Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.
This journal is © the Partner Organisations 2024

Supporting Information

Nickel-free Cross-electrophile Coupling of Unactivated Alkyl Bromides with Thiosulfonates and Sulfinyl Sulfones

Qiujin Fan[1], Yanchuang Zhao[1], Jin-Tao Liang[1], Yan Zhang[1], Yuenian Xu[1], Qingqing Zhang[1], Hua Zhu[2], Min Jiang[1]* and Xinxin Shao[1]*

[1]College of Material, Chemistry and Chemical Engineering, Key Laboratory of Organosilicon Chemistry and Material Technology of Ministry of Education, Hangzhou Normal University, Hangzhou 311121, People's Republic of China

[2]Sichuan Qingmu Pharmaceutical Co., Ltd., Meishan City, 620036, People's Republic of China.

E-mail: xxshao@hznu.edu.cn, jiang-m18@hznu.edu.cn

Table of Contents

I. General information

General procedures. Unless specifically stated, all reagents were commercially obtained and where appropriate, purified prior to use. For example, dichloromethane (dichlormethane) was freshly distilled from CaH_2; toluene, ether (Et_2O) was dried and distilled from metal sodium and benzophenone. Other commercially available reagents and solvents were used directly without purification. Reactions were monitored by thin layer chromatography (TLC) using silica gel plates. Flash column chromatography was performed over silica (200 – 300 mesh). ^{1}H, ^{13}C, ^{19}F NMR spectra were recorded on a Bruker 400 MHz or 500 MHz spectrometer in $CDCl_3$ or d_6-DMSO. Multiplicities were given as: s (singlet); d (doublet); dd (doublets of doublet); t (triplet); q (quartet); td (triplet of doublets); tt (triplet of triplets) ddd (doublet of doublet of doublets) or m (multiplets). High resolution mass spectra (HRMS) of the products were obtained on a Bruker Daltonics micro TOF-spectrometer. High resolution mass spectra (HRMS) of the products were obtained on a Agilent Technologies micro Q-TOF-spectrometer. Light Source: The photoreactors used in this research were bought from GeAo Chem Technology Co., Ltd. (blue LEDs, 1W for every light bulb; light intensity = 32.8 mw/cm^2; every Schlenk tube was irradiated by 4 light bulbs from the side).

Reagents. The following chemicals were used as received: Acetyl chloride (Energy-Chemical), 1-(2-Bromoethyl)-4-chlorobenzene (Leyan), (Bromomethyl)cyclopropane (Energy-Chemical), ((3-Bromopropoxy)methyl)benzene (Bide), 11-Bromoundecan-1-ol (Leyan), Benzoyl chloride (Energy-Chemical), 6-Bromohexanoic acid (Energy-Chemical), 3-Bromopropan-1-ol (Energy-Chemical), 4-(Benzo[*d*][1,3]dioxol-5-yl)butan-2-one (Energy-Chemical), 6-Bromohexan-1-ol (Leyan), 5-Bromopentanoic acid (Energy-Chemical), 6-Bromohex-1-ene (Leyan), 2-(1-(4-Chlorobenzoyl)-5-methoxy-2-methyl-1H-indol-3-yl)acetic acid (Energy-Chemical), 5-Bromopent-1-ene (Leyan), 3-Chlorobenzoperoxoic acid (Energy-Chemical), 9,10-Dihydroanthracene (Bide), 1,6-Dibromohexane (Energy-Chemical),

Dicyclohexylmethanediimine (Energy-Chemical), 1,3-Dibromo-5,5-dimethylimidazolidine-2,4-dione (Bide), 1,4-Dibromobutane (Leyan), 1,2-Dicyclohexyldisulfane (Adamas), 1,2-Diphenyldisulfane (Energy-Chemical), 1,2-Di-*p*-tolyldisulfane (Leyan), 4-Dimethylaminopyridine (Energy-Chemical), 2,6-Di-*tert*-butyl-4-methylphenol (Energy-Chemical), 2,3-Dihydro-1*H*-inden-2-ol (Leyan), 3-(4,5-Diphenyl-4,5-dihydrooxazol-2-yl)propanoic acid (Energy-Chemical), 5-(2,5-Dimethylphenoxy)-2,2-dimethylpentanoic acid (Energy-Chemical), (2*E*,6*E*)-3,7-Dimethylnona-2,6-dien-1-ol (Energy-Chemical), 4-Hydroxybenzonitrile (Energy-Chemical), 4-Hydroxybenzaldehyde (Energy-Chemical), 1-(4-Hydroxyphenyl)ethan-1-one (Leyan), 2-(1*H*-Indol-3-yl)ethan-1-ol (Energy-Chemical), 4-Hydroxybenzoate (Leyan), 4-Iodophenol (Energy-Chemical), 9*H*-Carbazole (Energy-Chemical), 4-Methoxyphenol (Energy-Chemical), Methyl Pent-4-yn-1-ol (Leyan), 4-Methoxybenzenethiol (Energy-Chemical), Perbromomethane (Energy-Chemical), Potassium 1,3-ioxoisoindolin-2-ide (Energy-Chemical), Potassium indol-1-ide (Energy-Chemical), ((Phenylsulfinyl)oxy)zinc (Cesium Carbonate), 4-Phenylbutan-2-ol (Leyan), 4-(4-Methoxyphenyl)butan-2-one (Leyan), (*R*)-2-(6-Methoxynaphthalen-2-yl)propanoic acid (Energy-Chemical), (1*R*,4*R*)-Bicyclo[2.2.1]hept-5-ene-2-carboxylic acid (Energy-Chemical), (*R*)-2,5,7,8-Tetramethyl-2-((4*R*,8*R*)-4,8,12-trimethyltridecyl)chroman-6-ol (Bide), Sodium benzenesulfinate (Leyan), Sodium 4-methylbenzenesulfinate (Leyan), Sodium 4-chlorobenzenesulfinate (Leyan), (*S*)-2-(3-Isobutylphenyl)propanoic acid (Energy-Chemical), Sodium periodate (Energy-Chemical), (13*S*)-3-Hydroxy-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydro-17*H*-cyclopenta[a]phenanthren-17-one (Energy-Chemical), Triphenylphosphane (Leyan), Thiophene-2-carbonyl chloride (Energy-Chemical), *tert*-Butylchlorodiphenylsilane (Bide), Triethylamine (Energy-Chemical), 1-(*tert*-Butoxycarbonyl)piperidine-4-carboxylic acid (Energy-Chemical), (*tert*-Butoxycarbonyl)-*L*-phenylalanine (Leyan).

II. Synthesis of starting materials

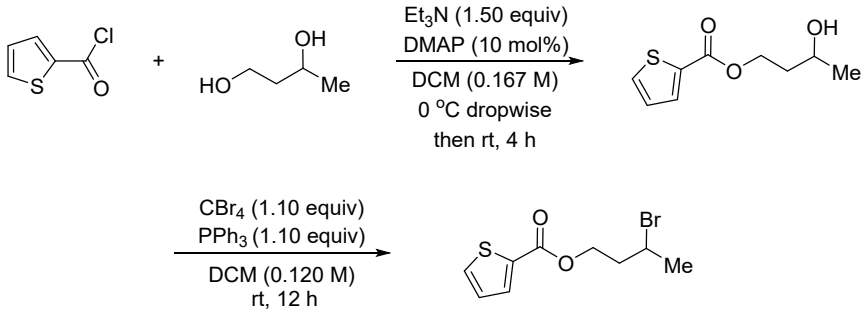
1. Synthesis of alkyl bromides 1f-1v, 1y-z, 1ar

The alkyl bromides **1f**, **1m**, **1ar**, **1y**, **1z** were synthesized according to our previous report, the spectral data match those previously reported[1].

The alkyl bromides **1i-k**, **1n**, **1r-1t** were synthesized according to our previous report, the spectral data match those previously reported[2].

The alkyl bromides **1g-1h**, **1l**, **1o-1q**, **1u-1v** were synthesized according to our previous report, the spectral data match those previously reported[3].

2. Synthesis of 3-bromobutyl thiophene-2-carboxylate 1w

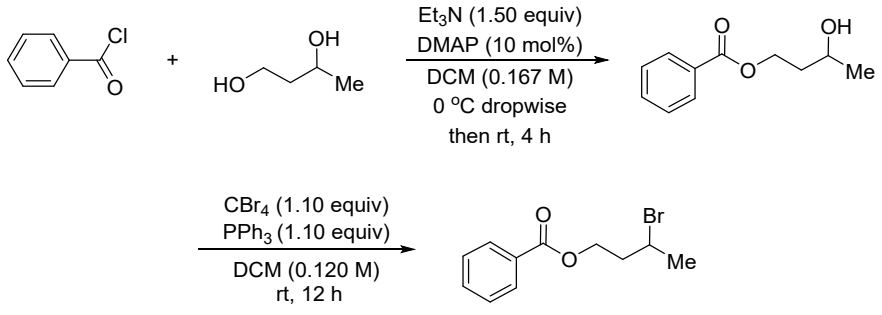


An oven-dried 200-mL round-bottom flask, equipped with a stirring bar, was charged with DMAP (0.244 g, 2.00 mmol, 0.100 equiv). The solid was evacuated and backfilled with nitrogen for three times. Then dry dichloromethane (100 mL), Et_3N (3.04 g, 30.0 mmol, 1.50 equiv) and butane-1,3-diol (1.98 g, 22.0 mmol, 1.10 equiv) were added under N_2 atmosphere. The thiophene-2-carbonyl chloride (2.93 g, 20.0 mmol, 1.00 equiv) was slowly added under stirring at 0 °C. Then, the mixture was allowed to stir at room temperature for 4 h. The mixture was poured into water (50.0 mL) and extracted with dichloromethane (25.0 mL x 3). The combined organic layers were washed with saturated NaCl aqueous solution (25.0 mL x 3), dried over Na_2SO_4 and filtered. The solvent was removed by rotary evaporation and the residue was purified by flash silica gel chromatography (Eluent: 100:1 to 10:1 petroleum ether: ethyl acetate). The product was isolated as a yellow liquid (2.57 g, 12.8 mmol,

64.2% yield) which is a known compound. The spectral data match those previously reported[4].

An oven-dried 50-mL round-bottom flask, equipped with a stirring bar, was charged with CBr_4 (1.09 g, 3.30 mmol, 1.10 equiv). The mixture was evacuated and backfilled with nitrogen for three times. Then dry dichloromethane (15.0 mL) and 3-hydroxybutyl thiophene-2-carboxylate (0.601 g, 3.00 mmol, 1.00 equiv) was added under N_2 atmosphere. A solution of PPh_3 (0.866 g, 3.30 mmol, 1.10 equiv) in dichlormethane (10.0 mL) was slowly added under stirring at 0 °C. Then, the mixture was stirred at room temperature for 12 h. The mixture was poured into water (25.0 mL) and extracted with dichloromethane (25.0 mL x 3). The combined organic layers were washed with saturated NaCl aqueous solution (25.0 mL x 3), dried over Na_2SO_4 and filtered. The solvent was removed by rotary evaporation and the residue was purified by flash silica gel chromatography (Eluent: 100:1 to 30:1 petroleum ether: ethyl acetate). The product was isolated as a colorless liquid (0.731 g, 2.78 mmol, 92.6% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.79 (1H, d, J = 4.0 Hz), 7.55 (1H, d, J = 5.1 Hz), 7.10 – 7.08 (1H, m), 4.52 – 4.46 (1H, m), 4.44 – 4.37 (1H, m), 4.31 – 4.23 (1H, m), 2.28 – 2.15 (2H, m), 1.78 (3H, d, J = 6.6 Hz); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 162.0, 133.6, 133.5, 132.6, 127.8, 63.2, 46.9, 39.8, 26.6; **HRMS** (ESI^+) $[M+Na]^+$ calc'd for $C_9H_{11}NaBrO_2S$: 284.9555, found: 284.9554.

3. Synthesis of 3-bromobutyl benzoate 1x

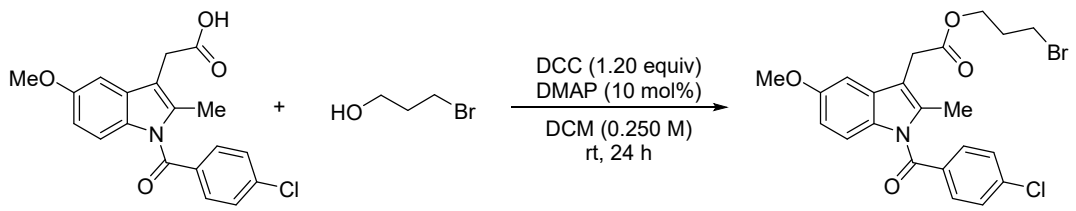


An oven-dried 200-mL round-bottom flask, equipped with a stirring bar, was charged with DMAP (0.122 g, 1.00 mmol, 0.100 equiv). The mixture was evacuated and backfilled with nitrogen for three times. Then the dry dichloromethane (50.0 mL), Et_3N (1.53 g, 15.0 mmol, 1.50 equiv) and butane-1,3-diol (1.08 g, 12.0 mmol,

1.20 equiv) was added under N_2 atmosphere. The benzoyl chloride (1.405 g, 10.0 mmol, 1.00 equiv) was slowly added under stirring at 0 °C. Then, the mixture was allowed to stir at room temperature for 4 h. The mixture was poured into water (50.0 mL) and extracted with dichloromethane (25.0 mL x 3). The combined organic layers were washed with saturated NaCl aqueous solution (25.0 mL x 3), dried over Na_2SO_4 and filtered. The solvent was removed by rotary evaporation and the residue was purified by flash silica gel chromatography (Eluent: 100:1 to 10:1 petroleum ether: ethyl acetate). The product was isolated as a colorless liquid (1.72 g, 1.73 mmol, 89.2% yield) which is a known compound. The spectral data match those previously reported[5].

An oven-dried 50-mL round-bottom flask, equipped with a stirring bar, was charged with CBr_4 (1.82 g, 5.50 mmol, 1.10 equiv). The mixture was evacuated and backfilled with nitrogen for three times. Then the dichloromethane (25.0 mL) and 3-hydroxybutyl benzoate (0.971 g, 5.00 mmol, 1.00 equiv) was added under N_2 atmosphere. A solution of PPh_3 (1.44 g, 5.50 mmol, 1.10 equiv) in dichloromethane (10.0 mL) was slowly added under stirring at 0 °C. Then, the mixture was allowed to stirat room temperature for 12 h. The mixture was poured into water (25.0 mL) and extracted with dichlormethane (25.0 mL x 3). The combined organic layers were washed with saturated NaCl aqueous solution (25.0 mL x 3), dried over Na_2SO_4 and filtered. The solvent was removed by rotary evaporation and the residue was purified by flash silica gel chromatography (Eluent: 100:1 to 20:1 petroleum ether: ethyl acetate). The product was isolated as a colorless liquid (0.997 g, 3.88 mmol, 77.6%) which is a known compound. The spectral data match those previously reported[6].

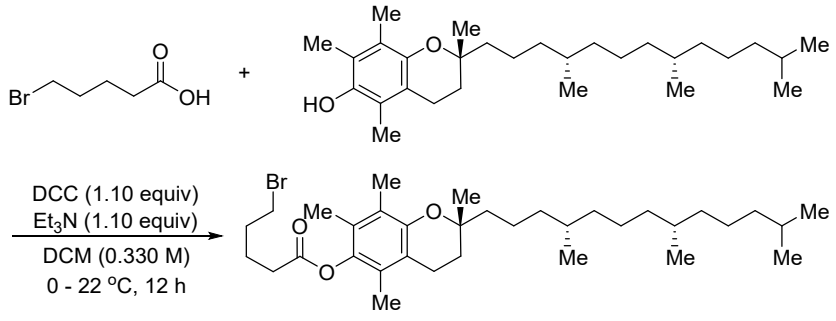
4. Synthesis of 3-bromopropyl 2-(1-(4-chlorobenzoyl)-5-methoxy-2-methyl-1*H*-indol-3-yl)acetate 1aa



An oven-dried 200-mL round-bottom flask, equipped with a stirring bar, was

charged with DMAP (0.183 g, 1.50 mmol, 0.100 equiv) and 2-(1-(4-chlorobenzoyl)-5- methoxy-2-methyl-1*H*-inden-3- yl)acetic acid (5.37 g, 15.0 mmol, 1.00 equiv). The mixture was evacuated and backfilled with nitrogen for three times. Then the dry dichlormethane (60.0 mL) and 3-bromopropan-1-ol (2.50 g, 18.0 mmol, 1.20 equiv) was added under N_2 atmosphere. A solution of DCC (3.71 g, 18.0 mmol, 1.20 equiv) in dichloromethane (36.0 mL) was slowly added under stirring at 0 °C. Then, the mixture was allowed to stir at room temperature for 24 h. The mixture was poured into water (50.0 mL) and extracted with dichloromethane (25.0 mL x 3). The combined organic layers were washed with saturated NaCl aqueous solution (25.0 mL x 3), dried over Na_2SO_4 and filtered. The solvent was removed by rotary evaporation and the residue was purified by flash silica gel chromatography (Eluent: 100:1 to 30:1 petroleum ether: ethyl acetate). The product was isolated as a white solid (5.20 g, 10.9 mmol, 72.7% yield). **M.p.** = 75.3 – 75.9 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.66 (2H, d, J = 8.5 Hz), 7.47 (2H, d, J = 8.4 Hz), 6.95 (1H, d, J = 2.5 Hz), 6.87 (1H, d, J = 9.0 Hz), 6.67 (1H, dd, J = 9.0, 2.6 Hz), 4.24 (2H, t, J = 6.0 Hz), 3.84 (3H, s), 3.68 (2H, s), 3.36 (2H, t, J = 6.5 Hz), 2.39 (3H, s), 2.18 – 2.12 (2H, m); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.7, 168.3, 156.1, 139.3, 135.9, 133.8, 131.2, 130.8, 130.6, 129.2, 115.0, 112.4, 111.7, 101.1, 62.7, 55.7, 31.5, 30.3, 29.3, 13.4; **HRMS** (ESI^+) $[M+Na]^+$ calc'd for $C_{22}H_{21}BrClNaNO_4$: 500.0235, found: 500.0229.

5. Synthesis of (*R*)-2,5,7,8-tetramethyl-2-((4*S*,8*S*)-4,8,12-trimethyltridecyl)chroman-6-yl 5-bromopentanoate 1ab



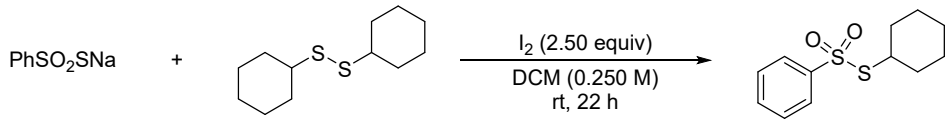
An oven-dried 200-mL round-bottom flask, equipped with a stirring bar, was charged with 5-bromopentanoic acid (1.81 g, 10.0 mmol, 1.00 equiv). The mixture was evacuated and backfilled with nitrogen for three times. Then dry dichloromethane

(30.0 mL) was added under N_2. The mixture was cooled to 0 °C and DCC (2.26 g, 11.1 mmol, 1.10 equiv) was added under N_2. The mixture was allowed to stir at room temperature for 0.5 h. Then (R)-2,5,7,8-tetramethyl-2-((4S,8S)-4,8,12-trimethyltridecyl)chroman-6-ol (4.77 g, 11.1 mmol, 1.10 equiv) was added under N_2. The mixture was stirred at room temperature for 12 h. The mixture was filtered and the solid was washed with dichloromethane. The combined organic layers were concentrated under vacuo. The solvent was removed by rotary evaporation and the residue was purified by flash silica gel chromatography to provide the desired product as a colorless liquid (5.00 g, 8.43 mmol, 84.3% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 3.44 (2H, t, J = 6.3 Hz), 2.62 (2H, t, J = 7.0 Hz), 2.58 (2H, t, J = 6.8 Hz), 2.09 (3H, s), 2.008 – 1.97 (4H, m), 1.97 – 1.89 (6H, m), 1.84 – 1.70 (2H, m), 1.578 – 1.47 (3H, m), 1.46 – 1.35 (4H, m), 1.32 – 1.18 (11H, m), 1.16 – 1.03 (6H, m), 0.878 – 0.84 (12H, m); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.7, 149.4, 140.5, 126.6, 124.9, 123.1, 117.4, 75.1, 39.4, 37.5, 37.5, 37.4, 33.1, 33.0, 32.9, 32.8, 32.2, 28.0, 24.9, 24.5, 23.7, 22.8, 22.7, 21.1, 20.7, 19.8, 19.8, 13.1, 12.2, 11.9 (three carbons were missing due to overlap); **HRMS** (ESI^+) $[M+Na]^+$ calc'd for $C_{34}H_{57}NaO_3S_2$: 615.3383, found: 615.3383.

6. Synthesis of *S*-alkylthiosulfonates 2a-g, 2i-n, 2q

The *S*-alkylthiosulfonates **2a-g**, **2i-n**, **2q** were synthesized according to our previous report, the spectral data match those previously reported[3].

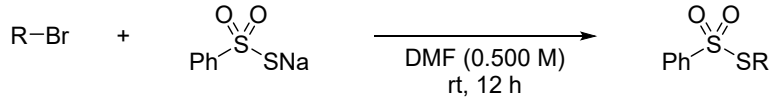
7. Synthesis of *S*-cyclohexyl benzenesulfonothioate 2h



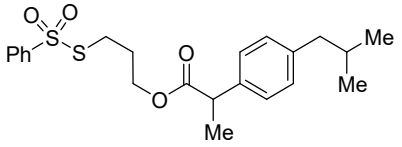
An oven-dried 100-mL round-bottom flask, equipped with a stirring bar, was charged with sodium benzenesulfonothioate (2.63 g, 16.0 mmol, 3.20 equiv), diiodine (2.54 g, 10.0 mmol, 2.00 equiv), Then dry dichlormethane (20.0 mL) and 1,2-dicyclohexyldisulfane (1.15 g, 5.00 mmol, 1.00 equiv) was added under N_2 atmosphere. The mixture was stirred at room temperature for 22 h. The mixture was poured into water (25.0 mL) and extracted with dichlormethane (25.0 mL x 3). The

combined organic layers were washed with saturated $Na_2S_2O_3$ aqueous solution (25.0 mL x 3), dried over Na_2SO_4 and filtered. The solvent was removed by rotary evaporation and the residue was purified by flash silica gel chromatography (Eluent: 100:1 to 20:1 petroleum ether: ethyl acetate). The product was isolated as a colorless liquid (2.42 g, 9.44 mmol, 94.4% yield) which is a known compound. The spectral data match those previously reported[7].

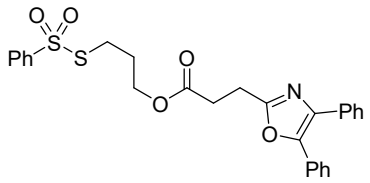
8. General Method A: Synthesis of *S*-alkylthiosulfonates 2o, 2r-v



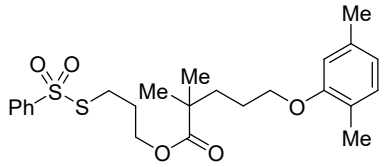
An oven-dried 100-mL round-bottom flask, equipped with a stir bar, was charged with sodium benzenesulfonothioate (2.35 g, 12.0 mmol, 1.20 equiv). The mixture was evacuated and backfilled with nitrogen for three times. Then alkyl bromide (10.0 mmol, 1.00 equiv) and dry DMF (20.0 mL) was added under N_2 atmosphere and the mixture was stirred at room temperature for 12 h. The mixture was diluted with H_2O (50.0 mL) and extracted with ethyl acetate (50.0 mL x 3). The combined organic layers were washed with saturated NaCl aqueous solution (50.0 mL x 5), dried over Na_2SO_4 and filtered. The solvent was removed by rotary evaporation and the residue was purified by flash silica gel chromatography.



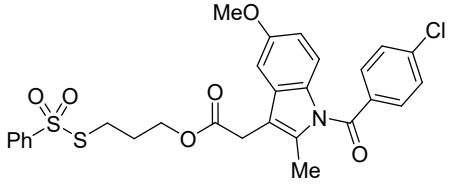
3-((Phenylsulfonyl)thio)propyl (*R*)-2-(4-isobutylphenyl)propanoate 2o: Prepared according to **General Method A** (Eluent: 200:1 to 10:1 petroleum ether: ethyl acetate) and the title compound was isolated as a colorless liquid (3.11 g, 7.41 mmol, 74.1% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.89 (2H, d, J = 7.1 Hz), 7.65 – 7.61 (1H, m), 7.55 – 7.51 (2H, m), 7.16 (2H, d, J = 8.1 Hz), 7.08 (2H, d, J = 7.9 Hz), 4.10 – 4.02 (2H, m), 3.68 – 3.63 (1H, m), 2.88 (2H, t, J = 7.2 Hz), 2.43 (2H, d, J = 7.2 Hz), 1.92 – 1.86 (2H, m), 1.84 – 1.79 (1H, m), 1.46 (3H, d, J = 7.1 Hz), 0.88 (6H, d, J = 6.6 Hz); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.5, 144.7, 140.8, 137.6, 133.8, 129.5, 129.4, 127.1, 127.0, 62.4, 45.1, 45.0, 32.5, 30.3, 28.2, 22.5, 18.4; **HRMS** (ESI$^+$) $[M+Na]^+$ calc'd for $C_{22}H_{28}NaO_4S_2$: 443.1321, found: 443.1337.



3-((Phenylsulfonyl)thio)propyl 3-(4,5-diphenyloxazol-2-yl)propanoate 2r: Prepared according to **General Method A** (Eluent: 200:1 to 3:1 petroleum ether: ethyl acetate) and the title compound was isolated as a colorless liquid (4.02 g, 7.92 mmol, 79.2% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.91 (2H, d, J = 7.4 Hz), 7.64 – 7.59 (3H, m), 7.57 – 7.52 (4H, m), 7.37 – 7.30 (6H, m), 4.14 (2H, t, J = 6.0 Hz), 3.16 (2H, t, J = 7.4 Hz), 3.03 (2H, t, J = 7.1 Hz), 2.88 (2H, t, J = 7.4 Hz), 2.02 – 1.95 (2H, m); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.9, 161.7, 145.6, 144.7, 135.2, 133.9, 132.5, 129.5, 129.0, 128.8, 128.7, 128.6, 128.2, 127.9, 127.1, 126.6, 62.6, 32.7, 31.1, 28.3, 23.5; **HRMS** (ESI^+) $[M+Na]^+$ calc'd for $C_{27}H_{25}NaNO_5S_2$: 530.1066, found: 530.1057.

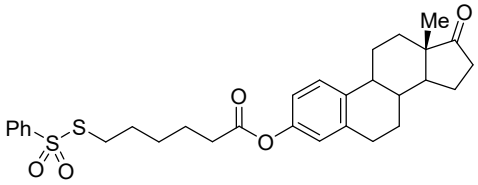


3-((Phenylsulfonyl)thio)propyl 5-(2,5-dimethylphenoxy)-2,2-dimethylpentanoate 2s: Prepared according to **General Method A** (Eluent: 200:1 to 10:1 petroleum ether: ethyl acetate) and the title compound was isolated as a colorless liquid (3.35 g, 7.21 mmol, 72.1% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.92 (2H, d, J = 7.1 Hz), 7.65 – 7.61 (1H, m), 7.57 – 7.52 (2H, m), 7.00 (1H, d, J = 7.4 Hz), 6.66 (1H, d, J = 7.5 Hz), 6.62 (1H, s), 4.07 (2H, t, J = 6.0 Hz), 3.93 – 3.90 (2H, m), 3.06 (2H, t, J = 7.2 Hz), 2.31 (3H, s), 2.17 (3H, s), 2.02 – 1.97 (2H, m), 1.72 – 1.68 (4H, m), 1.20 (6H, s); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 176.6, 155.9, 143.7, 135.6, 132.9, 129.4, 128.4, 126.0, 122.5, 119.8, 111.0, 66.9, 61.3, 41.2, 36.1, 31.7, 27.3, 24.2, 24.2, 20.5, 14.9; **HRMS** (ESI^+) $[M+Na]^+$ calc'd for $C_{224}H_{32}NaO_5S_2$: 487.1583, found: 487.1604.

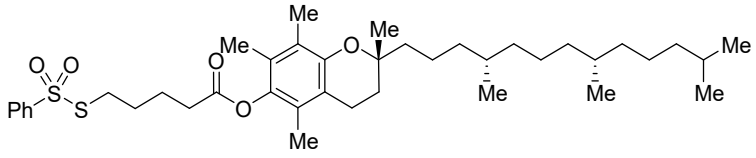


3-((Phenylsulfonyl)thio)propyl 2-(1-(4-chlorobenzoyl)-5-methoxy-2-methyl-1*H*-indol-3-yl)acetate 2t: Prepared according to **General Method A** (Eluent: 200:1 to 1:1 petroleum ether: ethyl acetate) and the title compound was isolated as a colorless

liquid (3.96 g, 6.93 mmol, 69.3% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.83 (2H, d, J = 7.0 Hz), 7.61 (2H, d, J = 8.5 Hz), 7.56 (1H, d, J = 7.3 Hz), 7.49 – 7.46 (2H, m), 7.40 (2H, d, J = 8.5 Hz), 6.93 (1H, d, J = 2.5 Hz), 6.89 (1H, d, J = 9.0 Hz), 6.64 (1H, dd, J = 9.0, 2.5 Hz), 4.07 (2H, t, J = 6.0 Hz), 3.77 (3H, s), 3.63 (2H, s), 2.95 (2H, t, J = 7.1 Hz), 2.34 (3H, s), 1.94 – 1.87 (2H, m); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.4, 168.0, 155.8, 144.3, 138.9, 135.7, 133.7, 131.0, 130.4, 130.5, 129.2, 128.9, 126.6, 114.8, 112.2, 111.4, 101.0, 62.6, 55.55, 32.4, 30.0, 27.9, 13.2; **HRMS** (ESI^+) $[M+H]^+$ calc'd for $C_{28}H_{27}ClNO_6S_2$: 572.0963, found: 572.0947.



(13*S*)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-3-yl 6-((phenylsulfonyl)thio)hexanoate 2u: Prepared according to **General Method A** (Eluent: 200:1 to 5:1 petroleum ether: ethyl acetate) and the title compound was isolated as a colorless liquid (3.53 g, 6.52 mmol, 65.2% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.94 (2H, d, J = 7.2 Hz), 7.66 – 7.61 (1H, m), 7.58 – 7.54 (2H, m), 7.28 (1H, d, J = 7.5 Hz), 6.84 – 6.78 (2H, m), 3.06 – 3.02 (2H, m), 2.92 – 2.89 (2H, m), 2.54 – 2.47 (3H, m), 2.42 – 2.37 (1H, m), 2.31 – 2.24 (1H, m), 2.19 – 2.12 (1H, m), 2.10 – 1.93 (3H, m), 1.77 – 1.74 (4H, m), 1.66 – 1.41 (6H, m), 0.90 (3H, s); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.7, 148.4, 144.7, 138.1, 137.5, 133.8, 129.4, 127.0, 126.4, 121.5, 118.7, 50.4, 47.9, 44.1, 38.0, 35.9, 35.6, 33.5, 31.6, 29.4, 28.2, 26.3, 25.8, 23.7, 21.6, 13.9 (one carbon was missing due to overlap); **HRMS** (ESI^+) $[M+H]^+$ calc'd for $C_{29}H_{34}NaO_5S_2$: 549.1740, found: 549.1744.

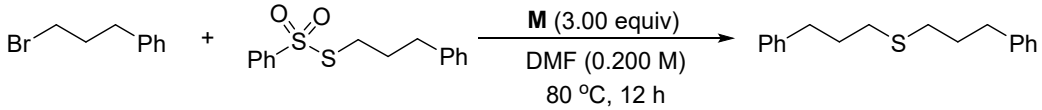


(*R*)-2,5,7,8-tetramethyl-2-((4*S*,8*S*)-4,8,12-trimethyltridecyl)chroman-6-yl 5-((phenylsulfonyl)thio)pentanoate 2v: Prepared according to **General Method D** (Eluent: 200:1 to 10:1 petroleum ether: ethyl acetate) and the title compound was isolated as a colorless liquid (4.99 g, 7.28 mmol, 72.8% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.95 (2H, d, J = 7.1 Hz), 7.66 – 7.61 (1H, m), 7.58 – 7.54 (2H, m), 3.05 (2H, t, J = 6.6 Hz), 2.60 – 2.53 (4H, m), 2.08 (3H, s), 1.97 (3H, s), 1.93 (3H, s), 1.84 – 1.72 (6H, m), 1.58 – 1.49 (4H, m), 1.42 – 1.33 (4H, m), 1.32 – 1.20 (10H, m), 1.16 – 1.04

(6H, m), 0.87 – 0.83 (12H, m); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.6, 149.5, 144.9, 140.5, 133.8, 129.5, 127.1, 126.6, 124.9, 123.2, 117.5, 75.2, 39.5, 37.6, 37.4, 35.7, 33.3, 32.9, 32.8, 28.5, 28.1, 24.9, 24.6, 24.0, 22.9, 22.8, 21.1, 20.7, 19.9, 19.8, 13.1, 12.3, 12.0 (one carbons were missing due to overlap); **HRMS** (ESI^+) $[M+Na]^+$ calc'd for $C_{40}H_{62}NaO_5S_2$: 709.3931, found: 709.3928.

III. Optimization of the reaction conditions

Table S1. Evaluation of different reductants

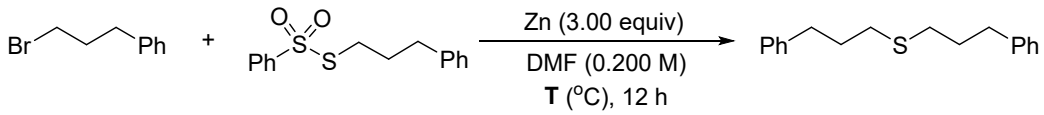


1a **2a** **3a**

entry	**M**	yield (%)[a]
1	Mn	<5
2	Cu	<5
3	Mg	<5
4	Zn	>99

Reaction condition: **1a** (0.200 mmol), **2a** (0.400 mmol), **M** (0.600 mmol), DMF (1.00 mL) at 80 °C for 12 h. [a]Yield was determined by ^{1}H NMR spectroscopy in the presence of CH_2Br_2 as an internal standard.

Table S2. Evaluation of different temperature

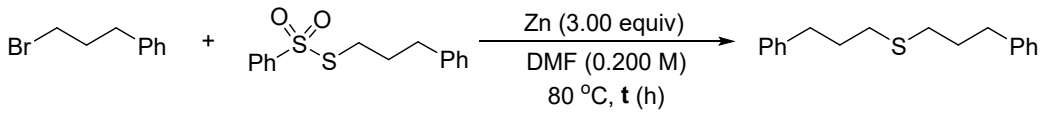


1a **2a** **3a**

entry	**T (°C)**	yield (%)[a]
1	22	34
2	40	56
3	60	96
4	80	>99

Reaction condition: **1a** (0.200 mmol), **2a** (0.400 mmol), Zn (0.600 mmol), DMF (1.00 mL) at **T** (°C) for 12 h. [a]Yield was determined by ^{1}H NMR spectroscopy in the presence of CH_2Br_2 as an internal standard.

Table S3. Evaluation of different time

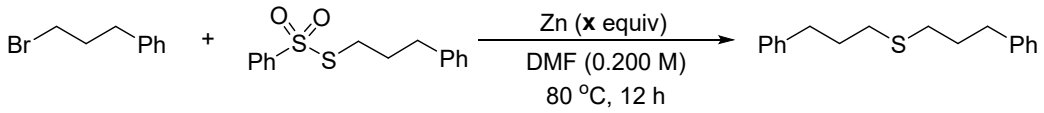


1a **2a** **3a**

entry	**t (h)**	yield (%)[a]
1	2	85
2	4	96
3	6	99
4	12	>99

Reaction condition: **1a** (0.200 mmol), **2a** (0.400 mmol), Zn (0.600 mmol), DMF (1.00 mL) at 80 °C for **t** (h). [a]Yield was determined by ^{1}H NMR spectroscopy in the presence of CH_2Br_2 as an internal standard.

Table S4. Evaluation of different amounts of Zn

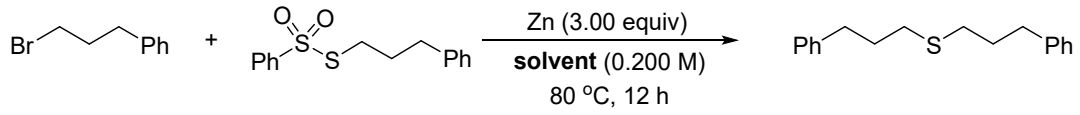


1a **2a** **3a**

entry	**x**	yield (%)[a]
1	1.50	86
2	3.00	>99

Reaction condition: **1a** (0.200 mmol), **2a** (0.400 mmol), Zn (0.200**x** mmol), DMF (1.00 mL) at 80 °C for 12 h. [a]Yield was determined by ^{1}H NMR spectroscopy in the presence of CH_2Br_2 as an internal standard.

Table S5. Evaluation of different solvents



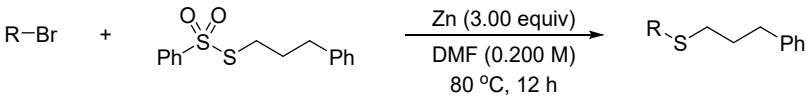
1a **2a** **3a**

entry	**solvent**	yield (%)[a]
1	MeOH	22
2	DCM	20
3	MeCN	18
4	THF	35
5	DMAc	>99
6	DMSO	93
7	DMF	>99

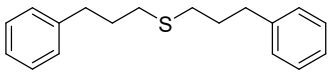
Reaction condition: **1a** (0.200 mmol), **2a** (0.400 mmol), Zn (0.600 mmol), **solvent** (1.00 mL) at 80 °C for 12 h. [a]Yield was determined by ^{1}H NMR spectroscopy in the presence of CH_2Br_2 as an internal standard.

IV. Substrate scope

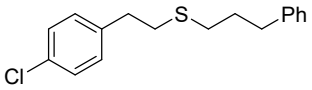
1. General Method B:



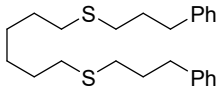
An oven-dried 25-mL glass schlenck, equipped with a stirring bar, was charged with zinc (98.1 mg, 1.50 mmol, 3.00 equiv) and *S*-(3-phenylpropyl) benzenesulfonothioate (292.4 mg, 1.00 mmol, 2.00 equiv). The mixture was evacuated and backfilled with nitrogen for three times. Then alkyl bromide (0.500 mmol, 1.00 equiv) and dry DMF (2.50 mL) was added under N_2 and the mixture was allowed to stir for 12 h at 80 °C. After cooling to room temperature, the mixture was diluted with NaCl aqueous solution (25.0 mL) and extracted with ethyl acetate (25.0 mL). The mixture was filtered through a celite pad and the organic layers were separated. The aqueous layer was extracted with ethyl acetate (10.0 mL x 3). The combined organic layers were washed with H_2O (25.0 mL x 5), dried over Na_2SO_4 and filtered. The solvent was removed by rotary evaporation and the residue was purified by flash silica gel chromatography.



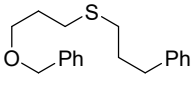
Bis(3-phenylpropyl)sulfane 3a: Prepared according to **General Method B** (Eluent: 200:1 to 50:1 petroleum ether: ethyl acetate) and the title compound was isolated as a colorless liquid (96.1 mg, 0.355 mmol, 71.1% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.29 – 7.25 (4H, m), 7.20 – 7.16 (6H, m), 2.70 (4H, t, J = 7.5 Hz), 2.51 (4H, t, J = 7.3 Hz), 1.92 – 1.85 (4H, m); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 141.7, 128.6, 128.5, 126.0, 34.9, 31.5, 31.2. Spectra were consistent with literature data[1].



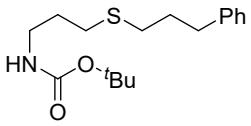
(4-Chlorophenethyl)(3-phenylpropyl)sulfane 3b: Prepared according to **General Method B** (Eluent: 200:1 to 50:1 petroleum ether: ethyl acetate) and the title compound was isolated as a colorless liquid (102.2 mg, 0.351 mmol, 70.2% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.30 – 7.23 (4H, m), 7.20 – 7.15 (3H, m), 7.11 – 7.08 (2H, m), 2.84 – 2.79 (2H, m), 2.74 – 2.67 (4H, m), 2.51 (2H, t, J = 9.3 Hz), 1.94 – 1.86 (2H, m); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 141.6, 139.1, 132.2, 130.0, 128.6, 128.6, 128.5, 126.1, 35.7, 34.9, 33.5, 31.7, 31.2. Spectra were consistent with literature data[1].



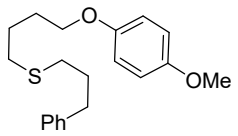
1,6-Bis((3-phenylpropyl)thio)hexane 3c: Prepared according to **General Method B** (2.00 mmol *S*-(3-phenylpropyl) benzenesulfonothioate, 3.00 mmol zinc were used) (Eluent: 200:1 to 20:1 petroleum ether: ethyl acetate) and the title compound was isolated as a colorless liquid (132.3 mg, 0.342 mmol, 68.4% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.33 – 7.29 (4H, m), 7.22 – 7.21 (6H, m), 2.75 (4H, t, J = 7.6 Hz), 2.56 – 2.51 (8H, m), 1.97 – 1.91 (4H, m), 1.62 – 1.56 (4H, t, J = 7.4 Hz), 1.43 – 1.39 (4H, m); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 141.7, 128.5, 128.4, 126.0, 34.9, 32.1, 31.5, 31.3, 29.6, 28.6; **HRMS** (FI) calc'd for $C_{24}H_{34}S_2$: 386.2098, found: 386.2096.



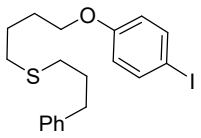
(3-(Benzyloxy)propyl)(3-phenylpropyl)sulfane 3d: Prepared according to **General Method B** (Eluent: 200:1 to 20:1 petroleum ether: ethyl acetate) and the title compound was isolated as a colorless liquid (125.8 mg, 0.419 mmol, 83.7% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.32 – 7.30 (4H, m), 7.28 – 7.25 (3H, m), 7.18 – 7.15 (3H, m), 4.48 (2H, s), 3.54 (2H, t, J = 6.2 Hz), 2.69 (2H, t, J = 7.6 Hz), 2.60 (2H, t, J = 7.3 Hz), 2.50 (2H, t, J = 7.3 Hz), 1.93 – 1.83 (4H, m); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 141.6, 138.5, 128.5, 128.4, 127.7, 127.6, 125.9, 73.0, 68.8, 34.9, 31.5, 31.2, 29.9, 28.8 (one carbon was missing due to overlap); **HRMS** (ESI$^+$) $[M+H]^+$ calc'd for $C_{19}H_{25}OS$: 301.1621, found: 301.1619.



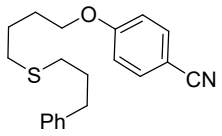
***tert*-Butyl (3-((3-phenylpropyl)thio)propyl)carbamate 3e:** Prepared according to **General Method B** (Eluent: 200:1 to 10:1 petroleum ether: ethyl acetate) and the title compound was isolated as a colorless liquid (119.1 mg, 0.385 mmol, 77.0% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.30 – 7.26 (2H, m), 7.20 – 7.17 (3H, m), 4.71 (1H, s), 3.22 – 3.17 (2H, m), 2.71 (2H, t, J = 7.6 Hz), 2.54 – 2.49 (4H, m), 1.93 – 1.86 (2H, m), 1.78 – 1.71 (2H, m), 1.44 (9H, s); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 156.0, 141.5, 128.5, 128.4, 126.0, 79.2, 39.7, 34.8, 31.4, 31.1, 29.8, 29.3, 28.5; **HRMS** (ESI$^+$) $[M+Na]^+$ calc'd for $C_{17}H_{27}NNaO_2S$: 332.1655, found: 332.1648.



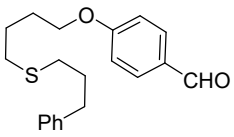
(4-(4-Methoxyphenoxy)butyl)(3-phenylpropyl)sulfane 3f: Prepared according to **General Method B** (Eluent: 200:1 to 20:1 petroleum ether: ethyl acetate) and the title compound was isolated as a colorless liquid (131.9 mg, 0.399 mmol, 79.8% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.34 – 7.30 (2H, m), 7.23 – 7.21 (3H, m), 6.86 (4H, s), 3.95 (2H, t, J = 6.1 Hz), 3.79 (3H, s), 2.76 (2H, t, J = 7.6 Hz), 2.63 – 2.55 (4H, m), 1.99 – 1.85 (4H, m), 1.83 – 1.75 (2H, m); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 153.8, 153.2, 141.6, 128.5, 128.4, 126.0, 115.5, 114.7, 68.0, 55.8, 34.9, 31.8, 31.5, 31.2, 28.6, 26.3; **HRMS** (ESI$^+$) $[M+Na]^+$ calc'd for $C_{20}H_{26}NaO_2S$: 353.1546, found: 353.1549.



(4-(4-Iodophenoxy)butyl)(3-phenylpropyl)sulfane 3g: Prepared according to **General Method B** (Eluent: 200:1 to 10:1 petroleum ether: ethyl acetate) and the title compound was isolated as a colorless liquid (184.8 mg, 0.433 mmol, 86.7% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.53 (2H, d, J = 8.8 Hz), 7.30 – 7.25 (2H, m), 7.20 – 7.17 (3H, m), 6.65 (2H, d, J = 8.8 Hz), 3.92 (2H, t, J = 6.2 Hz), 2.72 (2H, t, J = 7.6 Hz), 2.58 – 2.51 (4H, m), 1.95 – 1.83 (4H, m), 1.79 – 1.70 (2H, m); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.9, 141.6, 138.3, 128.6, 128.5, 126.0, 117.0, 82.7, 67.6, 34.9, 31.8, 31.5, 31.3, 28.4, 26.2; **HRMS** (FI) calc'd for $C_{19}H_{23}OIS$: 426.0506, found: 426.0509.

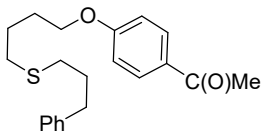


4-(4-((3-Phenylpropyl)thio)butoxy)benzonitrile 3h: Prepared according to **General Method B** (Eluent: 200:1 to 10:1 petroleum ether: ethyl acetate) and the title compound was isolated as a colorless liquid (129.3 mg, 0.397 mmol, 79.5% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.54 (2H, d, J = 9.0 Hz), 7.29 – 7.25 (2H, m), 7.20 – 7.16 (3H, m), 6.90 (2H, d, J = 8.9 Hz), 3.99 (2H, t, J = 6.2 Hz), 2.71 (2H, t, J = 7.6 Hz), 2.57 (2H, t, J = 7.2 Hz), 2.52 (2H, t, J = 7.3 Hz), 1.94 – 1.86 (4H, m), 1.78 – 1.71 (2H, m); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 162.2, 141.5, 133.9, 128.4, 128.3, 125.9, 119.3, 115.1, 103.7, 67.7, 34.8, 31.6, 31.4, 31.1, 28.0, 25.9; **HRMS** (ESI^+) $[M+Na]^+$ calc'd for $C_{20}H_{23}NNaOS$: 348.1393, found: 348.1381.

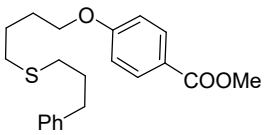


4-(4-((3-Phenylpropyl)thio)butoxy)benzaldehyde 3i: Prepared according to **General Method B** (Eluent: 200:1 to 10:1 petroleum ether: ethyl acetate) and the title compound was isolated as a colorless liquid (159.4 mg, 0.485 mmol, 97.1% yield). **^{1}H**

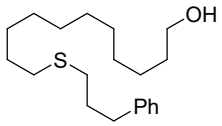
NMR (400 MHz, $CDCl_3$) δ 9.86 (1H, s), 7.81 (2H, d, J = 8.6 Hz), 7.29 – 7.25 (2H, m), 7.20 – 7.17 (3H, m), 6.97 (2H, d, J = 8.7 Hz), 4.04 (2H, t, J = 6.2 Hz), 2.72 (2H, t, J = 7.6 Hz), 2.58 (2H, t, J = 7.2 Hz), 2.53 (2H, t, J = 7.3 Hz), 1.95 – 1.87 (4H, m), 1.82 – 1.73 (2H, m); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 190.8, 164.1, 141.5, 132.0, 129.8, 128.5, 128.4, 126.0, 114.8, 67.8, 34.8, 31.7, 31.4, 31.2, 28.2, 26.1; **HRMS** (ESI^+) $[M+Na]^+$ calc'd for $C_{20}H_{24}NaO_2S$: 351.1389, found: 351.1389.



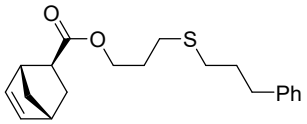
1-(4-(4-((3-Phenylpropyl)thio)butoxy)phenyl)ethan-1-one 3j: Prepared according to **General Method B** (Eluent: 200:1 to 10:1 petroleum ether: ethyl acetate) and the title compound was isolated as a colorless liquid (150.3 mg, 0.439 mmol, 87.8% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.91 (2H, d, J = 8.9 Hz), 7.29 – 7.24 (2H, m), 7.19 – 7.16 (3H, m), 6.89 (2H, d, J = 8.8 Hz), 4.01 (2H, t, J = 6.2 Hz), 2.71 (2H, t, J = 7.6 Hz), 2.57 (2H, t, J = 7.3 Hz), 2.54 – 2.51 (5H, m), 1.94 – 1.86 (4H, m), 1.79 – 1.72 (2H, m); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 196.7, 162.9, 141.5, 130.6, 130.2, 128.4, 128.4, 125.9, 114.1, 67.6, 34.8, 31.6, 31.4, 31.1, 28.2, 26.3, 26.0; **HRMS** (ESI^+) $[M+H]^+$ calc'd for $C_{21}H_{27}O_2S$: 343.1726, found: 343.1714.



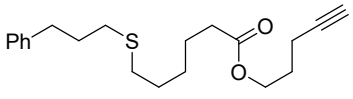
Methyl 4-(4-((3-phenylpropyl)thio)butoxy)benzoate 3k: Prepared according to **General Method B** (Eluent: 200:1 to 10:1 petroleum ether: ethyl acetate) and the title compound was isolated as a colorless liquid (145.0 mg, 0.404 mmol, 80.9% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.97 (2H, d, J = 8.7 Hz), 7.29 – 7.23 (2H, m), 7.19 – 7.15 (3H, m), 6.88 (2H, d, J = 8.9 Hz), 3.99 (2H, t, J = 6.2 Hz), 3.86 (3H, s), 2.71 (2H, t, J = 7.6 Hz), 2.57 (2H, t, J = 7.2 Hz), 2.52 (2H, t, J = 7.3 Hz), 1.94 – 1.85 (2H, m), 1.78 – 1.71 (2H, m); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.9, 162.8, 141.6, 131.6, 128.5, 128.4, 126.0, 122.5, 114.0, 67.6, 51.9, 34.9, 31.7, 31.4, 31.2, 28.3, 26.1; **HRMS** (ESI^+) $[M+Na]^+$ calc'd for $C_{21}H_{26}NaO_3S$: 381.1495, found: 381.1499.



11-((3-Phenylpropyl)thio)undecan-1-ol 3l: Prepared according to **General Method B** (Eluent: 200:1 to 10:1 petroleum ether: ethyl acetate) and the title compound was isolated as a white solid (135.5 mg, 0.420 mmol, 84.0% yield). **M.p.** = 33.4 – 34.1 ^{o}C . **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.29 – 7.25 (2H, m), 7.19 – 7.17 (3H, m), 3.61 (2H, t, J = 6.7 Hz), 2.71 (2H, t, J = 7.6 Hz), 2.53 – 2.47 (4H, m), 1.94 – 1.86 (2H, m), 1.71 (1H, s), 1.59 – 1.52 (4H, m), 1.37 – 1.27 (14H, m); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 141.7, 128.5, 128.4, 126.0, 63.0, 34.9, 32.8, 32.1, 31.5, 31.3, 29.7, 29.6, 29.6, 29.6, 29.5, 29.3, 29.0, 25.8; **HRMS** (ESI^+) $[M+H]^+$ calc'd for $C_{20}H_{35}OS$: 323.2403, found: 323.2406.

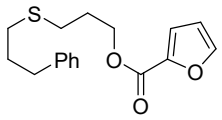


4-((3-Phenylpropyl)thio)butyl (1*R*,2*S*,4*R*)-bicyclo[2.2.1]hept-5-ene-2-carboxylate 3m: Prepared according to **General Method B** (Eluent: 200:1 to 20:1 petroleum ether: ethyl acetate) and the title compound was isolated as a colorless liquid (129.1 mg, 0.391 mmol, 78.1% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.30 – 7.24 (2H, m), 7.20 – 7.17 (3H,m), 6.19 – 6.17 (1H, m), 5.92 – 5.90 (1H, m), 4.12 – 4.08 (2H, m), 3.19 (1H, s), 2.95 – 2.88 (2H, m), 2.72 (2H, t, J = 7.6 Hz), 2.58 – 2.50 (4H, m), 1.99 – 1.81 (5H, m), 1.44 – 1.39 (2H, m), 1.26 (1H, d, J = 7.9 Hz); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.7, 141.5, 137.9, 132.3, 128.5, 128.4, 126.0, 62.8, 49.7, 45.8, 43.4, 42.6, 34.8, 31.4, 31.1, 29.2, 28.8, 28.5; **HRMS** (ESI^+) $[M+Na]^+$ calc'd for $C_{20}H_{26}NaO_2S$: 353.1546, found: 353.1551.

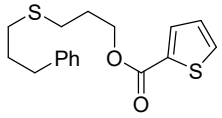


Pent-4-yn-1-yl 6-((3-phenylpropyl)thio)hexanoate 3n: Prepared according to **General Method B** (Eluent: 200:1 to 20:1 petroleum ether: ethyl acetate) and the title compound was isolated as a colorless liquid (122.2 mg, 0.367 mmol, 73.5% yield). **^{1}H**

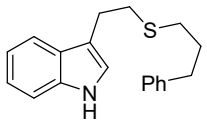
NMR (400 MHz, $CDCl_3$) δ 7.29 – 7.25 (2H, m), 7.19 – 7.16 (3H, m), 4.16 (2H, t, J = 6.3 Hz), 2.71 (2H, t, J = 7.6 Hz), 2.52 – 2.47 (4H, m), 2.32 – 2.26 (4H, m), 1.97 (1H, s), 1.93 – 1.80 (4H, m), 1.66 – 1.54 (4H, m), 1.44 – 1.36 (2H, m); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.5, 141.6, 128.5, 128.3, 125.9, 83.0, 69.1, 62.8, 34.8, 34.1, 31.8, 31.4, 31.2, 29.3, 28.3, 27.5, 24.5, 15.2; **HRMS** (ESI^+) $[M+Na]^+$ calc'd for $C_{20}H_{28}NaO_2S$: 355.1702, found: 355.1702.



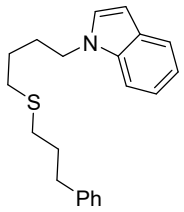
3-((3-Phenylpropyl)thio)propyl furan-2-carboxylate 3o: Prepared according to **General Method B** (Eluent: 200:1 to 20:1 petroleum ether: ethyl acetate) and the title compound was isolated as a colorless liquid (125.0 mg, 0.411 mmol, 82.1% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.79 (1H, dd, J = 3.8, 1.3 Hz), 7.53 (1H, dd, J = 5.0, 1.3 Hz), 7.29 – 7.24 (2H, m), 7.20 – 7.16 (3H, m), 7.10 – 7.08 (1H, m), 4.38 (2H, t, J = 6.2 Hz), 2.71 (2H, t, J = 7.6 Hz), 2.64 (2H, t, J = 7.3 Hz), 2.54 (2H, t, J = 7.3 Hz), 2.04 – 1.97 (2H, m), 1.95 – 1.88 (2H, m); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 162.2, 141.5, 133.8, 133.5, 132.5, 128.5, 128.4, 127.8, 126.0, 63.8, 34.8, 31.5, 31.1, 28.9, 28.4; **HRMS** (ESI^+) $[M+Na]^+$ calc'd for $C_{17}H_{20}NaO_3S$: 327.1025, found: 327.1027.



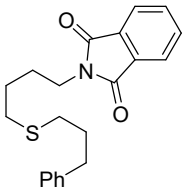
3-((3-Phenylpropyl)thio)propyl thiophene-2-carboxylate 3p: Prepared according to **General Method B** (Eluent: 200:1 to 20:1 petroleum ether: ethyl acetate) and the title compound was isolated as a yellow liquid (123.8 mg, 0.386 mmol, 77.3% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.55 (1H, d, J = 1.6 Hz), 7.29 – 7.25 (2H, m), 7.19 – 7.15 (4H, m), 6.49 – 6.48 (1H, m), 4.38 (2H, t, J = 6.3 Hz), 2.71 (2H, t, J = 7.6 Hz), 2.62 (2H, t, J = 7.3 Hz), 2.53 (2H, t, J = 7.3 Hz), 2.03 – 1.96 (2H, m), 1.94 – 1.87 (2H, m); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.6, 146.3, 144.6, 141.4, 128.4, 128.4, 125.9, 117.9, 111.8, 63.5, 34.7, 31.4, 31.0, 28.7, 28.3; **HRMS** (ESI^+) $[M+Na]^+$ calc'd for $C_{17}H_{20}NaO_2S_2$: 343.0797, found: 343.0797.



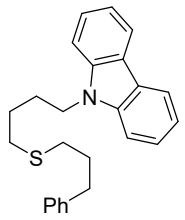
3-(2-((3-Phenylpropyl)thio)ethyl)-1*H*-indole 3q: Prepared according to **General Method B** (Eluent: 200:1 to 10:1 petroleum ether: ethyl acetate) and the title compound was isolated as a colorless liquid (120.6 mg, 0.408 mmol, 81.6% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.83 (1H, s), 7.57 (1H, d, J = 7.8 Hz), 7.30 – 7.25 (3H, m), 7.20 – 7.15 (4H, m), 7.13 – 7.09 (1H, m), 6.94 (1H, s), 3.02 (2H, t, J = 7.8 Hz), 2.84 (2H, t, J = 7.7 Hz), 2.69 (2H, t, J = 7.6 Hz), 2.56 (2H, t, J = 7.3 Hz), 1.94 – 1.87 (2H, m); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 141.7, 136.3, 128.6, 128.5, 127.2, 126.0, 122.1, 121.7, 119.4, 118.8, 115.0, 111.3, 34.9, 32.7, 31.7, 31.3, 26.1. The spectral data match those previously reported[8].



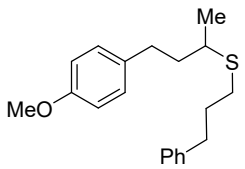
1-(4-((3-phenylpropyl)thio)butyl)-1*H*-indole 3r: Prepared according to **General Method B** (Eluent: 200:1 to 10:1 petroleum ether: ethyl acetate) and the title compound was isolated as a colorless liquid (130.2 mg, 0.402 mmol, 80.5% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.62 (1H, d, J = 7.9 Hz), 7.31 (1H, d, J = 8.2 Hz), 7.28 – 7.24 (2H, m), 7.21 – 7.13 (4H, m), 7.10 – 7.07 (1H, m), 7.04 (1H, d, J = 3.2 Hz), 6.47 (1H, d, J = 3.1 Hz), 4.07 (2H, t, J = 7.0 Hz), 2.66 (2H, t, J = 7.6 Hz), 2.46 – 2.40 (4H, m), 1.93 – 1.87 (2H, m), 1.85 – 1.80 (2H, m), 1.57 – 1.50 (2H, m); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 141.6, 136.0, 128.7, 128.5, 128.4, 127.8, 126.0, 121.5, 121.1, 119.3, 109.4, 101.2, 46.0, 34.8, 31.6, 31.4, 31.2, 29.3, 26.9; **HRMS** (ESI^+) $[M+H]^+$ calc'd for $C_{21}H_{26}NS$: 324.1780, found: 324.1782.



2-(4-((3-Phenylpropyl)thio)butyl)isoindoline-1,3-dione 3s: Prepared according to **General Method B** (Eluent: 200:1 to 10:1 petroleum ether: ethyl acetate) and the title compound was isolated as a colorless liquid (131.9 mg, 0.373 mmol, 74.6% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.84 – 7.82 (2H, m), 7.71 – 7.69 (2H, m), 7.29 – 7.25 (2H, m), 7.19 – 7.15 (3H, m), 3.69 (2H, t, J = 7.1 Hz), 2.70 (2H, t, J = 7.6 Hz), 2.56 – 2.48 (4H, m), 1.92 – 1.85 (2H, m), 1.82 – 1.75 (2H, m), 1.65 – 1.58 (2H, m); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.4, 141.6, 134.0, 132.1, 128.5, 128.4, 125.9, 123.2, 37.5, 34.8, 31.5, 31.5, 31.2, 27.8, 26.9; **HRMS** (ESI^+) $[M+H]^+$ calc'd for $C_{21}H_{24}NO_2S$: 354.1522, found: 354.1512.

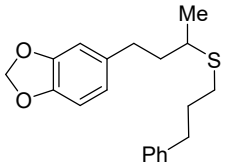


9-(4-((3-Phenylpropyl)thio)butyl)-9H-carbazole 3t: Prepared according to **General Method B** (Eluent: 200:1 to 10:1 petroleum ether: ethyl acetate) and the title compound was isolated as a colorless liquid (141.5 mg, 0.379 mmol, 75.8% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.24 (2H, d, J = 7.8 Hz), 7.62 – 7.57 (2H, m), 7.51 (2H, d, J = 8.2 Hz), 7.43 – 7.32 (5H, m), 7.30 – 7.28 (2H, m), 4.38 (2H, t, J = 7.0 Hz), 2.78 (2H, t, J = 7.6 Hz), 2.60 – 2.52 (4H, m), 2.11 – 2.04 (2H, m), 2.00 – 1.92 (2H, m), 1.77 – 1.69 (2H, m); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 141.5, 140.3, 128.5, 128.4, 125.9, 125.8, 122.9, 120.4, 118.9, 108.7, 42.5, 34.8, 31.7, 31.4, 31.1, 28.0, 27.2; **HRMS** (ESI^+) $[M+Na]^+$ calc'd for $C_{25}H_{27}NNaS$: 396.1756, found: 396.1763.

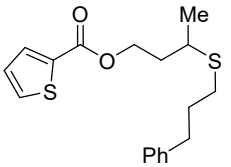


(4-(4-Methoxyphenyl)butan-2-yl)(3-phenylpropyl)sulfane 3u: Prepared according to **General Method B** (3.00 equiv $MgCl_2$, 100 ^{o}C were used) (Eluent: 200:1 to 100:1 petroleum ether: ethyl acetate) and the title compound was isolated as a colorless liquid (93.7 mg, 0.298 mmol, 59.6% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.30 – 7.26 (2H, m), 7.21 – 7.17 (3H, m), 7.10 (2H, d, J = 8.6 Hz), 6.82 (2H, d, J = 8.6 Hz),

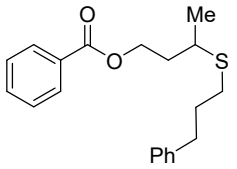
3.78 (3H, s), 2.75 – 2.66 (5H, m), 2.52 (2H, t, *J* = 7.3 Hz), 1.92 – 1.86 (2H, m), 1.85 – 1.71 (2H, m), 1.29 (3H, d, *J* = 6.8 Hz); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 157.9, 141.8, 134.1, 129.4, 128.6, 128.5, 126.0, 113.9, 55.4, 39.3, 39.0, 35.1, 32.4, 31.5, 29.6, 21.7; **HRMS** (ESI^+) $[M+H]^+$ calc'd for $C_{20}H_{27}OS$: 315.1777, found: 315.1773.



5-(3-((3-Phenylpropyl)thio)butyl)benzo[*d*][1,3]dioxole 3v: Prepared according to **General Method B** (3.00 equiv $MgCl_2$, 100 °C were used) (Eluent: 200:1 to 100:1 petroleum ether: ethyl acetate) and the title compound was isolated as a colorless liquid (113.9 mg, 0.347 mmol, 69.4% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.31 – 7.26 (2H, m), 7.22 – 7.17 (3H, m), 6.72 (1H, d, *J* = 7.9 Hz), 6.68 (1H, d, *J* = 1.7 Hz), 6.63 (1H, dd, *J* = 7.9, 1.7 Hz), 5.92 – 5.91 (2H, m), 2.74 – 2.69 (3H, m), 2.68 – 2.64 (2H, m), 2.52 (2H, t, *J* = 7.3 Hz), 1.93 – 1.85 (2H, m), 1.83 – 1.69 (2H, m), 1.28 (3H, d, *J* = 6.7 Hz); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 147.7, 145.7, 141.7, 135.9, 128.6, 128.5, 126.0, 121.3, 109.0, 108.3, 100.9, 39.3, 39.0, 35.1, 33.0, 31.5, 29.6, 21.7; **HRMS** (ESI^+) $[M+Na]^+$ calc'd for $C_{20}H_{24}NaO_2S$: 351.1389, found: 351.1384.

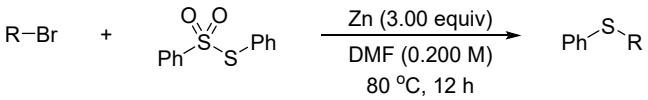


3-((3-Phenylpropyl)thio)butyl thiophene-2-carboxylate 3w: Prepared according to **General Method B** (3.00 equiv $MgCl_2$, 100 °C were used) (Eluent: 200:1 to 100:1 petroleum ether: ethyl acetate) and the title compound was isolated as a colorless liquid (97.8 mg, 0.292 mmol, 58.5% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.83 (1H, dd, *J* = 3.7, 1.3 Hz), 7.56 (1H, dd, *J* = 5.0, 1.3 Hz), 7.32 – 7.29 (2H, m), 7.23 – 7.21 (3H, m), 7.13 – 7.11 (1H, m), 4.48 (2H, t, *J* = 6.4 Hz), 3.00 – 2.93 (1H, m), 2.76 (2H, t, *J* = 7.6 Hz), 2.60 (2H, t, *J* = 7.3 Hz), 2.02 – 1.93 (4H, m), 1.39 (3H, d, *J* = 6.8 Hz); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 162.1, 141.5, 133.8, 133.4, 132.4, 128.5, 128.4, 127.8, 125.9, 62.9, 36.8, 35.8, 34.9, 31.3, 29.7, 21.8; **HRMS** (ESI^+) $[M+H]^+$ calc'd for $C_{18}H_{23}O_2S_2$: 335.1134, found: 335.1133.

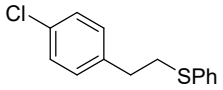


3-((3-Phenylpropyl)thio)butyl benzoate 3x: Prepared according to **General Method B** (3.00 equiv $MgCl_2$, 100 °C were used) (Eluent: 200:1 to 50:1 petroleum ether: ethyl acetate) and the title compound was isolated as a yellow liquid (100.1 mg, 0.305 mmol, 60.9% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.03 (2H, d, J = 7.0 Hz), 7.57 – 7.53 (1H, m), 7.44 – 7.40 (2H, m), 7.28 – 7.23 (2H, m), 7.19 – 7.15 (3H, m), 4.46 (2H, t, J = 6.4 Hz), 2.98 – 2.90 (1H, m), 2.71 (t, J = 7.6 Hz, 2H), 2.56 (t, J = 7.3 Hz, 2H), 2.04 – 1.94 (2H, m), 1.93 – 1.87 (2H, m), 1.35 (3H, d, J = 6.8 Hz); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.6, 141.6, 133.0, 130.3, 129.6, 128.5, 128.5, 126.0, 62.8, 37.0, 36.0, 35.0, 31.4, 29.8, 21.8 (one carbon was missing due to overlap); **HRMS** (ESI^+) $[M+H]^+$ calc'd for $C_{20}H_{25}O_2S$: 329.1570, found: 329.1564.

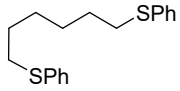
2. General Method C:



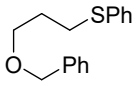
An oven-dried 25-mL glass schlenck, equipped with a stirring bar, was charged with zinc (98.1 mg, 1.50 mmol, 3.00 equiv) and *S*-phenyl benzenesulfonothioate (250 mg, 1.00 mmol, 2.00 equiv). The mixture was evacuated and backfilled with nitrogen for three times. Then aryl bromide (0.500 mmol, 1.00 equiv) and dry DMF (2.50 mL) was added under N_2 and the mixture was allowed to stir for 12 h at 80 °C. After cooling to room temperature, the mixture was diluted with NaCl aqueous solution (25.0 mL) and extracted with ethyl acetate (25.0 mL). The mixture was filtered through a celite pad and the organic layers were separated. The aqueous layer was extracted with ethyl acetate (10.0 mL x 3). The combined organic layers were washed with H_2O (25.0 mL x 5), dried over Na_2SO_4 and filtered. The solvent was removed by rotary evaporation and the residue was purified by flash silica gel chromatography.



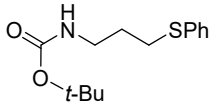
(4-Chlorophenethyl)(phenyl)sulfane 3y: Prepared according to **General Method C** (Eluent: 300:1 to 100:1 petroleum ether: ethyl acetate) and the title compound was isolated as a colorless liquid (107.1 mg, 0.431 mmol, 86.1% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.40 (2H, d, J = 6.8 Hz), 7.36 – 7.33 (2H, m), 7.31 (2H, d, J = 8.3 Hz), 7.27 – 7.22 (1H, m), 7.16 (2H, d, J = 8.3 Hz), 3.18 (2H, t, J = 8.2 Hz), 2.93 (2H, t, J = 7.2 Hz); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 138.7, 136.1, 132.3, 130.0, 129.5, 129.1, 128.7, 126.3, 35.1, 35.0. Spectra were consistent with literature data[1].



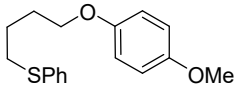
1,6-Bis(phenylthio)hexane 3z: Prepared according to **General Method C** (2.00 mmol *S*-phenyl benzenesulfonothioate, 3.00 mmol zinc were used) (Eluent: 200:1 to 100:1 petroleum ether: ethyl acetate) and the title compound was isolated as a white solid (99.2 mg, 0.328 mmol, 65.6% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.31 – 7.29 (4H, m), 7.27 – 7.23 (4H, m), 7.16 – 7.12 (2H, m), 2.89 (4H ,t, J = 7.3 Hz), 1.66 – 1.59 (4H, m), 1.45 – 1.38 (4H, m); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 136.9, 128.9, 128.9, 125.8, 33.5, 29.0, 28.4. Spectra were consistent with literature data[9].



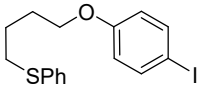
(3-(Benzyloxy)propyl)(phenyl)sulfane 3aa: Prepared according to **General Method C** (Eluent: 200:1 to 50:1 petroleum ether: ethyl acetate) and the title compound was isolated as a white solid (130.4 mg, 0.434 mmol, 86.8% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.34 – 7.29 (6H, m), 7.28 – 7.22 (3H, m), 7.15 – 7.11 (1H, m), 4.46 (2H, s), 3.55 (2H, t, J = 6.0 Hz), 3.02 (2H, t, J = 7.2 Hz), 1.95 – 1.88 (2H, m); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 138.4, 136.6, 129.0, 128.9, 128.4, 127.6, 127.6, 125.8, 73.0, 68.5, 30.4, 29.5. Spectra were consistent with literature data[10].



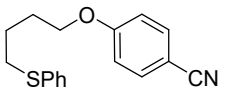
***tert*-Butyl (3-(phenylthio)propyl)carbamate 3ab:** Prepared according to **General Method C** (Eluent: 200:1 to 50:1 petroleum ether: ethyl acetate) and the title compound was isolated as a colorless liquid (102.7 mg, 0.384 mmol, 76.9% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.33 (2H, d, J = 6.9 Hz), 7.30 – 7.26 (2H, m), 7.20 – 7.16 (1H, m), 4.79 (1H, s), 3.27 – 3.22 (2H, m), 2.94 (2H, t, J = 7.2 Hz), 1.85 – 1.78 (2H, m), 1.45 (9H, s); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 156.0, 136.2, 129.2, 128.9, 126.0, 79.2, 39.4, 30.9, 29.4, 28.4. Spectra were consistent with literature data[11].



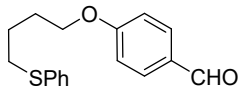
(4-(4-Methoxyphenoxy)butyl)(phenyl)sulfane 3ac: Prepared according to **General Method C** (Eluent: 200:1 to 50:1 petroleum ether: ethyl acetate) and the title compound was isolated as a white solid (127.2 mg, 0.441 mmol, 88.2% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.32 (2H, d, J = 7.8 Hz), 7.27 – 7.23 (2H, m), 7.17 – 7.13 (1H, m), 6.82 – 6.78 (4H, m), 3.89 (2H, t, J = 6.0 Hz), 3.73 (3H, s), 2.96 (2H, t, J = 7.0 Hz), 1.91 – 1.84 (2H, m), 1.84 – 1.77 (2H, m); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 153.8, 153.1, 136.7, 129.1, 128.9, 125.9, 115.5, 114.7, 67.9, 55.8, 33.4, 28.5, 25.9. Spectra were consistent with literature data[1].



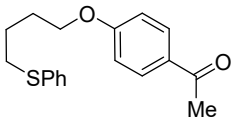
(4-(4-Iodophenoxy)butyl)(phenyl)sulfane 3ad: Prepared according to **General Method C** (Eluent: 200:1 to 50:1 petroleum ether: ethyl acetate) and the title compound was isolated as a white solid (150.3 mg, 0.391 mmol, 78.2% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.50 (2H, d, J = 8.8 Hz), 7.31 (2H, d, J = 7.5 Hz), 7.27 – 7.23 (2H, m), 7.17 – 7.13 (1H, m), 6.61 (2H, d, J = 8.8 Hz), 3.87 (2H, t, J = 6.1 Hz), 2.95 (2H, t, J = 7.0 Hz), 1.91 – 1.84 (2H, m), 1.82 – 1.75 (2H, m); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.8, 138.2, 136.5, 129.2, 128.9, 125.9, 116.9, 82.7, 67.4, 33.3, 28.2, 25.7. Spectra were consistent with literature data[1].



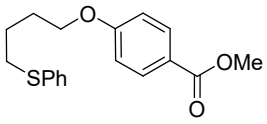
4-(4-(Phenylthio)butoxy)benzonitrile 3ae: Prepared according to **General Method C** (Eluent: 200:1 to 50:1 petroleum ether: ethyl acetate) and the title compound was isolated as a white solid (105.8 mg, 0.409 mmol, 81.7% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.53 (2H, d, J = 8.7 Hz), 7.32 (2H, d, J = 7.2 Hz), 7.28 – 7.25 (2H, m), 7.19 – 7.15 (1H, m), 6.88 (2H, d, J = 8.7 Hz), 3.98 (2H, t, J = 6.1 Hz), 2.97 (2H, t, J = 7.1 Hz), 1.97 – 1.90 (2H, m), 1.85 – 1.78 (2H, m); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 162.1, 136.3, 133.9, 129.1, 128.9, 126.0, 119.2, 115.1, 103.7, 67.6, 33.2, 27.9, 25.5; **HRMS** (ESI^+) $[M+Na]^+$ calc'd for $C_{17}H_{17}NaNOS$: 306.0923, found: 306.0915.



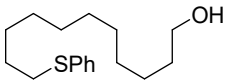
4-(4-(Phenylthio)butoxy)benzaldehyde 3af: Prepared according to **General Method C** (Eluent: 200:1 to 50:1 petroleum ether: ethyl acetate) and the title compound was isolated as a white solid (123.4 mg, 0.431 mmol, 86.2% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.85 (1H, s), 7.80 (2H, d, J = 8.7 Hz), 7.32 (2H, d, J = 7.0 Hz), 7.28 – 7.24 (2H, m), 7.18 – 7.14 (1H, m), 6.94 (2H, d, J = 8.8 Hz), 4.01 (2H, t, J = 6.1 Hz), 2.98 (2H, t, J = 7.1 Hz), 1.98 – 1.91 (2H, m), 1.86 – 1.78 (2H, m); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 190.8, 163.9, 136.3, 131.9, 129.8, 129.1, 128.9, 125.9, 114.7, 67.6, 33.2, 28.0, 25.6. Spectra were consistent with literature data[1].



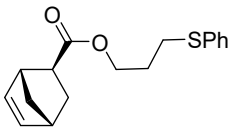
1-(4-(4-(Phenylthio)butoxy)phenyl)ethan-1-one 3ag: Prepared according to **General Method C** (Eluent: 200:1 to 50:1 petroleum ether: ethyl acetate) and the title compound was isolated as a white solid (124.8 mg, 0.416 mmol, 83.1% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.91 (2H, d, J = 8.9 Hz), 7.33 (2H, d, J = 7.1 Hz), 7.29 – 7.25 (2H, m), 7.19 – 7.15 (1H, m), 6.89 (2H, d, J = 8.9 Hz), 4.02 (2H, t, J = 6.2 Hz), 2.99 (2H, t, J = 7.2 Hz), 2.54 (3H, s), 1.98 – 1.91 (2H, m), 1.87 – 1.79 (2H, m); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 196.8, 162.9, 136.4, 130.6, 130.3, 129.3, 129.0, 126.0, 114.2, 67.6, 33.4, 28.1, 26.4, 25.7. Spectra were consistent with literature data[1].



Methyl 4-(4-(phenylthio)butoxy)benzoate 3ah: Prepared according to **General Method C** (Eluent: 200:1 to 50:1 petroleum ether: ethyl acetate) and the title compound was isolated as a white solid (142.7 mg, 0.451 mmol, 90.2% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.97 (2H, d, J = 8.5 Hz), 7.32 (2H, d, J = 7.3 Hz), 7.28 – 7.24 (2H, m), 7.18 – 7.13 (1H, m), 6.86 (2H, d, J = 8.5 Hz), 3.98 (2H, t, J = 6.1 Hz), 3.86 (3H, s), 2.97 (2H, t, J = 7.1 Hz), 1.96 – 1.89 (2H, m), 1.85 – 1.78 (2H, m); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.8, 162.7, 136.4, 131.6, 129.2, 128.9, 126.0, 122.5, 114.1, 67.4, 51.9, 33.3, 28.1, 25.7. Spectra were consistent with literature data[1].

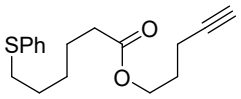


11-(Phenylthio)undecan-1-ol 3ai: Prepared according to **General Method C** (Eluent: 200:1 to 5:1 petroleum ether: ethyl acetate) and the title compound was isolated as a colorless liquid (112.7 mg, 0.402 mmol, 80.4% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.34 (2H, d, J = 7.3 Hz), 7.31 – 7.29 (2H, m), 7.19 – 7.16 (1H, m), 3.64 (2H, t, J = 6.7 Hz), 2.93 (2H, t, J = 7.4 Hz), 1.88 (1H, s), 1.70 – 1.63 (2H, m), 1.61 – 1.54 (2H, m), 1.45 – 1.40 (2H, m), 1.37 – 1.29 (12H, m); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 137.1, 128.9, 128.8, 125.7, 63.0, 33.6, 32.8, 29.6, 29.6, 29.5, 29.5, 29.2, 29.2, 28.9, 25.8; **HRMS** (ESI$^+$) $[M+Na]^+$ calc'd for $C_{17}H_{28}NaOS$: 303.1753, found: 303.1751.

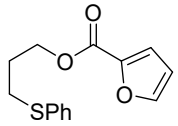


3-(Phenylthio)propyl (1*R*,2*S*,4*R*)-bicyclo[2.2.1]hept-5-ene-2-carboxylate 3aj: Prepared according to **General Method C** (Eluent: 200:1 to 20:1 petroleum ether: ethyl acetate) and the title compound was isolated as a colorless liquid (117.1 mg, 0.406 mmol, 81.2% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.37 (2H, d, J = 6.9 Hz), 7.33 – 7.29 (2H, m), 7.23 – 7.18 (1H, m), 6.22 – 6.20 (1H, m), 5.95 – 5.92 (1H, m), 4.15 (2H, td, J = 6.2, 2.0 Hz), 3.22 (1H, s), 3.00 (2H, t, J = 5.9 Hz), 2.98 – 2.95 (1H, m), 2.92 (1H, s), 1.99 – 1.94 (2H, m), 1.92 – 1.89 (1H, m), 1.47 – 1.44 (2H, m), 1.29

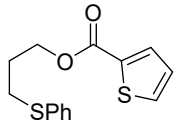
(1H, d, J = 7.6 Hz); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.6, 137.8, 136.0, 132.3, 129.3, 128.9, 126.1, 62.5, 49.6, 45.7, 43.3, 42.5, 30.2, 29.2, 28.4. Spectra were consistent with literature data[1].



Pent-4-yn-1-yl 6-(phenylthio)hexanoate 3ak: Prepared according to **General Method C** (Eluent: 200:1 to 30:1 petroleum ether: ethyl acetate) and the title compound was isolated as a colorless liquid (120.5 mg, 0.416 mmol, 83.1% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.32 – 7.20 (2H, m), 7.28 – 7.25 (2H, m), 7.18 – 7.14 (1H, m), 4.16 (2H, t, J = 6.3 Hz), 2.91 (2H, t, J = 7.3 Hz), 2.31 – 2.25 (4H, m), 1.97 (1H, t, J = 2.7 Hz), 1.87 – 1.81 (2H, m), 1.69 – 1.59 (4H, m), 1.49 – 1.41 (2H, m); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.5, 136.7, 129.0, 128.9, 125.8, 83.0, 69.1, 62.8, 34.1, 33.4, 28.8, 28.2, 27.5, 24.5, 15.2; **HRMS** (ESI^+) $[M+H]^+$ calc'd for $C_{17}H_{23}O_2S$: 291.1413, found: 291.1415.

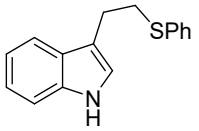


3-(Phenylthio)propyl furan-2-carboxylate 3al: Prepared according to **General Method C** (Eluent: 200:1 to 30:1 petroleum ether: ethyl acetate) and the title compound was isolated as a colorless liquid (117.0 mg, 0.446 mmol, 89.2% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.79 (1H, dd, J = 2.5, 1.3 Hz), 7.53 (1H, dd, J = 3.7, 1.3 Hz), 7.36 – 7.33 (2H, m), 7.19 – 7.14 (1H, m), 7.09 – 7.07 (1H, m), 4.39 (2H, t, J = 6.2 Hz), 3.04 (2H, t, J = 7.2 Hz), 2.09 – 2.02 (2H, m); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 162.1, 135.9, 133.7, 133.5, 132.5, 129.4, 129.0, 127.8, 126.2, 63.5, 30.2, 28.4. Spectra were consistent with literature data[1].

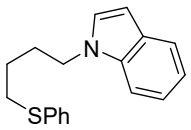


3-(Phenylthio)propyl thiophene-2-carboxylatee 3am: Prepared according to **General Method C** (Eluent: 200:1 to 50:1 petroleum ether: ethyl acetate) and the title compound was isolated as a colorless liquid (122.1 mg, 0.439 mmol, 87.7% yield). **^{1}H**

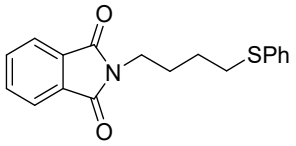
NMR (400 MHz, $CDCl_3$) δ 7.57 – 7.56 (1H, m), 7.35 (2H, d, J = 7.2 Hz), 7.29 – 7.25 (2H, m), 7.19 – 7.16 (2H, m), 6.50 – 6.49 (1H, m), 4.40 (2H, t, J = 6.2 Hz), 3.04 (2H, t, J = 7.2 Hz), 2.09 – 2.03 (2H, m); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.6, 146.4, 144.6, 135.9, 129.4, 129.0, 126.2, 118.0, 111.9, 63.3, 30.2, 28.4. Spectra were consistent with literature data[1].



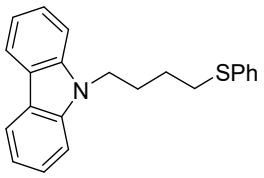
3-(2-(Phenylthio)ethyl)-1*H*-indole 3an: Prepared according to **General Method C** (Eluent: 200:1 to 50:1 petroleum ether: ethyl acetate) and the title compound was isolated as a colorless liquid (112.9 mg, 0.446 mmol, 89.1% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.85 (1H, s), 7.54 (1H, d, J = 7.8 Hz), 7.36 (2H, d, J = 7.2 Hz), 7.31 – 7.26 (3H, m), 7.20 – 7.15 (2H, m), 7.13 – 7.09 (1H, m), 6.97 (1H, s), 3.24 (2H, t, J = 7.3 Hz), 3.08 (2H, t, J = 7.7 Hz); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 136.7, 136.3, 129.2, 129.0, 127.2, 126.0, 122.2, 121.9, 119.5, 118.7, 114.7, 111.3, 34.3, 25.4. Spectra were consistent with literature data[1].



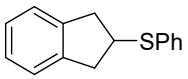
1-(4-(Phenylthio)butyl)-1*H*-indole 3ao: Prepared according to **General Method C** (Eluent: 200:1 to 50:1 petroleum ether: ethyl acetate) and the title compound was isolated as a colorless liquid (118.5 mg, 0.421 mmol, 84.2% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.61 (1H, d, J = 7.8 Hz), 7.27 (1H, d, J = 8.2 Hz), 7.25 – 7.22 (3H, m), 7.21 – 7.16 (2H, m), 7.14 – 7.11 (1H, m), 7.10 – 7.06 (1H, m), 6.97 (1H, d, J = 3.2 Hz), 6.45 (1H, d, J = 3.1 Hz), 4.01 (2H, t, J = 7.0 Hz), 2.81 (2H, t, J = 7.1 Hz), 1.93 – 1.86 (2H, m), 1.60 – 1.53 (2H, m); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 136.3, 135.9, 129.4, 129.0, 128.6, 127.7, 126.1, 121.5, 121.0, 119.3, 109.4, 101.1, 45.8, 33.3, 29.1, 26.4. Spectra were consistent with literature data[1].



2-(4-(Phenylthio)butyl)isoindoline-1,3-dione 3ap: Prepared according to **General Method C** (Eluent: 200:1 to 50:1 petroleum ether: ethyl acetate) and the title compound was isolated as a white solid (124.9 mg, 0.401 mmol, 80.2% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.82 – 7.79 (2H, m), 7.70 – 7.68 (2H, m), 7.29 (2H, d, J = 7.1 Hz), 7.25 – 7.21 (2H, m), 7.14 – 7.10 (1H, m), 3.68 (2H, t, J = 7.1 Hz), 2.94 (2H, t, J = 7.2 Hz), 1.86 – 1.79 (2H, m), 1.70 – 1.63 (2H, m); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.3, 136.3, 133.9, 132.0, 129.3, 128.8, 125.9, 123.2, 37.3, 33.1, 27.6, 26.2. Spectra were consistent with literature data[1].

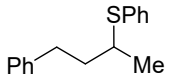


9-(4-(Phenylthio)butyl)-9*H*-carbazole 3aq: Prepared according to **General Method C** (Eluent: 200:1 to 50:1 petroleum ether: ethyl acetate) and the title compound was isolated as a white solid (140.4 mg, 0.424 mmol, 84.7% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.06 (2H, d, J = 7.7 Hz), 7.43 – 7.39 (2H, m), 7.30 (2H, d, J = 8.2 Hz), 7.23 – 7.17 (6H, m), 7.14 – 7.10 (1H, m), 4.19 (2H, t, J = 7.1 Hz), 2.80 (2H, t, J = 7.1 Hz), 1.97 – 1.90 (2H, m), 1.66 – 1.58 (2H, m); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 140.4, 136.3, 129.5, 129.0, 126.1, 125.7, 122.9, 120.5, 118.9, 108.7, 42.5, 33.6, 28.0, 26.7. Spectra were consistent with literature data[1].

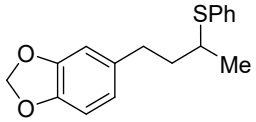


(2,3-Dihydro-1*H*-inden-2-yl)(phenyl)sulfane 3ar: Prepared according to **General Method C** (3.00 equiv $MgCl_2$ was used) (Eluent: 200:1 to 50:1 petroleum ether: ethyl acetate) and the title compound was isolated as a colorless liquid (102.4 mg, 0.452 mmol, 90.5% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.39 (2H, d, J = 8.1 Hz), 7.31 – 7.27 (2H, m), 7.22 – 7.13 (5H, m), 4.13 – 4.06 (1H, m), 3.35 (2H, dd, J = 16.1, 7.5 Hz), 2.99 (2H, dd, J = 16.2, 5.9 Hz); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 141.6, 136.2,

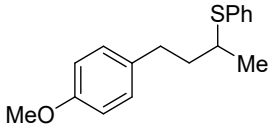
130.6, 129.0, 126.8, 126.5, 124.6, 45.3, 40.3. Spectra were consistent with literature data[1].



Phenyl(4-phenylbutan-2-yl)sulfane 3as: Prepared according to **General Method C** (3.00 equiv $MgCl_2$ was used) (Eluent: 200:1 to 50:1 petroleum ether: ethyl acetate) and the title compound was isolated as a colorless liquid (113.3 mg, 0.467 mmol, 93.5% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.36 – 7.33 (2H, m), 7.28 – 7.23 (4H, m), 7.21 – 7.15 (4H, m), 3.23 – 3.14 (1H, m), 2.84 – 2.71 (2H, m), 1.96 – 1.87 (1H, m), 1.85 – 1.76 (1H, m), 1.30 (3H, d, J = 6.7 Hz); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 141.8, 135.2, 132.1, 128.9, 128.6, 128.5, 126.8, 126.0, 42.6, 38.3, 33.3, 21.3. Spectra were consistent with literature data[1].



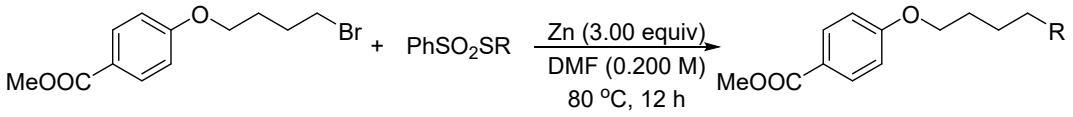
5-(3-(Phenylthio)butyl)benzo[*d*][1,3]dioxole 3at: Prepared according to **General Method C** (3.00 equiv $MgCl_2$ was used) (Eluent: 200:1 to 50:1 petroleum ether: ethyl acetate) and the title compound was isolated as a colorless liquid (115.7 mg, 0.404 mmol, 80.8% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.26 (2H, d, J = 7.0 Hz), 7.19 – 7.15 (2H, m), 7.13 – 7.08 (1H, m), 6.62 (1H, d, J = 7.8 Hz), 6.55 (1H, s), 6.51 (1H, d, J = 7.9 Hz), 5.79 (2H, s), 3.12 – 3.03 (1H, m), 2.66 – 2.54 (2H, m), 1.82 – 1.73 (1H, m), 1.71 – 1.62 (1H, m), 1.20 (3H, d, J = 6.7 Hz); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 147.6, 145.7, 135.5, 135.1, 132.1, 128.9, 126.8, 121.2, 108.9, 108.2, 100.8, 42.4, 38.5, 32.9, 21.3; **HRMS** (ESI$^+$) $[M+Na]^+$ calc'd for $C_{17}H_{18}NaO_2S$: 309.0920, found: 309.0912.



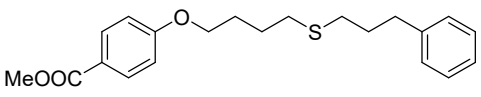
(4-(4-Methoxyphenyl)butan-2-yl)(phenyl)sulfane 3au: Prepared according to **General Method C** (3.00 equiv $MgCl_2$ was used) (Eluent: 200:1 to 50:1 petroleum ether: ethyl acetate) and the title compound was isolated as a colorless liquid (113.0

mg, 0.415 mmol, 83.0% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.35 (2H, d, J = 7.4 Hz), 7.27 – 7.23 (2H, m), 7.21 – 7.17 (1H, m), 7.07 (2H, d, J = 8.6 Hz), 6.81 (2H, d, J = 8.6 Hz), 3.76 (3H, s), 3.22 – 3.14 (1H, m), 2.78 – 2.65 (2H, m), 1.95 – 1.84 (1H, m), 1.81 – 1.72 (1H, m), 1.30 (3H, d, J = 6.7 Hz); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 157.9, 135.2, 133.7, 132.0, 129.4, 128.9, 126.8, 113.9, 55.3, 42.5, 38.5, 32.3, 21.3. Spectra were consistent with literature data[1].

3. General Method D:

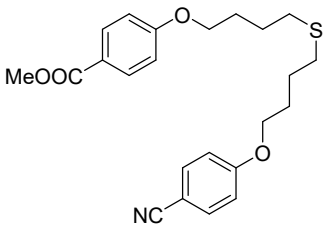


An oven-dried 25-mL glass schlenck, equipped with a stirring bar, was charged with zinc (98.1 mg, 1.50 mmol, 3.00 equiv) and methyl 4-(4-bromobutoxy)benzoate (287.2 mg, 1.00 mmol, 2.00 equiv). The mixture was evacuated and backfilled with nitrogen for three times. Then *S*-phenyl benzenesulfonothioate (0.500 mmol, 1.00 equiv) and dry DMF (2.50 mL) were added under N_2 and the mixture was allowed to stir for 12 h at 80 °C. After cooling to room temperature, the mixture was diluted with saturated NaCl aqueous solution (15.0 mL) and ethyl acetate (15.0 mL). The mixture was filtered through a celite pad and the organic layers were separated. The aqueous layer was diluted with H_2O (25.0 mL) and extracted with ethyl acetate (25.0 mL x 3). The combined organic layers were washed with H_2O (25.0 mL x 5), dried over Na_2SO_4 and filtered. The solvent was removed by rotary evaporation and the residue was purified by flash silica gel chromatography.

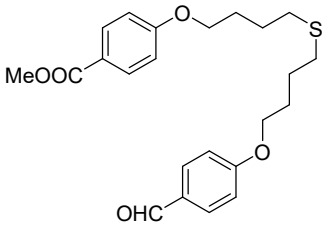


Methyl 4-(4-((3-phenylpropyl)thio)butoxy)benzoate 3k: Prepared according to **General Method D** (Eluent: 200:1 to 10:1 petroleum ether: ethyl acetate) and the title compound was isolated as a colorless liquid (145.0 mg, 0.404 mmol, 80.9% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.97 (2H, d, J = 8.8 Hz), 7.29 – 7.25 (2H, m), 7.18 – 7.16 (3H, m), 6.88 (2H, d, J = 8.9 Hz), 3.99 (2H, t, J = 6.2 Hz), 3.86 (3H, s), 2.71 (2H, t,

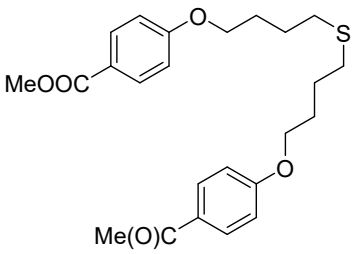
J = 7.6 Hz), 2.56 (2H, t, J = 7.2 Hz), 2.52 (2H, t, J = 7.3 Hz), 1.94 – 1.85 (4H, m), 1.81 – 1.71 (2H, m); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.9, 162.8, 141.6, 131.6, 128.5, 128.4, 126.0, 122.5, 114.0, 67.6, 51.9, 34.8, 31.7, 31.4, 31.2, 28.2, 26.1; **HRMS** (ESI^+) $[M+Na]^+$ calc'd for $C_{21}H_{26}NaO_3S$: 381.1495, found: 381.1499.



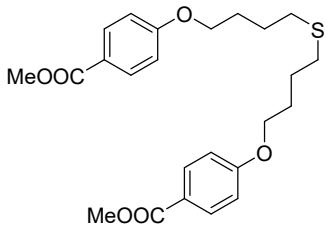
Methyl 4-(4-((4-(4-cyanophenoxy)butyl)thio)butoxy)benzoate 3av: Prepared according to **General Method D** (Eluent: 200:1 to 10:1 petroleum ether: ethyl acetate) and the title compound was isolated as a white solid (143.0 mg, 0.346 mmol, 69.2% yield). **M.p.** = 86.4 – 87.0 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.93 (2H, d, J = 8.5 Hz), 7.51 (2H, d, J = 8.4 Hz), 6.89 – 6.85 (4H, m), 4.00 – 3.96 (4H, m), 3.84 (3H, s), 2.57 (4H, t, J = 7.2 Hz), 1.92 – 1.88 (4H, m), 1.82 – 1.74 (4H, m); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.7, 162.7, 162.2, 134.0, 131.5, 122.4, 119.2, 115.1, 114.0, 103.7, 67.7, 67.5, 51.8, 31.7, 31.6, 28.2, 28.0, 26.0, 25.9; **HRMS** (ESI^+) $[M+Na]^+$ calc'd for $C_{23}H_{27}NNaO_4S$: 336.1553, found: 436.1563.



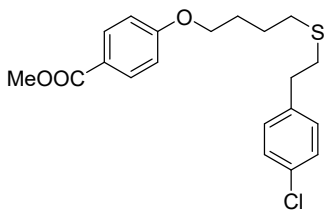
Methyl 4-(4-((4-(4-formylphenoxy)butyl)thio)butoxy)benzoate 3aw: Prepared according to **General Method D** (Eluent: 200:1 to 10:1 petroleum ether: ethyl acetate) and the title compound was isolated as a white solid (146.2 mg, 0.351 mmol, 70.2% yield). **M.p.** = 80.3 – 80.7 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.82 (1H, s), 7.93 (2H, d, J = 8.7 Hz), 7.77 (2H, d, J = 8.6 Hz), 6.94 (2H, d, J = 8.4 Hz), 6.85 (2H, d, J = 8.8 Hz), 4.02 – 3.96 (4H, m), 3.83 (3H, s), 2.57 (4H, t, J = 7.2 Hz), 1.91 – 1.84 (4H, m), 1.79 – 1.71 (4H, m); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 190.7, 166.7, 164.0, 162.7, 131.9, 131.5, 129.7, 122.4, 114.7, 114.0, 67.7, 67.5, 51.8, 31.6, 31.6, 28.2, 28.1, 26.0, 26.0; **HRMS** (ESI^+) $[M+Na]^+$ calc'd for $C_{23}H_{28}NaO_5S$: 439.1550, found: 439.1546.



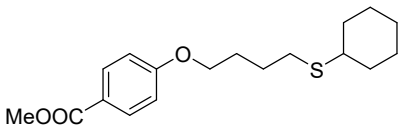
Methyl 4-(4-((4-(4-acetylphenoxy)butyl)thio)butoxy)benzoate 3ax: Prepared according to **General Method D** (Eluent: 200:1 to 10:1 petroleum ether: ethyl acetate) and the title compound was isolated as a white solid (156.3 mg, 0.363 mmol, 72.6% yield). **M.p.** = 80.1 – 80.5 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.86 (2H, d, J = 8.4 Hz), 7.80 (2H, d, J = 8.4 Hz), 6.79 (4H, m), 3.93 – 3.89 (4H, m), 3.76 (3H, s), 2.50 (4H, t, J = 7.1 Hz), 2.43 (3H, s), 1.84 – 1.77 (4H, m), 1.72 – 1.64 (4H, m); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 196.6, 166.7, 162.8, 162.6, 131.5, 130.5, 130.1, 122.3, 114.0, 113.9, 67.5, 67.4, 51.8, 31.6, 28.1, 26.3, 26.0 (three carbons were missing due to the overlap); **HRMS** (ESI^+) $[M+Na]^+$ calc'd for $C_{24}H_{30}NaO_5S$: 453.1706, found: 453.1719.



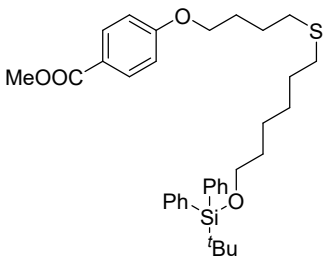
Dimethyl 4,4'-((thiobis(butane-4,1-diyl))bis(oxy))dibenzoate 3ay: Prepared according to **General Method D** (Eluent: 200:1 to 10:1 petroleum ether: ethyl acetate) and the title compound was isolated as a white solid (174.0 mg, 0.389 mmol, 77.9% yield). **M.p.** = 72.4 – 72.8 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.94 (4H, d, J = 8.4 Hz), 6.85 (4H, d, J = 8.4 Hz), 3.98 (4H, t, J = 6.2 Hz), 3.84 (6H, s), 2.57 (4H, t, J = 7.1 Hz), 1.91 – 1.84 (4H, m), 1.79 – 1.71 (4H, m); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.8, 162.7, 131.5, 122.4, 114.0, 67.5, 51.8, 31.7, 28.2, 26.1; **HRMS** (ESI^+) $[M+Na]^+$ calc'd for $C_{24}H_{30}NaO_6S$: 469.1655, found: 469.1667.



Methyl 4-(4-((4-chlorophenethyl)thio)butoxy)benzoate 3az: Prepared according to **General Method D** (Eluent: 200:1 to 10:1 petroleum ether: ethyl acetate) and the title compound was isolated as a colorless liquid (162.3 mg, 0.428 mmol, 85.7% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.97 (2H, d, J = 8.9 Hz), 7.23 (2H, d, J = 8.4 Hz), 7.11 (2H, d, J = 8.4 Hz), 6.87 (2H, d, J = 8.9 Hz), 3.98 (2H, t, J = 6.2 Hz), 3.86 (3H, s), 2.85 – 2.81 (2H, m), 2.75 – 2.71 (2H, m), 2.57 (2H, t, J = 7.2 Hz), 1.92 – 1.83 (2H, m), 1.80 – 1.71 (2H, m); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.7, 162.7, 138.9, 132.0, 131.5, 129.8, 128.5, 122.4, 114.0, 67.4, 51.8, 35.5, 33.4, 31.9, 28.1, 26.0; **HRMS** (ESI^+) $[M+Na]^+$ calc'd for $C_{20}H_{23}ClNaO_3S$: 401.0949, found: 401.0949.

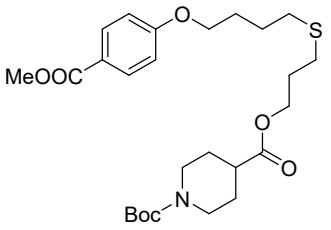


Methyl 4-(4-(cyclohexylthio)butoxy)benzoate 3aaa: Prepared according to **General Method D** (Eluent: 200:1 to 20:1 petroleum ether: ethyl acetate) and the title compound was isolated as a colorless liquid (146.1 mg, 0.453 mmol, 90.6% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.95 (2H, d, J = 8.8 Hz), 6.87 (2H, d, J = 8.9 Hz), 3.85 (2H, t, J = 6.3 Hz), 3.87 (3H, s), 2.65 – 2.62 (1H, m), 2.59 (2H, t, J = 7.3 Hz), 1.97 – 1.91 (2H, m), 1.91 – 1.85 (2H, m), 1.78 – 1.71 (4H, m), 1.62 – 1.55 (1H, m), 1.33 – 1.20 (5H, m); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.9, 162.8, 131.6, 122.5, 114.1, 67.6, 51.9, 43.5, 33.8, 29.8, 28.3, 26.5, 26.2, 25.9; **HRMS** (ESI^+) $[M+Na]^+$ calc'd for $C_{18}H_{26}NaO_3S$: 345.1495, found: 345.1507.

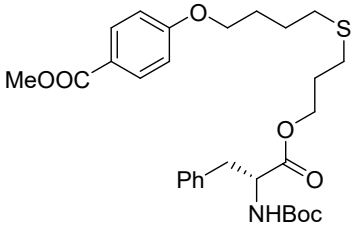


Methyl 4-(4-((6-((*tert*-butyldiphenylsilyl)oxy)hexyl)thio)butoxy)benzoate 3aab: Prepared according to **General Method D** (Eluent: 200:1 to 10:1 petroleum ether:

ethyl acetate) and the title compound was isolated as a colorless liquid (165.0 mg, 0.285 mmol, 57.0% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.99 (2H, d, J = 8.8 Hz), 7.70 – 7.67 (4H, m), 7.45 – 7.37 (6H, m), 6.91 (2H, d, J = 8.8 Hz), 4.04 (2H, t, J = 6.2 Hz), 3.89 (3H, s), 3.68 (2H, t, J = 6.4 Hz), 2.59 (2H, t, J = 7.2 Hz), 2.52 (2H, t, J = 7.4 Hz), 1.96 – 1.88 (2H, m), 1.83 – 1.74 (2H, m), 1.66 – 1.53 (4H, m), 1.43 – 1.35 (4H, m), 1.06 (9H, s); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.8, 162.8, 135.6, 134.0, 131.6, 129.5, 127.6, 122.4, 114.0, 67.5, 63.8, 51.8, 32.4, 32.0, 31.7, 29.6, 28.6, 28.2, 26.9, 26.1, 25.4, 19.2; **HRMS** (ESI^+) $[M+Na]^+$ calc'd for $C_{34}H_{46}NaO_4SSi$: 601.2778, found: 601.2780.

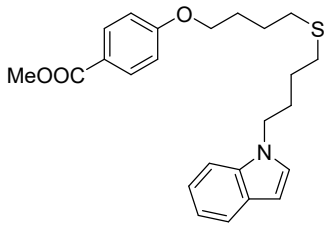


1-(*tert*-Butyl) 4-(3-((4-(4-(methoxycarbonyl)phenoxy)butyl)thio)propyl) piperidine-1,4-dicarboxylate 3aac: Prepared according to **General Method D** (Eluent: 200:1 to 10:1 petroleum ether: ethyl acetate) and the title compound was isolated as a colorless liquid (164.8 mg, 0.323 mmol, 64.7% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.92 (2H, d, J = 8.9 Hz), 6.84 (2H, d, J = 8.9 Hz), 4.13 (2H, t, J = 6.3 Hz), 3.97 (4H, t, J = 6.2 Hz), 3.82 (3H, s), 2.78 (2H, t, J = 12.5 Hz), 2.55 – 2.51 (4H, m), 2.42 – 2.36 (1H, m), 1.88 – 1.83 (6H, m), 1.75 – 1.70 (2H, m), 1.60 – 1.55 (2H, m), 1.40 (9H, s); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.3, 166.7, 162.6, 154.6, 131.5, 122.4, 114.0, 79.5, 67.4, 63.0, 51.7, 43.0, 41.0, 31.7, 28.6, 28.3, 28.1, 27.9, 25.9 (one carbon was missing due to overlap); **HRMS** (ESI^+) $[M+Na]^+$ calc'd for $C_{26}H_{39}NNaO_7S$: 532.2339, found: 532.2344.

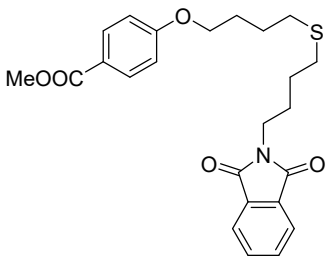


Methyl(*R*)-4-((6-benzyl-2,2-dimethyl-4,7-dioxo-3,8-dioxa-12-thia-5-azahexadecan-16-yl)oxy)benzoate 3aad: Prepared according to **General Method D**

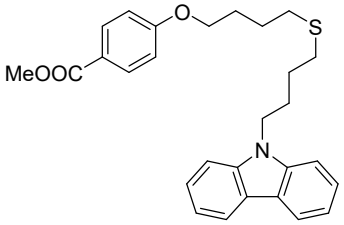
(Eluent: 200:1 to 10:1 petroleum ether: ethyl acetate) and the title compound was isolated as a colorless liquid (159.9 mg, 0.293 mmol, 58.6% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.98 (2H, d, J = 8.8 Hz), 7.30 – 7.23 (3H, m), 7.14 (2H, d, J = 6.7 Hz), 6.89 (2H, d, J = 8.9 Hz), 5.05 (1H, d, J = 8.3 Hz), 4.59 – 4.54 (1H, m), 4.20 – 4.16 (2H, m), 4.02 (2H, t, J = 6.2 Hz), 3.87 (3H, s), 3.07 (2H, d, J = 6.3 Hz), 2.56 (2H, t, J = 7.2 Hz), 2.47 (2H, t, J = 7.2 Hz), 1.94 – 1.82 (4H, m), 1.78 – 1.73 (2H, m), 1.41 (9H, s); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 172.0, 166.9, 162.7, 155.1, 136.0, 131.0, 129.3, 128.6, 127.1, 122.5, 114.1, 79.9, 67.5, 63.9, 54.5, 51.9, 38.5, 31.7, 28.4, 28.3, 28.2, 26.0; **HRMS** (ESI^+) $[M+Na]^+$ calc'd for $C_{29}H_{39}NNaO_7S$: 568.2339, found: 568.2353.



