Supplementary Information

BINOL-derived bifunctional sulfide catalysts for asymmetric synthesis of 3,3-disubstituted phthalides via bromolactonization

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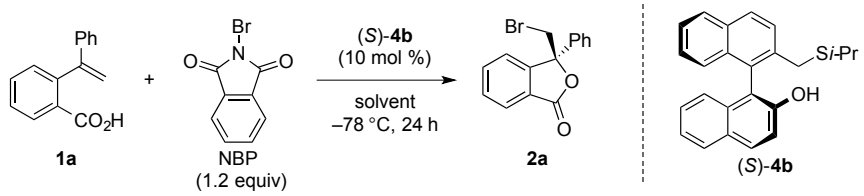
General Information

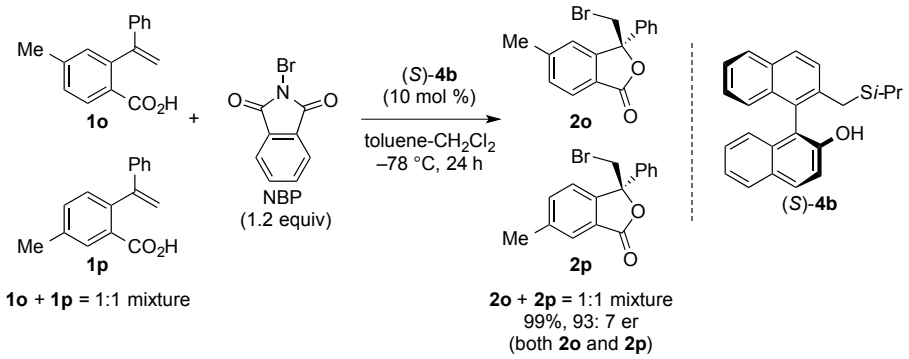
^{1}H and ^{13}C NMR spectra were measured on a JEOL JNM-AL 400 NMR instrument (400 MHz for ^{1}H NMR and 100 MHz for ^{13}C NMR). Tetramethylsilane (TMS) served as the internal standard (0 ppm) for ^{1}H NMR, and $CDCl_3$ served as the internal standard (77.0 ppm) for ^{13}C NMR. The following abbreviations were used to express the multiplicities: s = singlet; d = doublet; t = triplet; m = multiplet; br = broad. High-resolution mass spectra (HRMS) were measured on a JEOL JMS-700N. Infrared spectra (IR) were measured on a JASCO FT/IR-4200 spectrometer. Optical rotations were measured on a JASCO P-2100 polarimeter. High performance liquid chromatography (HPLC) was performed on Shimadzu LC-20AT and SPD-20A instruments using Daicel Chiralpak IA-3, IB-3, IC-3, IE-3, or Chiralcel OD-3 columns (4.6 mm × 250 mm). All reactions were monitored by thin-layer chromatography using Merck precoated TLC plates (silica gel 60GF-254, 0.25 mm), with visualization by the use of UV lamp (254 nm), or dyes such as $KMnO_4$. The products were purified by flash column chromatography on silica gel. Dehydrated solvents were purchased from Kanto Chemical.

Table S1 Optimization of the reaction solvents[a]



Entry	Solvent	Yield[b] (%)	er[c]
1	CH_2Cl_2 (2 mL)	99	78:22
2	toluene (2 mL)	88	80:20
3	hexane (1 mL)-CH_2Cl_2 (1 mL)	91	85:15
4	toluene (1 mL)-CH_2Cl_2 (1 mL)	94	91: 9
5	toluene (1.5 mL)-CH_2Cl_2 (0.5 mL)	98	94: 6

[a] Reaction conditions: **1a** (0.10 mmol), NBP (0.12 mmol), (*S*)-**4b** (10 mol %, 0.010 mmol), solvent (2 mL), –78 °C, 24 h. [b] Yield of isolated product **2a**. [c] Determined by HPLC analysis on a chiral stationary phase.



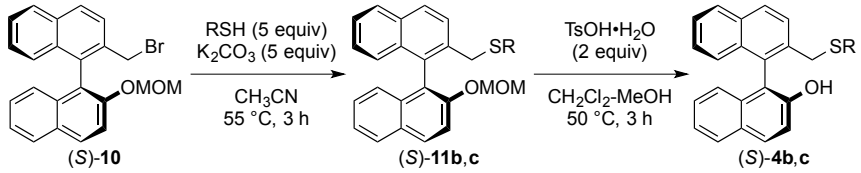
Scheme S1 Additional substrate scope.

Experimental Section

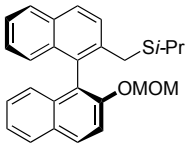
1. Synthesis of catalysts.

Catalysts (*S*)-**3a**, **4a**, and **5a** were prepared according to the literature.[1]

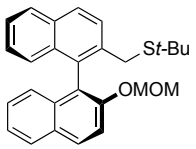
Synthesis of catalysts (*S*)-4b and 4c.



To a solution of (*S*)-**10**[2] (1.4 mmol) in CH_3CN (7 mL) was added K_2CO_3 (7.0 mmol) and RSH (7.0 mmol). The mixture was then warmed to 55 °C and stirred for 3 h. The mixture was cooled to room temperature and quenched by saturated aqueous NH_4Cl. The resulting solution was extracted with ethyl acetate for three times. The organic extracts were dried over Na_2SO_4 and evaporated. The residue was purified by flash column chromatography on silica gel (hexane/ethyl acetate = 100:1–30:1 as eluent) to afford (*S*)-**11**.

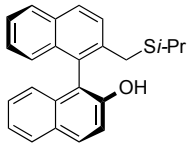


(*S*)-**11b**: 96% yield. $[\alpha]^{22}_D$ –82.0 (*c* = 1.3, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93–7.98 (m, 2H), 7.83–7.90 (m, 3H), 7.60 (d, *J* = 9.2 Hz, 1H), 7.41 (dt, *J* = 1.2, 7.6 Hz, 1H), 7.35 (t, *J* = 0.8, 7.6 Hz, 1H), 7.15–7.24 (m, 3H), 7.04 (d, *J* = 8.8 Hz, 1H), 5.10 (d, *J* = 6.8 Hz, 1H), 4.97 (d, *J* = 7.2 Hz, 1H), 3.56 (d, *J* = 13.6 Hz, 1H), 3.51 (d, *J* = 14.0 Hz, 1H), 3.16 (s, 3H), 2.58 (septet, *J* = 6.8 Hz, 1H), 0.97 (d, *J* = 6.8 Hz, 3H), 0.86 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.6, 135.8, 134.0, 133.0, 132.6, 132.5, 129.74, 129.67, 128.0, 127.9, 127.3, 126.5, 126.4, 126.0, 125.6, 125.4, 124.1, 122.1, 116.5, 94.9, 55.9, 34.8, 33.2, 23.15, 23.06; IR (neat): 3056, 2957, 2923, 1507, 1245, 1149, 1066, 1033, 1013, 814, 751 cm^{-1}; HRMS (FAB) calcd for $C_{26}H_{26}O_2S$: 402.1654 ($[M]^+$), found 402.1654.

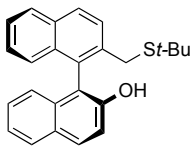


(*S*)-**11c**: 96% yield. $[\alpha]^{22}_{D}$ –96.5 (*c* = 1.5, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86–7.97 (m, 4H), 7.78 (d, *J* = 8.0 Hz, 1H), 7.61 (d, *J* = 9.2 Hz, 1H), 7.40 (dt, *J* = 1.2, 7.2 Hz, 1H), 7.34 (t, *J* = 1.2, 7.6 Hz, 1H), 7.16–7.24 (m, 3H), 7.05 (d, *J* = 8.4 Hz, 1H), 5.10 (d, *J* = 7.2 Hz, 1H), 4.98 (d, *J* = 6.8 Hz, 1H), 3.55 (d, *J* = 12.0 Hz, 1H), 3.50 (d, *J* = 12.4 Hz, 1H), 3.17 (s, 3H), 1.01 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.5, 135.0, 133.8, 133.0, 132.6, 132.5, 129.5, 127.9, 127.8, 127.7, 127.5, 126.3, 126.1, 125.8, 125.6, 125.2, 123.9, 122.0, 116.3, 94.8, 55.7, 42.3, 31.3, 30.3; IR (neat): 3056, 2958, 2898, 1148, 1033, 1013, 905, 812, 728 cm^{-1}; HRMS (FAB) calcd for $C_{27}H_{28}O_2S$: 416.1810 ($[M]^+$), found 416.1809.

To a solution of (*S*)-**11** (1.3 mmol) in CH_2Cl_2 (4 mL)-MeOH (4 mL) was added *p*-toluenesulfonic acid monohydrate (2.6 mmol), and the mixture was heated at 50 °C for 3 h. After cooled to room temperature, water was added to this reaction mixture and the mixture was evaporated to remove MeOH. Organic compounds were extracted with CH_2Cl_2 for three times. The combined organic layer was dried over Na_2SO_4 and concentrated. The residue was purified by flash column chromatography on silica gel (hexane/ethyl acetate = 100:1–10:1 as eluent) to afford (*S*)-**4**.



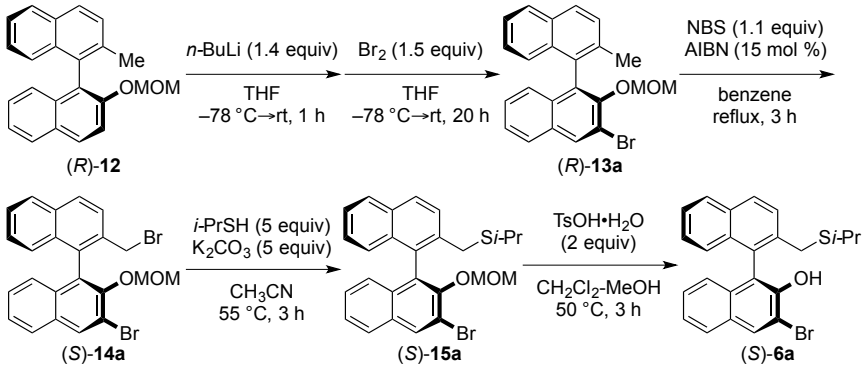
(*S*)-**4b**: 85% yield. $[\alpha]^{22}_{D}$ –94.2 (*c* = 0.90, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.0 Hz, 1H), 7.91–7.94 (m, 2H), 7.87 (d, *J* = 8.4 Hz, 1H), 7.75 (d, *J* = 8.8 Hz, 1H), 7.47 (dt, *J* = 1.2, 7.4 Hz, 1H), 7.28–7.38 (m, 3H), 7.18–7.24 (m, 2H), 6.95 (d, *J* = 8.4 Hz, 1H), 5.09 (s, 1H), 3.64 (d, *J* = 12.8 Hz, 1H), 3.48 (d, *J* = 13.2 Hz, 1H), 2.65 (septet, *J* = 6.6 Hz, 1H), 1.03 (d, *J* = 6.8 Hz, 3H), 1.00 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.4, 137.8, 133.7, 133.2, 133.0, 130.1, 129.5, 129.3, 129.1, 128.13, 128.09, 127.7, 127.0, 126.7, 126.1, 125.9, 124.6, 123.5, 118.2, 117.3, 35.5, 33.2, 23.1, 22.9; IR (neat): 3421, 3057, 2958, 2924, 1507, 1203, 1173, 1146, 911, 818, 749 cm^{-1}; HRMS (FAB) calcd for $C_{24}H_{22}OS$: 358.1391 ($[M]^+$), found 358.1389.



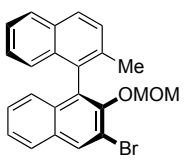
(*S*)-**4c**: 54% yield. $[\alpha]^{22}_{D}$ –50.8 (*c* = 1.1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.8 Hz, 1H), 7.86–7.93 (m, 3H), 7.70 (d, *J* = 8.8 Hz, 1H), 7.46 (dt, *J* = 1.2, 7.4 Hz, 1H), 7.16–7.38 (m, 5H), 6.95 (d, *J* =

8.8 Hz, 1H), 3.66 (d, J = 10.8 Hz, 1H), 3.49 (d, J = 10.4 Hz, 1H), 1.08 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.6, 136.7, 133.7, 133.3, 133.1, 129.93, 129.88, 129.3, 129.2, 128.1, 128.0, 127.8, 126.9, 126.6, 126.1, 125.9, 124.7, 123.5, 118.6, 117.6, 43.3, 31.5, 30.3; IR (neat): 3394, 3056, 2959, 1507, 1457, 1363, 1203, 1171, 1146, 818, 750 cm^{-1}; HRMS (FAB) calcd for $C_{25}H_{24}OS$: 372.1548 ([M]$^+$), found 372.1550.

Synthesis of catalysts (*S*)-6a.



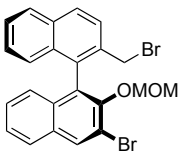
To a solution of (*R*)-**12**[3] (0.60 mmol) in THF (3 mL) was added 1.6 M hexane solution of *n*-BuLi (0.84 mmol) dropwise at –78 °C under N_2 atmosphere. The mixture was then warmed to room temperature and stirred for 1 h. The mixture was again cooled to –78 °C, and to the solution was added Br_2 (0.90 mmol). The mixture was then warmed to room temperature and stirred for 20 h. After cooled to 0 °C, saturated aqueous Na_2SO_3 was added to this reaction mixture and the mixture was evaporated to remove THF. Organic compounds were extracted with ethyl acetate for three times. The combined organic layer was dried over Na_2SO_4 and concentrated. The residue was purified by flash column chromatography on silica gel (hexane/ethyl acetate = 100:1–10:1 as eluent) to afford (*R*)-**13a**.



(*R*)-**13a**: 64% yield. $[\alpha]^{22}_D$ –23.6 (c = 0.93, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (s, 1H), 7.81–7.89 (m, 3H), 7.50 (d, J = 8.4 Hz, 1H), 7.38–7.44 (m, 2H), 7.22–7.28 (m, 2H), 7.15 (d, J = 8.4 Hz, 1H), 7.06 (d, J = 7.2 Hz, 1H), 4.78 (d, J = 5.2 Hz, 1H), 4.65 (d, J = 5.6 Hz, 1H), 2.62 (s, 3H), 2.15 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.0, 135.7, 133.2, 132.7, 132.4, 131.9, 131.7, 131.5, 130.4, 128.5, 128.1, 127.8, 127.0, 126.8, 126.3, 126.01, 125.96, 125.92,

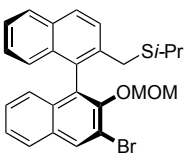
124.9, 117.7, 98.7, 56.5, 20.5; IR (neat): 3051, 2949, 2922, 1233, 1157, 1076, 987, 957, 919, 902, 812, 745 cm^{-1}; HRMS (FAB) calcd for $C_{23}H_{19}BrO_2$: 406.0568 ($[M]^+$), found 406.0568.

A mixture of (*R*)-**13a** (0.50 mmol), *N*-bromosuccinimide (NBS) (0.55 mmol), and 2,2'-azobis(isobutyronitrile) (AIBN) (0.075 mmol) in benzene (5 mL) was refluxed for 3 h. After cooled to room temperature, water was added to this reaction mixture. Organic compounds were extracted with ethyl acetate for three times. The combined organic layer was dried over Na_2SO_4 and concentrated. The residue was purified by flash column chromatography on silica gel (hexane/ethyl acetate = 100:1–10:1 as eluent) to afford (*S*)-**14a**.



(*S*)-**14a**: 88% yield. $[\alpha]^{22}_D$ +42.6 (*c* = 1.7, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (s, 1H), 7.99 (d, *J* = 8.8 Hz, 1H), 7.90 (d, *J* = 8.0 Hz, 1H), 7.83 (d, *J* = 8.0 Hz, 1H), 7.76 (d, *J* = 8.8 Hz, 1H), 7.43–7.50 (m, 2H), 7.25–7.31 (m, 2H), 7.15 (d, *J* = 8.8 Hz, 1H), 7.07 (d, *J* = 8.8 Hz, 1H), 4.82 (d, *J* = 6.0 Hz, 1H), 4.69 (d, *J* = 6.0 Hz, 1H), 4.45 (d, *J* = 10.8 Hz, 1H), 4.30 (d, *J* = 10.4 Hz, 1H), 2.56 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.3, 134.7, 133.2, 133.0, 132.9, 132.7, 132.4, 131.6, 129.2, 128.5, 127.9, 127.5, 126.94, 126.90, 126.8, 126.7, 126.6, 126.5, 126.3, 117.4, 99.0, 56.4, 32.7; IR (neat): 3056, 2951, 1233, 1203, 1157, 991, 958, 930, 904, 821, 748, 730 cm^{-1}; HRMS (FAB) calcd for $C_{23}H_{19}Br_2O_2$: 484.9752 ($[M+H]^+$), found 484.9752.

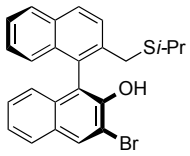
(*S*)-**15a** was synthesized from (*S*)-**14a** in a similar manner for the synthesis of (*S*)-**11b**.



(*S*)-**15a**: 99% yield. $[\alpha]^{21}_D$ +14.2 (*c* = 0.48, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (s, 1H), 7.95 (d, *J* = 8.8 Hz, 1H), 7.80–7.89 (m, 3H), 7.40–7.45 (m, 2H), 7.22–7.28 (m, 2H), 7.15 (d, *J* = 8.8 Hz, 1H), 7.08 (d, *J* = 8.8 Hz, 1H), 4.78 (d, *J* = 5.6 Hz, 1H), 4.61 (d, *J* = 5.6 Hz, 1H), 3.68 (d, *J* = 13.6 Hz, 1H), 3.50 (d, *J* = 13.6 Hz, 1H), 2.60 (s, 3H), 2.52 (septet, *J* = 6.8 Hz, 1H), 0.97 (d, *J* = 6.8 Hz, 3H), 0.80 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.1,

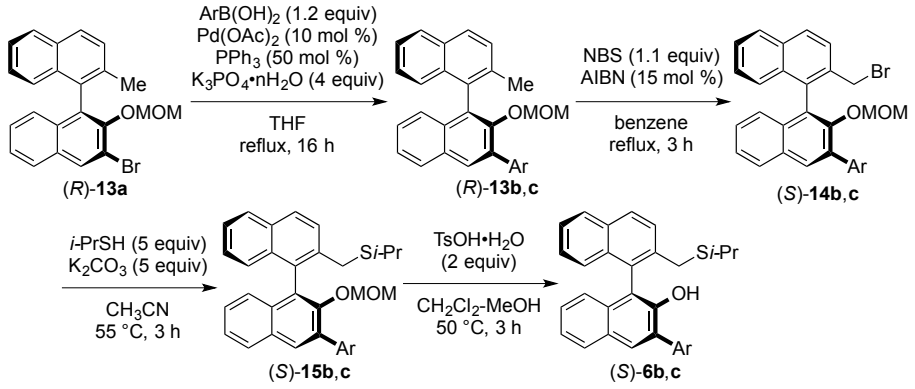
136.5, 133.1, 132.8, 132.4, 131.6, 131.5, 129.4, 128.6, 127.9, 127.3, 126.9, 126.7, 126.5, 126.4, 126.1, 125.6, 117.5, 98.8, 56.5, 35.0, 33.3, 23.0, 22.9; IR (neat): 3053, 2960, 2923, 1158, 991, 957, 814, 750 cm^{-1}; HRMS (FAB) calcd for $C_{26}H_{25}BrO_2S$: 480.0759 ($[M]^+$), found 480.0758.

Catalyst (*S*)-**6a** was synthesized from (*S*)-**15a** in a similar manner for the synthesis of catalyst (*S*)-**4b**.



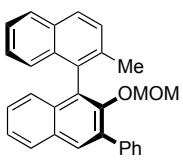
(*S*)-**6a**: 71% yield. $[\alpha]^{22}_D$ –62.6 (*c* = 1.6, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 8.29 (s, 1H), 8.00 (d, *J* = 8.4 Hz, 1H), 7.92 (d, *J* = 8.0 Hz, 1H), 7.76–7.80 (m, 2H), 7.46 (t, *J* = 7.2 Hz, 1H), 7.35 (t, *J* = 7.2 Hz, 1H), 7.21–7.30 (m, 2H), 7.14 (d, *J* = 8.4 Hz, 1H), 6.95 (d, *J* = 8.4 Hz, 1H), 5.58 (s, 1H), 3.60 (d, *J* = 13.2 Hz, 1H), 3.47 (d, *J* = 13.2 Hz, 1H), 2.63 (septet, *J* = 6.6 Hz, 1H), 1.02 (d, *J* = 6.8 Hz, 3H), 0.98 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.6, 137.1, 133.0, 132.9, 132.7, 132.1, 129.8, 129.6, 129.3, 128.1, 127.5, 127.1, 127.0, 126.9, 126.0, 125.7, 125.0, 124.6, 119.3, 112.6, 35.4, 33.1, 23.0, 22.9; IR (neat): 3502, 3056, 2958, 2922, 1507, 1359, 1263, 1200, 1147, 909, 824, 815, 748, 735 cm^{-1}; HRMS (FAB) calcd for $C_{24}H_{21}BrOS$: 436.0496 ($[M]^+$), found 436.0496.

Synthesis of catalysts (*S*)-6b and 6c.

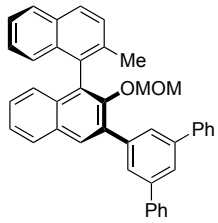


A mixture of (*R*)-**13a** (0.30 mmol), $ArB(OH)_2$ (0.36 mmol), $Pd(OAc)_2$ (0.030 mmol), PPh_3 (0.15 mmol), and K_3PO_4•nH_2O (1.2 mmol) in THF (5 mL) was refluxed for 16 h. The mixture was cooled to room temperature and quenched by saturated aqueous

NH_4Cl. The mixture was evaporated to remove THF. The resulting solution was extracted with ethyl acetate for three times. The organic extracts were dried over Na_2SO_4 and evaporated. The residue was purified by flash column chromatography on silica gel (hexane/ethyl acetate = 100:1–10:1 as eluent) to afford (*R*)-**13b** or **13c**.

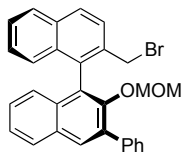


(*R*)-**13b**: 89% yield. $[\alpha]^{21}_D$ –47.9 (*c* = 2.4, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86–7.96 (m, 4H), 7.71–7.73 (m, 2H), 7.22–7.53 (m, 9H), 7.11 (d, *J* = 8.0 Hz, 1H), 4.29 (d, *J* = 6.0 Hz, 1H), 4.23 (d, *J* = 5.6 Hz, 1H), 2.26 (s, 3H), 2.24 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.5, 139.0, 135.6, 133.4, 132.9, 132.5, 132.0, 131.0, 130.3, 129.6, 128.9, 128.6, 128.3, 128.0, 127.8, 127.7, 127.2, 126.4, 126.2, 126.0, 125.8, 125.2, 124.8, 98.4, 55.9, 20.7; IR (neat): 3054, 2923, 1156, 1076, 987, 964, 925, 813, 750, 701 cm^{-1}; HRMS (FAB) calcd for $C_{29}H_{24}O_2$: 404.1776 ($[M]^+$), found 404.1777.



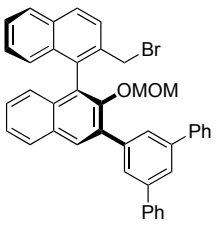
(*R*)-**13c**: 77% yield. $[\alpha]^{21}_D$ –59.6 (*c* = 1.4, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (s, 1H), 7.82–7.95 (m, 6H), 7.71–7.73 (m, 4H), 7.24–7.54 (m, 12H), 7.11 (d, *J* = 8.4 Hz, 1H), 4.40 (d, *J* = 6.4 Hz, 1H), 4.34 (d, *J* = 6.4 Hz, 1H), 2.30 (s, 3H), 2.26 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.7, 141.8, 141.0, 140.1, 135.6, 135.4, 133.4, 133.0, 132.4, 132.0, 131.0, 130.4, 129.0, 128.8, 128.6, 128.1, 127.79, 127.75, 127.50, 127.46, 127.3, 126.5, 126.3, 126.0, 125.8, 125.3, 125.0, 124.8, 98.6, 55.9, 20.7; IR (neat): 3051, 2972, 1168, 1157, 989, 966, 755, 704, 690 cm^{-1}; HRMS (FAB) calcd for $C_{41}H_{32}O_2$: 556.2402 ($[M]^+$), found 556.2402.

(*S*)-**14b** and **14c** were synthesized from (*R*)-**13b** or **13c** in a similar manner for the synthesis of (*S*)-**14a**.



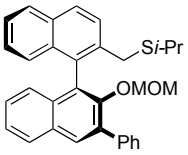
(*S*)-**14b**: 97% yield. $[\alpha]^{20}_D$ +44.1 (*c* = 1.2, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88–8.00 (m, 4H), 7.79 (d, *J* = 8.4 Hz, 1H), 7.71–7.73 (m, 2H), 7.24–7.49 (m, 8H), 7.11 (d, *J* = 8.8 Hz, 1H), 4.52 (d, *J* = 10.4 Hz, 1H), 4.46 (d, *J* = 10.4 Hz, 1H), 4.29 (d, *J* = 6.0 Hz, 1H), 4.23 (d, *J* = 6.4 Hz, 1H), 2.23 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.8, 138.7, 135.2, 134.5, 133.5,

133.1, 133.0, 131.1, 130.9, 129.5, 128.7, 128.4, 127.94, 127.87, 127.6, 127.4, 127.1, 127.0, 126.6, 126.5, 126.33, 126.28, 125.5, 98.5, 55.9, 33.0; IR (neat): 3055, 2952, 2898, 1155, 990, 966, 750, 701 cm^{-1}; HRMS (FAB) calcd for $C_{29}H_{23}BrO_2$: 482.0881 ($[M]^+$), found 482.0884.

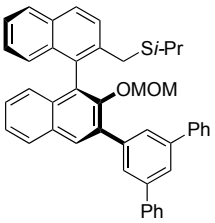


(*S*)-**14c**: 87% yield. $[\alpha]^{25}_D$ +18.1 (*c* = 2.3, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 8.11 (s, 1H), 7.89–7.99 (m, 5H), 7.71–7.83 (m, 6H), 7.25–7.50 (m, 11H), 7.12 (d, *J* = 8.8 Hz, 1H), 4.54 (d, *J* = 10.4 Hz, 1H), 4.48 (d, *J* = 10.8 Hz, 1H), 4.40 (d, *J* = 6.0 Hz, 1H), 4.34 (d, *J* = 6.4 Hz, 1H), 2.26 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.9, 141.9, 140.9, 139.7, 135.0, 134.6, 133.5, 133.10, 133.05, 131.2, 130.9, 128.83, 128.77, 127.95, 127.86, 127.6, 127.5, 127.32, 127.27, 127.12, 127.08, 126.61, 126.58, 126.3, 125.6, 125.1, 98.7, 55.9, 33.1; IR (neat): 3056, 2954, 2929, 1155, 1073, 1001, 968, 752, 739, 698 cm^{-1}; HRMS (FAB) calcd for $C_{41}H_{31}BrO_2Na$: 657.1405 ($[M+Na]^+$), found 657.1413.

(*S*)-**15b** and **15c** were synthesized from (*S*)-**14b** or **14c** in a similar manner for the synthesis of (*S*)-**11b**.

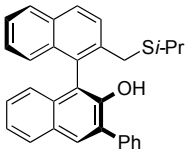


(*S*)-**15b**: 78% yield. $[\alpha]^{21}_D$ +45.5 (*c* = 1.5, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.86–7.97 (m, 5H), 7.71–7.73 (m, 2H), 7.35–7.48 (m, 5H), 7.21–7.29 (m, 3H), 7.12 (d, *J* = 8.4 Hz, 1H), 4.27 (d, *J* = 5.6 Hz, 1H), 4.21 (d, *J* = 5.6 Hz, 1H), 3.80 (d, *J* = 14.0 Hz, 1H), 3.69 (d, *J* = 13.6 Hz, 1H), 2.56 (septet, *J* = 6.8 Hz, 1H), 2.20 (s, 3H), 1.01 (d, *J* = 6.4 Hz, 3H), 0.82 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.6, 138.9, 136.4, 135.4, 133.32, 133.27, 132.5, 130.9, 130.7, 129.5, 128.3, 128.2, 127.90, 127.87, 127.80, 127.31, 127.27, 126.9, 126.33, 126.26, 126.1, 125.4, 125.3, 98.4, 55.8, 35.0, 33.5, 23.1, 23.0; IR (neat): 3054, 2957, 2925, 1156, 990, 965, 752, 701 cm^{-1}; HRMS (FAB) calcd for $C_{32}H_{30}O_2S$: 478.1967 ($[M]^+$), found 478.1966.

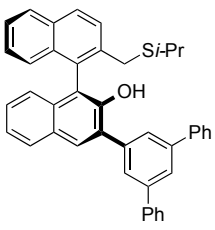


(*S*)-**15c**: 65% yield. $[\alpha]^{24}_{D}$ +22.3 (*c* = 1.9, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (s, 1H), 7.82–7.96 (m, 7H), 7.72–7.74 (m, 4H), 7.37–7.50 (m, 8H), 7.22–7.31 (m, 3H), 7.13 (d, *J* = 8.4 Hz, 1H), 4.37 (d, *J* = 6.0 Hz, 1H), 4.32 (d, *J* = 5.6 Hz, 1H), 3.82 (d, *J* = 14.4 Hz, 1H), 3.70 (d, *J* = 13.6 Hz, 1H), 2.60 (septet, *J* = 6.8 Hz, 1H), 2.24 (s, 3H), 1.04 (d, *J* = 6.8 Hz, 3H), 0.85 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.8, 141.9, 141.0, 139.9, 136.4, 135.2, 133.4, 133.3, 132.5, 130.9, 130.8, 128.8, 128.2, 127.99, 127.96, 127.8, 127.5, 127.4, 127.3, 126.9, 126.4, 126.3, 126.2, 125.45, 125.41, 125.0, 98.6, 55.9, 35.1, 33.6, 23.2, 23.1; IR (neat): 3056, 2956, 2924, 1154, 1000, 966, 912, 882, 752, 738, 697 cm^{-1}; HRMS (FAB) calcd for $C_{44}H_{39}O_2S$: 631.2671 ($[M+H]^+$), found 631.2673.

Catalyst (*S*)-**6b** and **6c** were synthesized from (*S*)-**15b** or **15c** in a similar manner for the synthesis of catalyst (*S*)-**4b**.



(*S*)-**6b**: 61% yield. $[\alpha]^{22}_{D}$ –87.7 (*c* = 0.50, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89–8.02 (m, 4H), 7.72–7.81 (m, 3H), 7.30–7.52 (m, 7H), 7.23 (dt, *J* = 1.6, 7.6 Hz, 1H), 6.97 (d, *J* = 8.4 Hz, 1H), 5.18 (s, 1H), 3.66 (d, *J* = 13.2 Hz, 1H), 3.55 (d, *J* = 13.2 Hz, 1H), 2.65 (septet, *J* = 6.8 Hz, 1H), 1.02 (d, *J* = 6.8 Hz, 3H), 0.97 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.9, 137.9, 137.7, 133.2, 133.1, 130.8, 130.2, 129.9, 129.6, 129.3, 129.1, 128.4, 128.1, 127.7, 127.5, 126.9, 126.6, 126.1, 125.9, 124.6, 123.9, 118.0, 35.3, 33.2, 23.1, 23.0; IR (neat): 3521, 3055, 2969, 1739, 1427, 1362, 1231, 751, 701 cm^{-1}; HRMS (FAB) calcd for $C_{30}H_{26}OS$: 434.1704 ($[M]^+$), found 434.1703.

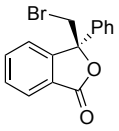


(*S*)-**6c**: 97% yield. $[\alpha]^{19}_{D}$ –37.5 (*c* = 0.74, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (s, 1H), 8.02 (d, *J* = 8.4 Hz, 1H), 7.91–7.96 (m, 4H), 7.79–7.84 (m, 2H), 7.71–7.73 (m, 4H), 7.45–7.50 (m, 5H), 7.32–7.40 (m, 5H), 7.23–7.27 (m, 1H), 6.99 (d, *J* = 8.0 Hz, 1H), 5.27 (s, 1H), 3.68 (d, *J* = 13.2 Hz, 1H), 3.57 (d, *J* = 12.8 Hz, 1H), 2.69 (septet, *J* = 6.8 Hz, 1H), 1.04 (d, *J* = 6.8 Hz, 3H), 0.99 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.9, 141.9, 141.1, 138.9, 137.8, 133.3, 133.1, 130.6, 130.3, 129.8, 129.4,

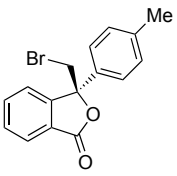
129.2, 128.8, 128.21, 128.18, 127.7, 127.6, 127.5, 127.4, 127.0, 126.8, 126.2, 125.9, 125.3, 124.6, 124.0, 118.2, 35.4, 33.3, 23.1, 23.0; IR (neat): 3525, 3057, 2960, 2925, 1742, 1709, 1507, 1227, 1159, 838, 738 cm^{-1}; HRMS (FAB) calcd for $C_{42}H_{34}OS$: 586.2330 ($[M]^+$), found 586.2330.

2. General procedure for asymmetric bromolactonizations.

To a solution of substrate **1**[4] (0.10 mmol) and catalyst (*S*)-**4b** (10 mol %, 0.010 mmol) in toluene (1.5 mL)-CH_2Cl_2 (0.5 mL) was cooled to –78 °C. After stirring for 10 min at –78 °C, *N*-bromophthalimide (NBP) (0.12 mmol) was added to the cooled reaction solution. The reaction mixture was stirred for 24 h at –78 °C. After 24 h, the reaction mixture was quenched with saturated aqueous Na_2SO_3 (4.0 mL) at –78 °C and stirred for 10 min at –78 °C. The quenched reaction mixture was diluted with CH_2Cl_2 (2 mL) and H_2O (2 mL), and warmed to room temperature. The organic materials were extracted with CH_2Cl_2 for three times (5.0 mL × 3). The combined extracts were dried over Na_2SO_4 and concentrated. The residue was purified by flash column chromatography on silica gel (hexane/ethyl acetate = 30:1–5:1 as eluent) to give product **2**. The enantioselectivity of the product **2** was determined by HPLC analysis on a chiral stationary phase.

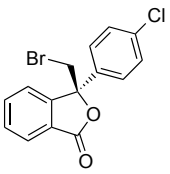


2a:[5] $[\alpha]^{23}_D$ +1.1 (*c* = 1.8, $CHCl_3$, 96:4 er); HPLC analysis: Daicel Chiralpak IC-3, hexane/2-propanol = 2:1, flow rate = 0.5 mL/min, 254 nm; retention time: 15.1 min (major) and 16.9 min (minor). ^1H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 7.6 Hz, 1H), 7.75 (dt, *J* = 1.2, 7.6 Hz, 1H), 7.67 (d, *J* = 7.2 Hz, 1H), 7.56–7.62 (m, 3H), 7.35–7.43 (m, 3H), 4.15 (d, *J* = 11.2 Hz, 1H), 4.09 (d, *J* = 11.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.9, 149.7, 137.4, 134.3, 129.9, 129.1, 129.0, 126.5, 126.0, 125.4, 122.5, 87.2, 37.9; IR (neat): 1766, 1287, 1086, 983, 754, 698 cm^{-1}.

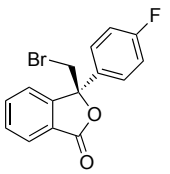


2b: $[\alpha]^{24}_D$ –5.0 (*c* = 0.96, $CHCl_3$, 90:10 er); HPLC analysis: Daicel Chiralpak IC-3, hexane/2-propanol = 2:1, flow rate = 0.5 mL/min, 254 nm; retention time: 17.5 min (major) and 19.3 min (minor). ^1H NMR (400 MHz, $CDCl_3$) δ 7.93 (dd, *J* = 0.8, 8.0 Hz, 1H), 7.73 (dt, *J* = 0.8, 7.6 Hz,

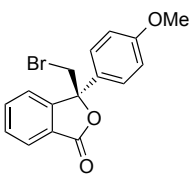
1H), 7.65 (dd, *J* = 0.8, 7.6 Hz, 1H), 7.58 (dt, *J* = 0.8, 7.6 Hz, 1H), 7.44 (d, *J* = 8.4 Hz, 2H), 7.20 (d, *J* = 8.0 Hz, 2H), 4.13 (d, *J* = 11.2 Hz, 1H), 4.07 (d, *J* = 11.2 Hz, 1H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.0, 149.9, 139.2, 134.4, 134.3, 129.9, 129.6, 126.5, 125.9, 125.4, 122.5, 87.3, 37.9, 21.0; IR (neat): 1763, 1286, 1082, 981, 819, 756, 718, 688 cm^{-1}; HRMS (FAB) calcd for $C_{16}H_{14}BrO_2$: 317.0177 ($[M+H]^+$), found 317.0177.



2c: $[\alpha]^{21}_D$ +1.8 (*c* = 1.2, $CHCl_3$, 91:9 er); HPLC analysis: Daicel Chiralpak IC-3, hexane/2-propanol = 5:1, flow rate = 0.5 mL/min, 254 nm; retention time: 21.6 min (major) and 23.4 min (minor). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 7.6 Hz, 1H), 7.76 (dt, *J* = 1.2, 7.6 Hz, 1H), 7.65 (d, *J* = 8.0 Hz, 1H), 7.61 (dt, *J* = 0.8, 7.2 Hz, 1H), 7.51 (d, *J* = 8.8 Hz, 2H), 7.38 (d, *J* = 8.8 Hz, 2H), 4.10 (d, *J* = 11.6 Hz, 1H), 4.04 (d, *J* = 11.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.6, 149.3, 136.0, 135.3, 134.5, 130.2, 129.2, 127.0, 126.3, 126.2, 122.5, 86.7, 37.5; IR (neat): 1765, 1492, 1286, 1080, 982, 829, 759, 686 cm^{-1}; HRMS (FAB) calcd for $C_{15}H_{11}BrClO_2$: 336.9631 ($[M+H]^+$), found 336.9632.

