Supporting Information

Synthesis of P-Chiral Phosphine Compounds by Palladium-Catalyzed C–P Coupling Reactions

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& These authors contributed equally to this work.

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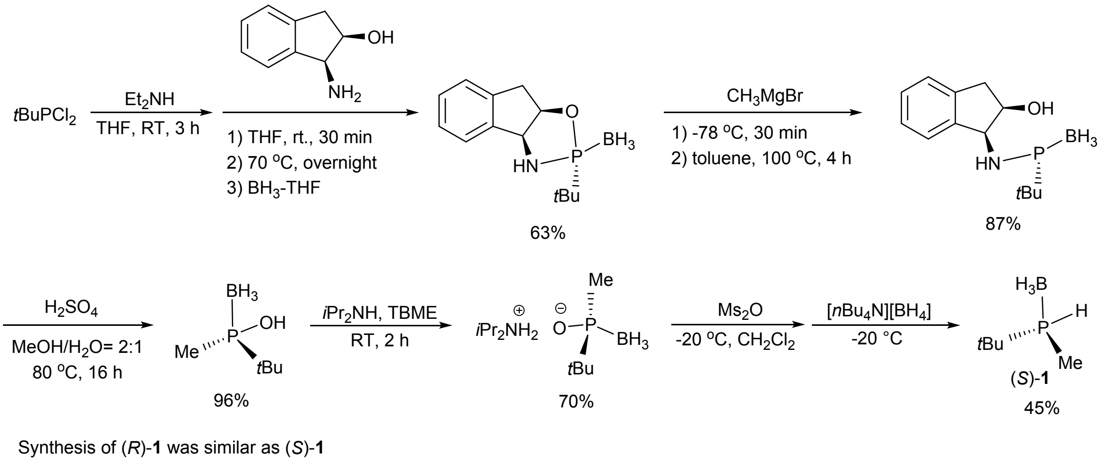
1. General considerations

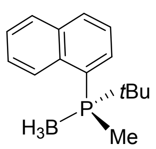
All manipulations of air-sensitive materials were carried out under an atmosphere of dry argon by using modified Schlenk line and glovebox techniques. Aryl halides, heteroaryl halides, bases, and catalysts were purchased from Alfa-Aesar and J&K Scientific Ltd. All solvents were distilled from appropriate drying agents under argon before use. The ^{1}H, ^{13}C, ^{19}F and ^{31}P NMR spectroscopic data were recorded on Bruker Mercury Plus 400 MHz NMR spectrometers. Chemical shifts (δ) for ^{1}H and ^{13}C are referenced to internal solvent resonances and reported relative to $SiMe_4$. Chemical shifts for ^{19}F are reported relative to an external $CFCl_3$ standard. Chemical shifts for ^{31}P are reported relative to an external 85% H_3PO_4 standard. High resolution mass analysis is performed on Varian 7.0T Fourier-transform mass spectrometry with ESI resource. High performance liquid chromatography (HPLC) was performed on Agilent 1100 series chromatographs using a Daicel Chiracel *AD-H* (4.6 mm Ø x 250 mm) or *OD-H* (4.6 mm Ø x 250 mm) or *AS-H* (4.6 mm Ø x 250 mm) column or *IBN-H* (4.6 mm Ø x 250 mm) with *n*-hexane/*i*-PrOH as an eluent. Microwave reaction was determined by Disover SP microwave instrument. (*S*)-*tert*- butyl(methyl)phosphine borane and (*R*)-*tert*- butyl(methyl)phosphine borane was synthesized according to the published procedures. [1]



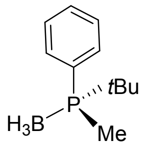
Scheme S1. Synthesis of optically pure P-stereogenic *tert*-butyl(methyl)phosphine borane[1]

2. Procedures for palladium-catalyzed C–P coupling reactions

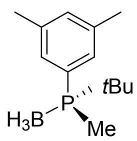
To a reaction tube, (*S*)-*tert*-butyl(methyl)phosphine borane (35.0 mg, 0.3 mmol), aryl and heteroaryl halides (0.5 mmol), $Pd(OAc)_2$ (3.4 mg, 0.015 mmol), dppf (27.7 mg, 0.03 mmol), *t*BuONa (57.6 mg, 0.6 mmol) and toluene (3 mL) were added under argon. The mixture was stirred for 72 h at room temperature. After removal of volatile materials under reduced pressure, the crude product was purified by chromatograph on silica gel. (*n*-hexane / dichloromethane).



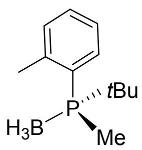
(*R*)-*tert*-butyl(methyl)(naphthalen-1-yl)phosphine Borane.[2] Performed according to the general procedure to afford 41.0 mg (71%) of (*R*)-**2a** as white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.90 (d, *J* = 8.0 Hz, 1 H, Ar), 7.99 (d, *J* = 8.0 Hz, 1 H, Ar), 7.87 (d, *J* = 8.0 Hz, 1 H, Ar), 7.75 - 7.80 (m, 1 H, Ar), 7.61 - 7.75 (m, 1 H, Ar), 7.49 - 7.53 (m, 2 H, Ar), 1.78 (d, J = 12.0 Hz, 3 H, CH_3), 1.16 (d, J = 16.0 Hz, 9 H, C(CH_3)$_3$), 0.79 - 1.57 (m, 3 H, BH_3). ^{13}C NMR (101 MHz, $CDCl_3$): δ 135.4 (d, J_{C-P} = 10.6 Hz, Ar), 133.9 (d, J_{C-P} = 7.7 Hz, Ar), 133.4 (d, J_{C-P} = 4.0 Hz, Ar), 132.4 (d, J_{C-P} = 2.6 Hz, Ar), 128.8 (s, Ar), 128.2 (d, J_{C-P} = 5.9 Hz, Ar), 126.6 (s, Ar), 126.3 (s, Ar), 125.0 (d, J_{C-P} = 44.8 Hz, Ar), 124.3 (d, J_{C-P} = 9.2 Hz, Ar), 30.5 (d, J_{C-P} = 31.5 Hz, C(CH_3)$_3$), 25.8 (d, J_{C-P} = 2.9 Hz, C(CH$_3$)$_3$), 8.9 (d, J_{C-P} = 39.6 Hz, CH$_3$). ^{31}P NMR (162 MHz, $CDCl_3$): δ 23.8 (q, J = 69.7 Hz). HPLC (Daicel Chiralcel AS-H, *n*-hexane/*i*-PrOH = 95/5, UV = 250 nm, flow rate = 1.0 mL/min) t_{R1} = 5.452 min (minor) and t_{R2} = 6.546 min (major), ee = 91%. $[\alpha]_D^{25}$ = +8.5 (c = 2.0, $CHCl_3$).



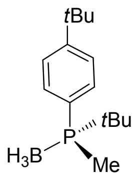
(*R*)-*tert*-butyl(methyl)(phenyl)phosphine Borane.[2] Performed according to the general procedure to afford 41 mg (71%) of (*R*)-**2b** as white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.71 (t, J = 8.0 Hz, 2 H, Ar), 7.39 – 7.58 (m, 3 H, Ar), 1.58 (d, J = 8.0 Hz, 3 H, CH_3), 1.11 (d, J = 12.0 Hz, 9 H, C(CH_3)$_3$), 0.12 – 0.97 (m, 3 H, BH_3). ^{13}C NMR (101 MHz, $CDCl_3$): δ 132.9 (d, J_{C-P} = 8.0 Hz, Ar), 131.1 (s, Ar), 128.3 (s, Ar), 128.2 (s, Ar), 28.5 (d, J_{C-P} = 33.3 Hz, C(CH_3)$_3$), 25.1 (d, J_{C-P} = 2.9 Hz, C(CH$_3$)$_3$), 5.2 (d, J_{C-P} = 37.8 Hz, CH$_3$). ^{31}P NMR (162 MHz, $CDCl_3$): δ 25.0 (q, J = 64.8 Hz). HPLC (Daicel Chiralcel AS-H, *n*-hexane/*i*-PrOH = 95/5, UV = 254 nm, flow rate = 1.0 mL/min) t_{R1} = 7.131 min (minor) and t_{R2} = 8.103 min (major), ee = 65%. $[\alpha]_D^{25}$ = +23.0 (c = 2.0, $CHCl_3$).



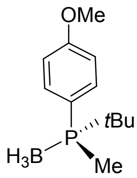
(*R*)-*tert*-butyl(3,5-dimethylphenyl)(methyl)phosphine Borane. Performed according to the general procedure to afford 50 mg (75%) of (*R*)-**2c** as yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30 (s, 1 H, Ar), 7.27 (s, 1 H, Ar), 7.12 (s, 1 H, Ar), 2.36 (s, 6 H, CH_3), 1.53 (d, J = 8.0 Hz, 3 H, CH_3), 1.10 (d, J = 12.0 Hz, 9 H, C(CH_3)$_3$), 0.24 – 0.86 (m, 3 H, BH_3). ^{13}C NMR (101 MHz, $CDCl_3$): δ 137.8 (d, J_{C-P} = 9.9 Hz, Ar), 132.8 (d, J_{C-P} = 2.6 Hz, Ar), 130.4 (d, J_{C-P} = 8.4 Hz, Ar), 127.2 (d, J_{C-P} = 50.3 Hz, Ar), 28.4 (d, J_{C-P} = 33.4 Hz, C(CH_3)$_3$), 25.2 (d, J_{C-P} = 2.6 Hz, C(CH$_3$)$_3$), 21.3 (s, CH$_3$), 5.3 (d, J_{C-P} = 37.8 Hz, CH$_3$). ^{31}P NMR (162 MHz, $CDCl_3$): δ 24.3 (q, J = 69.7 Hz). HRMS (ESI): m/z: $[M+H-BH_3]^+$ calculated for $C_{13}H_{22}P$: 209.1454, found 209.1455. HPLC (Daicel Chiralcel AS-H, *n*-hexane/*i*-PrOH = 95/5, UV = 220 nm, flow rate = 1.0 mL/min) t_{R1} = 4.240 min (minor) and t_{R2} = 5.678 min (major), ee = 94%. $[\alpha]_D^{25}$ = +38.0 (c = 2.0, $CHCl_3$).



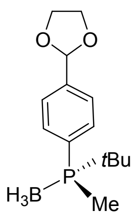
(*R*)-*tert*-butyl(methyl)(*o*-tolyl)phosphine Borane.[2] Performed according to the general procedure to afford 34 mg (42%) of (*R*)-**2d** as white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52 - 7.56 (m, 1 H, Ar), 7.37 (t, J = 8.0 Hz, 1 H, Ar), 7.13 – 7.26 (m, 2 H, Ar), 2.66 (s, 3 H, CH_3), 1.64 (d, J = 8.0 Hz, 3 H, CH_3), 1.14 (d, J = 16.0 Hz, 9 H, C(CH_3)$_3$), 0.43 – 1.10 (m, 3 H, BH_3). ^{13}C NMR (101 MHz, $CDCl_3$): δ 144.1 (d, J_{C-P} = 10.5 Hz, Ar), 133.9 (d, J_{C-P} = 6.1 Hz, Ar), 132.1 (d, J_{C-P} = 8.8 Hz, Ar), 131.0 (d, J_{C-P} = 2.4 Hz, Ar), 125.7 (d, J_{C-P} = 46.0 Hz, Ar), 125.3 (d, J_{C-P} = 8.3 Hz, Ar), 30.5 (d, J_{C-P} = 31.9 Hz, C(CH_3)$_3$), 25.4 (d, J_{C-P} = 2.7 Hz, C(CH$_3$)$_3$), 23.3 (d, J = 3.3 Hz, CH$_3$), 8.8 (d, J_{C-P} = 39.0 Hz, CH$_3$). ^{31}P NMR (162 MHz, $CDCl_3$): δ 25.1 (q, J = 61.6 Hz). HPLC (Daicel Chiralcel OD-H, *n*-hexane/*i*-PrOH = 98/2, UV = 230 nm, flow rate = 0.5 mL/min) t_{R1} = 12.580 min (minor) and t_{R2} = 14.134 min (major), ee = 90%. $[\alpha]_D^{25}$= +1.0 (c = 2.0, $CHCl_3$).



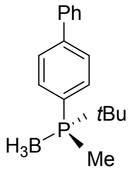
(*R*)-*tert*-butyl(4-(tert-butyl)phenyl)(methyl)phosphine Borane. Performed according to the general procedure to afford 67.5 mg (90%) of (*R*)-**2e** as yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61 – 7.65 (m, 2 H, Ar), 7.45 – 7.47 (m, 2 H, Ar), 1.55 (d, *J* = 8.0 Hz, 3 H, CH_3), 1.33 (s, 9 H, $C(CH_3)_3$), 1.11 (d, *J* = 12.0 Hz, 9 H, $C(CH_3)_3$), 0.48 – 1.05 (m, 3 H, BH_3). ^{13}C NMR (101 MHz, $CDCl_3$): δ 154.4 (d, $J_{C\text{-}P}$ = 2.4 Hz, Ar), 132.7 (d, $J_{C\text{-}P}$ = 8.4 Hz, Ar), 125.3 (d, $J_{C\text{-}P}$ = 9.7 Hz, Ar), 124.2 (d, $J_{C\text{-}P}$ = 6.1 Hz, Ar), 34.9 (s, $C(CH_3)_3$), 31.2 (s, $C(CH_3)_3$), 28.6 (d, $J_{C\text{-}P}$ = 33.3 Hz, $C(CH_3)_3$), 25.2 (d, $J_{C\text{-}P}$ = 3.0 Hz, $C(CH_3)_3$), 5.4 (d, $J_{C\text{-}P}$ = 30.3 Hz, CH_3). ^{31}P NMR (162 MHz, $CDCl_3$): δ 23.7 (q, *J* = 66.4 Hz). HRMS (ESI): m/z: $[M+H\text{-}BH_3]^+$ calculated for $C_{15}H_{26}P$:237.1767, found 237.1766. HPLC (Daicel Chiralcel AS-H, *n*-hexane/*i*-PrOH = 99/1, UV = 234 nm, flow rate = 1 mL/min) t_{R1} = 5.365 min (major) and t_{R2} = 6.045 min (minor), ee = 90%. $[\alpha]_D^{25}$ = +13.0 (c = 2.0, $CHCl_3$).



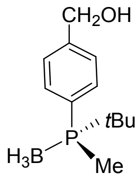
(*R*)-*tert*-butyl(4-methoxyphenyl)(methyl)phosphine Borane. Performed according to the general procedures to afford 47 mg (70%) of (*R*)-**2f** as white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61 - 7.65 (m, 2 H, Ar), 6.96 – 6.98 (m, 2 H, Ar), 3.85 (s, 3 H, OCH_3), 1.54 (d, *J* = 8.0 Hz, 3 H, CH_3), 1.09 (d, *J* = 16.0 Hz, 9 H, $C(CH_3)_3$). 0.35 – 0.91 (m, 3 H, BH_3). ^{13}C NMR (101 MHz, $CDCl_3$): δ 161.8 (d, $J_{C\text{-}P}$ = 2.4 Hz, Ar), 134.5 (d, $J_{C\text{-}P}$ = 9.4 Hz, Ar), 118.4 (d, $J_{C\text{-}P}$ = 6.2 Hz, Ar), 113.9 (d, $J_{C\text{-}P}$ = 10.3 Hz, Ar), 55.3 (s, OCH_3), 28.7 (d, $J_{C\text{-}P}$ = 30.3 Hz, $C(CH_3)_3$), 25.2 (d, $J_{C\text{-}P}$ = 2.7 Hz, $C(CH_3)_3$), 5.5 (d, $J_{C\text{-}P}$ = 30.3 Hz, CH_3). ^{31}P NMR (162 MHz, $CDCl_3$): δ 23.2 (q, *J* = 61.6 Hz). HRMS (ESI): m/z: $[M+H\text{-}BH_3]^+$ calculated for $C_{12}H_{20}OP$: 211.1246, found 211.1248. HPLC (Daicel Chiralcel AS-H, *n*-hexane/*i*-PrOH = 98/2, UV = 254 nm, flow rate = 0.8 mL/min) t_{R1} =21.843 min (minor) and t_{R2} = 23.093 (major), ee = 98%. $[\alpha]_D^{25}$ = +5.0 (c = 2.0, $CHCl_3$).



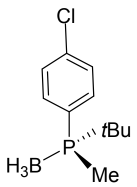
(*R*)-(4-(1,3-dioxolan-2-yl)phenyl)(*tert*-butyl)(methyl)phosphine Borane. Performed according to the general procedure to afford 34 mg (42%) of (*R*)-**2g** as yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.69 – 7.78 (m, 2 H, Ar), 7.56 – 7.58 (m, 2 H, Ar), 5.84 (s, 1 H, CH), 4.10 – 4.15 (m, 2 H, CH_2), 4.04 – 4.09 (m, 2 H, CH_2), 1.57 (d, *J* = 9.7 Hz, 3 H, CH_3), 1.10 (d, *J* = 14.0 Hz, 9 H, $C(CH_3)_3$), 0.13 – 0.99 (m, 3 H, BH_3). ^{13}C NMR (101 MHz, $CDCl_3$): δ 141.1 (s, Ar), 133.0 (d, $J_{C\text{-}P}$ = 8.1 Hz, Ar), 128.7 (d, $J_{C\text{-}P}$ = 50.5 Hz, Ar), 126.3 (d, $J_{C\text{-}P}$ = 9.1 Hz, Ar), 103.0 (s, CH), 65.4 (s, CH_2), 28.6 (d, $J_{C\text{-}P}$ = 40.4 Hz, $C(CH_3)_3$), 25.1(d, $J_{C\text{-}P}$ = 2.7 Hz, $C(CH_3)_3$), 5.3 (d, $J_{C\text{-}P}$ = 40.4 Hz, CH_3). ^{31}P NMR (162 MHz, $CDCl_3$): δ 25.2 (q, *J* = 66.4 Hz). HRMS (ESI): m/z: $[M+H\text{-}BH_3]^+$ calculated for $C_{14}H_{22}O_2P$: 253.1352, found 253.1352. HPLC (Daicel Chiralcel AS-H, *n*-hexane/*i*-PrOH = 98/2, UV = 250 nm, flow rate = 1.0 mL/min) t_{R1} = 26.610 min (major) and t_{R2} = 34.227 min (minor), ee = 89%. $[\alpha]_D^{25}$ = +11.0 (c = 2.0, $CHCl_3$).



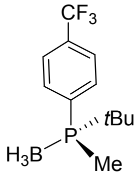
(*R*)-(4-(1,3-dioxolan-2-yl)phenyl)(*tert*-butyl)(methyl)phosphine Borane. Performed according to the general procedure to afford 34 mg (42%) of (*R*)-**2h** as yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75 – 7.80 (m, 2 H, Ar), 7.66 – 7.68 (m, 2 H, Ar), 7.60 – 7.61 (m, 2 H, Ar), 7.45 – 7.49 (m, 2 H, Ar), 7.37 – 7.41 (m, 1 H, Ar), 1.61 (d, *J* = 9.7 Hz, 3 H, C*H*$_3$), 1.15 (d, *J* = 14.0 Hz, 9 H, C(C*H*$_3$)$_3$), 0.41 – 0.88 (m, 3 H, B*H*$_3$). ^{13}C NMR (101 MHz, $CDCl_3$): δ 143.9 (s, Ar), 139.9 (s, Ar), 133.3 (d, $J_{C\text{-}P}$ = 8.7 Hz, Ar), 128.9 (s, Ar), 128.0 (s, Ar), 127.2 (s, Ar), 126.9 (d, $J_{C\text{-}P}$ = 9.5 Hz, Ar), 126.3 (d, $J_{C\text{-}P}$ = 51.3 Hz, Ar), 28.6 (d, $J_{C\text{-}P}$ = 34.3 Hz, *C*(CH$_3$)$_3$), 25.0 (d, $J_{C\text{-}P}$ = 24.2 Hz, C(*C*H$_3$)$_3$), 5.3 (d, $J_{C\text{-}P}$ = 37.4 Hz, *C*H$_3$). ^{31}P NMR (162 MHz, $CDCl_3$): δ 24.7 (q, *J* = 66.4 Hz). HRMS (ESI): m/z: $[M+H\text{-}BH_3]^+$ calculated for $C_{17}H_{22}P$: 257.1454, found 257.1454. HPLC (Daicel Chiralcel OD-H, *n*-hexane/*i*-PrOH = 95/5, UV = 250 nm, flow rate = 0.8 mL/min) t_{R1} = 7.891 min (major) and t_{R2} = 8.692 min (minor), ee = 79%. $[\alpha]_D^{25}$ = +11.0 (c = 2.0, $CHCl_3$).



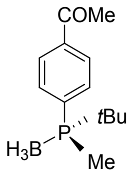
(*R*)-4-(borane *tert*-butyl(methyl)phosphino)phenyl)methanol. Performed according to the general procedure to afford 64 mg (95%) of (*R*)-**2i** as white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68 (t, *J* = 8.7 Hz, 2 H, Ar), 7.44 (d, *J* = 7.6 Hz, 2 H, Ar), 4.72 (s, 2 H, C*H*$_2$), 2.37 (s, 1 H, CH$_2$O*H*), 1.56 (d, *J* = 9.7 Hz, 3 H, C*H*$_3$), 1.09 (d, *J* = 14.0 Hz, 9 H, C(C*H*$_3$)$_3$), 0.17 – 0.91 (m, 3 H, B*H*$_3$). ^{13}C NMR (101 MHz, $CDCl_3$): δ 144.1 (s, Ar), 133.0 (d, $J_{C\text{-}P}$ = 8.4 Hz, Ar), 126.4 (d, $J_{C\text{-}P}$ = 51.5 Hz, Ar), 126.4 (d, $J_{C\text{-}P}$ = 10.1 Hz, Ar), 64.4 (s, *C*H$_2$), 28.4 (d, $J_{C\text{-}P}$ = 33.0 Hz, *C*(CH$_3$)$_3$), 25.0 (d, $J_{C\text{-}P}$ = 2.6 Hz, C(*C*H$_3$)$_3$), 5.2 (d, $J_{C\text{-}P}$ = 37.8 Hz, *C*H$_3$). ^{31}P NMR (162 MHz, $CDCl_3$): δ 24.6 (q, *J* = 68.0 Hz). HRMS (ESI): m/z: $[M+H\text{-}BH_3]^+$ calculated for $C_{12}H_{20}OP$: 211.1246, found 211.1246. HPLC (Daicel Chiralcel OD-H, *n*-hexane/*i*-PrOH = 90/10, UV = 254 nm, flow rate = 1.0 mL/min) t_{R1} = 9.399 min (major) and t_{R2} = 12.921 min (minor), ee = 84%. $[\alpha]_D^{25}$ = +58.0 (c = 2.0, $CHCl_3$).



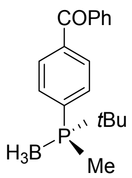
(*R*)-*tert*-butyl(4-chlorophenyl)(methyl)phosphine Borane. Performed according to the general procedure to afford 46 mg (68%) of (*R*)-**2j** as white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61 – 7.69 (m, 2 H, Ar), 7.41 – 7.48 (m, 2 H, Ar), 1.57 (d, *J* = 9.7 Hz, 3 H, C*H*$_3$), 1.10 (d, *J* = 14.1 Hz, 9 H, C(C*H*$_3$)$_3$), 0.11 - 0.95 (m, 3 H, B*H*$_3$). ^{13}C NMR (101 MHz, $CDCl_3$): δ 137.8 (s, Ar), 134.2 (d, $J_{C\text{-}P}$ = 8.9 Hz, Ar), 128.6 (d, $J_{C\text{-}P}$ = 9.9 Hz, Ar), 126.6 (d, $J_{C\text{-}P}$ = 50.5 Hz, Ar), 28.6 (d, $J_{C\text{-}P}$ = 30.3 Hz, *C*(CH$_3$)$_3$), 25.1 (d, $J_{C\text{-}P}$ = 2.7 Hz, C(*C*H$_3$)$_3$), 5.3 (d, $J_{C\text{-}P}$ = 38.4 Hz, *C*H$_3$). ^{31}P NMR (162 MHz, $CDCl_3$): δ 25.5 (q, *J* = 59.9 Hz). HRMS (ESI): m/z: $[M+H\text{-}BH_3]^+$ calculated for $C_{11}H_{17}ClP$: 215.0751, found 215.0752. HPLC (Daicel Chiralcel AS-H, *n*-hexane/*i*-PrOH = 99/1, UV = 234 nm, flow rate = 1.0 mL/min) t_{R1} = 9.339 min (major) and t_{R2} = 11.765 min (minor), ee = 94%. $[\alpha]_D^{25}$ = +1.5 (c = 2.0, $CHCl_3$).



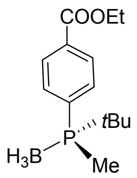
(*R*)-*tert*-butyl(methyl)(4-(trifluoromethyl)phenyl)phosphine Borane. Performed according to the general procedure to afford 47 mg (60%) of (*R*)-**2k** as yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.83 - 7.88 (m, 2 H, Ar), 7.72 (d, *J* = 8.0 Hz, 2 H, Ar), 1.61 (d, *J* = 9.5 Hz, 3 H, C*H*$_3$), 1.12 (d, *J* = 14.2 Hz, 9 H, C(C*H*$_3$)$_3$), 0.21 – 0.94 (m, 3 H, B*H*$_3$). ^{13}C NMR (101 MHz, $CDCl_3$): δ 133.3 (d, $J_{C\text{-}P}$ = 8.4 Hz, Ar), 133.2 (d, $J_{C\text{-}F}$ = 2.0 Hz, Ar), 133.0 (d, $J_{C\text{-}F}$ = 5.1 Hz, Ar), 132.4 (s, Ar), 123.6 (q, $J_{C\text{-}F}$ = 273.7 Hz, *C*F$_3$), 122.2 (s, Ar), 28.6 (d, $J_{C\text{-}P}$ = 32.6 Hz, *C*(CH$_3$)$_3$), 25.1 (d, $J_{C\text{-}P}$ = 2.6 Hz, C(*C*H$_3$)$_3$), 5.2 (d, $J_{C\text{-}P}$ = 37.0 Hz, *C*H$_3$). ^{31}P NMR (162 MHz, $CDCl_3$): δ 26.9 (q, *J* = 40.5 Hz). ^{19}F NMR (377 MHz, $CDCl_3$): δ -63.1 (s). HRMS (ESI): m/z: $[M+H-BH_3]^+$ calculated for $C_{12}H_{17}F_3P$: 249.1014, found 249.1016. HPLC (Daicel Chiralcel AS-H, *n*-hexane/*i*-PrOH = 99/1, UV = 254 nm, flow rate = 1.0 mL/min) t_{R1} = 6.392 min (minor) ang t_{R2} = 6.672 min (major), ee = 89%. $[\alpha]_D^{25}$ = +5.5 (c = 2.0, $CHCl_3$).



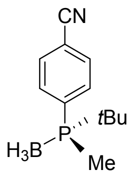
(*R*)-1-(4-(borane *tert*-butyl(methyl)phosphino)phenyl)ethan-1-one. Performed according to the general procedure to afford 20 mg (28%) of (*R*)-**2l** as white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95 – 8.05 (m, 2 H, Ar), 7.82 (t, *J* = 7.4 Hz, 2 H, Ar), 2.64 (d, *J* = 2.8 Hz, 3 H, COC*H*$_3$), 1.61 (d, *J* = 6.8 Hz, 3 H, C*H*$_3$), 1.12 (d, *J* = 14.2 Hz, 9 H, C(C*H*$_3$)$_3$). ^{13}C NMR (101 MHz, $CDCl_3$): δ 197.6 (s, *C*OCH$_3$), 138.8 (s, Ar), 133.2 (d, $J_{C\text{-}P}$ = 8.1 Hz, Ar), 127.7 (d, $J_{C\text{-}P}$ = 9.1 Hz, Ar), 28.8 (d, $J_{C\text{-}P}$ =30.3 Hz, *C*(CH$_3$)$_3$), 28.5(s, CO*C*H$_3$), 25.1 (d, $J_{C\text{-}P}$ = 2.7 Hz, C(*C*H$_3$)$_3$), 5.2 (d, $J_{C\text{-}P}$ = 38.4 Hz, *C*H$_3$). ^{31}P NMR (162 MHz, $CDCl_3$): δ 26.5 (q, *J* = 61.6 Hz). HRMS (ESI): m/z: $[M+H-BH_3]^+$ calculated for $C_{13}H_{20}OP$: 223.1246, found 223.1247. HPLC (Daicel Chiralcel OD-H, *n*-hexane/*i*-PrOH = 90/10, UV = 254 nm, flow rate = 1.0 mL/min) t_{R1} = 7.292 min (major) and t_{R2} = 8.536 min (minor), ee = 63%. $[\alpha]_D^{25}$ = +1.5 (c = 2.0, $CHCl_3$).



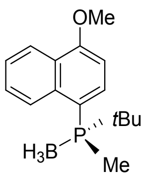
(*R*)-(4-(borane *tert*-butyl(methyl)phosphino)phenyl)(phenyl)methanone. Performed according to the general procedure to afford 22 mg (25%) of (*R*)-**2m** as yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77 – 7.90 (m, 6 H, Ar), 7.61 – 7.65 (m, 1 H, Ar), 7.49 – 7.53 (m, 2 H, Ar), 1.63 (d, *J* = 8.0 Hz, 3 H, C*H*$_3$), 1.14 (d, *J* = 12.0 Hz, 9 H, C(C*H*$_3$)$_3$), 0.11 – 1.02 (m, 3 H, B*H*$_3$). ^{13}C NMR (101 MHz, $CDCl_3$): δ 196.1 (s, *C*O), 139.8 (s, Ar), 136.8 (s, Ar), 133.0 (s, Ar), 132.8 (d, $J_{C\text{-}P}$ = 8.1 Hz, Ar), 132.4 (s, Ar), 131.6 (s, Ar), 130.2(s, Ar), 129.4 (d, $J_{C\text{-}P}$ = 10.0 Hz, Ar), 128.5 (s, Ar), 126.5 (s, Ar), 28.7 (d, $J_{C\text{-}P}$ =32.3 Hz, *C*(CH$_3$)$_3$), 25.2 (d, $J_{C\text{-}P}$ = 2.7 Hz, C(*C*H$_3$)$_3$), 5.2 (d, $J_{C\text{-}P}$ = 37.4 Hz, *C*H$_3$). ^{31}P NMR (162 MHz, $CDCl_3$): δ 26.5 (q, *J* = 76.1 Hz). HRMS (ESI): m/z: $[M+H-BH_3]^+$ calculated for $C_{18}H_{22}P$: 285.1408, found 285.1413. HPLC (Daicel Chiralcel OD-H, *n*-hexane/*i*-PrOH = 98/2, UV = 250 nm, flow rate = 1.0 mL/min) t_{R1} = 54.504 min (minor) and t_{R2} = 57.362 min (major), ee = 65%. $[\alpha]_D^{25}$ = +52.0 (c = 2.0, $CHCl_3$).



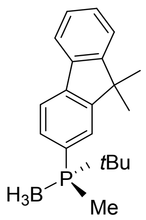
(*R*)-ethyl 4-(borane *tert*-butyl(methyl)phosphino)benzoate. Performed according to the general procedure to afford 50 mg (63%) of (*R*)-**2n** as yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.08 – 8.14 (m, 2 H, Ar), 7.76 – 7.83 (m, 2 H, Ar), 4.41 (q, *J* = 7.0 Hz, 2 H, CH_2CH_3), 1.61 (d, *J* = 9.8 Hz, 3 H, CH_2CH_3), 1.41 (t, *J* = 7.0 Hz, 3 H, CH_3), 1.11 (d, *J* = 14.0 Hz, 9 H, $C(CH_3)_3$), 0.19 – 0.94 (m, 3 H, BH_3). ^{13}C NMR (101 MHz, $CDCl_3$): δ 165.9 (s, CO_2Et), 133.4 (d, $J_{C\text{-}P}$ = 2.0 Hz, Ar), 132.9 (d, $J_{C\text{-}P}$ = 8.3 Hz, Ar), 132.8 (d, $J_{C\text{-}P}$ = 2.0 Hz, Ar), 129.1 (d, $J_{C\text{-}P}$ = 9.5 Hz, Ar), 61.4 (s, $CO_2CH_2CH_3$), 28.7 (d, $J_{C\text{-}P}$ = 33.3 Hz, $C(CH_3)_3$), 25.1(d, $J_{C\text{-}P}$ = 2.8 Hz, $C(CH_3)_3$), 14.3 (s, $CO_2CH_2CH_3$), 5.2 (d, $J_{C\text{-}P}$ = 37.4 Hz, CH_3). ^{31}P NMR (162 MHz, $CDCl_3$): δ 26.4 (q, *J* = 66.4 Hz). HRMS (ESI): m/z: $[M+H-BH_3]^+$ calculated for $C_{14}H_{22}O_2P$: 253.1352, found 253.1353. HPLC (Daicel Chiralcel OD-H, *n*-hexane/*i*-PrOH = 98/2, UV = 230 nm, flow rate = 0.8 mL/min) t_{R1} = 15.308 min (major) and t_{R2} = 16.976 min (minor), ee = 92%. $[\alpha]_D^{25}$ = +11.0 (c = 2.0, $CHCl_3$).



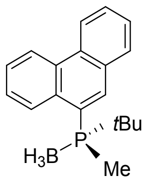
(*R*)-4-(borane *tert*-butyl(methyl)phosphino)benzonitrile. Performed according to the general procedure to afford 24 mg (36%) of (*R*)-**2o** as white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85 (d, *J* = 6.0 Hz, 2 H, Ar), 7.77 (d, *J* = 5.0 Hz, 2 H, Ar), 1.63 (d, *J* = 7.0 Hz, 3 H, CH_3), 0.98 – 1.19 (d, *J* = 14.0 Hz, 9 H, $C(CH_3)_3$), 0.11 – 0.95 (m, 3 H, BH_3). ^{13}C NMR (101 MHz, $CDCl_3$): δ 134.3 (d, $J_{C\text{-}P}$ = 44.4 Hz, Ar), 133.5 (d, $J_{C\text{-}P}$ = 7.1 Hz, Ar), 131.7 (d, $J_{C\text{-}P}$ = 8.1 Hz, Ar), 117.9 (s, *C*N), 115.0 (d, $J_{C\text{-}P}$ = 40.0 Hz, Ar), 28.6 (d, $J_{C\text{-}P}$ =30.3 Hz, $C(CH_3)_3$), 25.1 (d, $J_{C\text{-}P}$ = 2.7 Hz, $C(CH_3)_3$), 5.1 (d, J_{CP} = 40.4 Hz, CH_3). ^{31}P NMR (162 MHz, $CDCl_3$): δ 28.1 (q, *J* = 71.3 Hz). HRMS (ESI): m/z: $[M+H-BH_3]^+$ calculated for $C_{12}H_{17}NP$: 206.1093, found 206.1094. HPLC (Daicel Chiralcel OD-H, *n*-hexane/*i*-PrOH = 90/10, UV = 250 nm, flow rate = 1.0 mL/min) t_{R1} = 7.383 min (major) and t_{R2} = 8.712 min (minor), ee = 74%. $[\alpha]_D^{25}$ = +4.7 (c = 2.0, $CHCl_3$).



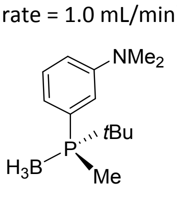
(*R*)-*tert*-butyl(4-methoxynaphthalen-1-yl)(methyl)phosphine Borane. Performed according to the general procedure to afford 37 mg (40%) of (*R*)-**2p** as white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.79 (d, *J* = 8.4 Hz, 1 H, Ar), 8.33 (d, *J* = 8.4 Hz, 1 H, Ar), 7.74 (s, 1 H, Ar), 7.47 - 7.63 (m, 2 H, Ar), 6.86 (d, *J* = 8.2 Hz, 1 H, Ar), 4.05 (s, 3 H, OCH_3), 1.76 (d, *J* = 9.0 Hz, 3H, CH_3), 1.15 (d, *J* = 14.0 Hz, 9 H, $C(CH_3)_3$), 0.21 - 0.88 (m, 3 H, BH_3). ^{13}C NMR (101 MHz, $CDCl_3$): δ 158.4 (d, $J_{C\text{-}P}$ = 3.0 Hz, Ar), 136.4 (d, $J_{C\text{-}P}$ = 11.1 Hz, Ar), 134.7 (d, $J_{C\text{-}P}$ = 6.1 Hz, Ar), 127.9 (d, $J_{C\text{-}P}$ = 5.1 Hz, Ar), 127.1 (s, Ar), 126.0 (d, $J_{C\text{-}P}$ = 8.1 Hz, Ar), 125.6 (s, Ar), 122.4 (s, Ar), 115.7 (d, $J_{C\text{-}P}$ = 49.5 Hz, Ar), 102.7 (d, $J_{C\text{-}P}$ = 11.1 Hz, Ar), 55.7 (s, O*Me*), 30.7 (d, $J_{C\text{-}P}$ = 32.3 Hz, $C(CH_3)_3$), 25.9 (d, $J_{C\text{-}P}$ = 3.0 Hz, $C(CH_3)_3$), 9.0 (d, $J_{C\text{-}P}$ = 39.4 Hz, CH_3). ^{31}P NMR (162 MHz, $CDCl_3$): δ 22.4 (q, *J* = 68.0 Hz). HRMS (ESI): m/z: $[M+H-BH_3]^+$ calculated for $C_{16}H_{22}OP$: 261.1403, found 261.1403. HPLC (Daicel Chiralcel OD-H, *n*-hexane/*i*-PrOH = 98/2, UV = 250 nm, flow rate = 1 mL/min) t_{R1} = 7.585 min (minor) and t_{R2} = 12.549 min (major), ee = 46%. $[\alpha]_D^{25}$ = +16.0 (c = 2.0, $CHCl_3$).



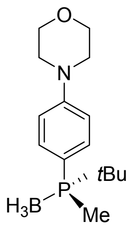
(*R*)-*tert*-butyl(9,9-dimethyl-9*H*-fluoren-2-yl)(methyl)phosphine Borane. Performed according to the general procedure to afford 76 mg (82%) of (*R*)-**2q** as white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72 – 7.81 (m, 3 H, Ar), 7.67 (t, *J* = 8.6 Hz, 1 H, Ar), 7.43 – 7.49 (m, 1 H, Ar), 7.34 – 7.38 (m, 2 H, Ar), 1.62 (t, *J* = 7.6 Hz, 3 H, C*H*3), 1.51 (d, *J* = 4.0 Hz, 6 H, C*H*3), 1.12 (d, *J* = 16.0 Hz, 9 H, $C(CH_3)_3$), 0.11 – 0.99 (m, 3 H, BH_3). ^{13}C NMR (101 MHz, $CDCl_3$): δ 154.1 (s, Ar), 153.5 (d, $J_{C\text{-}P}$ = 9.1 Hz, Ar), 142.2 (s, Ar), 138.0 (d, $J_{C\text{-}P}$ = 10.0 Hz, Ar), 131.8 (s, Ar), 131.7 (d, $J_{C\text{-}P}$ = 5.0 Hz, Ar), 128.4 (s, Ar), 127.2 (d, $J_{C\text{-}P}$ = 8.1 Hz, Ar), 126.0 (s, Ar), 122.8 (s, Ar), 120.7 (s, Ar), 119.7 (d, $J_{C\text{-}P}$ = 10.0 Hz, Ar), 47.0 (s, $C(CH_3)_2$), 28.6 (d, $J_{C\text{-}P}$ = 34.4 Hz, $C(CH_3)_3$), 27.0 (s, $C(CH_3)_2$), 25.2 (d, $J_{C\text{-}P}$ = 2.8 Hz, $C(CH_3)_3$), 5.5 (d, $J_{C\text{-}P}$ = 38.4 Hz, CH_3). ^{31}P NMR (162 MHz, $CDCl_3$): δ 25.3 (q, *J* = 72.9 Hz). HRMS (ESI): m/z: $[M+H-BH_3]^+$ calculated for $C_{20}H_{26}P$: 297.1767, found 297.1769. HPLC (Daicel Chiralcel IBN-H, *n*-hexane/*i*-PrOH = 99/1, UV = 254 nm, flow rate = 0.5 mL/min) t_{R1} = 11.612 min (minor) and t_{R2} = 12.325 min (major), ee = 74%. $[\alpha]_D^{25}$ = +7.5 (c = 2.0, $CHCl_3$).



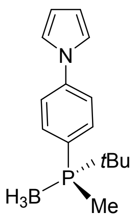
(*R*)-*tert*-butyl(methyl)(phenanthren-9-yl)phosphine Borane. Performed according to the general procedure to afford 79 mg (85%) of (*R*)-**2r** as white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.96 (d, *J* = 8.1 Hz, 1 H, Ar), 8.68 – 8.74 (m, 2 H, Ar), 8.08 (d, *J* = 12.4 Hz, 1 H, Ar), 7.94 (d, *J* = 7.7 Hz, 1 H, Ar), 7.61 – 7.80 (m, 4 H, Ar), 1.87 (d, *J* = 9.0 Hz, 3 H, CH_3), 1.21 (d, *J* = 14.1 Hz, 9 H, $C(CH_3)_3$), 0.11 - 0.94 (m, 3 H, BH_3). ^{13}C NMR (101 MHz, $CDCl_3$): δ 136.2 (d, $J_{C\text{-}P}$ = 4.0 Hz, Ar), 132.7 (d, $J_{C\text{-}P}$ = 7.1 Hz, Ar), 131.7 (d, $J_{C\text{-}P}$ = 2.0 Hz, Ar), 130.6 (d, $J_{C\text{-}P}$ = 7.1 Hz, Ar), 130.0 (d, $J_{C\text{-}P}$ = 10.0 Hz, Ar), 129.5 (s, Ar), 129.4 (d, $J_{C\text{-}P}$ = 17.2 Hz, Ar), 128.8 (s, Ar), 127.1 (d, $J_{C\text{-}P}$ = 6.1 Hz, Ar), 126.6 (s, Ar), 124.3 (d, $J_{C\text{-}P}$ = 47.5 Hz, Ar), 122.8 (d, $J_{C\text{-}P}$ = 38.4 Hz, Ar), 30.7 (d, $J_{C\text{-}P}$ = 30.3 Hz, $C(CH_3)_3$), 26.1 (d, $J_{C\text{-}P}$ = 2.8 Hz, $C(CH_3)_3$), 9.2 (d, $J_{C\text{-}P}$ = 40.4 Hz, CH_3). ^{31}P NMR (162 MHz, $CDCl_3$): δ 24.6 (q, *J* = 58.3 Hz). HRMS (ESI): m/z: $[M+H-BH_3]^+$ calculated for $C_{19}H_{22}P$: 281.1454, found 281.1455. HPLC (Daicel Chiralcel AS-H, *n*-hexane/*i*-PrOH = 90/10, UV = 254 nm, flow rate = 1.0 mL/min) t_{R1} = 13.414 min (minor) and t_{R2} = 28.472 min (major), ee =91%. $[\alpha]_D^{25}$ = +13.5 (c = 2.0, $CHCl_3$).



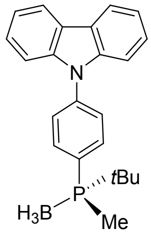
(*R*)-3-(borane *tert*-butyl(methyl)phosphino)-N,N-dimethylaniline. Performed according to the general procedure to afford 37 mg (52%) of (*R*)-**3a** as yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.26 – 7.39 (m, 1 H, Ar), 7.09 (d, *J* = 12.0 Hz, 1 H, Ar), 6.92 – 6.96 (m, 1 H, Ar), 6.82 (d, *J* = 8.0 Hz, 1 H, Ar), 2.98 (s, 6 H, $N(CH_3)_2$), 1.54 (d, *J* = 12.0 Hz, 3 H, CH_3), 1.12 (d, *J* = 24.0 Hz, 9 H, $C(CH_3)_3$), 0.18 – 0.74 (m, 3 H, BH_3) . ^{13}C NMR (101 MHz, $CDCl_3$): δ 150.1 (d, $J_{C\text{-}P}$ = 11.8 Hz, Ar), 128.8 (d, $J_{C\text{-}P}$ = 10.3 Hz, Ar), 127.3 (d, $J_{C\text{-}P}$ = 51.5 Hz, Ar), 120.1 (d, $J_{C\text{-}P}$ = 6.0 Hz, Ar), 117.2 (d, $J_{C\text{-}P}$ = 12.8 Hz, Ar), 114.8 (d, $J_{C\text{-}P}$ = 2.3 Hz, Ar), 40.4 (s, $N(CH_3)_2$), 28.5 (d, $J_{C\text{-}P}$ = 30.3 Hz, $C(CH_3)_3$), 25.4 (d, $J_{C\text{-}P}$ = 2.7 Hz, $C(CH_3)_3$), 5.4 (d, $J_{C\text{-}P}$ = 38.4 Hz, CH_3). ^{31}P NMR (162 MHz, $CDCl_3$): δ 25.6 (q, *J* = 64.8 Hz). HRMS (ESI): m/z: $[M+H-BH_3]^+$ calculated for $C_{13}H_{23}NP$: 224.1563, found 224.1562. HPLC (Daicel Chiralcel OD-H, *n*-hexane/*i*-PrOH = 98/2, UV = 250 nm, flow rate = 0.8 mL/min) t_{R1} = 8.667 min (minor) and t_{R2} = 10.155 min (major), ee = 80%. $[\alpha]_D^{25}$ = +24.0 (c = 2.0, $CHCl_3$).



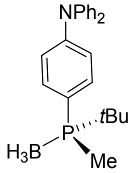
(*R*)-4-(4-(borane *tert*-butyl(methyl)phosphino)phenyl)morpholine. Performed according to the general procedure to afford 44 mg (53%) of (*R*)-**3b** as white solid. ^1H NMR (400 MHz, $CDCl_3$): δ 7.55 – 7.60 (m, 2 H, Ar), 6.91 – 6.94 (m, 2 H, Ar), 3.84 – 3.87 (m, 4 H, C*H₂*), 3.23 – 3.25 (m, 4 H, C*H₂*), 1.52 (d, *J* = 9.7 Hz, 3 H, C*H₃*), 1.09 (d, *J* = 13.9 Hz, 9 H, C(C*H₃*)₃), 0.25 – 0.84 (m, 3 H, B*H₃*). ^{13}C NMR (101 MHz, $CDCl_3$): δ 152.8 (d, J_{C-P} = 3.0 Hz, Ar), 134.1 (d, J_{C-P} = 9.1 Hz, Ar), 116.0 (d, J_{C-P} = 56.6 Hz, Ar), 114.1 (d, J_{C-P} = 10.1 Hz, Ar), 66.6 (s, *C*H₂), 47.8 (s, *C*H₂), 28.7 (d, J_{C-P} = 34.3 Hz, *C*(CH₃)₃), 25.1 (d, J_{C-P} = 3.0 Hz, C(*C*H₃)₃), 5.3 (d, J_{C-P} = 38.4 Hz, *C*H₃). ^{31}P NMR (162 MHz, $CDCl_3$): δ 22.4 (q, *J* = 74.5 Hz). HRMS (ESI): m/z: $[M+H-BH_3]^+$ calculated for $C_{15}H_{25}NOP$: 266.1668, found 266.1668. HPLC (Daicel Chiralcel OD-H, *n*-hexane/*i*-PrOH = 90/10, UV = 250 nm, flow rate = 1.0 mL/min) t_{R1} = 11.953 min (major) and t_{R2} = 16.618 min (minor), ee = 46%. $[\alpha]_D^{25}$ = +24.0 (c = 2.0, $CHCl_3$).



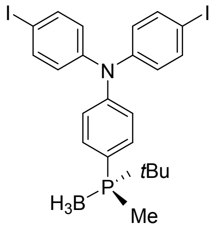
(*R*)-1-(4-(borane *tert*-butyl(methyl)phosphino)phenyl)-1*H*-pyrrole. Performed according to the general procedure to afford 57 mg (74%) of (*R*)-**3c** as white solid. ^1H NMR (400 MHz, $CDCl_3$): δ 7.74 – 7.79 (m, 2 H, Ar), 7.46 – 7.49 (m, 2 H, Ar), 7.13 – 7.15 (m, 2 H, Ar), 6.38 – 6.39 (m, 2 H, Ar), 1.59 (d, *J* = 3.0 Hz, 3 H, C*H₃*), 1.13 (d, *J* = 4.0 Hz, 9 H, C(C*H₃*)₃), 0.11 – 1.07 (m, 3 H, B*H₃*). ^{13}C NMR (101 MHz, $CDCl_3$): δ 142.7 (d, J_{C-P} = 3.0 Hz, Ar), 134.4 (d, J_{C-P} = 9.9 Hz, Ar), 124.2 (d, J_{C-P} = 51.2 Hz, Ar), 119.5 (d, J_{C-P} = 10.0 Hz, Ar), 119.0 (s, Ar), 111.4 (s, Ar), 28.7 (d, J_{C-P} = 33.3 Hz, *C*(CH₃)₃), 25.1 (d, J_{C-P} = 3.0 Hz, C(*C*H₃)₃), 5.3 (d, J_{C-P} = 37.4 Hz, *C*H₃). ^{31}P NMR (162 MHz, $CDCl_3$): δ 24.6 (q, *J* = 68.0 Hz). HRMS (ESI): m/z: $[M+H-BH_3]^+$ calculated for $C_{15}H_{21}NP$: 246.1406, found 246.1407. HPLC (Daicel Chiralcel OD-H, *n*-hexane/*i*-PrOH = 98/2, UV = 254 nm, flow rate = 0.8 mL/min) t_{R1} = 13.659 min (minor) and t_{R2} = 15.300 min (major), ee = 94%. $[\alpha]_D^{25}$ = +0.5 (c = 2.0, $CHCl_3$).



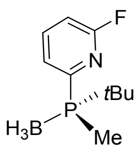
(*R*)-9-(4-(borane *tert*-butyl(methyl)phosphino)phenyl)-9*H*-carbazole. Performed according to the general procedure to afford 67.8 mg (63%) of (*R*)-**3d** as white solid. ^1H NMR (400 MHz, $CDCl_3$): δ 8.15 (d, *J* = 8.0 Hz, 2 H, Ar), 7.93 – 7.98 (m, 2 H, Ar), 7.70 – 7.72 (m, 2 H, Ar), 7.41 – 7.49 (m, 4 H, Ar), 7.30 – 7.34 (m, 2 H, Ar), 1.67 (d, *J* = 8.0 Hz, 3 H, C*H₃*), 1.21 (d, *J* = 16.0 Hz, 9 H, C(C*H₃*)₃), 0.26 – 0.93 (m, 3 H, B*H₃*). ^{13}C NMR (101 MHz, $CDCl_3$): δ 140.5 (d, J_{C-P} = 2.0 Hz, Ar), 140.2 (s, Ar), 134.5 (d, J_{C-P} = 9.1 Hz, Ar), 126.7 (s, Ar), 126.3 (d, J_{C-P} = 10.0 Hz, Ar), 126.1 (s, Ar), 123.7 (s, Ar), 120.5 (d, J_{C-P} = 6.1 Hz, Ar), 109.7 (s, Ar), 28.7 (d, J_{C-P} = 33.3 Hz, *C*(CH₃)₃), 25.2 (d, J_{C-P} = 3.0 Hz, C(*C*H₃)₃), 5.4 (d, $J_{C\text{-}P}$ = 37.4 Hz, CH_3). ^{31}P NMR (162 MHz, $CDCl_3$): δ 25.6 (q, J = 53.5 Hz). HRMS (ESI): m/z: $[M+H-BH_3]^+$ calculated for $C_{23}H_{25}NP$: 346.1719, found 346.1721. HPLC (Daicel Chiralcel AS-H, *n*-hexane/*i*-PrOH = 98/2, UV = 254 nm, flow rate = 0.5 mL/min) t_{R1} = 18.239 min (major) and t_{R2} = 20.275 min (minor), ee = 69%. $[\alpha]_D^{25}$ = +4.5 (c = 2.0, $CHCl_3$).



(*R*)-4-(borane *tert*-butyl(methyl)phosphino)-*N*,*N*-diphenylaniline. Performed according to the general procedure to afford 58 mg (47%) of (*R*)-**3e** as white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46 – 7.51 (m, 2 H, Ar), 7.28 – 7.32 (m, 4 H, Ar), 7.09 – 7.14 (m, 6 H, Ar), 7.02 – 7.04 (m, 2 H, Ar), 1.52 (d, J = 8.0 Hz, 3 H, CH_3), 1.11 (d, J = 12.0 Hz, 9 H, $C(CH_3)_3$), 0.26 – 0.86 (m, 3 H, BH_3). ^{13}C NMR (101 MHz, $CDCl_3$): δ 150.3 (d, $J_{C\text{-}P}$ = 2.0 Hz, Ar), 146.7 (s, Ar), 133.8 (d, $J_{C\text{-}P}$ = 9.1 Hz, Ar), 125.6 (s, Ar), 124.2 (s, Ar), 120.4 (d, $J_{C\text{-}P}$ = 10.0 Hz, Ar), 118.4 (s, Ar), 117.8 (s, Ar), 28.7 (d, $J_{C\text{-}P}$ = 33.3 Hz, $C(CH_3)_3$), 25.2 (d, $J_{C\text{-}P}$ = 3.0 Hz, $C(CH_3)_3$), 5.4 (d, $J_{C\text{-}P}$ = 38.4 Hz, CH_3) ^{31}P NMR (162 MHz, $CDCl_3$): δ 25.4 (q, J = 61.6 Hz). HRMS (ESI): m/z: $[M+H-BH_3]^+$ calculated for $C_{23}H_{27}NP$: 348.1876, found 348.1877. HPLC (Daicel Chiralcel OD-H, *n*-hexane/*i*-PrOH = 98/2, UV = 250 nm, flow rate = 1.0 mL/min) t_{R1} = 5.476 min (minor) and t_{R2} = 5.912 min (major), ee = 84%. $[\alpha]_D^{25}$ = +8.0 (c = 2.0, $CHCl_3$).

