Supporting Information

Access to Disulfides through Ligand controlling Nickel-catalyzed Dithiosulfonate and Alkyl Halides

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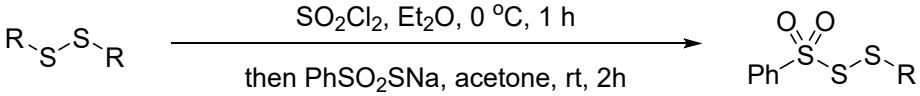
1. General Information

Unless otherwise stated, all commercially available compounds are used as specified without further purification. All reactions were carried out in flame-dried sealed tubes with magnetic stirring. The solvents used for chromatographic analysis were of analytical grade and did not require further purification. Anhydrous DMSO, was purchased from Beijing InnoChem Science & Technology Co., Ltd. Analytical thin-layer chromatography (TLC) was performed on silica gel, visualized by I_2 or irradiation with UV light. For column chromatography, 200-300 mesh silica gel was used. Flash chromatography was performed with SepaBean® machine of Santai Technologies. ^{1}H-NMR and ^{13}C-NMR were recorded on a BRUKER 300 MHz or 400 MHz spectrometer in $CDCl_3$. Chemical shifts (δ) were reported referenced to an internal tetramethylsilane standard or the $CDCl_3$ residual peak (δ 7.26) for 1H NMR. Chemical shifts of 13C NMR are reported relative to $CDCl_3$ (δ 77.16). Data are reported in the following order: chemical shift (δ) in ppm; multiplicities are indicated s (singlet), bs (broad singlet), d (doublet), t (triplet), m (multiplet); coupling constants (J) are in Hertz (Hz). Melting points were measured on an Electrothermal digital melting point apparatus and were uncorrected. IR spectra were recorded on a BRUKER VERTEX 70 spectrophotometer and are reported in terms of frequency of absorption (cm^{-1}). HRMS spectra were obtained by using BRUKER micrOTOF-Q III instrument with ESI or EI source.

2. Synthesis of Substrates

Synthesis of 1a-1g according to the following procedure[1]

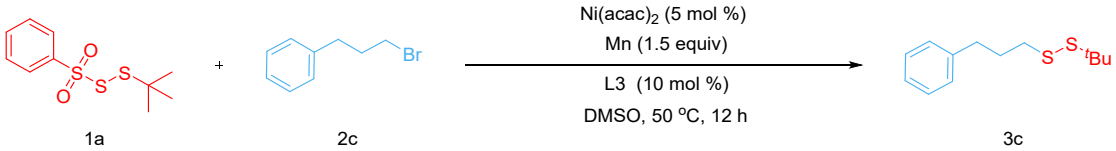


A flame-dried Schlenk-tube equipped with a magnetic stir bar was sealed with a septum, and degassed by alternating vacuum evacuation and argon backfilling (three times) before a solution of RSSR (10.00 mmol, 1.0 equiv) in Et_2O (40 mL) was added. SO_2Cl_2 (1.350 g, 10.00 mmol, 1.0 equiv) was slowly added to the result solution at 0 °C and the mixture was stirred at the same temperature for 1 h. Then a solution of $PhSO_2SNa$[2](3.919 g, 20.00 mmol, 2.0 equiv) in acetone (50 mL) was added slowly at 0 °C and then the mixture was allowed to warm to room temperature stirred for 2 h. The precipitate was filtered and the filtrate was evaporated under reduced pressure with the aid of a rotary evaporator the crude residue was purified by column chromatography to give the desired product.

Synthesis of alkyl halides

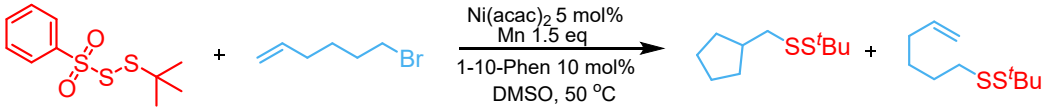
Alkyl halides 2a-2r are commercially available from Energy Chemical, Aladdin, Leyan, Alfa Aesar China. All commercially available substrates were used as received. Alkyl halides 2s[3,4], 2t[5] and 2u[5], were prepared according to previously reported literature procedures.

3. General procedures



1a 2c 3c

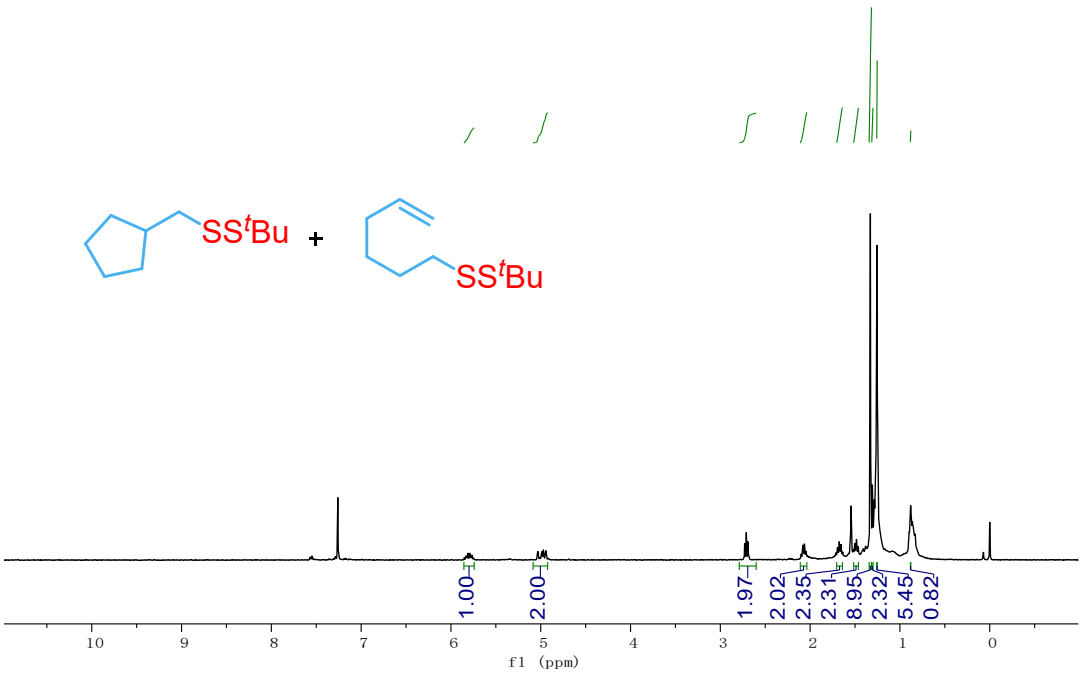
In glovebox, an oven-dried screw-capped 8-mL vial equipped with a magnetic stir bar was charged with dithiosulfonylation (**1a**) (73.4 mg, 0.28 mmol), 1- bromo-3-phenylpropane (**2c**) (39.8 mg, 0.2 mmol), $Ni(acac)_2$ (2.6 mg, 5.0 mol %), **L3** (3.6 mg, 10 mol %), Mn (16.5 mg, 2.5 equiv.), DMSO (1.5 mL) was added via syringe and the mixture was stirred at 50 °C for 12 h. After 12 h, the crude reaction mixture was diluted with ethyl acetate (20 mL) and washed with water (20 mL × 3). The organic layer was dried over Na_2SO_4, filtered, and concentrated. The residue was purified by flash chromatography to afford pure product 3c.



1a 2v 3v 3v'

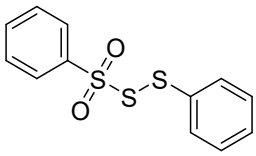
3v/3v': 78% yield: 1.64:1

In glovebox, an oven-dried screw-capped 8-mL vial equipped with a magnetic stir bar was charged with dithiosulfonylation (**1a**) (73.4 mg, 0.28 mmol), 6-bromohex-1-ene (**2v**) (32.4 mg, 0.2 mmol), $Ni(acac)_2$ (2.6 mg, 5.0 mol %), **L3** (3.6 mg, 10 mol %), Mn (16.5 mg, 2.5 equiv.), DMSO (1.5 mL) was added via syringe and the mixture was stirred at 50 °C for 12 h. After 12 h, the crude reaction mixture was diluted with ethyl acetate (20 mL) and washed with water (20 mL × 3). The organic layer was dried over Na_2SO_4, filtered, and concentrated. The residue was purified by flash chromatography to afford pure product 3v and 3v'.



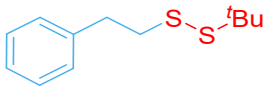
^{1}H NMR Spectra of 3v and 3v' (400 MHz, $CDCl_3$)

4. Spectroscopic Data of Compounds



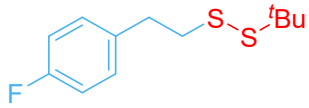
SS-phenyl benzenesulfono(dithioperoxoate) (1g)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.49 (t, *J* = 8.4 Hz, 3H), 7.36 (dt, *J* = 15.6, 7.3 Hz, 3H), 7.26 (d, *J* = 7.1 Hz, 4H).**^{13}C NMR** (101 MHz, Chloroform-*d*) δ 142.9, 136.6, 133.7, 131.4, 129.5, 128.8, 127.8, 127.6. HRMS (ESI): calcd. for $C_{12}H_{11}S_3O_2$ [M+H]+: 282.9916, found: 282.9916.



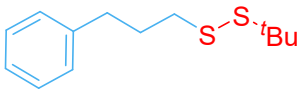
1-(tert-butyl)-2-phenethyldisulfane (3a)

Colorless liquid. yield 46% (20.8 mg, 0.2 mmol scale), and purified by flash column chromatography on silica gel (PE). **IR (neat)**: ν =2961, 2928, 1452, 1361, 1164, 747, 699, 489 cm^{-1}. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.31 (dd, *J* = 8.4, 6.3 Hz, 2H), 7.26 – 7.17 (m, 3H), 2.98 (q, *J* = 3.3 Hz, 4H), 1.36 (s, 9H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 140.3, 128.6, 128.5, 126.4, 47.9, 41.9, 35.8, 30.0. HRMS (ESI): calcd. for $C_{12}H_{18}S_2Na$ [M+Na]+: 249.0742, found: 249.0748.



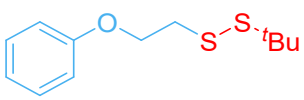
1-(tert-butyl)-2-(4-fluorophenethyl)disulfane (3b)

Colorless liquid. yield 58% (20.8 mg, 0.2 mmol scale), and purified by flash column chromatography on silica gel (PE). **IR (neat)**: ν =2962, 1508, 1223, 1161, 823 cm^{-1}. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.16 (dd, *J* = 8.5, 5.5 Hz, 2H), 6.98 (t, *J* = 8.7 Hz, 2H), 2.97 – 2.89 (m, 4H), 1.35 (s, 9H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 162.8, 160.3, 135.8, 135.8, 130.1, 130.0, 115.4, 115.1, 47.9, 41.9, 41.9, 34.9, 30.0. **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -116.79. HRMS (ESI): calcd. for $C_{12}H_{17}FS_2Na$ [M+Na]+: 267.0648, found: 267.0645.



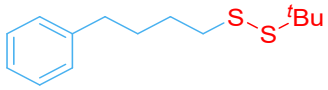
1-(tert-butyl)-2-(3-phenylpropyl)disulfane (3c)

Colorless liquid. yield 70% (33.6 mg, 0.2 mmol scale), and purified by flash column chromatography on silica gel (PE). **IR (neat)**: ν =2958, 2928, 1450, 1165, 741, 697 cm^{-1}. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.31 (dd, *J* = 8.0, 6.8 Hz, 2H), 7.24 – 7.19 (m, 3H), 2.74 (td, *J* = 7.5, 5.5 Hz, 4H), 2.08 – 1.99 (m, 2H), 1.35 (s, 9H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 141.4, 128.5, 128.4, 125.9, 47.8, 39.9, 34.5, 30.7, 30.0. HRMS (ESI): calcd. for $C_{13}H_{20}S_2Na$ [M+Na]+: 263.0899 , found: 263.0905.



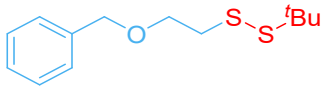
1-(tert-butyl)-2-(2-phenoxyethyl)disulfane (3d)

Colorless liquid. yield 50% (24.2 mg, 0.2 mmol scale), and purified by flash column chromatography on silica gel (PE). **IR (neat)**: ν =2962, 1235, 1165, 1024, 750, 689 cm^{-1}. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.30 (dd, *J* = 8.7, 7.3 Hz, 2H), 6.99 – 6.91 (m, 3H), 4.23 (t, *J* = 7.0 Hz, 2H), 3.06 (t, *J* = 7.0 Hz, 2H), 1.37 (s, 9H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 158. 5, 129.5, 121.0, 114.7, 66.5, 48.0, 39.0, 29.9. HRMS (ESI): calcd. for $C_{12}H_{18}OS_2Na$ [M+Na]+: 265.0691 , found: 265.0698.



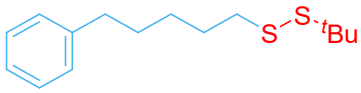
1-(tert-butyl)-2-(4-phenylbutyl)disulfane (3e)

Colorless liquid. yield 62% (31.5 mg, 0.2 mmol scale), and purified by flash column chromatography on silica gel (PE). **IR (neat)**: ν =2934, 1454, 1361, 1165, 745, 697 cm^{-1}. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.32 – 7.27 (m, 2H), 7.22 – 7.17 (m, 3H), 2.78 – 2.72 (m, 2H), 2.69 – 2.62 (m, 2H), 1.73 (qd, *J* = 3.7, 2.4, 1.9 Hz, 4H), 1.34 (s, 9H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 142.2, 128.4, 128.3, 125.8, 47.7, 40.8, 35.5, 30.3, 30.0, 29.0. HRMS (ESI): calcd. for $C_{14}H_{23}$ [M+H]+: 255.1236, found: 255.1233.



1-(2-(benzyloxy)ethyl)-2-(tert-butyl)disulfane (3f)

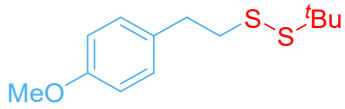
Colorless liquid. yield 62% (31.7 mg, 0.2 mmol scale), and purified by flash column chromatography on silica gel (PE). **IR (neat)**: ν =2961, 2858, 1360, 1096, 736 cm^{-1}. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.26 (d, *J* = 4.4 Hz, 4H), 7.23 – 7.19 (m, 1H), 4.47 (s, 2H), 3.63 (t, *J* = 6.7 Hz, 2H), 2.84 (t, *J* = 6.7 Hz, 2H), 1.25 (s, 9H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 138. 1, 128.4, 127.7, 127.7, 73.1, 68.9, 47.9, 40.3, 29.9. HRMS (ESI): calcd. for $C_{13}H_{20}OS_2Na$ [M+Na]+: 279.0848 , found: 279.0858.



1-(tert-butyl)-2-(5-phenylpentyl)disulfane (3g)

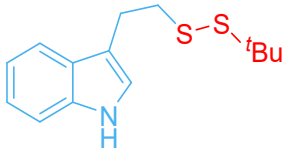
Colorless liquid. yield 63% (33.7 mg, 0.2 mmol scale), and purified by flash column chromatography on silica gel (PE). **IR (neat)**: ν =2927, 2856, 1455, 1165, 740, 698 cm^{-1}. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.32 – 7.27 (m, 2H), 7.19 (ddt, *J* = 7.5, 3.0, 1.8 Hz, 3H), 2.74 – 2.69 (m, 2H), 2.66 – 2.61 (m, 2H), 1.68 (ddt, *J* = 21.0, 15.4, 7.5 Hz, 4H), 1.50 – 1.41 (m, 2H), 1.35 (s, 9H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 142.5, 128.4, 128.3, 125.7, 47.7, 40.8, 35.8, 31.1, 30.0, 29.2, 28.2.

HRMS (ESI): calcd. for $C_{15}H_{24}S_2Na$ [M+Na]+: 291.1212 , found: 291.1221.



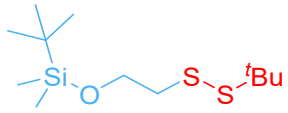
1-(*tert*-butyl)-2-(4-methoxyphenethyl)disulfane (3h)

Colorless liquid. yield 48% (24.5 mg, 0.2 mmol scale), and purified by flash column chromatography on silica gel (PE). **IR (neat)**: ν =2960, 1510, 1243, 1170, 1034, 816 cm^{-1}. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.12 (d, *J* = 8.7 Hz, 2H), 6.84 (d, *J* = 8.6 Hz, 2H), 3.79 (s, 3H), 2.92 (s, 4H), 1.35 (s, 9H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 158.1, 132.3, 129.5, 113.9, 55.3, 47.9, 42.2, 34.9, 30.0. HRMS (ESI): calcd. for $C_{13}H_{20}OS_2Na$ $[M+Na]^+$: 279.0848 , found: 279.0858.



3-(2-(*tert*-butyldisulfanyl)ethyl)-1H-indole (3i)

Yellow solid. yield 70% (37.1 mg, 0.2 mmol scale), and purified by flash column chromatography on silica gel (PE). **Mp**: 27.1-27.5 °C. **IR (neat)**: ν =3412, 2959, 1452, 1353, 1162, 738 cm^{-1}. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.89 (s, 1H), 7.60 (ddt, *J* = 7.9, 1.5, 0.8 Hz, 1H), 7.31 (dt, *J* = 8.2, 1.0 Hz, 1H), 7.22 – 7.15 (m, 1H), 7.12 (ddd, *J* = 8.0, 7.0, 1.1 Hz, 1H), 6.98 (d, *J* = 2.3 Hz, 1H), 3.15 – 3.10 (m, 2H), 3.02 (ddd, *J* = 8.2, 6.7, 1.2 Hz, 2H), 1.34 (s, 9H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 136.3, 127.2, 122.1, 121.9, 119.4, 118.7, 114.6, 111.3, 47.9, 41.1, 30.1, 25.5. HRMS (ESI): calcd. for $C_{14}H_{19}NS_2Na$ $[M+Na]^+$: 288.0851, found: 288.0859.

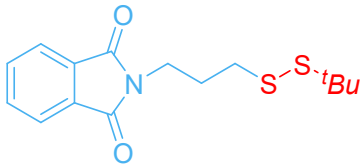


***tert*-butyl(2-(tert-butyldisulfanyl)ethoxy)dimethylsilane (3j)**

Colorless liquid. yield 51% (28.5 mg, 0.2 mmol scale), and purified by flash column chromatography on silica gel (PE). **IR (neat)**: ν =2954, 2858, 1253, 1089, 835, 775 cm^{-1}. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 3.75 (t, *J* = 6.9 Hz, 2H), 2.74 (t, *J* = 6.9 Hz, 2H), 1.26 (s, 9H), 0.82 (s, 9H), -0.00 (s, 6H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 62.2, 47.7, 43.0, 29.9, 25.9, 18.4, -5.2. HRMS (ESI): calcd. for $C_{12}H_{28}OS_2NaSi$ $[M+Na]^+$: 303.1243 , found: 303.1253.

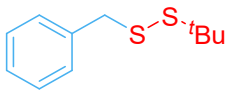
ethyl 6-(tert-butyldisulfanyl)hexanoate (3k)

Colorless liquid. yield 24% (12.6 mg, 0.2 mmol scale), and purified by flash column chromatography on silica gel (PE). **IR (neat)**: ν =2931, 1733, 1250, 1168, 1029 cm^{-1}. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 4.12 (q, *J* = 7.1 Hz, 2H), 2.69 (t, *J* = 7.4 Hz, 2H), 2.30 (t, *J* = 7.5 Hz, 2H), 1.70 – 1.61 (m, 4H), 1.46 – 1.38 (m, 2H), 1.32 (s, 9H), 1.25 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 173.6, 60.3, 47.7, 40.6, 34.2, 30.0, 28.9, 28.0, 24.6, 14.3. HRMS (ESI): calcd. for $C_{12}H_{24}O_2S_2Na$ $[M+Na]^+$: 287.1110 , found: 287.1119.



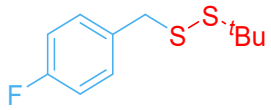
2-(3-(tert-butyldisulfanyl)propyl)isoindoline-1,3-dione (3l)

Colorless liquid. yield 66% (40.7 mg, 0.2 mmol scale), and purified by flash column chromatography on silica gel (PE). **IR (neat)**: ν =1706, 1393, 1359, 1165, 1008, 715 cm^{-1}. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.83 (dd, *J* = 5.4, 3.1 Hz, 2H), 7.70 (dd, *J* = 5.4, 3.1 Hz, 2H), 3.76 (t, *J* = 6.9 Hz, 2H), 2.74 – 2.68 (m, 2H), 2.05 (p, *J* = 7.1 Hz, 2H), 1.29 (s, 9H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 168.3, 134.0, 132.1, 123.2, 47.8, 37.7, 36.9, 29.9, 28.3. HRMS (ESI): calcd. for $C_{15}H_{19}NO_2S_2Na$ $[M+Na]^+$: 332.0749 , found: 332.0758.



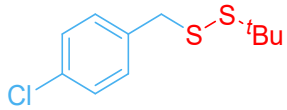
1-benzyl-2-(tert-butyl)disulfane (3m)

Colorless liquid. yield 78% (33.0 mg, 0.2 mmol scale), and purified by flash column chromatography on silica gel (PE). **IR (neat)**: ν =2961, 1455, 1164, 763, 696 cm^{-1}. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.35 – 7.28 (m, 4H), 7.29 – 7.24 (m, 1H), 3.94 (s, 2H), 1.34 (s, 9H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 137.4, 129.2, 128.5, 127.4, 48.1, 45.8, 30.0. HRMS (ESI): calcd. for $C_{11}H_{17}S_2$ $[M+H]^+$: 213.0766, found: 213.0773.



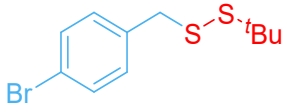
1-(tert-butyl)-2-(4-fluorobenzyl)disulfane (3n)

Yellow liquid. yield 75% (34.5 mg, 0.2 mmol scale), and purified by flash column chromatography on silica gel (PE). **IR (neat)**: ν =2962, 1507, 1225, 1159, 833 cm^{-1}. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.30 – 7.24 (m, 2H), 6.99 (t, *J* = 8.7 Hz, 2H), 3.89 (s, 2H), 1.33 (s, 9H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 163.4, 160.9, 133.3, 133.2, 130.9, 130.8, 115.5, 115.3, 48.1, 44.8, 30.0, 29.9. **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -114.93. HRMS (ESI): calcd. for $C_{11}H_{15}FS_2Na$ $[M+Na]^+$: 253.0491 , found: 253.0499.



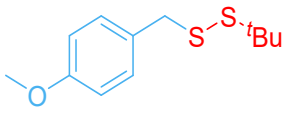
1-(tert-butyl)-2-(4-chlorobenzyl)disulfane (3o)

Colorless liquid. yield 74% (36.4 mg, 0.2 mmol scale), and purified by flash column chromatography on silica gel (PE). **IR (neat)**: ν =2962, 1486, 1164, 1091, 824, 496 cm^{-1}. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.31 – 7.27 (m, 2H), 7.24 (d, *J* = 8.5 Hz, 2H), 3.88 (s, 2H), 1.34 (s, 9H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 136.0, 133.2, 130.6, 128.7, 48.2, 44.8, 30.0. HRMS (ESI): calcd. for $C_{11}H_{15}ClS_2Na$ $[M+Na]^+$: 269.0196 , found: 269.0199.



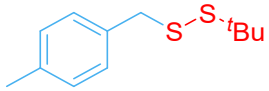
1-(4-bromobenzyl)-2-(tert-butyl)disulfane (3p)

Colorless solid. yield 71% (41.1 mg, 0.2 mmol scale), and purified by flash column chromatography on silica gel (PE). **Mp**: 28.0-28.4 °C. **IR (neat)**: ν =2959, 1479, 1161, 829, 488 cm^{-1}. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.44 (d, *J* = 8.4 Hz, 2H), 7.18 (d, *J* = 8.4 Hz, 2H), 3.86 (s, 2H), 1.34 (s, 9H).**^{13}C NMR** (100 MHz, Chloroform-*d*) δ 136.5, 131.6, 130.9, 121.3, 48.2, 44.8, 30.0. HRMS (ESI): calcd. for $C_{11}H_{15}BrS_2Na$ $[M+Na]^+$: 312.9691 , found: 312.9688.



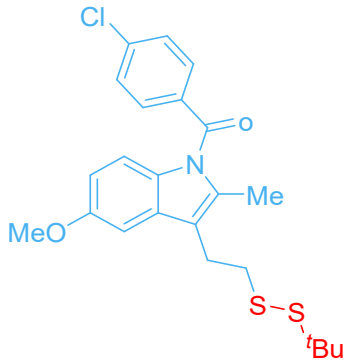
1-(tert-butyl)-2-(4-methoxybenzyl)disulfane (3q)

Yellow liquid. yield 70% (33.8 mg, 0.2 mmol scale), and purified by flash column chromatography on silica gel (PE). **IR (neat)**: ν =2959, 1509, 1243, 1168, 1032, 828 cm^{-1}. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.24 (d, *J* = 8.6 Hz, 2H), 6.86 (d, *J* = 8.6 Hz, 2H), 3.91 (s, 2H), 3.80 (s, 3H), 1.36 (s, 9H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 159.0, 130.4, 129.4, 114.0, 55.3, 48.0, 45.2, 30.1. HRMS (ESI): calcd. for $C_{12}H_{18}OS_2Na$ $[M+Na]^+$: 265.0691 , found: 265.0687.



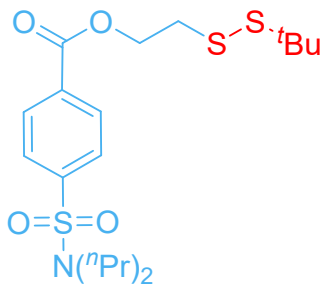
1-(tert-butyl)-2-(4-methylbenzyl)disulfane (3r)

Colorless liquid. yield 69% (31.1 mg, 0.2 mmol scale), and purified by flash column chromatography on silica gel (PE). **IR (neat)**: ν =2961, 1457, 1164, 813, 469 cm^{-1}. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.21 (d, *J* = 8.1 Hz, 2H), 7.13 (d, *J* = 7.8 Hz, 2H), 3.92 (s, 2H), 2.34 (s, 3H), 1.36 (s, 9H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 137.1, 134.3, 129.2, 129.1, 48.0, 45.6, 30.1, 21.2. HRMS (ESI): calcd. for $C_{12}H_{18}S_2Na$ $[M+Na]^+$: 249.0742 , found: 249.0733.