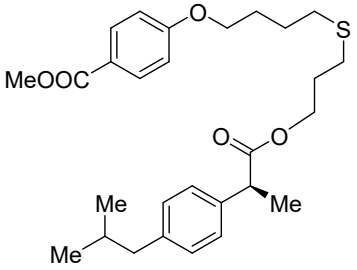
Methyl 4-(4-((4-(1H-indol-1-yl)butyl)thio)butoxy)benzoate 3aae: Prepared according to **General Method D** (Eluent: 200:1 to 10:1 petroleum ether: ethyl acetate) and the title compound was isolated as a yellow liquid (167.2 mg, 0.406 mmol, 81.2% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.07 (2H, d, J = 8.8 Hz), 7.72 (1H, d, J = 7.8 Hz), 7.41 (1H, d, J = 8.2 Hz), 7.31 – 7.27 (1H, m), 7.21 – 7.18 (1H, m), 7.14 (1H, d, J = 3.1 Hz), 6.95 (2H, d, J = 8.8 Hz), 6.57 (1H, d, J = 3.1 Hz), 4.15 (2H, t, J = 7.0 Hz), 4.00 (2H, t, J = 6.2 Hz), 3.95 (3H, s), 2.57 – 2.52 (4H, m), 2.02 – 1.95 (2H, m), 1.92 – 1.87 (2H, m), 1.80 – 1.73 (2H, m), 1.67 – 1.59 (2H, m); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.7, 162.7, 135.8, 131.5, 128.5, 127.6, 122.3, 121.3, 120.9, 119.2, 114.0, 109.3, 101.0, 67.4, 51.7, 45.8, 31.6, 31.5, 29.1, 28.1, 26.8, 25.9; **HRMS** (ESI^+) $[M+Na]^+$ calc'd for $C_{24}H_{29}NNaO_3S$: 434.1760, found: 434.1760.



Methyl 4-(4-((4-(1,3-dioxoisoindolin-2-yl)butyl)thio)butoxy)benzoate 3aaf: Prepared according to **General Method D** (Eluent: 200:1 to 10:1 petroleum ether: ethyl acetate) and the title compound was isolated as a yellow liquid (153.9 mg, 0.349 mmol, 69.7% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.88 (2H, d, J = 8.8 Hz), 7.75 – 7.72 (2H, m), 7.63 – 7.61 (2H, m), 6.81 (2H, d, J = 8.8 Hz), 3.94 (2H, t, J = 6.2 Hz), 3.79 (3H, s), 3.62 (2H, t, J = 7.0 Hz), 2.54 – 2.33 (4H, m), 1.85 – 1.79 (2H, m), 1.78 – 1.65 (4H, m), 1.60 – 1.53 (2H, m); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.2, 166.6, 162.6, 133.8, 131.9, 131.4, 123.0, 122.2, 113.9, 67.4, 51.7, 37.3, 31.6, 31.3, 28.1, 27.7, 26.7, 26.0; **HRMS** (ESI^+) $[M+Na]^+$ calc'd for $C_{24}H_{27}NNaO_5S$: 464.1502, found: 464.1496.

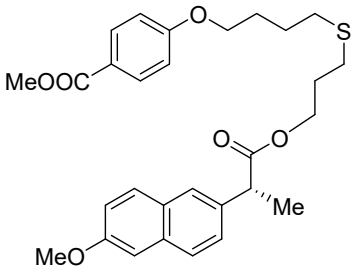


Methyl 4-(4-((4-(9*H*-carbazol-9-yl)butyl)thio)butoxy)benzoate 3aag: Prepared according to **General Method D** (Eluent: 200:1 to 10:1 petroleum ether: ethyl acetate) and the title compound was isolated as a yellow liquid (173.1 mg, 0.375 mmol, 75.0% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.06 (2H, d, J = 7.8 Hz), 7.95 (2H, d, J = 8.9 Hz), 7.44 – 7.40 (2H, M), 7.34 (2H, d, J = 8.2 Hz), 7.21 – 7.17 (2H, m), 6.81 (2H, d, J = 8.9 Hz), 4.22 (2H, t, J = 7.0 Hz), 3.86 – 3.83 (5H, m), 2.43 – 2.38 (4H, q, J = 7.2 Hz), 1.95 – 1.88 (2H, m), 1.78 – 1.71 (2H, m), 1.64 – 1.54 (4H, m); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.8, 162.7, 140.3, 131.5, 125.6, 122.8, 122.4, 120.3, 118.8, 114.0, 108.6, 67.4, 51.8, 42.5, 31.7, 31.7, 28.1, 28.0, 27.1, 26.0; **HRMS** (ESI^+) $[M+Na]^+$ calc'd for $C_{28}H_{31}NNaO_3S$: 484.1917, found: 484.1912.

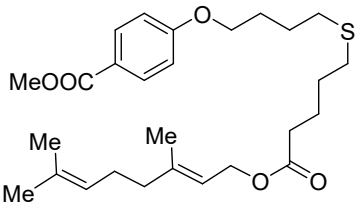


Methyl(*S*)-4-(4-((3-((2-(4-isobutylphenyl)propanoyl)oxy)propyl)thio)butoxy)benzo-

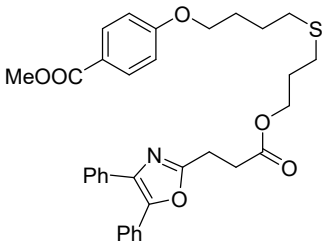
ate 3aah: Prepared according to **General Method D** (Eluent: 200:1 to 5:1 petroleum ether: ethyl acetate) and the title compound was isolated as a colorless liquid (178.0 mg, 0.366 mmol, 73.2% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.98 (2H, d, J = 8.8 Hz), 7.19 (2H, d, J = 8.1 Hz), 7.08 (2H, d, J = 8.2 Hz), 6.89 (2H, d, J = 8.9 Hz), 4.21 – 4.10 (2H, m), 4.05 – 3.94 (2H, t, J = 5.5 Hz), 3.86 (3H, s), 3.71 – 3.66 (1H, m), 2.50 (2H, t, J = 7.2 Hz), 2.45 – 2.11 (4H, m), 1.90 – 1.79 (5H, m), 1.77 – 1.68 (2H, m), 1.48 (3H, d, J = 7.4 Hz), 0.88 (6H, d, J = 6.8 Hz); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.5, 166.7, 162.7, 140.5, 137.8, 131.6, 129.3, 127.1, 122.5, 114.0, 67.5, 63.1, 51.8, 45.1, 45.0, 31.7, 30.2, 28.7, 28.3, 28.2, 26.0, 22.4, 18.4; **HRMS** (ESI^+) $[M+Na]^+$ calc'd for $C_{28}H_{38}NaO_5S$: 509.2332, found: 509.2334.



Methyl (*R*)-4-(4-((3-((2-(6-methoxynaphthalen-2-yl)propanoyl)oxy)propyl)thio) butoxy)benzoate 3aai: Prepared according to **General Method D** (Eluent: 200:1 to 5:1 petroleum ether: ethyl acetate) and the title compound was isolated as a colorless liquid (176.0 mg, 0.345 mmol, 68.9% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.97 (2H, d, J = 8.8 Hz), 7.69 – 7.65 (3H, m), 7.39 (1H, dd, J = 8.4, 1.9 Hz), 7.12 (1H, d, J = 8.9 Hz), 7.08 (1H, s), 6.86 (d, J = 8.9 Hz, 2H), 4.22 – 4.10 (2H, m), 3.91 (t, J = 6.2 Hz, 2H), 3.86 (6H, s), 3.85 – 3.83 (1H, m), 2.39 (4H, td, J = 7.4, 2.4 Hz), 1.87 – 1.81 (2H, m), 1.79 – 1.74 (2H, m), 1.64 – 1.59 (2H, m), 1.56 (3H, d, J = 7.1 Hz); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.5, 166.8, 162.7, 157.6, 135.7, 133.7, 131.6, 129.2, 128.9, 127.1, 126.2, 125.9, 122.4, 119.0, 114.0, 105.6, 67.5, 63.2, 55.2, 51.8, 45.4, 31.7, 28.7, 28.3, 28.1, 25.9, 18.4; **HRMS** (ESI^+) $[M+Na]^+$ calc'd for $C_{29}H_{34}NaO_6S$: 533.1968, found: 533.1970.

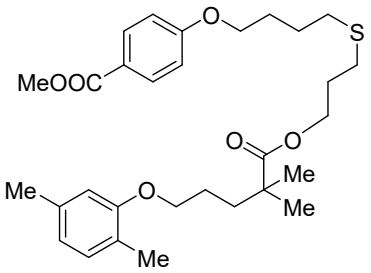


Methyl(*E*)-4-(4-((5-((3,7-dimethylocta-2,6-dien-1-yl)oxy)-5-oxopentyl)thio)butoxy)benzoate 3aaj: Prepared according to **General Method D** (Eluent: 200:1 to 10:1 petroleum ether: ethyl acetate) and the title compound was isolated as a colorless liquid (163.0 mg, 0.342 mmol, 68.4% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.97 (2H, d, J = 8.8 Hz), 6.89 (2H, d, J = 8.9 Hz), 5.37 – 5.33 (1H, m), 5.10 – 5.07 (1H, m), 4.56 (2H, d, J = 7.2 Hz), 4.01 (2H, t, J = 6.2 Hz), 3.87 (3H, s), 2.57 (2H, t, J = 7.2 Hz), 2.52 (2H, t, J = 7.2 Hz), 2.32 (2H, t, J = 7.3 Hz), 2.14 – 2.04 (4H, m), 1.94 – 1.87 (2H, m), 1.78 – 1.72 (7H, m), 1.67 (3H, s), 1.59 (3H, m); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.2, 166.7, 162.7, 142.4, 132.0, 131.5, 123.5, 122.4, 119.2, 114.0, 67.5, 60.9, 51.7, 33.8, 32.1, 31.6, 31.5, 29.0, 28.2, 26.6, 26.0, 25.6, 24.1, 23.4, 17.6; **HRMS** (ESI^+) $[M+Na]^+$ calc'd for $C_{27}H_{40}NaO_5S$: 499.2489, found: 499.2484.

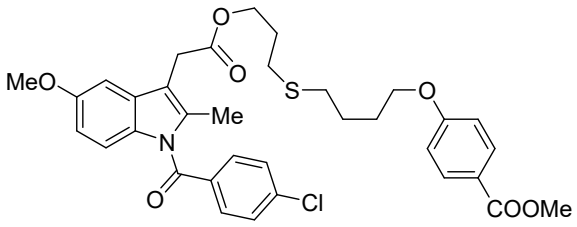


Methyl4-(4-((3-((3-(4,5-diphenyloxazol-2-yl)propanoyl)oxy)propyl)thio)butoxy)benzoate 3aak: Prepared according to **General Method D** (Eluent: 200:1 to 10:1 petroleum ether: ethyl acetate) and the title compound was isolated as a colorless liquid (146.9 mg, 0.256 mmol, 51.2% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.86 (2H, d, J = 8.8 Hz), 7.53 (2H, d, J = 6.7 Hz), 7.46 (2H, d, J = 6.4 Hz), 7.27 – 7.17 (6H, m), 6.77 (2H, d, J = 8.7 Hz), 4.12 (2H, t, J = 6.3 Hz), 3.87 (2H, t, J = 6.2 Hz), 3.75 (3H, s), 3.07 (2H, t, J = 7.4 Hz), 2.81 (2H, t, J = 7.4 Hz), 2.47 – 2.41 (4H, m), 1.84 – 1.72 (4H, m), 1.66 – 1.59 (2H, m); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.8, 166.7, 162.7, 161.7, 145.3, 135.0, 132.4, 131.5, 128.9, 128.6, 128.5, 128.4, 128.0, 127.8, 126.4, 122.4, 114.0, 67.5, 63.3, 51.8, 31.7, 31.0, 28.6, 28.4,

28.2, 26.0, 23.5; **HRMS** (ESI$^+$) [M+Na]$^+$ calc'd for $C_{33}H_{35}NNaO_6S$: 596.2077, found: 596.2079.

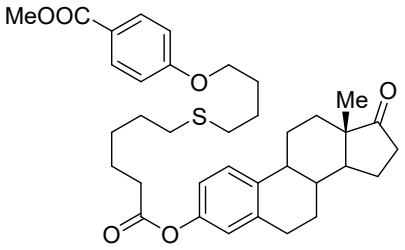


Methyl 4-(4-((3-((5-(2,5-dimethylphenoxy)-2,2-dimethylpentanoyl)oxy)propyl) thio)butoxy)benzoate 3aal: Prepared according to **General Method D** (Eluent: 200:1 to 5:1 petroleum ether: ethyl acetate) and the title compound was isolated as a colorless liquid (225.5 mg, 0.425 mmol, 85.0% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.99 (2H, d, J = 8.8 Hz), 7.01 (1H, d, J = 7.5 Hz), 6.89 (2H, d, J = 8.9 Hz), 6.66 (1H, d, J = 7.4 Hz), 6.62 (1H, s), 4.19 (2H, t, J = 6.2 Hz), 3.98 (2H, t, J = 6.2 Hz), 3.92 – 3.90 (2H, m), 3.88 (3H, s), 2.62 – 2.57 (4H, m), 2.32 (3H, s), 2.20 (3H, s), 1.97 – 1.88 (4H, m), 1.81 – 1.74 (6H, m), 1.25 (6H, s); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 177.5, 166.7, 162.6, 156.8, 136.3, 131.5, 130.2, 123.3, 122.3, 120.6, 113.9, 111.9, 67.7, 67.4, 62.9, 51.7, 42.0, 37.0, 31.7, 28.7, 28.4, 28.1, 25.9, 25.1, 25.0, 21.3, 15.7; **HRMS** (ESI$^+$) [M+Na]$^+$ calc'd for $C_{30}H_{42}NaO_6S$: 553.2594, found: 553.2607.

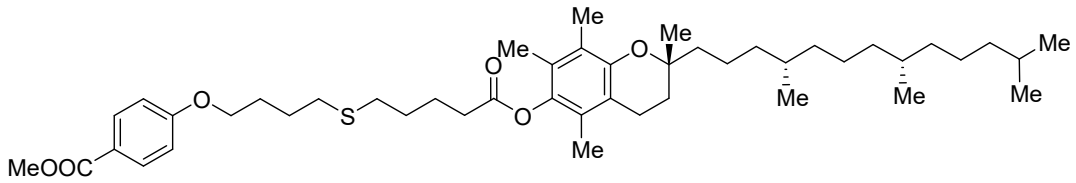


Methyl 4-(4-((3-(2-(1-(4-chlorobenzoyl)-5-methoxy-2-methyl-1H-indol-3-yl)aceto-xy)propyl)thio)butoxy)benzoate 3aam: Prepared according to **General Method D** (Eluent: 200:1 to 5:1 petroleum ether: ethyl acetate) and the title compound was isolated as a colorless liquid (236.6 mg, 0.371 mmol, 74.1% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.95 (2H, d, J = 8.8 Hz), 7.63 (2H, d, J = 8.4 Hz), 7.44 (2H, d, J = 8.5 Hz), 6.96 (1H, d, J = 2.5 Hz), 6.87 (3H, d, J = 9.0 Hz), 6.66 (1H, d, J = 9.0 Hz), 4.20 (2H, t, J = 6.2 Hz), 3.98 (2H, t, J = 4.8 Hz), 3.86 (3H, s), 3.82 (3H, s), 3.66 (2H, s), 2.51 – 2.47 (4H, m), 2.37 (3H, s), 1.92 – 1.82 (4H, m), 1.74 – 1.67 (2H, m); **^{13}C**

NMR (101 MHz, $CDCl_3$) δ 170.7, 168.1, 166.7, 162.6, 156.0, 139.1, 135.8, 133.8, 131.5, 131.1, 130.7, 130.5, 129.0, 122.3, 115.9, 113.9, 112.5, 111.5, 101.2, 67.4, 63.5, 55.6, 51.8, 31.7, 30.3, 28.6, 28.3, 28.1, 25.9, 13.3; **HRMS** (ESI^+) $[M+Na]^+$ calc'd for $C_{34}H_{36}ClNNaO_7S$: 316.0226, found: 316.0214.



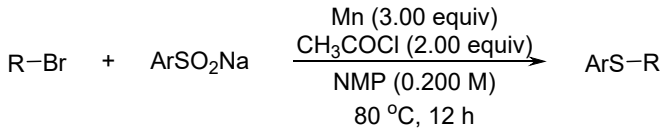
Methyl 4-(4-((6-(((13*S*)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[*a*]phenanthren-3-yl)oxy)-6-oxohexyl)thio)butoxy)benzoate 3aan: Prepared according to **General Method D** (Eluent: 200:1 to 5:1 petroleum ether: ethyl acetate) and the title compound was isolated as a white solid (226.3 mg, 0.382 mmol, 76.4% yield). **M.p.** = 81.0 – 81.6 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.97 (2H, d, J = 8.4 Hz), 7.27 (1H, d, J = 8.7 Hz), 6.89 (2H, d, J = 8.4 Hz), 6.84 (1H, d, J = 7.7 Hz), 6.80 (1H, s), 4.01 (2H, t, J = 6.2 Hz), 3.86 (3H, s), 2.91 – 2.88 (2H, m), 2.61 – 2.53 (6H, m), 2.39 – 2.32 (1H, m), 2.31 – 2.22 (1H, m), 2.18 – 1.67 (13H, m), 1.63 – 1.37 (6H, m), 0.89 (3H, s); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 172.0, 166.7, 162.7, 148.5, 137.9, 137.3, 131.5, 126.3, 122.4, 121.5, 118.7, 114.0, 67.5, 51.8, 50.3, 47.8, 44.0, 37.9, 35.8, 33.8, 31.7, 31.6, 31.5, 29.3, 28.9, 28.2, 26.3, 26.0, 25.7, 24.1, 21.5, 13.8 (one carbon was missing due to overlap); **HRMS** (ESI^+) $[M+Na]^+$ calc'd for $C_{35}H_{44}NaO_6S$: 615.2751, found: 615.2748.



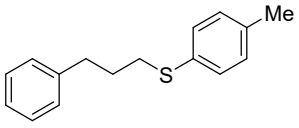
Methyl 4-(4-((5-oxo-5-(((*R*)-2,5,7,8-tetramethyl-2-((4*S*,8*S*)-4,8,12-trimethyltridecyl)chroman-6-yl)oxy)pentyl)thio)butoxy)benzoate 3aao: Prepared according to **General Method D** (Eluent: 200:1 to 5:1 petroleum ether: ethyl acetate) and the title compound was isolated as a colorless liquid (256.8 mg, 0.341 mmol, 68.2% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.97 (2H, d, J = 8.9 Hz), 6.88 (2H, d, J = 8.8 Hz), 4.01

(2H, t, J = 6.2 Hz), 3.87 (3H, s), 2.64 – 2.55 (8H, m), 2.09 (3H, s), 2.00 (3H, s), 1.96 (3H, s), 1.93 – 1.87 (4H, m), 1.82 – 1.70 (6H, m), 1.57 – 1.49 (3H, m), 1.45 – 1.34 (4H, m), 1.32 – 1.18 (11H, m), 1.16 – 1.10 (3H, m), 1.09 – 1.01 (3H, m), 0.87 – 0.84 (12H, m); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 172.0, 166.8, 162.8, 149.4, 140.5, 131.6, 126.6, 124.9, 123.0, 122.5, 117.4, 114.1, 75.1, 67.6, 51.8, 39.4, 37.5, 37.5, 37.3, 33.6, 32.8, 32.7, 31.8, 31.7, 31.1, 29.3, 28.3, 28.0, 26.1, 24.8, 24.5, 24.3, 22.8, 22.7, 21.1, 20.6, 19.8, 19.7, 13.1, 12.2, 11.9; **HRMS** (ESI^+) $[M+Na]^+$ calc'd for $C_{46}H_{72}NaO_6S$: 775.4942, found: 775.4934.

4. General Method E:

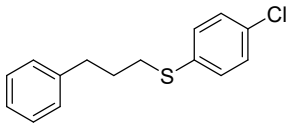


A 120 °C oven-dried 25-mL glass schlenck, equipped with a stirring bar, was charged with manganese (82.4 mg, 1.50 mmol, 3.00 equiv) and aryl sodium benzene sulfonate (1.00 mmol, 2.00 equiv). The mixture was evacuated and backfilled with nitrogen for three times. Then alkyl bromide (0.500 mmol, 1.00 equiv), acetyl chloride (78.5 mg, 1.00 mmol, 2.00 equiv) and dry NMP (2.50 mL) was added under N_2 and the mixture was allowed to stir for 12 h at 80 °C. After cooling to room temperature, the mixture was diluted with saturated NaCl aqueous solution (15.0 mL) and ethyl acetate (15.0 mL). The mixture was filtered through a celite pad and the organic layers were separated. The aqueous layer was diluted with H_2O (25.0 mL) and extracted with ethyl acetate (25.0 mL x 3). The combined organic layers were washed with H_2O (25.0 mL x 5), dried over Na_2SO_4 and filtered. The solvent was removed by rotary evaporation and the residue was purified by flash silica gel chromatography.

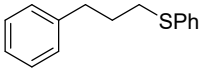


(3-Phenylpropyl)(*p*-tolyl)sulfane 3aap: Prepared according to **General Method E** (Eluent: 200:1 to 100:1 petroleum ether: ethyl acetate) and the title compound was isolated as a yellow liquid (73.5 mg, 0.303 mmol, 60.6% yield). **^{1}H NMR** (400 MHz,

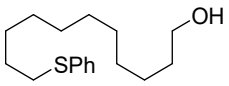
$CDCl_3$) δ 7.27 – 7.20 (4H, m), 7.18 – 7.13 (3H, m), 7.06 (2H, d, J = 7.9 Hz), 2.85 (2H, t, J = 7.3 Hz), 2.72 (2H, t, J = 7.5 Hz), 2.29 (3H, s), 1.95 – 1.88 (2H, m); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 141.5, 136.1, 132.8, 130.1, 129.7, 128.6, 128.5, 126.0, 34.7, 33.7, 30.8, 21.1. Spectra were consistent with literature data[12].



(4-Chlorophenyl)(3-phenylpropyl)sulfane 3aaq: Prepared according to **General Method E** (Eluent: 200:1 to 100:1 petroleum ether: ethyl acetate) and the title compound was isolated as a colorless liquid (61.0 mg, 0.232 mmol, 46.4% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.29 – 7.25 (2H, m), 7.23 – 7.18 (5H, m), 7.15 (2H, d, J = 6.9 Hz), 2.90 – 2.83 (2H, t, J = 7.2 Hz), 2.73 (2H, t, J = 7.5 Hz), 1.97 – 1.89 (2H, m); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 141.2, 135.2, 131.8, 130.5, 129.1, 128.6, 128.5, 126.2, 34.7, 33.1, 30.6. Spectra were consistent with literature data[13].

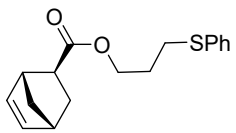


Phenyl(3-phenylpropyl)sulfane 3aar: Prepared according to **General Method E** (Eluent: 200:1 to 100:1 petroleum ether: ethyl acetate) and the title compound was isolated as a colorless liquid (93.0 mg, 0.407 mmol, 81.4% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 77.30 – 7.22 (6H, m), 7.19 – 7.12 (4H, m), 2.90 (2H, t, J = 7.2 Hz), 2.73 (2H, t, J = 7.5 Hz), 1.95 (2H, m); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 141.4, 136.6, 129.1, 128.9, 128.6, 128.5, 126.1, 125.9, 34.9, 32.9, 30.7. Spectra were consistent with literature data[1].

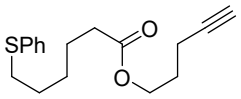


11-(Phenylthio)undecan-1-ol 3ai: Prepared according to **General Method E** (Eluent: 200:1 to 100:1 petroleum ether: ethyl acetate) and the title compound was isolated as a white solid (119.6 mg, 0.426 mmol, 85.3% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.34 (2H, d, J = 7.3 Hz), 7.31 – 7.29 (2H, m), 7.19 – 7.16 (1H, m), 3.64 (2H, t, J = 6.7 Hz), 2.93 (2H, t, J = 7.4 Hz), 1.88 (1H, s), 1.70 – 1.63 (2H, m), 1.61 – 1.54 (2H, m), 1.45 – 1.40 (2H, m), 1.37 – 1.29 (12H, m); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 137.1,

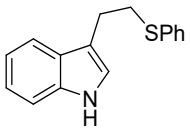
128.9, 128.8, 125.7, 63.0, 33.6, 32.8, 29.6, 29.6, 29.5, 29.5, 29.2, 29.2, 28.9, 25.8; **HRMS** (ESI^+) $[M+Na]^+$ calc'd for $C_{17}H_{28}NaOS$: 303.1753, found: 303.1751.



3-(Phenylthio)propyl (1*R*,2*S*,4*R*)-bicyclo[2.2.1]hept-5-ene-2-carboxylate 3aaj: Prepared according to **General Method E** (Eluent: 200:1 to 20:1 petroleum ether: ethyl acetate) and the title compound was isolated as a colorless liquid (111.9 mg, 0.388 mmol, 77.6% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.37 (2H, d, J = 6.9 Hz), 7.33 – 7.29 (2H, m), 7.23 – 7.18 (1H, m), 6.22 – 6.20 (1H, m), 5.95 – 5.92 (1H, m), 4.15 (2H, td, J = 6.2, 2.0 Hz), 3.22 (1H, s), 3.00 (2H, t, J = 5.9 Hz), 2.98 – 2.95 (1H, m), 2.92 (1H, s), 1.99 – 1.94 (2H, m), 1.92 – 1.89 (1H, m), 1.47 – 1.44 (2H, m), 1.29 (1H, d, J = 7.6 Hz); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.6, 137.8, 136.0, 132.3, 129.3, 128.9, 126.1, 62.5, 49.6, 45.7, 43.3, 42.5, 30.2, 29.2, 28.4. Spectra were consistent with literature data[1].

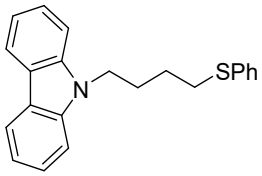


Pent-4-yn-1-yl 6-(phenylthio)hexanoate 3ak: Prepared according to **General Method E** (Eluent: 200:1 to 100:1 petroleum ether: ethyl acetate) and the title compound was isolated as a colorless liquid (120.2 mg, 0.414 mmol, 82.8% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.32 – 7.20 (2H, m), 7.28 – 7.25 (2H, m), 7.18 – 7.14 (1H, m), 4.16 (2H, t, J = 6.3 Hz), 2.91 (2H, t, J = 7.3 Hz), 2.31 – 2.25 (4H, m), 1.97 (1H, t, J = 2.7 Hz), 1.87 – 1.81 (2H, m), 1.69 – 1.59 (4H, m), 1.49 – 1.41 (2H, m); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.5, 136.7, 129.0, 128.9, 125.8, 83.0, 69.1, 62.8, 34.1, 33.4, 28.8, 28.2, 27.5, 24.5, 15.2; **HRMS** (ESI^+) $[M+H]^+$ calc'd for $C_{17}H_{23}O_2S$: 291.1413, found: 291.1415.



3-(2-(Phenylthio)ethyl)-1*H*-indole 3an: Prepared according to **General Method E** (Eluent: 200:1 to 20:1 petroleum ether: ethyl acetate) and the title compound was

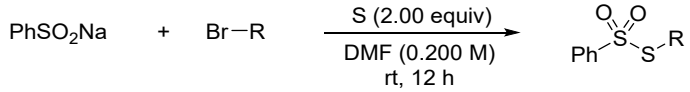
isolated as a white solid (115.6 mg, 0.456 mmol, 91.3% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.85 (1H, s), 7.54 (1H, d, J = 7.8 Hz), 7.36 (2H, d, J = 7.2 Hz), 7.31 – 7.26 (3H, m), 7.20 – 7.15 (2H, m), 7.13 – 7.09 (1H, m), 6.97 (1H, s), 3.24 (2H, t, J = 7.3 Hz), 3.08 (2H, t, J = 7.7 Hz); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 136.7, 136.3, 129.2, 129.0, 127.2, 126.0, 122.2, 121.9, 119.5, 118.7, 114.7, 111.3, 34.3, 25.4. Spectra were consistent with literature data[1].



9-(4-(Phenylthio)butyl)-9*H*-carbazole 3aq: Prepared according to **General Method E** (Eluent: 200:1 to 20:1 petroleum ether: ethyl acetate) and the title compound was isolated as a white solid (135.6 mg, 0.409 mmol, 81.8% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.06 (2H, d, J = 7.7 Hz), 7.43 – 7.39 (2H, m), 7.30 (2H, d, J = 8.2 Hz), 7.23 – 7.17 (6H, m), 7.14 – 7.10 (1H, m), 4.19 (2H, t, J = 7.1 Hz), 2.80 (2H, t, J = 7.1 Hz), 1.97 – 1.90 (2H, m), 1.66 – 1.58 (2H, m); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 140.4, 136.3, 129.5, 129.0, 126.1, 125.7, 122.9, 120.5, 118.9, 108.7, 42.5, 33.6, 28.0, 26.7. Spectra were consistent with literature data[1].

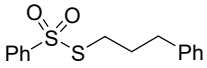
V. Synthetic applications of current method

1. <u>General Method F:</u> Modified synthesis of alkyl substiuted thiosulfonates from S powder.

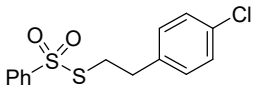


An oven-dried 25-mL glass schlenck,s equipped with a stirring bar, was charged with *S* powder (64.1 mg, 2.00 mmol, 2.00 equiv) and sodium benzenesulfinate (32.8 mg, 2.00 mmol, 2.00 equiv). The mixture was evacuated and backfilled with

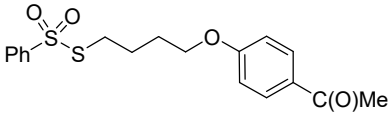
nitrogen for three times. Then the dry DMF (5.00 mL) and alkyl bromide (1.00 mmol, 1.00 equiv) was added under N_2 atmosphere. The mixture was allowed to stir at room temperature for 12 h. The mixture was poured into water (25.0 mL) and extracted with ethyl acetate (25.0 mL x 3). The combined organic layers were washed with saturated NaCl aqueous solution (25.0 mL x 5), dried over Na_2SO_4 and filtered. The solvent was removed by rotary evaporation and the residue was purified by flash silica gel chromatography.



***S*-(3-phenylpropyl) benzenesulfonothioate 2a:** Prepared according to **General Method F** (Eluent: 200:1 to 20:1 petroleum ether: ethyl acetate) and the title compound was isolated as a colorless liquid (187.6 mg, 0.642 mmol, 64.2% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.85 (2H, d, J = 7.2 Hz), 7.60 – 7.56 (1H, m), 7.50 – 7.46 (2H, m), 7.25 – 7.20 (2H, m), 7.18 – 7.14 (1H, m), 7.03 (2H, d, J = 6.8 Hz), 2.93 (2H, t, J = 7.3 Hz), 2.58 (2H, t, J = 7.4 Hz), 1.93 – 1.86 (2H, m); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 144.5, 1402, 133.6 129.3, 128.4, 128.3, 126.8, 126.1, 35.2, 34.2, 30.1. Spectra were consistent with literature data[3].

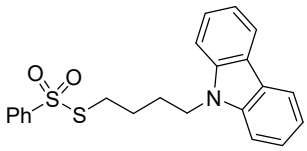


***S*-(4-chlorophenethyl) benzenesulfonothioate 2g:** Prepared according to **General Method F** (Eluent: 200:1 to 20:1 petroleum ether: ethyl acetate) and the title compound was isolated as a colorless liquid (214.1 mg, 0.684 mmol, 68.4% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.91 (2H, d, J = 7.2 Hz), 7.65 – 7.61 (1H, m), 7.57 – 7.53 (2H, m), 7.20 (2H, d, J = 8.4 Hz), 7.00 (2H, d, J = 8.4 Hz), 3.20 (2H, t, J = 7.5 Hz), 2.87 (2H, t, J = 7.5 Hz); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 144.6, 137.0, 133.8, 132.5, 129.9, 129.4, 128.7, 126.8, 37.0, 34.3. Spectra were consistent with literature data[3].



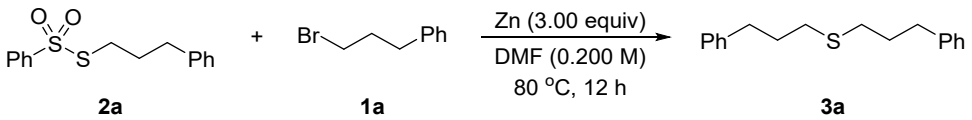
***S*-(4-(4-acetylphenoxy)butyl) benzenesulfonothioate 2e:** Prepared according to **General Method F** (Eluent: 200:1 to 10:1 petroleum ether: ethyl acetate) and the title

compound was isolated as a colorless liquid (307.2 mg, 0.843 mmol, 84.3% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.85 – 7.82 (4H, m), 7.57 – 7.53 (1H, m), 7.48 – 7.44 (2H, m), 6.78 (2H, d, J = 8.8 Hz), 3.86 (2H, t, J = 5.3 Hz), 3.00 (2H, t, J = 6.8 Hz), 2.45 (3H, s), 1.76 – 1.70 (4H, m); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 196.5, 162.4, 144.4, 133.6, 130.4, 130.0, 129.2, 126.6, 113.9, 67.0, 35.5, 27.5, 26.2, 25.3. Spectra were consistent with literature data[3].



***S*-(4-(9*H*-carbazol-9-yl)butyl) benzenesulfonothioate 2n:** Prepared according to **General Method F** (Eluent: 200:1 to 10:1 petroleum ether: ethyl acetate) and the title compound was isolated as a colorless liquid (302.0 mg, 0.764 mmol, 76.4% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.18 (2H, d, J = 7.7 Hz), 7.89 (2H, d, J = 7.2 Hz), 7.55 – 7.49 (3H, m), 7.43 – 7.40 (2H, m), 7.36 – 7.31 (4H, m), 4.16 (2H, t, J = 6.8 Hz), 2.92 (2H, t, J = 7.1 Hz), 1.83 – 1.76 (2H, m), 1.60 – 1.52 (2H, m); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 144.5, 140.0, 133.5, 129.1, 126.6, 125.6, 122.6, 120.2, 118.9, 108.5, 41.9, 35.6, 27.6, 26.2. Spectra were consistent with literature data[3].

2. Synthesis of 3a on 10.0 mmol scale:

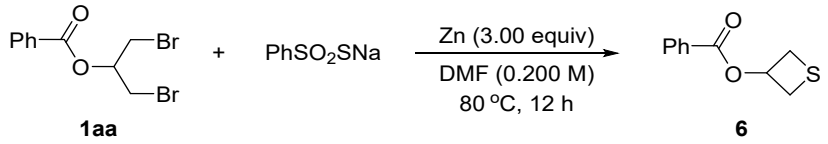


2a **1a** **3a**

An oven-dried 100-mL round-bottom flask, equipped with a stirring bar, was charged with zinc (1.96 g, 30.0 mmol, 3.00 equiv). The mixture was evacuated and backfilled with nitrogen for three times. Then the dry DMF (50.0 mL), *S*-(3-phenylpropyl) benzenesulfonothioate (5.85 g, 20.0 mmol, 2.00 equiv) and (3-bromopropyl)benzene (1.99 g, 10.0 mmol, 1.00 equiv) were added under N_2 atmosphere. The mixture was allowed to stir at 80 °C for 12 h. After cooling to room temperature, the mixture was diluted with water (50.0 mL) and ethyl acetate (25.0 mL). The mixture was filtered through a celite pad and the organic layers were

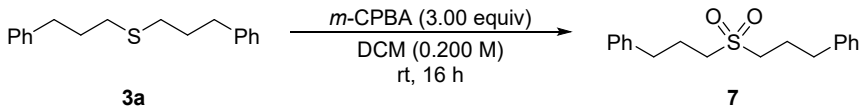
separated. The aqueous layer was extracted with ethyl acetate (25.0 mL x 3). The combined organic layers were washed with saturated NaCl aqueous solution (25.0 mL x 5), dried over Na_2SO_4 and filtered. The solvent was removed by rotary evaporation and the residue was purified by flash silica gel chromatography (Eluent: 200:1 to 100:1 petroleum ether: ethyl acetate). The product **3a** was isolated as a colorless liquid (2.09 g, 7.73 mmol, 77.3% yield). The spectral data match those previously reported[1].

3. Synthesis of (sulfonylbis(propane-3,1-diyl))dibenzene 6:



An oven-dried 25-mL glass schlenck, equipped with a stirring bar, was charged with zinc (98.1 mg, 1.50 mmol, 3.00 equiv) and sodium benzenesulfonothioate (98.1 mg, 0.500 mmol, 1.00 equiv). The mixture was evacuated and backfilled with nitrogen for three times. Then dry DMF (2.50 mL) and 1,3-dibromopropan-2-yl benzoate (160.9 mg, 0.500 mmol, 1.00 equiv) were added under N_2 atmosphere. The mixture was allowed to stir at 80 °C for 12 h. After cooling to room temperature, the mixture was diluted with water (25.0 mL) and extracted with ethyl acetate (25.0 mL x 3). The combined organic layers were washed with saturated NaCl aqueous solution (25.0 mL x 5), dried over Na_2SO_4 and filtered. The solvent was removed by rotary evaporation and the residue was purified by flash silica gel chromatography (Eluent: 200:1 to 20:1 petroleum ether: ethyl acetate). The product **6** was isolated as a colorless liquid (54.3 mg, 0.280 mmol, 56.0% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.03 (2H, d, J = 6.9 Hz), 7.60 – 7.56 (1H, m), 7.47 – 7.42 (2H, m), 5.90 – 5.82 (1H, m), 3.65 – 3.61 (2H, m), 3.44 – 3.40 (2H, dd, J = 9.8, 7.8 Hz); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.2, 133.4, 129.8, 129.6, 128.5, 68.7, 35.2. The spectral data match those previously reported[8].

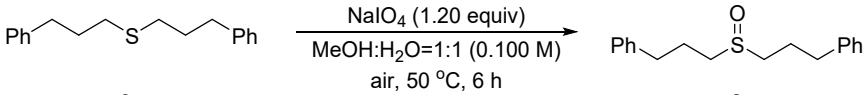
4. Synthesis of (sulfonylbis(propane-3,1-diyl))dibenzene 7



3a **7**

An oven-dried 25-mL glass schlenck, equipped with a stirring bar, was charged with *m*-CPBA (304.5 mg, 1.50 mmol, 3.00 equiv) at 0 °C. The mixture was evacuated and backfilled with nitrogen for three times. Then the dry dichlormethane (2.50 mL) and bis(3-phenylpropyl)sulfane (135.2 g, 0.500 mmol, 1.00 equiv) was added under N_2 atmosphere. Then, the mixture was stirred at room temperature for 16 h. After the completion of the reaction, the mixture was poured into saturated sodium carbonate to quench, and extracted with dichloromethane (25.0 mL x 3). The combined organic layers were washed with H_2O (25.0 mL x 3), dried over Na_2SO_4 and filtered. The solvent was removed by rotary evaporation and the residue was purified by flash silica gel chromatography (Eluent: 100:1 to 3:1 petroleum ether: ethyl acetate) to provide the desired product **7** as a white solid (146.2 mg, 0.483 mmol, 96.6% yield).**^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.29 – 7.25 (4H, m), 7.21 – 7.17 (2H, m), 7.13 (4H, d, J = 7.1 Hz), 2.90 – 2.80 (4H, t, J = 8.0 Hz), 2.71 (4H, t, J = 7.4 Hz), 2.12 – 2.04 (4H, m); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 139.8, 128.6, 128.4, 126.4, 51.7, 34.1, 23.3. The spectral data match those previously reported[14].

5. Synthesis of (sulfinylbis(propane-3,1-diyl))dibenzene 8



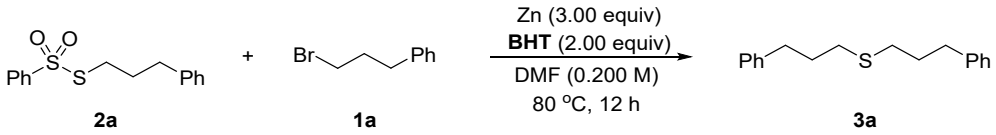
3a **8**

An oven-dried 25-mL glass schlenck, equipped with a stirring bar, was charged with bis(3-phenylpropyl)sulfane (135.2 g, 0.500 mmol, 1.00 equiv), $NaIO_4$ (128.4 mg, 0.600 mmol, 1.20 equiv) and MeOH:H_2O = 1:1 (5.00 mL) under air atmosphere. The mixture was stirred at 50 °C for 6 h. The mixture was diluted with H_2O (25.0 mL) and extracted with ethyl acetate (30.0 mL × 3). The combined organic layers were washed with H_2O (25.0 mL), dried over Na_2SO_4 and filtered. The solvent was removed by rotary evaporation and the residue was purified by flash silica gel chromatography (Eluent: 100:1 to 1:1 petroleum ether: ethyl acetate) to provide the desired product **8** as a white solid (93.1 mg, 0.325 mmol, 65.0% isolated yield).**^{1}H NMR** (400 MHz,

$CDCl_3$) δ 7.30 – 7.27 (4H, m), 7.21 (2H, d, J = 7.2 Hz), 7.16 (4H, d, J = 6.9 Hz), 2.78 – 2.72 (4H, m), 2.69 – 2.53 (4H, m), 2.12 – 2.04 (4H, m); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 140.4, 128.6, 128.5, 126.3, 51.6, 34.7, 24.2. The spectral data match those previously reported[15].

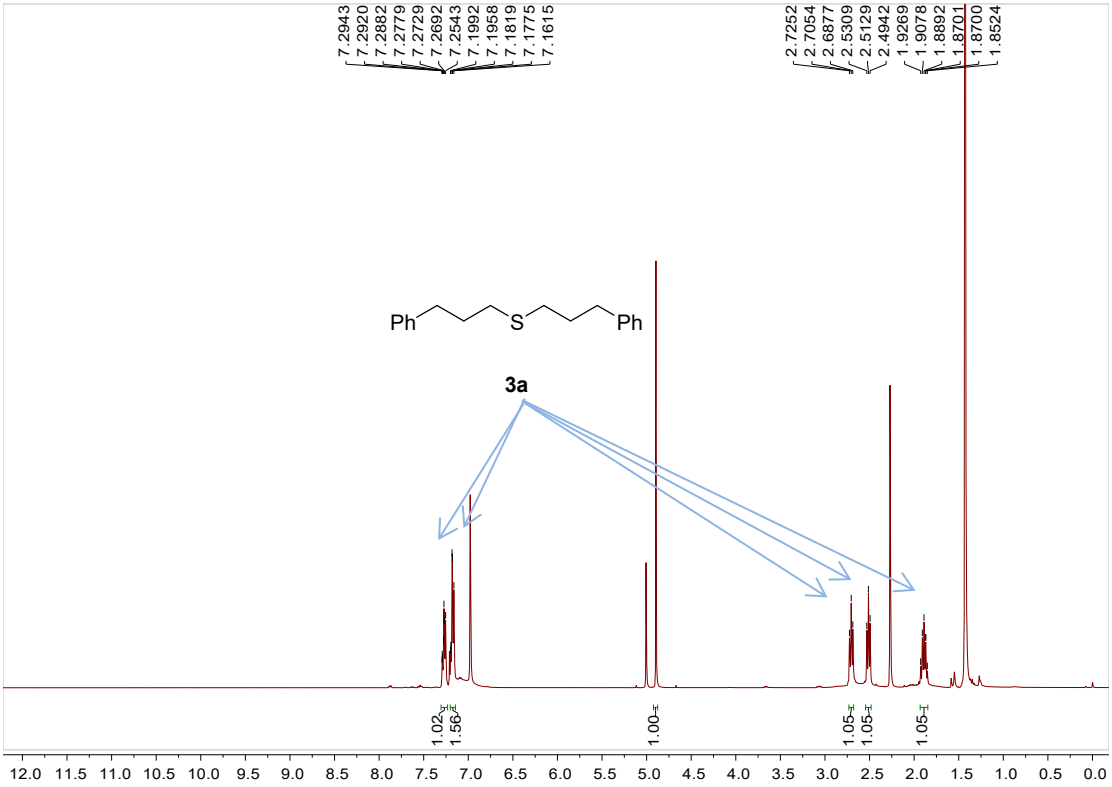
VI. Mechanistic studies

1. Radical trapping experiments employing BHT and 9,10-dihydroanthracene

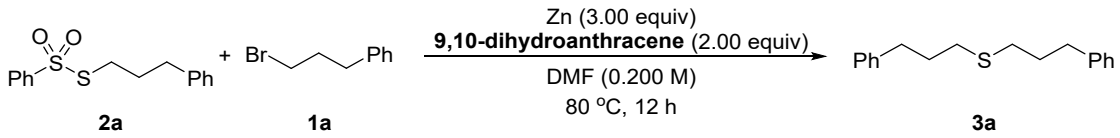


2a **1a** **3a**

An oven-dried 25-mL glass schlenck, equipped with a stirring bar, was charged with zinc (19.6 mg, 0.300 mmol, 3.00 equiv) and BHT (44.1 mg, 0.200 mmol, 2.00 equiv). The mixture was evacuated and backfilled with nitrogen for three times. Then the dry DMF (0.500 mL), *S*-(3-phenylpropyl) benzenesulfonothioate **2a** (58.4 mg, 0.200 mmol, 2.00 equiv) and (3-bromopropyl)benzene **1a** (19.9 mg, 0.100 mmol, 1.00 equiv) were added under N_2 atmosphere. The mixture was allowed to stir at 80 °C for 12 h. After cooling to room temperature, the mixture was diluted with saturated NaCl aqueous solution (15.0 mL) and ethyl acetate (15.0 mL). The mixture was filtered through a celite pad and the organic layers were separated. The aqueous layer was extracted with ethyl acetate (25.0 mL x 3). The combined organic layers were washed with saturated NaCl aqueous solution (10.0 mL x 5), dried over Na_2SO_4 and filtered. The solvent was removed by rotary evaporation, the crude mixture was subjected to ^{1}H NMR spectroscopy in the presence of CH_2Br_2 (34.8 mg, 0.200 mmol). Crude ^{1}H NMR yield of **3a** is >99.0%.

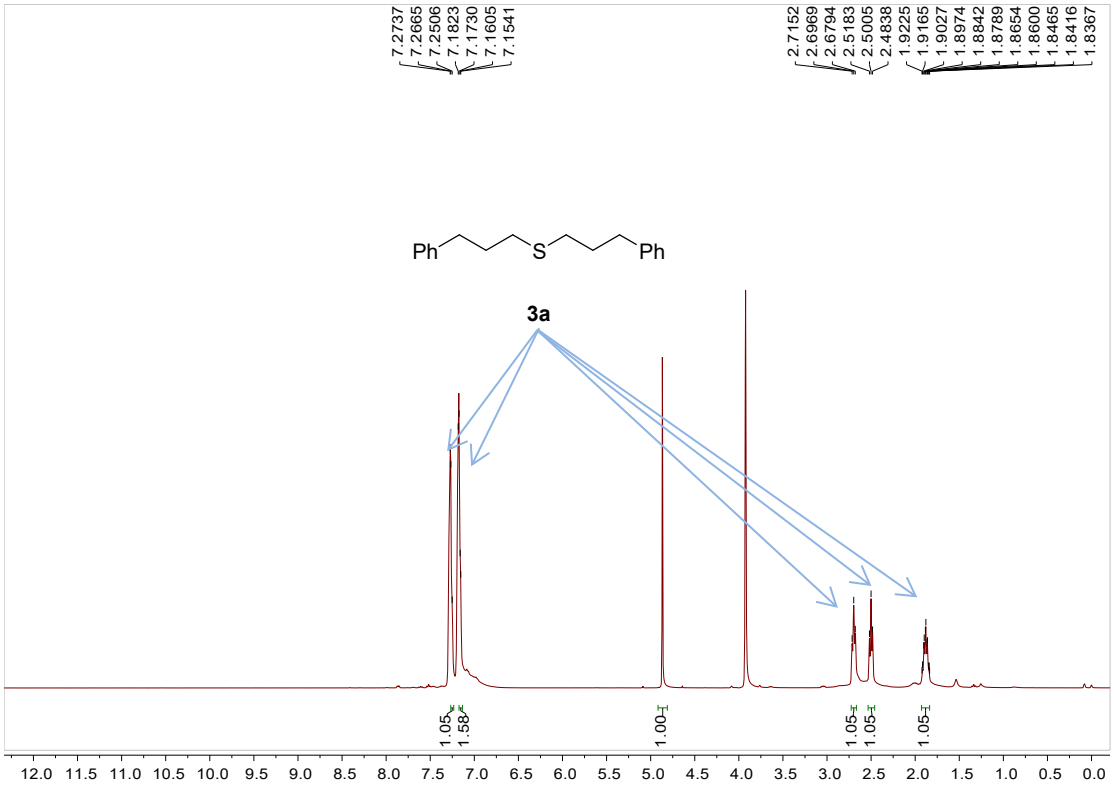


Supplementary Fig. S1. BHT as the additive in the reductive coupling.



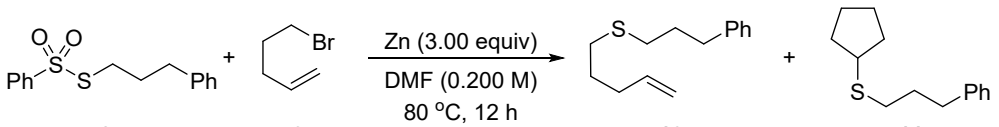
An oven-dried 25-mL glass schlenck, equipped with a stirring bar, was charged with zinc (19.6 mg, 0.300 mmol, 3.00 equiv) and 9,10-dihydroanthracene (36.0 mg, 0.200 mmol, 2.00 equiv). The mixture was evacuated and backfilled with nitrogen for three times. Then dry DMF (0.500 mL), *S*-(3-phenylpropyl) benzenesulfonothioate **2a** (58.4 mg, 0.200 mmol, 2.00 equiv) and (3-bromopropyl)benzene **1a** (19.9 g, 0.100 mmol, 1.00 equiv) were added under N_2 atmosphere. The mixture was allowed to stir at 80 °C for 12 h. After cooling to room temperature, the mixture was diluted with saturated NaCl aqueous solution (15.0 mL) and ethyl acetate (15.0 mL). The mixture was filtered through a celite pad and the organic layers were separated. The aqueous layer was extracted with ethyl acetate (25.0 mL x 3). The combined organic layers were washed with saturated NaCl aqueous solution (10.0 mL x 5), dried over Na_2SO_4 and filtered. The solvent was removed by rotary evaporation, the crude mixture was subjected to ^1H NMR spectroscopy in the presence of CH_2Br_2 (34.8 mg,

0.200 mmol). Crude ^{1}H NMR yield of **3a** is >99.0%.



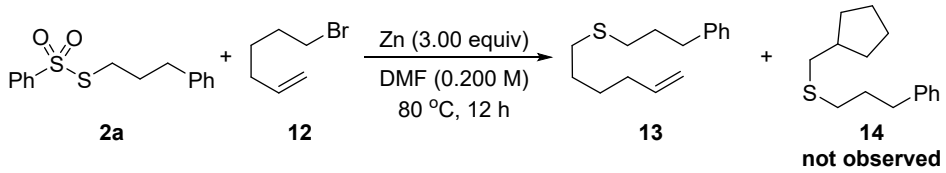
Supplementary Fig. S2. 9,10-dihydroanthracene as the additive in the reductive coupling.

2. Radical ring-closed experiment employing 5-bromopent-1-ene



An oven-dried 25-mL glass schlenck, equipped with a stirring bar, was charged with zinc (98.1 mg, 1.50 mmol, 3.00 equiv). The mixture was evacuated and backfilled with nitrogen for three times. Then the dry DMF (2.50 mL), *S*-(3-phenylpropyl) benzenesulfonothioate **2a** (292.4 mg, 1.00 mmol, 2.00 equiv) and 5-bromopent-1-ene **9** (74.5 mg, 0.500 mmol, 1.00 equiv) were added under N_2 atmosphere. The mixture was allowed to stir at 80 °C for 12 h. After cooling to room temperature, the mixture was diluted with saturated NaCl aqueous solution (15.0 mL) and ethyl acetate (15.0 mL). The mixture was filtered through a celite pad and the organic layers were separated. The aqueous layer was extracted with ethyl acetate (25.0 mL x 3). The combined organic layers were washed with saturated NaCl

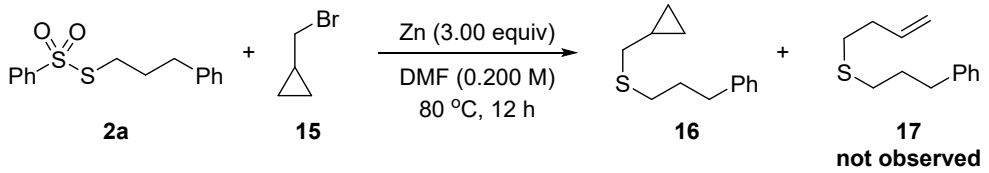
aqueous solution (25.0 mL x 5), dried over Na_2SO_4 and filtered. The solvent was removed by rotary evaporation and the residue was purified by flash silica gel chromatography (Eluent: 200:1 to 100:1 petroleum ether: ethyl acetate) to provide the desired product **10** as a colorless liquid (84.5 mg, 0.383 mmol, 76.6% yield). However, compound **11** was not observed. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.30 – 7.26 (2H, m), 7.20 – 7.16 (3H, m), 5.83 – 5.73 (1H, m), 5.05 – 4.96 (2H, m), 2.71 (2H, t, J = 7.6 Hz), 2.53 – 2.49 (4H, m), 2.17 – 2.11 (2H, m), 1.94 – 1.86 (2H, m), 1.70 – 1.62 (2H, m); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 141.7, 137.9, 128.6, 128.5, 126.0, 115.3, 34.9, 32.9, 31.5, 31.3, 28.9 (one carbon was missing due to the overlap); **HRMS** (ESI^+) $[M+H]^+$ calc'd for $C_{14}H_{20}S$: 221.1350, found: 221.1350.



2a **12** **13** **14** **not observed**

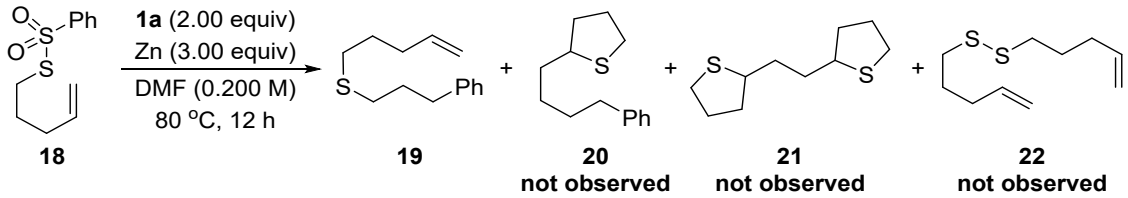
An oven-dried 25-mL glass schlenck, equipped with a stirring bar, was charged with zinc (98.1 mg, 1.50 mmol, 3.00 equiv). The mixture was evacuated and backfilled with nitrogen for three times. Then dry DMF (2.50 mL), *S*-(3-phenylpropyl) benzenesulfonothioate **2a** (292.4 mg, 1.00 mmol, 2.00 equiv) and 6-bromohex-1-ene **12** (81.5 mg, 0.500 mmol, 1.00 equiv) were added under N_2 atmosphere. The mixture was allowed to stir at 80 °C for 12 h. After cooling to room temperature, the mixture was diluted with saturated NaCl aqueous solution (15.0 mL) and ethyl acetate (15.0 mL). The mixture was filtered through a celite pad and the organic layers were separated. The aqueous layer was extracted with ethyl acetate (25.0 mL x 3). The combined organic layers were washed with saturated NaCl aqueous solution (25.0 mL x 5), dried over Na_2SO_4 and filtered. The solvent was removed by rotary evaporation and the residue was purified by flash silica gel chromatography (Eluent: 200:1 to 100:1 petroleum ether: ethyl acetate) to provide the desired product **13** as a colorless liquid (88.2 mg, 0.376 mmol, 75.2% yield). However, compound **14** was not observed. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.29 – 7.26 (2H, m), 7.20 – 7.16 (3H, m), 5.84 – 5.74 (1H, m), 5.03 – 4.93 (2H, m), 2.71 (2H, t, J = 7.6 Hz), 2.53 – 2.48 (4H, m), 2.08 –

2.02 (2H, m), 1.93 – 1.86 (2H, m), 1.62 – 1.56 (2H, m), 1.51 – 1.43 (2H, m); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 141.7, 138.6, 128.5, 128.4, 126.0, 114.7, 34.9, 33.4, 31.9, 31.5, 31.2, 29.2, 28.2; **HRMS** (ESI^+) $[M+H]^+$ calc'd for $C_{15}H_{22}S$: 235.1515, found: 235.1517.



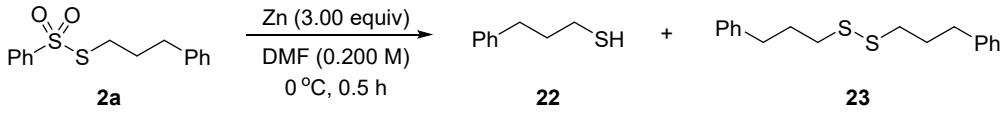
An oven-dried 25-mL glass schlenck, equipped with a stirring bar, was charged with zinc (98.1 mg, 1.50 mmol, 3.00 equiv). The mixture was evacuated and backfilled with nitrogen for three times. Then the dry DMF (2.50 mL), *S*-(3-phenylpropyl) benzenesulfonothioate **2a** (292.4 mg, 1.00 mmol, 2.00 equiv) and (bromomethyl)cyclopropane **15** (67.5 mg, 0.500 mmol, 1.00 equiv) were added under N_2 atmosphere. The mixture was allowed to stir at 80 °C for 12 h. After cooling to room temperature, the mixture was diluted with saturated NaCl aqueous solution (15.0 mL) and ethyl acetate (15.0 mL). The mixture was filtered through a celite pad and the organic layers were separated. The aqueous layer was extracted with ethyl acetate (25.0 mL x 3). The combined organic layers were washed with saturated NaCl aqueous solution (25.0 mL x 5), dried over Na_2SO_4 and filtered. The solvent was removed by rotary evaporation and the residue was purified by flash silica gel chromatography (Eluent: 200:1 to 100:1 petroleum ether: ethyl acetate) to provide the desired product as a colorless liquid (81.7 mg, 0.396 mmol, 79.2% isolated yield). However, compound **17** was not observed. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.30 – 7.26 (2H, m), 7.20 – 7.16 (3H, m), 2.72 (2H, t, J = 7.6 Hz), 2.59 (2H, t, J = 7.3 Hz), 2.44 (2H, d, J = 6.9 Hz), 1.95 – 1.88 (2H, m), 1.01 – 0.91 (1H, m), 0.57 – 0.52 (2H, m), 0.20 – 0.16 (2H, m); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 141.7, 128.5, 128.4, 125.9, 37.5, 35.0, 31.4, 31.4, 11.3, 5.4. Spectra were consistent with literature data[8].

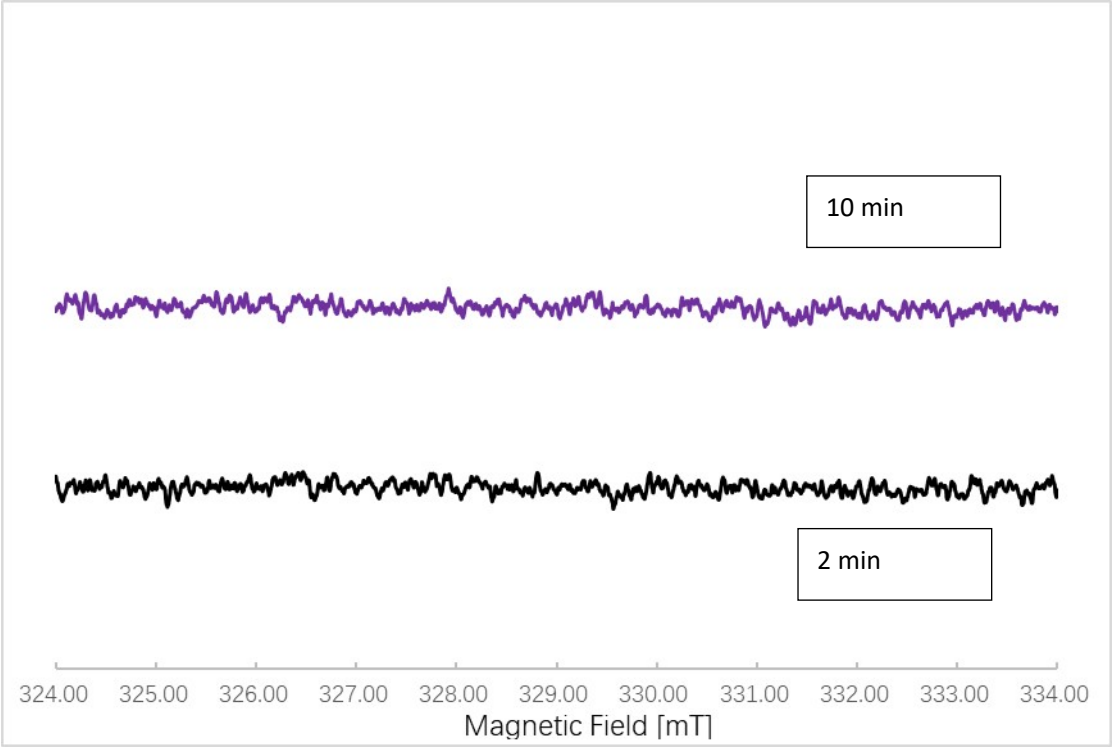
3. Radical ring-closed experiment employing *S*-(pent-4-en-1-yl) benzenesulfonothioate



An oven-dried 25-mL glass schlenck, equipped with a stirring bar, was charged with zinc (98.1 mg, 1.50 mmol, 3.00 equiv). The mixture was evacuated and backfilled with nitrogen for three times. Then dry DMF (2.50 mL), (3-bromopropyl)benzene **1a** (99.5 mg, 0.500 mmol, 1.00 equiv) and *S*-(pent-4-en-1-yl) benzenesulfonothioate **18** (242.4 mg, 1.00 mmol, 2.00 equiv) were added under N_2 atmosphere. The mixture was allowed to stir at 80 °C for 12 h. After cooling to room temperature, the mixture was diluted with saturated NaCl aqueous solution (15.0 mL) and ethyl acetate (15.0 mL). The mixture was filtered through a celite pad and the organic layers were separated. The aqueous layer was extracted with ethyl acetate (25.0 mL x 3). The combined organic layers were washed with saturated NaCl aqueous solution (25.0 mL x 5), dried over Na_2SO_4 and filtered. The solvent was removed by rotary evaporation and the residue was purified by flash silica gel chromatography (Eluent: 200:1 to 100:1 petroleum ether: ethyl acetate) to provide the desired product as a colorless liquid (89.4 mg, 0.405 mmol, 81.0% yield). However, compound **20**, compound **21** and compound **22** were not observed. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.29 – 7.25 (2H, m), 7.19 – 7.16 (3H, m), 5.82 – 5.72 (1H, m), 5.05 – 4.95 (2H, m), 2.71 (2H, t, J = 7.6 Hz), 2.52 – 2.48 (4H, m), 2.17 – 2.11 (2H, m), 1.93 – 1.86 (2H, m), 1.69 – 1.62 (2H, m); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 141.6, 137.9, 128.5, 128.4, 126.0, 115.2, 34.9, 32.9, 31.5, 31.5, 31.3, 28.9; **HRMS** (ESI^+) $[M+H]^+$ calc'd for $C_{14}H_{20}S$: 221.1350, found: 221.1358.

4. Electron paramagnetic resonance (EPR) study





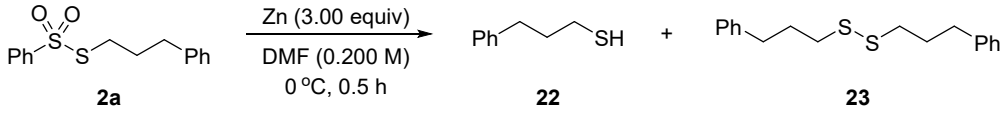
Supplementary Fig. S3. Electron paramagnetic resonance (EPR) study.

To gain more insight into the possible radical intermediates, we carried out paramagnetic resonance (EPR) studies (X band, 10.0 GHz) by using 5,5-dimethyl-pyrroline N-oxide (DMPO) as free radical spin-trapping agent (**Supplementary Fig. S3**). In equation 1, an oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar was charged with a mixture of **7a** (0.200 mmol), Zn (0.200 mmol), **2a** (0.1 mmol) followed by the addition of DMF (1.00 mL), the mixture was stirred for 5 min at RT, then 11.5 uL of DMPO (100 mM) was added to the mixture through syringe, after that, the mixture was stirred for 2 min, 20 uL of the mixture was transferred to a capillary tube, the tubes was charged into a EPR tube and then the mixture was measured. After the former mentioned mixture was stirred for 10 min, 20 uL of the mixture was transferred to a capillary tube, the tubes were charged into a EPR tube and then the mixture was measured again. Both no signal was found.

The EPR experiment was taken on a JEOL JES X320 EPR instrument. Sulfur-centered radical measurement conditions: Frequency 9.222 MHz; Power 1 mW; Center Field 329.0 mT; Sweep Width 10 mT, Modulation Width 0.1 mT; Amplitude 8×100; Sweep time 1 min; Time constant 0.1 s.

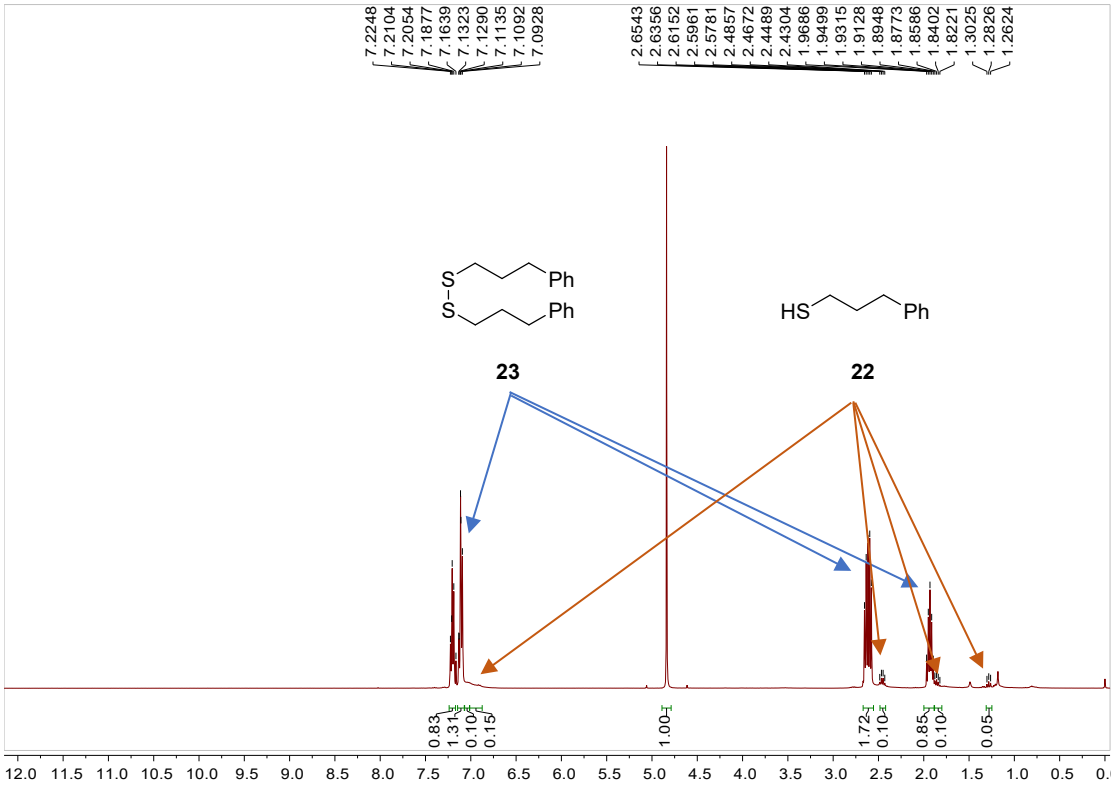
5. Control experiments in absence of alkyl bromide at different

temperature

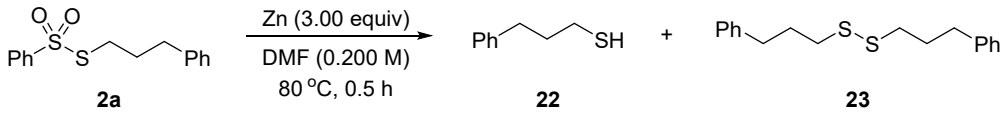


2a **22** **23**

An oven-dried 25-mL glass schlenck, equipped with a stirring bar, was charged with zinc (39.2 mg, 0.600 mmol, 3.00 equiv). The mixture was evacuated and backfilled with nitrogen for three times. Then dry DMF (0.500 mL), *S*-(3-phenylpropyl) benzenesulfonothioate **2a** (58.4 mg, 0.200 mmol, 2.00 equiv) were added under N_2 atmosphere. The mixture was allowed to stir at 0 °C for 0.5 h. The mixture was then diluted with saturated NaCl aqueous solution (15.0 mL) and ethyl acetate (15.0 mL). The mixture was filtered through a celite pad and the organic layers were separated. The aqueous layer was extracted with ethyl acetate (25.0 mL x 3). The combined organic layers were washed with saturated NaCl aqueous solution (10.0 mL x5), dried over Na_2SO_4 and filtered. The solvent was removed by rotary evaporation, the crude mixture was subjected to ^{1}H NMR spectroscopy in the presence of CH_2Br_2 (34.8 mg, 0.200 mmol). Crude ^{1}H NMR yield of **22** is 10.0%, and the ^{1}H NMR yield of **23** is 86.0%.

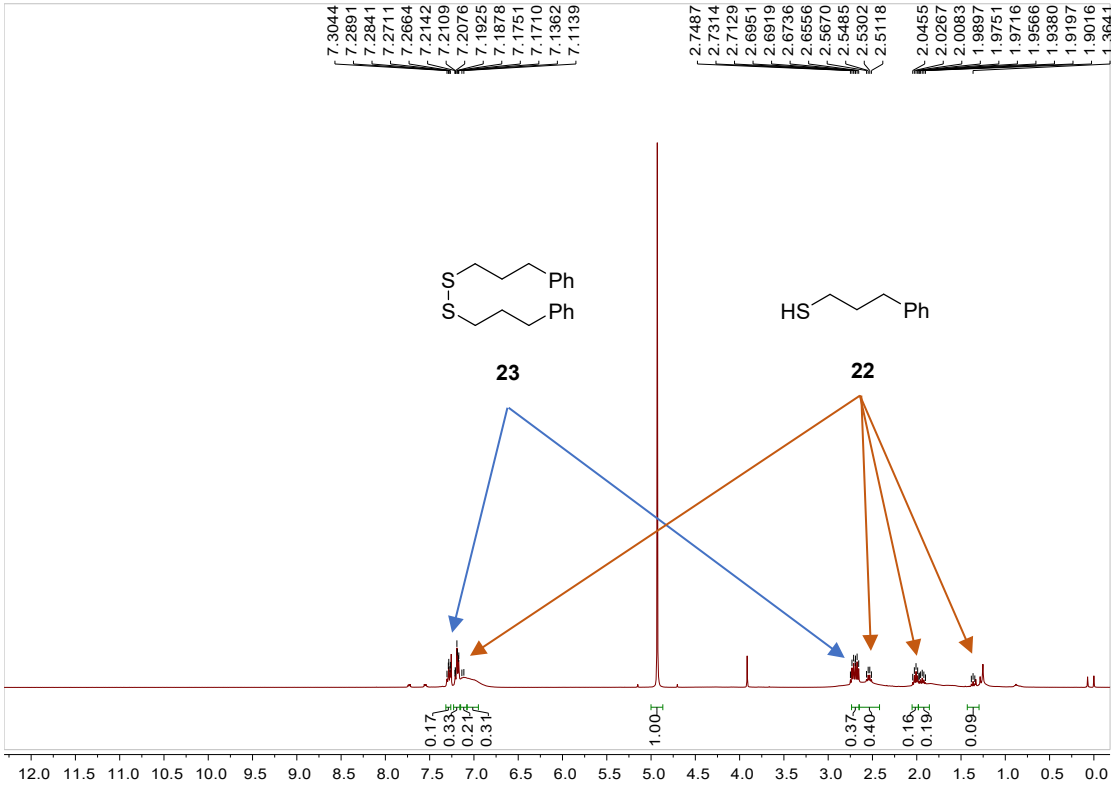


Supplementary Fig. S4. Detection of thiol employing 2a.

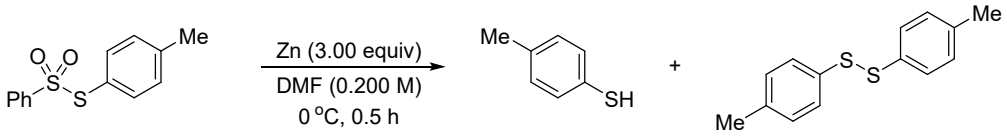


2a **22** **23**

An oven-dried 25-mL glass schlenck, equipped with a stirring bar, was charged with zinc (39.2 mg, 0.600 mmol, 3.00 equiv). The mixture was evacuated and backfilled with nitrogen for three times. Then dry DMF (0.500 mL), *S*-(3-phenylpropyl) benzenesulfonothioate **2a** (58.4 mg, 0.200 mmol, 2.00 equiv) wereadded under N_2 atmosphere. The mixture was allowed to stir at 80 °C for 0.5 h. The mixture was allowed to stir at 80 °C for 12 h. After cooling to room temperature, the mixture was diluted with saturated NaCl aqueous solution (15.0 mL) and ethyl acetate (15.0 mL). The mixture was filtered through a celite pad and the organic layers were separated. The aqueous layer was extracted with ethyl acetate (25.0 mL x 3). The combined organic layers were washed with saturated NaCl aqueous solution (10.0 mL x 5), dried over Na_2SO_4 and filtered. The solvent was removed by rotary evaporation, the crude mixture was subjected to ^{1}H NMR spectroscopy in the presence of CH_2Br_2 (34.8 mg, 0.200 mmol). Crude yield of **22** is 20.0% ^{1}H NMR yield, and the ^{1}H NMR yield of **23** is 17.0%.

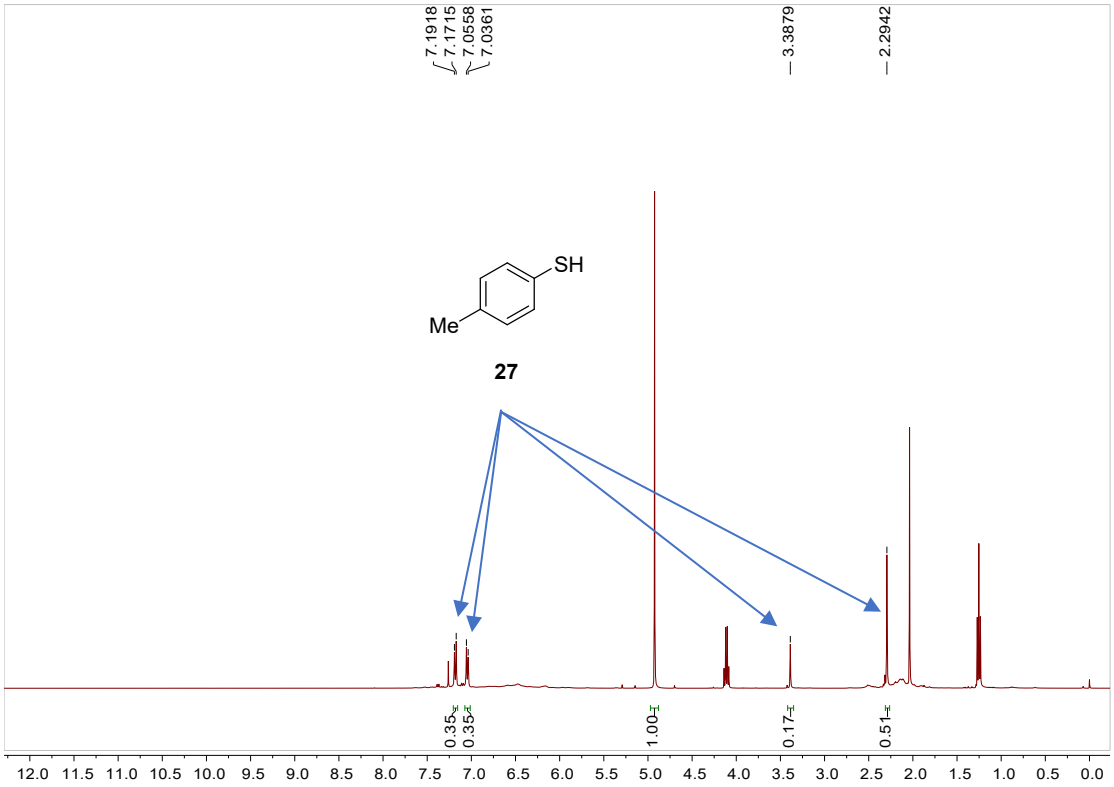


Supplementary Fig. S5. The detection of thiol employing reagent 2a.

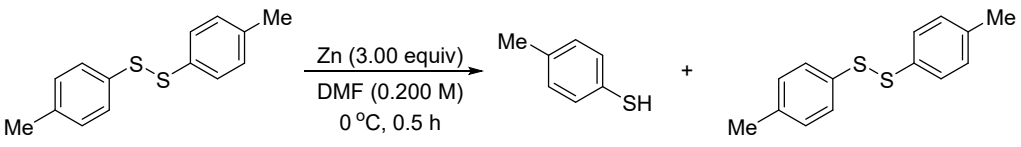


24 **26** **25**

An oven-dried 25-mL glass schlenck, equipped with a stirring bar, was charged with zinc (39.2 mg, 0.600 mmol, 3.00 equiv). The mixture was evacuated and backfilled with nitrogen for three times. Then the dry DMF (0.500 mL), *S*-(p-tolyl) benzenesulfonothioate **24** (52.9 mg, 0.200 mmol, 2.00 equiv) was added under N_2 atmosphere. The mixture was allowed to stir at 0 °C for 0.5 h. The mixture was then diluted with saturated NaCl aqueous solution (15.0 mL) and ethyl acetate (15.0 mL). The mixture was filtered through a celite pad and the organic layers were separated. The aqueous layer was extracted with ethyl acetate (25.0 mL x 3). The combined organic layers were washed with saturated NaCl aqueous solution (10.0 mL x 5), dried over Na_2SO_4 and filtered. The solvent was removed by rotary evaporation, the crude mixture was subjected to ^{1}H NMR spectroscopy in the presence of CH_2Br_2 (34.8 mg, 0.200 mmol). Crude ^{1}H NMR yield of **26** is 35.0%, and compound **25** was not observed.

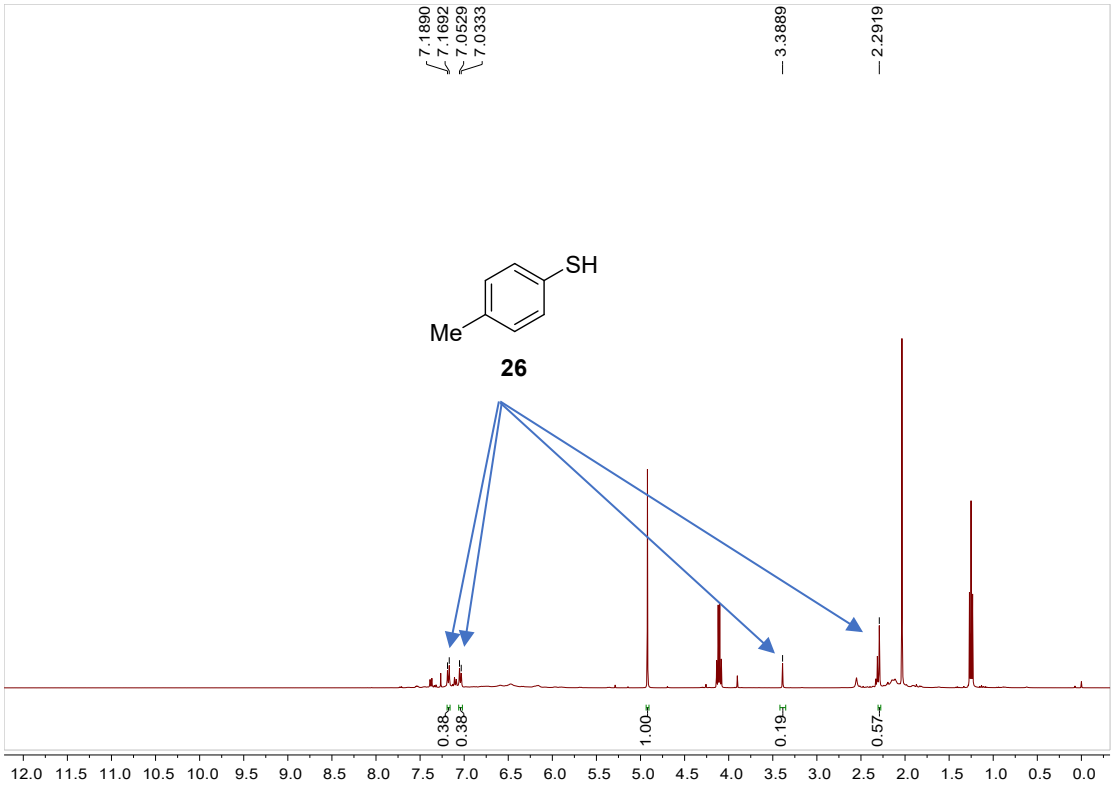


Supplementary Fig. S6. Detection of thiolphenol employing reagent 24.



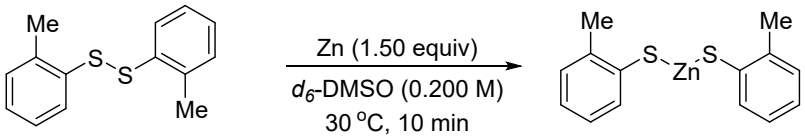
25 **26** **25**

An oven-dried 25-mL glass schlenck, equipped with a stirring bar, was charged with zinc (39.2 mg, 0.600 mmol, 3.00 equiv). The mixture was evacuated and backfilled with nitrogen for three times. Then dry DMF (0.500 mL), disulfide **25** (49.6 mg, 0.200 mmol, 2.00 equiv) was added under N_2 atmosphere. The mixture was allowed to stir at 0 °C for 0.5 h. The mixture was then diluted with saturated NaCl aqueous solution (15.0 mL) and ethyl acetate (15.0 mL). The mixture was filtered through a celite pad and the organic layers were separated. The aqueous layer was extracted with ethyl acetate (25.0 mL x 3). The combined organic layers were washed with saturated NaCl aqueous solution (10.0 mL x 5), dried over Na_2SO_4 and filtered. The solvent was removed by rotary evaporation, the crude mixture was subjected to ^{1}H NMR spectroscopy in the presence of CH_2Br_2 (34.8 mg, 0.200 mmol). Crude ^{1}H NMR yield of **26** is 38.0%, and compound **25** was not observed.



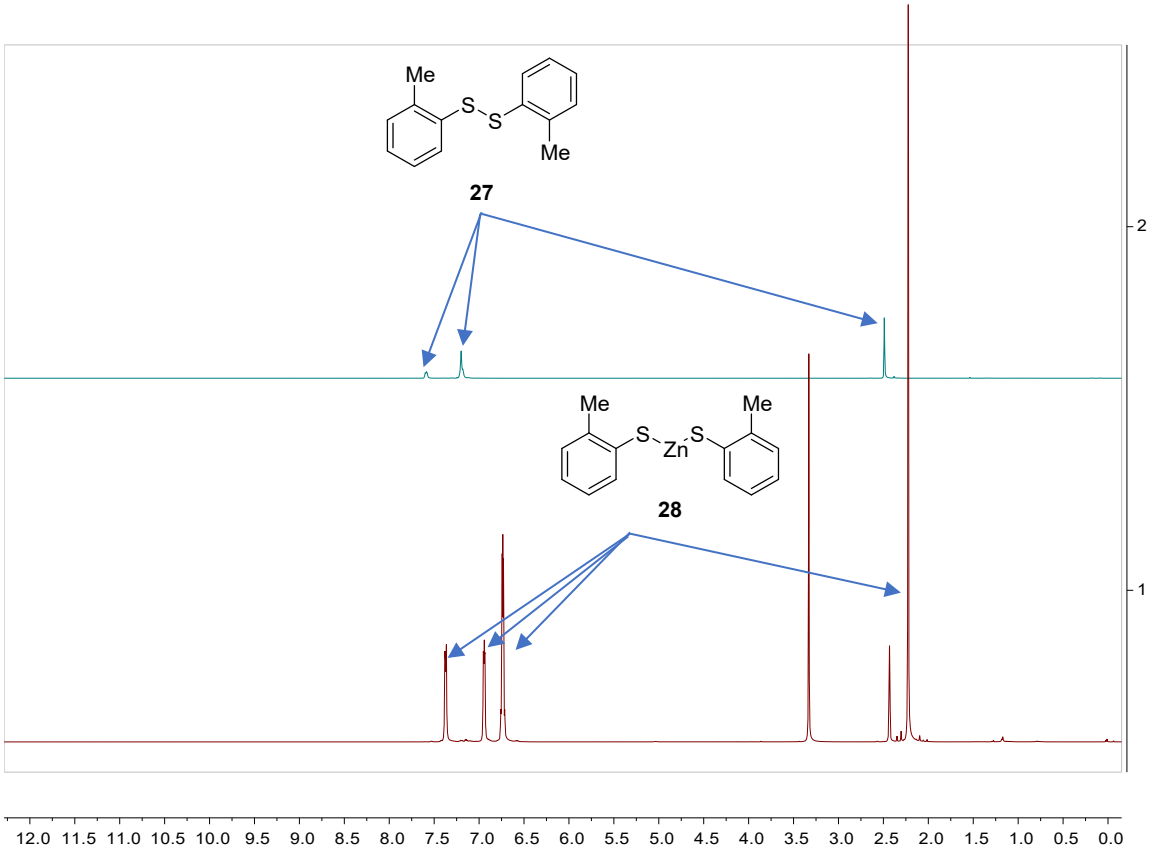
Supplementary Fig. S7. The detection of thiolphenol employing 25.

6. Observation of zinc thiolate

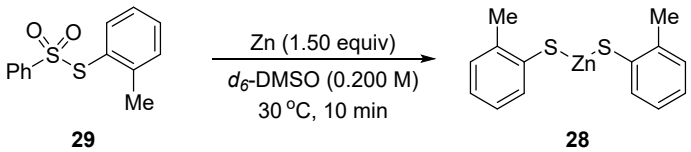


27 **28**

An oven-dried 25-mL glass schlenck, equipped with a stirring bar, was charged with zinc (19.6 mg, 0.300 mmol, 1.50 equiv). The mixture was evacuated and backfilled with nitrogen for three times. Then the d_6-DMSO (0.500 mL), disulfide **27** (49.3 mg, 0.200 mmol, 2.00 equiv) was added under N_2 atmosphere. The mixture was stirred at 30 °C for 10 min. After cooling to room temperature, the crude mixture was subjected to ^{1}H NMR spectroscopy. A new set of peaks was observed with full conversion of the disulfide.

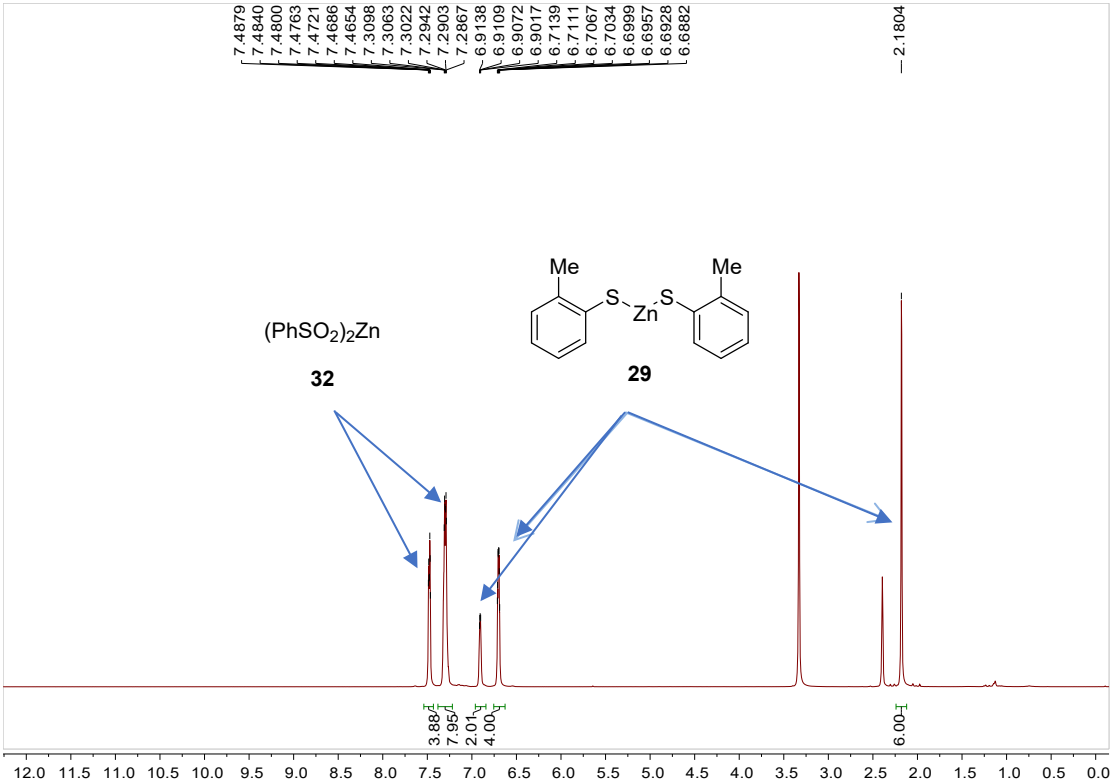


Supplementary Fig. S8. The detection of zinc thiolate employing disulfide 27.



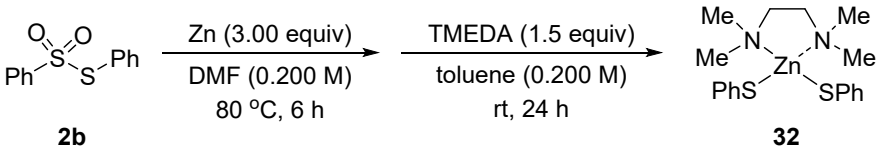
29 **28**

An oven-dried 25-mL glass schlenck, equipped with a stirring bar, was charged with zinc (19.6 mg, 0.300 mmol, 1.50 equiv). The mixture was evacuated and backfilled with nitrogen for three times. Then the d_6-DMSO (0.500 mL), *S*-(o-tolyl) benzenesulfonothioate **29** (52.8 mg, 0.200 mmol, 2.00 equiv) was added under N_2 atmosphere. The mixture was stirred at 30 °C for 10 min. After cooling to room temperature, the crude mixture was subjected to ^{1}H NMR spectroscopy. A new set of peaks with was observed with full conversion of the disulfide.



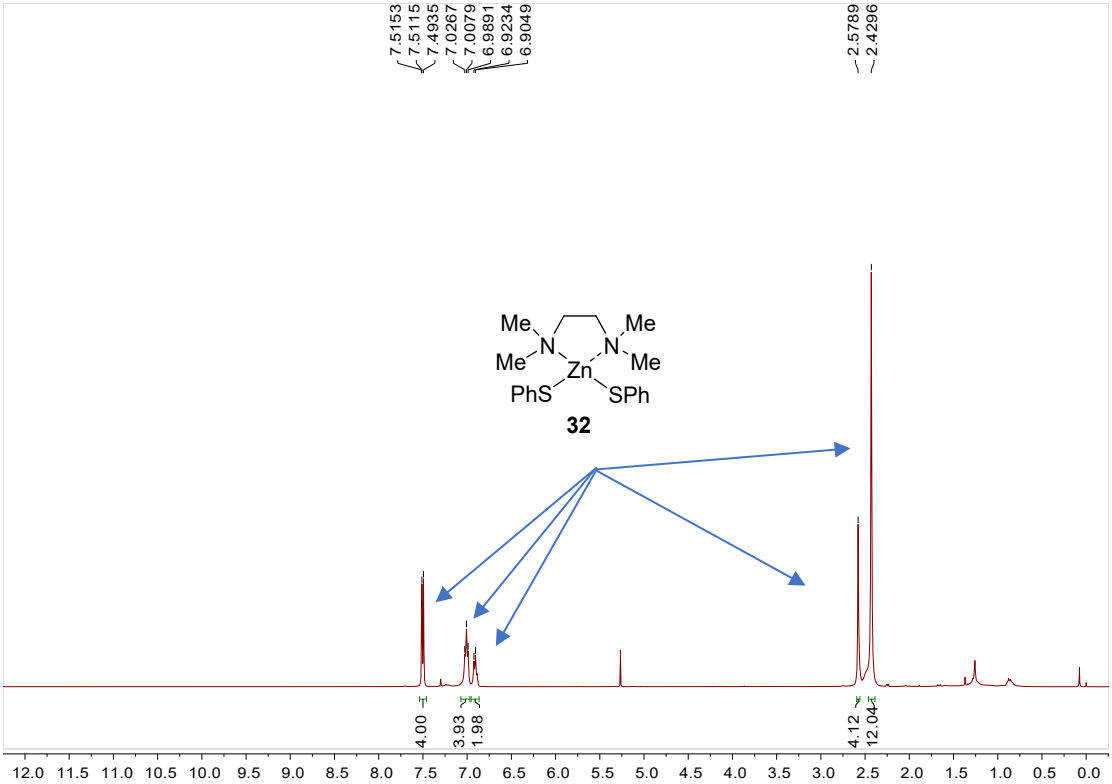
Supplementary Fig. S9. The detection of zinc thiolate employing 29.

7. Isolation of zinc thiolate

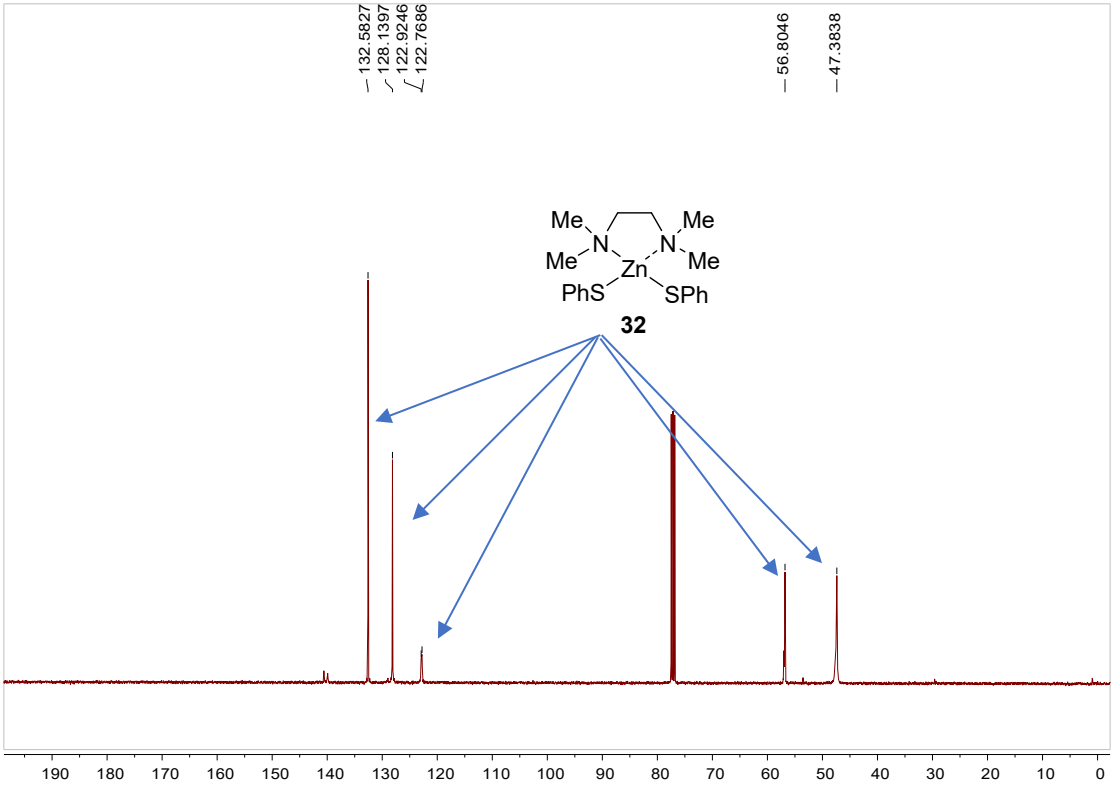


An oven-dried 50-mL glass schlenck, equipped with a stirring bar, was charged with zinc (0.981 g, 15.0 mmol, 3.00 equiv). The mixture was evacuated and backfilled with nitrogen for three times. Then dry DMF (10.0 mL), *S*-phenyl benzenesulfonothioate **2b** (1.25 g, 5.00 mmol, 1.00 equiv) was added under N_2

atmosphere. The mixture was stirred at 80 °C for 6 h. After the completion of the reaction, filtered and the solvent was removed by rotary evaporation. The mixture was evacuated and backfilled with nitrogen for three times. Then dry toluene (10.0 mL), TMEDA (0.872 g, 7.50 mmol, 1.50 equiv) were added under N_2 atmosphere. The mixture was stirred at room temperature for 24 h. The solvent was removed by rotary evaporation, the mixture was poured into water (25.0 mL) and dichloromethane (25.0 mL), filtered. extracted with dichloromethane (25.0 mL x 3). The combined organic layers were washed with saturated NaCl aqueous solution (10.0 mL x 5), dried over Na_2SO_4 and filtered. The solvent was removed by rotary evaporation, the product **32** was isolated as a white solid (1.68 g, 4.20 mmol, 84.0% yield) which is a known compound. The structure was further confirmed by X-ray analysis. The spectral data match those previously reported[1].

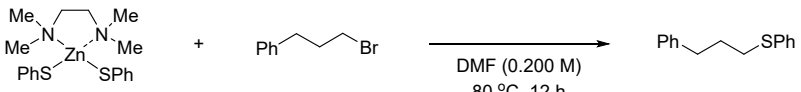


Supplementary Fig. S10. The ^{1}H NMR of zinc thiolate 32.



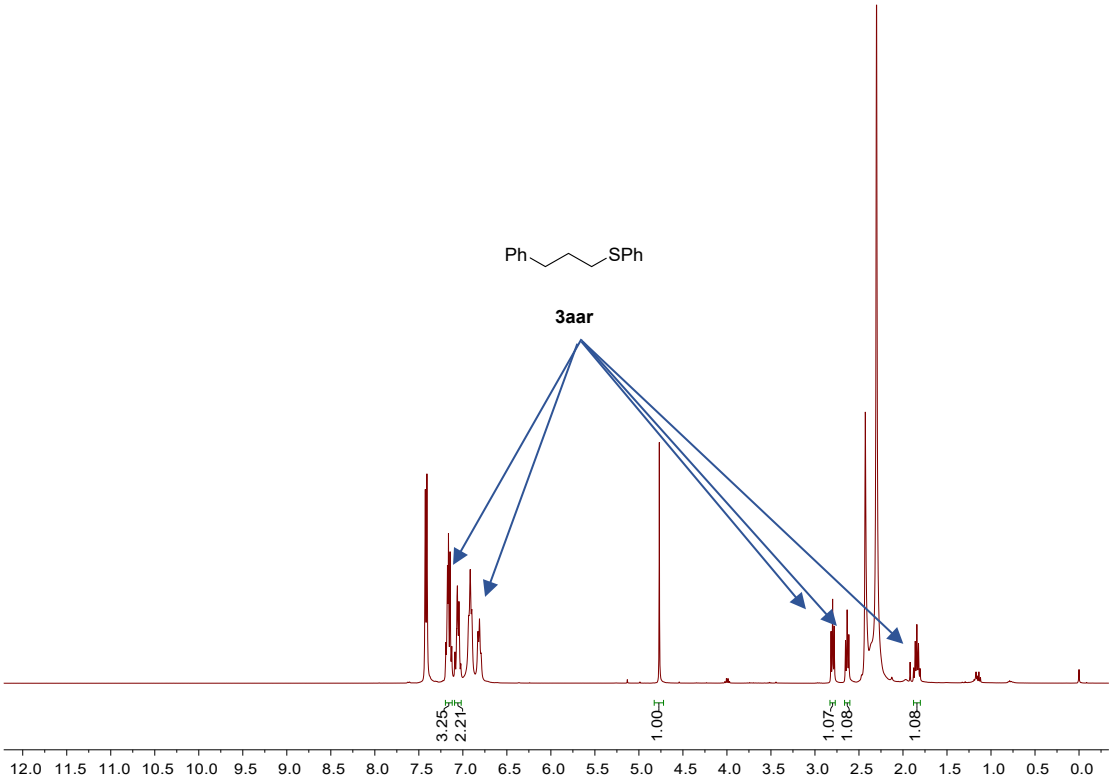
Supplementary Fig. S11. The ^{13}C NMR of zinc thiolate 32.

8. The reactivity of Zinc thiolate in the reaction with alkyl bromide 1a.



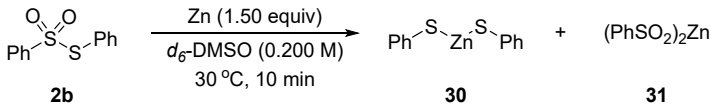
An oven-dried 25-mL glass schlenck, equipped with a stirring bar, was charged with TMEDA-ligated zinc thiolate (159.9 mg, 0.400 mmol, 2.00 equiv). It was evacuated and backfilled with nitrogen for three times. Then the DMF (1.00 mL) and (3-bromopropyl)benzene (39.8 mg, 0.200 mmol, 1.00 equiv) was added under N_2 atmosphere. The mixture was allowed to stir at 80 °C for 12 h. After cooling to room temperature, the mixture was diluted with saturated NaCl aqueous solution (15.0 mL) and ethyl acetate (15.0 mL). The mixture was filtered through a celite pad and the organic layers were separated. The aqueous layer was extracted with ethyl acetate (25.0 mL x 3). The combined organic layers were washed with saturated NaCl aqueous solution (25.0 mL x 5), dried over Na_2SO_4 and filtered. The solvent was removed by rotary evaporation, the crude mixture was subjected to ^1H NMR

spectroscopy in the presence of CH_2Br_2 (34.8 mg, 0.200 mmol). Crude ^1H NMR yield of **3aar** is >99.0%.



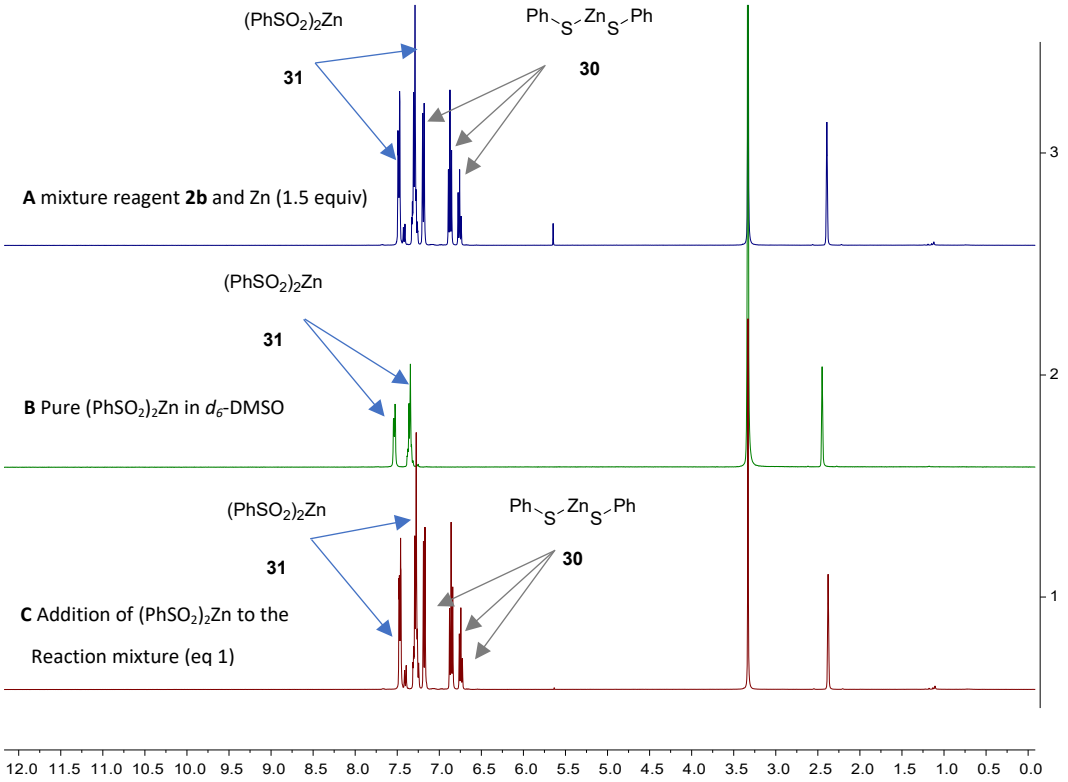
Supplementary Fig. S12. The crude ^1H NMR of the reaction between Zinc thiolate and alkyl bromide.

9. The observation of $(PhSO_2)_2Zn$.



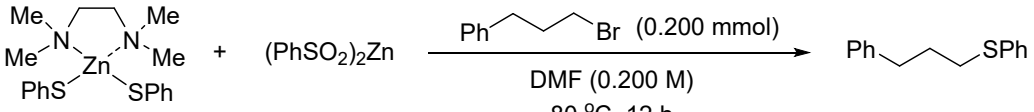
2b **30** **31**

An oven-dried 25-mL glass schlenck, equipped with a stirring bar, was charged with zinc (19.6 mg, 0.300 mmol, 1.50 equiv). The mixture was evacuated and backfilled with nitrogen for three times. Then the d_6-DMSO (0.500 mL), *S*-phenyl benzenesulfonothioate **2b** (50.6 mg, 0.200 mmol, 1.00 equiv) was added under N_2 atmosphere. The mixture was stirred at 30 °C for 10 min. After cooling to room temperature, the crude mixture was subjected to ^1H NMR spectroscopy. A new set of peaks with was observed with full conversion of the disulfide.



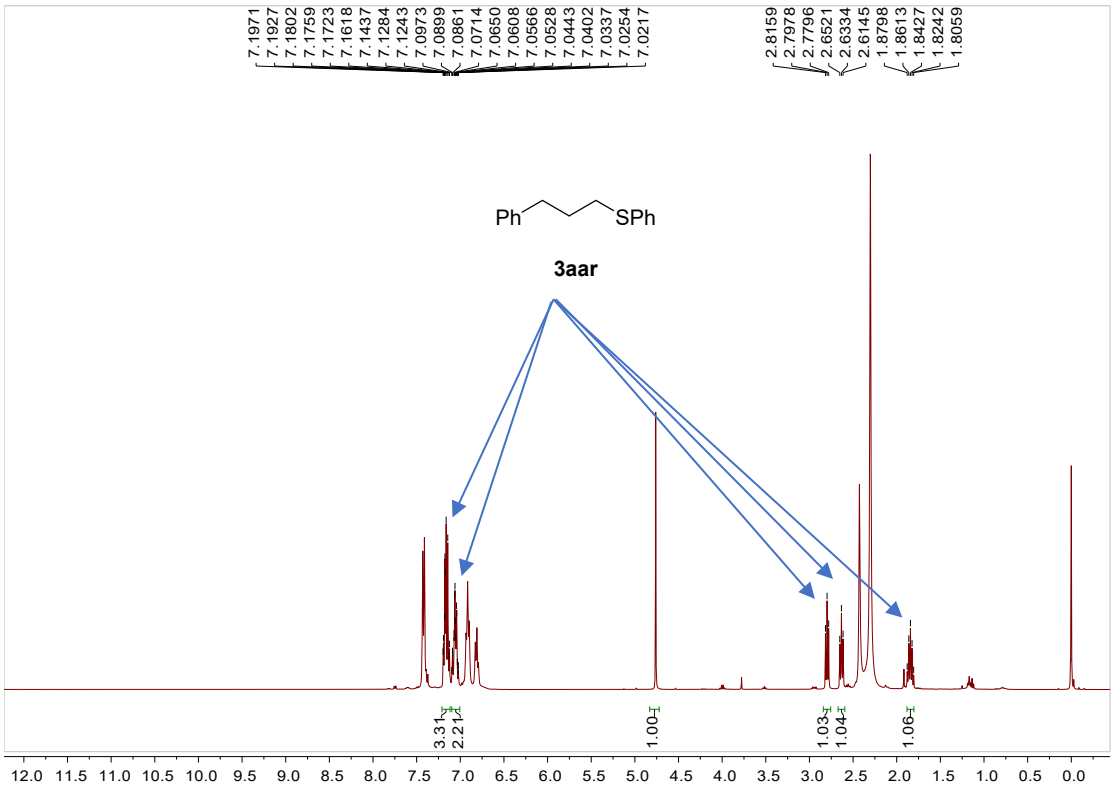
Supplementary Fig. S13. The observation of $(PhSO_2)_2Zn$.

