Supporting Information

Efficient approach for the design of effective chiral quaternary phosphonium salts in asymmetric conjugate additions

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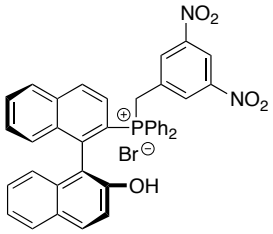
General Information

^{1}H NMR spectra were measured on a JEOL JNM-FX 400 NMR instrument (400 MHz for ^{1}H NMR). ^{13}C NMR spectra were measured on JEOL JNM-FX 400 NMR and JEOL JNM-ECA 500 NMR instruments (100 and 125 MHz for ^{13}C NMR). ^{31}P NMR spectra were measured on a JEOL JNM-ECA 500 NMR instrument (200 MHz for ^{31}P 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; q = quartet; m = multiplet; br = broad. High performance liquid chromatography (HPLC) was performed on Shimadzu 10A instruments using Daicel Chiralpak AD-H, AD-3, or Chiralcel OD-H (4.6 mm × 250 mm) columns. High-resolution mass spectra (HRMS) were performed on BRUKER microTOF focus–KR. Optical rotations were measured on a JASCO DIP-1000 digital polarimeter. All reactions were monitored by thin-layer chromatography carried out on Merck precoated TLC plates (silica gel 60GF-254, 0.25 mm), visualization by using UV (254 nm), or dyes such as $KMnO_4$. The products were purified by flash column chromatography on silica gel 60N [Kanto Chemical Co., Inc. (spherical, neutral)] or Merck preparative thin layer chromatography on silica gel (PLC 60 F254, 0.5 mm). All simple chemicals were purchased and used as received.

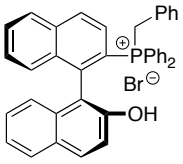
Experimental Section

General Procedure for the Synthesis of Chiral Phosphonium Salts 9.

A solution of (*S*)-OH-MOP[1] (0.05 mmol) and alkyl halide (0.06 mmol) in toluene (1.0 mL) was stirred for 10 h at 110 °C. The mixture was concentrated, and the residue was purified by column chromatography on silica gel (CH_2Cl_2/MeOH = 50:1–10:1 as eluent) to give a phosphonium salt **9** (91–97% yield).

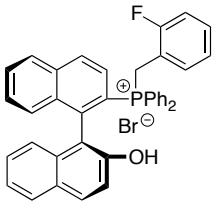


9l: $[\alpha]^{30}_D$ = –76.3 (*c* = 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.74 (s, 1H), 8.74 (d, *J* = 1.2 Hz, 1H), 8.33 (d, *J* = 1.2 Hz, 2H), 7.95–8.15 (m, 2H), 7.91 (d, *J* = 8.0 Hz, 1H), 7.83 (d, *J* = 9.2 Hz, 1H), 7.62–7.78 (m, 5H), 7.53 (d, *J* = 8.8 Hz, 1H), 7.49 (d, *J* = 8.0 Hz, 1H), 7.39–7.46 (m, 1H), 7.32–7.38 (m, 1H), 7.19–7.31 (m, 2H), 7.12–7.19 (m, 1H), 6.93–7.10 (m, 2H), 6.71–6.89 (m, 3H), 6.63 (d, *J* = 8.0 Hz, 1H), 6.17–6.48 (m, 1H), 4.75–5.05 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.9, 147.7 (d, $J_{C–P}$ = 3.3 Hz), 147.4 (d, $J_{C–P}$ = 9.1 Hz), 135.8 (d, $J_{C–P}$ = 2.5 Hz), 134.7 (d, $J_{C–P}$ = 2.5 Hz), 134.0, 133.9, 133.5 (d, $J_{C–P}$ = 9.9 Hz), 133.3, 133.2 (d, $J_{C–P}$ = 7.4 Hz), 132.3 (d, $J_{C–P}$ = 3.3 Hz), 131.8, 131.7 (d, $J_{C–P}$ = 4.9 Hz), 130.9 (d, $J_{C–P}$ = 10.7 Hz), 130.5, 130.4 (d, $J_{C–P}$ = 13.1 Hz), 128.5, 128.3, 128.1, 128.0, 127.9, 127.8, 127.5, 126.8, 123.9, 123.2, 119.6, 119.1 (d, $J_{C–P}$ = 86.4 Hz), 117.8, 117.4 (d, $J_{C–P}$ = 89.7 Hz), 115.1, 115.0, 112.7 (d, $J_{C–P}$ = 88.1 Hz), 27.5 (d, $J_{C–P}$ = 48.6 Hz); ^{31}P NMR (200 MHz, $CDCl_3$) δ 24.6; HRMS (ESI-TOF) calcd for $C_{39}H_{28}N_2O_5P^+$: 635.1730 ($[M]^+$), found 635.1730.

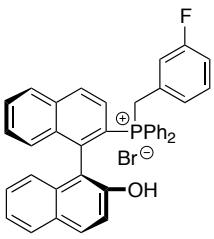


9a: $[\alpha]^{29}_D$ = –28.3 (*c* = 1.04, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.04 (s, 1H), 7.99 (d, *J* = 9.6 Hz, 1H), 7.91 (d, *J* = 8.0 Hz, 1H), 7.62–7.81 (m, 5H), 7.50–7.61 (m, 4H), 7.30–7.41 (m, 2H), 7.12–7.24 (m, 5H), 7.00–7.11 (m, 3H), 6.91–6.99 (m, 2H), 6.81–6.91 (m, 3H), 6.65–6.72 (m, 1H), 5.28 (dd, *J* = 14.4, 14.4 Hz, 1H), 3.84 (dd, *J* = 13.2, 14.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.3, 146.1 (d, $J_{C–P}$ = 9.9 Hz), 135.4 (d, $J_{C–P}$ = 2.4 Hz), 134.1 (d, $J_{C–P}$ = 2.5 Hz), 133.7, 133.54, 133.50, 133.3 (d, $J_{C–P}$ = 9.1 Hz), 132.8 (d, $J_{C–P}$ = 3.3 Hz), 131.9 (d, $J_{C–P}$ = 9.8 Hz), 131.3, 131.2 (d, $J_{C–P}$ = 5.7 Hz), 129.9, 129.8 (d, $J_{C–P}$ = 12.4 Hz), 128.6, 128.5 (d, $J_{C–P}$ = 13.2 Hz), 128.3, 128.2 (d, $J_{C–P}$ = 3.3 Hz), 127.96 (d, $J_{C–P}$ = 10.7 Hz), 127.95, 127.75, 127.73 (d, $J_{C–P}$ = 12.3 Hz), 127.5, 126.9 (d, $J_{C–P}$ = 9.0 Hz), 126.7, 123.7, 122.9, 119.8 (d, $J_{C–P}$ = 87.3 Hz), 119.6, 118.6 (d, $J_{C–P}$ = 85.6 Hz), 114.74, 114.68, 114.2 (d, $J_{C–P}$ = 87.2 Hz), 29.2 (d, $J_{C–P}$ = 46.9 Hz); ^{31}P NMR (200 MHz,

$CDCl_3$) δ 24.0; HRMS (ESI-TOF) calcd for $C_{39}H_{30}OP^+$: 545.2029 ($[M]^+$), found 545.2040.

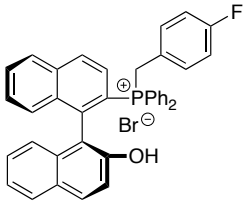


9b: $[\alpha]^{22}_D$ = –16.7 (*c* = 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.98 (s, 1H), 7.95 (d, *J* = 9.2 Hz, 1H), 7.94 (d, *J* = 8.0 Hz, 1H), 7.82 (dd, *J* = 2.8, 9.0 Hz, 1H), 7.61–7.77 (m, 4H), 7.46–7.61 (m, 4H), 7.31–7.43 (m, 2H), 7.12–7.30 (m, 5H), 7.03–7.11 (m, 2H), 6.90–7.03 (m, 3H), 6.74–6.89 (m, 2H), 6.69 (d, *J* = 8.4 Hz, 1H), 5.17 (dd, *J* = 15.4, 15.4 Hz, 1H), 4.10 (dd, *J* = 13.8, 14.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.6 (dd, $J_{C–P}$ = 6.2 Hz, $J_{C–F}$ = 248.9 Hz), 154.2, 146.2 (d, $J_{C–P}$ = 9.0 Hz), 135.5 (d, $J_{C–P}$ = 2.5 Hz), 134.2 (d, $J_{C–P}$ = 3.3 Hz), 133.7 (d, $J_{C–P}$ = 13.2 Hz), 133.5, 133.39, 133.38, 133.33, 133.30, 133.28, 133.0 (d, $J_{C–P}$ = 3.3 Hz), 132.0 (d, $J_{C–P}$ = 9.8 Hz), 131.4, 130.4 (dd, $J_{C–P}$ = 3.3 Hz, $J_{C–F}$ = 8.3 Hz), 130.0, 129.6 (d, $J_{C–P}$ = 12.3 Hz), 128.5 (d, $J_{C–P}$ = 13.1 Hz), 128.3 (d, $J_{C–P}$ = 10.7 Hz), 128.1, 128.0, 127.9, 127.8, 127.6, 126.7, 124.5 (dd, $J_{C–P}$ = 3.3 Hz, $J_{C–F}$ = 3.3 Hz), 123.6, 122.9, 119.64, 119.55 (d, $J_{C–P}$ = 86.4 Hz), 118.3 (d, $J_{C–P}$ = 85.6 Hz), 115.3 (dd, $J_{C–P}$ = 2.9 Hz, $J_{C–F}$ = 22.3 Hz), 114.7 (dd, $J_{C–P}$ = 8.2 Hz, $J_{C–F}$ = 14.8 Hz), 114.6, 114.5, 114.2 (d, $J_{C–P}$ = 84.8 Hz), 23.0 (d, $J_{C–P}$ = 49.4 Hz); ^{31}P NMR (200 MHz, $CDCl_3$) δ 23.6; HRMS (ESI-TOF) calcd for $C_{39}H_{29}FOP^+$: 563.1935 ($[M]^+$), found 563.1935.

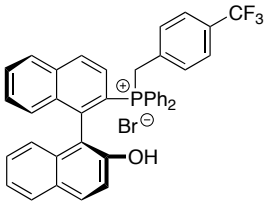


9c: $[\alpha]^{25}_D$ = –30.2 (*c* = 0.82, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.25 (s, 1H), 7.92 (d, *J* = 8.8 Hz, 2H), 7.63–7.85 (m, 5H), 7.56–7.63 (m, 2H), 7.54 (d, *J* = 9.2 Hz, 1H), 7.53 (d, *J* = 8.0 Hz, 1H), 7.29–7.44 (m, 2H), 6.97–7.24 (m, 6H), 6.83–6.95 (m, 4H), 6.74–6.83 (m, 1H), 6.66 (d, *J* = 8.4 Hz, 1H), 6.55–6.63 (m, 1H), 5.49 (dd, *J* = 15.2, 15.2 Hz, 1H), 3.97 (dd, *J* = 13.6, 14.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.2 (dd, $J_{C–P}$ = 3.7 Hz, $J_{C–F}$ = 248.9 Hz), 154.6, 146.6 (d, $J_{C–P}$ = 9.0 Hz), 135.6 (d, $J_{C–P}$ = 2.5 Hz), 134.3 (d, $J_{C–P}$ = 2.5 Hz), 133.8 (d, $J_{C–P}$ = 13.2 Hz), 133.5, 133.4 (d, $J_{C–P}$ = 9.1 Hz), 132.6 (d, $J_{C–P}$ = 3.3 Hz), 131.6 (d, $J_{C–P}$ = 9.9 Hz), 131.5, 130.2 (dd, $J_{C–P}$ = 3.3 Hz, $J_{C–F}$ = 8.2 Hz), 130.1, 130.0 (d, $J_{C–P}$ = 12.3 Hz), 129.6 (dd, $J_{C–P}$ = 8.2 Hz, $J_{C–F}$ = 8.2 Hz), 128.5 (d, $J_{C–P}$ = 10.7 Hz), 128.3 (d, $J_{C–P}$ = 12.4 Hz), 128.1, 128.0, 127.8, 127.7, 127.6 (d, $J_{C–P}$ = 13.2 Hz), 127.4 (dd, $J_{C–P}$ = 5.8 Hz, $J_{C–F}$ = 3.3 Hz), 126.6, 123.8, 122.9, 120.2 (d, $J_{C–P}$ = 87.2 Hz), 119.9, 118.5 (d, $J_{C–P}$ = 85.6 Hz), 118.1 (dd, $J_{C–P}$ = 5.4 Hz, $J_{C–F}$ = 22.7 Hz), 115.3 (dd, $J_{C–P}$ = 3.7 Hz, $J_{C–F}$ = 21.0 Hz), 114.84, 114.78, 113.8 (d, $J_{C–P}$ = 88.1 Hz), 28.5 (d, $J_{C–P}$ = 46.9 Hz); ^{31}P NMR (200 MHz, $CDCl_3$) δ 24.1; HRMS (ESI-TOF) calcd for $C_{39}H_{29}FOP^+$: 563.1935 ($[M]^+$), found

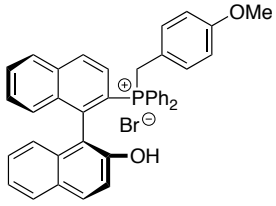
563.1928.



9d: $[\alpha]^{26}_{D}$ = –31.1 (*c* = 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.07 (s, 1H), 7.87–8.00 (m, 2H), 7.72–7.84 (m, 3H), 7.56–7.72 (m, 4H), 7.53 (d, *J* = 8.8 Hz, 1H), 7.52 (d, *J* = 7.6 Hz, 1H), 7.28–7.43 (m, 2H), 7.12–7.23 (m, 3H), 7.02–7.12 (m, 2H), 6.91–7.00 (m, 2H), 6.79–6.91 (m, 3H), 6.72 (dd, *J* = 8.4, 8.4 Hz, 2H), 6.67 (d, *J* = 8.0 Hz, 1H), 5.44 (dd, *J* = 15.2, 15.2 Hz, 1H), 4.00 (dd, *J* = 13.2, 15.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.4 (dd, $J_{C–P}$ = 4.1 Hz, $J_{C–F}$ = 249.4 Hz), 154.3, 146.4 (d, $J_{C–P}$ = 9.1 Hz), 135.5 (d, $J_{C–P}$ = 2.5 Hz), 134.2 (d, $J_{C–P}$ = 2.4 Hz), 133.7 (d, $J_{C–P}$ = 13.1 Hz), 133.43, 133.42 (d, $J_{C–P}$ = 9.1 Hz), 133.1 (dd, $J_{C–P}$ = 5.8 Hz, $J_{C–F}$ = 8.3 Hz), 132.5 (d, $J_{C–P}$ = 3.3 Hz), 131.5 (d, $J_{C–P}$ = 9.9 Hz), 131.4, 130.0, 129.9, 128.6 (d, $J_{C–P}$ = 10.6 Hz), 128.2 (d, $J_{C–P}$ = 12.4 Hz), 128.04, 127.96, 127.8, 127.6, 127.5, 126.6, 123.8, 122.93, 122.87 (dd, $J_{C–P}$ = 8.2 Hz, $J_{C–F}$ = 3.3 Hz), 120.1 (d, $J_{C–P}$ = 87.3 Hz), 119.7, 118.5 (d, $J_{C–P}$ = 84.8 Hz), 115.6 (dd, $J_{C–P}$ = 3.3 Hz, $J_{C–F}$ = 21.5 Hz), 114.92, 114.87, 113.9 (d, $J_{C–P}$ = 88.1 Hz), 27.9 (d, $J_{C–P}$ = 46.9 Hz); ^{31}P NMR (200 MHz, $CDCl_3$) δ 23.8; HRMS (ESI-TOF) calcd for $C_{39}H_{29}FOP^+$: 563.1935 ($[M]^+$), found 563.1931.

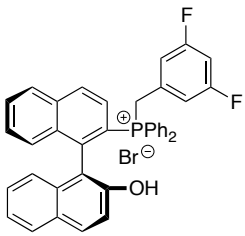


9e: $[\alpha]^{26}_{D}$ = –40.0 (*c* = 1.01, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.97 (s, 1H), 7.93 (d, *J* = 8.4 Hz, 1H), 7.90 (d, *J* = 9.2 Hz, 1H), 7.76–7.86 (m, 2H), 7.58–7.75 (m, 5H), 7.53 (d, *J* = 8.8 Hz, 1H), 7.52 (d, *J* = 6.8 Hz, 1H), 7.35–7.45 (m, 1H), 7.28–7.35 (m, 3H), 7.11–7.24 (m, 5H), 7.01–7.10 (m, 2H), 6.81–6.93 (m, 2H), 6.76 (dd, *J* = 8.8, 10.8 Hz, 1H), 6.66 (d, *J* = 8.8 Hz, 1H), 5.72 (dd, *J* = 15.6, 15.6 Hz, 1H), 4.04–4.26 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.0, 146.4 (d, $J_{C–P}$ = 8.4 Hz), 135.4 (d, $J_{C–P}$ = 2.5 Hz), 134.2 (d, $J_{C–P}$ = 2.4 Hz) 133.6 (d, $J_{C–P}$ = 13.1 Hz), 133.4 (d, $J_{C–P}$ = 8.4 Hz), 133.3, 132.4 (d, $J_{C–P}$ = 2.4 Hz), 131.8 (d, $J_{C–P}$ = 4.8 Hz), 131.35, 131.27 (d, $J_{C–P}$ = 9.5 Hz), 121.983 (dq, $J_{C–P}$ = 3.6 Hz, $J_{C–F}$ = 32.3 Hz), 129.978, 129.87, 128.4 (d, $J_{C–P}$ = 9.5 Hz), 128.1 (d, $J_{C–P}$ = 13.1 Hz), 128.0 (d, $J_{C–P}$ = 8.4 Hz), 127.8, 127.7, 127.44, 127.43 (d, $J_{C–P}$ = 13.1 Hz), 126.6, 125.2 (m), 123.7, 123.5 (q, $J_{C–F}$ = 273.3 Hz), 122.9, 119.7 (d, $J_{C–P}$ = 86.1 Hz), 119.4, 118.2 (d, $J_{C–P}$ = 84.9 Hz), 114.82, 114.78, 113.5 (d, $J_{C–P}$ = 88.6 Hz), 28.2 (d, $J_{C–P}$ = 46.6 Hz); ^{31}P NMR (200 MHz, $CDCl_3$) δ 24.1; HRMS (ESI-TOF) calcd for $C_{40}H_{29}F_3OP^+$: 613.1903 ($[M]^+$), found 613.1893.

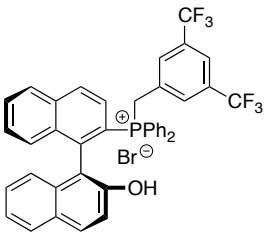


9f: $[\alpha]^{27}_{D}$ = –49.2 (*c* = 1.03, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.98 (s, 1H), 7.97 (d, *J* = 9.2 Hz, 1H), 7.92 (d, *J* = 8.4

Hz, 1H), 7.78 (dd, J = 3.2, 8.8 Hz, 1H), 7.61–7.73 (m, 4H), 7.47–7.61 (m, 4H), 7.29–7.43 (m, 2H), 7.11–7.23 (m, 4H), 7.03–7.10 (m, 1H), 6.88–7.01 (m, 3H), 6.73–6.83 (m, 2H), 6.68 (d, J = 8.4 Hz, 1H), 6.56 (d, J = 8.4 Hz, 2H), 5.14 (dd, J = 15.0, 15.0 Hz, 1H), 3.79 (dd, J = 12.8, 15.2 Hz, 1H), 3.69 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.5 (d, $J_{C–P}$ = 3.5 Hz), 154.5, 146.2 (d, $J_{C–P}$ = 9.5 Hz), 135.5 (d, $J_{C–P}$ = 2.4 Hz), 134.1 (d, $J_{C–P}$ = 2.4 Hz), 133.7 (d, $J_{C–P}$ = 13.1 Hz), 133.6, 133.5 (d, $J_{C–P}$ = 8.4 Hz), 132.7 (d, $J_{C–P}$ = 2.4 Hz), 132.5 (d, $J_{C–P}$ = 6.0 Hz), 131.9 (d, $J_{C–P}$ = 9.5 Hz), 131.4, 130.0, 129.8 (d, $J_{C–P}$ = 13.3 Hz), 128.7 (d, $J_{C–P}$ = 10.8 Hz), 128.4 (d, $J_{C–P}$ = 13.1 Hz), 128.04, 128.00 (d, $J_{C–P}$ = 6.0 Hz), 127.8, 127.69, 127.69 (d, $J_{C–P}$ = 12.0 Hz), 126.6, 123.8, 122.9, 120.2 (d, $J_{C–P}$ = 87.4 Hz), 119.9, 118.9 (d, $J_{C–P}$ = 83.8 Hz), 118.3 (d, $J_{C–P}$ = 8.4 Hz), 114.8 (d, $J_{C–P}$ = 4.8 Hz), 114.4 (d, $J_{C–P}$ = 87.4 Hz), 114.12, 114.10, 55.2, 28.5 (d, $J_{C–P}$ = 46.6 Hz); ^{31}P NMR (200 MHz, $CDCl_3$) δ 23.2; HRMS (ESI-TOF) calcd for $C_{40}H_{32}O_2P^+$: 575.2134 ($[M]^+$), found 575.2122.

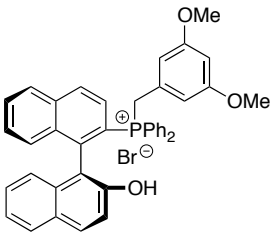


9g: $[\alpha]^{27}_D$ = –40.8 (c = 0.98, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.90 (s, 1H), 7.94 (d, J = 8.0 Hz, 1H), 7.87 (d, J = 8.8 Hz, 1H), 7.75–7.84 (m, 3H), 7.57–7.75 (m, 4H), 7.52 (d, J = 8.8 Hz, 1H), 7.51 (d, J = 8.0 Hz, 1H), 7.28–7.44 (m, 2H), 7.11–7.25 (m, 3H), 7.00–7.11 (m, 2H), 6.77–6.94 (m, 3H), 6.48–6.73 (m, 4H), 5.66 (dd, J = 15.6, 15.6 Hz, 1H), 4.17 (dd, J = 14.2, 14.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.3 (ddd, $J_{C–P}$ = 3.3 Hz, $J_{C–F}$ = 12.8, 250.1 Hz), 154.1, 146.4 (d, $J_{C–P}$ = 9.1 Hz), 135.6 (d, $J_{C–P}$ = 2.5 Hz), 134.3 (d, $J_{C–P}$ = 2.4 Hz), 133.7 (d, $J_{C–P}$ = 13.2 Hz), 133.31, 133.30 (d, $J_{C–P}$ = 9.0 Hz), 132.5 (d, $J_{C–P}$ = 2.5 Hz), 131.5, 131.4, 131.2 (dt, $J_{C–P}$ = 9.1 Hz, $J_{C–F}$ = 9.1 Hz), 130.1, 129.9, 128.4 (d, $J_{C–P}$ = 10.7 Hz), 128.2 (d, $J_{C–P}$ = 12.3 Hz), 128.1, 128.0, 127.9, 127.7, 127.6, 127.5, 126.6, 123.8, 123.0, 119.7 (d, $J_{C–P}$ = 87.2 Hz), 119.6, 118.1 (d, $J_{C–P}$ = 85.6 Hz), 114.81, 114.75, 114.5 (ddd, $J_{C–P}$ = 6.4 Hz, $J_{C–F}$ = 6.4, 20.3 Hz), 113.4 (d, $J_{C–P}$ = 88.9 Hz), 103.6 (dd, $J_{C–P}$ = 3.3 Hz, $J_{C–F}$ = 25.1 Hz), 28.2 (d, $J_{C–P}$ = 48.6 Hz); ^{31}P NMR (200 MHz, $CDCl_3$) δ 24.1; HRMS (ESI-TOF) calcd for $C_{39}H_{28}F_2OP^+$: 581.1840 ($[M]^+$), found 581.1856.

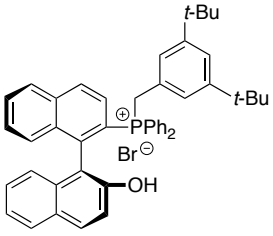


9h: $[\alpha]^{29}_D$ = –43.3 (c = 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.82 (s, 1H), 7.93 (d, J = 8.4 Hz, 1H), 7.79–7.90 (m, 3H), 7.59–7.78 (m, 6H), 7.44–7.58 (m, 4H), 7.37–7.44 (m, 1H), 7.31–7.36 (m, 1H), 7.20–7.31 (m, 2H), 7.12–7.20 (m, 1H), 6.98–7.11 (m, 2H), 6.78–6.96 (m, 2H), 6.72 (dd, J = 8.8, 10.8 Hz, 1H), 6.65 (d, J = 8.4, 1H), 6.00 (dd, J = 15.6, 15.6 Hz, 1H),

4.28–4.55 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.1, 146.9 (d, $J_{C–P}$ = 9.5 Hz), 135.7 (d, $J_{C–P}$ = 2.5 Hz), 134.4 (d, $J_{C–P}$ = 2.4 Hz) 133.8 (d, $J_{C–P}$ = 13.1 Hz), 133.4, 133.3, 132.6 (d, $J_{C–P}$ = 2.4 Hz), 131.8, 131.5, 131.4 (dq, $J_{C–P}$ = 2.5 Hz, $J_{C–F}$ = 33.5 Hz), 131.3 (d, $J_{C–P}$ = 10.8 Hz), 130.7 (d, $J_{C–P}$ = 8.4 Hz), 130.2, 130.1 (d, $J_{C–P}$ = 12.0 Hz), 128.27, 128.22, 128.18, 128.12, 128.0, 127.944 (d, $J_{C–P}$ = 13.1 Hz), 127.939, 127.8, 127.5, 126.7, 123.8, 123.0, 122.5 (q, $J_{C–F}$ = 274.1 Hz), 121.7 (m), 119.8, 119.2 (d, $J_{C–P}$ = 87.4 Hz), 117.7 (d, $J_{C–P}$ = 86.1 Hz), 114.95, 114.90, 113.0 (d, $J_{C–P}$ = 88.5 Hz), 28.3 (d, $J_{C–P}$ = 47.9 Hz); ^{31}P NMR (200 MHz, $CDCl_3$) δ 24.4; HRMS (ESI-TOF) calcd for $C_{41}H_{28}F_6OP^+$: 681.1776 ([M]$^+$), found 681.1753.

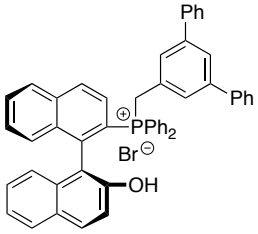


9i: $[\alpha]^{22}_D$ = –38.8 (*c* = 1.02, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.15 (s, 1H), 7.94 (d, *J* = 9.2 Hz, 1H), 7.91 (d, *J* = 8.4 Hz, 1H), 7.72–7.84 (m, 3H), 7.57–7.72 (m, 4H), 7.55 (d, *J* = 9.2 Hz, 1H), 7.53 (d, *J* = 7.6 Hz, 1H), 7.29–7.44 (m, 2H), 7.02–7.24 (m, 5H), 6.84–6.99 (m, 3H), 6.68 (d, *J* =8.0 Hz, 1H), 6.24 (q, *J* = 2.4 Hz, 1H), 6.11 (t, *J* = 2.4 Hz, 2H), 5.21 (dd, *J* = 15.0, 15.0 Hz, 1H), 3.86 (dd, *J* = 13.0, 14.6 Hz, 1H), 3.35 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.4 (d, $J_{C–P}$ = 3.6 Hz), 154.4, 146.3 (d, $J_{C–P}$ = 9.6 Hz), 135.4 (d, $J_{C–P}$ = 2.4 Hz), 134.1 (d, $J_{C–P}$ = 2.4 Hz), 133.6 (d, $J_{C–P}$ = 13.1 Hz), 133.4 (d, $J_{C–P}$ = 9.6 Hz), 132.6 (d, $J_{C–P}$ = 2.4 Hz), 131.6 (d, $J_{C–P}$ = 9.6 Hz), 131.3, 129.9, 129.8 (d, $J_{C–P}$ = 12.0 Hz), 128.8 (d, $J_{C–P}$ = 7.1 Hz), 128.7 (d, $J_{C–P}$ = 10.9 Hz), 128.3, 128.2, 127.94, 127.90, 127.85, 127.7, 127.6, 127.5 (d, $J_{C–P}$ = 12.3 Hz), 126.6, 123.7, 122.9, 120.2 (d, $J_{C–P}$ = 87.4 Hz), 119.7, 118.6 (d, $J_{C–P}$ = 83.8 Hz), 114.83, 114.79, 114.3 (d, $J_{C–P}$ = 88.6 Hz), 108.9 (d, $J_{C–P}$ = 4.9 Hz), 101.0 (d, $J_{C–P}$ = 3.5 Hz), 55.1, 28.9 (d, $J_{C–P}$ = 46.8 Hz); ^{31}P NMR (200 MHz, $CDCl_3$) δ 24.1; HRMS (ESI-TOF) calcd for $C_{41}H_{34}O_3P^+$: 605.2240 ([M]$^+$), found 605.2231.

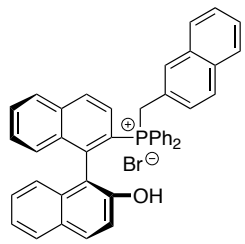


9j: $[\alpha]^{27}_D$ = –40.8 (*c* = 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.11 (s, 1H), 7.95 (d, *J* = 8.8 Hz, 1H), 7.88 (d, *J* = 8.4 Hz, 1H), 7.74 (dd, *J* = 3.2, 9.2 Hz, 1H), 7.55–7.69 (m, 8H), 7.30–7.42 (m, 2H), 7.18–7.29 (m, 4H), 7.12–7.18 (m, 1H), 6.95–7.10 (m, 3H), 6.87 (dd, *J* =8.8, 10.8 Hz, 1H), 6.66 (d, *J* = 8.8 Hz, 1H), 6.64 (t, *J* = 2.2 Hz, 2H), 5.01 (dd, *J* = 14.8, 14.8 Hz, 1H), 3.77 (dd, *J* = 13.2, 14.8 Hz, 1H), 0.99 (s, 18H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.5, 151.1 (d, $J_{C–P}$ = 3.6 Hz), 146.2 (d, $J_{C–P}$ = 9.6 Hz), 135.3 (d, $J_{C–P}$ = 2.5 Hz), 133.9 (d, $J_{C–P}$ = 2.4 Hz), 133.6, 133.5 (d, $J_{C–P}$ = 13.3 Hz), 133.3 (d, $J_{C–P}$ = 9.6 Hz),

133.0 (d, J_{C-P} = 3.5 Hz), 132.3 (d, J_{C-P} = 9.5 Hz), 131.2, 129.9, 129.4 (d, J_{C-P} = 11.9 Hz), 128.5 (d, J_{C-P} = 13.1 Hz), 128.2 (d, J_{C-P} = 10.8 Hz), 128.0, 127.9, 127.84, 127.77, 127.66, 127.58, 126.6, 125.56 (d, J_{C-P} = 12.0 Hz), 125.54 (d, J_{C-P} = 8.4 Hz), 123.6, 122.7, 122.0 (d, J_{C-P} = 3.6 Hz), 119.8 (d, J_{C-P} = 87.4 Hz), 119.7, 118.7 (d, J_{C-P} = 84.9 Hz), 114.6 (d, J_{C-P} = 87.4 Hz), 114.52, 114.49, 34.4, 30.9, 30.2 (d, J_{C-P} = 46.6 Hz); ^{31}P NMR (200 MHz, $CDCl_3$) δ 23.6; HRMS (ESI-TOF) calcd for $C_{47}H_{46}OP^+$: 657.3281 ($[M]^+$), found 657.3263.

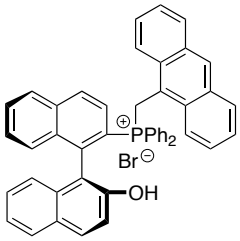


9k: $[\alpha]^{26}_D$ = –57.4 (*c* = 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.01 (s, 1H), 7.96 (d, *J* = 9.6 Hz, 1H), 7.72–7.87 (m, 3H), 7.61–7.71 (m, 4H), 7.47–7.61 (m, 4H), 7.34–7.44 (m, 2H), 7.20–7.34 (m, 8H), 7.02–7.20 (m, 9H), 6.86–7.02 (m, 3H), 6.70 (d, *J* =8.4 Hz, 1H), 5.49 (dd, *J* = 14.4, 14.4 Hz, 1H), 3.90–4.20 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.4, 146.5 (d, J_{C-P} = 8.4 Hz), 141.7 (d, J_{C-P} = 2.4 Hz), 139.4, 135.5, 134.1 (d, J_{C-P} = 2.4 Hz), 133.6 (d, J_{C-P} = 13.1 Hz), 133.5, 133.4 (d, J_{C-P} = 9.5 Hz), 132.7, 131.8 (d, J_{C-P} = 9.6 Hz), 131.3, 129.9, 129.7 (d, J_{C-P} = 12.0 Hz), 128.7 (d, J_{C-P} = 6.0 Hz), 128.6, 128.4 (d, J_{C-P} = 13.3 Hz), 128.1 (d, J_{C-P} = 8.4 Hz), 127.9, 127.8, 127.7, 127.6, 127.5, 126.6, 125.3 (d, J_{C-P} = 3.6 Hz), 123.7, 122.8, 119.8 (d, J_{C-P} = 86.3 Hz), 119.7, 118.4 (d, J_{C-P} = 84.9 Hz), 114.68, 114.64, 114.1 (d, J_{C-P} = 87.4 Hz), 29.3 (d, J_{C-P} = 47.9 Hz); ^{31}P NMR (200 MHz, $CDCl_3$) δ 24.1; HRMS (ESI-TOF) calcd for $C_{51}H_{38}OP^+$: 697.2655 ($[M]^+$), found 697.2630.

