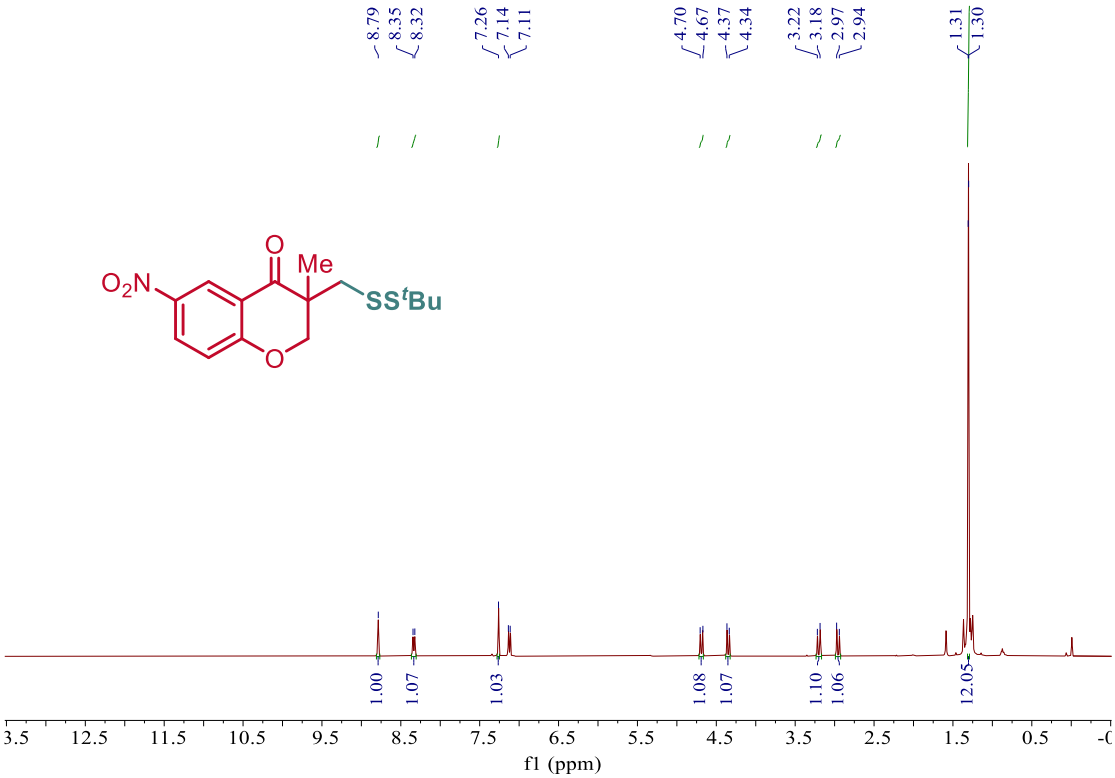
^{1}H NMR Spectrum of 3-((*tert*-Butyldisulfaneyl)methyl)-3-methylchroman-4-one 5o



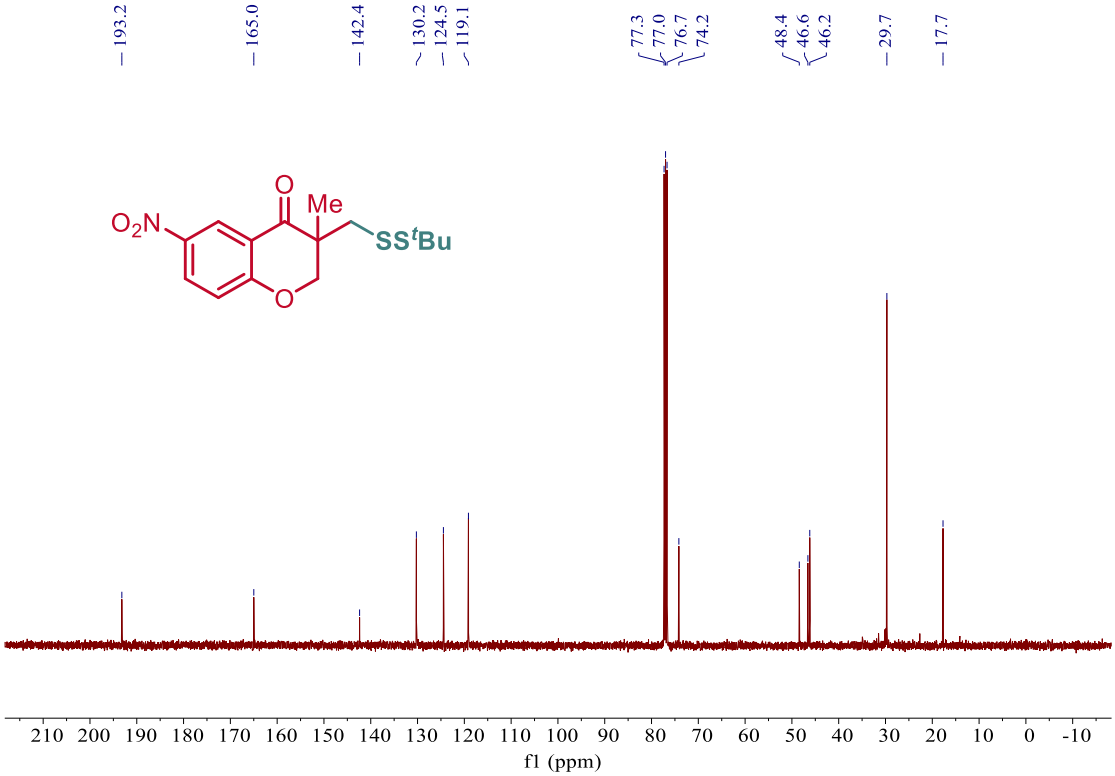
^{13}C NMR Spectrum of 3-((*tert*-Butyldisulfaneyl)methyl)-3-methylchroman-4-one 5o