10. The reactivity of TMEDA-ligated zinc thiolate 32



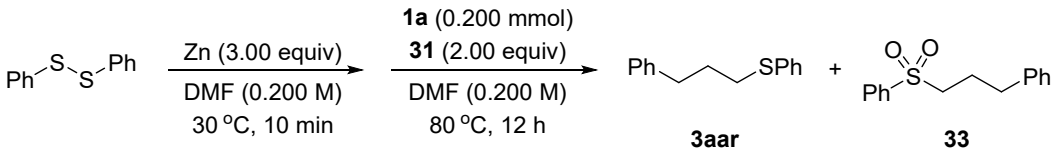
An oven-dried 25-mL glass schlenck, equipped with a stirring bar, was charged with TMEDA-ligated zinc thiolate (159.9 mg, 0.400 mmol, 2.00 equiv) and bis(phenylsulfonyl)zinc (123.0 mg, 0.400 mmol, 2.00 equiv). The mixture was evacuated and backfilled with nitrogen for three times. Then the DMF (1.00 mL) and (3-bromopropyl)benzene (39.8 mg, 0.200 mmol, 1.00 equiv) was added under N_2 atmosphere. The mixture was allowed to stir at 80 °C for 12 h. After cooling to room temperature, the mixture was diluted with saturated NaCl aqueous solution (15.0 mL) and ethyl acetate (15.0 mL). The mixture was filtered through a celite pad and the organic layers were separated. The aqueous layer was extracted with ethyl acetate (25.0 mL x 3). The combined organic layers were washed with saturated NaCl aqueous solution (25.0 mL x 5), dried over Na_2SO_4 and filtered. The solvent was removed by rotary evaporation, the crude mixture was subjected to ^1H NMR

spectroscopy in the presence of CH_2Br_2 (34.8 mg, 0.200 mmol). Crude ^1H NMR yield of **3aar** is >99.0%.



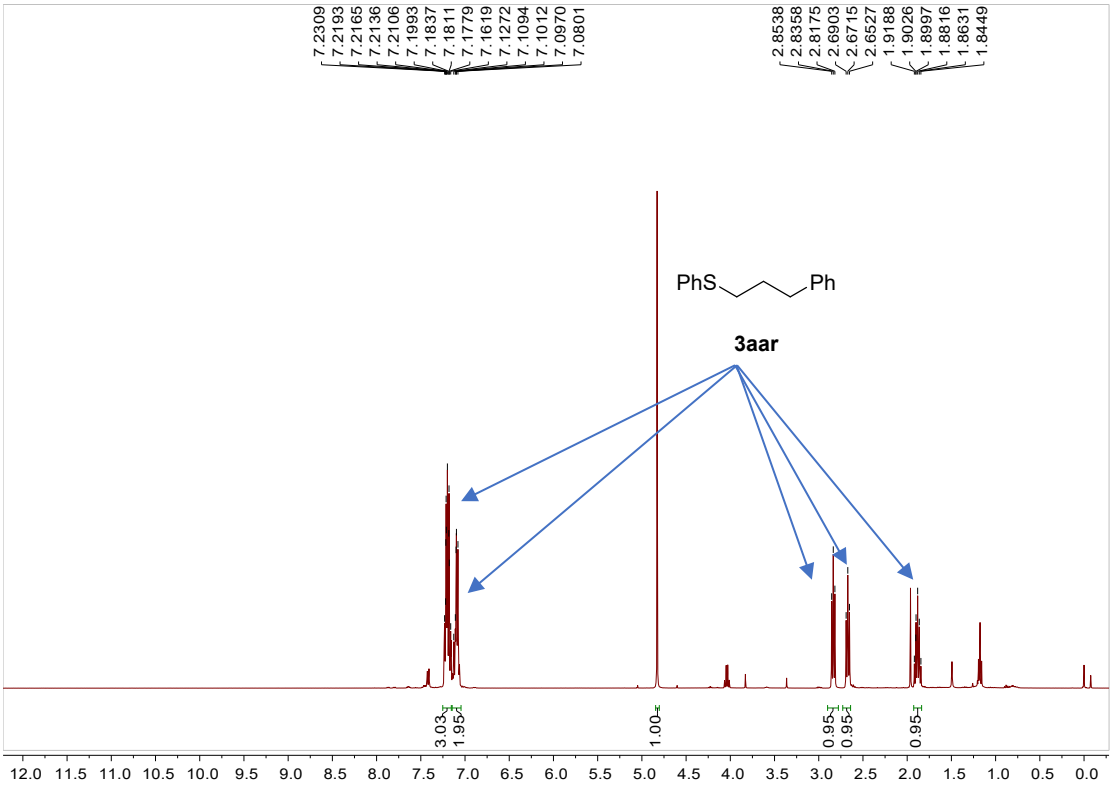
Supplementary Fig. S14. The detection of zinc thiolate employing 3aar.

11. Chemo-selective formation of sulfide

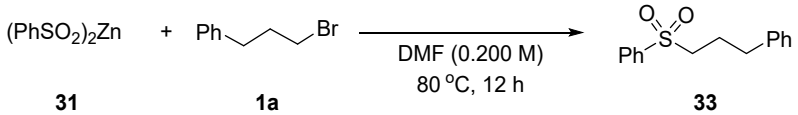


An oven-dried 25-mL glass schlenck, equipped with a stirring bar, was charged with zinc (39.2 mg, 0.600 mmol, 3.00 equiv) and 1,2-diphenyldisulfane (87.3 mg, 0.400 mmol, 2.00 equiv). The mixture was evacuated and backfilled with nitrogen for three times. Then the DMF (1.00 mL) was added under N_2 atmosphere. The mixture was allowed to stir at 30 °C for 10 min. After cooling to room temperature, the (3-bromopropyl)benzene **1a** (39.8 mg, 0.200 mmol, 1.00 equiv) and sulfinate **31** (123.0 mg, 0.400 mmol, 2.00 equiv) was added under N_2 atmosphere. The mixture was allowed to stir at 80 °C for 12 h. After cooling to room temperature, the mixture was diluted with saturated NaCl aqueous solution (15.0 mL) and ethyl acetate (15.0 mL). The mixture was filtered through a celite pad and the organic layers were

separated. The aqueous layer was extracted with ethyl acetate (25.0 mL x 3). The combined organic layers were washed with saturated NaCl aqueous solution (25.0 mL x 5), dried over Na_2SO_4 and filtered. The solvent was removed by rotary evaporation, the crude mixture was subjected to ^1H NMR spectroscopy in the presence of CH_2Br_2 (34.8 mg, 0.200 mmol). Crude ^1H NMR yield of **3aar** is 95.0%, and compound **33** was not observed.



Supplementary Fig. S15. Chemo-selective formation of sulfide 3aar.

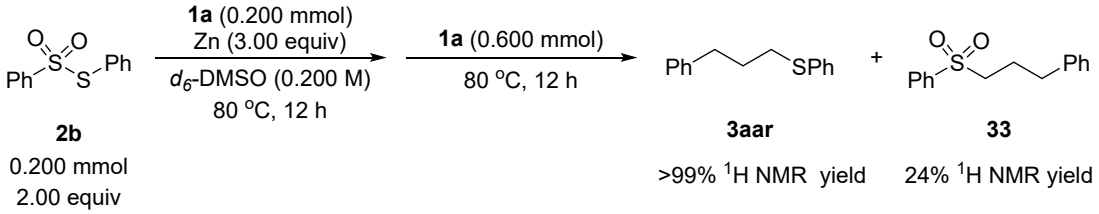


31 **1a** **33**

An oven-dried 25-mL glass schlenck, equipped with a stirring bar, was charged with bis(phenylsulfonyl)zinc **31** (307.6 mg, 1.00 mmol, 2.00 equiv). The mixture was evacuated and backfilled with nitrogen for three times. Then the DMF (1.00 mL) and (3-bromopropyl)benzene **1a** (99.5 mg, 0.500 mmol, 1.00 equiv) was added under N_2 atmosphere. The mixture was allowed to stir at 80 °C for 12 h. After cooling to room temperature, the mixture was poured into water (25.0 mL) and extracted with ethyl acetate (25.0 mL x 3). The combined organic layers were washed with saturated NaCl

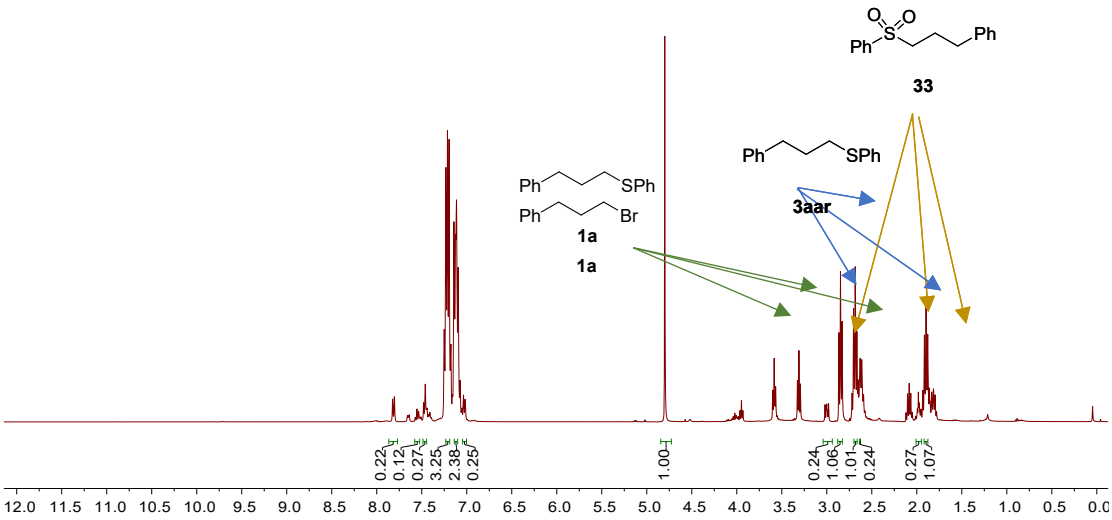
aqueous solution (25.0 mL x 5), dried over Na_2SO_4 and filtered. The solvent was removed by rotary evaporation and the residue was purified by flash silica gel chromatography (Eluent: 200:1 to 10:1 petroleum ether: ethyl acetate). The product was isolated as a white solid (71.2 mg, 0.273 mmol, 54.6% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.87 (2H, d, J = 7.0 Hz), 7.65 – 7.61 (1H, m), 7.55 – 7.52 (2H, m), 7.28 – 7.24 (2H, m), 7.20 – 7.16 (1H, m), 7.09 (2H, d, J = 6.9 Hz), 3.09 – 3.05 (2H, m), 2.68 (2H, t, J = 7.5 Hz), 2.07 – 1.99 (2H, m); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 139.9, 139.0, 133.7, 129.3, 128.6, 128.4, 128.0, 126.4, 55.4, 34.0, 24.2. The spectral data match those previously reported[16].

12. Chemo-selective formation of sulfide



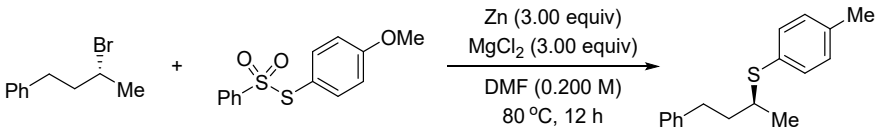
An oven-dried 25-mL glass schlenck, equipped with a stirring bar, was charged with zinc (39.2 mg, 0.600 mmol, 3.00 equiv). It was evacuated and backfilled with nitrogen for three times. Then dry DMF (1.00 mL), *S*-phenyl benzenesulfonothioate (50.6 mg, 0.200 mmol, 1.00 equiv) and (3-bromopropyl)benzene (39.8 mg, 0.200 mmol, 1.00 equiv) were added under N_2 atmosphere. The mixture was allowed to stir at 80 °C for 12 h. After cooling to room temperature, the 3-bromopropyl)benzene (119.5 mg, 0.600 mmol, 3.00 equiv) were added under N_2 atmosphere. The mixture was allowed to stir at 80 °C for 12 h. After cooling to room temperature, the mixture was then diluted with saturated NaCl aqueous solution (15.0 mL) and ethyl acetate (15.0 mL). The mixture was filtered through a celite pad and the organic layers were separated. The aqueous layer was extracted with ethyl acetate (25.0 mL x 3). The combined organic layers were washed with saturated NaCl aqueous solution (10.0 mL x 5), dried over Na_2SO_4 and filtered. The solvent was removed by rotary evaporation, the crude mixture was subjected to ^{1}H NMR spectroscopy in the presence of CH_2Br_2 (34.8 mg, 0.200 mmol). Crude ^{1}H NMR yield of **3aar** is >99.0%, and the ^{1}H NMR

yield of **33** is 24.0%.



Supplementary Fig. S16. Two-step experiment to investigate the formation of active species.

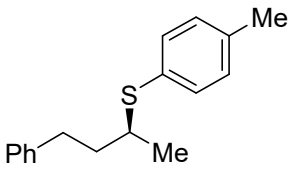
13. Thiolation of optically pure secondary alkyl bromide:



34 **35** **36**

An oven-dried 25-mL glass schlenck, equipped with a stirring bar, was charged with *S*-(4-methoxyphenyl) benzenesulfonothioate **35** (280.4 mg, 1.00 mmol, 2.00 equiv), magnesium chloride (142.8 mg 1.50 mmol, 3.00 equiv) and zinc (98.1 mg 1.50 mmol, 3.00 equiv). The mixture was evacuated and backfilled with nitrogen for three times. Then the DMF (2.50 mL) and (*R*)-(3-bromobutyl)benzene **34** (106.6 mg, 0.500 mmol, 1.00 equiv, 98% ee) was added under N_2 atmosphere. The mixture was stirred at 80 °C for 12 h. After cooling to room temperature, the mixture diluted with NaCl aqueous solution (15.0 mL) and ethyl acetate (15.0 mL). The mixture was filtered through a celite pad and the organic layers were separated. The

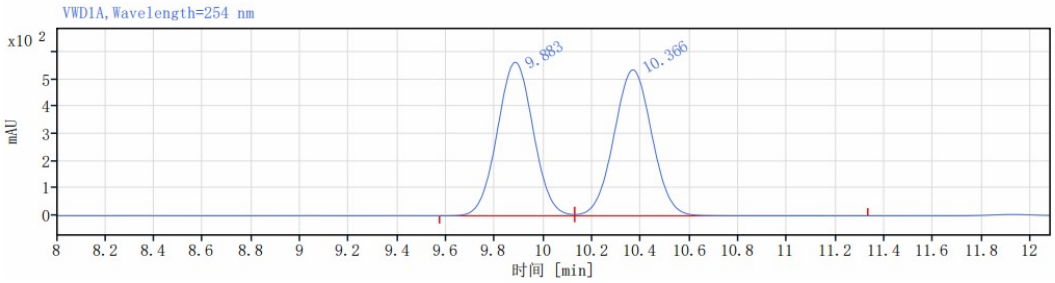
aqueous layer was extracted with ethyl acetate (25.0 mL x 3). The combined organic layers were washed with saturated NaCl aqueous solution (25.0 mL x 5), dried over Na_2SO_4 and filtered. The solvent was removed by rotary evaporation and the residue was purified by flash silica gel chromatography.



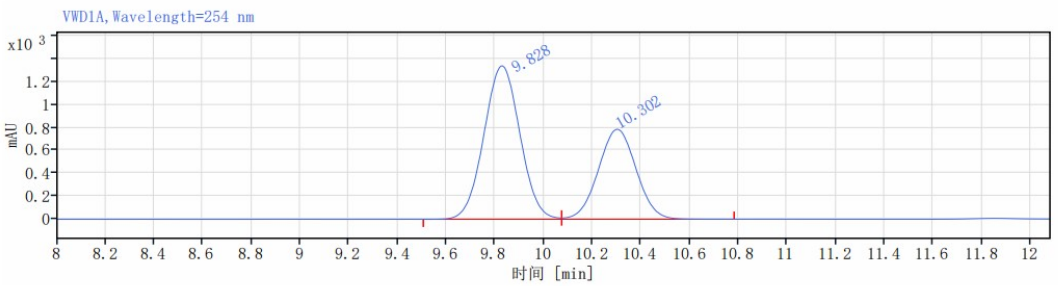
(*S*)-(4-phenylbutan-2-yl)(p-tolyl)sulfane 36: Prepared according to **General Method C** (3.00 equiv $MgCl_2$, 80 °C were used) (Eluent: 200:1 to 20:1 petroleum ether: ethyl acetate) and the title compound was isolated as a colorless liquid (102.8 mg, 0.401 mmol, 80.2% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.36 (2H, d, J = 8.5 Hz), 7.28 – 7.24 (2H, m), 7.18 – 7.15 (3H, m), 6.81 (2H, d, J = 8.8 Hz), 3.76 (3H, s), 3.04 – 3.95 (1H, m), 2.81 – 2.71 (2H, m), 1.91 – 1.70 (2H, m), 1.25 (3H, d, J = 6.9 Hz); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.4, 141.9, 135.8, 128.5, 128.4, 125.9, 124.7, 114.4, 55.3, 43.9, 38.1, 33.2, 21.3. The spectral data match those previously reported[1].

HPLC analysis: The enantiomeric excess (23% ee) was determined on a Lux® 5μm Cellulose-1 (5% iPrOH in hexane, 0.5 mL/min, 35 °C, γ = 254 nm), t_R (minor) = 10.30 min, t_R (major) = 9.83 min.

HPLC traces for compound **36**:

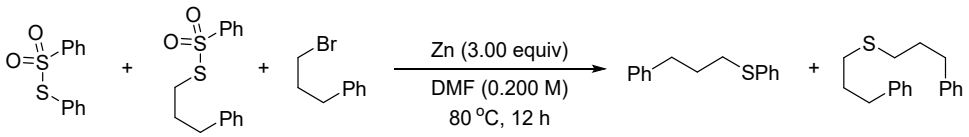


Resolution Time (min)	Width (min)	Area	Height	Area %
9.883	0.556	5793.2	563.4	49.95
10.366	1.204	5804.4	535.6	50.05
		Total VWD1A	11597.5	



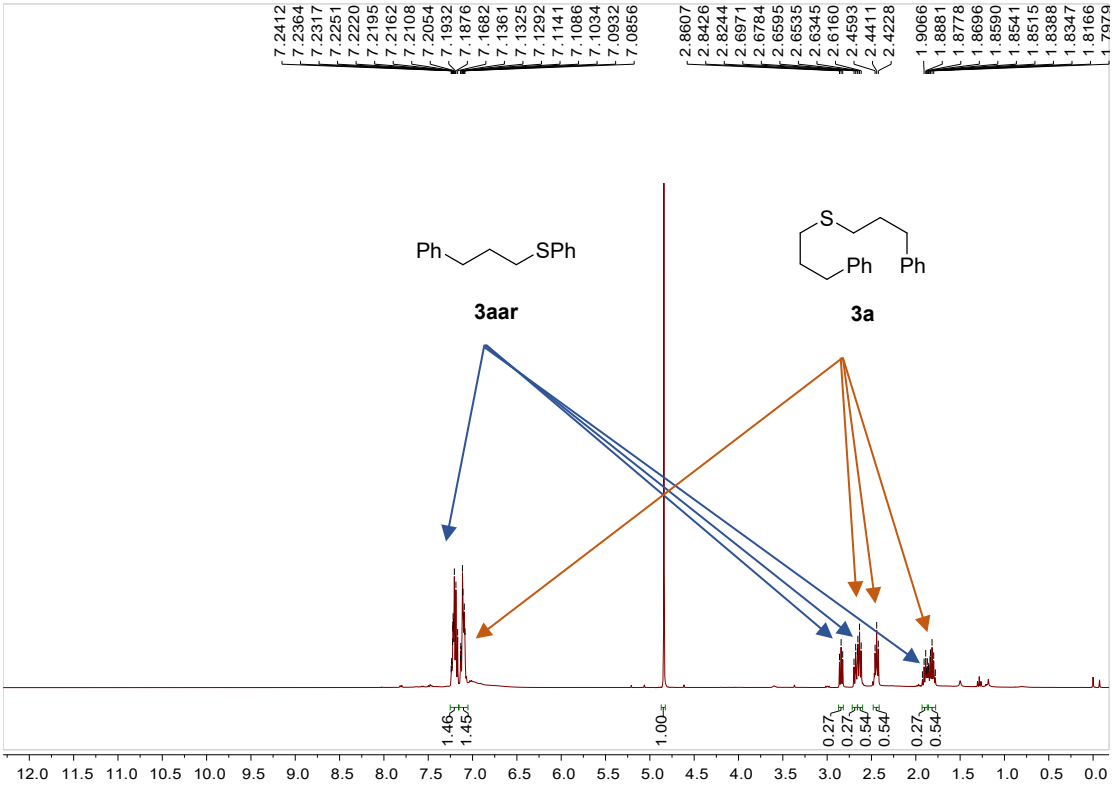
Resolution Time (min)	Width (min)	Area	Height	Area %
9.828	0.569	13789.9	1340.1	61.88
10.302	0.709	8495.3	785.8	38.12
		Total VWD1A	22285.2	

14. Competitive thiolation of alkyl bromide employing aryl and alkyl-substituted thiolsufonate 2a and 2b.:



2b **2a** **1a** **3aar** **3a**

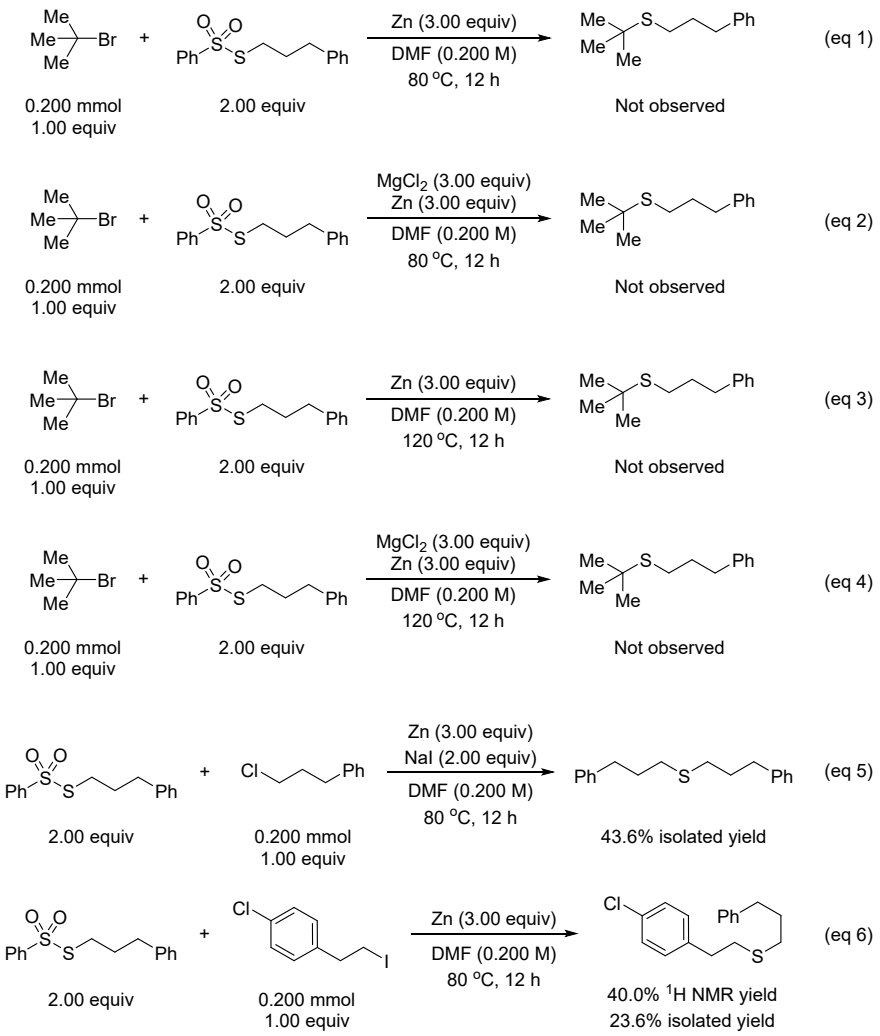
An oven-dried 25-mL glass schlenck, equipped with a stirring bar, was charged with **2b** (25.0 mg, 0.10 mmol, 1.00 equiv), zinc (19.6 mg 0.30 mmol, 3.00 equiv). The mixture was evacuated and backfilled with nitrogen for three times. Then the DMF (1.00 mL), **2a** (29.2 mg, 0.100 mmol, 1.00 equiv) and **1a** (19.9 mg, 0.100 mmol, 1.00 equiv) was added under N_2 atmosphere. The mixture was stirred at 80 °C for 12 h. After cooling to room temperature, the mixture diluted with NaCl aqueous solution (15.0 mL) and ethyl acetate (15.0 mL). The mixture was filtered through a celite pad and the organic layers were separated. The aqueous layer was extracted with ethyl acetate (25.0 mL x 3). The combined organic layers were washed with saturated NaCl aqueous solution (25.0 mL x 5), dried over Na_2SO_4 and filtered. The solvent was removed by rotary evaporation, the crude mixture was subjected to ^{1}H NMR spectroscopy in the presence of CH_2Br_2 (34.8 mg, 0.200 mmol). Crude ^{1}H NMR yield of **3aar** is 54.0%, and crude ^{1}H NMR yield of **3a** is 54.0%.



Supplementary Fig. S17. The detection of 3a and 3aar.

VII. The results of other alkyl substrates.

We have tried the tertiary alkyl bromide, alkyl chloride and iodide. The results were summarized in Figure S1. The tertiary substrate such as 2-bromo-2-methylpropane failed to give the final product with the full recovery of 2-bromo-2-methylpropane and full conversion of the thiolating reagent even 120 ^{o}C was employed (Supplementary Fig. S18, eq 1-4). In addition, primary alkyl chloride could be applied in the reaction and the final product was isolated in 43.6% isolated yield (Supplementary Fig. S18, eq 5). Primary alkyl iodide gave the corresponding product in 40.0% ^{1}H NMR yields (Supplementary Fig. S18, eq 6).

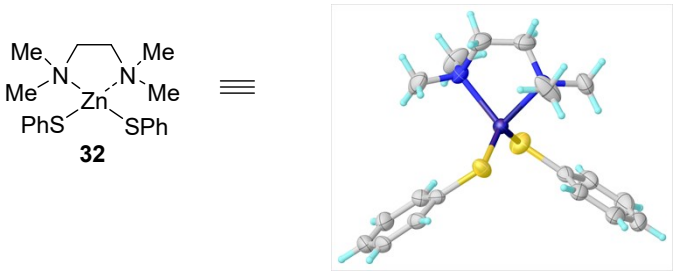


Supplementary Fig. S18. Attempts employing tertiary alkyl bromide, alkyl chloride and iodide

VIII. Crystallographic data

Colorless crystals of **32** were slowly grown from methanol solution of the compound at 22 °C. For X-ray structure analyses, the oil-coated crystals were mounted onto a loop, and the diffraction data were collected on a Bruker Smart Apex II CCD diffractometer with graphite-monochromated Mo Kα (λ = 0.71073 Å). An empirical (multi-scan) absorption correction was applied with the program SADABS. The structures were solved by Olex2 with the ShelXT solution program using the intrinsic phasing method and subsequently refined on F2 by using full-matrix least-squares techniques (SHELXL-2014). If not noted otherwise, all non-hydrogen atoms were refined anisotropically, and hydrogen atoms were located at calculated positions

or found in the ΔF map. Figures of the solid-state molecular structures were generated using XP as implemented in the SHELXTL program.



Supplementary Fig. 15. ORTEP drawing of 2321469 with 50% thermal ellipsoid.

Table 1 Crystal data and structure refinement for mo231102a.

Identification code	mo231102a
Empirical formula	$C_{18}H_{25}N_2S_2Zn$
Formula weight	398.89
Temperature/K	296.15
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	21.00(2)
b/Å	12.476(13)
c/Å	15.346(16)
α/°	90
β/°	90.41(2)
γ/°	90
Volume/Å^3	4020(7)
Z	8
ρ_{calc}g/cm^3	1.318
μ/mm^{-1}	1.430
F(000)	1672.0
Crystal size/mm^3	0.15 × 0.12 × 0.12
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	1.94 to 61.212
Index ranges	$-29 \le h \le 29$, $-17 \le k \le 17$, $-21 \le l \le 21$
Reflections collected	64914
Independent reflections	11523 [R_{int} = 0.0579, R_{sigma} = 0.0453]
Data/restraints/parameters	11523/0/411
Goodness-of-fit on F^2	1.018
Final R indexes [I>=2σ (I)]	R_1 = 0.0419, wR_2 = 0.0989
Final R indexes [all data]	R_1 = 0.0895, wR_2 = 0.1179

Largest diff. peak/hole / e Å^{-3} 0.50/-0.31

Table 2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for mo231102a. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
Zn(1)	8384.5(2)	7119.3(2)	5324.3(2)	44.78(9)
S(1)	8970.0(4)	8564.2(6)	4921.1(6)	72.6(2)
S(2)	7738.7(4)	6037.7(6)	4508.6(5)	61.65(19)
N(1)	8941.9(10)	6019.3(17)	6076.7(14)	52.0(5)
N(2)	7958.0(10)	7562.6(18)	6514.7(14)	54.2(5)
C(1)	9632.7(14)	6141(3)	5928(2)	89.8(11)
C(2)	8751(2)	4910(2)	5923(3)	106.2(14)
C(3)	8816.5(17)	6337(3)	6972.1(19)	80.6(10)
C(4)	8179.4(19)	6707(3)	7127(2)	92.7(11)
C(5)	7256.7(15)	7531(4)	6473(2)	90.6(11)
C(6)	8165(2)	8622(3)	6819(3)	102.7(13)
C(7)	9523.1(8)	8133.9(18)	4143.6(12)	64.7(8)
C(8)	9481.6(9)	7145.1(16)	3729.7(14)	72.8(9)
C(9)	9939.5(13)	6847.4(19)	3126.5(14)	96.8(13)
C(10)	10438.9(10)	7539(3)	2937.2(13)	107.1(16)
C(11)	10480.5(8)	8527(2)	3351.1(16)	112.6(16)
C(12)	10022.6(10)	8825.0(17)	3954.3(14)	84.6(11)
C(13)	7113.4(12)	6819(2)	4059.6(16)	50.7(6)
C(14)	7090.8(14)	7924(2)	4095.2(18)	60.3(7)
C(15)	6577.7(16)	8478(3)	3730(2)	78.7(10)
C(16)	6093.2(17)	7937(4)	3319(2)	86.8(12)
C(17)	6117.1(14)	6848(4)	3258(2)	81.1(11)
C(18)	6616.5(13)	6289(3)	3627.4(17)	64.2(8)
Zn(2)	6589.0(2)	2812.1(2)	6953.4(2)	47.29(9)
S(3)	5887.0(4)	1722.8(6)	7637.0(5)	64.4(2)
S(4)	7283.6(4)	4012.5(6)	7542.7(5)	65.4(2)
N(3)	6153.7(11)	3703(2)	5916.0(15)	64.9(6)
N(4)	6988.7(14)	1847(2)	5964.8(18)	80.6(8)
C(19)	6782(3)	737(4)	6016(4)	168(3)
C(20)	7684.3(19)	1864(4)	5972(3)	128.1(18)
C(21)	6739(4)	2338(7)	5175(3)	240(5)
C(22)	6403(3)	3190(4)	5133(2)	137(2)
C(23)	6343.5(17)	4848(3)	5914(2)	89.9(11)
C(24)	5455.2(15)	3669(4)	5954(3)	103.9(14)
C(25)	7846.0(12)	3338(2)	8207.3(16)	49.9(6)

Table 2 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for mo231102a. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
C(26)	8306.6(13)	3946(2)	8636.3(17)	58.2(7)
C(27)	8765.7(14)	3479(3)	9160(2)	71.0(8)
C(28)	8774.5(15)	2394(3)	9271(2)	77.2(9)
C(29)	8325.1(16)	1774(3)	8858(2)	75.1(9)
C(30)	7860.3(14)	2232(2)	8332(2)	63.1(7)
C(31)	5396.5(12)	2557(2)	8263.2(16)	52.7(6)
C(32)	5476.6(15)	3652(3)	8363(2)	70.2(8)
C(33)	5065.0(19)	4243(3)	8864(2)	90.7(11)
C(34)	4573.9(18)	3767(4)	9294(2)	92.1(11)
C(35)	4489.3(14)	2693(4)	9215(2)	81.4(10)
C(36)	4887.3(13)	2090(3)	8698.4(19)	64.9(8)

Table 3 Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for mo231102a. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Zn(1)	42.29(16)	49.84(17)	42.23(16)	1.37(12)	1.84(11)	0.20(12)
S(1)	76.0(5)	63.3(5)	78.9(5)	8.4(4)	22.6(4)	-13.8(4)
S(2)	62.7(4)	55.8(4)	66.1(4)	-7.0(3)	-18.4(3)	4.6(3)
N(1)	50.1(12)	53.9(13)	51.8(12)	0.8(10)	-9.6(10)	2.9(10)
N(2)	56.8(13)	55.8(13)	50.1(13)	-5.7(10)	12.5(10)	-2.5(11)
C(1)	53.6(18)	128(3)	88(2)	22(2)	-8.8(17)	17.9(19)
C(2)	118(3)	49.3(18)	150(4)	-7(2)	-71(3)	13(2)
C(3)	99(3)	93(2)	50.4(18)	11.7(17)	-2.7(17)	15(2)
C(4)	111(3)	110(3)	58(2)	14(2)	17.8(19)	13(2)
C(5)	62(2)	130(3)	80(2)	-21(2)	24.7(17)	-8(2)
C(6)	128(3)	79(2)	102(3)	-37(2)	40(2)	-19(2)
C(7)	50.0(16)	93(2)	51.2(16)	26.1(16)	2.5(12)	6.4(15)
C(8)	71(2)	92(2)	55.2(17)	22.7(17)	5.8(15)	24.1(17)
C(9)	101(3)	130(3)	60(2)	26(2)	6.5(19)	53(3)
C(10)	75(3)	176(4)	70(2)	46(3)	21(2)	49(3)
C(11)	55(2)	186(5)	97(3)	54(3)	11(2)	-1(3)
C(12)	57.8(18)	127(3)	69(2)	31(2)	-0.2(16)	-11.2(19)
C(13)	45.7(14)	68.3(17)	38.1(13)	2.3(12)	-0.4(10)	-3.7(12)
C(14)	56.4(16)	73(2)	51.9(16)	3.7(14)	0.5(13)	5.9(14)

Table 3 Anisotropic Displacement Parameters ($Å^2×10^3$) for mo231102a. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C(15)	79(2)	93(2)	63.3(19)	10.3(18)	7.2(17)	30(2)
C(16)	60(2)	141(4)	59(2)	10(2)	-1.6(16)	29(2)
C(17)	43.6(16)	149(4)	50.7(17)	6(2)	-2.8(13)	-10(2)
C(18)	53.8(16)	92(2)	47.2(15)	3.1(15)	0.5(13)	-15.4(15)
Zn(2)	45.46(16)	52.85(18)	43.64(16)	-1.77(13)	5.36(12)	-6.82(13)
S(3)	73.4(5)	54.6(4)	65.4(4)	-1.1(3)	19.9(4)	-15.5(4)
S(4)	64.1(4)	50.8(4)	80.9(5)	7.8(4)	-18.5(4)	-12.5(3)
N(3)	61.8(15)	82.3(17)	50.7(13)	11.0(12)	-6.0(11)	-13.6(13)
N(4)	79.3(19)	90(2)	73.1(18)	-24.5(15)	20.1(14)	6.7(15)
C(19)	145(4)	118(4)	244(7)	-108(4)	84(4)	-32(3)
C(20)	88(3)	155(4)	142(4)	-50(3)	56(3)	-2(3)
C(21)	351(11)	326(10)	44(2)	-29(4)	-2(4)	215(9)
C(22)	232(6)	138(4)	43(2)	4(2)	-1(3)	54(4)
C(23)	84(2)	83(2)	102(3)	38(2)	-12(2)	-8.6(19)
C(24)	63(2)	139(4)	110(3)	44(3)	-31(2)	-21(2)
C(25)	50.3(14)	53.5(15)	45.8(14)	2.5(12)	4.2(11)	-9.5(12)
C(26)	58.9(16)	66.4(17)	49.2(15)	2.1(13)	2.0(12)	-14.8(14)
C(27)	58.9(18)	95(2)	58.4(18)	7.3(17)	-2.5(14)	-19.6(17)
C(28)	57.9(19)	101(3)	73(2)	23(2)	-0.5(16)	3.5(18)
C(29)	82(2)	64.2(19)	80(2)	21.7(17)	6.6(18)	6.5(17)
C(30)	67.2(18)	55.0(17)	67.1(18)	5.3(14)	1.0(15)	-9.8(14)
C(31)	51.6(15)	66.6(17)	40.0(13)	6.7(12)	0.7(11)	-6.5(13)
C(32)	76(2)	68.0(19)	67.4(19)	-5.5(15)	20.1(16)	-11.0(16)
C(33)	106(3)	75(2)	90(3)	-7(2)	26(2)	12(2)
C(34)	78(2)	116(3)	83(2)	0(2)	21.5(19)	24(2)
C(35)	48.2(17)	126(3)	70(2)	18(2)	13.3(15)	1.8(19)
C(36)	54.5(16)	85(2)	55.4(17)	12.7(15)	0.1(13)	-12.0(15)

Table 4 Bond Lengths for mo231102a.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Zn(1)	S(1)	2.2705(18)	Zn(2)	S(3)	2.2678(16)
Zn(1)	S(2)	2.2810(16)	Zn(2)	S(4)	2.2737(17)
Zn(1)	N(1)	2.137(2)	Zn(2)	N(3)	2.141(3)
Zn(1)	N(2)	2.114(3)	Zn(2)	N(4)	2.116(3)
S(1)	C(7)	1.755(2)	S(3)	C(31)	1.755(3)

Table 4 Bond Lengths for mo231102a.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
S(2)	C(13)	1.771(3)	S(4)	C(25)	1.768(3)
N(1)	C(1)	1.478(4)	N(3)	C(22)	1.461(5)
N(1)	C(2)	1.460(4)	N(3)	C(23)	1.483(4)
N(1)	C(3)	1.456(4)	N(3)	C(24)	1.469(4)
N(2)	C(4)	1.494(4)	N(4)	C(19)	1.453(5)
N(2)	C(5)	1.474(4)	N(4)	C(20)	1.461(5)
N(2)	C(6)	1.466(4)	N(4)	C(21)	1.452(6)
C(3)	C(4)	1.436(5)	C(21)	C(22)	1.278(7)
C(7)	C(8)	1.3900	C(25)	C(26)	1.391(4)
C(7)	C(12)	1.3900	C(25)	C(30)	1.393(4)
C(8)	C(9)	1.3900	C(26)	C(27)	1.380(4)
C(9)	C(10)	1.3900	C(27)	C(28)	1.365(5)
C(10)	C(11)	1.3900	C(28)	C(29)	1.371(5)
C(11)	C(12)	1.3900	C(29)	C(30)	1.385(4)
C(13)	C(14)	1.381(4)	C(31)	C(32)	1.386(4)
C(13)	C(18)	1.399(4)	C(31)	C(36)	1.392(4)
C(14)	C(15)	1.394(4)	C(32)	C(33)	1.375(4)
C(15)	C(16)	1.371(5)	C(33)	C(34)	1.365(5)
C(16)	C(17)	1.363(5)	C(34)	C(35)	1.357(5)
C(17)	C(18)	1.378(5)	C(35)	C(36)	1.379(5)

Table 5 Bond Angles for mo231102a.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
S(1)	Zn(1)	S(2)	129.88(6)	S(3)	Zn(2)	S(4)	128.90(6)
N(1)	Zn(1)	S(1)	111.19(9)	N(3)	Zn(2)	S(3)	112.30(9)
N(1)	Zn(1)	S(2)	103.75(9)	N(3)	Zn(2)	S(4)	102.90(9)
N(2)	Zn(1)	S(1)	105.16(8)	N(4)	Zn(2)	S(3)	104.66(11)
N(2)	Zn(1)	S(2)	112.03(9)	N(4)	Zn(2)	S(4)	113.80(10)
N(2)	Zn(1)	N(1)	86.27(11)	N(4)	Zn(2)	N(3)	86.09(13)
C(7)	S(1)	Zn(1)	107.74(10)	C(31)	S(3)	Zn(2)	106.50(12)
C(13)	S(2)	Zn(1)	108.92(12)	C(25)	S(4)	Zn(2)	109.86(11)
C(1)	N(1)	Zn(1)	112.64(19)	C(22)	N(3)	Zn(2)	103.4(2)
C(2)	N(1)	Zn(1)	111.94(18)	C(22)	N(3)	C(23)	108.8(3)
C(2)	N(1)	C(1)	109.9(3)	C(22)	N(3)	C(24)	112.5(3)
C(3)	N(1)	Zn(1)	103.46(18)	C(23)	N(3)	Zn(2)	112.84(19)
C(3)	N(1)	C(1)	107.6(2)	C(24)	N(3)	Zn(2)	112.2(2)
C(3)	N(1)	C(2)	111.0(3)	C(24)	N(3)	C(23)	107.2(3)

Table 5 Bond Angles for mo231102a.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C(4)	N(2)	Zn(1)	102.98(19)	C(19)	N(4)	Zn(2)	112.5(2)
C(5)	N(2)	Zn(1)	112.64(19)	C(19)	N(4)	C(20)	108.2(4)
C(5)	N(2)	C(4)	108.3(3)	C(20)	N(4)	Zn(2)	112.8(2)
C(6)	N(2)	Zn(1)	112.60(19)	C(21)	N(4)	Zn(2)	102.4(3)
C(6)	N(2)	C(4)	110.7(3)	C(21)	N(4)	C(19)	110.0(5)
C(6)	N(2)	C(5)	109.4(3)	C(21)	N(4)	C(20)	110.8(5)
C(4)	C(3)	N(1)	114.7(3)	C(22)	C(21)	N(4)	126.1(4)
C(3)	C(4)	N(2)	114.3(3)	C(21)	C(22)	N(3)	121.6(4)
C(8)	C(7)	S(1)	122.85(14)	C(26)	C(25)	S(4)	118.2(2)
C(8)	C(7)	C(12)	120.0	C(26)	C(25)	C(30)	117.4(3)
C(12)	C(7)	S(1)	117.15(15)	C(30)	C(25)	S(4)	124.4(2)
C(7)	C(8)	C(9)	120.0	C(27)	C(26)	C(25)	121.8(3)
C(10)	C(9)	C(8)	120.0	C(28)	C(27)	C(26)	120.0(3)
C(9)	C(10)	C(11)	120.0	C(27)	C(28)	C(29)	119.6(3)
C(12)	C(11)	C(10)	120.0	C(28)	C(29)	C(30)	121.1(3)
C(11)	C(12)	C(7)	120.0	C(29)	C(30)	C(25)	120.2(3)
C(14)	C(13)	S(2)	124.0(2)	C(32)	C(31)	S(3)	125.0(2)
C(14)	C(13)	C(18)	117.7(3)	C(32)	C(31)	C(36)	116.9(3)
C(18)	C(13)	S(2)	118.2(2)	C(36)	C(31)	S(3)	118.0(2)
C(13)	C(14)	C(15)	120.4(3)	C(33)	C(32)	C(31)	120.9(3)
C(16)	C(15)	C(14)	120.7(4)	C(34)	C(33)	C(32)	121.2(4)
C(17)	C(16)	C(15)	119.6(3)	C(35)	C(34)	C(33)	119.0(3)
C(16)	C(17)	C(18)	120.3(3)	C(34)	C(35)	C(36)	120.7(3)
C(17)	C(18)	C(13)	121.2(3)	C(35)	C(36)	C(31)	121.2(3)

Table 6 Torsion Angles for mo231102a.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
Zn(1)	S(1)	C(7)	C(8)	13.61(14)	Zn(2)	S(3)	C(31)	C(32)	-5.2(3)
Zn(1)	S(1)	C(7)	C(12)	-165.71(9)	Zn(2)	S(3)	C(31)	C(36)	175.00(19)
Zn(1)	S(2)	C(13)	C(14)	9.3(2)	Zn(2)	S(4)	C(25)	C(26)	-179.04(18)
Zn(1)	S(2)	C(13)	C(18)	-171.93(18)	Zn(2)	S(4)	C(25)	C(30)	0.9(3)
Zn(1)	N(1)	C(3)	C(4)	35.2(4)	Zn(2)	N(3)	C(22)	C(21)	6.7(8)
Zn(1)	N(2)	C(4)	C(3)	35.8(4)	Zn(2)	N(4)	C(21)	C(22)	4.5(11)
S(1)	C(7)	C(8)	C(9)	-179.30(15)	S(3)	C(31)	C(32)	C(33)	179.6(3)
S(1)	C(7)	C(12)	C(11)	179.34(14)	S(3)	C(31)	C(36)	C(35)	178.8(2)
S(2)	C(13)	C(14)	C(15)	-179.5(2)	S(4)	C(25)	C(26)	C(27)	-179.4(2)
S(2)	C(13)	C(18)	C(17)	-179.6(2)	S(4)	C(25)	C(30)	C(29)	179.2(2)

Table 6 Torsion Angles for mo231102a.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
N(1)	C(3)	C(4)	N(2)	-51.7(5)	N(4)	C(21)	C(22)	N(3)	-8.5(14)
C(1)	N(1)	C(3)	C(4)	154.6(3)	C(19)	N(4)	C(21)	C(22)	124.4(10)
C(2)	N(1)	C(3)	C(4)	-85.0(4)	C(20)	N(4)	C(21)	C(22)	-116.0(9)
C(5)	N(2)	C(4)	C(3)	155.3(3)	C(23)	N(3)	C(22)	C(21)	126.9(8)
C(6)	N(2)	C(4)	C(3)	-84.7(4)	C(24)	N(3)	C(22)	C(21)	-114.5(8)
C(7)	C(8)	C(9)	C(10)	0.0	C(25)	C(26)	C(27)	C(28)	-0.2(5)
C(8)	C(7)	C(12)	C(11)	0.0	C(26)	C(25)	C(30)	C(29)	-0.8(4)
C(8)	C(9)	C(10)	C(11)	0.0	C(26)	C(27)	C(28)	C(29)	0.0(5)
C(9)	C(10)	C(11)	C(12)	0.0	C(27)	C(28)	C(29)	C(30)	-0.2(5)
C(10)	C(11)	C(12)	C(7)	0.0	C(28)	C(29)	C(30)	C(25)	0.6(5)
C(12)	C(7)	C(8)	C(9)	0.0	C(30)	C(25)	C(26)	C(27)	0.6(4)
C(13)	C(14)	C(15)	C(16)	-1.1(5)	C(31)	C(32)	C(33)	C(34)	1.5(6)
C(14)	C(13)	C(18)	C(17)	-0.7(4)	C(32)	C(31)	C(36)	C(35)	-1.0(4)
C(14)	C(15)	C(16)	C(17)	-0.7(5)	C(32)	C(33)	C(34)	C(35)	-0.8(6)
C(15)	C(16)	C(17)	C(18)	1.6(5)	C(33)	C(34)	C(35)	C(36)	-0.8(6)
C(16)	C(17)	C(18)	C(13)	-0.9(5)	C(34)	C(35)	C(36)	C(31)	1.7(5)
C(18)	C(13)	C(14)	C(15)	1.7(4)	C(36)	C(31)	C(32)	C(33)	-0.6(5)

Table 7 Hydrogen Atom Coordinates (Å×104) and Isotropic Displacement Parameters (Å2×103) for mo231102a.

Atom	*x*	*y*	*z*	U(eq)
H(1A)	9730.2	5934.01	5341.34	135
H(1B)	9863.76	5693.07	6328.44	135
H(1C)	9752.82	6875.69	6017.23	135
H(2A)	8299.68	4842.46	5997.85	159
H(2B)	8967.51	4450.34	6331.3	159
H(2C)	8861.94	4705.85	5340.55	159
H(3A)	8901.12	5730.28	7350.52	97
H(3B)	9111.68	6902.91	7132.91	97
H(4A)	8156.02	6979.07	7717.86	111
H(4B)	7890.92	6101.92	7082.23	111
H(5A)	7104.11	8115.92	6122.7	136
H(5B)	7087.87	7591.83	7050.73	136
H(5C)	7121.39	6865.25	6218.87	136
H(6A)	8620.71	8631.02	6876.24	154
H(6B)	7976.68	8770.36	7374.04	154
H(6C)	8033.88	9156.98	6405.77	154

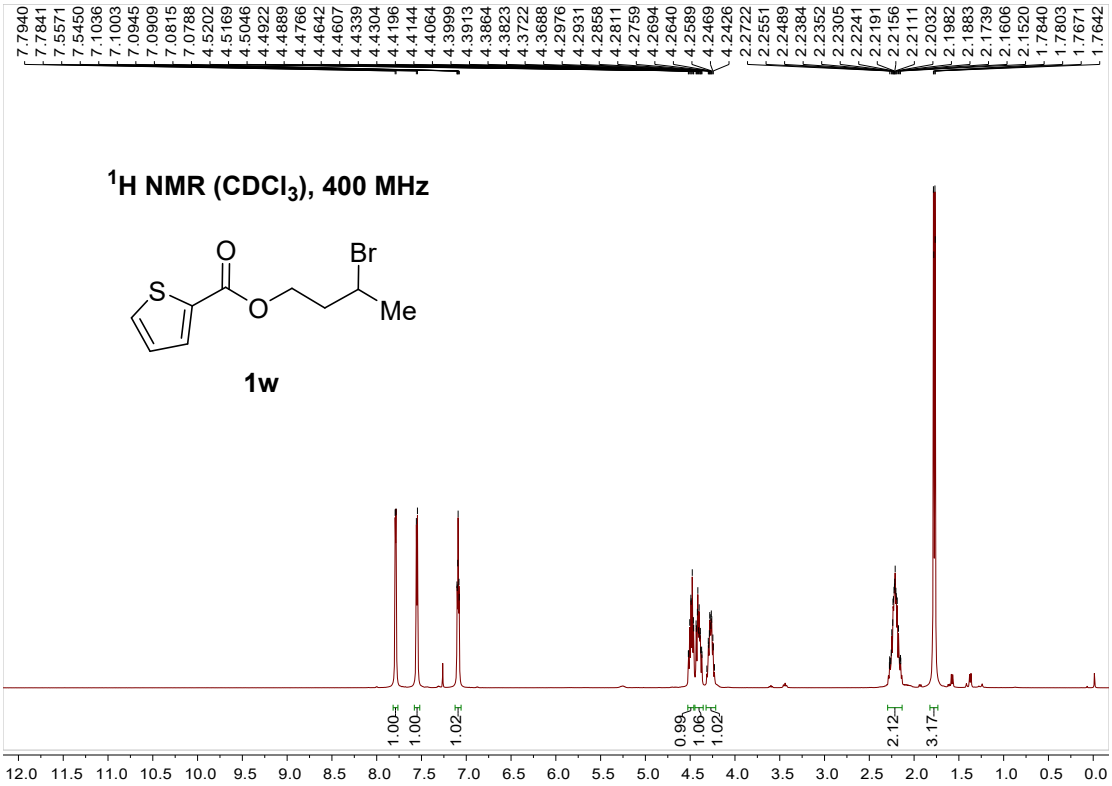
Table 7 Hydrogen Atom Coordinates (Å×104) and Isotropic Displacement Parameters (Å2×103) for mo231102a.

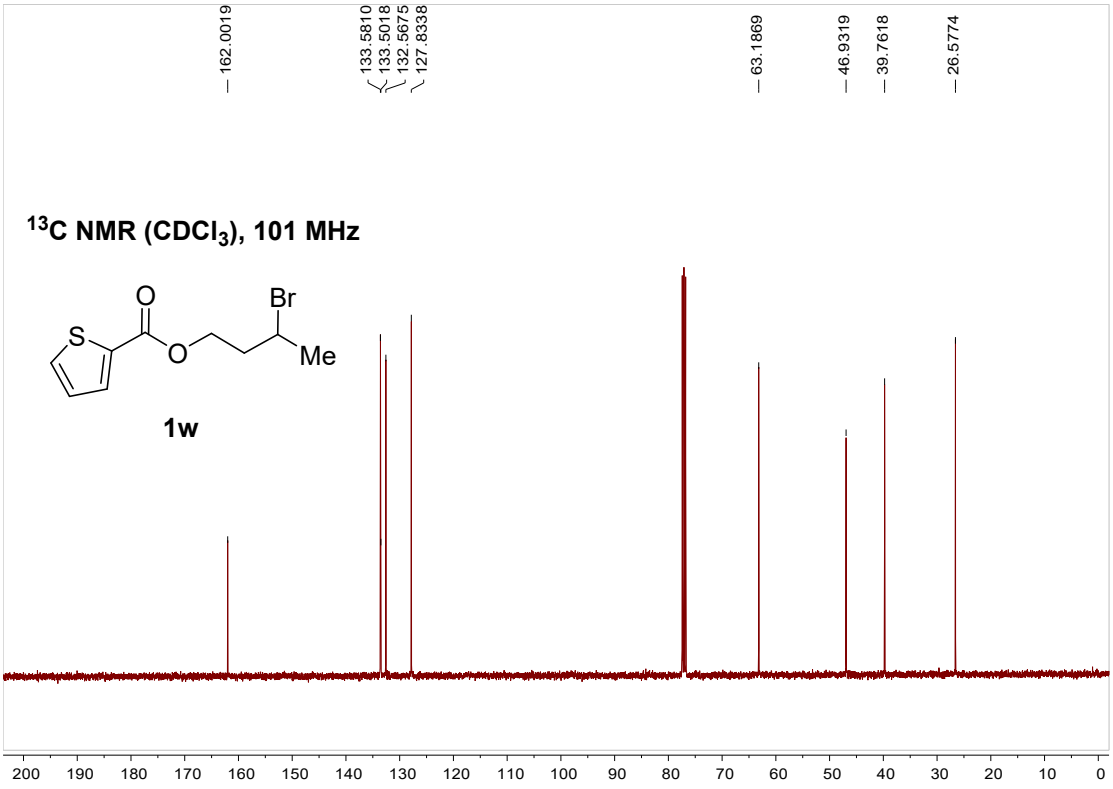
Atom	*x*	*y*	*z*	U(eq)
H(8)	9147.42	6682.74	3856.35	87
H(9)	9911.65	6185.85	2849.55	116
H(10)	10745.26	7339.33	2533.59	128
H(11)	10814.65	8989.7	3224.43	135
H(12)	10050.43	9486.61	4231.24	101
H(14)	7419.75	8301.27	4364.21	72
H(15)	6563.79	9221.39	3766.44	94
H(16)	5750.27	8311.49	3081.95	104
H(17)	5794.73	6479.84	2966.41	97
H(18)	6623.36	5544.82	3588.52	77
H(19A)	6909.21	440.31	6567.76	253
H(19B)	6972.88	332.75	5554.33	253
H(19C)	6326.54	704.24	5960.52	253
H(20A)	7830.26	2593.02	5967.46	192
H(20B)	7840.22	1497.99	5466.68	192
H(20C)	7839.43	1511.98	6488.16	192
H(21)	6833.35	2000.88	4651.08	289
H(22)	6314.06	3491.36	4591.17	165
H(23A)	6203.71	5182.48	6442.32	135
H(23B)	6151.2	5201.77	5422.91	135
H(23C)	6798.56	4900.16	5875.11	135
H(24A)	5314.81	2936.82	5945.18	156
H(24B)	5279.62	4041.11	5459.77	156
H(24C)	5314.79	4007.29	6480.16	156
H(26)	8304.88	4686.23	8568.21	70
H(27)	9069.14	3904.41	9437.89	85
H(28)	9083.21	2076.39	9623.45	93
H(29)	8332.51	1034.38	8932.66	90
H(30)	7556.76	1800.01	8062.29	76
H(32)	5813.54	3993.29	8087.45	84
H(33)	5122.17	4979.69	8910.22	109
H(34)	4301.26	4172.05	9637.25	110
H(35)	4159.34	2359.39	9511.52	98
H(36)	4814.33	1357.95	8639.68	78

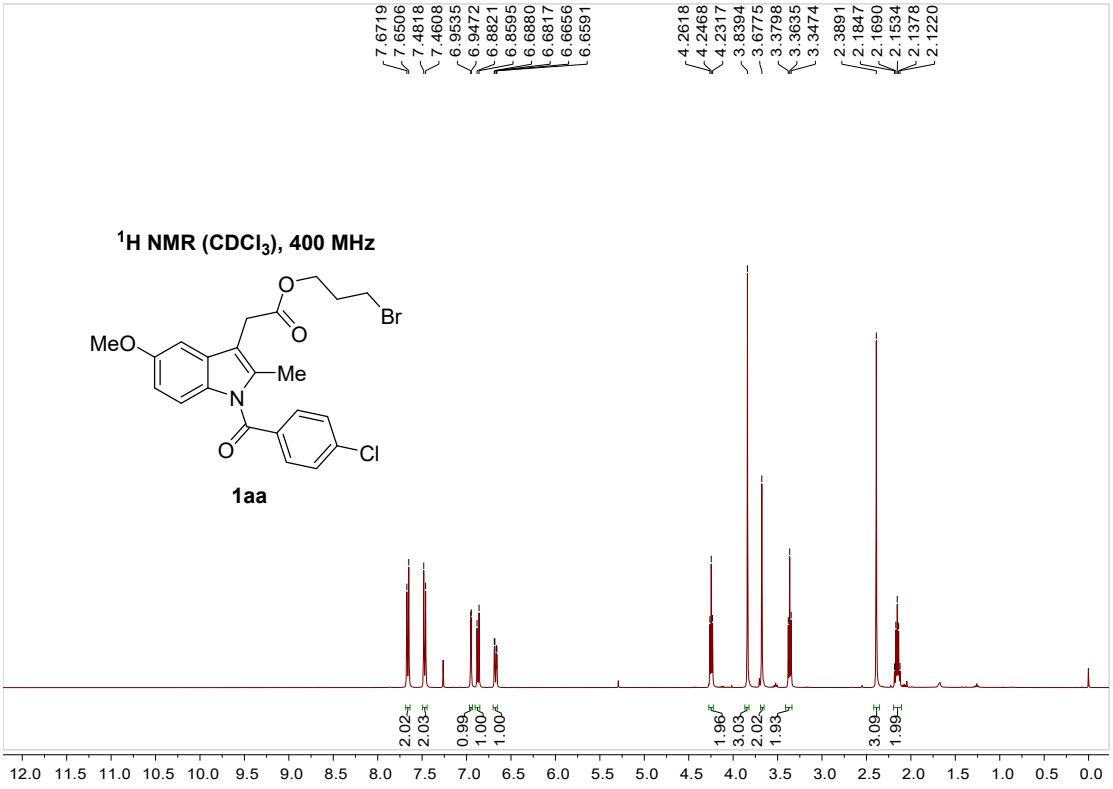
IX. References

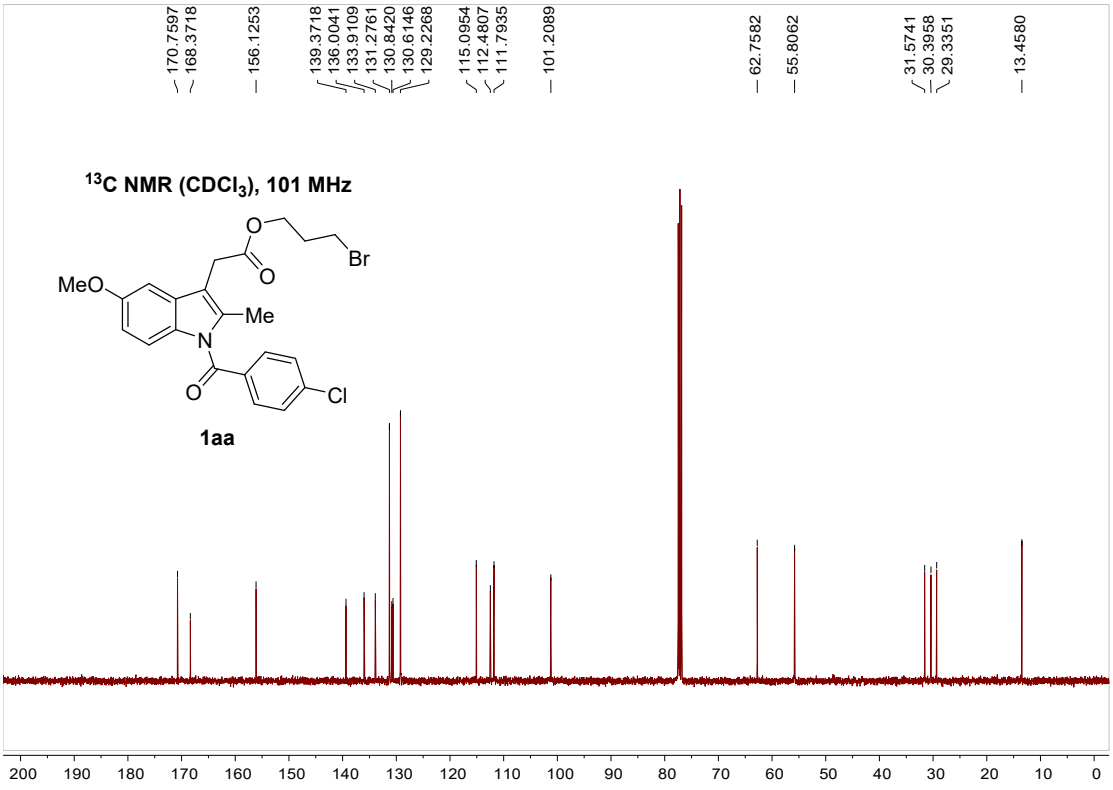
1. Xu, Y.; Zhang, Y.; Liu, Y.; Sun, W.; Huang, J.; He, H.; Wu, Y.; Liu, W.; Ni, S.; Xiao, X.; Shao, S., *Sci. China. Chem.* **2023**. Doi: 10.1007/s11426-023-1795-9.
2. Xing, S.; Zhu, Y.; Liu, W.; Liu, Y.; Zhang, J.; Zhang, H.; Wang, Y.; Ni, S.; Shao, X., *Org. Lett.* **2022**, *24*, 3378-3383.
3. Zhang, Y.; Fan, Q.; Ye, Z.; Xu, Y.; Cao, Y.; Liu, Y.; Liu, W.; Shao, X., *Cell. Rep. Phy Sci.* **2023**, *4*, 101696-101709.
4. Zhang, J.; Jiang, M.; Wang, C.; Guo, K.; Li, Q.; Ma, C.; Ni, S.; Chen, G.; Zong, Y.; Lu, H.; Xu, L.; Shao, X., *Nat. Commun.* **2022**, *13*, 7961-7970.
5. K., J.-d. A.; G., T. B., *Org. Lett.* **2011**, *4*, 2988-2991.
6. Wang, C.; Dong, G., *J. Am. Chem. Soc.* **2018**, *140*, 6057-6061.
7. Mampuys, P.; Zhu, Y.; Sergeyev, S.; Ruijter, E.; Orru, R.; Van Doorslaer, S.; Maes, B., *Org.Lett.* **2016**, *18*, 2808-2811.
8. Fang, Y.; Rogge, T.; Ackermann, L.; Wang, S.; Ji, S., *Nat. Commun.* **2018**, *9*, 2240-2249.
9. Xu, H.; Liang, Y.; Zhou, X.; Feng, Y., *Org. Biomol. Chem.* **2012**, *10*, 2562-2568.
10. Jones, C.; Schley, N., *Org. Biomol. Chem.* **2019**, *17*, 1744-1748.
11. Kennemur, J.; Kortman, G.; Hull, K., *J. Am. Chem. Soc.* **2016**, *138*, 11914-11919.
12. B., P. R.; B., M. S., *J. Am. Chem. Soc. 129*, 3068-3069.
13. Saito, K.; Kondo, K.; Akiyama, T., *Org. Lett.* **2015**, *17*, 3366-3369.
14. Meng, Y.; Wang, M.; Jiang, X., *CCS Chem.* **2021**, *3*, 17-24.
15. Shi, R.; Hu, X., *Angew. Chem. Int. Ed.* **2019**, *58*, 7454-7458.
16. Yang, Y.; Li, Y.; Lv, G.; He, D.; Li, J., *Org. Lett.* **2022**, *24*, 5115-5119.

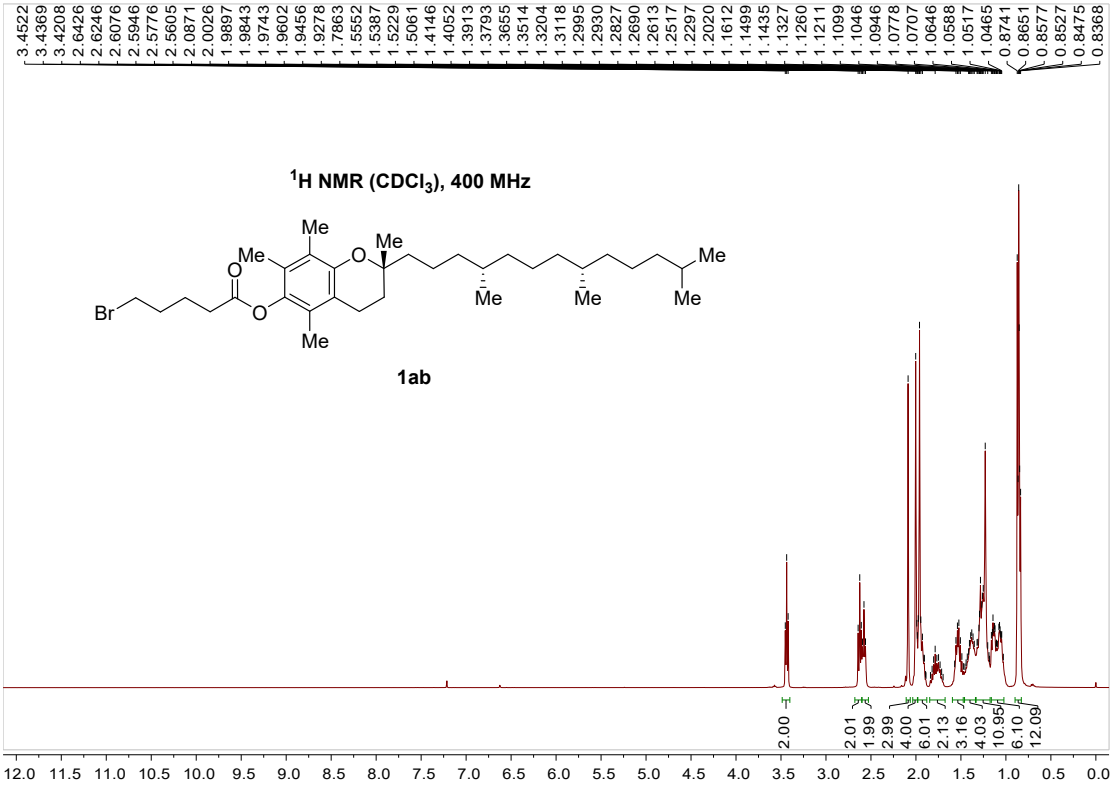
X. NMR spectra

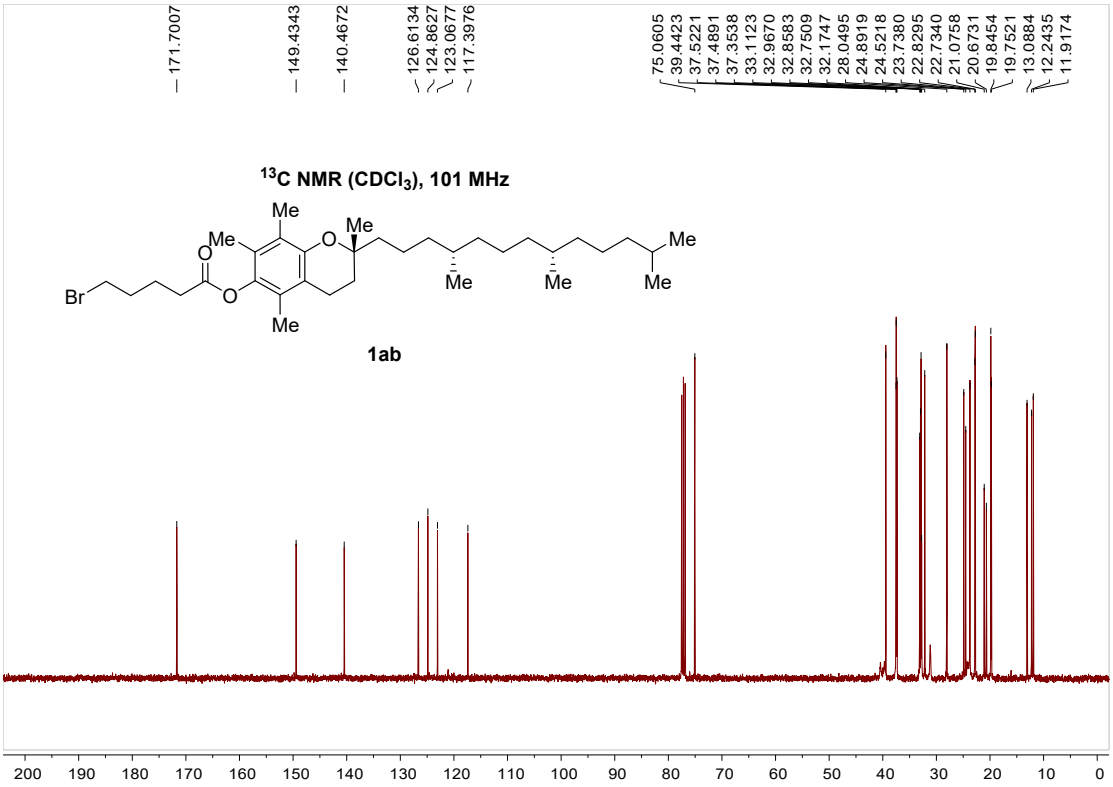


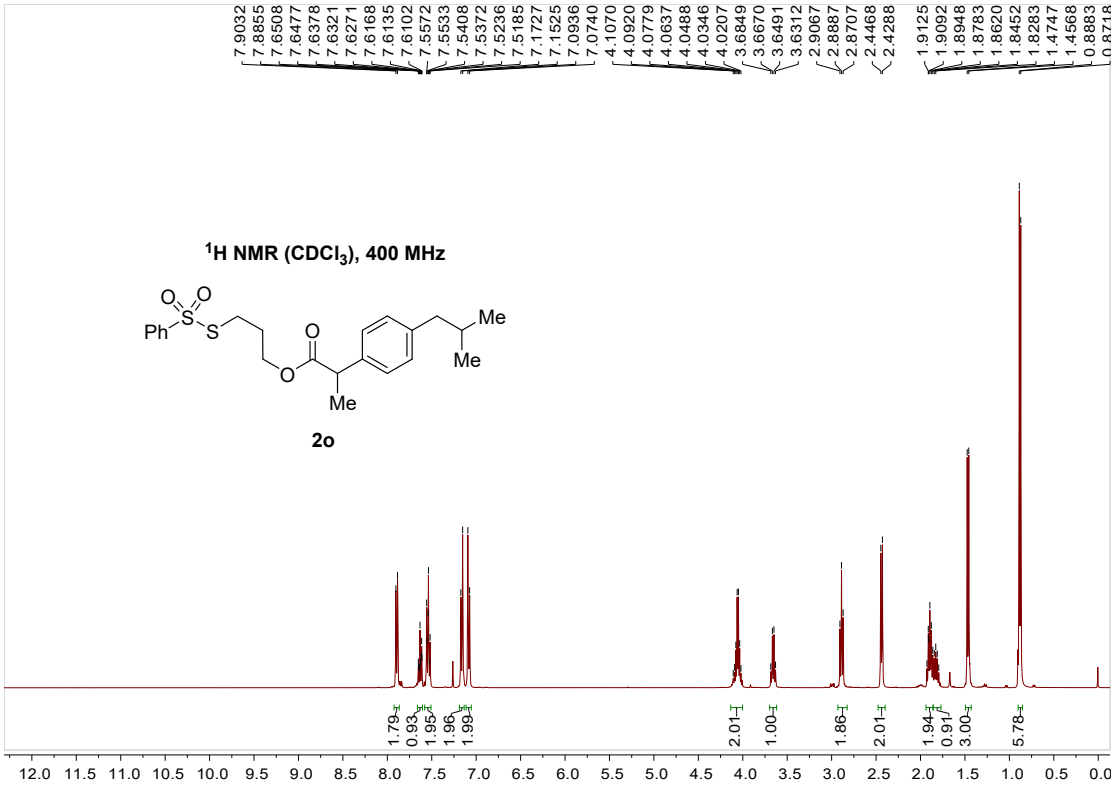


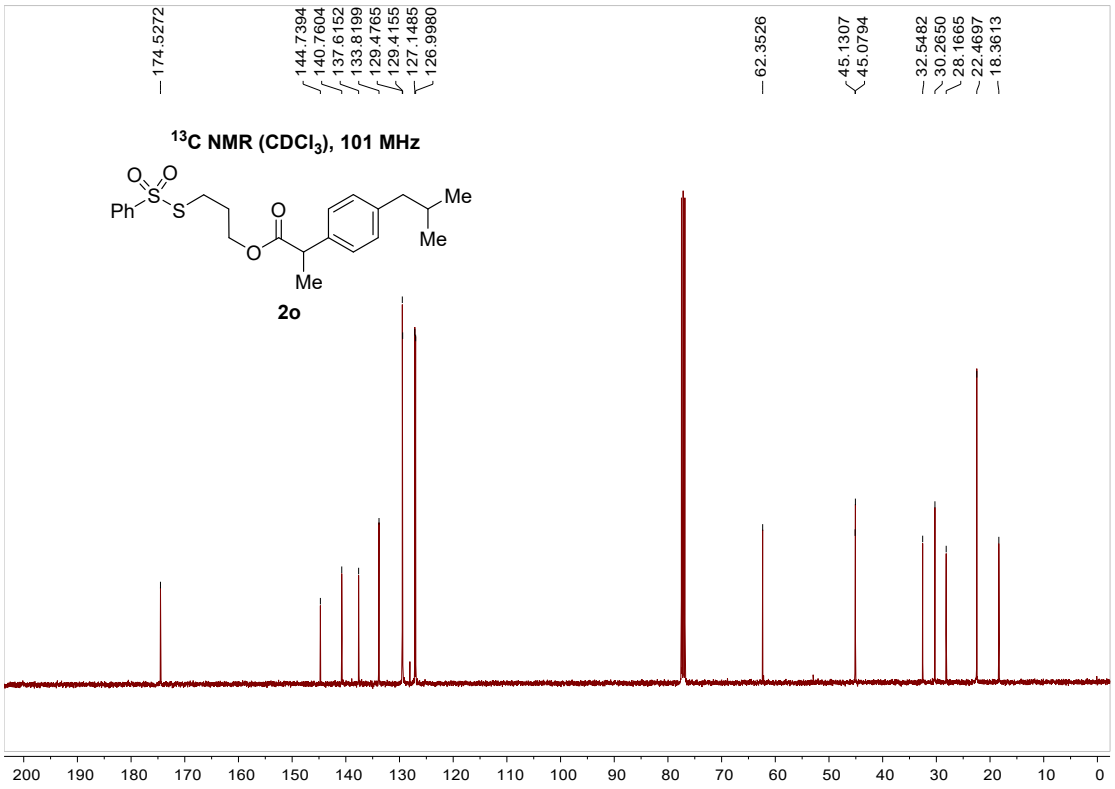

7.6719
7.6506
7.4818
7.4608
6.9535
6.9472
6.8821
6.8595
6.6880
6.6817
6.6656
6.6591
4.2618
4.2468
4.2317
3.8394
3.6775
3.3798
3.3635
3.3474
2.3891
2.1847
2.1690
2.1534
2.1378
2.1220
1H NMR (CDCl3), 400 MHz
MeO
Me
N
O
Br
Cl
1aa
2.02
2.03
0.99
1.00
1.00
1.96
3.03
2.02
1.93
3.09
1.99
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

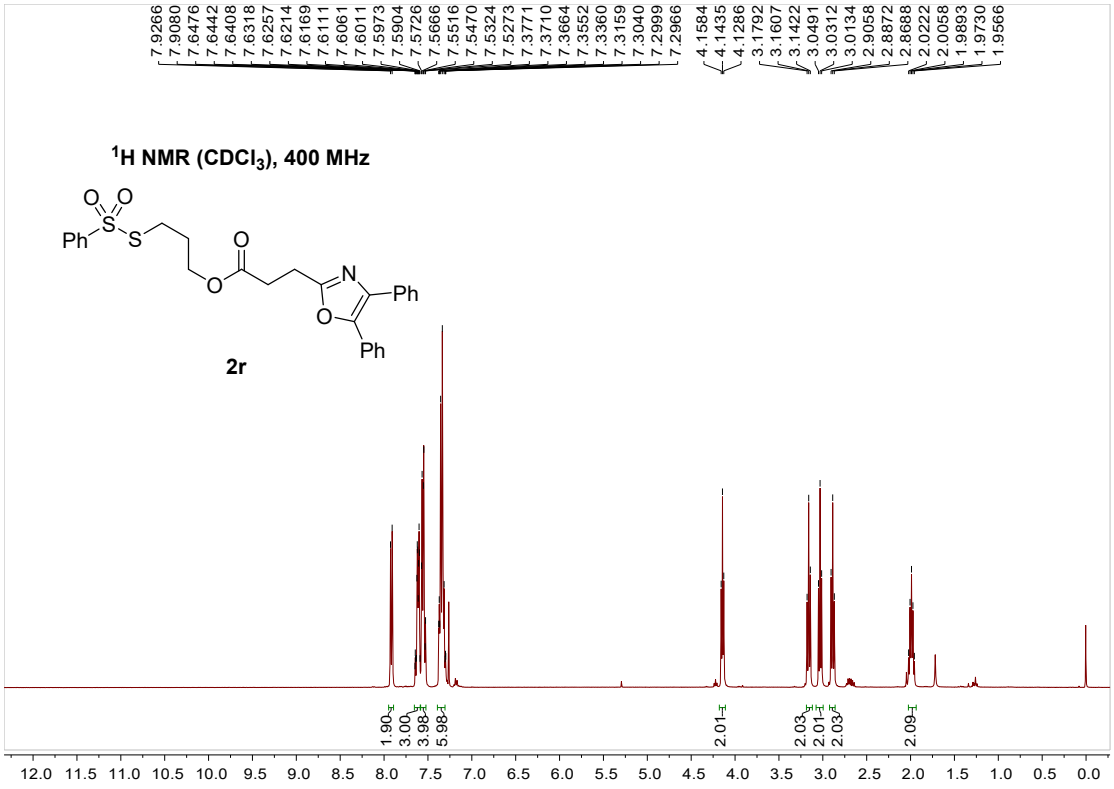

170.7597
168.3718
156.1253
139.3718
136.0041
133.9109
131.2761
130.8420
130.6146
129.2268
115.0954
112.4807
111.7935
101.2089
62.7582
55.8062
31.5741
30.3958
29.3351
13.4580
13C NMR (CDCl3), 101 MHz
MeO
Me
N
O
Br
Cl
1aa
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

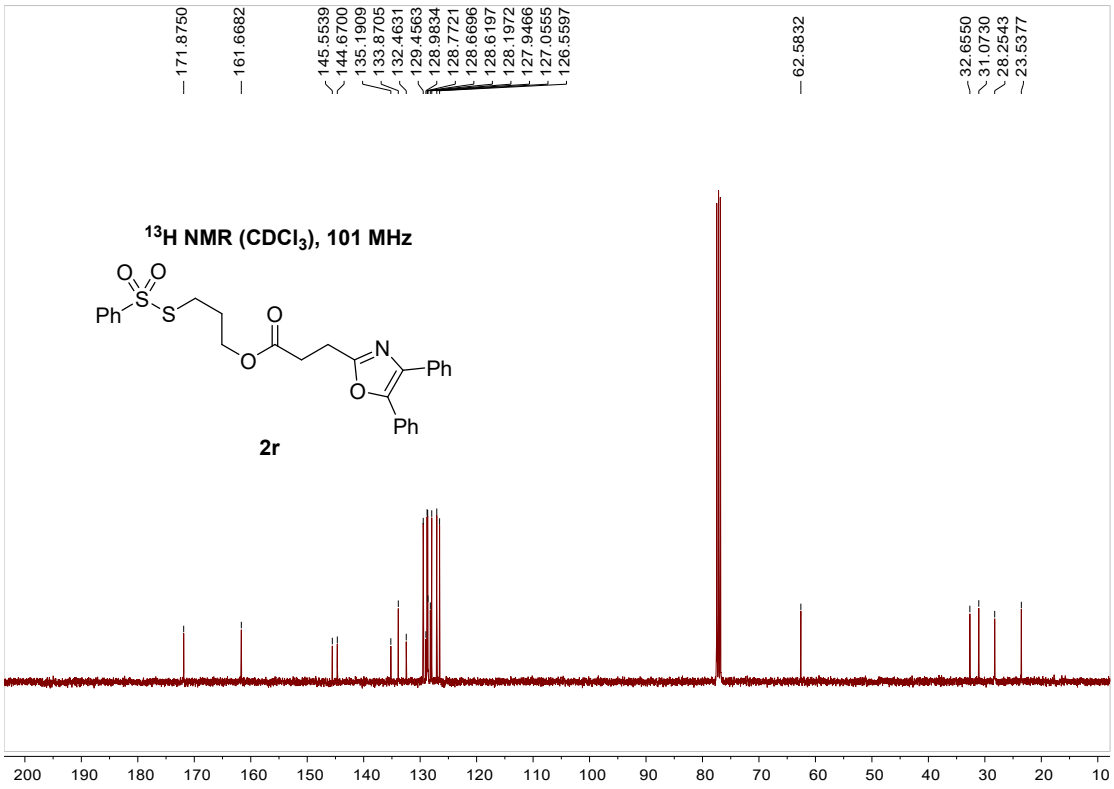

3.4522 3.4369 3.4208 2.6426 2.6246 2.6076 2.5946 2.5776 2.5605 2.0871 2.0026 1.9897 1.9843 1.9743 1.9602 1.9456 1.9278 1.7863 1.5552 1.5387 1.5229 1.5061 1.4146 1.4052 1.3913 1.3793 1.3655 1.3514 1.3204 1.3118 1.2995 1.2930 1.2827 1.2690 1.2613 1.2517 1.2297 1.2020 1.1612 1.1499 1.1435 1.1327 1.1260 1.1211 1.1099 1.1046 1.0946 1.0778 1.0707 1.0646 1.0588 1.0517 1.0465 0.8741 0.8651 0.8577 0.8527 0.8475 0.8368
^{1}H NMR ($CDCl_3$), 400 MHz
Me
Me
O
Me
O
Me
Me
Me
Me
Br
O
Me
1ab
2.00
2.01
1.99
2.99
4.00
6.01
2.13
3.16
4.03
10.95
6.10
12.09
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

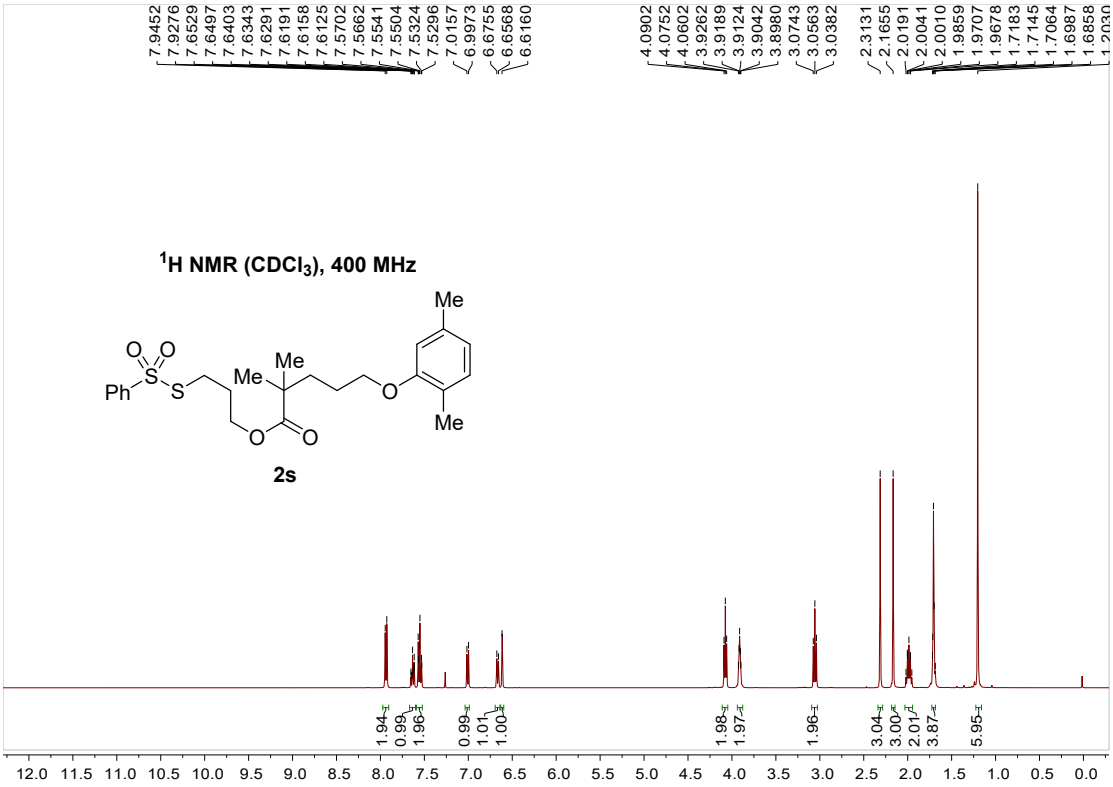

171.7007
149.4343
140.4672
126.6134
124.8627
123.0677
117.3976
75.0605
39.4423
37.5221
37.4891
37.3538
33.1123
32.9670
32.8583
32.7509
32.1747
28.0495
24.8919
24.5218
23.7380
22.8295
22.7340
21.0758
20.6731
19.8454
19.7521
13.0884
12.2435
11.9174
^{13}C NMR ($CDCl_3$), 101 MHz
Me
Me
O
Me
O
Me
Me
Me
Me
Br
O
Me
1ab
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

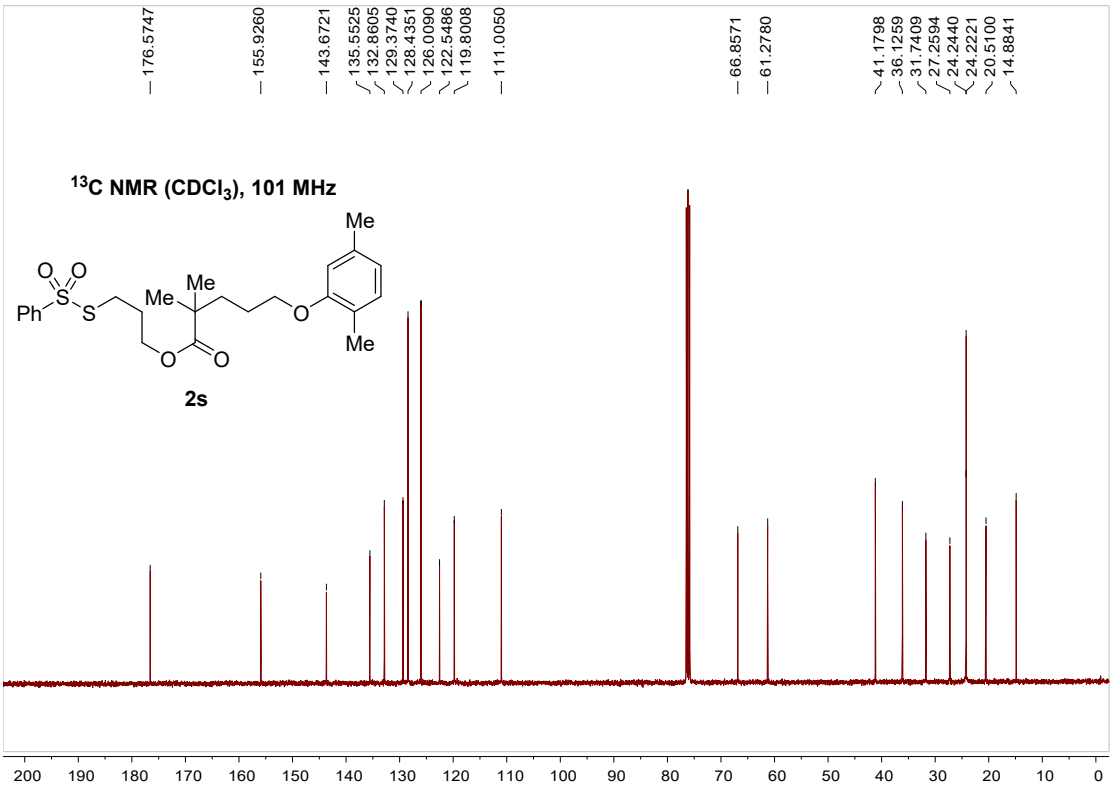

7.9032
7.8855
7.6508
7.6477
7.6378
7.6321
7.6271
7.6168
7.6135
7.6102
7.5572
7.5533
7.5408
7.5372
7.5236
7.5185
7.1727
7.1525
7.0936
7.0740
4.1070
4.0920
4.0779
4.0637
4.0488
4.0346
4.0207
3.6849
3.6670
3.6491
3.6312
2.9067
2.8887
2.8707
2.4468
2.4288
1.9125
1.9092
1.8948
1.8783
1.8620
1.8452
1.8283
1.4747
1.4568
0.8883
0.8718
1H NMR (CDCl3), 400 MHz
Ph
S
O
O
O
O
Me
Me
Me
2o
1.79
0.93
1.95
1.96
1.99
2.01
1.00
1.86
2.01
1.94
0.91
3.00
5.78
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

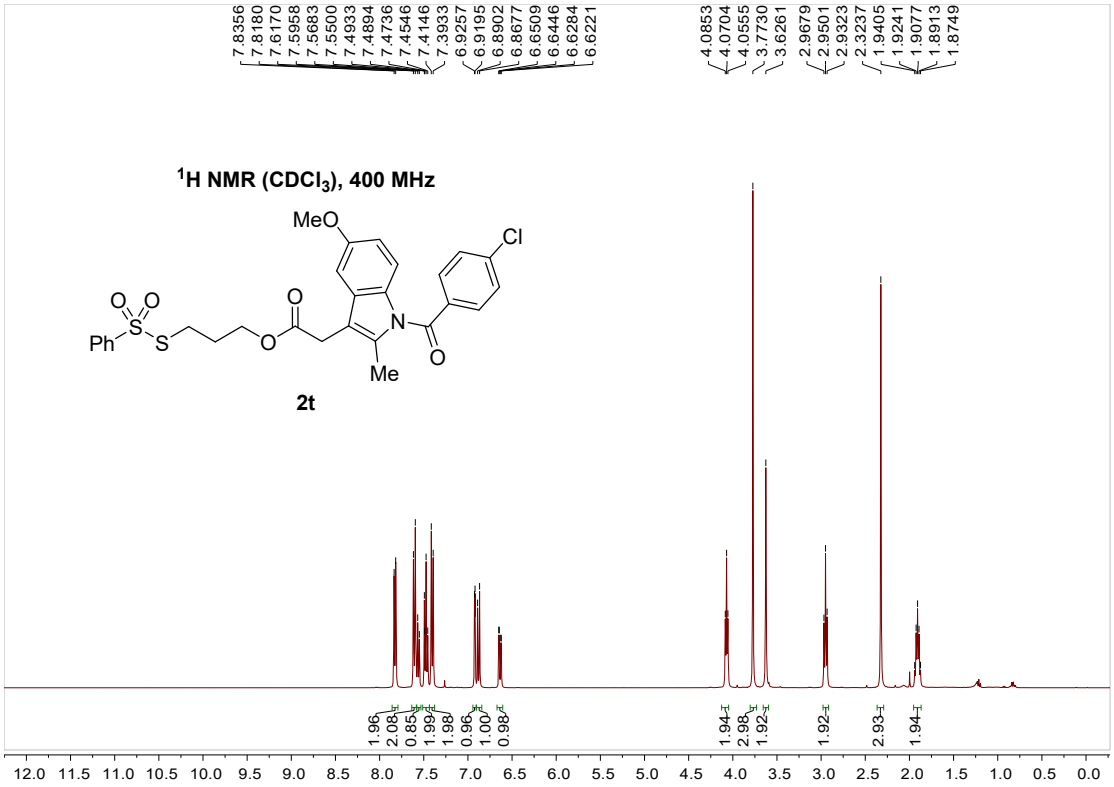

174.5272
144.7394
140.7604
137.6152
133.8199
129.4765
129.4155
127.1485
126.9980
62.3526
45.1307
45.0794
32.5482
30.2650
28.1665
22.4697
18.3613
13C NMR (CDCl3), 101 MHz
Ph
S
O
O
O
O
Me
Me
Me
2o
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

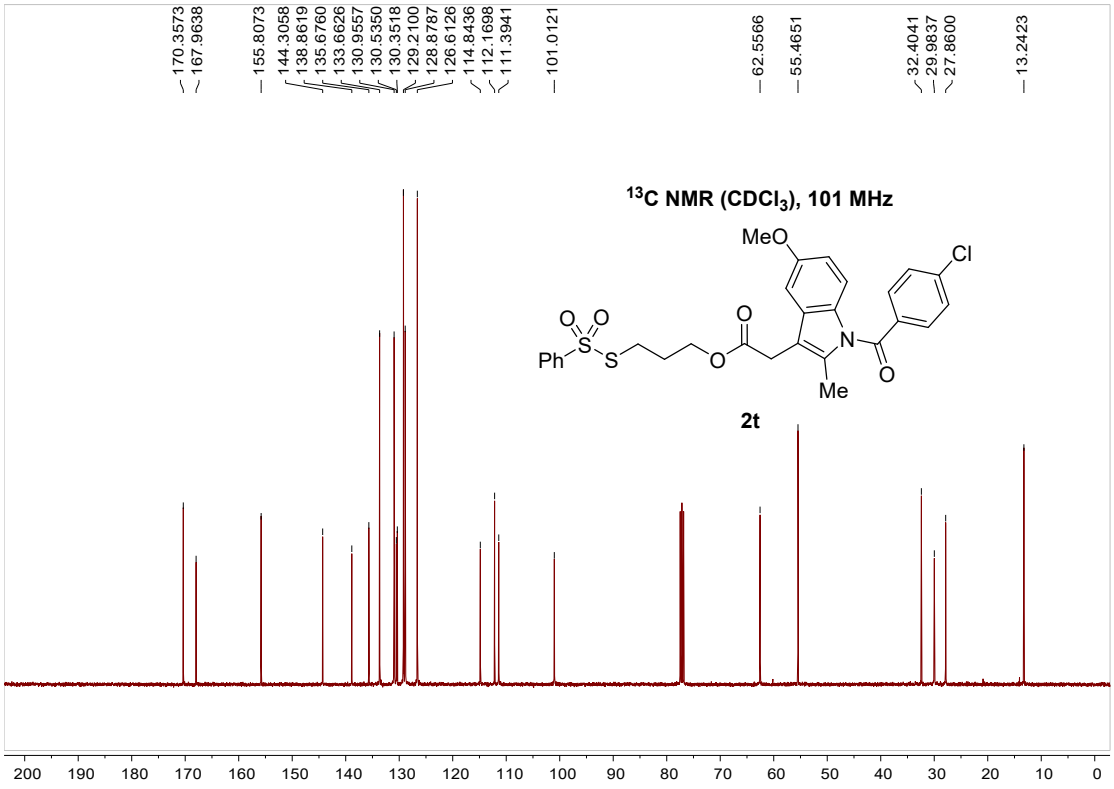

7.9266
7.9080
7.6476
7.6442
7.6408
7.6318
7.6257
7.6214
7.6169
7.6111
7.6061
7.6011
7.5973
7.5904
7.5726
7.5666
7.5516
7.5470
7.5324
7.5273
7.3771
7.3710
7.3664
7.3552
7.3360
7.3159
7.3040
7.2999
7.2966
4.1584
4.1435
4.1286
3.1792
3.1607
3.1422
3.0491
3.0312
3.0134
2.9058
2.8872
2.8688
2.0222
2.0058
1.9893
1.9730
1.9566
1H NMR (CDCl3), 400 MHz
Ph
S
O
O
O
O
N
Ph
O
Ph
2r
1.90
3.00
3.98
5.98
2.01
2.03
2.01
2.03
2.09
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

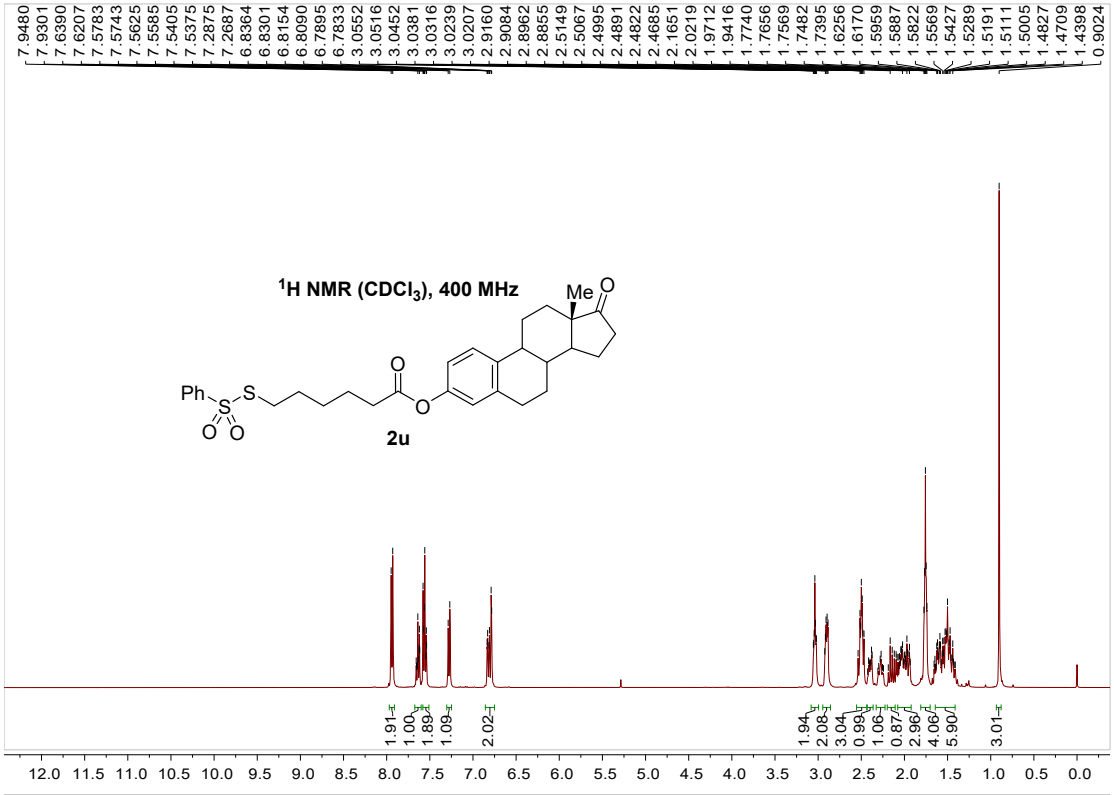

171.8750
161.6682
145.5539
144.6700
135.1909
133.8705
132.4631
129.4563
128.9834
128.7721
128.6696
128.6197
128.1972
127.9466
127.0555
126.5597
62.5832
32.6550
31.0730
28.2543
23.5377
13H NMR (CDCl3), 101 MHz
Ph
S
O
O
O
O
N
Ph
O
Ph
2r
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10

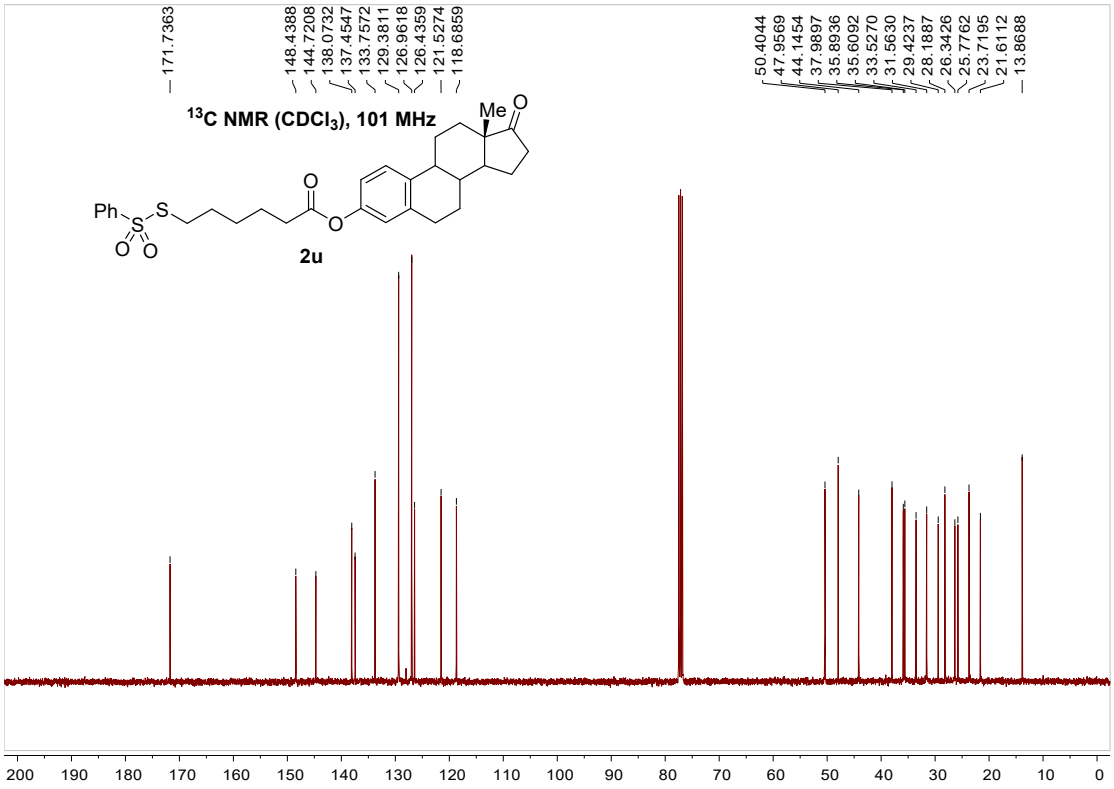

7.9452
7.9276
7.6529
7.6497
7.6403
7.6343
7.6291
7.6191
7.6158
7.6125
7.5702
7.5662
7.5541
7.5504
7.5324
7.5296
7.0157
6.9973
6.6755
6.6568
6.6160
4.0902
4.0752
4.0602
3.9262
3.9189
3.9124
3.9042
3.8980
3.0743
3.0563
3.0382
2.3131
2.1655
2.0191
2.0041
2.0010
1.9859
1.9707
1.9678
1.7183
1.7145
1.7064
1.6987
1.6858
1H NMR (CDCl3), 400 MHz
Me
Me
Me
Ph
S
O
O
O
O
Me
2s
1.94
0.99
1.96
0.99
1.01
1.00
1.98
1.97
1.96
3.04
3.00
2.01
3.87
5.95
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

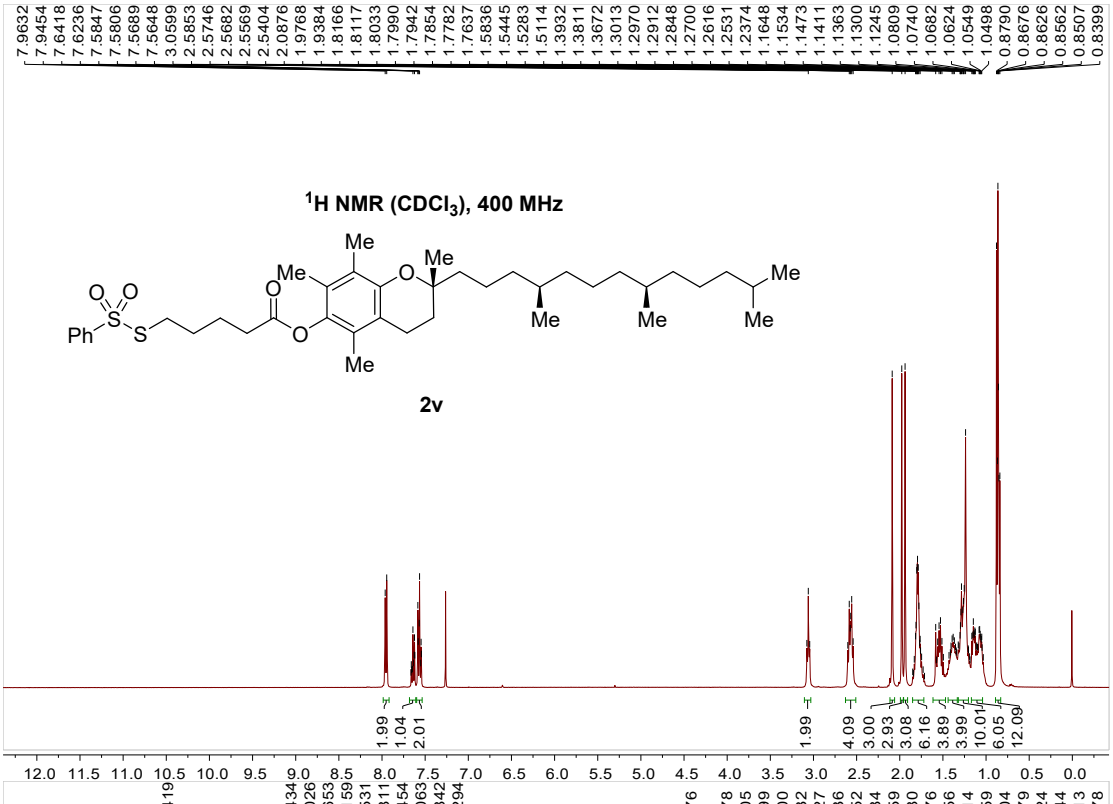

176.5747
155.9260
143.6721
135.5525
132.8605
129.3740
128.4351
126.0090
122.5486
119.8008
111.0050
66.8571
61.2780
41.1798
36.1259
31.7409
27.2594
24.2440
24.2221
20.5100
14.8841
13C NMR (CDCl3), 101 MHz
Me
Me
Me
Ph
S
O
O
O
O
Me
2s
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