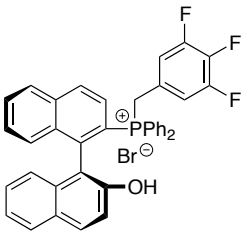


9m: $[\alpha]^{27}_D$ = –103.4 (*c* = 1.01, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.41 (s, 1H), 8.00 (d, *J* = 8.8 Hz, 1H), 7.87 (d, *J* = 8.4 Hz, 1H), 7.52–7.81 (m, 9H), 7.29–7.51 (m, 7H), 7.10–7.29 (m, 5H), 7.05 (t, *J* = 7.6 Hz, 1H), 6.89–7.01 (m, 3H), 6.84 (dd, *J* = 9.0, 10.6 Hz, 1H), 6.69 (d, *J* =8.0 Hz, 1H), 5.41 (dd, *J* = 15.2, 15.2 Hz, 1H), 4.00 (dd, *J* = 13.8, 13.8 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.5, 146.2 (d, J_{C-P} = 9.5 Hz), 135.4 (d, J_{C-P} = 2.5 Hz), 134.1 (d, J_{C-P} = 2.5 Hz), 133.6 (d, J_{C-P} = 12.0 Hz), 133.5, 133.4 (d, J_{C-P} = 9.6 Hz), 132.72, 132.70, 132.67, 132.64, 132.4 (d, J_{C-P} = 2.4 Hz), 131.7 (d, J_{C-P} = 8.8 Hz), 131.3, 130.9 (d, J_{C-P} = 7.1 Hz), 129.9, 129.7 (d, J_{C-P} = 11.9 Hz), 128.6 (d, J_{C-P} = 10.8 Hz), 128.4, 128.3, 128.2 (d, J_{C-P} = 2.4 Hz), 128.0, 127.91, 127.88, 127.7, 127.62, 127.59, 127.3, 126.6, 126.4, 126.2, 124.3 (d, J_{C-P} = 8.4 Hz), 123.7, 122.8, 119.7 (d, J_{C-P} = 86.1 Hz), 119.6, 118.6 (d, J_{C-P} = 85.0 Hz), 114.73, 114.69, 114.3 (d, J_{C-P} = 88.5 Hz), 29.3 (d, J_{C-P} = 46.6 Hz); ^{31}P NMR (200 MHz, $CDCl_3$) δ 23.4; HRMS (ESI-TOF) calcd for $C_{43}H_{32}OP^+$: 595.2185 ($[M]^+$),

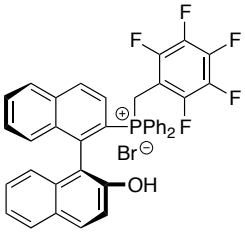
found 595.2179.



9n: $[\alpha]^{26}_{D}$ = 116.6 (*c* = 1.02, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.61 (s, 1H), 8.23–8.34 (m, 2H), 7.95 (d, *J* = 8.4 Hz, 1H), 7.80–7.93 (m, 3H), 7.68–7.80 (m, 5H), 7.66 (d, *J* = 8.4 Hz, 1H), 7.47–7.62 (m, 2H), 7.35–7.47 (m, 4H), 7.18–7.32 (m, 3H), 7.02–7.18 (m, 3H), 6.42–7.00 (m, 7H), 5.20 (dd, *J* = 15.0, 15.0 Hz, 1H), 3.81 (dd, *J* = 15.6, 15.6 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.8, 145.7 (d, $J_{C–P}$ = 7.5 Hz), 135.1 (d, $J_{C–P}$ = 2.4 Hz), 134.1, 134.05, 134.01, 133.9, 133.8, 133.6 (d, $J_{C–P}$ = 13.3 Hz), 131.6, 130.8 (d, $J_{C–P}$ = 5.9 Hz), 130.6 (d, $J_{C–P}$ = 4.8 Hz), 130.2, 129.6 (d, $J_{C–P}$ = 13.1 Hz), 129.1 (d, $J_{C–P}$ = 13.3 Hz), 128.9, 128.8, 128.5, 128.41, 128.38, 128.29, 128.1, 127.8, 127.2, 126.2, 124.7, 123.8, 123.5, 123.0 (br), 120.4, 120.3 (d, $J_{C–P}$ = 85.0 Hz), 118.0 (d, $J_{C–P}$ = 10.9 Hz), 117.1 (d, $J_{C–P}$ = 83.8 Hz), 116.9 (d, $J_{C–P}$ = 81.4 Hz), 115.3, 115.2, 25.0 (d, $J_{C–P}$ = 44.4 Hz); ^{31}P NMR (200 MHz, $CDCl_3$) δ 23.0; HRMS (ESI-TOF) calcd for $C_{47}H_{34}OP^+$: 645.2342 ($[M]^+$), found 645.2329.

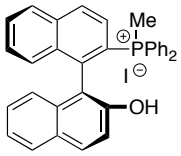


9o: $[\alpha]^{27}_{D}$ = –53.4 (*c* = 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.93 (s, 1H), 7.89–8.03 (m, 3H), 7.82 (d, *J* = 9.2 Hz, 1H), 7.79 (dd, *J* = 3.2, 9.2 Hz, 1H), 7.58–7.75 (m, 4H), 7.49 (d, *J* = 9.2 Hz, 1H), 7.48 (d, *J* = 8.0 Hz, 1H), 7.33–7.41 (m, 1H), 7.28–7.33 (m, 1H), 7.11–7.24 (m, 3H), 7.02–7.10 (m, 1H), 6.95–7.02 (m, 1H), 6.70–6.89 (m, 5H), 6.65 (d, *J* = 8.4 Hz, 1H), 5.70 (dd, *J* = 15.4, 15.4 Hz, 1H), 4.51 (dd, *J* = 14.0, 14.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.0, 151.4 (m), 149.4 (m), 146.6 (d, $J_{C–P}$ = 9.6 Hz), 139.3 (dtd, $J_{C–P}$ = 3.5 Hz, $J_{C–F}$ = 15.4, 255.1 Hz), 135.6 (d, $J_{C–P}$ = 2.4 Hz), 134.2 (d, $J_{C–P}$ = 2.4 Hz), 133.7 (d, $J_{C–P}$ = 13.3 Hz), 133.5 (d, $J_{C–P}$ = 9.6 Hz), 133.3, 132.2 (d, $J_{C–P}$ = 2.5 Hz), 131.4, 131.1 (d, $J_{C–P}$ = 9.6 Hz), 130.08, 130.06 (d, $J_{C–P}$ = 11.9 Hz), 128.5 (d, $J_{C–P}$ = 10.8 Hz), 128.1, 128.0, 127.9, 127.8 (d, $J_{C–P}$ = 12.0 Hz), 127.5, 127.4 (d, $J_{C–P}$ = 13.3 Hz), 126.6, 124.1 (m), 123.9, 123.0, 119.9 (d, $J_{C–P}$ = 83.9 Hz), 119.5, 118.0 (d, $J_{C–P}$ = 86.1 Hz), 115.9 (m), 115.0, 114.9, 113.3 (d, $J_{C–P}$ = 88.5 Hz), 27.1 (d, $J_{C–P}$ = 47.9 Hz); ^{31}P NMR (200 MHz, $CDCl_3$) δ 24.1; HRMS (ESI-TOF) calcd for $C_{39}H_{27}F_3OP^+$: 599.1746 ($[M]^+$), found 599.1755.



9p: $[\alpha]^{27}_{D}$ = –10.0 (*c* = 0.99, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.11 (s, 1H), 8.04 (dd, *J* = 3.0, 9.0 Hz, 1H), 7.99 (d, *J* = 8.8 Hz, 1H), 7.87 (dd, *J* = 1.4, 9.0 Hz, 1H), 7.23–7.76 (m, 14H), 7.09–7.22

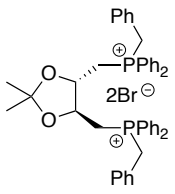
(m, 3H), 7.00–7.08 (m, 1H), 6.61 (d, J = 8.8 Hz, 1H), 5.02–5.29 (m, 1H), 3.98 (dd, J = 14.6, 14.6 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.3, 146.2 (d, $J_{C–P}$ = 9.5 Hz), 146.0 (br m), 144.0 (br m), 142.2 (br m), 140.1 (br m), 138.2 (br m), 136.2 (br m), 135.6 (d, $J_{C–P}$ = 2.4 Hz), 134.6 (d, $J_{C–P}$ = 2.4 Hz), 134.2 (d, $J_{C–P}$ = 2.4 Hz), 133.7 (d, $J_{C–P}$ = 13.3 Hz), 133.5, 133.3 (d, $J_{C–P}$ = 10.9 Hz), 132.8 (d, $J_{C–P}$ = 10.8 Hz), 131.5, 130.2, 129.5 (d, $J_{C–P}$ = 13.1 Hz), 129.1, 129.0, 128.9, 128.2, 128.1, 128.0, 127.7, 127.5, 127.1 (d, $J_{C–P}$ = 12.0 Hz), 126.9, 123.3, 123.0, 119.4, 117.6 (d, $J_{C–P}$ = 86.1 Hz), 117.0 (d, $J_{C–P}$ = 86.3 Hz), 114.1 (d, $J_{C–P}$ = 88.6 Hz), 113.94, 113.89, 103.6 (br m), 20.4 (d, $J_{C–P}$ = 52.6 Hz); ^{31}P NMR (200 MHz, $CDCl_3$) δ 22.9; HRMS (ESI-TOF) calcd for $C_{39}H_{25}F_5OP^+$: 635.1558 ($[M]^+$), found 635.1561.



9q: $[\alpha]^{27}_D$ = –3.5 (c = 1.03, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.59 (br, 1H), 8.09 (dd, J = 3.0, 9.0 Hz, 1H), 7.96 (d, J = 8.4 Hz, 1H), 7.91 (d, J = 9.2 Hz, 1H), 7.59–7.76 (m, 4H), 7.38–7.58 (m, 6H), 7.31–7.38 (m, 2H), 7.19–7.31 (m, 4H), 7.07–7.18 (m, 1H), 6.83–6.99 (m, 1H), 6.50 (d, J = 8.4 Hz, 1H), 2.31 (d, J = 13.2 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.8, 145.2 (d, $J_{C–P}$ = 8.4 Hz), 135.6 (d, $J_{C–P}$ = 2.4 Hz), 134.4 (d, $J_{C–P}$ = 2.4 Hz), 133.9 (d, $J_{C–P}$ = 2.4 Hz), 133.6 (d, $J_{C–P}$ = 13.1 Hz), 133.2, 132.3 (d, $J_{C–P}$ = 9.6 Hz), 131.9 (d, $J_{C–P}$ = 10.8 Hz), 131.4, 130.1, 130.0 (d, $J_{C–P}$ = 13.1 Hz), 129.5 (d, $J_{C–P}$ = 13.1 Hz), 128.3 (d, $J_{C–P}$ = 9.6 Hz), 128.0, 127.8, 127.6 (d, $J_{C–P}$ = 13.3 Hz) 127.3, 126.8, 123.6, 123.1, 121.0 (d, $J_{C–P}$ = 88.6 Hz), 119.2, 119.0 (d, $J_{C–P}$ = 88.5 Hz), 115.9 (d, $J_{C–P}$ = 92.1 Hz), 114.4, 114.3, 11.0 (d, $J_{C–P}$ = 57.4 Hz); ^{31}P NMR (200 MHz, $CDCl_3$) δ 21.0; HRMS (ESI-TOF) calcd for $C_{33}H_{26}OP^+$: 469.1716 ($[M]^+$), found 469.1703.

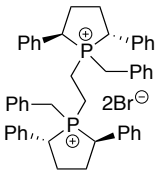
General Procedure for the Synthesis of Bis-Phosphonium Bromides 1–3.

A solution of a chiral bisphosphine (0.05 mmol) and benzyl bromide (0.11 mmol) in toluene (1.0 mL) was stirred for 10 h at 110 °C. The mixture was concentrated, and the residue was purified by column chromatography on silica gel (CH_2Cl_2/MeOH = 50:1–10:1 as eluent) to give a phosphonium salt (89–95% yield).

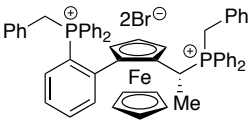


1: $[\alpha]^{26}_D$ = 12.4 (c = 0.96, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94–8.06 (m, 4H), 7.83–7.94 (m, 4H), 7.67–7.77 (m, 4H), 7.54–7.65 (m, 8H), 7.15–7.22 (m, 2H), 7.06–7.15 (m, 4H), 6.94–7.04 (m, 4H), 4.64–4.91 (m, 6H), 4.40–4.55 (m, 2H), 3.45–3.66 (m, 2H), 1.17 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 134.4 (d, $J_{C–P}$ = 2.4 Hz), 134.2 (d, $J_{C–P}$ = 2.4 Hz), 133.5 (d, $J_{C–P}$ = 14.4 Hz), 133.4 (d, $J_{C–P}$ = 14.4 Hz), 130.2 (d, $J_{C–P}$ = 6.0 Hz),

129.3 (d, $J_{C–P}$ = 9.5 Hz), 129.2 (d, $J_{C–P}$ = 8.4 Hz), 128.3 (d, $J_{C–P}$ = 3.6 Hz), 127.7 (d, $J_{C–P}$ = 3.6 Hz), 126.5 (d, $J_{C–P}$ = 8.4 Hz), 116.58 (d, $J_{C–P}$ = 85.0 Hz), 116.55 (d, $J_{C–P}$ = 83.8 Hz), 110.6, 74.6 (dd, $J_{C–P}$ = 5.9, 15.6 Hz), 30.0 (d, $J_{C–P}$ = 46.6 Hz), 26.0, 22.0 (d, $J_{C–P}$ = 53.9 Hz); ^{31}P NMR (200 MHz, $CDCl_3$) δ 26.0; HRMS (ESI-TOF) calcd for $C_{45}H_{46}O_2P_2^{2+}$: 340.1481 ($[M]^{2+}$), found 340.1470.



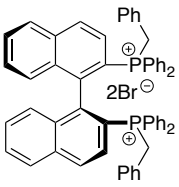
2: $[\alpha]^{25}_D$ = 25.1 (*c* = 0.96, DMSO); ^{1}H NMR (400 MHz, DMSO-d_6) δ 6.75–7.70 (m, 30H), 2.15–5.45 (br m, 20H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 132.1, 131.1, 130.5, 129.3, 129.22, 129.15, 129.10, 128.42, 128.37, 128.2, 127.9, 127.1 (d, $J_{C–P}$ = 4.9 Hz), 127.0 (d, $J_{C–P}$ = 4.8 Hz), 41.7, 41.6, 41.41, 41.37, 41.2, 41.1, 30.9, 30.3, 25.6 (d, $J_{C–P}$ = 18.0 Hz), 25.5 (d, $J_{C–P}$ = 17.9 Hz), 12.6 (d, $J_{C–P}$ = 16.8 Hz), 12.5 (d, $J_{C–P}$ = 18.0 Hz); ^{31}P NMR (200 MHz, DMSO-d_6) δ 47.1; HRMS (ESI-TOF) calcd for $C_{48}H_{50}P_2^{2+}$: 344.1688 ($[M]^{2+}$), found 344.1676.



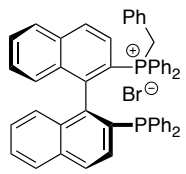
3: $[\alpha]^{26}_D$ = –59.5 (*c* = 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.00–9.15 (m, 1H), 8.30–8.52 (m, 1H), 6.96–7.95 (m, 23H), 6.48–6.94 (m, 9H), 6.05–6.23 (m, 1H), 5.09–5.25 (m, 1H), 4.61–4.81 (m, 1H), 4.36 (br, 1H), 4.20 (s, 5H), 3.95 (s, 1H), 3.38–3.80 (m, 3H), 2.33 (dd, *J* = 2.6, 18.2 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.2 (d, $J_{C–P}$ = 7.3 Hz), 138.6 (d, $J_{C–P}$ = 7.3 Hz), 136.7, 136.0 (d, $J_{C–P}$ = 10.8 Hz), 135.4, 135.0 (d, $J_{C–P}$ = 7.3 Hz), 134.6, 134.4, 133.6, 132.8 (d, $J_{C–P}$ = 7.1 Hz), 130.3 (d, $J_{C–P}$ = 11.9 Hz), 129.8 (d, $J_{C–P}$ = 13.3 Hz), 129.3, 129.1, 129.0, 128.9 (d, $J_{C–P}$ = 13.1 Hz), 127.8 (d, $J_{C–P}$ = 12.0 Hz), 127.3, 127.0 (d, $J_{C–P}$ = 8.4 Hz), 126.4, 125.1 (d, $J_{C–P}$ = 8.4 Hz), 118.4 (d, $J_{C–P}$ = 83.8 Hz), 117.3 (d, $J_{C–P}$ = 87.4 Hz), 115.4 (d, $J_{C–P}$ = 81.4 Hz), 115.1 (d, $J_{C–P}$ = 79.0 Hz), 111.7 (d, $J_{C–P}$ = 77.8 Hz), 87.6, 85.6 (br), 71.3, 71.2, 68.0, 67.4, 29.5 (d, $J_{C–P}$ = 41.9 Hz), 29.3 (br), 27.3 (d, $J_{C–P}$ = 39.5 Hz), 18.9; ^{31}P NMR (200 MHz, $CDCl_3$) δ 37.3, 24.1; HRMS (ESI-TOF) calcd for $C_{56}H_{50}FeP_2^{2+}$: 420.1364 ($[M]^{2+}$), found 420.1366.

Synthesis of BINAP-Derived Phosphonium Bromides 4 and 7.

A solution of BINAP (0.05 mmol) and benzyl bromide (0.11 mmol) in toluene (1.0 mL) was stirred for 12 h at 110 °C. The mixture was concentrated, and the residue was purified by column chromatography on silica gel (CH_2Cl_2/MeOH = 50:1–10:1 as eluent) to give mono-phosphonium bromide **7** (81% yield) and bis-phosphonium bromide **4** (19% yield).



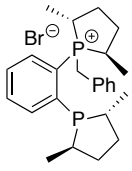
4: $[\alpha]^{25}_{D}$ = 153.6 (*c* = 0.99, DMSO); ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.98–8.23 (m, 6H), 7.73–7.84 (m, 2H), 7.66 (t, *J* = 7.6 Hz, 2H), 7.54–7.62 (m, 2H), 7.42–7.53 (m, 4H), 7.24–7.38 (m, 6H), 6.98–7.24 (m, 12H), 6.78–6.97 (m, 8H), 4.74–5.25 (m, 4H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 140.5 (d, $J_{C–P}$ = 4.9 Hz), 140.4 (d, $J_{C–P}$ = 4.8 Hz), 134.92, 134.91, 134.88, 134.80, 134.5, 133.7, 133.6, 133.5, 131.4 (d, $J_{C–P}$ = 6.0 Hz), 131.1 (d, $J_{C–P}$ = 13.1 Hz), 130.4, 129.31, 129.27, 129.22, 129.19, 129.08, 128.7 (d, $J_{C–P}$ = 8.4 Hz), 128.5 (d, $J_{C–P}$ = 3.6 Hz), 127.8 (d, $J_{C–P}$ = 8.4 Hz), 127.0, 116.4 (d, $J_{C–P}$ = 86.1 Hz), 116.1 (d, $J_{C–P}$ = 83.8 Hz), 115.3 (d, $J_{C–P}$ = 81.4 Hz), 31.4 (d, $J_{C–P}$ = 46.8 Hz); ^{31}P NMR (200 MHz, DMSO-d_6) δ 22.6; HRMS (ESI-TOF) calcd for $C_{58}H_{46}P_2^{2+}$: 402.1532 ($[M]^{2+}$), found 402.1520.



7: $[\alpha]^{25}_{D}$ = –60.1 (*c* = 1.04, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (dd, *J* = 2.8, 8.8 Hz, 1H), 7.91 (d, *J* = 8.0 Hz, 1H), 7.78–7.88 (m, 1H), 7.69 (t, *J* = 9.4 Hz, 2H), 7.11–7.57 (m, 19H), 7.08 (t, *J* = 7.6 Hz, 2H), 6.94–7.04 (m, 3H), 6.74–6.93 (m, 6H), 6.62–6.72 (m, 1H), 6.36 (d, *J* = 8.4 Hz, 1H), 4.45–4.60 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.65 (d, $J_{C–P}$ = 7.1 Hz), 146.58 (d, $J_{C–P}$ = 7.1 Hz), 139.7 (d, $J_{C–P}$ = 3.6 Hz), 139.4 (d, $J_{C–P}$ = 4.8 Hz), 136.6 (d, $J_{C–P}$ = 14.4 Hz), 135.3, 135.2, 134.5 (d, $J_{C–P}$ = 2.5 Hz), 134.24 (d, $J_{C–P}$ = 3.5 Hz), 134.16, 134.0, 133.9 (d, $J_{C–P}$ = 2.4 Hz), 133.8, 133.7, 133.6, 133.3 (d, $J_{C–P}$ = 8.3 Hz), 133.1 (d, $J_{C–P}$ = 2.4 Hz), 133.0 (d, $J_{C–P}$ = 3.6 Hz), 132.8 (d, $J_{C–P}$ = 6.0 Hz), 132.6, 132.5, 132.3, 131.0 (d, $J_{C–P}$ = 4.8 Hz), 129.9, 129.4, 129.3 (d, $J_{C–P}$ = 13.1 Hz), 129.1, 129.0, 128.9 (d, $J_{C–P}$ = 13.1 Hz), 128.51, 128.47, 128.44, 128.3 (d, $J_{C–P}$ = 3.6 Hz), 128.1, 128.0, 127.6 (d, $J_{C–P}$ = 13.1 Hz), 127.5, 127.3, 127.0, 126.6 (d, $J_{C–P}$ = 8.4 Hz), 125.8, 117.2 (d, $J_{C–P}$ = 85.0 Hz), 116.7 (d, $J_{C–P}$ = 87.4 Hz), 113.7 (d, $J_{C–P}$ = 85.0 Hz), 31.3 (d, $J_{C–P}$ = 46.8 Hz); ^{31}P NMR (200 MHz, $CDCl_3$) δ 23.4, –15.4; HRMS (ESI-TOF) calcd for $C_{51}H_{39}P_2^{+}$: 713.2522 ($[M]^{+}$), found 713.2510.

Synthesis of Mono-Phosphonium Bromide 5.

A solution of Me-DuPHOS (0.05 mmol) and benzyl bromide (0.11 mmol) in toluene (1.0 mL) was stirred for 10 h at 110 °C. The mixture was concentrated, and the residue was purified by column chromatography on silica gel (CH_2Cl_2/MeOH = 50:1–10:1 as eluent) to give mono-phosphonium bromide **5** (90% yield).

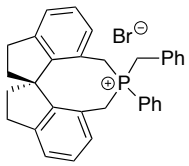


5: $[\alpha]^{28}_{D}$ = 108.7 (*c* = 1.03, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93–8.05 (m, 1H), 7.81–7.89 (m, 1H), 7.66–7.80 (m, 2H), 7.15–7.37 (m,

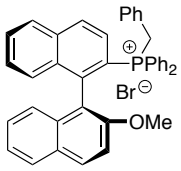
5H), 4.58 (d, J = 14.8 Hz, 2H), 3.57–3.79 (m, 2H), 2.66–2.80 (m, 1H), 2.10–2.62 (m, 5H), 1.84–2.00 (m, 1H), 1.65–1.84 (m, 4H), 1.44–1.64 (m, 2H), 1.36 (dd, J = 7.2, 19.2 Hz, 3H), 1.18 (dd, J = 7.4, 18.2 Hz, 3H), 0.82 (dd, J = 7.2, 10.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.6 (dd, $J_{C–P}$ = 10.7, 29.6 Hz), 137.3 (dd, $J_{C–P}$ = 2.5, 11.6 Hz), 135.0 (dd, $J_{C–P}$ = 10.7, 11.5 Hz), 133.7 (d, $J_{C–P}$ = 3.3 Hz), 131.2 (dd, $J_{C–P}$ = 1.6, 11.5 Hz), 129.94, 129.93, 129.88, 129.20, 129.17, 129.11, 128.4 (d, $J_{C–P}$ = 3.2 Hz), 127.5 (dd, $J_{C–P}$ = 36.7, 72.1 Hz), 40.0 (d, $J_{C–P}$ = 8.2 Hz), 37.6 (d, $J_{C–P}$ = 2.5 Hz), 36.9 (d, $J_{C–P}$ = 3.3 Hz), 35.3 (d, $J_{C–P}$ = 9.9 Hz), 33.5 (dd, $J_{C–P}$ = 9.1, 48.6 Hz), 32.4 (dd, $J_{C–P}$ = 4.5, 46.5 Hz), 32.2 (d, $J_{C–P}$ = 42.0 Hz), 31.9 (d, $J_{C–P}$ = 8.2 Hz), 31.8 (d, $J_{C–P}$ = 9.0 Hz), 19.9 (d, $J_{C–P}$ = 31.3 Hz), 17.0 (dd, $J_{C–P}$ = 3.3, 5.0 Hz), 16.3 (d, $J_{C–P}$ = 3.3 Hz), 14.3 (dd, $J_{C–P}$ = 3.3, 4.9 Hz); ^{31}P NMR (200 MHz, $CDCl_3$) δ 50.0 (d, J = 10.8 Hz), 1.4 (d, J = 11.0 Hz); HRMS (ESI-TOF) calcd for $C_{25}H_{35}P_2^+$: 397.2209 ($[M]^+$), found 397.2214.

General Procedure for the Synthesis of Chiral Phosphonium Bromides 6 and 8.

A solution of monophosphine (0.05 mmol) and benzyl bromide (0.06 mmol) in toluene (1.0 mL) was stirred for 10 h at 110 °C. The mixture was concentrated, and the residue was purified by column chromatography on silica gel (CH_2Cl_2/MeOH = 50:1–10:1 as eluent) to give a phosphonium bromide (93–95% yield).



6: $[\alpha]^{24}_D$ = –179.0 (c = 1.01, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75–7.87 (m, 2H), 7.58–7.70 (m, 2H), 7.45–7.55 (m, 2H), 7.34–7.43 (m, 2H), 7.15–7.25 (m, 3H), 7.08 (dd, J = 1.8, 7.4 Hz, 1H), 6.95–7.04 (m, 2H), 6.74–6.84 (m, 1H), 6.40 (dd, J = 2.8, 7.6 Hz, 1H), 4.44–4.67 (m, 3H), 4.21 (dd, J = 15.0, 15.0 Hz, 1H), 3.59–3.75 (m, 2H), 2.94–3.20 (m, 3H), 2.87 (dd, J = 8.4, 16.4 Hz, 1H), 2.28 (ddd, J = 3.8, 6.6, 12.6 Hz, 2H), 1.83–2.07 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.1 (d, $J_{C–P}$ = 5.8 Hz), 147.3 (d, $J_{C–P}$ = 5.8 Hz), 145.0 (d, $J_{C–P}$ = 4.1 Hz), 144.2 (d, $J_{C–P}$ = 3.3 Hz), 134.4 (d, $J_{C–P}$ = 2.5 Hz), 133.3 (d, $J_{C–P}$ = 8.3 Hz), 130.5 (d, $J_{C–P}$ = 5.7 Hz), 130.2 (d, $J_{C–P}$ = 6.6 Hz), 129.7 (d, $J_{C–P}$ = 4.9 Hz), 129.3 (d, $J_{C–P}$ = 12.3 Hz), 129.0 (d, $J_{C–P}$ = 2.5 Hz), 128.5 (d, $J_{C–P}$ = 3.3 Hz), 128.1 (d, $J_{C–P}$ = 3.2 Hz), 128.0 (d, $J_{C–P}$ = 9.1 Hz), 127.6 (d, $J_{C–P}$ = 3.2 Hz), 126.2 (d, $J_{C–P}$ = 4.1 Hz), 125.4 (d, $J_{C–P}$ = 3.2 Hz), 122.1 (d, $J_{C–P}$ = 9.1 Hz), 121.9 (d, $J_{C–P}$ = 7.4 Hz), 115.4 (d, $J_{C–P}$ = 79.9 Hz), 61.8 (d, $J_{C–P}$ = 2.5 Hz), 38.1, 37.8, 30.1, 30.0, 28.0 (d, $J_{C–P}$ = 42.8 Hz), 24.8 (d, $J_{C–P}$ = 46.1 Hz), 20.8 (d, $J_{C–P}$ = 46.1 Hz); ^{31}P NMR (200 MHz, $CDCl_3$) δ 27.1; HRMS (ESI-TOF) calcd for $C_{32}H_{30}P^+$: 445.2080 ($[M]^+$), found 445.2062.

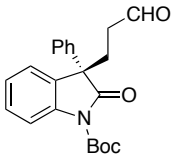


8: $[\alpha]^{24}_D$ = –67.0 (c = 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$)

δ 8.10 (dd, J = 3.0, 9.0 Hz, 1H), 8.04 (d, J = 8.4 Hz, 1H), 7.64–7.78 (m, 3H), 7.59 (d, J = 8.4 Hz, 1H), 7.39–7.53 (m, 3H), 7.31–7.38 (m, 2H), 7.09–7.31 (m, 10H), 7.00–7.09 (m, 3H), 6.87–6.96 (m, 2H), 6.66 (d, J = 8.8 Hz, 1H), 5.07–5.23 (m, 1H), 4.70–4.85 (m, 1H), 3.62 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.5, 144.7 (d, $J_{C–P}$ = 8.4 Hz), 135.5 (d, $J_{C–P}$ = 2.4 Hz), 133.5 (d, $J_{C–P}$ = 2.5 Hz), 133.34, 133.32, 133.2, 133.1, 132.9 (d, $J_{C–P}$ = 9.6 Hz), 132.7 (d, $J_{C–P}$ = 9.5 Hz), 132.1, 131.0 (d, $J_{C–P}$ = 6.0 Hz), 129.8, 128.9, 128.8, 128.71, 128.66, 128.62, 128.56, 128.51, 128.3 (d, $J_{C–P}$ = 3.6 Hz), 128.2, 128.0 (d, $J_{C–P}$ = 3.6 Hz), 127.94, 127.85, 127.7, 127.2, 126.8 (d, $J_{C–P}$ = 8.4 Hz), 126.6, 124.0, 123.8, 117.7 (d, $J_{C–P}$ = 85.0 Hz), 117.5 (d, $J_{C–P}$ = 85.6 Hz), 116.91, 116.86, 114.7 (d, $J_{C–P}$ = 86.1 Hz), 112.0, 55.5, 30.8 (d, $J_{C–P}$ = 46.6 Hz); ^{31}P NMR (200 MHz, $CDCl_3$) δ 22.3; HRMS (ESI-TOF) calcd for $C_{40}H_{32}OP^+$: 559.2185 ($[M]^+$), found 559.2189.

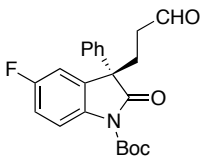
General Procedure for the Catalytic Asymmetric Conjugate Addition of 3-Substituted Oxindoles.

A solution of catalyst (*S*)-**9l** (36 μl, 1.4 × 10^{-3} M, 0.1 mol %) in CH_2Cl_2 was added to reaction vessel, and the solvent was completely evaporated and dried under vacuo. To the reaction vessel was added 3-substituted oxindole **10** (0.050 mmol) and mesitylene (1.0 mL), and the solution was cooled to 0 °C. To this reaction mixture was added water (1.0 mL) and acrolein (0.15 mmol), and stirred for 48 h at 0 °C. The reaction mixture was diluted with Et_2O, and organic phase was separated. The aqueous phase was extracted with Et_2O. The combined extracts were dried over Na_2SO_4 and concentrated. The residue was purified by column chromatography on silica gel (hexane/ethyl acetate as eluent) to give product **11**. The enatiomeric excess of the product **11** was determined by chiral HPLC analysis. The absolute configurations of products **11** and **13** were confirmed by comparison of the optical rotations of products **11a**, **11b**, **13a**, and **13b** with the literature value.[2]

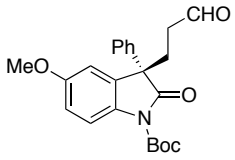


11a:[2] $[\alpha]^{30}_D$ = –66.9 (c = 1.02, $CHCl_3$), HPLC analysis (90% ee): Daicel Chiralpak AD-3, hexane/2-propanol = 20:1, flow rate = 0.5 mL/min, 224 nm; retention time: 14.9 min (major) and 20.7 min (minor). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.64 (s, 1H), 7.95 (d, J = 8.8 Hz, 1H), 7.38 (ddd, J = 1.9, 7.1, 8.3 Hz, 1H), 7.16–7.35 (m, 7H), 2.80 (ddd, J = 4.9, 11.1, 14.6 Hz, 1H), 2.52 (ddd, J = 4.4, 11.2, 14.0 Hz, 1H), 2.33–2.46 (m, 1H), 2.15 (dddd, J = 1.1, 4.5, 11.0, 17.8 Hz, 1H), 1.63 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.2, 176.3, 149.1, 139.9, 139.1, 130.0, 128.9, 128.7, 127.8, 126.9, 124.8, 124.6, 115.4, 84.7, 55.8, 39.3,

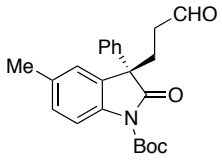
30.2, 28.0; IR (neat) 2980, 2932, 1790, 1761, 1724, 1479, 1462, 1344, 1287, 1250, 1148, 841, 756, 696 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{22}H_{23}NO_4Na^+$: 388.1519 ($[M+Na]^+$), found 388.1505.



11b:[2] $[\alpha]^{33}_D$ = –40.7 (*c* = 0.98, $CHCl_3$), HPLC analysis (88% ee): Daicel Chiralpak AD-H, hexane/2-propanol = 20:1, flow rate = 0.5 mL/min, 224 nm; retention time: 15.0 min (major) and 16.5 min (minor). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.66 (s, 1H), 7.95 (dd, *J* = 4.8, 9.2 Hz, 1H), 7.22–7.43 (m, 5H), 7.09 (ddd, *J* = 2.3, 8.9, 8.9 Hz, 1H), 6.92 (dd, *J* = 2.8, 8.0 Hz, 1H), 2.81 (ddd, *J* = 4.4, 11.0, 13.6 Hz, 1H), 2.34–2.58 (m, 2H), 2.11–2.26 (m, 1H), 1.62 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.9, 175.9, 160.0 (d, J_{C-F} = 246.1 Hz), 149.1, 138.6, 135.8 (d, J_{C-F} = 2.5 Hz), 132.1 (d, J_{C-F} = 7.4 Hz), 128.9, 128.1, 126.8, 116.8 (d, J_{C-F} = 7.4 Hz), 115.5 (d, J_{C-F} = 23.1 Hz), 112.0 (d, J_{C-F} = 24.7 Hz), 84.9, 56.0, 39.2, 30.0, 28.0; IR (neat) 2982, 2930, 1792, 1765, 1728, 1481, 1296, 1267, 1250, 1146, 841, 721, 696 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{22}H_{22}FNO_4Na^+$: 406.1425 ($[M+Na]^+$), found 406.1419.