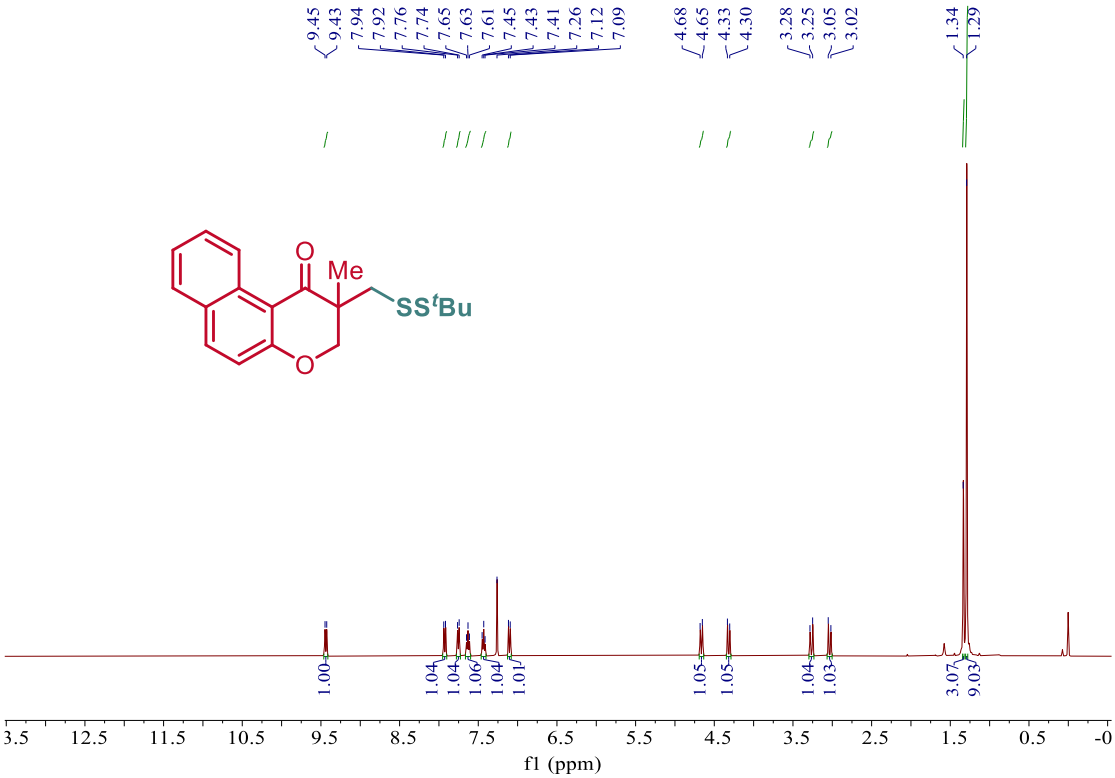
^{1}H NMR Spectrum of 3-((*tert*-Butyldisulfaneyl)methyl)-3-methyl-6-nitrochroman-4-one 5p



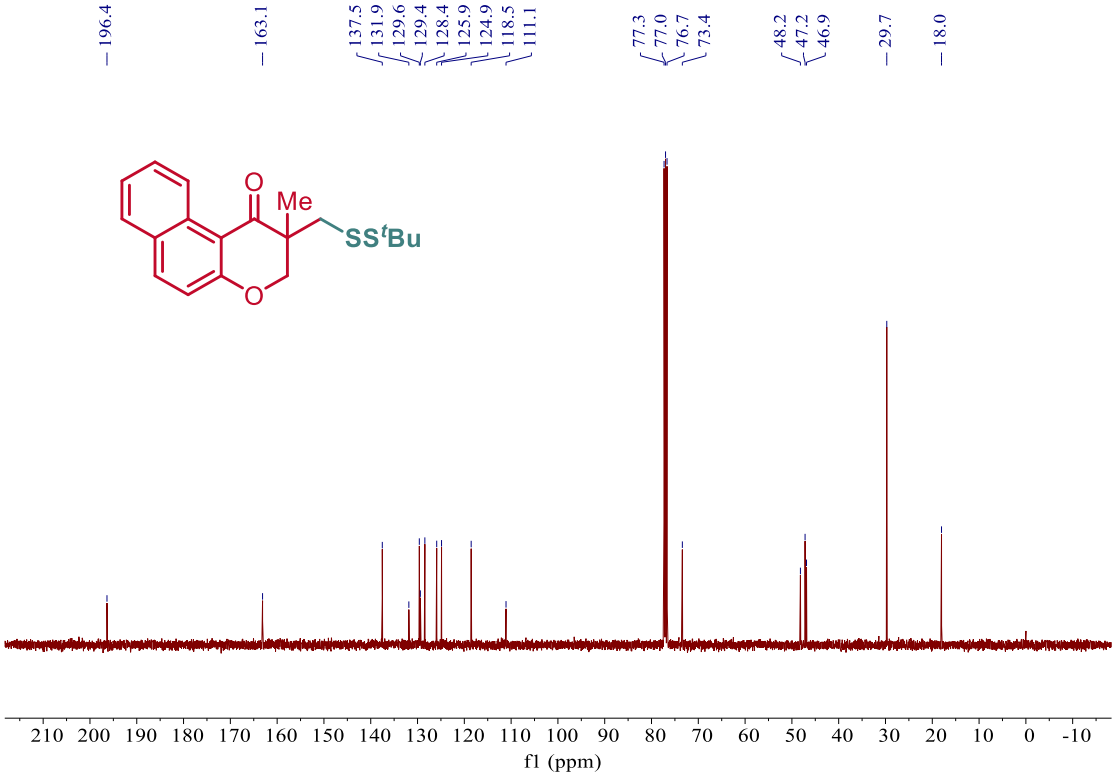
^{13}C NMR Spectrum of 3-((*tert*-Butyldisulfaneyl)methyl)-3-methyl-6-nitrochroman-4-one 5p



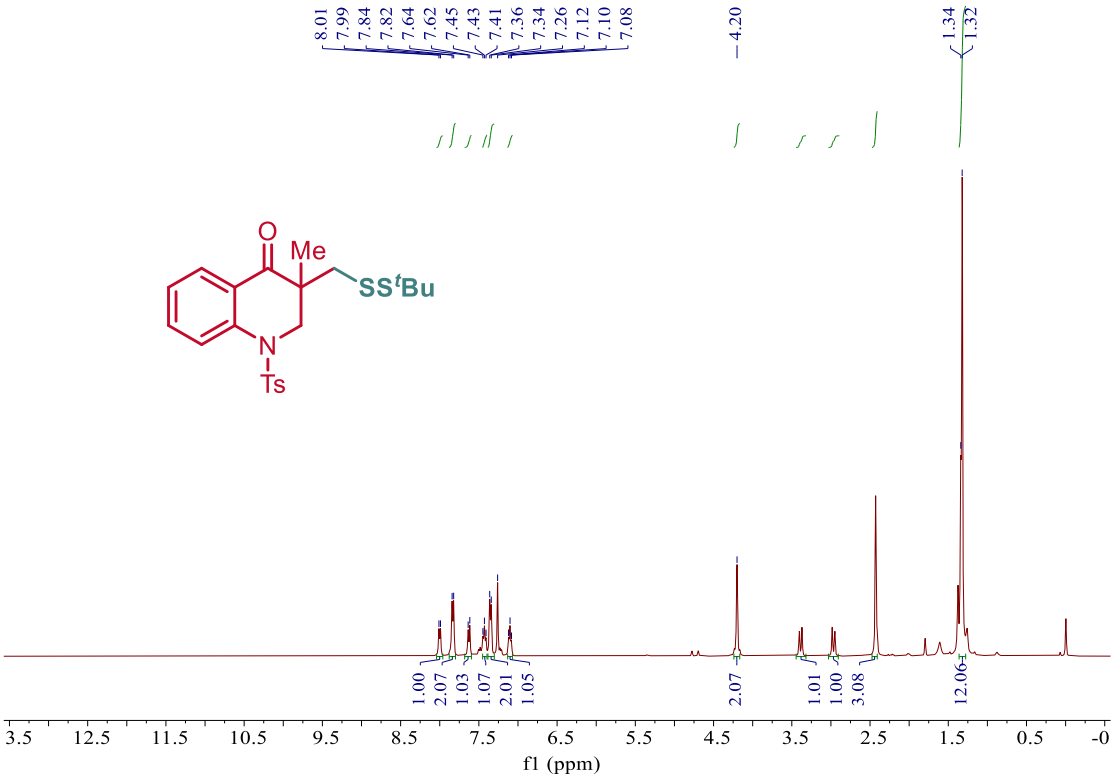
^{1}H NMR Spectrum of 2-((*tert*-Butyldisulfaneyl)methyl)-2-methyl-2,3-dihydro-1*H*-benzo[*f*]chromen-1-one 5q