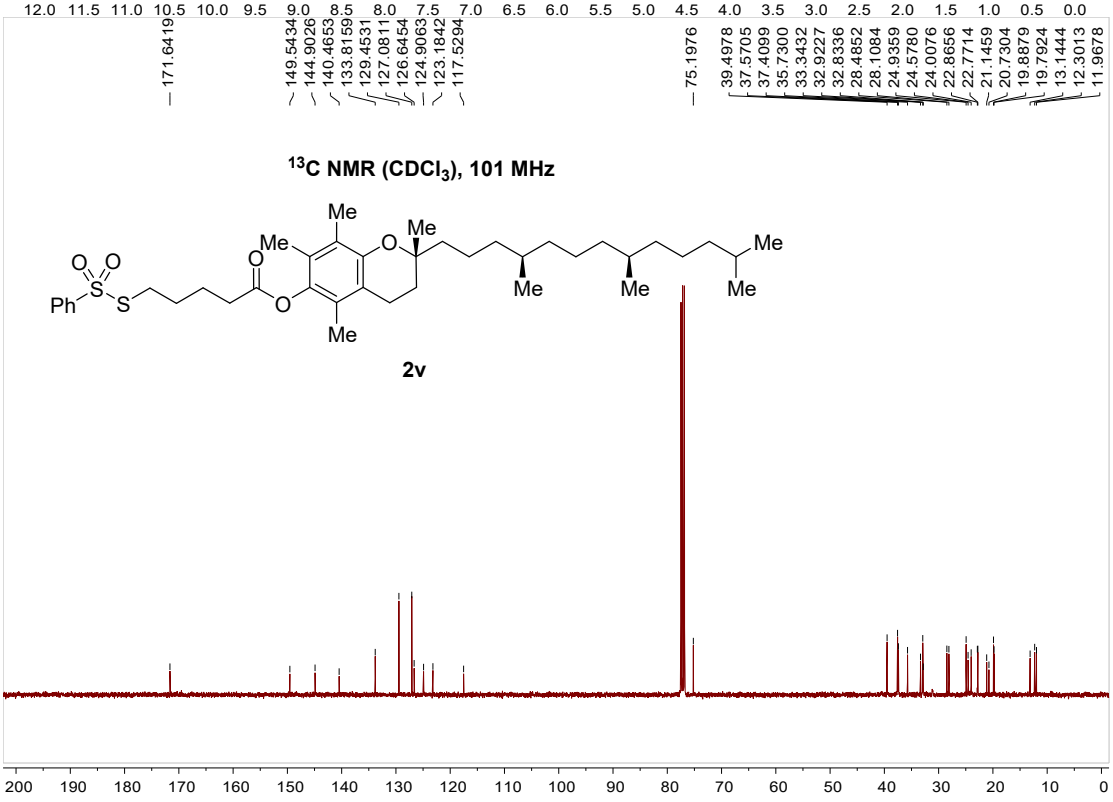

7.8356
7.8180
7.6170
7.5958
7.5683
7.5500
7.4933
7.4894
7.4736
7.4546
7.4146
7.3933
6.9257
6.9195
6.8902
6.8677
6.6509
6.6446
6.6284
6.6221
4.0853
4.0704
4.0555
3.7730
3.6261
2.9679
2.9501
2.9323
2.3237
1.9405
1.9241
1.9077
1.8913
1.8749
1H NMR (CDCl3), 400 MHz
MeO
Cl
O
O
Ph
S
S
O
O
N
O
Me
2t
1.96
2.08
0.85
1.99
1.98
0.96
1.00
0.98
1.94
2.98
1.92
1.92
2.93
1.94
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

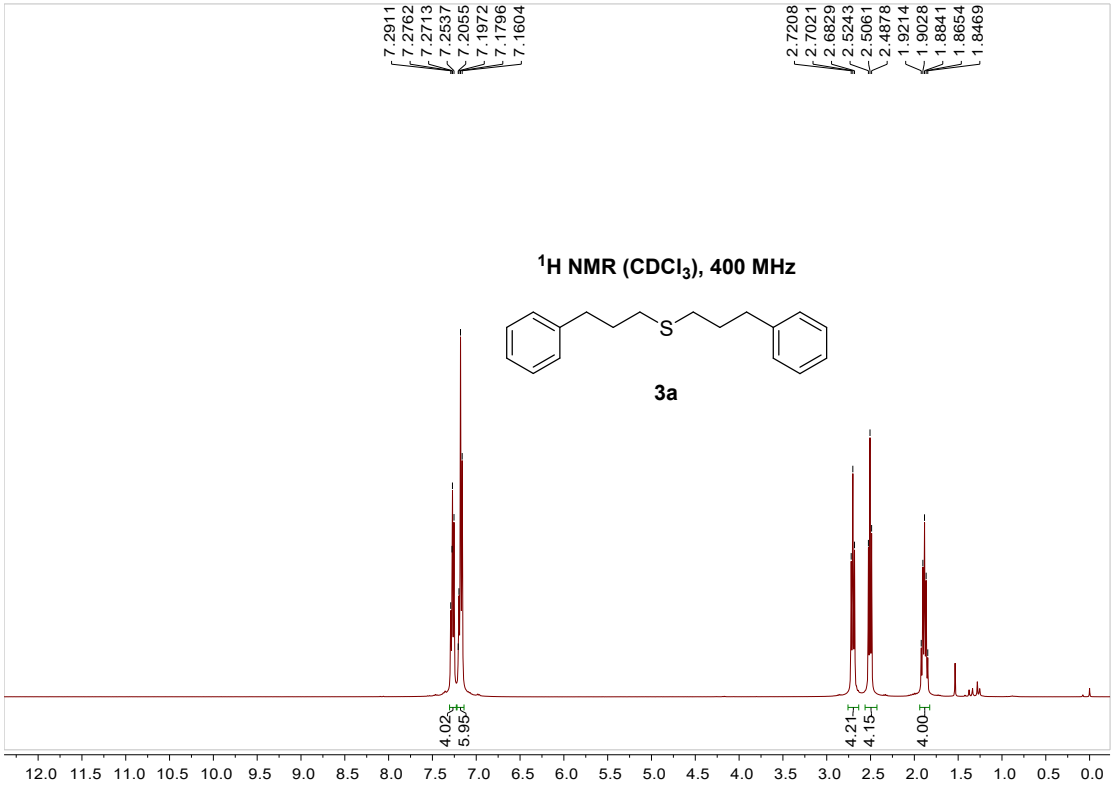

170.3573
167.9638
155.8073
144.3058
138.8619
135.6760
133.6626
130.9557
130.5350
130.3518
129.2100
128.8787
126.6126
114.8436
112.1698
111.3941
101.0121
62.5566
55.4651
32.4041
29.9837
27.8600
13.2423
13C NMR (CDCl3), 101 MHz
MeO
Cl
O
O
Ph
S
S
O
O
N
O
Me
2t
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

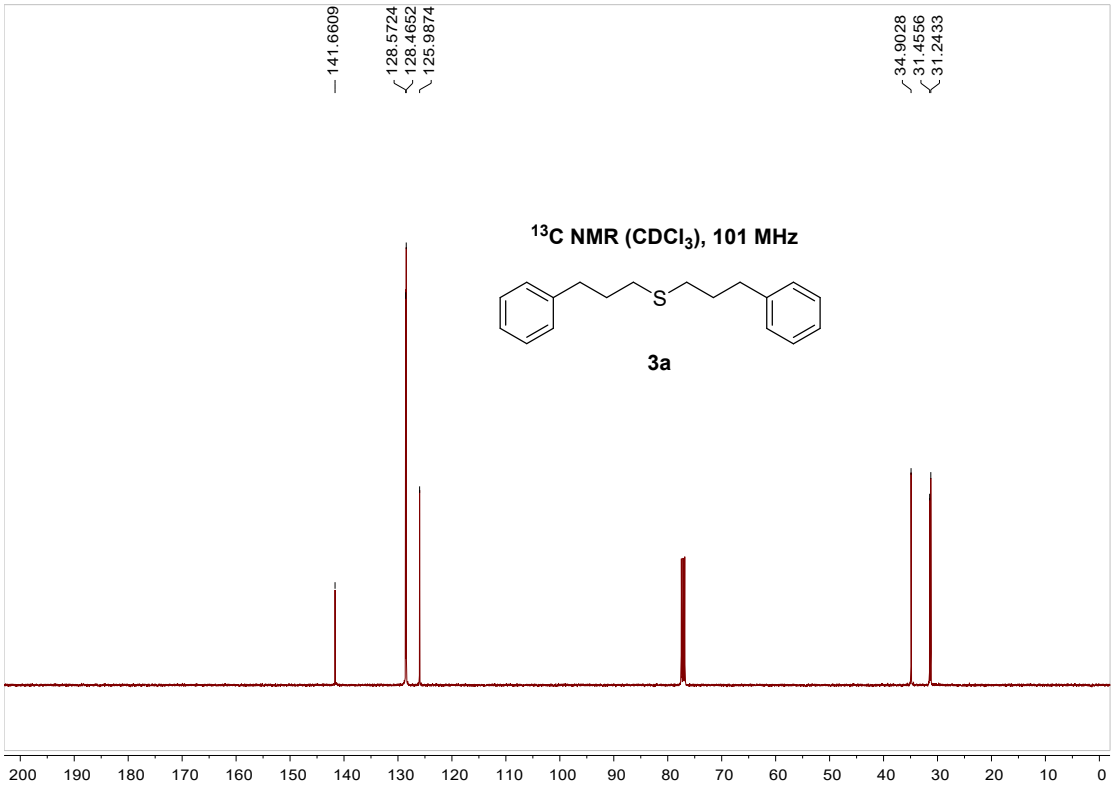

^{1}H NMR ($CDCl_3$), 400 MHz
2u

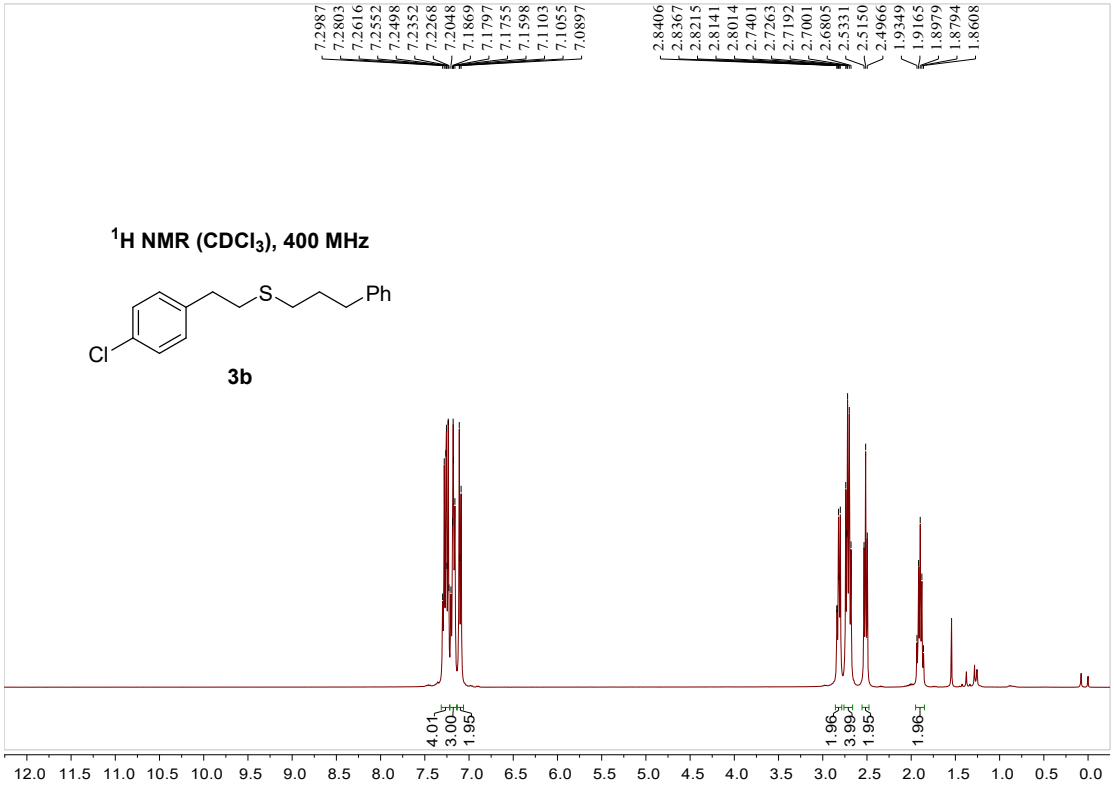

^{13}C NMR ($CDCl_3$), 101 MHz
2u


7.9632 7.9454 7.6418 7.6236 7.5847 7.5806 7.5689 7.5648 3.0599 2.5853 2.5746 2.5682 2.5569 2.5404 2.0876 1.9768 1.9384 1.8166 1.8117 1.8033 1.7990 1.7942 1.7854 1.7782 1.7637 1.5836 1.5445 1.5283 1.5114 1.3932 1.3811 1.3672 1.3013 1.2970 1.2912 1.2848 1.2700 1.2616 1.2531 1.2374 1.1648 1.1534 1.1473 1.1411 1.1363 1.1300 1.1245 1.0809 1.0740 1.0682 1.0624 1.0549 1.0498 0.8790 0.8676 0.8626 0.8562 0.8507 0.8399
1H NMR (CDCl3), 400 MHz
Me
Me
Me
O
O
O
O
Ph
S
S
O
Me
Me
Me
Me
Me
2v
1.99 1.04 2.01 1.99 4.09 3.00 2.93 3.08 6.16 3.89 3.99 10.01 6.05 12.09
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0


171.6419 149.5434 144.9026 140.4653 133.8159 129.4531 127.0811 126.6454 124.9063 123.1842 117.5294 75.1976 39.4978 37.5705 37.4099 35.7300 33.3432 32.9227 32.8336 28.4852 28.1084 24.9359 24.5780 24.0076 22.8656 22.7714 21.1459 20.7304 19.8879 19.7924 13.1444 12.3013 11.9678
13C NMR (CDCl3), 101 MHz
Me
Me
Me
O
O
O
O
Ph
S
S
O
Me
Me
Me
Me
Me
2v
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

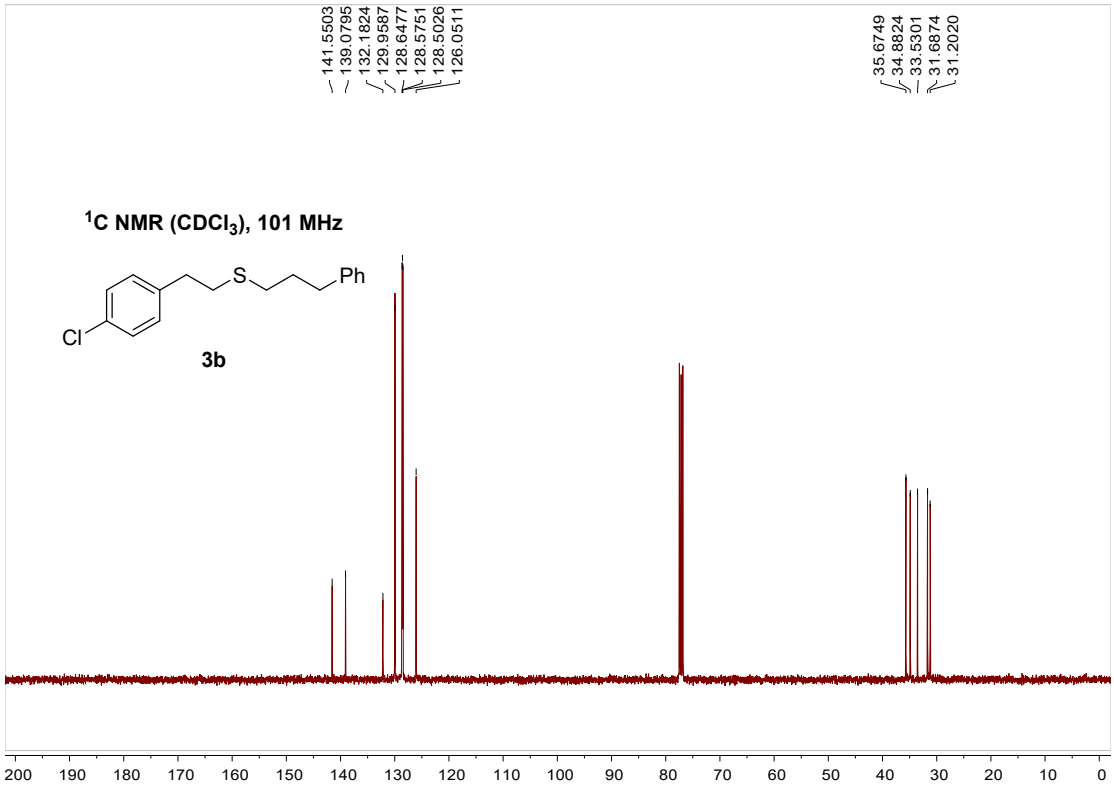

7.2911
7.2762
7.2713
7.2537
7.2055
7.1972
7.1796
7.1604
2.7208
2.7021
2.6829
2.5243
2.5061
2.4878
1.9214
1.9028
1.8841
1.8654
1.8469
^{1}H NMR ($CDCl_3$), 400 MHz
S
3a
4.02
5.95
4.21
4.15
4.00
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0


141.6609
128.5724
128.4652
125.9874
34.9028
31.4556
31.2433
^{13}C NMR ($CDCl_3$), 101 MHz
S
3a
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0



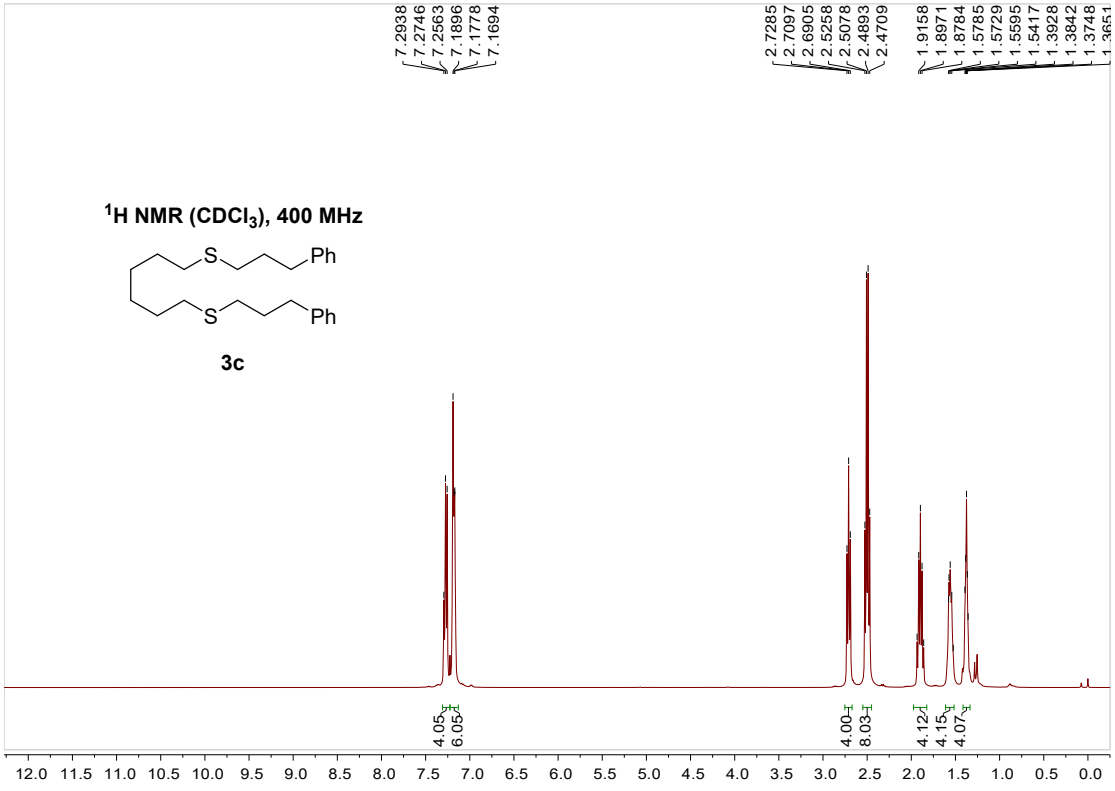
^{1}H NMR ($CDCl_3$), 400 MHz

3b



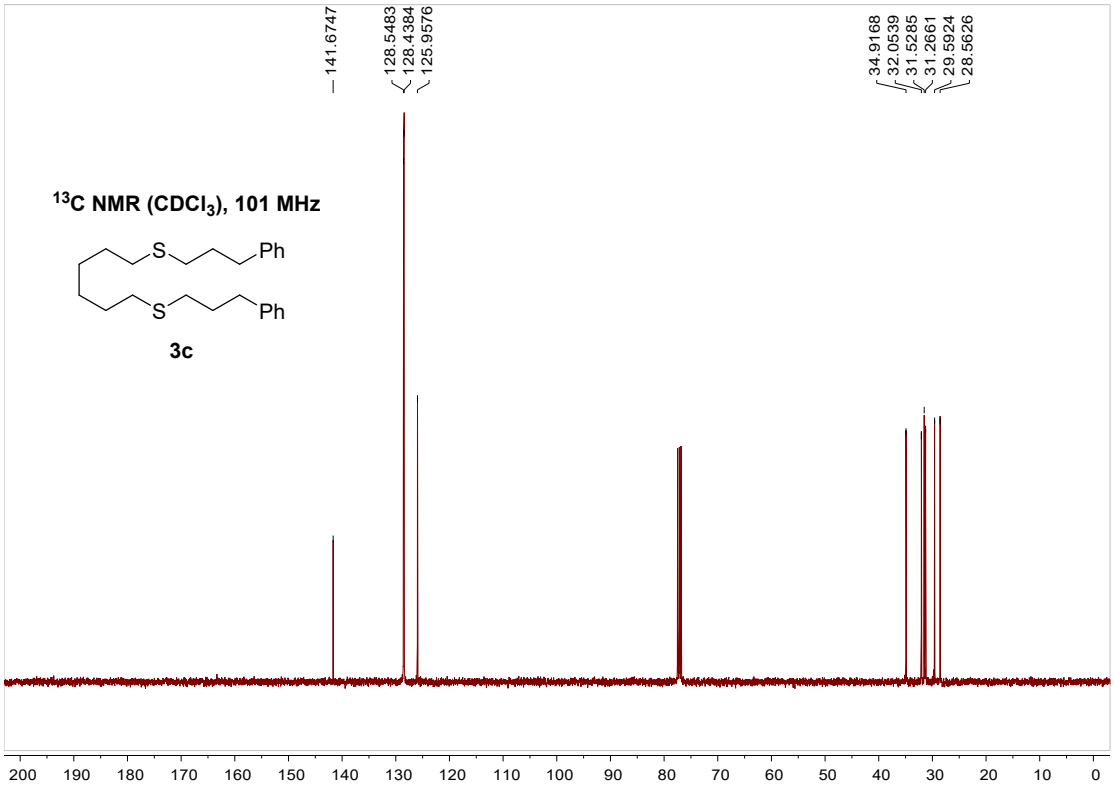
^{1}C NMR ($CDCl_3$), 101 MHz

3b



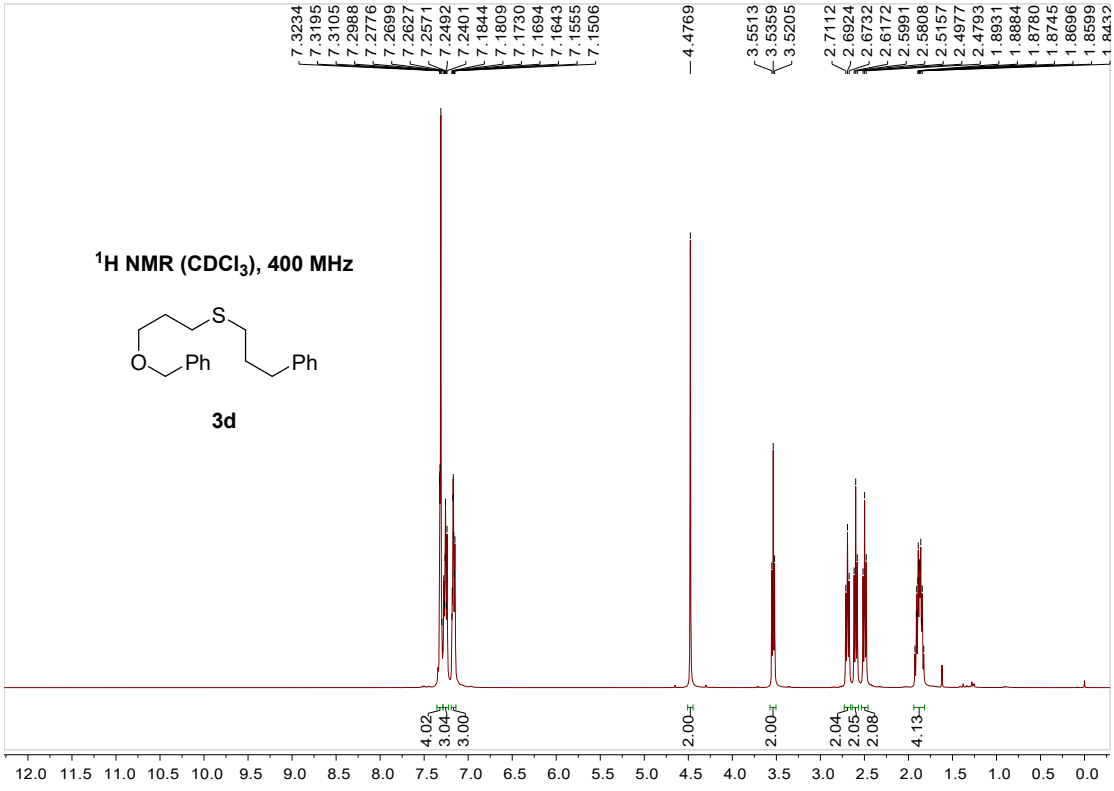
^{1}H NMR ($CDCl_3$), 400 MHz

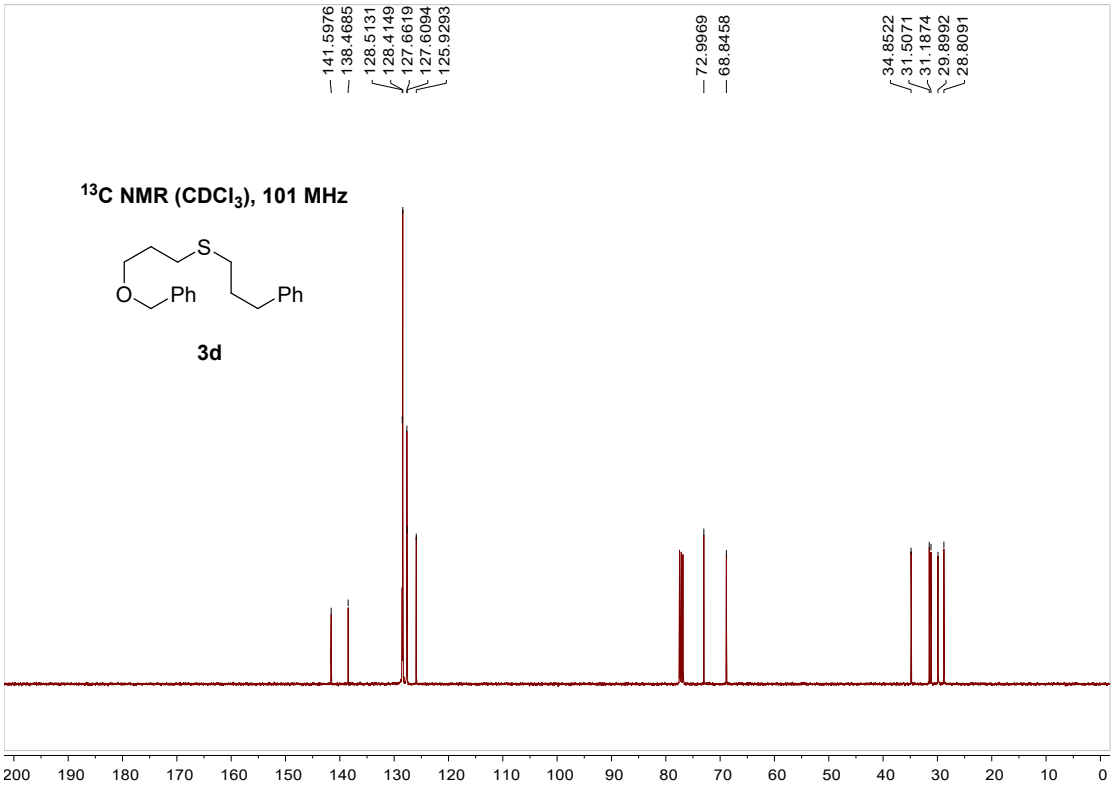
3c

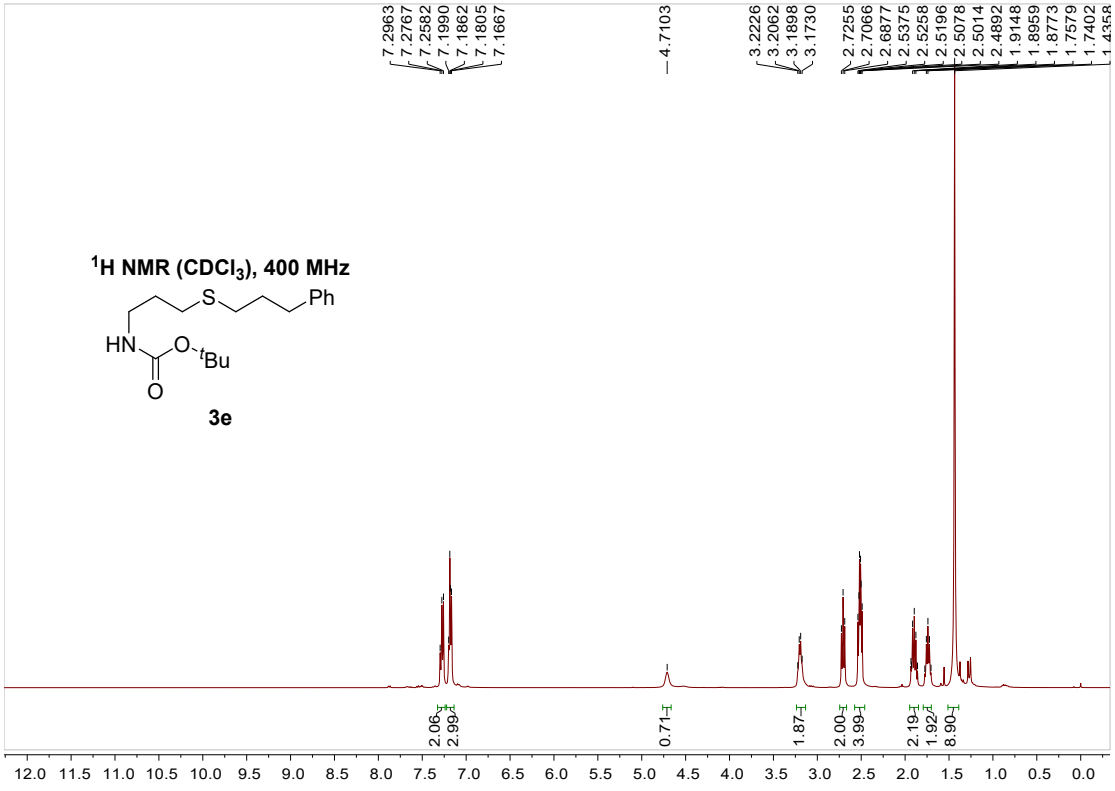


^{13}C NMR ($CDCl_3$), 101 MHz

3c

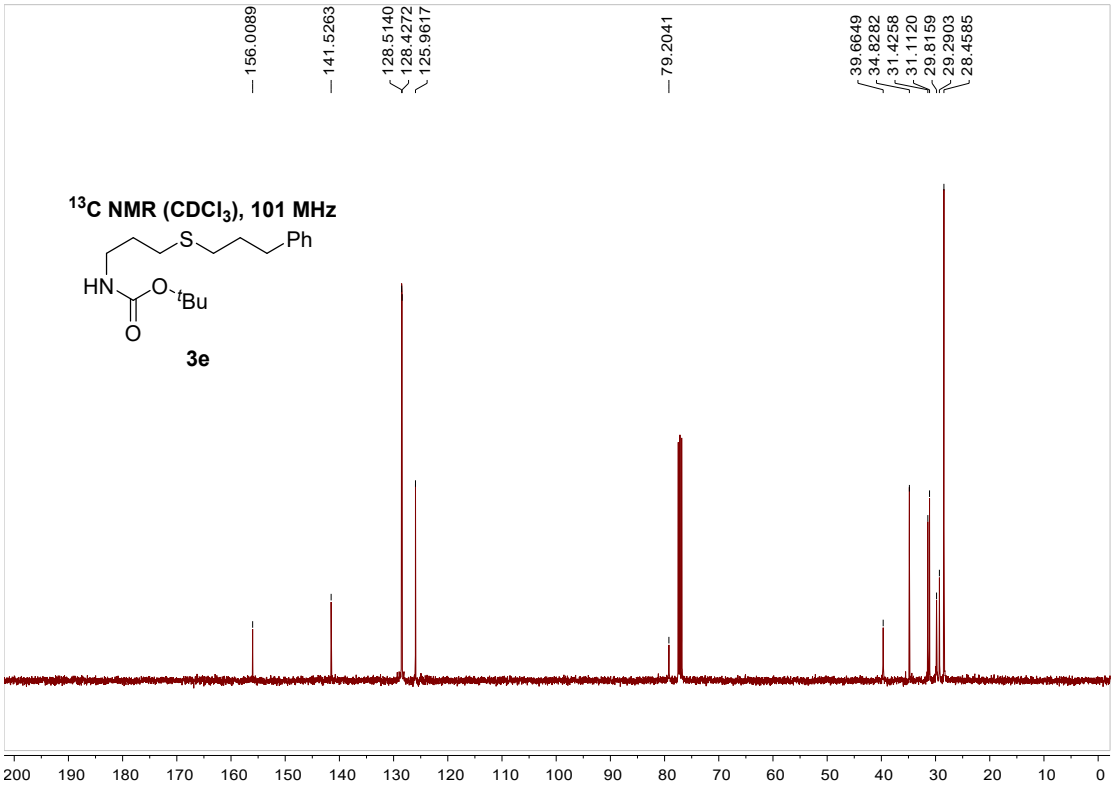

7.3234
7.3195
7.3105
7.2988
7.2776
7.2699
7.2627
7.2571
7.2492
7.2401
7.1844
7.1809
7.1730
7.1694
7.1643
7.1555
7.1506
4.4769
3.5513
3.5359
3.5205
2.7112
2.6924
2.6732
2.6172
2.5991
2.5808
2.5157
2.4977
2.4793
1.8931
1.8884
1.8780
1.8745
1.8696
1.8599
^{1}H NMR ($CDCl_3$), 400 MHz
S
O
Ph
Ph
3d
4.02
3.04
3.00
2.00
2.00
2.04
2.05
2.08
4.13
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0


141.5976
138.4685
128.5131
128.4149
127.6619
127.6094
125.9293
72.9969
68.8458
34.8522
31.5071
31.1874
29.8992
28.8091
^{13}C NMR ($CDCl_3$), 101 MHz
S
O
Ph
Ph
3d
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0



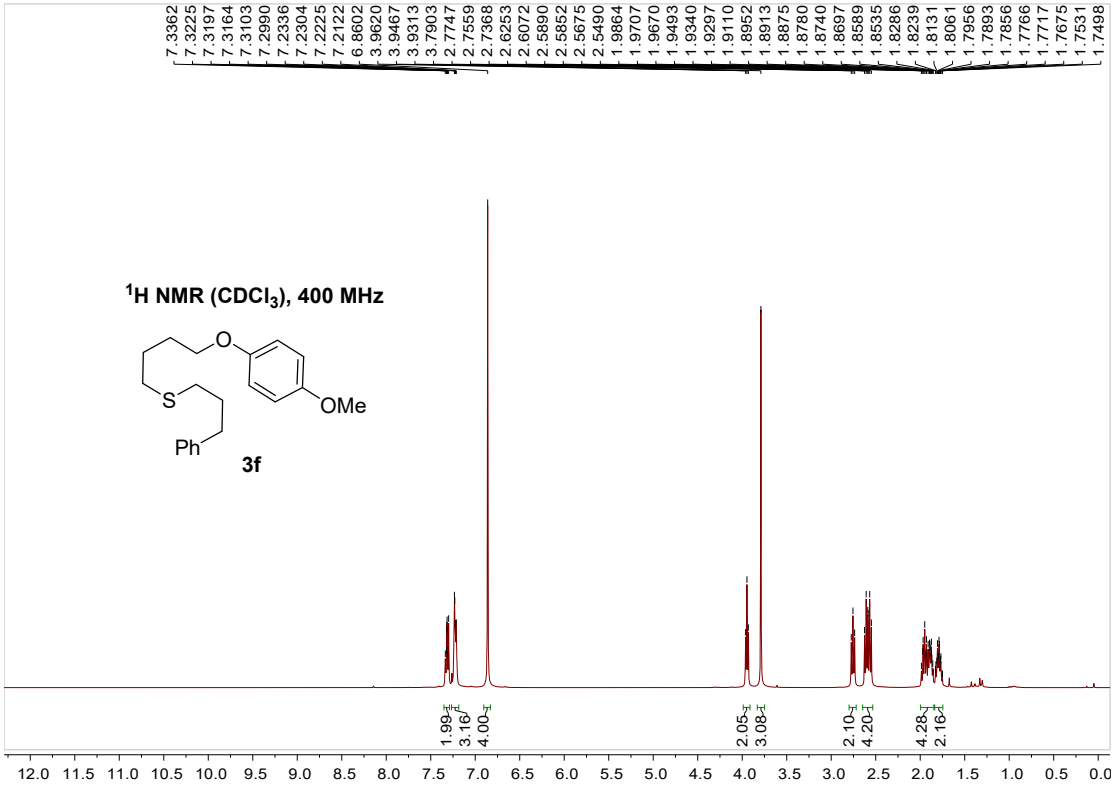
^{1}H NMR ($CDCl_3$), 400 MHz

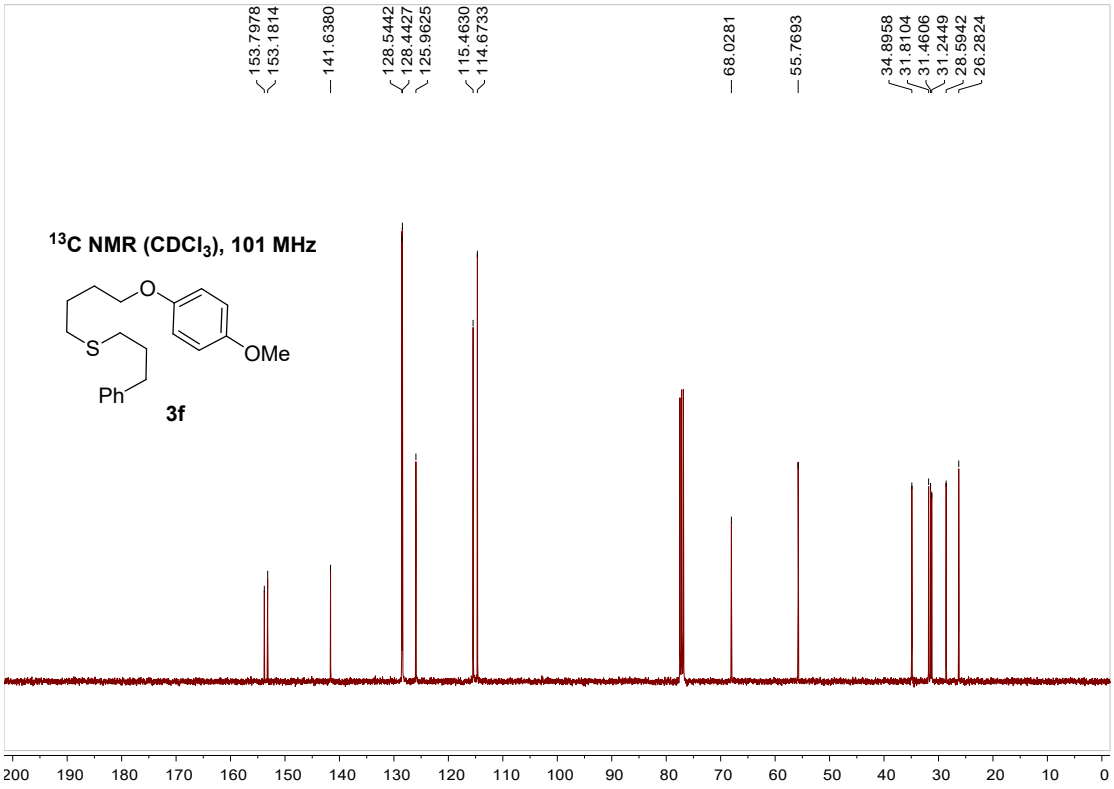
3e

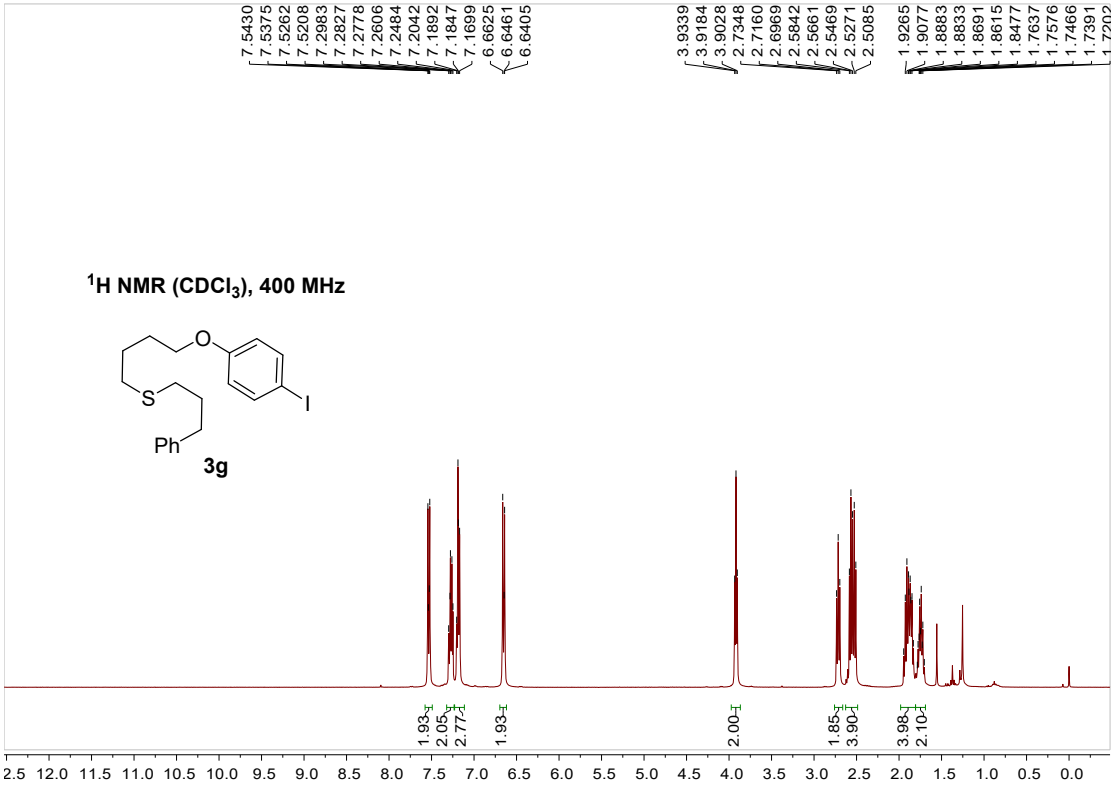


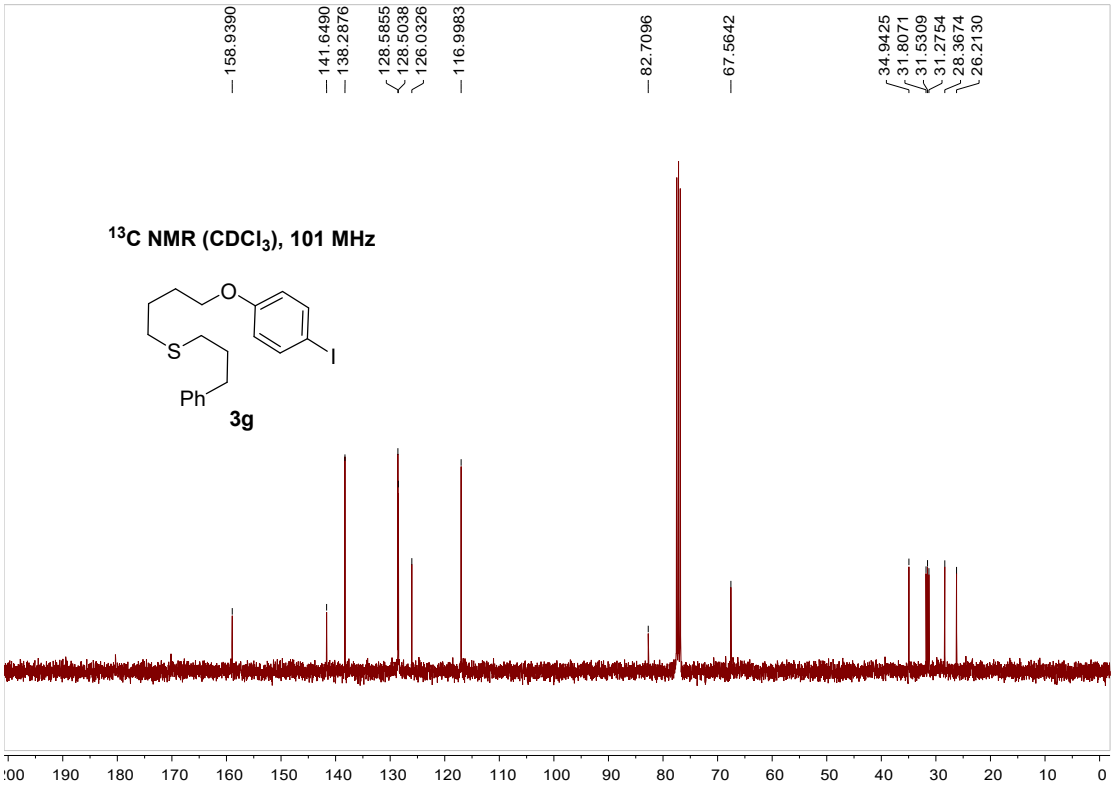
^{13}C NMR ($CDCl_3$), 101 MHz

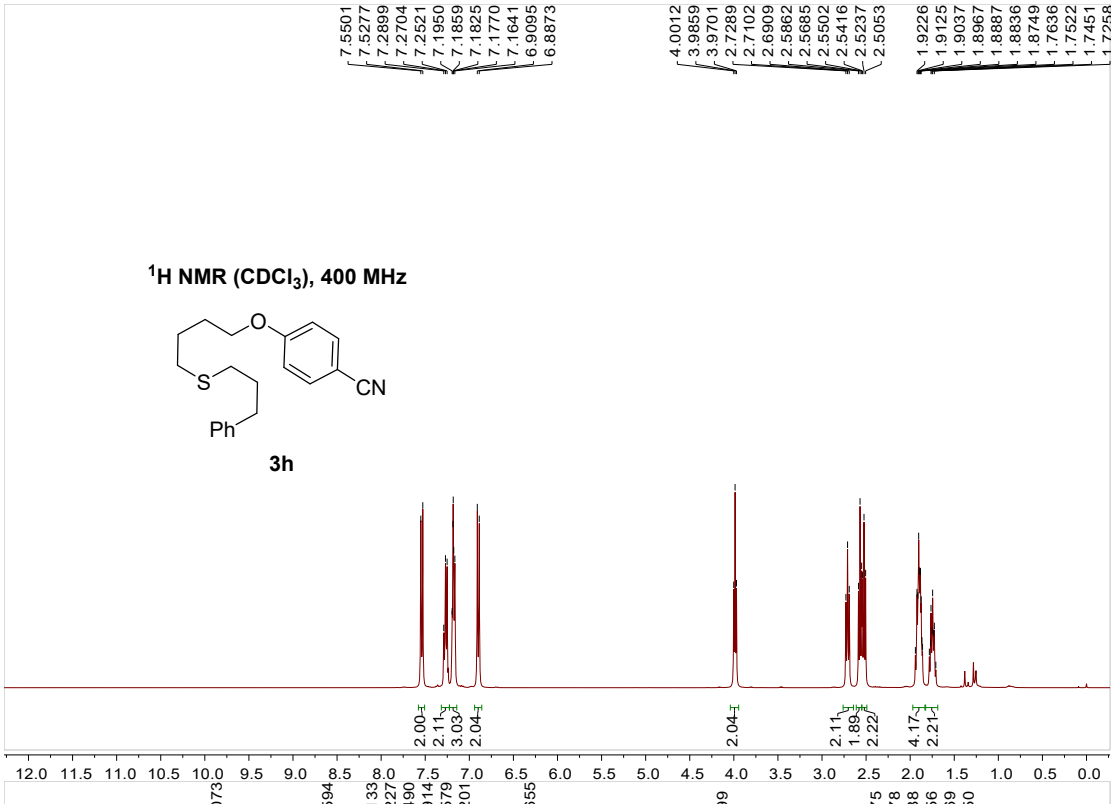
3e

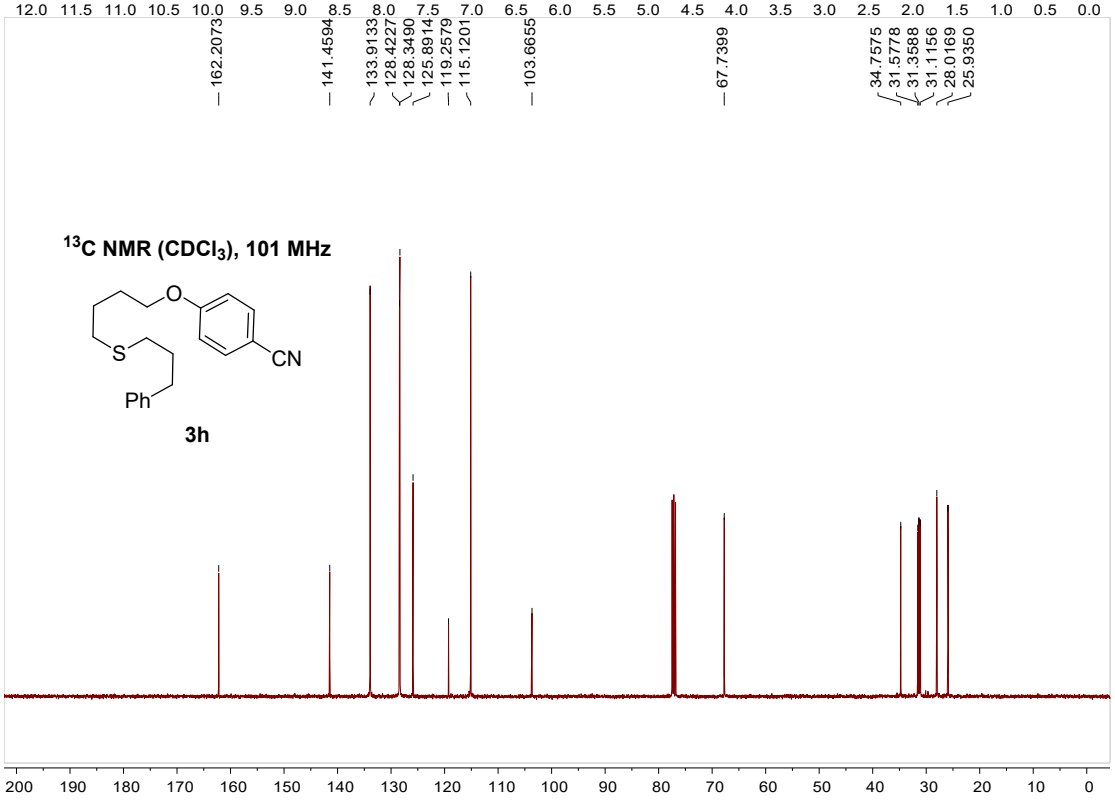

^{1}H NMR ($CDCl_3$), 400 MHz
O
S
OMe
Ph
3f

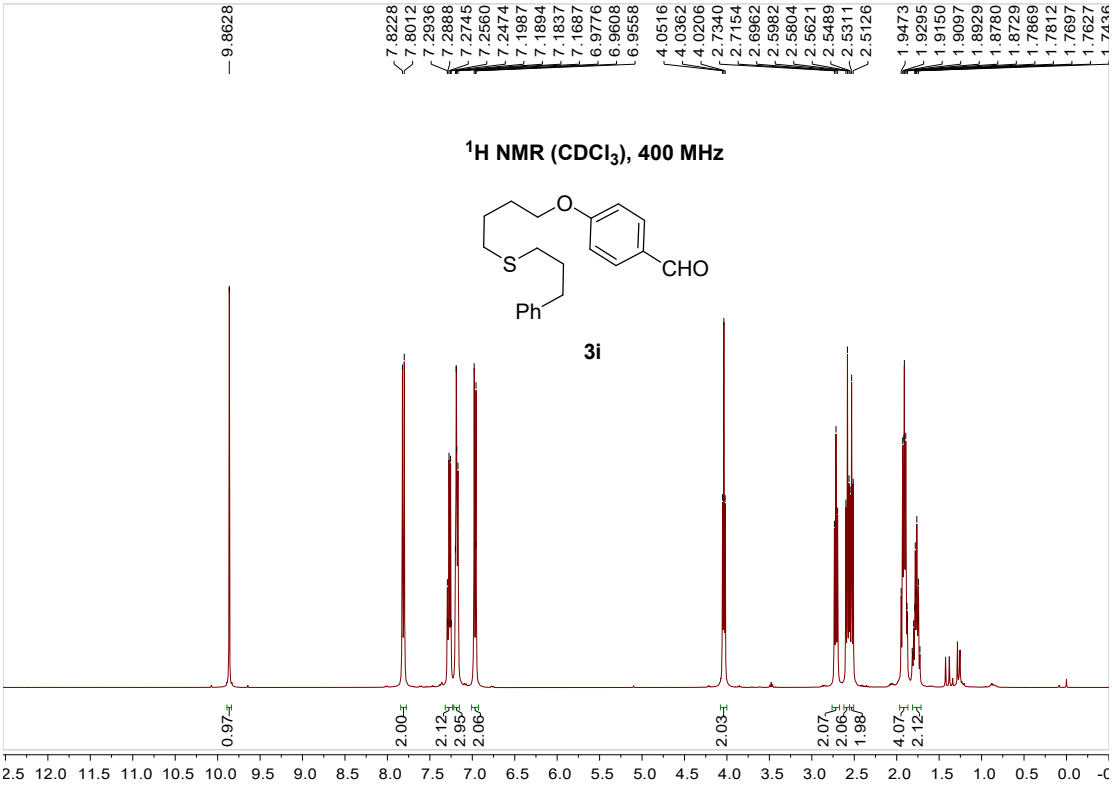

^{13}C NMR ($CDCl_3$), 101 MHz
O
S
OMe
Ph
3f

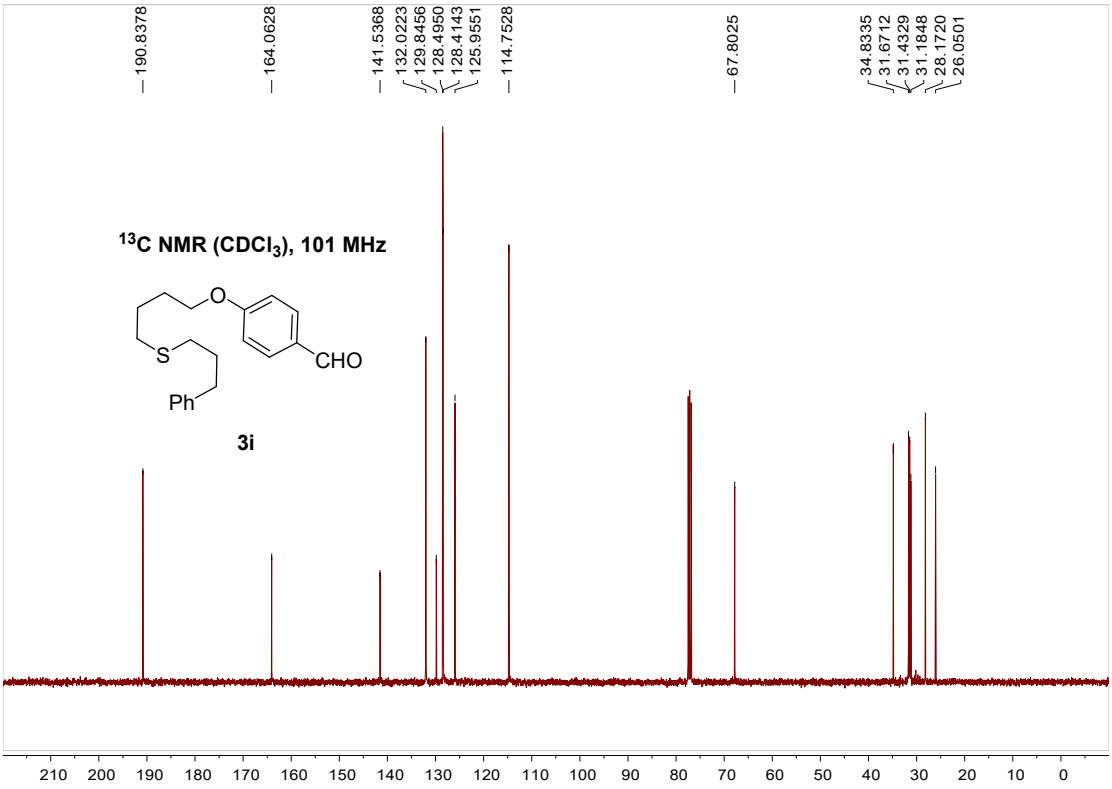

7.5430
7.5375
7.5262
7.5208
7.2983
7.2827
7.2778
7.2606
7.2484
7.2042
7.1892
7.1847
7.1699
6.6625
6.6461
6.6405
3.9339
3.9184
3.9028
2.7348
2.7160
2.6969
2.5842
2.5661
2.5469
2.5271
2.5085
1.9265
1.9077
1.8883
1.8833
1.8691
1.8615
1.8477
1.7637
1.7576
1.7466
1.7391
1.7202
^{1}H NMR (CDCl$_3$), 400 MHz
O
S
I
Ph
3g
1.93
2.05
2.77
1.93
2.00
1.85
3.90
3.98
2.10
2.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

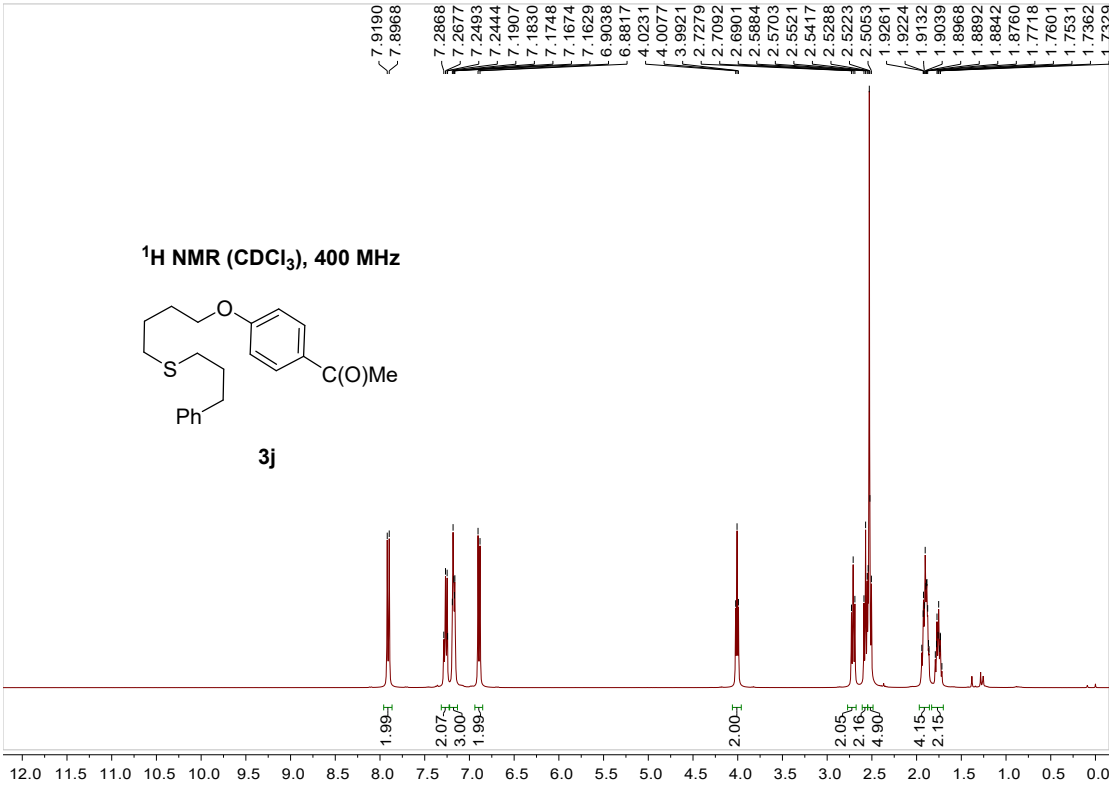

158.9390
141.6490
138.2876
128.5855
128.5038
126.0326
116.9983
82.7096
67.5642
34.9425
31.8071
31.5309
31.2754
28.3674
26.2130
^{13}C NMR (CDCl$_3$), 101 MHz
O
S
I
Ph
3g
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

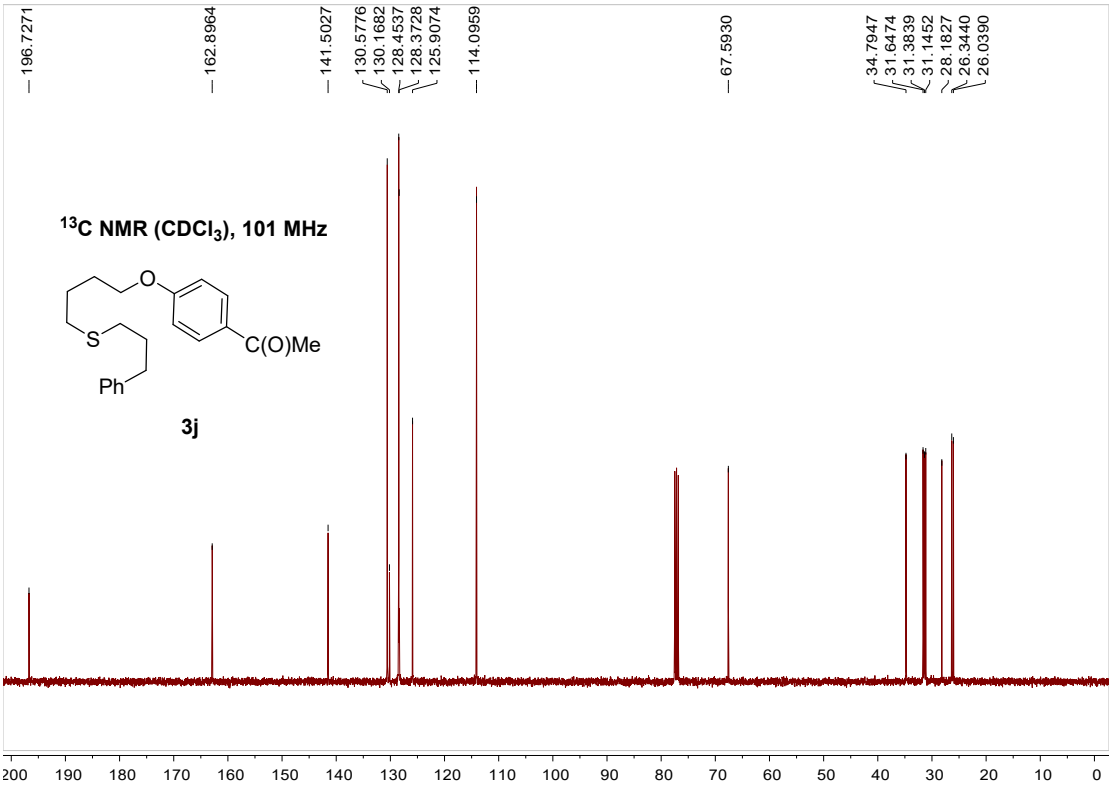

7.5501
7.5277
7.2899
7.2704
7.2521
7.1950
7.1859
7.1825
7.1770
7.1641
6.9095
6.8873
4.0012
3.9859
3.9701
2.7289
2.7102
2.6909
2.5862
2.5685
2.5502
2.5416
2.5237
2.5053
1.9226
1.9125
1.9037
1.8967
1.8887
1.8836
1.8749
1.7636
1.7522
1.7451
^{1}H NMR ($CDCl_3$), 400 MHz
O
S
CN
Ph
3h
2.00
2.11
3.03
2.04
2.04
2.11
1.89
2.22
4.17
2.21
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

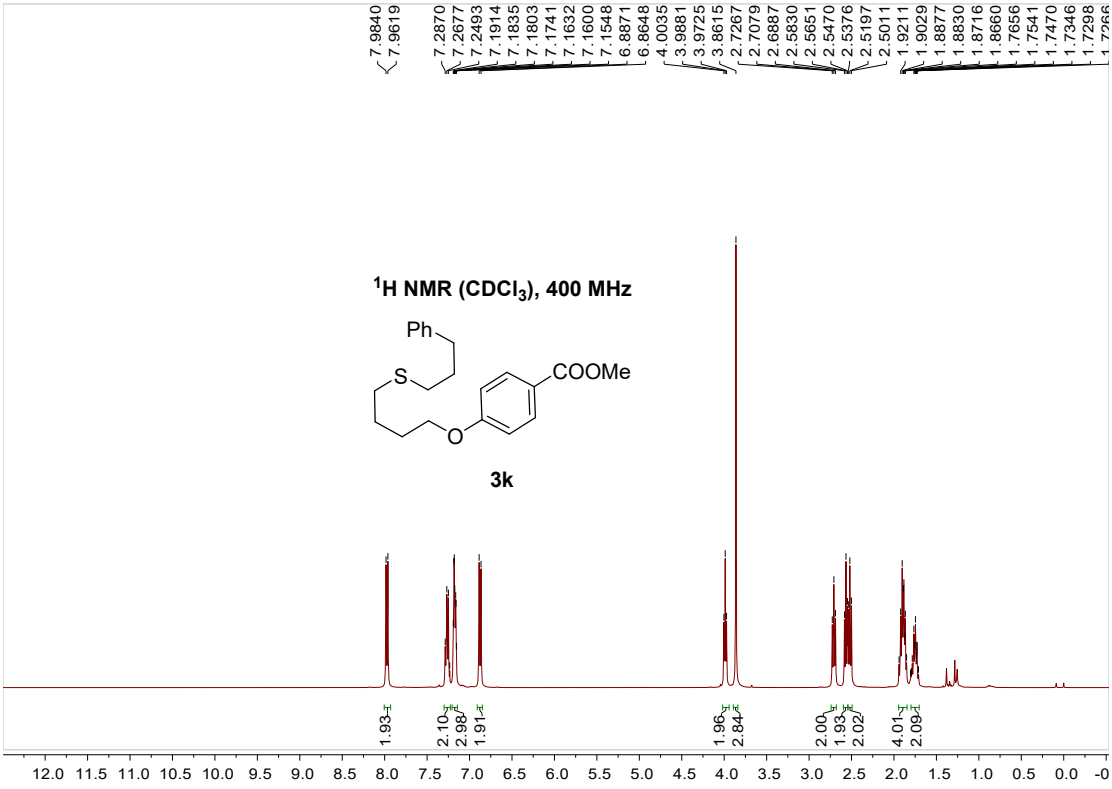

162.2073
141.4594
133.9133
128.4227
128.3490
125.8914
119.2579
115.1201
103.6655
67.7399
34.7575
31.5778
31.3588
31.1156
28.0169
25.9350
^{13}C NMR ($CDCl_3$), 101 MHz
O
S
CN
Ph
3h
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

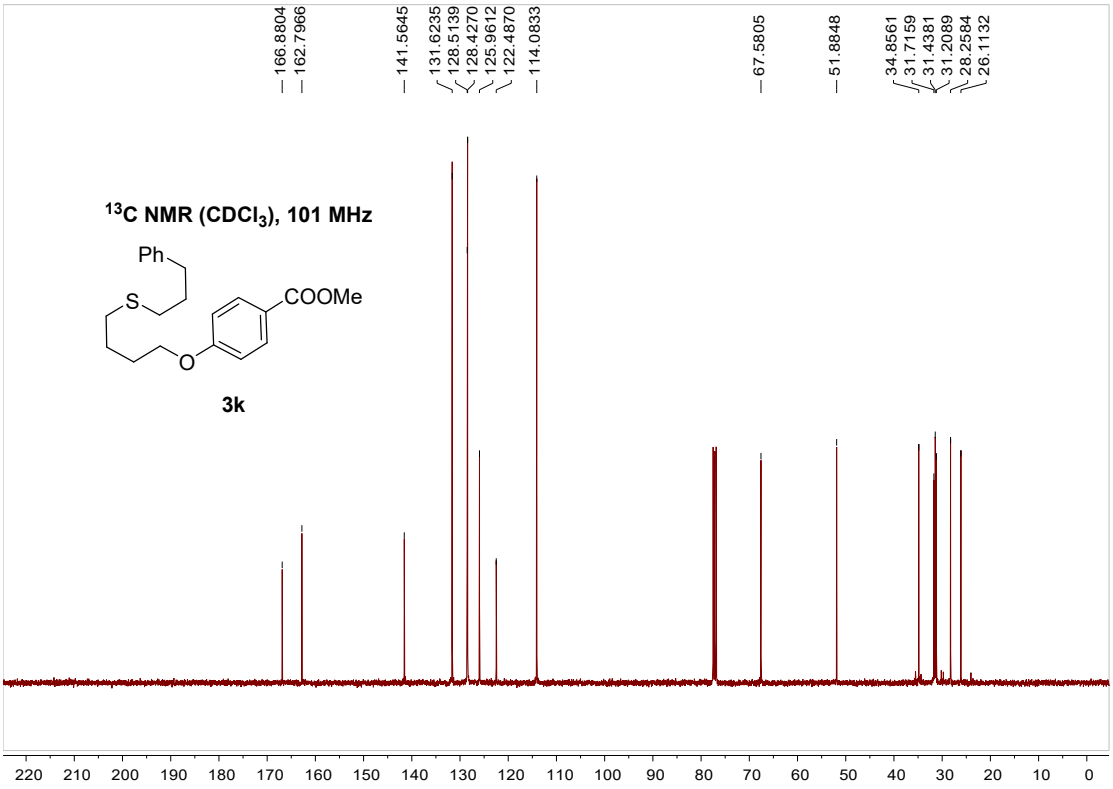

9.8628
7.8228
7.8012
7.2936
7.2888
7.2745
7.2560
7.2474
7.1987
7.1894
7.1837
7.1687
6.9776
6.9608
6.9558
4.0516
4.0362
4.0206
2.7340
2.7154
2.6962
2.5982
2.5804
2.5621
2.5489
2.5311
2.5126
1.9473
1.9295
1.9150
1.9097
1.8929
1.8780
1.8729
1.7869
1.7812
1.7697
1.7627
1H NMR (CDCl3), 400 MHz
O
S
CHO
Ph
3i
0.97
2.00
2.12
2.95
2.06
2.03
2.07
2.06
1.98
4.07
2.12

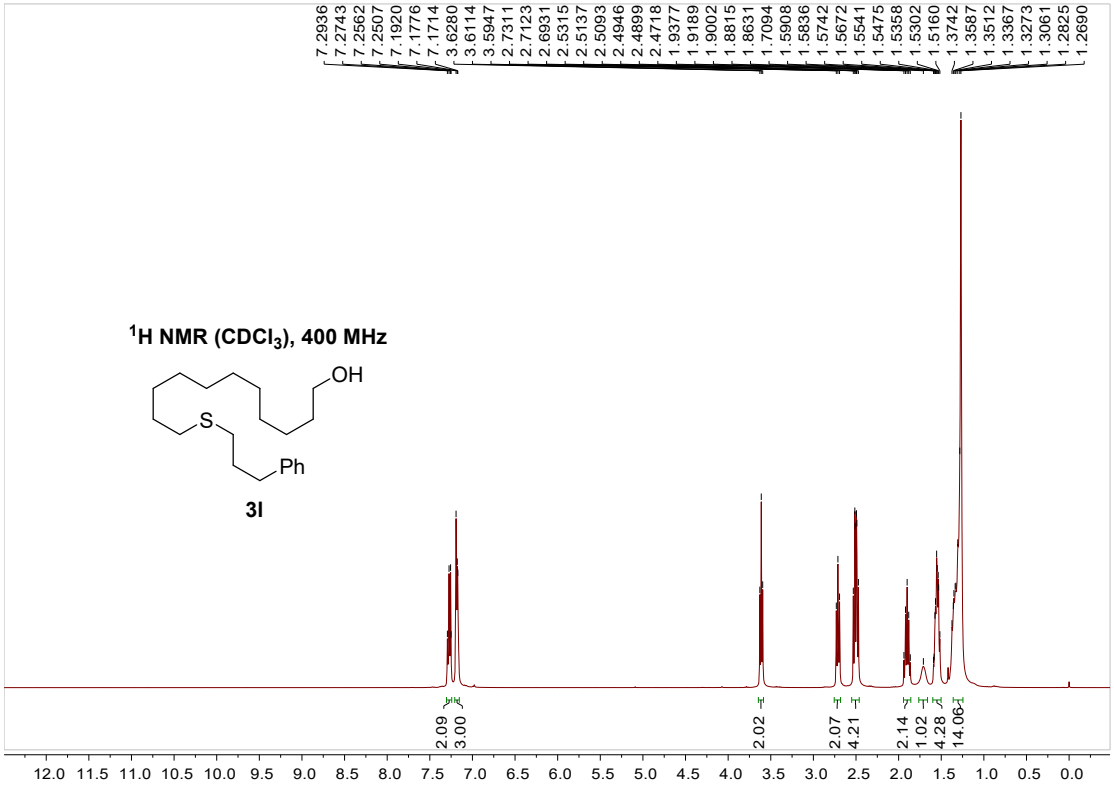

190.8378
164.0628
141.5368
132.0223
129.8456
128.4950
128.4143
125.9551
114.7528
67.8025
34.8335
31.6712
31.4329
31.1848
28.1720
26.0501
13C NMR (CDCl3), 101 MHz
O
S
CHO
Ph
3i

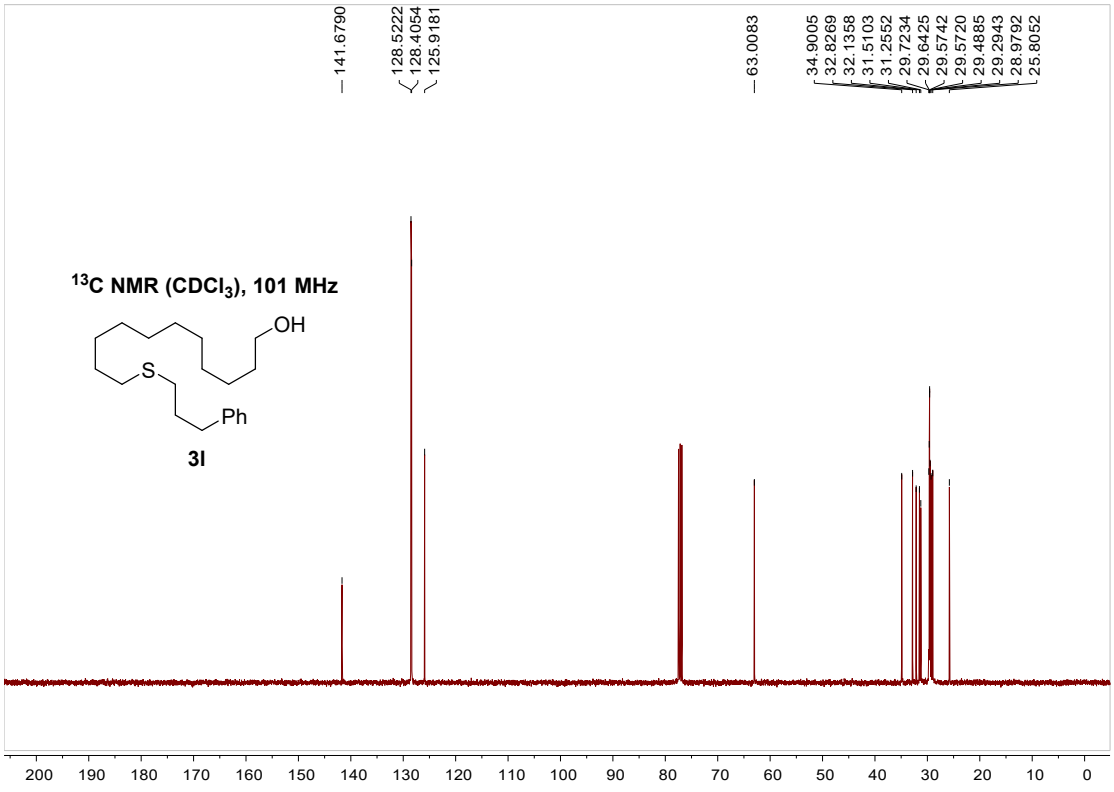

7.9190
7.8968
7.2868
7.2677
7.2493
7.2444
7.1907
7.1830
7.1748
7.1674
7.1629
6.9038
6.8817
4.0231
4.0077
3.9921
2.7279
2.7092
2.6901
2.5884
2.5703
2.5521
2.5417
2.5288
2.5223
2.5053
1.9261
1.9224
1.9132
1.9039
1.8968
1.8892
1.8842
1.8760
1.7718
1.7601
1.7531
1.7362
1H NMR (CDCl3), 400 MHz
O
S
C(O)Me
Ph
3j
1.99
2.07
3.00
1.99
2.00
2.05
2.16
4.90
4.15
2.15
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

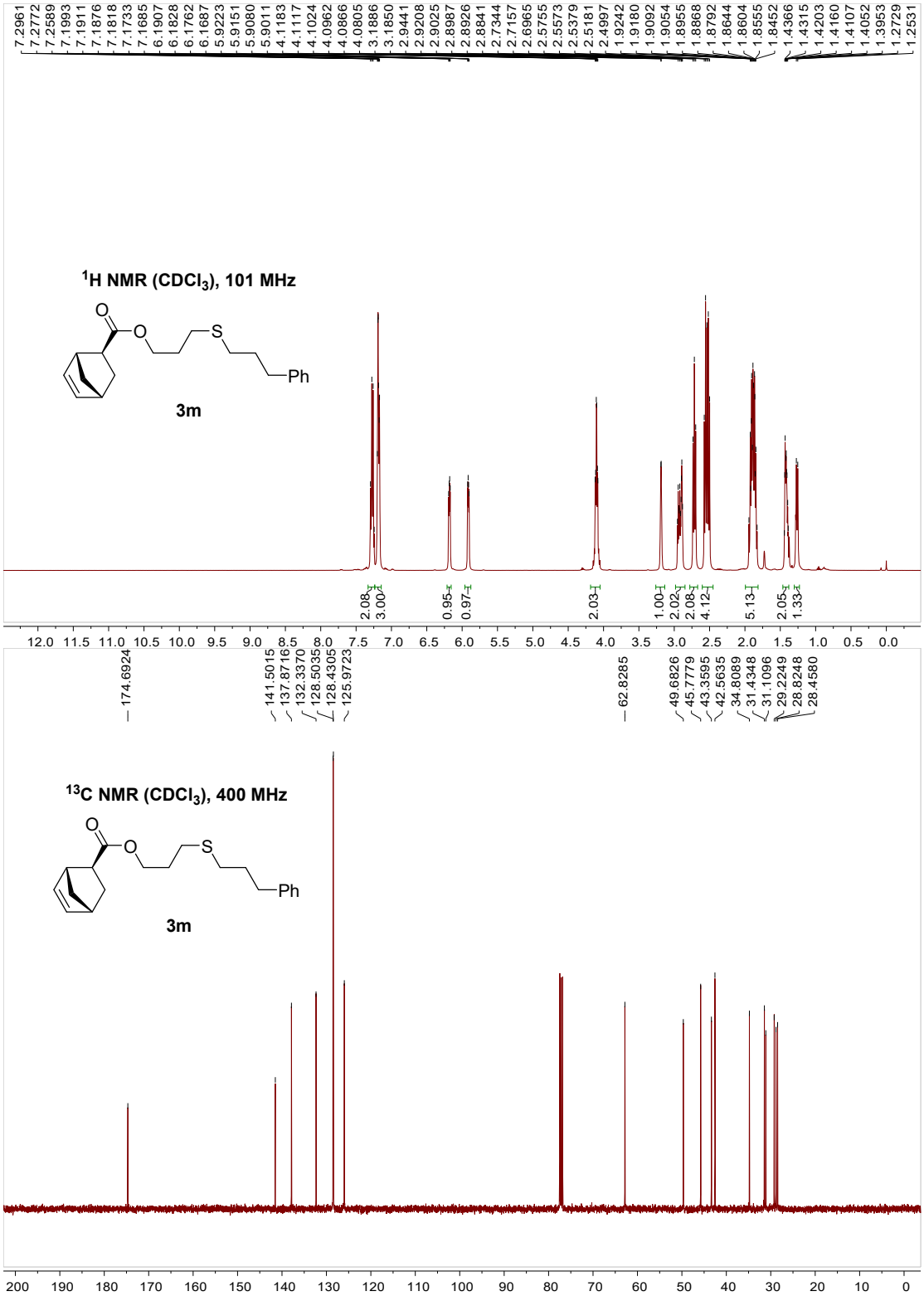

196.7271
162.8964
141.5027
130.5776
130.1682
128.4537
128.3728
125.9074
114.0959
67.5930
34.7947
31.6474
31.3839
31.1452
28.1827
26.3440
26.0390
13C NMR (CDCl3), 101 MHz
O
S
C(O)Me
Ph
3j
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

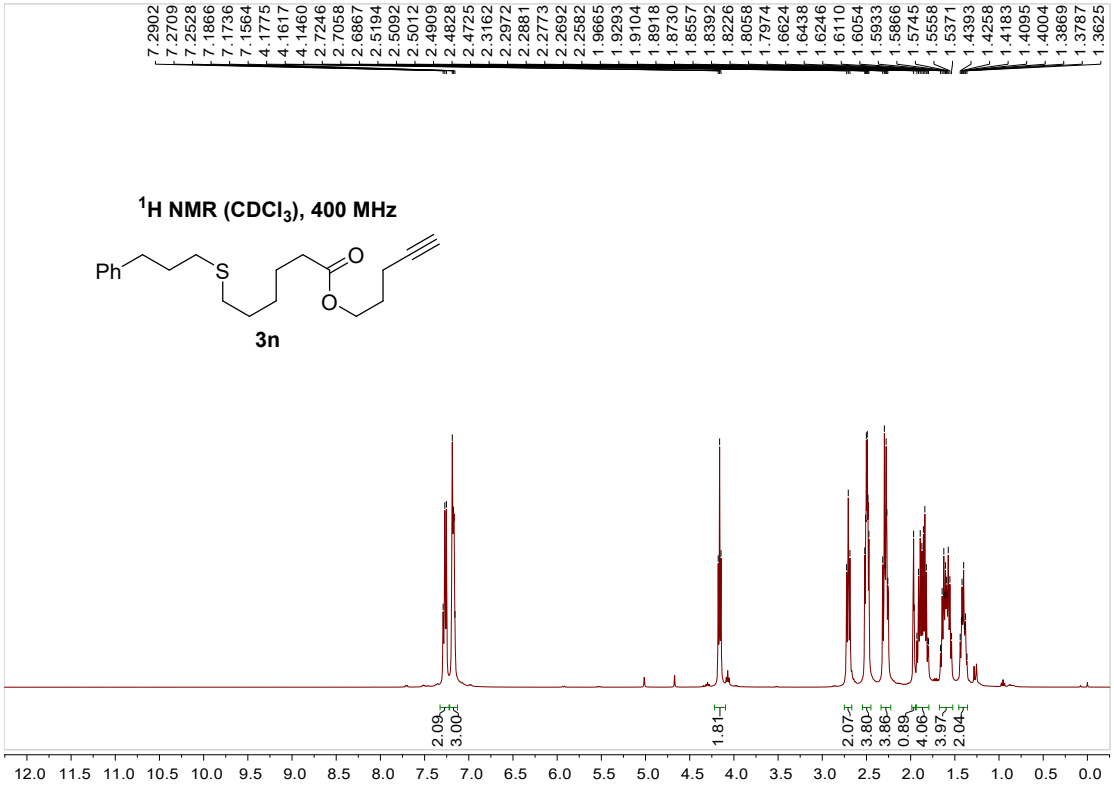

^{1}H NMR (CDCl$_3$), 400 MHz
Ph
S
O
COOMe
3k

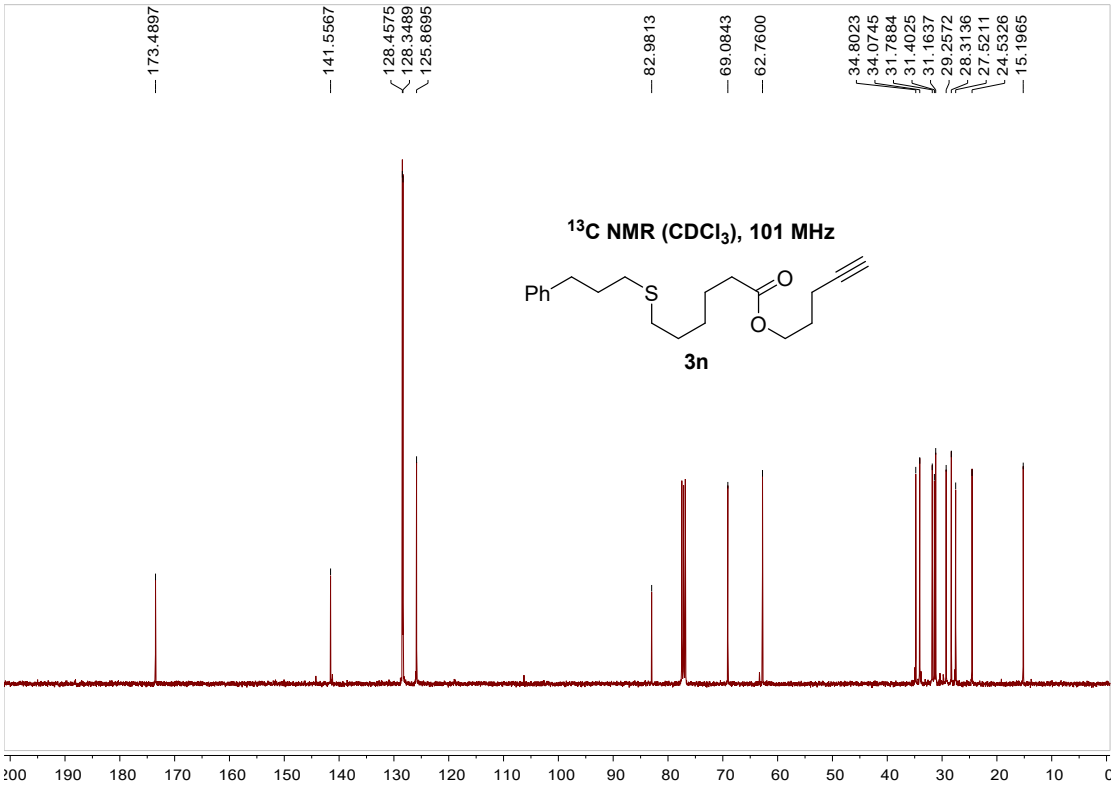

^{13}C NMR (CDCl$_3$), 101 MHz
Ph
S
O
COOMe
3k

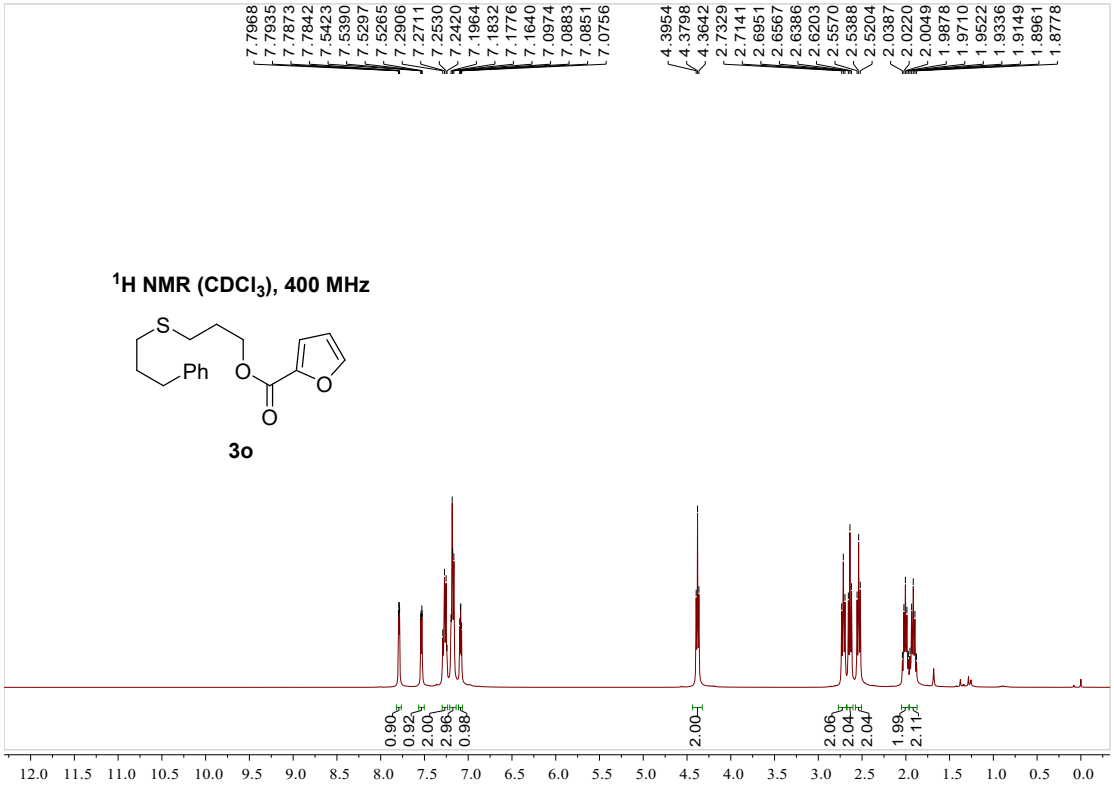

7.2936
7.2743
7.2562
7.2507
7.1920
7.1776
7.1714
3.6280
3.6114
3.5947
2.7311
2.7123
2.6931
2.5315
2.5137
2.5093
2.4946
2.4899
2.4718
1.9377
1.9189
1.9002
1.8815
1.8631
1.7094
1.5908
1.5836
1.5742
1.5672
1.5541
1.5475
1.5358
1.5302
1.5160
1.3742
1.3587
1.3512
1.3367
1.3273
1.3061
1.2825
1.2690
1H NMR (CDCl3), 400 MHz
OH
S
Ph
3l
2.09
3.00
2.02
2.07
4.21
2.14
1.02
4.28
14.06
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0


141.6790
128.5222
128.4054
125.9181
63.0083
34.9005
32.8269
32.1358
31.5103
31.2552
29.7234
29.6425
29.5742
29.5720
29.4885
29.2943
28.9792
25.8052
13C NMR (CDCl3), 101 MHz
OH
S
Ph
3l
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0


7.2961
7.2772
7.2589
7.1993
7.1911
7.1876
7.1818
7.1733
7.1685
6.1907
6.1828
6.1762
6.1687
5.9223
5.9151
5.9080
5.9011
4.1183
4.1117
4.1024
4.0962
4.0866
4.0805
3.1886
3.1850
2.9441
2.9208
2.9025
2.8987
2.8926
2.8841
2.7344
2.7157
2.6965
2.5755
2.5573
2.5379
2.5181
2.4997
1.9242
1.9180
1.9092
1.9054
1.8955
1.8868
1.8792
1.8644
1.8604
1.8555
1.8452
1.4366
1.4315
1.4203
1.4160
1.4107
1.4052
1.3953
1.2729
1.2531
^{1}H NMR (CDCl$_3$), 101 MHz
O
O
S
Ph
3m
2.08
3.00
0.95
0.97
2.03
1.00
2.02
2.08
4.12
5.13
2.05
1.33
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
174.6924
141.5015
137.8716
132.3370
128.5035
128.4305
125.9723
62.8285
49.6826
45.7779
43.3595
42.5635
34.8089
31.4348
31.1096
29.2249
28.8248
28.4580
^{13}C NMR (CDCl$_3$), 400 MHz
O
O
S
Ph
3m
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

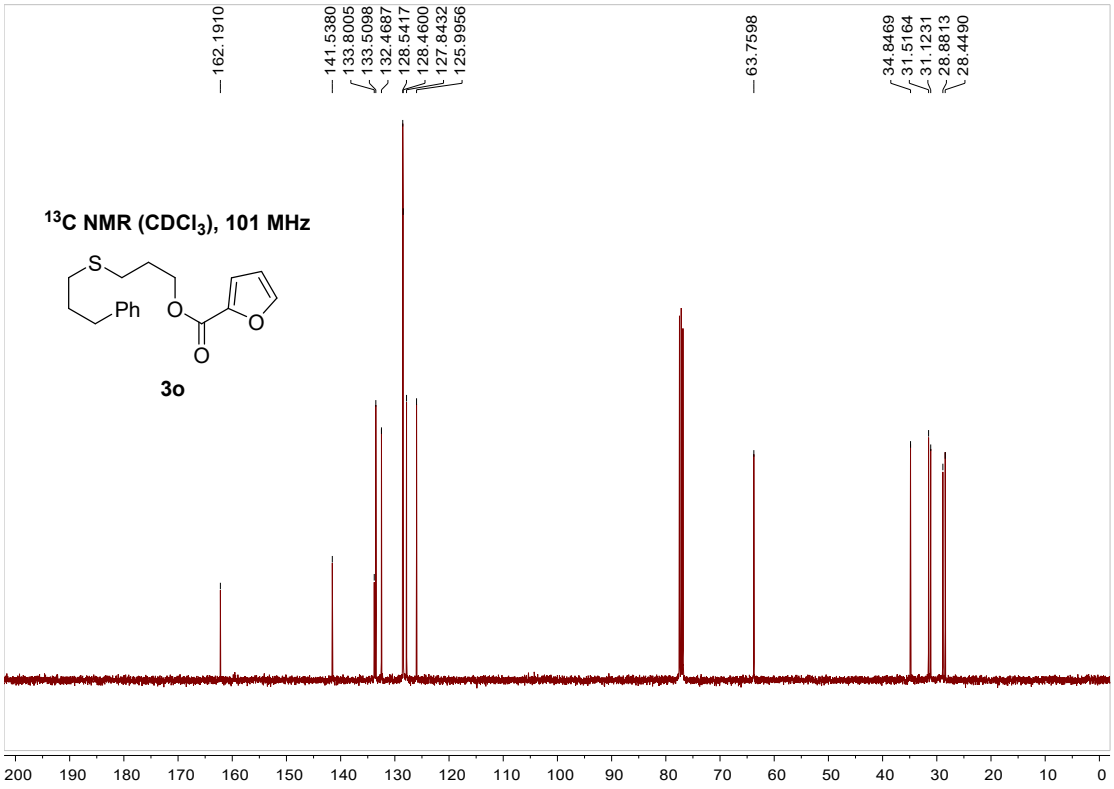

7.2902
7.2709
7.2528
7.1866
7.1736
7.1564
4.1775
4.1617
4.1460
2.7246
2.7058
2.6867
2.5194
2.5092
2.5012
2.4909
2.4828
2.4725
2.3162
2.2972
2.2881
2.2773
2.2692
2.2582
1.9665
1.9293
1.9104
1.8918
1.8730
1.8557
1.8392
1.8226
1.8058
1.7974
1.6624
1.6438
1.6246
1.6110
1.6054
1.5933
1.5866
1.5745
1.5558
1.5371
1.4393
1.4258
1.4183
1.4095
1.4004
1.3869
1.3787
1.3625
1H NMR (CDCl3), 400 MHz
Ph
S
O
O
3n
2.09
3.00
1.81
2.07
3.80
3.86
0.89
4.06
3.97
2.04
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0


173.4897
141.5567
128.4575
128.3489
125.8695
82.9813
69.0843
62.7600
34.8023
34.0745
31.7884
31.4025
31.1637
29.2572
28.3136
27.5211
24.5326
15.1965
13C NMR (CDCl3), 101 MHz
Ph
S
O
O
3n
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0



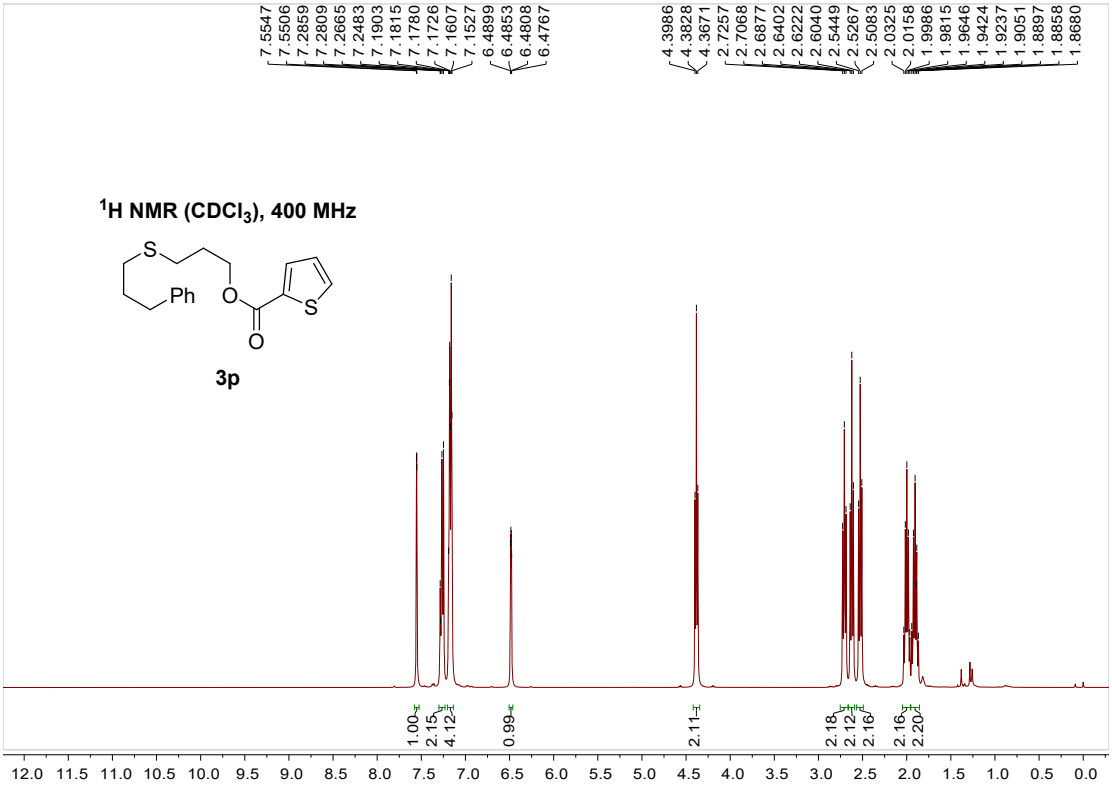
^{1}H NMR ($CDCl_3$), 400 MHz

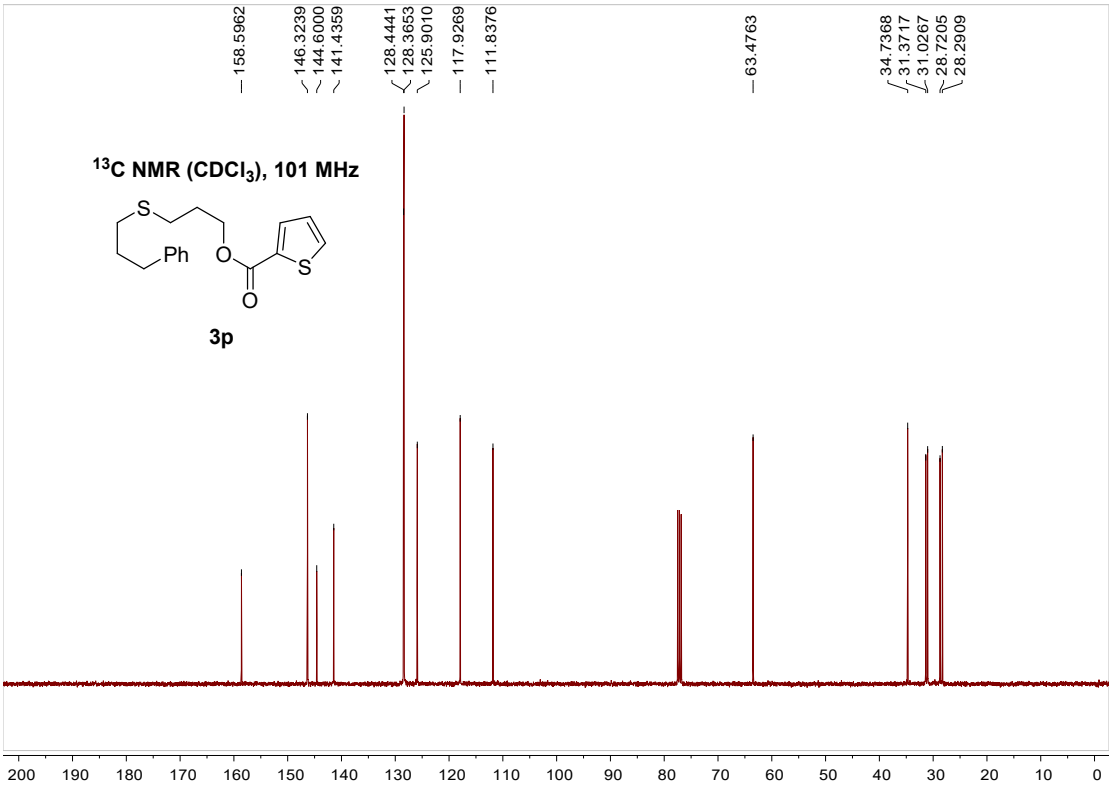
3o

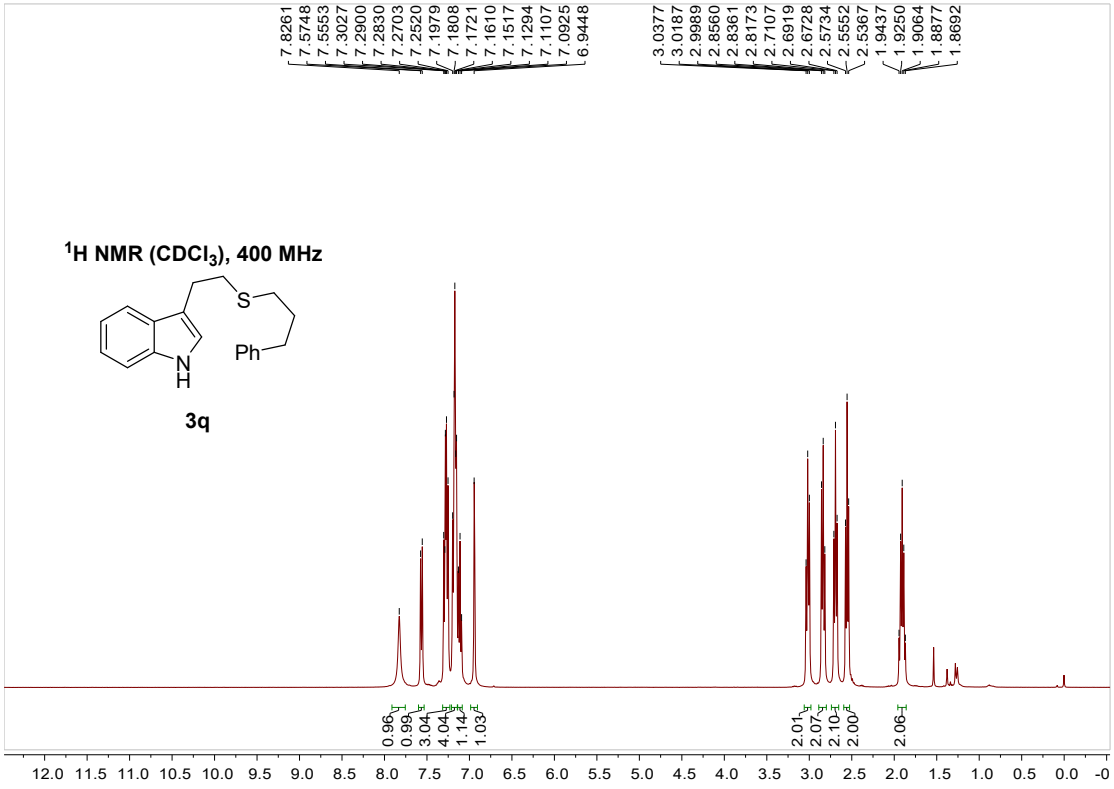


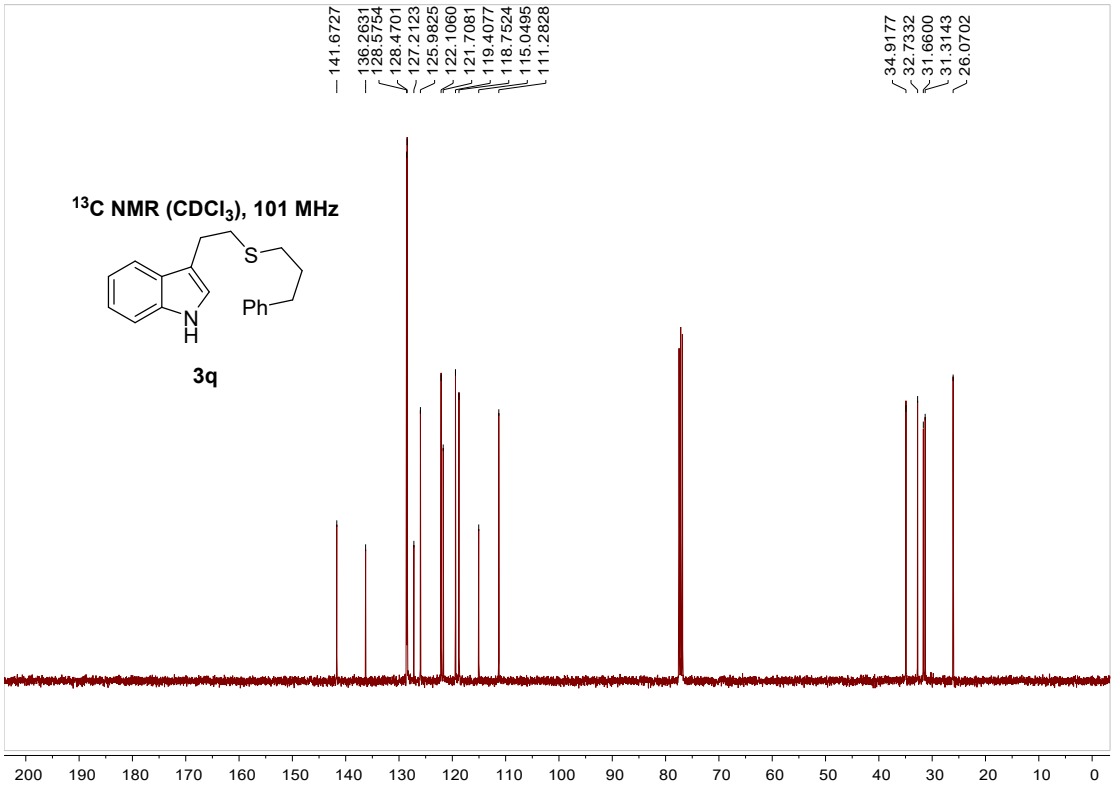
^{13}C NMR ($CDCl_3$), 101 MHz

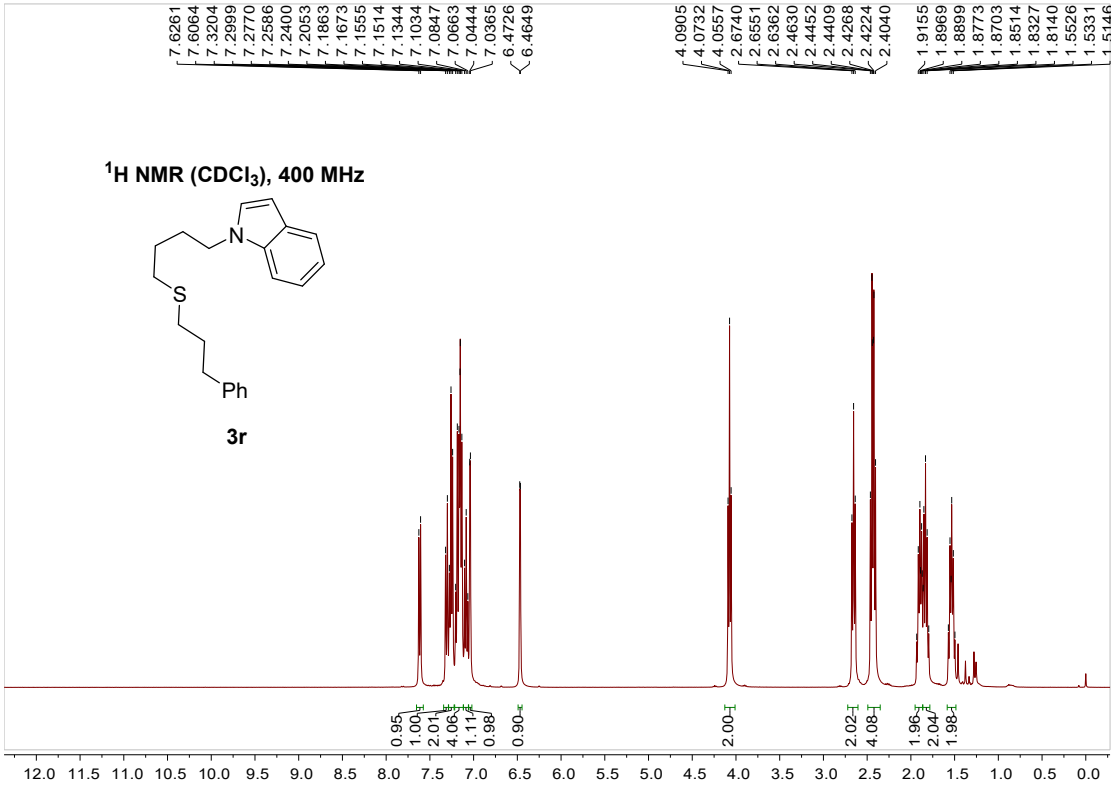
3o

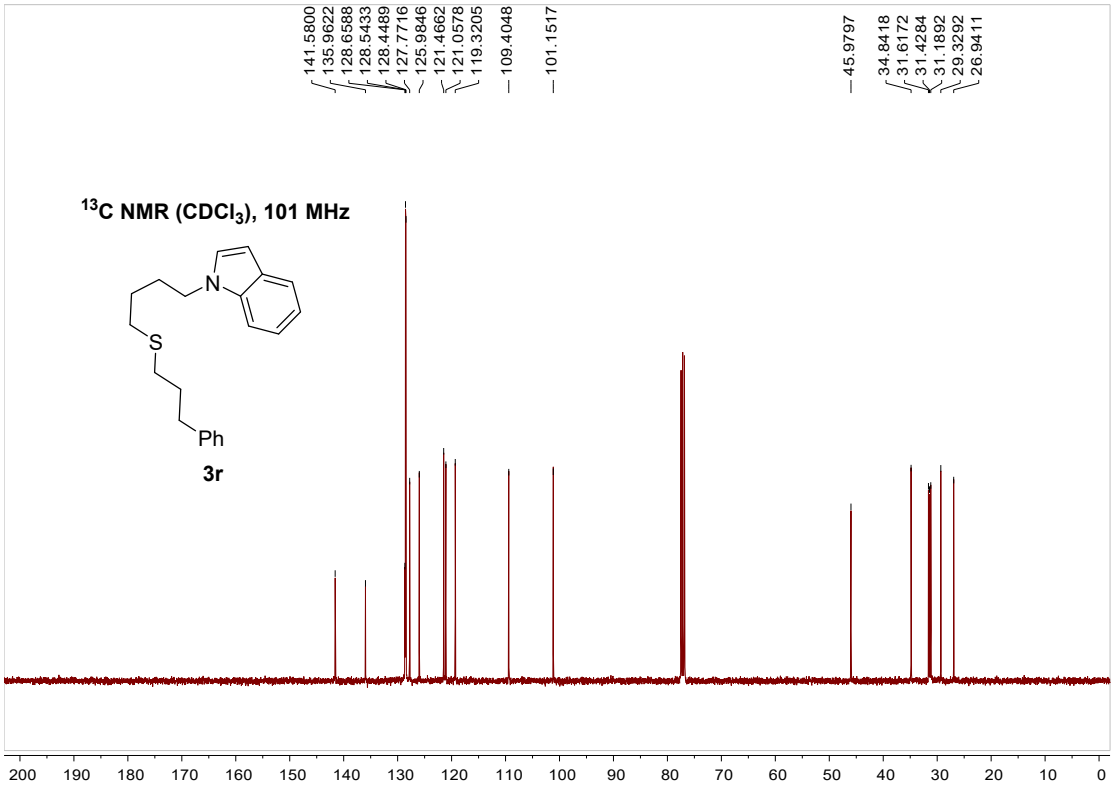

7.5547
7.5506
7.2859
7.2809
7.2665
7.2483
7.1903
7.1815
7.1780
7.1726
7.1607
7.1527
6.4899
6.4853
6.4808
6.4767
4.3986
4.3828
4.3671
2.7257
2.7068
2.6877
2.6402
2.6222
2.6040
2.5449
2.5267
2.5083
2.0325
2.0158
1.9986
1.9815
1.9646
1.9424
1.9237
1.9051
1.8897
1.8858
1.8680
1H NMR (CDCl3), 400 MHz
S
Ph
O
O
S
O
3p
1.00
2.15
4.12
0.99
2.11
2.18
2.12
2.16
2.16
2.20
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

