

The Pummerer Synthesis of Chromanes Reveals a Competition Between Cyclization and Unprecedented Reductive Chlorination

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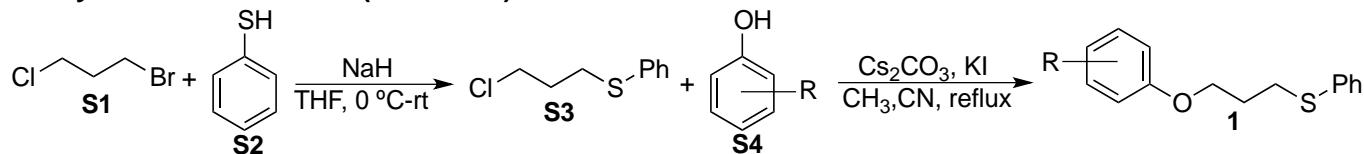
1. Experimental Procedures

1.1 General information

All reactions were performed under an atmosphere of argon. All solvents were distilled from appropriate drying agents prior to use. All reagents were used as received from commercial suppliers. Reactions progress was monitored by thin layer chromatography (TLC) performed on aluminum plates coated with silica gel F₂₅₄ with 0.2 mm thickness. Flash column chromatography was performed using silica gel 60 (230-400 mesh). Neat infrared spectra were recorded using a THERMO NICOLET-NEXUS (FT-IR) with PIKE MIRacle ATR cell. Wavenumbers (vmax) are reported in cm⁻¹. High Resolution Mass spectrometry was recorded using an Agilent 5973 (70 eV) spectrometer, using electrospray ionization (ESI). All ¹H NMR and C¹³ NMR spectra were recorded using a BRUKER Avance III HD Ascend 400 spectrometer. Chemical shifts are given in parts per million (ppm, δ), referenced to the TMS (¹H and ¹³C) and trifluoracetic acid (¹⁹F), solvent peak of CDCl₃ defined at δ = 7.26 ppm (¹H NMR) and δ = 77.16 (¹³C NMR). Coupling constants are quoted in Hz (J). ¹H NMR splitting patterns were designated as singlet (s), doublet (d), triplet (t), quartet (q) and multiplet (m). Splitting patterns that could not be interpreted or easily visualized were designated as multiplet (m) or broad (br).

2. Preparation of Starting Materials

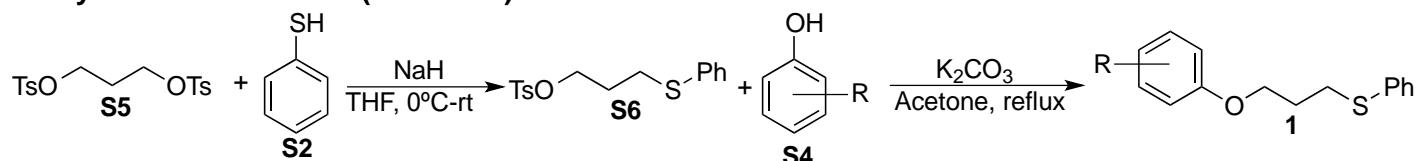
2.1 Synthesis of Sulfides (Method A)



To a suspension of sodium hydride (60% w.t. in mineral oil) (26.5 mmol, 1.06 g) in THF (32 mL) at 0°C was added drop-wise thiophenol **S2** (26.5 mmol, 2.8 mL). The reaction mixture was vigorously stirred at the same temperature for 1 hour, then, 1-bromo-3-chloropropane **S1** (31.8 mmol, 3.1mL) was added. The reaction mixture was stirred at room temperature by 24 h. When the reaction was finished, water was added to eliminate the sodium hydride excess. The aqueous layer was extracted with AcOEt (3 x 20 mL). The organic layer was dried over Na₂SO₄, filtered and the solvent was evaporated *in vacuo*. The crude mixture was purified using flash chromatography with cyclohexane as the eluent to afford the pure product **S3**. (25 mmol, 4.66 g, 95%)

To a solution of potassium iodide (0.3 equiv.) in acetonitrile was added (3-chloropropyl)(phenyl)sulfide **S3** (1 equiv.), the reaction mixture was stirred a room temperature by 20 min, and then cesium carbonate (1.8 equiv.) and the corresponding phenol **S4** (1.2 equiv.) were added; the reaction mixture was heated under reflux by 24 to 48 h (following by TLC), when the starting materials were completely consumed the reaction was quenched with water. The aqueous layer was extracted with AcOEt (3 x 20 mL). The organic phases were combined and dried over Na₂SO₄ and the solvent was evaporated *in vacuo*. The crude mixture was purified using flash chromatography with CH_x:DCM (8:2) as the eluent to afford the pure product **1**. With yields between 53 and 97 %

2.2 Synthesis of Sulfides (Method B)

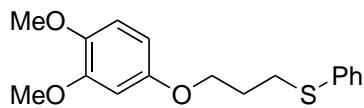


To a suspension of NaH (60% w.t. in mineral oil) (4.7 mmol, 188 mg) in dried THF (30 mL), thiophenol **S2** (4.7 mmol, 0.49 mL) was slowly added at 0°C. The mixture was stirred at the same temperature for 30 min, then, propane-1,3-diyldibenzenesulfonate **S5** (5.2 mmol, 2 g) was slowly added. The reaction

mixture was stirred at 0°C for 20 h followed by water addition (10 mL) and extraction with AcOEt (3 x 20 mL). The organic layer was dried over anhydrous Na₂SO₄, filtered and evaporated to dryness. The residue was purified by flash chromatography using CH_x:DCM (2:1) as eluent to afford **S6** (2.8 mmol, 908 mg, 60%) as a colorless oil.

3-(phenylthio)propyl-4-methylbenzenesulfonate **S6** (1 equiv.) was dissolved in acetone (10 mL), then, the corresponding phenol **S4** (1.05 equiv.) and K₂CO₃ (2.1 equiv.) were added and the reaction mixture was stirred under reflux for 24 hours. Then, the reaction mixture was cooled to room temperature, followed by water addition (10 mL) and extraction with AcOEt (3 x 20 mL). The combined organic extracts were washed with brine, dried over anhydrous Na₂SO₄, filtered and concentrated under reduced pressure. The crude product was purified by flash chromatography using cyclohexane as eluent; the pure products¹ were obtained with yields between 67 and 89%.

(3-(3,4-Dimethoxyphenoxy)propyl)(phenyl)sulfide (1a).



According to the general procedure, (Method A): (3-chloropropyl)(phenyl)sulfide (1.61 mmol, 300 mg), 3,4-dimethoxyphenol (1.93 mmol, 297 mg), cesium carbonate (2.90 mmol, 944.6 mg) potassium iodide (0.48 mmol, 79.7 mg) and acetonitrile (5.2 mL) were used to obtain **1a** as a colorless oil (1.29 mmol, 392 mg, 80%).

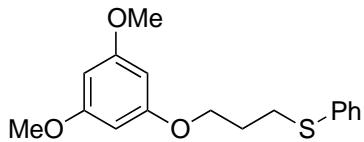
¹H NMR (400 MHz, CDCl₃) δ: 7.35 (dd, *J* = 8.4, 1.2 Hz, 2H), 7.27 (t, *J* = 7.6 Hz, 2H), 7.11 – 7.20 (m, 1H), 6.76 (d, *J* = 8.8 Hz, 1H), 6.50 (d, *J* = 2.8 Hz, 1H), 6.38 (dd, *J* = 8.8, 2.8 Hz, 1H), 4.02 (t, *J* = 6.0 Hz, 2H), 3.84 (s, 3H), 3.82 (s, 3H), 3.11 (t, *J* = 7.1 Hz, 2H), 1.90 – 2.28 (m, 2H).

¹³C NMR (100 MHz CDCl₃) δ: 153.5, 149.9, 143.6, 136.3, 129.2, 129.0, 126.0, 111.9, 103.9, 100.9, 66.6, 56.5, 55.9, 30.3, 29.0.

FT-IR (neat) ν(cm⁻¹): 3046, 2936, 1590, 1467, 1140, 1063, 683.

HRMS (ESI): Calcd. for C₁₇H₁₀O₃S (M+Na⁺), 327.1031; found: 327.1035.

(3-(3,5-Dimethoxyphenoxy)propyl)(phenyl)sulfide (1b).



According to the general procedure, (Method A): (3-chloropropyl)(phenyl)sulfide (2.15 mmol, 400 mg), 3,5-dimethoxyphenol (2.58 mmol, 397 mg), cesium carbonate (3.87 mmol, 1.26 g), potassium iodide (0.64 mmol, 106 mg) and acetonitrile (7.0 mL) were used to obtain **1b** as a colorless oil (1.74 mmol, 529 mg, 81%).

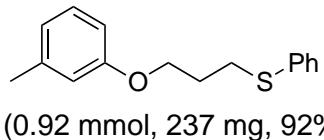
¹H NMR (400 MHz, CDCl₃) δ: 7.31 – 7.38 (m, 2H), 7.28 (dd, *J* = 10.5, 5.0 Hz, 2H), 7.18 (t, *J* = 7.3 Hz, 1H), 6.03 – 6.13 (m, 3H), 4.04 (t, *J* = 6.0 Hz, 2H), 3.76 (s, 6H), 3.11 (t, *J* = 7.1 Hz, 2H), 1.97 – 2.17 (m, 2H).

¹³C NMR (100 MHz, CDCl₃) δ: 161.7, 160.9, 136.3, 129.4, 129.1, 126.2, 93.5, 93.2, 66.2, 55.5, 30.4, 29.0.

FT-IR (neat) ν(cm⁻¹): 3050, 2939, 1593, 1469, 1145, 1060, 686.

HRMS (ESI): Calcd. for C₁₇H₁₀O₃S (M+Na⁺), 327.1031; found: 327.1029.

Phenyl(3-(*m*-tolyloxy)propyl)sulfide (1c).



According to the general procedure, (Method A): (3-chloropropyl)(phenyl)sulfide (1 mmol, 186 mg), 3-methylphenol (1.2 mmol, 223 mg), cesium carbonate (1.8 mmol, 586 mg), potassium iodide (0.3 mmol, 49.8 mg) and acetonitrile (4.0 mL) were used to obtain **1c** as a colorless oil (0.92 mmol, 237 mg, 92%).

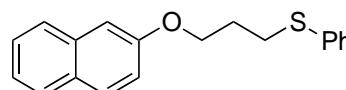
¹H NMR (400 MHz, CDCl₃) δ: 7.35 (d, *J* = 7.8 Hz, 2H), 7.24 – 7.30 (m, 2H), 7.11 – 7.20 (m, 2H), 6.76 (d, *J* = 7.5 Hz, 1H), 6.66 – 6.73 (m, 2H), 4.06 (t, *J* = 6.0 Hz, 2H), 3.12 (t, *J* = 7.1 Hz, 2H), 2.32 (s, 3H), 1.98 – 2.15 (m, 2H).

¹³C NMR (100 MHz CDCl₃) δ: 158.9, 139.6, 136.4, 129.3, 129.3, 129.1, 126.1, 121.7, 115.5, 111.5, 66.1, 30.4, 29.1, 21.7.

FT-IR (neat) ν(cm⁻¹): 3147, 1605, 1460, 1150, 1121, 705.

HRMS (ESI): Calcd. for C₁₆H₁₈OS (M+Na⁺), 281.0976; found: 281.0976.

(3-(Naphthalen-2-yloxy)propyl)(phenyl)sulfide (1d).



According to the general procedure, (Method A): (3-chloropropyl)(phenyl)sulfide (2.68 mmol, 500 mg), β-naphthol (3.21 mmol, 462 mg), cesium carbonate (4.82 mmol, 1.57g), potassium iodide (0.8 mmol, 133 mg) and acetonitrile (10.0 mL) were used to obtain **1d** as a colorless oil (1.74 mmol, 512 mg, 65%).

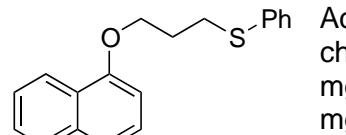
¹H NMR (400 MHz, CDCl₃) δ: 7.67 – 7.78 (m, 3H), 7.43 (t, *J* = 7.1 Hz, 1H), 7.25 – 7.39 (m, 5H), 7.09 – 7.20 (m, 3H), 4.19 (t, *J* = 6.0 Hz, 2H), 3.17 (t, *J* = 7.1 Hz, 2H), 2.09 – 2.26 (m, 2H).

¹³C NMR (100 MHz CDCl₃) δ: 156.9, 136.3, 134.7, 129.5, 129.4, 129.1, 129.1, 127.8, 126.9, 126.5, 126.2, 123.8, 119.0, 106.8, 66.2, 30.4, 29.0.

FT-IR (neat) ν(cm⁻¹): 3060, 2940, 1570, 1399, 1238, 1097, 736, 692.

HRMS (ESI): Calcd. for C₁₉H₁₈OS (M+Na⁺), 317.0976; found: 317.0976.

(3-(Naphthalen-1-yloxy)propyl)(phenyl)sulfide (1e).



According to the general procedure, (Method A): (3-chloropropyl)(phenyl)sulfide (2.68 mmol, 500 mg), α-naphthol (3.22 mmol, 463 mg), cesium carbonate (4.82 mmol, 1.57g), potassium iodide (0.8 mmol, 133 mg) and acetonitrile (10.0 mL) were used to obtained **1e** as a colorless oil (2.22 mmol, 654 mg, 83%).

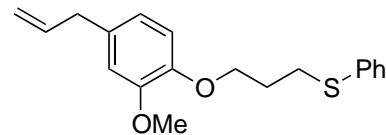
¹H NMR (400 MHz, CDCl₃) δ: 8.22 – 8.30 (m, 1H), 7.76 – 7.83 (m, 1H), 7.43 – 7.72 (m, 2H), 7.33 – 7.44 (m, 4H), 7.24 – 7.31 (m, 2H), 7.17 (t, *J* = 7.4 Hz, 1H), 6.79 (d, *J* = 7.4 Hz, 1H), 4.26 (t, *J* = 5.9 Hz, 2H), 3.24 (t, *J* = 7.1 Hz, 2H), 2.19 – 2.33 (m, 2H).

¹³C NMR (100 MHz CDCl₃) δ: 154.6, 136.3, 134.6, 129.4, 129.1, 127.6, 126.5, 126.2, 125.9, 125.3, 122.1, 120.4, 108.5, 104.8, 66.3, 30.6, 29.2.

FT-IR (neat) ν(cm⁻¹): 3051, 2927, 1577, 1384, 1265, 1099, 767, 690.

HRMS (ESI): Calcd. for C₁₉H₁₈OS (M+Na⁺), 317.0976; found: 317.0977.

(3-(4-Allyl-2-methoxyphenoxy)propyl)(phenyl)sulfide (1f).



According to the general procedure, (Method A): (3-chloropropyl)(phenyl)sulfide (2.15 mmol, 400 mg), eugenol (2.58 mmol, 0.4 mL), cesium carbonate (3.87 mmol, 1.26 g) potassium iodide (0.6 mmol, 99.6 mg) and acetonitrile (7.5 mL) were used to obtain **1f** as a colorless oil (0.97 mmol, 274 mg, 45%).

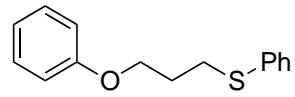
¹H NMR (400 MHz, CDCl₃) δ: 7.31 – 7.40 (m, 2H), 7.23 – 7.30 (m, 2H), 7.10 – 7.21 (m, 1H), 6.80 (d, *J* = 7.8 Hz, 1H), 6.62 – 6.74 (m, 2H), 5.86 – 6.05 (m, 1H), 4.98 – 5.16 (m, 2H), 4.11 (t, *J* = 6.2 Hz, 2H), 3.84 (s, 3H), 3.33 (dt, *J* = 6.7, 1.8 Hz, 2H), 3.13 (t, *J* = 7.1 Hz, 2H), 2.01 – 2.21 (m, 2H).

¹³C NMR (100 MHz CDCl₃) δ: 149.6, 146.7, 137.8, 136.4, 133.3, 129.3, 129.0, 126.0, 120.6, 115.8, 113.8, 112.5, 67.6, 56.0, 40.0, 30.3, 29.0.

FT-IR (neat) ν(cm⁻¹): 3055, 2935, 1508, 1257, 1230, 1138, 1026, 736, 690.

HRMS (ESI): Calcd. for C₁₉H₂₂O₂S (M+Na⁺), 337.1238; found: 337.1234.

(3-Phenoxypropyl)(phenyl)sulfide (1g).



According to the general procedure, (Method A): (3-chloropropyl)(phenyl)sulfide (3.22 mmol, 600 mg), phenol (3.86 mmol, 363 mg), cesium carbonate (5.80 mmol, 1.89 g), potassium iodide (0.97 mmol, 161 mg) and acetonitrile (12.0 mL) were used to obtain 1g as a colorless oil (2.90 mmol, 707 mg, 90%).

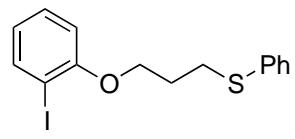
¹H NMR (400 MHz, CDCl₃) δ: 7.35 (d, J = 7.3 Hz, 2H), 7.23 – 7.31 (m, 4H), 7.17 (t, J = 7.3 Hz, 1H), 6.94 (t, J = 7.4 Hz, 1H) 7.01 (d, J = 7.9 Hz, 2H), 4.08 (t, J = 6.0 Hz, 2H), 3.12 (t, J = 7.1 Hz, 2H), 1.98 – 2.20 (m, 2H).

¹³C NMR (100 MHz CDCl₃) δ: 158.9, 136.3, 129.6, 129.3, 129.1, 126.1, 120.9, 114.6, 66.0, 30.3, 29.0.

FT-IR (neat) ν(cm⁻¹): 3050, 2928, 1585, 1481, 1470, 1439, 1242, 1038, 750.

HRMS (ESI): Calcd. for C₁₅H₁₆OS (M+Na⁺), 267.0820; found: 267.0823.

(3-(2-Iodophenoxy)propyl)(phenyl)sulfide (1h).



According to the general procedure, (Method A): (3-chloropropyl)(phenyl)sulfide (1.6 mmol, 300 mg), 2-iodophenol (1.9 mmol, 418 mg), cesium carbonate (2.9 mmol, 945 mg, 1.8 equiv), potassium iodide (0.5 mmol, 83 mg) and acetonitrile (7.0 mL) were used to obtain 1h as a colorless oil (1.2 mmol, 444 mg, 75%).

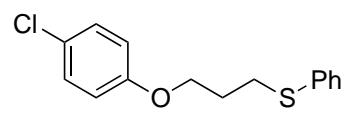
¹H NMR (400 MHz, CDCl₃) δ: 7.77 (dd, J = 7.8, 1.7 Hz, 1H), 7.36 – 7.41 (m, 2H), 7.24 – 7.31 (m, 3H), 7.16 (t, J = 7.3 Hz, 1H), 6.78 (dd, J = 8.3, 1.4 Hz, 1H), 6.71 (td, J = 7.5, 1.5 Hz, 1H), 4.12 (t, J = 5.7 Hz, 2H), 3.24 (t, J = 7.1 Hz, 2H), 2.06 – 2.26 (m, 2H).

¹³C NMR (100 MHz CDCl₃) δ: 157.4, 139.6, 136.3, 129.6, 129.2, 129.1, 126.0, 122.7, 112.2, 86.8 (C), 67.2, 30.2, 29.1.

FT-IR (neat) ν(cm⁻¹): 3059, 2920, 2850, 1462, 1242, 1018, 736, 690.

HRMS (ESI): Calcd. for C₁₅H₁₅IOS (M+Na⁺), 292.9786; found: 292.9785.

(3-(4-Chlorophenoxy)propyl)(phenyl)sulfide (1i).



According to the general procedure, (Method A): (3-chloropropyl)(phenyl)sulfide (2.69 mmol, 550 mg), 4-chlorophenol (3.22 mmol, 0.32 mL), cesium carbonate (4.84 mmol, 1.57g), potassium iodide (0.8 mmol, 134 mg) and acetonitrile (10.0 mL) were used to obtain 1i as a colorless oil (2.56 mmol, 712 mg, 95%).

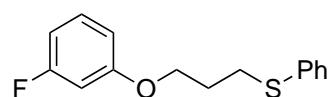
¹H NMR (400 MHz, CDCl₃) δ: 7.35 (d, J = 7.7 Hz, 2H), 7.24 – 7.31 (m, 2H), 7.15 – 7.24 (m, 3H), 6.80 (d, J = 8.9 Hz, 2H), 4.04 (t, J = 6.0 Hz, 2H), 3.11 (t, J = 7.0 Hz, 2H), 2.03 – 2.16 (m, 2H).

¹³C NMR (100 MHz CDCl₃) δ: 157.6, 136.2, 129.5, 129.5, 129.1, 126.2, 125.8, 115.9, 66.5, 30.3, 29.0.

FT-IR (neat) ν(cm⁻¹): 1582, 1489, 1439, 1389, 1169, 1092, 783, 737.

HRMS (ESI): Calcd. for C₁₅H₁₅ClOS (M+Na⁺), 301.0430; found: 301.0428.

(3-(3-Fluorophenoxy)propyl)(phenyl)sulfide (1j).



According to the general procedure, (Method A): (3-chloropropyl)(phenyl)sulfide (3.2 mmol, 600 mg), 3-fluorophenol (3.8 mmol,

0.35 mL), cesium carbonate (5.8 mmol, 1.9 g), potassium iodide (0.96 mmol, 159 mg) and acetonitrile (10.0 mL) were used to obtain **1j** as a colorless oil (1.95 mmol, 511 mg, 61%).

¹H NMR (400 MHz, CDCl₃) δ: 7.36 (d, *J* = 7.9 Hz, 2H), 7.25 – 7.32 (m, 2H), 7.13 – 7.24 (m, 2H), 6.54 – 6.70 (m, 3H), 4.05 (t, *J* = 6.0 Hz, 2H), 3.11 (t, *J* = 7.0 Hz, 2H), 2.01 – 2.17 (m, 2H).

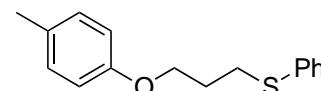
¹³C NMR (100 MHz CDCl₃) δ: 163.8 (d, *J_{C-F}* = 245.1 Hz), 160.3 (d, *J_{C-F}* = 10.8 Hz), 136.2, 130.3 (d, *J_{C-F}* = 10.2 Hz), 129.4, 129.1, 126.2, 110.4 (d, *J_{C-F}* = 2.9 Hz), 107.7 (d, *J_{C-F}* = 21.3 Hz), 102.3 (d, *J_{C-F}* = 24.7 Hz), 66.4, 30.3, 28.9.

¹⁹F NMR (374 MHz CDCl₃) δ: -112.69 (s).

FT-IR (neat) ν(cm⁻¹): 3074, 2943, 1589, 1489, 1261, 1134, 1029, 736, 679.

HRMS (ESI): Calcd. for C₁₅H₁₅FOS (M+Na⁺), 285.0725; found: 285.0720.

Phenyl(3-(*p*-tolyloxy)propyl)sulfide (**1k**).

 According to the general procedure, (Method A): (3-chloropropyl)(phenyl)sulfide (2.69 mmol, 500 mg), *p*-cresol (3.22 mmol, 0.34 mL), cesium carbonate (4.8 mmol, 1.57 g), potassium iodide (0.8 mmol, 133 mg, 0.3 equiv) and acetonitrile (10.0 mL) were used to obtain **1k** as a colorless oil (2.60 mmol, 671 mg, 97%).

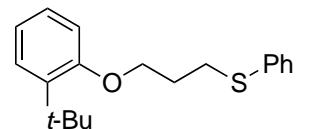
¹H NMR (400 MHz, CDCl₃) δ: 7.35 (d, *J* = 8.0 Hz, 2H), 7.25 – 7.30 (m, 2H), 7.17 (t, *J* = 7.3 Hz, 1H), 7.07 (d, *J* = 8.3 Hz, 2H), 6.79 (d, *J* = 8.6 Hz, 2H), 4.04 (t, *J* = 6.0 Hz, 2H), 3.11 (t, *J* = 7.0 Hz, 2H), 2.28 (s, 3H), 2.03 – 2.16 (m, 2H).

¹³C NMR (100 MHz CDCl₃) δ: 156.8, 136.4, 130.1, 130.0, 129.3, 129.1, 126.1, 114.5, 66.3, 30.3, 29.1, 20.6.

FT-IR (neat) ν(cm⁻¹): 3050, 2920, 1508, 1238, 1033, 737, 690.

HRMS (ESI): Calcd. for C₁₆H₁₈OS (M+Na⁺), 281.0976; found: 281.0980.

(3-(2-(tert-butyl)phenoxy)propyl)(phenyl)sulfide (**1l**).

 According to the general procedure, (Method A): (3-chloropropyl)(phenyl)sulfide (2.95 mmol, 550 mg), 2-(tert-butyl)phenol (3.54 mmol, 0.54 mL), cesium carbonate (5.31 mmol, 1.73 g) potassium iodide (0.9 mmol, 148 mg) and acetonitrile (10.0 mL) were used to obtain **1l** as a colorless oil (2.07 mmol, 621 mg, 70%).

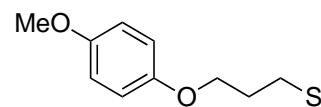
¹H NMR (400 MHz, CDCl₃) δ: 7.38 (d, *J* = 8.1 Hz, 2H) 7.25 – 7.33 (m, 3H), 7.12 – 7.23 (m, 2H), 6.90 (t, *J* = 7.5 Hz, 1H), 6.86 (d, *J* = 8.1 Hz, 1H), 4.11 (t, *J* = 5.7 Hz, 2H), 3.18 (t, *J* = 7.2 Hz, 2H), 2.09 – 2.26 (m, 2H), 1.39 (s, 9H).

¹³C NMR (100 MHz CDCl₃) δ: 157.7, 138.0, 136.2, 129.4, 129.1, 127.2, 126.8, 126.1, 120.5, 111.9, 66.1, 35.0, 30.9, 30.0, 29.4.

FT-IR (neat) ν(cm⁻¹): 3051, 2940, 1582, 1485, 1389, 1230, 1169, 1092, 740.

HRMS (ESI): Calcd. for C₁₉H₂₄OS (M+Na⁺), 323.1446; found: 323.1445.

(3-(4-Methoxyphenoxy)propyl)(phenyl)sulfide (**1m**).

 According to the general procedure, (Method A): (3-chloropropyl)(phenyl)sulfide (2.15 mmol, 400 mg), 4-methoxyphenol (2.58 mmol, 320 mg), cesium carbonate (2.87 mmol, 1.26 g) potassium iodide (0.64 mmol, 107 mg) and acetonitrile (7.3 mL) were used to obtain **1m** as a colorless oil (1.46 mmol, 400 mg, 68%).

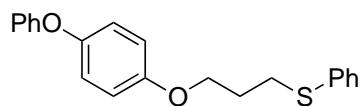
¹H NMR (400 MHz, CDCl₃) δ: 7.35 (d, *J* = 8.0 Hz, 2H), 7.27 (t, *J* = 7.4 Hz, 2H), 7.18 (t, *J* = 6.1 Hz, 1H), 6.83 (s, 4H), 4.03 (t, *J* = 6.0 Hz, 2H), 3.77 (s, 3H), 3.12 (t, *J* = 7.1 Hz, 2H), 1.94 – 2.18 (m, 2H).

¹³C NMR (100 MHz CDCl₃) δ: 154.0, 153.1, 136.4, 129.3, 129.1, 126.1, 115.6, 114.8, 66.8, 55.9, 30.3, 29.1.

FT-IR (neat) ν(cm⁻¹): 3054, 2950, 1580, 1278, 1117, 1038, 737, 692.

HRMS (ESI): Calcd. for C₁₆H₁₈O₂S (M+Na⁺), 297.0925; found: 297.0928.

(3-(4-Phenoxyphenoxy)propyl)(phenyl)sulfide (1n).



According to the general procedure, (Method A): (3-chloropropyl)(phenyl)sulfide (1.94 mmol, 361 mg), 4-phenoxyphenol (2.33 mmol, 435 mg), cesium carbonate (3.49 mmol, 1.14 g) potassium iodide (0.58 mmol, 97 mg) and acetonitrile (6.5 mL) were used to obtain **1n** as an orange oil (1.78 mmol, 599 mg, 92%).

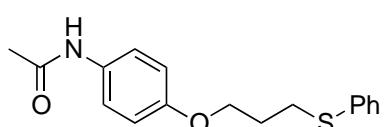
¹H NMR (400 MHz, CDCl₃) δ: 7.33 – 7.38 (m, 2H), 7.24 – 7.32 (m, 4H), 7.18 (t, J = 7.3 Hz, 1H), 7.04 (t, J = 7.4 Hz, 1H), 6.91 – 7.00 (m, 4H), 6.83 – 6.89 (m, 2H), 4.06 (t, J = 5.9 Hz, 2H), 3.13 (t, J = 7.1 Hz, 2H), 2.05 – 2.16 (m, 2H).

¹³C NMR (100 MHz CDCl₃) δ: 158.6, 155.2, 150.3, 136.3, 129.8, 129.4, 129.1, 126.2, 122.6, 121.0, 117.7, 115.7, 66.6, 30.3, 29.1.

FT-IR (neat) ν(cm⁻¹): 3056, 2942, 1490, 1280, 1125, 1050, 738, 691.

HRMS (ESI): Calcd. for C₂₁H₂₀O₂S (M+Na⁺), 359.1082; found: 359.1079.

N-(4-(3-(Phenylthio)propoxy)phenyl)acetamide (1o).



According to the general procedure, (Method A): (3-chloropropyl)(phenyl)sulfide (2.95 mmol, 550 mg, 1.0 equiv), N-(4-hydroxyphenyl)acetamide (3.54 mmol, 534 mg), cesium carbonate (5.31 mmol, 1.73 g) potassium iodide (0.9 mmol, 148 mg) and acetonitrile (12.0 mL) were used to obtain **1o** as a white solid (2.65 mmol, 799 mg, 90%). m.p. 87-88 °C.

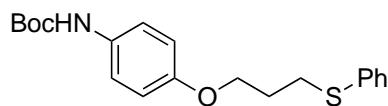
¹H NMR (400 MHz, CDCl₃) δ: 7.32 – 7.39 (m, 4H), 7.25 – 7.30 (m, 2H), 7.14 – 7.20 (m, 1H), 6.81 – 6.86 (m, 2H), 4.04 (t, J = 6.0 Hz, 2H), 3.11 (t, J = 7.1 Hz, 2H), 2.15 (s, 3H), 2.04 – 2.13 (m, 2H).

¹³C NMR (100 MHz CDCl₃) δ: 168.3, 155.8, 136.3, 131.2, 129.4, 129.1, 126.2, 122.0, 114.9, 66.4, 30.3, 29.0, 24.5.

FT-IR (neat) ν(cm⁻¹): 3150, 3043, 2954, 1508, 1238, 1033, 744, 690.

HRMS (ESI): Calcd. for C₁₇H₁₉NO₂S (M+Na⁺), 324.1034; found: 324.1034.

tert-butyl (4-(3-(phenylthio)propoxy)phenyl)carbamate (1p).



According to the general procedure, (Method A): (3-chloropropyl)(phenyl)sulfide (2.48 mmol, 461 mg), *tert*-butyl (4-hydroxyphenyl)carbamate (2.98 mmol, 622 mg), cesium carbonate (4.46 mmol, 1.45 g) potassium iodide (0.74 mmol, 123 mg) and acetonitrile (10.0 mL) were used to obtain **1p** as a white solid (2.20 mmol, 793 mg, 89%). m.p. 99-100 °C.

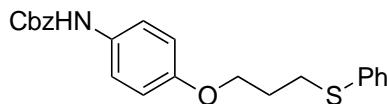
¹H NMR (400 MHz, CDCl₃) δ: 7.33 – 7.37 (m, 2H), 7.21 – 7.30 (m, 4H), 7.14 – 7.20 (m, 1H), 6.79 – 6.84 (m, 2H), 4.03 (t, J = 6.0 Hz, 2H), 3.11 (t, J = 7.1 Hz, 2H), 2.02 – 2.13 (m, 2H), 1.51 (s, 9H).

¹³C NMR (100 MHz CDCl₃) δ: 155.0, 153.3, 136.3, 131.7, 129.3, 129.1, 126.1, 120.6, 115.0, 80.4, 66.5, 30.3, 29.1, 28.5.

FT-IR (neat) ν(cm⁻¹): 3356, 3040, 2978, 1693, 1516, 1230, 1153, 732, 644.

HRMS (ESI): Calcd. for C₂₀H₂₅NO₃S (M+Na⁺), 382.1453; found: 382.1455.

Benzyl (4-(3-(phenylthio)propoxy)phenyl)carbamate (1q).



According to the general procedure, (Method B): 3-(phenylthio)propyl 4-methylbenzenesulfonate (1.04 mmol, 335 mg), benzyl (4-hydroxyphenyl)carbamate (0.99 mmol, 240 mg), potassium carbonate (2.08 mmol, 387 mg), Cetone (5.0 mL) were used to obtain **1q** as a white solid (0.93 mmol, 333 mg, 89%) m.p. 97–98 °C.

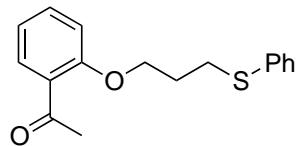
¹H NMR (400 MHz, CDCl₃) δ: 7.58 – 7.77 (m, 2H), 7.47 – 7.56 (m, 3H), 7.32 – 7.43 (m, 5H), 7.21 – 7.30 (m, 2H), 6.79 (d, *J* = 9.0 Hz, 2H), 6.61 (brs, 1H), 5.18 (s, 2H), 3.87 – 4.15 (m, 2H), 3.00 – 3.12 (m, 1H), 2.86 – 2.98 (m, 1H), 2.15 – 2.36 (m, 1H), 1.96 – 2.16 (m, 1H).

¹³C NMR (100 MHz CDCl₃) δ: 155.4, 153.8, 136.3, 131.1, 129.4, 129.1, 128.8, 128.5, 128.5, 128.5, 126.2, 120.8, 115.1, 67.1, 66.5, 30.4, 29.1.

FT-IR (neat) ν(cm⁻¹): 3317, 3066, 2920, 1693, 1531, 1235, 1060, 732, 690.

HRMS (ESI): Calcd. for C₂₃H₂₃NO₃S (M+Na⁺), 416.1296; found: 416.1294.

1-(2-(3-(Phenylthio)propoxy)phenyl)ethanone (1r).



According to the general procedure, (Method A): (3-chloropropyl)(phenyl)sulfide (2 mmol, 572 mg), 1-(2-hydroxyphenyl)ethanone (2.4 mmol, 0.3 mL), cesium carbonate (3.6 mmol, 1.2 g) potassium iodide (0.6 mmol, 100 mg) and acetonitrile (12.0 mL) were used to obtain **1r** as a colorless oil (1.12 mmol, 320 mg, 56%).

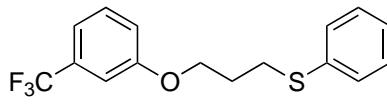
¹H NMR (400 MHz, CDCl₃) δ: 7.73 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.40 – 7.47 (m, 1H), 7.33 – 7.39 (m, 2H), 7.25 – 7.32 (m, 2H), 7.16 – 7.22 (m, 1H), 6.99 (t, *J* = 7.7 Hz, 1H), 6.93 (d, *J* = 8.3 Hz, 1H), 4.18 (t, *J* = 6.0 Hz, 2H), 3.14 (t, *J* = 7.0 Hz, 2H), 2.60 (s, 3H), 2.13 – 2.23 (m, 2H).

¹³C NMR (100 MHz CDCl₃) δ: 199.8, 158.2, 135.9, 133.7, 130.6, 129.8, 129.2, 128.6, 126.5, 120.9, 112.5, 66.8, 32.1, 30.8, 29.1.

FT-IR (neat) ν(cm⁻¹): 2928, 1597, 1481, 1358, 1292, 1161, 1026, 690.

HRMS (ESI): Calcd. for C₁₇H₁₈O₂S (M+Na⁺), 309.0925; found: 309.0928.

Phenyl(3-(3-(trifluoromethyl)phenoxy)propyl)sulfide (1s).



According to the general procedure, (Method A): (3-chloropropyl)(phenyl)sulfide (2.95 mmol, 550 mg), 3-(trifluoromethyl)phenol (3.5 mmol, 0.43 mL), cesium carbonate (5.31 mmol, 1.7 g) potassium iodide (0.9 mmol, 146.9 mg) and acetonitrile (10.0 mL) were used to obtain **1s** as a colorless oil (2.63 mmol, 819 mg, 89%).

¹H NMR (400 MHz, CDCl₃) δ: 7.33 – 7.42 (m, 3H), 7.25 – 7.32 (m, 2H), 7.15 – 7.23 (m, 2H), 7.10 (s, 1H), 7.04 (d, *J* = 8.3 Hz, 1H), 4.11 (t, *J* = 5.8 Hz, 2H), 3.13 (t, *J* = 6.9 Hz, 2H), 2.01 – 2.32 (m, 2H).

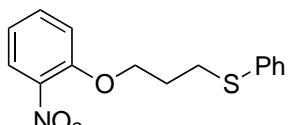
¹³C NMR (100 MHz CDCl₃) δ: 159.1, 136.1, 131.9 (q, *J*_{C-F} = 32.2 Hz), 130.1, 129.5, 129.1, 126.3, 124.1 (q, *J*_{C-F} = 272.2 Hz), 118.1, 117.6 (q, *J*_{C-F} = 3.8 Hz), 111.4 (q, *J*_{C-F} = 3.6 Hz), 66.4, 30.3, 28.9.

¹⁹F NMR (376 MHz, CDCl₃) δ: -63.64 (s).

FT-IR (neat) ν(cm⁻¹): 3059, 2927, 1589, 1450, 1327, 1122, 1033, 736, 690.

HRMS (ESI): Calcd. for C₁₆H₁₅F₃OS (M+Na⁺), 335.0693; found: 335.0692.

(3-(2-Nitrophenoxy)propyl)(phenyl)sulfide (1t).



According to the general procedure, (Method A): (3-chloropropyl)(phenyl)sulfide (3.22 mmol, 600 mg), 2-nitrophenol (3.86 mmol, 537 mg), cesium carbonate (5.80 mmol, 1.9 g) potassium iodide (0.97 mmol, 160 mg) and acetonitrile (10.0 mL) were used to obtain **1t** as a yellow solid

(1.84 mmol, 532 mg, 57%) m.p. 59-60 °C.

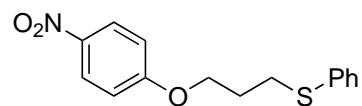
¹H NMR (400 MHz, CDCl₃) δ: 7.84 (d, *J* = 8.1 Hz, 1H), 7.49 (t, *J* = 7.9 Hz, 1H), 7.36 (d, *J* = 8.2 Hz, 2H), 7.26 (t, *J* = 7.4 Hz, 2H), 7.15 (t, *J* = 7.4 Hz, 1H), 7.01 (t, *J* = 7.9 Hz, 2H), 4.21 (t, *J* = 5.7 Hz, 2H), 3.18 (t, *J* = 6.8 Hz, 2H), 2.07 – 2.23 (m, 2H).

¹³C NMR (100 MHz CDCl₃) δ: 157.5 (**C**), 136.2 (**C**), 129.5 (**CH**), 129.4 (**CH**), 129.1 (**CH**), 126.2 (**CH**), 125.8 (**C**), 115.9 (**CH**), 66.4 (**CH₂**), 30.2 (**CH₂**), 28.9 (**CH₂**).

FT-IR (neat) ν(cm⁻¹): 3070, 2953, 1585, 1499, 1330, 1269, 1017, 735, 689.

HRMS (ESI): Calcd. for C₁₅H₁₅NO₃S (M+Na⁺), 312.0670; found: 312.0671.

(3-(4-Nitrophenoxy)propyl)(phenyl)sulfide (1u).



According to the general procedure, (Method A): (3-chloropropyl)(phenyl)sulfide (2.69 mmol, 500 mg), 4-nitrophenol (3.22 mmol, 447 mg), cesium carbonate (4.84 mmol, 1.6 g) potassium iodide (0.8 mmol, 132.8 mg) and acetonitrile (10.0 mL) were used to obtain **1u** as a pale yellow solid (1.42 mmol, 412 mg, 53%) m.p. 62-63 °C.

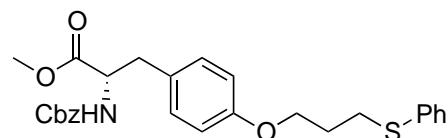
¹H NMR (400 MHz, CDCl₃) δ: 8.10 – 8.39 (m, 2H), 7.36 (d, *J* = 8.9 Hz, 2H), 7.23 – 7.32 (m, 2H), 7.18 (t, *J* = 7.3 Hz, 1H), 6.93 (d, *J* = 9.2 Hz, 2H), 4.17 (t, *J* = 6.0 Hz, 2H), 3.13 (t, *J* = 6.9 Hz, 2H), 2.01 – 2.37 (m, 2H).

¹³C NMR (100 MHz CDCl₃) δ: 163.9, 141.7, 135.9, 129.6, 129.2, 126.4, 126.1, 114.6, 66.9, 30.2, 28.7.

FT-IR (neat) ν(cm⁻¹): 3080, 2954, 1589, 1492, 1338, 1261, 1014, 733, 686.

HRMS (ESI): Calcd. for C₁₅H₁₅NO₃S (M+Na⁺), 312.0670; found: 321.0669.

(S)-Methyl 2-((benzyloxy)carbonyl)amino-3-(4-(3-(phenylthio)propoxy)phenyl)propanoate (1v).



According to the general procedure, (Method B): 3-(phenylthio)propyl 4-methylbenzenesulfonate (1.2 mmol, 387 mg), (*R*)-methyl 2-((benzyloxy)carbonyl)amino-3-(4-hydroxyphenyl)propanoate (1.14 mmol, 375 mg), potassium carbonate (2.39 mmol, 329 mg), acetone (6.0 mL) were used to obtain **1v** as a colorless oil (0.76 mmol, 364 mg, 67%).

¹H NMR (400 MHz, CDCl₃) δ: 7.30 – 7.39 (m, 7H), 7.20 – 7.29 (m, 2H), 7.16 (t, *J* = 7.3 Hz, 1H), 6.97 (d, *J* = 8.6 Hz, 2H), 6.77 (d, *J* = 8.6 Hz, 2H), 5.21 (d, *J* = 8.1 Hz, 1H), 5.08 (d, *J* = 3.7 Hz, 2H), 4.54 – 4.65 (m, 1H), 4.17 (t, *J* = 6.0 Hz, 2H), 3.71 (s, 3H), 3.10 (t, *J* = 7.1 Hz, 2H), 2.96 – 3.06 (m, 2H), 2.00 – 2.14 (m, 2H).

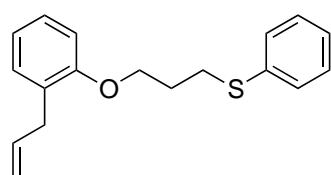
¹³C NMR (100 MHz CDCl₃) δ: 172.2, 158.1, 155.8, 136.4, 136.3, 130.4, 129.3, 129.1, 128.6, 128.3, 128.2, 127.8, 126.1, 114.8, 67.1, 66.1, 55.0, 52.4, 37.5, 30.3, 29.0.

FT-IR (neat) ν(cm⁻¹): 3336, 3032, 2947, 1716, 1508, 1242, 1026, 736, 694.

HRMS (ESI): Calcd. for C₂₇H₂₉NO₅S (M+Na⁺), 502.1664; found: 502.1667.

[α]²⁵_D = +36.69 (c = 1.0 in CHCl₃).

(3-(2-Allylphenoxy)propyl)(phenyl)sulfide (1w).



According to the general procedure, (Method A): (3-chloropropyl)(phenyl)sulfide (2.2 mmol, 400 mg), 4 2-allylphenol (2.64 mmol, 354 mg), cesium carbonate (3.96 mmol, 1.3 g) potassium iodide (0.66 mmol, 109 mg) and acetonitrile (10.0 mL) were used to obtain **1w** as a colorless oil (1.94 mmol, 551 mg, 88%).

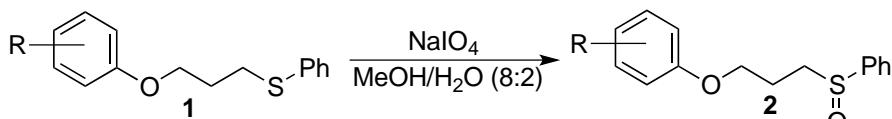
¹H NMR (400 MHz, CDCl₃) δ: 7.30 – 7.39 (m, 2H), 7.19 – 7.31 (m, 2H), 7.07 – 7.21 (m, 3H), 6.88 (t, *J* = 7.4 Hz, 1H), 6.80 (d, *J* = 8.1 Hz, 1H), 5.90 – 6.04 (m, 1H), 4.86 – 5.13 (m, 2H), 4.05 (t, *J* = 5.8 Hz, 2H), 3.38 (d, *J* = 6.6 Hz, 2H), 3.12 (t, *J* = 7.2 Hz, 2H), 2.03 – 2.21 (m, 2H).

¹³C NMR (100 MHz CDCl₃) δ: 156.5, 137.1 (CH), 136.4, 130.0, 129.2, 129.1, 128.8, 127.5, 126.1, 120.7, 115.5, 111.2, 66.1, 34.6, 30.4, 29.2.

FT-IR (neat) ν(cm⁻¹): 3074, 2920, 1585, 1492, 1238, 1026, 736, 690.

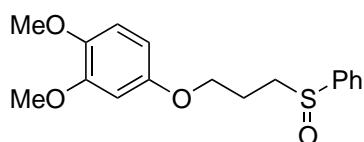
HRMS (ESI): Calcd. for C₁₈H₂₀OS (M+Na⁺), 307.1133; found: 307.1133.

2.3 General procedure for oxidation of sulfides



A solution of NaIO₄ (1.5 equiv) in water (1.2 mL/mmol) was added to a solution of sulfide (1.0 equiv) in methanol (7.3 mL/mmol). This mixture was stirred at room temperature for around 30 hours until complete conversion of the starting material (followed by TLC). Then, the reaction mixture was concentrated *in vacuo*, and the residue was extracted three times with DCM (3 x 20 mL). The combined organic extracts were washed with brine, dried over anhydrous Na₂SO₄, filtered and concentrated under reduced pressure. The crude product was purified by flash chromatography using DCM as eluent; the pure products **2** were obtained with yields between 53 and 100%.

1,2-Dimethoxy-4-(3-(phenylsulfinyl)propoxy)benzene (2a).



According to the general procedure, (3-(3,4-dimethoxyphenoxy)propyl)(phenyl)sulfide **1a** (1.64 mmol, 500 mg), sodium periodate (2.46 mmol, 525 mg) and MeOH/H₂O (8:2) (15 mL) were used to obtain **2a** as a colorless oil (1.38 mmol, 442 mg, 84%).

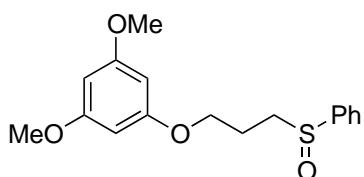
¹H NMR (400 MHz, CDCl₃) δ: 7.61 – 7.68 (m, 2H), 7.46 – 7.58 (m, 3H), 6.75 (d, *J* = 8.7 Hz, 1H), 6.47 (d, *J* = 2.8 Hz, 1H), 6.34 (dd, *J* = 8.7, 2.8 Hz, 1H), 4.00 – 4.09 (m, 1H), 3.91 – 4.00 (m, 1H), 3.84 (s, 3H), 3.82 (s, 3H), 2.99 – 3.17 (m, 1H), 2.84 – 2.99 (m, 1H), 2.16 – 2.36 (m, 1H), 1.95 – 2.16 (m, 1H).

¹³C NMR (100 MHz, CDCl₃) δ: 153.2, 150.0, 143.8, 143.8, 131.3, 129.4, 124.2, 111.9, 103.9, 100.9, 66.8, 56.6, 56.0, 54.0, 22.4.

FT-IR (neat) ν(cm⁻¹): 3055, 2938, 1540, 1240, 1119, 1051, 739, 695.

HRMS (ESI): Calcd. for C₁₇H₂₀O₄S (M+Na⁺), 343.0980; found: 343.0985.

1,3-Dimethoxy-5-(3-(phenylsulfinyl)propoxy)benzene (2b).



According to the general procedure, (3-(3,5-dimethoxyphenoxy)propyl)(phenyl)sulfide **1b** (1.73 mmol, 527 mg), sodium periodate (2.60 mmol, 555 mg) and MeOH/H₂O (8:2) (16 mL) were used to obtain **2b** as a colorless oil (1.38 mmol, 443 mg, 80%).

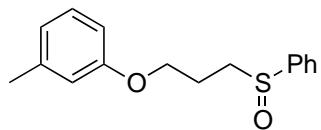
¹H NMR (400 MHz, CDCl₃) δ: 7.64 (dd, *J* = 7.9, 1.5 Hz, 2H), 7.47 – 7.56 (m, 3H), 6.08 (t, *J* = 2.1 Hz, 1H), 6.03 (d, *J* = 2.1 Hz, 2H), 3.90 – 4.08 (m, 2H), 3.75 (s, 6H), 2.84 – 3.12 (m, 2H), 1.96 – 2.35 (m, 2H).

¹³C NMR (100 MHz, CDCl₃) δ: 161.7, 160.6, 143.8, 131.2, 129.4, 124.2, 93.6, 93.4, 66.3, 55.5, 53.9, 22.3.

FT-IR (neat) ν (cm⁻¹): 3055, 2939, 1593, 1469, 1145, 1064, 817, 748, 690.

HRMS (ESI): Calcd. for C₁₇H₂₀O₄S (M+Na⁺), 343.0980; found: 343.0979.

1-Methyl-3-(phenylsulfinyl)propoxybenzene (2c).



According to the general procedure phenyl(3-(*m*-tolyloxy)propyl)sulfide **1c** (1.59 mmol, 411 mg), sodium periodate (2.39 mmol, 510 mg) and MeOH/H₂O (8:2) (14 mL) were used to obtain **2c** as a colorless oil (1.32 mmol, 362 mg, 83%).

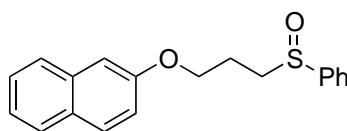
¹H NMR (400 MHz, CDCl₃) δ : 7.56 – 7.69 (m, 2H), 7.43 – 7.56 (m, 3H), 7.14 (t, *J* = 7.8 Hz, 1H), 6.76 (d, *J* = 7.5 Hz, 1H), 6.56 – 6.69 (m, 2H), 4.03 – 4.12 (m, 1H), 3.87 – 4.03 (m, 1H), 3.00 – 3.14 (m, 1H), 2.88 – 2.99 (m, 1H), 2.31 (s, 3H), 2.16 – 2.28 (m, 1H), 1.97 – 2.14 (m, 1H).

¹³C NMR (100 MHz CDCl₃) δ : 158.7, 143.8, 139.7, 131.2, 129.4, 129.4, 124.2, 122.0, 115.5, 111.5, 66.1, 54.0, 22.4, 21.6.

FT-IR (neat) ν (cm⁻¹): 3055, 2916, 1561, 1473, 1242, 1168, 1087, 1026, 744, 690.

HRMS (ESI): Calcd. for C₁₆H₁₈O₂S (M+Na⁺), 297.0925; found: 297.0927.

2-(3-(Phenylsulfinyl)propoxy)naphthalene (2d).



According to the general procedure, (3-(naphthalen-2-yloxy)propyl)(phenyl)sulfide **1d** (1.75 mmol, 515 mg), sodium periodate (2.62 mmol, 560 mg) and MeOH/H₂O (8:2) (16 mL) were used to obtain **2d** as a colorless oil (1.38 mmol, 428 mg, 79%).

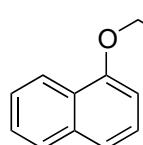
¹H NMR (400 MHz, CDCl₃) δ : 7.68 – 7.78 (m, 3H), 7.62 – 7.67 (m, 2H), 7.48 – 7.56 (m, 3H), 7.40 – 7.46 (m, 1H), 7.30 – 7.37 (m, 1H), 7.11 (d, *J* = 2.5 Hz, 1H), 7.08 (s, 1H), 4.18 – 4.26 (m, 1H), 4.08 – 4.16 (m, 1H), 3.06 – 3.18 (m, 1H), 2.93 – 3.05 (m, 1H), 2.26 – 2.40 (m, 1H), 2.09 – 2.25 (m, 1H).

¹³C NMR (100 MHz CDCl₃) δ : 156.6, 143.7, 134.6, 131.2, 129.5, 129.2, 127.8, 126.9, 126.6, 124.2, 123.9, 118.8, 106.9, 66.3, 53.9, 22.3.

FT-IR (neat) ν (cm⁻¹): 3055, 2237, 1597, 1466, 1443, 1258, 1215, 1180, 1022, 690.

HRMS (ESI): Calcd. for C₁₉H₁₈O₂S (M+Na⁺), 333.0925; found: 333.0928.

1-(3-(Phenylsulfinyl)propoxy)naphthalene (2e).



According to the general procedure, (3-(naphthalen-1-yloxy)propyl)(phenyl)sulfide **1e** (2.14 mmol, 632 mg), sodium periodate (3.22 mmol, 688 mg) and MeOH/H₂O (8:2) (19 mL) were used to obtain **2e** as a colorless oil (1.78 mmol, 551 mg, 83%).

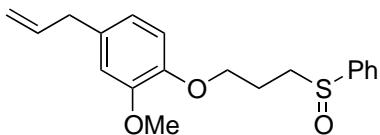
¹H NMR (400 MHz, CDCl₃) δ : 8.18 (dd, *J* = 7.5, 2.1 Hz, 1H), 7.73 – 7.84 (m, 1H), 7.60 – 7.70 (m, 2H), 7.40 – 7.57 (m, 6H), 7.35 (t, *J* = 7.9 Hz, 1H), 6.76 (d, *J* = 7.3 Hz, 1H), 4.24 – 4.31 (m, 1H), 4.14 – 4.23 (m, 1H), 3.12 – 3.27 (m, 1H), 2.94 – 3.09 (m, 1H), 2.33 – 2.51 (m, 1H), 2.11 – 2.31 (m, 1H).

¹³C NMR (100 MHz CDCl₃) δ : 154.3, 143.8, 134.6, 131.2, 129.4, 127.7, 126.6, 125.9, 125.6, 125.4, 124.2, 121.9, 120.7, 104.9, 66.4, 54.1, 22.3.

FT-IR (neat) ν (cm⁻¹): 3051, 2927, 1577, 1388, 1269, 1099, 1011, 771, 690.

HRMS (ESI): Calcd. for C₁₉H₁₈O₂S (M+Na⁺), 333.0925; found: 333.0920.

4-Allyl-2-methoxy-1-(3-(phenylsulfinyl)propoxy)benzene (2f).



According to the general procedure, (3-(4-allyl-2-methoxyphenoxy)propyl)(phenyl)sulfide **1f** (0.87 mmol, 260 mg), sodium periodate (1.3 mmol, 278 mg) and MeOH/H₂O (8:2) (8 mL) were used to obtain **2f** as a colorless oil (0.64 mmol, 209 mg, 73%).

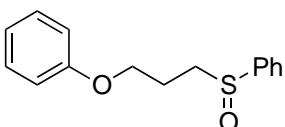
¹H NMR (400 MHz, CDCl₃) δ: 7.58 – 7.72 (m, 2H), 7.42 – 7.50 (m, 3H), 6.77 (d, *J* = 7.9 Hz, 1H), 6.63 – 6.72 (m, 2H), 5.84 – 6.07 (m, 1H), 4.97 – 5.16 (m, 2H), 4.09 – 4.18 (m, 1H), 3.98 – 4.07 (m, 1H), 3.82 (s, 3H), 3.32 (dd, *J* = 6.7, 1.5 Hz, 2H), 3.05 – 3.18 (m, 1H), 2.89 – 3.04 (m, 1H), 2.19 – 2.38 (m, 1H), 2.02 – 2.20 (m, 1H).

¹³C NMR (100 MHz CDCl₃) δ: 149.7, 146.4, 143.8, 137.7, 133.8, 131.1, 129.4, 124.2, 120.7, 115.8, 114.4, 112.5, 68.0, 55.9, 54.0, 39.9, 22.5.

FT-IR (neat) ν(cm⁻¹): 3055, 2935, 1508, 1257, 1226, 1138, 1022, 744, 690.

HRMS (ESI): Calcd. for C₁₉H₂₂O₃S (M+Na⁺), 353.1187; found: 353.1183.

((3-Phenoxypropyl)sulfinyl)benzene (2g).



According to the general procedure, (3-phenoxypropyl)(phenyl)sulfide **1g** (5.5 mmol, 1343 mg), sodium periodate (8.2 mmol, 1.77 g) and MeOH/H₂O (8:2) (50 mL) were used to obtain **2g** as a colorless oil (4.07 mmol, 1.06 g, 74%).

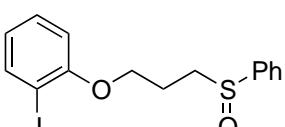
¹H NMR (400 MHz, CDCl₃) δ: 7.61 – 7.67 (m, 2H), 7.48 – 7.56 (m, 3H), 7.27 (m, 2H), 6.95 (t, *J* = 7.3 Hz, 1H), 6.85 (d, *J* = 8.0 Hz, 2H), 4.05 – 4.14 (m, 1H), 3.97 – 4.05 (m, 1H), 3.03 – 3.14 (m, 1H), 2.88 – 3.01 (m, 1H), 2.19 – 2.33 (m, 1H), 2.02 – 2.18 (m, 1H).

¹³C NMR (100 MHz CDCl₃) δ: 158.6, 143.7, 131.2, 129.6, 129.4, 124.2, 121.1, 114.6, 66.1, 53.9, 22.3.

FT-IR (neat) ν(cm⁻¹): 3050, 2932, 1593, 1481, 1473, 1445, 1242, 1065, 1040, 781, 753.

HRMS (ESI): Calcd. for C₁₅H₁₆O₂S (M+Na⁺), 283.0769; found: 283.0767.

1-Iodo-2-(3-(phenylsulfinyl)propoxy)benzene (2h).



According to the general procedure, (3-(2-iodophenoxy)propyl)(phenyl)sulfide **1h** (1.2 mmol, 444 mg), sodium periodate (1.8 mmol, 384 mg) and MeOH/H₂O (8:2) (11 mL) were used to obtain **2h** as a colorless oil (1 mmol, 384 mg, 83%).

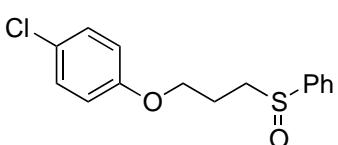
¹H NMR (400 MHz, CDCl₃) δ: 7.75 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.59 – 7.69 (m, 2H), 7.41 – 7.58 (m, 3H), 7.21 – 7.33 (m, 1H), 6.62 – 6.80 (m, 2H), 4.10 – 4.21 (m, 1H), 3.99 – 4.10 (m, 1H), 3.19 – 3.34 (m, 1H), 2.96 – 3.09 (m, 1H), 2.23 – 2.41 (m, 1H), 2.06 – 2.23 (m, 1H).

¹³C NMR (100 MHz CDCl₃) δ: 157.0, 143.7, 139.5, 131.1, 129.7, 129.4, 124.2, 123.0, 112.3, 86.7, 67.2, 53.6, 22.2.

FT-IR (neat) ν(cm⁻¹): 3054, 2241, 1582, 1466, 1246, 1161, 721, 690.

HRMS (ESI): Calcd. for C₁₅H₁₅IO₂S (M+Na⁺), 408.9735; found: 408.9725.

1-Chloro-4-(3-(phenylsulfinyl)propoxy)benzene (2i).



According to the general procedure, (3-(4-chlorophenoxy)propyl)(phenyl)sulfide **1i** (2.8 mmol, 778 mg), sodium periodate (4.2 mmol, 898 mg) and MeOH/H₂O (8:2) (25 mL) were used to obtain **2i** as a yellow-brownish solid (2.46 mmol, 724 mg, 88%). m.p. 53-54 °C.

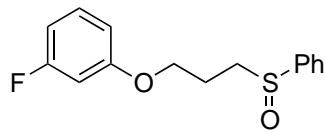
¹H NMR (400 MHz, CDCl₃) δ: 7.66 – 7.69 (m, 2H), 7.49 – 7.57 (m, 2H), 7.15 – 7.24 (m, 3H), 6.74 – 6.80 (m, 2H), 4.02 – 4.09 (m, 1H), 3.95 – 4.02 (m, 1H), 3.00 – 3.14 (m, 1H), 2.84 – 2.98 (m, 1H), 2.17 – 2.35 (m, 1H), 1.99 – 2.16 (m, 1H).

¹³C NMR (100 MHz CDCl₃) δ: 157.3, 143.8, 131.2, 129.5, 129.4, 125.9, 124.1, 115.9, 66.6, 53.8, 22.3.

FT-IR (neat) ν(cm⁻¹): 3052, 2943, 1477, 1087, 1242, 1022, 740, 690, 543.

HRMS (ESI): Calcd. for C₁₅H₁₅ClO₂S (M+Na⁺), 317.0379; found: 317.0360.

1-Fluoro-3-(3-(phenylsulfinyl)propoxy)benzene (2j).



According to the general procedure, (3-(3-fluorophenoxy)propyl)(phenyl)sulfide **1j** (1.54 mmol, 403 mg), sodium periodate (2.31 mmol, 494 mg) and MeOH/H₂O (8:2) (14 mL) were used to obtain **2j** as a colorless oil (1.5 mmol, 417 mg, 97%).

¹H NMR (400 MHz, CDCl₃) δ: 7.64 (d, J = 7.1 Hz, 2H), 7.46 – 7.58 (m, 3H), 7.14 – 7.24 (m, 1H), 6.60 – 6.70 (m, 2H), 6.53 – 6.59 (m, 1H), 4.02 – 4.15 (m, 1H), 3.91 – 4.03 (m, 1H), 3.01 – 3.14 (m, 1H), 2.79 – 2.99 (m, 1H), 2.17 – 2.38 (m, 1H), 2.02 – 2.17 (m, 1H).

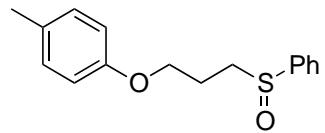
¹³C NMR (100 MHz CDCl₃) δ: 163.7 (d, J = 245.4 Hz), 160.0 (d, J = 10.7 Hz), 143.7, 131.2, 130.4 (d, J = 10.2 Hz), 129.4, 124.1, 110.3 (d, J = 3.0 Hz), 108.0 (d, J = 21.4 Hz), 102.4 (d, J = 24.8 Hz), 66.5, 53.8, 22.2.

¹⁹F NMR (376 MHz, CDCl₃) δ: -112.19 (s).

FT-IR (neat) ν(cm⁻¹): 3059, 2943, 1589, 1489, 1280, 1134, 1026, 744, 682.

HRMS (ESI): Calcd. for C₁₅H₁₅FO₂S (M+Na⁺), 301.0674; found: 301.0685.

1-Methyl-4-(3-(phenylsulfinyl)propoxy)benzene (2k).



According to the general procedure phenyl(3-(*p*-tolyloxy)propyl)sulfide **1k** (2.6 mmol, 671 mg), sodium periodate (3.9 mmol, 834 mg) and MeOH/H₂O (8:2) (24 mL) were used to obtain **2k** as an orange oil (2.02 mmol, 555 mg, 78%).

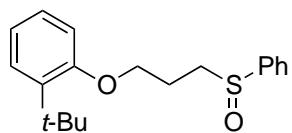
¹H NMR (400 MHz, CDCl₃) δ: 7.60 – 7.66 (m, 2H), 7.48 – 7.56 (m, 3H), 7.06 (d, J = 8.3 Hz, 2H), 6.75 (d, J = 8.5 Hz, 2H), 4.02 – 4.13 (m, 1H), 3.92 – 4.02 (m, 1H), 3.01 – 3.14 (m, 1H), 2.86 – 2.99 (m, 1H), 2.17 – 2.36 (m, 4H), 2.00 – 2.15 (m, 1H).

¹³C NMR (100 MHz CDCl₃) δ: 156.5, 143.8, 131.2, 130.4, 130.0, 129.4, 124.2, 114.5, 66.3, 54.0, 22.4, 20.6.

FT-IR (neat) ν(cm⁻¹): 3050, 2920, 1508, 1234, 1022, 813, 748, 690.

HRMS (ESI): Calcd. for C₁₆H₁₈O₂S (M+Na⁺), 297.0925; found: 297.0928.

1-(tert-butyl)-2-(3-(phenylsulfinyl)propoxy)benzene (2l).



According to the general procedure, (3-(2-(*tert*-butyl)phenoxy)propyl)(phenyl)sulfide **1l** (2.07 mmol, 623 mg, 1.0 equiv), sodium periodate (3.1 mmol, 664 mg, 1.5 equiv) and MeOH/H₂O (8:2) (18 mL) were used to obtain **2l** as a colorless oil (1.97 mmol, 621 mg, 95%).

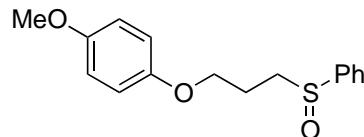
¹H NMR (400 MHz, CDCl₃) δ: 7.64 (d, J = 6.9 Hz, 2H), 7.48 – 7.57 (m, 3H), 7.27 (d, J = 8.8 Hz, 1H), 7.15 (t, J = 7.7 Hz, 1H), 6.90 (t, J = 7.5 Hz, 1H), 6.81 (d, J = 8.1 Hz, 1H), 3.99 – 4.18 (m, 2H), 3.09 – 3.22 (m, 1H), 2.91 – 3.06 (m, 1H), 2.23 – 2.40 (m, 1H), 2.05 – 2.23 (m, 1H), 1.34 (s, 9H).

¹³C NMR (100 MHz CDCl₃) δ: 157.4, 143.6, 137.9, 131.2, 129.4, 127.2, 126.9, 124.1, 120.7, 111.9, 66.1, 54.1, 34.9, 30.0, 22.3.

FT-IR (neat) ν (cm⁻¹): 3055, 2951, 1489, 1442, 1230, 1087, 1026, 744, 690.

HRMS (ESI): Calcd. for C₁₉H₂₄O₂S (M+Na⁺), 339.1395; found: 339.1395.

1-Methoxy-4-(3-(phenylsulfinyl)propoxy)benzene (2m)



According to the general procedure, (3-(4-methoxyphenoxy)propyl) (phenyl)sulfide **1m** (1.38 mmol, 379 mg), sodium periodate (2.07 mmol, 443 mg) and MeOH/H₂O (8:2) (13 mL) were used to obtain **2m** as an orange oil (1.13 mmol, 328 mg, 82%).

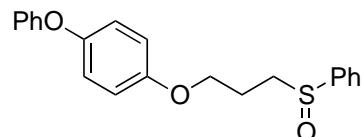
¹H NMR (400 MHz, CDCl₃) δ : 7.58 – 7.75 (m, 2H), 7.45 – 7.59 (m, 3H), 6.80 (d, J = 3.2 Hz, 4H), 4.00 – 4.08 (m, 1H), 3.93 – 4.00 (m, 1H), 3.76 (s, 3H), 3.00 – 3.18 (m, 1H), 2.85 – 3.01 (m, 1H), 2.15 – 2.37 (m, 1H), 1.98 – 2.09 (m, 1H).