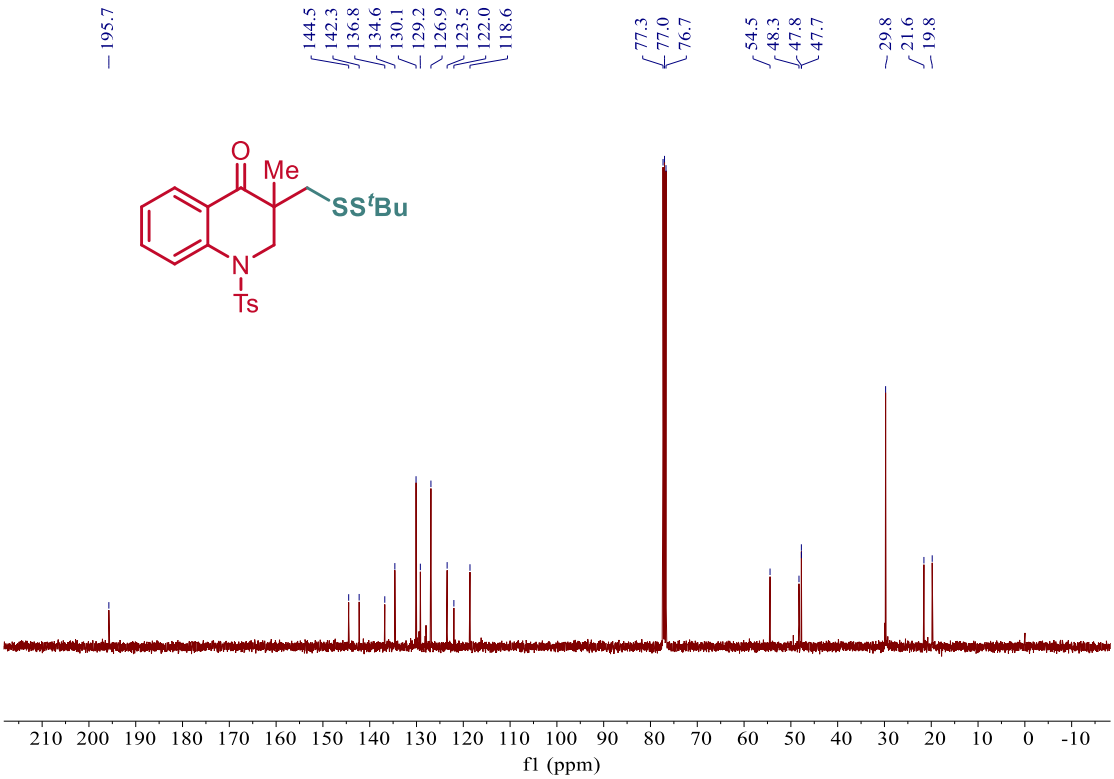
^{13}C NMR Spectrum of 2-((*tert*-Butyldisulfaneyl)methyl)-2-methyl-2,3-dihydro-1*H*-benzo[*f*]chromen-1-one 5q



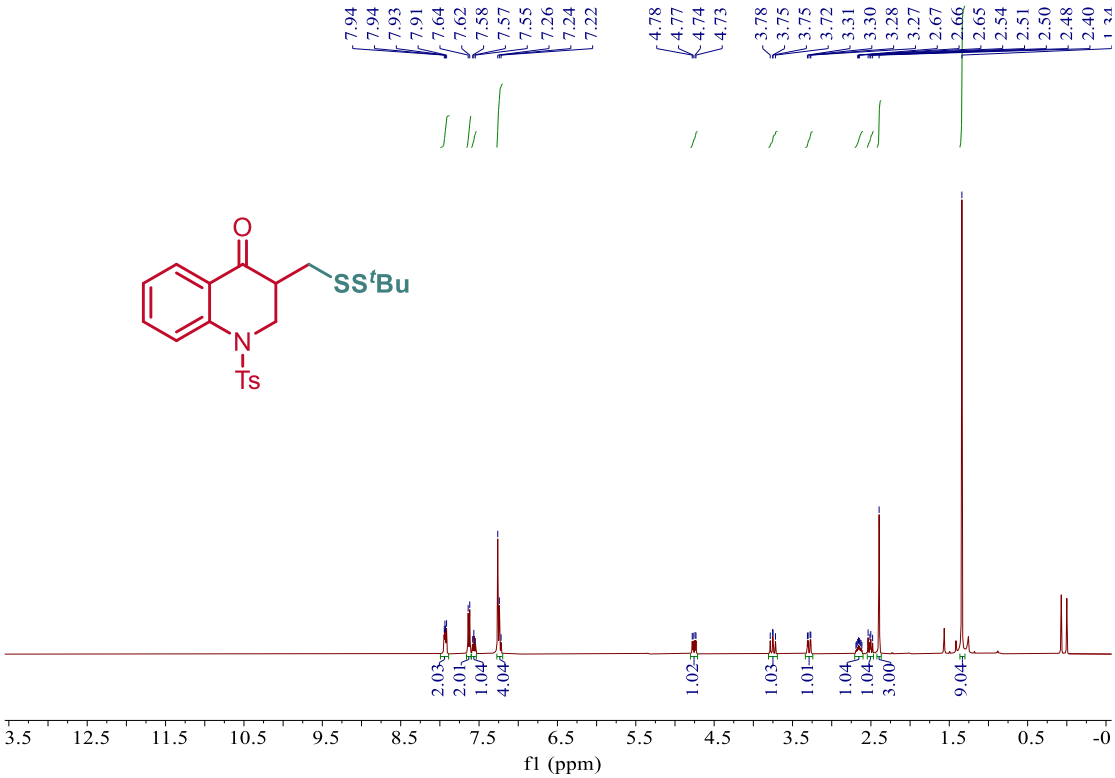
^{1}H NMR Spectrum of 3-((*tert*-Butyldisulfaneyl)methyl)-3-methyl-1-tosyl-2,3-dihydroquinolin-4(1*H*)-one 5r