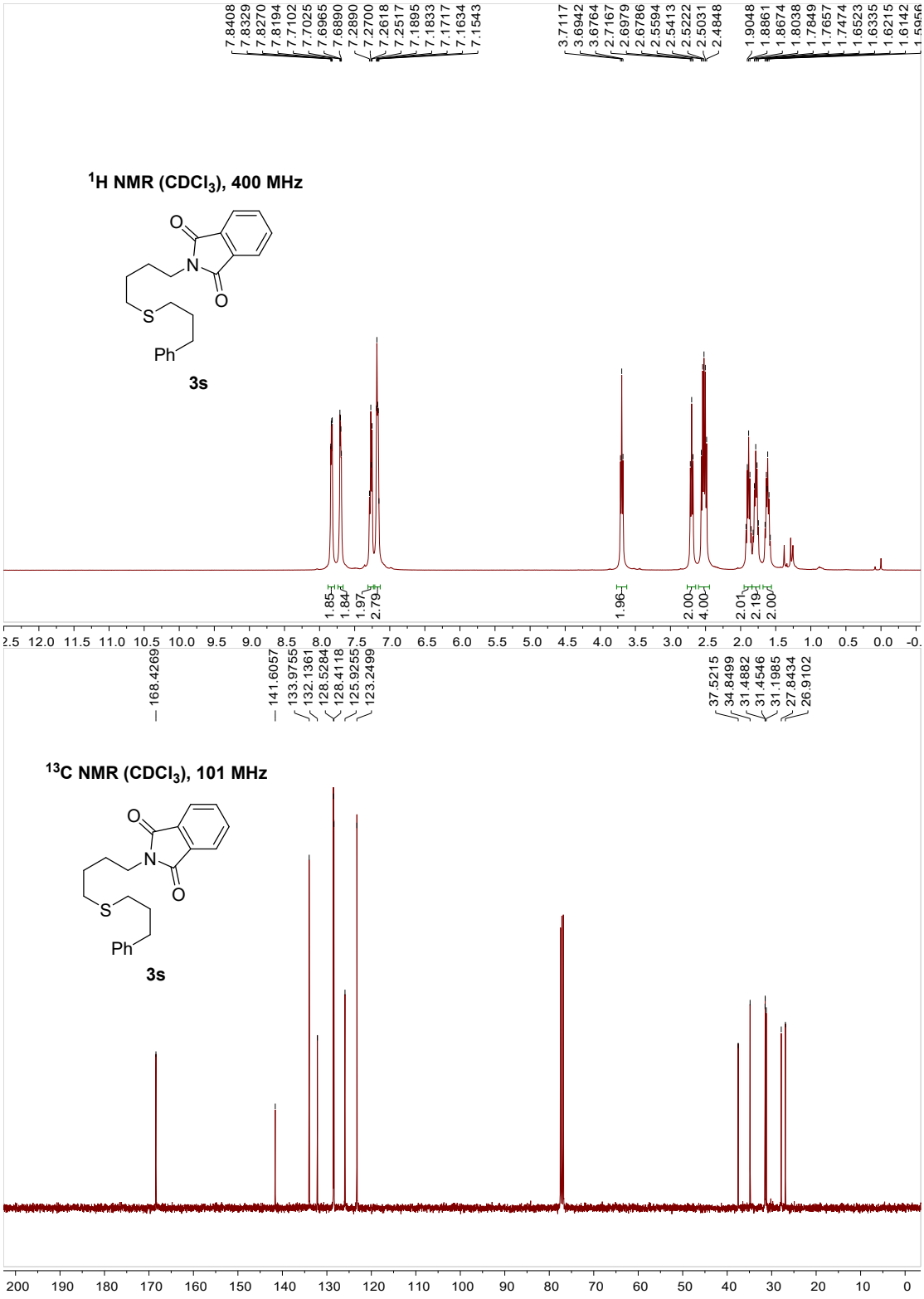

158.5962
146.3239
144.6000
141.4359
128.4441
128.3653
125.9010
117.9269
111.8376
63.4763
34.7368
31.3717
31.0267
28.7205
28.2909
13C NMR (CDCl3), 101 MHz
S
Ph
O
O
S
O
3p
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

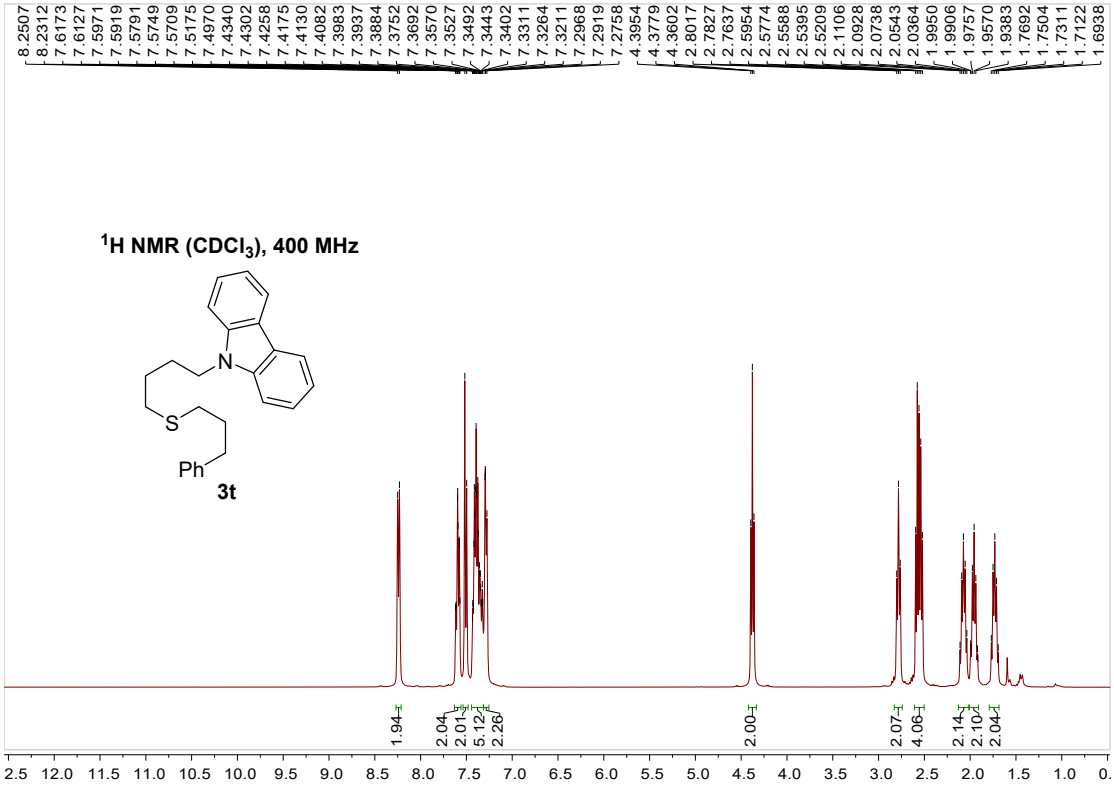

7.8261
7.5748
7.5553
7.3027
7.2900
7.2830
7.2703
7.2520
7.1979
7.1808
7.1721
7.1610
7.1517
7.1294
7.1107
7.0925
6.9448
3.0377
3.0187
2.9989
2.8560
2.8361
2.8173
2.7107
2.6919
2.6728
2.5734
2.5552
2.5367
1.9437
1.9250
1.9064
1.8877
1.8692
^{1}H NMR ($CDCl_3$), 400 MHz
S
Ph
N
H
3q
0.96
0.99
3.04
4.04
1.14
1.03
2.01
2.07
2.10
2.00
2.06
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0

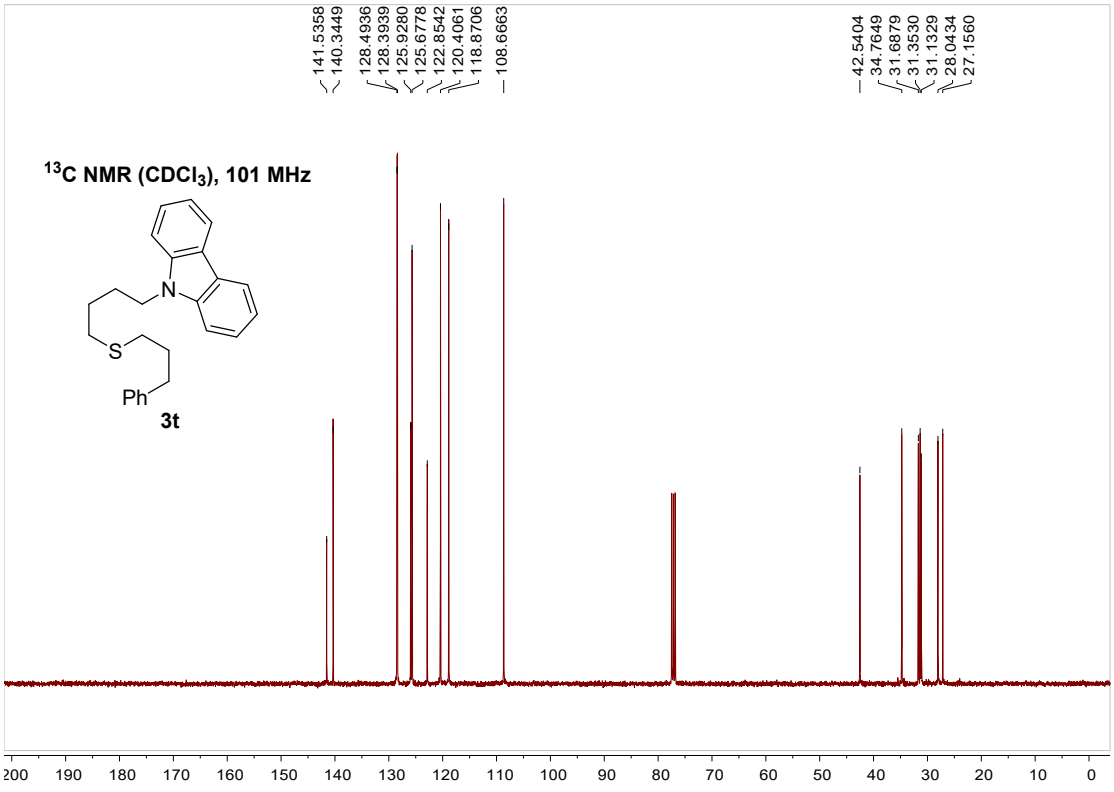

141.6727
136.2631
128.5754
128.4701
127.2123
125.9825
122.1060
121.7081
119.4077
118.7524
115.0495
111.2828
34.9177
32.7332
31.6600
31.3143
26.0702
^{13}C NMR ($CDCl_3$), 101 MHz
S
Ph
N
H
3q
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

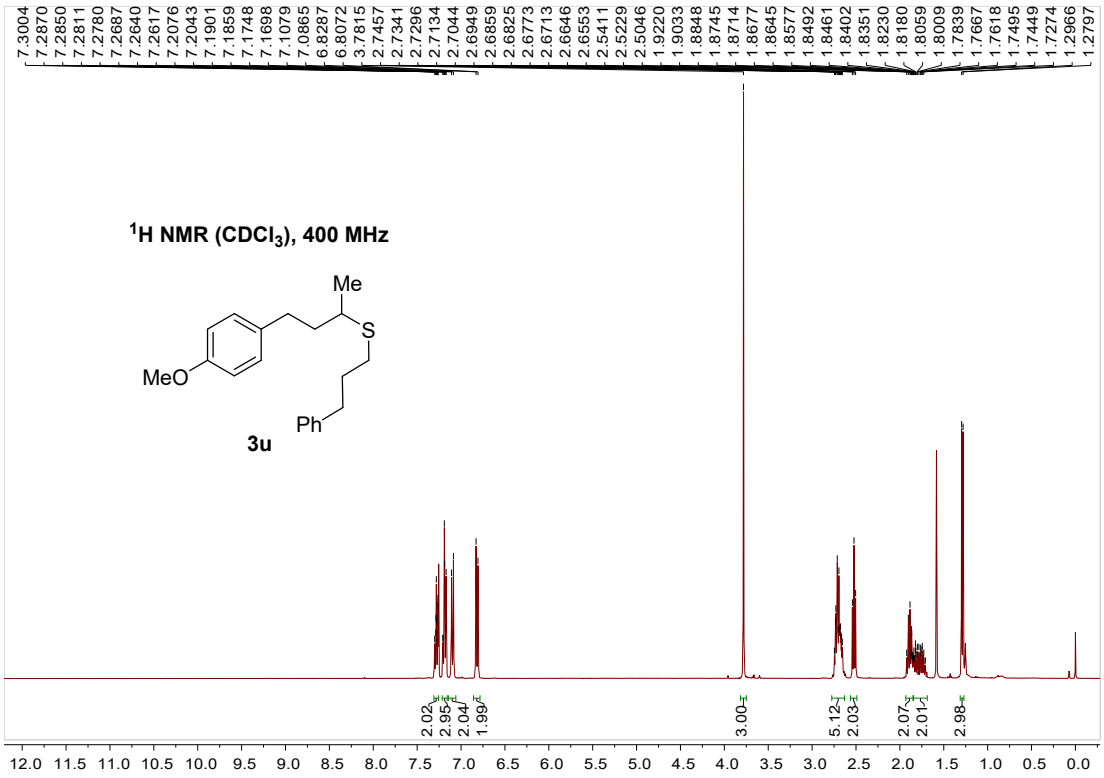

7.6261
7.6064
7.3204
7.2999
7.2770
7.2586
7.2400
7.2053
7.1863
7.1673
7.1555
7.1514
7.1344
7.1034
7.0847
7.0663
7.0444
7.0365
6.4726
6.4649
4.0905
4.0732
4.0557
2.6740
2.6551
2.6362
2.4630
2.4452
2.4409
2.4268
2.4224
2.4040
1.9155
1.8969
1.8899
1.8773
1.8703
1.8514
1.8327
1.8140
1.5526
1.5331
1.5146
^{1}H NMR ($CDCl_3$), 400 MHz
N
S
Ph
3r
0.95
1.00
2.01
4.06
1.11
0.98
0.90
2.00
2.02
4.08
1.96
2.04
1.98
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

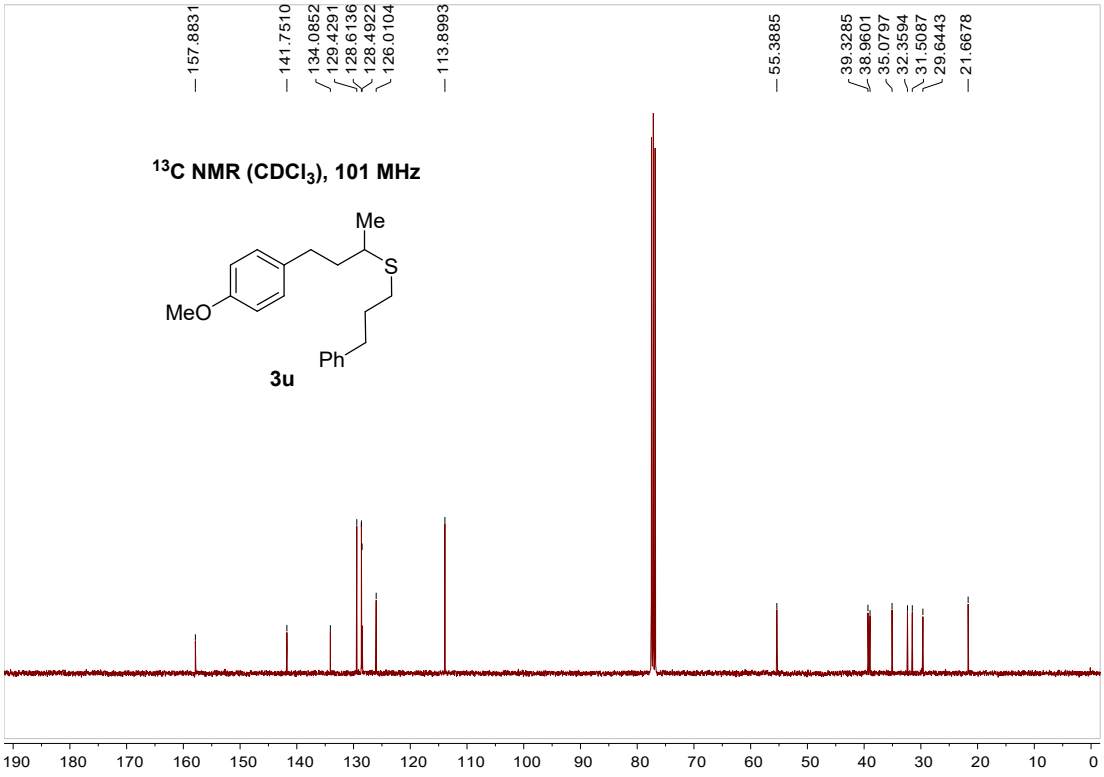

141.5800
135.9622
128.6588
128.5433
128.4489
127.7716
125.9846
121.4662
121.0578
119.3205
109.4048
101.1517
45.9797
34.8418
31.6172
31.4284
31.1892
29.3292
26.9411
^{13}C NMR ($CDCl_3$), 101 MHz
N
S
Ph
3r
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

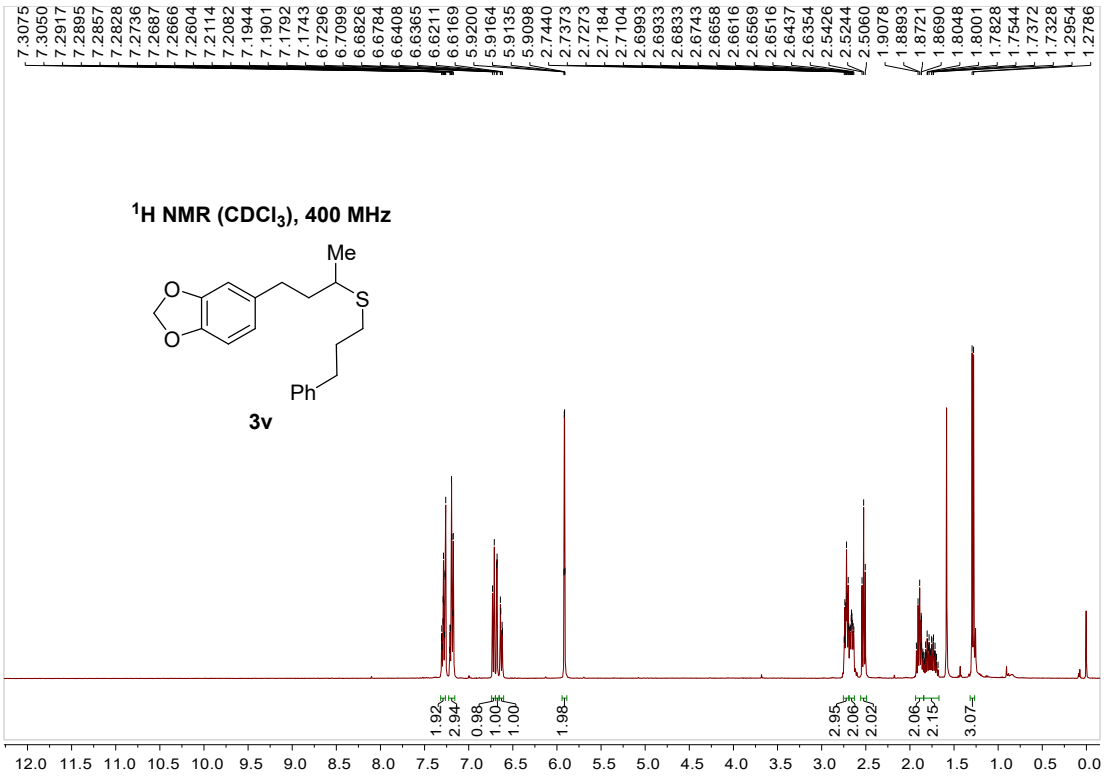

7.8408
7.8329
7.8270
7.8194
7.7102
7.7025
7.6965
7.6890
7.2890
7.2700
7.2618
7.2517
7.1895
7.1833
7.1717
7.1634
7.1543
3.7117
3.6942
3.6764
2.7167
2.6979
2.6786
2.5594
2.5413
2.5222
2.5031
2.4848
1.9048
1.8861
1.8674
1.8038
1.7849
1.7657
1.7474
1.6523
1.6335
1.6215
1.6142
1H NMR (CDCl3), 400 MHz
O
N
O
S
Ph
3s
1.85
1.84
1.97
2.79
1.96
2.00
4.00
2.01
2.19
2.00
168.4269
141.6057
133.9755
132.1361
128.5284
128.4118
125.9255
123.2499
37.5215
34.8499
31.4882
31.4546
31.1985
27.8434
26.9102
13C NMR (CDCl3), 101 MHz
O
N
O
S
Ph
3s

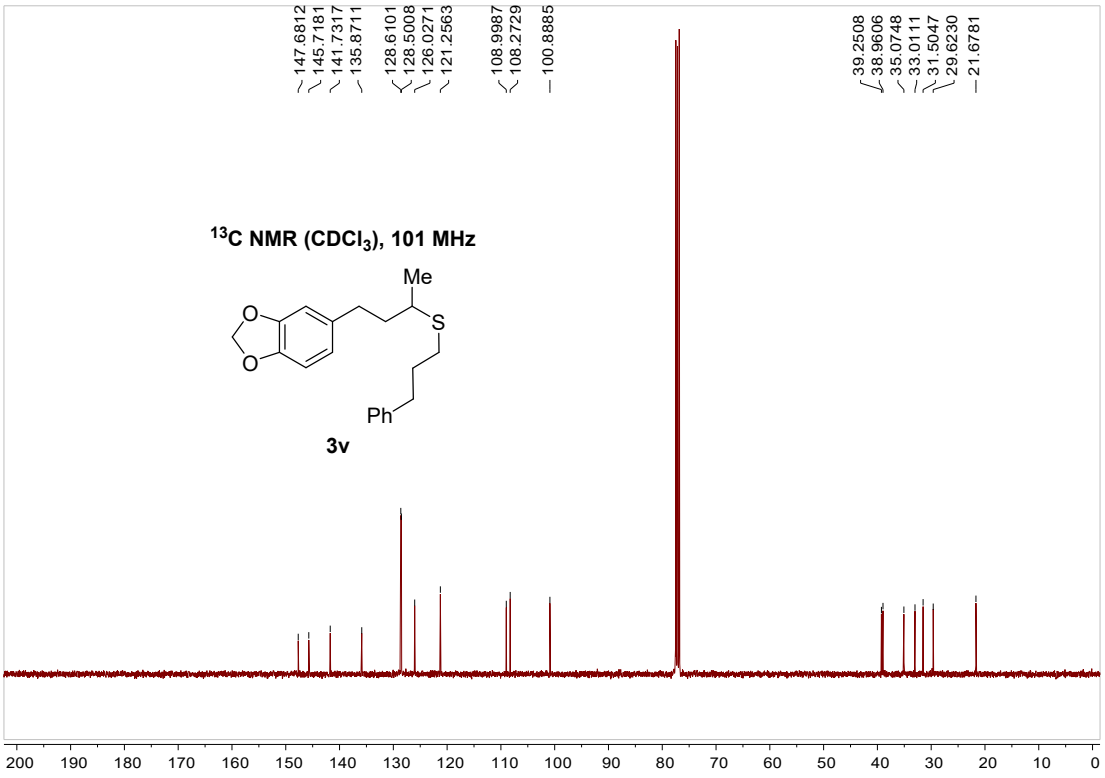

8.2507
8.2312
7.6173
7.6127
7.5971
7.5919
7.5791
7.5749
7.5709
7.5175
7.4970
7.4340
7.4302
7.4258
7.4175
7.4130
7.4082
7.3983
7.3937
7.3884
7.3752
7.3692
7.3570
7.3527
7.3492
7.3443
7.3402
7.3311
7.3264
7.3211
7.2968
7.2919
7.2758
4.3954
4.3779
4.3602
2.8017
2.7827
2.7637
2.5954
2.5774
2.5588
2.5395
2.5209
2.1106
2.0928
2.0738
2.0543
2.0364
1.9950
1.9906
1.9757
1.9570
1.9383
1.7692
1.7504
1.7311
1.7122
1.6938
1H NMR (CDCl3), 400 MHz
N
S
Ph
3t
1.94
2.04
2.01
5.12
2.26
2.00
2.07
4.06
2.14
2.10
2.04
2.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0

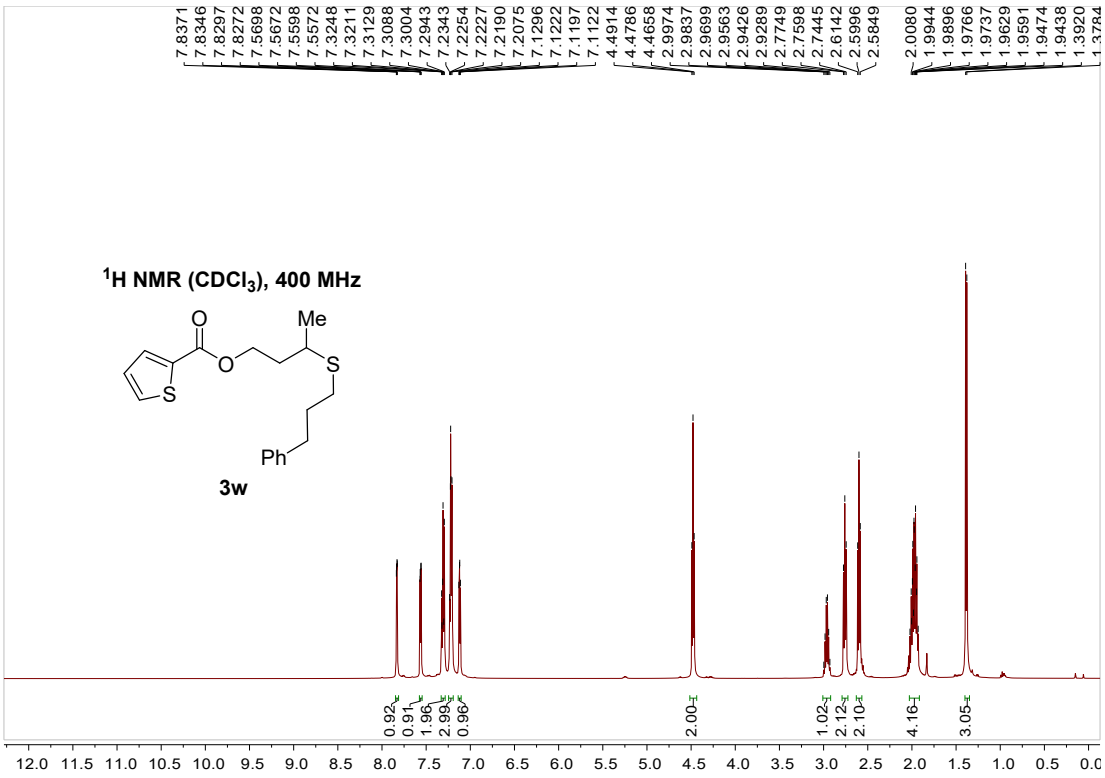

141.5358
140.3449
128.4936
128.3939
125.9280
125.6778
122.8542
120.4061
118.8706
108.6663
42.5404
34.7649
31.6879
31.3530
31.1329
28.0434
27.1560
13C NMR (CDCl3), 101 MHz
N
S
Ph
3t
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

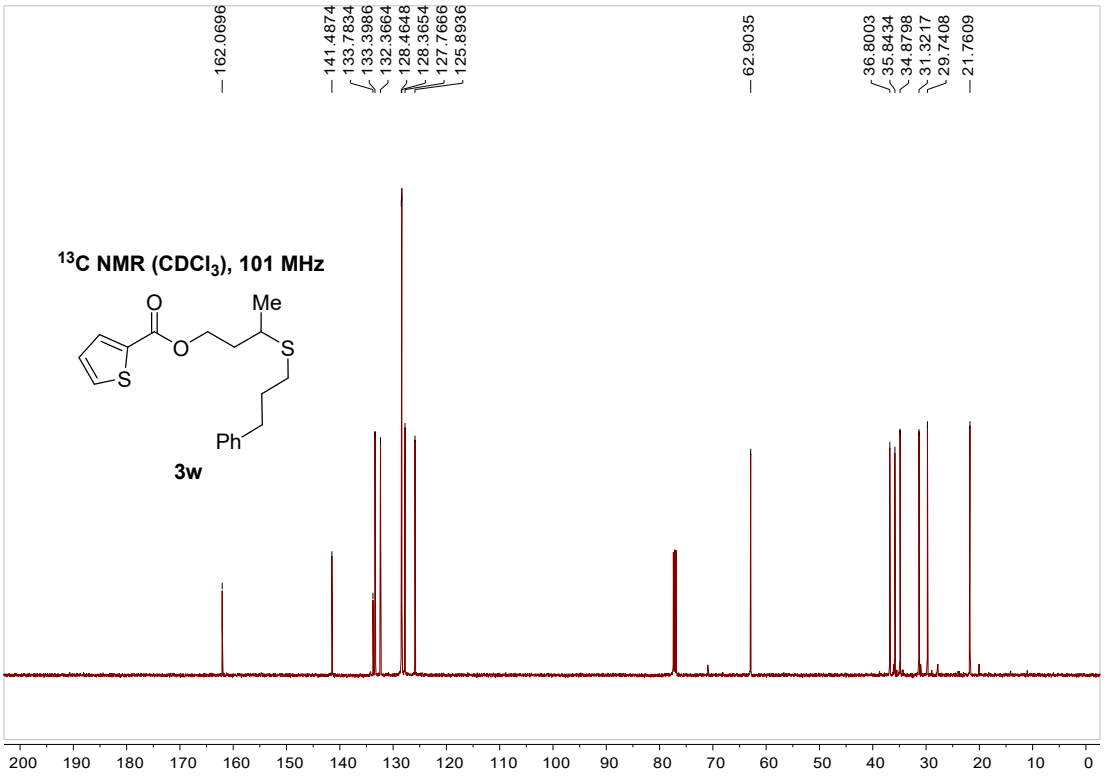

7.3004
7.2870
7.2850
7.2811
7.2780
7.2687
7.2640
7.2617
7.2076
7.2043
7.1901
7.1859
7.1748
7.1698
7.1079
7.0865
6.8287
6.8072
3.7815
2.7457
2.7341
2.7296
2.7134
2.7044
2.6949
2.6859
2.6825
2.6773
2.6713
2.6646
2.6553
2.5411
2.5229
2.5046
1.9220
1.9033
1.8848
1.8745
1.8714
1.8677
1.8645
1.8577
1.8492
1.8461
1.8402
1.8351
1.8230
1.8180
1.8059
1.8009
1.7839
1.7667
1.7618
1.7495
1.7449
1.7274
1.2966
1.2797
^{1}H NMR (CDCl$_3$), 400 MHz
Me
S
MeO
Ph
3u
2.02
2.95
2.04
1.99
3.00
5.12
2.03
2.07
2.01
2.98
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

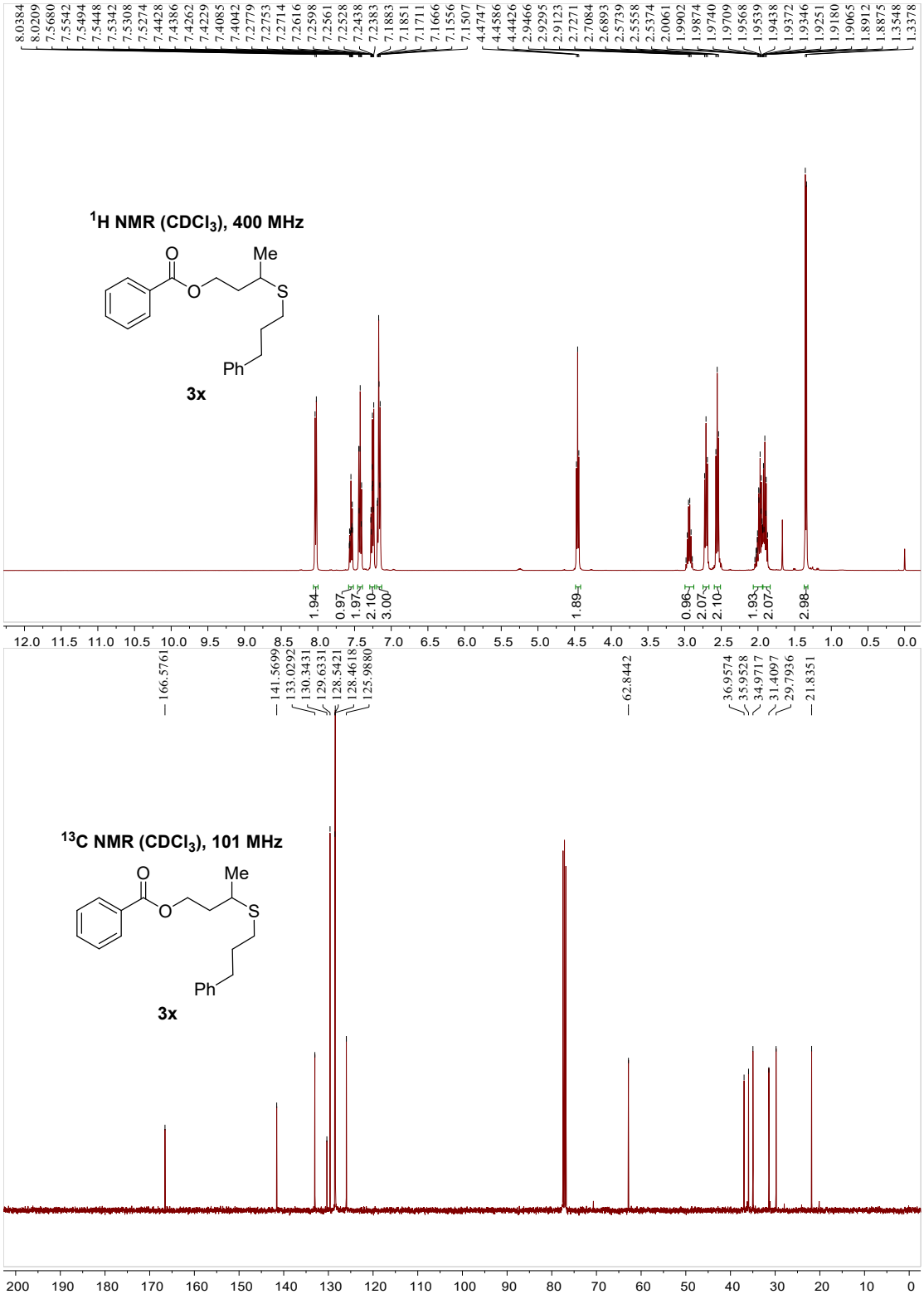

157.8831
141.7510
134.0852
129.4291
128.6136
128.4922
126.0104
113.8993
55.3885
39.3285
38.9601
35.0797
32.3594
31.5087
29.6443
21.6678
^{13}C NMR (CDCl$_3$), 101 MHz
Me
S
MeO
Ph
3u
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

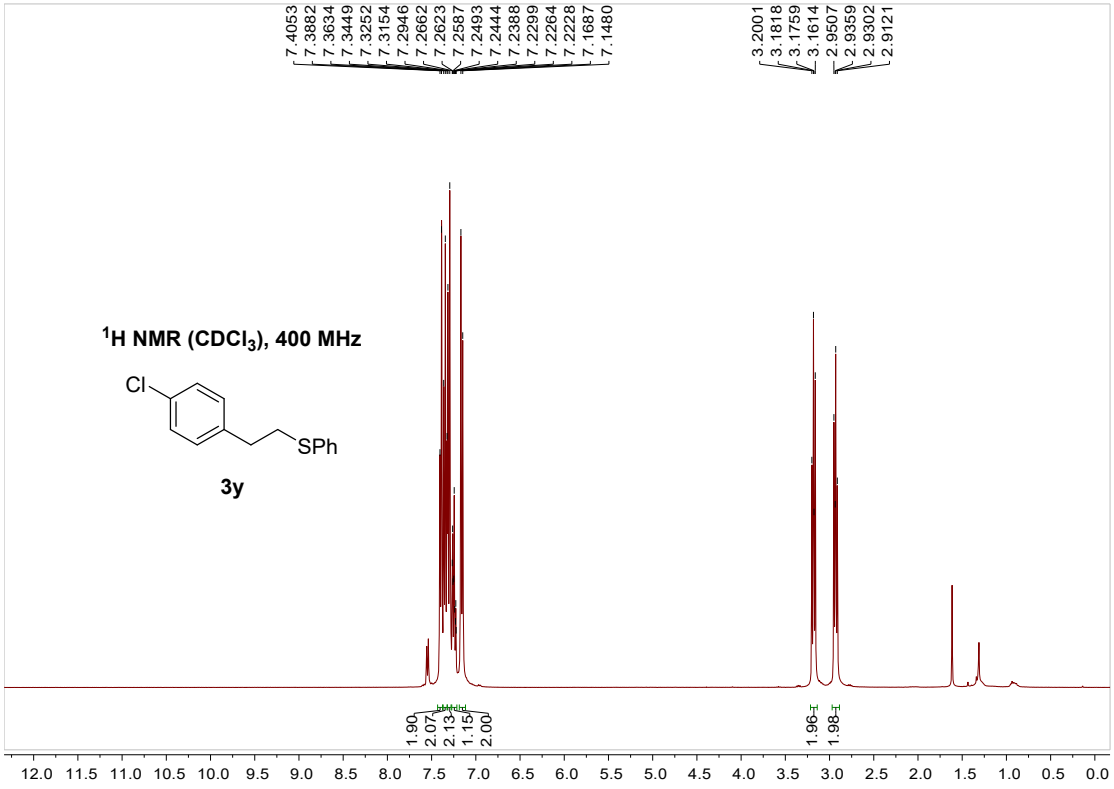

7.3075 7.3050 7.2917 7.2895 7.2857 7.2828 7.2736 7.2687 7.2666 7.2604 7.2114 7.2082 7.1944 7.1901 7.1792 7.1743 7.7296 6.7099 6.6826 6.6784 6.6408 6.6365 6.6211 6.6169 5.9200 5.9164 5.9135 5.9098 2.7440 2.7373 2.7273 2.7184 2.7104 2.6993 2.6933 2.6833 2.6743 2.6658 2.6616 2.6569 2.6516 2.6437 2.6354 2.5426 2.5244 2.5060 1.9078 1.8893 1.8721 1.8690 1.8048 1.8001 1.7828 1.7544 1.7372 1.7328 1.2954 1.2786
1H NMR (CDCl3), 400 MHz
Me
O
O
S
Ph
3v
1.92 2.94 0.98 1.00 1.00 1.98 2.95 2.06 2.02 2.06 2.15 3.07
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

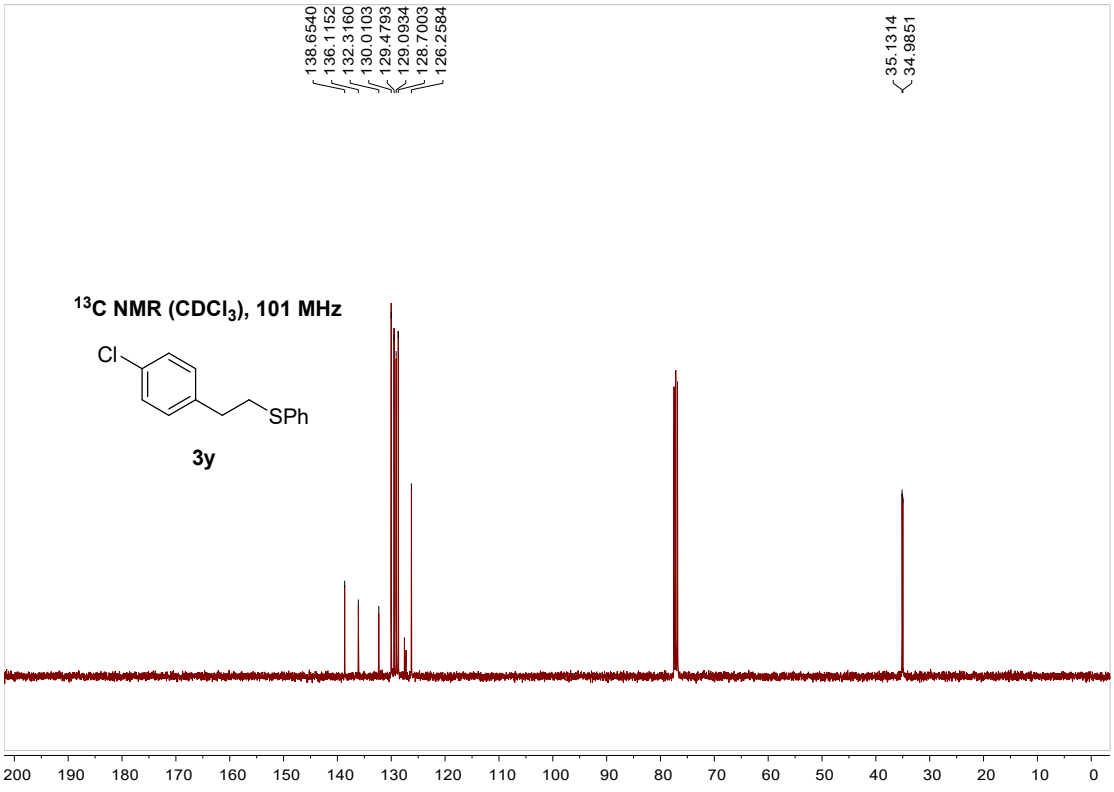

147.6812 145.7181 141.7317 135.8711 128.6101 128.5008 126.0271 121.2563 108.9987 108.2729 100.8885
39.2508 38.9606 35.0748 33.0111 31.5047 29.6230 21.6781
13C NMR (CDCl3), 101 MHz
Me
O
O
S
Ph
3v
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

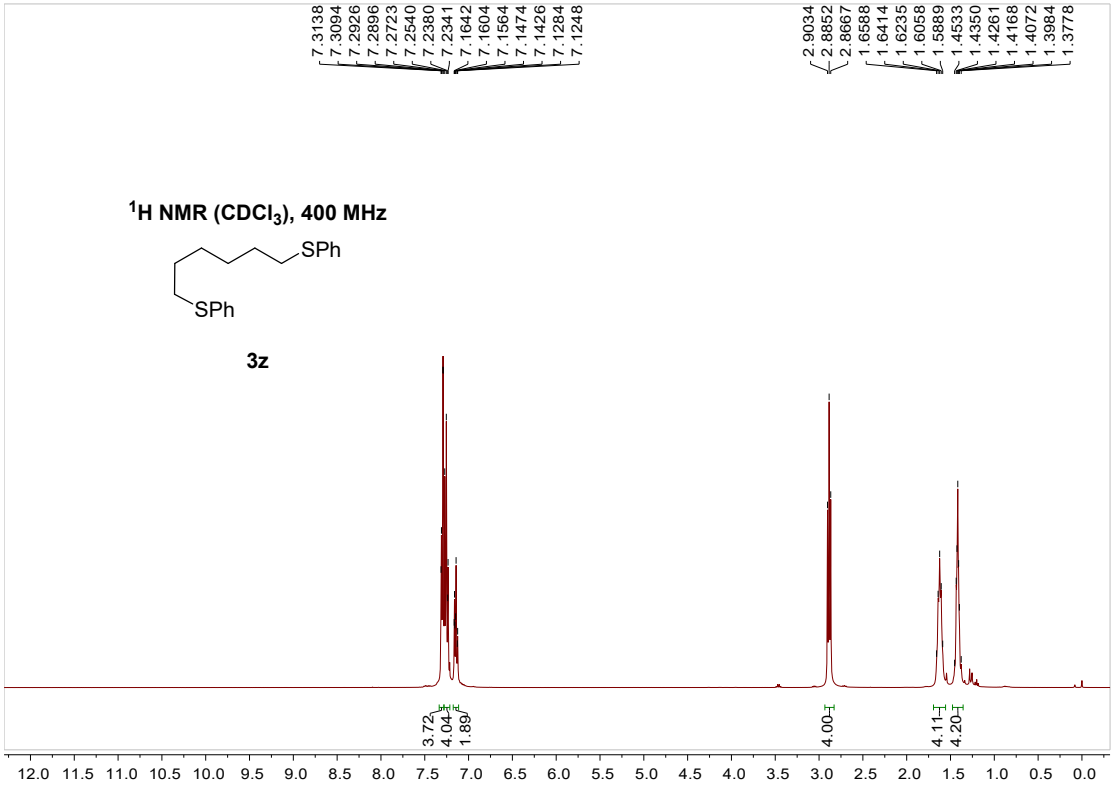

7.8371
7.8346
7.8297
7.8272
7.5698
7.5672
7.5598
7.5572
7.3248
7.3211
7.3129
7.3088
7.3004
7.2943
7.2343
7.2254
7.2227
7.2190
7.2075
7.1296
7.1222
7.1197
7.1122
4.4914
4.4786
4.4658
2.9974
2.9837
2.9699
2.9563
2.9426
2.9289
2.7749
2.7598
2.7445
2.6142
2.5996
2.5849
2.0080
1.9944
1.9896
1.9766
1.9737
1.9629
1.9591
1.9474
1.9438
1.3920
1.3784
^{1}H NMR ($CDCl_3$), 400 MHz
O
Me
O
S
S
Ph
3w
0.92
0.91
1.96
2.99
0.96
2.00
1.02
2.12
2.10
4.16
3.05
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

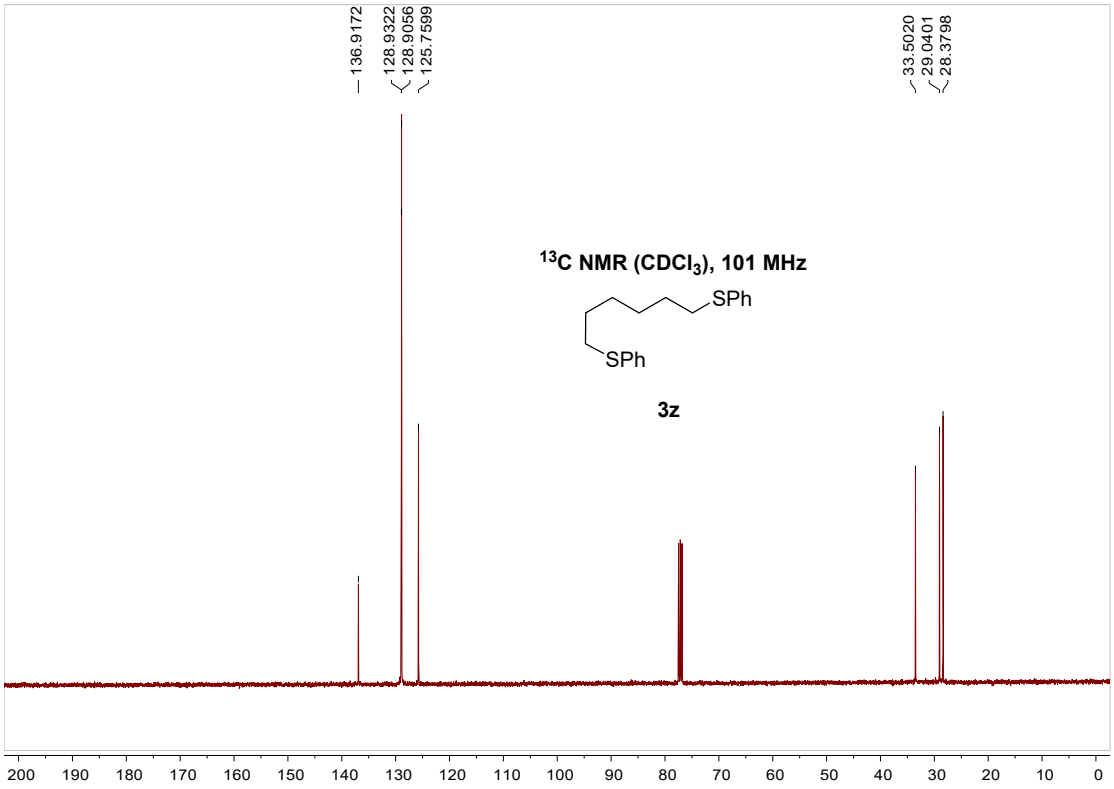

162.0696
141.4874
133.7834
133.3986
132.3664
128.4648
128.3654
127.7666
125.8936
62.9035
36.8003
35.8434
34.8798
31.3217
29.7408
21.7609
^{13}C NMR ($CDCl_3$), 101 MHz
O
Me
O
S
S
Ph
3w
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

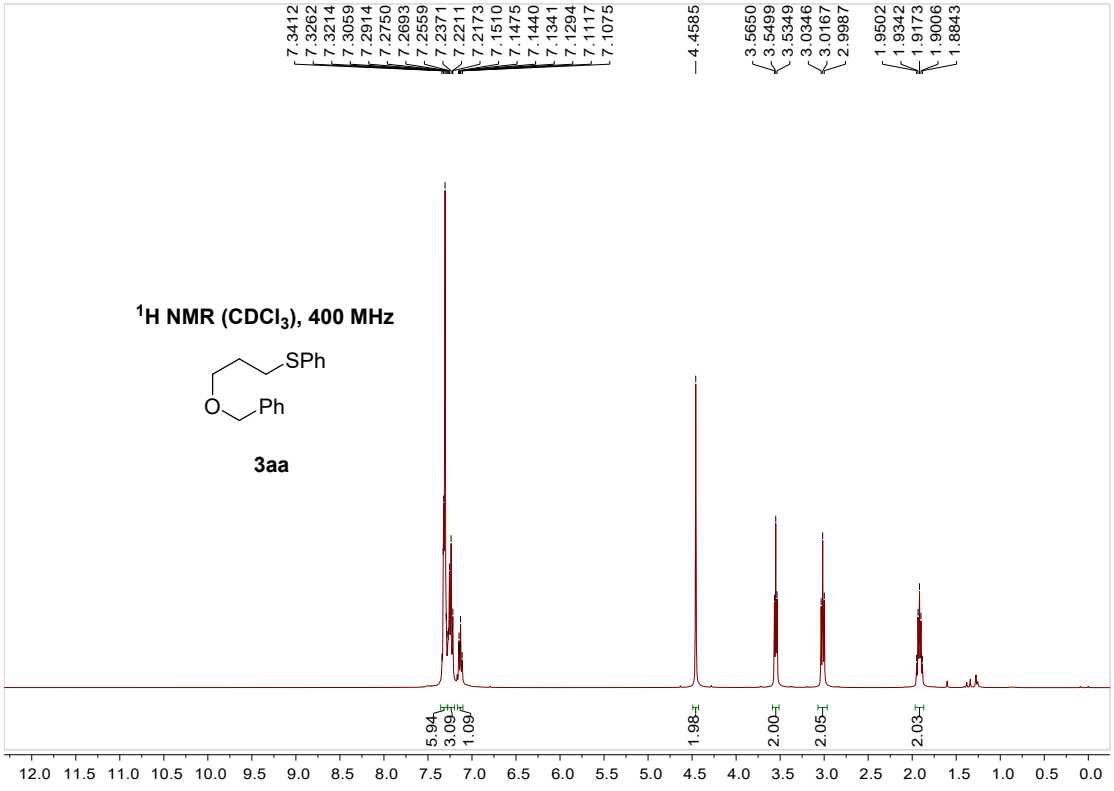

8.0384
8.0209
7.5680
7.5542
7.5494
7.5448
7.5342
7.5308
7.5274
7.4428
7.4386
7.4262
7.4229
7.4085
7.4042
7.2779
7.2753
7.2714
7.2616
7.2598
7.2561
7.2528
7.2438
7.2383
7.1883
7.1851
7.1711
7.1666
7.1556
7.1507
4.4747
4.4586
4.4426
2.9466
2.9295
2.9123
2.7271
2.7084
2.6893
2.5739
2.5558
2.5374
2.0061
1.9902
1.9874
1.9740
1.9709
1.9568
1.9539
1.9438
1.9372
1.9346
1.9251
1.9180
1.9065
1.8912
1.8875
1.3548
1.3378
1H NMR (CDCl3), 400 MHz
O
Me
O
S
Ph
3x
1.94
0.97
1.97
2.10
3.00
1.89
0.96
2.07
2.10
1.93
2.07
2.98
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
166.5761
141.5699
133.0292
130.3431
129.6331
128.5421
128.4618
125.9880
62.8442
36.9574
35.9528
34.9717
31.4097
29.7936
21.8351
13C NMR (CDCl3), 101 MHz
O
Me
O
S
Ph
3x
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

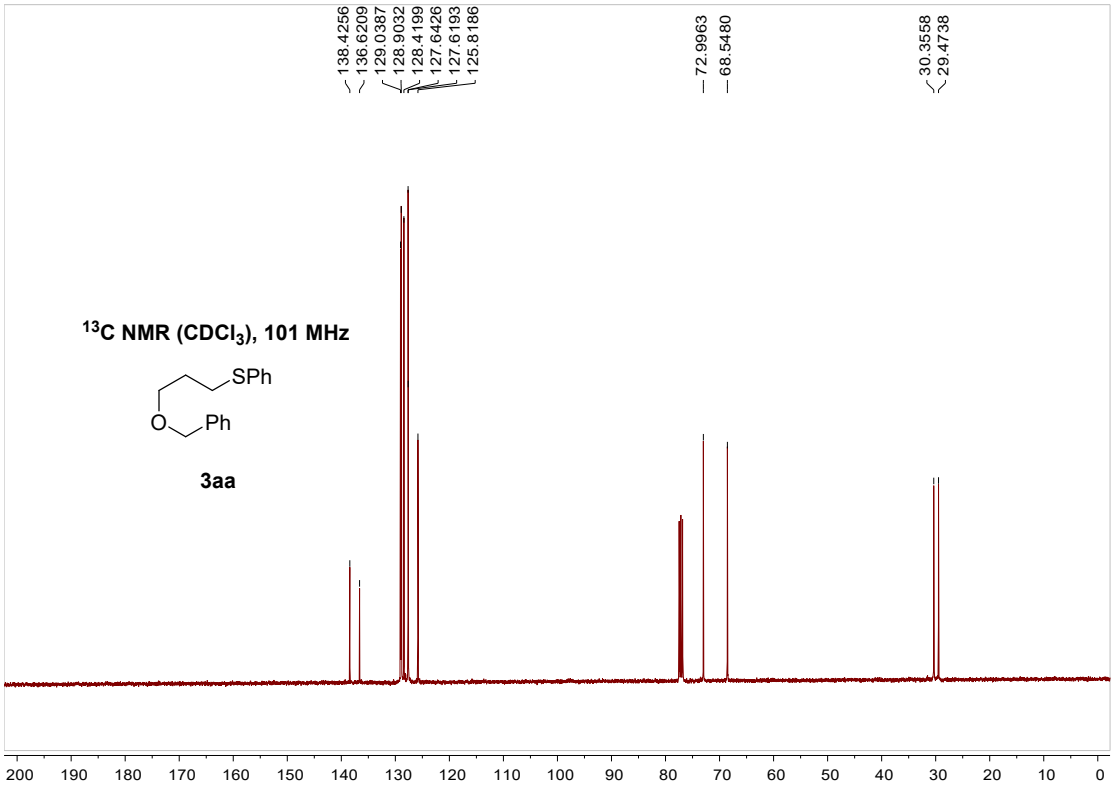

7.4053
7.3882
7.3634
7.3449
7.3252
7.3154
7.2946
7.2662
7.2623
7.2587
7.2493
7.2444
7.2388
7.2299
7.2264
7.2228
7.1687
7.1480
3.2001
3.1818
3.1759
3.1614
2.9507
2.9359
2.9302
2.9121
1H NMR (CDCl3), 400 MHz
Cl
SPh
3y
1.90
2.07
2.13
1.15
2.00
1.96
1.98
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

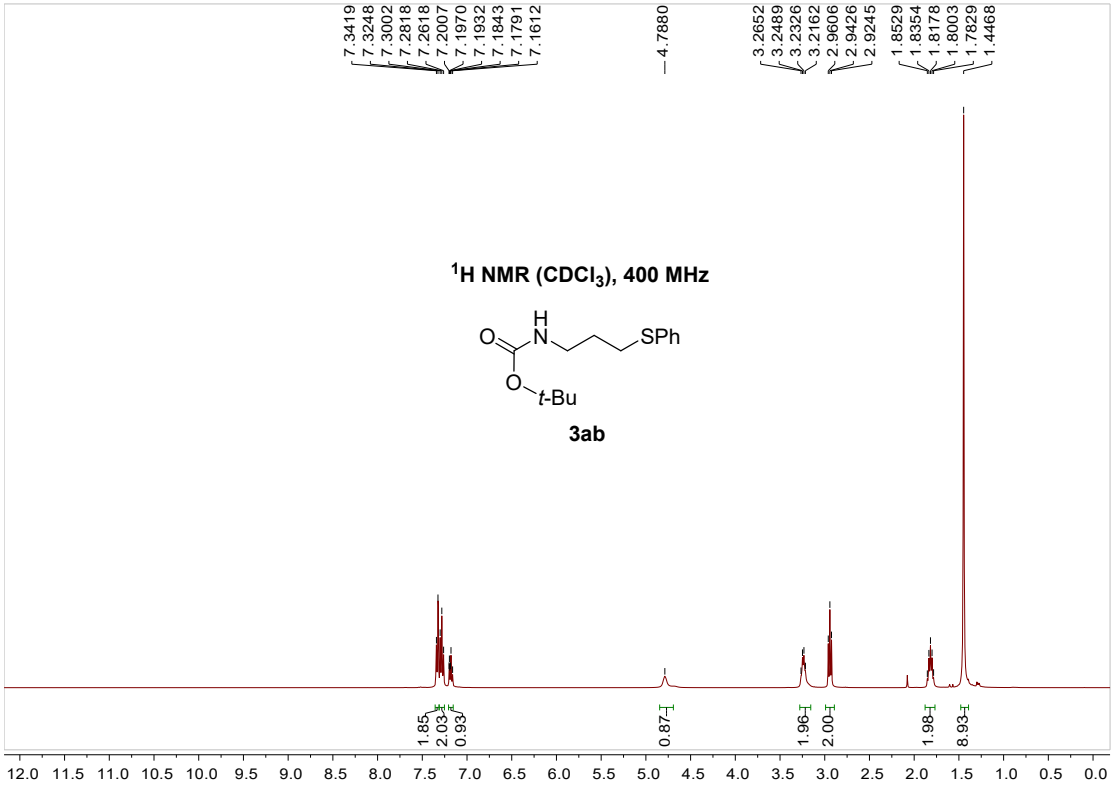

138.6540
136.1152
132.3160
130.0103
129.4793
129.0934
128.7003
126.2584
35.1314
34.9851
13C NMR (CDCl3), 101 MHz
Cl
SPh
3y
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

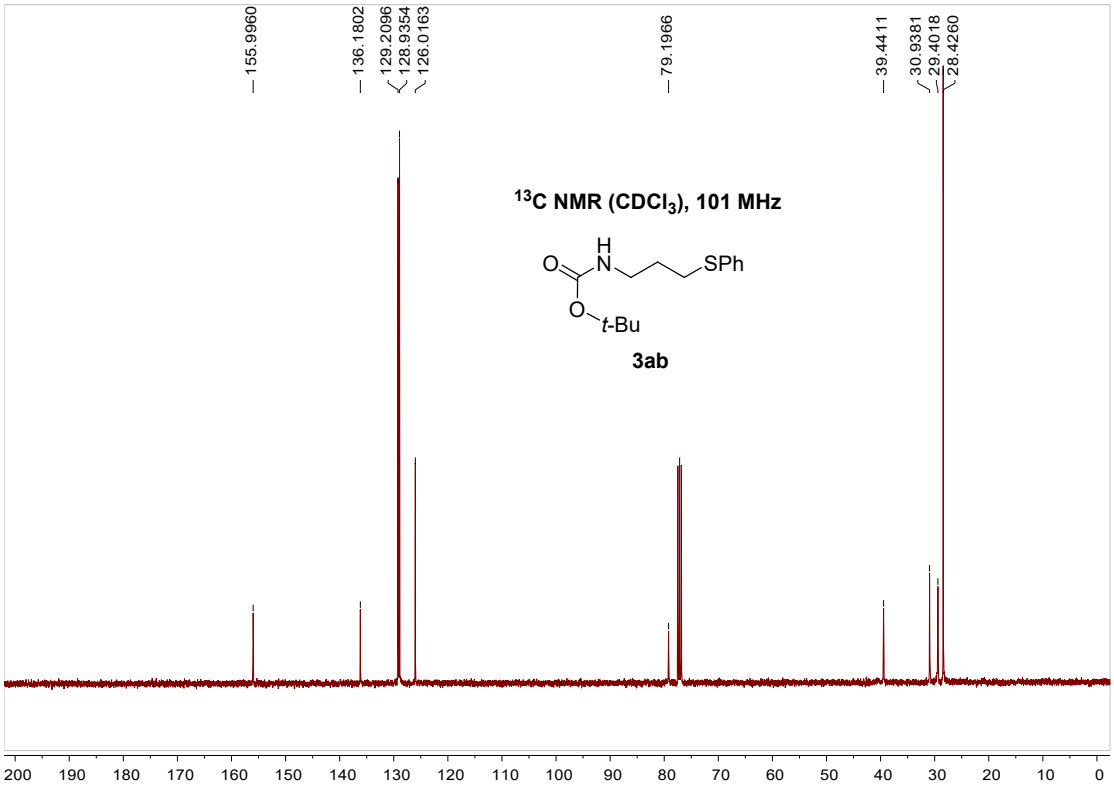

7.3138
7.3094
7.2926
7.2896
7.2723
7.2540
7.2380
7.2341
7.1642
7.1604
7.1564
7.1474
7.1426
7.1284
7.1248
2.9034
2.8852
2.8667
1.6588
1.6414
1.6235
1.6058
1.5889
1.4533
1.4350
1.4261
1.4168
1.4072
1.3984
1.3778
1H NMR (CDCl3), 400 MHz
SPh
SPh
3z
3.72
4.04
1.89
4.00
4.11
4.20
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

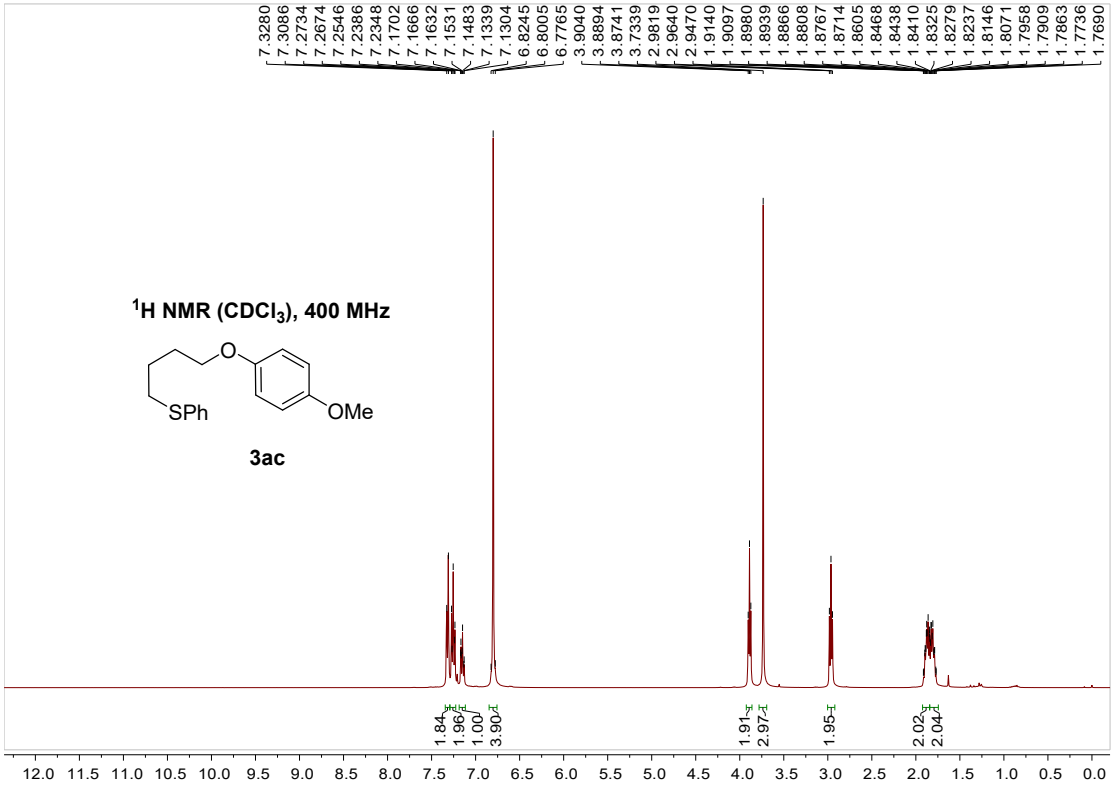

136.9172
128.9322
128.9056
125.7599
33.5020
29.0401
28.3798
13C NMR (CDCl3), 101 MHz
SPh
SPh
3z
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

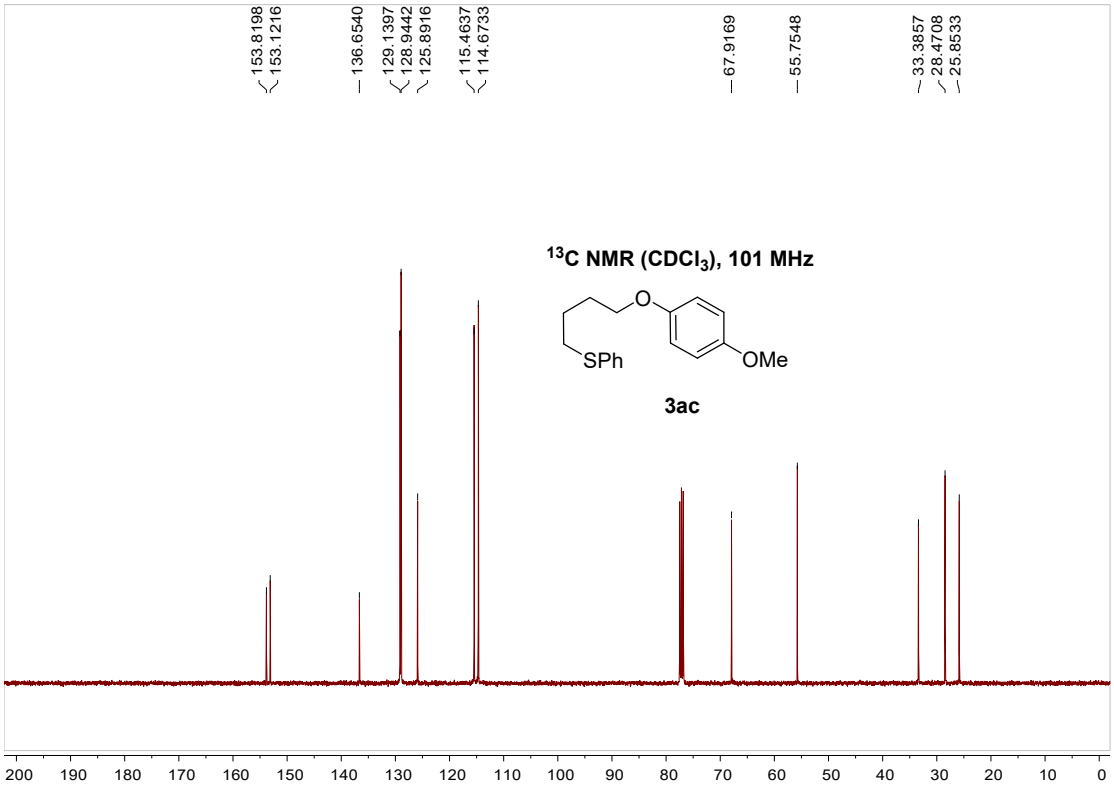

7.3412
7.3262
7.3214
7.3059
7.2914
7.2750
7.2693
7.2559
7.2371
7.2211
7.2173
7.1510
7.1475
7.1440
7.1341
7.1294
7.1117
7.1075
4.4585
3.5650
3.5499
3.5349
3.0346
3.0167
2.9987
1.9502
1.9342
1.9173
1.9006
1.8843
^{1}H NMR ($CDCl_3$), 400 MHz
SPh
O
Ph
3aa
5.94
3.09
1.09
1.98
2.00
2.05
2.03
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

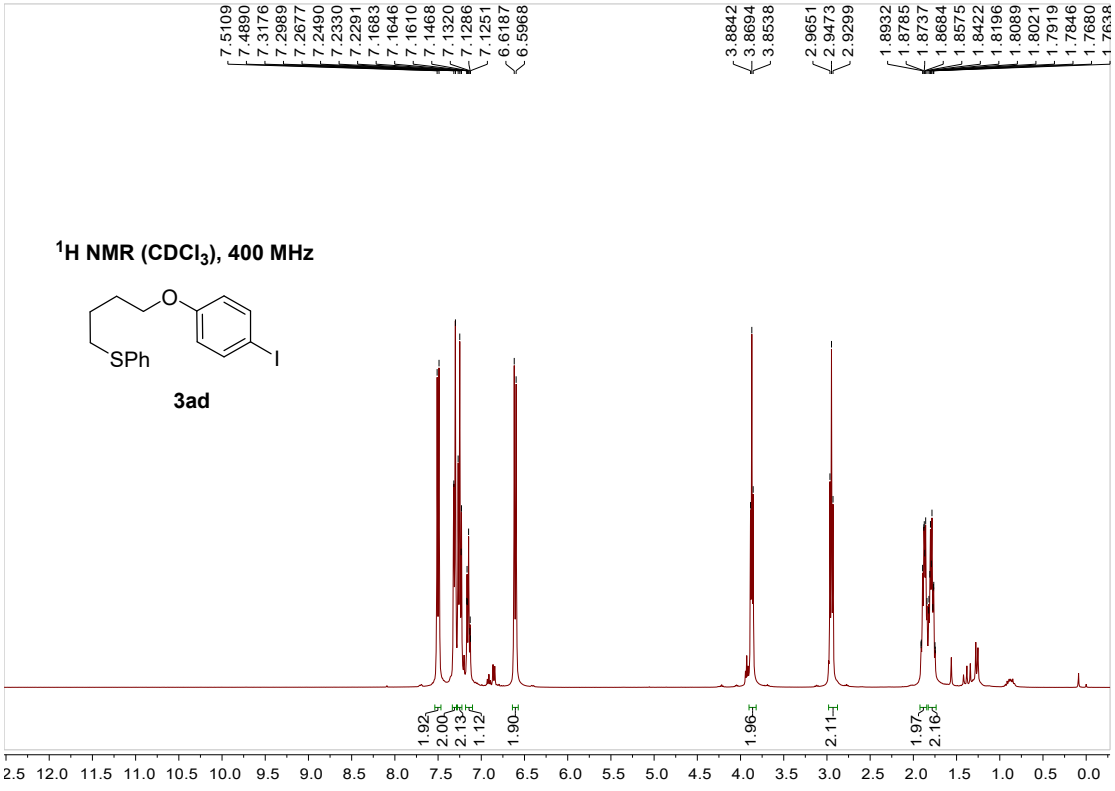

138.4256
136.6209
129.0387
128.9032
128.4199
127.6426
127.6193
125.8186
72.9963
68.5480
30.3558
29.4738
^{13}C NMR ($CDCl_3$), 101 MHz
SPh
O
Ph
3aa
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

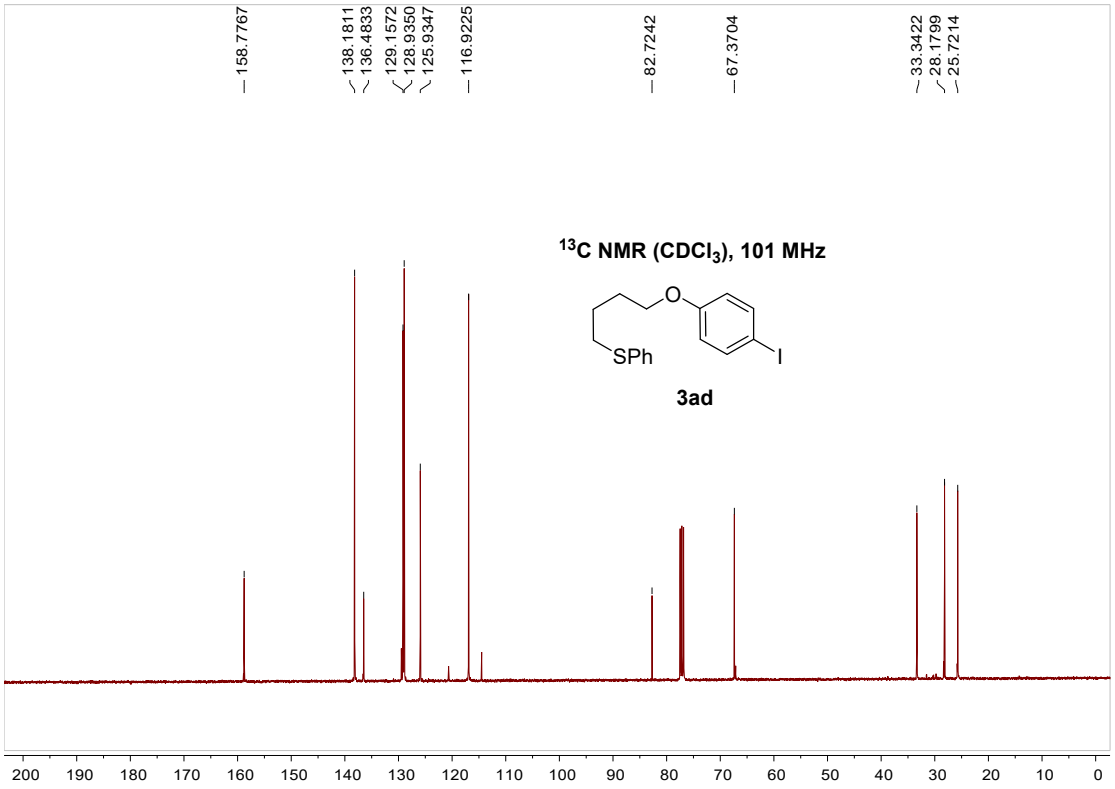

7.3419
7.3248
7.3002
7.2818
7.2618
7.2007
7.1970
7.1932
7.1843
7.1791
7.1612
4.7880
3.2652
3.2489
3.2326
3.2162
2.9606
2.9426
2.9245
1.8529
1.8354
1.8178
1.8003
1.7829
1.4468
1H NMR (CDCl3), 400 MHz
O
H
N
SPh
O
t-Bu
3ab
1.85
2.03
0.93
0.87
1.96
2.00
1.98
8.93
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

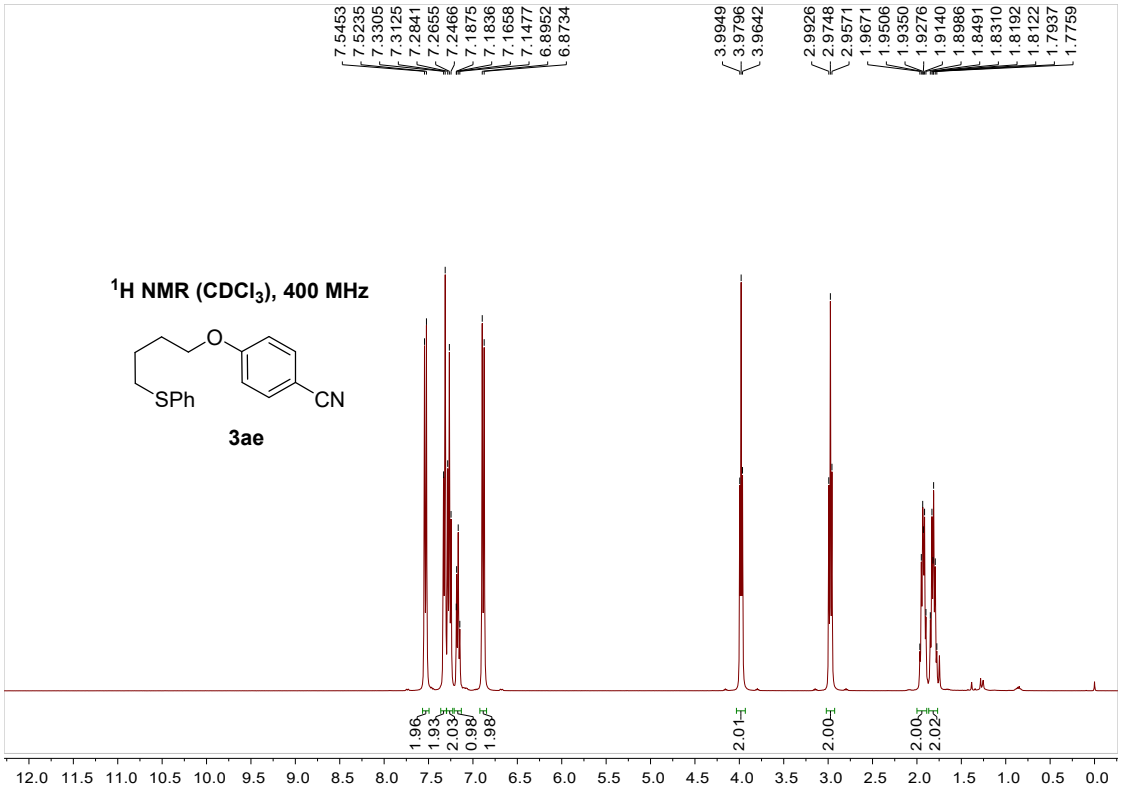

155.9960
136.1802
129.2096
128.9354
126.0163
79.1966
39.4411
30.9381
29.4018
28.4260
13C NMR (CDCl3), 101 MHz
O
H
N
SPh
O
t-Bu
3ab
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

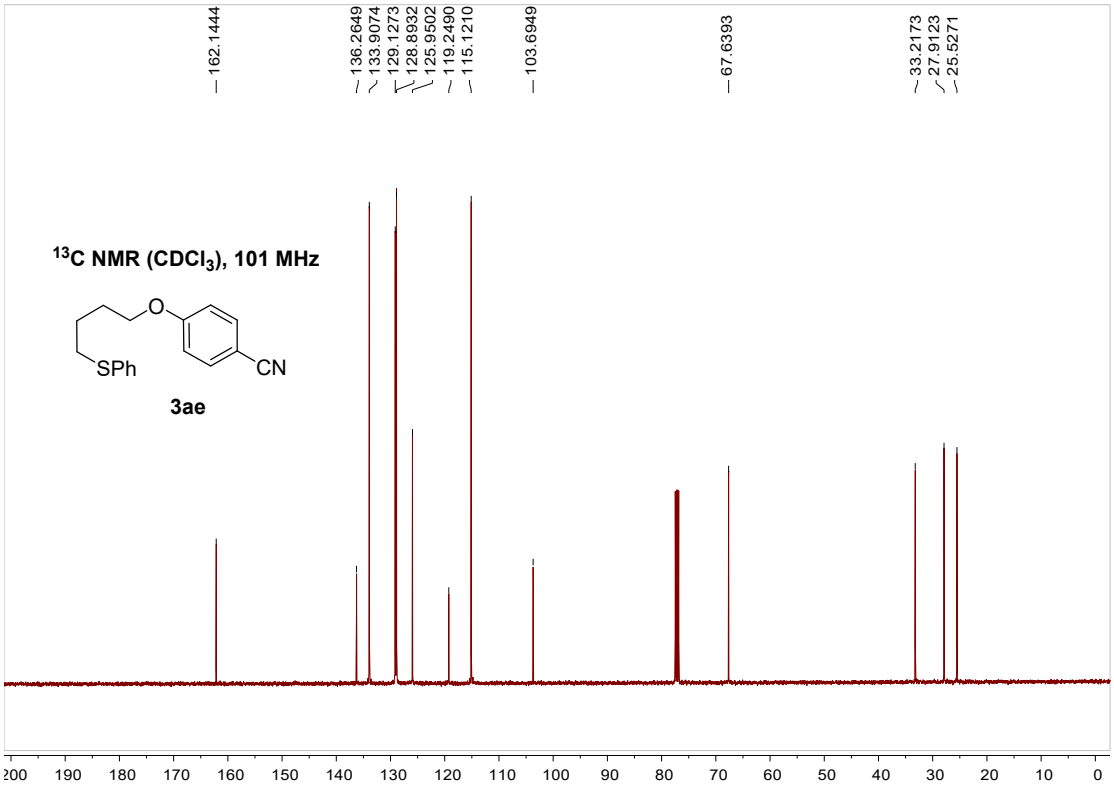

7.3280
7.3086
7.2734
7.2674
7.2546
7.2386
7.2348
7.1702
7.1666
7.1632
7.1531
7.1483
7.1339
7.1304
6.8245
6.8005
6.7765
3.9040
3.8894
3.8741
3.7339
2.9819
2.9640
2.9470
1.9140
1.9097
1.8980
1.8939
1.8866
1.8808
1.8767
1.8714
1.8605
1.8468
1.8438
1.8410
1.8325
1.8279
1.8237
1.8146
1.8071
1.7958
1.7909
1.7863
1.7736
1.7690
1H NMR (CDCl3), 400 MHz
O
SPh
OMe
3ac
1.84
1.96
1.00
3.90
1.91
2.97
1.95
2.02
2.04
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

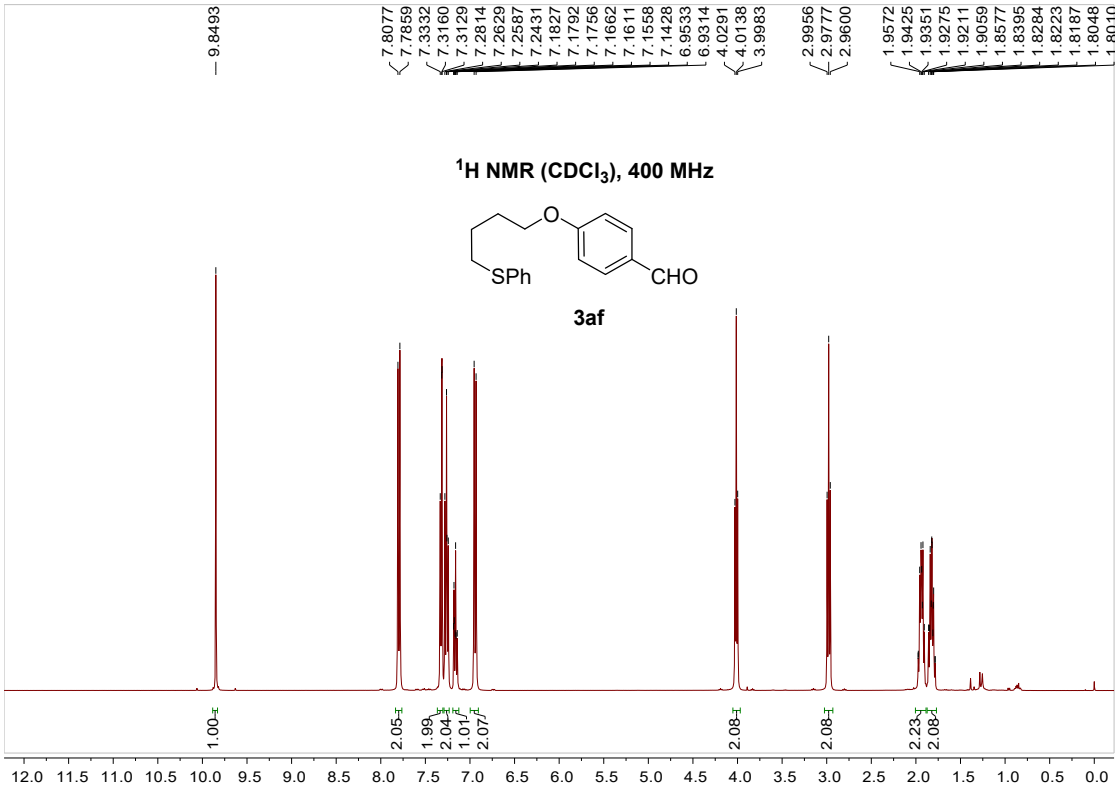

153.8198
153.1216
136.6540
129.1397
128.9442
125.8916
115.4637
114.6733
67.9169
55.7548
33.3857
28.4708
25.8533
13C NMR (CDCl3), 101 MHz
O
SPh
OMe
3ac
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0


7.5109
7.4890
7.3176
7.2989
7.2677
7.2490
7.2330
7.2291
7.1683
7.1646
7.1610
7.1468
7.1320
7.1286
7.1251
6.6187
6.5968
3.8842
3.8694
3.8538
2.9651
2.9473
2.9299
1.8932
1.8785
1.8737
1.8684
1.8575
1.8422
1.8196
1.8089
1.8021
1.7919
1.7846
1.7680
1.7638
1H NMR (CDCl3), 400 MHz
O
SPh
I
3ad
1.92
2.00
2.13
1.12
1.90
1.96
2.11
1.97
2.16
2.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0


158.7767
138.1811
136.4833
129.1572
128.9350
125.9347
116.9225
82.7242
67.3704
33.3422
28.1799
25.7214
13C NMR (CDCl3), 101 MHz
O
SPh
I
3ad
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

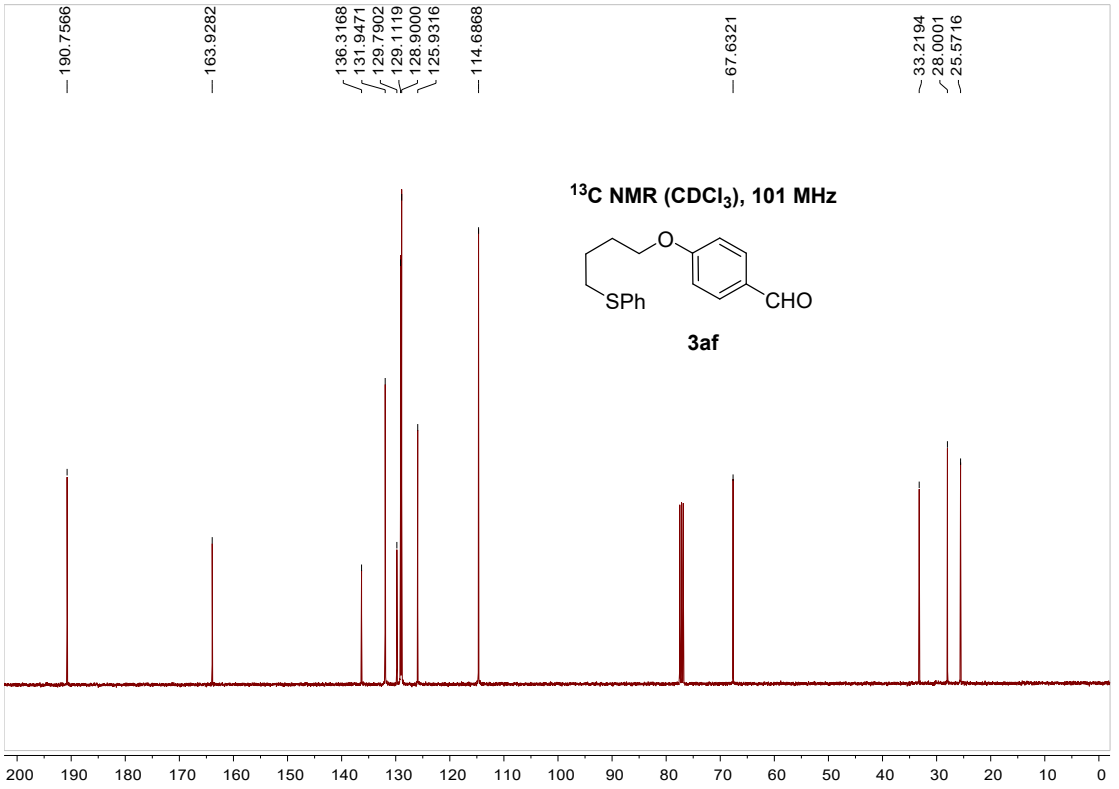

7.5453
7.5235
7.3305
7.3125
7.2841
7.2655
7.2466
7.1875
7.1836
7.1658
7.1477
6.8952
6.8734
3.9949
3.9796
3.9642
2.9926
2.9748
2.9571
1.9671
1.9506
1.9350
1.9276
1.9140
1.8986
1.8491
1.8310
1.8192
1.8122
1.7937
1.7759
1H NMR (CDCl3), 400 MHz
O
SPh
CN
3ae
1.96
1.93
2.03
0.98
1.98
2.01
2.00
2.00
2.02
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0


162.1444
136.2649
133.9074
129.1273
128.8932
125.9502
119.2490
115.1210
103.6949
67.6393
33.2173
27.9123
25.5271
13C NMR (CDCl3), 101 MHz
O
SPh
CN
3ae
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0



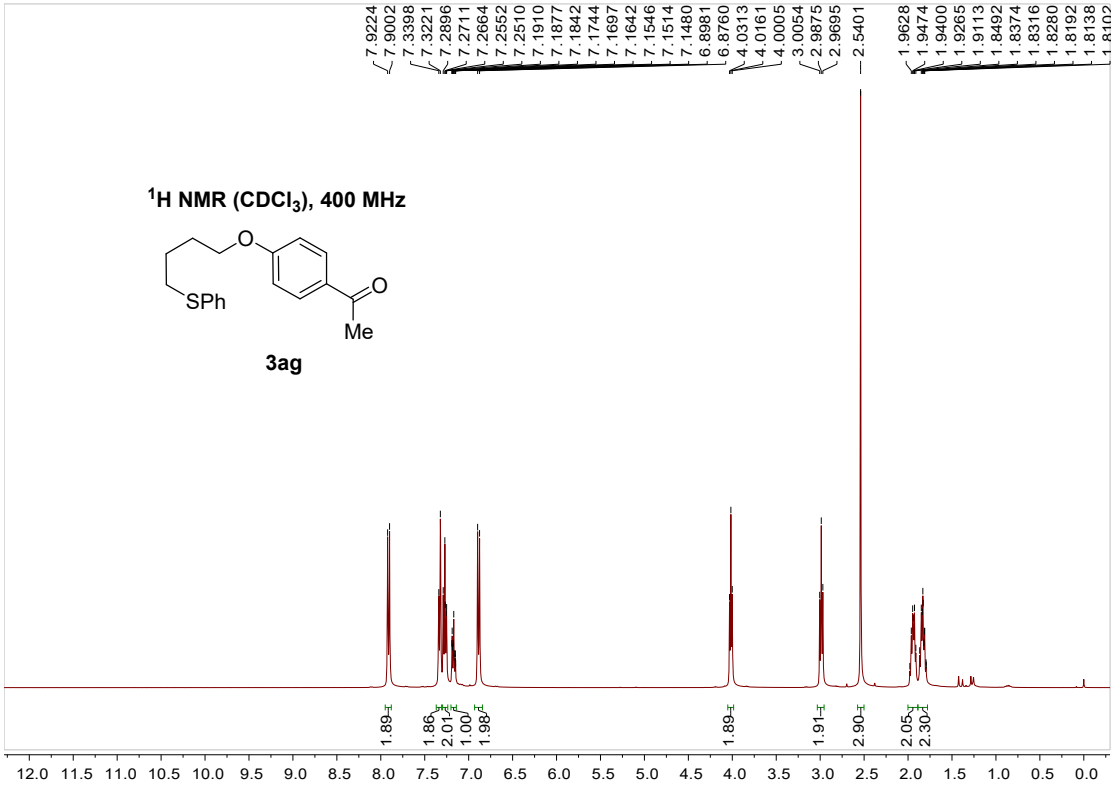
^{1}H NMR ($CDCl_3$), 400 MHz

3af



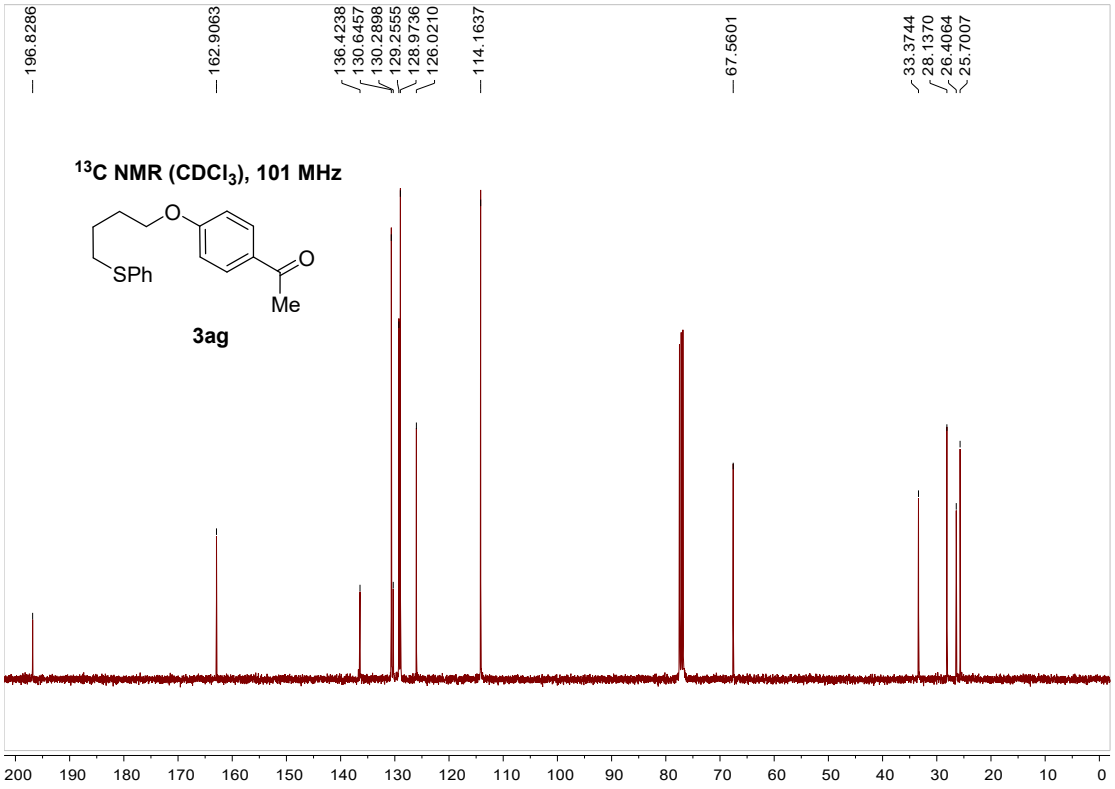
^{13}C NMR ($CDCl_3$), 101 MHz

3af



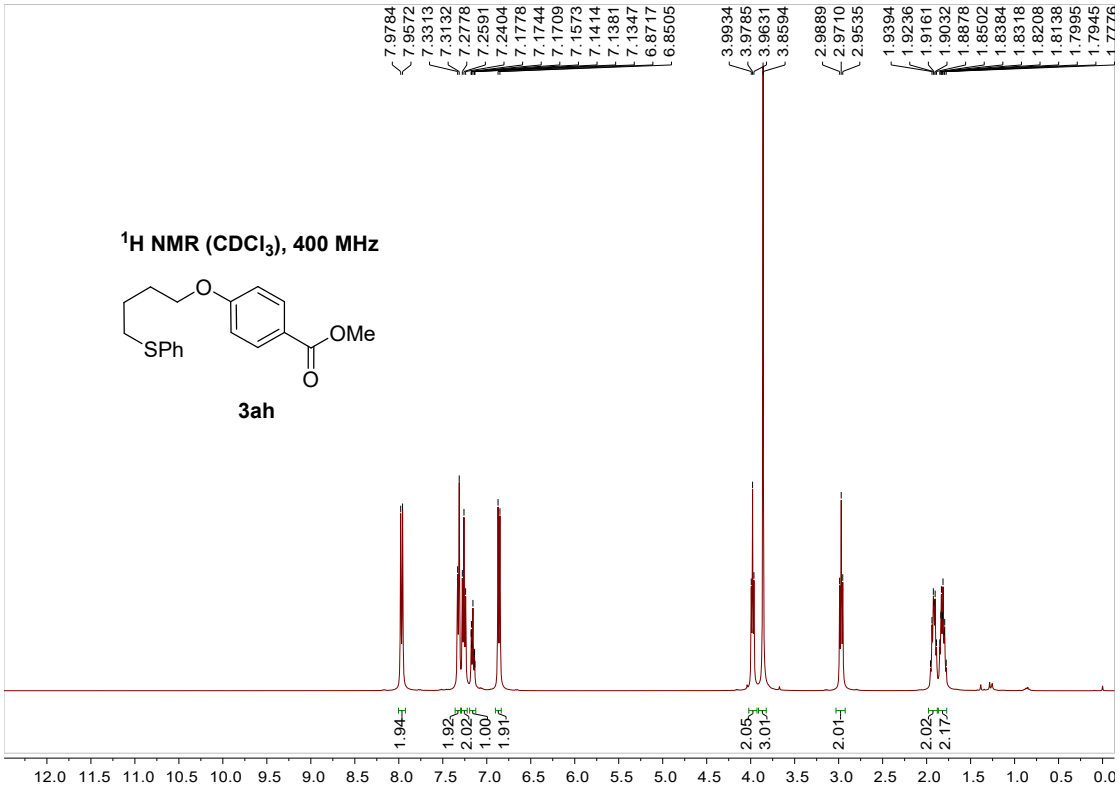
^{1}H NMR ($CDCl_3$), 400 MHz

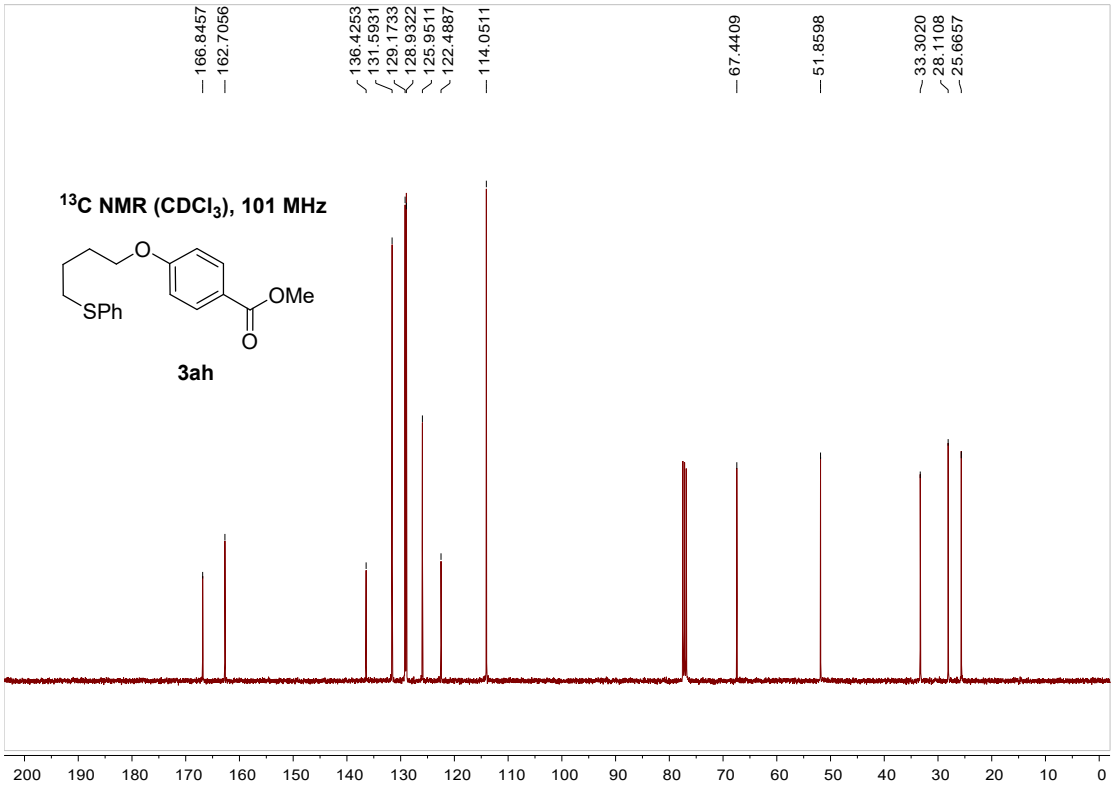
3ag

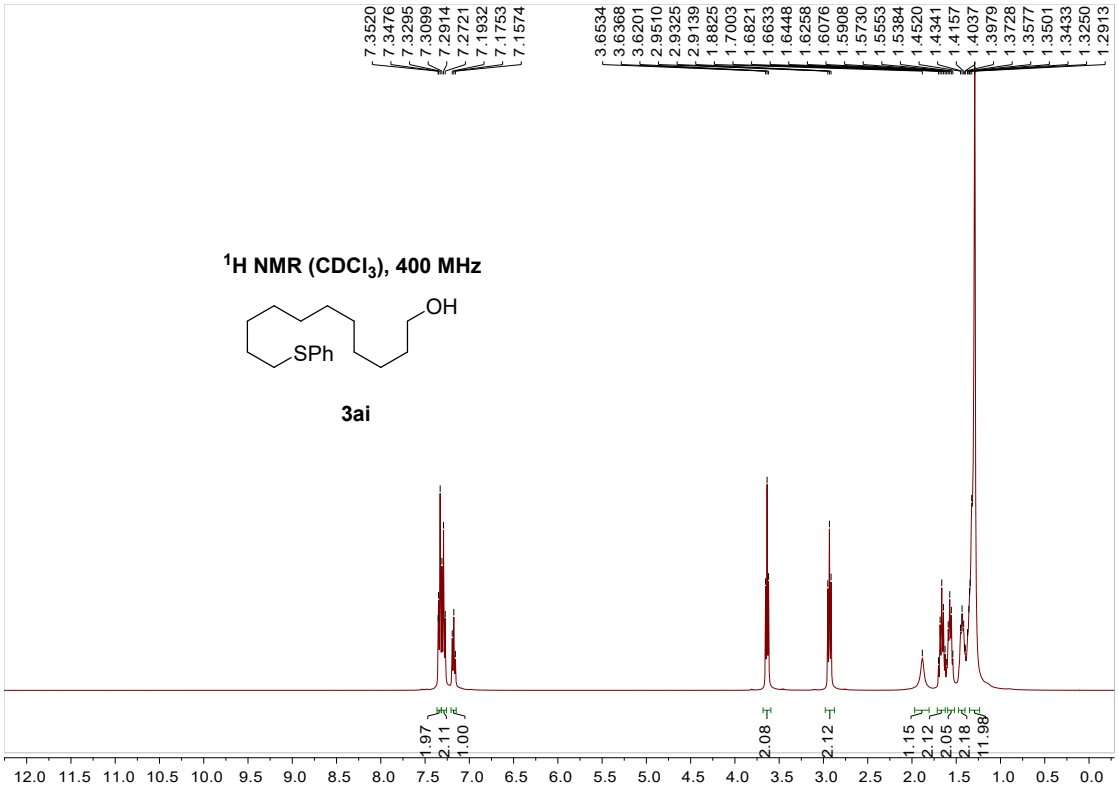


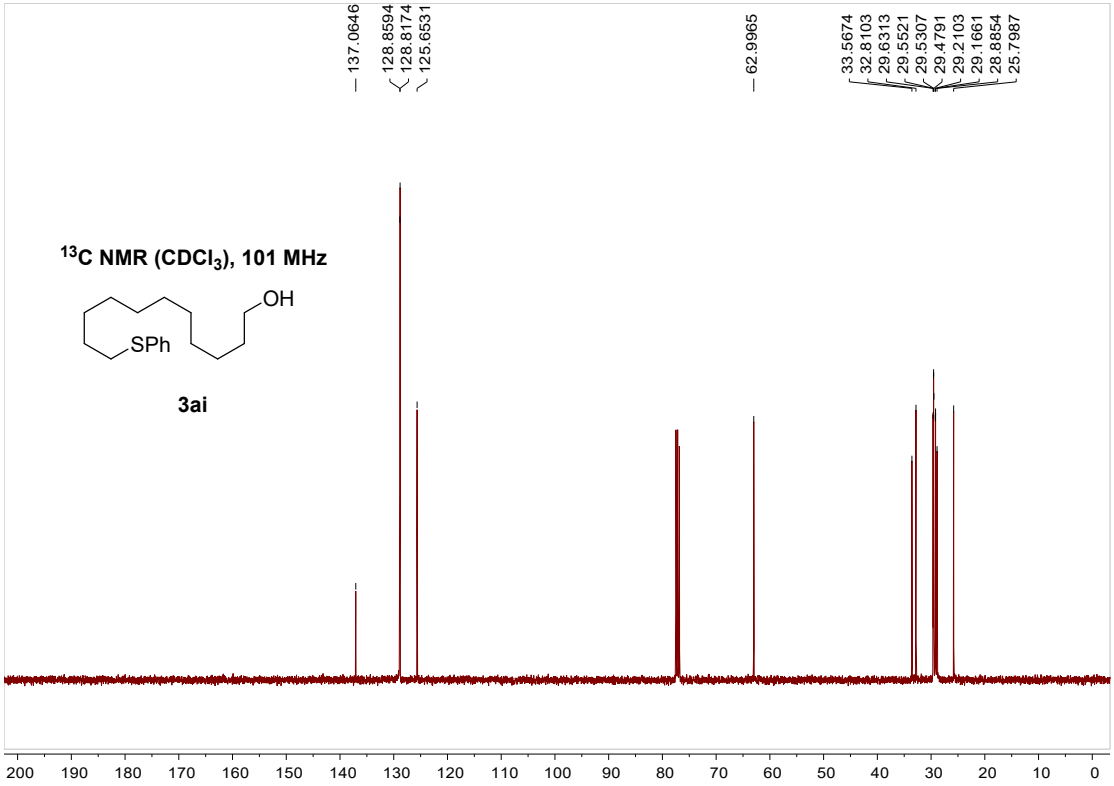
^{13}C NMR ($CDCl_3$), 101 MHz

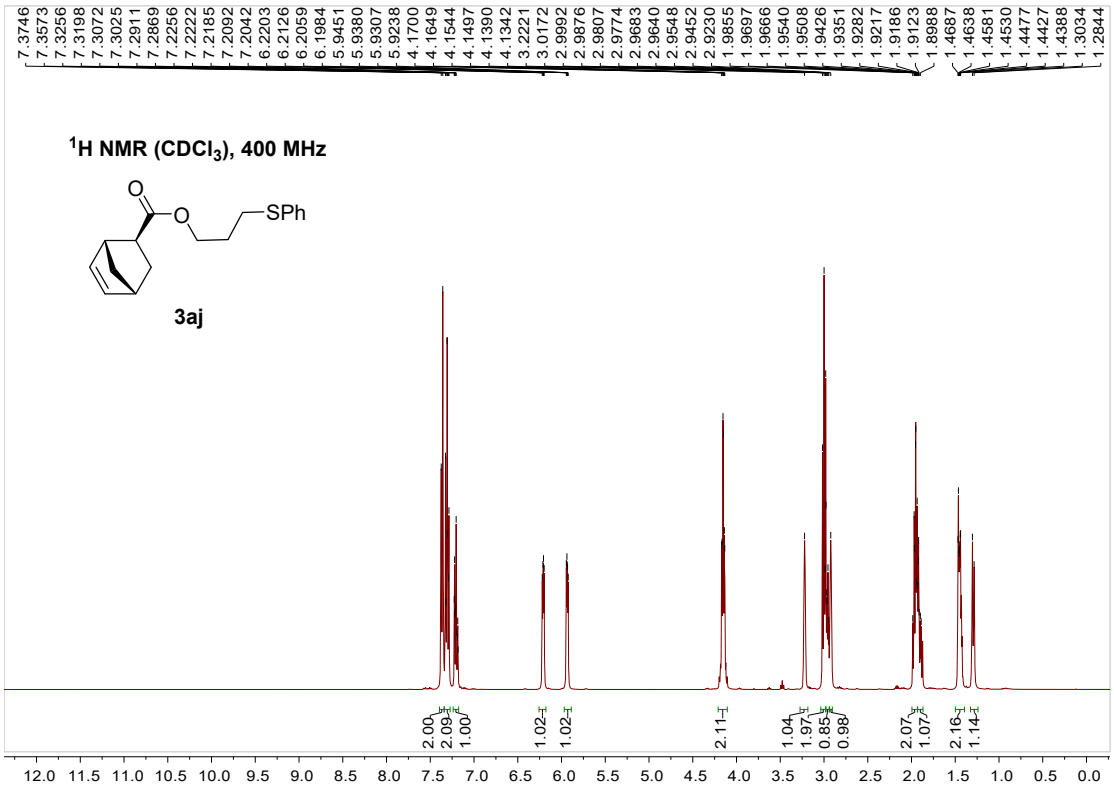
3ag

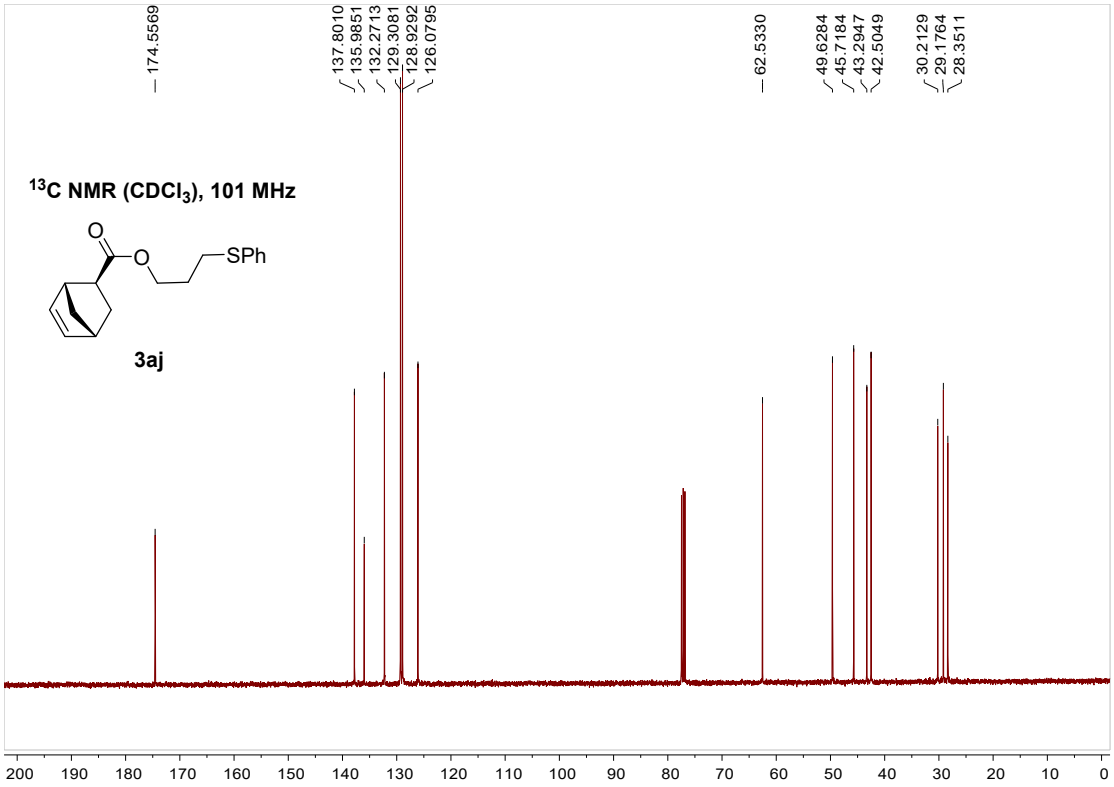

7.9784
7.9572
7.3313
7.3132
7.2778
7.2591
7.2404
7.1778
7.1744
7.1709
7.1573
7.1414
7.1381
7.1347
6.8717
6.8505
3.9934
3.9785
3.9631
3.8594
2.9889
2.9710
2.9535
1.9394
1.9236
1.9161
1.9032
1.8878
1.8502
1.8384
1.8318
1.8208
1.8138
1.7995
1.7945
1.7776
1H NMR (CDCl3), 400 MHz
O
SPh
OMe
O
3ah
1.94
1.92
2.02
1.00
1.91
2.05
3.01
2.01
2.02
2.17
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