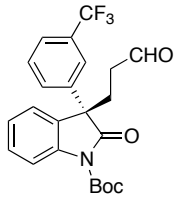


11c: $[\alpha]^{30}_D$ = –74.3 (*c* = 1.00, $CHCl_3$), HPLC analysis (90% ee): Daicel Chiralpak AD-H, hexane/2-propanol = 20:1, flow rate = 0.5 mL/min, 224 nm; retention time: 23.4 min (major) and 34.9 min (minor). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.65 (s, 1H), 7.88 (d, *J* = 9.2 Hz, 1H), 7.19–7.43 (m, 5H), 6.90 (dd, *J* = 2.6, 9.0 Hz, 1H), 6.73 (d, *J* = 2.8 Hz, 1H), 3.80 (s, 3H), 2.81 (ddd, *J* = 4.4, 11.0, 13.4 Hz, 1H), 2.31–2.58 (m, 2H), 2.16 (ddd, *J* = 4.4, 11.4, 17.2 Hz, 1H), 1.62 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.3, 176.3, 157.1, 149.2, 139.2, 133.2, 131.4, 128.8, 127.8, 126.9, 116.4, 113.6, 110.8, 84.5, 56.2, 55.6, 39.3, 30.1, 28.1; IR (neat) 2980, 2934, 1788, 1759, 1724, 1487, 1296, 1277, 1248, 1152, 843, 723, 696 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{23}H_{25}NO_5Na^+$: 418.1625 ($[M+Na]^+$), found 418.1612.

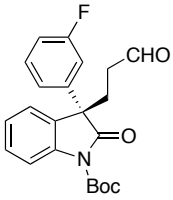


11d: $[\alpha]^{28}_D$ = –73.4 (*c* = 0.90, $CHCl_3$), HPLC analysis (90% ee): Daicel Chiralpak AD-3, hexane/2-propanol = 20:1, flow rate = 0.5 mL/min, 224 nm; retention time: 15.3 min (major) and 20.7 min (minor). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.65 (s, 1H), 7.81 (d, *J* = 8.4 Hz, 1H), 7.23–7.42 (m, 5H), 7.13–7.21 (m, 1H), 6.98 (d, *J* = 1.2 Hz, 1H), 2.80 (ddd, *J* = 4.6, 11.2, 13.8 Hz, 1H), 2.49 (ddd, *J* = 4.1, 11.6, 13.5 Hz, 1H), 2.28–2.44 (m, 4H), 2.15 (dddd, *J* = 1.2, 4.3, 11.1, 17.5 Hz 1H), 1.62 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$)

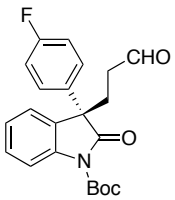
δ 200.4, 176.5, 149.2, 139.4, 137.5, 134.5, 130.1, 129.4, 128.7, 127.8, 126.9, 125.0, 115.2, 84.5, 55.9, 39.4, 30.2, 28.1, 21.1; IR (neat) 2980, 2928, 1790, 1761, 1726, 1489, 1337, 1300, 1279, 1250, 1152, 820, 721, 696 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{23}H_{25}NO_4Na^+$: 402.1676 ($[M+Na]^+$), found 402.1662.



11e: $[\alpha]^{30}_D$ = –68.1 (*c* = 0.89, $CHCl_3$), HPLC analysis (90% ee): Daicel Chiralpak AD-3, hexane/2-propanol = 20:1, flow rate = 0.5 mL/min, 224 nm; retention time: 11.2 min (major) and 12.9 min (minor). ^1H NMR (400 MHz, $CDCl_3$) δ 9.64 (s, 1H), 7.97 (d, *J* = 8.8 Hz, 1H), 7.51–7.63 (m, 3H), 7.38–7.50 (m, 2H), 7.24–7.32 (m, 1H), 7.16–7.23 (m, 1H), 2.81 (ddd, *J* = 4.9, 10.7, 13.7 Hz, 1H), 2.52 (ddd, *J* = 4.2, 11.2, 13.8 Hz, 1H), 2.34–2.46 (m, 1H), 2.12 (dddd, *J* = 1.0, 4.4, 11.0, 18.0 Hz, 1H), 1.64 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.8, 175.7, 148.9, 140.2, 139.9, 131.1 (q, $J_{C–F}$ = 32.6 Hz), 130.6, 129.4, 129.3, 128.9, 125.1, 124.8 (q, $J_{C–F}$ = 3.8 Hz), 124.6, 123.9 (q, $J_{C–F}$ = 273.5 Hz), 123.7 (q, $J_{C–F}$ = 3.8 Hz), 115.7, 85.0, 55.6, 39.2, 30.6, 28.0; IR (neat) 2982, 2930, 1790, 1761, 1728, 1479, 1327, 1287, 1250, 1148, 1125, 841, 756, 700 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{23}H_{22}F_3NO_4Na^+$: 456.1393 ($[M+Na]^+$), found 456.1393.

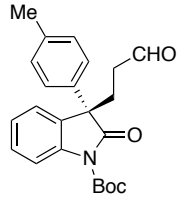


11f: $[\alpha]^{31}_D$ = –71.1 (*c* = 0.93, $CHCl_3$), HPLC analysis (91% ee): Daicel Chiralpak AD-3, hexane/2-propanol = 20:1, flow rate = 0.5 mL/min, 224 nm; retention time: 14.3 min (major) and 17.8 min (minor). ^1H NMR (400 MHz, $CDCl_3$) δ 9.64 (s, 1H), 7.96 (d, *J* = 8.0 Hz, 1H), 7.37–7.46 (m, 1H), 7.22–7.35 (m, 2H), 7.17–7.22 (m, 1H), 7.09–7.16 (m, 1H), 7.03 (ddd, *J* = 2.1, 2.1, 10.5 Hz, 1H), 6.93–7.01 (m, 1H), 2.77 (ddd, *J* = 4.7, 10.9, 13.7 Hz, 1H), 2.51 (ddd, *J* = 4.4, 11.4, 13.8, 1H), 2.32–2.45 (m, 1H), 2.06–2.21 (m, 1H), 1.63 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.0, 175.8, 162.9 (d, $J_{C–F}$ = 247.8 Hz), 149.0, 141.6 (d, $J_{C–F}$ = 6.6 Hz), 139.9, 130.2 (d, $J_{C–F}$ = 9.1 Hz), 129.3, 129.2, 124.9, 124.6, 122.7 (d, $J_{C–F}$ = 2.5 Hz), 115.5, 114.8 (d, $J_{C–F}$ = 20.6 Hz), 114.4 (d, $J_{C–F}$ = 23.8 Hz), 84.9, 55.6, 39.2, 30.3, 28.0; IR (neat) 2980, 2930, 1790, 1761, 1726, 1481, 1464, 1344, 1287, 1250, 1148, 839, 756 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{22}H_{22}FNO_4Na^+$: 406.1425 ($[M+Na]^+$), found 406.1413.

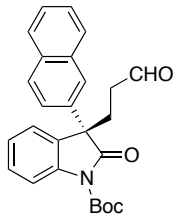


11g: $[\alpha]^{31}_D$ = –70.9 (*c* = 0.93, $CHCl_3$), HPLC analysis (91% ee): Daicel Chiralpak AD-3, hexane/2-propanol = 20:1, flow rate = 0.5 mL/min, 224 nm; retention time: 15.5 min (major) and 19.5 min (minor). ^1H NMR (400 MHz, $CDCl_3$) δ 9.63 (s, 1H), 7.95 (d, *J* = 8.0 Hz, 1H),

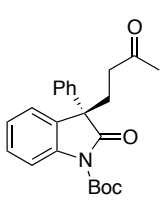
7.36–7.47 (m, 1H), 7.21–7.36 (m, 3H), 7.14–7.21 (m, 1H), 6.94–7.06 (m, 2H), 2.77 (ddd, J = 3.8, 11.0, 13.6 Hz, 1H), 2.49 (ddd, J = 4.2, 11.0, 13.6, 1H), 2.31–2.44 (m, 1H), 2.03–2.21 (m, 1H), 1.63 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.1, 176.2, 162.3 (d, J_{C-F} = 248.6 Hz), 149.0, 139.9, 134.9 (d, J_{C-F} = 2.4 Hz), 129.6, 129.1, 128.8 (d, J_{C-F} = 8.3 Hz), 124.9, 124.6, 115.6 (d, J_{C-F} = 21.4 Hz), 115.5, 84.8, 55.2, 39.3, 30.5, 28.0; IR (neat) 2980, 2928, 1790, 1763, 1728, 1508, 1344, 1287, 1250, 1150, 841, 756 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{22}H_{22}FNO_4Na^+$: 406.1425 ([M+Na]$^+$), found 406.1418.



11h: $[\alpha]^{30}_D$ = –52.7 (c = 0.96, $CHCl_3$), HPLC analysis (88% ee): Daicel Chiralpak AD-H, hexane/2-propanol = 20:1, flow rate = 0.5 mL/min, 224 nm; retention time: 15.5 min (major) and 21.3 min (minor). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.64 (t, J = 1.0 Hz, 1H), 7.94 (d, J = 8.4 Hz, 1H), 7.37 (ddd, J = 1.8, 7.2, 8.4 Hz, 1H), 7.16–7.25 (m, 4H), 7.07–7.15 (m, 2H), 2.78 (ddd, J = 4.8, 11.0, 13.8 Hz, 1H), 2.50 (ddd, J = 4.6, 11.2, 13.8 Hz, 1H), 2.24–2.44 (m, 4H), 2.14 (dddd, J = 1.3, 4.5, 11.1, 17.9 Hz, 1H), 1.62 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.3, 176.4, 149.2, 139.9, 137.6, 136.2, 130.2, 129.5, 128.8, 126.8, 124.8, 124.6, 115.4, 84.6, 55.5, 39.4, 30.2, 28.1, 20.9; IR (neat) 2980, 2930, 1792, 1763, 1726, 1479, 1344, 1287, 1250, 1148, 841, 756 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{23}H_{25}NO_4Na^+$: 402.1676 ([M+Na]$^+$), found 402.1668.

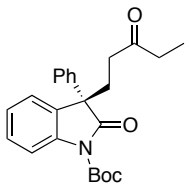


11i: $[\alpha]^{28}_D$ = –26.1 (c = 0.98, $CHCl_3$), HPLC analysis (91% ee): Daicel Chiralpak AD-H, hexane/2-propanol = 20:1, flow rate = 0.5 mL/min, 224 nm; retention time: 22.8 min (major) and 29.1 min (minor). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.67 (s, 1H), 7.99 (d, J = 8.0 Hz, 1H), 7.70–7.84 (m, 4H), 7.37–7.53 (m, 4H), 7.21–7.33 (m, 2H), 2.93 (ddd, J = 4.9, 11.1, 13.9 Hz, 1H), 2.63 (ddd, J = 4.7, 11.3, 14.1 Hz, 1H), 2.38–2.53 (m, 1H), 2.14–2.28 (m, 1H), 1.63 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.3, 176.3, 149.2, 139.9, 136.5, 133.1, 132.7, 130.1, 129.0, 128.7, 128.2, 127.4, 126.4, 126.3, 126.0, 124.9, 124.69, 124.68, 115.5, 84.7, 56.0, 39.4, 30.1, 28.1; IR (neat) 2980, 2932, 1788, 1761, 1724, 1479, 1342, 1287, 1250, 1146, 816, 754 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{26}H_{25}NO_4Na^+$: 438.1676 ([M+Na]$^+$), found 438.1681.



13a:[2] $[\alpha]^{32}_D$ = –44.3 (c = 1.10, $CHCl_3$), HPLC analysis (90% ee): Daicel Chiralpak AD-H, hexane/2-propanol = 20:1, flow rate = 0.5 mL/min, 224 nm; retention time: 14.9 min (major) and 21.3 min (minor). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, J = 8.0 Hz, 1H), 7.35–7.42 (m, 1H),

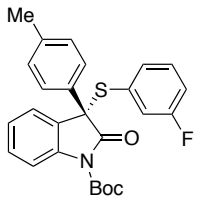
7.15–7.34 (m, 7H), 2.75 (ddd, J = 4.5, 11.3, 13.7 Hz, 1H), 2.49 (ddd, J = 4.2, 11.6, 13.8 Hz, 1H), 2.29–2.42 (m, 1H), 2.03–2.13 (m, 1H), 2.01, (s, 3H), 1.63 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.0, 176.5, 149.2, 139.8, 139.4, 130.4, 128.7, 127.7, 126.9, 124.74, 124.71, 115.3, 84.6, 55.9, 38.7, 31.7, 29.9, 28.1; IR (neat) 2980, 2928, 1790, 1763, 1728, 1479, 1464, 1346, 1288, 1250, 1148, 841, 758, 696 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{23}H_{25}NO_4Na^+$: 402.1676 ([M+Na]$^+$), found 402.1669.



13b:[2] $[\alpha]^{29}_D$ = –43.8 (c = 1.00, $CHCl_3$), HPLC analysis (90% ee): Daicel Chiralpak AD-H, hexane/2-propanol = 20:1, flow rate = 0.5 mL/min, 224 nm; retention time: 14.5 min (major) and 19.7 min (minor). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, J = 8.4 Hz, 1H), 7.34–7.44 (m, 1H), 7.15–7.34 (m, 7H), 2.75 (ddd, J = 5.1, 11.1, 14.1 Hz, 1H), 2.52 (ddd, J = 4.6, 11.4, 14.2 Hz, 1H), 2.14–2.40 (m, 3H), 2.04 (ddd, J = 4.9, 11.3, 17.1 Hz, 1H), 1.63 (s, 9H), 0.95 (t, J = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.7, 176.5, 149.2, 139.8, 139.5, 130.4, 128.69, 128.68, 127.7, 126.9 124.8, 124.7, 115.3, 84.6, 56.0, 37.4, 35.9, 31.8, 28.1, 7.6; IR (neat) 2978, 2936, 1792, 1763, 1728, 1479, 1462, 1346, 1288, 1250, 1148, 841, 758, 696 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{24}H_{27}NO_4Na^+$: 416.1832 ([M+Na]$^+$), found 416.1821.

Typical Procedure for the Catalytic Asymmetric Sulfenylation of 3-Substituted Oxindole.

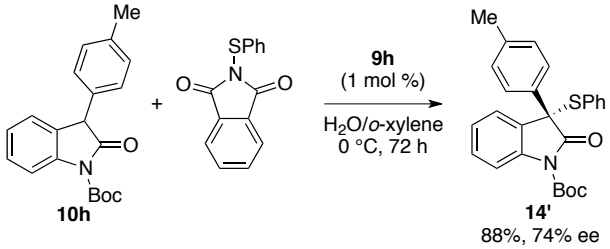
To a solution of catalyst **9h** (0.00050 mmol) and 3-aryloxindole **10h** (0.050 mmol) in *o*-xylene (1.0 mL) was added *N*-(arylthio)phthalimide (0.060 mmol) and water (1.0 mL) at 0 °C. After stirring for 48 h at 0 °C, the reaction mixture was diluted with ethyl acetate and organic phase was separated. The aqueous phase was extracted with ethyl acetate. The combined extracts were dried over Na_2SO_4 and concentrated. The residue was purified by preparative thin layer chromatography on silica gel (hexane/ethyl acetate as eluent) to give product **14**. The enatiomeric excess of the product **14** was determined by chiral HPLC analysis.



14: $[\alpha]^{26}_D$ = 106.1 (c = 0.97, $CHCl_3$), HPLC analysis (80% ee): Daicel Chiralcel OD-H, hexane/2-propanol = 40:1, flow rate = 0.5 mL/min, 224 nm; retention time: 8.7 min (major) and 11.9 min (minor). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53–7.64 (m, 3H), 7.42–7.49 (m, 1H), 7.22–7.31 (m, 2H), 7.19 (d, J = 8.0 Hz, 2H), 7.01–7.09 (m, 1H), 6.96

(ddd, J = 1.1, 2.5, 8.5 Hz, 1H), 6.87–6.94 (m, 2H), 2.35 (s, 3H), 1.55 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.2, 161.8 (d, $J_{C–F}$ = 251.0 Hz), 148.6, 139.3, 138.6, 132.3, 132.1 (d, $J_{C–F}$ = 3.2 Hz), 131.4 (d, $J_{C–F}$ = 8.2 Hz), 129.5 (d, $J_{C–F}$ = 9.1 Hz), 129.4, 129.2, 128.4, 128.2, 126.2, 124.6, 123.1 (d, $J_{C–F}$ = 22.2 Hz), 116.8 (d, $J_{C–F}$ = 20.6 Hz), 114.7, 84.3, 62.6, 27.9, 21.1; IR (neat) 1764, 1733, 1476, 1466, 1343, 1301, 1290, 1250, 1216, 1148, 1093, 880, 752 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{26}H_{24}FNO_3SNa^+$: 472.1353 ([M+Na]$^+$), found 472.1365.

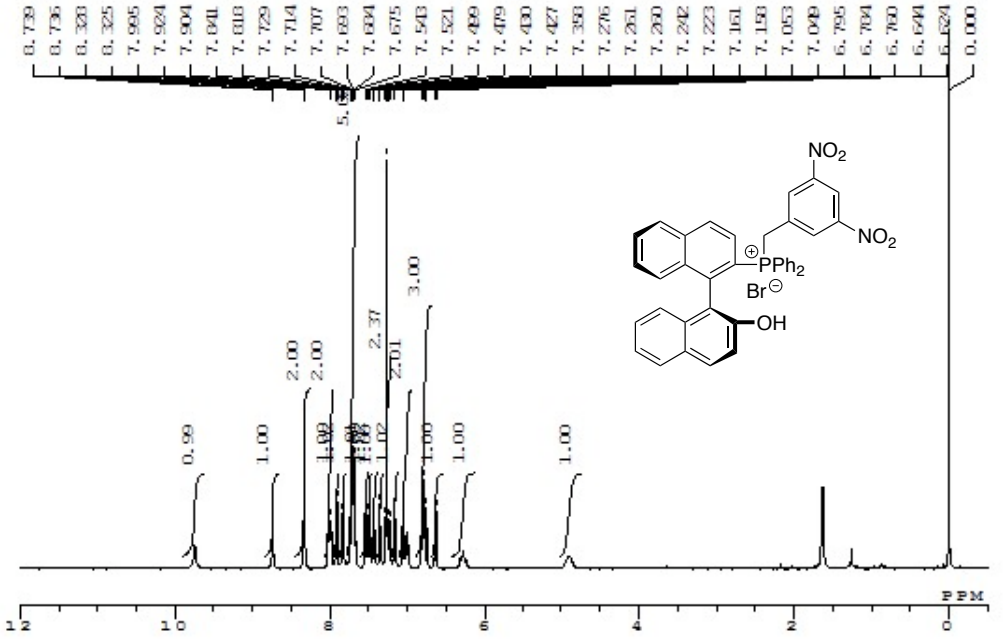
The absolute configuration of product **14** was confirmed by comparison of the optical rotation of related compound **14'** with the literature value.[3] The product **14'** was synthesized by the above-mentioned method.



14':[3] [α]$^{30}_D$ = 88.0 (c = 1.14, $CHCl_3$; 74% ee) [lit.[3] [α]$^{22}_D$ = –173.7 (c = 1.0, $CHCl_3$; 97% ee for (*R*))], HPLC analysis (74% ee): Daicel Chiralcel OD-H, hexane/2-propanol = 98:2, flow rate = 1.0 mL/min, 224 nm; retention time: 4.7 min (major) and 5.9 min (minor). [lit.[3] Daicel Chiralcel OD-H, hexane/2-propanol = 98:2, flow rate = 1.0 mL/min, 210 nm; retention time: 5.1 min (*S*) and 7.5 min (*R*)]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52–7.61 (m, 3H), 7.39–7.46 (m, 1H), 7.21–7.25 (m, 3H), 7.18 (d, J = 8.4 Hz, 2H), 7.11–7.16 (m, 2H), 7.04–7.11 (m, 2H), 2.34 (s, 3H), 1.53 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.5, 148.6, 139.3, 138.4, 136.5, 132.6, 129.7, 129.5, 129.3, 128.9, 128.8, 128.33, 128.27, 126.2, 124.4, 114.7, 84.0, 62.6, 28.0, 21.1; IR (neat) 1764, 1731, 1477, 1466, 1343, 1301, 1290, 1250, 1148, 1092, 752 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{26}H_{25}NO_3SNa^+$: 454.1447 ([M+Na]$^+$), found 454.1447.