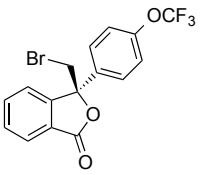


2d: $[\alpha]^{22}_D$ –13.0 (*c* = 2.3, $CHCl_3$, 93:7 er); HPLC analysis: Daicel Chiralpak IC-3, hexane/2-propanol = 2:1, flow rate = 0.5 mL/min, 254 nm; retention time: 14.1 min (major) and 14.9 min (minor). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 7.6 Hz, 1H), 7.76 (dt, *J* = 1.2, 7.6 Hz, 1H), 7.60–7.67 (m, 2H), 7.52–7.57 (m, 2H), 7.06–7.12 (m, 2H), 4.11 (d, *J* = 11.2 Hz, 1H), 4.05 (d, *J* = 11.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.6, 162.9 (d, *J* = 249 Hz), 149.5, 134.4, 133.3 (d, *J* = 3.3 Hz), 130.1, 127.6 (d, *J* = 9.1 Hz), 126.5, 126.1, 122.6, 116.0 (d, *J* = 21.4 Hz), 86.8, 37.7; IR (neat): 1764, 1508, 1232, 1081, 983, 837, 689 cm^{-1}; HRMS (FAB) calcd for $C_{15}H_{11}BrFO_2$: 320.9926 ($[M+H]^+$), found 320.9925.

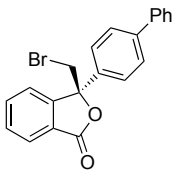


2e: $[\alpha]^{22}_D$ –18.9 (*c* = 1.6, $CHCl_3$, 82:18 er); HPLC analysis: Daicel Chiralpak IC-3, hexane/2-propanol = 2:1, flow rate = 0.5 mL/min, 254 nm; retention time: 22.7 min (major) and 26.0 min (minor). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 7.2 Hz, 1H), 7.75 (dt, *J* = 0.8, 7.2 Hz, 1H), 7.64 (d, *J* = 7.6 Hz, 1H), 7.60 (dt, *J* = 0.8, 7.2 Hz, 1H), 7.46 (d, *J* = 8.8 Hz, 2H), 6.91 (d, *J* = 8.8 Hz, 2H), 4.12 (d, *J* = 12.0 Hz, 1H), 4.06 (d, *J* = 11.2 Hz, 1H), 3.80 (s, 3H); ^{13}C

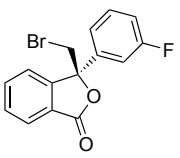
NMR (100 MHz, $CDCl_3$) δ 168.9, 160.1, 149.9, 134.2, 129.9, 129.3, 127.0, 126.7, 126.0, 122.6, 114.2, 87.2, 55.3, 37.9; IR (neat): 1763, 1608, 1511, 1466, 1285, 1254, 1180, 1084, 1031, 982, 832, 729, 689 cm^{-1}; HRMS (FAB) calcd for $C_{16}H_{14}BrO_3$: 333.0126 ($[M+H]^+$), found 333.0126.



2f: $[\alpha]^{20}_D$ –4.0 (*c* = 1.2, $CHCl_3$, 96:4 er); HPLC analysis: Daicel Chiralcel OD-3, hexane/2-propanol = 4:1, flow rate = 0.5 mL/min, 254 nm; retention time: 14.2 min (major) and 17.5 min (minor). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (dd, *J* = 0.8, 7.6 Hz, 1H), 7.77 (t, *J* = 7.6 Hz, 1H), 7.68 (d, *J* = 7.6 Hz, 1H), 7.61–7.65 (m, 3H), 7.26 (d, *J* = 8.8 Hz, 2H), 4.11 (d, *J* = 11.2 Hz, 1H), 4.06 (d, *J* = 11.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.5, 149.6, 149.3, 136.1, 134.6, 130.2, 127.3, 126.4, 126.2, 122.5, 121.2, 120.3 (q, *J* = 257 Hz), 86.6, 37.5; IR (neat): 1773, 1257, 1167, 1083, 984, 760 cm^{-1}; HRMS (FAB) calcd for $C_{16}H_{11}BrF_3O_3$: 386.9844 ($[M+H]^+$), found 386.9844.

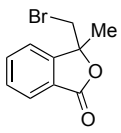


2g: $[\alpha]^{25}_D$ +3.9 (*c* = 1.0, $CHCl_3$, 88:12 er); HPLC analysis: Daicel Chiralpak IC-3, hexane/2-propanol = 2:1, flow rate = 0.5 mL/min, 254 nm; retention time: 18.6 min (major) and 21.5 min (minor). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (dd, *J* = 0.8, 7.6 Hz, 1H), 7.76 (dt, *J* = 0.8, 7.6 Hz, 1H), 7.70 (d, *J* = 8.0 Hz, 1H), 7.54–7.65 (m, 7H), 7.42–7.46 (m, 2H), 7.36 (dt, *J* = 1.6, 7.6 Hz, 1H), 4.18 (d, *J* = 11.2 Hz, 1H), 4.12 (d, *J* = 11.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.9, 149.7, 142.1, 139.9, 136.3, 134.4, 130.0, 128.9, 127.8, 127.6, 127.1, 126.5, 126.0, 125.9, 122.5, 87.2, 37.8; IR (neat): 1766, 1286, 1083, 983, 765, 731, 695 cm^{-1}; HRMS (FAB) calcd for $C_{21}H_{16}BrO_2$: 379.0334 ($[M+H]^+$), found 379.0334.

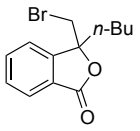


2h: $[\alpha]^{19}_D$ +3.6 (*c* = 0.63, $CHCl_3$, 93:7 er); HPLC analysis: Daicel Chiralpak IC-3, hexane/2-propanol = 2:1, flow rate = 0.5 mL/min, 254 nm; retention time: 12.4 min (major) and 14.5 min (minor). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 7.6 Hz, 1H), 7.76 (dt, *J* = 0.8, 7.6 Hz, 1H), 7.60–7.67 (m, 2H), 7.35–7.42 (m, 2H), 7.26–7.30 (m, 1H), 7.05–7.10 (m, 1H), 4.11 (d, *J* = 11.2 Hz, 1H), 4.05 (d, *J* = 11.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.5, 162.8 (d, *J* = 247 Hz), 149.3, 140.0 (d, *J* = 6.6 Hz), 134.5, 130.7 (d, *J* = 8.3 Hz), 130.2, 126.4, 126.2, 122.5,

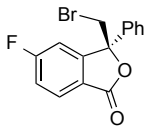
121.1 (d, J = 3.3 Hz), 116.2 (d, J = 21.4 Hz), 113.0 (d, J = 23.9 Hz), 86.6, 37.5; IR (neat): 1767, 1285, 1084, 963, 756, 701 cm^{-1}; HRMS (FAB) calcd for $C_{15}H_{11}BrFO_2$: 320.9926 ($[M+H]^+$), found 320.9926.



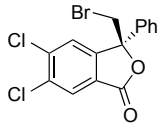
2i:[5] HPLC analysis: Daicel Chiralpak IC-3, hexane/2-propanol = 2:1, flow rate = 0.5 mL/min, 254 nm; retention time: 17.6 min (major) and 20.1 min (minor). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, J = 7.6 Hz, 1H), 7.71 (dt, J = 0.8, 7.2 Hz, 1H), 7.58 (dt, J = 1.2, 7.6 Hz, 1H), 7.52 (dd, J = 0.8, 7.6 Hz, 1H), 3.75 (d, J = 11.2 Hz, 1H), 3.72 (d, J = 11.2 Hz, 1H), 1.83 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.9, 151.1, 134.3, 129.8, 126.2, 125.9, 121.4, 84.5, 37.8, 24.2; IR (neat): 1756, 1286, 1100, 1031, 764, 696 cm^{-1}.



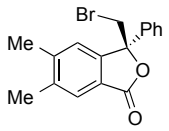
2j: HPLC analysis: Daicel Chiralpak IC-3, hexane/2-propanol = 2:1, flow rate = 0.5 mL/min, 254 nm; retention time: 12.9 min (major) and 14.1 min (minor). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (dd, J = 0.8, 8.0 Hz, 1H), 7.71 (dt, J = 0.8, 7.6 Hz, 1H), 7.57 (dt, J = 0.8, 7.6 Hz, 1H), 7.49 (d, J = 7.6 Hz, 1H), 3.76 (d, J = 10.4 Hz, 1H), 3.73 (d, J = 10.8 Hz, 1H), 2.17–2.24 (m, 1H), 1.99–2.07 (m, 1H), 1.21–1.35 (m, 3H), 0.91–1.02 (m, 1H), 0.83 (t, J = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.2, 150.1, 134.2, 129.7, 126.9, 125.8, 121.6, 87.0, 37.0, 36.4, 25.4, 22.5, 13.7; IR (neat): 2957, 2932, 2871, 1760, 1466, 1286, 1077, 969, 765, 698 cm^{-1}; HRMS (FAB) calcd for $C_{13}H_{16}BrO_2$: 283.0334 ($[M+H]^+$), found 283.0332.



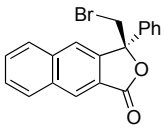
2k: $[\alpha]^{23}_D$ –3.2 (c = 1.0, $CHCl_3$, 91:9 er); HPLC analysis: Daicel Chiralpak IB-3, hexane/2-propanol = 10:1, flow rate = 0.5 mL/min, 254 nm; retention time: 23.6 min (minor) and 24.9 min (major). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (dd, J = 4.8, 8.4 Hz, 1H), 7.52–7.55 (m, 2H), 7.39–7.45 (m, 3H), 7.28–7.34 (m, 2H), 4.12 (d, J = 11.2 Hz, 1H), 4.08 (d, J = 11.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.8, 166.4 (d, J = 243 Hz), 152.5 (d, J = 9.0 Hz), 137.0, 129.4, 129.1, 128.3 (d, J = 10.7 Hz), 125.3, 122.7 (d, J = 1.7 Hz), 118.2 (d, J = 23.9 Hz), 110.1 (d, J = 24.7 Hz), 86.6, 37.4; IR (neat): 2956, 2923, 2851, 1774, 1290, 1262, 1077, 700 cm^{-1}; HRMS (FAB) calcd for $C_{15}H_{11}BrFO_2$: 320.9926 ($[M+H]^+$), found 320.9928.



2l: $[\alpha]^{18}_{D}$ –34.5 (*c* = 1.1, $CHCl_3$, 82:18 er); HPLC analysis: Daicel Chiralpak IE-3, hexane/2-propanol = 10:1, flow rate = 0.5 mL/min, 254 nm; retention time: 25.4 min (minor) and 27.7 min (major). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (s, 1H), 7.74 (s, 1H), 7.50–7.52 (m, 2H), 7.40–7.46 (m, 3H), 4.12 (d, *J* = 11.2 Hz, 1H), 4.08 (d, *J* = 11.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.6, 148.8, 139.4, 136.5, 135.2, 129.6, 129.2, 127.5, 126.4, 125.2, 124.6, 86.9, 37.3; IR (neat): 1774, 1448, 1386, 1300, 1274, 1181, 1087, 991, 957, 893, 762, 701, 636 cm^{-1}; HRMS (FAB) calcd for $C_{15}H_{10}BrCl_2O_2$: 370.9241 ($[M+H]^+$), found 370.9239.



2m: $[\alpha]^{23}_{D}$ –9.4 (*c* = 1.9, $CHCl_3$, 90:10 er); HPLC analysis: Daicel Chiralpak IC-3, hexane/2-propanol = 2:1, flow rate = 0.5 mL/min, 254 nm; retention time: 21.4 min (major) and 23.2 min (minor). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (s, 1H), 7.54–7.57 (m, 2H), 7.34–7.42 (m, 4H), 4.12 (d, *J* = 11.6 Hz, 1H), 4.05 (d, *J* = 11.2 Hz, 1H), 2.42 (s, 3H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.2, 147.9, 144.6, 139.3, 137.9, 128.95, 128.90, 126.2, 125.4, 124.4, 123.2, 86.8, 38.1, 21.0, 20.0; IR (neat): 1765, 1090, 763, 748, 695 cm^{-1}; HRMS (FAB) calcd for $C_{17}H_{16}BrO_2$: 331.0334 ($[M+H]^+$), found 331.0333.

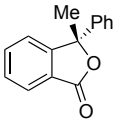


2n: $[\alpha]^{22}_{D}$ –77.6 (*c* = 1.0, $CHCl_3$, 88:12 er); HPLC analysis: Daicel Chiralpak IE-3, hexane/2-propanol = 4:1, flow rate = 0.5 mL/min, 254 nm; retention time: 38.5 min (minor) and 41.9 min (major). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51 (s, 1H), 7.99–8.07 (m, 3H), 7.56–7.70 (m, 4H), 7.35–7.44 (m, 3H), 4.23 (d, *J* = 11.2 Hz, 1H), 4.19 (d, *J* = 11.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.8, 143.6, 138.0, 136.1, 133.4, 129.9, 129.3, 129.1, 129.0, 128.6, 127.5, 127.4, 125.5, 124.0, 121.8, 87.4, 38.6; IR (neat): 1762, 1169, 1087, 1075, 980, 765, 747, 737, 697, 659 cm^{-1}; HRMS (FAB) calcd for $C_{19}H_{14}BrO_2$: 353.0177 ($[M+H]^+$), found 353.0179.

3. Conversions of product 2a.

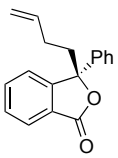
To a solution of product **2a** (0.10 mmol) in toluene (5 mL) was added 2,2'-azobis(isobutyronitrile) (AIBN) (0.010 mmol) and tributyltin hydride (0.30 mmol). The reaction mixture was warmed to 100 °C and stirred for 24 h. After 24 h, the reaction

mixture was cooled to room temperature and quenched with saturated aqueous $NaHCO_3$ (10 mL). The organic materials were extracted with ethyl acetate for three times (5.0 mL × 3). The combined extracts were dried over Na_2SO_4 and concentrated. The residue was purified by flash column chromatography on silica gel (hexane/ethyl acetate = 70:1–10:1 as eluent) to give product **7**.



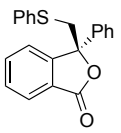
7:[6] $[\alpha]^{28}_D$ +61.3 (*c* = 0.97, $CHCl_3$, 96:4 er); HPLC analysis: Daicel Chiralpak IC-3, hexane/2-propanol = 2:1, flow rate = 0.5 mL/min, 254 nm; retention time: 15.7 min (major) and 16.8 min (minor). ^1H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 7.6 Hz, 1H), 7.66 (dt, *J* = 0.8, 7.2 Hz, 1H), 7.52 (t, *J* = 7.2 Hz, 1H), 7.44–7.48 (m, 3H), 7.30–7.38 (m, 3H), 2.05 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.9, 154.2, 140.7, 134.3, 129.1, 128.7, 128.3, 125.8, 125.1, 122.0, 87.5, 27.3; IR (neat): 1756, 1286, 1267, 1027, 768, 755, 694 cm^{-1}.

To a solution of product **2a** (0.10 mmol) in benzene (2 mL) was added 2,2'-azobis(isobutyronitrile) (AIBN) (0.30 mmol) and allyltributyltin (1.0 mmol). The reaction mixture was warmed to 80 °C and stirred for 24 h. After 24 h, the reaction mixture was cooled to room temperature and quenched with saturated aqueous $NaHCO_3$ (10 mL). The organic materials were extracted with ethyl acetate for three times (5.0 mL × 3). The combined extracts were dried over Na_2SO_4 and concentrated. The residue was purified by flash column chromatography on silica gel (hexane/ethyl acetate = 70:1–10:1 as eluent) to give product **8**.



8: $[\alpha]^{21}_D$ +92.5 (*c* = 1.7, $CHCl_3$, 96:4 er); HPLC analysis: Daicel Chiralpak IC-3, hexane/2-propanol = 2:1, flow rate = 0.5 mL/min, 254 nm; retention time: 11.4 min (major) and 12.2 min (minor). ^1H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 7.6 Hz, 1H), 7.67 (dt, *J* = 1.2, 7.6 Hz, 1H), 7.50–7.56 (m, 4H), 7.28–7.39 (m, 3H), 5.68–5.78 (m, 1H), 4.90–4.96 (m, 2H), 2.54–2.62 (m, 1H), 2.25–2.32 (m, 1H), 1.99–2.08 (m, 1H), 1.84–1.94 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.0, 152.7, 140.3, 137.0, 134.3, 129.2, 128.8, 128.1, 125.9, 125.5, 124.9, 122.1, 115.2, 89.7, 39.4, 28.0; IR (neat): 3065, 2920, 1761, 1286, 1089, 772, 752, 700 cm^{-1}; HRMS (FAB) calcd for $C_{18}H_{17}O_2$: 265.1229 ($[M+H]^+$), found 265.1228.

To a solution of product **2a** (0.10 mmol) in CH_3CN (1 mL) was added K_2CO_3 (0.20 mmol) and thiophenol (0.30 mmol). The reaction mixture was warmed to 75 °C and stirred for 24 h. After 24 h, the reaction mixture was cooled to room temperature and quenched with saturated aqueous NH_4Cl (5 mL). The organic materials were extracted with ethyl acetate for three times (5.0 mL × 3). The combined extracts were dried over Na_2SO_4 and concentrated. The residue was purified by flash column chromatography on silica gel (hexane/ethyl acetate = 30:1–5:1 as eluent) to give product **9**.



9: $[\alpha]^{22}_D$ +34.7 (*c* = 2.5, $CHCl_3$, 96:4 er); HPLC analysis: Daicel Chiralpak IC-3, hexane/2-propanol = 2:1, flow rate = 0.5 mL/min, 254 nm; retention time: 18.7 min (major) and 22.7 min (minor). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92–7.94 (m, 1H), 7.47–7.54 (m, 4H), 7.32–7.40 (m, 4H), 7.12–7.20 (m, 5H), 3.90 (d, *J* = 14.0 Hz, 1H), 3.86 (d, *J* = 14.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.4, 150.3, 139.1, 135.8, 133.8, 131.2, 129.5, 128.81, 128.80, 128.7, 127.0, 126.8, 125.7, 125.3, 122.7, 88.6, 46.3; IR (neat): 1761, 1285, 1086, 980, 740, 688 cm^{-1}; HRMS (FAB) calcd for $C_{21}H_{17}O_2S$: 333.0949 ($[M+H]^+$), found 333.0949.

4. Determination of the absolute configuration of products 2, 7, 8, and 9.

The absolute configurations of products **2**, **7**, **8**, and **9** were confirmed by comparison of an optical rotation value for product **7** with the literature.[6]

5. Details of computational method.

All calculations were performed with the Gaussian 09 package.[7] The transition structure was partially optimized at the B3LYP/6-31LAN (LANL2DZ for Br and 6-31G* for the rest) level. The structure around the reaction center was only frozen (forming C^1-O length: 2.33 Å, C^2-Br bond: 2.13 Å, C^1-C^2-Br angle: 102.3°) corresponding to the previous TS model[1] while the other moiety was fully optimized. For the major enantiomer, two possible plausible TS models (**TS-O** and **TS-N**) were investigated depending on the position of deprotonation by succinimide anion. **TS-N** is energetically more favored than

TS-O (Fig. S1). The molecular structures were depicted by using the CYLview v1.0.561 β.[8]

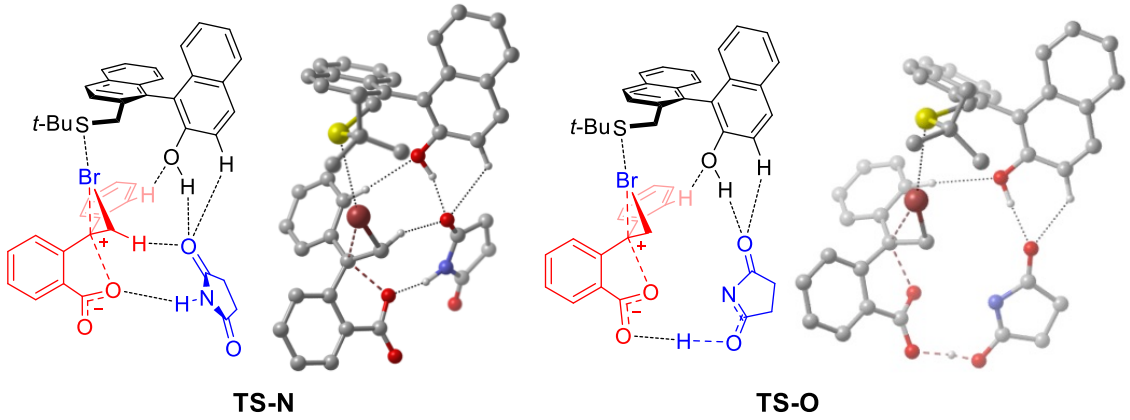


Fig. S1 3D structures of plausible TS models.

Cartesian coordination

TS-N

SCF Done: E(RB3LYP) = -2543.00706396 A.U.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.429662	3.631282	3.221177
2	6	0	2.630432	2.868687	2.091483
3	6	0	2.805187	1.458179	2.172968
4	6	0	2.786561	0.854864	3.473118
5	6	0	2.575190	1.667756	4.620180
6	6	0	2.395805	3.027290	4.501575
7	1	0	2.301132	4.706750	3.130671
8	1	0	2.662413	3.343584	1.117217
9	6	0	3.001304	0.637998	1.008437
10	6	0	2.991536	-0.543949	3.579884
11	1	0	2.564182	1.191717	5.598231
12	1	0	2.238955	3.639570	5.385725
13	6	0	3.188766	-1.309923	2.458453
14	6	0	3.180086	-0.738166	1.156026
15	1	0	2.993306	-1.003634	4.565574
16	1	0	3.345172	-2.379606	2.556235
17	6	0	3.046024	1.280779	-0.345161
18	6	0	4.289405	1.445568	-1.042019
19	6	0	1.876184	1.733786	-0.947978
20	6	0	5.538914	1.066388	-0.472602
21	6	0	4.303551	2.026321	-2.354861

22	6	0	1.893682	2.305503	-2.249161
23	6	0	6.719660	1.232652	-1.163825
24	1	0	5.554086	0.652675	0.530492
25	6	0	5.537181	2.178753	-3.041489
26	6	0	3.075237	2.440685	-2.932851
27	1	0	0.951764	2.620316	-2.690721
28	6	0	6.724784	1.788760	-2.465029
29	1	0	7.658485	0.938376	-0.701673
30	1	0	5.524919	2.616377	-4.037391
31	1	0	3.081581	2.872512	-3.930918
32	1	0	7.662516	1.911929	-2.999704
33	6	0	3.419972	-1.622995	-0.055243
34	1	0	3.034445	-1.134634	-0.950424
35	1	0	4.497300	-1.773792	-0.196104
36	16	0	2.624395	-3.283758	0.107771
37	6	0	3.288597	-4.220916	-1.370677
38	8	0	0.702249	1.628195	-0.270270
39	1	0	-0.028811	2.027720	-0.791016
40	6	0	2.521254	-5.553912	-1.337809
41	1	0	1.443563	-5.395688	-1.450320
42	1	0	2.860355	-6.192891	-2.162670
43	1	0	2.694951	-6.093250	-0.399929
44	6	0	4.795314	-4.478749	-1.217322
45	1	0	5.371002	-3.547139	-1.211599
46	1	0	5.011667	-5.022351	-0.292314
47	1	0	5.157262	-5.079868	-2.062267
48	6	0	-4.546877	4.275240	-1.510262
49	6	0	-3.564014	5.417583	-1.788956
50	6	0	-2.178499	4.754420	-1.808284
51	6	0	-2.455615	3.271496	-1.578488
52	7	0	-3.799003	3.089618	-1.434789
53	1	0	-3.832879	5.887723	-2.739960
54	1	0	-1.509255	5.114607	-1.019793
55	1	0	-3.675518	6.178978	-1.011425
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TS-O