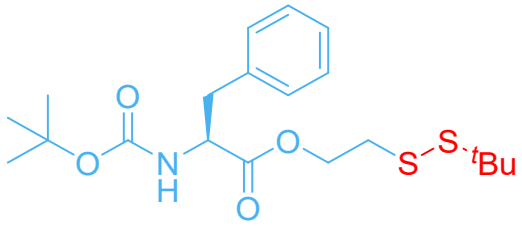
(3-(2-(tert-Butyldisulfaneyl)ethyl)-5-methoxy-2-methyl-1H-indol-1-yl)(4-chlorophenyl)methanone (11r) (3s)

Yellow solid. yield 69% (31.1 mg, 0.2 mmol scale), and purified by flash column chromatography on silica gel (PE:EA = 10:1). **Mp**: 80.0-80.4 °C. **IR (neat)**: ν =2961, 1682, 1362, 1312, 1220 cm^{-1}. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.67 – 7.63 (m, 2H), 7.49 – 7.43 (m, 2H), 6.97 – 6.87 (m, 2H), 6.67 (dd, *J* = 9.0, 2.6 Hz, 1H), 3.84 (s, 3H), 3.03 (dd, *J* = 9.2, 6.7 Hz, 2H), 2.91 (dd, *J* = 8.6, 6.1 Hz, 2H), 2.35 (s, 3H), 1.36 (s, 9H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 168.3, 156.0, 139.1, 134.8, 134.1, 131.1, 131.0, 130.8, 129.1, 117.8, 115.1, 111.3, 101.1, 55.7, 48.0, 39.7, 30.0, 24.3, 13.5. HRMS (ESI): calcd. for $C_{23}H_{26}ClNOS_2Na$ $[M+Na]^+$: 454.1037 , found: 454.1047.



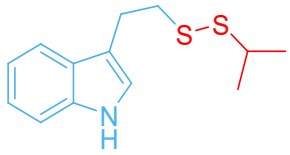
2-(tert-butyldisulfanyl)ethyl 4-(N,N-dipropylsulfamoyl)benzoate (3t)

Colorless liquid. yield 40% (34.6 mg, 0.2 mmol scale), and purified by flash column chromatography on silica gel (PE:EA = 10:1). **IR (neat)**: ν =2965, 1725, 1267, 1159, 1097, 732, 602 cm^{-1}. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.16 (d, *J* = 8.6 Hz, 2H), 7.88 – 7.84 (m, 2H), 4.58 (t, *J* = 6.6 Hz, 2H), 3.11 – 3.02 (m, 6H), 1.58 – 1.48 (m, 4H), 1.34 (s, 9H), 1.25 (s, 1H), 0.85 (t, *J* = 7.4 Hz, 6H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 165.0, 144.4, 133.3, 130.3, 127.0, 63.7, 49.9, 48.1, 38.5, 29.9, 21.9, 11.2. HRMS (ESI): calcd. for $C_{19}H_{31}NO_4S_3Na$ $[M+Na]^+$: 456.1307 , found: 456.1304.



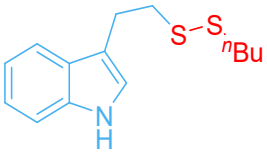
2-(tert-butyldisulfanyl)ethyl (tert-butoxycarbonyl)-L-phenylalaninate (3u)

Colorless liquid. yield 51% (42.1 mg, 0.2 mmol scale), and purified by flash column chromatography on silica gel (PE:EA = 10:1). **IR (neat)**: ν =2968, 1709, 1498, 1358, 1159, 1055 cm^{-1}. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.32 – 7.21 (m, 3H), 7.18 – 7.12 (m, 2H), 5.00 (d, *J* = 8.4 Hz, 1H), 4.58 (d, *J* = 7.9 Hz, 1H), 4.33 (td, *J* = 7.0, 2.3 Hz, 2H), 3.18 – 2.96 (m, 2H), 2.83 (t, *J* = 6.8 Hz, 2H), 1.41 (s, 9H), 1.34 (s, 9H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 155.1, 136.0, 129.4, 128.5, 127.0, 79.9, 63.5, 54.5, 48.0, 38.4, 38.1, 29.9, 28.3. HRMS (ESI): calcd. for $C_{20}H_{31}NO_4S_2Na$ $[M+Na]^+$: 436.1587 , found: 436.1581.



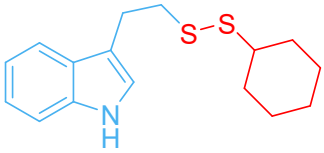
3-(2-(isopropyldisulfanyl)ethyl)-1H-indole (4a)

Yellow liquid. yield 61% (30.6 mg, 0.2 mmol scale), and purified by flash column chromatography on silica gel (PE). **IR (neat)**: ν =3411, 2960, 1449, 1235, 738, 473 cm^{-1}. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.90 (s, 1H), 7.60 (dt, *J* = 7.9, 1.0 Hz, 1H), 7.32 (dd, *J* = 8.0, 1.1 Hz, 1H), 7.19 (tt, *J* = 8.0, 1.1 Hz, 1H), 7.15 – 7.08 (m, 1H), 6.99 (dd, *J* = 2.3, 1.0 Hz, 1H), 3.18 – 3.10 (m, 2H), 3.05 – 2.97 (m, 3H), 1.32 (dd, *J* = 6.8, 1.0 Hz, 6H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 136.3, 127.2, 122.1, 121.8, 119.4, 118.7, 114.6, 111.2, 41.3, 40.4, 25.5, 22.7. HRMS (ESI): calcd. for $C_{13}H_{18}NS_2$ $[M+H]^+$: 252.0875, found: 252.0882.



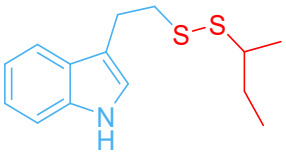
3-(2-(butyldisulfanyl)ethyl)-1H-indole (4b)

Yellow liquid. yield 63% (33.4 mg, 0.2 mmol scale), and purified by flash column chromatography on silica gel (PE). **IR (neat)**: ν =3412, 2922, 1452, 738, 472 cm^{-1}. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.96 (s, 1H), 7.65 (dq, *J* = 7.9, 0.9 Hz, 1H), 7.37 (dt, *J* = 8.1, 1.0 Hz, 1H), 7.23 (ddd, *J* = 8.2, 7.0, 1.3 Hz, 1H), 7.16 (ddd, *J* = 8.0, 7.0, 1.1 Hz, 1H), 7.06 – 7.01 (m, 1H), 3.25 – 3.14 (m, 2H), 3.11 – 3.01 (m, 2H), 2.81 – 2.70 (m, 2H), 1.78 – 1.66 (m, 2H), 1.45 (h, *J* = 7.4 Hz, 2H), 0.96 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 136.3, 127.3, 122.1, 121.9, 119.4, 118.7, 114.6, 111.2, 39.5, 39.0, 31.4, 25.5, 21.7, 13.8. HRMS (ESI): calcd. for $C_{14}H_{20}NS_2$ $[M+H]^+$: 266.1032, found: 266.1029.



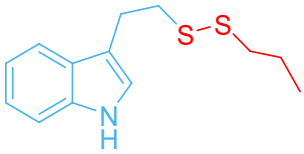
3-(2-(cyclohexyldisulfanyl)ethyl)-1H-indole (4c)

Yellow solid. yield 63% (33.4 mg, 0.2 mmol scale), and purified by flash column chromatography on silica gel (PE). **Mp**: 30.1-30.4 °C. **IR (neat)**: ν =3409, 2924, 2850, 1448, 738 cm^{-1}. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.96 (s, 1H), 7.63 (dd, *J* = 7.9, 1.1 Hz, 1H), 7.37 (dt, *J* = 8.1, 1.0 Hz, 1H), 7.22 (ddd, *J* = 8.2, 7.0, 1.3 Hz, 1H), 7.15 (ddd, *J* = 8.0, 7.0, 1.1 Hz, 1H), 7.05 (d, *J* = 2.4 Hz, 1H), 3.21 – 3.12 (m, 2H), 3.07 – 2.98 (m, 2H), 2.76 (tt, *J* = 10.8, 3.7 Hz, 1H), 2.11 – 2.01 (m, 2H), 1.85 – 1.73 (m, 2H), 1.48 – 1.18 (m, 6H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 136.3, 127.2, 122.1, 121.8, 119.4, 118.7, 114.6, 111.2, 49.7, 40.5, 33.0, 26.1, 25.7, 25.4. HRMS (ESI): calcd. for $C_{16}H_{22}NS_2$ $[M+H]^+$: 292.1188, found: 292.1195.



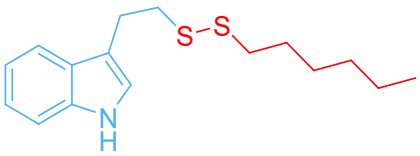
3-(2-(sec-butyldisulfanyl)ethyl)-1H-indole (4d)

Yellow liquid. yield 63% (33.4 mg, 0.2 mmol scale), and purified by flash column chromatography on silica gel (PE). **IR (neat)**: ν =3412, 2961, 2919, 1450, 739 cm^{-1}. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.95 (s, 1H), 7.67 – 7.62 (m, 1H), 7.37 (dt, *J* = 8.2, 1.0 Hz, 1H), 7.23 (ddd, *J* = 8.2, 7.0, 1.3 Hz, 1H), 7.16 (ddd, *J* = 8.0, 7.0, 1.2 Hz, 1H), 7.04 (d, *J* = 2.4 Hz, 1H), 3.22 – 3.14 (m, 2H), 3.09 – 2.99 (m, 2H), 2.81 (q, *J* = 6.7 Hz, 1H), 1.76 (ddd, *J* = 13.8, 7.4, 6.4 Hz, 1H), 1.59 (dt, *J* = 14.1, 7.2 Hz, 1H), 1.35 (d, *J* = 6.8 Hz, 3H), 1.02 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 136.3, 127.2, 122.1, 121.8, 119.4, 118.7, 114.6, 111.2, 48.2, 40.2, 29.0, 25.5, 20.3, 11.6. HRMS (ESI): calcd. for $C_{14}H_{19}NS_2Na$ [M+Na]+: 288.0851, found: 288.0850.



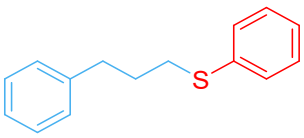
3-(2-(propyldisulfanyl)ethyl)-1H-indole (4e)

Yellow liquid. yield 58% (29.1 mg, 0.2 mmol scale), and purified by flash column chromatography on silica gel (PE). **IR (neat)**: ν =3412, 2958, 1451, 1087, 738 cm^{-1}. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.97 (s, 1H), 7.63 (dq, *J* = 7.8, 0.9 Hz, 1H), 7.37 (dt, *J* = 8.1, 1.0 Hz, 1H), 7.21 (ddd, *J* = 8.2, 7.0, 1.3 Hz, 1H), 7.14 (ddd, *J* = 8.0, 7.0, 1.1 Hz, 1H), 7.05 (dd, *J* = 2.3, 1.1 Hz, 1H), 3.22 – 3.14 (m, 2H), 3.08 – 2.99 (m, 2H), 2.76 – 2.65 (m, 2H), 1.74 (h, *J* = 7.3 Hz, 2H), 1.01 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 136.3, 127.2, 122.1, 121.8, 119.4, 118.7, 114.6, 111.2, 41.3, 39.4, 25.4, 22.6, 13.2. HRMS (ESI): calcd. for $C_{13}H_{17}NS_2Na$ [M+Na]+: 274.0695, found: 274.0702.



3-(2-(hexyldisulfanyl)ethyl)-1H-indole (4f)

Yellow liquid. yield 58% (34.0 mg, 0.2 mmol scale), and purified by flash column chromatography on silica gel (PE). **IR (neat)**: ν =3417, 2920, 2855, 1455, 739 cm^{-1}. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.98 (s, 1H), 7.62 (dd, *J* = 7.9, 1.1 Hz, 1H), 7.37 (dd, *J* = 8.1, 1.1 Hz, 1H), 7.21 (ddd, *J* = 8.2, 7.0, 1.3 Hz, 1H), 7.13 (ddd, *J* = 8.0, 7.0, 1.1 Hz, 1H), 7.05 (d, *J* = 2.4 Hz, 1H), 3.21 – 3.13 (m, 2H), 3.08 – 2.98 (m, 2H), 2.79 – 2.66 (m, 2H), 1.75 – 1.64 (m, 3H), 1.27 (d, *J* = 3.1 Hz, 4H), 0.89 (t, *J* = 6.8 Hz, 4H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 136.3, 127.2, 122.1, 121.8, 119.4, 118.7, 114.6, 111.2, 39.3, 31.5, 29.7, 29.3, 28.3, 25.4, 22.6, 14.1. HRMS (ESI): calcd. for $C_{16}H_{23}NS_2Na$ $[M+Na]^+$: 316.1164 , found: 316.1157.



phenyl(3-phenylpropyl)sulfane (4g)

Yellow liquid. yield 90% (50.7 mg, 0.2 mmol scale), and purified by flash column chromatography on silica gel (PE). **IR (neat)**: ν =2925, 1483, 1444, 736, 692, 483 cm^{-1}. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.25 – 7.14 (m, 6H), 7.13 – 7.04 (m, 4H), 2.86 – 2.79 (m, 2H), 2.66 (t, *J* = 7.6 Hz, 2H), 1.88 (p, *J* = 7.4 Hz, 2H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 141.3, 136.6, 129.2, 128.9, 128.5, 128.4, 126.0, 125.9, 34.7, 32.9, 30.7. HRMS (ESI): calcd. for $C_{15}H_{16}SNa$ $[M+Na]^+$: 251.0865 , found: 251.0875.

5. References

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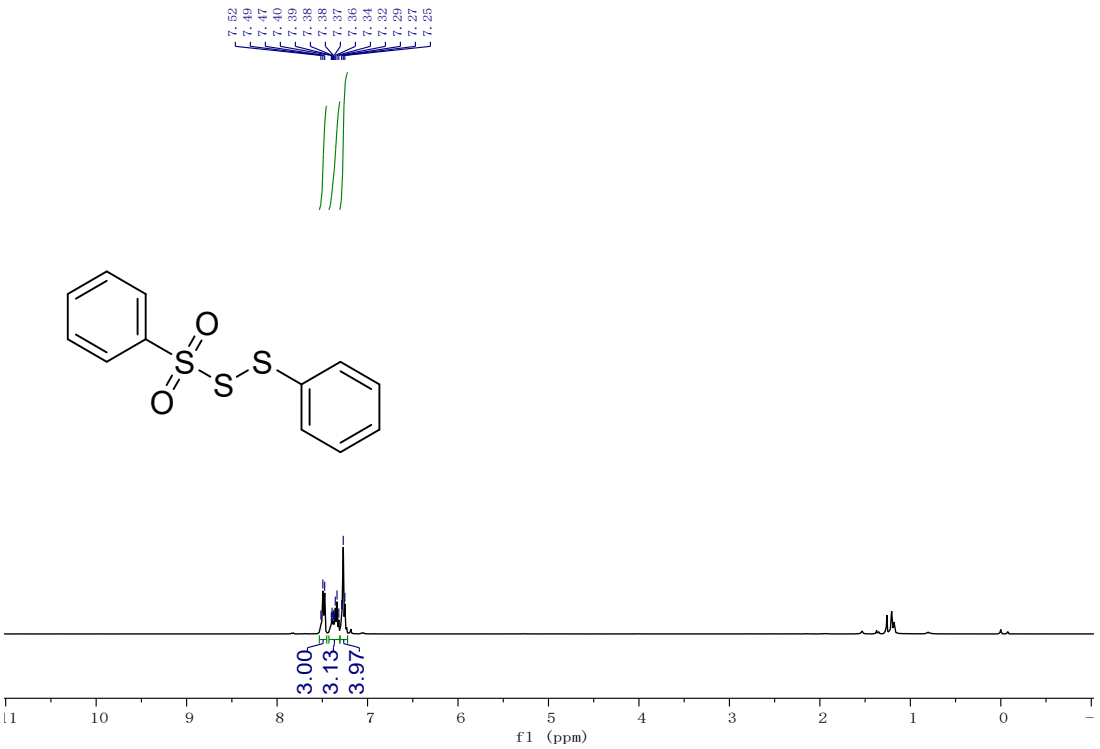
[2] W. Gao, J. Tian, Y. Shang, X. F. Jiang, *Chem. Sci*. 2020, **11**, 3903.

[3] H.-Q. Cao, H.-N. Liu, Z.-Y. Liu, B. Qiao, F.-G. Z, J.-A. Ma, *Org. Lett*. 2020, **22**, 6414–6419.

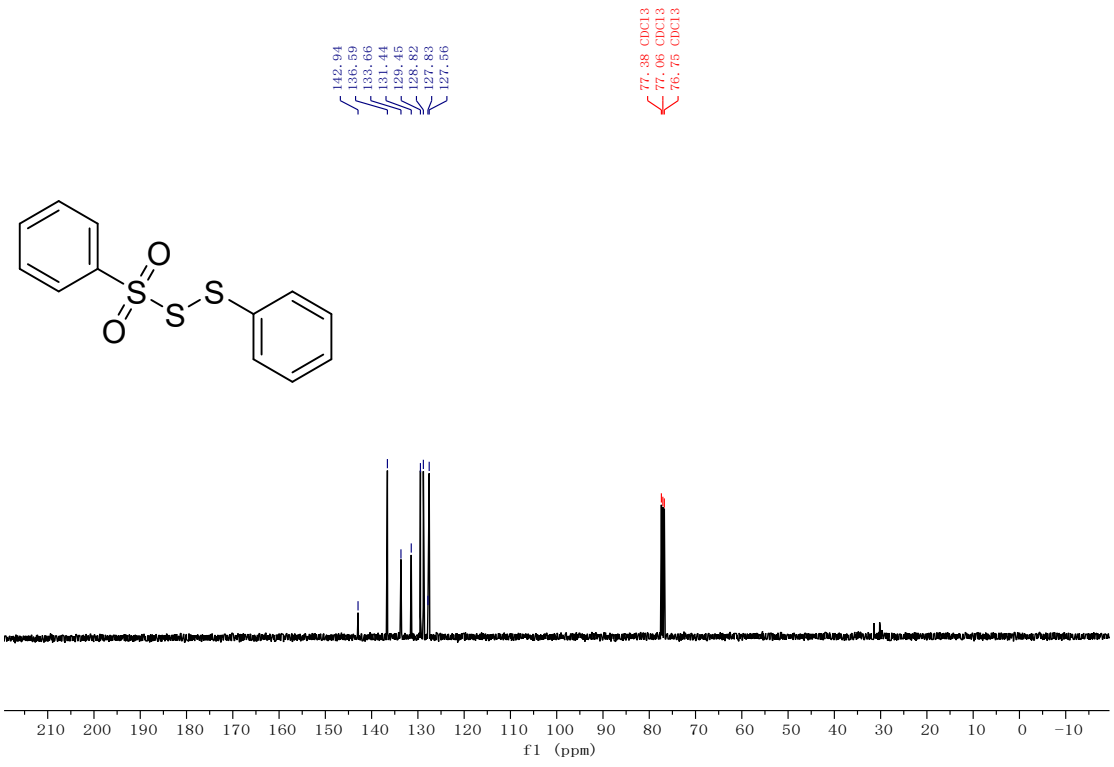
[4] S. Li, C. Lian, G. Yue, J. Zhang, D. Qiu, and F. Mo, *J. Org. Chem.* 2022, **87**, 4291–4297

[5] X. Ren,Q. Ke,Y. Zhou,J. Jiao,G. Li,S. Cao,X. Wang,Q. Gao, X. Wang. Angew. Chem. Int. Ed. 2023, 62, e2023021.

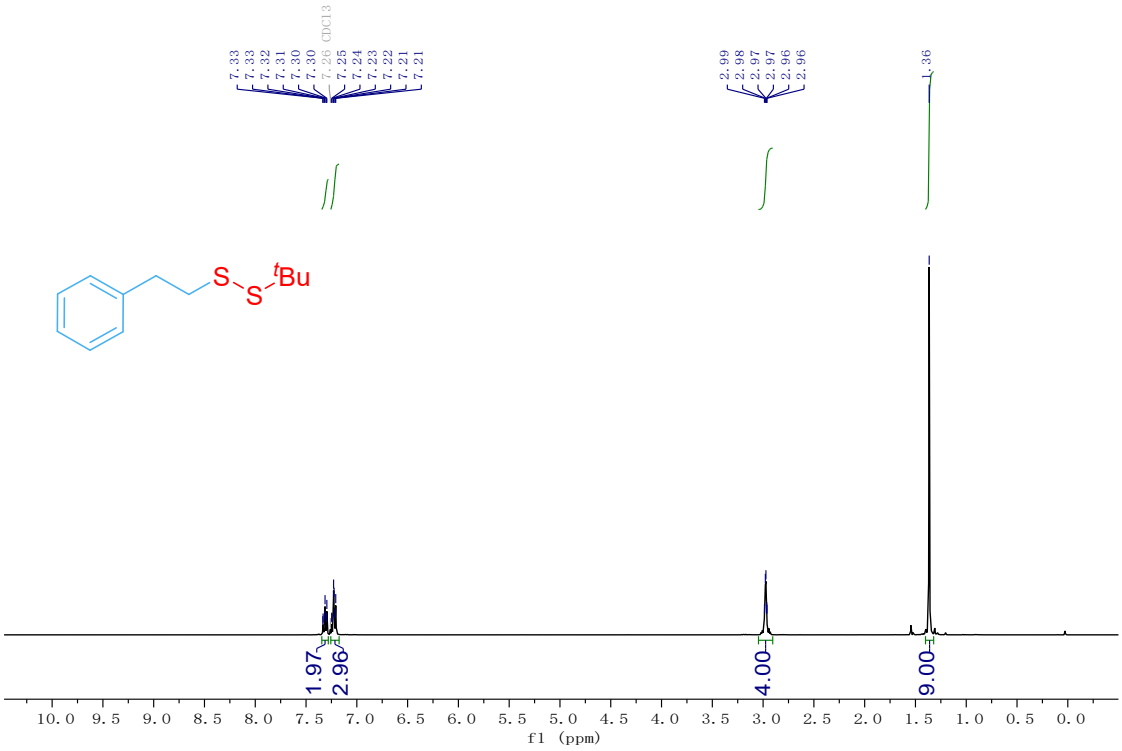
6. Copies of ^{1}H、^{13}C、^{19}F NMR Spectra for compounds



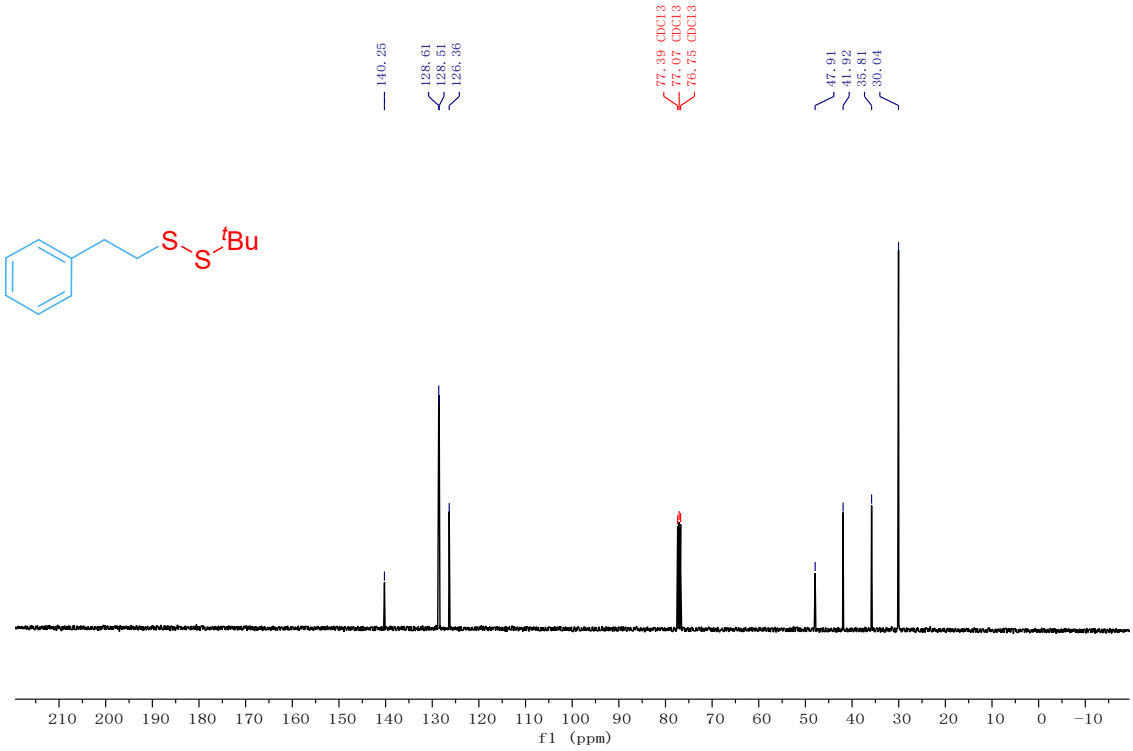
^{1}H NMR Spectra of 1g (400 MHz, $CDCl_3$) (400 MHz, $CDCl_3$)



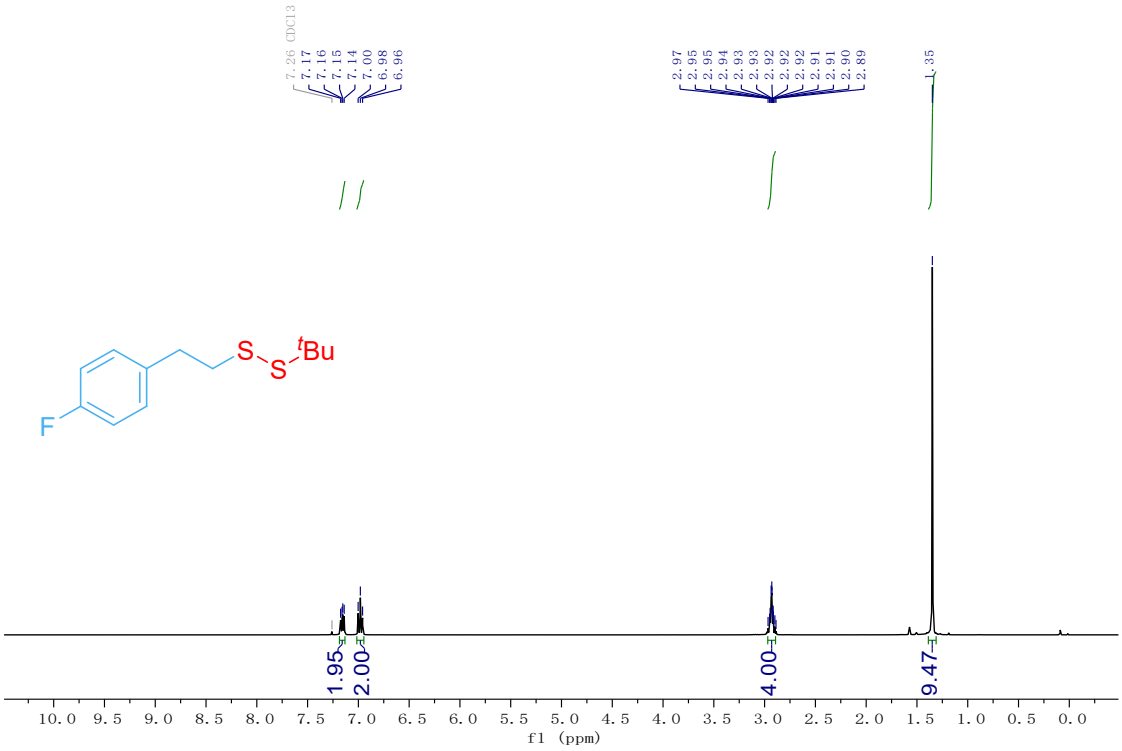
^{13}C NMR Spectra of 1g (100 MHz, $CDCl_3$)