References

1. (*a*) T. Hayashi, *J. Organomet. Chem.*, 1999, **576**, 195; (*b*) T. Hayashi, *Acc. Chem. Res.*, 2000, **33**, 354; (*c*) Y. Uozumi, M. Kawatsura and T. Hayashi, *Org. Synth.*, 2002, **78**, 1.
2. R. He, C. Ding and K. Maruoka, *Angew. Chem., Int. Ed.*, 2009, **48**, 4559.
3. X. Li, C. Liu, X.-S. Xue and J.-P. Cheng, *Org. Lett.*, 2012, **14**, 4374.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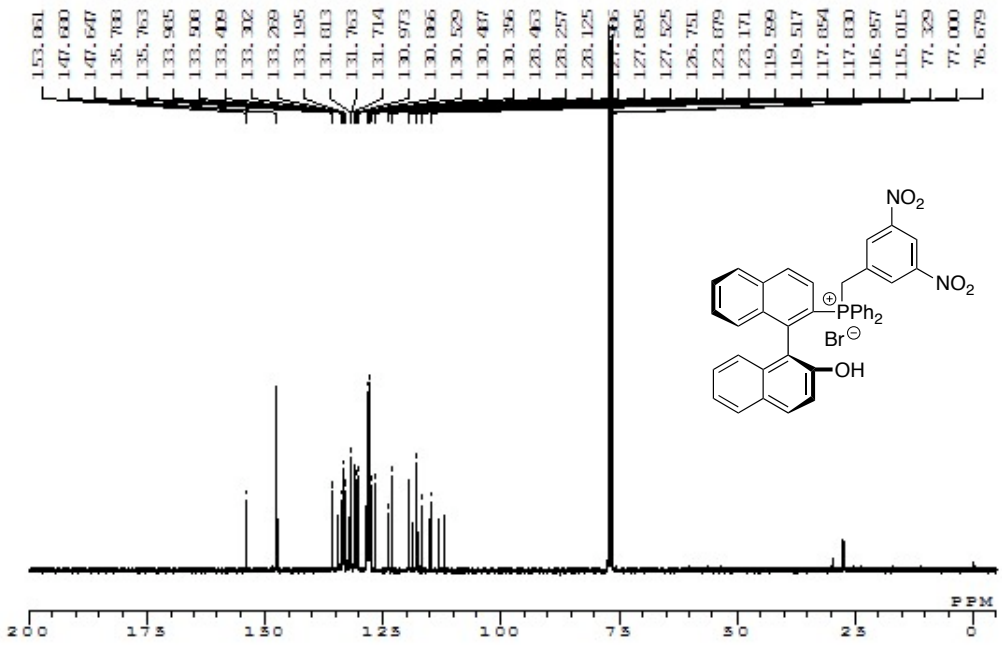
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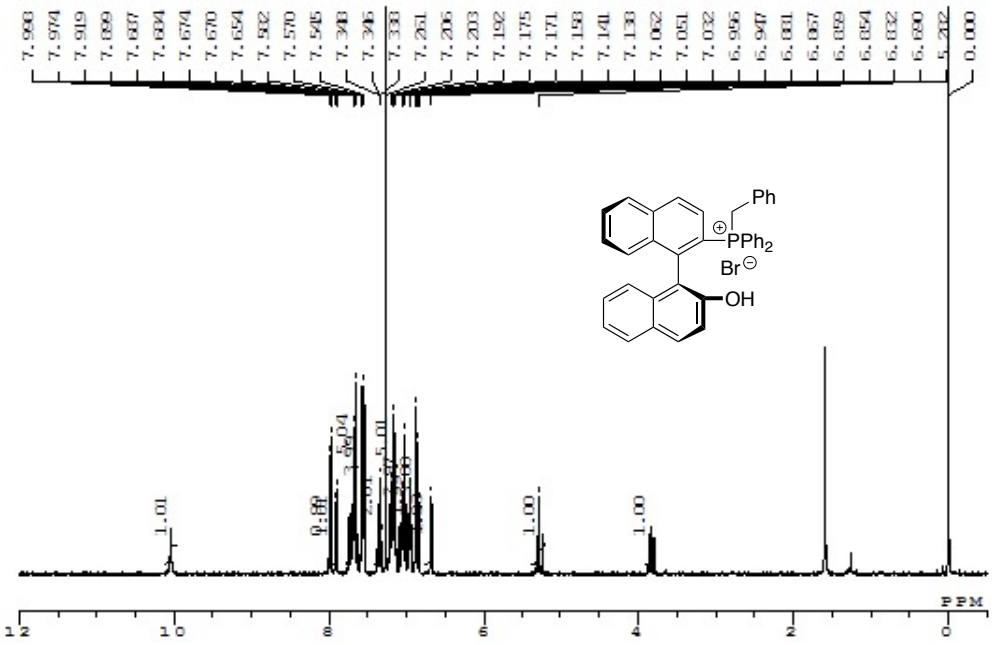
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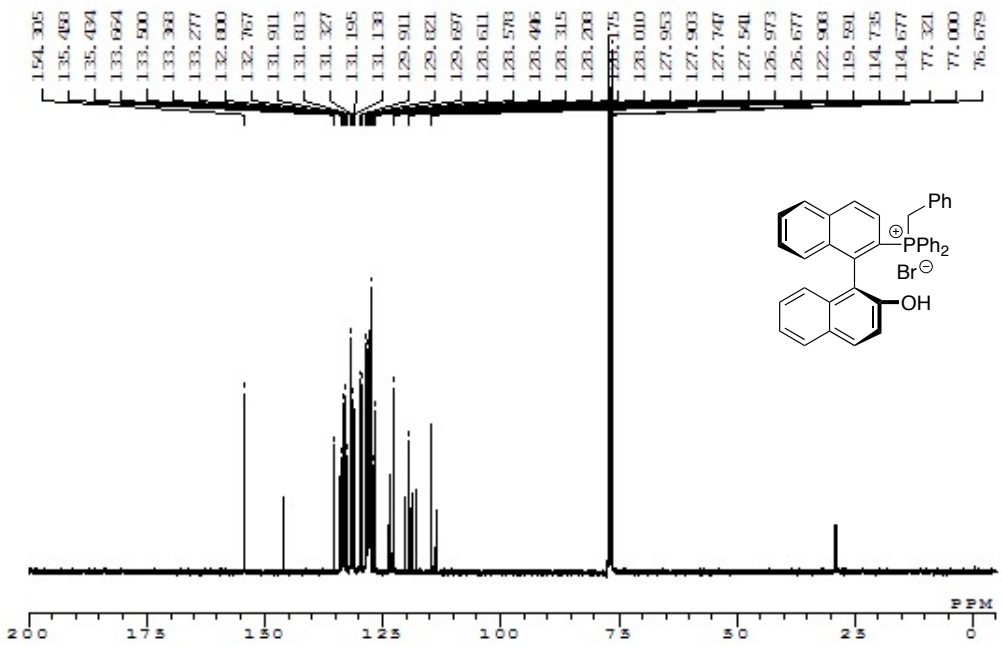
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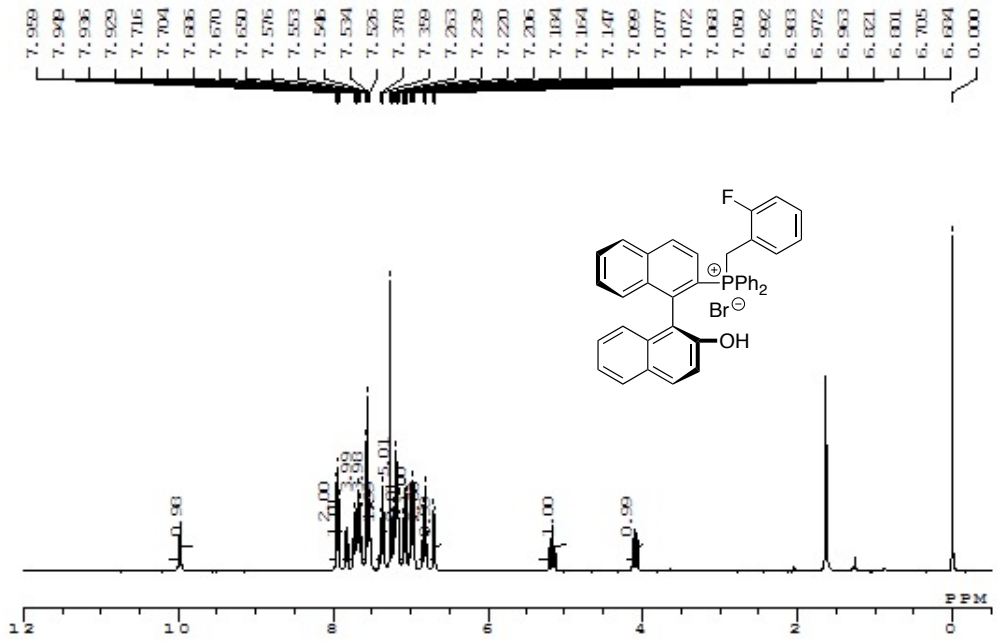
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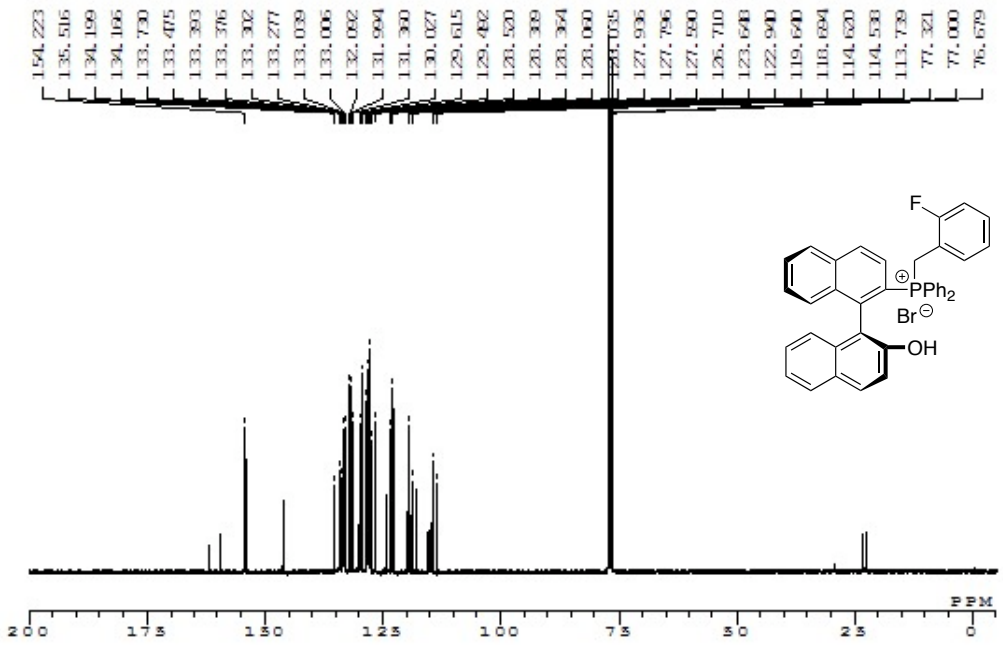
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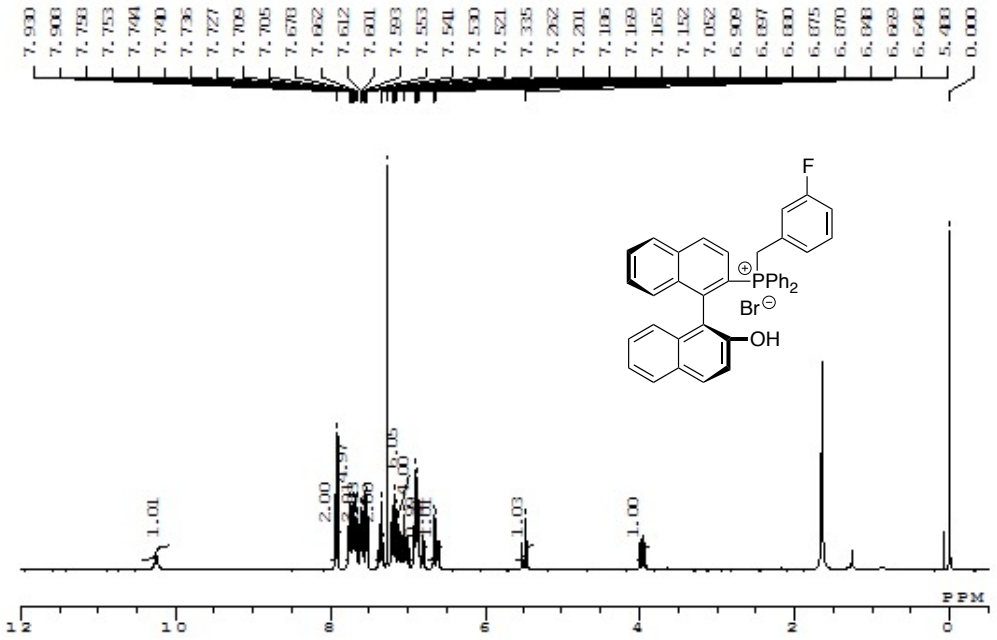
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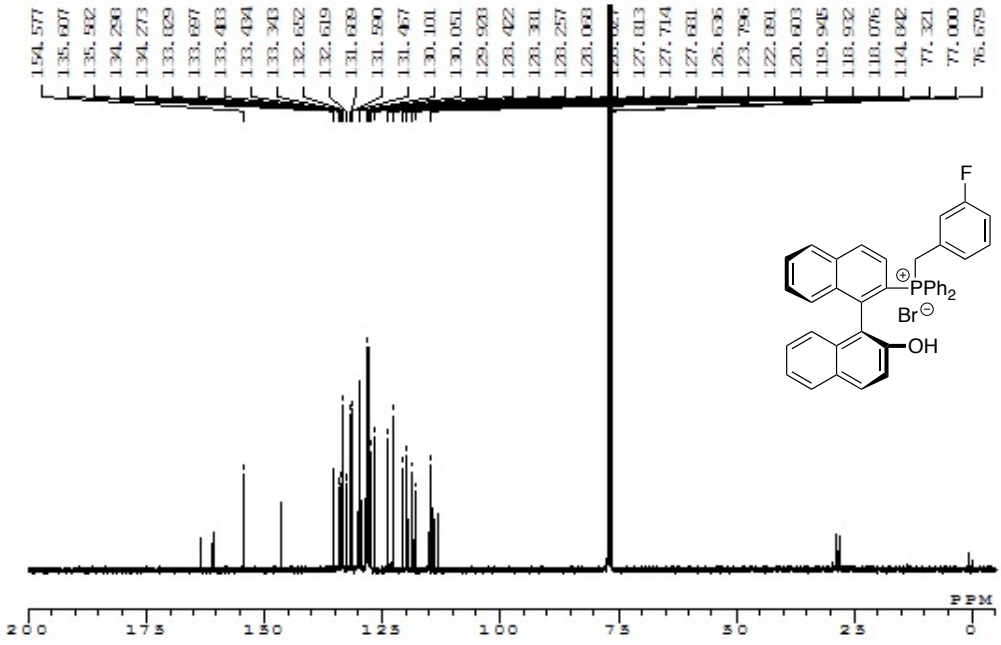
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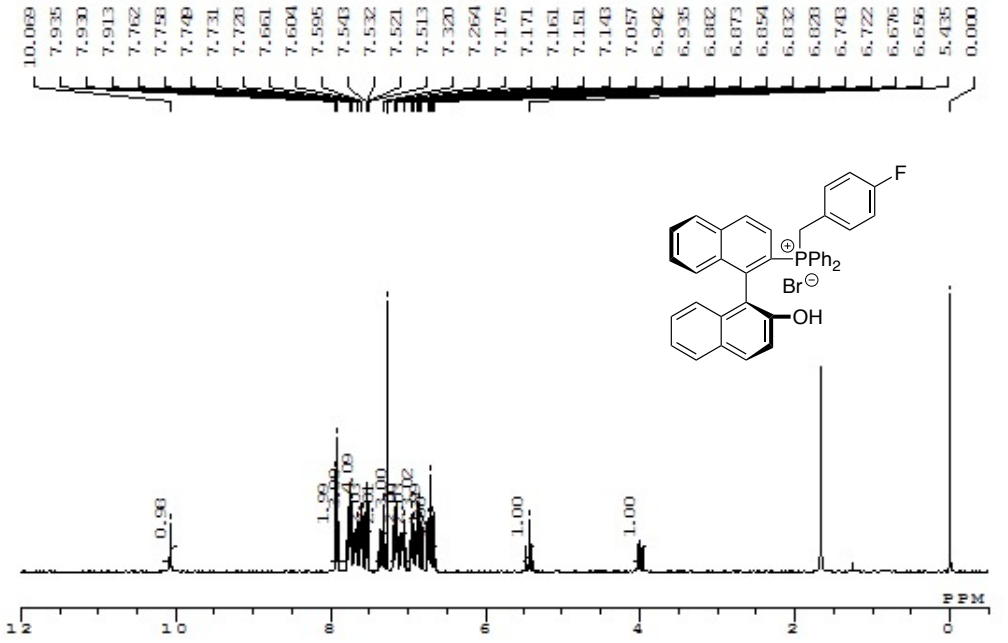
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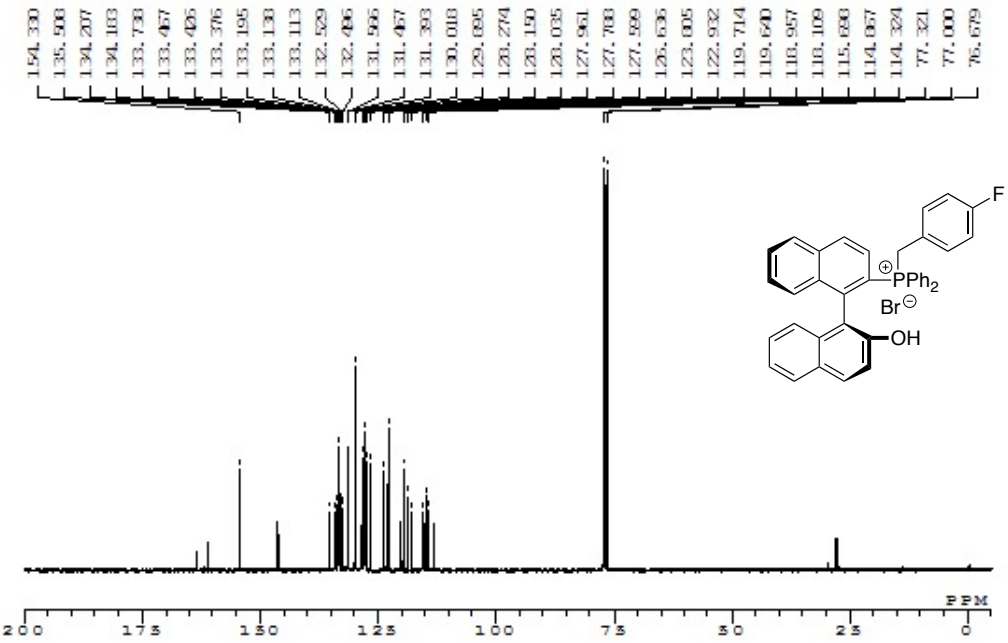
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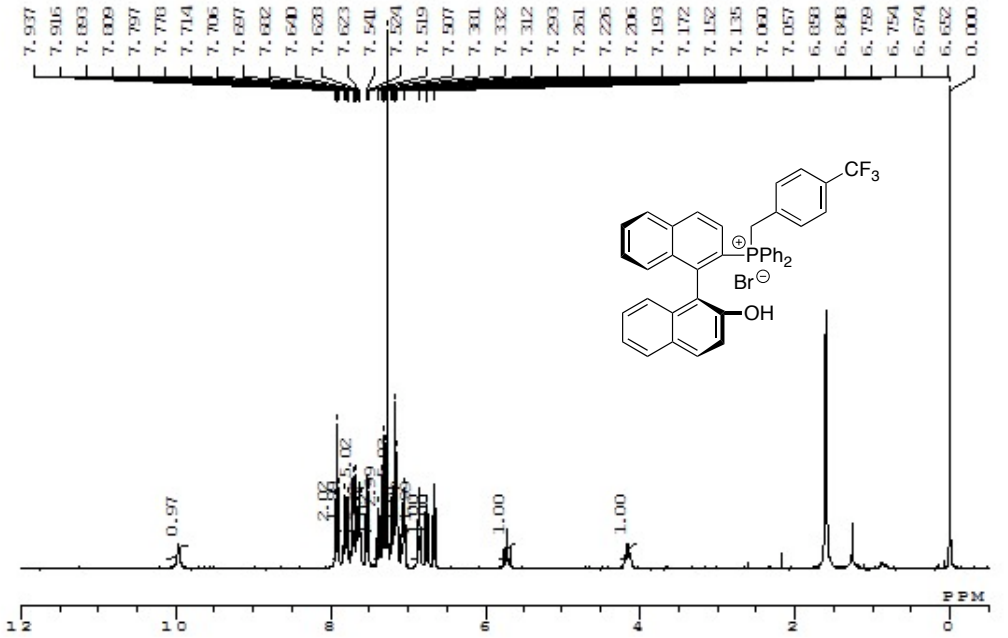
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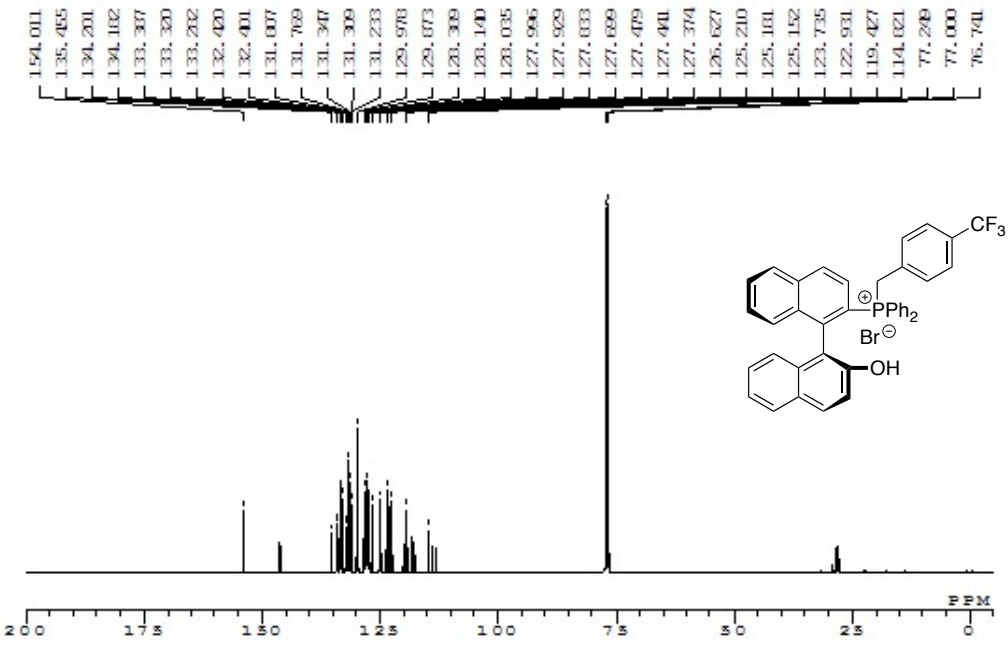
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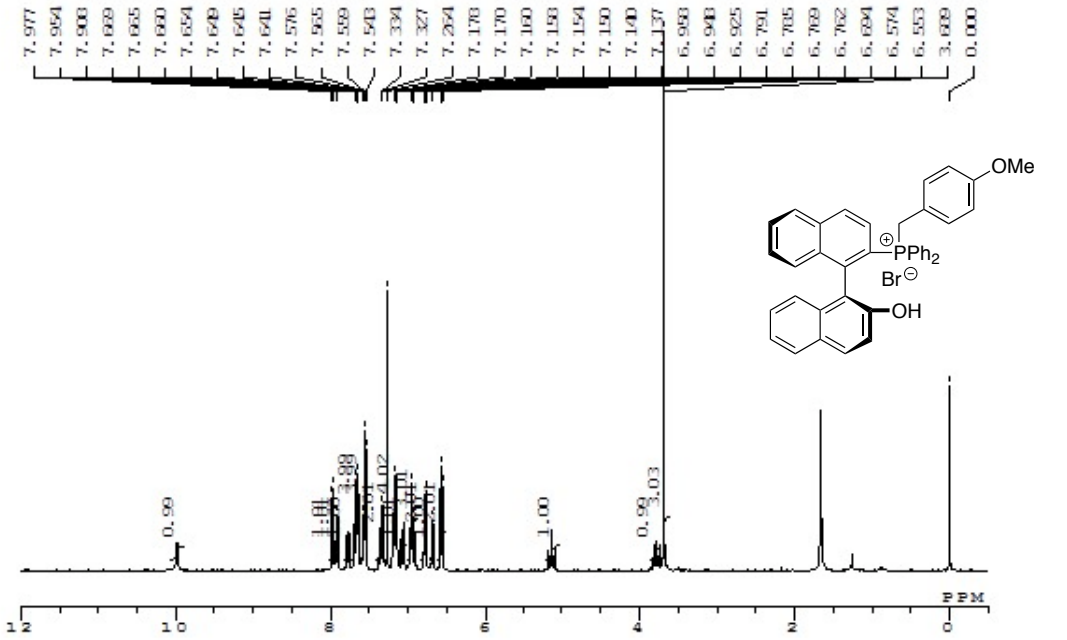
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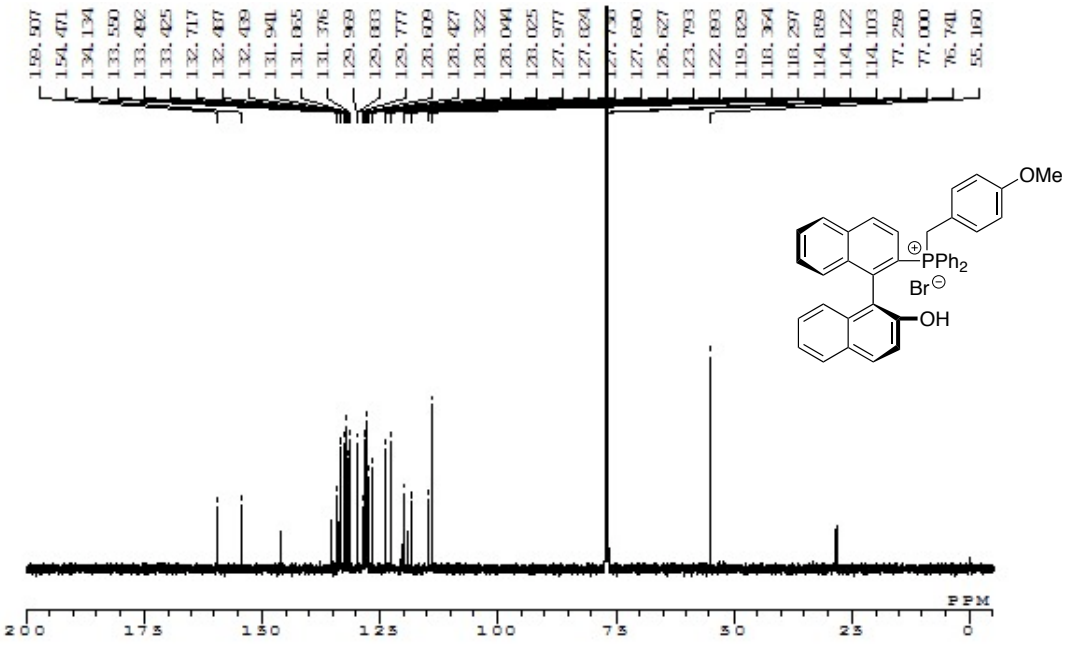
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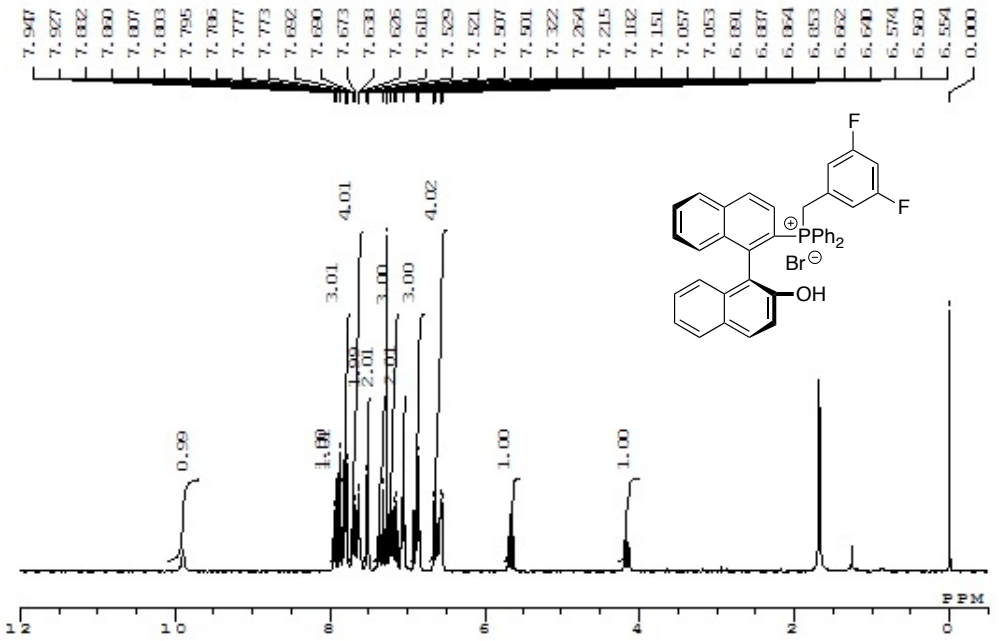
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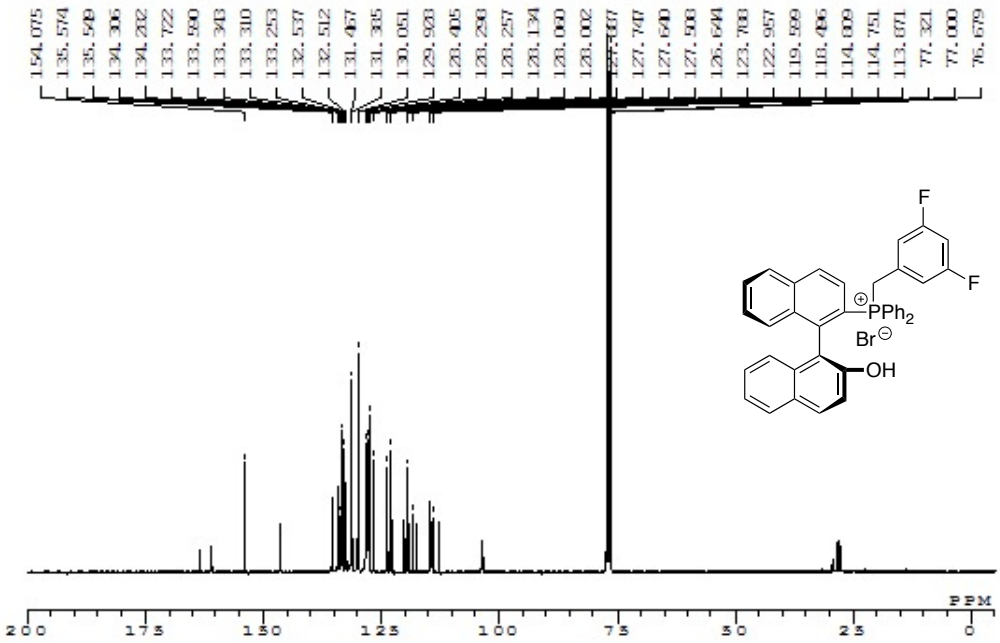
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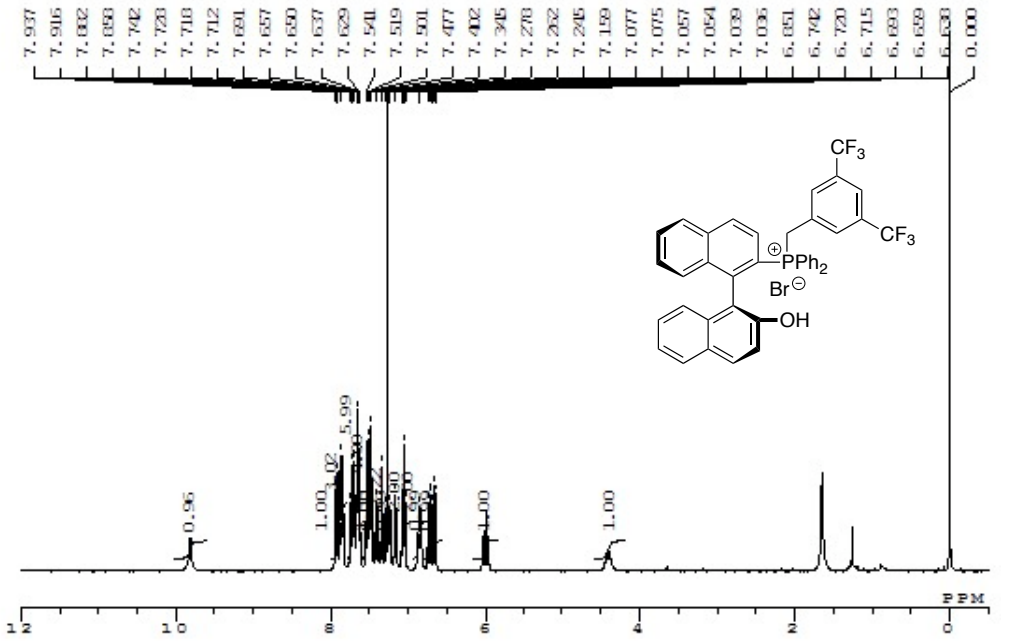