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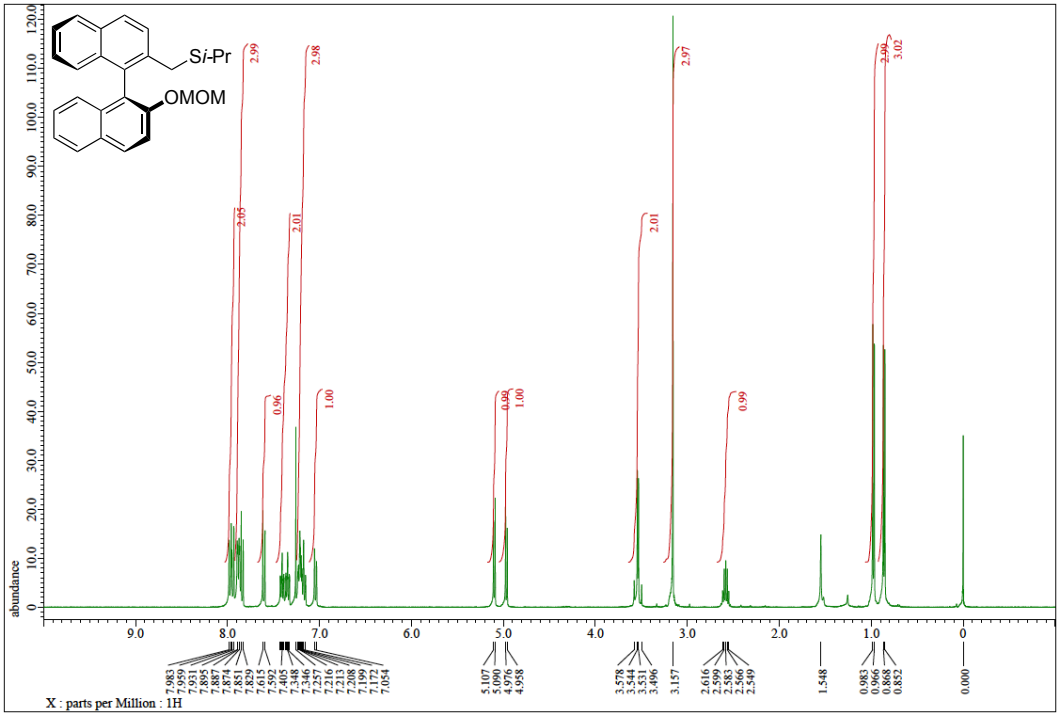
NMR Charts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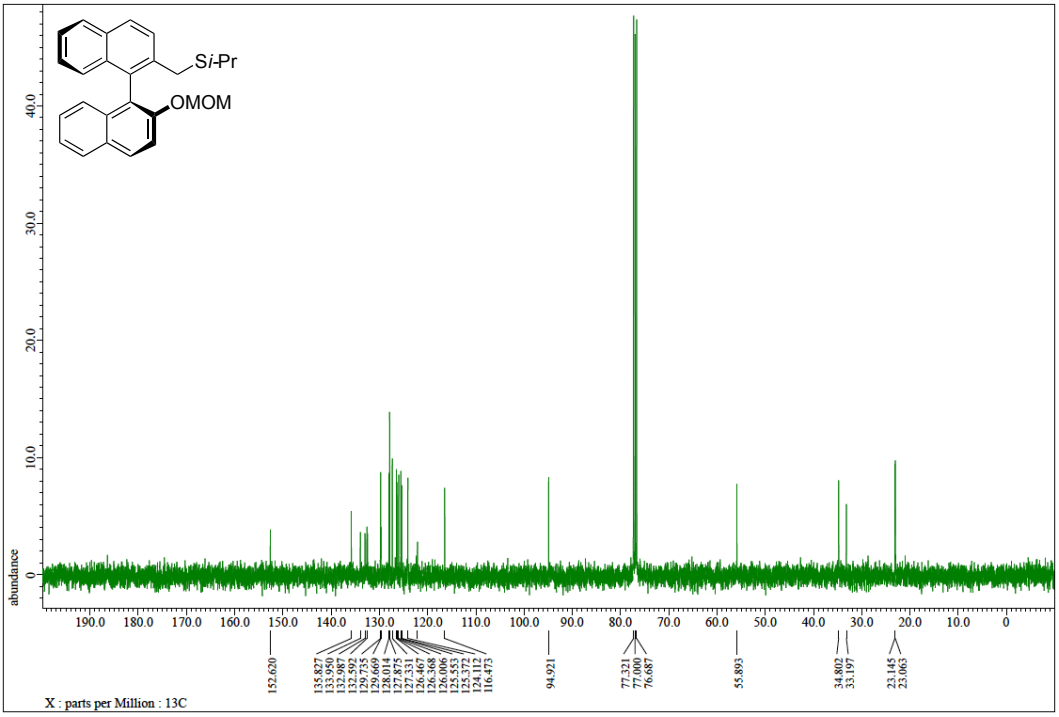
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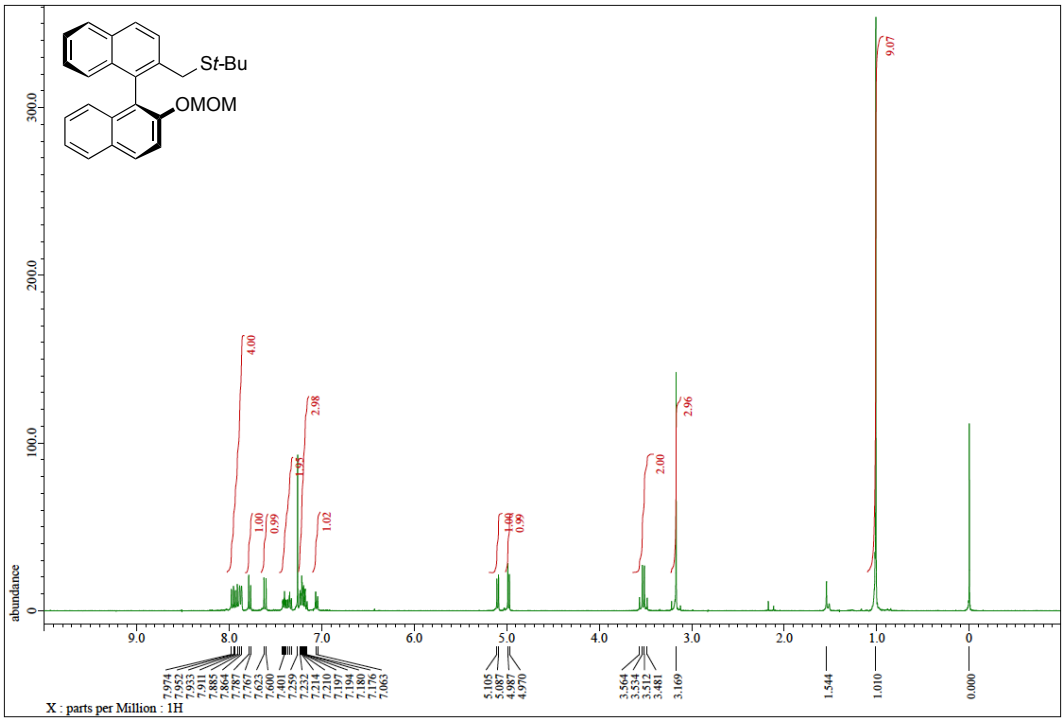
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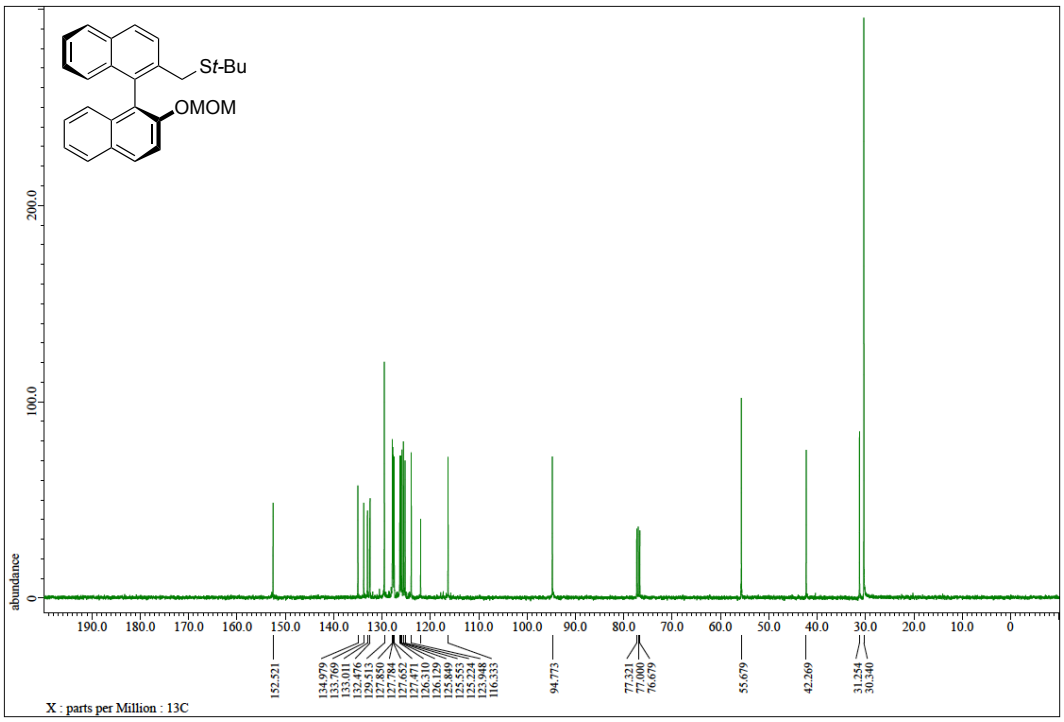
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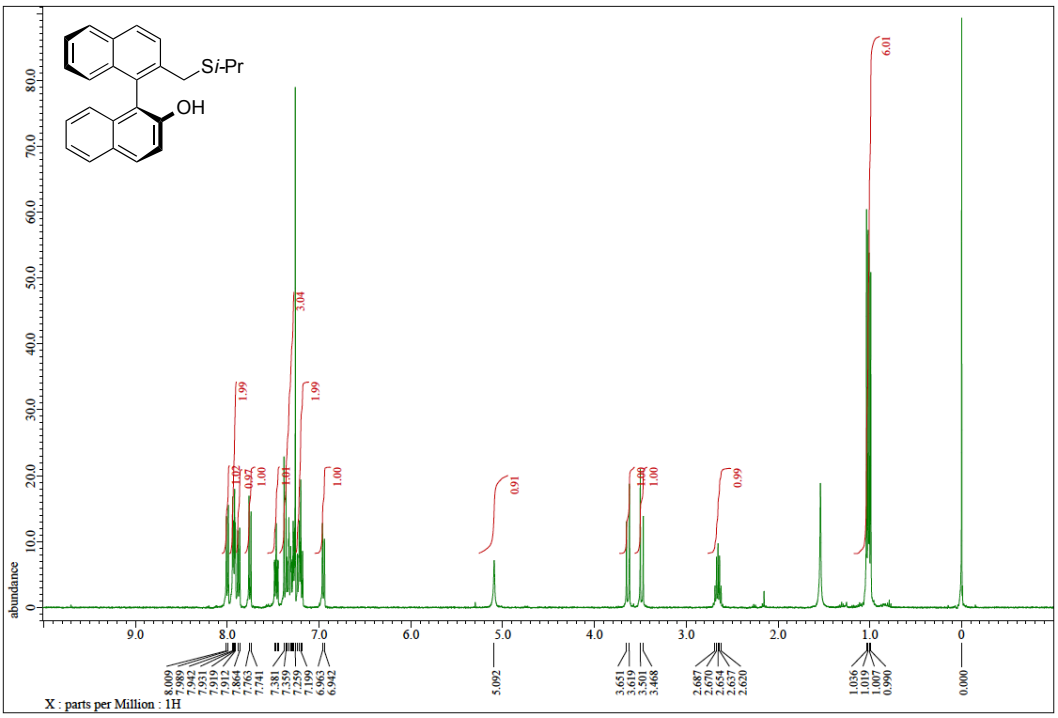
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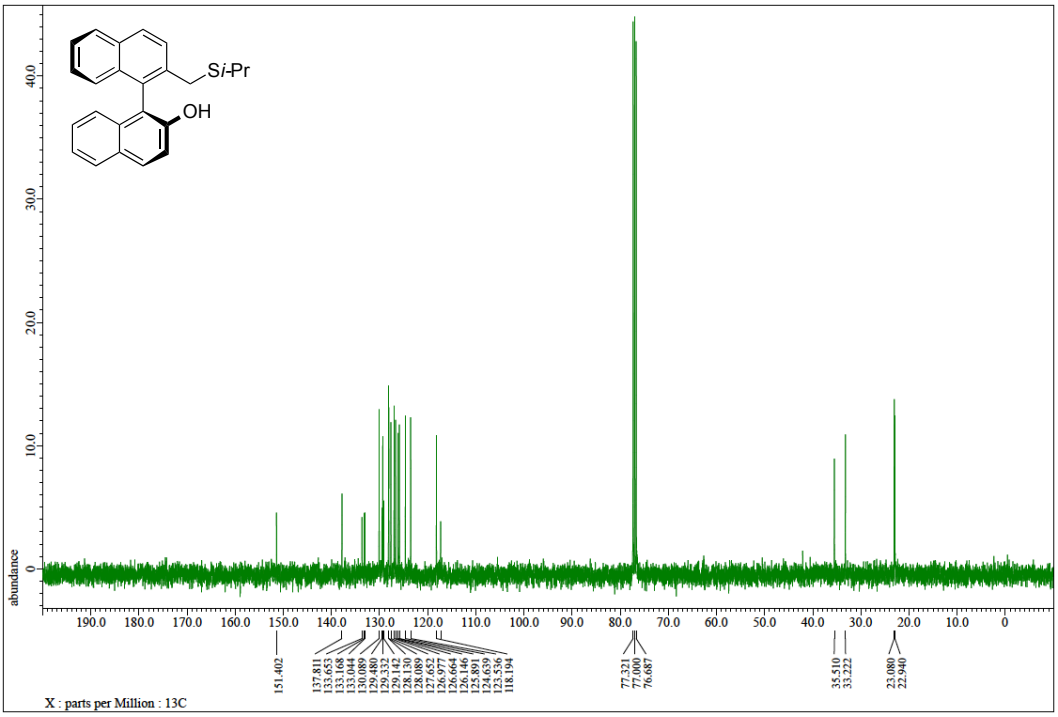
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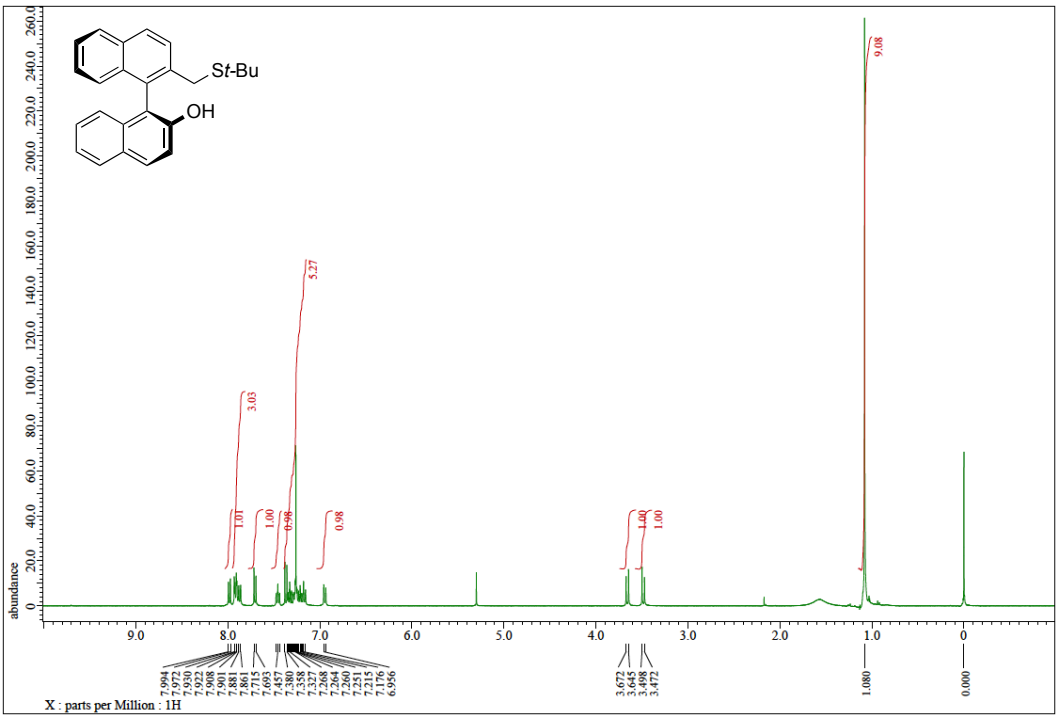
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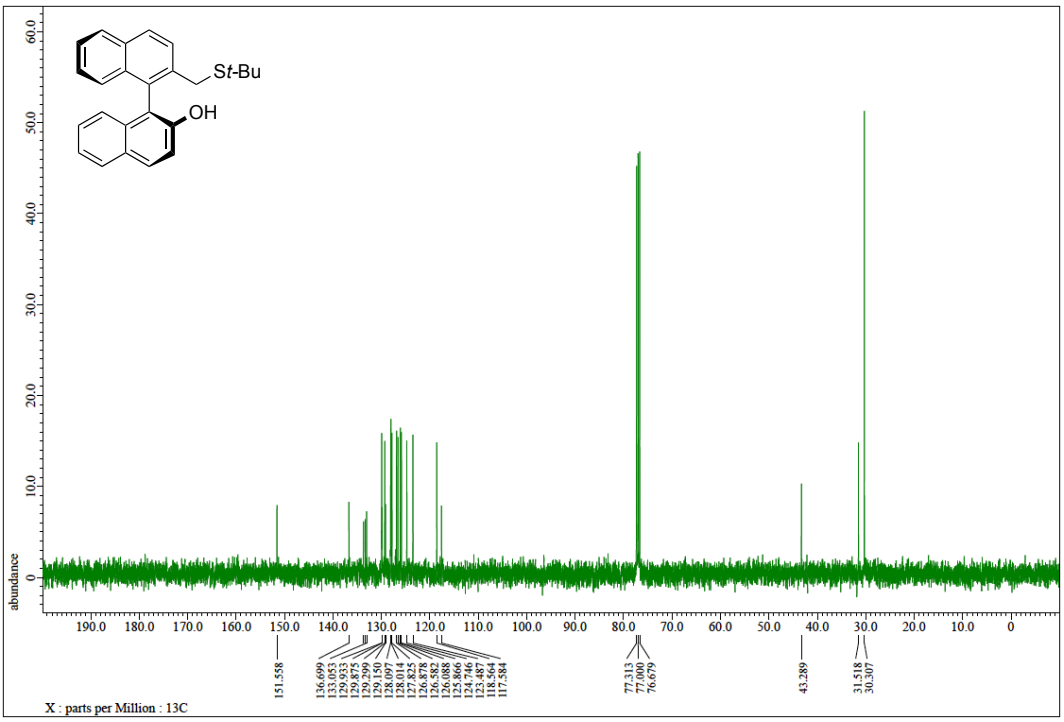
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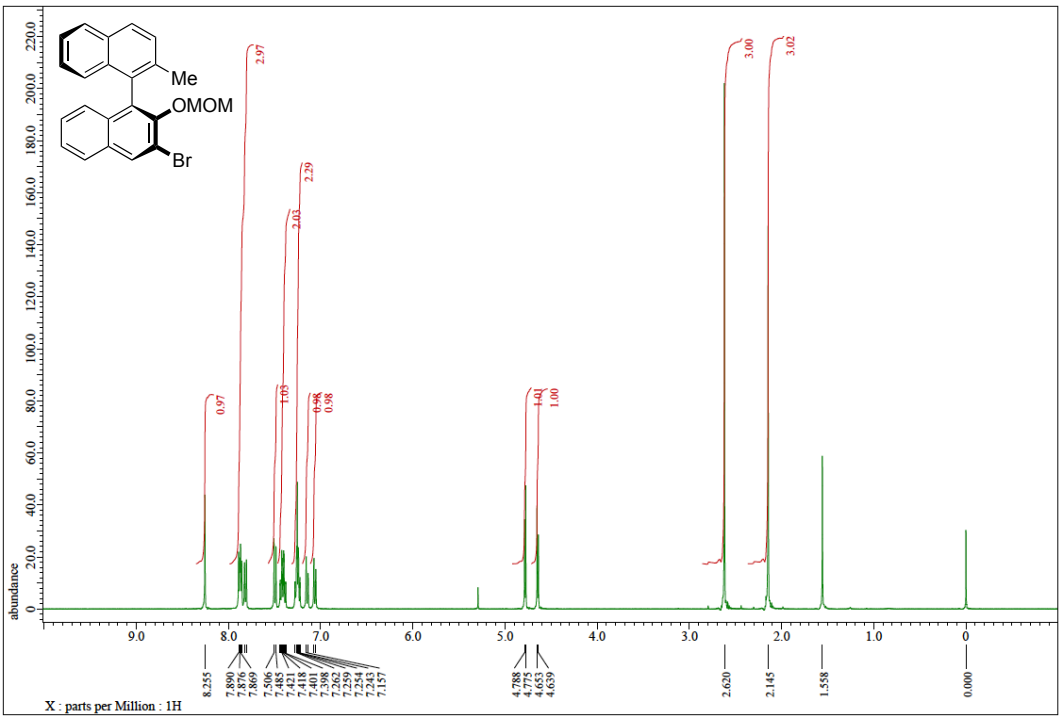
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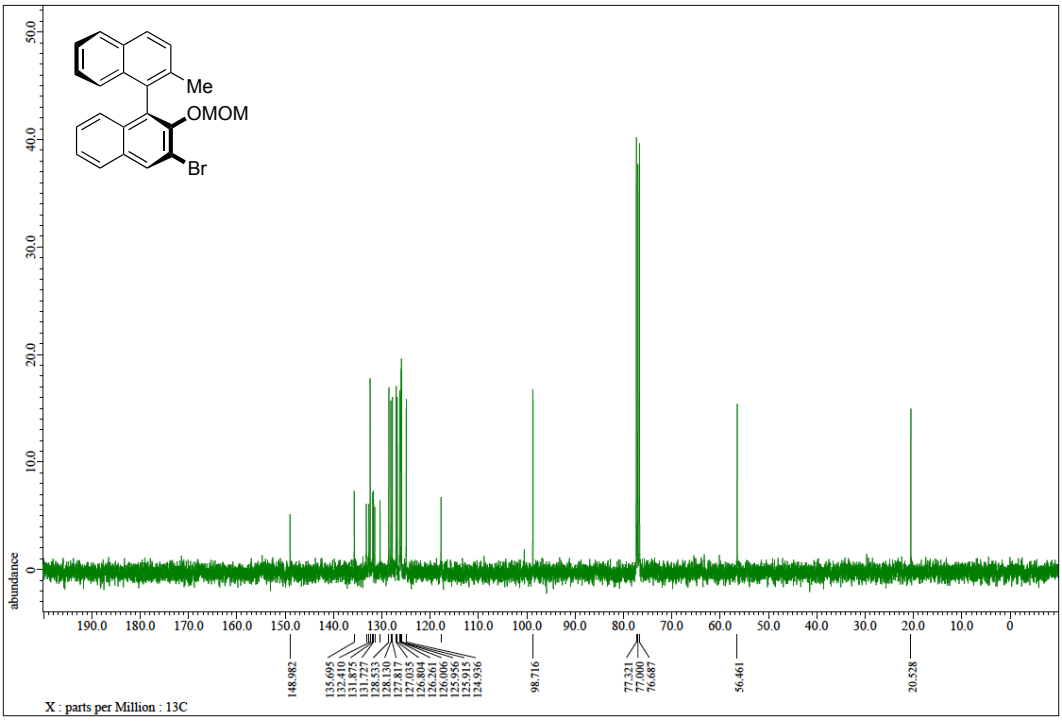
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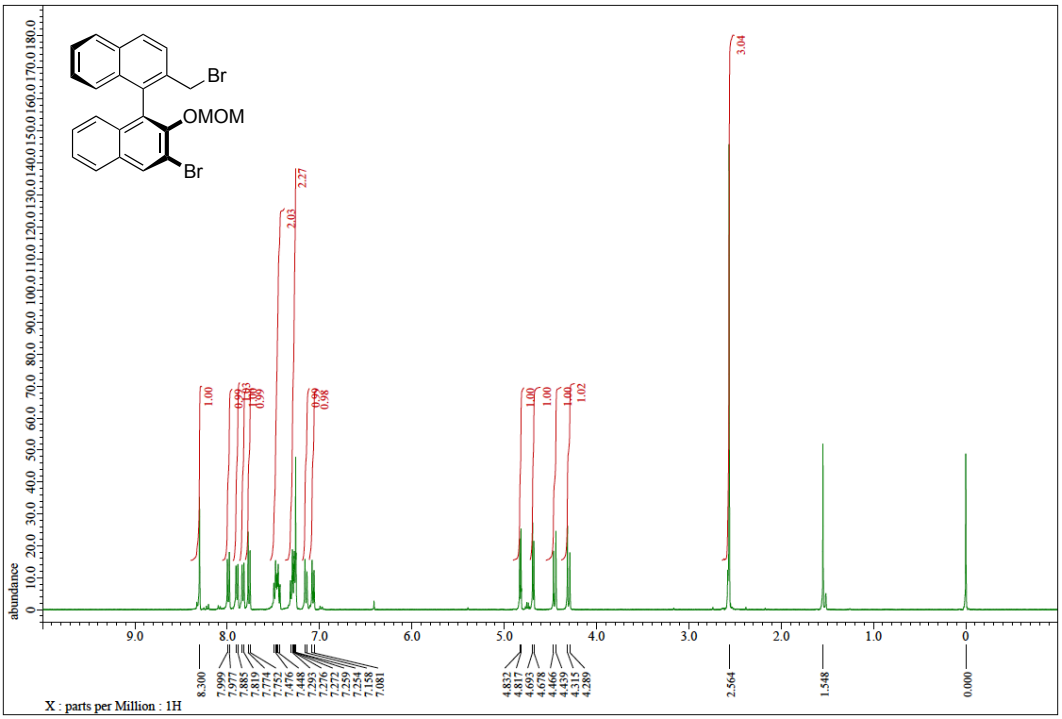
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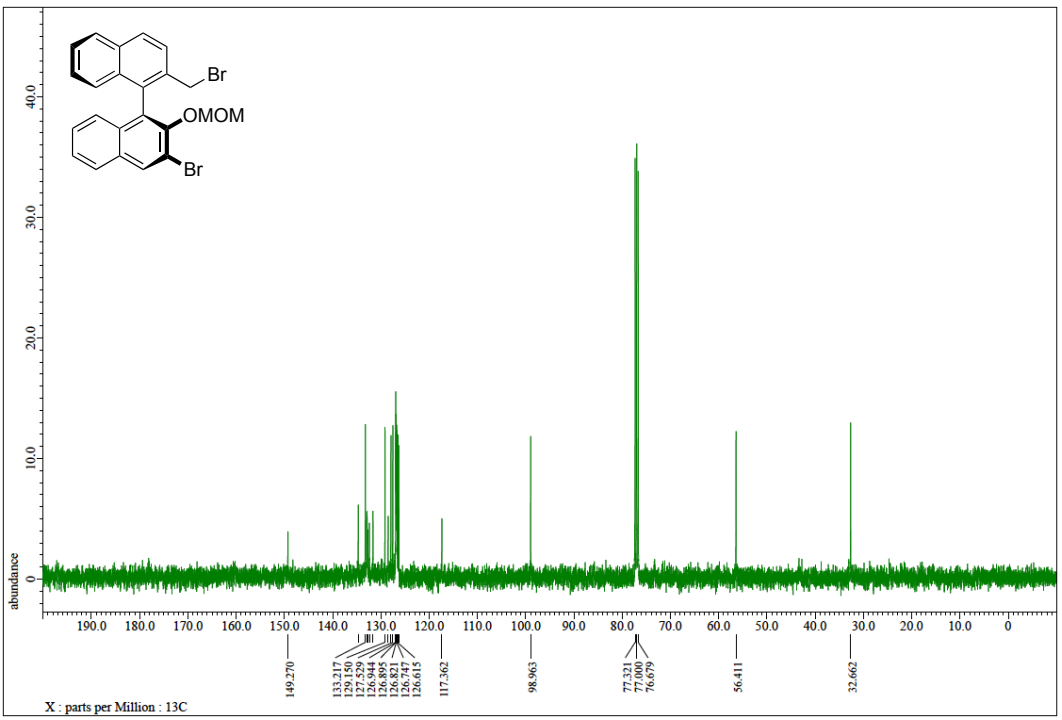
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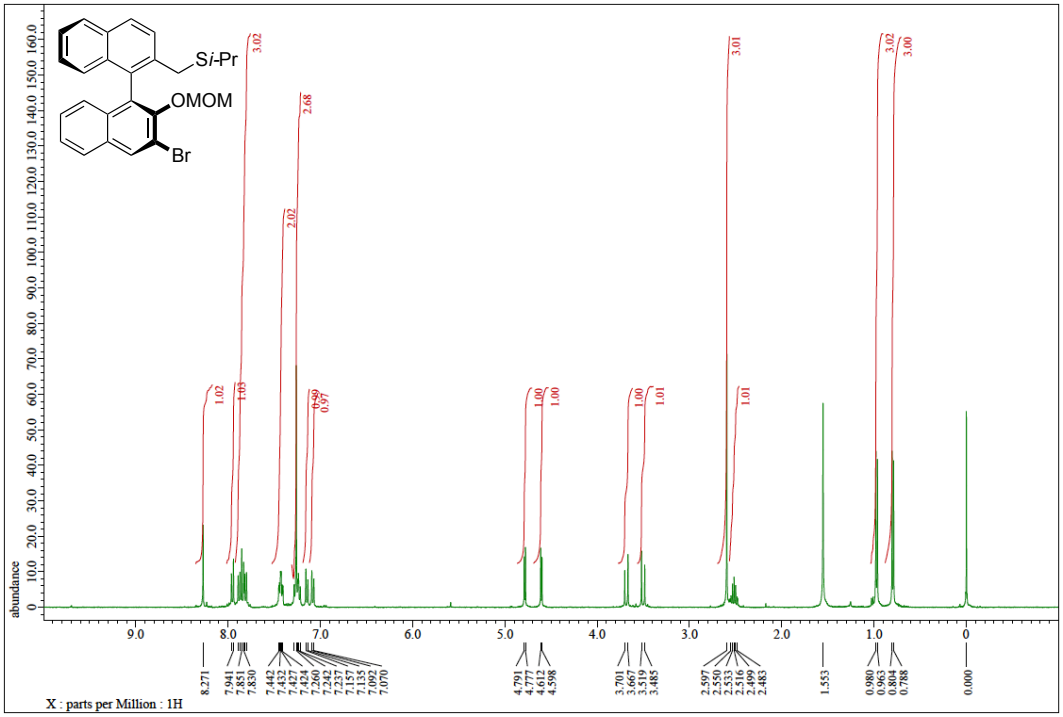
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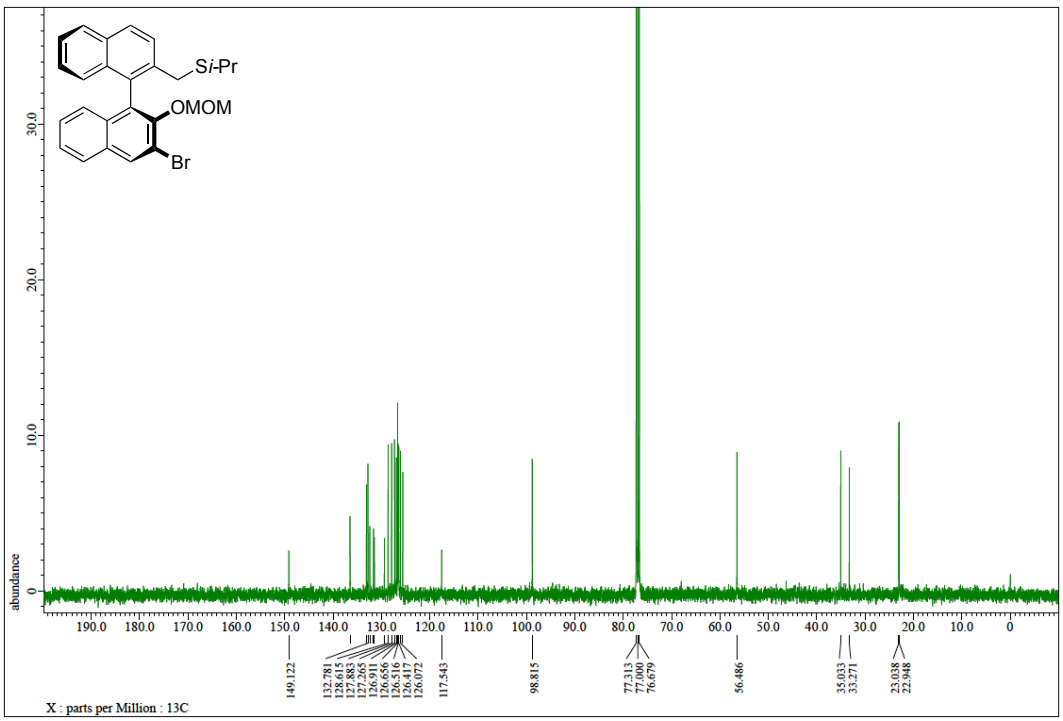
