Angewandte Chemie
Eine Zeitschrift der Gesellschaft Deutscher Chemiker

Supporting Information

Arynes as Radical Acceptors: TEMPO-Mediated Cascades Comprising Addition, Cyclization, and Trapping

*Maximilian Scherübl, Constantin G. Daniliuc, and Armido Studer**

anie_202012654_sm_miscellaneous_information.pdf

Table of Contents

1. General information

All reactions involving air or moisture sensitive reagents were carried out in flame-dried glass ware under argon atmosphere using standard Schlenk techniques. Solvents used in reactions were either freshly distilled or obtained in extra-dry grade from commercial sources. Diethyl ether (Et_2O) was refluxed over potassium and freshly distilled from K-Na-alloy (4:1) afterwards. Tetrahydrofuran (THF) was refluxed over sodium and distilled from potassium afterwards. Acetonitrile (MeCN, 99.9%, Extra Dry over Molecular Sieves) and *n*-hexane (*n*-hexane, 96+%, Extra Dry over Molecular Sieves) were purchased from Acros Organics. Solvents for extraction and for flash chromatography were distilled. All chemicals were purchased from ABCR, Acros Organics, Alfa Aesar, Sigma Aldrich, Fluka, Fluorochem and TCI and were used as received. Flash chromatography (FC) was performed on Merck silica gel 60 (40 – 63 µm) with an excess argon pressure up to 0.5 bar. Merck silica gel 60 F254 plates were used for thin layer chromatography (TLC) using UV light (254/366 nm) or oxidation with $KMnO_4$ (1.5 g $KMnO_4$, 10 g K_2CO_3, 1 mL aqueous 2 M NaOH, 200 mL H_2O) for detection. Melting points (m.p.) were determined with a Stuart SMP10 and are uncorrected. Infrared spectra (IR) were measured on a Digilab 3100 FT-IR Excalibur Series spectrometer and the position of the absorption bands is given in wave numbers v (cm^{-1}). ^{1}H NMR (300 MHz, 400 MHz, 500 MHz and 600 MHz), ^{13}C NMR (75 MHz, 100 MHz, 126 MHz and 151 MHz) and ^{19}F NMR (282 MHz and 564 MHz) spectra were measured on a Bruker DPX 300, Bruker AV 300, Bruker AV 400, Agilent DD2 500 or an Agilent DD2 600 spectrometer. The multiplicity of all signals were described as *s* (singlet), *d* (doublet), *t* (triplet), *q* (quartet) and *m* (multiplet). Chemical shifts (δ in ppm) were referenced on the residual peak of $CDCl_3$ (^{1}H NMR: δ = 7.26; ^{13}C NMR: δ = 77.16) or benzene-d^6 (^{1}H-NMR: δ = 7.16; ^{13}C-NMR: δ = 128.06). HRMS (ESI) was recorded on a Bruker Daltonics Micro-TOF, or a Thermo Fisher Scientific LTQ Orbitrap XL and peaks are given in m/z. GC-HRMS (EI) was recorded on a Thermo Fisher Scientific Exactive GC-MS. Medium Pressure Liquid Chromatography (MPLC) was used with an automatic flash-system by Reverleris® IES from Grace Davidson with C18 Reverleris® cartridges 4 g as stationary phase. Detection was carried out with UV absorption (λ = 210 nm, 230 nm).

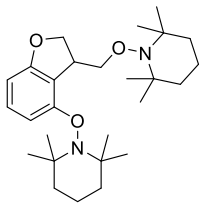
TEMPO (2,2,6,6-tetramethylpiperidin-1-yl)oxyl) was purified by sublimation at 0.5 mbar and 40 °C before use.

X-Ray diffraction: Data sets for compounds **1e**, **1h** and **3**were collected with a Bruker D8 Venture CMOS diffractometer. Programs used: data collection: APEX3 V2016.1-0[1] (Bruker AXS Inc., **2016**); cell refinement: SAINT V8.37A (Bruker AXS Inc., **2015**); data reduction: SAINT V8.37A (Bruker AXS Inc., **2015**); absorption correction, SADABS V2014/7 (Bruker AXS Inc., **2014**); structure solution *SHELXT-2015*[2] (Sheldrick, G. M. *Acta Cryst.,* **2015**, *A71*, 3-8); structure refinement *SHELXL-2015*[3] (Sheldrick, G. M. *Acta Cryst.,* **2015**, *C71* (1), 3-8) and graphics, *XP*[4] (Version 5.1, Bruker AXS Inc., Madison, Wisconsin, USA, **1998**). *R*-values are given for observed reflections, and *w*R^2 values are given for all reflections.

2. Procedures

2.1 Synthesis of cyclized bisalkoxyamines

2,2,6,6-Tetramethyl-1-((4-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)-2,3-dihydrobenzofuran-3-yl)methoxy)piperidine (1a)



1a

A flame-dried Schlenk tube was charged with CsF (46 mg, 0.30 mmol, 3.0 equiv.), TEMPO (78 mg, 0.50 mmol, 5.0 equiv.), 18-crown-6 ether (79 mg, 0.30 mmol, 3.0 equiv.) and dissolved in dry *n*-hexane (2.0 mL, 0.1 M). Allyl ether **4a** (35 mg, 0.10 mmol, 1.0 equiv.) was added and the red solution was stirred at room temperature for 2 h. The crude mixture was concentrated *in vacuo* and directly purified via flash column chromatography (SiO_2, Et_2O:*n*-pentane = 1%). The desired product was obtained as a white solid (52.5 mg, 0.118 mmol, 59%).

^{1}H-NMR (599 MHz, C_6D_6): δ (ppm) 7.16 (d, 1H), 7.01 (t, *J* = 8.1 Hz, 1H), 6.59 (d, *J* = 7.8 Hz, 1H), 4.76 (dd, *J* = 9.0, 4.7 Hz, 1H), 4.54 (dd, *J* = 8.4, 3.9 Hz, 1H), 4.49 (t, *J* = 8.7 Hz, 1H), 3.99 (dd, *J* = 10.9, 8.4 Hz, 1H), 3.82 (ddt, *J* = 10.8, 8.6, 4.4 Hz, 1H), 1.52 – 1.45 (m, 4H), 1.44 – 1.38 (m, 3H), 1.36 – 1.31 (m, 3H), 1.22 (d, *J* = 5.2 Hz, 6H), 1.18 – 1.11 (m, 8H), 1.13 (s, 3H), 1.10 (s, 6H), 1.06 (s, 3H).

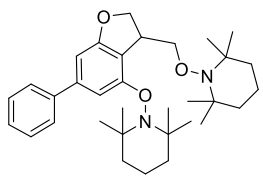
^{13}C-NMR (151 MHz, C_6D_6): δ (ppm) 162.4, 161.1, 129.6, 128.4, 128.1, 128.0, 110.7, 107.4, 102.8, 77.7, 75.5, 60.7, 60.4, 60.1, 59.9, 41.3, 40.0, 39.9, 39.8, 33.8, 33.6, 32.8, 32.7, 21.1, 20.7, 20.3, 20.1, 17.5, 17.3.

HR-MS (ESI): calc. for $C_{27}H_{45}N_2O_3^+$ $[M+H]^+$ 445.3425 found 445.3425.

FTIR (neat): ν(cm^{-1}) 2974, 2935, 1601, 1461, 1377, 1359, 1328, 1261, 1246, 1281, 1183, 1130, 1084, 1041, 1020, 994, 971, 955, 937, 876, 845, 777.

T_{melt} = 114 – 118°C.

2,2,6,6-tetramethyl-1-((6-phenyl-3-(((2,2,6,6-tetramethylpiperidin-1-yl)oxy)methyl)-2,3-dihydrobenzofuran-4-yl)oxy)piperidine (1b)



1b

Allyl ether **4b** (94.5 mg, 0.200 mmol, 1.0 equiv.), TEMPO (156 mg, 1.00 mmol, 5.0 equiv.), CsF (91 mg, 0.60 mmol, 3.0 equiv.) and 18-crown 6-ether (158 mg, 0.600 mmol, 3.0 equiv.) were dissolved in dry *n*-hexane (2.0 mL, 0.1 M) and stirred at room temperature for 3.5 h. Purification via flash column chromatography (SiO_2, gradient diethyl ether in *n*-pentane = 0.5 to 1%) furnished the product as a white solid (10:1 mixture with analogue TEMPO adduct **6e**, corrected yield: 44 mg, 0.084 mmol, 42%).

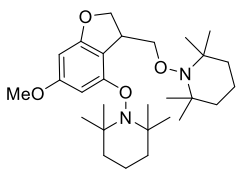
^{1}H-NMR (500 MHz, C_6D_6): δ (ppm) 7.64 – 7.59 (m, 3H), 7.24 – 7.15 (m, 2H), 7.12 – 7.05 (m, 1H), 6.92 (d, *J* = 1.1 Hz, 1H), 4.82 (dd, *J* = 8.9, 4.8 Hz, 1H), 4.62 – 4.41 (m, 2H), 4.04 (dd, *J* = 11.0, 8.4 Hz, 1H), 3.87 (ddt, *J* = 10.9, 8.6, 4.4 Hz, 1H), 1.55 – 1.00 (m, 36H).

^{13}C-NMR (126 MHz, C_6D_6): δ (ppm) 162.9, 161.1, 143.7, 142.6, 129.0, 127.6, 127.4, 109.9, 106.7, 102.1, 77.7, 75.9, 60.8, 60.5, 60.1, 60.0, 41.2, 40.0 (2xC), 39.8, 39.7, 33.9, 33.6, 33.0, 32.9, 21.1, 20.8, 20.3, 20.2, 17.5, 17.3.

HR-MS (ESI): calc. for $C_{33}H_{49}N_2O_3^+$ $[M+H]^+$ 521.3738 found 521.3746.

FTIR (neat): ν(cm^{-1}) 2974, 2869, 1595, 1573, 1478, 1468, 1450, 1413, 1358, 1319, 1295, 1245, 1207, 1183, 1158, 1132, 1036, 994, 942, 840, 829, 762, 696.

1-((6-Methoxy-3-(((2,2,6,6-tetramethylpiperidin-1-yl)oxy)methyl)-2,3-dihydrobenzofuran-4-yl)oxy)-2,2,6,6-tetramethylpiperidine (1c)



1c

Allyl ether **4c** (85 mg, 0.20 mmol, 1.0 equiv.), TEMPO (156 mg, 1.00 mmol, 5.0 equiv.), CsF (91 mg, 0.60 mmol, 3.0 equiv.) and 18-crown 6-ether (158 mg, 0.600 mmol, 3.0 equiv.) were dissolved in dry *n*-hexane (2.0 mL, 0.1 M) and stirred at room temperature for 3 h. Purification via flash column chromatography (SiO_2, diethyl ether in *n*-pentane = 0.5%) furnished the product as a white solid (5:1 mixture with analogue TEMPO adduct **6e**, corrected yield: 30 mg, 0.059 mmol, 30%).

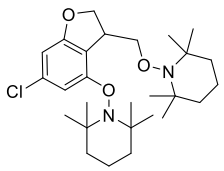
^{1}H-NMR (500 MHz, C_6D_6): δ (ppm) 7.01 (d, *J* = 2.2 Hz, 1H), 6.25 (d, *J* = 2.1 Hz, 1H), 4.80 (dd, *J* = 9.0, 4.7 Hz, 1H), 4.61 – 4.45 (m, 2H), 4.00 (dd, *J* = 10.9, 8.5 Hz, 1H), 3.81 (ddt, *J* = 10.8, 8.6, 4.5 Hz, 1H), 3.33 (s, 3H), 1.53 – 1.02 (m, 36H).

^{13}C-NMR (126 MHz, C_6D_6): δ (ppm) 163.2, 162.5, 161.3, 103.0, 95.3, 88.9, 78.1, 76.2, 60.7, 60.5, 60.1, 59.9, 55.0, 41.0, 40.0, 39.8, 39.7, 33.8, 33.6, 32.9, 32.8, 21.1, 20.8, 20.3, 20.1, 17.5, 17.3.

HR-MS (ESI): calc. for $C_{28}H_{46}N_2NaO_4^+$ $[M+H]^+$ 497.3350 found 497.3344.

FTIR (neat): ν(cm^{-1}) 2977, 2932, 2848, 1625, 1600, 1489, 1469, 1434, 1373,1364, 1262, 1244, 1184, 1132, 1040, 979, 956, 923, 874, 832, 796, 779.

1-((6-Chloro-3-(((2,2,6,6-tetramethylpiperidin-1-yl)oxy)methyl)-2,3-dihydrobenzofuran-4-yl)oxy)-2,2,6,6-tetramethylpiperidine (1d)



1d

Allyl ether **4d** (86 mg, 0.20 mmol, 1.0 equiv.), TEMPO (156 mg, 1.00 mmol, 5.0 equiv.), CsF (91 mg, 0.60 mmol, 3.0 equiv.) and 18-crown 6-ether (158 mg, 0.600 mmol, 3.0 equiv.) were dissolved in dry *n*-hexane (2.0 mL, 0.1 M) and stirred at room temperature for 3 h. Purification via flash column chromatography (SiO_2, diethyl ether in *n*-pentane = 0.5%) furnished the product as a white solid (5:1 mixture with analogue TEMPO adduct **6e**, corrected yield: 47 mg, 0.097 mmol, 49%).

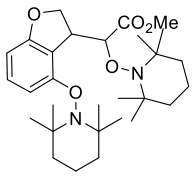
^{1}H-NMR (500 MHz, C_6D_6): δ (ppm) 7.37 (d, *J* = 1.8 Hz, 1H), 6.64 (d, *J* = 1.7 Hz, 1H), 4.67 (dd, *J* = 9.0, 4.8 Hz, 1H), 4.43 (dd, *J* = 8.5, 4.0 Hz, 1H), 4.39 (t, *J* = 8.8 Hz, 1H), 3.90 (dd, *J* = 10.8, 8.5 Hz, 1H), 3.67 (ddt, *J* = 10.7, 8.7, 4.4 Hz, 1H), 1.53 – 1.05 (m, 29H), 1.01 (s, 3H), 0.99 (s, 3H).

^{13}C-NMR (126 MHz, C_6D_6): δ (ppm) 162.8, 161.0, 135.0, 109.6, 108.1, 103.9, 77.4, 76.2, 60.8, 60.6, 60.1, 60.0, 40.9, 40.0, 39.63, 39.55, 33.8, 33.5, 32.7, 32.5, 21.1, 20.7, 20.2, 20.1, 17.5, 17.2.

HR-MS (ESI): calc. for $C_{27}H_{44}ClN_2O_3^+$ $[M+H]^+$ 479.3035 found 479.3031.

FTIR (neat): ν(cm^{-1}) 3003, 2972, 2932, 2875, 1599, 1464, 1420, 1372, 1362, 1324, 1261,1242, 1209, 1182, 1132, 1039, 992, 973, 955, 934, 882, 842, 820.

Methyl 2-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)-2-(4-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)-2,3-dihydrobenzofuran-3-yl)acetate (1e)



1e

Sulfonic ester **4e** (103 mg, 0.250 mmol, 1.0 equiv.), TEMPO (195 mg, 1.25 mmol, 5.0 equiv.) and CsF (114 mg, 0.750 mmol, 3.0 equiv.) were dissolved in dry MeCN (2.5 mL, 0.1 M) and stirred at room temperature for 2 h. Purification via flash column chromatography (SiO_2, diethyl ether in *n*-pentane = 5%) furnished the product as a white solid (mixture of diastereoisomers, *dr* = 5:1 determined by ^{1}H-NMR, 52.3 mg, 0.104 mmol, 42%). Note: The major diastereoisomer was separated via Medium Pressure Liquid Chromatography (Reverleris® IES from Grace Davidson with C18 Reverleris® cartridges 4 g as stationary phase, gradient H_2O:MeCN = 25:75 to 15:85 over 30 min, elution time *t* = 14 – 18 min).

Major diastereoisomer:

^{1}H-NMR (500 MHz, C_6D_6): δ (ppm) 7.09 (dd, *J* = 8.3, 0.7 Hz, 1H), 7.02 (t, *J* = 8.1 Hz, 1H), 6.58 (d, *J* = 7.7 Hz, 1H), 5.57 (dd, *J* = 9.2, 3.4 Hz, 1H), 5.16 (d, *J* = 0.8 Hz, 1H), 4.47 (t, *J* = 9.5 Hz, 1H), 3.75 (dd, *J* = 9.8, 3.4 Hz, 1H), 3.36 (s, 3H), 1.61 – 0.87 (m, 36H).

^{13}C-NMR (126 MHz, C_6D_6): δ (ppm) 173.3, 162.9, 160.8, 130.2, 112.1, 107.4, 102.8, 83.1, 72.3, 61.1, 60.3, 51.1, 44.6, 41.0, 40.3, 39.9, 33.1, 32.9, 20.9, 20.7, 17.4, 17.3.

Minor diastereoisomer:

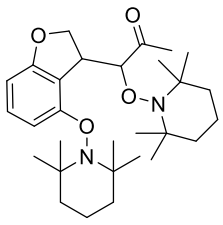
^{1}H-NMR (500 MHz, C_6D_6): δ (ppm) 7.12 – 7.07 (m, 1H), 6.97 (t, *J* = 8.1 Hz, 1H), 6.50 (d, *J* = 7.8 Hz, 1H), 5.53 (dd, *J* = 9.0, 3.8 Hz, 1H), 5.17 (d, *J* = 5.3 Hz, 1H), 4.43 – 4.36 (m, 1H), 4.37 – 4.28 (m, 1H), 3.15 (s, 3H), 1.60 – 0.95 (m, 36H).

^{13}C-NMR (126 MHz, C_6D_6): δ (ppm) 171.4, 162.6, 161.2, 130.1, 108.6, 106.7, 102.4, 84.5, 71.9, 60.7, 60.6, 50.8, 43.9, 40.6, 40.3, 40.0, 33.0, 32.1, 21.2, 20.7, 17.44, 17.38.

HR-MS (ESI): calc. for $C_{29}H_{47}N_2O_5^+$ $[M+H]^+$ 503.3479 found 503.3490.

FTIR (neat): ν(cm^{-1}) 3004, 2974, 2933, 2870, 1745, 1602, 1470, 1378, 1364, 1329, 1312, 1262, 1251, 1234, 1209, 1184, 1171, 1133, 1088, 1046, 1026, 995, 973, 958, 912, 878, 794, 765.

1-((2,2,6,6-Tetramethylpiperidin-1-yl)oxy)-1-(4-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)-2,3-dihydrobenzofuran-3-yl)propan-2-one (1f)



1f

Allyl ether **4f** (85 mg, 0.20 mmol, 1.0 equiv.), TEMPO (156 mg, 1.00 mmol, 5.0 equiv.) and CsF (91 mg, 0.60 mmol, 3.0 equiv.) were dissolved in dry acetonitrile (2.0 mL, 0.1 M) and stirred at room temperature for 3 h. Purification via flash column chromatography (SiO_2, diethyl ether in *n*-pentane = 5%) furnished the product as a colorless oil (*dr* = 3:1 determined by ^{1}H-NMR, 57 mg, 0.061 mmol, 58%).

Major diastereoisomer:

^{1}H-NMR (500 MHz, C_6D_6): δ (ppm) 7.14 – 7.05 (m, 1H), 7.00 (t, *J* = 7.9 Hz, 1H), 6.55 (d, *J* = 7.6 Hz, 1H), 5.41 – 5.30 (m, 1H), 5.07 (s, 1H), 4.37 (t, *J* = 9.1 Hz, 1H), 3.63 – 3.45 (m, 1H), 2.16 (s, 3H), 1.66 – 0.68 (m, 36H).

^{13}C-NMR (126 MHz, C_6D_6): δ (ppm) 208.5, 162.7, 160.5, 129.9, 112.2, 107.4, 102.8, 85.9, 72.1, 61.0, 60.2, 42.9, 40.9, 40.3, 39.8, 33.0, 32.8, 21.0, 20.8, 17.3, 17.2.

Minor diastereoisomer:

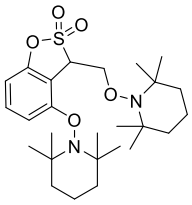
^{1}H-NMR (500 MHz, C_6D_6): δ (ppm) 7.14 – 7.05 (m, 1H), 6.97 – 6.93 (m, 1H), 6.47 (d, *J* = 7.8 Hz, 1H), 5.13 (dd, *J* = 9.1, 2.6 Hz, 1H), 5.01 (d, *J* = 5.2 Hz, 1H), 4.37 (t, *J* = 9.1 Hz, 1H), 4.26 (t, *J* = 9.1 Hz, 1H), 1.94 (s, 3H), 1.66 – 0.68 (m, 36H).

^{13}C-NMR (126 MHz, C_6D_6): δ (ppm) 206.0, 162.0, 160.8, 130.2, 109.4, 107.3, 102.8, 89.8, 71.9, 60.7, 60.4, 43.4, 40.6, 40.2, 39.9, 32.9, 32.5, 29.3, 21.0, 20.7, 17.4, 17.3.

HR-MS (ESI): calc. for $C_{29}H_{46}N_2NaO_4^+$ $[M+Na]^+$ 509.3350 found 509.3348.

FTIR (neat): ν(cm^{-1}) 2973, 2932, 2871, 1722, 1601, 1468, 1377, 1363, 1348, 1328, 1261, 1249, 1208, 1183, 1170, 1132, 1084, 1046, 1024, 984, 973, 957, 790, 763.

4-((2,2,6,6-Tetramethylpiperidin-1-yl)oxy)-3-(((2,2,6,6-tetramethylpiperidin-1-yl)oxy)methyl)-3H-benzo[d][1,2]oxathiole 2,2-dioxide (1g)



1g

Sulfonic ester **4g** (81 mg, 0.20 mmol, 1.0 equiv.), TEMPO (156 mg, 1.00 mmol, 5.0 equiv.) and CsF (91 mg, 0.60 mmol, 3.0 equiv.) were dissolved in dry MeCN (2.0 mL, 0.1 M) and stirred at room temperature for 2 h. Purification via flash column chromatography (SiO_2, gradient diethyl ether in *n*-pentane = 1% to 2%) furnished the product as a white solid (46 mg, 0.092 mmol, 46%).

^{1}H-NMR (599 MHz, C_6D_6): δ (ppm) 7.18 (dd, *J* = 8.7, 0.7 Hz, 1H), 6.79 (t, *J* = 8.4 Hz, 1H), 6.32 (d, *J* = 7.8 Hz, 1H), 4.73 (dd, *J* = 9.7, 3.6 Hz, 1H), 4.66 (dd, *J* = 9.6, 3.5 Hz, 1H), 4.43 (t, *J* = 9.6 Hz, 1H), 1.51 – 1.30 (m, 11H), 1.25 (d, *J* = 9.3 Hz, 5H), 1.21 (s, 3H), 1.08 (m, 5H), 1.03 (s, 3H), 0.91 (s, 3H), 0.79 (s, 3H), 0.34 – 0.24 (m, 3H).

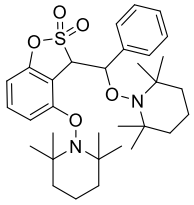
^{13}C-NMR (151 MHz, C_6D_6): δ (ppm) 160.4, 151.5, 130.5, 111.0, 105.7, 104.7, 72.4, 61.0, 60.7, 60.6, 60.5, 60.4, 40.1, 40.1, 39.9, 39.8, 33.6, 33.4, 32.6, 32.3, 21.3, 20.8, 20.3, 20.1, 17.4, 17.1.

HR-MS (ESI): calc. for $C_{26}H_{43}N_2O_5S^+$ $[M+H]^+$ 495.2887 found 495.2895.

FTIR (neat): ν(cm^{-1}) 2978, 2930, 2876, 2848, 1617, 1588, 1458, 1378, 1364, 1263, 1210, 1179, 1130, 1066, 1020, 987, 970, 953, 937, 797, 782, 769, 713.

T_{melt} = 143 – 146°C.

3-(Phenyl((2,2,6,6-tetramethylpiperidin-1-yl)oxy)methyl)-4-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)-3H-benzo[d][1,2]oxathiole 2,2-dioxide (1h)



1h

Sulfonic ester **4h** (96 mg, 0.20 mmol, 1.0 equiv.), TEMPO (156 mg, 1.00 mmol, 5.0 equiv.) and CsF (91 mg, 0.60 mmol, 3.0 equiv.) were dissolved in dry MeCN (2.0 mL, 0.1 M) and stirred at room temperature for 30 min. Purification via flash column chromatography (SiO_2, gradient diethyl ether in *n*-pentane = 1% to 2%) furnished the product as a white solid (47 mg, 0.083 mmol, 41%). Note: the product was obtained as an inseparable mixture of diasteroisomers (*dr* = 3:1). Note: the major diastereoisomer was separated by preparative TLC and used for X-ray crystallography.

Major diastereoisomer:

^{1}H-NMR (599 MHz, $CDCl_3$): δ (ppm) 7.37 (d, *J* = 7.4 Hz, 2H), 7.28 (d, *J* = 8.7 Hz, 1H), 7.15 - 7.08 (m, 3H), 7.06 (t, *J* = 8.4 Hz, 1H), 6.37 (d, *J* = 8.0 Hz, 1H), 5.77 (s, 1H), 5.16 (s, 1H), 1.78 – 1.31 (m, 18H), 1.28 (s, 6H), 1.21 (s, 3H), 1.07 (s, 3H), 0.84 (s, 3H), 0.48 (s, 3H).

^{13}C-NMR (151 MHz, $CDCl_3$): δ (ppm) 160.5, 150.2, 138.8, 130.2, 128.1, 127.8, 127.7, 111.7, 104.3, 88.5, 65.8, 61.5, 60.6, 40.4, 39.9, 33.0, 32.4, 21.18, 21.16, 17.2, 17.0.

Minor diastereoisomer:

^{1}H-NMR (599 MHz, $CDCl_3$): δ (ppm) 7.35 (d, *J* = 8.7 Hz, 2H), 7.21 – 7.07 (m, 5H), 6.34 (d, *J* = 7.7 Hz, 1H), 5.62 (d, *J* = 3.4 Hz, 1H), 5.56 – 5.44 (m, 1H), 1.84 – 1.32 (m, 21H), 1.26 (s, 6H), 1.13 (s, 3H), 0.97 (s, 3H), 0.79 (s, 3H).

^{13}C-NMR (151 MHz, $CDCl_3$): δ (ppm) 150.8, 130.4, 128.2, 127.1, 111.7, 110.9, 108.7, 104.5, 84.9, 33.0, 32.9, 32.7, 32.4, 17.3, 17.0.

Major or Minor diastereoisomer:

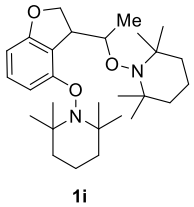
^{13}C-NMR (151 MHz, $CDCl_3$): δ (ppm) 66.0, 64.1, 60.7, 60.6, 59.9, 35.2, 34.2, 33.5, 21.3, 20.8, 20.7, 20.6, 20.5.

HR-MS (ESI): calc. for $C_{32}H_{47}N_2O_5S^+$ $[M+H]^+$ 571.3200 found 571.3220.

T_{melt} = > 152°C decomposition.

FTIR (neat): ν(cm^{-1}) 2977, 1617, 1595, 1470, 1377, 1264, 1207, 1189, 1168, 1133, 1015, 805, 776, 767, 703.

2,2,6,6-Tetramethyl-1-(1-(4-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)-2,3-dihydrobenzofuran-3-yl)ethoxy)piperidine (1i)



1i

Allyl ether **4i** (74 mg, 0.20 mmol, 1.0 equiv.), TEMPO (156 mg, 1.00 mmol, 5.0 equiv.), CsF (91 mg, 0.60 mmol, 3.0 equiv.) and 18-crown 6-ether (158 mg, 0.600 mmol, 3.0 equiv.) were dissolved in dry *n*-hexane (2.0 mL, 0.1 M) and stirred at room temperature for 3.5 h. Purification via flash column chromatography (SiO_2, diethyl ether in *n*-pentane = 0.5%) furnished the product as a white solid (inseparable mixture of diastereoisomers, *dr* = 5:1 determined by ^{1}H-NMR, 34.9 mg, 0.076 mmol, 38%).

Major diastereoisomer:

^{1}H-NMR (500 MHz, C_6D_6): δ (ppm) 7.19 – 7.13 (m, 1H), 7.05 – 6.99 (m, 1H), 6.59 (d, *J* = 7.8 Hz, 1H), 4.88 – 4.80 (m, 2H), 4.46 (t, *J* = 9.4 Hz, 1H), 4.17 (dt, *J* = 9.4, 4.6 Hz, 1H), 1.57 – 1.13 (m, 33H), 1.09 (s, 3H), 1.08 (s, 3H).

^{13}C-NMR (126 MHz, C_6D_6): δ (ppm) 162.5, 160.7, 129.4, 111.8, 107.1, 102.7, 78.8, 72.3, 60.7, 60.3, 45.3, 40.7, 39.9, 32.8, 32.7, 21.2, 20.8, 17.7, 17.4, 14.9.

Minor diastereoisomer (Note: In the ^{13}C-NMR of the mixture no signals of the minor product were detected):

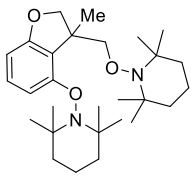
^{1}H-NMR (500 MHz, C_6D_6): δ (ppm) 7.20 – 7.14 (m, 1H), 7.06 – 7.01 (m, 1H), 6.62 (d, *J* = 7.8 Hz, 1H), 5.00 (dd, *J* = 8.6, 2.4 Hz, 1H), 4.57 – 4.50 (m, 1H), 4.22 (t, *J* = 8.6 Hz, 1H), 3.36 (ddd, *J* = 8.6, 4.5, 2.5 Hz, 1H), 1.59 – 1.03 (m, 39H).

HR-MS (ESI): calc. for $C_{28}H_{47}N_2O_3^+$ $[M+H]^+$ 459.3581 found 459.3584.

T_{melt} = > 138 °C decomposition.

FTIR (neat): ν(cm^{-1}) 2974, 2931, 1600, 1463, 1378, 1363, 1328, 1261, 1248, 1209, 1183, 1132, 1076, 1023, 973, 957, 927, 783, 763.

2,2,6,6-Tetramethyl-1-((3-methyl-3-(((2,2,6,6-tetramethylpiperidin-1-yl)oxy)methyl)-2,3-dihydrobenzofuran-4-yl)oxy)piperidine (1j)



1j

Allyl ether **4j** (74 mg, 0.20 mmol, 1.0 equiv.), TEMPO (156 mg, 1.00 mmol, 5.0 equiv.), CsF (91 mg, 0.60 mmol, 3.0 equiv.) and 18-crown 6-ether (158 mg, 0.600 mmol, 3.0 equiv.) were dissolved in dry *n*-hexane (2.0 mL, 0.1 M) and stirred at room temperature for 7 h. Purification via flash column chromatography (SiO_2, diethyl ether in *n*-pentane = 0.5%) furnished the product as a white solid (10:1 mixture with analogue TEMPO adduct **6e**, corrected yield: 36 mg, 0.079 mmol, 40%).

^{1}H-NMR (500 MHz, C_6D_6): δ (ppm) 7.20 (dd, *J* = 8.5, 0.9 Hz, 1H), 7.00 (t, *J* = 8.1 Hz, 1H), 6.59 (dd, *J* = 7.9, 0.8 Hz, 1H), 4.86 (d, *J* = 8.7 Hz, 1H), 4.54 (dd, *J* = 8.2, 1.1 Hz, 1H), 4.17 (dd, *J* = 8.7, 1.1 Hz, 1H), 4.11 (d, *J* = 8.2 Hz, 1H), 1.69 (s, 3H), 1.63 – 0.94 (m, 36H).

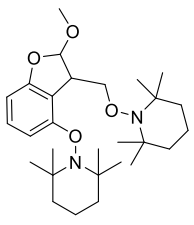
^{13}C-NMR (126 MHz, C_6D_6): δ (ppm) 161.8, 161.2, 129.5, 115.8, 107.5, 103.1, 81.1, 80.5, 60.6, 60.5, 60.3, 60.2, 47.9, 40.2, 40.0, 39.92, 39.88, 33.75, 33.73, 32.62, 32.56, 21.9, 21.25, 21.16, 20.34, 20.26, 17.4, 17.3.

HR-MS (ESI): calc. for $C_{28}H_{47}N_2O_3^+$ $[M+H]^+$ 459.3581 found 459.3582.

T_{melt} = 113-115 °C.

FTIR (neat): ν(cm^{-1}) 2978, 2966, 2933, 2872, 1598, 1486, 1496, 1454, 1377, 1360, 1324, 1262, 1252, 1209, 1181, 1129, 1045, 1024, 990, 970, 956, 786.

1-((2-methoxy-3-(((2,2,6,6-tetramethylpiperidin-1-yl)oxy)methyl)-2,3-dihydrobenzofuran-4-yl)oxy)-2,2,6,6-tetramethylpiperidine (1k)



1k

Acetal **4k** (77 mg, 0.20 mmol, 1.0 equiv.), TEMPO (156 mg, 1.00 mmol, 5.0 equiv.), CsF (91 mg, 0.60 mmol, 3.0 equiv.) and 18-crown 6-ether (158 mg, 0.600 mmol, 3.0 equiv.) were dissolved in dry *n*-hexane (2.0 mL, 0.1 M) and stirred at room temperature for 3.5 h. Purification via flash column chromatography (SiO_2, gradient diethyl ether in *n*-pentane = 0% to 2%) furnished the product as a white solid (inseparable mixture of diastereoisomers, dr = 1.5:1 determined by ^{1}H-NMR, 59.3 mg, 0.125 mmol, 62%).

Major diastereoisomer:

^{1}H-NMR (500 MHz, C_6D_6): δ (ppm) 7.19 (dd, *J* = 8.4, 0.8 Hz, 1H), 7.03 (t, *J* = 8.2 Hz, 1H), 6.63 (d, *J* = 8.2 Hz, 1H), 5.91 (d, *J* = 1.1 Hz, 1H), 4.52 (dd, *J* = 7.7, 3.1 Hz, 1H), 4.05 – 3.92 (m, 2H), 3.39 (s, 3H), 1.57 – 0.84 (m, 36H).

^{13}C-NMR (126 MHz, C_6D_6): δ (ppm) 161.0, 160.3, 129.6, 110.9, 109.9, 108.1, 103.1, 75.2, 60.7, 60.51, 60.49, 60.4, 55.6, 48.3, 40.0, 39.9 (2xC), 39.8, 32.81, 32.78, 32.77, 32.5, 21.6, 21.00, 20.97, 20.6, 17.5, 17.3.

Minor diastereoisomer:

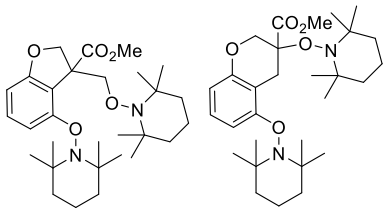
^{1}H-NMR (500 MHz, C_6D_6): δ (ppm) 7.22 (dd, *J* = 8.5, 0.8 Hz, 1H), 7.00 (td, *J* = 8.3, 1.0 Hz, 1H), 6.62 (d, *J* = 8.5 Hz, 1H), 5.45 (d, *J* = 6.0 Hz, 1H), 4.95 (dd, *J* = 8.1, 4.3 Hz, 1H), 4.59 – 4.51 (m, 1H), 3.77 (dt, *J* = 10.6, 5.0 Hz, 1H), 3.38 (s, 3H), 1.74 – 0.87 (m, 36H).

^{13}C-NMR (126 MHz, C_6D_6): δ (ppm) 161.3, 160.2, 129.0, 109.5, 108.3, 108.1, 103.1, 73.0, 60.11, 60.05, 60.0, 59.9, 55.8, 46.2, 40.2, 40.1, 40.0, 39.91, 33.89, 33.8, 33.6, 33.1, 20.4, 20.2, 20.12, 20.11, 17.6, 17.4.

HR-MS (ESI): calc. for $C_{28}H_{47}N_2O_4^+$ $[M+H]^+$ 475.3530 found 475.3538.

FTIR (neat): ν(cm^{-1}) 2974, 2928, 1601, 1460, 1378, 1359, 1328, 1259, 1184, 1131, 1111, 1046, 1015, 994, 972, 951, 909, 857, 777, 726.

Methyl 4-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)-3-(((2,2,6,6-tetramethylpiperidin-1-yl)oxy)methyl)-2,3-dihydrobenzofuran-3-carboxylate (1l) and methyl 3,5-bis((2,2,6,6-tetramethylpiperidin-1-yl)oxy)chromane-3-carboxylate (1l')



1l 1l'

Acrylate **4l** (82 mg, 0.20 mmol, 1.0 equiv.), TEMPO (156 mg, 1.00 mmol, 5.0 equiv.) and CsF (91 mg, 0.60 mmol, 3.0 equiv.) were dissolved in dry MeCN (2.0 mL, 0.1 M) and stirred at room temperature for 4 h. Purification via flash column chromatography (SiO_2, gradient diethyl ether in *n*-pentane = 1% to 2%) furnished the product as a pale yellow solid (inseparable mixture of regioisomers, 6-*endo*:5-*exo* = 1.5:1.0 determined by ^{1}H-NMR, 44 mg, 0.088 mmol, 44%).

*5-exo product **1l**:*

^{1}H-NMR (500 MHz, C_6D_6): δ (ppm) 7.19 (dd, *J* = 8.4, 0.7 Hz, 1H), 6.99 – 6.94 (m, 1H), 6.55 (dd, *J* = 7.9, 0.7 Hz, 1H), 5.37 (d, *J* = 6.7 Hz, 1H), 5.35 (d, *J* = 6.0 Hz, 1H), 4.90 (d, *J* = 9.0 Hz, 1H), 4.11 (d, *J* = 8.4 Hz, 1H), 3.38 (s, 3H), 1.67 – 0.96 (m, 36H).

^{13}C-NMR (126 MHz, C_6D_6): δ (ppm) 171.9, 162.2, 161.2, 130.7, 110.6, 107.6, 103.1, 78.3, 77.8, 60.7, 60.6, 60.4, 60.3, 57.6, 51.9, 40.5, 40.1, 39.93, 39.86, 33.6, 33.3, 32.7, 32.2, 21.3, 20.8, 20.24, 20.19, 17.4, 17.3.

*6-endo product **1l'**:*

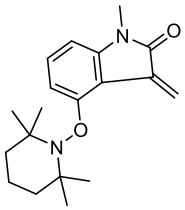
^{1}H-NMR (500 MHz, C_6D_6): δ (ppm) 7.27 (dd, *J* = 8.3, 1.0 Hz, 1H), 7.00 (t, *J* = 7.5 Hz, 1H), 6.73 – 6.68 (m, 1H), 4.55 (dd, *J* = 10.0, 2.0 Hz, 1H), 4.08 (d, *J* = 10.0 Hz, 1H), 3.80 (dd, *J* = 17.3, 1.8 Hz, 1H), 3.67 (d, *J* = 17.3 Hz, 1H), 3.32 (s, 3H), 1.67 – 0.96 (m, 36H).

^{13}C-NMR (126 MHz, C_6D_6): δ (ppm) 172.5, 161.7, 155.2, 126.8, 109.0, 108.5, 107.5, 80.1, 70.1, 60.8, 60.5, 60.3, 60.1, 51.8, 41.1, 41.0, 39.9, 39.8, 34.0, 33.7, 32.9, 32.8, 26.0, 21.0, 20.89, 20.88, 20.8, 17.5, 17.4.

HR-MS (ESI): calc. for $C_{29}H_{47}N_2O_5^+$ $[M+H]^+$ 503.3479 found 503.3471.

FTIR (neat): ν(cm^{-1}) 3005, 2975, 2935, 2875, 1739, 1723, 1684, 1631, 1607, 1592, 1462, 1453, 1435, 1376, 1363, 1350, 1318, 1284, 1249, 1210, 1183, 1170, 1132, 1115, 1096, 1069, 1045, 1026, 999, 955, 840, 776, 711.

1-Methyl-3-methylene-4-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)indolin-2-one (1m)



1m

Amide **4m** (76 mg, 0.20 mmol, 1.0 equiv.), TEMPO (156 mg, 1.00 mmol, 5.0 equiv.) and CsF (91 mg, 0.60 mmol, 3.0 equiv.) were dissolved in dry MeCN (2.0 mL, 0.1 m) and stirred at room temperature for 1 h. Purification via flash column chromatography (SiO_2, gradient diethyl ether in *n*-pentane = 3% to 25%) furnished the product as a yellow oil (24 mg, 0.076 mmol, 38%).

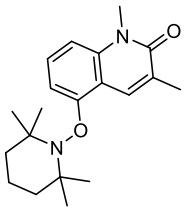
^{1}H-NMR (599 MHz, $CDCl_3$): δ (ppm) 7.30 (d, *J* = 8.6 Hz, 1H), 7.18 – 7.13 (m, 1H), 6.49 (s, 1H), 6.37 (d, *J* = 7.6 Hz, 1H), 6.32 (s, 1H), 3.23 (s, 3H), 1.74 – 1.58 (m, 5H), 1.48 – 1.42 (m, 1H), 1.29 (s, 6H), 1.03 (s, 6H).

^{13}C-NMR (151 MHz, $CDCl_3$): δ (ppm) 167.7, 160.4, 144.4, 134.3, 130.2, 120.9, 110.1, 106.4, 100.5, 60.6, 39.8, 32.4, 26.4, 21.4, 17.2.

HR-MS (ESI): calc. for $C_{19}H_{26}N_2O_2Na^+$ $[M+Na]^+$ 337.1886 found 337.1889.

FTIR (neat): ν(cm^{-1}) 2937, 2933, 2870, 1717, 1662, 1639, 1610, 1596, 1465, 1395, 1378, 1364, 1325, 1305, 1256, 1229, 1209, 1183, 1146, 1131, 1101, 1060, 970, 954, 925, 875, 843, 789, 751.

1,3-Dimethyl-5-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)quinolin-2(1H)-one (1n)



1n

Amide **4n** (79 mg, 0.200 mmol, 1.0 equiv.), TEMPO (156 mg, 1.00 mmol, 5.0 equiv.) and CsF (91 mg, 0.60 mmol, 3.0 equiv.) were dissolved in dry MeCN (2.0 mL, 0.1 m) and stirred at room temperature for 6 h. The mixture was concentrated and purification via flash column chromatography (SiO_2, gradient diethyl ether in *n*-pentane = 20% to 50%) furnished the product as a pale yellow oil (39 mg, 0.118 mmol, 59%).

^{1}H-NMR (500 MHz, C_6D_6): δ (ppm) 8.10 – 7.99 (m, 1H), 7.36 (dd, *J* = 8.2, 0.9 Hz, 1H), 7.12 (t, *J* = 8.3 Hz, 1H), 6.37 (d, *J* = 8.4 Hz, 1H), 3.35 (s, 3H), 2.32 (d, *J* = 1.3 Hz, 3H), 1.55 – 1.09 (m, 6H), 1.21 (s, 6H), 1.03 (s, 6H).

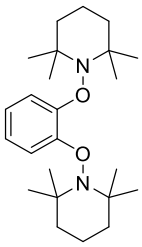
^{13}C-NMR (126 MHz, C_6D_6): δ (ppm) 162.4, 159.2, 140.9, 129.4, 129.0, 128.6, 108.6, 107.0, 106.2, 60.9, 39.9, 32.6, 29.7, 21.0, 18.5, 17.3.

HR-MS (ESI): calc. for $C_{20}H_{28}N_2NaO_2^+$ $[M+Na]^+$ 351.2043 found 351.2042.

FTIR (neat): ν(cm^{-1}) 2972, 2933, 1659, 1644, 1594, 1479, 1467, 1415, 1377, 1363, 1328, 1274, 1256, 1241, 1208, 1172, 1128, 1083, 1034, 1023, 995, 953, 909, 866, 789.

2.2 Synthesis of TEMPO-benzyne bisadduct 3

1,2-Bis((2,2,6,6-tetramethylpiperidin-1-yl)oxy)benzene (3)



3

2-(Trimethylsilyl)phenyl trifluoromethanesulfonate (**2**, 298 mg, 1.00 mmol, 1.0 equiv.), TEMPO (781 mg, 5.00 mmol, 5.0 equiv.), CsF (456 mg, 3.00 mmol, 3.0 equiv.) and 18-crown-6 ether (792 mg, 3.00 mmol, 3.00 equiv.) were dissolved in dry *n*-hexane (10 mL, 0.1 M). After stirring at room temperature for 3.5 h the mixture was diluted with water (10 mL) and extracted with pentane (3x50 mL). The organic layers were washed with sat. aq. NaCl solution (100 mL), dried over $MgSO_4$ and concentrated under reduced pressure. Ice-cold MeOH was added and then decanted until all red TEMPO was removed. The product was dried under high vacuum and obtained as a white solid (189 mg, 0.486 mmol, 48%). NOTE: the product is not stable on silica and decomposes on the TLC plate.

^{1}H-NMR (599 MHz, C_6D_6): δ (ppm) 7.69 – 7.63 (m, 2H), 6.88 – 6.84 (m, 2H), 1.58 – 1.45 (m, 6H), 1.41 – 1.38 (m, 3H), 1.37 (s, 12H), 1.21 – 1.17 (m, 3H), 1.15 (s, 12H).

^{13}C-NMR (151 MHz, C_6D_6): δ (ppm) 150.3, 120.0, 114.9, 60.6, 39.8, 33.0, 20.8, 17.4.

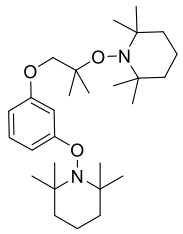
HR-MS (ESI): calc. for $C_{24}H_{41}N_2O_2^+$ $[M+H]^+$ 389.3163 found 389.3169.

FTIR (neat): n(cm^{-1}) 3006, 2980, 2929, 1584, 1474, 1375, 1361, 1329, 1266, 1216, 1172, 1129, 1096, 1048, 1029, 997, 955, 939, 874, 817, 795, 745, 713.

T_{melt} = > 125°C decomposition.

2.3 Synthesis of HAT-bisalkoxyamines

2,2,6,6-Tetramethyl-1-((2-methyl-1-(3-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)phenoxy)propan-2-yl)oxy)piperidine (6a)



6a

Ether **5a** (74 mg, 0.20 mmol, 1.0 equiv.), TEMPO (156 mg, 1.00 mmol, 5.0 equiv.), CsF (91 mg, 0.60 mmol, 3.0 equiv.) and 18-crown 6-ether (158 mg, 0.600 mmol, 3.0 equiv.) were dissolved in dry *n*-hexane (2.0 mL, 0.1 M) and stirred at room temperature for 4 h. Purification via flash column chromatography (SiO_2, gradient Et_2O in *n*-pentane = 0.5 to 1%) furnished the product as a colorless oil (49 mg, 0.106 mmol, 53%).

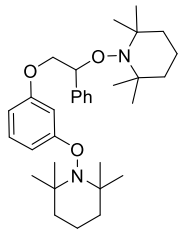
^{1}H-NMR (599 MHz, C_6D_6): δ (ppm) 7.20 (s, 1H), 7.09 (t, *J* = 8.2 Hz, 1H), 6.98 (s, 1H), 6.57 (ddd, *J* = 8.1, 2.4, 0.8 Hz, 1H), 3.97 (s, 2H), 1.48 (s, 6H), 1.47 – 1.30 (m, 12H), 1.21 (s, 6H), 1.18 (s, 6H), 1.17 (s, 6H), 1.12 (s, 6H).

^{13}C-NMR (151 MHz, C_6D_6): δ (ppm) 165.4, 160.9, 129.8, 128.4, 107.1, 106.9, 79.0, 75.5, 60.5, 59.7, 41.2, 39.9, 35.1, 32.9, 24.8, 20.9, 20.7, 17.5, 17.3.

HR-MS (ESI): calc. for $C_{28}H_{49}N_2O_3^+$ $[M+H]^+$ 461.3738 found 461.3741.

FTIR (neat): ν(cm^{-1}) 2976, 2931, 2871, 1588, 1489, 1467, 1378, 1363, 1298, 1273, 1259, 1240, 1209, 1163, 1127, 1046, 956, 930, 879, 757, 687.

2,2,6,6-Tetramethyl-1-(3-(2-phenyl-2-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)ethoxy)phenoxy)piperidine (6b)



6b

Ether **5b** (84 mg, 0.20 mmol, 1.0 equiv.), TEMPO (156 mg, 1.00 mmol, 5.0 equiv.), CsF (91 mg, 0.60 mmol, 3.0 equiv.) and 18-crown 6-ether (158 mg, 0.600 mmol, 3.0 equiv.) were dissolved in dry *n*-hexane (2.0 mL, 0.1 M) and stirred at room temperature for 7 h. Purification via flash column chromatography (SiO_2, gradient Et_2O in *n*-pentane = 0.5 to 1%) furnished the product as a white solid (54 mg, 0.107 mmol, 54%).

^{1}H-NMR (599 MHz, C_6D_6): δ (ppm) 7.41 – 7.36 (m, 2H), 7.20 – 7.14 (m, 2H), 7.12 – 7.07 (m, 2H), 7.04 (t, *J* = 8.2 Hz, 1H), 6.94 (s, 1H), 6.49 (ddd, *J* = 8.1, 2.4, 0.9 Hz, 1H), 5.19 (t, *J* = 5.8 Hz, 1H), 4.49 (dd, *J* = 9.8, 5.6 Hz, 1H), 4.16 (dd, *J* = 9.8, 6.0 Hz, 1H), 1.54 – 1.26 (m, 17H), 1.20 (s, 6H), 1.17 – 1.10 (m, 4H), 1.09 (s, 3H), 1.08 (s, 3H), 0.82 (s, 3H).

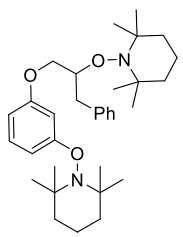
^{13}C-NMR (151 MHz, C_6D_6): δ (ppm) 165.3, 160.4, 141.6, 129.7, 128.4, 128.3, 107.1, 85.2, 70.8, 60.52, 60.51, 39.9, 32.8, 20.6, 17.6, 17.3.

HR-MS (ESI): calc. for $C_{32}H_{49}N_2O_3^+$ $[M+H]^+$ 509.3738 found 509.3747.

T_{melt} = 119–120 °C.

FTIR (neat): ν(cm^{-1}) 3005, 2970, 2933, 1593, 1467, 1377, 1363, 1328, 1274, 1255, 1241, 1209, 1171, 1127, 1083, 1034, 1023, 995, 973, 952, 924, 913, 866, 805, 701.

2,2,6,6-Tetramethyl-1-(3-(3-phenyl-2-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)propoxy)phenoxy)piperidine (6c)



6c

Ether **5c** (87 mg, 0.20 mmol, 1.0 equiv.), TEMPO (156 mg, 1.00 mmol, 5.0 equiv.), CsF (91 mg, 0.60 mmol, 3.0 equiv.) and 18-crown 6-ether (158 mg, 0.600 mmol, 3.0 equiv.) were dissolved in dry *n*-hexane (2.0 mL, 0.1 M) and stirred at room temperature for 8 h. Purification via flash column chromatography (SiO_2, CH_2Cl_2 in *n*-pentane = 20%) furnished the product as a colorless oil (49 mg, 0.093 mmol, 47%).

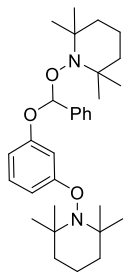
^{1}H-NMR (599 MHz, C_6D_6): δ (ppm) 7.28 – 7.24 (m, 2H), 7.20 (br s, 1H), 7.12 (m, 2H), 7.10 – 7.02 (m, 2H), 6.93 (br s, 1H), 6.56 (dd, *J* = 8.2, 2.4 Hz, 1H), 4.45 – 4.35 (m, 1H), 4.20 – 4.02 (m, 2H), 3.23 – 3.11 (m, 2H), 1.57 – 1.06 (m, 36H).

^{13}C-NMR (151 MHz, C_6D_6): δ (ppm) 165.4, 160.6, 139.4, 129.8, 128.5, 126.4, 107.0, 106.9, 101.6, 82.2, 67.5, 60.8, 60.5, 59.9, 40.7, 39.96, 39.95, 37.9, 34.5, 34.0, 32.9, 20.8, 20.67, 20.65, 17.6, 17.3. Note: some TMP signals overlap

HR-MS (ESI): calc. for $C_{33}H_{51}N_2O_3^+$ $[M+H]^+$ 523.3894 found 523.3894.

FTIR (neat): ν(cm^{-1}) 2974, 2928, 2871, 1589, 1489, 1453, 1377, 1362, 1330, 1298, 1275, 1257, 1241, 1209, 1165, 1130, 1083, 1033, 993, 971, 956, 937, 846, 829, 759, 699.

2,2,6,6-Tetramethyl-1-(3-(phenyl((2,2,6,6-tetramethylpiperidin-1-yl)oxy)methoxy)phenoxy)piperidine (6d)



6d

Ether **5d** (81 mg, 0.20 mmol, 1.0 equiv.), TEMPO (156 mg, 1.00 mmol, 5.0 equiv.), CsF (91 mg, 0.60 mmol, 3.0 equiv.) and 18-crown 6-ether (158 mg, 0.600 mmol, 3.0 equiv.) were dissolved in dry *n*-hexane (2.0 mL, 0.1 M) and stirred at room temperature for 8 h. Purification via flash column chromatography (SiO_2, Et_2O in *n*-pentane = 5%) furnished the product as a colorless oil (46 mg, 0.093 mmol, 47%).