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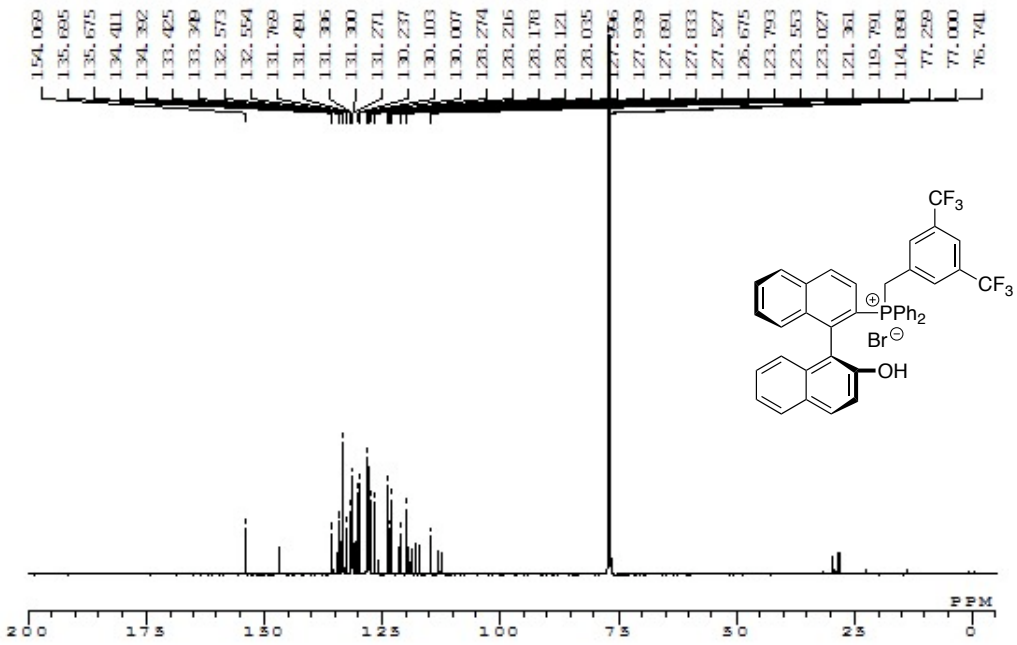
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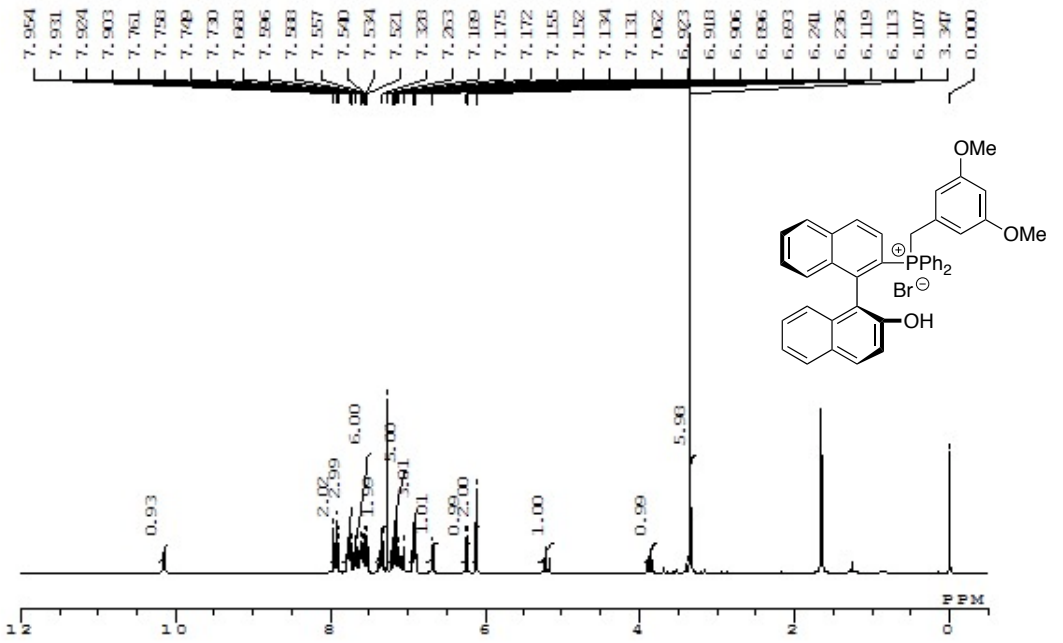
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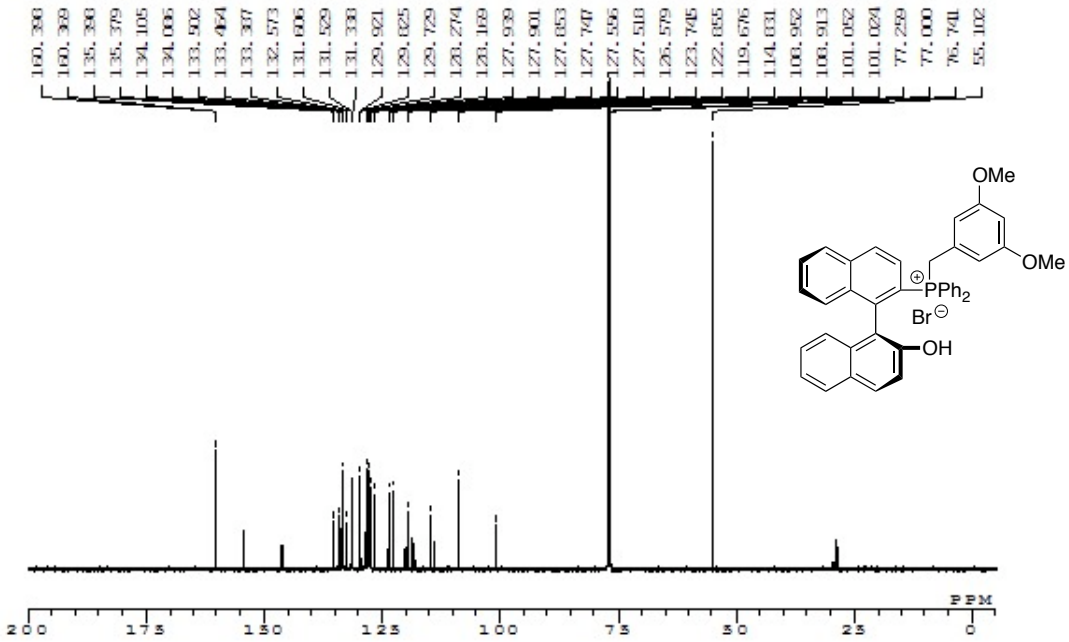
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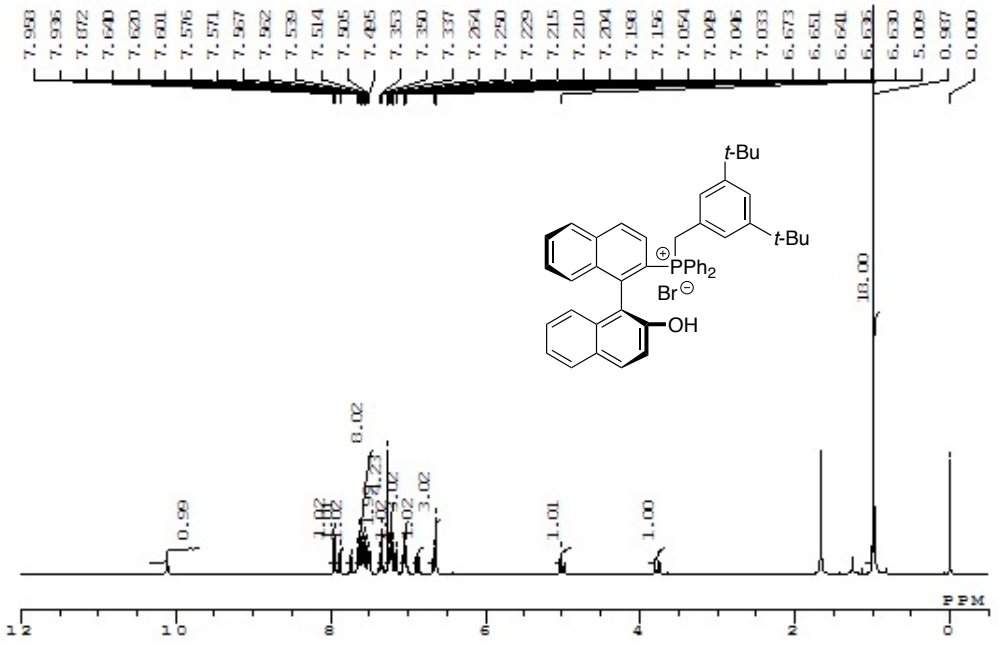
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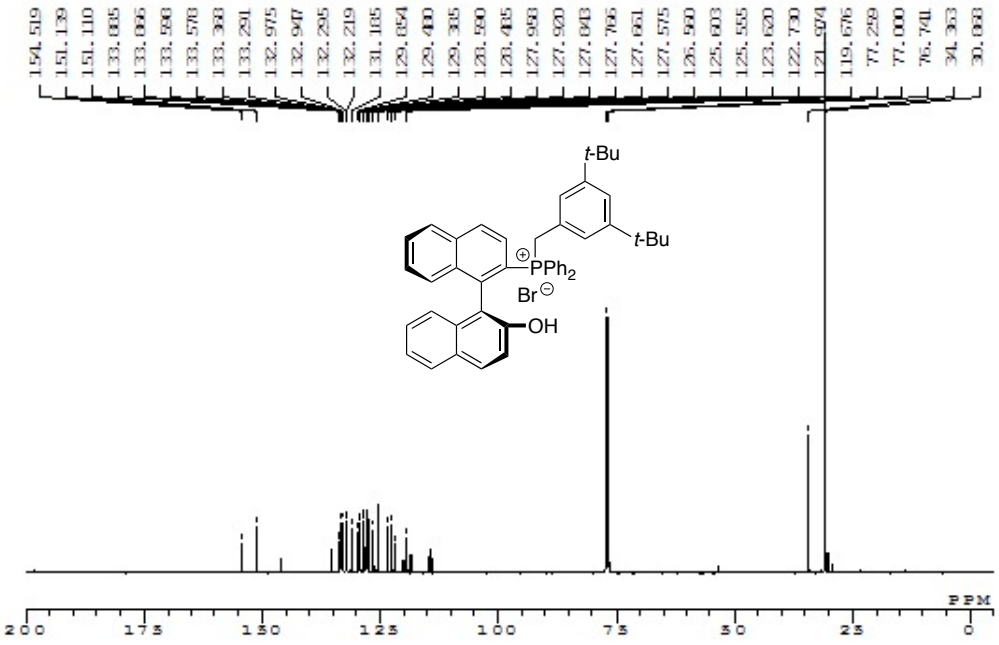
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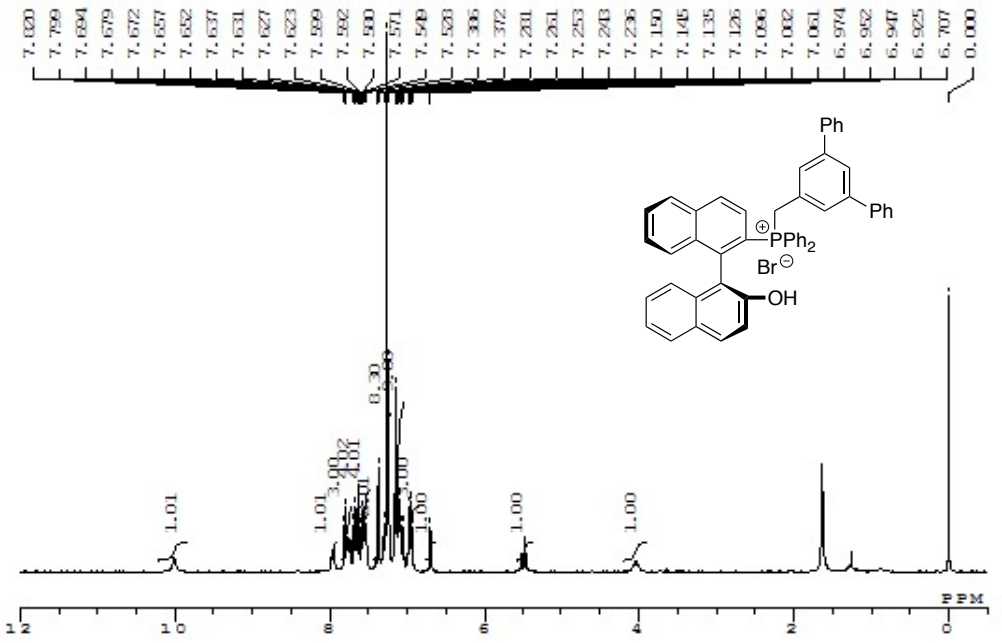
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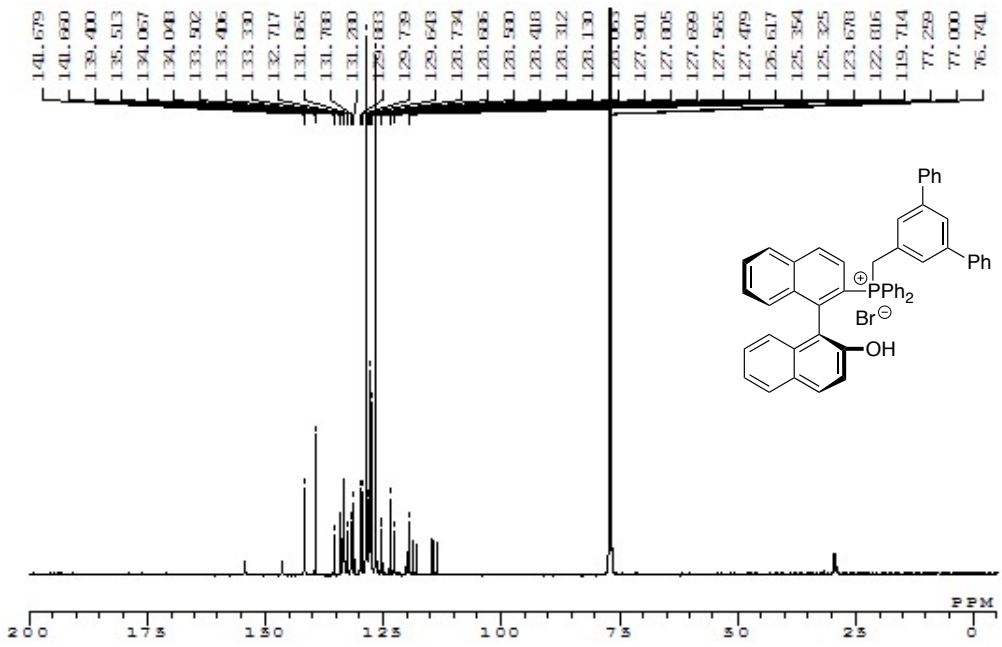
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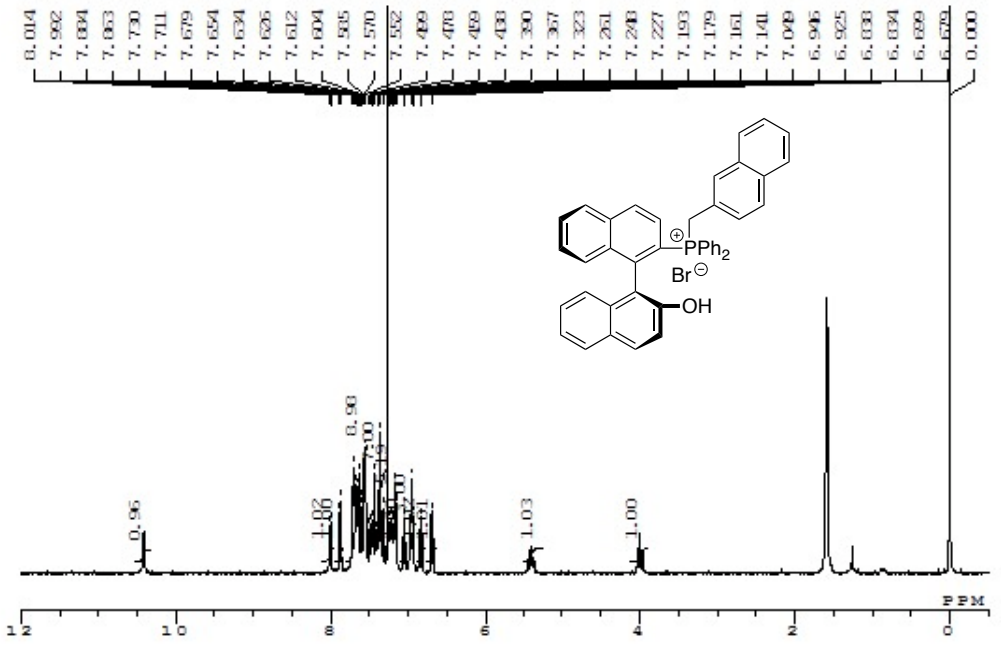
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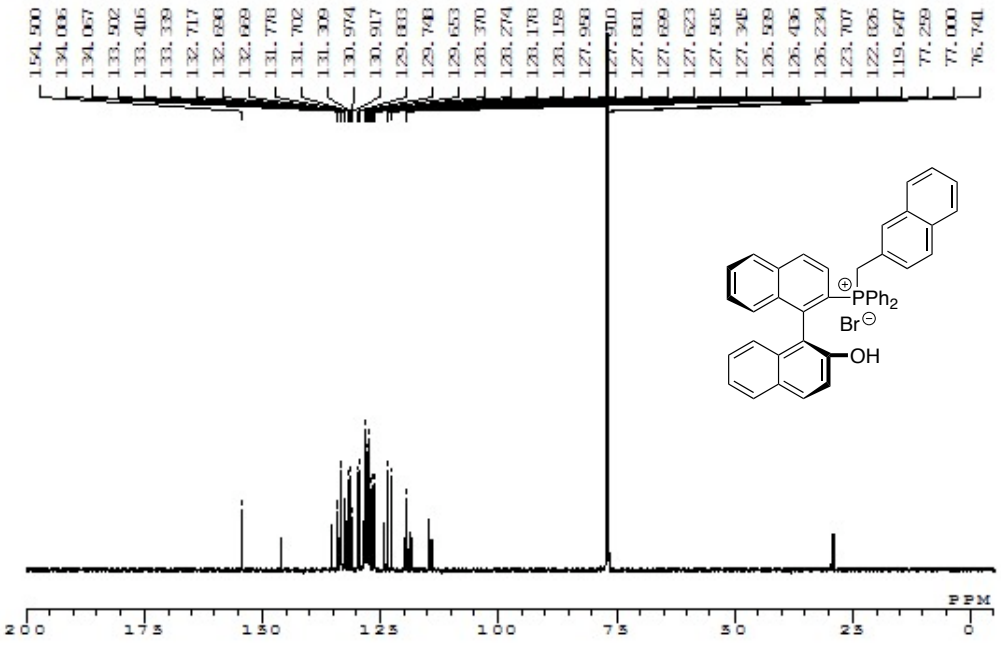
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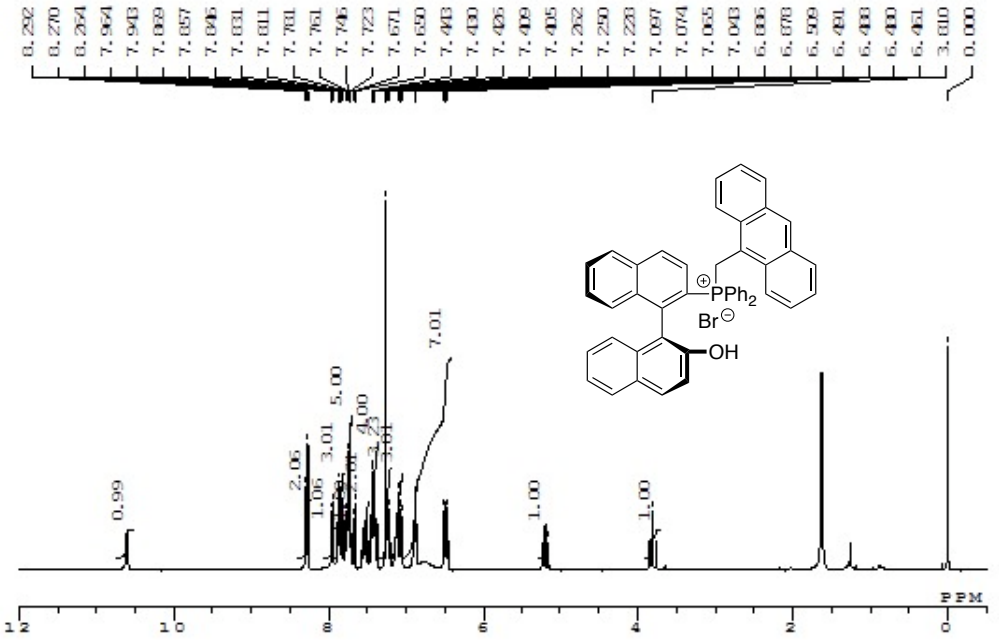
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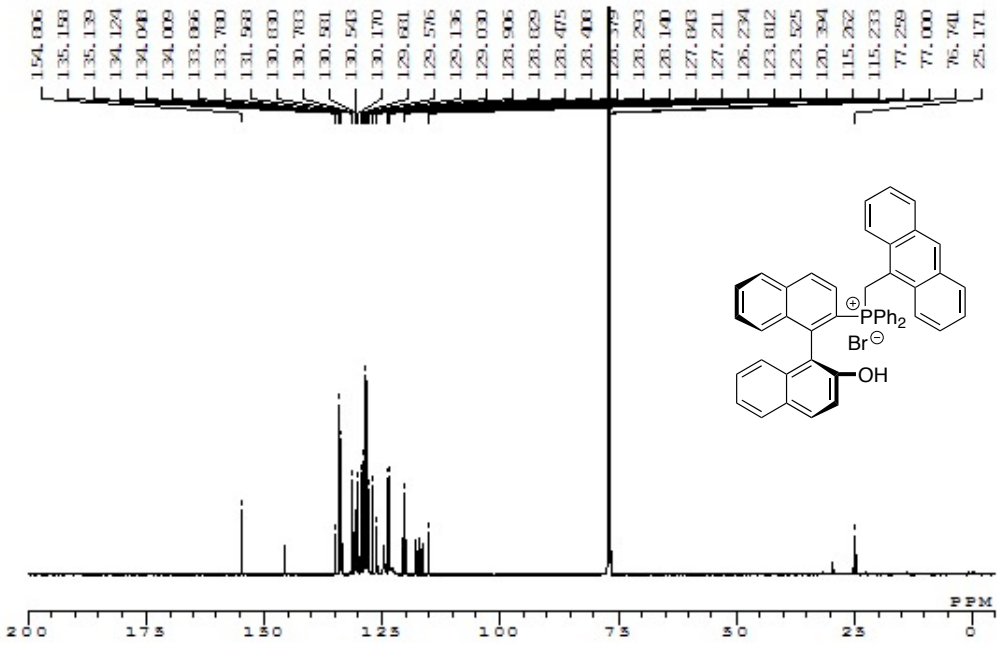
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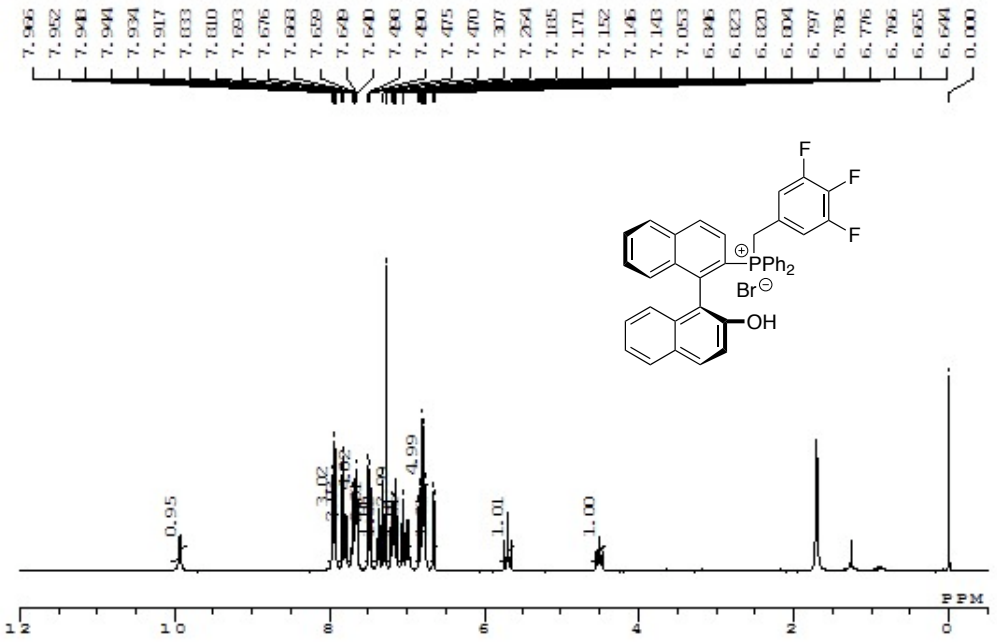
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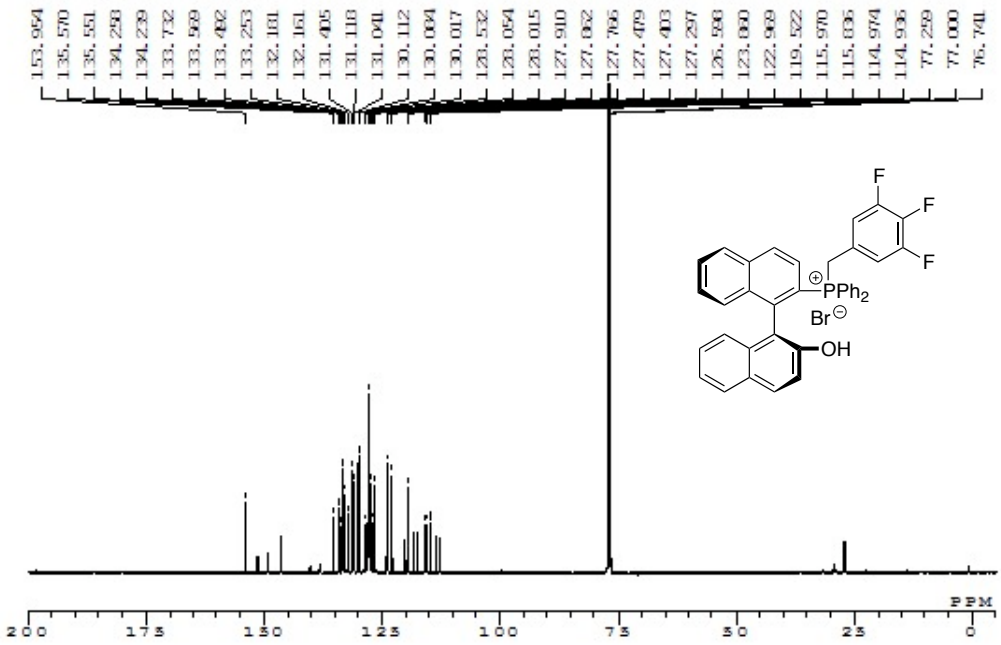
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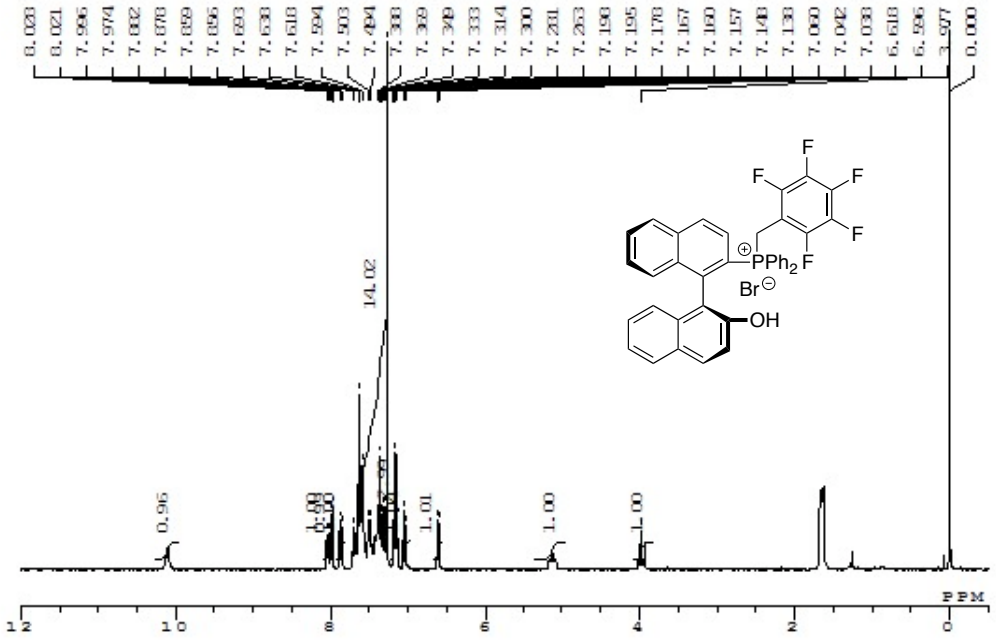
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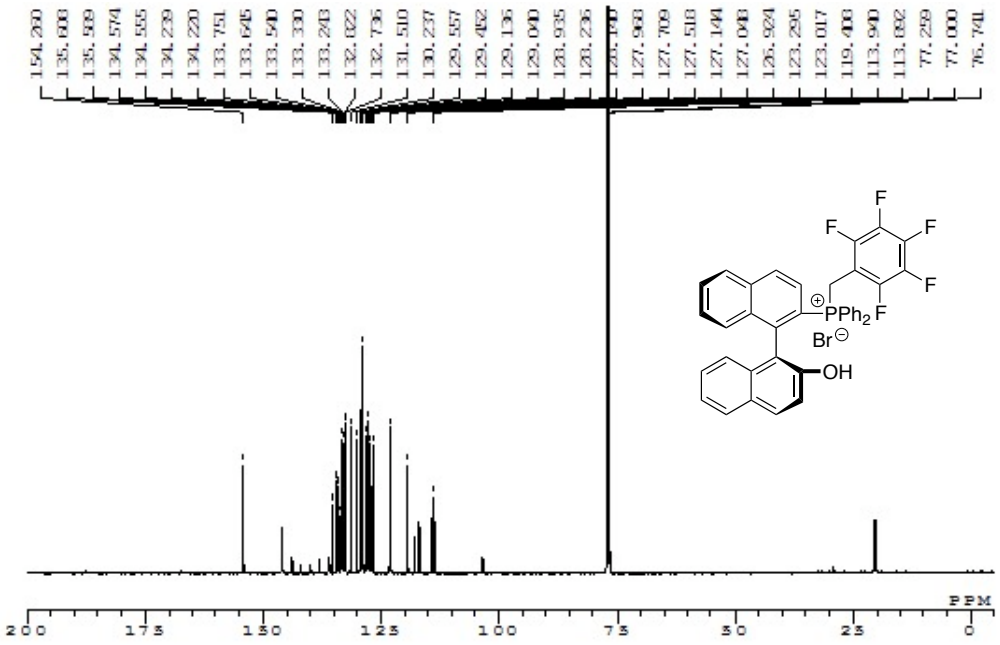
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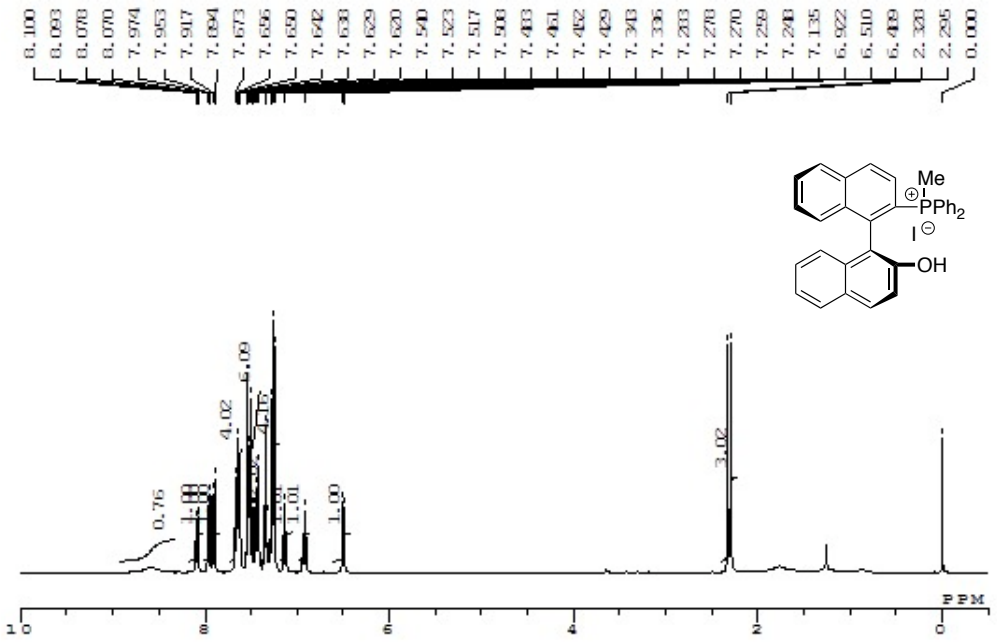
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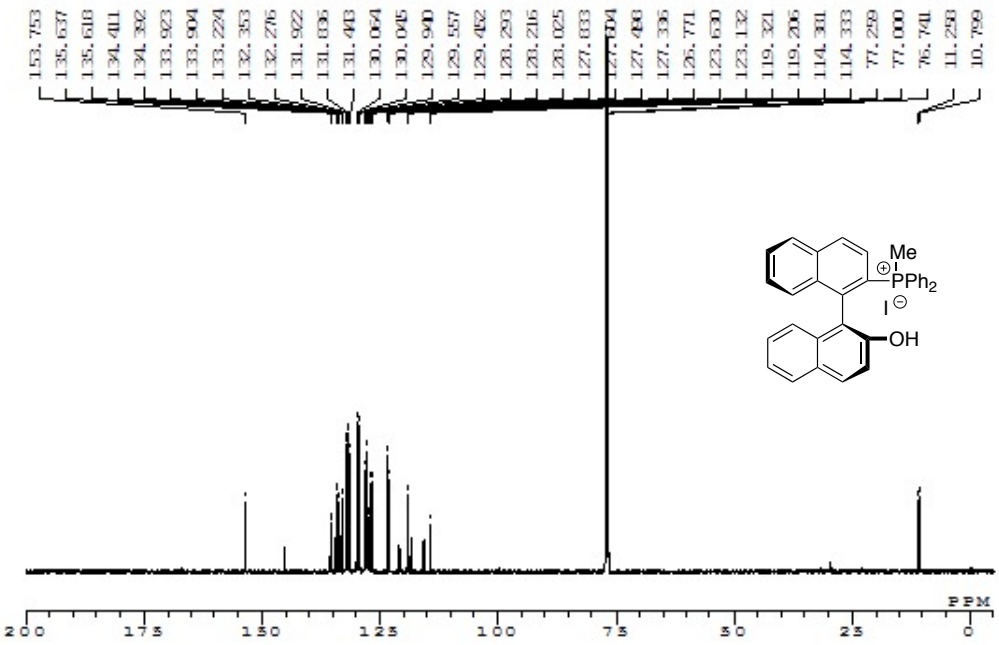
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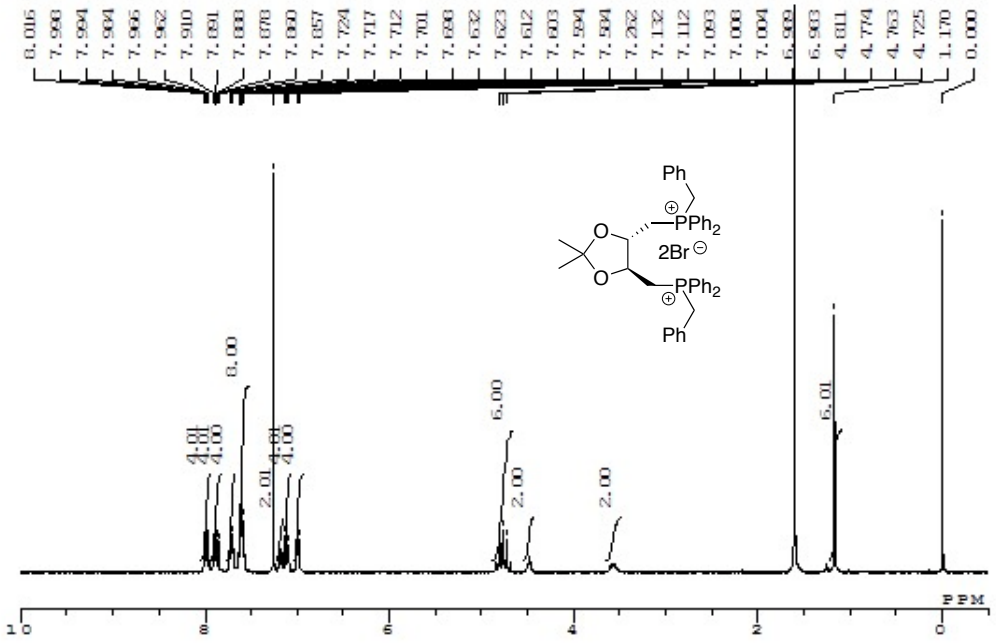
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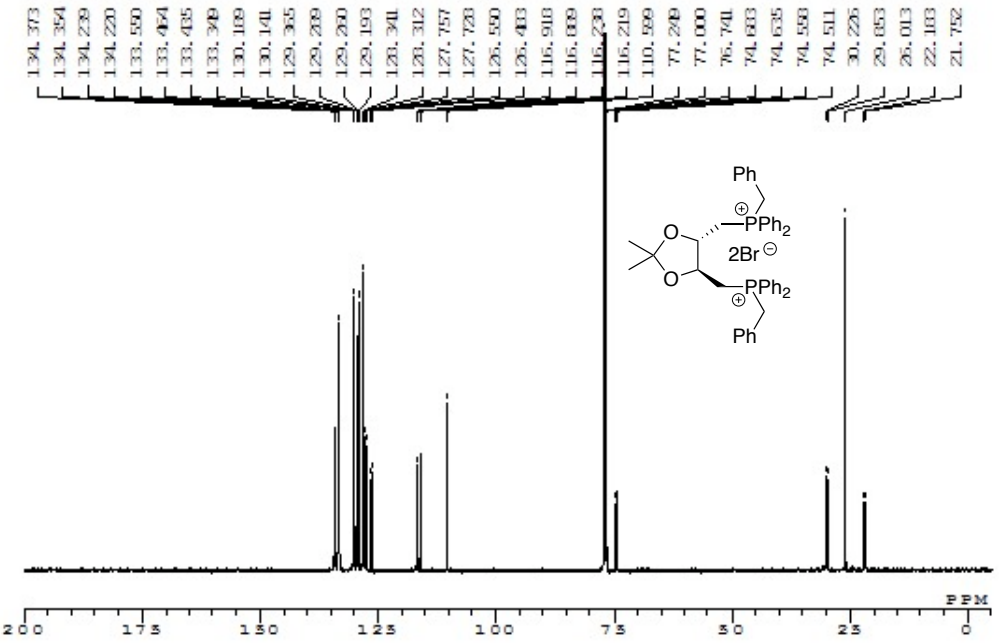
