Supporting Information

Asymmetric synthesis of spirocyclic isobenzofuranones *via* squaramide catalyzed sulfa-Michael desymmetrization reaction

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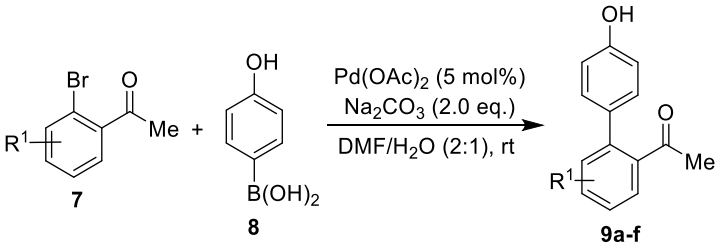
1. General Information:

All commercially available compounds were purchased from Sigma-Aldrich, Tokyo Chemical Industry Co., Ltd. (TCI) Chemicals, Spectrochem Pvt. Ltd., and BLD Pharmatech (India) Pvt. Ltd. (BLD pharma) and used as received without further purification. The catalysts **C-1** to **C-4,**[1] **C-6**[2] and **C-7**[3] were prepared from the methods known in the literature. The catalyst **C-5** is commercially available and used as it is. All reactions were performed in oven-dried glassware. All the solvents for routine isolation of products and chromatography were laboratory reagent grade and distilled before use. The molecular sieves (4 Å) were activated at 300 °C for 2 hours in an oven. Analytical thin-layer chromatography (TLC) was performed on the TLC Silica Gel 60 F254 Aluminium Sheets (MERCK), and UV light (254 nm) was used for the visualization. The flash column chromatography was performed on Combiflash NextGen 300 using silica gel (230 - 400 mesh), and the column chromatography was performed on the glass column using silica gel (60 - 120 mesh). ^{1}H NMR and ^{13}C NMR spectra were recorded on the JEOL JNM-ECZ500R/S3 500MHz NMR Spectrometer at 500 MHz, and 125 MHz, respectively, and TMS was used as an internal reference for ^{1}H NMR. NMR data are reported as follows: chemical shift (δ) in ppm; multiplicities are indicated s (singlet), br s (broad singlet), br m (broad multiplet), d (doublet), t (triplet), m (multiplet), dd (double doublet); and coupling constants (J) are in Hertz (Hz). Enantiomeric excesses were measured on an Agilent 1260 Infinity II HPLC instrument by using Diacel Chiralpak IA, IB, IK and IF columns. Optical rotations were measured on a Rudolph Research Analytical, Autopol I. Melting points were measured on a Buchi melting point M-565 apparatus. High-resolution mass spectra (HRMS) were recorded on a Waters Xevo Q-TOF Mass Spectrometer using the electrospray ionization (ESI) technique. Infrared spectral data were recorded on a PerkinElmer Spectrum Two FT-IR.

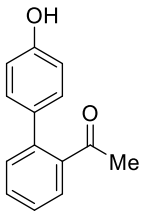
2. Experimental Procedures and Characterization Data:

General procedure for the synthesis of 9a-f: [4]



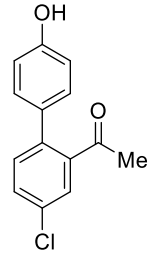
To a solution of substituted 2-bromoacetophenone derivatives **7** (3.0 to 6.0 mmol, 1.0 eq.) and Na_2CO_3 (2.0 eq.) in DMF : H_2O (v:v = 2 :1, 8 to 16 mL) was added phenylboronic acid (**8**, 3.6 to 7.2 mmol, 1.2 eq.). The reaction mixture was stirred at room temperature for 5 minutes. Palladium (II) acetate (5 mol%) was then added, and the reaction mixture was allowed to stir at room temperature until complete consumption of **7** (monitored by TLC). After completion of the reaction, water was added, and the reaction mixture was extracted with ethyl acetate (3 × 30 mL). The combined organic phase was washed with water and brine and dried over anhydrous Na_2SO_4. The organic phase was filtered and concentrated under vacuum to yield the crude product, which was purified by column chromatography (silica gel, *n*-hexane : EtOAc = 9 :1 to 7 : 3 as eluent) to afford **9a-f**.

1-(4'-Hydroxy-[1,1'-biphenyl]-2-yl)ethan-1-one (9a)



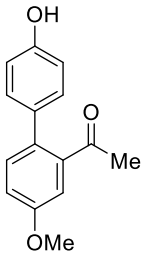
The title compound was prepared by performing the reaction at 3.0 mmol scale; White solid; **m.p.**: 120-121 °C; **Yield**: 457 mg, 72%; $\mathbf{R_f}$: 0.35 (*n*-hexane : ethyl acetate = 7 : 3); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.54 – 7.49 (m, 2H, Ar*H*), 7.40 – 7.38 (m, 2H, Ar*H*), 7.20 – 7.18 (m, 2H, Ar*H*), 6.90 – 6.88 (m, 2H, Ar*H*), 6.80 (br s, 1H, –O*H*), 2.07 (s, 3H, –COC*H*$_3$); **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$) δ 207.3, 156.3, 140.7, 140.5, 132.7, 131.1, 130.4, 130.2 (2C), 127.9, 127.2, 115.9 (2C), 30.6; **HRMS** (ESI, m/z) calcd for $C_{14}H_{13}O_2^+$ $[M+H]^+$: 213.0916, found: 213.0915; **IR**: ν_{max}/cm^{-1} 3363, 3023, 2923, 2852, 1669, 1611, 1516, 1474, 1353, 1263, 1233, 1172, 835, 765, 754.

1-(4-Chloro-4'-hydroxy-[1,1'-biphenyl]-2-yl)ethan-1-one (9b)



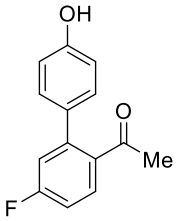
The title compound was prepared by performing the reaction at 3.0 mmol scale; White solid; **m.p.**: 135 - 136 °C; **Yield**: 450 mg, 61%; $\mathbf{R_f}$: 0.42 (*n*-hexane : ethyl acetate = 7 : 3); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.50 (d, *J* = 2.5 Hz, 1H, Ar*H*), 7.46 (dd, *J* = 8.0, 2.0 Hz, 1H, Ar*H*), 7.32 (d, *J* = 8.5 Hz, 1H, Ar*H*), 7.18 – 7.16 (m, 2H, Ar*H*), 6.90 – 6.88 (m, 2H, Ar*H*), 6.09 (br s, 1H, –O*H*), 2.04 (s, 3H, –COCH_3); **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$) δ 156.3, 141.9, 138.7, 133.4, 131.7 (2C), 130.9, 130.2 (2C), 127.8 (2C), 116.0 (2C), 30.4; **HRMS** (ESI, m/z) calcd for $C_{14}H_{12}O_2Cl^+$ $[M+H]^+$: 247.0526, found: 247.0500; **IR**: ν_{max}/cm^{-1} 3356, 2926, 2854, 1677, 1608, 1590, 1480, 1263, 1188, 822, 750, 519.

1-(4'-Hydroxy-4-methoxy-[1,1'-biphenyl]-2-yl)ethan-1-one (9c)



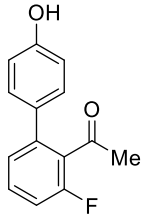
The title compound was prepared by performing the reaction at 3.5 mmol scale; White solid; **m.p.**: 148 - 149 °C; **Yield**: 177 mg, 21%; $\mathbf{R_f}$: 0.40 (*n*-hexane : ethyl acetate = 7 : 3); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.30 – 7.28 (m, 1H, Ar*H*), 7.18 – 7.17 (m, 2H, Ar*H*), 7.05 – 7.03 (m, 2H, Ar*H*), 6.88 – 6.87 (m, 2H, Ar*H*), 5.34 (br s, 1H, –O*H*), 3.86 (s, 3H, –OCH_3), 2.02 (s, 3H, –COCH_3); **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$) δ 205.9, 158.8, 155.6, 141.8, 133.0, 132.9, 131.6, 130.3 (2C), 117.3, 115.8 (2C), 112.4, 55.7, 30.6; **HRMS** (ESI, m/z) calcd for $C_{15}H_{15}O_3^+$ $[M+H]^+$: 243.1021, found: 243.1025; **IR**: ν_{max}/cm^{-1} 3325, 2917, 2849, 1677, 1611, 1497, 1246, 1128, 815, 795, 509.

1-(5-Fluoro-4'-hydroxy-[1,1'-biphenyl]-2-yl)ethan-1-one (9d)



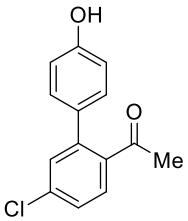
The title compound was prepared by performing the reaction at 6.0 mmol scale; Orange solid; **m.p.**: 98-99 °C; **Yield**: 982 mg, 71%; $\mathbf{R_f}$: 0.54 (*n*-hexane : ethyl acetate = 7 : 3); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.58 – 7.55 (m, 1H, Ar*H*), 7.20 – 7.18 (m, 2H, Ar*H*), 7.09 – 7.06 (m, 2H, Ar*H*), 6.91 – 6.89 (m, 2H, Ar*H*), 6.07 (s, 1H, –O*H*), 2.03 (s, 3H, –COCH_3); **^{13}C{^{1}H}{^{19}F} NMR** (125 MHz, $CDCl_3$) δ 204.9, 163.9, 156.5, 143.4, 136.9, 132.0, 130.7, 130.2 (2C), 117.1, 116.0 (2C), 114.2, 30.5; **[^{19}F] NMR** (471 MHz, $CDCl_3$) δ −108.6; **HRMS** (ESI, m/z) calcd for $C_{14}H_{12}O_2F^+$ $[M+H]^+$: 231.0821, found: 231.0836; **IR**: ν_{max}/cm^{-1} 3346, 2925, 2853, 1671, 1603, 1573, 1355, 1266, 1183, 837, 750.

1-(3-Fluoro-4'-hydroxy-[1,1'-biphenyl]-2-yl)ethan-1-one (9e)



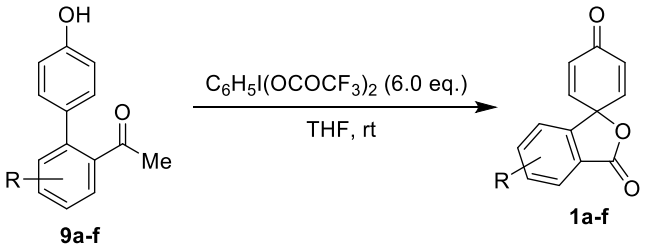
The title compound was prepared by performing the reaction at 3.5 mmol scale; White solid; **m.p.**: 131 - 132 °C; **Yield**: 457 mg, 66%; **R**$_f$: 0.48 (*n*-hexane : ethyl acetate = 7 : 3); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.43 – 7.38 (m, 1H, Ar*H*), 7.19 – 7.15 (m, 3H, Ar*H*), 7.10 – 7.07 (m, 1H, Ar*H*), 6.85 – 6.82 (m, 2H, Ar*H*), 6.04 – 5.93 (m, 1H, –O*H*), 2.24 (s, 3H, –COCH_3); **^{13}C{^{1}H}{^{19}F} NMR** (125 MHz, $CDCl_3$) δ 203.0, 158.8, 156.2, 141.4, 131.2, 131.0, 130.2 (2C), 129.2, 125.9, 115.9 (2C), 114.5, 32.5; **[^{19}F] NMR** (471 MHz, $CDCl_3$) δ −116.8; **HRMS** (ESI, m/z) calcd for $C_{14}H_{12}O_2F^+$ $[M+H]^+$: 231.0821, found: 231.0818; **IR**: ν_{max}/cm^{-1} 3325, 1687, 1608, 1518, 1463, 1234, 1099, 800, 535.

1-(5-Chloro-4'-hydroxy-[1,1'-biphenyl]-2-yl)ethan-1-one (9f)



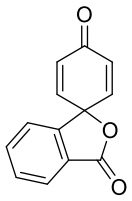
The title compound was prepared by performing the reaction at 3.0 mmol scale; White solid; **m.p.**: 130-131 °C; **Yield**: 662 mg, 90%; **R$_f$**: 0.47 (*n*-hexane : ethyl acetate = 7 : 3); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.49 – 7.47 (m, 1H, Ar*H*), 7.37 – 7.35 (m, 2H, Ar*H*), 7.20 – 7.18 (m, 2H, Ar*H*), 6.90 – 6.89 (m, 2H, Ar*H*), 5.61 (s, 1H, –O*H*), 2.02 (s, 3H, –COCH_3); **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$) δ 204.8, 156.4, 142.2, 139.0, 136.9, 131.9, 130.3 (2C), 129.6, 127.3, 116.0 (2C), 30.5; **HRMS** (ESI, m/z) calcd for $C_{14}H_{12}O_2Cl^+$ $[M+H]^+$: 247.0526, found: 247.0500; **IR**: ν_{max}/cm^{-1} 3189, 1656, 1609, 1589, 1436, 1274, 1216, 1099, 823, 595.

General procedure for the synthesis of 1a-f: [5]



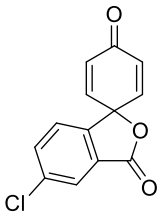
To a solution of **9** (0.3 to 2.6 mmol, 1.0 eq.) in THF (2.0 to 18.0 mL) was added $C_6H_5I(OCOCF_3)_2$ (6.0 eq.). The mixture was stirred at room temperature in the air until complete consumption of **9** (monitored by TLC). The solvent was removed under reduced pressure, and the residue was directly purified by flash column chromatography (silica gel, *n*-hexane : EtOAc = 9 :1 to 7 : 3 as eluent) to afford the desired products **1a-f**.

3'*H*-Spiro[cyclohexane-1,1'-isobenzofuran]-2,5-diene-3',4-dione (1a)



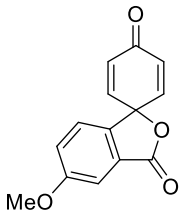
The title compound was prepared by performing the reaction at 2.6 mmol scale; White solid; **m.p.**: 184-185 °C; **Yield**: 182 mg, 33%; $\mathbf{R_f}$: 0.61 (*n*-hexane : ethyl acetate = 7 : 3); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.01 – 8.00 (m, 1H, Ar*H*), 7.77 – 7.74 (m, 1H, Ar*H*), 7.67 – 7.64 (m, 1H, Ar*H*), 7.33 (d, *J* = 7.5 Hz, 1H, Ar*H*), 6.70 – 6.67 (m, 2H, –C*H*=CHC=O), 6.46 – 6.42 (m, 2H, –CH=C*H*C=O); **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$) δ 184.4, 169.1, 146.6, 144.4 (2C), 135.3, 130.8, 129.9 (2C), 126.9, 125.7, 122.6, 80.5; **HRMS** (ESI, m/z) calcd for $C_{13}H_9O_3^+$ $[M+H]^+$: 213.0552, found: 213.0541; **IR**: ν_{max}/cm^{-1} 2917, 2850, 1755, 1671, 1467, 1242, 1091, 950, 690.

5'-Chloro-3'*H*-spiro[cyclohexane-1,1'-isobenzofuran]-2,5-diene-3',4-dione (1b)



The title compound was prepared by performing the reaction at 0.6 mmol scale; White solid; **m.p.**: 145-146 °C **Yield**: 133 mg, 90%; $\mathbf{R_f}$: 0.48 (*n*-hexane : ethyl acetate = 7 : 3); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.96 – 7.95 (m, 1H, Ar*H*), 7.70 – 7.68 (dd, *J* = 8.0, 2.0 Hz, 1H, Ar*H*), 7.27 – 7.24 (m, 1H, Ar*H*), 6.65 – 6.63 (m, 2H, –C*H*=CHC=O), 6.45 – 6.43 (m, 2H, –CH=C*H*C=O); **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$) δ 184.1, 167.6, 144.9, 143.7 (2C), 137.4, 135.7, 130.3 (2C), 127.6, 126.8, 123.9, 80.4; **HRMS** (ESI, m/z) calcd for $C_{13}H_8O_3Cl^+$ $[M+H]^+$: 247.0162, found: 247.0140; **IR**: ν_{max}/cm^{-1} 2918, 2850, 1775, 1673, 1263, 1233, 977, 959, 836, 748.

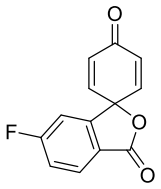
5'-Methoxy-3'*H*-spiro[cyclohexane-1,1'-isobenzofuran]-2,5-diene-3',4-dione (1c)



The title compound was prepared by performing the reaction at 0.3 mmol scale; White solid; **m.p.**: 154-155 °C **Yield**: 38 mg, 52%; $\mathbf{R_f}$: 0.46 (*n*-hexane : ethyl acetate = 7 : 3); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.40 – 7.39 (m, 1H, Ar*H*), 7.27 – 7.25 (m, 1H, Ar*H*), 7.17 (dd, *J* = 8.5, 0.5 Hz, 1H, Ar*H*), 6.64 – 6.62 (m, 2H, –C*H*=CHC=O), 6.41 – 6.39 (m, 2H, –CH=C*H*C=O), 3.90 (s, 3H, –OCH_3); **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$) δ 184.5, 169.2, 162.0, 144.7 (2C), 138.5, 129.8 (2C), 127.4, 124.2, 123.4, 108.7, 80.3, 56.1; **HRMS** (ESI, m/z) calcd for $C_{14}H_{11}O_4^+$ $[M+H]^+$: 243.0657, found: 243.0658; **IR**: ν_{max}/cm^{-1} 2916, 2850, 1770, 1670, 1422, 1232, 1062, 947, 865, 844, 754, 629, 546.

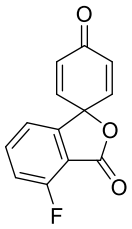
6'-Fluoro-3'*H*-spiro[cyclohexane-1,1'-isobenzofuran]-2,5-diene-3',4-dione (1d)

The title compound was prepared by performing the reaction at 0.6 mmol scale; Colourless wax; **Yield**: 103 mg, 75%; $\mathbf{R_f}$: 0.53 (*n*-hexane : ethyl acetate = 7 : 3); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.02 – 7.99 (m, 1H, Ar*H*), 7.35 – 7.31 (m, 1H, Ar*H*), 6.99 – 6.98 (m, 1H, Ar*H*), 6.67



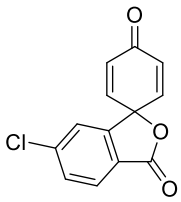
– 6.65 (m, 2H, –C*H*=CHC=O), 6.46 – 6.44 (m, 2H, –CH=C*H*C=O); **^{13}C{^{1}H}{^{19}F} NMR** (125 MHz, $CDCl_3$) δ 184.0, 167.8, 149.7, 143.7 (2C), 130.4 (2C), 129.3, 119.1, 109.9, 107.7, 106.5, 79.8; **[^{19}F] NMR** (471 MHz, $CDCl_3$) δ −99.7; **HRMS** (ESI, m/z) calcd for $C_{13}H_8O_3F^+$ $[M+H]^+$: 231.0469, found: 231.0469; **IR**: ν_{max}/cm^{-1} 2921, 2851, 1779, 1674, 1267, 1077, 972, 861, 764, 750.

4'-Fluoro-3'*H*-spiro[cyclohexane-1,1'-isobenzofuran]-2,5-diene-3',4-dione (1e)



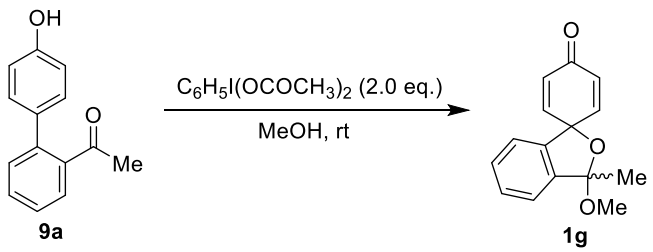
The title compound was prepared by performing the reaction at 1.0 mmol scale; White solid; **m.p.**: 217-218 °C; **Yield**: 87 mg, 38%; **R$_f$**: 0.38 (*n*-hexane : ethyl acetate = 7 : 3); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.75 – 7.70 (m, 1H, Ar*H*), 7.29 – 7.25 (m, 1H, Ar*H*), 7.09 (d, *J* = 7.7 Hz, 1H, Ar*H*), 6.67 (d, *J* = 10.0 Hz, 2H, –C*H*=CHC=O), 6.44 (d, *J* = 10.0 Hz, 2H, –CH=C*H*C=O); **^{13}C{^{1}H}{^{19}F} NMR** (125 MHz, $CDCl_3$) δ 184.1, 165.0, 160.1, 149.1, 143.7 (2C), 137.8, 130.3 (2C), 118.6, 117.94, 113.7, 80.1; **[^{19}F] NMR** (471 MHz, $CDCl_3$) δ −111.4; **HRMS** (ESI, m/z) calcd for $C_{13}H_8O_3F^+$ $[M+H]^+$: 231.0457, found: 231.0422; **IR**: ν_{max}/cm^{-1} 2921, 2851, 1779, 1674, 1267, 1077, 972, 861, 764, 750.

6'-Chloro-3'*H*-spiro[cyclohexane-1,1'-isobenzofuran]-2,5-diene-3',4-dione (1f)



The title compound was prepared by performing the reaction at 0.3 mmol scale; Colourless wax; **Yield**: 60 mg, 81%; **R$_f$**: 0.70 (*n*-hexane : ethyl acetate = 7 : 3); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.93 (dd, *J* = 8.0, 0.5 Hz, 1H, Ar*H*), 7.61 (dd, *J* = 8.0, 1.5 Hz, 1H, Ar*H*), 7.29 (dd, *J* = 1.5, 0.5 Hz, 1H, Ar*H*), 6.66 – 6.64 (m, 2H, –C*H*=CHC=O), 6.47 – 6.45 (m, 2H, –CH=C*H*C=O); **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$) δ 184.0, 167.9, 148.5, 143.6 (2C), 142.2, 131.6, 130.4 (2C), 128.0, 124.2, 123.1, 79.9; **HRMS** (ESI, m/z) calcd for $C_{13}H_8O_3Cl^+$ $[M+H]^+$: 247.0162, found: 247.0140; **IR**: ν_{max}/cm^{-1} 2918, 2850, 1775, 1673, 1263, 1233, 977, 959, 836, 748.

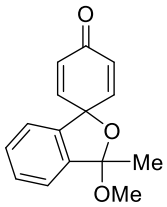
Procedure for the synthesis of 1g: [6]



9a **1g**

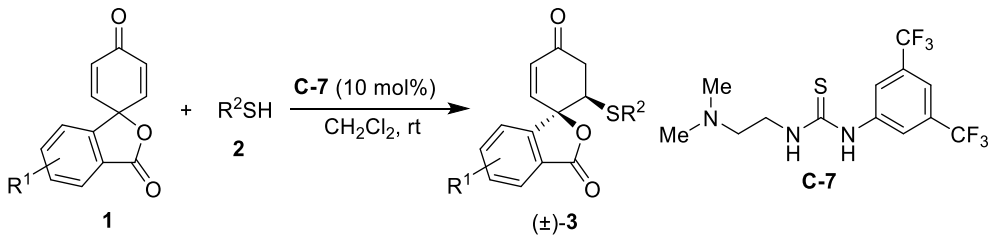
To a solution of **9a** (1.0 mmol, 1.0 eq.) in methanol (5.0 mL) was added $C_6H_5I(OCOCH_3)_2$ (2.0 eq.). The mixture was stirred at room temperature in the air until complete consumption of starting material **9a** (monitored by TLC). The solvent was removed under reduced pressure, and the residue was directly purified by flash column chromatography (silica gel, *n*-hexane : EtOAc = 9 :1 to 7 : 3 as eluent)) to afford the desired product**1g**.

3'-Methoxy-3'-methyl-3'*H*-spiro[cyclohexane-1,1'-isobenzofuran]-2,5-dien-4-one (1g)



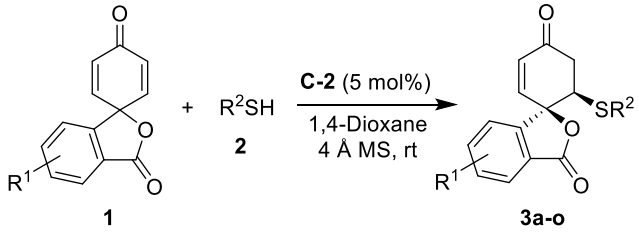
White solid; **m.p.**: 151-152 °C; **Yield**: 110 mg, 45%; $\mathbf{R_f}$: 0.70 (*n*-hexane : ethyl acetate = 7 : 3); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.44 – 7.37 (m, 3H, Ar*H*), 7.04 (d, *J* = 7.5 Hz, 1H, Ar*H*), 6.91 (dd, *J* = 9.5, 2.5 Hz, 1H, –C*H*=CHC=O), 6.69 (dd, *J* = 10.5, 3.0 Hz, 1H, –C*H*=CHC=O), 6.26 (d, *J* = 10.0 Hz, 2H, –CH=C*H*C=O), 3.25 (s, 3H, –OCH_3), 1.84 (s, 3H, –CH_3); **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$) δ 185.6, 149.3, 148.7, 141.2, 138.7, 130.1, 129.7, 127.9, 127.7, 123.1, 122.3, 112.2, 81.7, 50.6, 26.5; **HRMS** (ESI, m/z) calcd for $C_{15}H_{15}O_3^+$ $[M+H]^+$: 243.1021, found: 243.1016; **IR**: ν_{max}/cm^{-1} 2918, 2850, 1775, 1673, 1263, 1233, 977, 959, 836, 748.

General procedure for the synthesis of racemic products:



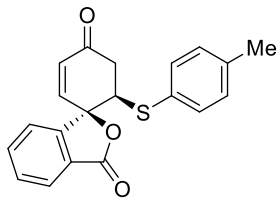
In a 10 mL reaction tube equipped with a magnetic stirring bar, the isobenzofuranone **1** (1.0 eq., 0.1 mmol) and thiourea catalyst **C-7** (10 mol%) were stirred in CH_2Cl_2 (1.0 mL) at room temperature. After 5 minutes, thiol **2** (1.0 eq.) was added, and the stirring was continued at the same temperature. After the complete consumption of 2,5-cyclohexadienone **1** (indicated by TLC), the crude product was directly purified by flash column chromatography (*n*-hexane : EtOAc = 8 : 2) to afford the racemic products.

General procedure for enantioselective desymmetrization reaction for the synthesis of 3a-o:



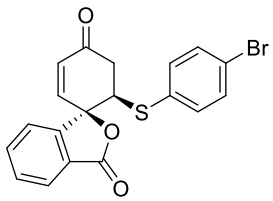
In a 10 mL reaction tube equipped with a magnetic stirring bar, the isobenzofuranone **1** (2.0 eq., 0.2 mmol) and catalyst **C-2** (5 mol%) were stirred in 1,4-dioxane (2.0 mL) in the presence of 4 Å molecular sieves (50 mg) at room temperature. After 5 minutes, thiol **2** (1.0 eq., 0.1 mmol) was added, and the stirring was continued at the same temperature. After the complete consumption of thiol **2** (indicated by TLC), the crude product was directly purified by flash column chromatography (*n*-hexane : EtOAc = 8 : 2) to afford the products **3a-o**.

6-(*p*-Tolylthio)-3'*H*-spiro[cyclohexane-1,1'-isobenzofuran]-2-ene-3',4-dione (3a)



Colourless wax; **Yield**: 30 mg, 89%; **R$_f$**: 0.11 (*n*-hexane : ethyl acetate = 8 : 2); $[\alpha]_D^{26}$ = +18.3; 92% ee; Daicel Chiralpak IA column, *n*-hexane : *i*-PrOH = 70 : 30, Flow rate: 1.0 mL/min; 254 nm, t_R = 15.39 min (major), t_R = 17.10 min (minor); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.01 – 8.00 (m, 1H, Ar*H*), 7.61 – 7.58 (m, 1H, Ar*H*), 7.54 – 7.50 (m, 1H, Ar*H*), 7.12 – 7.10 (m, 1H, Ar*H*), 6.91 (d, *J* = 8.0 Hz, 2H, Ar*H*), 6.85 (d, *J* = 8.0 Hz, 2H, Ar*H*), 6.61 (d, *J* = 10.0 Hz, 1H, –C*H*=CHCO), 6.30 (d, *J* = 9.5 Hz, 1H, –CH=C*H*CO), 3.85 (dd, *J* = 10.5, 7.0 Hz, 1H, –C*H*SAr), 3.07 – 3.05 (m, 2H, –CH_2–), 2.26 (s, 3H, ArCH_3); **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$) δ 196.6, 169.1, 149.8, 143.4, 138.7, 134.5, 133.9 (2C), 132.9, 130.4, 129.8 (2C), 129.5, 127.3, 126.1, 121.6, 82.7, 53.8, 42.6, 21.2; **HRMS** (ESI, m/z) calcd for $C_{20}H_{17}O_3S^+$ $[M+H]^+$: 337.0898, found: 337.0911; **IR**: ν_{max}/cm^{-1} 2925, 2853, 1671, 1603, 1573, 1518, 1478, 1266, 837, 750.

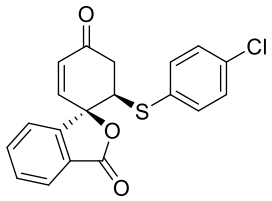
6-[(4-Bromophenyl)thio]-3'*H*-spiro[cyclohexane-1,1'-isobenzofuran]-2-ene-3',4-dione (3b)



Colourless wax; **Yield**: 31 mg, 77%; **R$_f$**: 0.14 (*n*-hexane : ethyl acetate = 8 : 2); $[\alpha]_D^{26}$ = +20.1; 91% ee; Daicel Chiralpak IK column, *n*-hexane : *i*-PrOH = 70 : 30, Flow rate: 1.0 mL/min; 290 nm, t_R = 17.62 min (minor), t_R = 23.28 min (major); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.0 Hz, 1H, Ar*H*), 7.62 – 7.58 (m, 1H, Ar*H*), 7.53 – 7.49 (m, 1H, Ar*H*), 7.23 – 7.21 (m, 2H, Ar*H*), 7.07 (d, *J* = 7.5 Hz, 1H, Ar*H*), 6.83 – 6.81 (m, 2H, Ar*H*), 6.63 (d, *J* = 10.0 Hz, 1H, –C*H*=CHCO), 6.33 (d, *J* = 10.0 Hz, 1H, –CH=C*H*CO), 3.91 – 3.88 (m, 1H, –C*H*SAr), 3.08 –

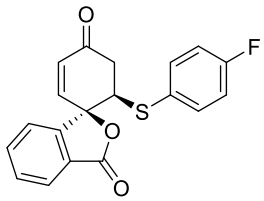
3.06 (m, 2H, –CH_2–); **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$) δ 196.1, 169.0, 149.6, 144.5, 143.2, 135.1 (2C), 134.6, 133.0, 132.2 (2C), 130.6, 127.2, 126.2, 122.9, 121.6, 82.5, 53.9, 42.4; **HRMS** (ESI, m/z) calcd for $C_{19}H_{14}O_3BrS^+$ $[M+H]^+$: 400.9847, found: 400.9865; **IR**: ν_{max}/cm^{-1} 2924, 2853, 1774, 1694, 1466, 1264, 1083, 930, 763, 746.

6-[(4-Chlorophenyl)thio]-3'*H*-spiro[cyclohexane-1,1'-isobenzofuran]-2-ene-3',4-dione (3c)



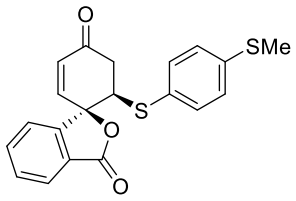
Colourless wax; **Yield**: 22 mg, 63%; **R_f**: 0.14 (*n*-hexane : ethyl acetate = 8 : 2); $[\alpha]_D^{26}$ = +17.6; 81% ee; Daicel Chiralpak IK column, *n*-hexane : *i*-PrOH = 70 : 30, Flow rate: 1.0 mL/min; 290 nm, t_R = 16.00 min (minor), t_R = 20.99 min (major); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.02 – 8.00 (m, 1H, Ar*H*), 7.62 – 7.58 (m, 1H, Ar*H*), 7.53 – 7.50 (m, 1H, Ar*H*), 7.08 – 7.06 (m, 3H, Ar*H*), 6.90 – 6.87 (m, 2H, Ar*H*), 6.63 (d, *J* = 10.0 Hz, 1H, –C*H*=CHCO), 6.33 (d, *J* = 10.0 Hz, 1H, –CH=C*H*CO), 3.91 – 3.87 (m, 1H, –C*H*SAr), 3.08 – 3.06 (m, 2H, –CH_2–); **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$) δ 196.1, 168.9, 149.6, 144.4, 143.2, 134.9 (2C), 134.5, 132.9, 131.7, 130.5, 129.2 (2C), 127.2, 126.1, 121.6, 82.4, 54.0, 42.4; **HRMS** (ESI, m/z) calcd for $C_{19}H_{14}O_3ClS^+$ $[M+H]^+$: 357.0352, found: 357.0362; **IR**: ν_{max}/cm^{-1} 2925, 2854, 1772, 1693, 1476, 1265, 1083, 929, 761, 733.

6-[(4-Fluorophenyl)thio]-3'*H*-spiro[cyclohexane-1,1'-isobenzofuran]-2-ene-3',4-dione (3d)



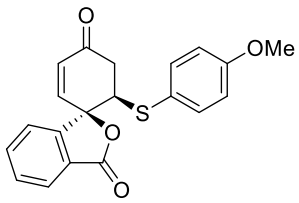
Colourless wax; **Yield**: 23 mg, 68%; **R_f**: 0.14 (*n*-hexane : ethyl acetate = 8 : 2); $[\alpha]_D^{26}$ = +14.2; 73% ee; Daicel Chiralpak IK column, *n*-hexane : *i*-PrOH = 70 : 30, Flow rate: 1.0 mL/min; 290 nm, t_R = 15.54 min (minor), t_R = 20.74 min (major); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.03 – 8.01 (m, 1H, Ar*H*), 7.62 – 7.59 (m, 1H, Ar*H*), 7.55 – 7.52 (m, 1H, Ar*H*), 7.09 – 7.08 (m, 1H, Ar*H*), 6.96 – 6.93 (m, 2H, Ar*H*), 6.82 – 6.78 (m, 2H, Ar*H*), 6.62 (d, *J* = 10.0 Hz, 1H, –C*H*=CHCO), 6.32 (d, *J* = 10.0 Hz, 1H, –CH=C*H*CO), 3.85 (m, 1H, –C*H*SAr), 3.06 – 3.04 (m, 2H, –CH_2–); **^{13}C{^{1}H}{^{19}F} NMR** (125 MHz, $CDCl_3$) δ 196.3, 169.0, 162.9, 149.7, 143.3, 136.1 (2C), 134.6, 132.9, 130.5, 128.3, 127.3, 126.2, 121.6, 116.2 (2C), 82.5, 54.2, 42.4; **[^{19}F] NMR** (471 MHz, $CDCl_3$) δ −112.0; **HRMS** (ESI, m/z) calcd for $C_{19}H_{14}O_3FS^+$ $[M+H]^+$: 341.0648, found: 341.0635; **IR**: ν_{max}/cm^{-1} 2918, 2850, 1771, 1692, 1489, 1261, 1083, 929, 749.

6-[(4-(methylthio)phenyl)thio]-3'*H*-spiro[cyclohexane-1,1'-isobenzofuran]-2-ene-3',4-dione (3e)



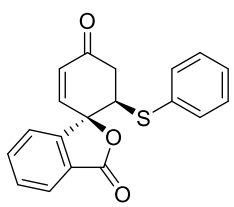
Colourless wax; **Yield**: 22 mg, 60%; **R**$_f$: 0.11 (*n*-hexane : ethyl acetate = 8 : 2); $[\alpha]_D^{26}$ = +17.2; 84% ee; Daicel Chiralpak IK column, *n*-hexane : *i*-PrOH = 70 : 30, Flow rate: 1.0 mL/min; 290 nm, t_R = 23.01 min (minor), t_R = 32.15 min (major); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.02 – 8.00 (m, 1H, Ar*H*), 7.61 – 7.58 (m, 1H, Ar*H*), 7.55 – 7.52 (m, 1H, Ar*H*), 7.12 – 7.11 (m, 1H, Ar*H*), 6.97 – 6.95 (m, 2H, Ar*H*), 6.88 – 6.86 (m, 2H, Ar*H*), 6.62 (d, *J* = 10.0 Hz, 1H, –C*H*=CHCO), 6.31 (d, *J* = 10.0 Hz, 1H, –CH=C*H*CO), 3.85 (dd, *J* = 10.5, 8.0 Hz, 1H, –C*H*SAr), 3.06 – 3.04 (m, 2H, –CH_2–), 2.43 (s, 3H, ArSCH_3); **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$) δ 196.4, 169.1, 149.8, 143.3, 140.0, 134.6, 134.3 (2C), 132.9, 130.5, 128.9, 127.3, 126.5 (2C), 126.1, 121.7, 82.6, 53.9, 42.5, 15.5; **HRMS** (ESI, m/z) calcd for $C_{20}H_{17}O_3S_2^+$ $[M+H]^+$: 369.0619, found: 369.0601; **IR**: ν_{max}/cm^{-1} 2925, 2853, 1671, 1603, 1573, 1518, 1478, 1266, 837, 750.

6-[(4-Methoxyphenyl)thio]-3'*H*-spiro[cyclohexane-1,1'-isobenzofuran]-2-ene-3',4-dione (3f)



Colourless wax; **Yield**: 10 mg, 28%; **R**$_f$: 0.08 (*n*-hexane : ethyl acetate = 8 : 2); $[\alpha]_D^{26}$ = +17.6; 69% ee; Daicel Chiralpak IF column, *n*-hexane : *i*-PrOH = 70 : 30, Flow rate: 1.0 mL/min; 254 nm, t_R = 20.37 min (minor), t_R = 23.98 min (major); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.03 – 8.02 (m, 1H, Ar*H*), 7.63 – 7.55 (m, 2H, Ar*H*), 7.14 – 7.12 (m, 1H, Ar*H*), 6.91 – 6.89 (m, 2H, Ar*H*), 6.65 – 6.63 (m, 2H, Ar*H*), 6.60 (d, *J* = 10.0 Hz, 1H, –C*H*=CHCO), 6.29 (d, *J* = 10.0 Hz, 1H, –CH=C*H*CO), 3.79 – 3.77 (m, 1H, –C*H*SAr), 3.75 (s, 3H, ArOCH_3), 3.03 – 3.01 (m, 2H, –CH_2–); **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$) δ 196.7, 169.2, 160.2, 150.0, 143.4, 136.1 (2C), 134.6, 132.8, 130.4, 127.4, 126.2, 123.4, 121.7, 114.6 (2C), 82.7, 55.5, 54.0, 42.5; **HRMS** (ESI, m/z) calcd for $C_{20}H_{17}O_4S^+$ $[M+H]^+$: 353.0848, found: 353.0843; **IR**: ν_{max}/cm^{-1} 2918, 2850, 1771, 1693, 1592, 1493, 1466, 1247, 1083, 929, 829, 762, 690.

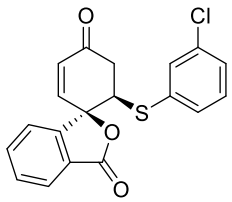
6-(Phenylthio)-3'*H*-spiro[cyclohexane-1,1'-isobenzofuran]-2-ene-3',4-dione (3g)



Colourless wax; **Yield**: 20 mg, 62%; **R**$_f$: 0.14 (*n*-hexane : ethyl acetate = 8 : 2); $[\alpha]_D^{26}$ = +15.3; 82% ee; Daicel Chiralpak IK column, *n*-hexane : *i*-PrOH = 70 : 30, Flow rate: 1.0 mL/min; 254 nm, t_R = 15.59 min (minor), t_R = 21.90 min (major); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.00 (d, *J* = 7.5

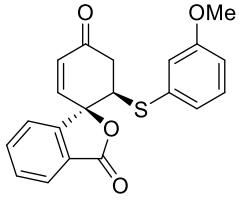
Hz, 1H, Ar*H*), 7.59 – 7.55 (m, 1H, Ar*H*), 7.49 – 7.46 (m, 1H, Ar*H*), 7.19 – 7.15 (m, 1H, Ar*H*), 7.11 – 7.06 (m, 3H, Ar*H*), 6.97 – 6.95 (m, 2H, Ar*H*), 6.62 (d, *J* = 10.0 Hz, 1H, –C*H*=CHCO), 6.32 (d, *J* = 10.0 Hz, 1H, –CH=C*H*CO), 3.92 (dd, *J* = 11.0, 6.5 Hz, 1H, –C*H*SPh), 3.11 – 3.08 (m, 2H, –C*H*$_2$–); **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$) δ 196.5, 169.1, 149.7, 144.4, 143.4, 134.5, 133.5 (2C), 133.3, 132.9, 130.4, 129.1 (2C), 128.3, 126.1, 121.6, 82.6, 53.8, 42.6 ; **HRMS** (ESI, m/z) calcd for $C_{19}H_{15}O_3S^+$ $[M+H]^+$: 323.0742, found: 323.0735; **IR**: ν_{max}/cm^{-1} 2919, 2851, 1771, 1693, 1466, 1274, 1266, 1083, 929, 763, 749.

6-[(3-Chlorophenyl)thio]-3'*H*-spiro[cyclohexane-1,1'-isobenzofuran]-2-ene-3',4-dione (3h)



Colourless wax; **Yield**: 22 mg, 62%; **R$_f$**: 0.14 (*n*-hexane : ethyl acetate = 8 : 2); $[\alpha]_D^{26}$ = +17.6; 86% ee; Daicel Chiralpak IA column, *n*-hexane : *i*-PrOH = 90 : 10, Flow rate: 1.0 mL/min; 254 nm, t_R = 16.23 min (major), t_R = 18.95 min (minor); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.02 – 8.00 (m, 1H, Ar*H*), 7.61 – 7.58 (m, 1H, Ar*H*), 7.47 – 7.44 (m, 1H, Ar*H*), 7.15 – 7.12 (m, 1H, Ar*H*), 7.06 – 7.02 (m, 2H, Ar*H*), 6.93 – 6.90 (m, 1H, Ar*H*), 6.76 – 6.75 (m, 1H, Ar*H*), 6.65 (d, *J* = 9.5 Hz, 1H, –C*H*=CHCO), 6.34 (d, *J* = 10.0 Hz, 1H, –CH=C*H*CO), 3.95 (dd, *J* = 10.0, 7.5 Hz, 1H, –C*H*SAr), 3.11 – 3.09 (m, 2H, –C*H*$_2$–); **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$) δ 196.0, 169.0, 149.4, 143.2, 135.4, 134.5, 134.3, 133.0, 132.9, 131.3, 130.7, 130.1, 128.5, 127.2, 126.1, 121.7, 82.3, 54.3, 42.4; **HRMS** (ESI, m/z) calcd for $C_{19}H_{14}O_3ClS^+$ $[M+H]^+$: 357.0352, found: 357.0363; **IR**: ν_{max}/cm^{-1} 2919, 2851, 1772, 1694, 1464, 1265, 1084, 930, 763, 748.

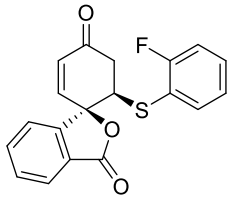
6-[(3-Methoxyphenyl)thio]-3'*H*-spiro[cyclohexane-1,1'-isobenzofuran]-2-ene-3',4-dione (3i)



Colourless wax; **Yield**: 30 mg, 85%; **R$_f$**: 0.08 (*n*-hexane : ethyl acetate = 8 : 2); $[\alpha]_D^{26}$ = +15.2; 84% ee; Daicel Chiralpak IK column, *n*-hexane : *i*-PrOH = 70 : 30, Flow rate: 1.0 mL/min; 290 nm, t_R = 18.37 min (minor), t_R = 25.14 min (major); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.00 – 7.98 (m, 1H, Ar*H*), 7.58 – 7.55 (m, 1H, Ar*H*), 7.50 – 7.47 (m, 1H, Ar*H*), 7.10 – 7.08 (m, 1H, Ar*H*), 7.03 – 7.00 (m, 1H, Ar*H*), 6.72 – 6.70 (m, 1H, Ar*H*), 6.63 (d, *J* = 9.5 Hz, 1H, –C*H*=CHCO), 6.60 – 6.58 (m, 1H, Ar*H*), 6.45 – 6.44 (m, 1H, Ar*H*), 6.32 (d, *J* = 10.0 Hz, 1H, –CH=C*H*CO), 3.97 (dd, *J* = 10.0, 7.5 Hz, 1H, –C*H*SAr), 3.70 (s, 3H, $ArOCH_3$), 3.10 – 3.08 (m, 2H, –C*H*$_2$–); **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$) δ 196.4, 169.1, 159.6, 149.7, 143.3, 134.4, 134.4, 132.9, 130.4, 129.8, 127.2, 126.0, 125.5, 121.7, 118.4, 114.3, 82.6, 55.4, 53.7, 42.5; **HRMS** (ESI,

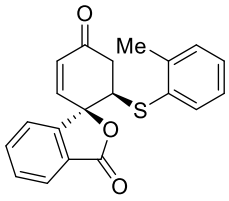
m/z) calcd for $C_{20}H_{17}O_4S^+$ $[M+H]^+$: 353.0848, found: 353.0865; **IR**: ν_{max}/cm^{-1} 2918, 2850, 1771, 1693, 1592, 1493, 1466, 1247, 1083, 929, 829, 762, 690.