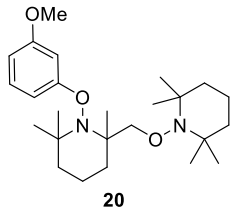
^{1}H-NMR (599 MHz, C_6D_6): δ (ppm) 7.71 – 7.59 (m, 2H), 7.46 (s, 1H), 7.14 (t, *J* = 7.7 Hz, 2H), 7.08 – 7.04 (m, 1H), 7.02 (t, *J* = 8.2 Hz, 1H), 6.83 (dd, *J* = 7.8, 4.6 Hz, 1H), 6.76 (dd, *J* = 8.1, 2.4 Hz, 1H), 6.61 (s, 1H), 1.62 (s, 3H), 1.60 – 1.30 (m, 12H), 1.27 (d, *J* = 5.8 Hz, 6H), 1.19 (s, 6H), 1.16 (s, 3H), 1.09 (s, 3H), 1.05 (s, 3H).

^{13}C-NMR (151 MHz, C_6D_6): δ (ppm) 165.2, 159.0, 139.6, 129.7, 128.61, 128.57, 128.4, 127.1, 110.3, 107.7, 107.5, 104.7, 61.3, 60.55, 60.51, 60.1, 40.8, 40.4, 40.1, 40.0, 34.1, 33.6, 32.9, 32.8, 21.1, 20.7, 20.6, 17.6, 17.4.

HR-MS (ESI): calc. for $C_{31}H_{47}N_2O_3^+$ $[M+H]^+$ 495.3581 found 495.3586.

FTIR (neat): ν(cm^{-1}) 2976, 2932, 2870, 1591, 1470, 1451, 1378, 1363, 1348, 1302, 1258, 1241, 1209, 1184, 1159, 1121, 1083, 1060, 1007, 985, 954, 919, 878, 802, 769, 695.

1-(3-Methoxyphenoxy)-2,2,6-trimethyl-6-(((2,2,6,6-tetramethylpiperidin-1-yl)oxy)methyl)piperidine (6e)



20

Methylether **5e** (330 mg, 1.00 mmol, 1.0 equiv.), TEMPO (469 mg, 3.00 mmol, 3.0 equiv.) and CsF (456 mg, 3.00 mmol, 3.0 equiv.) were dissolved in dry MeCN (10 mL, 0.1 M) and stirred at room temperature for 8 h. Purification via flash column chromatography (SiO_2, gradient Et_2O in *n*-pentane = 1% to 2%) furnished the product as a white solid (63 mg, 0.150 mmol, 15%, mixture of two diastereoisomers dr = 1:1).

^{1}H-NMR (599 MHz, $CDCl_3$): δ (ppm) 7.09 (dt, *J* = 12.0, 8.2 Hz, 2H), 6.85 – 6.66 (m, 4H), 6.42 (dt, *J* = 8.3, 2.3 Hz, 2H), 4.16 (d, *J* = 8.0 Hz, 1H), 4.10 (d, *J* = 8.0 Hz, 1H), 3.78 (s, 6H), 3.58 (d, *J* = 7.5 Hz, 1H), 3.54 (d, *J* = 7.6 Hz, 1H), 2.11 – 2.06 (m, 1H), 2.03 (dq, *J* = 13.4, 2.6 Hz, 1H), 1.73 – 0.77 (m, 70H).

^{13}C-NMR (151 MHz, $CDCl_3$): δ (ppm) 164.9, 164.5, 160.4, 129.3, 129.2, 106.8, 106.7, 105.7, 105.3, 84.3, 75.0, 64.0, 63.9, 62.8, 60.8, 60.4, 55.3, 39.90, 39.88, 39.81, 39.75, 39.72, 36.1, 35.1, 33.3, 33.2, 33.1, 32.9, 32.7, 27.0, 22.5, 21.6, 21.1, 20.50, 20.47, 20.0, 17.3, 17.2, 17.1, 16.6, 16.3, 14.2. Multiple carbon signals overlap.

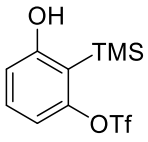
HR-MS (ESI): calc. for $C_{25}H_{42}N_2NaO_3^+$ $[M+Na]^+$ 441.3088 found 441.3086.

T_{melt} = 60–62 °C.

FTIR (neat): ν(cm^{-1}) 2977, 2933, 2870, 1600, 1489, 1471, 1453, 1373, 1360, 1279, 1255, 1188, 1166, 1130, 1041, 1023, 993, 956, 861, 797, 763.

2.4 Synthesis of starting materials

3-Hydroxy-2-(trimethylsilyl)phenyl trifluoromethanesulfonate (7)



7

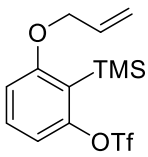
2-Bromoresorcinol (3.03 g, 16.0 mmol, 1.0 equiv.) and hexamethyldisilazane (HMDS, 7.4 mL, 35.3 mmol, 2.2 equiv.) were dissolved in dry THF (30 mL, 0.53 m) and heated to 65°C for 15 h. The solution was concentrated under reduced pressure and high vacuum and then dissolved in dry THF (40 mL, 0.4 m). The mixture was cooled to −94°C (acetone/liquid nitrogen bath) and *n*-BuLi (1.6 M in hexanes, 11.0 mL, 17.6 mmol1.1 equiv.) was added portion wise over 10 min. After 30 min trifluoromethanesulfonic anhydride (4.0 mL, 24.1 mmol, 1.5 equiv.) was added portion wise over 15 min. After 2 h at −94°C the reaction was finished by adding aqueous hydrochloric acid (2 m, 20 mL). The suspension was extracted with diethyl ether (3×150 mL). The organic layers were washed with sat. aq. $NaHCO_3$ solution (3×100 mL), sat. aq. NaCl solution (100 mL), dried over $MgSO_4$ and concentrated. The crude product was purified via flash column chromatography on silica gel (SiO_2, gradient diethyl ether in *n*-pentane = 5% to 20%) to furnish the desired product as a pale yellow oil (3.19 g, 10.2 mmol, 63%). Spectroscopic data are in accordance with those described in the literature.[1]

^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) 7.28 (t, *J* = 8.2 Hz, 1H), 6.95 (d, *J* = 8.3 Hz, 1H), 6.70 (dd, *J* = 8.1, 0.6 Hz, 1H), 5.30 – 5.16 (m, 1H), 0.44 (s, 9H).

^{13}C-NMR (101 MHz, $CDCl_3$): δ (ppm) 161.8, 155.3, 131.6, 123.5, 120.3, 118.6, 117.1, 114.8, 114.0, 112.7, 0.8.

HR-MS (ESI): calc. for $C_{10}H_{13}F_3NaO_4SSi^+$ $[M+Na]^+$ 337.0148 found 337.0141.

3-(Allyloxy)-2-(trimethylsilyl)phenyl trifluoromethanesulfonate (4a)



4a

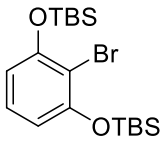
Phenol **7** (943 mg, 3.00 mmol, 1.0 equiv.), allyl bromide (0.65 mL, 7.5 mmol, 2.5 equiv.), *tetra-n*-butyl ammonium bromide (967 mg, 3.00 mmol, 1.0 equiv.) and $K_3PO_4 \cdot H_2O$ (2.07 g, 9.00 mmol, 3.0 equiv.) were dissolved in water (27 mL, 0.11 M) and stirred for 2 h. The aq. solution was diluted with water (80 mL) and extracted with diethyl ether (3 x 100 mL). The combined organic layers were washed with sat. aq. NaCl solution (100 mL), dried over $MgSO_4$ and concentrated under reduced pressure. The crude product was purified via flash column chromatography on silica gel (SiO_2, gradient diethyl ether in in *n*-pentane = 0% to 1%) to obtain the product as a colorless oil (414 mg, 1.17 mmol, 39%). Spectroscopic data are in accordance with those described in the literature.[2]

^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) 7.34 (t, *J* = 8.3 Hz, 1H), 6.94 (d, *J* = 8.4 Hz, 1H), 6.81 (d, *J* = 8.2 Hz, 1H), 6.05 (ddt, *J* = 17.2, 10.7, 5.4 Hz, 1H), 5.40 (dq, *J* = 17.2, 1.5 Hz, 1H), 5.31 (dq, *J* = 10.4, 1.3 Hz, 1H), 4.56 (dt, *J* = 5.5, 1.5 Hz, 2H), 0.38 (s, 9H).

^{13}C-NMR (101 MHz, , $CDCl_3$): δ (ppm) 164.6, 154.8, 132.7, 131.7, 121.2, 118.8 (q, *J* = 320.8 Hz), 118.5, 113.0, 110.6, 69.7, 1.1.

HR-MS (ESI): calc. for $C_{10}H_{13}F_3NaO_4SSi^+$ $[M+Na]^+$ 337.0148 found 337.0141.

((2-Bromo-1,3-phenylene)bis(oxy))bis(*tert*-butyldimethylsilane) (8)



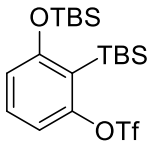
8

2-Bromoresorcinol (2.50 g, 13.2 mmol, 1.0 equiv.), *tert*-butyldimethylsilyl chloride (5.98 g, 39.7 mmol, 3.0 equiv.) and imidazole (2.07 g, 30.4 mmol, 2.3 equiv.) were dissolved in DMF (28 mL, 0.48 M). After 14 h at room temperature sat. aq. NH_4Cl solution (50 mL) was added and the mixture was extracted with *n*-pentane (3 x 100 mL). The combined org. phases were washed wit sat. aq. NaCl solution (100 mL), dried over $MgSO_4$ and concentrated under reduced pressure. Purification via flash column chromatography (SiO_2, *n*-pentane) afforded the desired product as a colorless oil (5.03 g, 12.3 mmol, 93%). Spectroscopic data are in accordance with those reported in literature.[3]

^{1}H-NMR (300 MHz, $CDCl_3$): δ (ppm) 6.99 (t, *J* = 8.2 Hz, 1H), 6.51 (d, *J* = 8.2 Hz, 2H), 1.04 (s, 18H), 0.24 (s, 12H).

^{13}C-NMR (75 MHz, $CDCl_3$): δ (ppm) 154.3, 127.4, 113.2, 109.5, 26.0, 18.6, −4.0.

2-(*tert*-Butyldimethylsilyl)-3-((*tert*-butyldimethylsilyl)oxy)phenyl trifluoromethanesulfonate (9)



9

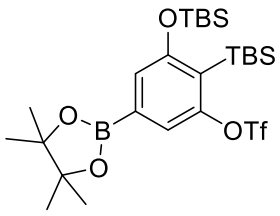
Aryl bromide **8** (4.94 g, 11.83 mmol, 1.0 equiv.) was dissolved in dry THF (30 mL, 0.4 M) and cooled to −94 °C (acetone/liquid N_2 bath). *n*-BuLi (1.6 M in n-hexane, 8.1 mL, 13.0 mmol, 1.1 equiv.) was added drop wise. After 30 min at −94 °C, Tf_2O (3.0 mL, 18 mmol, 1.5 equiv.) was added drop wise and stirred for 20 min. The reaction was finished by addition of sat. aq. NH_4Cl solution (15 mL) and the mixture was extracted with Et_2O (3 x 90 mL). The combined org. phases were washed with sat. aq. NaCl solution (50 mL), dried over $MgSO_4$ and concentrated *in vacuo*. Purification via flash column chromatography (SiO_2, *n*-pentane) afforded the desired product as a white solid (4.87 g, 10.4 mmol, 87%). Spectroscopic data are in accordance with those reported in literature.[3]

^{1}H-NMR (500 MHz, $CDCl_3$): δ (ppm) 7.25 (t, *J* = 8.4 Hz, 1H), 6.99 (dd, *J* = 8.4, 0.7 Hz, 1H), 6.79 (dd, *J* = 8.3, 0.7 Hz, 1H), 1.00 (s, 9H), 0.92 (s, 9H), 0.40 (s, 6H), 0.34 (s, 6H).

^{13}C-NMR (126 MHz, $CDCl_3$, , ^{1}H/^{19}F decoupled): δ (ppm) 162.5, 157.1, 131.1, 119.0, 118.7, 117.0, 110.9, 27.1, 27.0, 19.8, 18.8, −1.2, −2.8.

^{19}F-NMR (470 MHz, $CDCl_3$): δ (ppm) −73.69.

2-(*tert*-Butyldimethylsilyl)-3-((*tert*-butyldimethylsilyl)oxy)-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl trifluoromethanesulfonate (10)



10

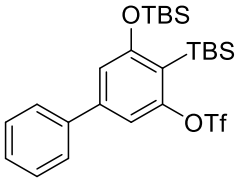
TBS-protected resorcinol **9** (3.80 g, 8.07 mmol, 1.0 equiv.), $[Ir(OMe)(1,5\text{-cod})]_2$ (184 mg, 0.202 mmol, 2.5 mol%), bis(pinacolato)diboron (3.08 g, 12.1 mmol, 1.5 equiv.) and 4,4′-di-*tert*-butyl-2,2′-dipyridyl (87 mg, 0.32 mmol, 4 mol%) were dissolved in dry *n*-hexane and stirred at 60 °C for 12 h. The mixture was concentrated under reduced pressure and purification via flash column chromatography (SiO_2, Et_2O in *n*-pentane = 10%) afforded the desired product as a white solid (4.69 g, 7.87 mmol, 97%). Spectroscopic data are in accordance with those reported in literature.[3]

^{1}H-NMR (500 MHz, $CDCl_3$): δ (ppm) 7.32 (s, 1H), 7.25 (s, 1H), 1.31 (s, 12H), 1.01 (s, 9H), 0.91 (s, 9H), 0.39 (s, 6H), 0.35 (s, 6H).

^{13}C-NMR (126 MHz, $CDCl_3$, ^{1}H/^{19}F decoupled): δ (ppm) 161.9, 156.8, 123.1, 122.1, 118.7, 116.2, 84.3, 27.2, 27.1, 25.0, 19.7, 18.8, −1.2, −2.8.

^{19}F-NMR (470 MHz, $CDCl_3$): δ (ppm) −73.64.

4-(*tert*-Butyldimethylsilyl)-5-((*tert*-butyldimethylsilyl)oxy)-[1,1'-biphenyl]-3-yl trifluoromethanesulfonate (11)



11

Arylpinacol ester **10** (592 mg, 0.992 mmol, 1.0 equiv.), bromobenzene (0.13 mL, 1.2 mmol, 1.25 equiv.), $Pd(OAc)_2$ (8.9 mg, 40 µmol, 4 mol%), SPhos (33 mg, 80 µmol, 8 mol%) and K_2CO_3 (274 mg, 1.98 mmol, 2.0 equiv.) were dissolved in dry toluene (5.0 mL, 0.2 M) and heated to 65 °C. After 30 h the mixture was concentrated under reduced pressure. Purification via flash column chromatography (SiO_2, *n*-pentane) afforded the desired product as a white solid (353 mg, 0.646 mmol, 65%). Spectroscopic data are in accordance with those reported in literature.[3]

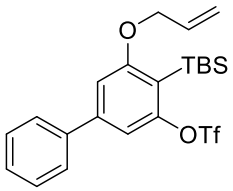
^{1}H-NMR (500 MHz, $CDCl_3$): δ (ppm) 7.54 – 7.43 (m, 4H), 7.43 – 7.37 (m, 1H), 7.22 (d, *J* = 1.3 Hz, 1H), 7.03 (d, *J* = 1.3 Hz, 1H), 1.04 (s, 9H), 0.96 (s, 9H), 0.42 (s, 6H), 0.38 (s, 6H).

^{13}C-NMR (126 MHz, $CDCl_3$, ^{1}H/^{19}F decoupled): δ (ppm) 162.7, 157.5, 144.5, 139.4, 129.3, 128.5, 126.9, 118.7, 117.5, 115.7, 109.9, 27.2, 27.1, 19.9, 18.9, −1.2, −2.7.

^{19}F-NMR (470 MHz, $CDCl_3$): δ (ppm) −73.60.

HR-MS (ESI): calc. $C_{25}H_{37}F_3NaO_4SSi_2^+$ $[M+Na]^+$ 569.1795 found 569.1796.

5-(Allyloxy)-4-(*tert*-butyldimethylsilyl)-[1,1'-biphenyl]-3-yl trifluoromethanesulfonate (4b)



4b

TBS-protected phenol **11** (327 mg, 0.598 mmol, 1.0 equiv.) was dissolved in dry THF (3.0 mL, 0.2 M) and cooled to −78 °C. Tetrabutylammonium fluoride (TBAF, 1 M in THF, 0.60 mL, 0.60 mmol, 1.01 equiv.) was added and it was stirred at −78 °C for 30 min. Sat. aq. NH_4Cl solution (2 mL) was added and the solution was diluted with water (20 mL). The mixture was extracted with Et_2O (3 x 30 mL) and the combined org. phases were washed with sat. aq. NaCl solution (20 mL), dried over $MgSO_4$ and concentrated under reduced pressure. The crude product, allyl bromide (0.18 mL, 1.5 mmol, 2.5 equiv.), TBAB (193 mg, 0.598 mmol, 1.0 equiv.) and $K_3PO_4 \cdot H_2O$ (415 mg, 1.80 mmol, 3.0 equiv.) were dissolved in water (5.4 mL, 0.11 M) and stirred for 1 h. The aq. solution was diluted with water (10 mL) and extracted with diethyl ether (3 x 35 mL). The combined organic layers were washed with sat. aq. NaCl solution (20 mL), dried over $MgSO_4$ and concentrated under reduced pressure. The crude product was purified via flash column chromatography on silica gel (SiO_2,*n*-pentane) to obtain the product as a white solid (164 mg, 0.347 mmol, 58% over two steps).

^{1}H-NMR (500 MHz, $CDCl_3$): δ (ppm) 7.59 – 7.51 (m, 2H), 7.50 – 7.37 (m, 3H), 7.21 (d, *J* = 1.3 Hz, 1H), 6.98 (d, *J* = 1.3 Hz, 1H), 6.09 (ddt, *J* = 17.3, 10.4, 5.7 Hz, 1H), 5.51 – 5.25 (m, 2H), 4.60 (dt, *J* = 5.8, 1.4 Hz, 2H), 0.96 (s, 9H), 0.42 (s, 6H).

^{13}C-NMR (126 MHz, $CDCl_3$, ^{1}H/^{19}F decoupled): δ (ppm) 165.0, 156.9, 145.4, 139.6, 132.8, 129.2, 128.6, 127.2, 119.0, 118.7, 116.6, 110.6, 108.9, 69.9, 27.3, 18.6, −1.5.

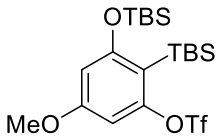
^{19}F-NMR (470 MHz, $CDCl_3$): δ (ppm) −73.67.

HR-MS (ESI): calc. $C_{22}H_{27}F_3NaO_4SSi^+$ $[M+Na]^+$ 495.1244 found 495.1222.

FTIR (neat): ν(cm^{-1}) 2956, 2930, 2858, 2364, 1600, 1543, 1506, 1420, 1399, 1364, 1307, 1212, 1142, 1109, 1037, 954, 895, 847, 822, 782, 761, 696.

T_{melt} = 86 – 89 °C.

2-(*tert*-Butyldimethylsilyl)-3-((*tert*-butyldimethylsilyl)oxy)-5-methoxyphenyl trifluoromethanesulfonate (12)



12

Arylpinacol ester **10** (716 mg, 1.20 mmol, 1.0 equiv.), $Cu(OAc)_2$ (8.9 mg, 40 µmol, 4 mol%), and K_2CO_3 (274 mg, 1.98 mmol, 2.0 equiv.) were dissolved in dry MeOH:1,4-dioxane (5.0 mL, 0.2 M) and heated to 65 °C. After 30 h the mixture was concentrated under reduced pressure. Purification via flash column chromatography (SiO_2, *n*-pentane) afforded the desired product as a white solid (353 mg, 0.646 mmol, 65%).

^{1}H-NMR (500 MHz, $CDCl_3$): δ (ppm) 6.59 (d, *J* = 2.0 Hz, 1H), 6.35 (d, *J* = 2.1 Hz, 1H), 3.77 (s, 3H), 1.01 (s, 9H), 0.90 (s, 9H), 0.36 (s, 6H), 0.34 (s, 6H).

^{13}C-NMR (126 MHz, $CDCl_3$, ^{1}H/^{19}F decoupled): δ (ppm) 163.1, 161.7, 157.7, 118.7, 110.2, 103.7, 97.9, 55.5, 27.12, 27.06, 19.8, 18.8, −1.3, −2.8.

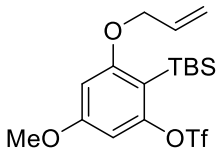
^{19}F-NMR (282 MHz, $CDCl_3$): δ (ppm) −73.57.

HR-MS (ESI): calc. $C_{20}H_{35}F_3NaO_5SSi_2^+$ $[M+Na]^+$ 523.1588 found 523.1580.

FTIR (neat): ν(cm^{-1}) 2958, 2931, 2859, 1604, 1560, 1473, 1415, 1318, 1261, 1245, 1206, 1141, 1091, 1047, 1017, 1003, 960, 840, 810, 781, 749.

T_{melt} = 62 – 64 °C.

3-(Allyloxy)-2-(*tert*-butyldimethylsilyl)-5-methoxyphenyl trifluoromethanesulfonate (4c)



4c

TBS-protected phenol **12** (244 mg, 0.487 mmol, 1.0 equiv.) was dissolved in dry THF (2.4 mL, 0.2 M) and cooled to −78 °C. Tetrabutylammonium fluoride (1 M in THF, 0.49 mL, 0.49 mmol, 1.01 equiv.) was added and it was stirred at −78 °C for 30 min. Sat. aq. NH_4Cl solution (2 mL) was added and the solution was diluted with water (20 mL). The mixture was extracted with Et_2O (3 x 30 mL) and the combined org. phases were washed with sat. aq. NaCl solution (20 mL), dried over $MgSO_4$ and concentrated under reduced pressure. The crude product, allyl bromide (0.15 mL, 1.2 mmol, 2.5 equiv.), TBAB (157 mg, 0.487 mmol, 1.0 equiv.) and K_3PO_4 (310 mg, 1.46 mmol, 3.0 equiv.) were dissolved in water (4.4 mL, 0.11 M) and stirred for 2 h. The aq. solution was diluted with water (5 mL) and extracted with diethyl ether (3 x 20 mL). The combined organic layers were washed with sat. aq. NaCl solution (20 mL), dried over $MgSO_4$ and concentrated under reduced pressure. The crude product was purified via flash column chromatography on silica gel (SiO_2,*n*-pentane) to obtain the product as a colorless oil (155 mg, 0.363 mmol, 75% over two steps).

^{1}H-NMR (300 MHz, $CDCl_3$): δ (ppm) 6.58 (d, *J* = 2.0 Hz, 1H), 6.37 (d, *J* = 2.0 Hz, 1H), 6.06 (ddt, *J* = 17.2, 10.4, 5.8 Hz, 1H), 5.45 – 5.19 (m, 2H), 4.50 (dt, *J* = 5.8, 1.4 Hz, 2H), 3.81 (s, 3H), 0.92 (s, 9H), 0.37 (s, 6H).

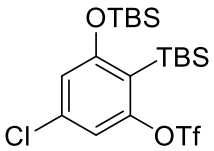
^{13}C-NMR (75 MHz, $CDCl_3$): δ (ppm) 165.5, 162.6, 157.2, 132.8, 118.9, 118.73 (q, *J* = 320.4 Hz), 109.3, 97.8, 97.5, 69.8, 55.6, 27.2, 18.6, −1.5.

^{19}F-NMR (282 MHz, $CDCl_3$): δ (ppm) −73.69.

HR-MS (ESI): calc. $C_{17}H_{25}F_3NaO_5SSi^+$ $[M+Na]^+$ 449.1036 found 449.1044.

FTIR (neat): ν(cm^{-1}) 2932, 2857, 1604, 1564, 1464, 1412, 1363, 1306, 1262, 1245, 1204, 1140, 1091, 1033, 959, 821, 811, 780, 688, 660, 600.

2-(*tert*-Butyldimethylsilyl)-3-((*tert*-butyldimethylsilyl)oxy)-5-chlorophenyl trifluoromethanesulfonate (13)



13

Arylpinacol ester **10** (716 mg, 1.20 mmol, 1.0 equiv.) and $CuCl_2$ (484 mg, 3.6 mmol, 3.0 equiv.) were dissolved in a mixture of H_2O:MeOH:1,4-dioxane (1:1:1, 12 mL, 0.1 M) and heated to 65 °C. After 16 h the mixture was concentrated under reduced pressure. Purification via flash column chromatography (SiO_2, *n*-pentane) afforded the desired product as a white solid (418 mg, 0.828 mmol, 69%).

^{1}H-NMR (500 MHz, $CDCl_3$): δ (ppm) 7.01 (d, *J* = 1.6 Hz, 1H), 6.79 (d, *J* = 1.6 Hz, 1H), 1.01 (s, 9H), 0.91 (s, 9H), 0.37 (s, 6H), 0.35 (s, 6H).

^{13}C-NMR (126 MHz, $CDCl_3$, ^{1}H/^{19}F decoupled): δ (ppm) 162.8, 156.8, 136.2, 118.6, 117.9, 117.6, 111.8, 27.1, 27.0, 19.8, 18.8, −1.3, −2.9.

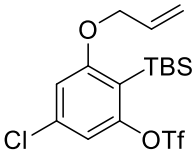
^{19}F-NMR (470 MHz, $CDCl_3$): δ (ppm) −73.55.

HR-MS (ESI): calc. $C_{19}H_{32}ClF_3NaO_4SSi_2^+$ $[M+Na]^+$ 527.1093 found 527.1102.

FTIR (neat): ν(cm^{-1}) 2960, 2932, 2890, 2861, 1585, 1549, 1473, 1425, 1389, 1281, 1252, 1213, 1178, 1143, 1059, 1014, 917, 838, 808, 788, 743.

T_{melt} = 64 – 67 °C.

3-(Allyloxy)-2-(*tert*-butyldimethylsilyl)-5-chlorophenyl trifluoromethanesulfonate (4d)



4d

TBS-protected phenol **13** (417 mg, 0.826 mmol, 1.0 equiv.) was dissolved in dry THF (4.1 mL, 0.2 M) and cooled to −78 °C. Tetrabutylammonium fluoride (1 M in THF, 0.83 mL, 0.83 mmol, 1.01 equiv.) was added and it was stirred at −78 °C for 30 min. Sat. aq. NH_4Cl solution (2 mL) was added and the solution was diluted with water (20 mL). The mixture was extracted with Et_2O (3 x 30 mL) and the combined org. phases were washed with sat. aq. NaCl solution (20 mL), dried over $MgSO_4$ and concentrated under reduced pressure. The crude product, allyl bromide (0.25 mL, 2.7 mmol, 2.5 equiv.), TBAB (266 mg, 0.826 mmol, 1.0 equiv.) and K_3PO_4 (526 mg, 2.48 mmol, 3.0 equiv.) were dissolved in water (7.5 mL, 0.11 M) and stirred for 2 h. The aq. solution was diluted with water (10 mL) and extracted with diethyl ether (3 x 25 mL). The combined organic layers were washed with sat. aq. NaCl solution (20 mL), dried over $MgSO_4$ and concentrated under reduced pressure. The

crude product was purified via flash column chromatography on silica gel (SiO_2,*n*-pentane) to obtain the product as a white solid (124 mg, 0.288 mmol, 35% over two steps).

^{1}H-NMR (500 MHz, $CDCl_3$): δ (ppm) 7.02 (d, *J* = 1.6 Hz, 1H), 6.78 (d, *J* = 1.6 Hz, 1H), 6.04 (ddt, *J* = 17.3, 10.4, 5.8 Hz, 1H), 5.45 – 5.27 (m, 2H), 4.51 (dt, *J* = 5.8, 1.3 Hz, 2H), 0.91 (s, 9H), 0.37 (s, 6H).

^{13}C-NMR (126 MHz, $CDCl_3$, ^{1}H/^{19}F decoupled): δ (ppm) 165.0, 156.2, 137.1, 132.1, 119.5, 118.6, 116.9, 112.4, 111.0, 70.1, 27.1, 18.5, -1.6.

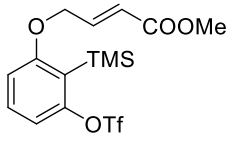
^{19}F-NMR (282 MHz, $CDCl_3$): δ (ppm) −73.65.

HR-MS (ESI): calc. $C_{16}H_{22}ClF_3NaO_4SSi^+$ $[M+Na]^+$ 453.0541 found 453.0546.

FTIR (neat): ν(cm^{-1}) 2954, 2932, 2859, 1584, 1555, 1472, 1422, 1392, 1364, 1252, 1208, 1182, 1139, 1060, 1035, 955, 929, 900, 845, 807, 781, 763, 688, 599.

T_{melt} = 42 – 44 °C.

Methyl *(E)*-4-(3-(((trifluoromethyl)sulfonyl)oxy)-2-(trimethylsilyl)phenoxy)but-2-enoate (4e)



4e

Phenol **7** (126 mg, 0.400 mmol, 1.0 equiv.), 3-bromo-2-methylpropene (70 µL, 0.6 mmol, 1.5 equiv.), *tetra*-*n*-butyl ammonium bromide (129 mg, 0.400 mmol, 1.0 eq) and $K_3PO_4 \cdot H_2O$ (276 mg, 1.20 mmol, 3.0 equiv.) were dissolved in water (3.6 mL, 0.11 M) and stirred for 4 h. The aq. solution was diluted with water (10 mL) and extracted with diethyl ether (3 x 30 mL). The combined organic layers were washed with sat. aq. NaCl solution (30 mL), dried over $MgSO_4$ and concentrated under reduced pressure. The crude product was purified via flash column chromatography on silica gel (SiO_2, gradient Et_2O in *n*-pentane = 5% to 10%) to obtain the product as a colorless oil (113 mg, 0.272 mmol, 68%).

^{1}H-NMR (500 MHz, $CDCl_3$): δ (ppm) 7.35 (t, *J* = 8.3 Hz, 1H), 7.08 (dt, *J* = 15.8, 4.4 Hz, 1H), 6.98 (dd, *J* = 8.4, 0.7 Hz, 1H), 6.77 (dd, *J* = 8.3, 0.7 Hz, 1H), 6.14 (dt, *J* = 15.8, 2.0 Hz, 1H), 4.75 (dd, *J* = 4.4, 2.0 Hz, 2H), 3.77 (s, 3H), 0.40 (s, 9H).

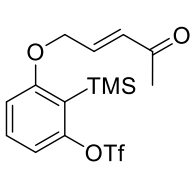
^{13}C-NMR (126 MHz, $CDCl_3$, ^{1}H/^{19}F decoupled): δ (ppm) 166.3, 164.0, 154.8, 141.8, 131.8, 122.6, 121.5, 118.8, 113.7, 110.7, 67.6, 52.0, 1.1.

^{19}F-NMR (470 MHz, $CDCl_3$): δ (ppm) −72.75.

HR-MS (ESI): calc. for $C_{15}H_{19}F_3NaO_6SSi^+$ $[M+Na]^+$ 435.0516 found 435.0539.

FTIR (neat): ν(cm^{-1}) 1726, 1669, 1596, 1567, 1435, 1418, 1310, 1277, 1247, 1206, 1173, 1138, 1119, 1089, 1041, 1023, 966, 933, 908, 835, 787, 796, 734, 713, 603.

(E)-3-((4-Oxopent-2-en-1-yl)oxy)-2-(trimethylsilyl)phenyl trifluoromethanesulfonate (4f)



4f

Allyl ether **4a** (142 mg, 0.400 mmol, 1.0 equiv.), methyl vinyl ketone (68 µL, 0.80 mmol, 2.0 equiv.) and Hoveyda-Grubbs II catalyst (2.5 mg, 4.0 µmol, 1 mol%) were dissolved in dry CH_2Cl_2 (2.1 mL, 1.9 M) and heated to 40 °C for 15 h. The crude product was concentrated under reduced pressure and purification via flash column chromatography (SiO_2, gradient of Et_2O in *n*-

pentane = 10% to 50%) yielded the enone as a pale yellow oil (98.0 mg, 0.247 mmol, 35%, *(E)/(Z)* > 20:1).

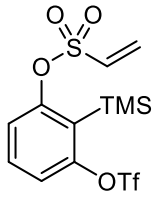
^{1}H-NMR (300 MHz, $CDCl_3$): δ (ppm) 7.35 (t, *J* = 8.3 Hz, 1H), 6.98 (d, *J* = 8.4 Hz, 1H), 6.88 (dt, *J* = 16.1, 4.5 Hz, 1H), 6.78 (d, *J* = 8.3 Hz, 1H), 6.37 (dt, *J* = 16.1, 1.9 Hz, 1H), 4.76 (dd, *J* = 4.5, 1.9 Hz, 2H), 2.29 (s, 3H), 0.39 (s, 9H).

^{13}C-NMR (75 MHz, $CDCl_3$): δ (ppm) 197.5, 164.0, 154.8, 140.1, 131.8, 131.4, 121.4, 118.74 (q, *J* = 320.8 Hz), 113.7, 110.7, 67.7, 27.7, 1.1.

HR-MS (ESI): calc. $C_{15}H_{19}F_3NaO_5SSi^+$ $[M+Na]^+$ 419.0567 found 419.0567.

FTIR (neat): ν(cm^{-1}) 1704, 1683, 1640, 1596, 1566, 1435, 1414, 1362, 1246, 1205, 1138, 1119, 1090, 1038, 969, 933, 836, 787, 767, 738, 712.

3-(((Trifluoromethyl)sulfonyl)oxy)-2-(trimethylsilyl)phenyl ethenesulfonate (4g)



4g

Phenol **7** (126 mg, 0.400 mmol, 1.0 equiv.) and 2-chloroethanesulfonyl chloride (50 µL, 0.48 mmol, 1.2 equiv.) were dissolved in dry CH_2Cl_2 (0.8 mL, 0.5 M) and cooled to 0 °C. NEt_3 (0.17 mL, 1.2 mmol, 3.0 equiv.) was added dropwise and the mixture was stirred at 0 °C for 1 h. The reaction was finished by addition of water (30 mL) and the aq. phase was extracted with CH_2Cl_2 (3 x 30 mL). The combines organic layers were washed with sat. aq. NaCl solution (50 mL), dried over $MgSO_4$ and concentrated *in vacuo*. Purification via flash column chromatography (SiO_2, Et_2O in *n*-pentane = 5%) afforded the desired product as a colorless oil (143 mg, 0.353 mmol, 88%).

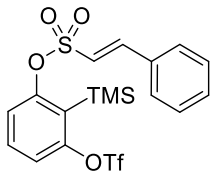
^{1}H-NMR (300 MHz, $CDCl_3$): δ (ppm) 7.52 – 7.39 (m, 2H), 7.30 (m, 1H), 6.70 (dd, *J* = 16.6, 9.8 Hz, 1H), 6.51 (d, *J* = 16.6 Hz, 1H), 6.26 (d, *J* = 9.8 Hz, 1H), 0.45 (s, 9H).

^{13}C-NMR (75 MHz, $CDCl_3$): δ (ppm) 155.0, 154.9, 132.7, 132.4, 131.8, 126.4, 120.2, 118.60 (q, *J* = 320.4 Hz), 118.55, 1.0.

HR-MS (ESI): calc. for $C_{12}H_{15}F_3NaO_6S_2Si^+$ $[M+Na]^+$ 426.9924 found 426.9927.

FTIR (neat): ν(cm^{-1}) 1597, 1565, 1420, 1377, 1250, 1206, 1163, 1136, 1117, 1058, 942, 875, 839, 801, 781, 762, 741, 711, 673, 598.

3-(((Trifluoromethyl)sulfonyl)oxy)-2-(trimethylsilyl)phenyl *(E)*-2-phenylethene-1-sulfonate (4h)



4h

Phenol **7** (126 mg, 0.400 mmol, 1.0 equiv.) and (*E*)-2-phenylethenesulfonyl chloride (89.2 mg, 0.440 mmol, 1.1 equiv.) were dissolved in dry CH_2Cl_2 - (1.1 mL, 0.35 M). NEt_3 (83 mL, 0.60 mmol, 1.5 mmol) was added drop wise and the mixture was stirred at room temperature for 1.5 h. The reaction was finished by adding water (12 mL) and the aqueous layer was extracted with CH_2Cl_2 (3 x 30 mL). The combined organic phases were washed with sat. aq. NaCl solution (40 mL), dried over $MgSO_4$ and concentrated *in vacuo*. The crude product was purified via flash column chromatography (SiO_2, Et_2O in *n*-pentane = 10%) to obtain sulfonic ester as a white solid (175 mg, 0.363 mmol, 91%).

^{1}H-NMR (300 MHz, $CDCl_3$): δ (ppm) 7.66 (d, *J* = 15.5 Hz, 1H), 7.56 – 7.39 (m, 7H), 7.30 (dd, *J* = 7.7, 1.4 Hz, 1H), 6.88 (d, *J* = 15.5 Hz, 1H), 0.46 (s, 9H).

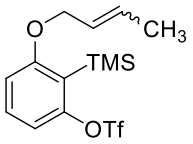
^{13}C-NMR (75 MHz, $CDCl_3$): δ (ppm) 155.3, 155.0, 147.0, 132.2, 131.8, 131.6, 129.5, 128.9, 126.5, 121.1, 120.4, 118.64 (q, *J* = 320.5 Hz), 118.4 , 1.1.

HR-MS (ESI): calc. for $C_{18}H_{19}F_3NaO_6S_2Si^+$ $[M+Na]^+$ 503.0237 found 503.0236.

FTIR (neat): ν(cm^{-1}) 1619, 1596, 1564, 1433, 1411, 1346, 1250, 1214, 1157, 1138, 1116, 1054, 982, 953, 875, 842, 827, 795, 774, 746, 712.

T_{melt} = 76 °C.

***(E)/(Z)*-3-(But-2-en-1-yloxy)-2-(trimethylsilyl)phenyl trifluoromethanesulfonate (4i)**



4i

Phenol **7** (189 mg, 0.600 mmol, 1.0 equiv.), crotyl bromide (mixture (*E*)/(*Z*), 0.15 mL, 1.5 mmol, 2.5 equiv.), *tetra-n*-butyl ammonium bromide (193 mg, 0.600 mmol, 1.0 eq) and $K_3PO_4 \cdot H_2O$ (415 mg, 1.80 mmol, 3.0 equiv.) were dissolved in water (5.5 mL, 0.11 M) and stirred for 1 h. The aq. solution was diluted with water (10 mL) and extracted with diethyl ether (3 x 30 mL). The combined organic layers were washed with sat. aq. NaCl solution (30 mL), dried over $MgSO_4$ and concentrated under reduced pressure. The crude product was purified via flash column chromatography on silica gel (SiO_2, *n*-pentane) to obtain the product as a colorless oil (inseparable (*E*)/(*Z*) mixture = 3.7:1.0, 99 mg, 0.27 mmol, 39%).

(E)-isomer:

^{1}H-NMR (500 MHz, $CDCl_3$): δ (ppm) 7.34 (t, *J* = 8.3 Hz, 1H), 6.93 (d, *J* = 8.4 Hz, 1H), 6.82 (d, *J* = 8.5 Hz, 1H), 5.85 (dqt, *J* = 15.3, 6.4, 1.2 Hz, 1H), 5.75 – 5.65 (m, 1H), 4.49 (dt, *J* = 6.1, 1.2 Hz, 2H), 1.77 (dq, *J* = 6.5, 1.2 Hz, 3H), 0.39 (s, 9H).

^{13}C-NMR (126 MHz, $CDCl_3$): δ (ppm), 130.9, 125.6, 110.6, 69.5, 17.9, 1.1.

(Z)-isomer:

^{1}H-NMR (500 MHz, $CDCl_3$): δ (ppm) 7.35 (t, *J* = 8.3 Hz, 1H), 6.95 (d, *J* = 8.3 Hz, 1H), 6.84 (d, *J* = 8.5 Hz, 1H), 5.80 – 5.75 (m, 1H), 5.74 – 5.67 (m, 1H), 4.61 (d, *J* = 6.2 Hz, 2H), 1.75 (ddd, *J* = 6.9, 1.6, 0.8 Hz, 3H), 0.38 (s, 9H).

^{13}C-NMR (126 MHz, $CDCl_3$): δ (ppm) 129.0, 125.0, 110.3, 64.4, 13.5, 1.0.

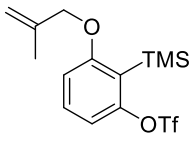
(E) or (Z)-isomer (or overlap of signals):

^{13}C-NMR (126 MHz, $CDCl_3$): δ (ppm) 164.8, 154.9, 131.6, 121.1, 118.8 (q, *J* = 320.8 Hz), 112.81 (q, *J* = 1.6 Hz),

HR-MS (ESI): calc. for $C_{14}H_{19}F_3NaO_4SSi^+$ $[M+Na]^+$ 391.0618 found 391.0607.

FTIR (neat): ν(cm^{-1}) 2956, 1596, 1566, 1437, 1418, 1247, 1205, 1161, 1139, 1116, 1081, 1057, 1019, 965, 935, 833, 786, 712, 602.

3-((2-Methylallyl)oxy)-2-(trimethylsilyl)phenyl trifluoromethanesulfonate (4j)



4j

Phenol **7** (251 mg, 0.800 mmol, 1.0 equiv.), 3-bromo-2-methylpropene (0.20 mL, 2.0 mmol, 2.5 equiv.), *tetra*-*n*-butyl ammonium bromide (258 mg, 0.800 mmol, 1.0 eq) and $K_3PO_4 \cdot H_2O$ (553 mg, 2.40 mmol, 3.0 equiv.) were dissolved in water (7.3 mL, 0.11 M) and stirred for 1 h. The aq. solution was diluted with water (20 mL) and extracted with diethyl ether (3 x 50 mL). The combined organic layers were washed with sat. aq. NaCl solution (50 mL), dried over $MgSO_4$ and concentrated under reduced pressure. The crude product was purified via flash column chromatography on silica gel (SiO_2, *n*-pentane) to obtain the product as a colorless oil (167 mg, 0.452 mmol, 56%).

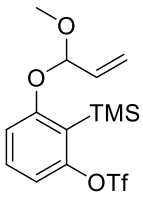
^{1}H-NMR (300 MHz, $CDCl_3$): δ (ppm) 7.34 (t, *J* = 8.3 Hz, 1H), 6.94 (d, *J* = 8.4 Hz, 1H), 6.82 (d, *J* = 8.3 Hz, 1H), 5.07 (s, 1H), 5.02 (s, 1H), 4.46 (s, 2H), 1.85 (s, 3H), 0.39 (s, 9H).

^{13}C-NMR (75 MHz, $CDCl_3$): δ (ppm) 164.8, 154.8, 140.2, 131.6, 121.0, 118.7 (q, *J* = 320.8 Hz), 113.8, 113.0, 110.6, 72.8, 19.8, 1.0.

HR-MS (ESI): calc. for $C_{14}H_{19}F_3NaO_4SSi^+$ $[M+Na]^+$ 391.0623 found 391.0620.

FTIR (neat): ν(cm^{-1}) 1596, 1566, 1418, 1247, 1205, 1139, 1117, 1024, 929, 829, 785, 769, 737, 712, 671, 641, 600.

3-((1-Methoxyallyl)oxy)-2-(trimethylsilyl)phenyl trifluoromethanesulfonate (4k)



4k

Phenol **7** (251 mg, 0.800 mmol, 1.0 equiv.), $Pd_2(dba)_3$ (9.2 mg, 16 µmol, 2 mol%) and (*R*)-BINAP (25 mg, 40 mmol, 5 mol%), NEt_3 (0.22 mL, 1.6 mmol, 2.0 equiv.), 1-methoxy-1,2-propadiene (0.16 mL, 2.0 mmol, 2.5 equiv.) and 4Å molecular sieve (powder, 400 mg) were dissolved in dry 1,4-dioxane (8.0 mL, 0.1 M) and stirred at room temperature for 20 h. The mixture was concentrated *in vacuo* and purification via flash column chromatography (SiO_2, Et_2O in *n*-pentane = 1%) afforded the desired acetal as a colorless oil (165 mg, 0.427 mmol, 53%).

^{1}H-NMR (500 MHz, $CDCl_3$): δ (ppm) 7.33 (t, *J* = 8.3 Hz, 1H), 7.09 (d, *J* = 8.3 Hz, 1H), 6.98 (d, *J* = 9.0 Hz, 1H), 5.99 (ddd, *J* = 17.4, 10.7, 5.1 Hz, 1H), 5.61 (dt, *J* = 5.1, 1.1 Hz, 1H), 5.53 (dt, *J* = 17.4, 1.1 Hz, 1H), 5.45 (dt, *J* = 10.7, 1.1 Hz, 1H), 3.39 (s, 3H), 0.40 (s, 9H).

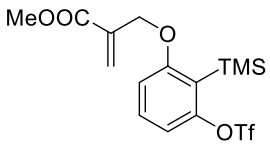
^{13}C-NMR (126 MHz, $CDCl_3$, ^{1}H/^{19}F decoupled): δ (ppm) 162.5, 154.8, 133.2, 131.6, 121.6, 120.4, 118.8, 113.7, 113.4, 101.3, 52.6, 1.2.

^{19}F-NMR (470 MHz, $CDCl_3$): δ (ppm) −72.84.

HR-MS (ESI): calc. for $C_{14}H_{19}F_3NaO_5SSi^+$ $[M+Na]^+$ 407.0567 found 407.0566.

FTIR (neat): ν(cm^{-1}) 1596, 1566, 1437, 1418, 1246, 1205, 1162, 1139, 1116, 983, 944, 835, 788, 767, 740.

Methyl 2-((3-(((trifluoromethyl)sulfonyl)oxy)-2-(trimethylsilyl)phenoxy)methyl)acrylate (4l)



4l

Phenol **7** (251 mg, 0.800 mmol, 1.0 equiv.), methyl 2-(bromomethyl)acrylate (0.24 mL, 2.0 mmol, 2.5 equiv.), *tetra*-*n*-butyl ammonium bromide (258 mg, 0.800 mmol, 1.0 eq) and $K_3PO_4 \cdot H_2O$ (553 mg, 2.40 mmol, 3.0 equiv.) were dissolved in water (7.3 mL, 0.11 M) and stirred for 2 h. The aq. solution was diluted with water (20 mL) and extracted with diethyl ether (3 x 50 mL). The combined organic layers were washed with sat. aq. NaCl solution (50 mL), dried over $MgSO_4$ and concentrated under reduced pressure. The crude product was purified via flash column chromatography on silica gel (SiO_2, Et_2O in *n*-pentane = 5%) to obtain the product as a colorless oil (184 mg, 0.447 mmol, 56%).

^{1}H-NMR (300 MHz, $CDCl_3$): δ (ppm) 7.36 (t, *J* = 8.3 Hz, 1H), 6.97 (d, *J* = 8.3 Hz, 1H), 6.83 (d, *J* = 8.2 Hz, 1H), 6.43 (d, *J* = 1.0 Hz, 1H), 5.94 (q, *J* = 1.4 Hz, 1H), 4.79 (s, 2H), 3.82 (s, 3H), 0.36 (s, 9H).

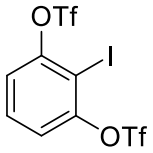
^{13}C-NMR (126 MHz, $CDCl_3$, ^{1}H/^{19}F decoupled): δ (ppm) 165.9, 164.2, 154.8, 135.5, 131.8, 127.8, 121.2, 118.8, 113.4, 110.7, 67.4, 52.3, 1.0.

^{19}F-NMR (470 MHz, $CDCl_3$): δ (ppm) −72.75.

HR-MS (ESI): calc. for $C_{15}H_{19}F_3NaO_6SSi^+$ $[M+Na]^+$ 435.0516 found 435.0506.

FTIR (neat): ν(cm^{-1}) 2956, 2362, 1727, 1596, 1437, 1420, 1314, 1249, 1209, 1164, 1141, 1051, 1036, 936, 846, 788, 742, 713, 607.

2-Iodo-1,3-phenylene bis(trifluoromethanesulfonate) (14)



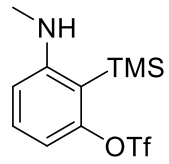
14

2-Iodoresorcinol[4] (4.55 g, 19.3 mmol, 1.0 equiv.) and *i*-Pr_2EtN (8.2 mL, 47 mmol, 2.44 equiv.) were dissolved in dry CH_2Cl_2 (28 mL, 0.7 M) and cooled to −78 °C. Tf_2O (7.4 mL, 44 mmol, 2.3 equiv.) was added dropwise and the mixture was stirred at -78 °C for 20 min. The brown solution was quenched by addition of water (30 mL) and extracted with CH_2Cl_2 (3x80 mL). The combined org. layers were washed with sat. aq. NaCl solution (100 mL), dried over $MgSO_4$ and concentrated *in vacuo*. The crude product was purified via flash column chromatography (SiO_2, *n*-pentane) to furnish the product as a pale yellow solid (8.84 g, 17.7 mmol, 92%). Spectroscopic data is in accordance to literature.[5]

^{1}H-NMR (500 MHz, $CDCl_3$): δ (ppm) 7.55 (dd, *J* = 8.7, 8.1 Hz, 1H), 7.38 (d, *J* = 8.3 Hz, 2H).

^{13}C-NMR (126 MHz, $CDCl_3$): δ (ppm) 151.8, 131.1, 121.7, 118.8 (q, *J* = 320.8 Hz), 87.7.

3-(Methylamino)-2-(trimethylsilyl)phenyl trifluoromethanesulfonate (15)



15

Aryl iodide **14** (1.00 g, 2.00 mmol, 1.0 equiv.) and *N,N*-bis(trimethylsilyl)methylamine (1.3 mL, 6.00 mmol, 3.0 equiv.) were dissolved in dry *n*-hexane (10 mL, 0.2 M) and cooled to 0 °C. *n*-BuLi (1.6 M in *n*-hexane, 2.75 mL, 4.40 mmol, 2.2 equiv.) was added slowly. After 15 min, water (50 mL) was added carefully in small portions and the mixture was extracted with Et_2O (3 x 30 mL). The combined org. phases were washed with sat. aq. NaCl solution (50 mL), dried over $MgSO_4$ and concentrated under reduced pressure. Purification via flash column chromatography (SiO_2, gradient Et_2O in *n*-pentane = 0.5% to 1%) afforded the desired amine as a yellow oil (240 mg, 0.734 mmol, 37%).

^{1}H-NMR (500 MHz, $CDCl_3$): δ (ppm) 7.28 (t, *J* = 8.3 Hz, 1H), 6.69 (d, *J* = 8.3 Hz, 1H), 6.54 (d, *J* = 8.3 Hz, 1H), 4.26 (s, *J* = 6.6 Hz, 1H), 2.86 (d, *J* = 5.1 Hz, 3H), 0.45 (s, 9H).

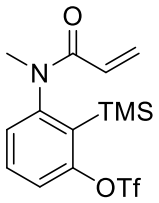
^{13}C-NMR (126 MHz, $CDCl_3$, ^{1}H/^{19}F decoupled): δ (ppm) 156.2, 155.8, 132.0, 118.7, 113.7, 109.0, 108.3, 31.2, 1.4.

^{19}F-NMR (470 MHz, $CDCl_3$): δ (ppm) −73.18.

HR-MS (ESI): calc. $C_{11}H_{16}F_3NNaO_3SSi^+$ $[M+Na]^+$ 350.0464 found 350.0467.

FTIR (neat): ν(cm^{-1}) 3495, 2957, 2822, 1602, 1560, 1506, 1452, 1416, 1309, 1247, 1204, 1136, 1073, 1046, 925, 829, 780, 737, 710, 671, 600.

3-(*N*-Methylacrylamido)-2-(trimethylsilyl)phenyl trifluoromethanesulfonate (4m)



4m

Aniline **15** (189 mg, 0.578 mmol, 1.0 equiv.) and acryloyl chloride (51 µL, 0.636 mmol, 1.1 equiv.) were dissolved in dry CH_2Cl_2 (2.9 ml, 0.2 M). NEt_3 (0.12 mL, 0.87 mmol, 1.5 equiv.) was added drop wise and the solution was stirred at room temperature for 2 h. The mixture was diluted with H_2O (10 mL) and sat. aq. NaCl solution (30 mL), and extracted with CH_2Cl_2 (3 x 50 mL). The combined org. phases were dried over $MgSO_4$ and concentrated *in vacuo*. Purification via flash column chromatography (SiO_2, Et_2O in *n*-pentane = 25%) afforded the desired amine as a yellow solid (86 mg, 0.225 mmol, 39%).

^{1}H-NMR (599 MHz, $CDCl_3$): δ (ppm) 7.50 (t, *J* = 8.1 Hz, 1H), 7.42 (d, *J* = 8.4 Hz, 1H), 7.11 (d, *J* = 7.8 Hz, 1H), 6.40 (dd, *J* = 16.7, 1.9 Hz, 1H), 5.90 (dd, *J* = 16.7, 10.3 Hz, 1H), 5.57 – 5.54 (m, 1H), 3.24 (s, 3H), 0.35 (s, 9H).

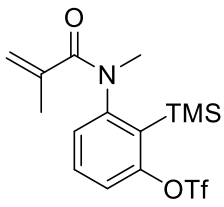
^{13}C-NMR (151 MHz, $CDCl_3$): δ (ppm) 165.6, 156.0, 150.2, 132.2, 132.1, 128.8, 128.7, 128.1, 119.61 (q, *J* = 1.6 Hz), 118.59 (q, *J* = 320.2 Hz), 38.5, 0.7.

HR-MS (ESI): calc. $C_{14}H_{18}F_3NNaO_4SSi^+$ $[M+Na]^+$ 404.0570 found 404.0583.