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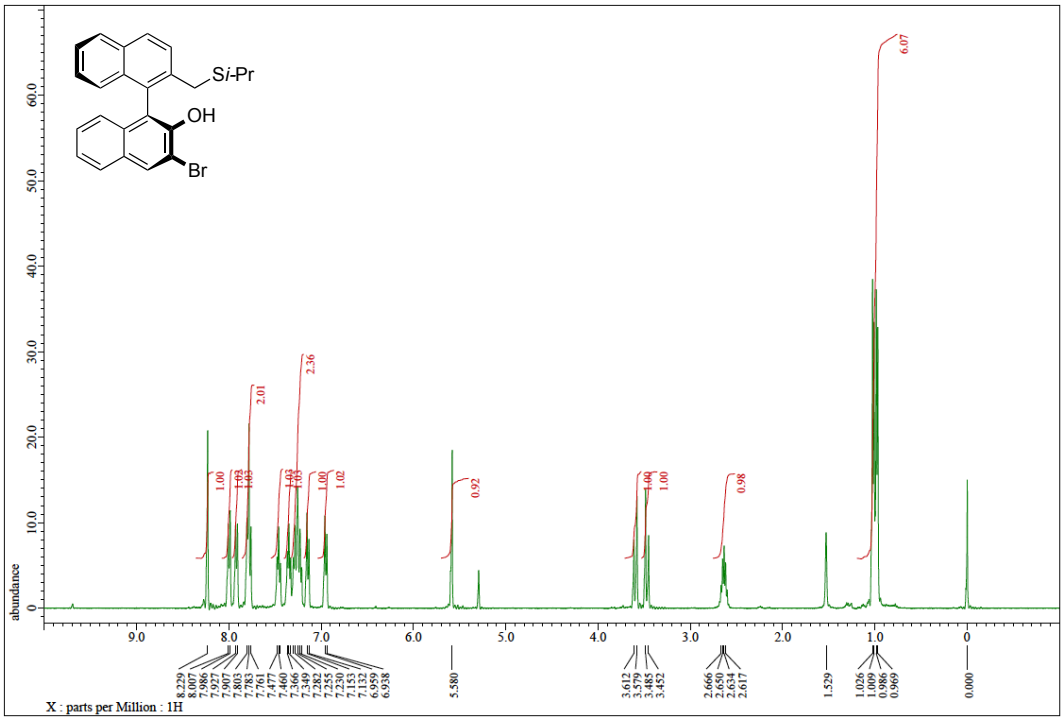
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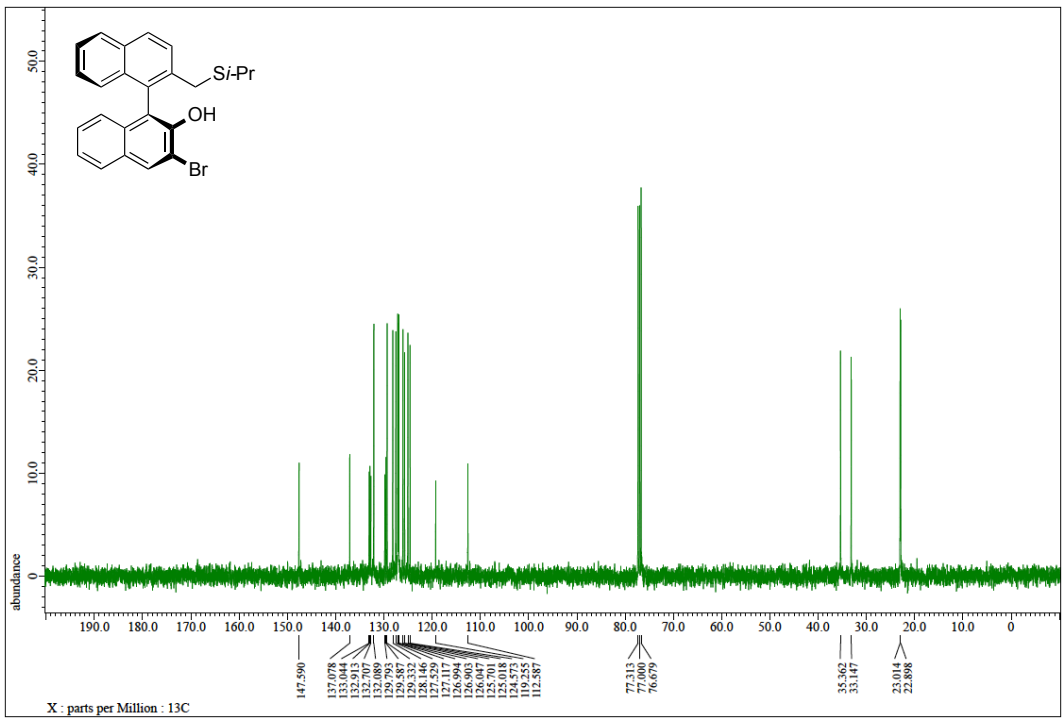
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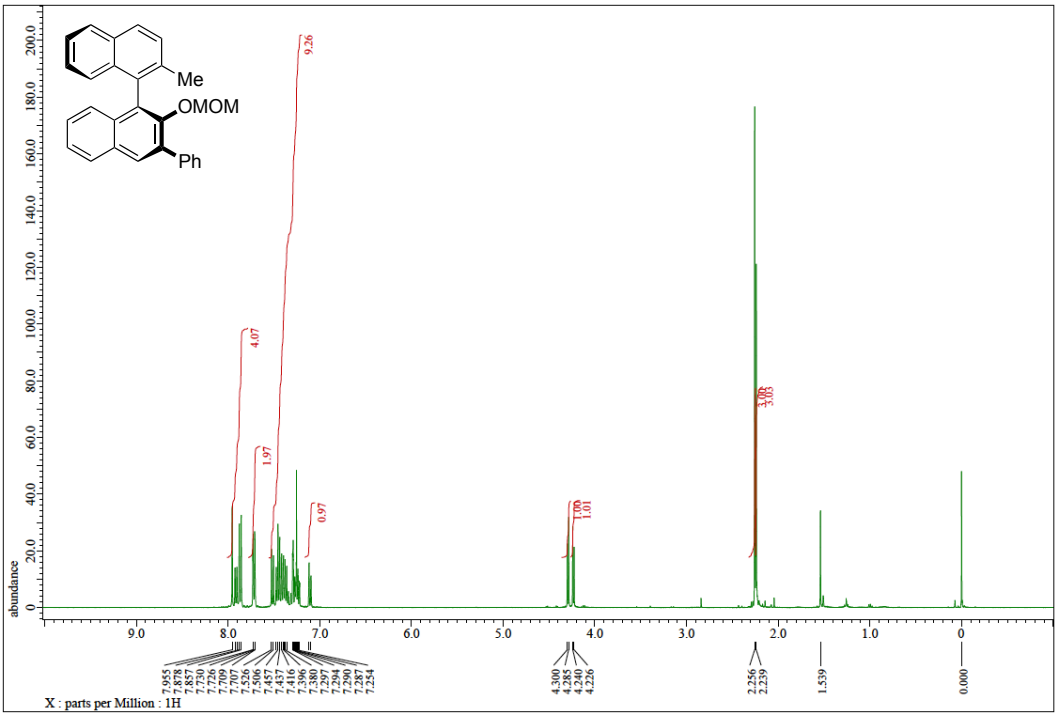
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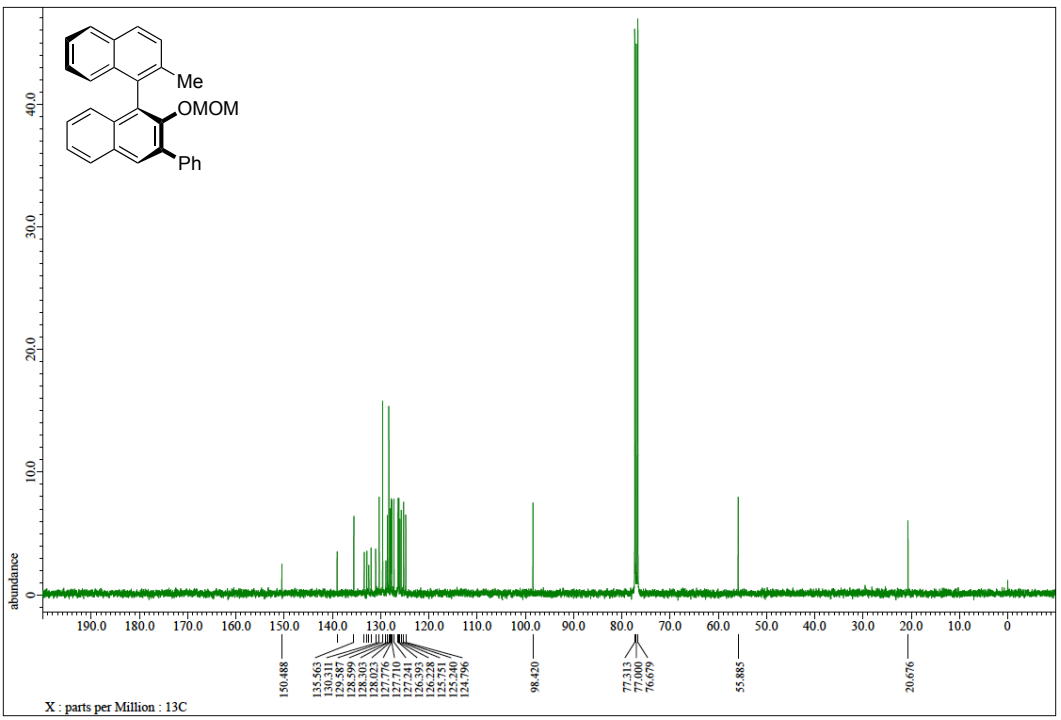
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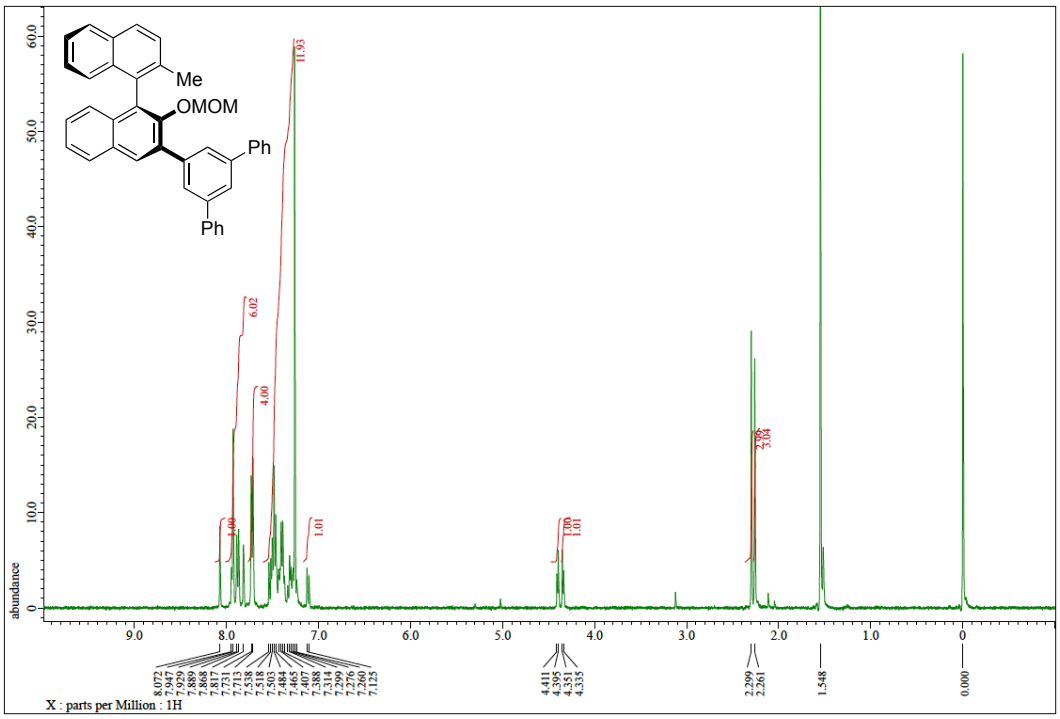
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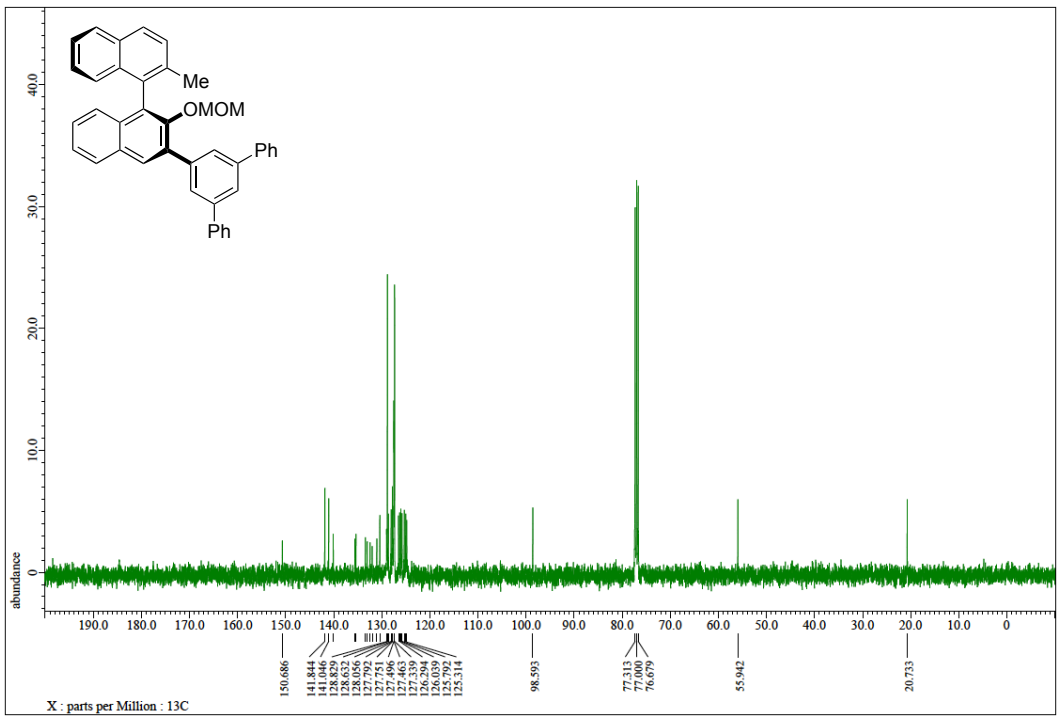
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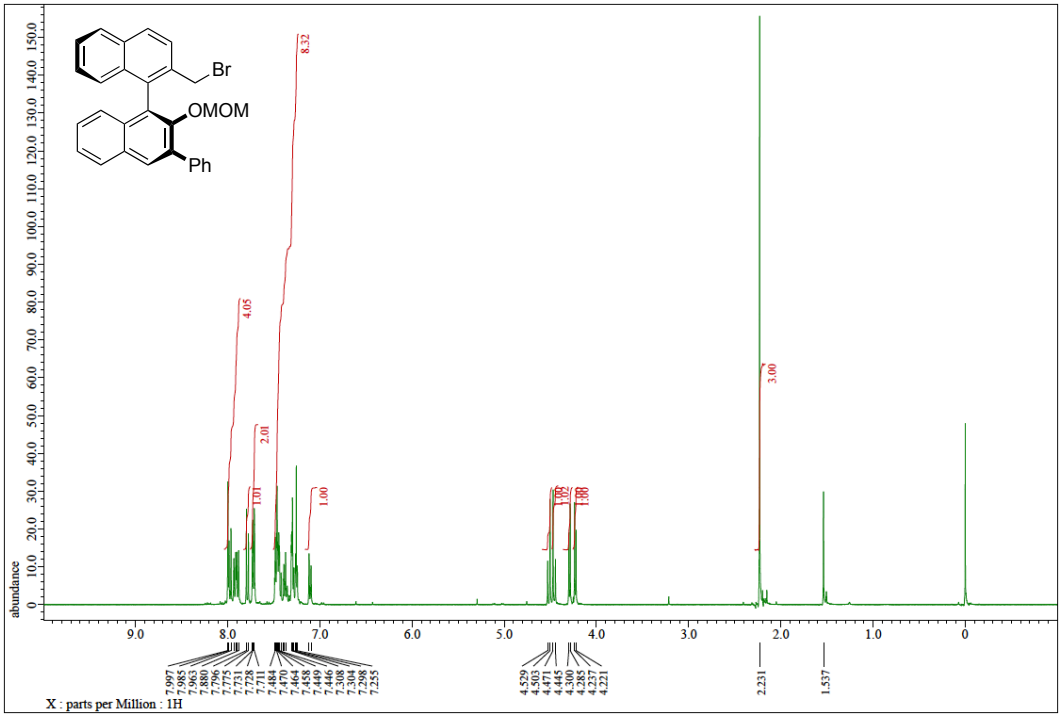
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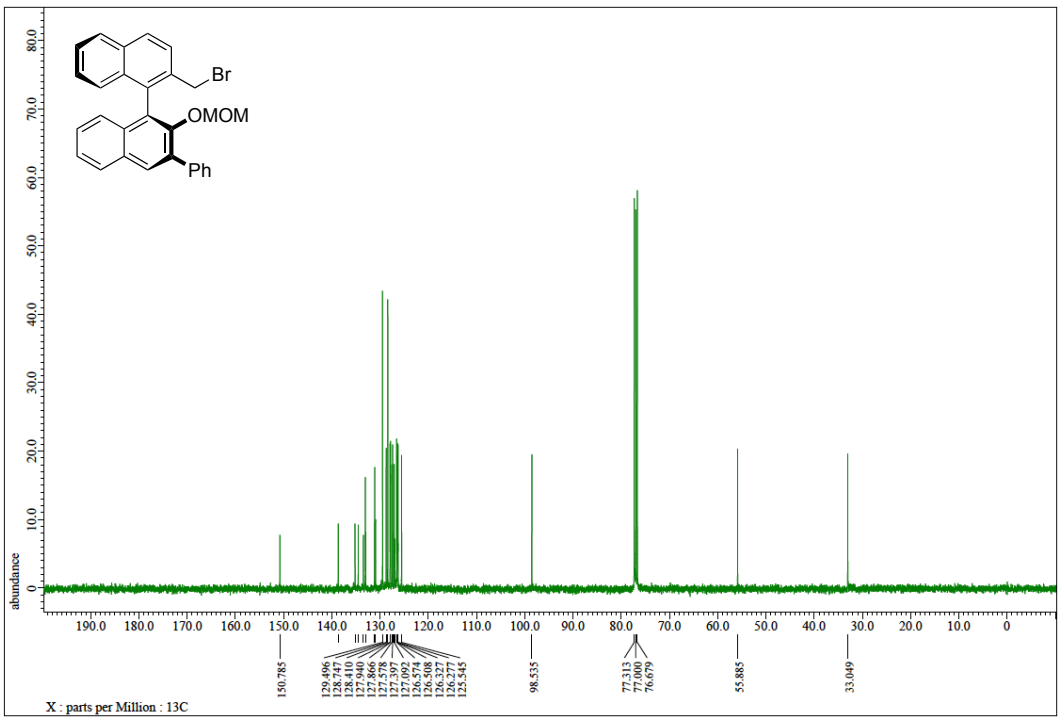
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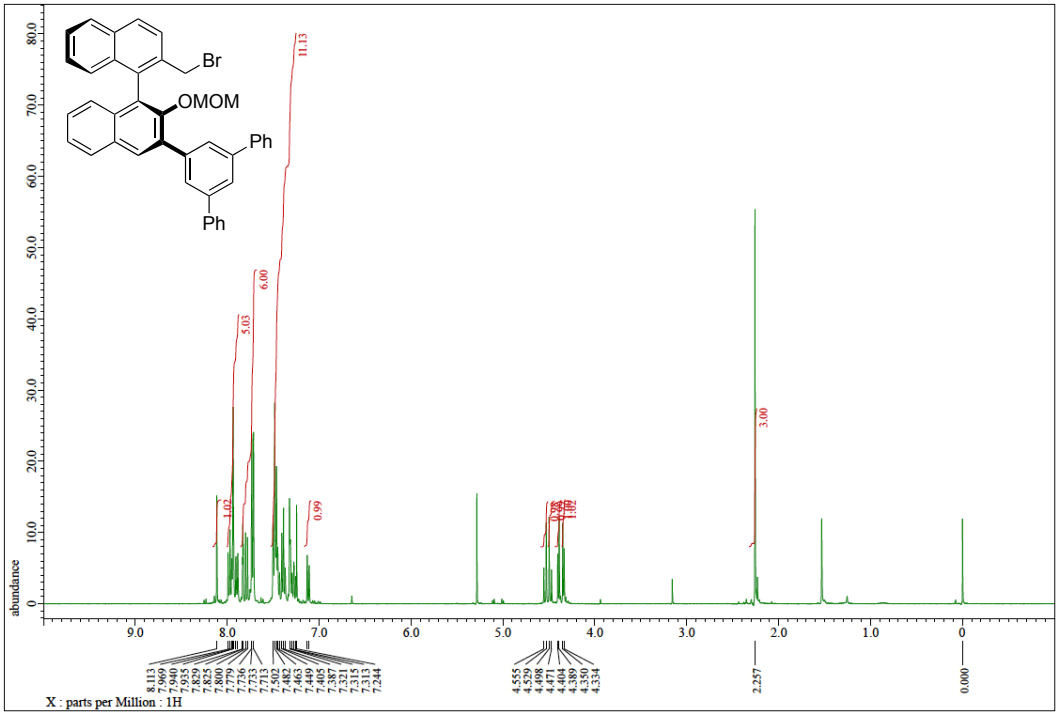
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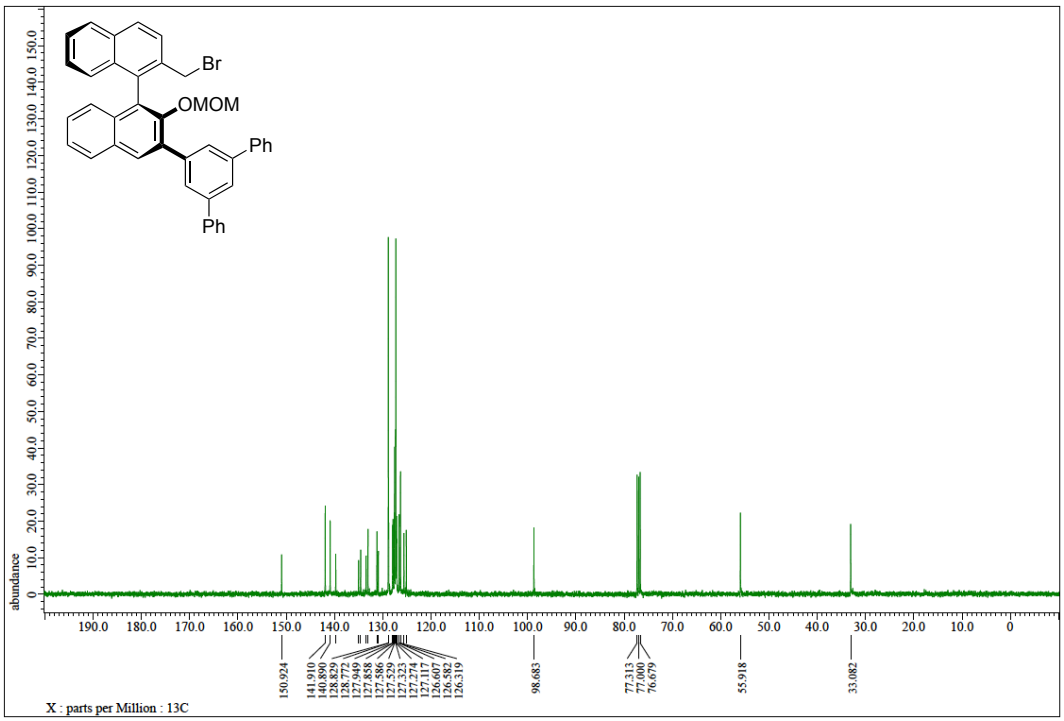
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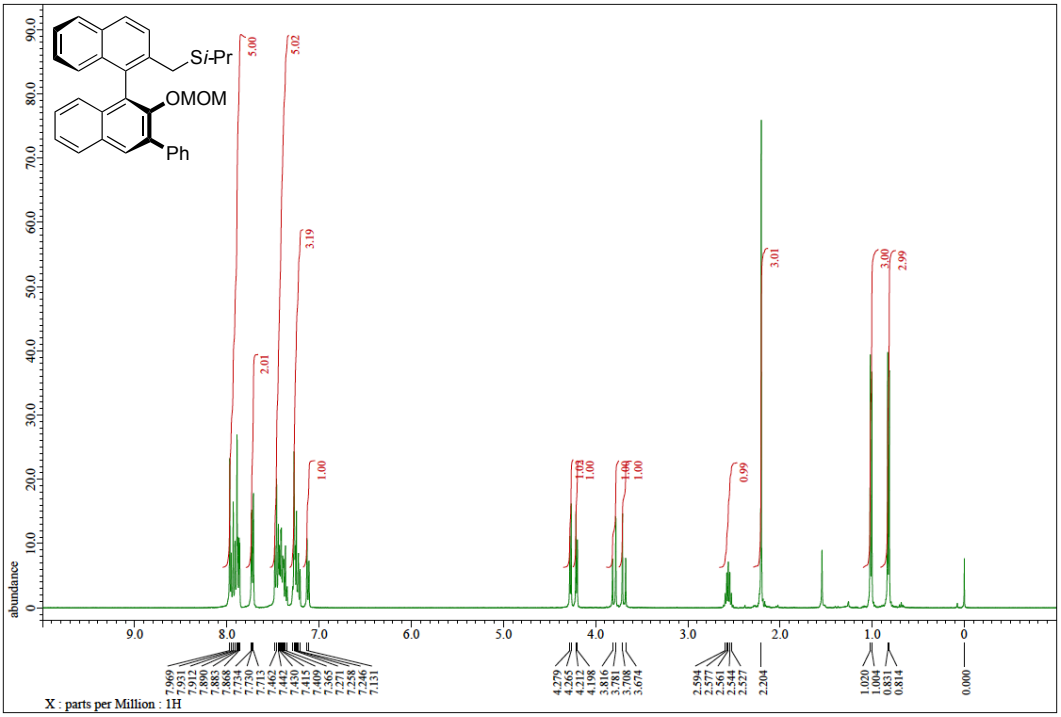
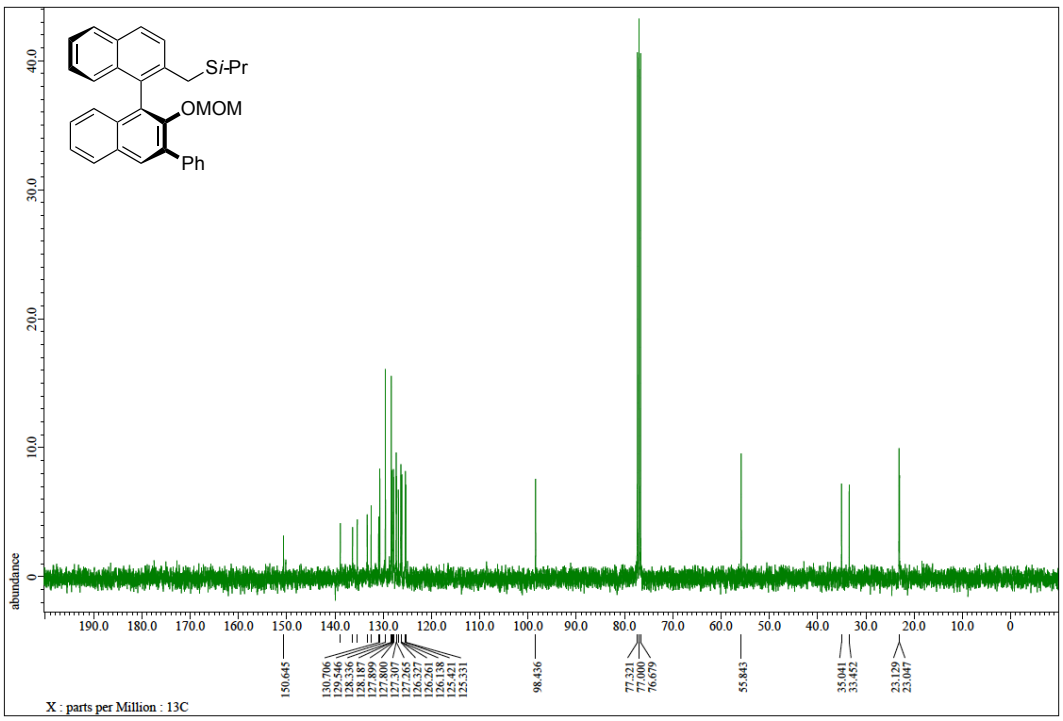
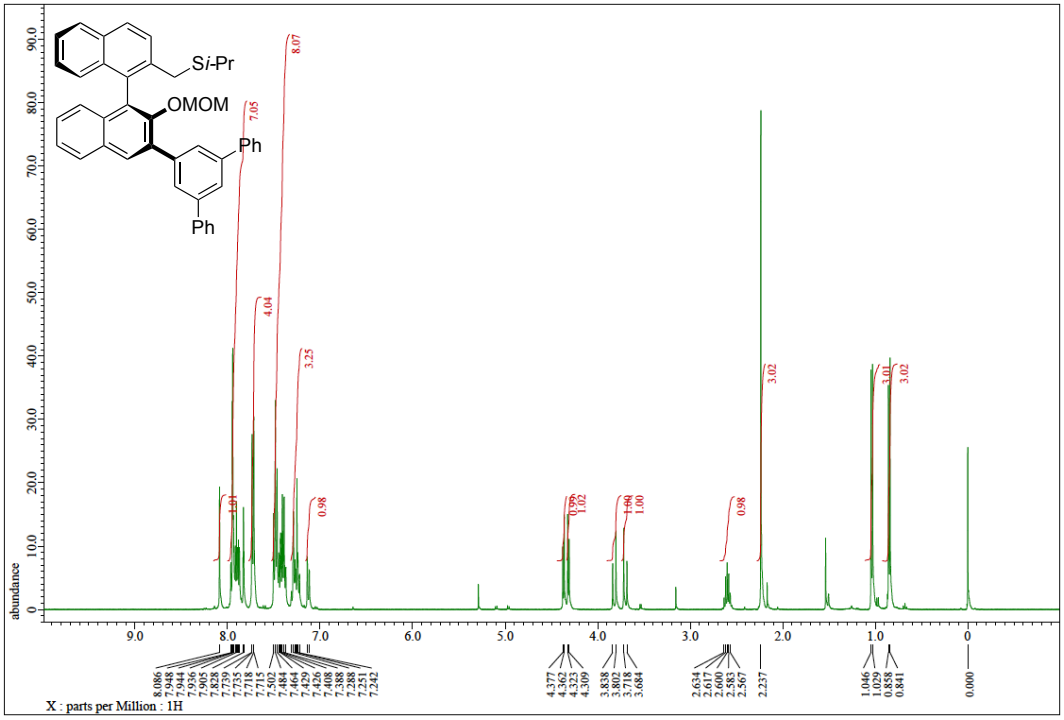
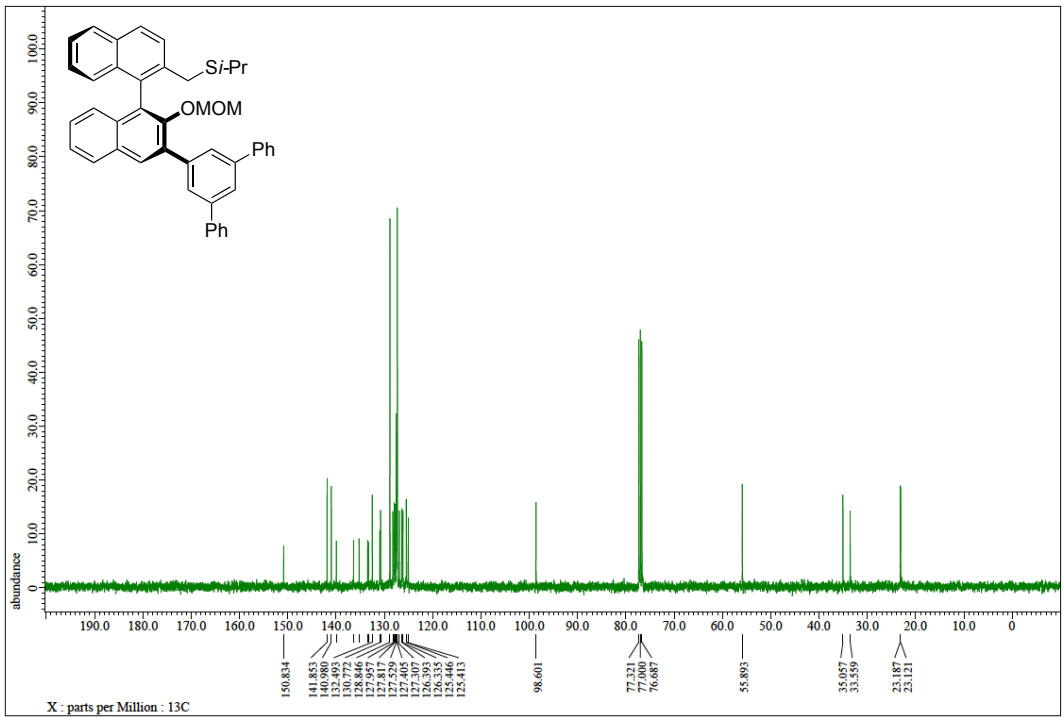
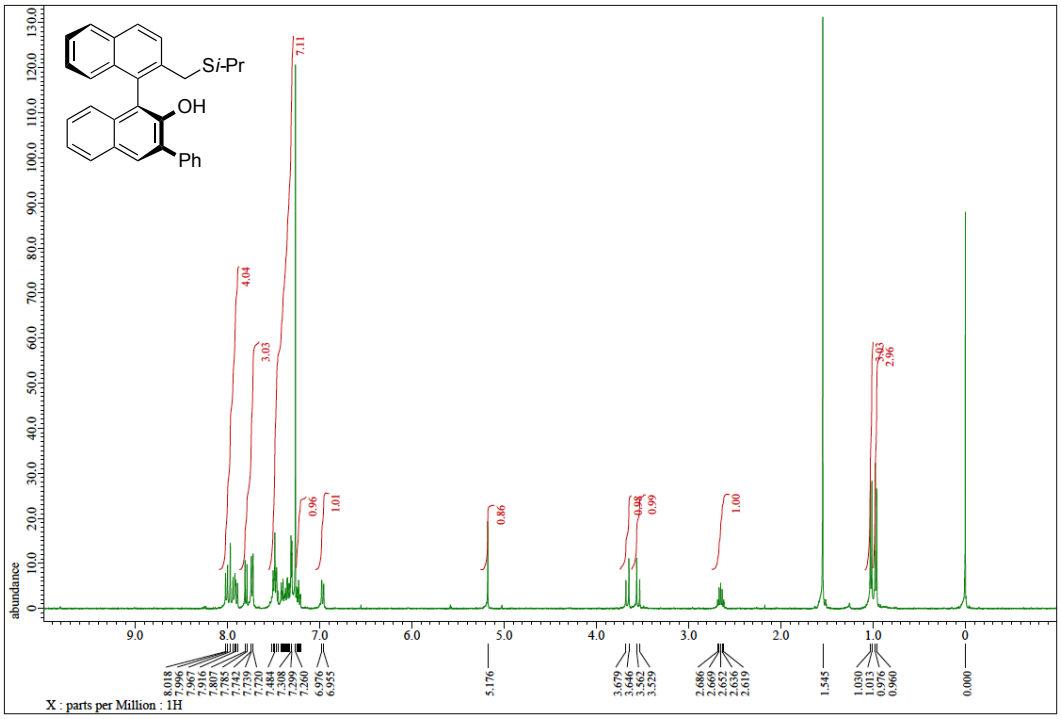
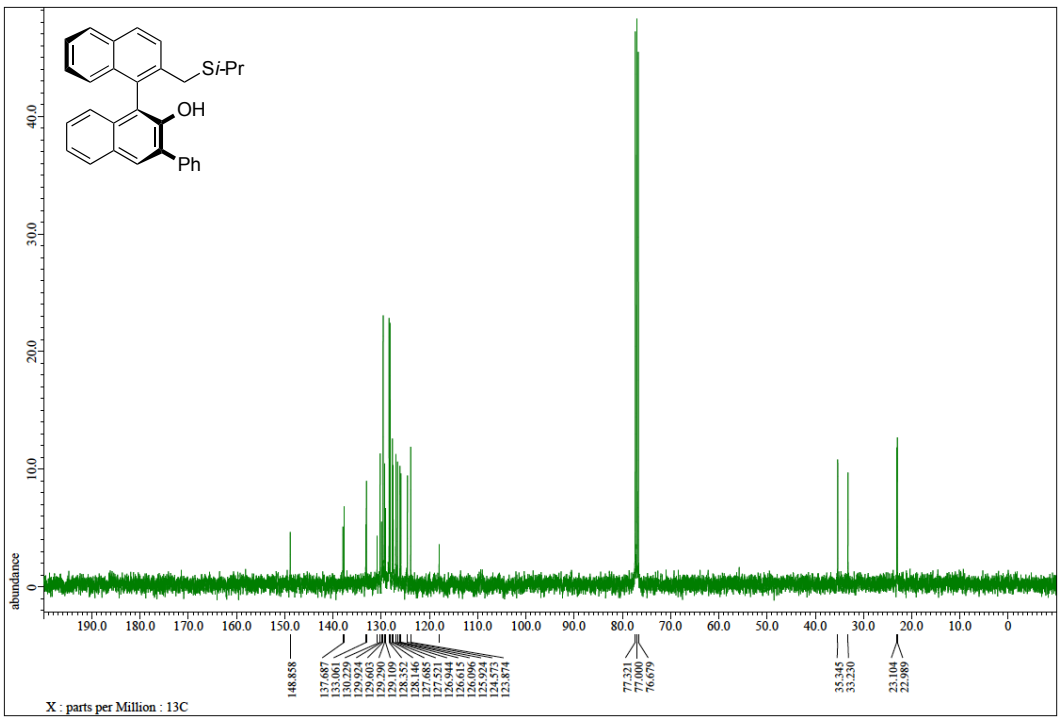