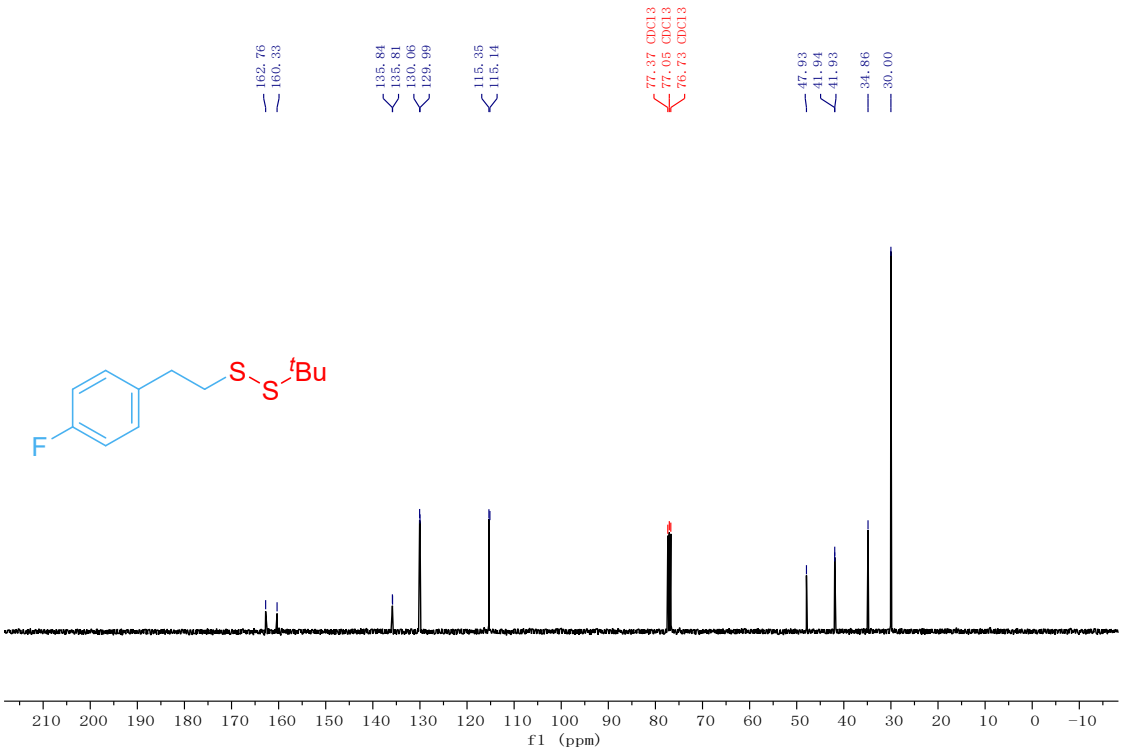
^{1}H NMR Spectra of 3a (400 MHz, $CDCl_3$) (400 MHz, $CDCl_3$)



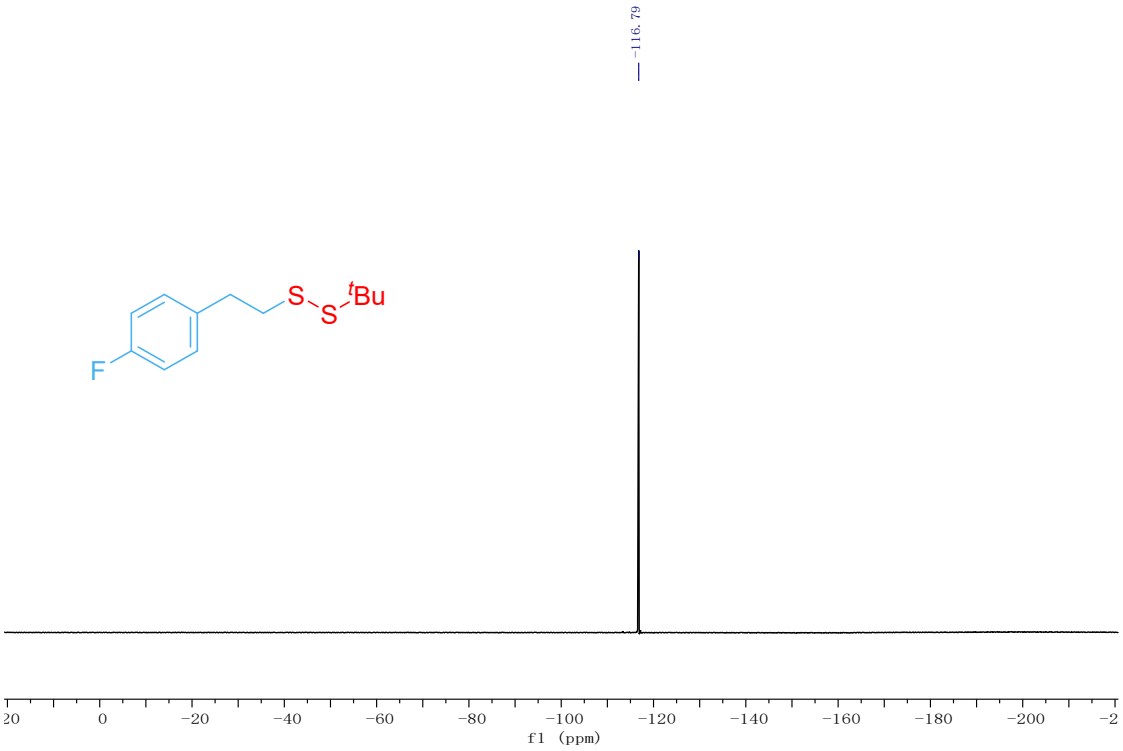
^{13}C NMR Spectra of 3a (100 MHz, $CDCl_3$)



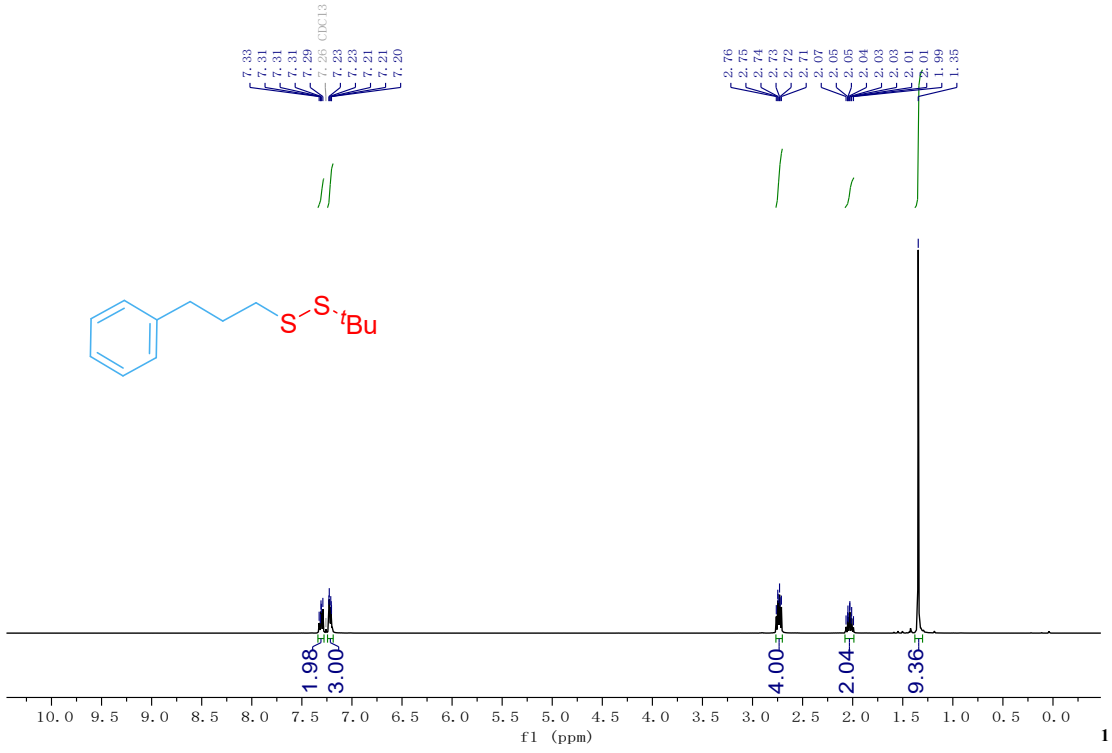
^{1}H NMR Spectra of 3b (400 MHz, $CDCl_3$) (400 MHz, $CDCl_3$)



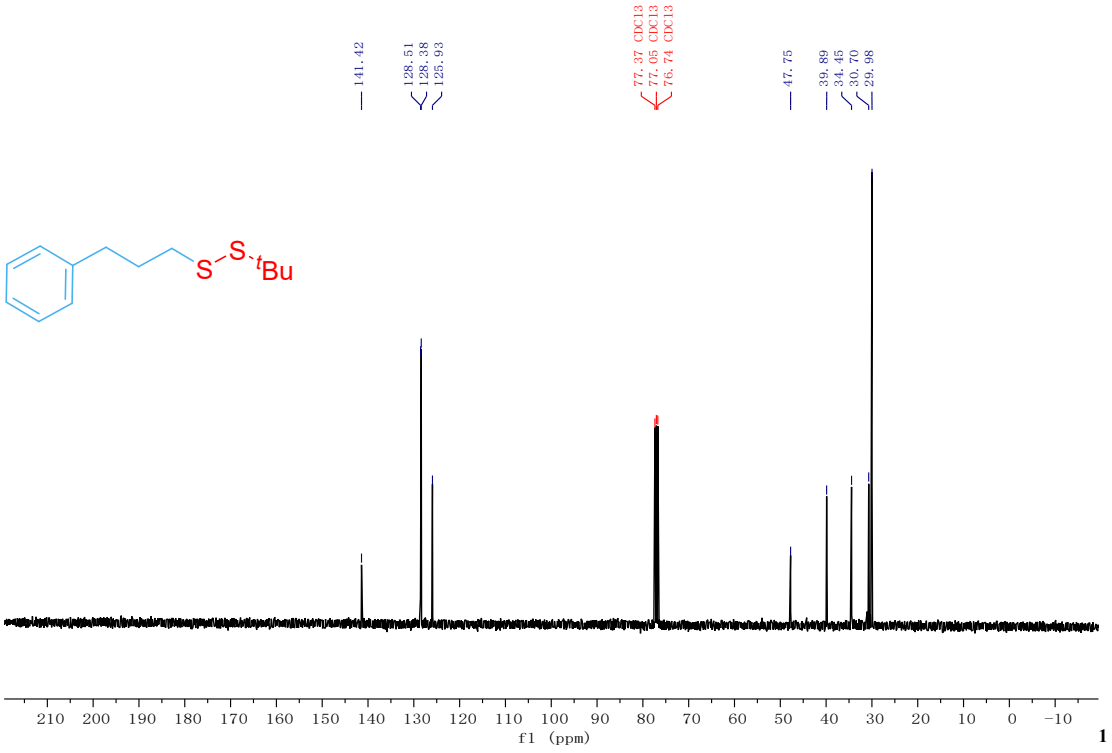
^{13}C NMR Spectra of 3b (100 MHz, $CDCl_3$)



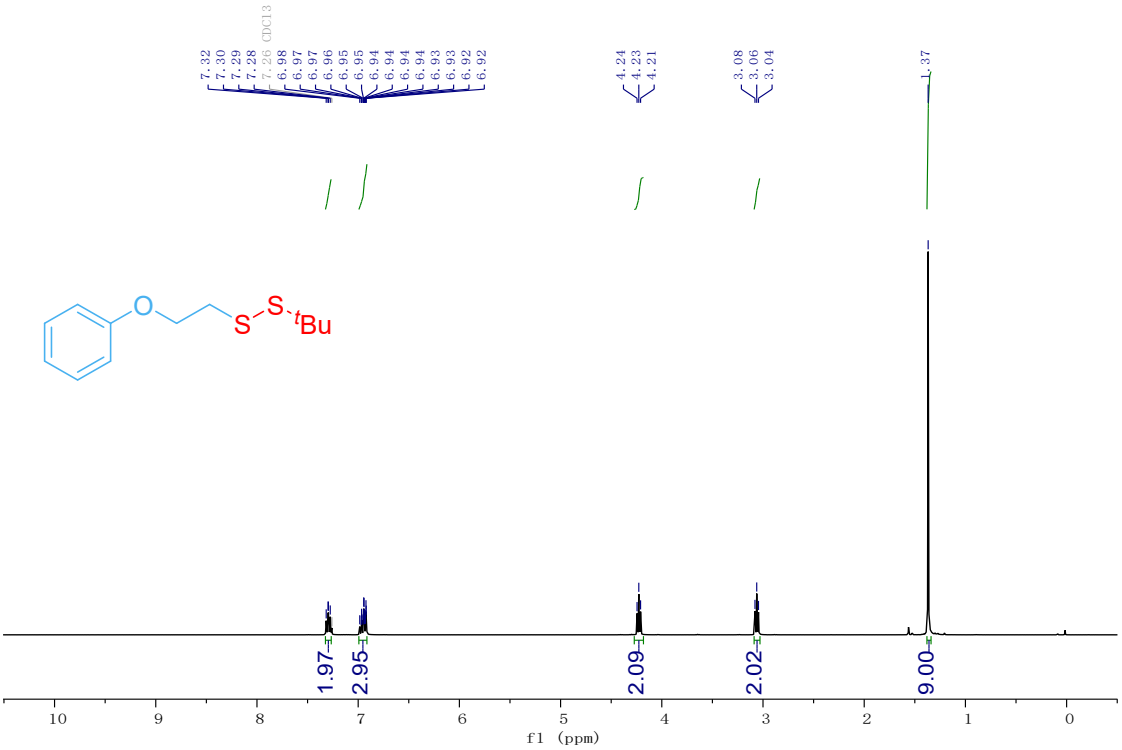
^{19}F NMR Spectra of 3b (376 MHz, $CDCl_3$)



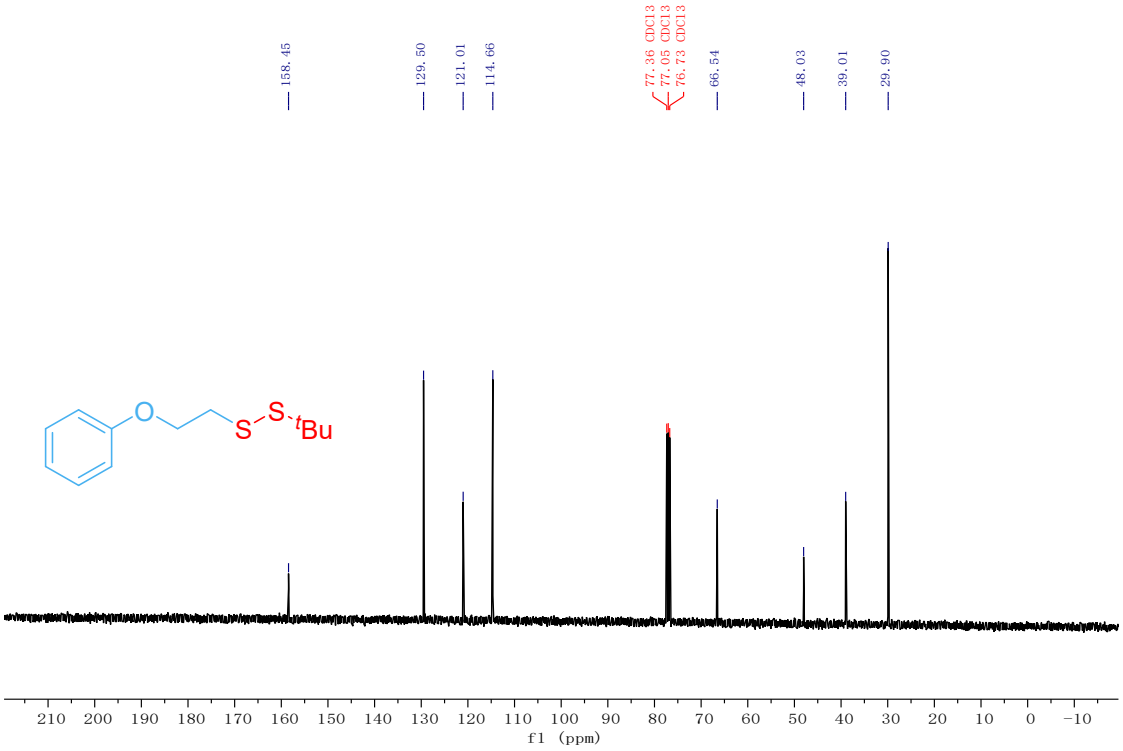
H NMR Spectra of 3c (400 MHz, $CDCl_3$) (400 MHz, $CDCl_3$)



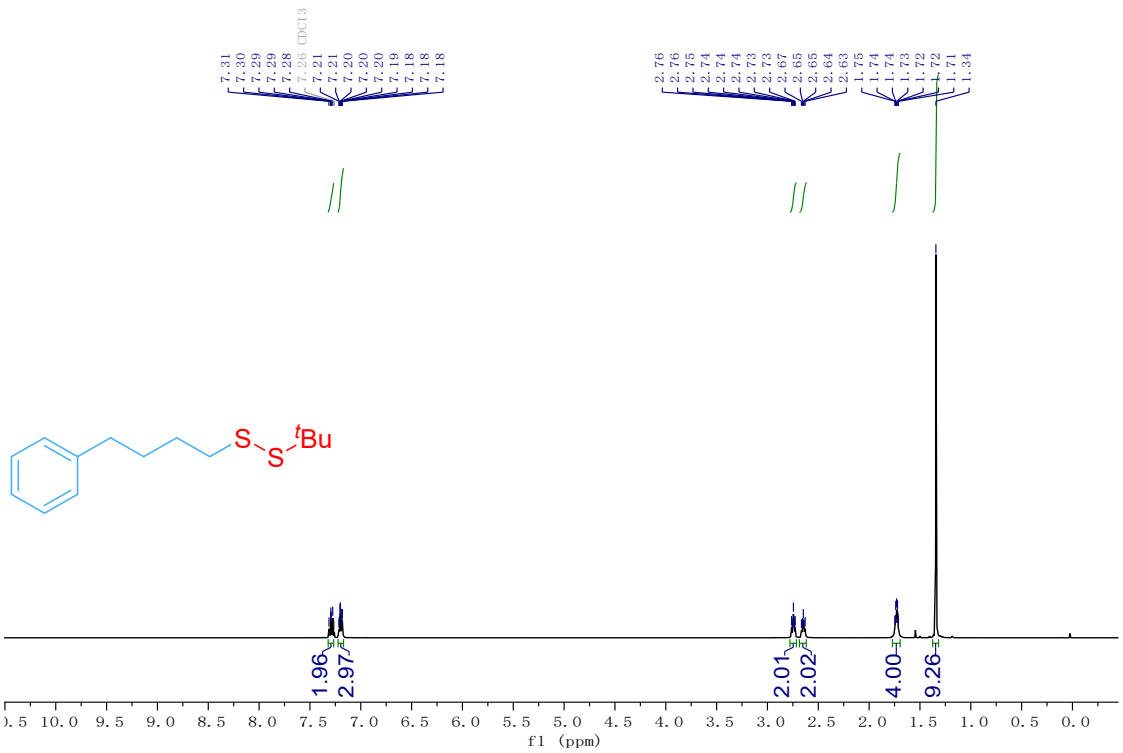
^{3}C NMR Spectra of 3c (100 MHz, $CDCl_3$)



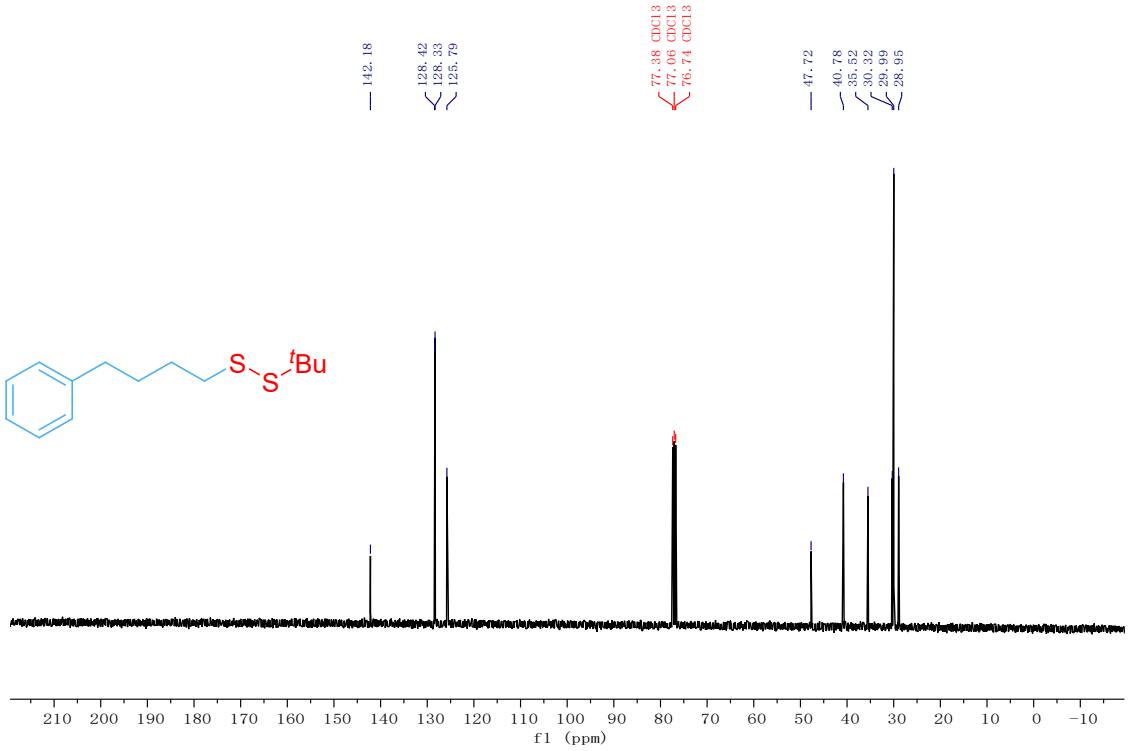
^{1}H NMR Spectra of 3d (400 MHz, $CDCl_3$) (400 MHz, $CDCl_3$)



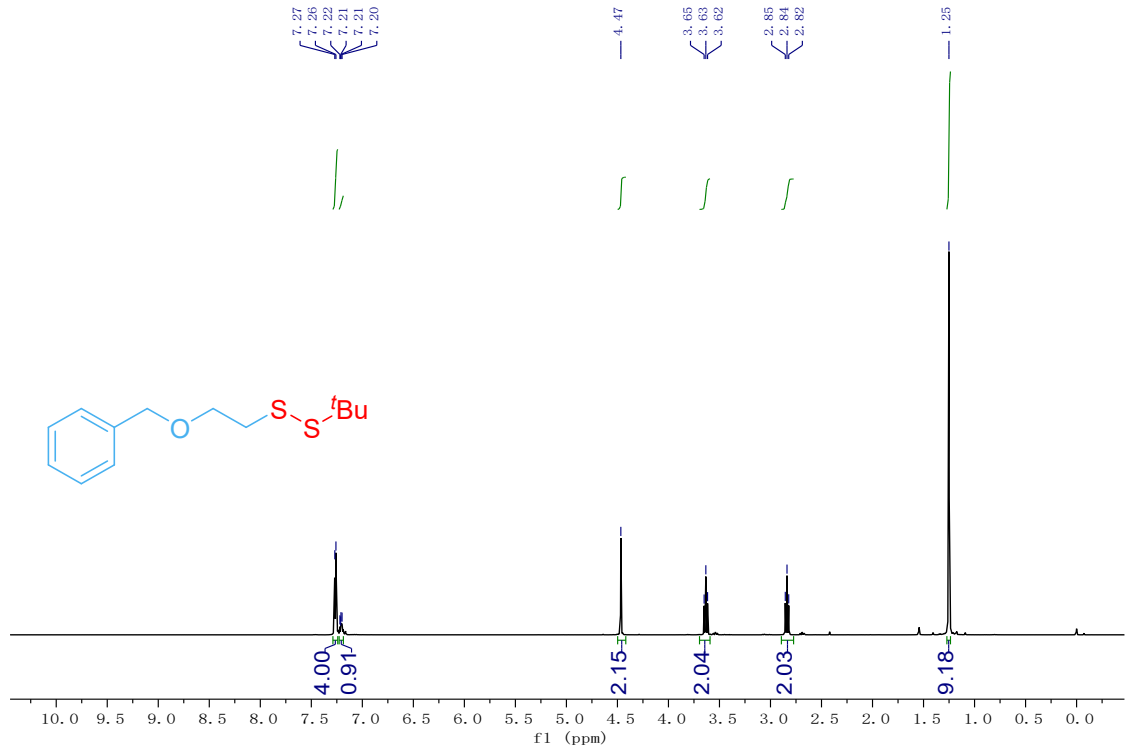
^{13}C NMR Spectra of 3d (100 MHz, $CDCl_3$)