FTIR (neat): ν(cm^{-1}) 1654, 1619, 1590, 1554, 1449, 1422, 1402, 1357, 1278, 1247, 1211, 1152, 1132, 1114, 1050, 971, 948, 883, 843, 813, 791, 762, 728, 697, 678, 661, 636, 607.

T_{melt} = 65 – 67 °C.

3-(*N*-Methylmethacrylamido)-2-(trimethylsilyl)phenyl trifluoromethanesulfonate (4n)



4n

Aniline **15** (189 mg, 0.578 mmol, 1.0 equiv.) and acryloyl chloride (51 µL, 0.636 mmol, 1.1 equiv.) were dissolved in dry CH_2Cl_2 (2.9 ml, 0.2 M). NEt_3 (0.12 mL, 0.87 mmol, 1.5 equiv.) was added drop wise and the solution was stirred at room temperature for 2 h. The mixture was diluted with H_2O (10 mL) and sat. aq. NaCl solution (30 mL), and extracted with CH_2Cl_2 (3 x 50 mL). The combined org. phases were dried over $MgSO_4$ and concentrated *in vacuo*. Purification via flash column chromatography (SiO_2, Et_2O in *n*-pentane = 25%) afforded the desired amine as a yellow solid (86 mg, 0.225 mmol, 39%). Note: a mixture of two rotamers ratio = 5:1) was obtained.

Major Rotamer:

^{1}H-NMR (599 MHz, $CDCl_3$): δ (ppm) 7.42 (t, *J* = 8.1 Hz, 1H), 7.36 (dd, *J* = 8.5, 1.0 Hz, 1H), 7.01 (dd, *J* = 7.8, 1.0 Hz, 1H), 5.11 (s, 1H), 4.89 (s, 1H), 3.21 (s, 3H), 1.75 (s, 4H), 0.41 (s, 9H).

^{13}C-NMR (151 MHz, $CDCl_3$, ^{1}H/^{19}F decoupled):): δ (ppm) 170.9, 156.3, 151.4, 140.1, 131.7, 130.9, 128.4, 121.1, 118.7, 118.6, 39.8, 21.0, 0.7.

Minor Rotamer:

^{1}H-NMR (599 MHz, $CDCl_3$): δ (ppm) 7.48 (t, *J* = 8.1 Hz, 1H), 7.34 (d, *J* = 7.0 Hz, 1H), 7.11 (d, *J* = 7.8 Hz, 1H), 5.35 (s, 1H), 5.26 (s, 1H), 3.28 (s, 3H), 2.05 (s, 3H), 0.39 (s, 9H).

^{13}C-NMR (151 MHz, $CDCl_3$, ^{1}H/^{19}F decoupled):): δ (ppm) 172.7, 156.0, 150.7, 140.4, 132.1, 131.1, 119.0, 118.6, 116.8, 41.7, 20.4, 0.9.

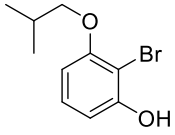
^{19}F-NMR (282 MHz, $CDCl_3$): δ (ppm) −73.83.

HR-MS (ESI): calc. $C_{15}H_{20}F_3NNaO_4SSi^+$ $[M+Na]^+$ 418.0727 found 418.0717.

FTIR (neat): ν(cm^{-1}) 1657, 1630, 1596, 1556, 1449, 1418, 1366, 1310, 1251, 1214, 1182, 1140, 1115, 1053, 1006, 961, 920, 872, 845, 805, 786, 757, 726.

T_{melt} = 42 – 44 °C.

2-Bromo-3-isobutoxyphenol (16)



16

2-Bromoresorcinol (600 mg, 3.17 mmol, 1.0 equiv.), K_2CO_3 (971 mg, 6.97 mmol., 2.2 equiv.) and 1-bromo-2-methylpropane (0.41 mL, 3.8 mmol, 1.2 equiv.) were dissolved in dry acetone (12 mL, 0.26 M) and heated to 55 °C for 15 h. The mixture was concentrated *in vacuo* and purified via flash column chromatography on silica gel (SiO_2, gradient diethyl ether in *n*-pentane = 5% to 10%) to obtain the product as a colorless oil (123 mg, 0.500 mmol, 16%).

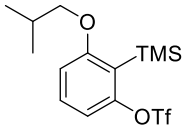
^{1}H-NMR (300 MHz, $CDCl_3$): δ (ppm) 7.13 (t, *J* = 8.2 Hz, 1H), 6.66 (dd, *J* = 8.2, 1.3 Hz, 1H), 6.45 (dd, *J* = 8.3, 1.2 Hz, 1H), 5.64 (s, 1H), 3.78 (d, *J* = 6.4 Hz, 2H), 2.15 (dp, *J* = 13.3, 6.6 Hz, 1H), 1.07 (d, *J* = 6.7 Hz, 6H).

^{13}C-NMR (75 MHz, $CDCl_3$): δ (ppm) 156.3, 153.7, 128.7, 108.3, 104.8, 100.7, 75.6, 28.5, 19.3.

HR-MS (ESI): calc. for $C_{10}H_{13}BrNaO_2^+$ $[M+Na]^+$ 266.9991 found 266.9998.

FTIR (neat): ν(cm^{-1}) 3507, 2958, 2929, 2873, 1594, 1483, 1461, 1395, 1368, 1326, 1269, 1200, 1164, 1072, 1055, 1031, 766, 703.

3-Isobutoxy-2-(trimethylsilyl)phenyl trifluoromethanesulfonate (5a)



5a

Phenol **16** (123 mg, 0.500 mmol, 1.0 equiv.) and HMDS (0.12 mL, 0.55 mmol, 1.1 equiv.) were dissolved in dry THF (0.92 mL, 0.53 M) and heated to 60 °C for 18 h. The solution was concentrated *in vacuo* and then redissolved in dry THF (1.3 mL, 0.4 M) and cooled to -78°C. *n*-BuLi (1.6 M in *n*-hexane, 0.34 mL, 0.55 mmol, 1.1 equiv.) was added drop wise and after 30 min at -78 °C, Tf_2O (0.13 mL, 0.75 mmol, 1.5 equiv.) was added. After 1 h the reaction was finished by addition of sat. aq. NH_4Cl solution (5 mL). The mixture was diluted with H_2O (40 mL) and extracted with diethyl ether (3 x 30 mL). The combines org. phases were washed with sat. aq. NaCl solution (30 mL), dried over $MgSO_4$ and concentrated under reduced pressure. The crude product was via flash column chromatography on silica gel (SiO_2, *n*-pentane) to obtain the product as a colorless oil (122 mg, 0.329 mmol, 66%).

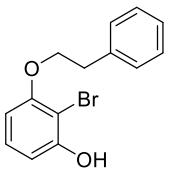
^{1}H-NMR (500 MHz, $CDCl_3$): δ (ppm) 7.34 (t, *J* = 8.3 Hz, 1H), 6.92 (d, *J* = 8.3 Hz, 1H), 6.82 (dd, *J* = 8.3, 0.7 Hz, 1H), 3.74 (d, *J* = 6.6 Hz, 2H), 2.15 (dp, *J* = 13.3, 6.7 Hz, 1H), 1.06 (d, *J* = 6.7 Hz, 6H), 0.39 (s, 9H).

^{13}C-NMR (126 MHz, $CDCl_3$): δ (ppm) 165.2, 154.9, 131.7, 120.7, 118.8 (q, J = 320.8 Hz), 112.7, 110.1, 75.6, 28.3, 19.7, 1.2.

HR-MS (ESI): calc. for $C_{14}H_{21}F_3NaO_4SSi^+$ $[M+Na]^+$ 393.0774 found 393.0766.

FTIR (neat): ν(cm^{-1}) 2962, 2877, 1596, 1566, 1473, 1437, 1419, 1247, 1205, 1162, 1139, 1117, 1038, 1015, 960, 938, 917, 842, 828, 785, 771, 738, 712, 602.

2-Bromo-3-phenethoxyphenol (17)



17

2-Bromoresorcinol (600 mg, 3.17 mmol, 1.0 equiv.), K_2CO_3 (971 mg, 6.97 mmol., 2.2 equiv.) and (2-bromoethyl)benzene (0.51 mL, 3.8 mmol, 1.2 equiv.) were dissolved in dry acetone (12 mL, 0.26 M) and heated to 55 °C for 15 h. The mixture was concentrated *in vacuo* and purified via flash column chromatography on silica gel (SiO_2, gradient diethyl ether in *n*-pentane = 5% to 10%) to obtain the product as a pale yellow oil (277 mg, 0.945 mmol, 30%).

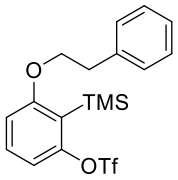
^{1}H-NMR (300 MHz, $CDCl_3$): δ (ppm) 7.40 – 7.28 (m, 4H), 7.31 – 7.21 (m, 1H), 7.13 (t, *J* = 8.2 Hz, 1H), 6.68 (dd, *J* = 8.3, 1.3 Hz, 1H), 6.45 (dd, *J* = 8.3, 1.3 Hz, 1H), 5.64 (s, 1H), 4.22 (t, *J* = 6.9 Hz, 2H), 3.16 (t, *J* = 6.9 Hz, 2H).

^{13}C-NMR (75 MHz, $CDCl_3$): δ (ppm) 155.9, 153.7, 138.2, 129.3, 128.7, 128.6, 126.7, 108.6, 104.8, 100.7, 70.1, 35.9.

HR-MS (ESI): calc. for $C_{15}H_{14}BrO_4^-$ $[M+HCOO]^-$ 337.0081 found 337.0065.

FTIR (neat): ν(cm^{-1}) 3497, 3027, 2935, 2881, 1594, 1482, 1461, 1387, 1324, 1268, 1194, 1165, 1074, 1031, 765, 700, 650.

3-Phenethoxy-2-(trimethylsilyl)phenyl trifluoromethanesulfonate (5b)



5b

Phenol **17** (235 mg, 0.800 mmol, 1.0 equiv.) and HMDS (0.18 mL, 0.88 mmol, 1.1 equiv.) were dissolved in dry THF (1.5 mL, 0.53 M) and heated to 60 °C for 18 h. The solution was concentrated *in vacuo* and then redissolved in dry THF (2.0 mL, 0.4 M) and cooled to −78°C. *n*-BuLi (1.6 M in *n*-hexane, 0.55 mL, 0.88 mmol, 1.1 equiv.) was added drop wise and after 30 min at -78 °C, Tf_2O (0.20 mL, 1.2 mmol, 1.5 equiv.) was added. After 1 h the reaction was finished by addition of sat. aq. NH_4Cl solution (5 mL). The mixture was diluted with H_2O (40 mL) and extracted with diethyl ether (3 x 30 mL). The combines org. phases were washed with sat. aq. NaCl solution (30 mL), dried over $MgSO_4$ and concentrated under reduced pressure. The crude product was via flash column chromatography on silica gel (SiO_2, *n*-pentane) to obtain the product as a colorless oil (207 mg, 0.496 mmol, 62%).

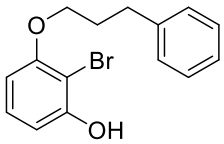
^{1}H-NMR (500 MHz, $CDCl_3$): δ (ppm) 7.36 - 7.31 (m, 3H), 7.30 - 7.24 (m, 3H), 6.94 (d, *J* = 8.3 Hz, 1H), 6.82 (d, *J* = 8.2 Hz, 1H), 4.22 (t, *J* = 7.3 Hz, 2H), 3.15 (t, *J* = 7.3 Hz, 2H), 0.34 (s, 9H).

^{13}C-NMR (126 MHz, $CDCl_3$): δ (ppm) 164.7, 154.9, 137.6, 131.7, 129.0, 128.8, 126.9, 120.9, 118.8 (q, *J* = 320.8 Hz), 112.9, 110.1, 69.4, 35.7, 1.1.

HR-MS (ESI): calc. for $C_{18}H_{21}F_3NaO_4SSi^+$ $[M+Na]^+$ 441.0774 found 441.0762.

FTIR (neat): ν(cm^{-1}) 1596, 1567, 1437, 1419, 1248, 1208, 1140, 1118, 1041, 938, 909, 843, 818, 786, 738, 699, 648, 607.

2-Bromo-3-(3-phenylpropoxy)phenol (18)



18

2-Bromoresorcinol (500 mg, 2.65 mmol, 1.0 equiv.), K_2CO_3 (804 mg, 5.82 mmol, 2.2 equiv.) and 1-bromo-3-phenylpropane (0.60 mL, 4.0 mmol, 1.5 equiv.) were dissolved in dry acetone (10 mL, 0.26 M) and heated to 55 °C for 15 h. The mixture was concentrated *in vacuo* and purified via flash column chromatography on silica gel (SiO_2, gradient diethyl ether in *n*-pentane = 5% to 10%) to obtain the product as a colorless oil (187 mg, 0.609 mmol, 23%).

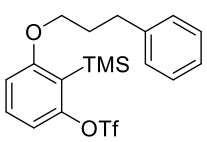
^{1}H-NMR (300 MHz, $CDCl_3$): δ (ppm) 7.38 – 7.19 (m, 5H), 7.15 (t, *J* = 8.2 Hz, 1H), 6.69 (dd, *J* = 8.2, 1.2 Hz, 1H), 6.44 (dd, *J* = 8.3, 1.1 Hz, 1H), 5.65 (s, 1H), 4.03 (t, *J* = 6.2 Hz, 2H), 2.90 (t, *J* = 7.6 Hz, 2H), 2.36 – 1.99 (m, 2H).

^{13}C-NMR (75 MHz, $CDCl_3$): δ (ppm) 156.1, 153.7, 141.5, 128.74, 128.70, 128.6, 126.1, 108.5, 104.9, 100.7, 68.1, 32.2, 30.9.

HR-MS (ESI): calc. for $C_{15}H_{15}BrNaO_2^+$ $[M+Na]^+$ 329.0148 found 329.0158.

FTIR (neat): ν(cm^{-1}) 3494, 3025, 2941, 2877, 1593, 1483, 1460, 1390, 1323, 1267, 1194, 1164, 1071, 1030, 915, 767, 748, 699, 652.

3-(3-Phenylpropoxy)-2-(trimethylsilyl)phenyl trifluoromethanesulfonate (5c)



5c

Phenol **18** (187 mg, 0.609 mmol, 1.0 equiv.) and HMDS (0.14 mL, 0.67 mmol, 1.1 equiv.) were dissolved in dry THF (1.1 mL, 0.53 M) and heated to 60 °C for 18 h. The solution was concentrated *in vacuo* and then redissolved in dry THF (1.5 mL, 0.4 M) and cooled to -78°C. *n*-BuLi (1.6 M in *n*-hexane, 0.42 mL, 0.67 mmol, 1.1 equiv.) was added drop wise and after 30 min at -78 °C, Tf_2O (0.15 mL, 0.91 mmol, 1.5 equiv.) was added. After 1 h the reaction was finished by addition of sat. aq. NH_4Cl solution (5 mL). The mixture was diluted with H_2O (40 mL) and extracted with diethyl ether (3 x 30 mL). The combines org. phases were washed with sat. aq. NaCl solution (30 mL), dried over $MgSO_4$ and concentrated under reduced pressure. The crude product was via flash column chromatography on silica gel (SiO_2, *n*-pentane) to obtain the product as a colorless oil (199 mg, 0.460 mmol, 76%).

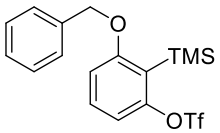
^{1}H-NMR (500 MHz, $CDCl_3$): δ (ppm) 7.25 – 7.20 (m, 3H), 7.17 – 7.10 (m, 3H), 6.85 (dd, *J* = 8.4, 0.7 Hz, 1H), 6.69 (dd, *J* = 8.3, 0.7 Hz, 1H), 3.90 (t, *J* = 6.4 Hz, 2H), 2.74 (dd, *J* = 8.7, 6.8 Hz, 2H), 2.22 – 2.00 (m, 2H), 0.34 (s, 9H).

^{13}C-NMR (126 MHz, $CDCl_3$): δ (ppm) 165.0, 154.9, 141.3, 131.7, 128.7, 128.6, 126.3, 120.7, 118.77 (q, *J* = 320.8 Hz), 112.8, 110.1, 67.9, 32.5, 31.0, 1.3.

HR-MS (ESI): calc. for $C_{19}H_{23}F_3NaO_4SSi^+$ $[M+Na]^+$ 455.0931 found 455.0941.

FTIR (neat): ν(cm^{-1}) 2953, 1596, 1566, 1436, 1416, 1247, 1205, 1139, 1118, 1038, 975, 932, 909, 835, 786, 736, 712, 699, 649, 606.

3-(Benzyloxy)-2-(trimethylsilyl)phenyl trifluoromethanesulfonate (5d)



5d

Phenol **7** (110 mg, 0.350 mmol, 1.0 equiv.), benzyl bromide (62 µL, 0.53 mmol, 1.5 equiv.), *tetra*-*n*-butyl ammonium bromide (113 mg, 0.350 mmol, 1.0 eq) and $K_3PO_4 \cdot H_2O$ (242 mg, 1.05 mmol, 3.0 equiv.) were dissolved in water (3.2 mL, 0.11 M) and stirred for 1 h. The aq. solution was diluted with water (7 mL) and extracted with diethyl ether (3 x 20 mL). The combined organic layers were washed with sat. aq. NaCl solution (20 mL), dried over $MgSO_4$ and concentrated under reduced pressure. The crude product was purified via flash column chromatography on silica gel (SiO_2, Et_2O in *n*-pentane = 1%) to obtain the product as a white solid (129 mg, 0.318 mmol, 91%). Spectroscopic data are in accordance with those reported in literature.[6]

^{1}H-NMR (300 MHz, $CDCl_3$): δ (ppm) 7.47 – 7.32 (m, 6H), 6.98 (d, *J* = 8.4 Hz, 2H), 6.90 (d, *J* = 8.2 Hz, 2H), 5.10 (s, 3H), 0.36 (s, 9H).

^{13}C-NMR (75 MHz, $CDCl_3$): δ (ppm) 164.8, 154.9, 136.2, 131.7, 128.8, 128.4, 127.9, 121.3, 118.81 (q, *J* = 320.8 Hz), 113.1, 110.7, 71.1, 1.1.

HR-MS (ESI): calc. $C_{17}H_{19}F_3NaO_4SSi^+$ $[M+Na]^+$ 427.0618 found 427.0597.

3. References synthetic procedures

[1] S. Yoshida, K. Shimomori, T. Nonaka, and T. Hosoya, *Chem.Lett.* **2015**, *44*, 1324–1326.

[2] J. Schwan, M. Kleoff, B. Hartmayer, P. Heretsch and M. Christman, *Org. Lett.* **2018**, *20*, 7661–7664.

[3] Y.-J. Kwon,Y.-K. Jeon,H.-B. Sim,I.-Y. Oh, I. Shin and W.-S. Kim, *Org. Lett.* **2017**, *19*, 6224-6227.

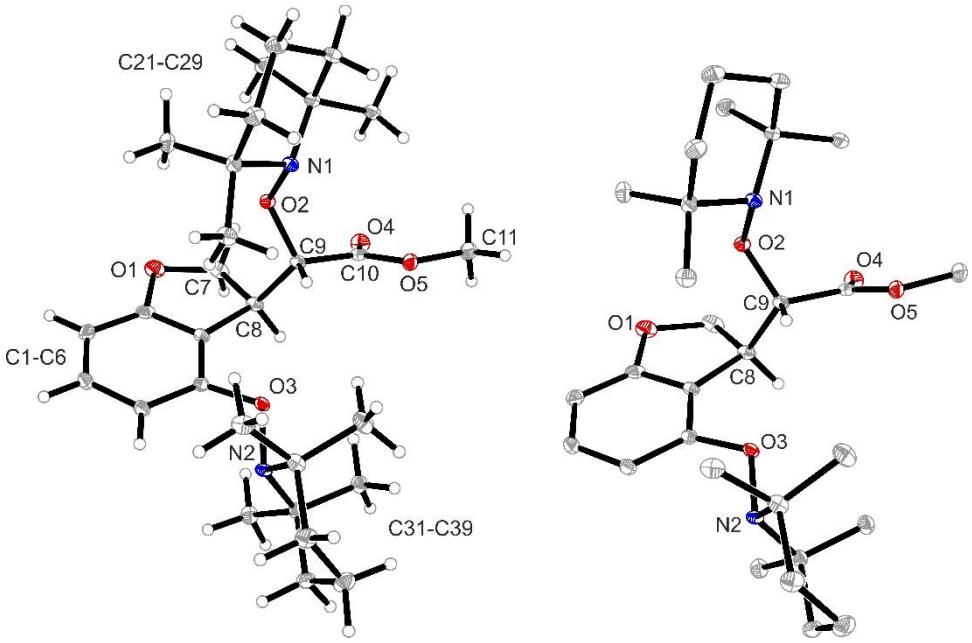
[4] T. Kitamuraand K. Otsubo, *J. Org. Chem.* **2012**, *77*, 6, 2978–2982.

[5] T. Hamura, T. Hosoya, H. Yamaguchi, Y. Kuriyama, M. Tanabe, M. Miyamoto, Y. Yasui, T. Matsumoto and K. Suzuki, *Helv. Chim. Acta* **2002**, *85*, 3589-3604.

[6] H. Takikawa*,* A. Nishii and K. Suzuki, *Synthesis* **2006,** *48,* 3331-3338.

4. X-ray crystal structures

X-ray crystal structure analysis of 1e: A colorless prism-like specimen of $C_{29}H_{46}N_2O_5$, approximate dimensions 0.123 mm x 0.173 mm x 0.286 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured on a Bruker D8 Venture PHOTON III Diffractometer system equipped with a micro focus tube Cu Ims (CuKα, λ = 1.54178 Å) and a MX mirror monochromator. A total of 1717 frames were collected. The total exposure time was 25.88 hours. The frames were integrated with the Bruker SAINT software package using a wide-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 50681 reflections to a maximum θ angle of 66.58° (0.84 Å resolution), of which 4705 were independent (average redundancy 10.772, completeness = 95.1%, R_{int} = 4.68%, R_{sig} = 2.33%) and 4253 (90.39%) were greater than $2\sigma(F^2)$. The final cell constants of a = 11.8849(2) Å, b = 13.4514(3) Å, c = 18.5190(4) Å, β = 108.3920(10)°, volume = 2809.38(10) $Å^3$, are based upon the refinement of the XYZ-centroids of 9923 reflections above 20 σ(I) with 8.277° < 2θ < 136.5°. Data were corrected for absorption effects using the Multi-Scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.919. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.8380 and 0.9250. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group $P2_1/n$, with Z = 4 for the formula unit, $C_{29}H_{46}N_2O_5$. The final anisotropic full-matrix least-squares refinement on F^2 with 334 variables converged at R1 = 3.28%, for the observed data and wR2 = 8.13% for all data. The goodness-of-fit was 1.046. The largest peak in the final difference electron density synthesis was 0.227 $e^-/Å^3$ and the largest hole was -0.174 $e^-/Å^3$ with an RMS deviation of 0.031 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.188 g/cm^3 and F(000), 1096 e^-. CCDC number: 2030809.



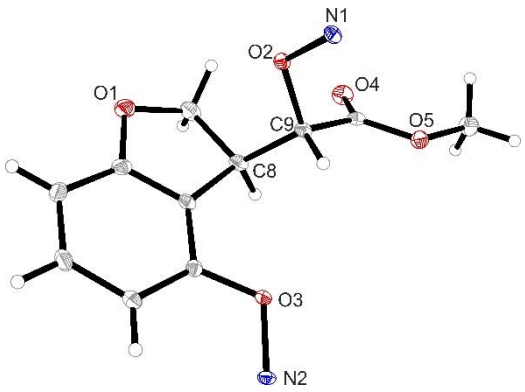


Figure S1: a) Crystal structure of compound **1e**. b) Hydrogen atoms except for the carbon atoms C8 and C9 were omitted for clarity. c) TEMPO units were omitted for clarity, only nitrogen atom is shown. Thermal ellipsoids are set at 30% probability.

X-ray crystal structure analysis of 1h: A colorless needle-like specimen of $C_{32}H_{46}N_2O_5S$, approximate dimensions 0.058 mm x 0.114 mm x 0.251 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured on a Bruker D8 Venture PHOTON III Diffractometer system equipped with a micro focus tube Cu Ims (CuK_α, λ = 1.54178 Å) and a MX mirror monochromator. A total of 1500 frames were collected. The total exposure time was 20.59 hours. The frames were integrated with the Bruker SAINT software package using a wide-frame algorithm. The integration of the data using an orthorhombic unit cell yielded a total of 61470 reflections to a maximum θ angle of 68.36° (0.83 Å resolution), of which 5695 were independent (average redundancy 10.794, completeness = 99.8%, R_{int} = 13.33%, R_{sig} = 5.55%) and 4693 (82.41%) were greater than $2\sigma(F^2)$. The final cell constants of a = 11.6625(2) Å, b = 12.2376(3) Å, c = 21.7465(5) Å, volume = 3103.68(12) $Å^3$, are based upon the refinement of the XYZ-centroids of 9986 reflections above 20 σ(I) with 8.131° < 2θ < 136.1°. Data were corrected for absorption effects using the Multi-Scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.916. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.7430 and 0.9310. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group $P2_12_12_1$, with Z = 4 for the formula unit, $C_{32}H_{46}N_2O_5S$. The final anisotropic full-matrix least-squares refinement on F^2 with 370 variables converged at R1 = 5.37%, for the observed data and wR2 = 14.29% for all data. The goodness-of-fit was 1.060. The largest peak in the final difference electron density synthesis was 0.454 $e^-/Å^3$ and the largest hole was -0.266 $e^-/Å^3$ with an RMS deviation of 0.056 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.221 g/cm^3 and F(000), 1232 e^-. CCDC number: 2030810.

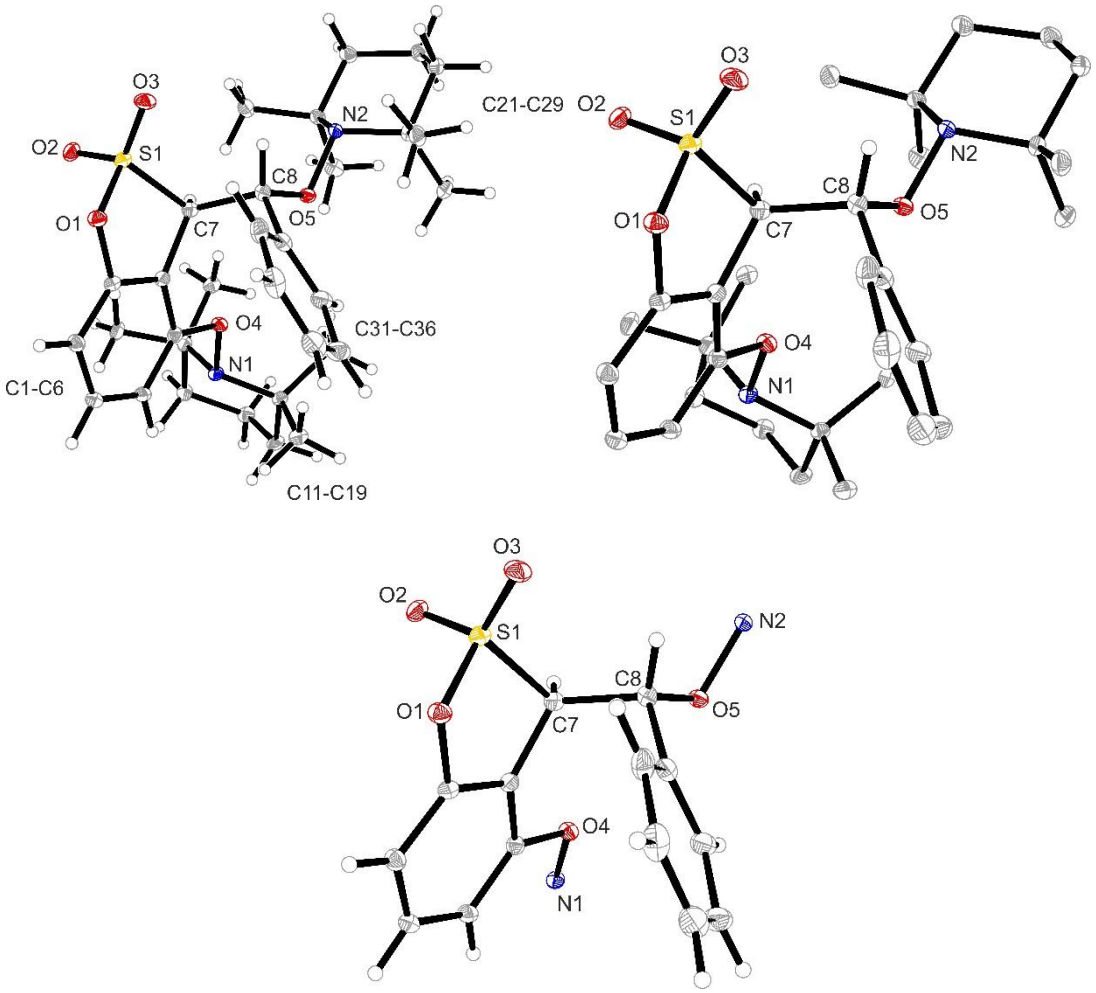


Figure S2: a) Crystal structure of compound **1h**. b) Hydrogen atoms except for the carbon atoms C7 and C8 were omitted for clarity. c) TEMPO units were omitted for clarity, only nitrogen atom is shown. Thermal ellipsoids are set at 15% probability.

X-ray crystal structure analysis of 3: A colorless prism-like specimen of $C_{24}H_{40}N_2O_2$, approximate dimensions 0.162 mm x 0.219 mm x 0.268 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. A total of 296 frames were collected. The total exposure time was 2.06 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 12808 reflections to a maximum θ angle of 26.72° (0.79 Å resolution), of which 2405 were independent (average redundancy 5.326, completeness = 98.2%, R_{int} = 3.79%, R_{sig} = 2.58%) and 2179 (90.60%) were greater than $2\sigma(F^2)$. The final cell constants of a = 13.0188(5) Å, b = 9.0818(3) Å, c = 20.2160(7) Å, β = 104.6330(10)°, volume = 2312.69(14) $Å^3$, are based upon the refinement of the XYZ-centroids of 6077 reflections above 20 σ(I) with 5.613° < 2θ < 53.43°. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.951. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.9810 and 0.9890. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group *C*2/*c*, with Z = 4 for the formula unit, $C_{24}H_{40}N_2O_2$. The final anisotropic full-matrix least-squares refinement on F^2 with 131 variables converged at R1 = 3.86%, for the observed data and wR2 = 9.32% for all data. The goodness-of-fit was 1.050. The largest peak in the final difference electron density synthesis was 0.297 $e^-/Å^3$ and

the largest hole was -0.186 $e^-/Å^3$ with an RMS deviation of 0.034 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.116 g/cm^3 and F(000), 856 e^-. CCDC number: 2030811.

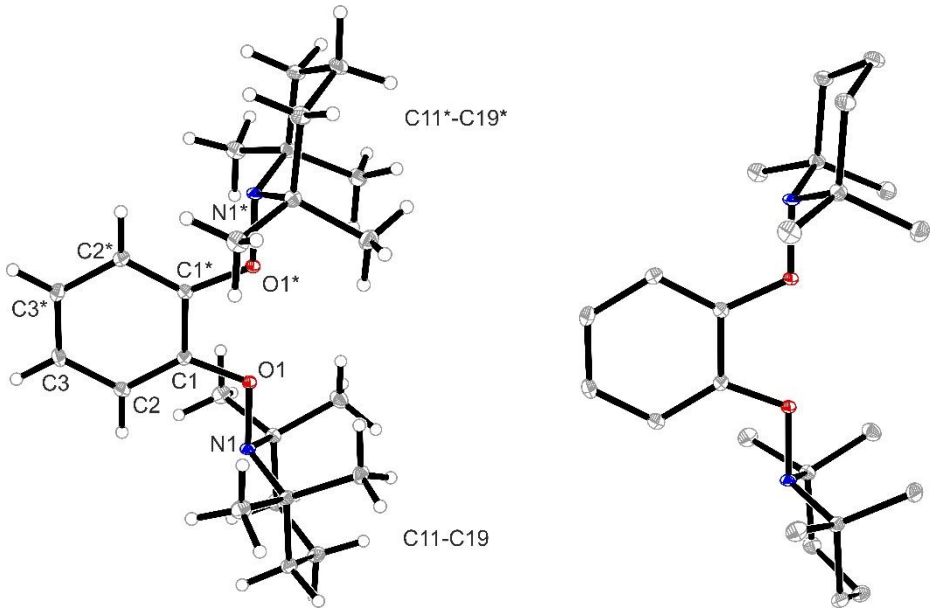


Figure S3: Crystal structure of compound **3**.
Thermal ellipsoids are set at 30% probability.

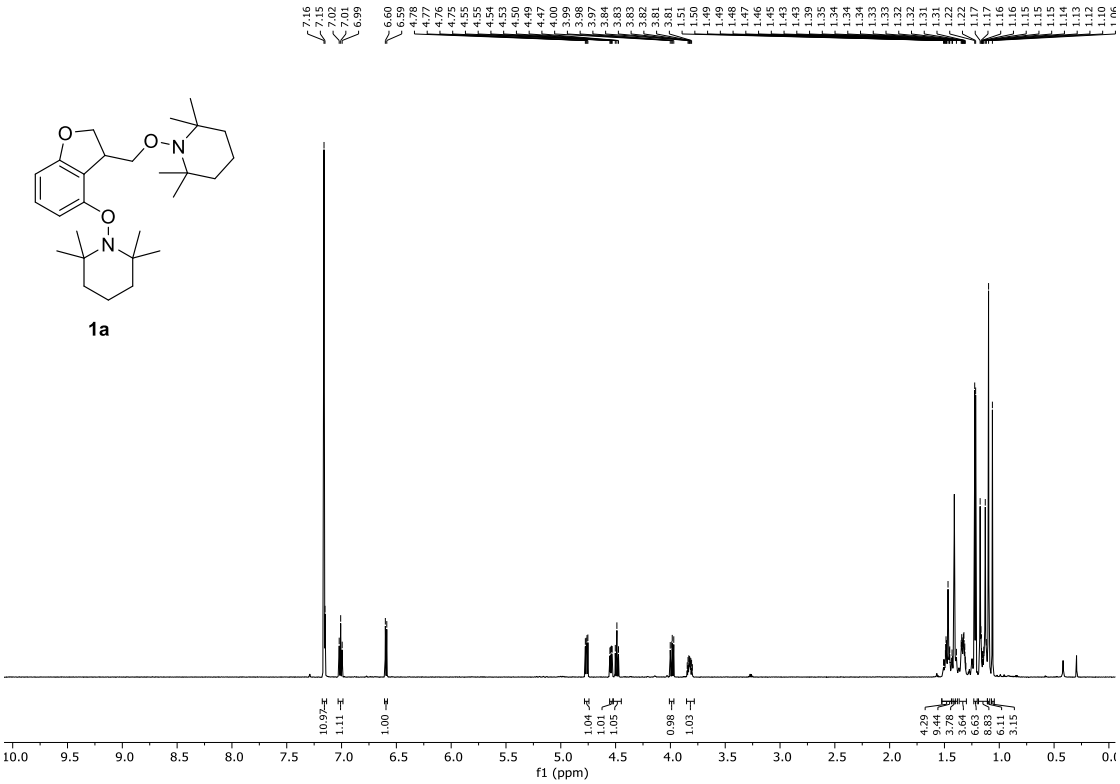
5. References X-ray crystallography

1. *APEX3* (**2016**), *SAINT* (**2015**) and *SADABS* (**2015**), Bruker AXS Inc., Madison, Wisconsin, USA.
2. Sheldrick, G. M., *SHELXT – Integrated space-group and crystal-structure determination*, *Acta Cryst.,* **2015**, *A71*, 3-8.
3. Sheldrick, G.M., *Crystal structure refinement with SHELXL*, *Acta Cryst.*, **2015**, *C71 (1)*, 3-8.
4. *XP – Interactive molecular graphics, Version 5.1,* Bruker AXS Inc., Madison, Wisconsin, USA, **1998**.

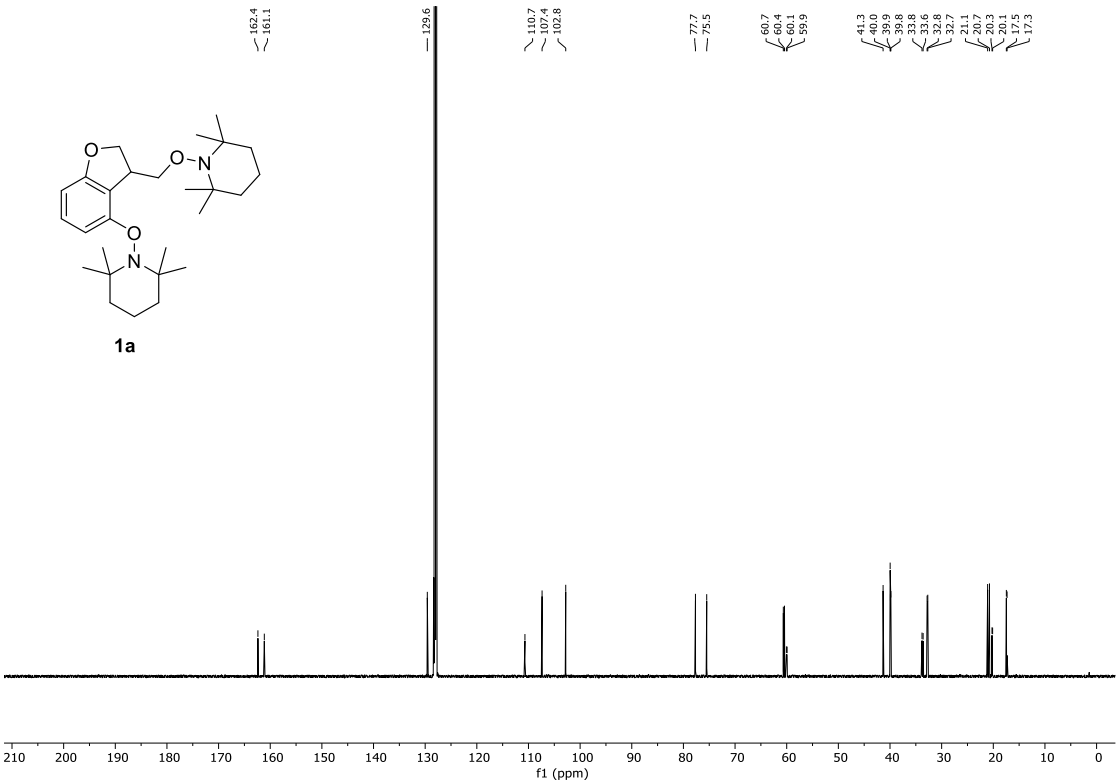
6. NMR-spectra

2,2,6,6-Tetramethyl-1-((4-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)-2,3-dihydrobenzofuran-3-yl)methoxy)piperidine (1a)

^{1}H-NMR (600 MHz, C_6D_6)

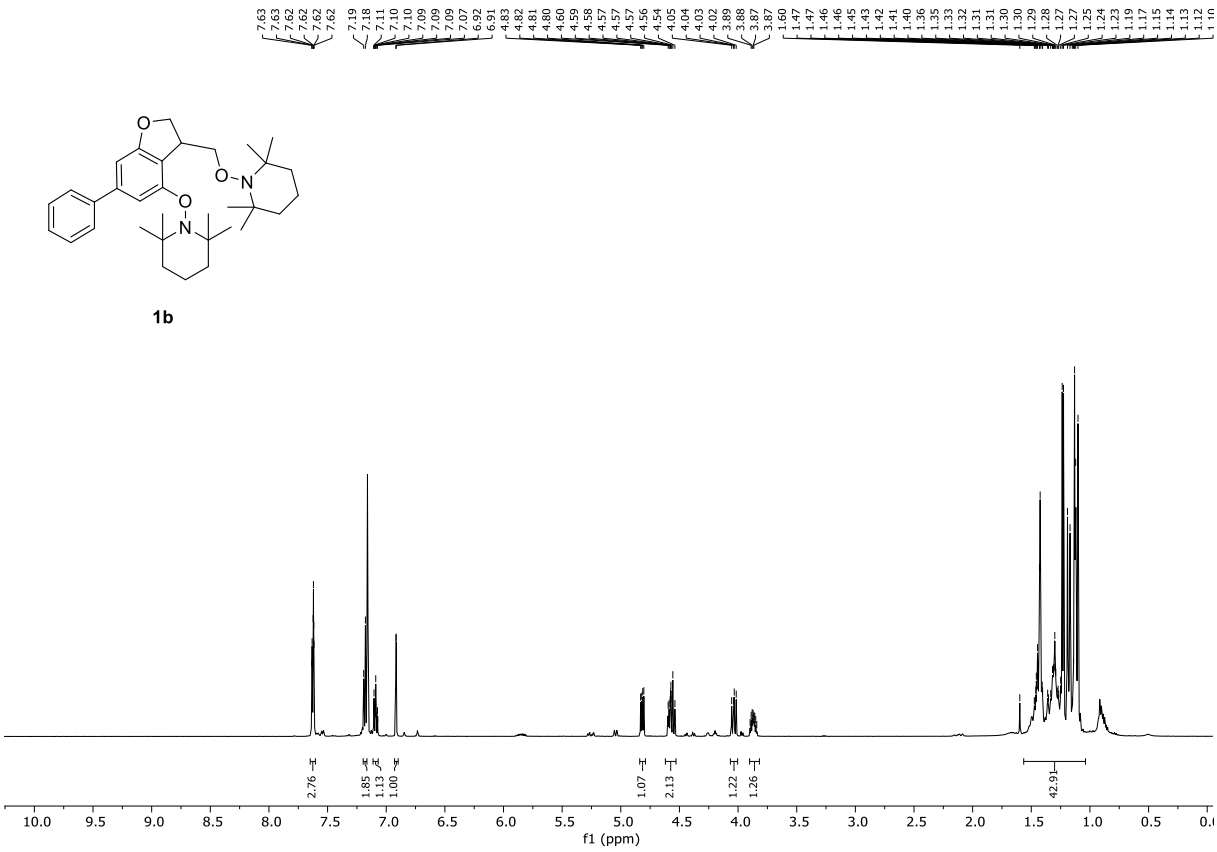


^{13}C-NMR (151 MHz, C_6D_6)



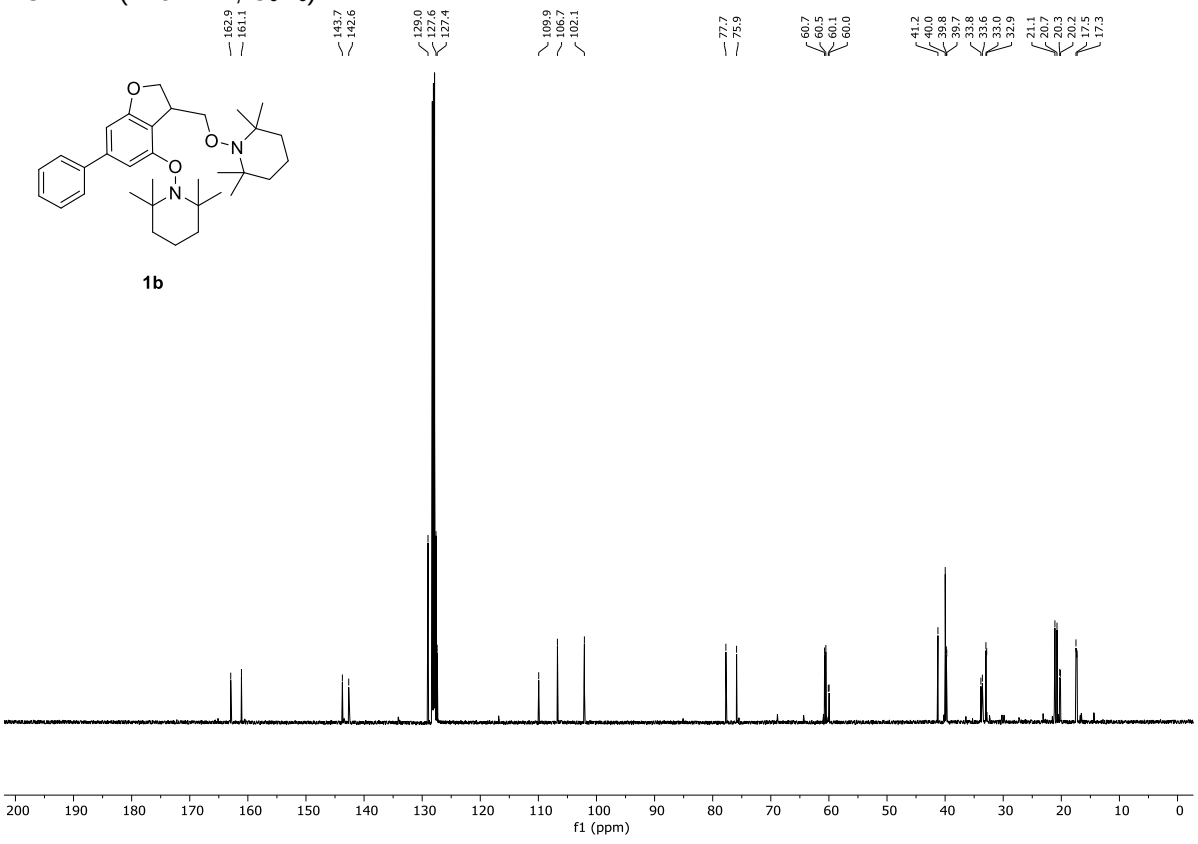
2,2,6,6-Tetramethyl-1-((6-phenyl-3-(((2,2,6,6-tetramethylpiperidin-1-yl)oxy)methyl)-2,3-dihydrobenzofuran-4-yl)oxy)piperidine (1b)

^{1}H-NMR (500 MHz, C_6D_6)



1b

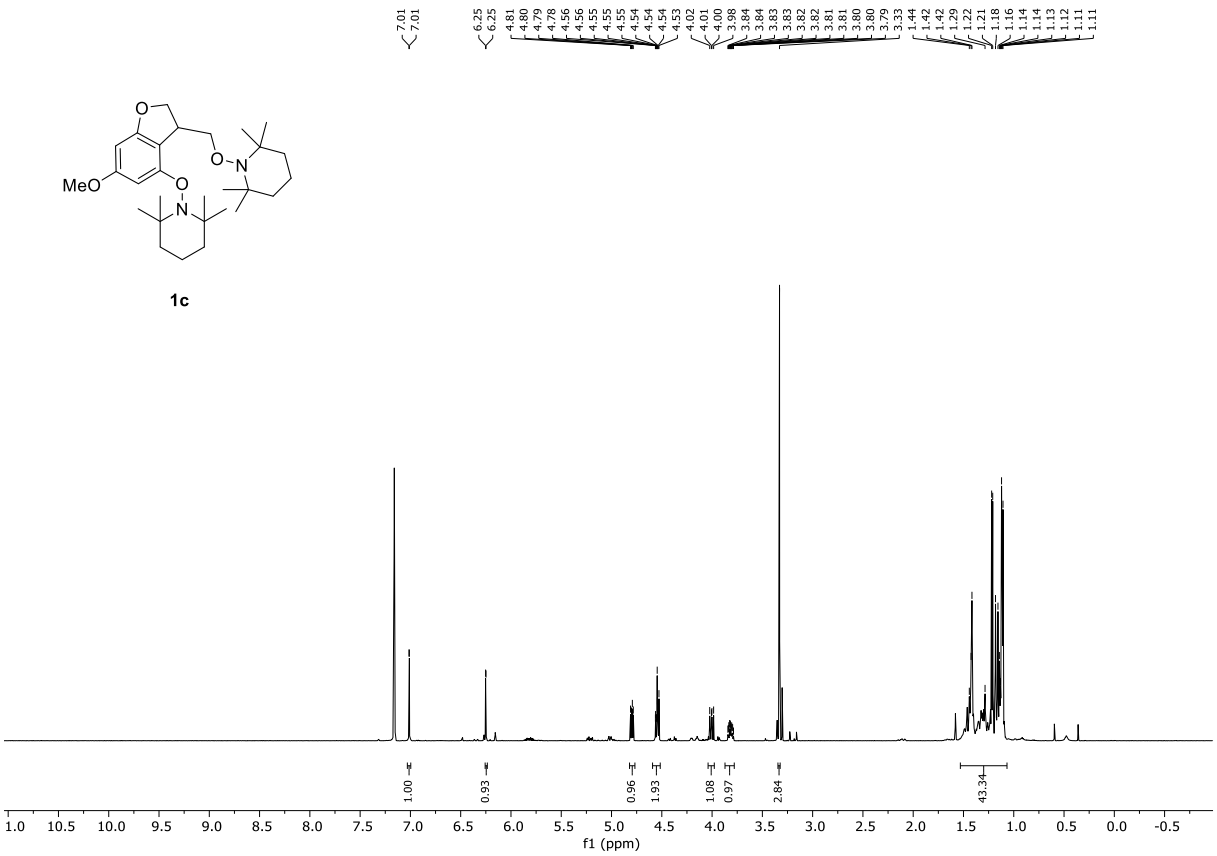
^{13}C-NMR (126 MHz, C_6D_6)



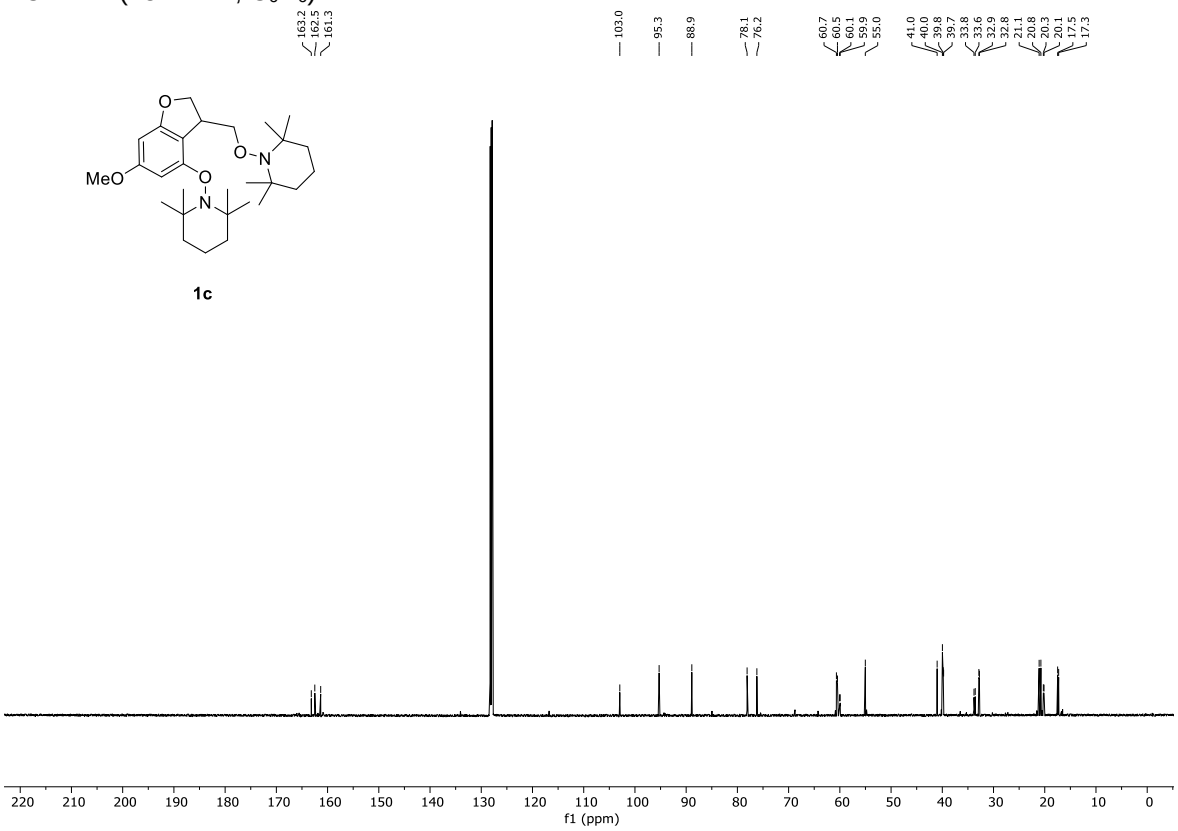
1b

2,2,6,6-Tetramethyl-1-((6-phenyl-3-(((2,2,6,6-tetramethylpiperidin-1-yl)oxy)methyl)-2,3-dihydrobenzofuran-4-yl)oxy)piperidine (1b)

^{1}H-NMR (500 MHz, C_6D_6)