Si-Pr
OMOM
Ph
abundance
X : parts per Million : 1H

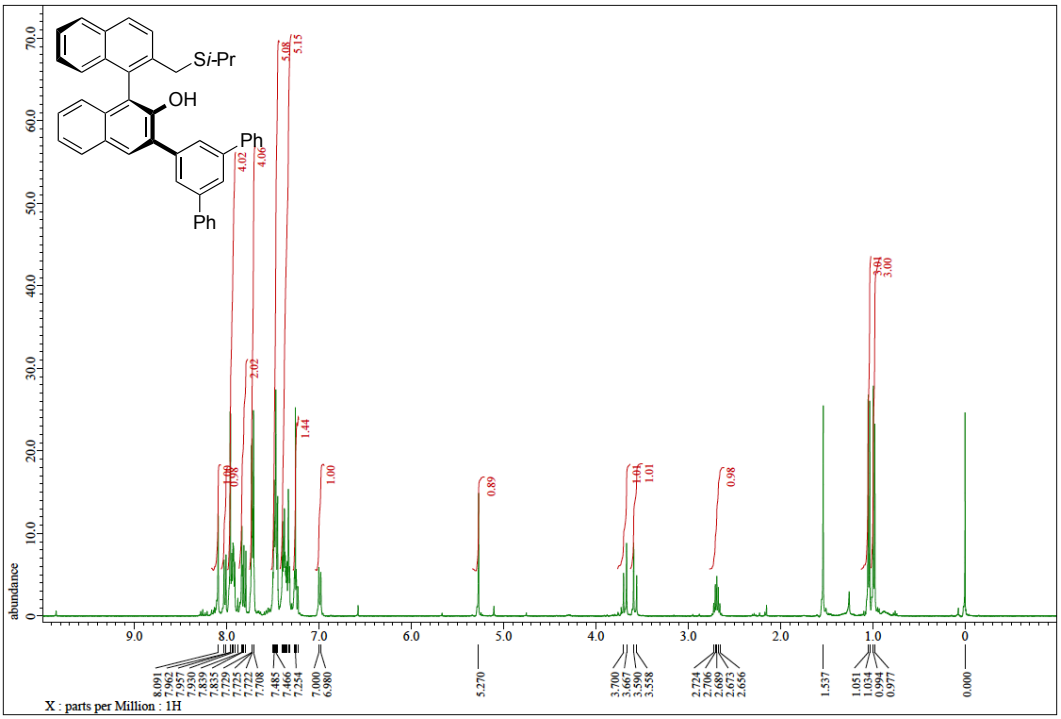

Si-Pr
OMOM
Ph
abundance
X : parts per Million : 13C

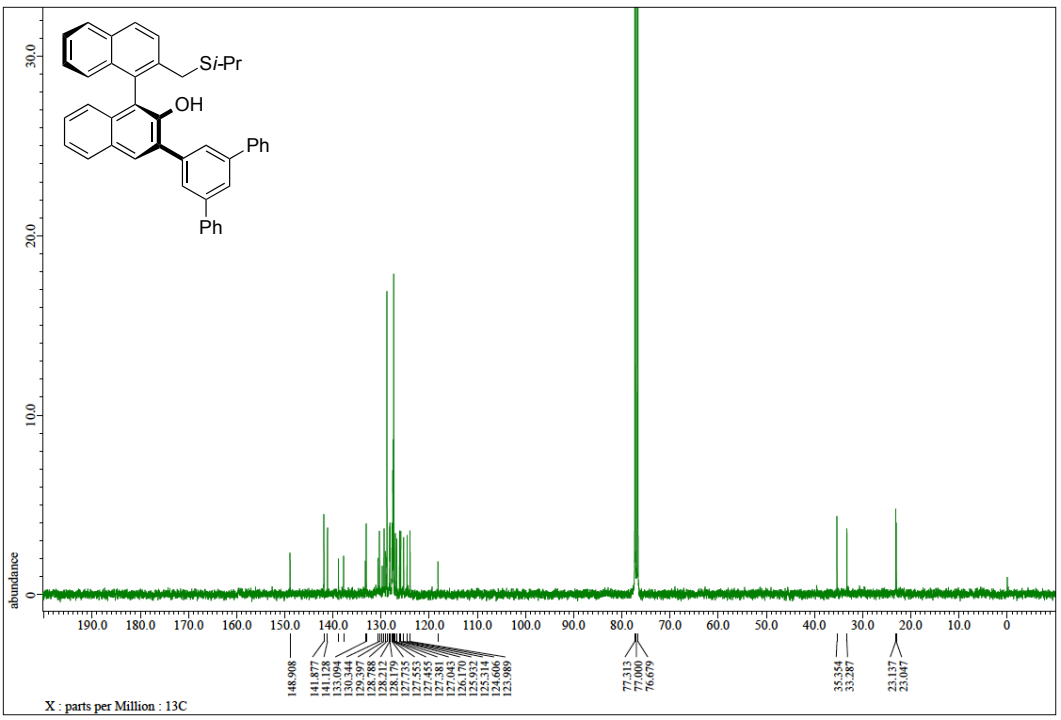

Si-Pr
OMOM
Ph
Ph
abundance
X : parts per Million : 1H

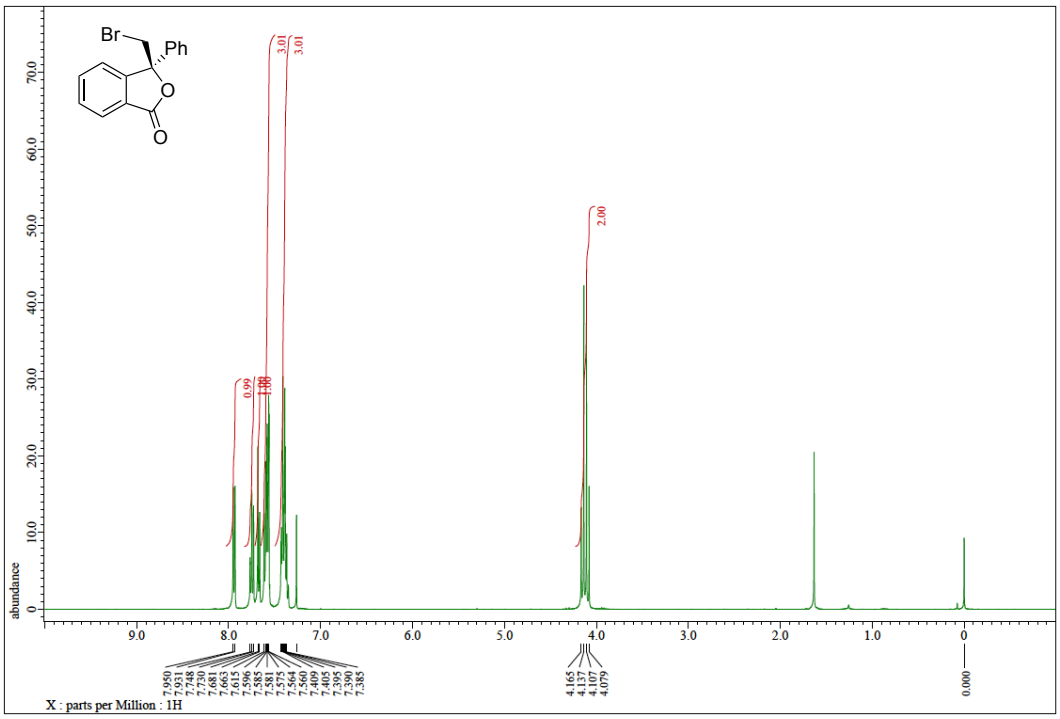

Si-Pr
OMOM
Ph
Ph
abundance
X : parts per Million : 13C

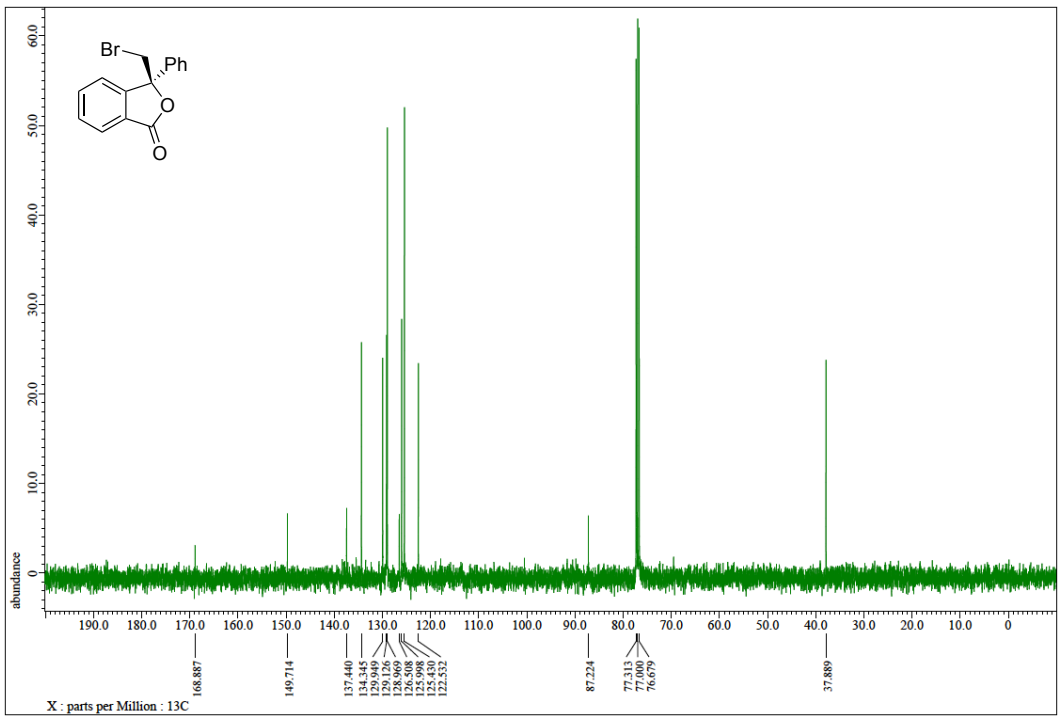

Si-Pr
OH
Ph
abundance
X : parts per Million : 1H

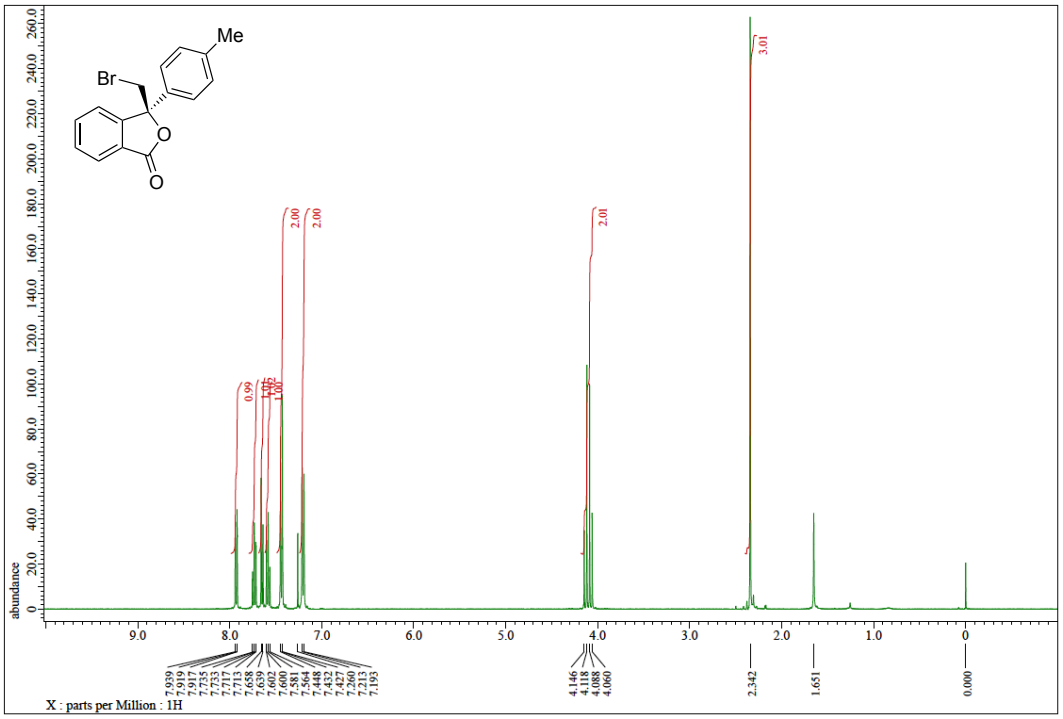

Si-Pr
OH
Ph
abundance
X : parts per Million : 13C

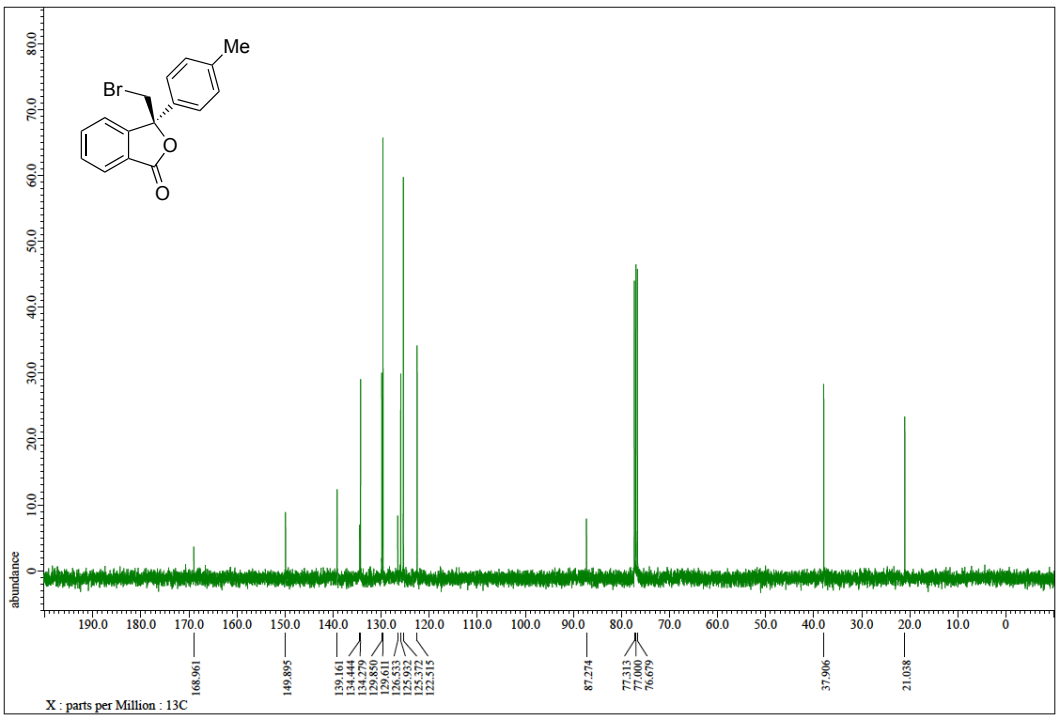

Si-Pr
OH
Ph
Ph
abundance
X : parts per Million : 1H

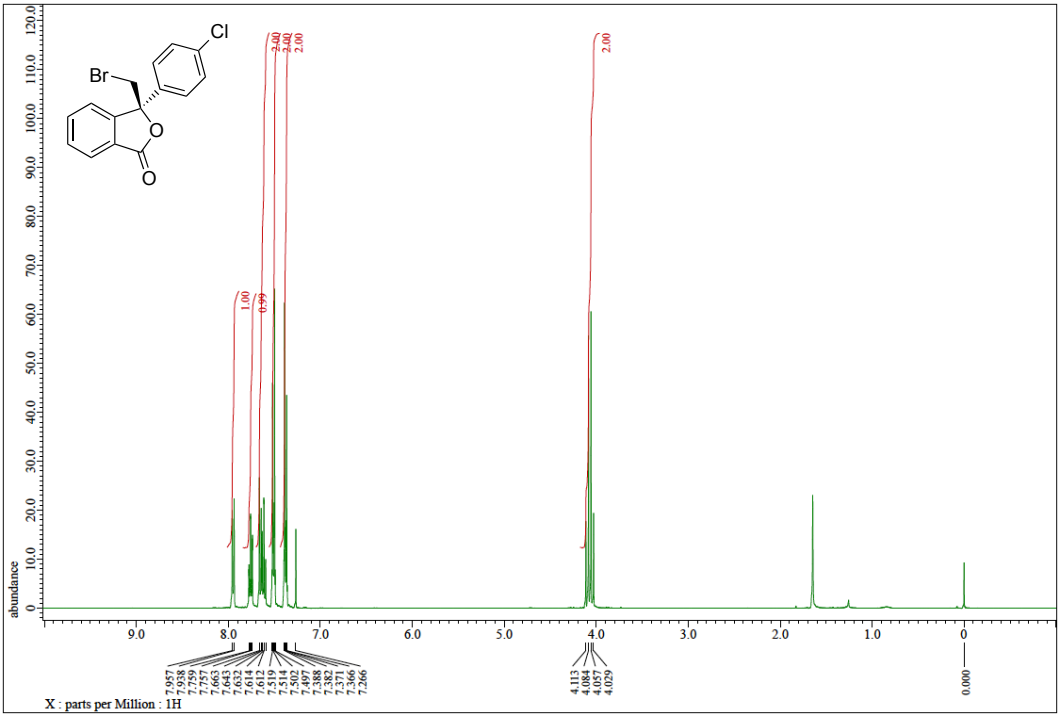

Si-Pr
OH
Ph
Ph
abundance
X : parts per Million : 13C

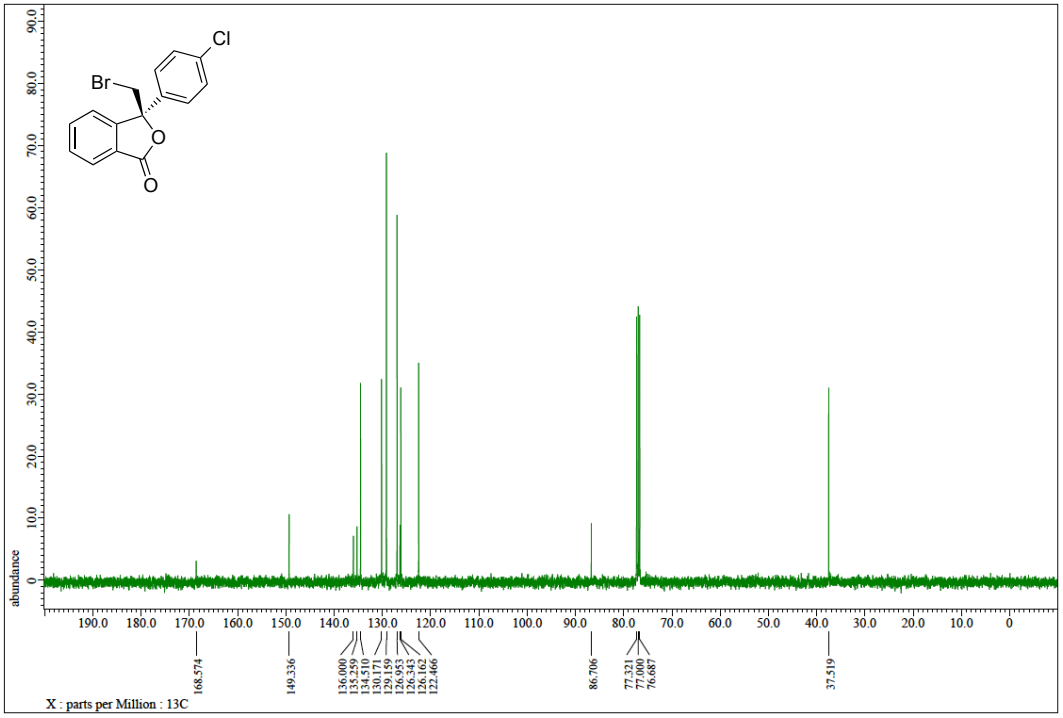

Br
Ph
O
O
abundance
X : parts per Million : 1H

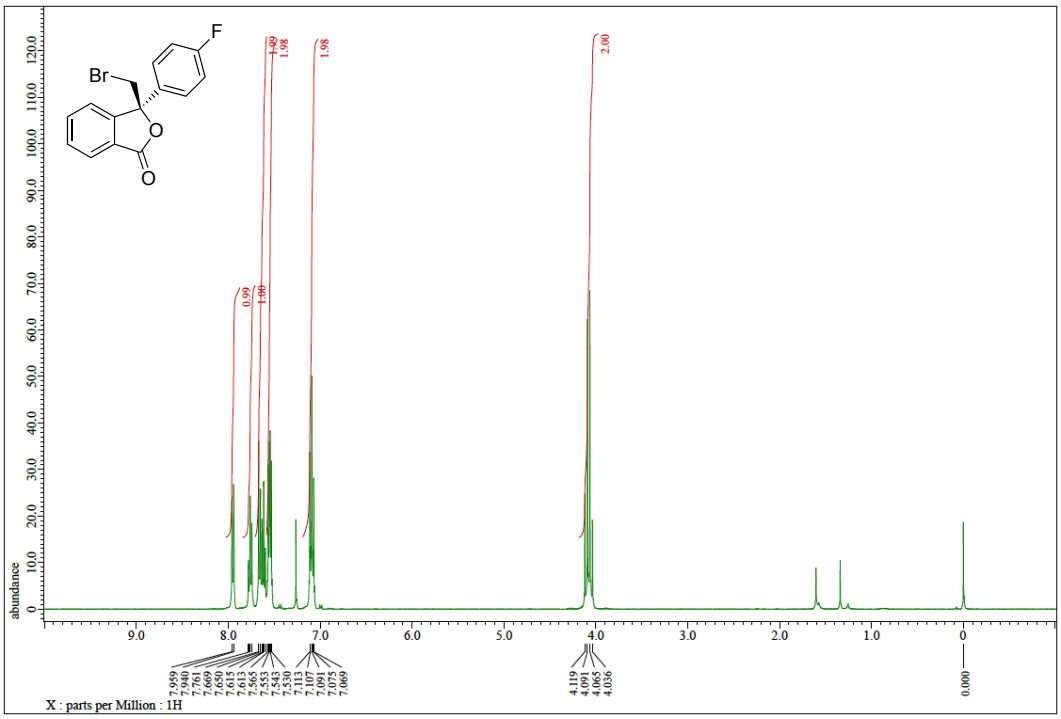

Br
Ph
O
O
abundance
X : parts per Million : 13C

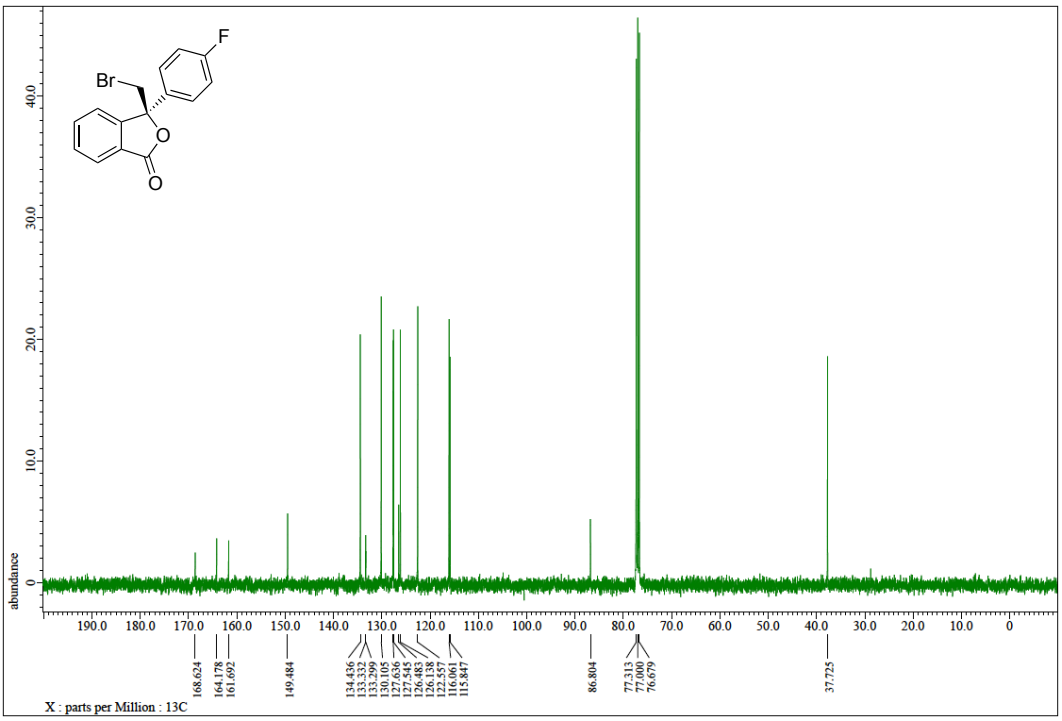

Me
Br
O
O
abundance
X : parts per Million : 1H

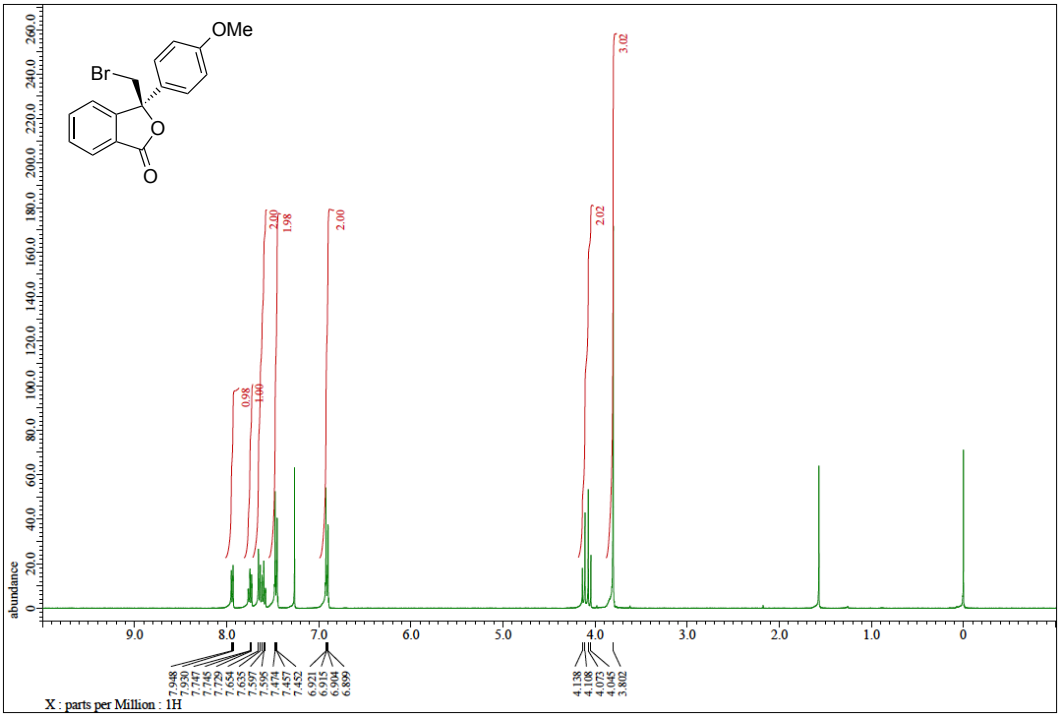

Me
Br
O
O
abundance
X : parts per Million : 13C

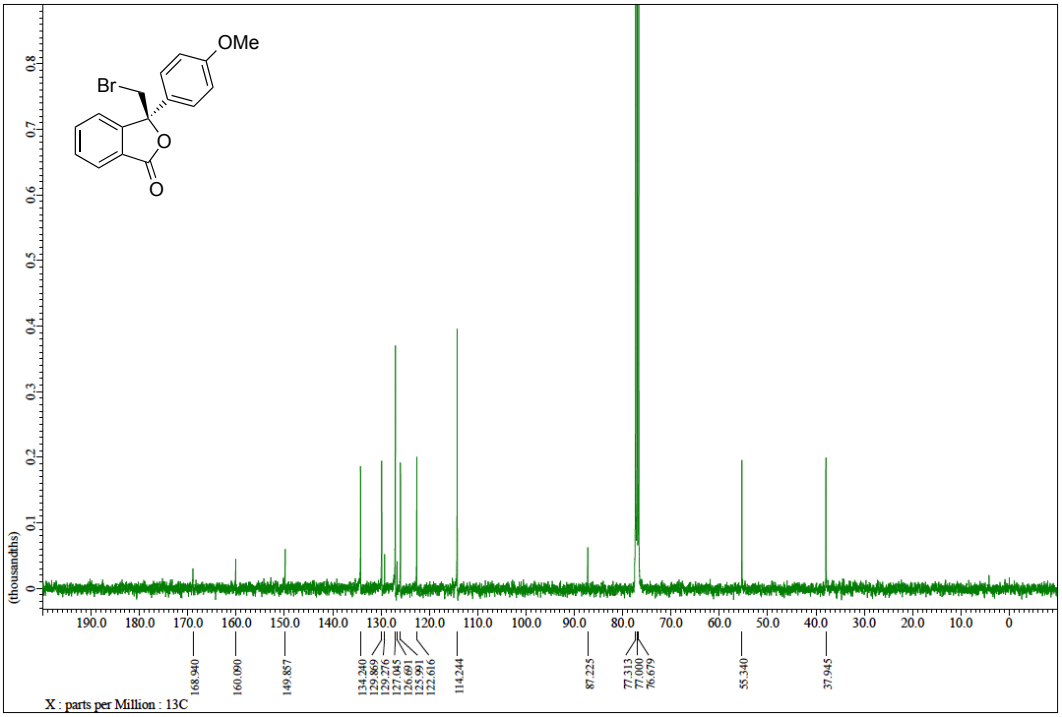

Cl
Br
O
O
abundance
X : parts per Million : 1H

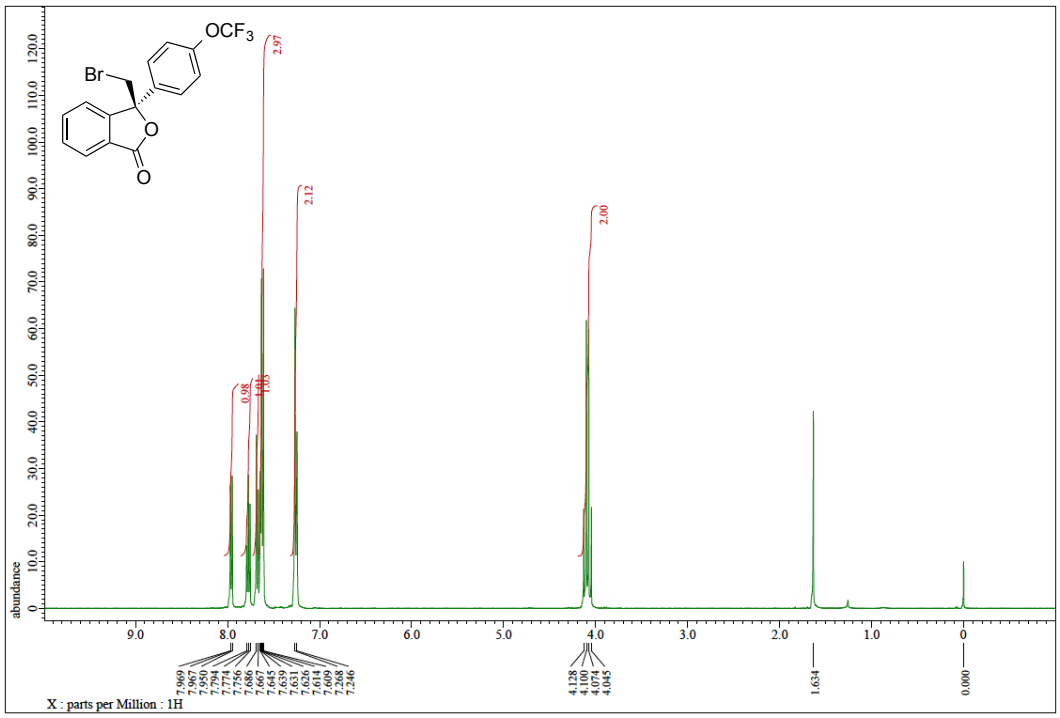

Cl
Br
O
O
abundance
X : parts per Million : 13C

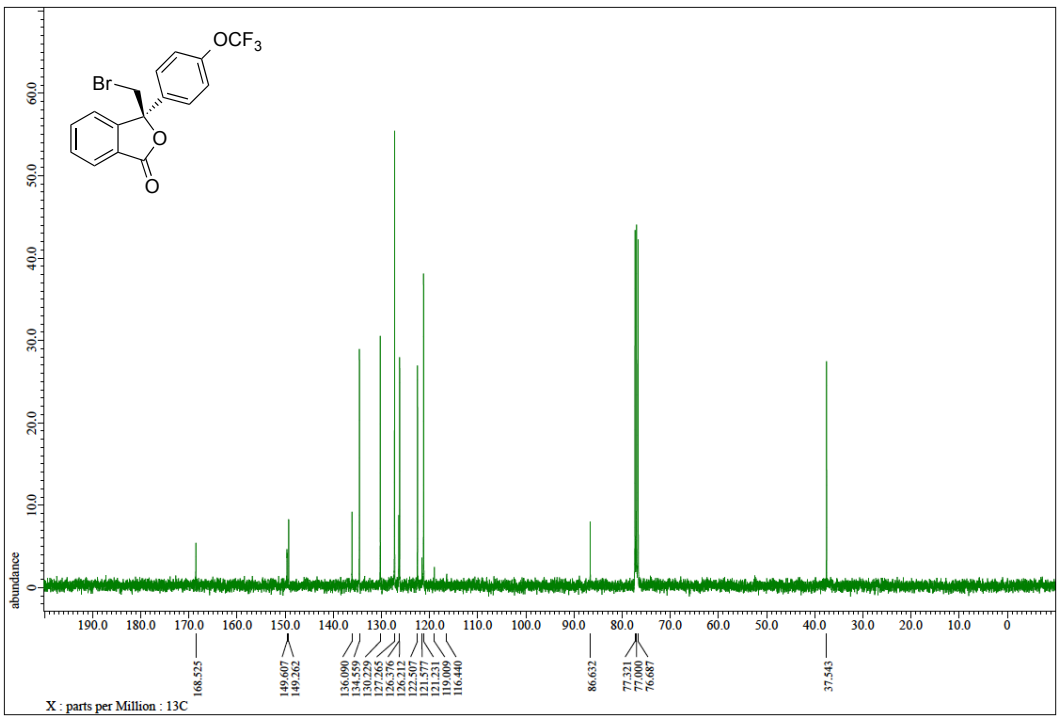

F
Br
O
O
abundance
X : parts per Million : 1H

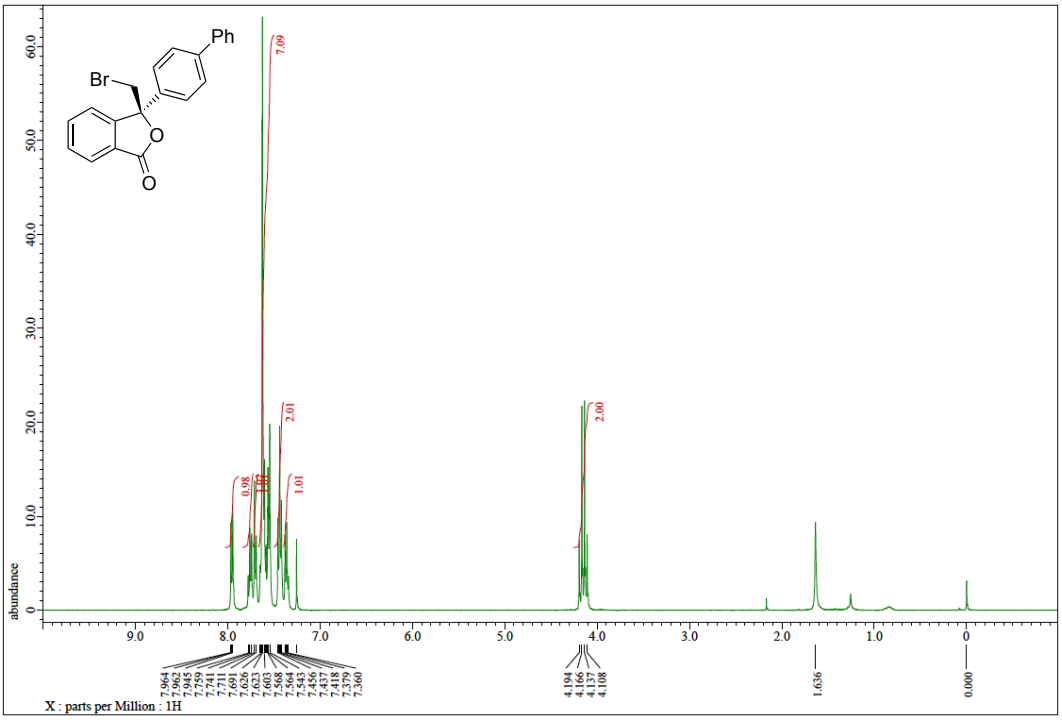

F
Br
O
O
abundance
X : parts per Million : 13C

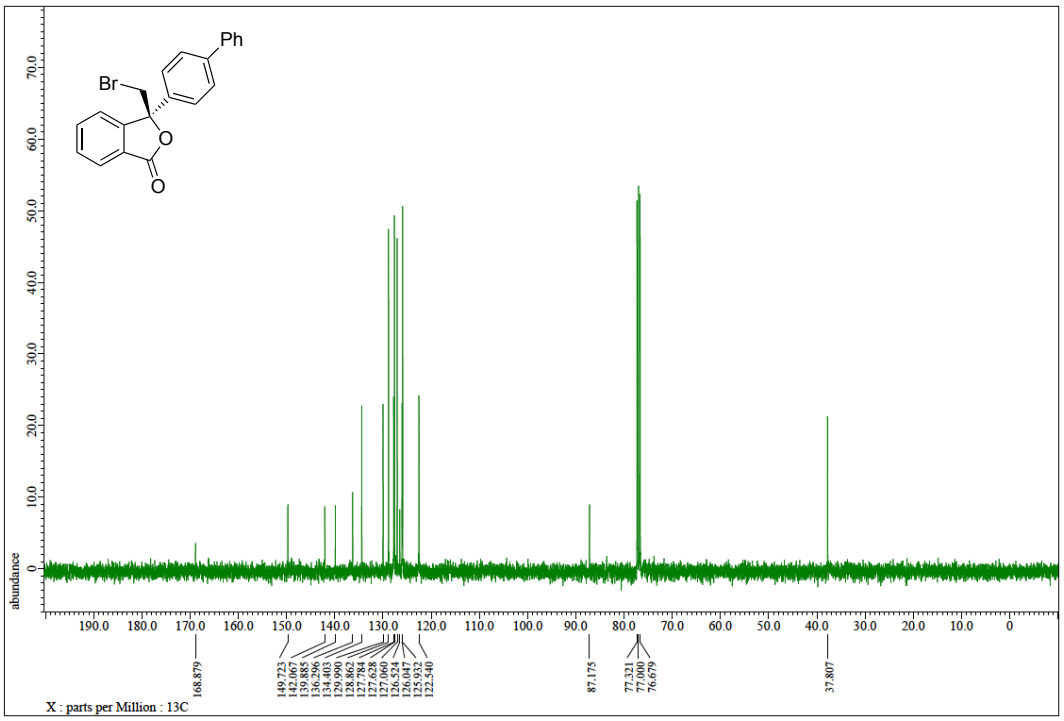

OMe
Br
O
O
abundance
X : parts per Million : 1H

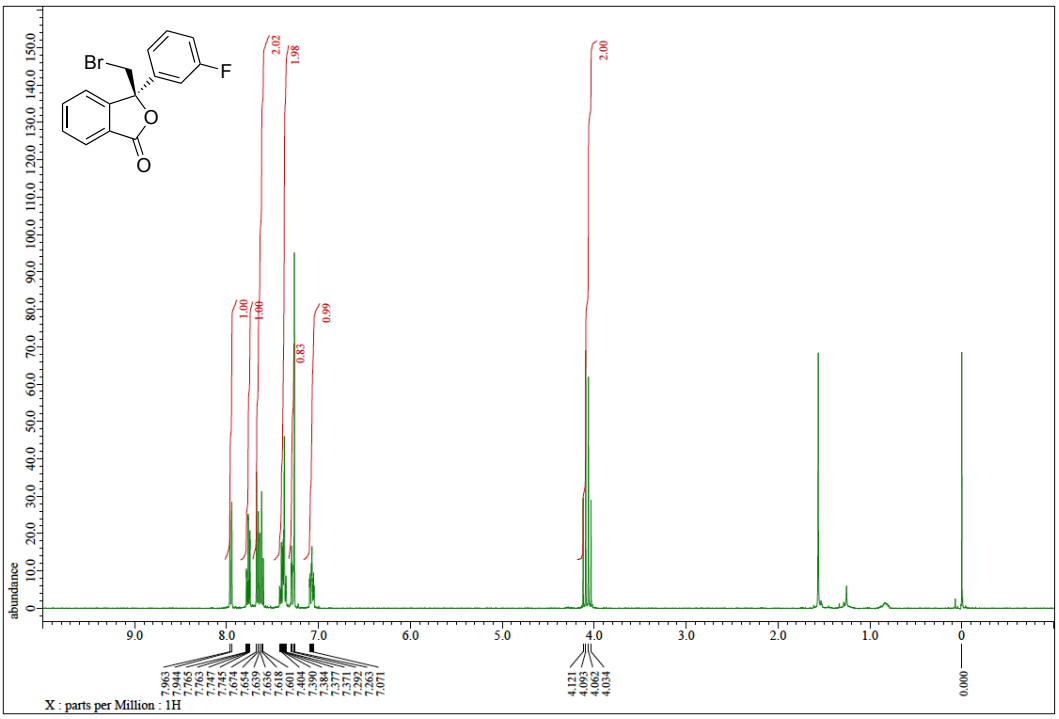

OMe
Br
O
O
(thousandths)
X : parts per Million : 13C

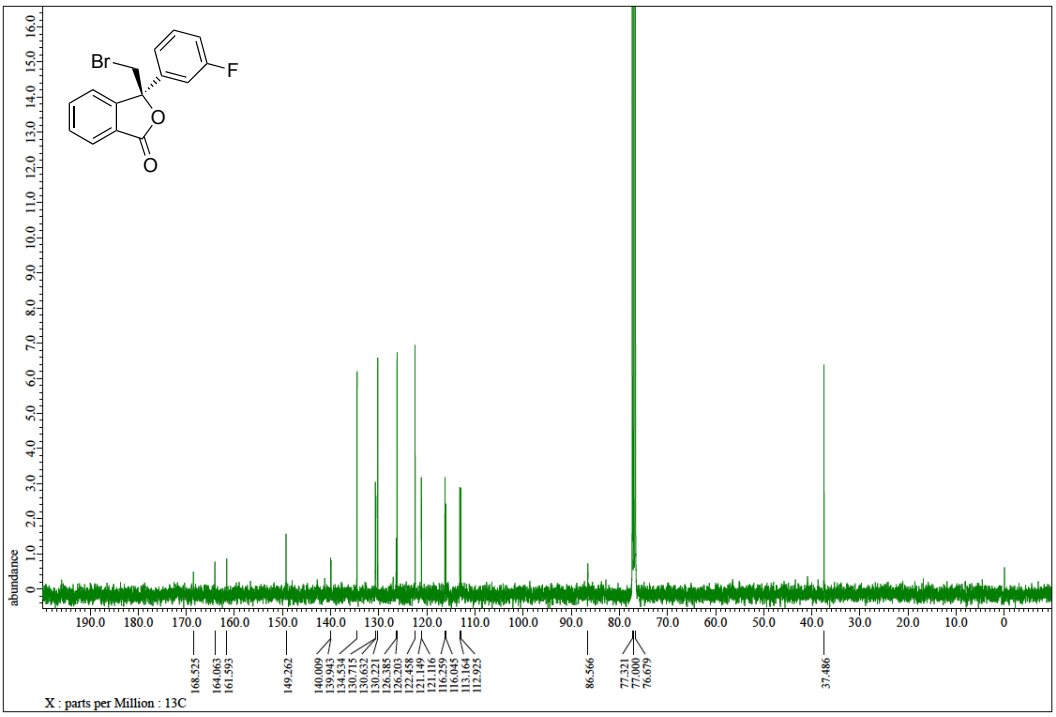

OCF3
Br
O
O
2.97
2.12
2.00
0.98
1.03
1.03
abundance
X : parts per Million : 1H

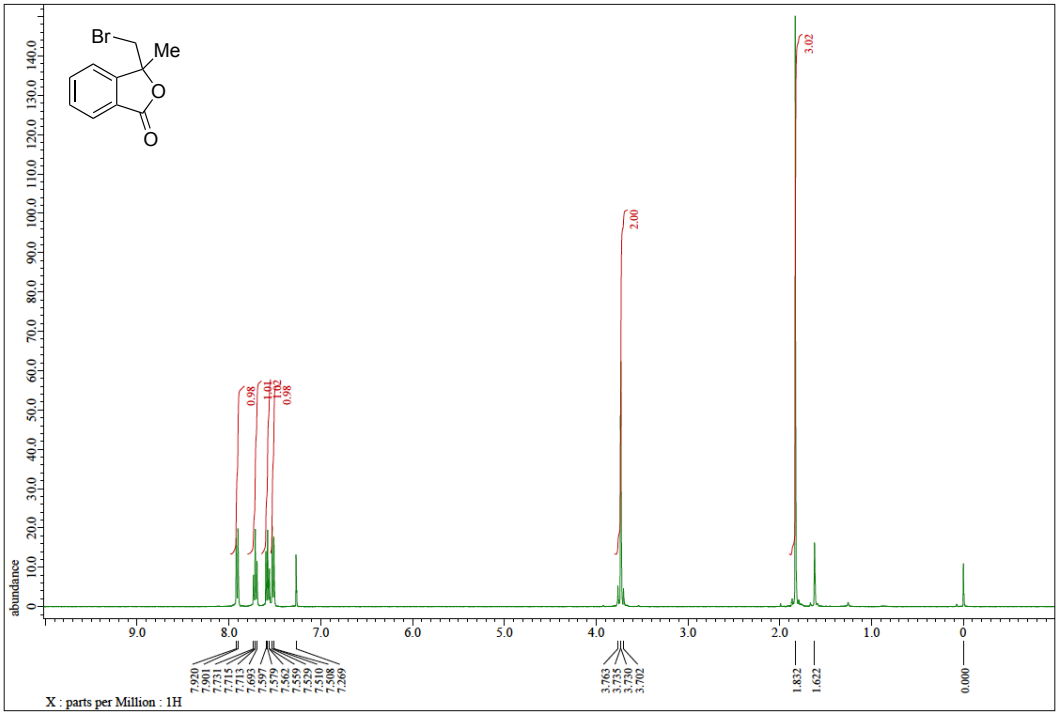

OCF3
Br
O
O
abundance
X : parts per Million : 13C

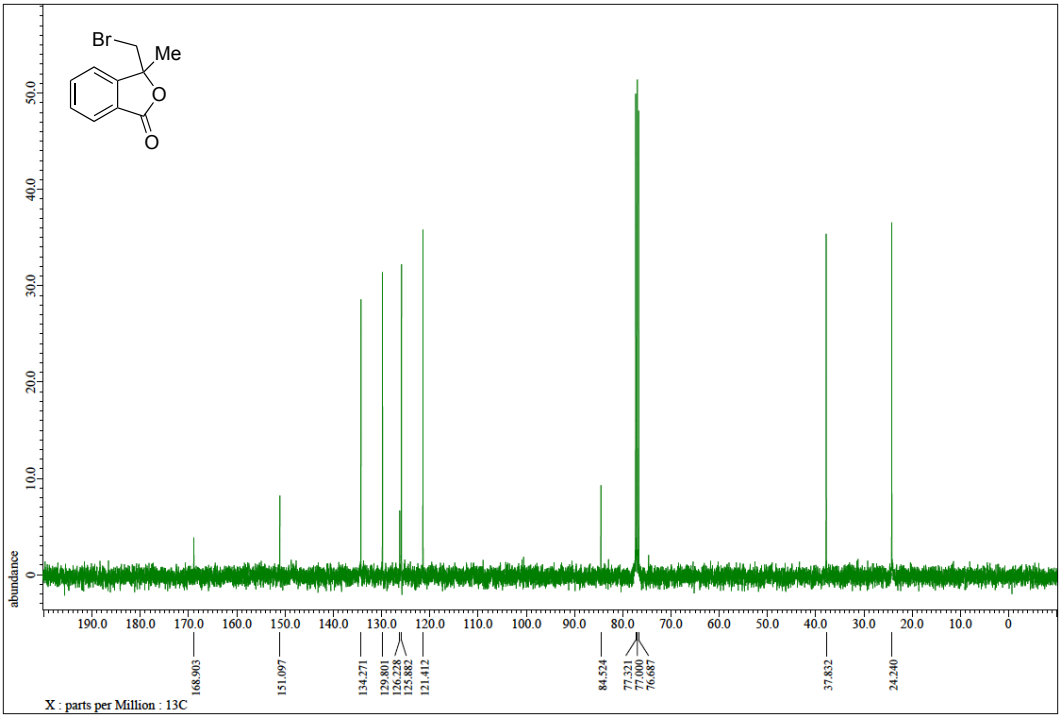

Ph
Br
O
O
abundance
7.09
2.01
2.00
1.01
0.98
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.964
7.962
7.945
7.759
7.741
7.711
7.691
7.626
7.623
7.603
7.568
7.564
7.543
7.456
7.437
7.418
7.379
7.360
4.194
4.166
4.137
4.108
1.636
0.000
X : parts per Million : 1H

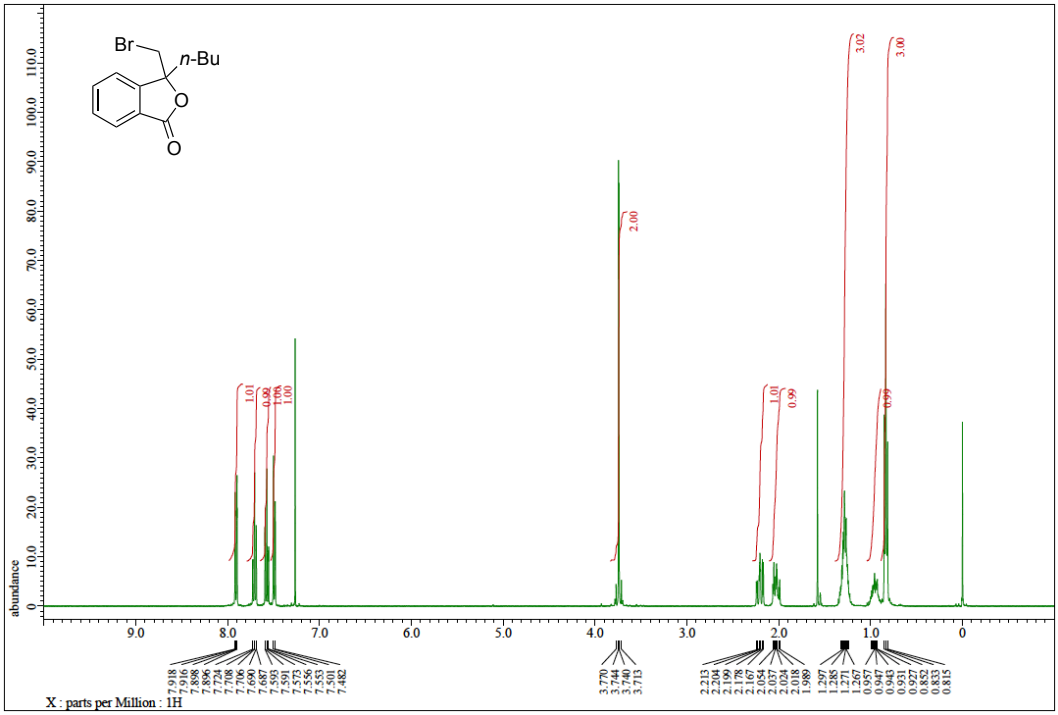

Ph
Br
O
O
abundance
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
168.879
149.723
147.067
139.885
136.296
134.403
129.990
128.862
127.784
127.628
127.060
126.524
126.047
125.823
122.540
87.175
77.321
77.000
76.679
37.807
X : parts per Million : 13C