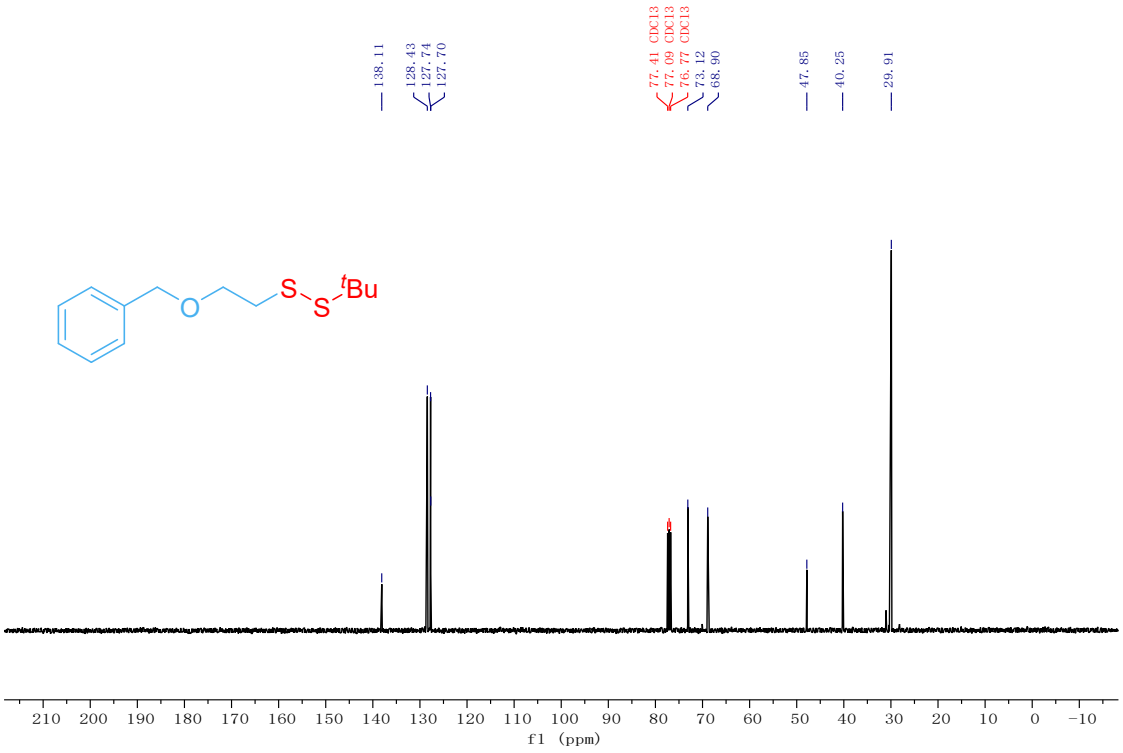
^{1}H NMR Spectra of 3e (400 MHz, $CDCl_3$) (400 MHz, $CDCl_3$)



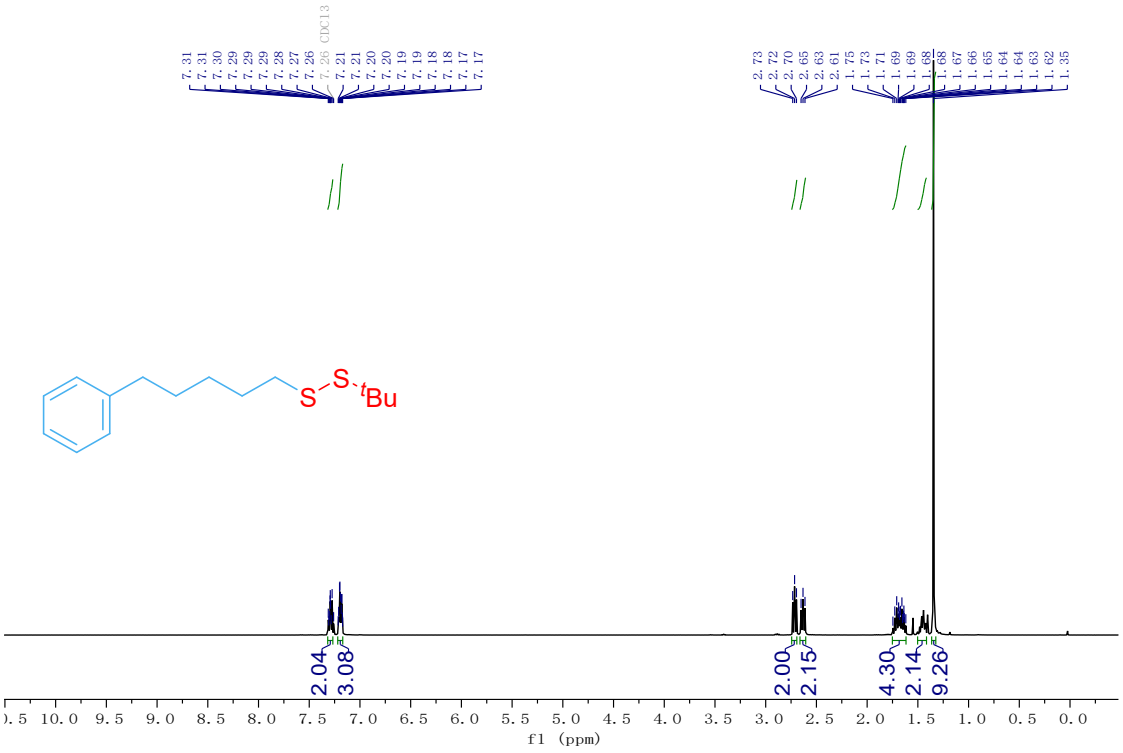
^{13}C NMR Spectra of 3e (100 MHz, $CDCl_3$)



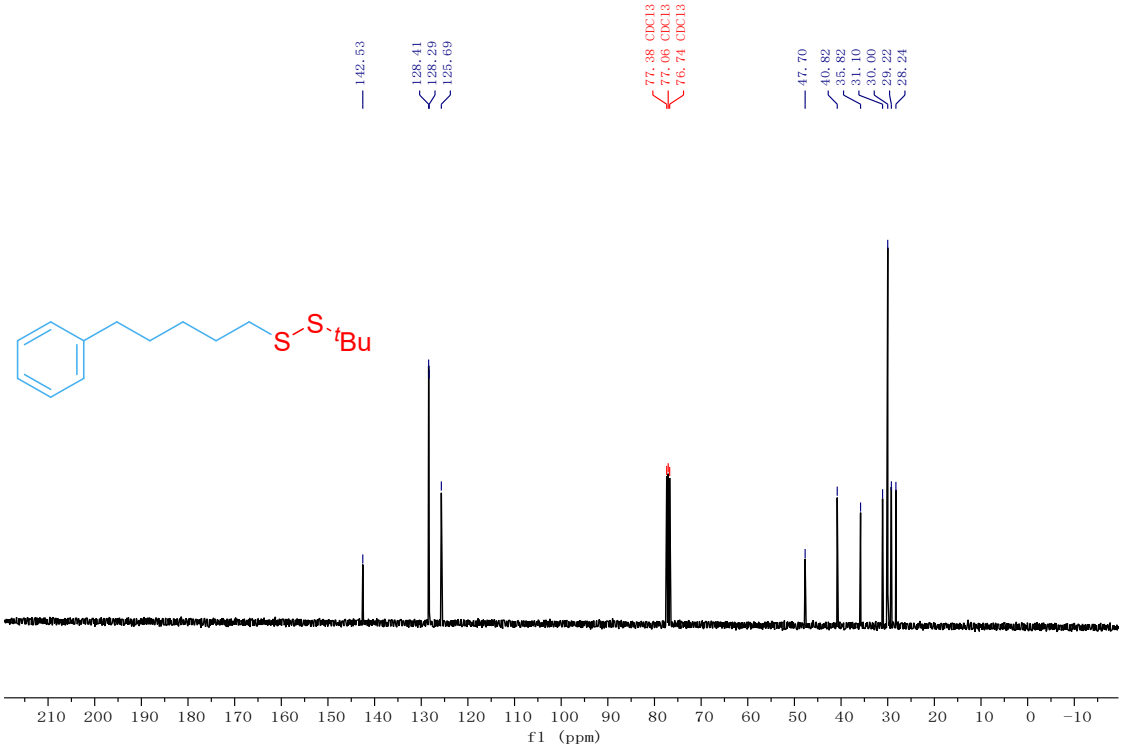
^{1}H NMR Spectra of 3f (400 MHz, $CDCl_3$) (400 MHz, $CDCl_3$)



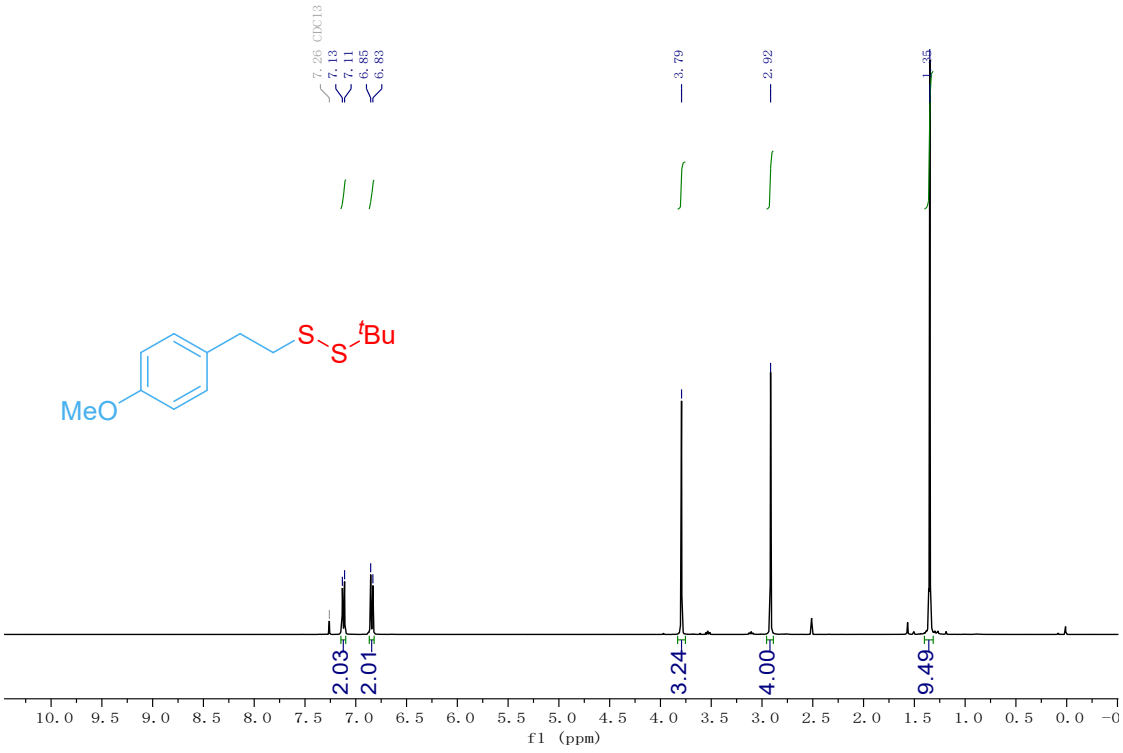
^{13}C NMR Spectra of 3f (100 MHz, $CDCl_3$)



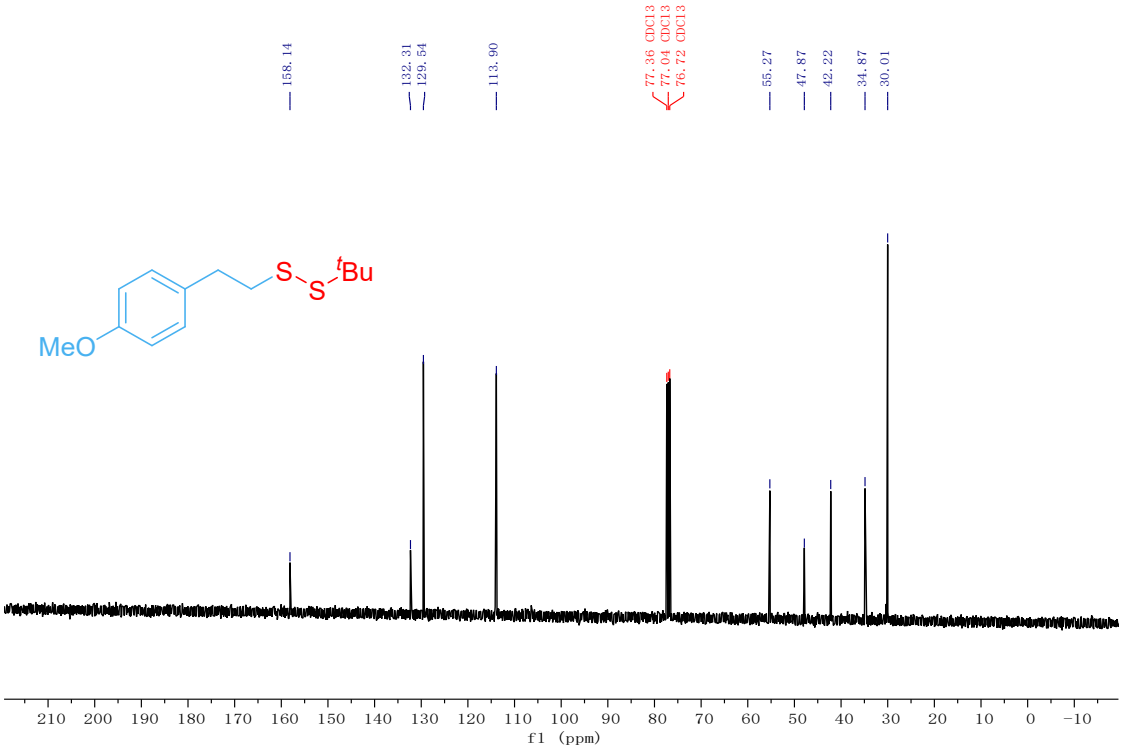
^{1}H NMR Spectra of 3g (400 MHz, $CDCl_3$) (400 MHz, $CDCl_3$)



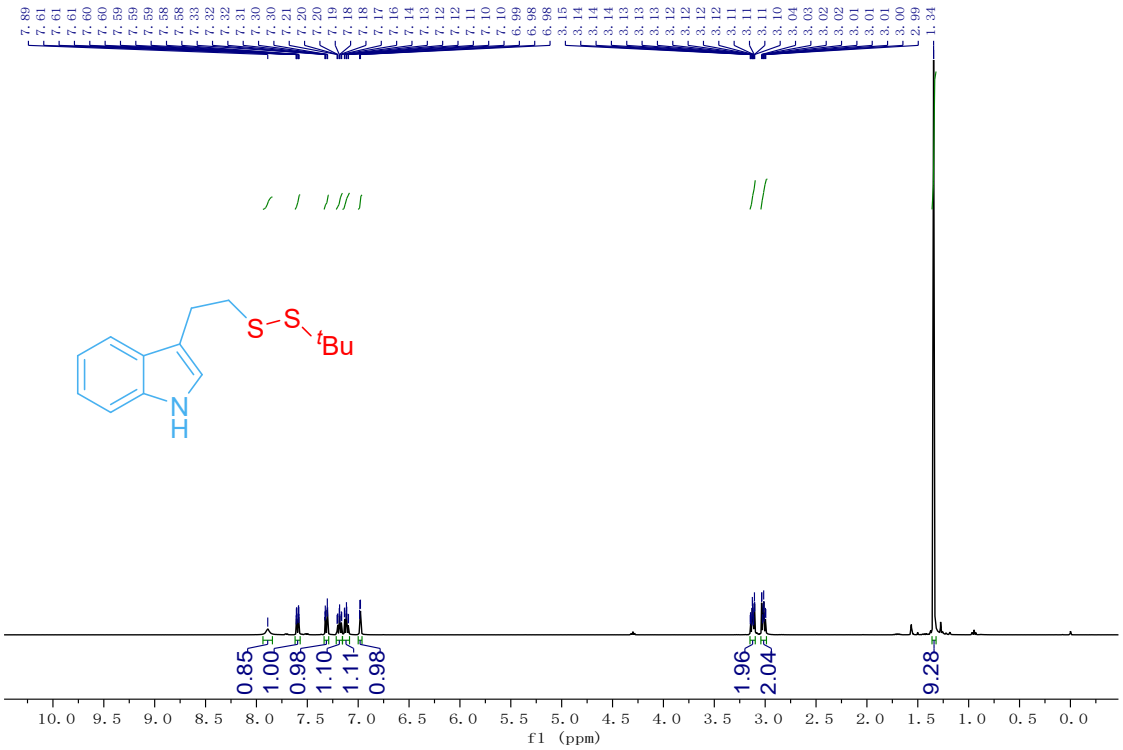
^{13}C NMR Spectra of 3g(100 MHz, $CDCl_3$)



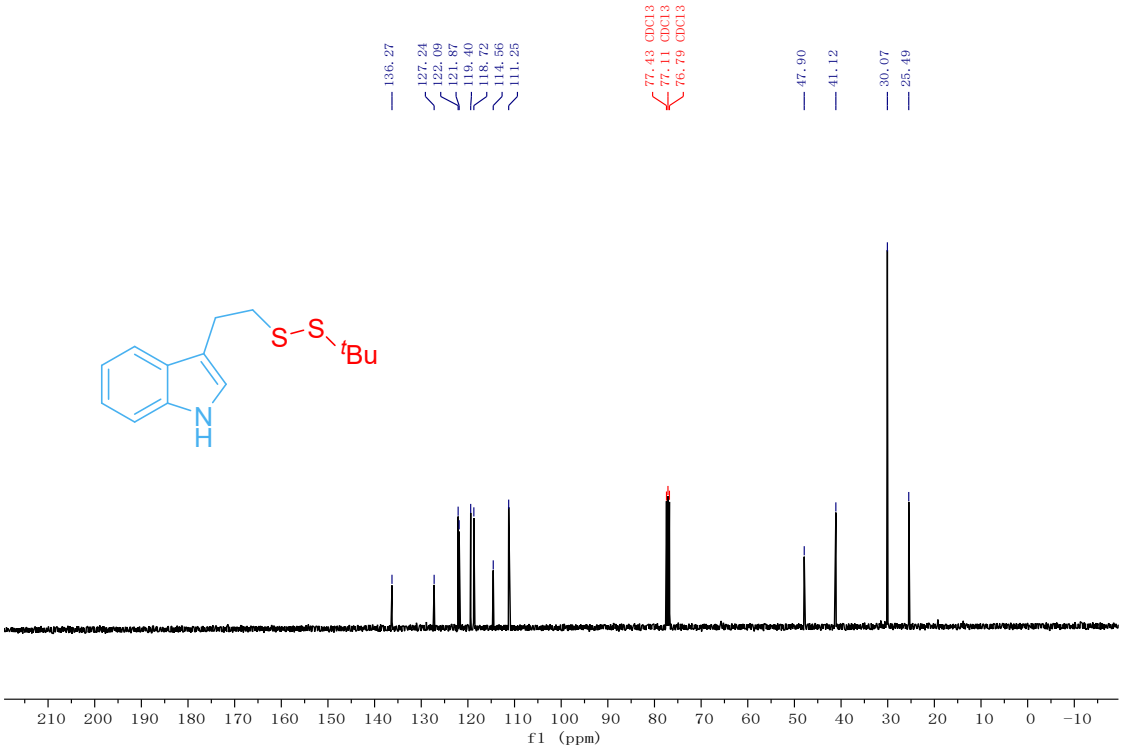
^{1}H NMR Spectra of 3h (400 MHz, $CDCl_3$) (400 MHz, $CDCl_3$)



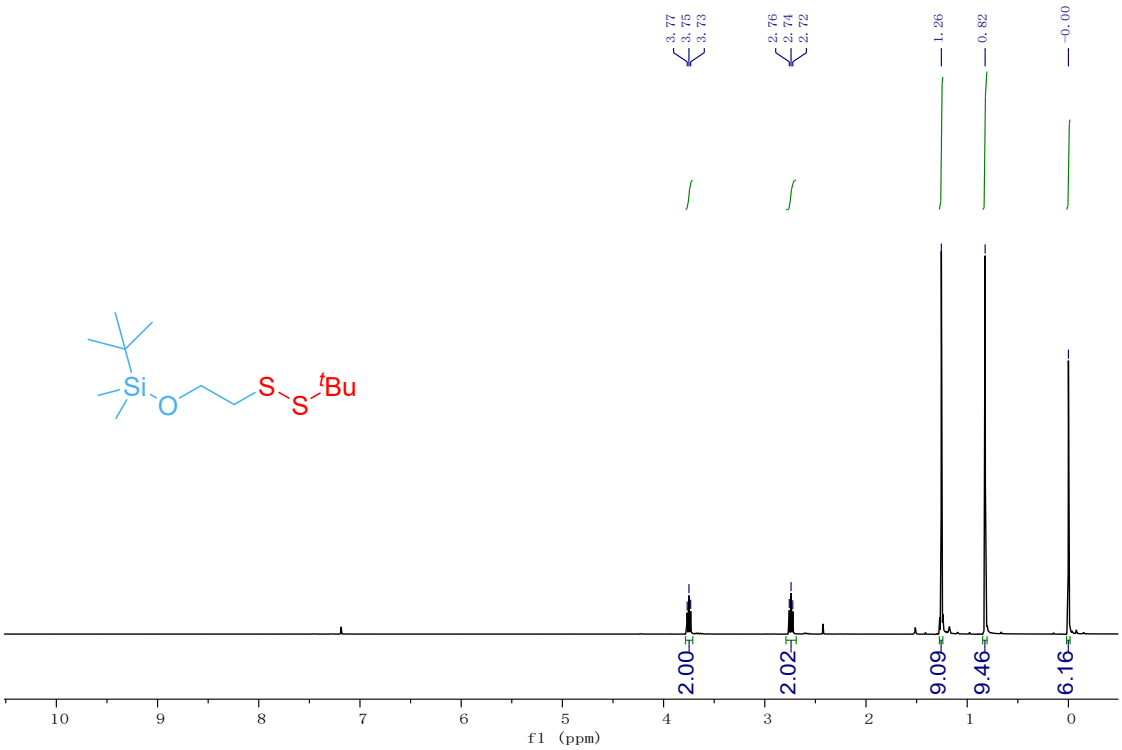
^{13}C NMR Spectra of 3h(100 MHz, $CDCl_3$)



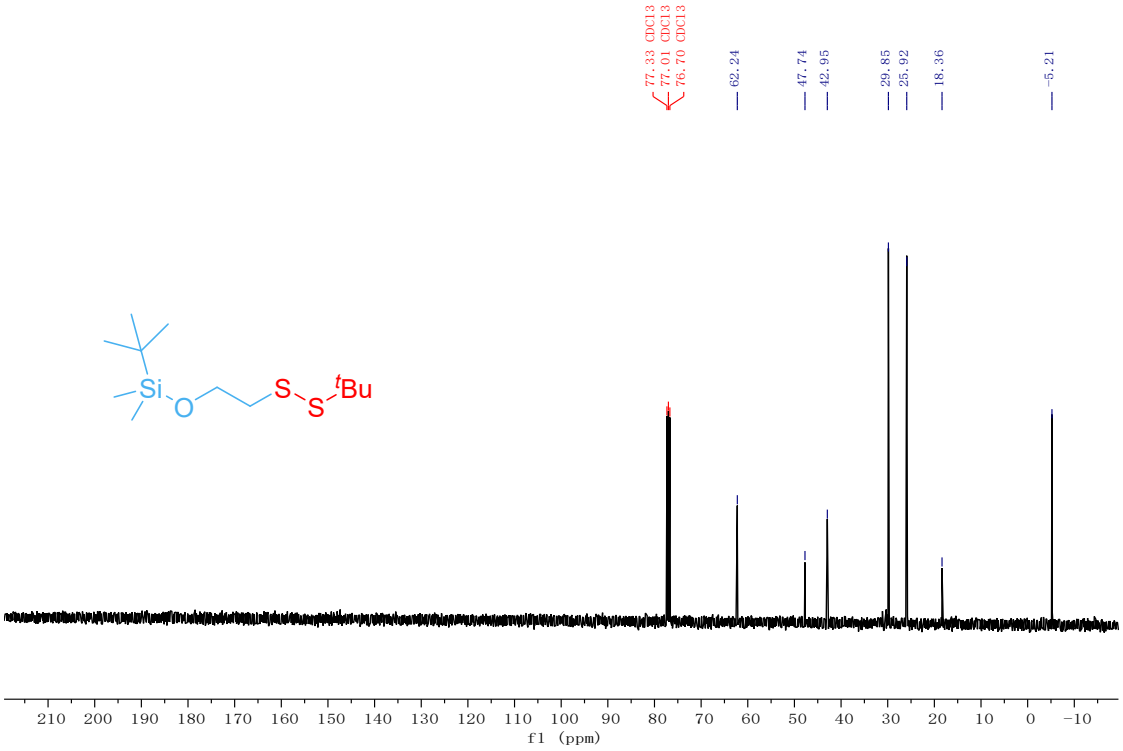
^{1}H NMR Spectra of 3i (400 MHz, $CDCl_3$) (400 MHz, $CDCl_3$)



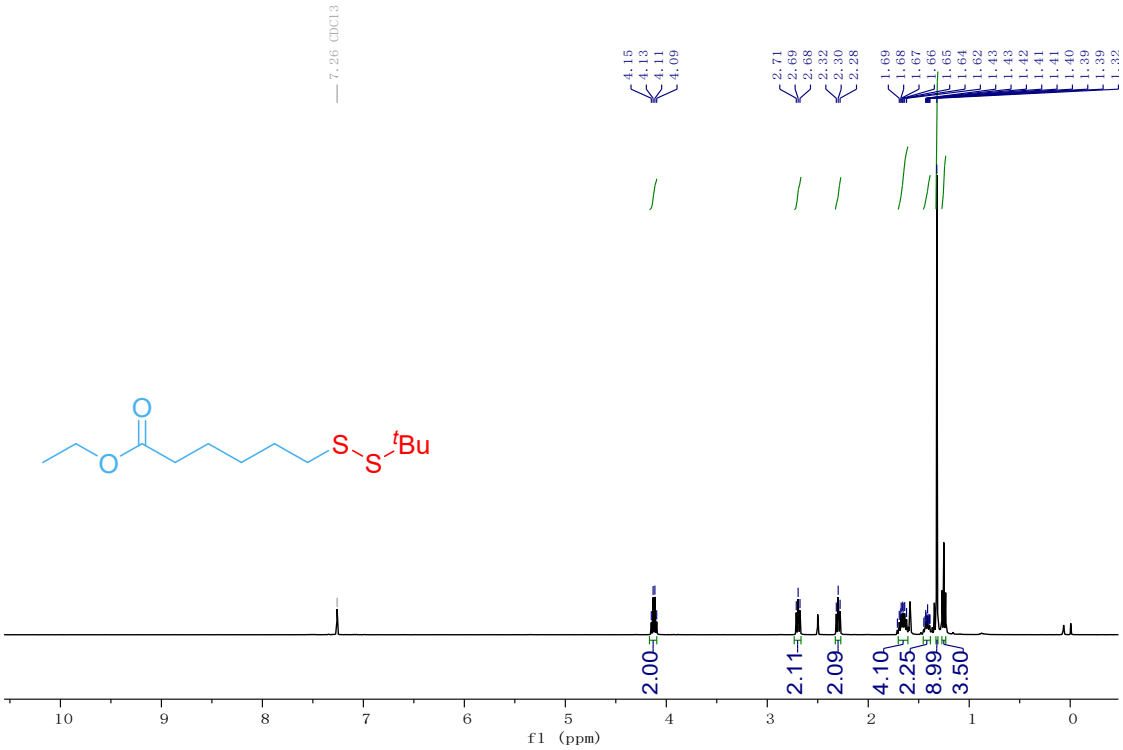
^{13}C NMR Spectra of 3i (100 MHz, $CDCl_3$)