6-[(2-Fluorophenyl)thio]-3'*H*-spiro[cyclohexane-1,1'-isobenzofuran]-2-ene-3',4-dione (3j)



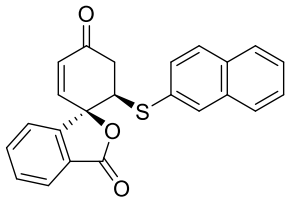
Colourless wax; **Yield**: 20 mg, 59%; $\mathbf{R_f}$: 0.11 (*n*-hexane : ethyl acetate = 8 : 2); $[\alpha]_D^{26}$ = +16.5; 84% ee; Daicel Chiralpak IK column, *n*-hexane : *i*-PrOH = 70 : 30, Flow rate: 1.0 mL/min; 290 nm, t_R = 16.27 min (minor), t_R = 22.28 min (major); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.99 – 7.97 (m, 1H, Ar*H*), 7.55 – 7.52 (m, 1H, Ar*H*), 7.44 – 7.41 (m, 1H, Ar*H*), 7.18 – 7.16 (m, 1H, Ar*H*), 7.07 (d, *J* = 7.5 Hz, 1H, Ar*H*), 6.94 – 6.91 (m, 1H, Ar*H*), 6.80 – 6.77 (m, 1H, Ar*H*), 6.72 – 6.69 (m, 1H, Ar*H*), 6.62 (d, *J* = 9.5 Hz, 1H, –C*H*=CHCO), 6.33 – 6.31 (dd, *J* = 10.0, 0.5 Hz, 1H, –CH=C*H*CO), 4.04 (dd, *J* = 12.5, 5.5 Hz, 1H, –C*H*SAr), 3.15 – 3.05 (m, 2H, –CH_2–); **^{13}C{^{1}H}{^{19}F} NMR** (125 MHz, $CDCl_3$) δ 196.1, 169.0, 162.5, 149.6, 143.3, 135.6, 134.4, 133.0, 130.8, 130.5, 127.1, 126.1, 124.4, 121.5, 120.2, 116.0, 82.4, 51.8, 42.0; **[^{19}F] NMR** (471 MHz, $CDCl_3$) δ −106.3; **HRMS** (ESI, m/z) calcd for $C_{19}H_{14}O_3FS^+$ $[M+H]^+$: 341.0648, found: 341.0632; **IR**: ν_{max}/cm^{-1} 2918, 2850, 1771, 1692, 1489, 1261, 1083, 929, 749.

6-(*o*-Tolylthio)-3'*H*-spiro[cyclohexane-1,1'-isobenzofuran]-2-ene-3',4-dione (3k)



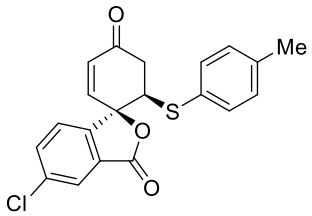
Colourless wax; **Yield**: 13 mg, 39%; $\mathbf{R_f}$: 0.17 (*n*-hexane : ethyl acetate = 8 : 2); $[\alpha]_D^{26}$ = 12.4; 65% ee; Daicel Chiralpak IK column, *n*-hexane : *i*-PrOH = 70 : 30, Flow rate: 1.0 mL/min; 254 nm, t_R = 14.81 min (minor), t_R = 21.50 min (major); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.00 – 7.99 (m, 1H, Ar*H*), 7.58 – 7.55 (m, 1H, Ar*H*), 7.50 – 7.47 (m, 1H, Ar*H*), 7.10 – 7.05 (m, 3H, Ar*H*), 6.93 – 6.90 (m, 1H, Ar*H*), 6.85 – 6.84 (m, 1H, Ar*H*), 6.61 (d, *J* = 10.0 Hz, 1H, –C*H*=CHCO), 6.31 (dd, *J* = 10.0, 1.0 Hz, 1H, –CH=C*H*CO), 3.86 (dd, *J* = 13.0, 4.5 Hz, 1H, –C*H*SAr), 3.20 – 3.05 (m, 2H, –CH_2–), 2.11 (s, 3H, ArCH_3); **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$) δ 196.5, 149.8, 143.5, 141.0, 134.5, 134.1, 132.8, 132.6, 130.6, 130.4, 130.1 128.5, 127.2, 126.5, 126.2, 121.6, 82.7, 52.9, 42.6, 20.9; **HRMS** (ESI, m/z) calcd for $C_{20}H_{17}O_3S^+$ $[M+H]^+$: 337.0898, found: 337.0900; **IR**: ν_{max}/cm^{-1} 2925, 2853, 1671, 1603, 1573, 1518, 1478, 1266, 837, 750.

6-(Naphthalen-2-ylthio)-3'*H*-spiro[cyclohexane-1,1'-isobenzofuran]-2-ene-3',4-dione (3l)



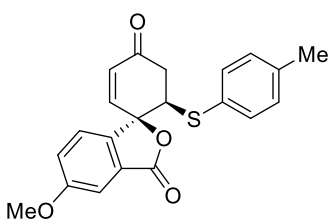
Colourless wax; **Yield**: 23 mg, 64%; **R_f**: 0.14 (*n*-hexane : ethyl acetate = 8 : 2); $[\alpha]_D^{26}$ = +18.9; 84% ee; Daicel Chiralpak IK column, *n*-hexane : *i*-PrOH = 70 : 30, Flow rate: 1.0 mL/min; 290 nm, t_R = 21.81 min (minor), t_R = 31.54 min (major); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.03 – 8.02 (m, 1H, Ar*H*), 7.75 – 7.73 (m, 1H, Ar*H*), 7.60 (d, *J* = 8.5 Hz, 1H, Ar*H*), 7.57 – 7.55 (m, 1H, Ar*H*), 7.48 – 7.45 (m, 3H, Ar*H*), 7.30 (d, *J* = 2.5 Hz, 1H, Ar*H*), 7.25 – 7.22 (m, 1H, Ar*H*), 7.09 (dd, *J* = 8.5, 2.0 Hz, 1H, Ar*H*), 6.99 – 6.97 (m, 1H, Ar*H*), 6.62 (d, *J* = 9.5 Hz, 1H, –C*H*=CHCO), 6.32 (d, *J* = 9.5 Hz, 1H, –CH=C*H*CO), 4.01 (t, *J* = 8.5 Hz, 1H, –C*H*SAr), 3.14 (d, *J* = 9.0 Hz, 2H, –CH_2–); **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$) δ 196.4, 169.2, 149.7, 144.4, 143.4, 134.3, 133.2, 133.1, 133.0, 132.7, 130.5, 130.0, 128.8, 127.7, 127.3, 126.9, 126.8, 126.0, 121.7, 82.6, 53.7, 42.6, 29.8 **HRMS** (ESI, m/z) calcd for $C_{23}H_{17}O_3S^+$ $[M+H]^+$: 373.0898, found: 373.0890; **IR**: ν_{max}/cm^{-1} 2918, 2851, 1773, 1693, 1466, 1265, 1084, 930, 734, 708.

5'-Chloro-6-(*p*-tolylthio)-3'*H*-spiro[cyclohexane-1,1'-isobenzofuran]-2-ene-3',4-dione (3m)



Colourless wax; **Yield**: 24 mg, 65%; **R_f**: 0.19 (*n*-hexane : ethyl acetate = 8 : 2); $[\alpha]_D^{26}$ = +19.8; 89% ee; Daicel Chiralpak IF column, *n*-hexane : *i*-PrOH = 70 : 30, Flow rate: 1.0 mL/min; 254 nm, t_R = 13.29 min (minor), t_R = 14.75 min (major); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.94 (dd, *J* = 2.0, 1.0 Hz, 1H, Ar*H*), 7.37 (dd, *J* = 8.0, 1.5 Hz, 1H, Ar*H*), 6.96 – 6.92 (m, 3H, Ar*H*), 6.86 – 6.85 (m, 2H, Ar*H*), 6.59 (d, *J* = 10.0 Hz, 1H, –C*H*=CHCO), 6.32 (d, *J* = 9.5 Hz, 1H, –CH=C*H*CO), 3.87 (dd, *J* = 11.5, 6.5 Hz, 1H, –C*H*SAr), 3.05 – 3.03 (m, 2H, –CH_2–), 2.29 (s, 3H, ArCH_3); **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$) δ 196.2, 167.7, 147.9, 142.7, 138.8, 136.9, 134.5, 133.6 (2C), 133.3, 129.9 (2C), 129.6, 129.0, 125.9, 122.9, 82.6, 53.9, 42.3, 21.2; **HRMS** (ESI, m/z) calcd for $C_{20}H_{16}O_3ClS^+$ $[M+H]^+$: 371.0509, found: 371.0502; **IR**: ν_{max}/cm^{-1} 2925, 2854, 1772, 1693, 1476, 1265, 1083, 929, 761, 733.

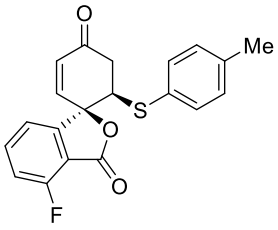
5'-Methoxy-6-(*p*-tolylthio)-3'*H*-spiro[cyclohexane-1,1'-isobenzofuran]-2-ene-3',4-dione (3n)



Colourless wax; **Yield**: 8 mg, 44%; **R_f**: 0.19 (*n*-hexane : ethyl acetate = 8 : 2); $[\alpha]_D^{26}$ = +12.3; 64% ee; Daicel Chiralpak IF column, *n*-hexane : *i*-PrOH = 70 : 30, Flow rate: 1.0 mL/min; 254 nm, t_R = 13.98 min (minor), t_R = 15.91 min (major); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.41 (d, *J* = 2.5 Hz, 1H, Ar*H*), 7.04 (dd, *J* = 8.5,

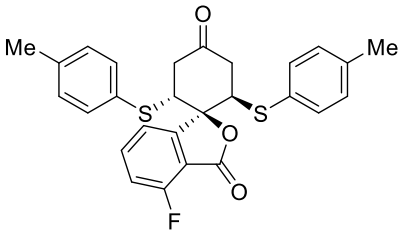
2.0 Hz, 1H, Ar*H*), 6.97 – 6.90 (m, 5H, Ar*H*), 6.60 (d, *J* = 10.0 Hz, 1H, –C*H*=CHCO), 6.28 (d, *J* = 10.0 Hz, 1H, –CH=C*H*CO), 3.91 (s, 3H, –OCH_3), 3.82 (dd, *J* = 10.0, 7.5 Hz, 1H, –C*H*SAr), 3.04 – 3.02 (m, 2H, –CH_2–), 2.27 (s, 3H, ArCH_3); **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$) δ 196.7, 169.2, 161.7, 143.8, 142.2, 138.7, 134.0 (2C), 132.8, 129.8 (2C), 129.6, 128.7, 123.1, 122.5, 108.0, 82.5, 56.1, 54.0, 42.5, 21.2; **HRMS** (ESI, m/z) calcd for $C_{21}H_{19}O_4S^+$ $[M+H]^+$: 367.1004, found: 367.1012; **IR**: ν_{max}/cm^{-1} 2925, 2854, 1772, 1693, 1476, 1265, 1083, 929, 761, 733.

4'-Fluoro-6-(p-tolylthio)-3'*H*-spiro[cyclohexane-1,1'-isobenzofuran]-2-ene-3',4-dione (3o)



Colourless wax; **Yield**: 8 mg, 23%; **R_f**: 0.08 (*n*-hexane : ethyl acetate = 8 : 2); $[\alpha]_D^{26}$ = +12.5; 59% ee; Daicel Chiralpak IK column, *n*-hexane : *i*-PrOH = 70 : 30, Flow rate: 1.0 mL/min; 290 nm, t_R = 19.05 min (minor), t_R = 24.38 min (major); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.49 (m, 1H, Ar*H*), 7.20 (t, *J* = 8.4 Hz, 1H, ArH), 6.94 – 6.90 (m, 4H, Ar*H*), 6.87 (d, *J* = 7.5 Hz, 1H, Ar*H*), 6.59 (d, *J* = 10.0 Hz, 1H, –C*H*=CHCO), 6.29 (d, *J* = 9.5 Hz, 1H, –CH=C*H*CO), 3.83 – 3.80 (m, 1H, –C*H*SAr), 3.02 (d, *J* = 9.5 Hz, 2H, –CH_2–), 2.26 (s, 3H, ArCH_3); **^{13}C{^{1}H}{^{19}F} NMR** (125 MHz, $CDCl_3$) δ 196.2, 165.0, 159.6, 152.4, 143.7, 142.5, 138.8, 137.0, 133.9 (2C), 133.1, 130.3, 129.9 (2C), 117.6, 117.5, 82.4, 53.6, 42.4, 21.2; **{^{19}F} NMR** (471 MHz, $CDCl_3$) δ −112.7; **HRMS** (ESI, m/z) calcd for $C_{20}H_{16}O_3FS^+$ $[M+H]^+$: 355.0804, found: 355.0813; **IR**: ν_{max}/cm^{-1} 2918, 2850, 1771, 1692, 1489, 1261, 1083, 929, 749.

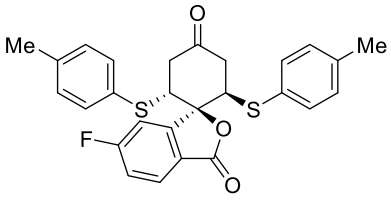
(2*R*,6*R*)-4'-Fluoro-2,6-bis(*p*-tolylthio)-3'*H*-spiro[cyclohexane-1,1'-isobenzofuran]-3',4-dione (4b)



Colourless wax; **Yield**: 20 mg, 42%; **R_f**: 0.38 (*n*-hexane : ethyl acetate = 8 : 2); $[\alpha]_D^{26}$ = −6.2; 20% ee; Daicel Chiralpak IK column, *n*-hexane : *i*-PrOH = 70 : 30, Flow rate: 1.0 mL/min; 254 nm, t_R = 17.09 min (minor), t_R = 21.58 min (major); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.46 – 7.44 (m, 1H, Ar*H*), 7.41 – 7.37 (m, 1H, Ar*H*), 7.22 – 7.18 (m, 1H, Ar*H*), 7.16 – 7.14 (m, 2H, Ar*H*), 7.09 – 7.07 (m, 2H, Ar*H*), 6.97 – 6.95 (m, 2H, Ar*H*), 6.92 – 6.90 (m, 2H, Ar*H*), 4.08 (dd, *J* = 13.0, 5.5 Hz, 1H, –C*H*SAr), 3.55 (dd, *J* = 4.0, 2.5 Hz, 1H, –C*H*SAr), 3.22 (dd, *J* = 15.0, 4.5 Hz, 1H,

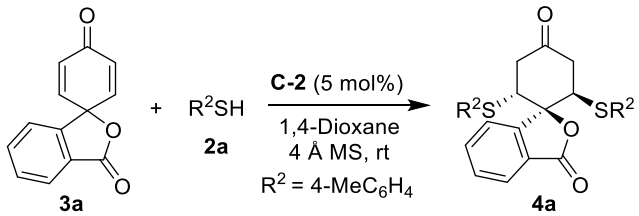
–CH_2–), 3.03 – 2.99 (m, 1H, –CH_2–), 2.88 – 2.83 (m, 1H, –CH_2–), 2.63 – 2.60 (m, 1H, –CH_2–), 2.30 (d, J = 3.0 Hz, 6H, 2 × ArCH_3); **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$) δ 204.3, 164.9, 159.7, 151.1, 139.5, 138.7, 135.6, 134.1 (2C), 133.7 (2C), 130.5 (2C), 129.9 (2C), 129.3, 127.3, 121.6, 117.1, 114.9, 87.5, 54.6, 51.5, 46.1, 43.5, 21.3 (2C); **{^{19}F} NMR** (471 MHz, $CDCl_3$) −114.1; **HRMS** (ESI, m/z) calcd for $C_{27}H_{24}O_3FS_2^+$ $[M+H]^+$: 479.1151, found: 479.1175; **IR**: ν_{max}/cm^{-1} 2917, 2850, 1772, 1729, 1466, 1264, 1179, 1088, 1017, 810, 734, 702.

(2*R*,6*R*)-6'-Fluoro-2,6-bis(*p*-tolylthio)-3'*H*-spiro[cyclohexane-1,1'-isobenzofuran]-3',4-dione (4c)



Colourless wax; **Yield**: 16 mg, 33%; **R$_f$**: 0.40 (*n*-hexane : ethyl acetate = 8 : 2); $[\alpha]_D^{26}$ = −10.5; 44% ee; Daicel Chiralpak IF column, *n*-hexane : *i*-PrOH = 70 : 30, Flow rate: 1.0 mL/min; 254 nm, t_R = 10.12 min (minor), t_R = 12.50 min (major); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.96 (dd, J = 9.0, 5.0 Hz, 1H, Ar*H*), 7.25 – 7.21 (m, 2H, Ar*H*), 7.18 – 7.16 (m, 2H, Ar*H*), 7.09 – 7.08 (m, 2H, Ar*H*), 6.97 – 6.95 (m, 2H, Ar*H*), 6.86 – 6.85 (m, 2H, Ar*H*), 4.11 – 4.07 (m, 1H, –C*H*SAr), 3.53 – 3.52 (m, 1H, –C*H*SAr), 3.25 – 3.21 (m, 1H, –CH_2–), 3.06 – 3.01 (m, 1H, –CH_2–), 2.88 – 2.82 (m, 1H, –CH_2–), 2.64 – 2.60 (m, 1H, –CH_2–), 2.30 (d, J = 2.5 Hz, 6H, 2 × ArCH_3); **^{13}C{^{1}H}{^{19}F} NMR** (125 MHz, $CDCl_3$); δ 204.2, 167.8, 165.7, 151.4, 139.5, 138.8, 134.1 (2C), 133.4 (2C), 130.5 (2C), 129.9 (2C), 129.5, 127.8, 127.3, 123.2, 118.3, 113.3, 87.0, 54.6, 51.8, 46.0, 43.4, 21.3, 21.2; **{^{19}F} NMR** (471 MHz, $CDCl_3$) δ −102.7; **HRMS** (ESI, m/z) calcd for $C_{27}H_{24}O_3FS^+$ $[M+H]^+$: 479.1151, found: 479.1143; **IR**: ν_{max}/cm^{-1} 2917, 2850, 1772, 1729, 1466, 1264, 1179, 1088, 1017, 810, 734, 702.

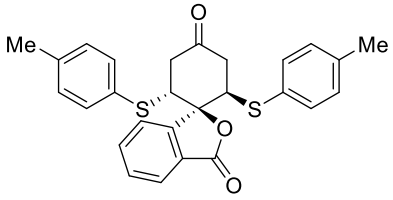
Procedure for the enantioselective synthesis of 4a:



In a 10 mL reaction tube equipped with a magnetic stirring bar, the isobenzofuranone **1a** (1.0 eq., 0.1 mmol) and catalyst **C-2** (5 mol%) were stirred in 1,4-dioxane (1.0 mL) in the presence of 4 Å molecular sieves (50 mg) at room temperature. After 5 minutes, thiol **2a** (1.0 eq., 0.1 mmol) was added, and the stirring was continued at the same temperature. After 24 hours, added more of **2a** (1.2 eq., 0.12 mmol). On the complete consumption of **1a** (indicated by TLC),

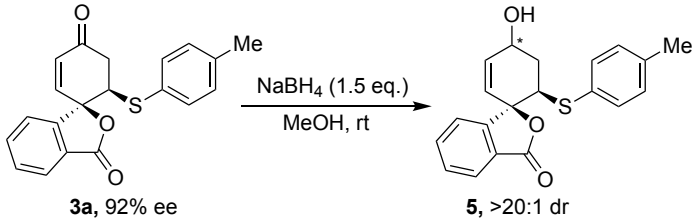
the crude product was directly purified by flash column chromatography (*n*-hexane : EtOAc = 8 : 2) to afford the products **4a**.

(2*R*,6*R*)-2,6-Bis(*p*-tolylthio)-3'*H*-spiro[cyclohexane-1,1'-isobenzofuran]-3',4-dione (4a)



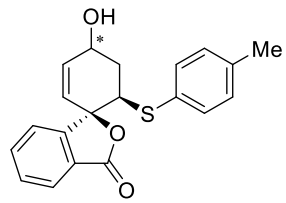
Colourless wax; **Yield**: 24 mg, 52%; **R$_f$**: 0.39 (*n*-hexane : ethyl acetate = 8 : 2); $[\alpha]_D^{26} = -20.8$; 77% ee; Daicel Chiralpak IK column, *n*-hexane : *i*-PrOH = 70 : 30, Flow rate: 1.0 mL/min; 254 nm, t_R = 14.50 min (minor), t_R = 18.51 min (major); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.00 – 7.98 (m, 1H, Ar*H*), 7.66 – 7.64 (m, 1H, Ar*H*), 7.59 – 7.55 (m, 1H, Ar*H*), 7.43 – 7.40 (m, 1H, Ar*H*), 7.16 – 7.14 (m, 2H, Ar*H*), 7.08 – 7.06 (m, 2H, Ar*H*), 6.94 – 6.92 (m, 2H, Ar*H*), 6.85 – 6.84 (m, 2H, Ar*H*), 4.10 (dd, *J* = 13.0, 5.5 Hz, 1H, –C*H*SAr), 3.54 (dd, *J* = 4.0, 2.5 Hz, 1H, –C*H*SAr), 3.25 (dd, *J* = 15.0, 4.5 Hz, 1H, –C*H*$_2$–), 3.04 – 3.00 (m, 1H, –C*H*$_2$–), 2.88 (dd, *J* = 15.5, 13.0 Hz, 1H, –C*H*$_2$–), 2.63 – 2.59 (m, 1H, –C*H*$_2$–), 2.29 (d, *J* = 3.0 Hz, 6H, 2 × $ArCH_3$); **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$) δ 204.7, 169.0, 148.7, 139.3, 138.5, 134.1 (2C), 133.7 (2C), 133.3, 130.5 (2C), 130.1, 129.8 (2C), 129.5, 127.6, 127.1, 125.8, 125.5, 87.6, 54.8, 51.7, 46.2, 43.5, 21.3 (2C); **HRMS** (ESI, m/z) calcd for $C_{27}H_{25}O_3S_2^+$ $[M+H]^+$: 461.1245, found: 461.1233; **IR**: ν_{max}/cm^{-1} 2917, 2850, 1772, 1729, 1466, 1264, 1179, 1088, 1017, 810, 734, 702.

Procedure for synthesis of 5 from 3a:



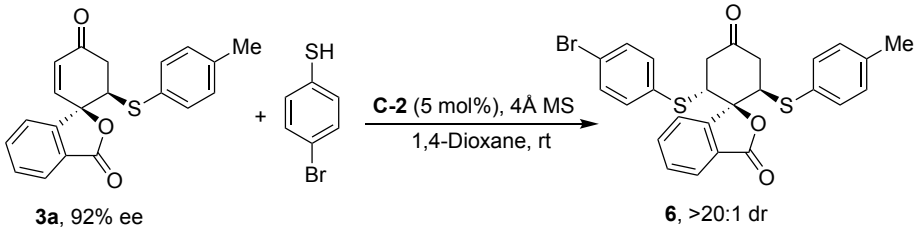
In a 10 mL reaction tube equipped with a magnetic stirring bar, the isobenzofuranone **3a** (1.0 eq., 0.1 mmol) dissolved in methanol (1.0 mL) at room temperature. Then $NaBH_4$ (1.5 equiv) was added, and the stirring was continued at the same temperature. After the complete consumption of **3a** (less than 5 minutes, indicated by TLC), the crude product was directly purified by flash column chromatography (*n*-hexane : EtOAc = 8 : 2) to afford the product **5.**

(1*R*,6*R*)-4-Hydroxy-6-(*p*-tolylthio)-3'*H*-spiro[cyclohexane-1,1'-isobenzofuran]-2-en-3'-one (5)



Colourless wax; **Yield**: 30 mg, 89%; **R**$_f$: 0.12 (*n*-hexane : ethyl acetate = 7 : 3); $[\alpha]_D^{26}$ = +25.7; 89% ee; Daicel Chiralpak IF column, *n*-hexane : *i*-PrOH = 70 : 30, Flow rate: 1.0 mL/min; 254 nm, t_R = 16.55 min (major), t_R = 18.68 min (minor); **^{1}H NMR** (500 MHz, DMSO-d_6) δ 7.86 (d, *J* = 7.5 Hz, 1H, Ar*H*), 7.68 – 7.65 (m, 1H, Ar*H*), 7.61 – 7.57 (m, 1H, Ar*H*), 7.49 (d, *J* = 7.5 Hz, 1H, Ar*H*), 7.01 – 6.95 (m, 4H, Ar*H*), 6.11 (d, *J* = 10.0 Hz, 1H, –C*H*), 5.47 (d, *J* = 10.0 Hz, 1H, –C*H*), 5.30 (d, *J* = 6.0 Hz, 1H, –OH), 4.40 – 4.37 (m, 1H, –C*H*OH), 3.82 (dd, *J* = 13.5, 3.0 Hz, 1H, –C*H*SAr), 2.34 – 2.30 (m, 1H, –CH_2–), 2.22 (s, 3H, ArCH_3), 1.85 – 1.78 (m, 1H, –CH_2–); **^{13}C{^{1}H} NMR** (125 MHz, DMSO-d_6) δ 169.2, 151.4, 139.9, 137.1, 134.6, 132.2 (2C), 129.9 (2C), 129.6 (2C), 126.5, 124.7, 124.5, 122.2, 84.3, 65.7, 51.0, 37.3, 20.6; **HRMS** (ESI, m/z) calcd for $C_{20}H_{19}O_3S^+$ $[M+H]^+$: 339.1055, found: 339.1059; **IR**: ν_{max}/cm^{-1} 3362, 2918, 2850, 1738, 1466, 1262, 931, 763, 750.

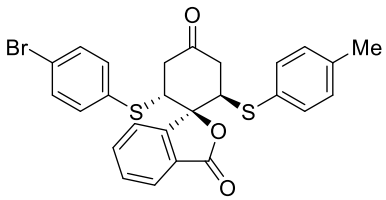
Procedure for synthesis of 6 from 3a:



3a, 92% ee **6**, >20:1 dr

In a 10 mL reaction tube equipped with a magnetic stirring bar, the isobenzofuranone (**3a**, 1.0 eq., 0.1 mmol) and catalyst **C-2** (5 mol%) were stirred in 1,4-dioxane (2.0 mL) in the presence of molecular sieves at 24 ℃. After 5 minutes, 4-bromothiophenol (1.0 eq., 0.1 mmol) was added, and the stirring was continued at the same temperature. After the complete consumption of **3a** (indicated by TLC), the crude product was directly purified by flash column chromatography (*n*-hexane : EtOAc = 8 : 2) to afford the product **6.**

(*1R*,2*R*,6*R*)-2-[(4-bromophenyl)thio]-6-(*p*-tolylthio)-3'*H*-spiro[cyclohexane-1,1'-isobenzofuran]-3',4-dione (6)



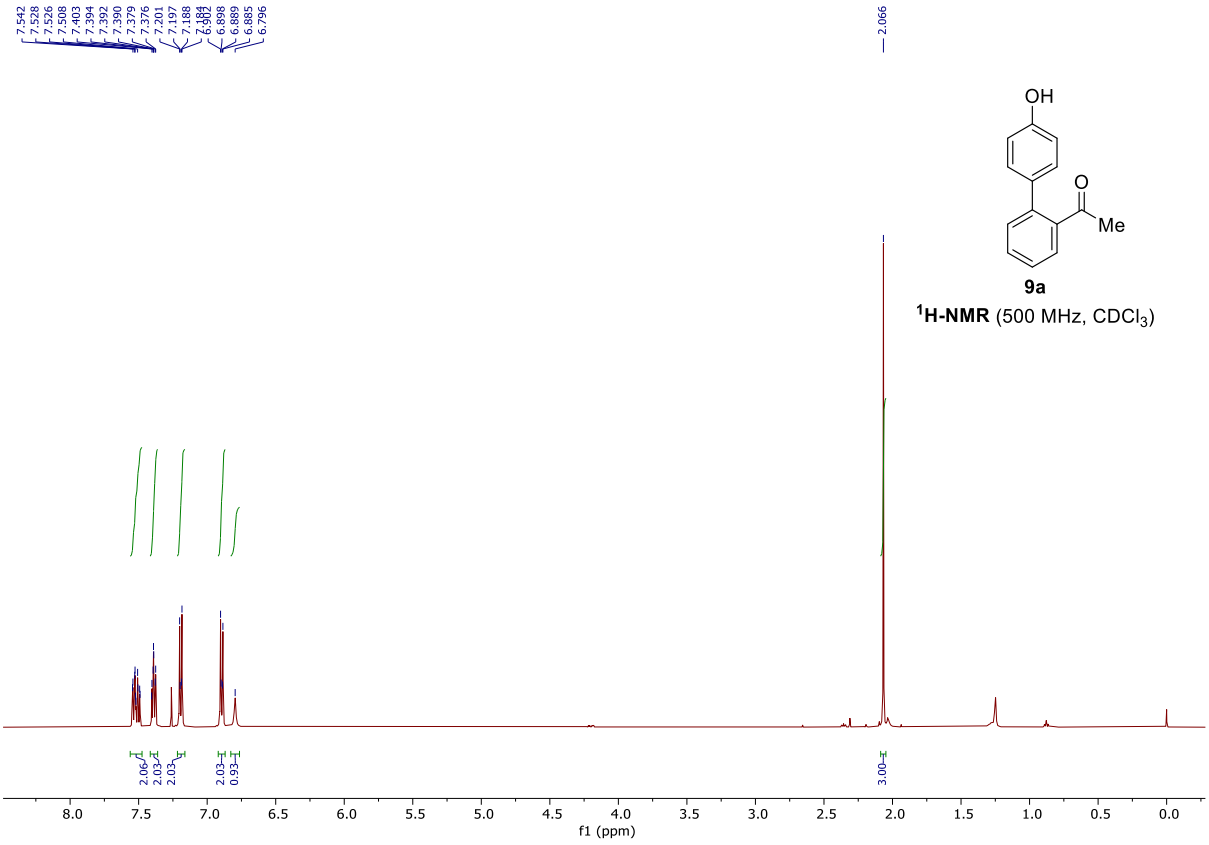
Colourless wax; **Yield**: 38 mg, 72%; **R**$_f$: 0.40 (*n*-hexane: ethyl acetate = 8 : 2); $[\alpha]_D^{26}$ = −14.8; 84% ee; Daicel Chiralpak IF column, *n*-hexane : *i*-PrOH = 70 : 30, Flow rate: 1.0 mL/min; 254 nm, t_R = 13.32 min (minor), t_R = 17.45 min (major); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.01 – 7.99 (m, 1H, Ar*H*), 7.59 – 7.56 (m, 2H, Ar*H*), 7.42 – 7.38 (m, 3H, Ar*H*), 7.11 – 7.10 (m, 2H, Ar*H*), 6.95 – 6.93 (m, 2H, Ar*H*), 6.85 – 6.84 (m, 2H, Ar*H*),

4.07 (dd, J = 12.5, 5.5 Hz, 1H, –C*H*SAr), 3.60 (dd, J = 4.5, 2.5 Hz, 1H, –C*H*SAr), 3.29 (dd, J = 15.0, 4.5 Hz, 1H, –CH_2–), 3.05 – 3.00 (m, 1H, –CH_2–), 2.89 (dd, J = 15.5, 13.0 Hz, 1H, –CH_2–), 2.61 – 2.57 (m, 1H, –CH_2–), 2.29 (s, 3H, ArCH_3); **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$) δ 204.3, 168.8, 148.5, 138.6, 135.0 (2C), 133.7 (2C), 133.4, 132.8 (2C), 130.4, 130.2, 129.9 (2C), 129.3, 127.1, 125.9, 125.3, 123.4, 87.3, 54.6, 51.8, 46.2, 43.6, 21.2; **HRMS** (ESI, m/z) calcd for $C_{26}H_{22}O_3BrS_2^+$ $[M+H]^+$: 525.0194, found: 525.0181; **IR**: ν_{max}/cm^{-1} 2922, 1770, 1718, 1466, 1251, 1086, 1008, 944, 809, 733, 692, 496.

References:

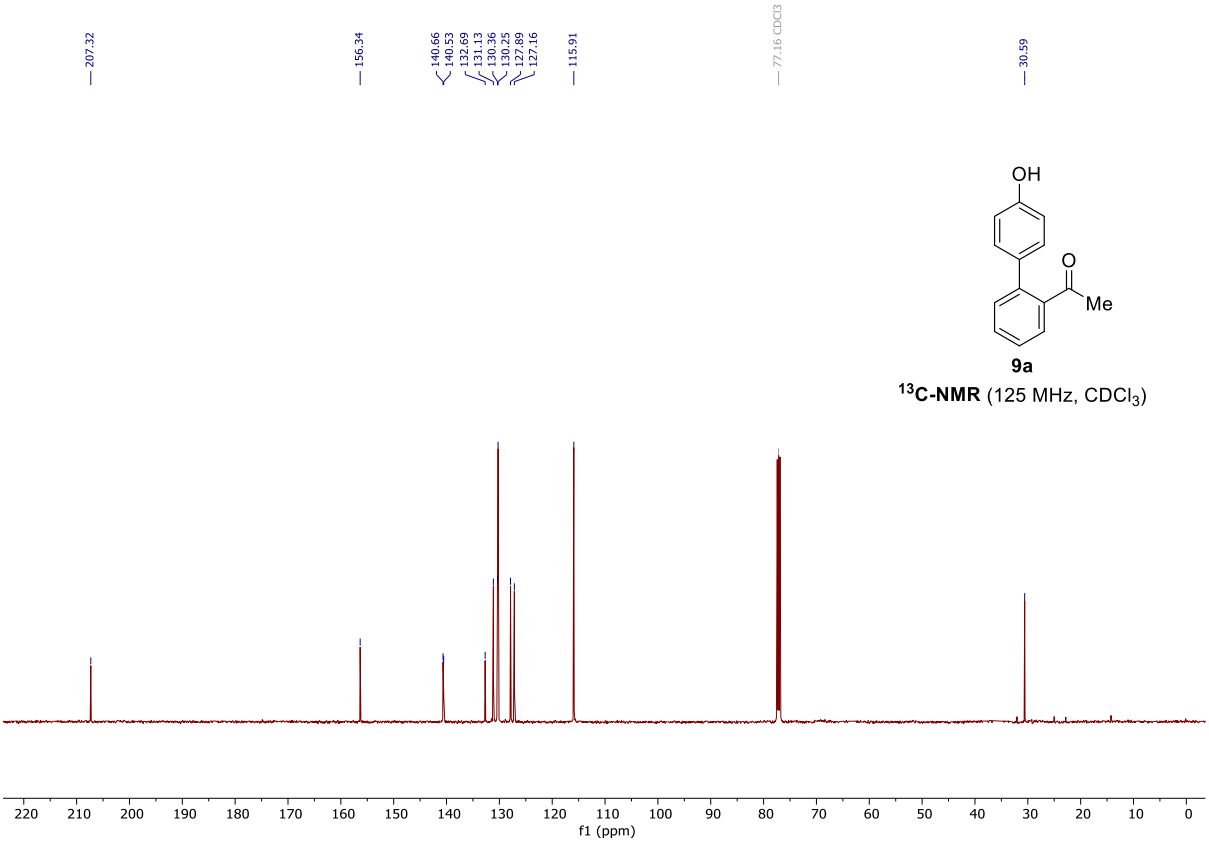
1. W. Yang and D.-M. Du, *Org. Lett*., 2010, **12**, 5450.
2. H. Li, Y. Wang, L. Tang, F. Wu, X. Liu, C. Guo, B. M. Foxman and L. Deng, *Angew. Chem., Int. Ed*., 2004, **117**, 107.
3. Y. Fan, M. Tiffner, J. Schorgenhumer, R. Robiettee, M. Waser and S. R. Kass, *J. Org. Chem*., 2018, **82**, 9991.
4. Y.-T. Jiang, Z.-Z. Yu, Y.-K Zhang and B. Wang, *Org. Lett*., 2018, **20**, 3728.
5. G.-H. Zhao, B.-Q. Li, S.-S. Wang, M. Liu, Y. Chen and B. Wang, *J. Org. Chem*., 2020, **85**, 9367.
6. S. Peng, J. He, L. Yang, H. Zhang, H. Li, M. Lang, C. Chen, J. Wang, *J. Org. Chem*., 2022, **87**, 6247.

NMR Spectra:



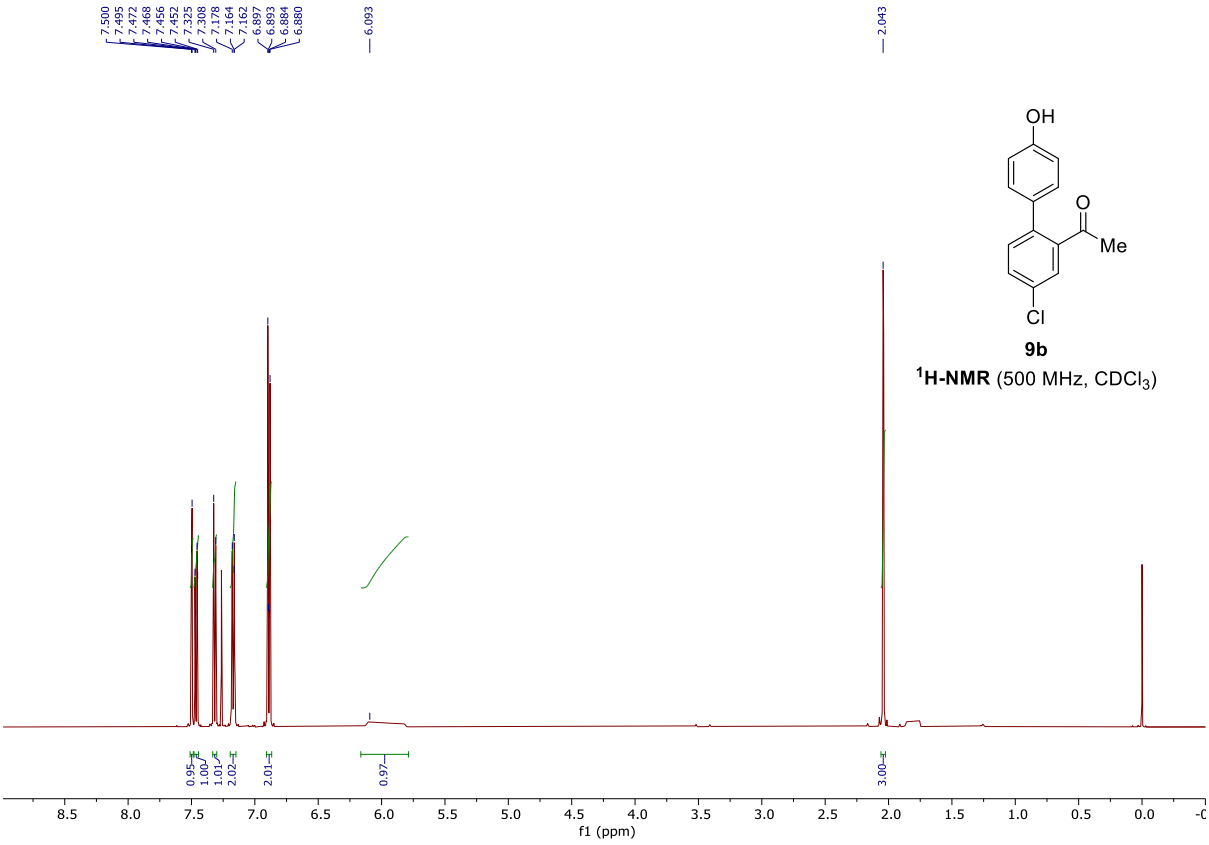
9a

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



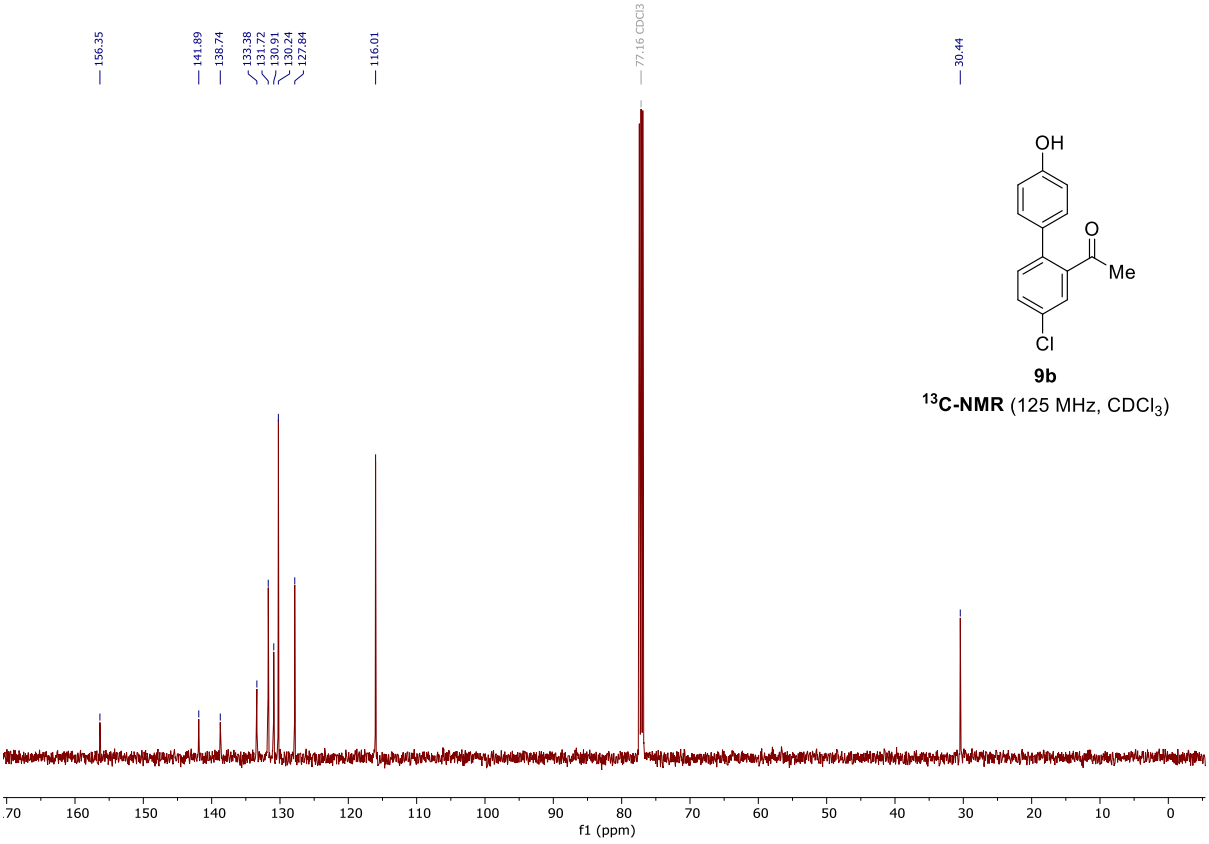
9a

^{13}C-NMR (125 MHz, $CDCl_3$)