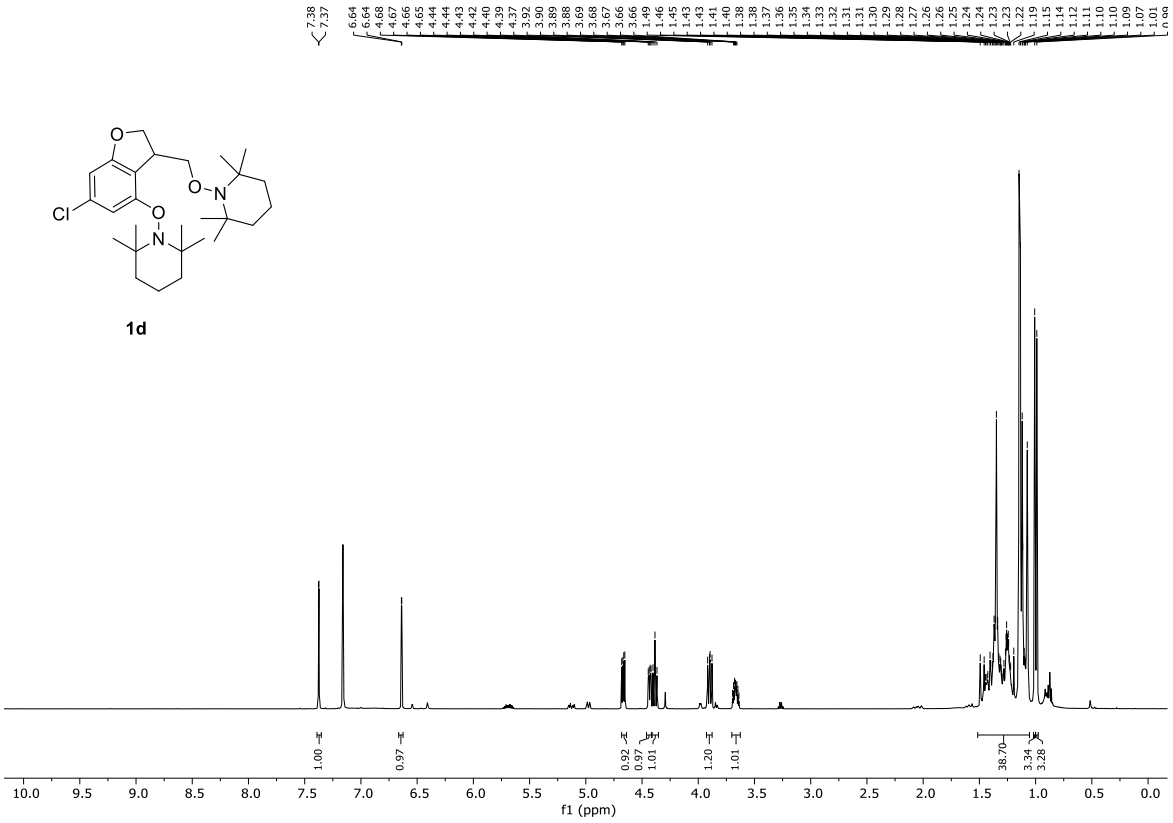


^{13}C-NMR (151 MHz, C_6D_6)

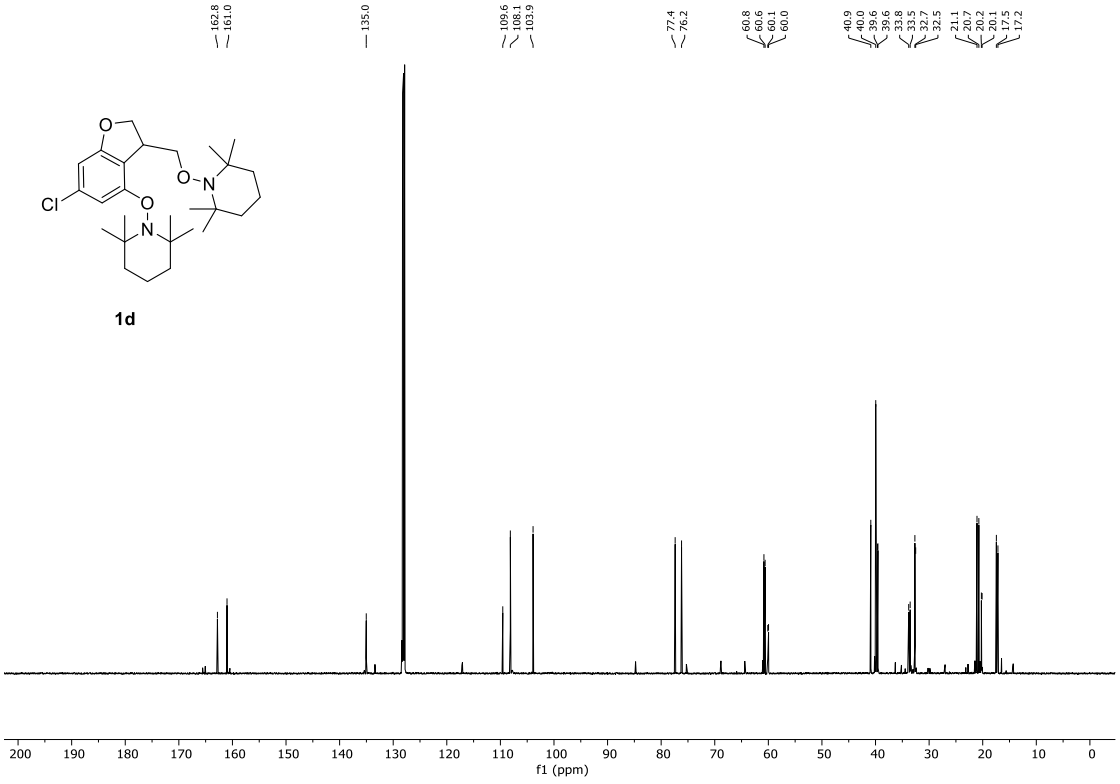


1-((6-Chloro-3-(((2,2,6,6-tetramethylpiperidin-1-yl)oxy)methyl)-2,3-dihydrobenzofuran-4-yl)oxy)-2,2,6,6-tetramethylpiperidine (1d)

^{1}H-NMR (500 MHz, C_6D_6)

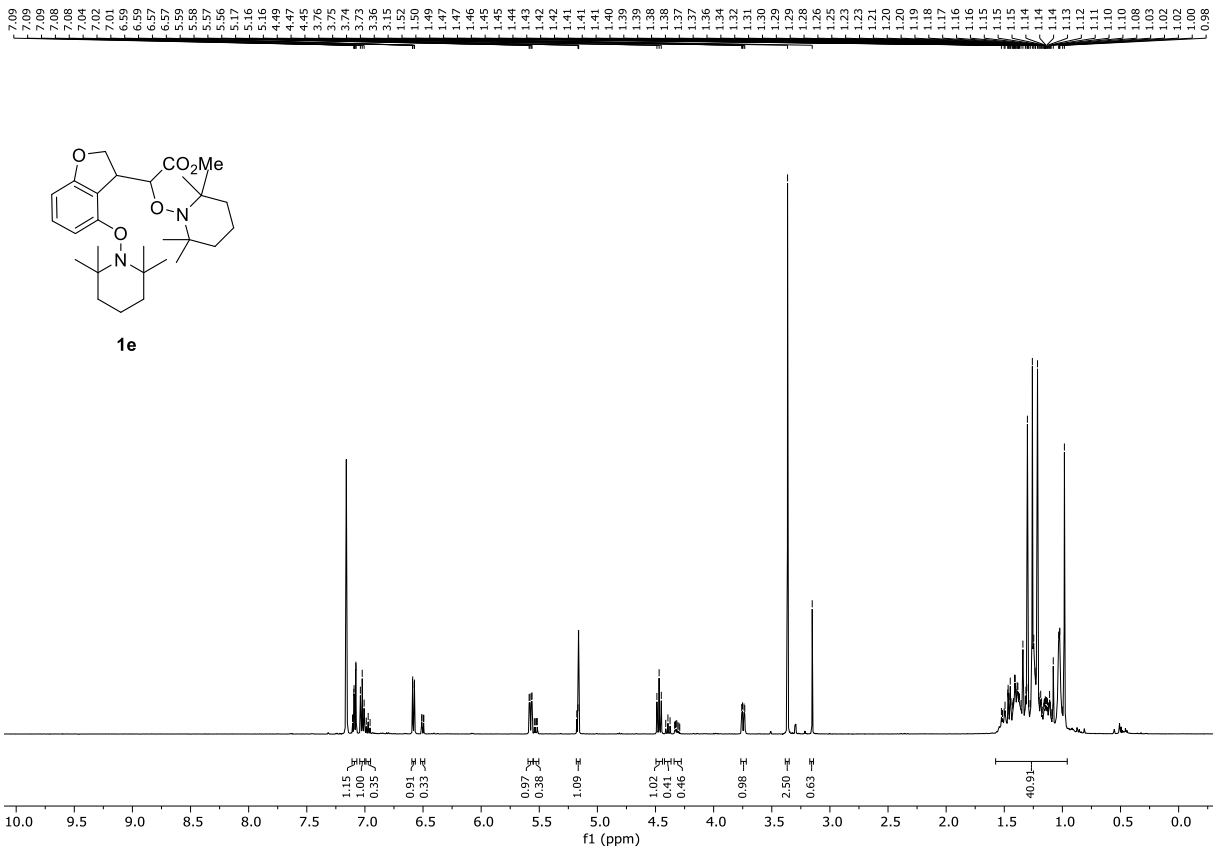


^{13}C-NMR (126 MHz, C_6D_6)



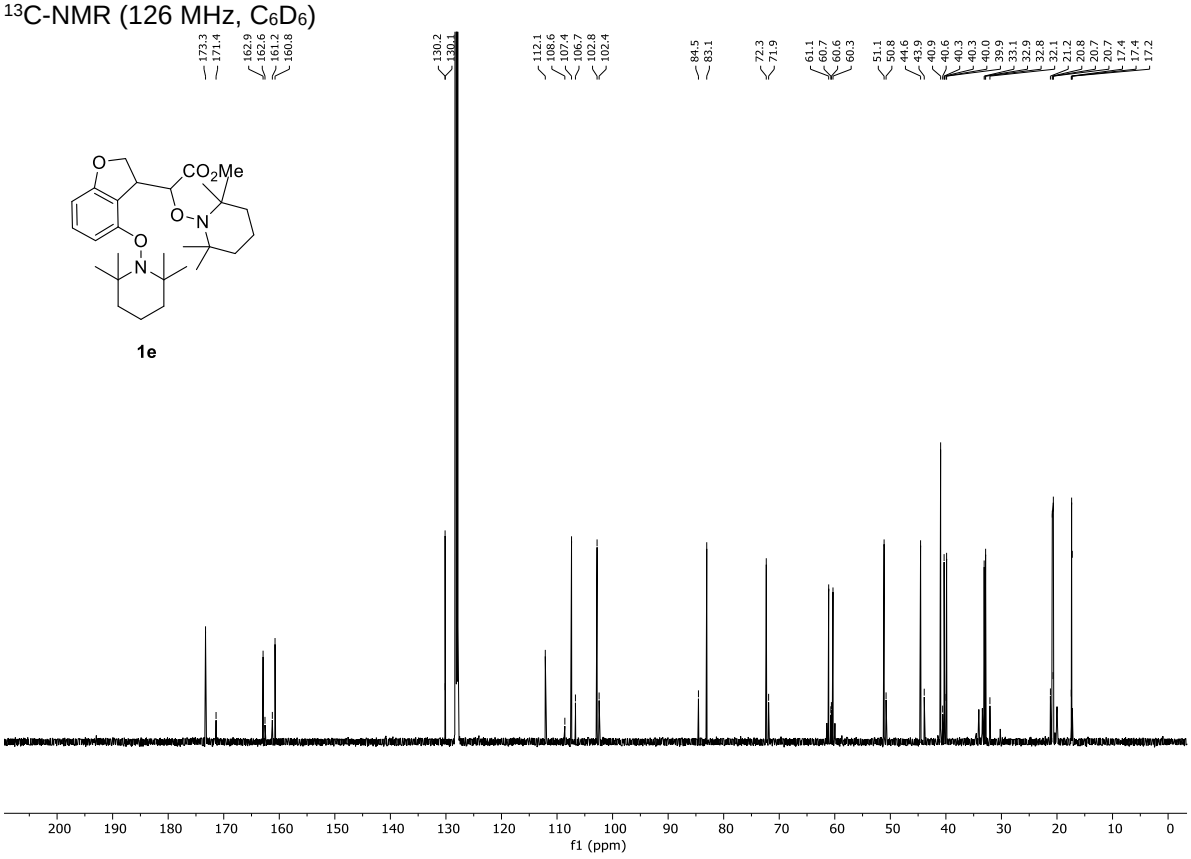
Methyl 2-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)-2-(4-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)-2,3-dihydrobenzofuran-3-yl)acetate (1e)

^{1}H-NMR (500 MHz, C_6D_6)



1e

^{13}C-NMR (126 MHz, C_6D_6)

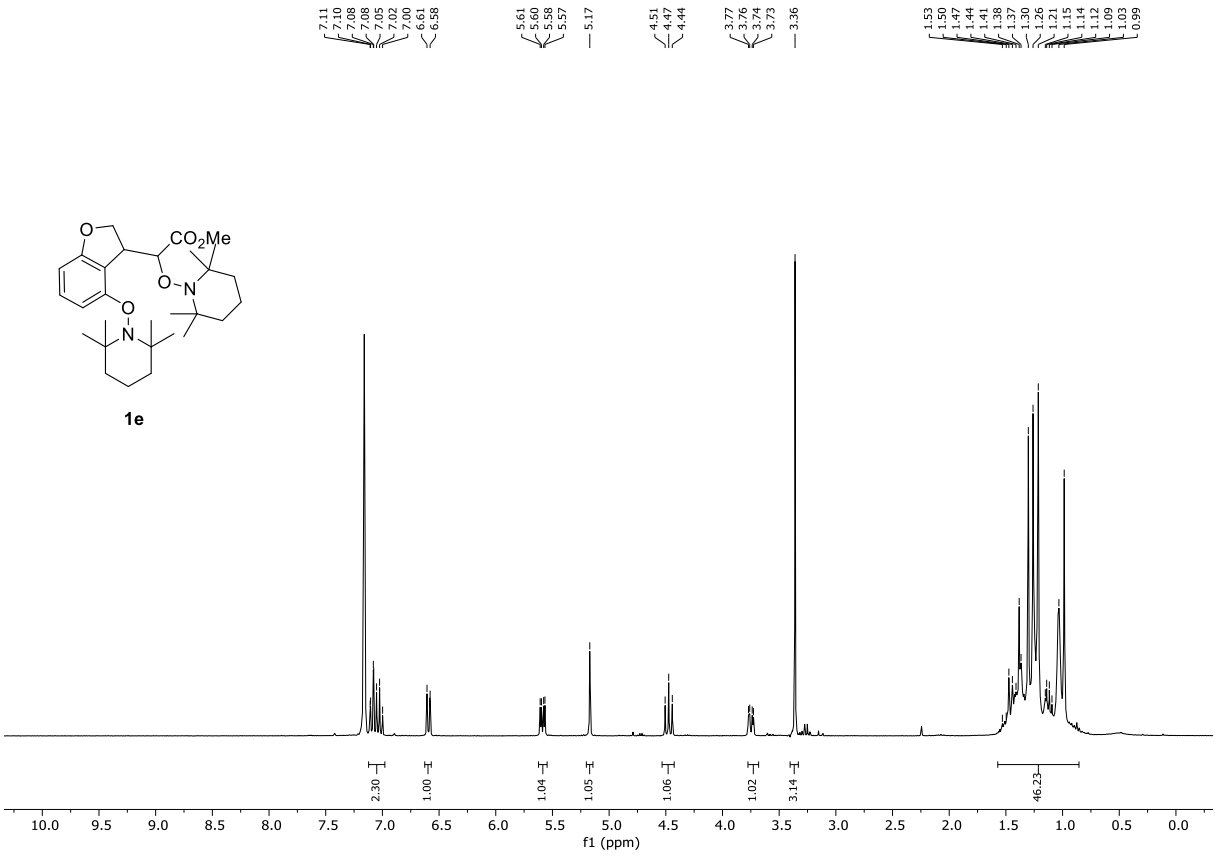


1e

Methyl 2-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)-2-(4-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)-2,3-dihydrobenzofuran-3-yl)acetate (1e)

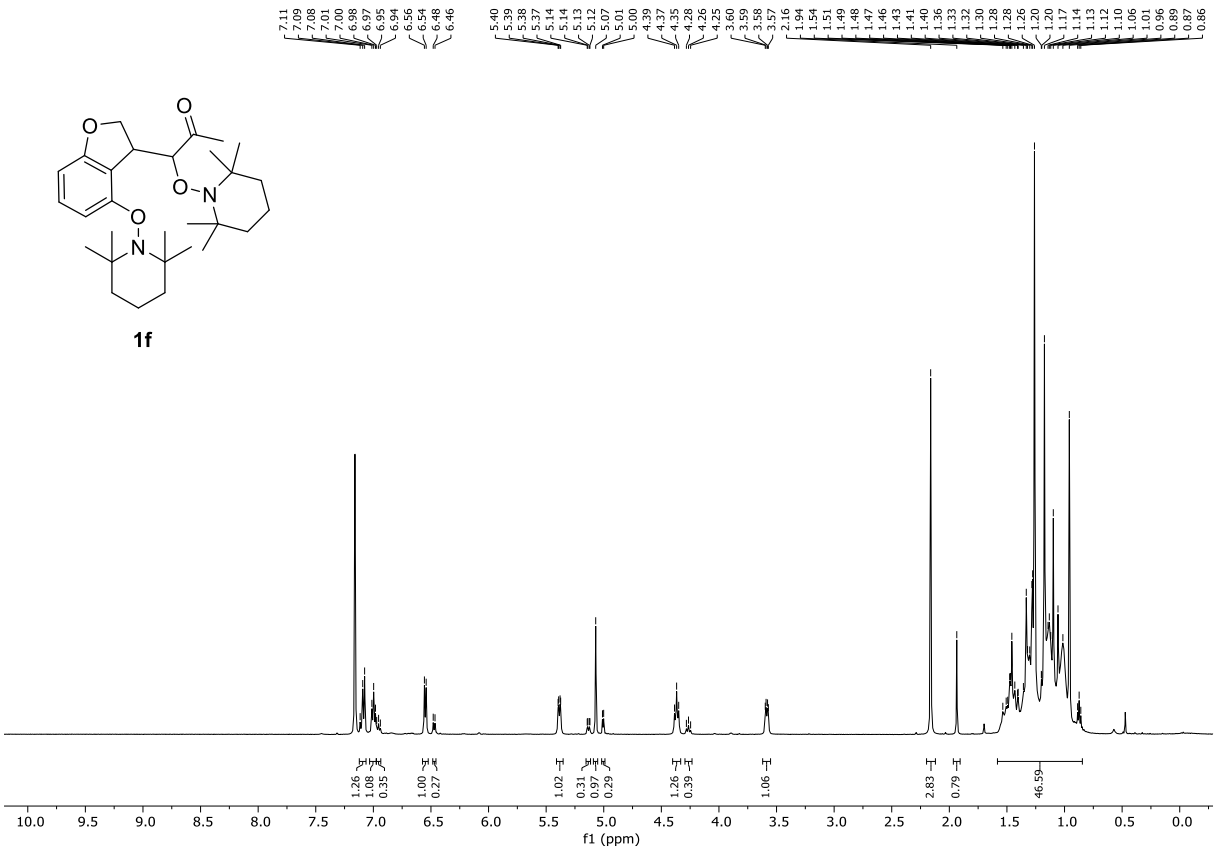
Major diastereomer of **1e** after separation via Medium Pressure Liquid Chromatography (MPLC) which was used for X-ray crystallography:

^{1}H-NMR (300 MHz, C_6D_6)

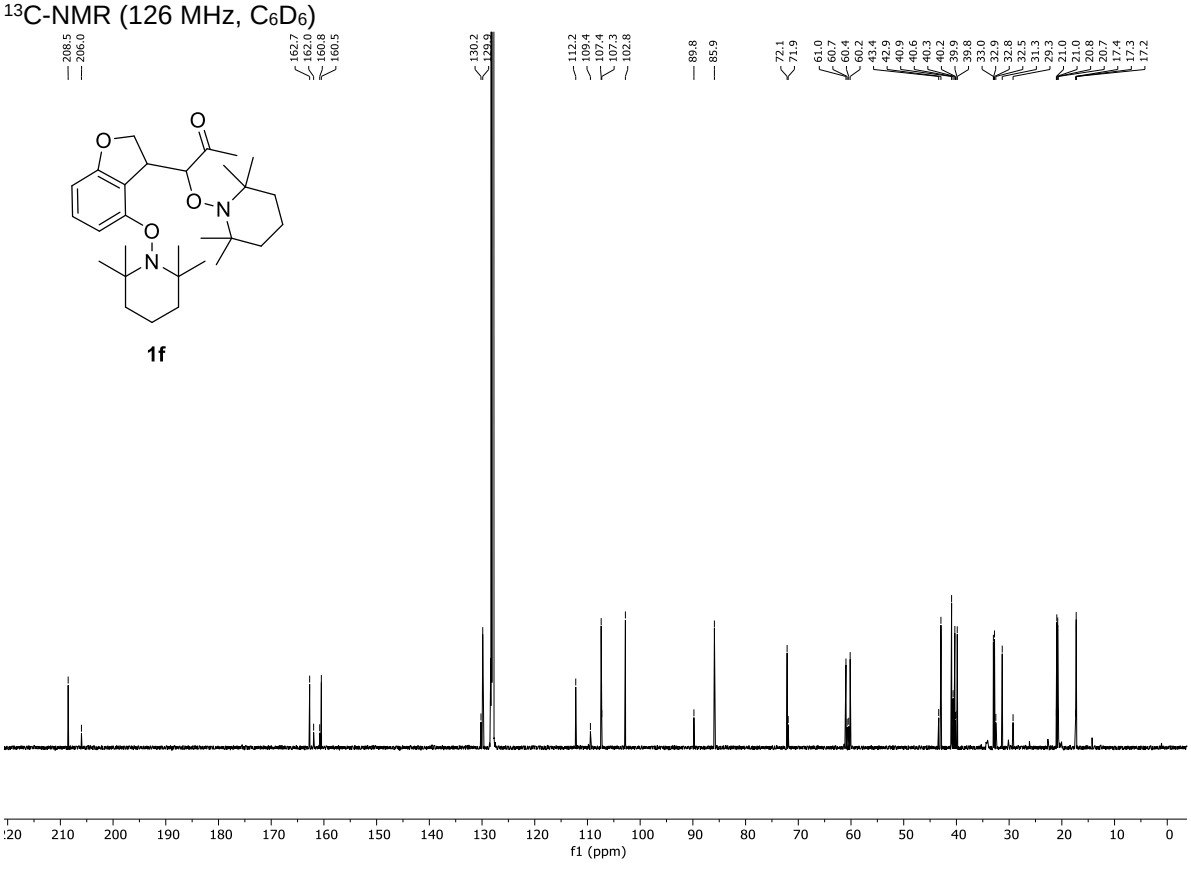


1-((2,2,6,6-Tetramethylpiperidin-1-yl)oxy)-1-(4-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)-2,3-dihydrobenzofuran-3-yl)propan-2-one (1f)

^{1}H-NMR (500 MHz, C_6D_6)

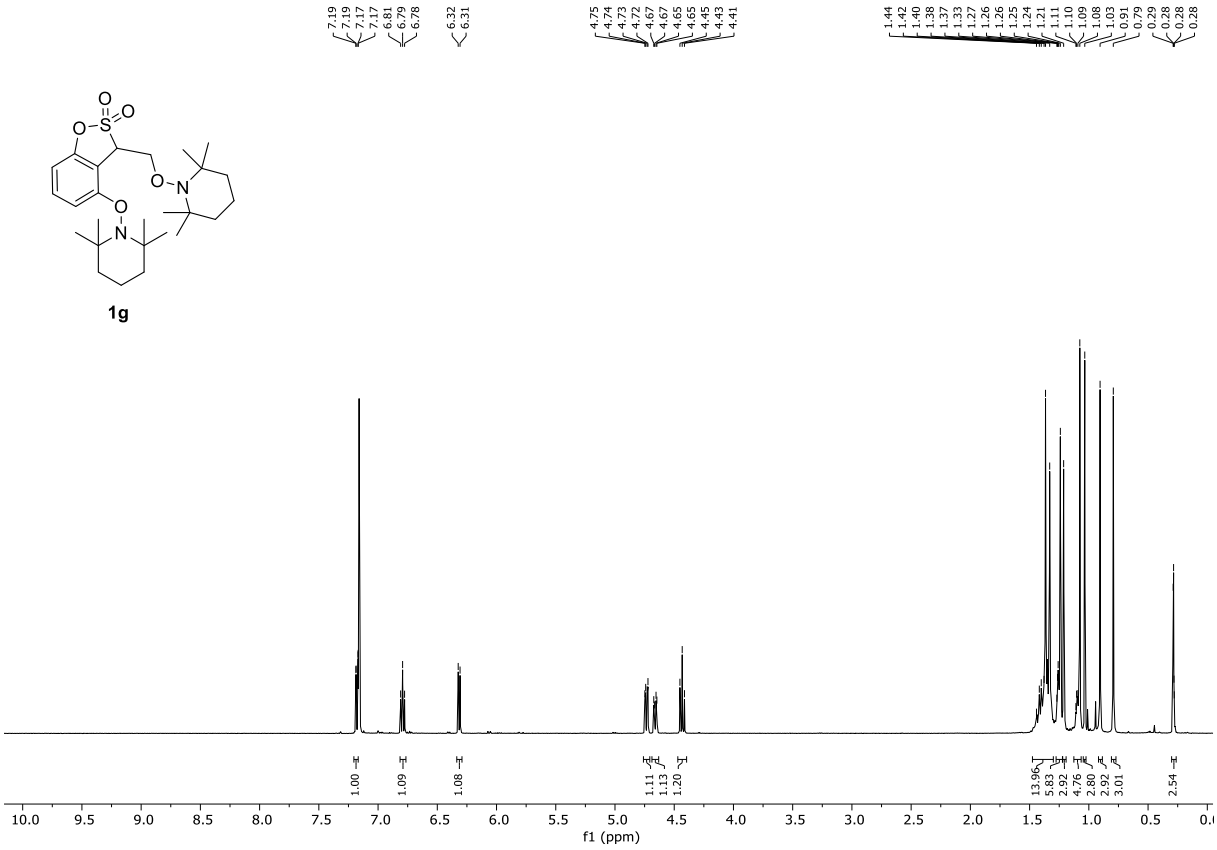


^{13}C-NMR (126 MHz, C_6D_6)



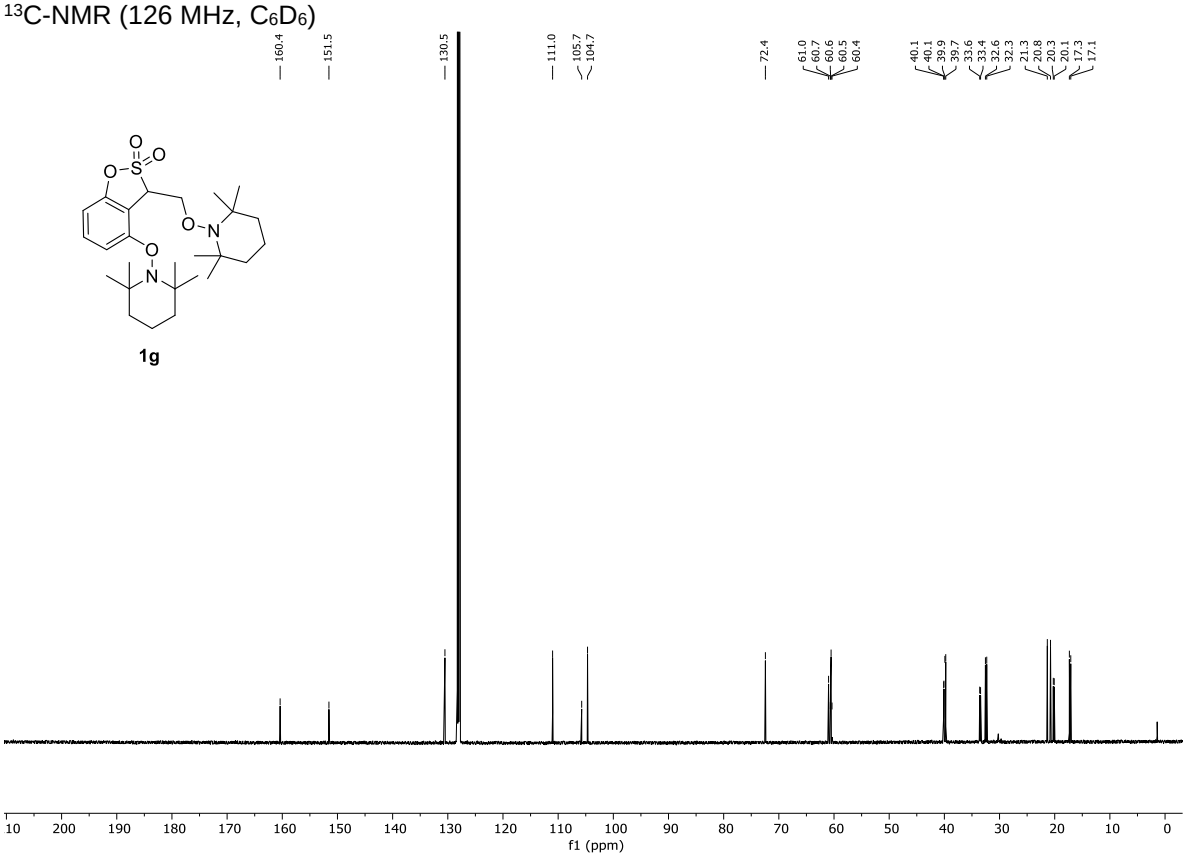
4-((2,2,6,6-Tetramethylpiperidin-1-yl)oxy)-3-(((2,2,6,6-tetramethylpiperidin-1-yl)oxy)methyl)-3H-benzo[d][1,2]oxathiole 2,2-dioxide (1g)

^{1}H-NMR (500 MHz, C_6D_6)



1g

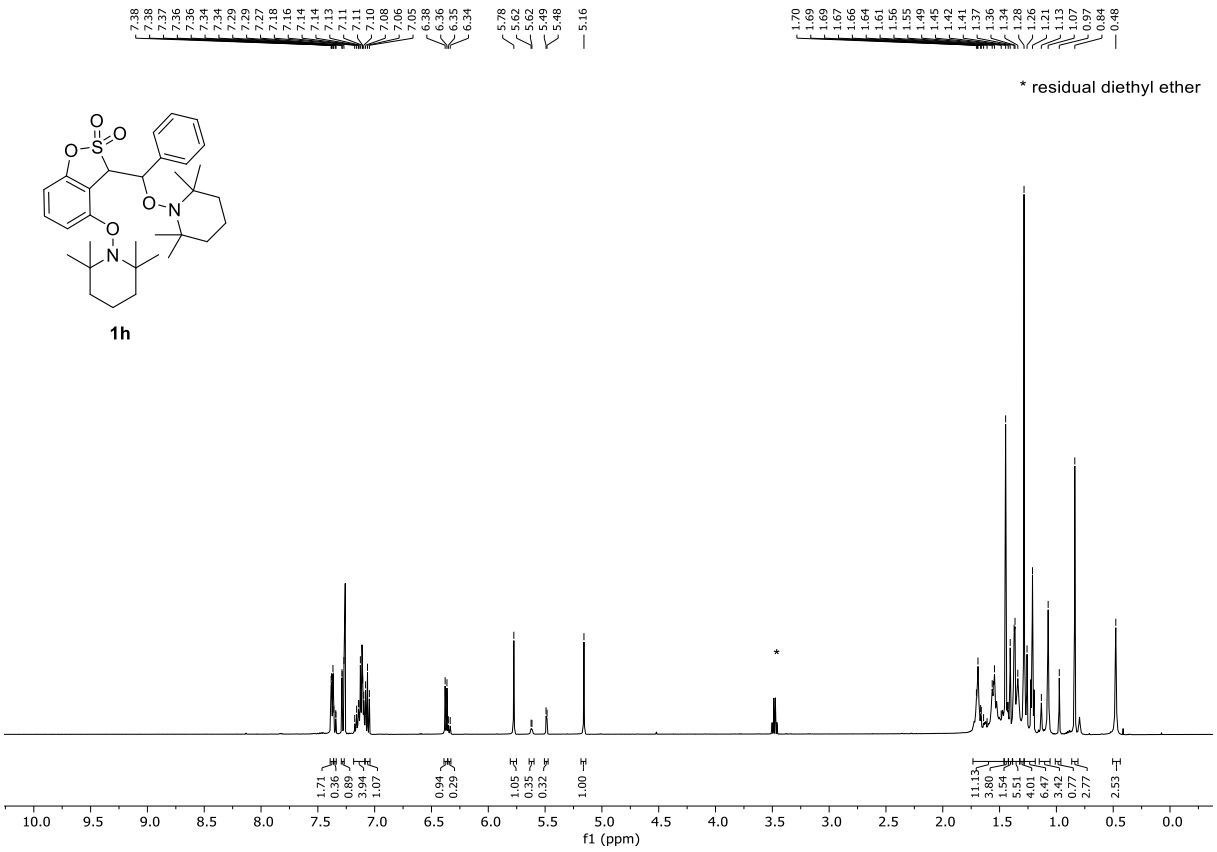
^{13}C-NMR (126 MHz, C_6D_6)



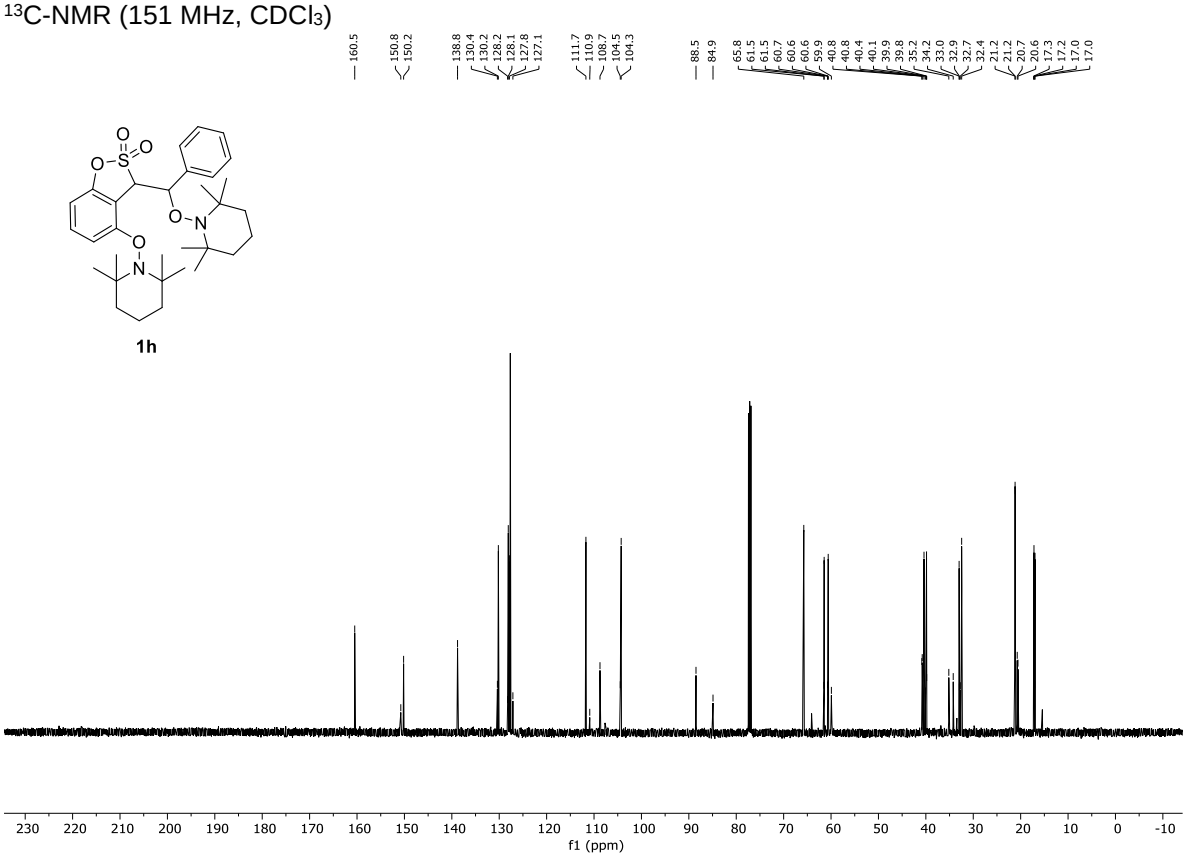
1g

3-(Phenyl((2,2,6,6-tetramethylpiperidin-1-yl)oxy)methyl)-4-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)-3H-benzo[d][1,2]oxathiole 2,2-dioxide (1h)

^{1}H-NMR (599 MHz, $CDCl_3$)



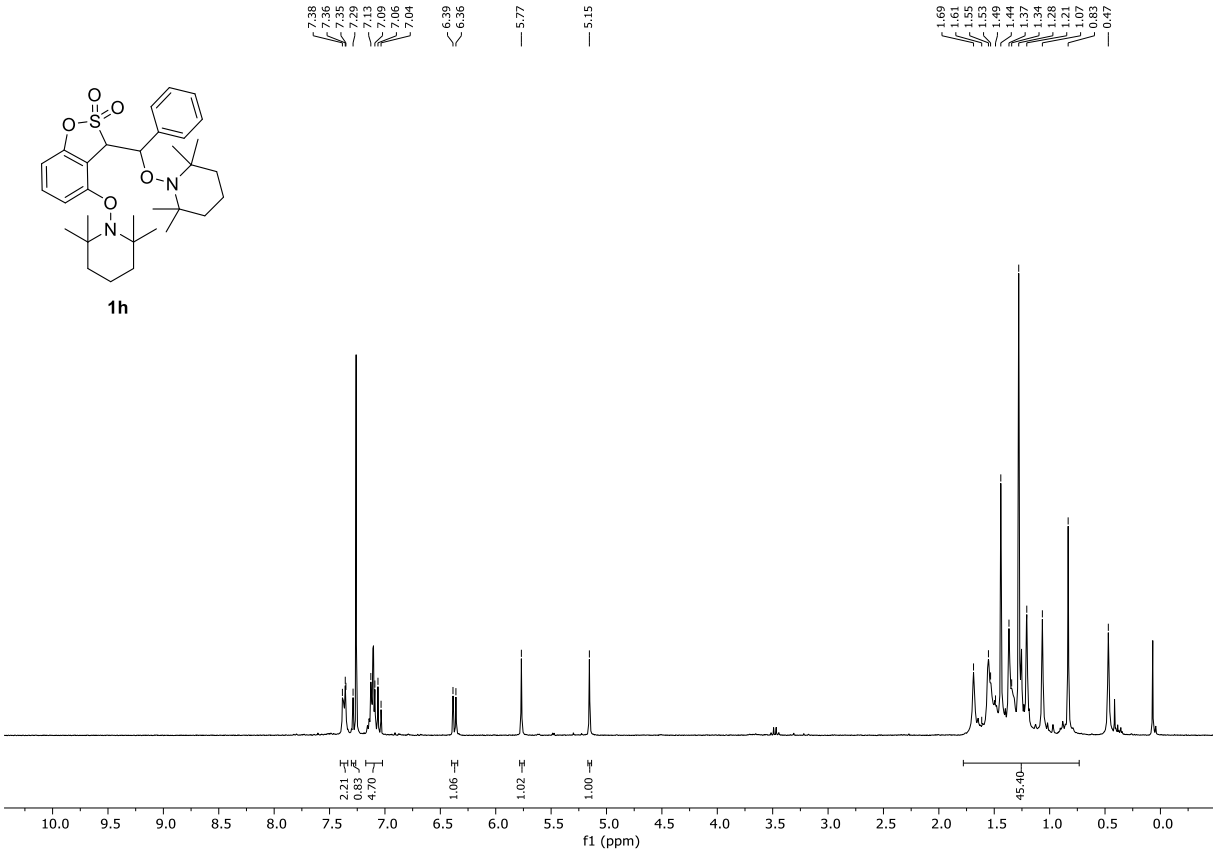
^{13}C-NMR (151 MHz, $CDCl_3$)



3-(Phenyl((2,2,6,6-tetramethylpiperidin-1-yl)oxy)methyl)-4-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)-3H-benzo[d][1,2]oxathiole 2,2-dioxide (1h)

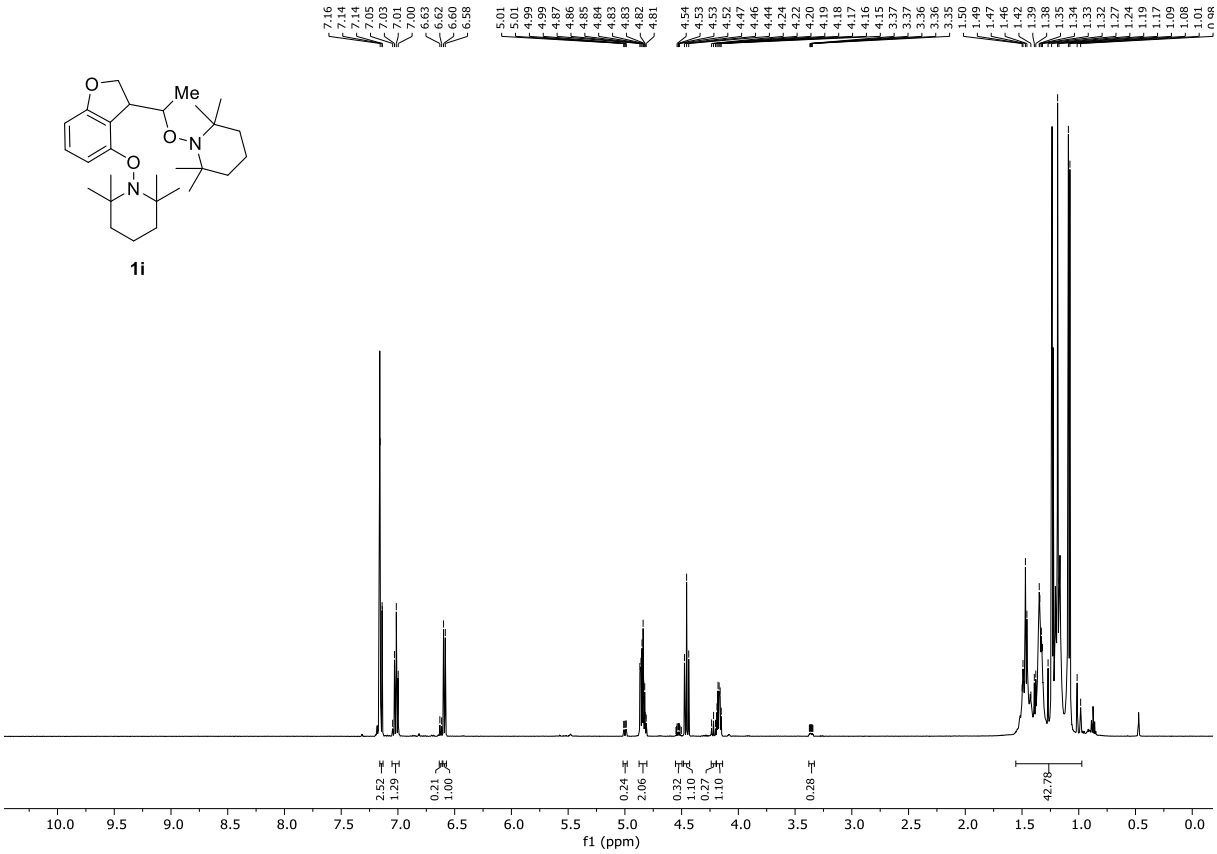
Major diastereomer of **1h** after separation via preparative TLC which was used for X-ray crystallography:

^{1}H-NMR (300 MHz, $CDCl_3$)

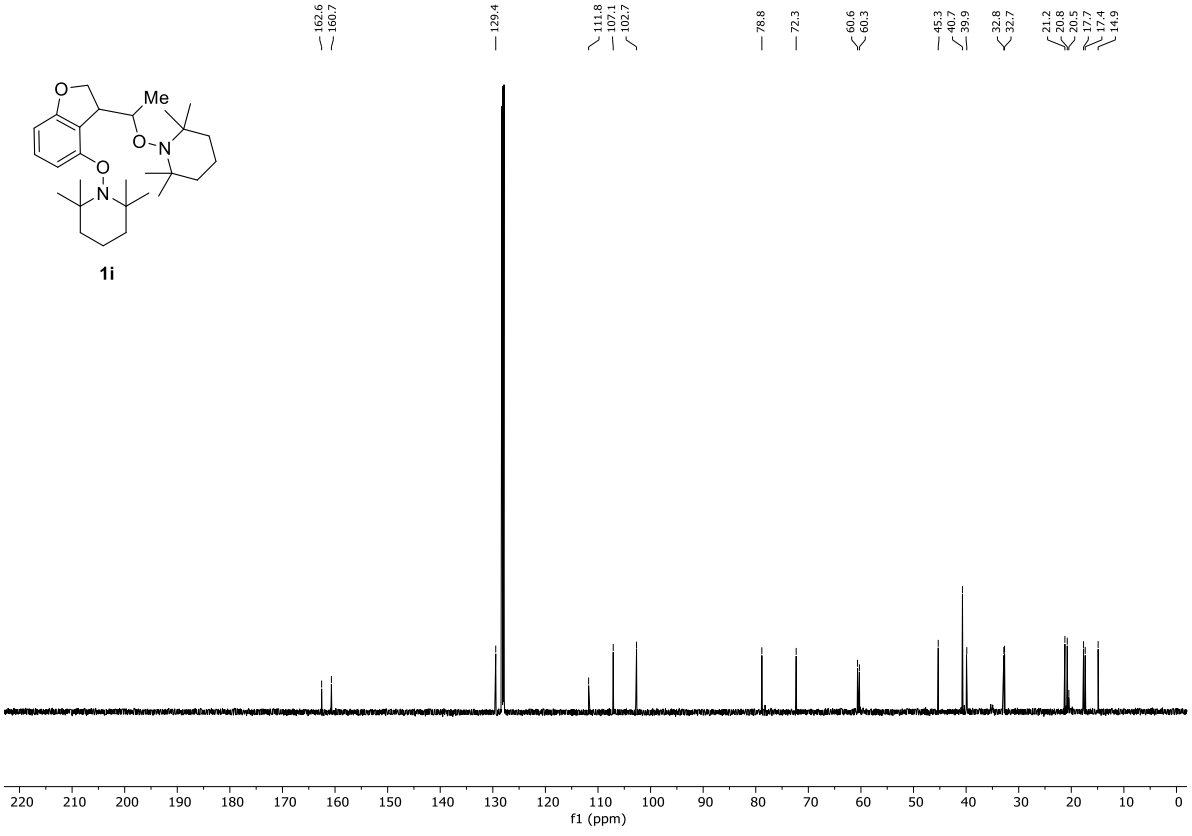


2,2,6,6-Tetramethyl-1-(1-(4-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)-2,3-dihydrobenzofuran-3-yl)ethoxy)piperidine (1i)

^{1}H-NMR (500 MHz, C_6D_6)

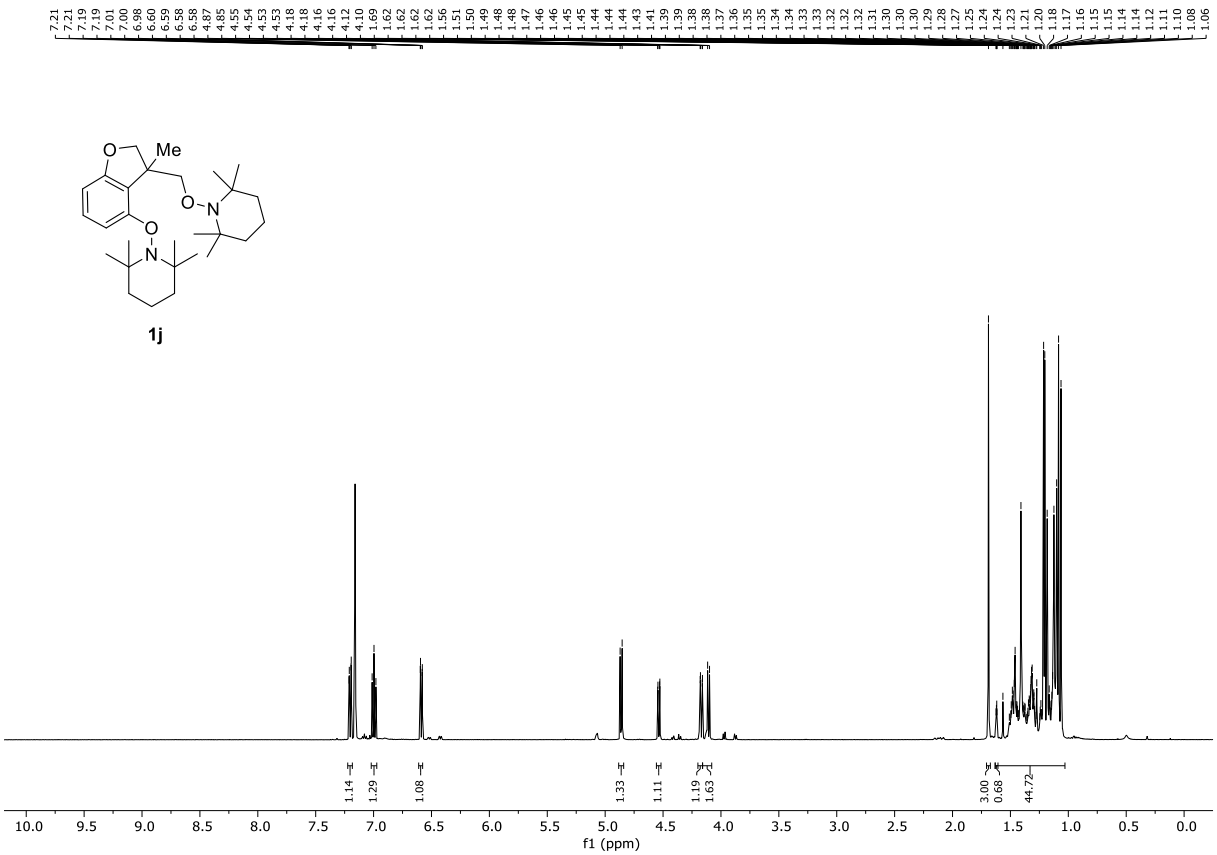


^{13}C-NMR (126 MHz, C_6D_6)

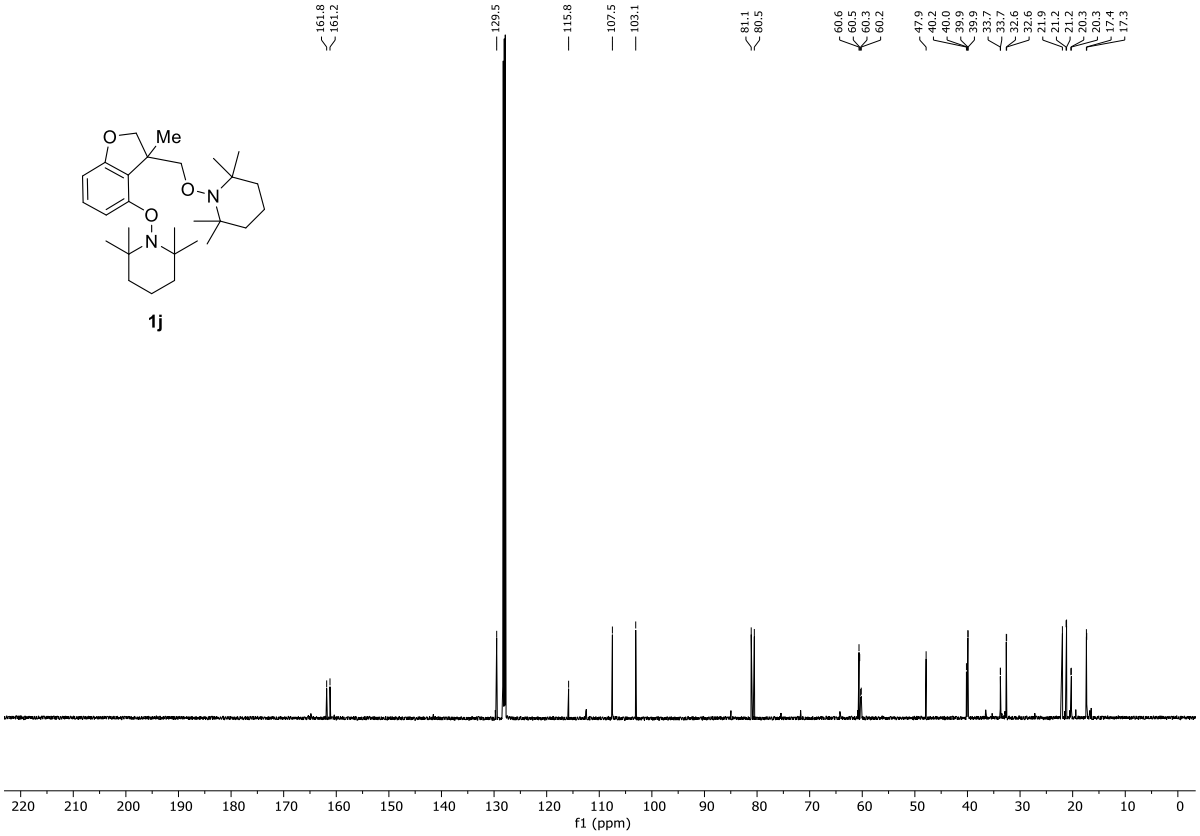


2,2,6,6-Tetramethyl-1-((3-methyl-3-(((2,2,6,6-tetramethylpiperidin-1-yl)oxy)methyl)-2,3-dihydrobenzofuran-4-yl)oxy)piperidine (1j)

^{1}H-NMR (500 MHz, C_6D_6)