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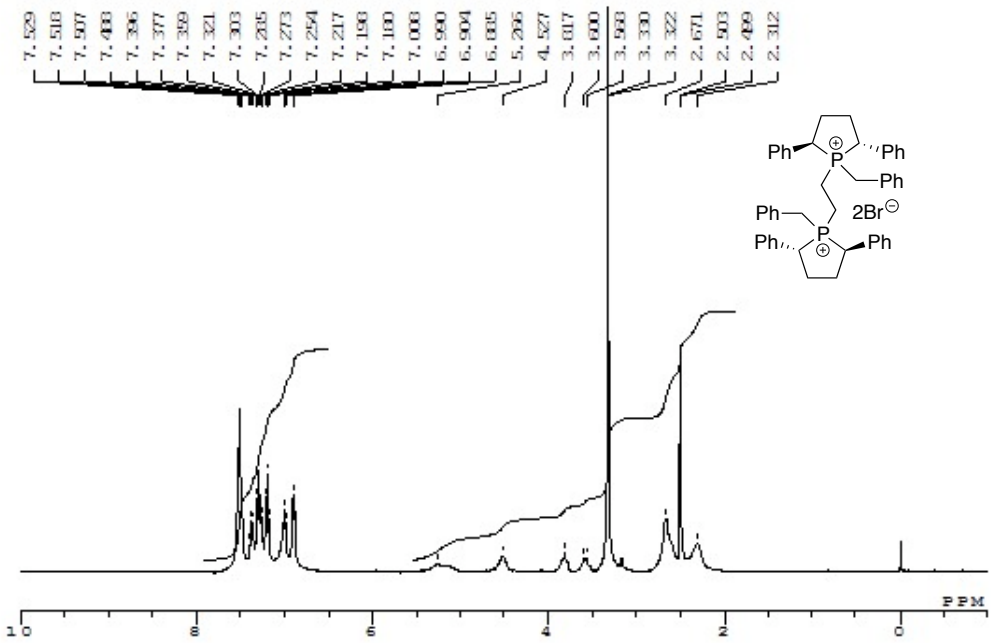
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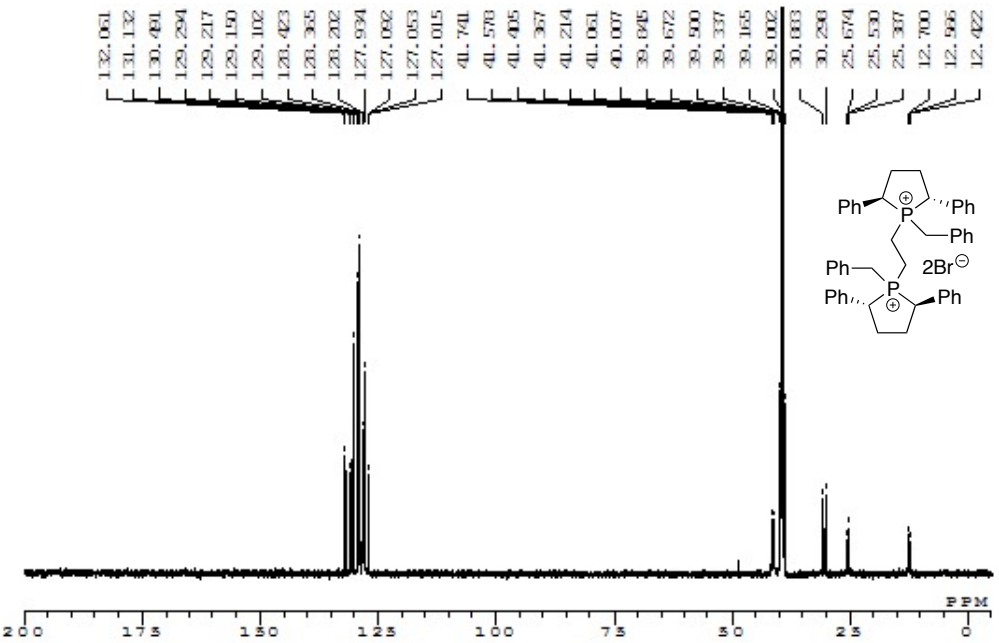
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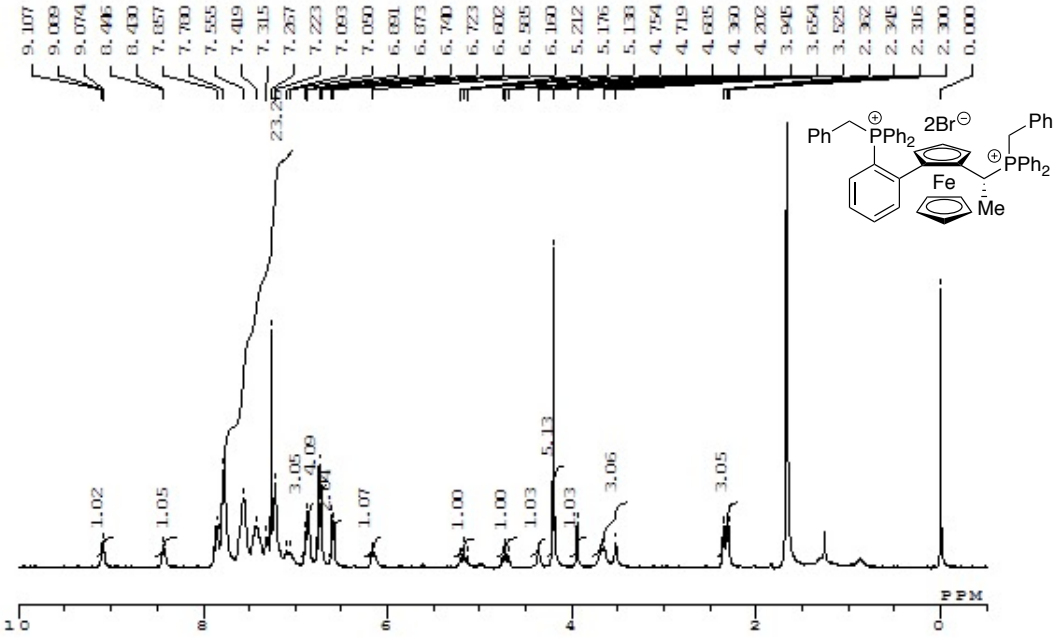
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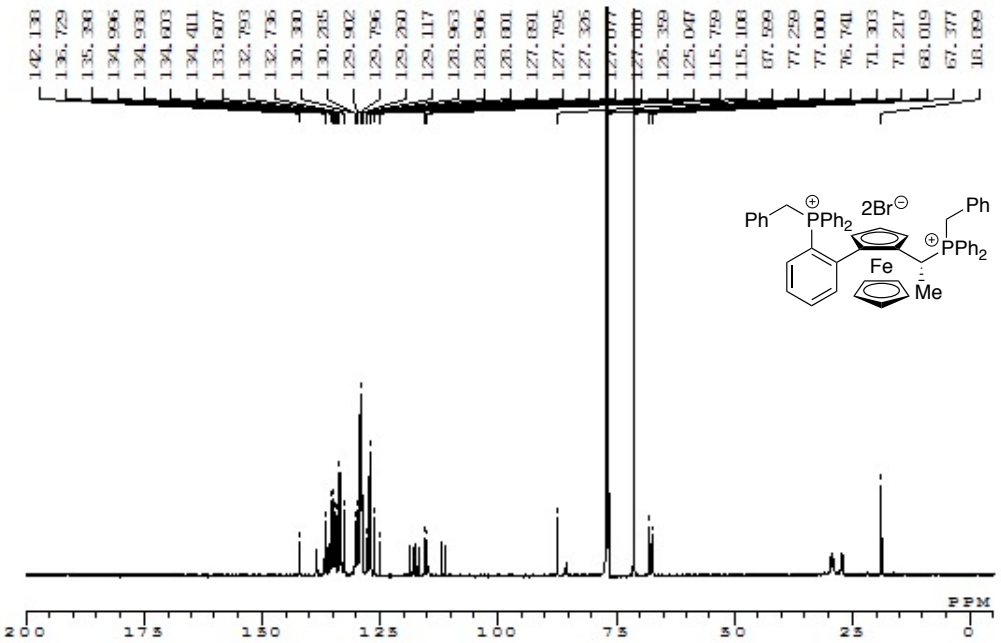
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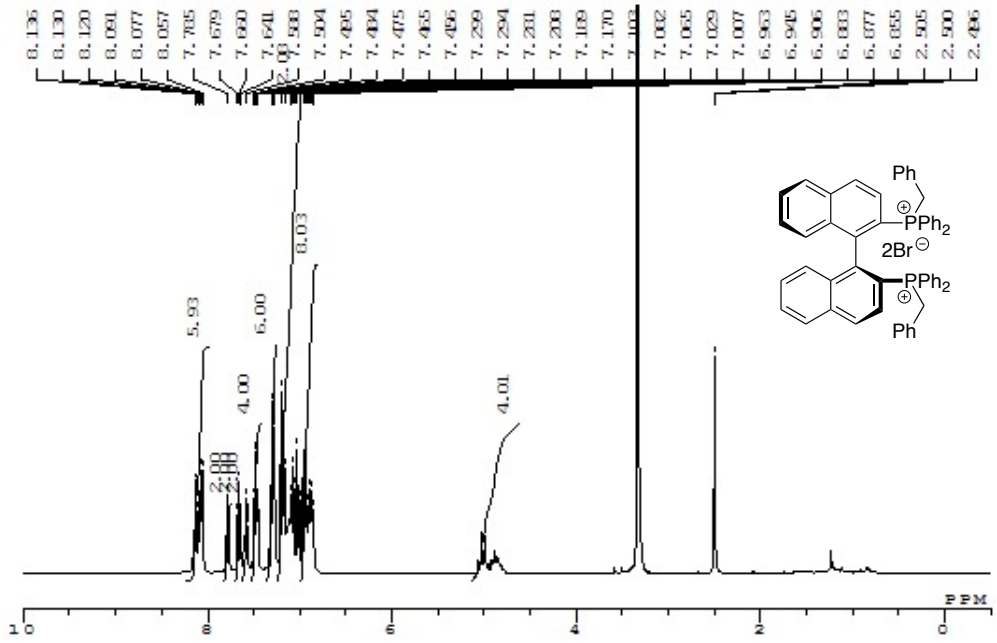
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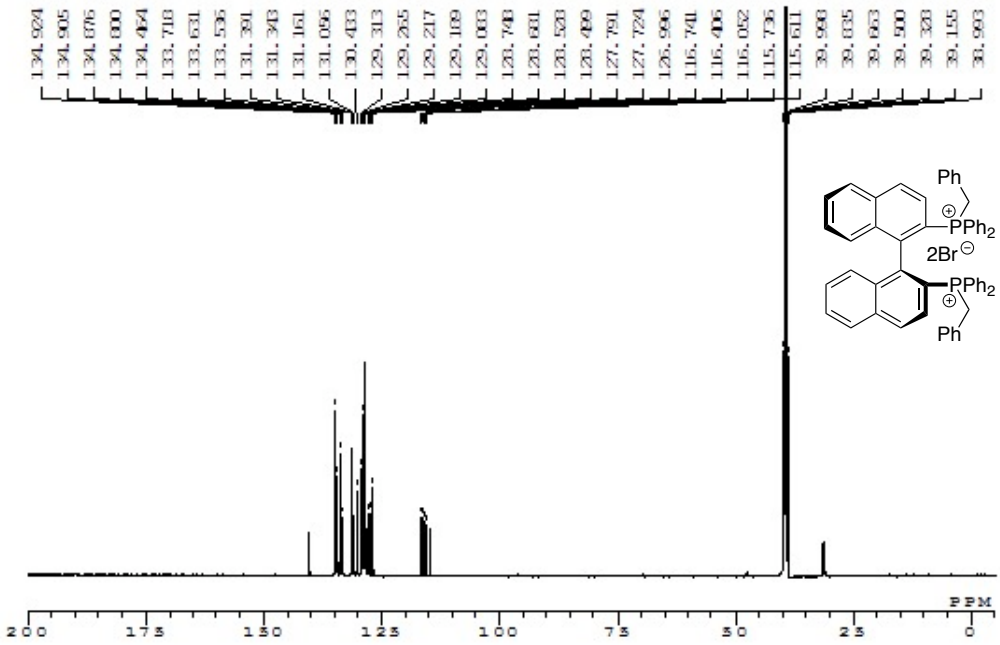
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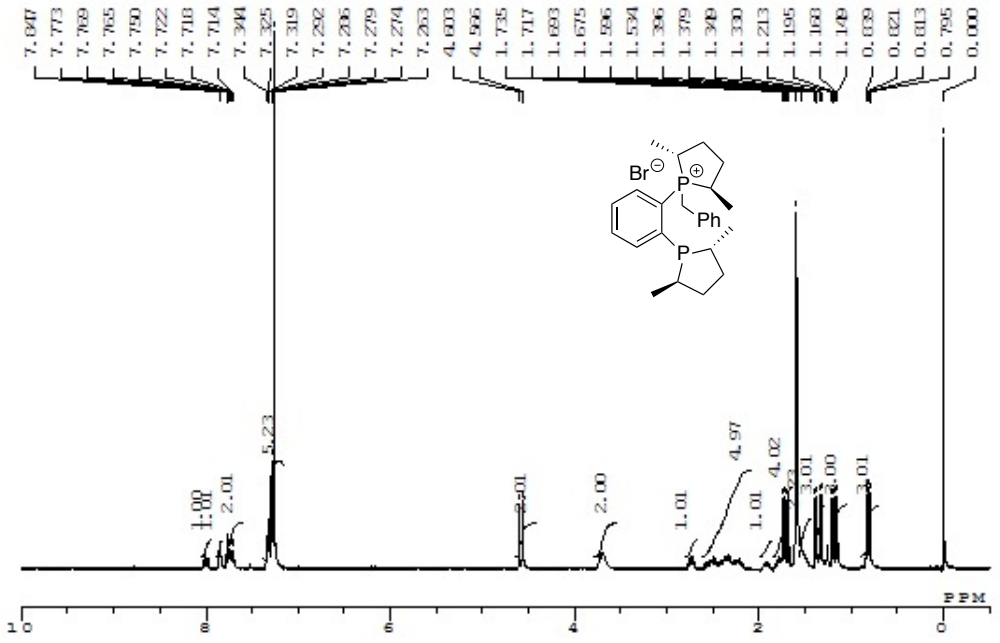
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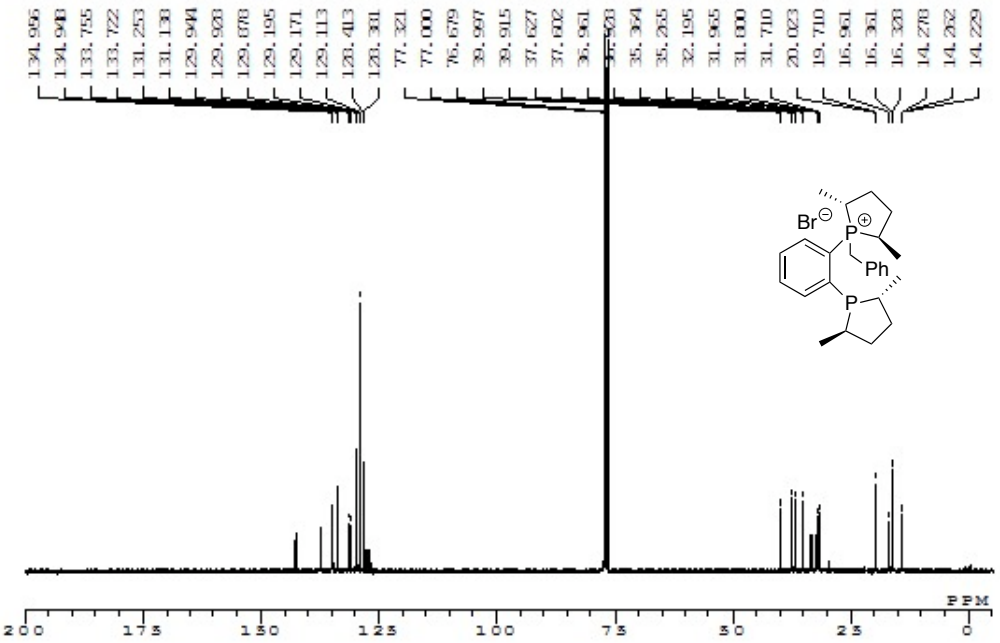
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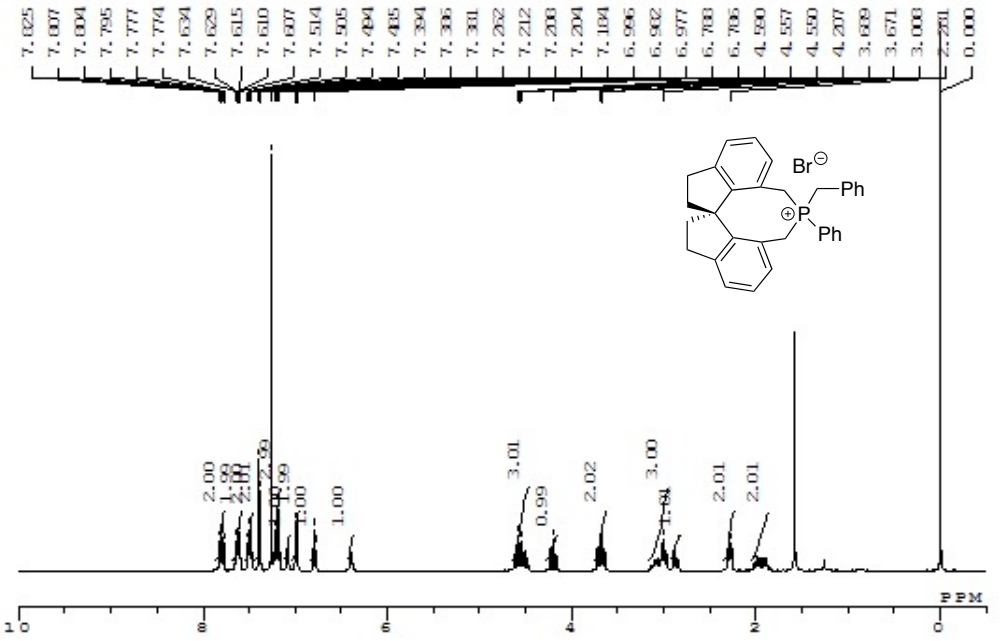
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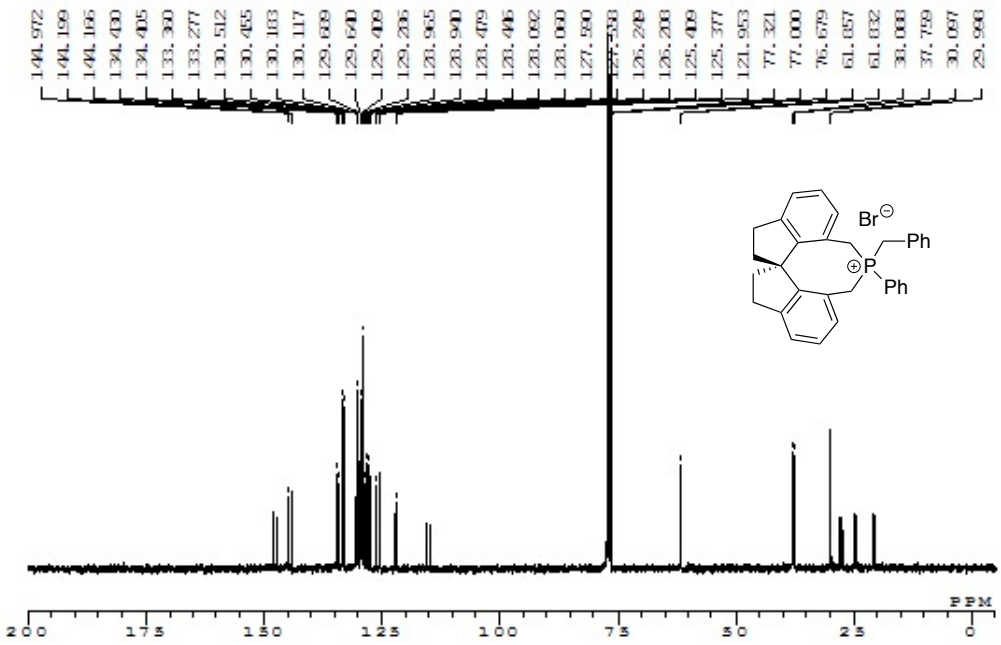
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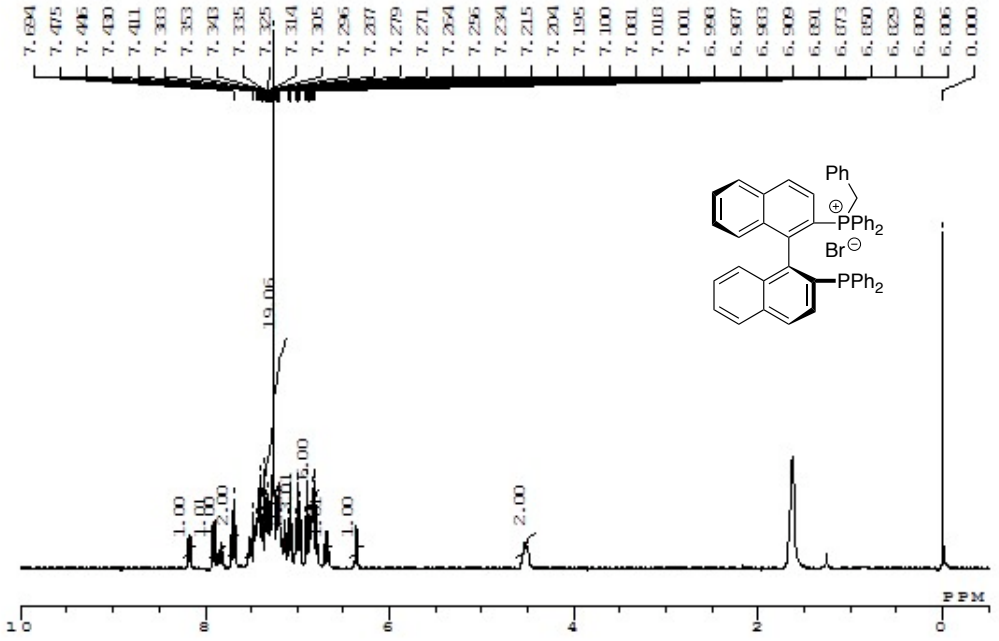
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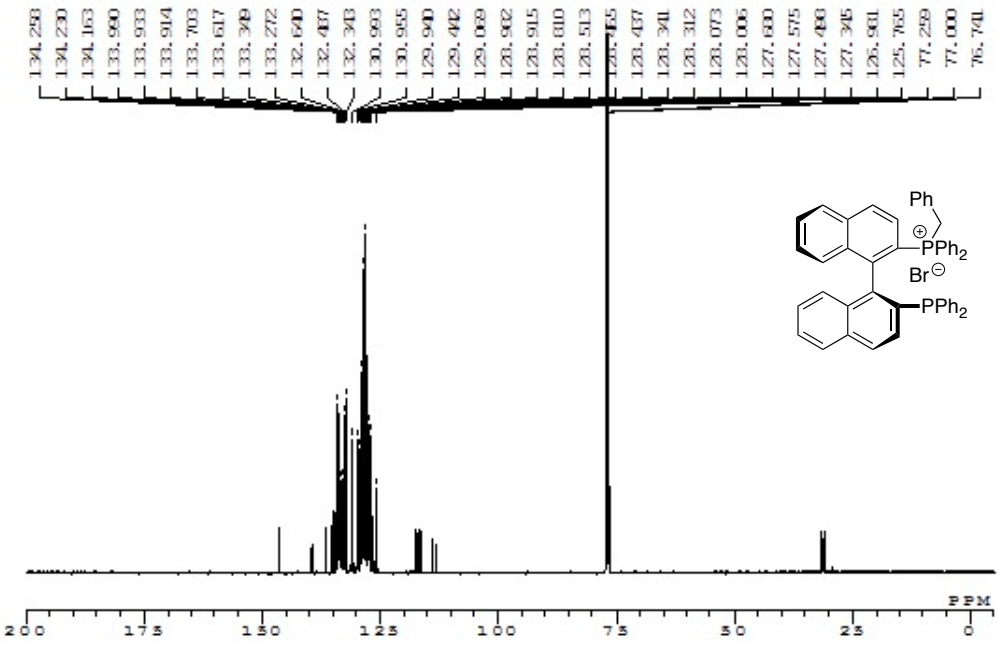
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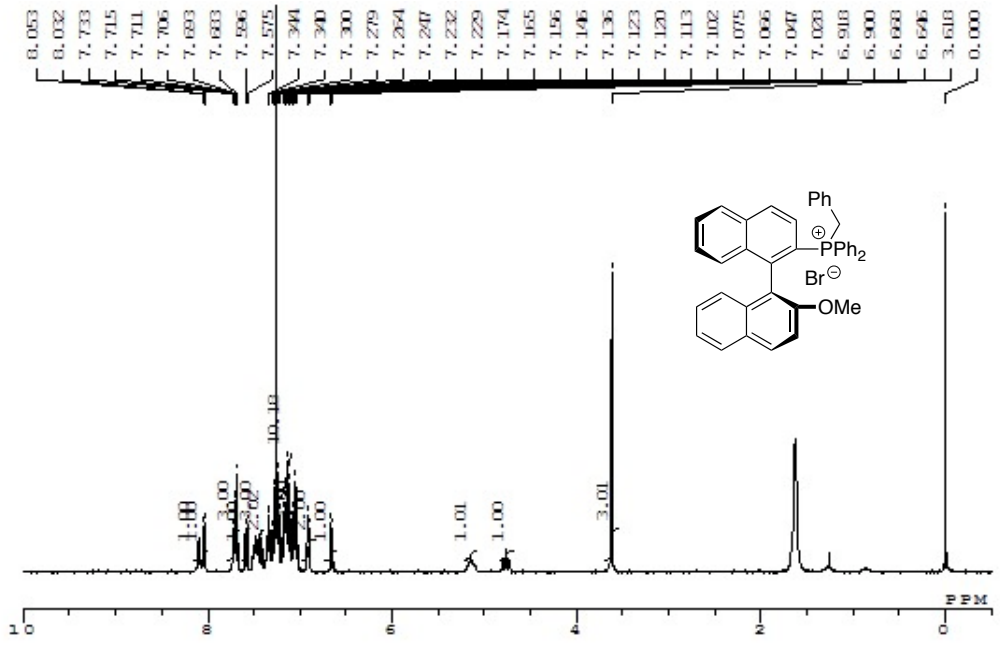
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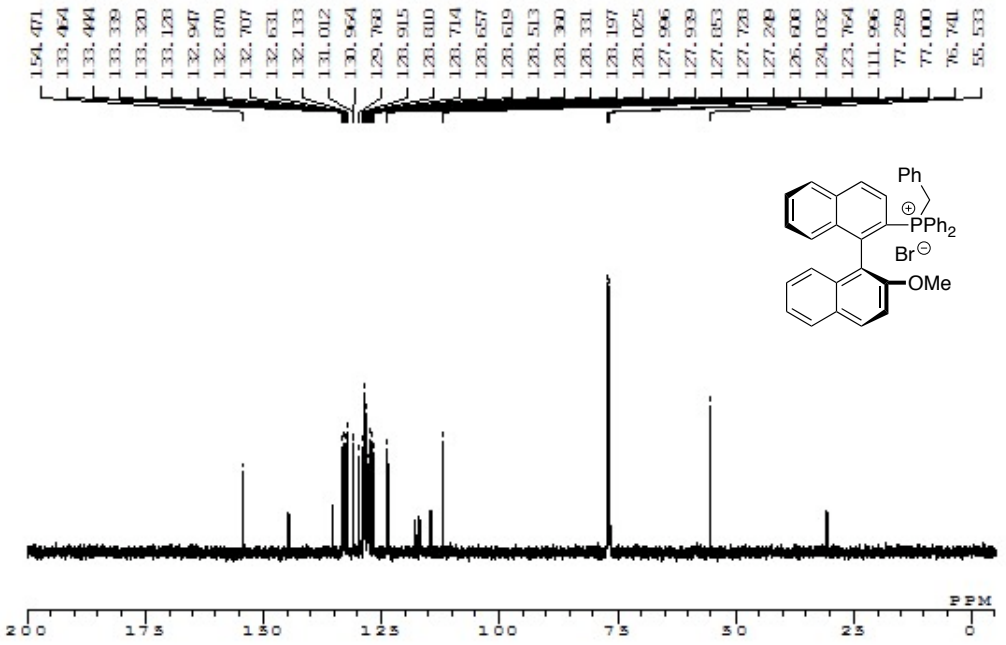
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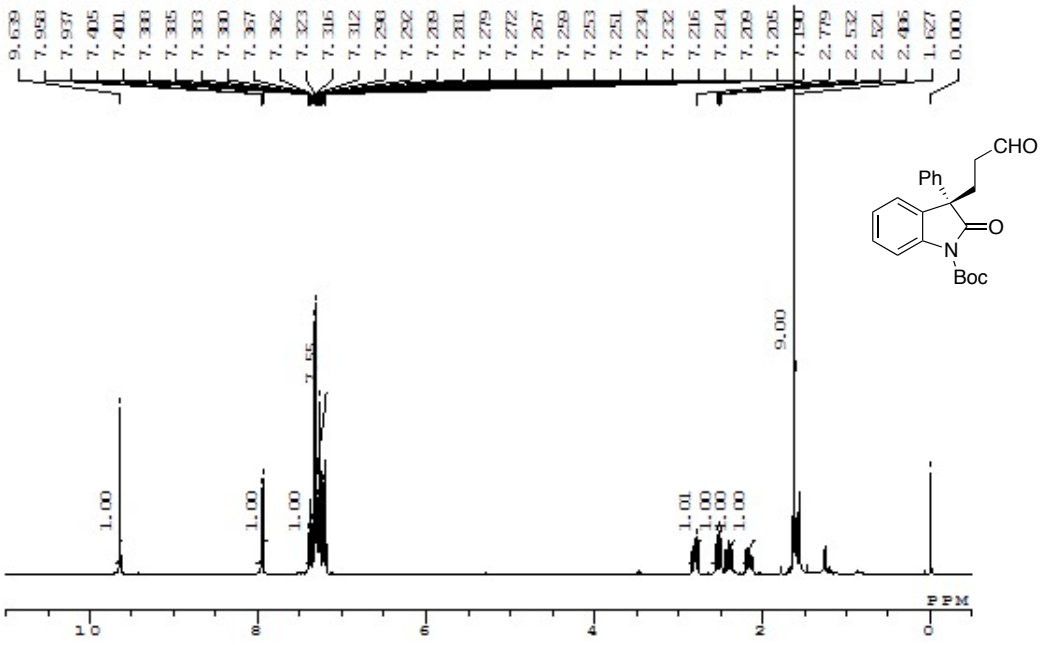
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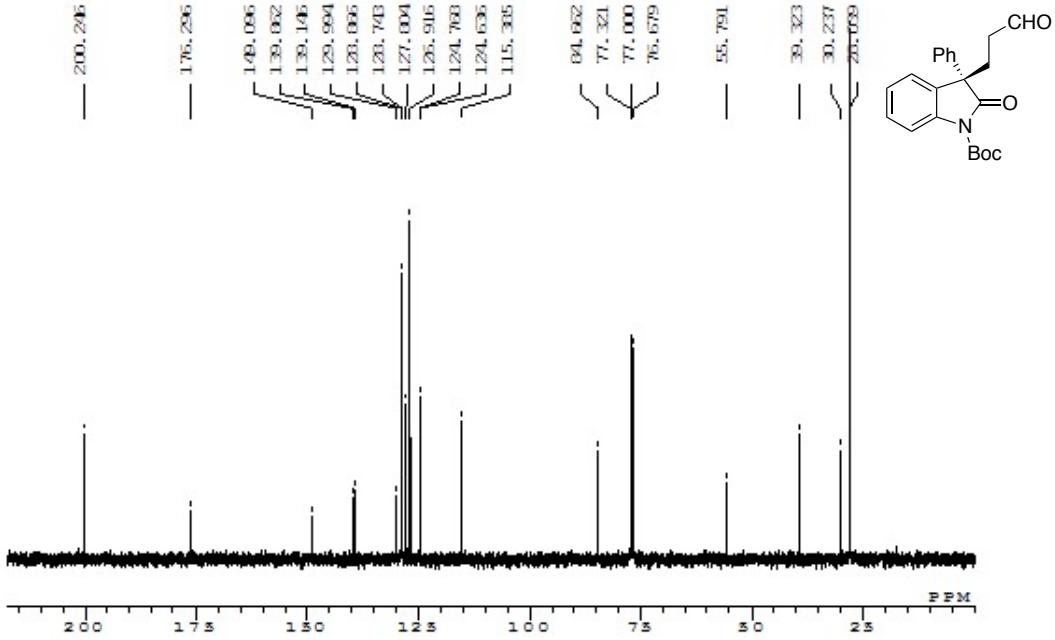
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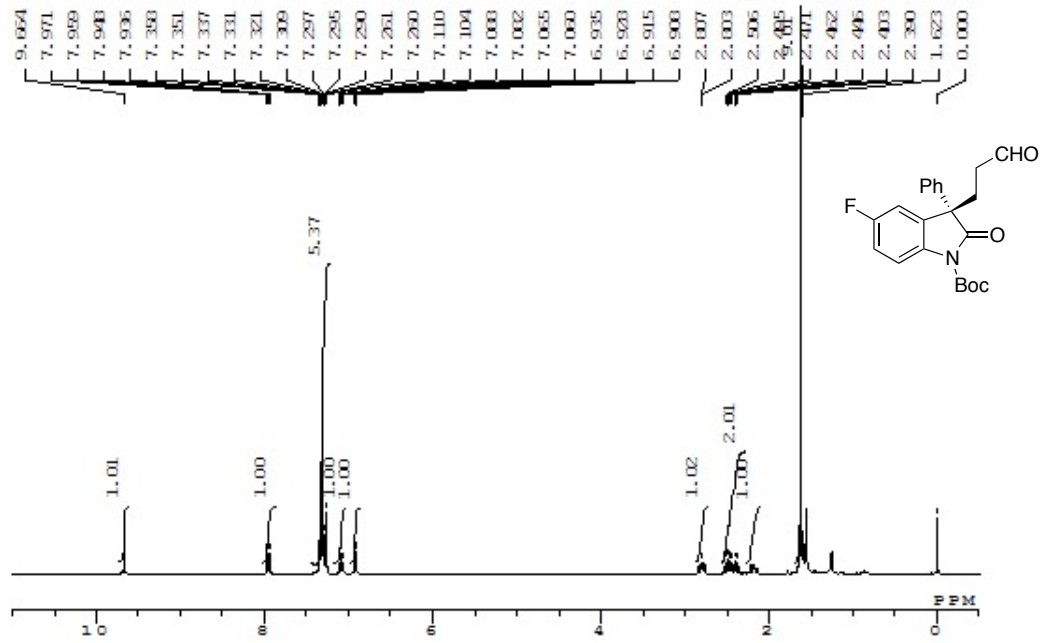
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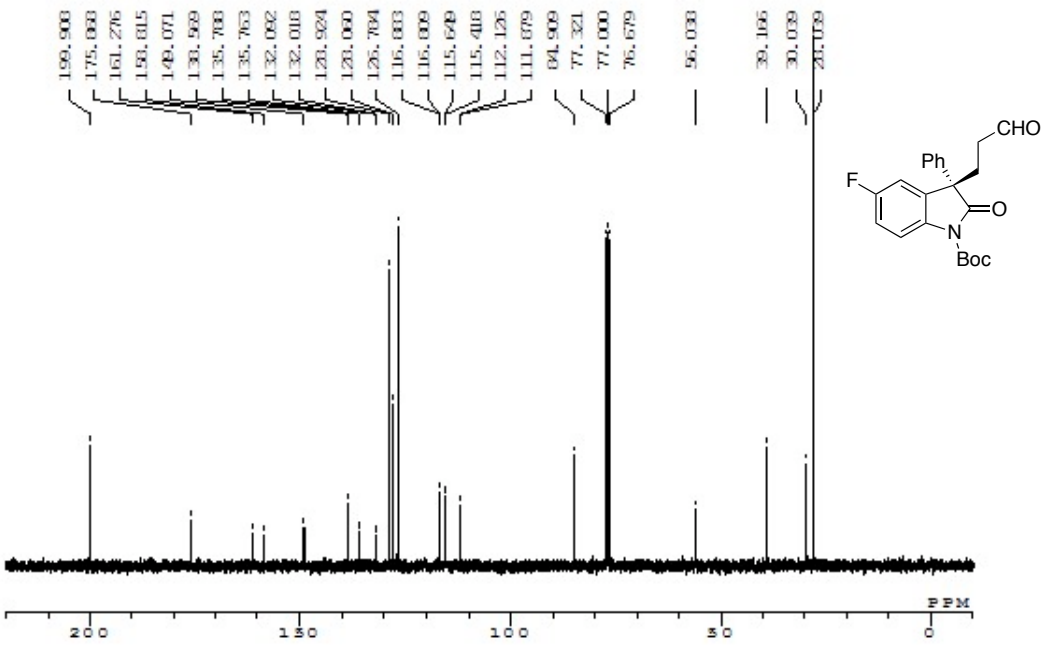
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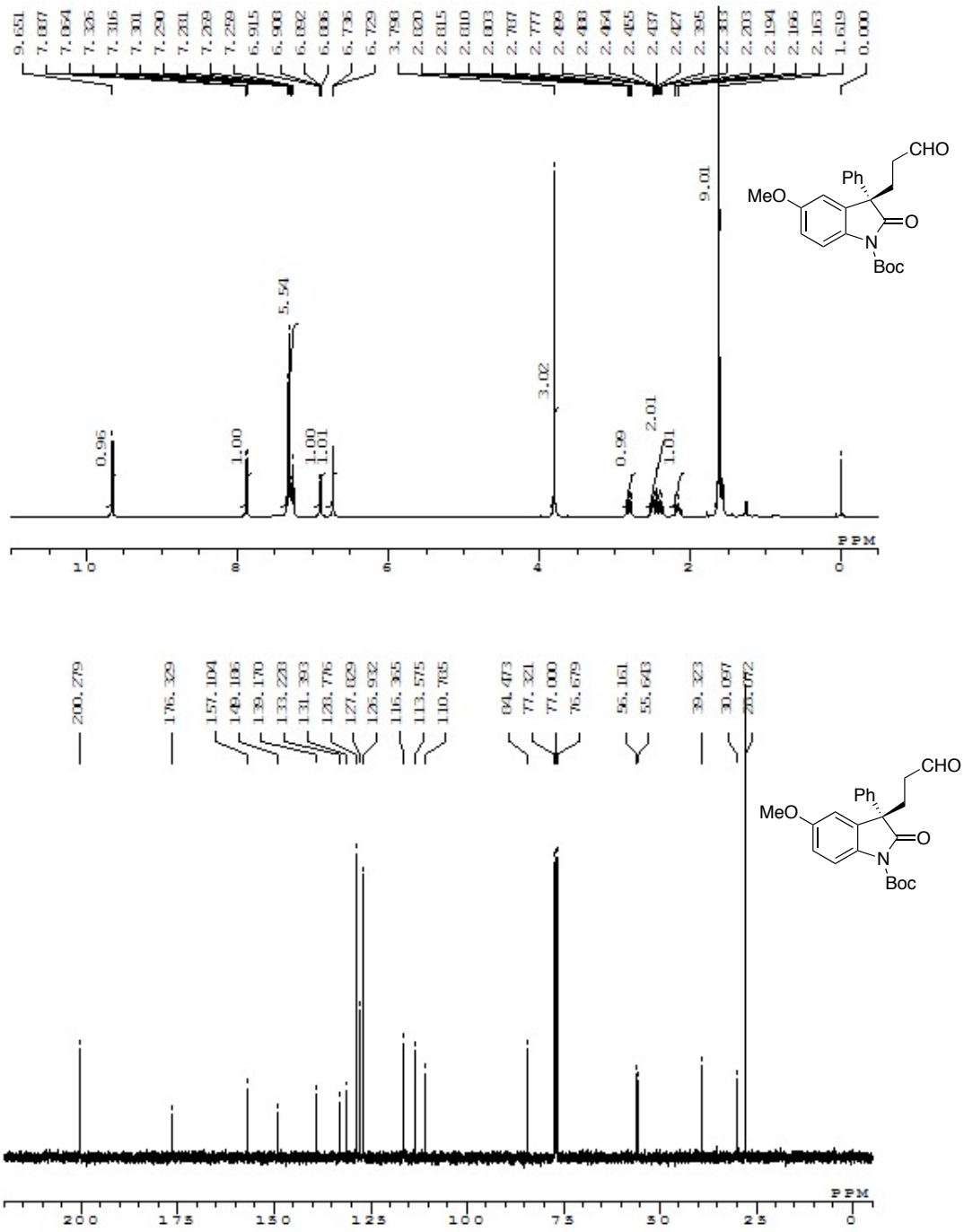
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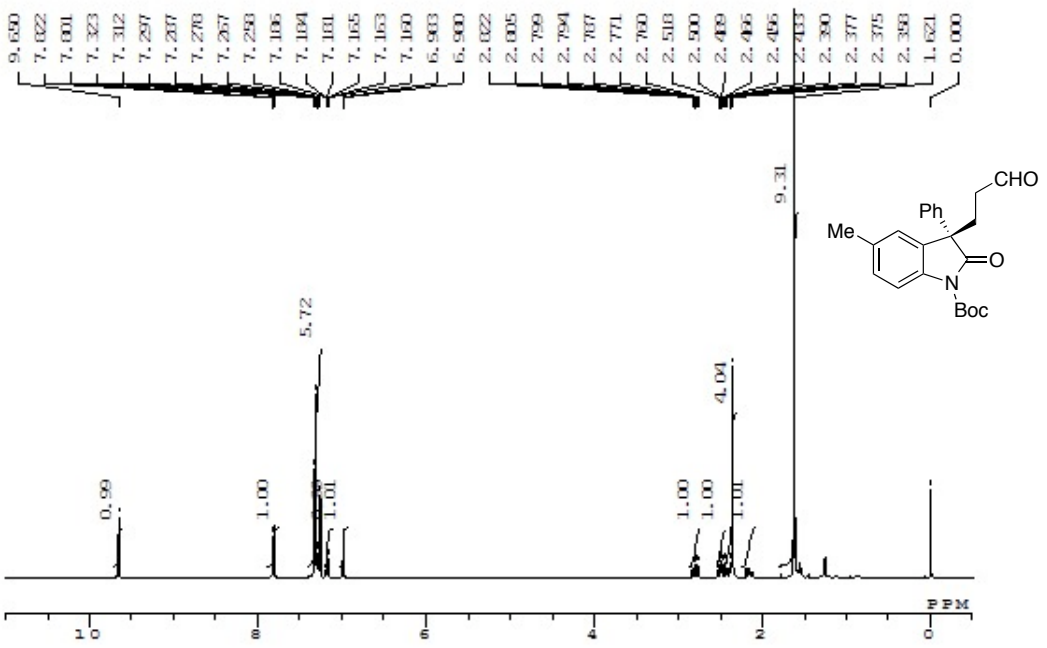