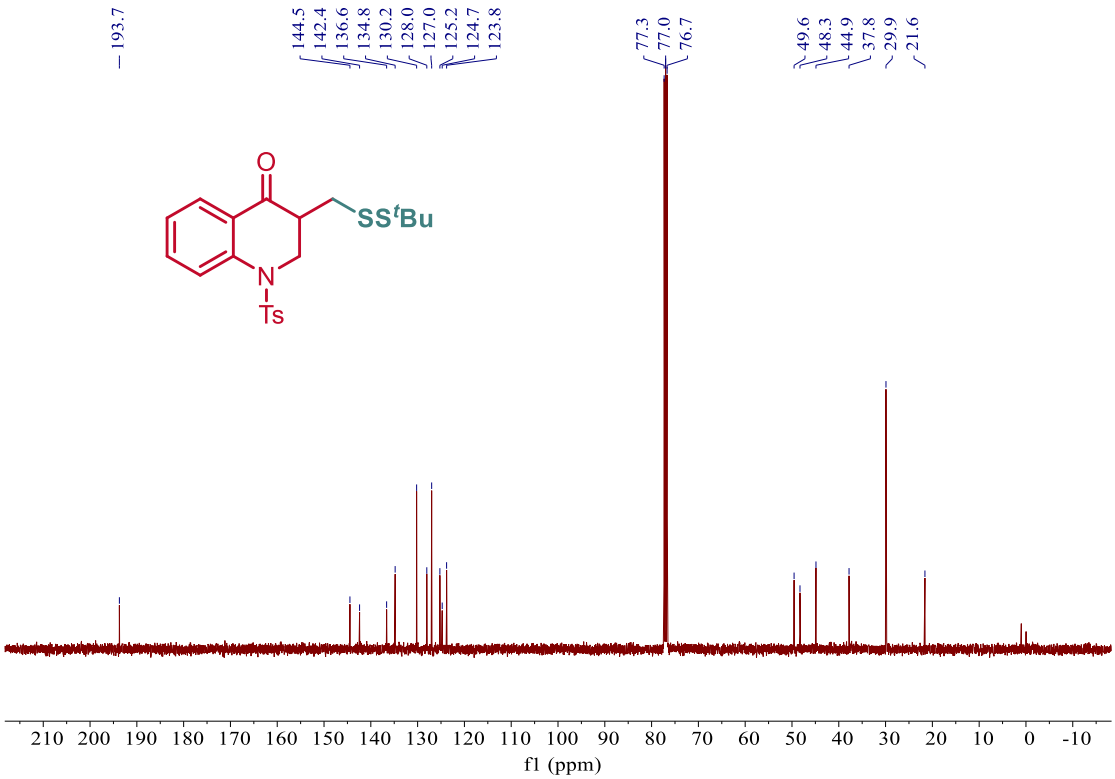
^{13}C NMR Spectrum of 3-((*tert*-Butyldisulfaneyl)methyl)-3-methyl-1-tosyl-2,3-dihydroquinolin-4(1*H*)-one 5r



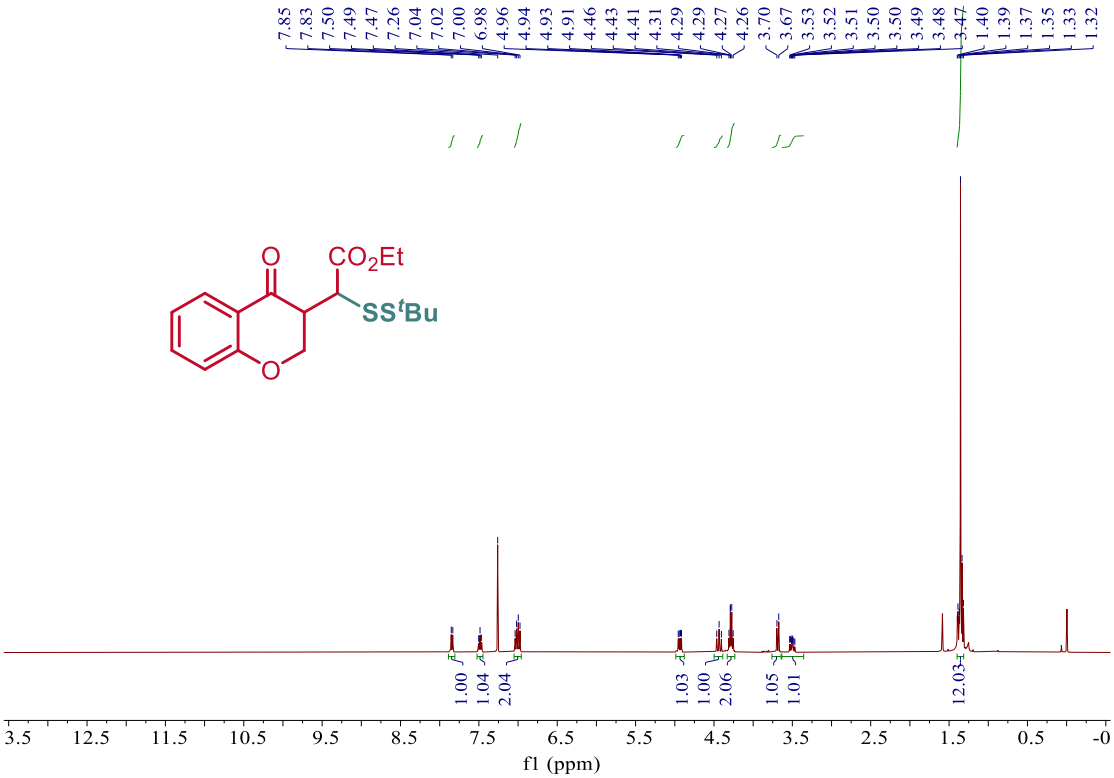
^{1}H NMR Spectrum of 3-((tert-Butyldisulfaneyl)methyl)-1-tosyl-2,3-dihydroquinolin-4(1*H*)-one 5s