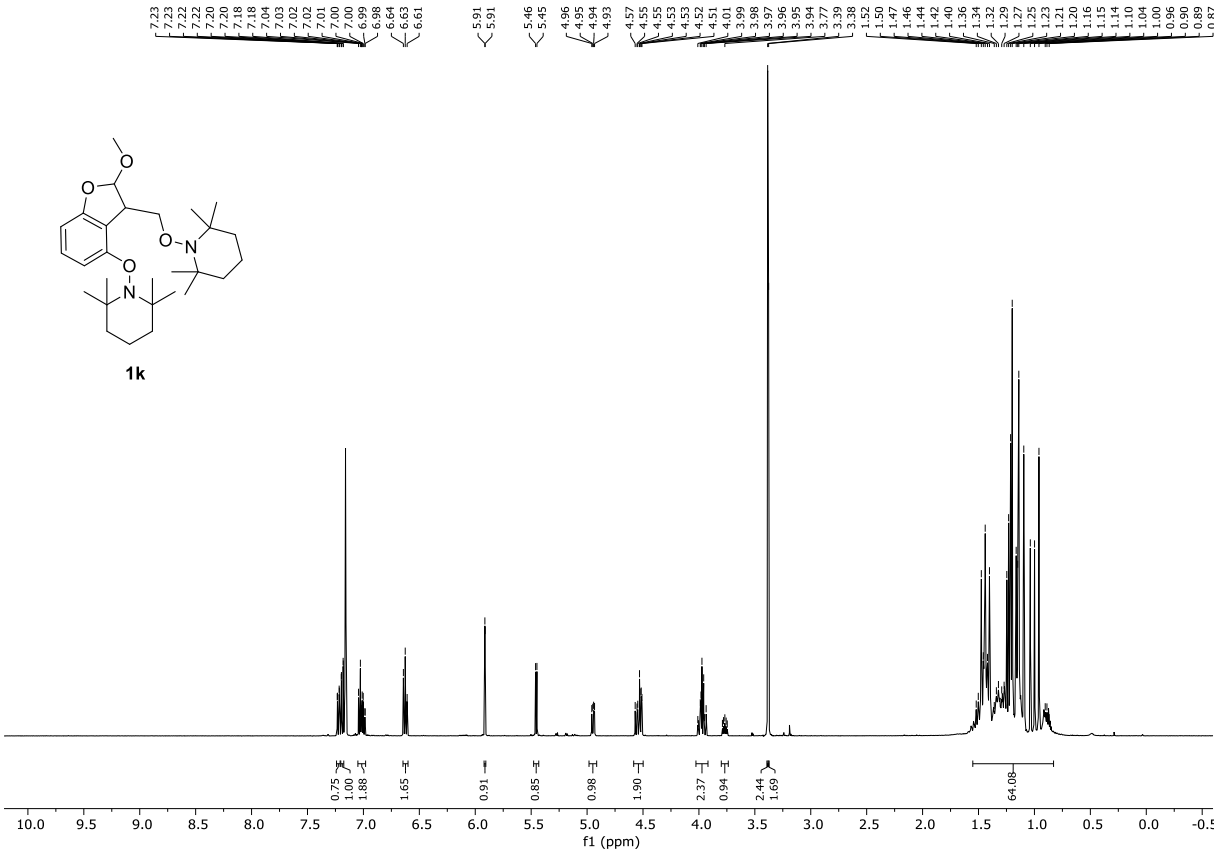


^{13}C-NMR (126 MHz, C_6D_6)

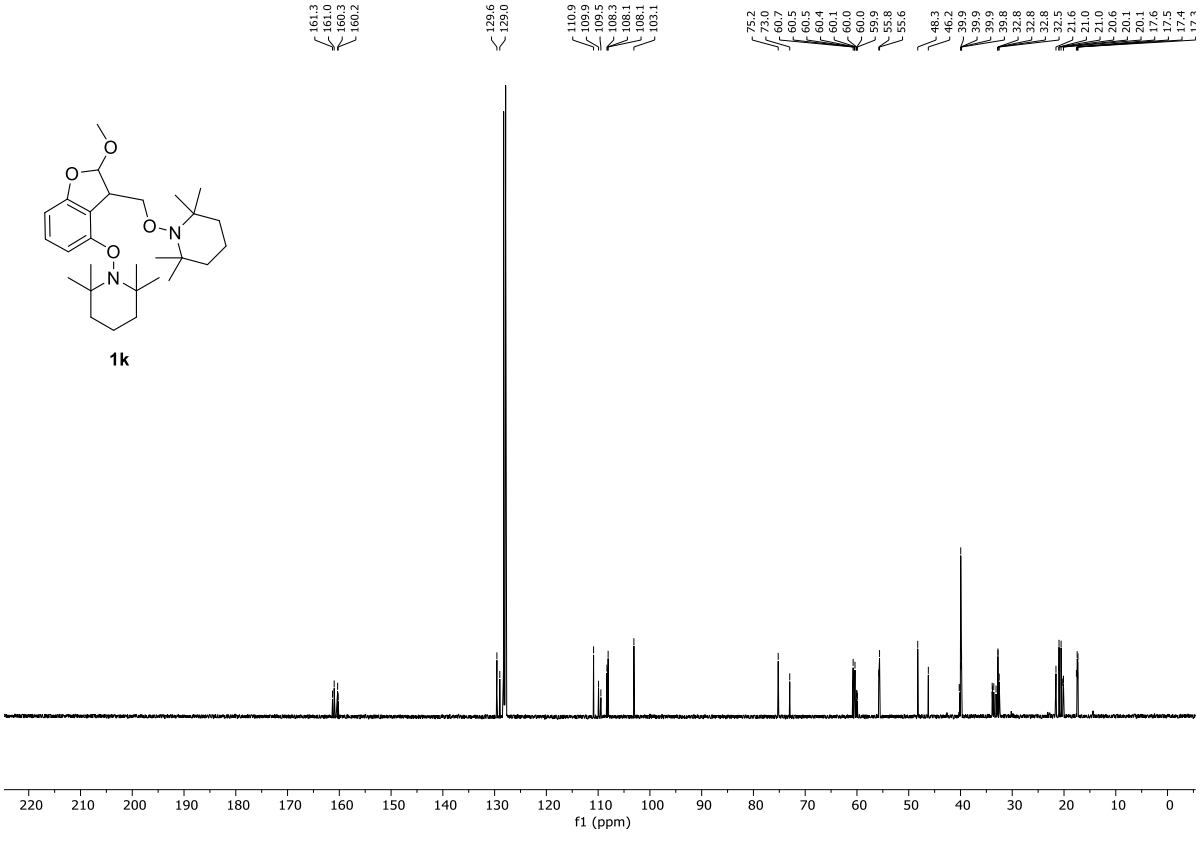


1-((2-Methoxy-3-(((2,2,6,6-tetramethylpiperidin-1-yl)oxy)methyl)-2,3-dihydrobenzofuran-4-yl)oxy)-2,2,6,6-tetramethylpiperidine (1k)

^{1}H-NMR (500 MHz, C_6D_6)

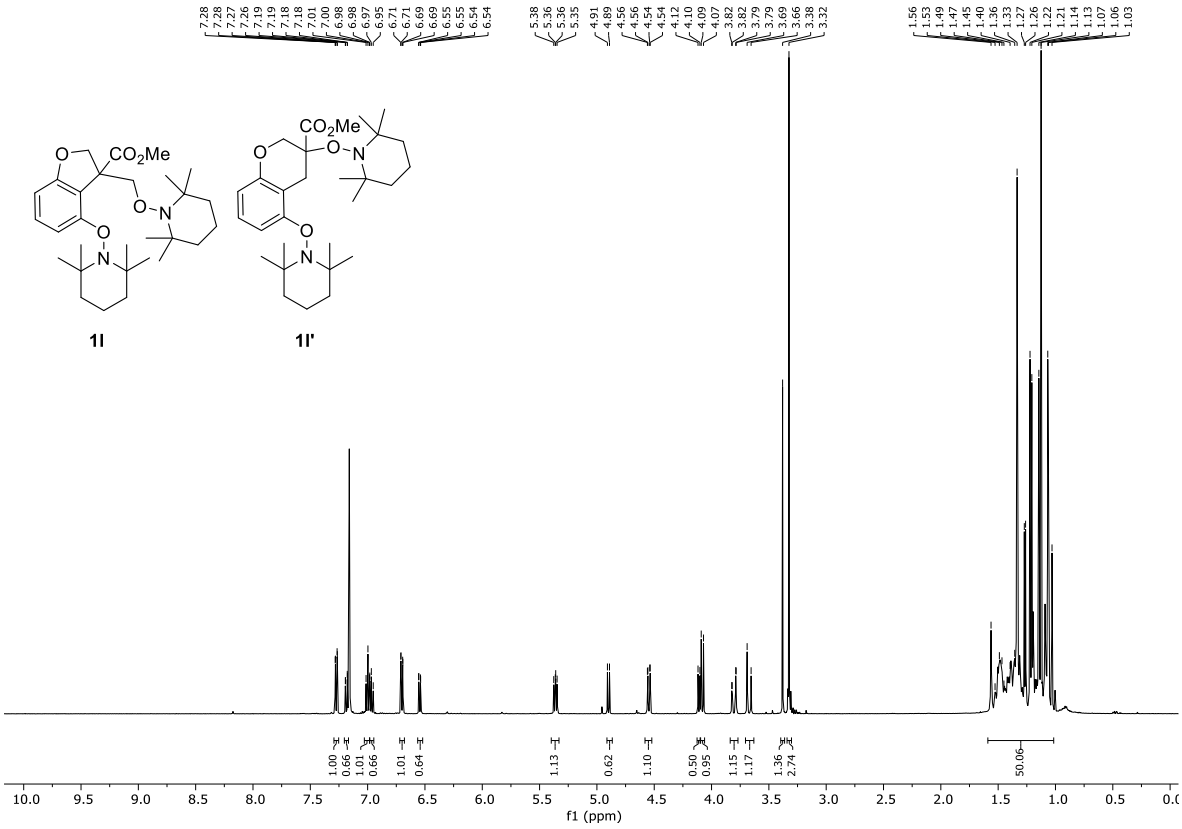


^{13}C-NMR (126 MHz, C_6D_6)

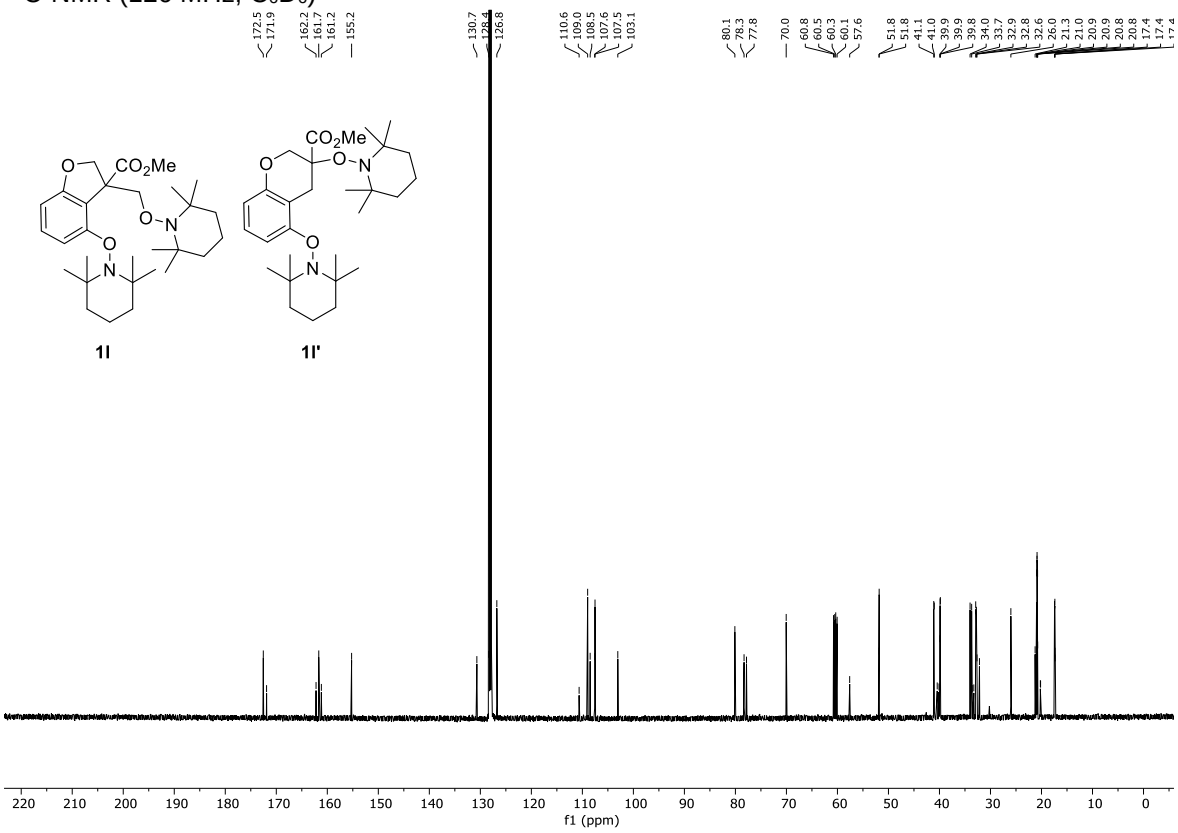


Methyl 4-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)-3-(((2,2,6,6-tetramethylpiperidin-1-yl)oxy)methyl)-2,3-dihydrobenzofuran-3-carboxylate (1l) and methyl 3,5-bis((2,2,6,6-tetramethylpiperidin-1-yl)oxy)chromane-3-carboxylate (1l')

^{1}H-NMR (500 MHz, C_6D_6)

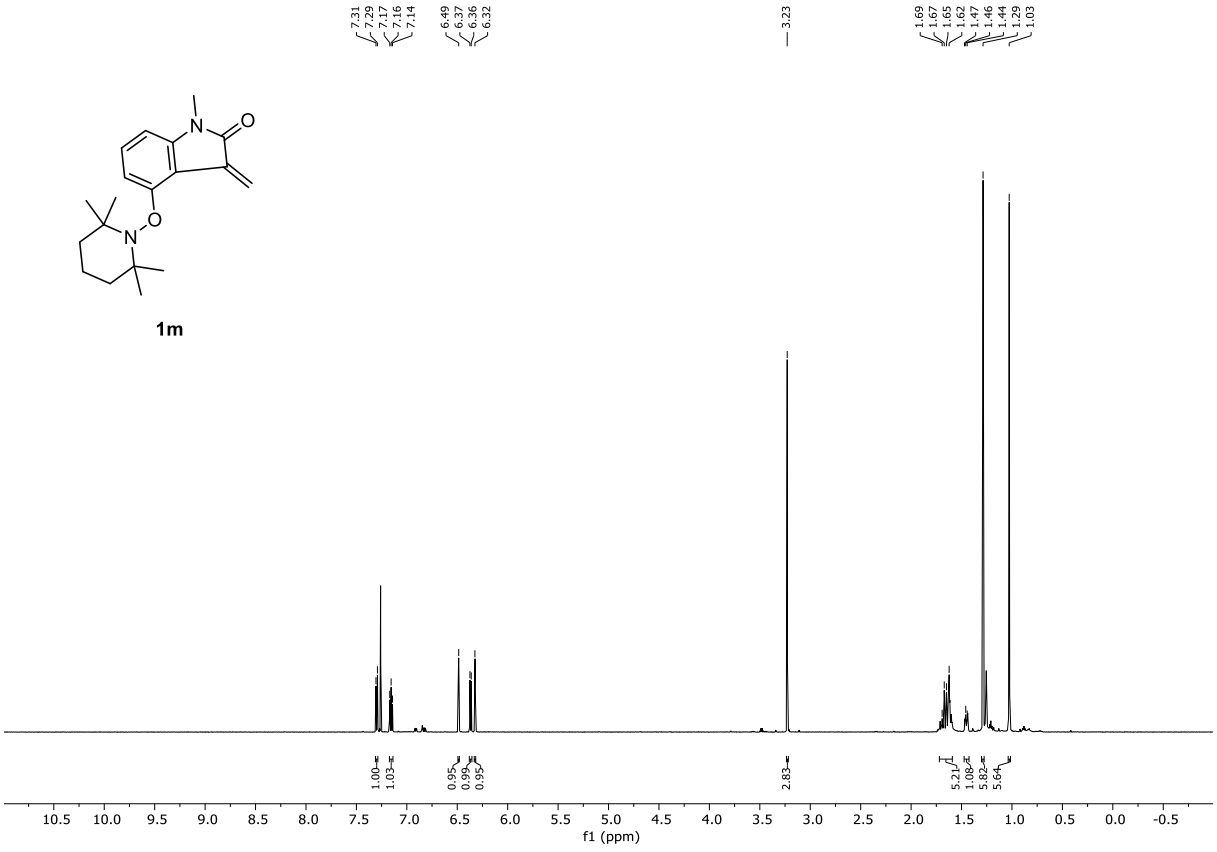


^{13}C-NMR (126 MHz, C_6D_6)

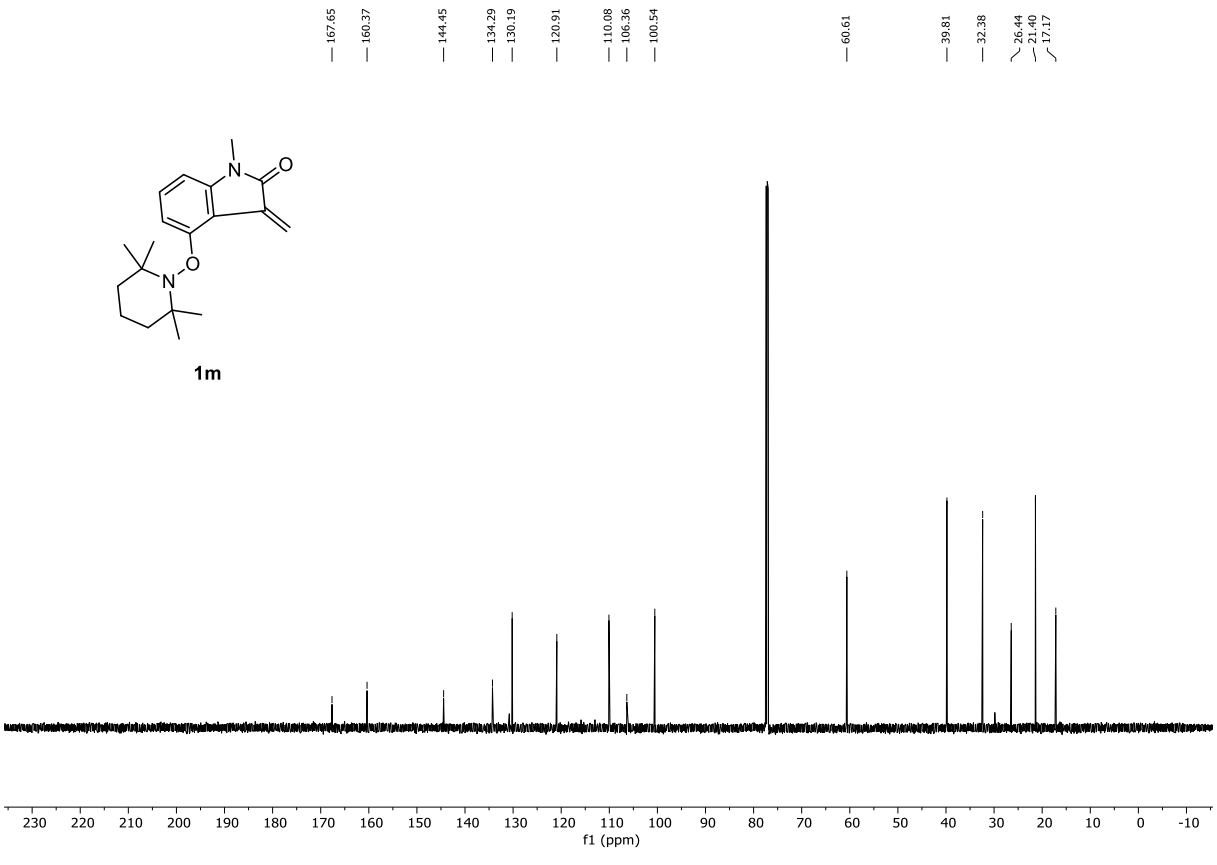


1-Methyl-3-methylene-4-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)indolin-2-one (1m)

^{1}H-NMR (599 MHz, $CDCl_3$)

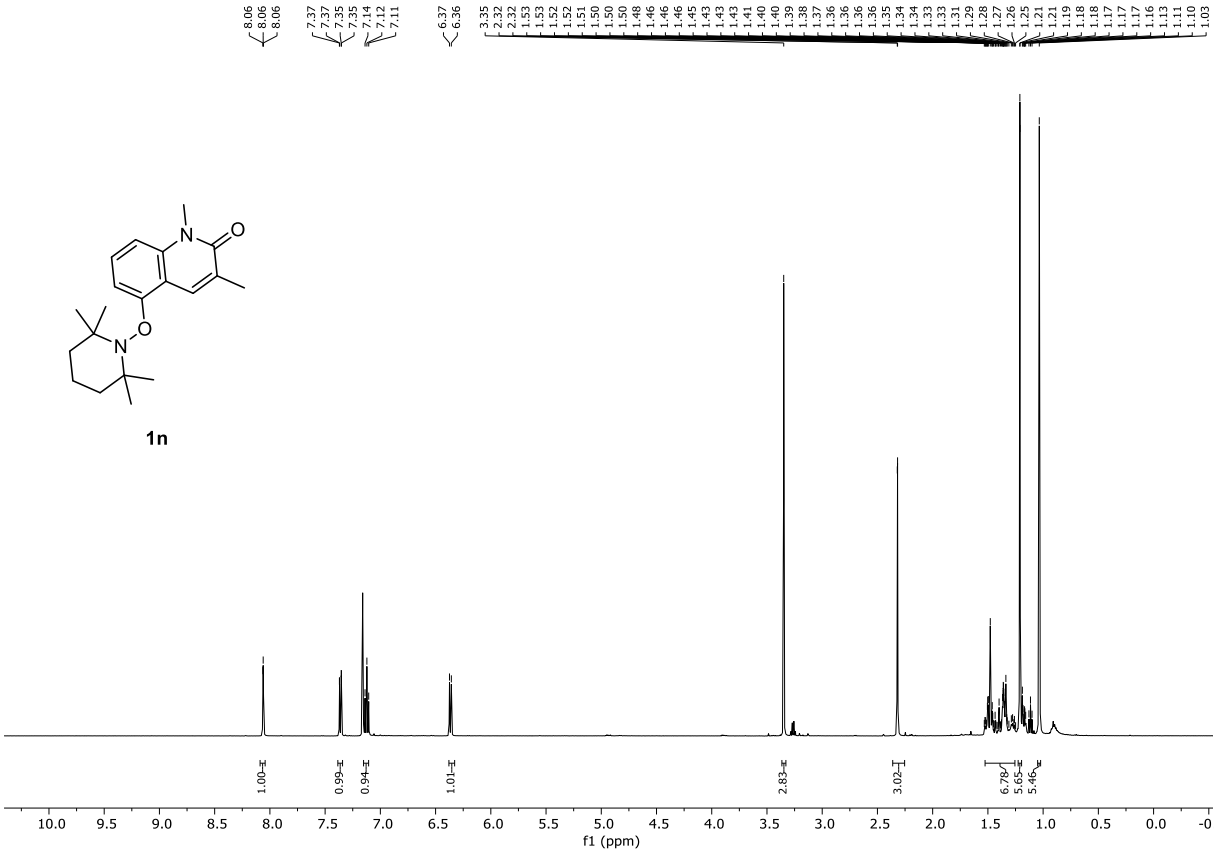


^{13}C-NMR (151 MHz, $CDCl_3$)



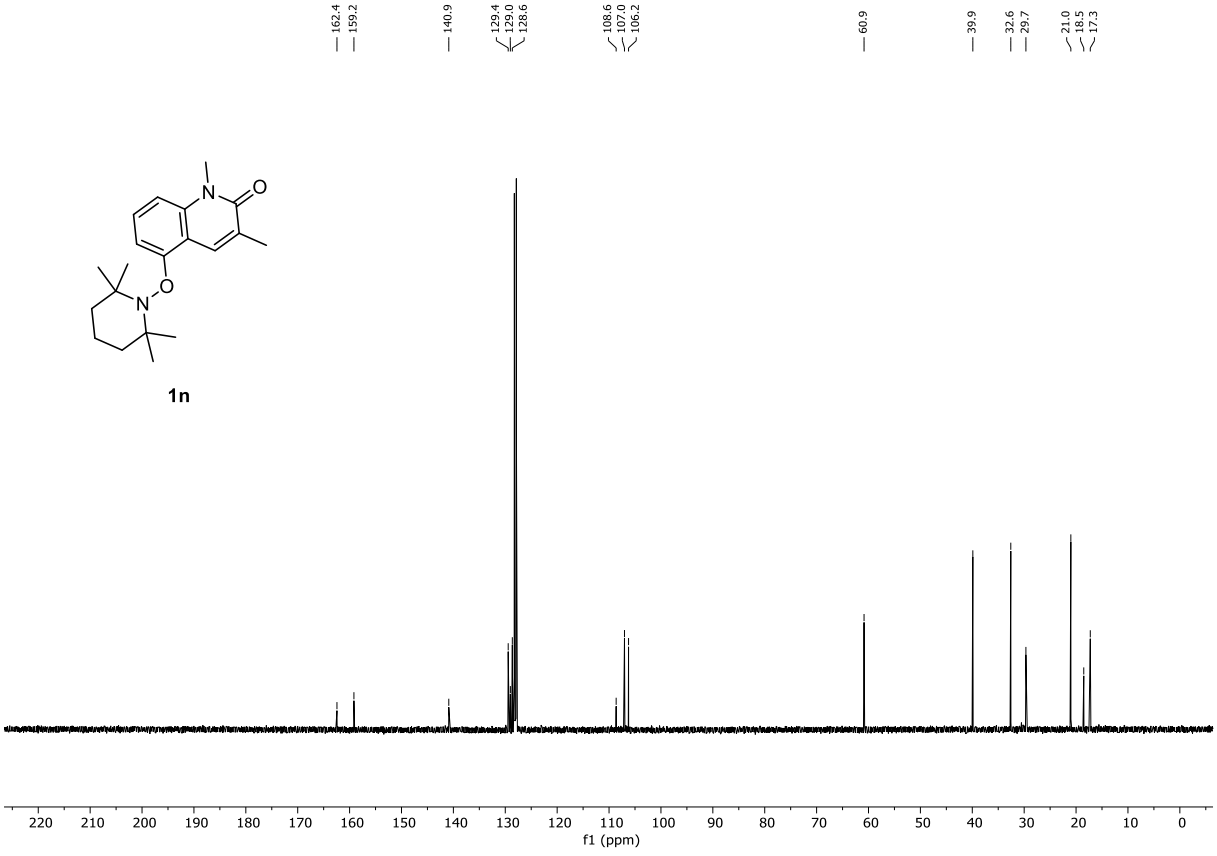
1,3-Dimethyl-5-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)quinolin-2(1H)-one (1n)

^{1}H-NMR (500 MHz, C_6D_6)



1n

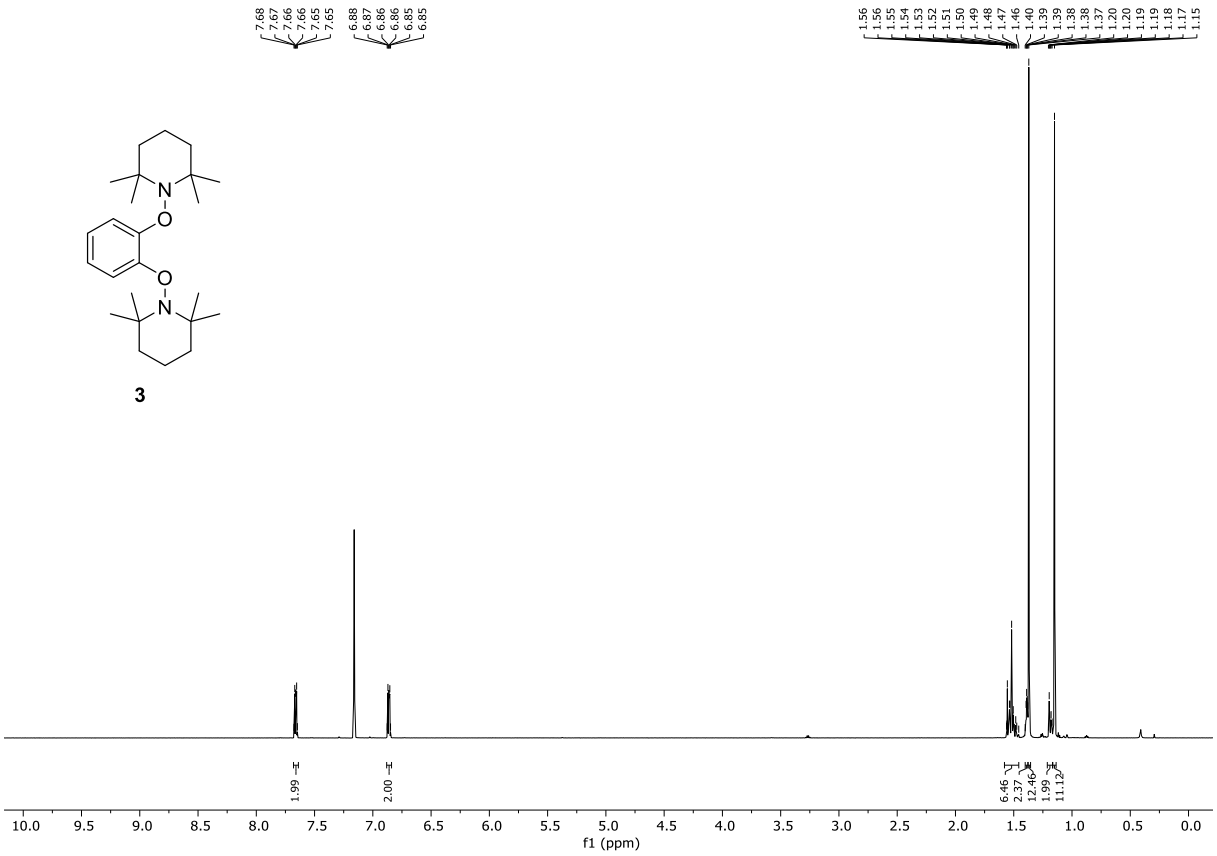
^{13}C-NMR (126 MHz, C_6D_6)



1n

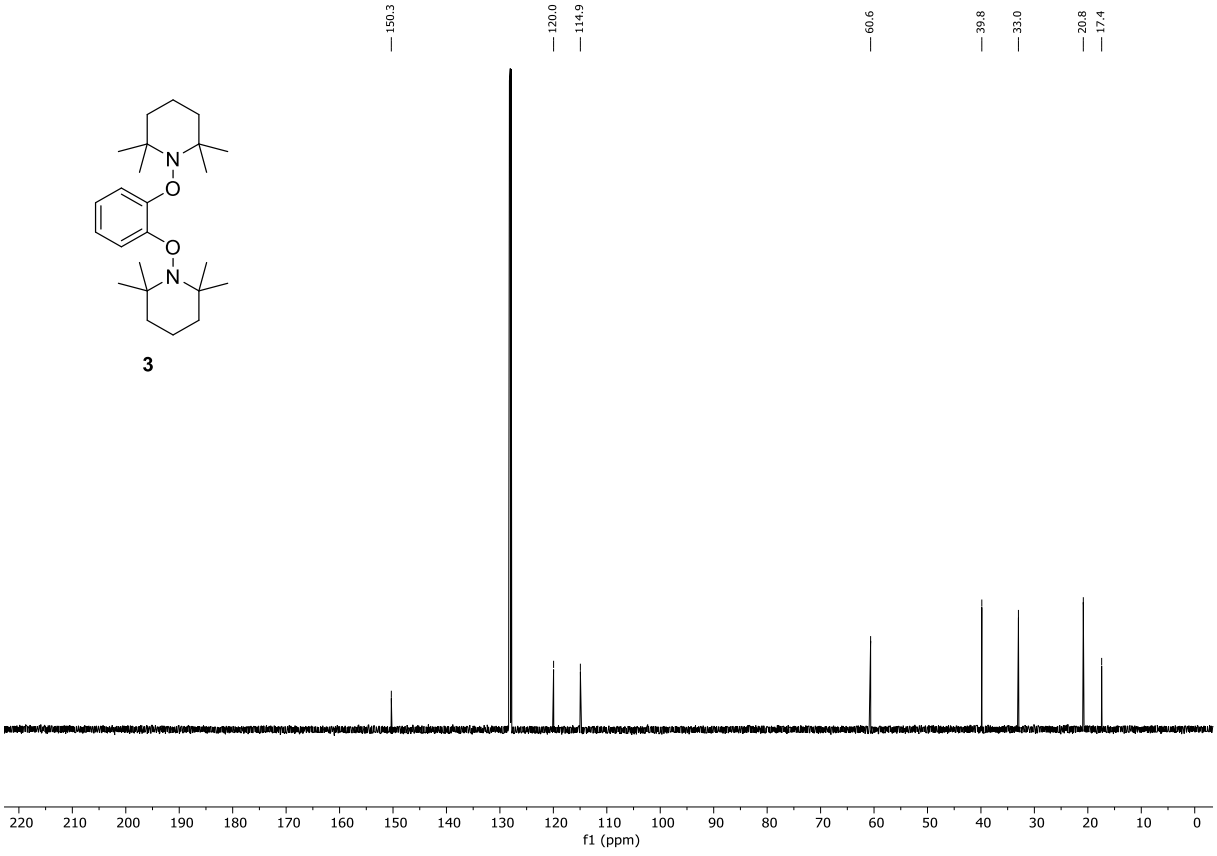
1,2-Bis((2,2,6,6-tetramethylpiperidin-1-yl)oxy)benzene (3)

^{1}H-NMR (599 MHz, C_6D_6)



3

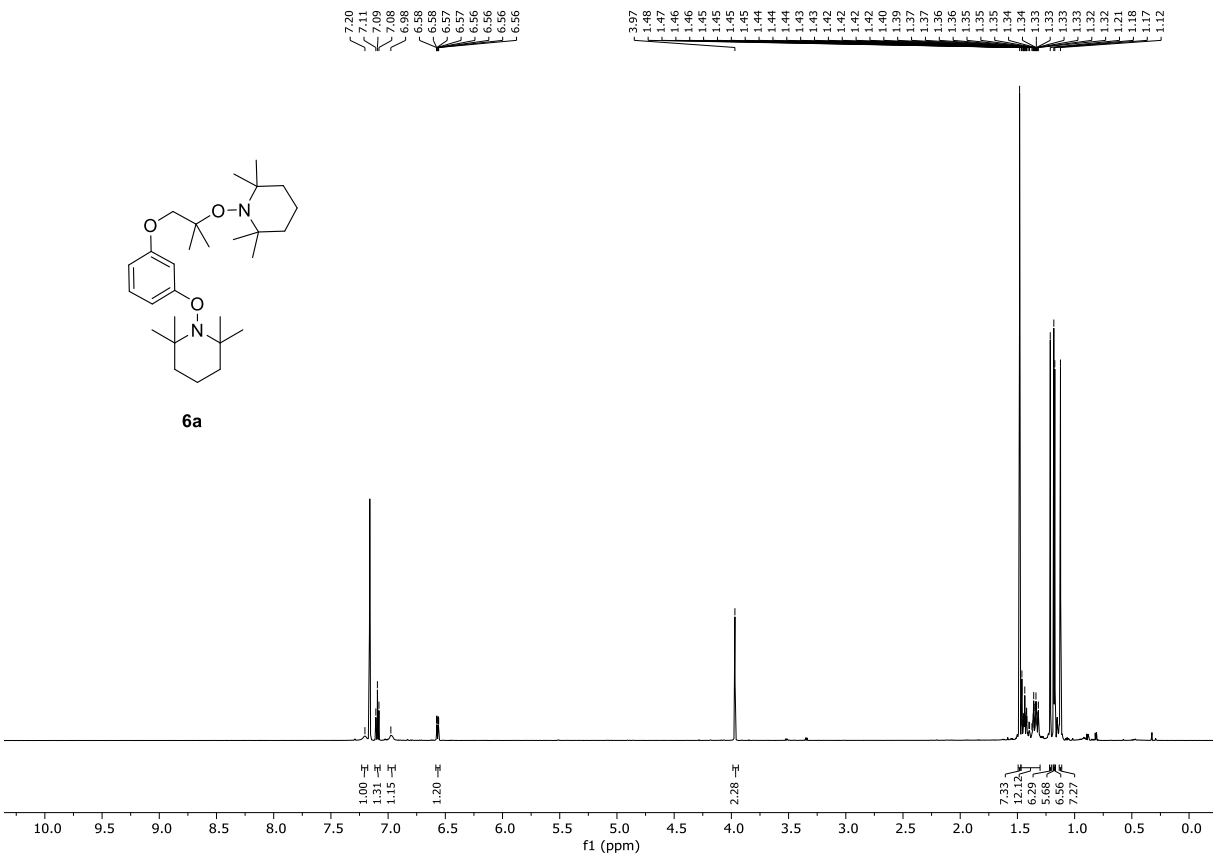
^{13}C-NMR (151 MHz, C_6D_6)



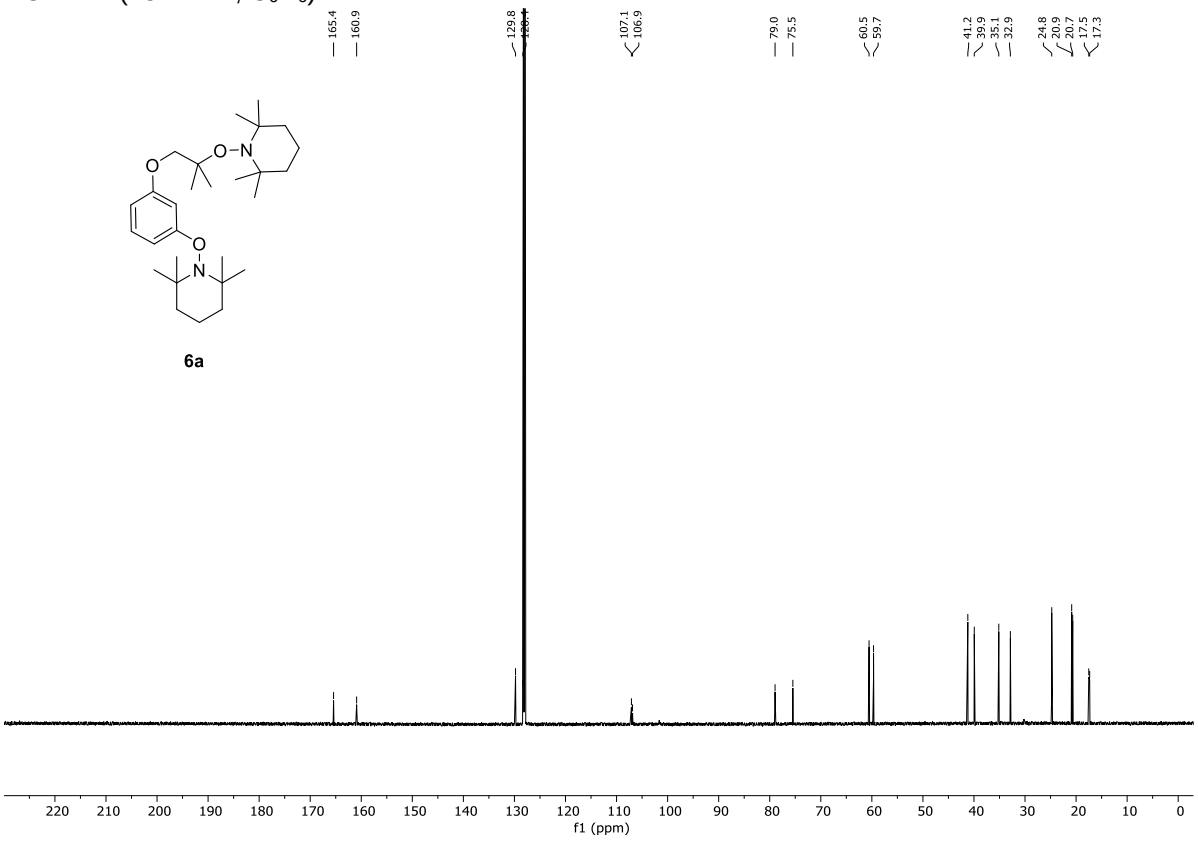
3

2,2,6,6-Tetramethyl-1-((2-methyl-1-(3-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)phenoxy)propan-2-yl)oxy)piperidine (6a)

^{1}H-NMR (600 MHz, C_6D_6)

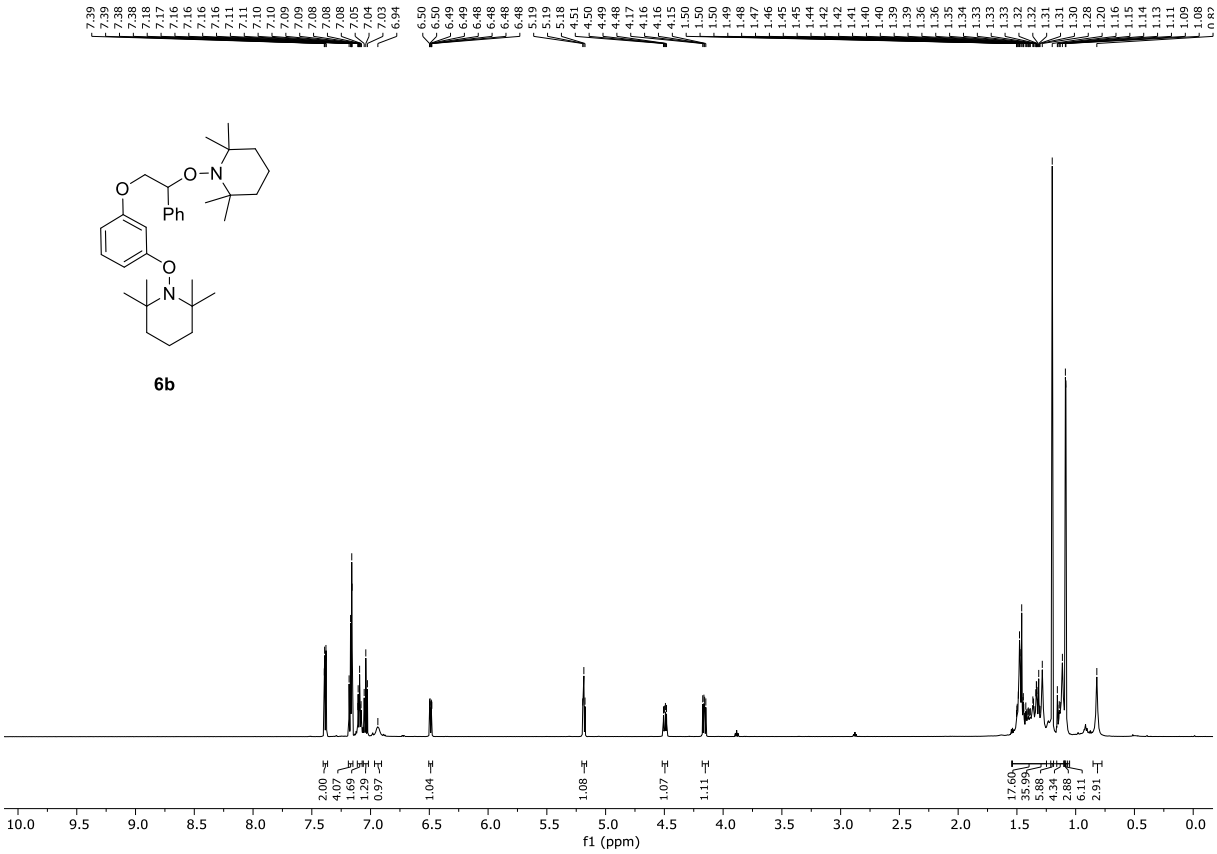


^{13}C-NMR (151 MHz, C_6D_6)

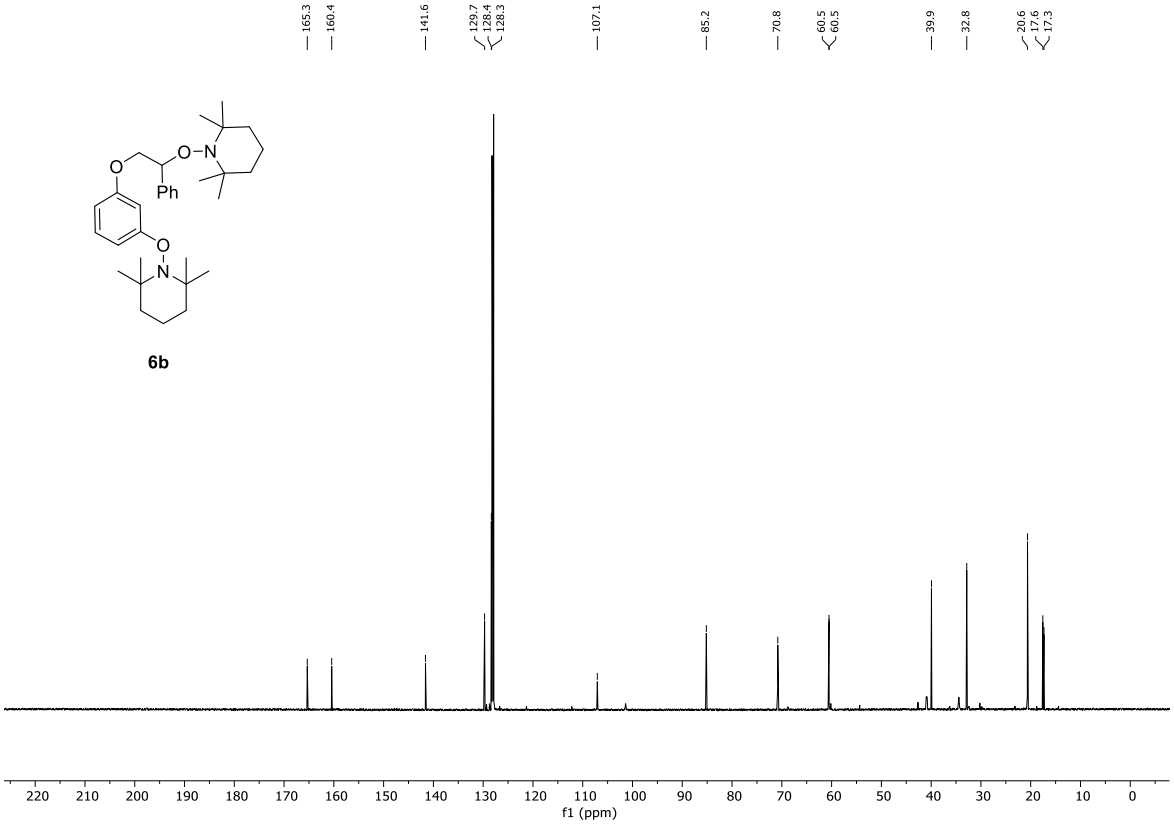


2,2,6,6-Tetramethyl-1-(3-(2-phenyl-2-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)ethoxy)phenoxy)piperidine (6b)

^{1}H-NMR (599 MHz, C_6D_6)

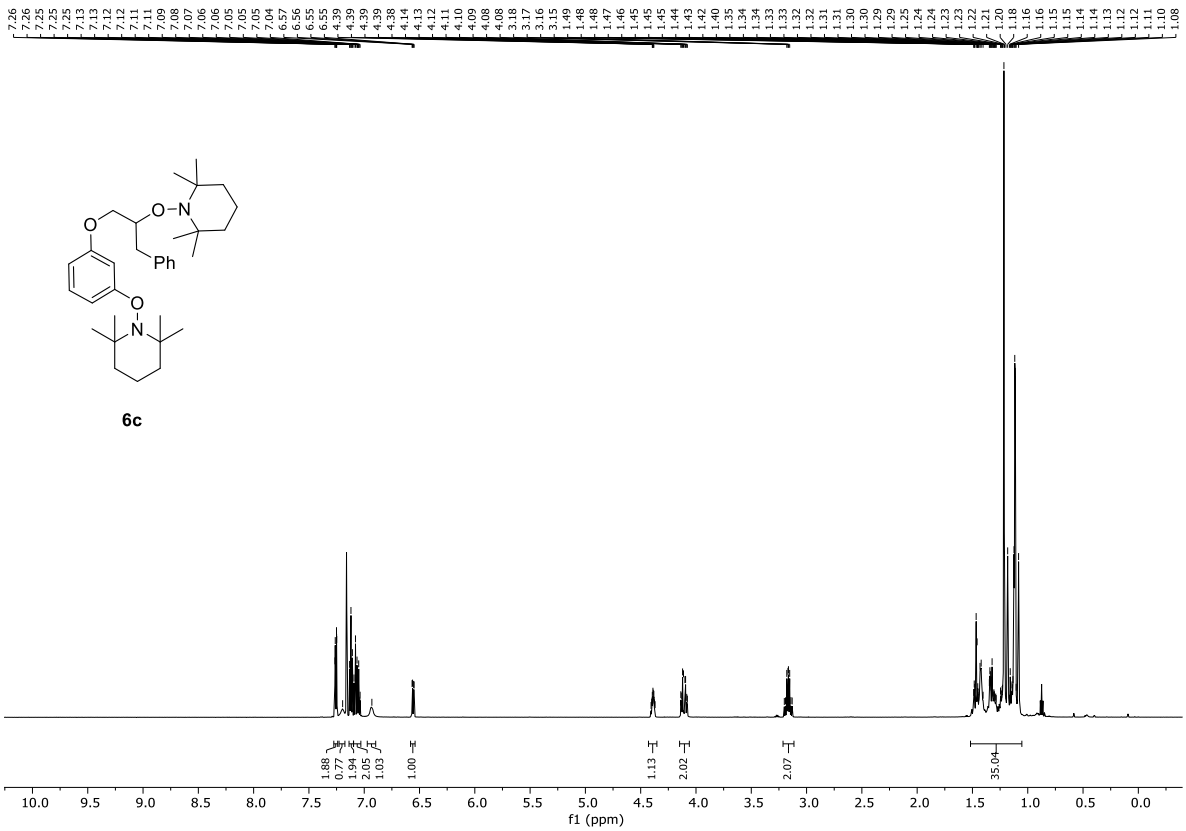


^{13}C-NMR (151 MHz, C_6D_6)

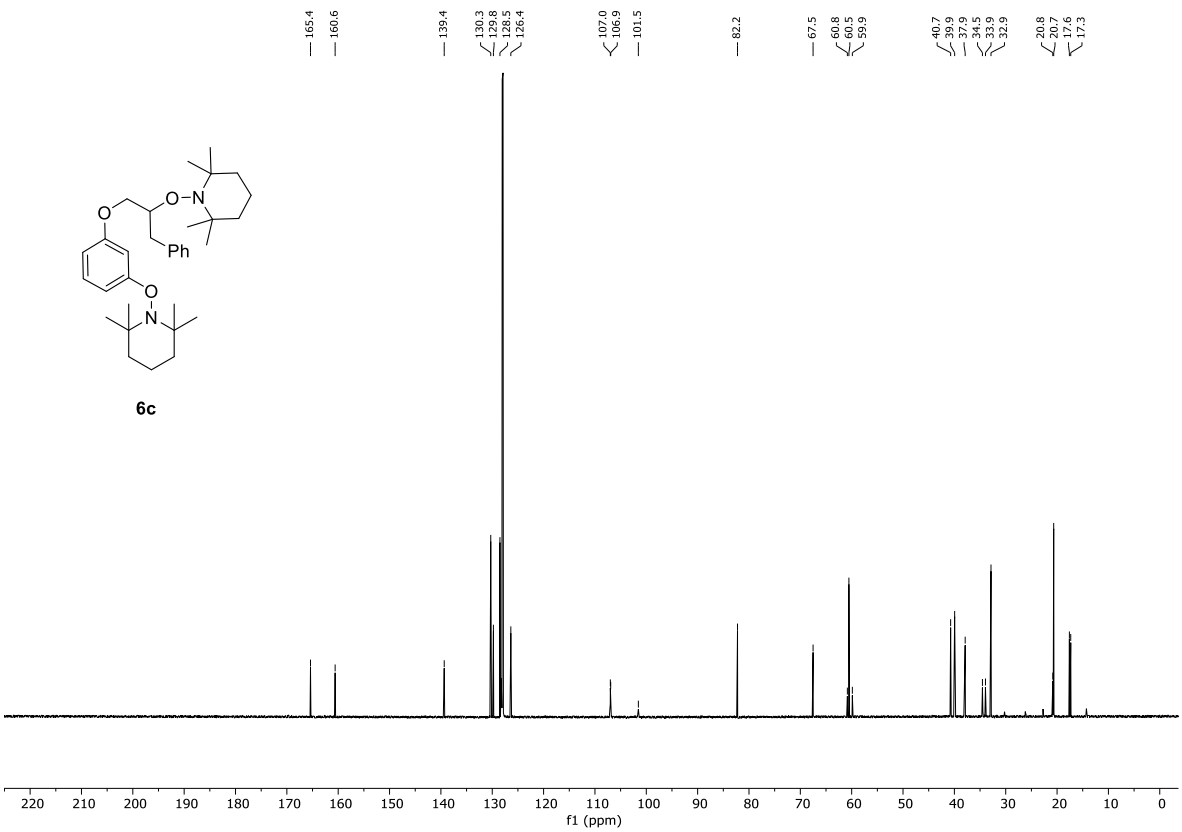


2,2,6,6-Tetramethyl-1-(3-(3-phenyl-2-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)propoxy)phenoxy)piperidine (6c)

^{1}H-NMR (599 MHz, C_6D_6)