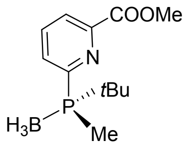


(*R*)-4-(borane *tert*-butyl(methyl)phosphino)-*N*,*N*-bis(4-iodophenyl)aniline. Performed according to the general procedure to afford 93.7 mg (51%) of (*R*)-**3f** as white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46 – 7.51 (m, 2 H, Ar), 7.28 – 7.32 (m, 4 H, Ar), 7.13 (d, J = 8.0 Hz, 4 H, Ar), 7.02 – 7.04 (m, 2 H, Ar), 1.52 (d, J = 8.0 Hz, 3 H, CH_3), 1.12 (d, J = 12.0 Hz, 9 H, $C(CH_3)_3$), 0.26 – 0.86 (m, 3 H, BH_3). ^{13}C NMR (101 MHz, $CDCl_3$): δ 149.2 (d, $J_{C\text{-}P}$ = 3.0 Hz, Ar), 146.1 (s, Ar), 138.6 (s, Ar), 134.0 (d, $J_{C\text{-}P}$ = 9.1 Hz, Ar), 127.7 (d, $J_{C\text{-}P}$ = 39.9 Hz, Ar), 121.6 (d, $J_{C\text{-}P}$ = 10.1 Hz, Ar), 120.5 (s, Ar), 87.6 (s, Ar), 28.6 (d, $J_{C\text{-}P}$ = 33.3 Hz, $C(CH_3)_3$), 25.2 (d, $J_{C\text{-}P}$ = 2.0 Hz, $C(CH_3)_3$), 5.3 (d, $J_{C\text{-}P}$ = 38.4 Hz, CH_3). ^{31}P NMR (162 MHz, $CDCl_3$): δ 23.7 (q, J = 38.9 Hz). HRMS (ESI): m/z: $[M+H-BH_3]^+$ calculated for $C_{23}H_{25}I_2NP$: 599.9808, found 599.9811. HPLC (Daicel Chiralcel OD-H, *n*-hexane/*i*-PrOH = 90/10, UV = 254 nm, flow rate = 1.0 mL/min) t_{R1} = 9.428 min (major) and t_{R2} = 11.065 min (minor), ee = 94%. $[\alpha]_D^{25}$ = +1.5 (c = 2.0, $CHCl_3$).

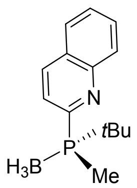


(*R*)-2-(borane *tert*-butyl(methyl)phosphino)-6-fluoropyridine. Performed according to the general procedure to afford 59 mg (62%) of (*R*)-**3g** as white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88 – 7.92 (m, 1 H, Ar), 7.69 – 7.73 (m, 1 H, Ar), 7.37 (d, J = 8.0 Hz, 1 H, Ar), 1.60 (d, J = 8.0 Hz, 3 H, CH_3), 1.11 (d, J = 16.0 Hz, 9 H, $C(CH_3)_3$), 0.26 – 0.98 (m, 3 H, BH_3). ^{13}C NMR (101 MHz, $CDCl_3$): δ 154.5 (d, $J_{C\text{-}P}$ = 61.6 Hz, Ar), 151.5 (d, $J_{C\text{-}P}$ = 11.1 Hz, Ar), 138.4 (d, $J_{C\text{-}P}$ = 10.0 Hz, Ar), 129.1 (d, $J_{C\text{-}P}$ = 23.2 Hz, Ar), 125.7 (d, $J_{C\text{-}P}$ = 2.0 Hz, Ar), 28.8 (d, $J_{C\text{-}P}$ = 32.3 Hz, $C(CH_3)_3$), 25.2 (d, $J_{C\text{-}P}$ = 3.0 Hz, $C(CH_3)_3$), 4.5 (d, $J_{C\text{-}P}$ = 39.4 Hz, CH_3). ^{31}P NMR (162 MHz, $CDCl_3$): δ 30.3 (q, J = 61.6 Hz). ^{19}F NMR (376 MHz, $CDCl_3$): δ -68.4 (s). HRMS (ESI): m/z: $[M+H-BH_3]^+$ calculated for $C_{10}H_{16}FNP$: 200.0999, found 200.1001. HPLC (Daicel

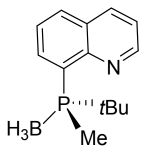
Chiralcel AS-H, *n*-hexane/*i*-PrOH = 98/2, UV = 250 nm, flow rate = 1.0 mL/min) t_{R1} = 11.503 min (minor) and t_{R2} = 12.124 min (major), ee = 97%. $[\alpha]_D^{25}$ = +12.0 (c = 2.0, $CHCl_3$).



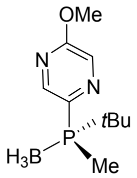
(*R*)-methyl 6-(borane *tert*-butyl(methyl)phosphino)picolinate. Performed according to the general procedure to afford 35.7 mg (47%) of (*R*)-**3h** as white solid. ^1H NMR (400 MHz, $CDCl_3$): ^1H NMR (400 MHz, $CDCl_3$): δ 8.11 – 8.15 (m, 2 H, Ar), 7.86 – 7.91 (m, 1 H, Ar), 3.97 (s, 3 H, C*H*$_3$), 1.66 (d, *J* = 8.0 Hz, 3 H, C*H*$_3$), 1.13 (d, *J* = 16.0 Hz, 9 H, C(C*H*$_3$)$_3$), 0.20 – 0.95 (m, 3 H, B*H*$_3$). ^{13}C NMR (101 MHz, $CDCl_3$): δ 165.2 (s, *C*O), 154.3 (d, $J_{C\text{-}P}$ = 64.6 Hz, Ar), 148.1 (d, $J_{C\text{-}P}$ = 11.1 Hz, Ar), 136.7 (d, $J_{C\text{-}P}$ = 8.1 Hz, Ar), 132.9 (d, $J_{C\text{-}P}$ = 25.3 Hz, Ar), 125.8 (d, $J_{C\text{-}P}$ = 2.0 Hz, Ar), 52.8 (s, *C*H$_3$), 28.8 (d, $J_{C\text{-}P}$ = 32.3 Hz, *C*(CH$_3$)$_3$), 25.3 (d, $J_{C\text{-}P}$ = 2.5 Hz, C(*C*H$_3$)$_3$), 4.6 (d, $J_{C\text{-}P}$ = 39.4 Hz, *C*H$_3$). ^{31}P NMR (162 MHz, $CDCl_3$): δ 30.3 (q, *J* = 66.4 Hz). HRMS (ESI): m/z: $[M+H-BH_3]^+$ calculated for $C_{12}H_{19}NO_2P$: 240.1148, found 240.1150. HPLC (Daicel Chiralcel AS-H, *n*-hexane/*i*-PrOH = 95/5, UV = 230 nm, flow rate = 1.0 mL/min) t_{R1} = 8.140 min (minor) and t_{R2} = 9.308 min (major), ee = 73%. $[\alpha]_D^{25}$ = +42.0 (c = 2.0, $CHCl_3$).



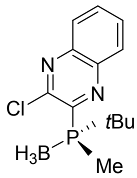
(*R*)-2-(borane *tert*-butyl(methyl)phosphino)quinoline. Performed according to the general procedure to afford 68 mg (56%) of (*R*)-**3i** as white solid. ^1H NMR (400 MHz, $CDCl_3$): δ 8.20 – 8.22 (m, 1 H, Ar), 8.15 (d, *J* = 8.0 Hz, 1 H, Ar), 8.02 – 8.05 (m, 1 H, Ar), 7.87 (d, *J* = 8.0 Hz, 1 H, Ar), 7.75 – 7.79 (m, 1 H, Ar), 7.60 – 7.64 (m, 1 H, Ar), 1.76 (d, *J* = 8.0 Hz, 3 H, C*H*$_3$), 1.18 (d, *J* = 16.0 Hz, 9 H, C(C*H*$_3$)$_3$), 0.25 – 1.11 (m, 3 H, B*H*$_3$). ^{13}C NMR (101 MHz, $CDCl_3$): δ 154.7 (s, Ar), 154.1 (s, Ar), 148.0 (d, $J_{C\text{-}P}$ = 13.1 Hz, Ar), 135.1 (d, $J_{C\text{-}P}$ = 10.0 Hz, Ar), 130.1 (s, Ar), 129.9 (s, Ar), 127.9 (s, Ar), 127.8 (s, Ar), 125.6 (d, $J_{C\text{-}P}$ = 26.3 Hz, Ar), 29.1 (d, $J_{C\text{-}P}$ = 32.3 Hz, *C*(CH$_3$)$_3$), 25.4 (d, $J_{C\text{-}P}$ = 3.0 Hz, C(*C*H$_3$)$_3$), 4.6 (d, $J_{C\text{-}P}$ = 40.4 Hz, *C*H$_3$). ^{31}P NMR (162 MHz, $CDCl_3$): δ 30.1 (q, *J* = 63.2 Hz). HRMS (ESI): m/z: $[M+H-BH_3]^+$ calculated for $C_{14}H_{19}NP$: 232.1250, found 232.1250. HPLC (Daicel Chiralcel AS-H, *n*-hexane/*i*-PrOH = 98/2, UV = 250 nm, flow rate = 0.8 mL/min) t_{R1} = 6.452 min (minor) and t_{R2} = 6.937 min (major), ee = 81%. $[\alpha]_D^{25}$ = +49.5 (c = 2.0, $CHCl_3$).



(*R*)-8-(borane *tert*-butyl(methyl)phosphino)quinoline. Performed according to the general procedure to afford 20.7 mg (20%) of (*R*)-**3j** as white solid. ^1H NMR (400 MHz, $CDCl_3$): δ 8.91 – 8.93 (m, 1 H, Ar), 8.50 – 8.55 (m, 1 H, Ar), 8.19 (d, *J* = 8.0 Hz, 1 H, Ar), 7.96 (d, *J* = 8.0 Hz, 1 H, Ar), 7.57 – 7.64 (m, 1 H, Ar), 7.42 – 7.45 (m, 1 H, Ar), 2.10 (d, *J* = 8.0 Hz, 3 H, C*H*$_3$), 1.18 (d, *J* = 12.0 Hz, 9 H, C(C*H*$_3$)$_3$), 0.26 - 0.90 (m, 3 H, B*H*$_3$). ^{13}C NMR (101 MHz, $CDCl_3$): δ 149.6 (d, $J_{C\text{-}P}$ = 2.0 Hz, Ar), 149.4 (s, Ar), 140.2 (d, $J_{C\text{-}P}$ = 16.2 Hz, Ar), 136.6 (s, Ar), 132.0 (d, $J_{C\text{-}P}$ = 2.5 Hz, Ar), 128.4 (d, $J_{C\text{-}P}$ = 5.1 Hz, Ar), 126.0 (s, Ar), 125.9 (s, Ar), 121.2 (s, Ar), 30.3 (d, $J_{C\text{-}P}$ = 34.3 Hz, *C*(CH$_3$)$_3$), 26.6 (d, $J_{C\text{-}P}$ = 3.0 Hz, C(*C*H$_3$)$_3$), 8.6 (d, $J_{C\text{-}P}$ = 39.4 Hz, *C*H$_3$). ^{31}P NMR (162 MHz, $CDCl_3$): δ 31.0 (q, *J* = 58.3 Hz). HRMS (ESI): m/z: $[M+H-BH_3]^+$ calculated for $C_{14}H_{19}NP$: 232.1250, found 232.1250. HPLC (Daicel Chiralcel OD-H, *n*-hexane/*i*-PrOH = 98/2 , UV = 250 nm, flow rate = 1.0 mL/min) t_{R1} = 6.324 min (minor) and t_{R2} = 7.473 min (major), ee = 71%. $[\alpha]_D^{25}$ = +42.0 (c = 2.0, $CHCl_3$).



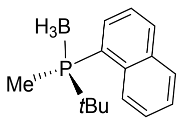
(*R*)-2-(borane *tert*-butyl(methyl)phosphino)-5-methoxypyrazine. Performed according to the general procedure to afford 40.0 mg (59%) of (*R*)-**3k** as white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.66 (s, 1 H, Ar), 8.31 (s, 1 H, Ar), 4.01 (s, 3 H, OCH_3), 1.58 (d, J = 8.0 Hz, 3 H, CH_3), 1.14 (d, J = 12.0 Hz, 9 H, $C(CH_3)_3$), 0.20 – 0.98 (m, 3 H, BH_3). ^{13}C NMR (101 MHz, $CDCl_3$): δ 161.0 (d, $J_{C\text{-}P}$ = 20.0 Hz, Ar), 147.5 (d, $J_{C\text{-}P}$ = 28.3 Hz, Ar), 138.7 (d, $J_{C\text{-}P}$ = 66.7 Hz, Ar), 136.2 (d, $J_{C\text{-}P}$ = 10.0 Hz, Ar), 55.0 (s, O*Me*), 28.9 (d, $J_{C\text{-}P}$ = 33.3 Hz, $C(CH_3)_3$), 25.3 (d, $J_{C\text{-}P}$ = 3.0 Hz, $C(CH_3)_3$), 4.7 (d, $J_{C\text{-}P}$ = 39.4 Hz, CH_3). ^{31}P NMR (162 MHz, $CDCl_3$): δ 24.4 (q, J = 59.9 Hz). HRMS (ESI): m/z: $[M+H-BH_3]^+$ calculated for $C_{10}H_{18}N_2OP$: 213.1151, found 213.1152. HPLC (Daicel Chiralcel OD-H, *n*-hexane/*i*-PrOH = 98/2, UV = 254 nm, flow rate = 0.8 mL/min) t_{R1} = 5.752 min (major) and t_{R2} = 6.206 min (minor), ee = 77%. $[\alpha]_D^{25}$ = +9.5 (c = 2.0, $CHCl_3$).



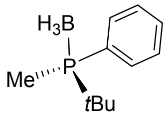
(*R*)-2-(borane *tert*-butyl(methyl)phosphino)-3-chloroquinoxaline. Performed according to the general procedure to afford 64 mg (76%) of (*R*)-**3l** as yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.15 – 8.17 (m, 1 H, Ar), 8.05 – 8.08 (m, 1 H, Ar), 7.83 – 7.92 (m, 2 H, Ar), 1.81 (d, J = 8.0 Hz, 3 H, CH_3), 1.28 (d, J = 12.0 Hz, 9 H, $C(CH_3)_3$), 0.18 – 1.14 (m, 3 H, BH_3). ^{13}C NMR (101 MHz, $CDCl_3$): δ 150.3 (d, $J_{C\text{-}P}$ = 22.6 Hz, Ar), 149.9 (d, $J_{C\text{-}P}$ = 9.3 Hz, Ar), 141.4 (s, Ar), 140.3 (s, Ar), 132.9 (s, Ar), 130.8 (s, Ar), 129.6 (s, Ar), 128.3 (s, Ar), 31.5 (d, $J_{C\text{-}P}$ = 29.3 Hz, $C(CH_3)_3$), 26.0 (d, $J_{C\text{-}P}$ = 2.0 Hz, $C(CH_3)_3$), 7.7 (d, $J_{C\text{-}P}$ = 41.4 Hz, CH_3). ^{31}P NMR (162 MHz, $CDCl_3$): δ 37.9 (q, J = 53.5 Hz). HRMS (ESI): m/z: $[M+H-BH_3]^+$ calculated for $C_{13}H_{17}ClN_2P$: 267.0812, found 267.0813. HPLC (Daicel Chiralcel OD-H, *n*-hexane/*i*-PrOH = 98/2 , UV = 254 nm, flow rate = 0.8 mL/min) t_{R1} = 11.847 min (minor) and t_{R2} = 13.672 min (major), ee = 94%. $[\alpha]_D^{25}$ = +2.5 (c = 2.0, $CHCl_3$).

3. Procedures of palladium-catalyzed C–P coupling reactions under microwave conditions

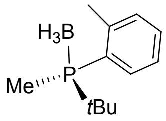
To a reaction tube, (*R*)-*tert*-butyl(methyl)phosphine borane (35 mg, 0.3 mmol), aryl and heteroaryl halides (0.5 mmol), $Pd(OAc)_2$ (3.37 mg, 0.015 mmol), dppf (27.75 mg, 0.03 mmol), *t*BuONa (57.66 mg, 0.60 mmol) and toluene (3 mL) were added under argon. The mixture was stirred for 6 h under microwave conditions. After removal of the volatile materials under reduced pressure, the crude product was purified by chromatograph on silica gel. (*n*-hexane / dichloromethane).



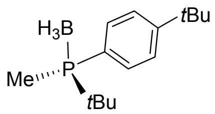
(*S*)-*tert*-butyl(methyl)(naphthalen-1-yl)phosphine Borane.[2] Performed according to the microwave reactions procedure to afford 47.2 mg (64%) of (*S*)-**2a** as white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.90 (d, J = 8.0 Hz, 1 H, Ar), 7.99 (d, J = 8.0 Hz, 1 H, Ar), 7.87 (d, J = 8.0 Hz, 1 H, Ar), 7.75 - 7.80 (m, 1 H, Ar), 7.61 - 7.75 (m, 1 H, Ar), 7.49 - 7.53 (m, 2 H, Ar), 1.78 (d, J = 12.0 Hz, 3 H, CH_3), 1.16 (d, J = 16.0 Hz, 9 H, $C(CH_3)_3$), 0.79 - 1.57 (m, 3 H, BH_3). ^{31}P NMR (162 MHz, $CDCl_3$): δ 23.9 (q, J = 66.4 Hz). HPLC (Daicel Chiralcel AS-H, *n*-hexane/*i*-PrOH = 95/5, UV = 250 nm, flow rate = 1.0 mL/min) t_{R1} = 5.430 min (major), ee = 99%. $[\alpha]_D^{25}$ = -23.0 (c = 2.0, $CHCl_3$).



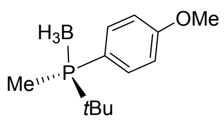
(*S*)-*tert*-butyl(methyl)(phenyl)phosphine Borane.[2] Performed according to the microwave reactions procedure to afford 50.6 mg (87%) of (*S*)-**2b** as white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.69 – 7.73 (m, 2 H, Ar), 7.43 – 7.52 (m, 3 H, Ar), 1.58 (d, *J* = 12.0 Hz, 3 H, C*H*$_3$), 1.11 (d, *J* = 12.0 Hz, 9 H, C(C*H*$_3$)$_3$), 0.24 – 1.07 (m, 3 H, B*H*$_3$). ^{31}P NMR (162 MHz, $CDCl_3$): δ 25.0 (q, *J* = 63.2 Hz). HPLC (Daicel Chiralcel AS-H, *n*-hexane/*i*-PrOH = 95/5, UV = 230 nm, flow rate = 1.0 mL/min) t_{R1} =7.908 min (major) and t_{R2} = 8.829 min (minor), ee = 99%. $[\alpha]_D^{25}$ = -14.5 (c = 2.0, $CHCl_3$).



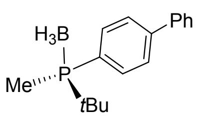
(*S*)-*tert*-butyl(methyl)(o-tolyl)phosphine Borane. [2] Performed according to the microwave reactions procedure to afford 40.7 mg (65%) of (*S*)-**2d** as white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52 – 7.56 (m, 1 H, Ar), 7.35 – 7.39 (m, 1 H, Ar), 7.23 – 7.26 (m, 2 H, Ar), 2.66 (s, 3 H, C*H*$_3$), 1.64 (d, *J* = 8.0 Hz, 3 H, C*H*$_3$), 1.14 (d, *J* = 16.0 Hz, 9 H, C(C*H*$_3$)$_3$), 0.19 – 1.10 (m, 3 H, B*H*$_3$). ^{31}P NMR (162 MHz, $CDCl_3$): δ 25.1 (q, *J* = 59.9 Hz). HPLC (Daicel Chiralcel OD-H, *n*-hexane/*i*-PrOH = 98/2, UV = 230 nm, flow rate = 0.5 mL/min) t_{R1} = 13.211 min (major) and t_{R2} = 14.302 min (minor), ee = 92%. $[\alpha]_D^{25}$ = -12.5 (c = 2.0, $CHCl_3$).



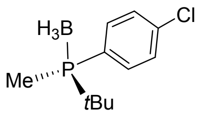
(*S*)-*tert*-butyl(4-(tert-butyl)phenyl)(methyl)phosphine Borane. Performed according to the microwave reactions procedure to afford 35.3 mg (50%) of (*S*)-**2e** as white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 – 7.65 (m, 2 H, Ar), 7.45 – 7.47 (m, 2 H, Ar), 1.55 (d, *J* = 8.0 Hz, 3 H, C*H*$_3$), 1.33 (s, 9 H, C(C*H*$_3$)$_3$), 1.11 (d, *J* = 12.0 Hz, 9 H, C(C*H*$_3$)$_3$), 0.18 – 1.05 (m, 3 H, B*H*$_3$). ^{31}P NMR (162 MHz, $CDCl_3$): δ 23.7 (q, *J* = 66.4 Hz). HPLC (Daicel Chiralcel AS-H, *n*-hexane/*i*-PrOH = 99/1, UV = 254 nm, flow rate = 1.0 mL/min) t_{R1} = 4.992 min (minor) and t_{R2} = 5.519 min (major), ee = 88%. $[\alpha]_D^{25}$ = -7.3 (c = 2.0, $CHCl_3$).



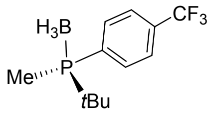
(*S*)-*tert*-butyl(4-methoxyphenyl)(methyl)phosphine Borane. Performed according to the microwave reactions procedure to afford 53.7 mg (80%) of (*S*)-**2f** as white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61 – 7.65 (m, 2 H, Ar), 6.96 – 6.98 (m, 2 H, Ar), 3.85 (s, 3 H, OC*H*$_3$), 1.54 (d, *J* = 8.0 Hz, 3 H, C*H*$_3$), 1.09 (d, *J* = 16.0 Hz, 9 H, C(C*H*$_3$)$_3$). 0.35 – 0.91 (m, 3 H, B*H*$_3$). ^{31}P NMR (162 MHz, $CDCl_3$): δ 23.2 (q, *J* = 69.7 Hz). HPLC (Daicel Chiralcel AS-H, n-hexane/i-PrOH = 98/2, UV = 250 nm, flow rate = 0.8 mL/min) t_{R1} = 21.932 min (major) and t_{R2} = 24.014 min (minor), ee = 95%. $[\alpha]_D^{25}$ = -8.3 (c = 2.0, $CHCl_3$).



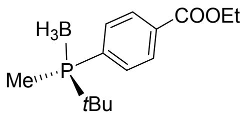
(*S*)-[1,1'-biphenyl]-4-yl(*tert*-butyl)(methyl)phosphine Borane. Performed according to the microwave reactions procedure to afford 57.4 mg (70%) of (*S*)-**2h** as white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75 – 7.81 (m, 2 H, Ar), 7.66 – 7.68 (m, 2 H, Ar), 7.61 (d, *J* = 4.0 Hz, 2 H, Ar), 7.45 – 7.49 (m, 2 H, Ar), 7.37 – 7.41 (m, 1 H, Ar), 1.61 (d, *J* = 12.0 Hz, 3 H, C*H*$_3$), 1.14 (d, *J* = 12.0 Hz, 9 H, C(C*H*$_3$)$_3$), 0.24 – 0.95 (m, 3 H, B*H*$_3$). ^{31}P NMR (162 MHz, $CDCl_3$): δ 24.7 (q, *J* = 77.8 Hz). HPLC (Daicel Chiralcel OD-H, n-hexane/i-PrOH = 95/5, UV = 250 nm, flow rate = 0.8 mL/min) t_{R1} = 7.872 min (minor) and t_{R2} = 8.778 min (major), ee = 93%. $[\alpha]_D^{25}$ = -12.0 (c = 2.0, $CHCl_3$).



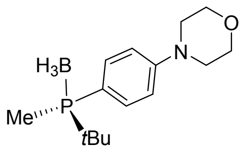
(*S*)-*tert*-butyl(4-chlorophenyl)(methyl)phosphine Borane. Performed according to the microwave reactions procedure to afford 46.6 mg (68%) of (*S*)-**2j** as white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.60 – 7.69 (m, 2 H, Ar), 7.37 – 7.51 (m, 2 H, Ar), 1.57 (d, J = 12.0 Hz, 3 H, CH_3), 1.10 (d, J = 16.0 Hz, 9 H, $C(CH_3)_3$), 0.22 – 0.85 (m, 3 H, BH_3). ^{31}P NMR (162 MHz, $CDCl_3$): δ 25.4 (q, J = 63.2 Hz). HPLC (Daicel Chiralcel AS-H, *n*-hexane/*i*-PrOH = 99/1, UV = 234 nm, flow rate = 1.0 mL/min) t_{R1} = 9.679 min (major) and t_{R2} = 12.252 min (minor), ee = 95%. $[\alpha]_D^{25}$ = -12.3 (c = 2.0, $CHCl_3$).



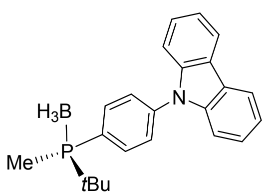
(*S*)-*tert*-butyl(methyl)(4-(trifluoromethyl)phenyl)phosphine Borane. Performed according to the microwave reactions procedure to afford 31.4 mg (40%) of (*S*)-**2k** as white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.83 – 7.88 (m, 2 H, Ar), 7.72 (d, J = 8.0 Hz, 2 H, Ar), 1.61 (d, J = 12.0 Hz, 3 H, CH_3), 1.13 (d, J = 12.0 Hz, 9 H, $C(CH_3)_3$), 0.25 – 0.85 (m, 3 H, BH_3). ^{31}P NMR (162 MHz, $CDCl_3$): δ 26.9 (q, J = 59.9 Hz). HPLC (Daicel Chiralcel AS-H, *n*-hexane/*i*-PrOH = 99/1, UV = 254 nm, flow rate = 1.0 mL/min) t_{R1} = 6.399 min (major) and t_{R2} = 6.745 min (minor), ee = 94%. $[\alpha]_D^{25}$ = -33.0 (c = 2.0, $CHCl_3$).



(*S*)-ethyl 4-(borane *tert*-butyl(methyl)phosphino)benzoate. Performed according to the microwave reactions procedure to afford 50.3 mg (63%) of (*S*)-**2n** as white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.10 – 8.12 (m, 2 H, Ar), 7.77 – 7.81 (m, 2 H, Ar), 4.41 (q, J = 7.1 Hz, 2 H, CH_2CH_3), 1.61 (d, J = 12.0 Hz, 3 H, CH_2CH_3), 1.39 – 1.43 (m, 3 H, CH_3), 1.11 (d, J = 16.0 Hz, 9 H, $C(CH_3)_3$), 0.21 – 0.87 (m, 3 H, BH_3). ^{31}P NMR (162 MHz, $CDCl_3$): δ 26.4 (q, J = 74.5 Hz). HPLC (Daicel Chiralcel OD-H, *n*-hexane/*i*-PrOH = 98/2, UV = 230 nm, flow rate = 0.8 mL/min) t_{R1} = 14.957 min (minor) and t_{R2} = 16.501 min (major), ee = 97%. $[\alpha]_D^{25}$ = -28.0 (c = 2.0, $CHCl_3$).

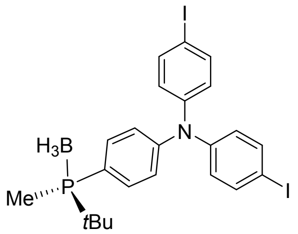


(*S*)-4-(4-(borane *tert*-butyl(methyl)phosphino)phenyl)morpholine. Performed according to the microwave reactions procedure to afford 65.8 mg (79%) of (*S*)-**3b** as white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 – 7.60 (m, 2 H, Ar), 6.91 – 6.94 (m, 2 H, Ar), 3.83 – 3.90 (m, 4 H, CH_2), 3.21 – 3.29 (m, 4 H, CH_2), 1.52 (d, J = 12.0 Hz, 3 H, CH_3), 1.09 (d, J = 16.0 Hz, 9 H, $C(CH_3)_3$), 0.19 – 0.88 (m, 3 H, BH_3). ^{31}P NMR (162 MHz, $CDCl_3$): δ 22.4 (q, J = 77.8 Hz). HPLC (Daicel Chiralcel OD-H, *n*-hexane/*i*-PrOH = 90/10, UV = 250 nm, flow rate = 1.0 mL/min) t_{R1} = 11.772 min (major) and t_{R2} = 16.287 min (minor), ee = 91%. $[\alpha]_D^{25}$ = -12.0 (c = 2.0, $CHCl_3$).

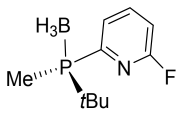


(*S*)-9-(4-(borane *tert*-butyl(methyl)phosphino)phenyl)-9*H*-carbazole. Performed according to the microwave reactions procedure to afford 52.1 mg (43%) of (*S*)-**3d** as white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.15 (d, J = 8.0

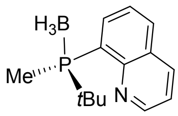
Hz, 2 H, Ar), 7.91 – 7.99 (m, 2 H, Ar), 7.67 – 7.74 (m, 2 H, Ar), 7.41 – 7.49 (m, 4 H, Ar), 7.29 – 7.35 (m, 2 H, Ar), 1.67 (d, *J* = 8.0 Hz, 3 H, C*H*$_3$), 1.21 (d, *J* = 16.0 Hz, 9 H, C(C*H*$_3$)$_3$), 0.26 – 0.93 (m, 3 H, B*H*$_3$). ^{31}P NMR (162 MHz, CDCl$_3$): δ 25.5 (q, *J* = 66.4 Hz). HPLC (Daicel Chiralcel AS-H, *n*-hexane/*i*-PrOH = 98/2, UV = 254 nm, flow rate = 0.5 mL/min) t_{R1} = 18.379 min (minor) and t_{R2} = 20.599 min (major), ee = 90%. $[\alpha]_D^{25}$ = -6.0 (c = 2.0, CHCl$_3$).



(*S*)-4-(borane *tert*-butyl(methyl)phosphino)-*N*,*N*-bis(4-iodophenyl)aniline. Performed according to the microwave reactions procedure to afford 81.5 mg (45%) of (*S*)-**3f** as white solid. ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.46 – 7.51 (m, 2 H, Ar), 7.28 – 7.32 (m, 4 H, Ar), 7.13 (d, *J* = 8.0 Hz, 4 H, Ar), 7.02 – 7.04 (m, 2 H, Ar), 1.52 (d, *J* = 8.0 Hz, 3 H, C*H*$_3$), 1.12 (d, *J* = 12.0 Hz, 9 H, C(C*H*$_3$)$_3$), 0.26 – 0.86 (m, 3 H, B*H*$_3$). ^{31}P NMR (162 MHz, CDCl$_3$): δ 23.7 (q, *J* = 45.4 Hz). HPLC (Daicel Chiralcel OD-H, *n*-hexane/*i*-PrOH = 90/10, UV = 254 nm, flow rate = 1.0 mL/min) t_{R1} = 9.797 min (minor) and t_{R2} = 11.418 min (major), ee = 95%. $[\alpha]_D^{25}$ = -6.5 (c = 2.0, CHCl$_3$).



(*S*)-2-(borane *tert*-butyl(methyl)phosphino)-6-fluoropyridine. Performed according to the microwave reactions procedure to afford 43.2 mg (56%) of (*S*)-**3g** as white solid. ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.88 – 7.92 (m, 1 H, Ar), 7.69 – 7.73 (m, 1 H, Ar), 7.37 (d, *J* = 8.0 Hz, 1 H, Ar), 1.60 (d, *J* = 8.0 Hz, 3 H, C*H*$_3$), 1.11 (d, *J* = 16.0 Hz, 9 H, C(C*H*$_3$)$_3$), 0.26 – 0.98 (m, 3 H, B*H*$_3$). ^{31}P NMR (162 MHz, CDCl$_3$): δ 30.5 (q, *J* = 61.6 Hz). HPLC (Daicel Chiralcel AS-H, *n*-hexane/*i*-PrOH = 98/2, UV = 250 nm, flow rate = 1.0 mL/min) t_{R1} = 11.471 min (major) and t_{R2} = 12.718 min (minor), ee = 93%. $[\alpha]_D^{25}$ = -34.0 (c = 2.0, CHCl$_3$).



(*S*)-8-(borane *tert*-butyl(methyl)phosphino)quinoline. Performed according to the microwave reactions procedure to afford 22.6 mg (26%) of (*S*)-**3j** as white solid. ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.91 – 8.93 (m, 1 H, Ar), 8.50 – 8.55 (m, 1 H, Ar), 8.19 (d, *J* = 8.0 Hz, 1 H, Ar), 7.96 (d, *J* = 8.0 Hz, 1 H, Ar), 7.57 – 7.64 (m, 1 H, Ar), 7.42 – 7.45 (m, 1 H, Ar), 2.10 (d, *J* = 8.0 Hz, 3 H, C*H*$_3$), 1.18 (d, *J* = 12.0 Hz, 9 H, C(C*H*$_3$)$_3$), 0.26 - 0.90 (m, 3 H, BH$_3$). ^{31}P NMR (162 MHz, CDCl$_3$): δ 31.0 (q, *J* = 63.2 Hz). HPLC (Daicel Chiralcel OD-H, *n*-hexane/*i*-PrOH = 98/2, UV = 250 nm, flow rate = 1.0 mL/min) t_{R1} = 6.791 min (major) and t_{R2} = 7.931 min (minor), ee = 71%. $[\alpha]_D^{25}$ = -27.0 (c = 2.0, CHCl$_3$).

4. X-ray structural determination

The X-ray date was collected on a Rigaku Saturn CCDC diffractometer using graphite-monochromated Mo K*α* radiation (λ = 0.71073 Å). The structure was solved by direct methods (SHELXS-97)[3] and refined by full-matrix least squares on F^2. All non-hydrogen atoms were refined anisotropically and hydrogen atoms by a riding model (SHELXL-97).[4] The crystal data and structural refinements details are listed in Table S1. CCDC 2017943 ((*S*)-**2q**), and CCDC 2017887 ((*R*)-**2h**) contain the supplementary crystallographic data for this paper. This data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table S1. Crystal Data and Summary of X-ray Data Collection for compound (*S*)-**2q** and (*R*)-**2h**

	(*S*)-**2q**	(*R*)-**2h**
formula	$C_{20}H_{28}BP$	$C_{17}H_{24}BP$
fw	310.20	270.14
T (K)	296	296
space group	P 21 21 21	P 21 21 21
crystal system	Orthorhombic	Orthorhombic
a (Å)	11.2902(16)	6.6359(9)
b (Å)	12.3392(18)	7.5137(10)
c (Å)	13.6341(19)	34.018(5)
α (deg.)	90°	90°
β (deg.)	90°	90°
γ (deg.)	90°	90°
V (Å3)	1899.4(5)	90(19)
Z	4	4
*d*calcd. (mg/cm3)	1.085	1.058
F(000)	672.0	584
GOF	1.078	1.248
R1 (*I* > 2*σ* (*I*))	0.0358	0.0840
*w*R2 (all data)	0.1017	0.1430

5. References

1. (*a*) E. Salomó, A. Prades, A. Riera, and X. Verdaguer, *J. Org. Chem.*, 2017, **82**, 7065; (*b*) E. Salomó, S. Orgué, A. Riera, X. Verdaguer, *Synthesis*, 2016, **48**, 2659.
2. D. Gatineau, L. Giordano and G. Buono, *J. Am. Chem. Soc.*, 2011, **133**, 10728.
3. G. M. Sheldrick, SHELXS-90/96, Program for Structure Solution, *Acta Crystallogr*. *Sect A* 1990, **46**, 467.
4. G. M. Sheldrick, SHELXL 97, Program for Crystal structure Refinement, University of Goettingen:Geottingen, Germany, 1997.

6. ^{1}H, ^{13}C, ^{19}F and ^{31}P NMR spectra for all products.