¹³C NMR (100 MHz CDCl₃) δ : 154.1, 152.8, 143.8, 131.1, 129.4, 124.2, 115.6, 114.8, 66.9, 55.9, 54.0, 22.4.

FT-IR (neat) ν (cm⁻¹): 3055, 2927, 1504, 1226, 1022, 825, 744, 690.

HRMS (ESI): Calcd. for C₁₆H₁₈O₃S (M+Na⁺), 313.0874; found: 313.0878.

1-Phenoxy-4-(3-(phenylsulfinyl)propoxy)benzene (2n)



According to the general procedure, (3-(4-phenoxyphenoxy)propyl) (phenyl)sulfide **1n** (1.78 mmol, 598 mg), sodium periodate (2.67 mmol, 571 mg) and MeOH/H₂O (8:2) (16 mL) were used to obtain **2n** as an orange oil (1.57 mmol, 551 mg, 88%).

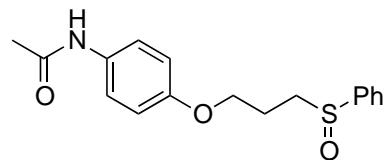
¹H NMR (400 MHz, CDCl₃) δ : 7.65 (d, J = 7.8 Hz, 2H), 7.47 – 7.58 (m, 3H), 7.29 (t, J = 7.8 Hz, 2H), 7.04 (t, J = 7.0 Hz, 1H), 6.94 (t, J = 8.6 Hz, 4H), 6.83 (d, J = 8.0 Hz, 2H), 4.04 – 4.12 (m, 1H), 3.96 – 4.03 (m, 1H), 3.02 – 3.14 (m, 1H), 2.87 – 3.00 (m, 1H), 2.20 – 2.36 (m, 1H), 2.01 – 2.17 (m, 1H).

¹³C NMR (100 MHz CDCl₃) δ : 158.5, 154.9, 150.6, 143.8, 131.2, 129.8, 129.4, 124.2, 122.7, 120.9, 117.8, 115.7, 66.8, 53.9, 22.4.

FT-IR (neat) ν (cm⁻¹): 2924, 1589, 1485, 1215, 1161, 1022, 748.

HRMS (ESI): Calcd. for C₂₁H₂₀O₃S (M+Na⁺), 375.1031; found: 375.1036.

N-(4-(3-(phenylsulfinyl)propoxy)phenyl)acetamide (2o)



According to the general procedure, N-(4-(3-(phenylthio)propoxy)phenyl) acetamide **1o** (2.65 mmol, 798 mg), sodium periodate (3.98 mmol, 851 mg) and MeOH/H₂O (8:2) (24 mL) were used to obtain **2o** as a white solid (2.65 mmol, 840 mg, 100%). m.p. 131–133 °C.

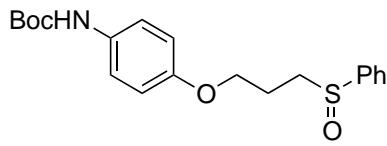
¹H NMR (400 MHz, CDCl₃) δ : 7.59 – 7.66 (m, 2H), 7.48 – 7.56 (m, 3H), 7.33 – 7.40 (m, 2H), 6.74 – 6.81 (m, 2H), 4.00 – 4.09 (m, 1H), 3.91 – 4.00 (m, 1H), 2.99 – 3.11 (m, 1H), 2.86 – 2.98 (m, 1H), 2.30 – 2.19 (m, 1H), 2.14 (s, 3H), 1.98 – 2.11 (m, 1H).

¹³C NMR (100 MHz CDCl₃) δ : 168.4, 155.4, 143.6, 131.5, 131.2, 129.4, 124.2, 122.0, 114.9, 66.5, 53.9, 24.5, 22.3.

FT-IR (neat) ν (cm⁻¹): 3313, 3074, 2873, 1670, 1508, 1234, 1041, 1018, 837, 690.

HRMS (ESI): Calcd. for C₁₇H₁₉NO₃S (M+Na⁺), 340.0983; found: 340.0975.

tert-butyl (4-(3-(phenylsulfinyl)propoxy)phenyl)carbamate (2p).



According to the general procedure, *tert*-butyl (4-(3-(phenylthio)propoxy)phenyl)carbamate **1p** (2.2 mmol, 791 mg), sodium periodate (3.3 mmol, 706 mg, 1.5 equiv) and MeOH/H₂O (8:2) (20 mL) were used to obtain **2p** as an orange oil (1.78 mmol, 669 mg, 81%). m.p. 106–107 °C.

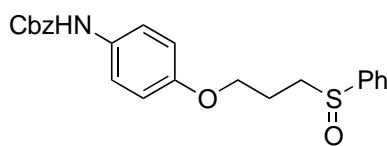
¹H NMR (400 MHz, CDCl₃) δ: 7.59 – 7.67 (m, 2H), 7.46 – 7.56 (m, 4H), 7.24 (d, *J* = 8.8 Hz, 1H), 6.73 – 6.81 (m, 2H), 4.00 – 4.08 (m, 1H), 3.92 – 4.00 (m, 1H), 2.99 – 3.12 (m, 1H), 2.84 – 2.99 (m, 1H), 2.17 – 2.32 (m, 1H), 1.97 – 2.15 (m, 1H), 1.50 (s, 9H).

¹³C NMR (100 MHz CDCl₃) δ: 154.7, 153.2, 143.8, 131.9, 131.2, 129.4, 124.2, 120.6, 115.0, 80.4, 66.6, 53.9, 28.5, 22.3.

FT-IR (neat) ν(cm⁻¹): 3271, 3055, 2974, 1712, 1512, 1226, 1157, 1018, 744, 690.

HRMS (ESI): Calcd. for C₂₀H₂₅NO₄S (M+Na⁺), 398.1402; found: 398.1399.

Benzyl (4-(3-(phenylsulfinyl)propoxy)phenyl)carbamate (2q).



According to the general procedure, benzyl (4-(3-(phenylthio)propoxy)phenyl)carbamate **1q** (0.66 mmol, 257.7 mg), sodium periodate (0.99 mmol, 212 mg) and MeOH/H₂O (8:2) (6 mL) were used to obtain **2q** as a white solid (0.49 mmol, 200 mg, 74%). m.p. 144–145 °C.

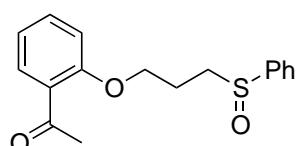
¹H NMR (400 MHz, CDCl₃) δ: 7.58 – 7.71 (m, 2H), 7.46 – 7.56 (m, 3H), 7.31 – 7.43 (m, 5H), 7.24 – 7.29 (m, 2H), 6.72 – 6.84 (m, 2H), 6.59 (br, 1H), 5.18 (s, 2H), 4.01 – 4.10 (m, 1H), 3.92 – 4.05 (m, 1H), 2.97 – 3.13 (m, 1H), 2.83 – 3.00 (m, 1H), 2.16 – 2.34 (m, 1H), 1.95 – 2.15 (m, 1H).

¹³C NMR (100 MHz CDCl₃) δ: 155.0 (C), 153.8 (C), 143.7 (C), 136.3 (C), 131.2 (CH), 129.4 (CH), 128.8 (CH), 128.5 (CH), 128.4 (CH), 124.2 (CH), 120.8 (C), 115.1 (CH), 67.1 (CH₂), 66.6 (CH₂), 53.9 (CH₂), 22.4 (CH₂).

FT-IR (neat) ν(cm⁻¹): 3290, 3062, 2962, 1716, 1516, 1215, 1045, 1022, 752, 690.

HRMS (ESI): Calcd. for C₂₃H₂₃NO₄S (M+Na⁺), 432.1245; found: 432.1245.

1-(2-(3-(phenylsulfinyl)propoxy)phenyl)ethanone (2r).



According to the general procedure, 1-(2-(3-(phenylthio)propoxy)phenyl)ethanone **1r** (1.5 mmol, 429 mg), sodium periodate (2.25 mmol, 481 mg) and MeOH/H₂O (8:2) (14 mL) were used to obtain **2r** as a colorless oil (1.11 mmol, 317 mg, 74%).

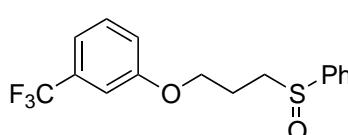
¹H NMR (400 MHz, CDCl₃) δ: 7.69 (d, *J* = 7.6 Hz, 1H), 7.63 (d, *J* = 6.8 Hz, 2H), 7.49 – 7.57 (m, 3H), 7.43 (t, *J* = 7.3 Hz, 1H), 7.00 (t, *J* = 7.5 Hz, 1H), 6.89 (d, *J* = 8.4 Hz, 1H), 4.07 – 4.25 (m, 2H), 3.03 – 3.17 (m, 1H), 2.87 – 3.01 (m, 1H), 2.53 (s, 3H), 2.28 – 2.42 (m, 1H), 2.09 – 2.24 (m, 1H).

¹³C NMR (100 MHz CDCl₃) δ: 199.7, 157.7, 143.5, 133.8, 131.3, 130.6, 129.5, 128.6, 124.1, 121.1, 112.4, 66.9, 53.5, 32.0, 22.1.

FT-IR (neat) ν(cm⁻¹): 3050, 2245, 1670, 1597, 1450, 1296, 1238, 1165, 1041, 690.

HRMS (ESI): Calcd. for C₁₇H₁₈O₃S (M+Na⁺), 325.0874; found: 325.0864.

1-(3-(phenylsulfinyl)propoxy)-3-(trifluoromethyl)benzene (2s).



According to the general procedure, phenyl(3-(3-(trifluoromethyl)phenoxy)propyl)sulfide **1s** (2.57 mmol, 802 mg), sodium

periodate (3.85 mmol, 823 mg) and MeOH/H₂O (8:2) (23 mL) were used to obtain **2s** as a white solid (2.29 mmol, 750 mg, 89%). m.p. 64–65 °C.

¹H NMR (400 MHz, CDCl₃) δ: 7.64 (d, *J* = 7.5 Hz, 2H), 7.46 – 7.57 (m, 3H), 7.37 (t, *J* = 8.0 Hz, 1H), 7.20 (d, *J* = 7.7 Hz, 1H), 7.07 (s, 1H), 7.01 (d, *J* = 8.2 Hz, 1H), 4.08 – 4.15 (m, 1H), 4.01 – 4.08 (m, 1H), 2.99 – 3.16 (m, 1H), 2.84 – 3.00 (m, 1H), 2.21 – 2.43 (m, 1H), 1.99 – 2.20 (m, 1H).

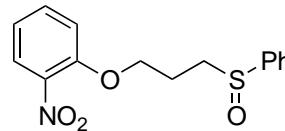
¹³C NMR (100 MHz CDCl₃) δ: 158.7, 143.6, 132.0 (q, *J* = 32.4 Hz), 131.2, 130.2, 129.4, 124.1, 124.0 (q, *J* = 272.4 Hz), 117.9, 117.8 (q, *J* = 3.8 Hz), 111.4 (q, *J* = 3.8 Hz), 66.5, 53.6, 22.2.

¹⁹F NMR (376 MHz, CDCl₃) δ: -63.49 (s).

FT-IR (neat) ν(cm⁻¹): 3051, 2933, 1587, 1440, 1235, 1035, 1022, 692.

HRMS (ESI): Calcd. for C₁₆H₁₅F₃O₂S (M+Na⁺), 351.0643; found: 351.0648.

1-Nitro-2-(3-(phenylsulfinyl)propoxy)benzene (2t).



According to the general procedure, (3-(2-nitrophenoxy)propyl)(phenyl)sulfide **1t** (1.85 mmol, 534 mg), sodium periodate (2.78 mmol, 594 mg) and MeOH/H₂O (8:2) (17 mL) were used to obtain **2t** as a white solid (1.55 mmol, 449 mg, 84%). m.p. 58–59 °C.

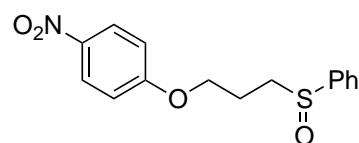
¹H NMR (400 MHz, CDCl₃) δ: 7.84 (d, *J* = 8.3 Hz, 1H), 7.64 (d, *J* = 7.4 Hz, 2H), 7.43 – 7.56 (m, 4H), 6.98 – 7.07 (m, 2H), 4.21 – 4.33 (m, 1H), 4.08 – 4.22 (m, 1H), 3.09 – 3.30 (m, 1H), 2.89 – 3.07 (m, 1H), 2.28 – 2.44 (m, 1H), 2.08 – 2.25 (m, 1H).

¹³C NMR (100 MHz CDCl₃) δ: 152.0, 143.5, 139.9, 134.4, 131.1, 129.4, 125.9, 124.1, 120.8, 114.6, 67.6, 53.0, 22.1.

FT-IR (neat) ν(cm⁻¹): 3055, 2939, 1604, 1519, 1346, 1249, 1014, 740, 690.

HRMS (ESI): Calcd. for C₁₅H₁₅NO₄S (M+Na⁺), 328.0619; found: 328.0628.

1-Nitro-4-(3-(phenylsulfinyl)propoxy)benzene (2u).



According to the general procedure, 4-(3-(phenylthio)propoxy)phenyl nitrate **1u** (1.6 mmol, 462 mg), sodium periodate (2.4 mmol, 513 mg) and MeOH/H₂O (8:2) (15 mL) were used to obtain **2u** as a white solid (1.6 mmol, 488 mg, 100%). m.p. 109–110 °C.

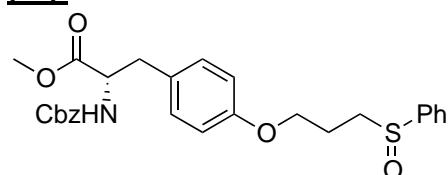
¹H NMR (400 MHz, CDCl₃) δ: 8.18 (d, *J* = 9.2 Hz, 2H), 7.60 – 7.68 (m, 2H), 7.47 – 7.59 (m, 3H), 6.91 (d, *J* = 9.2 Hz, 2H), 4.15 – 4.22 (m, 1H), 4.08 – 4.15 (m, 1H), 3.03 – 3.14 (m, 1H), 2.88 – 2.99 (m, 1H), 2.27 – 2.41 (m, 1H), 2.08 – 2.22 (m, 1H).

¹³C NMR (100 MHz CDCl₃) δ: 163.6, 143.5, 141.9, 131.3, 129.5, 126.1, 124.1, 114.5, 67.1, 53.3, 22.1.

FT-IR (neat) ν(cm⁻¹): 3074, 2951, 1589, 1504, 1300, 1107, 1249, 1018, 856, 744, 690.

HRMS (ESI): Calcd. for C₁₅H₁₅NO₄S (M+Na⁺), 328.0619; found: 328.0621.

(2S)-Methyl 2-(((benzyloxy)carbonyl)amino)-3-(4-(3-(phenylsulfinyl)propoxy)phenyl)propanoate (2v).



According to the general procedure, methyl 2-(((benzyloxy)carbonyl)amino)-3-(4-(3-(phenylthio)propoxy)phenyl)propanoate **1v** (0.7 mmol, 339 mg), sodium periodate (1.05 mmol, 224 mg) and MeOH/H₂O (7:3) (6 mL) were used to obtain **2v** as a colorless oil. (0.58 mmol, 288 mg, 83%).

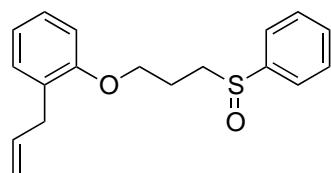
¹H NMR (400 MHz, CDCl₃) δ: 7.59 – 7.71 (m, 2H), 7.44 – 7.57 (m, 3H), 7.29 – 7.38 (m, 5H), 6.98 (d, *J* = 8.6 Hz, 2H), 6.75 (d, *J* = 8.6 Hz, 2H), 5.20 (d, *J* = 8.3 Hz, 1H), 5.09 (d, *J* = 2.8 Hz, 2H), 4.52 – 4.68 (m, 1H), 4.01 – 4.10 (m, 1H), 3.92 – 4.00 (m, 1H), 3.72 (s, 3H), 2.98 – 3.14 (m, 3H), 2.86 – 2.99 (m, 1H), 2.18 – 2.36 (m, 1H), 1.98 – 2.15 (m, 1H).

^{13}C NMR (100 MHz CDCl_3) δ : 172.1 (C), 157.8 (C), 155.7 (C), 143.7 (C), 136.4 (C), 131.2 (CH), 130.4 (CH), 129.4 (CH), 128.7 (CH), 128.3 (CH), 128.2 (CH), 128.1 (C), 124.2 (CH), 114.7 (CH), 67.1 (CH_2), 66.2 (CH_2), 55.0 (CH), 53.9 (CH_2), 52.5 (CH_3), 37.5 (CH_2), 22.4 (CH_2).

FT-IR (neat) $\nu(\text{cm}^{-1})$: 3267, 3055, 2951, 1712, 1512, 1238, 1211, 1022, 744, 694.

HRMS (ESI): Calcd. for $\text{C}_{27}\text{H}_{29}\text{NO}_6\text{S}$ ($\text{M}+\text{Na}^+$), 518.1613; found: 518.1604.

1-Allyl-2-(3-(phenylsulfinyl)propoxy)benzene (2w).



According to the general procedure, (3-(2-allylphenoxy)propyl)(phenyl)sulfide **1w** (1.17 mmol, 500 mg), sodium periodate (2.64 mmol, 564 mg) and MeOH/H₂O (8:2) (12 mL) were used to obtain **2w** as a colorless oil (0.92 mmol, 277 mg, 79%).

^1H NMR (400 MHz, CDCl_3) δ : 7.63 (dd, $J = 7.9, 1.6$ Hz, 2H), 7.45 – 7.58 (m, 3H), 7.06 – 7.21 (m, 2H), 6.90 (t, $J = 7.4$ Hz, 1H), 6.78 (d, $J = 8.1$ Hz, 1H), 6.01 – 6.85 (m, 1H), 4.99 – 5.04 (m, 1H), 4.92 – 4.99 (m, 1H), 4.06 – 4.13 (m, 1H), 3.96 – 4.05 (m, 1H), 3.33 (d, $J = 6.5$ Hz, 2H), 3.04 – 3.16 (m, 1H), 2.88 – 3.00 (m, 1H), 2.20 – 2.36 (m, 1H), 2.02 – 2.18 (m, 1H).

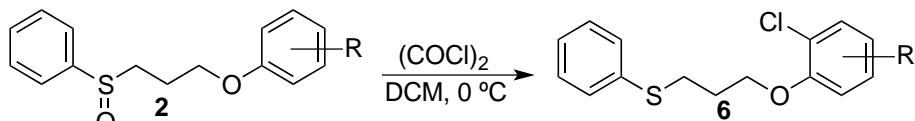
^{13}C NMR (100 MHz CDCl_3) δ : 156.2, 143.8, 137.1, 131.2, 130.1, 129.4, 128.6, 127.5, 124.1, 121.0, 115.5, 111.2, 66.1, 53.9, 34.6, 22.4.

FT-IR (neat) $\nu(\text{cm}^{-1})$: 3059, 2912, 1597, 1492, 1442, 1238, 1022, 748, 690.

HRMS (ESI): Calcd. for $\text{C}_{18}\text{H}_{20}\text{O}_2\text{S}$ ($\text{M}+\text{Na}^+$), 300.1184; found: 300.1190.

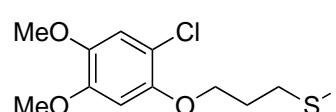
3. Reductive Chlorination: Synthesis of Chlorinated Sulfides

3.1 General Procedure



To a solution of the corresponding sulfoxide **2** (1 equiv.) in dry DCM at 0°C, oxalyl chloride (1.2 equiv) was added. The mixture was stirred at the same temperature for 1 hour (complete conversion was observed by TLC). Then, NaOH (1M) was added to neutralize. The aqueous layer was extracted with DCM (3 x 20 mL) and the combined organic extracts were combined, washed with brine, dried over anhydrous Na_2SO_4 , filtered and concentrated under reduced pressure. The crude mixture was purified using flash chromatography to afford the pure product **6**.

(3-(2-Chloro-4,5-dimethoxyphenoxy)propyl)(phenyl)sulfide (6a).



According to the general procedure, 1,2-Dimethoxy-4-(3-(phenylsulfinyl)propoxy)benzene **2a** (1 mmol, 320 mg), oxalyl chloride (1.2 mmol, 0.1 mL) and DCM (6.0 mL) were used to obtain **6a** as a yellow oil (0.99 mmol, 335 mg, 99%).

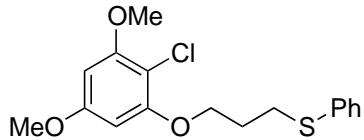
^1H NMR (400 MHz, CDCl_3) δ : 7.35 (d, $J = 7.6$ Hz, 2H), 7.21 – 7.29 (m, 2H), 7.15 (t, $J = 7.3$ Hz, 1H), 6.87 (s, 1H), 6.53 (s, 1H), 4.09 (t, $J = 5.9$ Hz, 2H), 3.82 (d, $J = 4.7$ Hz, 6H), 3.18 (t, $J = 7.0$ Hz, 2H), 1.88 – 2.34 (m, 2H).

^{13}C NMR (101 MHz, CDCl_3) δ : 148.6, 148.5, 144.0, 136.3, 129.2, 129.1, 126.1, 114.2, 113.7, 101.1, 68.8, 56.7, 56.4, 30.1, 29.3.

FT-IR (neat) $\nu(\text{cm}^{-1})$: 3055, 2935, 1504, 1438, 1168, 1026, 736, 690.

HRMS (ESI): Calcd. for $\text{C}_{17}\text{H}_{19}\text{ClO}_3\text{S}$ ($\text{M}+\text{Na}^+$), 361.0641; found: 361.0645.

(3-(2-Chloro-3,5-dimethoxyphenoxy)propyl)(phenyl)sulfide (6b).



According to the general procedure, 1,3-Dimethoxy-5-(3-(phenylsulfinyl)propoxy)benzene **2b** (1.05 mmol, 336 mg), oxalyl chloride (1.26 mmol, 0.1 mL) and DCM (6.4 mL) were used to obtain **6b** as a colorless oil (1.02 mmol, 345 mg, 97%).

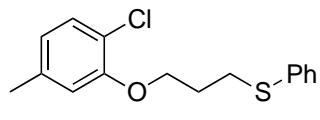
¹H NMR (400 MHz, CDCl₃) δ: 7.29 – 7.39 (m, 2H), 7.19 – 7.29 (m, 2H), 7.06 – 7.19 (m, 1H), 6.17 (d, *J* = 2.7 Hz, 1H), 6.14 (d, *J* = 2.5 Hz, 1H), 4.10 (t, *J* = 5.9 Hz, 2H), 3.87 (s, 3H), 3.78 (s, 3H), 3.18 (t, *J* = 7.0 Hz, 2H), 2.02 – 2.30 (m, 2H).

¹³C NMR (100 MHz, CDCl₃) δ: 159.4, 156.7, 155.9, 136.2, 129.1, 129.1, 126.0, 103.4, 92.7, 92.0, 67.3, 56.4, 56.7, 29.9, 29.0.

FT-IR (neat) u(cm⁻¹): 3050, 2939, 1585, 1438, 1230, 1161, 1041, 1118, 736, 690.

HRMS (ESI): Calcd. for C₁₇H₁₉ClO₃S (M+Na⁺), 361.0641; found: 361.0644.

(3-(2-Chloro-5-methylphenoxy)propyl)(phenyl)sulfide (6c).



According to the general procedure, 1-methyl-3-(3-(phenylsulfinyl)propoxy)benzene **2c** (1.02 mmol, 262 mg), oxalyl chloride (1.22 mmol, 0.1 mL) and DCM (4.8 mL) were used to obtain **6c** as a colorless oil (1.01 mmol, 298 mg, 99%).

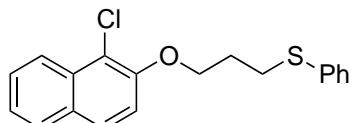
¹H NMR (400 MHz, CDCl₃) δ: 7.32 – 7.38 (m, 2H), 7.24 – 7.31 (m, 2H), 7.14 – 7.23 (m, 2H), 6.75 (d, *J* = 3.0 Hz, 1H), 6.65 (dd, *J* = 8.7, 3.0 Hz, 1H), 4.03 (t, *J* = 6.0 Hz, 2H), 3.11 (t, *J* = 7.1 Hz, 2H), 2.33 (s, 3H), 1.99 – 2.18 (m, 2H).

¹³C NMR (100 MHz CDCl₃) δ: 157.5, 137.1, 136.2, 129.7, 129.4, 129.1, 126.2, 126.0, 117.2, 113.2, 66.4, 30.3, 29.0, 20.5.

FT-IR (neat) u(cm⁻¹): 3055, 2947, 1577, 1477, 1242, 1168, 1029, 736, 690.

HRMS (ESI): Calcd. for C₁₆H₁₇ClOS (M+Na⁺), 315.0586; found: 315.0588.

(3-((1-Choronaphthalen-2-yl)oxy)propyl)(phenyl)sulfide (6d).



According to the general procedure, 2-(3-(phenylsulfinyl)propoxy)naphthalene **2d** (1 mmol, 310 mg), oxalyl chloride (1.2 mmol, 0.1 mL) and DCM (6 mL) were used to obtain **6d** as an orange oil (0.98 mmol, 322 mg, 98%).

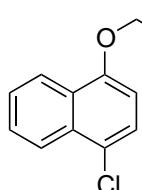
¹H NMR (400 MHz, CDCl₃) δ: 8.22 (d, *J* = 8.5 Hz, 1H), 7.79 (d, *J* = 8.2 Hz, 1H), 7.73 (d, *J* = 8.9 Hz, 1H), 7.52 – 7.62 (m, 1H), 7.46 – 7.33 (m, 3H), 7.31 – 7.20 (m, 3H), 7.14 (t, *J* = 7.4 Hz, 1H), 4.29 (t, *J* = 5.9 Hz, 2H), 3.24 (t, *J* = 7.1 Hz, 2H), 2.25 – 2.14 (m, 2H).

¹³C NMR (100 MHz, CDCl₃) δ: 152.0, 136.3, 132.1, 129.9, 129.3, 129.1, 128.2, 128.1, 127.6, 126.1, 124.6, 123.7, 117.9, 115.4, 68.3, 30.1, 29.4.

FT-IR (neat) u(cm⁻¹): 3070, 2943, 1589, 1462, 1354, 1242, 1022, 782, 686, 520.

HRMS (ESI): Calcd. for C₁₉H₁₇ClOS (M+Na⁺), 351.0586; found: 351.0588.

(3-((4-Choronaphthalen-1-yl)oxy)propyl)(phenyl)sulfane (6e).



According to the general procedure, 1-(3-(phenylsulfinyl)propoxy)naphthalene **2e** (1.06 mmol, 329 mg), oxalyl chloride (1.27 mmol, 0.1 mL) and DCM (6 mL) were used to obtain **6e** as an orange oil (1.04 mmol, 342 mg, 98%).

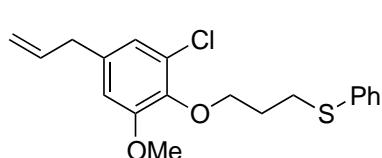
¹H NMR (400 MHz, CDCl₃) δ: 8.25 – 8.29 (m, 1H), 8.17 – 8.22 (m, 1H), 7.58 – 7.65 (m, 1H), 7.49 – 7.57 (m, 1H), 7.34 – 7.46 (m, 3H), 7.21 – 7.31 (m, 2H), 7.13 – 7.21 (m, 1H), 6.68 (d, J = 8.3 Hz, 1H), 4.19 – 4.26 (m, 2H), 3.22 (t, J = 7.1 Hz, 2H), 2.17 – 2.31 (m, 2H).

¹³C NMR (100 MHz, CDCl₃) δ: 153.8, 136.2, 131.5, 129.5, 129.1, 127.6, 126.8, 126.3, 126.1, 125.9, 124.4, 123.4, 122.5, 104.9, 66.6, 30.6, 29.1.

FT-IR (neat) u(cm⁻¹): 3055, 2927, 1585, 1373, 1261, 1238, 1083, 736, 690, 524.

HRMS (ESI): Calcd. for C₁₉H₁₇ClOS (M+Na⁺), 351.0586; found: 351.0574.

(3-(4-Allyl-2-chloro-6-methoxyphenoxy)propyl)(phenyl)sulfane (6f).



According to the general procedure, 4-allyl-2-methoxy-1-(3-(phenylsulfinyl)propoxy)benzene **2f** (0.56 mmol, 196 mg), oxalyl chloride (0.71 mmol, 0.05 mL) and DCM (3.5 mL) were used to obtain **6f** as a colorless oil (0.34 mmol, 117 mg, 60%).

¹H NMR (400 MHz, CDCl₃) δ: 7.33 – 7.40 (m, 2H), 7.24 – 7.31 (m, 2H), 7.13 – 7.21 (m, 1H), 6.85 (s, 1H), 6.70 (s, 1H), 5.88 – 6.02 (m, 1H), 4.92 – 5.27 (m, 2H), 4.09 (t, J = 6.2 Hz, 2H), 3.83 (s, 3H), 3.42 (d, J = 6.4 Hz, 2H), 3.13 (t, J = 7.0 Hz, 2H), 1.98 – 2.30 (m, 2H).

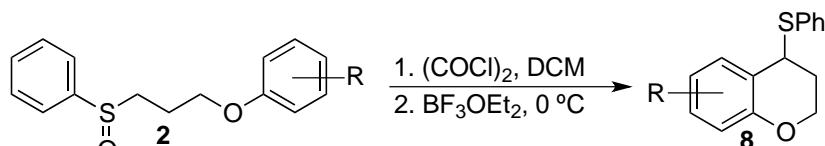
¹³C NMR (100 MHz CDCl₃) δ: 148.4, 147.3, 136.2, 136.0, 129.9, 129.4, 129.1, 126.2, 124.9, 116.3, 114.6, 113.6, 67.6, 56.3, 37.4, 30.2, 28.8.

FT-IR (neat) u(cm⁻¹): 3074, 2935, 1581, 1504, 1257, 1165, 1026, 736, 690.

HRMS (ESI): Calcd. for C₁₉H₂₁ClO₂S (M+Na⁺), 371.0848; found: 371.0855.

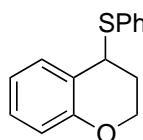
4. Classic Pummerer cyclization: Synthesis of Chromanes

4.1 General Procedure



To a solution of the corresponding sulfoxide **2** (1 equiv.) in dry DCM at 0°C, oxalyl chloride (1.2 equiv) was added. The mixture was stirred at the same temperature for 1 hour (complete conversion was observed by TLC). Then, BF₃.OEt₂ (3 equiv) was added and the reaction mixture was stirred for 1 hour. The reaction was quenched with NaOH (1M). The aqueous layer was extracted with DCM (3 x 15 mL), the combined organic extracts were washed with brine, dried over anhydrous Na₂SO₄, filtered and concentrated under reduced pressure. The crude mixture was purified using flash chromatography to afford the pure product **8**.

4-(Phenylthio)chromane (8g).



According to the general procedure, ((3-phenoxypropyl)sulfinyl)benzene **2g** (4.16 mmol, 1.08 g), oxalyl chloride (5.0 mmol, 0.4 mL), boron trifluoride diethyl etherate (12.48 mmol, 1.6 mL) and DCM (20.0 mL) were used to obtain **8g** as a colorless oil (3.6 mmol, 886 mg, 88%).

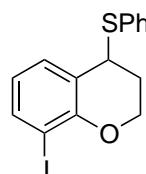
¹H NMR (400 MHz, CDCl₃) δ: 7.47 (d, J = 7.1 Hz, 2H), 7.27 – 7.40 (m, 4H), 7.09 – 7.20 (m, 1H), 6.88 (t, J = 7.5 Hz, 1H), 6.82 (t, J = 8.2 Hz, 1H), 4.42 – 4.67 (m, 2H), 4.06 – 4.30 (m, 1H), 2.15 – 2.43 (m, 1H), 1.86 – 2.12 (m, 1H).

¹³C NMR (100 MHz CDCl₃) δ: 155.1, 134.9, 132.2, 131.1, 129.3, 129.1, 127.5, 120.9, 120.4, 117.2, 62.3, 42.9, 27.8.

FT-IR (neat) ν (cm⁻¹): 3050, 2931, 1607, 1581, 1452, 1315, 1269, 1230, 1117, 1045, 779, 748.

HRMS (ESI): Calcd. for C₁₅H₁₄OS (M+Na⁺), 265.0663; found: 265.0670.

8-Iodo-4-(phenylthio)chromane (8h).



According to the general procedure, 1-iodo-2-(3-(phenylsulfinyl)propoxy)benzene **2h** (1 mmol, 385 mg), oxalyl chloride (1.2 mmol, 0.1 mL), boron trifluoride diethyl etherate (3 mmol, 0.37 mL) and DCM (6.5 mL) were used to obtain **8h** as a colorless oil (0.95 mmol, 349 mg, 95%).

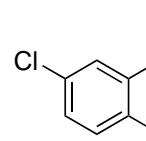
¹H NMR (400 MHz, CDCl₃) δ : 7.65 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.42 – 7.49 (m, 3H), 7.28 – 7.38 (m, 3H), 6.64 (t, *J* = 7.8 Hz, 1H), 4.59 (td, *J* = 11.3, 2.2 Hz, 1H), 4.42 – 4.49 (m, 1H), 4.20 – 4.30 (m, 1H), 2.15 – 2.35 (m, 1H), 1.97 – 2.11 (m, 1H).

¹³C NMR (100 MHz CDCl₃) δ : 153.8, 138.9, 134.5, 132.6, 131.4, 129.4, 127.9, 122.0, 121.9, 85.5, 63.5, 43.3, 27.7.

FT-IR (neat) ν (cm⁻¹): 3055, 2916, 1469, 1435, 1234, 1080, 1014, 736, 690.

HRMS (ESI): Calcd. for C₁₅H₁₃IOS (M+Na⁺), 390.9629; found: 390.9619.

6-Chloro-4-(phenylthio)chromane (8i).



According to the general procedure, 1-chloro-4-(3-(phenylsulfinyl)propoxy)benzene **2i** (1.02 mmol, 300 mg), oxalyl chloride (1.22 mmol, 0.1 mL), boron trifluoride diethyl etherate (3.06 mmol, 0.38 mL) and DCM (6.9 mL) were used to obtain **8i** as a colorless oil (0.88 mmol, 243 mg, 86%).

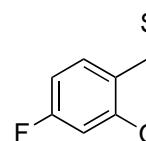
¹H NMR (400 MHz, CDCl₃) δ : 7.45 (d, *J* = 7.4 Hz, 2H), 7.27 – 7.40 (m, 4H), 7.09 (dd, *J* = 8.8, 2.8 Hz, 1H), 6.75 (d, *J* = 8.7 Hz, 1H), 4.33 – 4.61 (m, 2H), 4.09 – 4.32 (m, 1H), 2.13 – 2.27 (m, 1H), 1.96 – 2.06 (m, 1H).

¹³C NMR (100 MHz CDCl₃) δ : 153.8, 134.4, 132.7, 130.5, 129.4, 129.1, 128.0, 125.1, 122.5, 118.6, 62.5, 43.0, 27.6.

FT-IR (neat) ν (cm⁻¹): 3071, 2928, 2882, 1578, 1481, 1261, 1227, 741, 690.

HRMS (ESI): Calcd. for C₁₅H₁₃ClOS (M+Na⁺), 299.0273; found: 299.0280.

7-Fluoro-4-(phenylthio)chromane (8j).



According to the general procedure, 1-fluoro-3-(3-(phenylsulfinyl)propoxy)benzene **2j** (1.02 mmol, 285 mg), oxalyl chloride (1.22 mmol, 0.1 mL), boron trifluoride diethyl etherate (3.06 mmol, 0.38 mL) and DCM (5.4 mL) were used to obtain **8j** as a colorless oil (1 mmol, 260 mg, 98%).

¹H NMR (400 MHz, CDCl₃) δ : 7.45 (d, *J* = 8.1 Hz, 2H), 7.20 – 7.39 (m, 4H), 6.38 – 6.81 (m, 2H), 4.37 – 4.58 (m, 2H), 4.09 – 4.32 (m, 1H), 2.10 – 2.36 (m, 1H), 1.89 – 2.12 (m, 1H).

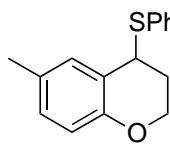
¹³C NMR (100 MHz CDCl₃) δ : 162.8 (d, *J* = 245.8 Hz), 156.2 (d, *J* = 12.2 Hz), 134.6, 132.5, 132.1 (d, *J* = 10.1 Hz), 129.3, 127.8, 116.9 (d, *J* = 3.1 Hz), 107.9 (d, *J* = 22.0 Hz), 104.2 (d, *J* = 24.3 Hz), 62.4, 42.6, 27.6.

¹⁹F NMR (376 MHz, CDCl₃) δ : -113.23 (s).

FT-IR (neat) ν (cm⁻¹): 3074, 2912, 1593, 1496, 1261, 1141, 1037, 737, 690.

HRMS (ESI): Calcd. for C₁₅H₁₃FOS (M+Na⁺), 283.0569; found: 283.0567.

6-Methyl-4-(phenylthio)chromane (8k).



According to the general procedure, 1-methyl-4-(3-(phenylsulfinyl)propoxy)benzene **2k** (1.1 mmol, 301 mg), oxalyl chloride (1.32 mmol, 0.11 mL), boron trifluoride diethyl etherate (3.3 mmol, 0.41 mL) and DCM (5.7 mL) were used to obtain **8k** as a colorless oil (0.77 mmol, 197 mg, 70%).

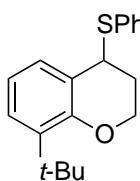
¹H NMR (400 MHz, CDCl₃) δ: 7.47 (dd, *J* = 8.2, 1.2 Hz, 2H), 7.26 – 7.37 (m, 3H), 7.14 (s, 1H), 6.96 (dd, *J* = 8.3, 2.1 Hz, 1H), 6.72 (d, *J* = 8.3 Hz, 1H), 4.42 – 4.62 (m, 2H), 4.10 – 4.30 (m, 1H), 2.17 – 2.30 (m, 4H), 1.93 – 2.06 (m, 1H).

¹³C NMR (100 MHz CDCl₃) δ: 153.0, 135.1, 132.2, 131.3, 129.9, 129.6, 129.3, 127.6, 120.4, 117.0, 62.3, 43.1, 27.9, 20.6.

FT-IR (neat) u(cm⁻¹): 3055, 2920, 1581, 1496, 1230, 1037, 813, 741, 691.

HRMS (ESI): Calcd. for C₁₆H₁₆OS (M+Na⁺), 279.0820; found: 279.0807.

8-(tert-butyl)-4-(phenylthio)chromane (8l).



According to the general procedure, 1-(*tert*-butyl)-2-(3-(phenylsulfinyl)propoxy)benzene **2l** (1.06 mmol, 334 mg), oxalyl chloride (1.27 mmol, 0.1 mL), boron trifluoride diethyl etherate (3.18 mmol, 0.40 mL) and DCM (6.3 mL) were used to obtain **8l** as a pale yellow oil (0.85 mmol, 255 mg, 81%).

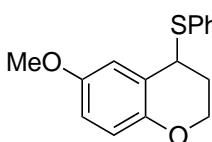
¹H NMR (400 MHz, CDCl₃) δ: 7.46 (d, *J* = 7.5 Hz, 2H), 7.34 (t, *J* = 7.4 Hz, 2H), 7.23 – 7.30 (m, 2H), 7.17 (d, *J* = 7.6 Hz, 1H), 6.83 (t, *J* = 7.7 Hz, 1H), 4.42 – 4.62 (m, 2H), 4.30 (d, *J* = 10.9 Hz, 1H), 2.14 – 2.32 (m, 1H), 1.96 – 2.09 (m, 1H), 1.36 (s, 9H).

¹³C NMR (100 MHz CDCl₃) δ: 154.3, 138.2, 135.3, 132.1, 129.4, 129.3, 127.4, 126.2, 120.9, 119.7, 61.6, 43.8, 35.1, 29.8, 27.8.

FTIR (neat) u(cm⁻¹): 3059, 2951, 1697, 1581, 1435, 1226, 1026, 737, 690.

HRMS (ESI): Calcd. for C₁₉H₂₂OS (M+Na⁺), 321.1289; found: 321.1267.

6-Methoxy-4-(phenylthio)chromane (8m).



According to the general procedure, 1-methoxy-4-(3-(phenylsulfinyl)propoxy)benzene **2m** (1 mmol, 275 mg), oxalyl chloride (1.2 mmol, 0.1 mL), boron trifluoride diethyl etherate (3 mmol, 0.38 mL) and DCM (5 mL) were used to obtain **8m** as a colorless oil (0.73 mmol, 199 mg, 73%).

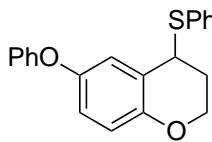
¹H NMR (400 MHz, CDCl₃) δ: 7.41 – 7.52 (m, 2H), 7.28 – 7.39 (m, 3H), 6.81 – 6.88 (m, 1H), 6.75 (d, *J* = 1.6 Hz, 2H), 4.37 – 4.59 (m, 2H), 4.09 – 4.27 (m, 1H), 3.74 (s, 3H), 2.17 – 2.32 (m, 1H), 1.91 – 2.10 (m, 1H).

¹³C NMR (100 MHz CDCl₃) δ: 153.3, 149.2, 134.9, 132.3, 129.3, 127.6, 121.2, 118.0, 116.3, 114.6, 62.4, 55.9, 43.3, 28.1.

FT-IR (neat) u(cm⁻¹): 3055, 2951, 1492, 1265, 1203, 1041, 740, 690.

HRMS (ESI): Calcd. for C₁₆H₁₆O₂S (M+Na⁺), 295.0769; found: 295.0780.

6-Phenoxy-4-(phenylthio)chromane (8n).



According to the general procedure, 1-Phenoxy-4-(3-(phenylsulfinyl)propoxy)benzene **2n** (1.02 mmol, 361 mg), oxalyl chloride (1.2 mmol, 0.1 mL), boron trifluoride diethyl etherate (3 mmol, 0.38 mL) and DCM (6.2 mL) were used to obtain **8n** as an orange oil (0.79 mmol, 264 mg, 77%).

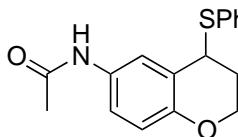
¹H NMR (400 MHz, CDCl₃) δ: 7.43 (d, *J* = 7.4 Hz, 2H), 7.23 – 7.33 (m, 5H), 7.00 – 7.06 (m, 2H), 6.94 (d, *J* = 8.3 Hz, 2H), 6.87 (dd, *J* = 8.8, 3.2 Hz, 1H), 6.80 (d, *J* = 8.8 Hz, 1H), 4.39 – 4.54 (m, 2H), 4.17 – 4.27 (m, 1H), 2.17 – 2.31 (m, 1H), 1.95 – 2.07 (m, 1H).

¹³C NMR (100 MHz CDCl₃) δ: 158.6, 151.4, 149.7, 134.7, 132.6, 129.8, 129.3, 127.8, 122.6, 122.0, 121.8, 121.1, 118.3, 117.8, 62.5, 43.2, 27.9.

FT-IR (neat) ν(cm⁻¹): 3051, 2945, 1589, 1485, 1211, 1142, 1042, 779, 752, 690.

HRMS (ESI): Calcd. for C₂₁H₁₈O₂S (M+Na⁺), 357.0925; found: 357.0914.

N-(4-(Phenylthio)chroman-6-yl)acetamide (8o).



According to the general procedure, *N*-(4-(3-(phenylsulfinyl)propoxy)phenyl) acetamide **2o** (1.01 mmol, 322 mg), oxalyl chloride (1.2 mmol, 0.1 mL), boron trifluoride diethyl etherate (3.03 mmol, 0.38 mL) and DCM (6 mL) were used to obtain **8o** as a colorless oil (0.71 mmol, 212 mg, 70%).

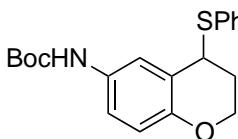
¹H NMR (400 MHz, CDCl₃) δ: 7.50 (d, *J* = 2.7 Hz, 1H), 7.40 – 7.48 (m, 3H), 7.20 – 7.36 (m, 3H), 6.76 (d, *J* = 8.8 Hz, 1H), 4.34 – 4.56 (m, 2H), 4.04 – 4.27 (m, 1H), 2.14 – 2.24 (m, 1H), 2.12 (s, 3H), 1.87 – 2.02 (m, 1H).

¹³C NMR (100 MHz CDCl₃) δ: 168.6, 152.1, 134.7, 132.3, 130.7, 129.3, 127.6, 123.3, 122.3, 121.0, 117.5, 62.4, 43.0, 27.7, 24.4.

FT-IR (neat) ν(cm⁻¹): 3278, 3070, 2924, 1658, 1496, 1230, 1037, 740, 691.

HRMS (ESI): Calcd. for C₁₇H₁₇NO₂S (M+Na⁺), 322.0878; found: 322.0855.

tert-butyl (4-(phenylthio)chroman-6-yl)carbamate (8p).



According to the general procedure, *tert*-butyl (4-(3-(phenylsulfinyl)propoxy)phenyl) carbamate **2p** (1.03 mmol, 388 mg), oxalyl chloride (1.23 mmol, 0.1 mL), boron trifluoride diethyl etherate (3.09 mmol, 0.39 mL) and DCM (6.4 mL) were used to obtain **8p** as an orange oil (0.33 mmol, 118 mg, 32%).

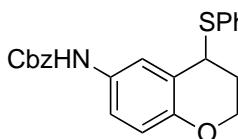
¹H NMR (400 MHz, CDCl₃) δ: 7.42 – 7.48 (m, 3H), 7.26 – 7.37 (m, 3H), 6.75 (d, *J* = 8.8 Hz, 1H), 6.32 – 6.35 (br, 1H), 4.38 – 4.56 (m, 2H), 4.10 – 4.28 (m, 1H), 2.13 – 2.30 (m, 1H), 1.89 – 2.04 (m, 1H), 1.51 (s, 9H).

¹³C NMR (100 MHz CDCl₃) δ: 153.3, 151.3, 134.8, 132.3, 131.1, 129.3, 129.1, 127.6, 121.0, 117.5, 80.4, 62.3, 43.0, 28.5, 27.7.

FTIR (KBr) ν(cm⁻¹): 3332, 3055, 2974, 1697, 1512, 1222, 1153, 1037, 741, 690.

HRMS (ESI): Calcd. for C₂₀H₂₃NO₃S (M+Na⁺), 380.1296; found: 380.1294.

Benzyl (4-(phenylthio)chroman-6-yl)carbamate (8q).



According to the general procedure, benzyl (4-(3-(phenylsulfinyl)propoxy)phenyl) carbamate **2q** (0.46 mmol, 185 mg), oxalyl chloride (0.54 mmol, 0.04 mL), boron trifluoride diethyl etherate (1.62 mmol, 0.2 mL) and DCM (3.3 mL) were used to obtain **8q** as a colorless oil (0.43 mmol, 168 mg, 93%).

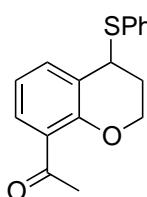
¹H NMR (400 MHz, CDCl₃) δ: 7.23 – 7.50 (m, 11H), 7.14 (d, *J* = 9.4 Hz, 1H), 6.77 (d, *J* = 8.8 Hz, 1H), 6.50 (brs, 1H), 5.19 (s, 2H), 4.39 – 4.55 (m, 2H), 4.16 – 4.28 (m, 1H), 2.14 – 2.32 (m, 1H), 1.92 – 2.07 (m, 1H).

¹³C NMR (100 MHz CDCl₃) δ: 153.9, 151.7, 136.3, 136.3, 134.8, 132.4, 129.3, 128.8, 128.4, 128.4, 127.7, 121.9, 121.3, 117.7, 115.1, 67.1, 62.4, 43.1, 27.8.

FT-IR (neat) u(cm⁻¹): 3313, 3059, 2951, 1705, 1496, 1207, 1056, 736, 690.

HRMS (ESI): Calcd. for C₂₃H₂₁NO₃S (M+Na⁺), 414.1140; found: 414.1148.

1-(4-(Phenylthio)chroman-8-yl)ethanone (8r).



According to the general procedure, 1-(2-(3-(phenylsulfinyl)propoxy)phenyl)ethanone **2r** (1 mmol, 302 mg), oxalyl chloride (1.2 mmol, 0.1 mL), boron trifluoride diethyl etherate (3 mmol, 0.37 mL) and DCM (5.9 mL) were used to obtain **8r** as a colorless oil (0.95 mmol, 270 mg, 95%).

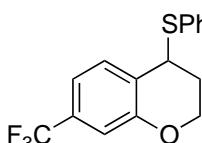
¹H NMR (400 MHz, CDCl₃) δ: 7.61 (d, *J* = 7.7 Hz, 1H), 7.46 (d, *J* = 7.2 Hz, 3H), 7.25 – 7.39 (m, 3H), 6.90 (t, *J* = 7.6 Hz, 1H), 4.47 – 4.70 (m, 2H), 4.29 – 4.44 (m, 1H), 2.59 (s, 3H), 2.18 – 2.35 (m, 1H), 1.97 – 2.11 (m, 1H).

¹³C NMR (100 MHz CDCl₃) δ: 199.8, 154.8, 135.4, 134.4, 132.6, 130.2, 129.4, 128.3, 127.9, 122.0, 120.0, 62.6, 43.2, 32.0, 27.1.

FT-IR (neat) u(cm⁻¹): 3050, 2934, 1670, 1585, 1470, 1439, 1358, 1273, 1084, 737, 690.

HRMS (ESI): Calcd. for C₁₇H₁₆O₂S (M+Na⁺), 307.0769; found: 307.0780.

4-(Phenylthio)-7-(trifluoromethyl)chromane (8s).



According to the general procedure, 1-(3-(phenylsulfinyl)propoxy)-3-(trifluoromethyl)benzene **2s** (1 mmol, 328 mg), oxalyl chloride (1.2 mmol, 0.1 mL), boron trifluoride diethyl etherate (3 mmol, 0.38 mL) and DCM (6.2 mL) were used to obtain **8s** as a colorless oil (0.95 mmol, 294 mg, 95%).

¹H NMR (400 MHz, CDCl₃) δ: 7.47 (d, *J* = 7.5 Hz, 2H), 7.41 (d, *J* = 7.9 Hz, 1H), 7.29 – 7.38 (m, *J* = 9.4, 7.9 Hz, 3H), 7.04 – 7.14 (m, 2H), 4.43 – 4.61 (m, 2H), 4.15 – 4.36 (m, 1H), 2.16 – 2.36 (m, 1H), 1.91 – 2.12 (m, 1H).

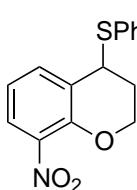
¹³C NMR (100 MHz CDCl₃) δ: 155.2, 134.2, 132.7, 131.20 (q, *J* = 32.6 Hz), 131.6, 129.4, 127.9, 124.8, 123.9 (q, *J* = 272.5 Hz), 116.7 (q, *J* = 3.8 Hz), 114.6 (q, *J* = 4.0 Hz), 62.6, 42.8, 27.4.

¹⁹F NMR (376 MHz, CDCl₃) δ: -63.80 (s).

FT-IR (neat) u(cm⁻¹): 3062, 2881, 1581, 1427, 1323, 1118, 1041, 740, 690.

HRMS (ESI): Calcd. for C₁₆H₁₃F₃OS (M+Na⁺), 333.0537; found: 333.0533.

8-Nitro-4-(phenylthio)chromane (8t).



According to the general procedure, 1-nitro-2-(3-(phenylsulfinyl)propoxy)benzene **2t** (1.06 mmol, 322 mg), oxalyl chloride (1.2 mmol, 0.11 mL), boron trifluoride diethyl etherate (3.18 mmol, 0.4 mL) and DCM (6.1 mL) were used to obtain **8t** as a white solid (0.57 mmol, 164 mg, 54%). m.p. 84–85 °C.

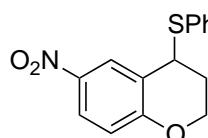
¹H NMR (400 MHz, CDCl₃): 7.70 – 7.78 (m, 1H), 7.51 (dd, *J* = 7.7, 1.9 Hz, 1H), 7.43 – 7.49 (m, 2H), 7.31 – 7.41 (m, 3H), 6.92 (td, *J* = 7.9, 1.8 Hz, 1H), 4.57 – 4.66 (m, 1H), 4.41 – 4.54 (m, 2H), 2.23 – 2.36 (m, 1H), 2.04 – 2.13 (m, 1H).

¹³C NMR (100 MHz CDCl₃) δ: 149.2, 139.3, 135.8, 133.6, 133.0, 129.5, 128.3, 125.3, 124.3, 119.3, 63.4, 42.8, 26.7.

FT-IR (neat) u(cm⁻¹): 3089, 2997, 1608, 1577, 1512, 1242, 1018, 737, 694.

HRMS (ESI): Calcd. for C₁₅H₁₃NO₃S (M+Na⁺), 310.0514; found: 310.0531.

6-Nitro-4-(phenylthio)chromane (8u).



According to the general procedure, 1-nitro-4-(3-(phenylsulfinyl)propoxy)benzene **2u** (1.01 mmol, 309 mg), oxalyl chloride (1.21 mmol, 0.1 mL), boron trifluoride diethyl etherate (3.03 mmol, 0.38 mL) and DCM (5.8 mL) were used to obtain **8u** as a white solid (0.73 mmol, 210 mg, 72%). m.p. 118–119 °C.

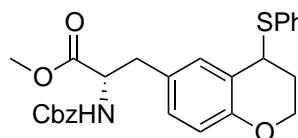
¹H NMR (400 MHz, CDCl₃) δ: 8.19 (d, *J* = 2.7 Hz, 1H), 8.04 (dd, *J* = 9.1, 2.7 Hz, 1H), 7.44 – 7.52 (m, 2H), 7.31 – 7.42 (m, 3H), 6.89 (d, *J* = 9.1 Hz, 1H), 4.61 (td, *J* = 11.4, 2.4 Hz, 1H), 4.48 (s, 1H), 4.31 – 4.42 (m, 1H), 2.19 – 2.30 (m, 1H), 2.04 – 2.13 (m, 1H).

¹³C NMR (100 MHz CDCl₃) δ: 160.4, 141.1, 133.5, 133.4, 129.6, 128.5, 127.3, 124.9, 121.7, 118.0, 63.3, 43.0, 27.0.

FT-IR (neat) u(cm⁻¹): 3078, 2931, 1581, 1508, 1330, 1253, 1026, 1006, 741, 691.

HRMS (ESI): Calcd. for C₁₅H₁₃NO₃S (M+Na⁺), 310.0514; found: 310.0502.

(2*R*)-Methyl 2-(((benzyloxy)carbonyl)amino)-3-(4-(phenylthio)chroman-6-yl)propanoate (8v).



According to the general procedure, (2*R*)-methyl 2-((benzyloxy carbonyl)amino)-3-(4-(3-(phenylsulfinyl)propoxy)phenyl)propanoate **2v** (0.64 mmol, 319 mg), oxalyl chloride (0.77 mmol, 0.06 mL), boron trifluoride diethyl etherate (1.92 mmol, 0.24 mL) and DCM (5.8 mL) were used to obtain **8v** as a colorless oil and as a 1:1 mixture of diastereoisomers (0.56 mmol, 267 mg, 87%).

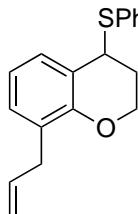
¹H NMR (400 MHz, CDCl₃) δ: 7.40 – 7.48 (m, 2H), 7.27 – 7.38 (m, 8H), 7.09 (d, *J* = 13.6 Hz, 1H), 6.87 (t, *J* = 10.3 Hz, 1H), 6.73 (dd, *J* = 8.3, 3.7 Hz, 1H), 5.23 (t, *J* = 8.3 Hz, 1H), 5.03 – 5.17 (m, 2H), 4.75 – 4.53 (m, 1H), 4.36 – 4.52 (m, 2H), 4.12 – 4.34 (m, 1H), 3.76 and 3.73 (2s, 3H), 2.89 – 3.26 (m, 2H), 2.11 – 2.35 (m, 1H), 2.02 – 1.89 (m, 1H).

¹³C NMR (100 MHz CDCl₃) δ: 172.2, 172.0, 155.8, 155.7, 154.4, 154.3, 136.4, 136.3, 134.8, 134.8, 132.3, 132.3, 131.8, 130.0, 129.9, 129.3, 129.3, 128.7, 128.6, 128.3, 128.3, 128.2, 127.7, 127.6, 127.4, 121.0, 120.9, 117.5, 117.4, 67.1, 67.0, 62.4, 62.3, 55.1, 55.0, 52.6, 52.5, 43.0, 42.9, 37.6, 37.5, 27.8, 27.7.

FT-IR (neat) u(cm⁻¹): 3036, 2924, 1716, 1496, 1234, 1207, 1041, 740, 691.

HRMS (ESI): Calcd. for C₂₇H₂₇NO₅S (M+Na⁺), 500.1508; found: 500.1512.

8-Allyl-4-(phenylthio)chromane (8w).



According to the general procedure, (1-allyl-2-(3-(phenylsulfinyl)propoxy)benzene **2w** (1.3 mmol, 390 mg), oxalyl chloride (1.56 mmol, 0.13 mL), boron trifluoride diethyl etherate (3.9 mmol, 0.49 mL) and DCM (7 mL) were used to obtain **8w** as a colorless oil (1.07 mmol, 301 mg, 82%).

¹H NMR (400 MHz, CDCl₃) δ: 7.47 (d, *J* = 6.9 Hz, 2H), 7.22 – 7.37 (m, 4H), 7.03 (d, *J* = 7.3 Hz, 1H), 6.84 (t, *J* = 7.6 Hz, 1H), 5.89 – 6.10 (m, 1H), 5.01 – 5.11 (m, 2H), 4.46 – 4.57 (m, 2H), 4.24 – 4.34 (m, 1H), 3.34 (d, *J* = 6.6 Hz, 2H), 2.17 – 2.30 (m, 1H), 1.98 – 2.09 (m,

1H).

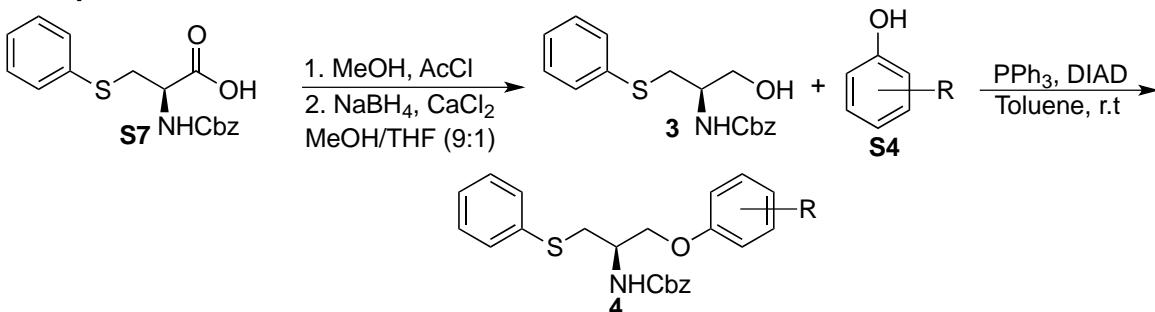
^{13}C NMR (100 MHz CDCl_3) δ : 152.9, 136.9, 135.1, 132.2, 129.3, 129.3, 129.2, 128.4, 127.5, 120.5, 120.0, 115.6, 62.3, 43.3, 34.2, 27.8.

FT-IR (neat) $\nu(\text{cm}^{-1})$: 3070, 2920, 2877, 1473, 1585, 1446, 1222, 1033, 748, 690.

HRMS (ESI): Calcd. for $\text{C}_{18}\text{H}_{18}\text{OS}$ ($\text{M}+\text{Na}^+$), 282.1078; found: 282.1072.

5. Synthesis of Aminochromane Precursors

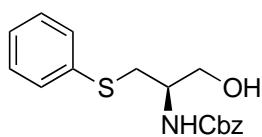
5.1 General procedure



To a solution of *N*-Z-S-phenyl-L-cysteine (9.1 mmol, 3 g) in methanol (36 mL) at 0°C was added dropwise AcCl (26.6 mmol, 1.8 mL). The reaction mixture was warm to room temperature and then, heated at reflux for 24 hours, then, methanol was evaporated *in vacuo*. The solid residue was washed with Ethyl ether:MeOH (9:1) to afford the methyl ester which was used without any further purification. The product was dissolved in EtOH:THF (9:1) (30 mL), and CaCl_2 (18.2 mmol, 2 g) was added, at 0°C, then NaBH_4 (36.4 mmol, 1.4g) was added; the reaction mixture was slowly heated to room temperature and stirred for 18 hours, after that, was poured into an ice/citric acid mixture and extracted with EtOAc (3 x 20 mL), the combined organic phases were washed with NaHCO_3 , then brine and dried over anhydrous Na_2SO_4 , filtered and the solvent evaporated in *vacuo*. The alcohol was obtained as a solid (7.7 mmol, 2.44 mg 85%).

To a solution of **3** (1 equiv) at 0°C in toluene were added, phenol **S4** (1.2 equiv), triphenylphosphine (1.2 equiv.), then, DIAD (1.2 equiv) was added drop-wise. After that, the reaction mixture was stirred at room temperature for 24 hours. Finally, the toluene was evaporated under reduce pressure. The crude mixture was purified by flash chromatography using CHx:DCM (9:1) to afford the pure product **4**.

(R)-Benzyl (1-hydroxy-3-(phenylthio)propan-2-yl)carbamate (3).



The product **3** was obtained as a white solid (7.7 mmol, 2.44 g, 85%), m.p. 72–73 °C.

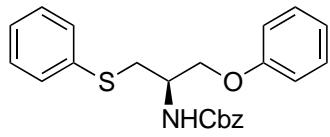
^1H NMR (400 MHz, CDCl_3) δ : 7.26 – 7.50 (m, 9H), 7.10 – 7.24 (m, 1H), 5.22 – 5.39 (m, 1H), 5.09 (s, 2H), 3.78 – 3.93 (m, 2H), 3.65 – 3.76 (m, 1H), 3.29 – 3.00 (m, 2H).

^{13}C NMR (100 MHz CDCl_3) δ : 156.3, 136.3, 135.3, 129.6, 129.2, 128.6, 128.2, 128.1, 126.6, 67.0, 63.3, 52.1, 34.9.

FT-IR (neat) $\nu(\text{cm}^{-1})$: 3225, 3062, 2935, 1689, 1531, 1280, 1238, 1010, 732, 686.

HRMS (ESI): Calcd. for $\text{C}_{17}\text{H}_{19}\text{NO}_3\text{S}$ ($\text{M}+\text{Na}^+$), 340.0983; found: 340.0991.

(R)-Benzyl (1-phenoxy-3-(phenylthio)propan-2-yl)carbamate (4a).



According to the general procedure, (*R*)-benzyl (1-hydroxy-3-(phenylthio)propan-2-yl)carbamate **3** (3.15 mmol, 1g), phenol (3.8 mmol, 357 mg), triphenylphosphine (3.8 mmol, 996 mg), DIAD (3.8 mmol, 0.75 mL)

and toluene (15 mL) were used to obtain **4a** as an orange oil (1.64 mmol,

645 mg, 52%).

¹H NMR (400 MHz, CDCl₃) δ: 7.39 – 7.45 (m, 2H), 7.32 – 7.39 (m, 5H), 7.21 – 7.30 (m, 4H), 7.16 (t, *J* = 7.4 Hz, 1H), 6.97 (t, *J* = 7.3 Hz, 1H), 6.85 (d, *J* = 8.4 Hz, 2H), 5.36 (d, *J* = 8.3 Hz, 1H), 5.12 (s, 2H), 4.13 – 4.29 (m, 2H), 3.99 (dd, *J* = 9.3, 4.2 Hz, 1H), 3.36 (dd, *J* = 13.9, 5.3 Hz, 1H), 3.20 (dd, *J* = 14.3, 7.4 Hz, 1H).

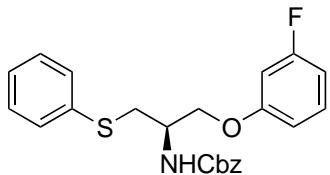
¹³C NMR (100 MHz CDCl₃) δ: 158.2, 155.8, 136.2, 135.3, 129.6, 129.3, 129.1, 128.6, 128.3, 128.2, 126.4, 121.3, 114.5, 67.0, 50.2, 34.6.

[α]²⁵D = -3.22 (c= 0.2, CH₃Cl).

FT-IR (neat) u(cm⁻¹): 3325, 3059, 2943, 1708, 1585, 1492, 1219, 1045, 737, 691.

HRMS (ESI): Calcd. for C₂₃H₂₃NO₃S (M+Na⁺), 416.1296; found: 416.1305.

(R)-Benzyl (1-(3-fluorophenoxy)-3-(phenylthio)propan-2-yl)carbamate (4b).



According to the general procedure, (*R*)-benzyl (1-hydroxy-3-(phenylthio)propan-2-yl)carbamate **3** (2.5 mmol, 800 mg), 3-fluorophenol (3 mmol, 0.27 mL), triphenylphosphine (3 mmol, 786 mg), DIAD (3 mmol, 0.59 mL) and toluene (13 mL) were used to obtain **4b** as a colorless oil (1.80 mmol, 740 mg, 72%).

¹H NMR (400 MHz, CDCl₃) δ: 7.30 – 7.45 (m, 7H), 7.22 – 7.29 (m, 2H), 7.11 – 7.22 (m, 2H), 6.67 (td, *J* = 8.3, 2.5 Hz, 1H), 6.62 (dd, *J* = 8.3, 2.4 Hz, 1H), 6.54 (d, *J* = 10.7 Hz, 1H), 5.32 (d, *J* = 8.6 Hz, 1H), 5.12 (s, 2H), 4.13 – 4.29 (m, 2H), 3.96 (dd, *J* = 9.2, 4.3 Hz, 1H), 3.27 – 3.43 (m, 1H), 3.07 – 3.23 (m, 1H).

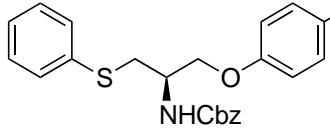
¹³C NMR (100 MHz CDCl₃) δ: 163.7 (d, *J*_{C-F} = 245.5 Hz), 159.6 (d, *J*_{C-F} = 10.6 Hz), 159.5, 136.3, 135.2, 130.4 (d, *J*_{C-F} = 10.1 Hz), 129.5, 129.2, 128.7, 128.4, 128.3, 126.6, 110.3 (d, *J*_{C-F} = 3.0 Hz), 108.3 (d, *J*_{C-F} = 21.3 Hz), 102.5 (d, *J*_{C-F} = 24.9 Hz), 67.5, 67.2, 50.2, 34.8.

[α]²⁵D = -13.71 (c= 1.0, CH₃Cl).

FT-IR (neat) u(cm⁻¹): 3317, 3062, 2935, 1697, 1489, 1261, 1134, 1026, 736, 690.

HRMS (ESI): Calcd. for C₂₃H₂₂FNO₃S (M+Na⁺), 434.1202; found: 434.1209.

(R)-Benzyl (1-(phenylthio)-3-(*p*-tolyloxy)propan-2-yl)carbamate (4c).