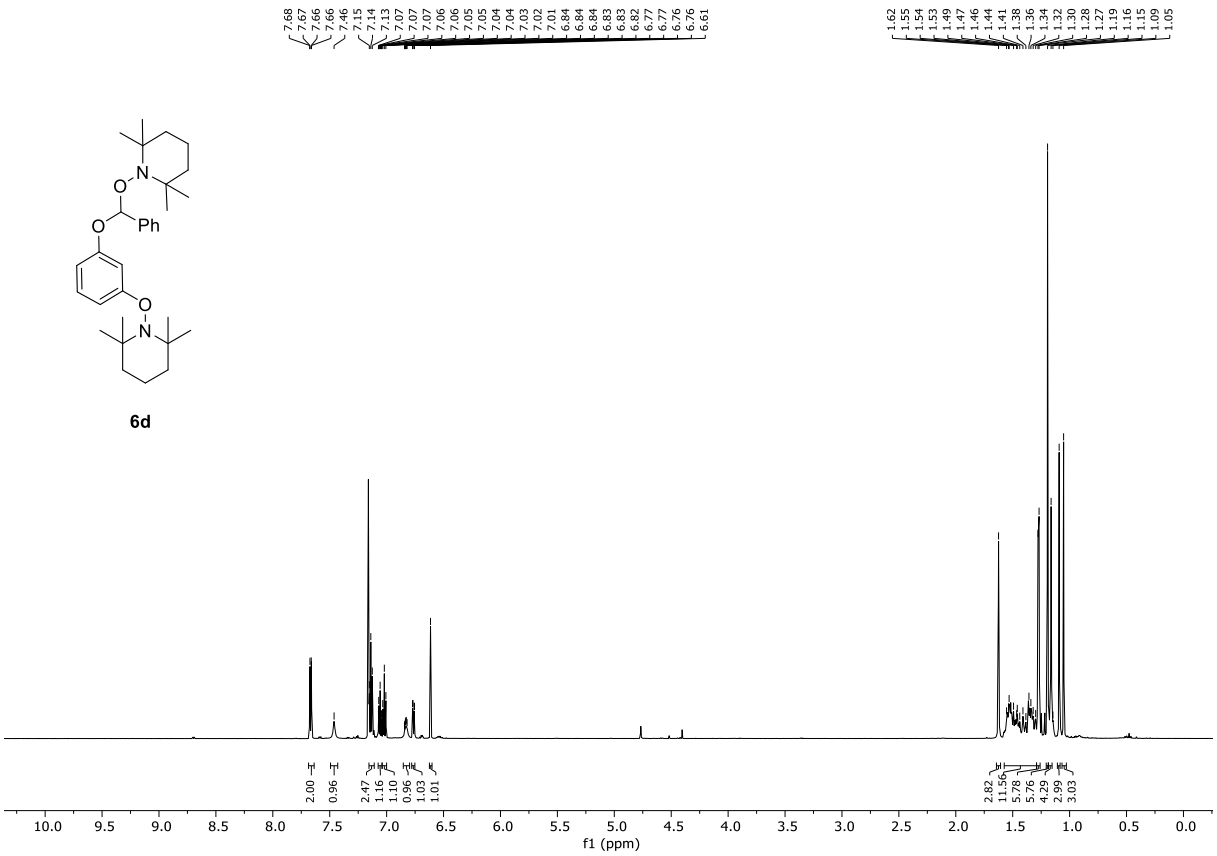


^{13}C-NMR (151 MHz, C_6D_6)

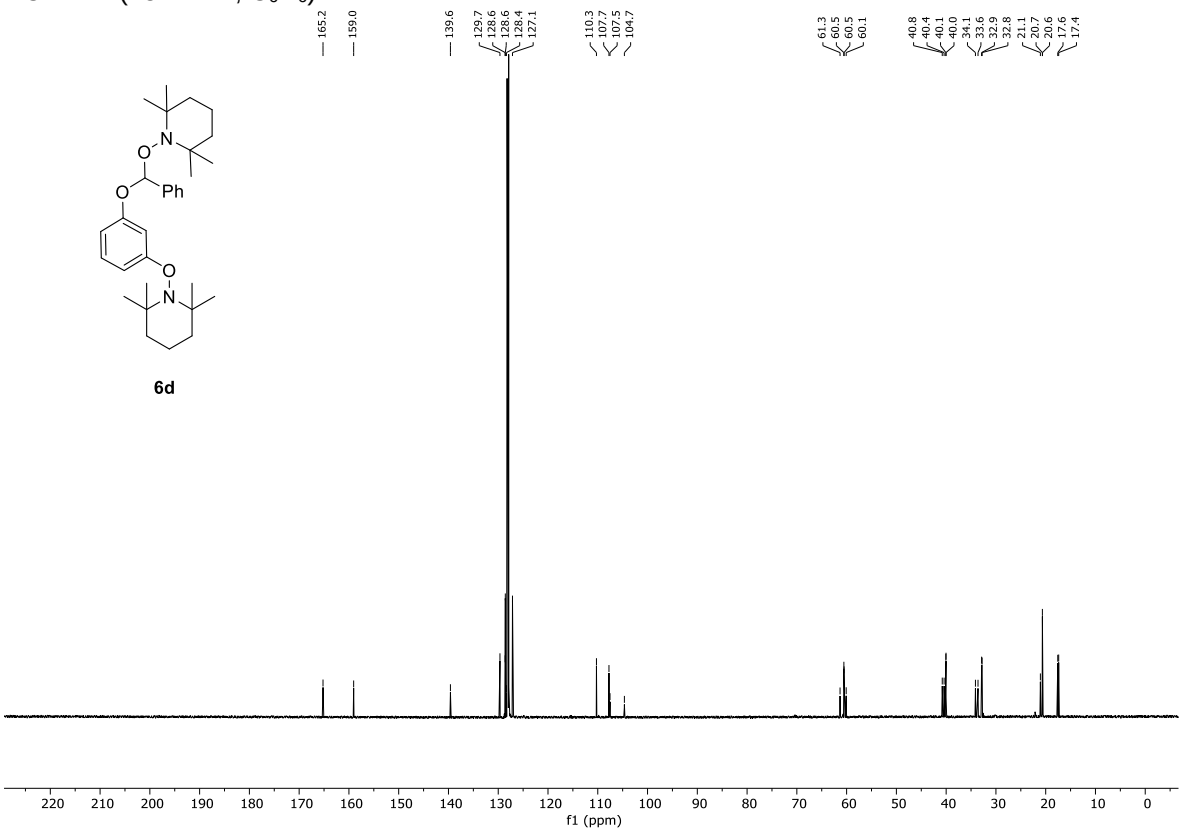


2,2,6,6-Tetramethyl-1-(3-(phenyl((2,2,6,6-tetramethylpiperidin-1-yl)oxy)methoxy)phenoxy)piperidine (6d)

^{1}H-NMR (599 MHz, C_6D_6)

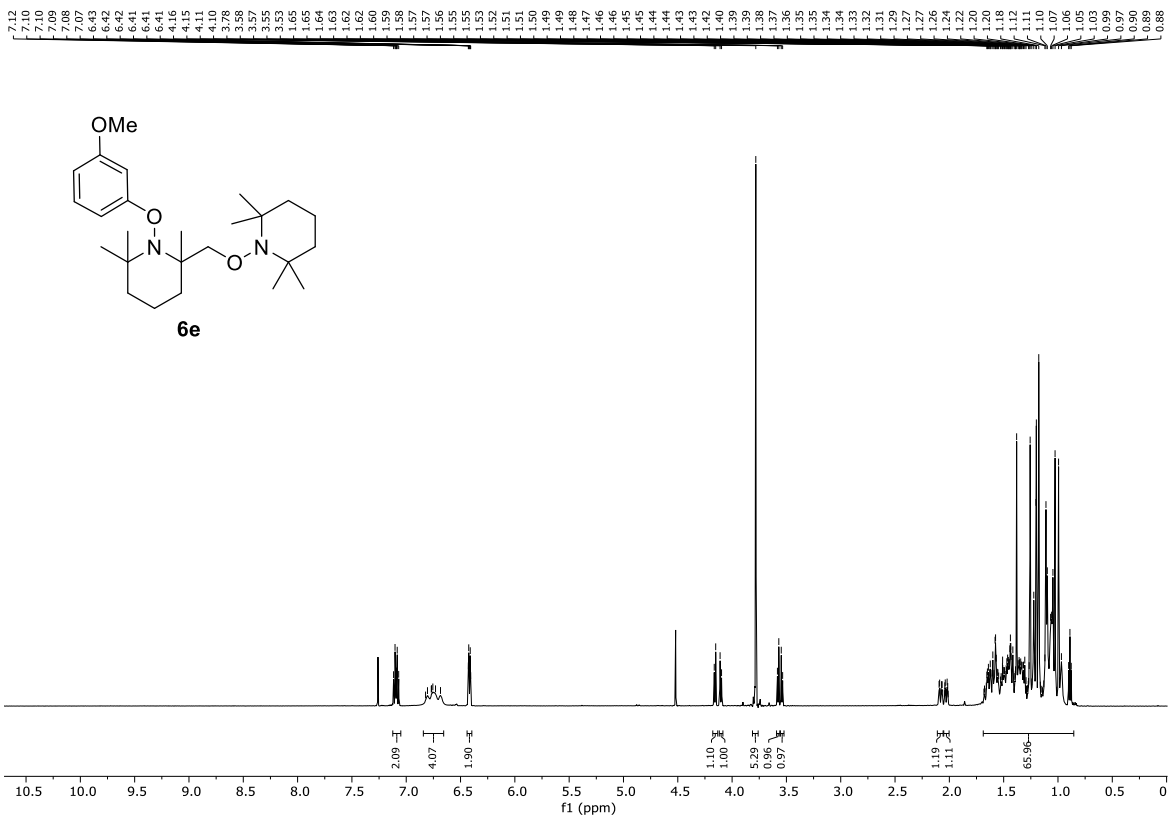


^{13}C-NMR (151 MHz, C_6D_6)

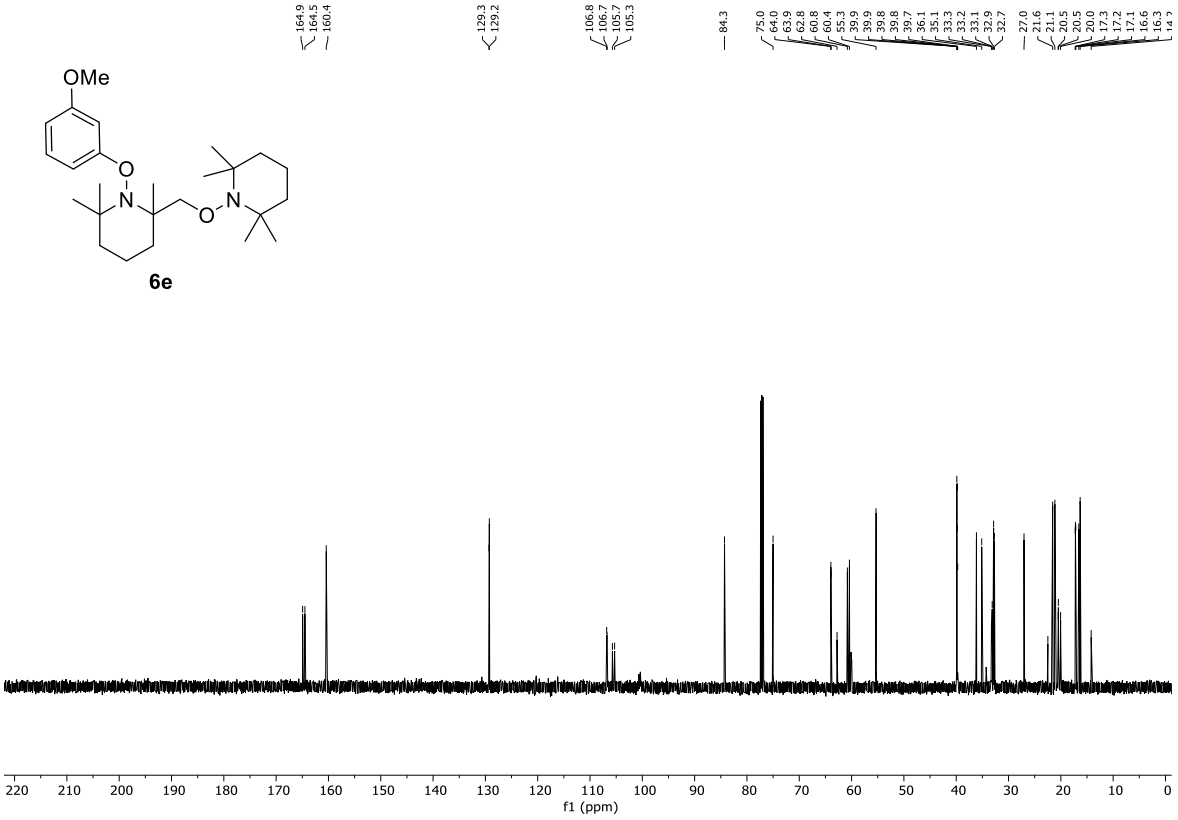


1-(3-Methoxyphenoxy)-2,2,6-trimethyl-6-(((2,2,6,6-tetramethylpiperidin-1-yl)oxy)methyl)piperidine (6e)

^{1}H-NMR (600 MHz, $CDCl_3$)

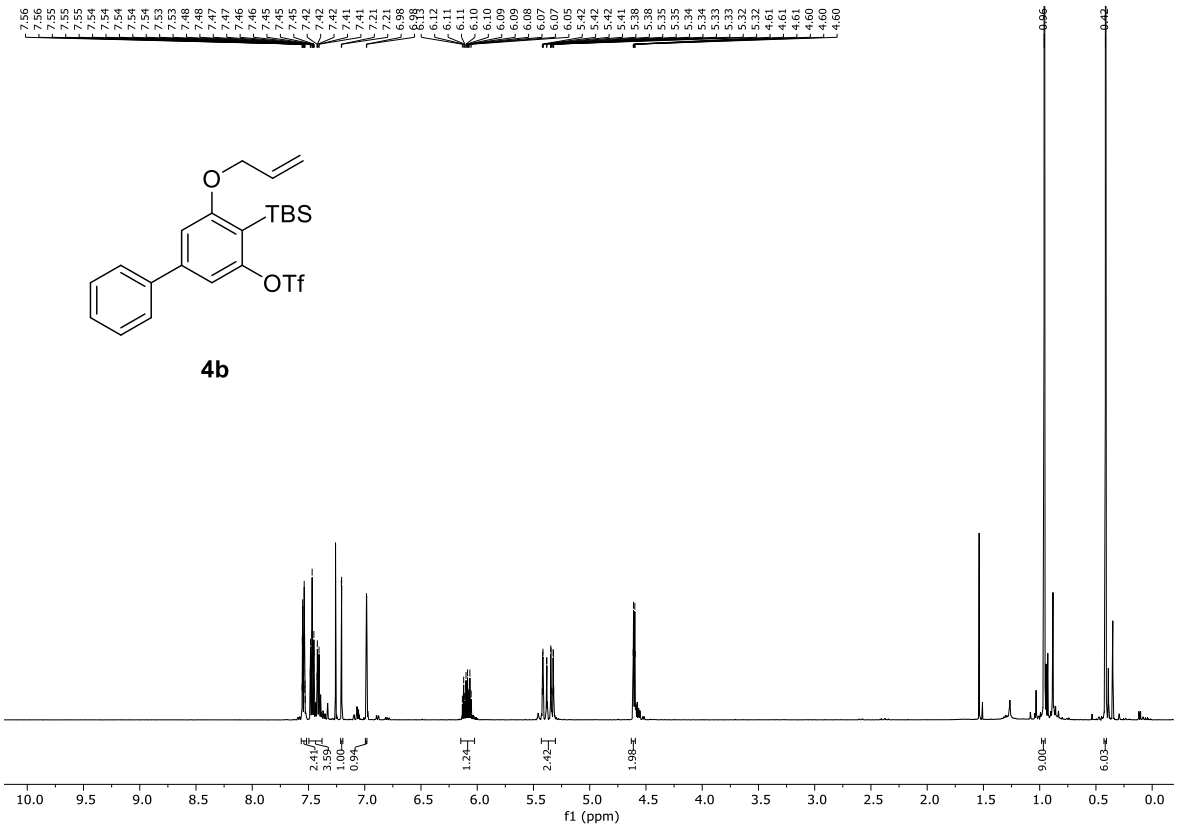


^{13}C-NMR (151 MHz, $CDCl_3$)

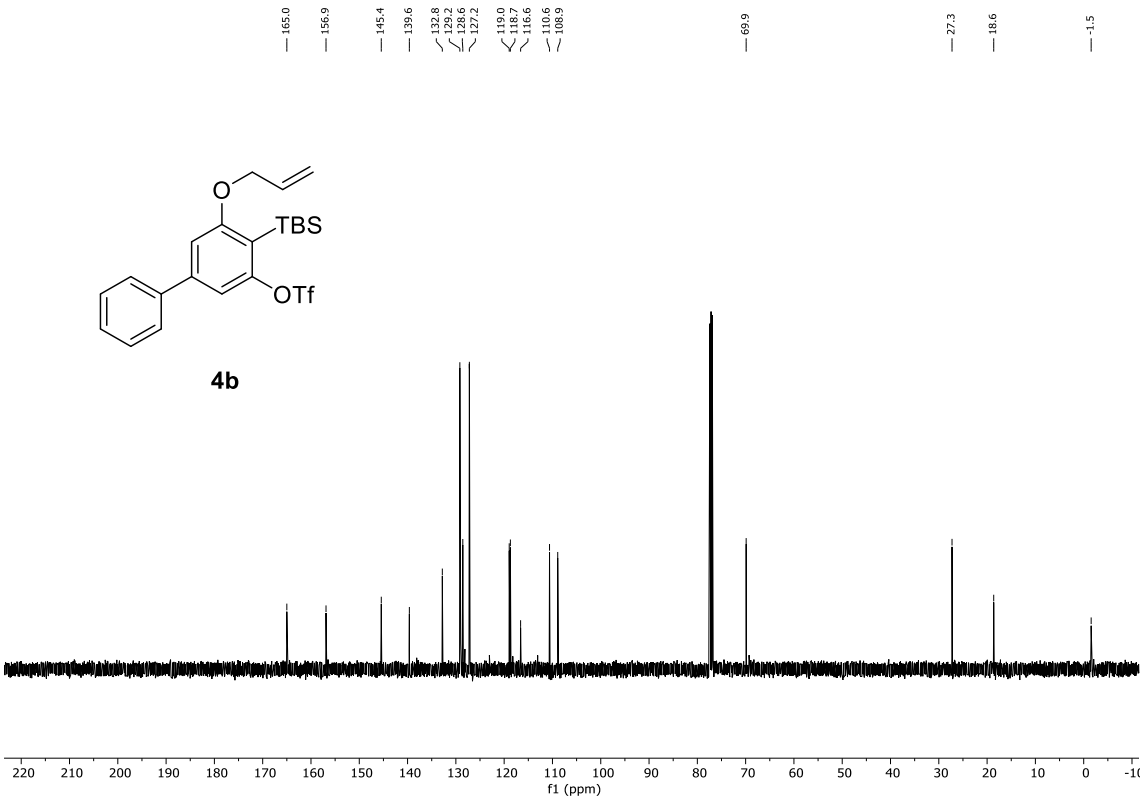


5-(Allyloxy)-4-(tert-butyldimethylsilyl)-[1,1'-biphenyl]-3-yl trifluoromethanesulfonate (4b)

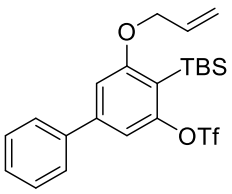
^{1}H-NMR (500 MHz, $CDCl_3$)



^{13}C-NMR (126 MHz, $CDCl_3$, ^{1}H/^{19}F decoupled)



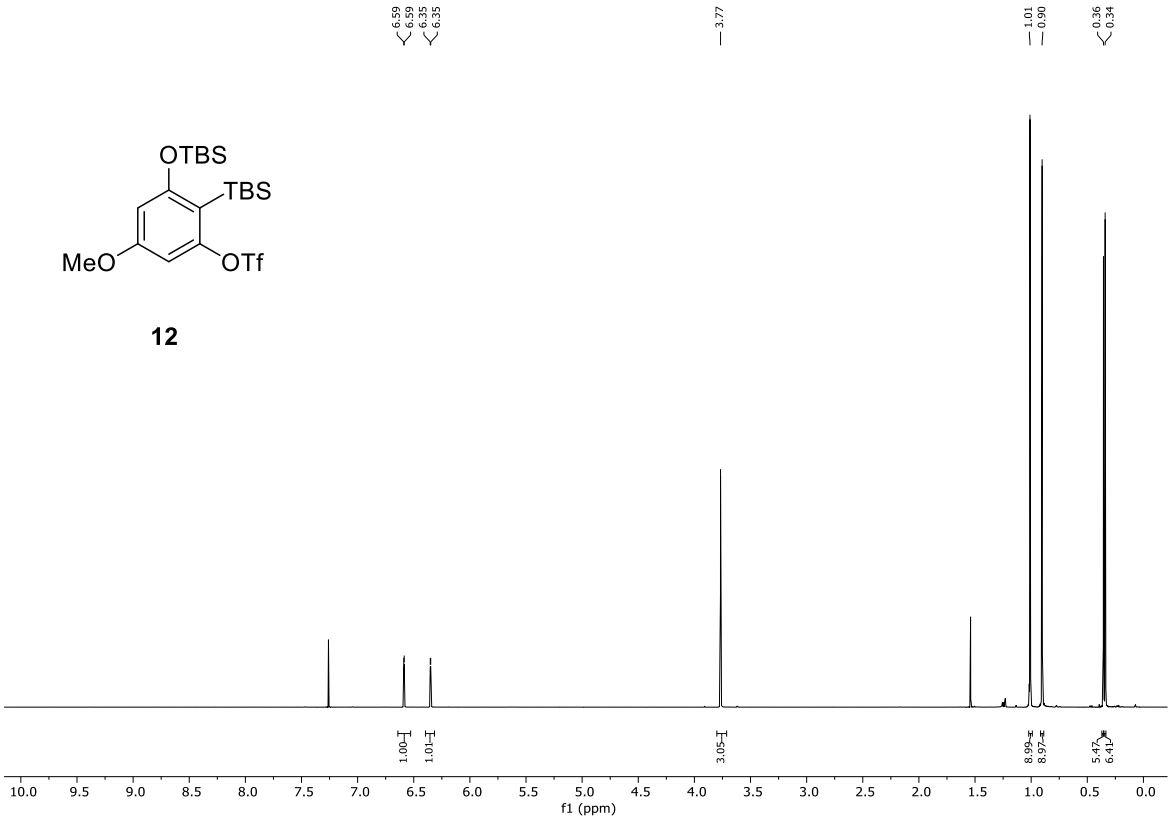
^{19}F-NMR (470 MHz, $CDCl_3$)



4b

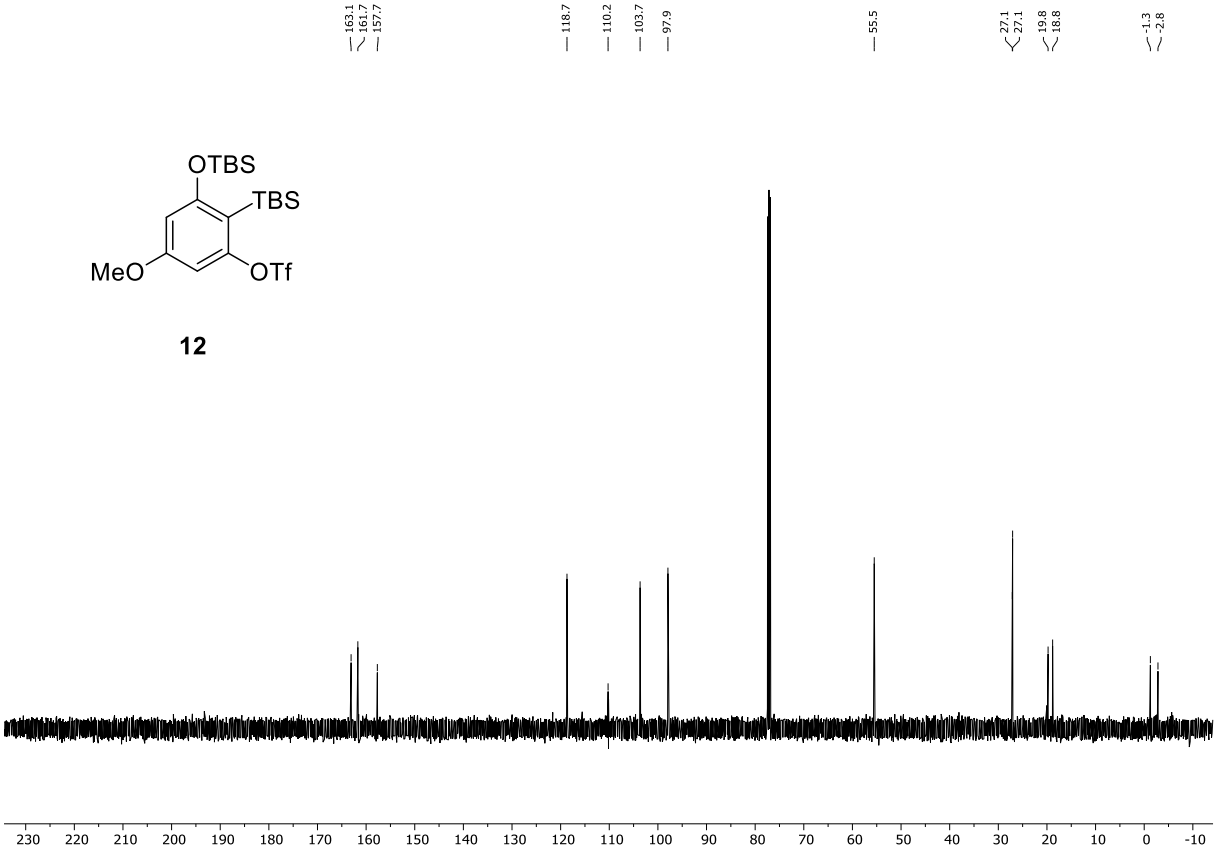
2-(*tert*-Butyldimethylsilyl)-3-((*tert*-butyldimethylsilyl)oxy)-5-methoxyphenyl trifluoromethanesulfonate (12)

^{1}H-NMR (500 MHz, $CDCl_3$)



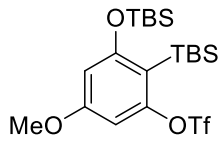
12

^{13}C-NMR (126 MHz, $CDCl_3$)



12

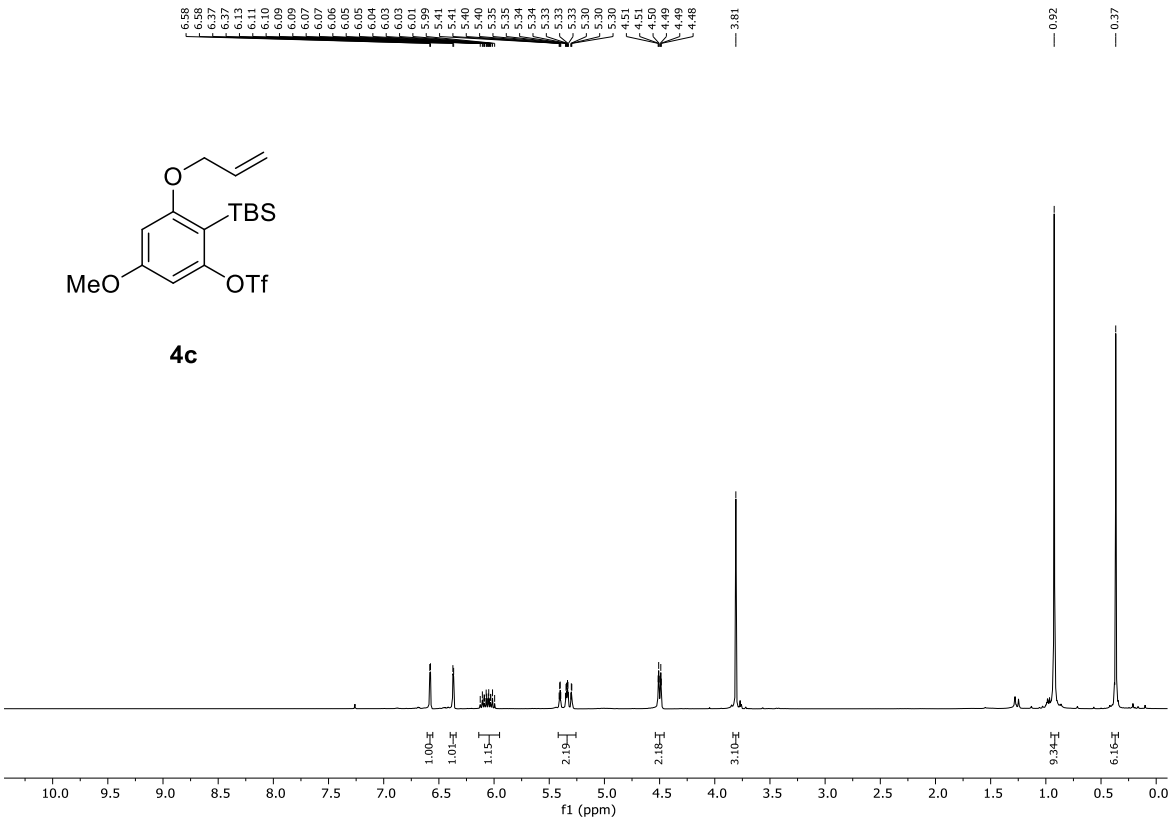
^{19}F-NMR (282 MHz, $CDCl_3$)



12

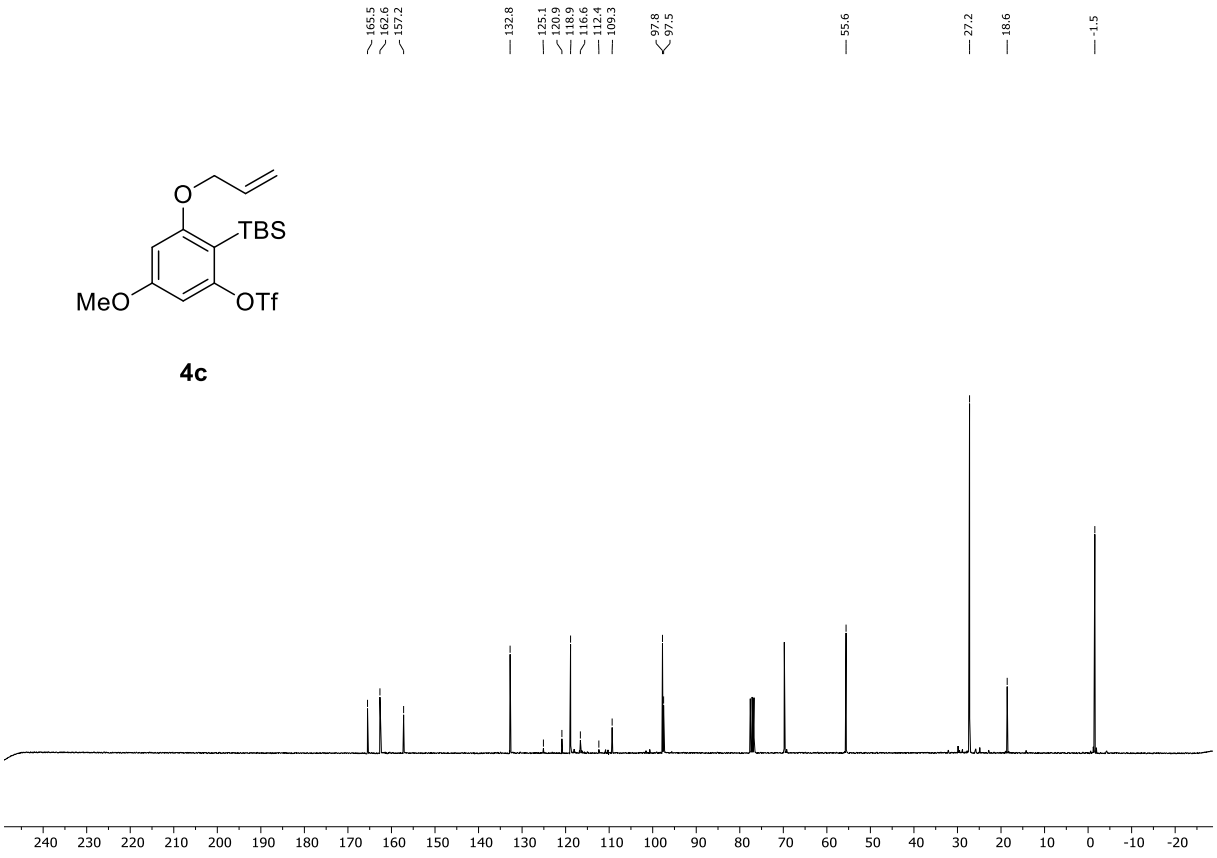
3-(Allyloxy)-2-(*tert*-butyldimethylsilyl)-5-methoxyphenyl trifluoromethanesulfonate (4c)

^{1}H-NMR (300 MHz, $CDCl_3$)



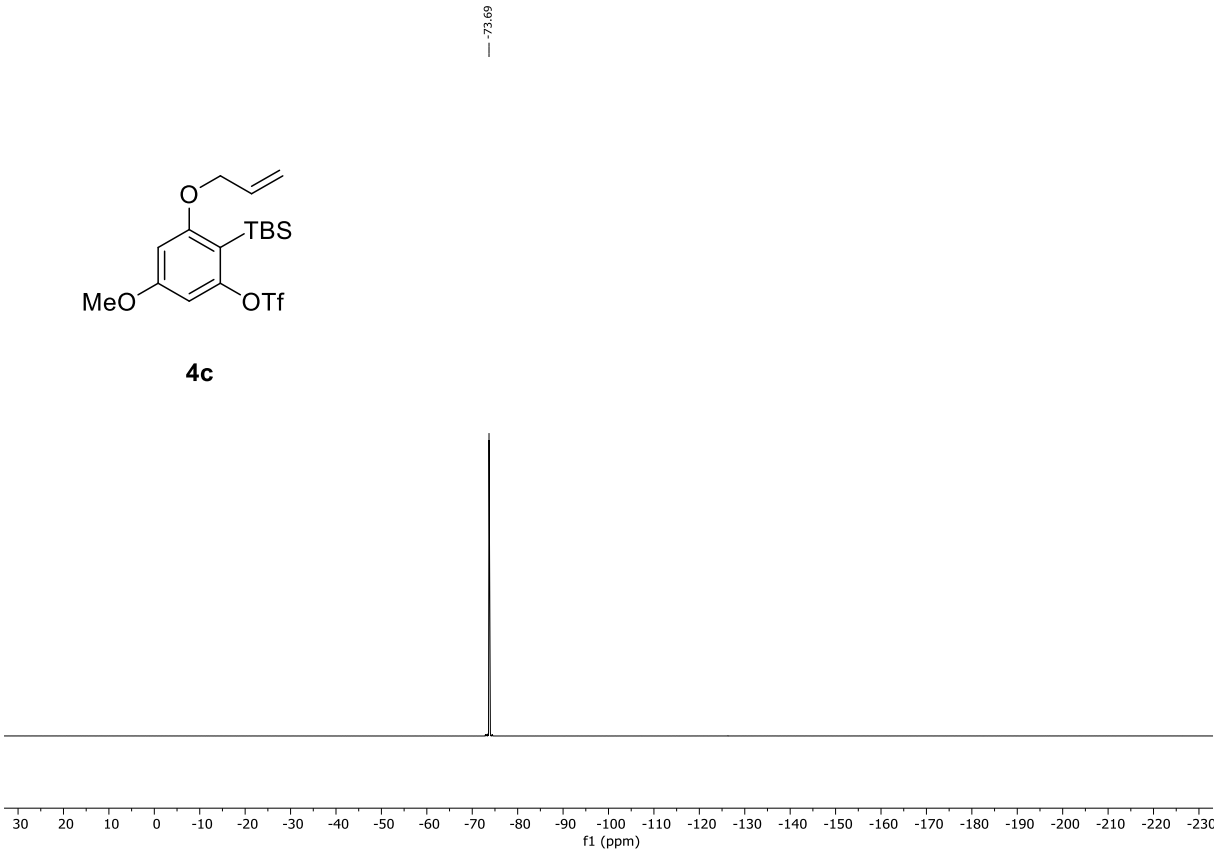
4c

^{13}C-NMR (75 MHz, $CDCl_3$)



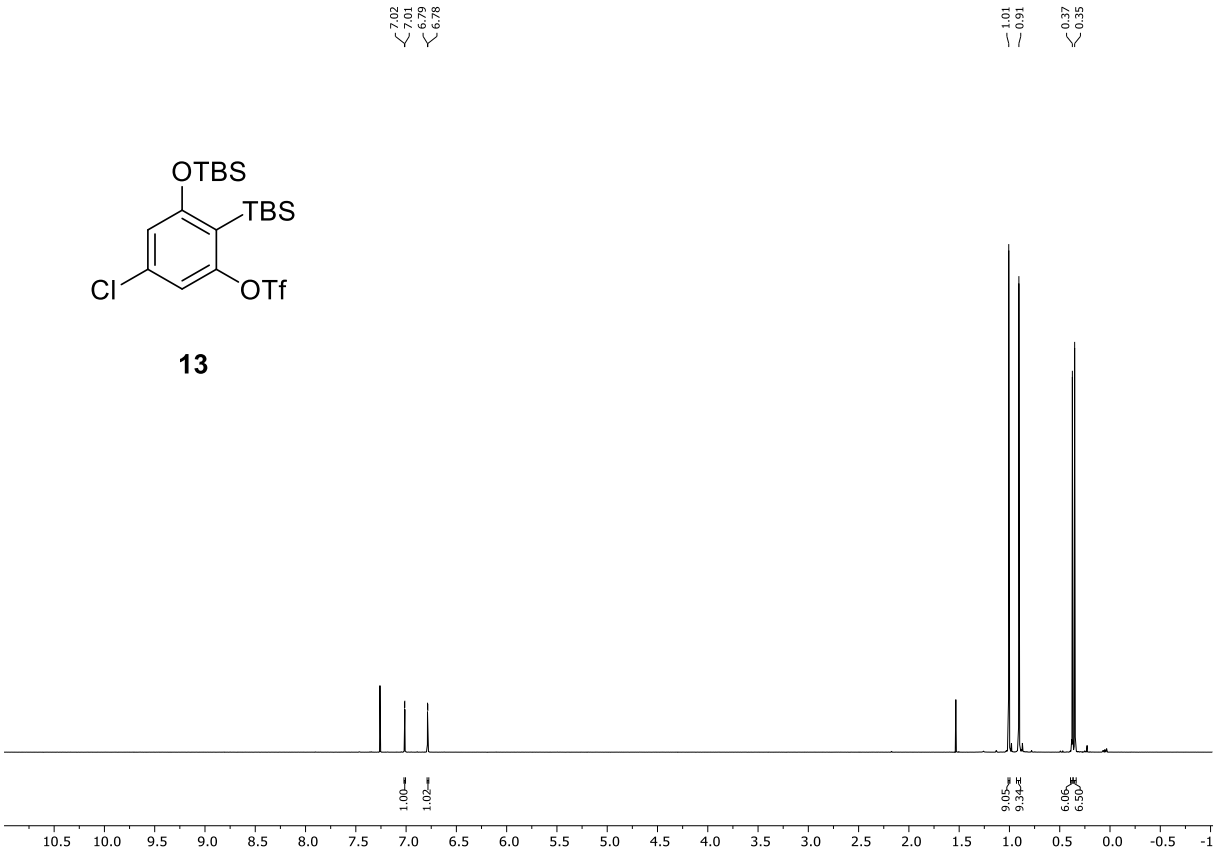
4c

^{19}F-NMR (282 MHz, $CDCl_3$)

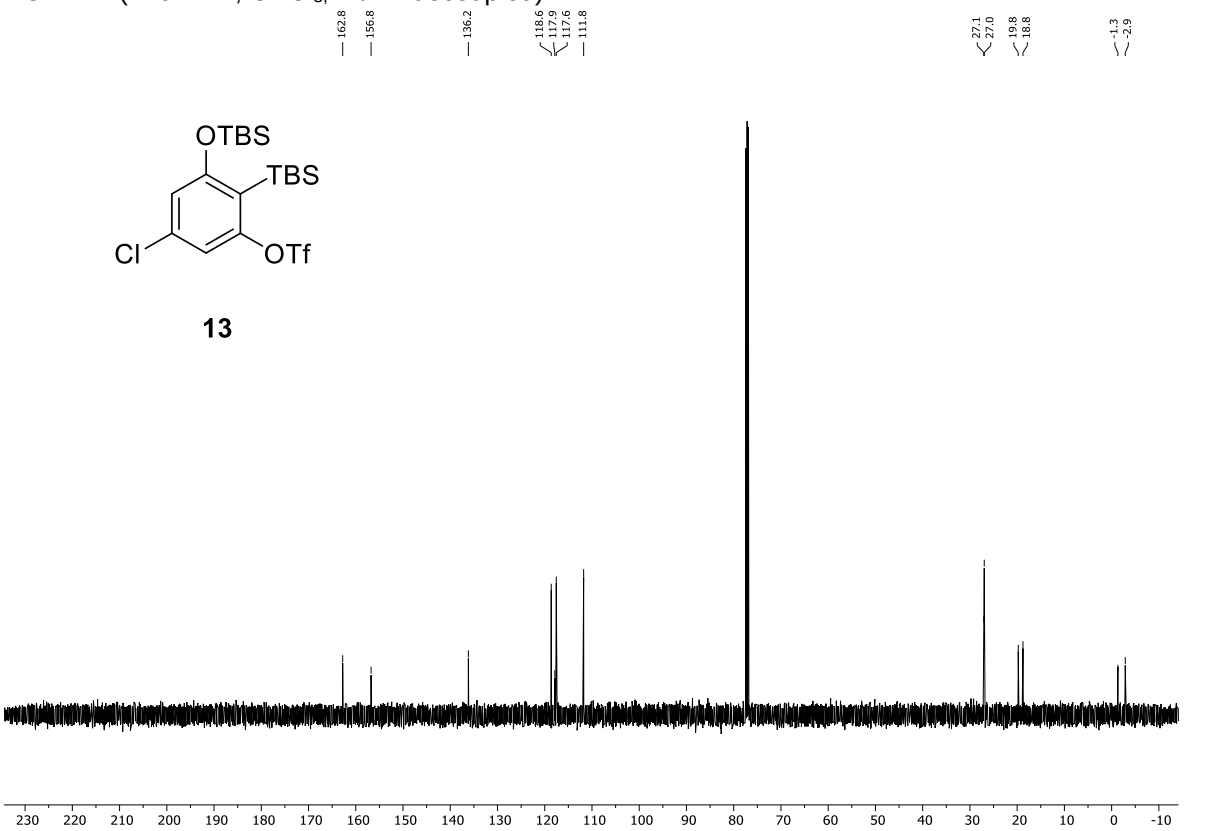


2-(*tert*-Butyldimethylsilyl)-3-((*tert*-butyldimethylsilyl)oxy)-5-chlorophenyl trifluoromethanesulfonate (13)

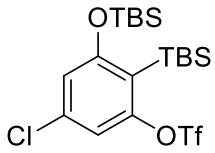
^{1}H-NMR (500 MHz, $CDCl_3$)



^{13}C-NMR (126 MHz, $CDCl_3$, ^{1}H/^{19}F decoupled)



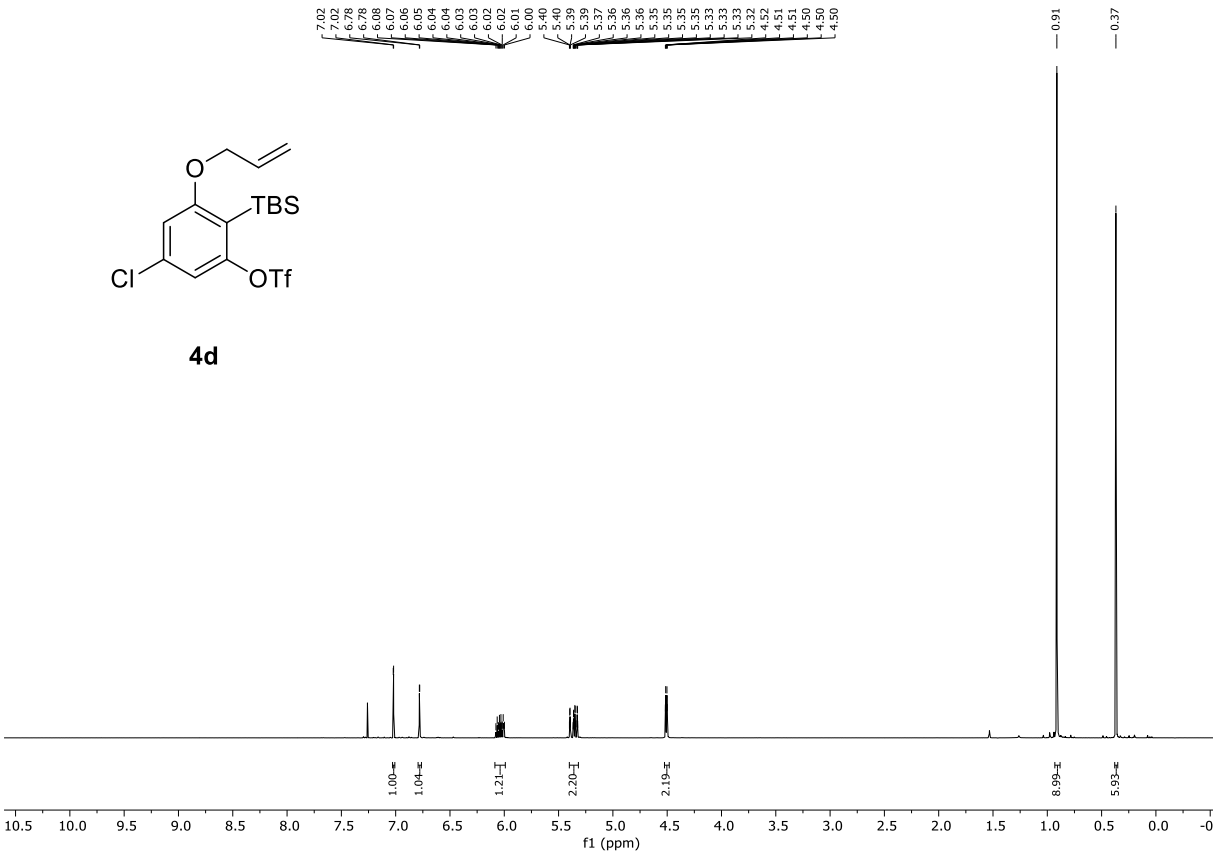
^{19}F-NMR (470 MHz, $CDCl_3$)



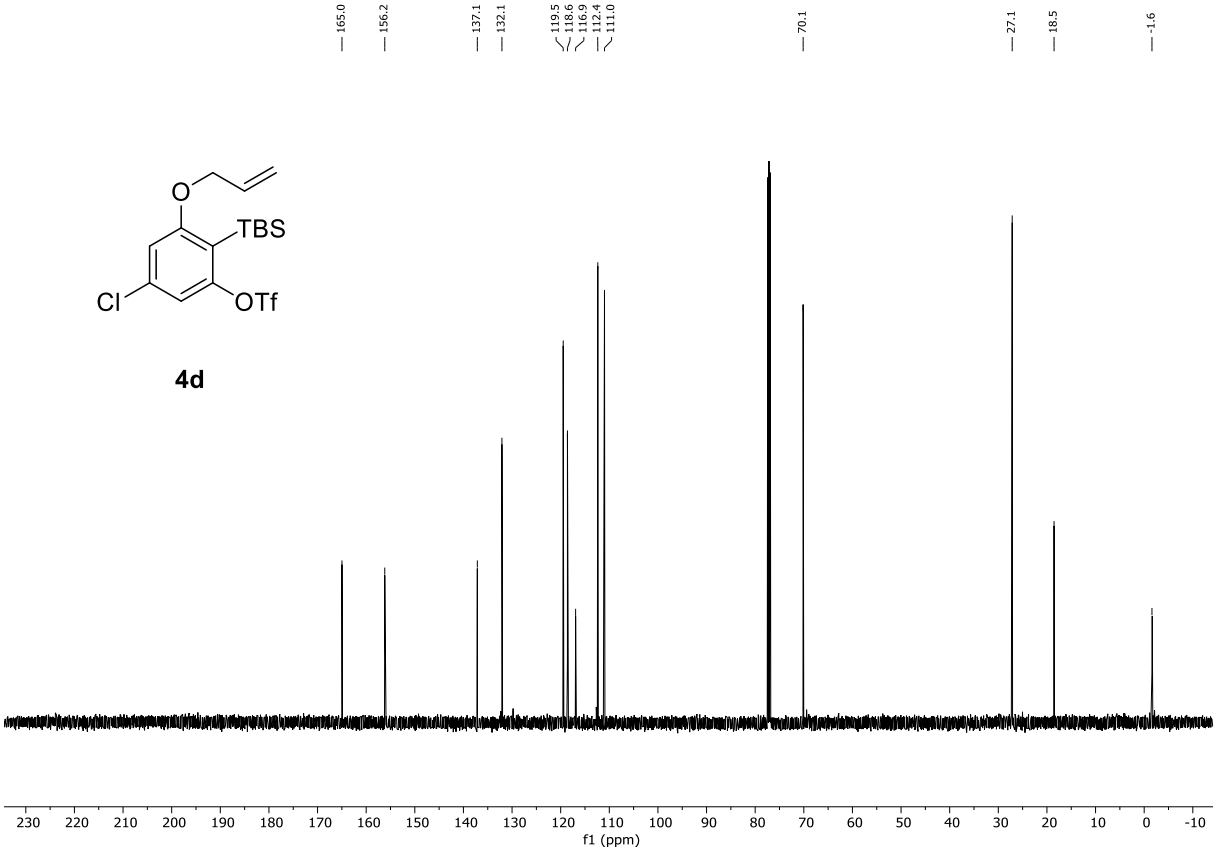
13

3-(Allyloxy)-2-(*tert*-butyldimethylsilyl)-5-chlorophenyl trifluoromethanesulfonate (4d)

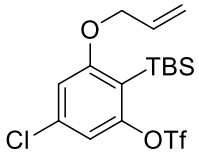
^{1}H-NMR (500 MHz, $CDCl_3$)



^{13}C-NMR (126 MHz, $CDCl_3$, ^{1}H/^{19}F decoupled)



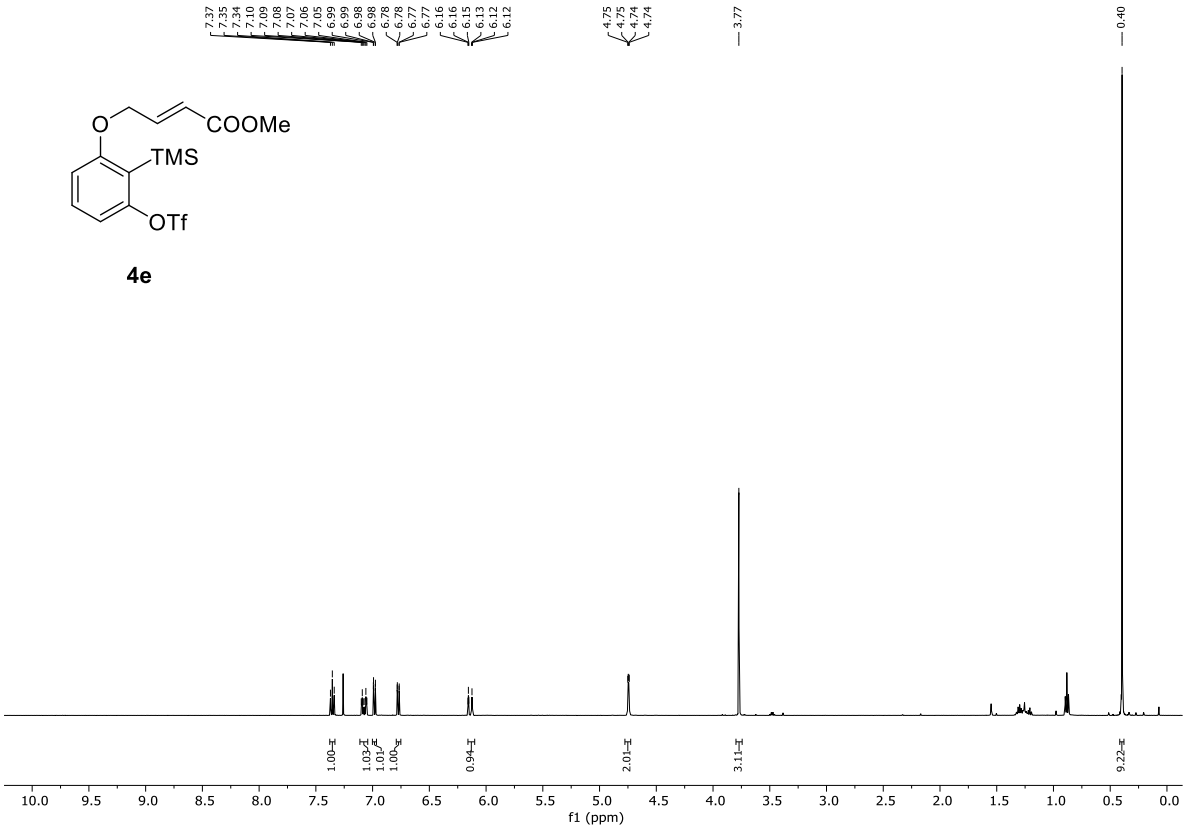
^{19}F-NMR (470 MHz, $CDCl_3$)