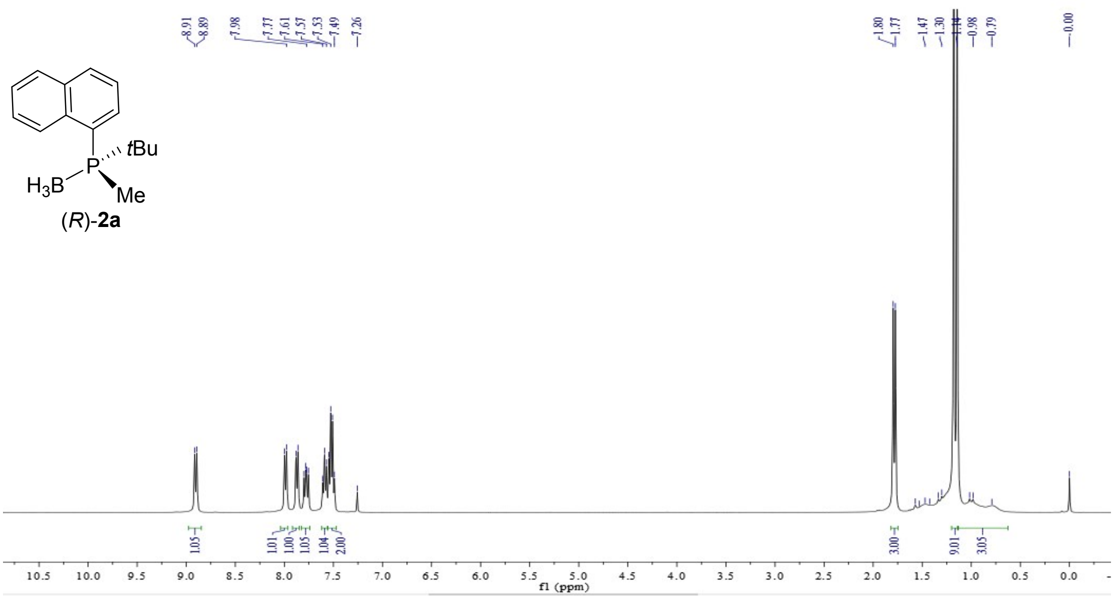


Figure S1. ^{1}H NMR spectrum of (*R*)-**2a** in $CDCl_3$

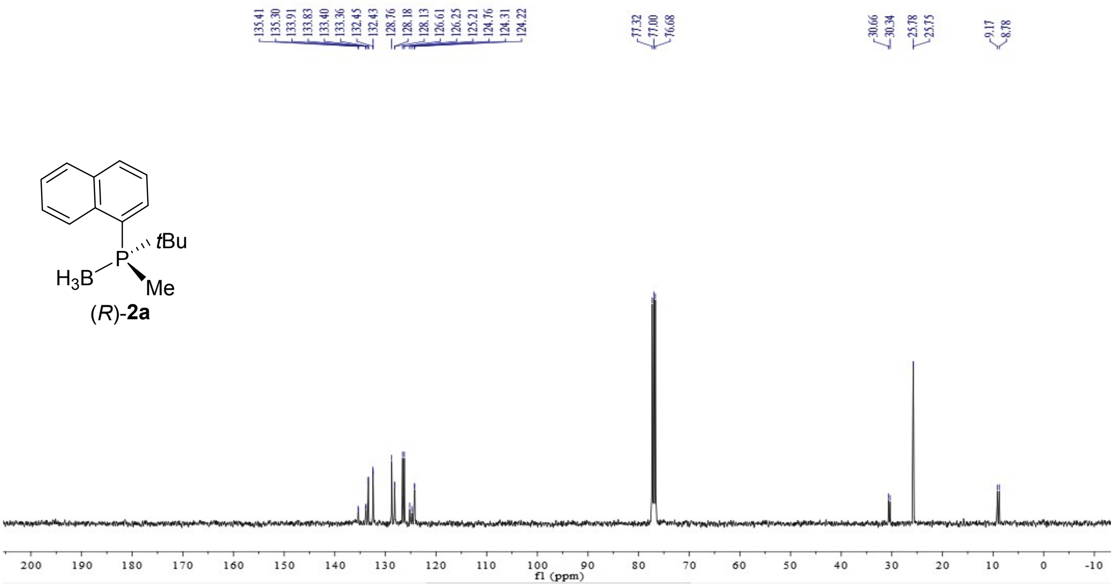


Figure S2. ^{13}C NMR spectrum of (*R*)-**2a** in $CDCl_3$

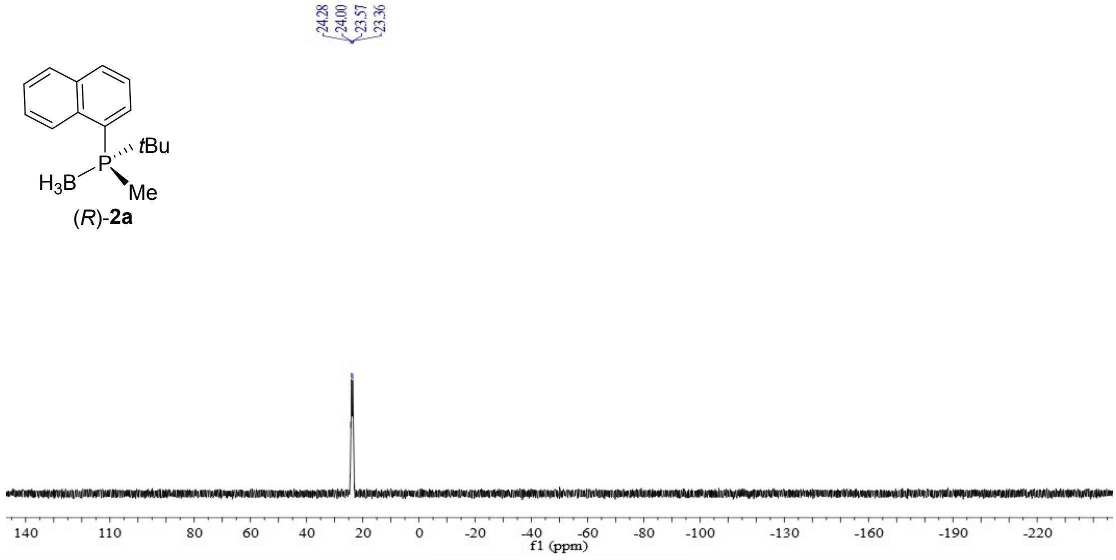


Figure S3. ^{31}P NMR spectrum of (*R*)-**2a** in $CDCl_3$

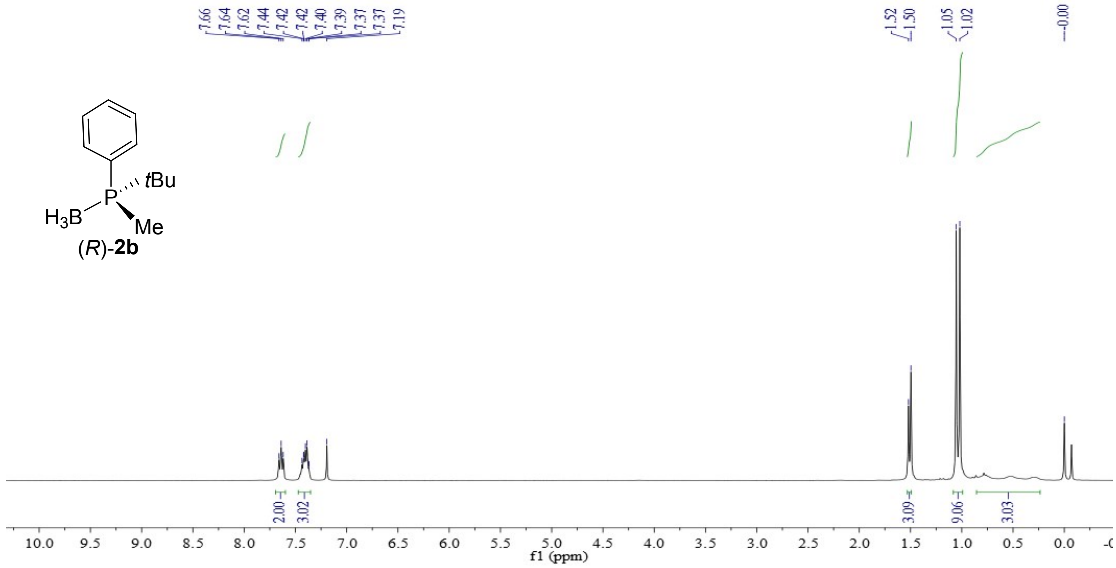


Figure S4. ^{1}H NMR spectrum of (*R*)-**2b** in $CDCl_3$

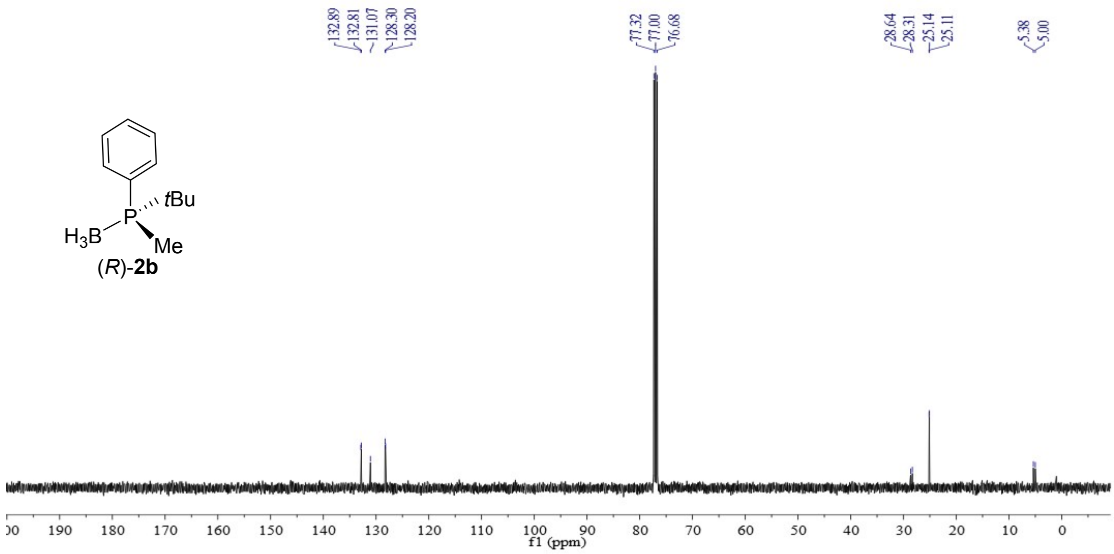


Figure S5. ^{13}C NMR spectrum of (*R*)-**2b** in $CDCl_3$

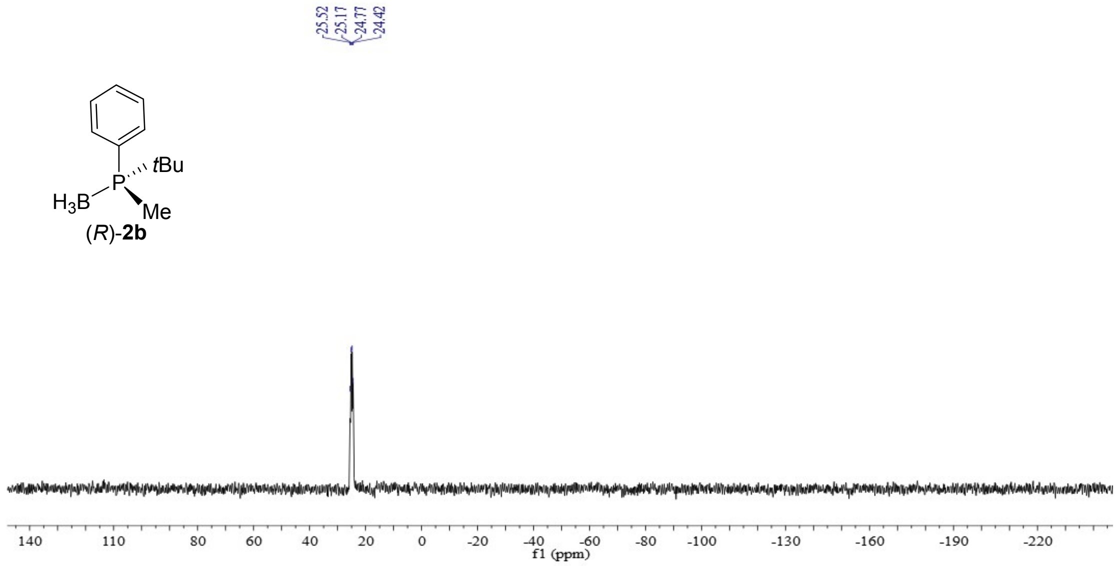


Figure S6. ^{31}P NMR spectrum of (*R*)-**2b** in $CDCl_3$

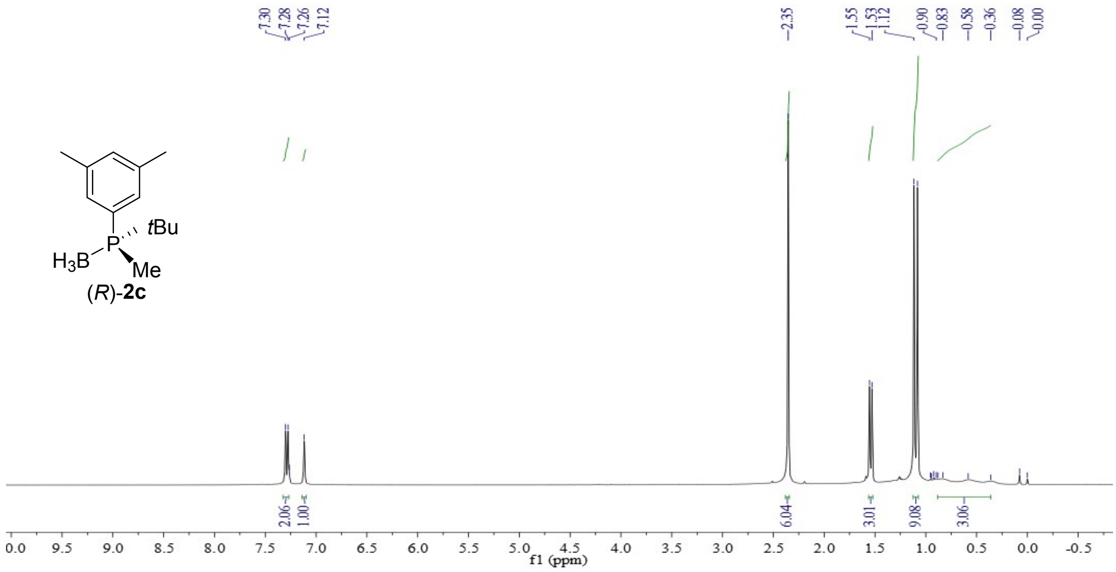


Figure S7. ^{1}H NMR spectrum of (*R*)-**2c** in $CDCl_3$

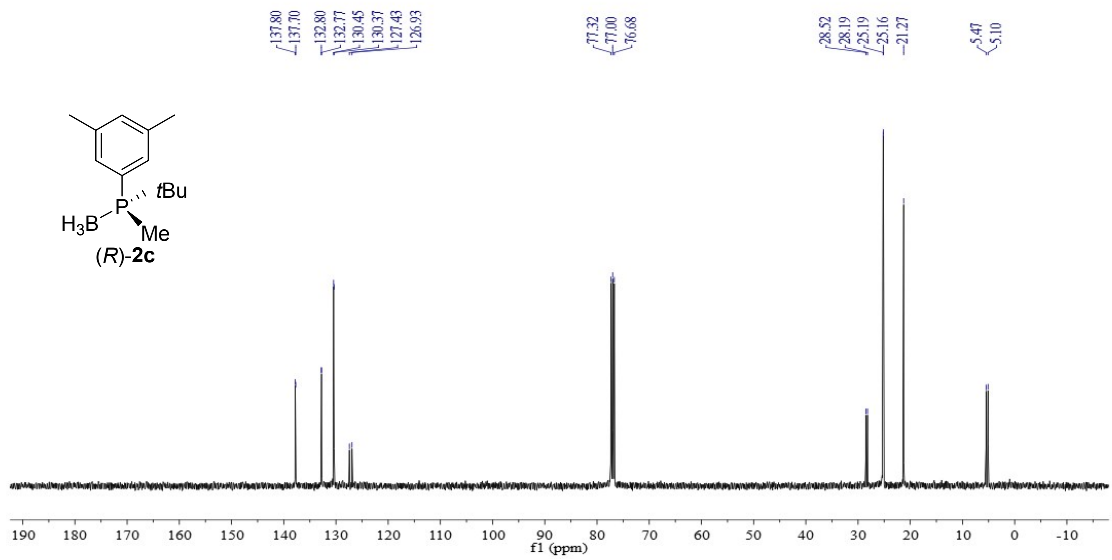


Figure S8. ^{13}C NMR spectrum of (*R*)-**2c** in $CDCl_3$

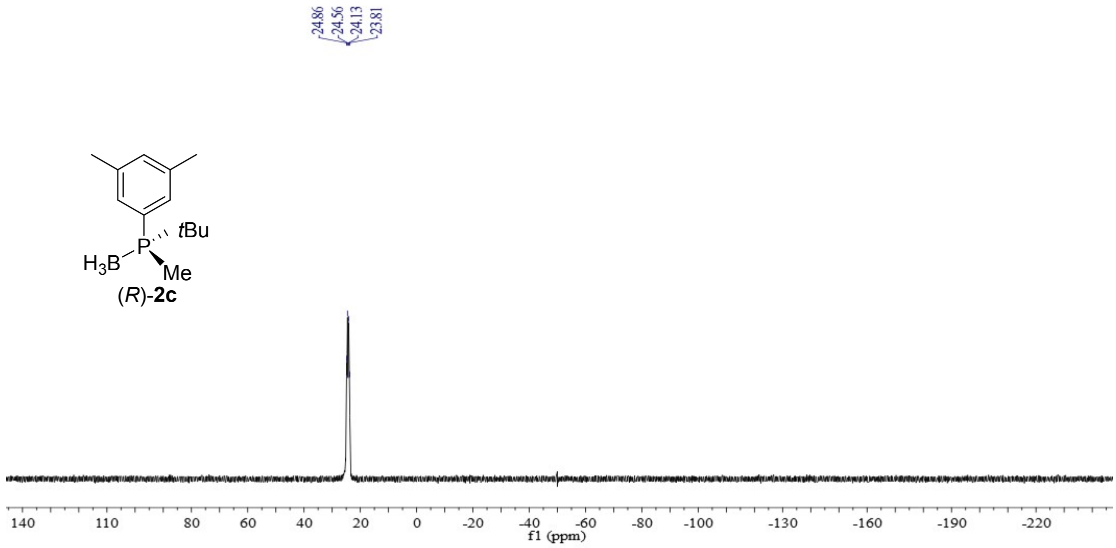


Figure S9. ^{31}P NMR spectrum of (*R*)-**2c** in $CDCl_3$

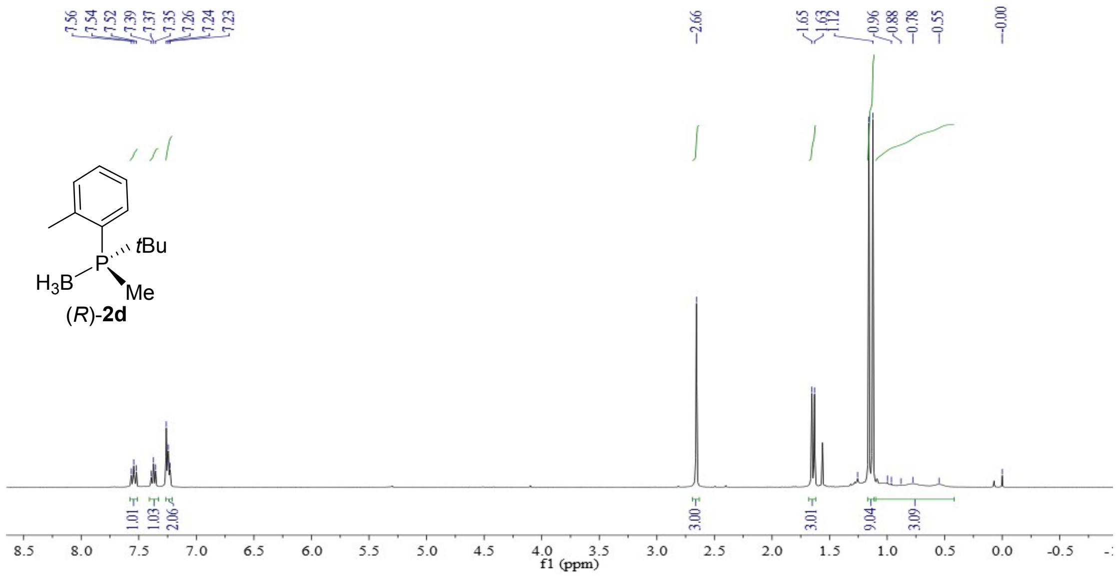


Figure S10. ^{1}H NMR spectrum of (*R*)-**2d** in $CDCl_3$

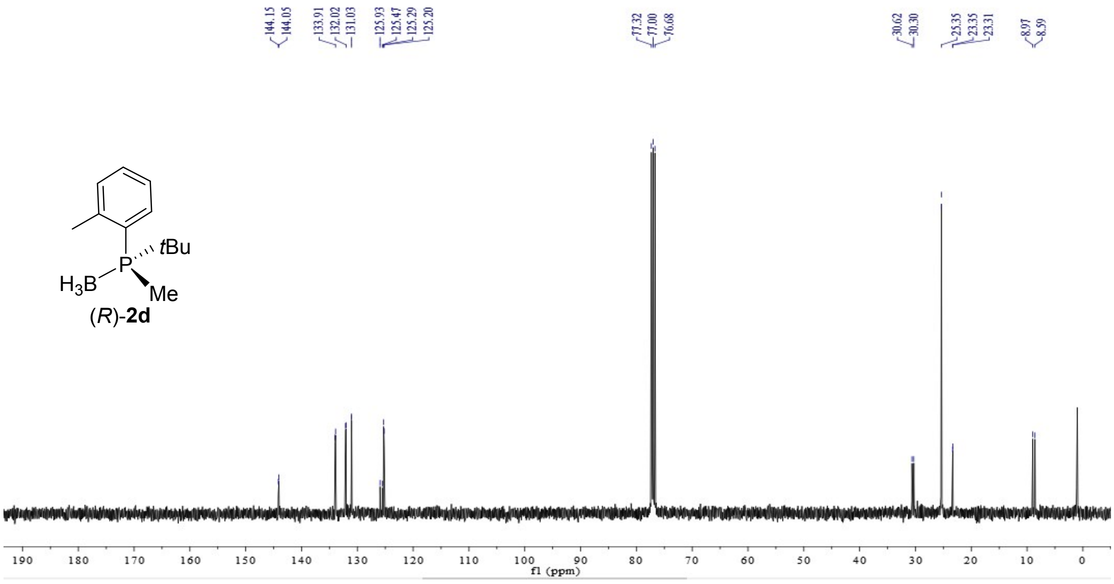


Figure S11. ^{13}C NMR spectrum of (*R*)-**2d** in $CDCl_3$

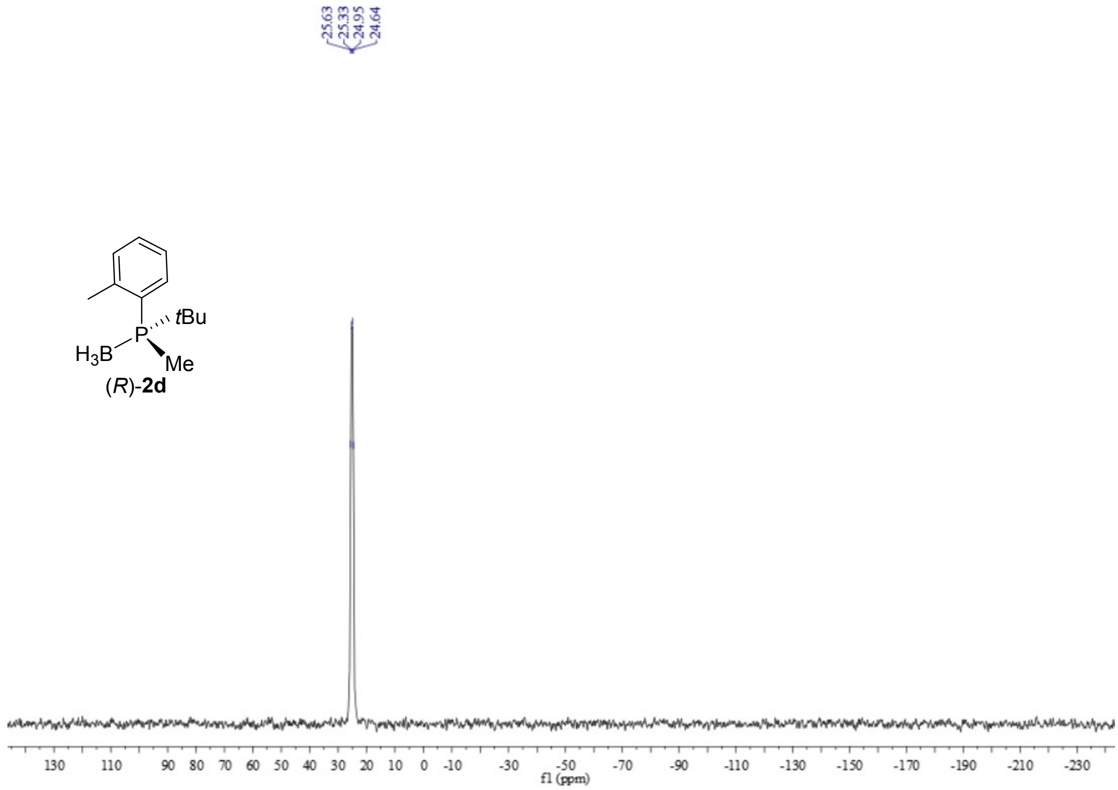


Figure S12. ^{31}P NMR spectrum of (*R*)-**2d** in $CDCl_3$

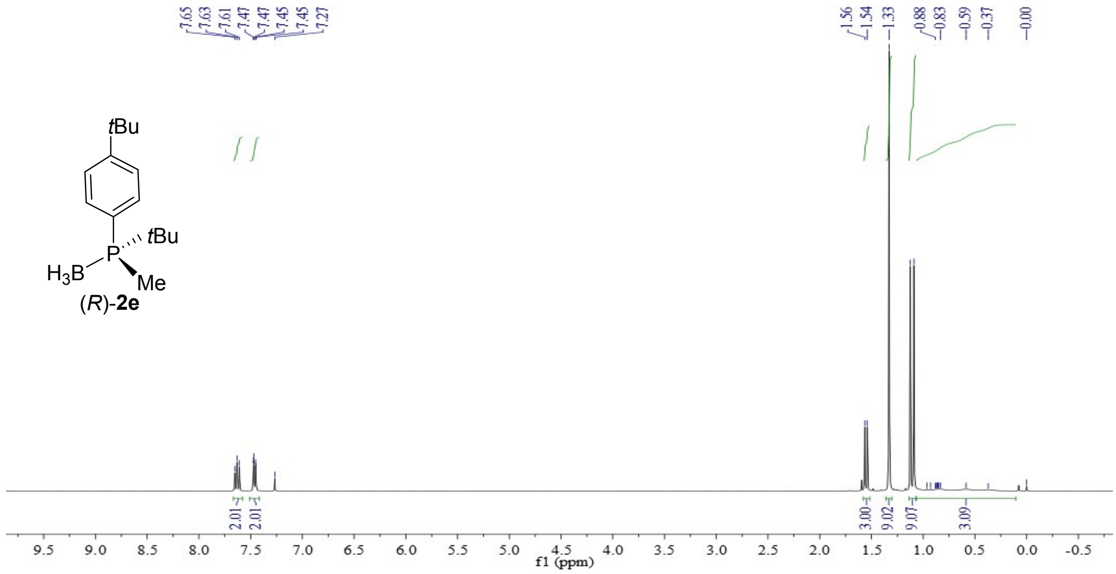


Figure S13. ^{1}H NMR spectrum of (*R*)-**2e** in $CDCl_3$

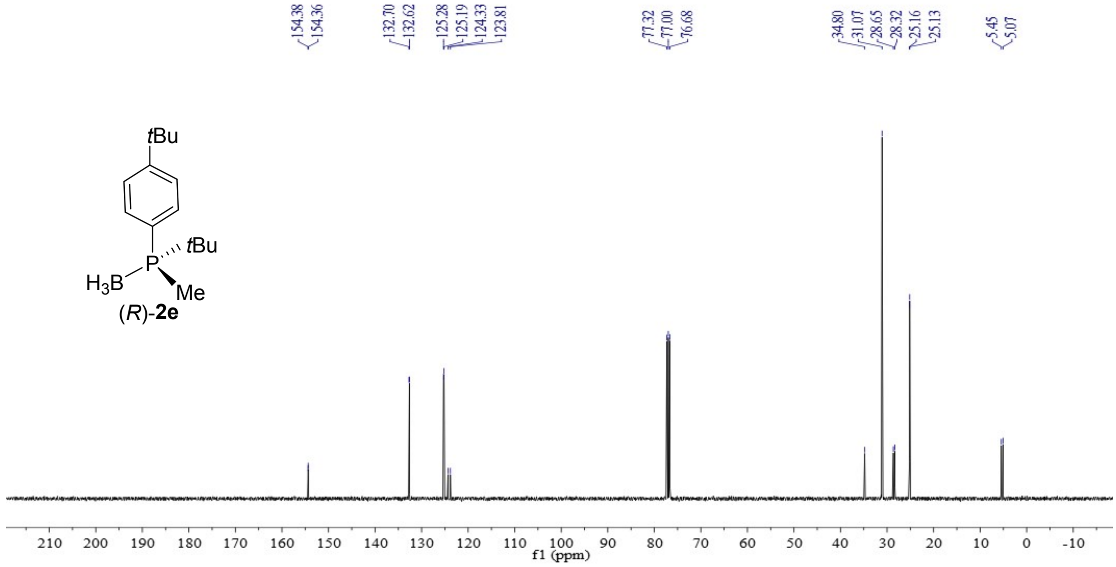


Figure S14. ^{13}C NMR spectrum of (*R*)-**2e** in $CDCl_3$

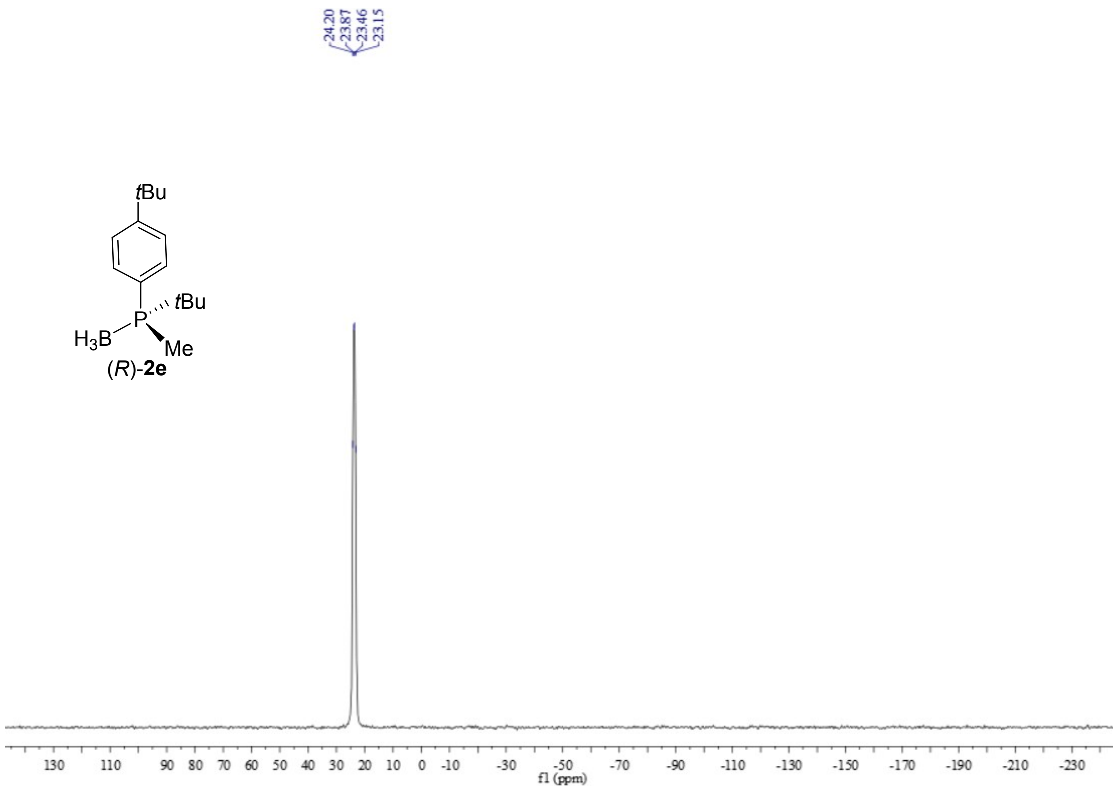


Figure S15. ^{31}P NMR spectrum of (*R*)-**2e** in $CDCl_3$

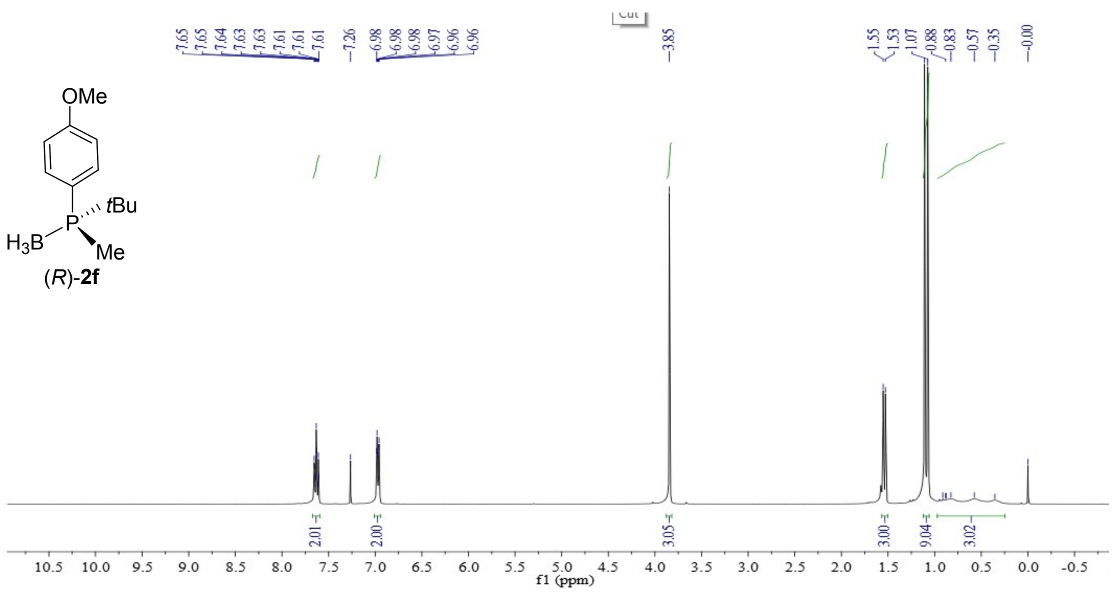


Figure S16. ^{1}H NMR spectrum of (*R*)-**2f** in $CDCl_3$

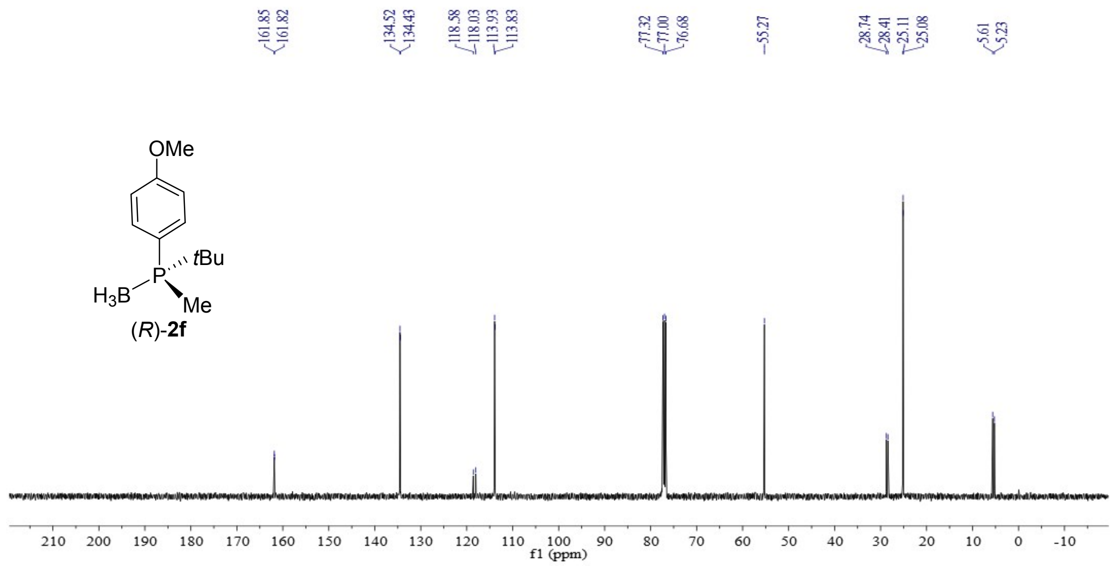


Figure S17. ^{13}C NMR spectrum of (*R*)-**2f** in $CDCl_3$

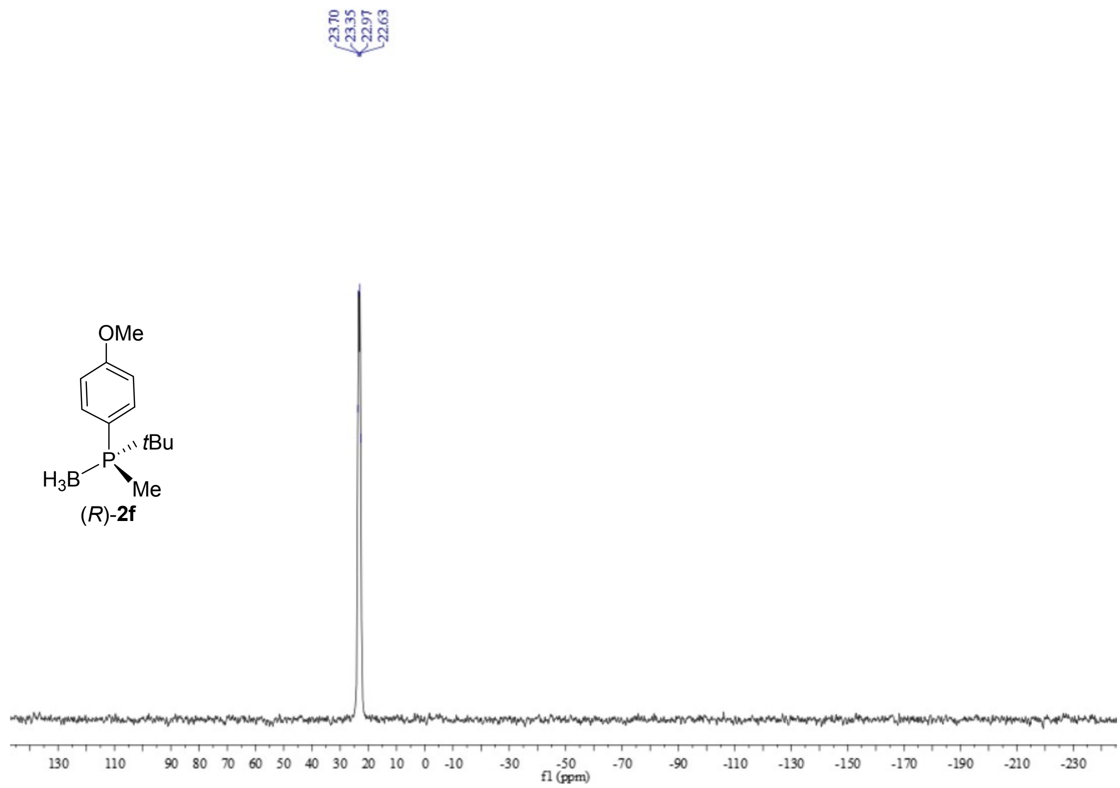


Figure S18. ^{31}P NMR spectrum of (*R*)-**2f** in $CDCl_3$

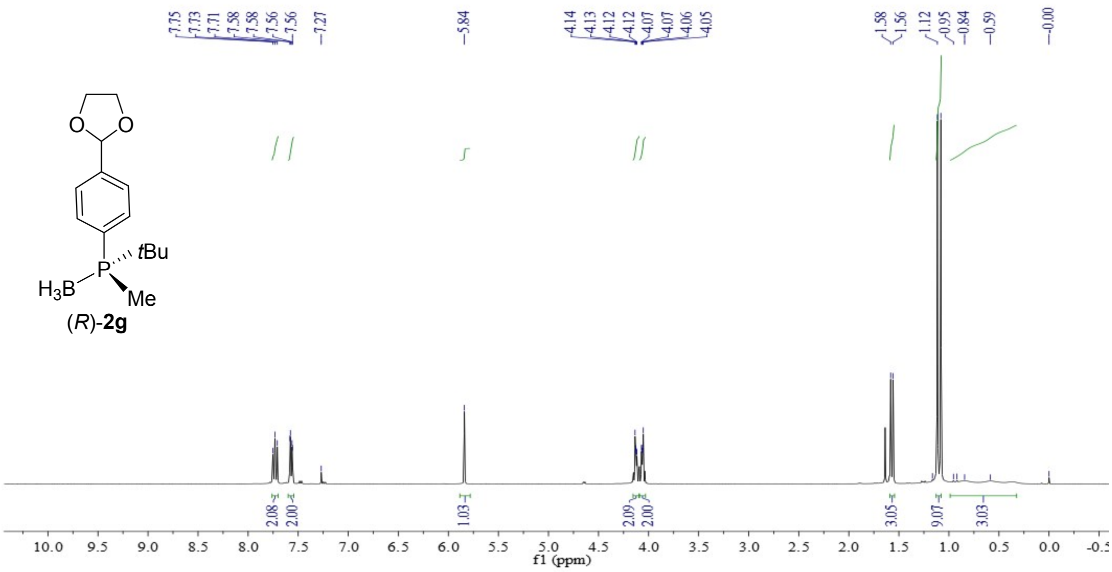


Figure S19. ^{1}H NMR spectrum of (*R*)-**2g** in $CDCl_3$

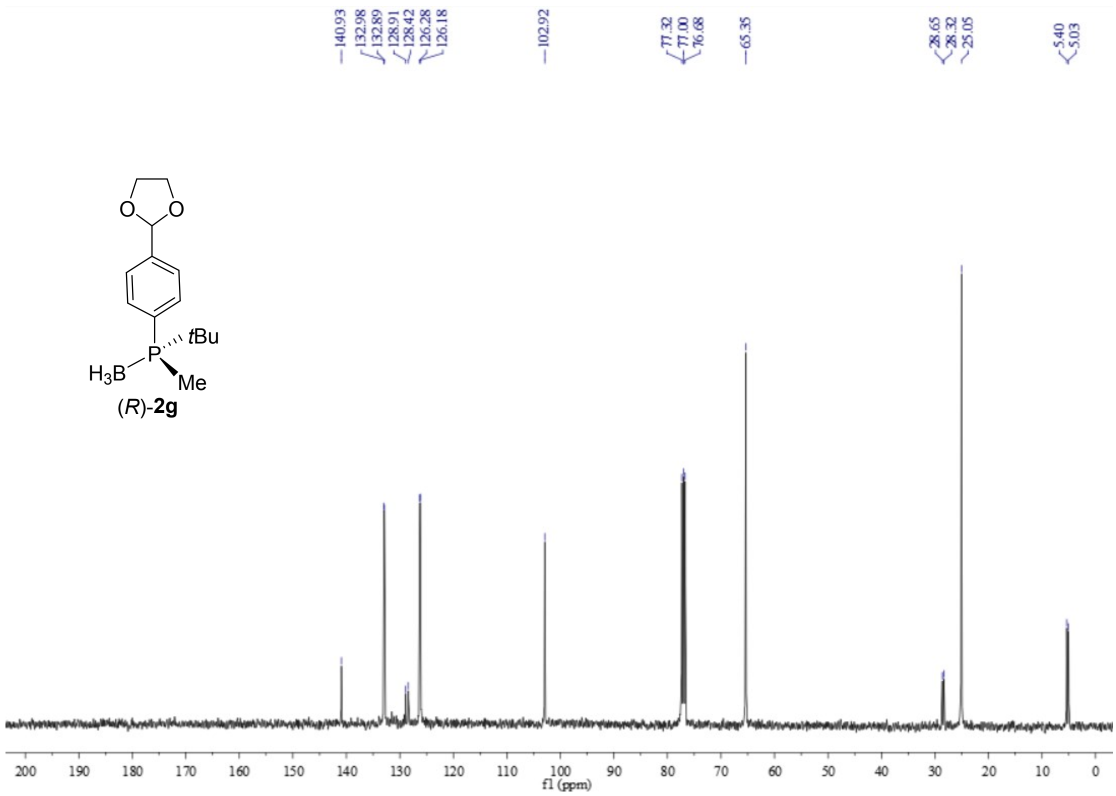


Figure S20. ^{13}C NMR spectrum of (*R*)-**2g** in $CDCl_3$

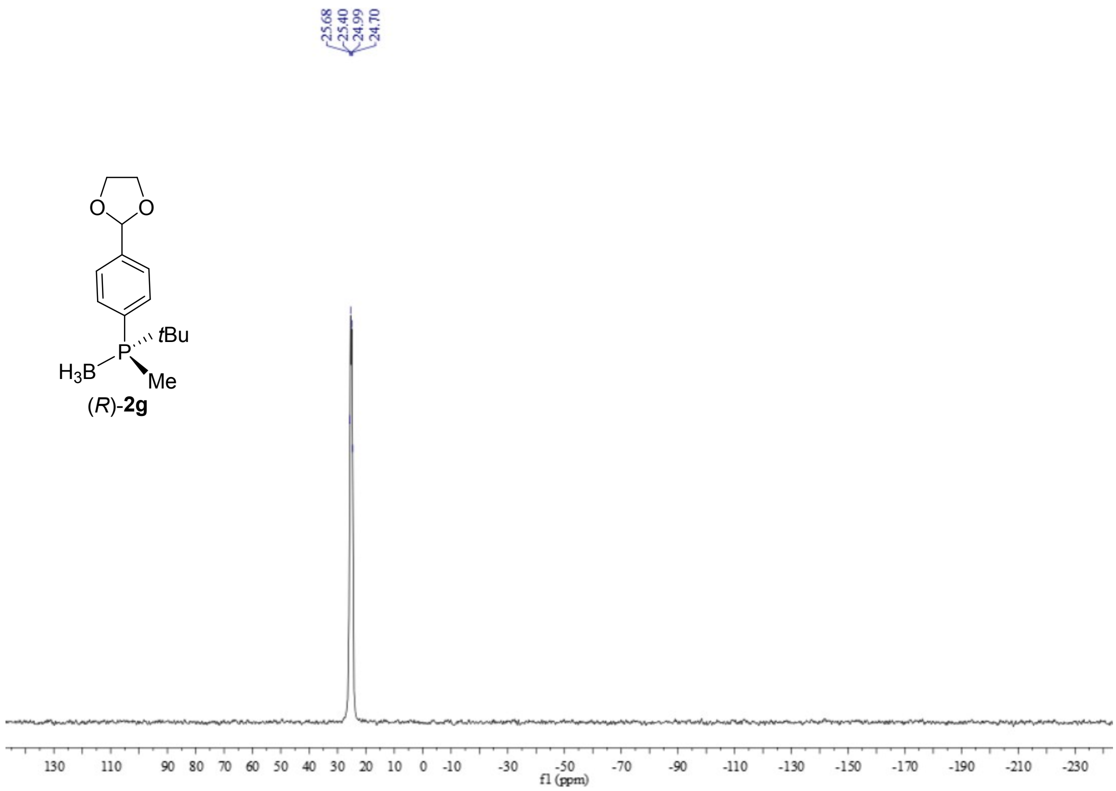


Figure S21. ^{31}P NMR spectrum of (*R*)-**2g** in $CDCl_3$

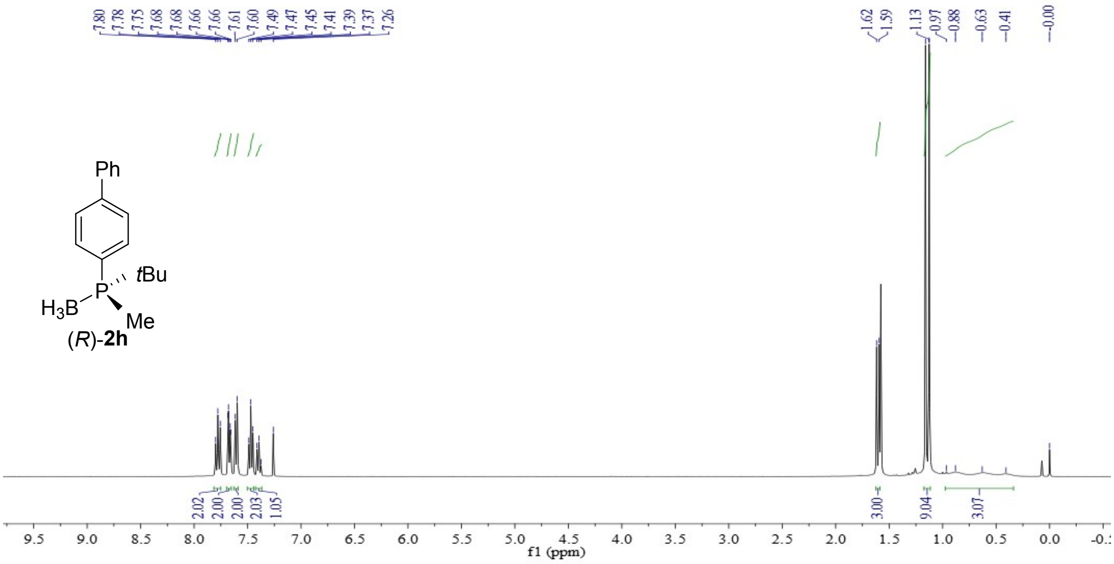


Figure S22. ^{1}H NMR spectrum of (*R*)-**2h** in $CDCl_3$

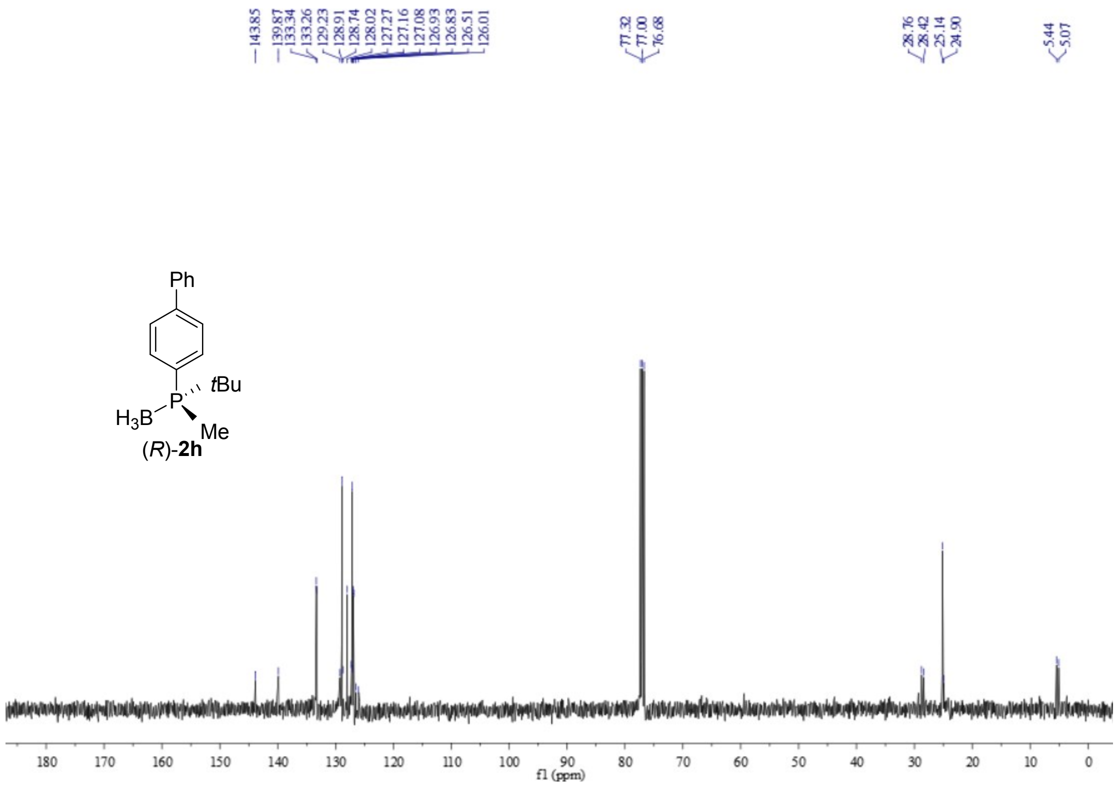


Figure S23. ^{13}C NMR spectrum of (*R*)-**2h** in $CDCl_3$

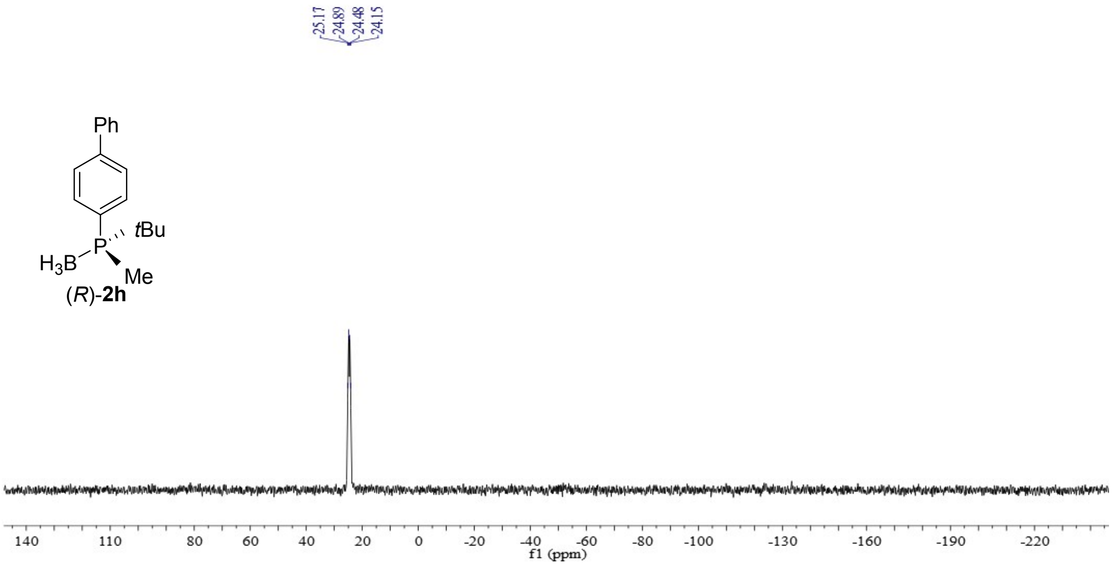


Figure S24. ^{31}P NMR spectrum of (*R*)-**2h** in $CDCl_3$

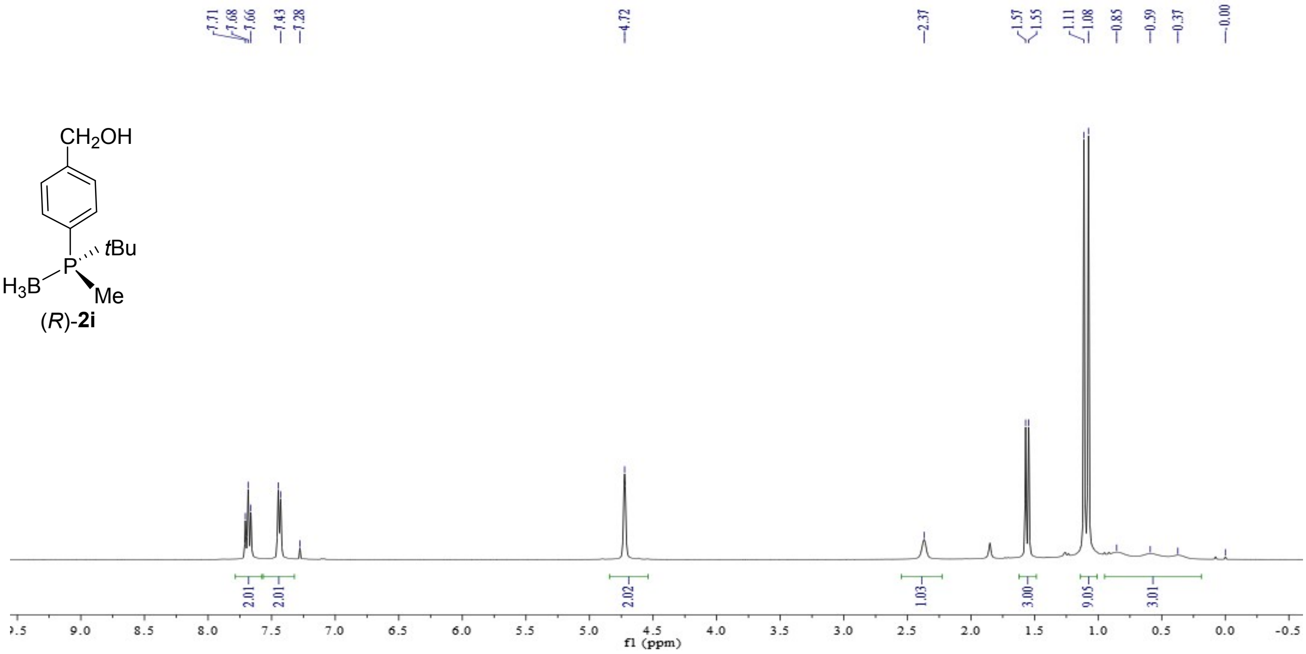


Figure S25. ^{1}H NMR spectrum of (*R*)-**2i** in $CDCl_3$

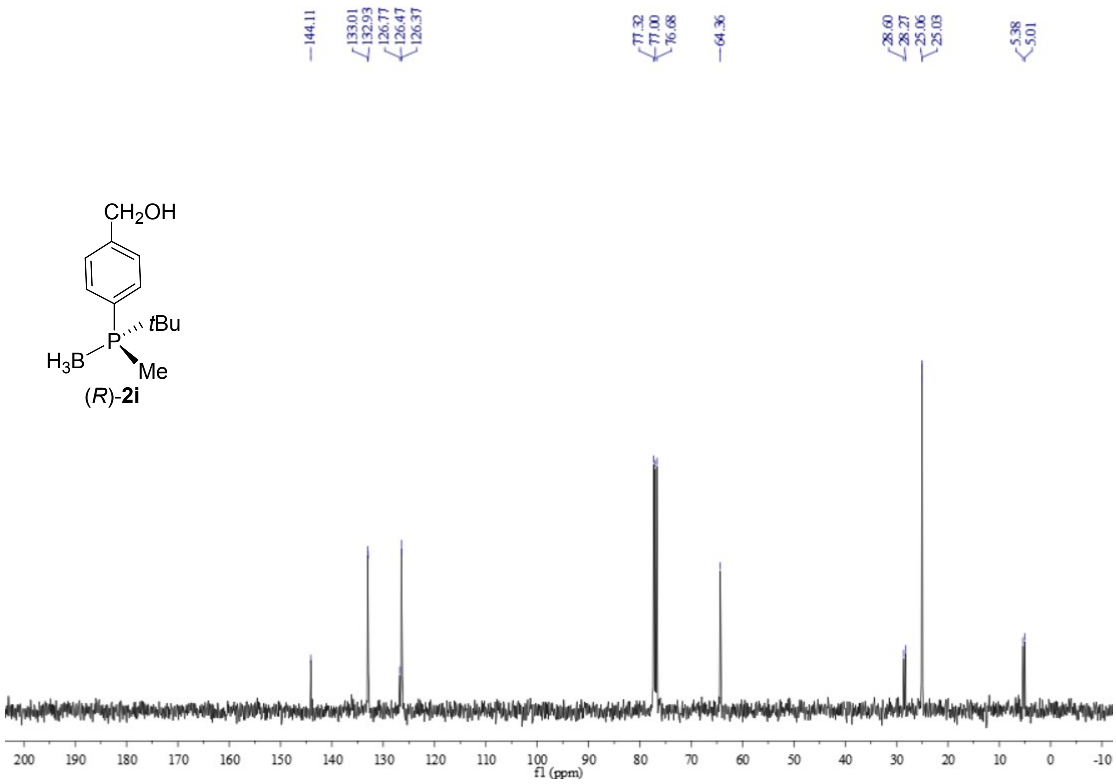


Figure S26. ^{13}C NMR spectrum of (*R*)-**2i** in $CDCl_3$

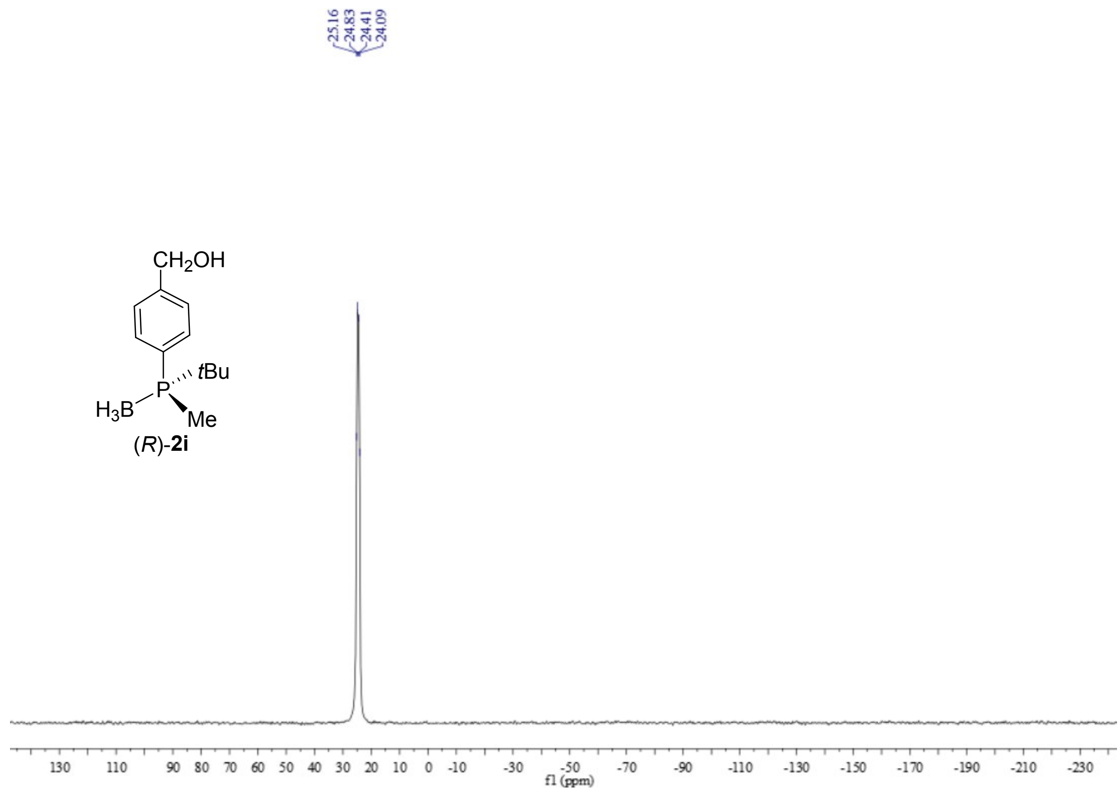


Figure S27. ^{31}P NMR spectrum of (*R*)-**2i** in $CDCl_3$

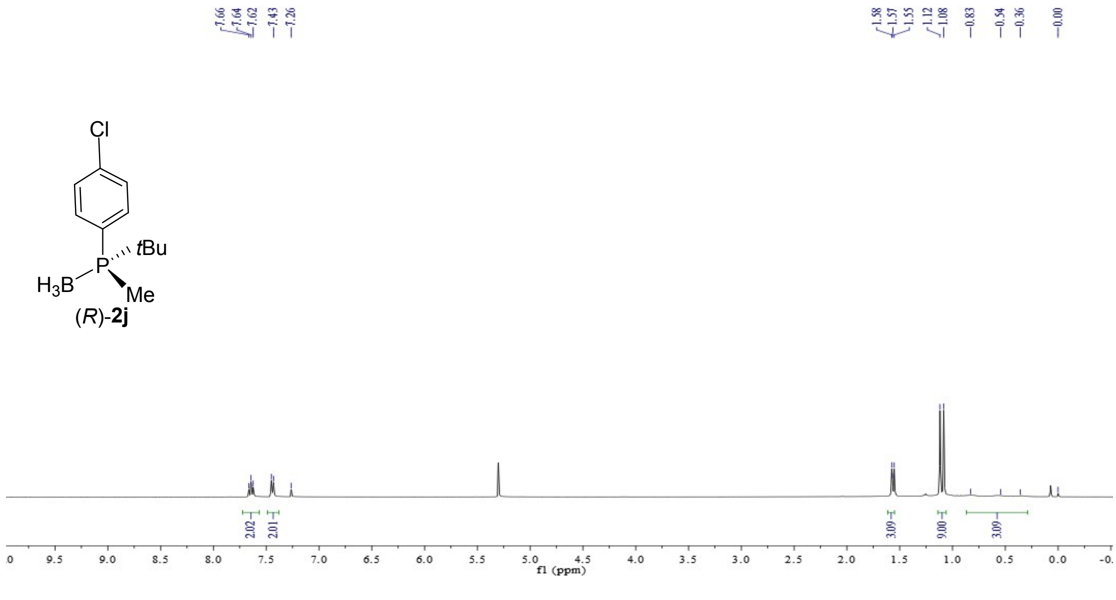


Figure S28. ^{1}H NMR spectrum of (*R*)-**2j** in $CDCl_3$

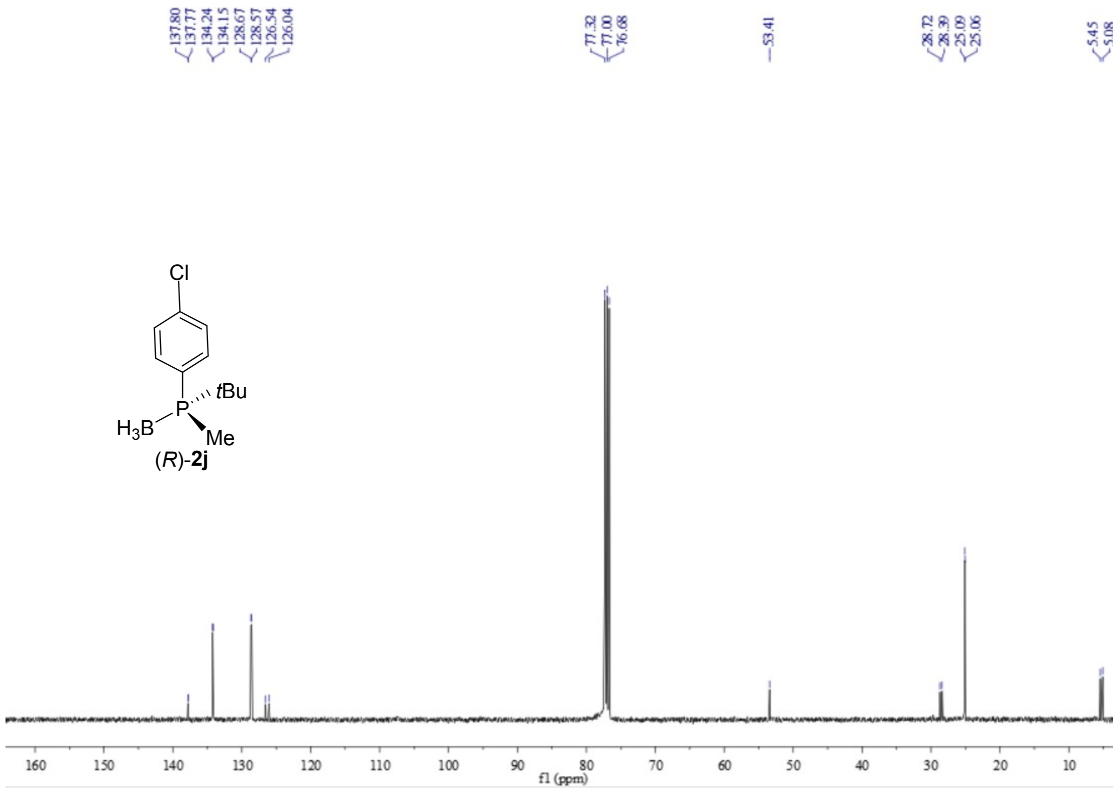


Figure S29. ^{13}C NMR spectrum of (*R*)-**2j** in $CDCl_3$

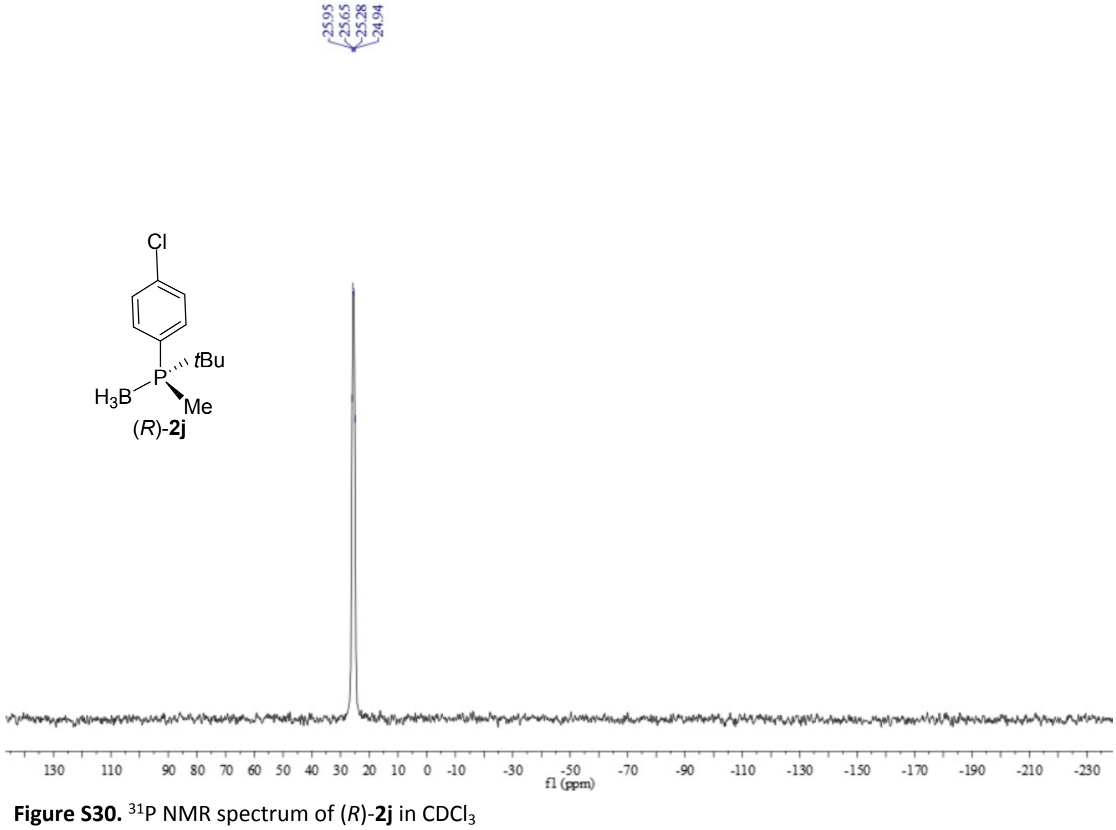


Figure S30. ^{31}P NMR spectrum of (*R*)-**2j** in $CDCl_3$

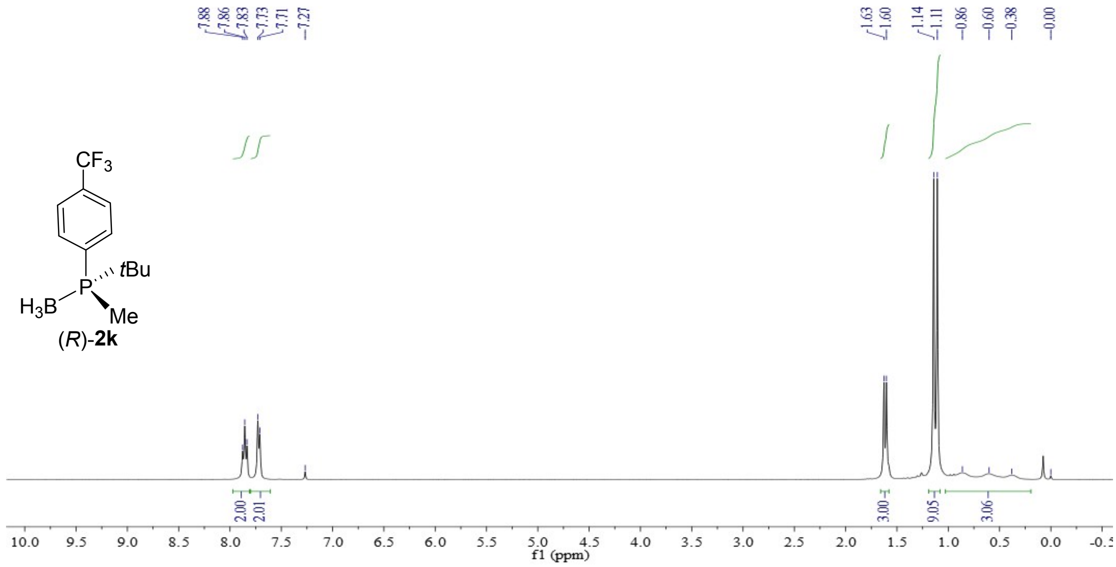


Figure S31. ^{1}H NMR spectrum of (*R*)-**2k** in $CDCl_3$

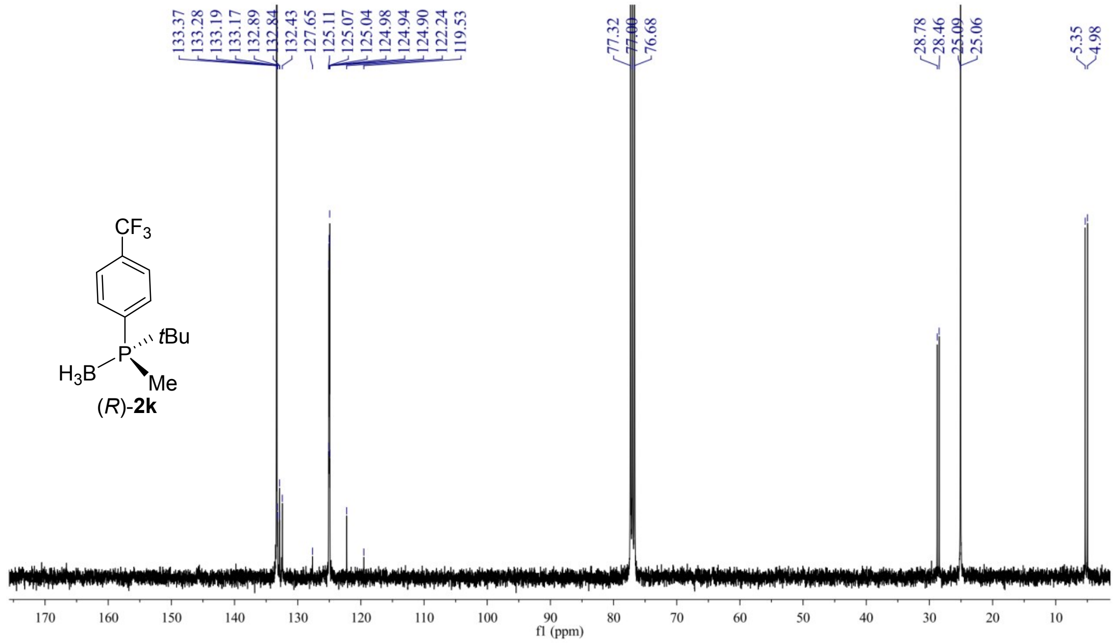