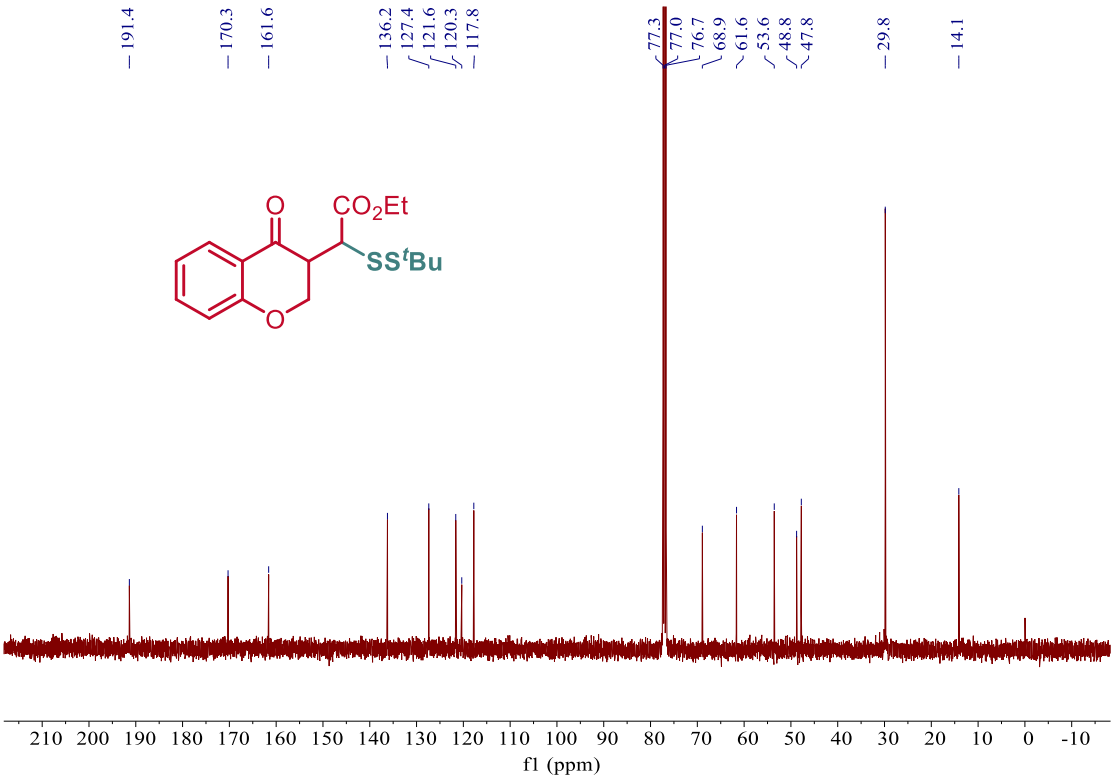
^{13}C NMR Spectrum of 3-((*tert*-Butyldisulfaneyl)methyl)-1-tosyl-2,3-dihydroquinolin-4(1*H*)-one 5s



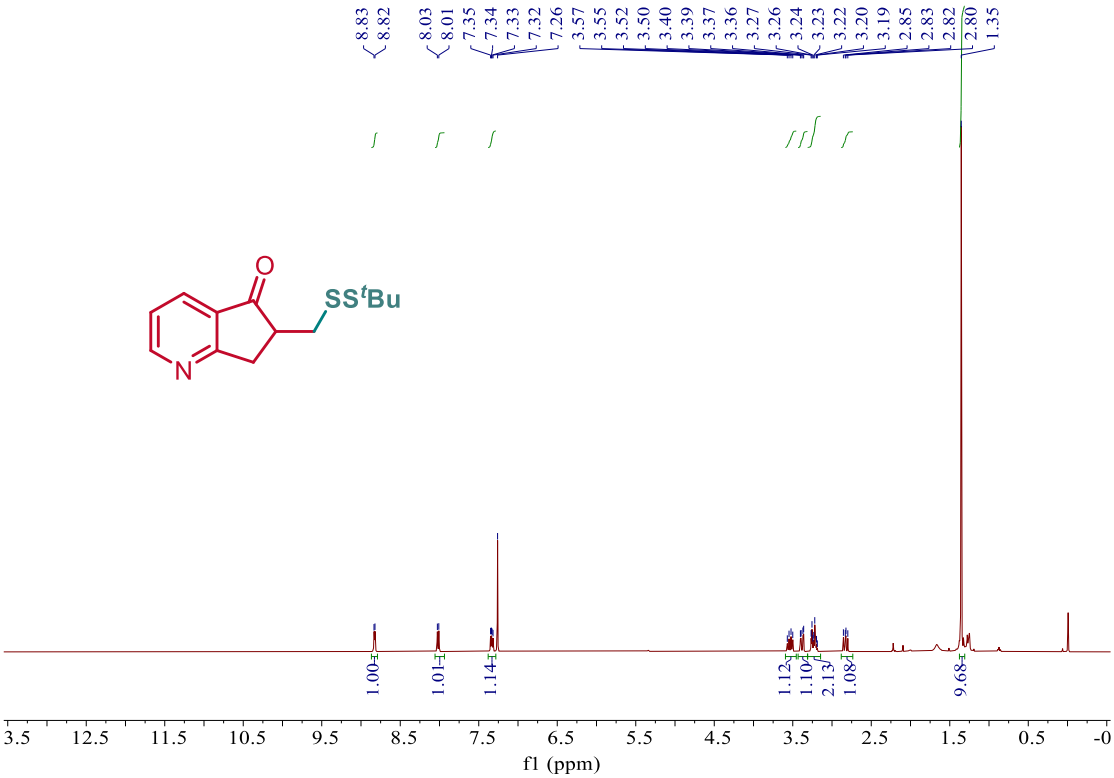
^{1}H NMR Spectrum of Ethyl 2-(*tert*-butyldisulfaneyl)-2-(4-oxochroman-3-yl) acetate 5t