According to the general procedure, (*R*)-benzyl (1-hydroxy-3-(phenylthio)propan-2-yl)carbamate **3** (1.26 mmol, 400 mg), 3-*p*-cresol (1.51 mmol, 0.16 mL), triphenylphosphine (1.51 mmol, 396 mg), DIAD (1.51 mmol, 0.30 mL) and toluene (7 mL) were used to obtain **4c** as a colorless oil (0.63 mmol, 257 mg, 50%).

¹H NMR (400 MHz, CDCl₃) δ: 7.39 – 7.46 (m, 2H), 7.32 – 7.39 (m, 5H), 7.23 – 7.31 (m, 2H), 7.17 (t, *J* = 7.3 Hz, 1H) 7.07 (d, *J* = 8.2, Hz, 2H), 6.75 (d, *J* = 8.4 Hz, 2H), 5.38 (d, *J* = 8.0 Hz, 1H), 5.12 (s, 2H), 4.10 – 4.33 (m, 2H), 3.88 – 4.01 (m, 1H), 3.36 (dd, *J* = 13.9, 5.4 Hz, 1H), 3.12 – 3.25 (m, 1H), 2.29 (s, 3H).

¹³C NMR (100 MHz CDCl₃) δ: 156.2, 155.9, 136.3, 135.4, 130.7, 130.1, 129.3, 129.2, 128.7, 128.4, 128.3, 126.4, 114.5, 67.3, 67.1, 50.2, 34.6, 20.6.

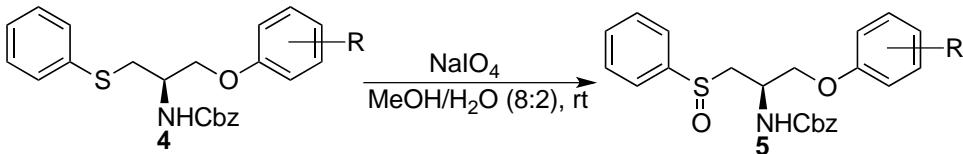
[α]²⁰D = -8.75 (c= 0.6, CH₃Cl).

FT-IR (neat) u(cm⁻¹): 3321, 3032, 2924, 1701, 1508, 1230, 1026, 736, 690.

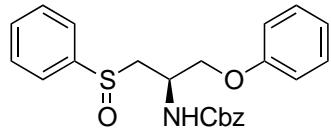
HRMS (ESI): Calcd. for C₂₄H₂₅NO₃S (M+Na⁺), 430.12453; found: 430.1455.

6. Synthesis of sulfoxides 5

6.1 Synthesis of sulfoxides 5.



Benzyl ((2*R*)-1-phenoxy-3-(phenylsulfinyl)propan-2-yl)carbamate (5a)



According to the general procedure of sulfides oxidation, (*R*)-benzyl (1-phenoxy-3-(phenylthio)propan-2-yl)carbamate **4a** (1.65 mmol, 650 mg), sodium periodate (2.5 mmol, 530 mg), and (MeOH/H₂O) (16 mL) were used to obtain **5a** as an orange oil and as a 1:1 mixture of diastereoisomers (1.50 mmol, 614 mg, 91%).

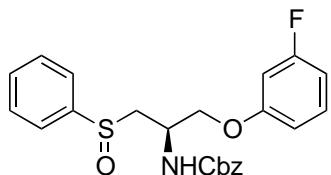
¹H NMR (400 MHz, CDCl₃) δ: 7.57 – 7.75 (m, 2H), 7.45 – 7.56 (m, 3H), 7.25 – 7.42 (m, 8H), 6.98 (t, *J* = 7.4 Hz, 1H), 6.81 – 6.92 (m, 2H), 5.99 (d, *J* = 7.7 Hz, 0.5H), 5.52 (d, *J* = 7.0 Hz, 0.5H), 5.13 (s, 1H), 5.10 (s, 1H), 4.51 – 4.64 (m, 0.5H), 4.38 – 4.49 (m, 0.5H), 4.18 – 4.30 (m, 1.5H), 4.07 (dd, *J* = 9.6, 4.4 Hz, 0.5H), 3.21 (dd, *J* = 12.9, 6.8 Hz, 1.5H), 3.09 (dd, *J* = 13.5, 4.4 Hz, 0.5H).

¹³C NMR (100 MHz CDCl₃) δ: 158.2, 155.9, 155.7, 143.8, 143.6, 136.3, 136.2, 131.4, 131.4, 129.7, 129.6, 129.5, 128.7, 128.4, 128.4, 128.3, 128.3, 124.2, 124.0, 121.7, 121.6, 114.7, 114.6, 68.7, 67.2, 58.9, 58.7, 48.0, 47.4.

FT-IR (neat) u(cm⁻¹): 3267, 3035, 2943, 1712, 1492, 1234, 1026, 748, 691.

HRMS (ESI): Calcd. for C₂₃H₂₃NO₄S (M+Na⁺), 432.1245; found: 432.1238.

Benzyl ((2*R*)-1-(3-fluorophenoxy)-3-(phenylsulfinyl)propan-2-yl)carbamate (5b).



According to the general procedure, (*R*)-benzyl (1-(3-fluorophenoxy)-3-(phenylthio)propan-2-yl)carbamate **4b** (1.8 mmol, 750 mg), sodium periodate (2.7 mmol, 577 mg), and (MeOH/H₂O) (20mL) were used to obtain **5b** as an orange oil and as a 1:1 mixture of diastereoisomers (1.69 mmol, 722 mg, 94%).

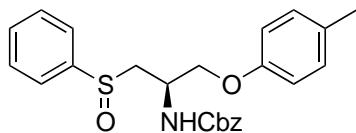
¹H NMR (400 MHz, CDCl₃) δ: 7.60 – 7.70 (m, 2H), 7.46 – 7.55 (m, 3H), 7.31 – 7.37 (m, 5H), 7.16 – 7.25 (m, 1H), 6.55 – 6.71 (m, 3H), 5.58 (brs, 0.5H), 5.12 (brs, 0.5H), 5.12 and 5.09 (2s, 2H), 4.47 – 4.61 (m, 0.5H), 4.34 – 4.47 (m, 0.5H), 4.15 – 4.25 (m, 1.5H), 4.04 (dd, *J* = 9.5, 4.8 Hz, 0.5H), 3.16 – 3.26 (m, 1.5H), 3.04 – 3.11 (m, 0.5H).

¹³C NMR (100 MHz CDCl₃) δ: 163.7 (d, *J*_{C-F} = 244.3 Hz), 159.4 (d, *J*_{C-F} = 10.5 Hz), 155.8 (A), 155.7 (B), 146.6 (A), 143.4 (B), 136.3 (A), 136.2 (B), 131.5 (A), 131.4 (B) 130.5 (d, *J*_{C-F} = 9.9 Hz), 129.6 (A), 129.5 (B), 128.7, 128.4 (A), 128.4 (B), 128.3 (A), 128.3 (B), 124.2 (A), 124.0 (B), 110.3 (d, *J*_{C-F} = 2.2 Hz), 108.5 (d, *J*_{C-F} = 21.2 Hz) (A), 108.5 (d, *J*_{C-F} = 21.2 Hz) (B), 102.7 (d, *J*_{C-F} = 24.9 Hz) (A), 102.6 (d, *J*_{C-F} = 25.0 Hz) (B), 68.9, 67.1, 58.5, 58.2, 47.8, 47.2.

FT-IR (neat) u(cm⁻¹): 3332, 3032, 2924, 1685, 1527, 1269, 1138, 1018, 748, 686.

HRMS (ESI): Calcd. For C₂₃H₂₂FNO₄S (M+Na⁺), 450.1151; found: 450.1148.

Benzyl ((2*R*)-1-(phenylsulfinyl)-3-(*p*-tolyloxy)propan-2-yl)carbamate (5c).



According to the general procedure, (*R*)-benzyl (1-(phenylthio)-3-(*p*-tolyloxy)propan-2-yl)carbamate **4c** (0.48 mmol, 145 mg), sodium periodate (0.72 mmol, 154 mg), and (MeOH/H₂O) (5 mL) were used to

obtain **5c** as an colorless oil and as a 1:1 mixture of diastereoisomers (0.44 mmol, 187 mg, 92%).

¹H NMR (400 MHz, CDCl₃) δ: 7.59 – 7.76 (m, 2H), 7.45 – 7.58 (m, 3H), 7.28 – 7.40 (m, 5H), 6.99 – 7.11 (m, 2H), 6.65 – 6.84 (m, 2H), 6.02 (brs, 0.5H), 5.56 (brs, 0.5H), 5.12 and 5.09 (2s, 2H), 4.50 – 4.61 (m, 0.5H), 4.34 – 4.45 (m, 0.5H), 4.13 – 4.31 (m, 1.5H), 3.94 – 4.10 (m, 0.5H), 3.16 – 3.26 (m, 1.5H), 2.98 – 3.12 (m, 0.6H), 2.28 (s, 3H).

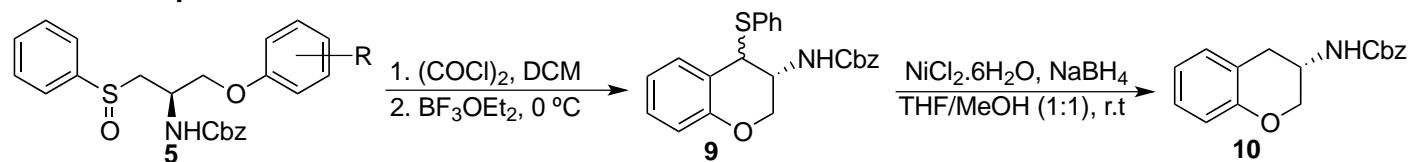
¹³C NMR (100 MHz CDCl₃) δ: 156.0, 155.8, 155.7, 155.6, 143.7, 143.5, 136.3, 136.2, 131.4, 131.4, 130.4, 130.3, 130.1, 130.1, 129.5, 129.5, 128.7, 128.7, 128.4, 128.3, 128.3, 128.3, 124.2, 124.0, 114.5, 114.5, 68.8, 68.5, 67.2, 67.1, 59.0, 58.9, 47.9, 47.3, 20.7, 20.6.

FT-IR (neat) u(cm⁻¹): 3265, 3055, 2940, 1698, 1480, 1225, 1026, 750, 689.

HRMS (ESI): Calcd. For C₂₄H₂₅NO₄S (M+Na⁺), 446.1402; found: 446.1405.

7. Synthesis of protected amino chromanes

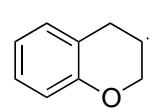
7.1 General procedure



To a solution of the corresponding sulfoxide **5** (1 equiv.) in dry DCM at 0°C, oxalyl chloride (1.2 equiv) was added. The mixture was stirred at the same temperature for 1 hour (complete conversion was observed by TLC). Then, BF_3OEt_2 (3 equiv) was added and the reaction mixture was stirred for 1 hour. The reaction was quenched with NaOH (1M). The aqueous layer was extracted with DCM (3 x 15 mL), the combined organic extracts were washed with brine, dried over anhydrous Na_2SO_4 , filtered and concentrated under reduced pressure. The crude product **9** was used in the next step without any purification.

Sodium borohydride (21 equiv.) was added to the solution of crude **9** and nickel chloride hexahydrate (7 equiv.) in THF:MeOH (1:1) in an ice bath. The reaction mixture was stirred at room temperature until the starting material was completely consumed (observed by TLC). After that, the reaction mixture was filtered through a pad of Celite, the solvent was evaporated *in vacuo*. The crude was purified by flash chromatography using CH_x:DCM (9:1).

(S)-Benzyl chroman-3-ylcarbamate (10a).

 According to the general procedure, benzyl ((2*R*)-1-phenoxy-3-(phenylsulfinyl)propan-2-yl)carbamate **5a** (0.9 mmol, 374 mg), oxalyl chloride (1.2 mmol, 0.09 mL), boron trifluoride diethyl etherate (2.7 mmol, 0.34 mL), DCM (8 mL), nickel chloride (6.4 mmol, 1.5 g), sodium borohydride (19 mmol, 718 mg), and THF:MeOH (14 mL) were used to obtain **10a** as a colorless oil (0.68 mmol, 192 mg, 75%).

¹H NMR (400 MHz, CDCl₃) δ: 7.27 – 7.42 (m, 5H), 7.13 (t, *J* = 8.4 Hz, 1H), 7.04 (d, *J* = 7.5 Hz, 1H), 6.89 (t, *J* = 7.3 Hz, 1H), 6.84 (d, *J* = 8.2 Hz, 1H), 5.01 – 5.27 (m, 3H), 4.21 – 4.33 (m, 1H), 4.06 – 4.22 (m, 2H), 3.12 (dd, *J* = 16.7, 5.2 Hz, 1H), 2.77 (dd, *J* = 16.7, 5.8 Hz, 1H).

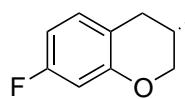
¹³C NMR (100 MHz CDCl₃) δ: 155.9, 153.9, 136.3, 130.6, 128.7, 128.4, 128.3, 127.9, 121.3, 119.2, 116.9, 68.3, 67.0, 44.0, 31.2.

$[\alpha]^{24}_{D} = -26.75$ (*c* = 0.6, CH₃Cl). Lit. $[\alpha]^{24}_{D} = -15.77$ (*c* = 1, CH₃Cl).

FT-IR (neat) u(cm⁻¹): 3317, 3032, 2927, 1693, 1492, 1222, 1064, 752, 694.

HRMS (ESI): Calcd. For C₁₇H₁₇NO₃ (M+Na⁺), 306.1106; found: 306.1112.

(S)-Benzyl (7-fluorochroman-3-yl)carbamate (10b).



According to the general procedure, benzyl ((2*R*)-1-(3-fluorophenoxy)-3-(phenylsulfinyl)propan-2-yl)carbamate **5b** (1 mmol, 430 mg), oxalyl chloride (1.2 mmol, 0.09 mL), boron trifluoride diethyl etherate (3 mmol, 0.38 mL), DCM (8.2 mL), nickel chloride (7 mmol, 1.7 g), sodium borohydride (21 mmol, 794 mg), and THF:MeOH (16 mL) were used to obtain **10b** as a colorless oil (0.7 mmol 211 mg, 70%).

¹H NMR (400 MHz CDCl₃) δ: 7.30 – 7.41 (m, 5H), 6.91 – 7.01 (m, 1H), 6.58 – 6.66 (m, 1H), 6.56 (dd, *J* = 10.0, 2.8 Hz, 1H), 4.88 – 5.24 (m, 3H), 4.19 – 4.30 (m, 1H), 4.01 – 4.18 (m, 2H), 3.06 (dd, *J* = 16.4, 5.4 Hz, 1H), 2.58 – 2.85 (m, 1H).

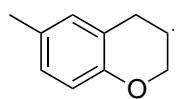
¹³C NMR (100 MHz CDCl₃) δ: 162.2 (d, *J_{C-F}* = 244), 155.8, 154.7 (d, *J_{C-F}* = 12.1), 136.2, 131.3 (d, *J_{C-F}* = 9.6), 128.7, 128.4, 128.3, 114.8 (d, *J_{C-F}* = 3.1), 108.6 (d, *J_{C-F}* = 22.0), 104.1 (d, *J_{C-F}* = 24.5), 68.4, 67.1, 43.8, 30.6.

[α]²⁴_D = -13.55 (c = 1, CH₃Cl).

FT-IR (neat) u(cm⁻¹): 3321, 3056, 2924, 1689, 1527, 1234, 1141, 1029, 732, 698.

HRMS (ESI): Calcd. For C₁₇H₁₆FNO₃ (M+Na⁺), 324.1012; found: 324.1019.

(S)-Benzyl (6-methylchroman-3-yl)carbamate (10c).



According to the general procedure, benzyl ((2*R*)-1-(phenylsulfinyl)-3-(*p*-tolyloxy)propan-2-yl)carbamate **5c** (0.22 mmol, 91 mg), oxalyl chloride (0.26 mmol, 0.02 mL), boron trifluoride diethyl etherate (0.66 mmol, 0.08 mL), DCM (2.0 mL), nickel chloride (1.47 mmol, 349 mg), sodium borohydride (4.4 mmol, 167 mg), and THF:MeOH (3.6 mL) were used to obtain **10c** as a colorless oil (0.16 mmol 48 mg, 73%).

¹H NMR (400 MHz CDCl₃) δ: 7.27 – 7.43 (m, 5H), 6.92 (dd, *J* = 10.0, 2.8 Hz, 1H), 6.84 (s, 1H), 6.73 (d, *J* = 8.3 Hz, 1H), 4.96 – 5.27 (m, 3H), 4.18 – 4.2 (m, 1H), 4.03 – 4.16 (m, 2H), 3.09 (dd, *J* = 16.8, 5.1 Hz, 1H), 2.66 – 2.78 (m, 1H), 2.24 (s, 3H).

¹³C NMR (100 MHz CDCl₃) δ: 155.9, 151.7, 136.3, 130.9, 130.6, 128.7, 128.4, 128.3, 128.3, 118.9, 116.6, 68.3, 67.0, 44.1, 31.2, 20.6.

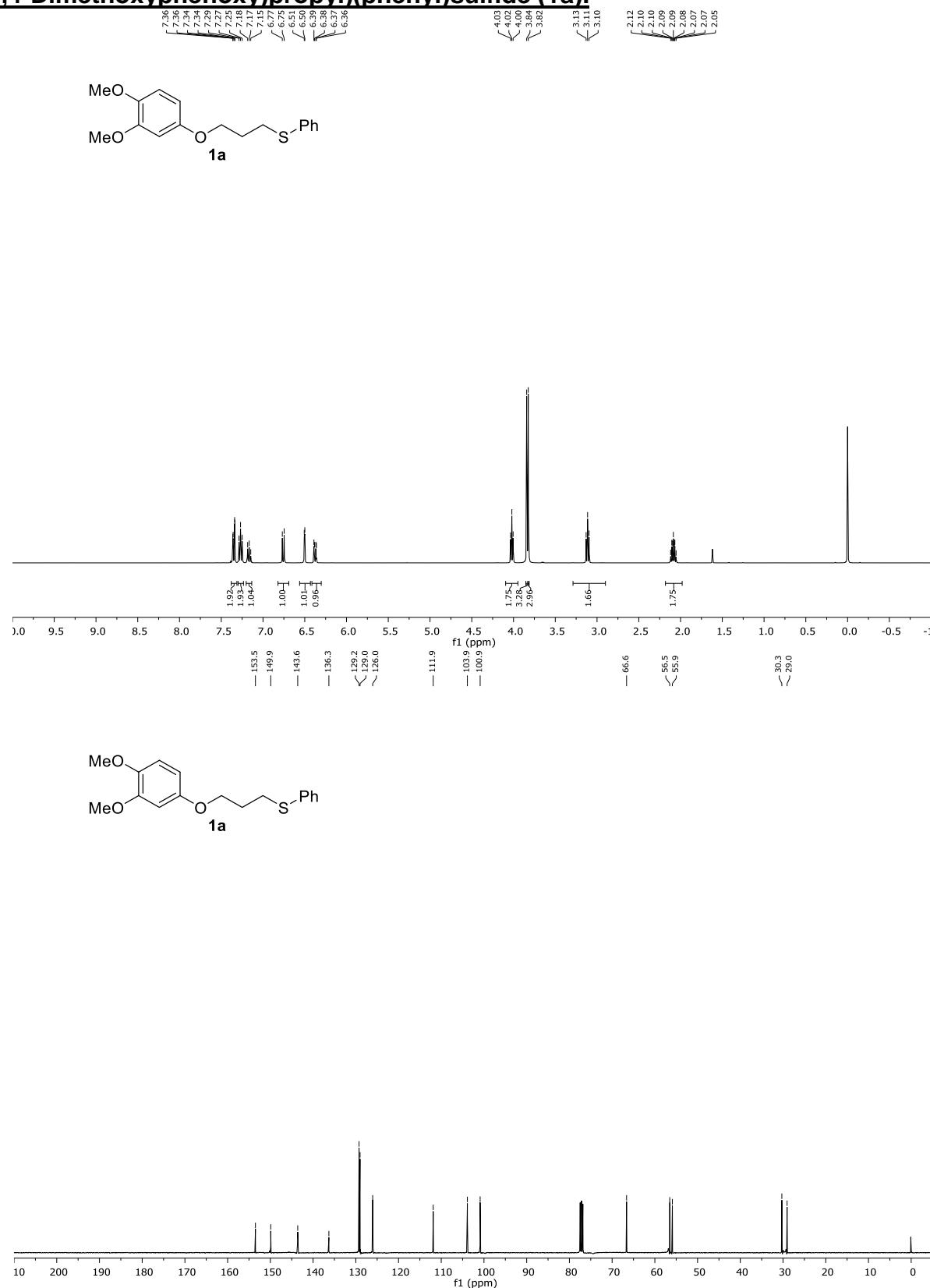
[α]²¹_D = -36.55 (c = 0.1, CH₃Cl).

FT-IR (neat) u(cm⁻¹): 3321, 3032, 2924, 1697, 1500, 1222, 1022, 740, 698.

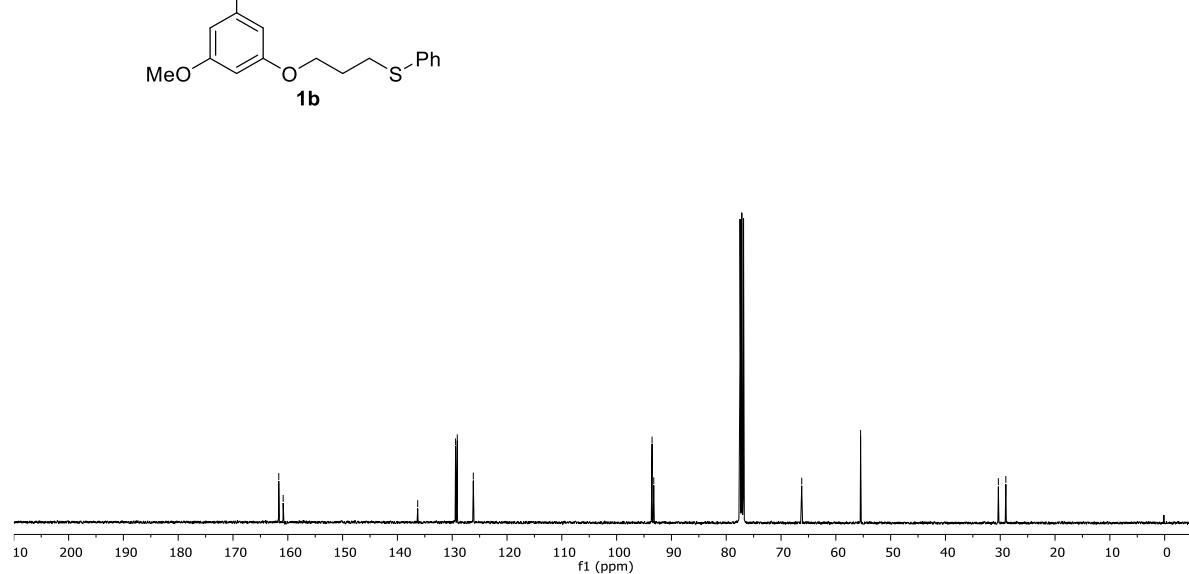
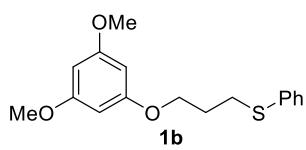
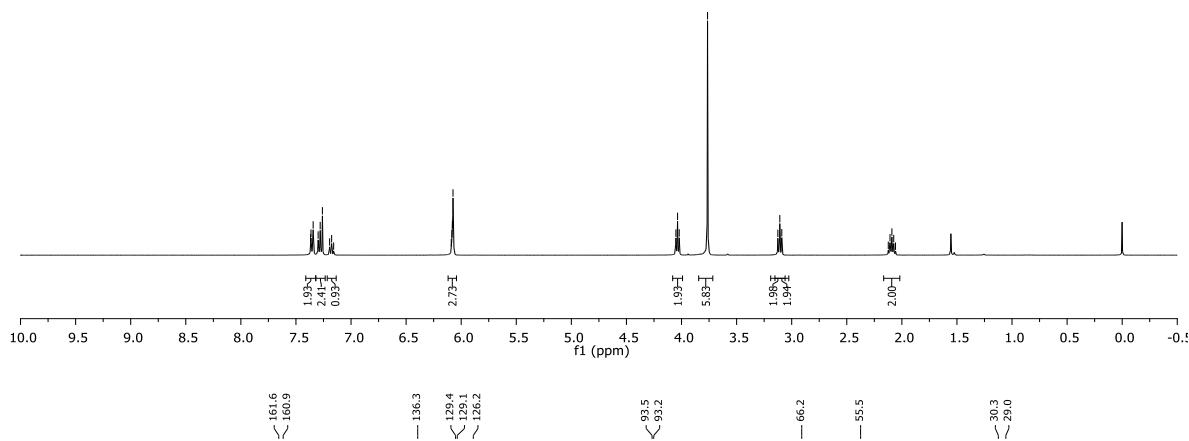
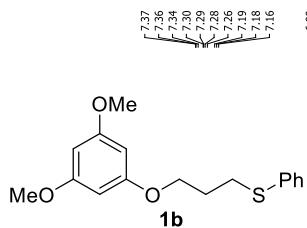
HRMS (ESI): Calcd. For C₁₈H₁₉NO₃ (M+Na⁺), 320.1263; found: 320.1266.

8. Copies of NMR Spectra

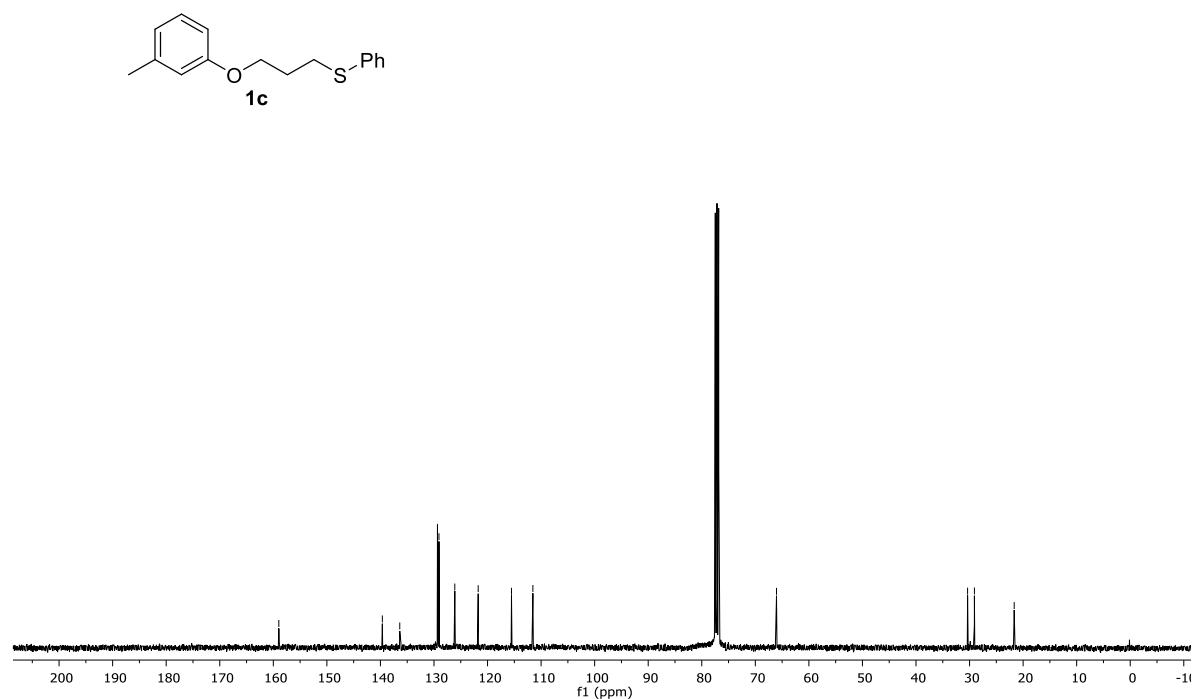
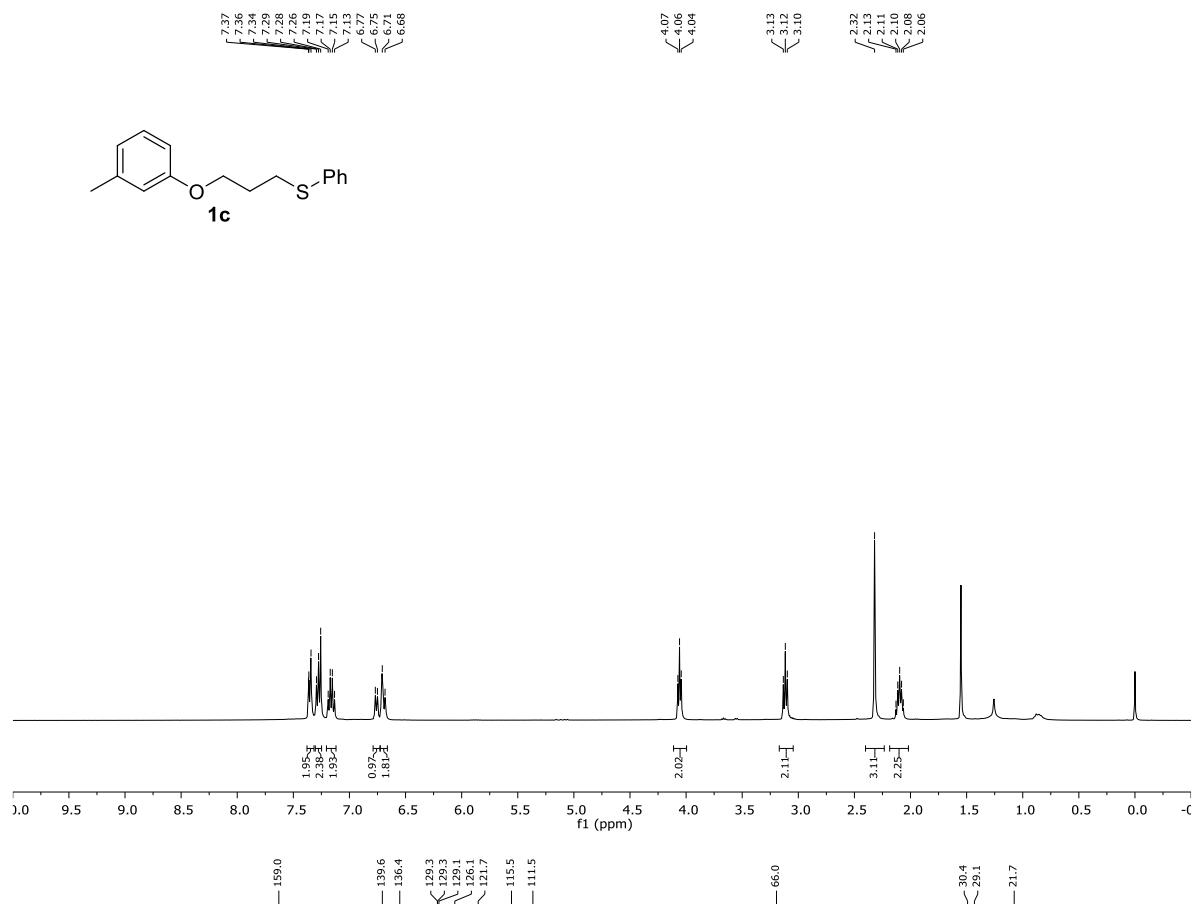
(3-(3,4-Dimethoxyphenoxy)propyl)(phenyl)sulfide (1a).



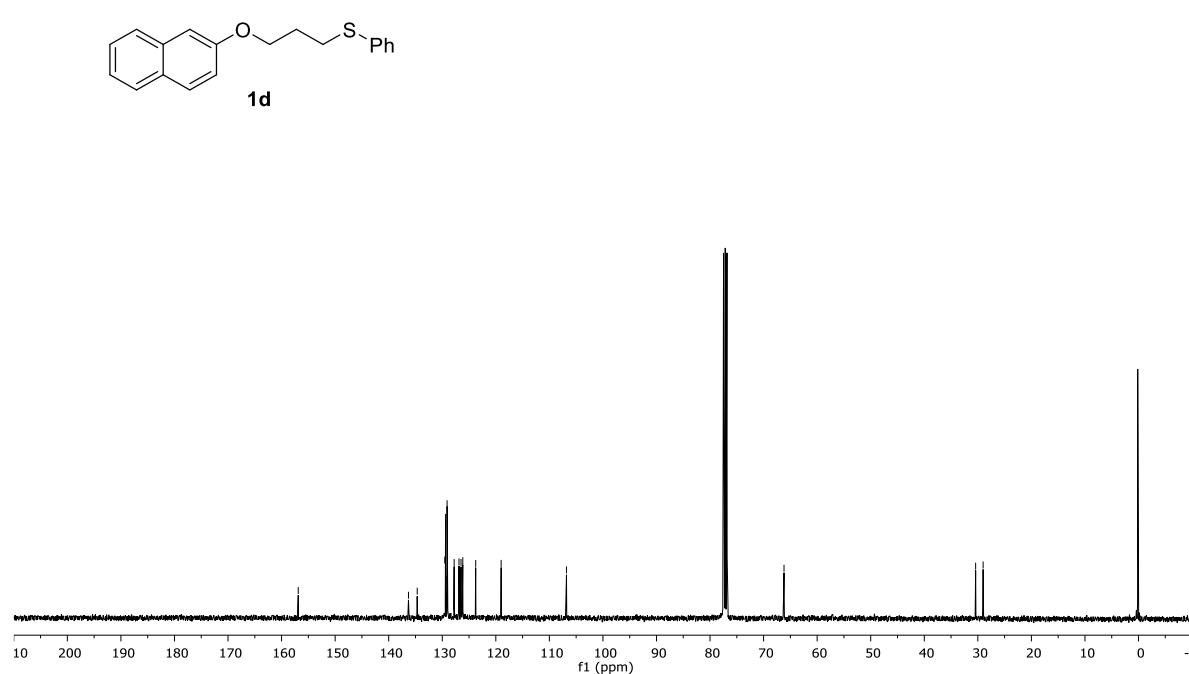
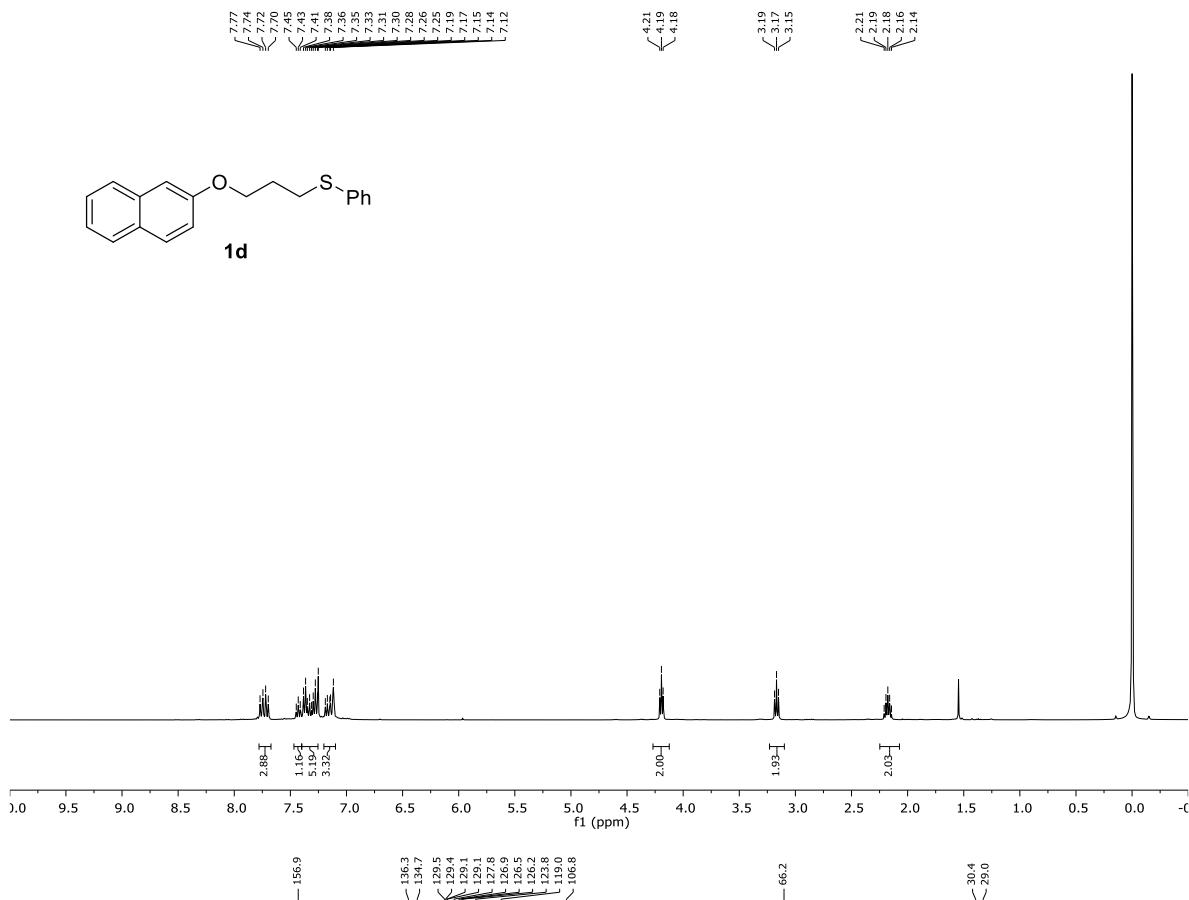
(3-(3,5-Dimethoxyphenoxy)propyl)(phenyl)sulfide (1b).



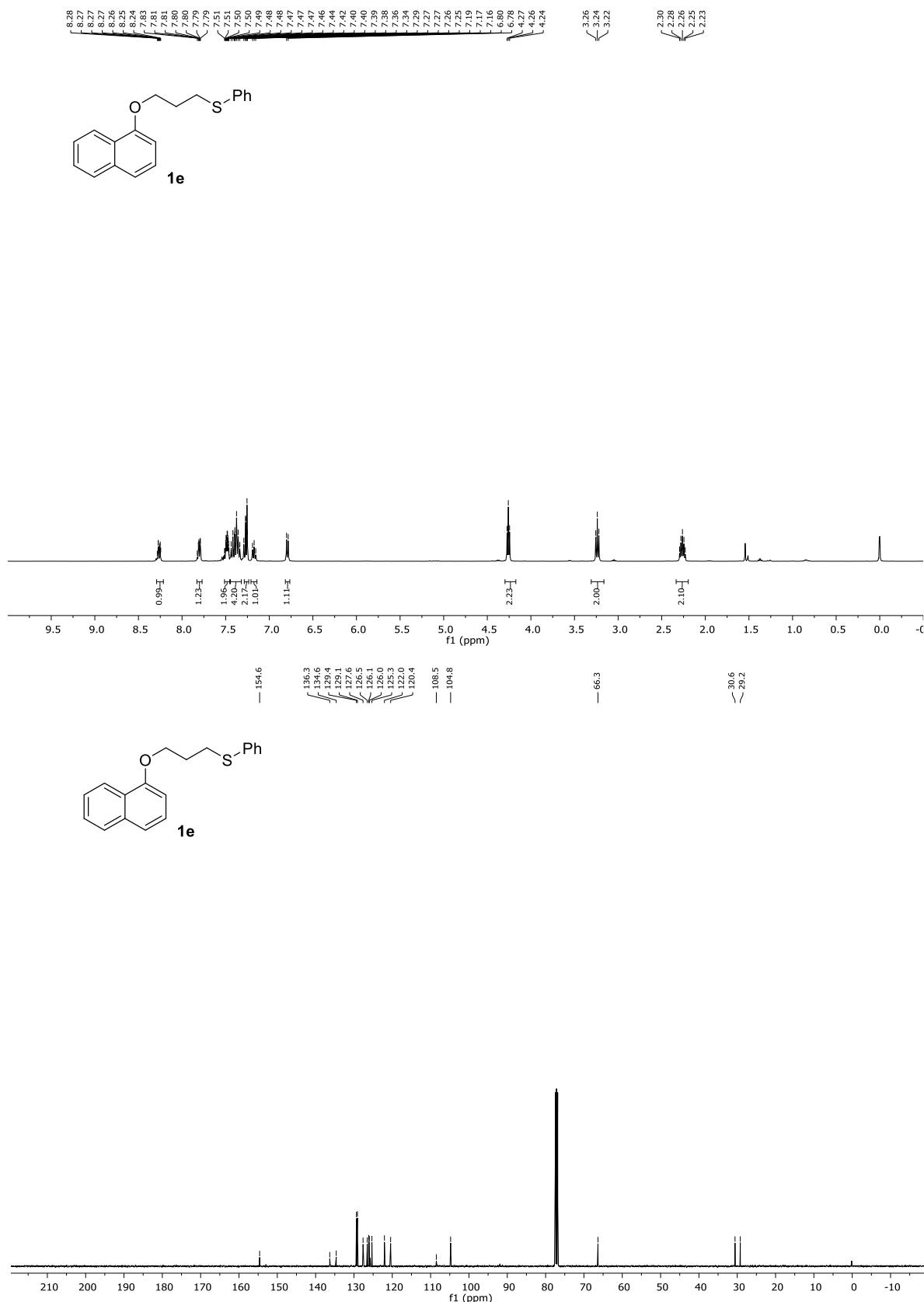
Phenyl(3-(*m*-tolyloxy)propyl)sulfide (1c**).**



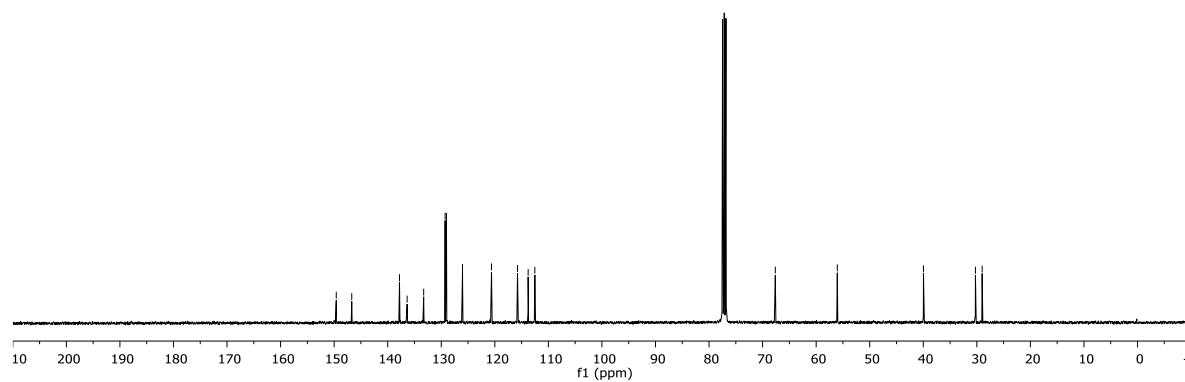
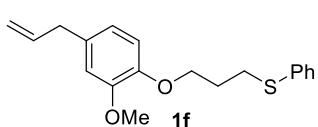
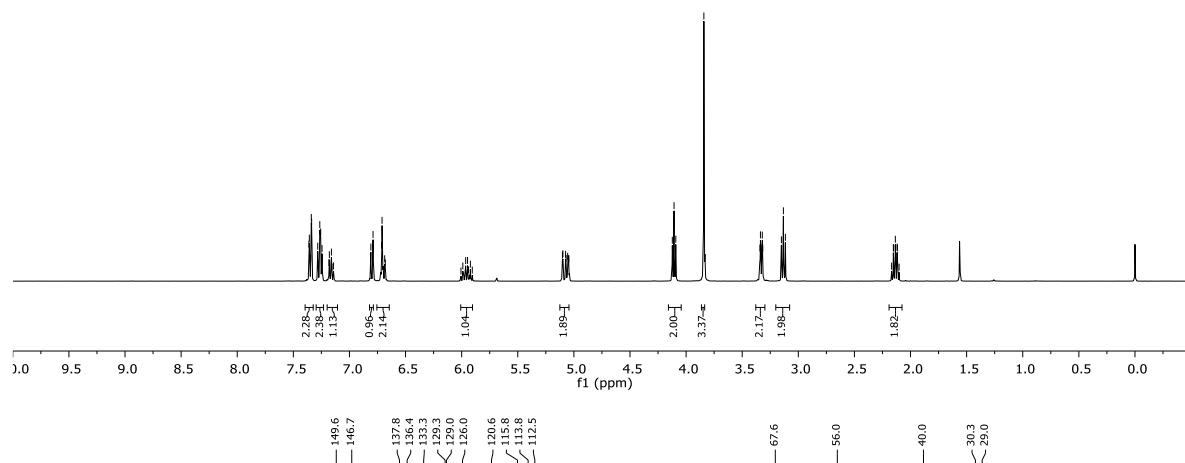
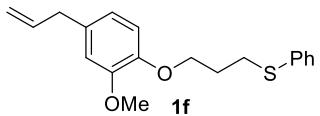
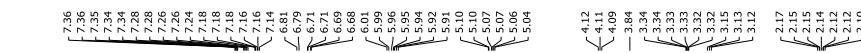
(3-(Naphthalen-2-yloxy)propyl)(phenyl)sulfide (1d**).**



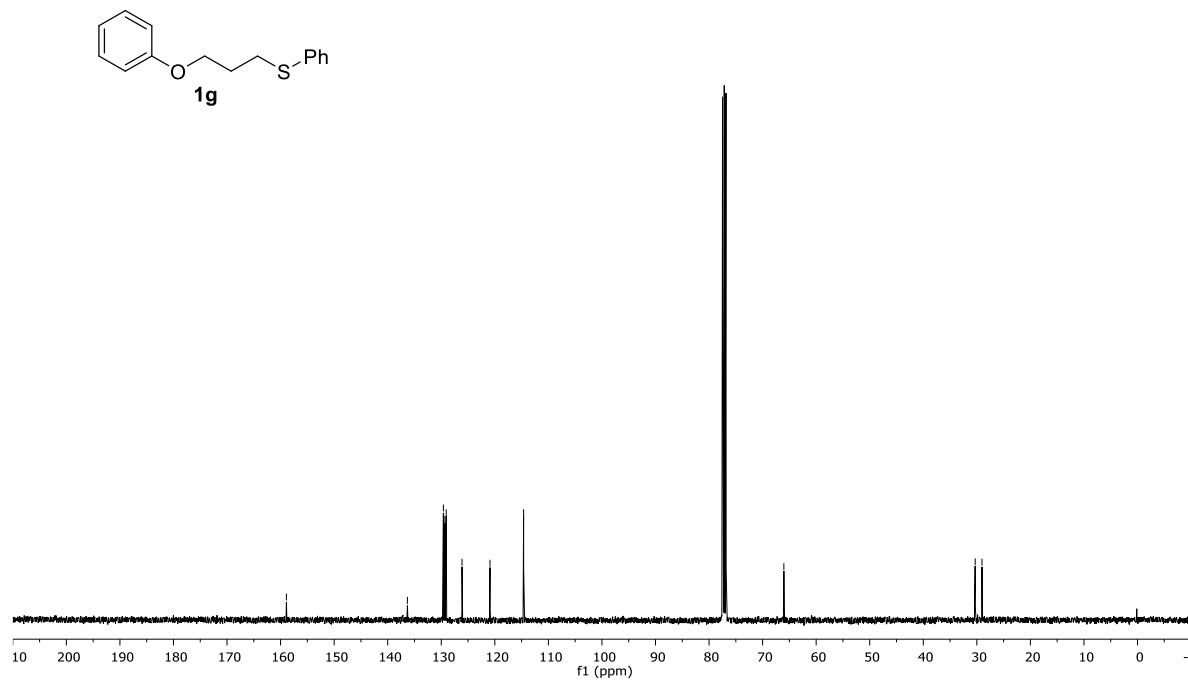
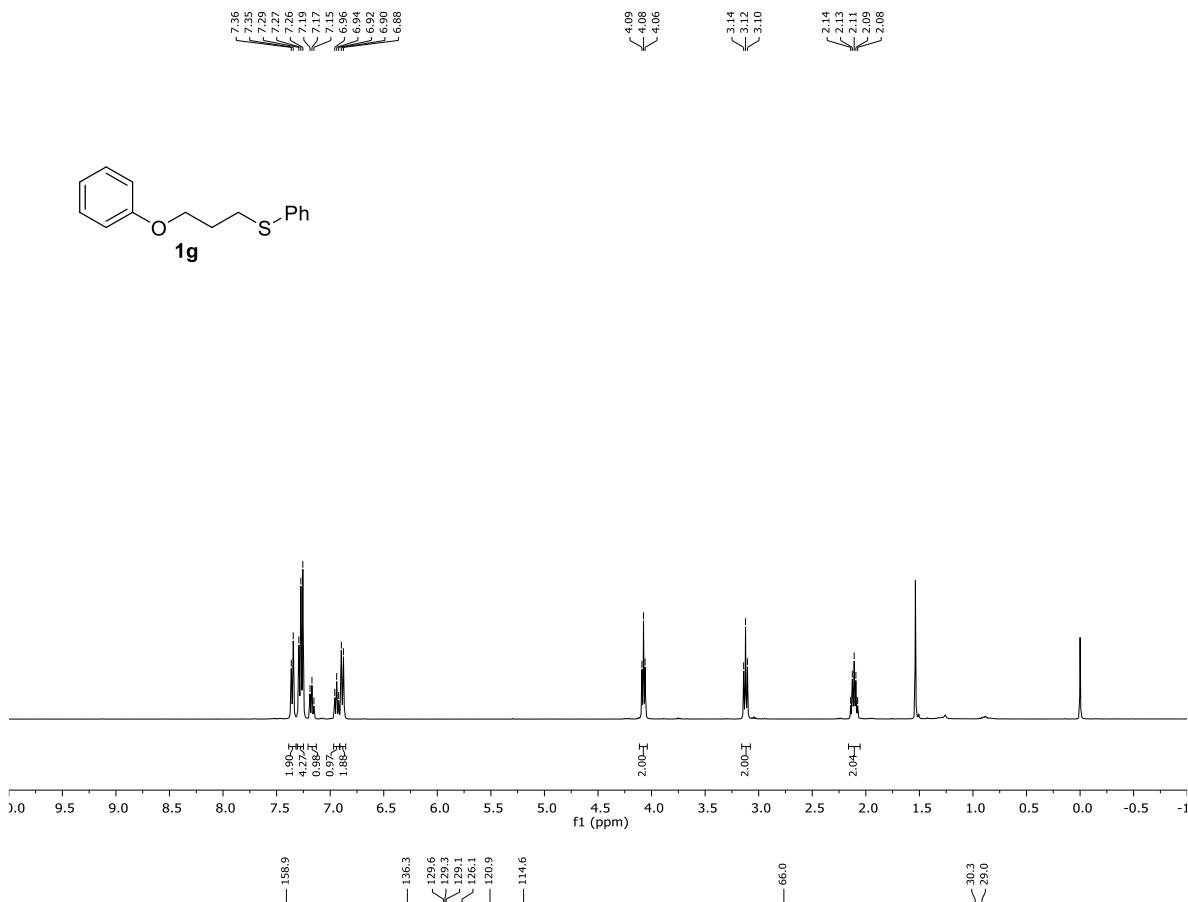
(3-(Naphthalen-1-yloxy)propyl)(phenyl)sulfide (1e).



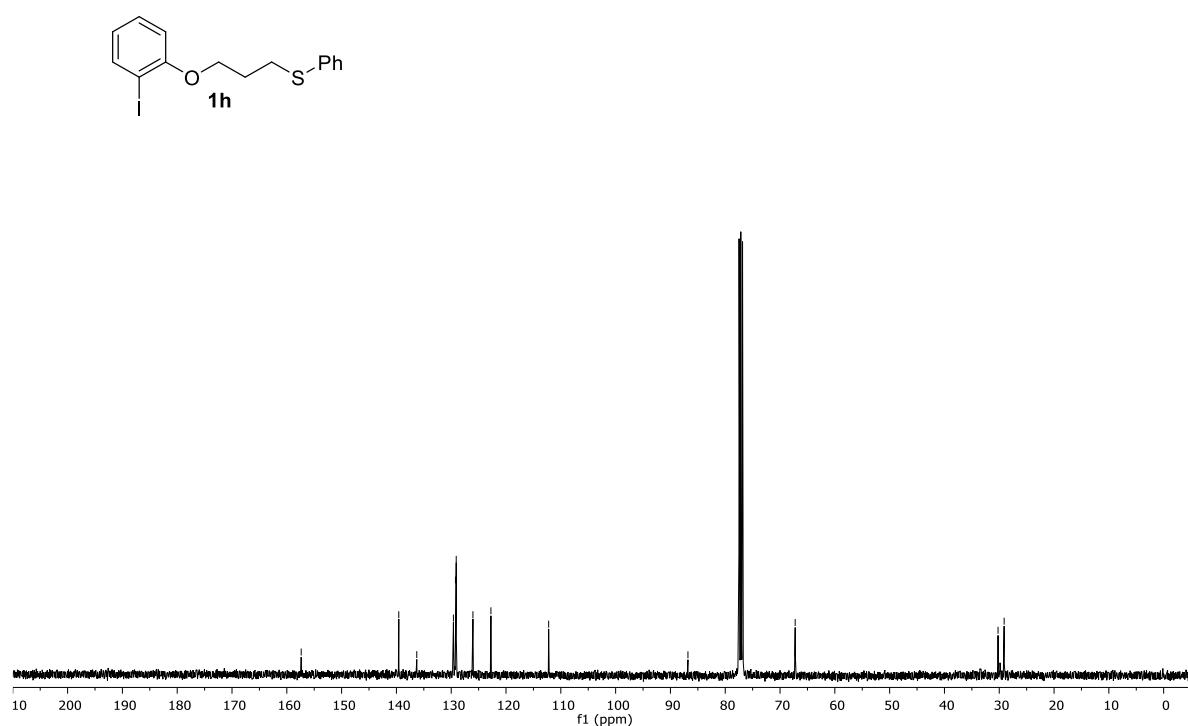
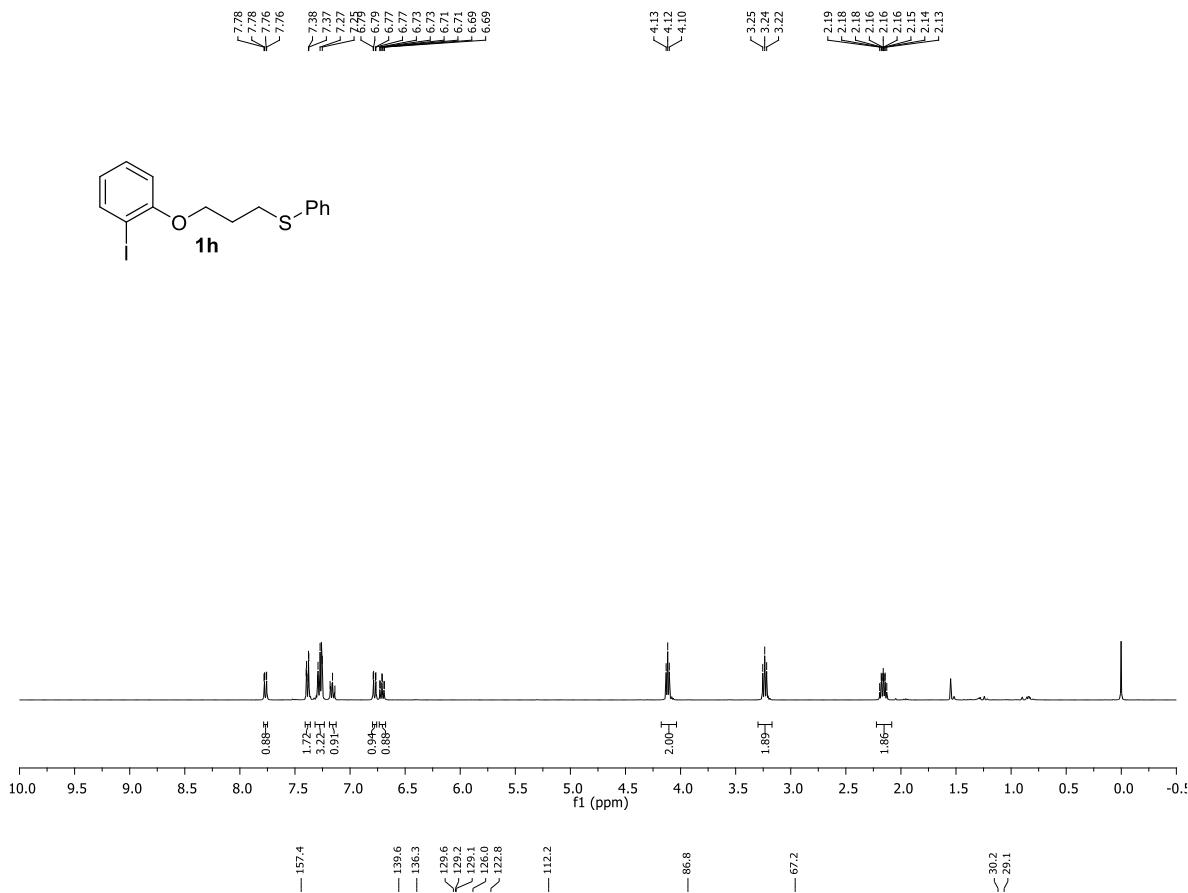
(3-(4-Allyl-2-methoxyphenoxy)propyl)(phenyl)sulfide (1f).



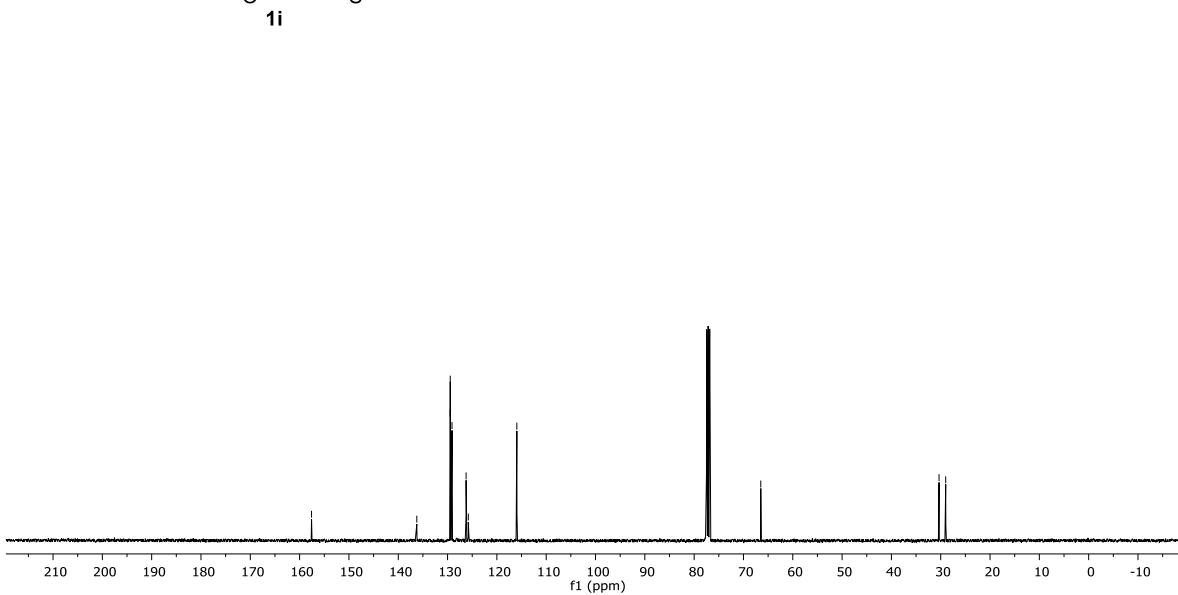
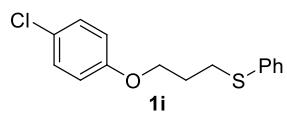
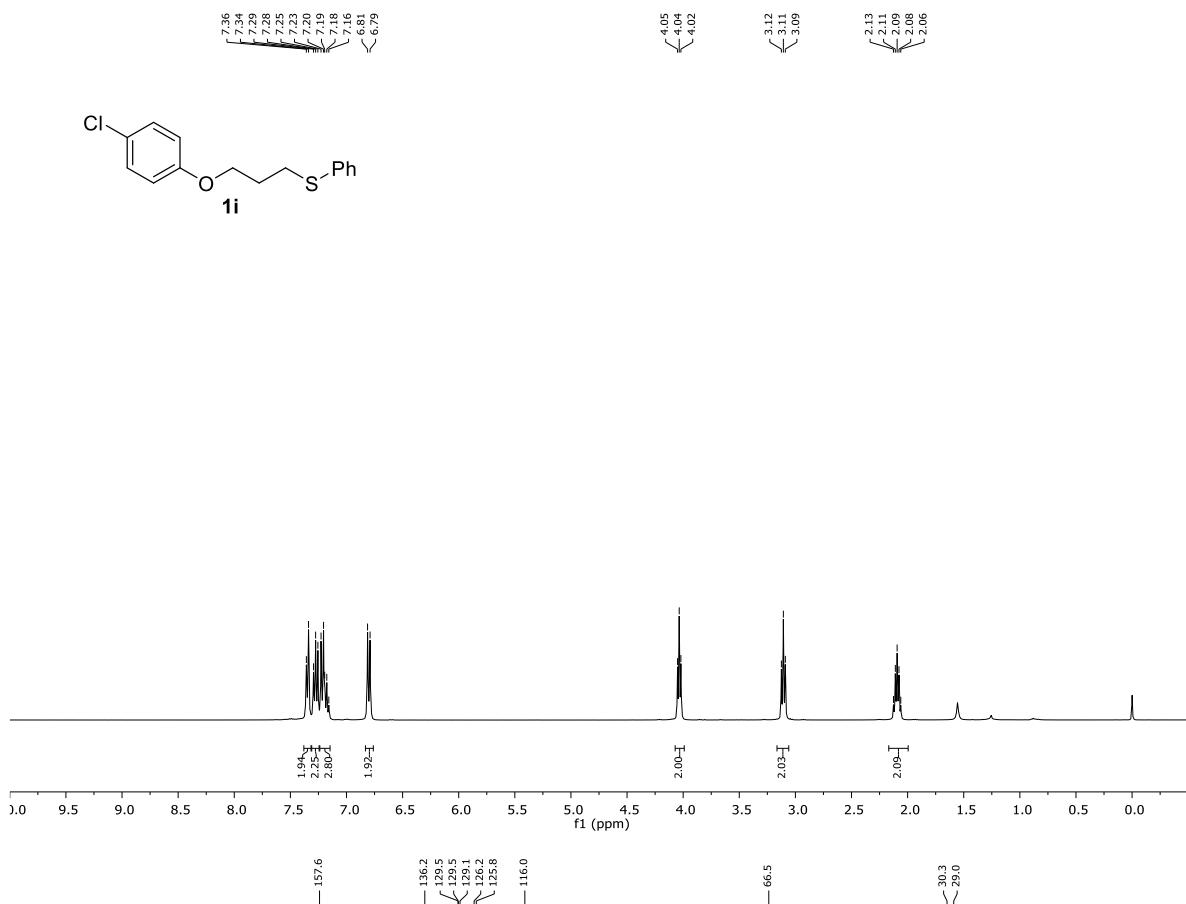
(3-Phenoxypropyl)(phenyl)sulfide (1g**).**



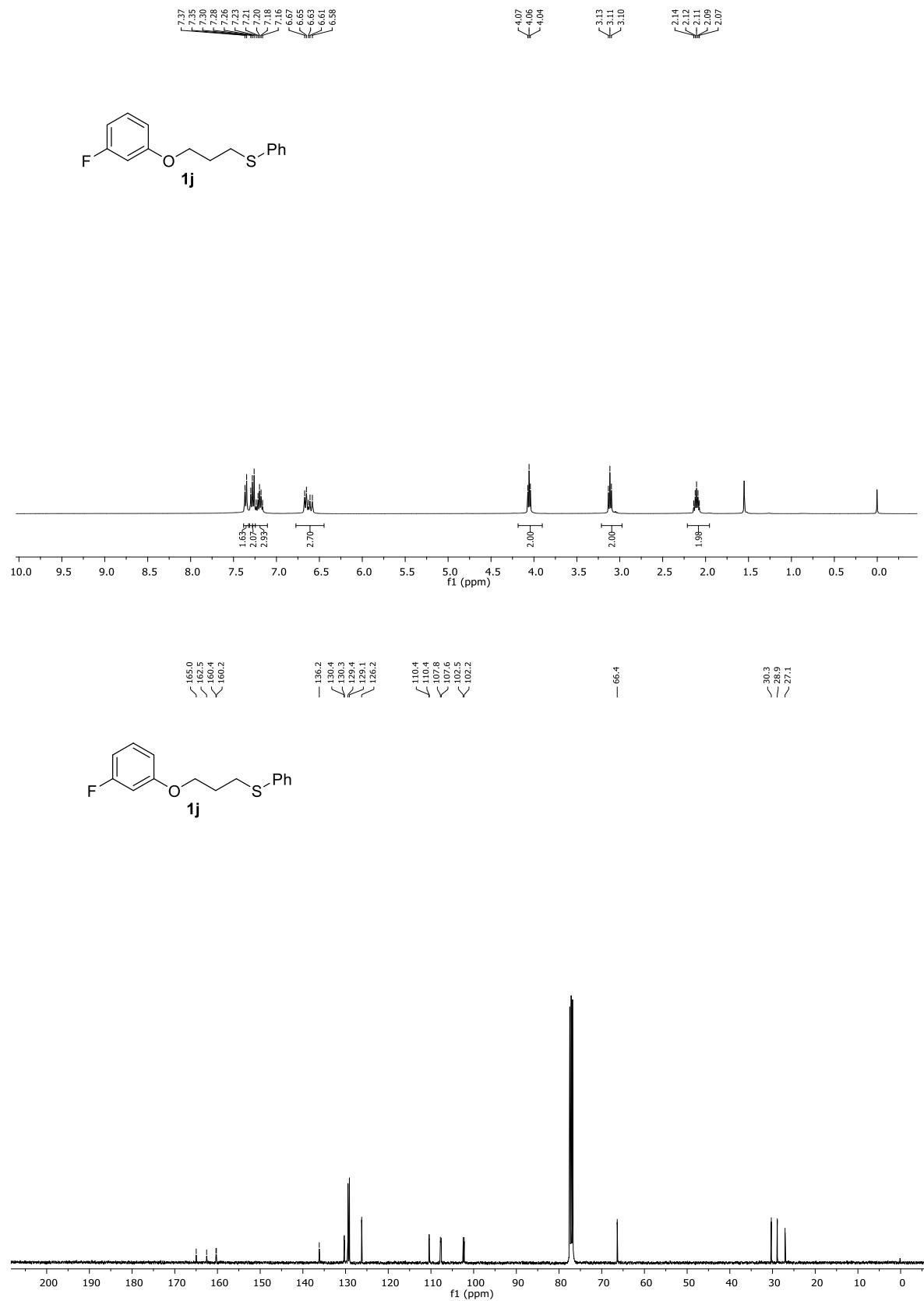
(3-(2-Iodophenoxy)propyl)(phenyl)sulfide (1h**).**



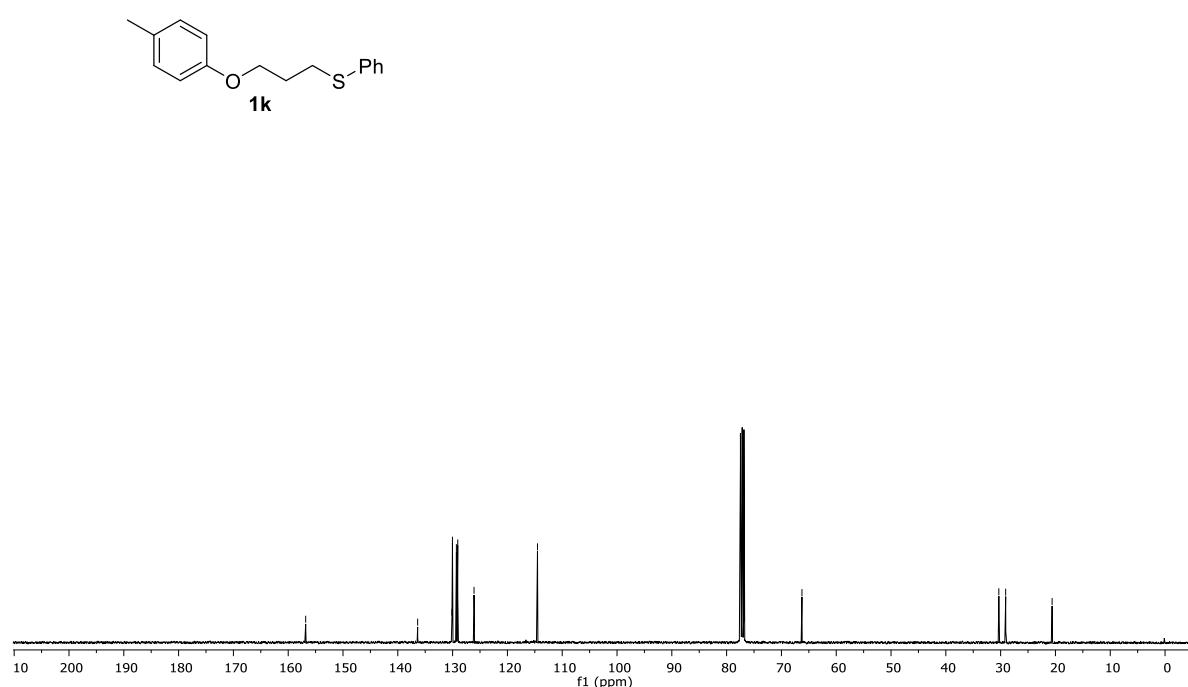
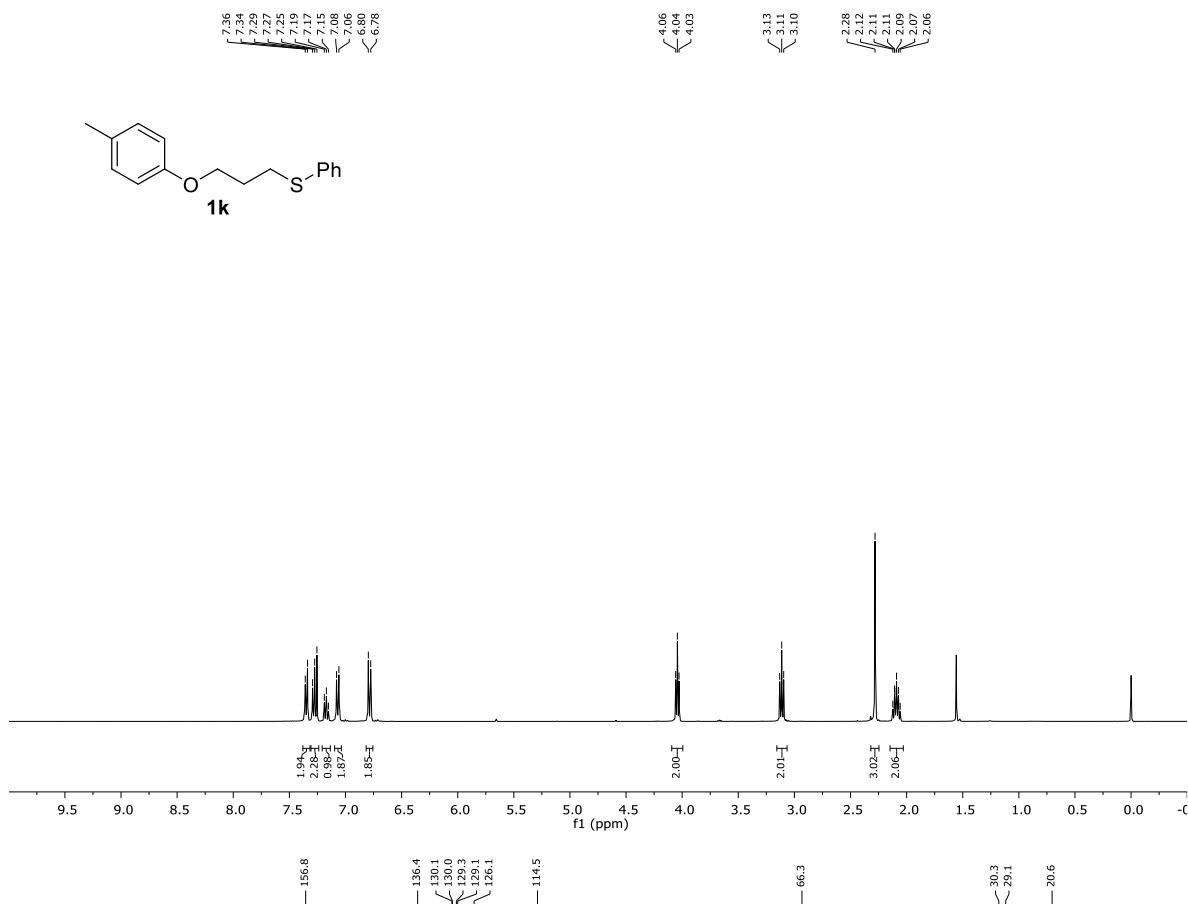
(3-(4-Chlorophenoxy)propyl)(phenyl)sulfide (1i)



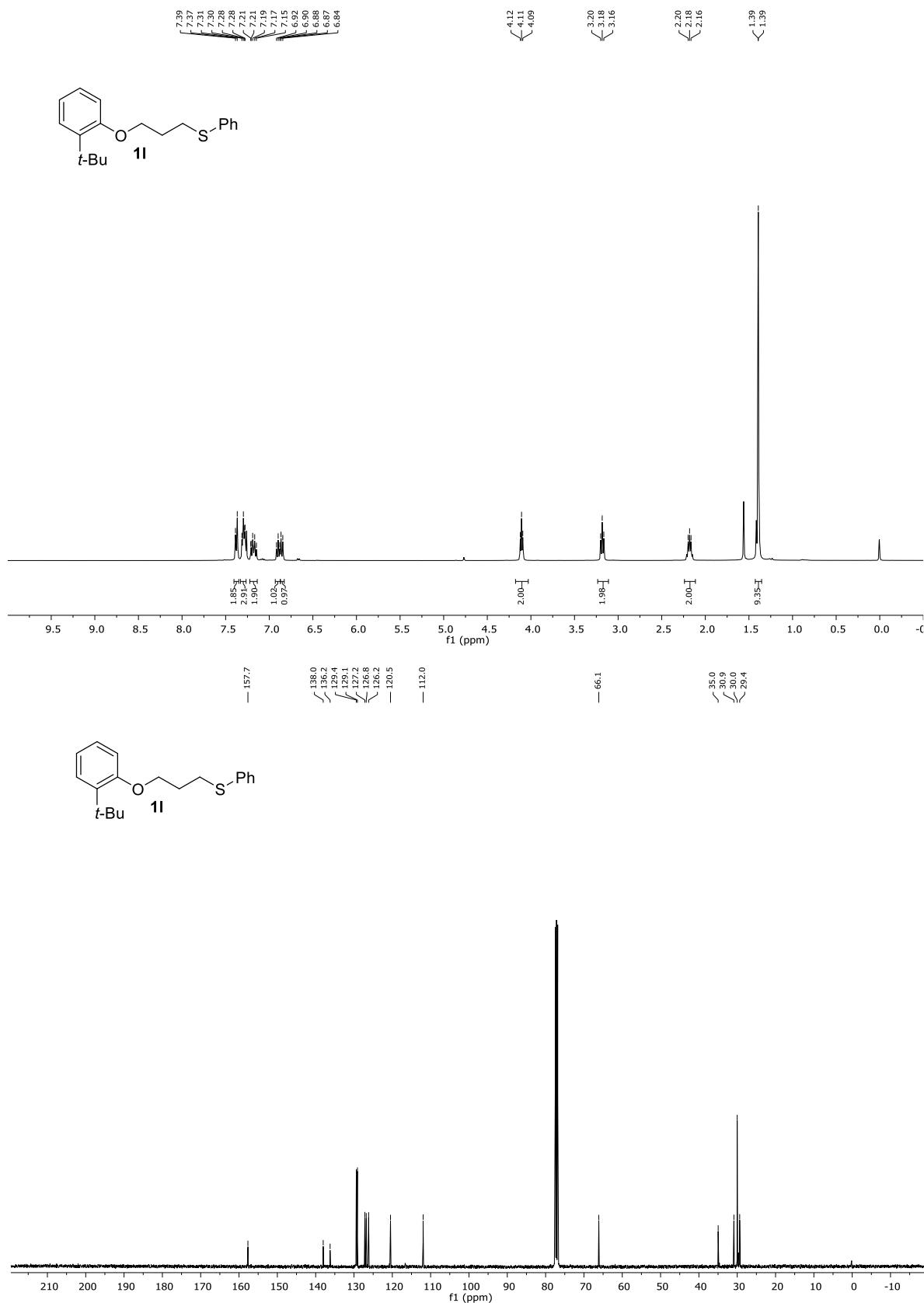
(3-(3-Fluorophenoxy)propyl)(phenyl)sulfide (1j).