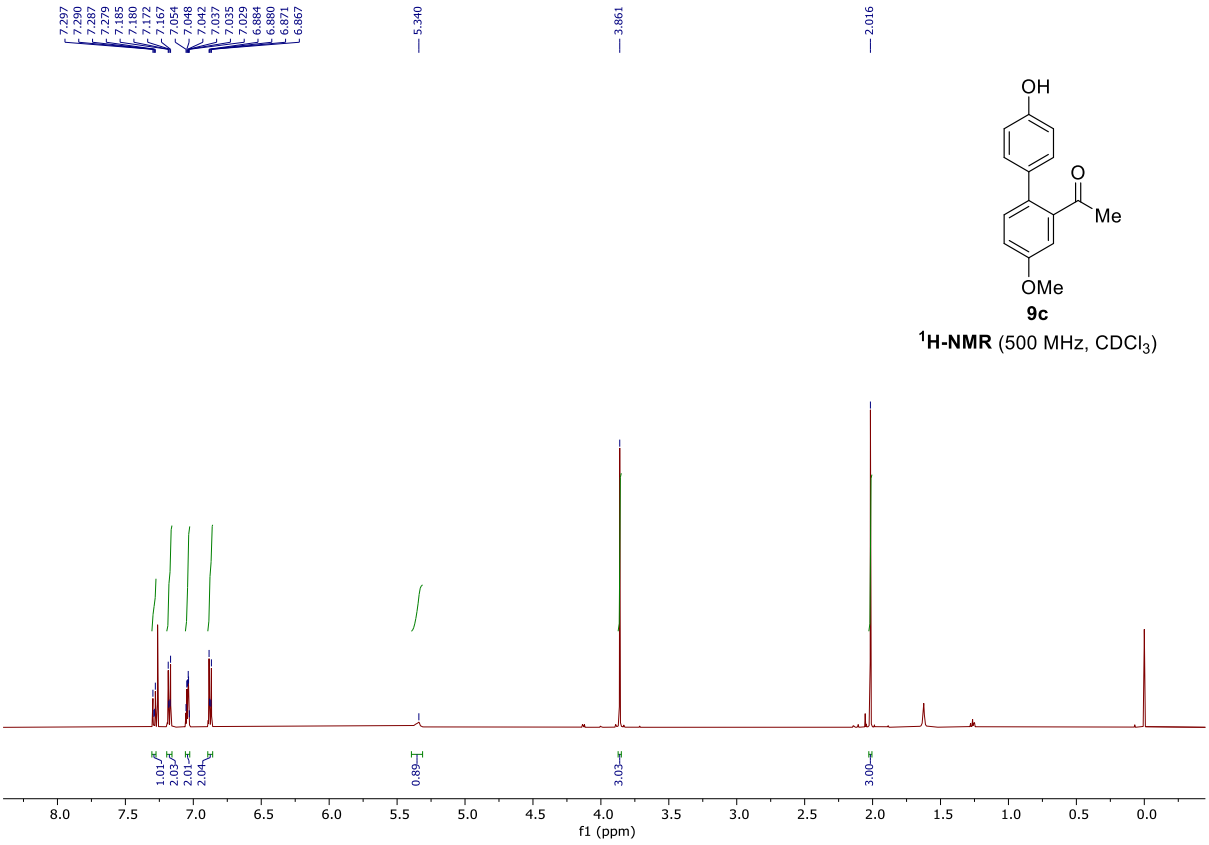
9b

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



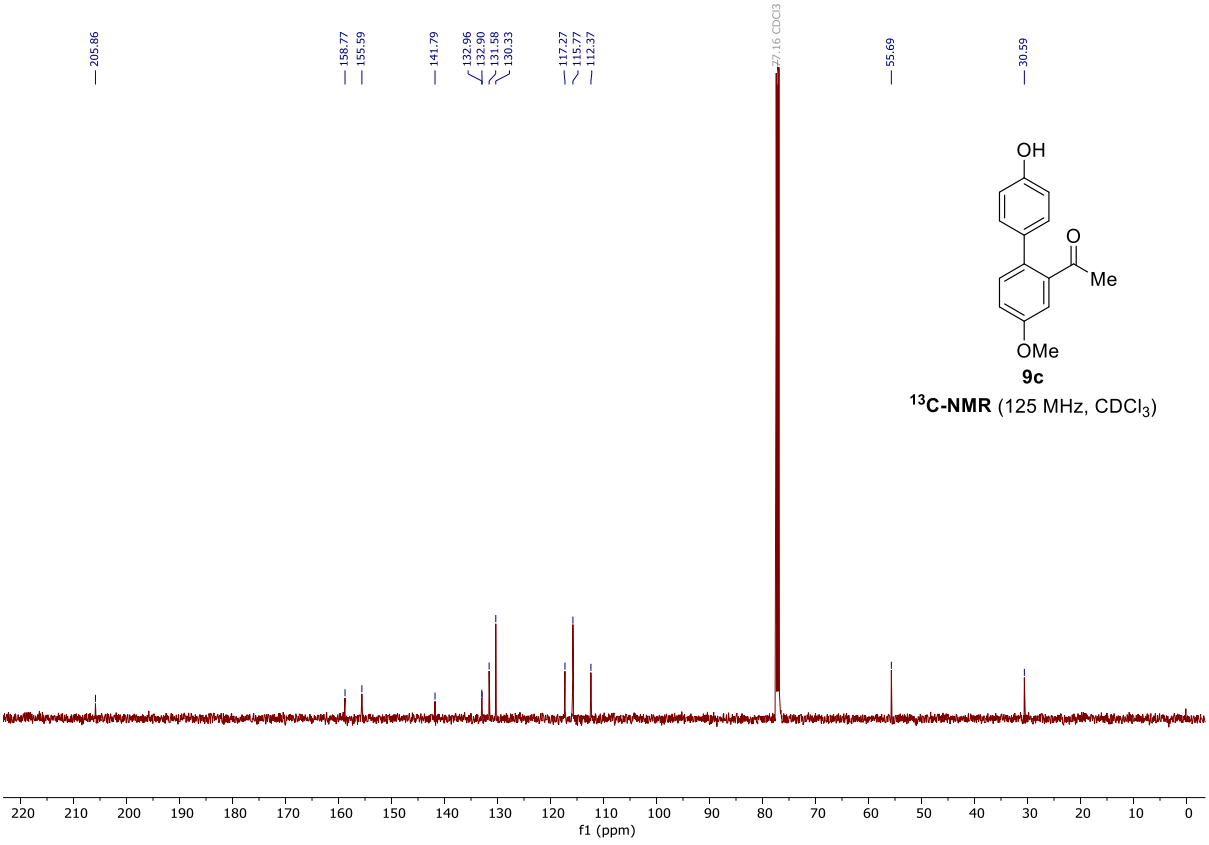
9b

^{13}C-NMR (125 MHz, $CDCl_3$)



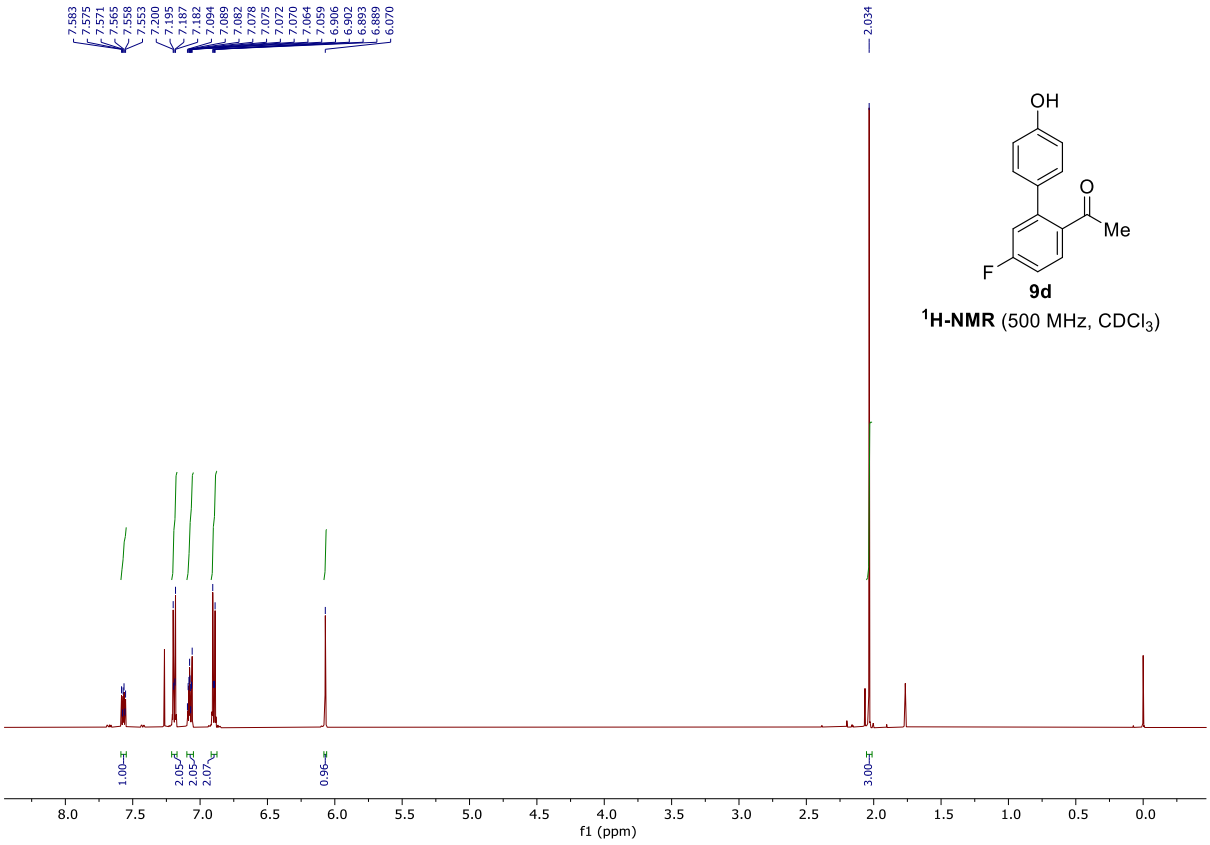
9c

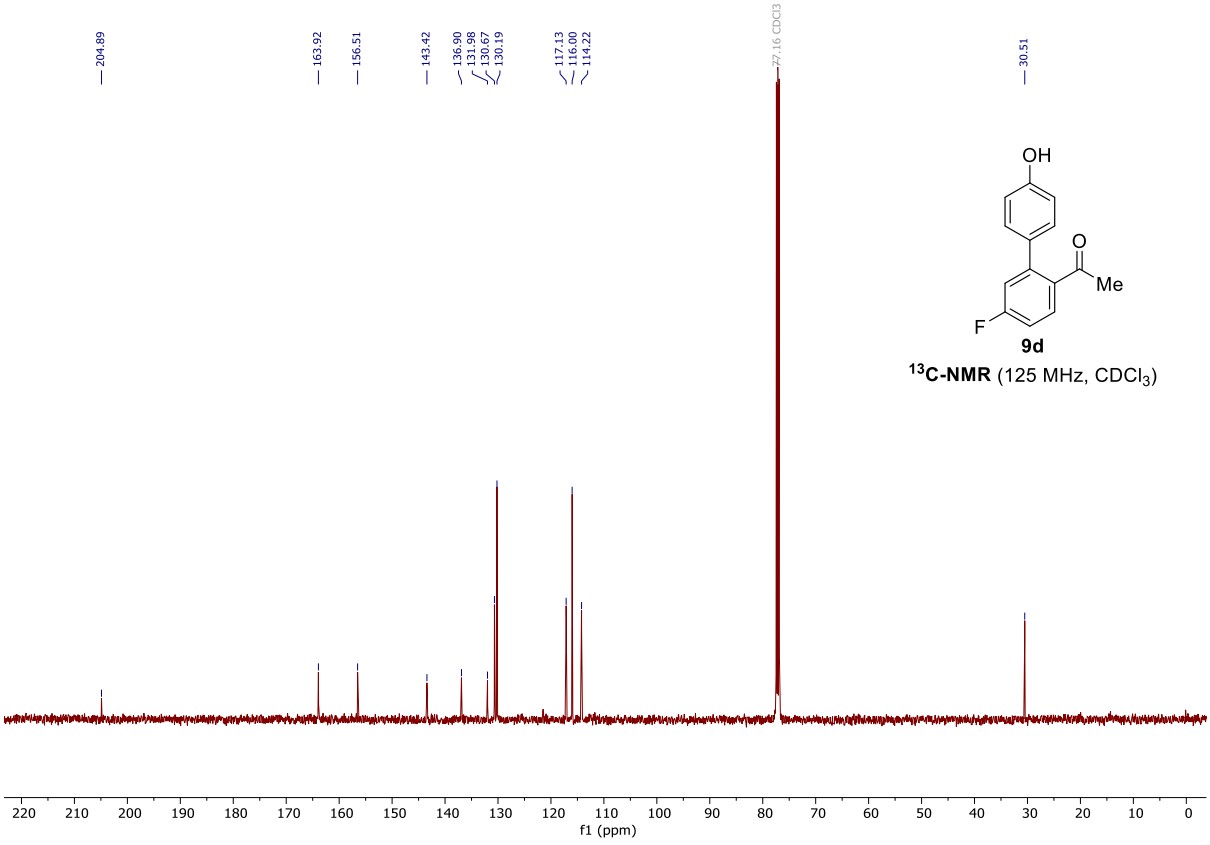
^{1}H-NMR (500 MHz, $CDCl_3$)

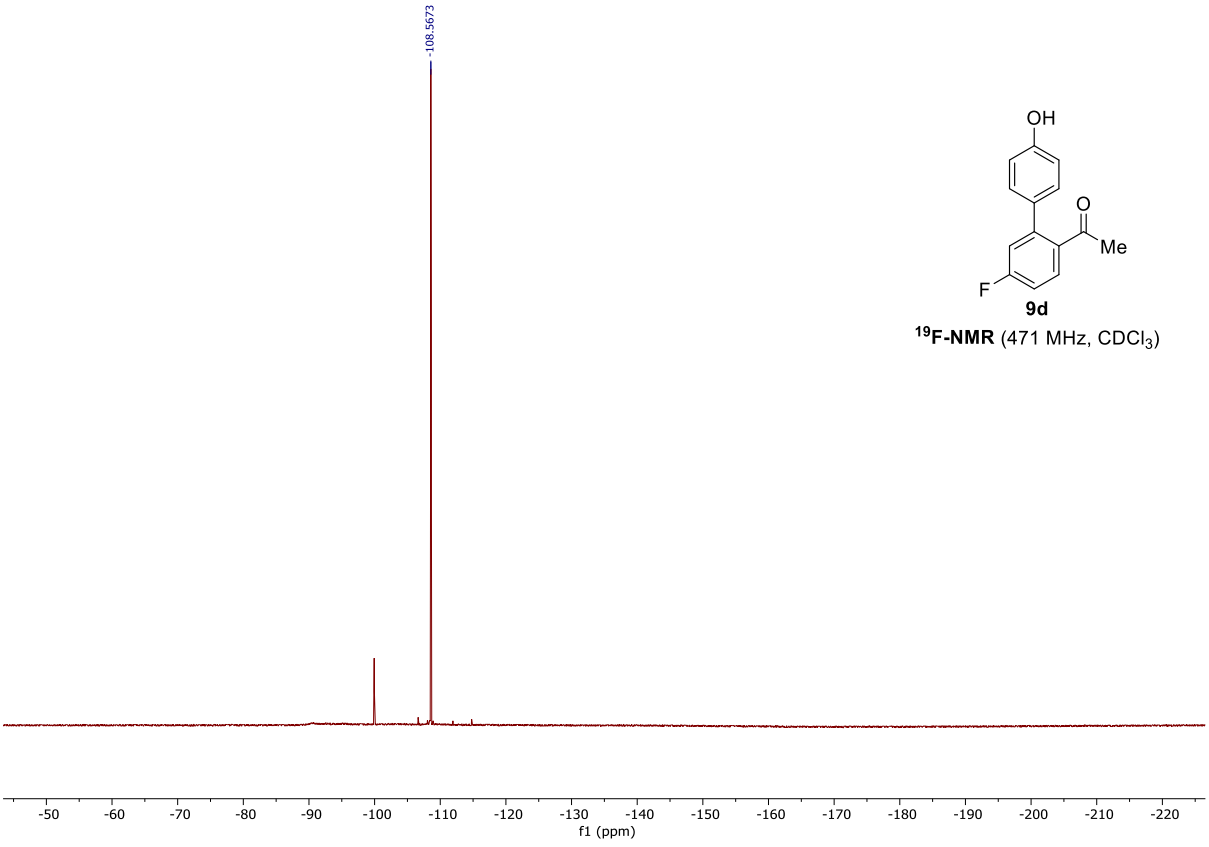


9c

^{13}C-NMR (125 MHz, $CDCl_3$)

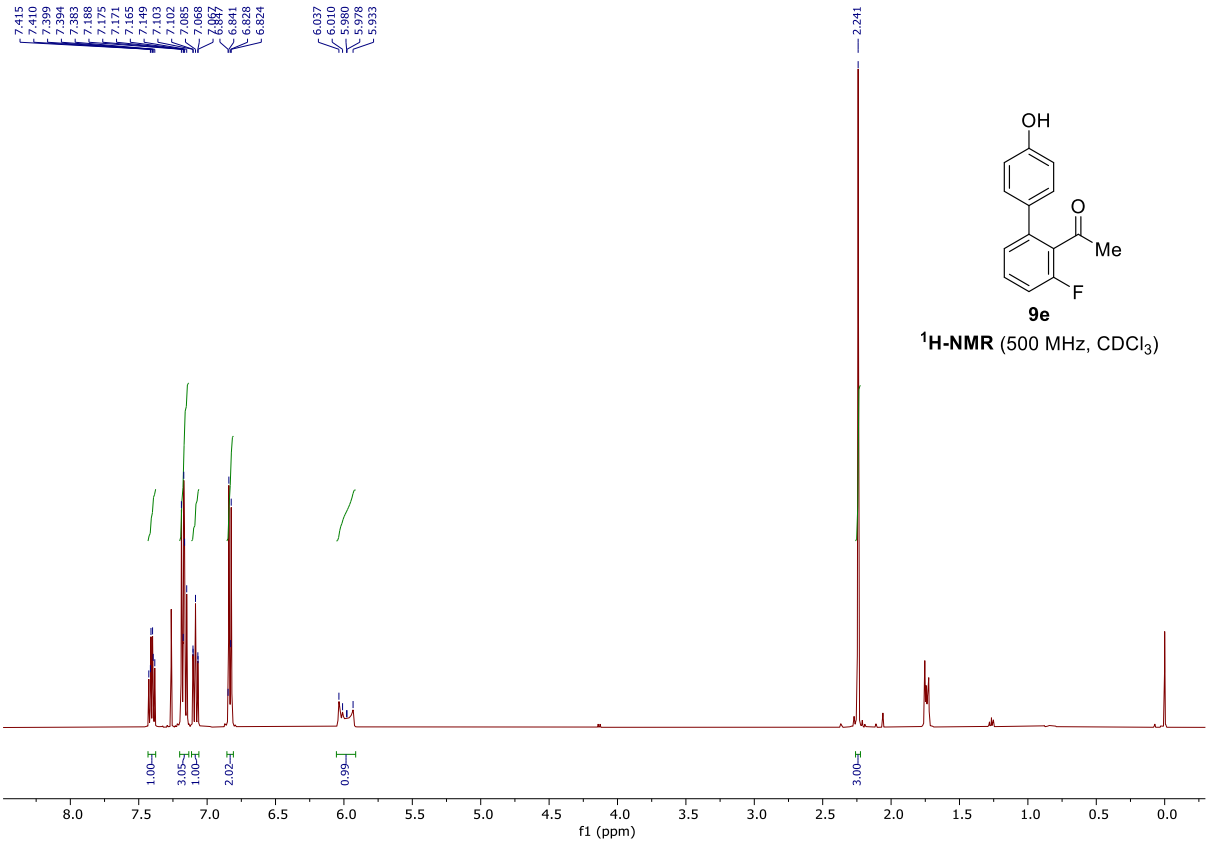

7.583
7.575
7.571
7.565
7.558
7.553
7.200
7.195
7.187
7.182
7.094
7.089
7.082
7.078
7.075
7.072
7.070
7.064
7.059
6.906
6.902
6.893
6.889
6.070
2.034
OH
O
Me
F
9d
1H-NMR (500 MHz, CDCl3)
1.00
2.05
2.05
2.07
0.96
3.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


204.89
163.92
156.51
143.42
136.90
131.98
130.67
130.19
117.13
116.00
114.22
77.16 CDCl3
30.51
OH
O
Me
F
9d
13C-NMR (125 MHz, CDCl3)
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



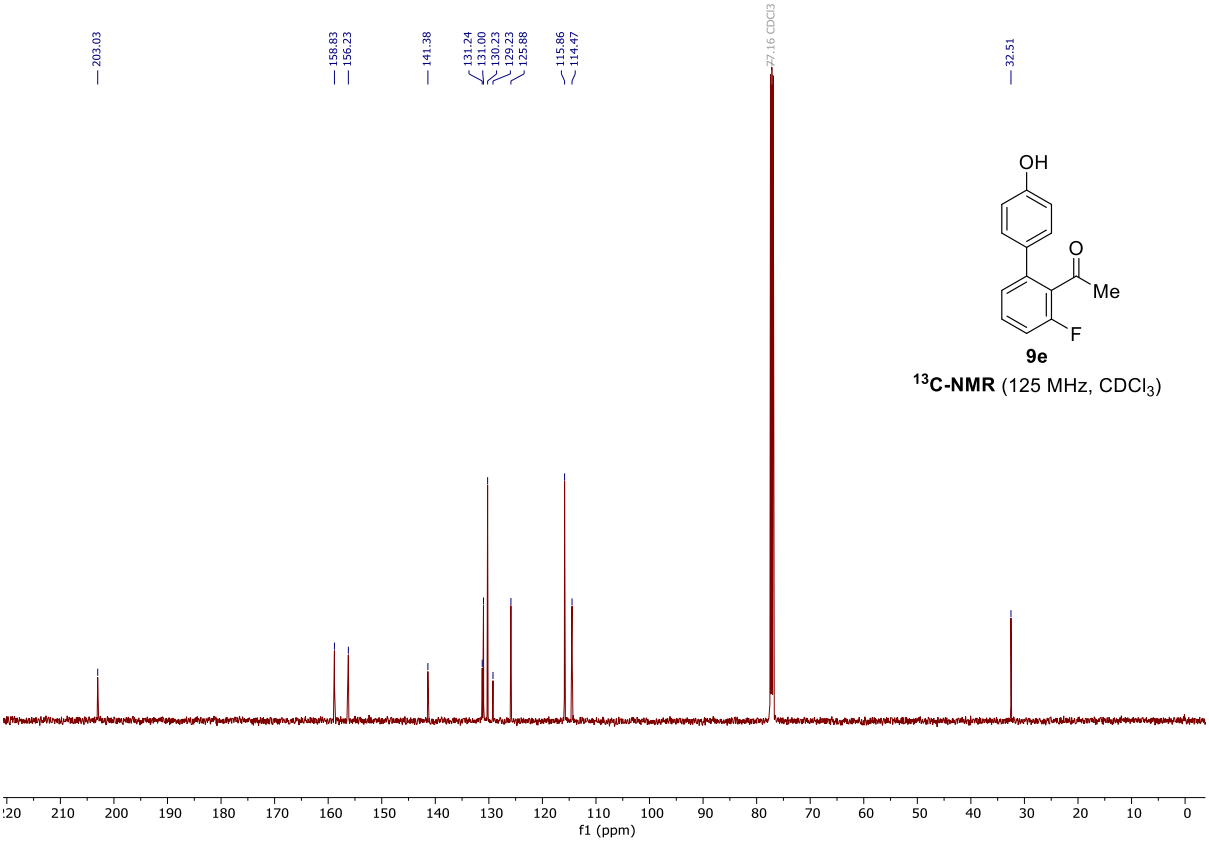
9d

^{19}F-NMR (471 MHz, $CDCl_3$)



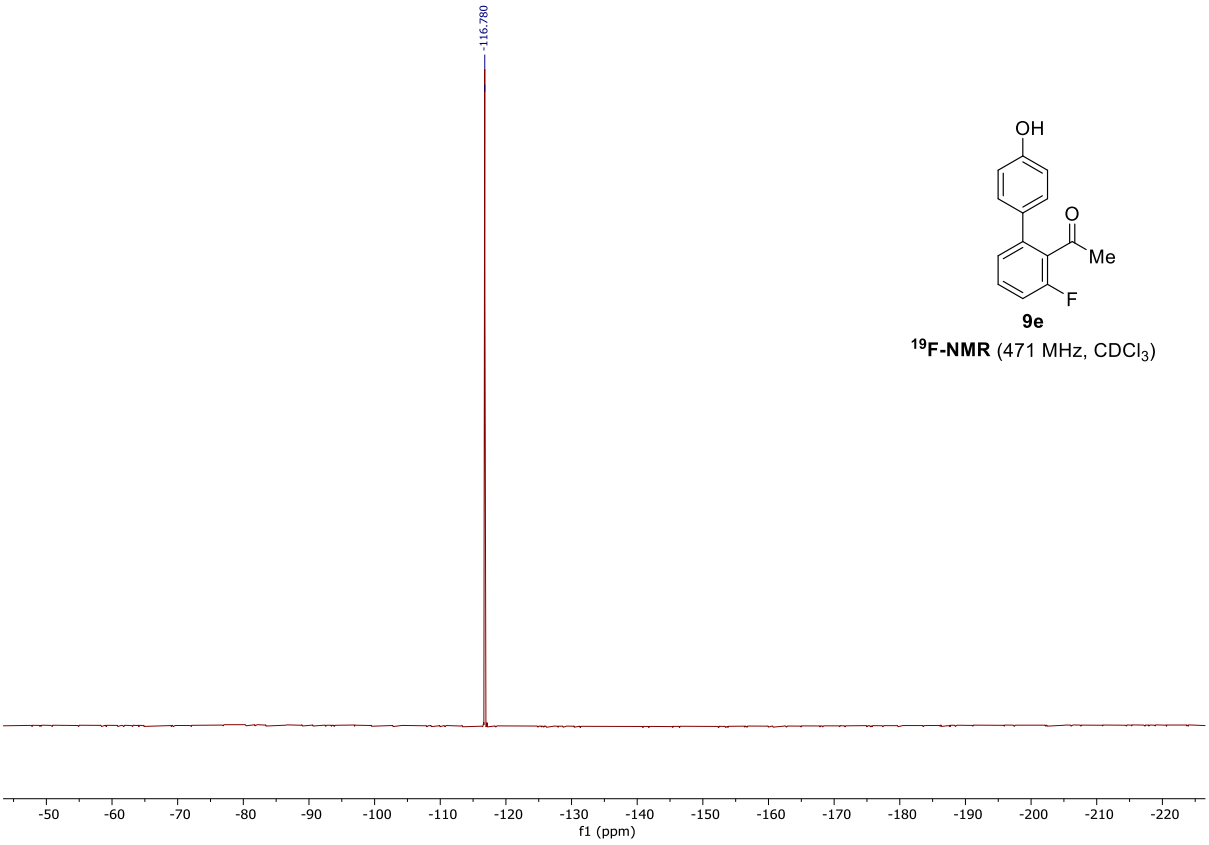
9e

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



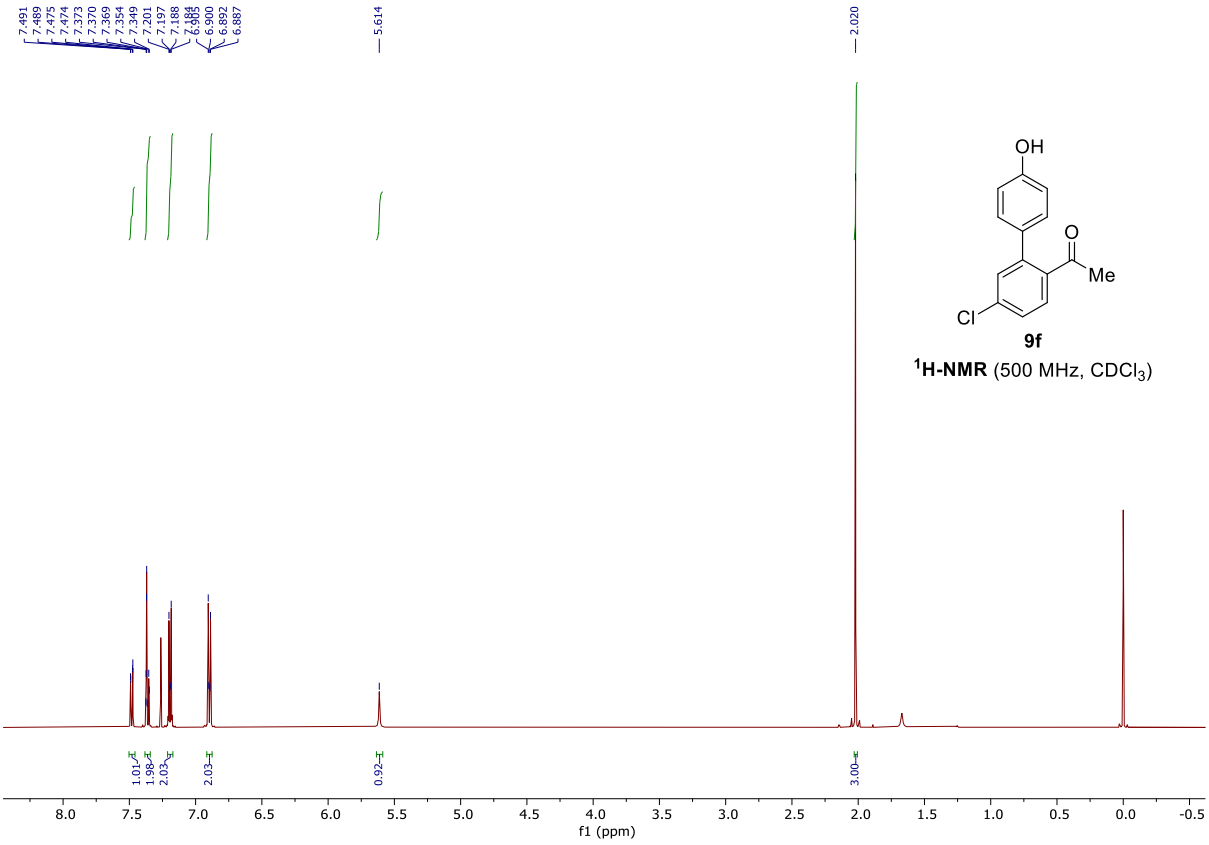
9e

^{13}C-NMR (125 MHz, $CDCl_3$)



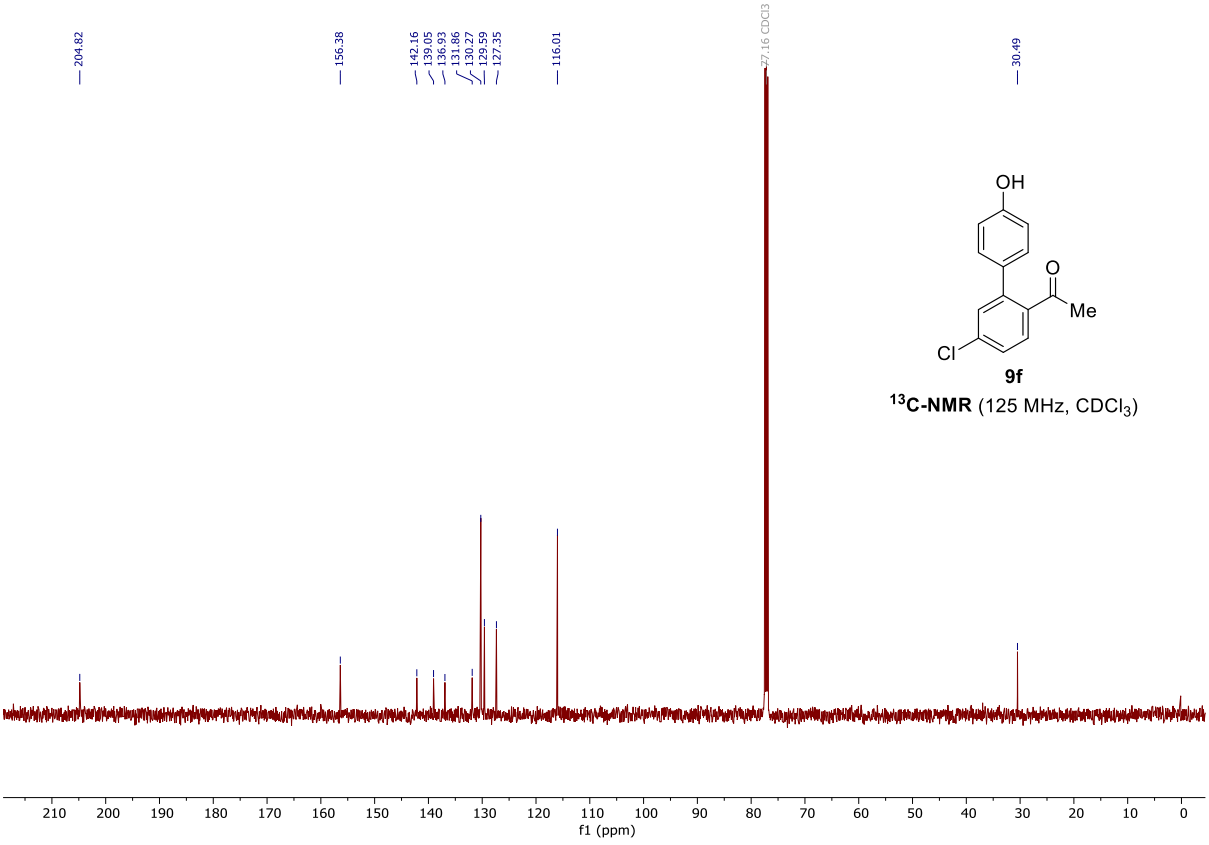
9e

^{19}F-NMR (471 MHz, $CDCl_3$)



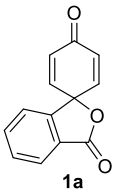
9f

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



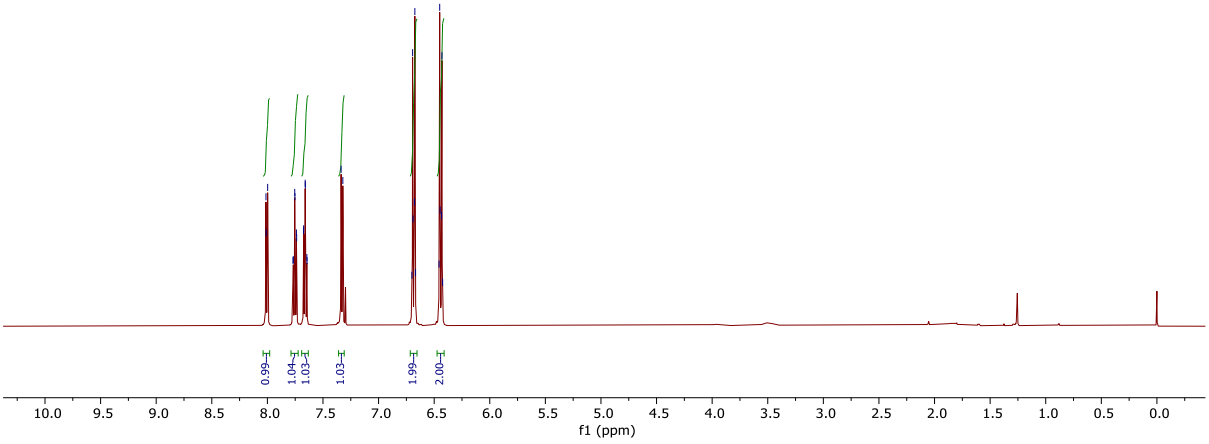
9f

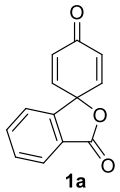
^{13}C-NMR (125 MHz, $CDCl_3$)



1a

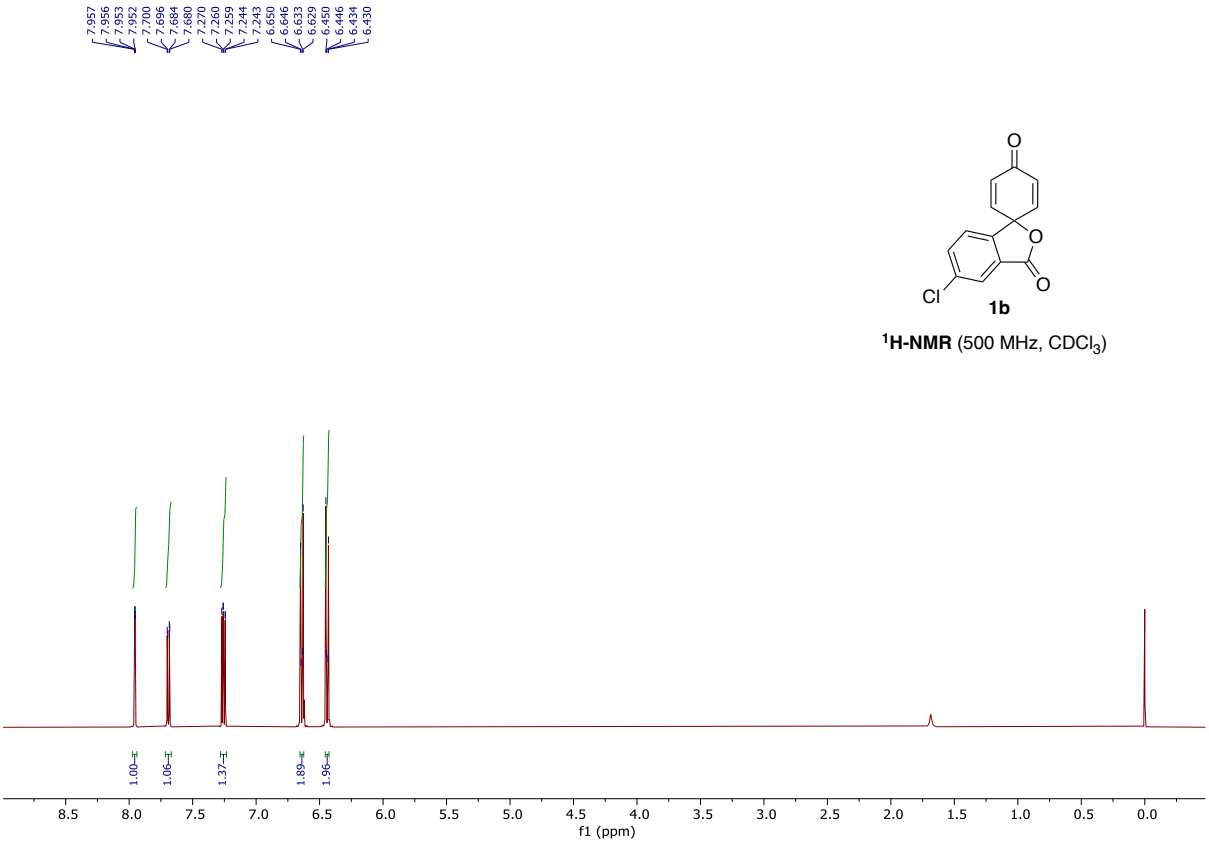
^{1}H-NMR (500 MHz, $CDCl_3$)





1a

^{13}C-NMR (125 MHz, $CDCl_3$)



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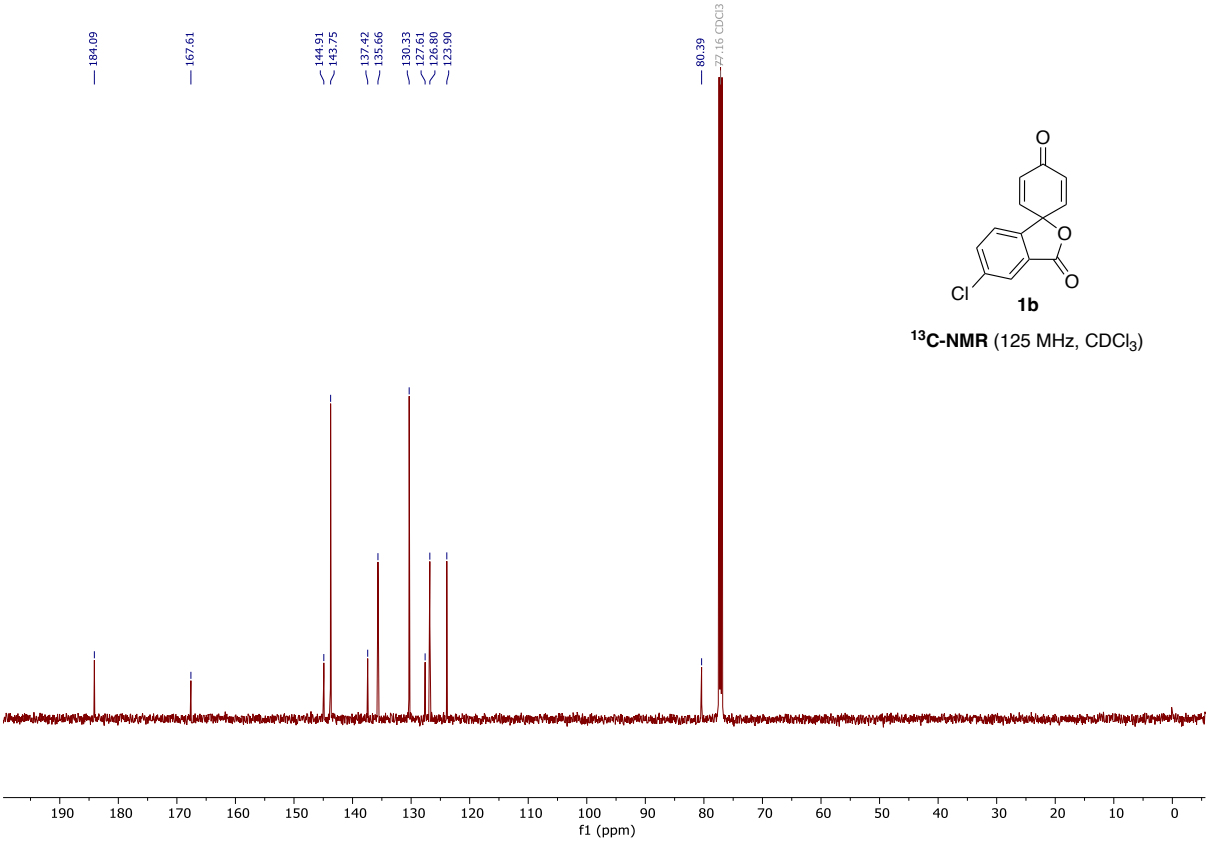

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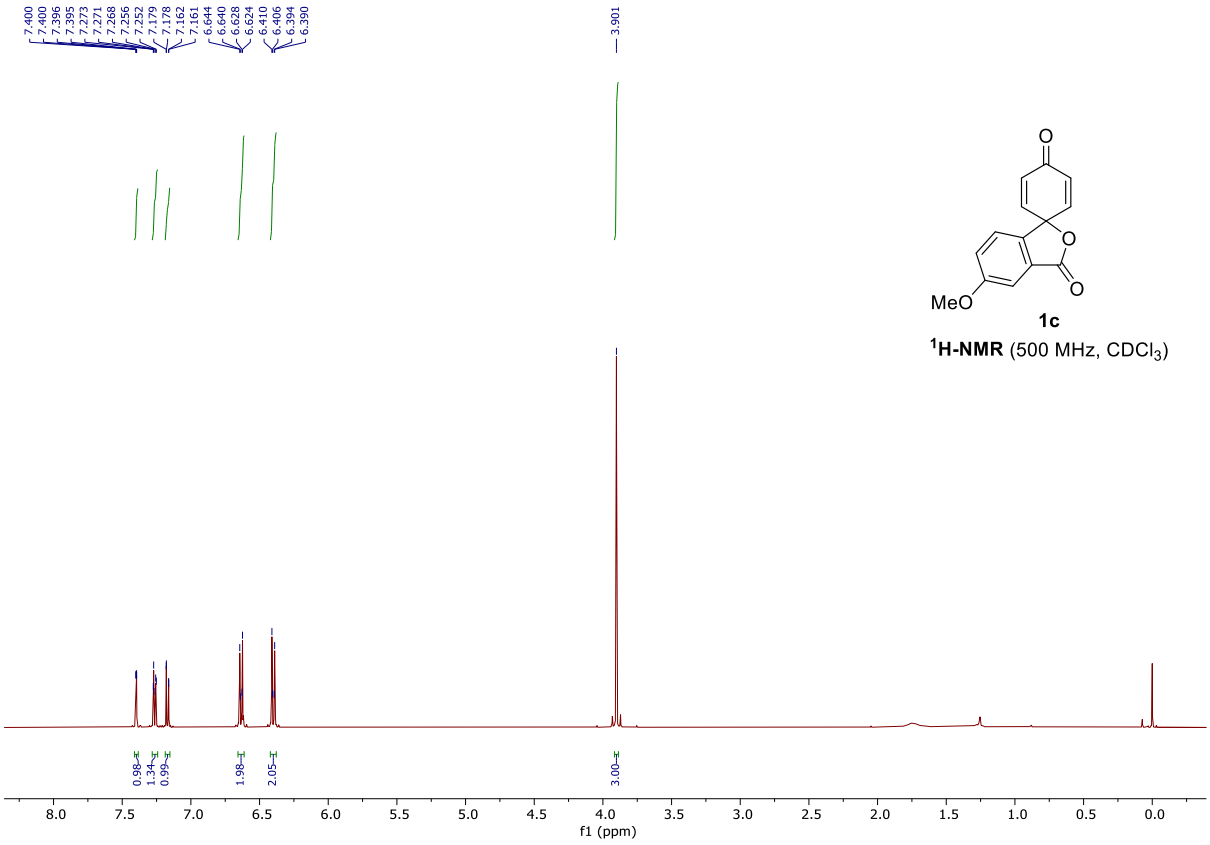
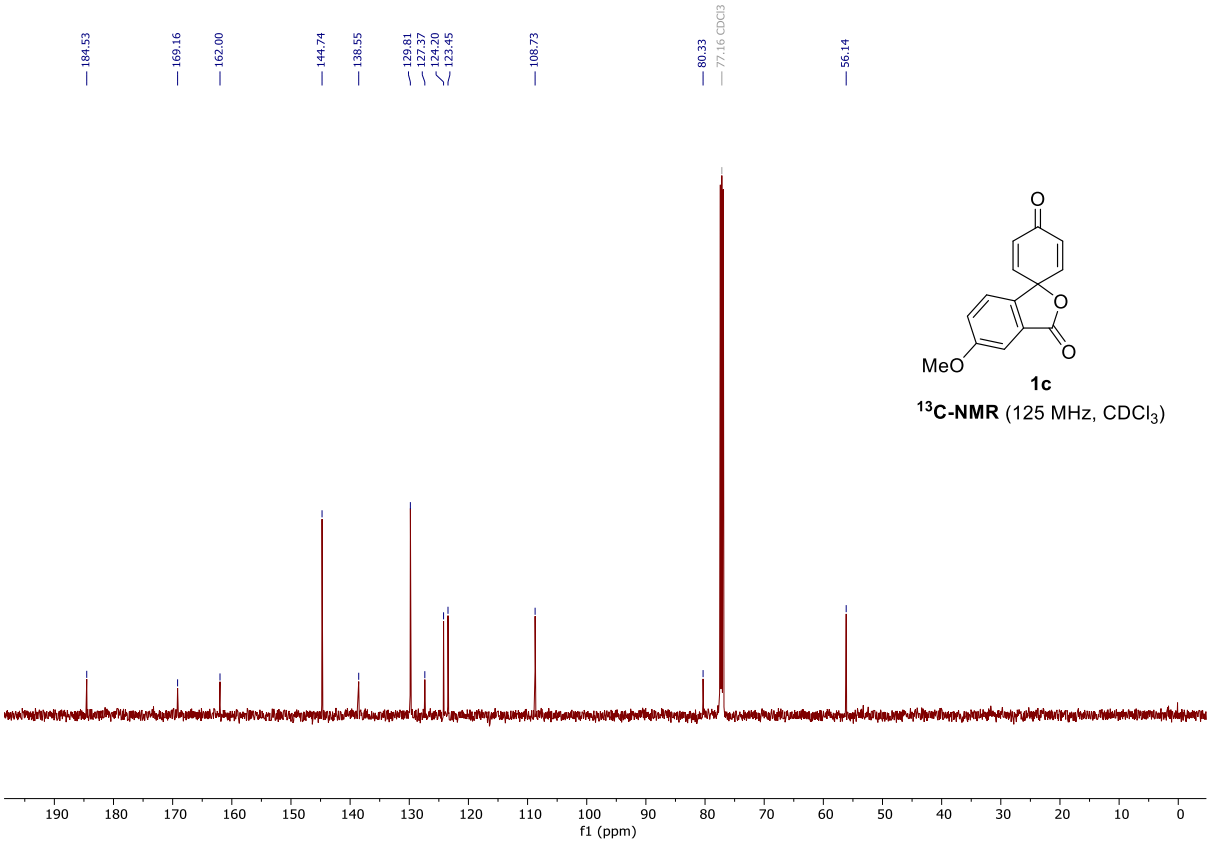