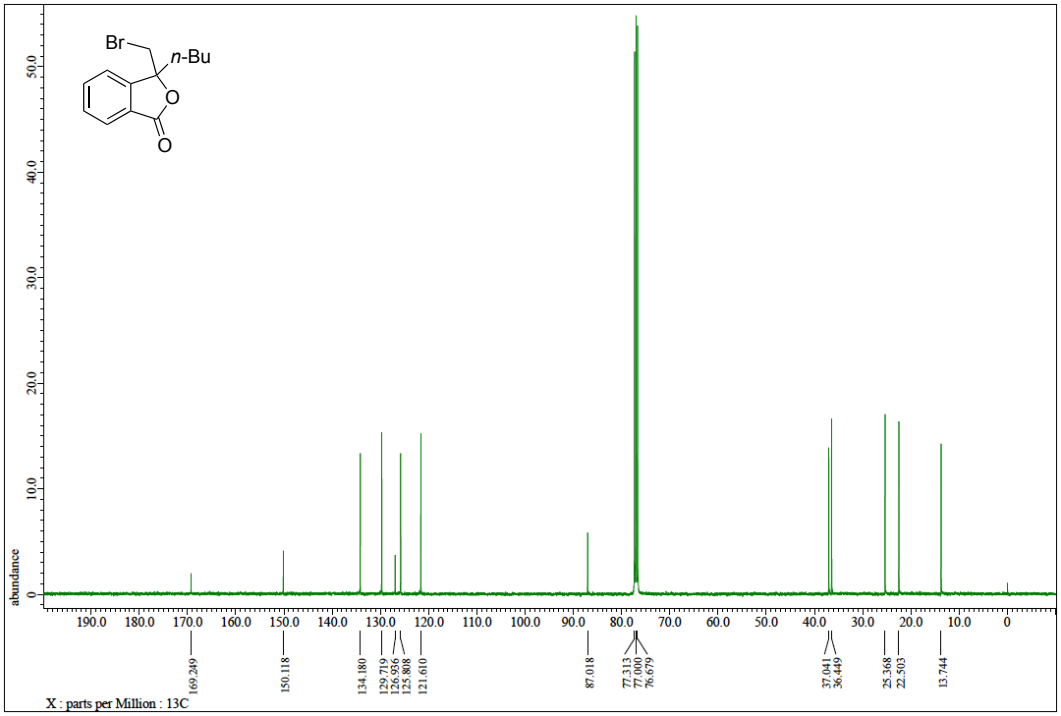

Br
F
O
O
2.02
1.98
2.00
1.00
1.00
0.83
0.99
abundance
X : parts per Million : 1H

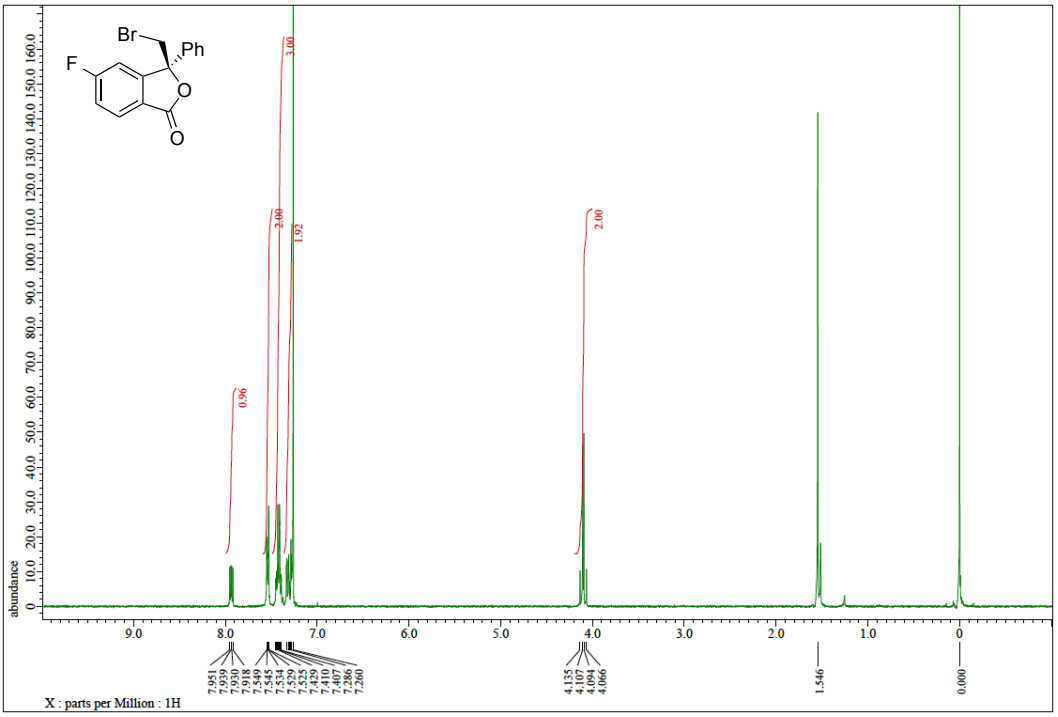

Br
F
O
O
abundance
X : parts per Million : 13C

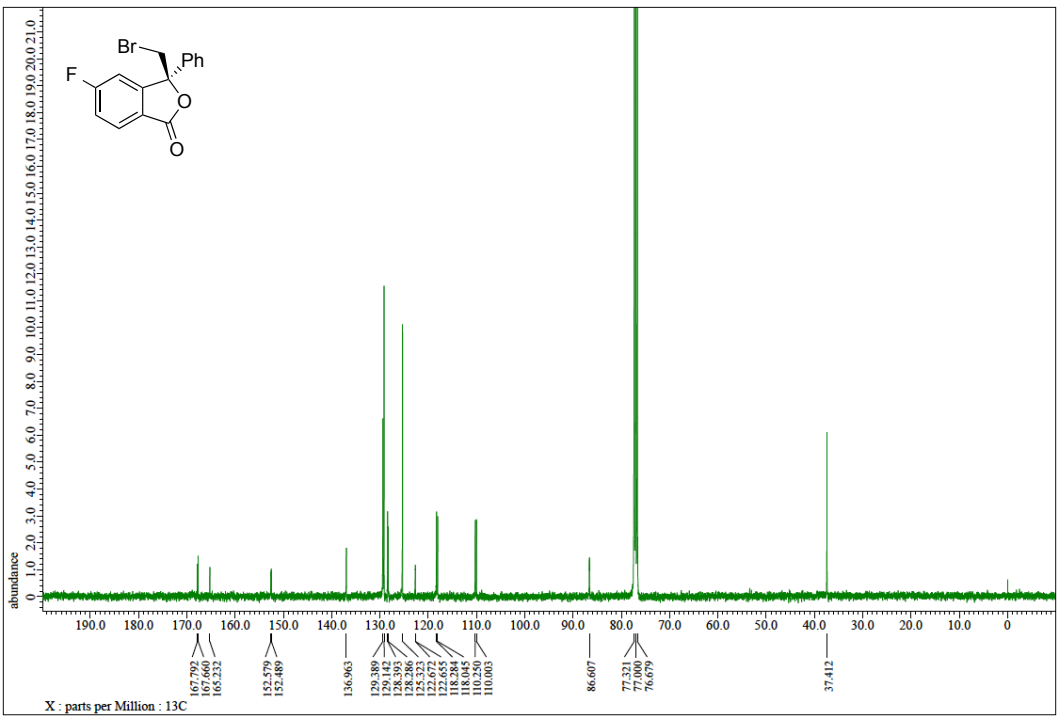

Br
Me
O
O
abundance
X : parts per Million : 1H

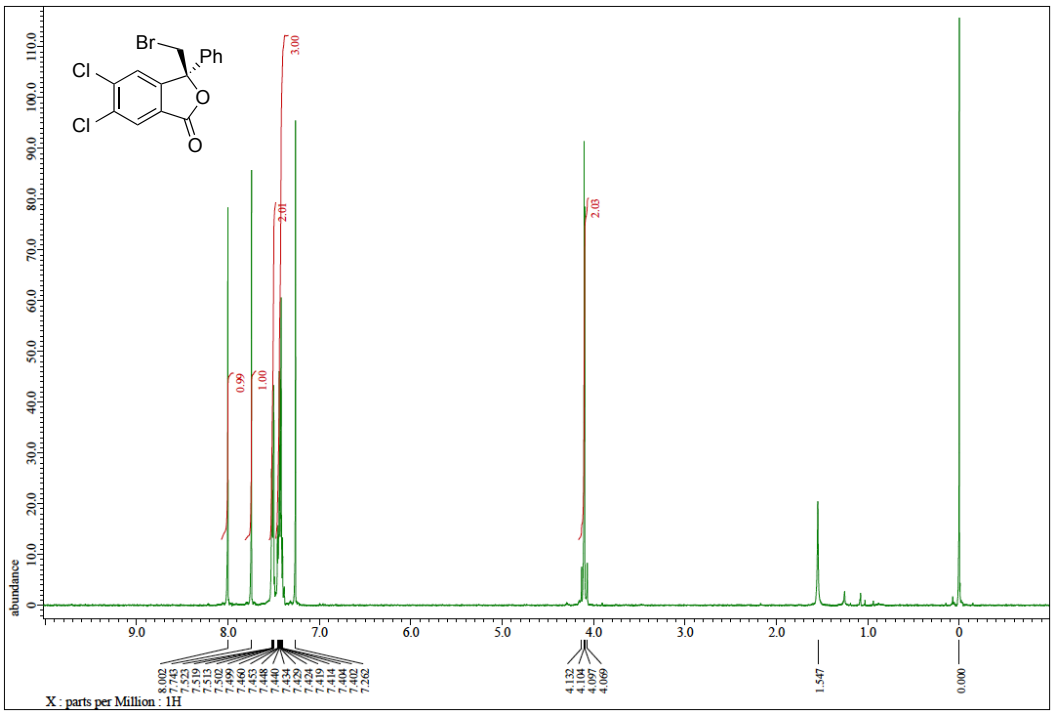

Br
Me
O
O
abundance
X : parts per Million : 13C

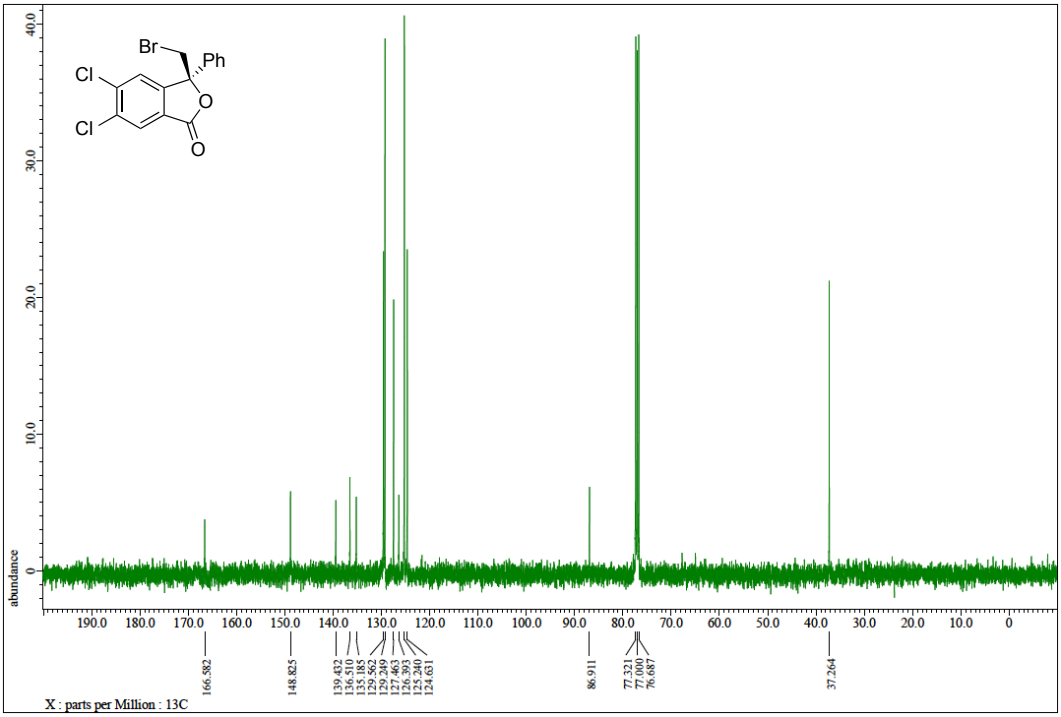

Br
n-Bu
O
O
abundance
X : parts per Million : 1H

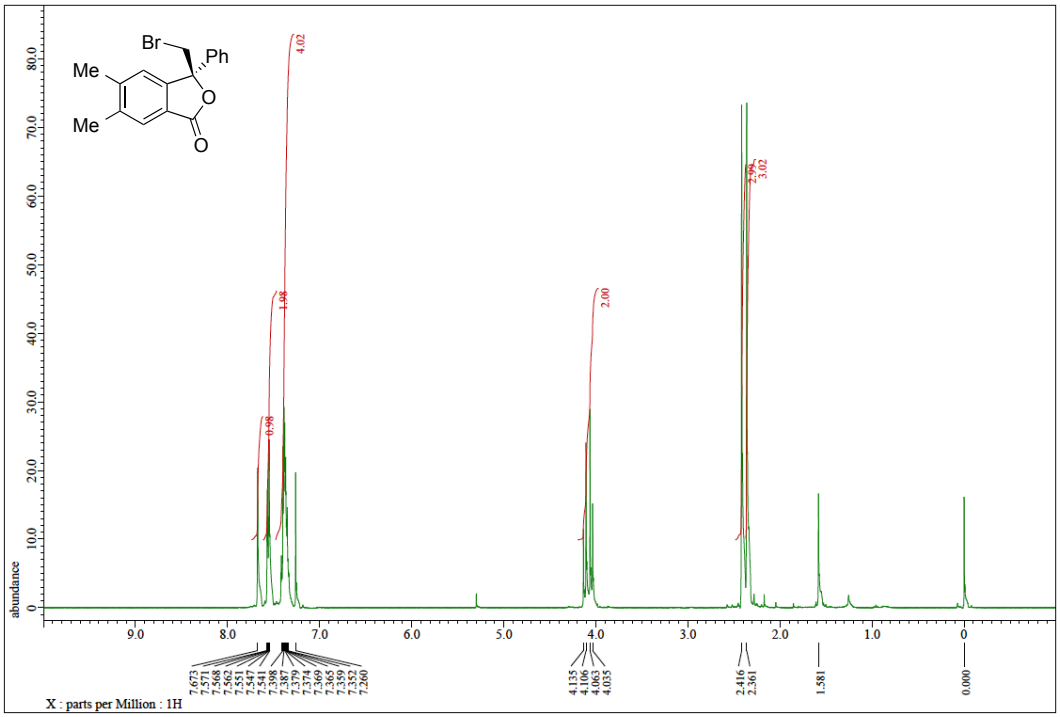

Br
n-Bu
O
O
abundance
X : parts per Million : 13C

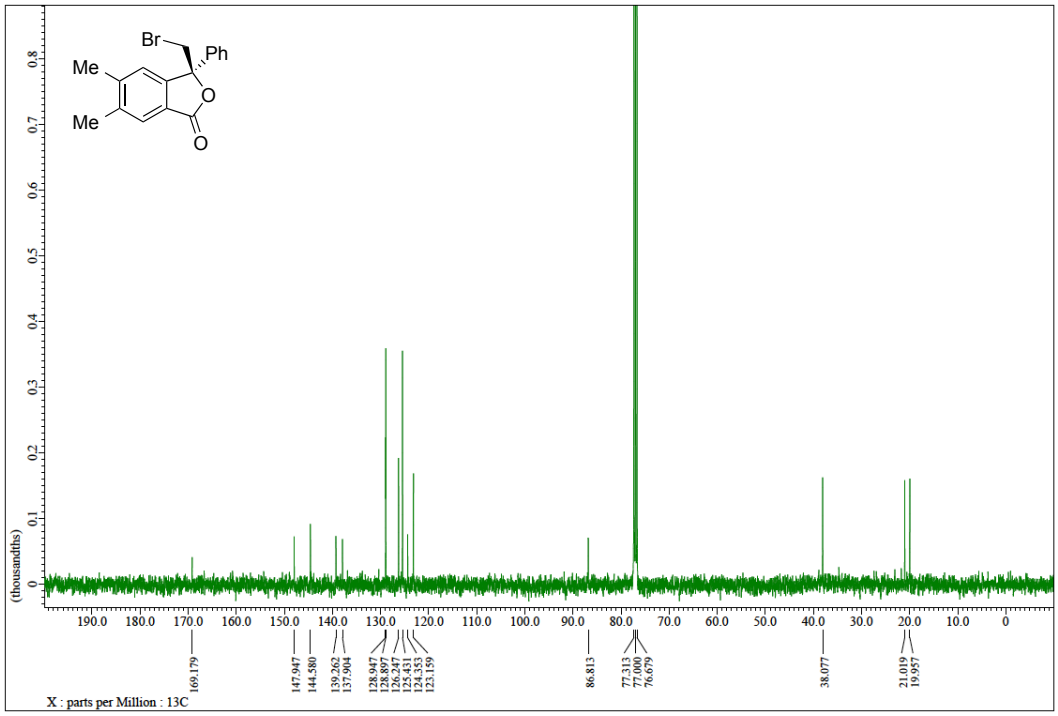

Br
Ph
F
O
O
abundance
X : parts per Million : 1H
7.951
7.939
7.930
7.918
7.549
7.545
7.534
7.529
7.525
7.429
7.410
7.407
7.286
7.260
4.135
4.107
4.094
4.066
1.546
0.000
0.96
3.00
2.00
1.92
2.00

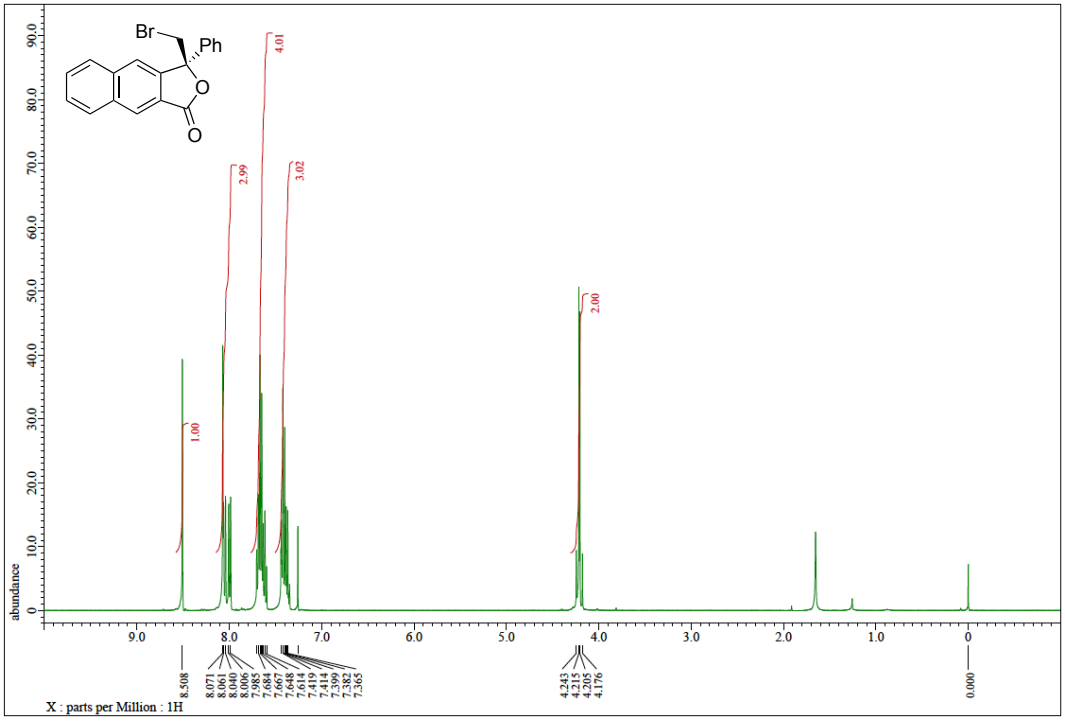

Br
Ph
F
O
O
abundance
X : parts per Million : 13C
167.792
167.660
165.232
152.579
152.489
136.963
129.389
129.142
128.393
128.286
125.323
122.675
122.565
118.284
118.045
110.250
110.003
86.607
77.321
77.000
76.679
37.412

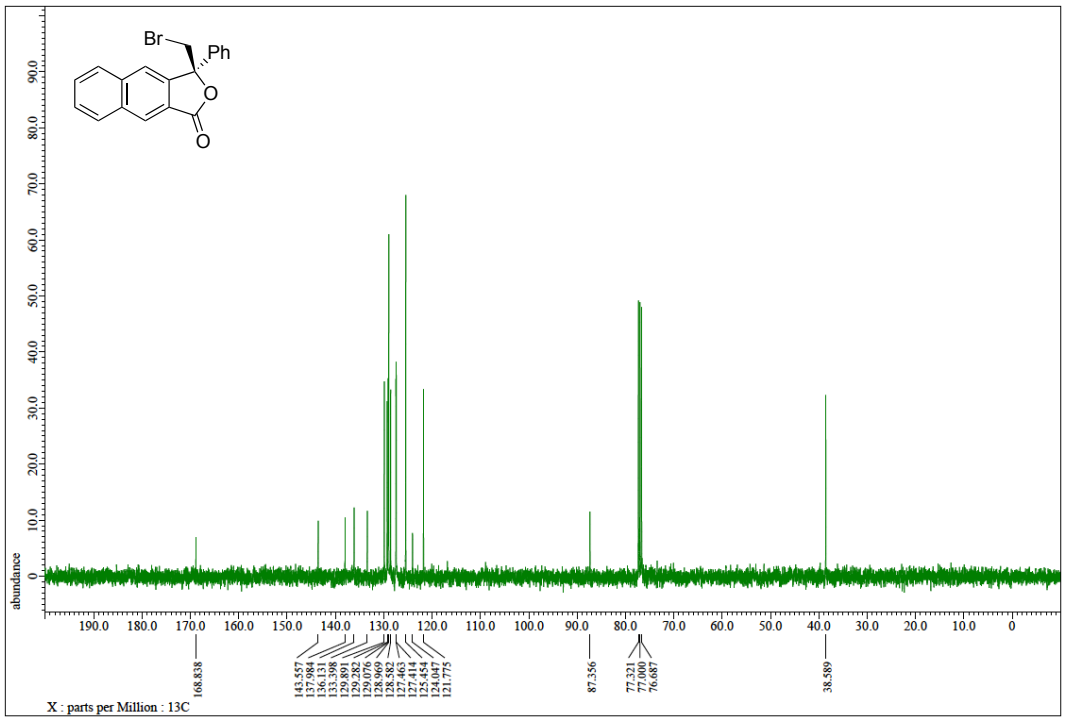

Br
Ph
Cl
Cl
O
O
abundance
X : parts per Million : 1H

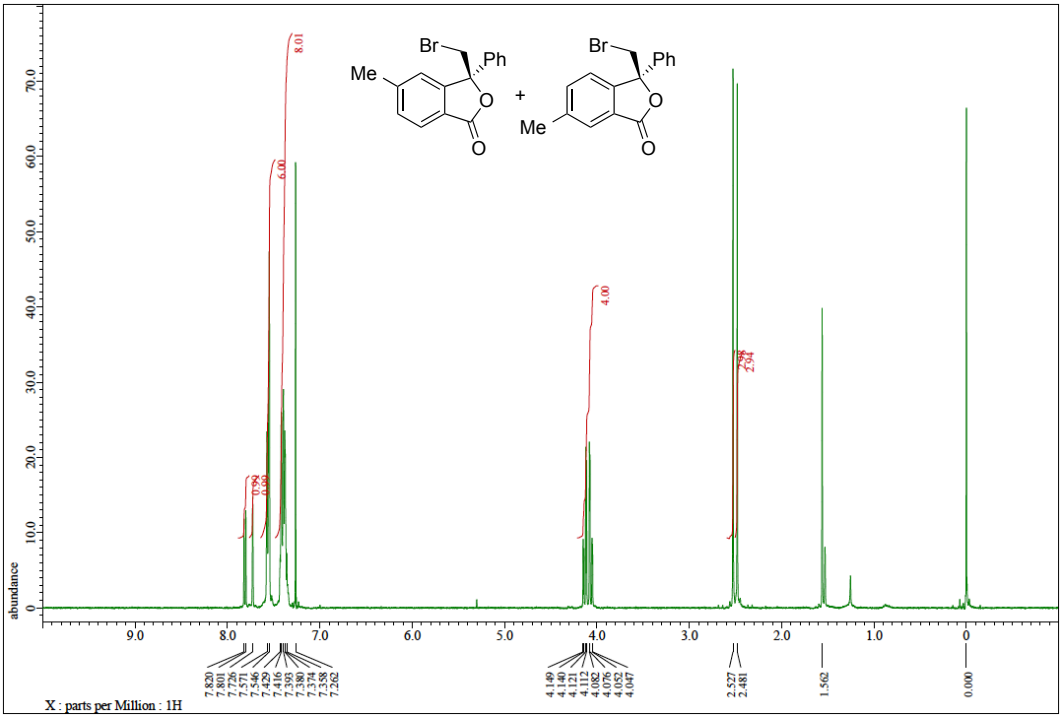

Br
Ph
Cl
Cl
O
O
abundance
X : parts per Million : 13C

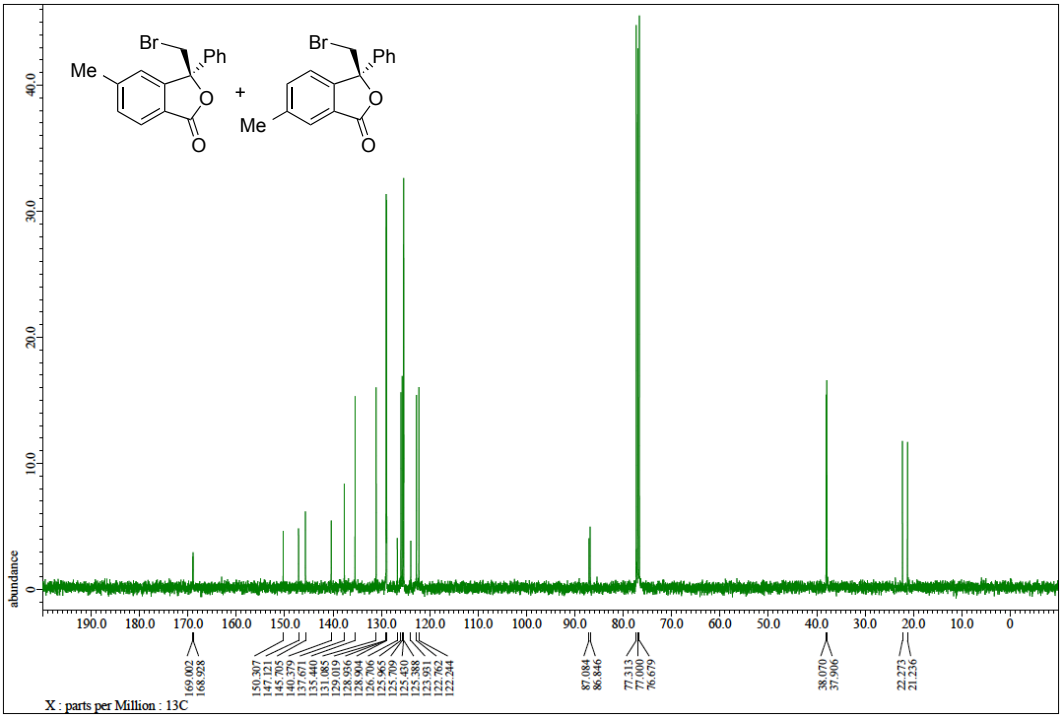

Br
Ph
Me
Me
O
O
4.02
1.98
0.98
2.00
3.02
abundance
X : parts per Million : 1H

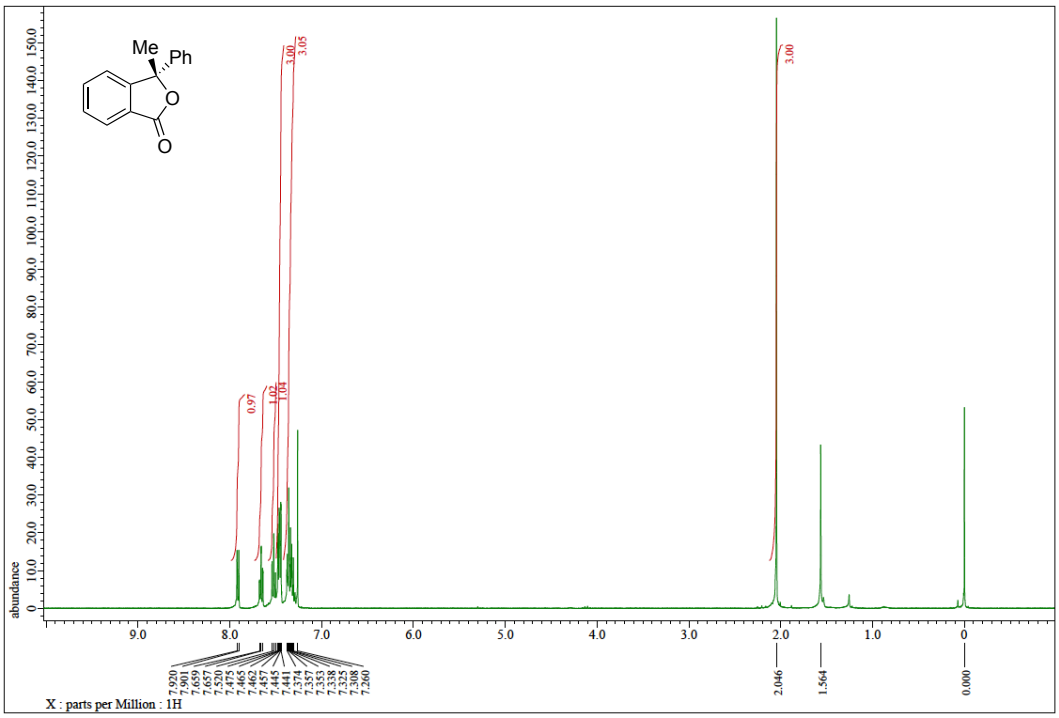

Br
Ph
Me
Me
O
O
(thousandths)
X : parts per Million : 13C

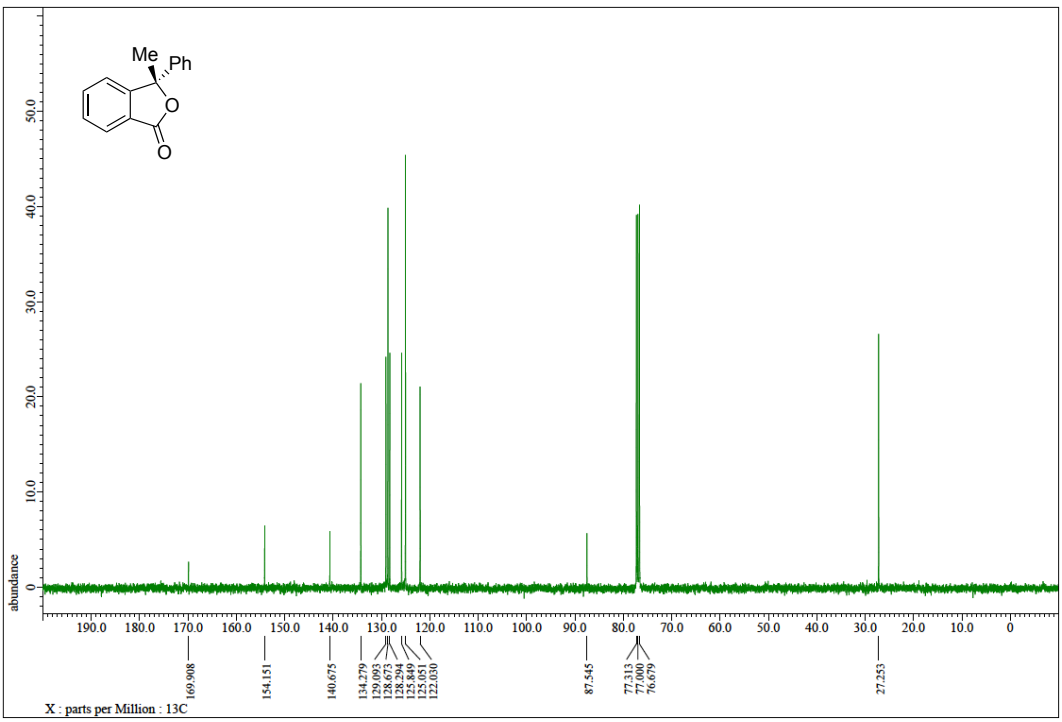

Br
Ph
O
O
abundance
1.00
2.99
4.01
3.02
2.00
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
8.508
8.071
8.061
8.040
8.006
7.985
7.684
7.666
7.648
7.614
7.419
7.414
7.398
7.382
7.365
4.243
4.215
4.208
4.176
0.000
X : parts per Million : 1H

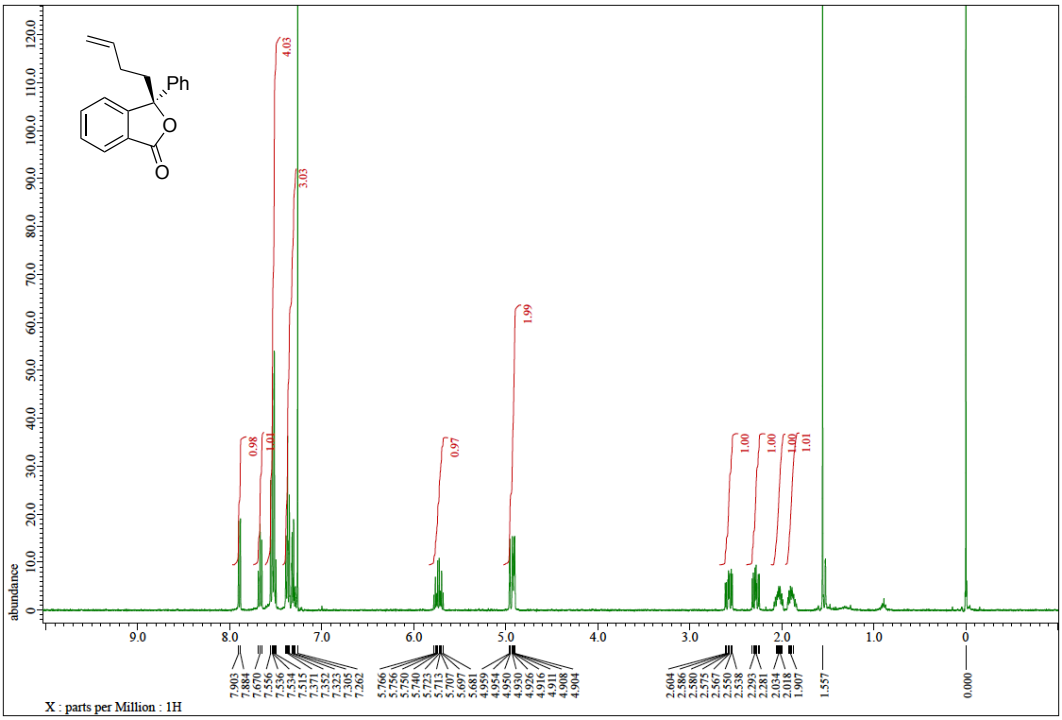

Br
Ph
O
O
abundance
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
168.838
143.557
137.984
135.131
133.398
129.891
129.282
129.076
128.969
128.832
127.463
127.414
125.454
124.047
121.775
87.356
77.321
77.000
76.687
38.589
X : parts per Million : 13C

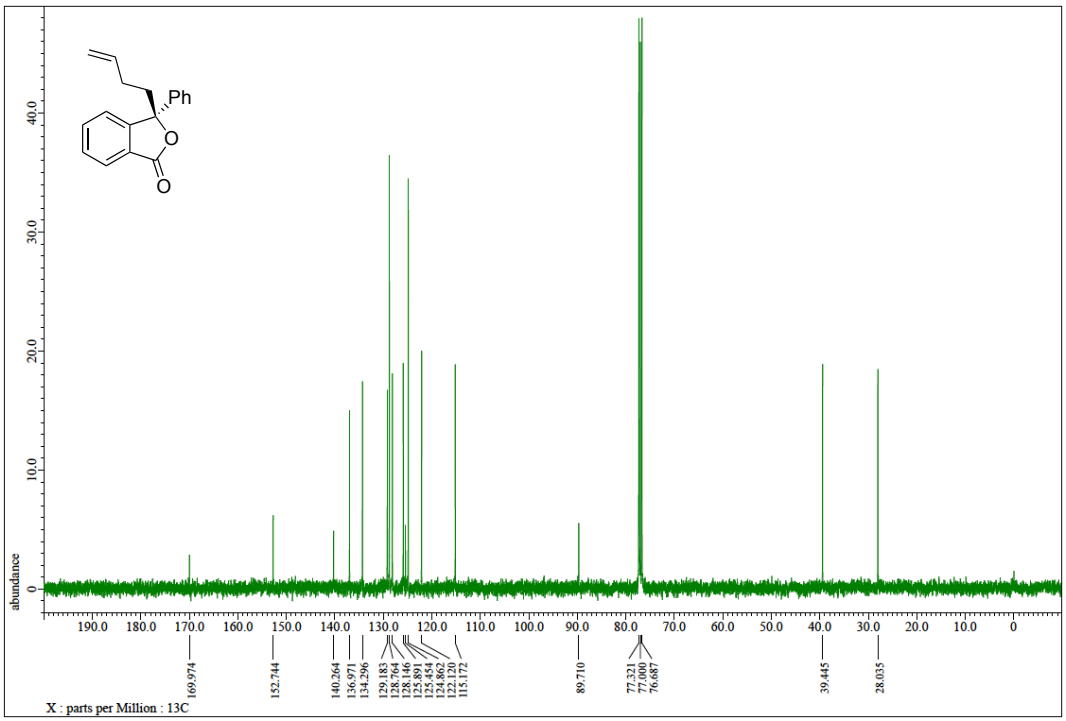

Br
Ph
Me
O
O
+
Br
Ph
Me
O
O
8.01
6.00
4.00
0.92
0.90
2.98
2.94
abundance
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.820
7.801
7.790
7.571
7.546
7.429
7.416
7.393
7.380
7.374
7.358
7.262
4.149
4.140
4.121
4.112
4.082
4.076
4.052
4.047
2.527
2.481
1.562
0.000
X : parts per Million : 1H

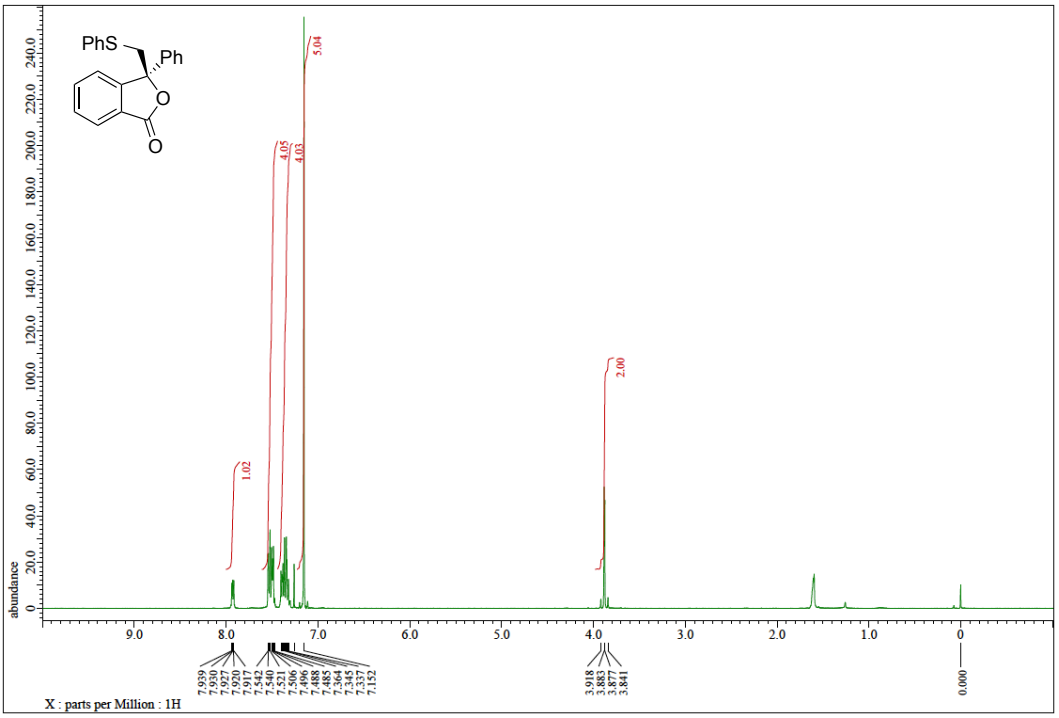

Br
Ph
Me
O
O
+
Br
Ph
Me
O
O
abundance
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
169.002
168.928
150.307
147.121
145.705
140.779
137.671
135.440
131.085
129.019
128.956
128.844
126.706
125.965
125.709
125.430
123.588
123.981
122.762
122.244
87.084
86.846
77.313
77.000
76.679
38.070
37.906
22.273
21.236
X : parts per Million : 13C