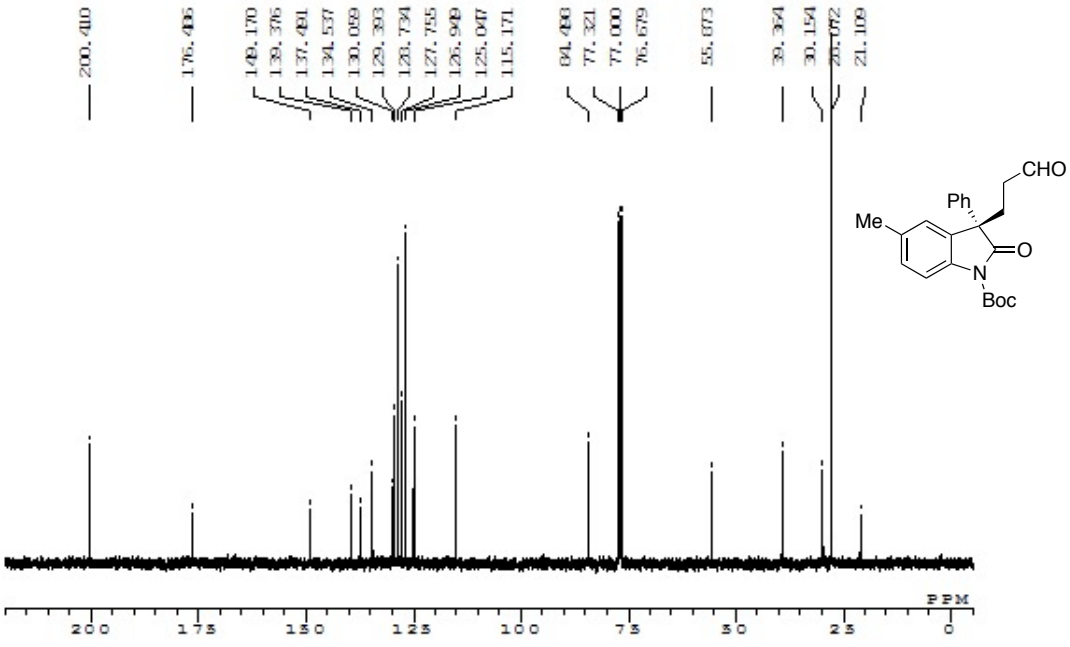

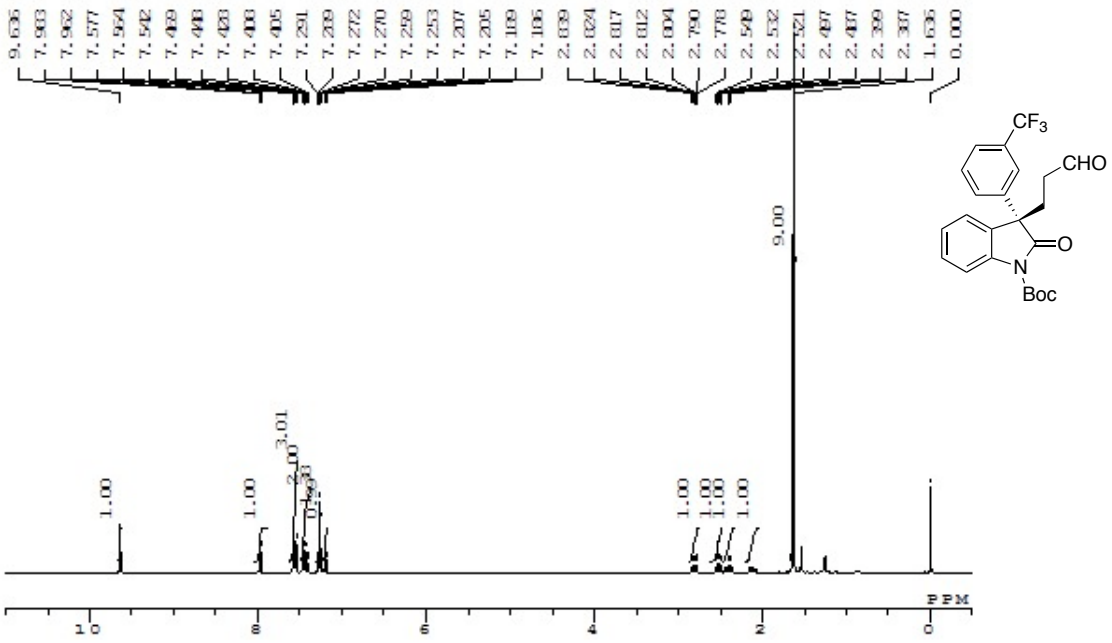
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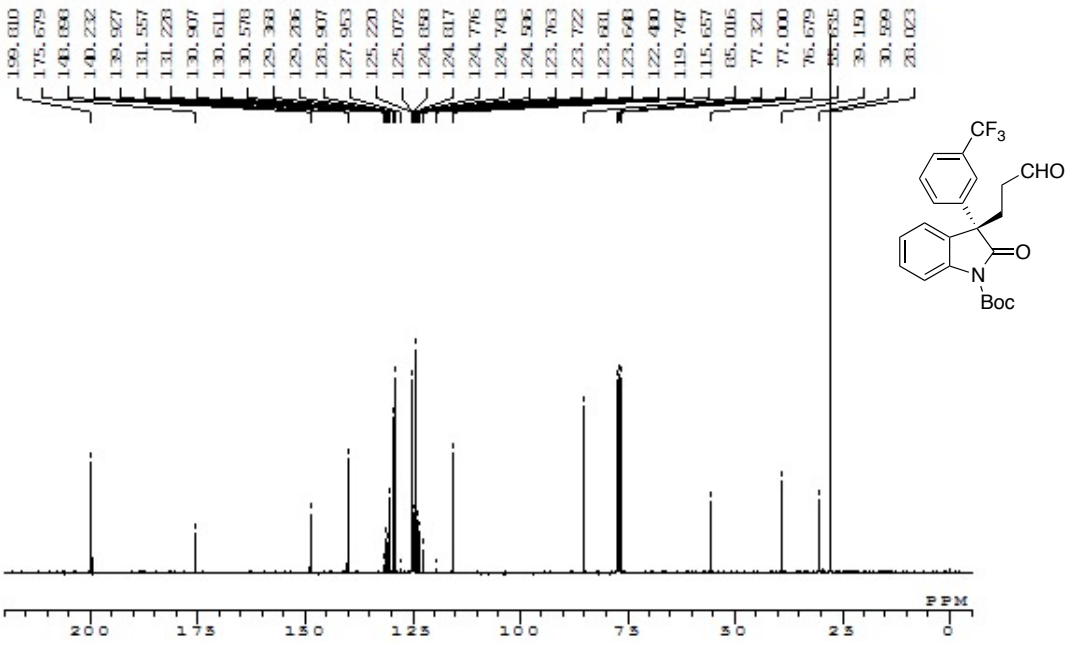
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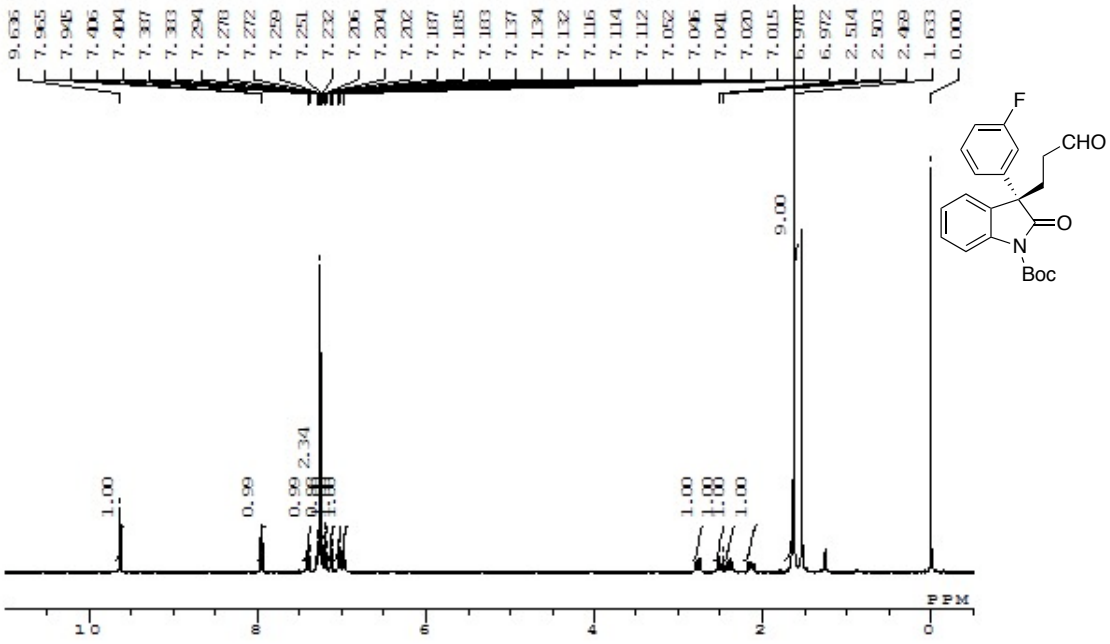
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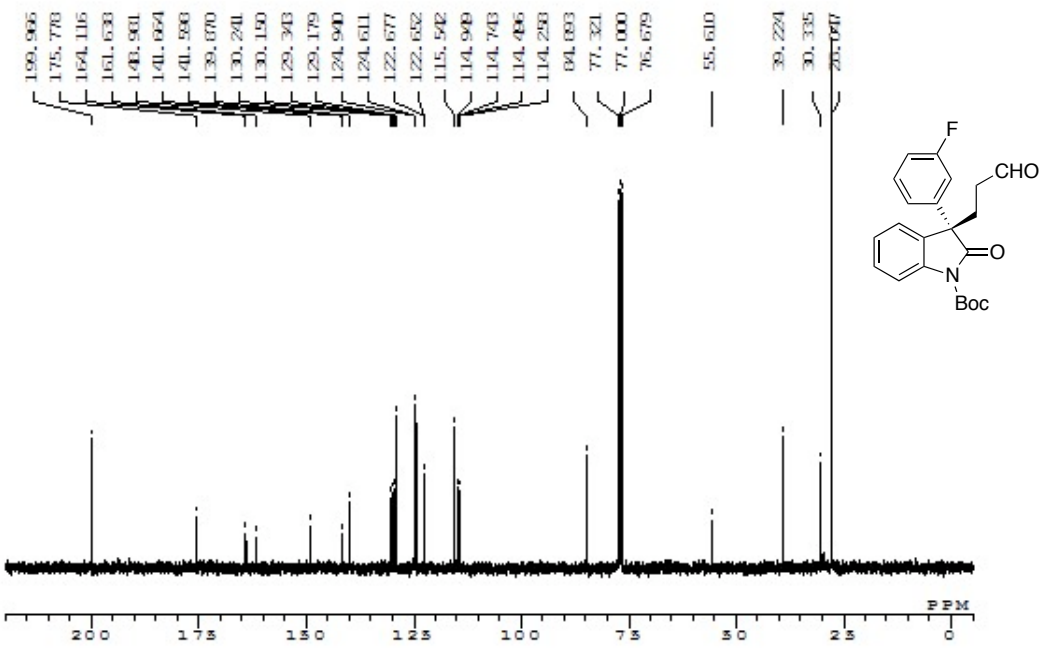
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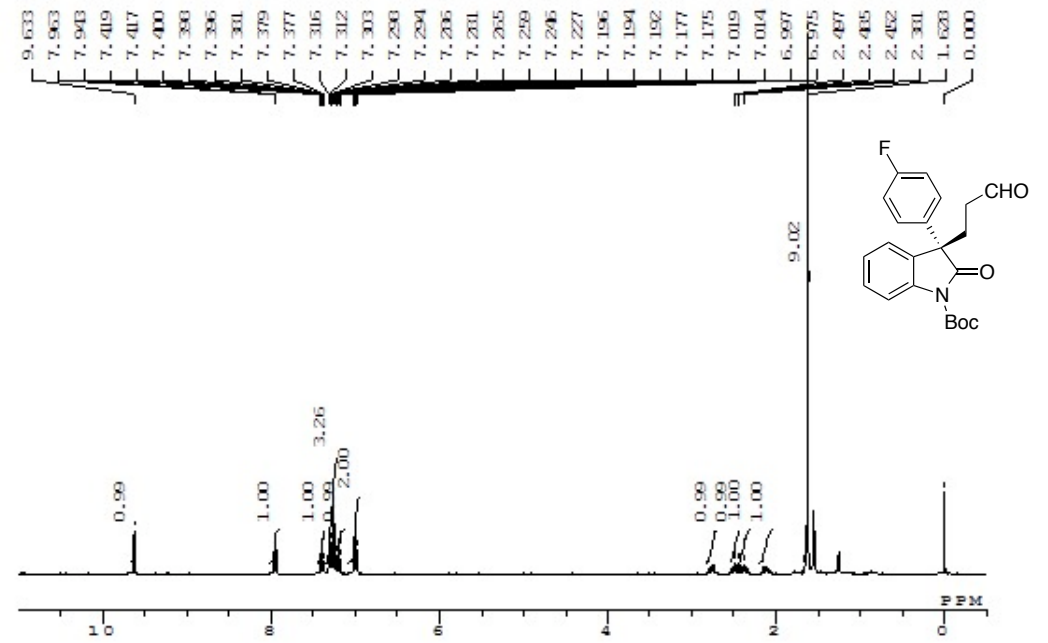

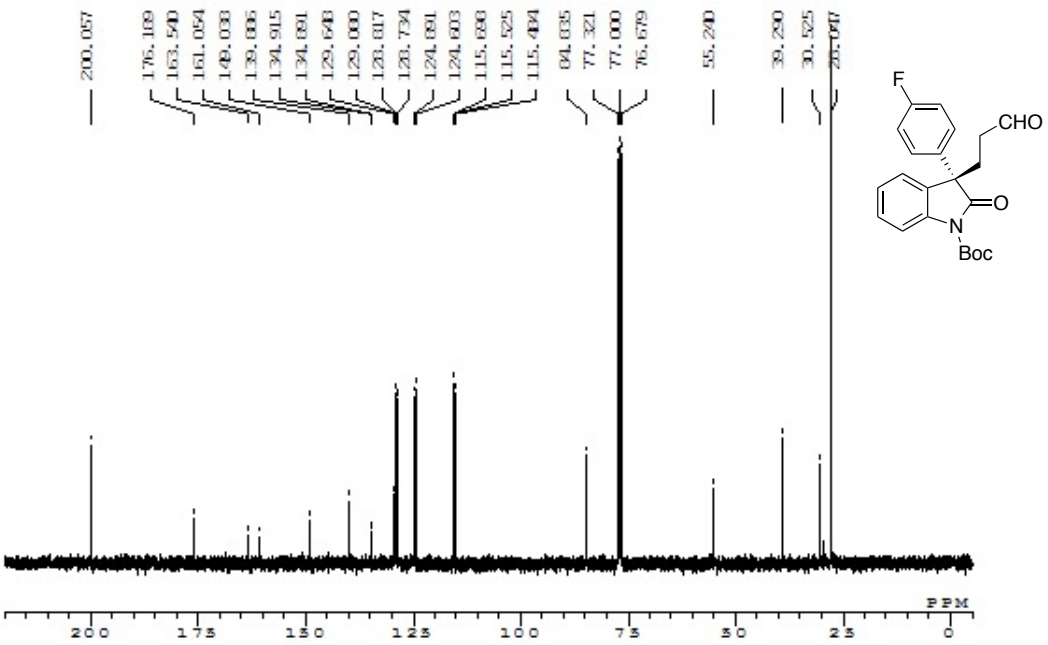

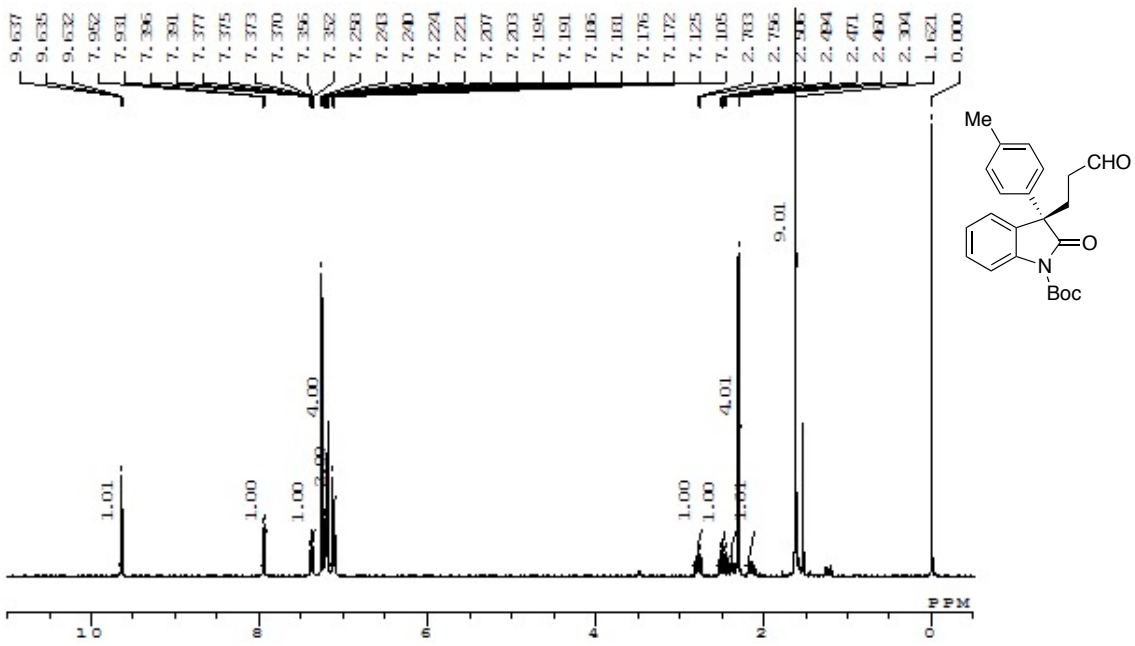
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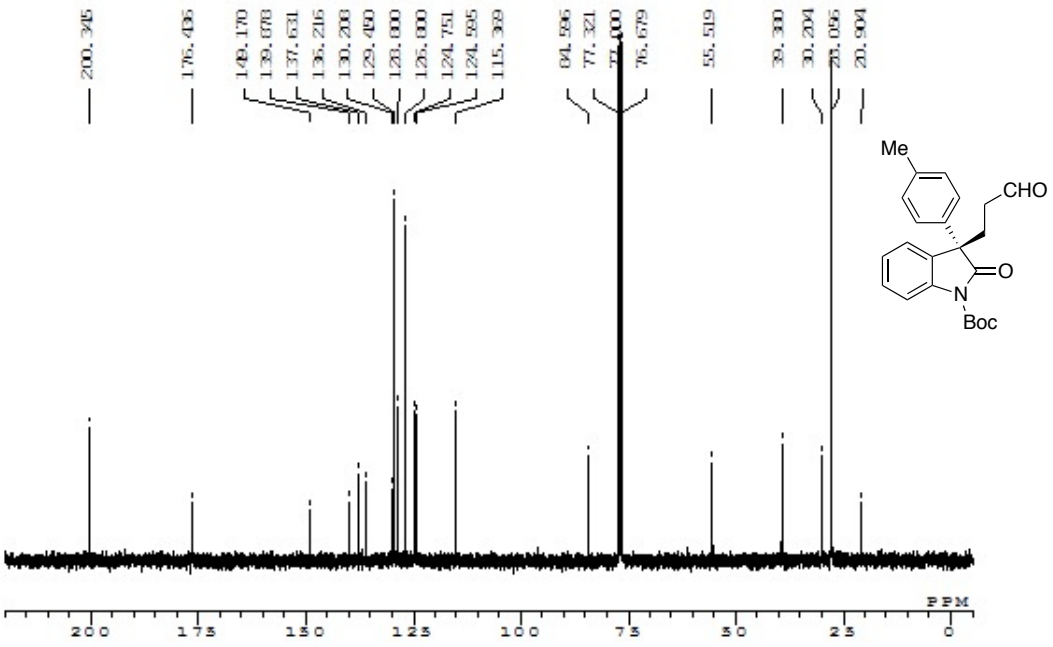
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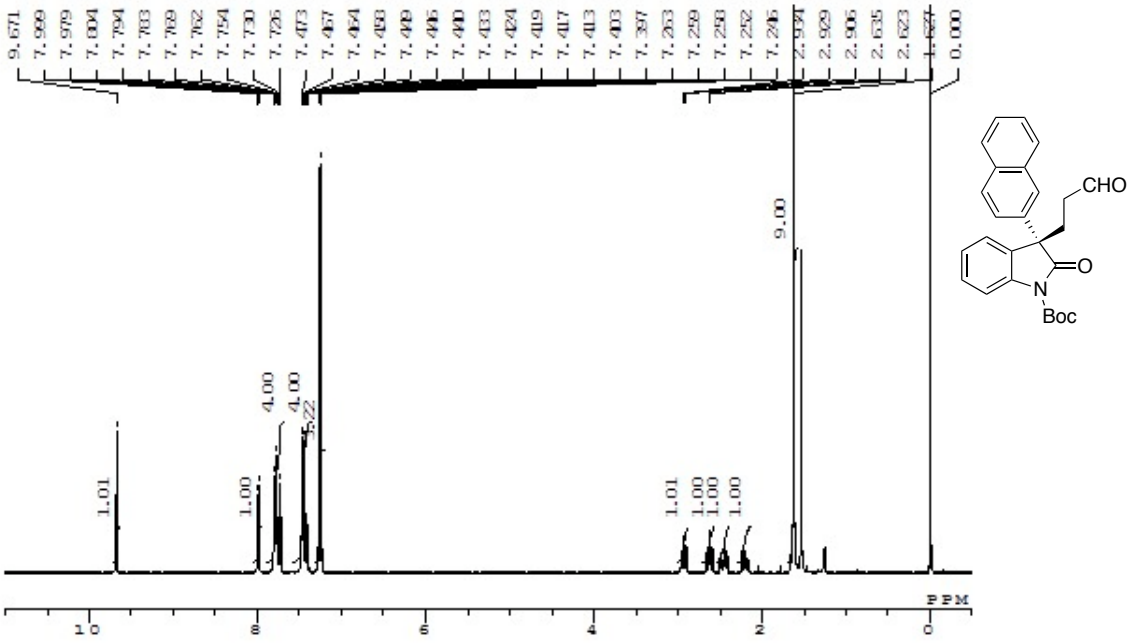
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7.979
7.804
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7.457
7.454
7.453
7.449
7.445
7.440
7.433
7.424
7.419
7.417
7.413
7.403
7.397
7.263
7.259
7.258
7.252
7.245
2.934
2.929
2.906
2.635
2.623
1.627
0.000
1.01
1.00
4.00
4.00
5.22
1.01
1.00
1.00
1.00
9.00
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Boc
PPM
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6
4
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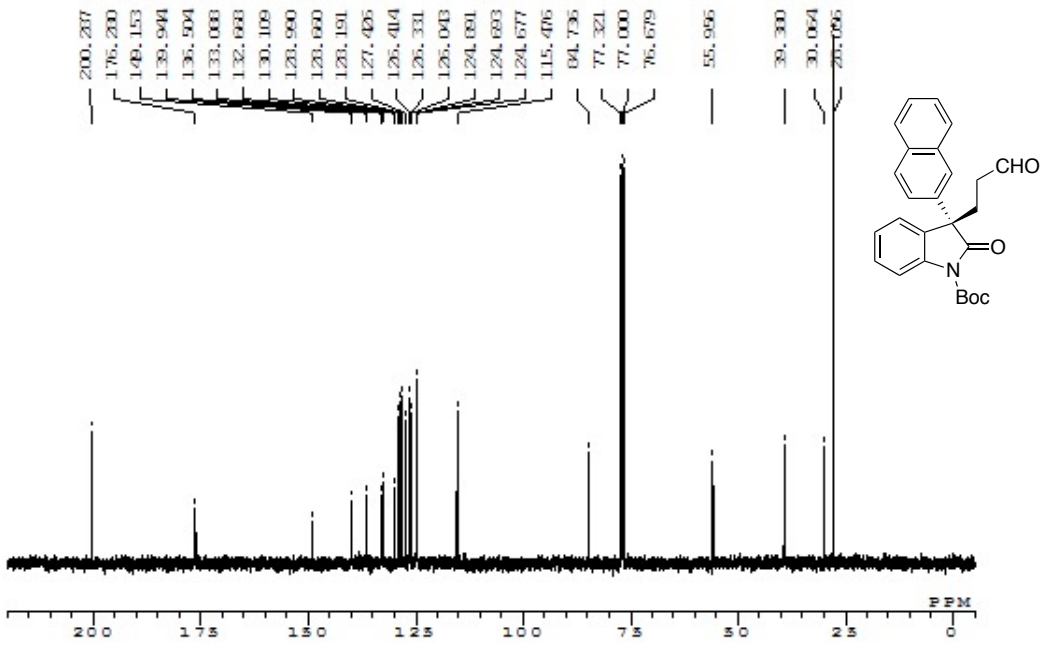
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130.109
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127.495
126.414
126.331
126.043
124.891
124.693
124.677
115.496
84.736
77.321
77.000
76.679
55.996
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28.196
CHO
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N
Boc
PPM
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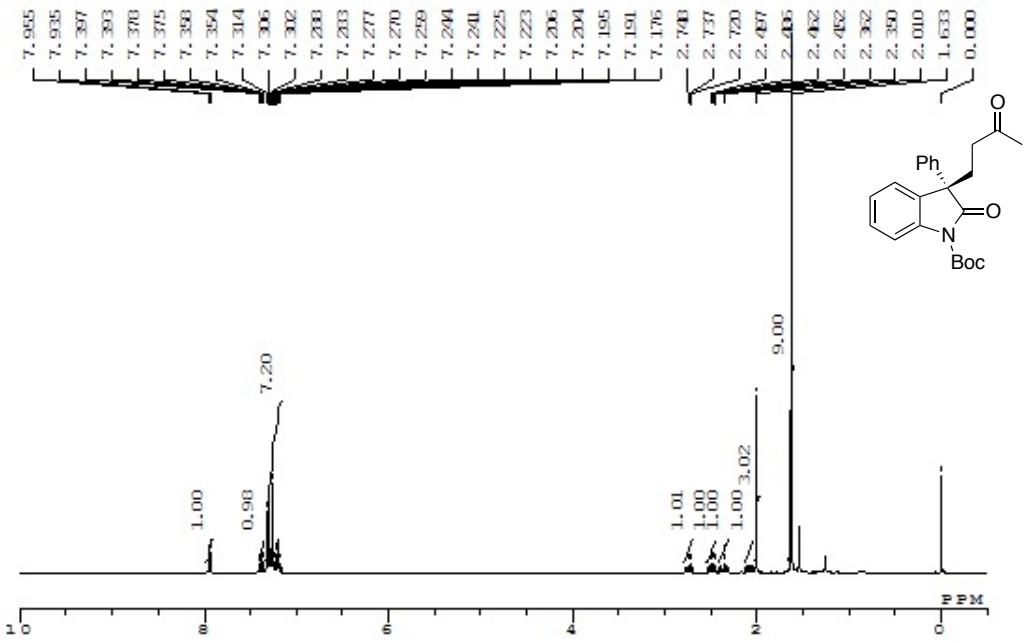
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7.283
7.277
7.270
7.259
7.244
7.241
7.225
7.223
7.206
7.204
7.195
7.191
7.176
2.743
2.737
2.720
2.497
2.482
2.452
2.362
2.350
2.010
1.633
0.000
Ph
O
N
Boc
9.00
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1.00
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PPM
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8
6
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2
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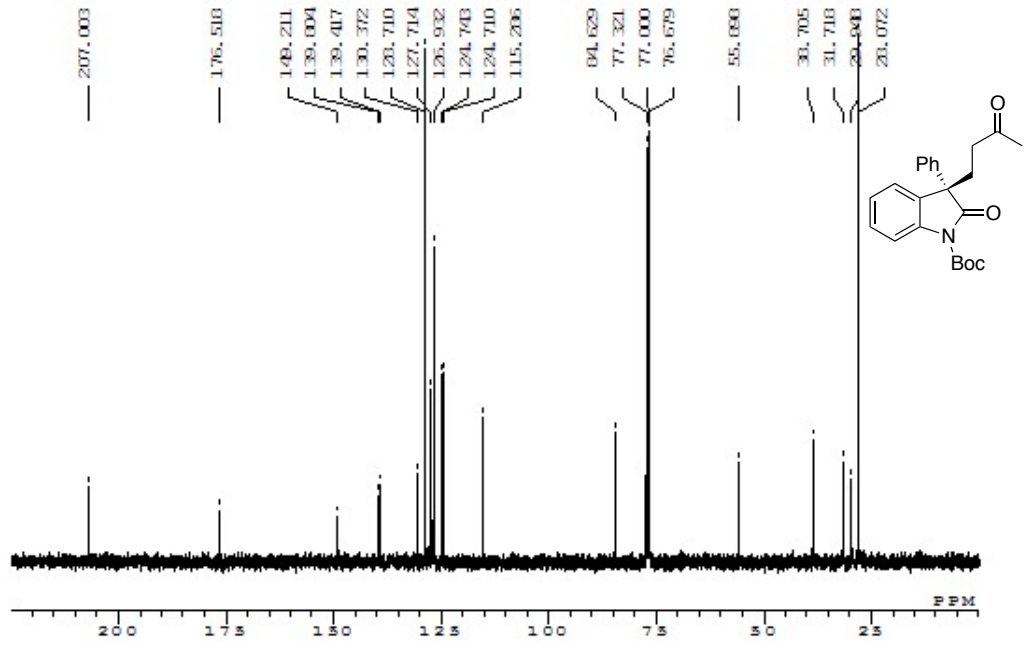
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77.000
76.679
55.888
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Ph
O
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Boc
PPM
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125
100
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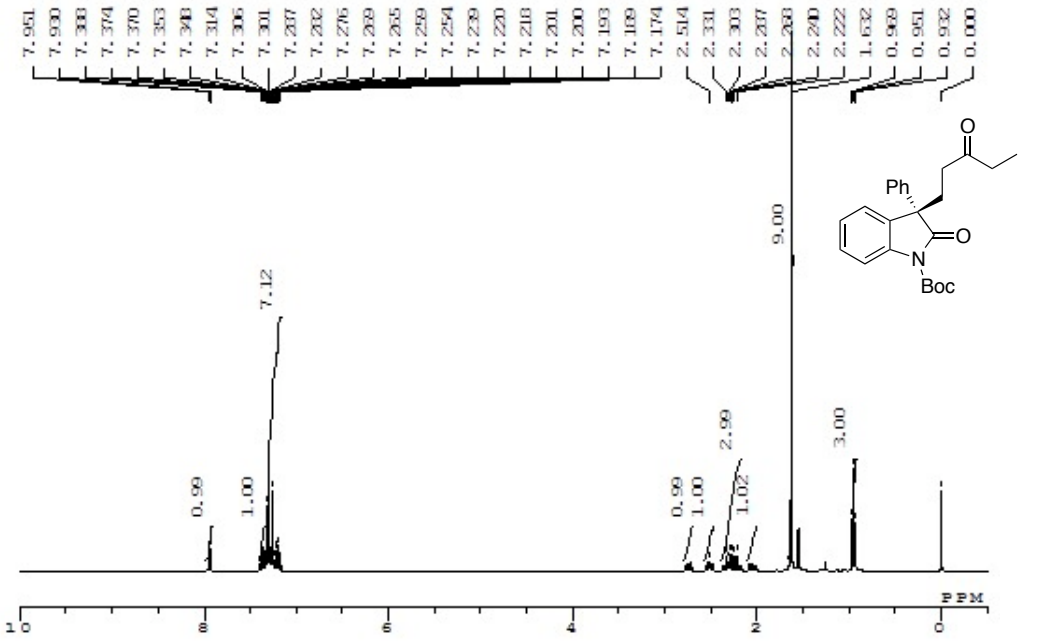
50
25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7.348
7.314
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7.301
7.237
7.232
7.276
7.269
7.265
7.259
7.254
7.229
7.220
7.218
7.201
7.200
7.193
7.189
7.174
2.514
2.331
2.303
2.287
2.268
2.240
2.222
1.632
0.969
0.951
0.932
0.000
9.00
7.12
0.99
1.00
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1.02
3.00
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Boc
PPM
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6
4
2
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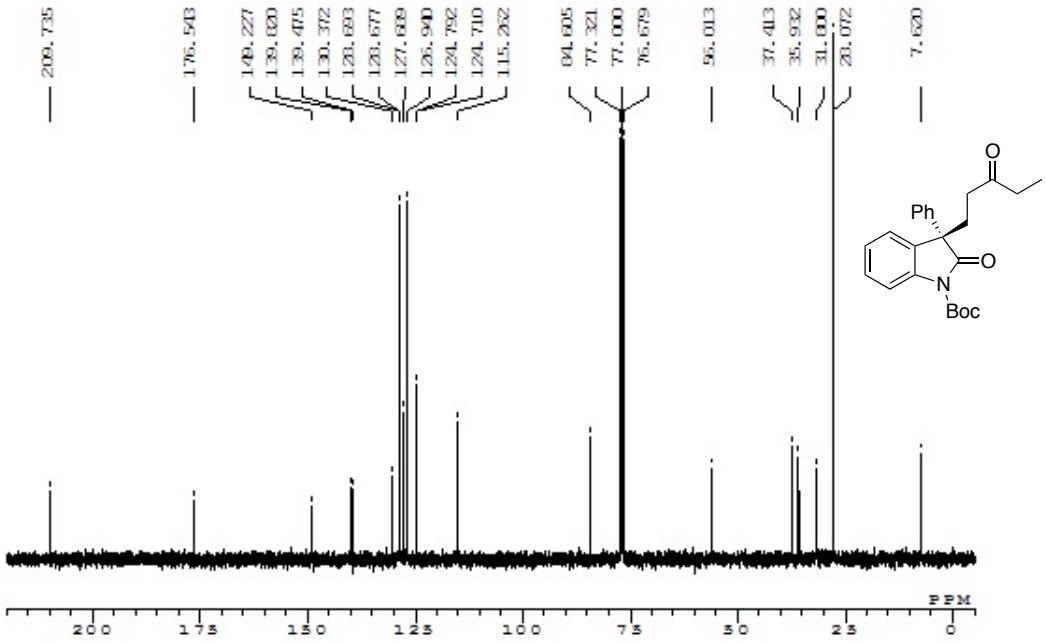
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124.710
115.262
84.605
77.321
77.000
76.679
56.013
37.413
35.932
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28.072
7.620
Ph
O
O
N
Boc
PPM
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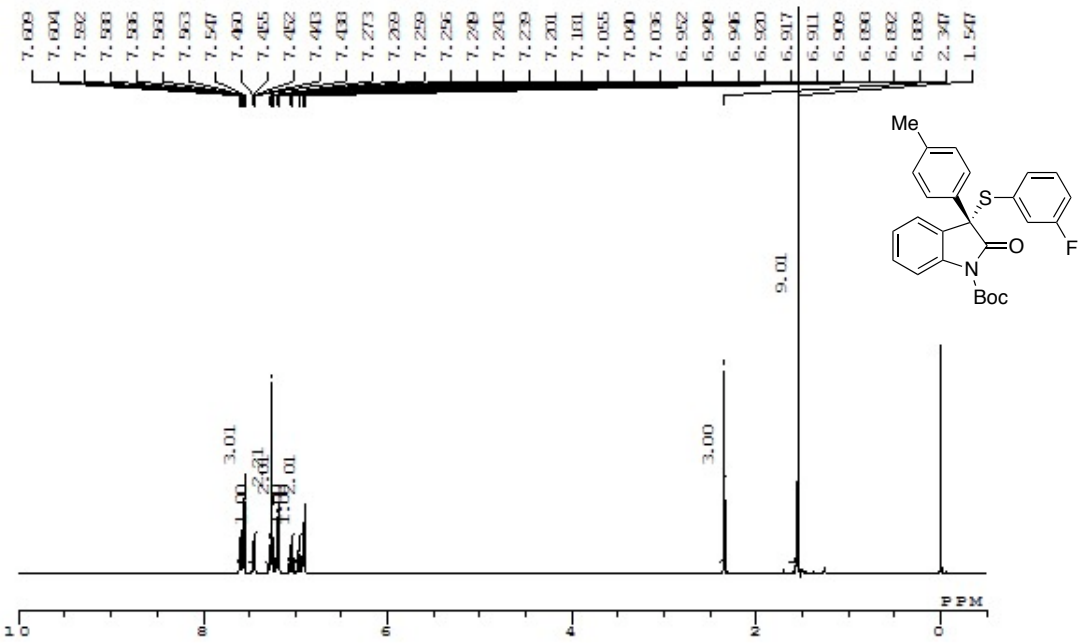
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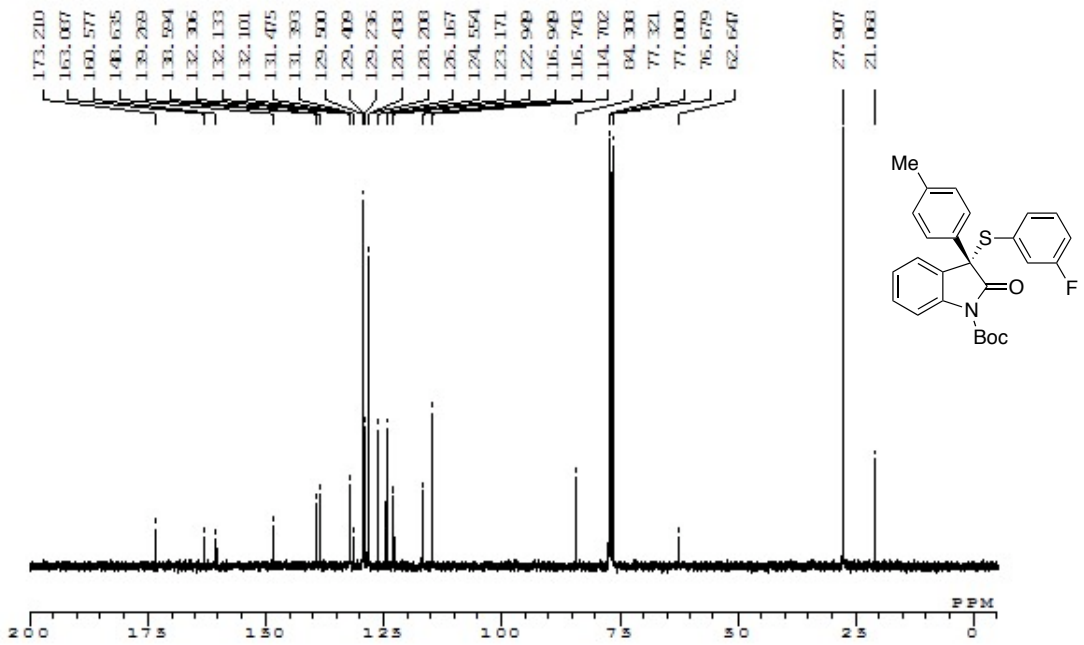
F
N
Boc
PPM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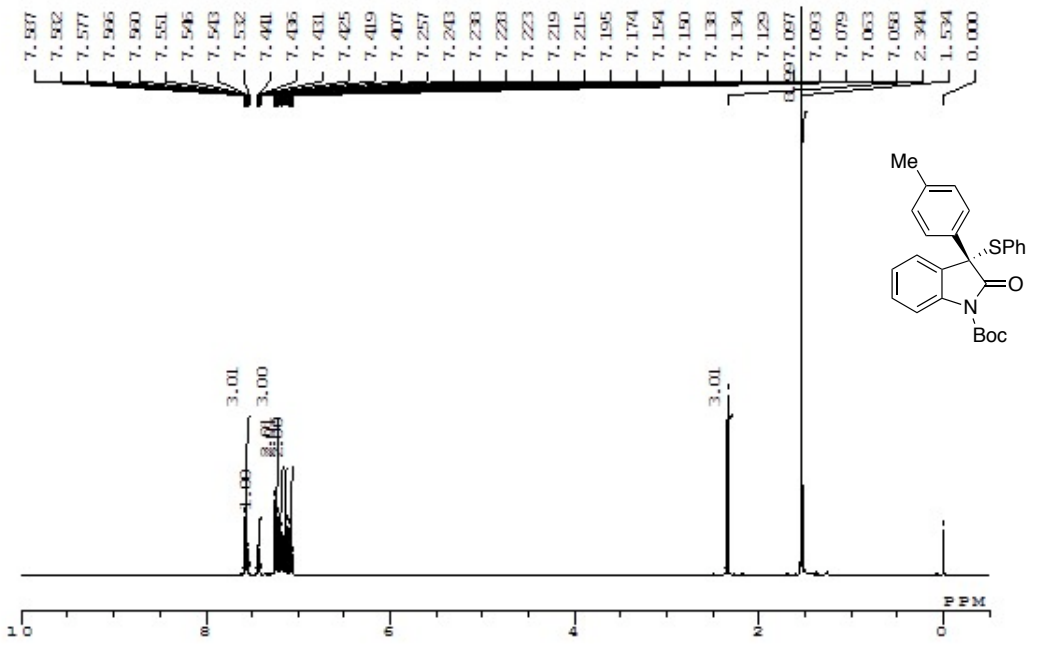
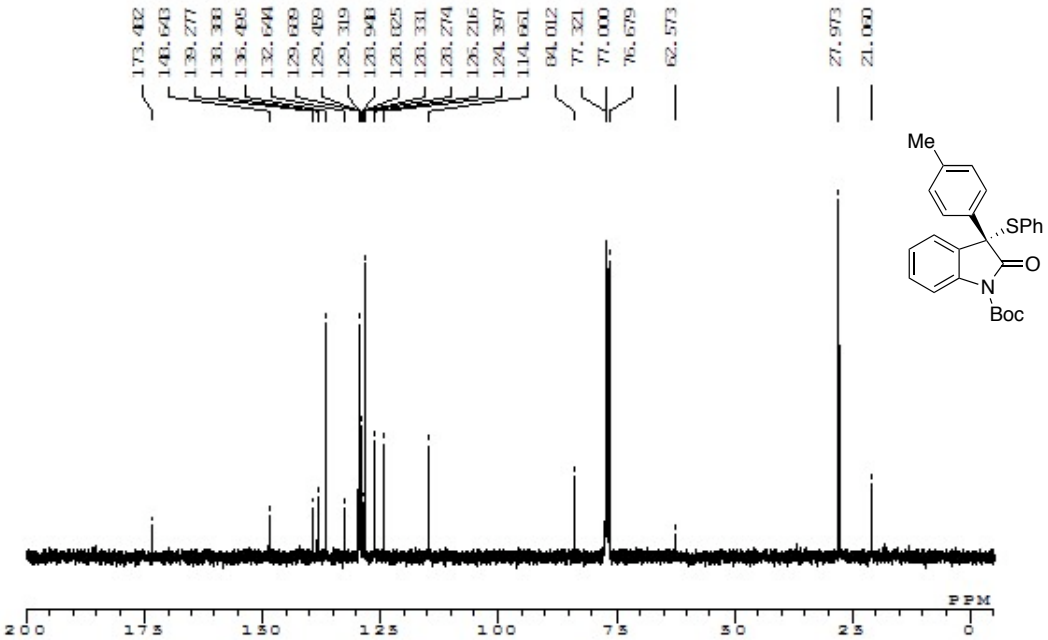
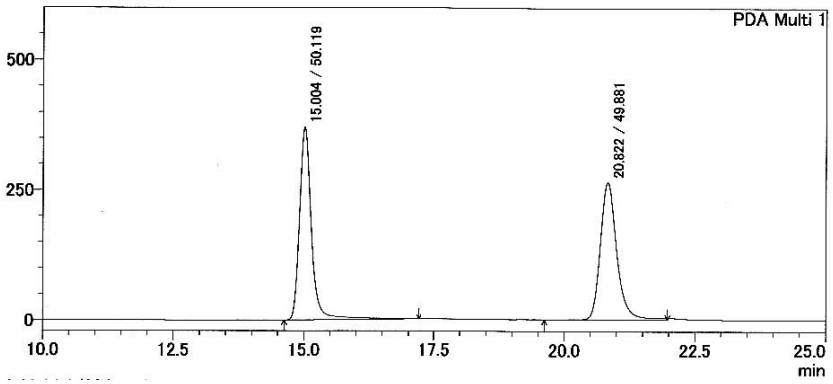
Boc
PPM