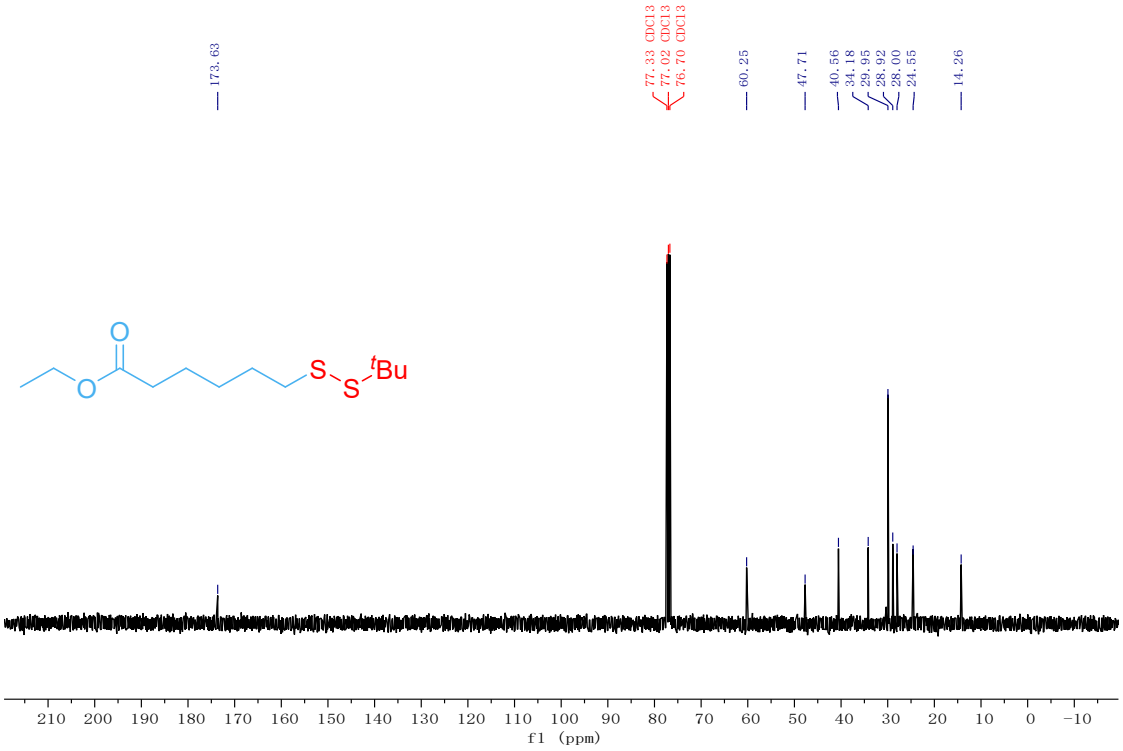
^{1}H NMR Spectra of 3j (400 MHz, $CDCl_3$) (400 MHz, $CDCl_3$)



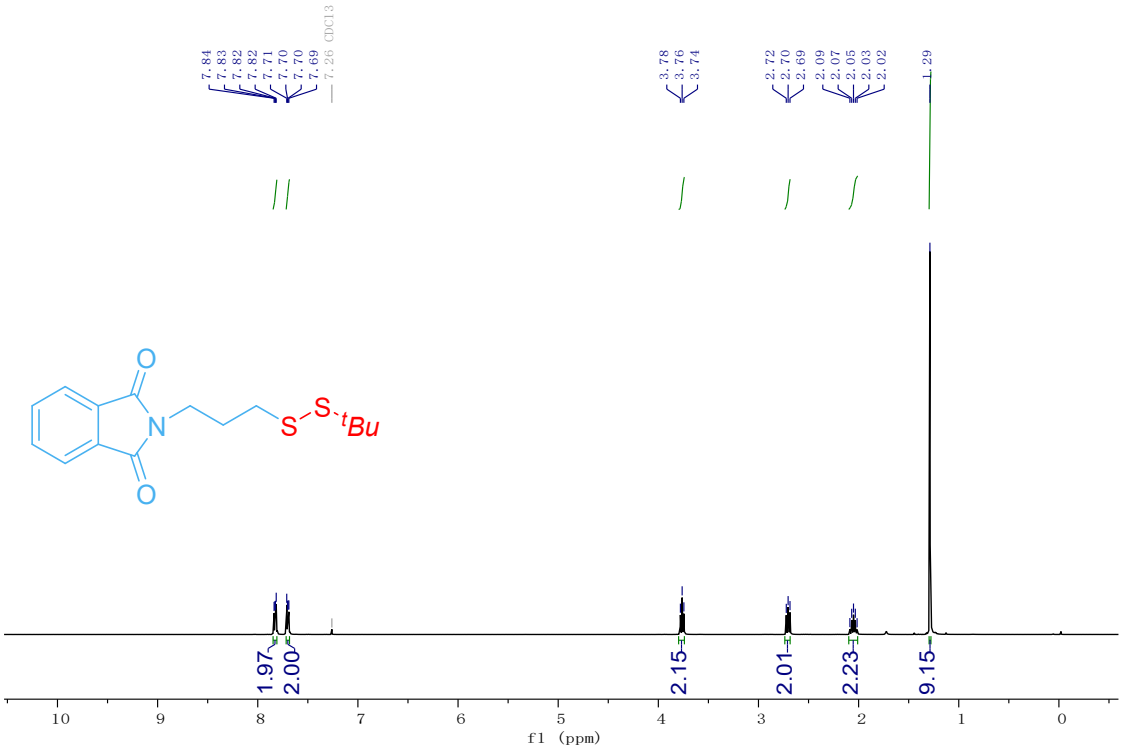
^{13}C NMR Spectra of 3j (100 MHz, $CDCl_3$)



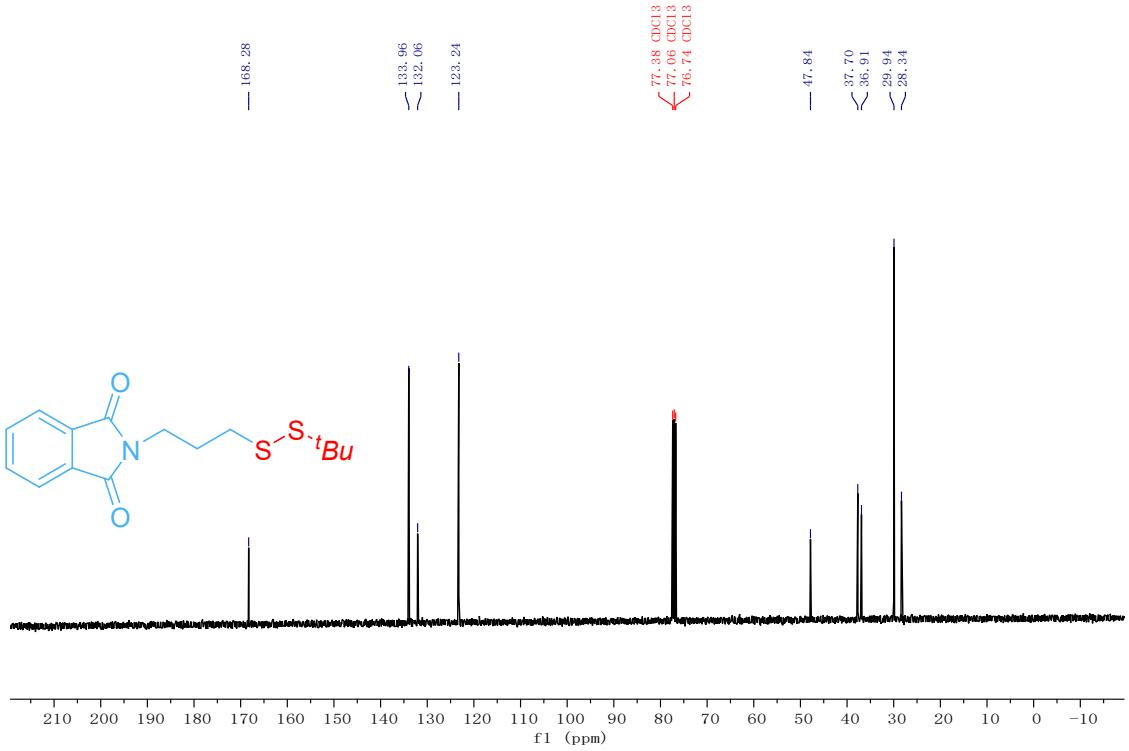
^{1}H NMR Spectra of 3k (400 MHz, $CDCl_3$) (400 MHz, $CDCl_3$)



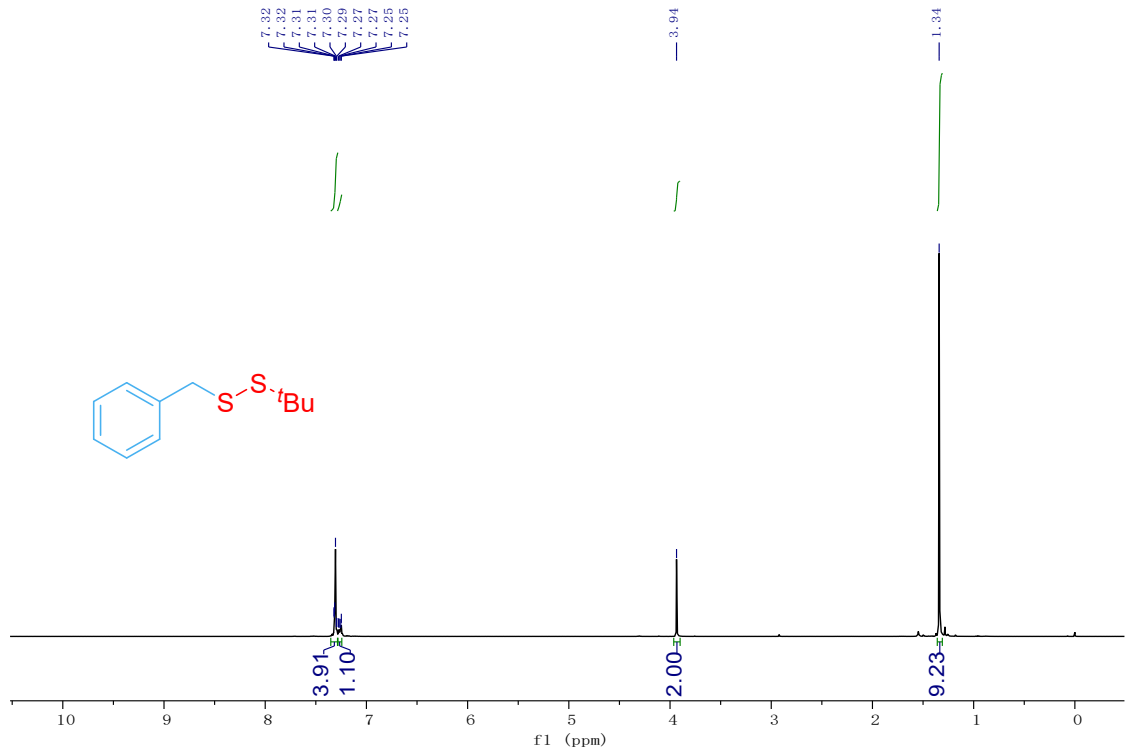
^{13}C NMR Spectra of 3k (100 MHz, $CDCl_3$)



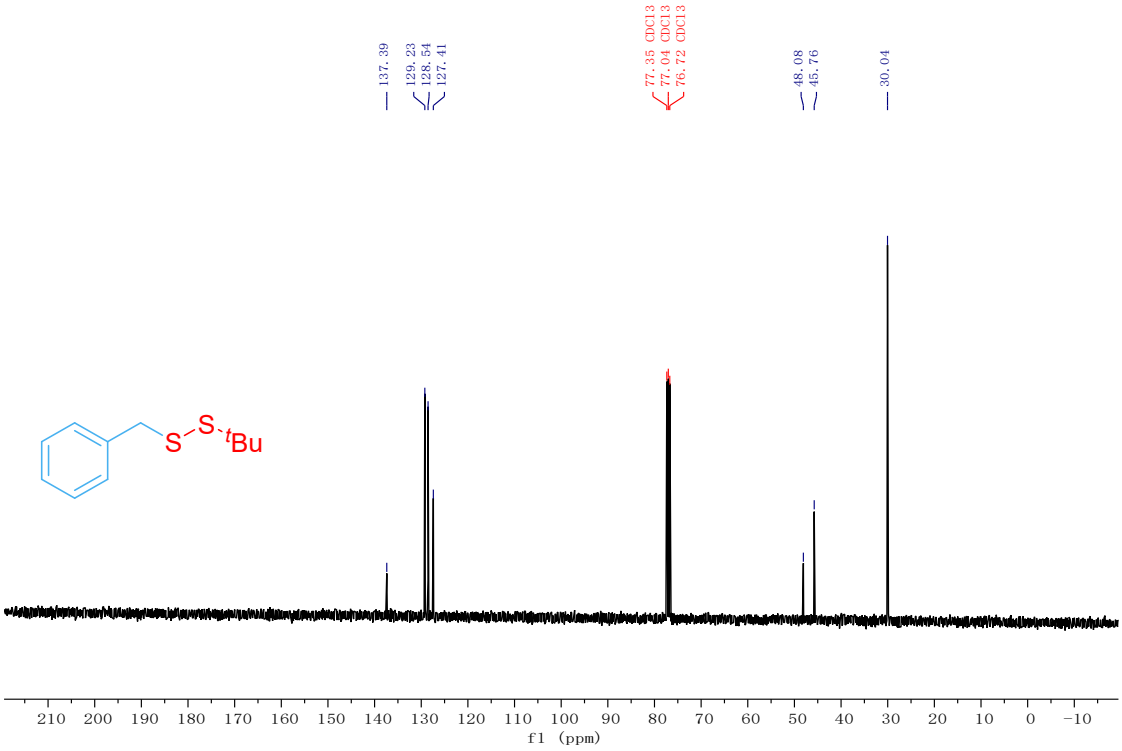
^{1}H NMR Spectra of 3l (400 MHz, $CDCl_3$) (400 MHz, $CDCl_3$)



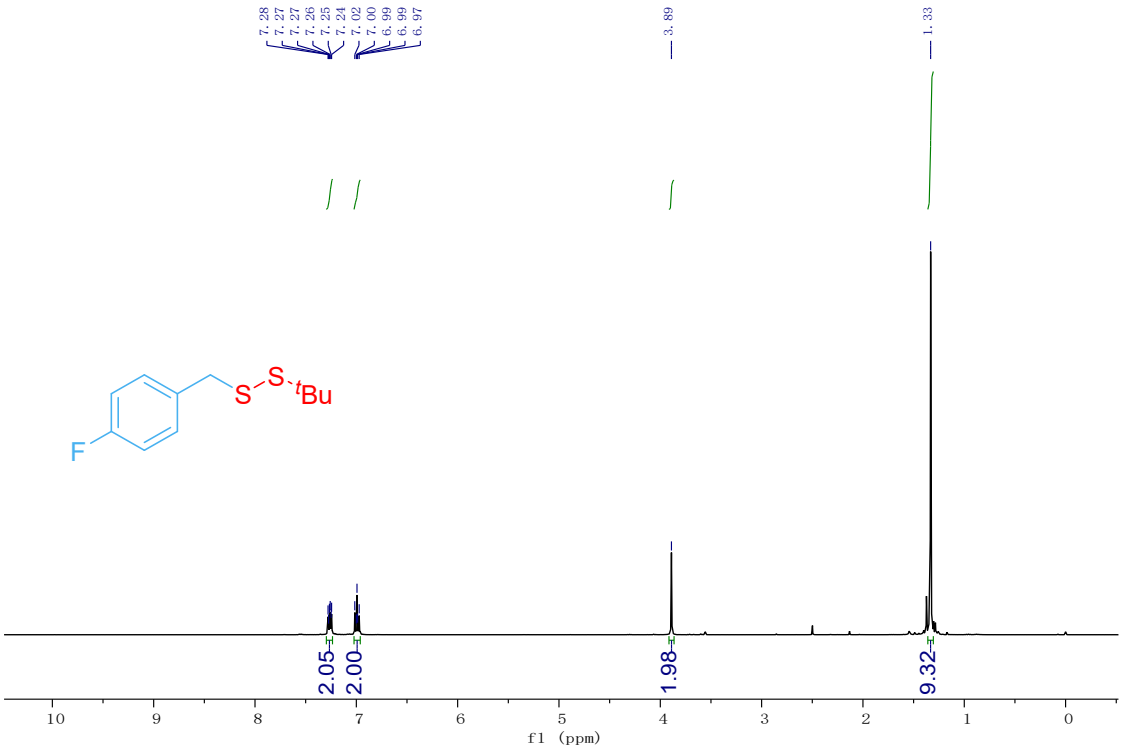
^{13}C NMR Spectra of 3l (100 MHz, $CDCl_3$)



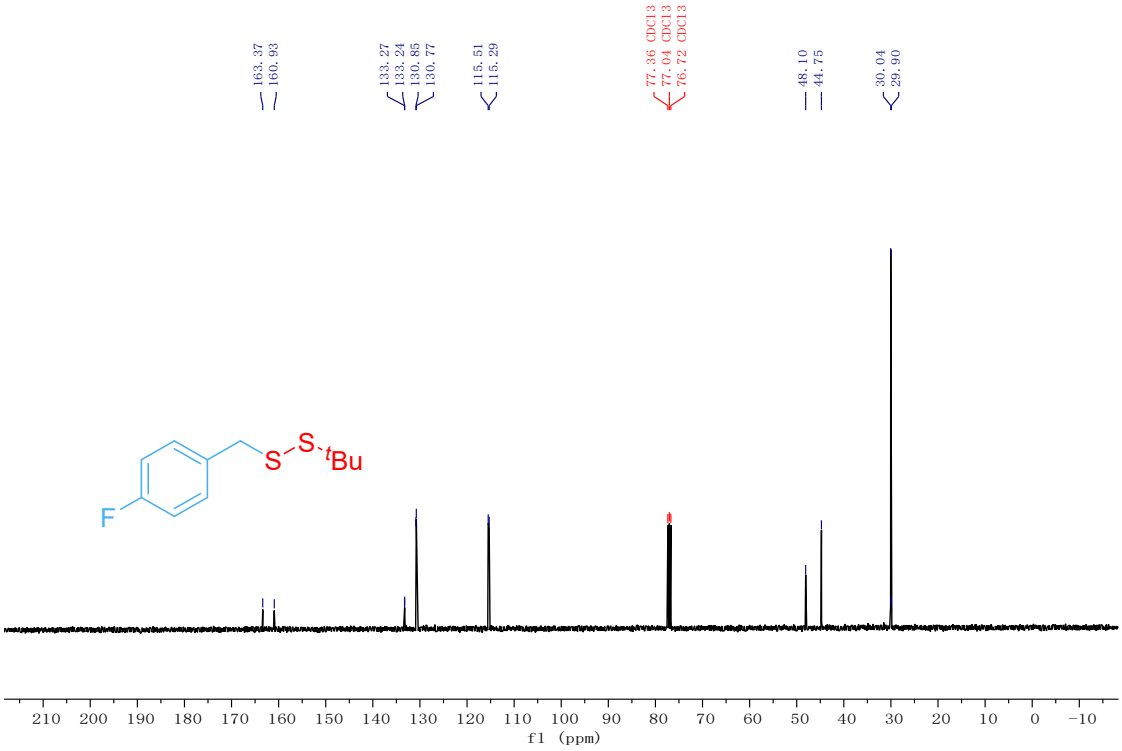
^{1}H NMR Spectra of 3m (400 MHz, $CDCl_3$) (400 MHz, $CDCl_3$)



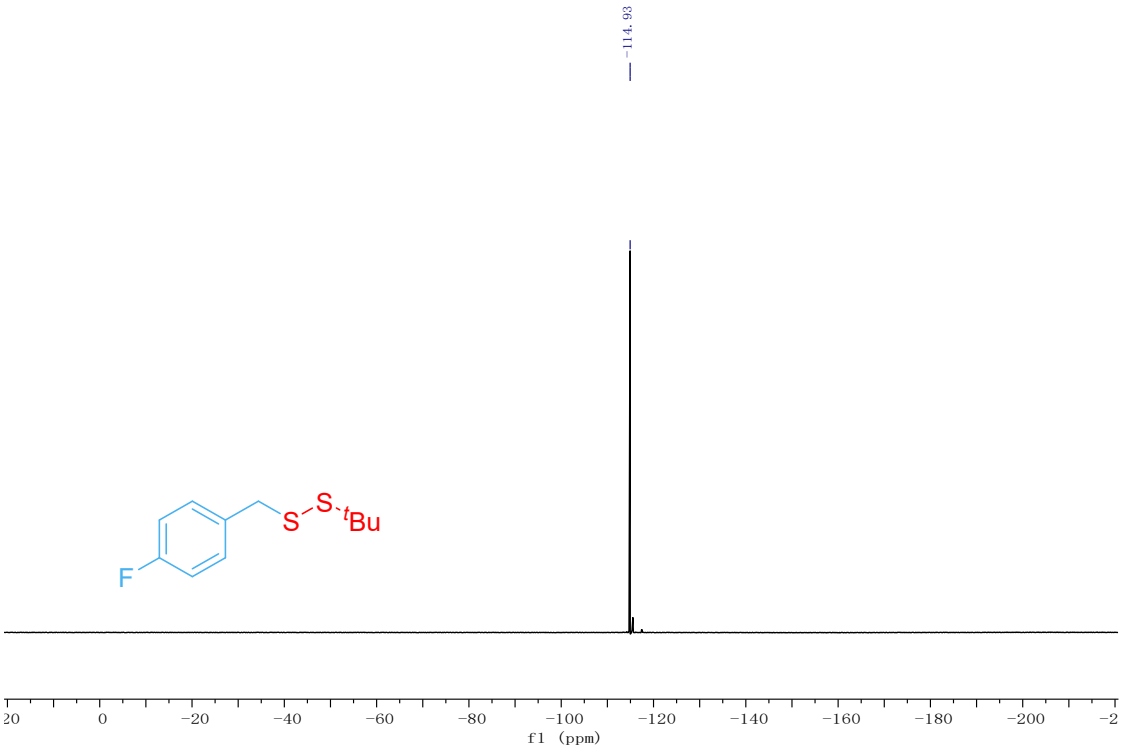
^{13}C NMR Spectra of 3m (100 MHz, $CDCl_3$)



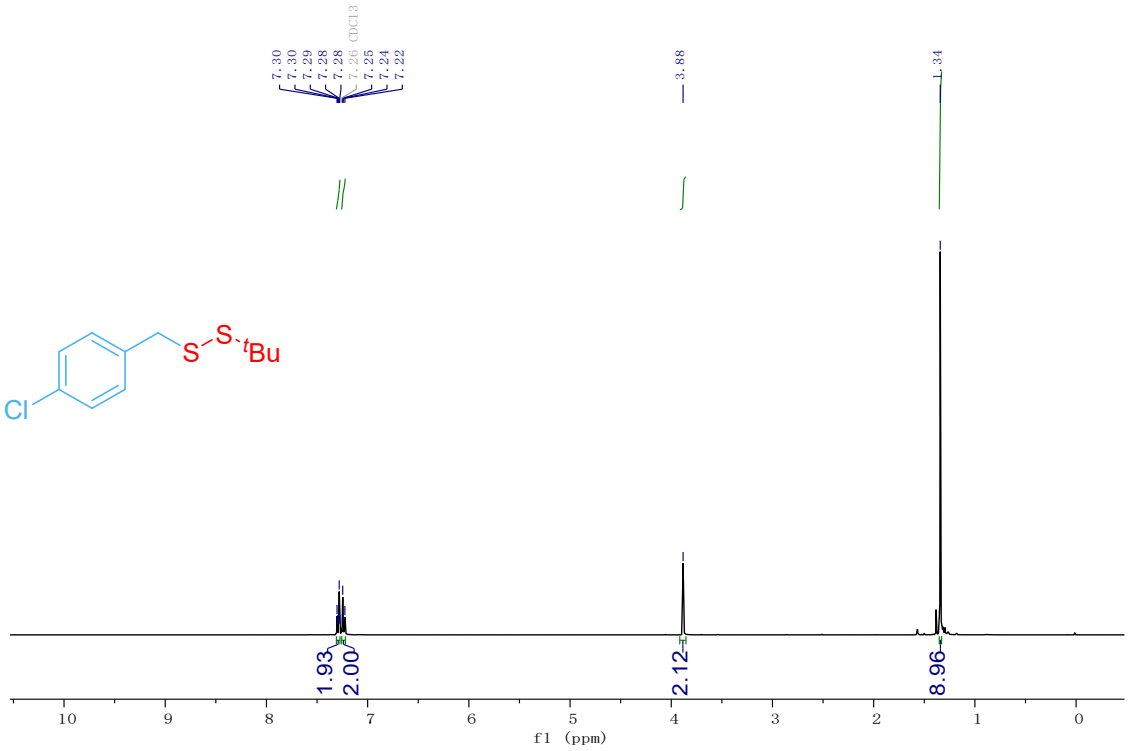
^{1}H NMR Spectra of 3n (400 MHz, $CDCl_3$) (400 MHz, $CDCl_3$)