Figure S32. ^{13}C NMR spectrum of (*R*)-**2k** in $CDCl_3$

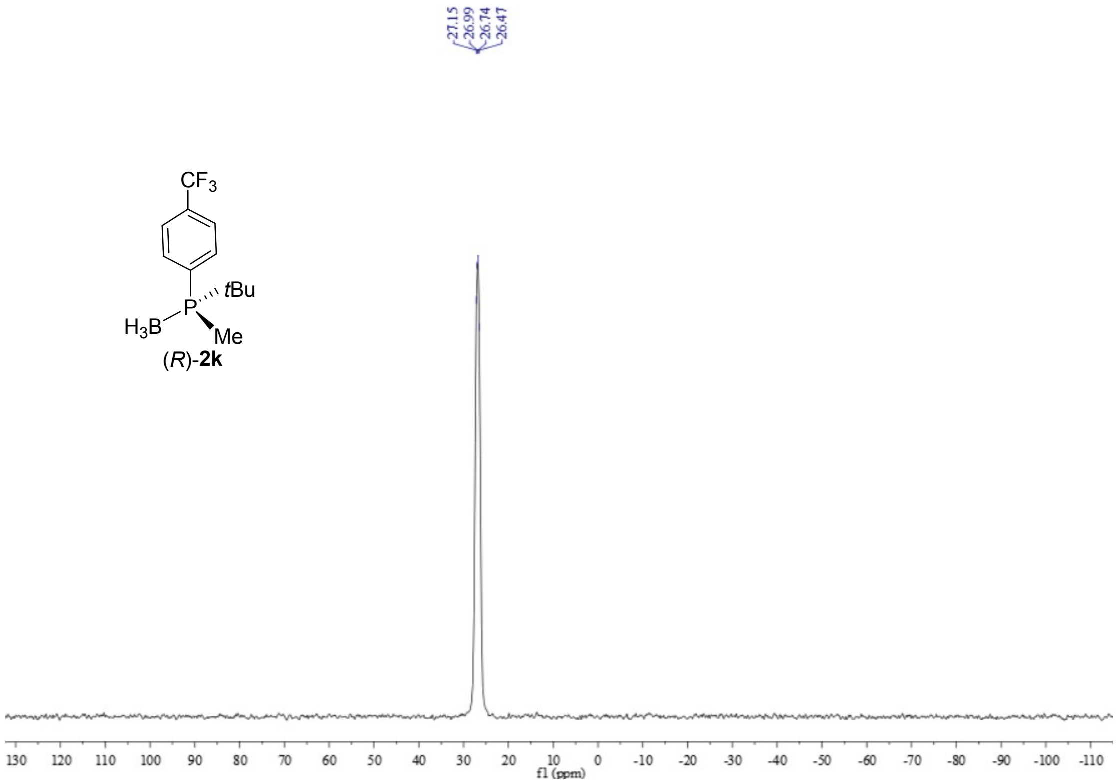


Figure S33. ^{31}P NMR spectrum of (*R*)-**2k** in $CDCl_3$

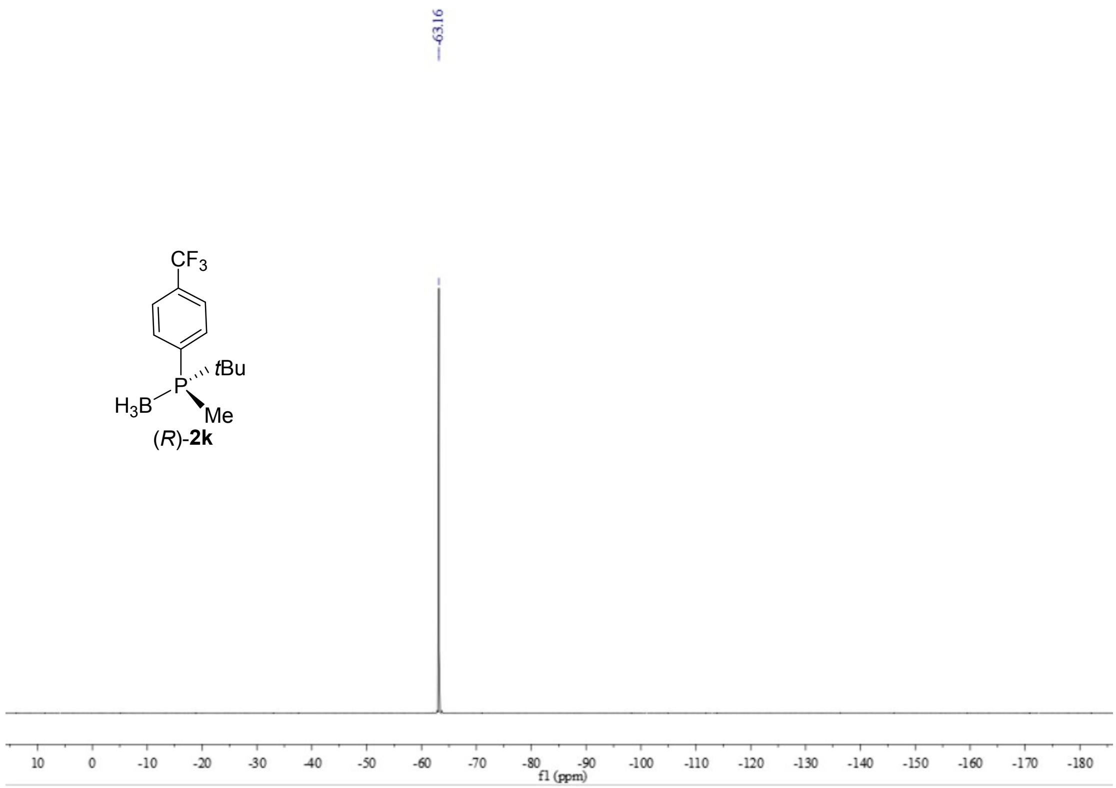


Figure S34. ^{19}F NMR spectrum of (*R*)-**2k** in $CDCl_3$

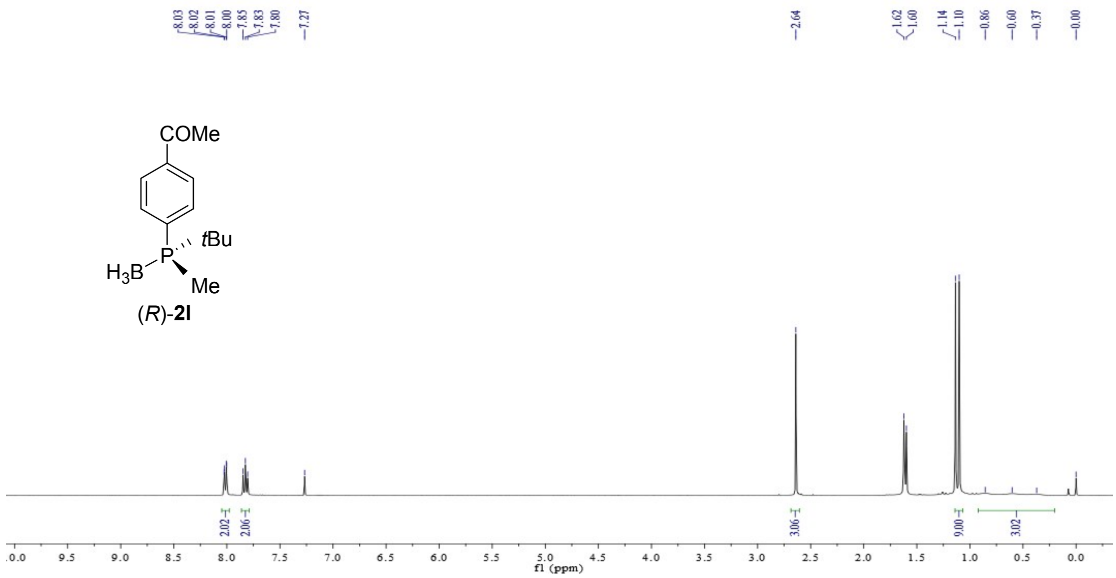


Figure S35. ^{1}H NMR spectrum of (*R*)-**2l** in $CDCl_3$

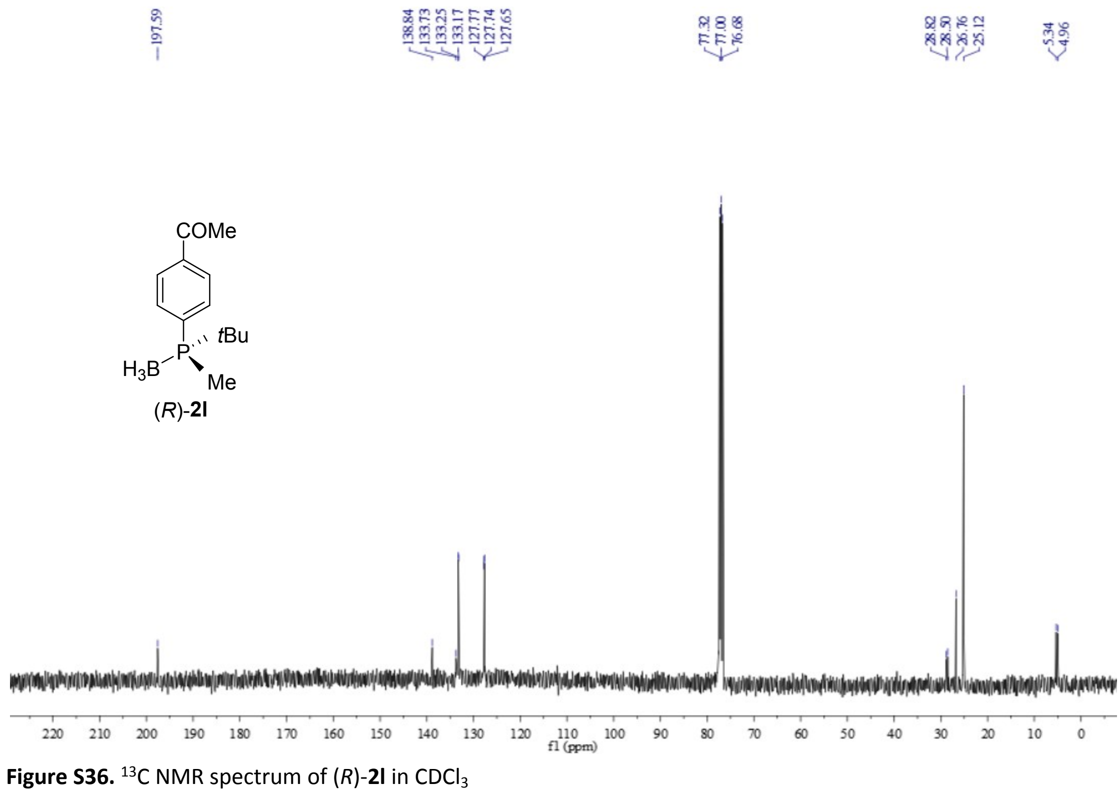


Figure S36. ^{13}C NMR spectrum of (*R*)-**2l** in $CDCl_3$

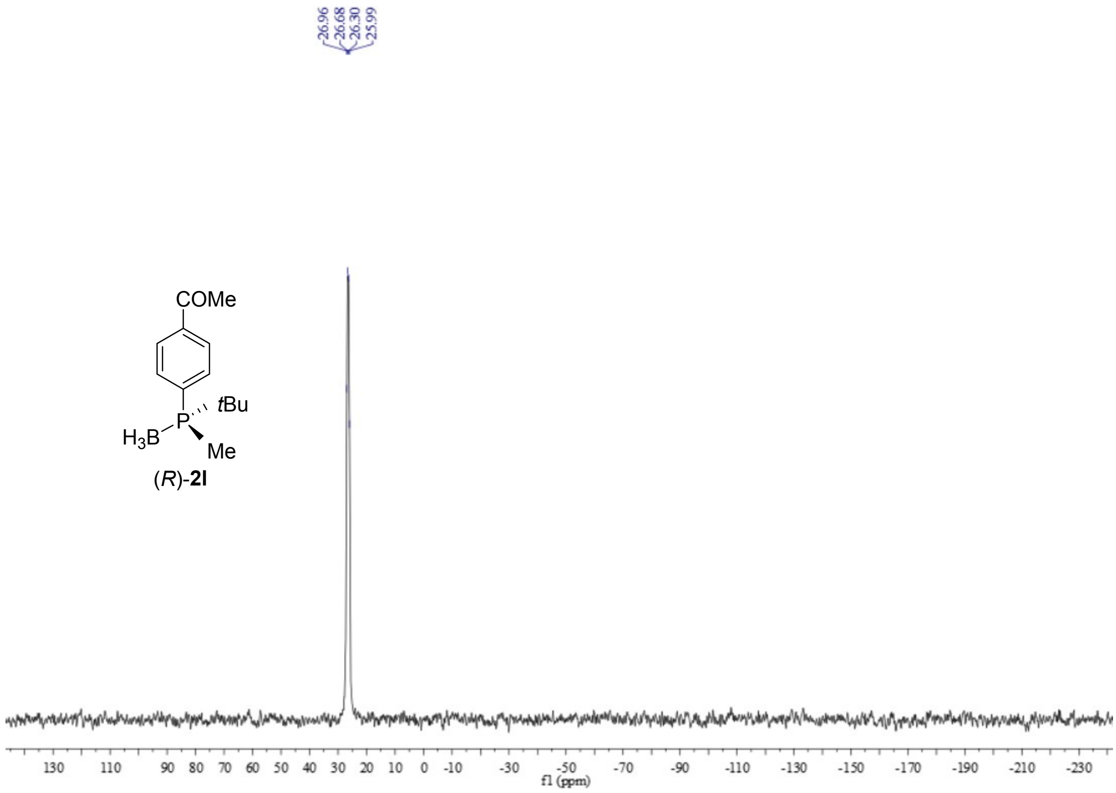


Figure S37. ^{31}P NMR spectrum of (*R*)-**2l** in $CDCl_3$

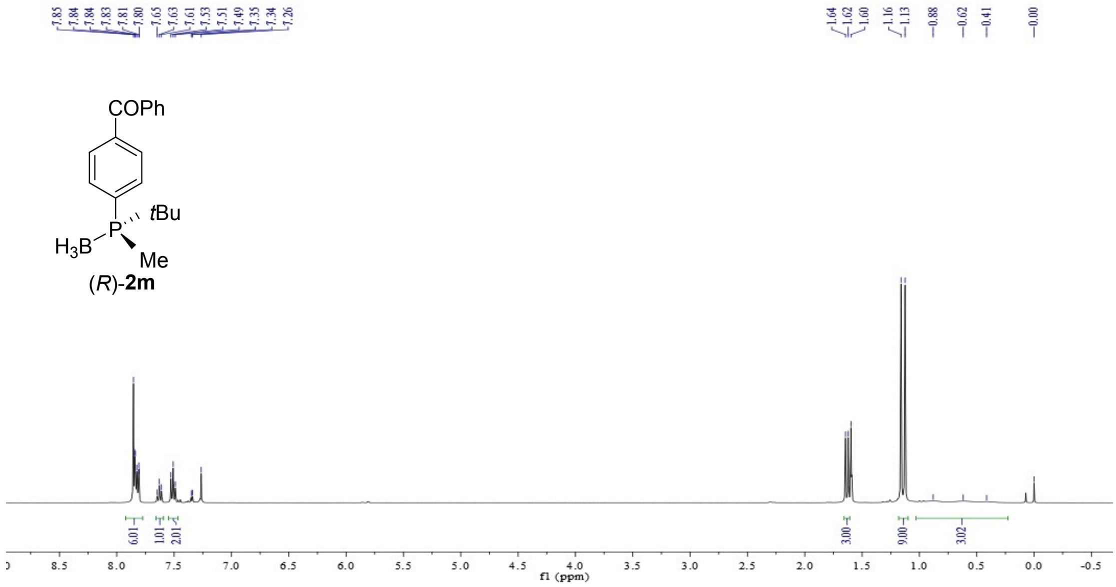


Figure S38. ^{1}H NMR spectrum of (*R*)-**2m** in $CDCl_3$

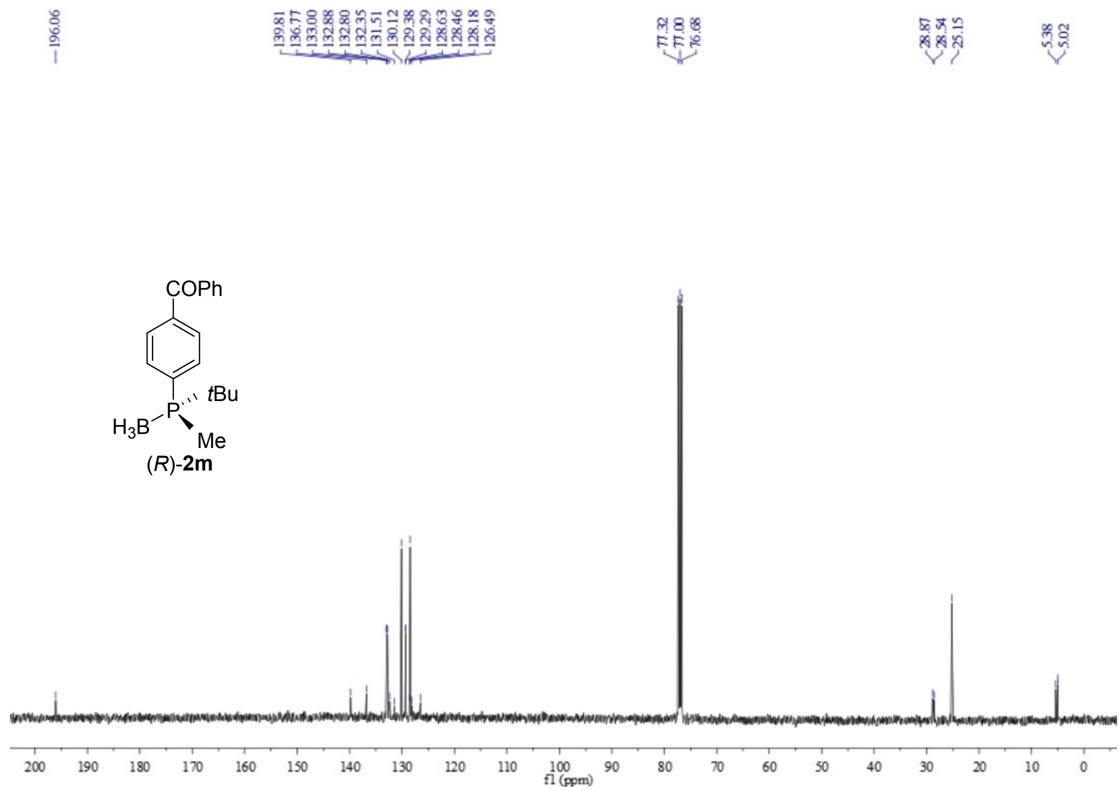


Figure S39. ^{13}C NMR spectrum of (*R*)-**2m** in $CDCl_3$

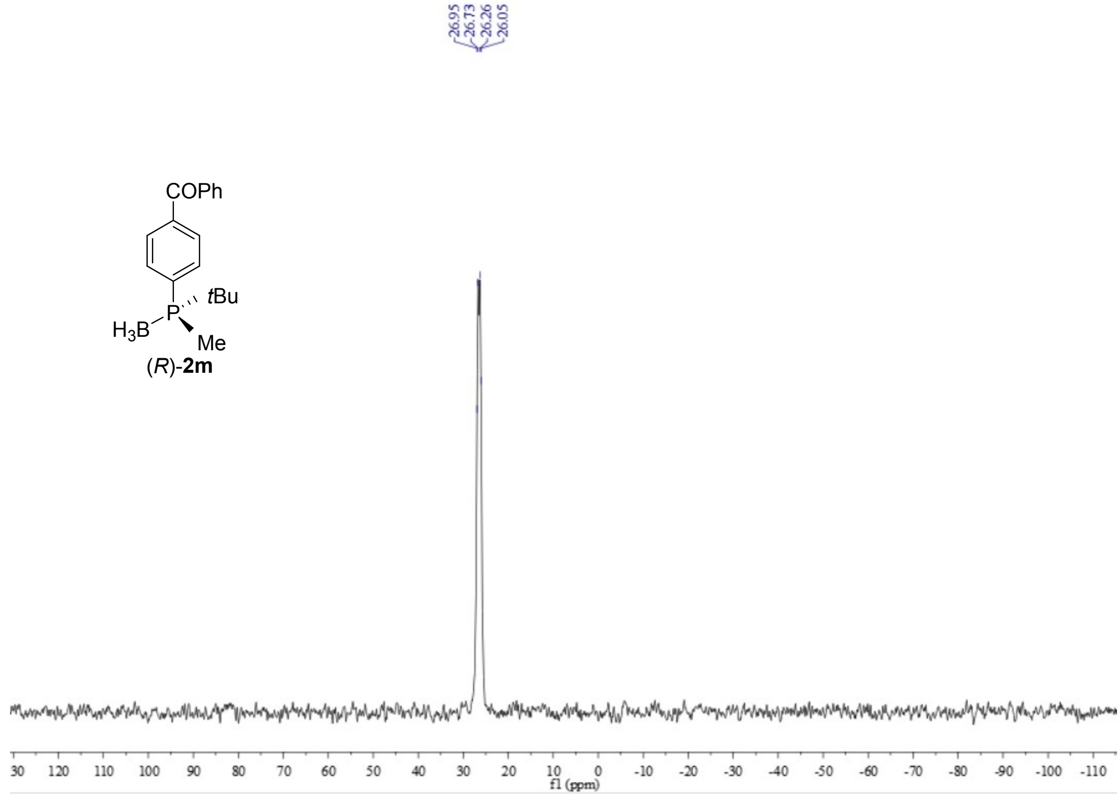


Figure S40. ^{31}P NMR spectrum of (*R*)-**2m** in $CDCl_3$

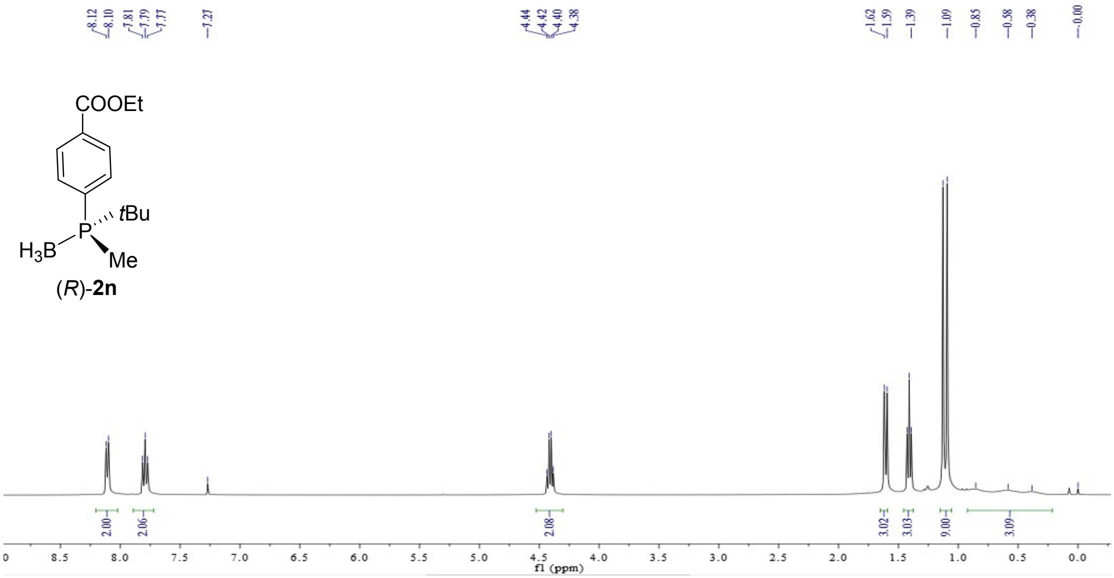


Figure S41. ^{1}H NMR spectrum of (*R*)-**2n** in $CDCl_3$

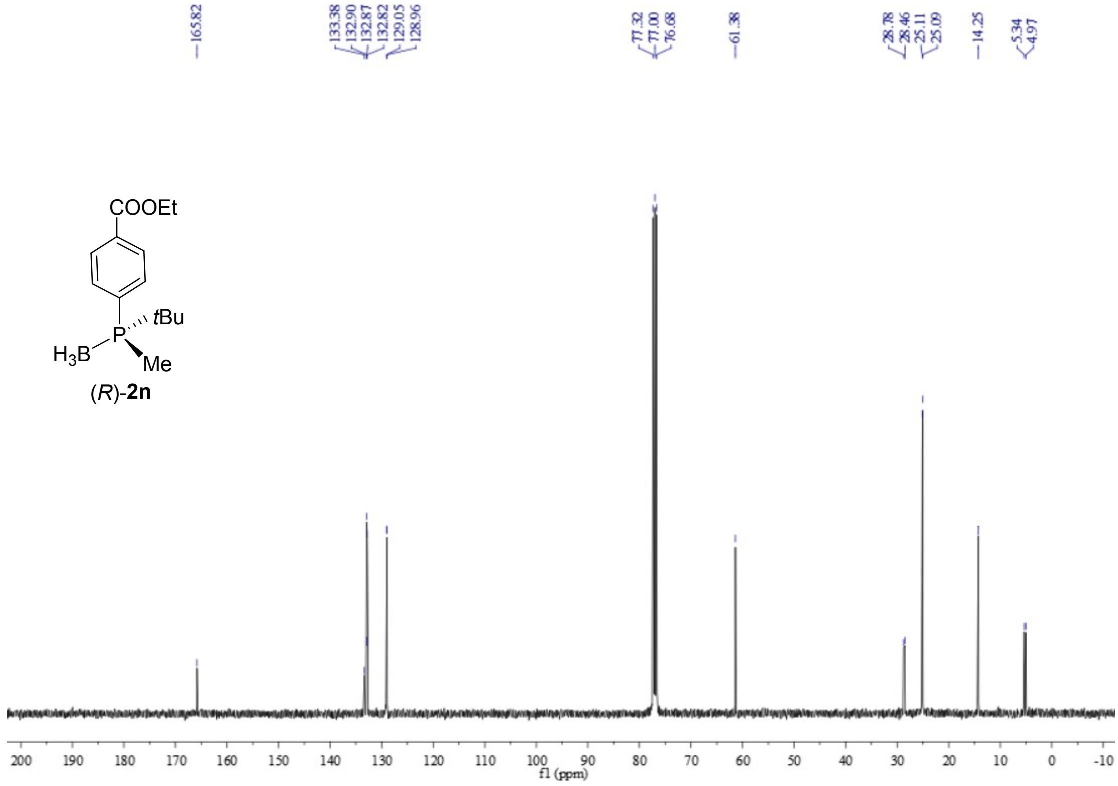


Figure S42. ^{13}C NMR spectrum of (*R*)-**2n** in $CDCl_3$

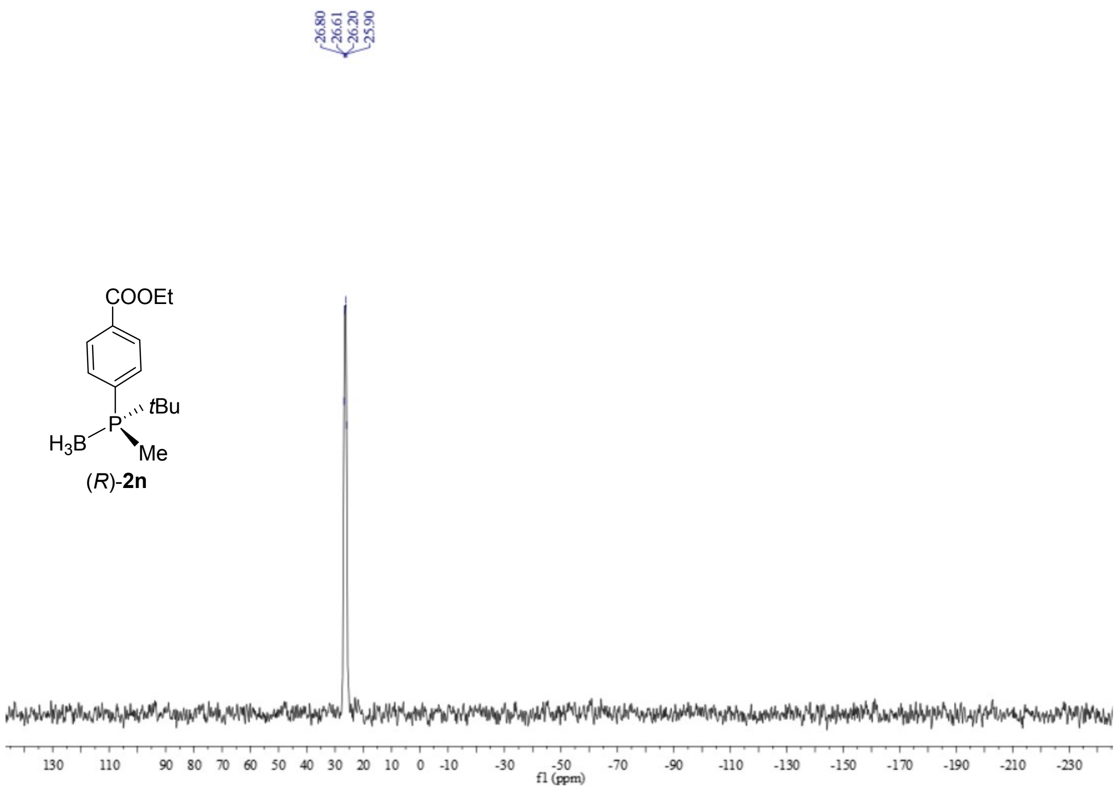


Figure S43. ^{31}P NMR spectrum of (*R*)-**2n** in $CDCl_3$

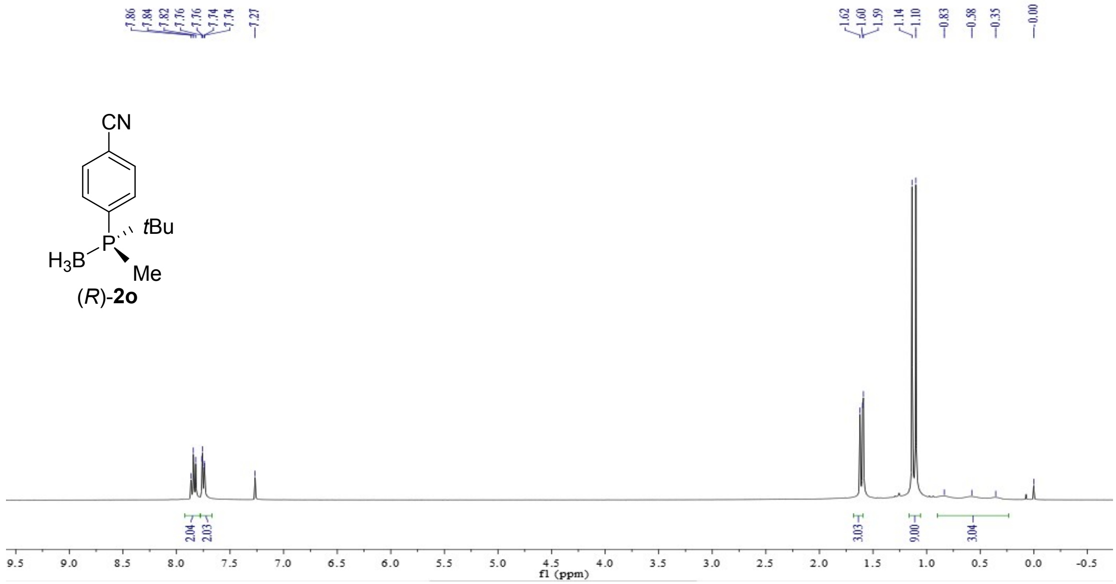


Figure S44. ^{1}H NMR spectrum of (*R*)-**2o** in $CDCl_3$

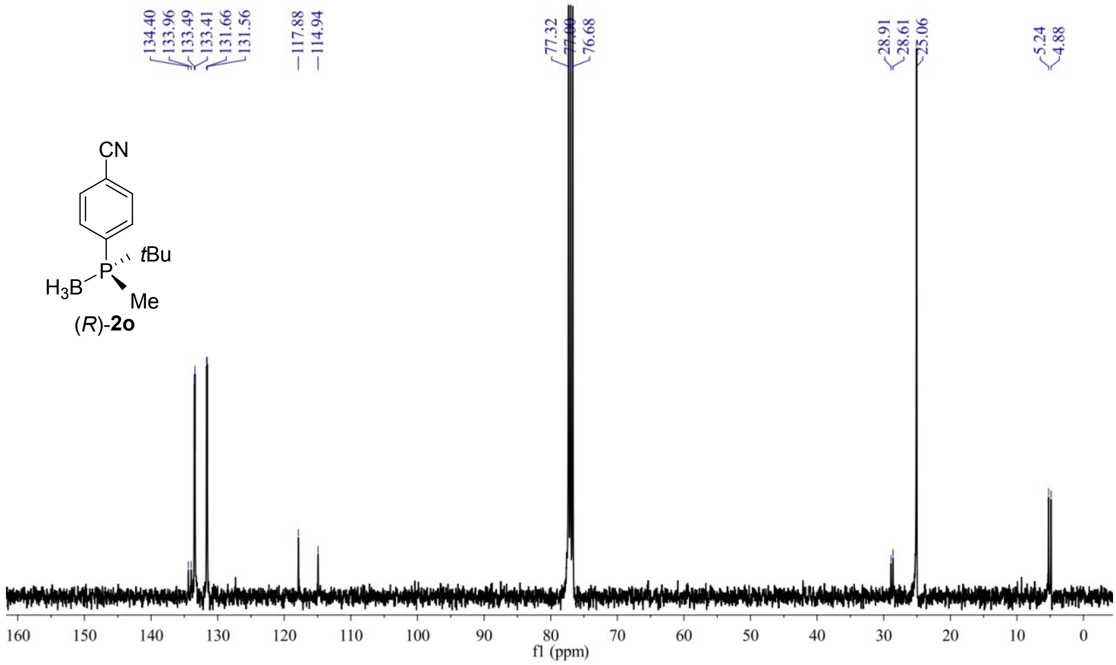


Figure S45. ^{13}C NMR spectrum of (*R*)-**2o** in $CDCl_3$

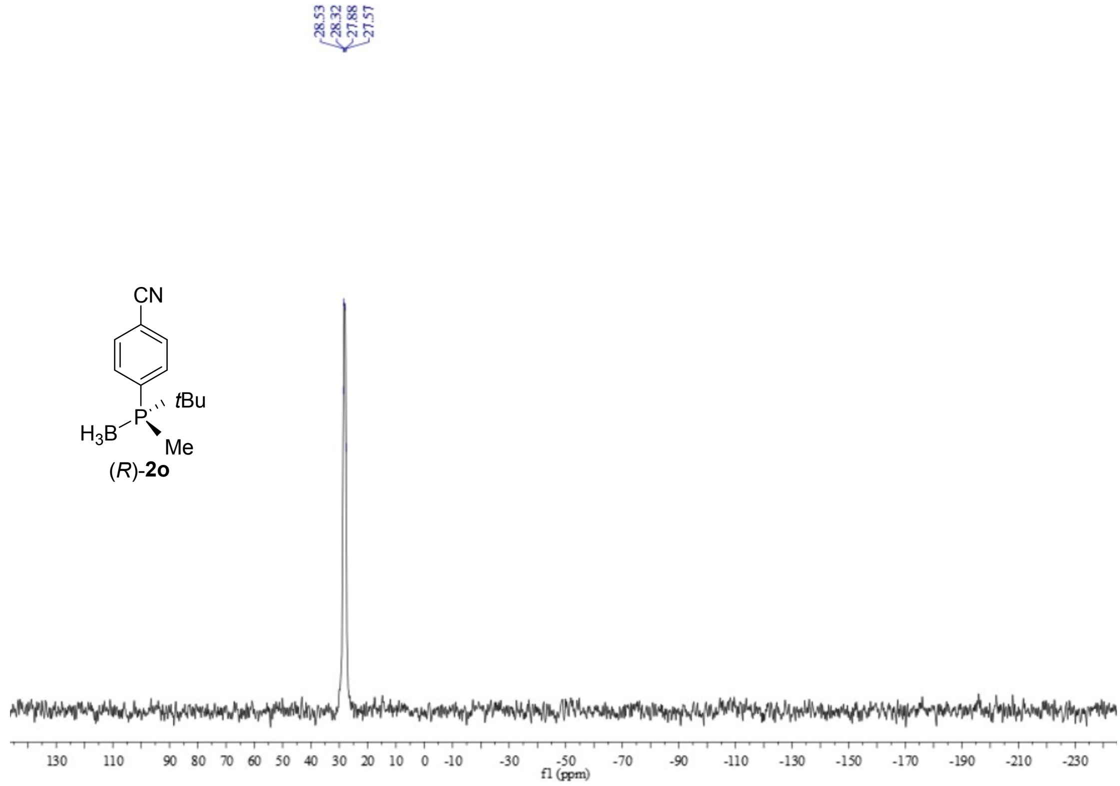


Figure S46. ^{31}P NMR spectrum of (*R*)-**2o** in $CDCl_3$

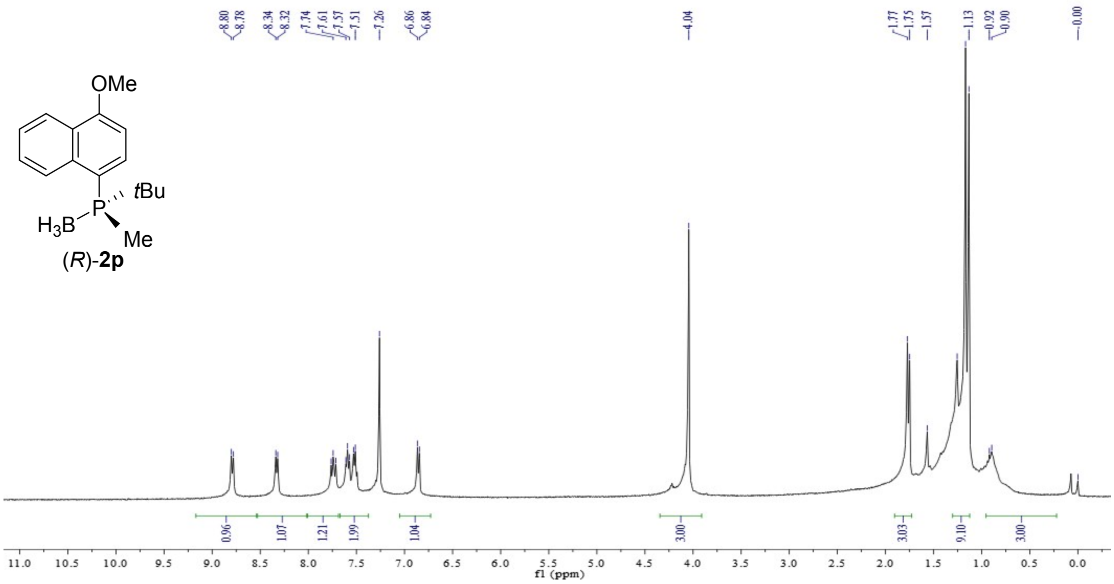


Figure S47. ^{1}H NMR spectrum of (*R*)-**2p** in $CDCl_3$

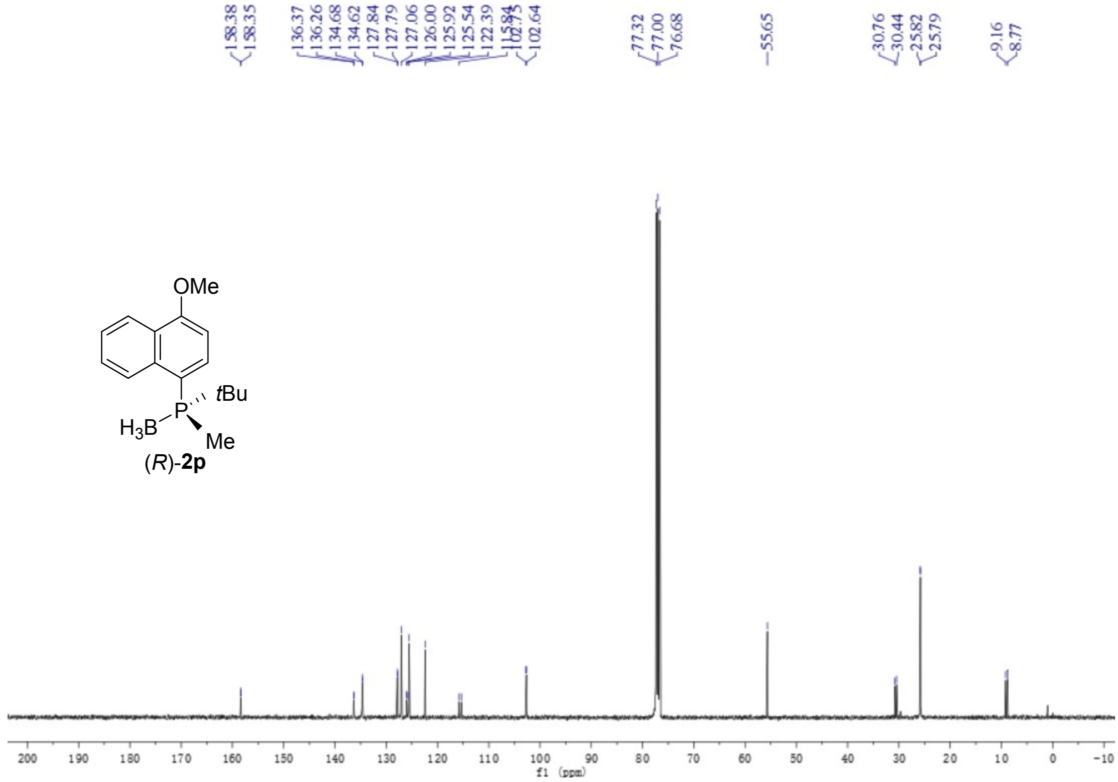


Figure S48. ^{13}C NMR spectrum of (*R*)-**2p** in $CDCl_3$

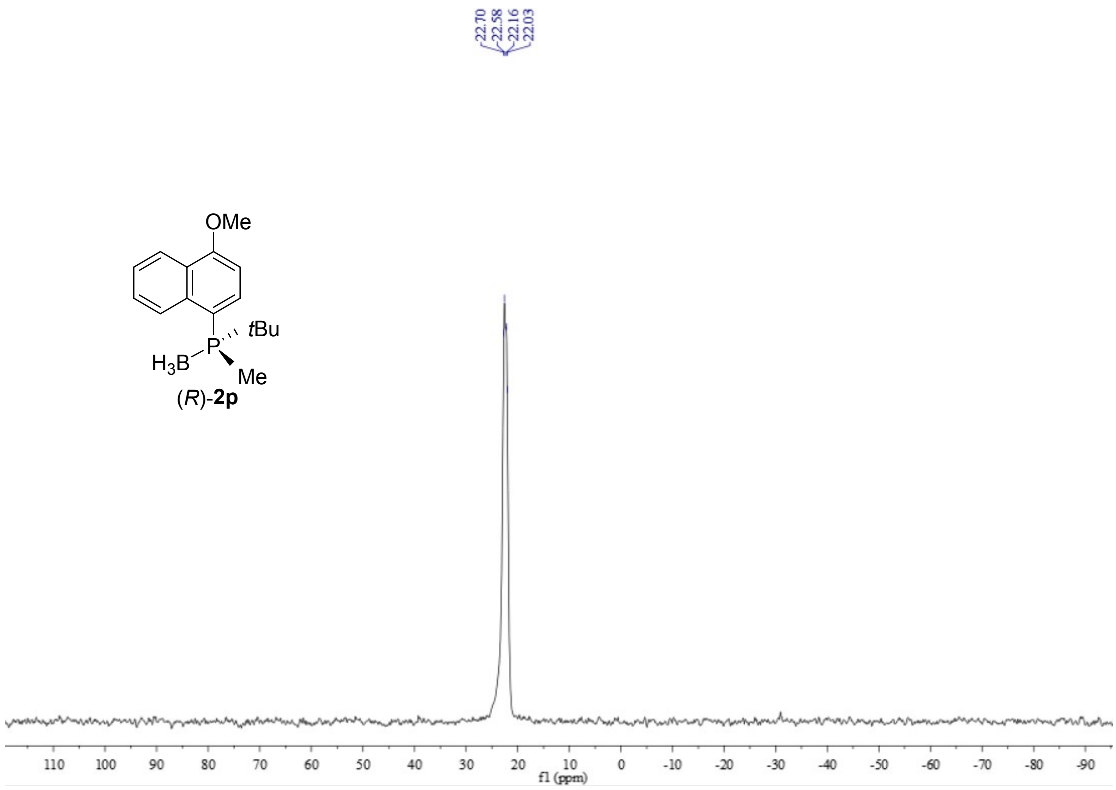


Figure S49. ^{31}P NMR spectrum of (*R*)-**2p** in $CDCl_3$

Figure S50. ^{1}H NMR spectrum of (*R*)-**2q** in $CDCl_3$

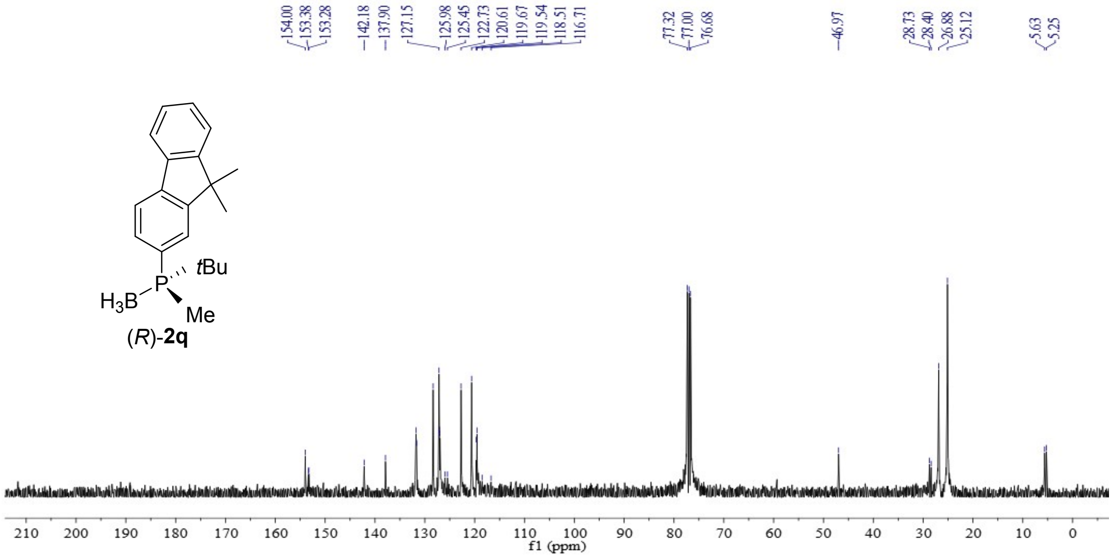


Figure S51. ^{13}C NMR spectrum of (*R*)-**2q** in $CDCl_3$

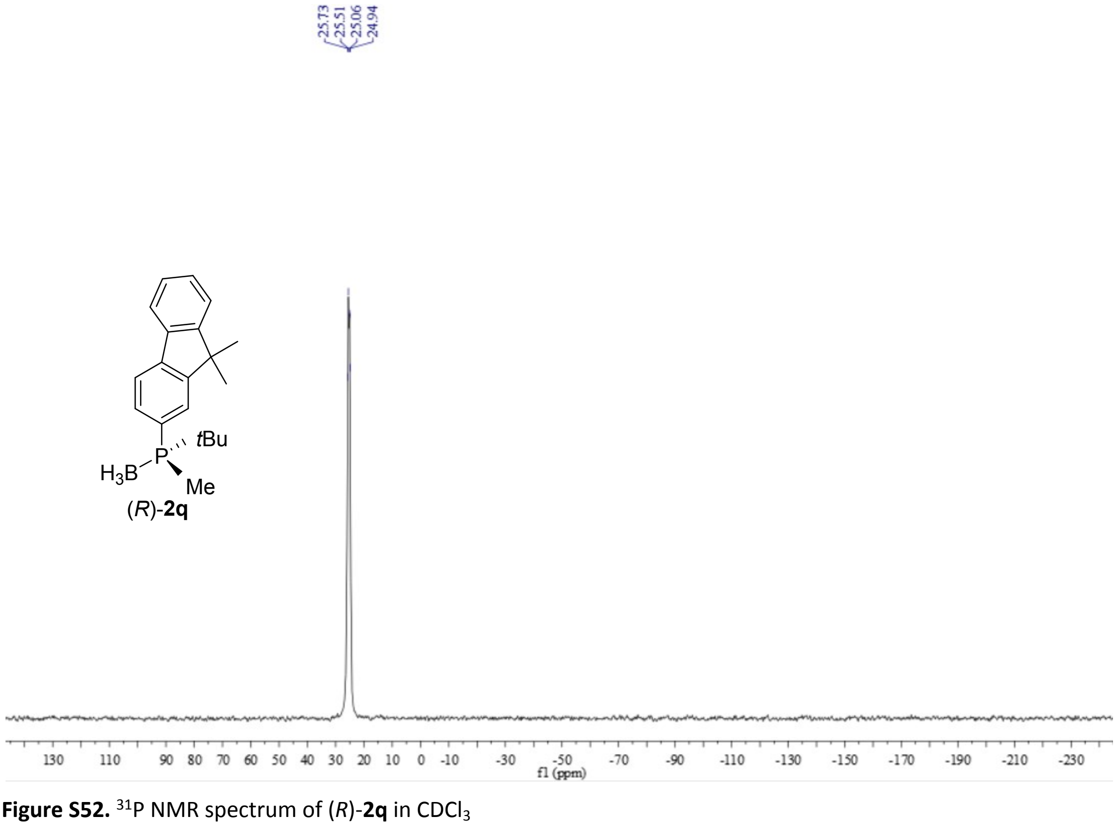


Figure S52. ^{31}P NMR spectrum of (*R*)-**2q** in $CDCl_3$

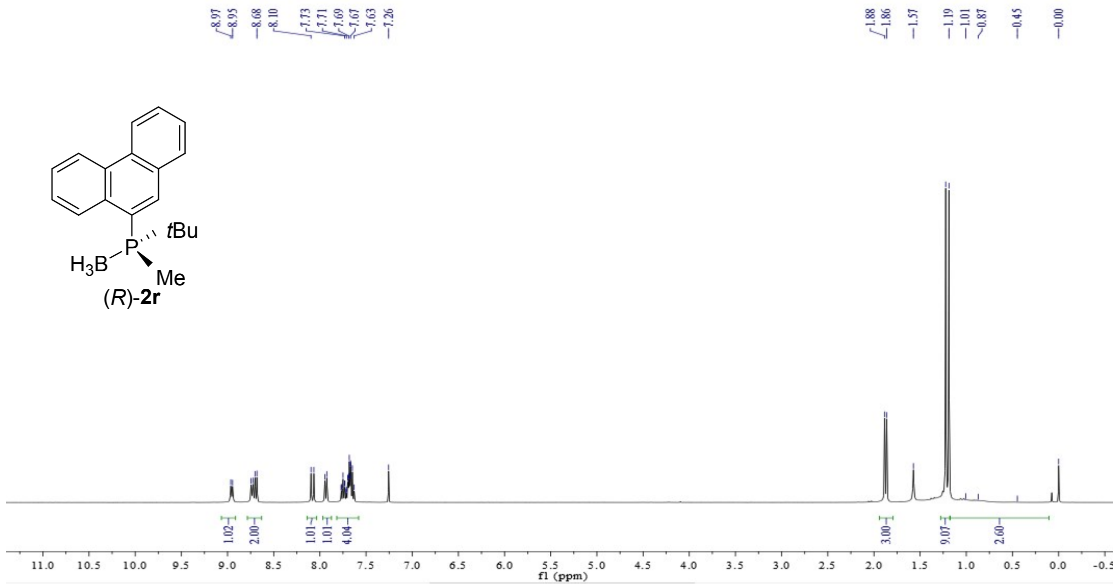


Figure S53. ^{1}H NMR spectrum of (*R*)-**2r** in $CDCl_3$

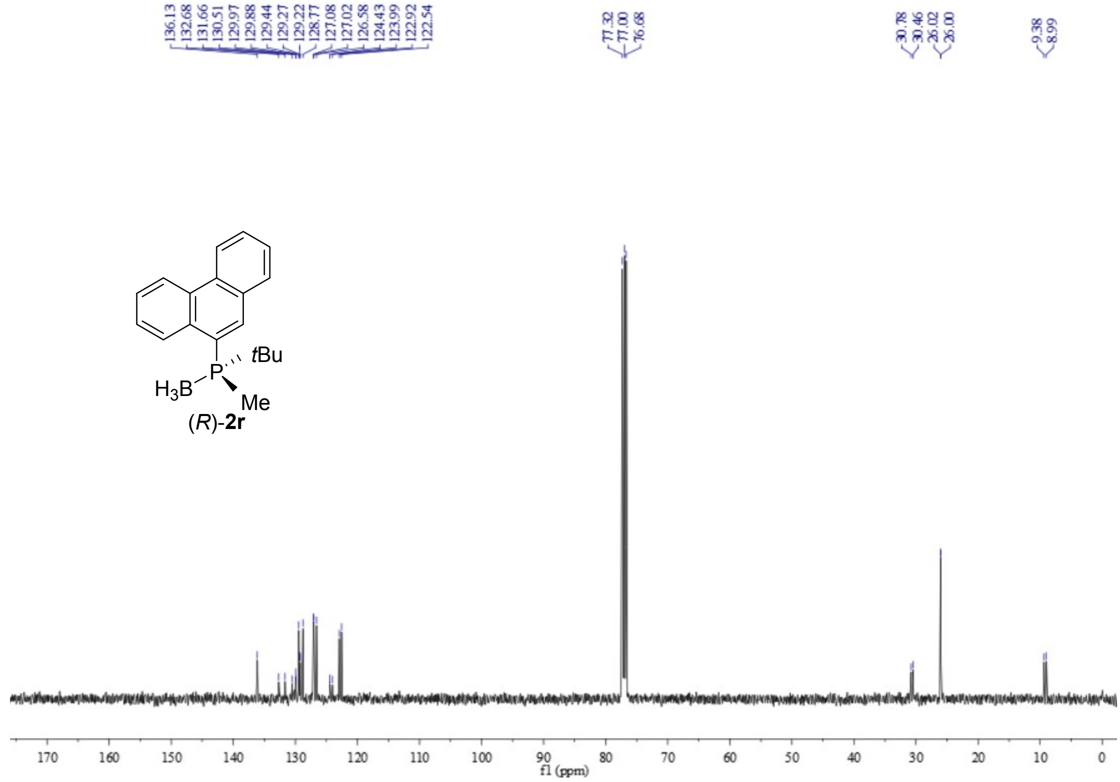


Figure S54. ^{13}C NMR spectrum of (*R*)-**2r** in $CDCl_3$

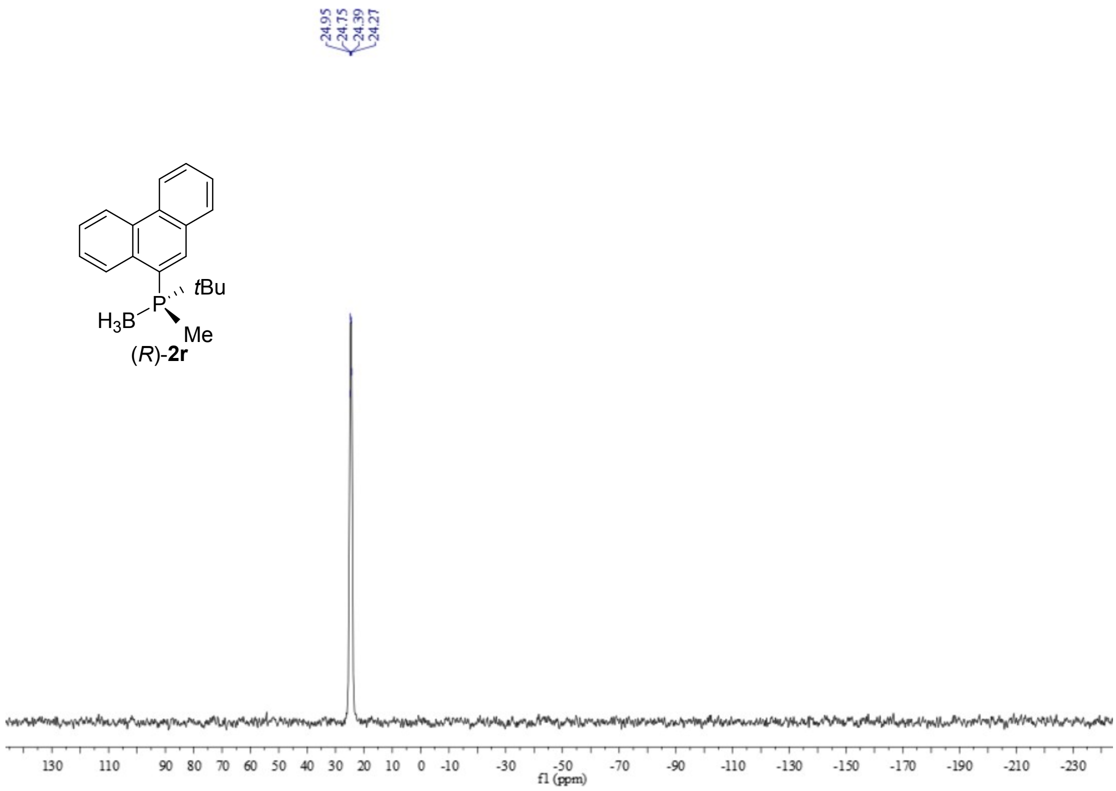


Figure S55. ^{31}P NMR spectrum of (*R*)-**2r** in $CDCl_3$

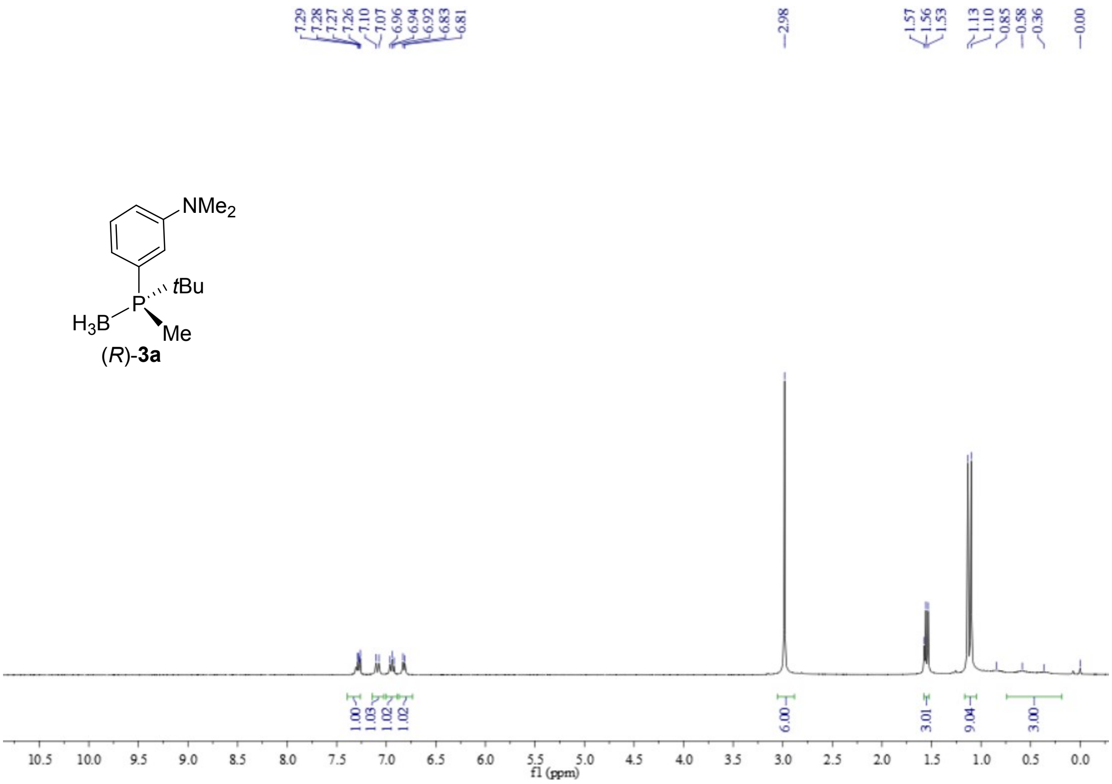


Figure S56. ^{1}H NMR spectrum of (*R*)-**3a** in $CDCl_3$

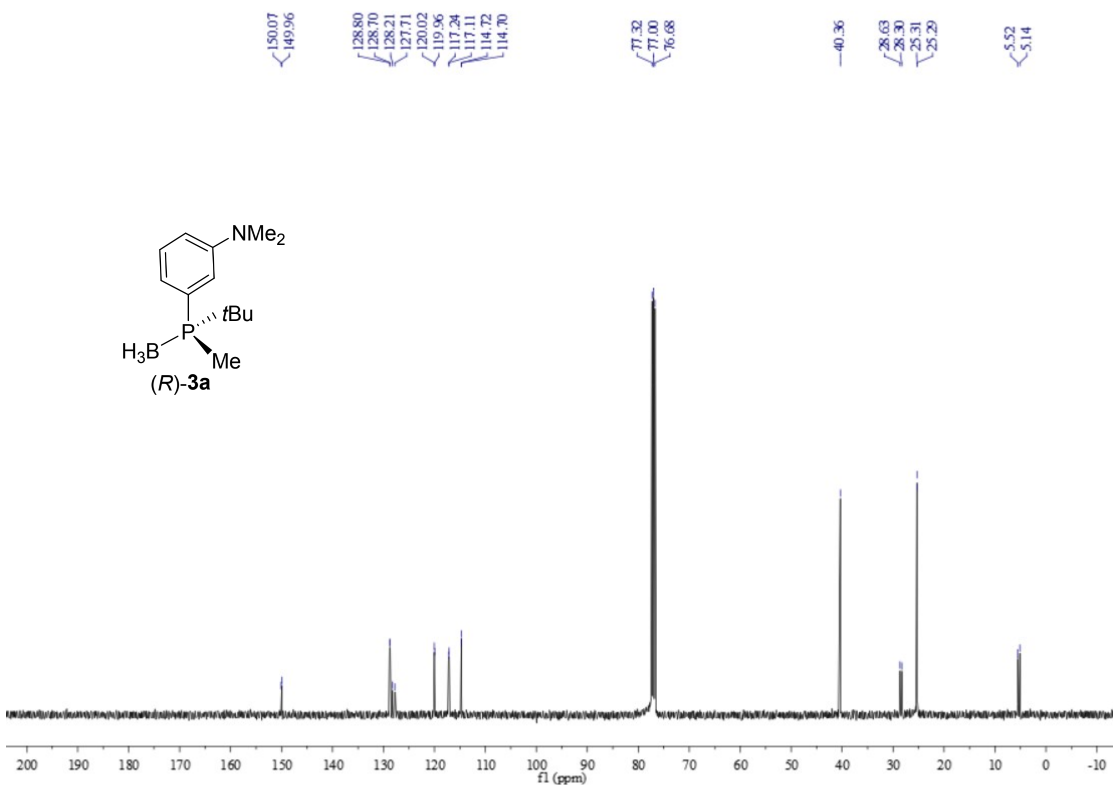


Figure S57. ^{13}C NMR spectrum of (*R*)-**3a** in $CDCl_3$

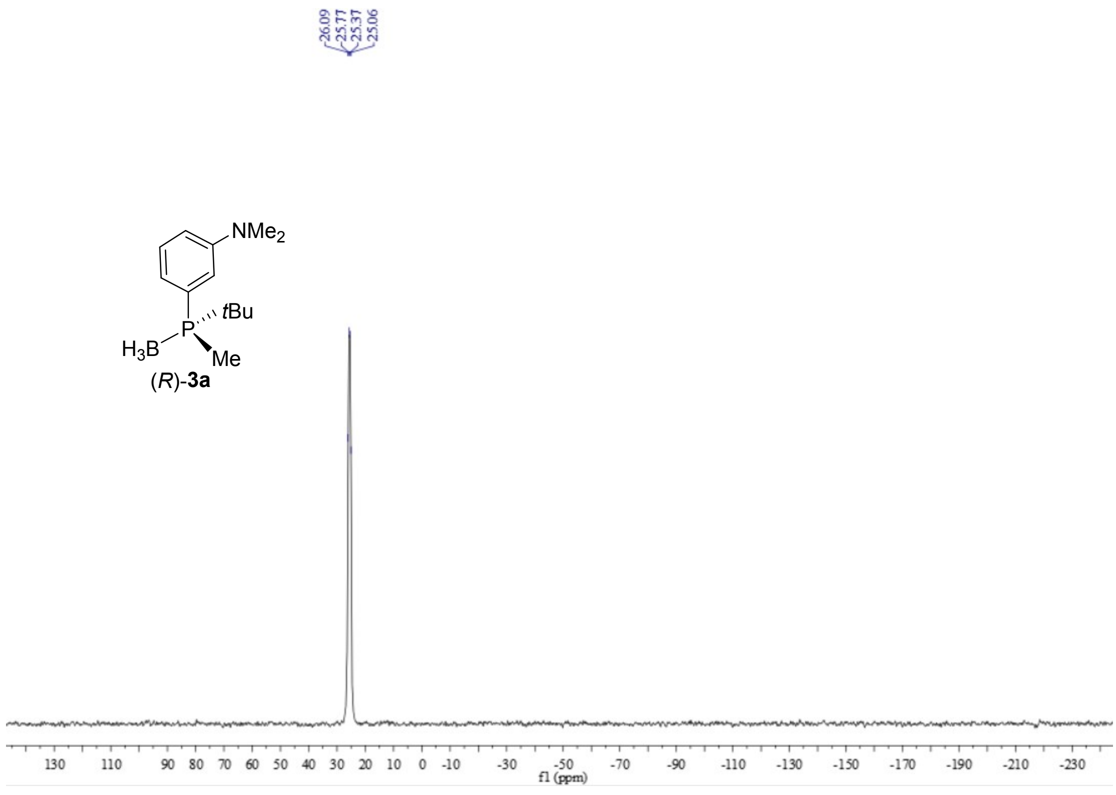


Figure S58. ^{31}P NMR spectrum of (*R*)-**3a** in $CDCl_3$

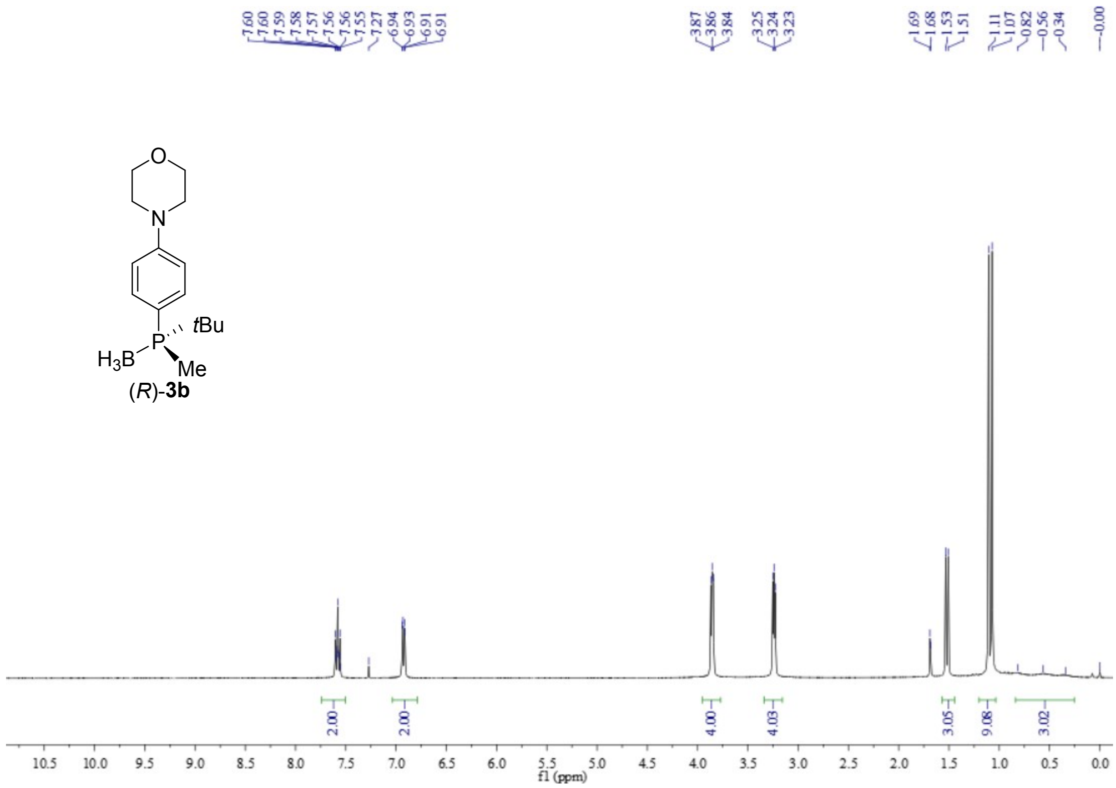


Figure S59. ^{1}H NMR spectrum of (*R*)-**3b** in $CDCl_3$

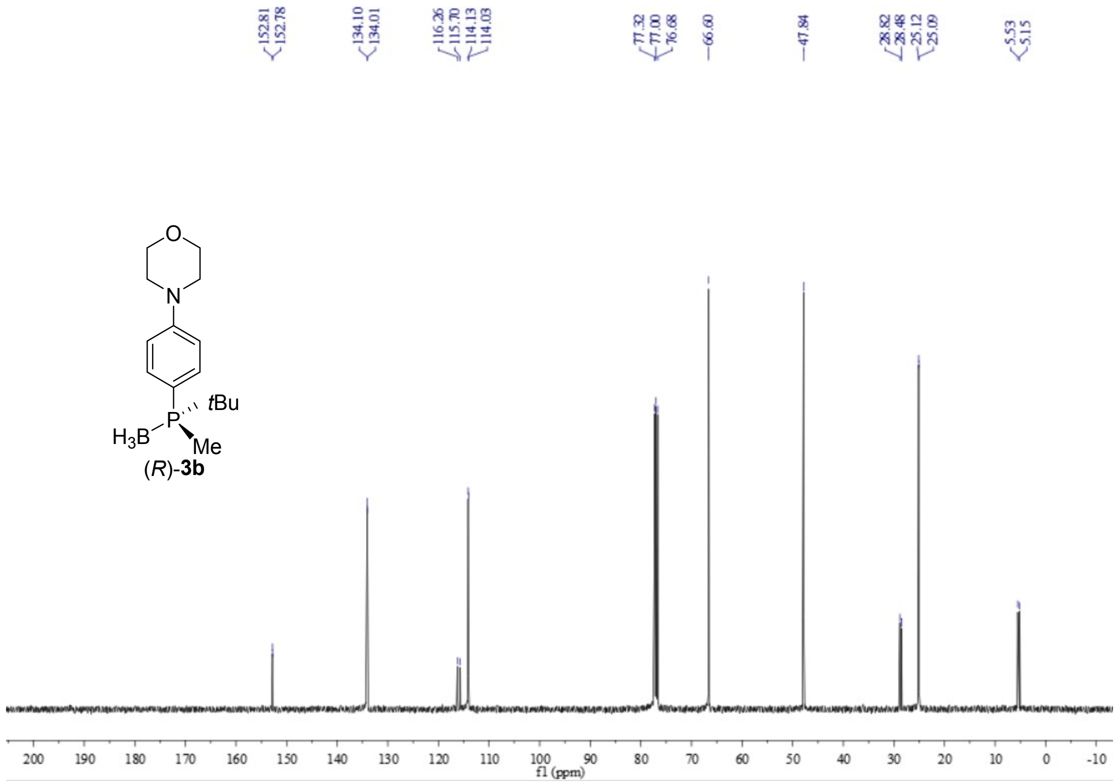


Figure S60. ^{13}C NMR spectrum of(*R*)-**3b** in $CDCl_3$

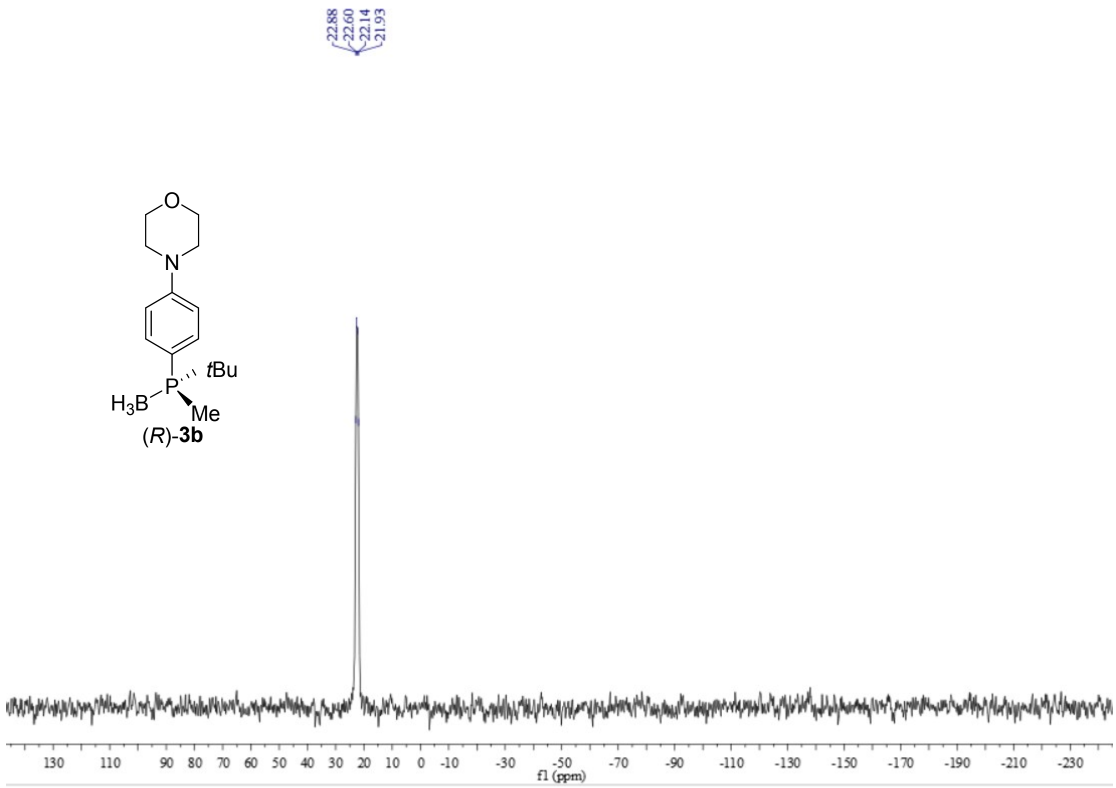


Figure S61. ^{31}P NMR spectrum of (*R*)-**3b** in $CDCl_3$

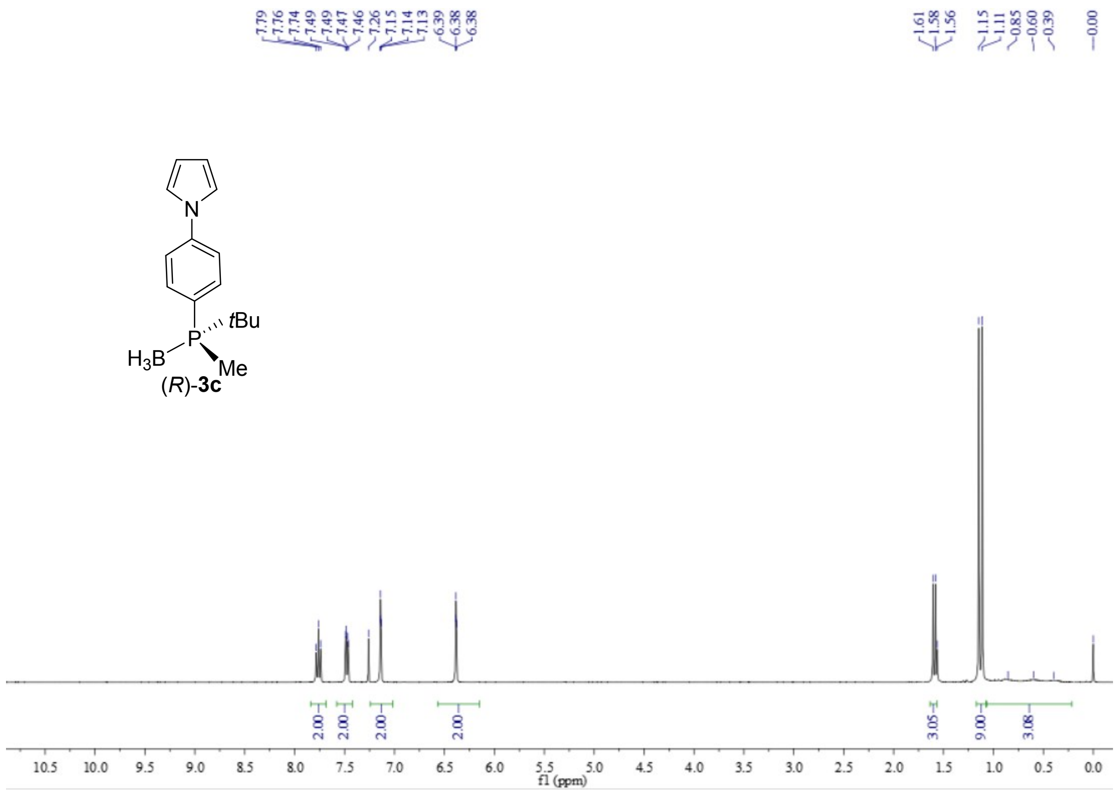


Figure S62. ^{1}H NMR spectrum of (*R*)-**3c** in $CDCl_3$

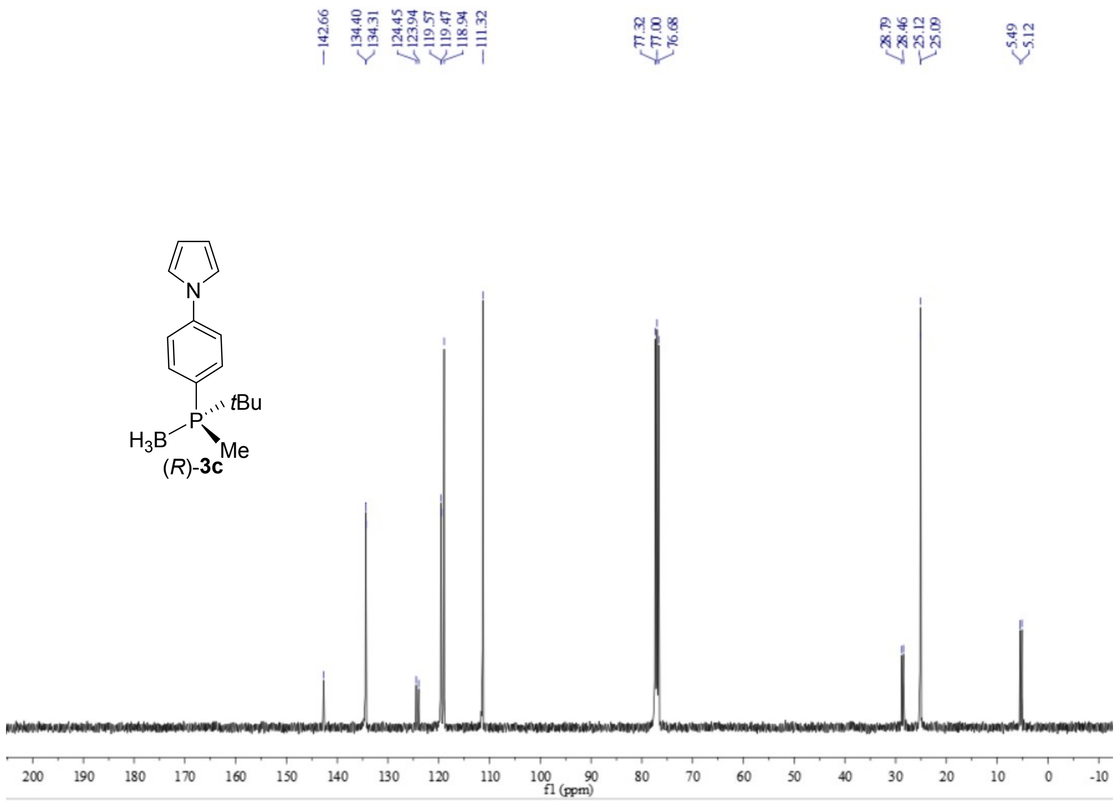


Figure S63. ^{13}C NMR spectrum of (*R*)-**3c** in $CDCl_3$