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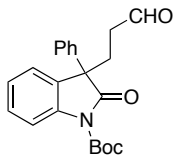
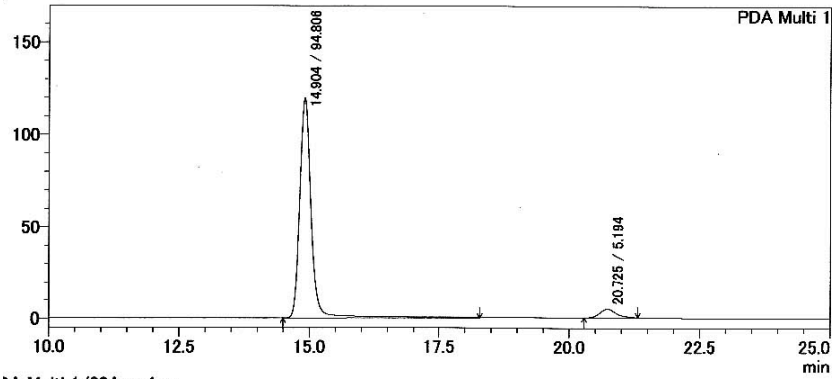
20.822 / 49.881
500
250
0
10.0
12.5
15.0
17.5
20.0
22.5
25.0
min


CHO
Ph
O
N
Boc


PDA Multi 1
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20.725 / 5.194
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100
50
0
10.0
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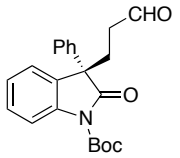
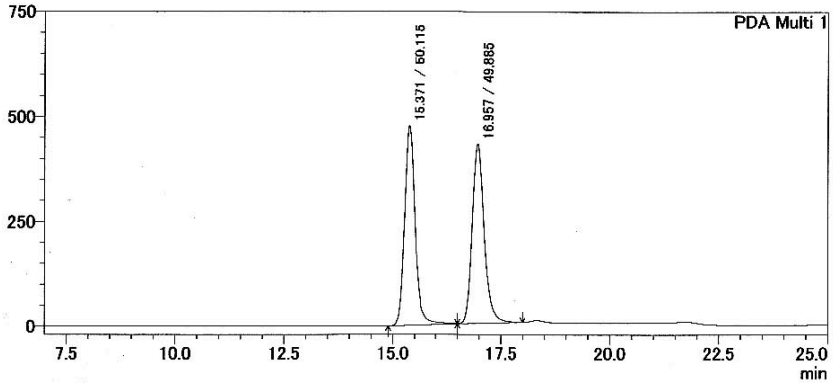
15.0
17.5
20.0
22.5
25.0
min


CHO
Ph
O
N
Boc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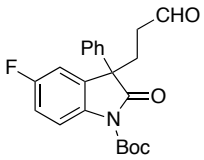
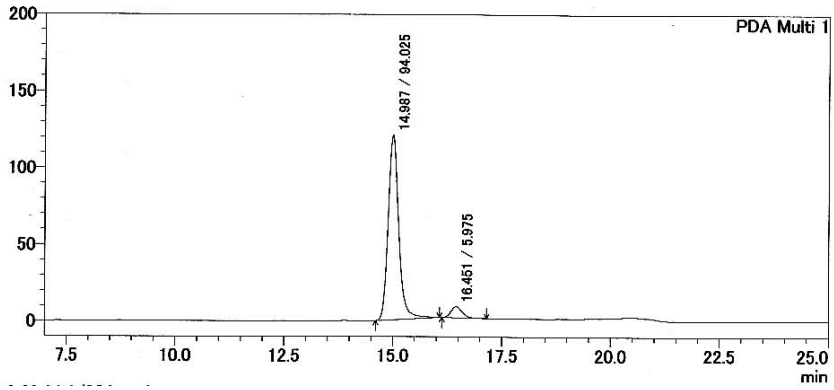
16.957 / 49.885
750
500
250
0
7.5
10.0
12.5
15.0
17.5
20.0
22.5
25.0
min


CHO
Ph
F
O
N
Boc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16.451 / 5.975
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150
100
50
0
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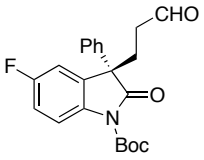
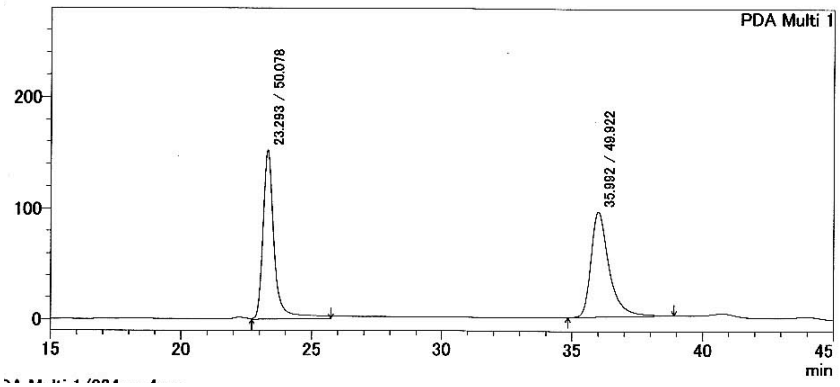
10.0
12.5
15.0
17.5
20.0
22.5
25.0
min


CHO
Ph
F
O
N
Boc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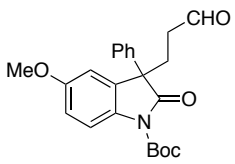
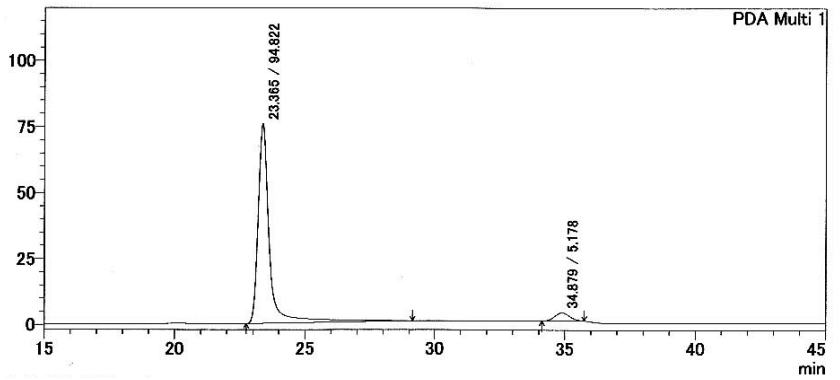
35.992 / 49.822
200
100
0
15
20
25
30
35
40
45
min


CHO
Ph
MeO
O
N
Boc


PDA Multi 1
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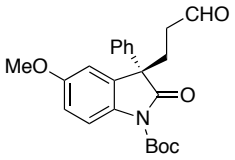
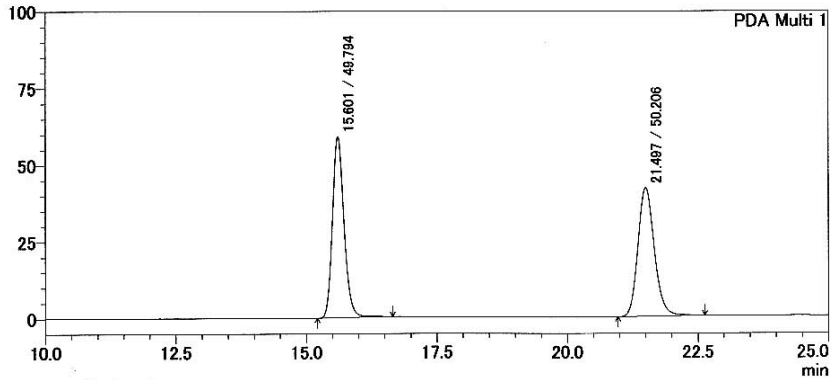
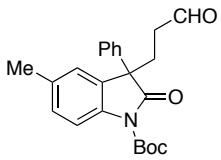
34.879 / 5.178
100
75
50
25
0
15
20
25
30
35
40
45
min


CHO
Ph
MeO
O
N
Boc


PDA Multi 1
15.601 / 49.794
21.497 / 50.206
100
75
50
25
0
10.0
12.5
15.0
17.5
20.0
22.5
25.0
min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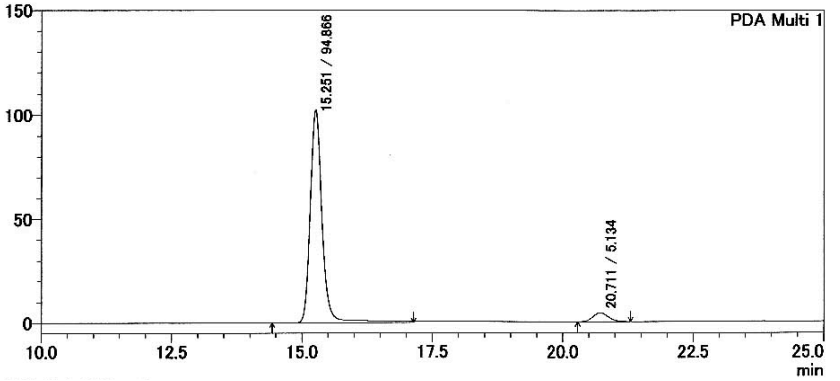
Ph
Me
O
N
Boc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20.711 / 5.134
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100
50
0
10.0
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17.5
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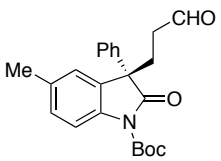
22.5
25.0
min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Me
O
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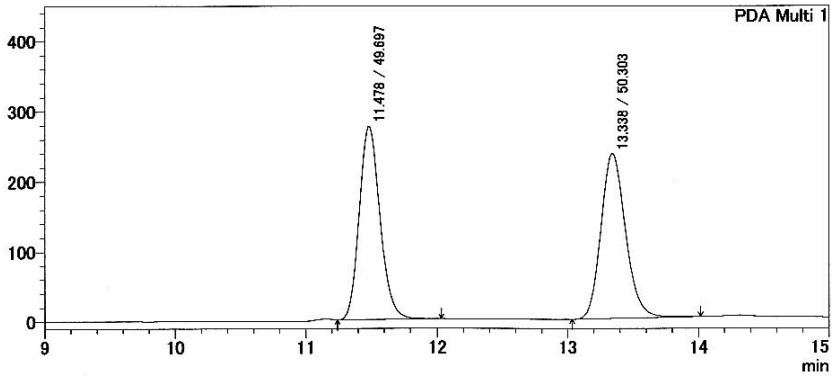
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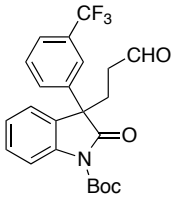
13.338 / 50.303
min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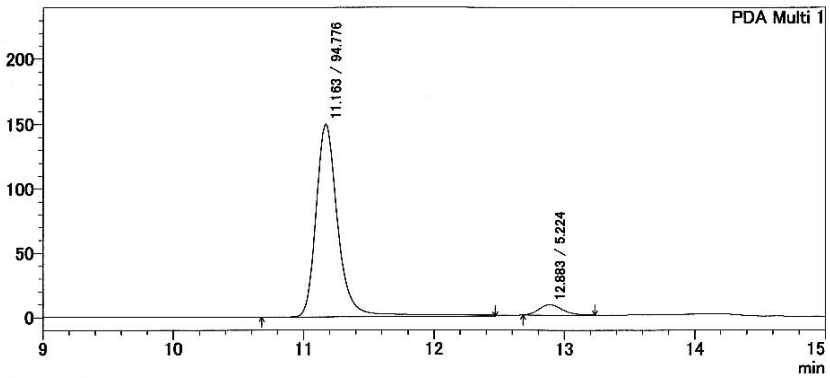
CHO
O
N
Boc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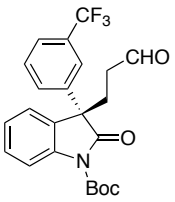
12.883 / 5.224
min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O
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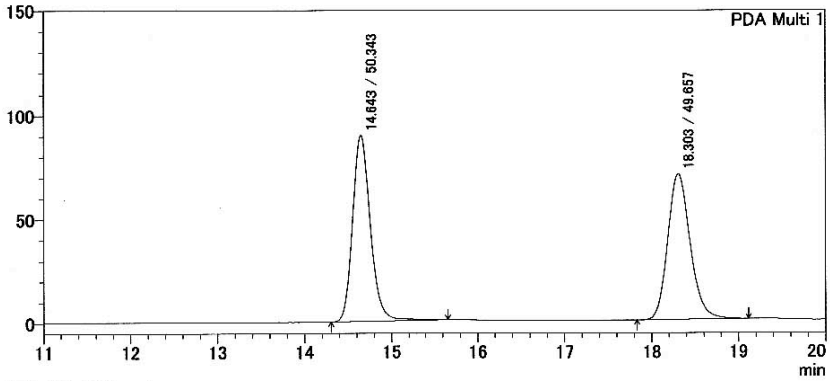
Boc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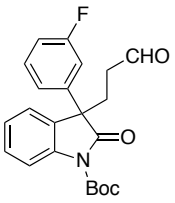
18.303 / 49.657
min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CHO
O
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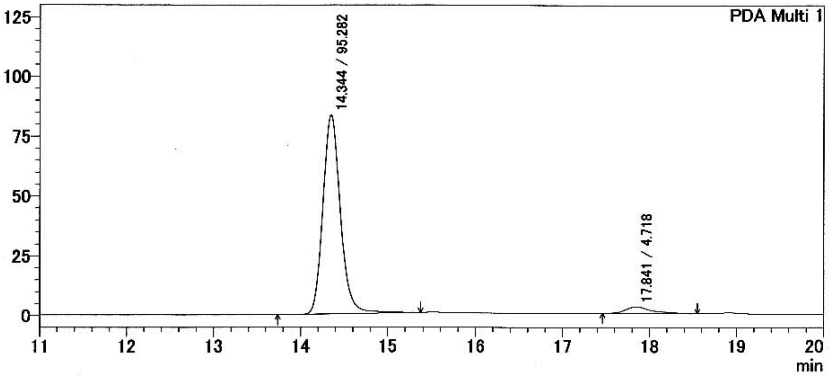
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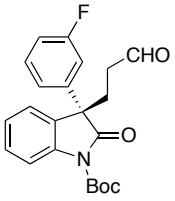
17.841 / 4.718
min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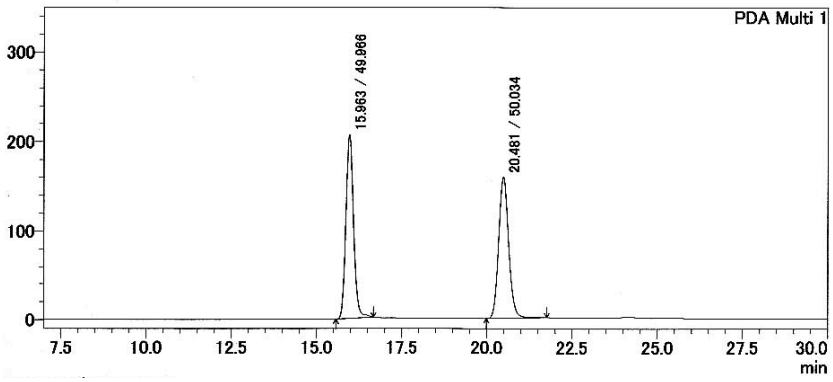
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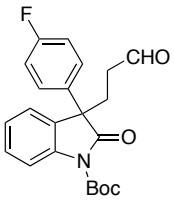
20.481 / 50.034
min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O
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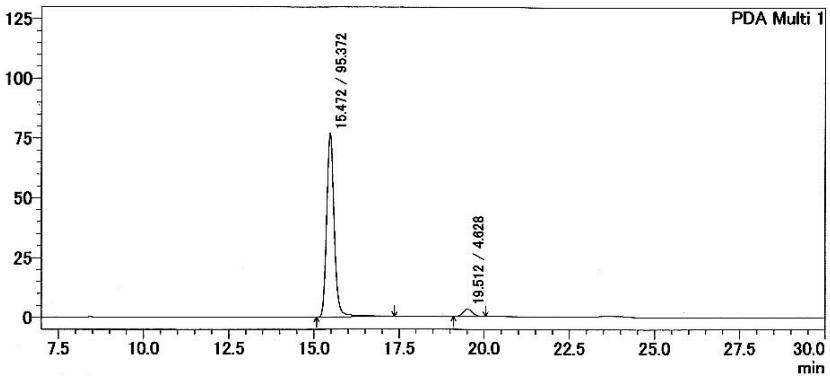
Boc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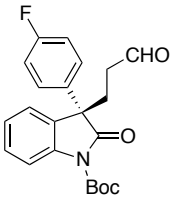
19.512 / 4.628
min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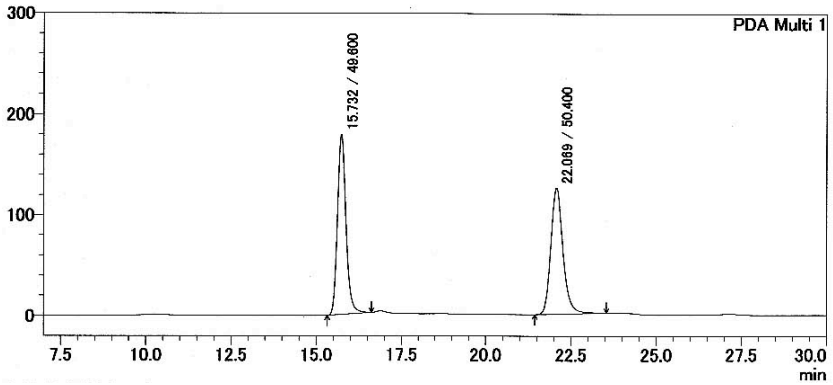
CHO
O
N
Boc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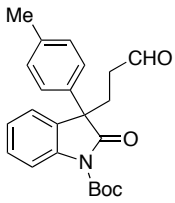
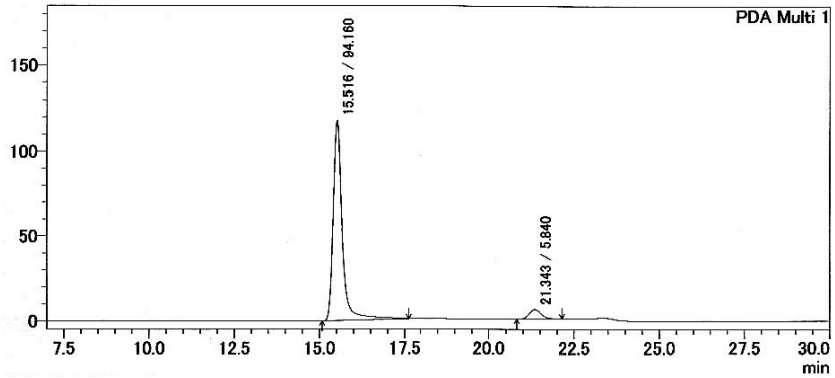
22.089 / 50.400
min


Me
CHO
O
N
Boc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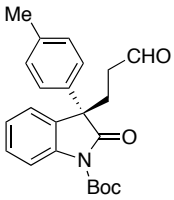
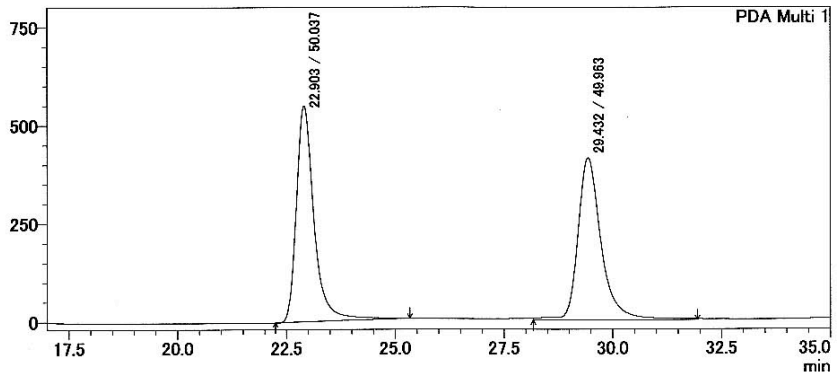
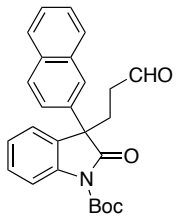
21.343 / 5.840
min


Me
CHO
O
N
Boc


PDA Multi 1
22.903 / 50.037
29.432 / 48.963
750
500
250
0
17.5
20.0
22.5
25.0
27.5
30.0
32.5
35.0
min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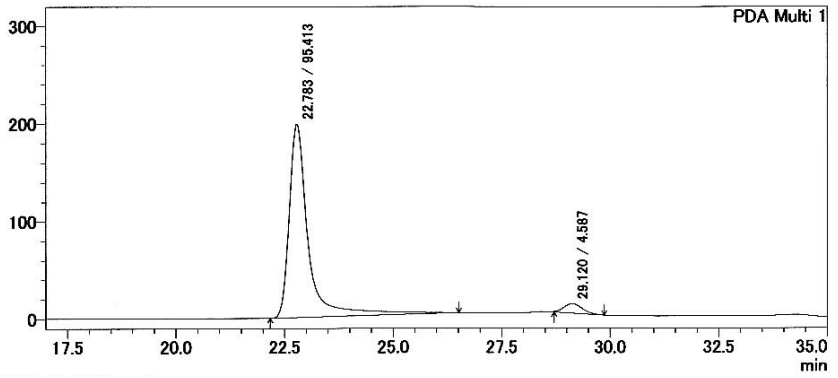
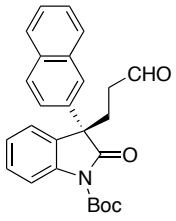

PDA Multi 1
22.783 / 95.413
29.120 / 4.587
300
200
100
0
17.5
20.0
22.5
25.0
27.5
30.0
32.5
35.0
min


CHO
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N
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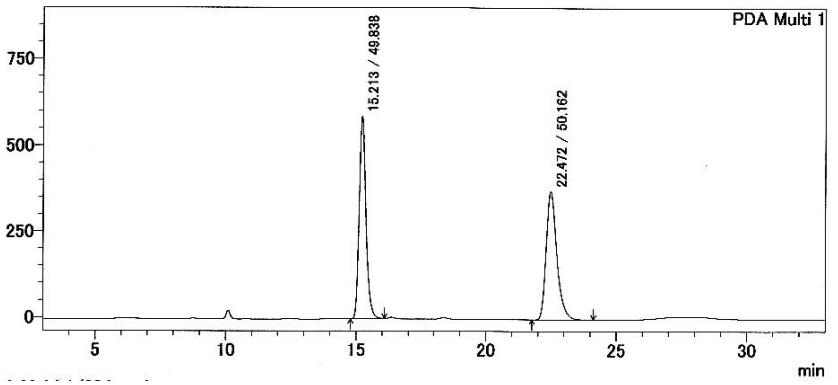
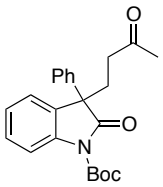

PDA Multi 1
15.213 / 49.838
22.472 / 50.162
750
500
250
0
5
10
15
20
25
30
min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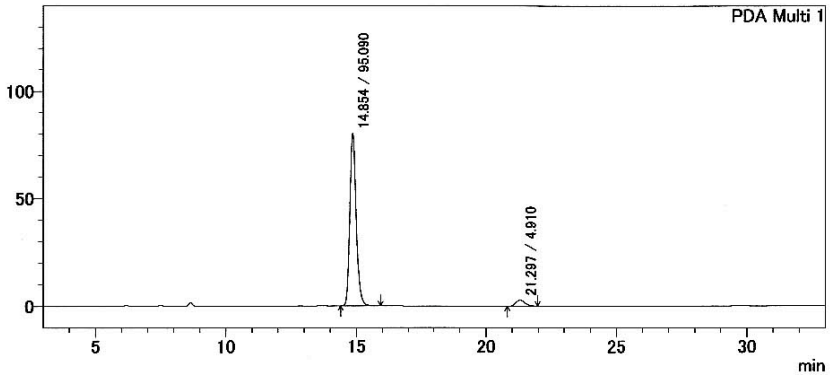
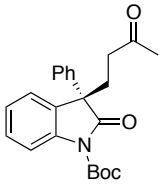

PDA Multi 1
14.854 / 95.090
21.297 / 4.910
100
50
0
5
10
15
20
25
30
min


O
Ph
O
N
Boc