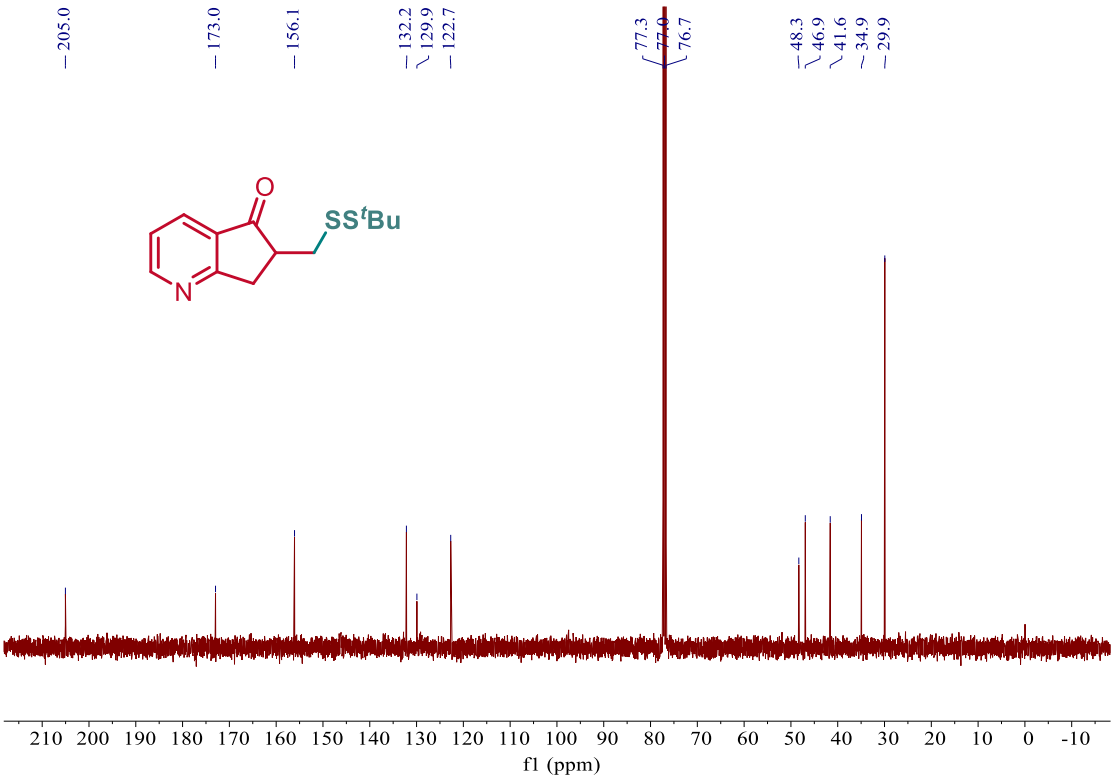
^{13}C NMR Spectrum of Ethyl 2-(*tert*-butyldisulfaneyl)-2-(4-oxochroman-3-yl) acetate 5t



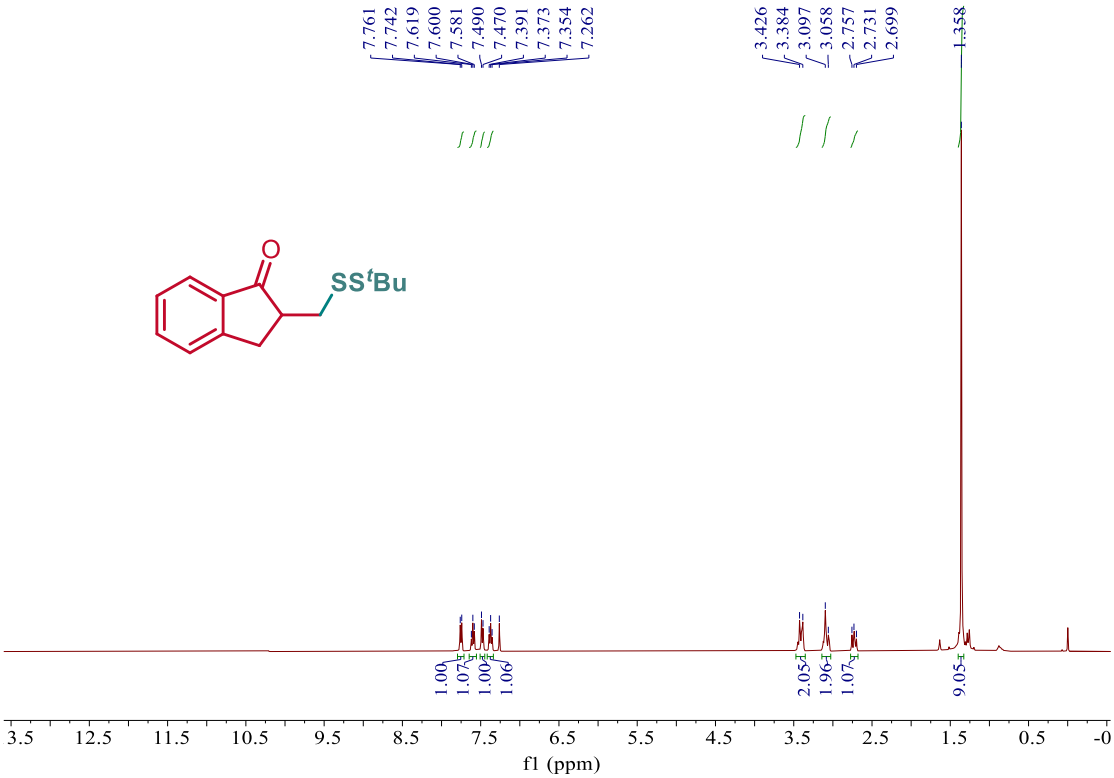
^{1}H NMR Spectrum of 6-((*tert*-Butyldisulfaneyl)methyl)-6,7-dihydro-5*H*-cyclopenta[*b*]pyridin-5-one 5u



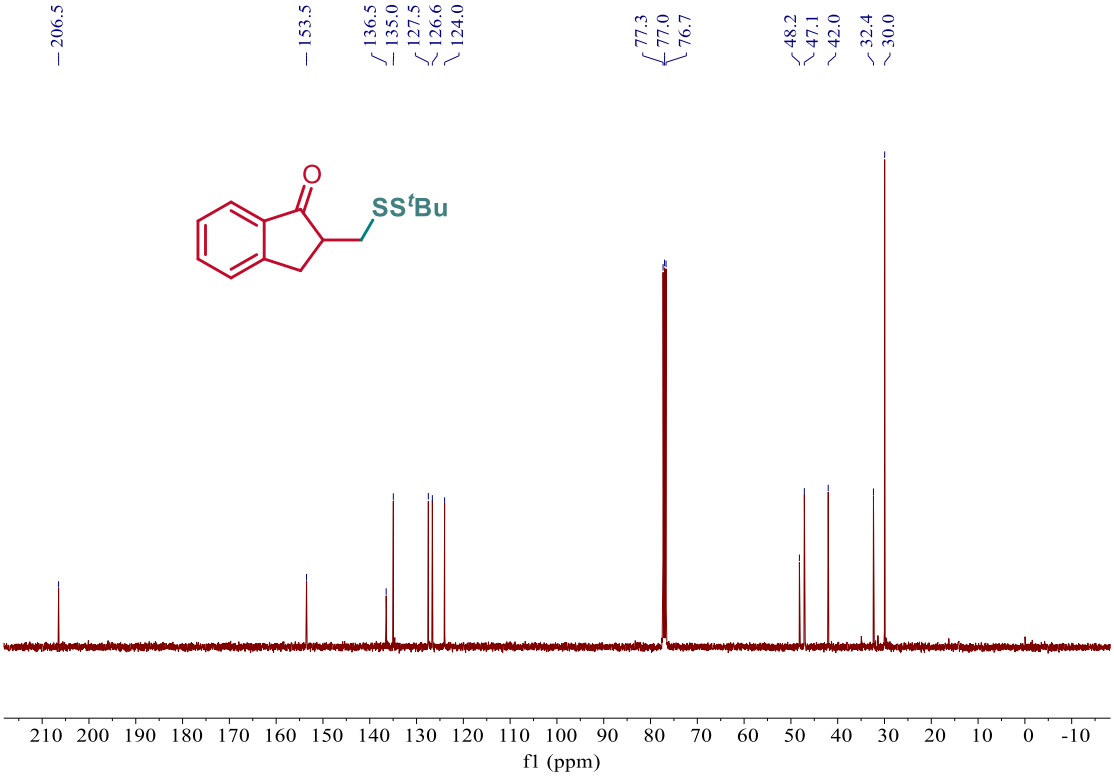
^{13}C NMR Spectrum of 6-((*tert*-Butyldisulfaneyl)methyl)-6,7-dihydro-5*H*-cyclopenta[*b*]pyridin-5-one 5u