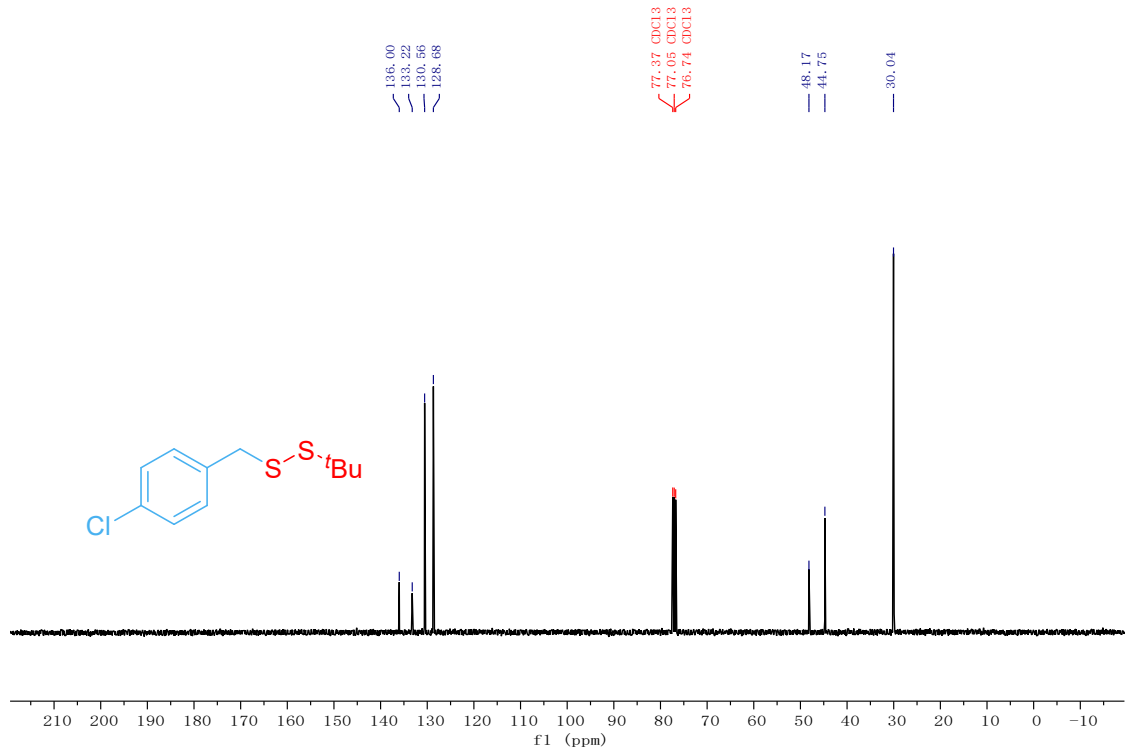
^{13}C NMR Spectra of 3n (100 MHz, $CDCl_3$)



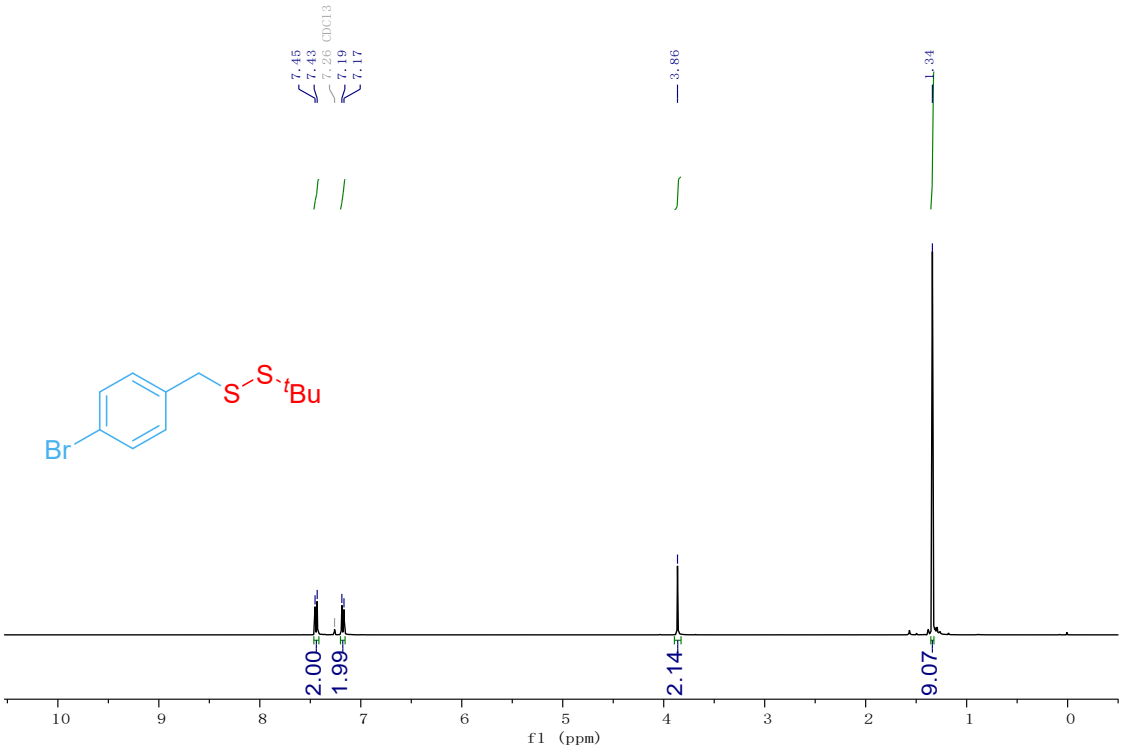
^{19}F NMR Spectra of 3n (376 MHz, $CDCl_3$)



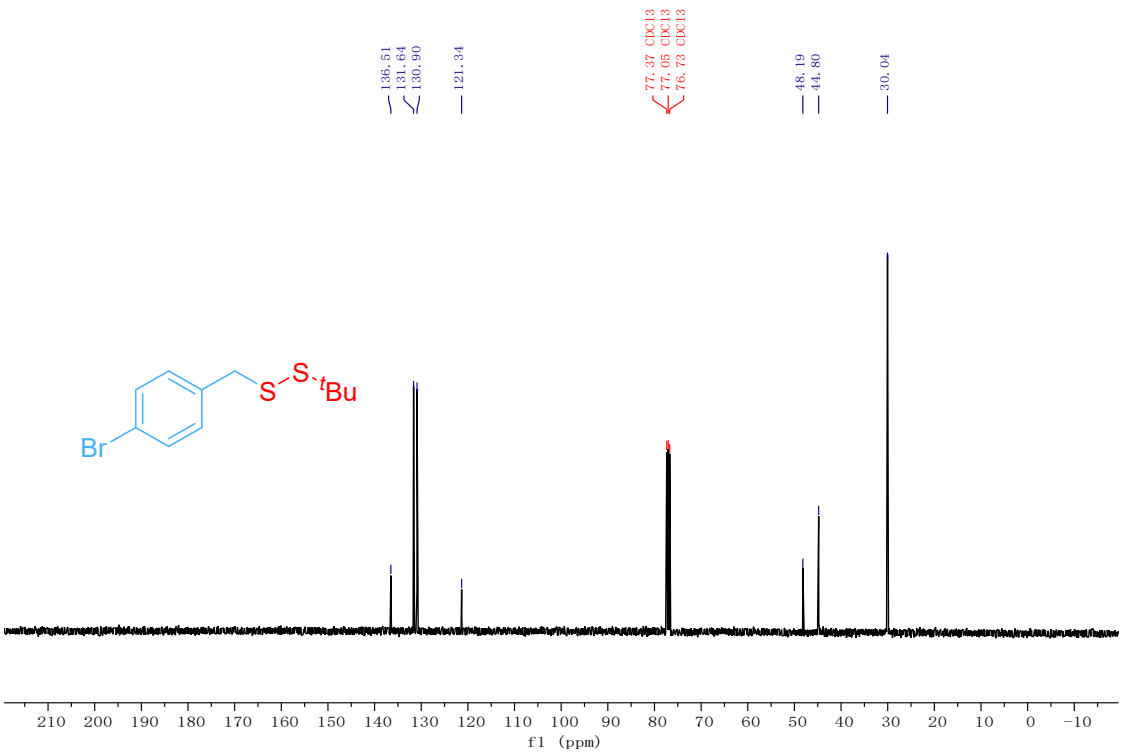
^{1}H NMR Spectra of 3o (400 MHz, $CDCl_3$) (400 MHz, $CDCl_3$)



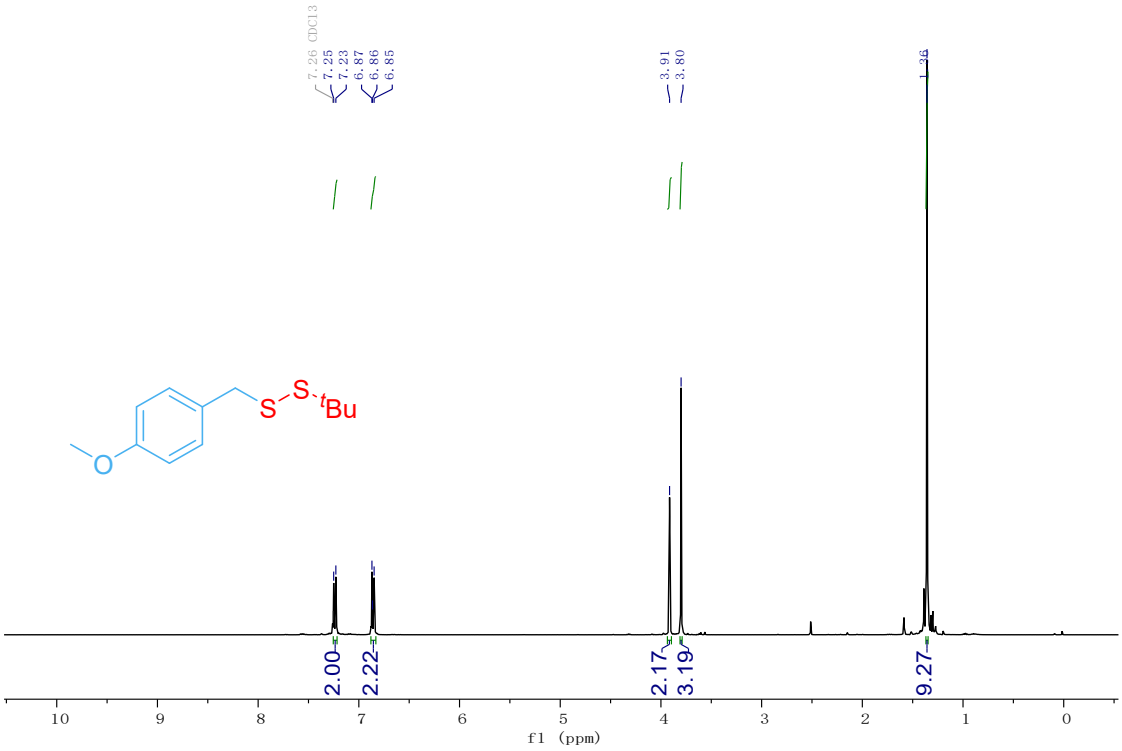
^{13}C NMR Spectra of 3o (100 MHz, $CDCl_3$)



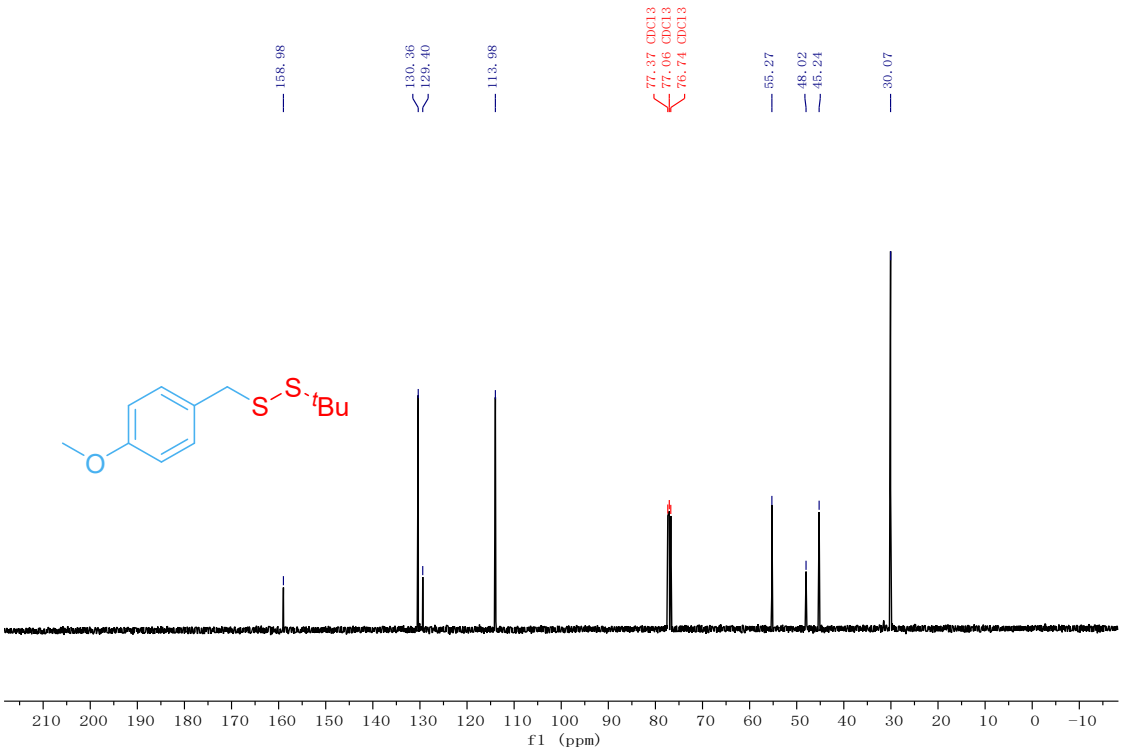
[1]H NMR Spectra of 3p (400 MHz, $CDCl_3$) (400 MHz, $CDCl_3$)



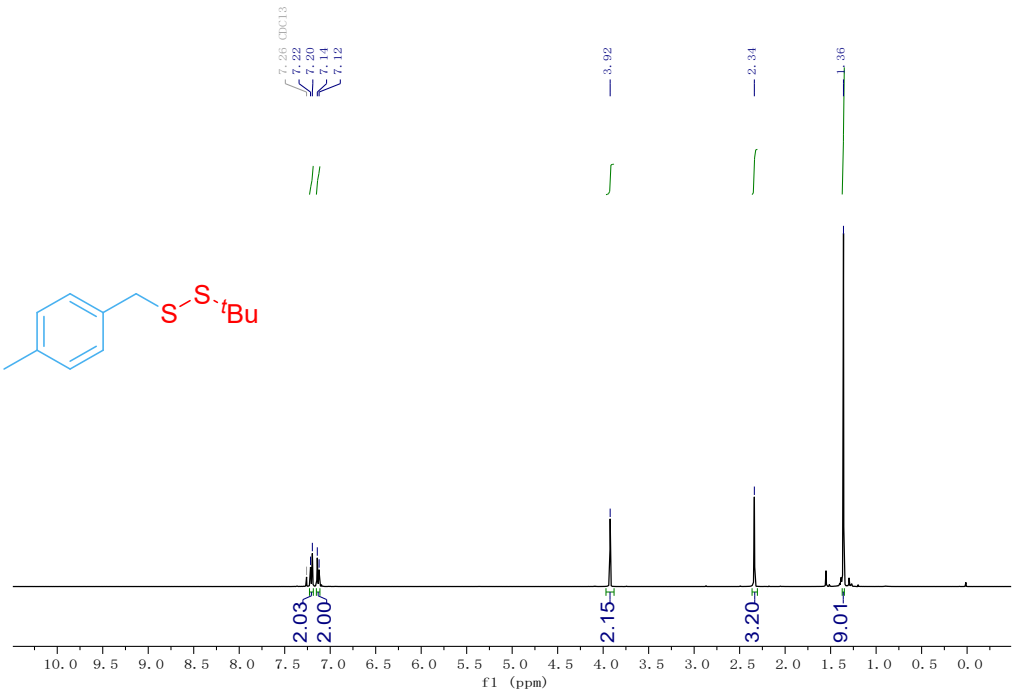
[13]C NMR Spectra of 3p (100 MHz, $CDCl_3$)



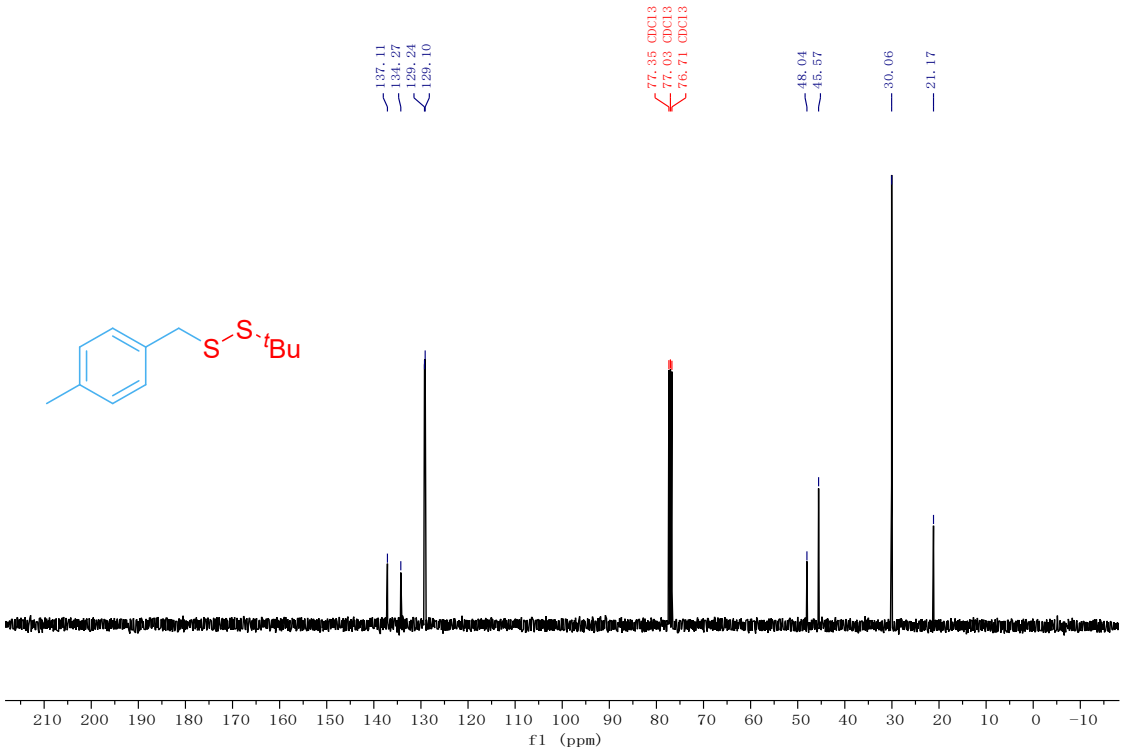
^{1}H NMR Spectra of 3q (400 MHz, $CDCl_3$) (400 MHz, $CDCl_3$)



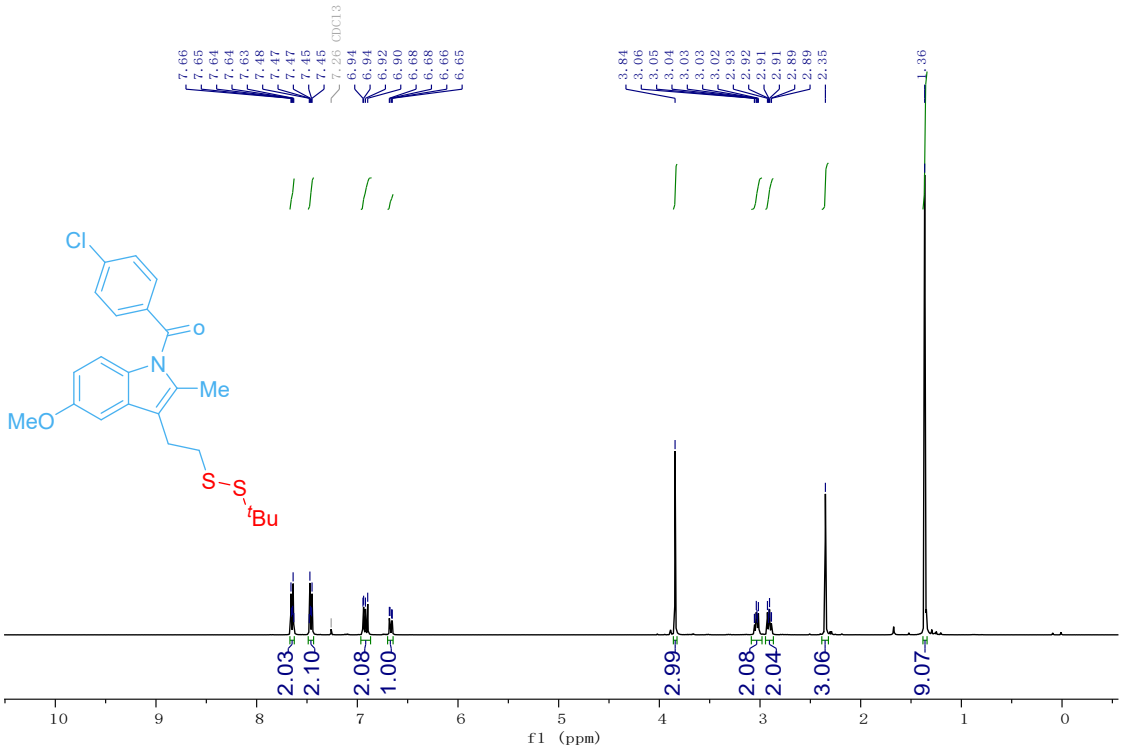
^{13}C NMR Spectra of 3q (100 MHz, $CDCl_3$)



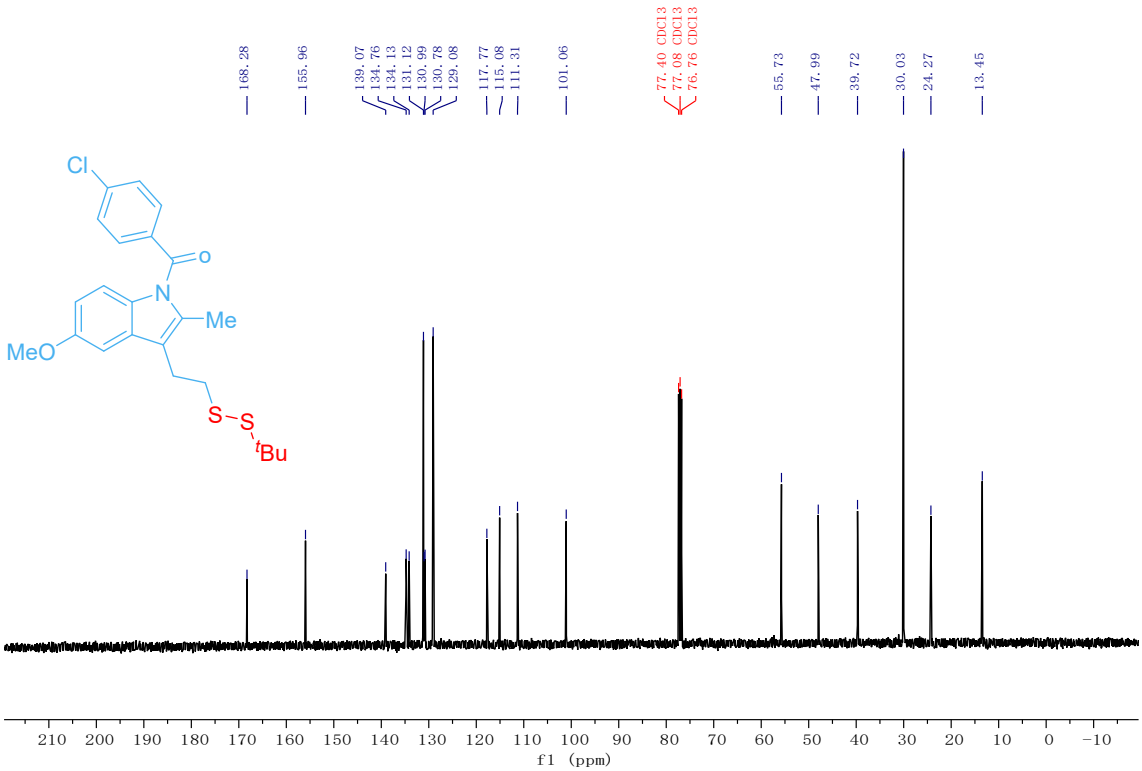
^{1}H NMR Spectra of 3r (400 MHz, $CDCl_3$) (400 MHz, $CDCl_3$)



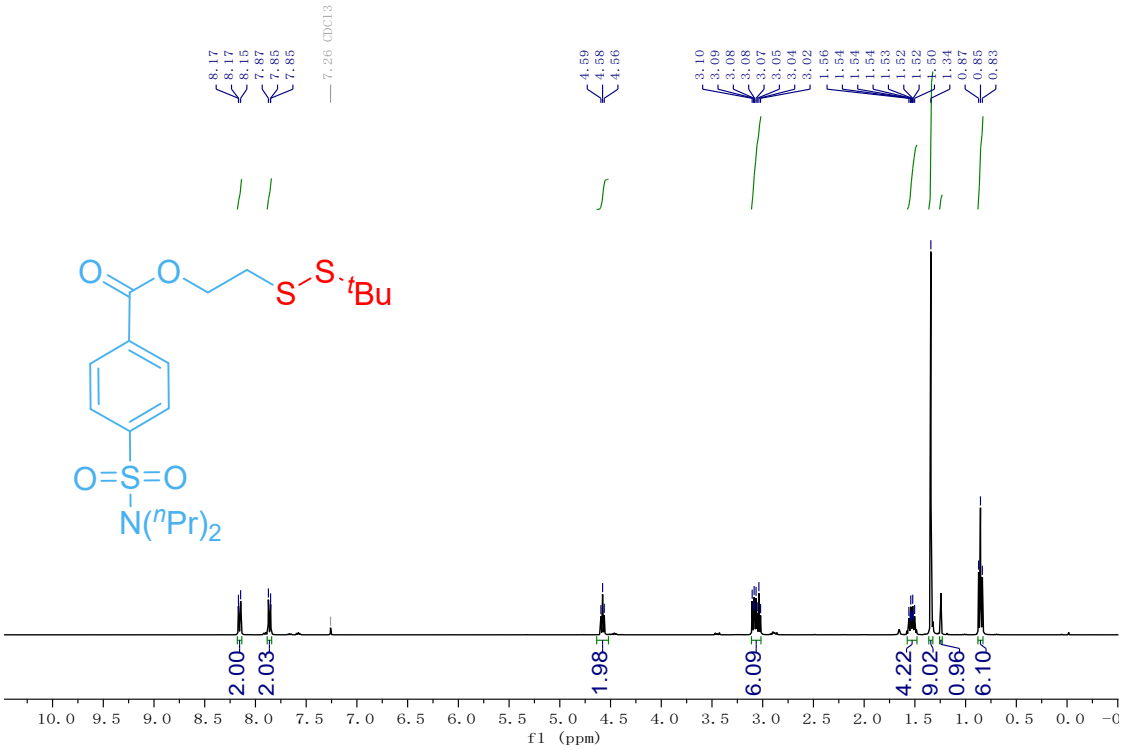
^{13}C NMR Spectra of 3r (100 MHz, $CDCl_3$)