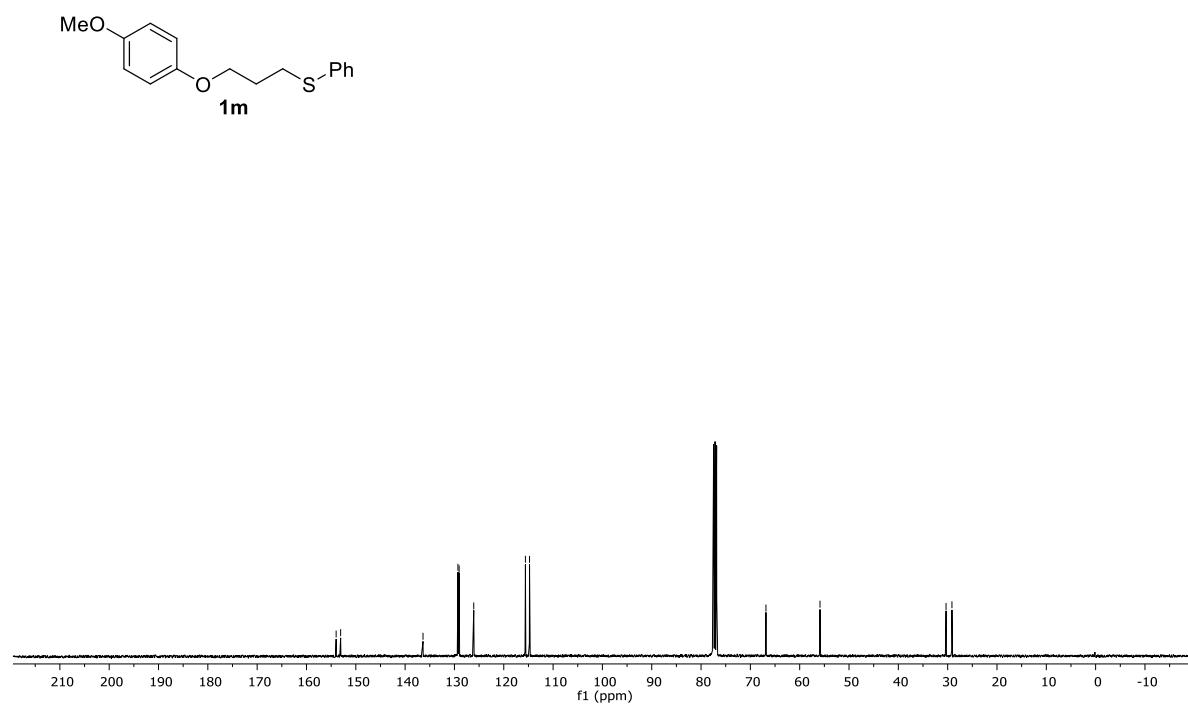
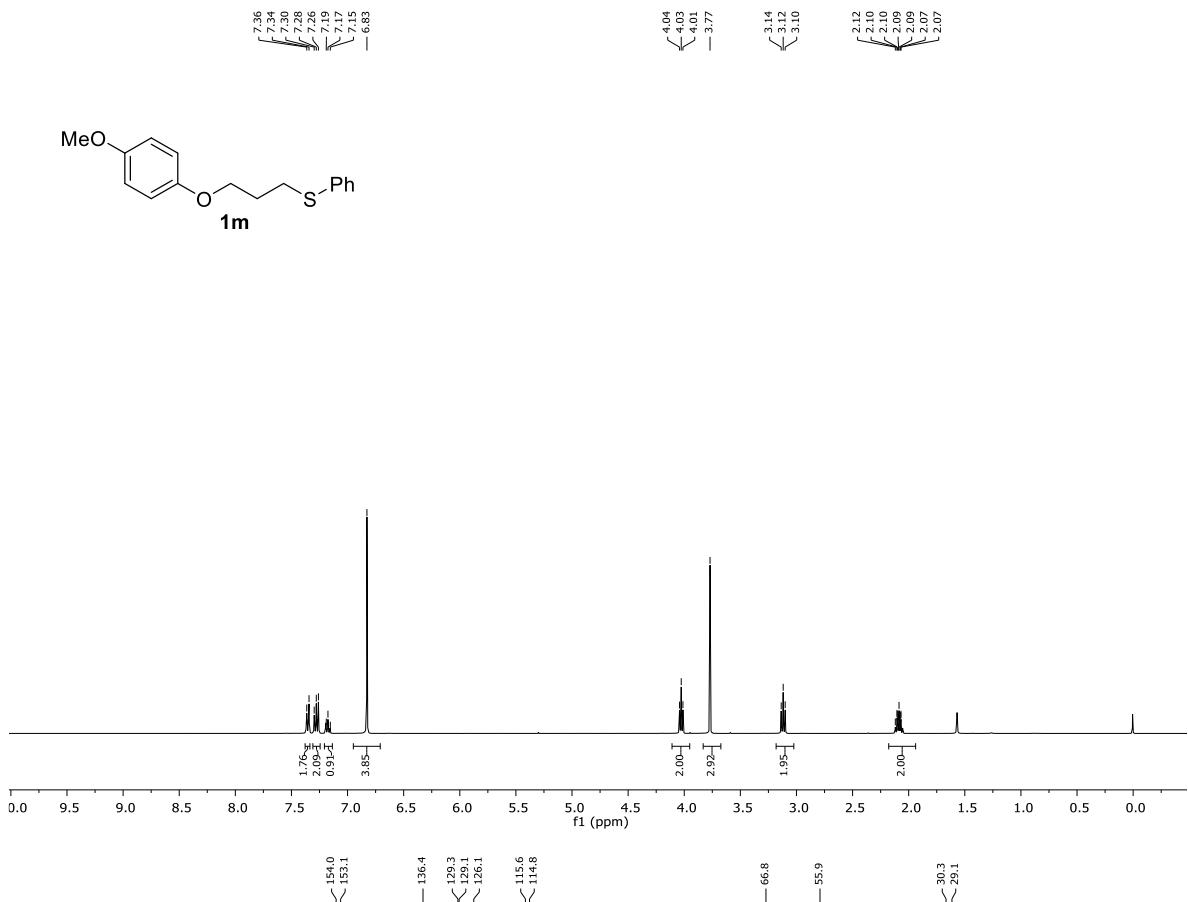
Phenyl(3-(*p*-tolyloxy)propyl)sulfide (1k**).**



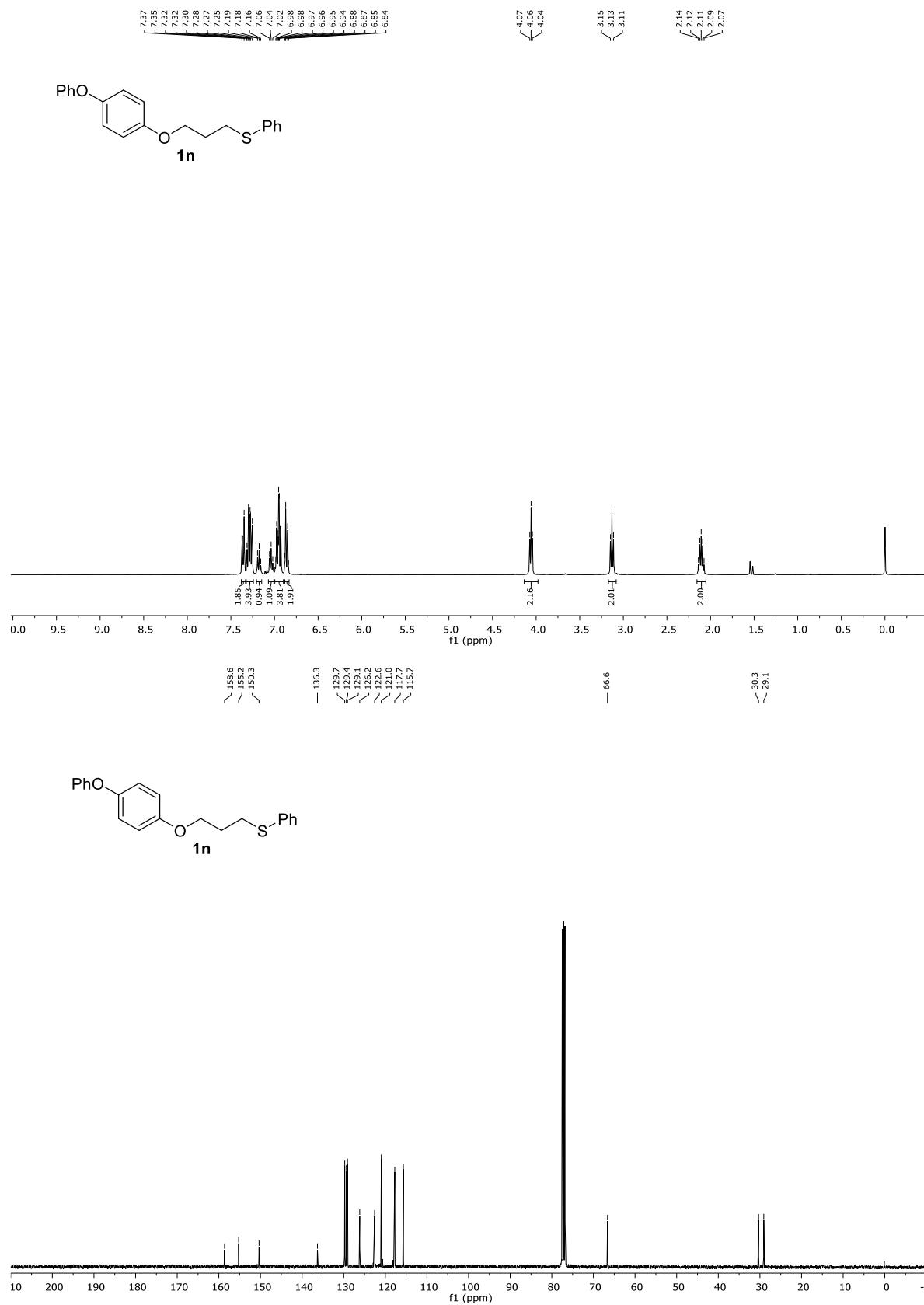
(3-(2-(tert-butyl)phenoxy)propyl)(phenyl)sulfide (1l**).**



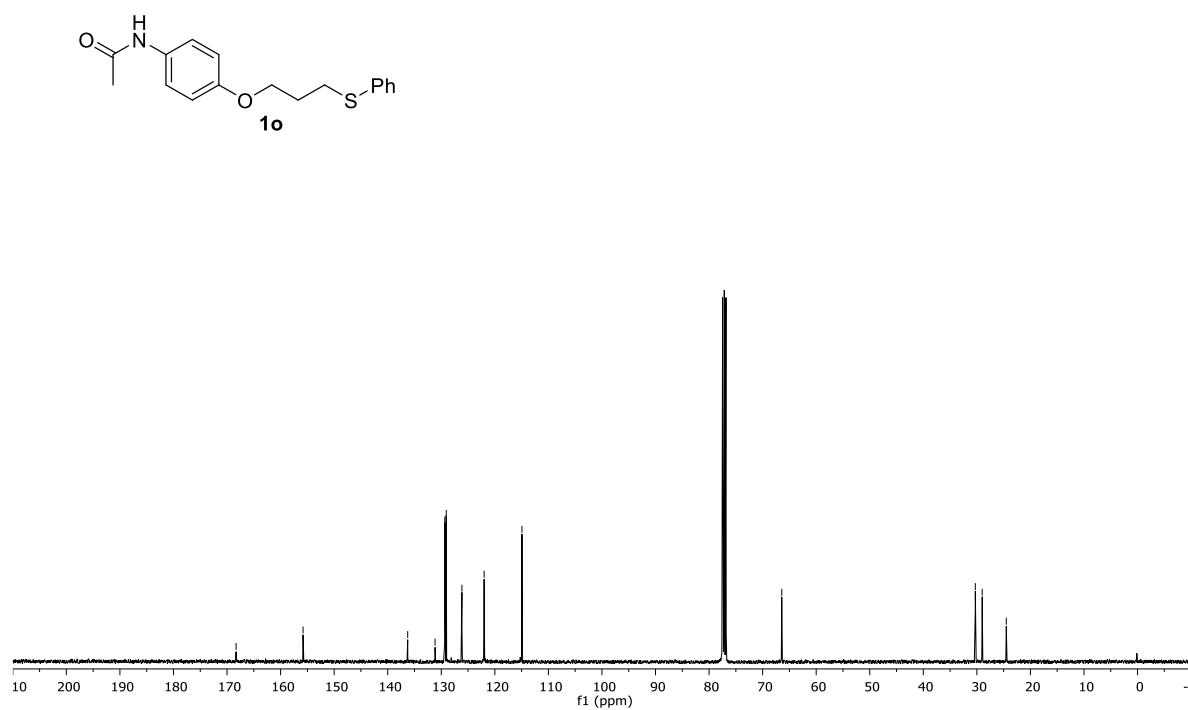
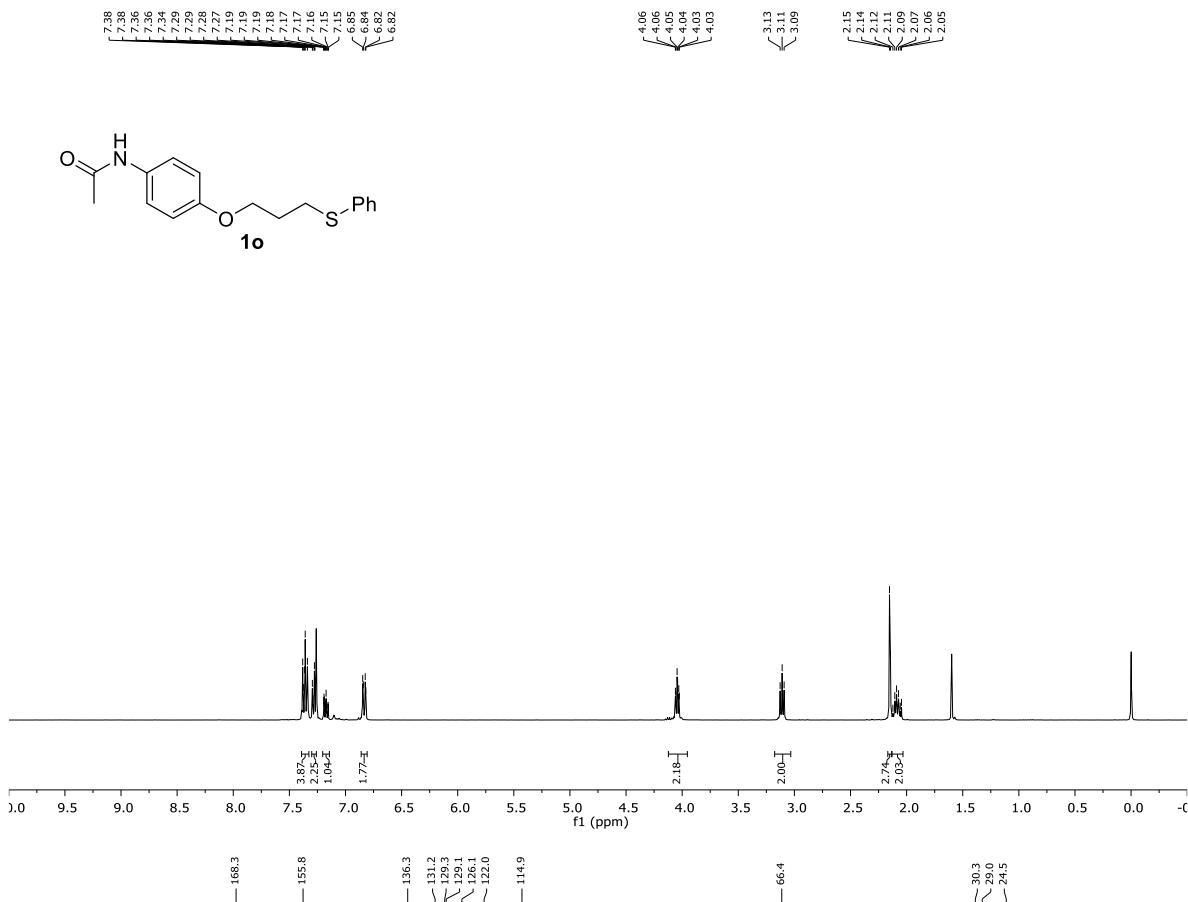
(3-(4-Methoxyphenoxy)propyl)(phenyl)sulfane (1m**).**



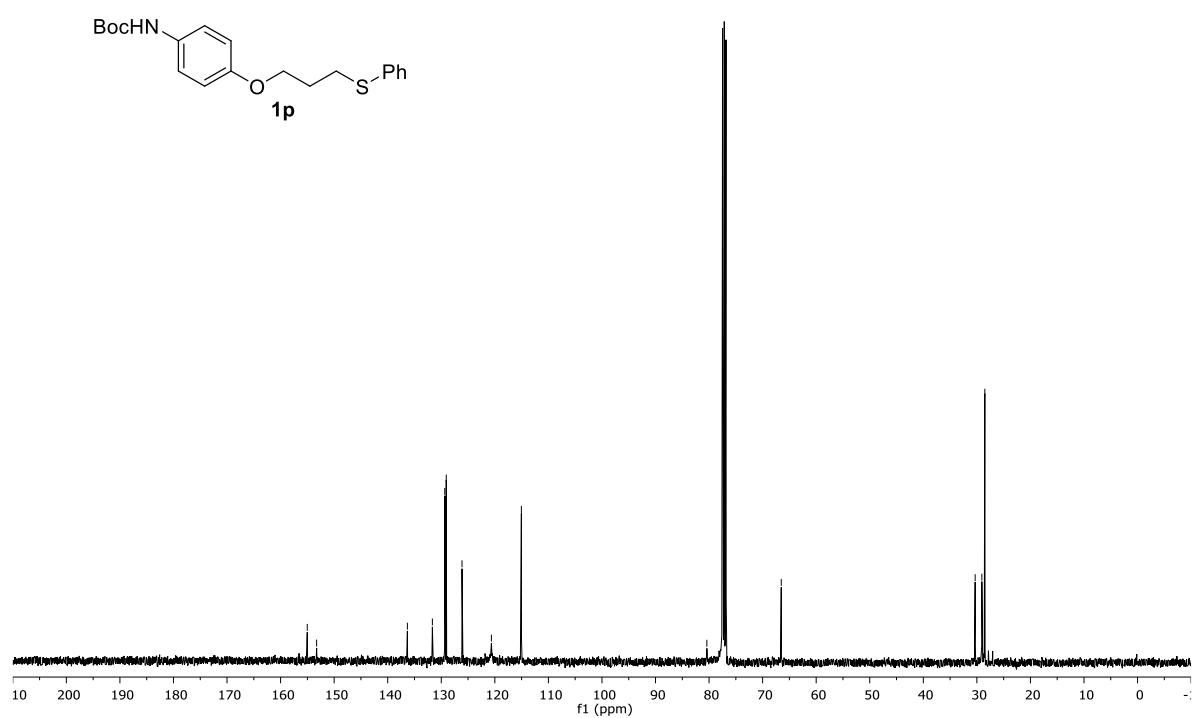
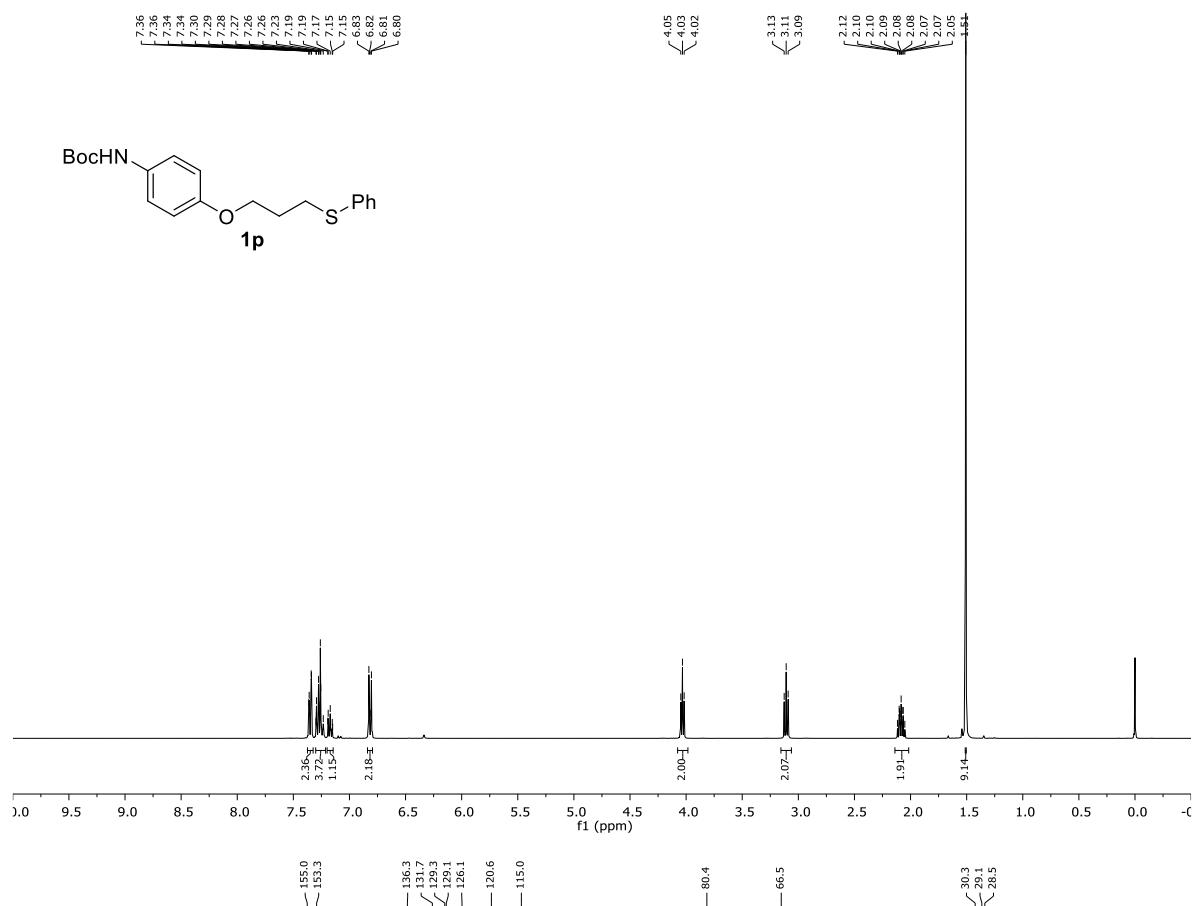
(3-(4-Phenoxyphenoxy)propyl)(phenyl)sulfide (1n**).**



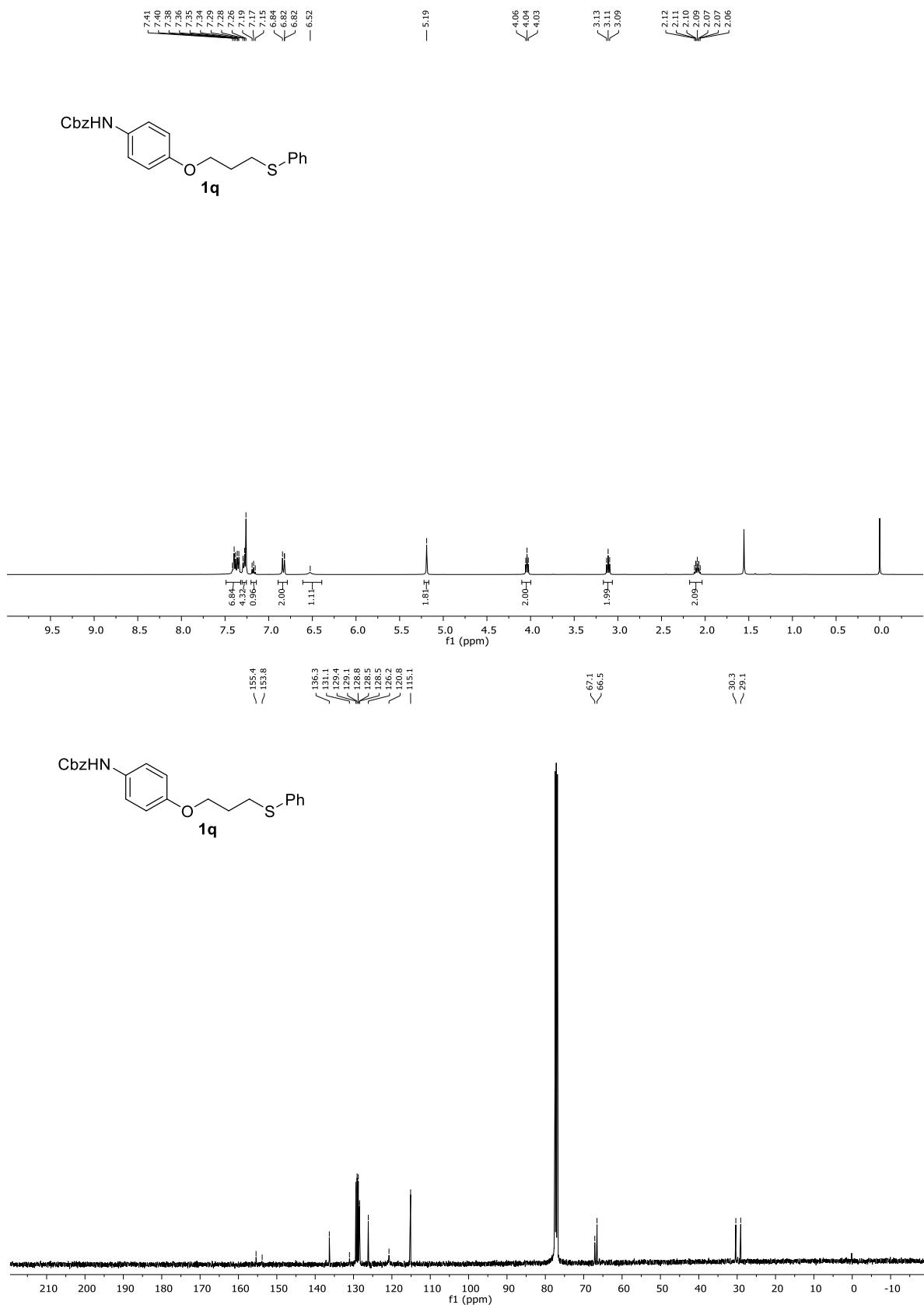
N-(4-(3-(Phenylthio)propoxy)phenyl)acetamide (1o).



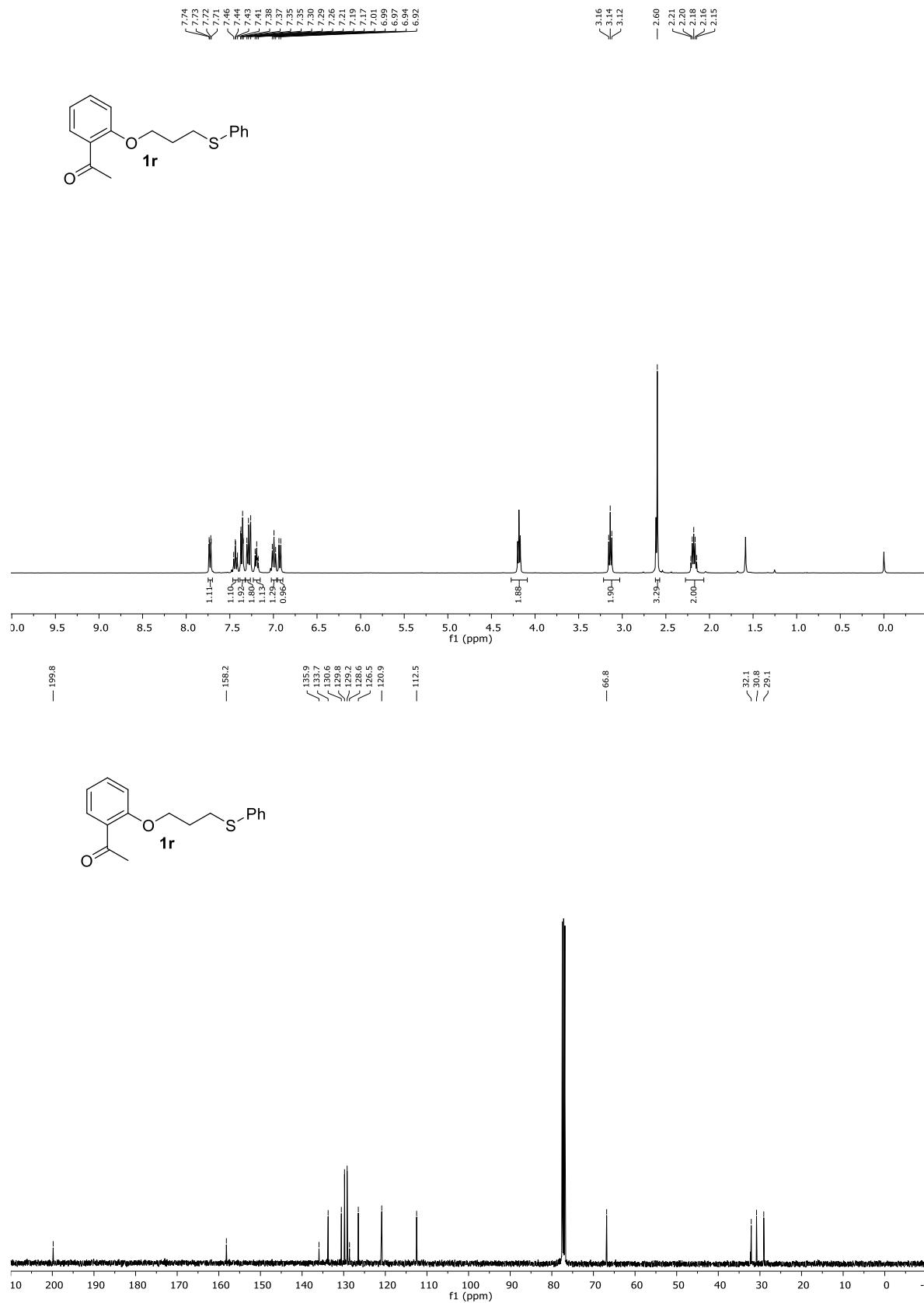
tert-butyl (4-(3-(phenylthio)propoxy)phenyl)carbamate (1p).



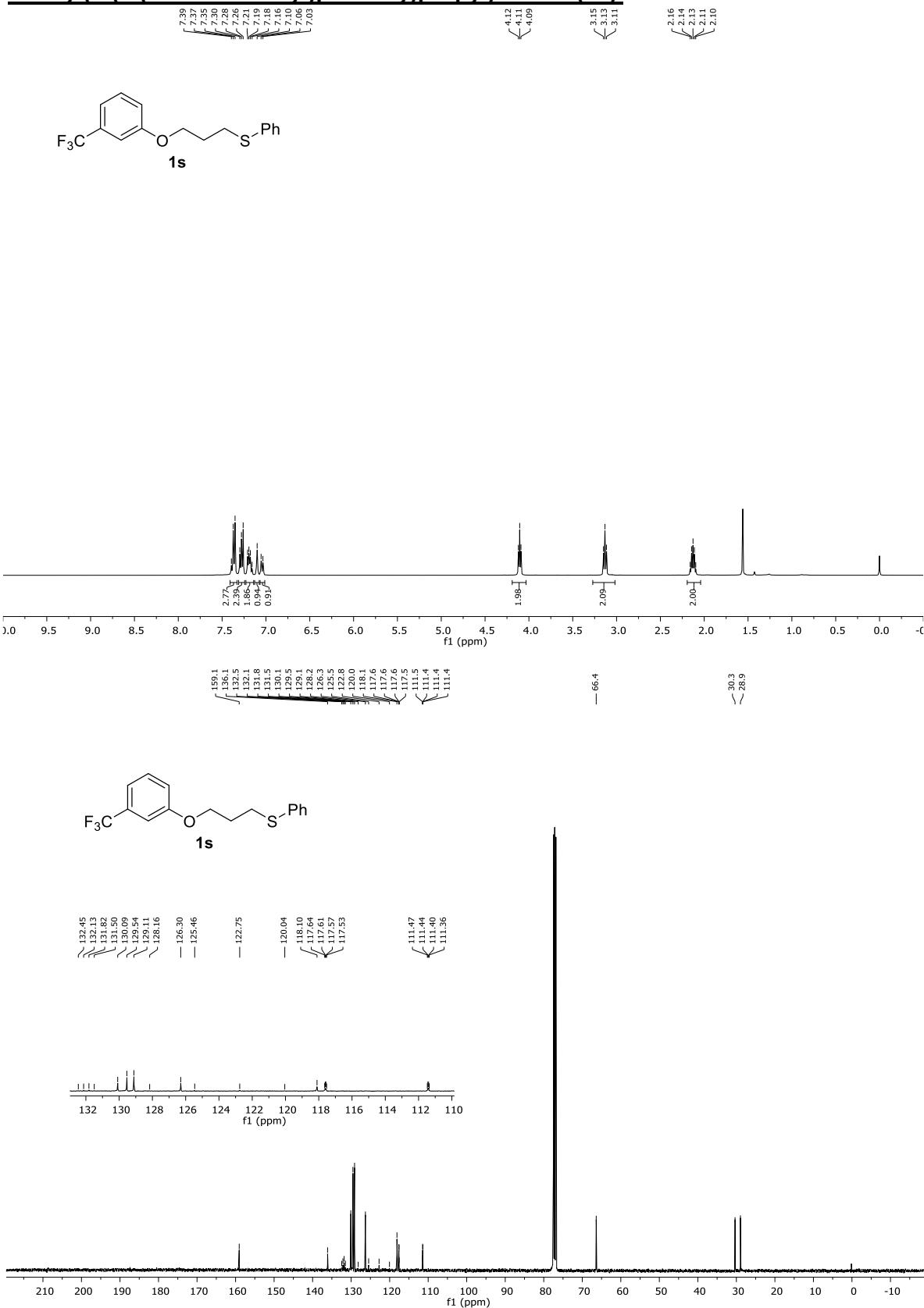
Benzyl (4-(3-(phenylthio)propoxy)phenyl)carbamate (1q).



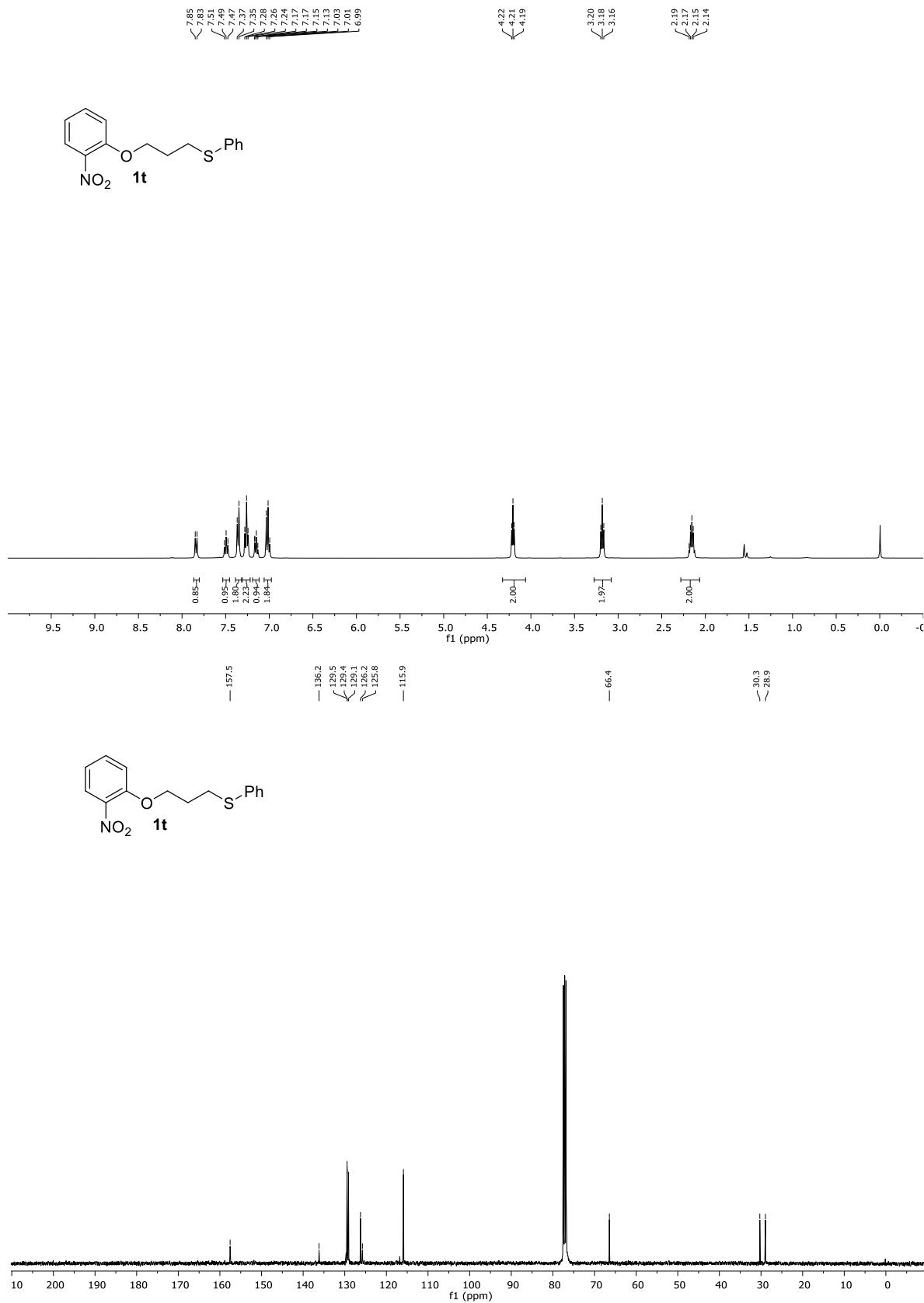
1-(2-(3-(Phenylthio)propoxy)phenyl)ethanone (1r).



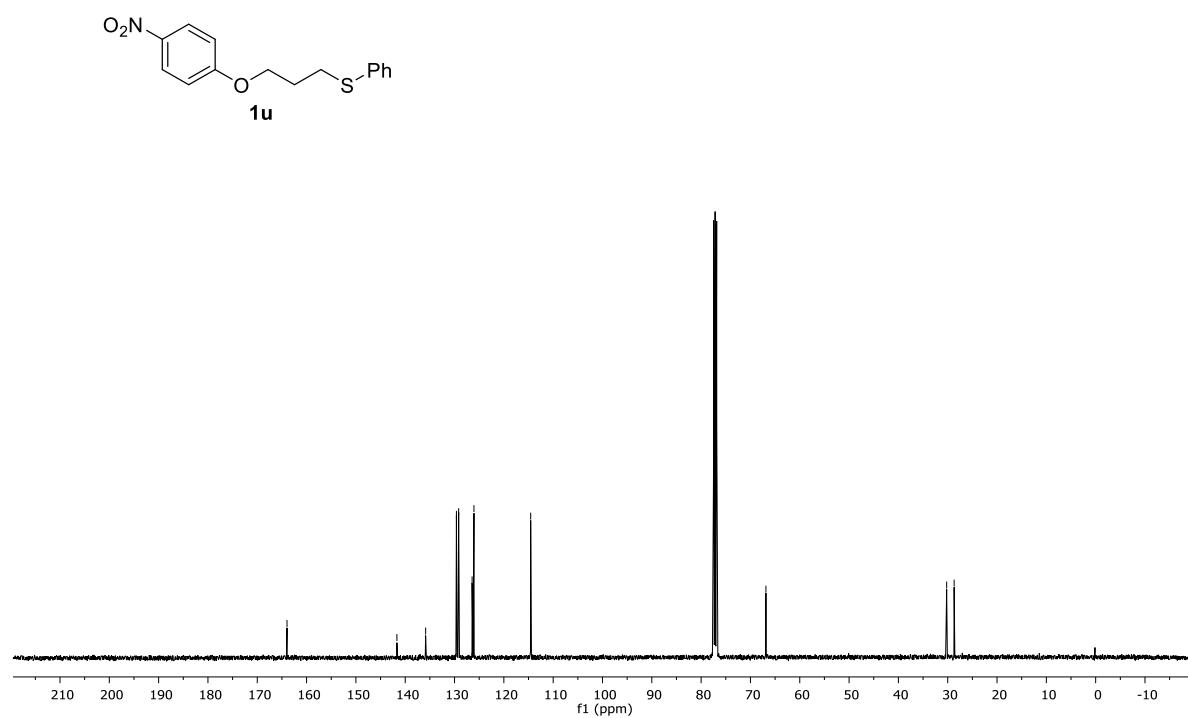
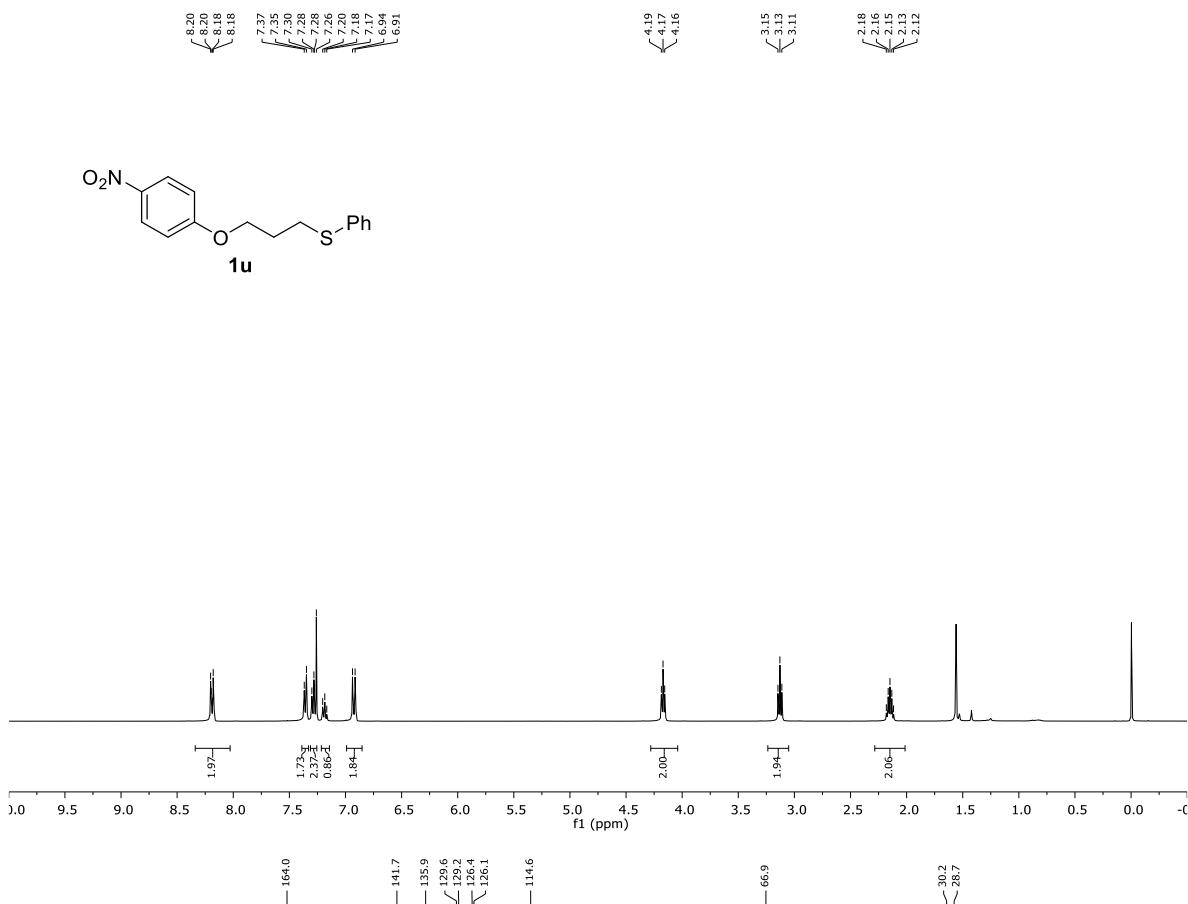
Phenyl(3-(3-(trifluoromethyl)phenoxy)propyl)sulfide (1s).



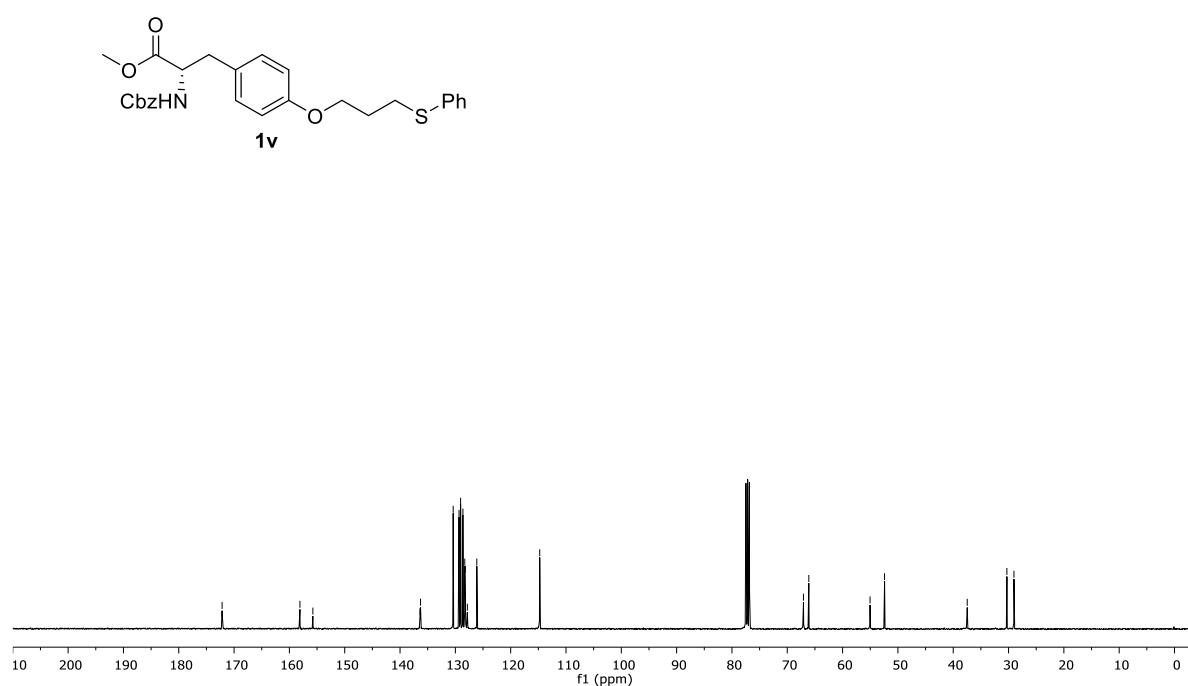
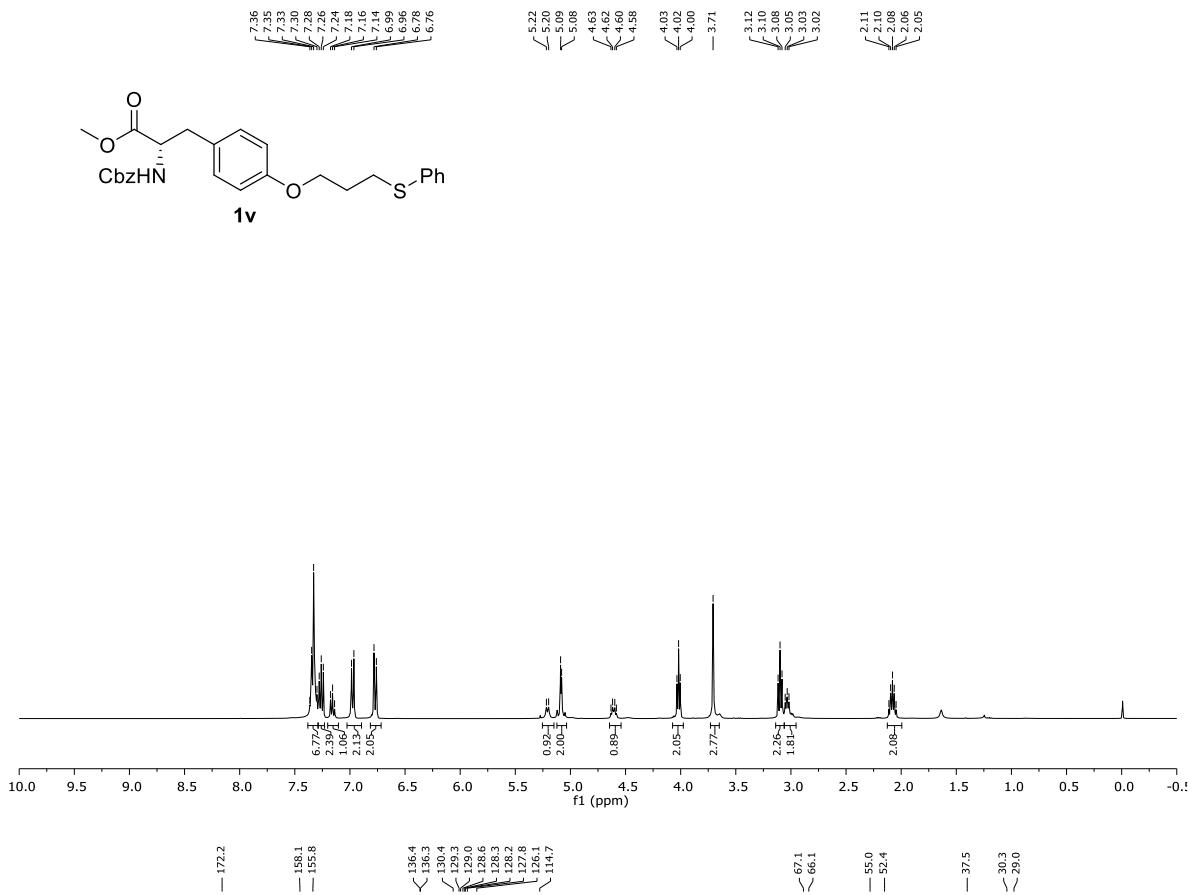
(3-(2-Nitrophenoxy)propyl)(phenyl)sulfide (1t**).**



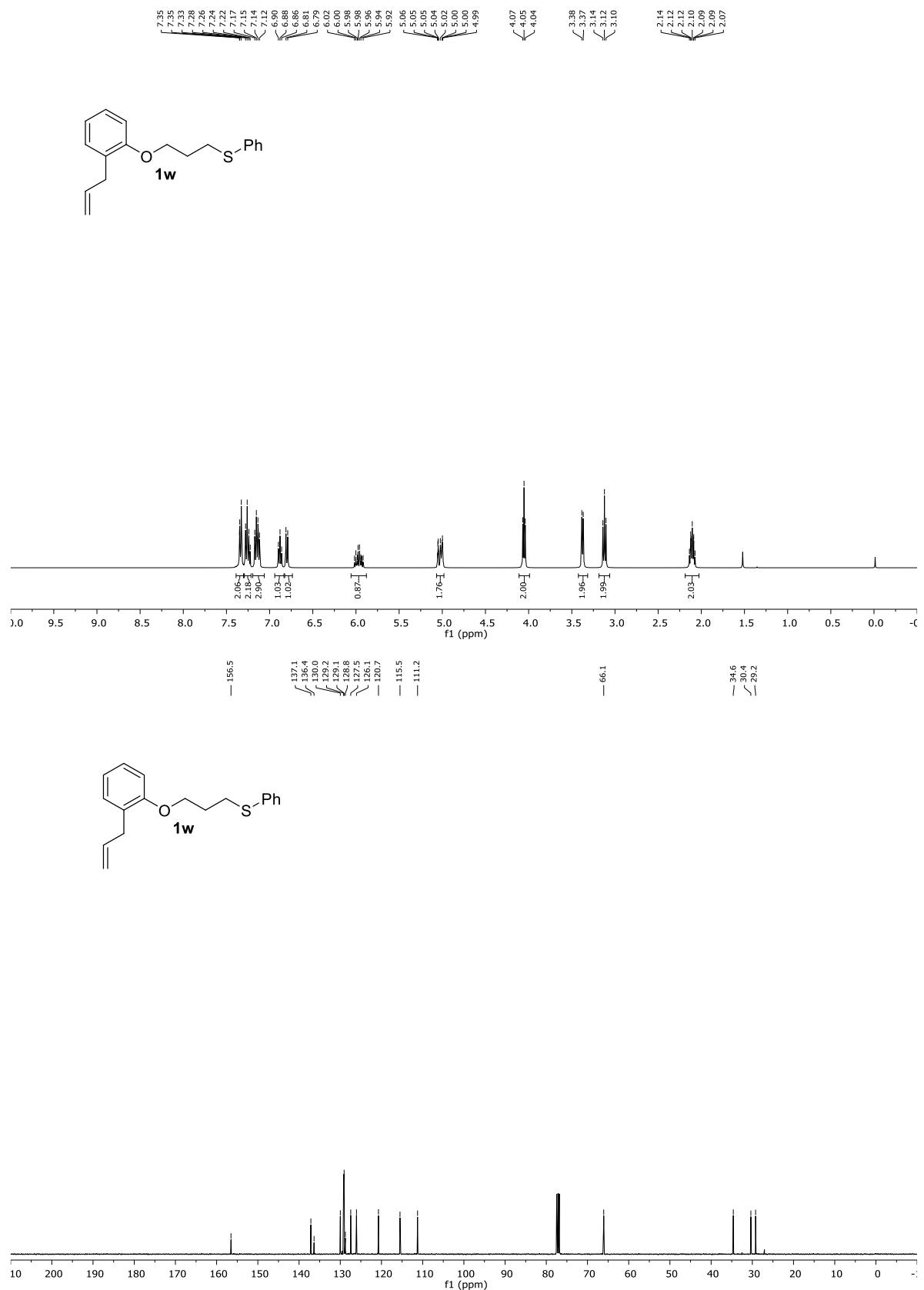
(3-(4-Nitrophenoxy)propyl)(phenyl)sulfide (1u).



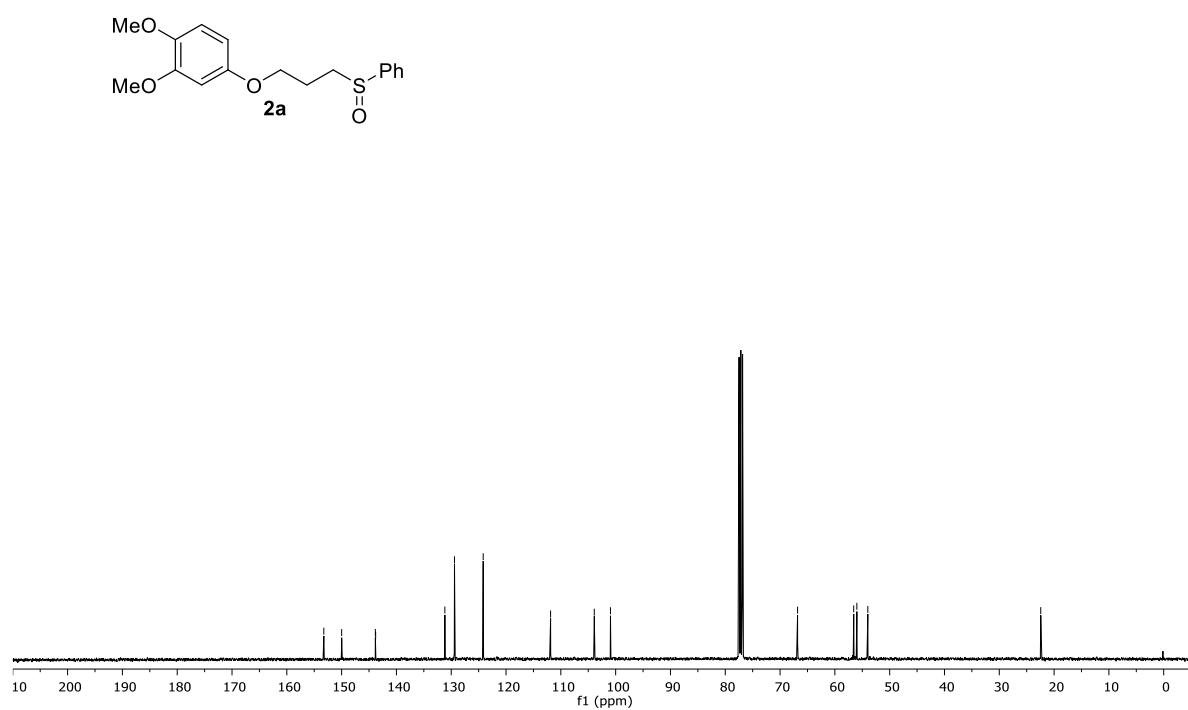
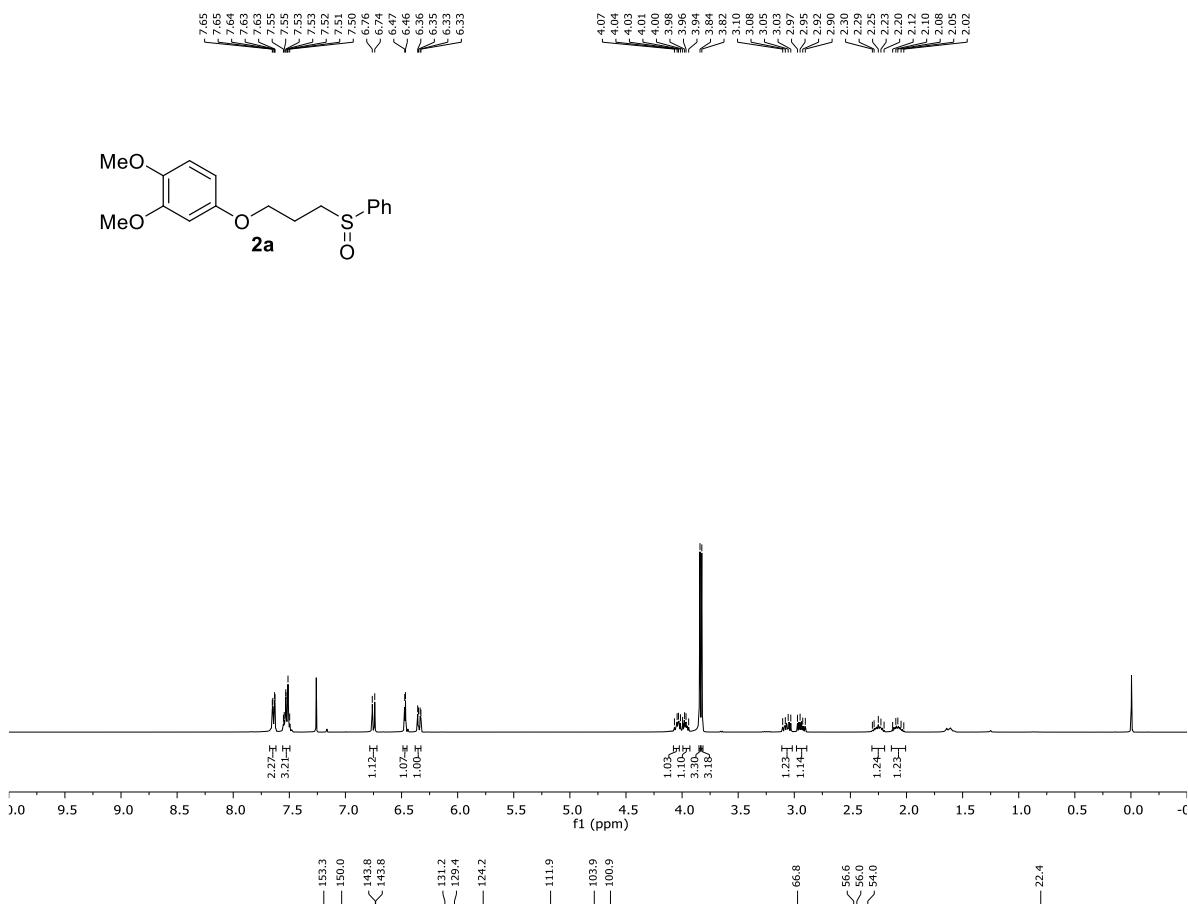
(S)-Methyl-2-(((benzyloxy)carbonyl)amino)-3-(4-(3-(phenylthio)propoxy)phenyl)propanoate (1v).