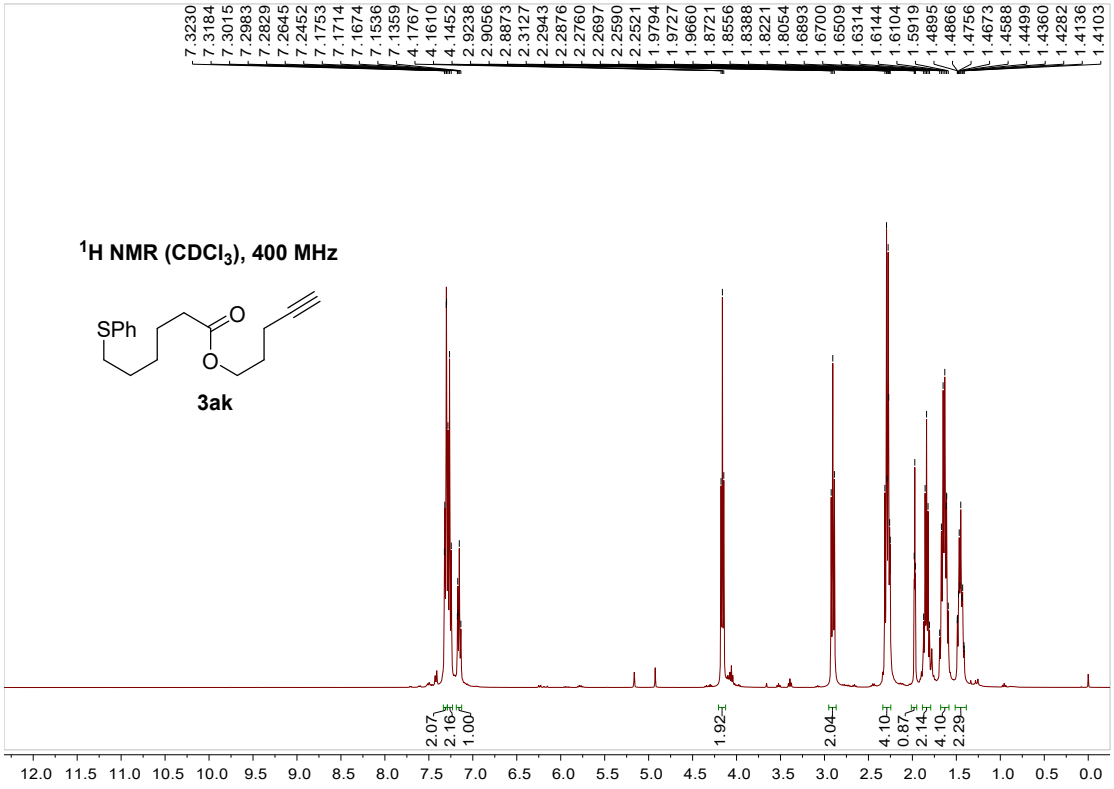

166.8457
162.7056
136.4253
131.5931
129.1733
128.9322
125.9511
122.4887
114.0511
67.4409
51.8598
33.3020
28.1108
25.6657
13C NMR (CDCl3), 101 MHz
O
SPh
OMe
O
3ah
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

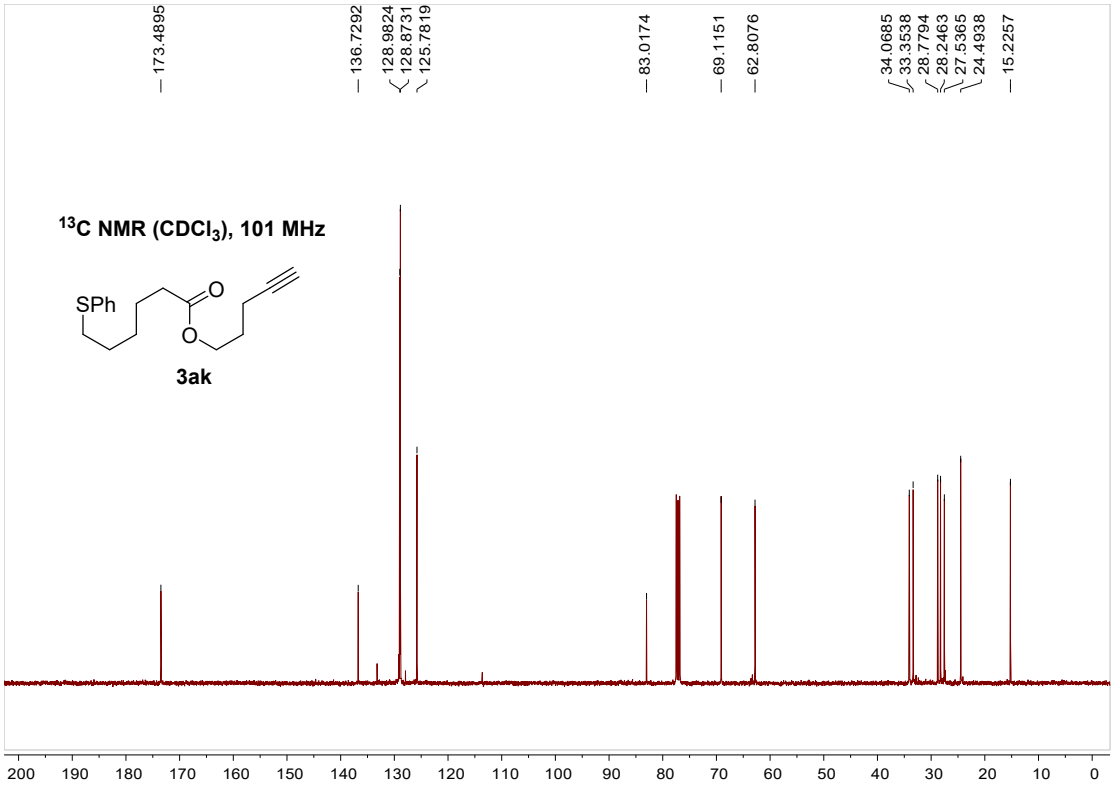

7.3520
7.3476
7.3295
7.3099
7.2914
7.2721
7.1932
7.1753
7.1574
3.6534
3.6368
3.6201
2.9510
2.9325
2.9139
1.8825
1.7003
1.6821
1.6633
1.6448
1.6258
1.6076
1.5908
1.5730
1.5553
1.5384
1.4520
1.4341
1.4157
1.4037
1.3979
1.3728
1.3577
1.3501
1.3433
1.3250
1.2913
1H NMR (CDCl3), 400 MHz
OH
SPh
3ai
1.97
2.11
1.00
2.08
2.12
1.15
2.12
2.05
2.18
11.98
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

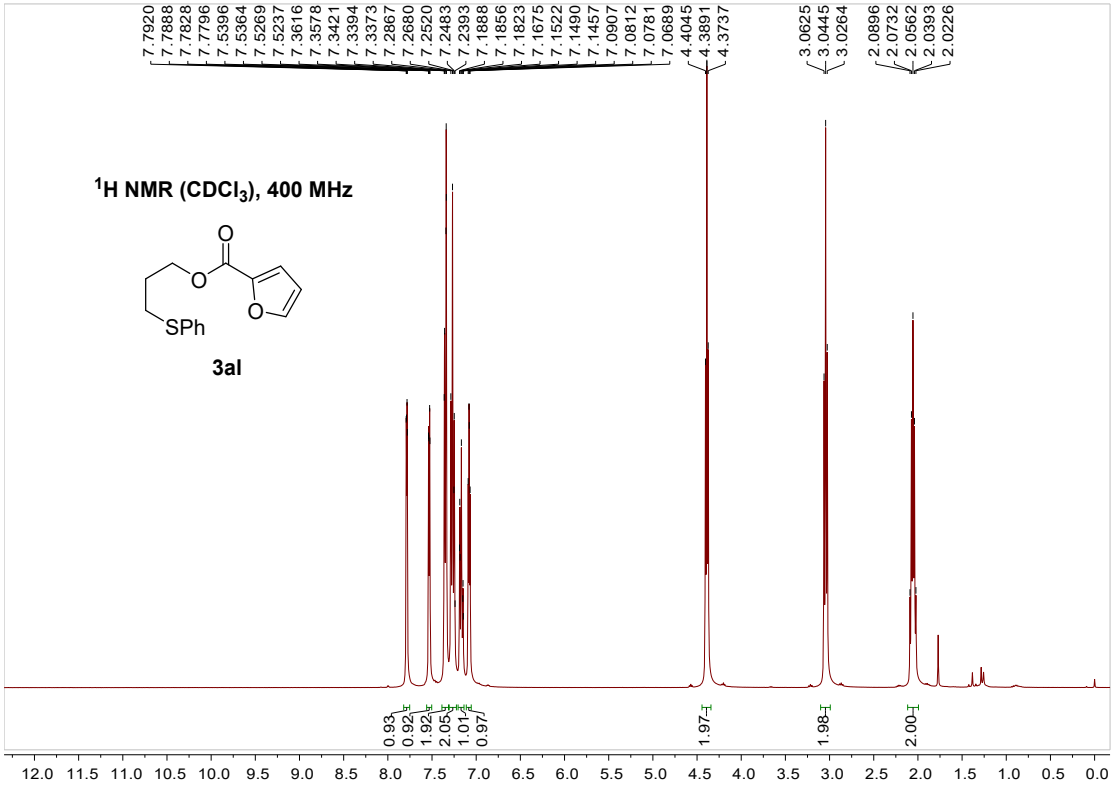

137.0646
128.8594
128.8174
125.6531
62.9965
33.5674
32.8103
29.6313
29.5521
29.5307
29.4791
29.2103
29.1661
28.8854
25.7987
13C NMR (CDCl3), 101 MHz
OH
SPh
3ai
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

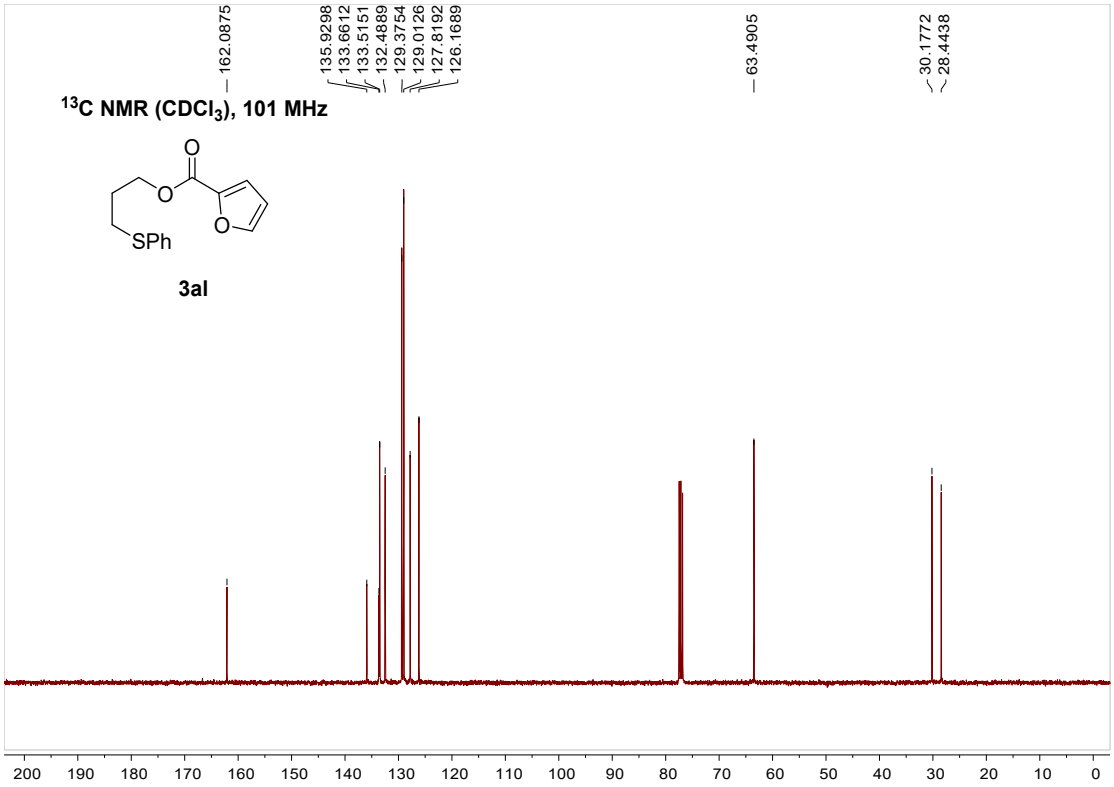

7.3746
7.3573
7.3256
7.3198
7.3072
7.3025
7.2911
7.2869
7.2256
7.2222
7.2185
7.2092
7.2042
6.2203
6.2126
6.2059
6.1984
5.9451
5.9380
5.9307
5.9238
4.1700
4.1649
4.1544
4.1497
4.1390
4.1342
3.2221
3.0172
2.9992
2.9876
2.9807
2.9774
2.9683
2.9640
2.9548
2.9452
2.9230
1.9855
1.9697
1.9666
1.9540
1.9508
1.9426
1.9351
1.9282
1.9217
1.9186
1.9123
1.8988
1.4687
1.4638
1.4581
1.4530
1.4477
1.4427
1.4388
1.3034
1.2844
^{1}H NMR (CDCl$_3$), 400 MHz
O
O
SPh
3aj
2.00
2.09
1.00
1.02
1.02
2.11
1.04
1.97
0.85
0.98
2.07
1.07
2.16
1.14
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

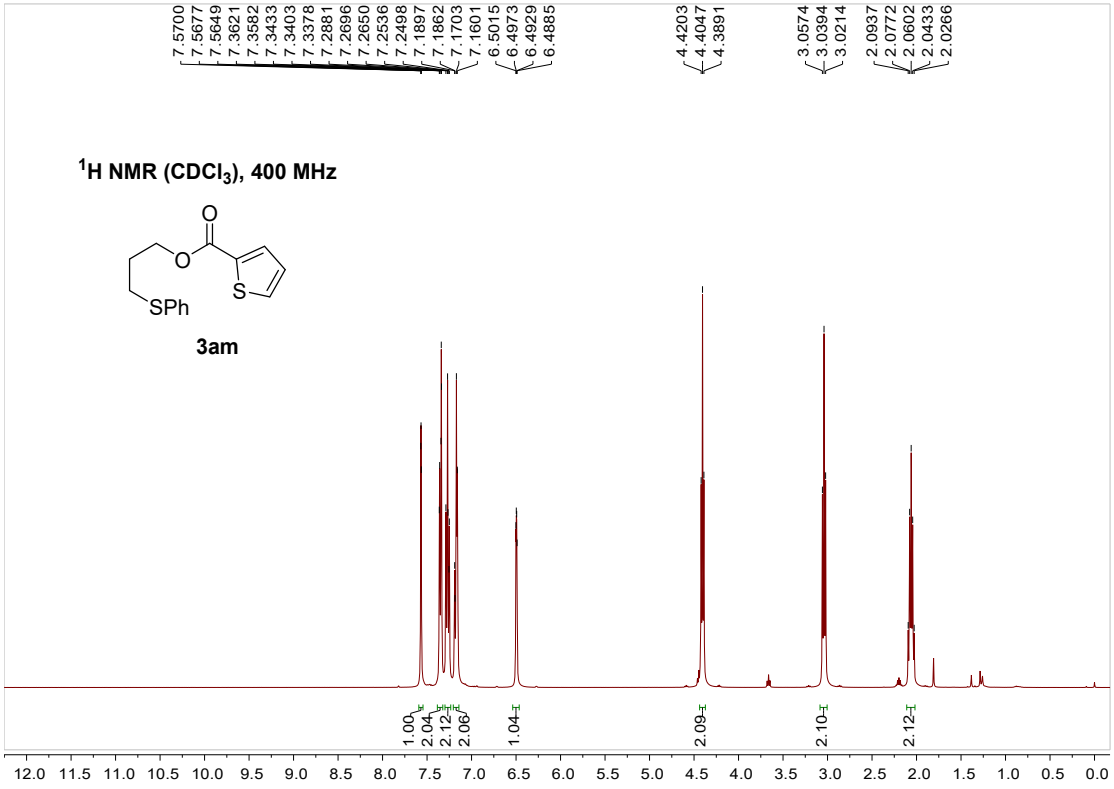

174.5569
137.8010
135.9851
132.2713
129.3081
128.9292
126.0795
62.5330
49.6284
45.7184
43.2947
42.5049
30.2129
29.1764
28.3511
^{13}C NMR (CDCl$_3$), 101 MHz
O
O
SPh
3aj
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

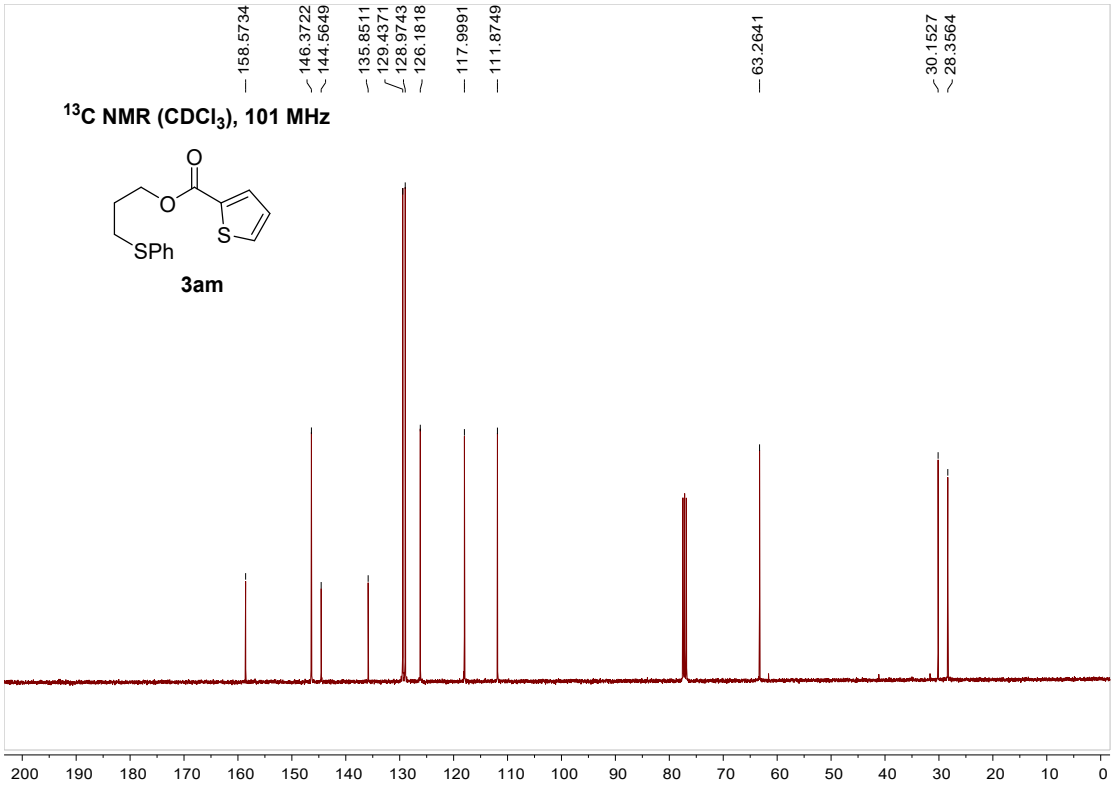

7.3230
7.3184
7.3015
7.2983
7.2829
7.2645
7.2452
7.1753
7.1714
7.1674
7.1536
7.1359
4.1767
4.1610
4.1452
2.9238
2.9056
2.8873
2.3127
2.2943
2.2876
2.2760
2.2697
2.2590
2.2521
1.9794
1.9727
1.9660
1.8721
1.8556
1.8388
1.8221
1.8054
1.6893
1.6700
1.6509
1.6314
1.6144
1.6104
1.5919
1.4895
1.4866
1.4756
1.4673
1.4588
1.4499
1.4360
1.4282
1.4136
1.4103
1H NMR (CDCl3), 400 MHz
SPh
O
O
3ak
2.07
2.16
1.00
1.92
2.04
4.10
0.87
2.14
4.10
2.29
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

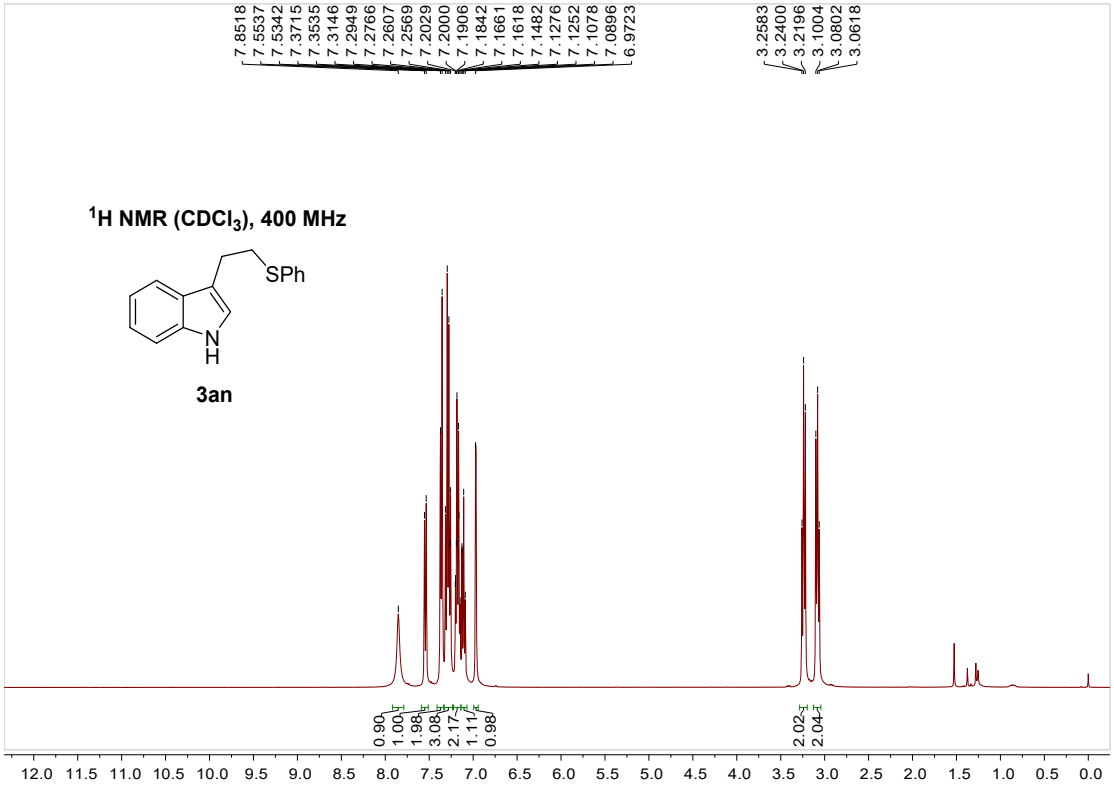

173.4895
136.7292
128.9824
128.8731
125.7819
83.0174
69.1151
62.8076
34.0685
33.3538
28.7794
28.2463
27.5365
24.4938
15.2257
13C NMR (CDCl3), 101 MHz
SPh
O
O
3ak
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

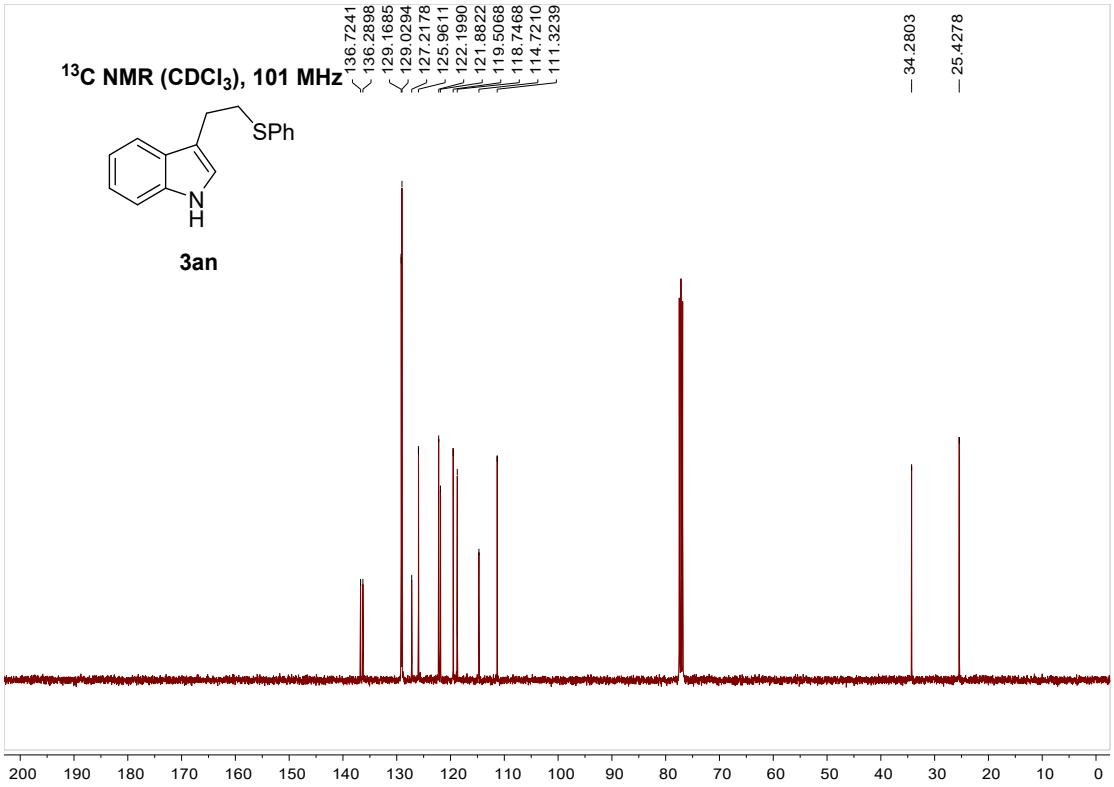

7.7920
7.7888
7.7828
7.7796
7.5396
7.5364
7.5269
7.5237
7.3616
7.3578
7.3421
7.3394
7.3373
7.2867
7.2680
7.2520
7.2483
7.2393
7.1888
7.1856
7.1823
7.1675
7.1522
7.1490
7.1457
7.0907
7.0812
7.0781
7.0689
4.4045
4.3891
4.3737
3.0625
3.0445
3.0264
2.0896
2.0732
2.0562
2.0393
2.0226
^{1}H NMR ($CDCl_3$), 400 MHz
O
O
O
SPh
3al
0.93
0.92
1.92
2.05
1.01
0.97
1.97
1.98
2.00
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

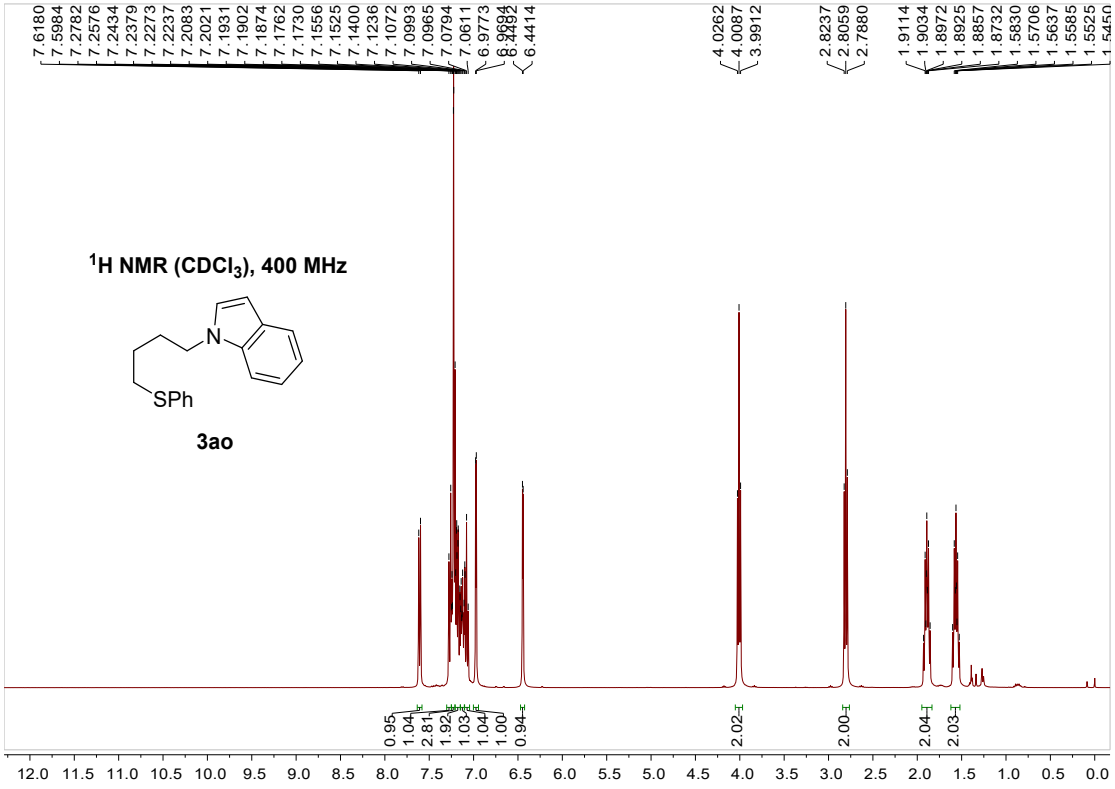

162.0875
135.9298
133.6612
133.5151
132.4889
129.3754
129.0126
127.8192
126.1689
63.4905
30.1772
28.4438
^{13}C NMR ($CDCl_3$), 101 MHz
O
O
O
SPh
3al
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0


7.5700
7.5677
7.5649
7.3621
7.3582
7.3433
7.3403
7.3378
7.2881
7.2696
7.2650
7.2536
7.2498
7.1897
7.1862
7.1703
7.1601
6.5015
6.4973
6.4929
6.4885
4.4203
4.4047
4.3891
3.0574
3.0394
3.0214
2.0937
2.0772
2.0602
2.0433
2.0266
1H NMR (CDCl3), 400 MHz
O
O
S
SPh
3am
1.00
2.04
2.12
2.06
1.04
2.09
2.10
2.12
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0


158.5734
146.3722
144.5649
135.8511
129.4371
128.9743
126.1818
117.9991
111.8749
63.2641
30.1527
28.3564
13C NMR (CDCl3), 101 MHz
O
O
S
SPh
3am
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

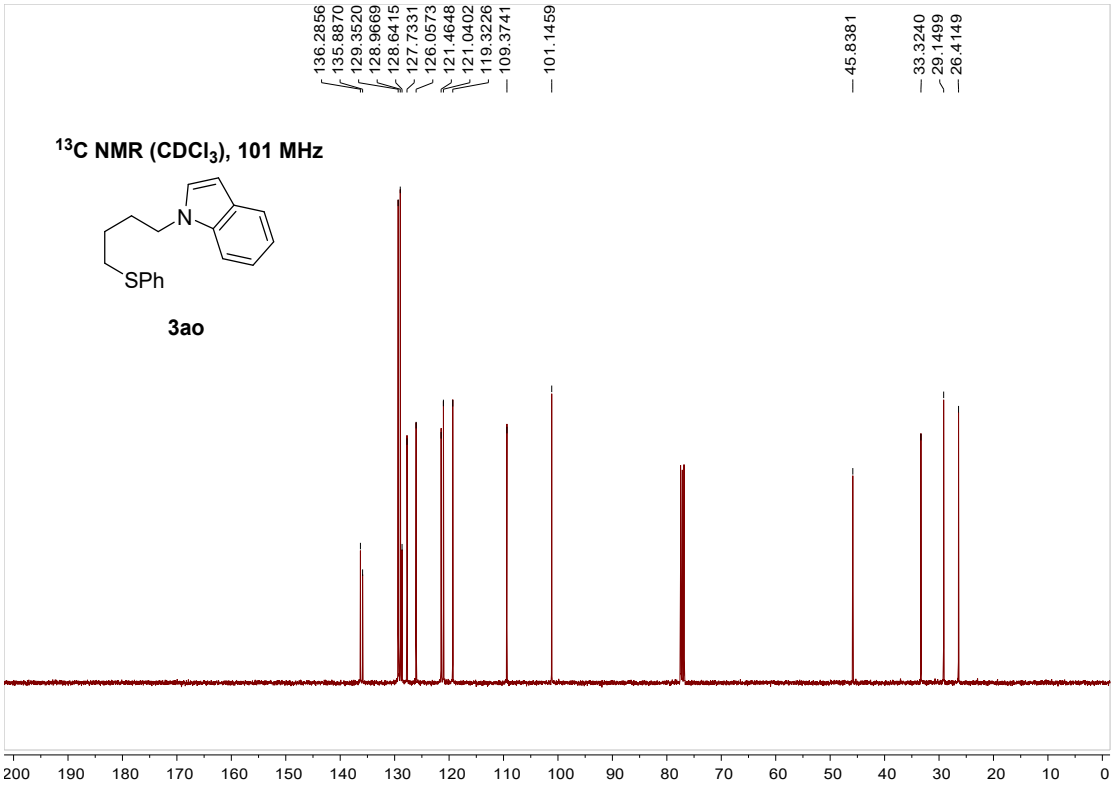

7.8518
7.5537
7.5342
7.3715
7.3535
7.3146
7.2949
7.2766
7.2607
7.2569
7.2029
7.2000
7.1906
7.1842
7.1661
7.1618
7.1482
7.1276
7.1252
7.1078
7.0896
6.9723
3.2583
3.2400
3.2196
3.1004
3.0802
3.0618
^{1}H NMR ($CDCl_3$), 400 MHz
SPh
N
H
3an
0.90
1.00
1.98
3.08
2.17
1.11
0.98
2.02
2.04
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0


136.7241
136.2898
129.1685
129.0294
127.2178
125.9611
122.1990
121.8822
119.5068
118.7468
114.7210
111.3239
34.2803
25.4278
^{13}C NMR ($CDCl_3$), 101 MHz
SPh
N
H
3an
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0



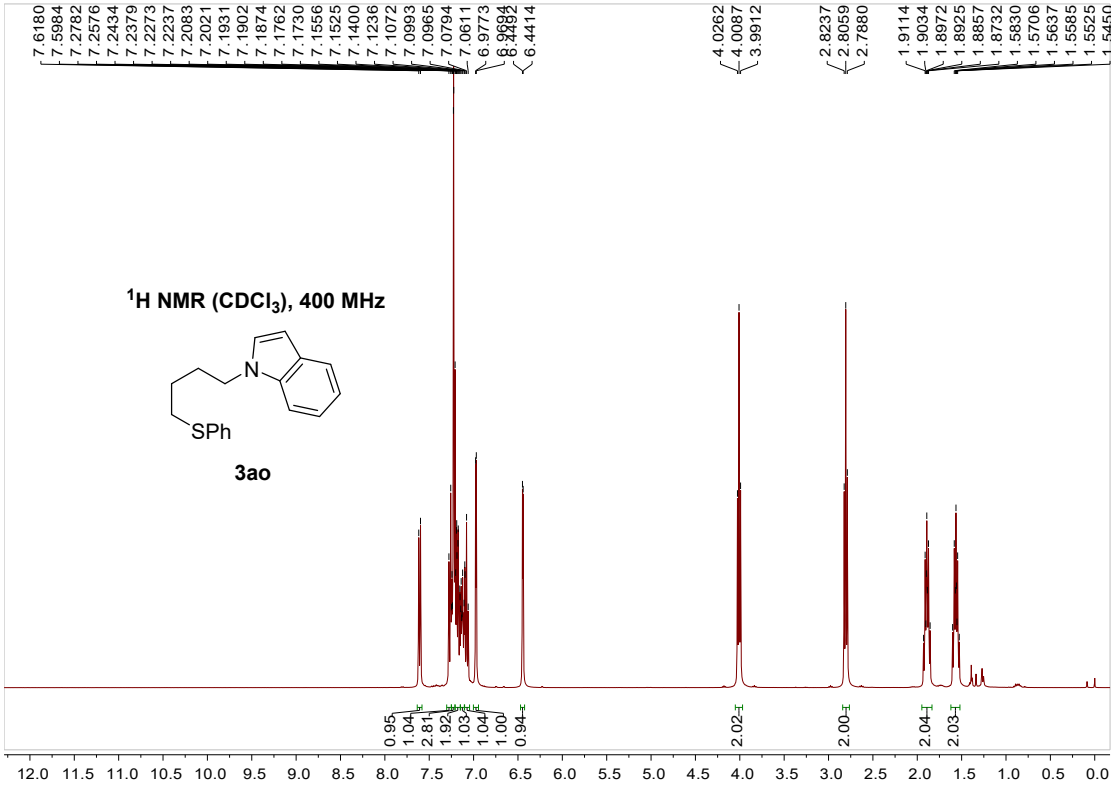
^{1}H NMR ($CDCl_3$), 400 MHz

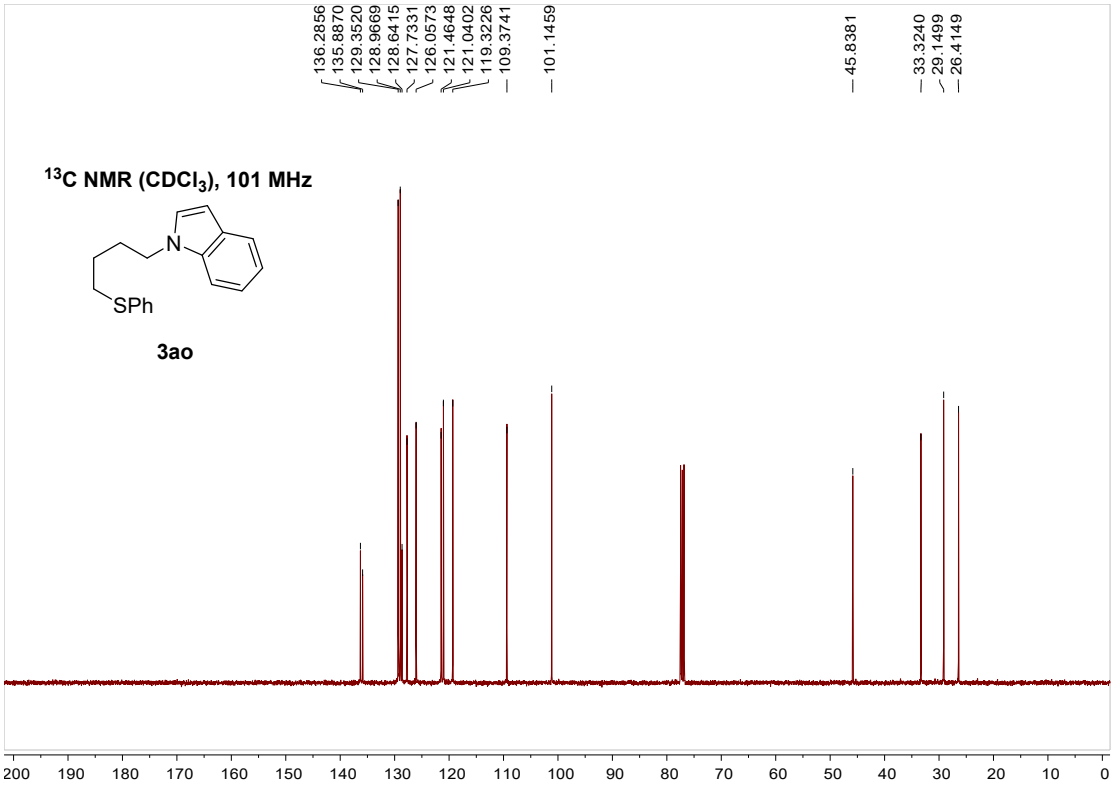
3ao

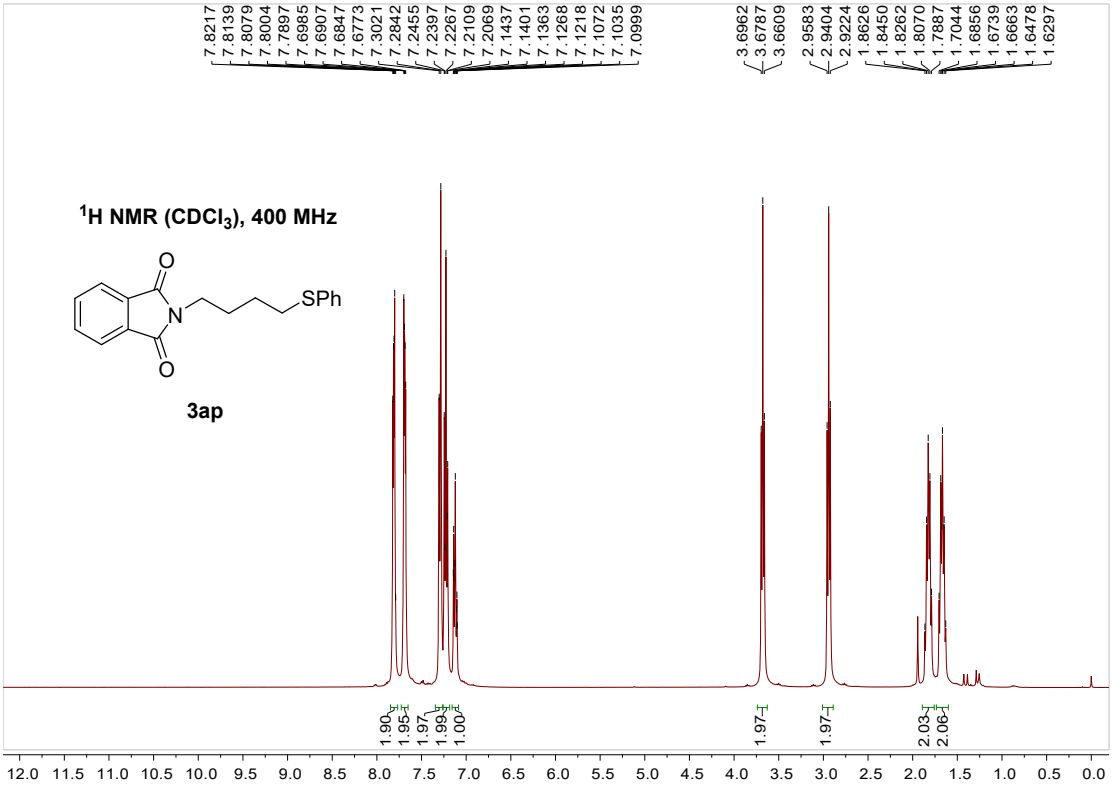


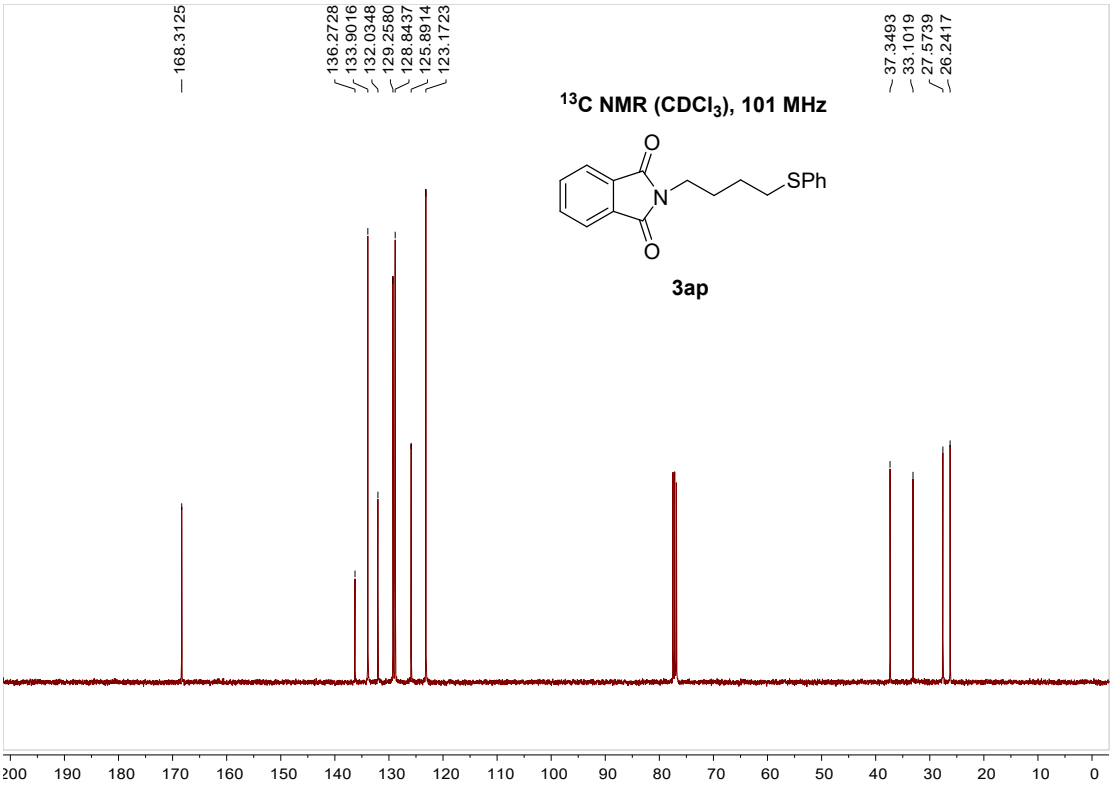
^{13}C NMR ($CDCl_3$), 101 MHz

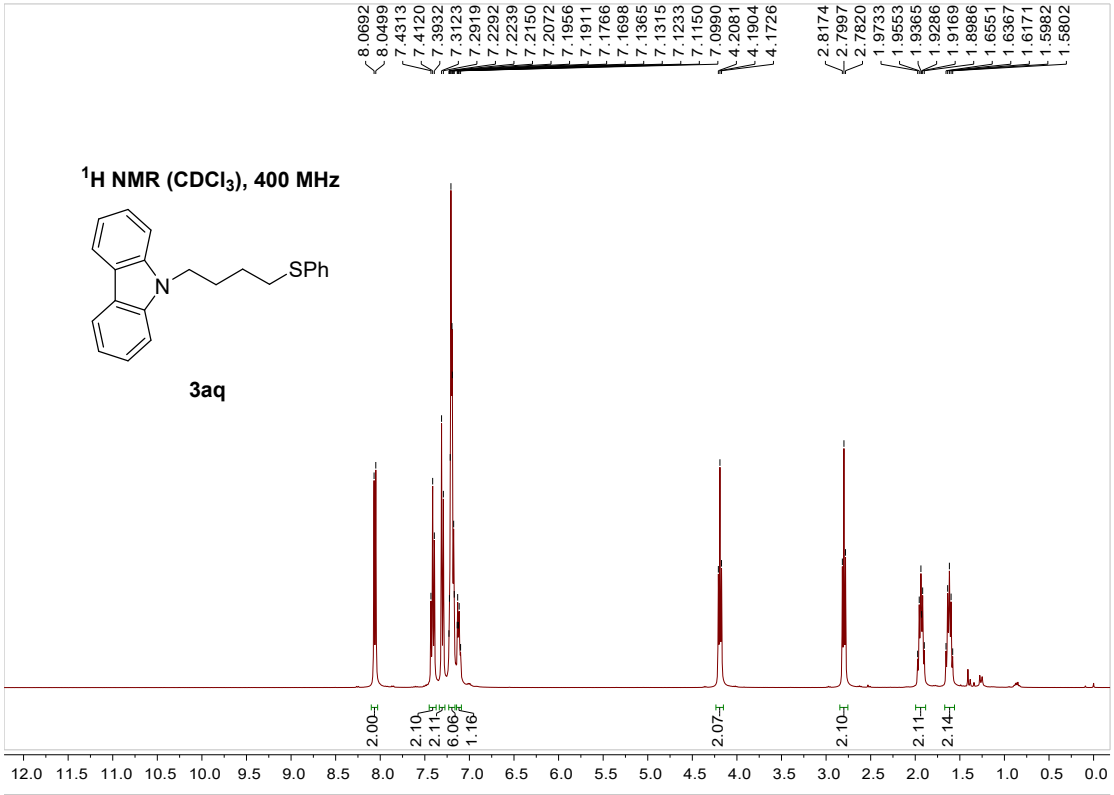
3ao

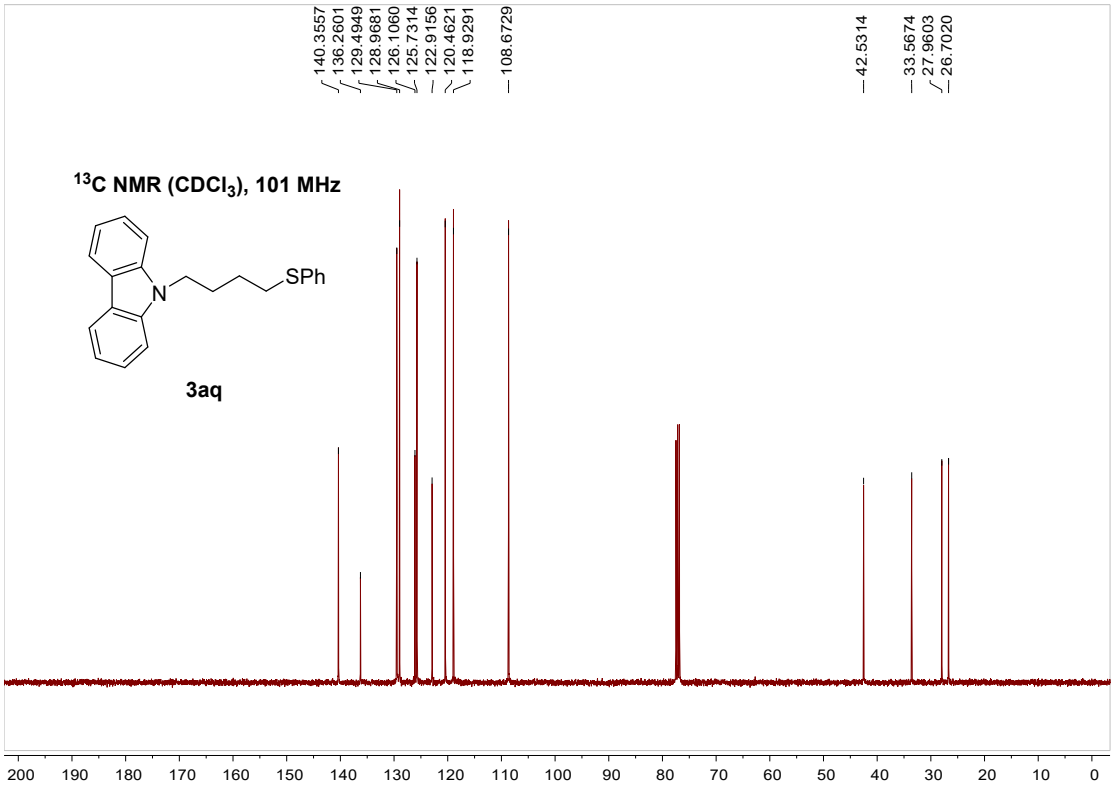

^{1}H NMR ($CDCl_3$), 400 MHz
SPh
3ao

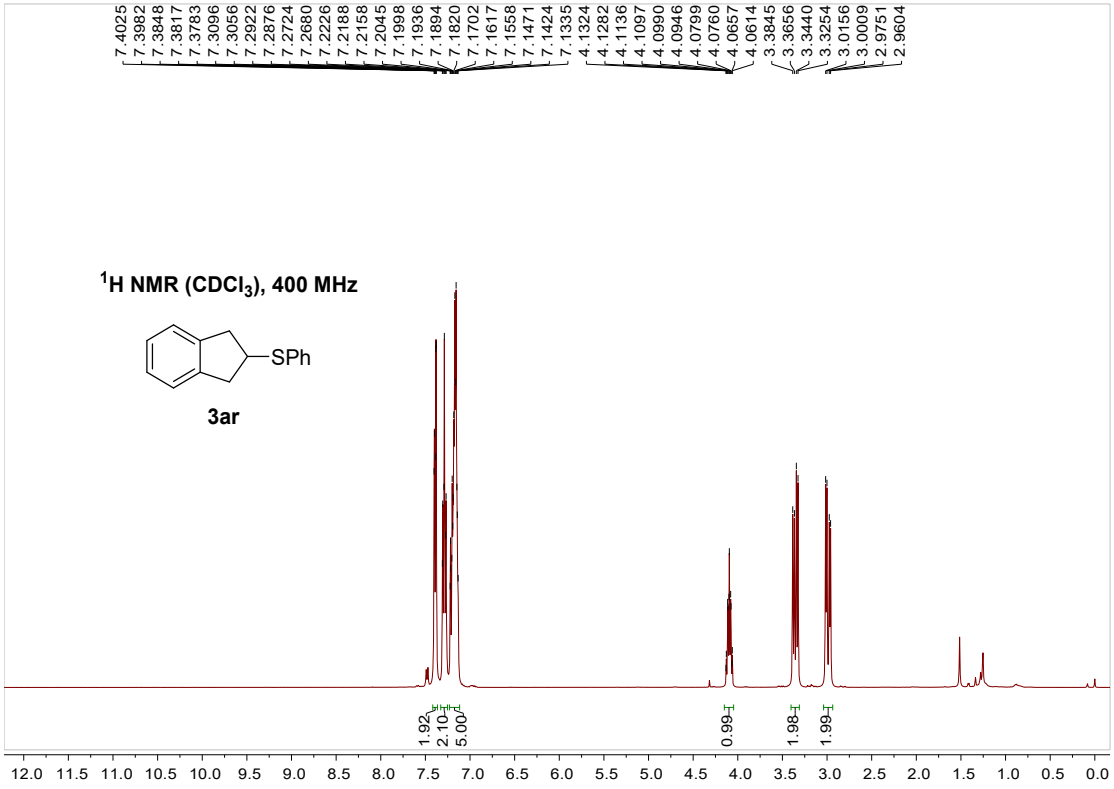

^{13}C NMR ($CDCl_3$), 101 MHz
SPh
3ao

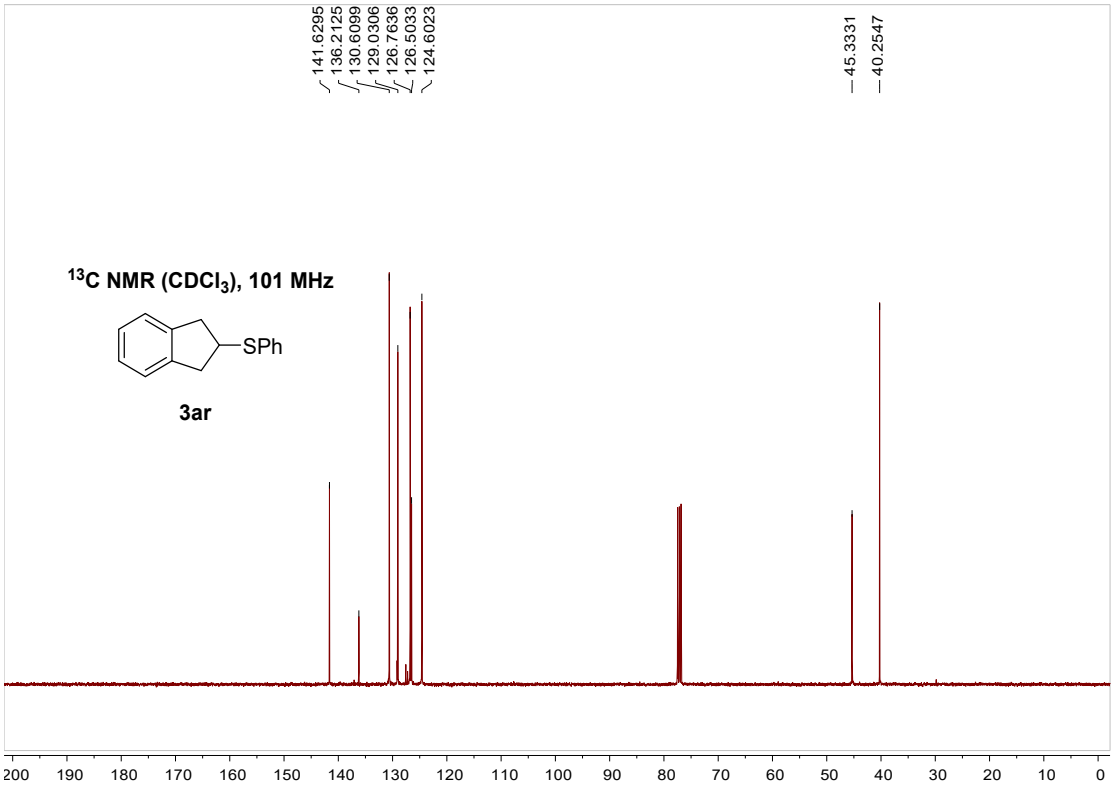

7.8217
7.8139
7.8079
7.8004
7.7897
7.6985
7.6907
7.6847
7.6773
7.3021
7.2842
7.2455
7.2397
7.2267
7.2109
7.2069
7.1437
7.1401
7.1363
7.1268
7.1218
7.1072
7.1035
7.0999
3.6962
3.6787
3.6609
2.9583
2.9404
2.9224
1.8626
1.8450
1.8262
1.8070
1.7887
1.7044
1.6856
1.6739
1.6663
1.6478
1.6297
^{1}H NMR (CDCl$_3$), 400 MHz
O
N
SPh
O
3ap
1.90
1.95
1.97
1.99
1.00
1.97
1.97
2.03
2.06
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

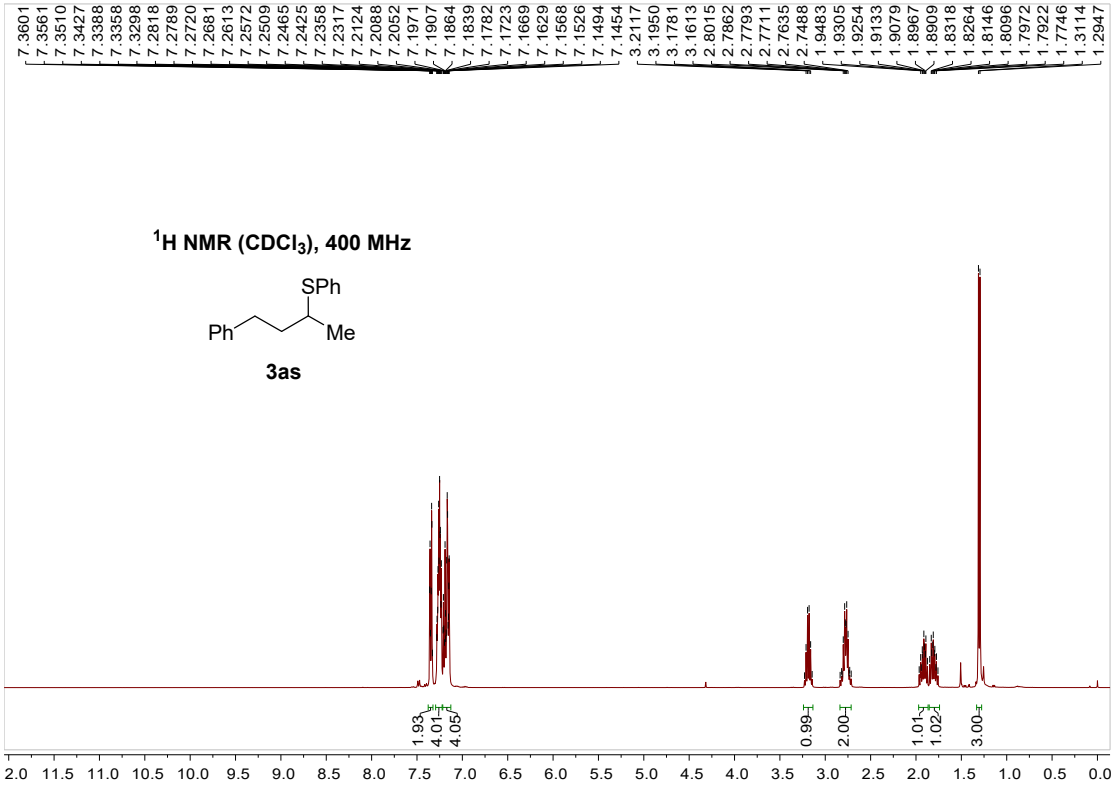

168.3125
136.2728
133.9016
132.0348
129.2580
128.8437
125.8914
123.1723
37.3493
33.1019
27.5739
26.2417
^{13}C NMR (CDCl$_3$), 101 MHz
O
N
SPh
O
3ap
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

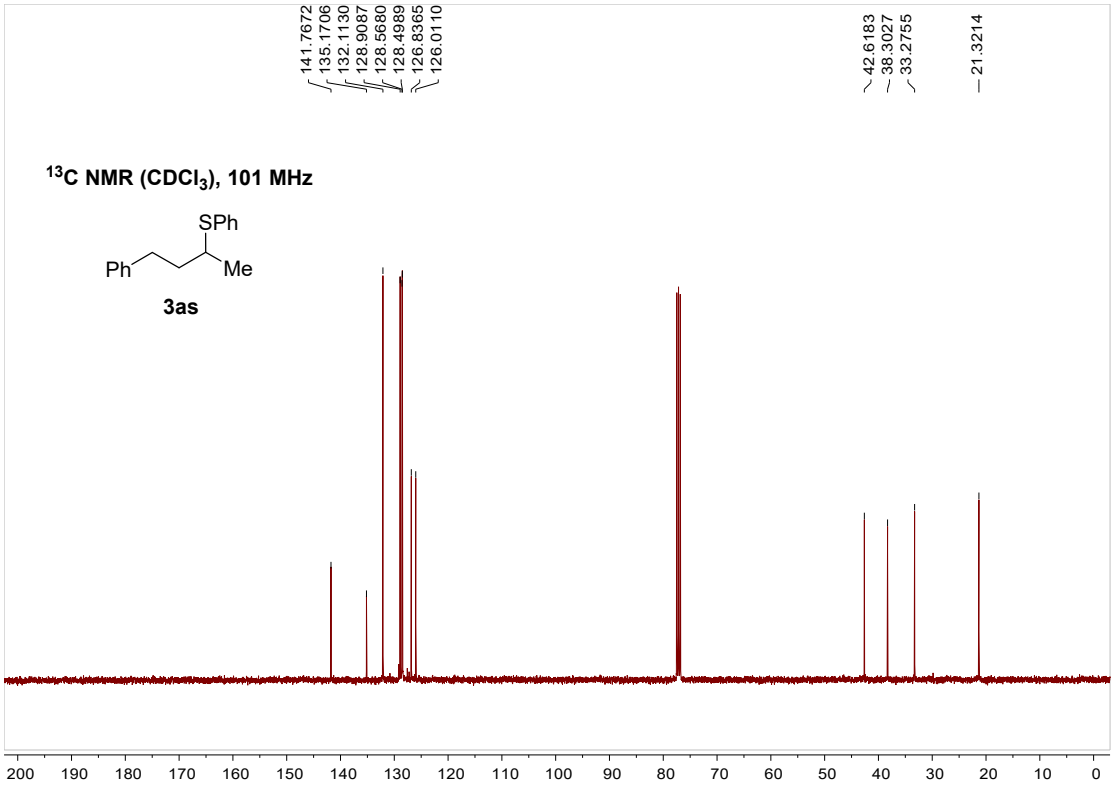

8.0692
8.0499
7.4313
7.4120
7.3932
7.3123
7.2919
7.2292
7.2239
7.2150
7.2072
7.1956
7.1911
7.1766
7.1698
7.1365
7.1315
7.1233
7.1150
7.0990
4.2081
4.1904
4.1726
2.8174
2.7997
2.7820
1.9733
1.9553
1.9365
1.9286
1.9169
1.8986
1.6551
1.6367
1.6171
1.5982
1.5802
^{1}H NMR ($CDCl_3$), 400 MHz
SPh
N
3aq
2.00
2.10
2.11
6.06
1.16
2.07
2.10
2.11
2.14
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

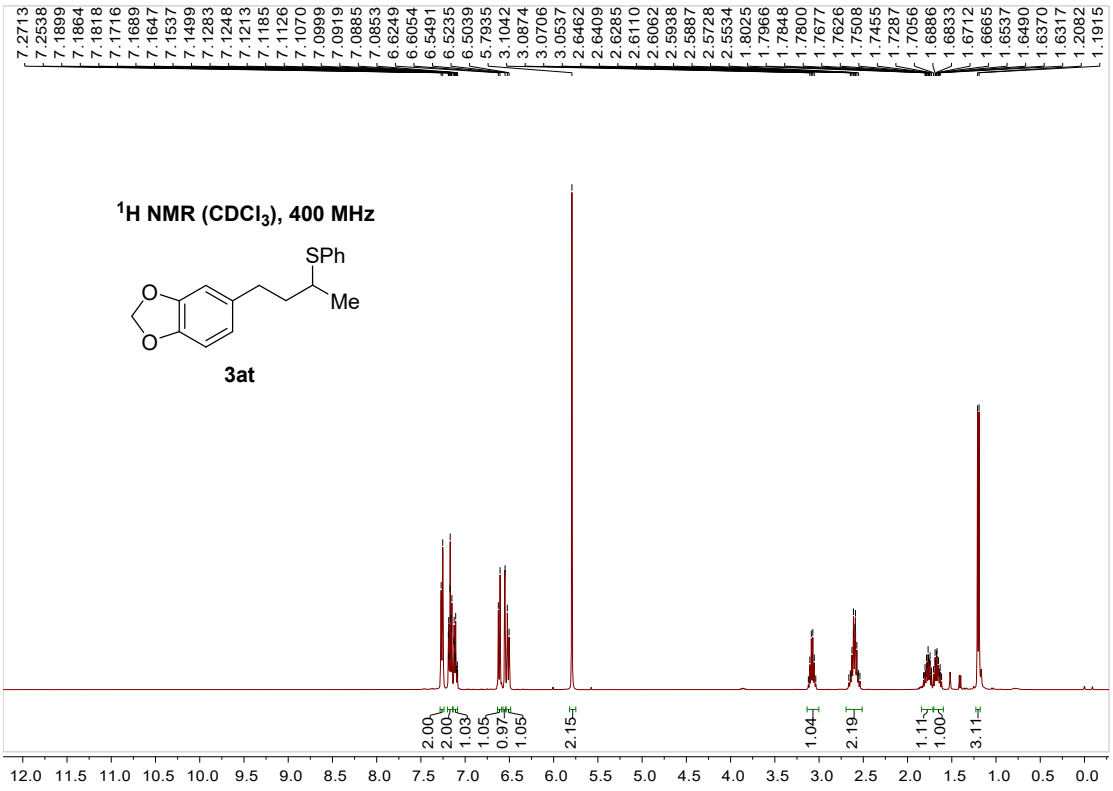

140.3557
136.2601
129.4949
128.9681
126.1060
125.7314
122.9156
120.4621
118.9291
108.6729
42.5314
33.5674
27.9603
26.7020
^{13}C NMR ($CDCl_3$), 101 MHz
SPh
N
3aq
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

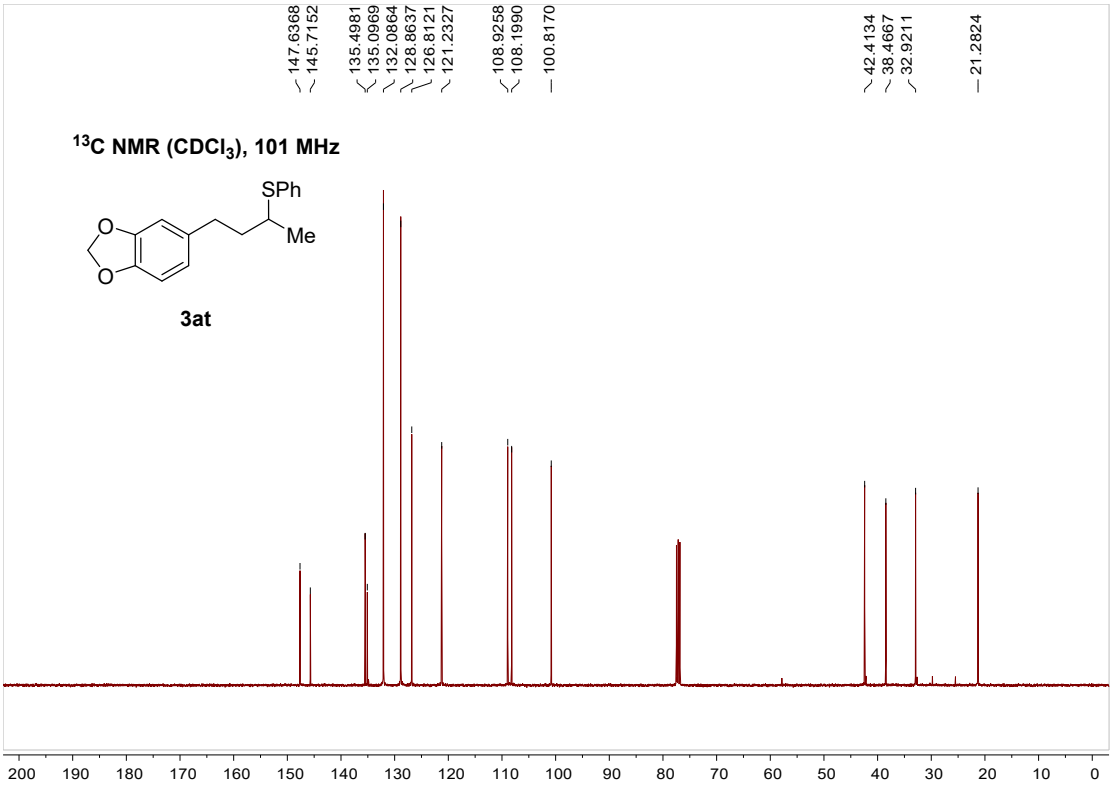

7.4025
7.3982
7.3848
7.3817
7.3783
7.3096
7.3056
7.2922
7.2876
7.2724
7.2680
7.2226
7.2188
7.2158
7.2045
7.1998
7.1936
7.1894
7.1820
7.1702
7.1617
7.1558
7.1471
7.1424
7.1335
4.1324
4.1282
4.1136
4.1097
4.0990
4.0946
4.0799
4.0760
4.0657
4.0614
3.3845
3.3656
3.3440
3.3254
3.0156
3.0009
2.9751
2.9604
1H NMR (CDCl3), 400 MHz
SPh
3ar
1.92
2.10
5.00
0.99
1.98
1.99
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

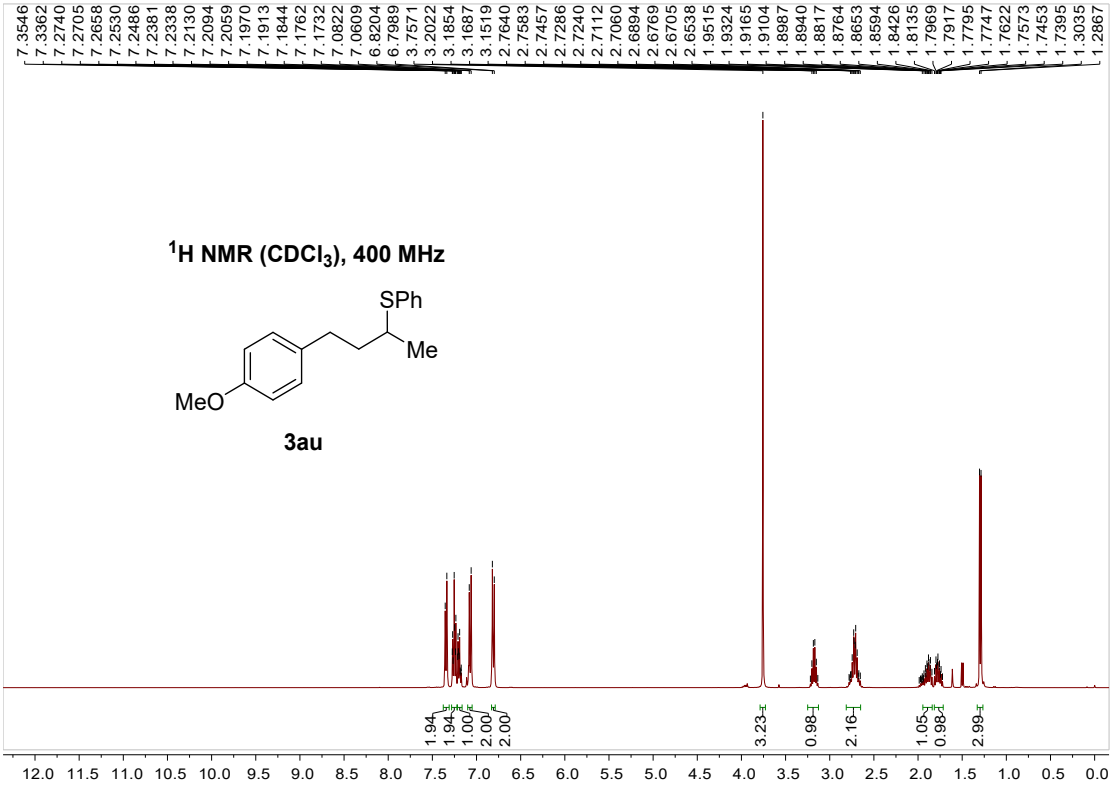

141.6295
136.2125
130.6099
129.0306
126.7636
126.5033
124.6023
45.3331
40.2547
13C NMR (CDCl3), 101 MHz
SPh
3ar
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

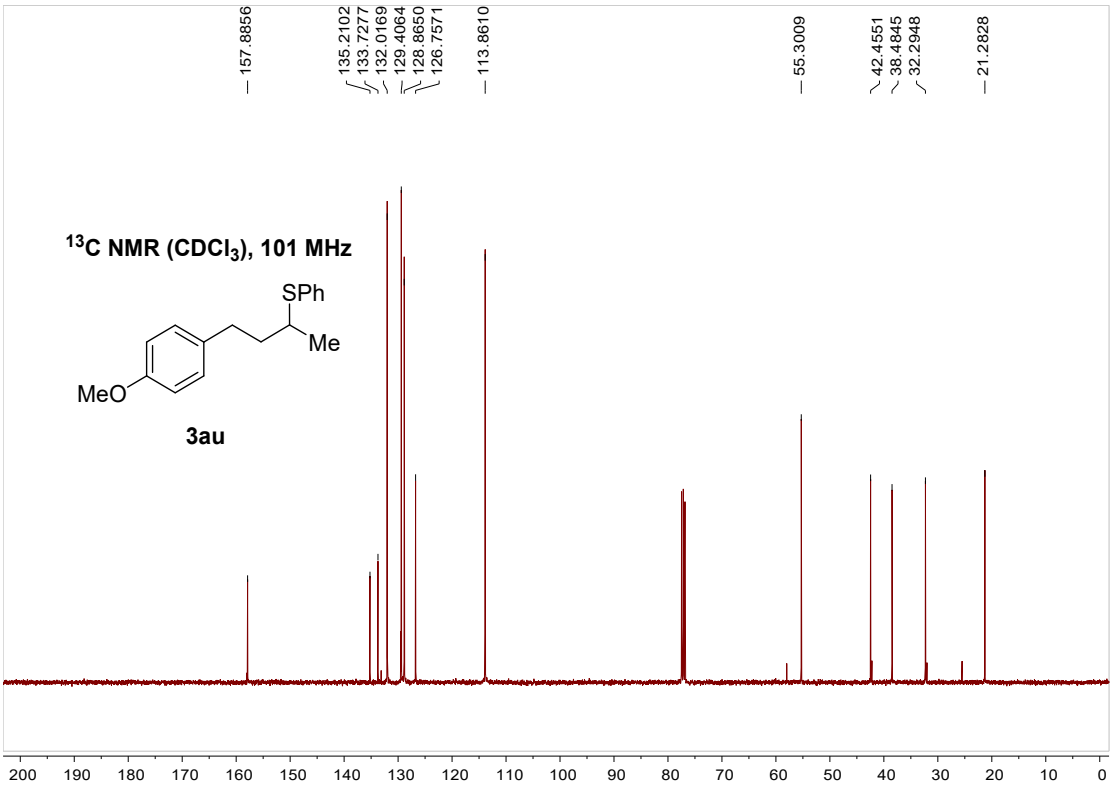

7.3601 7.3561 7.3510 7.3427 7.3388 7.3358 7.3298 7.2818 7.2789 7.2720 7.2681 7.2613 7.2572 7.2509 7.2465 7.2425 7.2358 7.2317 7.2124 7.2088 7.2052 7.1971 7.1907 7.1864 7.1839 7.1782 7.1723 7.1669 7.1629 7.1568 7.1526 7.1494 7.1454
3.2117 3.1950 3.1781 3.1613 2.8015 2.7862 2.7793 2.7711 2.7635 2.7488 1.9483 1.9305 1.9254 1.9133 1.9079 1.8967 1.8909 1.8318 1.8264 1.8146 1.8096 1.7972 1.7922 1.7746 1.3114 1.2947
1H NMR (CDCl3), 400 MHz
SPh
Ph
Me
3as
1.93 4.01 4.05 0.99 2.00 1.01 1.02 3.00
2.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

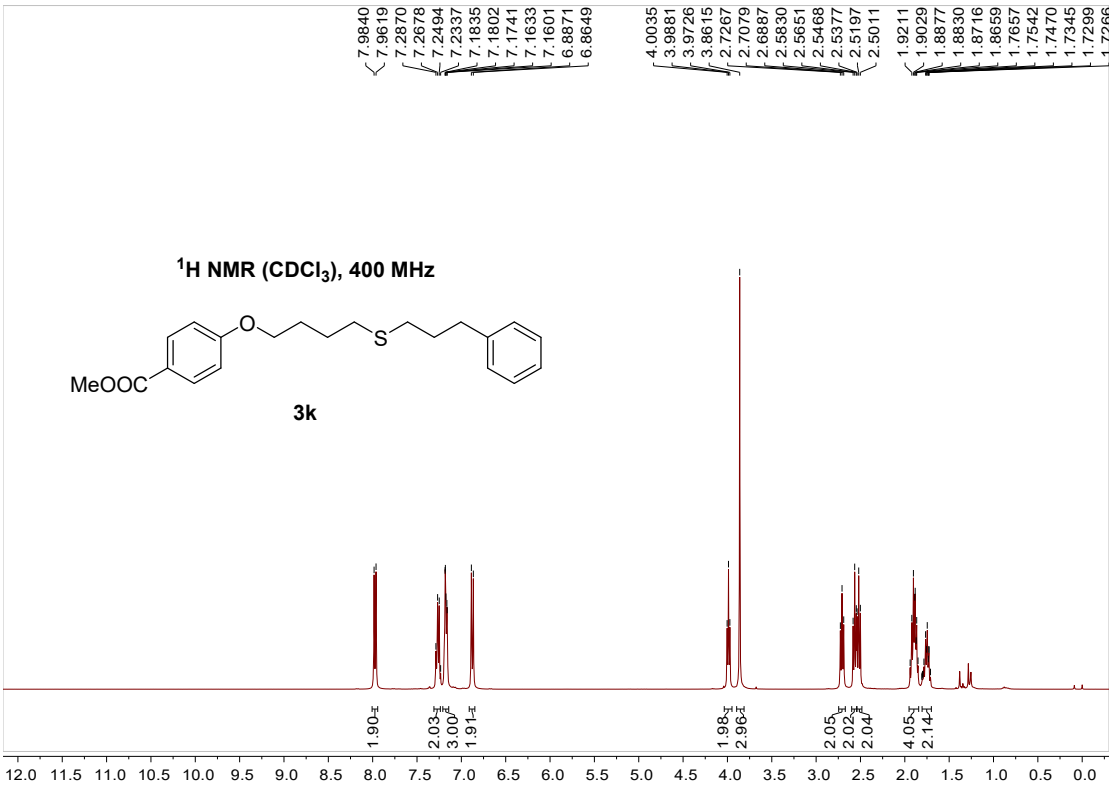

141.7672 135.1706 132.1130 128.9087 128.5680 128.4989 126.8365 126.0110
42.6183 38.3027 33.2755 21.3214
13C NMR (CDCl3), 101 MHz
SPh
Ph
Me
3as
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0


7.2713 7.2538 7.1899 7.1864 7.1818 7.1716 7.1689 7.1647 7.1537 7.1499 7.1283 7.1248 7.1213 7.1185 7.1126 7.1070 7.0999 7.0919 7.0885 7.0853 6.6249 6.6054 6.5491 6.5235 6.5039 5.7935 3.1042 3.0874 3.0706 3.0537 2.6462 2.6409 2.6285 2.6110 2.6062 2.5938 2.5887 2.5728 2.5534 1.8025 1.7966 1.7848 1.7800 1.7677 1.7626 1.7508 1.7455 1.7287 1.7056 1.6886 1.6833 1.6712 1.6665 1.6537 1.6490 1.6370 1.6317 1.2082 1.1915
^{1}H NMR ($CDCl_3$), 400 MHz
SPh
Me
O
O
3at
2.00 2.00 1.03 1.05 0.97 1.05 2.15 1.04 2.19 1.11 1.00 3.11
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0


147.6368 145.7152 135.4981 135.0969 132.0864 128.8637 126.8121 121.2327 108.9258 108.1990 100.8170 42.4134 38.4667 32.9211 21.2824
^{13}C NMR ($CDCl_3$), 101 MHz
SPh
Me
O
O
3at
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

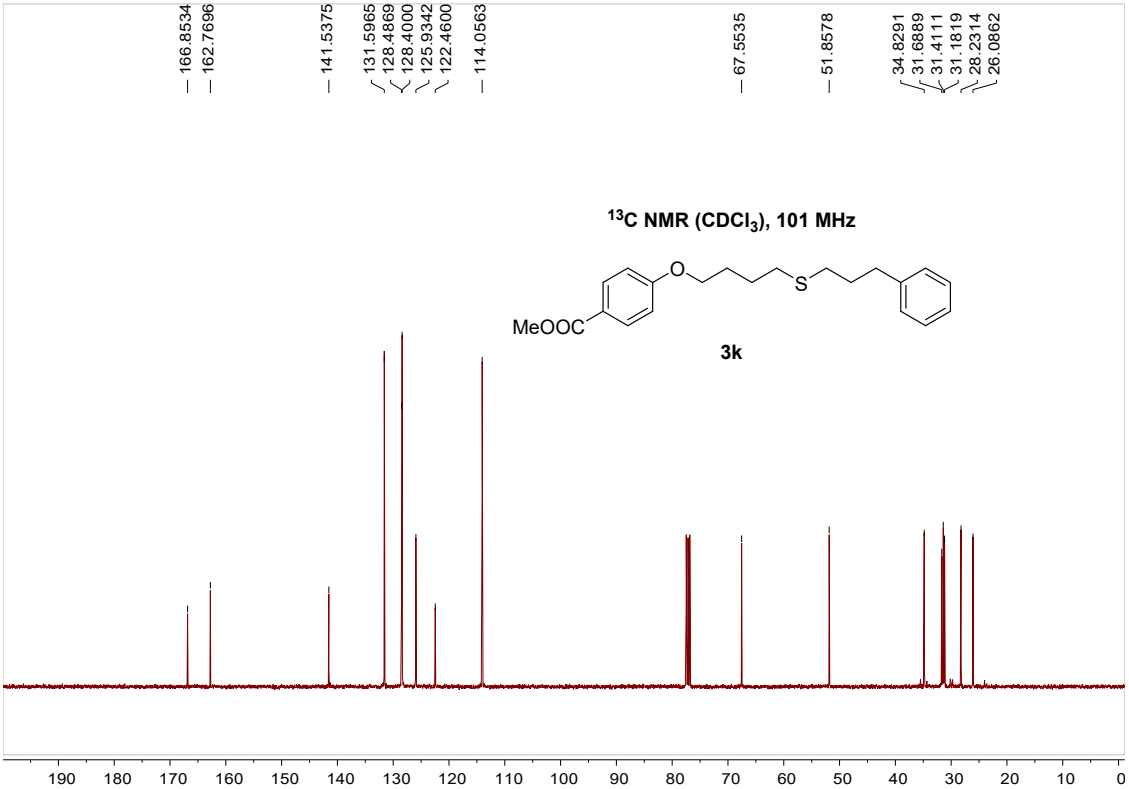

7.3546 7.3362 7.2740 7.2705 7.2658 7.2530 7.2486 7.2381 7.2338 7.2130 7.2094 7.2059 7.1970 7.1913 7.1844 7.1762 7.1732 7.0822 7.0609 6.8204 6.7989 3.7571 3.2022 3.1854 3.1687 3.1519 2.7640 2.7583 2.7457 2.7286 2.7240 2.7112 2.7060 2.6894 2.6769 2.6705 2.6538 1.9515 1.9324 1.9165 1.9104 1.8987 1.8940 1.8817 1.8764 1.8653 1.8594 1.8426 1.8135 1.7969 1.7917 1.7795 1.7747 1.7622 1.7573 1.7453 1.7395 1.3035 1.2867
1H NMR (CDCl3), 400 MHz
SPh
Me
MeO
3au
1.94 1.94 1.00 2.00 2.00 3.23 0.98 2.16 1.05 0.98 2.99
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0


157.8856
135.2102 133.7277 132.0169 129.4064 128.8650 126.7571
113.8610
55.3009
42.4551 38.4845 32.2948
21.2828
13C NMR (CDCl3), 101 MHz
SPh
Me
MeO
3au
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0



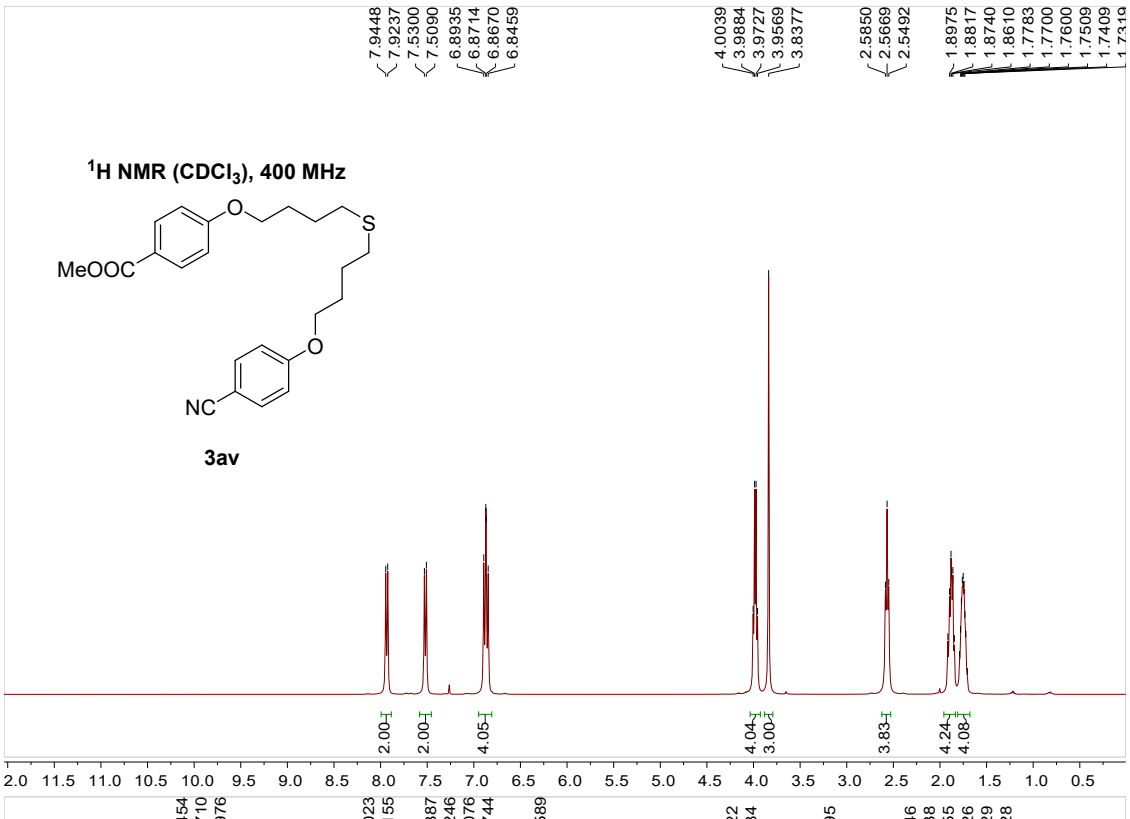
^{1}H NMR ($CDCl_3$), 400 MHz

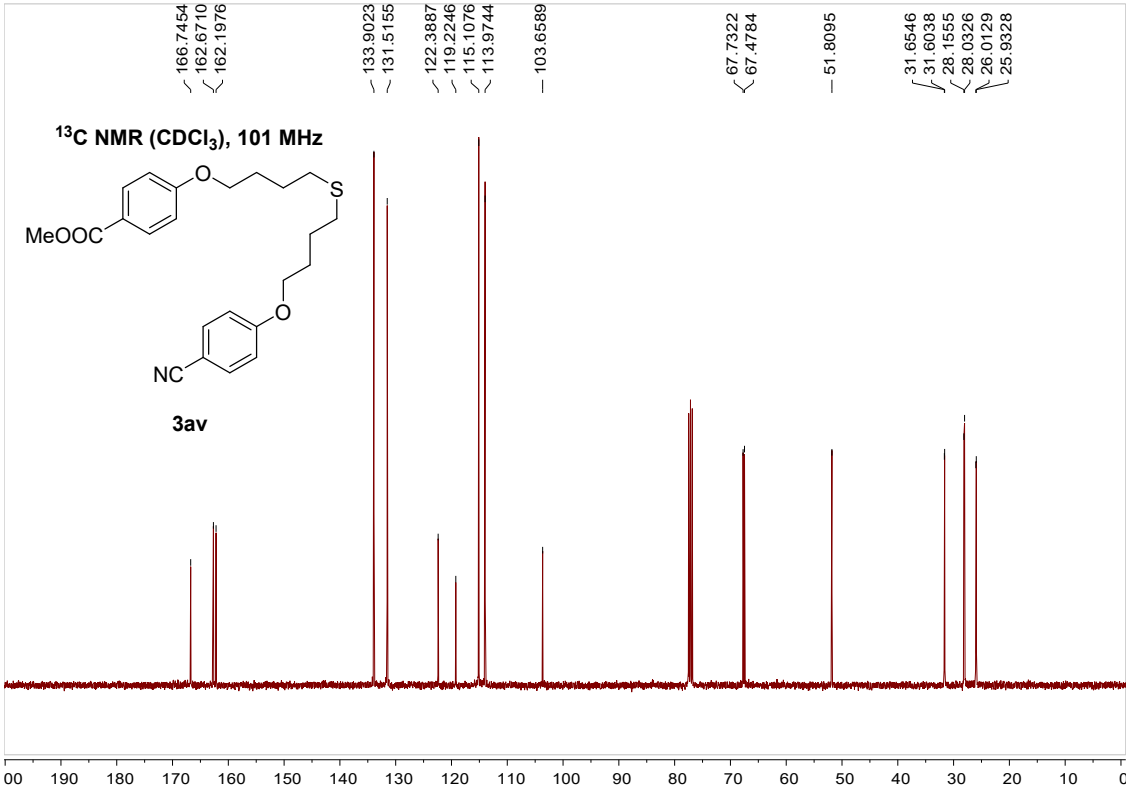
3k

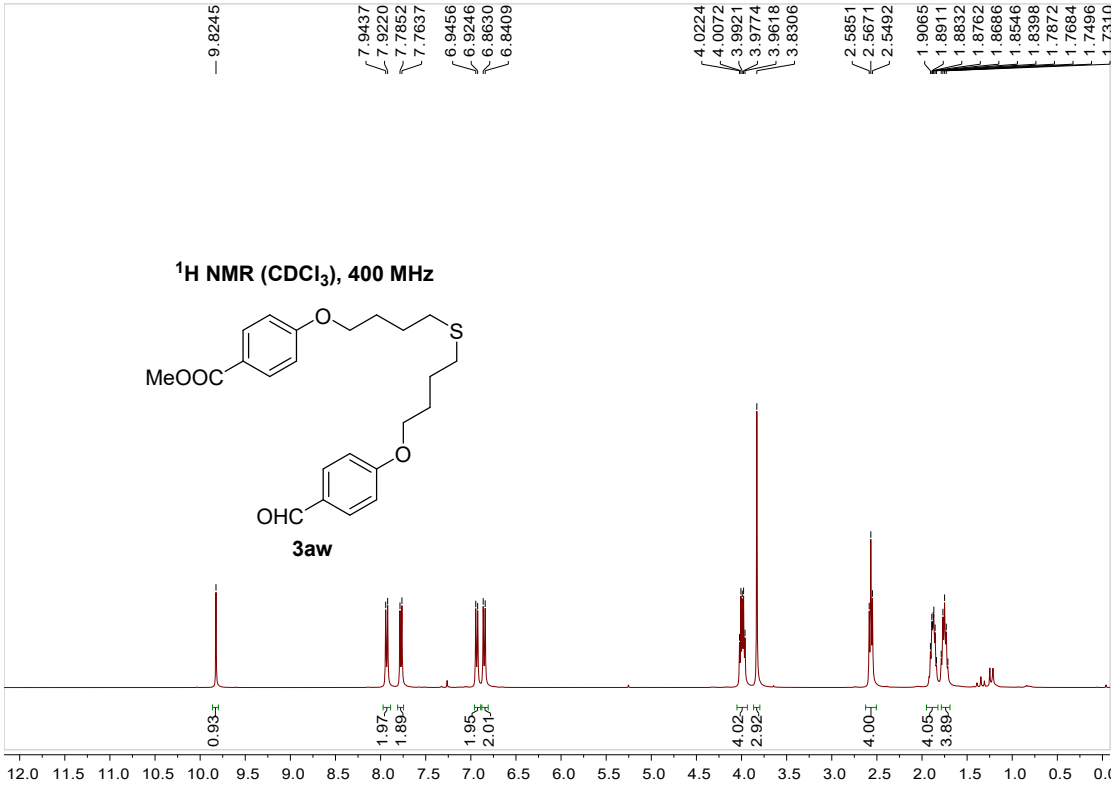


^{13}C NMR ($CDCl_3$), 101 MHz

3k

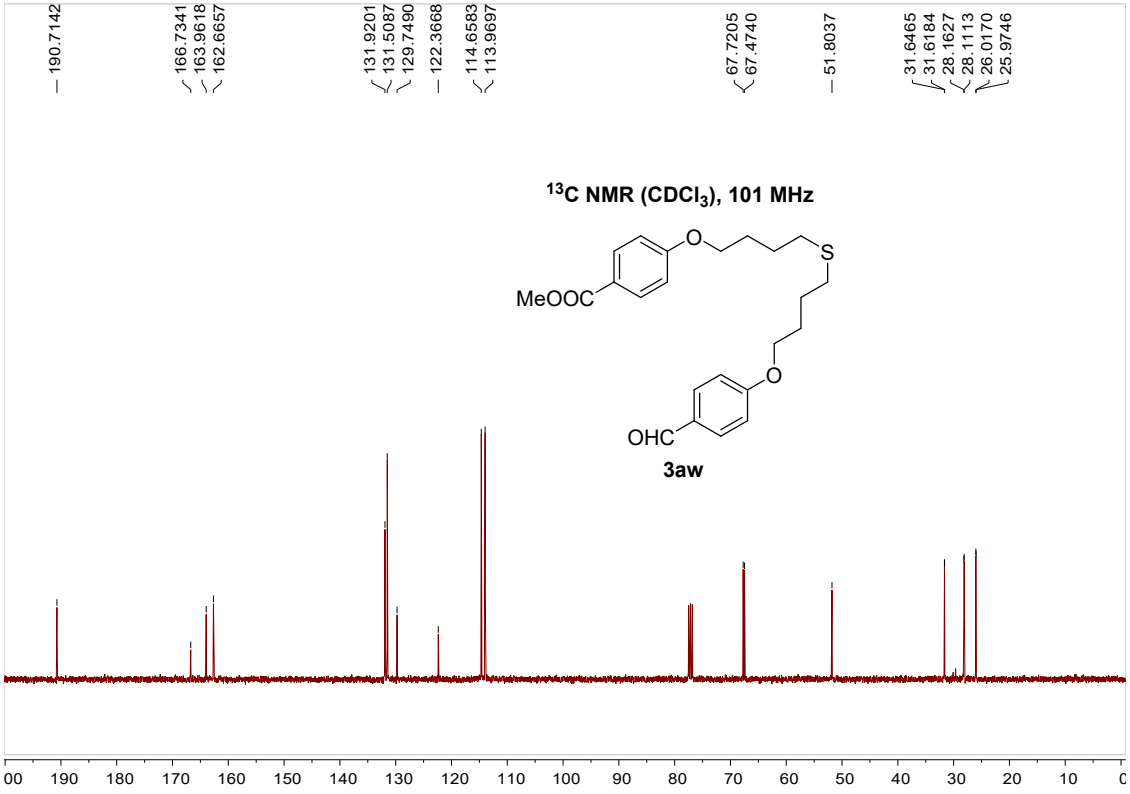

7.9448
7.9237
7.5300
7.5090
6.8935
6.8714
6.8670
6.8459
4.0039
3.9884
3.9727
3.9569
3.8377
2.5850
2.5669
2.5492
1.8975
1.8817
1.8740
1.8610
1.7783
1.7700
1.7600
1.7509
1.7409
1.7319
^{1}H NMR ($CDCl_3$), 400 MHz
MeOOC
O
S
O
NC
3av
2.00
2.00
4.05
4.04
3.00
3.83
4.24
4.08
2.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5


166.7454
162.6710
162.1976
133.9023
131.5155
122.3887
119.2246
115.1076
113.9744
103.6589
67.7322
67.4784
51.8095
31.6546
31.6038
28.1555
28.0326
26.0129
25.9328
^{13}C NMR ($CDCl_3$), 101 MHz
MeOOC
O
S
O
NC
3av
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0



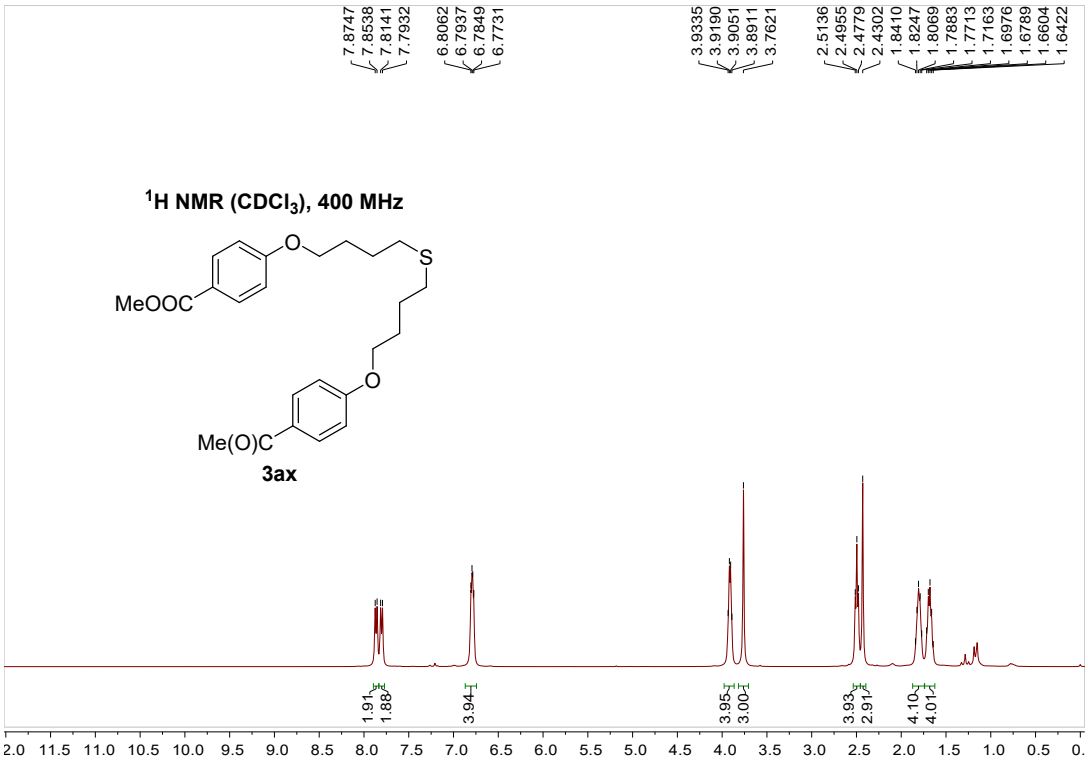
^{1}H NMR ($CDCl_3$), 400 MHz

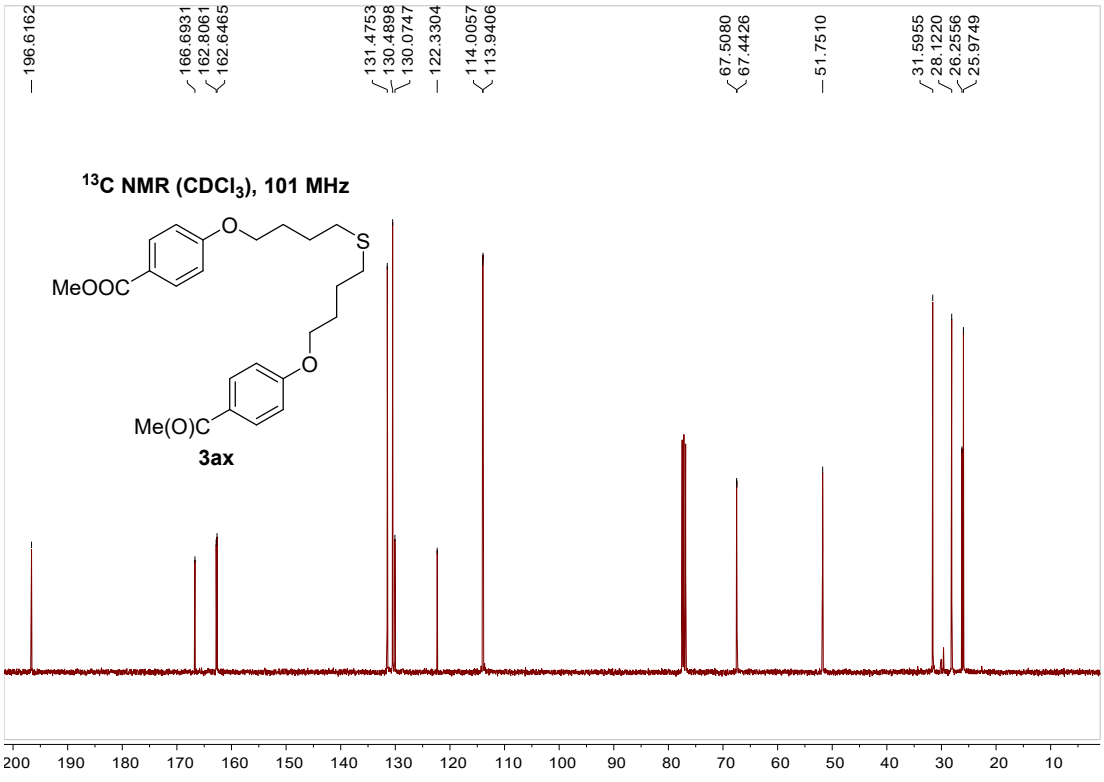
3aw

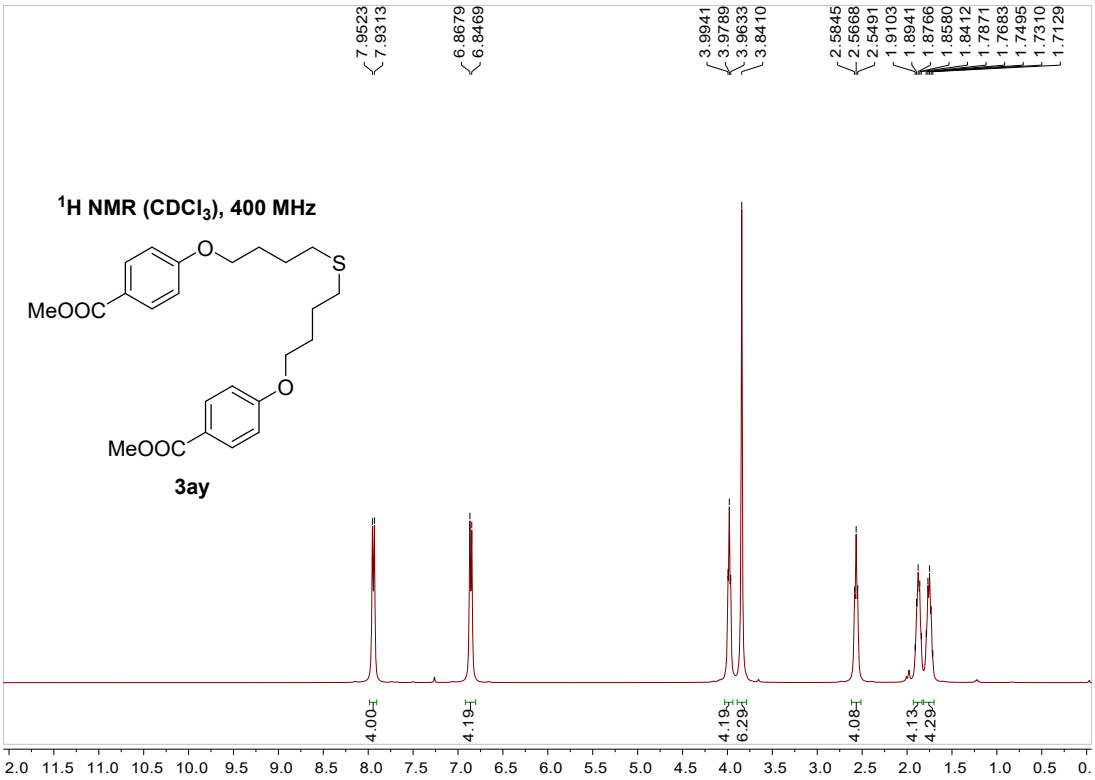


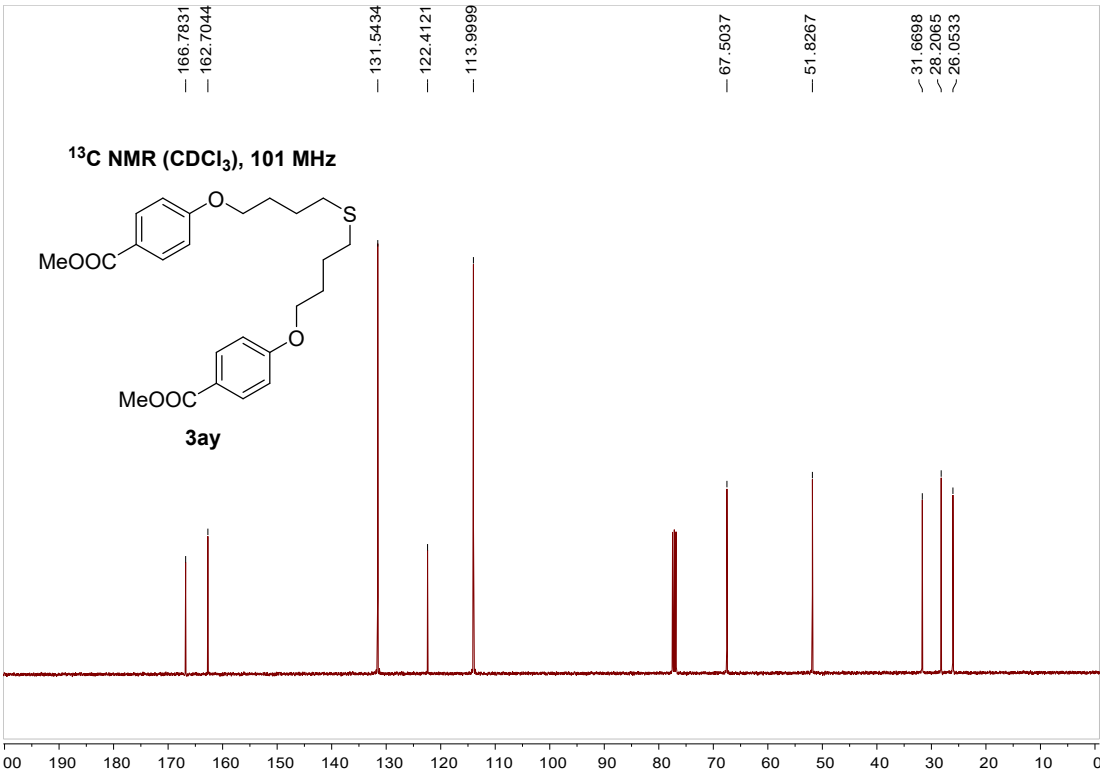
^{13}C NMR ($CDCl_3$), 101 MHz

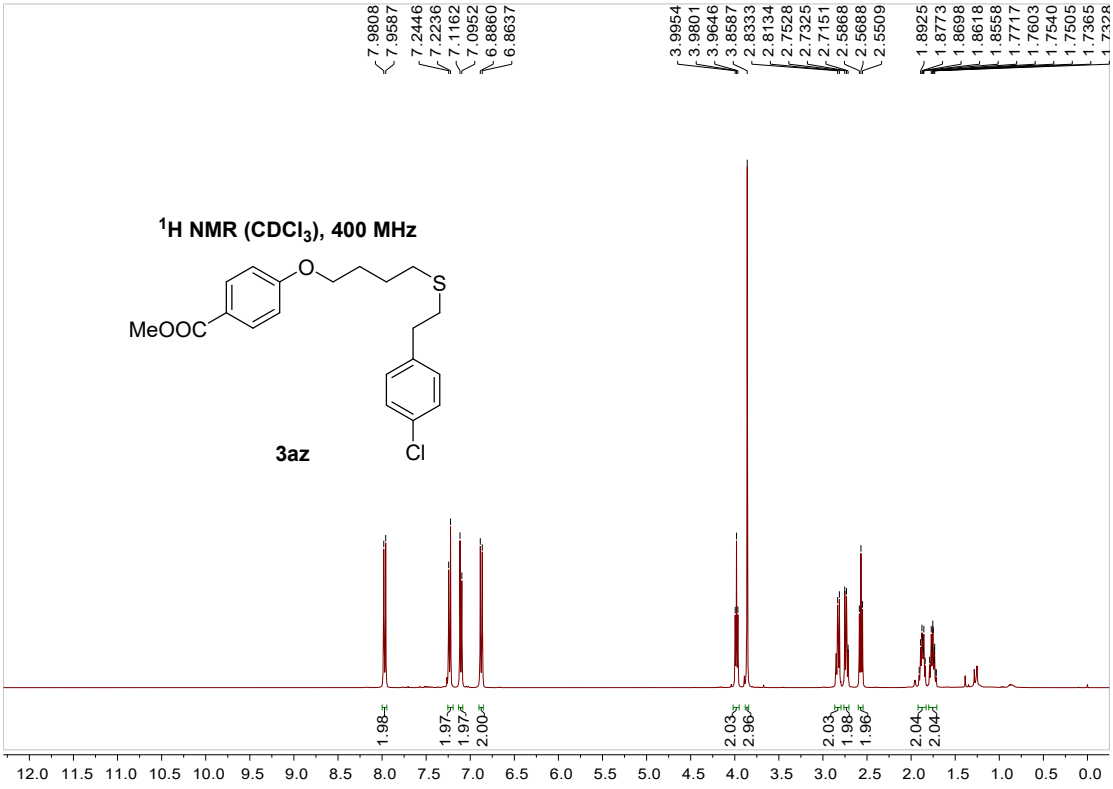
3aw

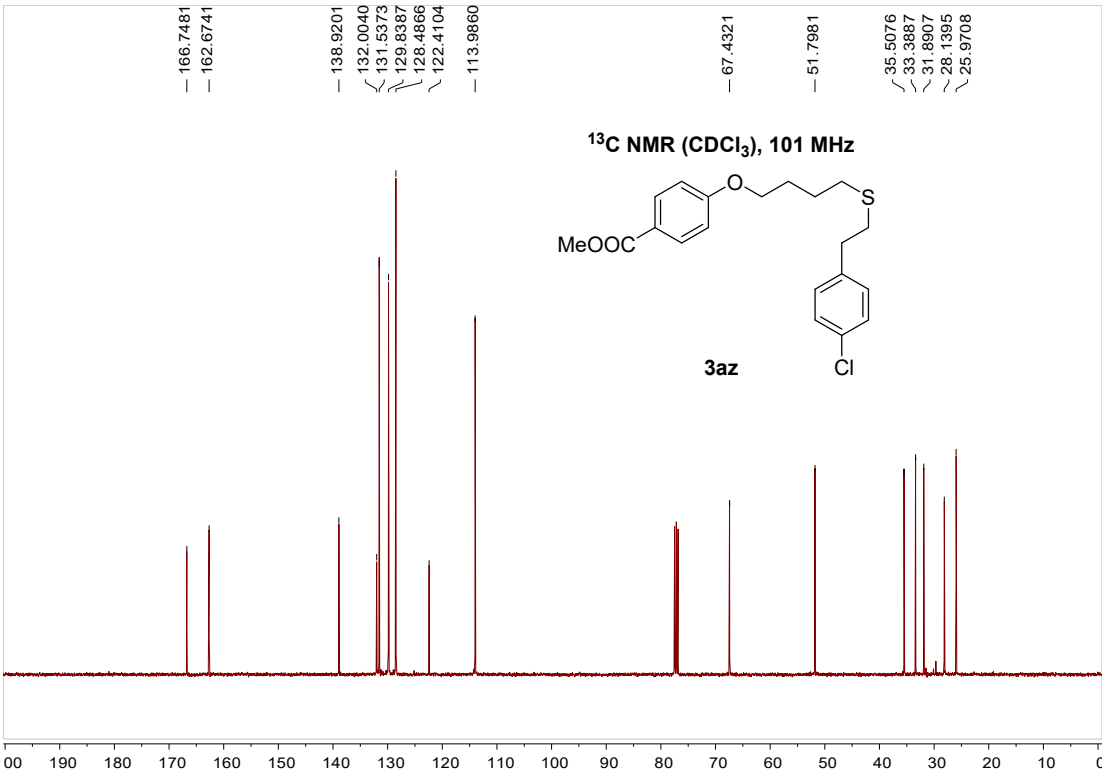

7.8747
7.8538
7.8141
7.7932
6.8062
6.7937
6.7849
6.7731
3.9335
3.9190
3.9051
3.8911
3.7621
2.5136
2.4955
2.4779
2.4302
1.8410
1.8247
1.8069
1.7883
1.7713
1.7163
1.6976
1.6789
1.6604
1.6422
1H NMR (CDCl3), 400 MHz
MeOOC
O
S
O
Me(O)C
3ax
1.91
1.88
3.94
3.95
3.00
3.93
2.91
4.10
4.01
2.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.