1c

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



1c

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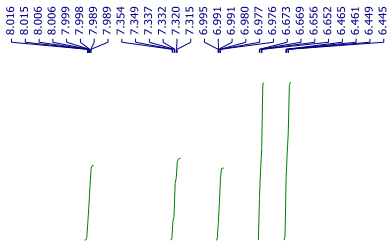

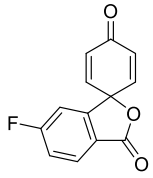

1d

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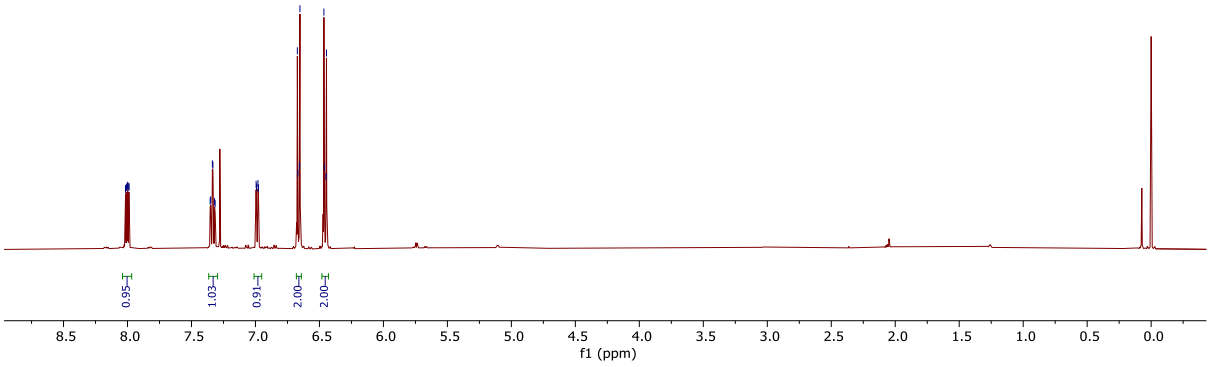
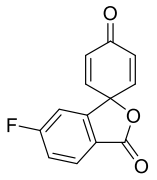
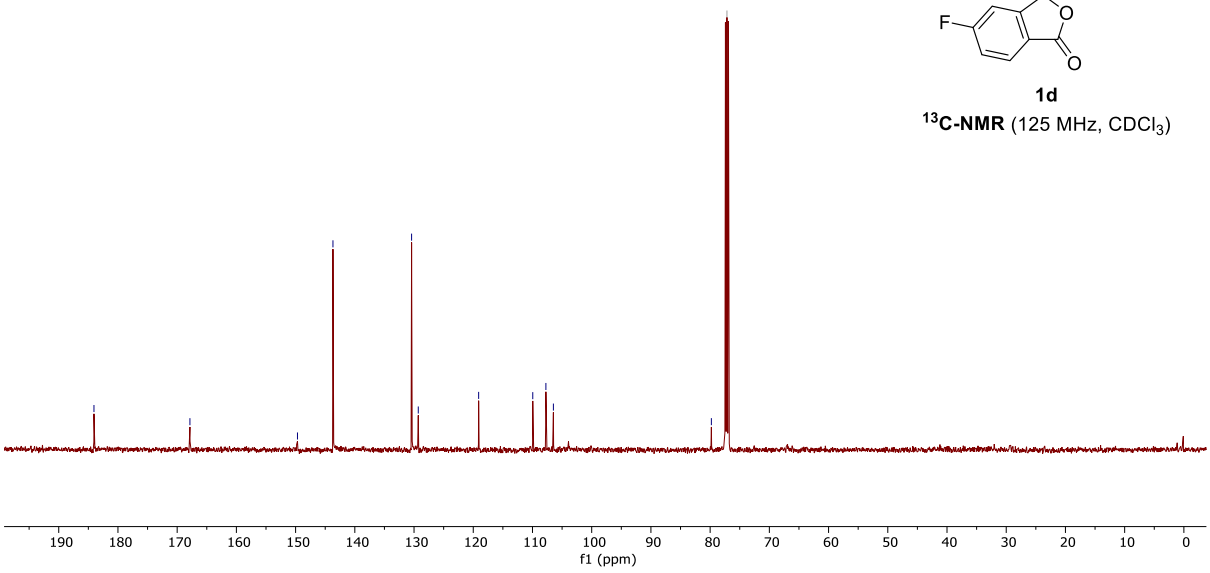
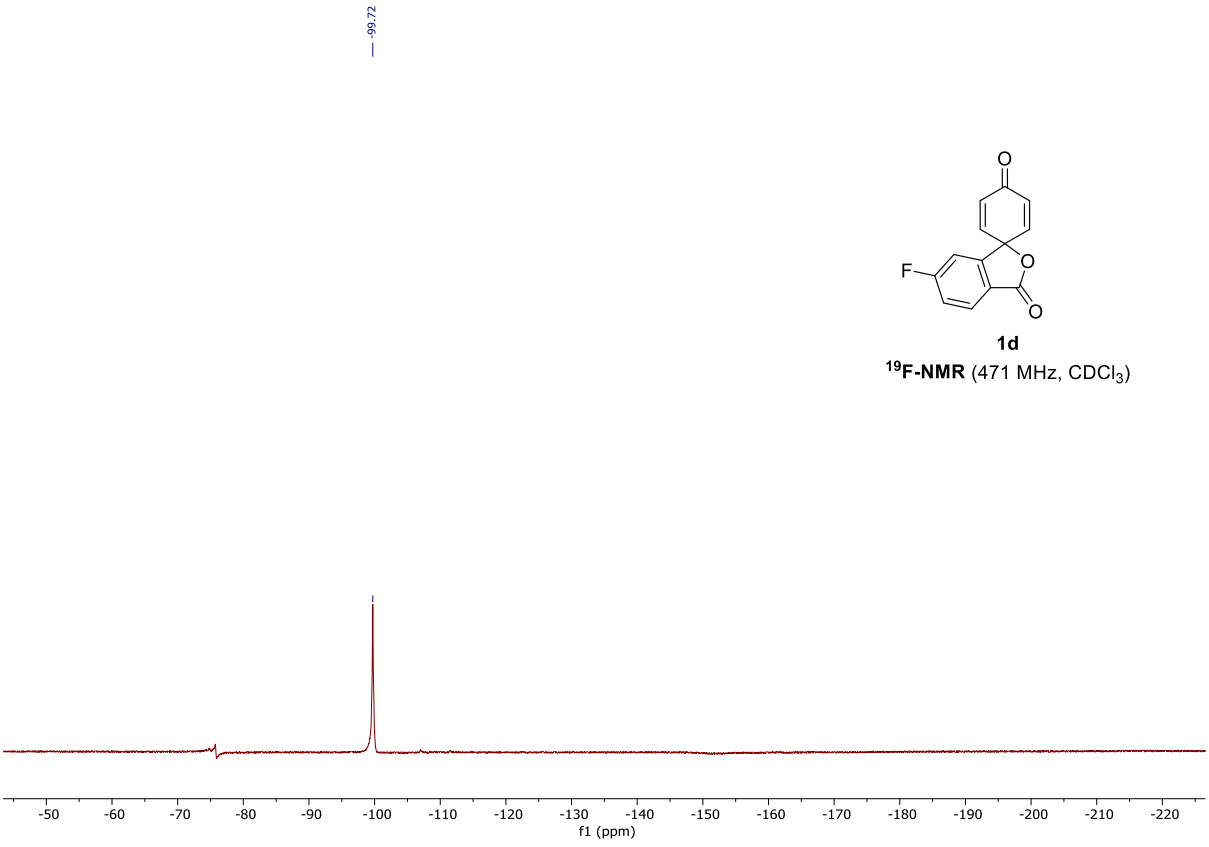




1d

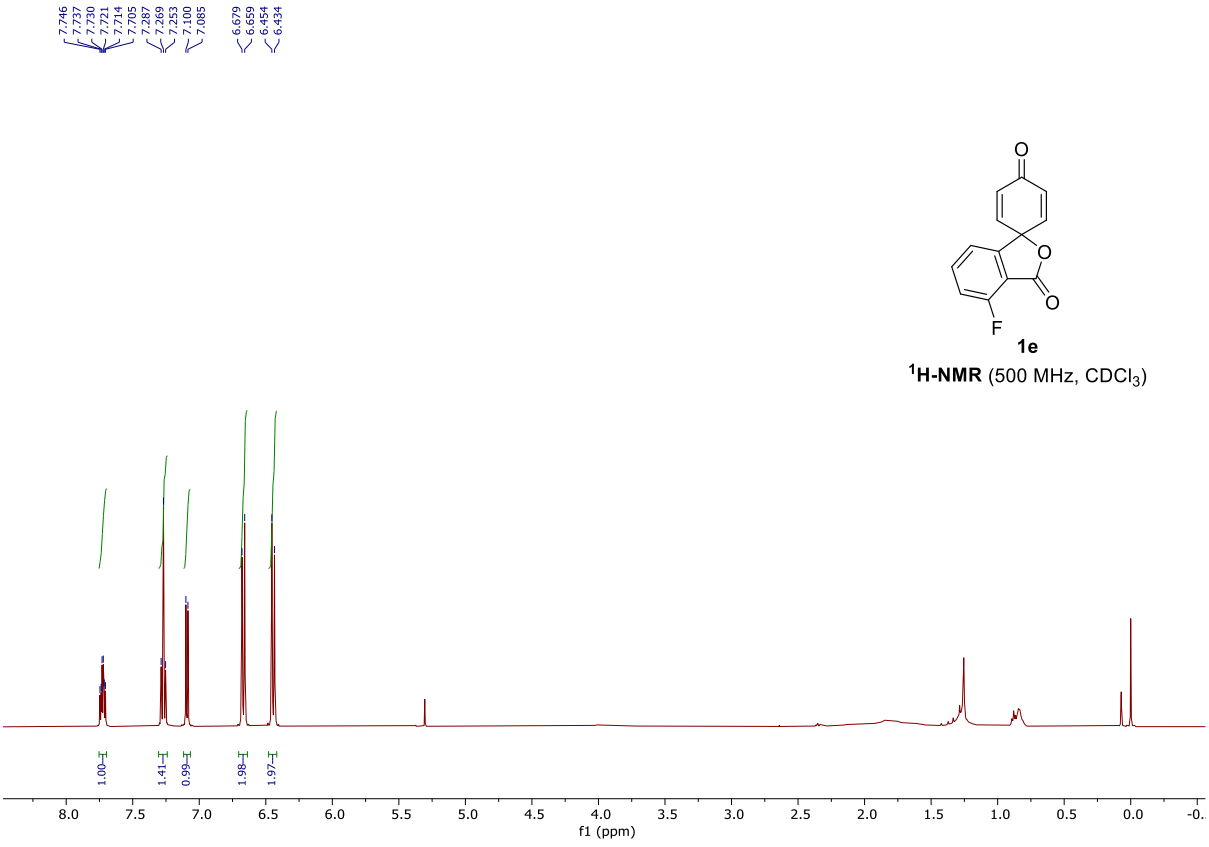
^{13}C-NMR (125 MHz, $CDCl_3$)





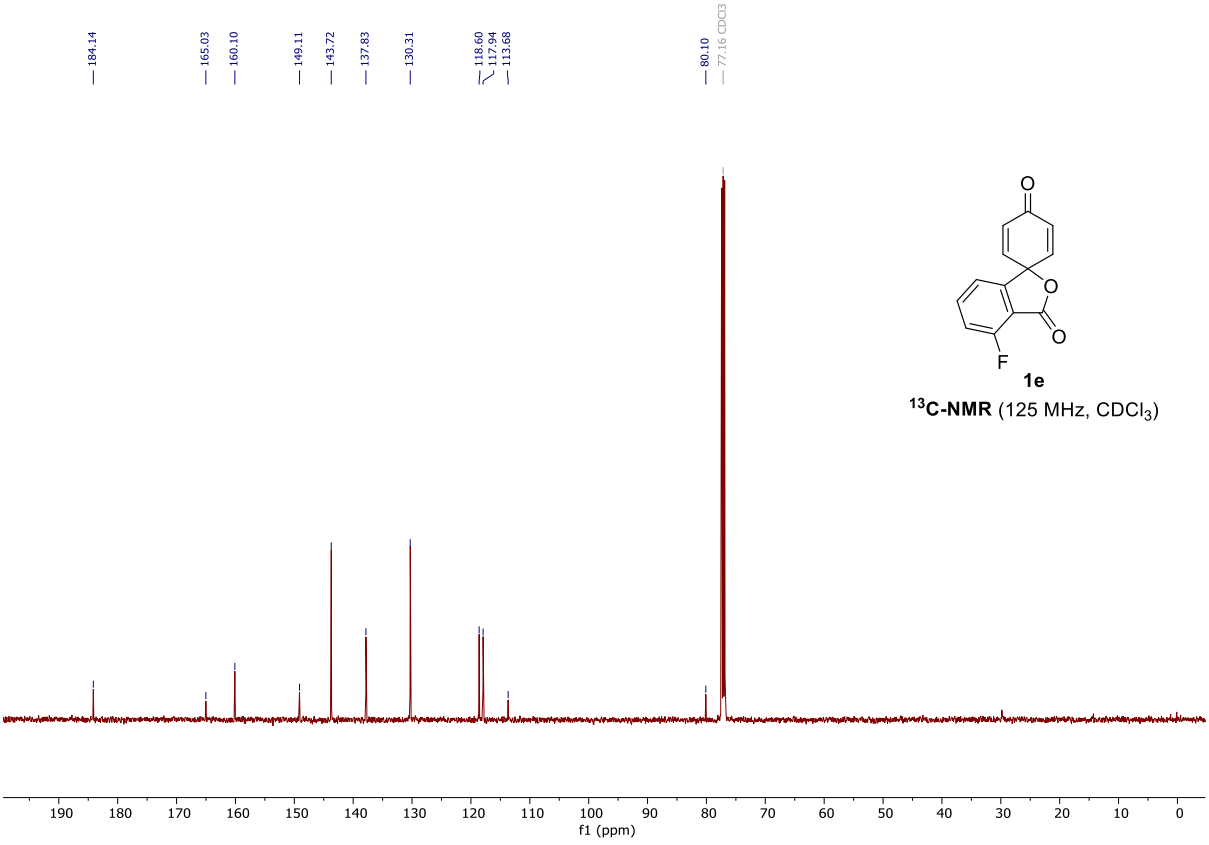
1d

^{19}F-NMR (471 MHz, $CDCl_3$)



1e

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



1e

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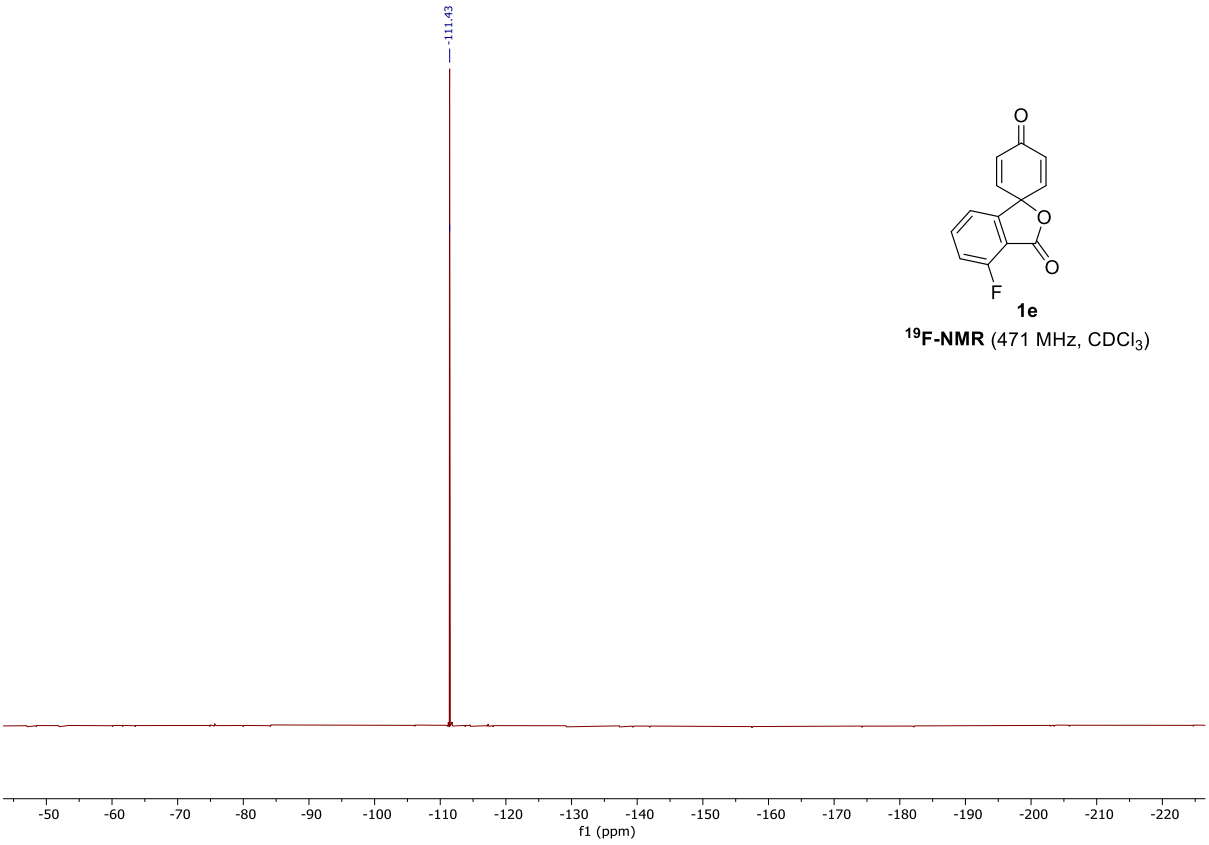

1e

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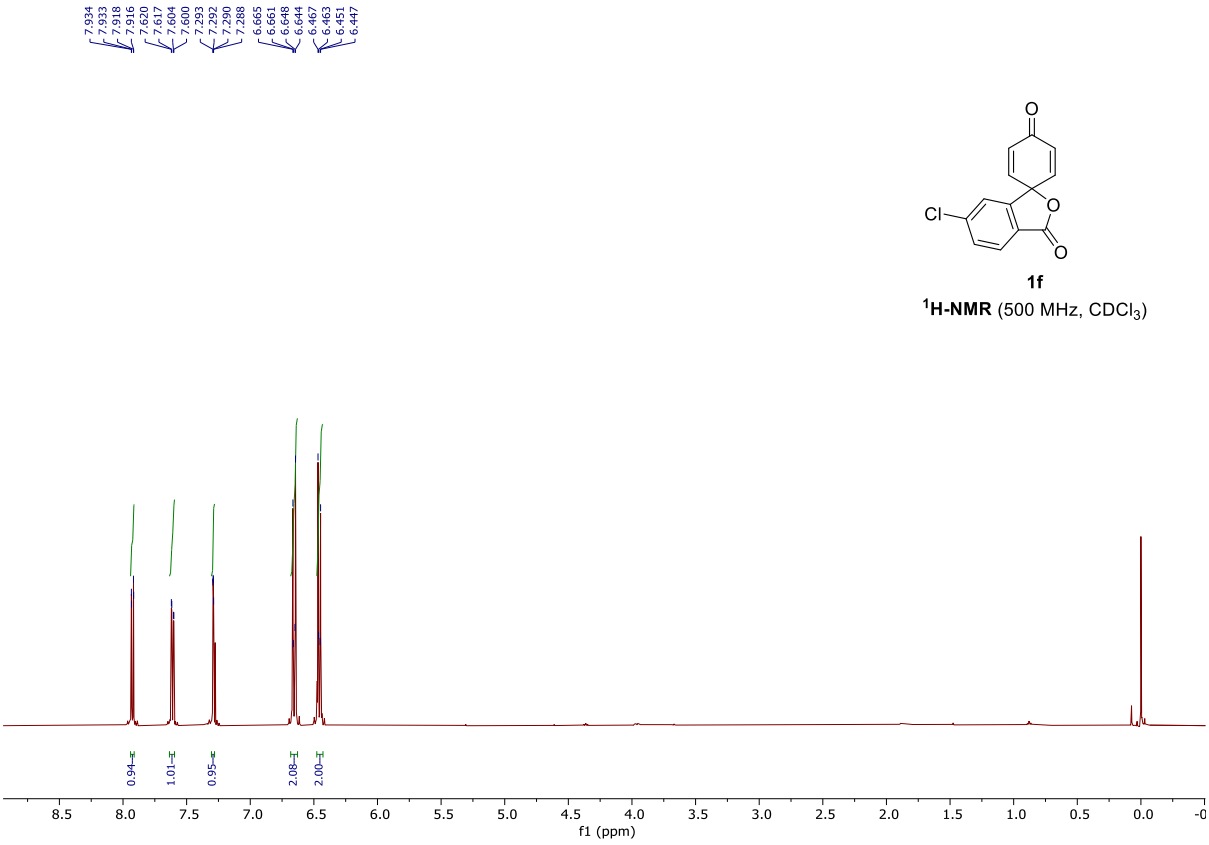

1f

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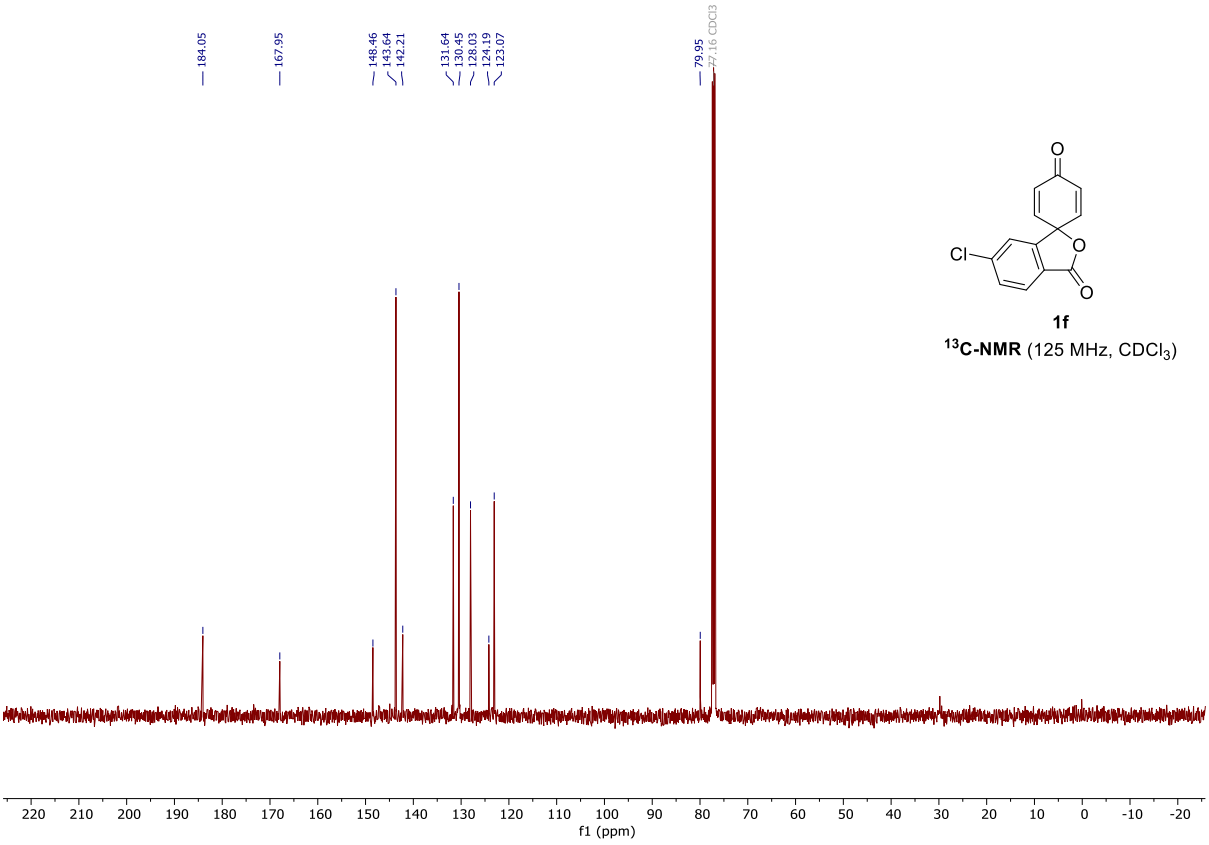

1f

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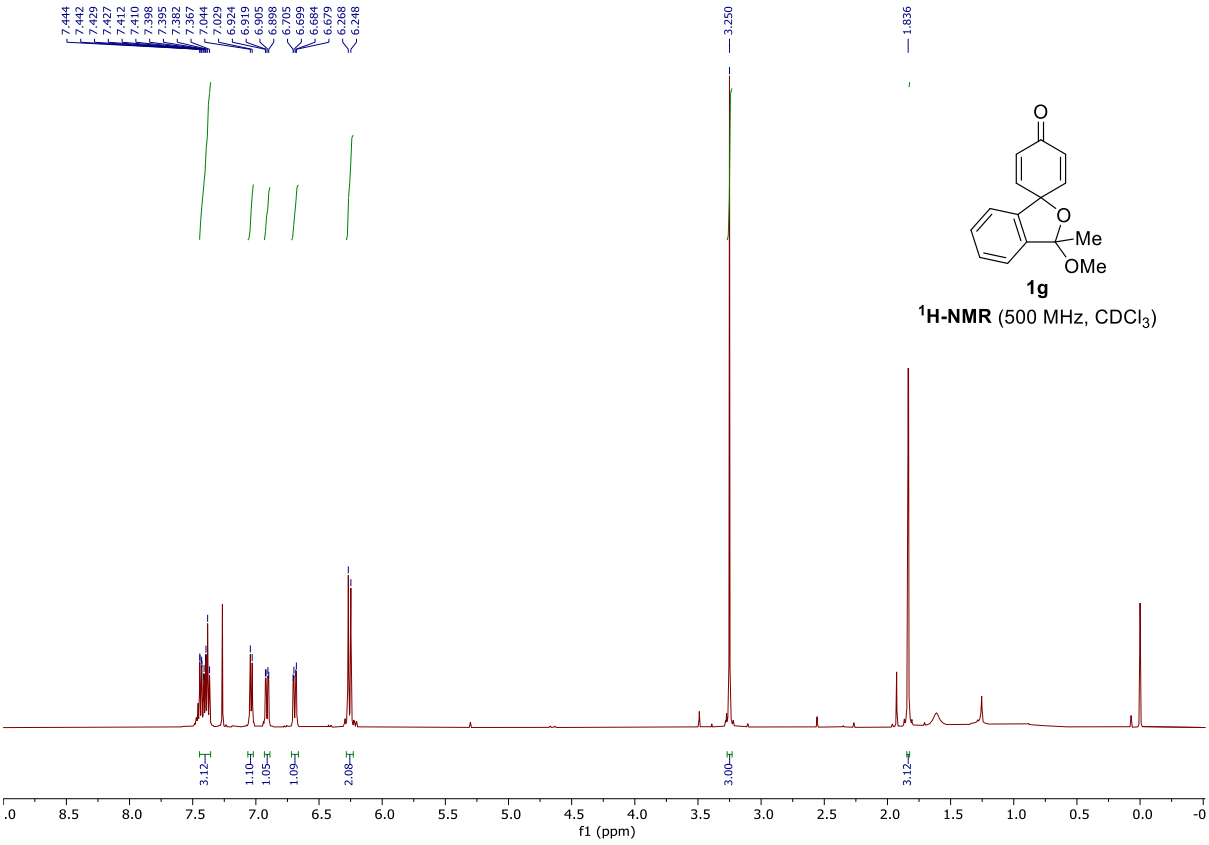
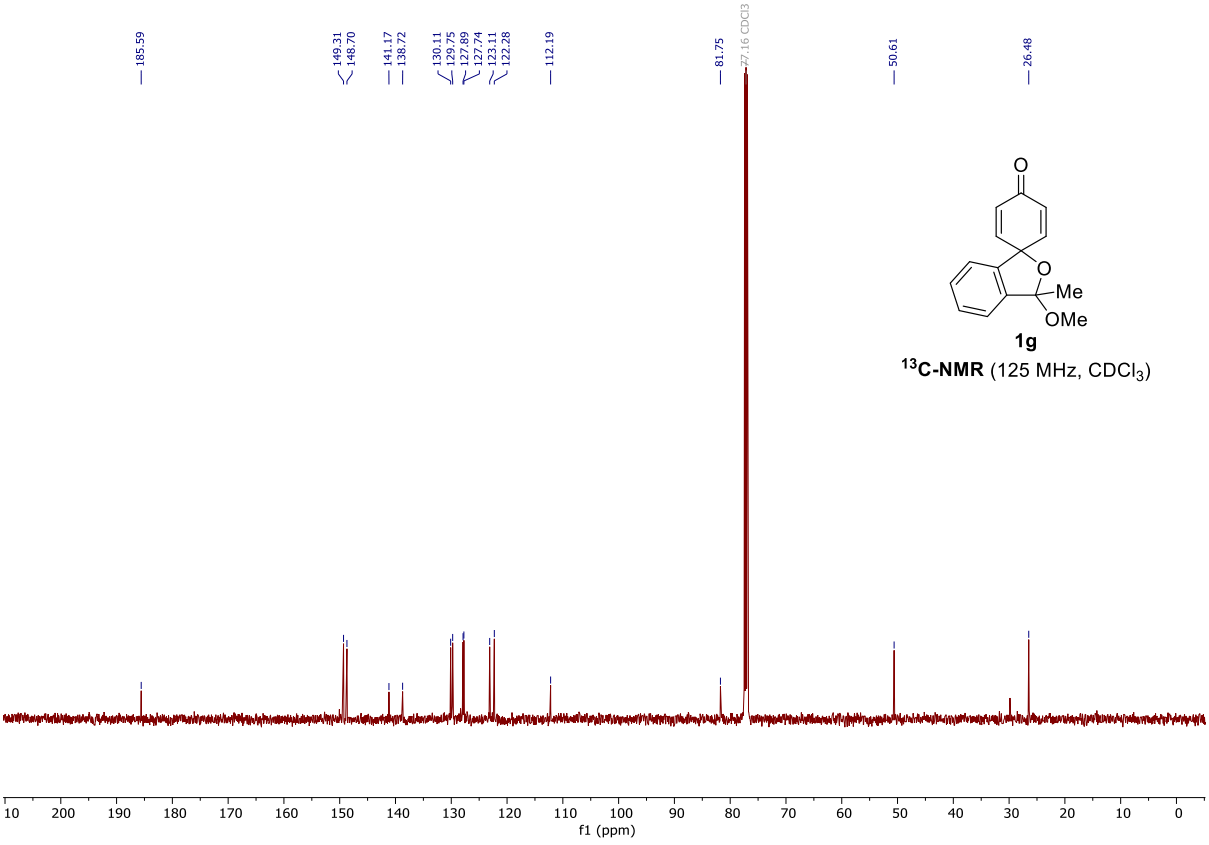


^{1}H-NMR (500 MHz, $CDCl_3$)



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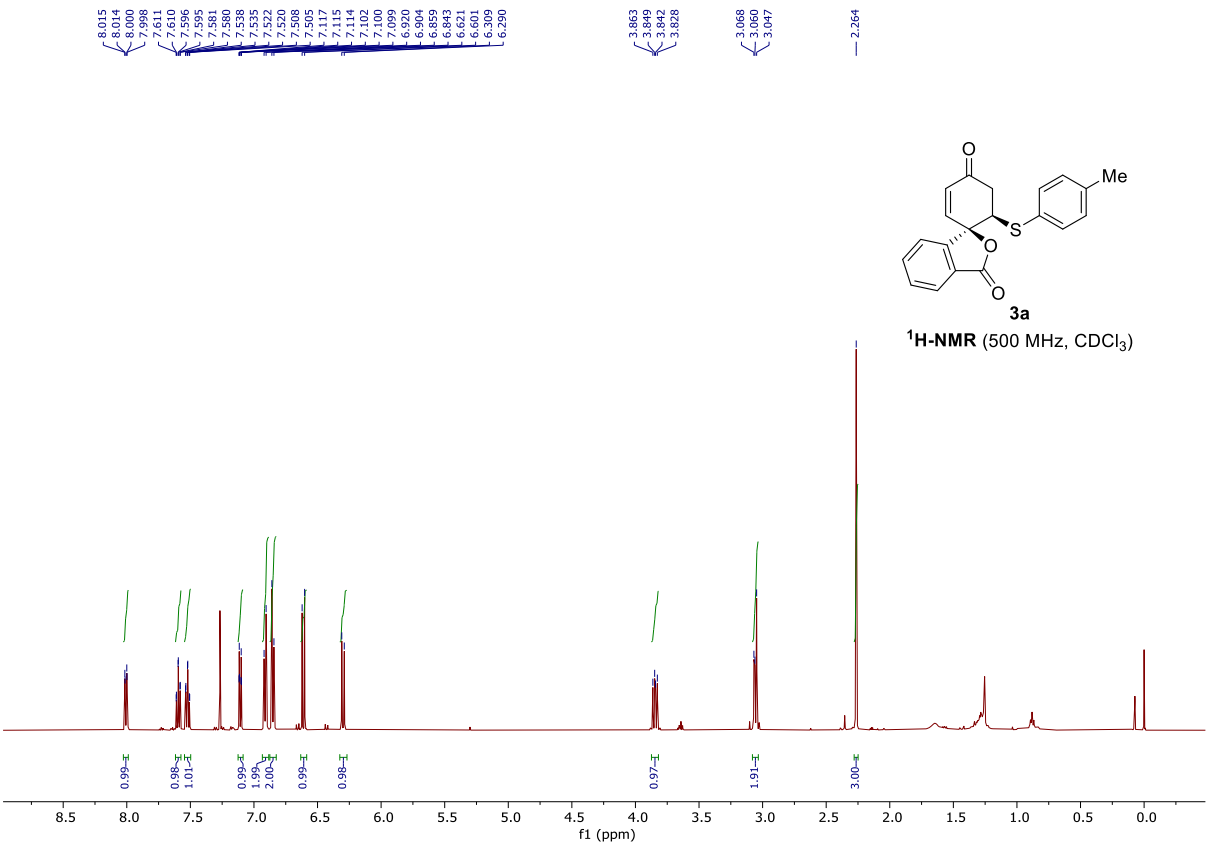
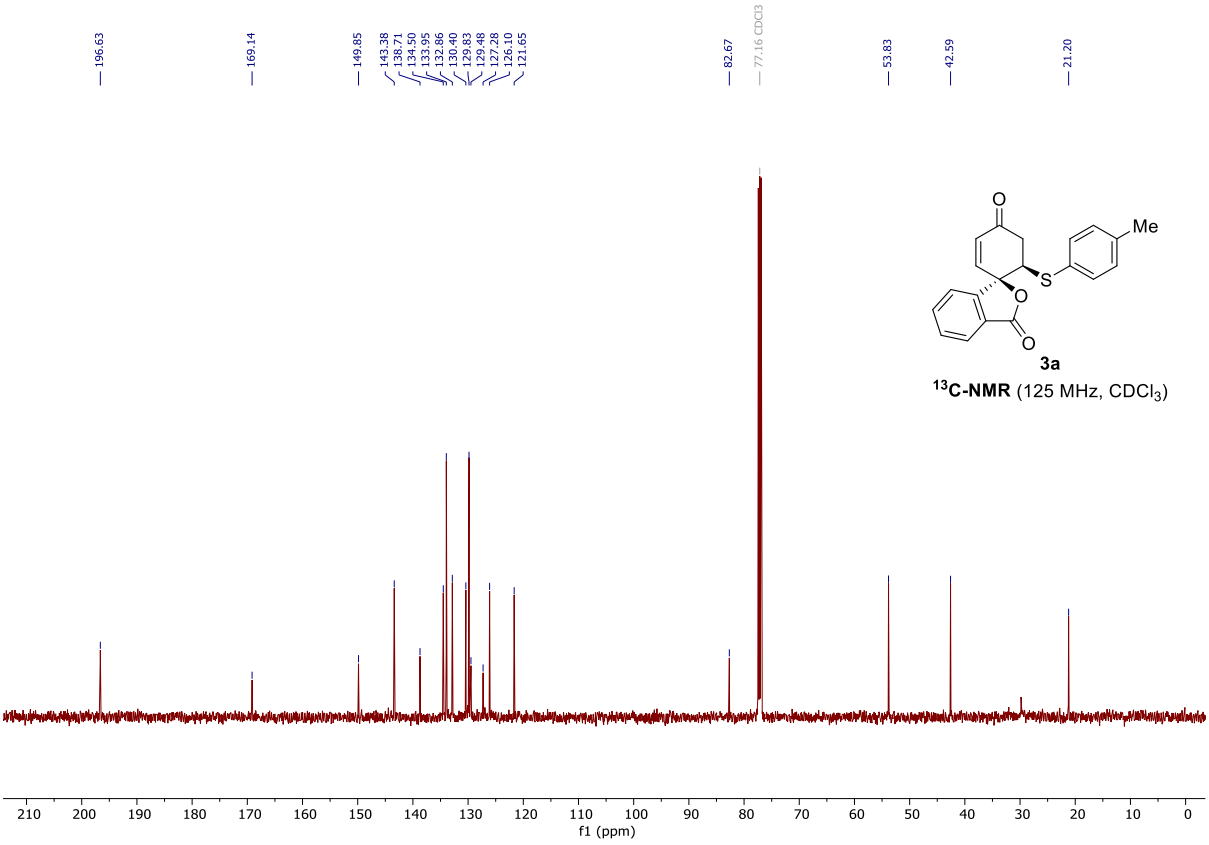
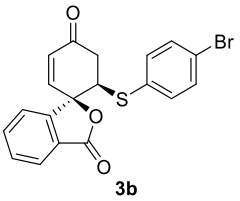


^{1}H-NMR (500 MHz, $CDCl_3$)

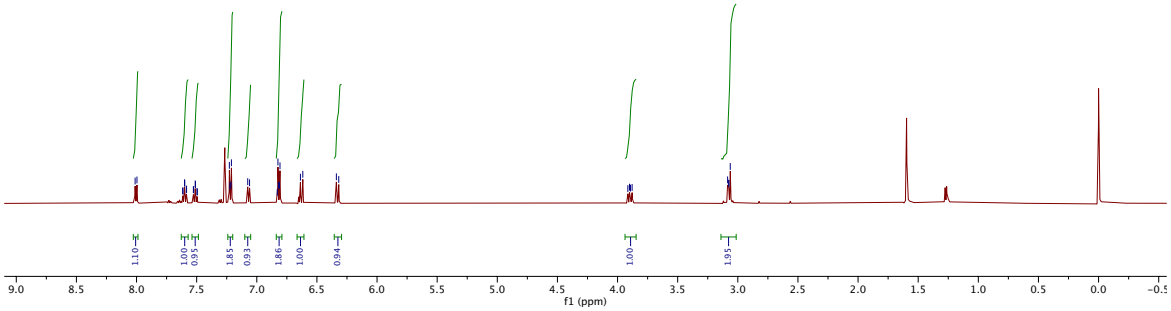


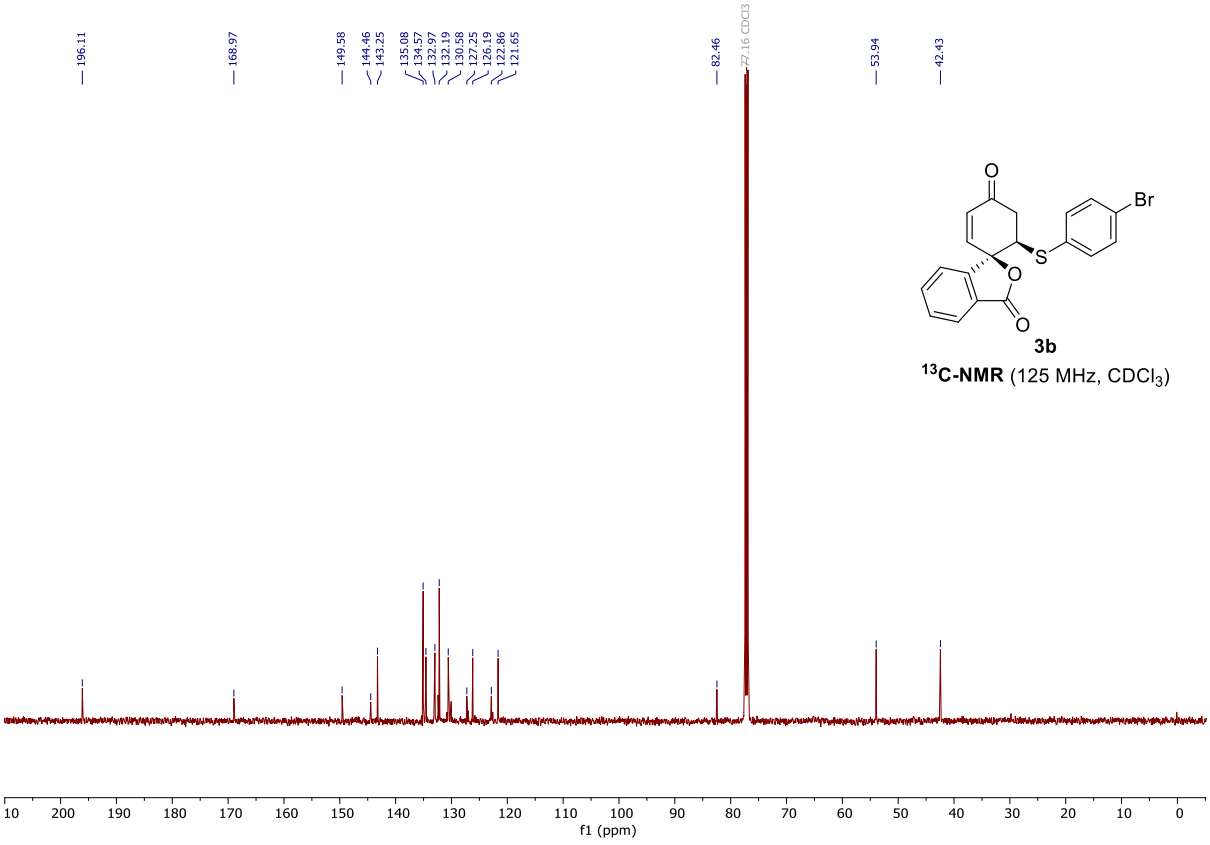
^{13}C-NMR (125 MHz, $CDCl_3$)



3b

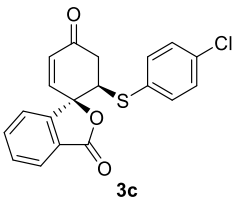
^{1}H-NMR (500 MHz, $CDCl_3$)