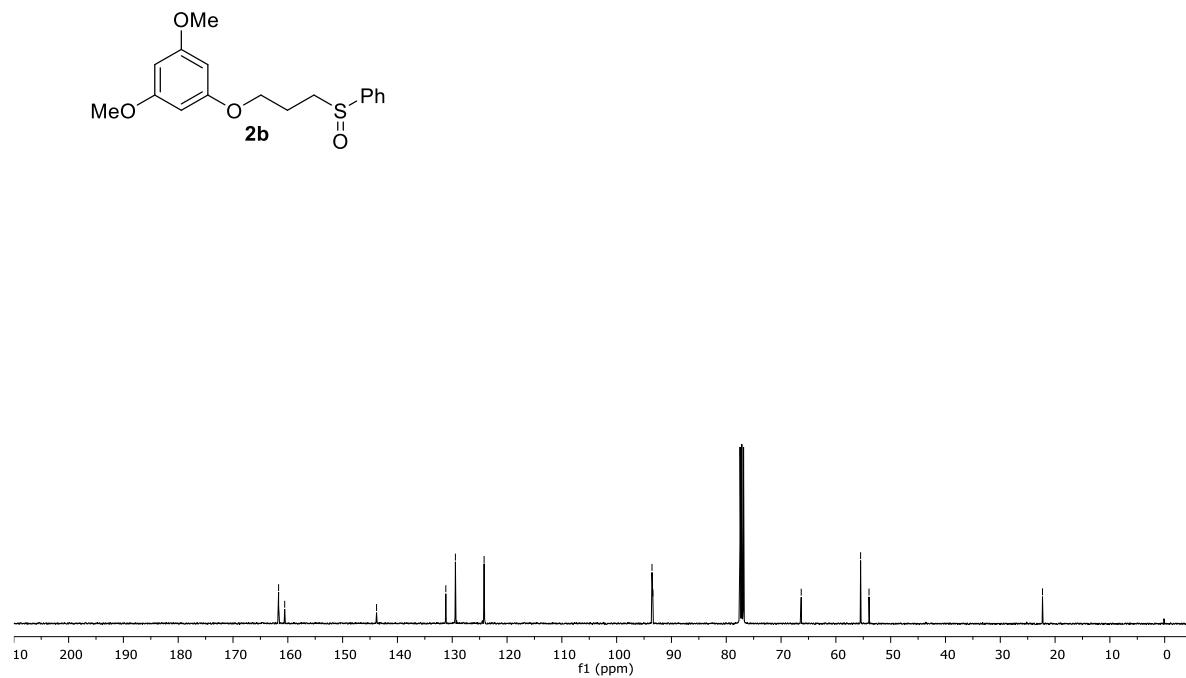
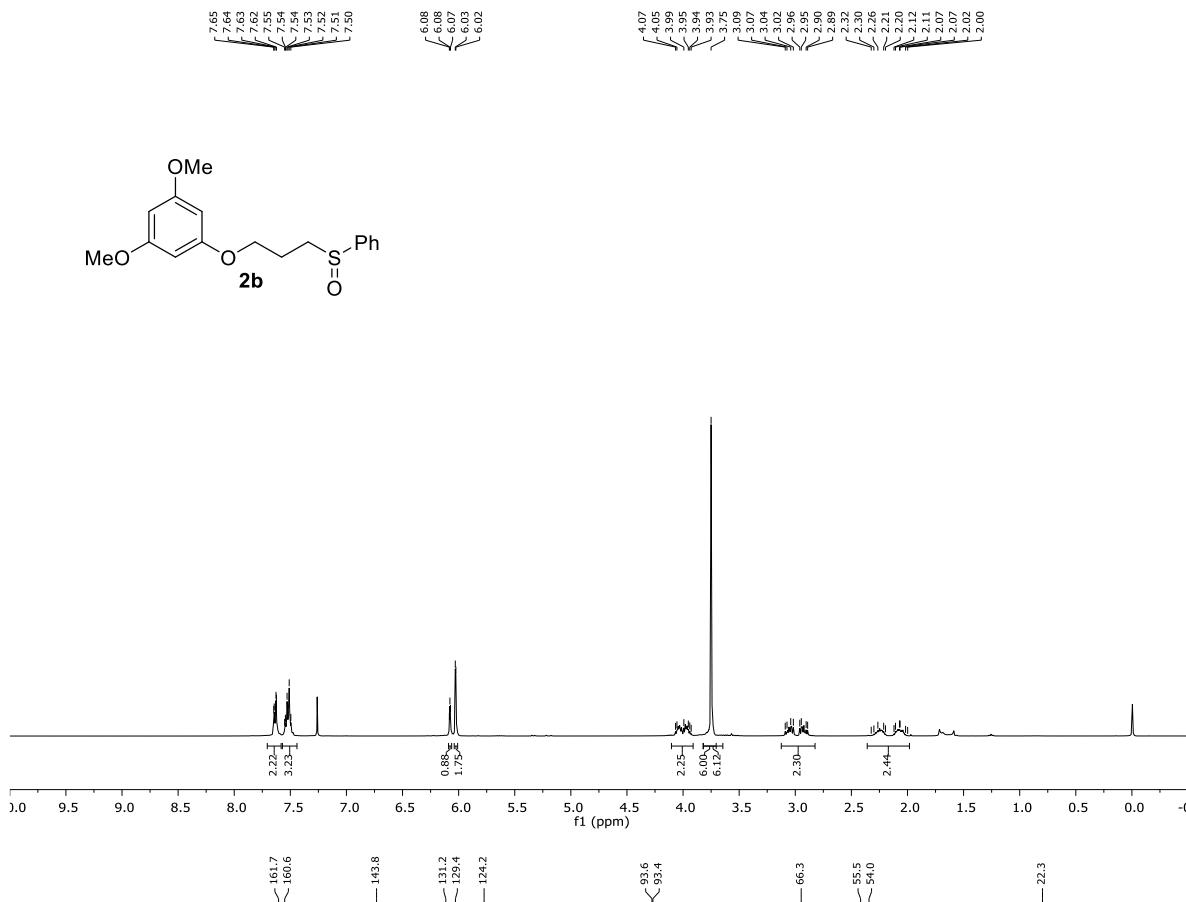
(3-(2-allylphenoxy)propyl)(phenyl)sulfide (1w).



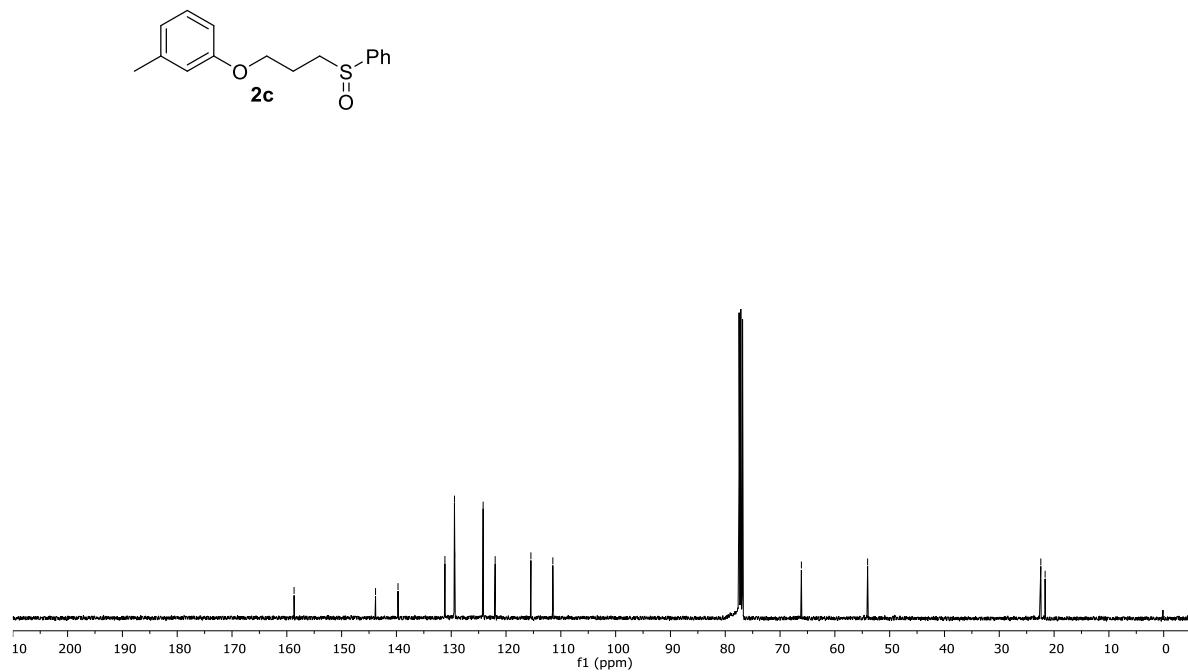
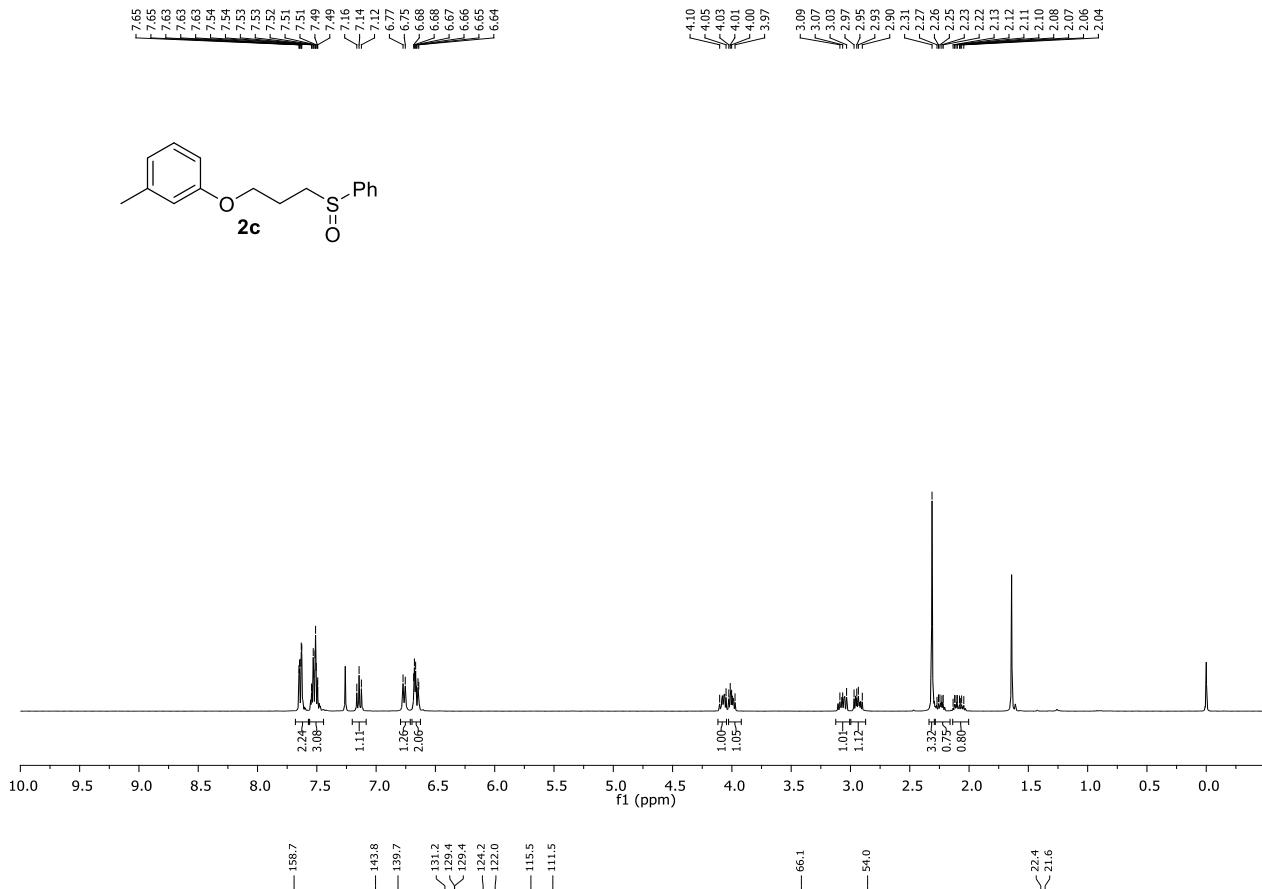
1,2-Dimethoxy-4-(3-(phenylsulfinyl)propoxy)benzene (2a).



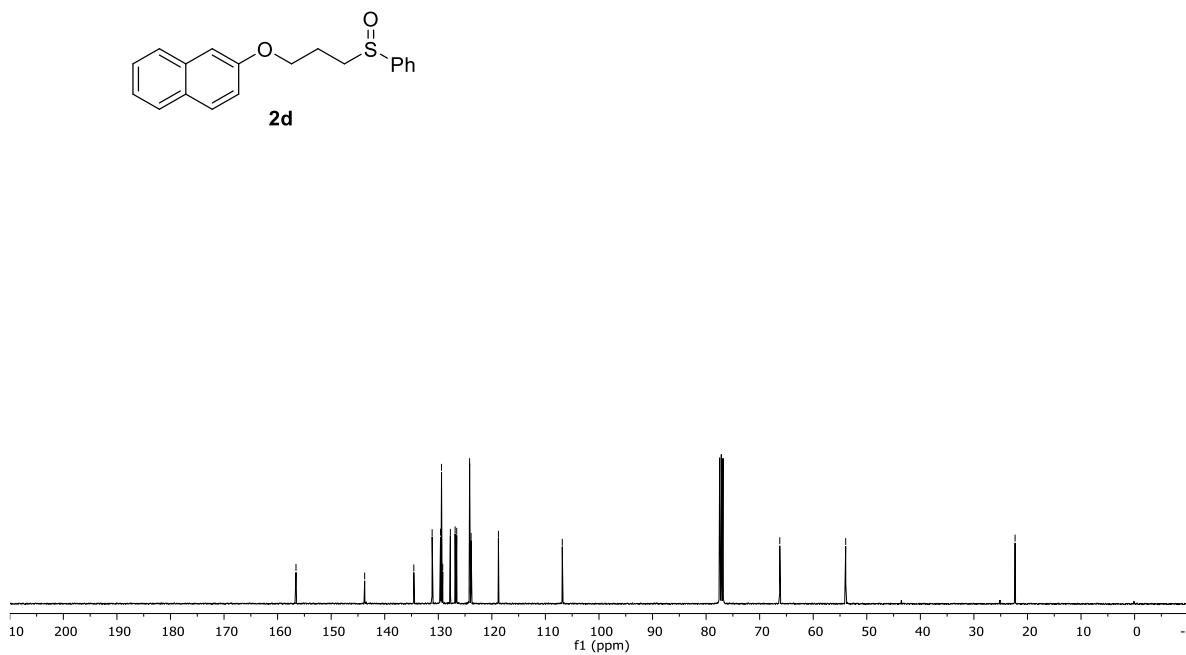
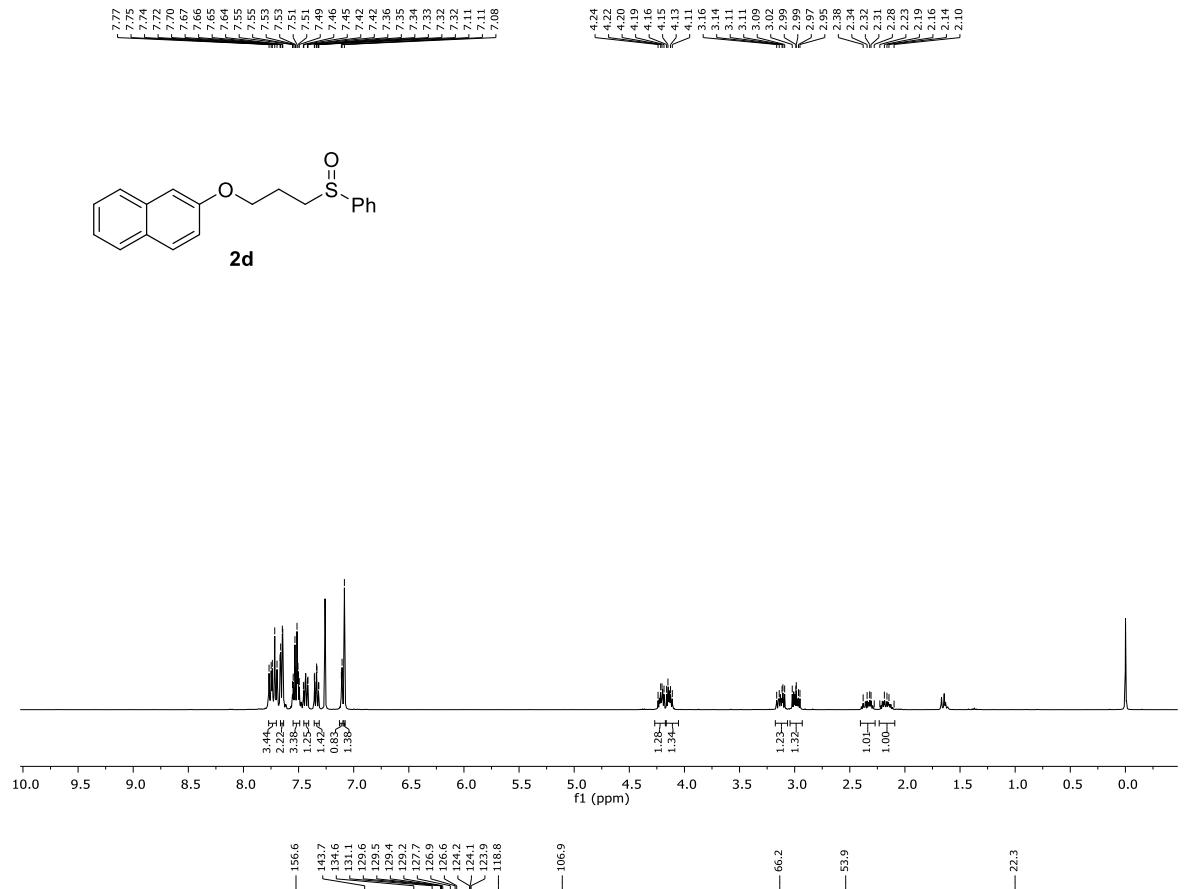
1,3-Dimethoxy-5-(3-(phenylsulfinyl)propoxy)benzene (2b).



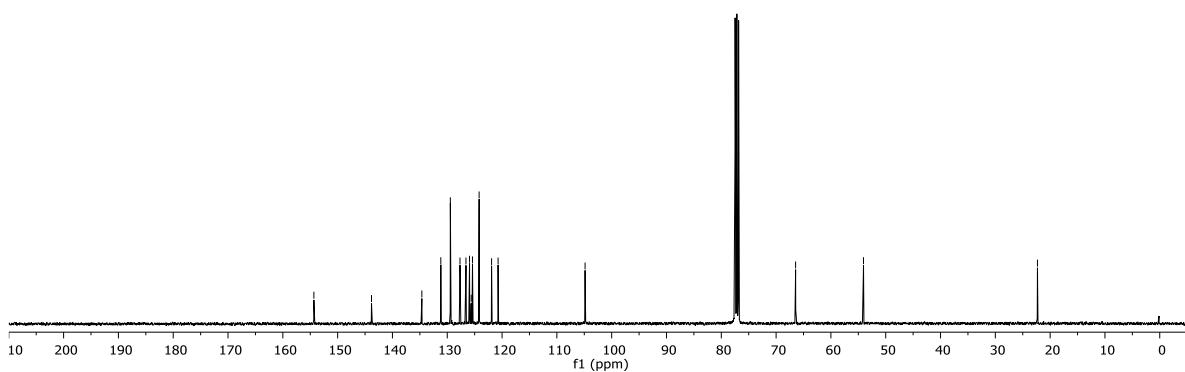
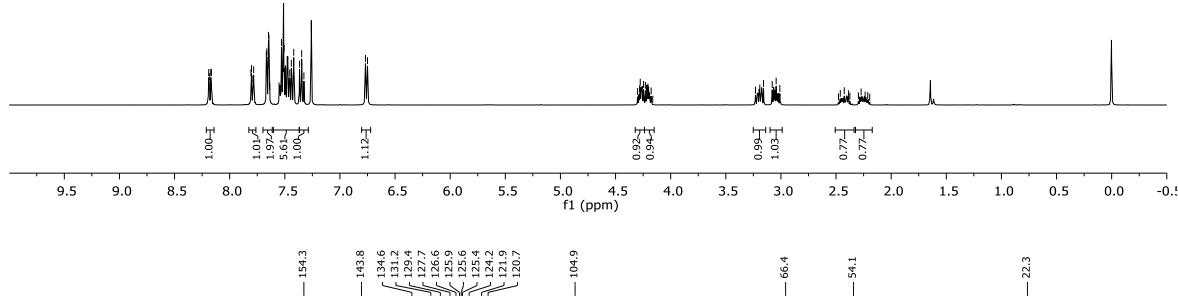
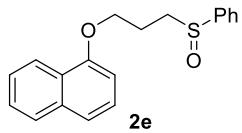
1-Methyl-3-(3-(phenylsulfinyl)propoxy)benzene (2c).



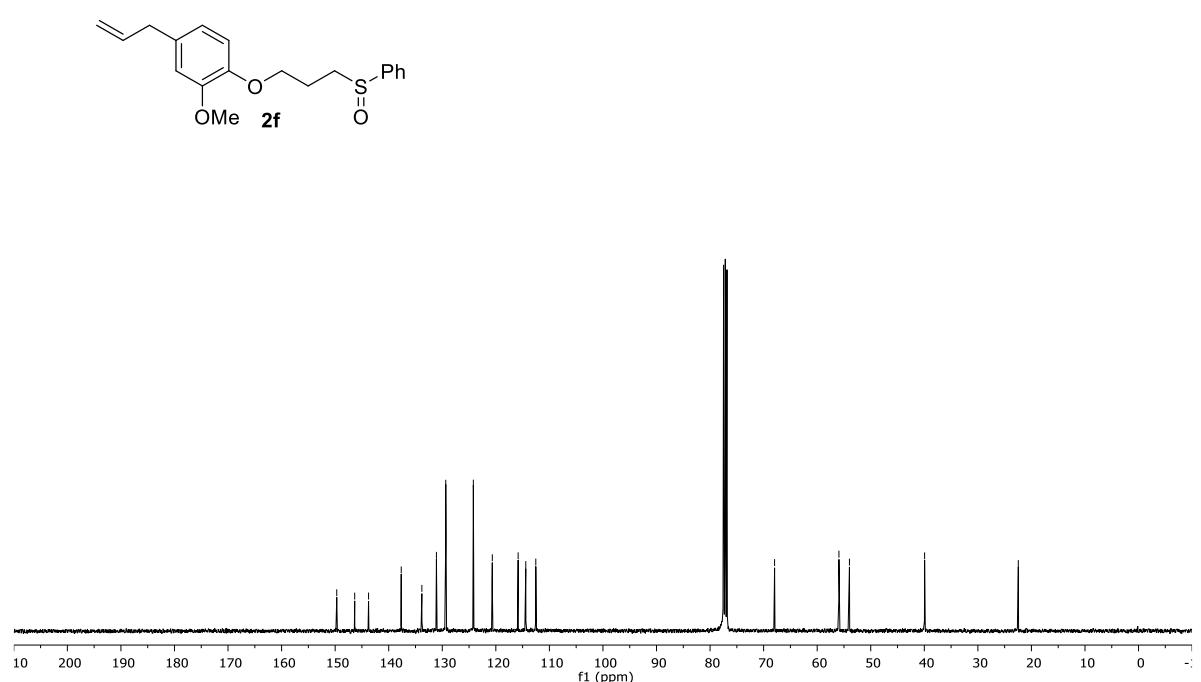
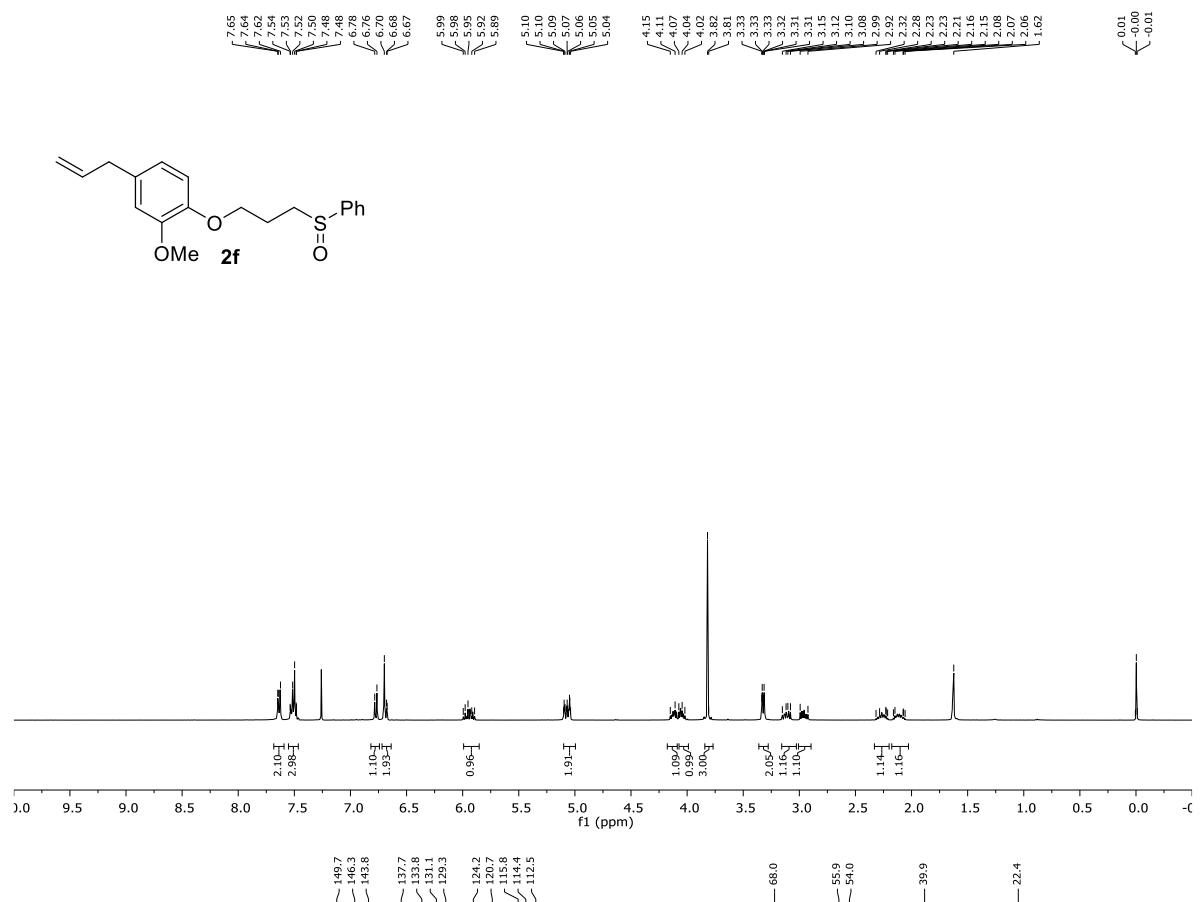
2-(3-(Phenylsulfinyl)propoxy)naphthalene (2d).



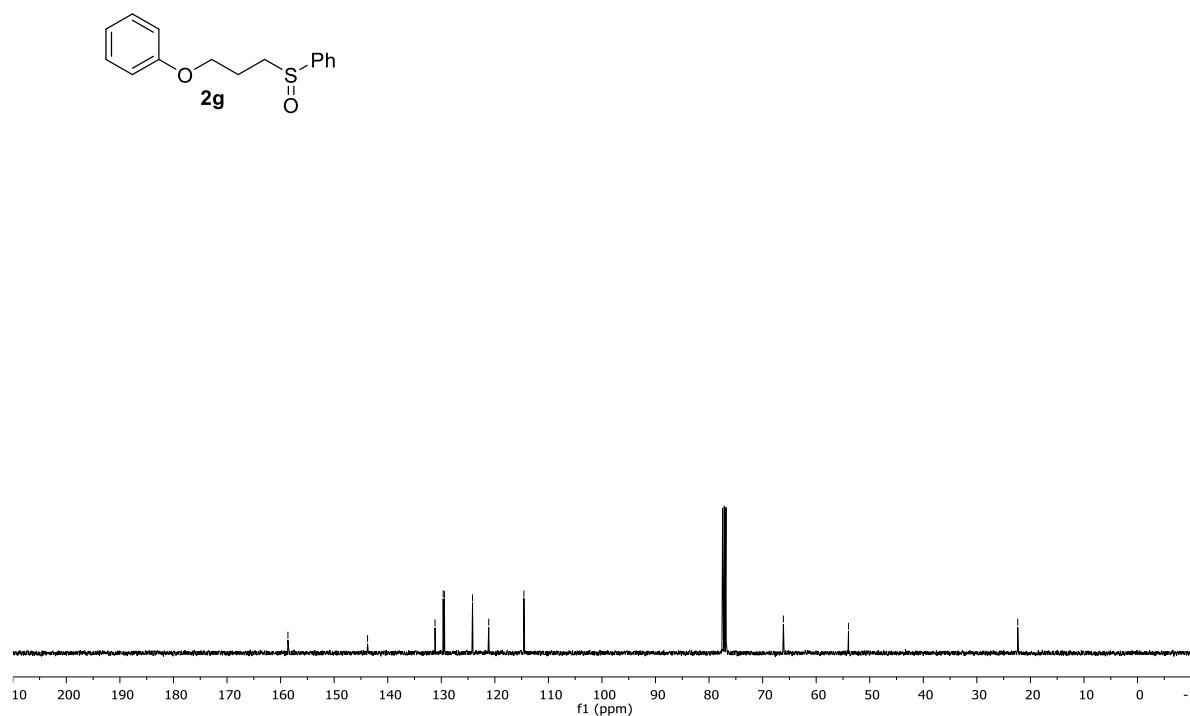
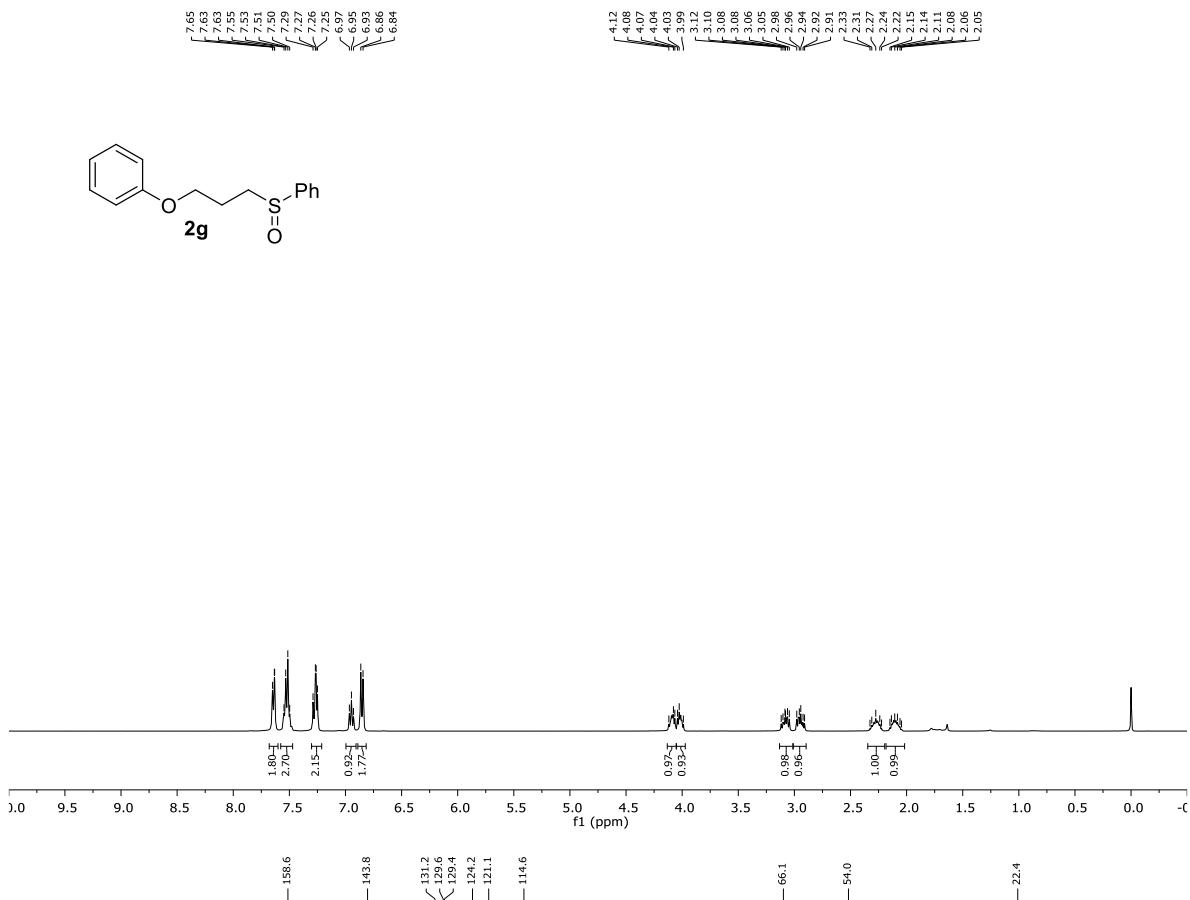
1-(3-(Phenylsulfinyl)propoxy)naphthalene (2e).



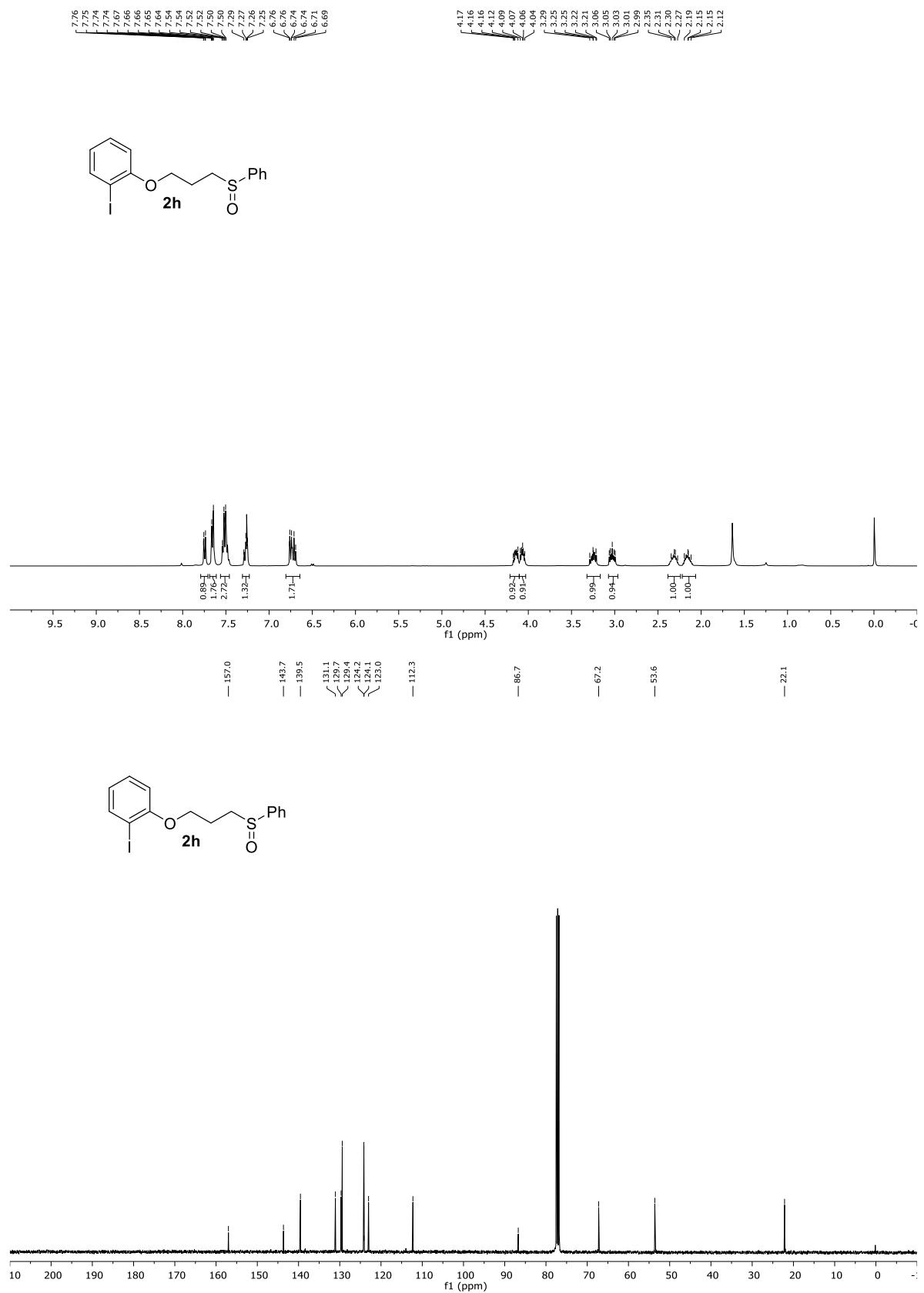
4-Allyl-2-methoxy-1-(3-(phenylsulfinyl)propoxy)benzene (2f).



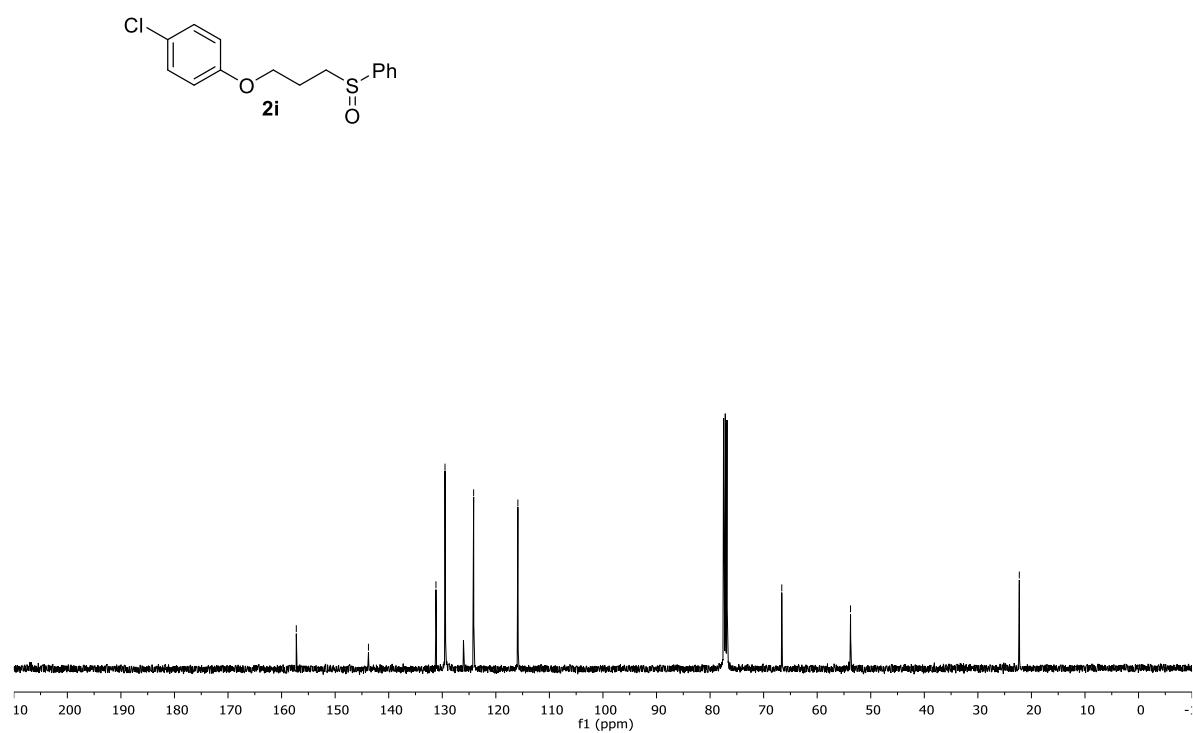
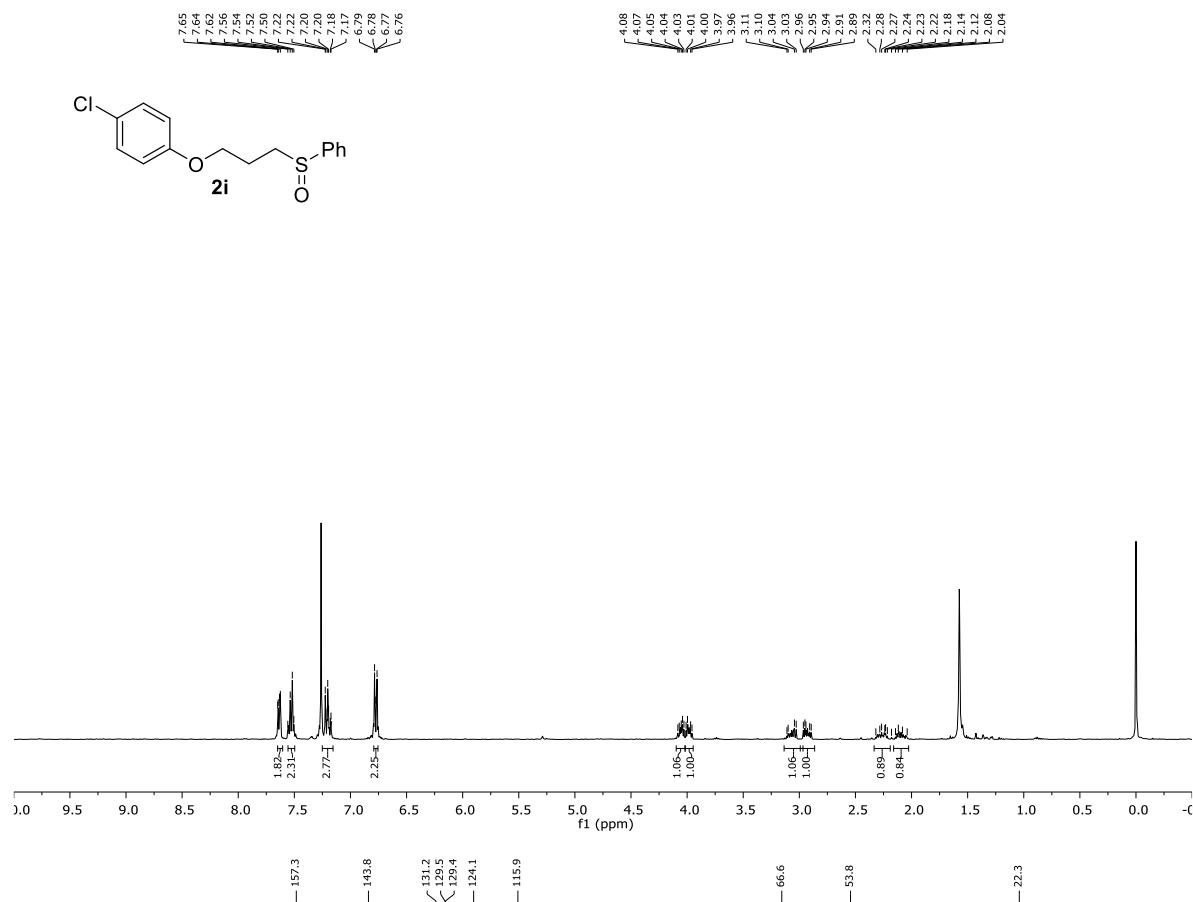
((3-Phenoxypropyl)sulfinyl)benzene (2g).



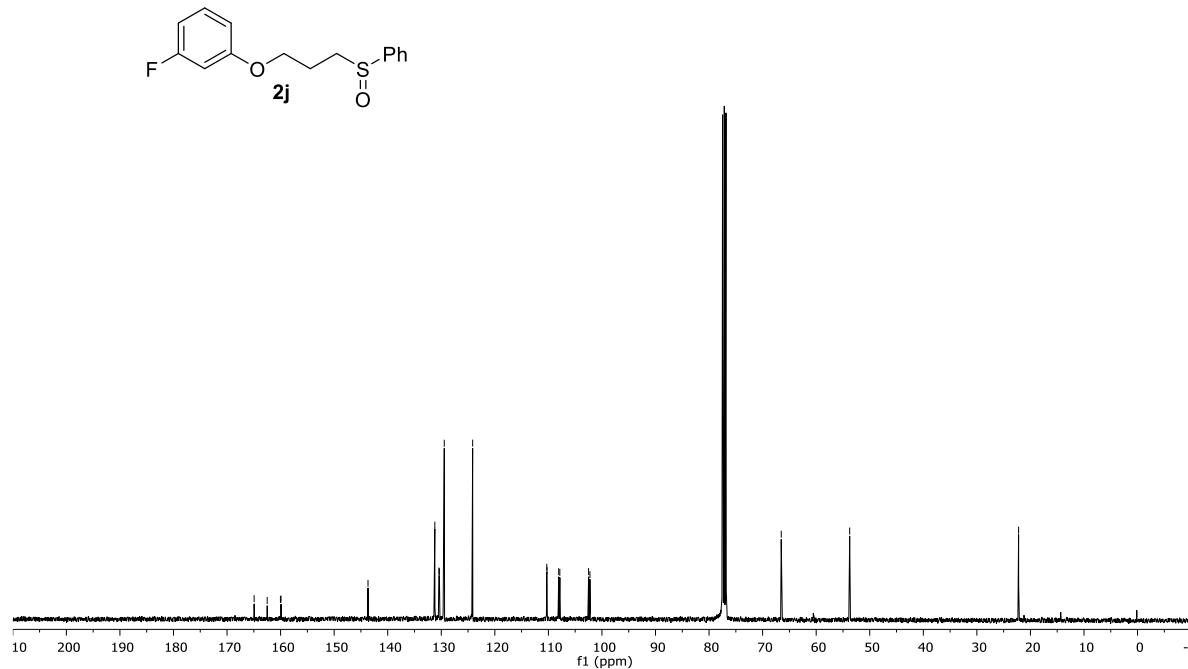
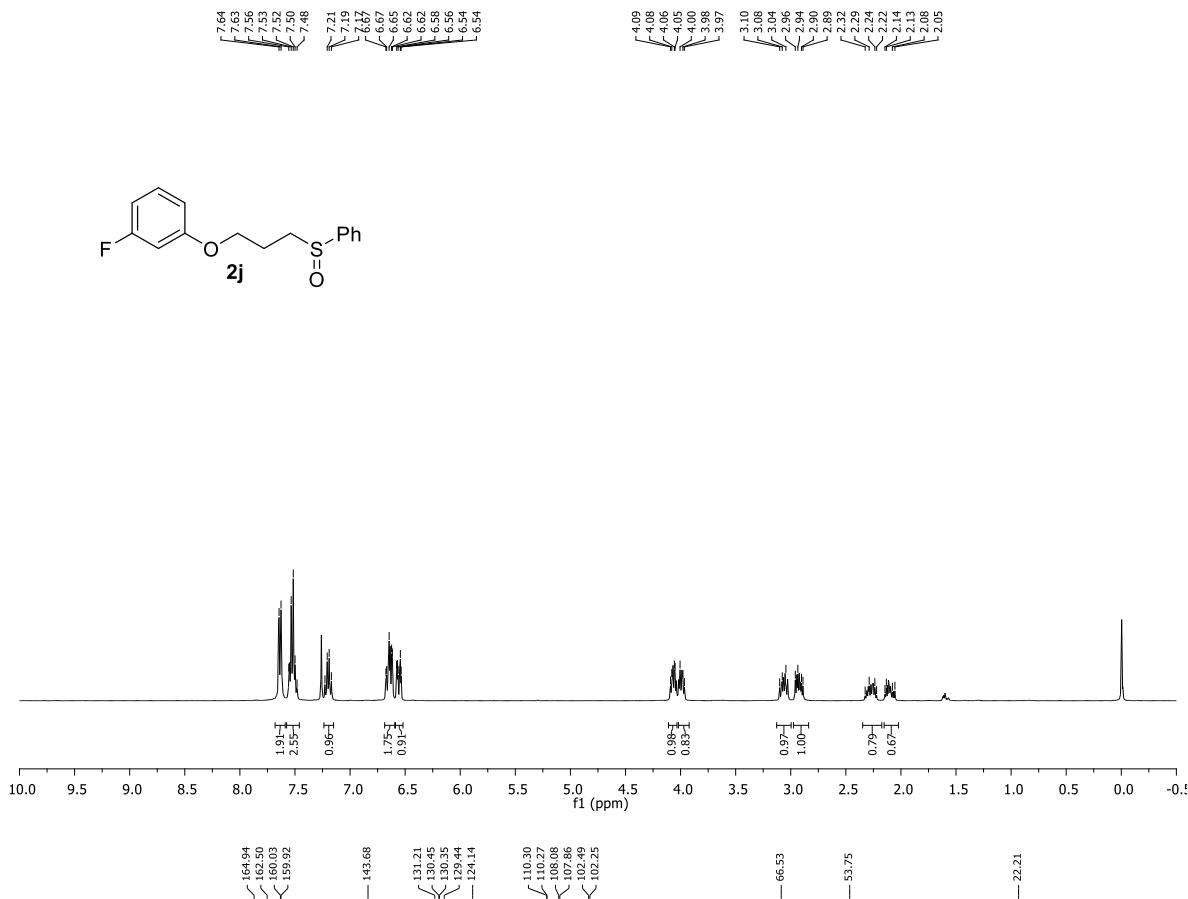
1-Iodo-2-(3-(phenylsulfinyl)propoxy)benzene (2h).



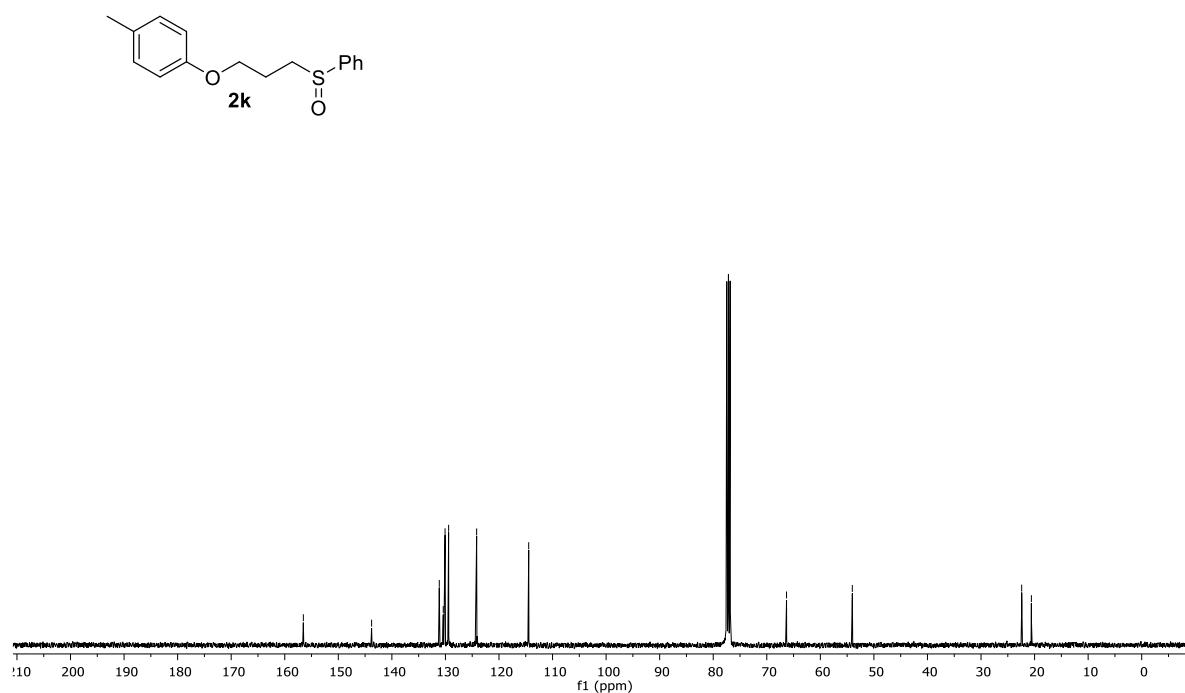
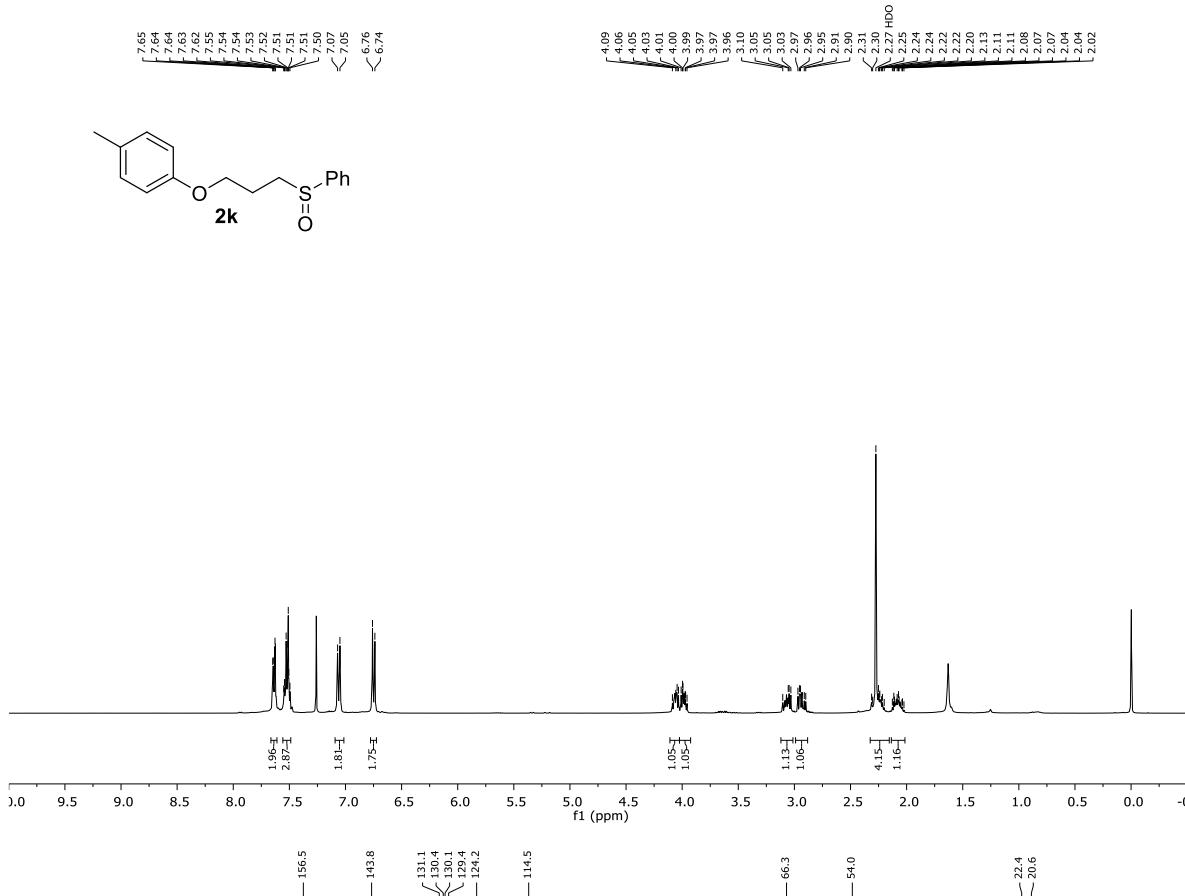
1-Chloro-4-(3-(phenylsulfinyl)propoxy)benzene (2i).



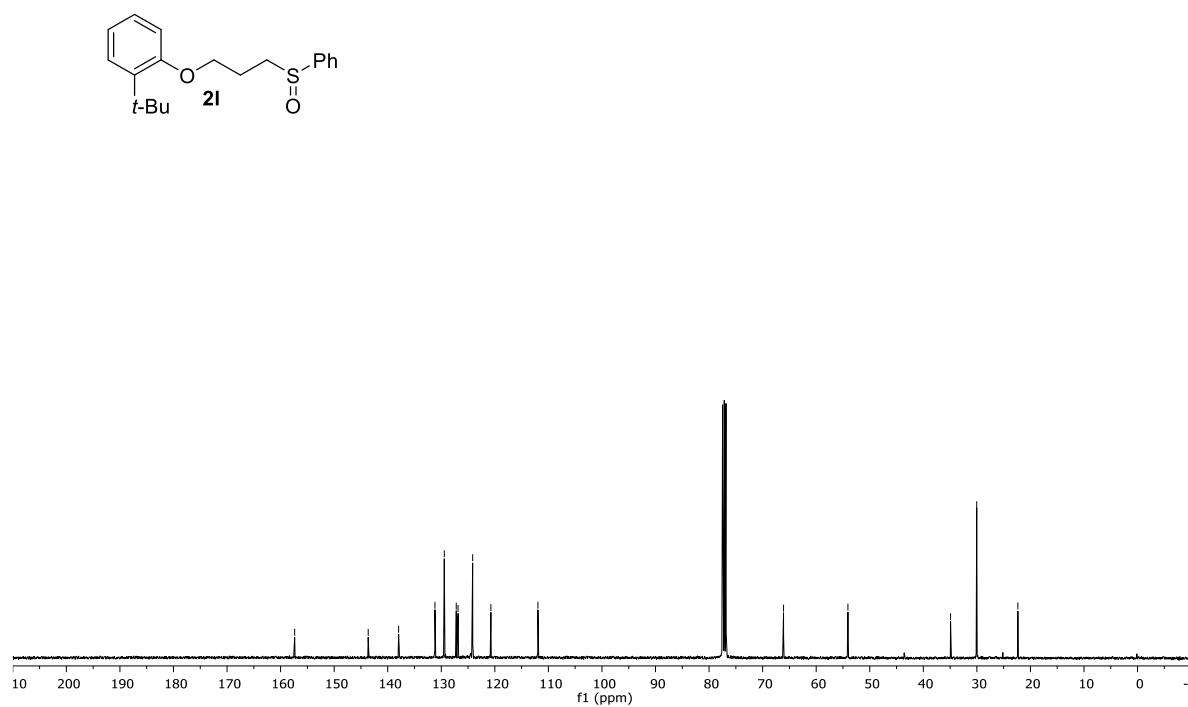
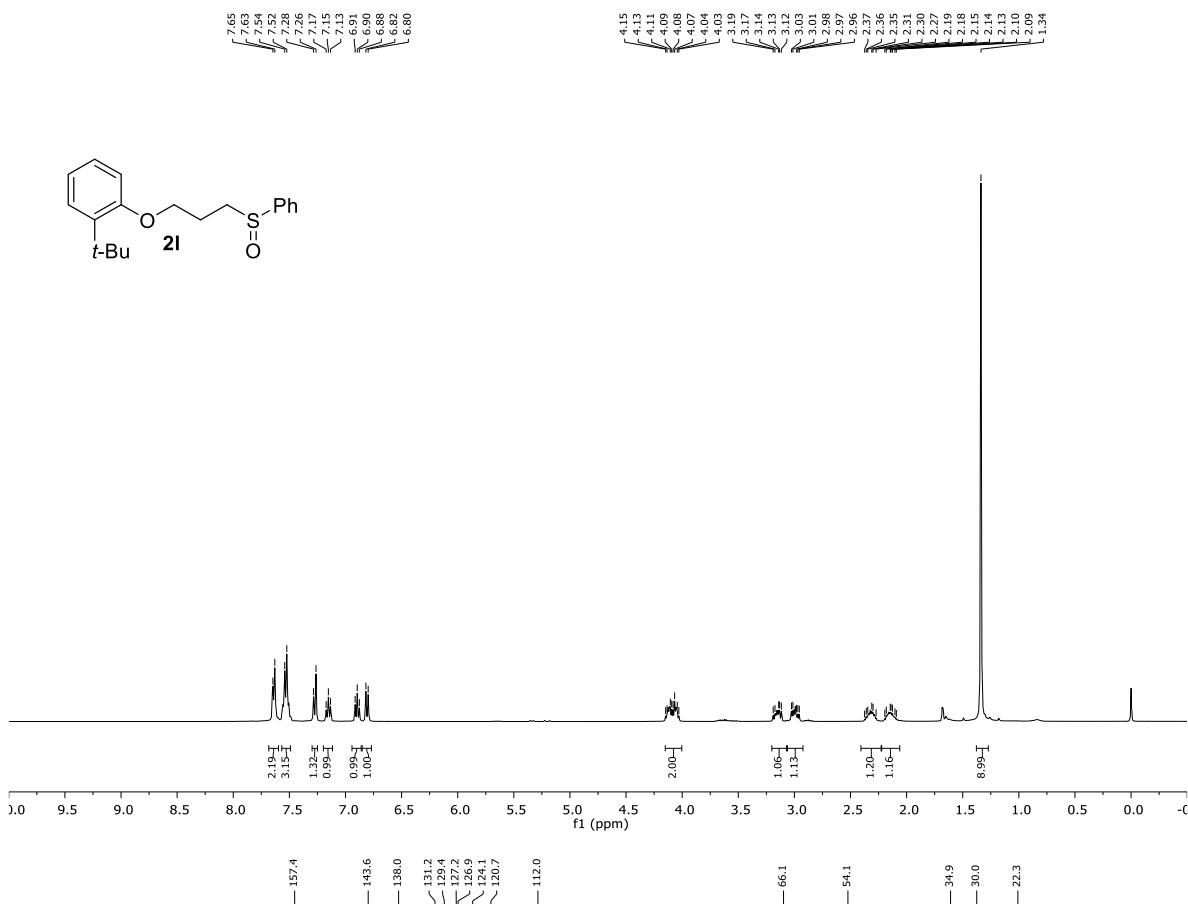
1-Fluoro-3-(3-(phenylsulfinyl)propoxy)benzene (2j).



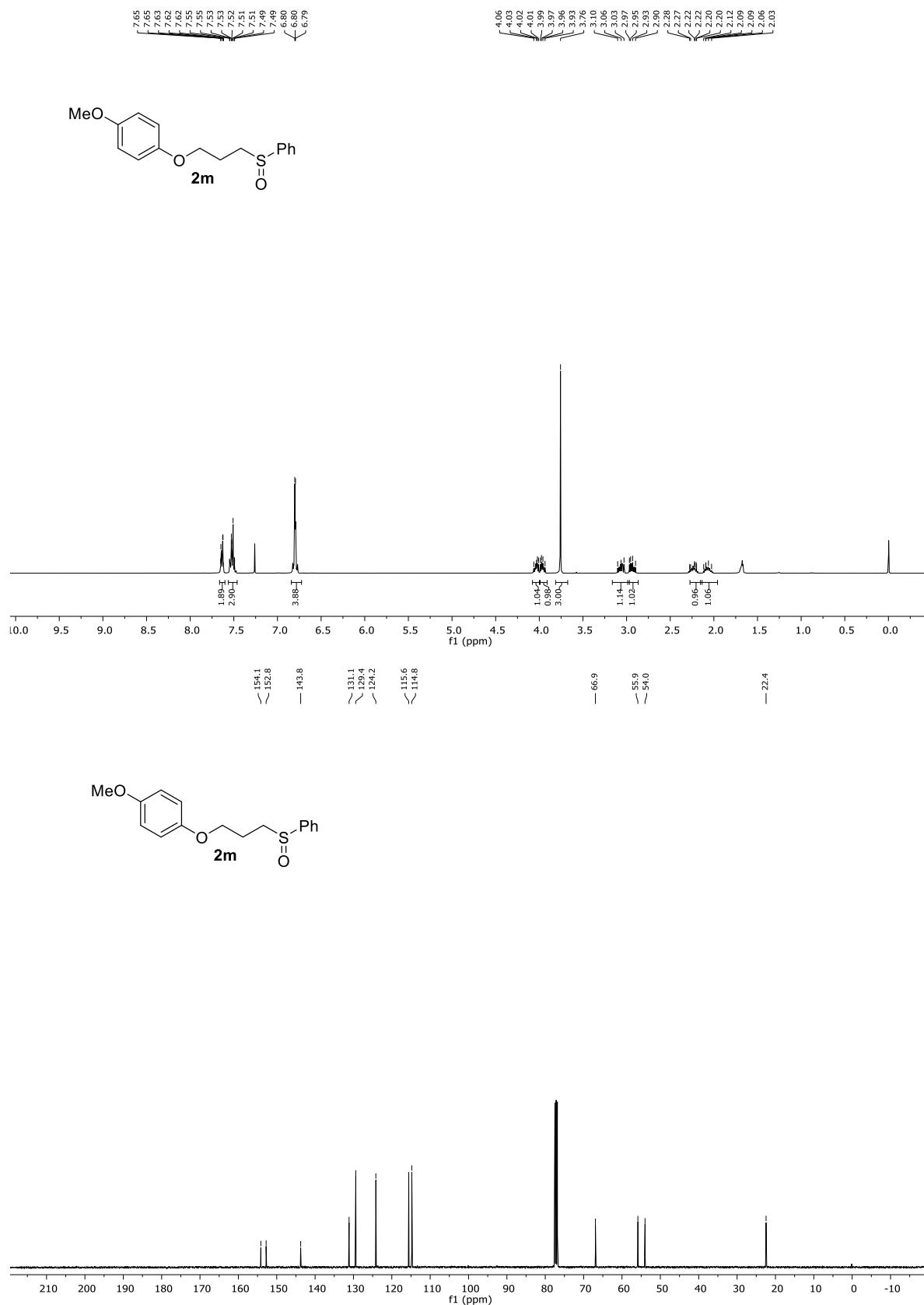
1-Methyl-4-(3-(phenylsulfinyl)propoxy)benzene (2k).