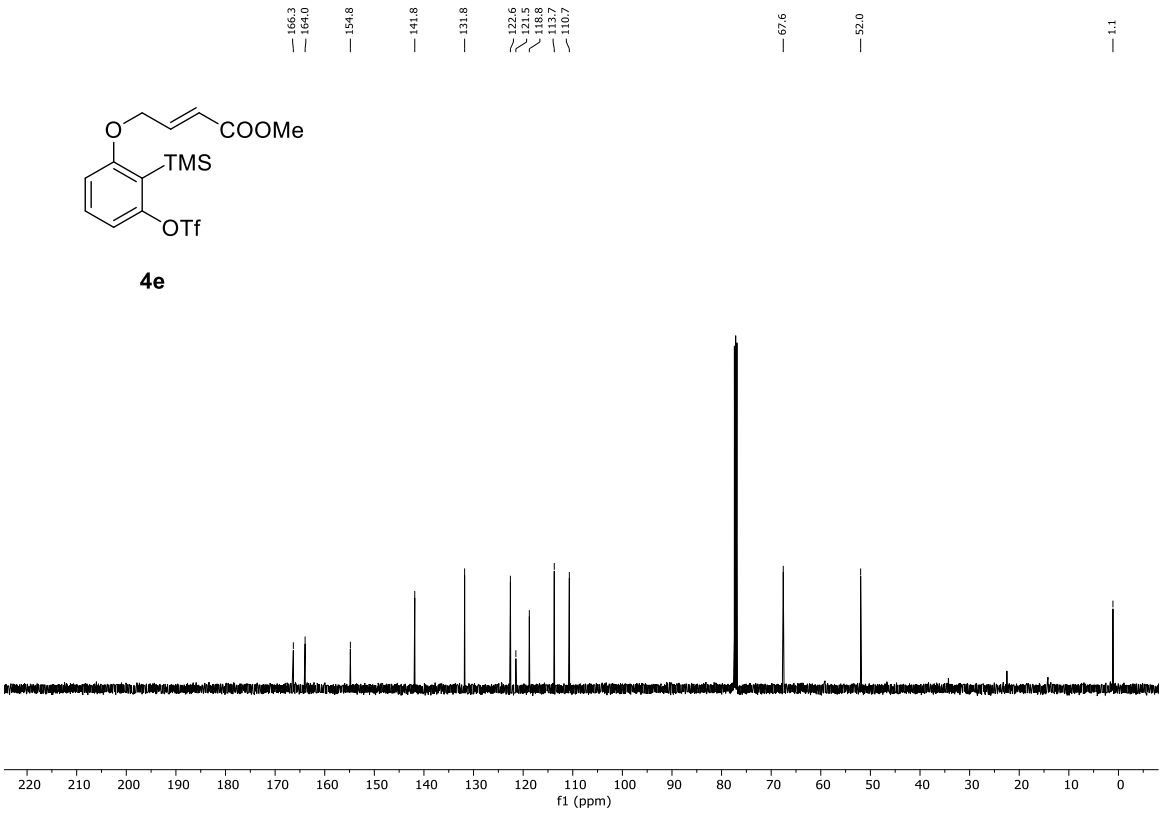
4d

Methyl *(E)*-4-(3-(((trifluoromethyl)sulfonyl)oxy)-2-(trimethylsilyl)phenoxy)but-2-enoate (4e)

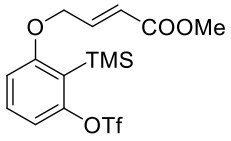
^{1}H-NMR (500 MHz, $CDCl_3$)



^{13}C-NMR (126 MHz, $CDCl_3$, ^{1}H/^{19}F decoupled)



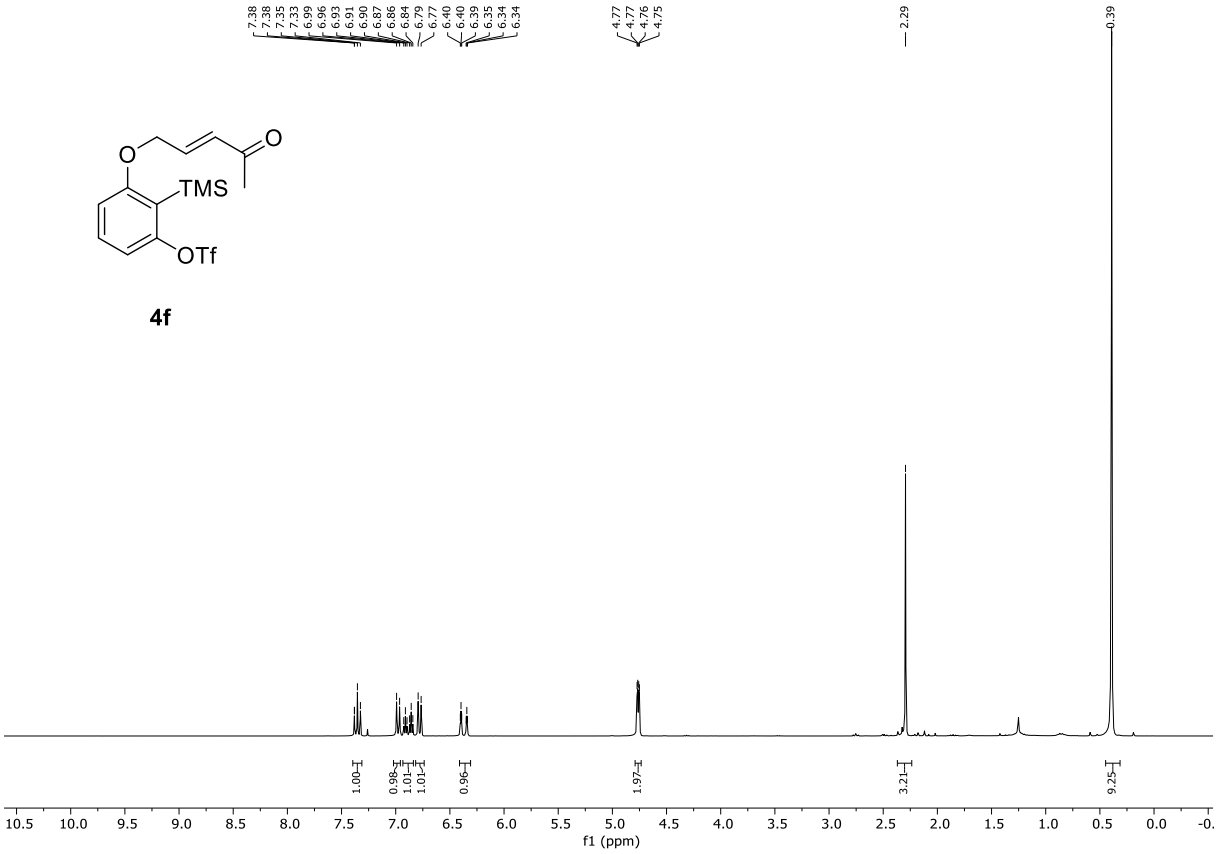
^{19}F-NMR (470 MHz, $CDCl_3$)



4e

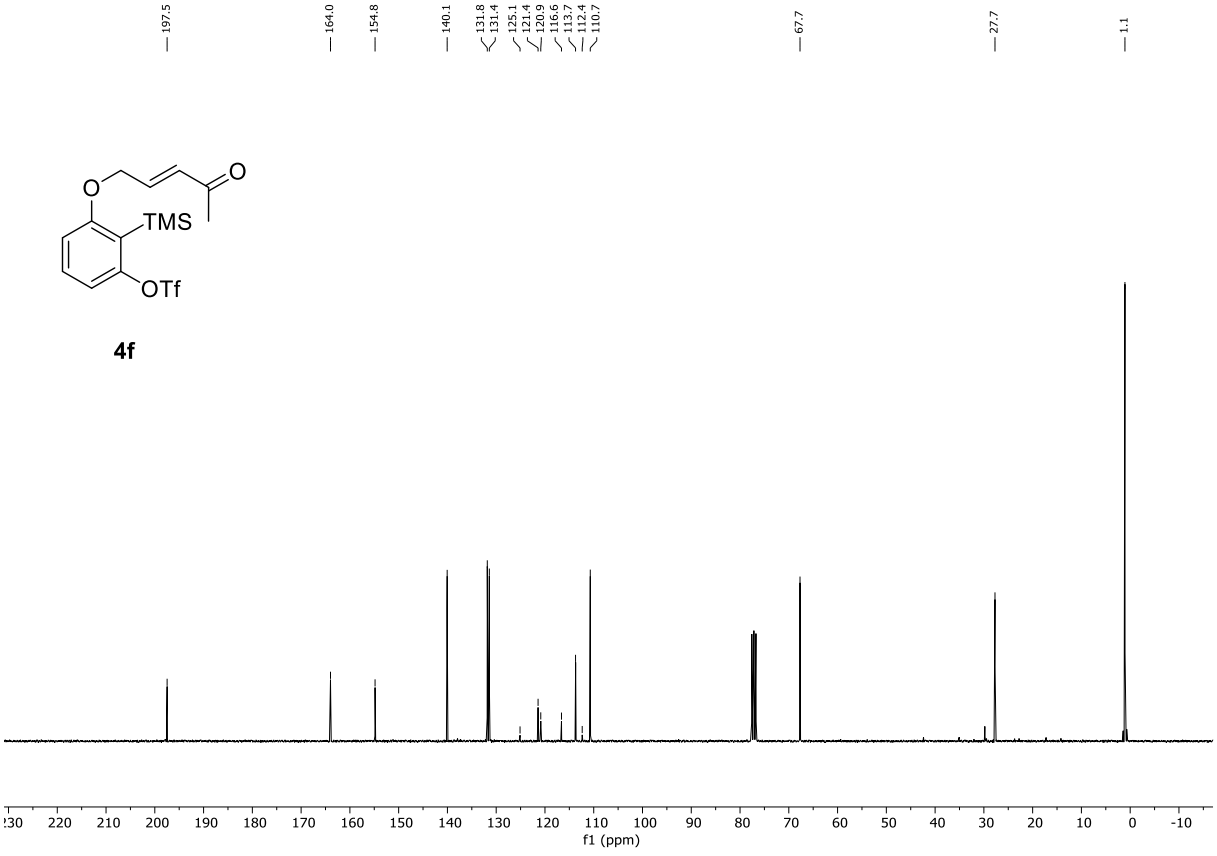
(E)-3-((4-Oxopent-2-en-1-yl)oxy)-2-(trimethylsilyl)phenyl trifluoromethanesulfonate (4f)

^{1}H-NMR (300 MHz, $CDCl_3$)



4f

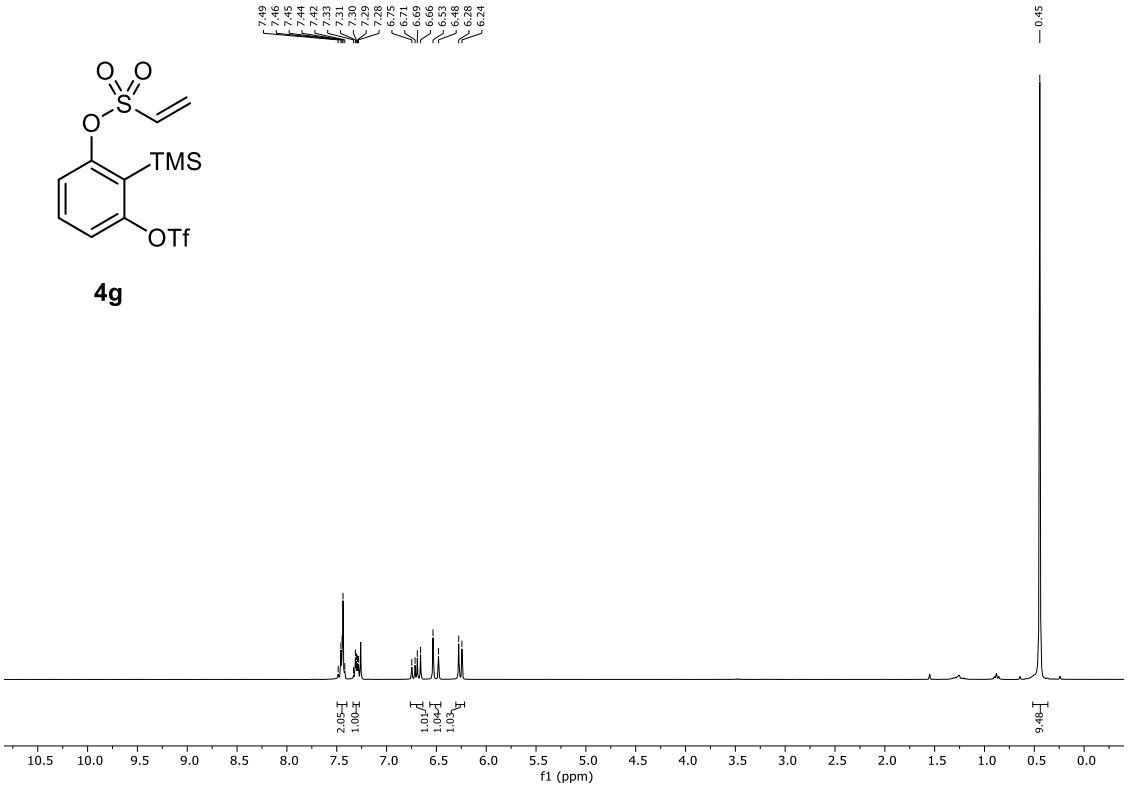
^{13}C-NMR (75 MHz, $CDCl_3$)



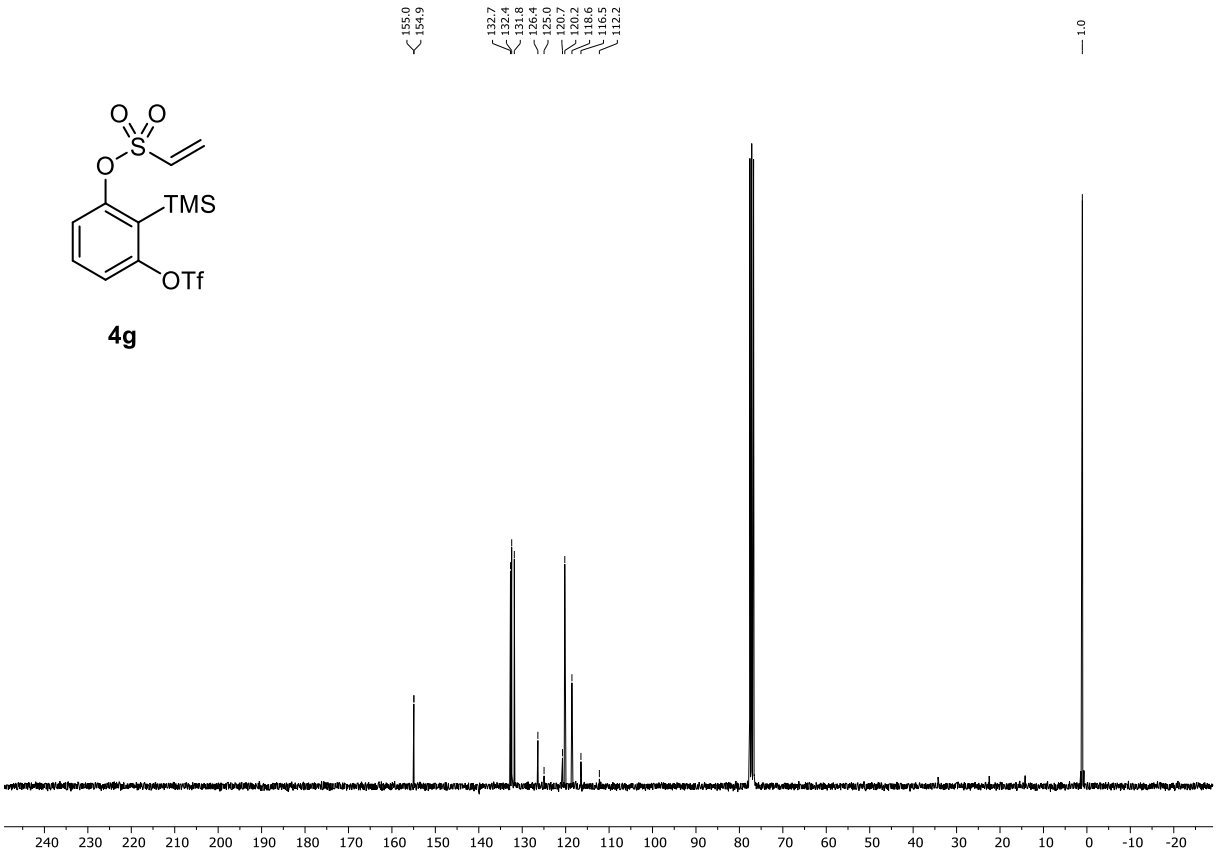
4f

3-(((Trifluoromethyl)sulfonyl)oxy)-2-(trimethylsilyl)phenyl ethenesulfonate (4g)

^{1}H-NMR (300 MHz, $CDCl_3$)

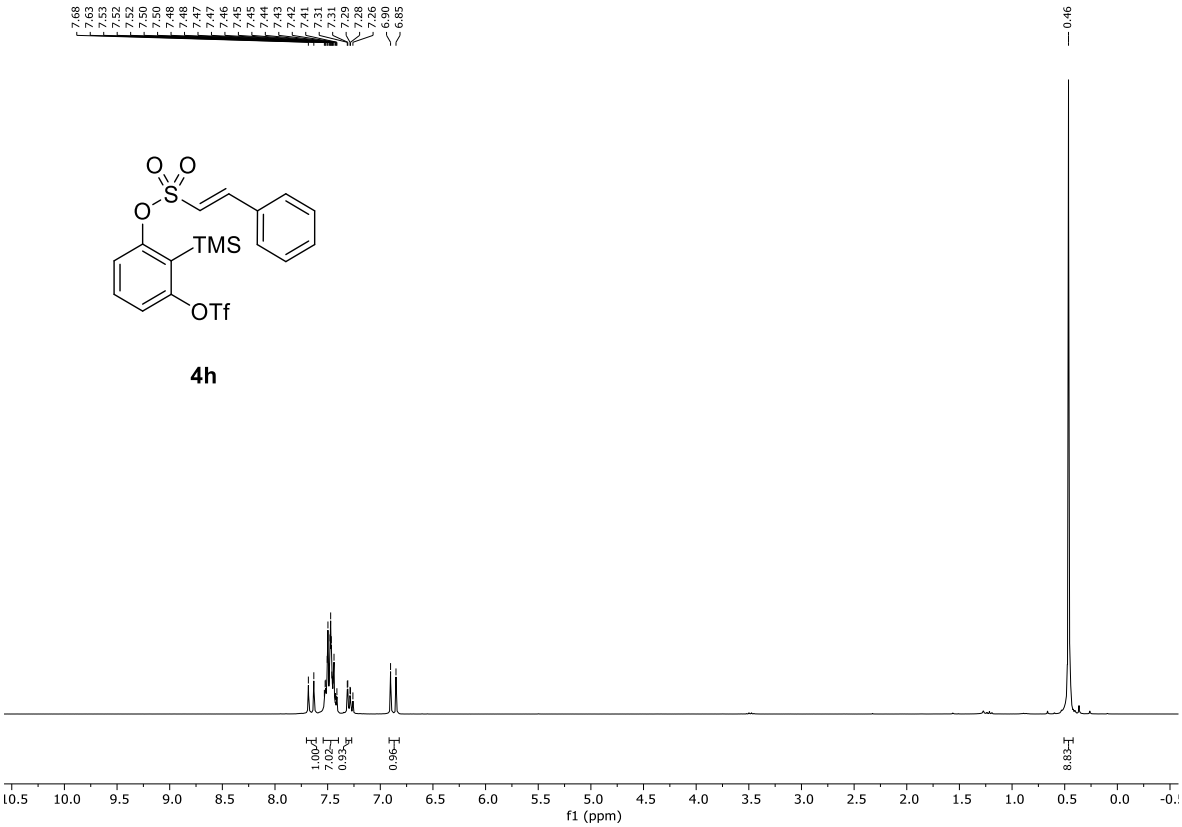


^{13}C-NMR (75 MHz, $CDCl_3$)



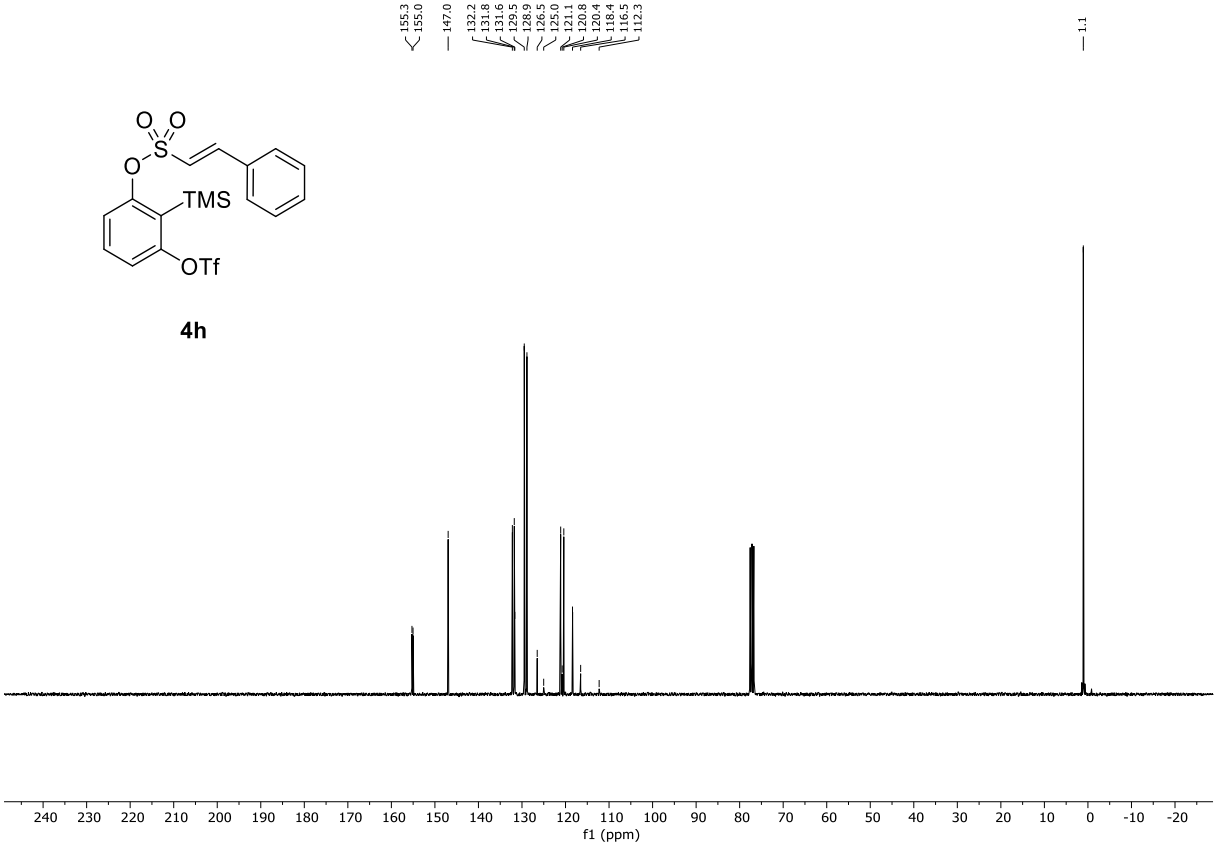
3-(((Trifluoromethyl)sulfonyl)oxy)-2-(trimethylsilyl)phenyl *(E)*-2-phenylethene-1-sulfonate (4h)

^{1}H-NMR (300 MHz, $CDCl_3$)



4h

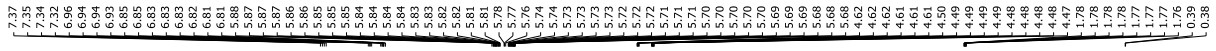
^{13}C-NMR (75 MHz, $CDCl_3$)

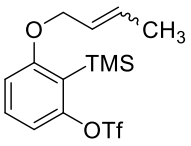


4h

(E)/(Z)-3-(But-2-en-1-yloxy)-2-(trimethylsilyl)phenyl trifluoromethanesulfonate (4i)

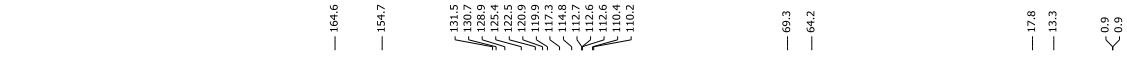
^{1}H-NMR (500 MHz, $CDCl_3$)

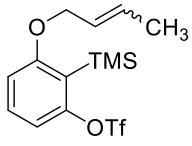




4i

^{13}C-NMR (126 MHz, $CDCl_3$)

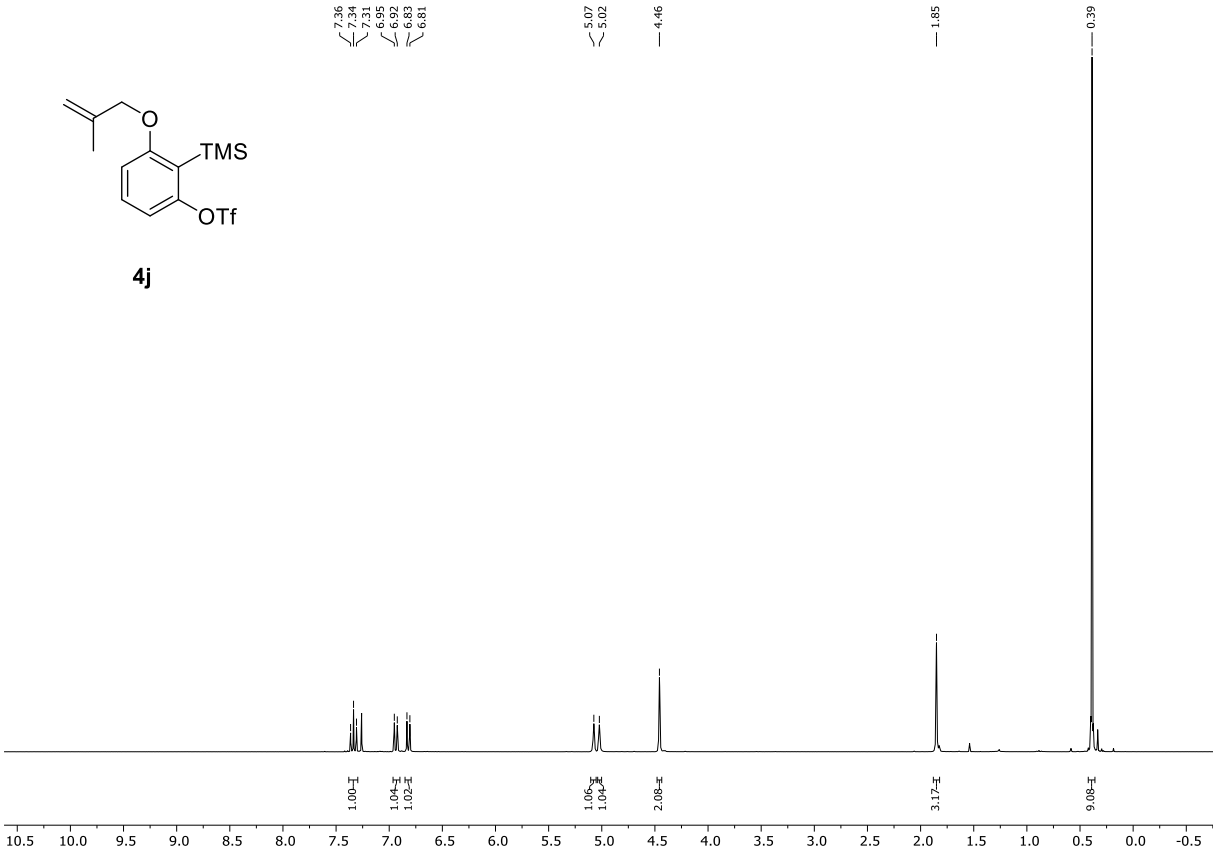




4i

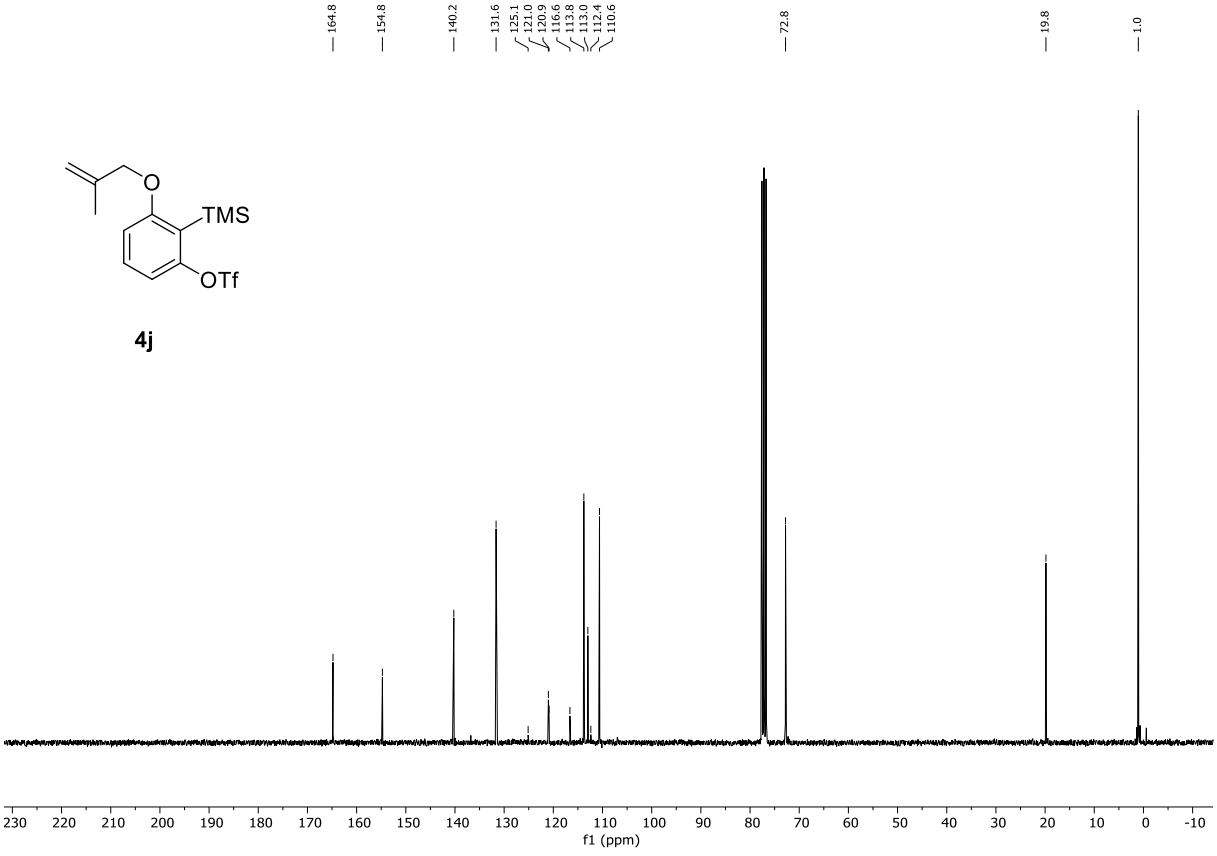
3-((2-Methylallyl)oxy)-2-(trimethylsilyl)phenyl trifluoromethanesulfonate (4j)

^{1}H-NMR (300 MHz, $CDCl_3$)



4j

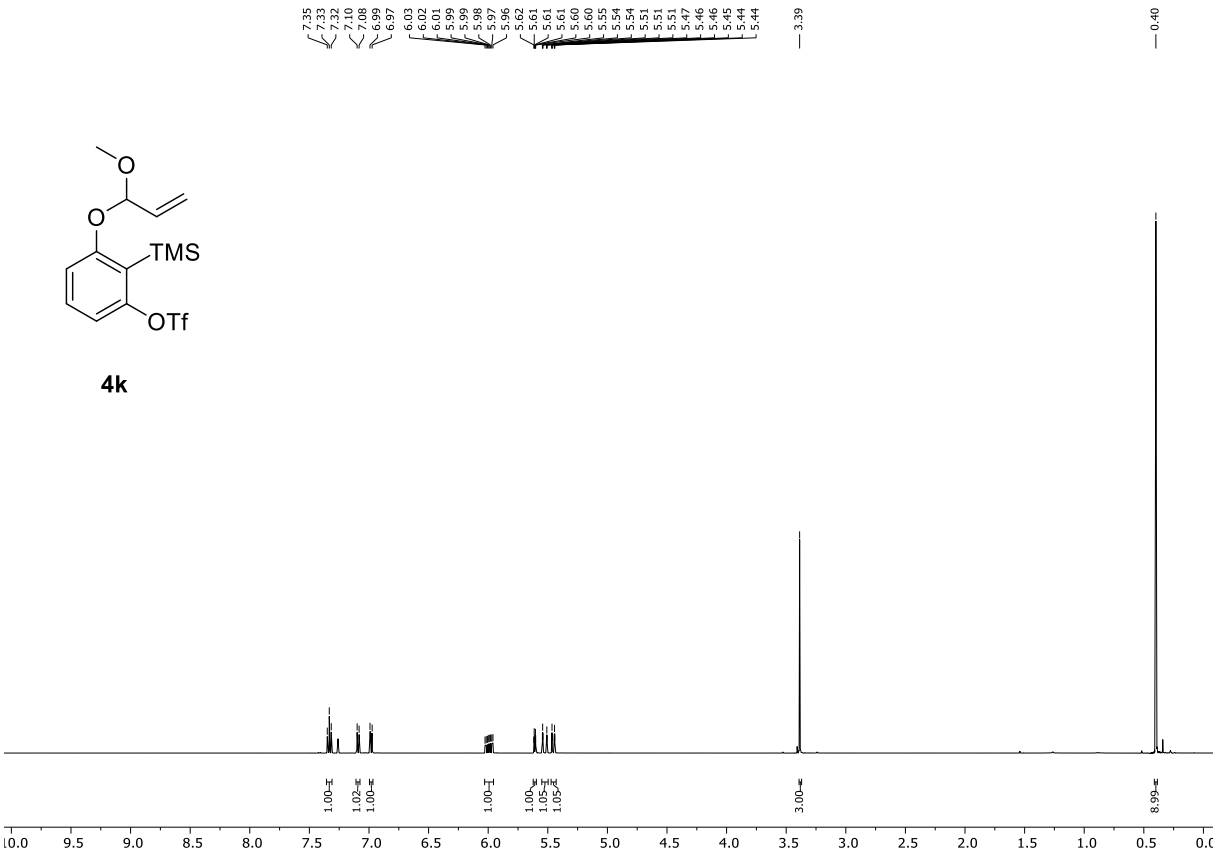
^{13}C-NMR (75 MHz, $CDCl_3$)



4j

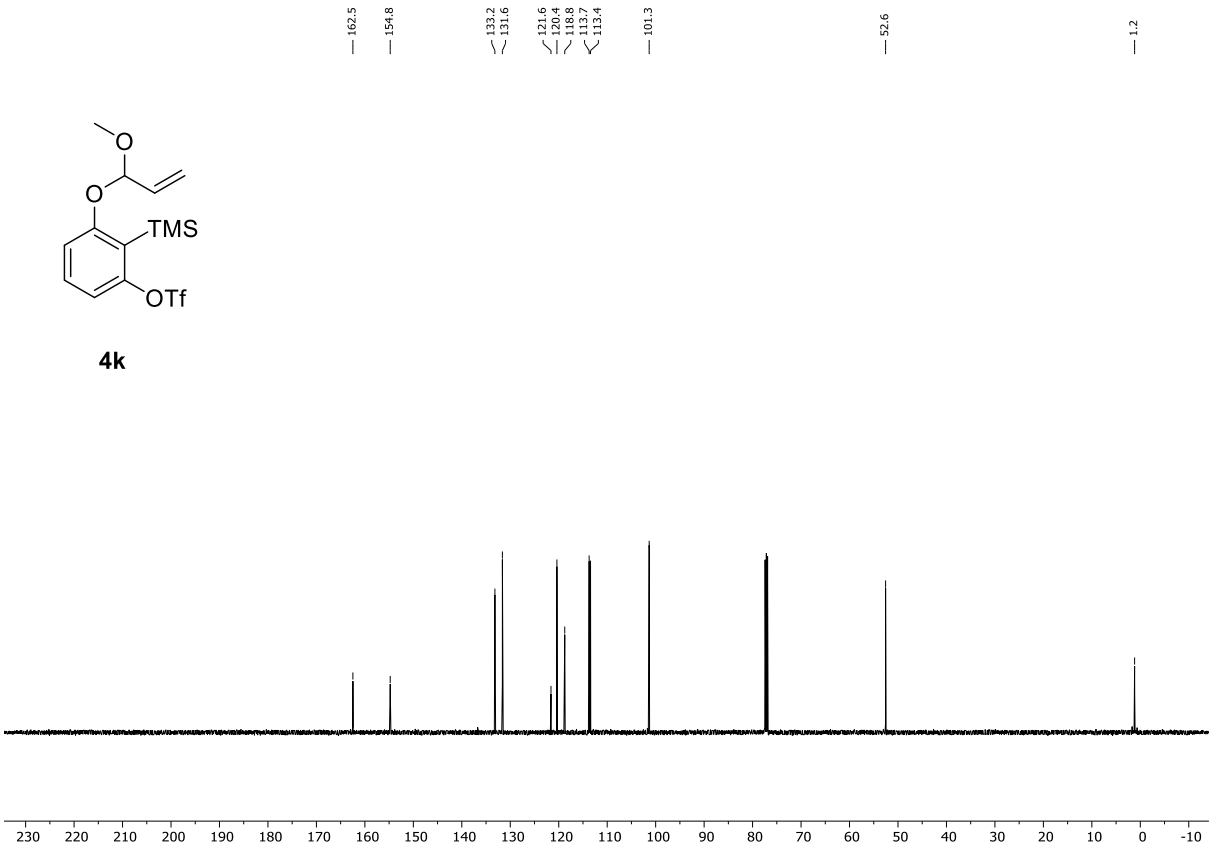
3-((1-Methoxyallyl)oxy)-2-(trimethylsilyl)phenyl trifluoromethanesulfonate (4k)

^{1}H-NMR (500 MHz, $CDCl_3$)



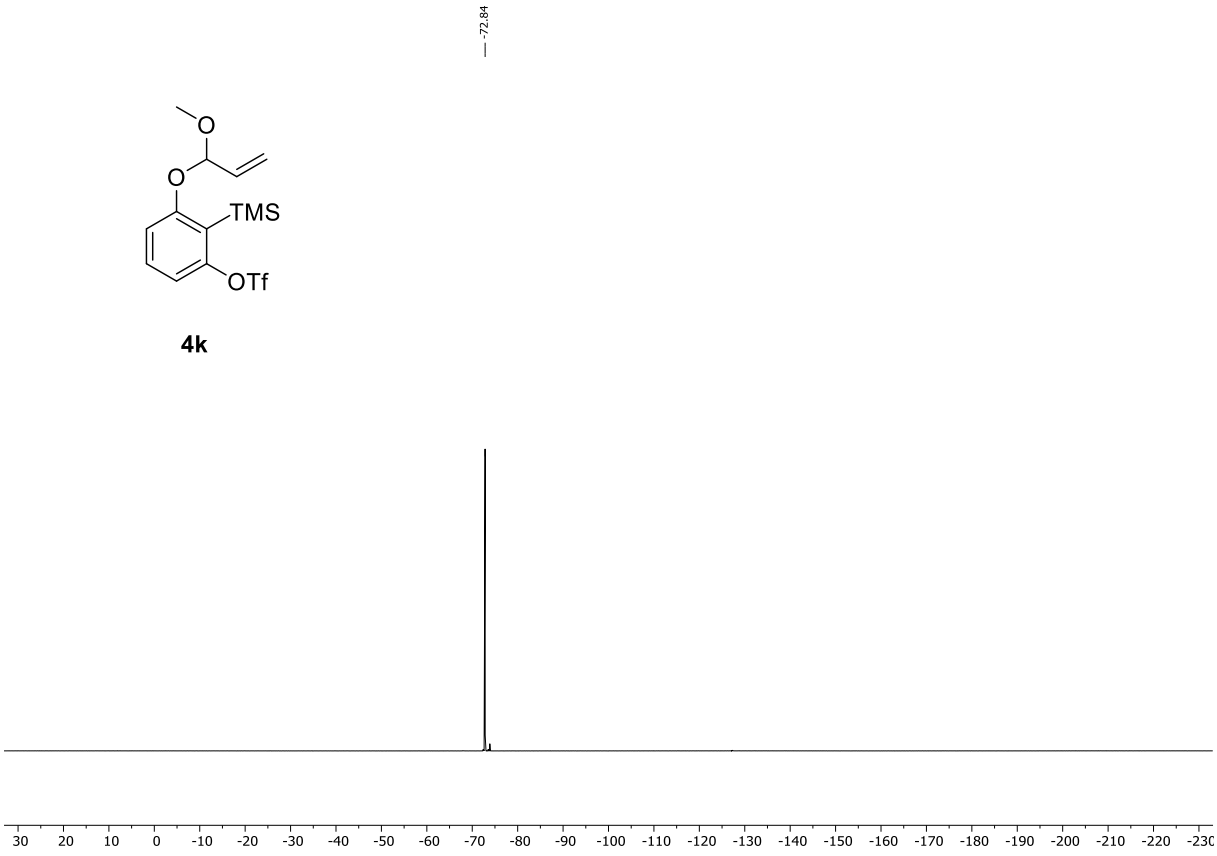
4k

^{13}C-NMR (126 MHz, $CDCl_3$, ^{1}H/^{19}F decoupled)



4k

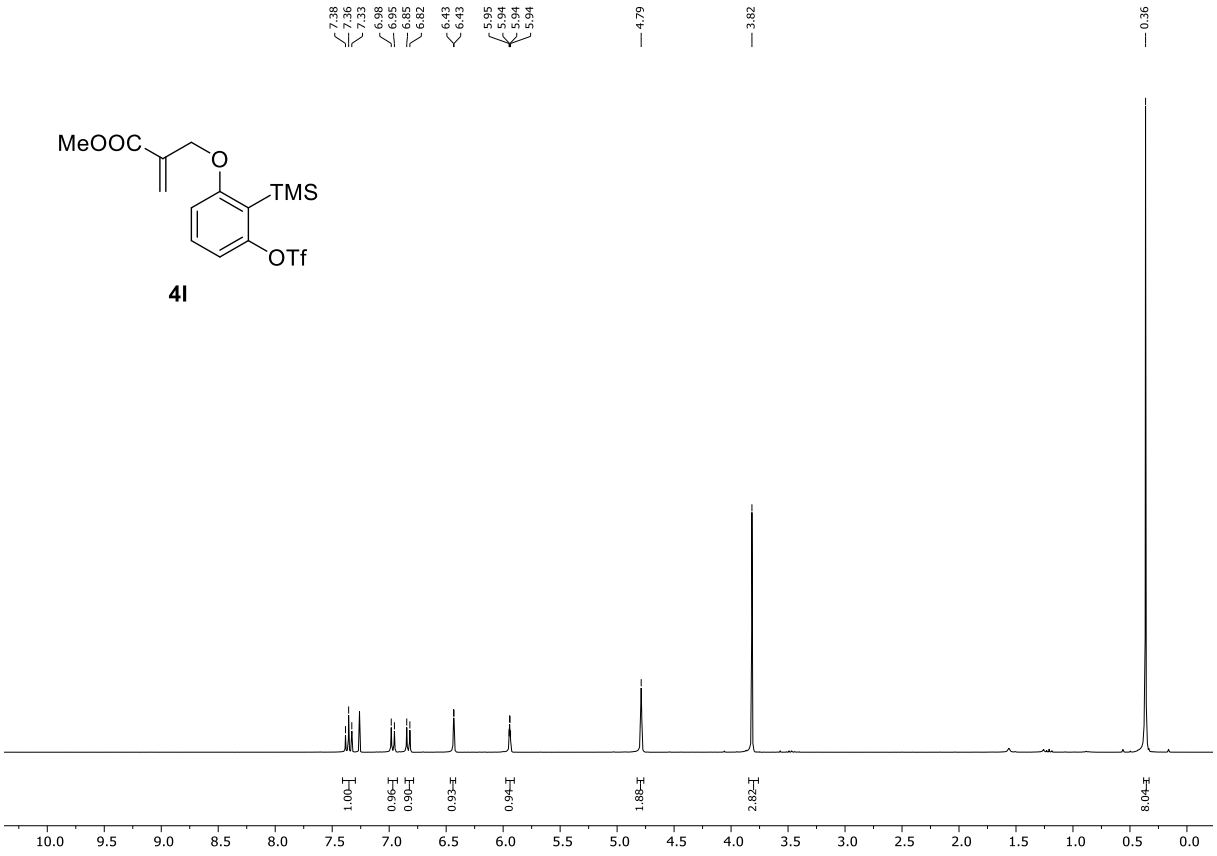
^{19}F-NMR (470 MHz, $CDCl_3$)



4k

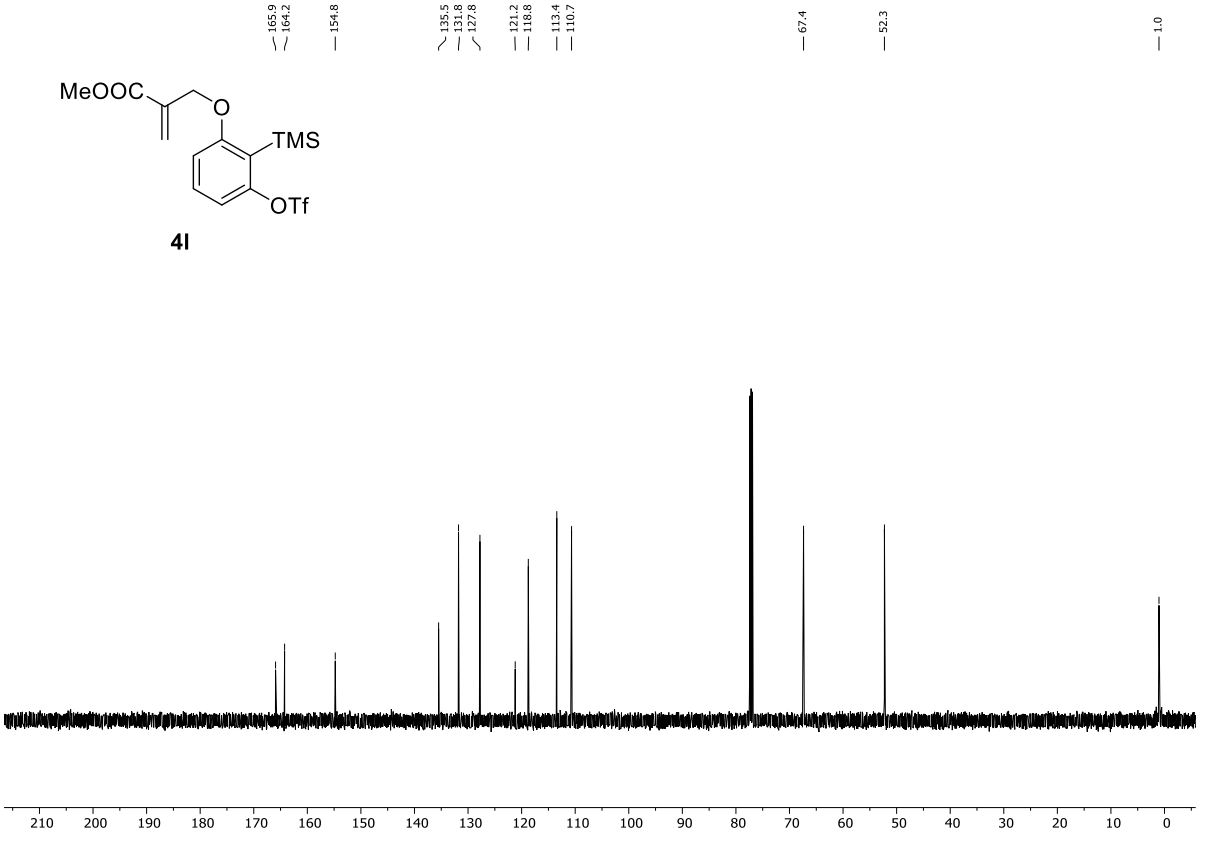
Methyl 2-((3-(((trifluoromethyl)sulfonyl)oxy)-2-(trimethylsilyl)phenoxy)methyl)acrylate (4l)

^{1}H-NMR (300 MHz, $CDCl_3$)



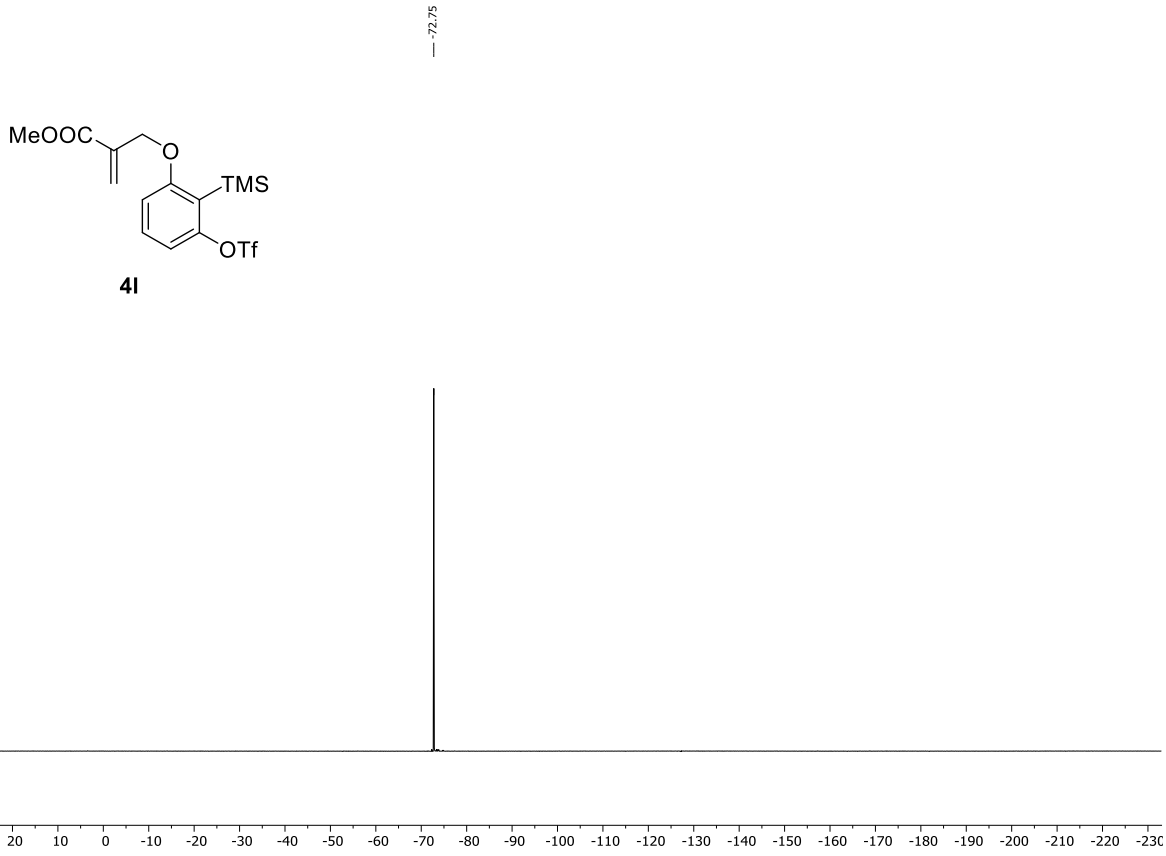
4l

^{13}C-NMR (126 MHz, $CDCl_3$, , ^{1}H/^{19}F decoupled)



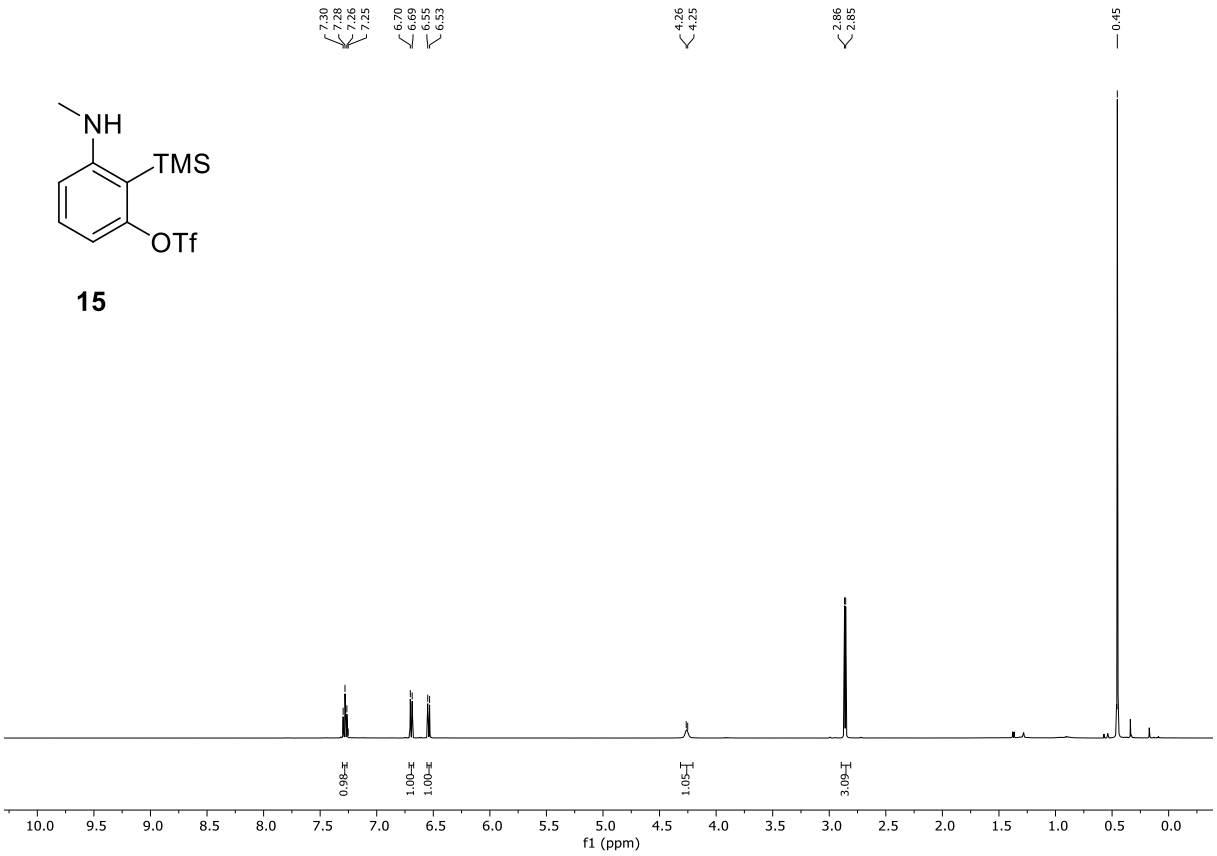
4l

^{19}F-NMR (282 MHz, $CDCl_3$)