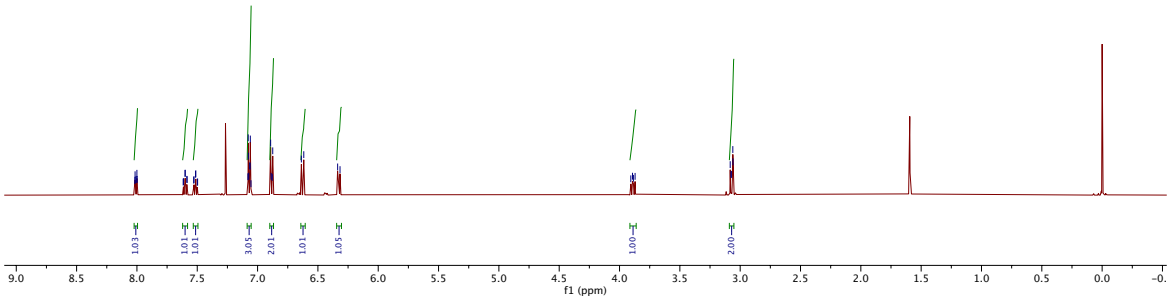
3b

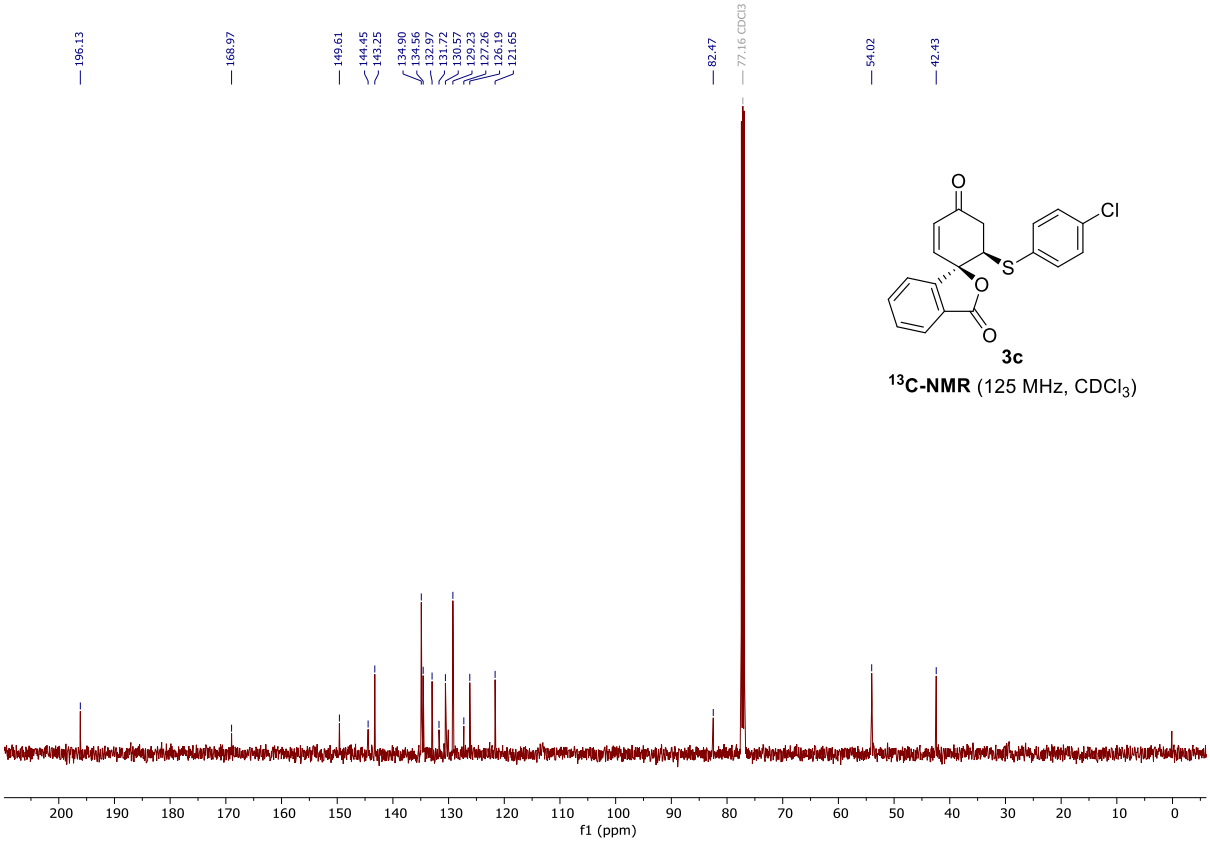
^{13}C-NMR (125 MHz, $CDCl_3$)



3c

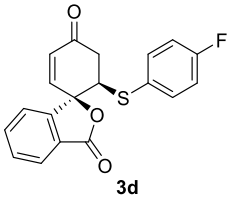
^{1}H-NMR (500 MHz, $CDCl_3$)





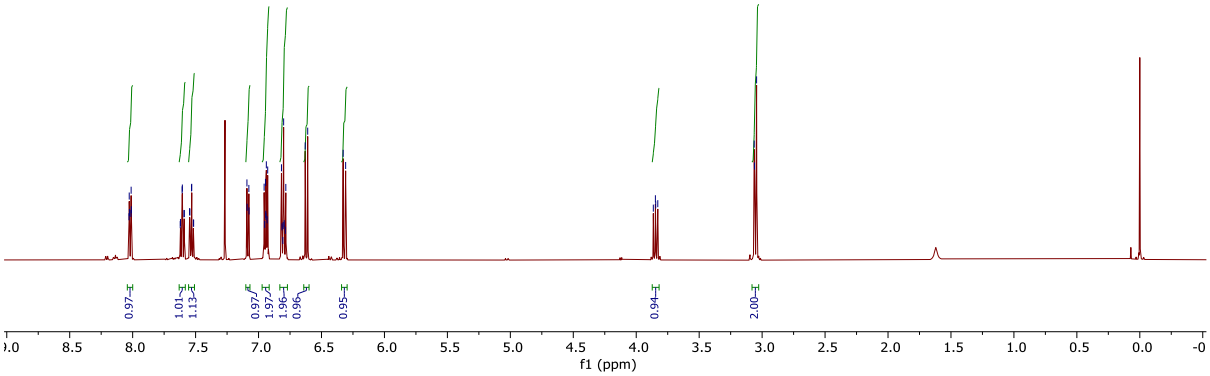
3c

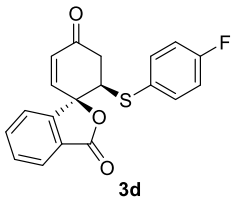
^{13}C-NMR (125 MHz, $CDCl_3$)



3d

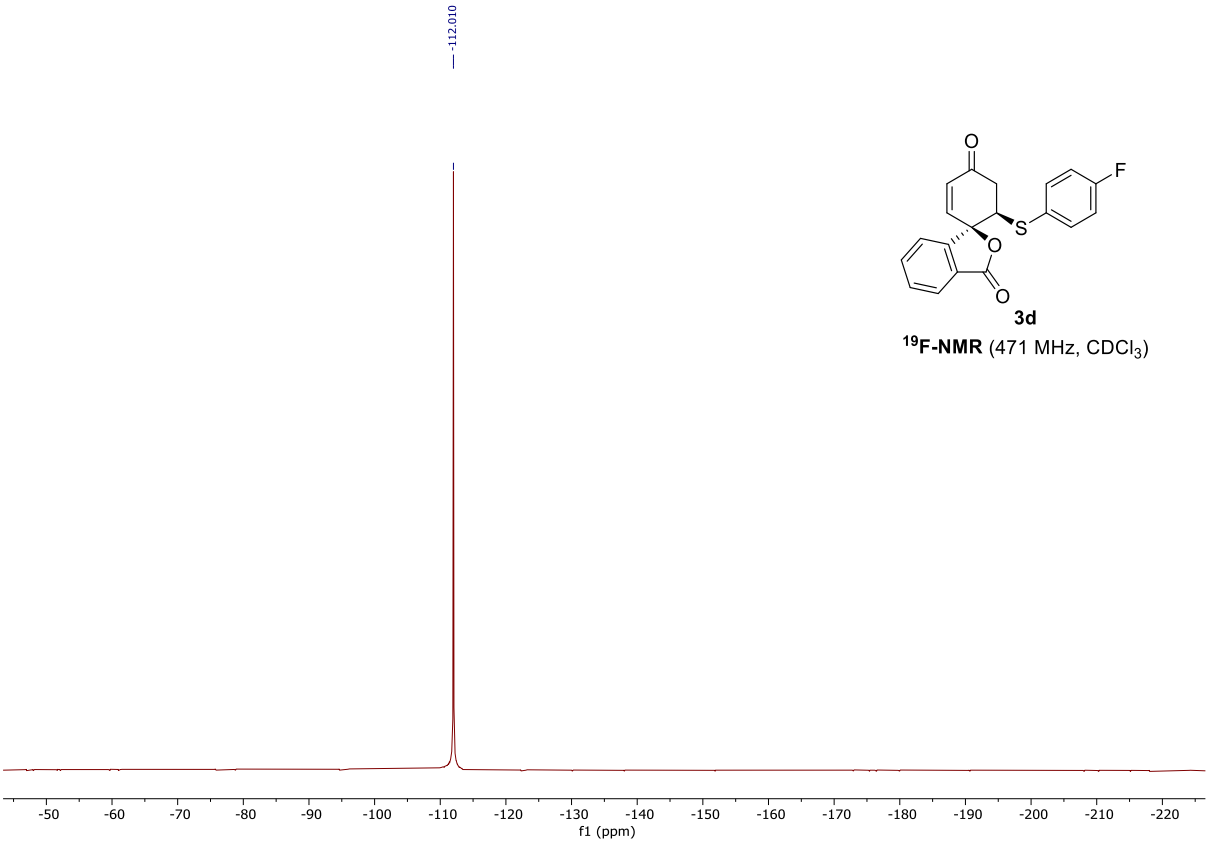
^{1}H-NMR (500 MHz, $CDCl_3$)





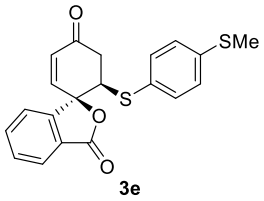
3d

^{13}C-NMR (125 MHz, $CDCl_3$)



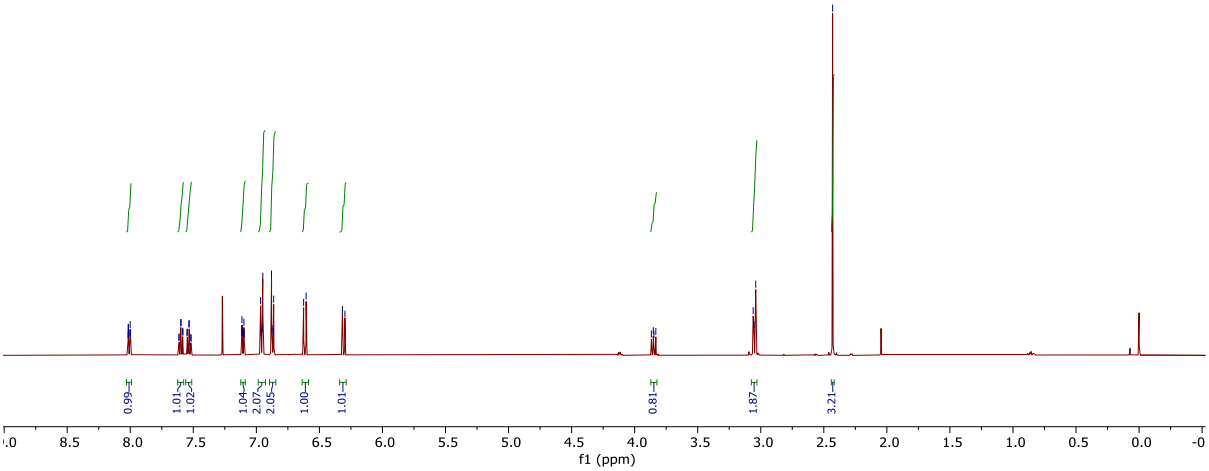
3d

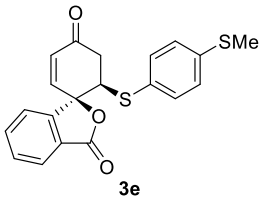
^{19}F-NMR (471 MHz, $CDCl_3$)



3e

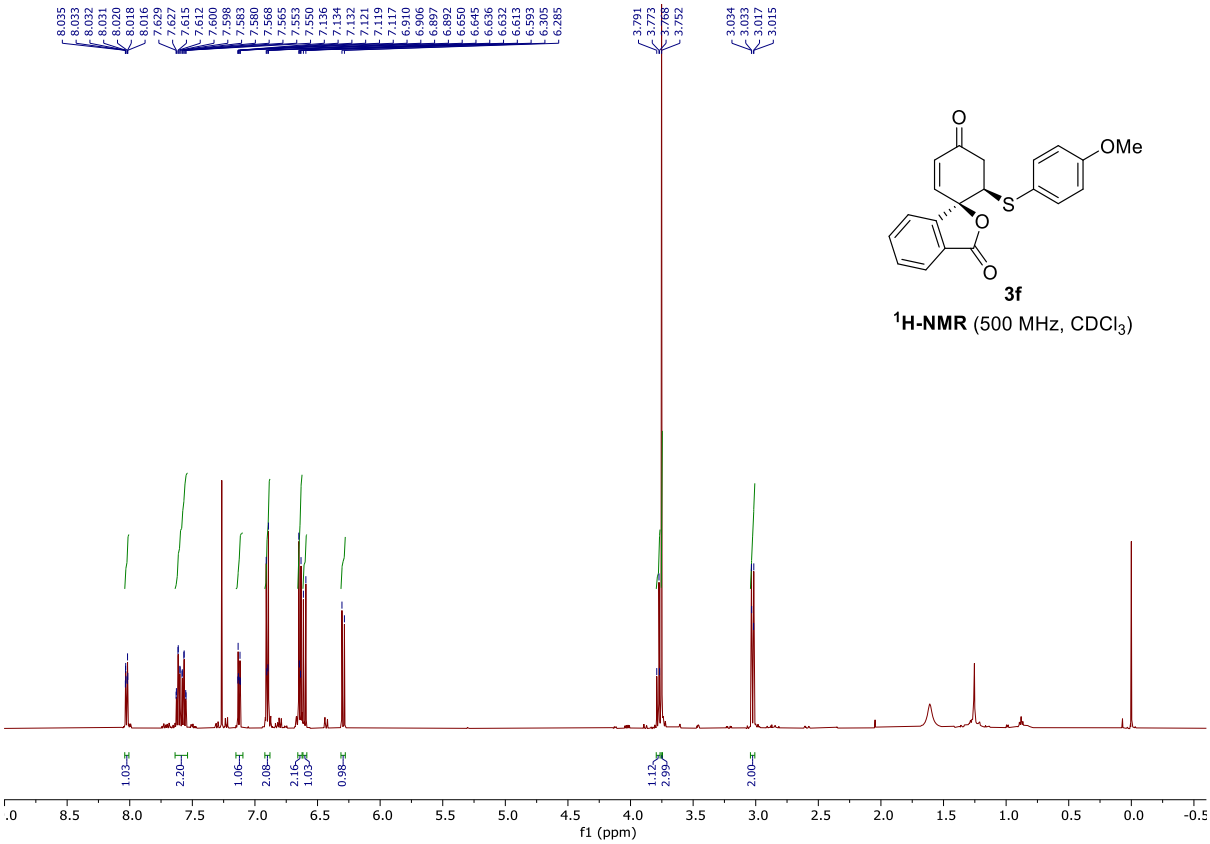
^{1}H-NMR (500 MHz, $CDCl_3$)





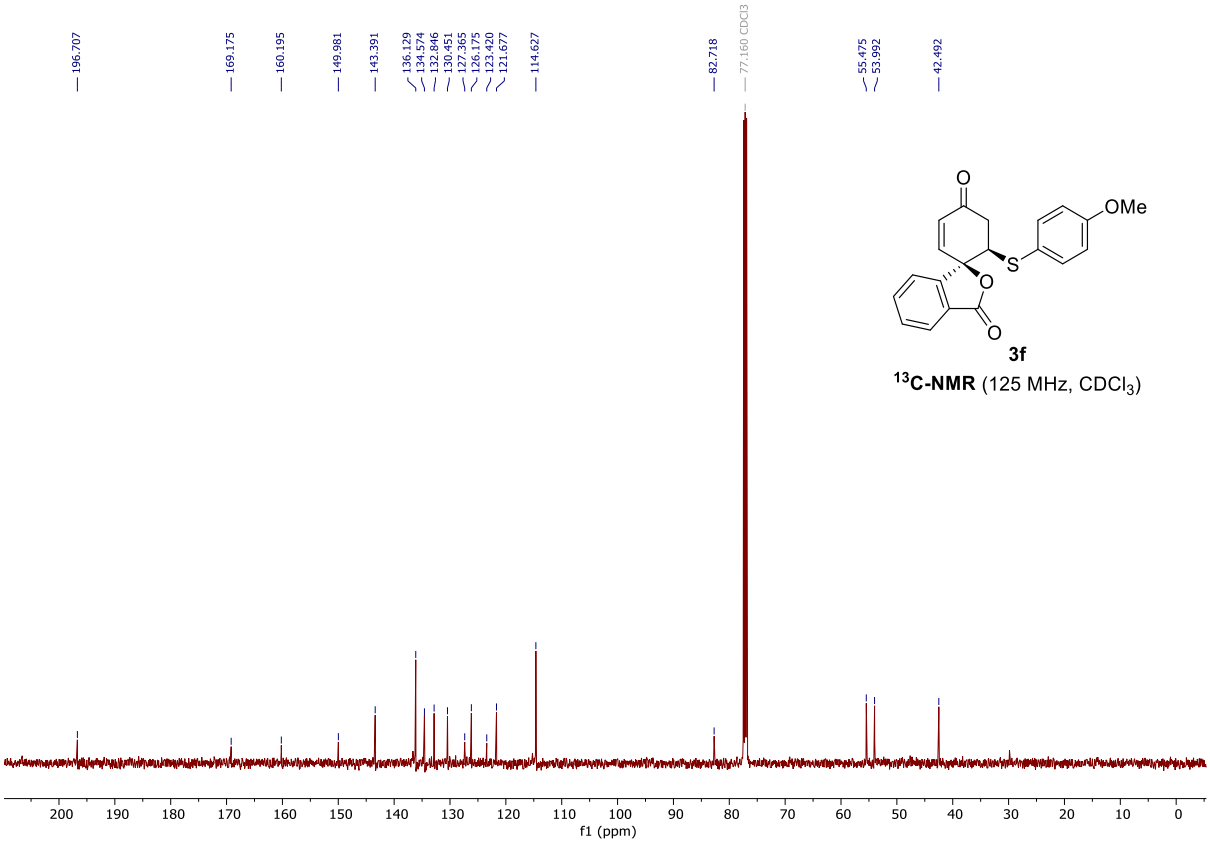
3e

^{13}C-NMR (125 MHz, $CDCl_3$)



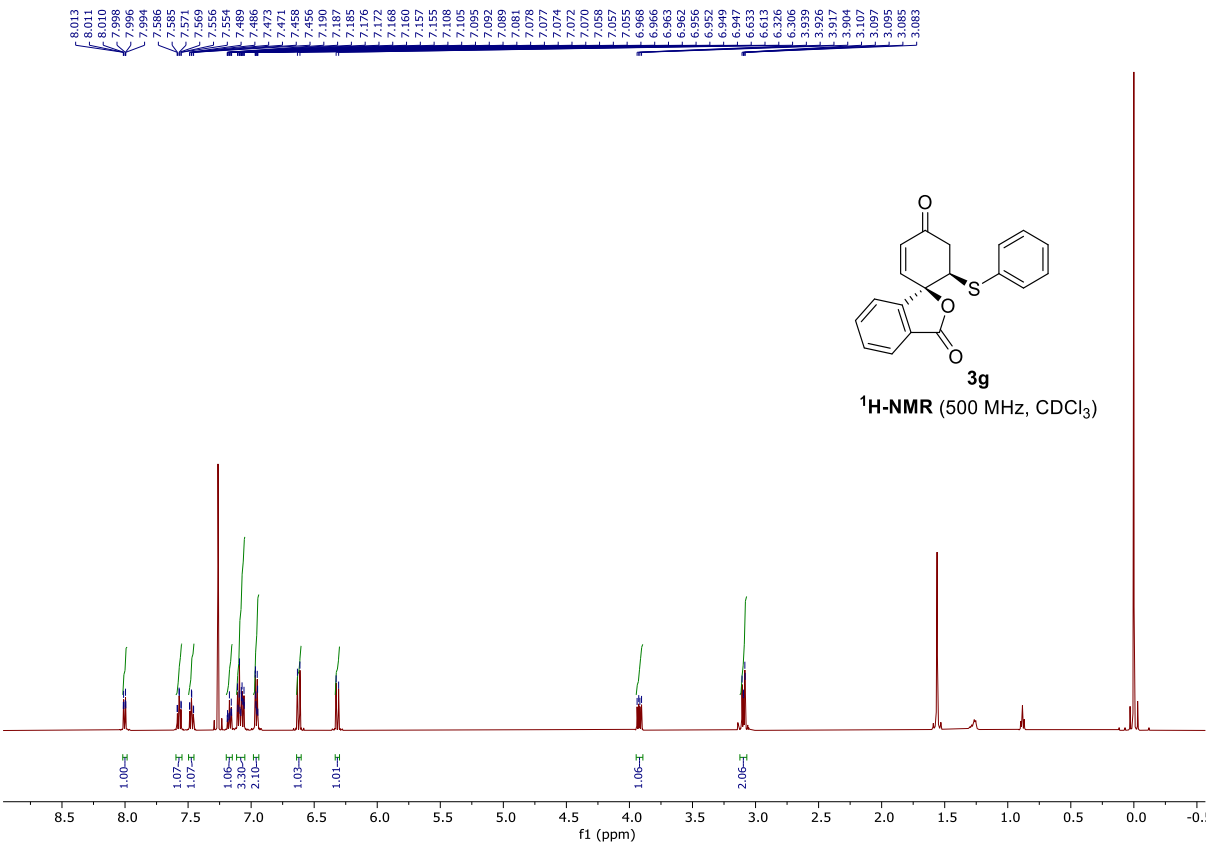
3f

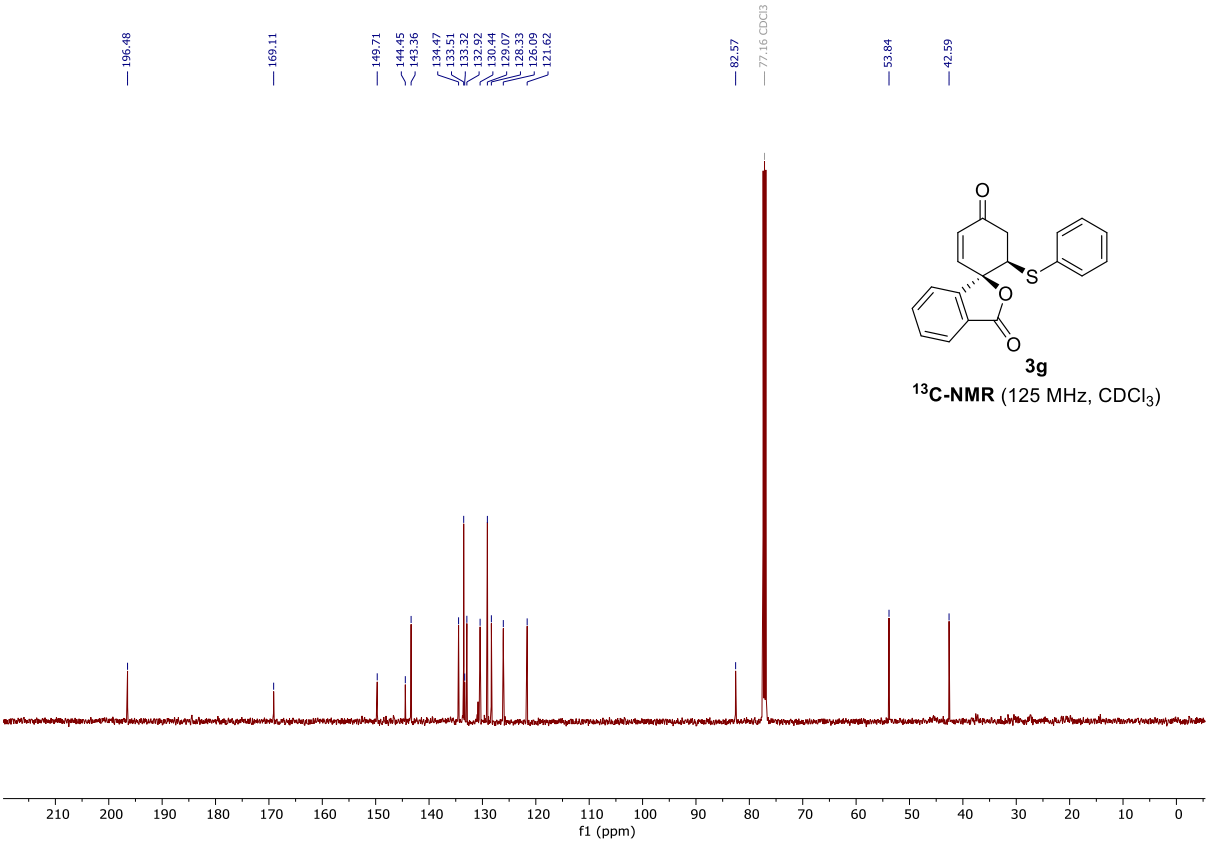
^{1}H-NMR (500 MHz, $CDCl_3$)

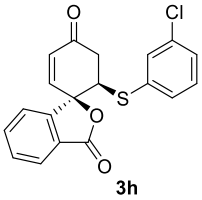


3f

^{13}C-NMR (125 MHz, $CDCl_3$)

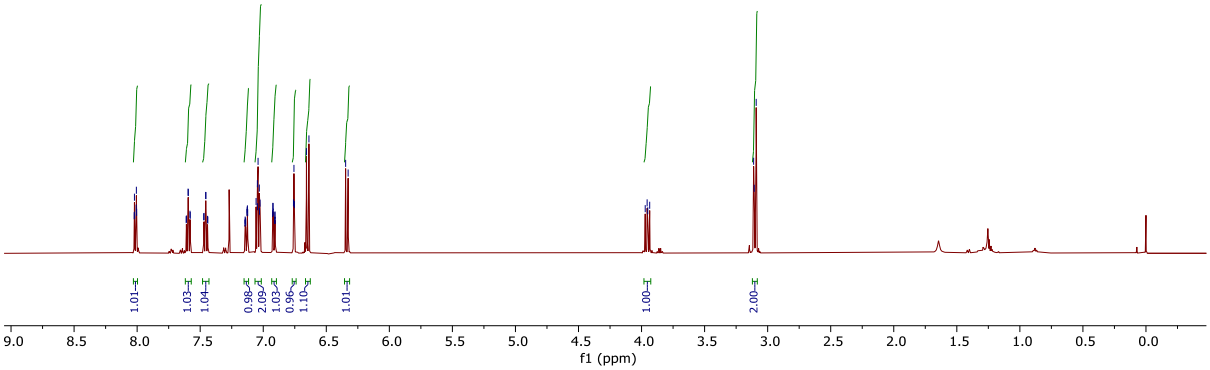

8.013
8.011
8.010
7.998
7.996
7.994
7.586
7.585
7.571
7.569
7.556
7.554
7.489
7.486
7.473
7.471
7.458
7.456
7.190
7.187
7.185
7.176
7.172
7.168
7.160
7.157
7.155
7.108
7.105
7.095
7.092
7.089
7.081
7.078
7.077
7.074
7.072
7.070
7.058
7.057
7.055
6.968
6.966
6.963
6.962
6.956
6.952
6.949
6.947
6.633
6.613
6.326
6.306
3.939
3.926
3.917
3.904
3.107
3.097
3.095
3.085
3.083
O
S
O
O
3g
1H-NMR (500 MHz, CDCl3)
1.00
1.07
1.07
1.06
3.30
2.10
1.03
1.01
1.06
2.06
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

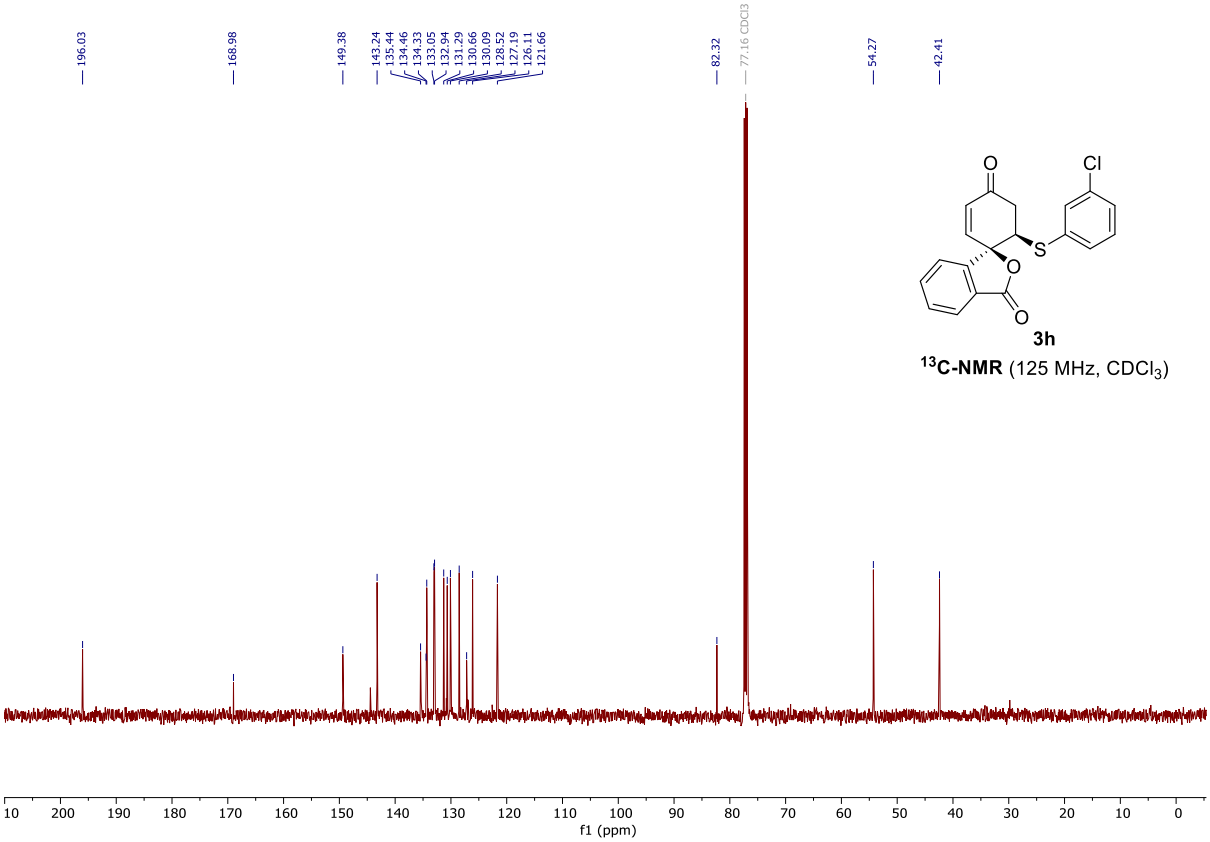

196.48
169.11
149.71
144.45
143.36
134.47
133.51
133.32
132.92
130.44
129.07
128.33
126.09
121.62
82.57
77.16 CDCl3
53.84
42.59
O
S
O
O
3g
13C-NMR (125 MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



3h

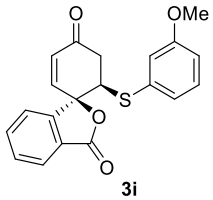
^{1}H-NMR (500 MHz, $CDCl_3$)





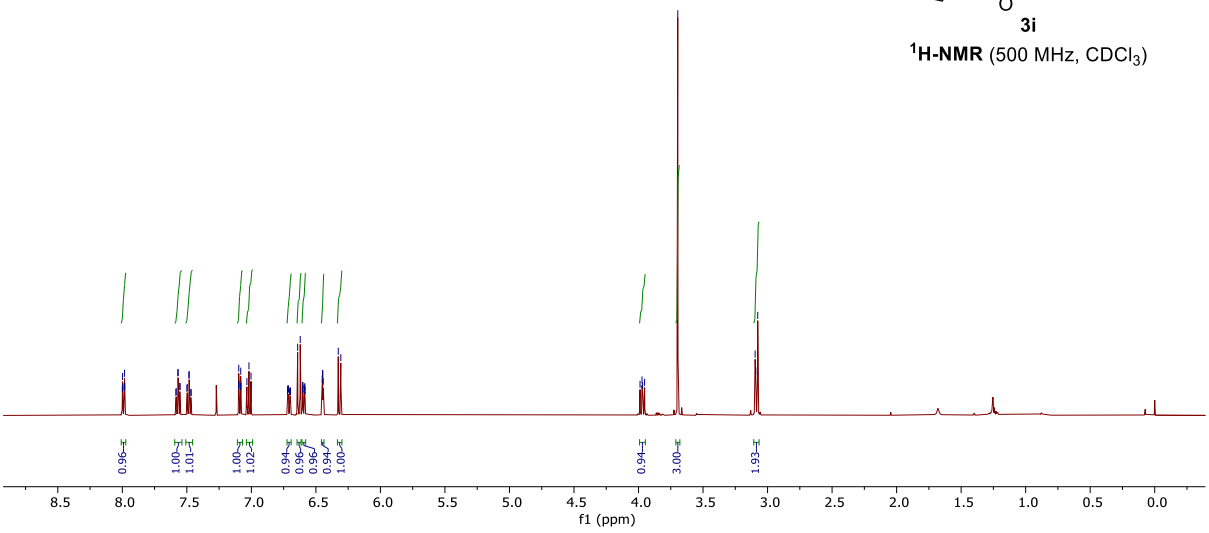
3h

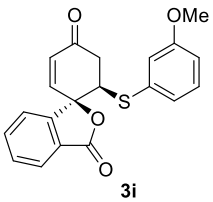
^{13}C-NMR (125 MHz, $CDCl_3$)



3i

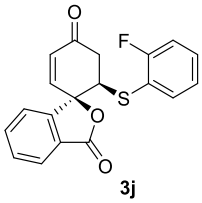
^{1}H-NMR (500 MHz, $CDCl_3$)





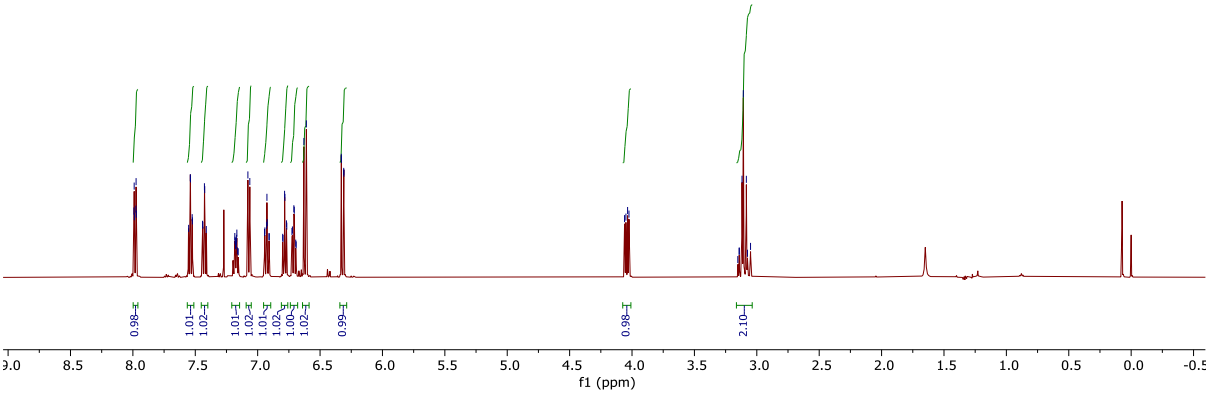
3i

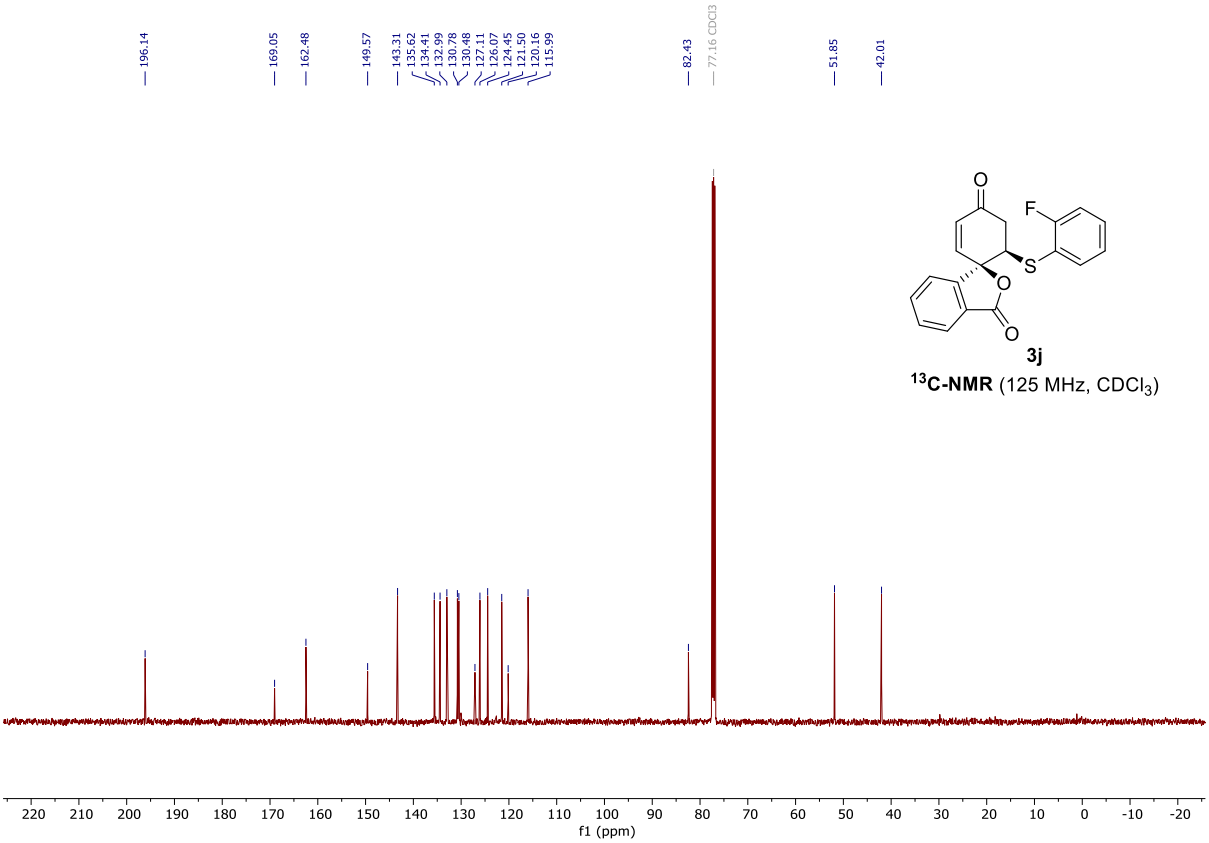
^{13}C-NMR (125 MHz, $CDCl_3$)



3j

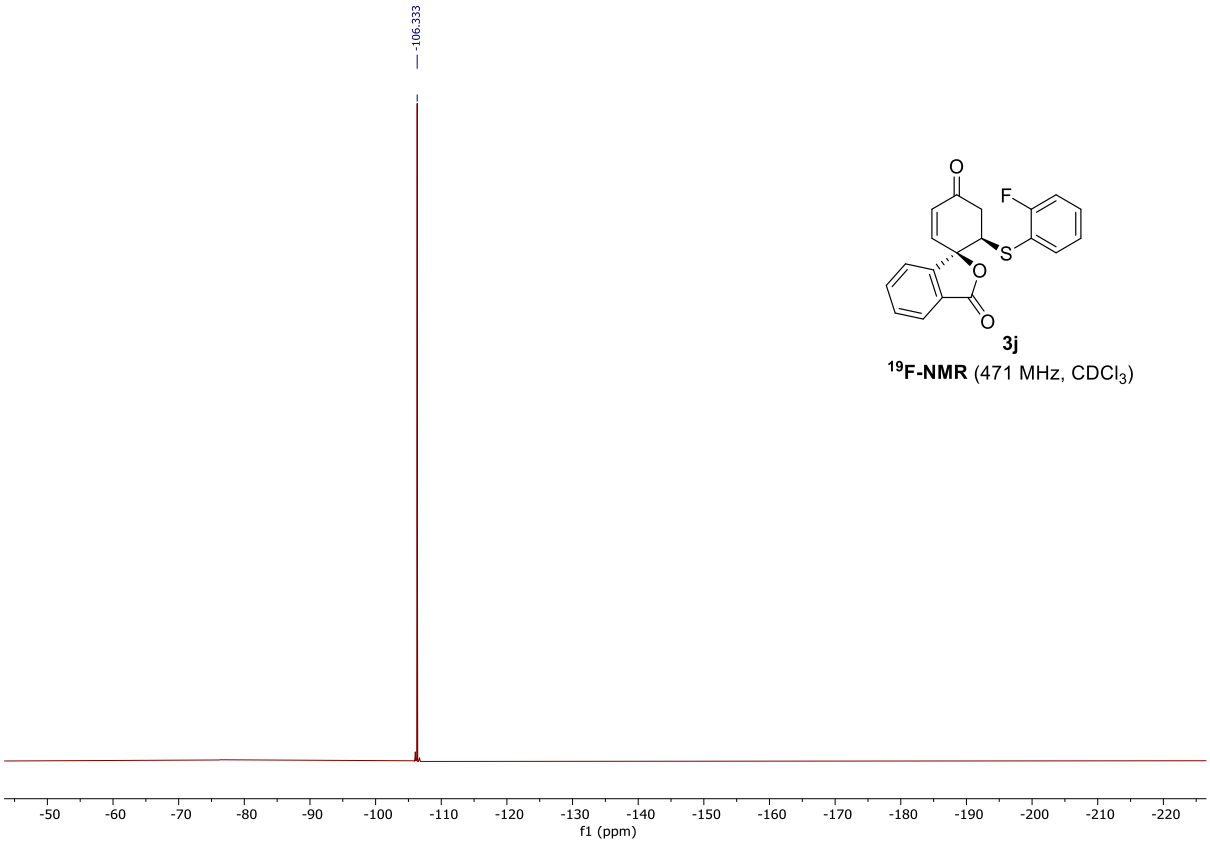
^{1}H-NMR (500 MHz, $CDCl_3$)





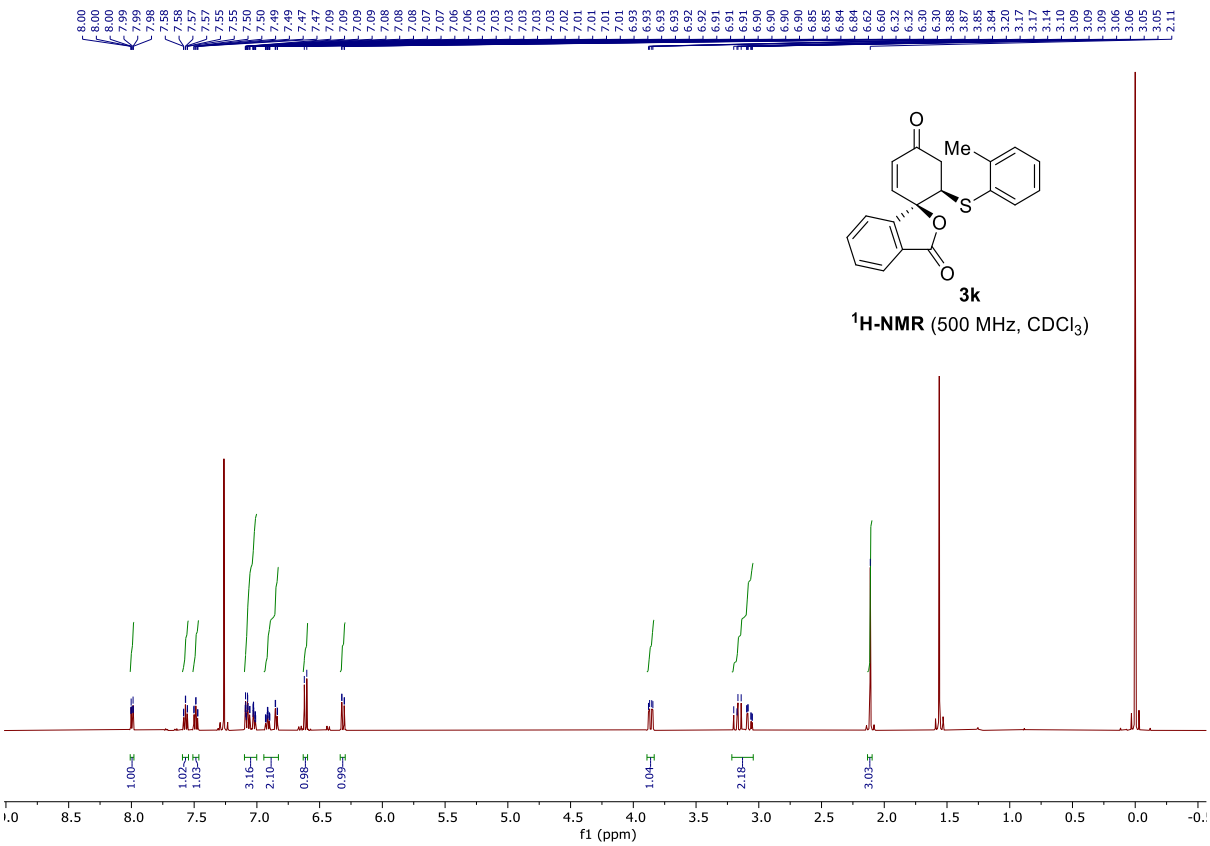
3j

^{13}C-NMR (125 MHz, $CDCl_3$)