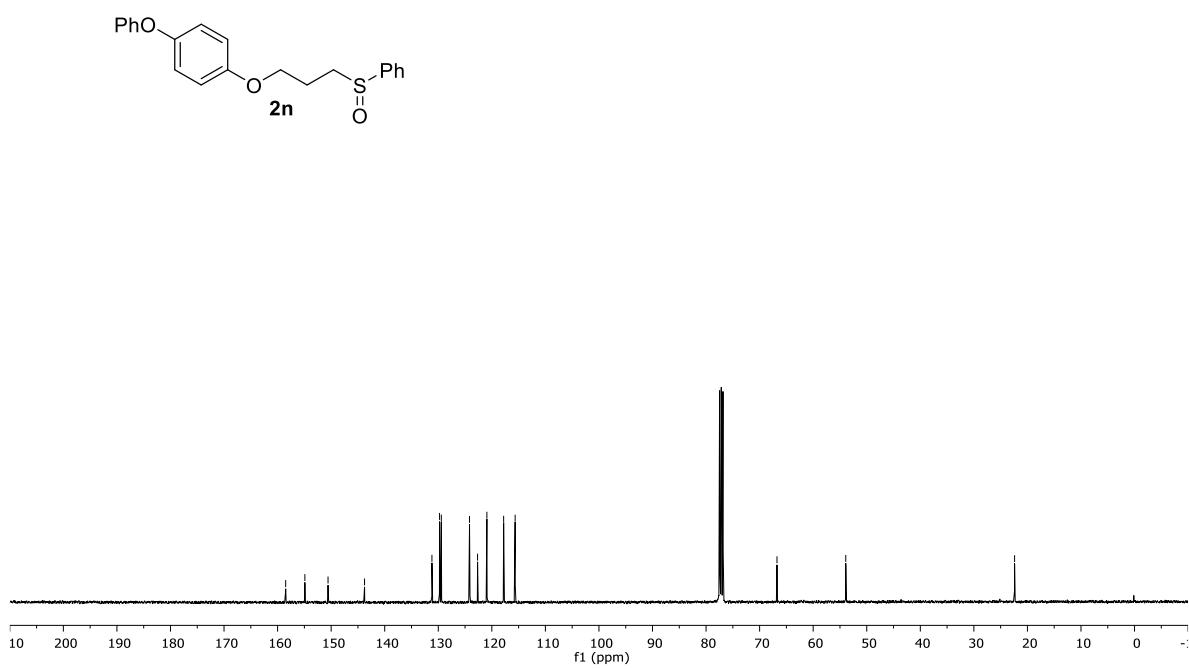
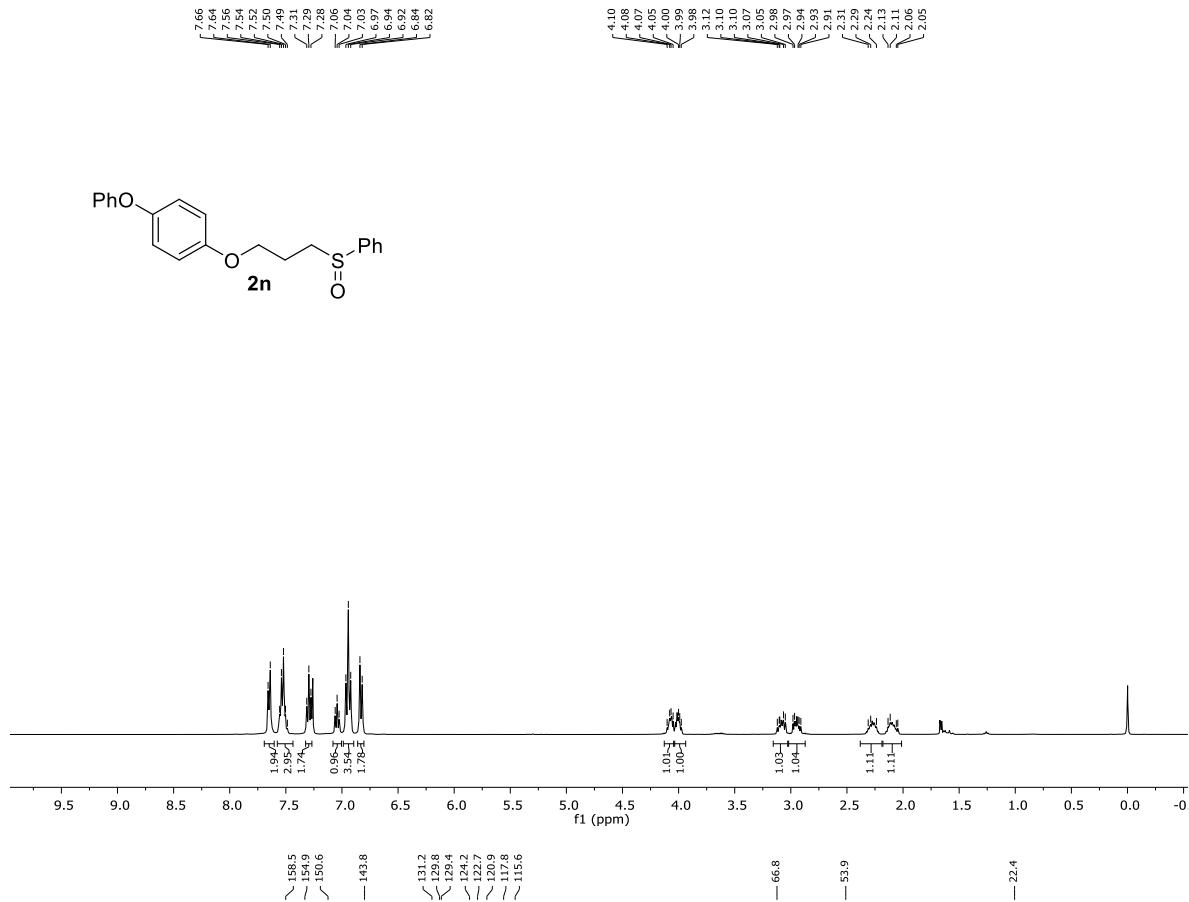
1-(tert-butyl)-2-(3-(phenylsulfinyl)propoxy)benzene (2l).



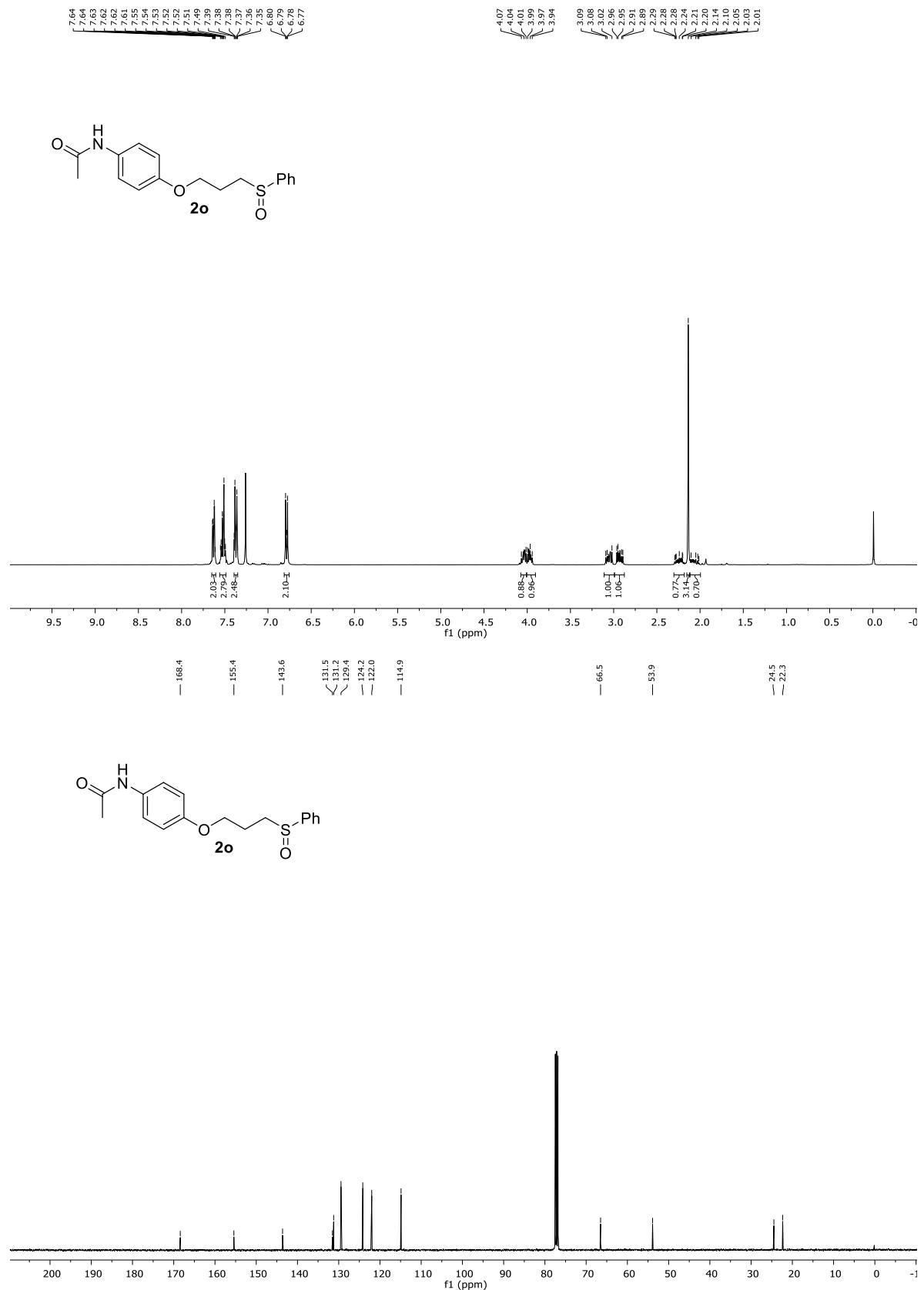
1-Methoxy-4-(3-(phenylsulfinyl)propoxy)benzene (2m).



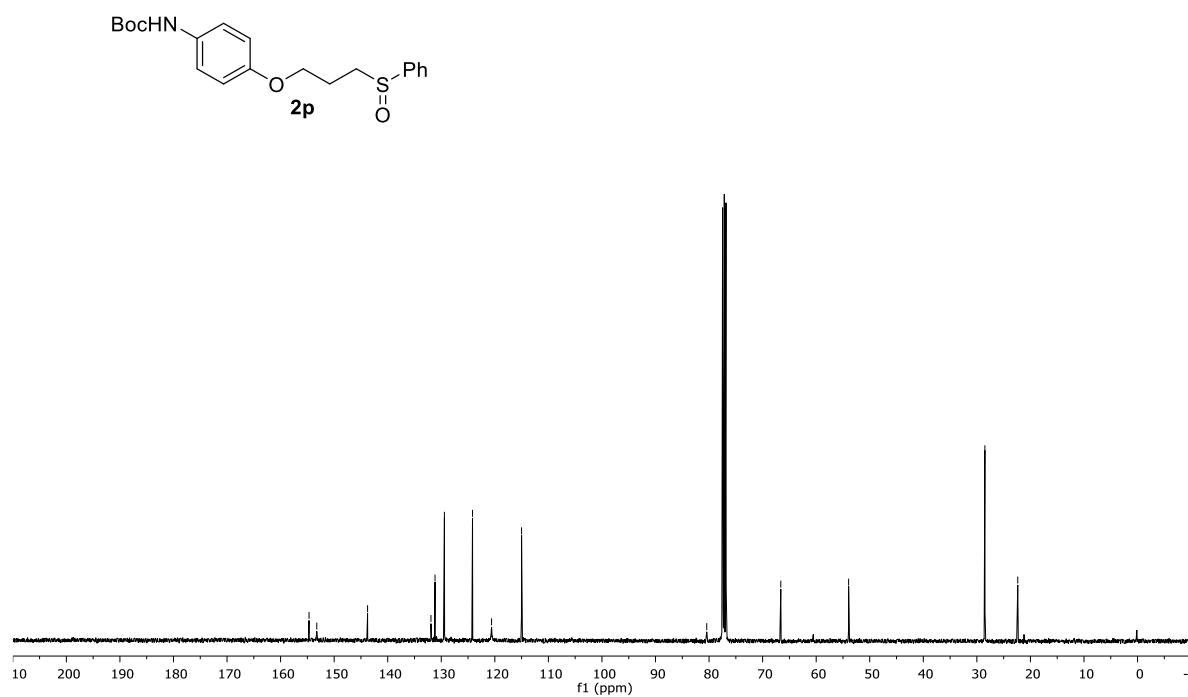
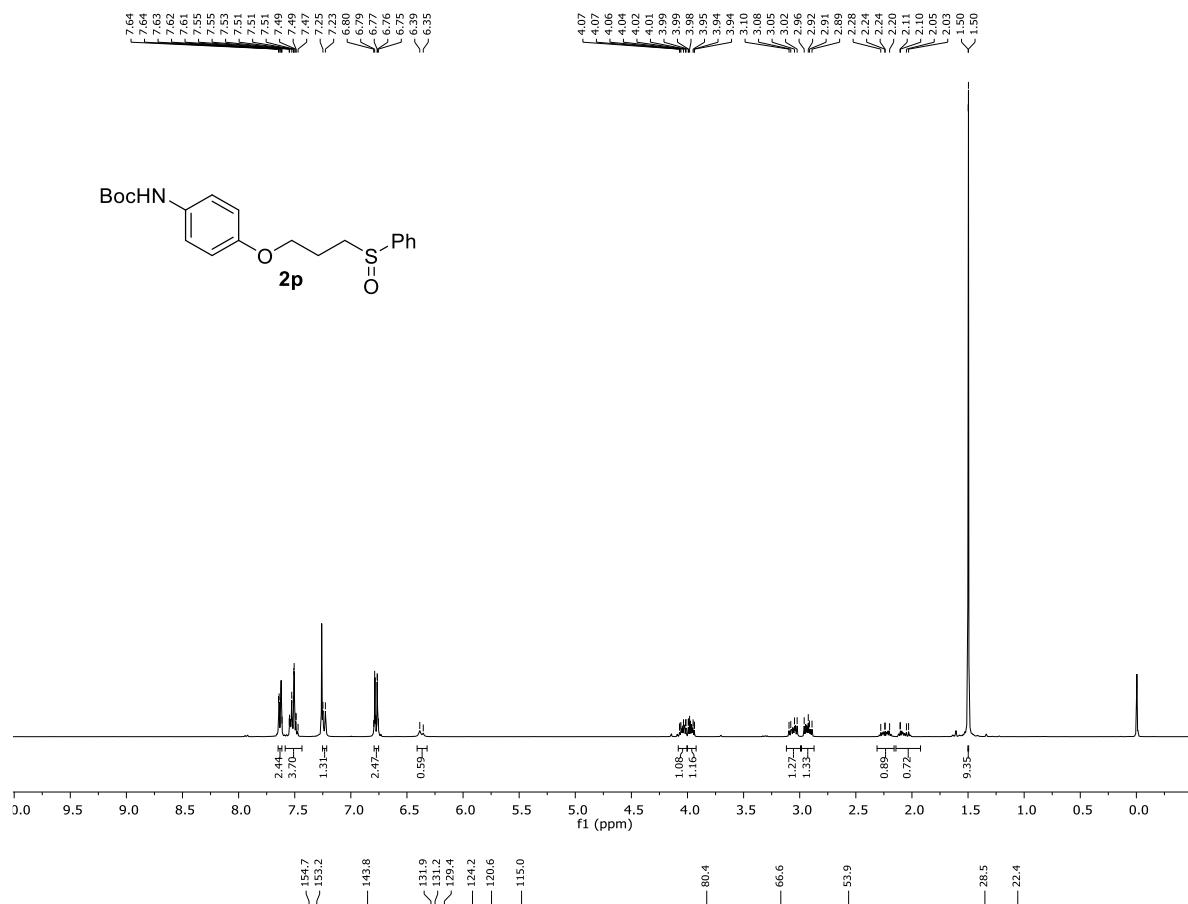
1-phenoxy-4-(3-(phenylsulfinyl)propoxy)benzene (2n**).**



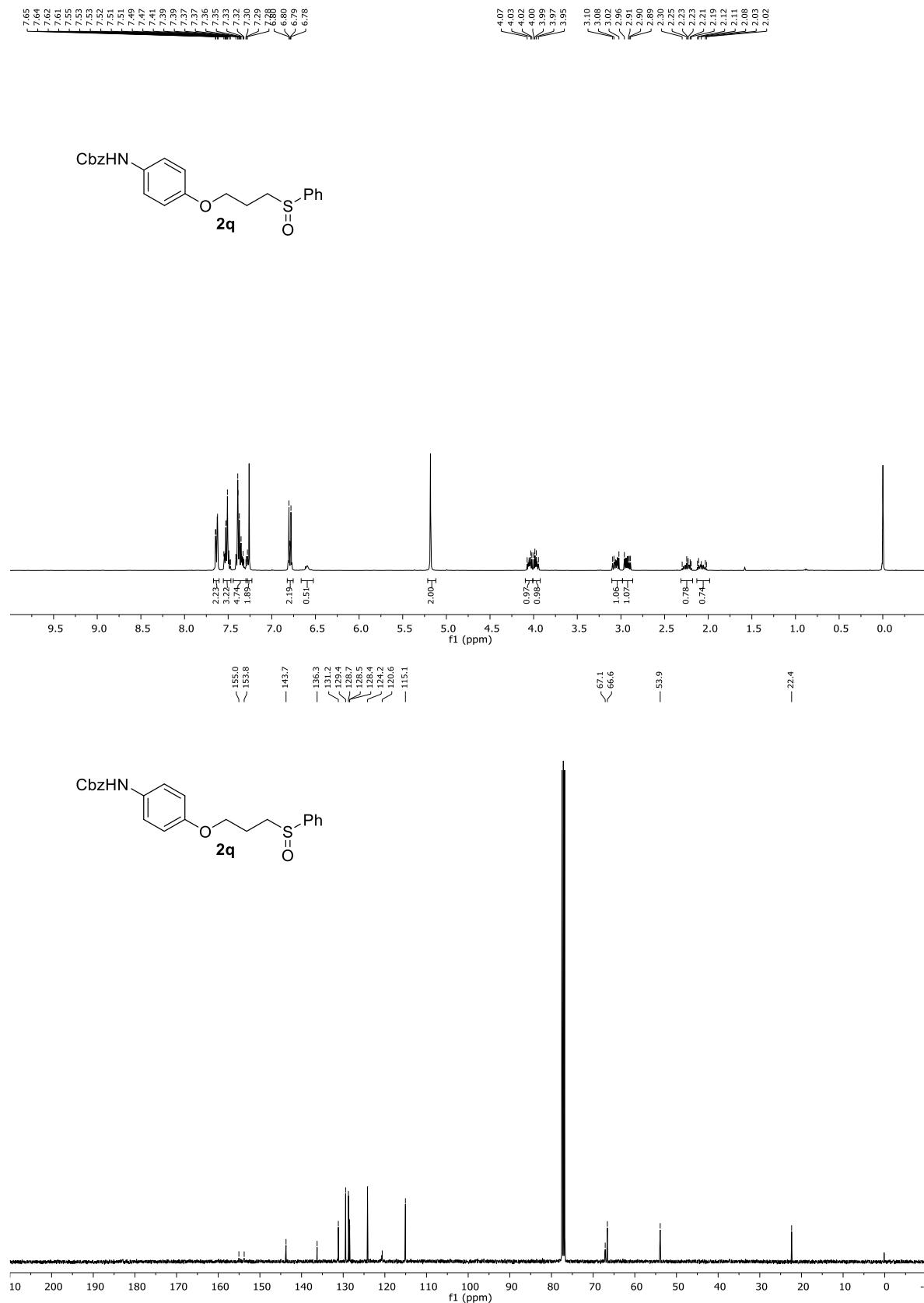
N-(4-(3-(phenylsulfinyl)propoxy)phenyl)acetamide (2o).



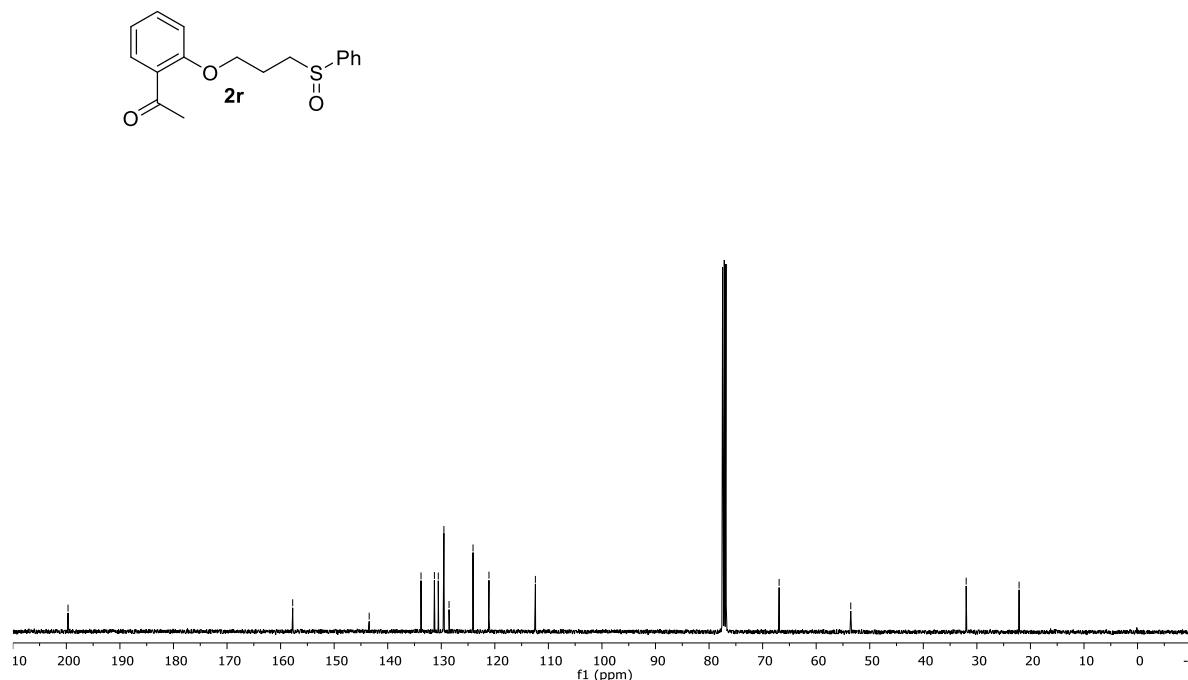
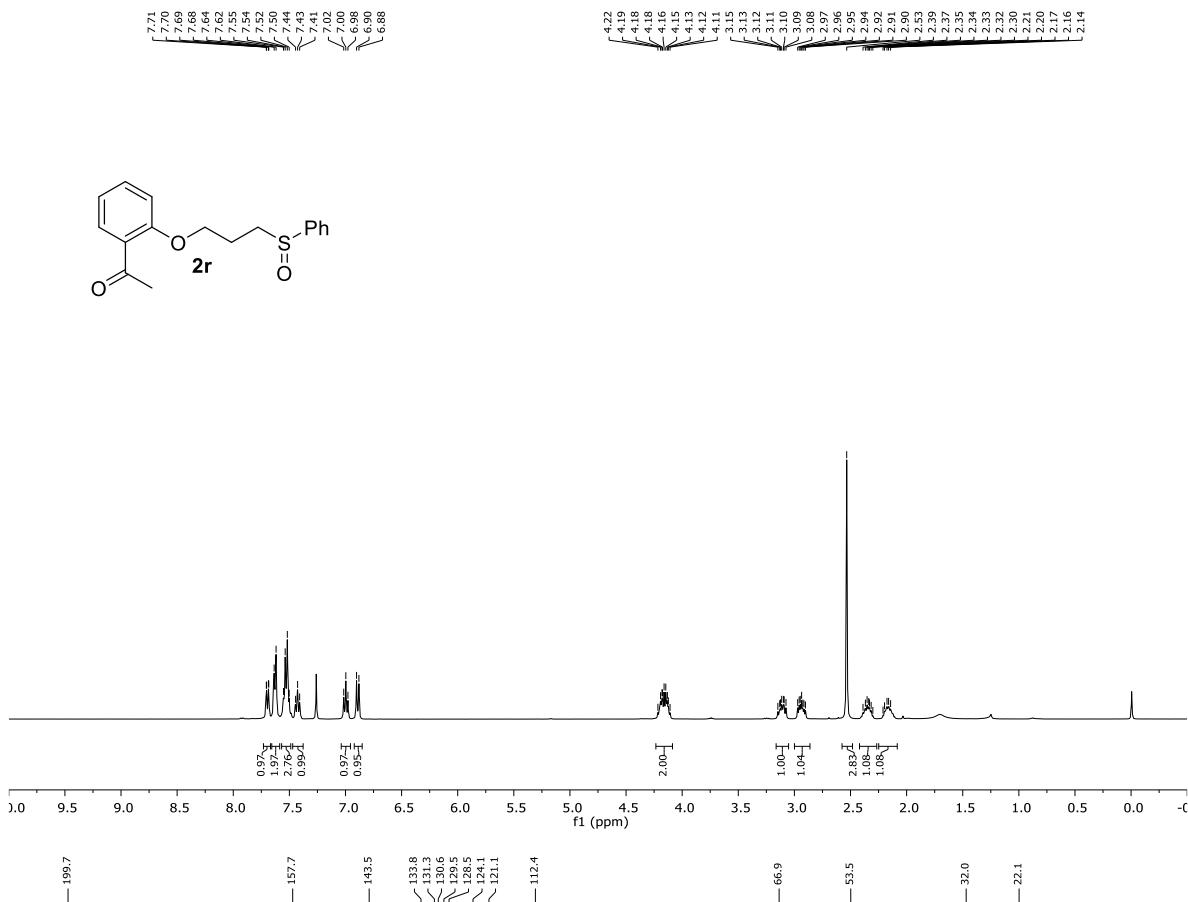
***tert*-butyl (4-(3-(phenylsulfinyl)propoxy)phenyl)carbamate (2p).**



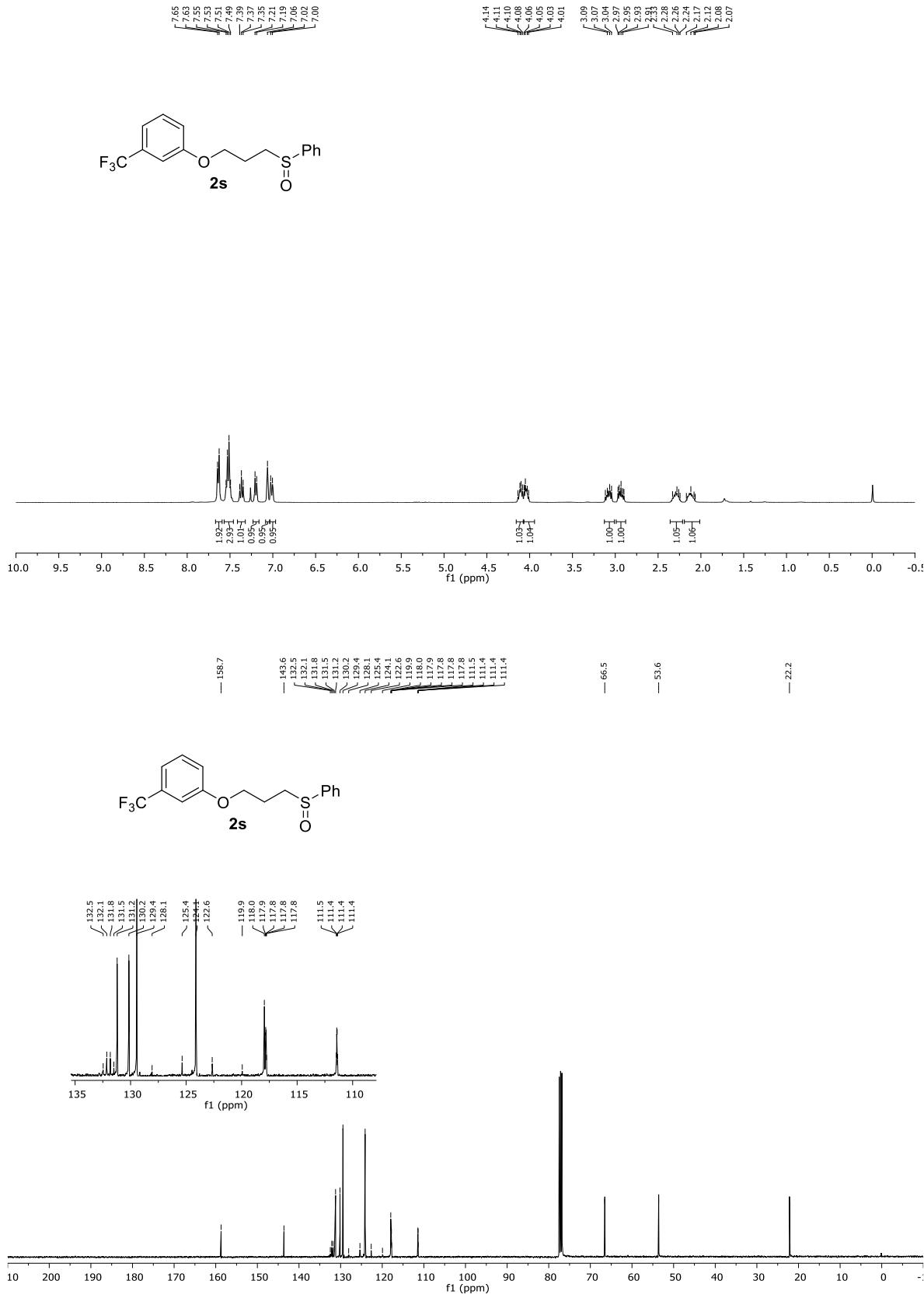
Benzyl (4-(3-(phenylsulfinyl)propoxy)phenyl)carbamate (2q).



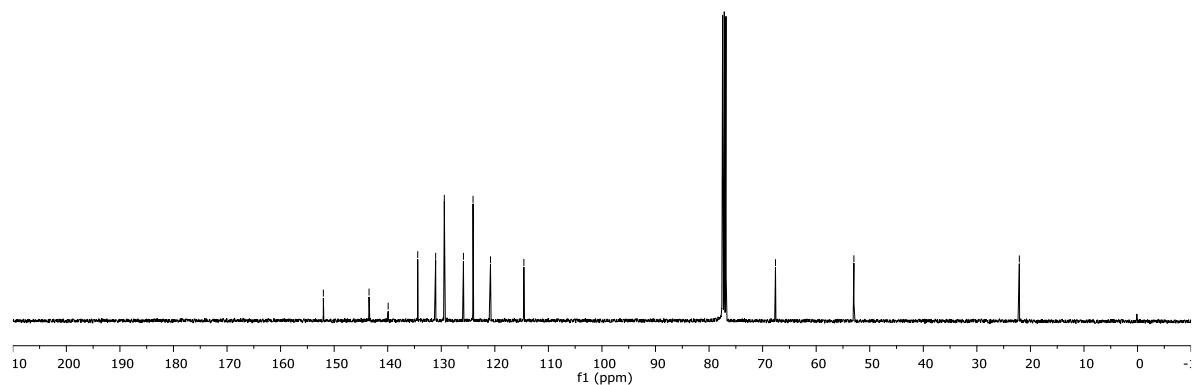
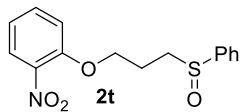
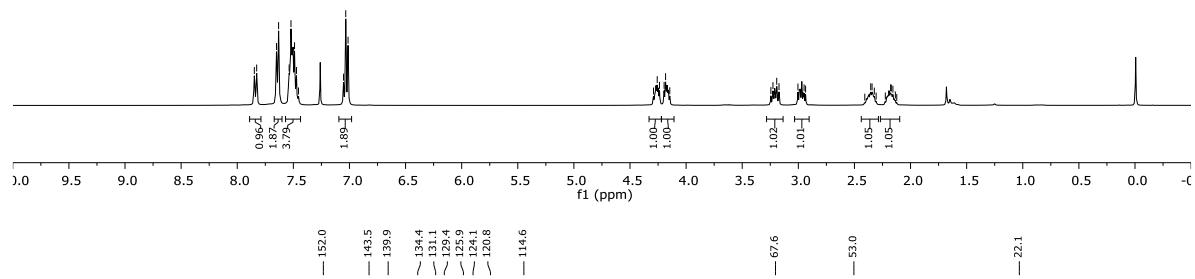
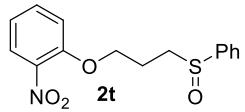
1-(2-(3-(Phenylsulfinyl)propoxy)phenyl)ethanone (2r).



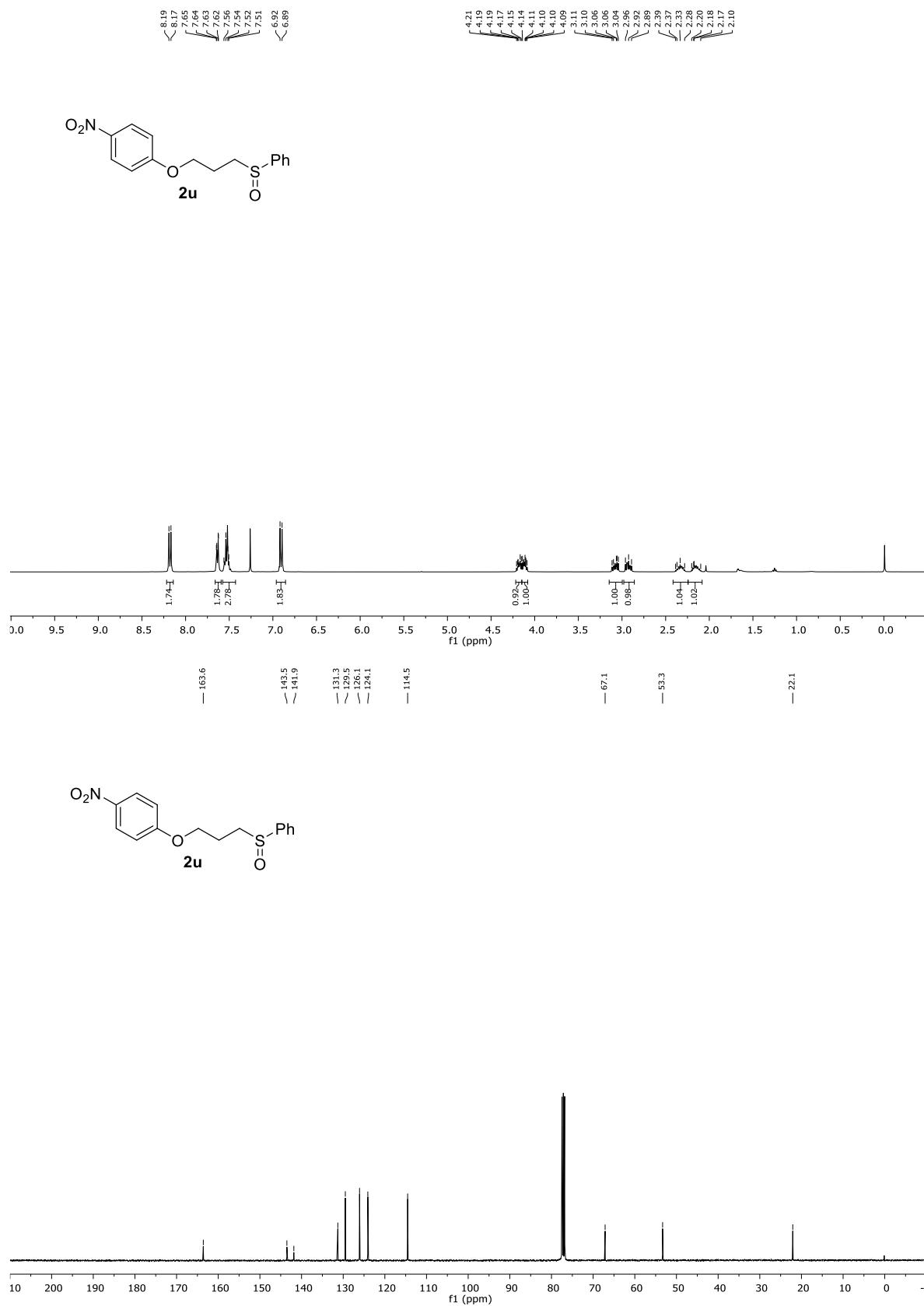
1-(3-(Phenylsulfinyl)propoxy)-3-(trifluoromethyl)benzene (2s).



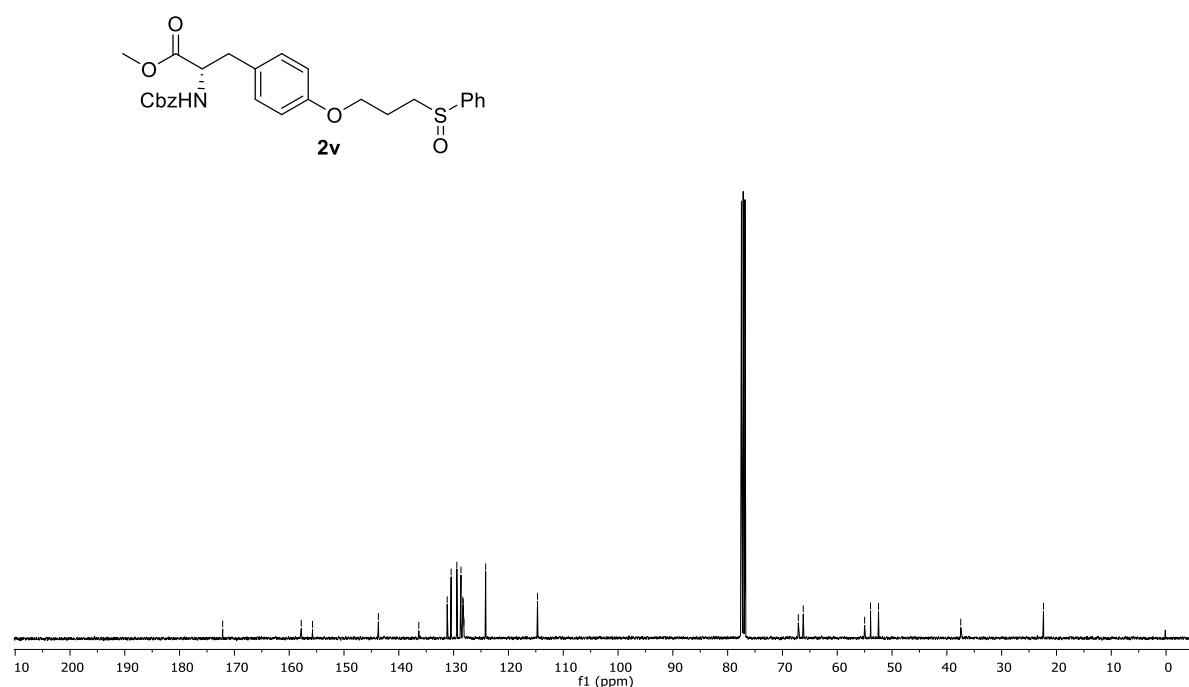
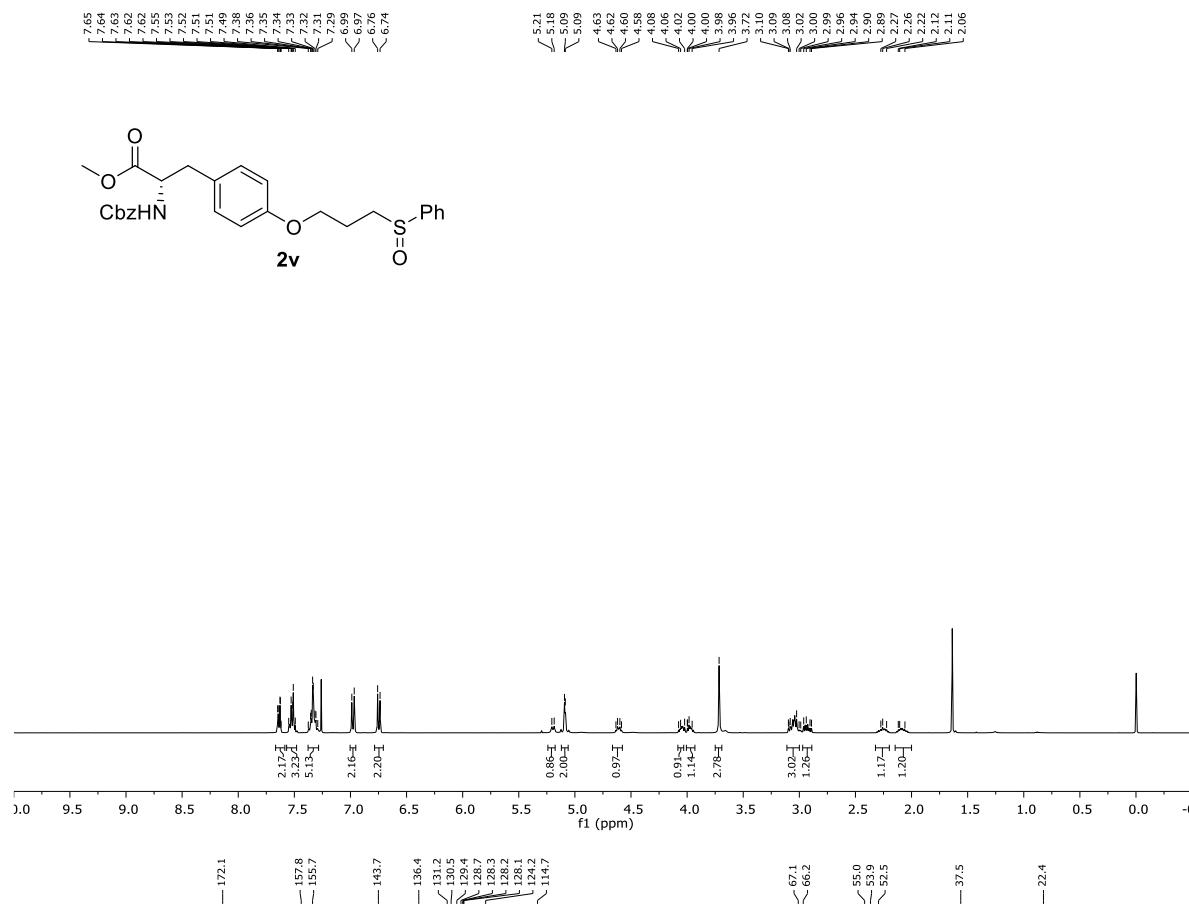
1-Nitro-2-(3-(phenylsulfinyl)propoxy)benzene (2t).



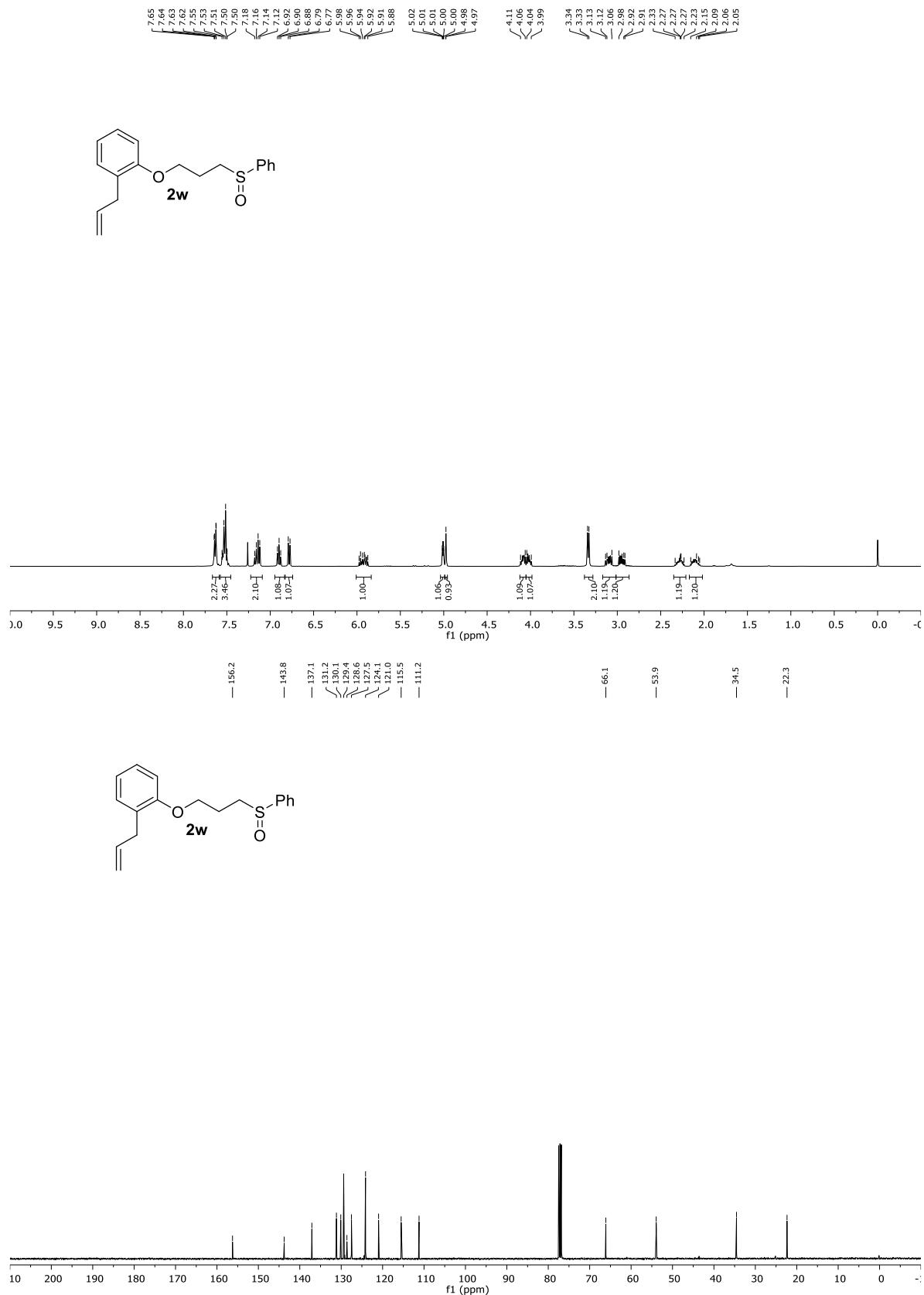
1-Nitro-4-(3-(phenylsulfinyl)propoxy)benzene (2u).



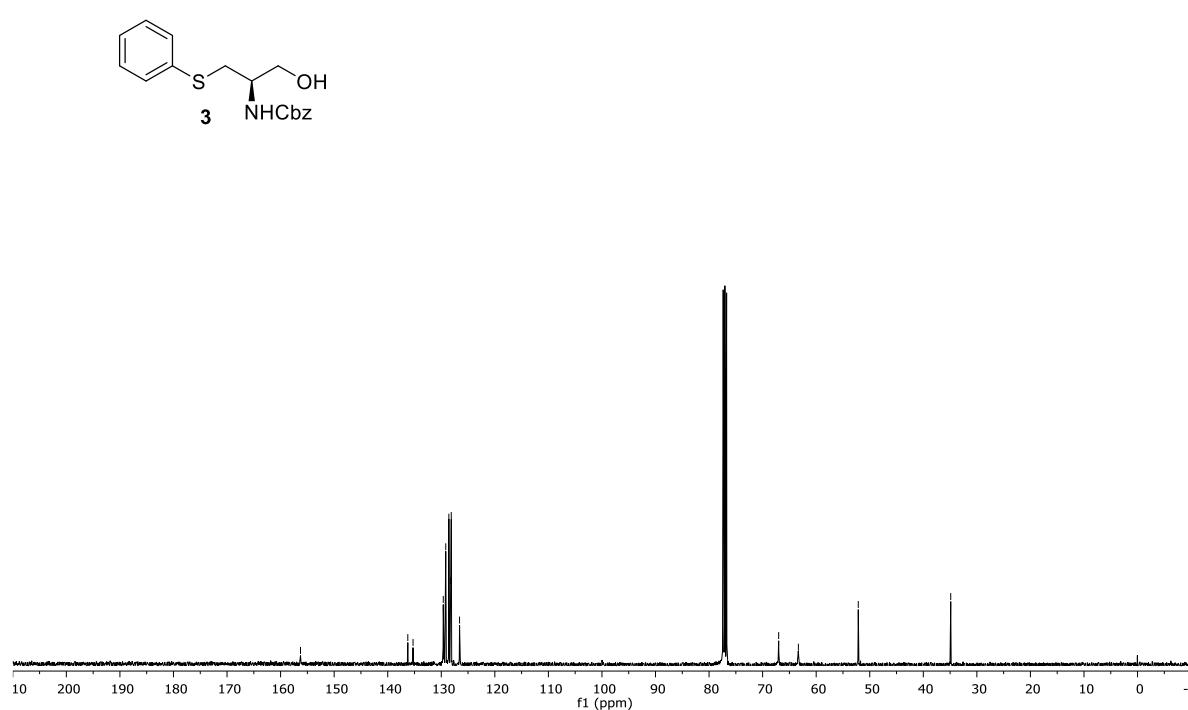
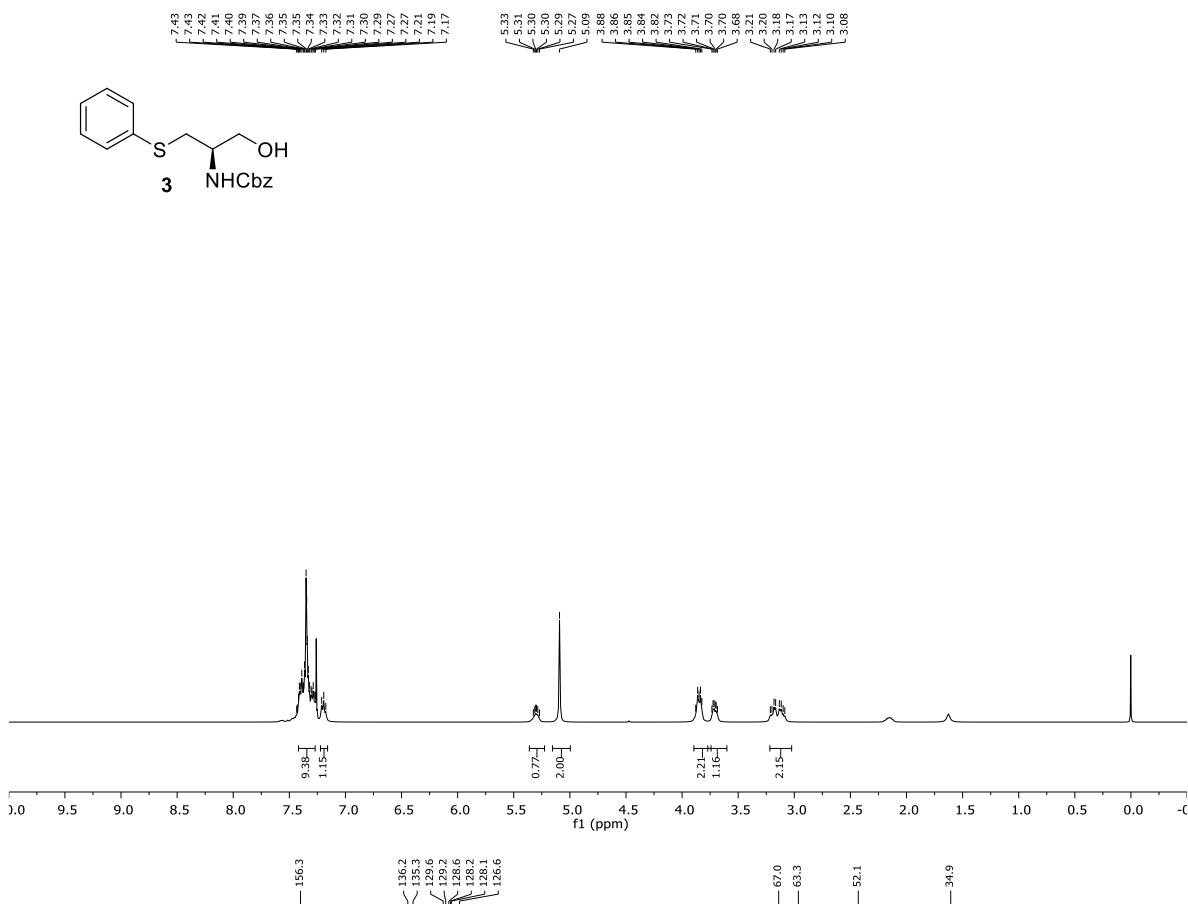
(2S)-Methyl-2-(((benzyloxy)carbonyl)amino)-3-(4-(phenylsulfinyl)propoxy)phenyl)propanoate (2v).



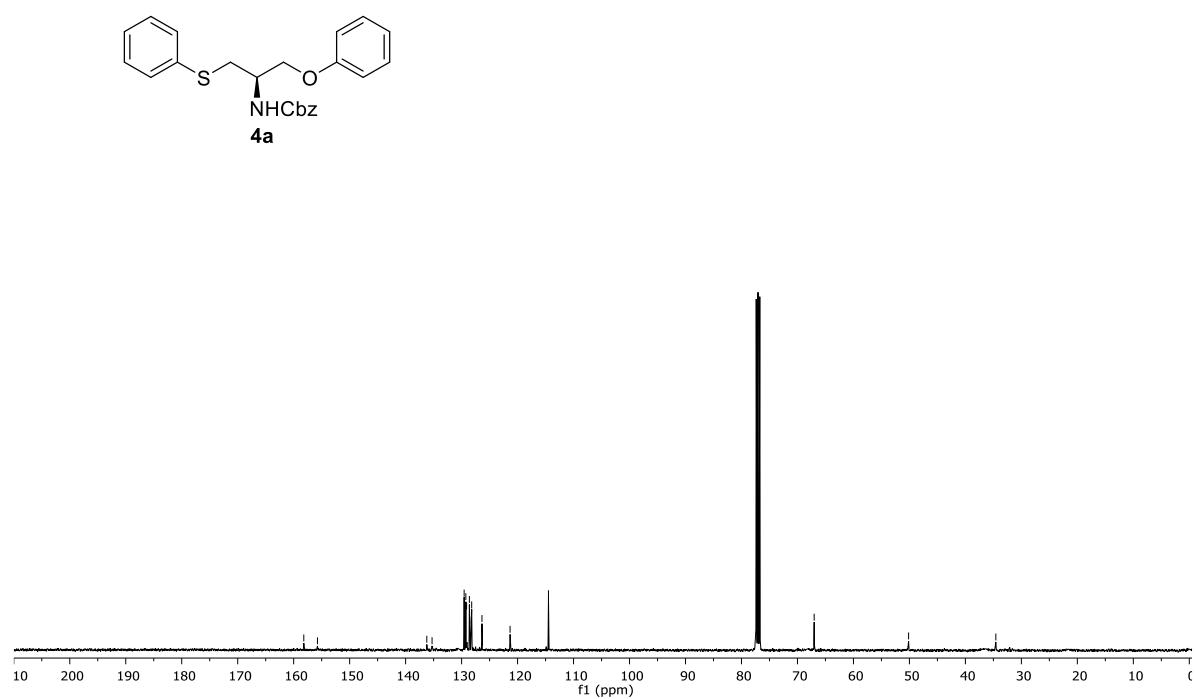
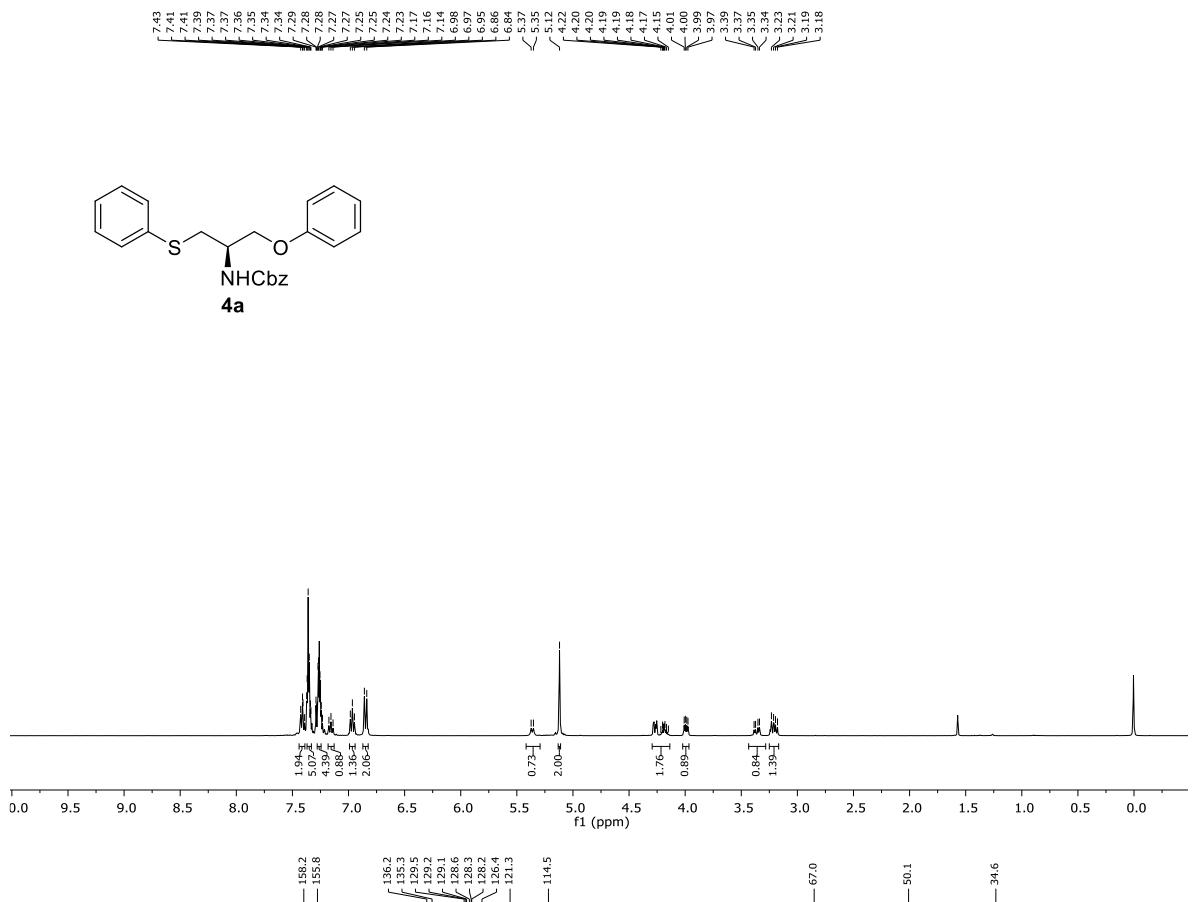
1-Allyl-2-(3-(phenylsulfinyl)propoxy)benzene (2w).



(R)-Benzyl(1-hydroxy-3-(phenylthio)propan-2-yl)carbamate (3).



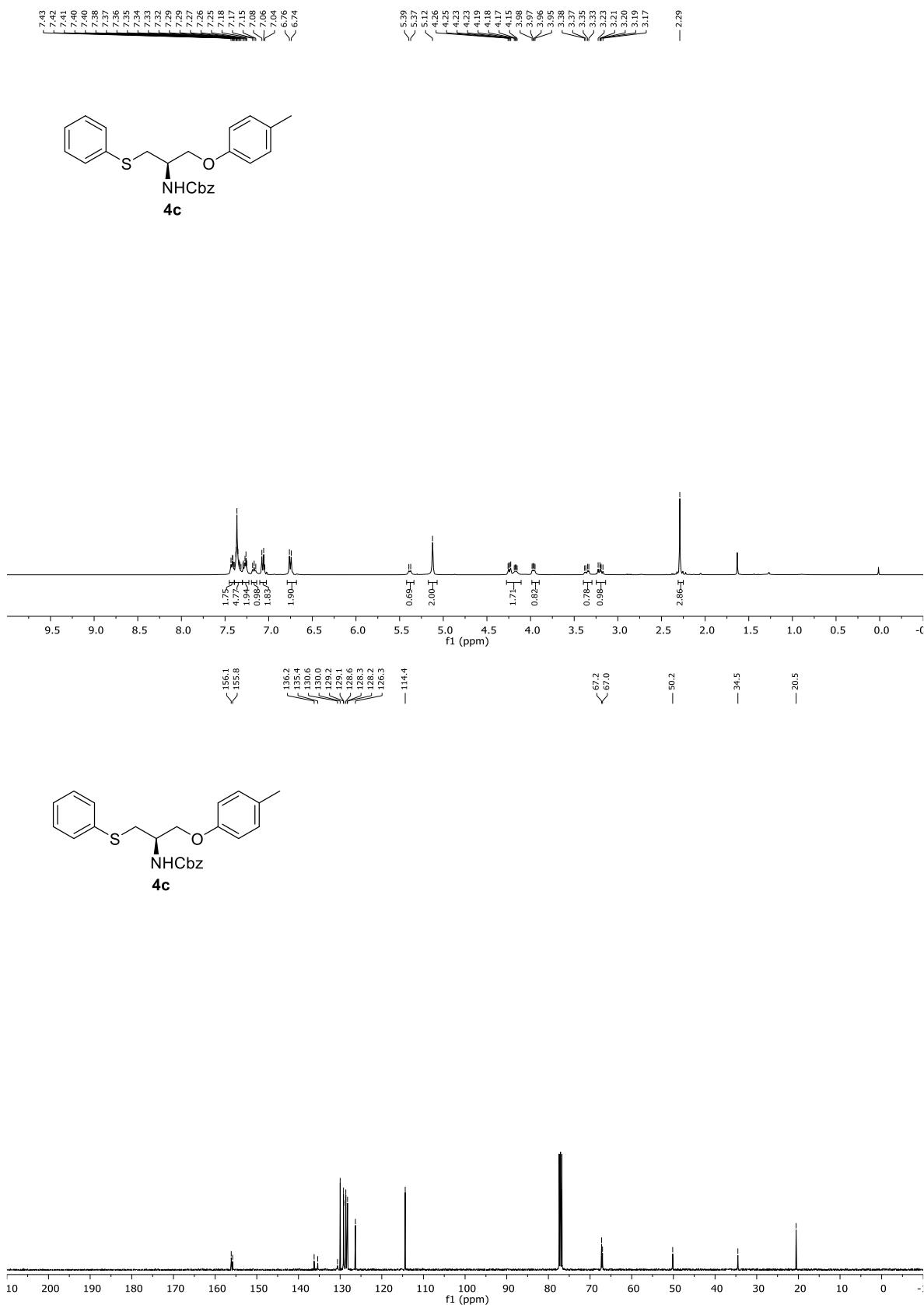
(R)-Benzyl (1-phenoxy-3-(phenylthio)propan-2-yl)carbamate (4a).



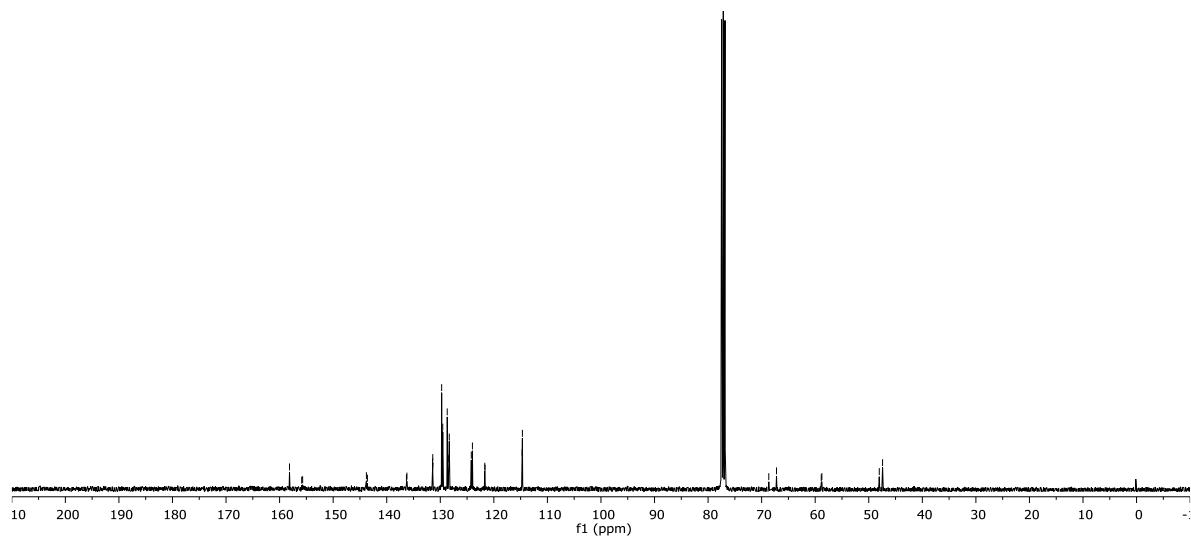
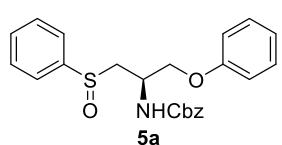
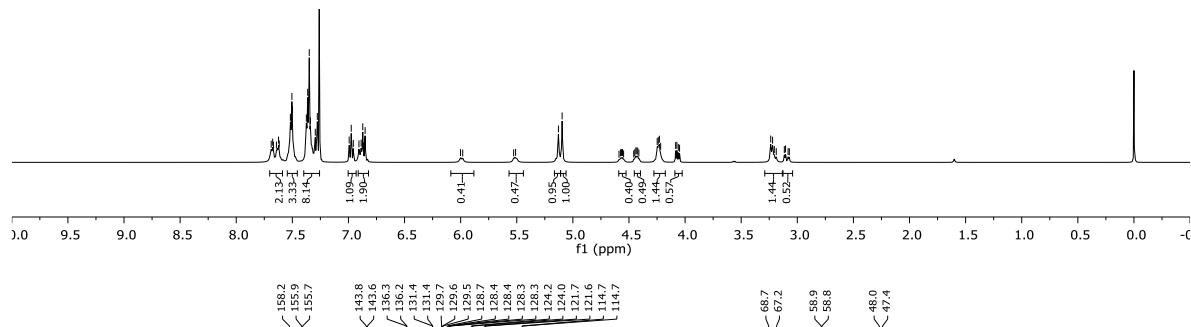
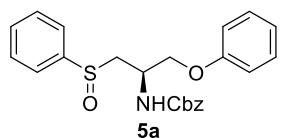
(R)-Benzyl (1-(3-fluorophenoxy)-3-(phenylthio)propan-2-yl)carbamate (4b).