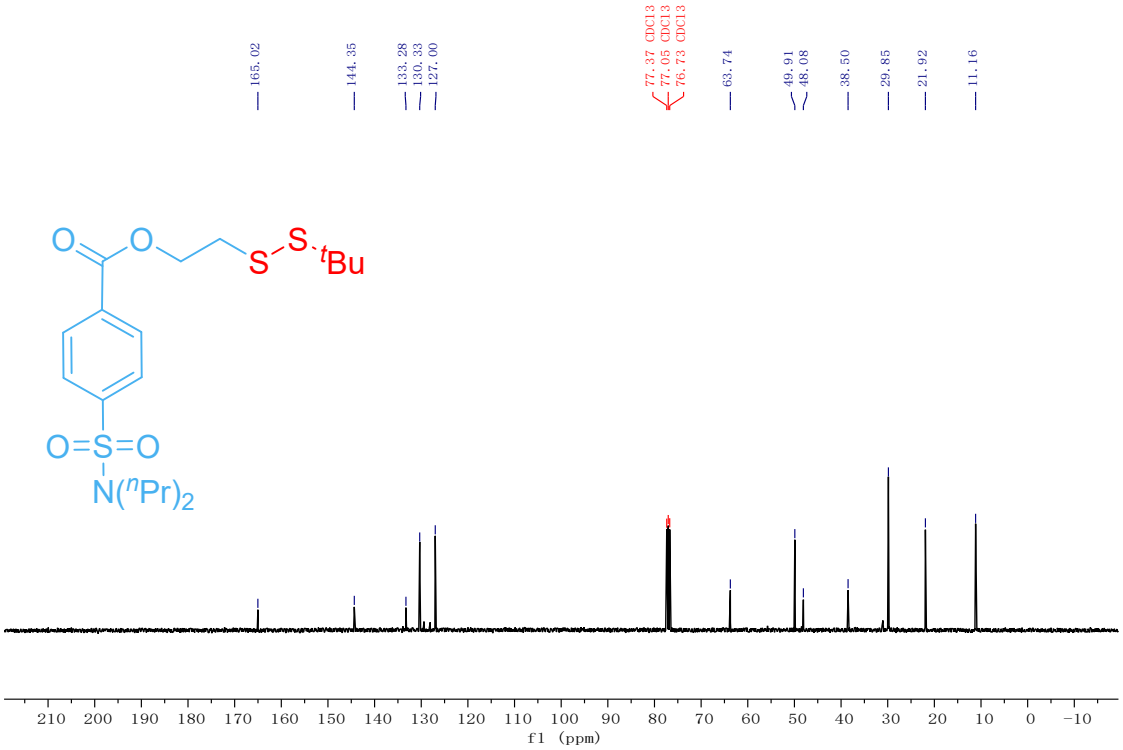
[1]H NMR Spectra of 3s (400 MHz, $CDCl_3$) (400 MHz, $CDCl_3$)



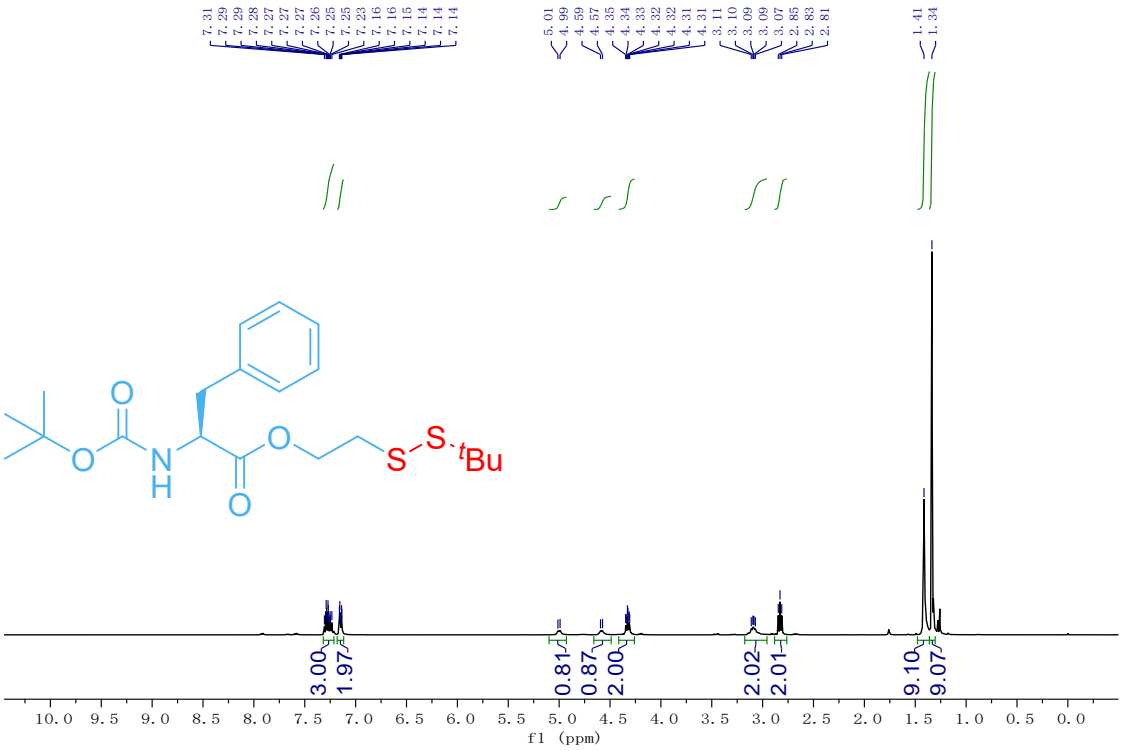
[13]C NMR Spectra of 3s (100 MHz, $CDCl_3$)



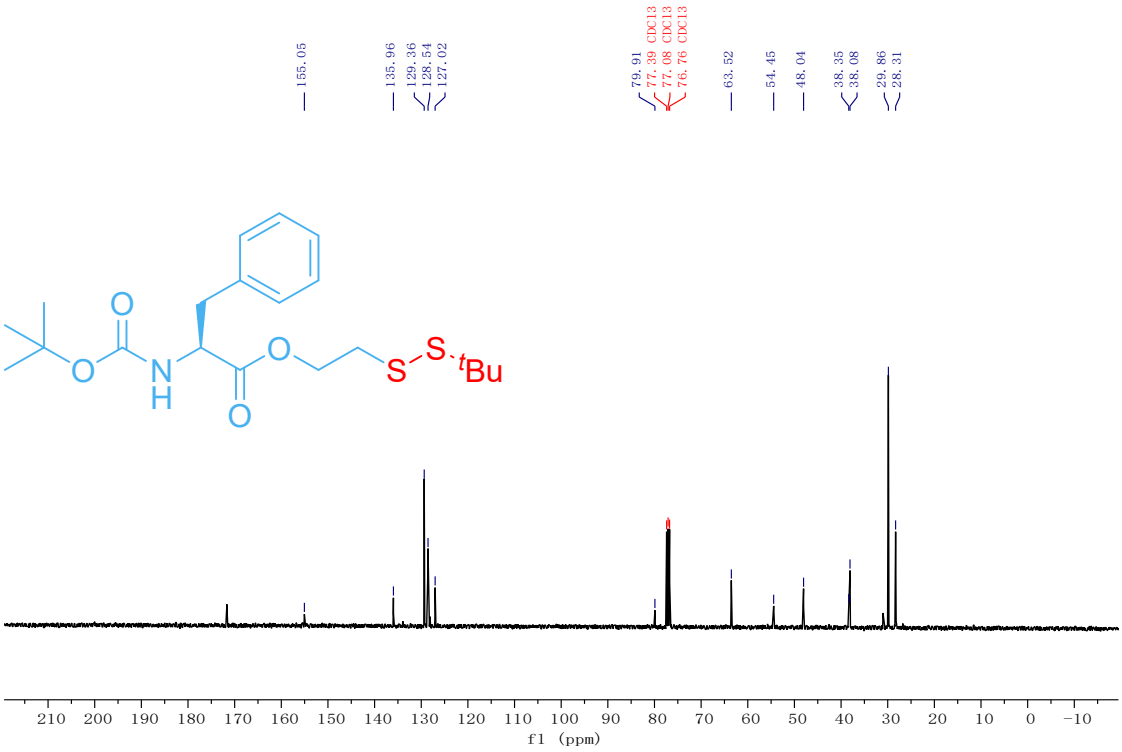
^{1}H NMR Spectra of 3t (400 MHz, $CDCl_3$) (400 MHz, $CDCl_3$)



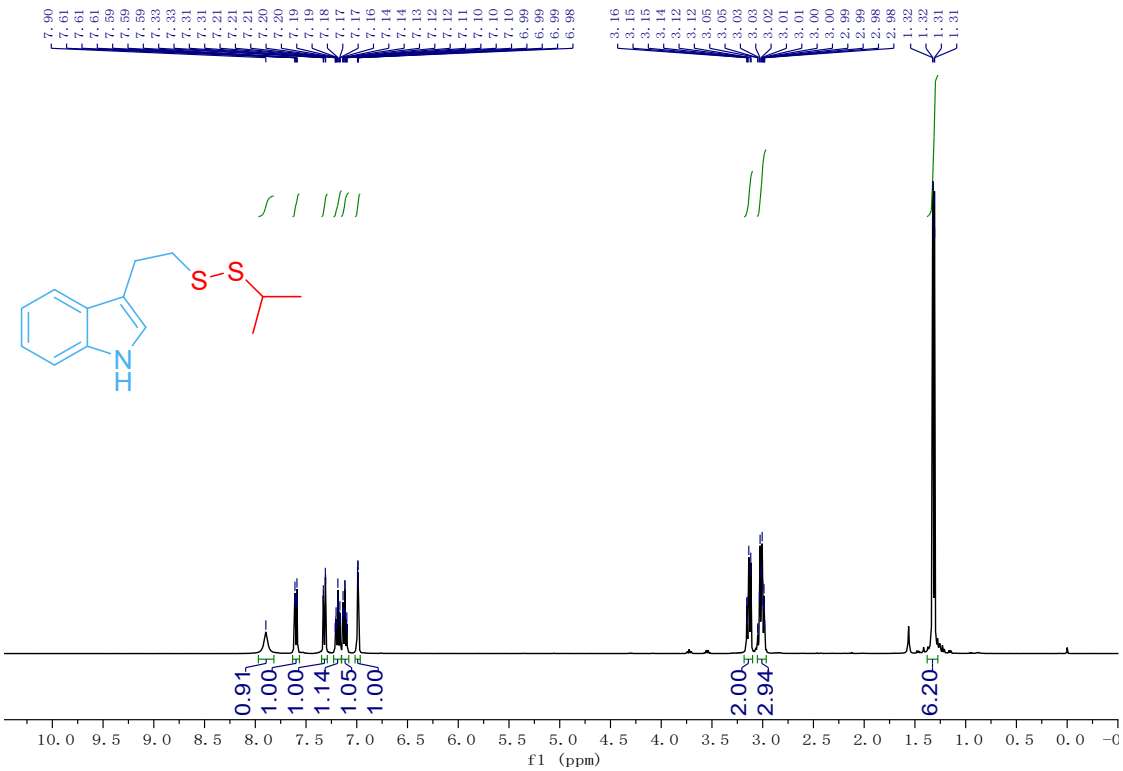
^{13}C NMR Spectra of 3t (100 MHz, $CDCl_3$)



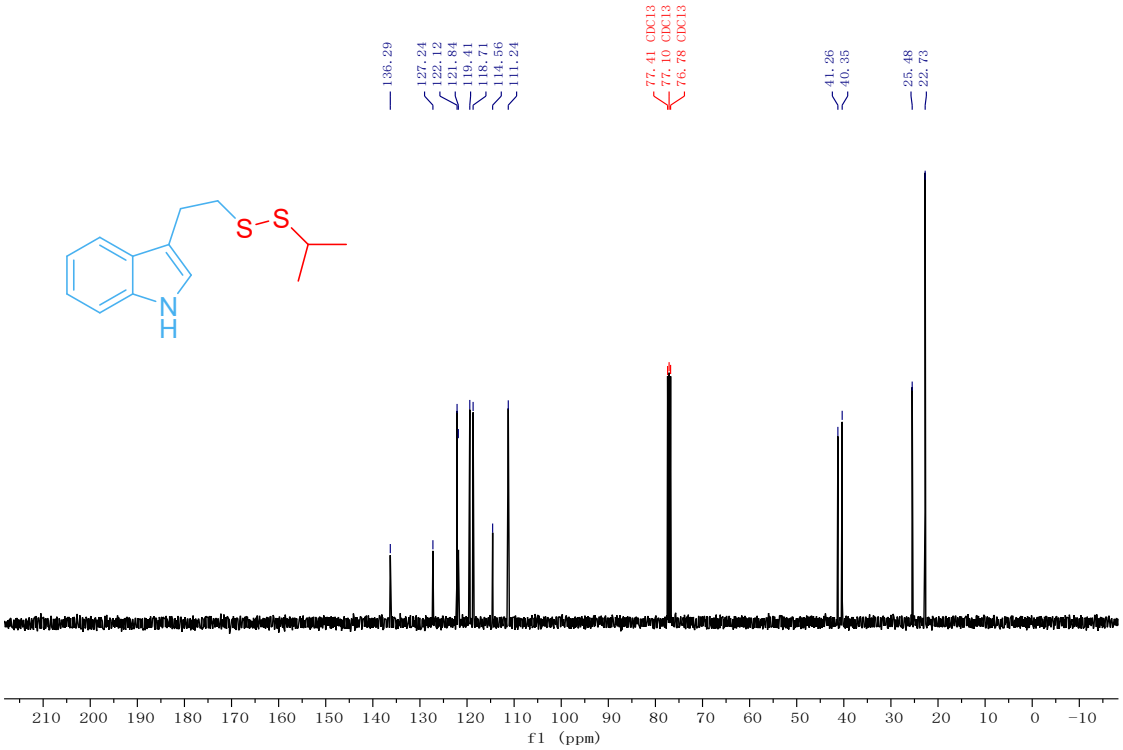
^{1}H NMR Spectra of 3u (400 MHz, $CDCl_3$) (400 MHz, $CDCl_3$)



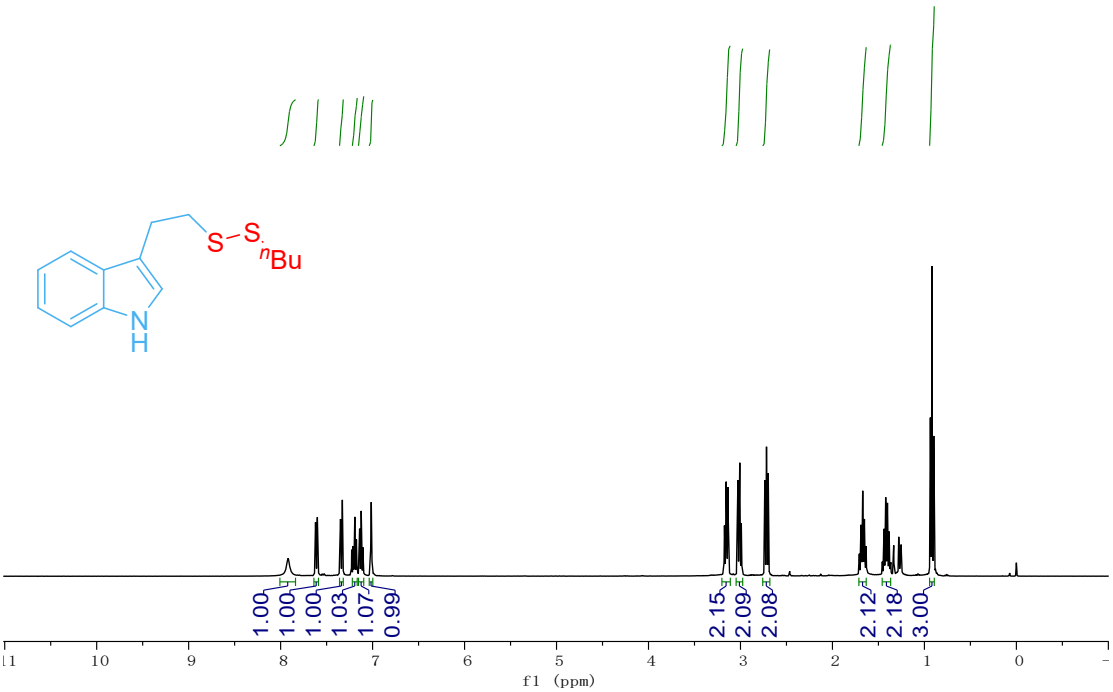
^{13}C NMR Spectra of 3u (100 MHz, $CDCl_3$)



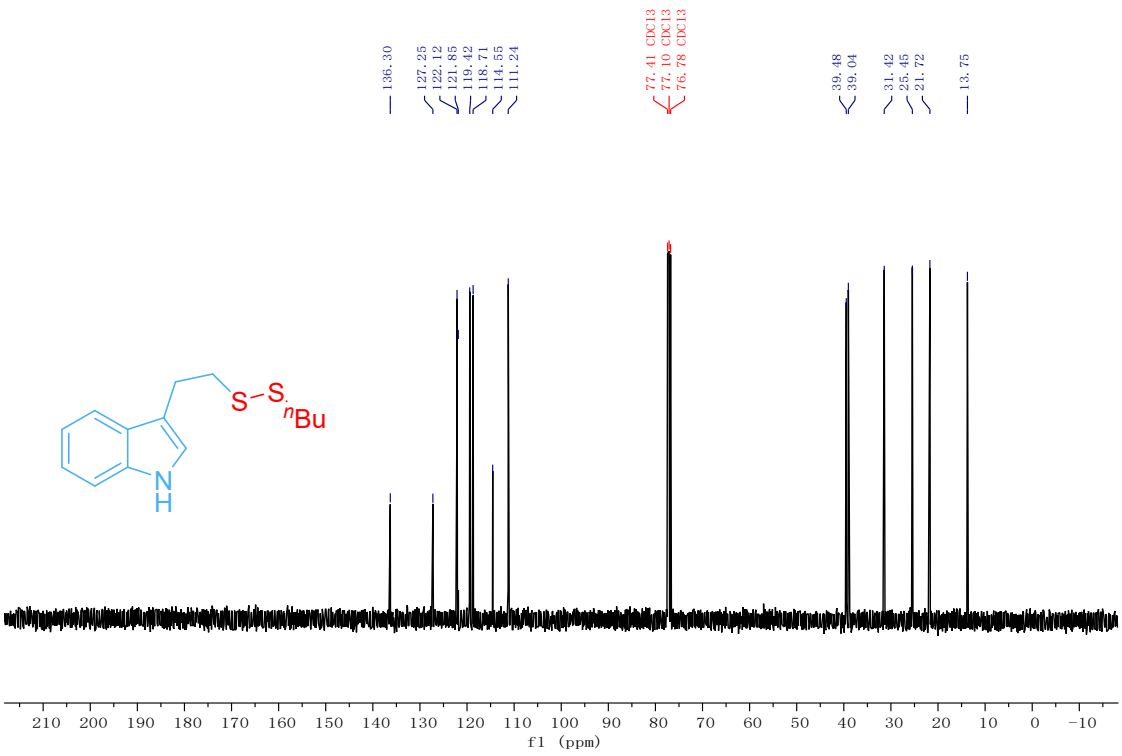
^{1}H NMR Spectra of 4a (400 MHz, $CDCl_3$) (400 MHz, $CDCl_3$)



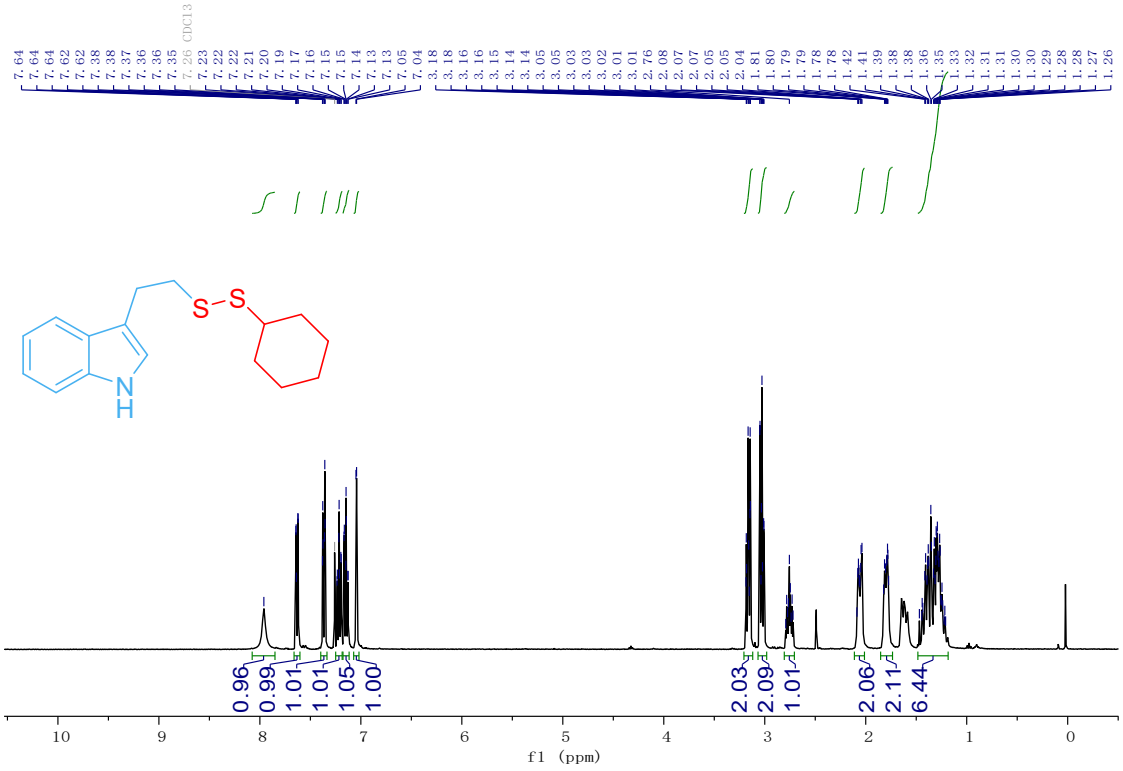
^{13}C NMR Spectra of 4a (100 MHz, $CDCl_3$)



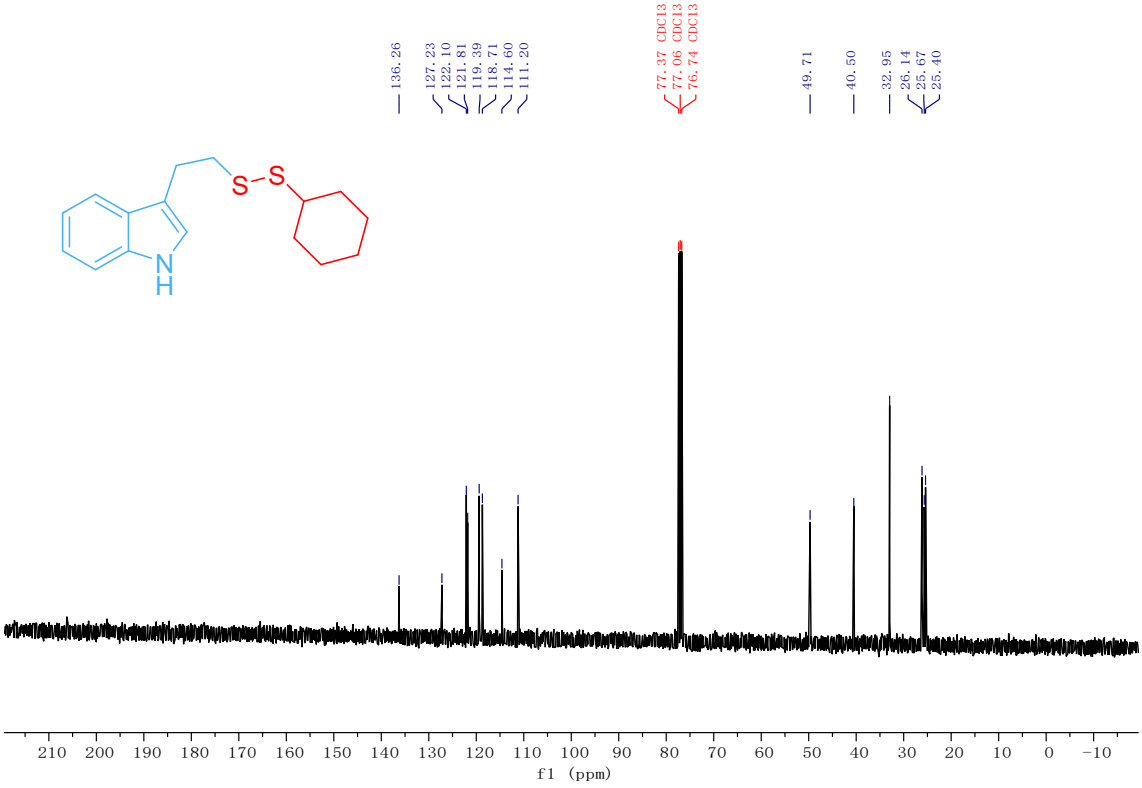
^{1}H NMR Spectra of 4b (400 MHz, $CDCl_3$) (400 MHz, $CDCl_3$)