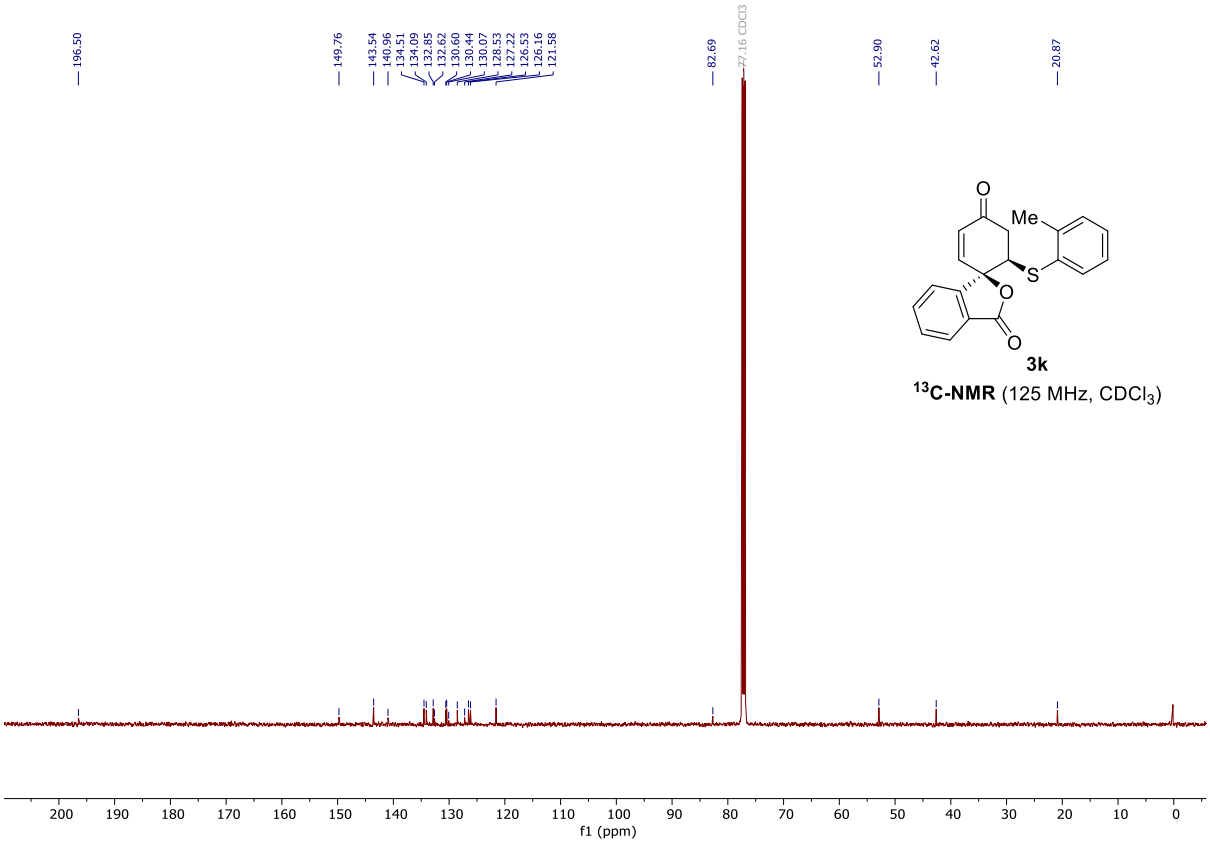


3j

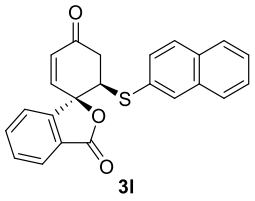
^{19}F-NMR (471 MHz, $CDCl_3$)



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

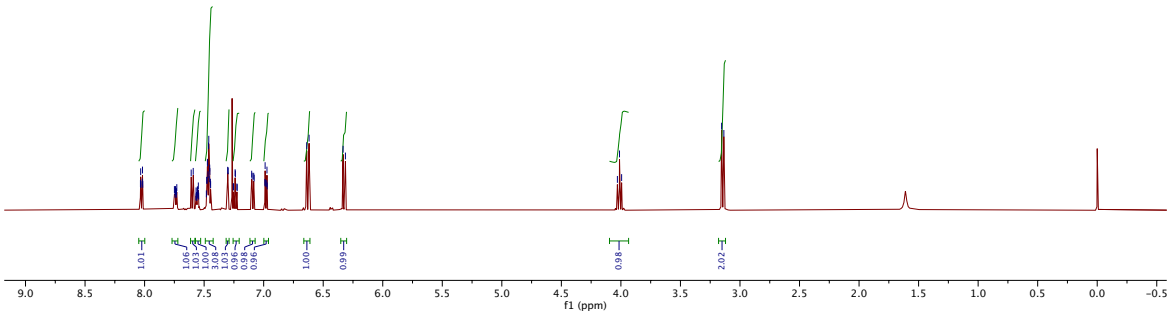


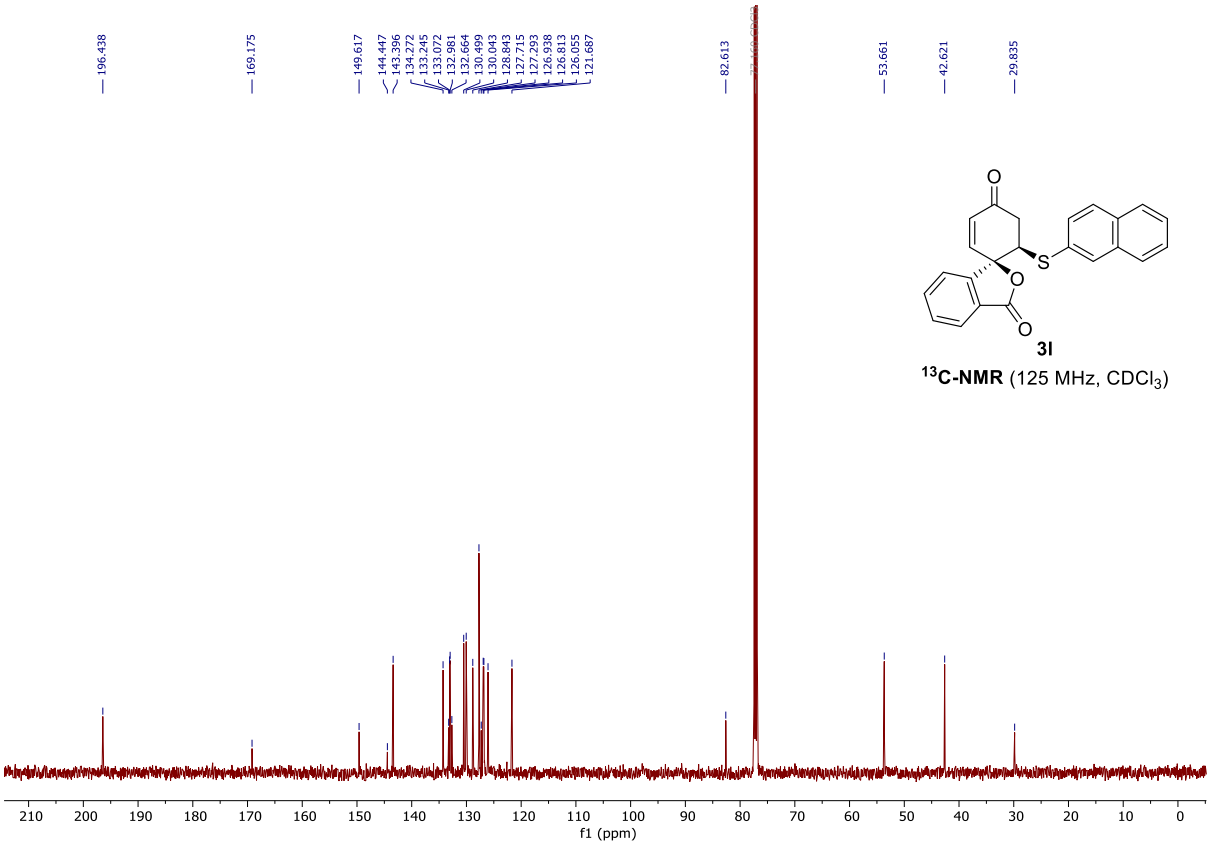
^{13}C-NMR (125 MHz, $CDCl_3$)



3l

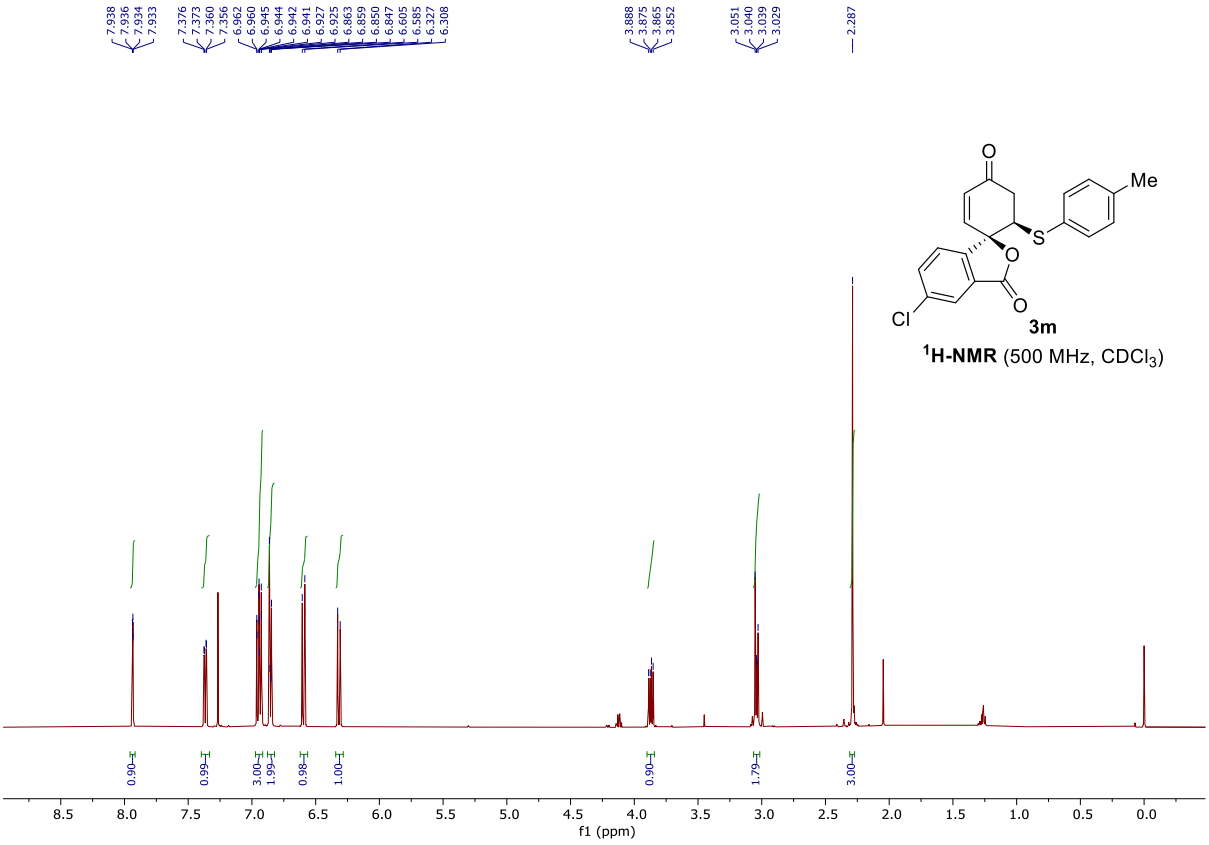
^{1}H-NMR (500 MHz, $CDCl_3$)



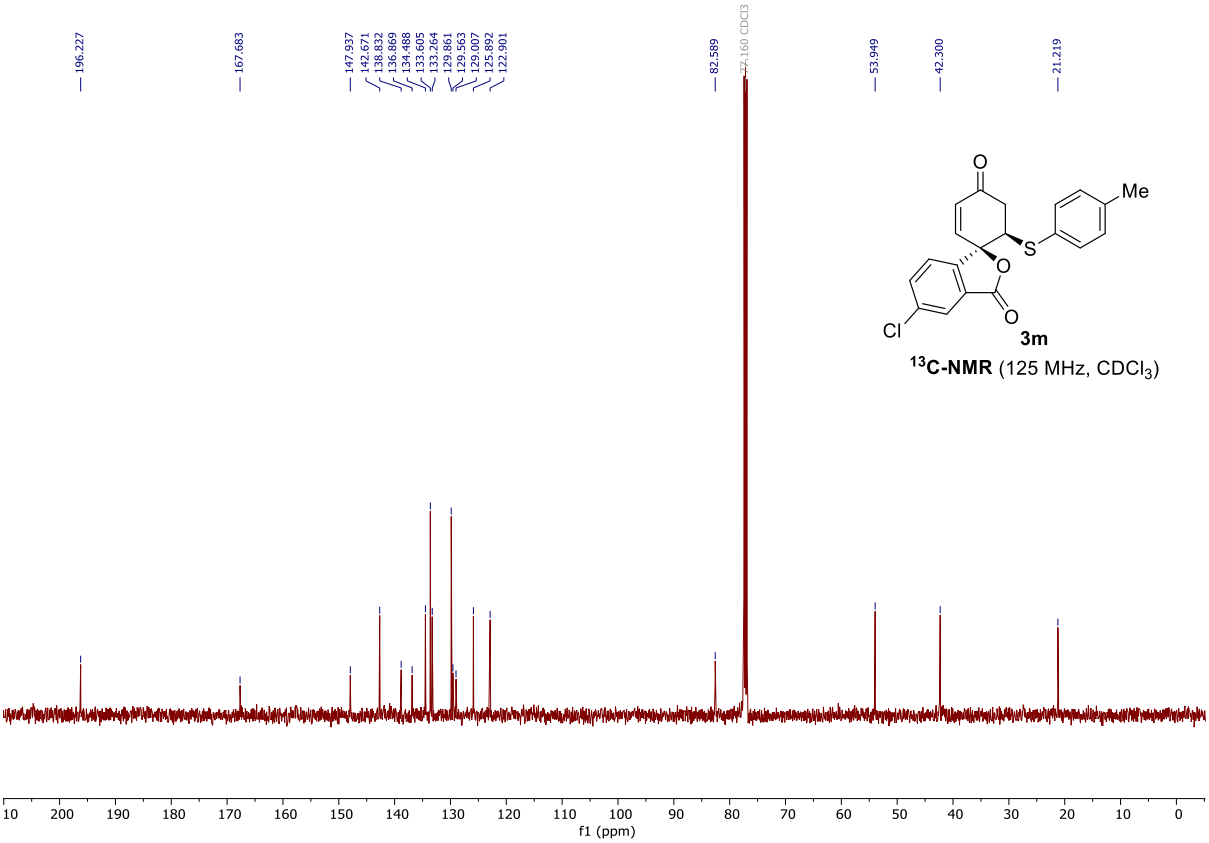


3l

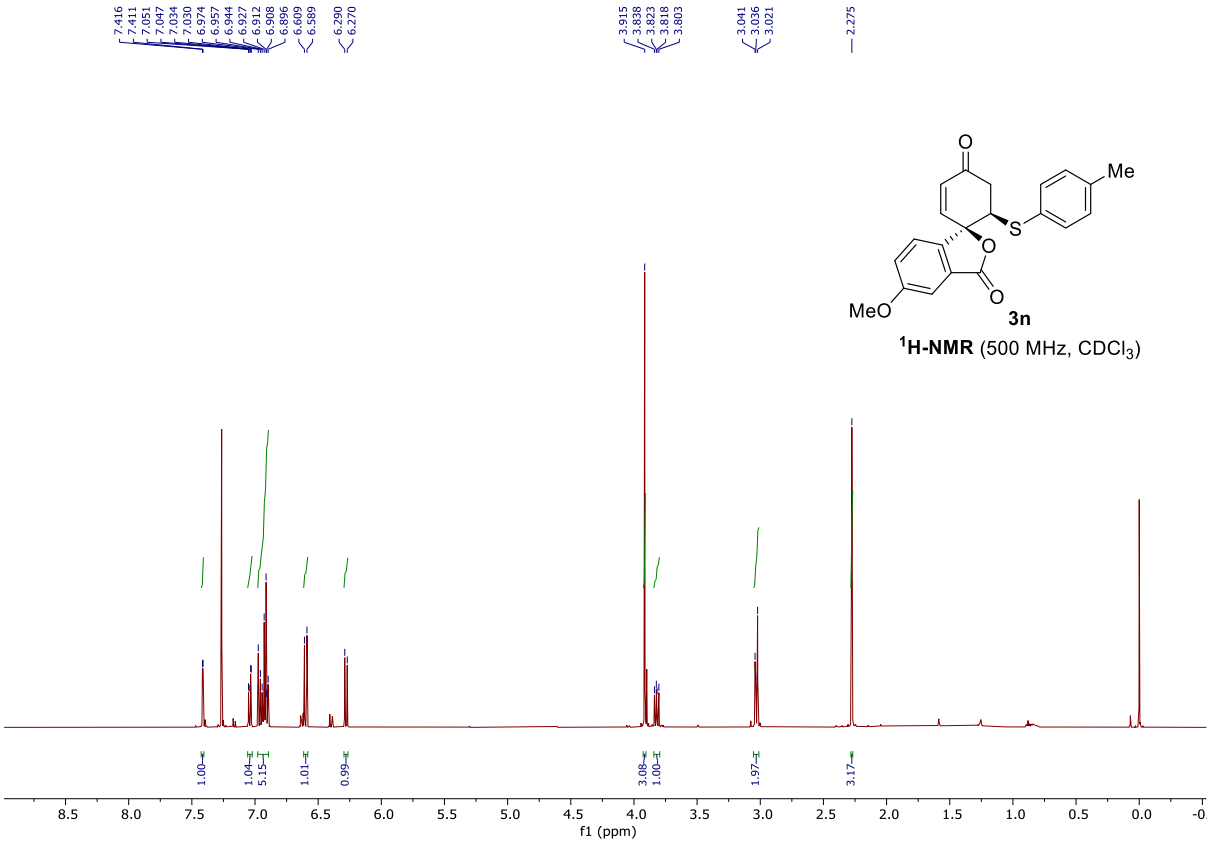
^{13}C-NMR (125 MHz, $CDCl_3$)



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

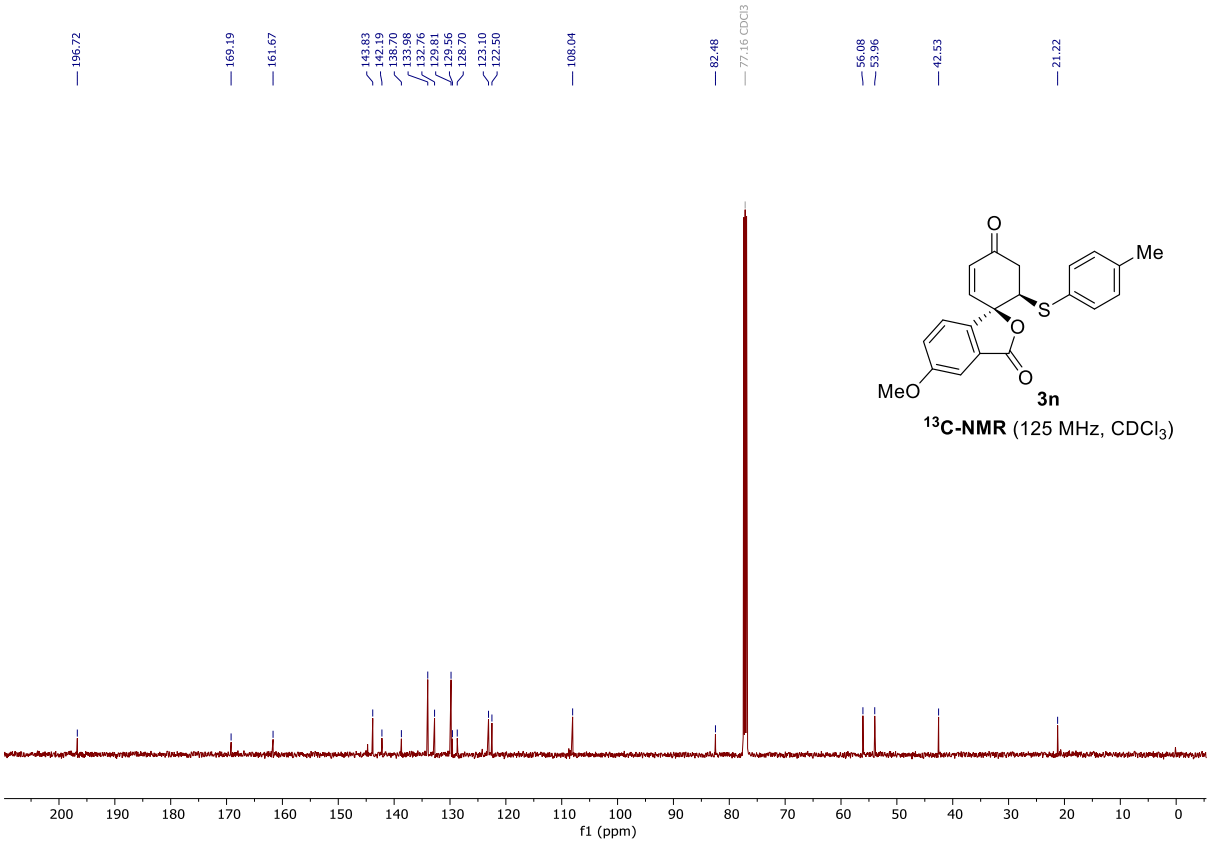


^{13}**C-NMR** (125 MHz, $CDCl_3$)



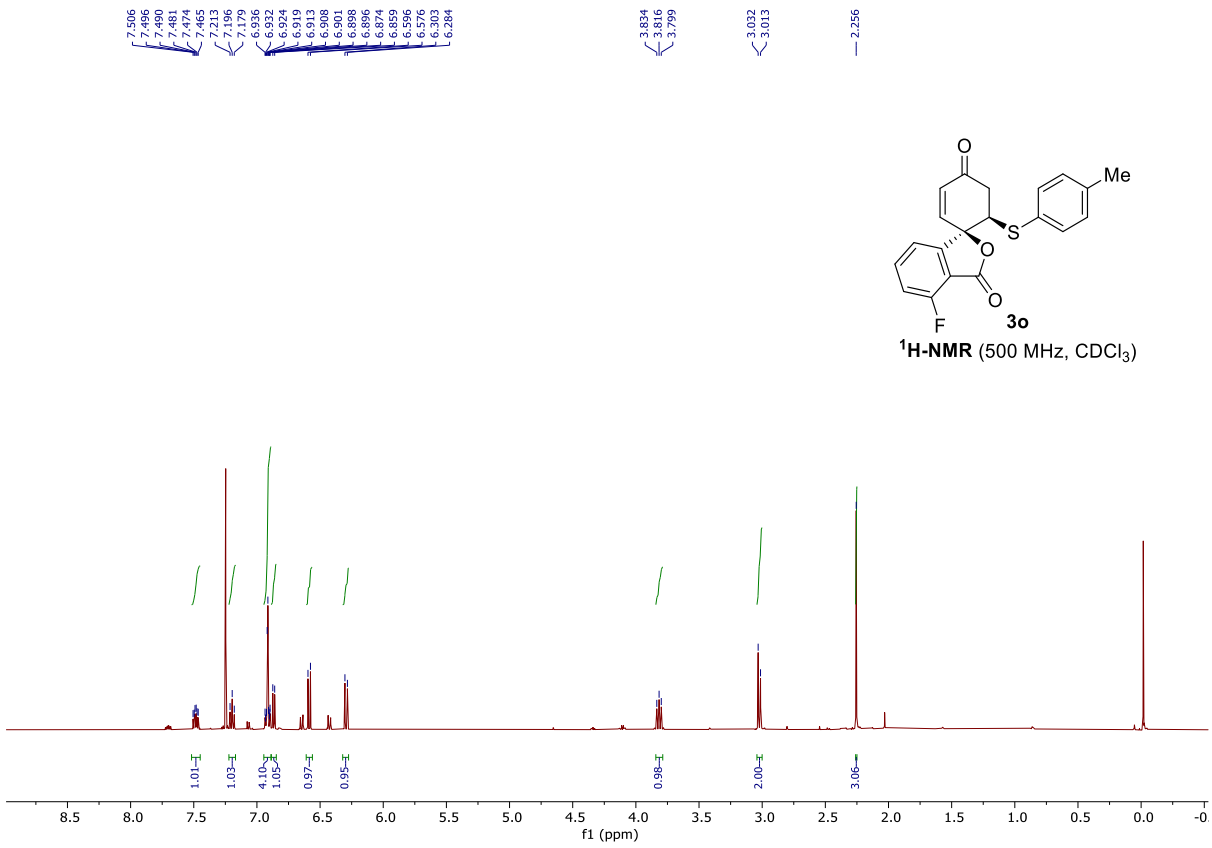
3n

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

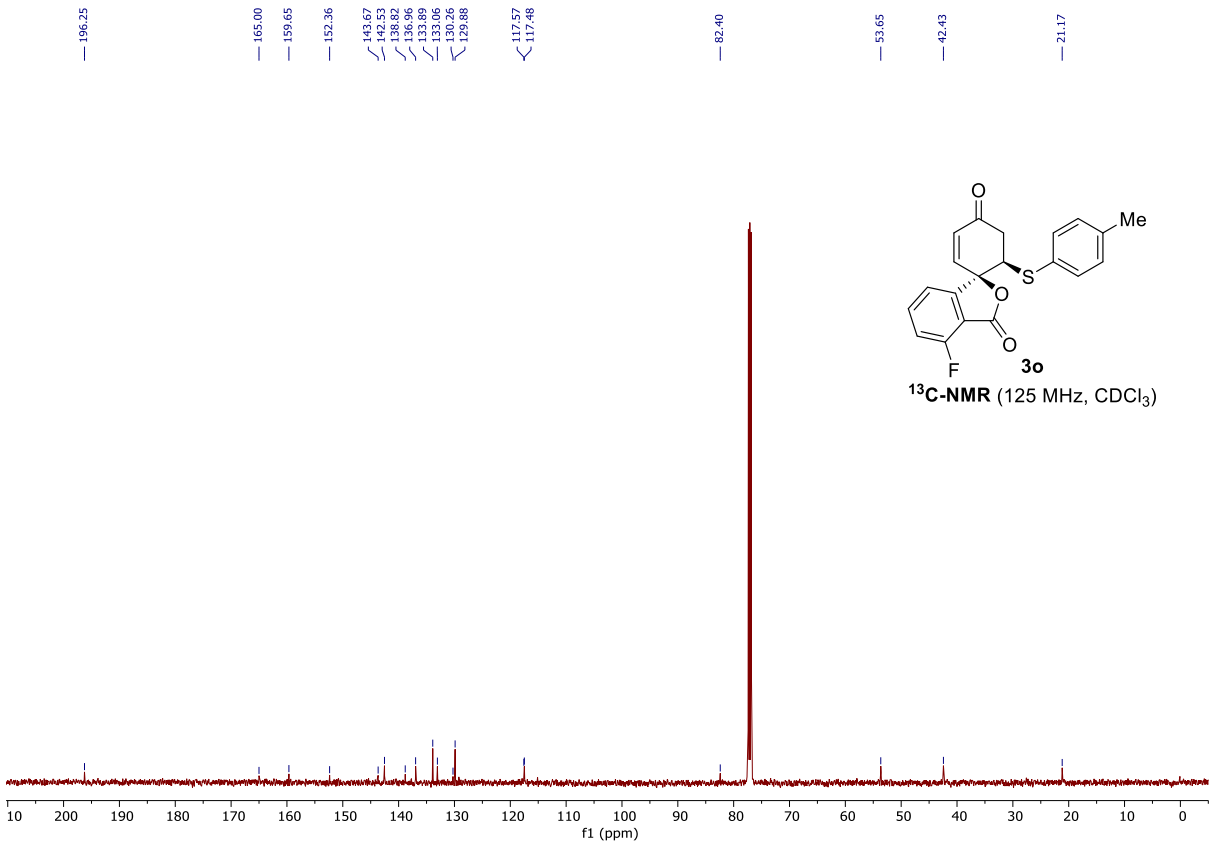


3n

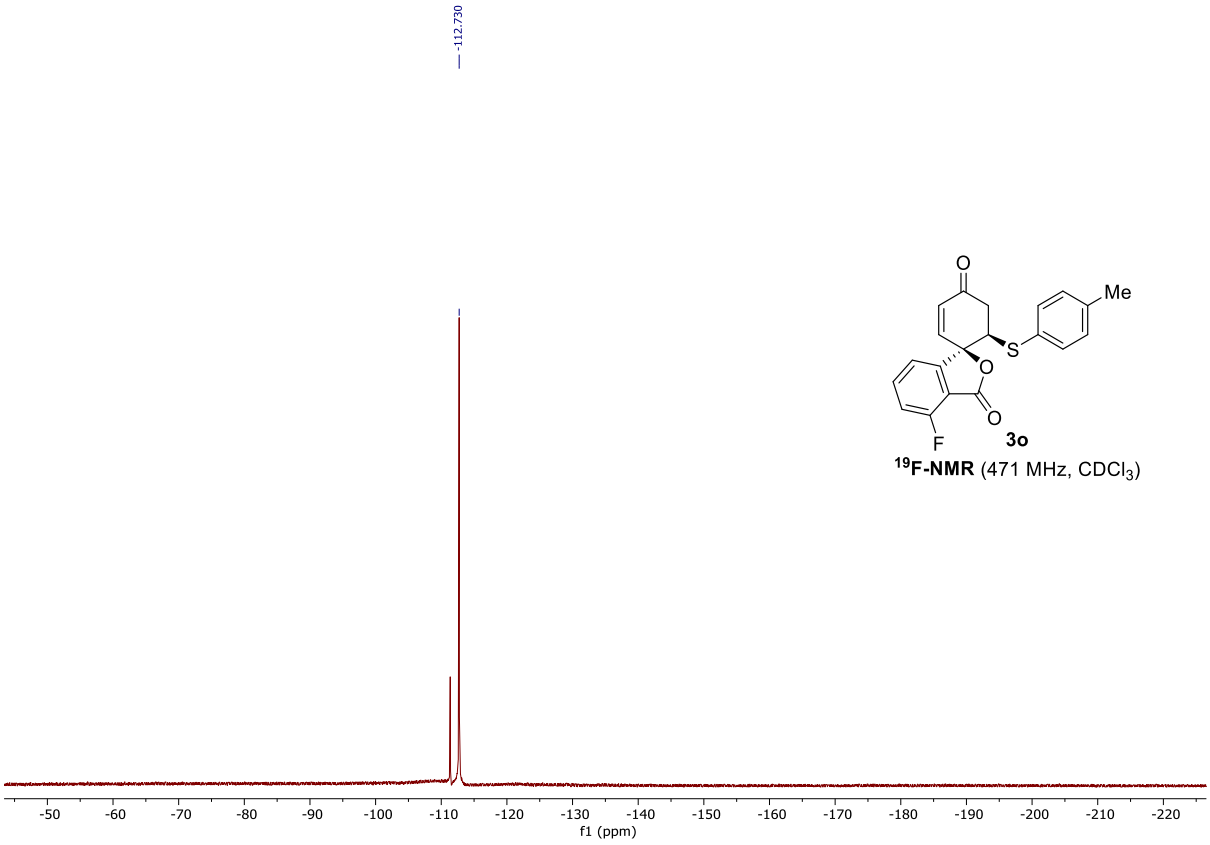
^{13}C-NMR (125 MHz, $CDCl_3$)



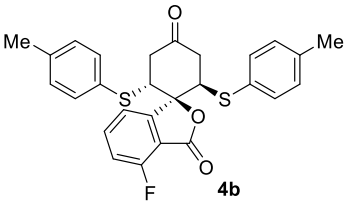
^{1}H-NMR (500 MHz, $CDCl_3$)



^{13}C-NMR (125 MHz, $CDCl_3$)

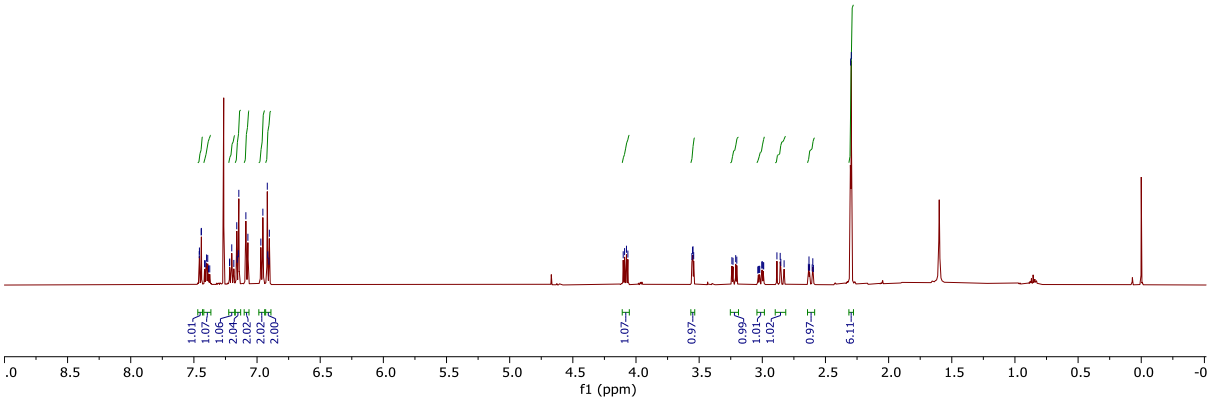


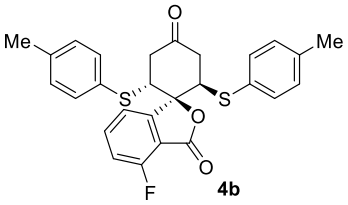
^{19}F-NMR (471 MHz, $CDCl_3$)



4b

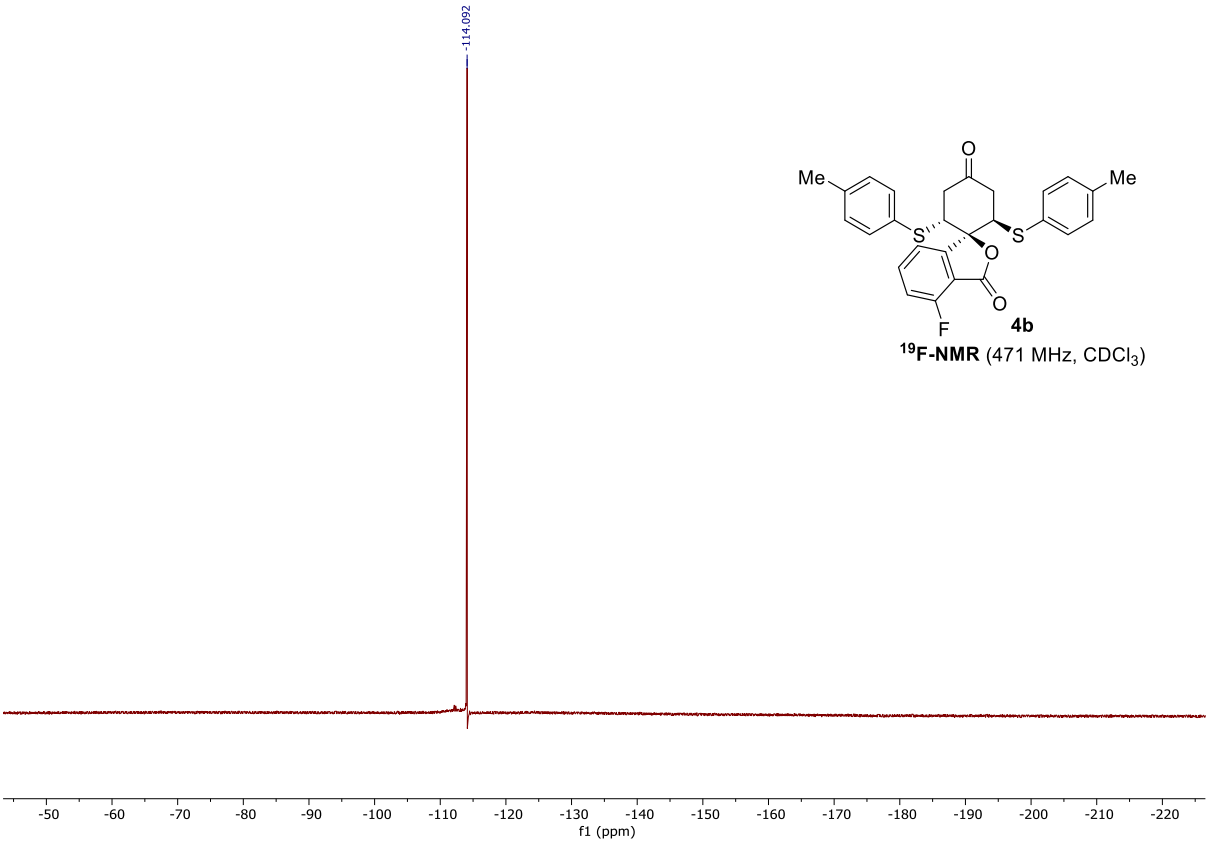
^{1}H-NMR (500 MHz, $CDCl_3$)



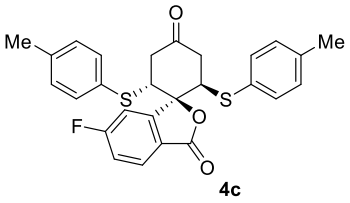


4b

^{13}C-NMR (125 MHz, $CDCl_3$)

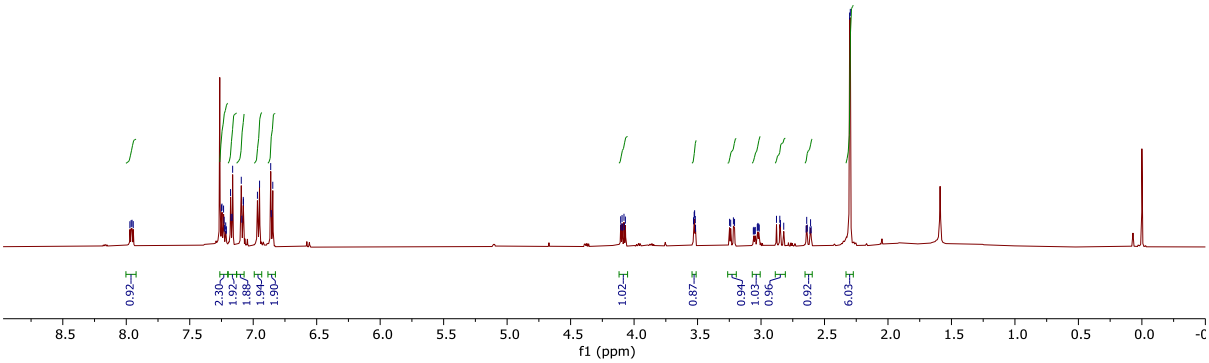


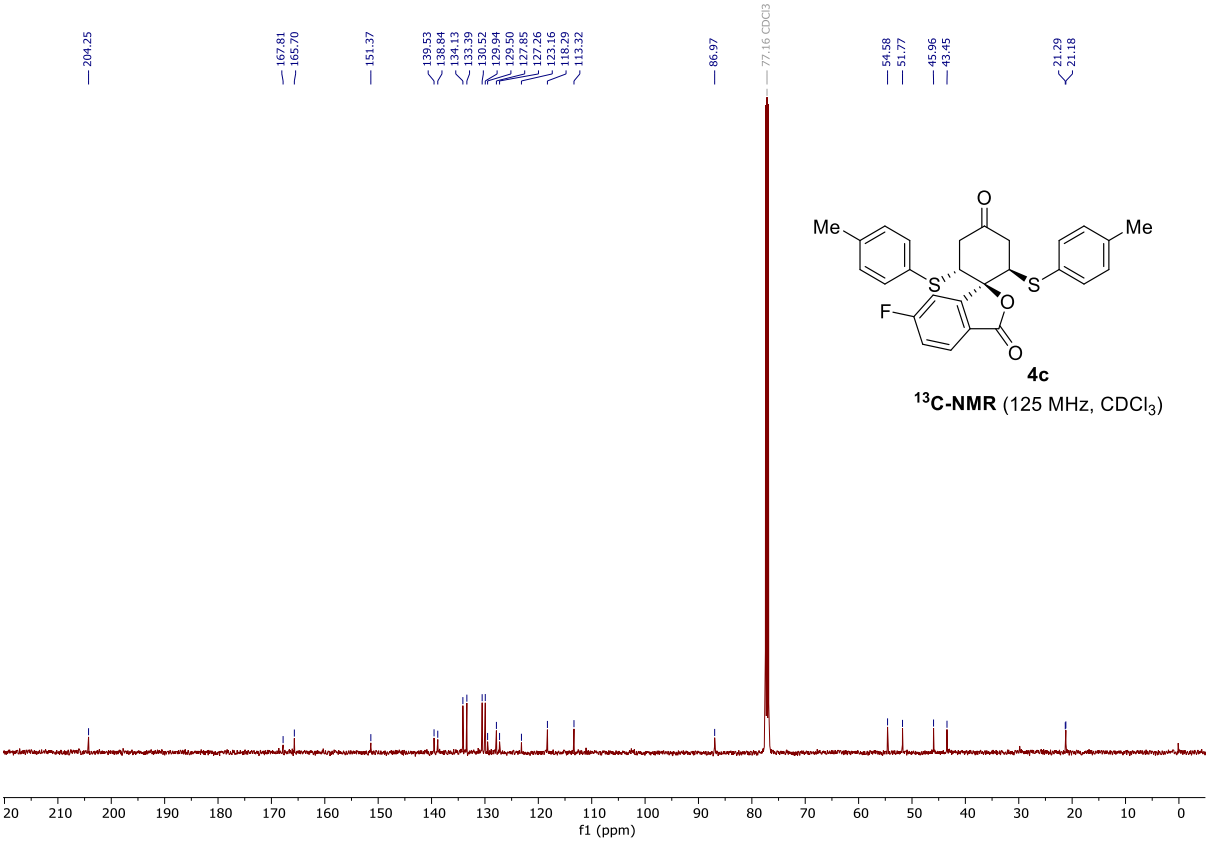
^{19}F-NMR (471 MHz, $CDCl_3$)



4c

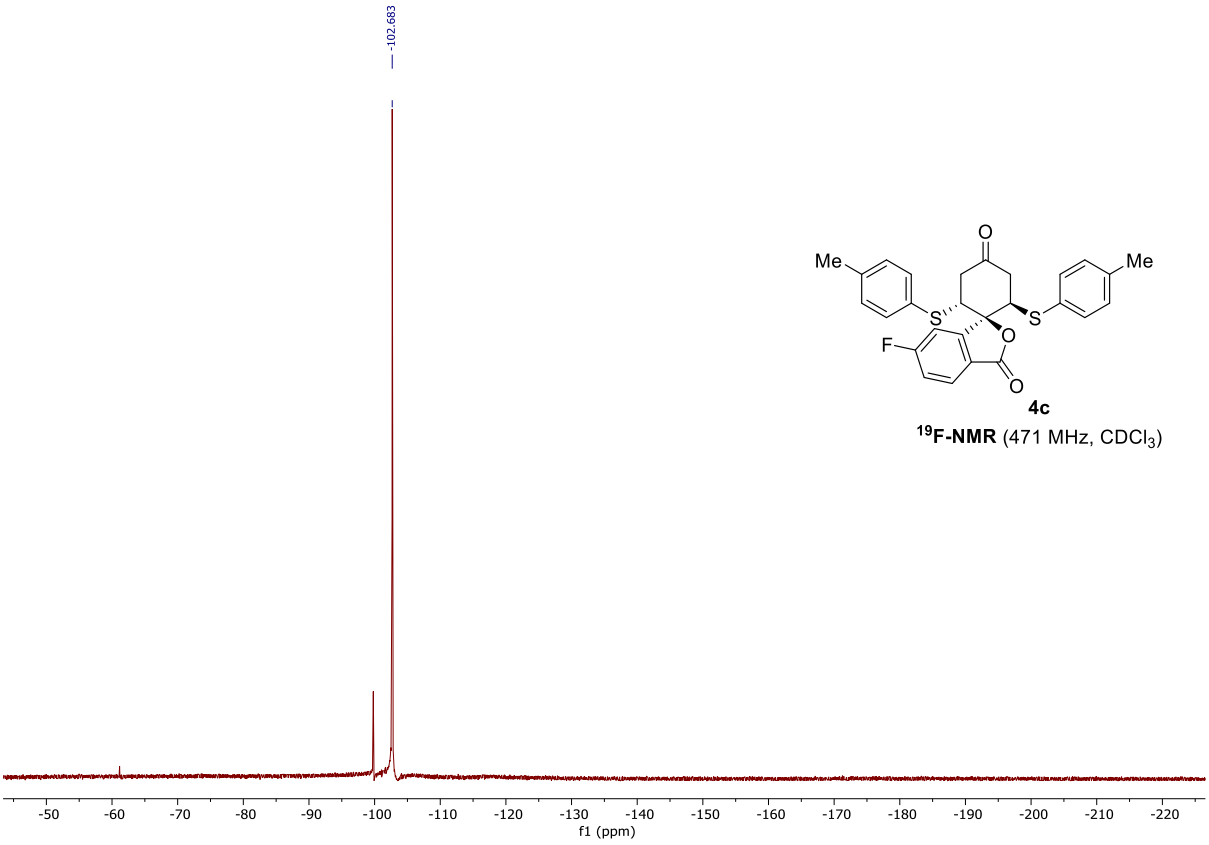
^{1}H-NMR (500 MHz, $CDCl_3$)





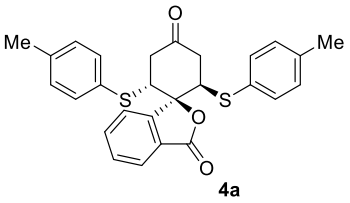
4c

^{13}C-NMR (125 MHz, $CDCl_3$)