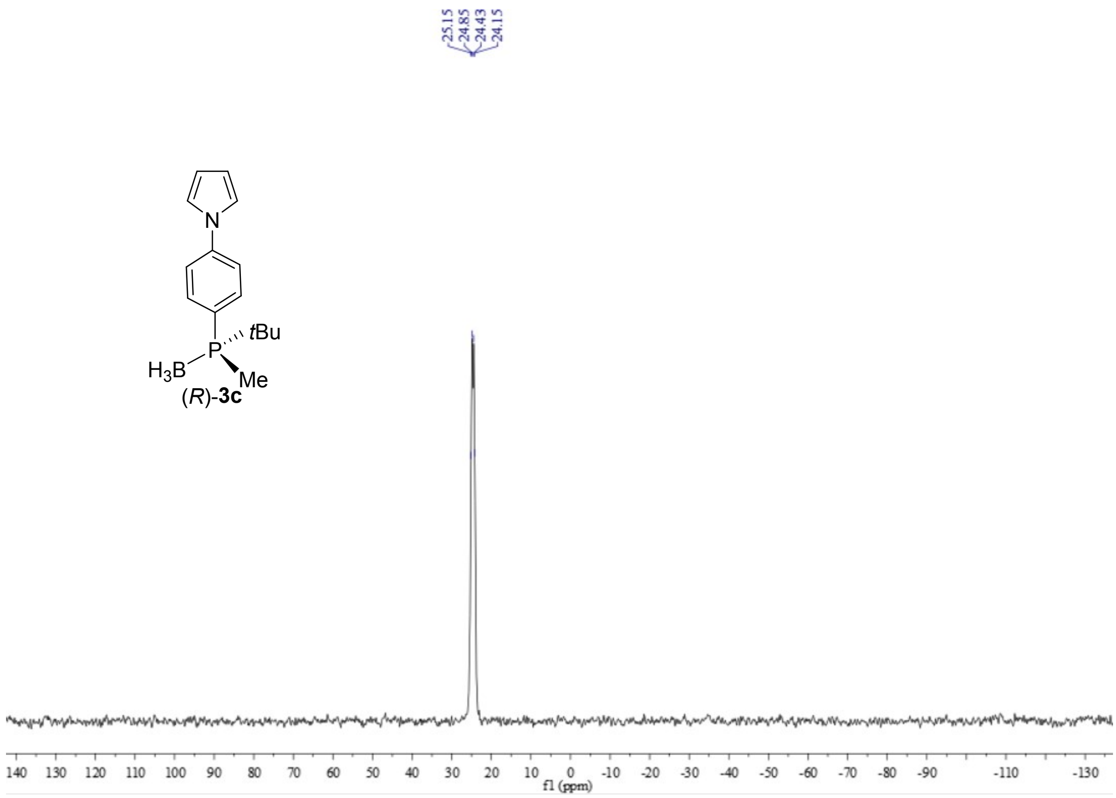


Figure S64. ^{31}P NMR spectrum of (*R*)-**3c** in $CDCl_3$

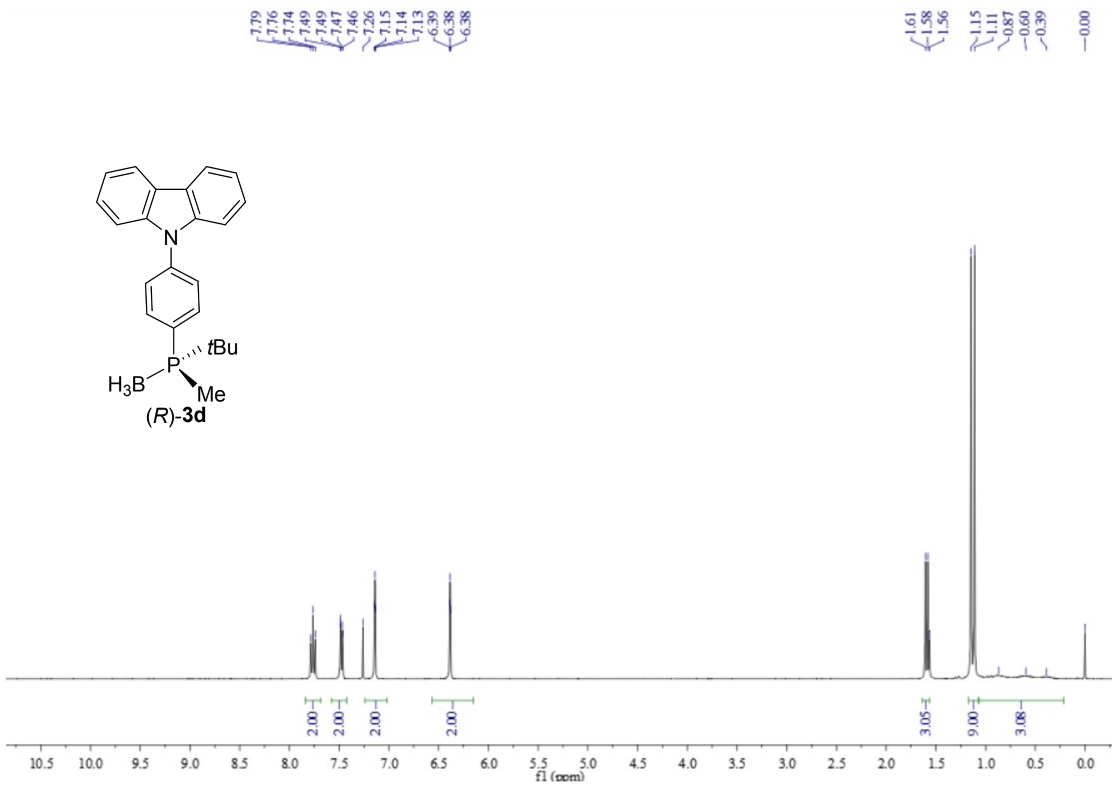


Figure S65. ^{1}H NMR spectrum of (*R*)-**3d** in $CDCl_3$

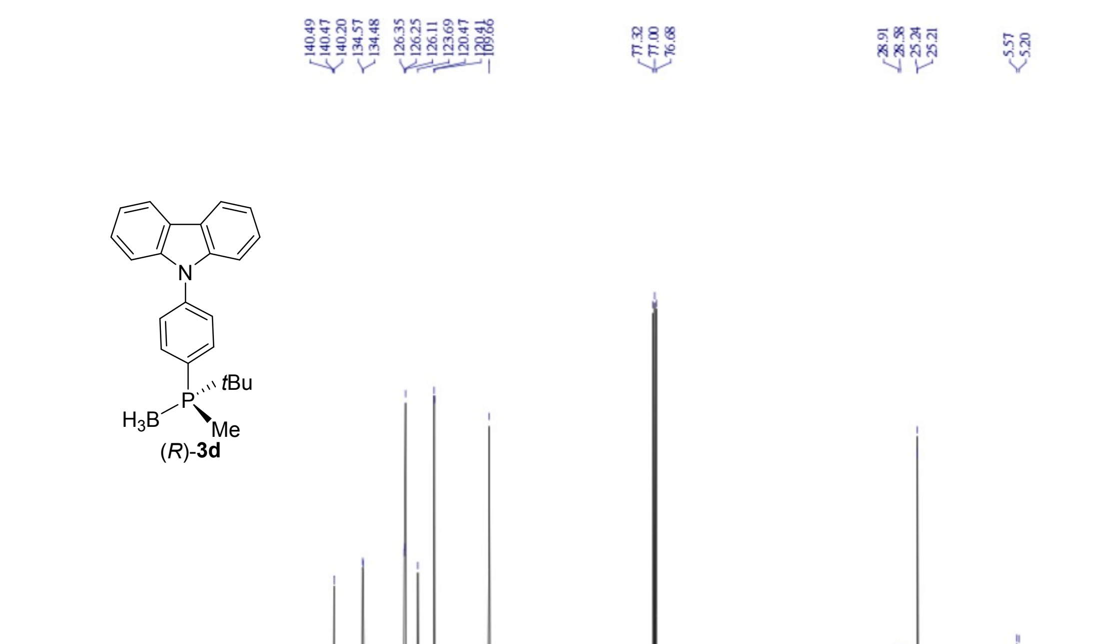


Figure S66. ^{13}C NMR spectrum of (*R*)-**3d** in $CDCl_3$

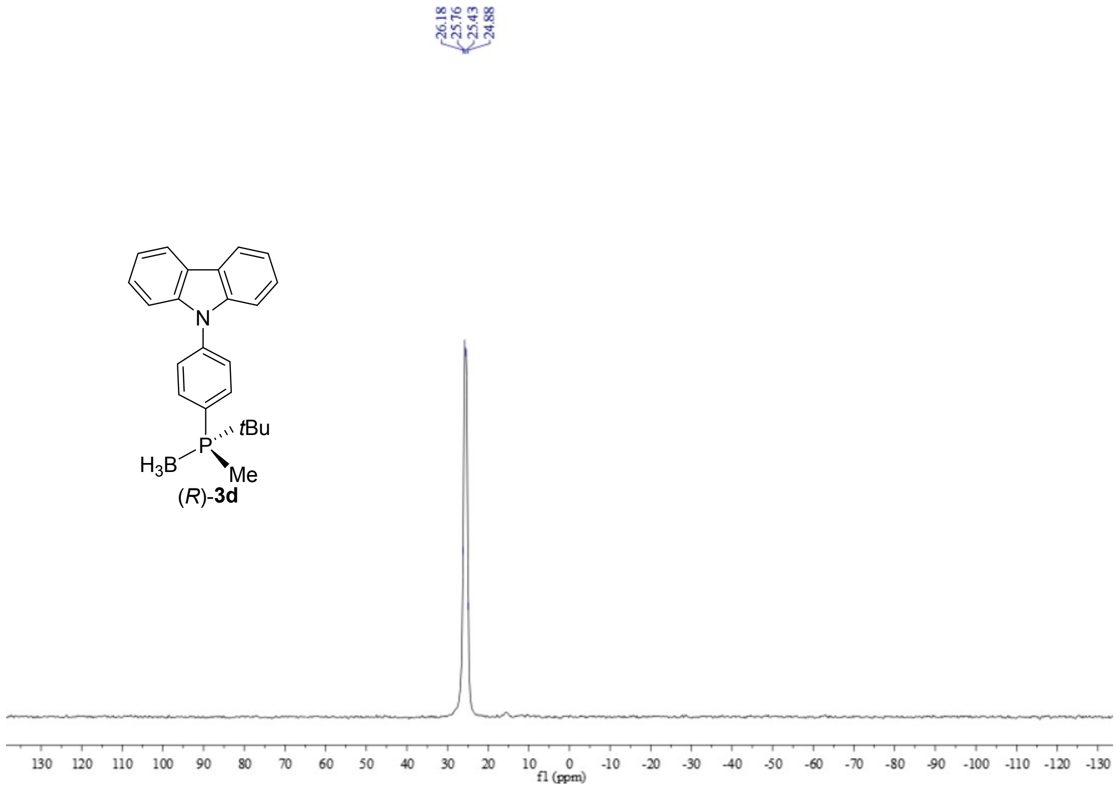


Figure S67. ^{31}P NMR spectrum of (*R*)-**3d** in $CDCl_3$

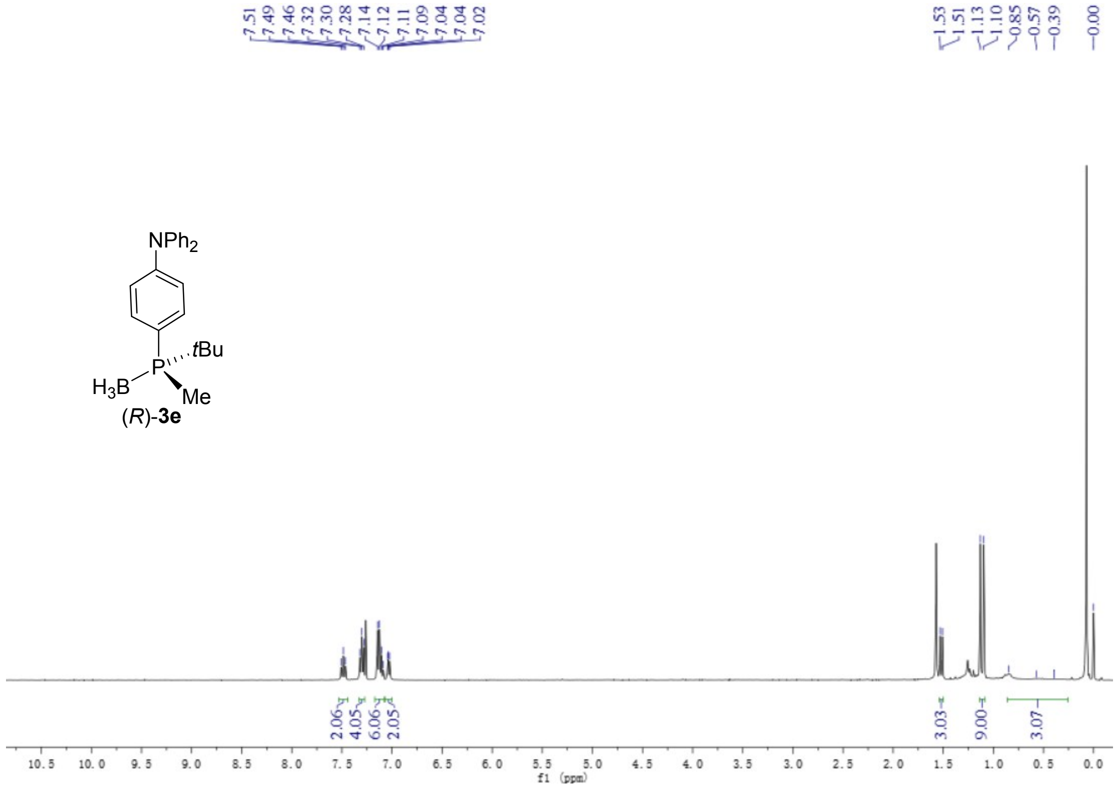


Figure S68. ^{1}H NMR spectrum of (*R*)-**3e** in $CDCl_3$

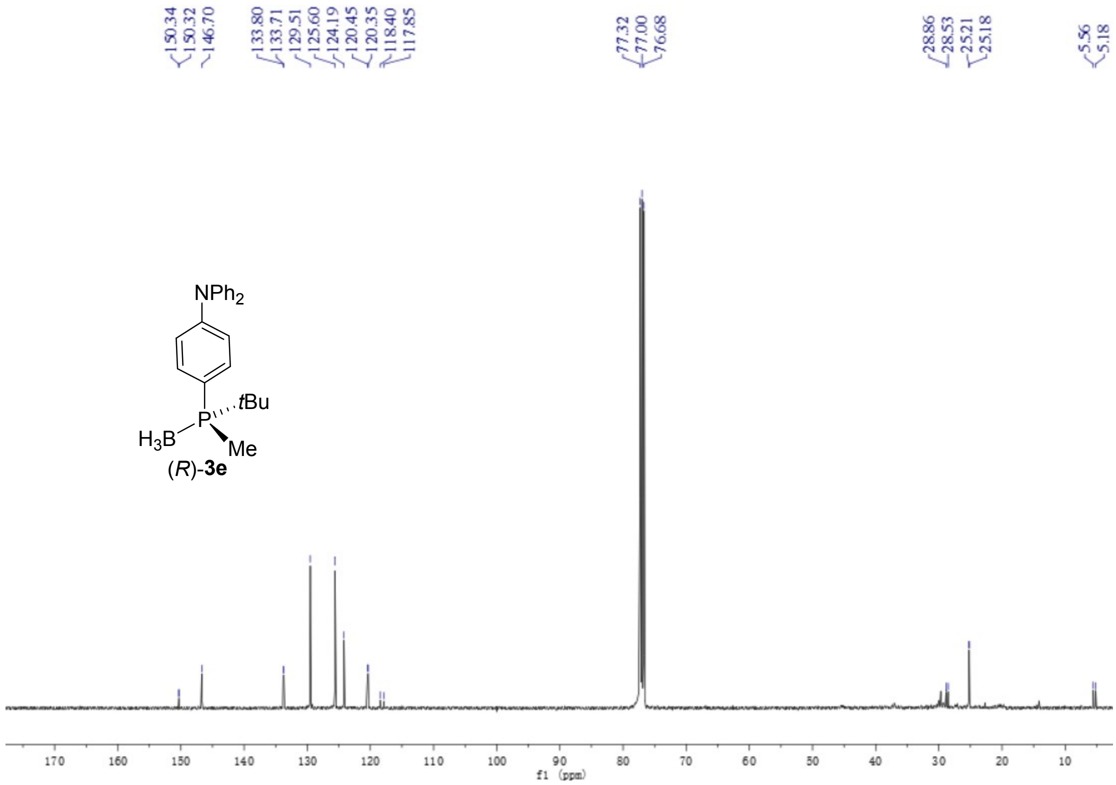


Figure S69. ^{13}C NMR spectrum of (*R*)-**3e** in $CDCl_3$

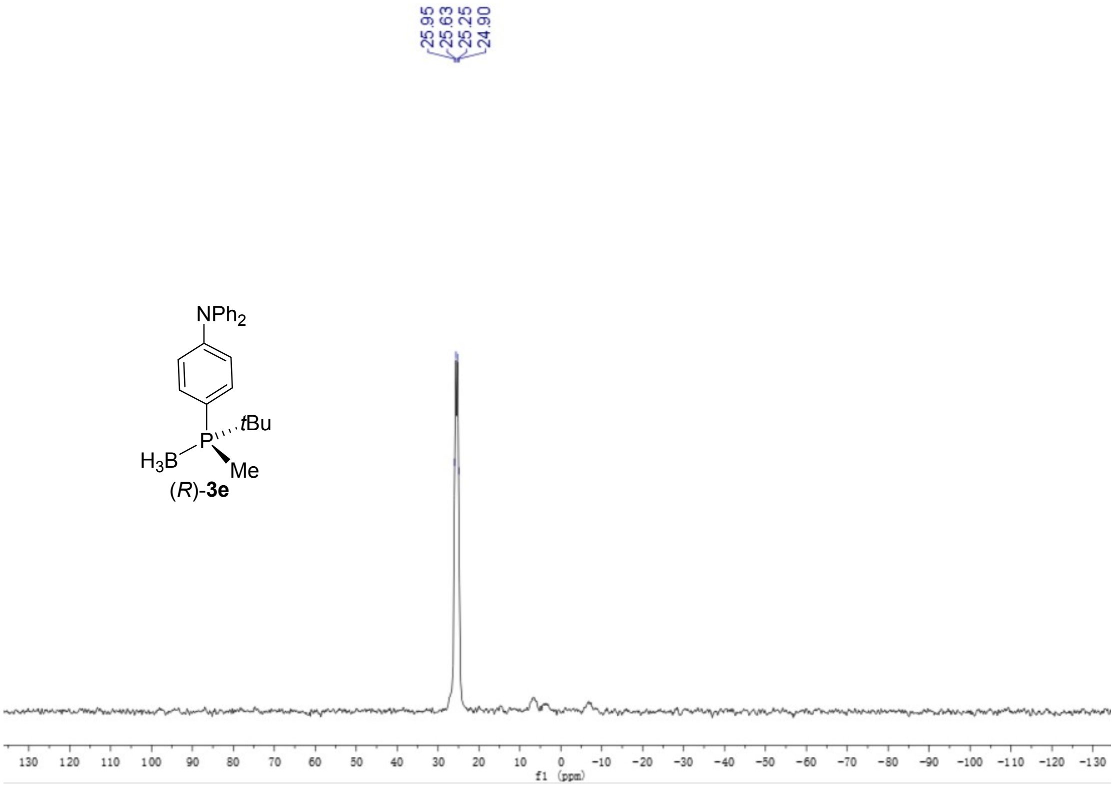


Figure S70. ^{31}P NMR spectrum of (*R*)-**3e** in $CDCl_3$

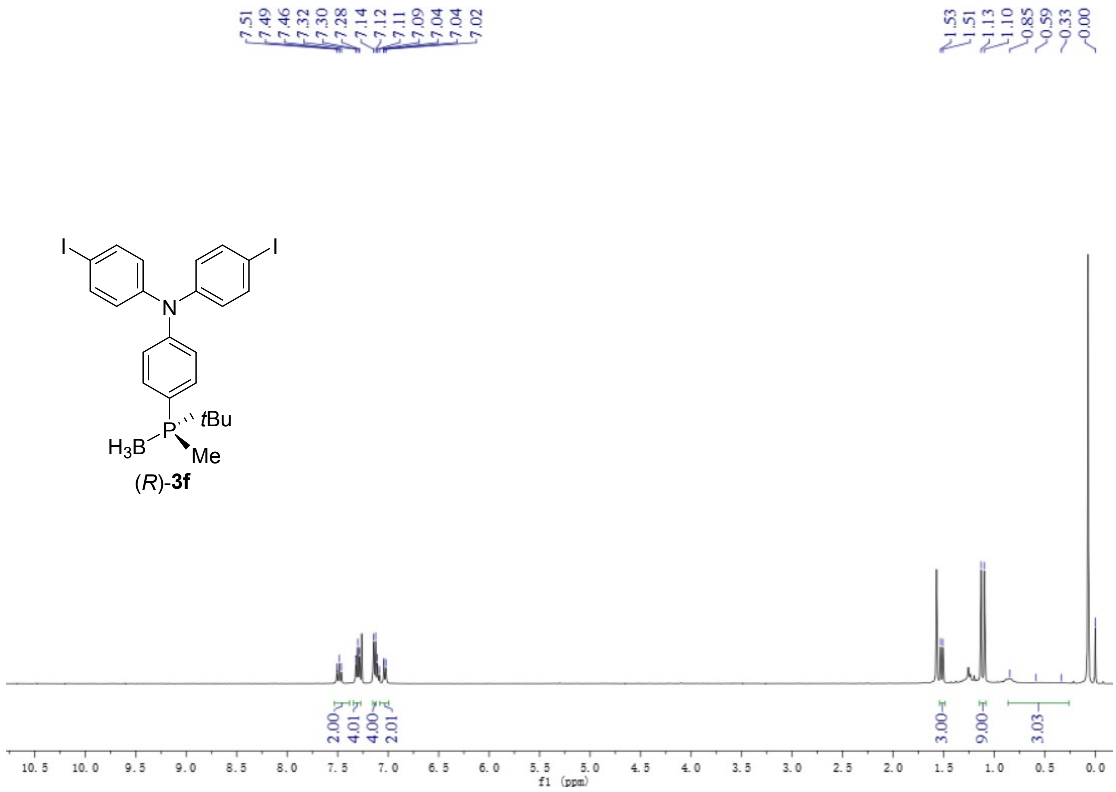


Figure S71. ^{1}H NMR spectrum of (*R*)-**3f** in $CDCl_3$

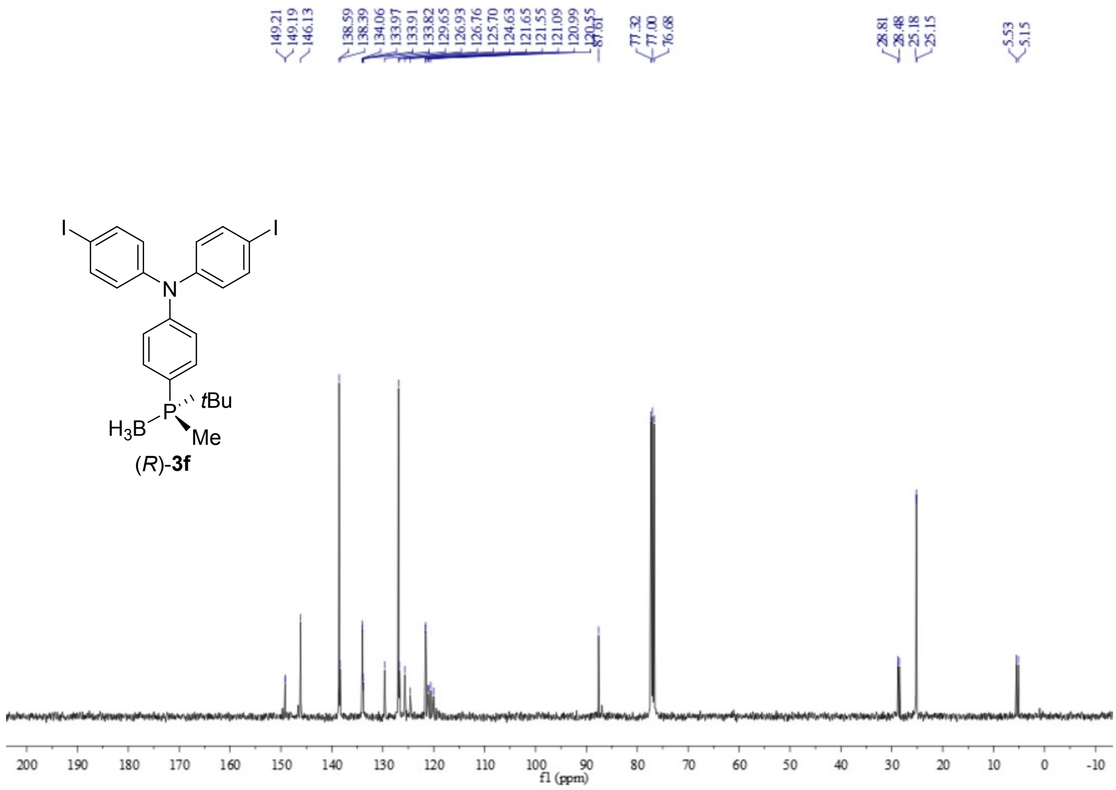


Figure S72. ^{13}C NMR spectrum of (*R*)-**3f** in $CDCl_3$

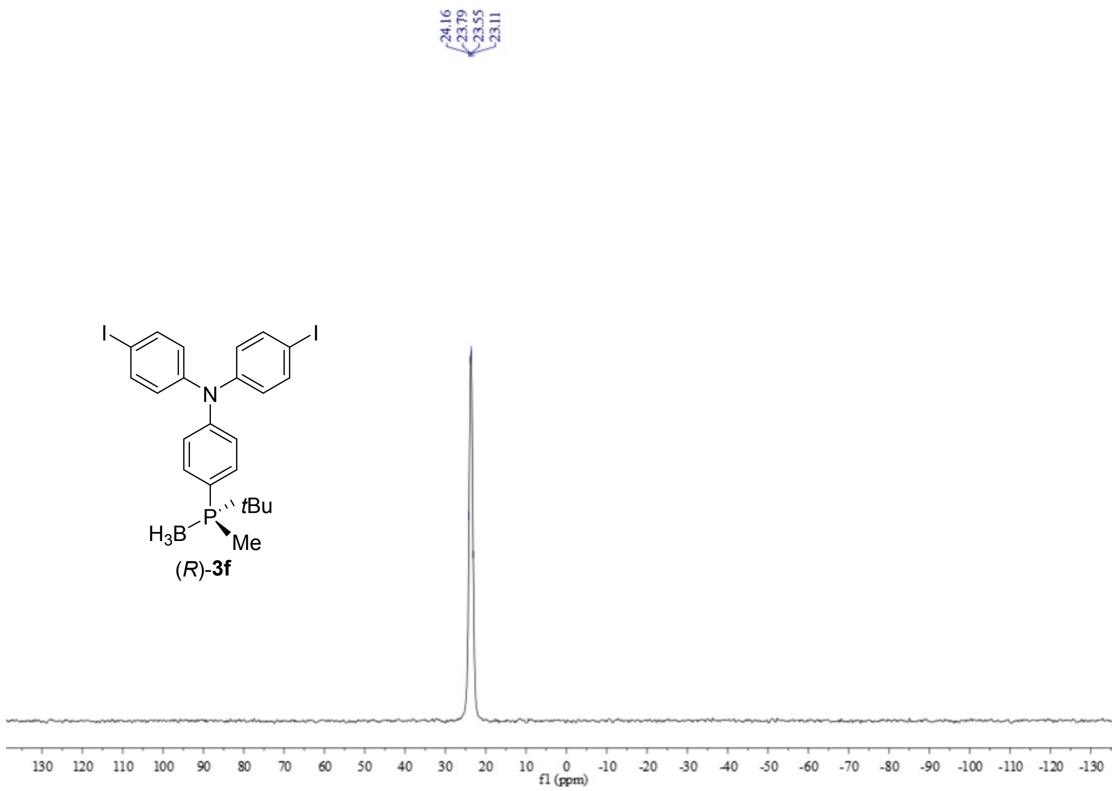


Figure S73. ^{31}P NMR spectrum of (*R*)-**3f** in $CDCl_3$

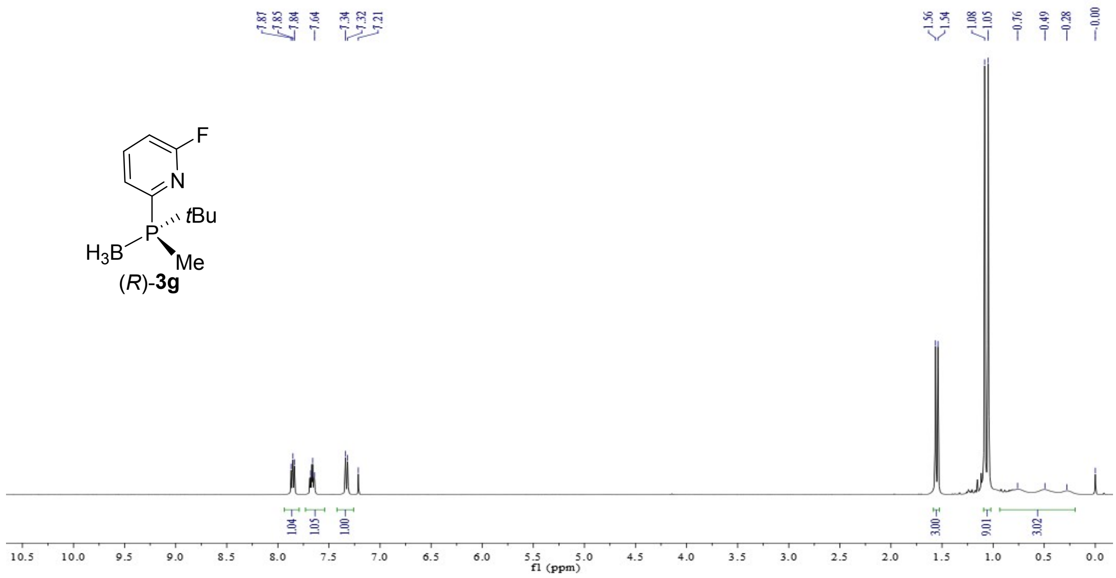


Figure S74. ^{1}H NMR spectrum of (*R*)-**3g** in $CDCl_3$

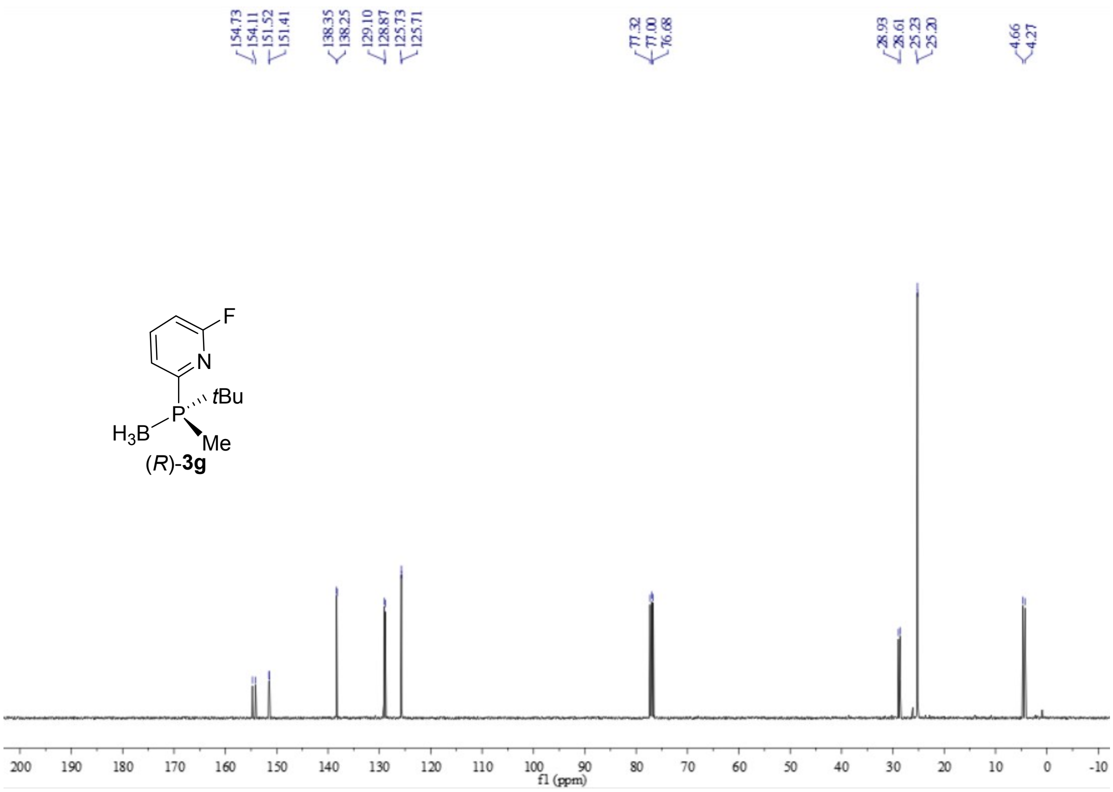


Figure S75. ^{13}C NMR spectrum of (*R*)-**3g** in $CDCl_3$

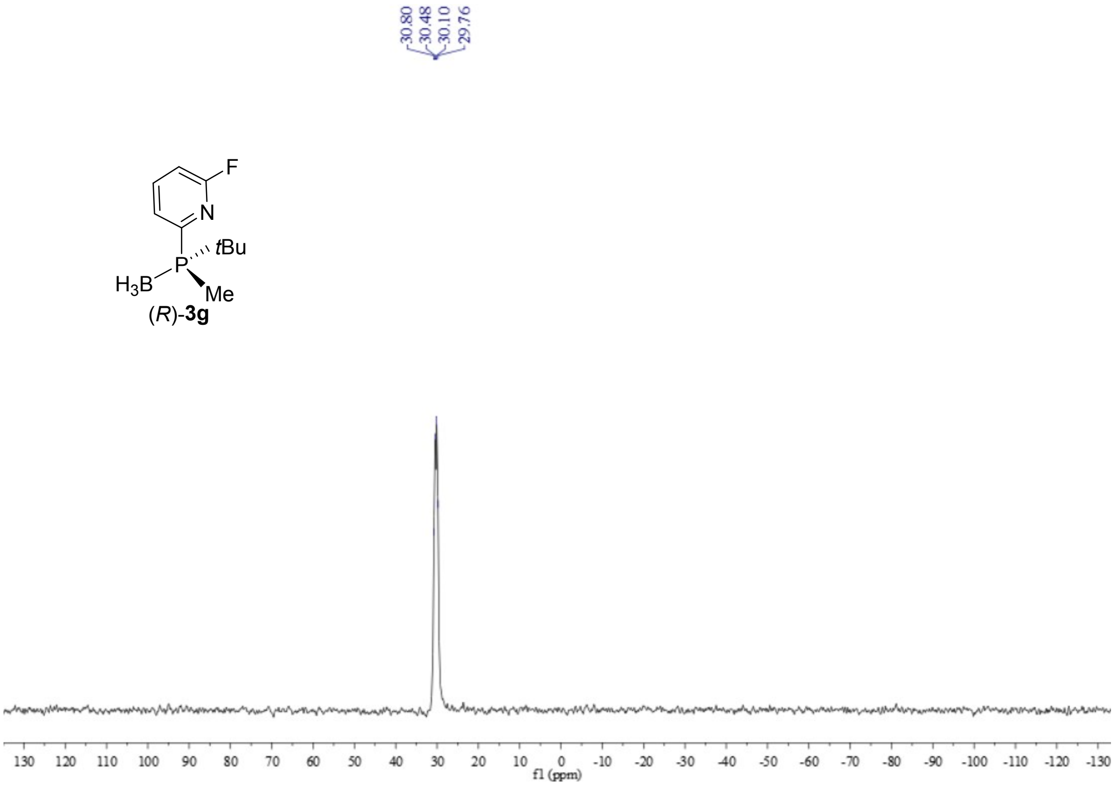


Figure S76. ^{31}P NMR spectrum of (*R*)-**3g** in $CDCl_3$

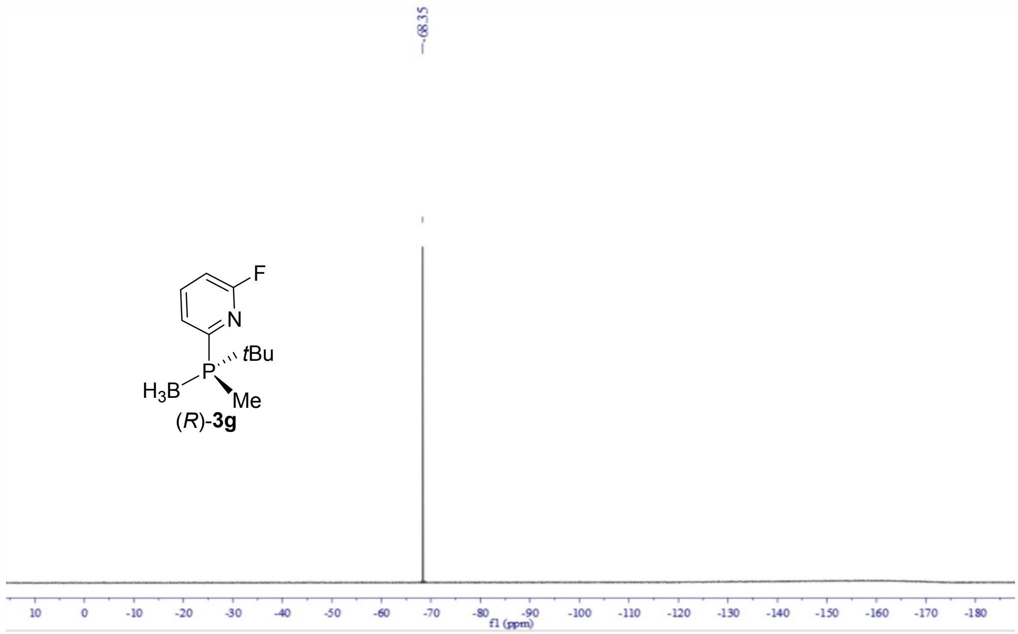


Figure S77. ^{19}F NMR spectrum of (*R*)-**3g** in $CDCl_3$

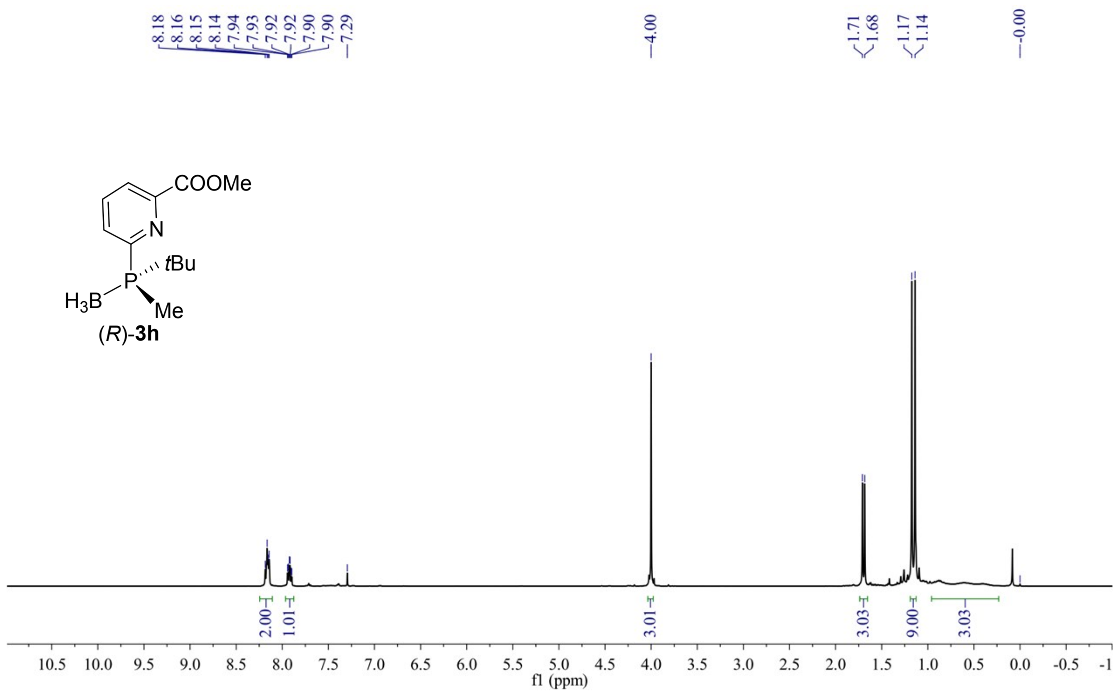


Figure S78. ^{1}H NMR spectrum of (*R*)-**3h** in $CDCl_3$

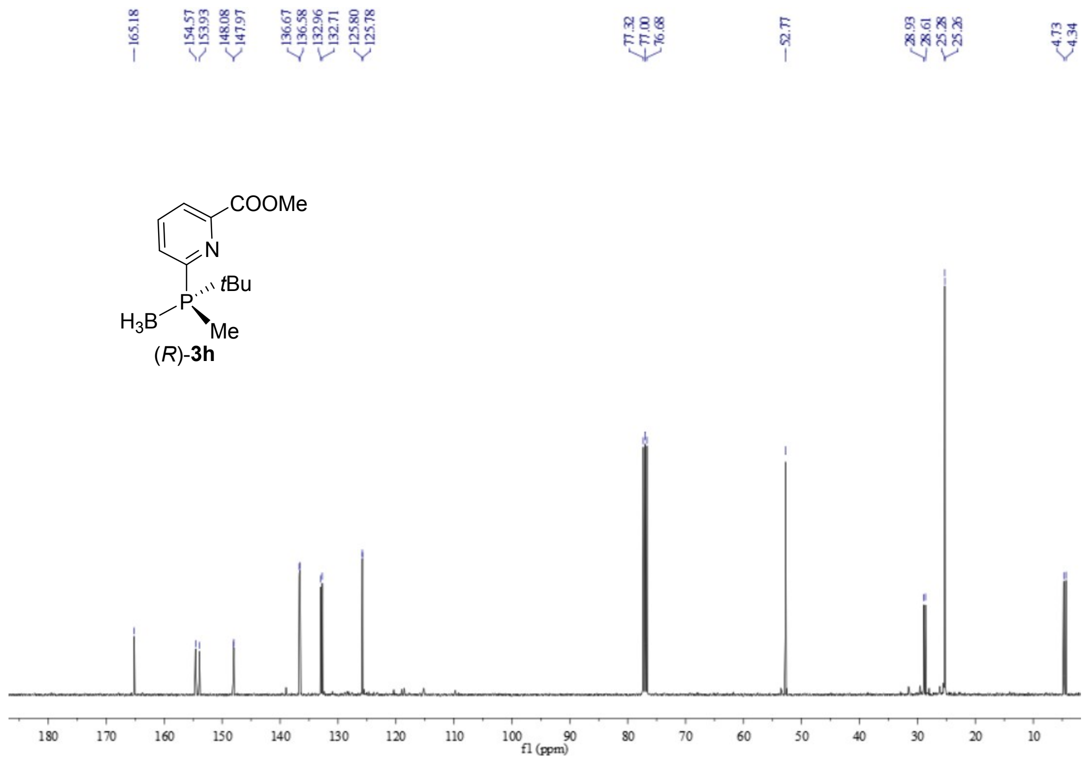


Figure S79. ^{13}C NMR spectrum of (*R*)-**3h** in $CDCl_3$

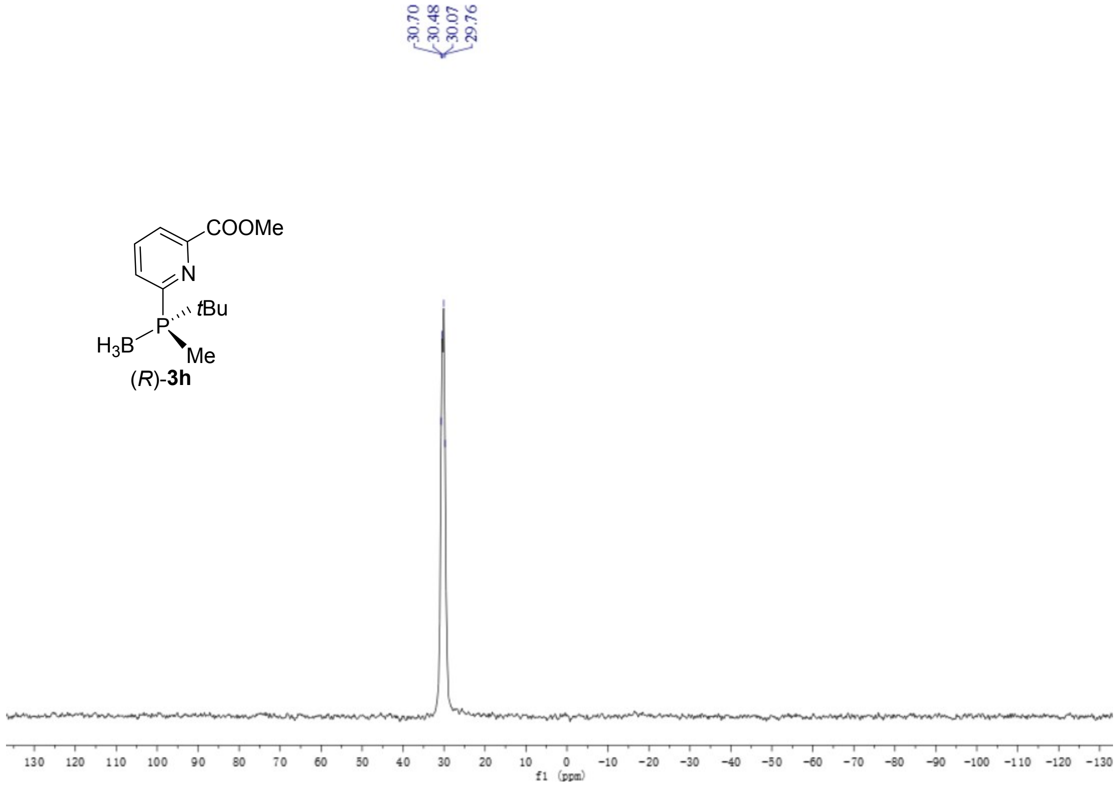


Figure S80. ^{31}P NMR spectrum of (*R*)-**3h** in $CDCl_3$

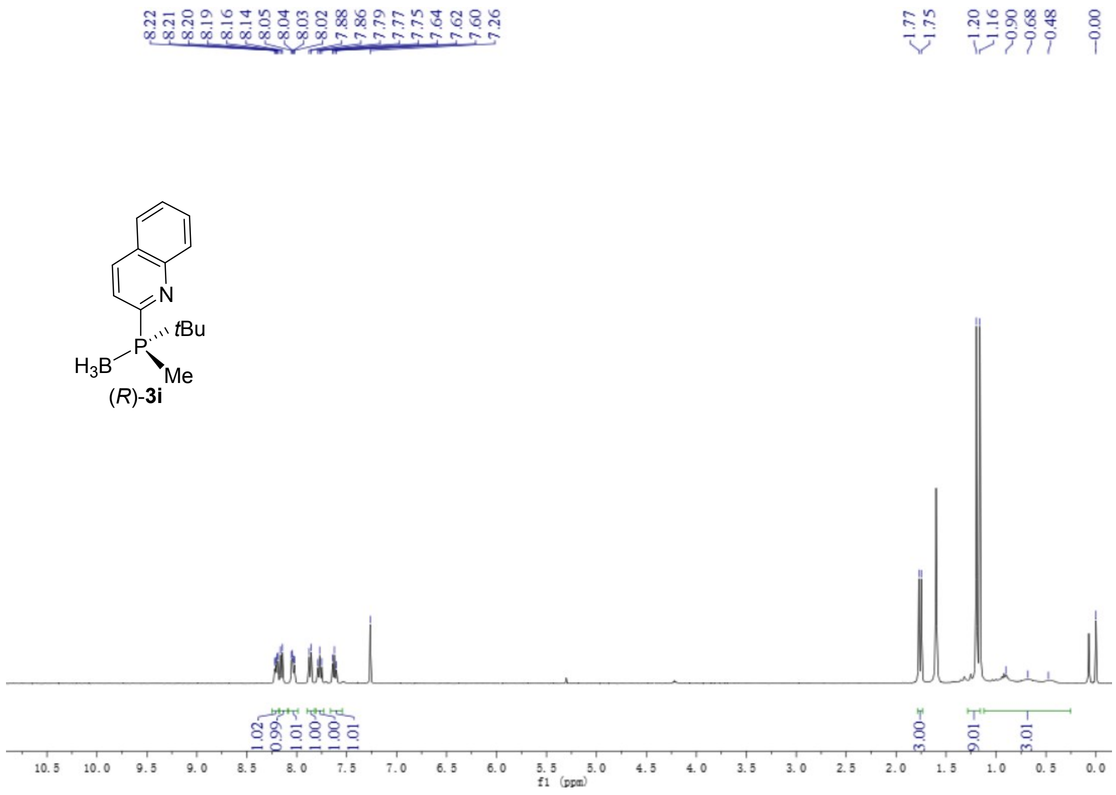


Figure S81. ^{1}H NMR spectrum of (*R*)-**3i** in $CDCl_3$

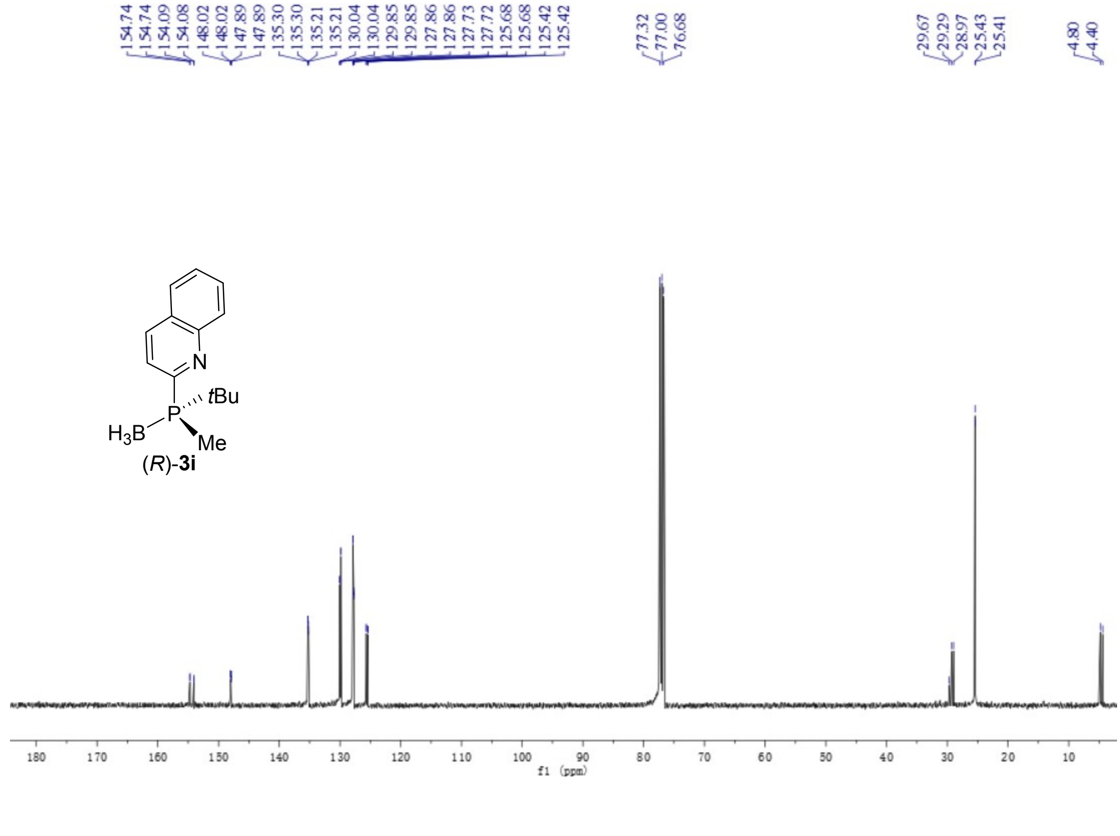


Figure S82. ^{13}C NMR spectrum of (*R*)-**3i** in $CDCl_3$

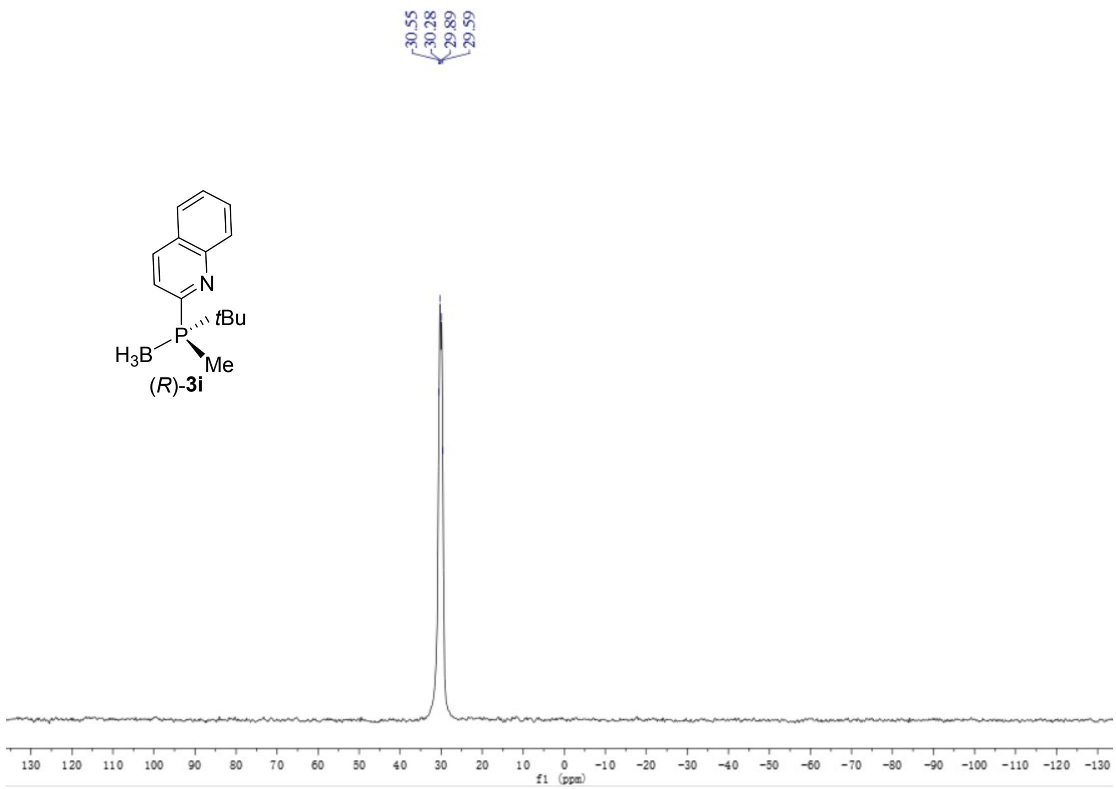


Figure S83. ^{31}P NMR spectrum of (*R*)-**3i** in $CDCl_3$

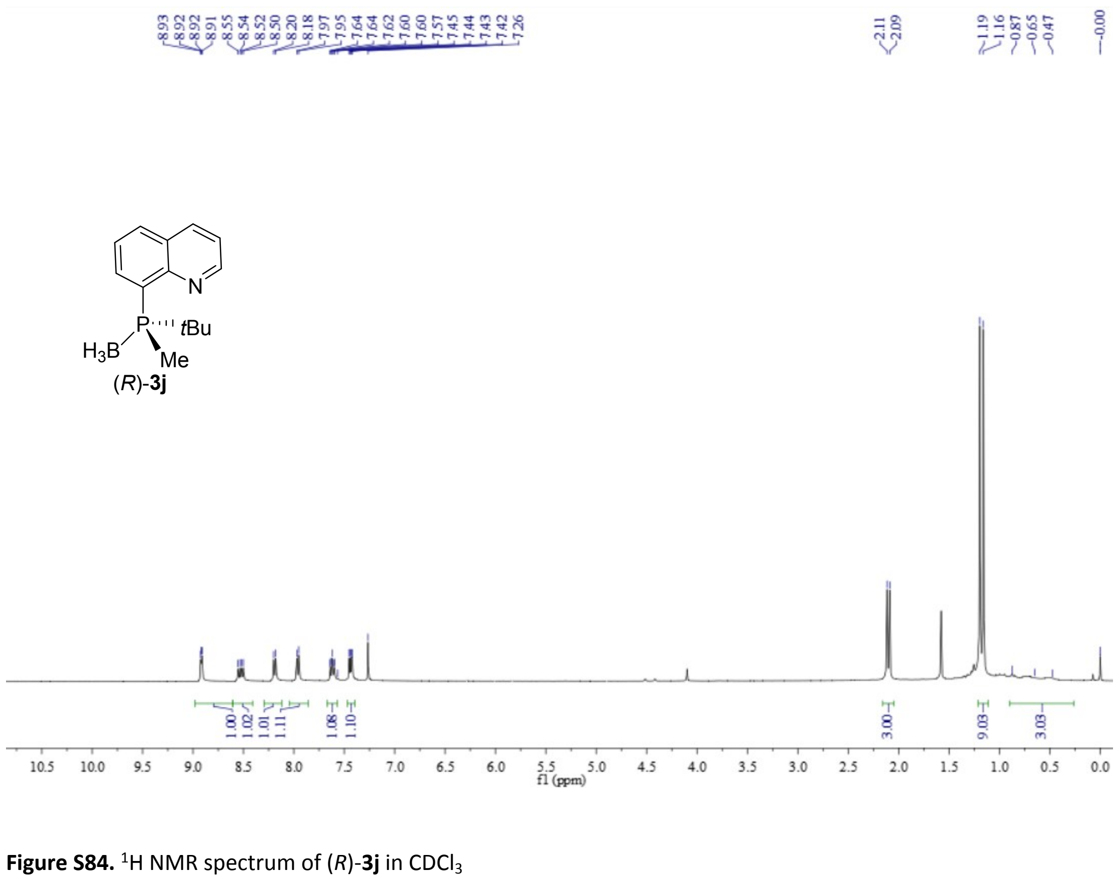


Figure S84. ^{1}H NMR spectrum of (*R*)-**3j** in $CDCl_3$

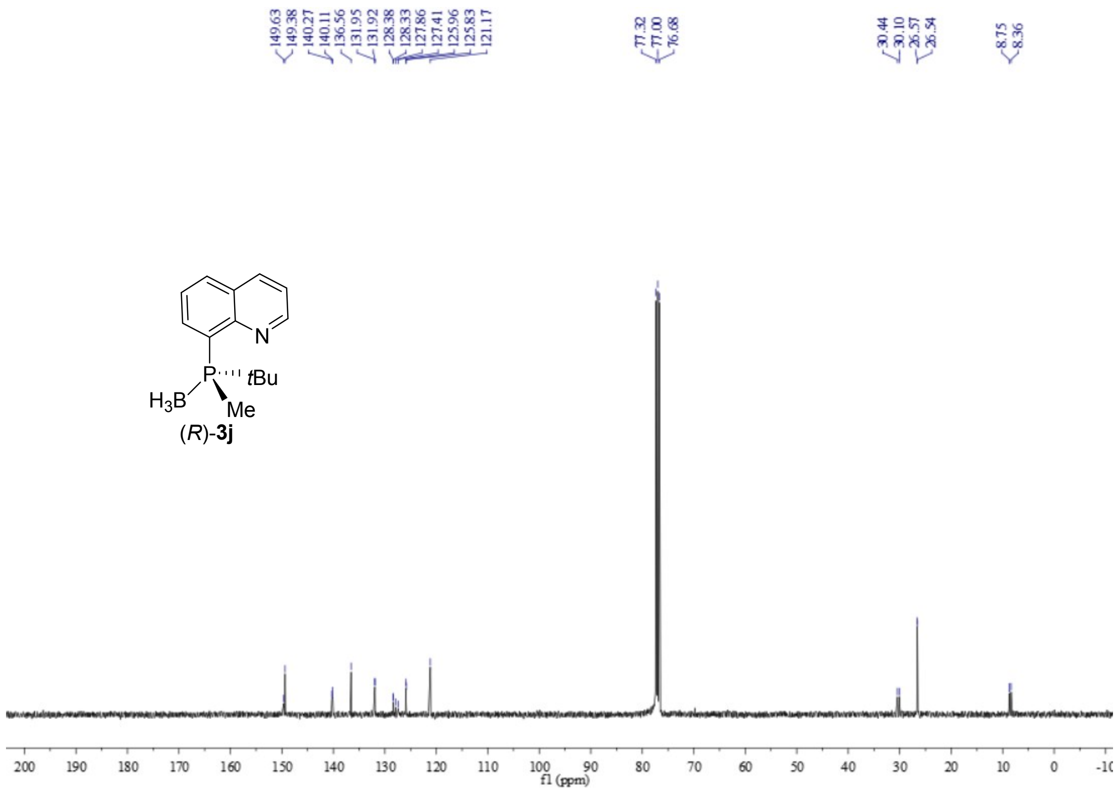


Figure S85. ^{13}C NMR spectrum of (*R*)-**3j** in $CDCl_3$

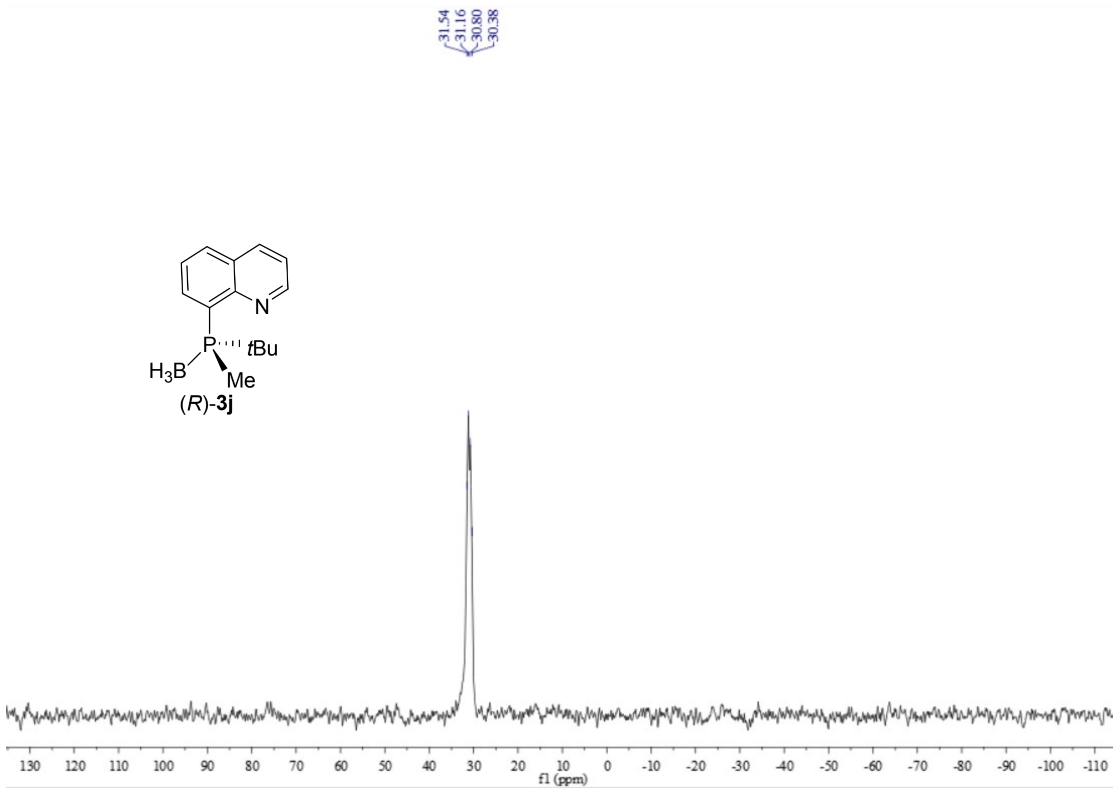


Figure S86. ^{31}P NMR spectrum of (*R*)-**3j** in $CDCl_3$

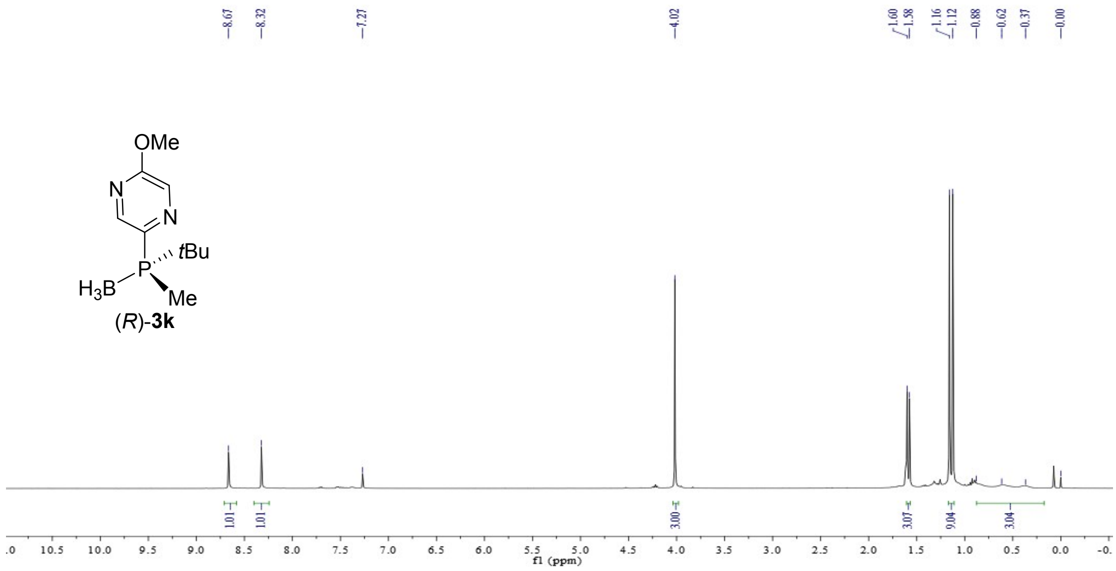


Figure S87. ^{1}H NMR spectrum of (*R*)-**3k** in $CDCl_3$

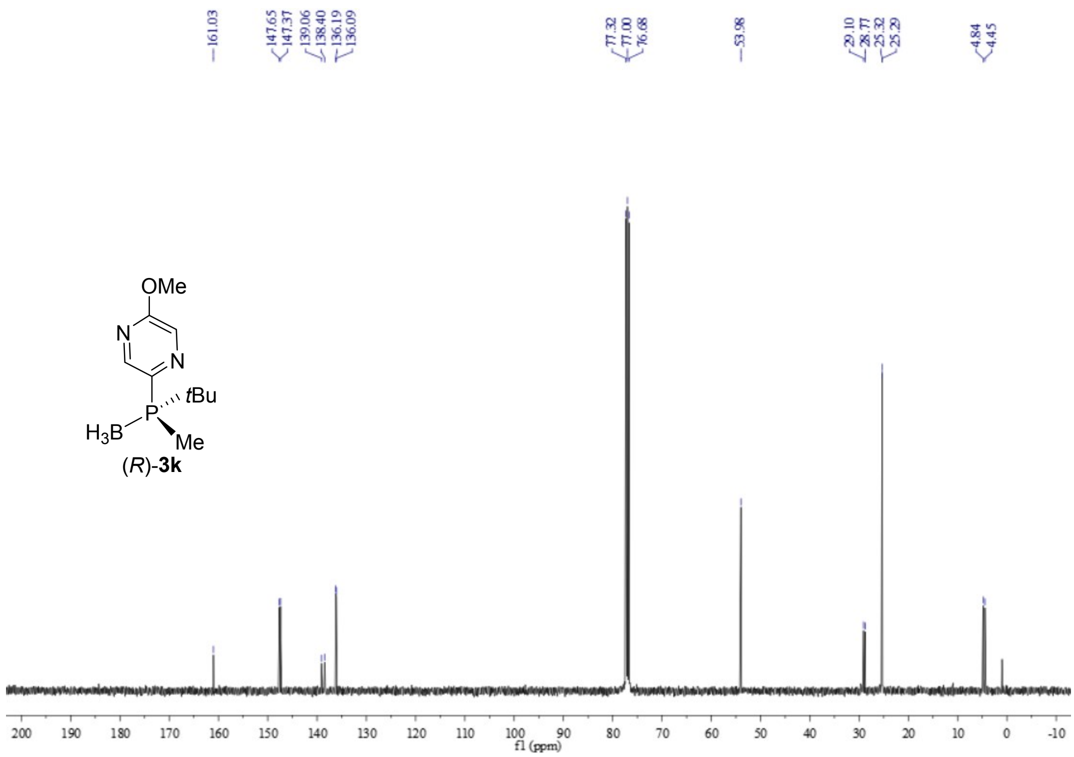


Figure S88. ^{13}C NMR spectrum of (*R*)-**3k** in $CDCl_3$

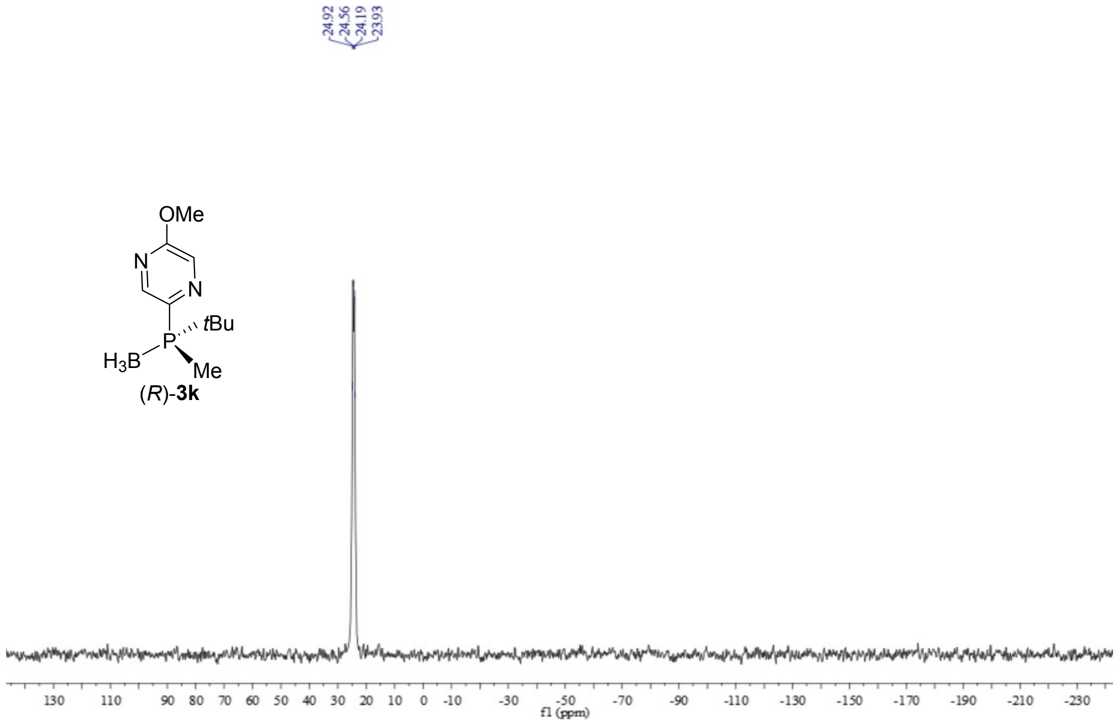


Figure S89. ^{31}P NMR spectrum of (*R*)-**3k** in $CDCl_3$

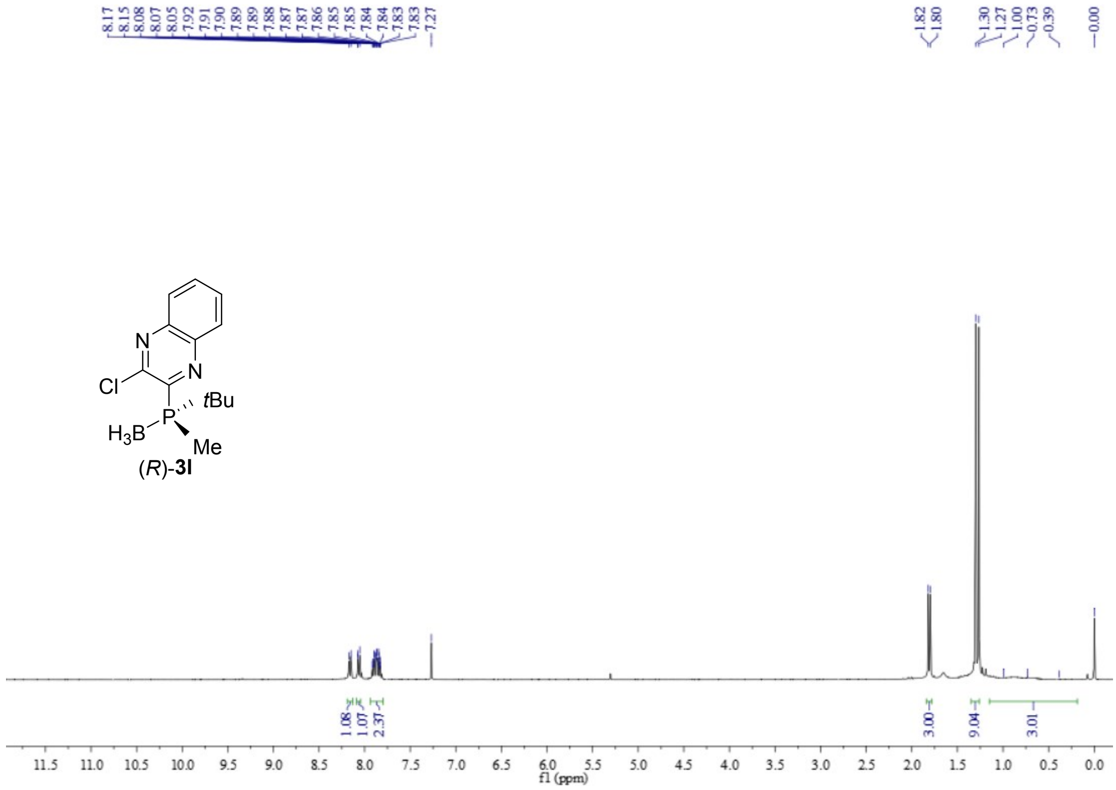


Figure S90. ^{1}H NMR spectrum of (*R*)-**3l** in $CDCl_3$

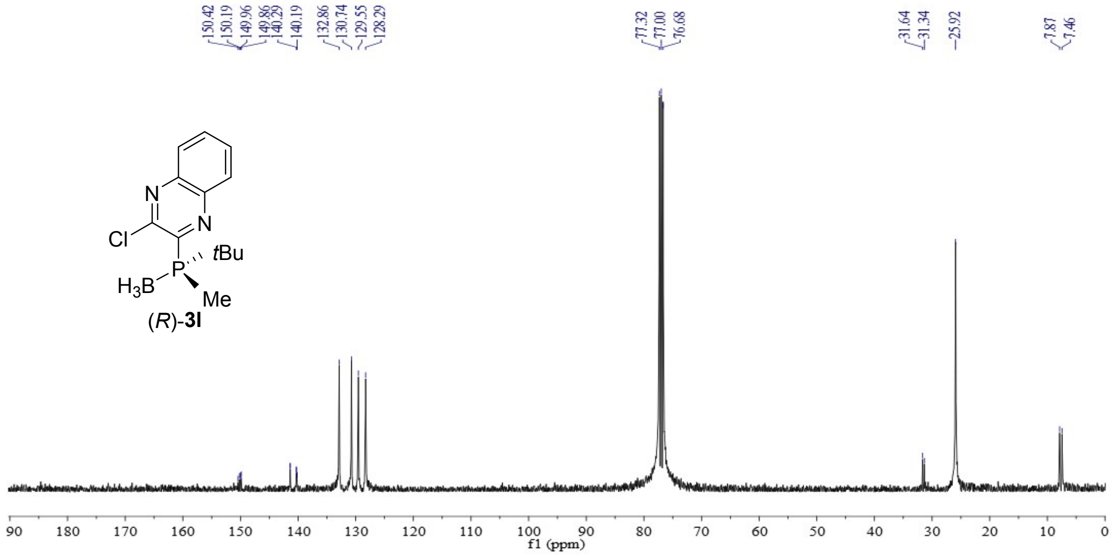


Figure S91. ^{13}C NMR spectrum of (*R*)-**3l** in $CDCl_3$

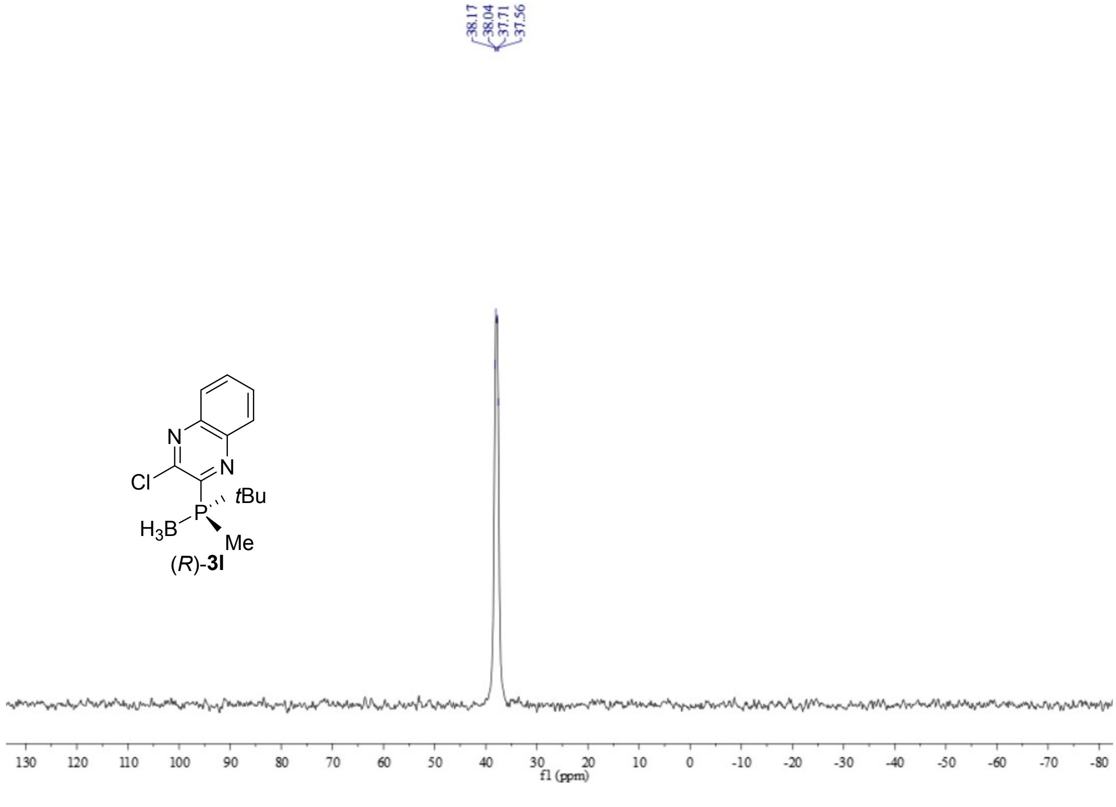


Figure S92. ^{31}P NMR spectrum of (*R*)-**3l** in $CDCl_3$

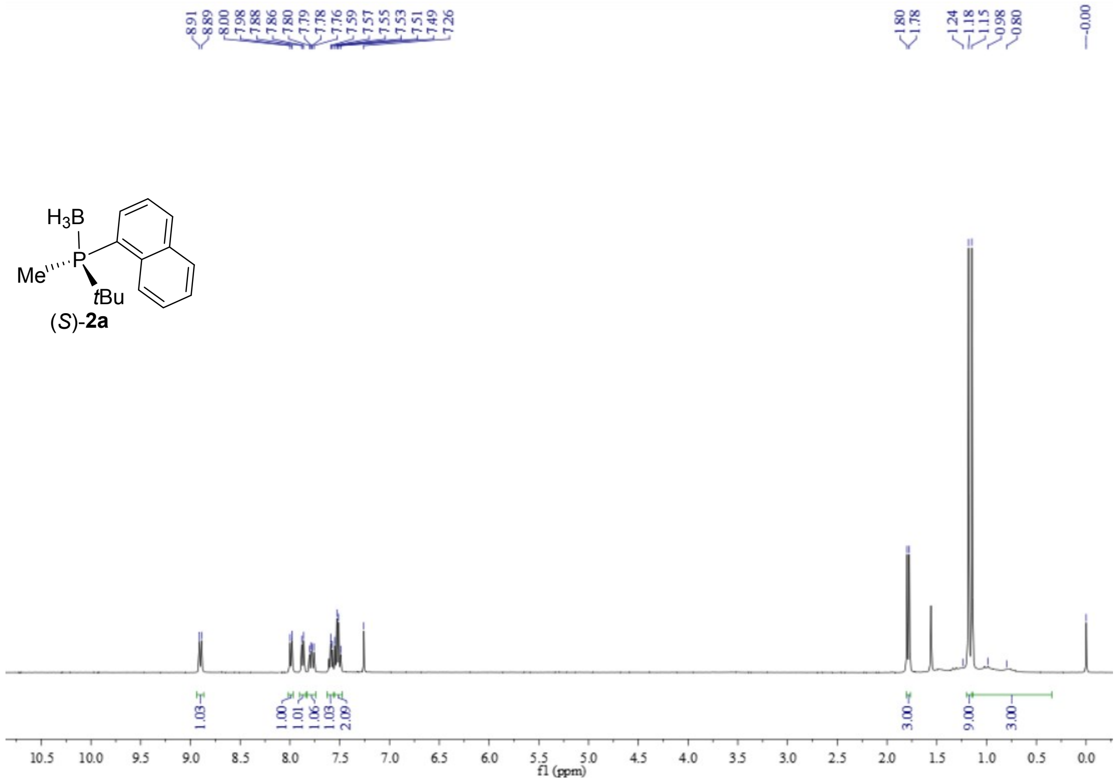


Figure S93. ^{1}H NMR spectrum of (*S*)-**2a** in $CDCl_3$

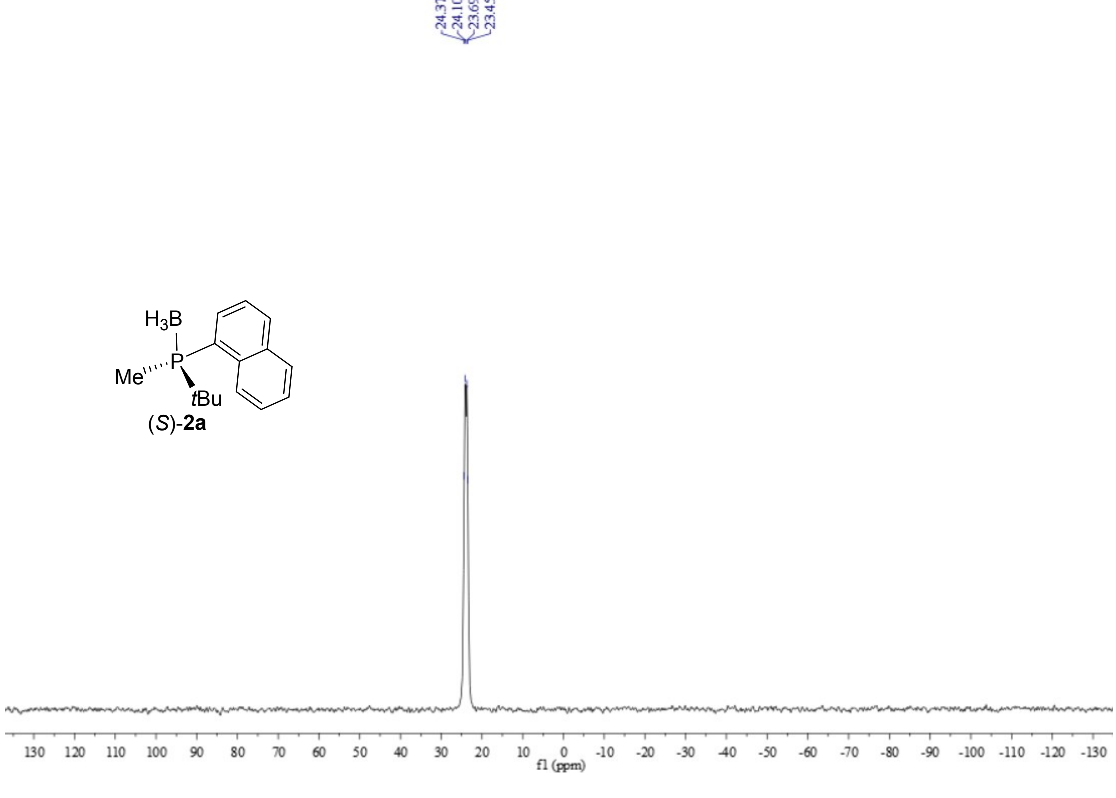


Figure S94. ^{31}P NMR spectrum of (*S*)-**2a** in $CDCl_3$

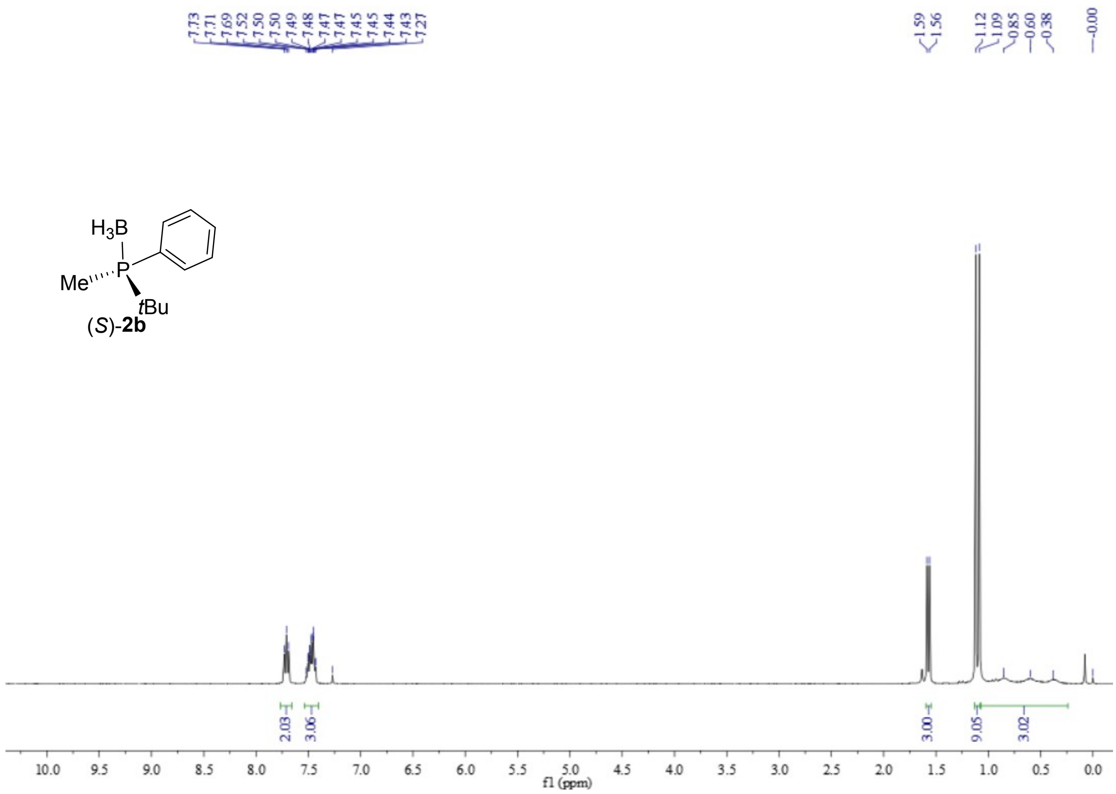