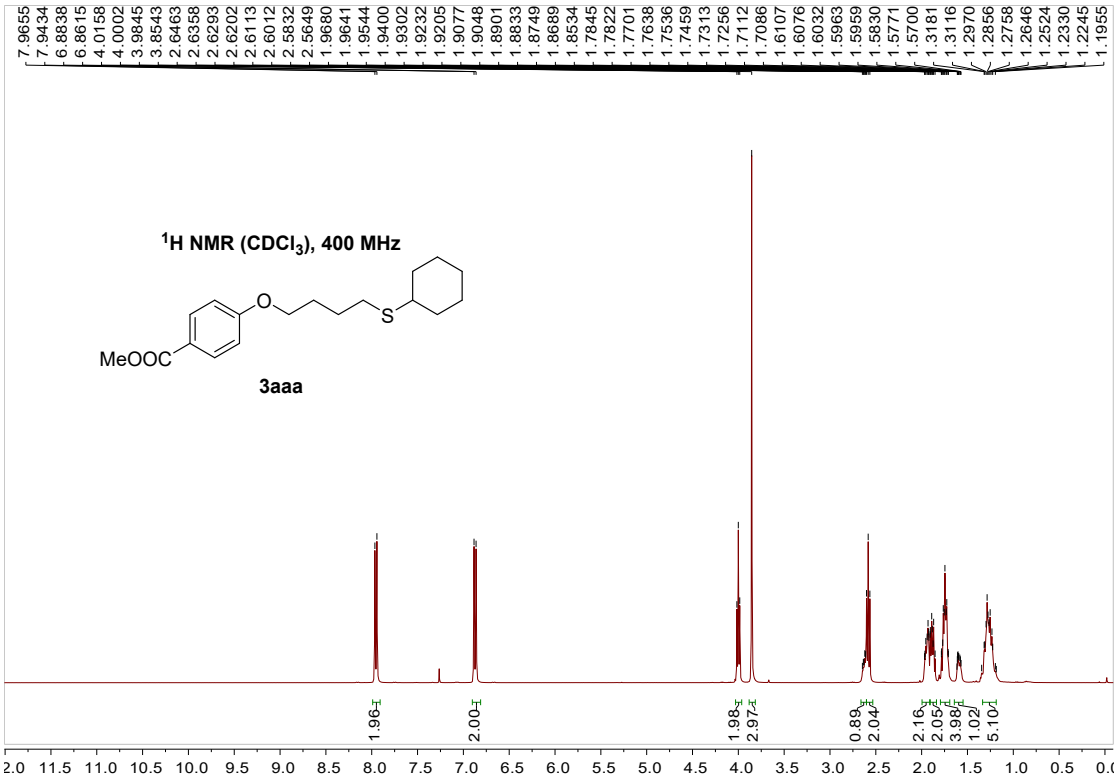

196.6162
166.6931
162.8061
162.6465
131.4753
130.4898
130.0747
122.3304
114.0057
113.9406
67.5080
67.4426
51.7510
31.5955
28.1220
26.2556
25.9749
13C NMR (CDCl3), 101 MHz
MeOOC
O
S
O
Me(O)C
3ax
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10

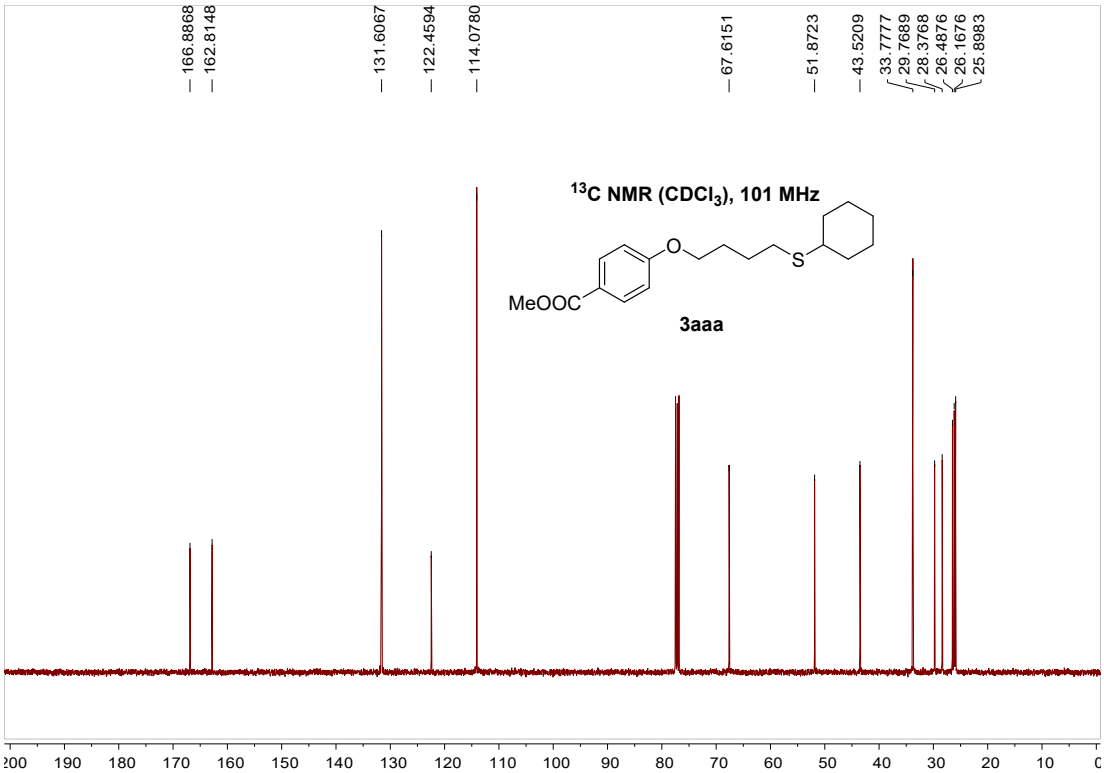

7.9523
7.9313
6.8679
6.8469
3.9941
3.9789
3.9633
3.8410
2.5845
2.5668
2.5491
1.9103
1.8941
1.8766
1.8580
1.8412
1.7871
1.7683
1.7495
1.7310
1.7129
^{1}H NMR (CDCl$_3$), 400 MHz
MeOOC
O
S
O
MeOOC
3ay
4.00
4.19
4.19
6.29
4.08
4.13
4.29
2.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.

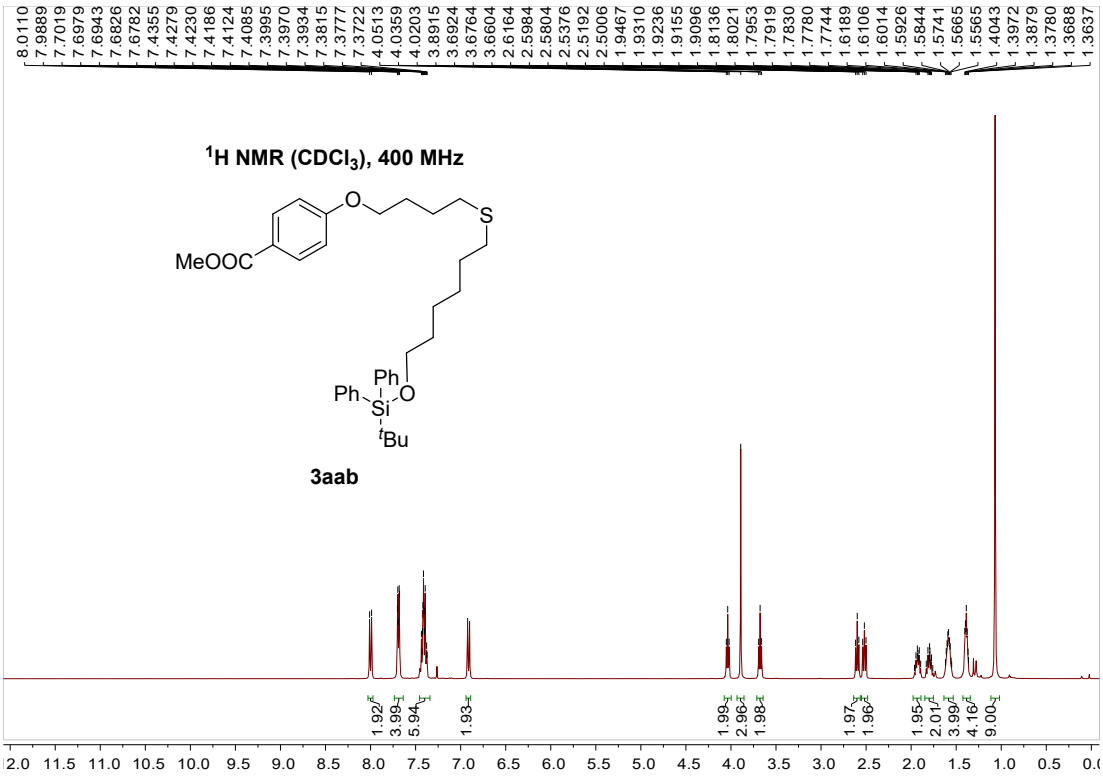

166.7831
162.7044
131.5434
122.4121
113.9999
67.5037
51.8267
31.6698
28.2065
26.0533
^{13}C NMR (CDCl$_3$), 101 MHz
MeOOC
O
S
O
MeOOC
3ay
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

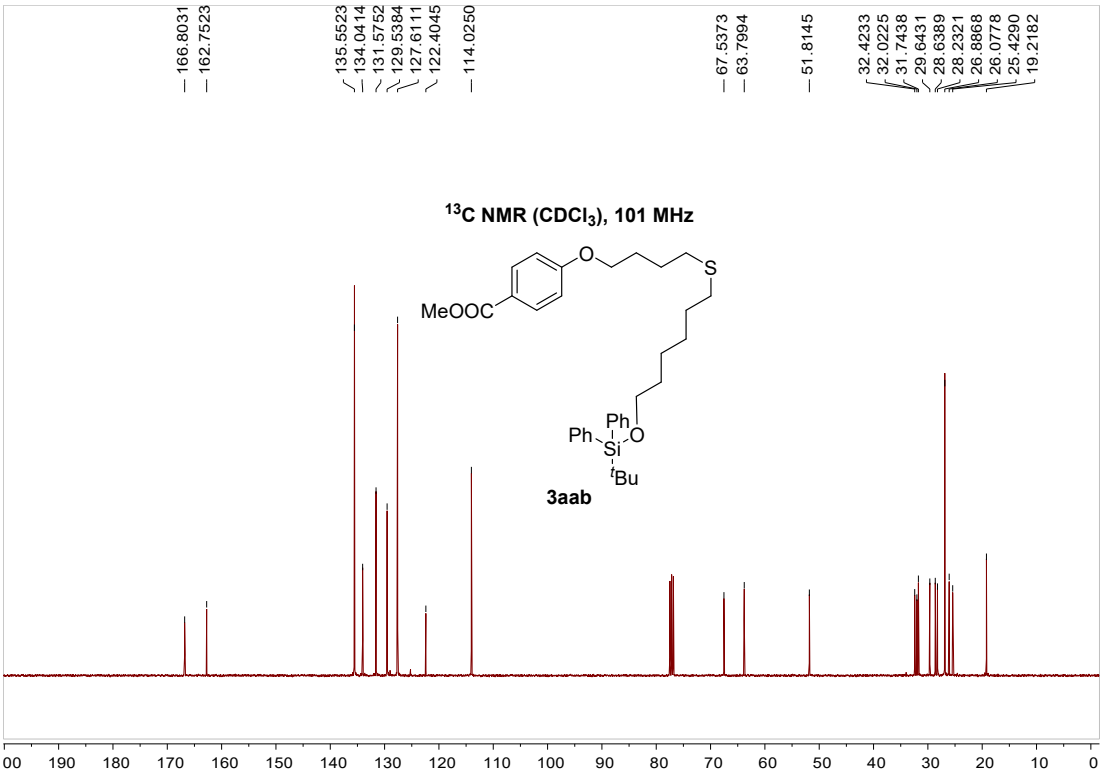

7.9808
7.9587
7.2446
7.2236
7.1162
7.0952
6.8860
6.8637
3.9954
3.9801
3.9646
3.8587
2.8333
2.8134
2.7528
2.7325
2.7151
2.5868
2.5688
2.5509
1.8925
1.8773
1.8698
1.8618
1.8558
1.7717
1.7603
1.7540
1.7505
1.7365
1.7328
1H NMR (CDCl3), 400 MHz
MeOOC
O
S
Cl
3az
1.98
1.97
1.97
2.00
2.03
2.96
2.03
1.98
1.96
2.04
2.04
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

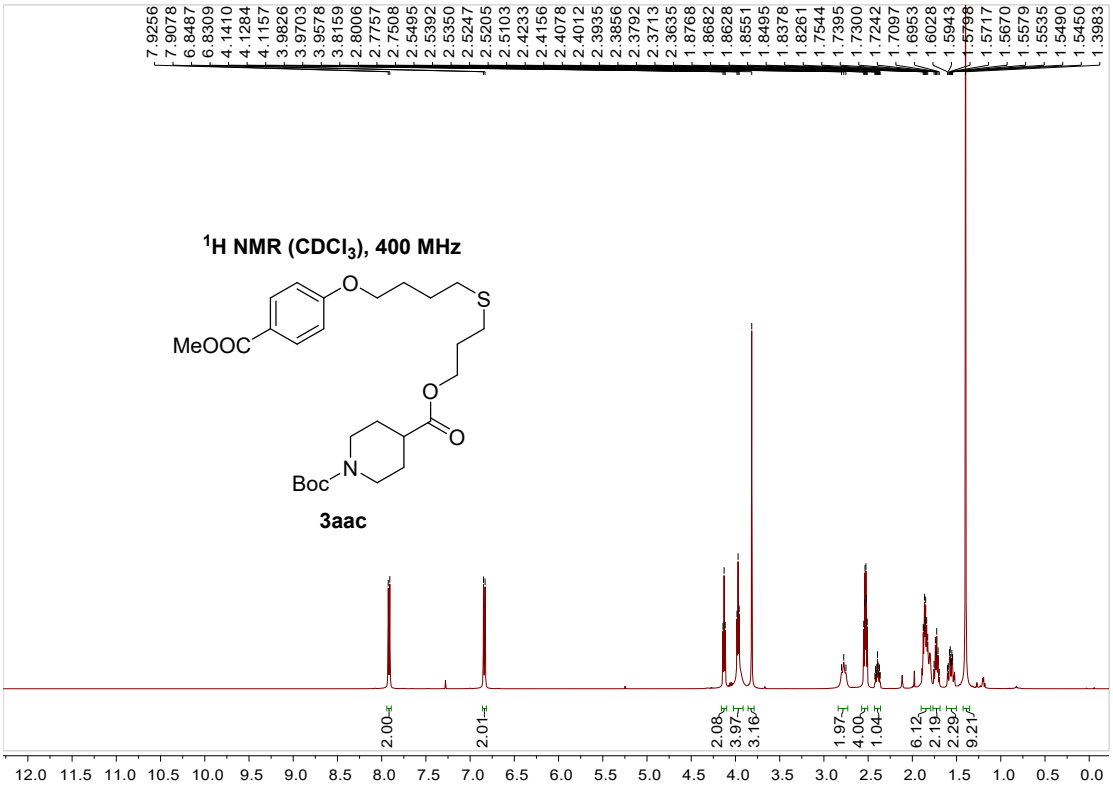

166.7481
162.6741
138.9201
132.0040
131.5373
129.8387
128.4866
122.4104
113.9860
67.4321
51.7981
35.5076
33.3887
31.8907
28.1395
25.9708
13C NMR (CDCl3), 101 MHz
MeOOC
O
S
Cl
3az
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

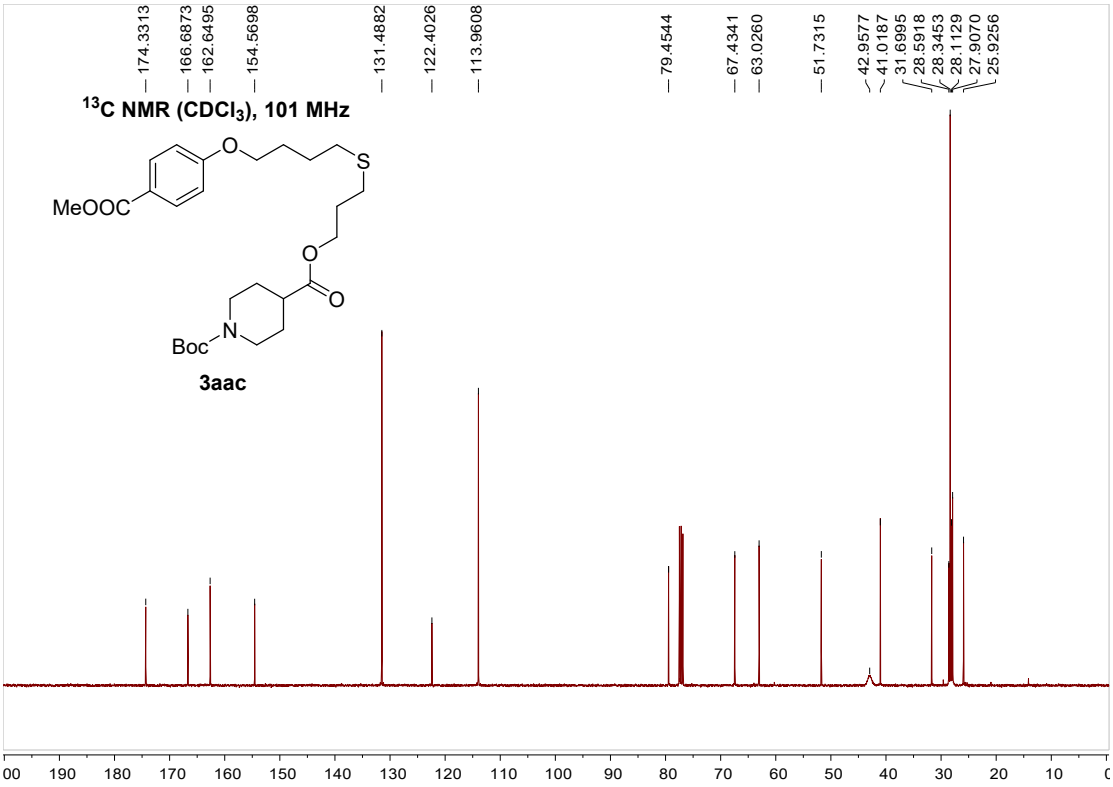

^{1}H NMR (CDCl$_3$), 400 MHz
MeOOC
O
S
3aaa

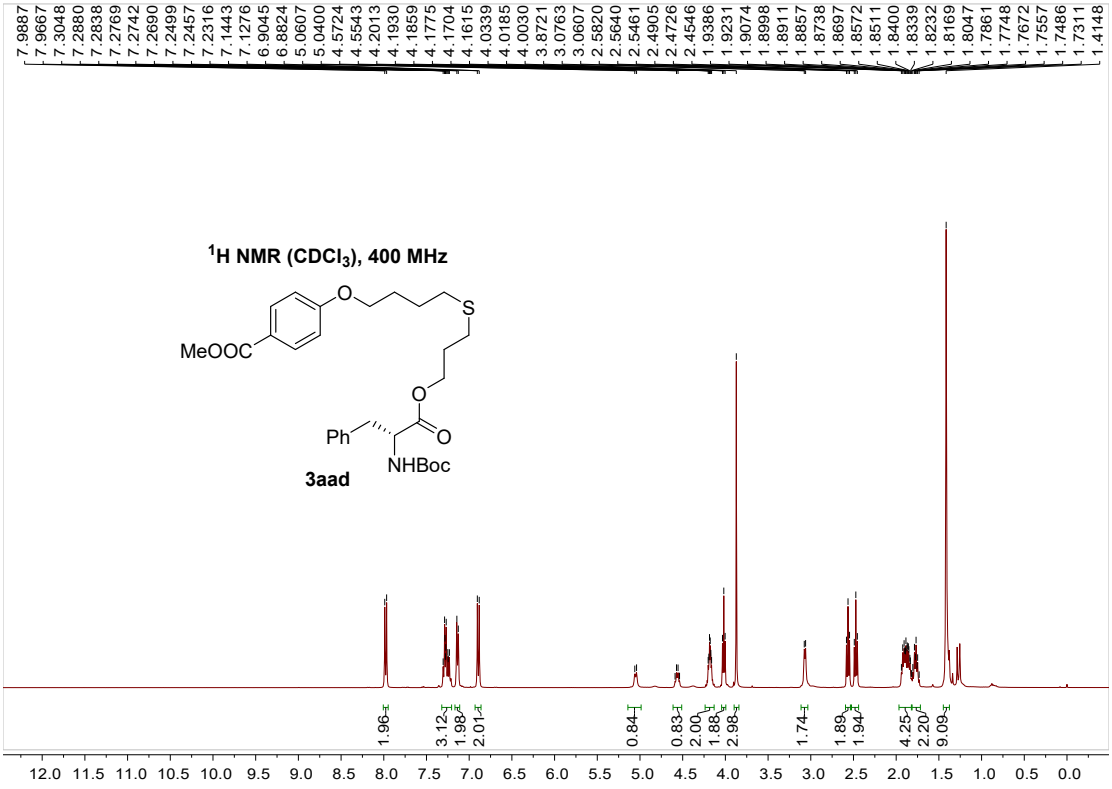

^{13}C NMR (CDCl$_3$), 101 MHz
MeOOC
O
S
3aaa

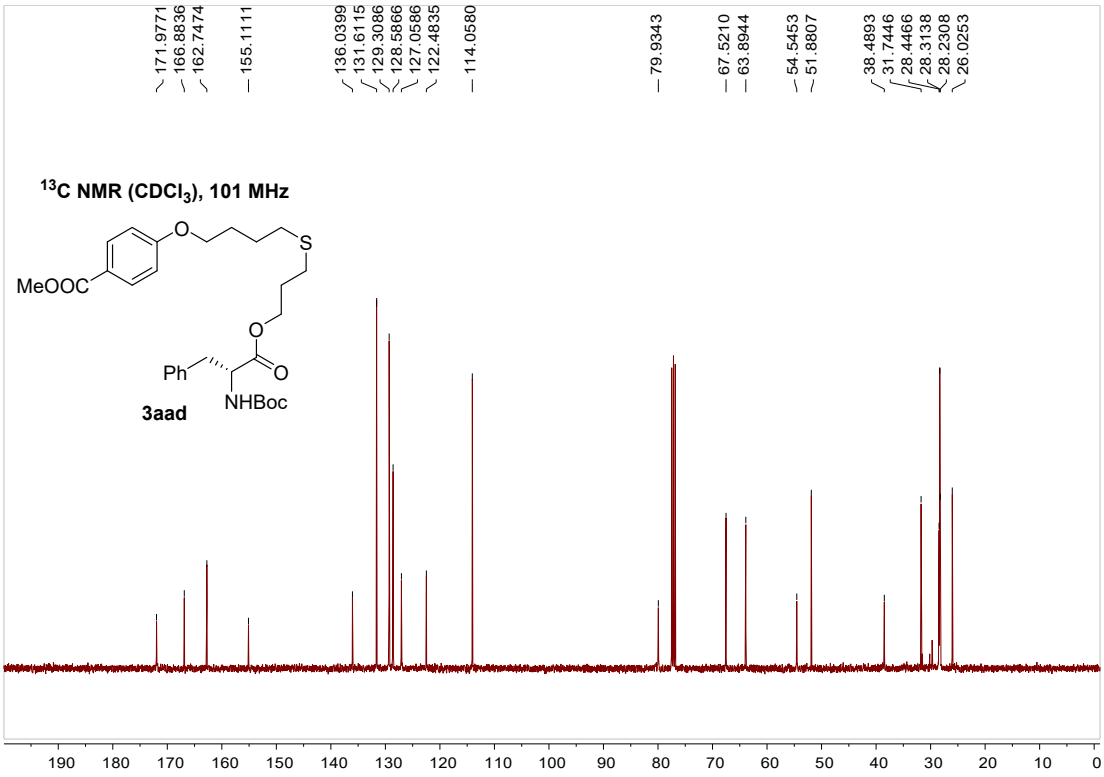

8.0110
7.9889
7.7019
7.6979
7.6943
7.6826
7.6782
7.4355
7.4279
7.4230
7.4186
7.4124
7.4085
7.3995
7.3970
7.3934
7.3815
7.3777
7.3722
4.0513
4.0359
4.0203
3.8915
3.6924
3.6764
3.6604
2.6164
2.5984
2.5804
2.5376
2.5192
2.5006
1.9467
1.9310
1.9236
1.9155
1.9096
1.8136
1.8021
1.7953
1.7919
1.7830
1.7780
1.7744
1.6189
1.6106
1.6014
1.5926
1.5844
1.5741
1.5665
1.5565
1.4043
1.3972
1.3879
1.3780
1.3688
1.3637
1H NMR (CDCl3), 400 MHz
MeOOC
O
S
Ph
Si
O
Ph
tBu
3aab
1.92
3.99
5.94
1.93
1.99
2.96
1.98
1.97
1.96
1.95
2.01
3.99
4.16
9.00
2.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

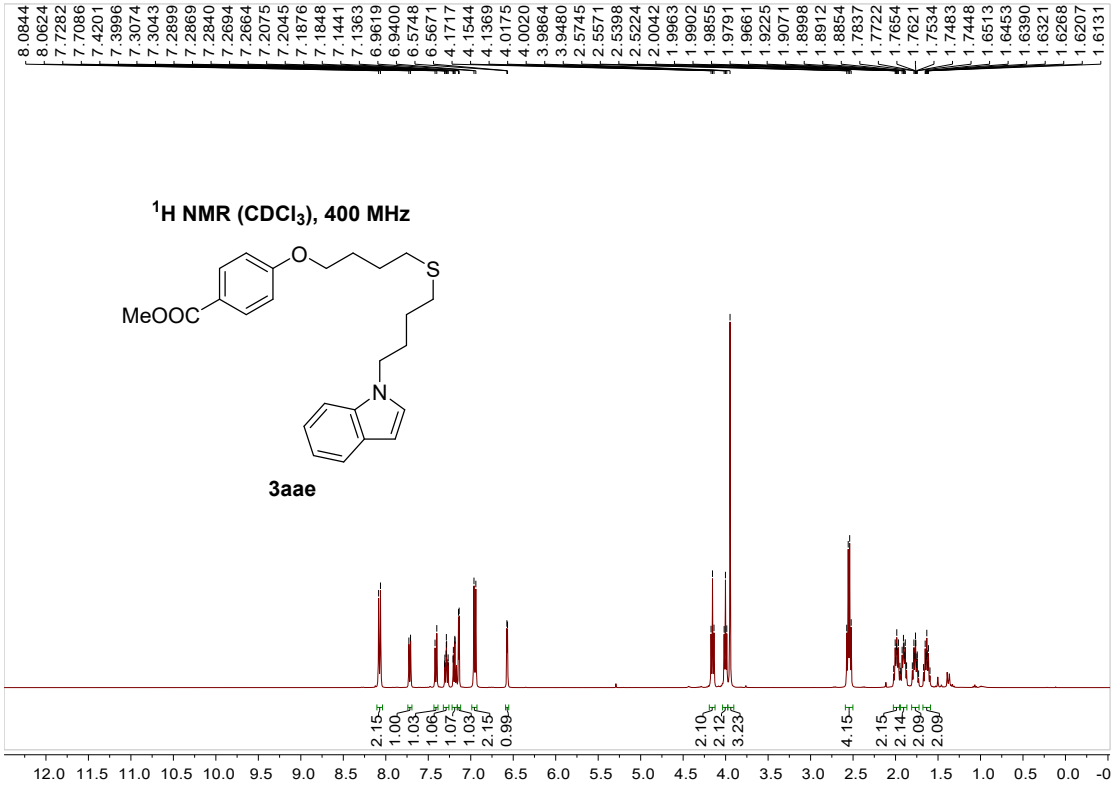

166.8031
162.7523
135.5523
134.0414
131.5752
129.5384
127.6111
122.4045
114.0250
67.5373
63.7994
51.8145
32.4233
32.0225
31.7438
29.6431
28.6389
28.2321
26.8868
26.0778
25.4290
19.2182
13C NMR (CDCl3), 101 MHz
MeOOC
O
S
Ph
Si
O
Ph
tBu
3aab
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

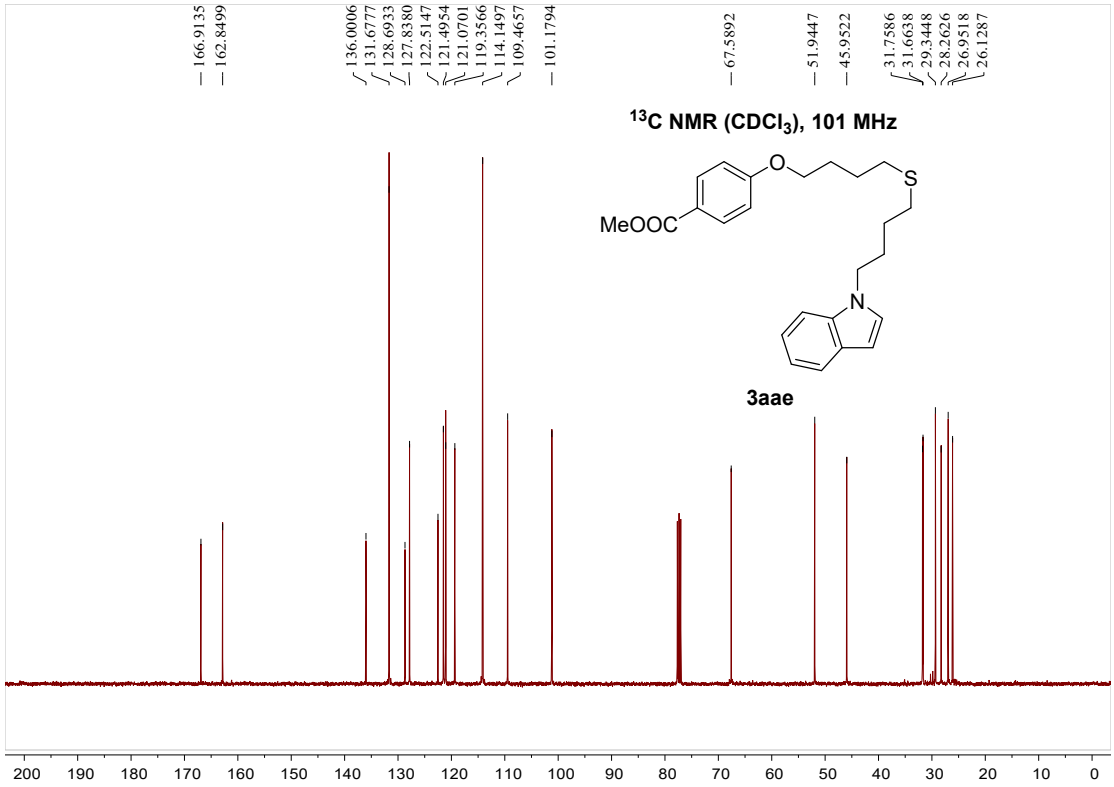

^{1}H NMR (CDCl$_3$), 400 MHz
MeOOC
O
S
O
O
N
Boc
3aac

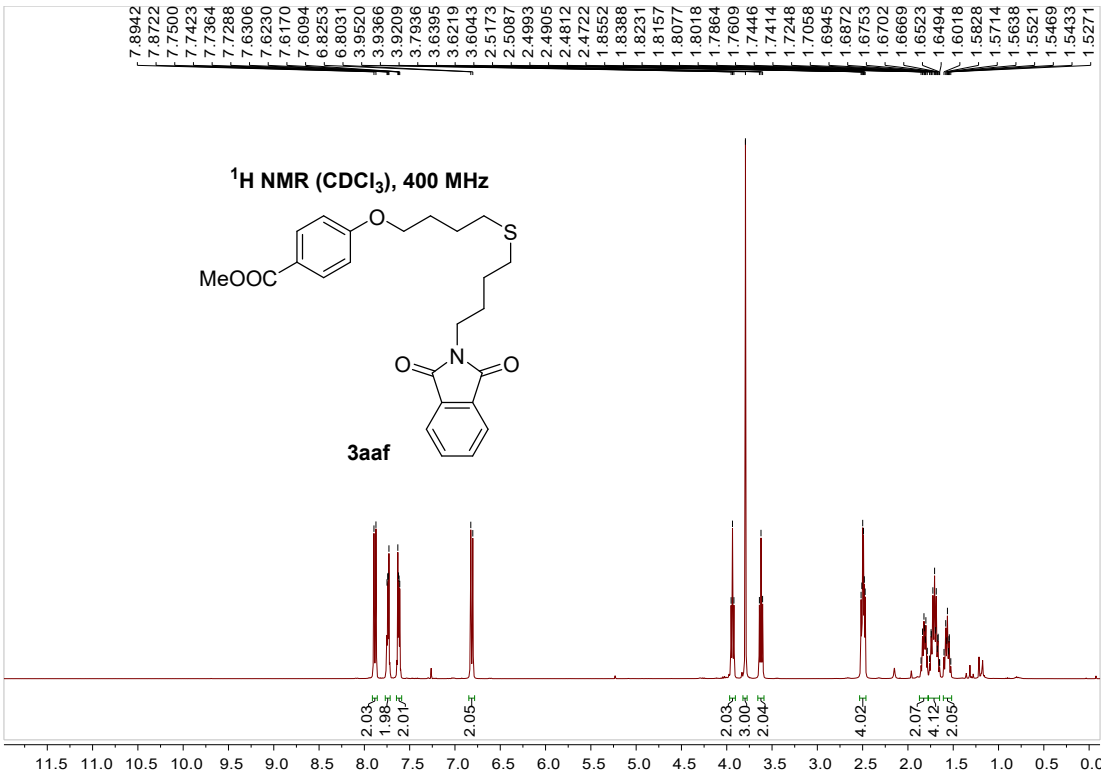

^{13}C NMR (CDCl$_3$), 101 MHz
MeOOC
O
S
O
O
N
Boc
3aac

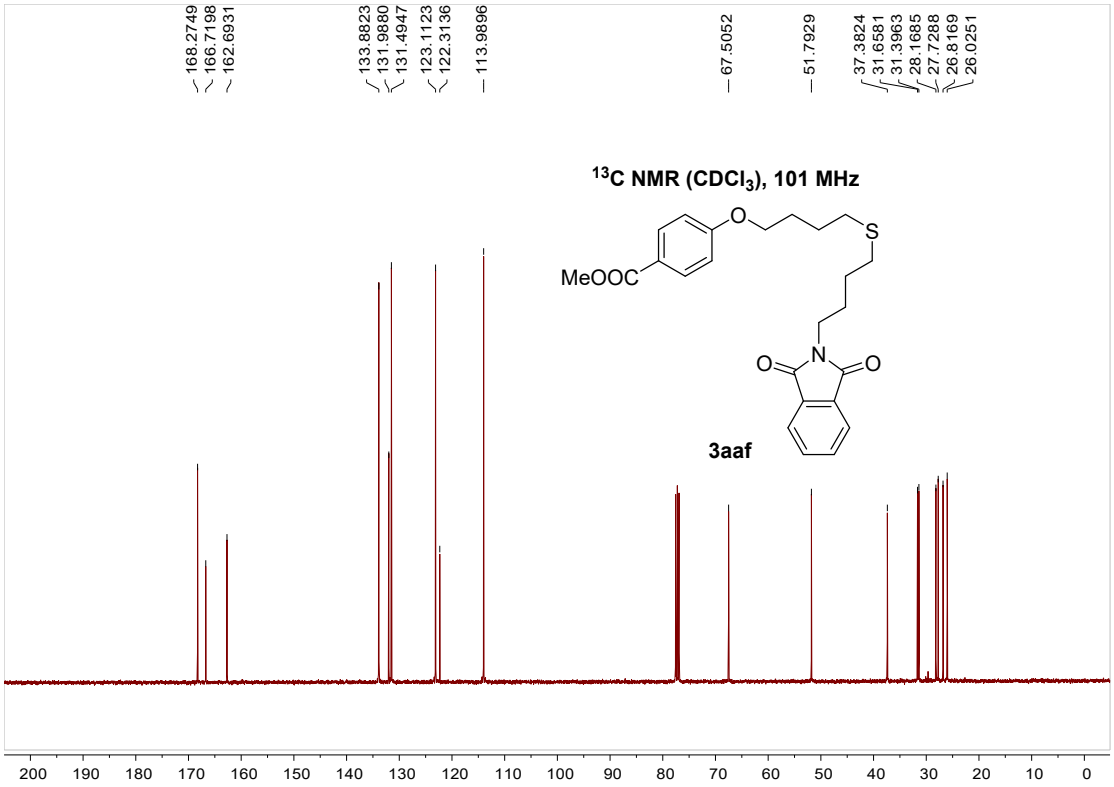

7.9887
7.9667
7.3048
7.2880
7.2838
7.2769
7.2742
7.2690
7.2499
7.2457
7.2316
7.1443
7.1276
6.9045
6.8824
5.0607
5.0400
4.5724
4.5543
4.2013
4.1930
4.1859
4.1775
4.1704
4.1615
4.0339
4.0185
4.0030
3.8721
3.0763
3.0607
2.5820
2.5640
2.5461
2.4905
2.4726
2.4546
1.9386
1.9231
1.9074
1.8998
1.8911
1.8857
1.8738
1.8697
1.8572
1.8511
1.8400
1.8339
1.8232
1.8169
1.8047
1.7861
1.7748
1.7672
1.7557
1.7486
1.7311
1.4148
^{1}H NMR (CDCl$_3$), 400 MHz
MeOOC
O
S
O
Ph
O
NHBoc
3aad
1.96
3.12
1.98
2.01
0.84
0.83
2.00
1.88
2.98
1.74
1.89
1.94
4.25
2.20
9.09
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

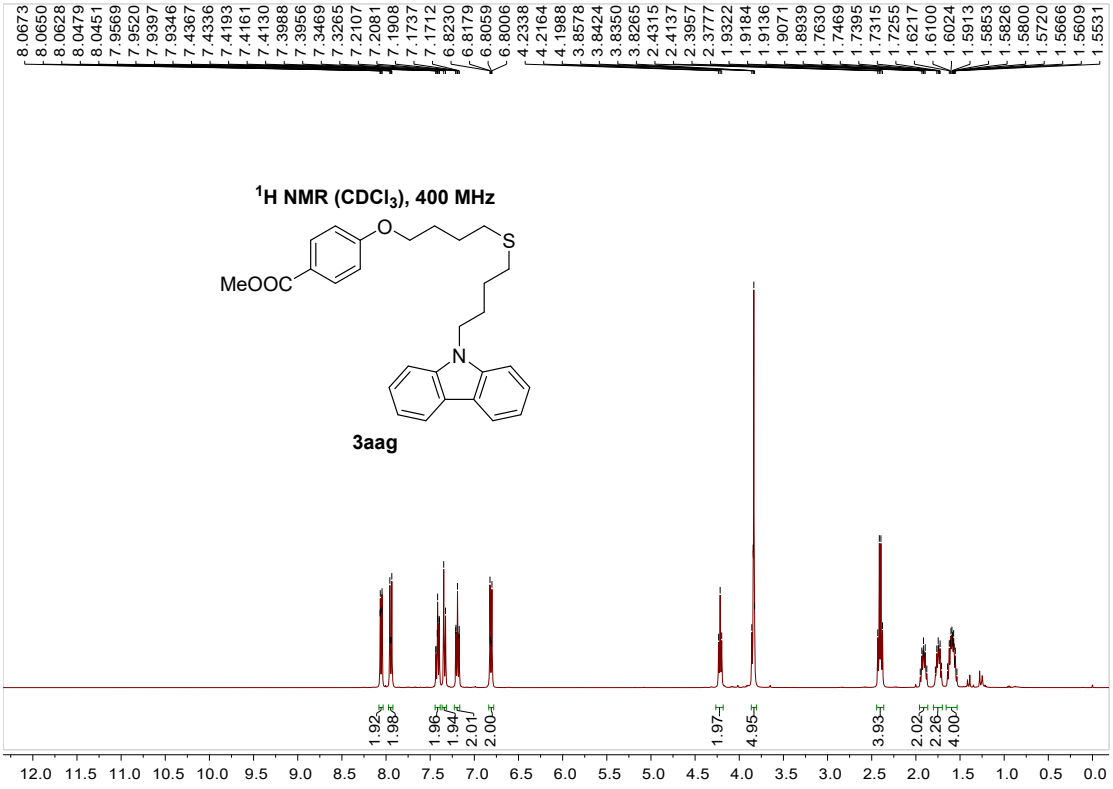

171.9771
166.8836
162.7474
155.1111
136.0399
131.6115
129.3086
128.5866
127.0586
122.4835
114.0580
79.9343
67.5210
63.8944
54.5453
51.8807
38.4893
31.7446
28.4466
28.3138
28.2308
26.0253
^{13}C NMR (CDCl$_3$), 101 MHz
MeOOC
O
S
O
Ph
O
NHBoc
3aad
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

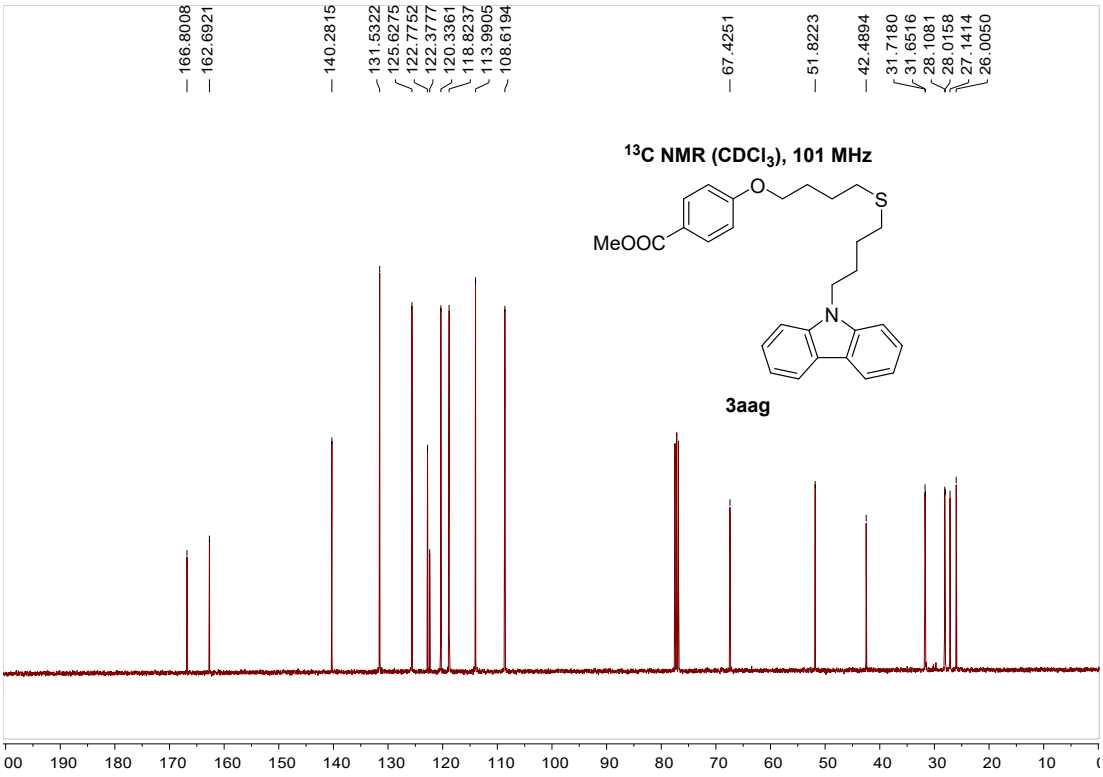

8.0844
8.0624
7.7282
7.7086
7.4201
7.3996
7.3074
7.3043
7.2899
7.2869
7.2840
7.2694
7.2664
7.2075
7.2045
7.1876
7.1848
7.1441
7.1363
6.9619
6.9400
6.5748
6.5671
4.1717
4.1544
4.1369
4.0175
4.0020
3.9864
3.9480
2.5745
2.5571
2.5398
2.5224
2.0042
1.9963
1.9902
1.9855
1.9791
1.9661
1.9225
1.9071
1.8998
1.8912
1.8854
1.7837
1.7722
1.7654
1.7621
1.7534
1.7483
1.7448
1.6513
1.6453
1.6390
1.6321
1.6268
1.6207
1.6131
^{1}H NMR (CDCl$_3$), 400 MHz
MeOOC
O
S
N
3aae
2.15
1.00
1.03
1.06
1.07
1.03
2.15
0.99
2.10
2.12
3.23
4.15
2.15
2.14
2.09
2.09
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0

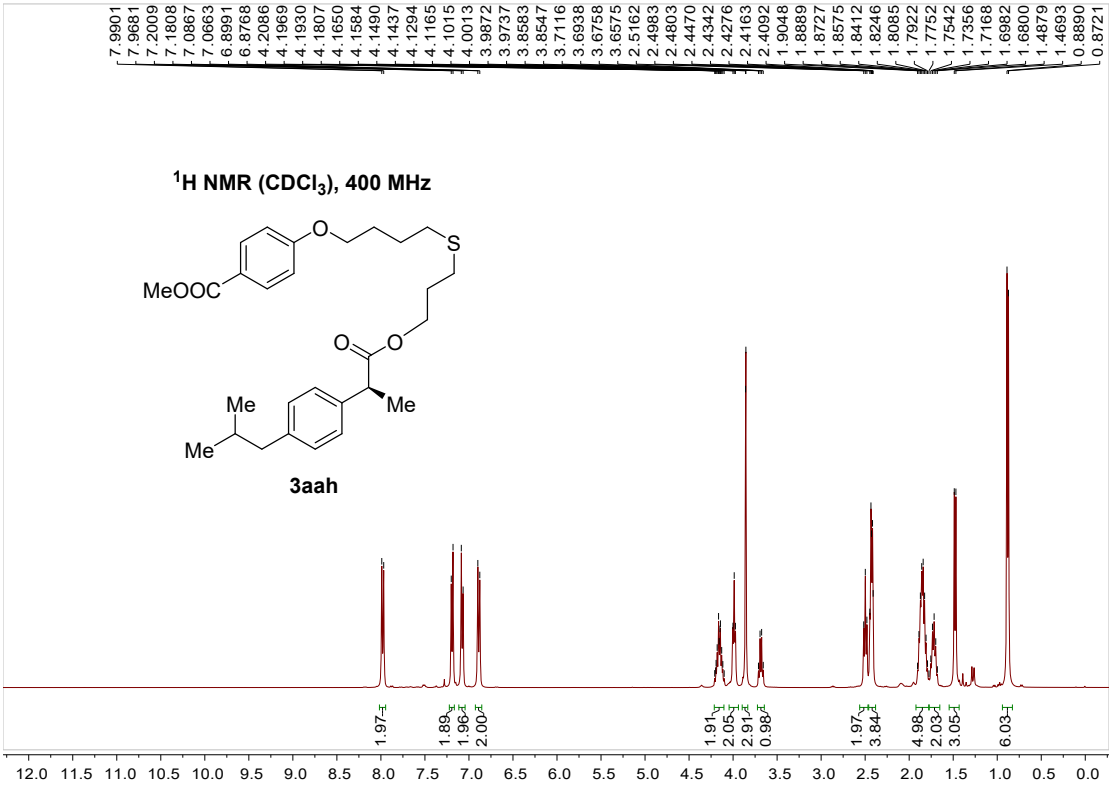

166.9135
162.8499
136.0006
131.6777
128.6933
127.8380
122.5147
121.4954
121.0701
119.3566
114.1497
109.4657
101.1794
67.5892
51.9447
45.9522
31.7586
31.6638
29.3448
28.2626
26.9518
26.1287
^{13}C NMR (CDCl$_3$), 101 MHz
MeOOC
O
S
N
3aae
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

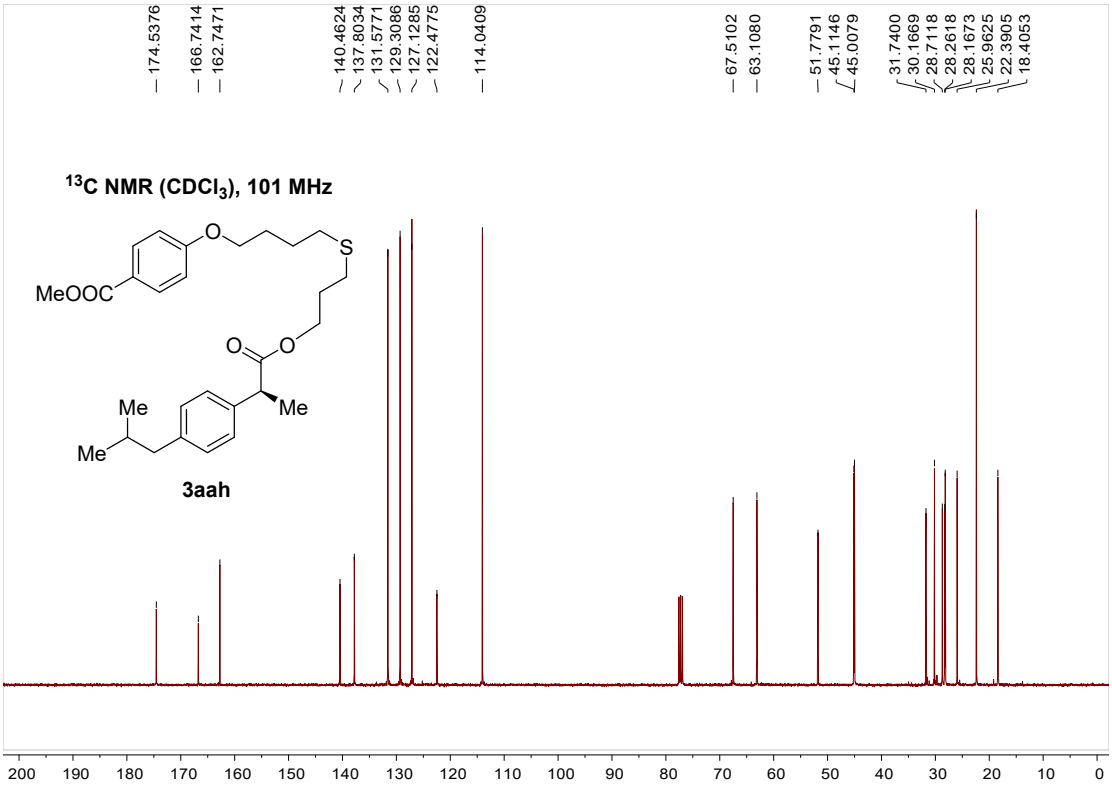

7.8942
7.8722
7.7500
7.7423
7.7364
7.7288
7.6306
7.6230
7.6170
7.6094
6.8253
6.8031
3.9520
3.9366
3.9209
3.7936
3.6395
3.6219
3.6043
2.5173
2.5087
2.4993
2.4905
2.4812
2.4722
1.8552
1.8388
1.8231
1.8157
1.8077
1.8018
1.7864
1.7609
1.7446
1.7414
1.7248
1.7058
1.6945
1.6872
1.6753
1.6702
1.6669
1.6523
1.6494
1.6018
1.5828
1.5714
1.5638
1.5521
1.5469
1.5433
1.5271
^{1}H NMR ($CDCl_3$), 400 MHz
MeOOC
O
S
N
O
O
3aaf
2.03
1.98
2.01
2.05
2.03
3.00
2.04
4.02
2.07
4.12
2.05
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

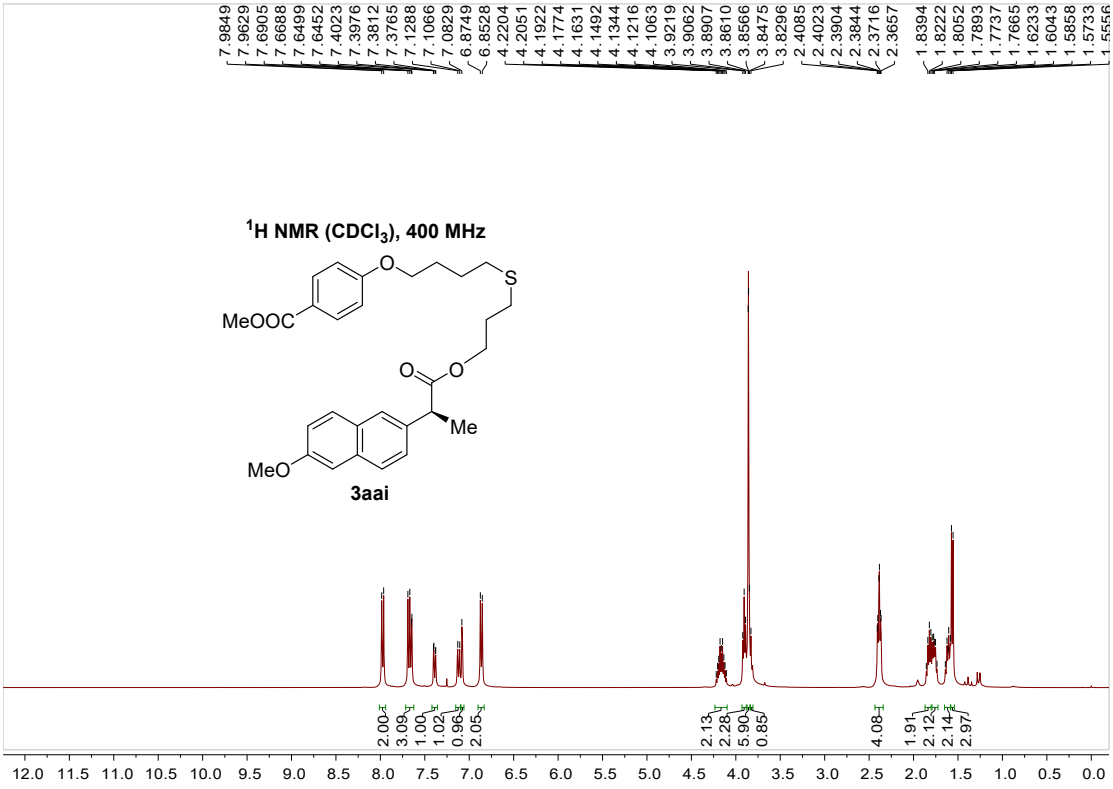

168.2749
166.7198
162.6931
133.8823
131.9880
131.4947
123.1123
122.3136
113.9896
67.5052
51.7929
37.3824
31.6581
31.3963
28.1685
27.7288
26.8169
26.0251
^{13}C NMR ($CDCl_3$), 101 MHz
MeOOC
O
S
N
O
O
3aaf
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

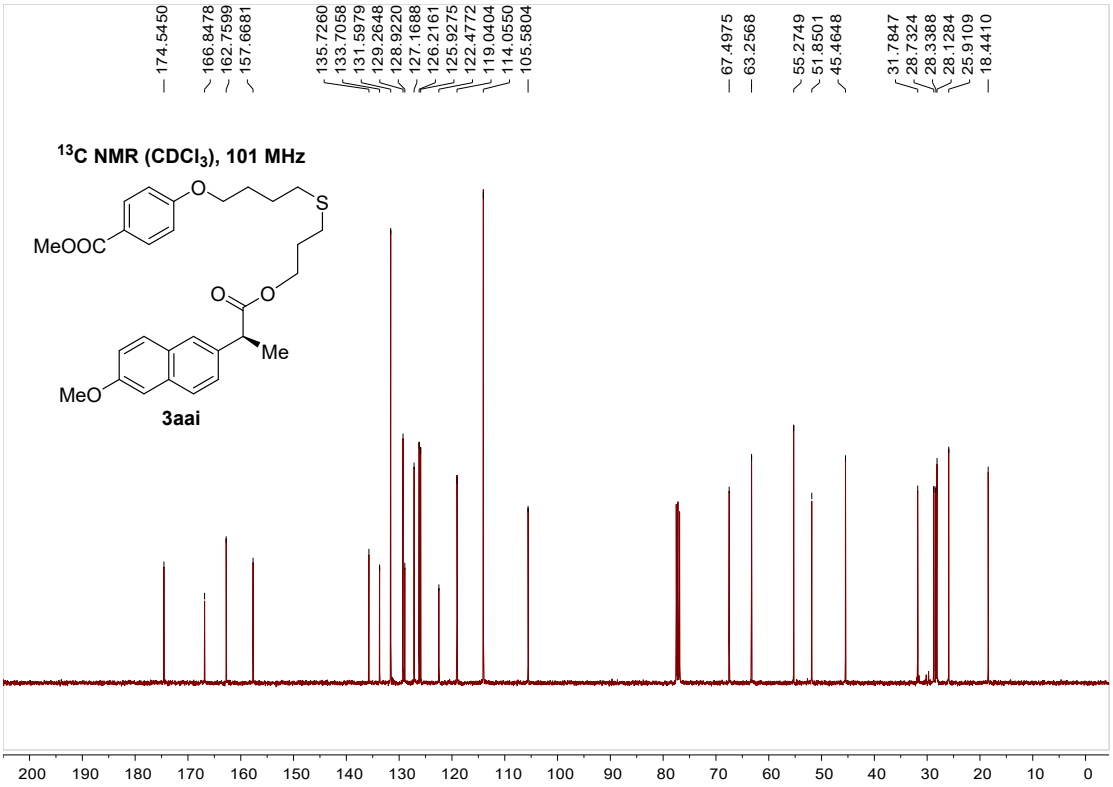

8.0673
8.0650
8.0628
8.0479
8.0451
7.9569
7.9520
7.9397
7.9346
7.4367
7.4336
7.4193
7.4161
7.4130
7.3988
7.3956
7.3469
7.3265
7.2107
7.2081
7.1908
7.1737
7.1712
6.8230
6.8179
6.8059
6.8006
4.2338
4.2164
4.1988
3.8578
3.8424
3.8350
3.8265
2.4315
2.4137
2.3957
2.3777
1.9322
1.9184
1.9136
1.9071
1.8939
1.7630
1.7469
1.7395
1.7315
1.7255
1.6217
1.6100
1.6024
1.5913
1.5853
1.5826
1.5800
1.5720
1.5666
1.5609
1.5531
^{1}H NMR ($CDCl_3$), 400 MHz
MeOOC
O
S
N
3aag
1.92
1.98
1.96
1.94
2.01
2.00
1.97
4.95
3.93
2.02
2.26
4.00
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

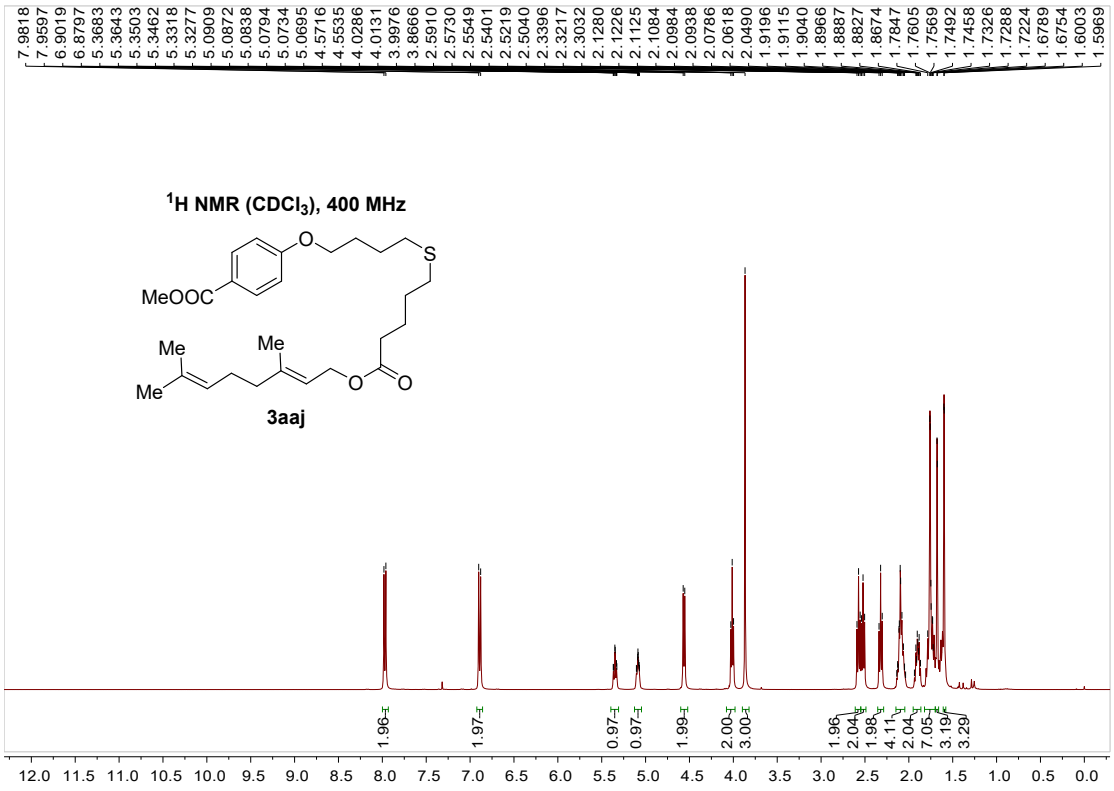

166.8008
162.6921
140.2815
131.5322
125.6275
122.7752
122.3777
120.3361
118.8237
113.9905
108.6194
67.4251
51.8223
42.4894
31.7180
31.6516
28.1081
28.0158
27.1414
26.0050
^{13}C NMR ($CDCl_3$), 101 MHz
MeOOC
O
S
N
3aag
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10

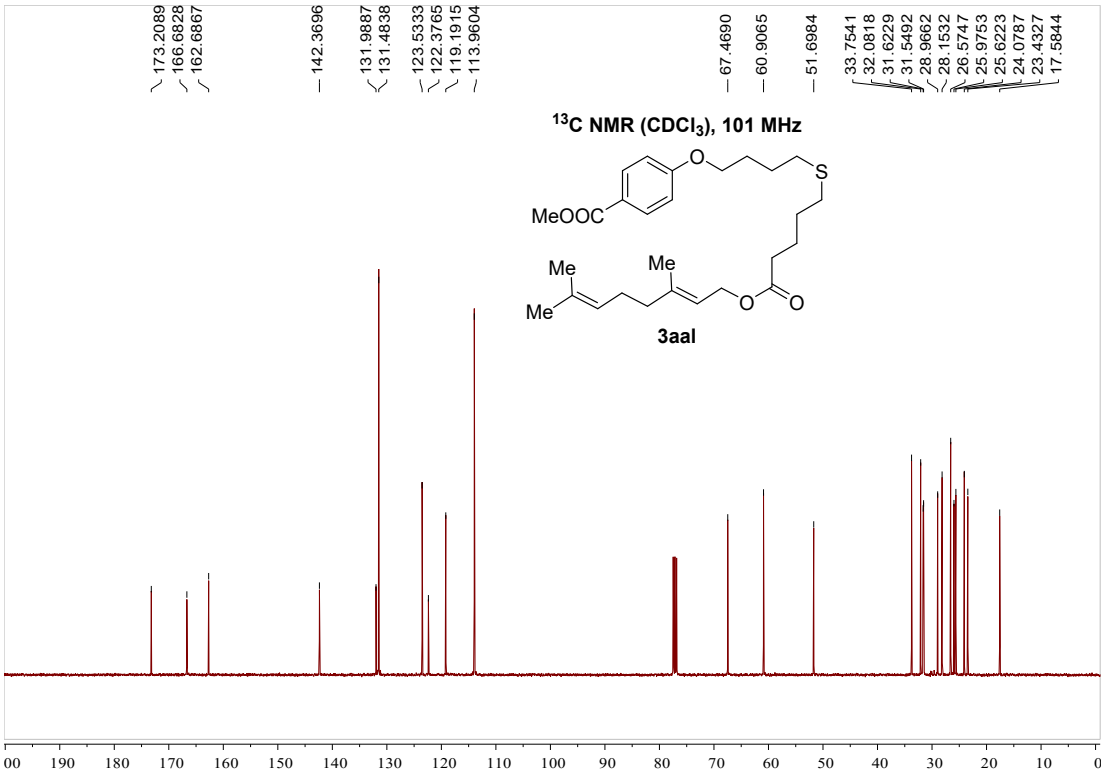

7.9901
7.9681
7.2009
7.1808
7.0867
7.0663
6.8991
6.8768
4.2086
4.1969
4.1930
4.1807
4.1650
4.1584
4.1490
4.1437
4.1294
4.1165
4.1015
4.0013
3.9872
3.9737
3.8583
3.8547
3.7116
3.6938
3.6758
3.6575
2.5162
2.4983
2.4803
2.4470
2.4342
2.4276
2.4163
2.4092
1.9048
1.8889
1.8727
1.8575
1.8412
1.8246
1.8085
1.7922
1.7752
1.7542
1.7356
1.7168
1.6982
1.6800
1.4879
1.4693
0.8890
0.8721
1H NMR (CDCl3), 400 MHz
MeOOC
O
S
O
O
Me
Me
Me
3aah
1.97
1.89
1.96
2.00
1.91
2.05
2.91
0.98
1.97
3.84
4.98
2.03
3.05
6.03
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

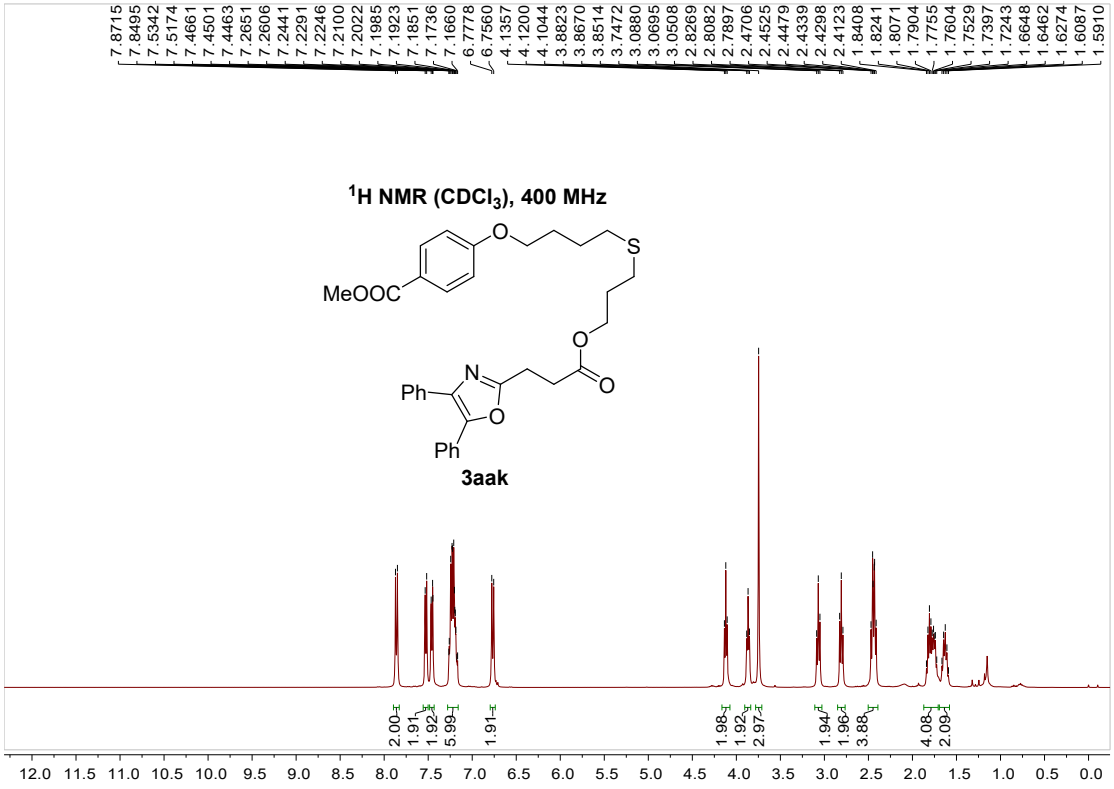

174.5376
166.7414
162.7471
140.4624
137.8034
131.5771
129.3086
127.1285
122.4775
114.0409
67.5102
63.1080
51.7791
45.1146
45.0079
31.7400
30.1669
28.7118
28.2618
28.1673
25.9625
22.3905
18.4053
13C NMR (CDCl3), 101 MHz
MeOOC
O
S
O
O
Me
Me
Me
3aah
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

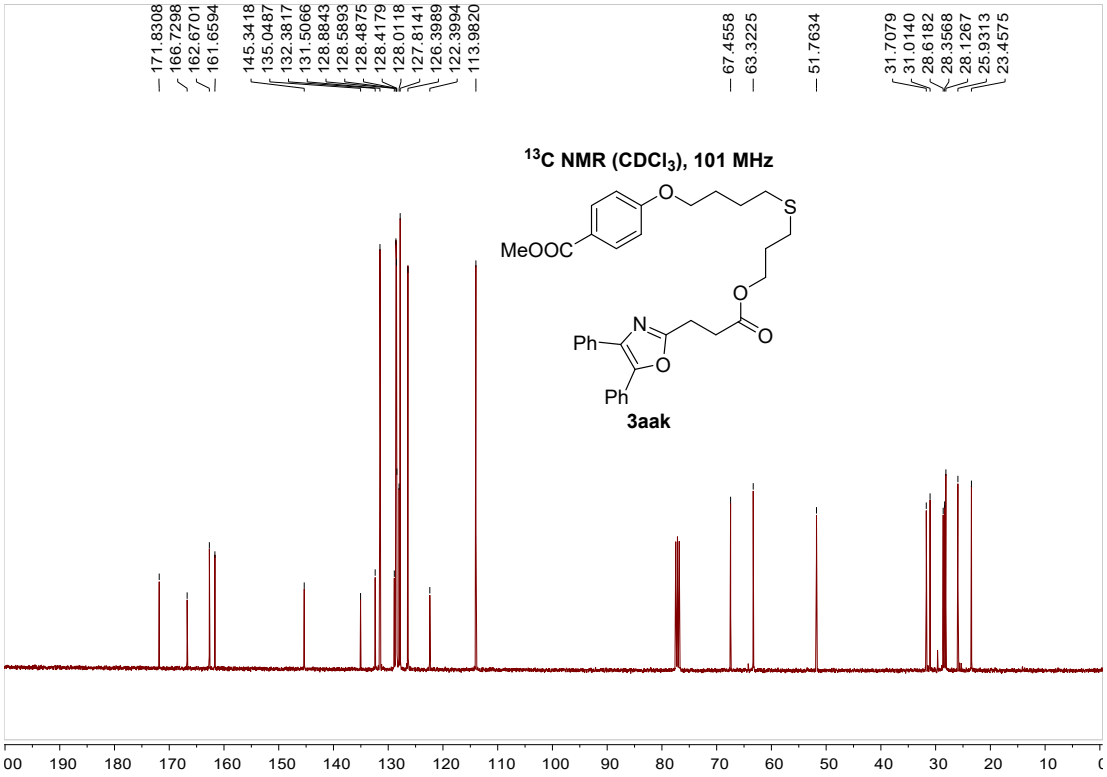

7.9849
7.9629
7.6905
7.6688
7.6499
7.6452
7.4023
7.3976
7.3812
7.3765
7.1288
7.1066
7.0829
6.8749
6.8528
4.2204
4.2051
4.1922
4.1774
4.1631
4.1492
4.1344
4.1216
4.1063
3.9219
3.9062
3.8907
3.8610
3.8566
3.8475
3.8296
2.4085
2.4023
2.3904
2.3844
2.3716
2.3657
1.8394
1.8222
1.8052
1.7893
1.7737
1.7665
1.6233
1.6043
1.5858
1.5733
1.5556
1H NMR (CDCl3), 400 MHz
MeOOC
O
S
O
O
Me
MeO
3aai
2.00
3.09
1.00
1.02
0.96
2.05
2.13
2.28
5.90
0.85
4.08
1.91
2.12
2.14
2.97
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

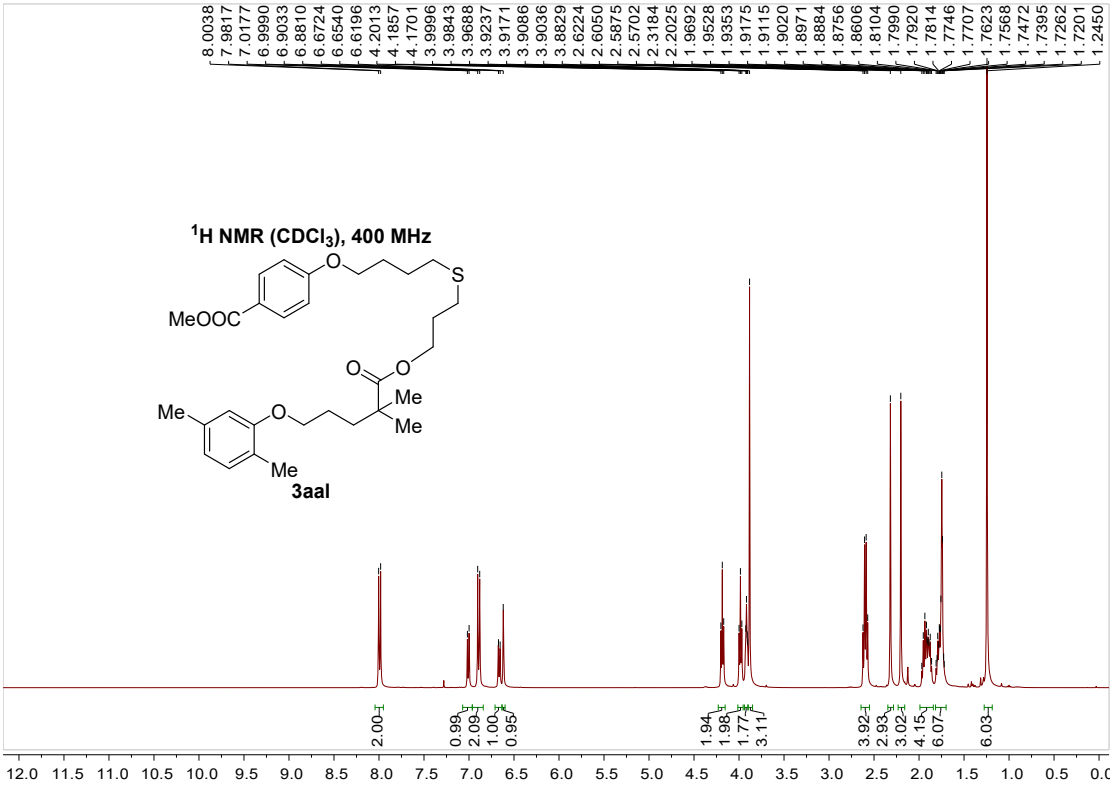

174.5450
166.8478
162.7599
157.6681
135.7260
133.7058
131.5979
129.2648
128.9220
127.1688
126.2161
125.9275
122.4772
119.0404
114.0550
105.5804
67.4975
63.2568
55.2749
51.8501
45.4648
31.7847
28.7324
28.3388
28.1284
25.9109
18.4410
13C NMR (CDCl3), 101 MHz
MeOOC
O
S
O
O
Me
MeO
3aai
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

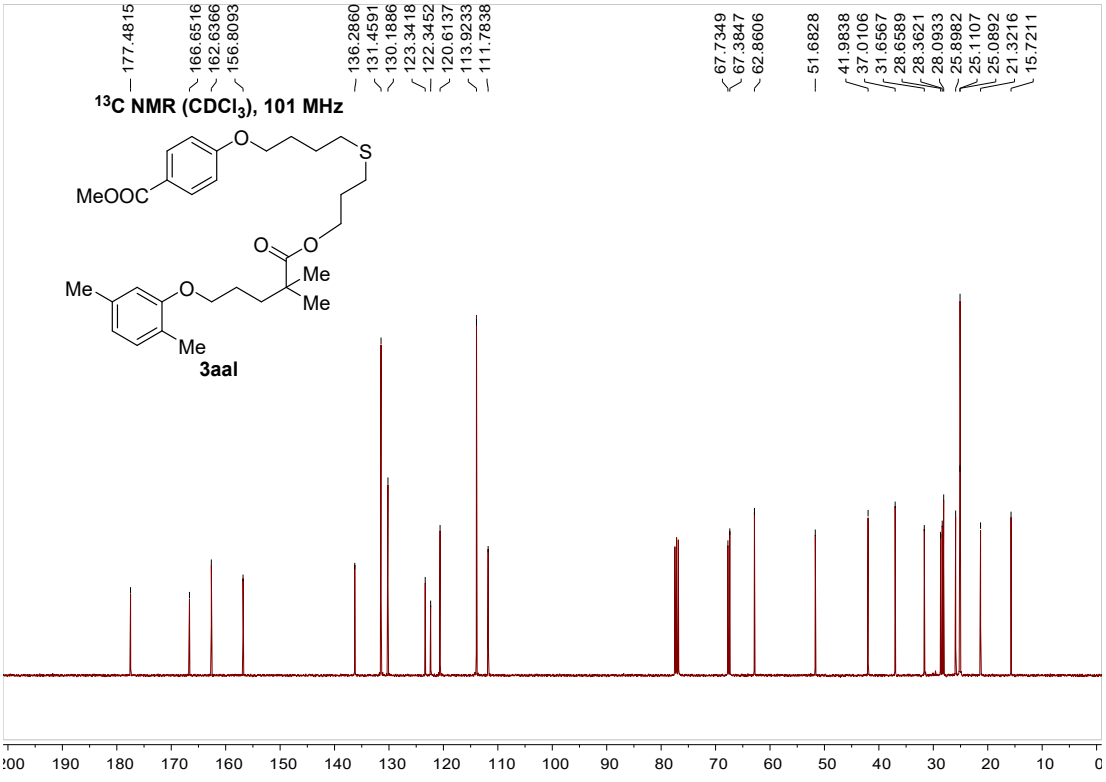

^{1}H NMR ($CDCl_3$), 400 MHz
MeOOC
O
S
Me
Me
Me
O
O
3aaj

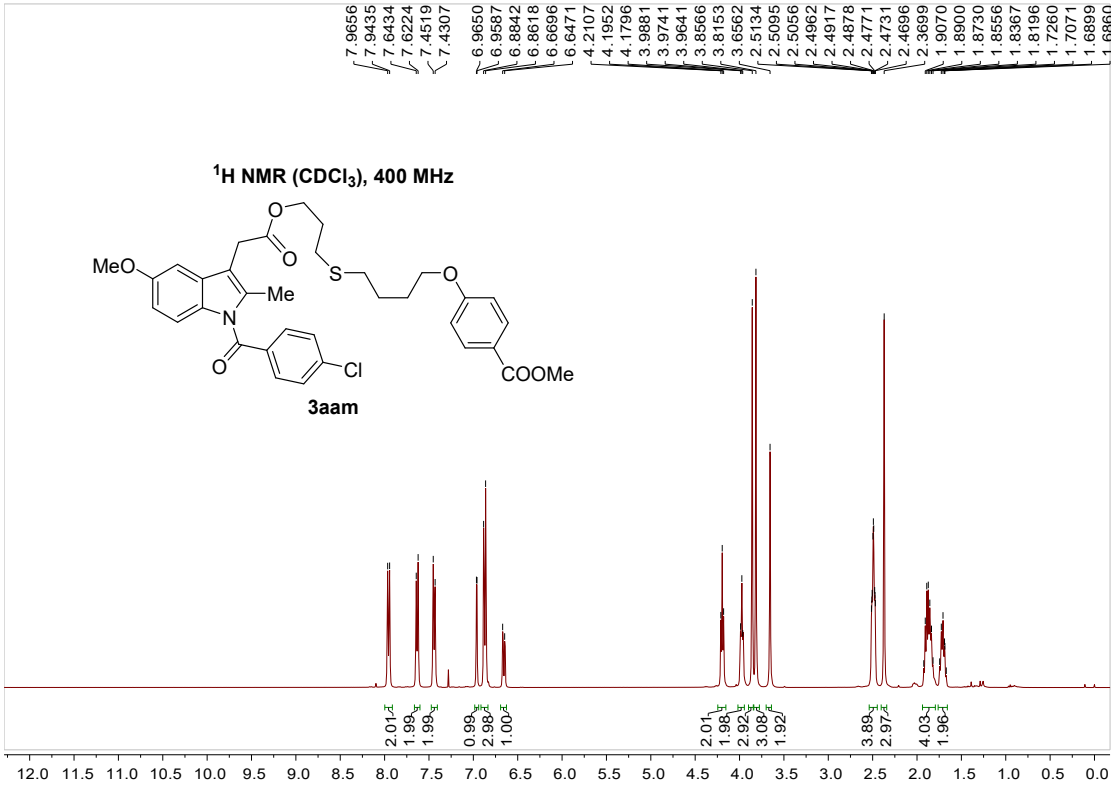

^{13}C NMR ($CDCl_3$), 101 MHz
MeOOC
O
S
Me
Me
Me
O
O
3aal

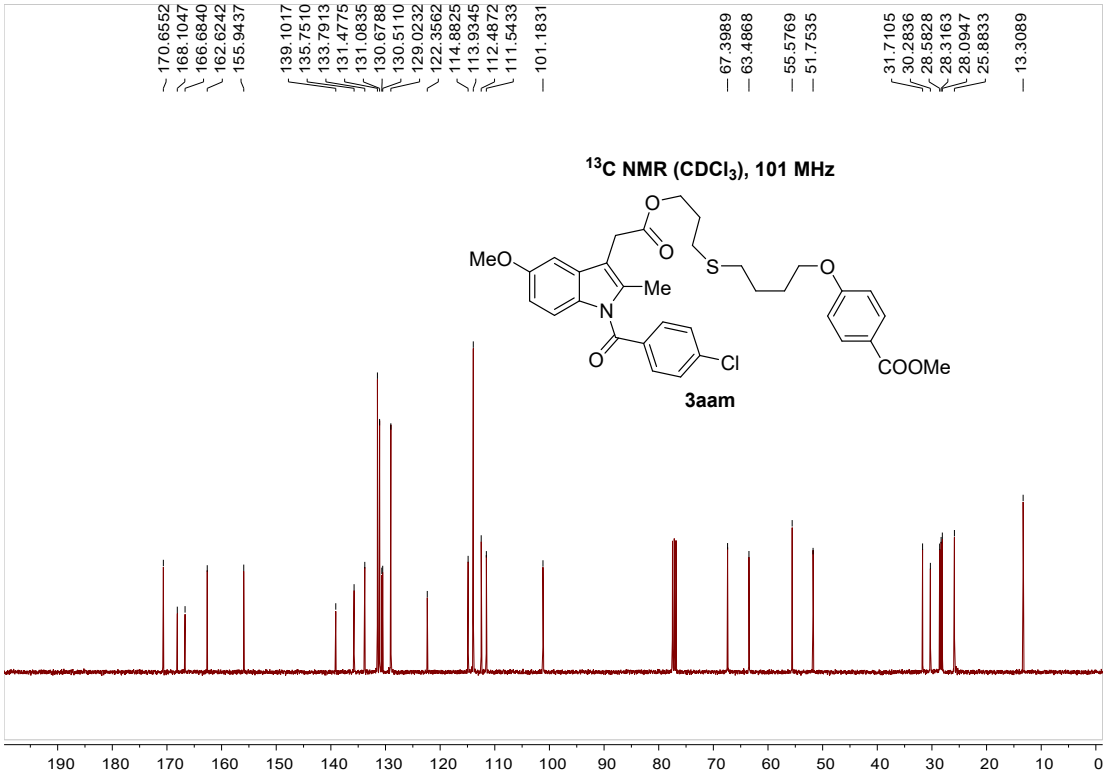

7.8715
7.8495
7.5342
7.5174
7.4661
7.4501
7.4463
7.2651
7.2606
7.2441
7.2291
7.2246
7.2100
7.2022
7.1985
7.1923
7.1851
7.1736
7.1660
6.7778
6.7560
4.1357
4.1200
4.1044
3.8823
3.8670
3.8514
3.7472
3.0880
3.0695
3.0508
2.8269
2.8082
2.7897
2.4706
2.4525
2.4479
2.4339
2.4298
2.4123
1.8408
1.8241
1.8071
1.7904
1.7755
1.7604
1.7529
1.7397
1.7243
1.6648
1.6462
1.6274
1.6087
1.5910
1H NMR (CDCl3), 400 MHz
MeOOC
O
S
O
N
Ph
O
O
Ph
3aak
2.00
1.91
1.92
5.99
1.91
1.98
1.92
2.97
1.94
1.96
3.88
4.08
2.09
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

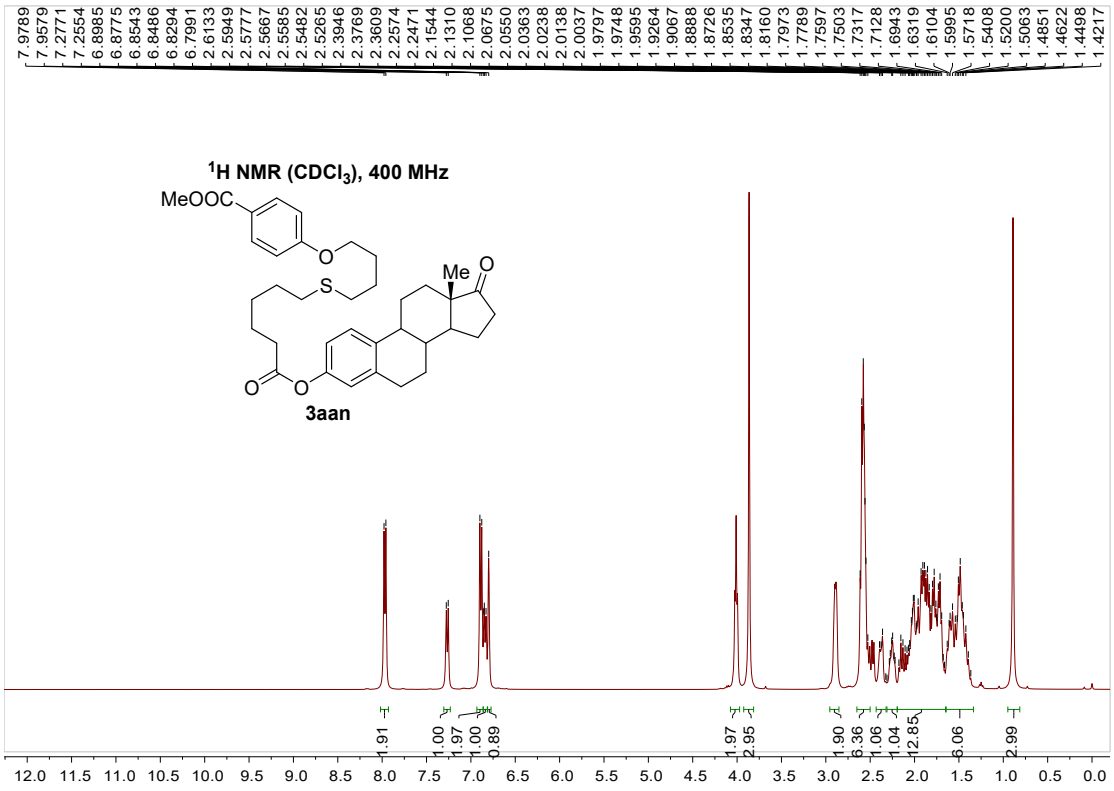

171.8308
166.7298
162.6701
161.6594
145.3418
135.0487
132.3817
131.5066
128.8843
128.5893
128.4875
128.4179
128.0118
127.8141
126.3989
122.3994
113.9820
67.4558
63.3225
51.7634
31.7079
31.0140
28.6182
28.3568
28.1267
25.9313
23.4575
13C NMR (CDCl3), 101 MHz
MeOOC
O
S
O
N
Ph
O
O
Ph
3aak
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

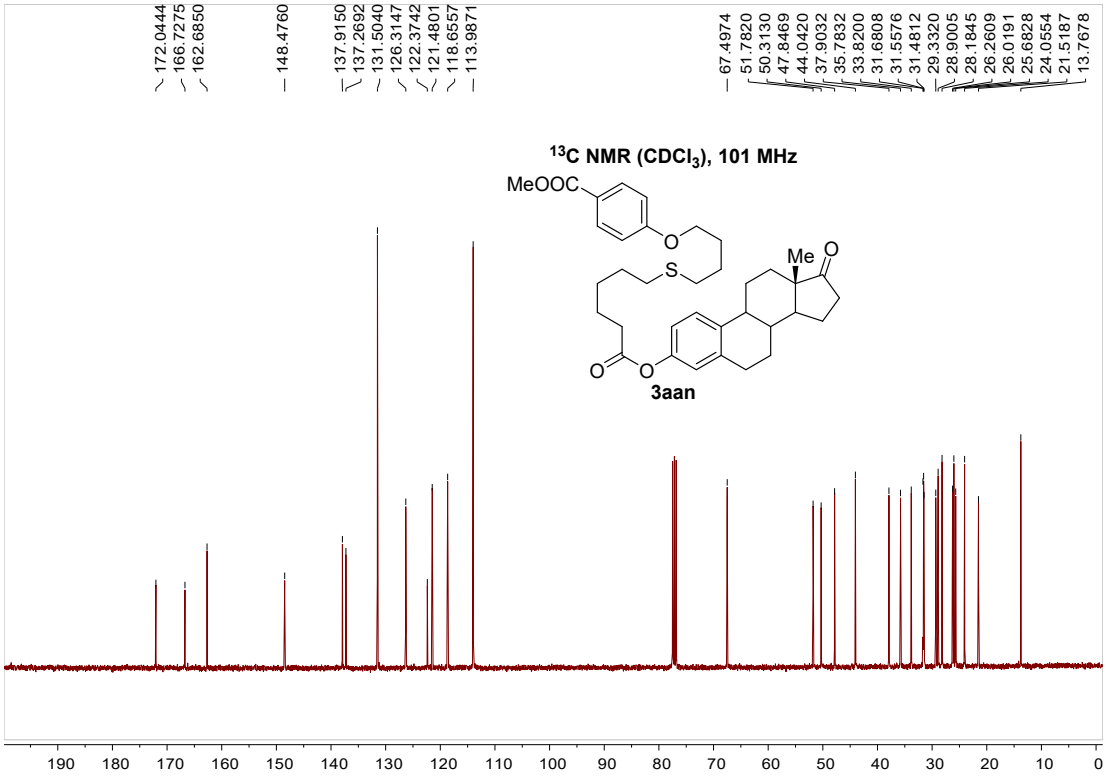

8.0038
7.9817
7.0177
6.9990
6.9033
6.8810
6.6724
6.6540
6.6196
4.2013
4.1857
4.1701
3.9996
3.9843
3.9688
3.9237
3.9171
3.9086
3.9036
3.8829
2.6224
2.6050
2.5875
2.5702
2.3184
2.2025
1.9692
1.9528
1.9353
1.9175
1.9115
1.9020
1.8971
1.8884
1.8756
1.8606
1.8104
1.7990
1.7920
1.7814
1.7746
1.7707
1.7623
1.7568
1.7472
1.7395
1.7262
1.7201
1.2450
^{1}H NMR (CDCl$_3$), 400 MHz
MeOOC
O
S
O
O
Me
Me
Me
O
Me
3aal
2.00
0.99
2.09
1.00
0.95
1.94
1.98
1.77
3.11
3.92
2.93
3.02
4.15
6.07
6.03
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

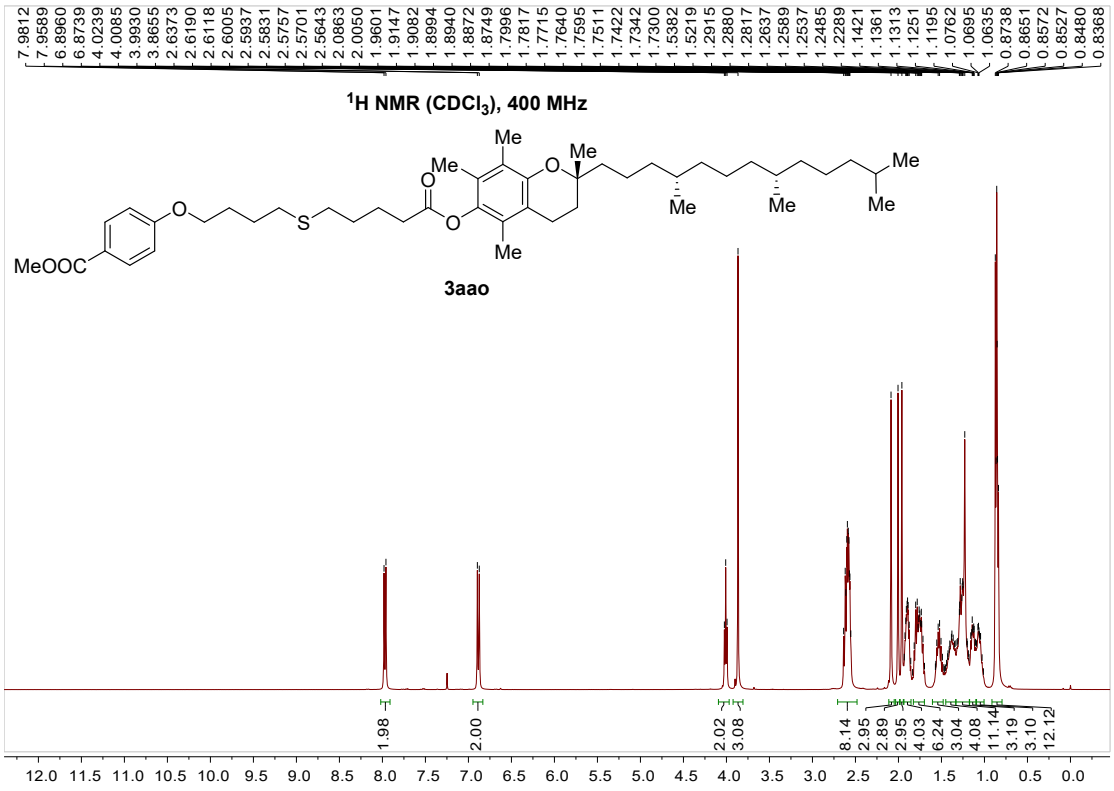

177.4815
166.6516
162.6366
156.8093
136.2860
131.4591
130.1886
123.3418
122.3452
120.6137
113.9233
111.7838
67.7349
67.3847
62.8606
51.6828
41.9838
37.0106
31.6567
28.6589
28.3621
28.0933
25.8982
25.1107
25.0892
21.3216
15.7211
^{13}C NMR (CDCl$_3$), 101 MHz
MeOOC
O
S
O
O
Me
Me
Me
O
Me
3aal
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