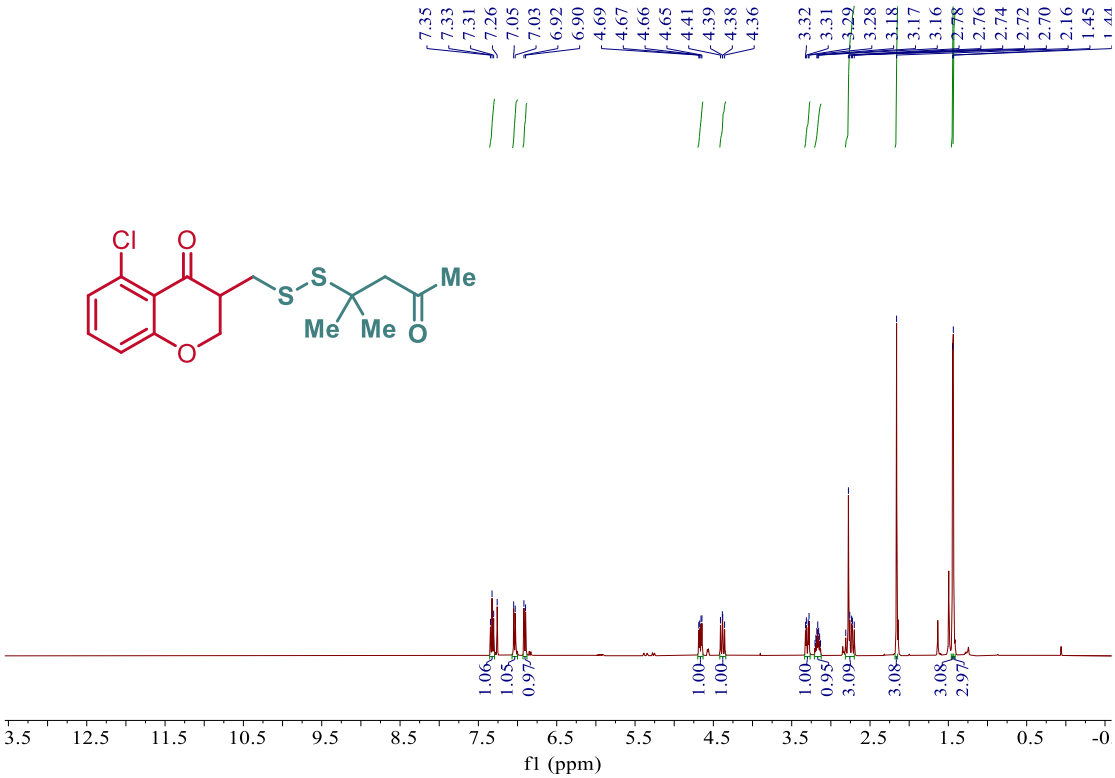
^{1}H NMR Spectrum of 2-((*tert*-Butyldisulfaneyl)methyl)-2,3-dihydro-1*H*-inden-1-one 5v



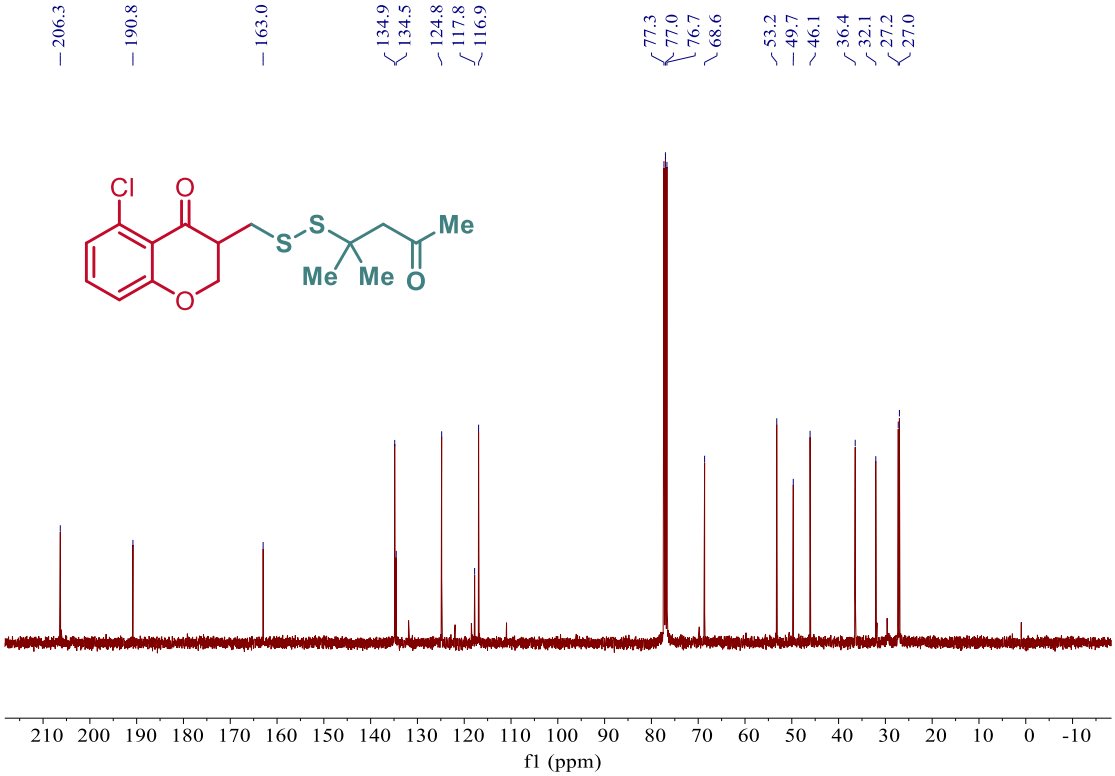
^{13}C NMR Spectrum of 2-((*tert*-Butyldisulfaneyl)methyl)-2,3-dihydro-1*H*-inden-1-one 5v