Figure S95. ^{1}H NMR spectrum of (*S*)-**2b** in $CDCl_3$

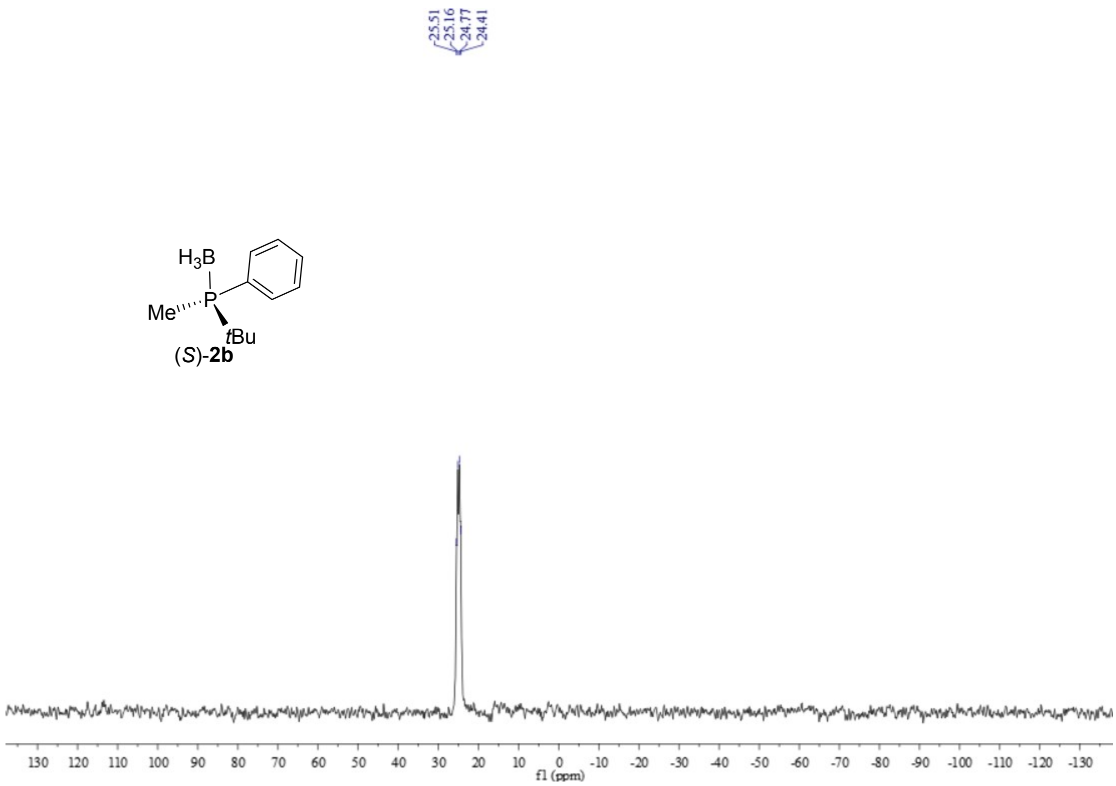


Figure S96. ^{31}P NMR spectrum of (*S*)-**2b** in $CDCl_3$

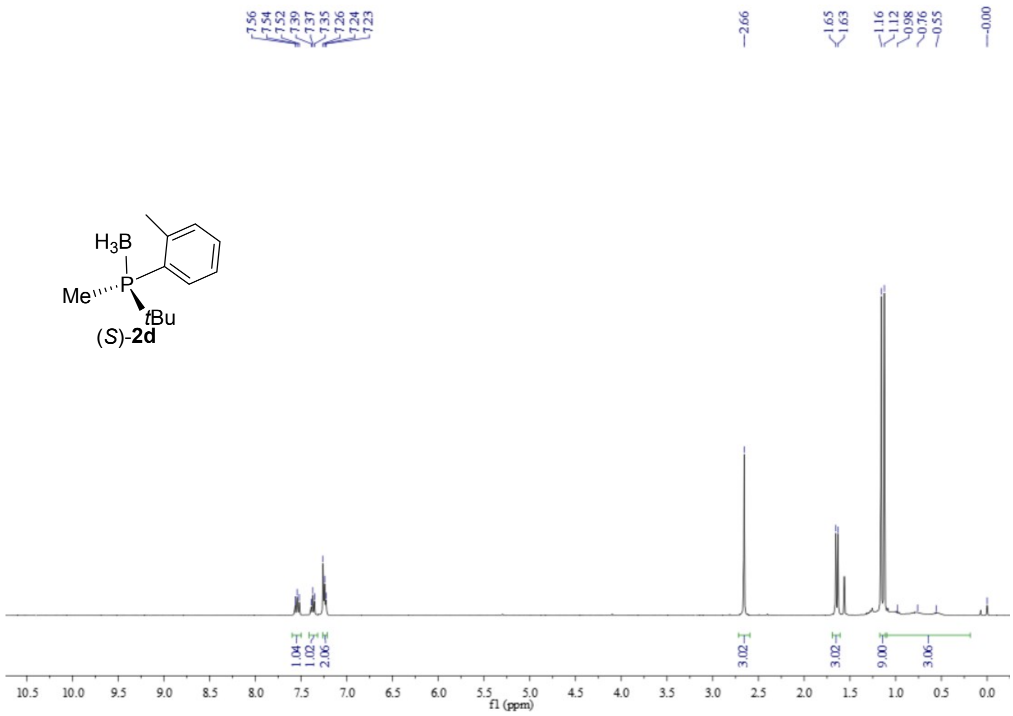


Figure S97. ^{1}H NMR spectrum of (*S*)-**2d** in $CDCl_3$

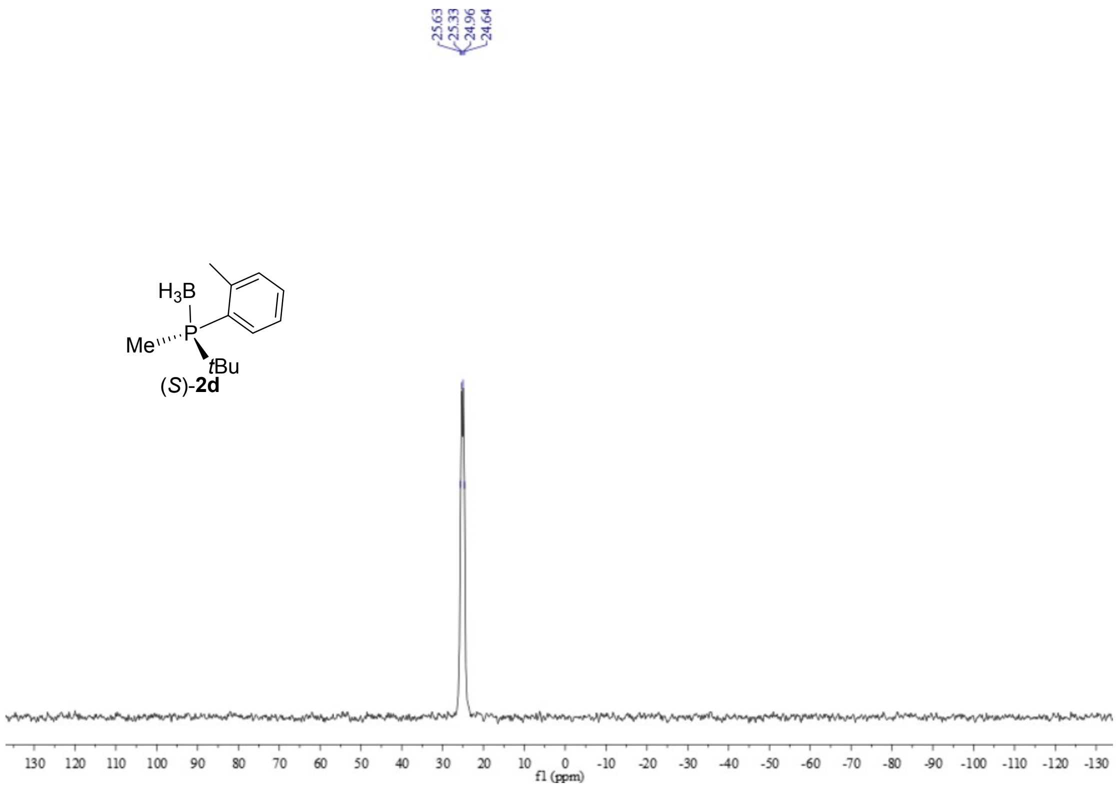


Figure S98. ^{31}P NMR spectrum of (*S*)-**2d** in $CDCl_3$

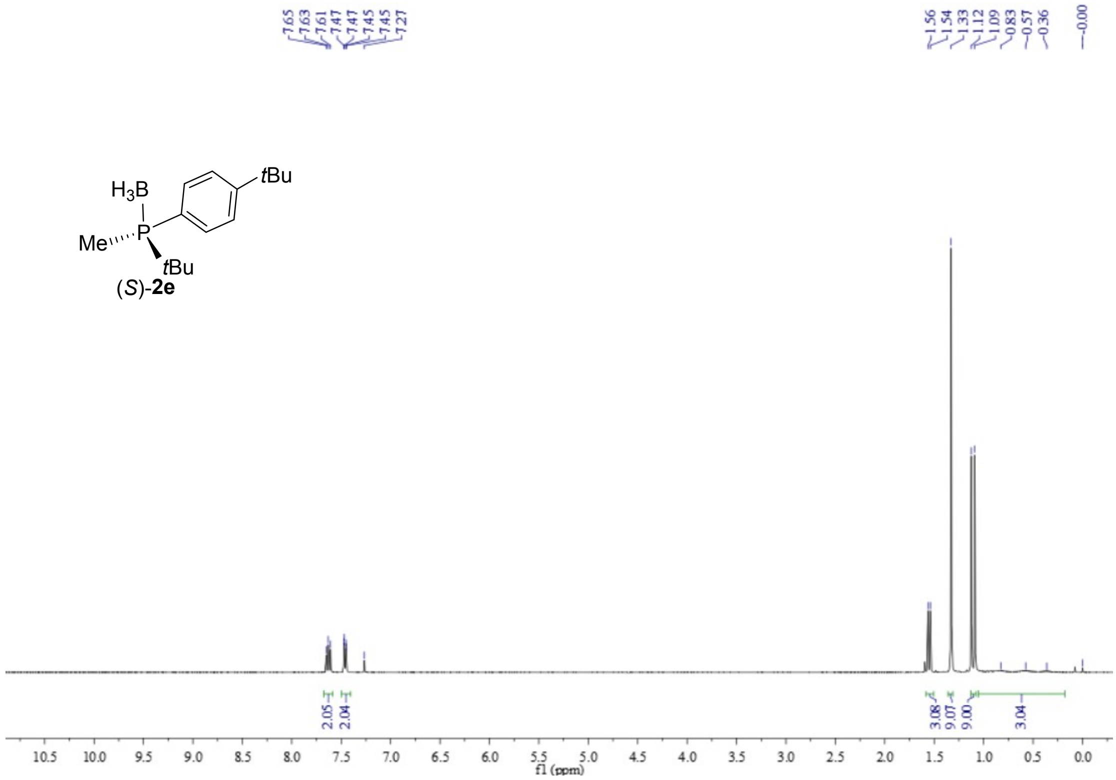


Figure S99. ^{1}H NMR spectrum of (*S*)-**2e** in $CDCl_3$

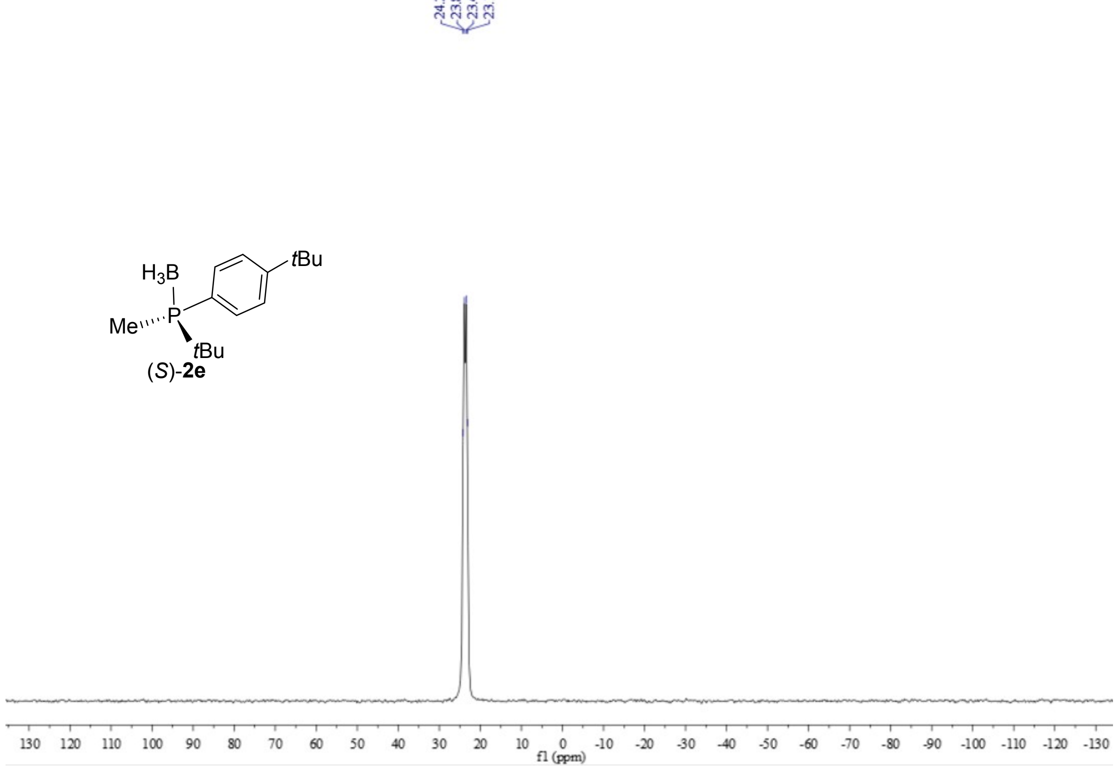


Figure S100. ^{31}P NMR spectrum of (*S*)-**2e** in $CDCl_3$

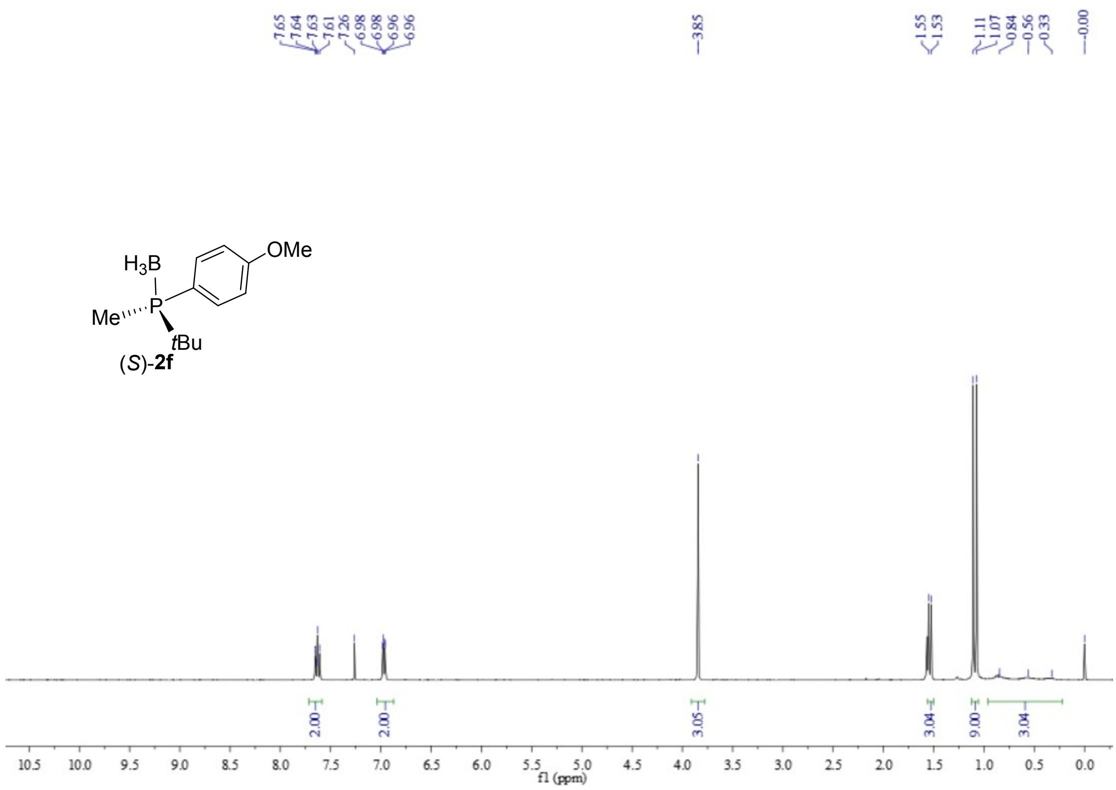


Figure S101. ^{1}H NMR spectrum of (*S*)-**2f** in $CDCl_3$

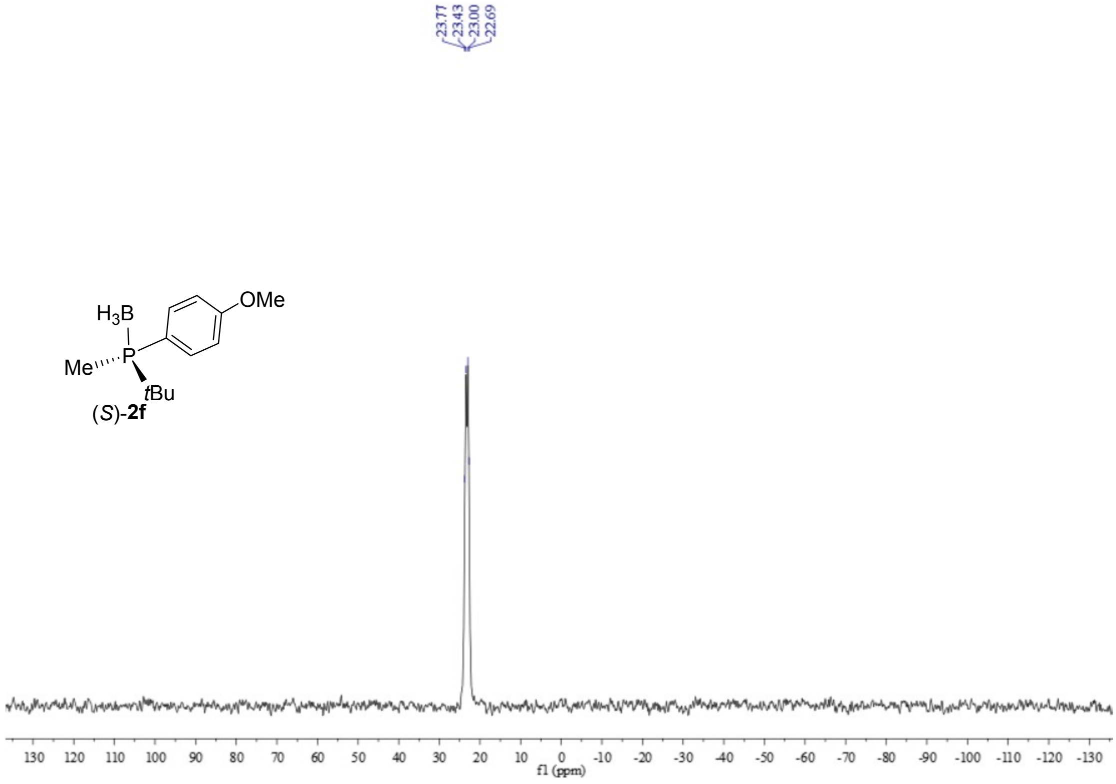


Figure S102. ^{31}P NMR spectrum of (*S*)-**2f** in $CDCl_3$

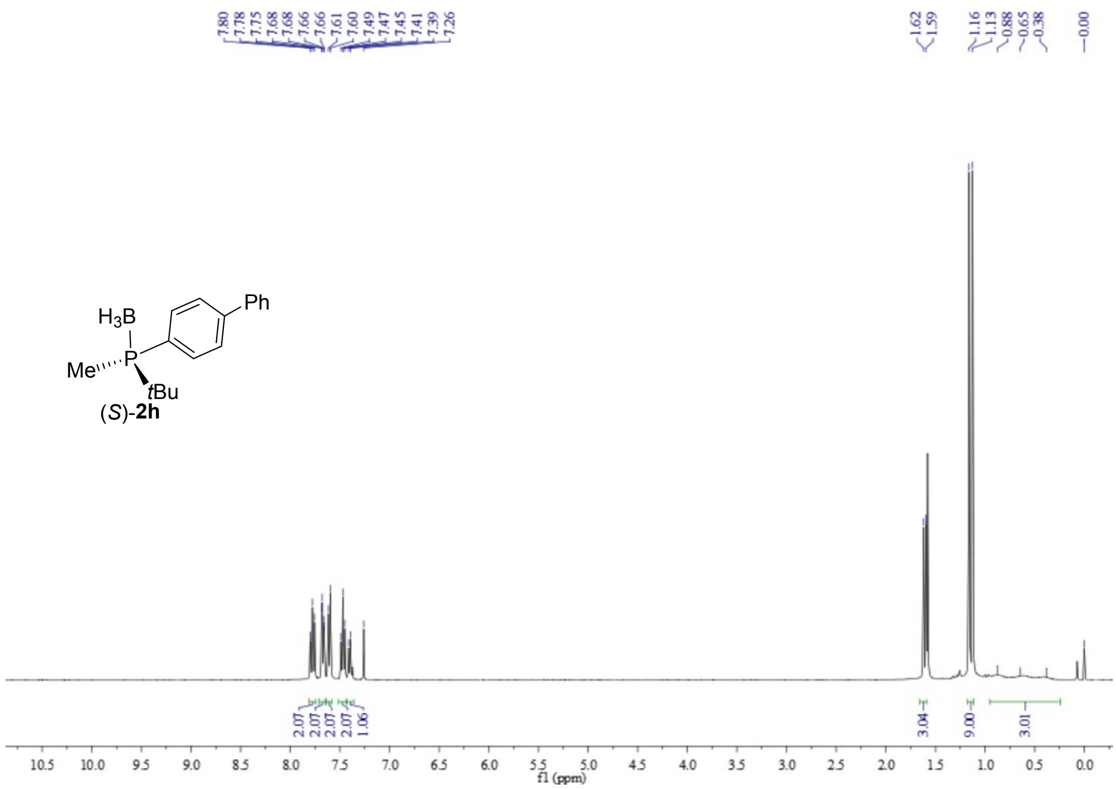


Figure S103. ^{1}H NMR spectrum of (*S*)-**2h** in $CDCl_3$

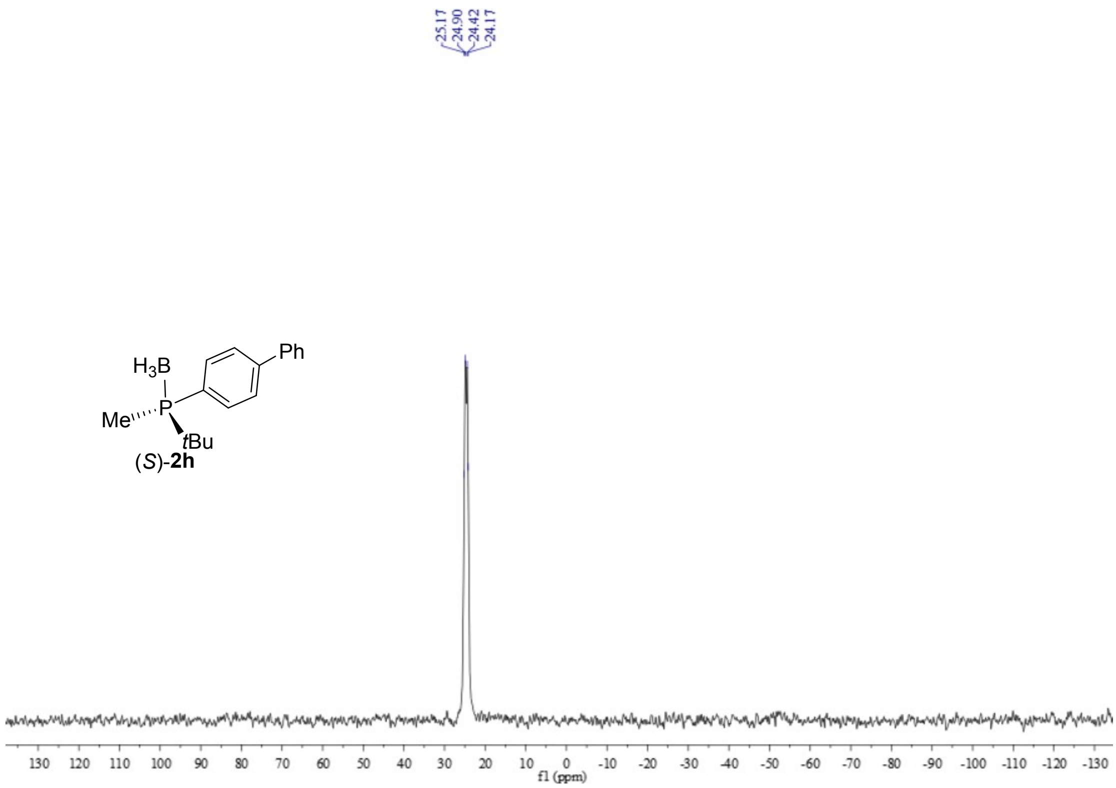


Figure S104. ^{31}P NMR spectrum of (*S*)-**2h** in $CDCl_3$

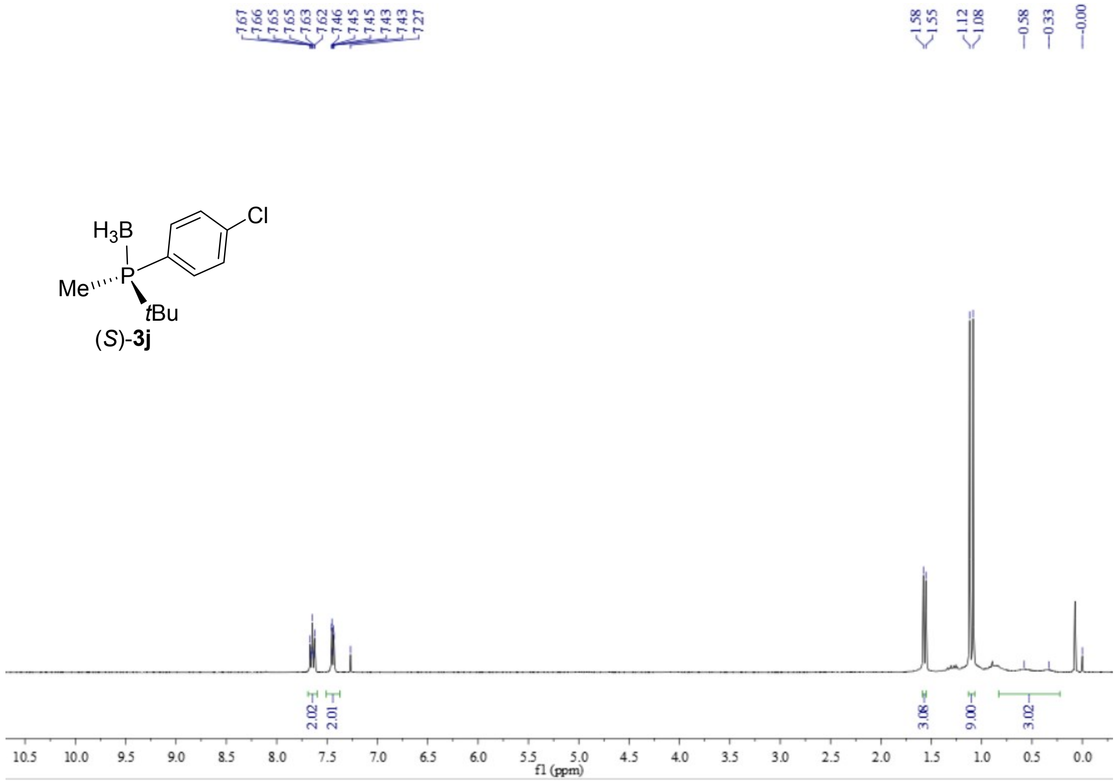


Figure S105. ^{1}H NMR spectrum of (*S*)-**3j** in $CDCl_3$

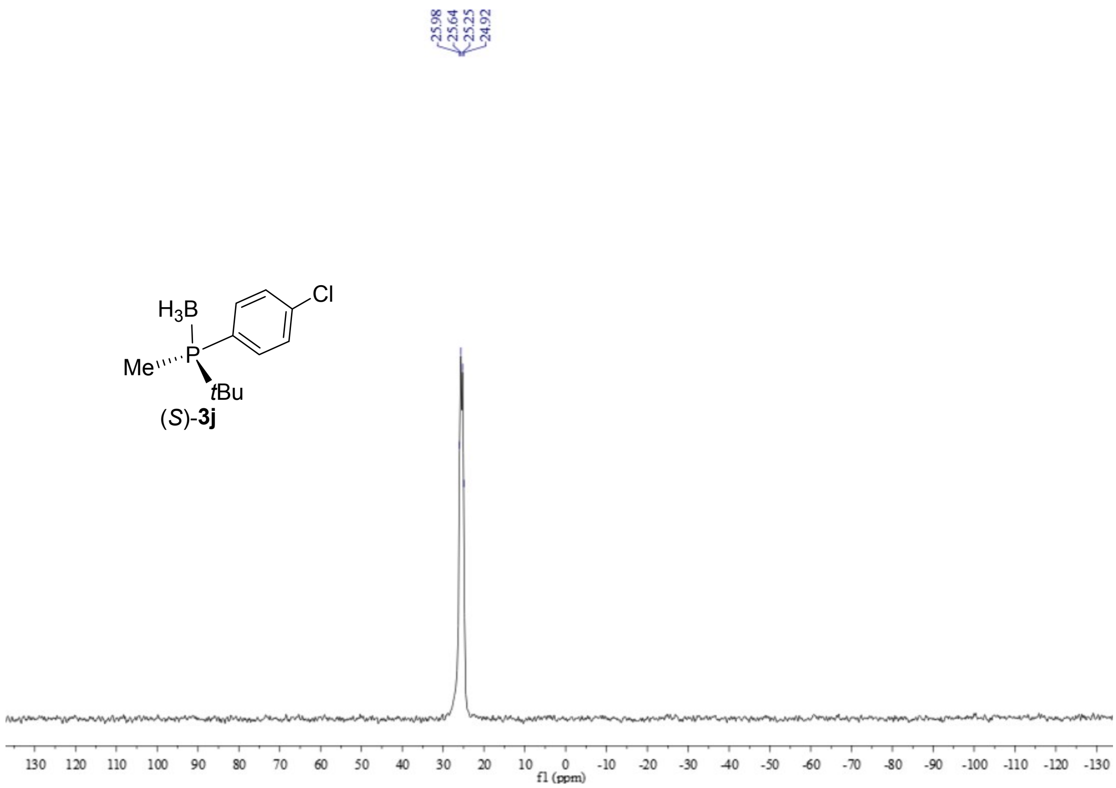


Figure S106. ^{31}P NMR spectrum of (*S*)-**3j** in $CDCl_3$

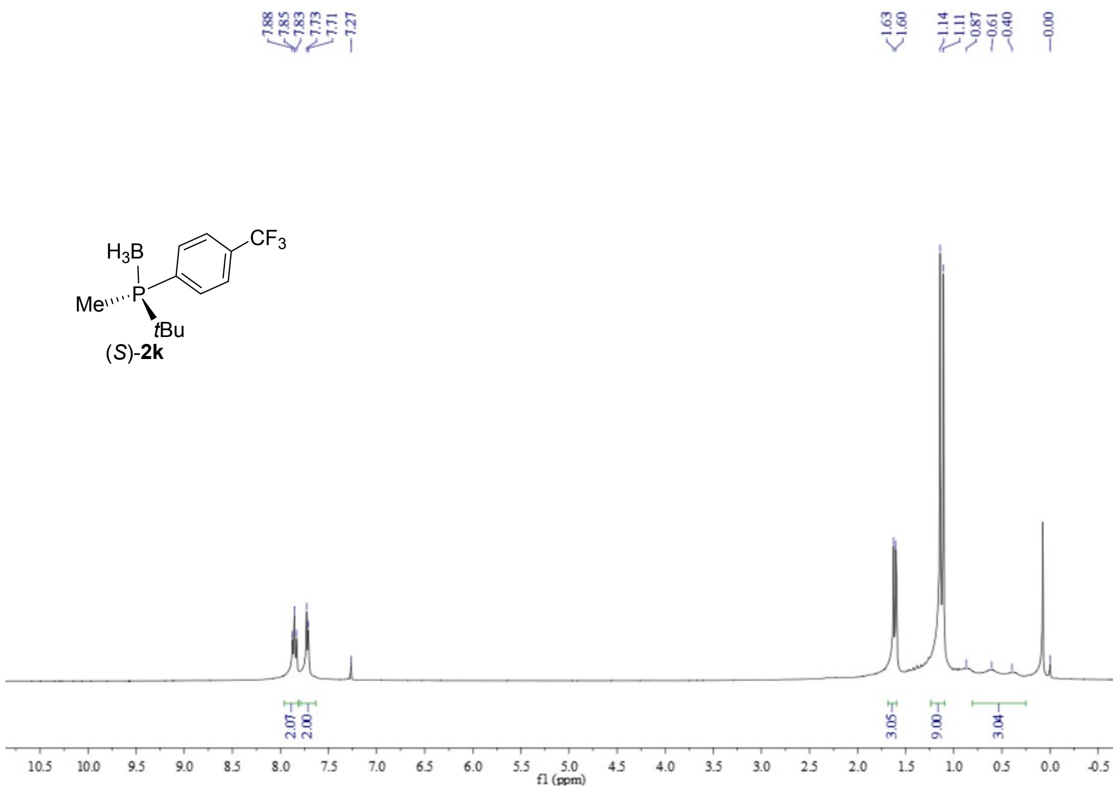


Figure S107. ^{1}H NMR spectrum of (*S*)-**2k** in $CDCl_3$

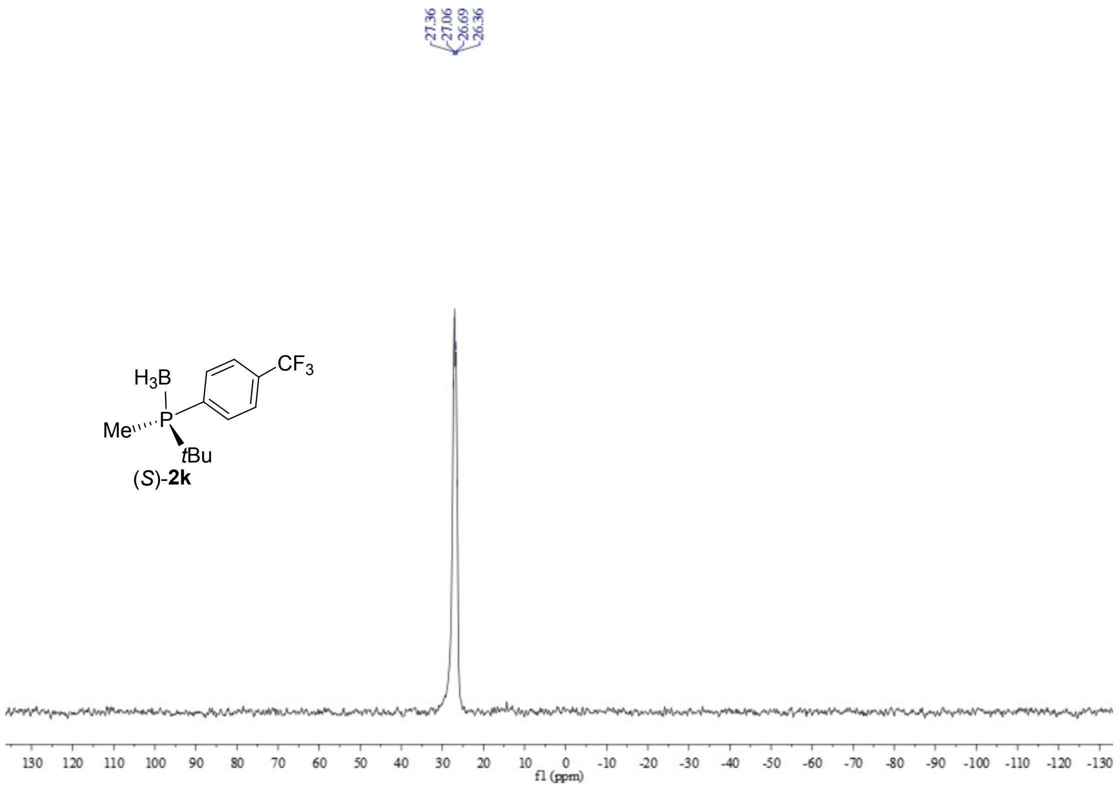


Figure S108. ^{31}P NMR spectrum of (*S*)-**2k** in $CDCl_3$

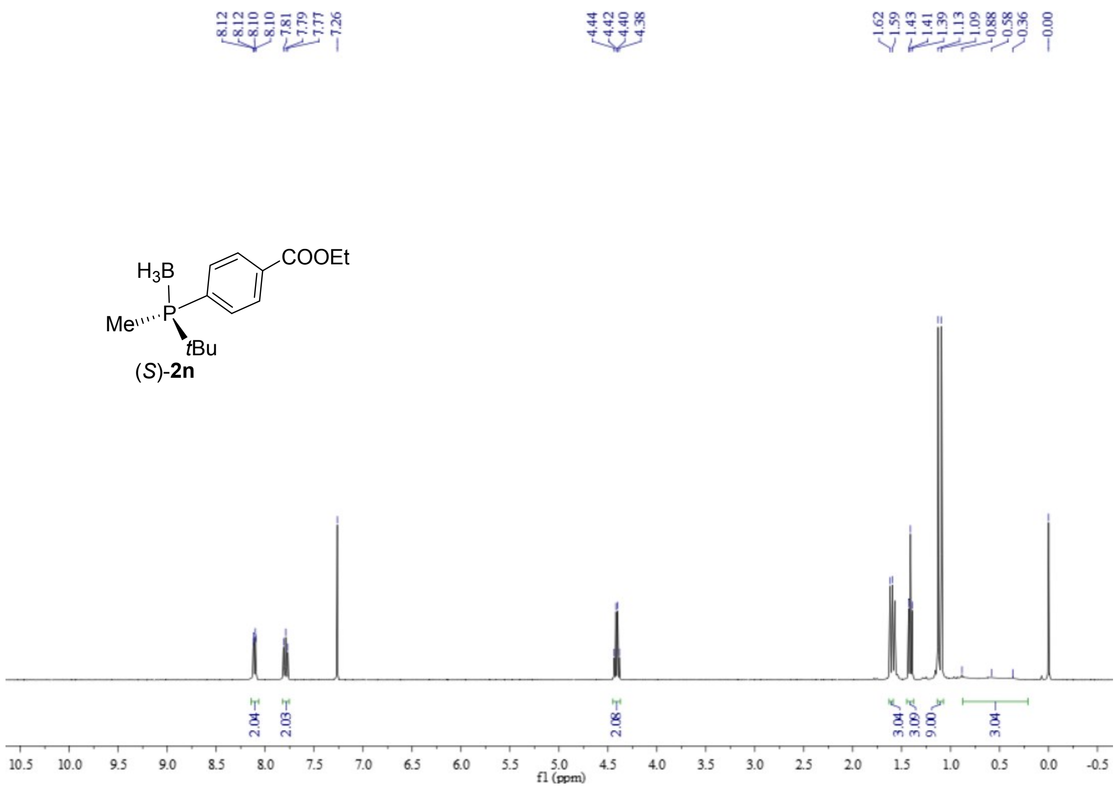


Figure S109. ^{1}H NMR spectrum of (*S*)-**2n** in $CDCl_3$

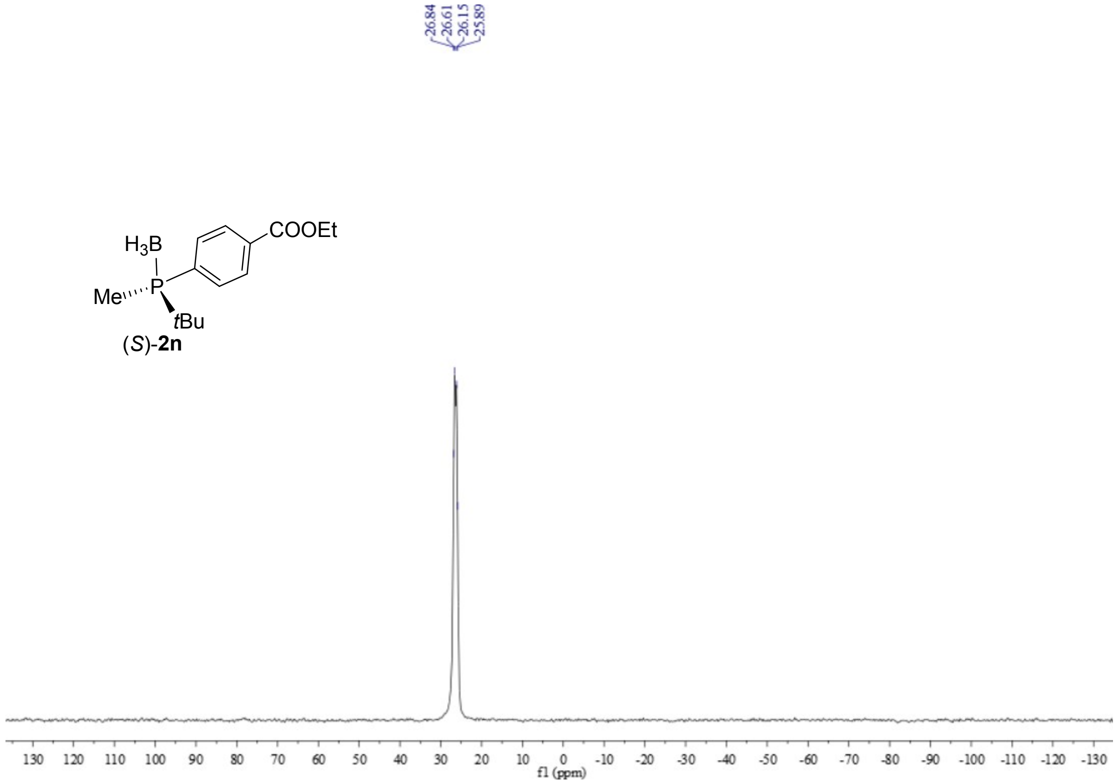


Figure S110. ^{31}P NMR spectrum of (*S*)-**2n** in $CDCl_3$

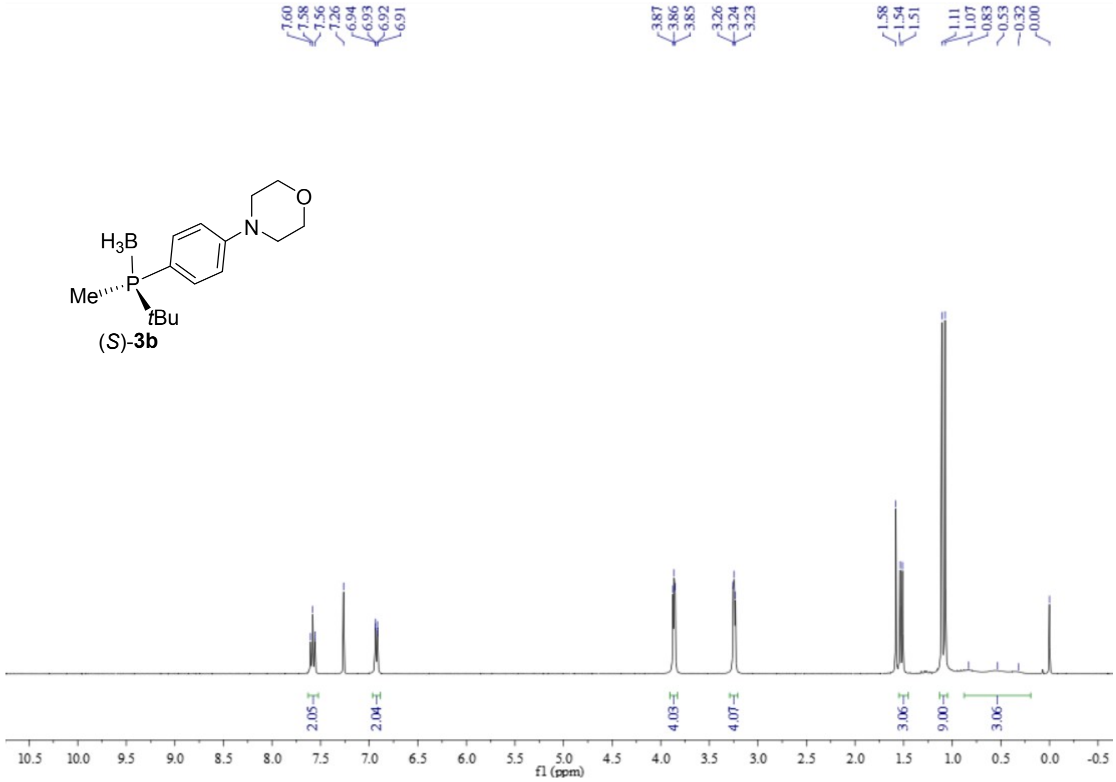


Figure S111. ^{1}H NMR spectrum of (*S*)-**3b** in $CDCl_3$

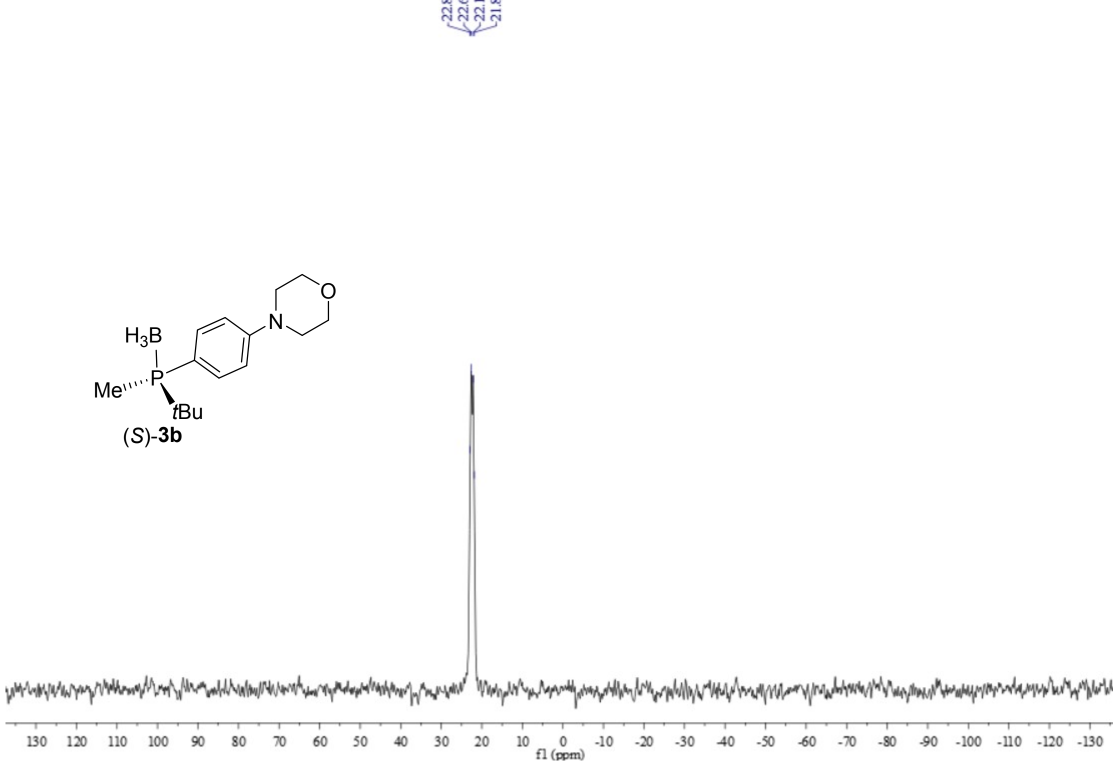


Figure S112. ^{31}P NMR spectrum of (*S*)-**3b** in $CDCl_3$

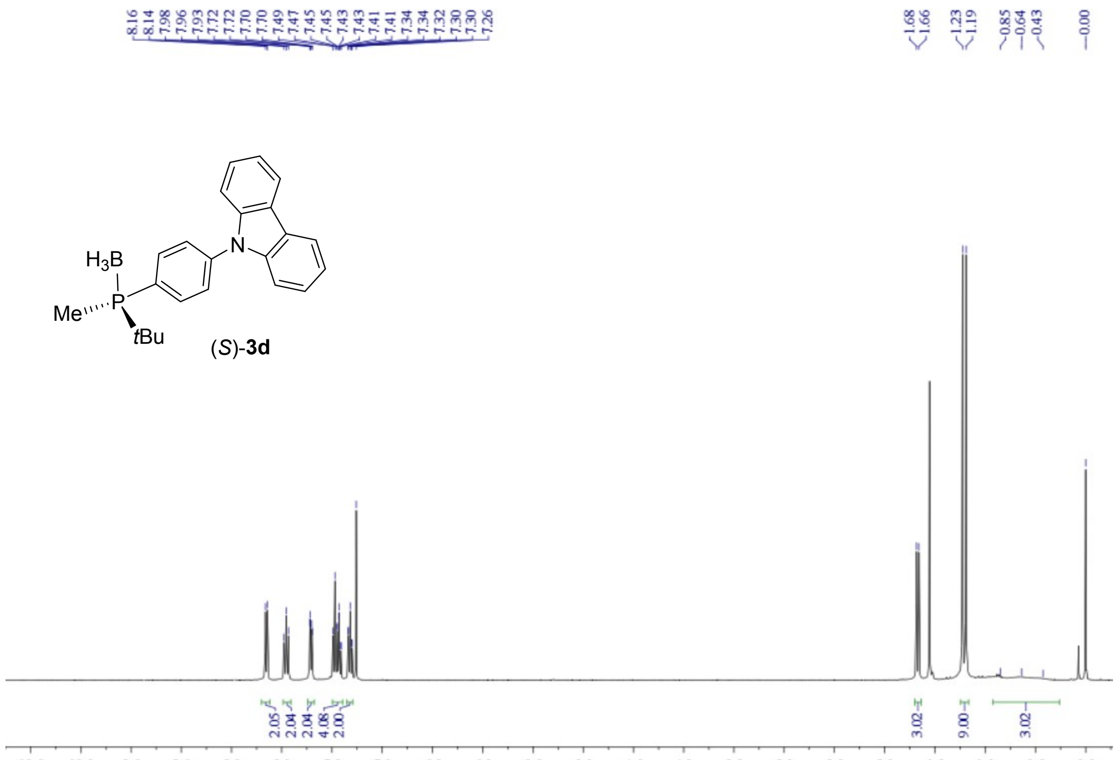


Figure S113. ^{1}H NMR spectrum of (*S*)-**3d** in $CDCl_3$

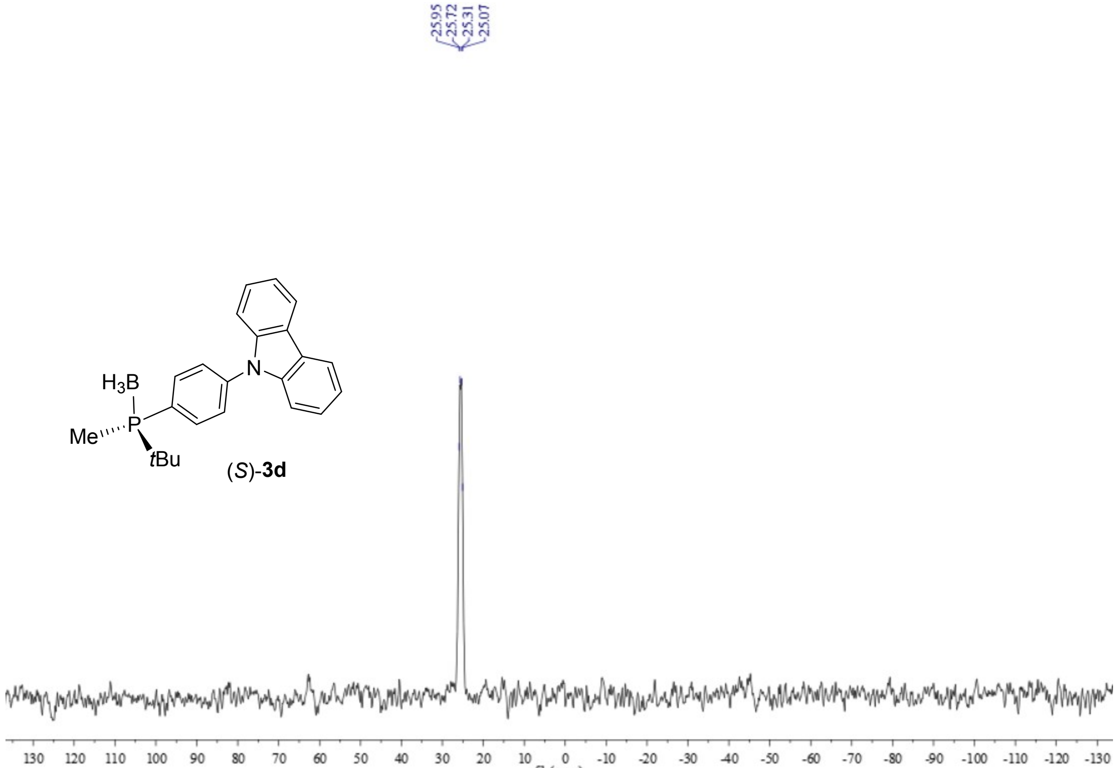


Figure S114. ^{31}P NMR spectrum of (*S*)-**3d** in $CDCl_3$

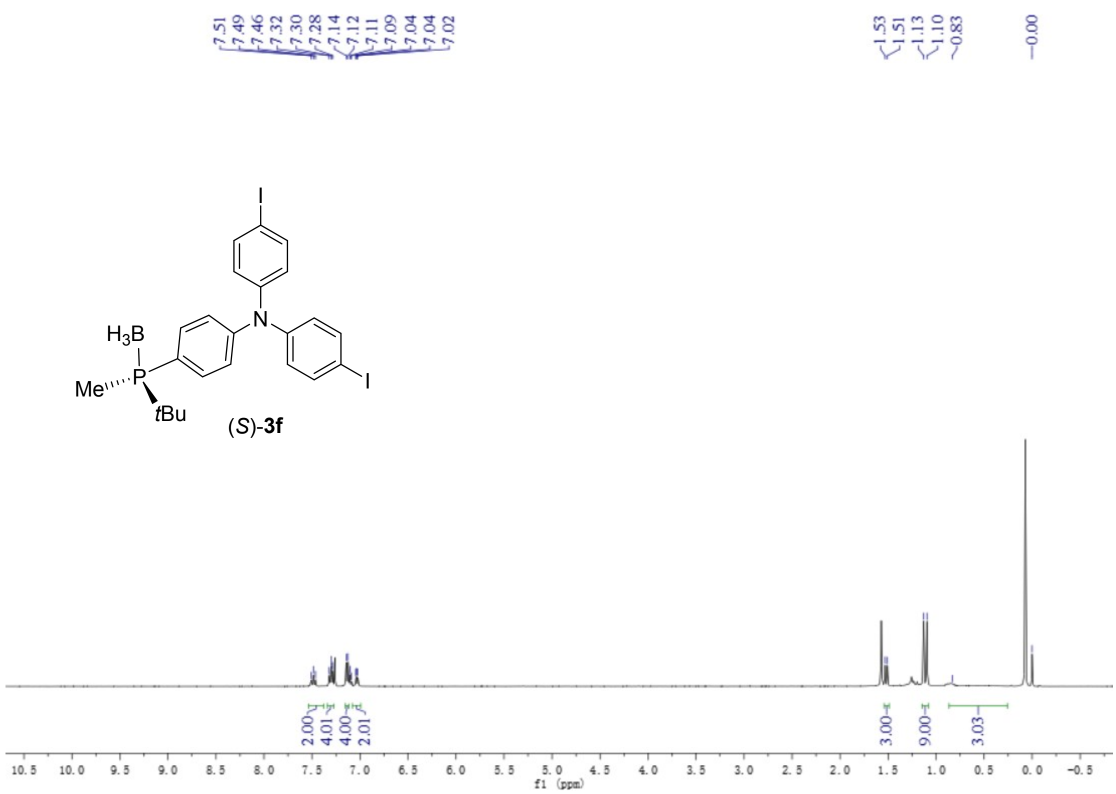


Figure S115. ^{1}H NMR spectrum of (*S*)-**3f** in $CDCl_3$

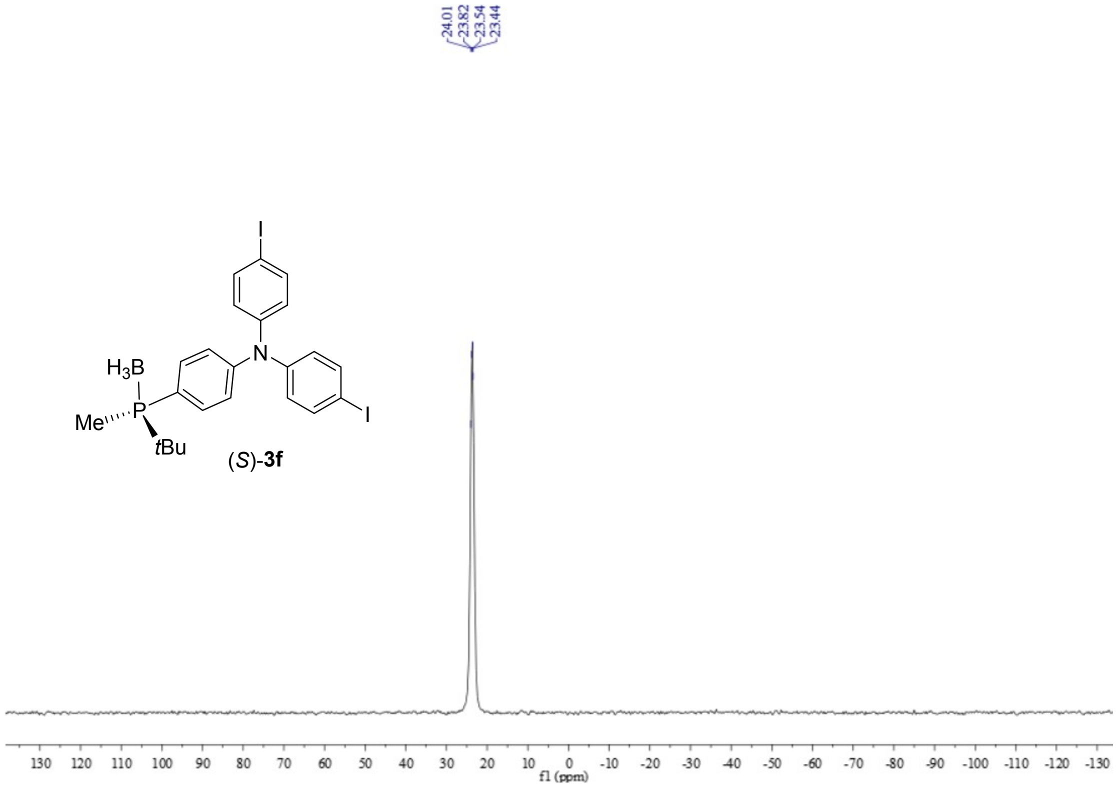


Figure S116. ^{31}P NMR spectrum of (*S*)-**3f** in $CDCl_3$

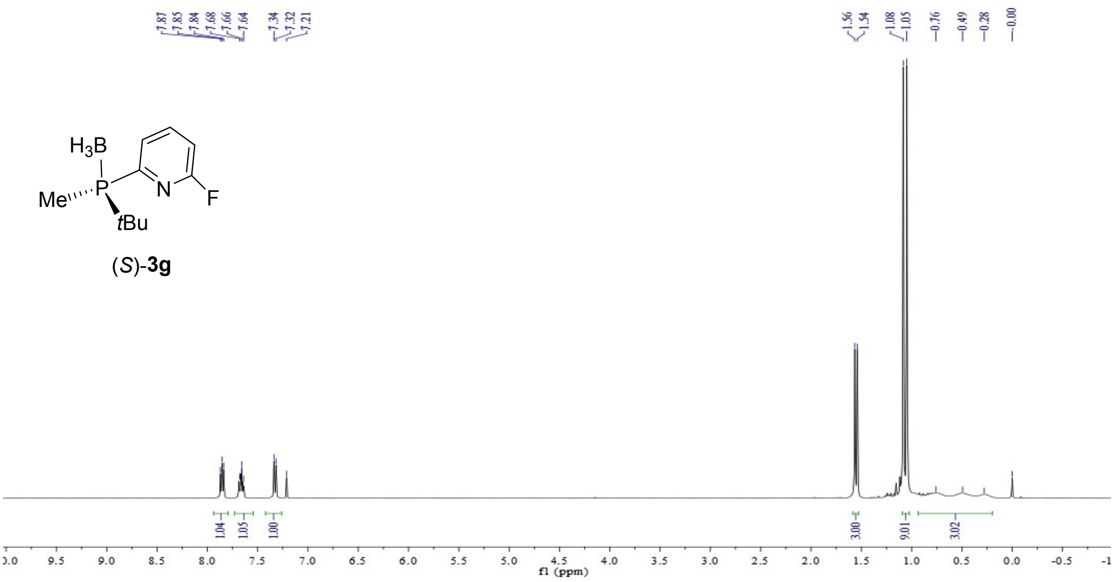


Figure S117. ^{1}H NMR spectrum of (*S*)-**3g** in $CDCl_3$

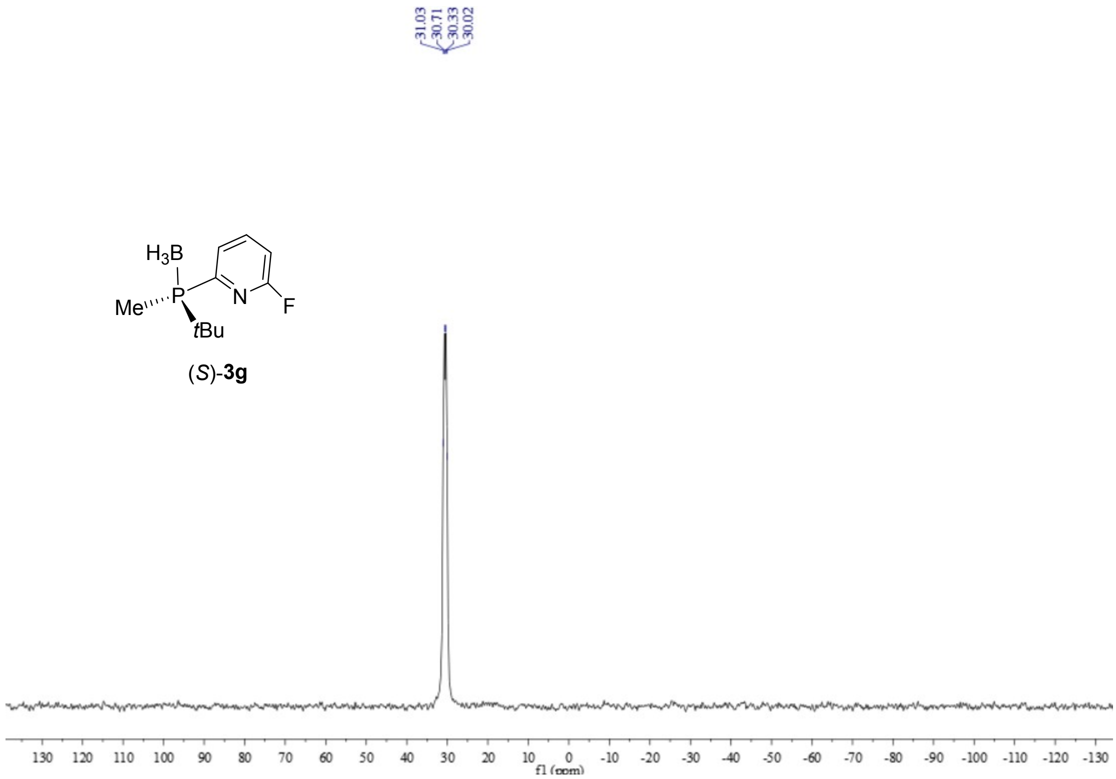


Figure S118. ^{31}P NMR spectrum of (*S*)-**3g** in $CDCl_3$

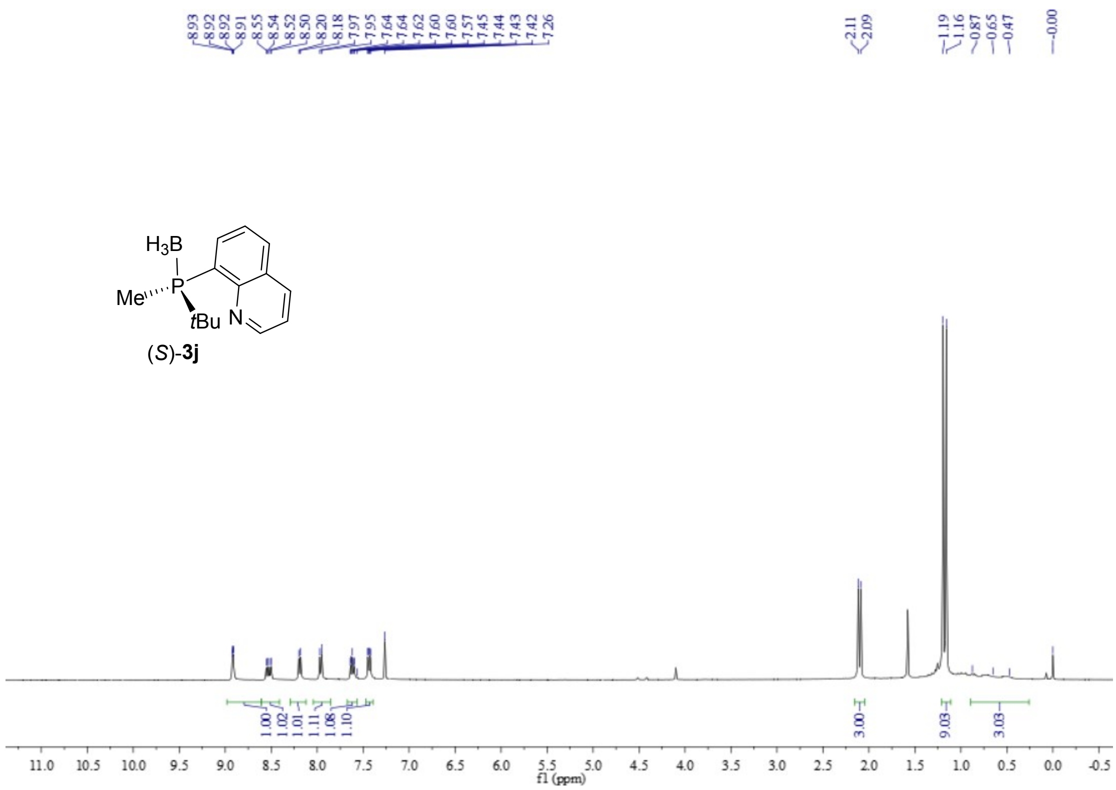


Figure S119. ^{1}H NMR spectrum of (*S*)-**3j** in $CDCl_3$

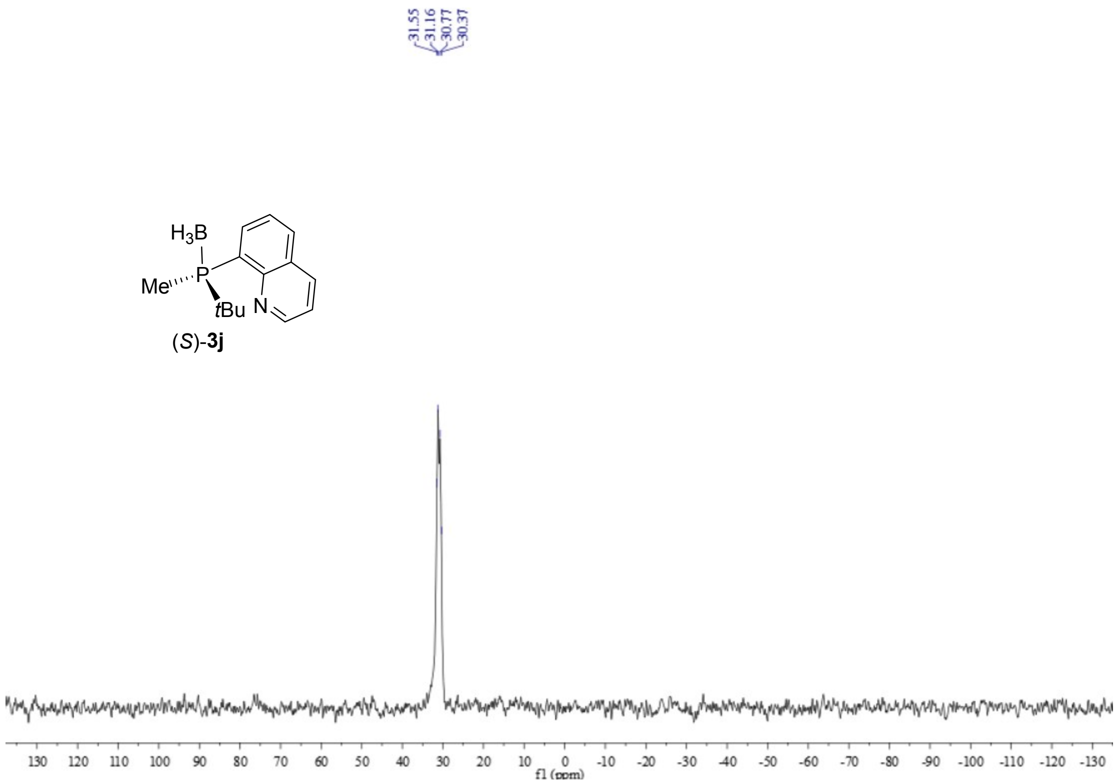
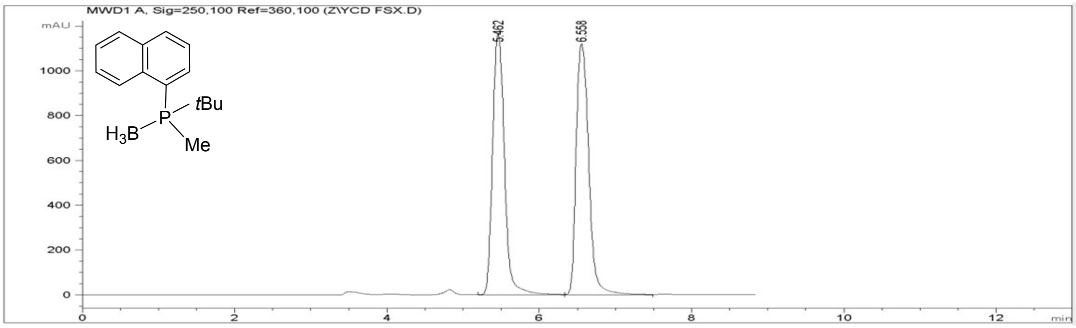


Figure S120. ^{31}P NMR spectrum of (*S*)-**3j** in $CDCl_3$

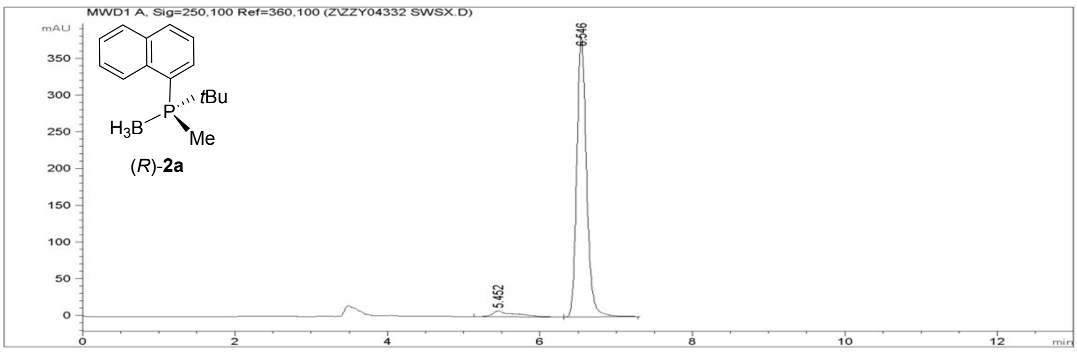
7. HPLC spectra for all products.

Chiral HPLC chromatographic analysis of (*R*)-**2a**

Condition: Daicel Chiralcel AS-H, *n*-hexane/*i*-PrOH = 95/5, UV = 250 nm, flow rate: 1.0 mL/min, retention time: t (minor) =5.452 min, t (major) = 6.546 min, ee = 91%.



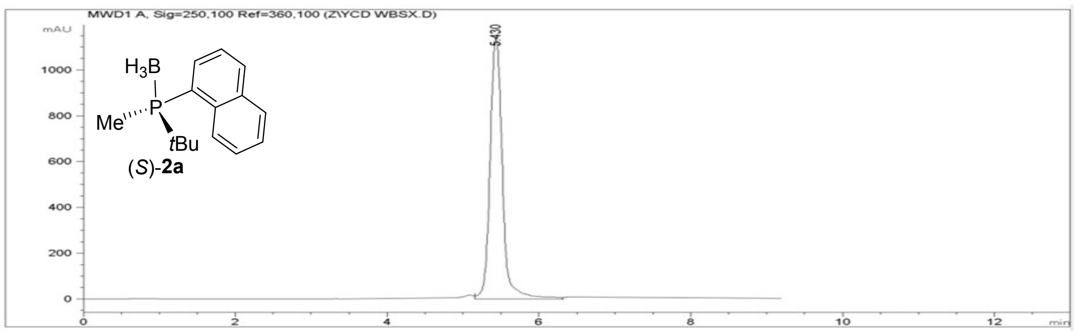
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.462	BV	0.1747	1.26782e4	1167.53125	49.5061
2	6.558	VV	0.1865	1.29312e4	1121.50928	50.4939