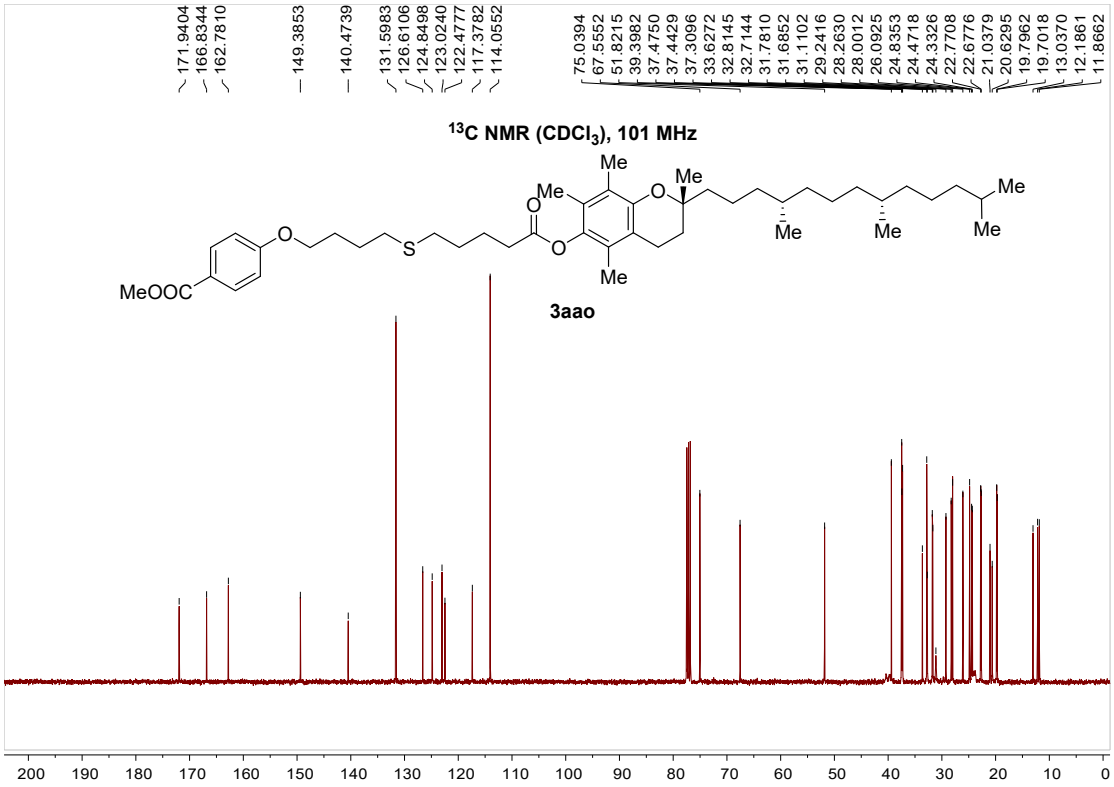

7.9656
7.9435
7.6434
7.6224
7.4519
7.4307
6.9650
6.9587
6.8842
6.8618
6.6696
6.6471
4.2107
4.1952
4.1796
3.9881
3.9741
3.9641
3.8566
3.8153
3.6562
2.5134
2.5095
2.5056
2.4962
2.4917
2.4878
2.4771
2.4731
2.4696
2.3699
1.9070
1.8900
1.8730
1.8556
1.8367
1.8196
1.7260
1.7071
1.6899
1.6860
^{1}H NMR ($CDCl_3$), 400 MHz
MeO
Me
N
O
S
O
Cl
COOMe
3aam
2.01
1.99
1.99
0.99
2.98
1.00
2.01
1.98
2.92
3.08
1.92
3.89
2.97
4.03
1.96
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

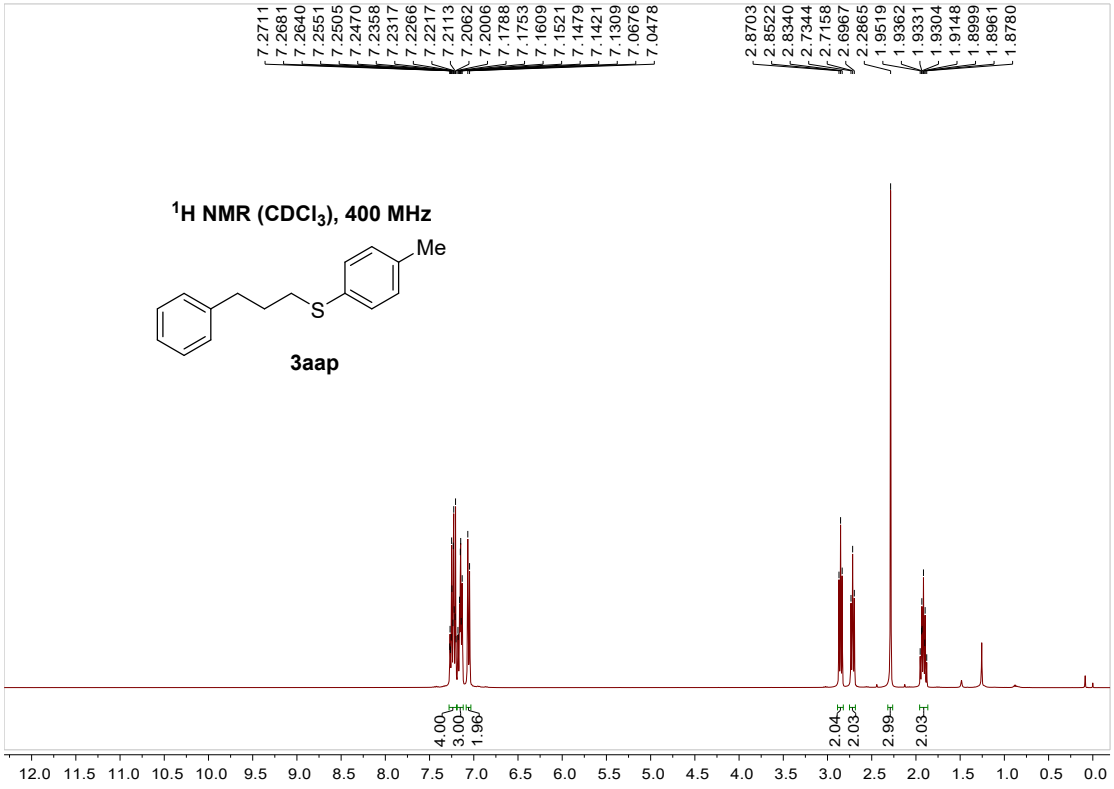

170.6552
168.1047
166.6840
162.6242
155.9437
139.1017
135.7510
133.7913
131.4775
131.0835
130.6788
130.5110
129.0232
122.3562
114.8825
113.9345
112.4872
111.5433
101.1831
67.3989
63.4868
55.5769
51.7535
31.7105
30.2836
28.5828
28.3163
28.0947
25.8833
13.3089
^{13}C NMR ($CDCl_3$), 101 MHz
MeO
Me
N
O
S
O
Cl
COOMe
3aam
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

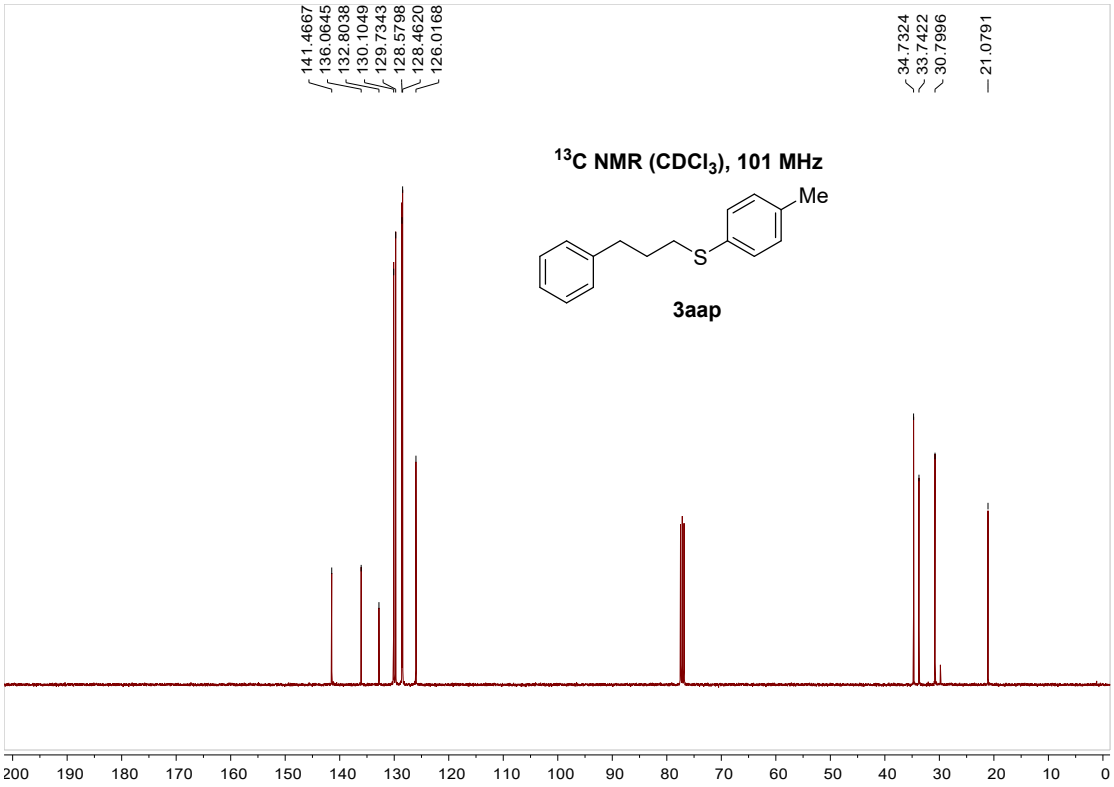

^{1}H NMR ($CDCl_3$), 400 MHz
MeOOC
O
S
Me
O
O
O
3aan

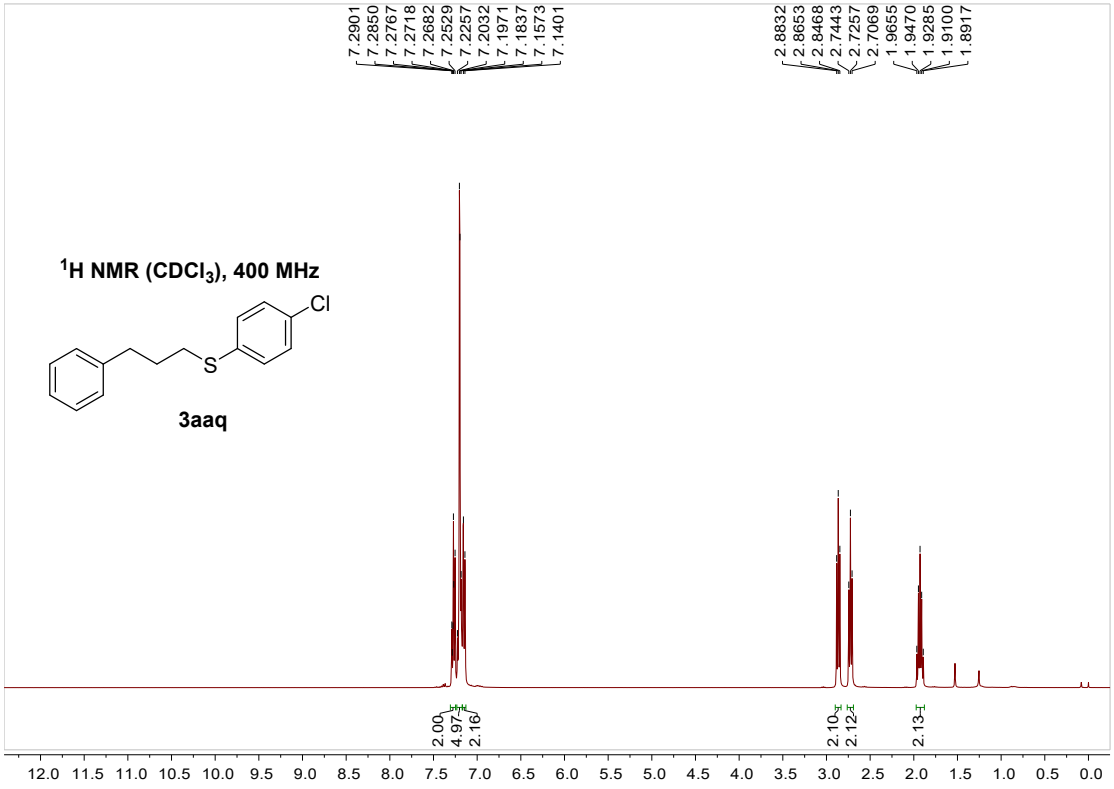

^{13}C NMR ($CDCl_3$), 101 MHz
MeOOC
O
S
Me
O
O
O
3aan

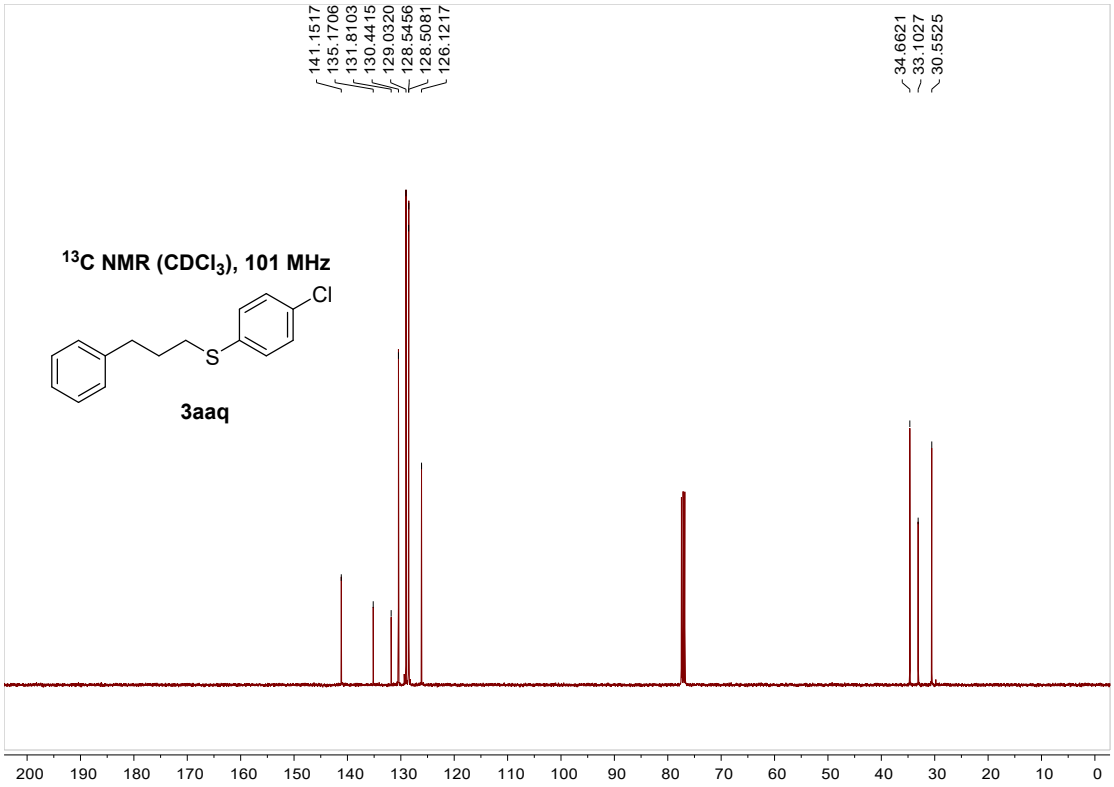

7.9812
7.9589
6.8960
6.8739
4.0239
4.0085
3.9930
3.8655
2.6373
2.6190
2.6118
2.6005
2.5937
2.5831
2.5757
2.5701
2.5643
2.0863
2.0050
1.9601
1.9147
1.9082
1.8994
1.8940
1.8872
1.8749
1.7996
1.7817
1.7715
1.7640
1.7595
1.7511
1.7422
1.7342
1.7300
1.5382
1.5219
1.2915
1.2880
1.2817
1.2637
1.2589
1.2537
1.2485
1.2289
1.1421
1.1361
1.1313
1.1251
1.1195
1.0762
1.0695
1.0635
0.8738
0.8651
0.8572
0.8527
0.8480
0.8368
1H NMR (CDCl3), 400 MHz
Me
Me
Me
O
O
Me
Me
Me
Me
O
S
O
MeOOC
3aao
1.98
2.00
2.02
3.08
8.14
2.95
2.89
2.95
4.03
6.24
3.04
4.08
11.14
3.19
3.10
12.12
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

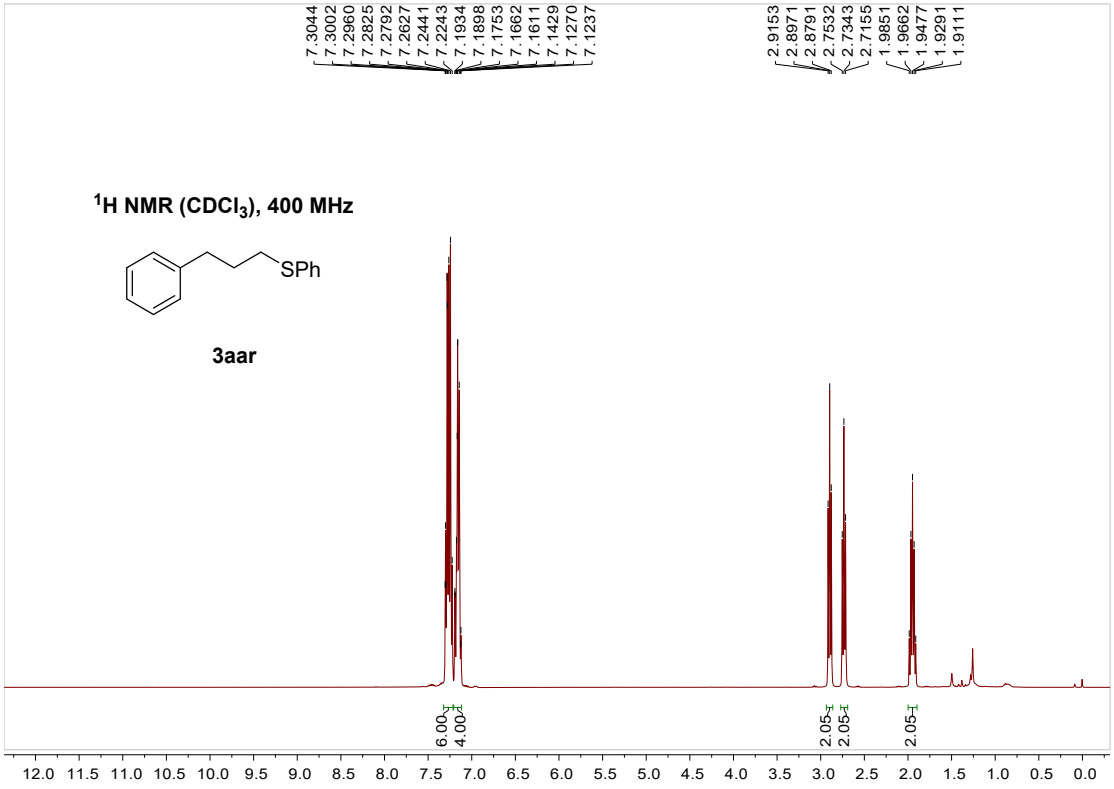

171.9404
166.8344
162.7810
149.3853
140.4739
131.5983
126.6106
124.8498
123.0240
122.4777
117.3782
114.0552
75.0394
67.5552
51.8215
39.3982
37.4750
37.4429
37.3096
33.6272
32.8145
32.7144
31.7810
31.6852
31.1102
29.2416
28.2630
28.0012
26.0925
24.8353
24.4718
24.3326
22.7708
22.6776
21.0379
20.6295
19.7962
19.7018
13.0370
12.1861
11.8662
13C NMR (CDCl3), 101 MHz
Me
Me
Me
O
O
Me
Me
Me
Me
O
S
O
MeOOC
3aao
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

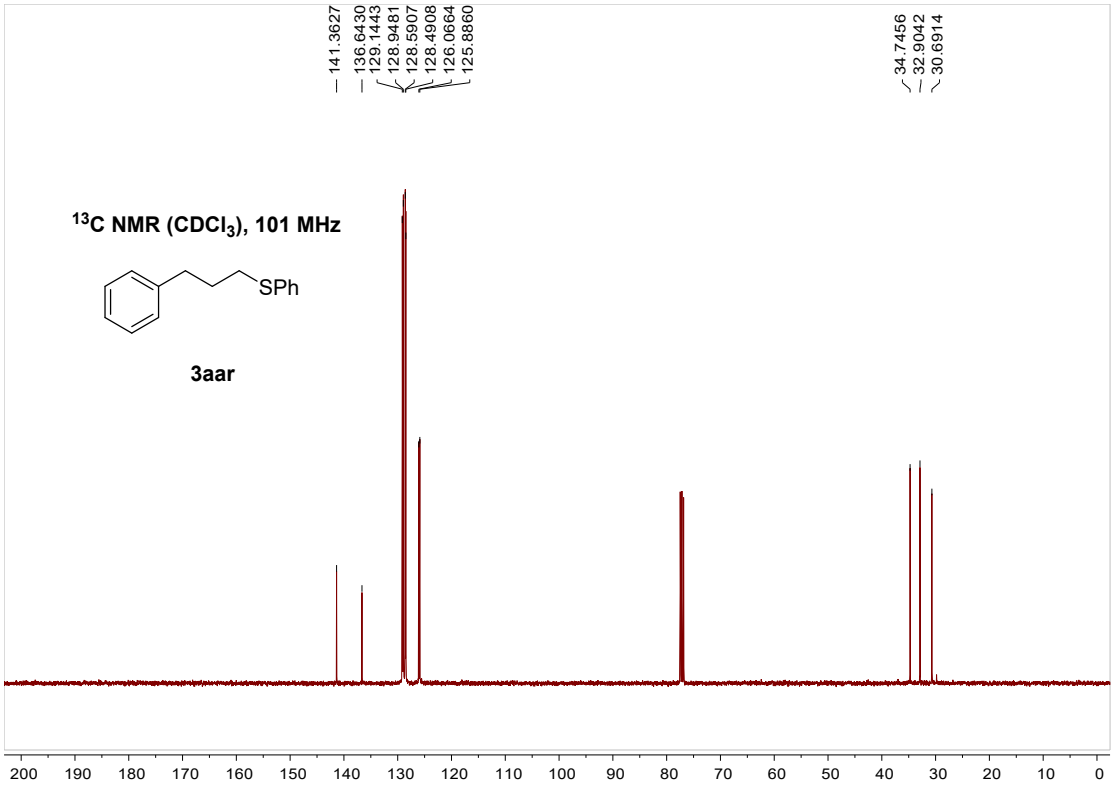

7.2711
7.2681
7.2640
7.2551
7.2505
7.2470
7.2358
7.2317
7.2266
7.2217
7.2113
7.2062
7.2006
7.1788
7.1753
7.1609
7.1521
7.1479
7.1421
7.1309
7.0676
7.0478
2.8703
2.8522
2.8340
2.7344
2.7158
2.6967
2.2865
1.9519
1.9362
1.9331
1.9304
1.9148
1.8999
1.8961
1.8780
1H NMR (CDCl3), 400 MHz
Me
S
3aap
4.00
3.00
1.96
2.04
2.03
2.99
2.03
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

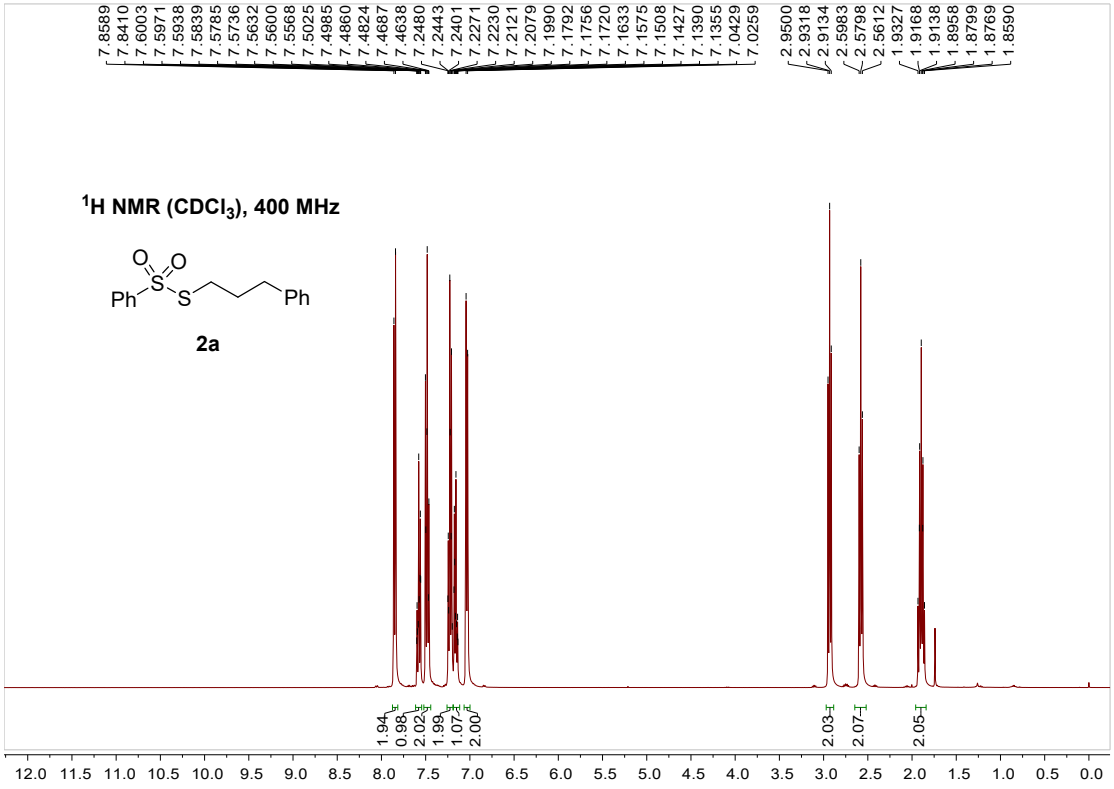

141.4667
136.0645
132.8038
130.1049
129.7343
128.5798
128.4620
126.0168
34.7324
33.7422
30.7996
21.0791
13C NMR (CDCl3), 101 MHz
Me
S
3aap
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

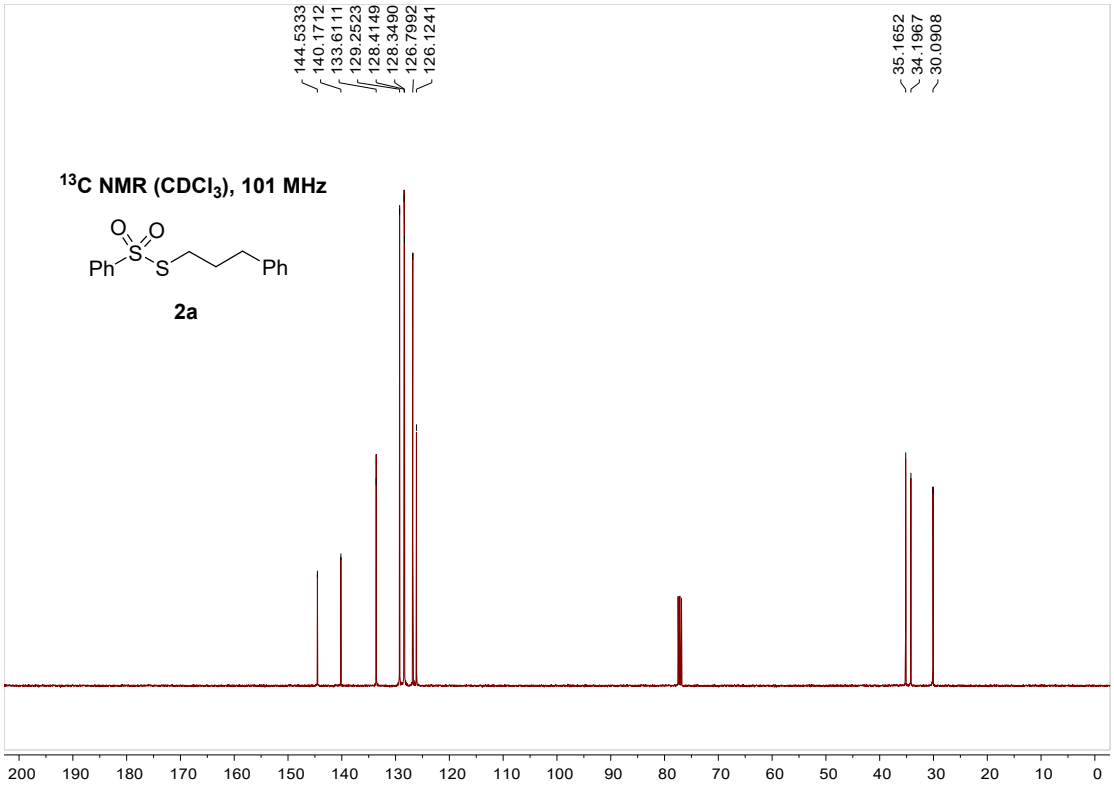

7.2901
7.2850
7.2767
7.2718
7.2682
7.2529
7.2257
7.2032
7.1971
7.1837
7.1573
7.1401
2.8832
2.8653
2.8468
2.7443
2.7257
2.7069
1.9655
1.9470
1.9285
1.9100
1.8917
^{1}H NMR ($CDCl_3$), 400 MHz
Cl
S
3aaq
2.00
4.97
2.16
2.10
2.12
2.13
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

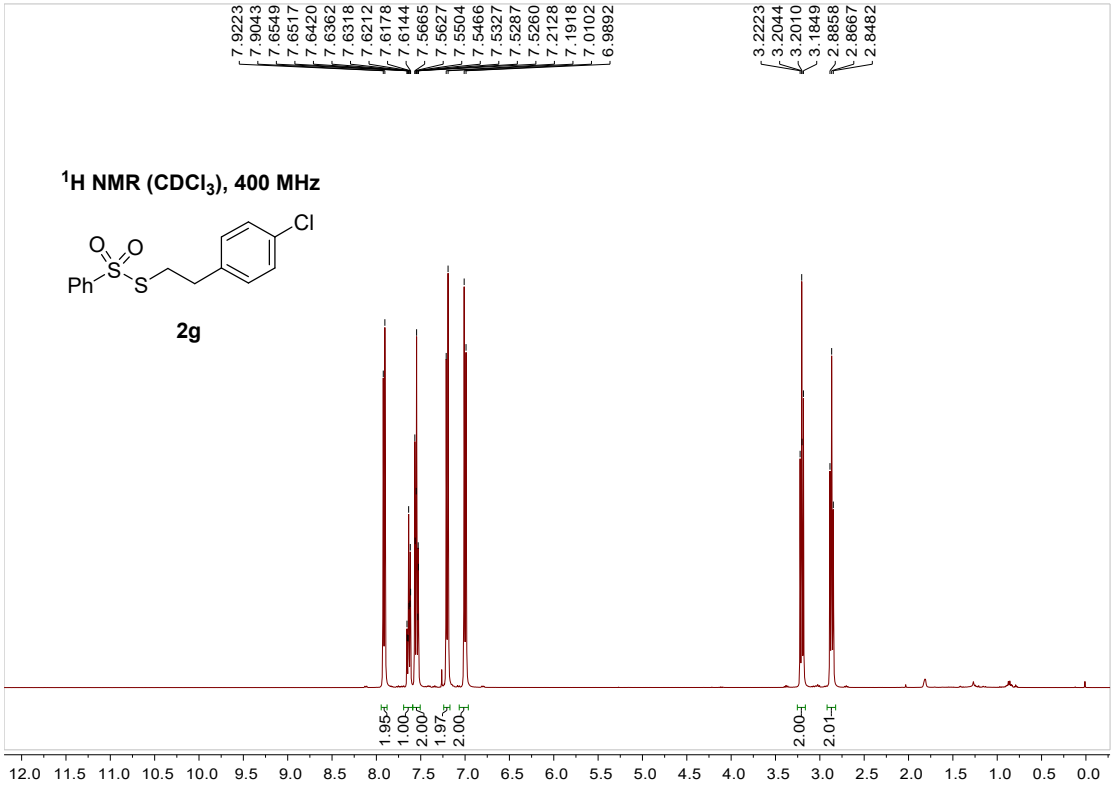

141.1517
135.1706
131.8103
130.4415
129.0320
128.5456
128.5081
126.1217
34.6621
33.1027
30.5525
^{13}C NMR ($CDCl_3$), 101 MHz
Cl
S
3aaq
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

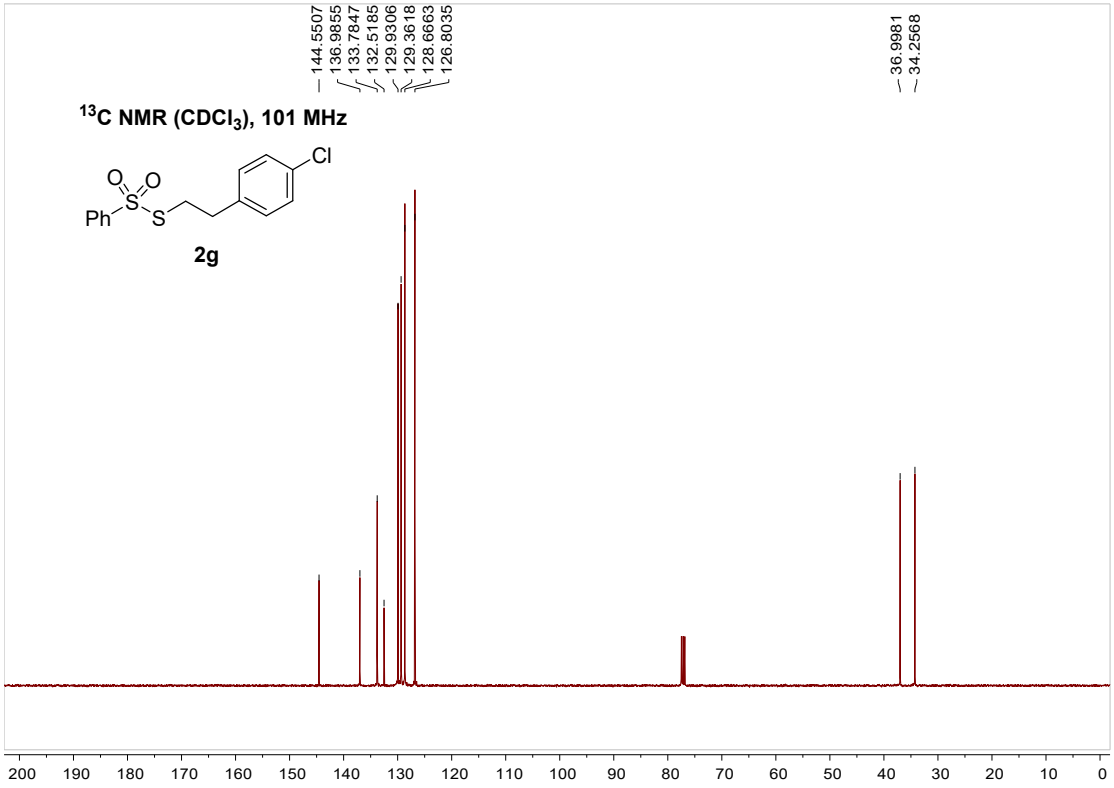

7.3044
7.3002
7.2960
7.2825
7.2792
7.2627
7.2441
7.2243
7.1934
7.1898
7.1753
7.1662
7.1611
7.1429
7.1270
7.1237
2.9153
2.8971
2.8791
2.7532
2.7343
2.7155
1.9851
1.9662
1.9477
1.9291
1.9111
1H NMR (CDCl3), 400 MHz
SPh
3aar
6.00
4.00
2.05
2.05
2.05
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

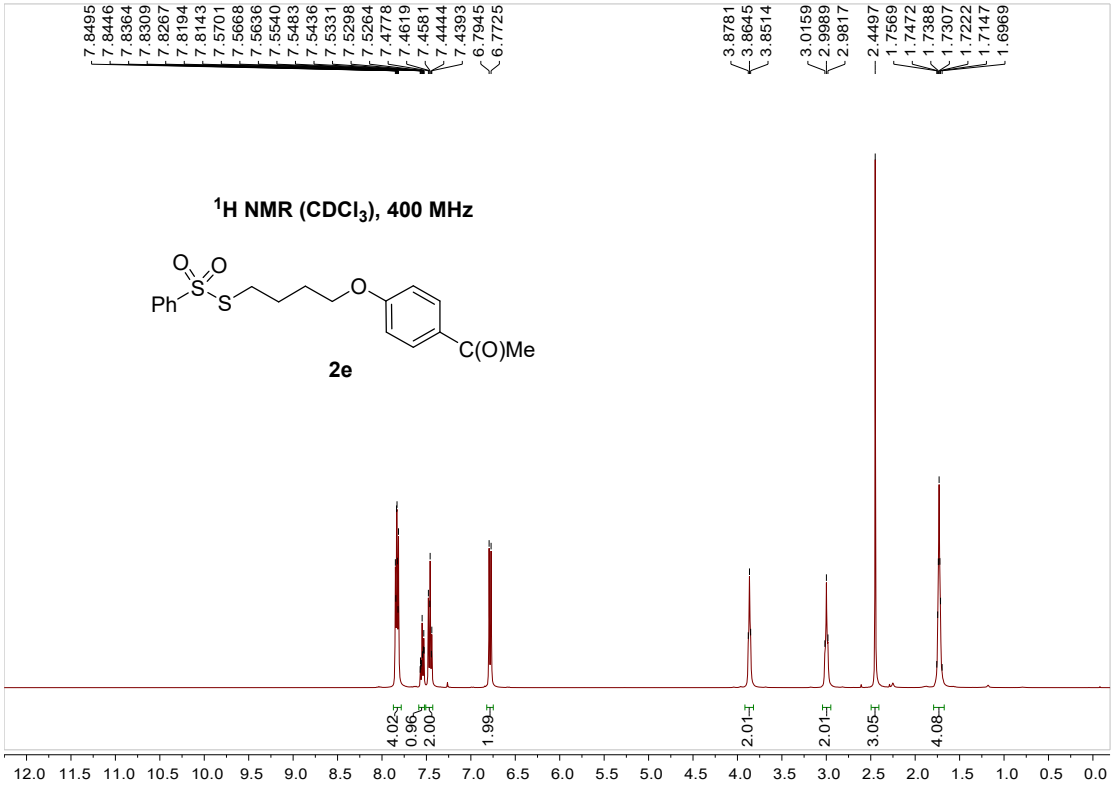

141.3627
136.6430
129.1443
128.9481
128.5907
128.4908
126.0664
125.8860
34.7456
32.9042
30.6914
13C NMR (CDCl3), 101 MHz
SPh
3aar
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

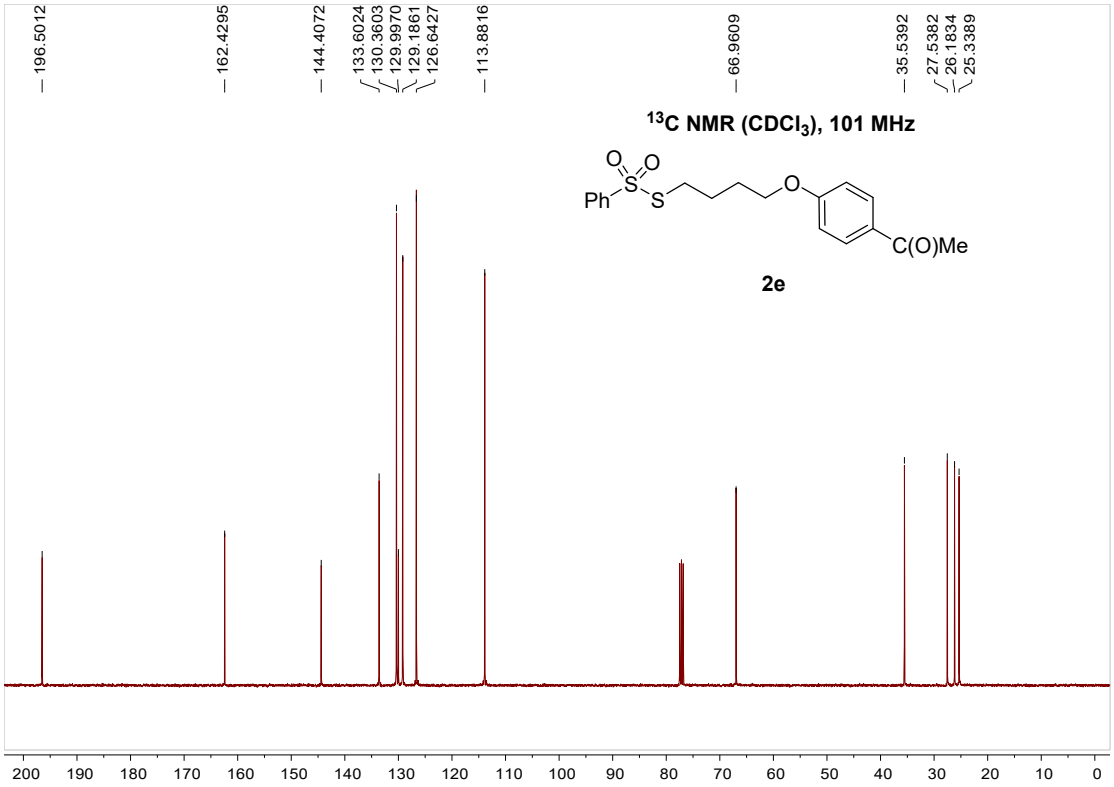

7.8589
7.8410
7.6003
7.5971
7.5938
7.5839
7.5785
7.5736
7.5632
7.5600
7.5568
7.5025
7.4985
7.4860
7.4824
7.4687
7.4638
7.2480
7.2443
7.2401
7.2271
7.2230
7.2121
7.2079
7.1990
7.1792
7.1756
7.1720
7.1633
7.1575
7.1508
7.1427
7.1390
7.1355
7.0429
7.0259
2.9500
2.9318
2.9134
2.5983
2.5798
2.5612
1.9327
1.9168
1.9138
1.8958
1.8799
1.8769
1.8590
1H NMR (CDCl3), 400 MHz
Ph
S
O
O
S
Ph
2a
1.94
0.98
2.02
1.99
1.07
2.00
2.03
2.07
2.05
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

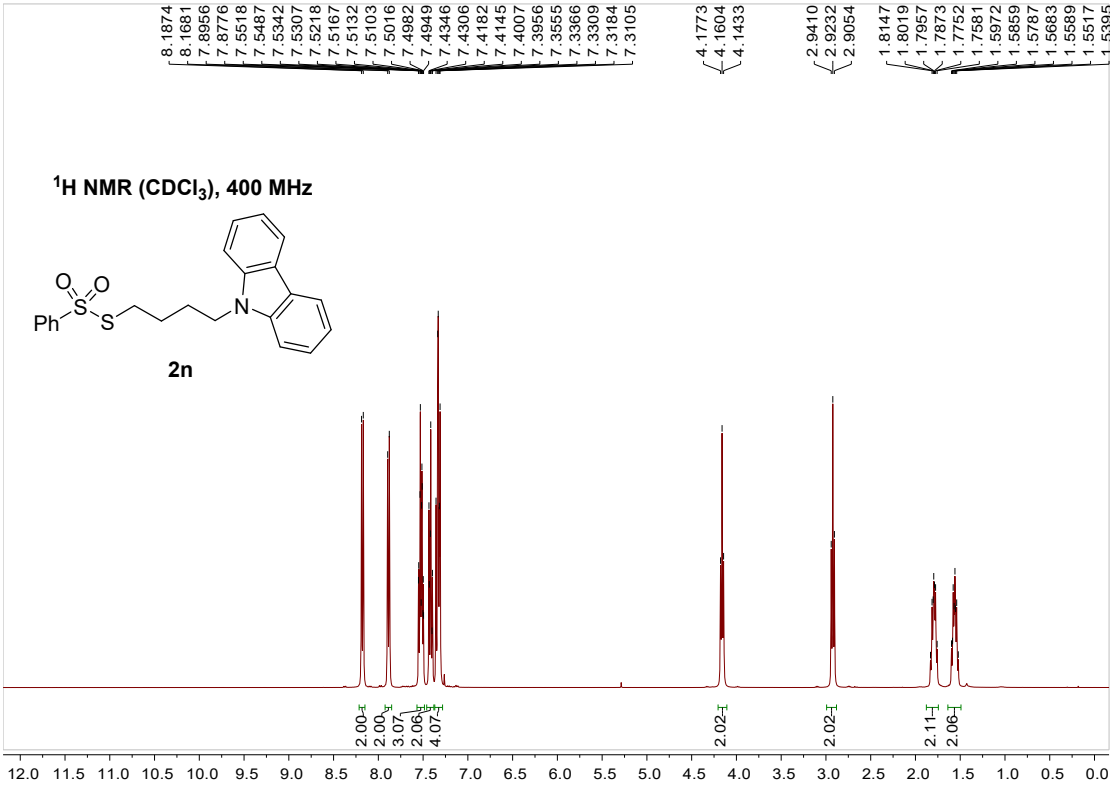

144.5333
140.1712
133.6111
129.2523
128.4149
128.3490
126.7992
126.1241
35.1652
34.1967
30.0908
13C NMR (CDCl3), 101 MHz
Ph
S
O
O
S
Ph
2a
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

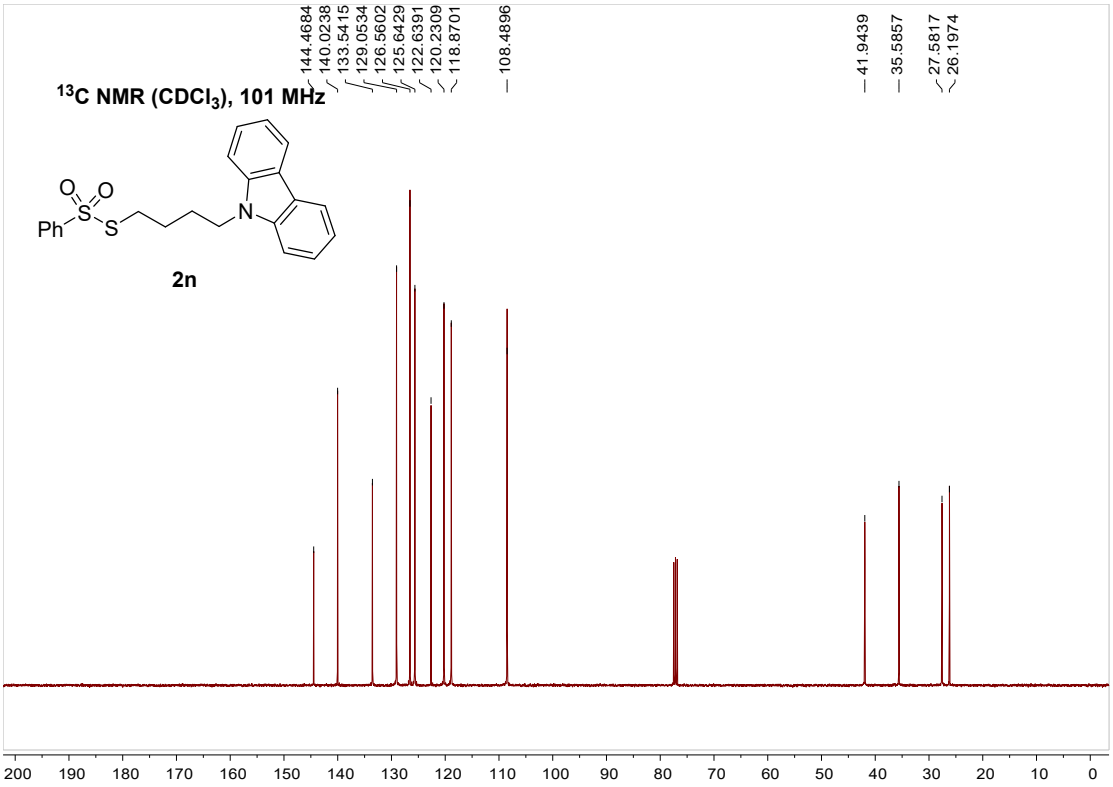

7.9223
7.9043
7.6549
7.6517
7.6420
7.6362
7.6318
7.6212
7.6178
7.6144
7.5665
7.5627
7.5504
7.5466
7.5327
7.5287
7.5260
7.2128
7.1918
7.0102
6.9892
3.2223
3.2044
3.2010
3.1849
2.8858
2.8667
2.8482
1H NMR (CDCl3), 400 MHz
Cl
O
O
S
Ph
S
2g
1.95
1.00
2.00
1.97
2.00
2.00
2.01
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

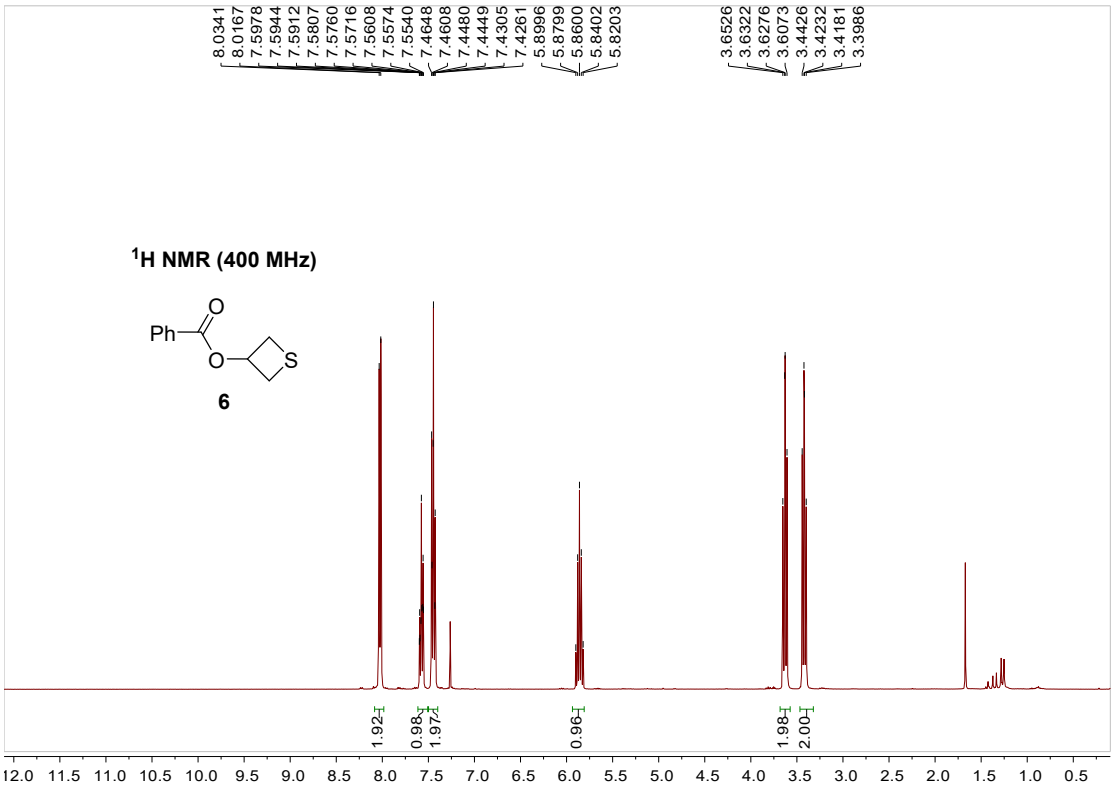

144.5507
136.9855
133.7847
132.5185
129.9306
129.3618
128.6663
126.8035
36.9981
34.2568
13C NMR (CDCl3), 101 MHz
Cl
O
O
S
Ph
S
2g
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

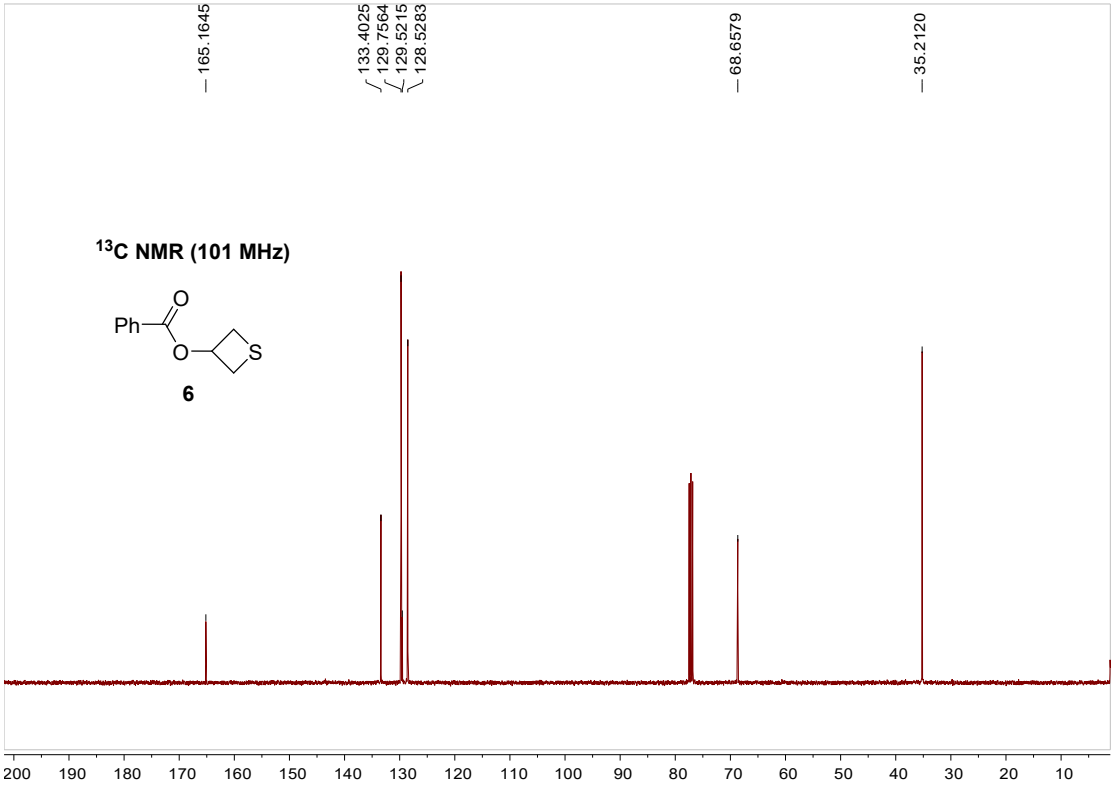

7.8495
7.8446
7.8364
7.8309
7.8267
7.8194
7.8143
7.5701
7.5668
7.5636
7.5540
7.5483
7.5436
7.5331
7.5298
7.5264
7.4778
7.4619
7.4581
7.4444
7.4393
6.7945
6.7725
3.8781
3.8645
3.8514
3.0159
2.9989
2.9817
2.4497
1.7569
1.7472
1.7388
1.7307
1.7222
1.7147
1.6969
^{1}H NMR (CDCl$_3$), 400 MHz
Ph
S
O
O
O
C(O)Me
2e
4.02
0.96
2.00
1.99
2.01
2.01
3.05
4.08
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

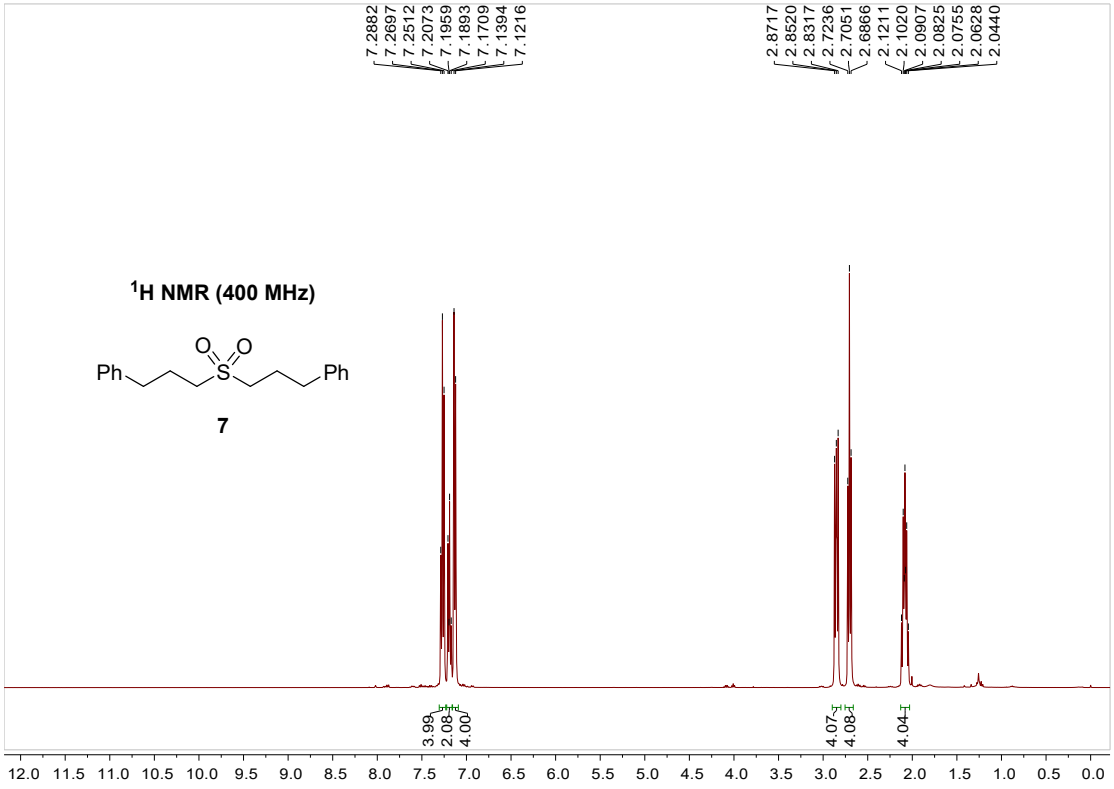

196.5012
162.4295
144.4072
133.6024
130.3603
129.9970
129.1861
126.6427
113.8816
66.9609
35.5392
27.5382
26.1834
25.3389
^{13}C NMR (CDCl$_3$), 101 MHz
Ph
S
O
O
O
C(O)Me
2e
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

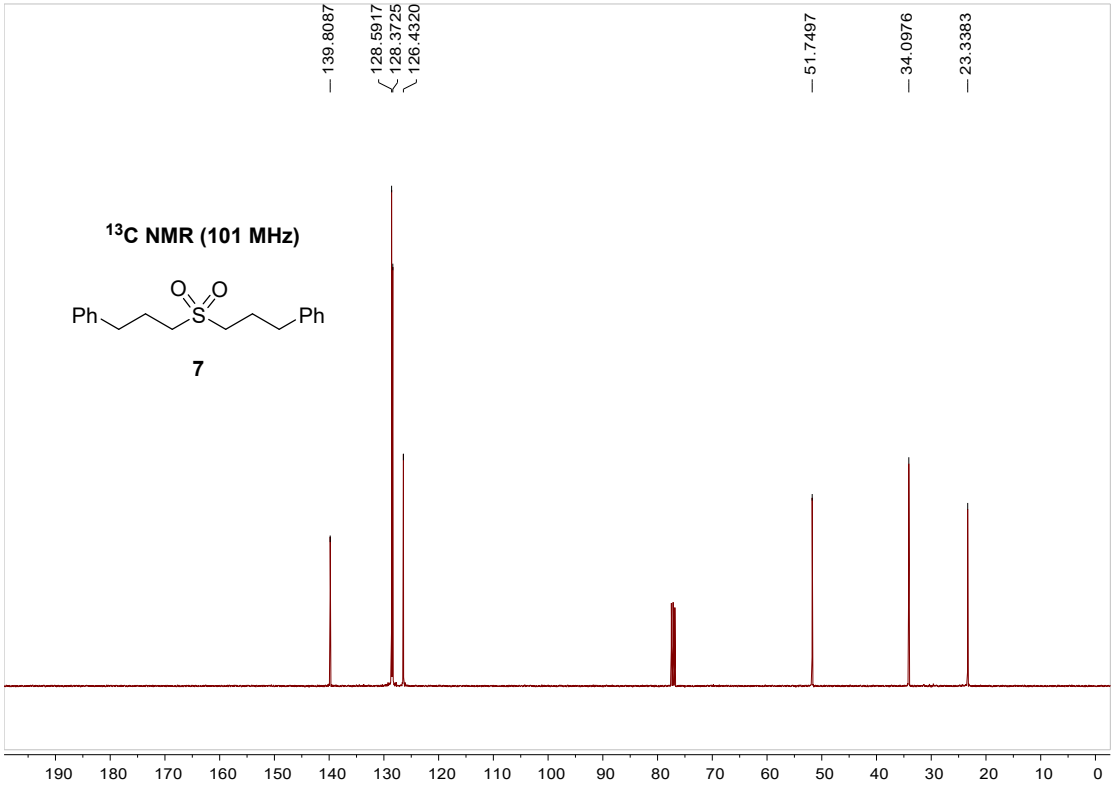

8.1874
8.1681
7.8956
7.8776
7.5518
7.5487
7.5342
7.5307
7.5218
7.5167
7.5132
7.5103
7.5016
7.4982
7.4949
7.4346
7.4306
7.4182
7.4145
7.4007
7.3956
7.3555
7.3366
7.3309
7.3184
7.3105
4.1773
4.1604
4.1433
2.9410
2.9232
2.9054
1.8147
1.8019
1.7957
1.7873
1.7752
1.7581
1.5972
1.5859
1.5787
1.5683
1.5589
1.5517
1.5395
1H NMR (CDCl3), 400 MHz
Ph
S
O
O
S
N
2n
2.00
2.00
3.07
2.06
4.07
2.02
2.02
2.11
2.06
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

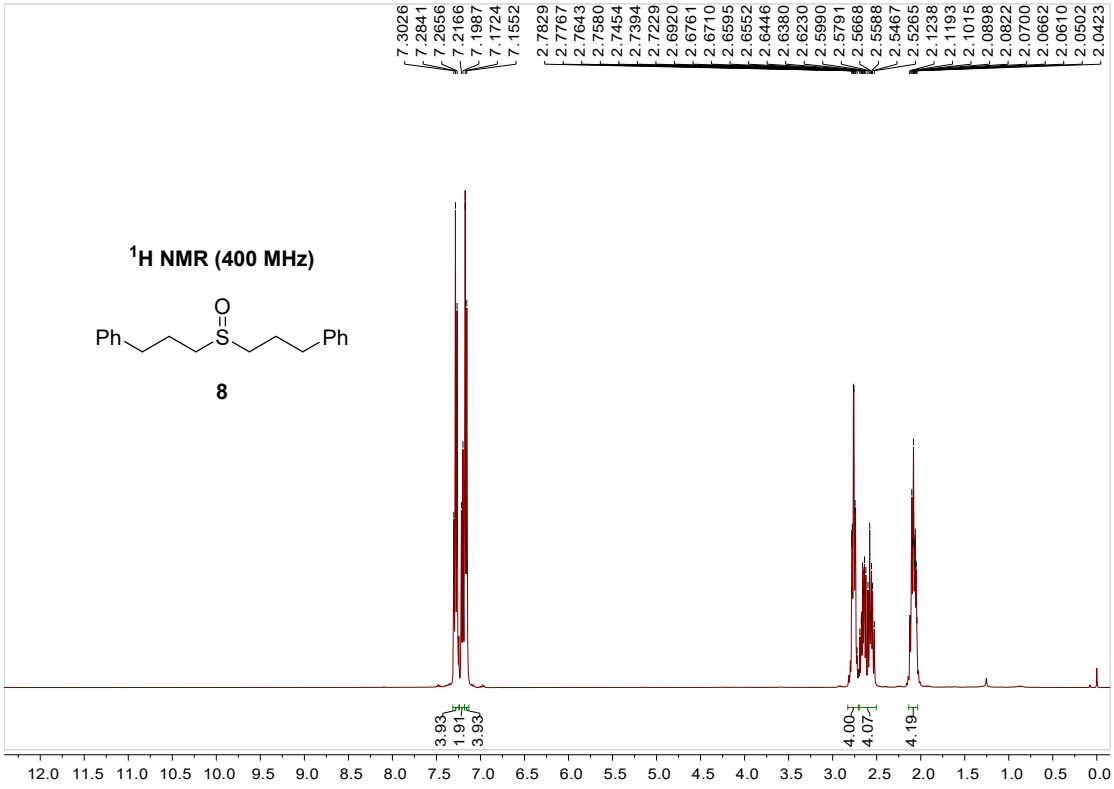

144.4684
140.0238
133.5415
129.0534
126.5602
125.6429
122.6391
120.2309
118.8701
108.4896
41.9439
35.5857
27.5817
26.1974
13C NMR (CDCl3), 101 MHz
Ph
S
O
O
S
N
2n
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

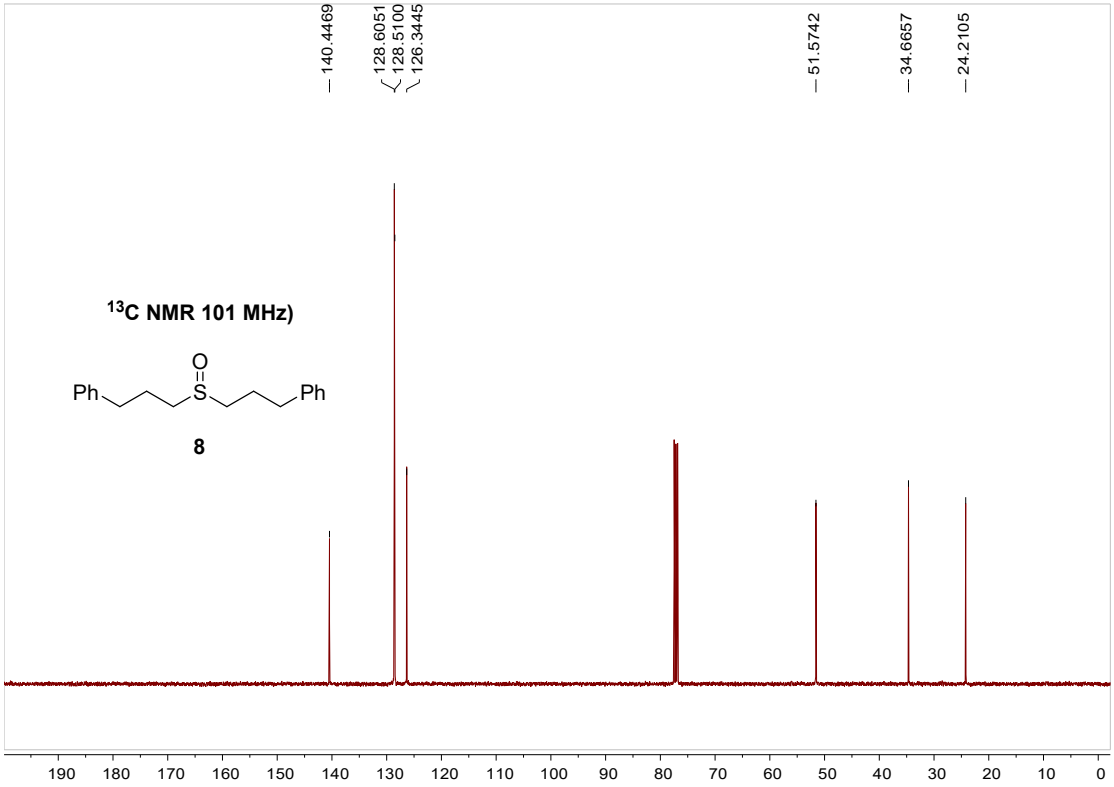

8.0341
8.0167
7.5978
7.5944
7.5912
7.5807
7.5760
7.5716
7.5608
7.5574
7.5540
7.4648
7.4608
7.4480
7.4449
7.4305
7.4261
5.8996
5.8799
5.8600
5.8402
5.8203
3.6526
3.6322
3.6276
3.6073
3.4426
3.4232
3.4181
3.3986
1H NMR (400 MHz)
Ph
O
O
S
6
1.92
0.98
1.97
0.96
1.98
2.00
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5

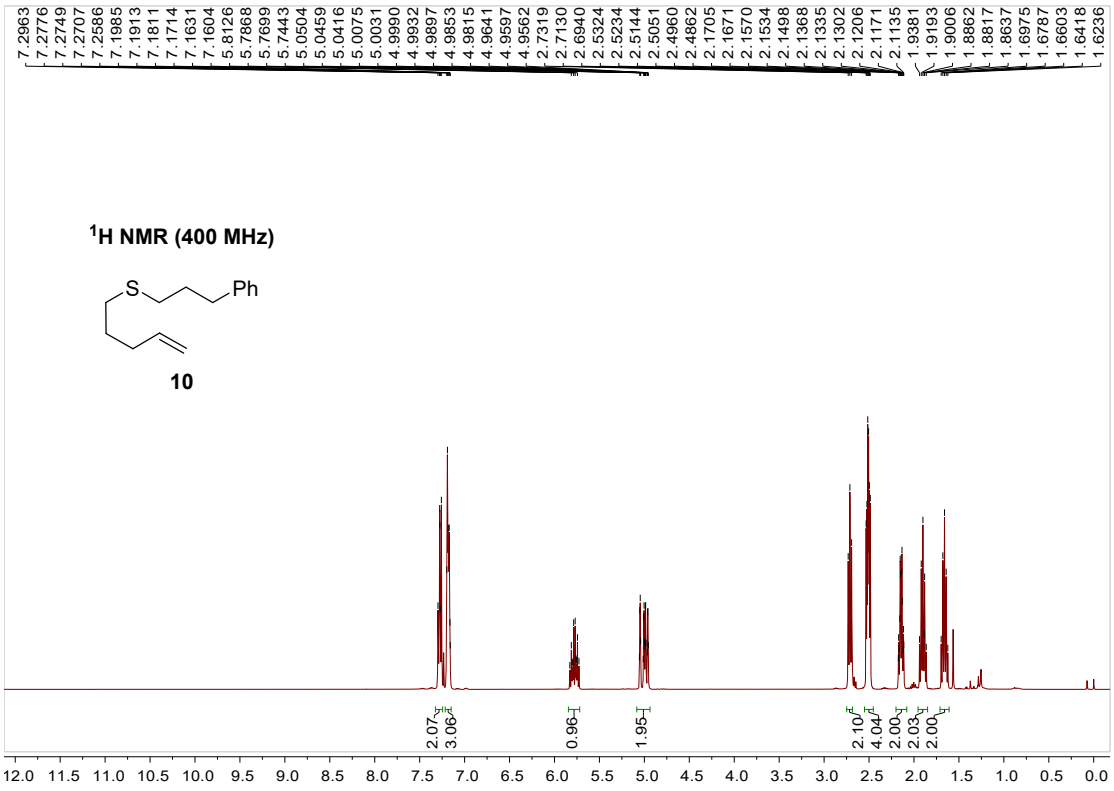

165.1645
133.4025
129.7564
129.5215
128.5283
68.6579
35.2120
13C NMR (101 MHz)
Ph
O
O
S
6
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10

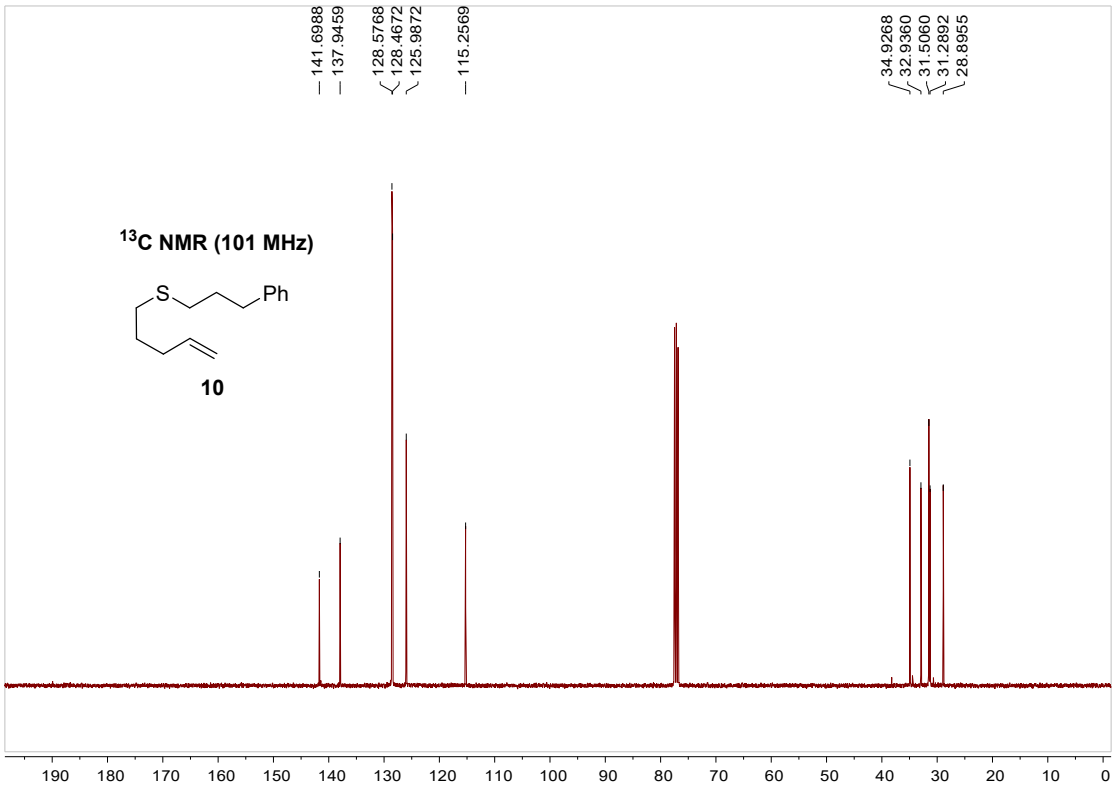

7.2882
7.2697
7.2512
7.2073
7.1959
7.1893
7.1709
7.1394
7.1216
2.8717
2.8520
2.8317
2.7236
2.7051
2.6866
2.1211
2.1020
2.0907
2.0825
2.0755
2.0628
2.0440
1H NMR (400 MHz)
O
O
S
Ph
Ph
7
3.99
2.08
4.00
4.07
4.08
4.04
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

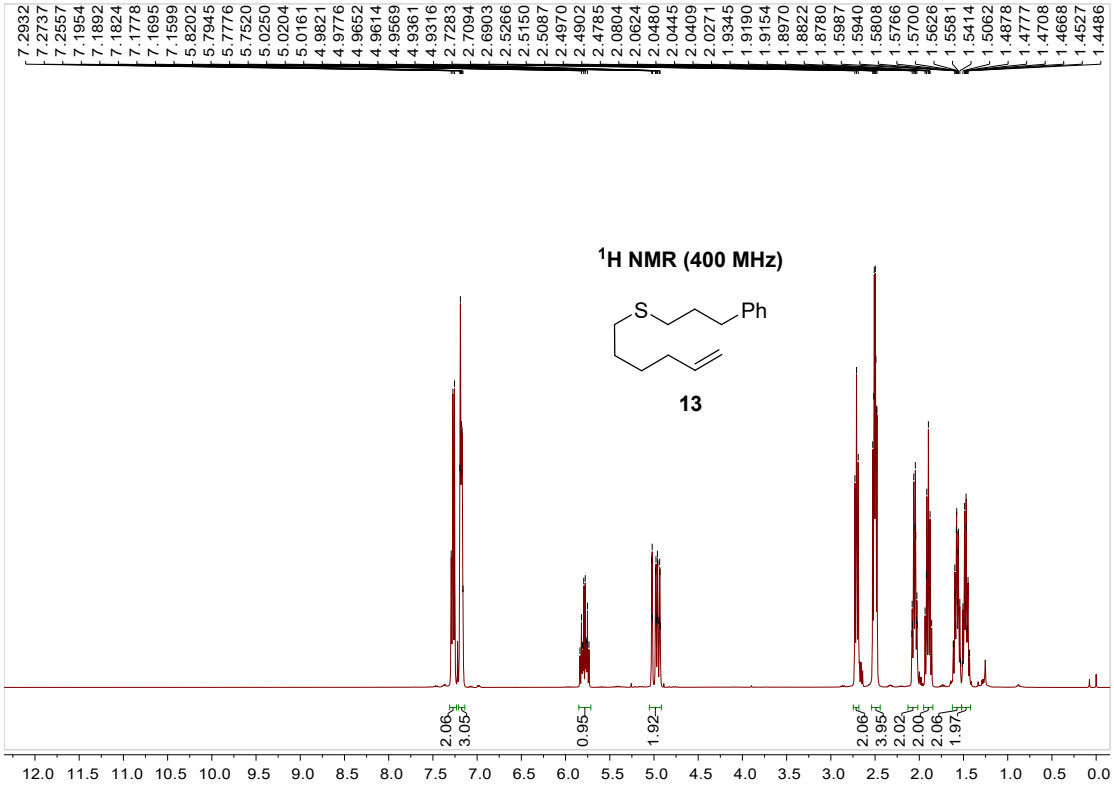

139.8087
128.5917
128.3725
126.4320
51.7497
34.0976
23.3383
13C NMR (101 MHz)
O
O
S
Ph
Ph
7
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

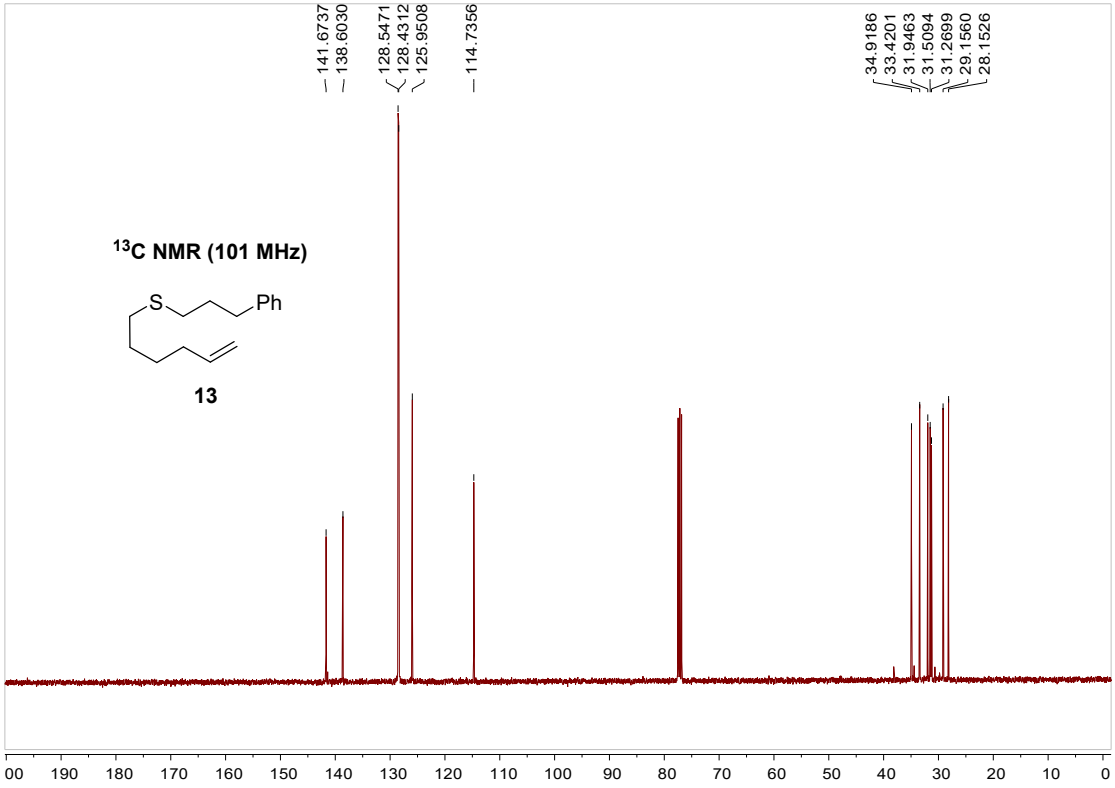

7.3026
7.2841
7.2656
7.2166
7.1987
7.1724
7.1552
2.7829
2.7767
2.7643
2.7580
2.7454
2.7394
2.7229
2.6920
2.6761
2.6710
2.6595
2.6552
2.6446
2.6380
2.6230
2.5990
2.5791
2.5668
2.5588
2.5467
2.5265
2.1238
2.1193
2.1015
2.0898
2.0822
2.0700
2.0662
2.0610
2.0502
2.0423
1H NMR (400 MHz)
O
Ph
S
Ph
8
3.93
1.91
3.93
4.00
4.07
4.19
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

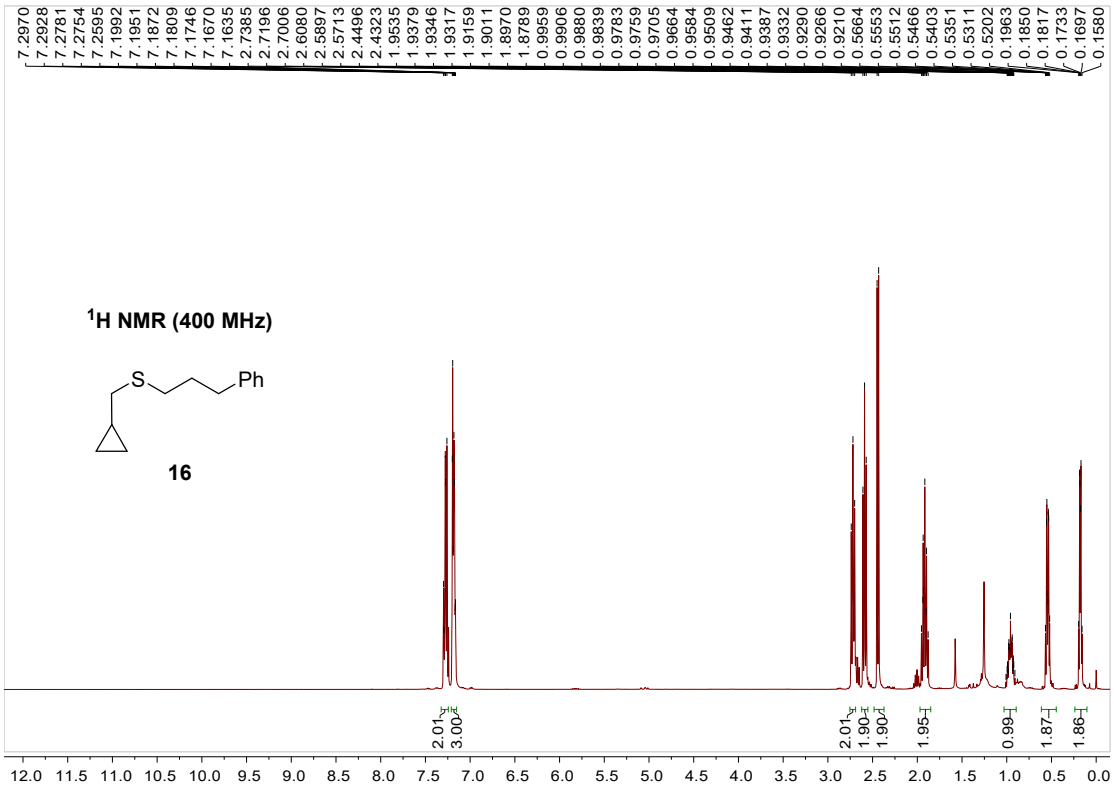

140.4469
128.6051
128.5100
126.3445
51.5742
34.6657
24.2105
13C NMR 101 MHz)
O
Ph
S
Ph
8
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

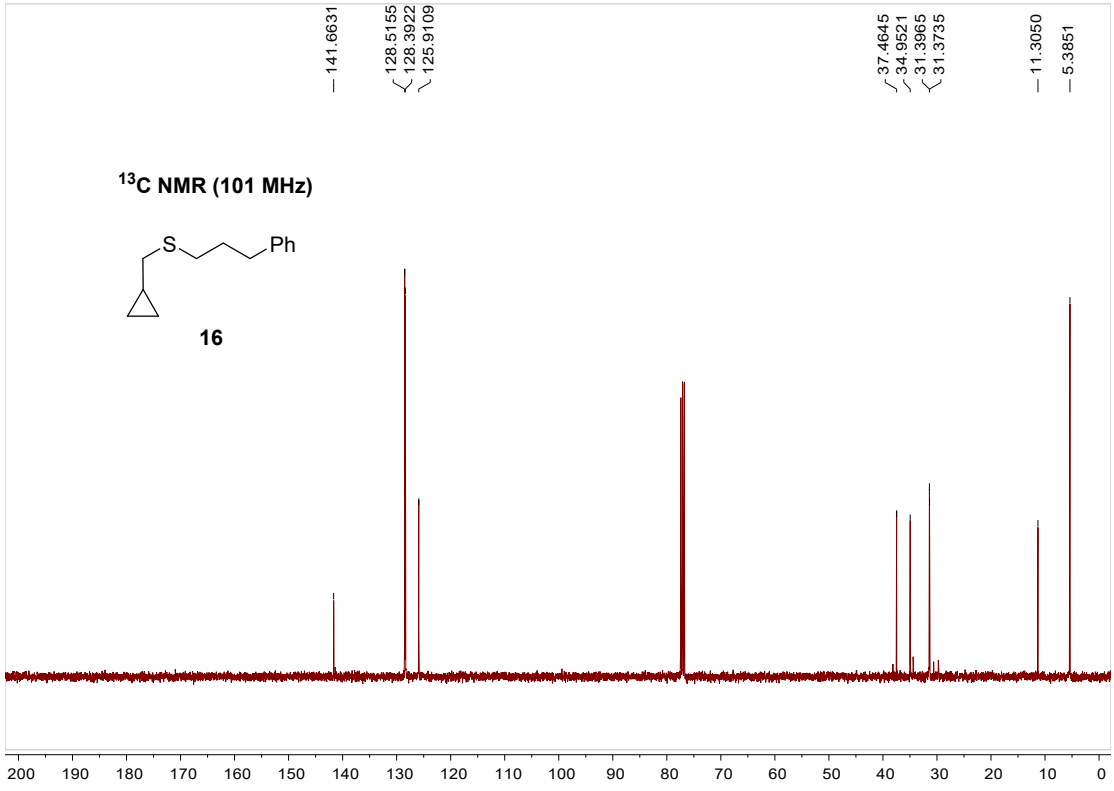

7.2963
7.2776
7.2749
7.2707
7.2586
7.1985
7.1913
7.1811
7.1714
7.1631
7.1604
5.8126
5.7868
5.7699
5.7443
5.0504
5.0459
5.0416
5.0075
5.0031
4.9990
4.9932
4.9897
4.9853
4.9815
4.9641
4.9597
4.9562
2.7319
2.7130
2.6940
2.5324
2.5234
2.5144
2.5051
2.4960
2.4862
2.1705
2.1671
2.1570
2.1534
2.1498
2.1368
2.1335
2.1302
2.1206
2.1171
2.1135
1.9381
1.9193
1.9006
1.8862
1.8817
1.8637
1.6975
1.6787
1.6603
1.6418
1.6236
1H NMR (400 MHz)
S
Ph
10
2.07
3.06
0.96
1.95
2.10
4.04
2.00
2.03
2.00
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

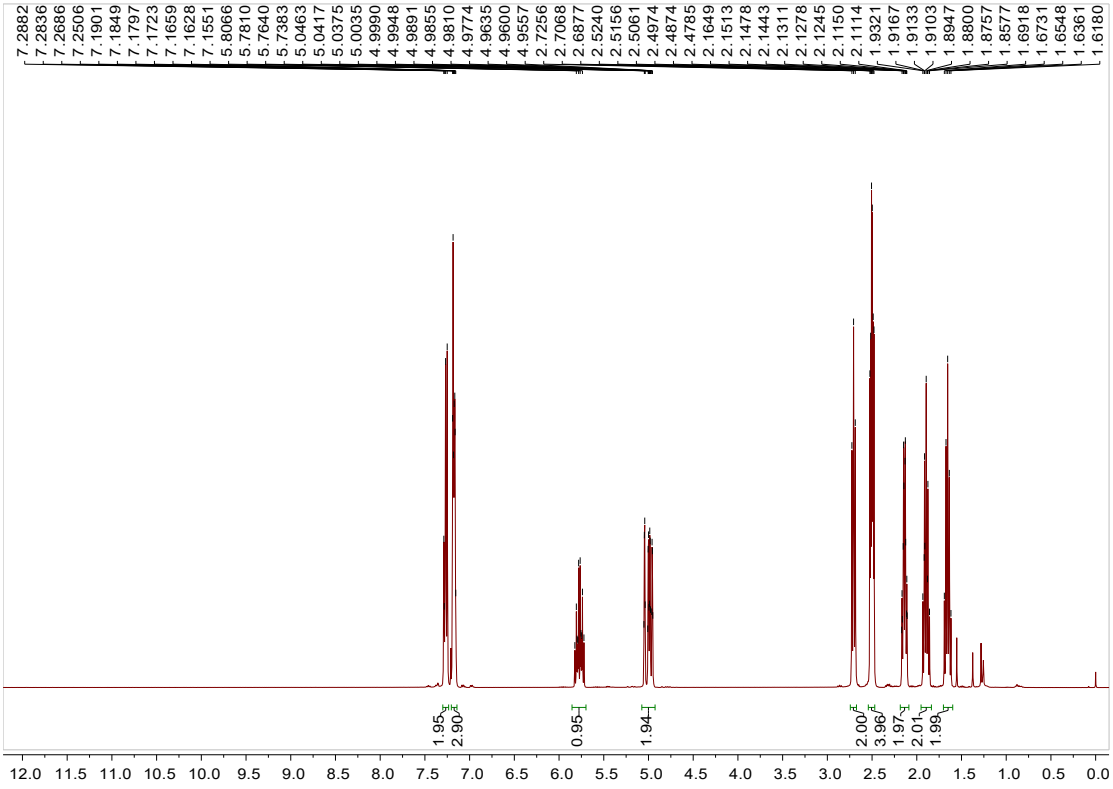

141.6988
137.9459
128.5768
128.4672
125.9872
115.2569
34.9268
32.9360
31.5060
31.2892
28.8955
13C NMR (101 MHz)
S
Ph
10
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

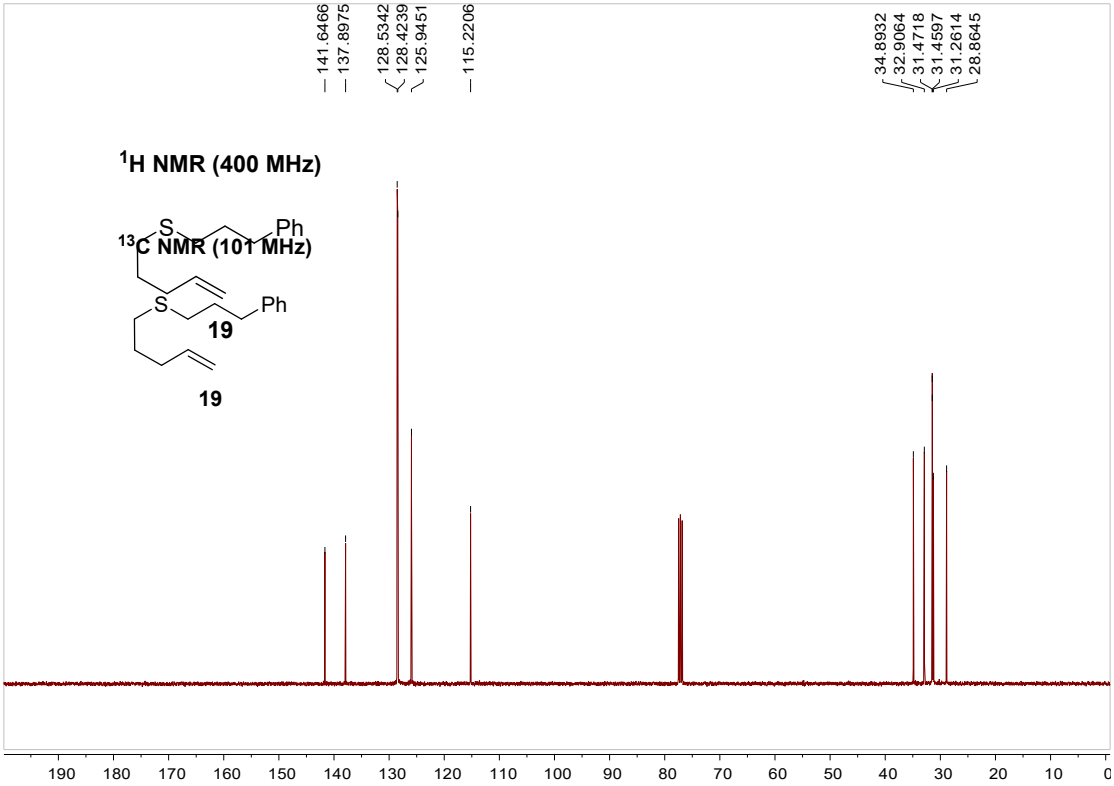

7.2932 7.2737 7.2557 7.1954 7.1892 7.1824 7.1778 7.1695 7.1599 5.8202 5.7945 5.7776 5.7520 5.0250 5.0204 5.0161 4.9821 4.9776 4.9652 4.9614 4.9569 4.9361 4.9316 2.7283 2.7094 2.6903 2.5266 2.5150 2.5087 2.4970 2.4902 2.4785 2.0804 2.0624 2.0480 2.0445 2.0409 2.0271 1.9345 1.9190 1.9154 1.8970 1.8822 1.8780 1.5987 1.5940 1.5808 1.5766 1.5700 1.5626 1.5581 1.5414 1.5062 1.4878 1.4777 1.4708 1.4668 1.4527 1.4486
^{1}H NMR (400 MHz)
S
Ph
13
2.06 3.05 0.95 1.92 2.06 3.95 2.02 2.00 2.06 1.97
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0


141.6737
138.6030
128.5471
128.4312
125.9508
114.7356
34.9186
33.4201
31.9463
31.5094
31.2699
29.1560
28.1526
^{13}C NMR (101 MHz)
S
Ph
13
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0


7.2970
7.2928
7.2781
7.2754
7.2595
7.1992
7.1951
7.1872
7.1809
7.1746
7.1670
7.1635
2.7385
2.7196
2.7006
2.6080
2.5897
2.5713
2.4496
2.4323
1.9535
1.9379
1.9346
1.9317
1.9159
1.9011
1.8970
1.8789
0.9959
0.9906
0.9880
0.9839
0.9783
0.9759
0.9705
0.9664
0.9584
0.9509
0.9462
0.9411
0.9387
0.9332
0.9290
0.9266
0.9210
0.5664
0.5553
0.5512
0.5466
0.5403
0.5351
0.5311
0.5202
0.1963
0.1850
0.1817
0.1733
0.1697
0.1580
1H NMR (400 MHz)
S
Ph
16
2.01
3.00
2.01
1.90
1.90
1.95
0.99
1.87
1.86
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0


141.6631
128.5155
128.3922
125.9109
37.4645
34.9521
31.3965
31.3735
11.3050
5.3851
13C NMR (101 MHz)
S
Ph
16
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0



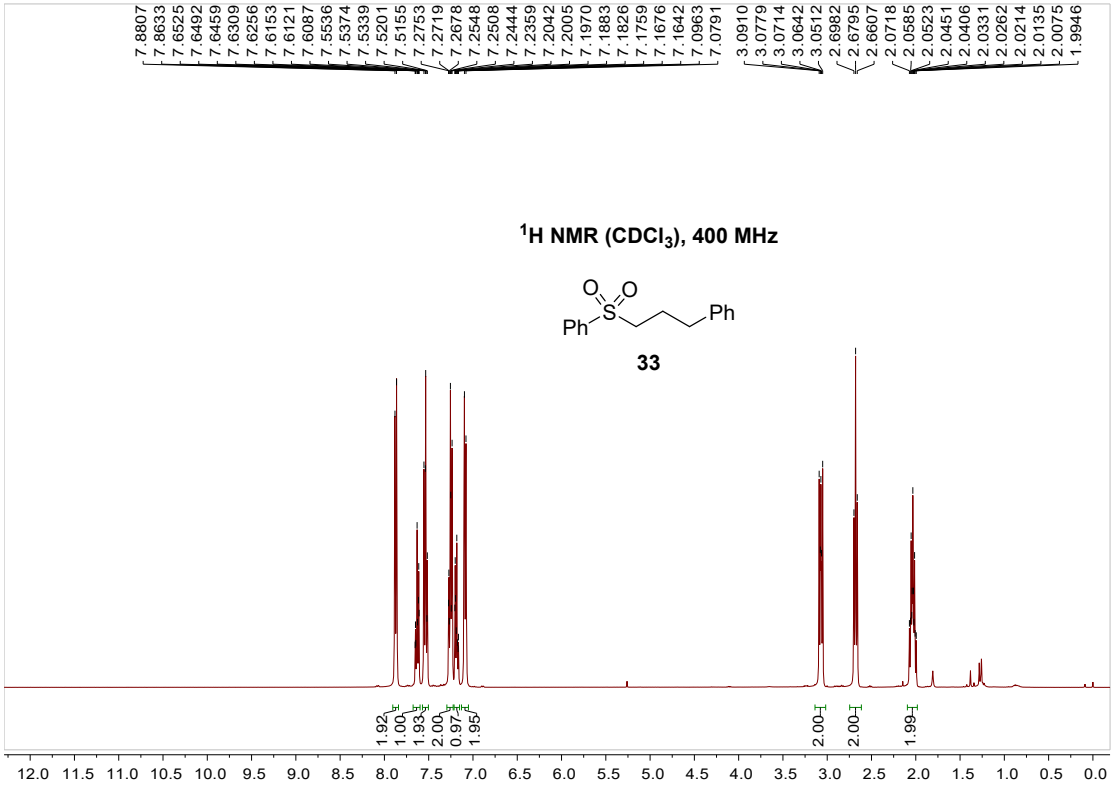


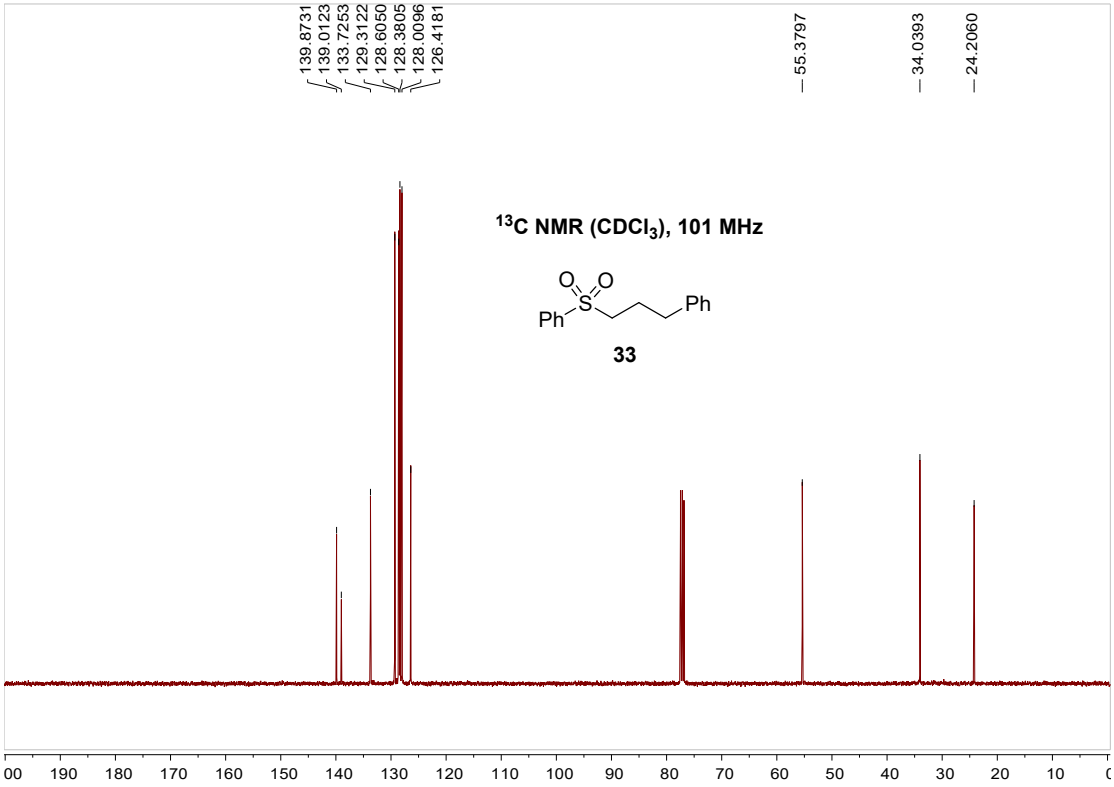
^{1}H NMR (400 MHz)

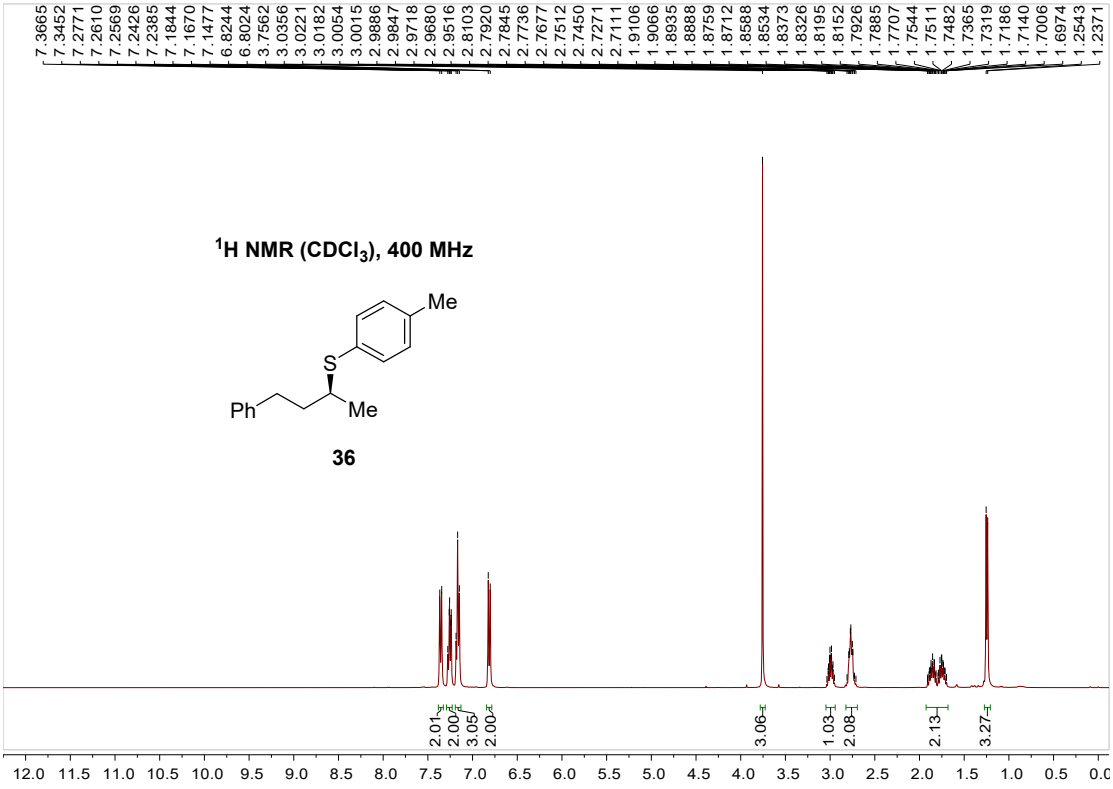
^{13}C NMR (101 MHz)

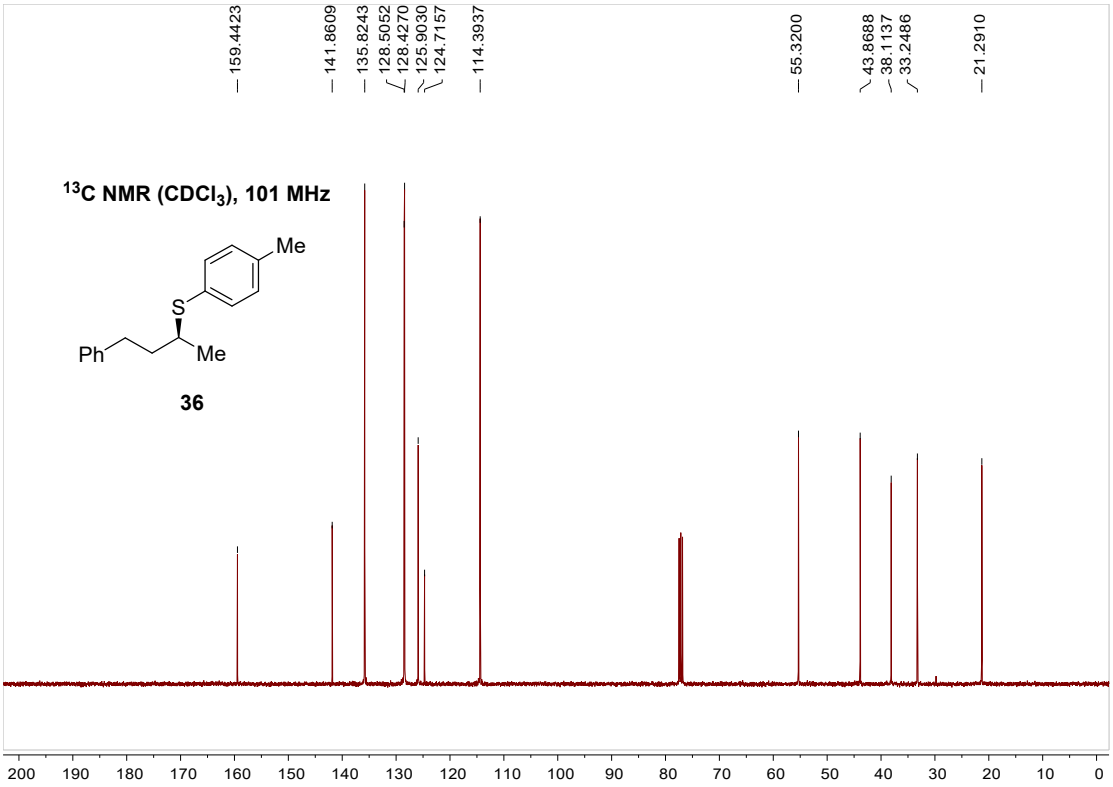
19

19


7.8807
7.8633
7.6525
7.6492
7.6459
7.6309
7.6256
7.6153
7.6121
7.6087
7.5536
7.5374
7.5339
7.5201
7.5155
7.2753
7.2719
7.2678
7.2548
7.2508
7.2444
7.2359
7.2042
7.2005
7.1970
7.1883
7.1826
7.1759
7.1676
7.1642
7.0963
7.0791
3.0910
3.0779
3.0714
3.0642
3.0512
2.6982
2.6795
2.6607
2.0718
2.0585
2.0523
2.0451
2.0406
2.0331
2.0262
2.0214
2.0135
2.0075
1.9946
1H NMR (CDCl3), 400 MHz
O
O
S
Ph
Ph
33
1.92
1.00
1.93
2.00
0.97
1.95
2.00
2.00
1.99
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0


139.8731
139.0123
133.7253
129.3122
128.6050
128.3805
128.0096
126.4181
55.3797
34.0393
24.2060
13C NMR (CDCl3), 101 MHz
O
O
S
Ph
Ph
33
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10


7.3665
7.3452
7.2771
7.2610
7.2569
7.2426
7.2385
7.1844
7.1670
7.1477
6.8244
6.8024
3.7562
3.0356
3.0221
3.0182
3.0054
3.0015
2.9886
2.9847
2.9718
2.9680
2.9516
2.8103
2.7920
2.7845
2.7736
2.7677
2.7512
2.7450
2.7271
2.7111
1.9106
1.9066
1.8935
1.8888
1.8759
1.8712
1.8588
1.8534
1.8373
1.8326
1.8195
1.8152
1.7926
1.7885
1.7707
1.7544
1.7511
1.7482
1.7365
1.7319
1.7186
1.7140
1.7006
1.6974
1.2543
1.2371
^{1}H NMR ($CDCl_3$), 400 MHz
Me
S
Ph
Me
36
2.01
2.00
3.05
2.00
3.06
1.03
2.08
2.13
3.27
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0


159.4423
141.8609
135.8243
128.5052
128.4270
125.9030
124.7157
114.3937
55.3200
43.8688
38.1137
33.2486
21.2910
^{13}C NMR ($CDCl_3$), 101 MHz
Me
S
Ph
Me
36
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0