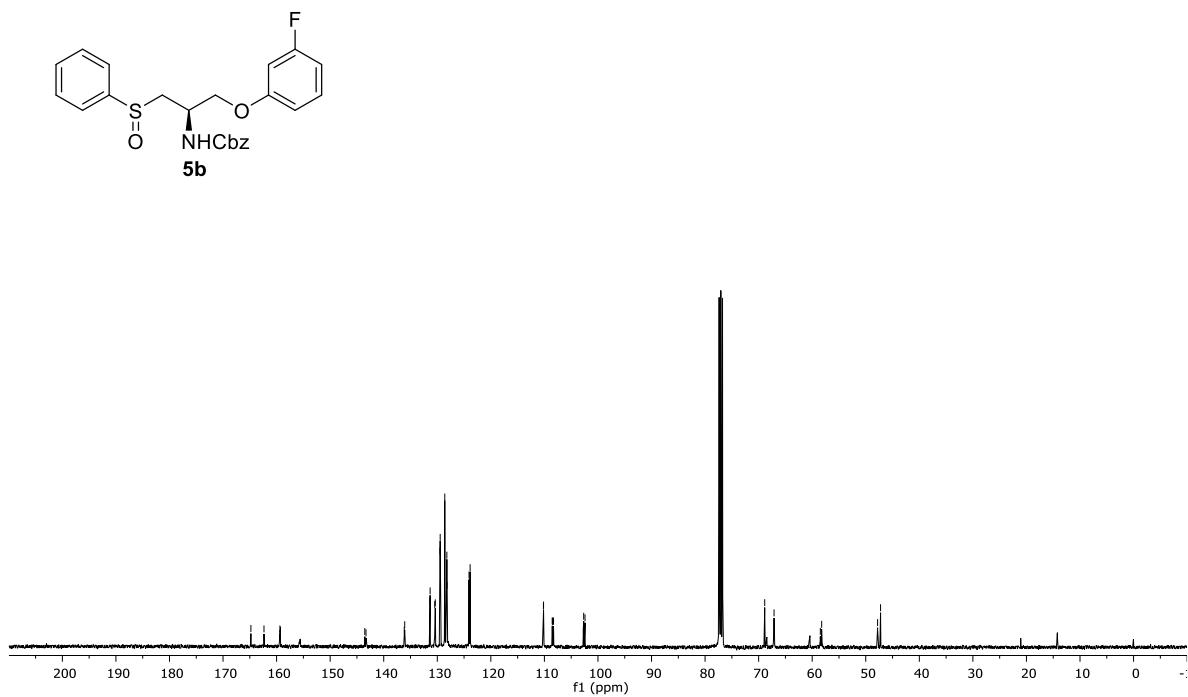
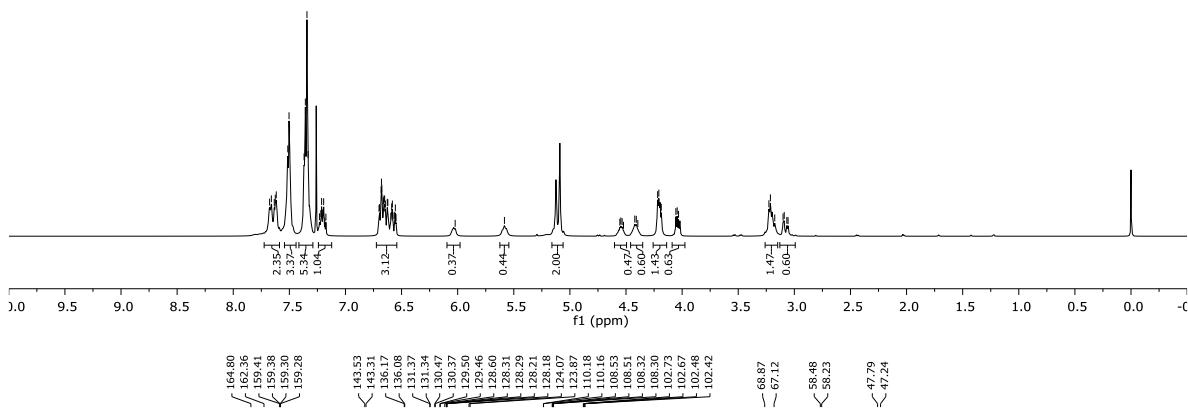
(R)-Benzyl-(1-(phenylthio)-3-(*p*-tolyloxy)propan-2-yl)carbamate (4c).



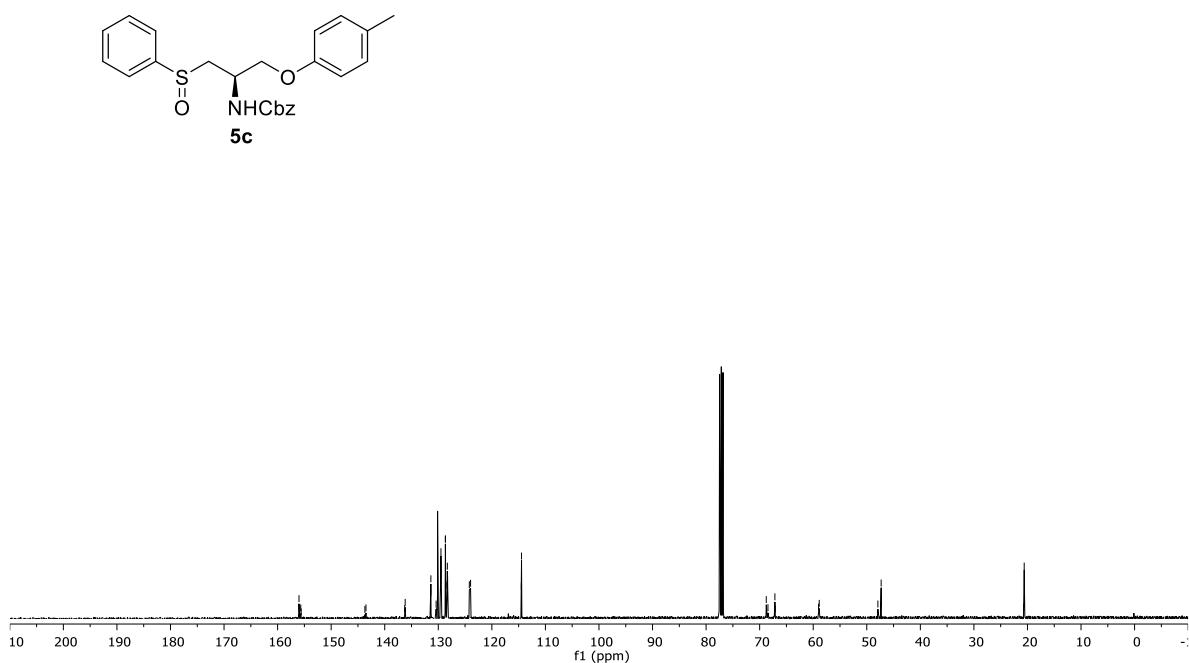
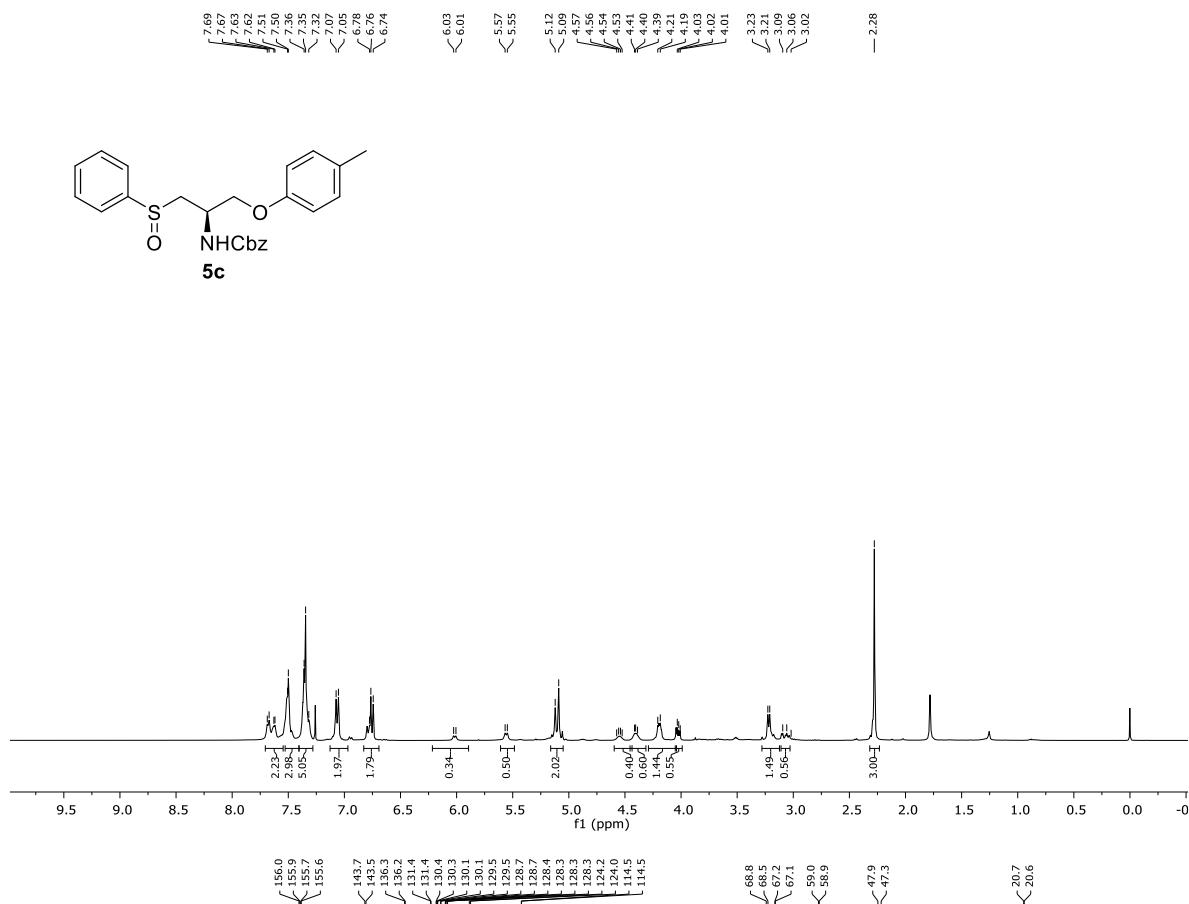
Benzyl ((2*R*)-1-phenoxy-3-(phenylsulfinyl)propan-2-yl)carbamate (5a).



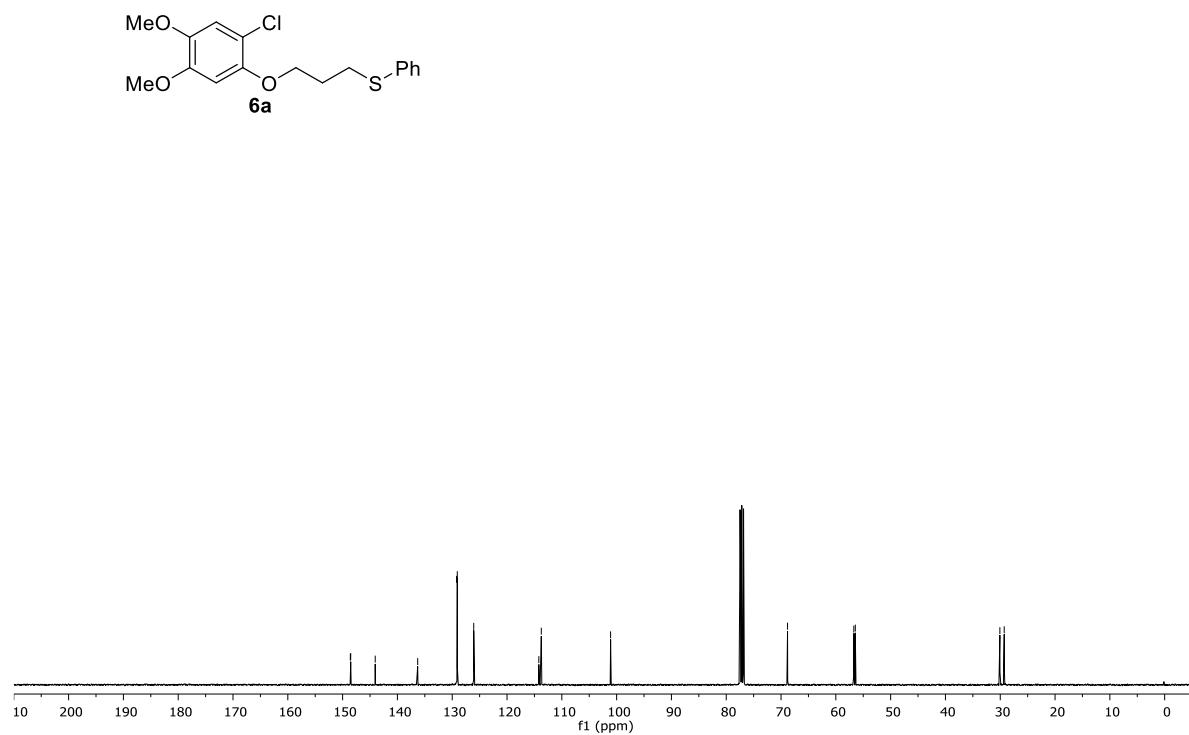
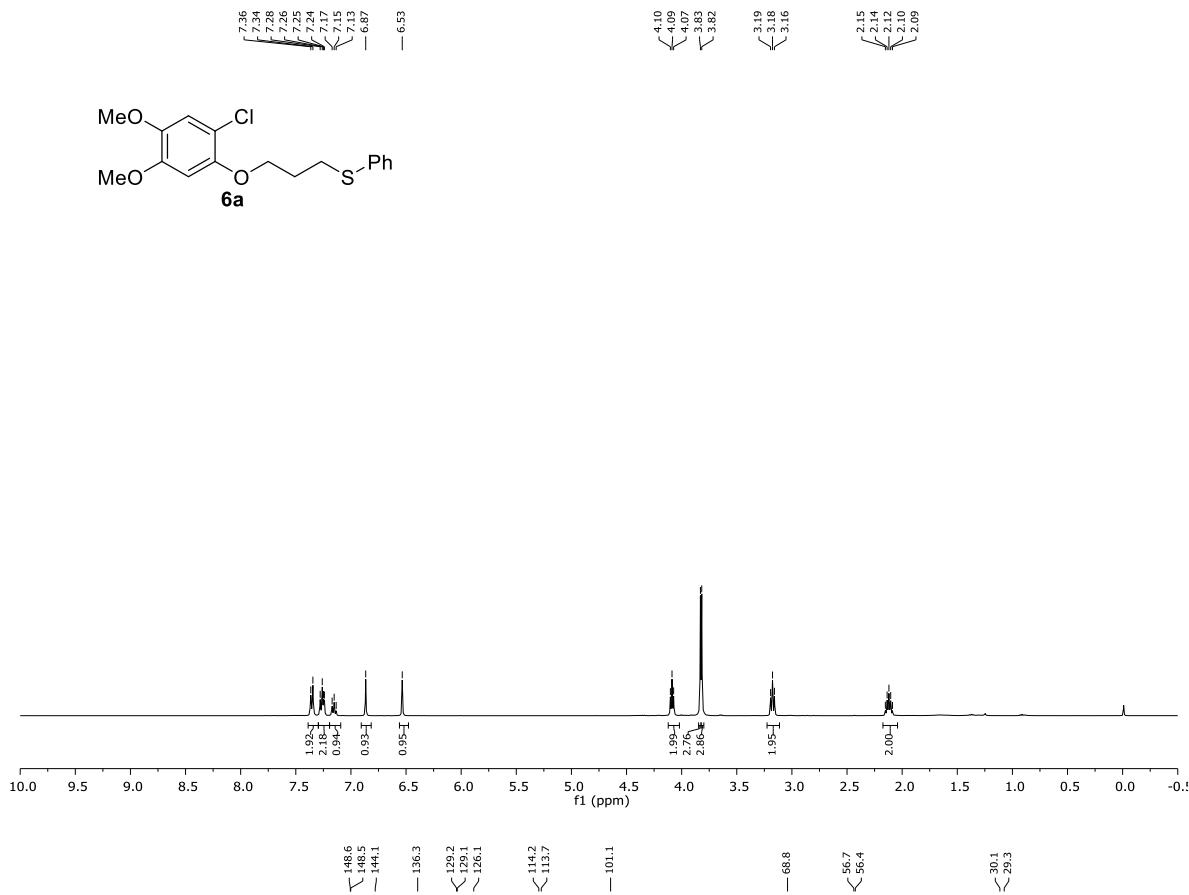
Benzyl ((2*R*)-1-(3-fluorophenoxy)-3-(phenylsulfinyl)propan-2-yl)carbamate (5b).



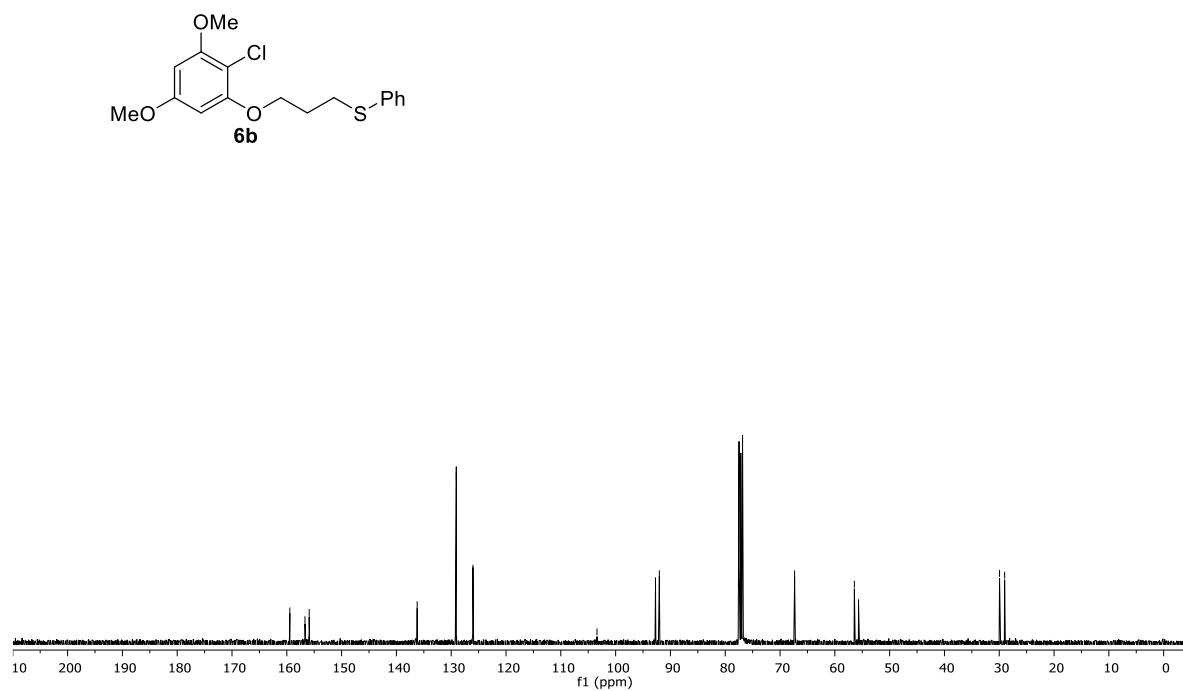
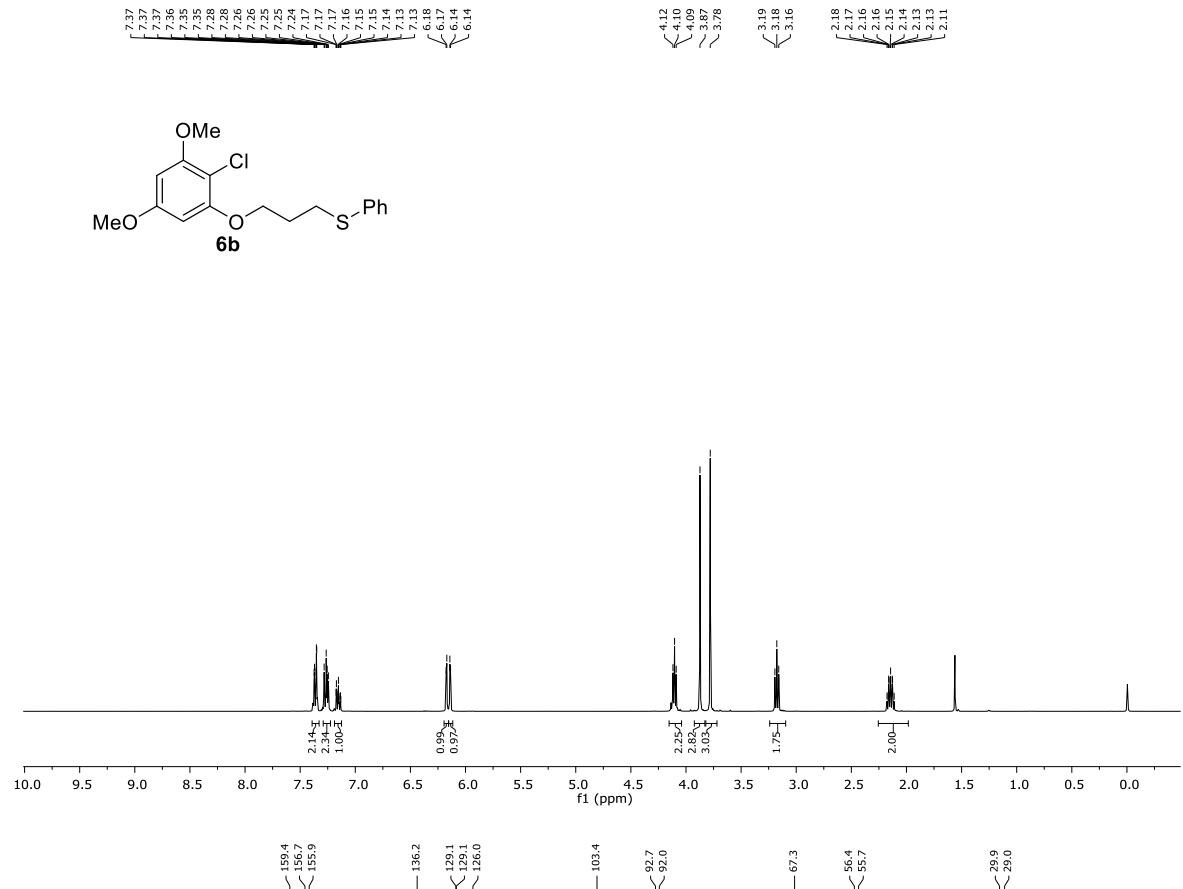
Benzyl ((2R)-1-(phenylsulfinyl)-3-(p-tolyloxy)propan-2-yl)carbamate (5c).



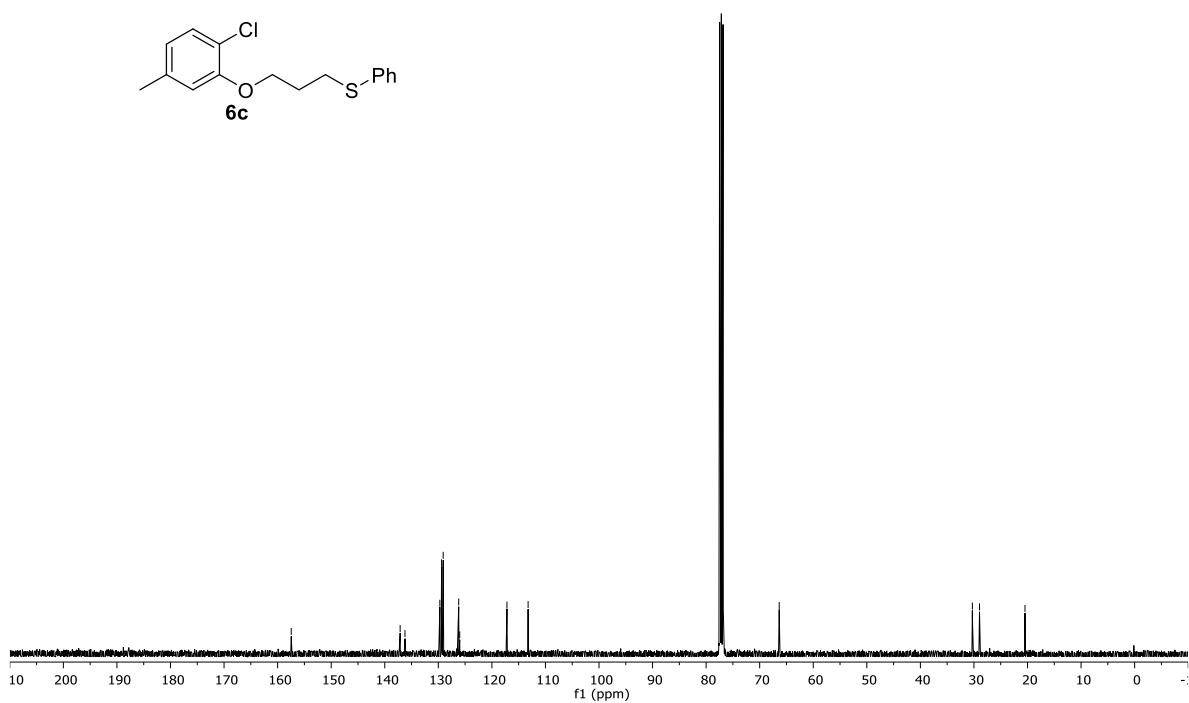
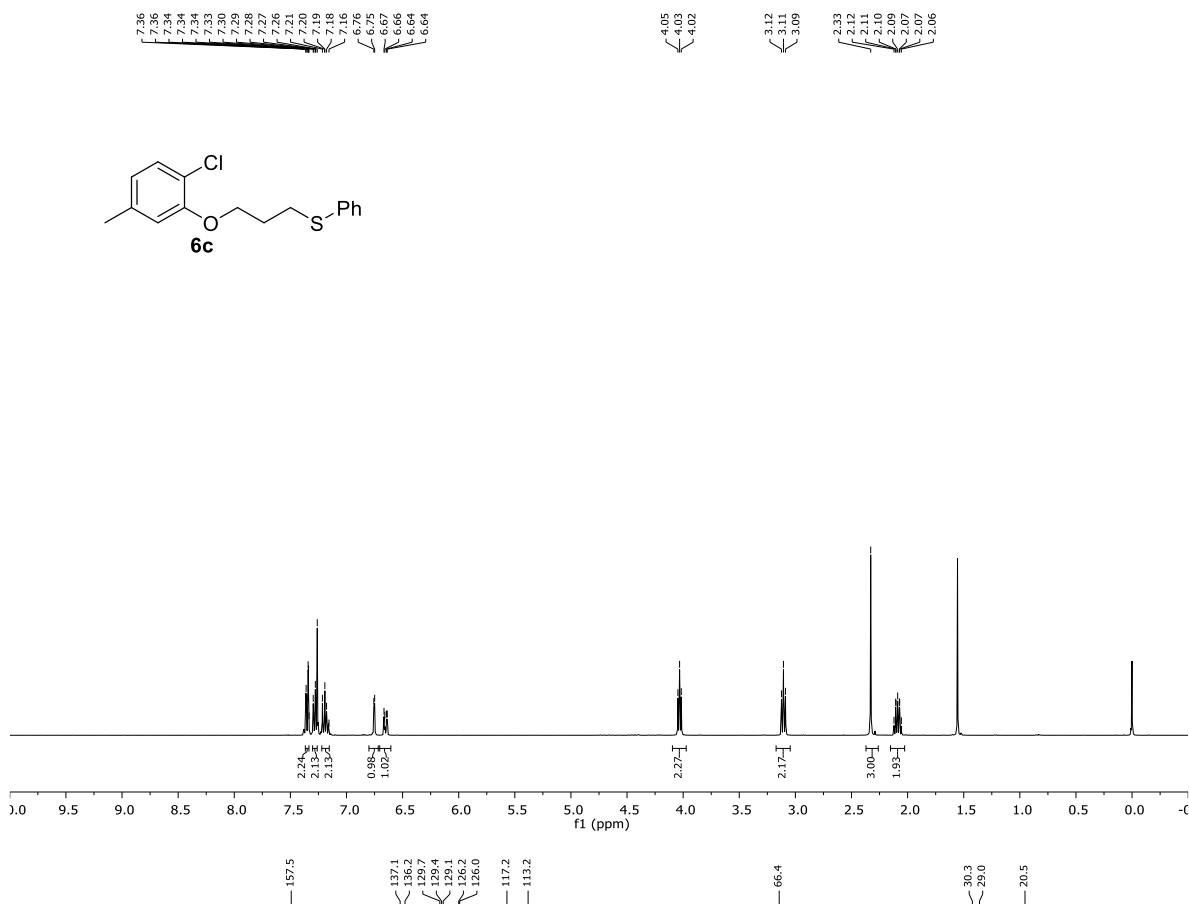
(3-(2-Chloro-4,5-dimethoxyphenoxy)propyl)(phenyl)sulfide (6a) .



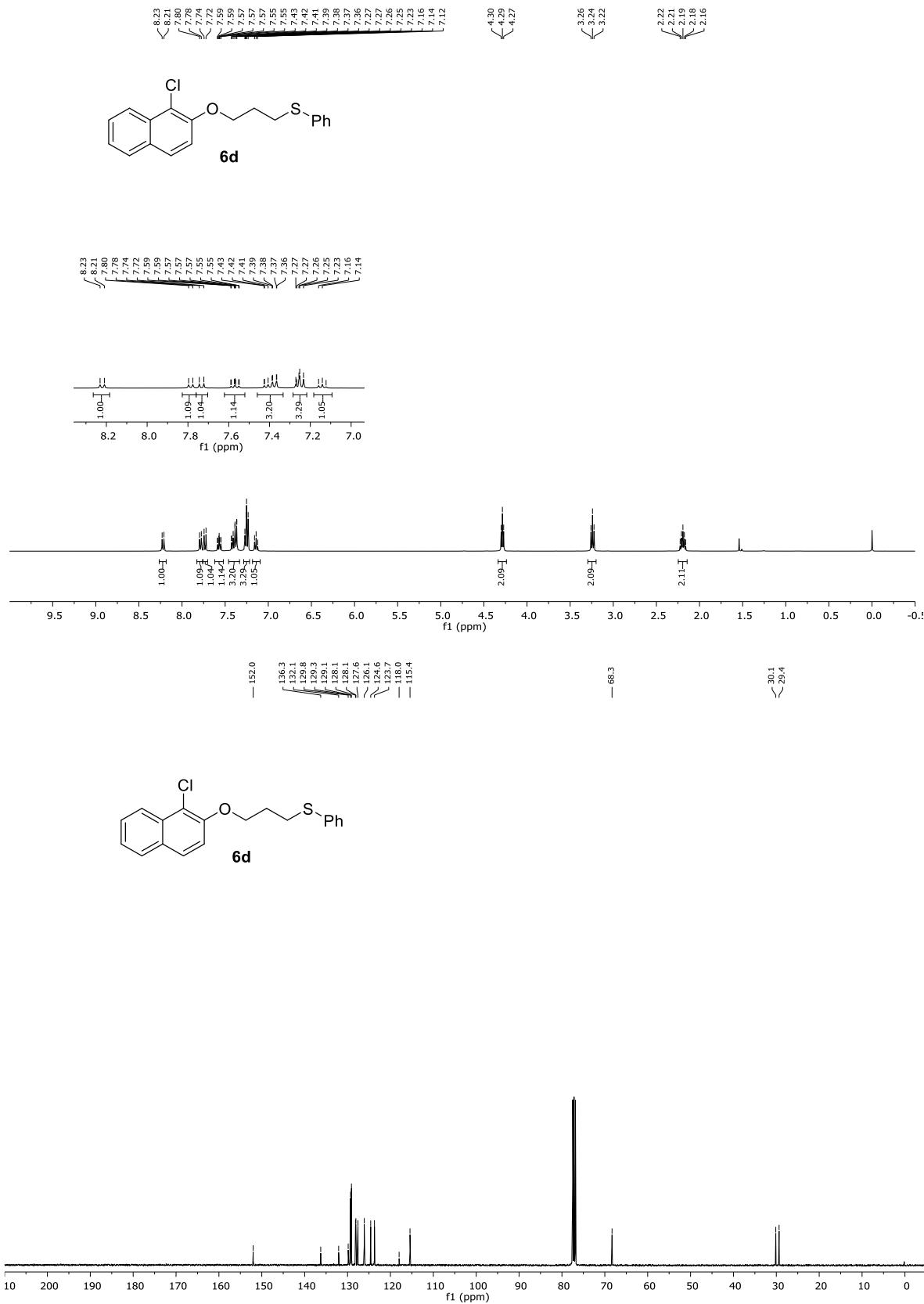
(3-(2-Chloro-3,5-dimethoxyphenoxy)propyl)(phenyl)sulfide (6b).



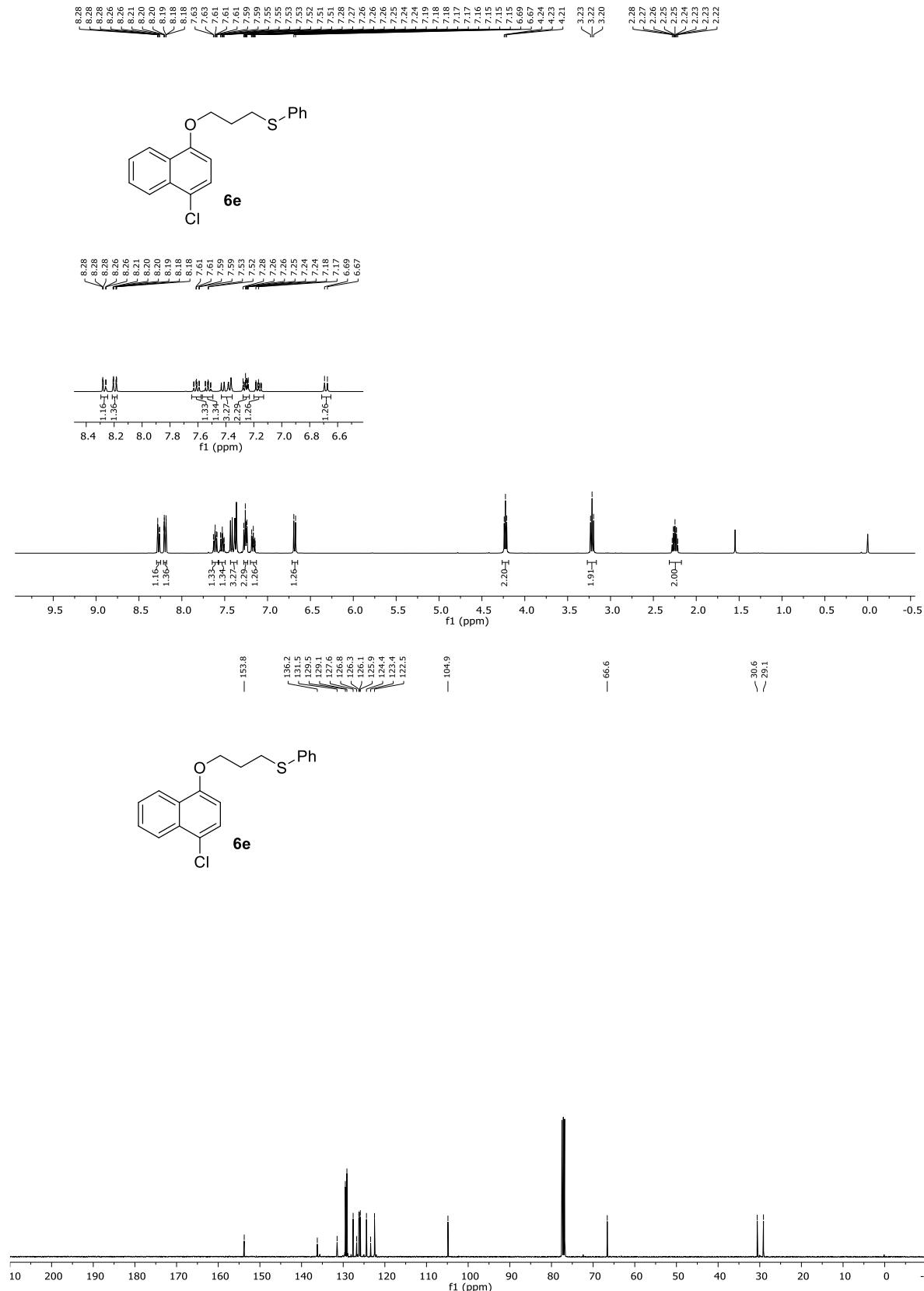
(3-(2-chloro-5-methylphenoxy)propyl)(phenyl)sulfide (6c).



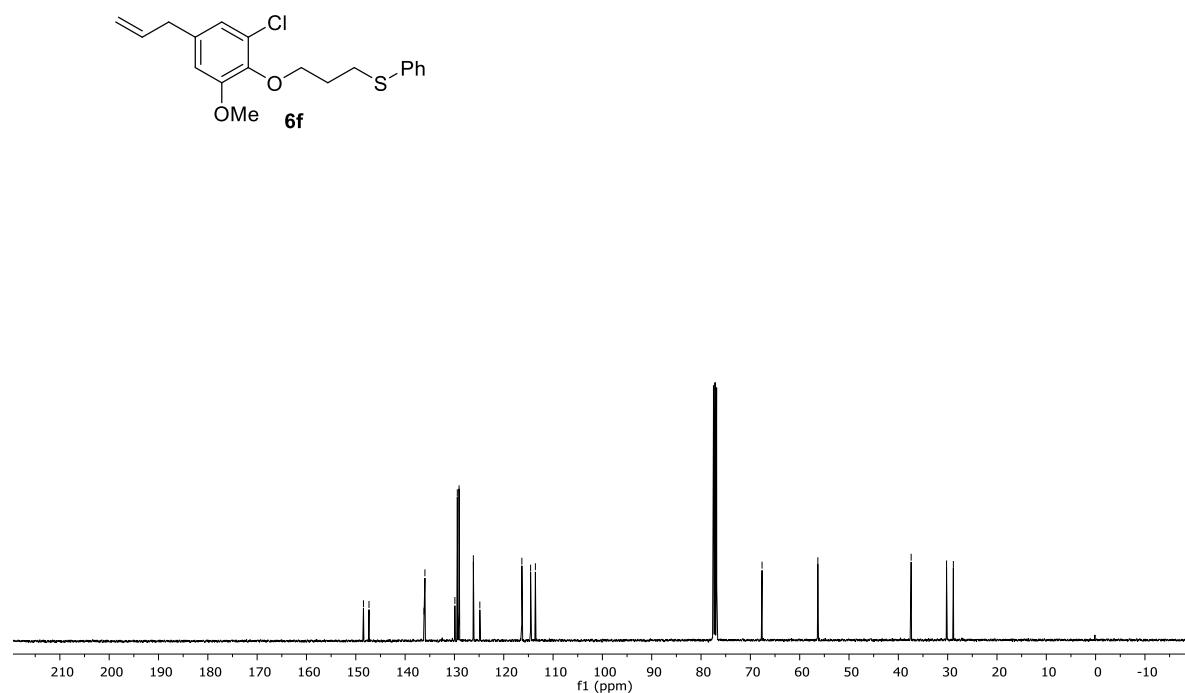
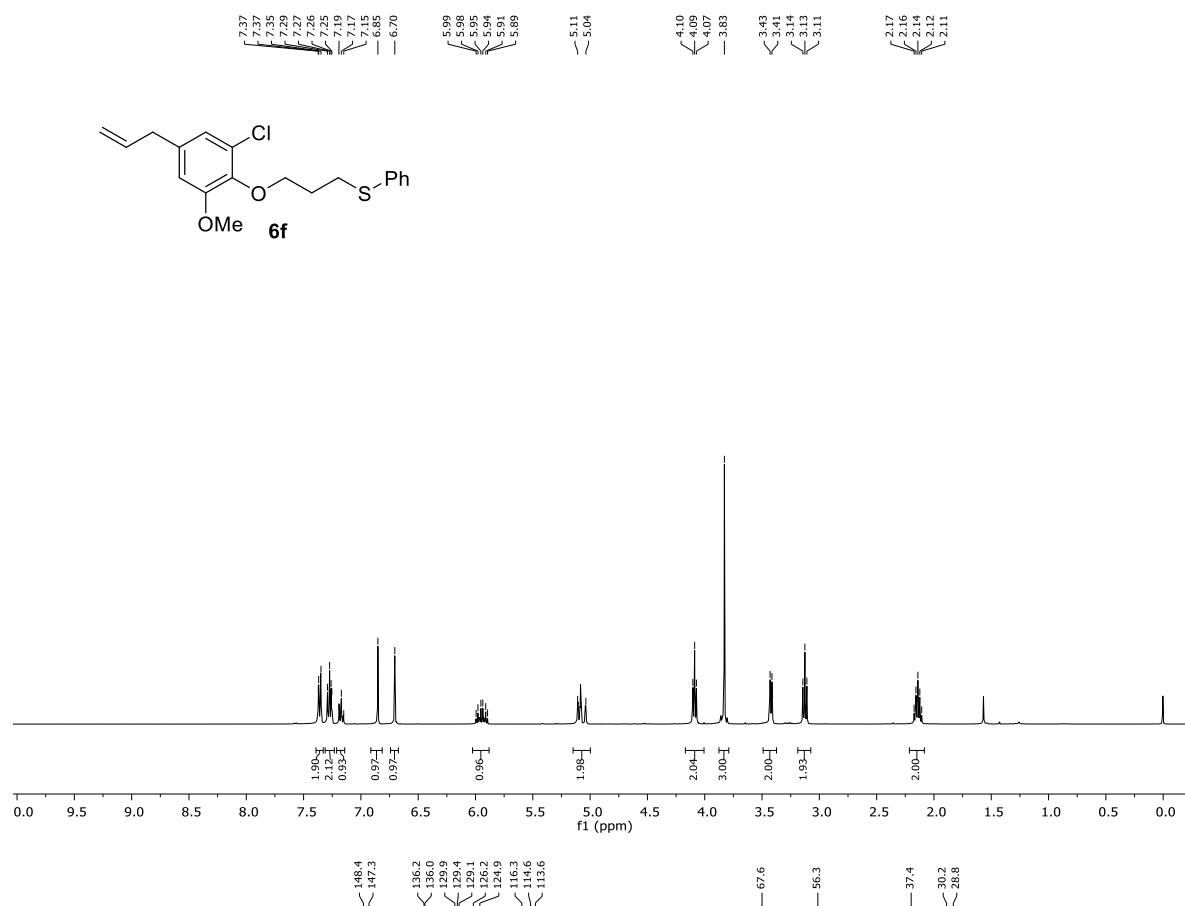
(3-((1-Chloronaphthalen-2-yl)oxy)propyl)(phenyl)sulfide (6d).



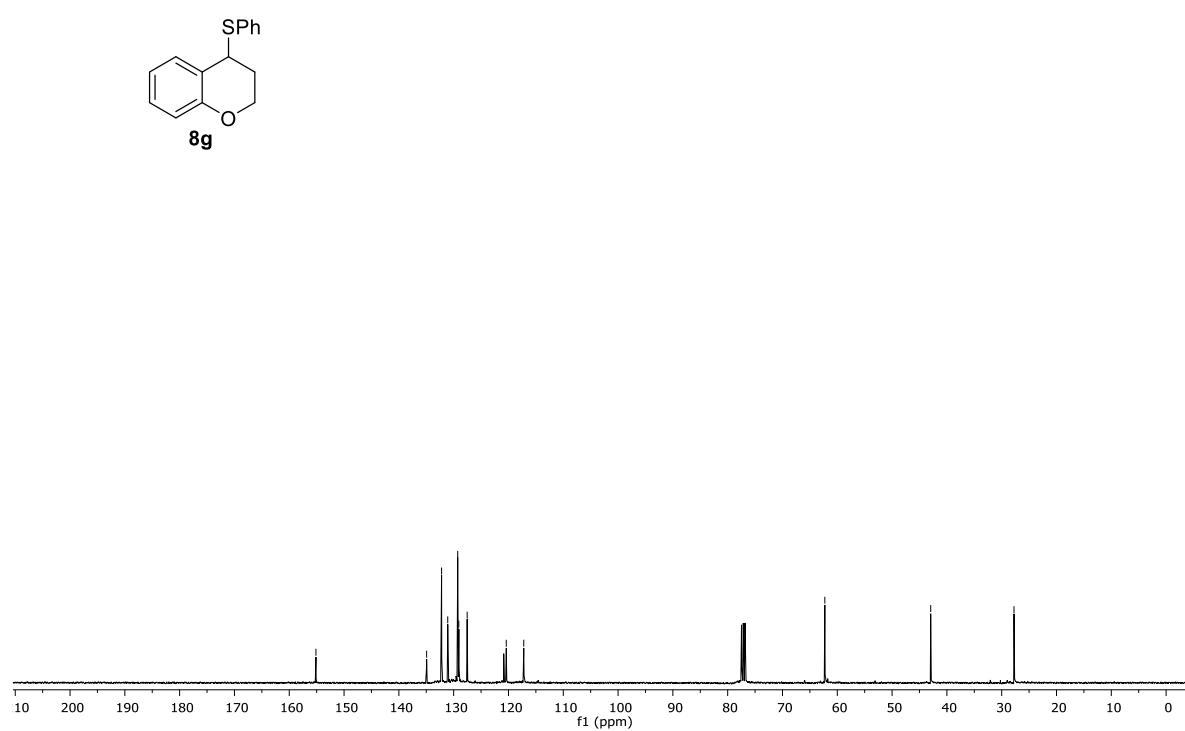
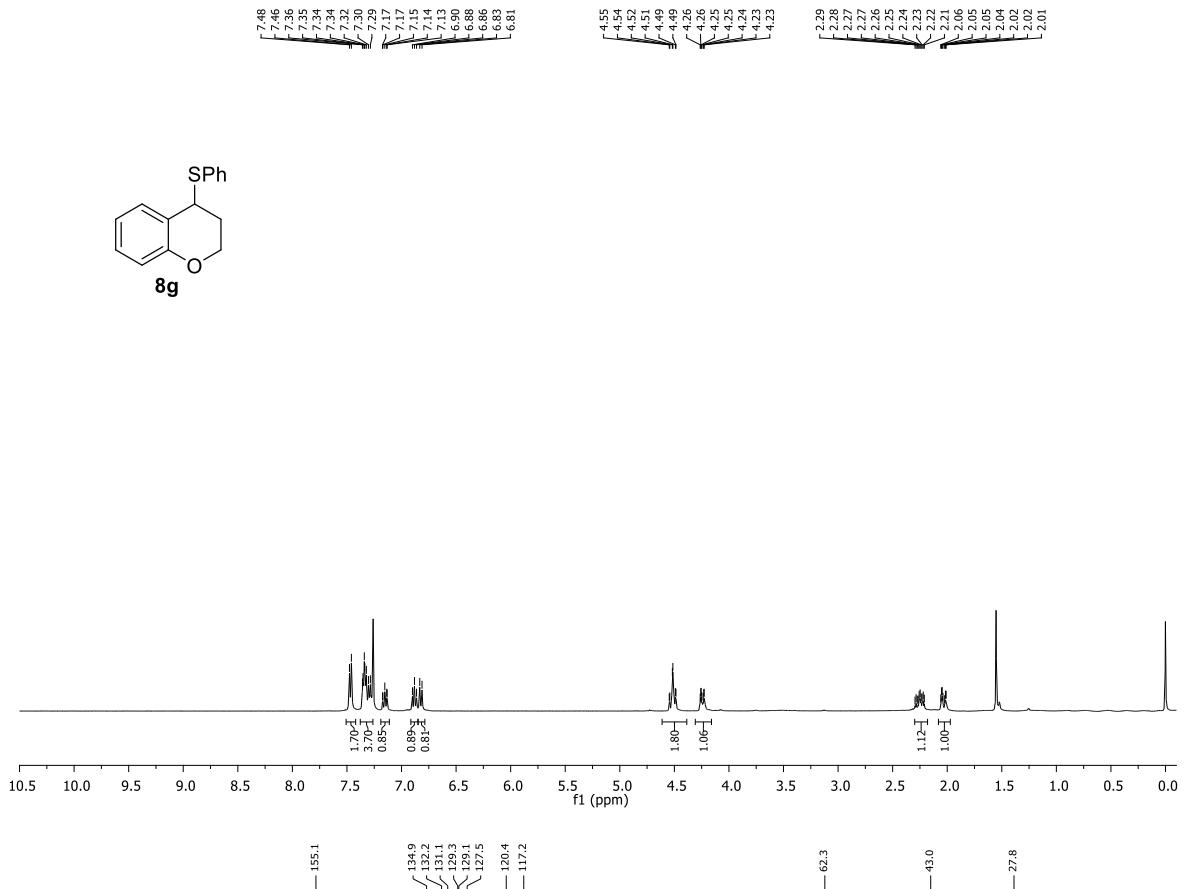
(3-((4-Chloronaphthalen-1-yl)oxy)propyl)(phenyl)sulfane (6e).



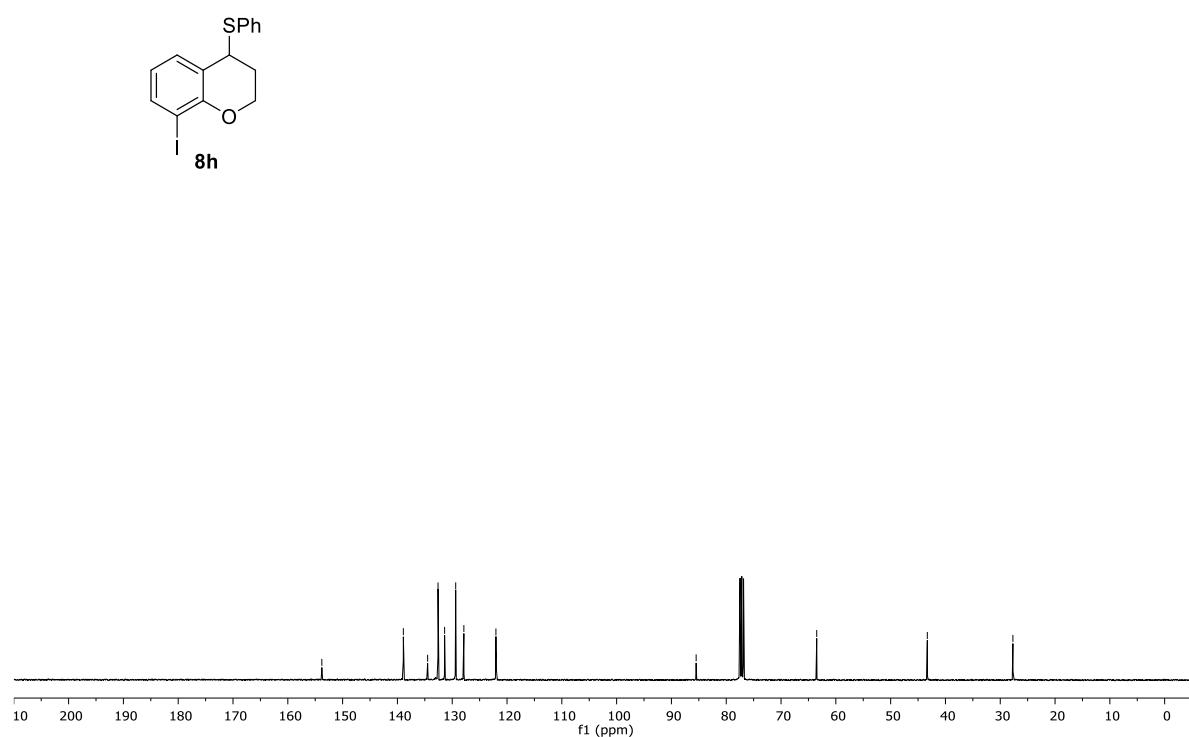
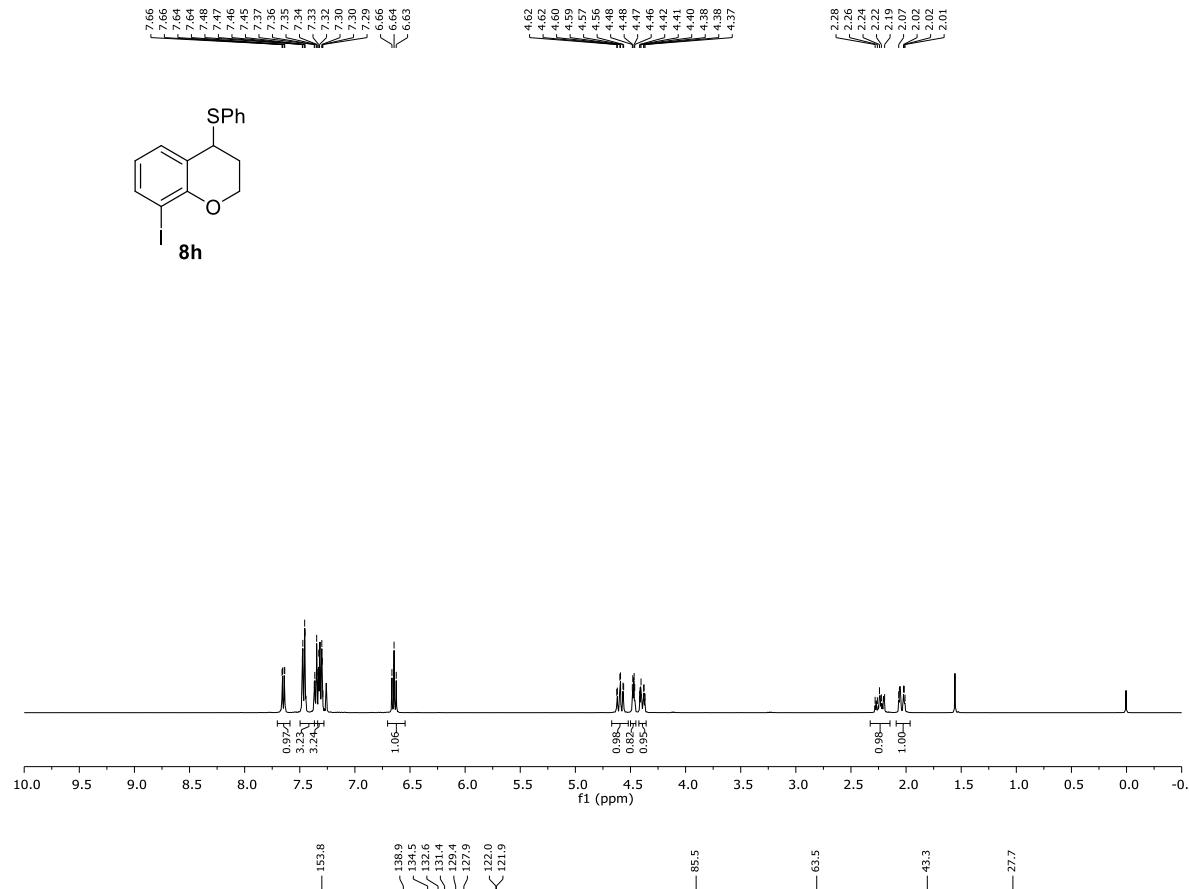
(3-(4-allyl-2-chloro-6-methoxyphenoxy)propyl)(phenyl)sulfane (6f).



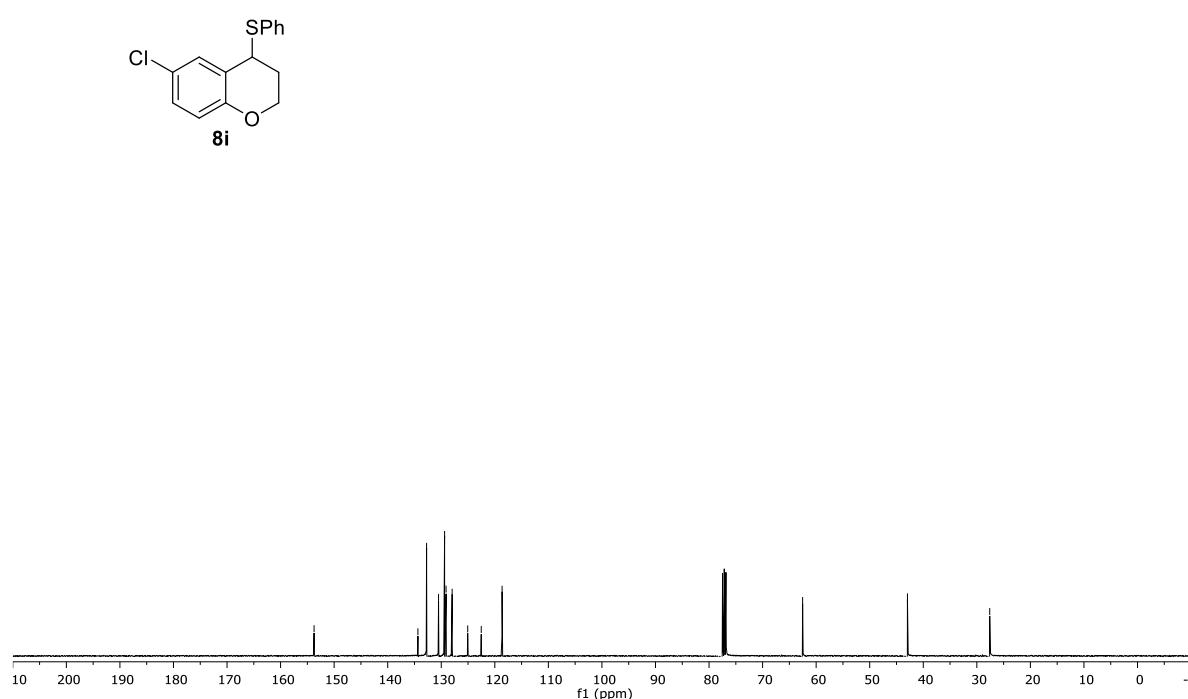
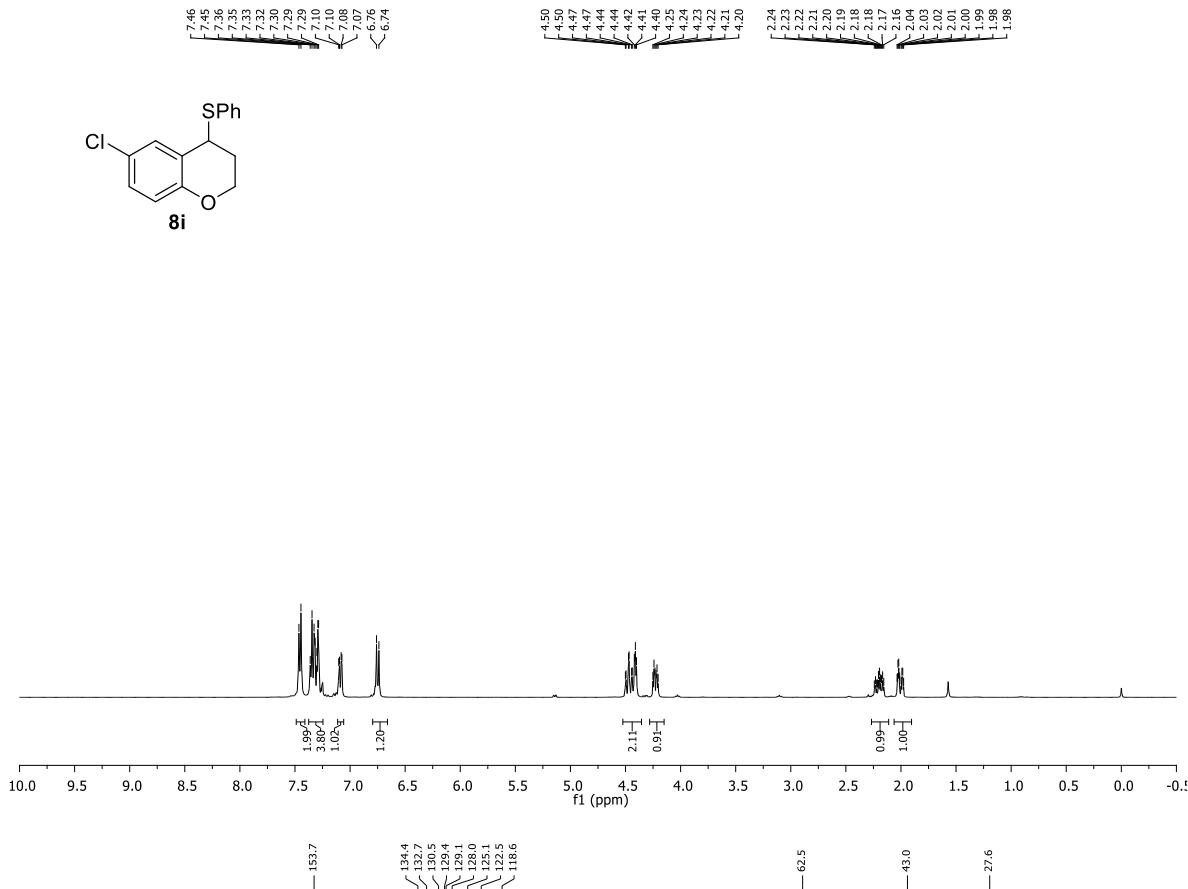
4-(phenylthio)chromane (8g).



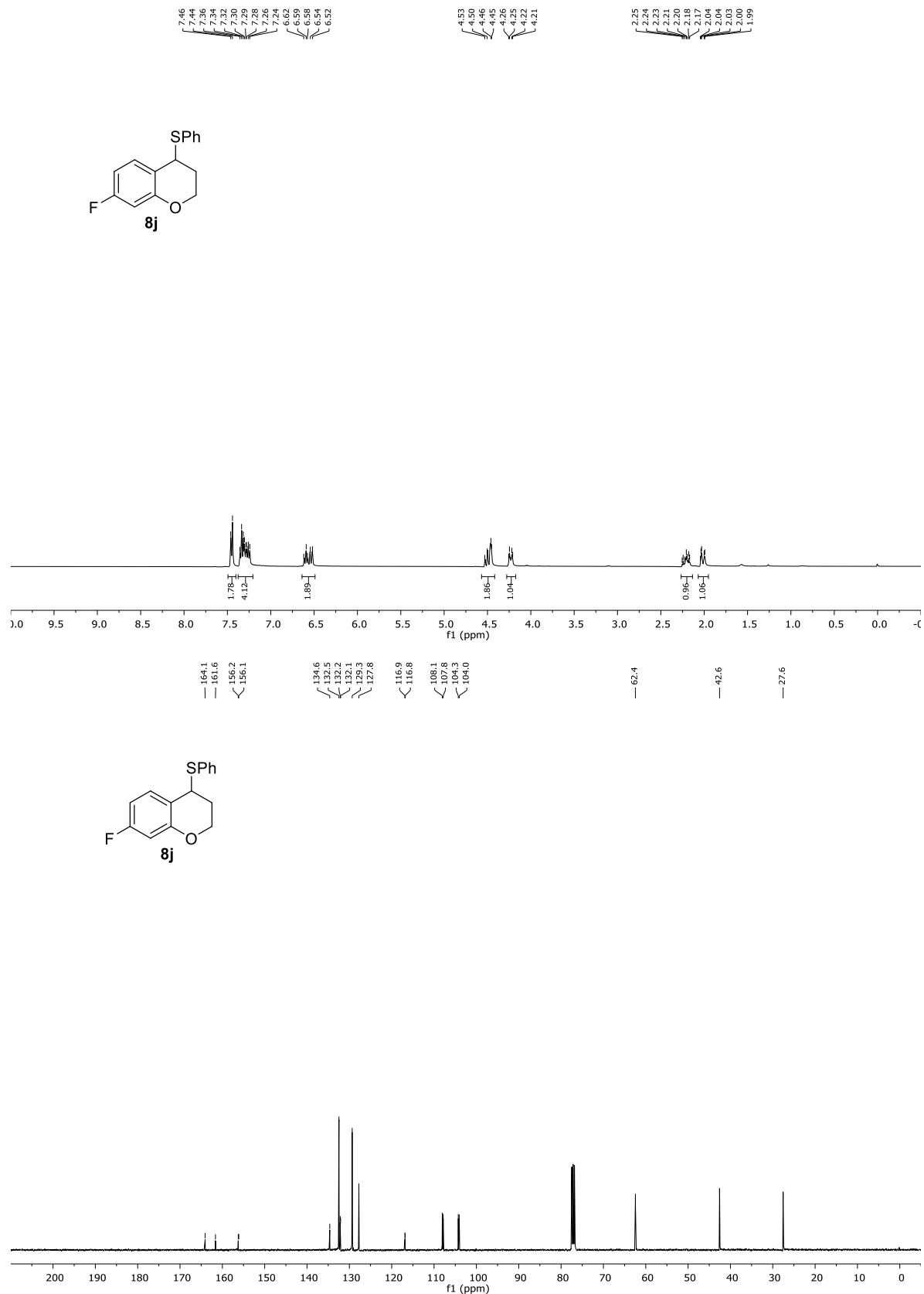
8-Iodo-4-(phenylthio)chromane (8h).



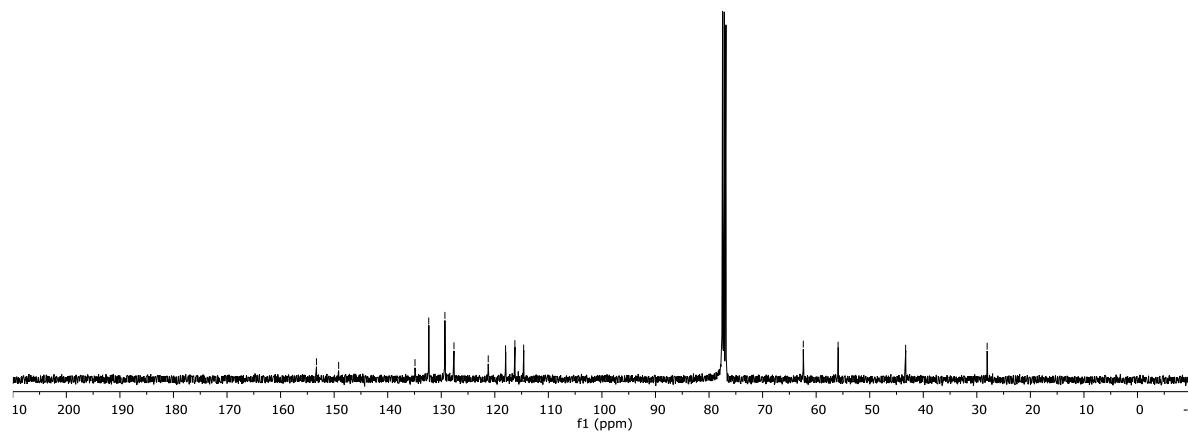
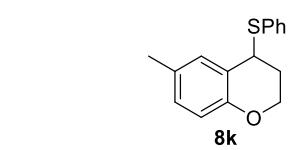
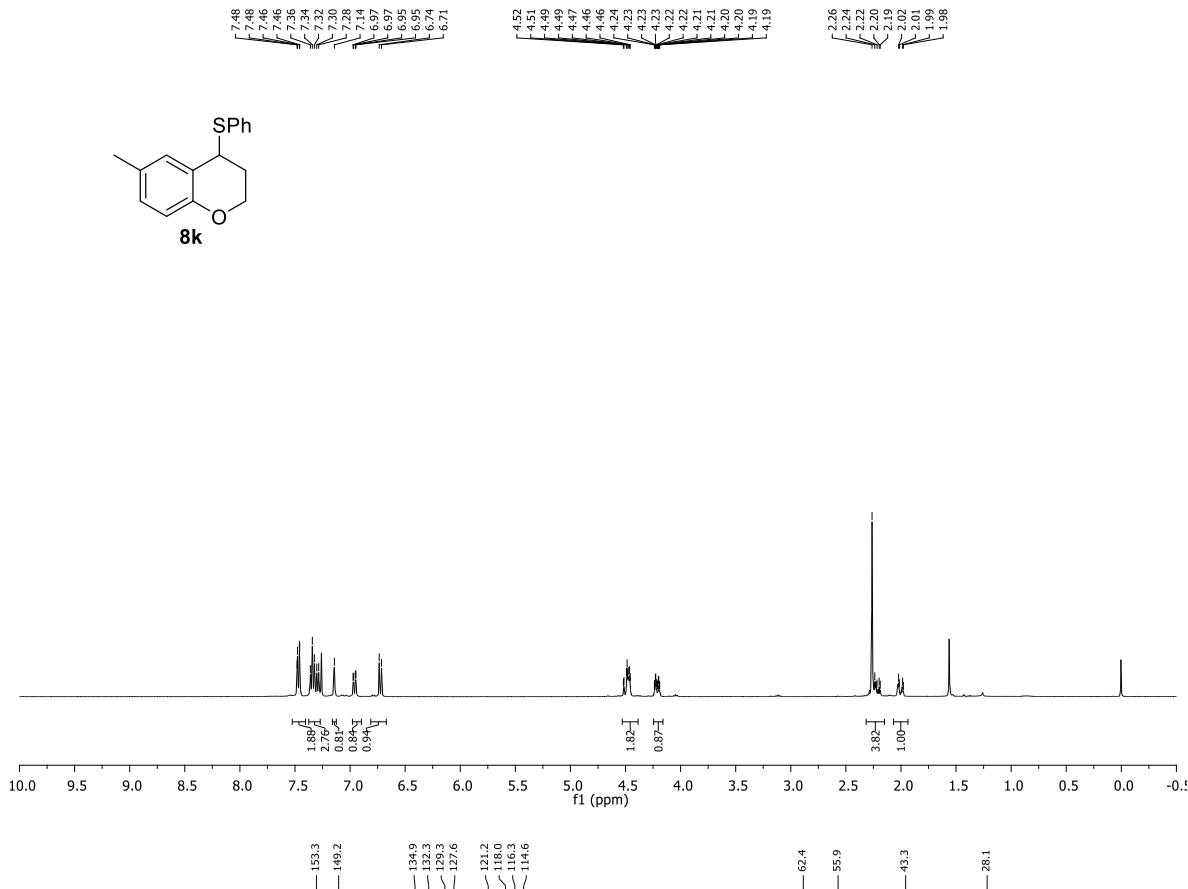
6-Chloro-4-(phenylthio)chromane (8i).