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.452	VV	0.2598	158.49107	7.97658	4.4623
2	6.546	VB	0.1358	3393.25806	381.34229	95.5377

Chiral HPLC chromatographic analysis of (*S*)-**2a**

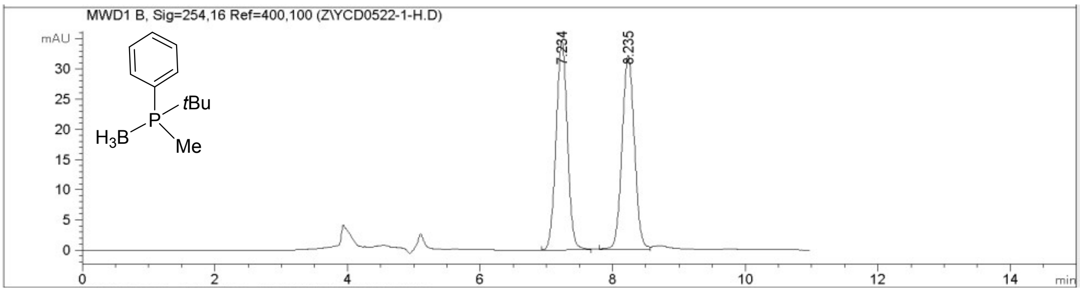
Condition: Daicel Chiralcel AS-H, *n*-hexane/*i*-PrOH = 95/5, UV = 250 nm, flow rate: 1.0 mL/min, retention time: t (major) = 5.430 min, ee = 99%.



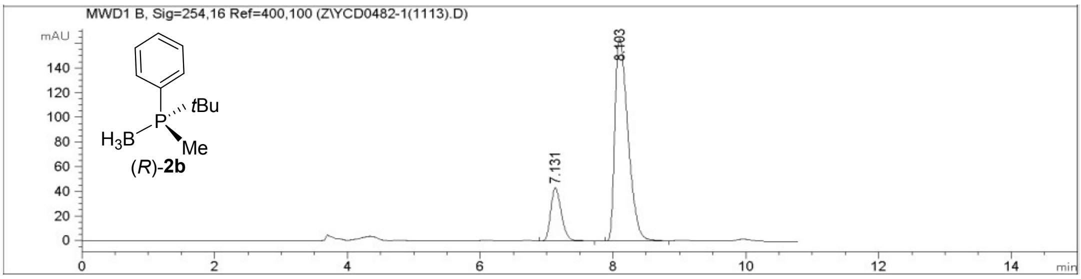
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.430	VV	0.1771	1.28394e4	1142.25513	100.0000

Chiral HPLC chromatographic analysis of (*R*)-**2b**

Condition: Daicel Chiralcel AS-H, *n*-hexane/*i*-PrOH = 95/5, UV = 254 nm, flow rate: 1.0 mL/min, retention time: t (minor) = 7.131 min, t (major) = 8.103 min, ee = 65%.



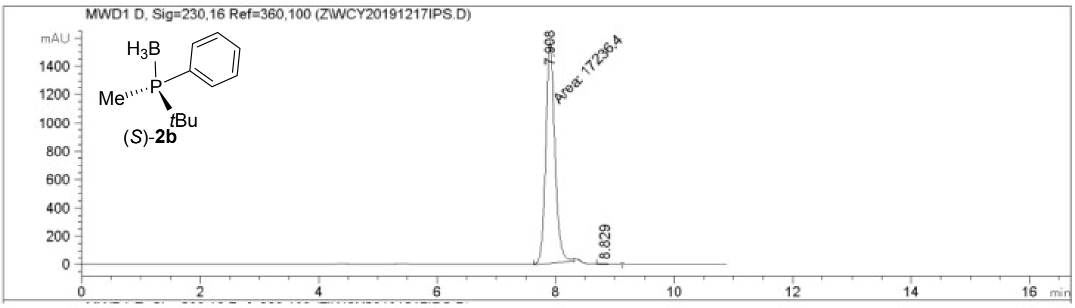
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.234	BB	0.1857	414.08304	34.58932	49.8892
2	8.235	BV	0.2009	415.92221	32.14756	50.1108



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.131	VB	0.1722	482.05902	43.19086	17.4976
2	8.103	BV	0.2155	2272.93848	164.24651	82.5024

Chiral HPLC chromatographic analysis of (*S*)-**2b**

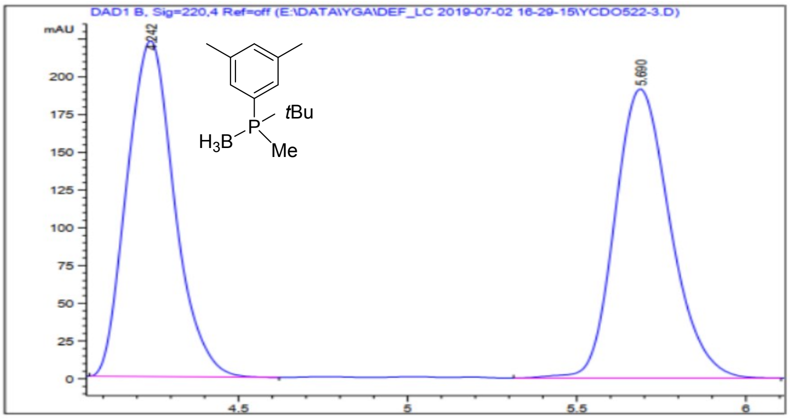
Condition: Daicel Chiralcel AS-H, *n*-hexane/*i*-PrOH = 95/5, UV = 230 nm, flow rate: 1.0 mL/min, retention time: t (major) = 7.908 min, t (minor) = 8.829 min, ee = 99%.



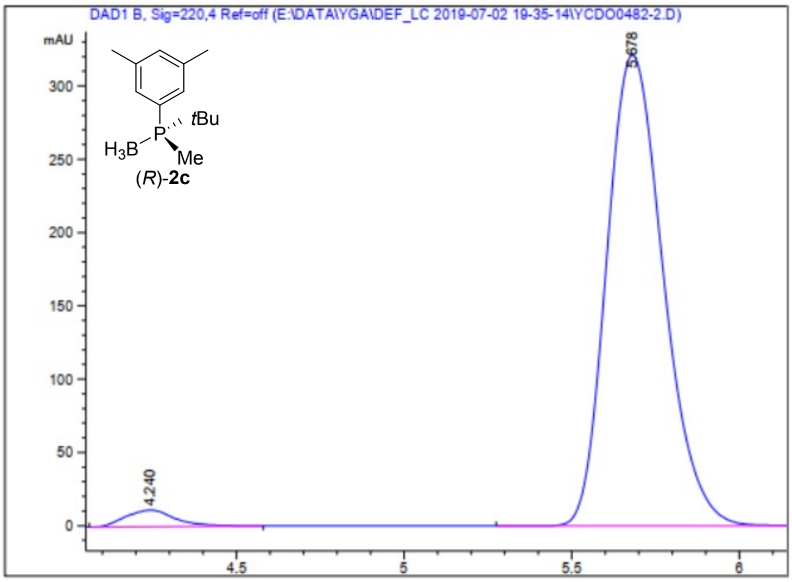
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.908	MM	0.1832	1.72364e4	1568.28149	99.5125
2	8.829	VBA	0.2526	84.43401	4.67756	0.4875

Chiral HPLC chromatographic analysis of (*R*)-**2c**

Condition: Daicel Chiralcel AS-H, *n*-hexane/*i*-PrOH = 95/5, UV = 220 nm, flow rate: 1.0 mL/min, retention time: t (minor) = 4.240 min, t (major) = 5.678 min, ee = 94%.



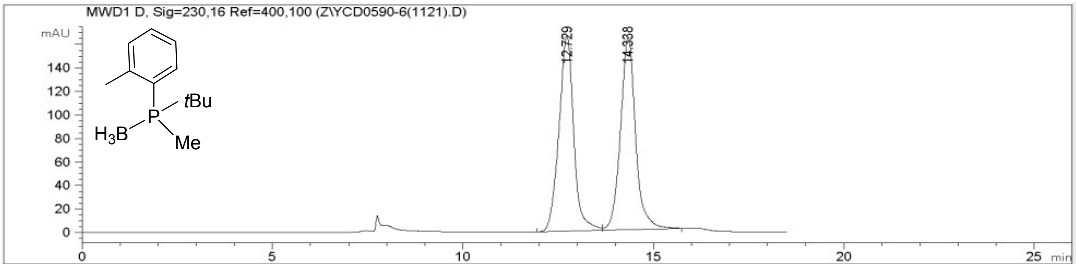
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	4.242	BB	0.1538	2173.64209	222.77597	49.9249
2	5.690	BB	0.1767	2180.18311	191.62512	50.0751



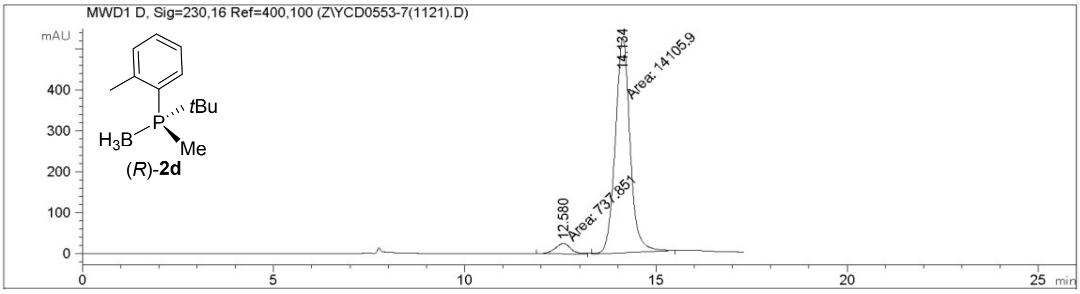
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	4.240	BB	0.1654	115.81202	11.31580	2.9885
2	5.678	BB	0.1845	3759.42749	321.34906	97.0115

Chiral HPLC chromatographic analysis of (*R*)-**2d**

Condition: Daicel Chiralcel OD-H, *n*-hexane/*i*-PrOH = 98/2, UV = 230 nm, flow rate: 0.5 mL/min, retention time: t (minor)= 12.580 min, t (major) = 14.134 min, ee = 90%.



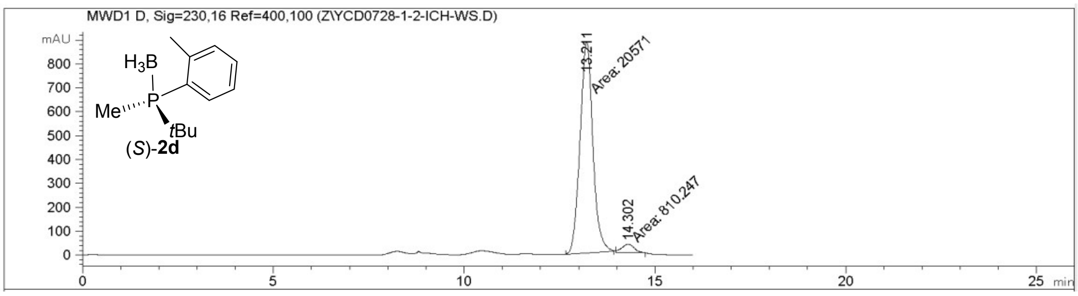
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.729	BV	0.4050	4483.72070	166.06494	49.8103
2	14.338	VB	0.4196	4517.87354	163.88429	50.1897



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.580	MM	0.4788	737.85126	25.68179	4.9708
2	14.134	MM	0.4498	1.41059e4	522.70612	95.0292

Chiral HPLC chromatographic analysis of (*S*)-**2d**

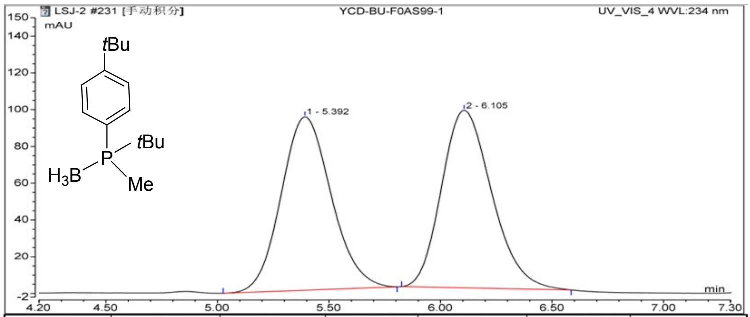
Condition: Daicel Chiralcel OD-H, *n*-hexane/*i*-PrOH = 98/2, UV = 230 nm, flow rate: 0.5 mL/min, retention time: t (major) = 13.211 min, t (minor) = 14.302 min, ee = 92%.



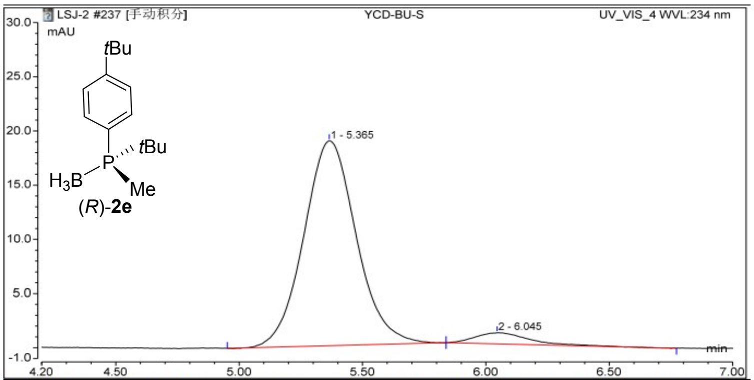
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.211	MM	0.3883	2.05710e4	883.04315	96.2105
2	14.302	MM	0.3746	810.24664	36.04960	3.7895

Chiral HPLC chromatographic analysis of (*R*)-**2e**