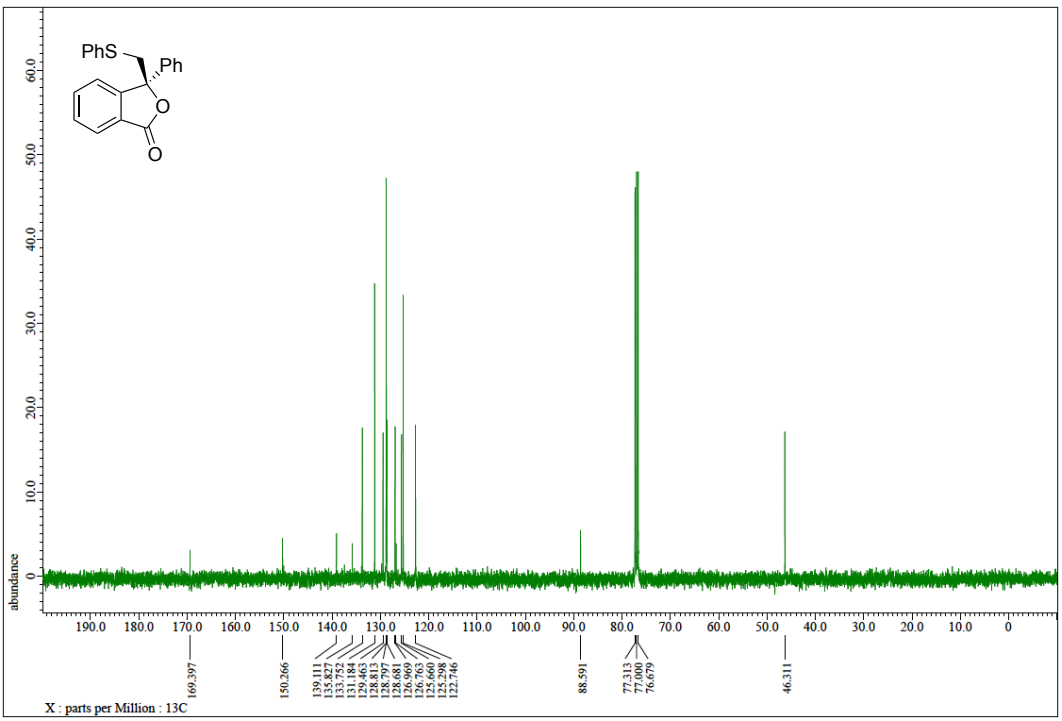

Me
Ph
O
O
abundance
X : parts per Million : 1H


Me
Ph
O
O
abundance
X : parts per Million : 13C

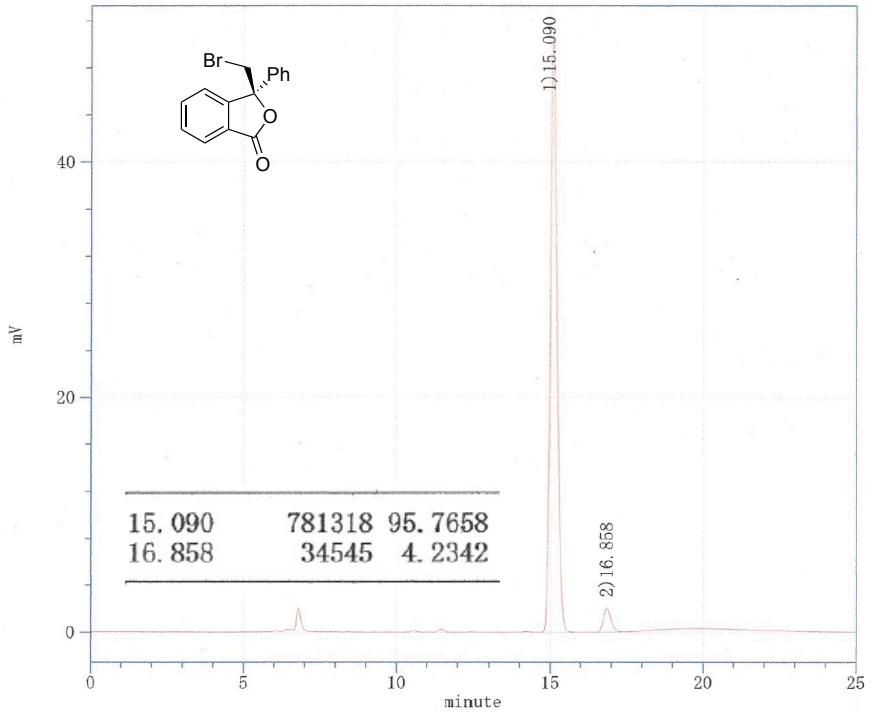

Ph
O
O
abundance
X : parts per Million : 1H

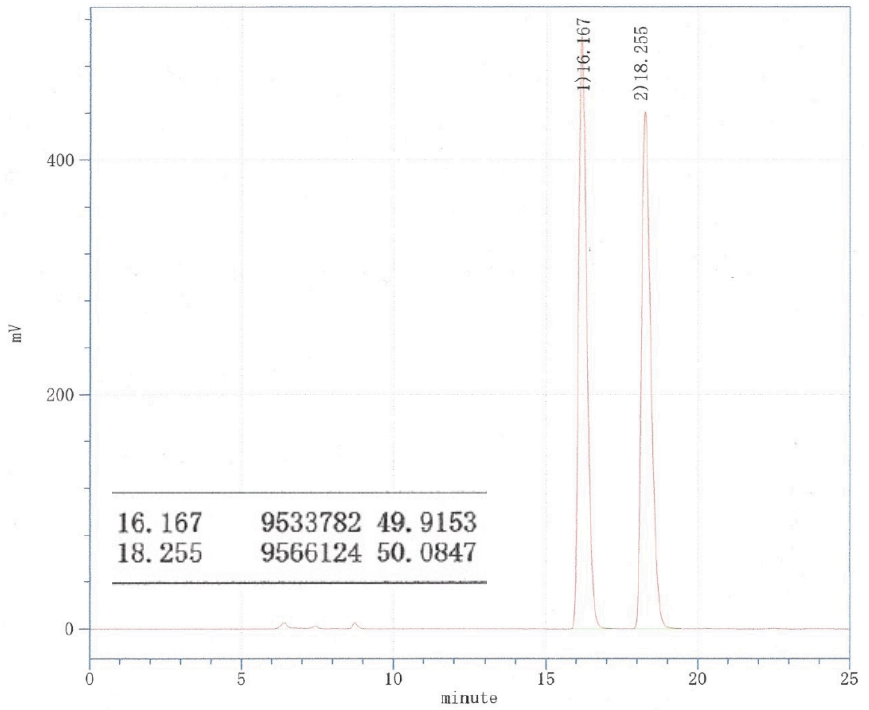

Ph
O
O
abundance
X : parts per Million : 13C

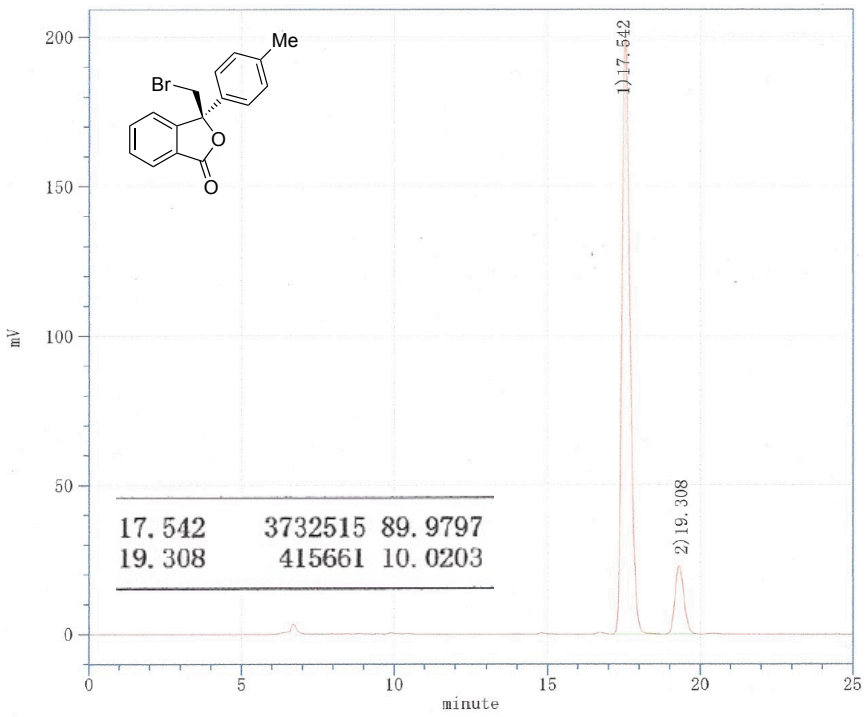

PhS
Ph
O
O
abundance
X : parts per Million : 1H

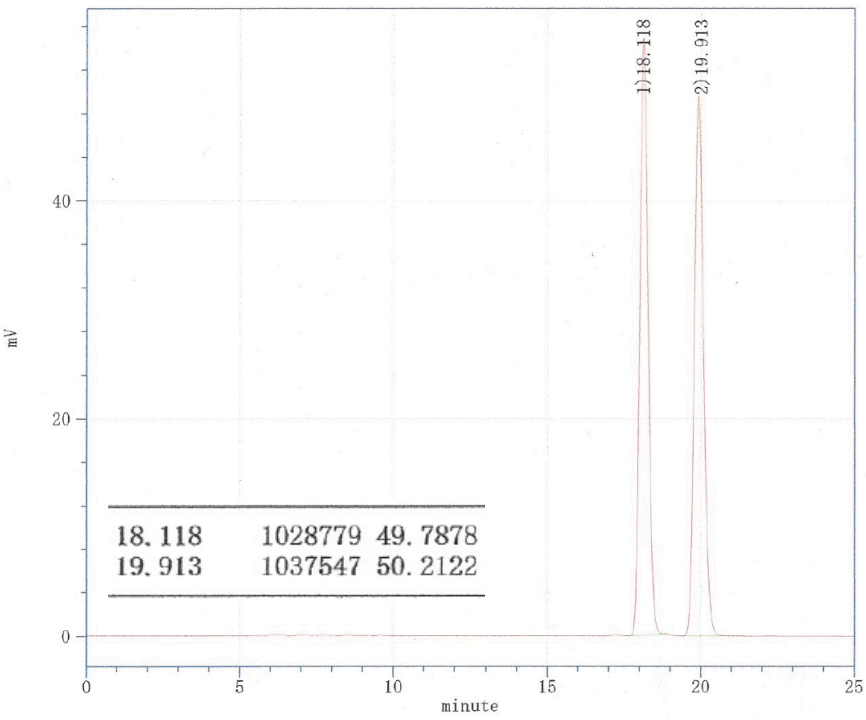

PhS
Ph
O
O
abundance
X : parts per Million : 13C

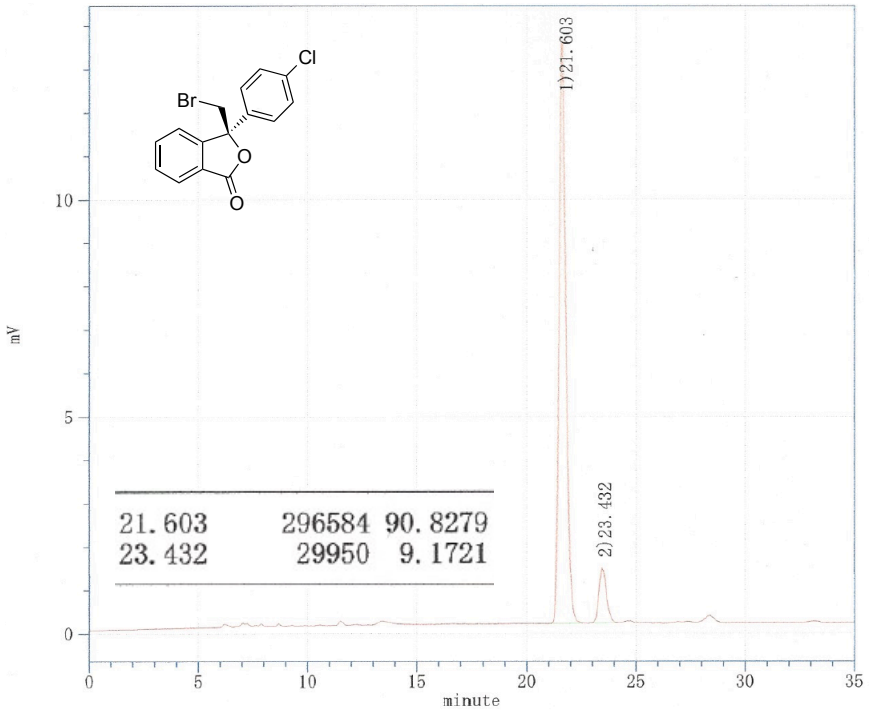
HPLC Charts

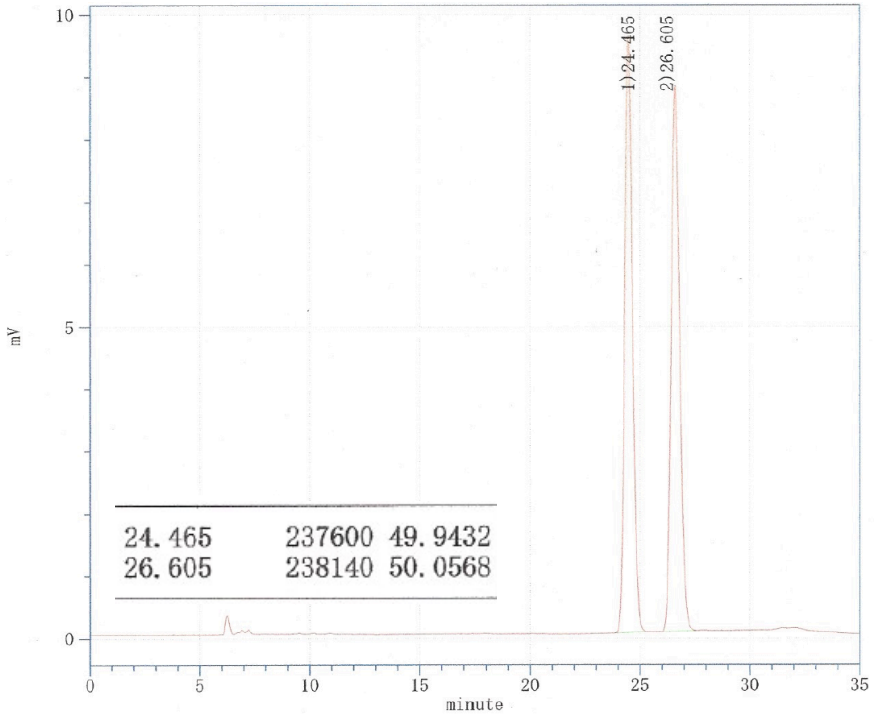

Br
Ph
O
O
1) 15.090
2) 16.858
mV
40
20
0
0
5
10
15
20
25
minute
15.090 781318 95.7658
16.858 34545 4.2342

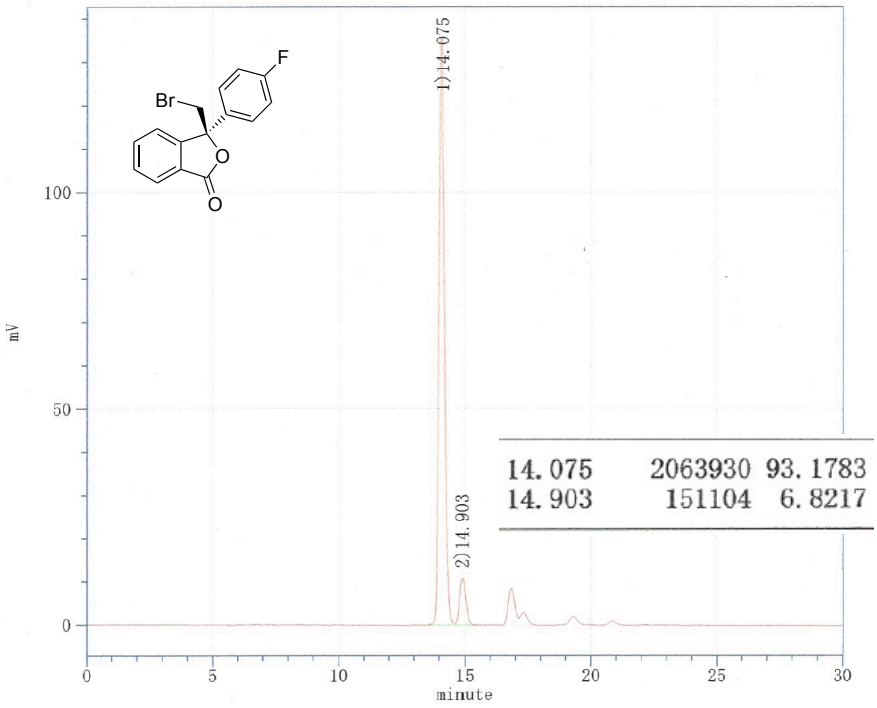

1) 16.167
2) 18.255
mV
400
200
0
0
5
10
15
20
25
minute
16.167 9533782 49.9153
18.255 9566124 50.0847

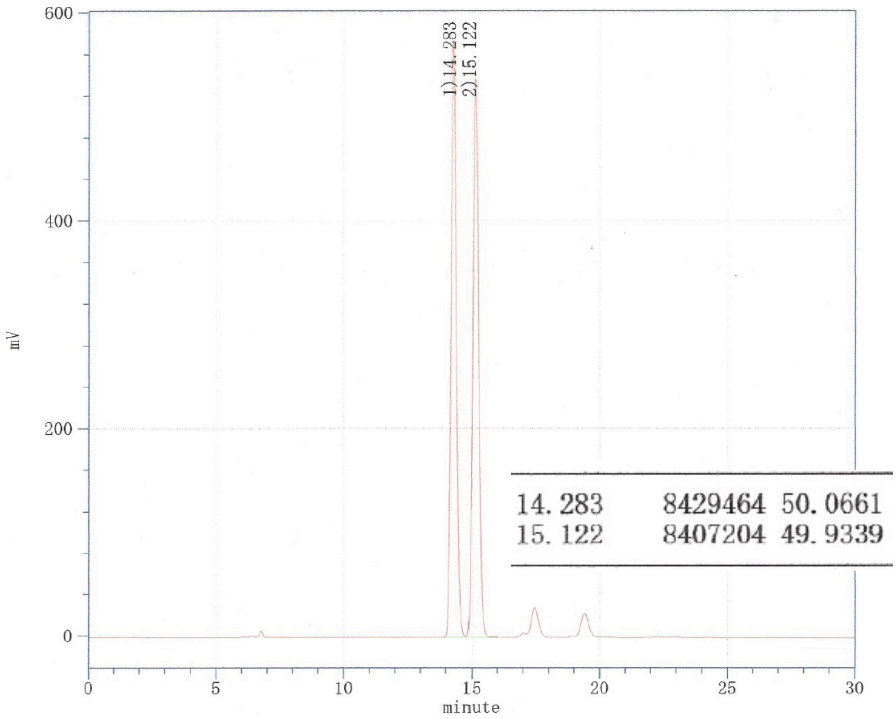

Me
Br
O
O
1) 17.542
2) 19.308
mV
minute
17.542 3732515 89.9797
19.308 415661 10.0203

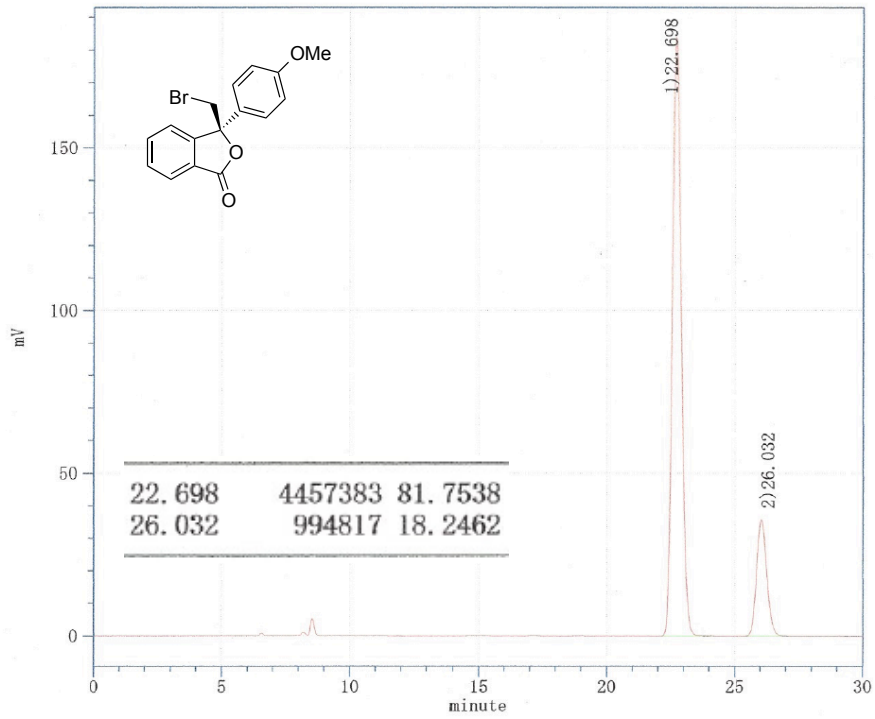

1) 18.118
2) 19.913
mV
minute
18.118 1028779 49.7878
19.913 1037547 50.2122

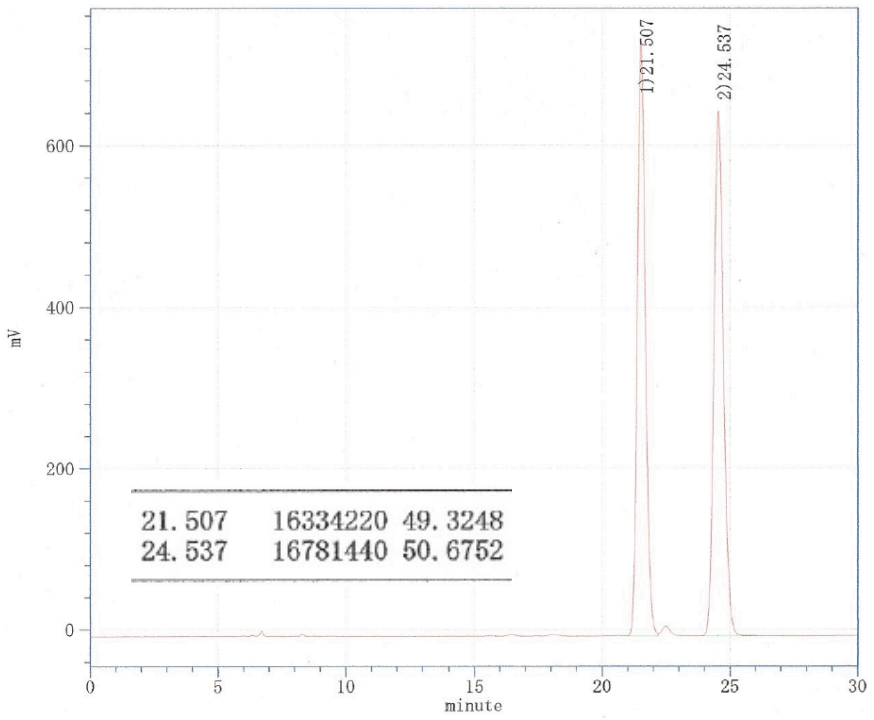

Cl
Br
O
O
1)21.603
2)23.432
mV
10
5
0
0
5
10
15
20
25
30
35
minute
21.603 296584 90.8279
23.432 29950 9.1721

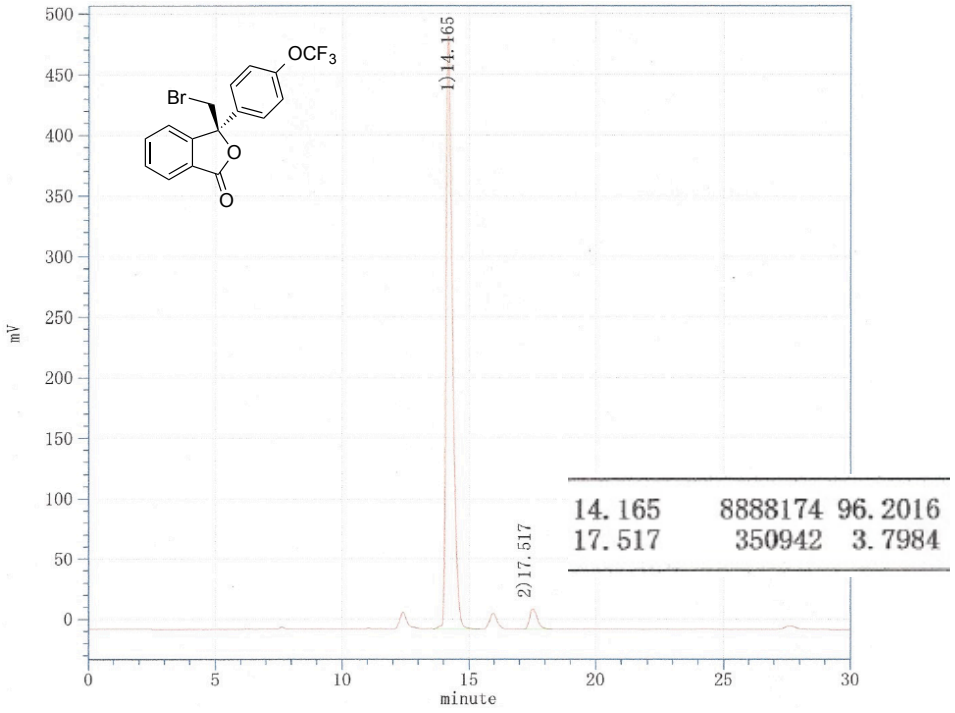

1)24.465
2)26.605
mV
10
5
0
0
5
10
15
20
25
30
35
minute
24.465 237600 49.9432
26.605 238140 50.0568

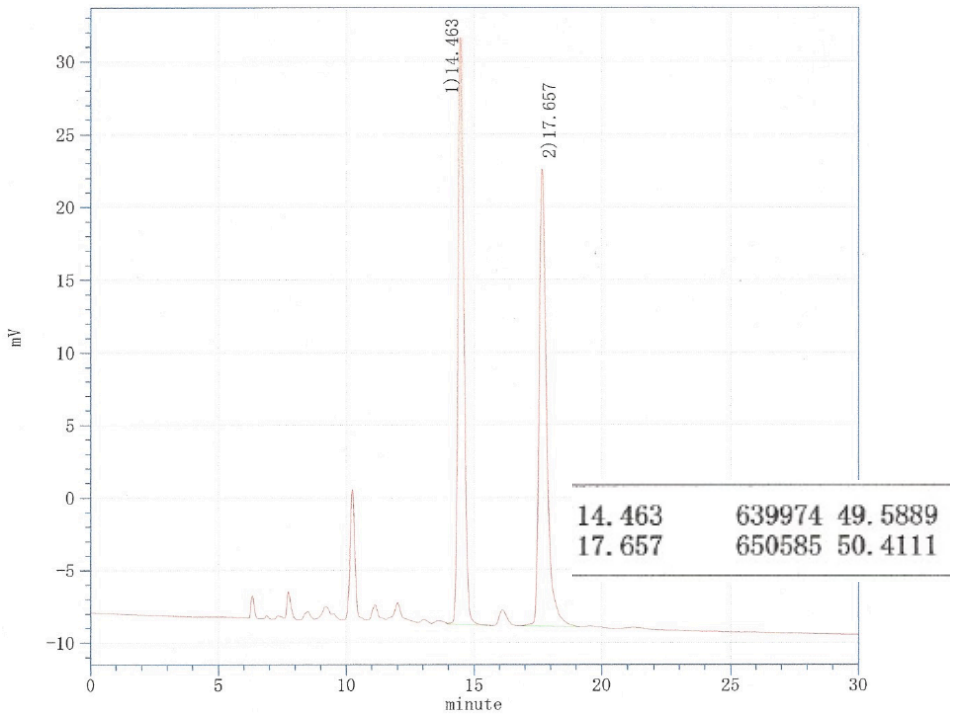

F
Br
O
O
1)14.075
2)14.903
100
50
0
mV
0
5
10
15
20
25
30
minute
14.075 2063930 93.1783
14.903 151104 6.8217

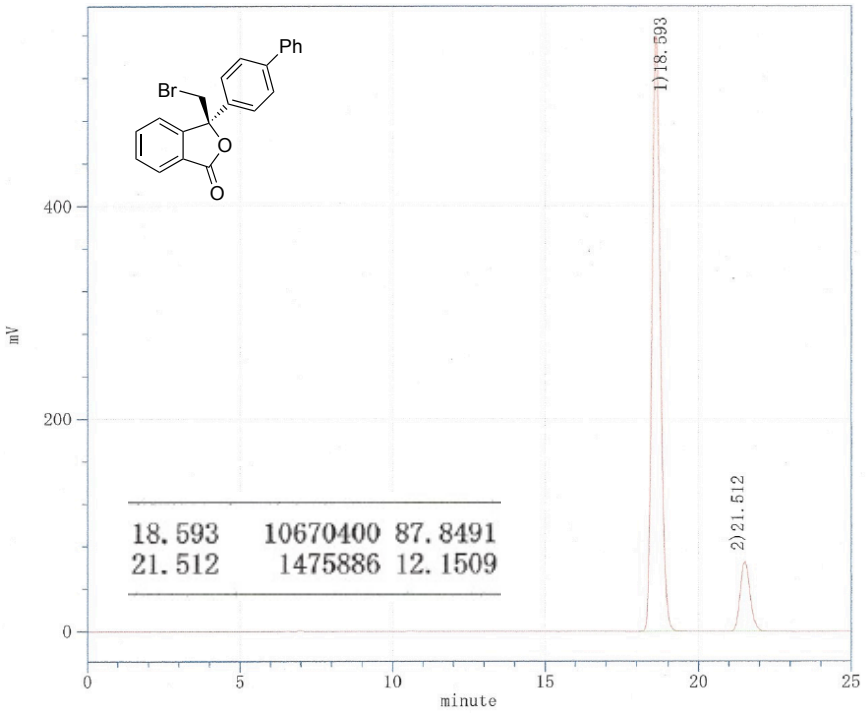

1)14.283
2)15.122
600
400
200
0
mV
0
5
10
15
20
25
30
minute
14.283 8429464 50.0661
15.122 8407204 49.9339

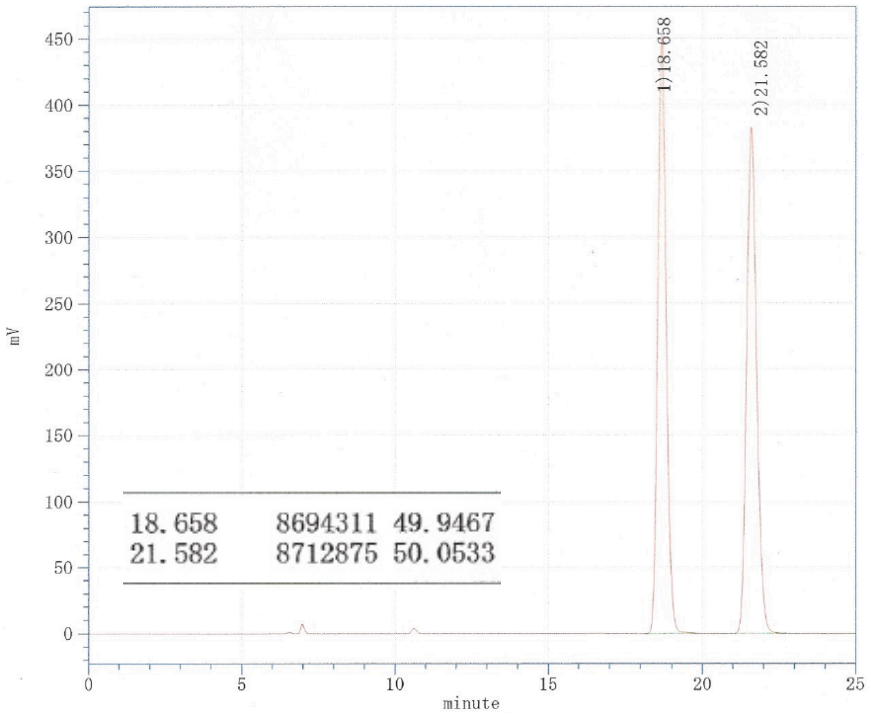

OMe
Br
O
O
1)22.698
2)26.032
mV
150
100
50
0
0
5
10
15
20
25
30
minute
22.698 4457383 81.7538
26.032 994817 18.2462

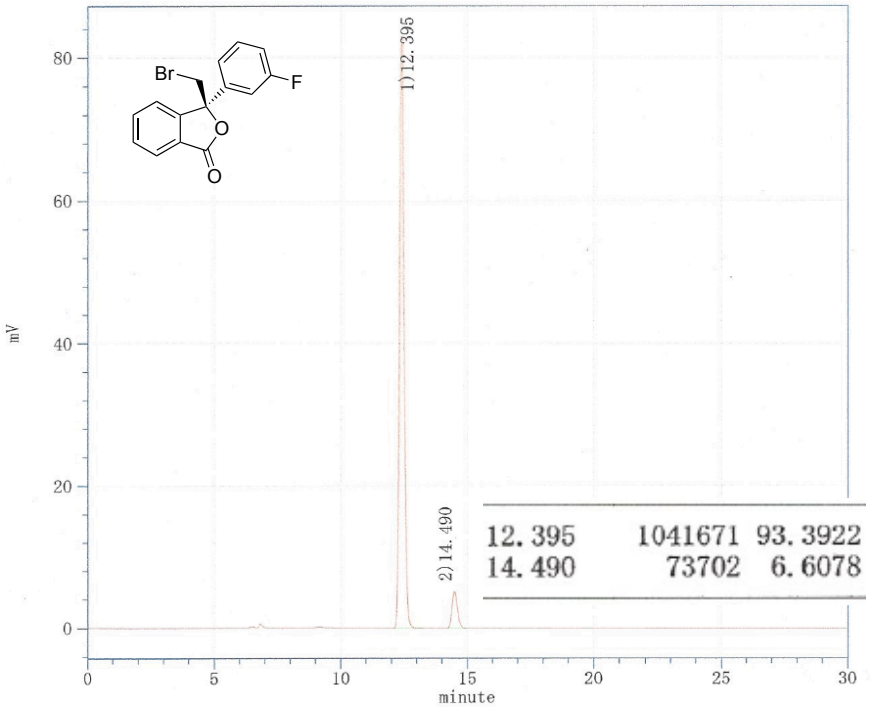

1)21.507
2)24.537
mV
600
400
200
0
0
5
10
15
20
25
30
minute
21.507 16334220 49.3248
24.537 16781440 50.6752

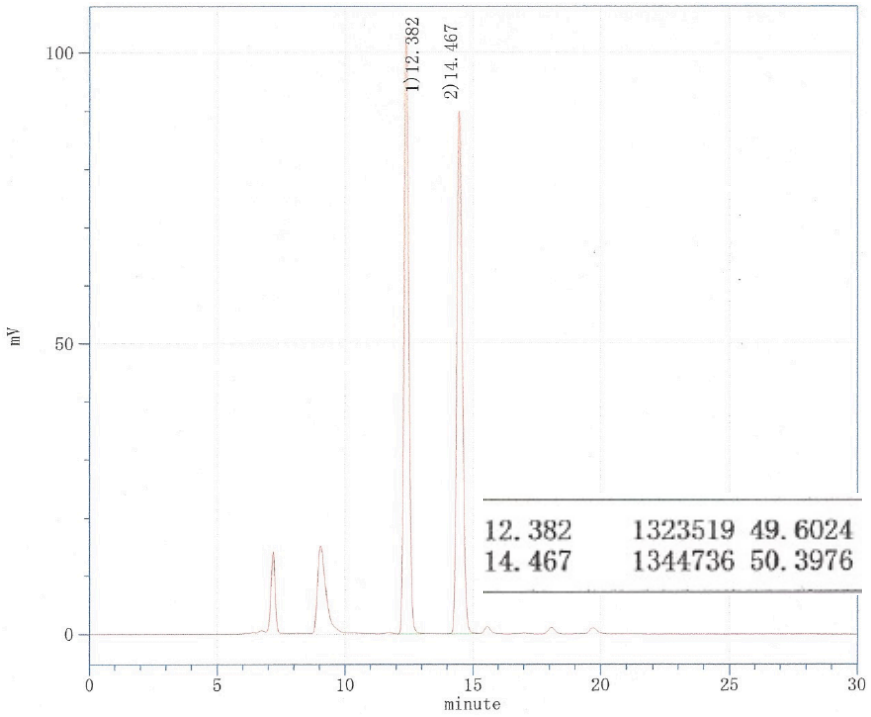

OCF3
Br
O
O
1) 14.165
2) 17.517
mV
minute
14.165 8888174 96.2016
17.517 350942 3.7984

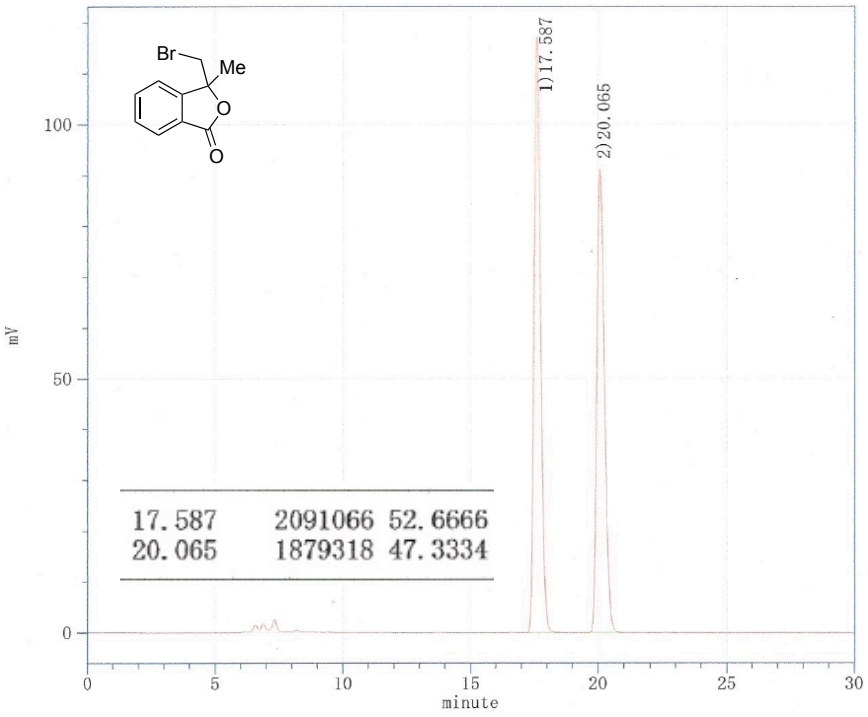

1) 14.463
2) 17.657
mV
minute
14.463 639974 49.5889
17.657 650585 50.4111

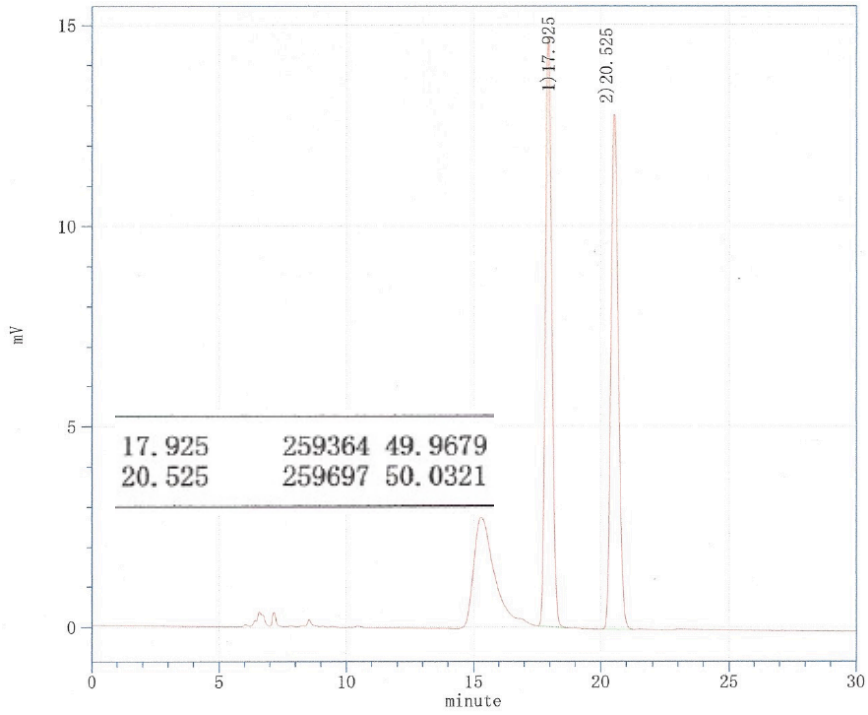

Ph
Br
O
O
1)18.593
2)21.512
mV
400
200
0
0
5
10
15
20
25
minute
18.593 10670400 87.8491
21.512 1475886 12.1509

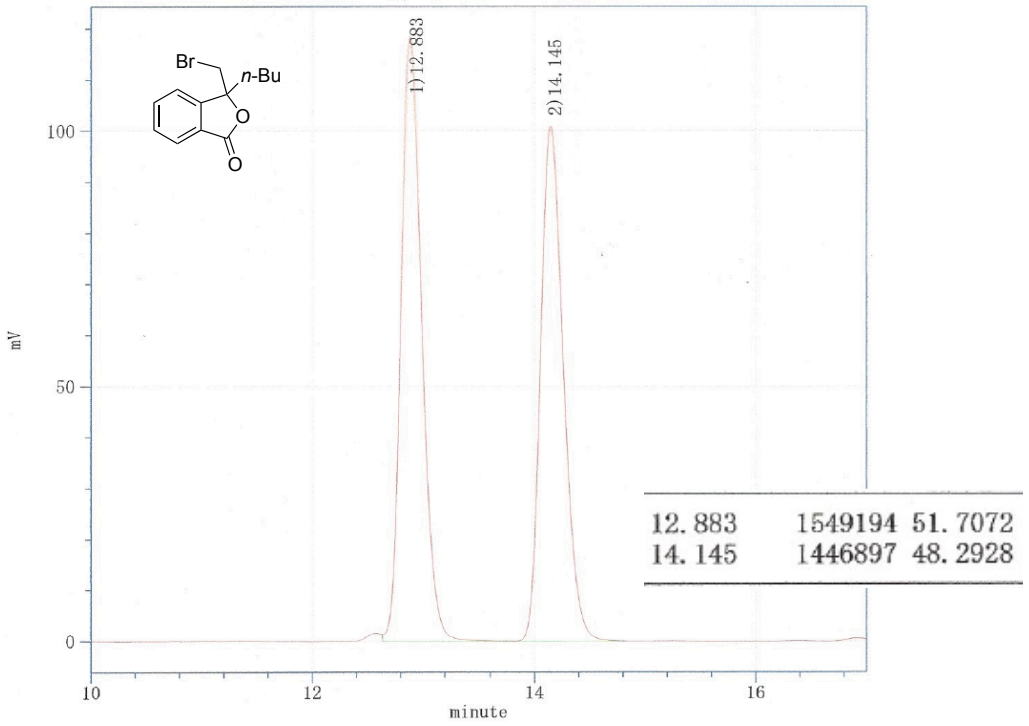

1)18.658
2)21.582
mV
450
400
350
300
250
200
150
100
50
0
0
5
10
15
20
25
minute
18.658 8694311 49.9467
21.582 8712875 50.0533