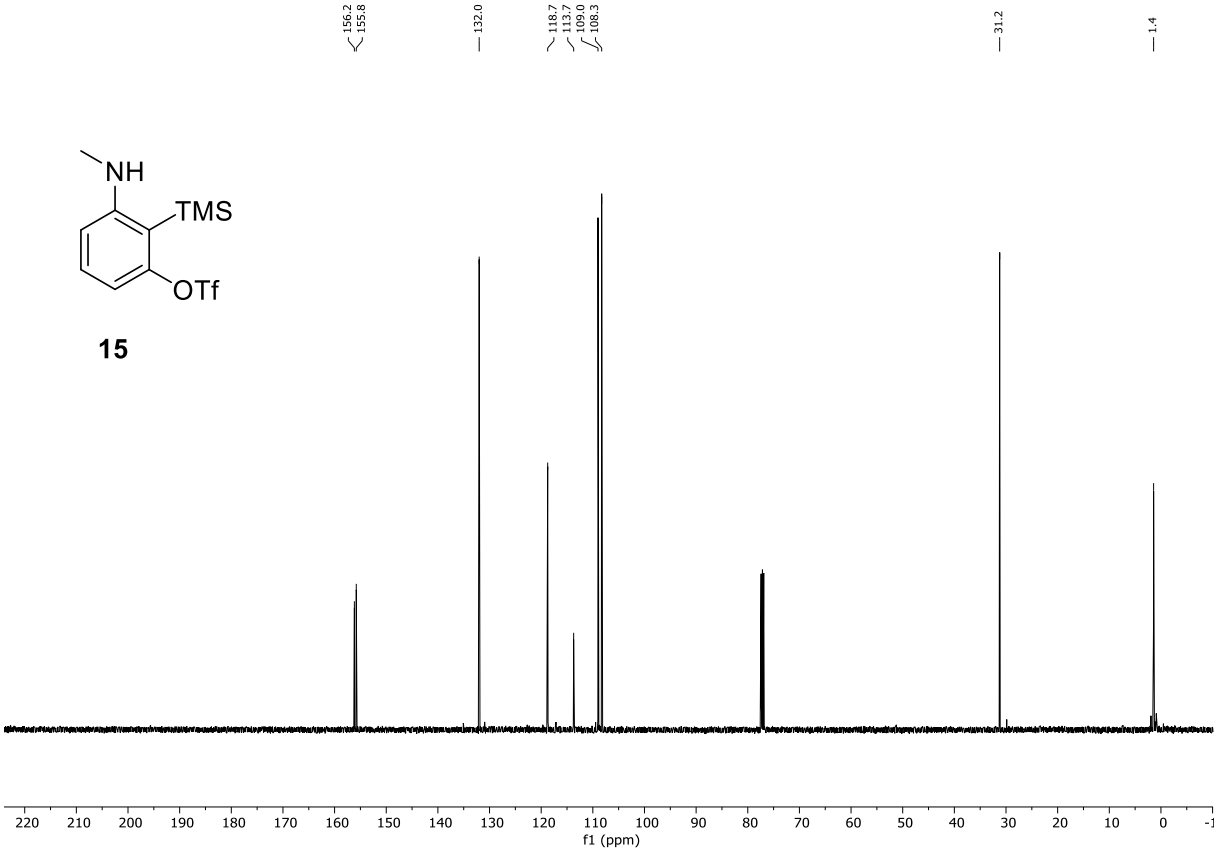


3-(Methylamino)-2-(trimethylsilyl)phenyl trifluoromethanesulfonate (15)

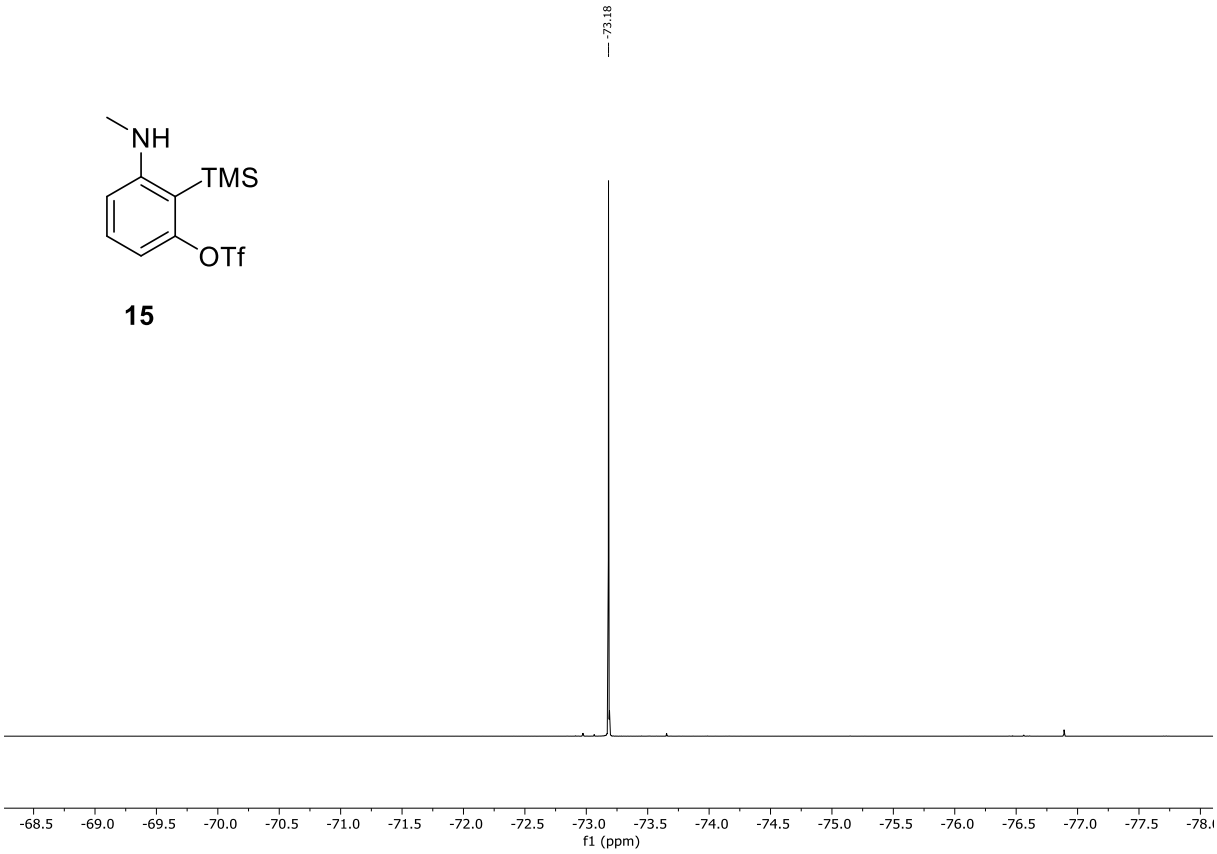
^{1}H-NMR (500 MHz, $CDCl_3$)



^{13}C-NMR (126 MHz, $CDCl_3$, , ^{1}H/^{19}F decoupled)

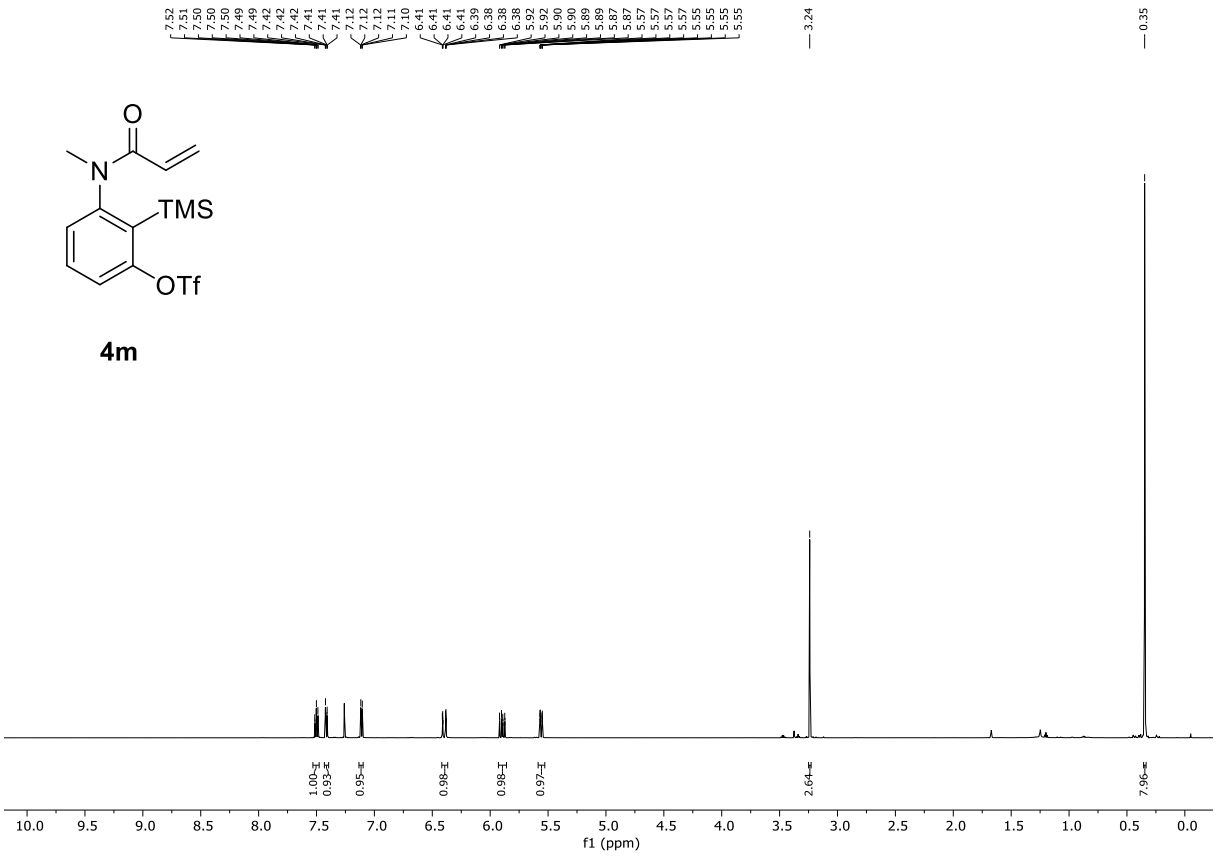


^{19}F-NMR (470 MHz, $CDCl_3$)

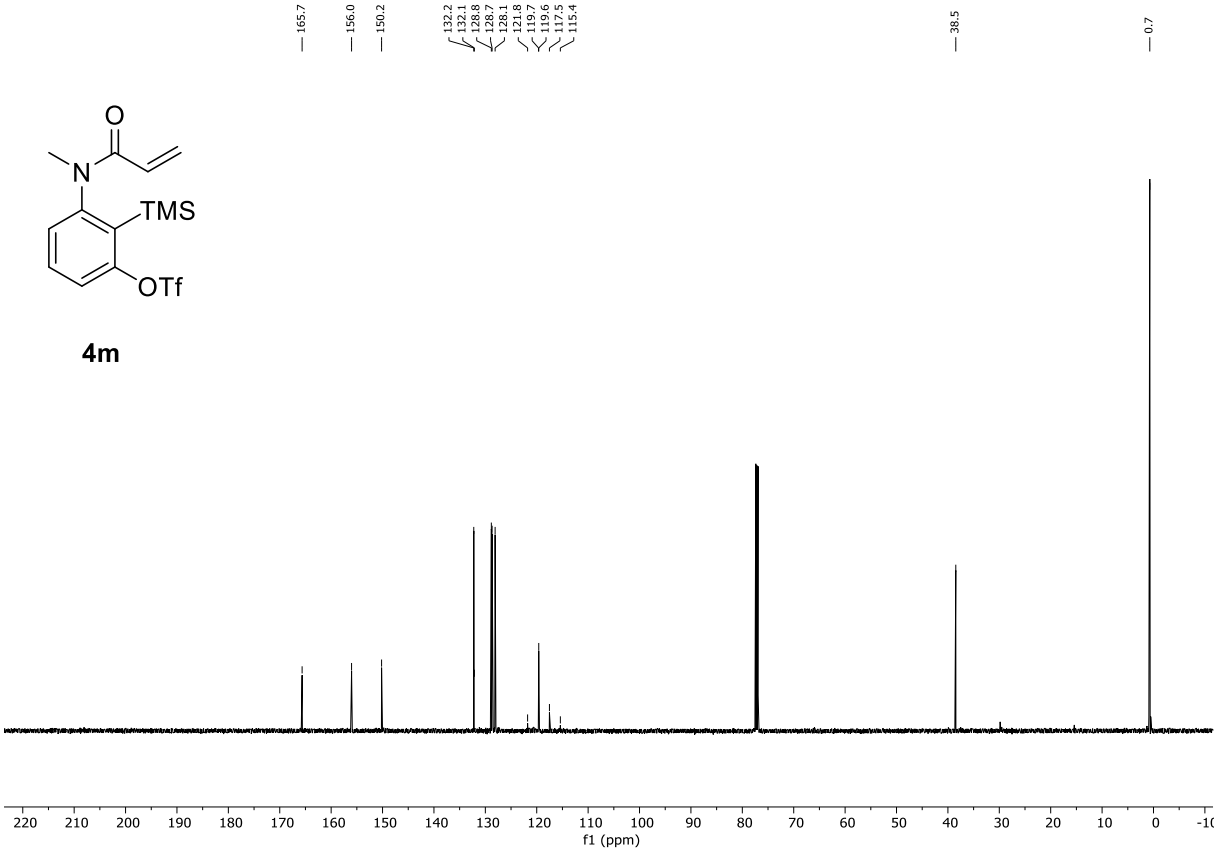


3-(*N*-Methylacrylamido)-2-(trimethylsilyl)phenyl trifluoromethanesulfonate (4m)

^{1}H-NMR (599 MHz, $CDCl_3$)

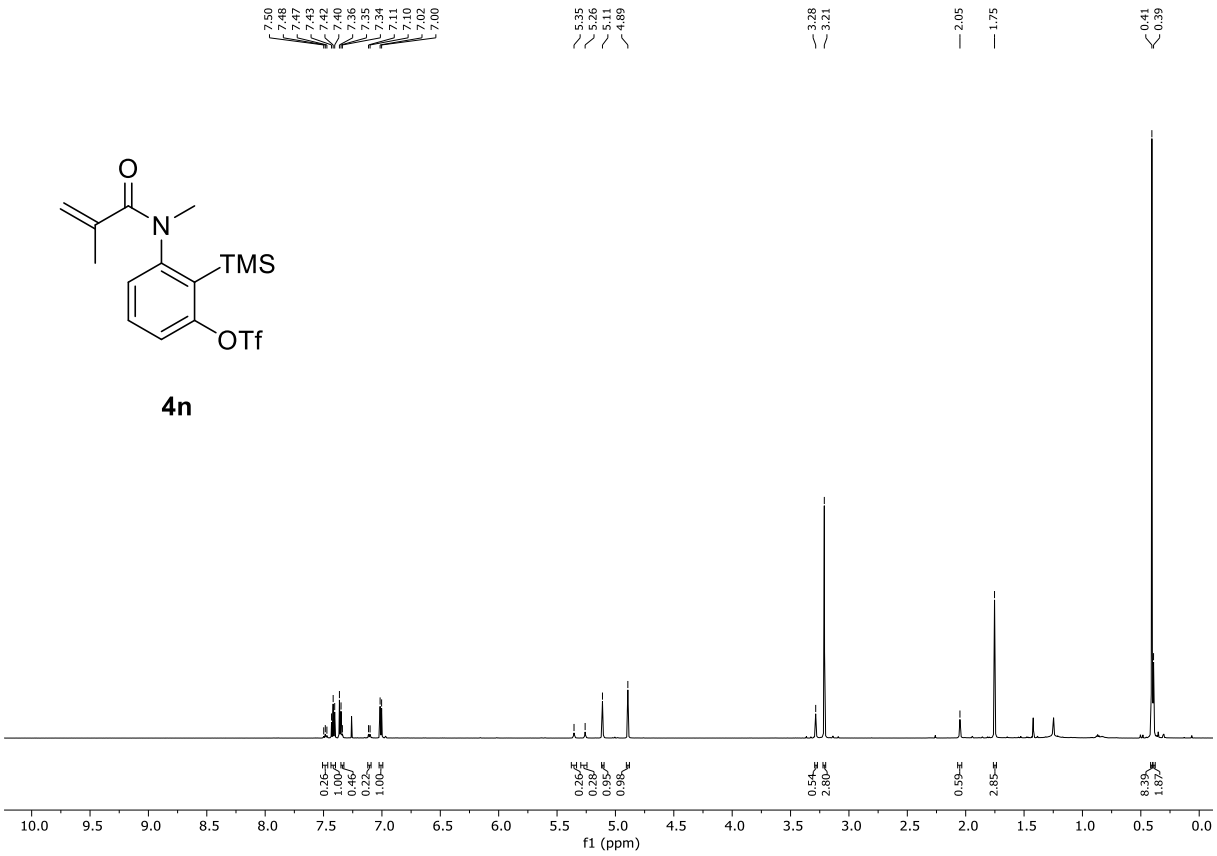


^{13}C-NMR (151 MHz, $CDCl_3$)

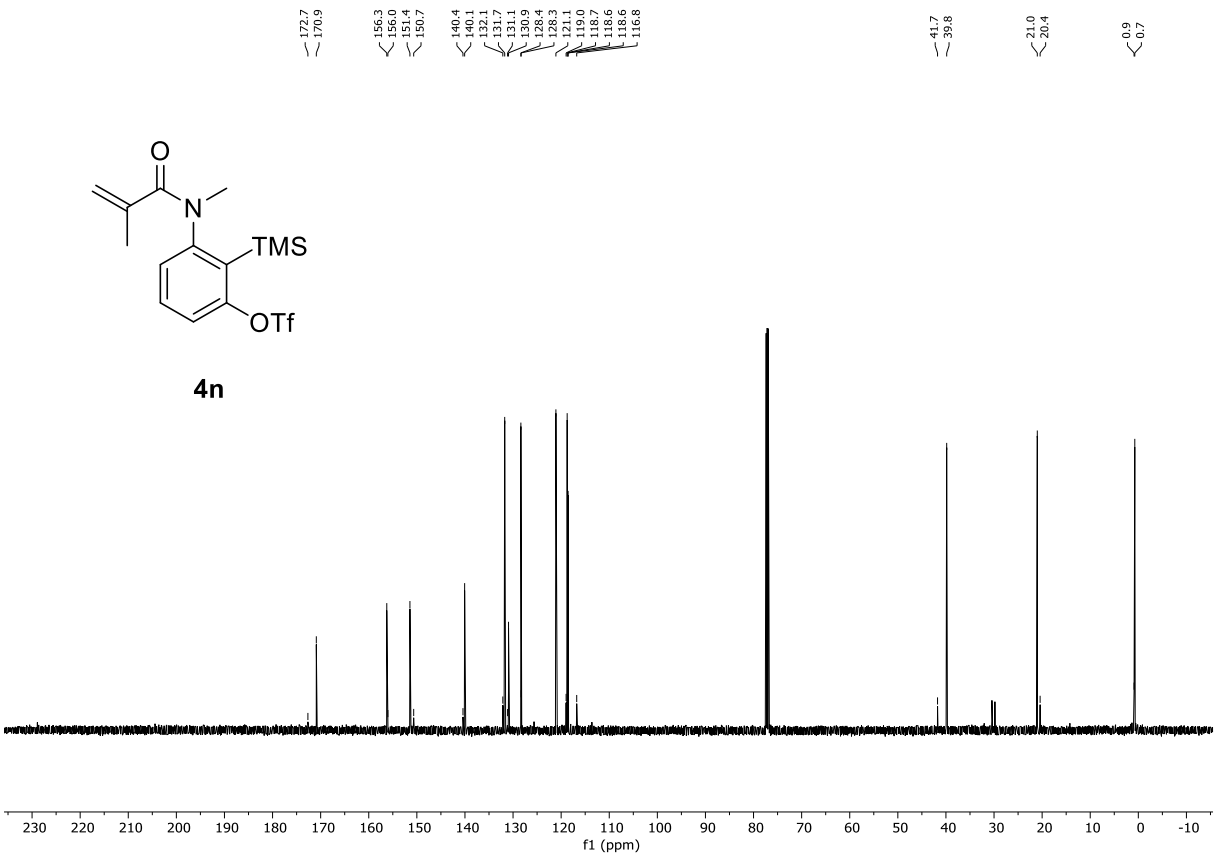


3-(*N*-Methylmethacrylamido)-2-(trimethylsilyl)phenyl trifluoromethanesulfonate (4n)

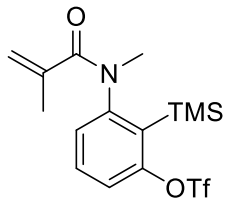
^{1}H-NMR (599 MHz, $CDCl_3$)



^{13}C-NMR (151 MHz, $CDCl_3$, ^{1}H/^{19}F decoupled)



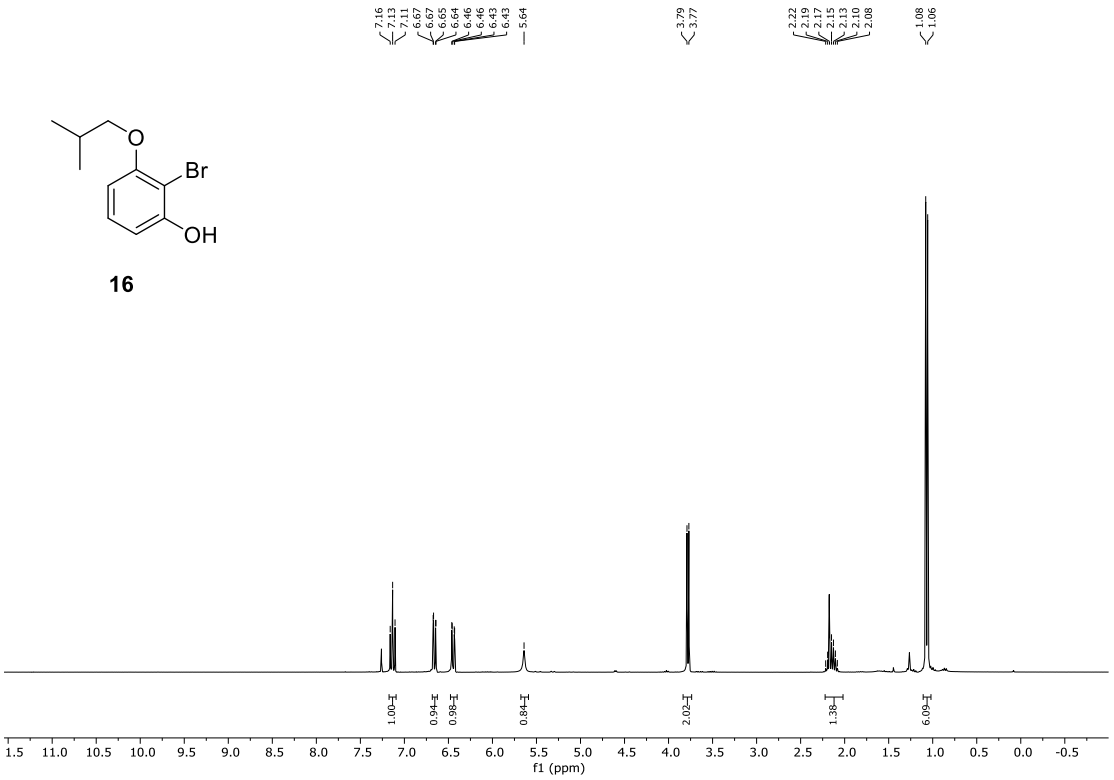
^{19}F-NMR (282 MHz, $CDCl_3$)



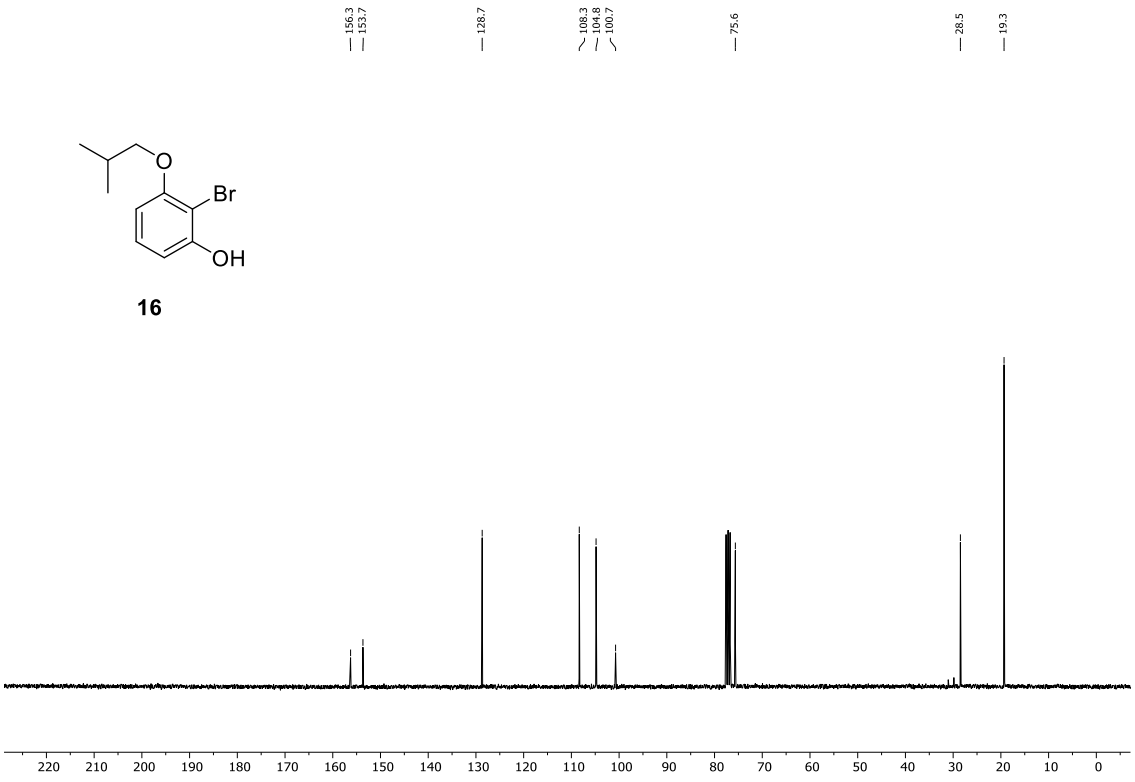
4n

2-Bromo-3-isobutoxyphenol (16)

^{1}H-NMR (300 MHz, $CDCl_3$)

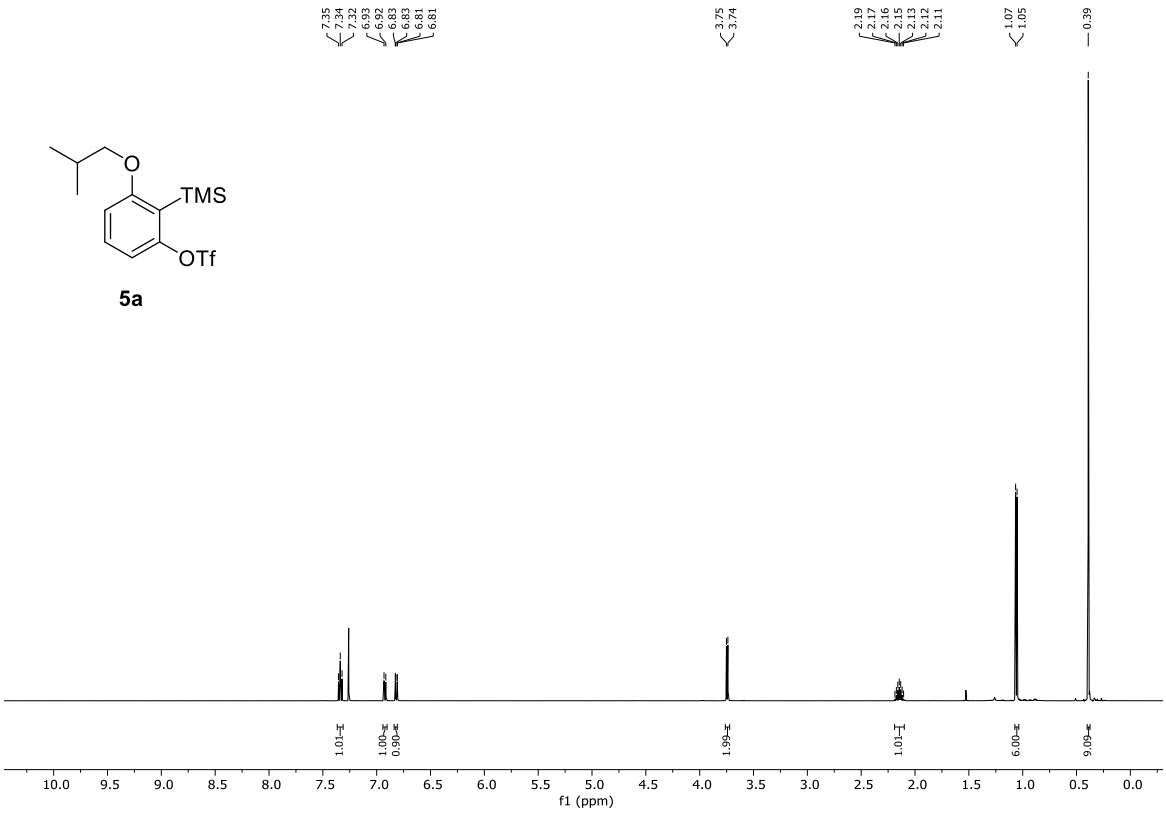


^{13}C-NMR (75 MHz, $CDCl_3$)



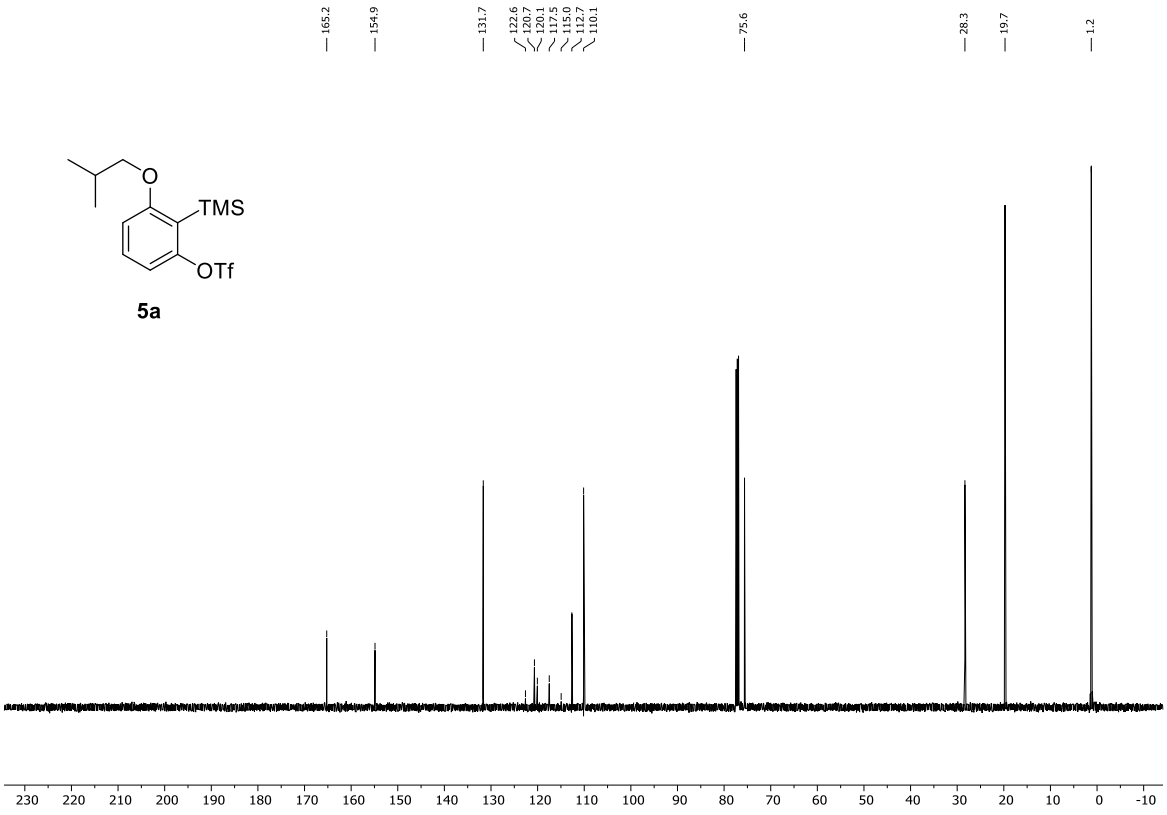
3-Isobutoxy-2-(trimethylsilyl)phenyl trifluoromethanesulfonate (5a)

^{1}H-NMR (500 MHz, $CDCl_3$)



5a

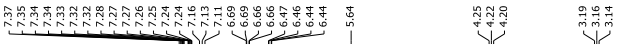
^{13}C-NMR (126 MHz, $CDCl_3$)

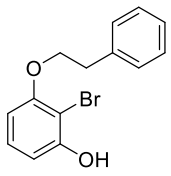


5a

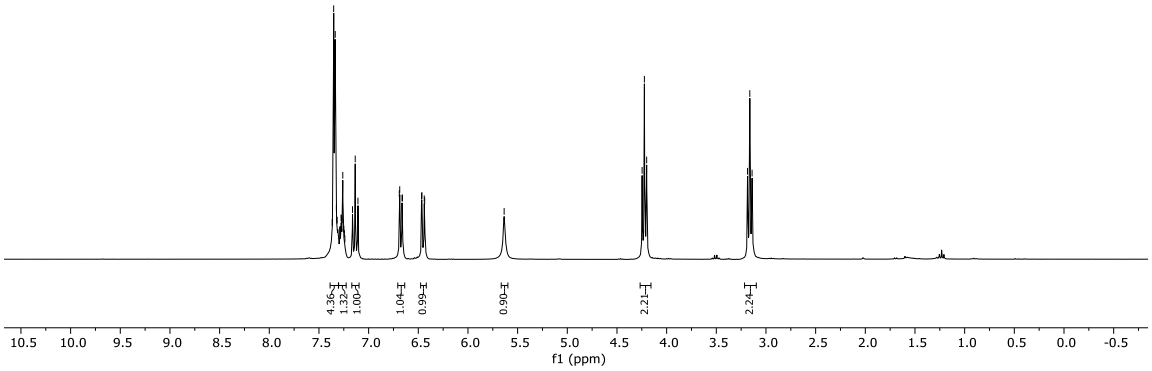
2-Bromo-3-phenethoxyphenol (17)

^{1}H-NMR (300 MHz, $CDCl_3$)

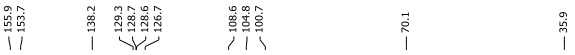


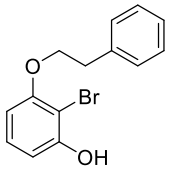


17

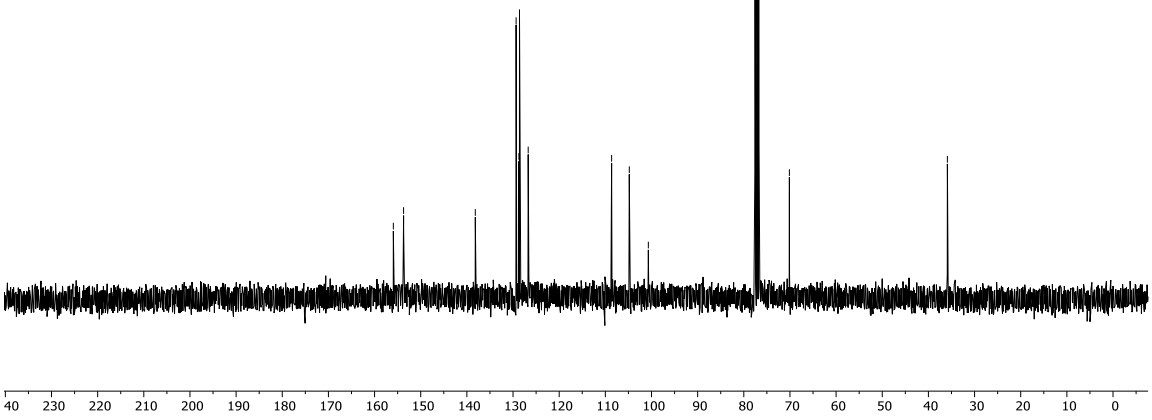


^{13}C-NMR (75 MHz, $CDCl_3$)





17

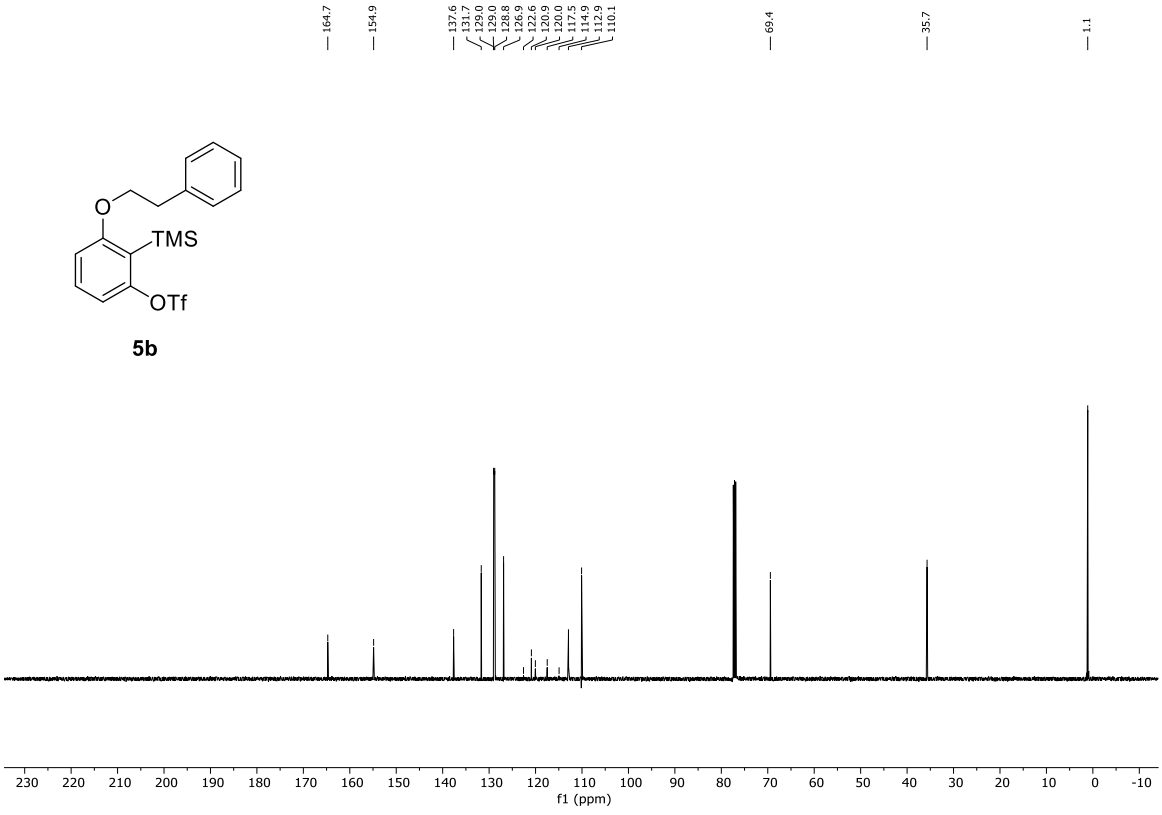


3-Phenethoxy-2-(trimethylsilyl)phenyl trifluoromethanesulfonate (5b)

^{1}H-NMR (500 MHz, $CDCl_3$)

5b

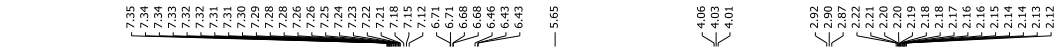
^{13}C-NMR (126 MHz, $CDCl_3$)

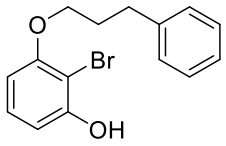


5b

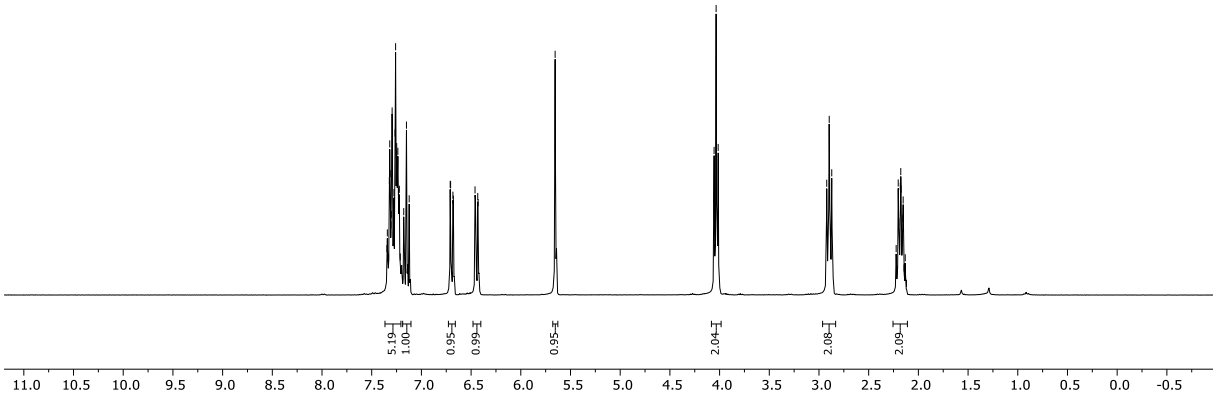
2-Bromo-3-(3-phenylpropoxy)phenol (18)

^{1}H-NMR (300 MHz, $CDCl_3$)

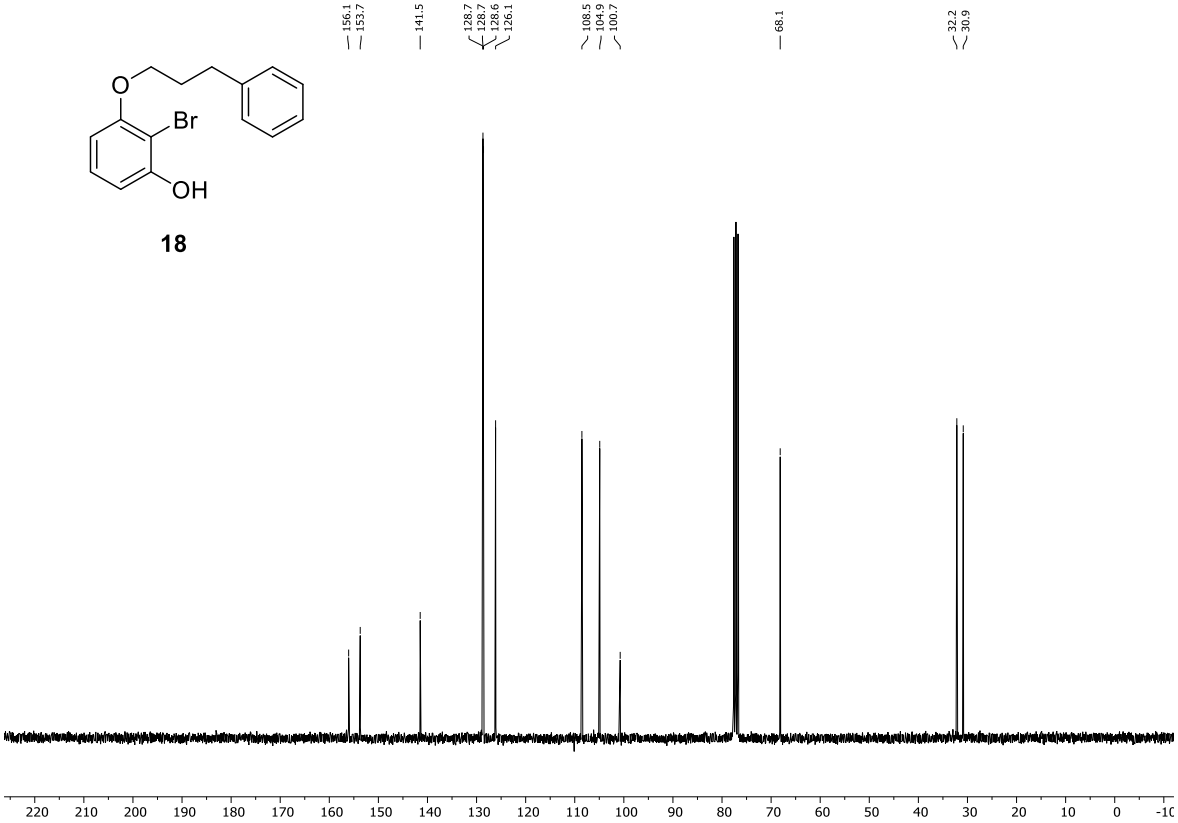




18



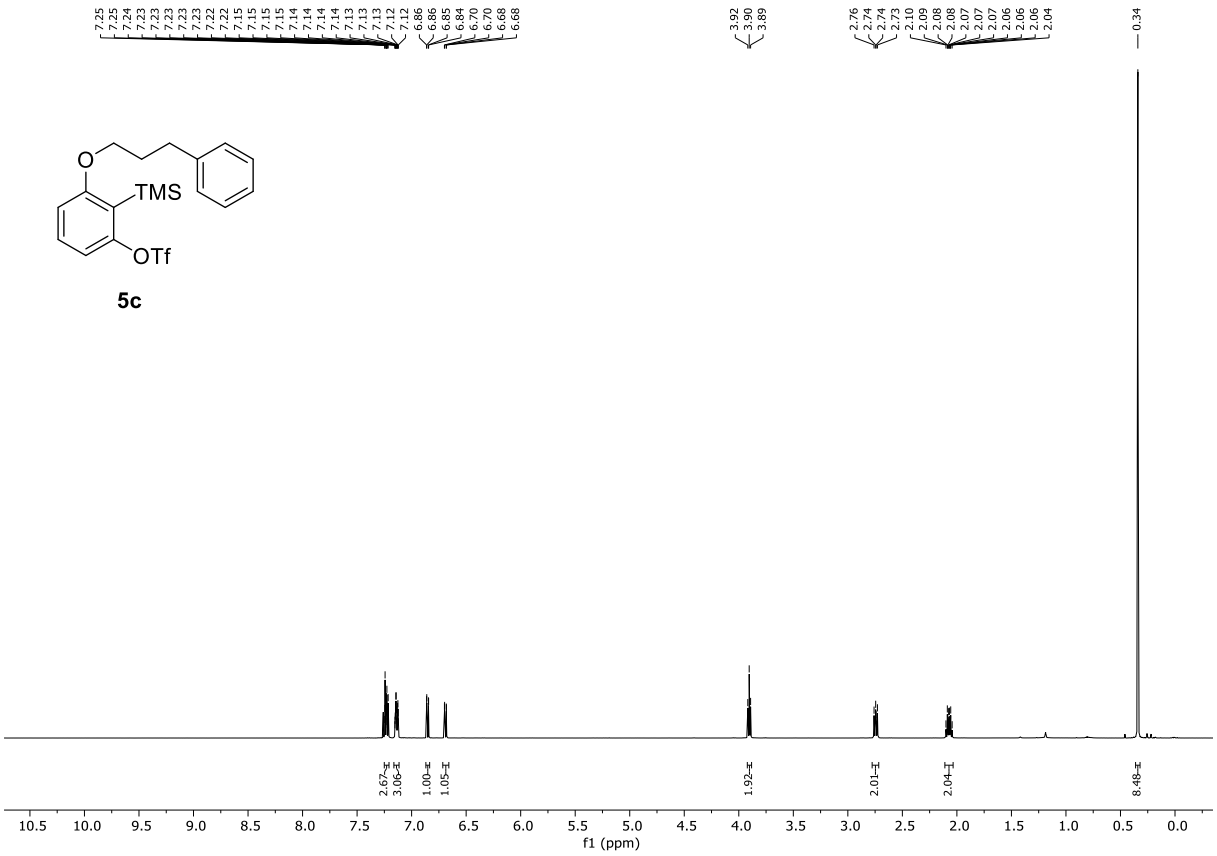
^{13}C-NMR (75 MHz, $CDCl_3$)



18

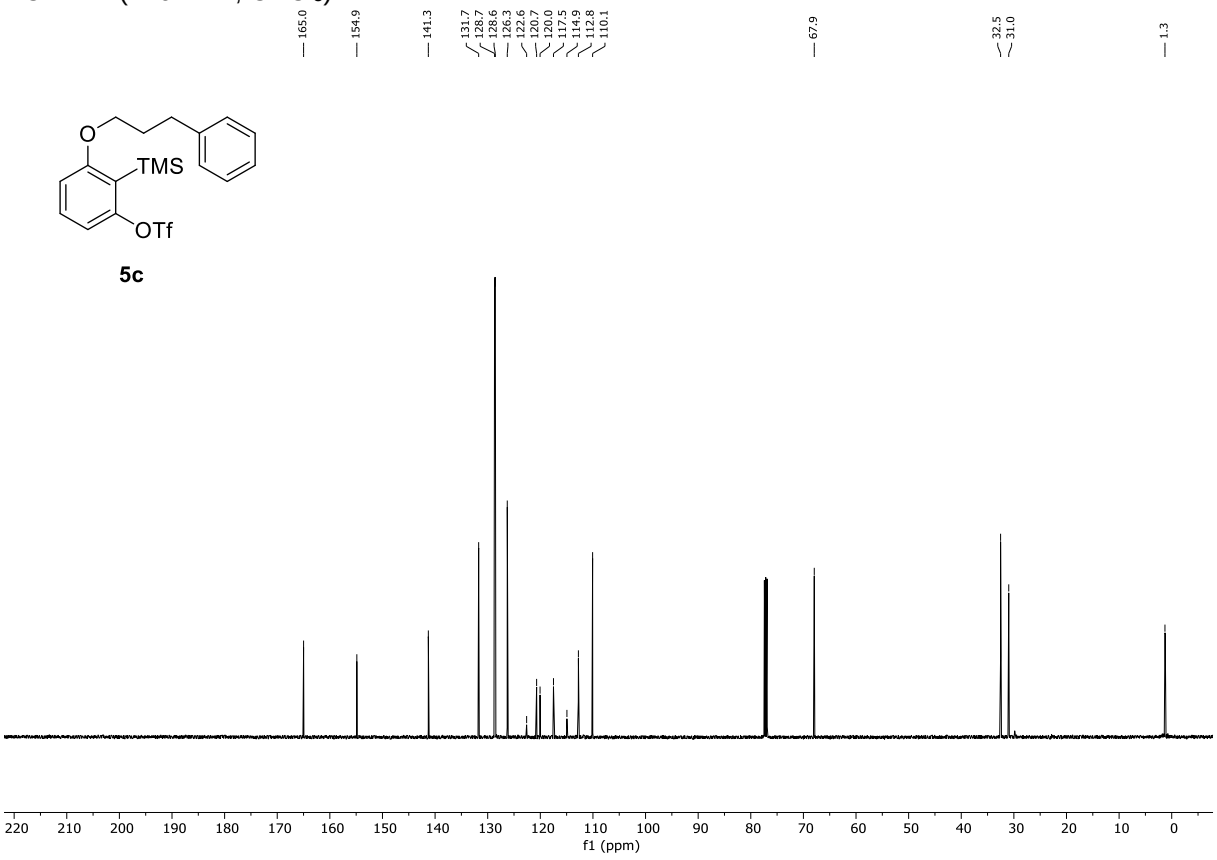
3-(3-Phenylpropoxy)-2-(trimethylsilyl)phenyl trifluoromethanesulfonate (5c)

^{1}H-NMR (500 MHz, $CDCl_3$)



5c

^{13}C-NMR (126 MHz, $CDCl_3$)



5c