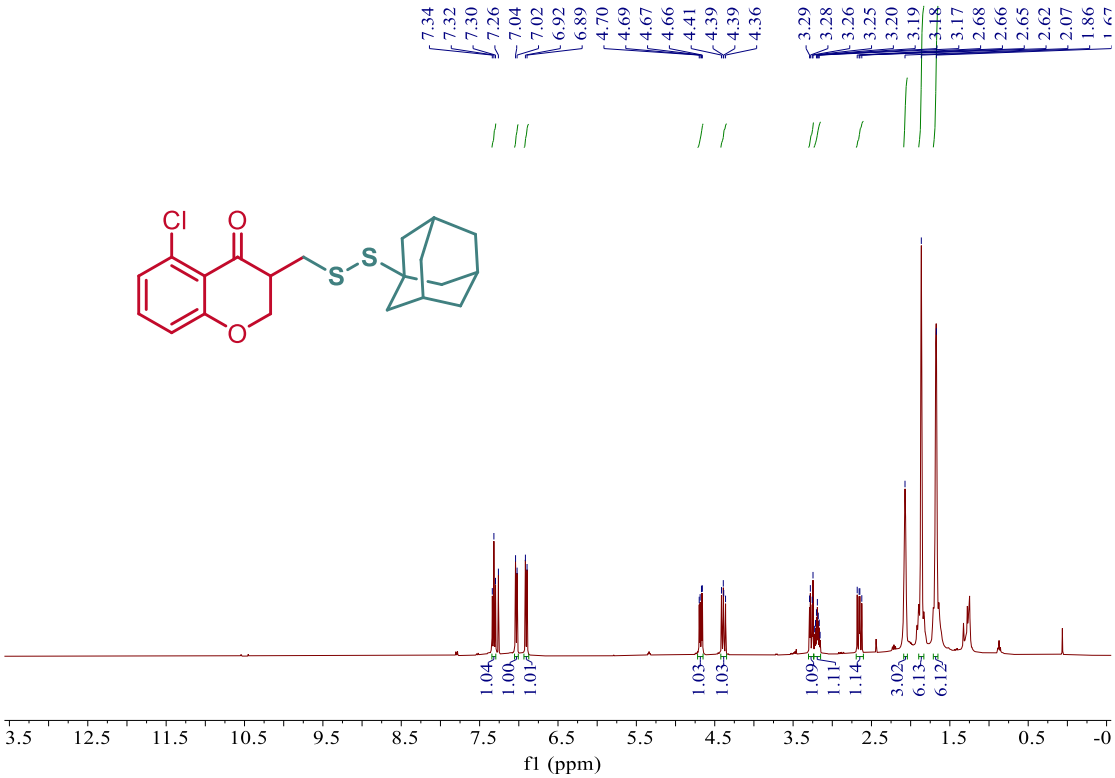
^{1}H NMR Spectrum of 5-Chloro-3-(((2-methyl-4-oxopentan-2-yl)disulfaneyl)methyl)chroman-4-one 5w



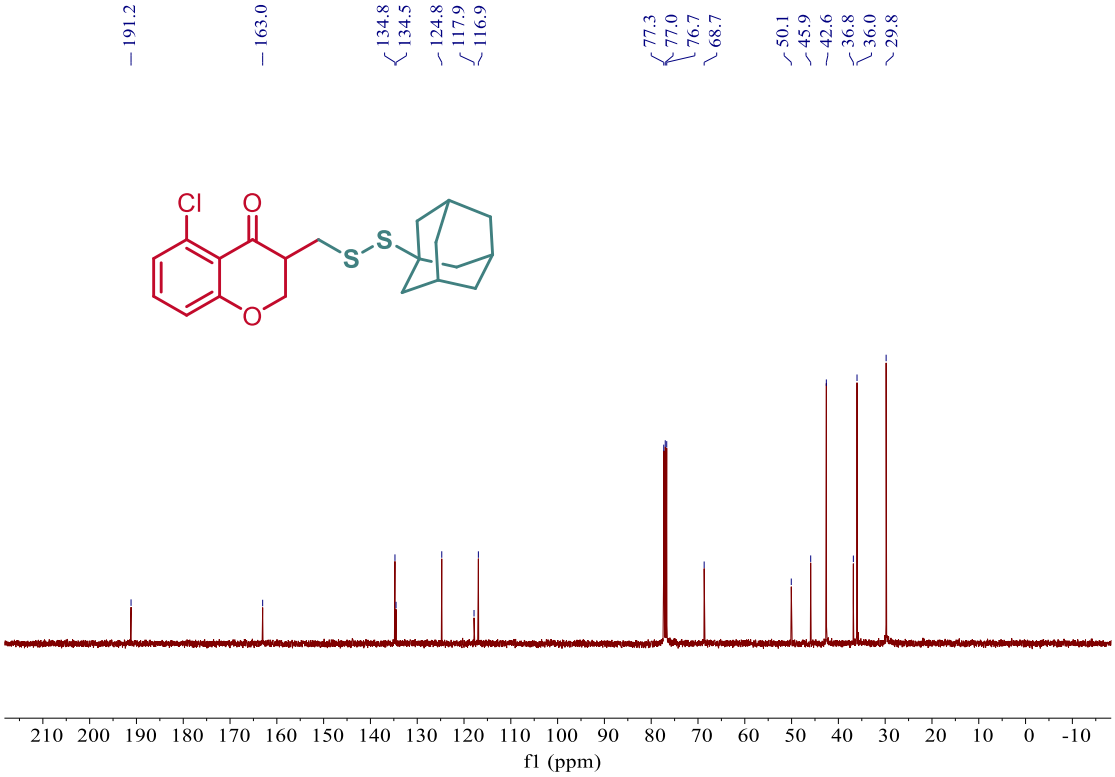
^{13}C NMR Spectrum of 5-Chloro-3-(((2-methyl-4-oxopentan-2-yl)disulfaneyl)methyl)chroman-4-one 5w



^{1}H NMR Spectrum of 3-((((3*R*,5*R*,7*R*)-Adamantan-1-yl)disulfaneyl)methyl)-5-chlorochroman-4-one 5x



^{13}C NMR Spectrum of 3-((((3*R*,5*R*,7*R*)-Adamantan-1-yl)disulfaneyl)methyl)-5-chlorochroman-4-one 5x



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