Br
F
O
O
1)12.395
2)14.490
mV
80
60
40
20
0
0
5
10
15
20
25
30
minute
12.395 1041671 93.3922
14.490 73702 6.6078

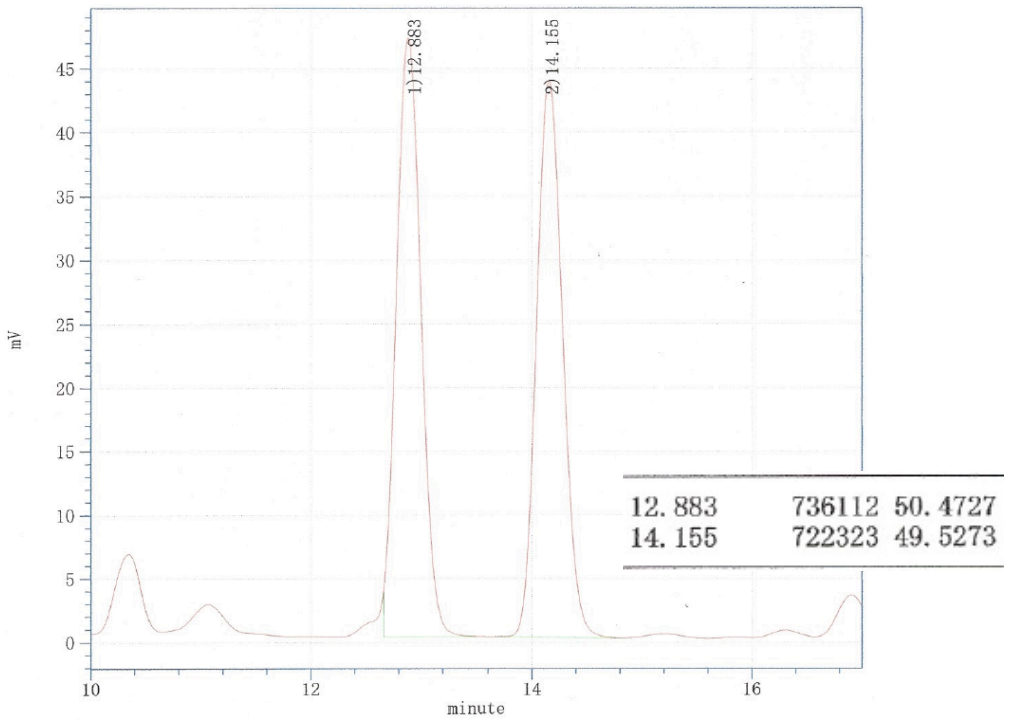

1)12.382
2)14.467
mV
100
50
0
0
5
10
15
20
25
30
minute
12.382 1323519 49.6024
14.467 1344736 50.3976


Br
Me
O
O
1) 17.587
2) 20.065
100
50
0
mV
17.587 2091066 52.6666
20.065 1879318 47.3334
0
5
10
15
20
25
30
minute

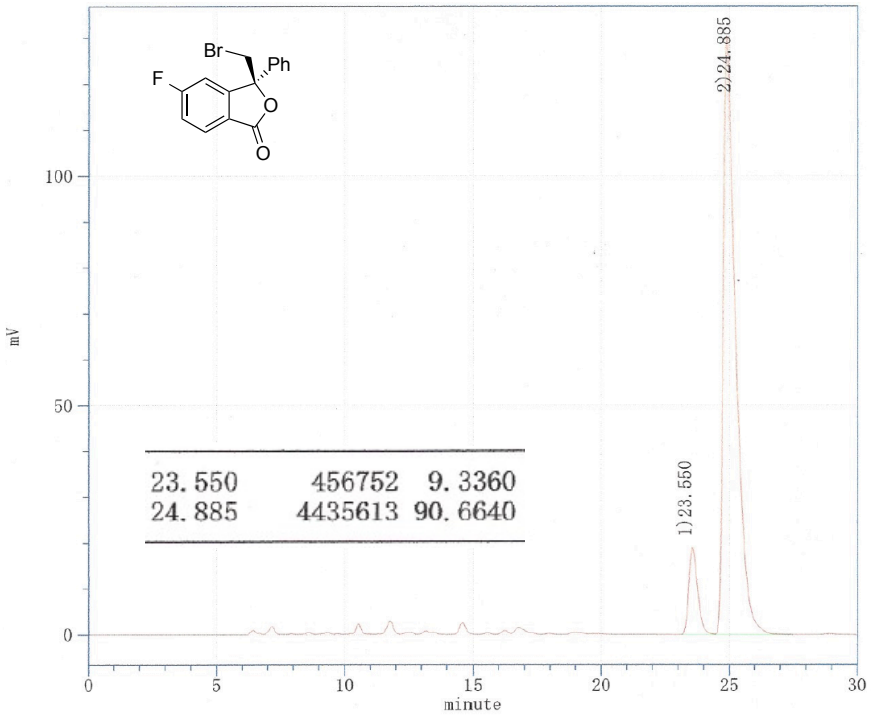

1) 17.925
2) 20.525
15
10
5
0
mV
17.925 259364 49.9679
20.525 259697 50.0321
0
5
10
15
20
25
30
minute

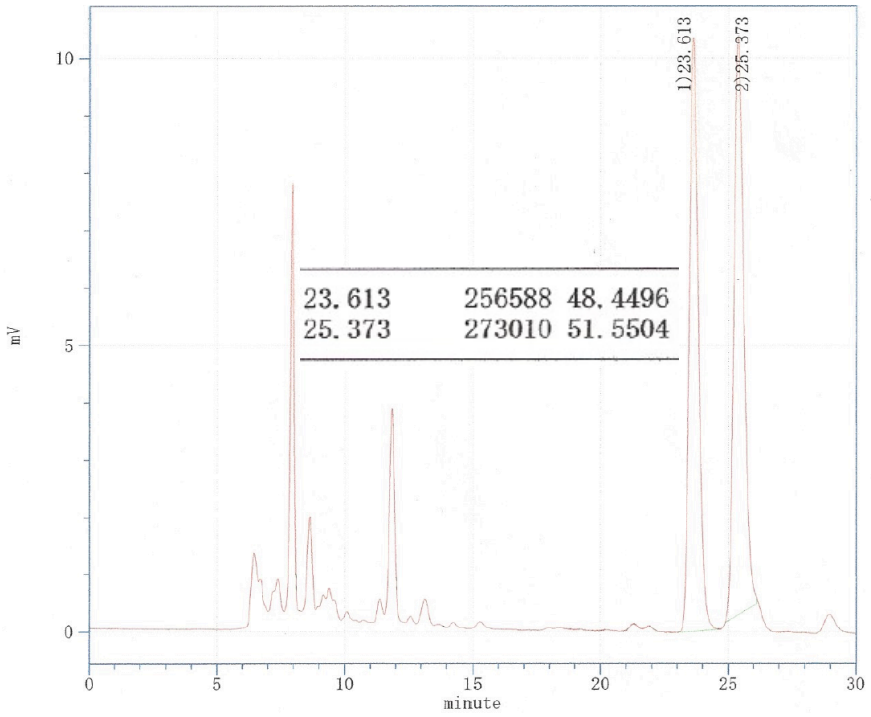


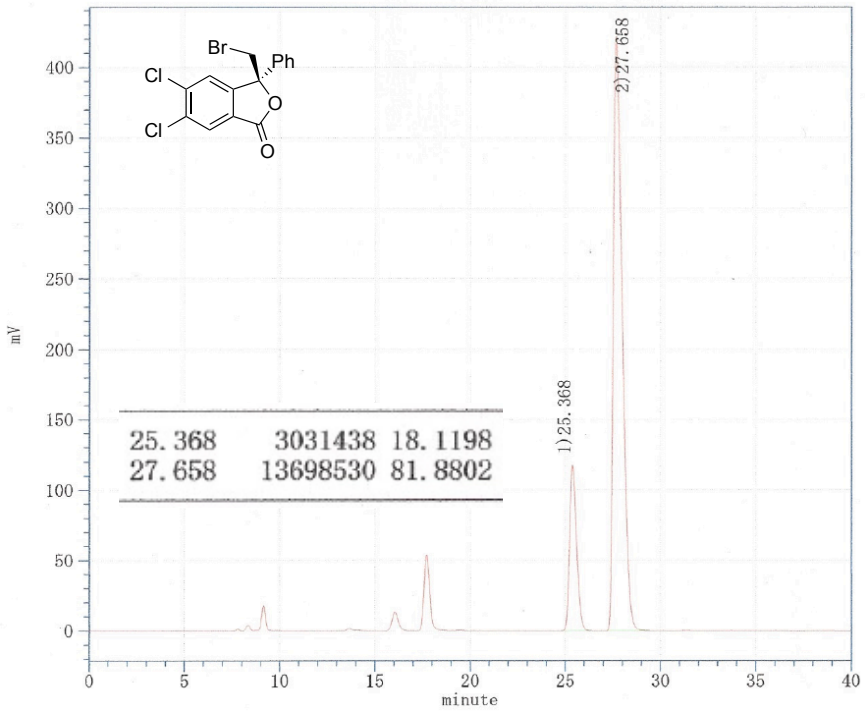
12.883	1549194	51.7072
14.145	1446897	48.2928

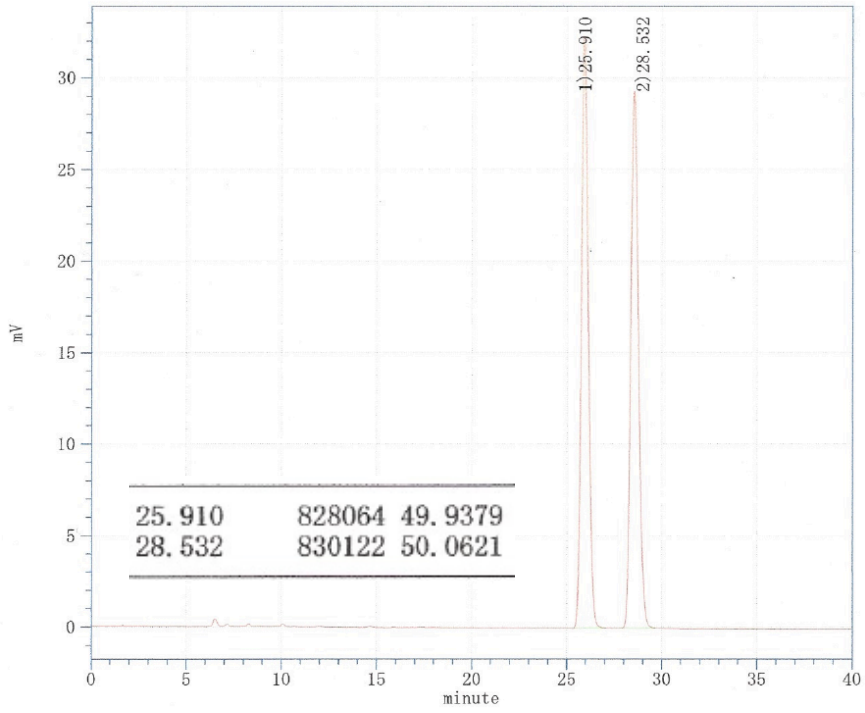


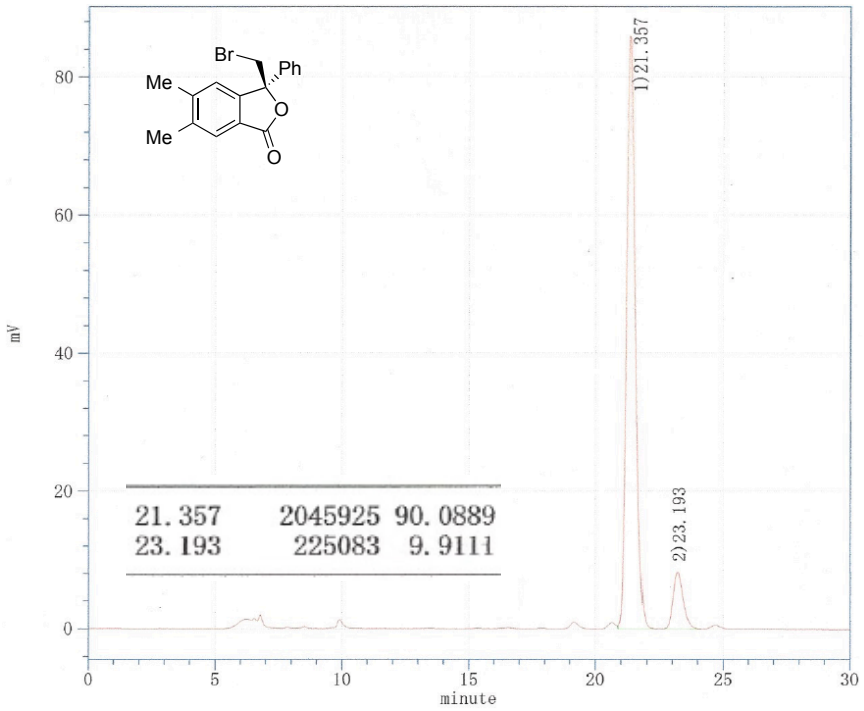
12.883	736112	50.4727
14.155	722323	49.5273

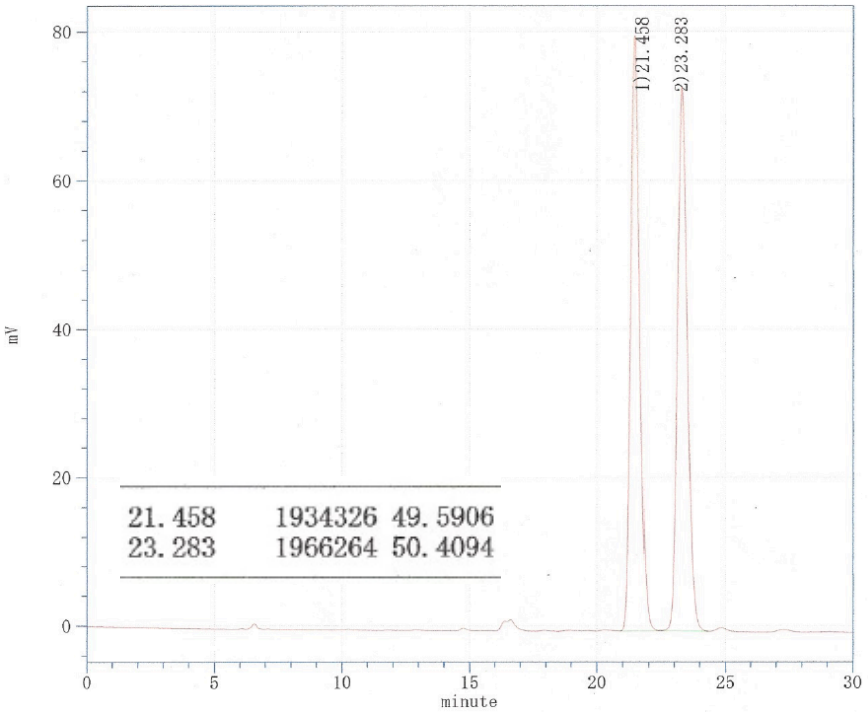

Br
Ph
F
O
O
2)24.885
1)23.550
100
50
0
mV
0
5
10
15
20
25
30
minute
23.550 456752 9.3360
24.885 4435613 90.6640

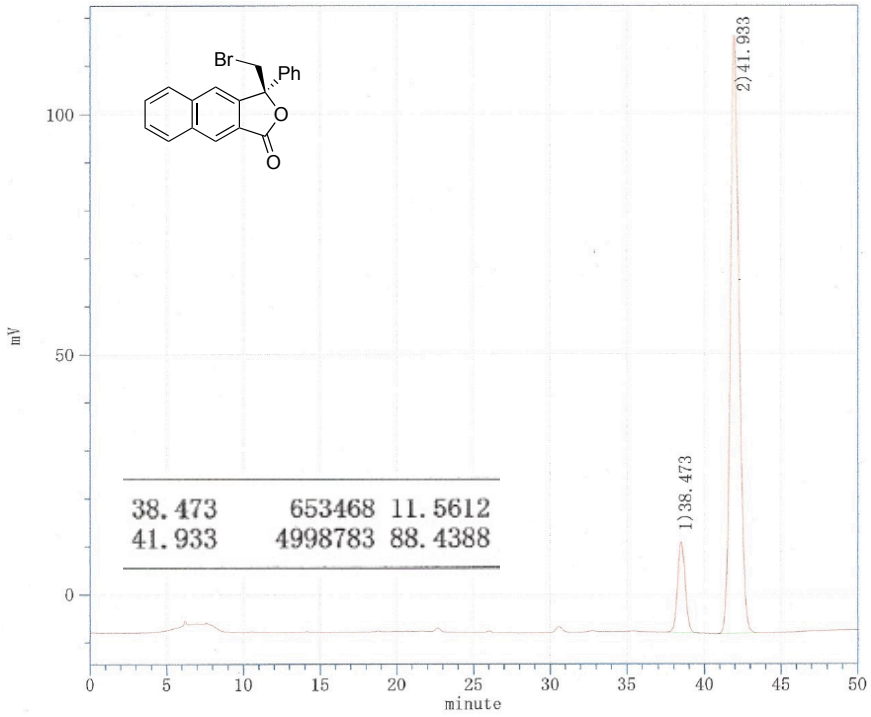

1)23.613
2)25.373
10
5
0
mV
0
5
10
15
20
25
30
minute
23.613 256588 48.4496
25.373 273010 51.5504

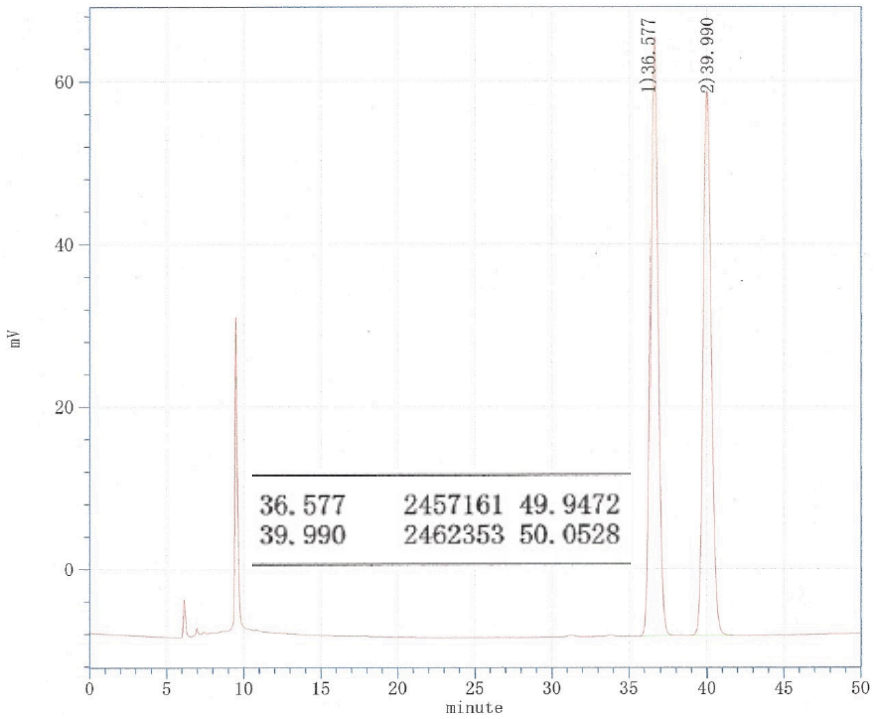

Br
Ph
Cl
Cl
O
O
mV
minute
1)25.368
2)27.658
25.368 3031438 18.1198
27.658 13698530 81.8802

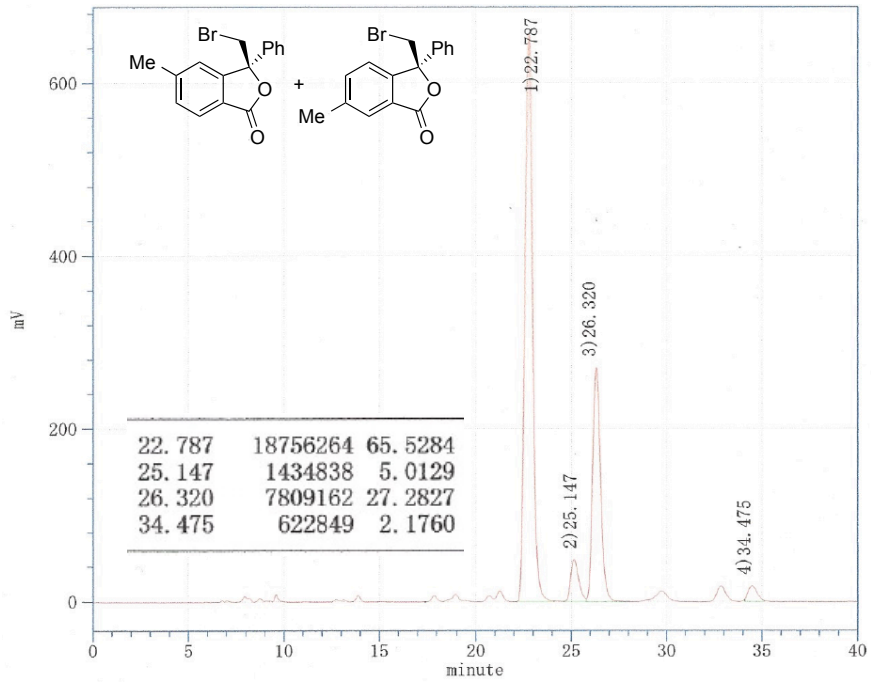

mV
minute
1)25.910
2)28.532
25.910 828064 49.9379
28.532 830122 50.0621


Br
Ph
Me
Me
O
O
1) 21.357
2) 23.193
mV
minute
21.357 2045925 90.0889
23.193 225083 9.9111

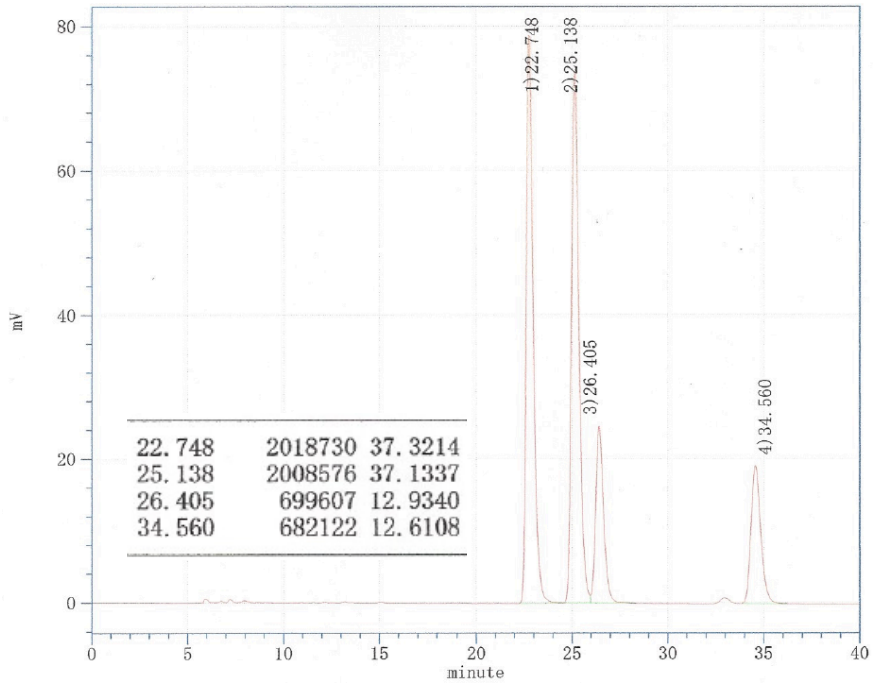

1) 21.458
2) 23.283
mV
minute
21.458 1934326 49.5906
23.283 1966264 50.4094

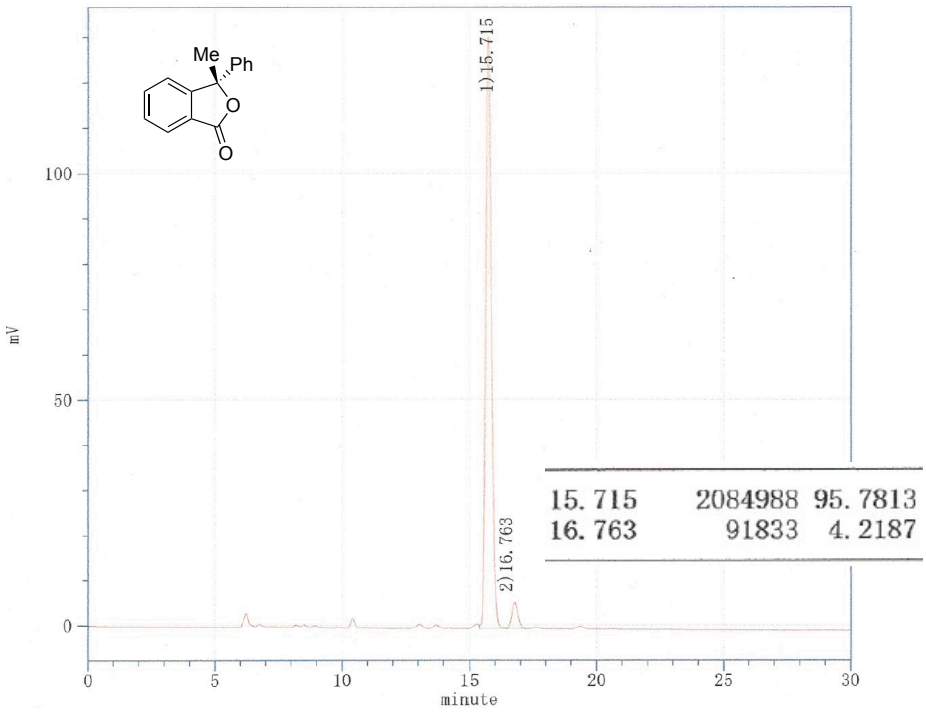

Br
Ph
O
O
100
50
0
mV
2) 41.933
1) 38.473
38.473 653468 11.5612
41.933 4998783 88.4388
0 5 10 15 20 25 30 35 40 45 50
minute

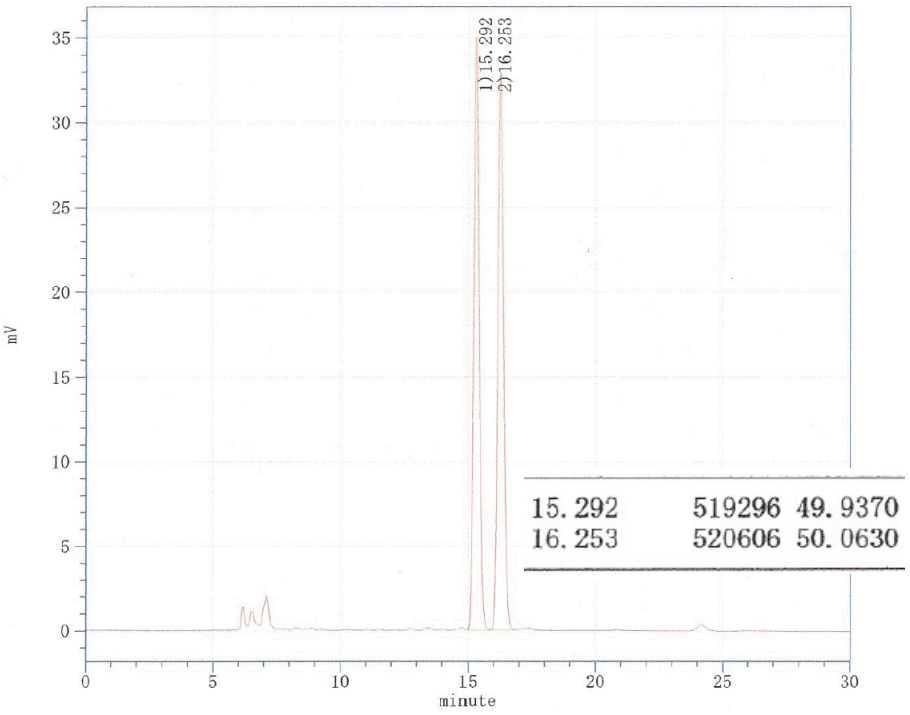

60
40
20
0
mV
1) 36.577
2) 39.990
36.577 2457161 49.9472
39.990 2462353 50.0528
0 5 10 15 20 25 30 35 40 45 50
minute

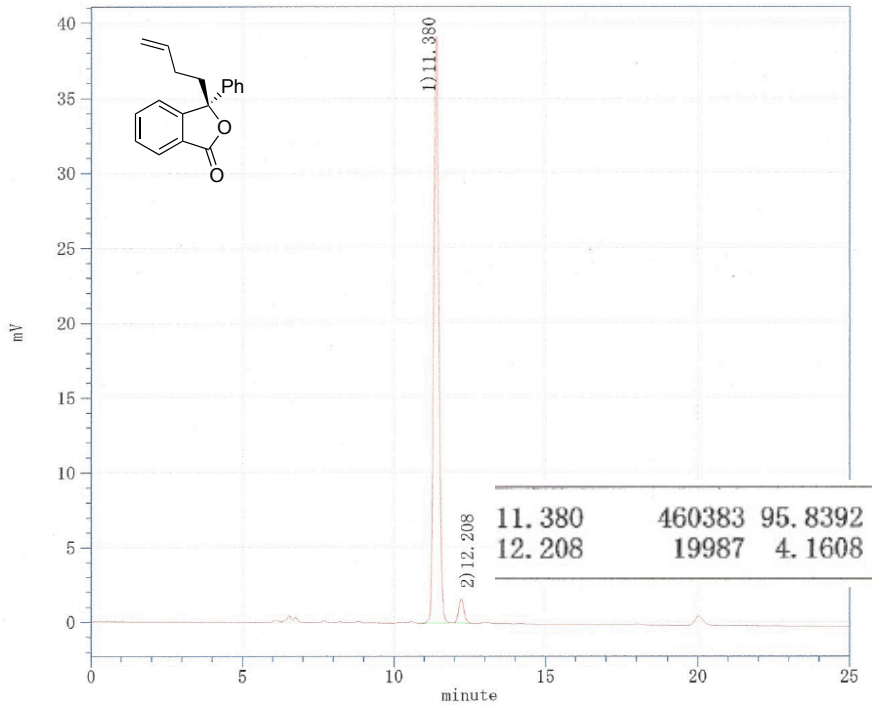


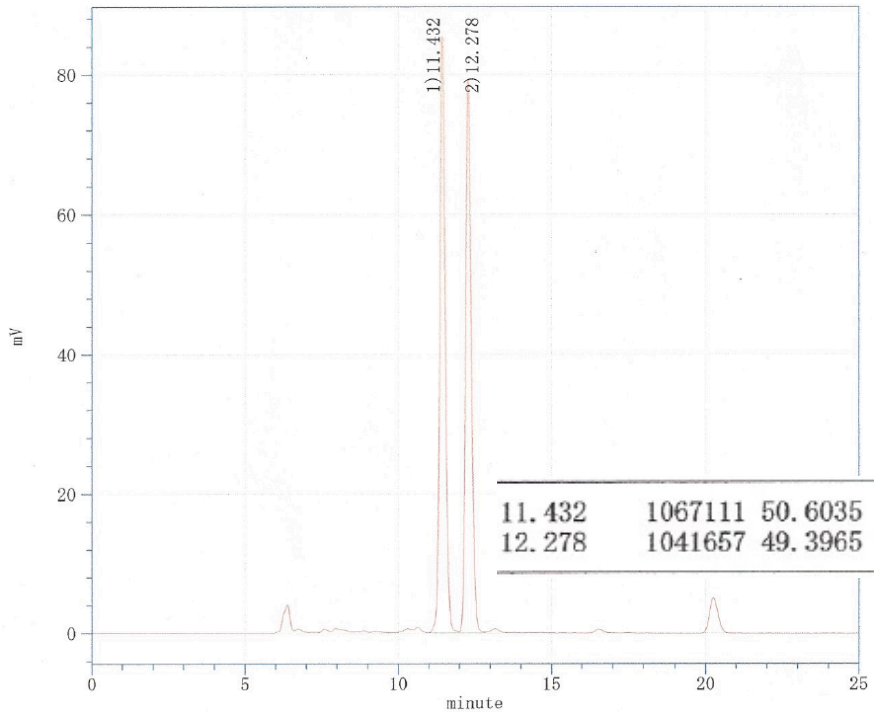
Daicel Chiralpak IA-3, hexane/2-propanol = 10:1, flow rate = 0.5 mL/min, 254 nm

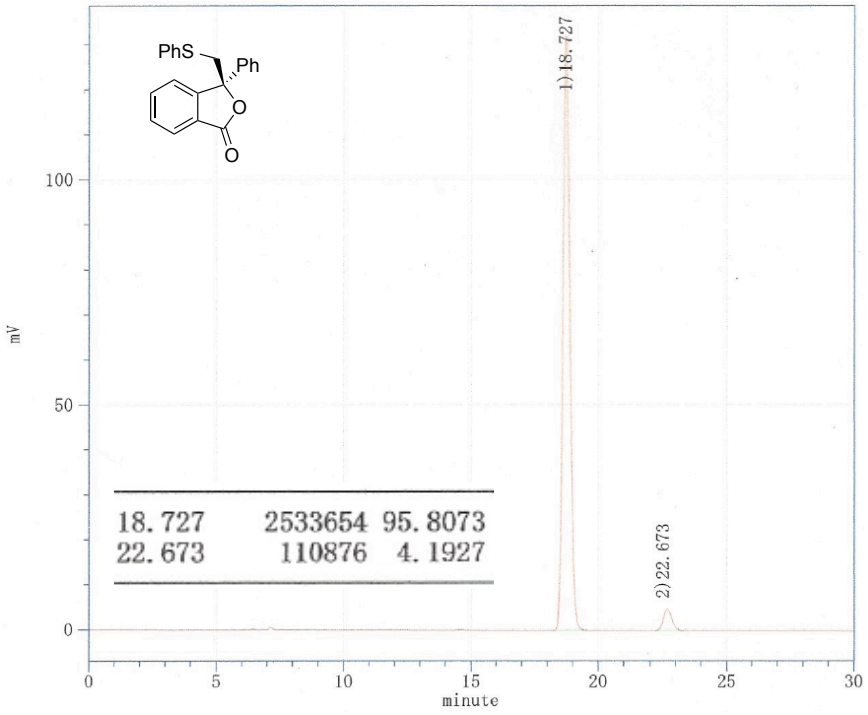


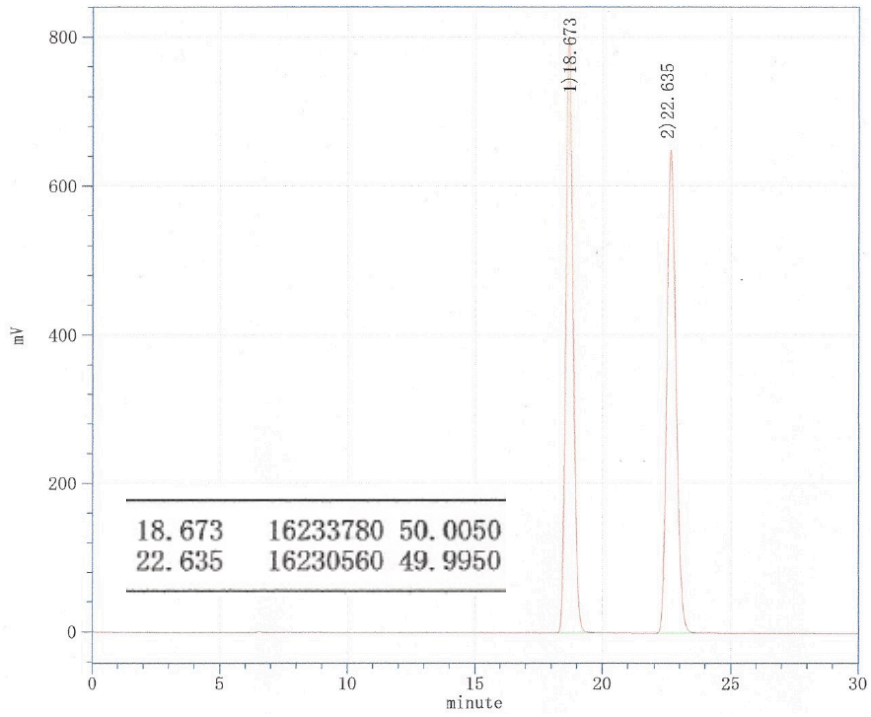

Me
Ph
O
O
1) 15.715
2) 16.763
100
50
0
mV
0
5
10
15
20
25
30
minute
15.715 2084988 95.7813
16.763 91833 4.2187


1) 15.292
2) 16.253
35
30
25
20
15
10
5
0
mV
0
5
10
15
20
25
30
minute
15.292 519296 49.9370
16.253 520606 50.0630


Ph
O
O
1) 11.380
2) 12.208
mV
minute
11.380 460383 95.8392
12.208 19987 4.1608


1) 11.432
2) 12.278
mV
minute
11.432 1067111 50.6035
12.278 1041657 49.3965


PhS
Ph
O
O
1) 18.727
2) 22.673
mV
100
50
0
0
5
10
15
20
25
30
minute
18.727 2533654 95.8073
22.673 110876 4.1927


1) 18.673
2) 22.635
mV
800
600
400
200
0
0
5
10
15
20
25
30
minute
18.673 16233780 50.0050
22.635 16230560 49.9950