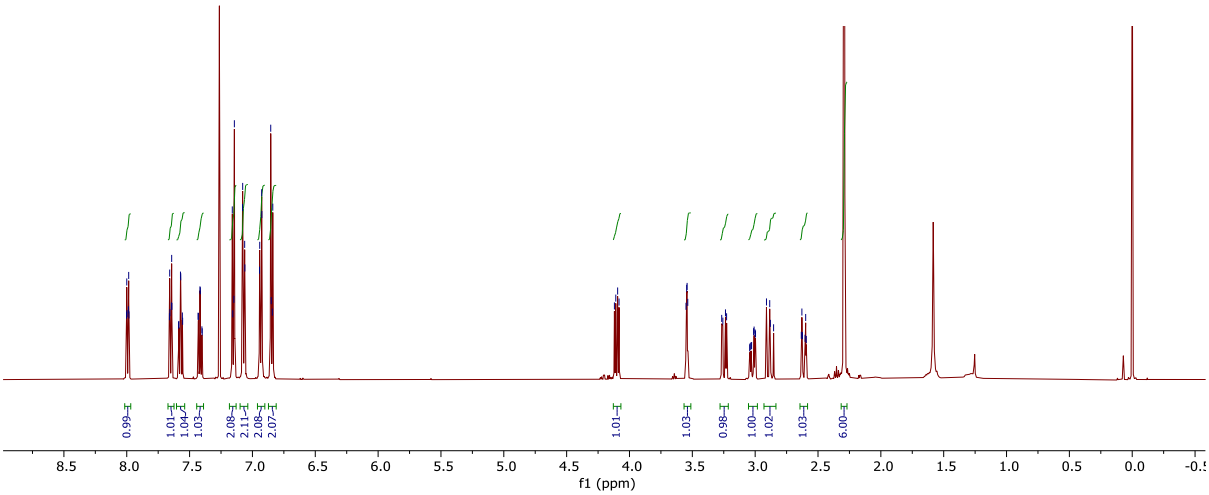
4c

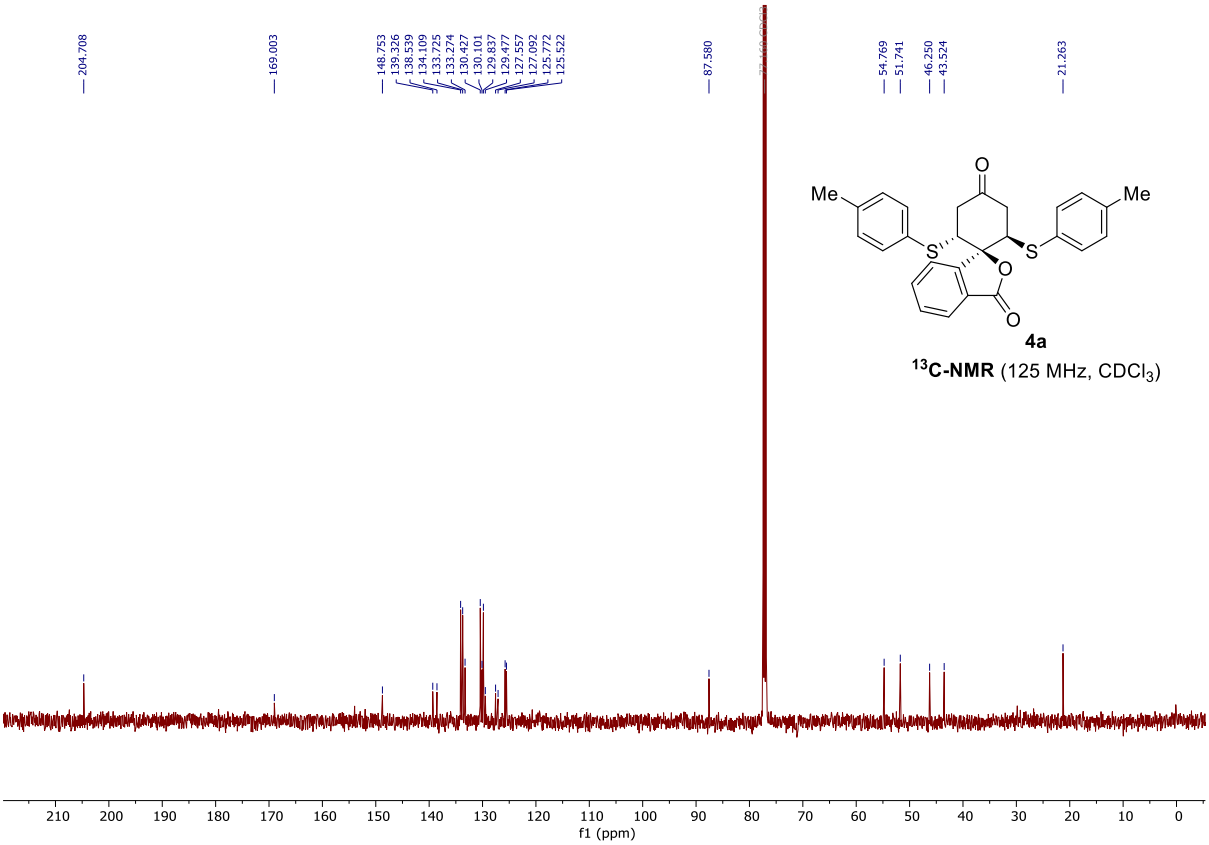
^{19}F-NMR (471 MHz, $CDCl_3$)



4a

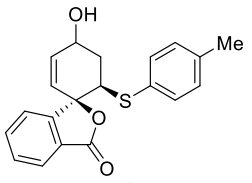
^{1}H-NMR (500 MHz, $CDCl_3$)





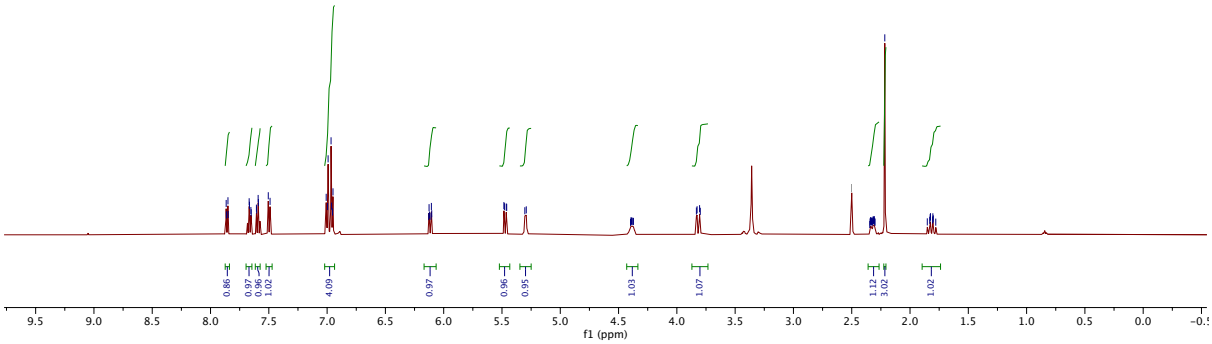
4a

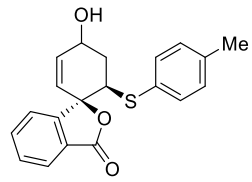
^{13}C-NMR (125 MHz, $CDCl_3$)



5

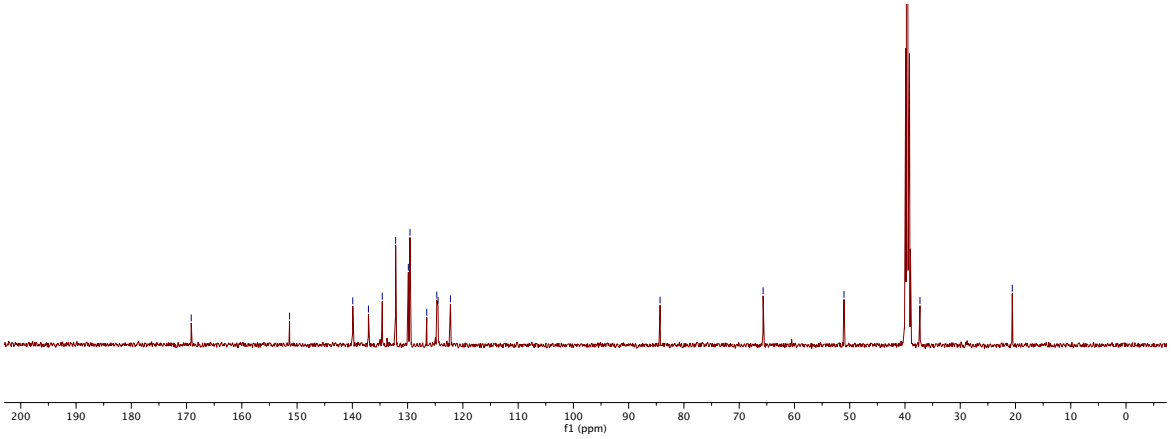
^{1}H-NMR (500 MHz, DMSO-d_6)

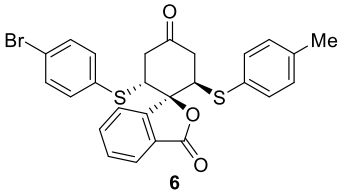




5

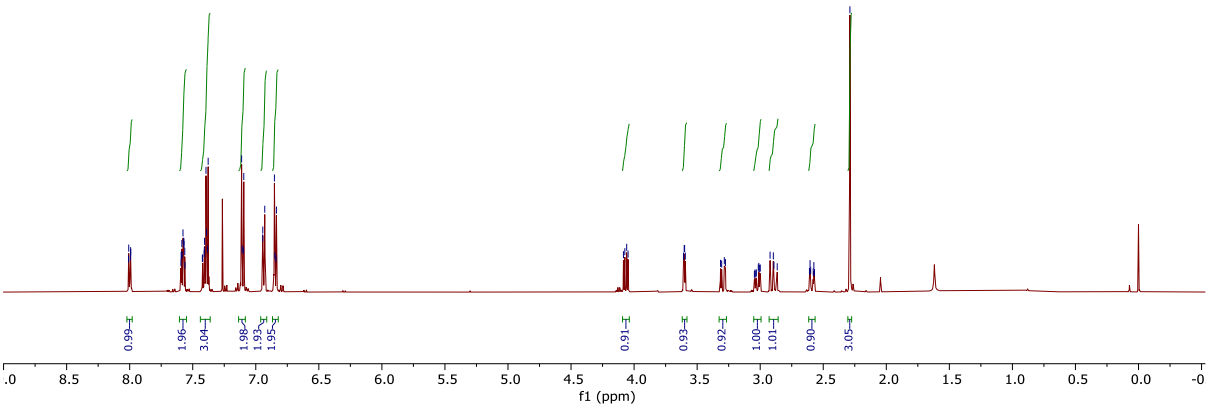
^{13}C-NMR (125 MHz, DMSO-d_6)

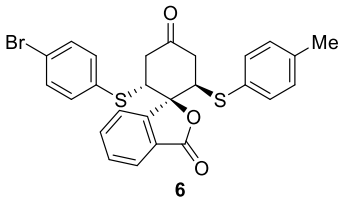




6

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





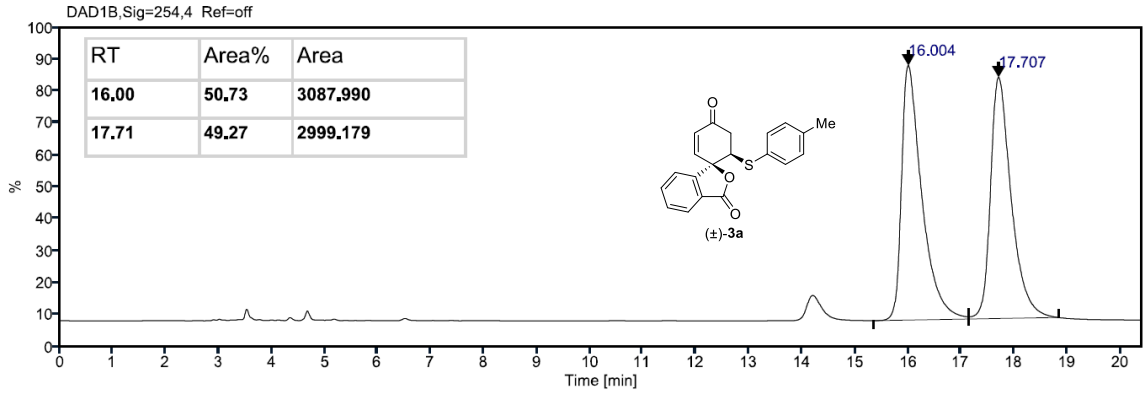
6

^{13}C-NMR (125 MHz, $CDCl_3$)

HPLC Chromatograms:

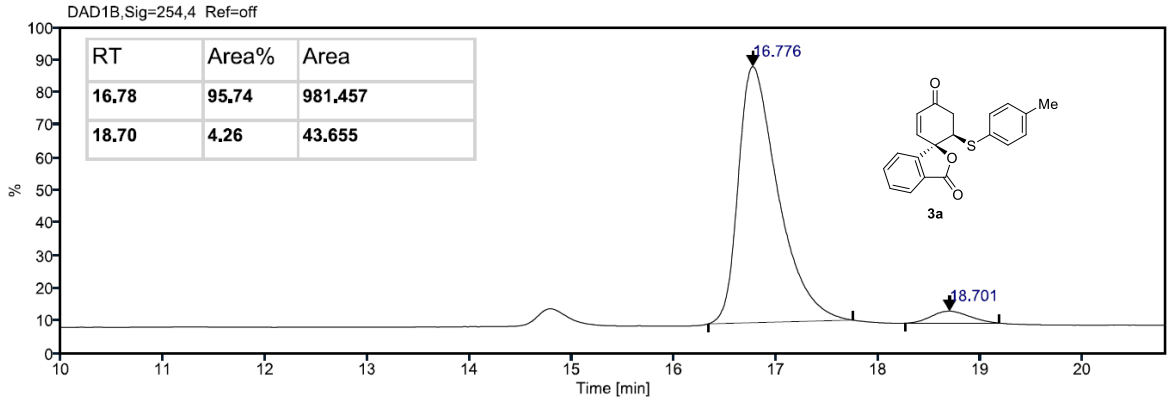
Sample ID: TC 575B

Acq. method: Chiralpak IA column, Flow rate: 1.0 mL/min, Hexane : IPA = 70 : 30



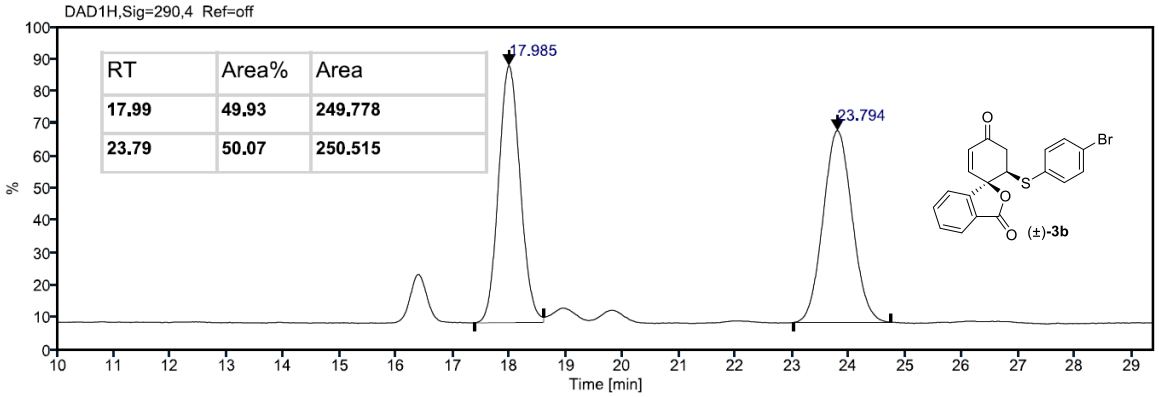
Sample ID: TC 596B

Acq. method: Chiralpak IA column, Flow rate: 1.0 mL/min, Hexane : IPA = 70 : 30



Sample ID: TC 685

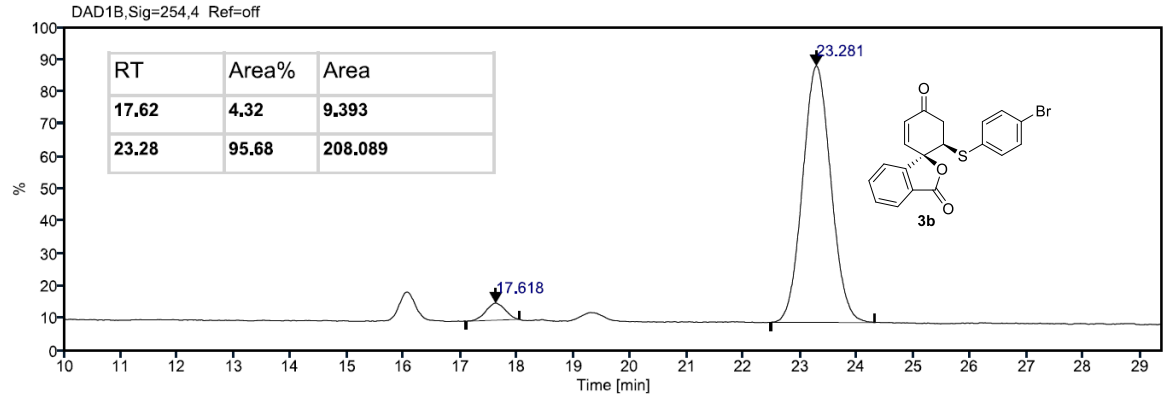
Acq. method: Chiralpak IK column, Flow rate: 1.0 mL/min, Hexane : IPA = 70 : 30



RT	Area%	Area
17.99	49.93	249.778
23.79	50.07	250.515

Sample ID: TC 673r

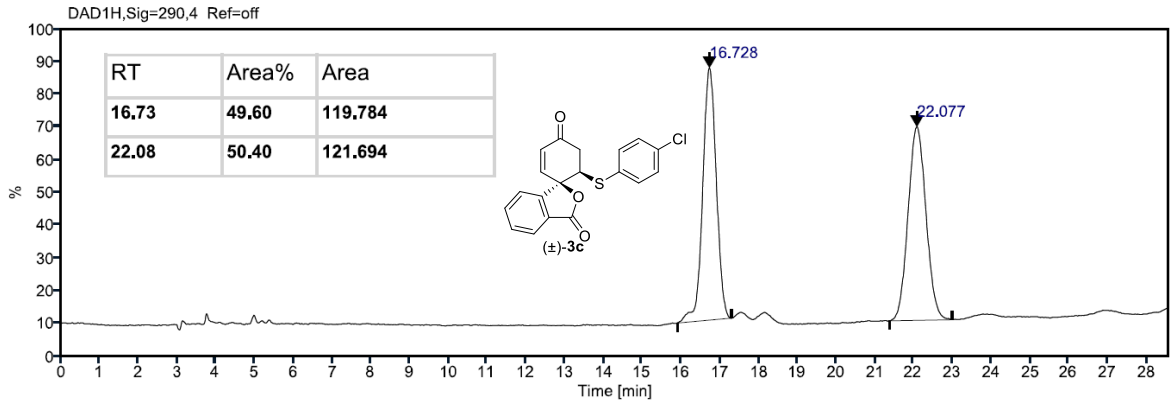
Acq. method: Chiralpak IK column, Flow rate: 1.0 mL/min, Hexane : IPA = 70 : 30



RT	Area%	Area
17.62	4.32	9.393
23.28	95.68	208.089

Sample ID: PS01 B

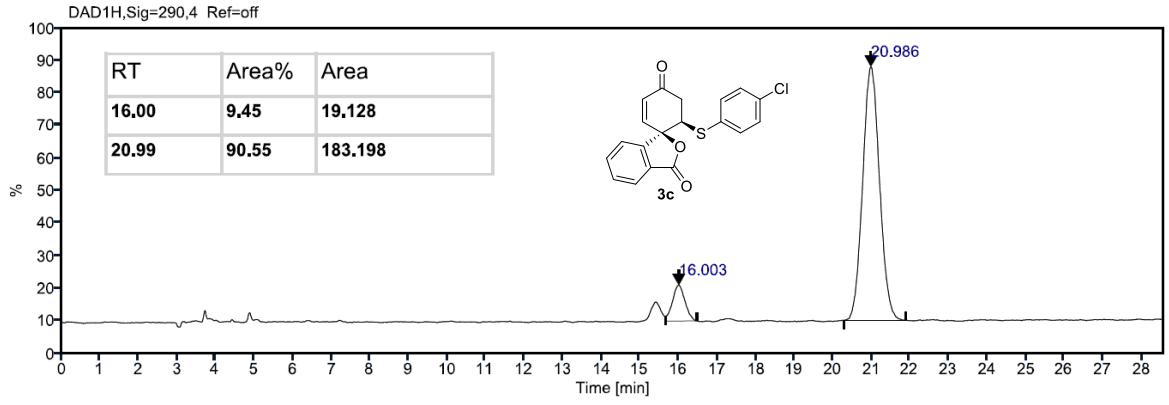
Acq. method: Chiralpak IK column, Flow rate: 1.0 mL/min, Hexane : IPA = 70 : 30



RT	Area%	Area
16.73	49.60	119.784
22.08	50.40	121.694

Sample ID: TC 703

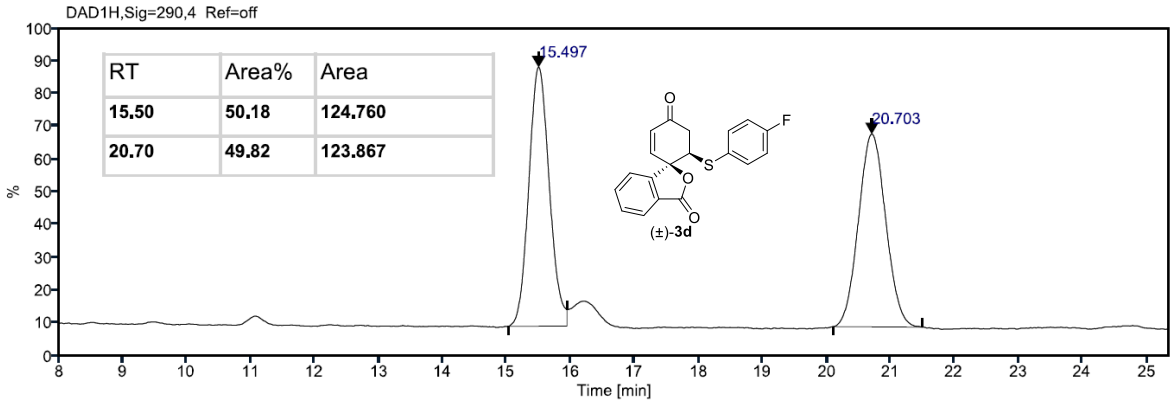
Acq. method: Chiralpak IK column, Flow rate: 1.0 mL/min, Hexane : IPA = 70 : 30



RT	Area%	Area
16.00	9.45	19.128
20.99	90.55	183.198

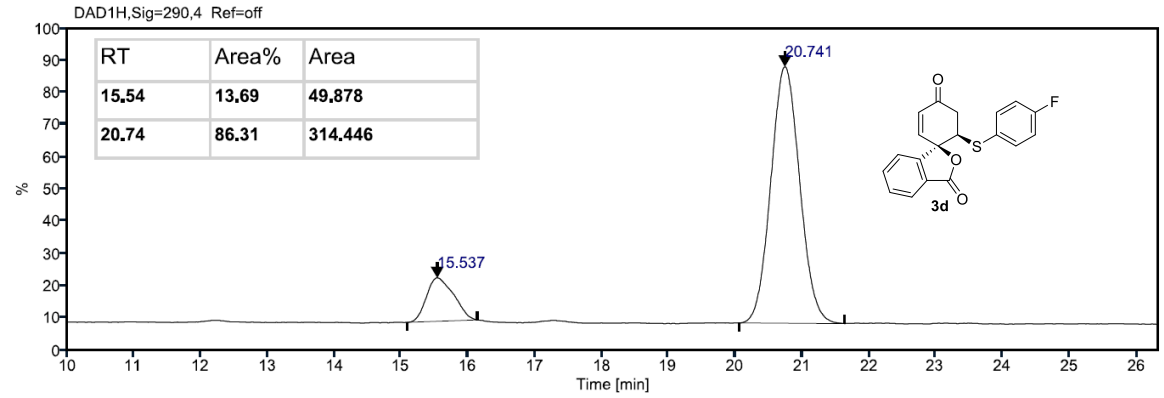
Sample ID: PS 4-F rac spot B

Acq. method: Chiralpak IK column, Flow rate: 1.0 mL/min, Hexane : IPA = 70 : 30



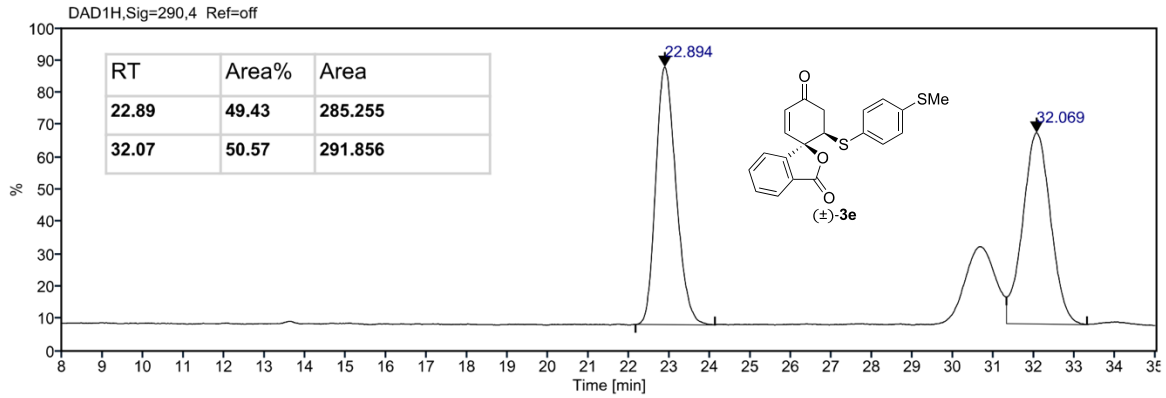
Sample ID: TC 707B

Acq. method: Chiralpak IK column, Flow rate: 1.0 mL/min, Hexane : IPA = 70 : 30



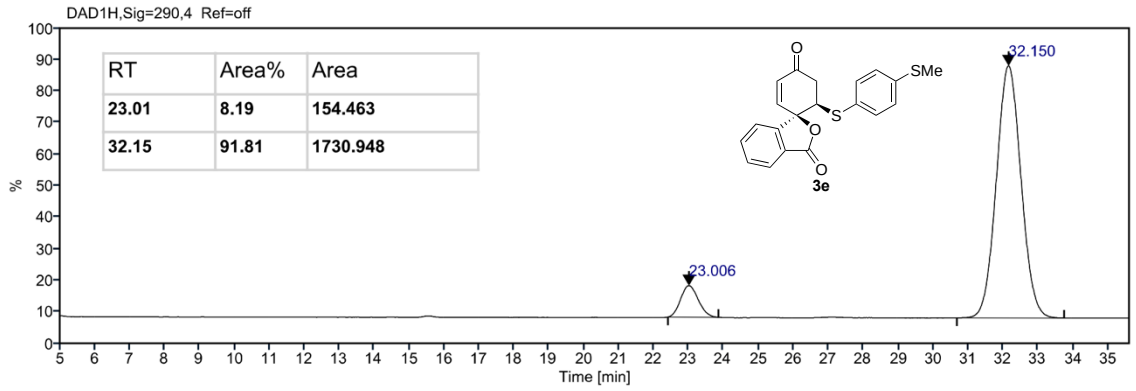
Sample ID: TC 692B

Acq. method: Chiralpak IK column, Flow rate: 1.0 mL/min, Hexane : IPA = 70 : 30



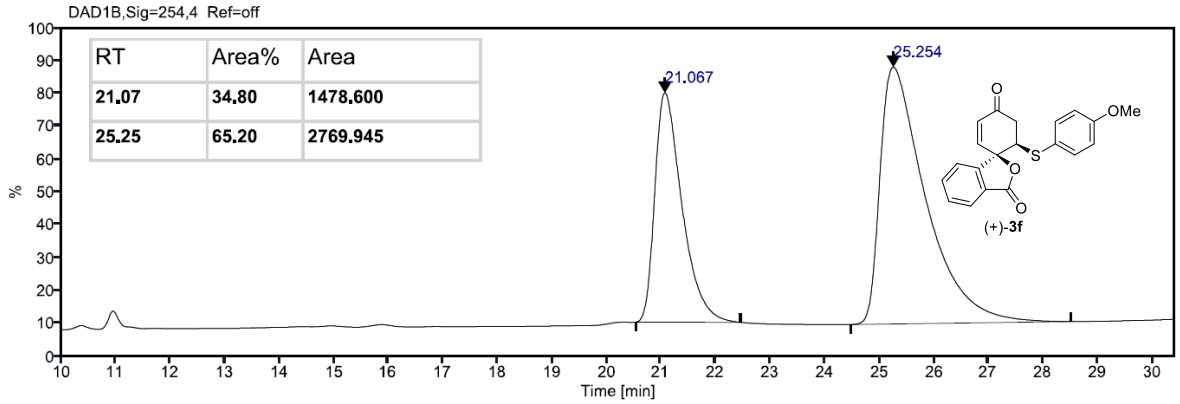
Sample ID: TC 721

Acq. method: Chiralpak IK column, Flow rate: 1.0 mL/min, Hexane : IPA = 70 : 30



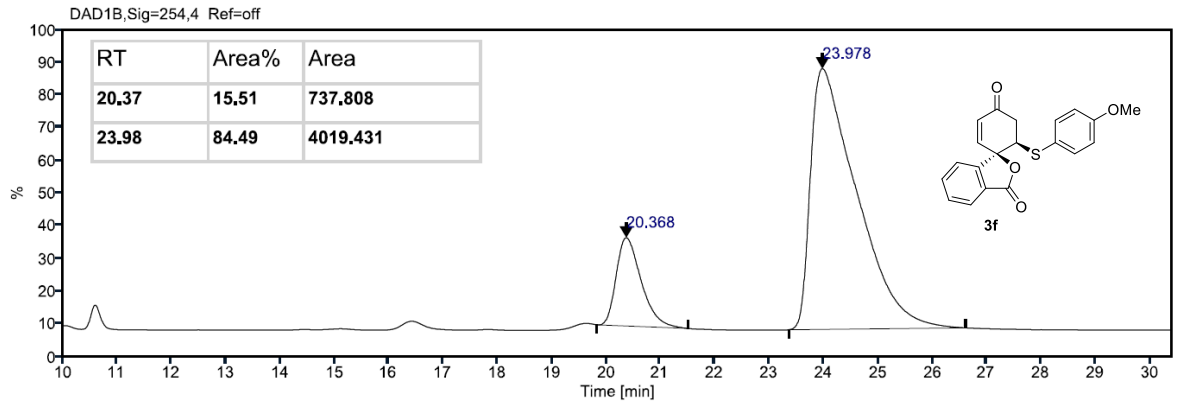
Sample ID: TC 837

Acq. method: Chiralpak IF column, Flow rate: 1.0 mL/min, Hexane : IPA = 70 : 30



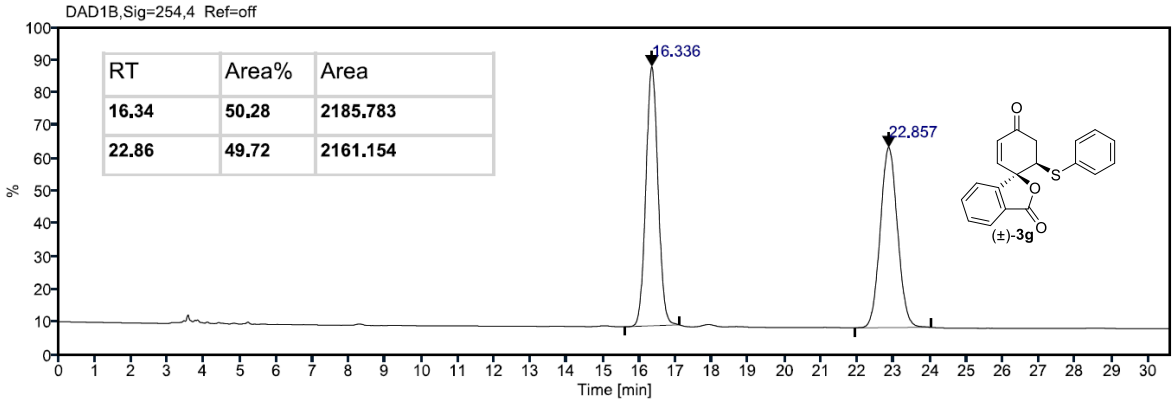
Sample ID: TC 725

Acq. method: Chiralpak IF column, Flow rate: 1.0 mL/min, Hexane : IPA = 70 : 30



Sample ID: TC 690Repeat

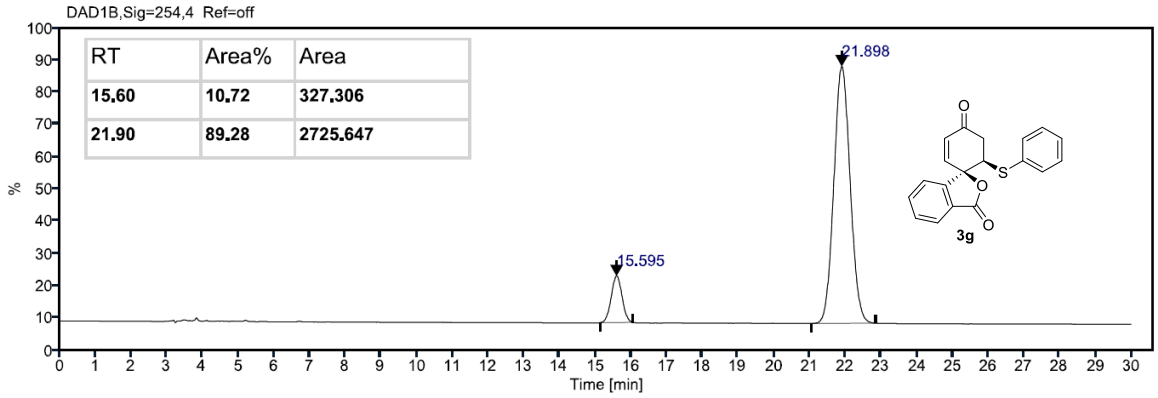
Acq. method: Chiralpak IK column, Flow rate: 1.0 mL/min, Hexane : IPA = 70 : 30



RT	Area%	Area
16.34	50.28	2185.783
22.86	49.72	2161.154

Sample ID: TC 722R

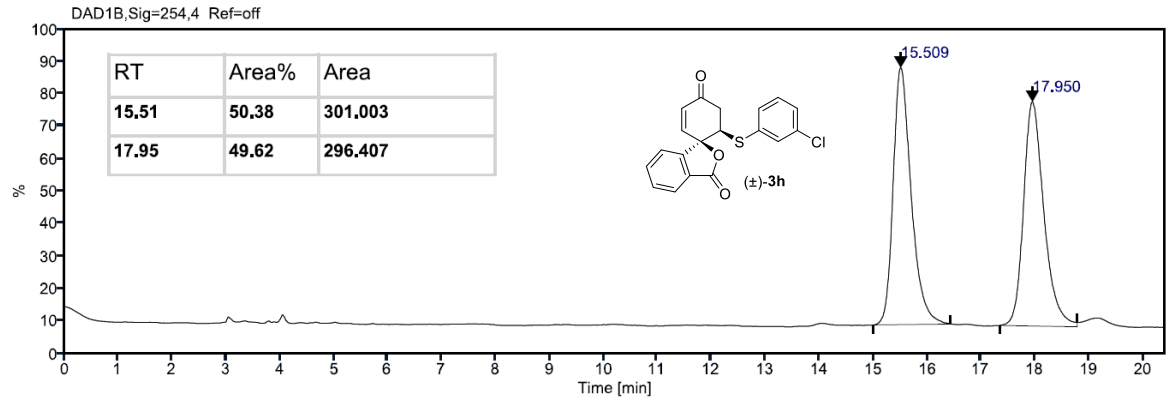
Acq. method: Chiralpak IK column, Flow rate: 1.0 mL/min, Hexane : IPA = 70 : 30



RT	Area%	Area
15.60	10.72	327.306
21.90	89.28	2725.647

Sample ID: D 3-Cl Rac

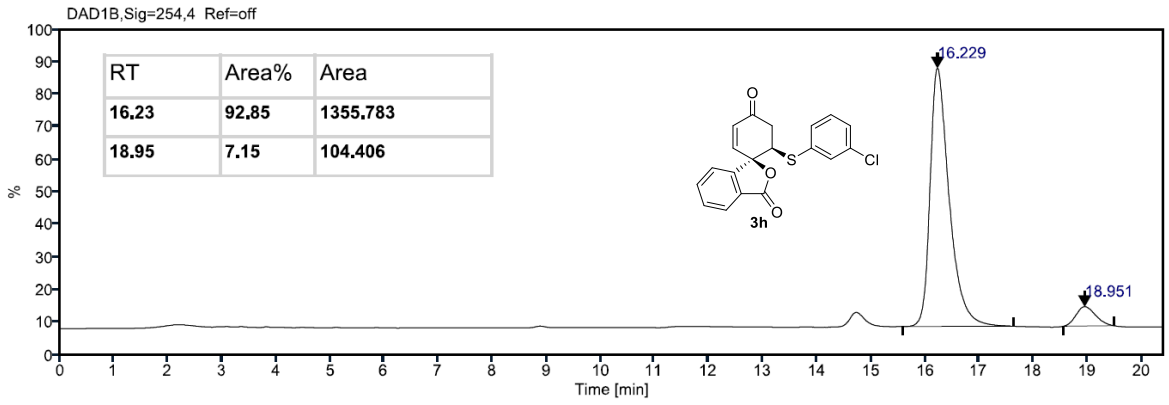
Acq. method: Chiralpak IA column, Flow rate: 1.0 mL/min, Hexane : IPA = 90 : 10



RT	Area%	Area
15.51	50.38	301.003
17.95	49.62	296.407

Sample ID: TC 695

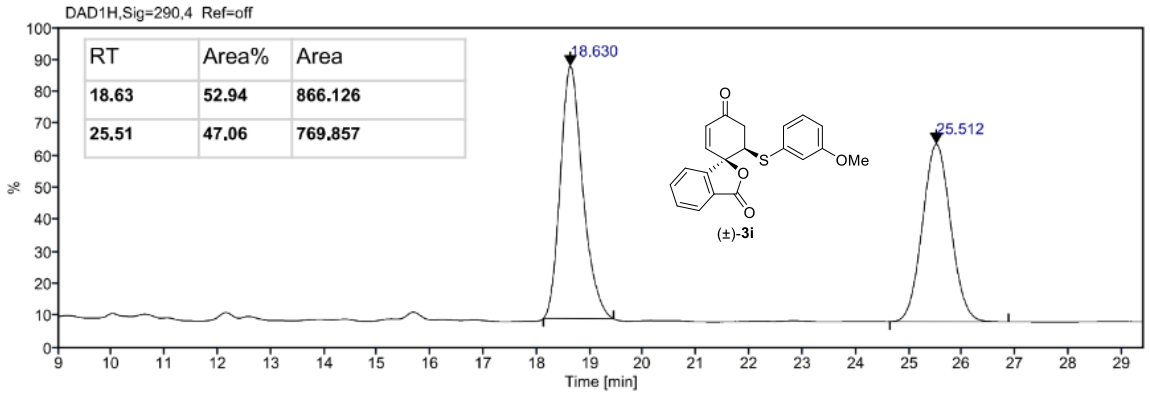
Acq. method: Chiralpak IA column, Flow rate: 1.0 mL/min, Hexane : IPA = 90 : 10



RT	Area%	Area
16.23	92.85	1355.783
18.95	7.15	104.406

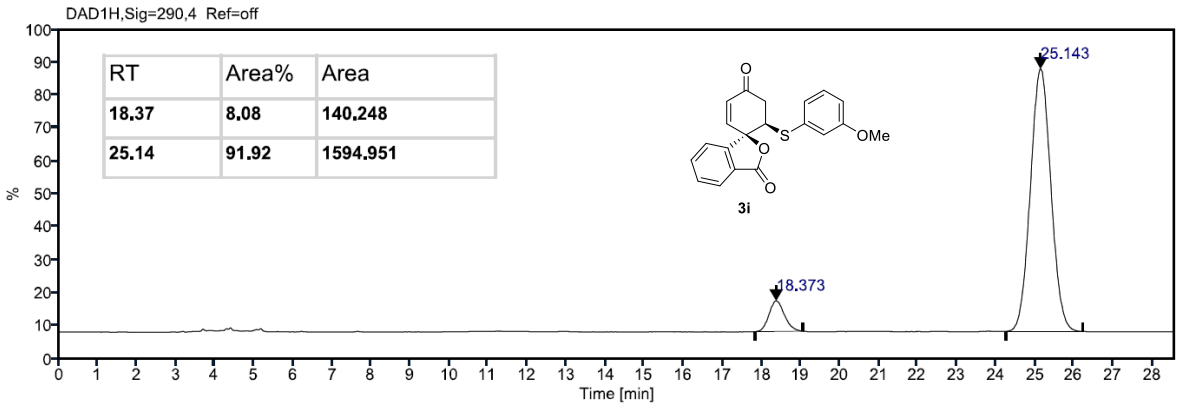
Sample ID: DS 3-OMe Rac

Acq. method: Chiralpak IK column, Flow rate: 1.0 mL/min, Hexane : IPA = 70 : 30



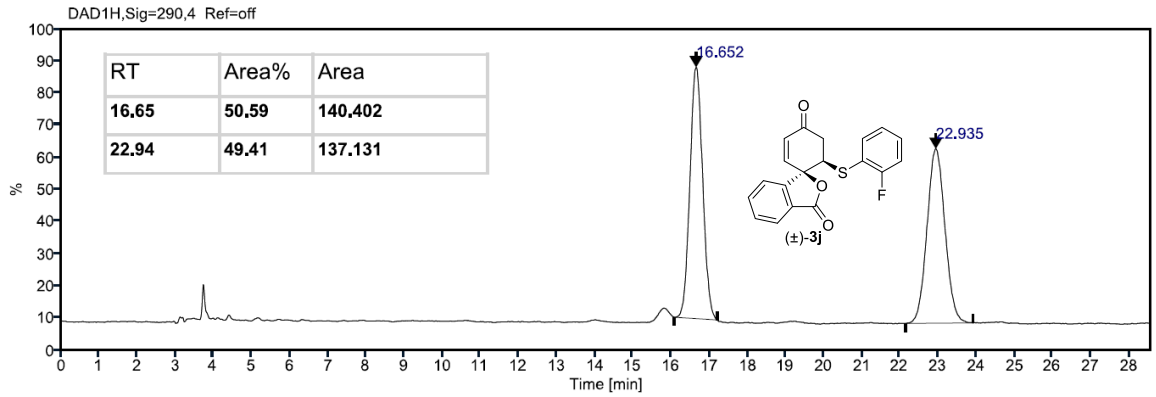
Sample ID: TC 696R

Acq. method: Chiralpak IK column, Flow rate: 1.0 mL/min, Hexane : IPA = 70 : 30



Sample ID: DS 2F rac

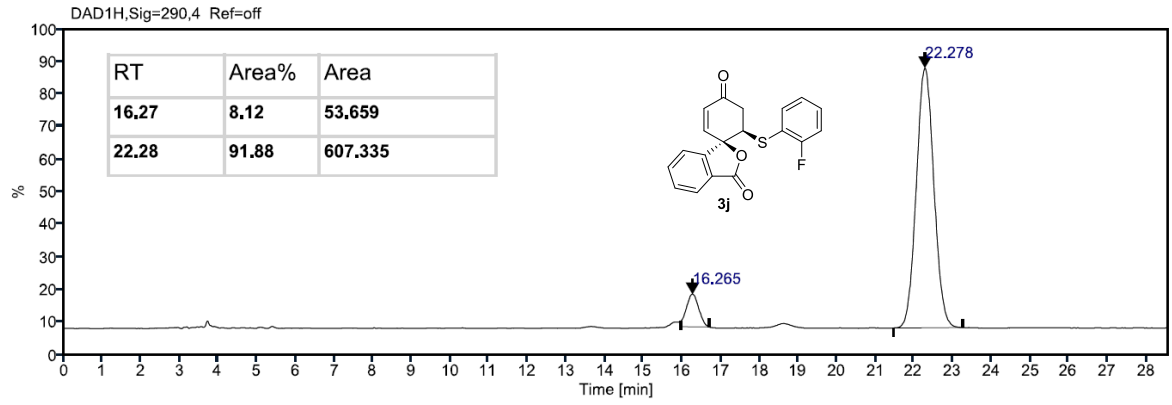
Acq. method: Chiralpak IK column, Flow rate: 1.0 mL/min, Hexane : IPA = 70 : 30



RT	Area%	Area
16.65	50.59	140.402
22.94	49.41	137.131

Sample ID: TC 694R

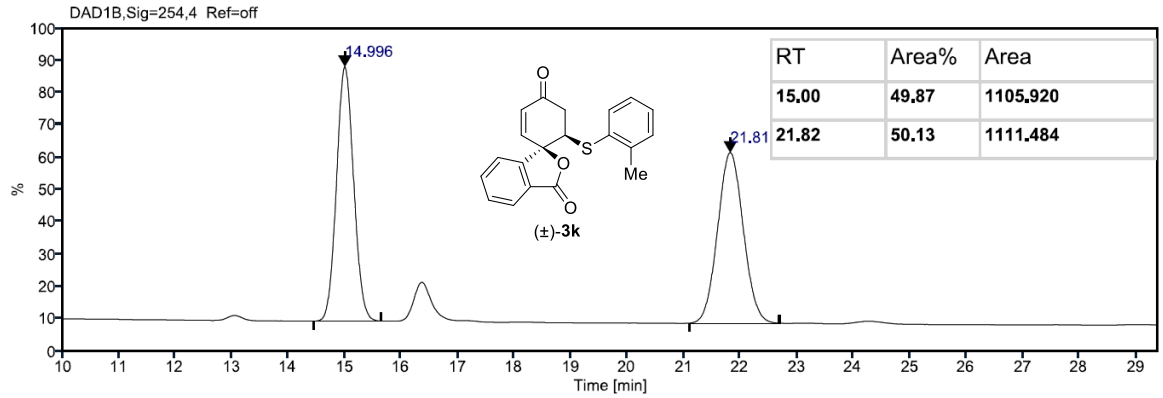
Acq. method: Chiralpak IK column, Flow rate: 1.0 mL/min, Hexane : IPA = 70 : 30