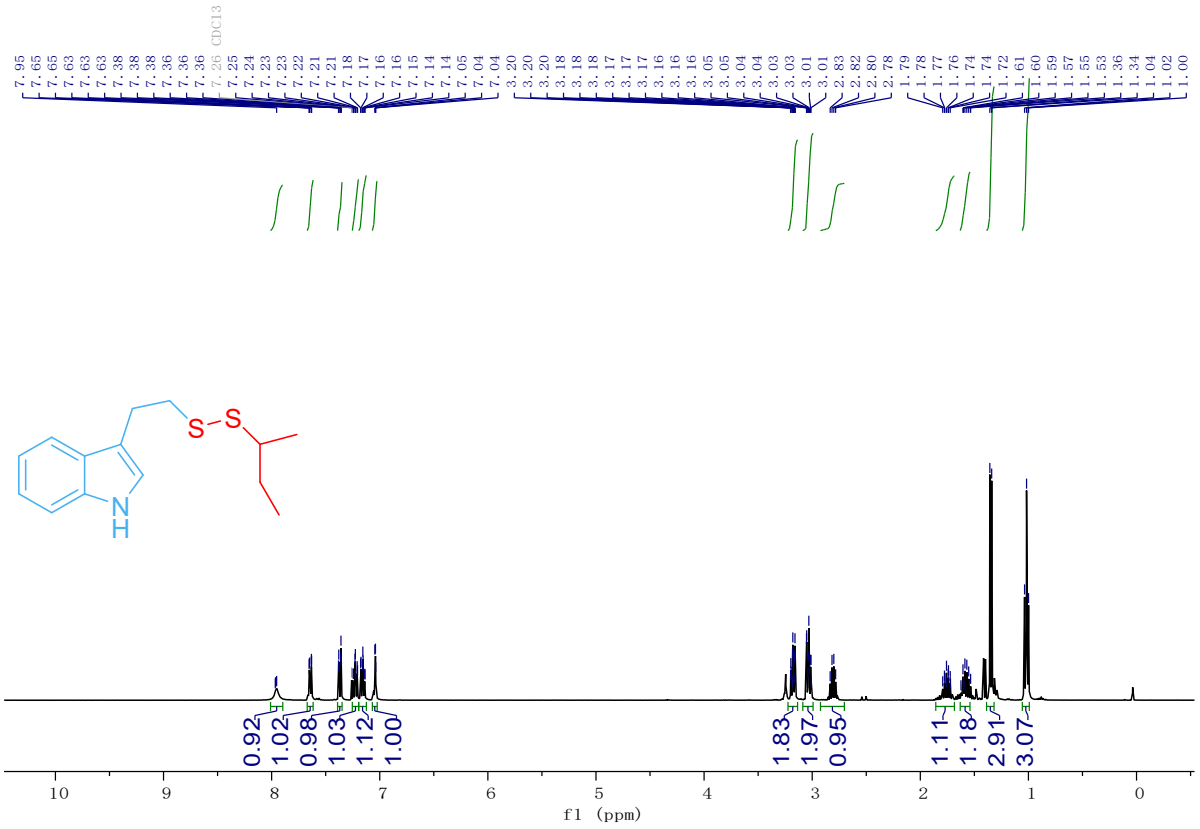
^{13}C NMR Spectra of 4b (100 MHz, $CDCl_3$)



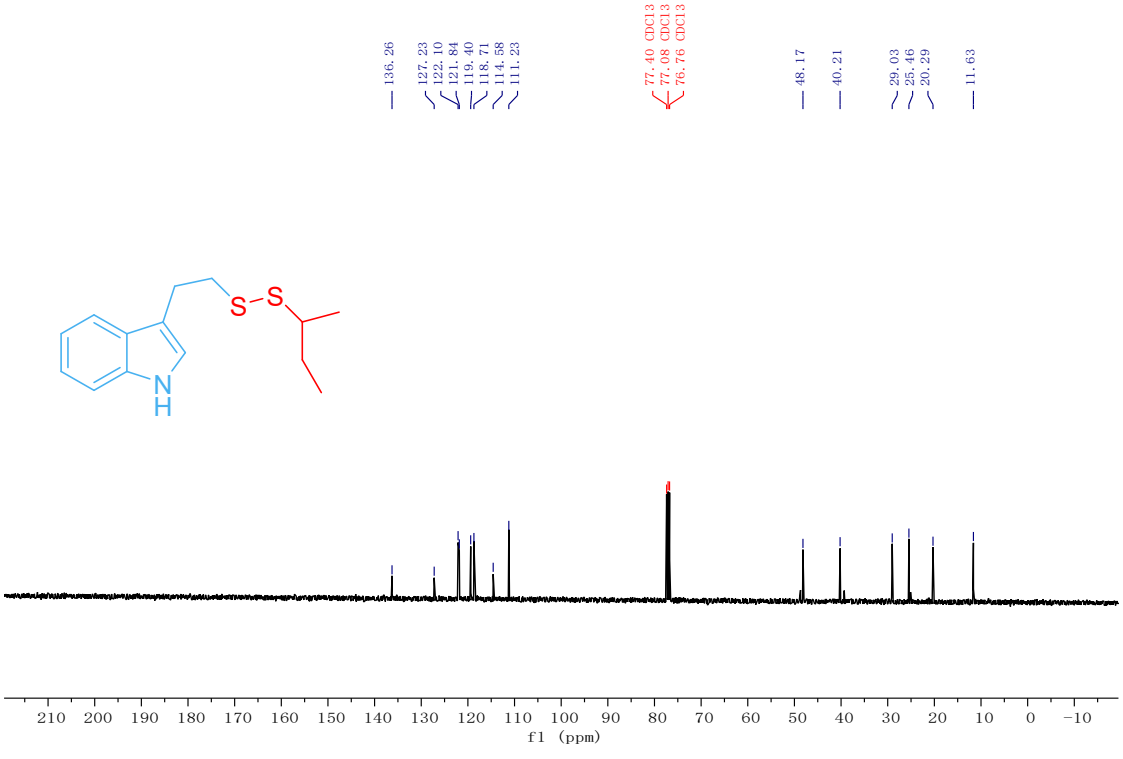
^{1}H NMR Spectra of 4c (400 MHz, $CDCl_3$) (400 MHz, $CDCl_3$)



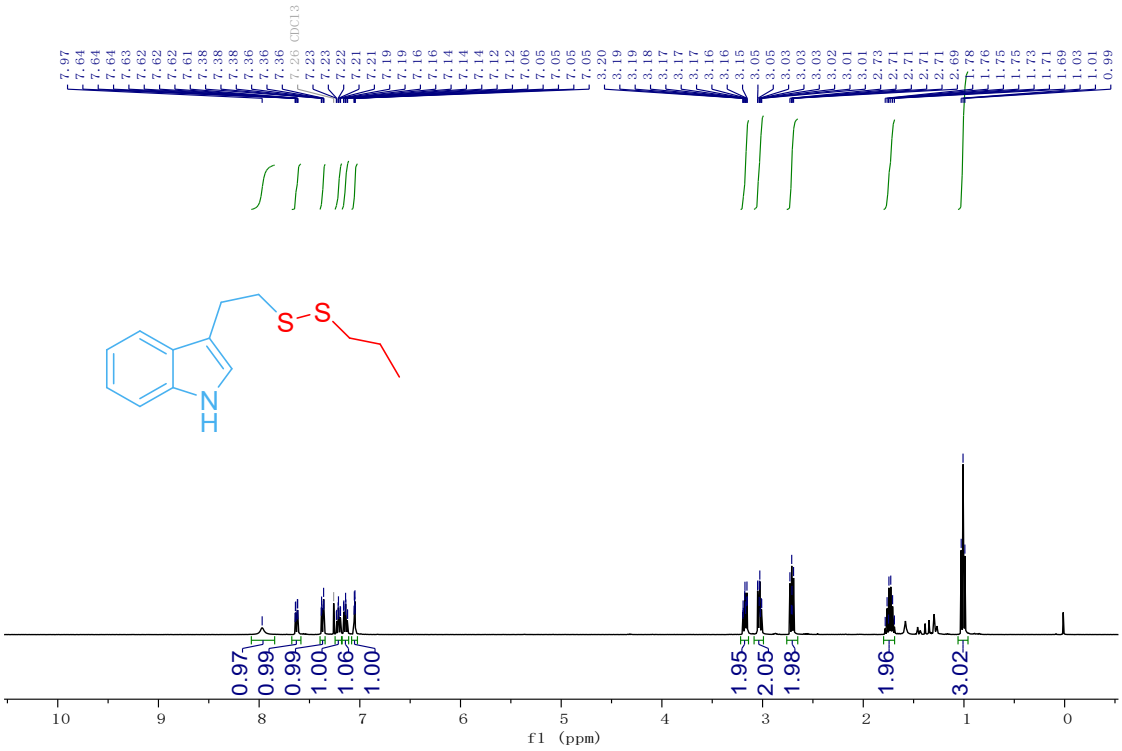
^{13}C NMR Spectra of 4c (100 MHz, $CDCl_3$)



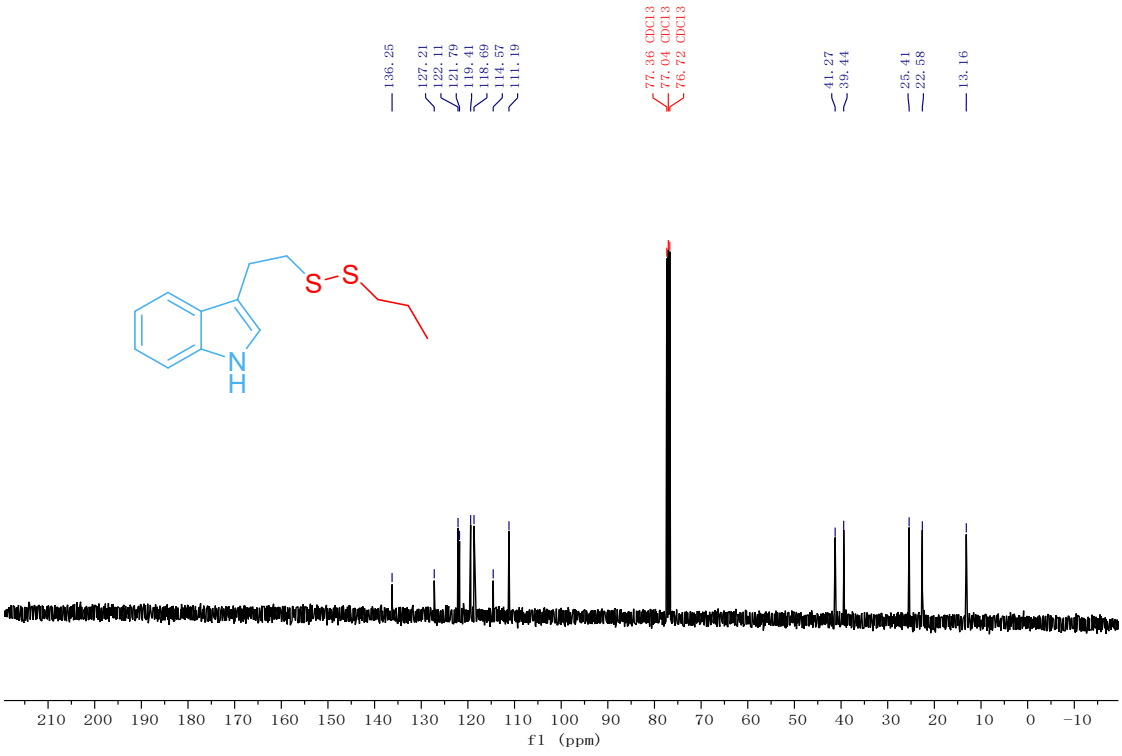
^{1}H NMR Spectra of 4d (400 MHz, $CDCl_3$) (400 MHz, $CDCl_3$)



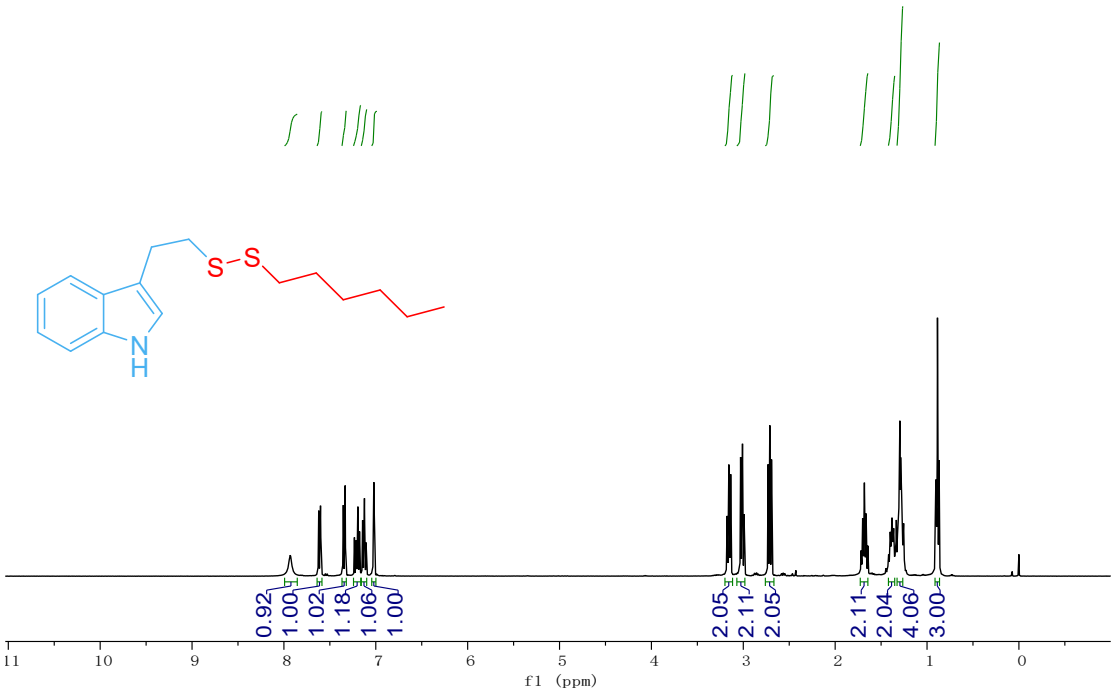
^{13}C NMR Spectra of 4d (100 MHz, $CDCl_3$)



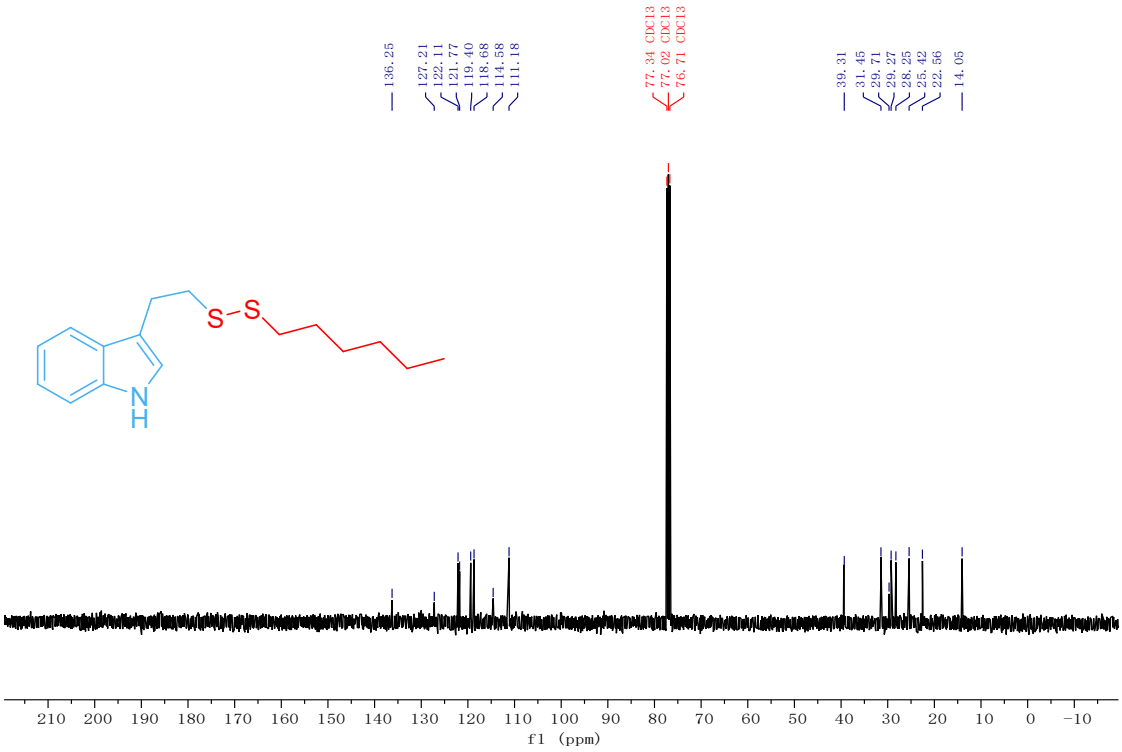
^{1}H NMR Spectra of 4e (400 MHz, $CDCl_3$) (400 MHz, $CDCl_3$)



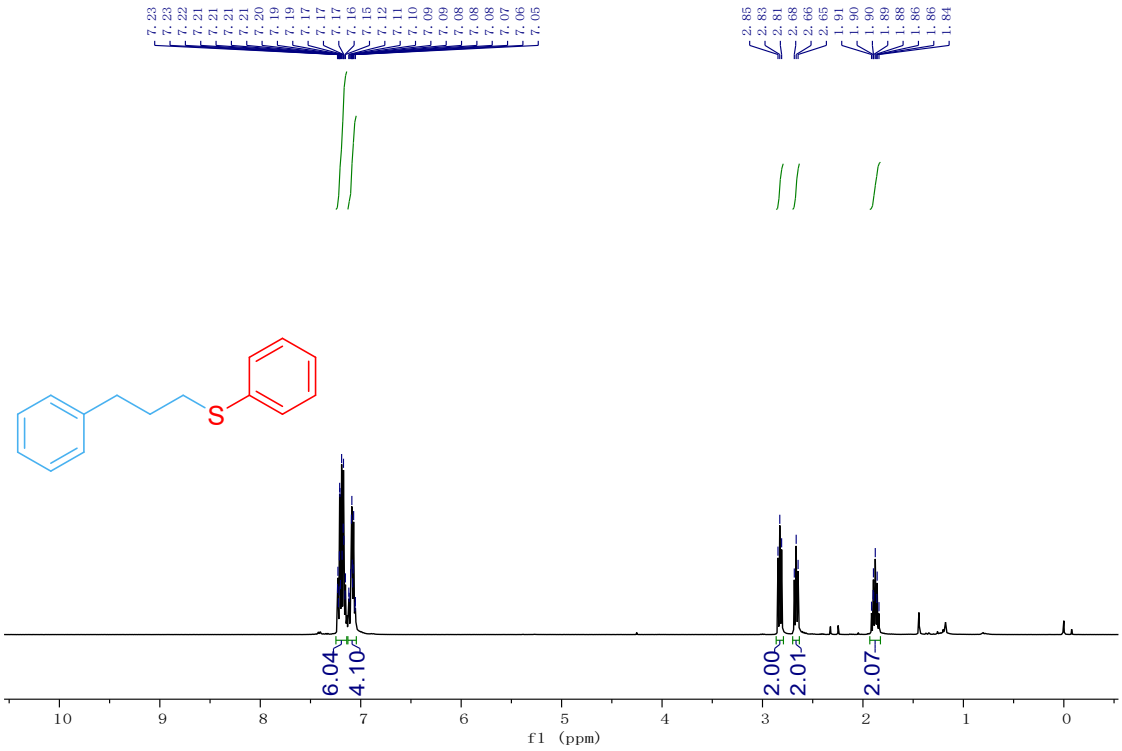
^{13}C NMR Spectra of 4e (100 MHz, $CDCl_3$)



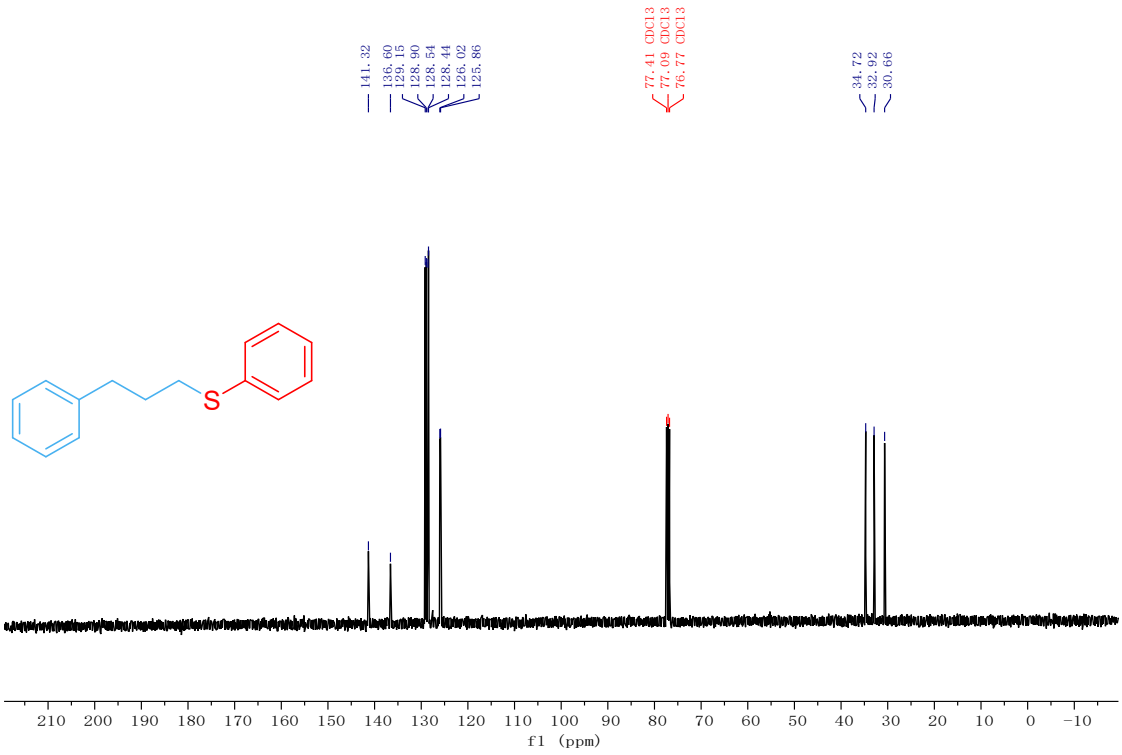
^{1}H NMR Spectra of 4f (400 MHz, $CDCl_3$) (400 MHz, $CDCl_3$)



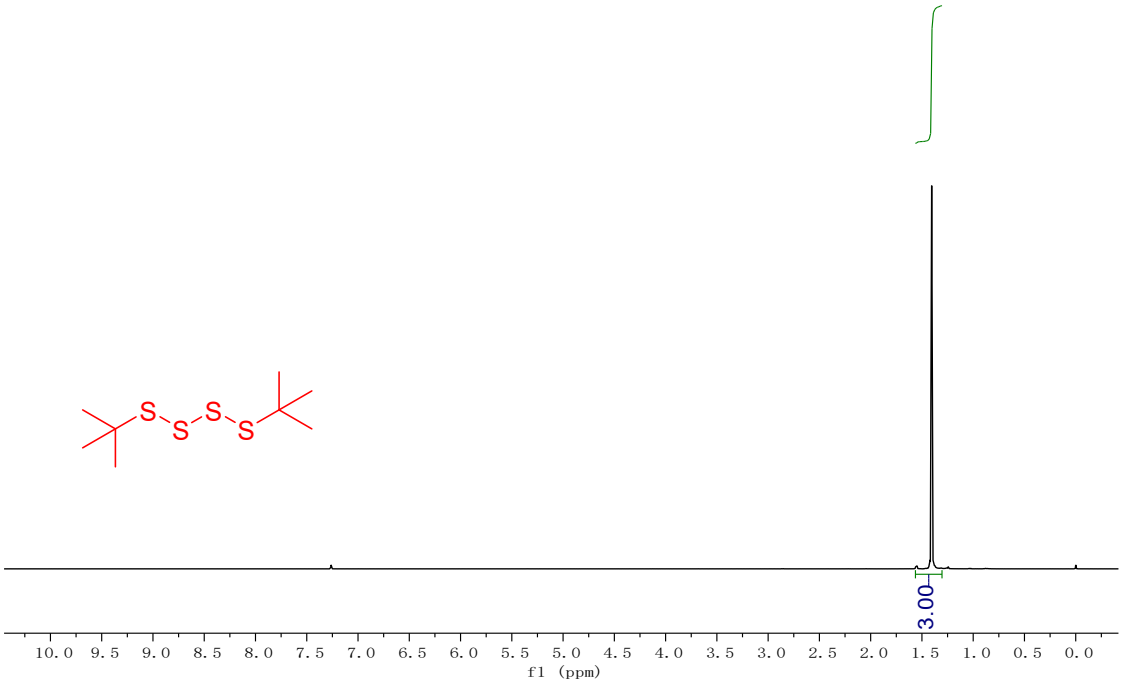
^{13}C NMR Spectra of 4f (100 MHz, $CDCl_3$)



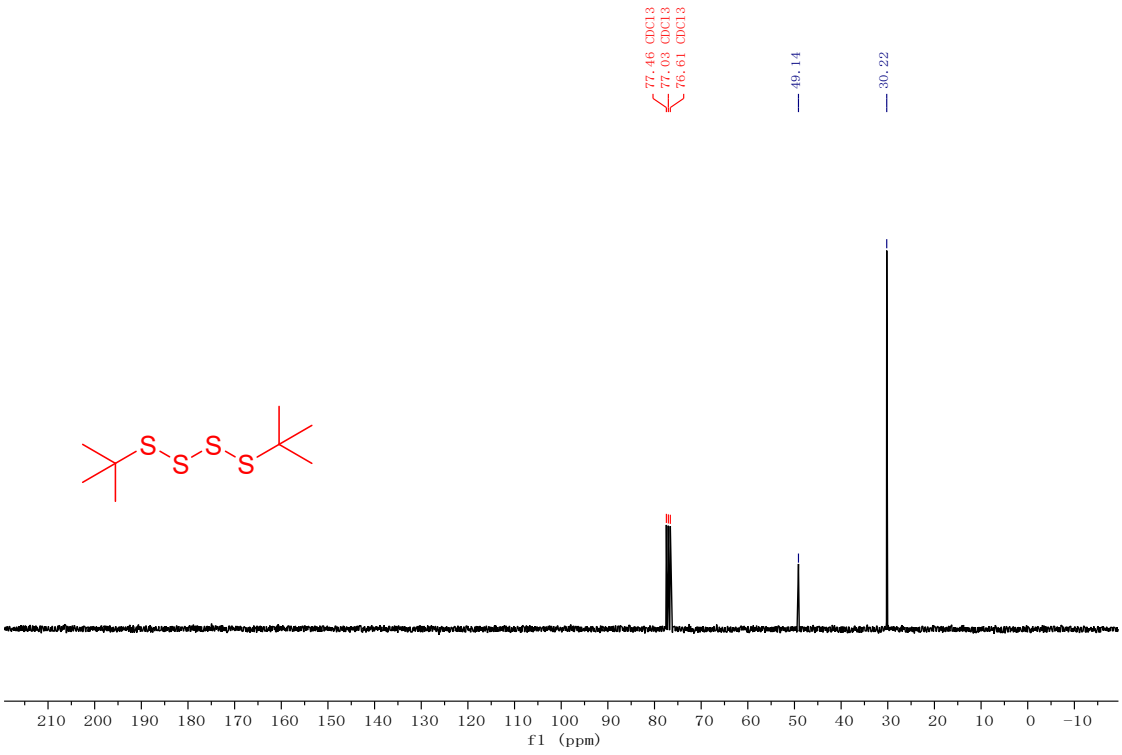
^{1}H NMR Spectra of 4g (400 MHz, $CDCl_3$) (400 MHz, $CDCl_3$)



^{13}C NMR Spectra of 4g (100 MHz, $CDCl_3$)



^{1}H NMR Spectra of 5a (400 MHz, $CDCl_3$) (400 MHz, $CDCl_3$)



^{13}C {1H} NMR Spectra of 5a (100 MHz, $CDCl_3$)