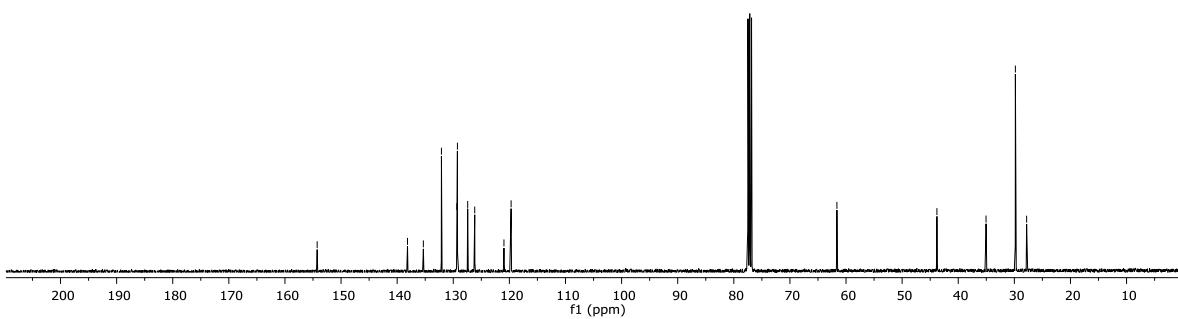
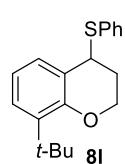
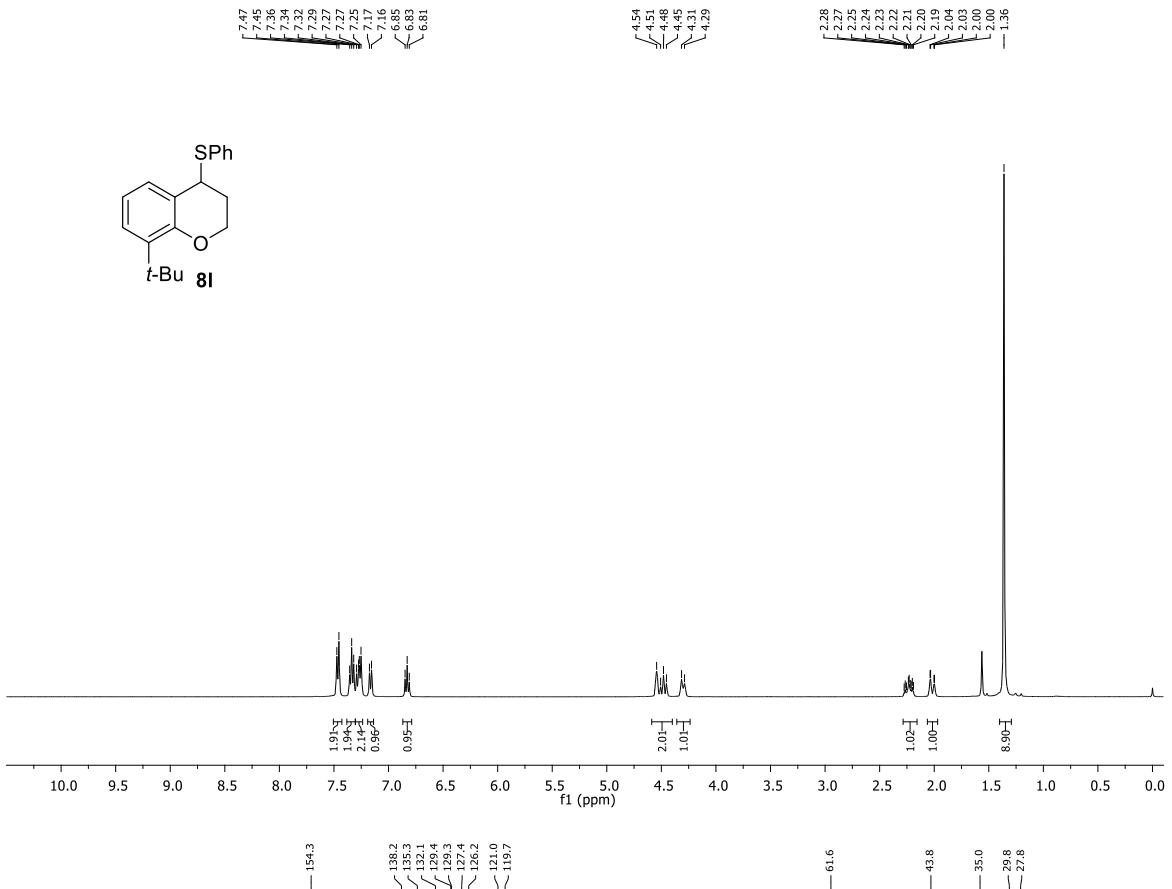
7-Fluoro-4-(phenylthio)chromane (8j).



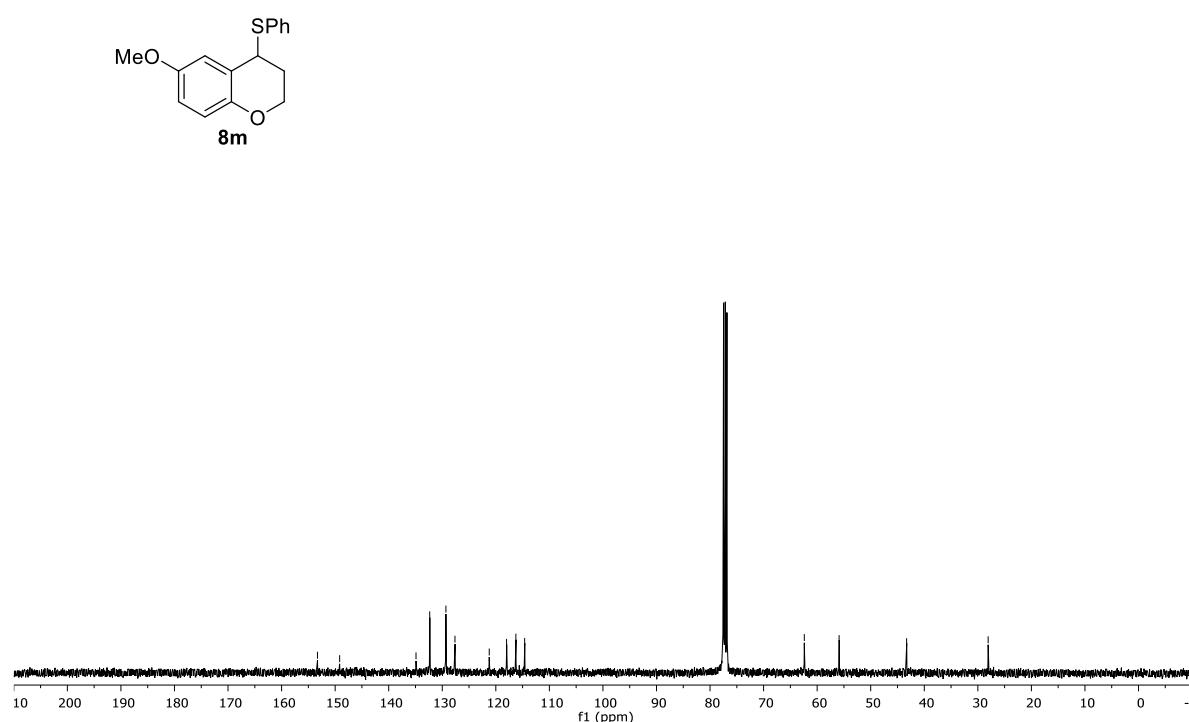
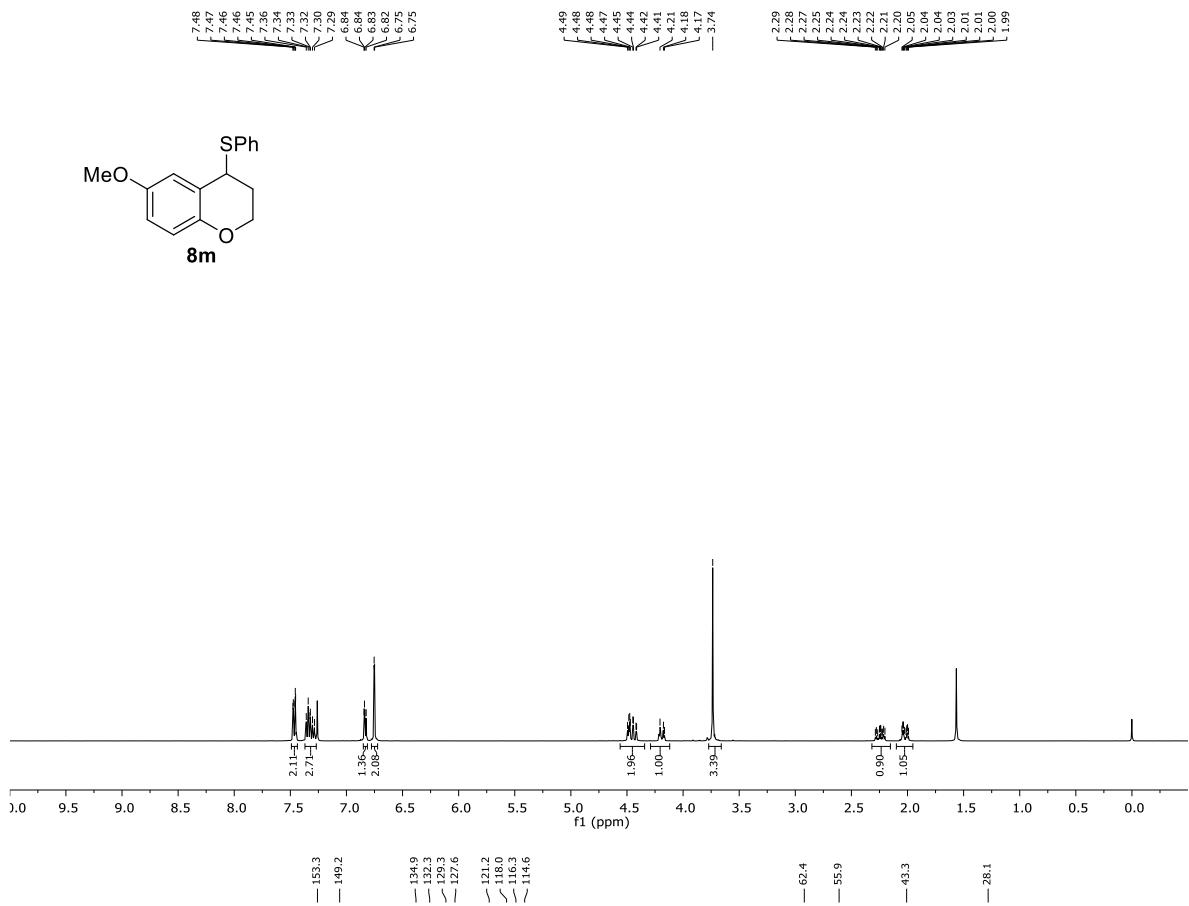
6-Methyl-4-(phenylthio)chromane (8k).



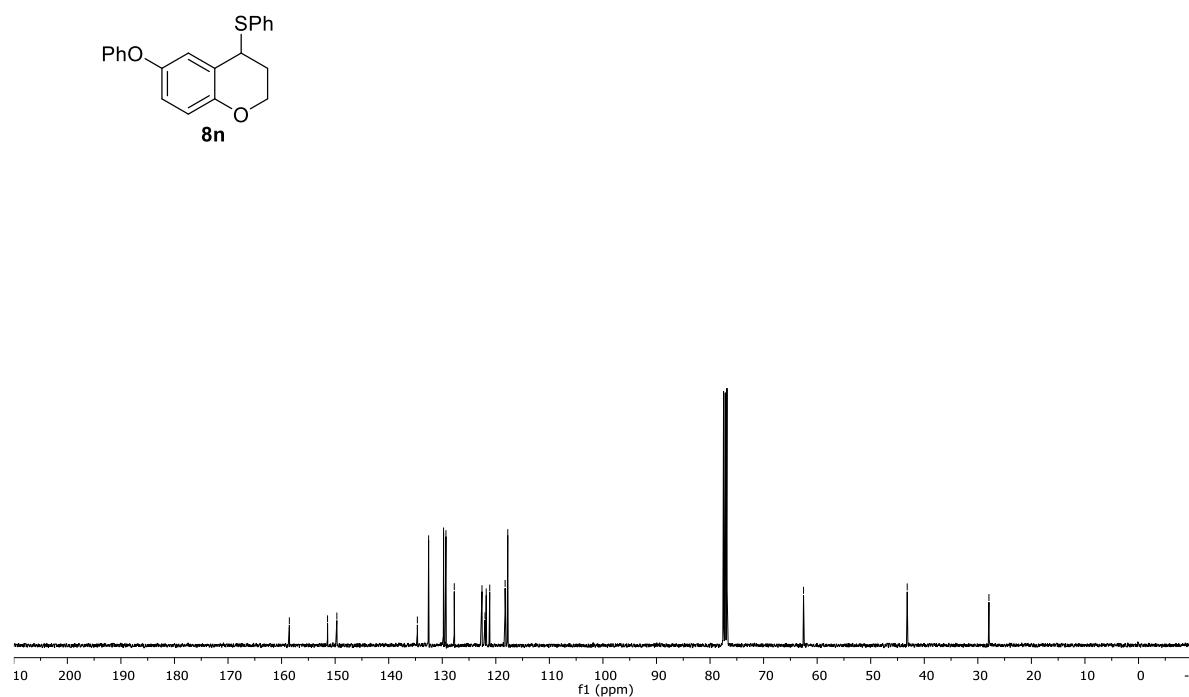
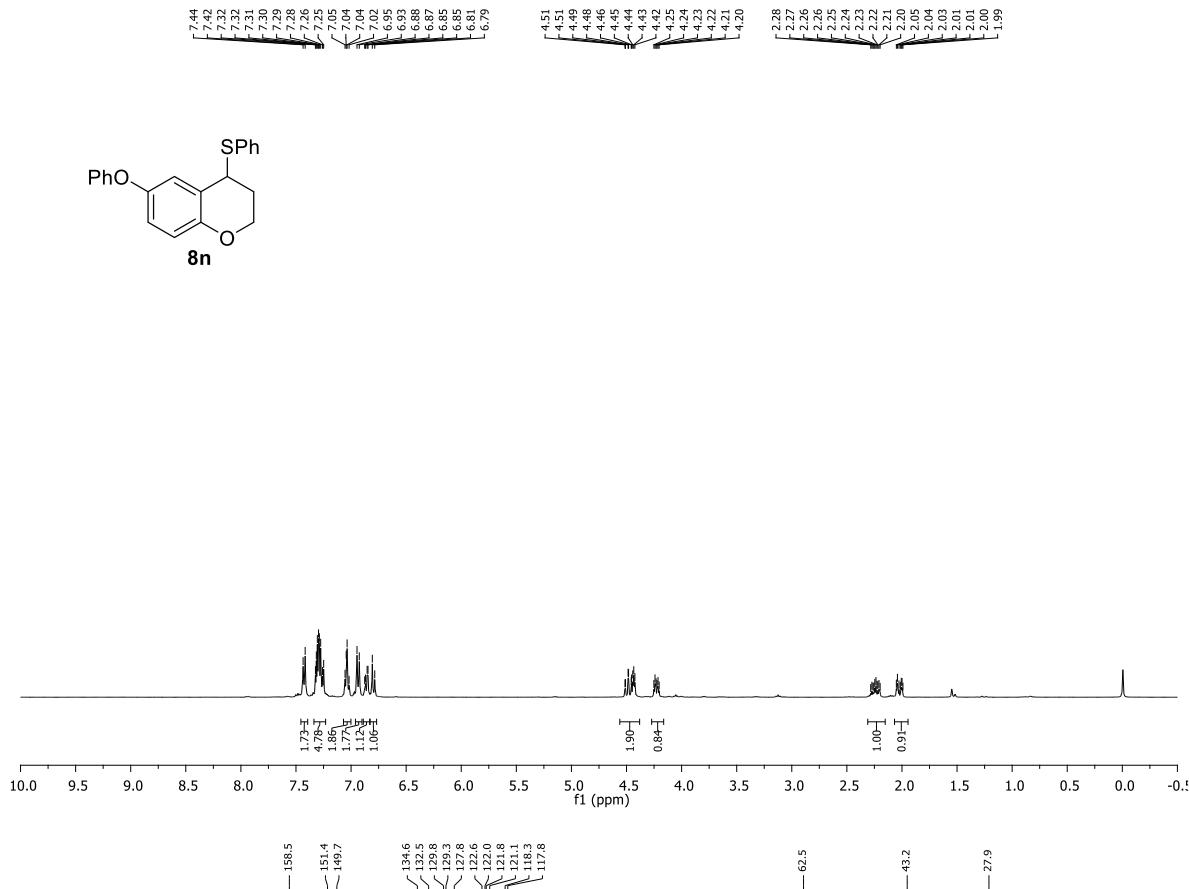
8-(*tert*-butyl)-4-(phenylthio)chromane (8l**)**



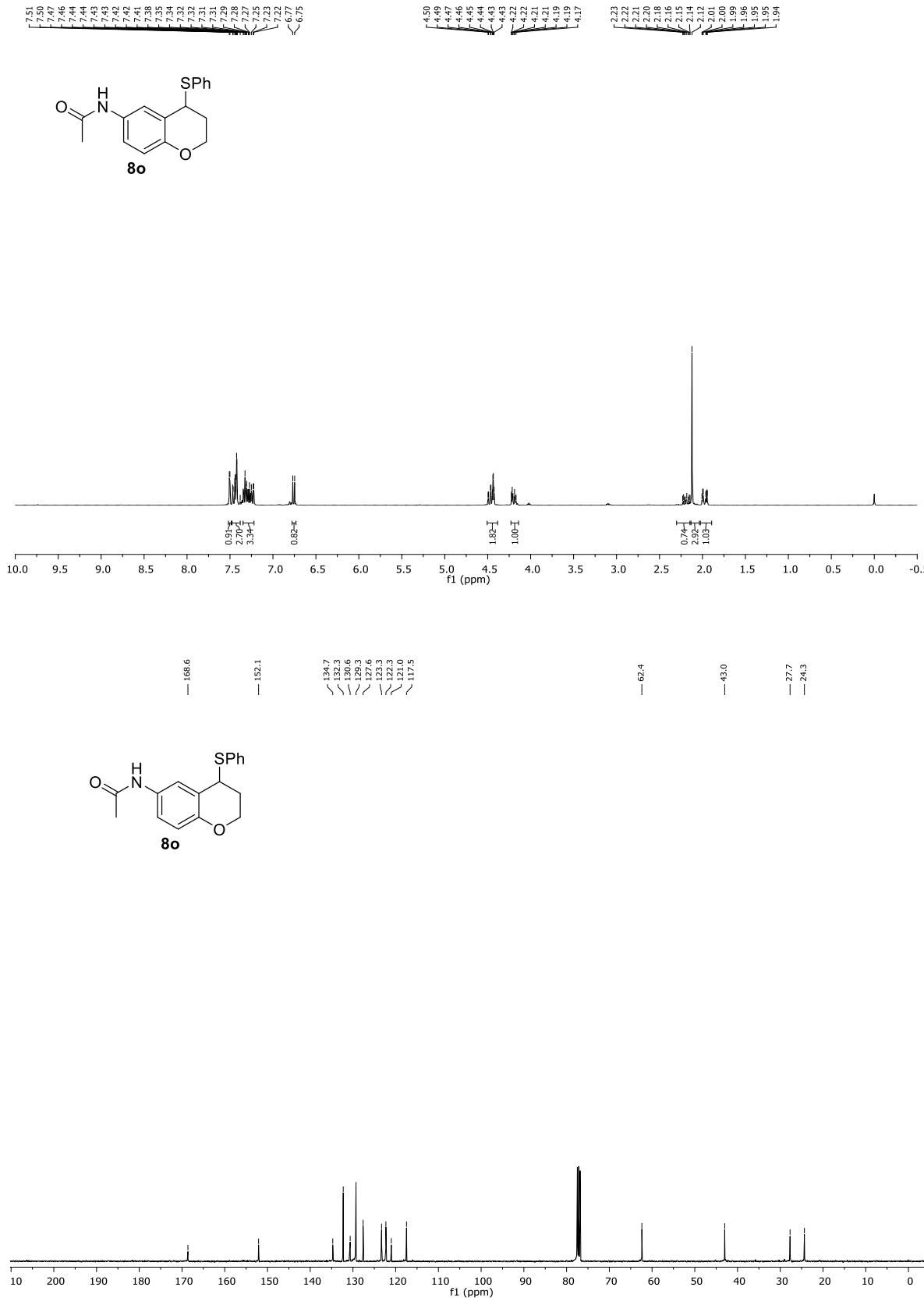
6-Methoxy-4-(phenylthio)chromane (8m).



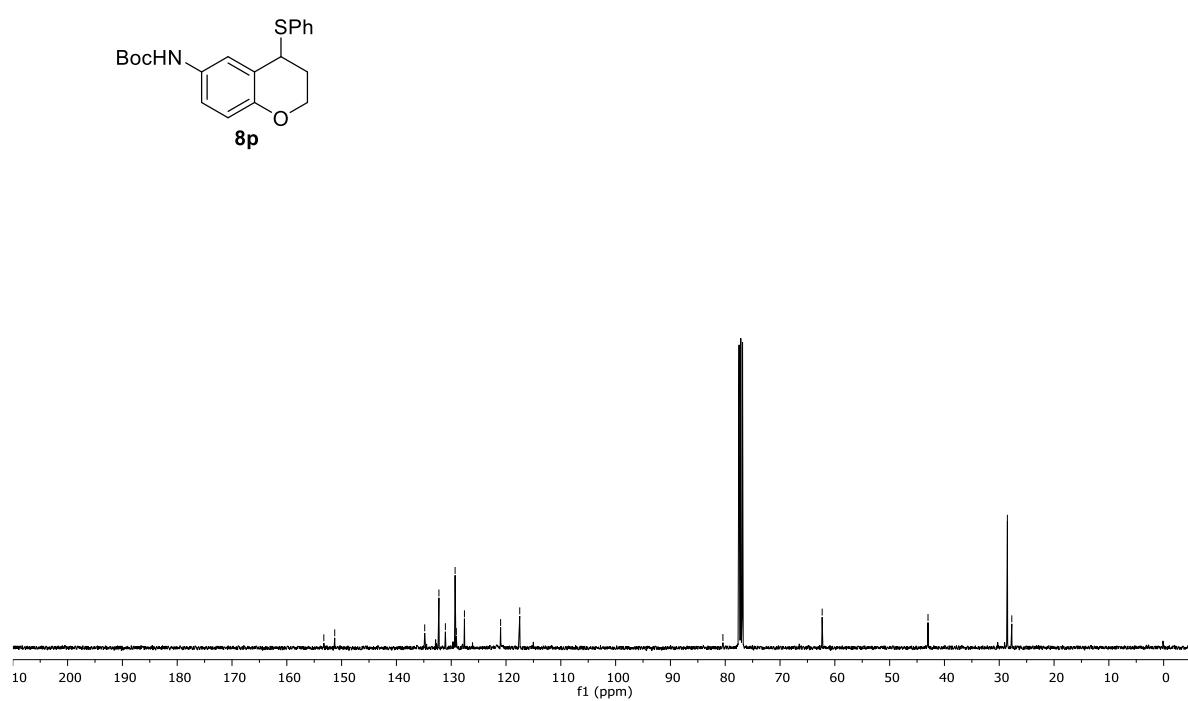
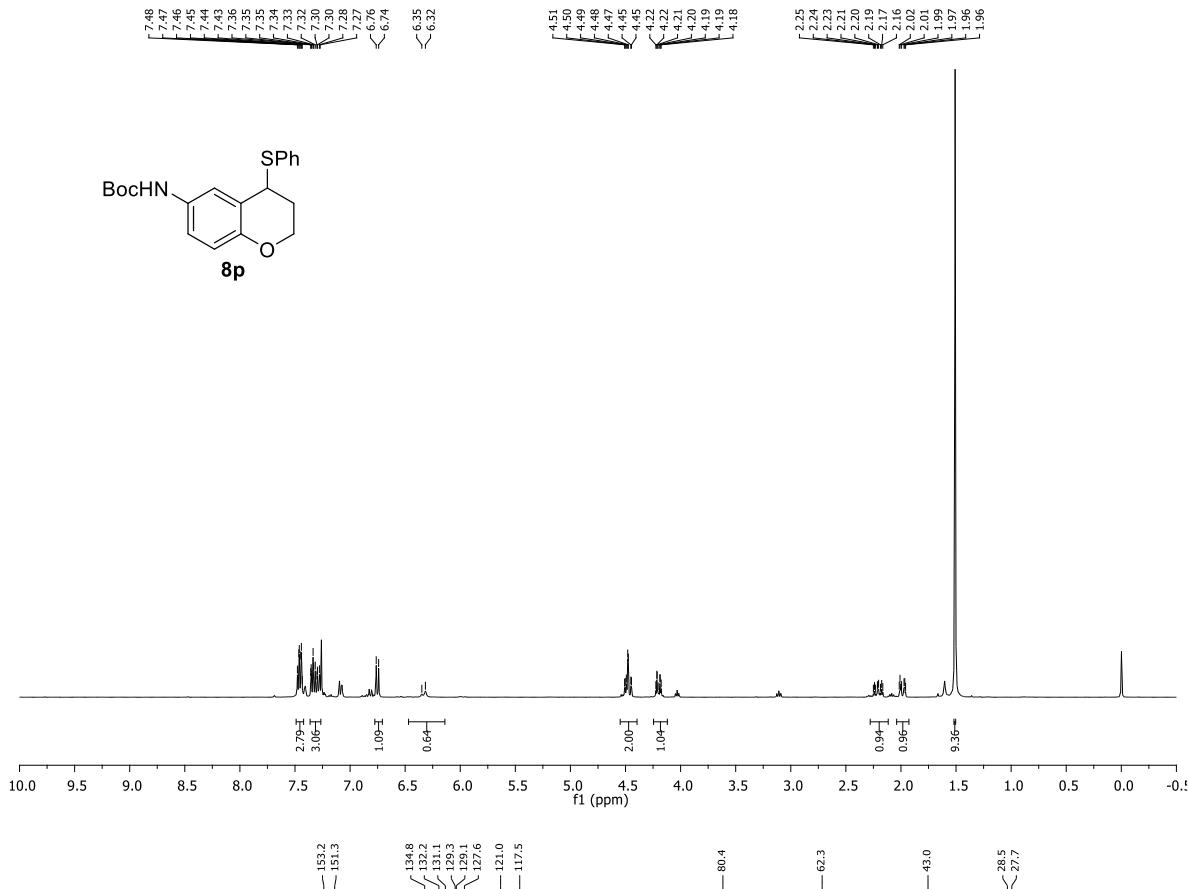
6-Phenoxy-4-(phenylthio)chromane (8n).



N-(4-(Phenylthio)chroman-6-yl)acetamide (8o).



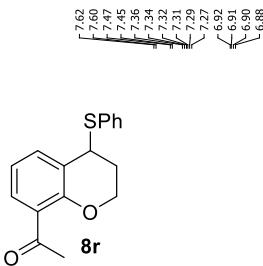
***tert*-butyl (4-(phenylthio)chroman-6-yl)carbamate (8p).**



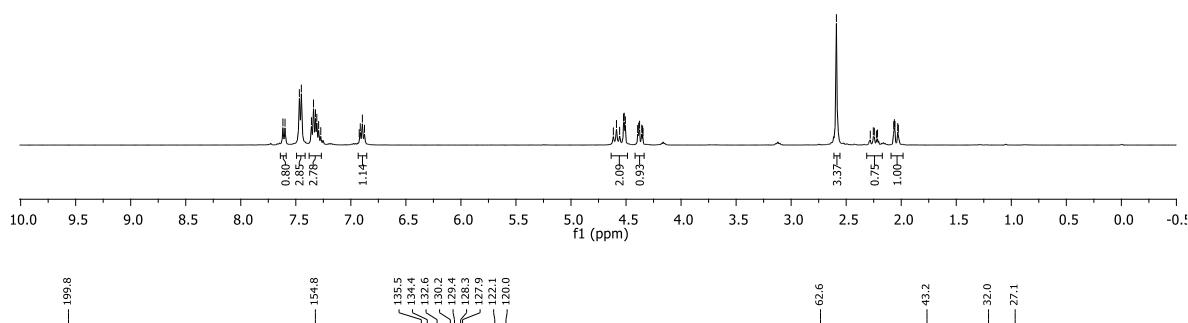
Benzyl (4-(phenylthio)chroman-6-yl)carbamate (8q).



1-(4-(Phenylthio)chroman-8-yl)ethanone (8r).



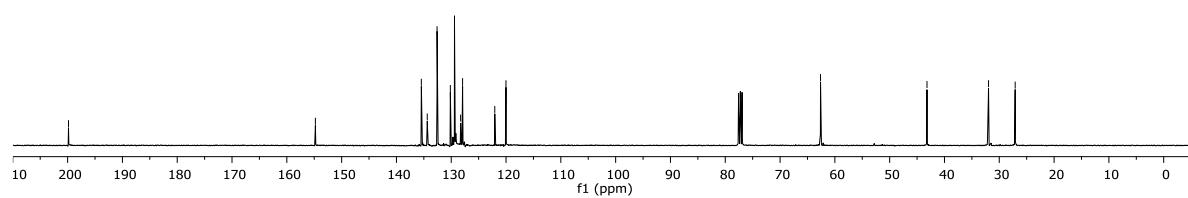
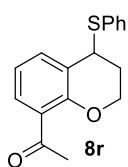
7.62
7.60
7.47
7.45
7.36
7.34
7.32
7.31
7.27
7.29
6.92
6.91
6.90
6.88



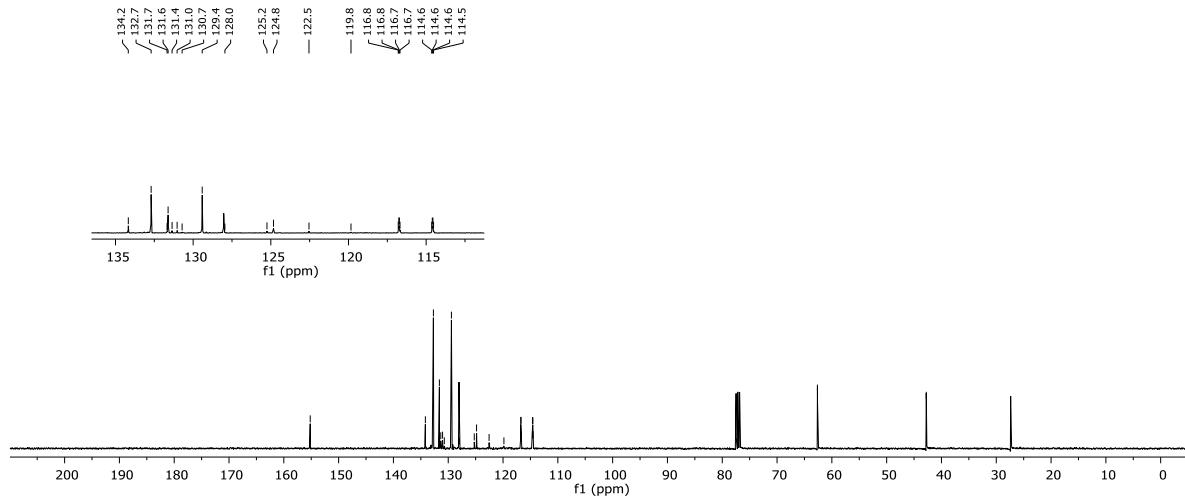
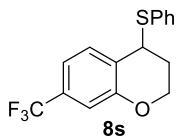
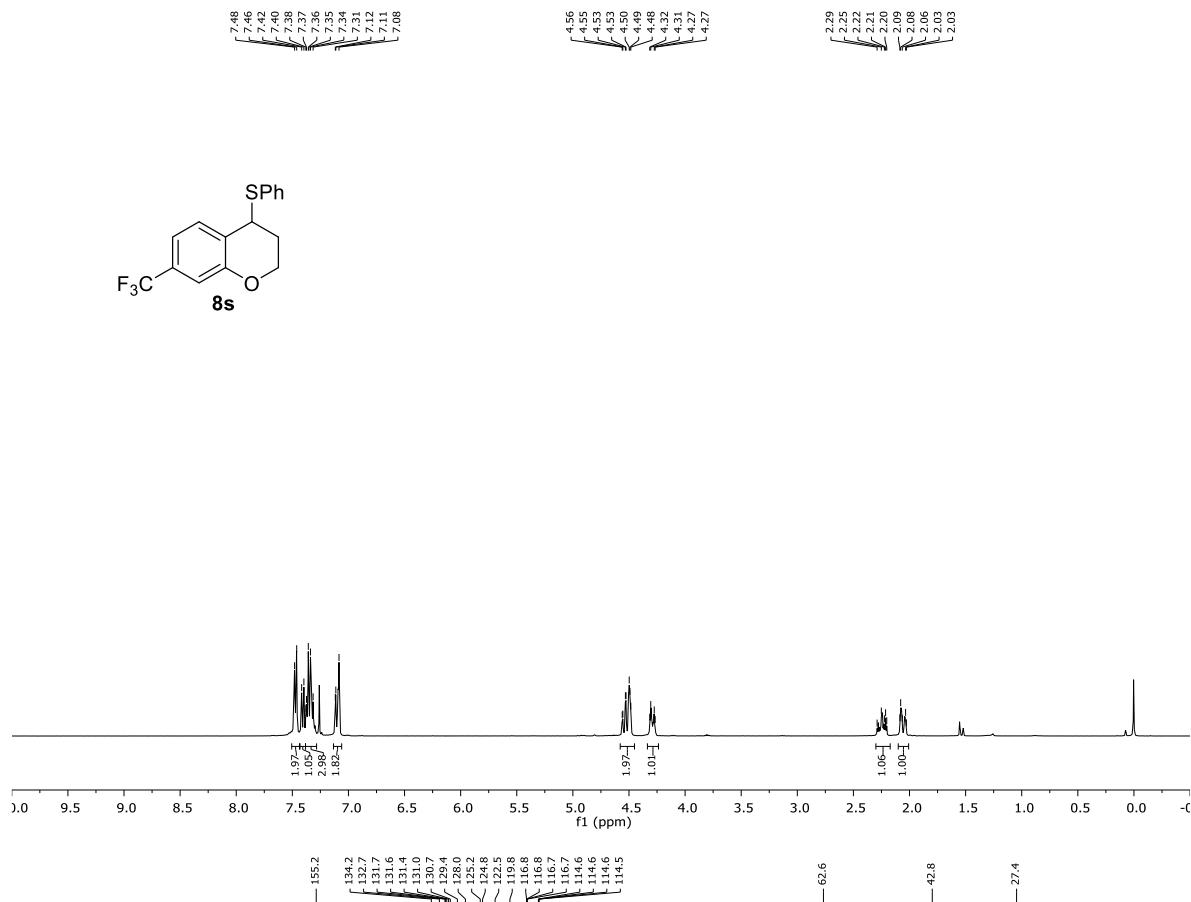
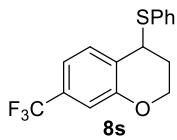
199.8

154.8
135.5
134.4
132.6
130.2
129.4
128.3
127.9
122.1
120.0

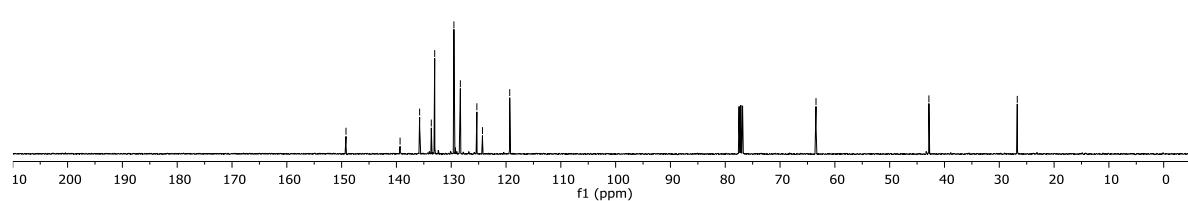
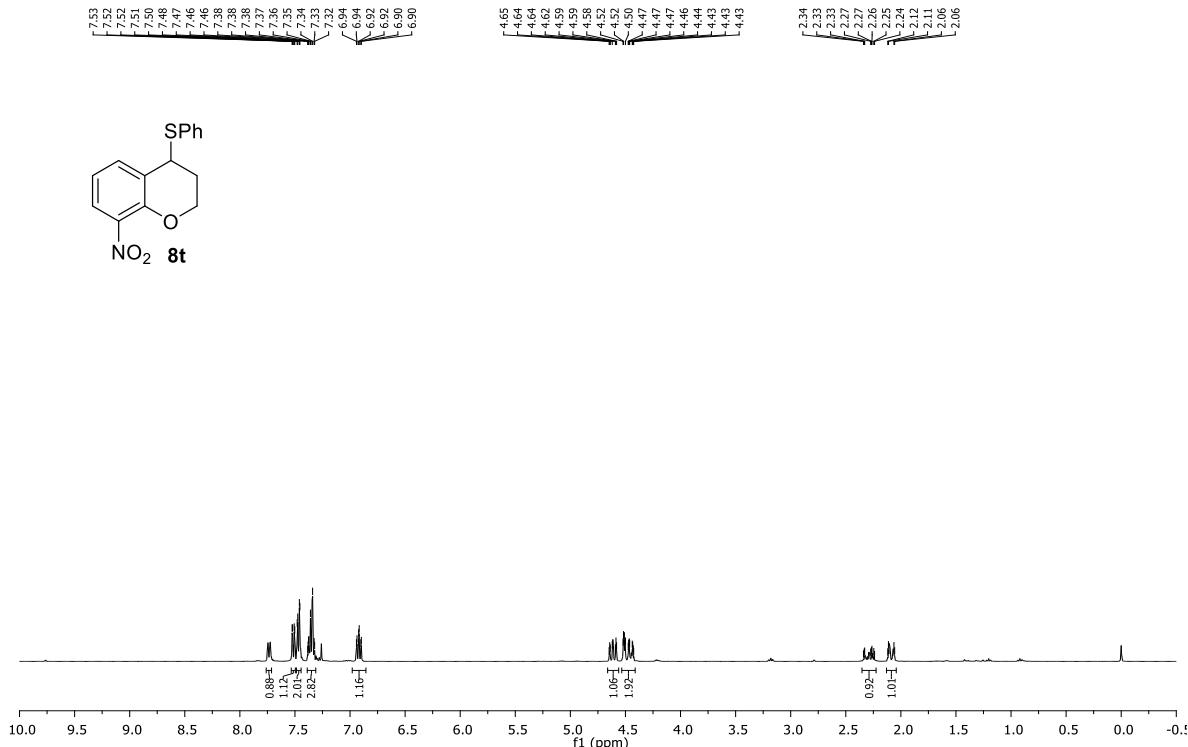
62.6
43.2
32.0
27.1



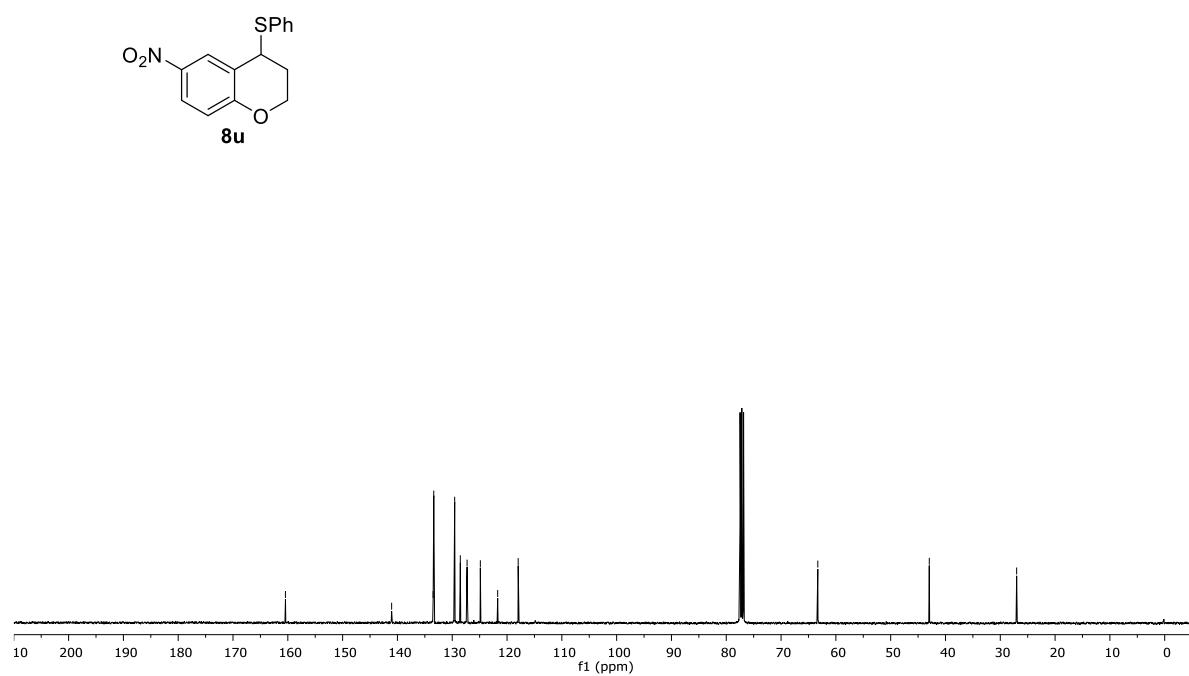
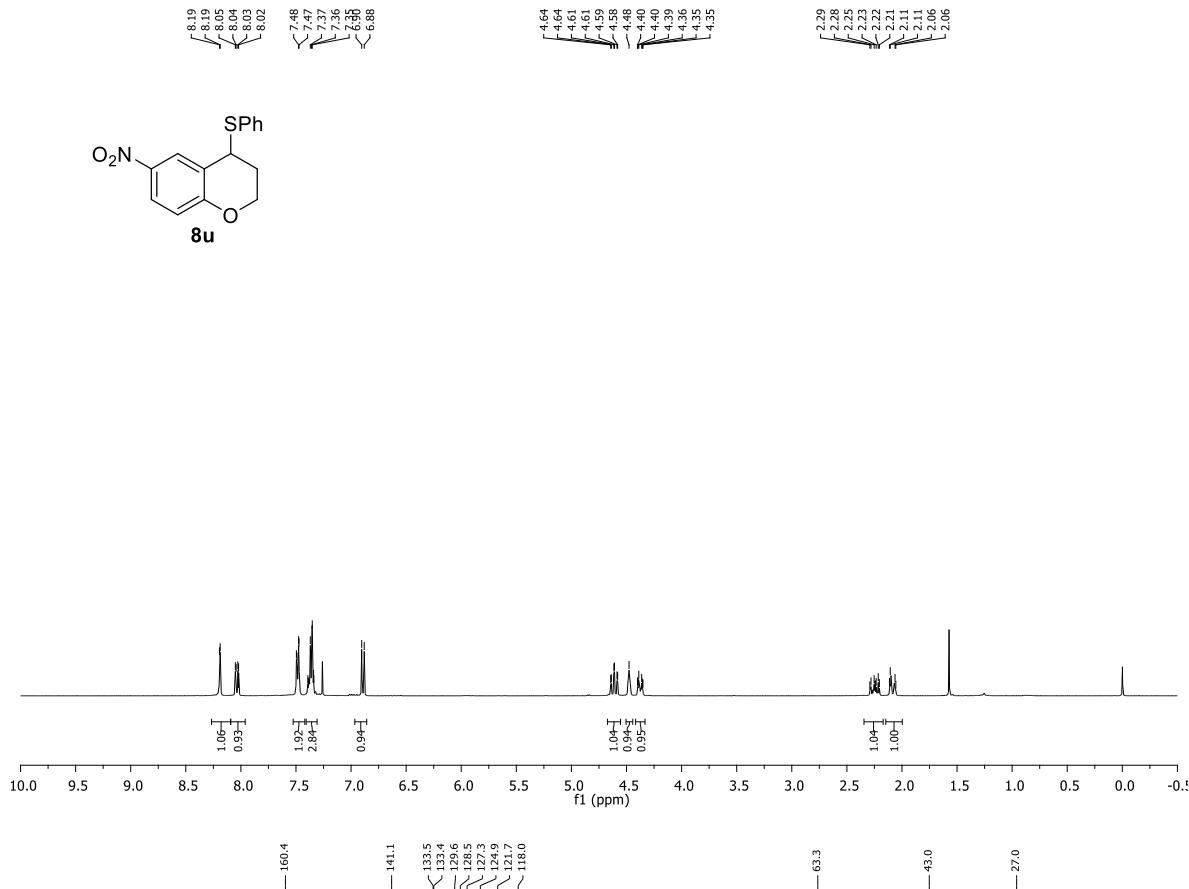
4-(Phenylthio)-7-(trifluoromethyl)chromane (8s).



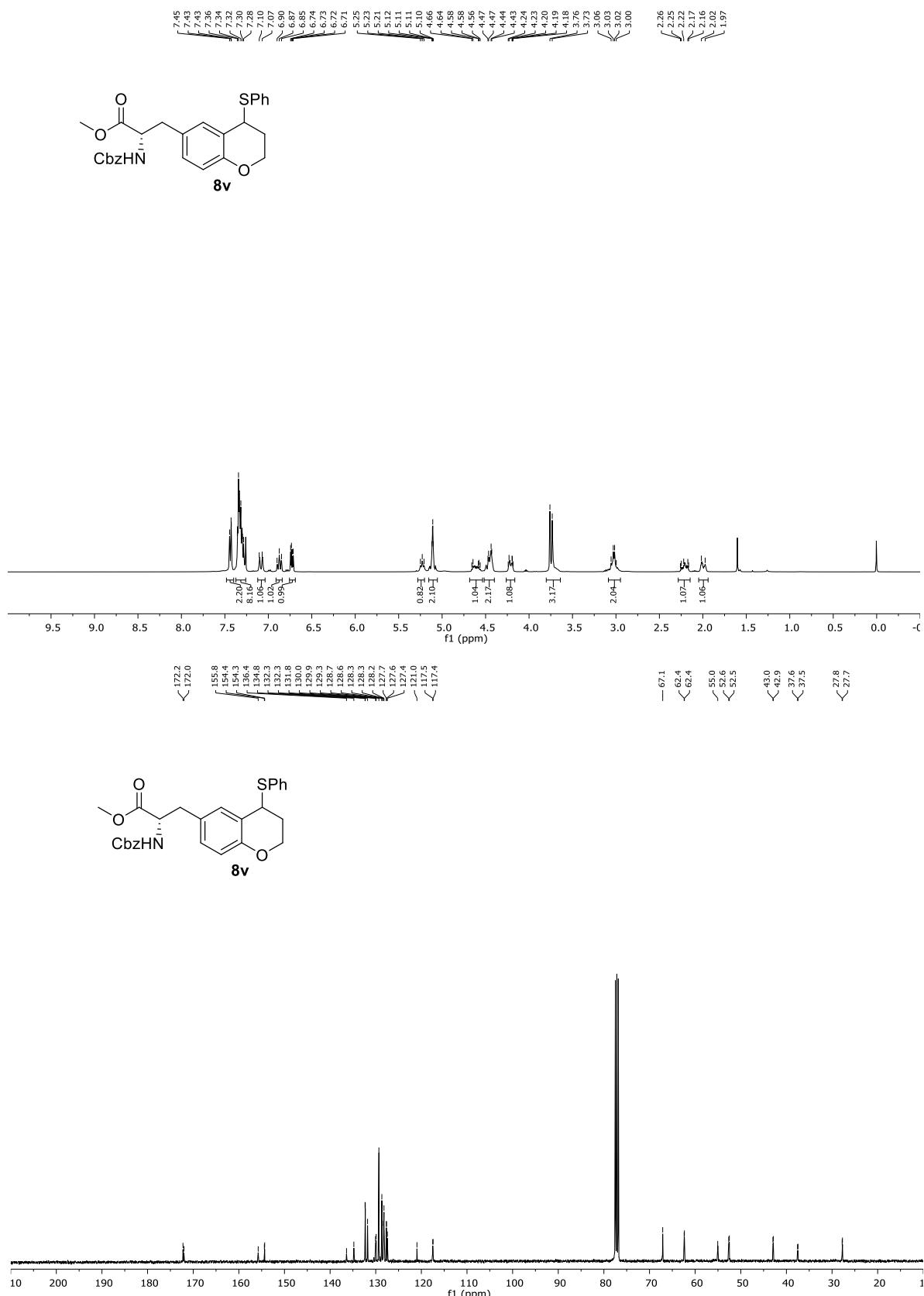
8-Nitro-4-(Phenylthio)chromane (8t).



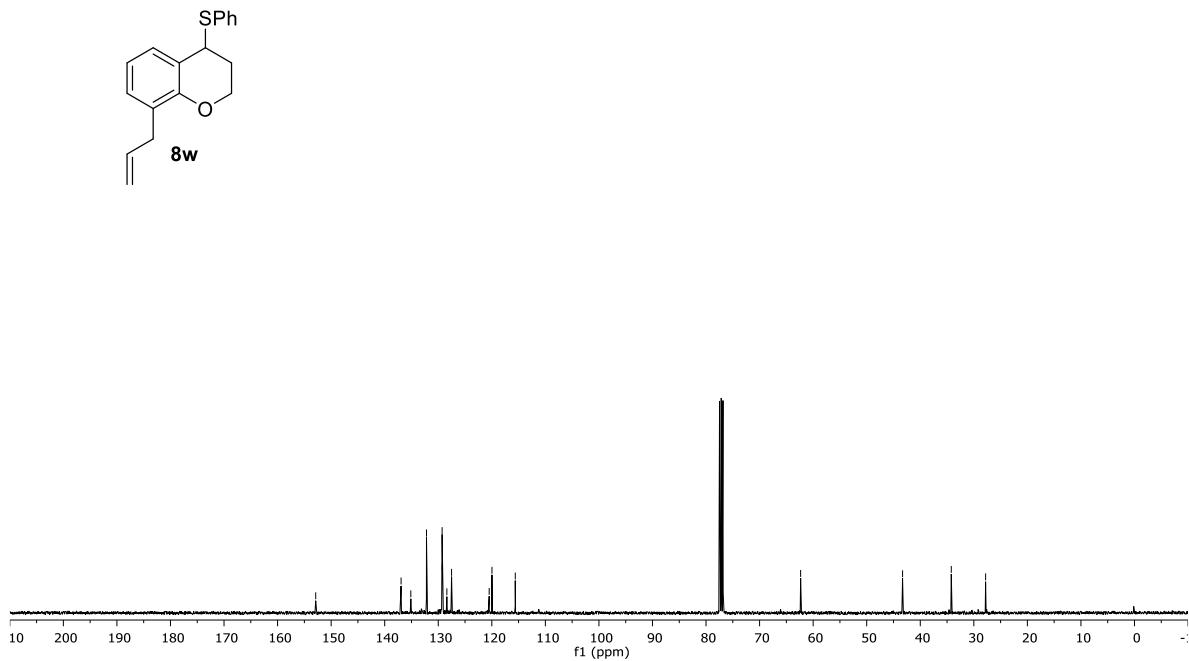
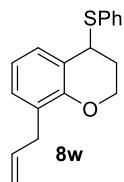
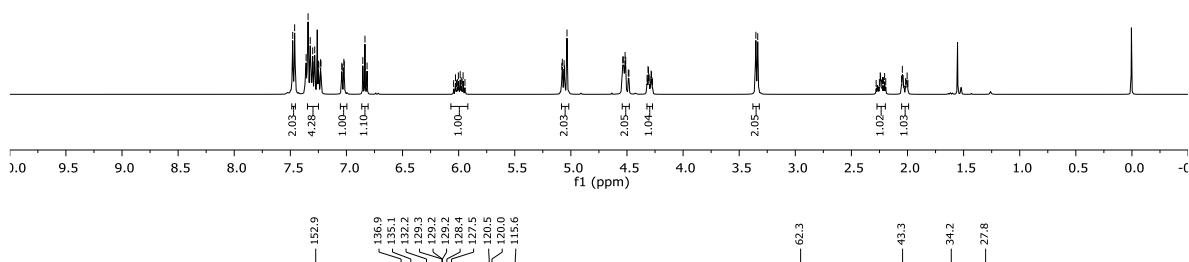
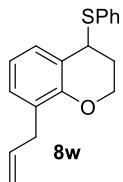
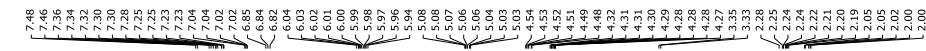
6-Nitro-4-(phenylthio)chromane (8u).



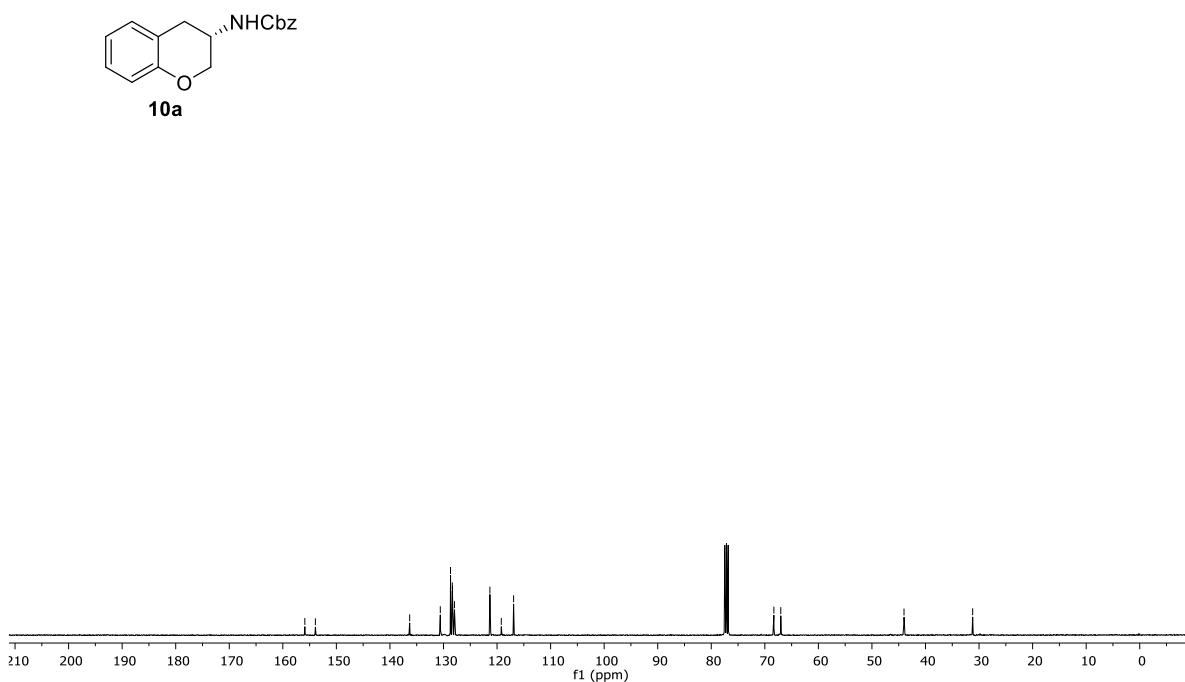
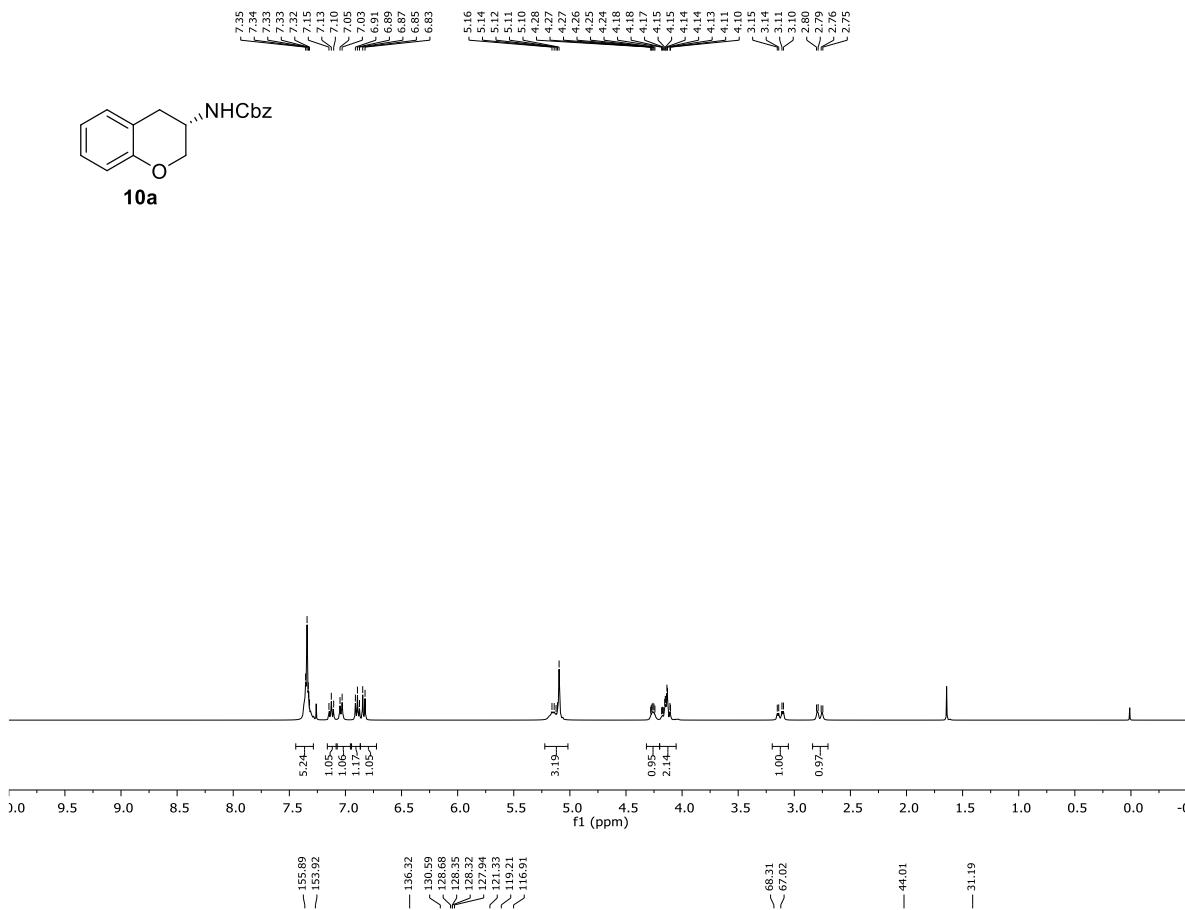
(2*R*)-Methyl 2-((benzyloxy)carbonyl)amino)-3-(4-(phenylthio)chroman-6-yl)propanoate (8v).



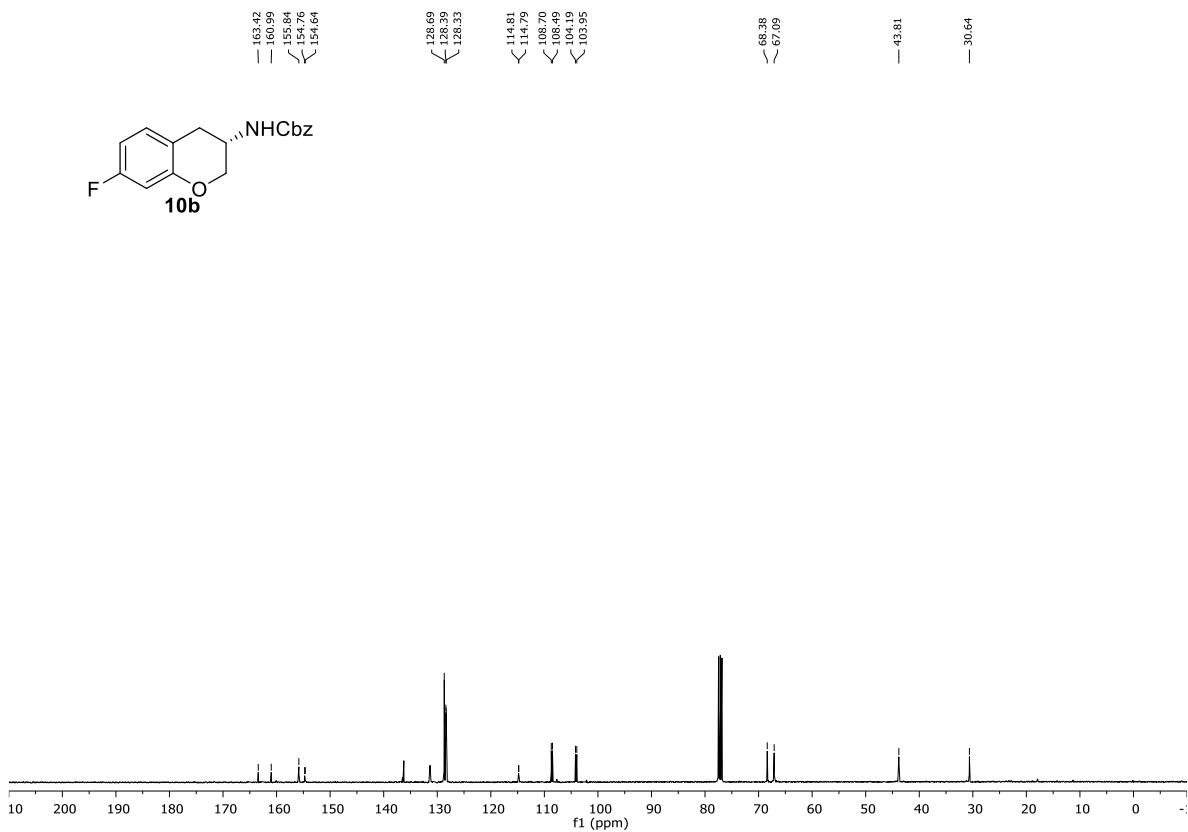
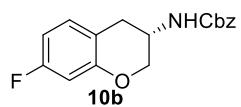
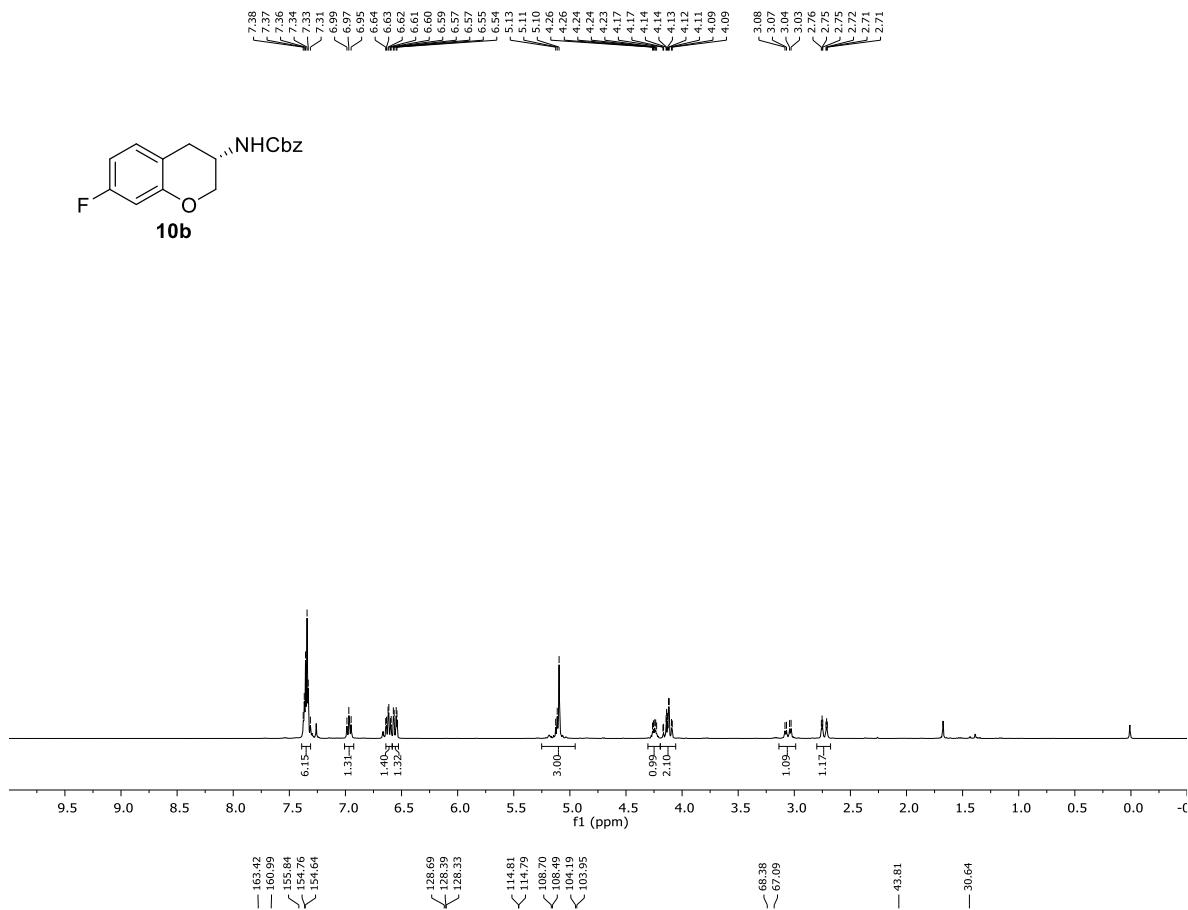
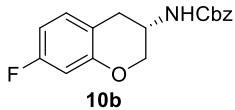
8-Allyl-4-(phenylthio)chromane (8w).



(S)-benzyl chroman-3-ylcarbamate (10a).



(S)-benzyl (7-fluorochroman-3-yl)carbamate (10b).



(S)-benzyl-(6-methylchroman-3-yl)carbamate (10c).