RT	Area%	Area
16.27	8.12	53.659
22.28	91.88	607.335

Sample ID: DS 2-Me Rac

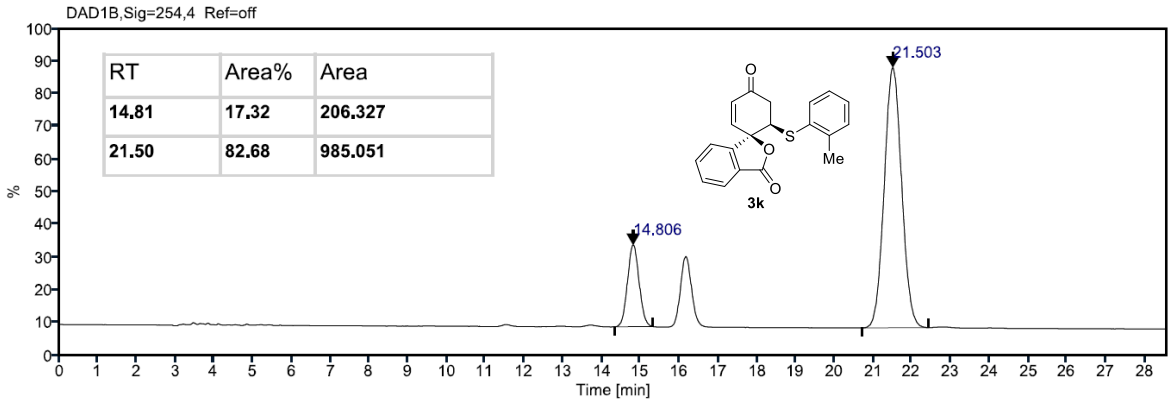
Acq. method: Chiralpak IK column, Flow rate: 1.0 mL/min, Hexane : IPA = 70 : 30



RT	Area%	Area
15.00	49.87	1105.920
21.82	50.13	1111.484

Sample ID: TC 693

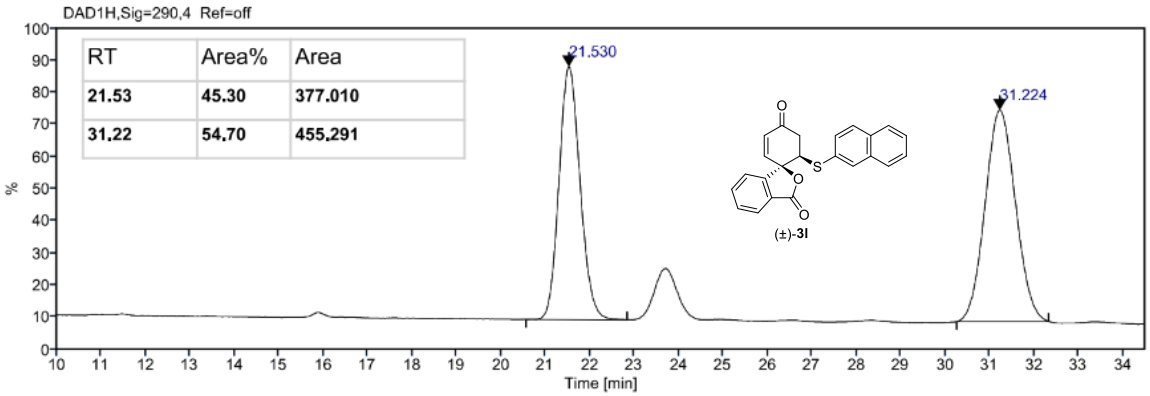
Acq. method: Chiralpak IK column, Flow rate: 1.0 mL/min, Hexane : IPA = 70 : 30



RT	Area%	Area
14.81	17.32	206.327
21.50	82.68	985.051

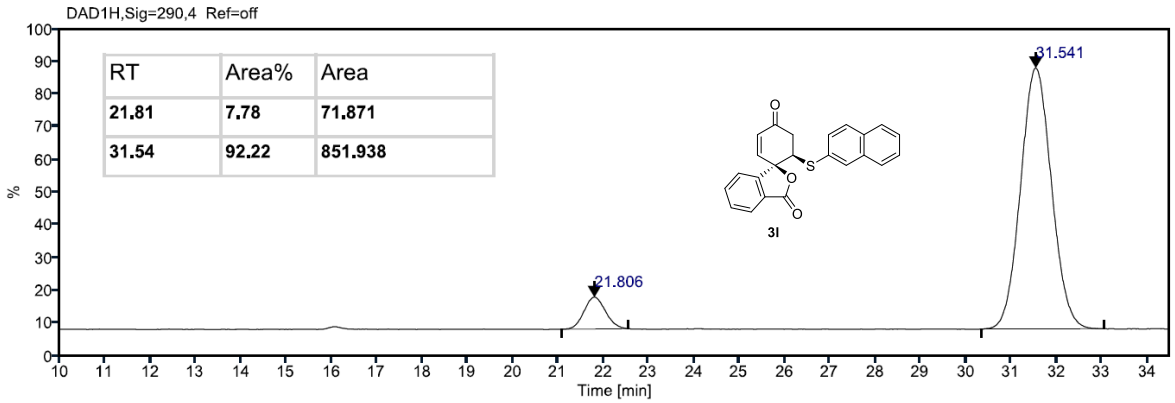
Sample ID: PS06B

Acq. method: Chiralpak IK column, Flow rate: 1.0 mL/min, Hexane : IPA = 70 : 30



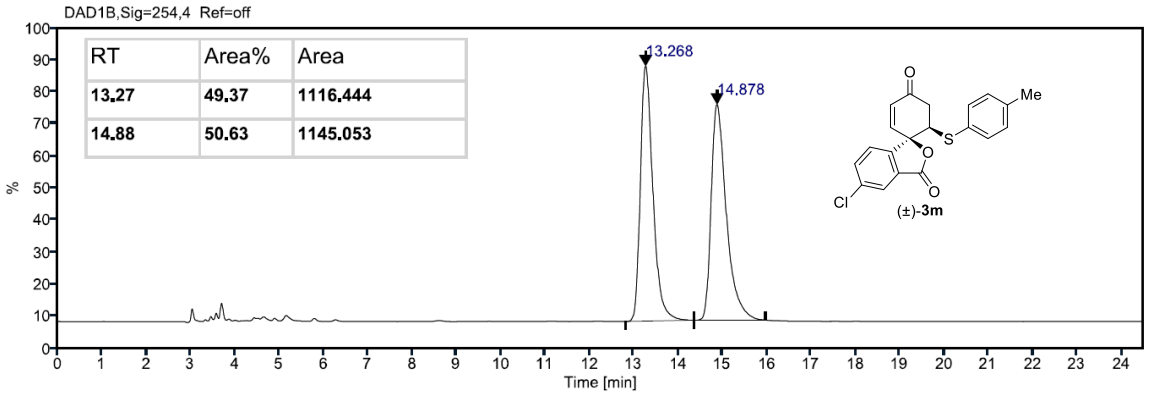
Sample ID: TC 708B r

Acq. method: Chiralpak IK column, Flow rate: 1.0 mL/min, Hexane : IPA = 70 : 30



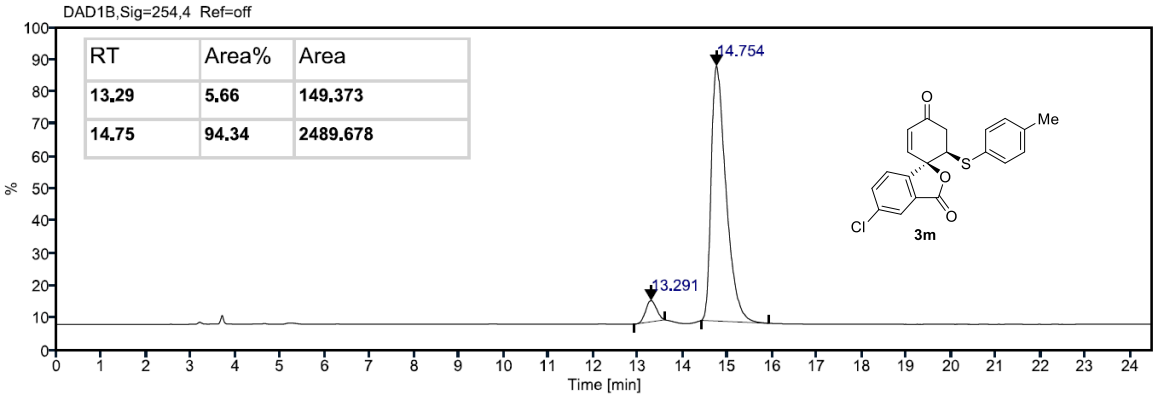
Sample ID: TC 812B

Acq. method: Chiralpak IF column, Flow rate: 1.0 mL/min, Hexane : IPA = 70 : 30



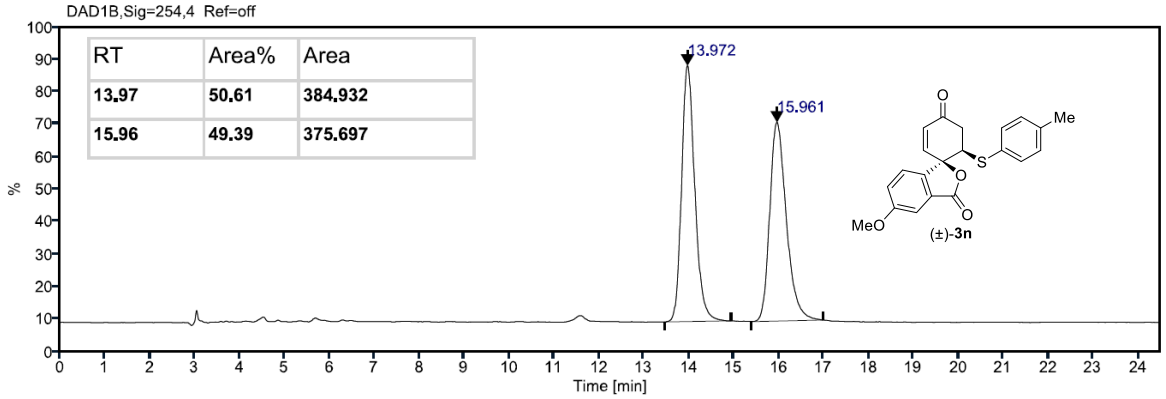
Sample ID: TC 805B

Acq. method: Chiralpak IF column, Flow rate: 1.0 mL/min, Hexane : IPA = 70 : 30



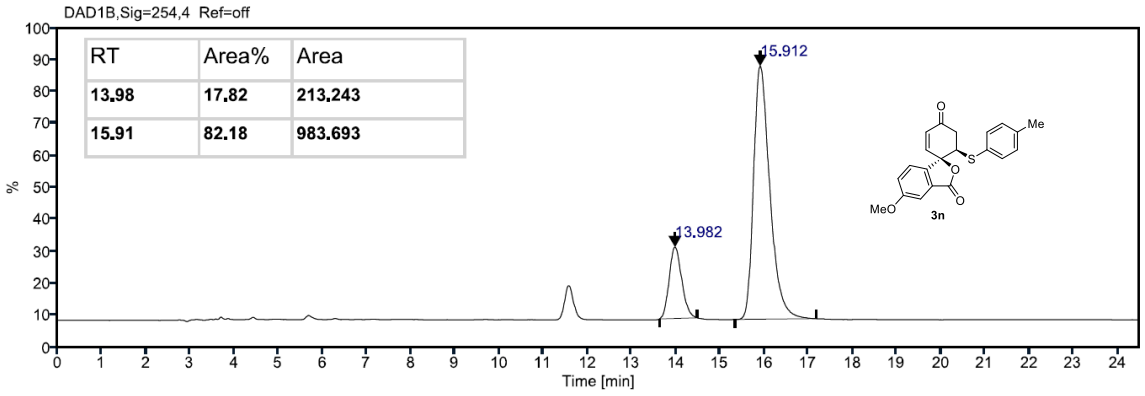
Sample ID: TC 818B

Acq. method: Chiralpak IF column, Flow rate: 1.0 mL/min, Hexane : IPA = 70 : 30



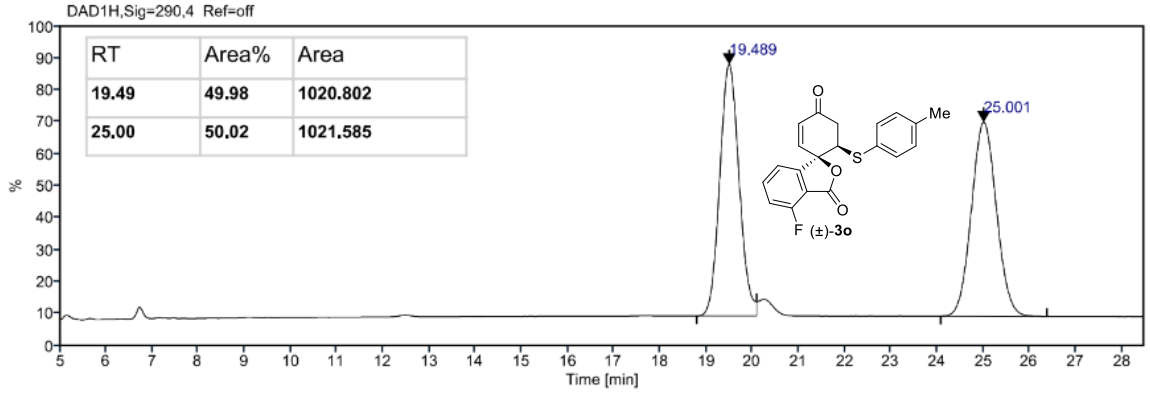
Sample ID: TC 815B

Acq. method: Chiralpak IF column, Flow rate: 1.0 mL/min, Hexane : IPA = 70 : 30



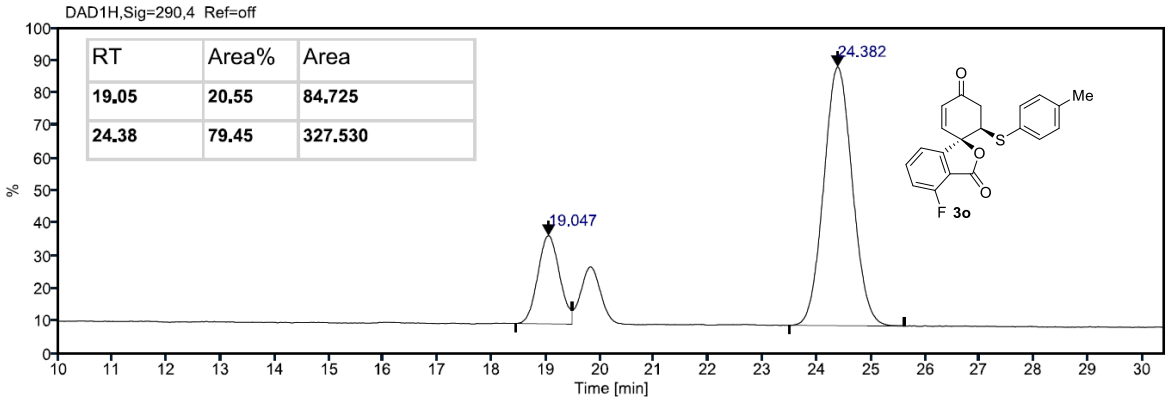
Sample ID: PS24

Acq. method: Chiralpak IK column, Flow rate: 1.0 mL/min, Hexane : IPA = 70 : 30



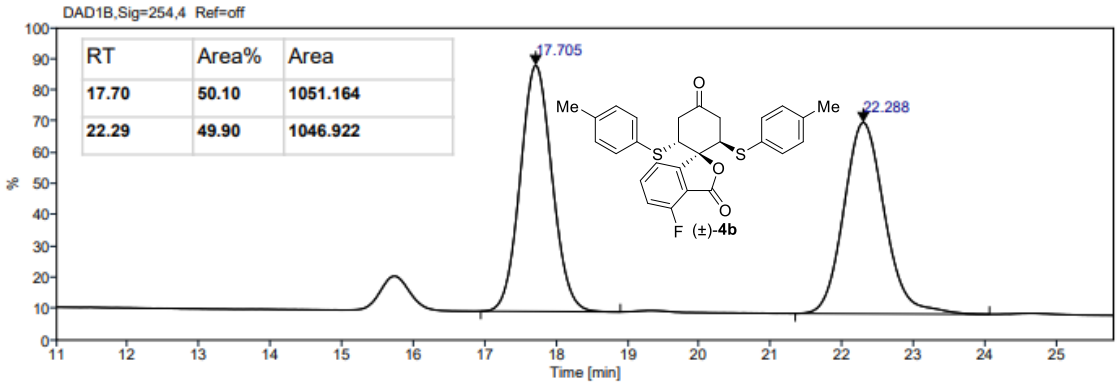
Sample ID: TC 732

Acq. method: Chiralpak IK column, Flow rate: 1.0 mL/min, Hexane : IPA = 70 : 30



Sample ID: DS TC F-dithiol 4-me rac

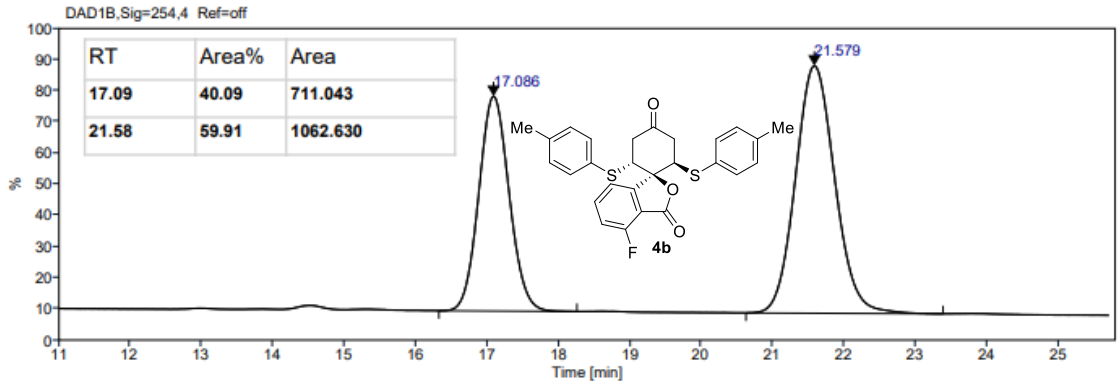
Acq. method: Chiralpak Ik column, Flow rate: 1.0 mL/min, Hexane : IPA = 70 : 30



RT	Area%	Area
17.70	50.10	1051.164
22.29	49.90	1046.922

Sample ID: Tc 795A

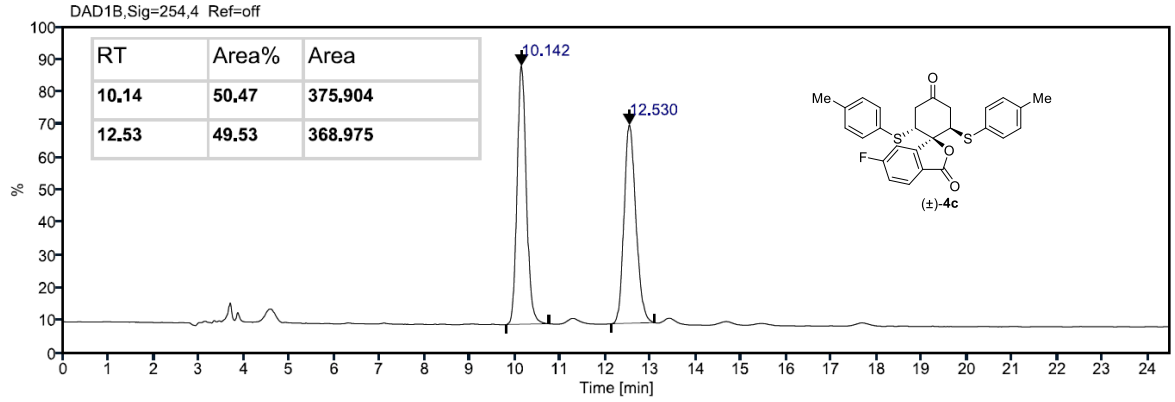
Acq. method: Chiralpak Ik column, Flow rate: 1.0 mL/min, Hexane : IPA = 70 : 30



RT	Area%	Area
17.09	40.09	711.043
21.58	59.91	1062.630

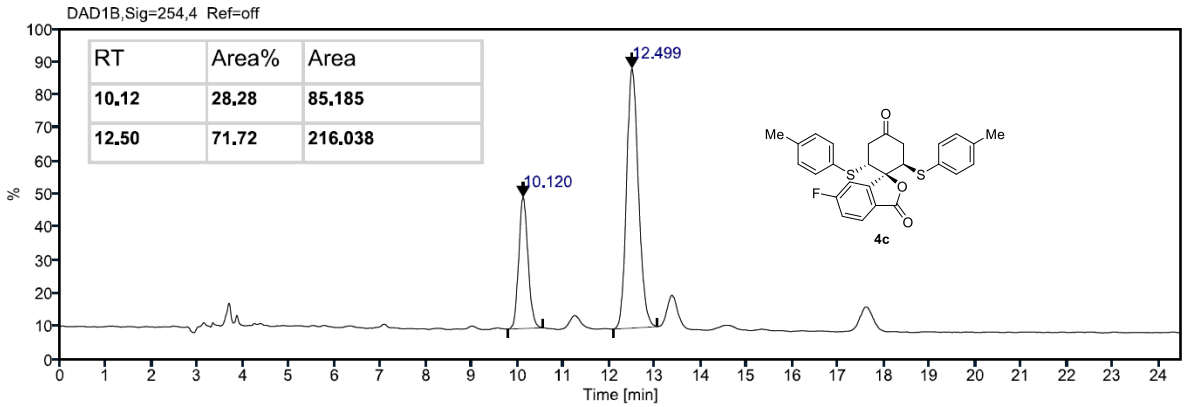
Sample ID: TC 802

Acq. method: Chiralpak IF column, Flow rate: 1.0 mL/min, Hexane : IPA = 70 : 30



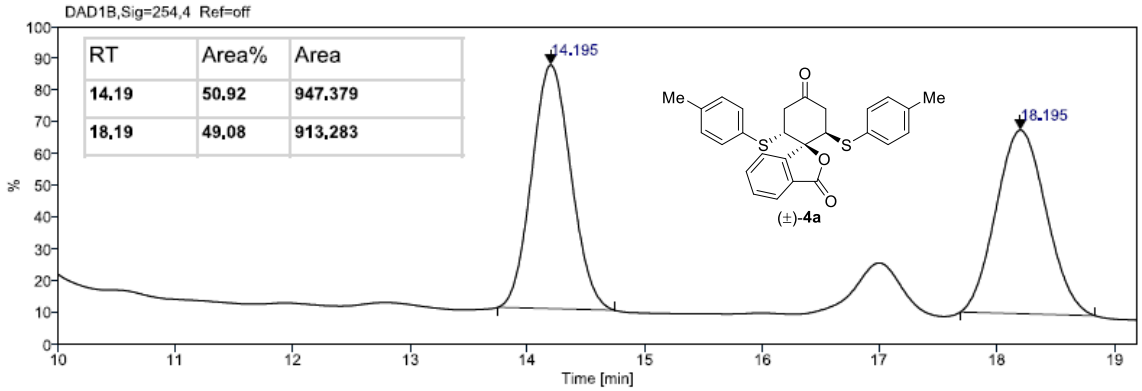
Sample ID: TC 789A

Acq. method: Chiralpak IF column, Flow rate: 1.0 mL/min, Hexane : IPA = 70 : 30



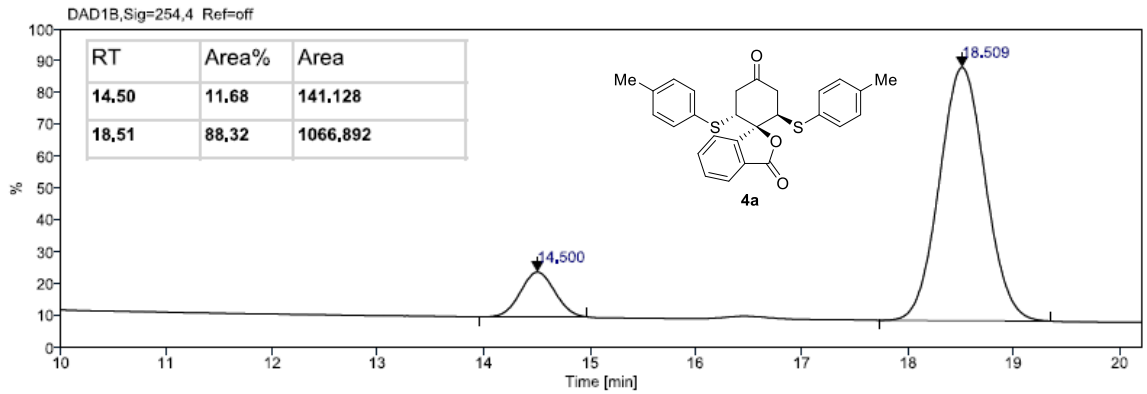
Sample ID: TC529A

Acq. method: Chiralpak IK column, Flow rate: 1.0 mL/min, Hexane : IPA = 70 : 30



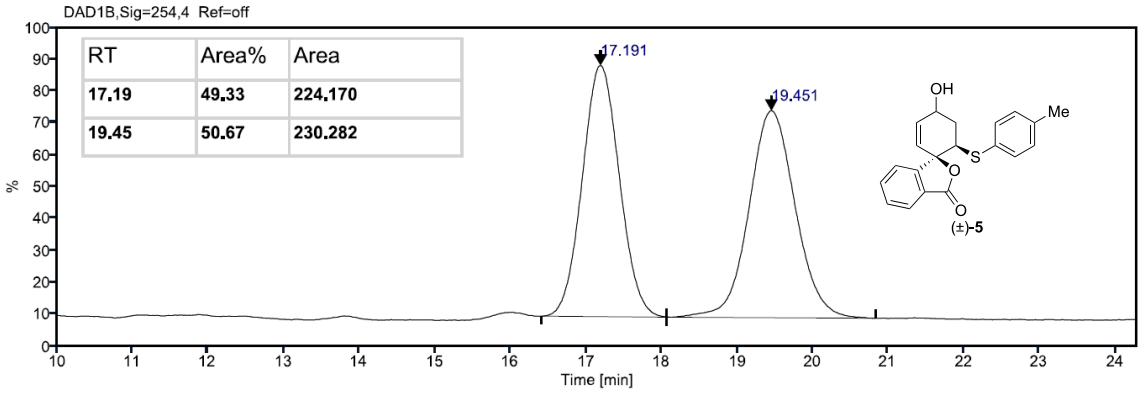
Sample ID: TC 705

Acq. method: Chiralpak IK column, Flow rate: 1.0 mL/min, Hexane : IPA = 70 : 30



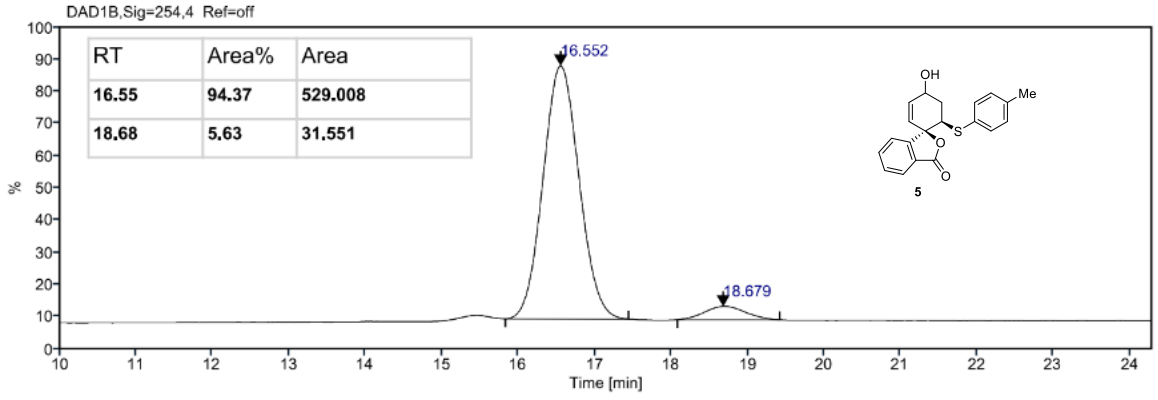
Sample ID: TC 748

Acq. method: Chiralpak IF column, Flow rate: 1.0 mL/min, Hexane : IPA = 70 : 30



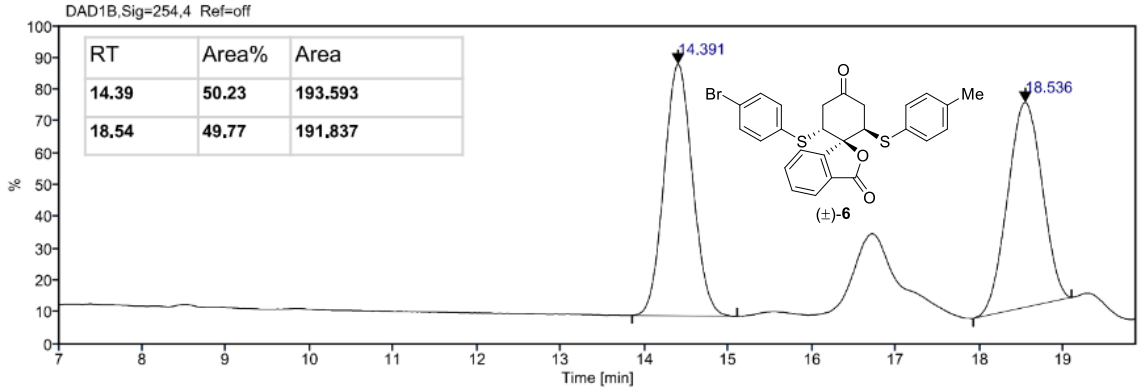
Sample ID: TC 836

Acq. method: Chiralpak IF column, Flow rate: 1.0 mL/min, Hexane : IPA = 70 : 30



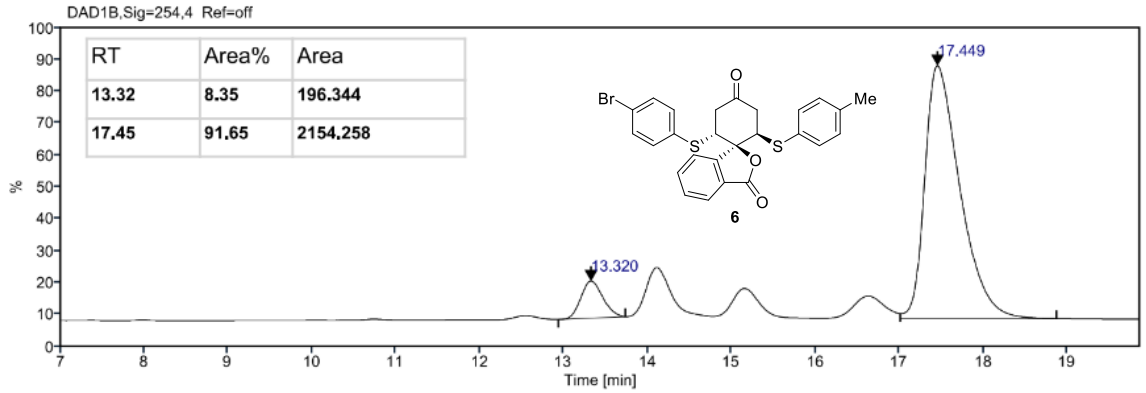
Sample ID: TC 749r2

Acq. method: Chiralpak IF column, Flow rate: 1.0 mL/min, Hexane : IPA = 70 : 30

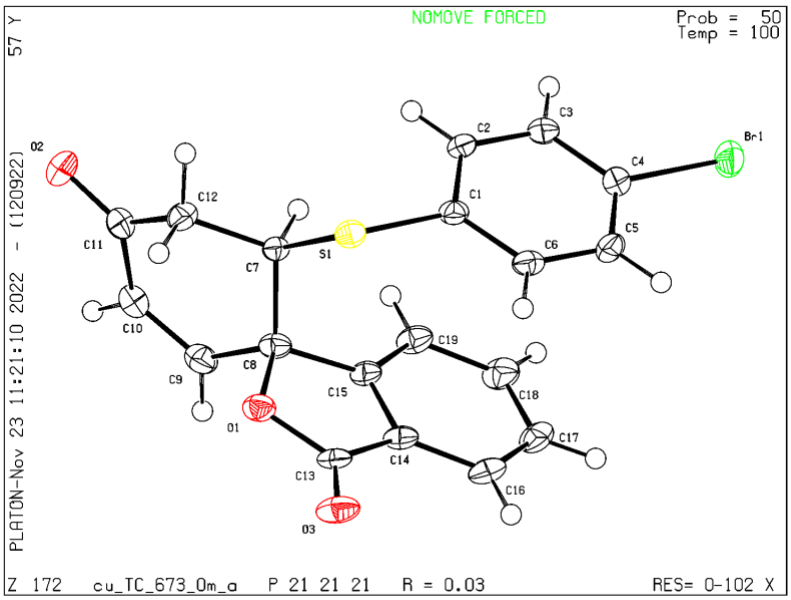


Sample ID: TC 778

Acq. method: Chiralpak IF column, Flow rate: 1.0 mL/min, Hexane : IPA = 70 : 30



Single Crystal X-ray Data of 3b:



cu_TC_673_0m_a

Table 1 Crystal data and structure refinement for cu_TC_673_0m_a.

Identification code	cu_TC_673_0m_a
Empirical formula	$C_{19}H_{13}BrO_3S$
Formula weight	401.26
Temperature/K	100(2)
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	7.6268(5)
b/Å	9.3115(7)
c/Å	24.2573(18)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	1722.7(2)
Z	4
ρ_{calc}g/cm^3	1.547
μ/mm^{-1}	4.504
F(000)	808.0
Crystal size/mm^3	? × ? × ?
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	7.288 to 133.008
Index ranges	-9 ≤ h ≤ 9, -10 ≤ k ≤ 11, -28 ≤ l ≤ 22
Reflections collected	15973
Independent reflections	3008 [R_{int} = 0.0511, R_{sigma} = 0.0335]
Data/restraints/parameters	3008/0/217
Goodness-of-fit on F^2	1.076
Final R indexes [I>=2σ (I)]	R_1 = 0.0252, wR_2 = 0.0632
Final R indexes [all data]	R_1 = 0.0261, wR_2 = 0.0641
Largest diff. peak/hole / e Å^{-3}	0.61/-0.38
Flack parameter	0.139(10)

Table 2 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for cu_TC_673_0m_a. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
Br1	3138.2(5)	9615.5(4)	3946.6(2)	34.59(14)
S1	10410.8(10)	6112.6(8)	4087.1(3)	19.25(18)
O1	10722(3)	3608(3)	3281.6(9)	22.1(5)
O2	10709(4)	1393(3)	5117.6(10)	33.4(6)
O3	11321(3)	4770(3)	2488.3(9)	29.7(6)
C1	8379(4)	7052(3)	4056.9(13)	18.7(6)
C2	7126(5)	6926(4)	4472.7(13)	21.6(7)
C3	5560(5)	7672(4)	4436.3(14)	23.4(7)
C4	5282(4)	8569(3)	3988.1(14)	23.3(7)
C5	6502(5)	8710(4)	3569.5(13)	22.8(7)
C6	8061(5)	7950(3)	3605.5(13)	19.7(6)
C7	9667(4)	4278(3)	4203.7(12)	16.5(6)
C8	9235(4)	3476(4)	3664.3(13)	19.2(7)
C9	8949(5)	1898(4)	3770.9(15)	23.9(7)
C10	9408(4)	1247(4)	4239.6(14)	24.0(7)
C11	10394(5)	1977(4)	4678.2(14)	24.5(7)
C12	11026(5)	3477(4)	4550.6(14)	23.0(7)
C13	10258(4)	4445(4)	2834.6(12)	20.9(7)
C14	8382(4)	4785(4)	2879.9(13)	20.3(7)
C15	7749(4)	4184(3)	3357.5(13)	19.0(7)
C16	7337(4)	5613(4)	2532.4(14)	25.2(7)
C17	5597(5)	5788(4)	2683.5(14)	27.5(8)
C18	4932(4)	5159(4)	3160.6(15)	27.5(8)
C19	6000(4)	4347(4)	3510.7(14)	23.1(7)

Table 3 Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for cu_TC_673_0m_a. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Br1	36.7(2)	39.6(2)	27.4(2)	7.25(17)	5.46(16)	18.60(17)
S1	19.1(3)	20.8(4)	17.8(4)	-0.7(3)	-0.7(3)	-2.3(3)
O1	19.5(11)	28.9(12)	17.9(11)	-2.7(10)	2.5(9)	1.7(9)
O2	45.9(16)	31.7(13)	22.6(13)	6.7(11)	-5.5(12)	8.5(12)
O3	24.6(12)	47.9(15)	16.5(11)	-4.5(12)	4.5(10)	-4.4(11)
C1	23.1(15)	18.3(14)	14.6(15)	-2.9(12)	-1.7(12)	-1.2(13)
C2	31.3(18)	21.2(15)	12.2(14)	0.2(12)	-1.5(14)	3.1(15)
C3	29.3(17)	26.1(17)	14.8(15)	0.6(13)	5.2(14)	4.5(15)
C4	27.8(16)	21.7(15)	20.3(16)	-2.1(14)	-3.1(15)	6.0(13)
C5	31.7(18)	20.4(15)	16.5(15)	4.2(13)	-1.6(13)	1.5(15)
C6	26.2(16)	18.3(14)	14.6(15)	-0.7(12)	1.9(14)	-4.2(14)
C7	17.6(14)	18.5(15)	13.4(14)	-0.8(12)	0.6(12)	1.2(12)
C8	17.4(15)	24.6(16)	15.7(15)	-2.5(13)	2.7(12)	-1.7(13)
C9	25.4(16)	22.3(16)	24.1(17)	-6.0(14)	0.2(14)	0.8(14)
C10	24.3(16)	20.4(16)	27.4(17)	-2.2(15)	1.8(14)	3.3(14)
C11	23.9(16)	26.2(17)	23.4(17)	-0.8(15)	1.7(14)	8.7(15)
C12	23.5(16)	28.1(18)	17.6(16)	-0.8(14)	-3.8(14)	3.2(14)
C13	24.1(16)	28.0(17)	10.7(14)	-5.7(13)	-0.5(13)	-1.7(15)
C14	21.3(15)	25.6(16)	14.1(14)	-5.3(13)	-1.6(12)	-4.6(14)
C15	20.4(16)	22.0(16)	14.6(15)	-3.6(12)	-4.0(12)	-2.2(12)
C16	29.3(17)	32.2(18)	14.0(15)	-2.1(14)	-4.5(13)	-5.2(15)
C17	27.1(17)	35.9(19)	19.6(17)	-0.7(15)	-9.8(14)	1.4(15)
C18	19.1(16)	40(2)	23.1(17)	-3.8(16)	-5.0(13)	0.0(14)
C19	19.0(15)	33.1(19)	17.3(15)	-1.2(15)	-1.0(12)	-4.0(14)

Table 4 Bond Lengths for cu_TC_673_0m_a.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Br1	C4	1.906(3)	C7	C8	1.542(4)
S1	C1	1.781(3)	C8	C15	1.507(4)
S1	C7	1.822(3)	C8	C9	1.508(5)
O1	C13	1.381(4)	C9	C10	1.336(5)
O1	C8	1.471(4)	C10	C11	1.470(5)
O2	C11	1.221(4)	C11	C12	1.510(5)
O3	C13	1.206(4)	C13	C14	1.469(5)
C1	C2	1.395(5)	C14	C15	1.374(5)
C1	C6	1.399(4)	C14	C16	1.393(5)
C2	C3	1.384(5)	C15	C19	1.393(5)
C3	C4	1.388(5)	C16	C17	1.386(5)
C4	C5	1.383(5)	C17	C18	1.393(5)
C5	C6	1.386(5)	C18	C19	1.399(5)
C7	C12	1.529(4)			

Table 5 Bond Angles for cu_TC_673_0m_a.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C1	S1	C7	101.31(14)	C9	C8	C7	110.9(3)
C13	O1	C8	110.2(2)	C10	C9	C8	123.4(3)
C2	C1	C6	119.8(3)	C9	C10	C11	122.7(3)
C2	C1	S1	121.7(2)	O2	C11	C10	121.8(3)
C6	C1	S1	118.5(2)	O2	C11	C12	121.9(3)
C3	C2	C1	120.2(3)	C10	C11	C12	116.3(3)
C2	C3	C4	119.0(3)	C11	C12	C7	110.3(3)
C5	C4	C3	121.9(3)	O3	C13	O1	121.1(3)
C5	C4	Br1	119.3(2)	O3	C13	C14	130.7(3)
C3	C4	Br1	118.7(3)	O1	C13	C14	108.2(3)
C4	C5	C6	118.8(3)	C15	C14	C16	122.3(3)
C5	C6	C1	120.2(3)	C15	C14	C13	108.5(3)
C12	C7	C8	112.1(3)	C16	C14	C13	129.1(3)
C12	C7	S1	109.4(2)	C14	C15	C19	121.1(3)
C8	C7	S1	112.9(2)	C14	C15	C8	109.3(3)
O1	C8	C15	103.4(3)	C19	C15	C8	129.5(3)
O1	C8	C9	107.5(3)	C17	C16	C14	116.9(3)
C15	C8	C9	113.7(3)	C16	C17	C18	121.3(3)
O1	C8	C7	109.3(2)	C17	C18	C19	121.3(3)
C15	C8	C7	111.6(3)	C15	C19	C18	117.0(3)

Table 6 Torsion Angles for cu_TC_673_0m_a.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
C7	S1	C1	C2	52.5(3)	C9	C10	C11	C12	-5.8(5)
C7	S1	C1	C6	-128.3(3)	O2	C11	C12	C7	-144.5(3)
C6	C1	C2	C3	0.8(5)	C10	C11	C12	C7	36.8(4)
S1	C1	C2	C3	180.0(3)	C8	C7	C12	C11	-57.0(4)
C1	C2	C3	C4	-1.6(5)	S1	C7	C12	C11	177.0(2)
C2	C3	C4	C5	1.8(5)	C8	O1	C13	O3	175.0(3)
C2	C3	C4	Br1	-179.1(3)	C8	O1	C13	C14	-5.4(3)
C3	C4	C5	C6	-1.2(5)	O3	C13	C14	C15	-179.0(3)
Br1	C4	C5	C6	179.6(2)	O1	C13	C14	C15	1.5(4)
C4	C5	C6	C1	0.4(5)	O3	C13	C14	C16	-1.5(6)
C2	C1	C6	C5	-0.3(5)	O1	C13	C14	C16	178.9(3)
S1	C1	C6	C5	-179.4(2)	C16	C14	C15	C19	1.7(5)
C1	S1	C7	C12	-148.3(2)	C13	C14	C15	C19	179.3(3)
C1	S1	C7	C8	86.2(2)	C16	C14	C15	C8	-174.8(3)
C13	O1	C8	C15	6.8(3)	C13	C14	C15	C8	2.9(4)
C13	O1	C8	C9	127.4(3)	O1	C8	C15	C14	-5.9(3)
C13	O1	C8	C7	-112.1(3)	C9	C8	C15	C14	-122.1(3)
C12	C7	C8	O1	-72.8(3)	C7	C8	C15	C14	111.5(3)
S1	C7	C8	O1	51.2(3)	O1	C8	C15	C19	178.1(3)
C12	C7	C8	C15	173.5(3)	C9	C8	C15	C19	61.8(5)
S1	C7	C8	C15	-62.5(3)	C7	C8	C15	C19	-64.6(4)
C12	C7	C8	C9	45.6(4)	C15	C14	C16	C17	-1.2(5)
S1	C7	C8	C9	169.6(2)	C13	C14	C16	C17	-178.4(3)
O1	C8	C9	C10	105.1(4)	C14	C16	C17	C18	-0.1(5)
C15	C8	C9	C10	-141.1(3)	C16	C17	C18	C19	1.1(6)
C7	C8	C9	C10	-14.4(5)	C14	C15	C19	C18	-0.7(5)
C8	C9	C10	C11	-6.0(5)	C8	C15	C19	C18	174.9(3)
C9	C10	C11	O2	175.4(3)	C17	C18	C19	C15	-0.6(5)

Table 7 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for cu_TC_673_0m_a.

Atom	*x*	*y*	*z*	U(eq)
H2	7346.72	6325.92	4781.75	26
H3	4689.99	7570.79	4713.78	28
H5	6275.38	9315.87	3262.67	27
H6	8915.56	8039.92	3322.82	24
H7	8563.18	4330.72	4425.06	20
H9	8413.67	1338.28	3489.99	29
H10	9085.05	270.65	4291.59	29
H12A	12149.87	3426.94	4347.08	28
H12B	11233.03	4005.1	4898.8	28
H16	7795.64	6038.07	2206.88	30
H17	4843.99	6346.83	2457.2	33
H18	3729.39	5284.81	3250.18	33
H19	5552.46	3924.84	3838.31	28