Condition: Daicel Chiralcel AS-H, *n*-hexane/*i*-PrOH = 99/1, UV = 234 nm, flow rate: 1 mL/min, retention time: t (major) = 5.365 min, t (minor) = 6.045 min, ee = 90%.



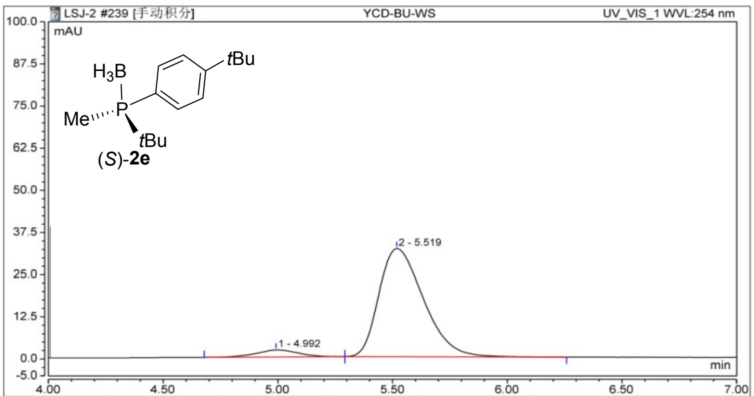
peak.number	retention_time min	peak.area mAU*min	peak.height mAU	peak.rel_area %	peak.rel_height %	peak.amount n.a.
1	5.392	24.571	94.334	49.33	49.42	n.a.
2	6.105	25.234	96.567	50.67	50.58	n.a.



peak.number	retention_time min	peak.area mAU*min	peak.height mAU	peak.rel_area %	peak.rel_height %	peak.amount n.a.
1	5.365	4.654	18.911	94.68	94.85	n.a.
2	6.045	0.262	1.028	5.32	5.15	n.a.

Chiral HPLC chromatographic analysis of (*S*)-**2e**

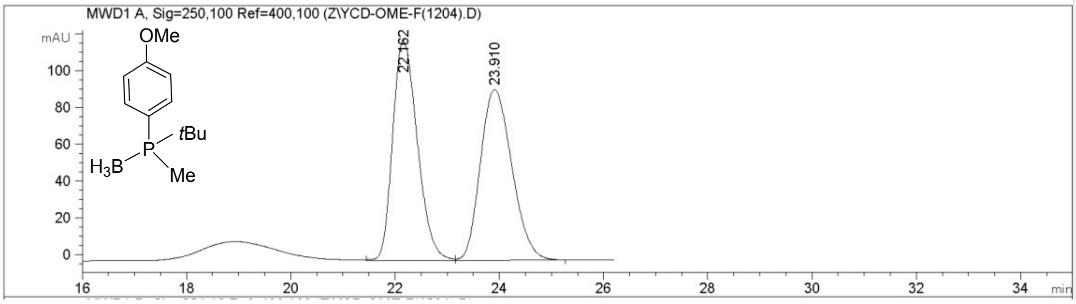
Condition: Daicel Chiralcel AS-H, *n*-hexane/*i*-PrOH = 99/1, UV = 254 nm, flow rate: 1.0 mL/min, retention time: t (minor) = 4.992 min, t (major) = 5.519 min, ee = 88%.



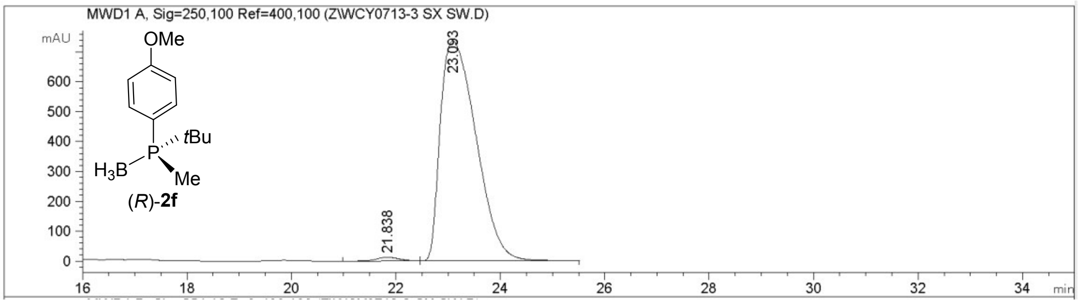
peak.number	retention_time min	peak.area mAU*min	peak.height mAU	peak.rel_area %	peak.rel_height %	peak.amount n.a.
1	4.992	0.444	2.081	5.78	6.09	n.a.
2	5.519	7.240	32.104	94.22	93.91	n.a.

Chiral HPLC chromatographic analysis of (*R*)-**2f**

Condition: Daicel Chiralcel AS-H, *n*-hexane/*i*-PrOH = 98/2, UV = 250 nm, flow rate: 0.8 mL/min, retention time: t (minor) = 21.843 min, t (major) = 23.093 min, ee = 98%.



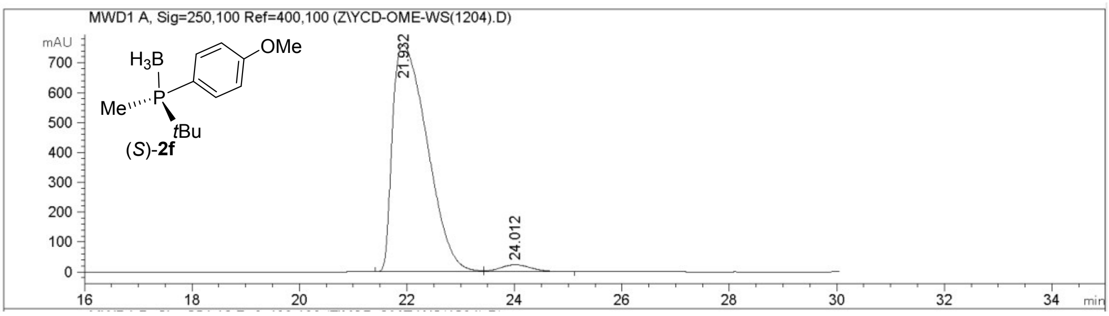
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.162	BV	0.5093	3923.07373	119.42327	50.1856
2	23.910	VB	0.6622	3894.06250	92.67391	49.8144



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.843	BV	0.4456	130.97234	4.47357	0.9432
2	23.093	VB	0.6927	1.37556e4	311.77374	99.0568

Chiral HPLC chromatographic analysis of (*S*)-**2f**

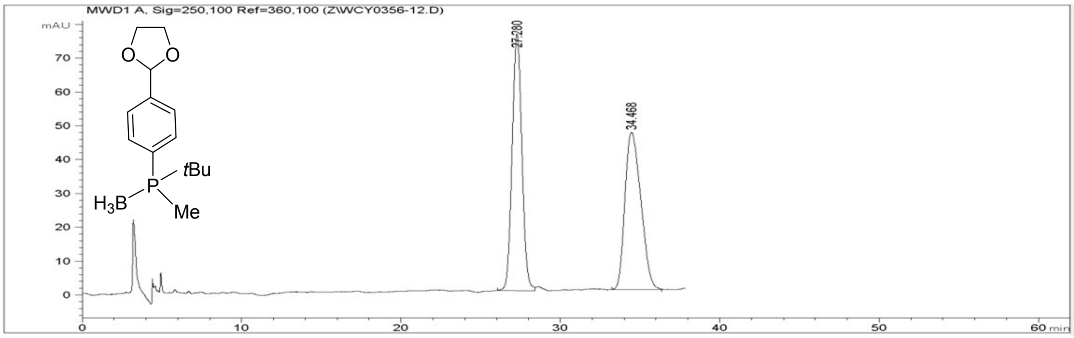
Condition: Daicel Chiralcel AS-H, *n*-hexane/*i*-PrOH = 98/2, UV = 250 nm, flow rate: 0.8 mL/min, retention time: t (major) = 21.932 min, t (minor)= 24.014 min, ee = 95%.



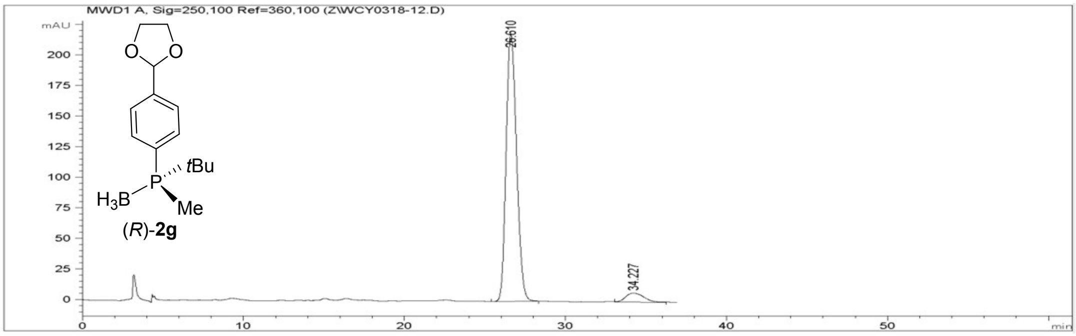
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.932	BB	0.6487	1.35912e4	327.13892	97.4981
2	24.014	BB	0.6021	348.76962	8.69236	2.5019

Chiral HPLC chromatographic analysis of (*R*)-**2g**

Condition: Daicel Chiralcel AS-H, *n*-hexane/*i*-PrOH = 98/2, UV = 250 nm, flow rate: 1.0 mL/min, retention time: t (major) = 26.610 min, t (minor) = 34.227 min, ee = 89%.



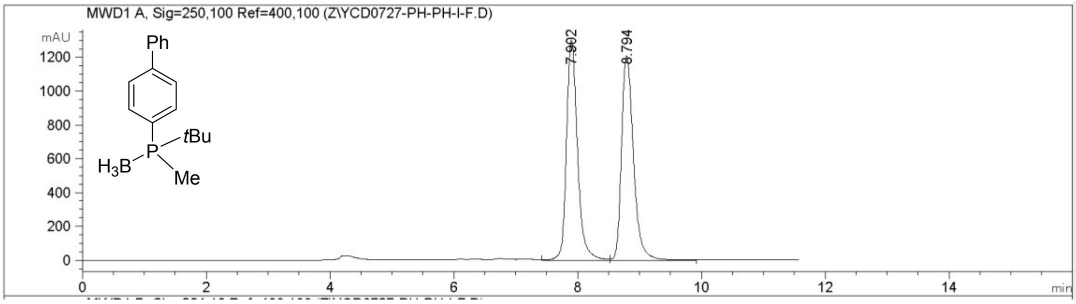
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	27.280	BB	0.6588	3230.39136	75.86506	50.0436
2	34.468	BB	1.0076	3224.76050	46.46822	49.9564



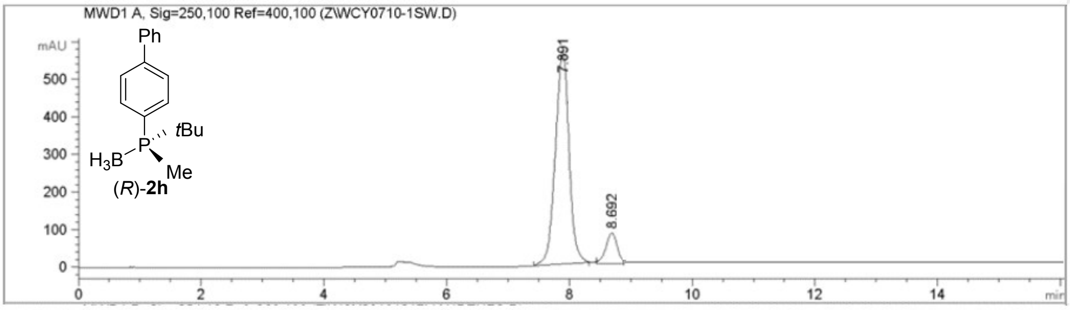
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	26.610	BB	0.6988	9841.18945	218.75577	94.5897
2	34.227	BB	0.9137	562.89392	7.29899	5.4103

Chiral HPLC chromatographic analysis of (*R*)-**2h**

Condition: Daicel Chiralcel OD-H, *n*-hexane/*i*-PrOH = 95/5, UV = 250 nm, flow rate: 0.8 mL/min, retention time: t (major) = 7.891 min, t (minor) = 8.692 min, ee = 79%.



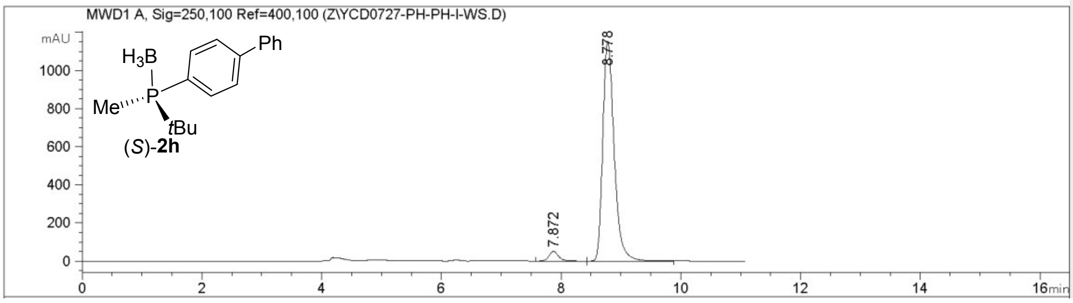
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.902	VV	0.1899	1.60491e4	1301.61743	49.7150
2	8.794	VV	0.2087	1.62331e4	1208.62646	50.2850



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.891	MM	0.2592	8811.94434	566.50598	89.0658
2	8.692	MM	0.2172	1081.80591	83.02530	10.9342

Chiral HPLC chromatographic analysis of (*S*)-**2h**

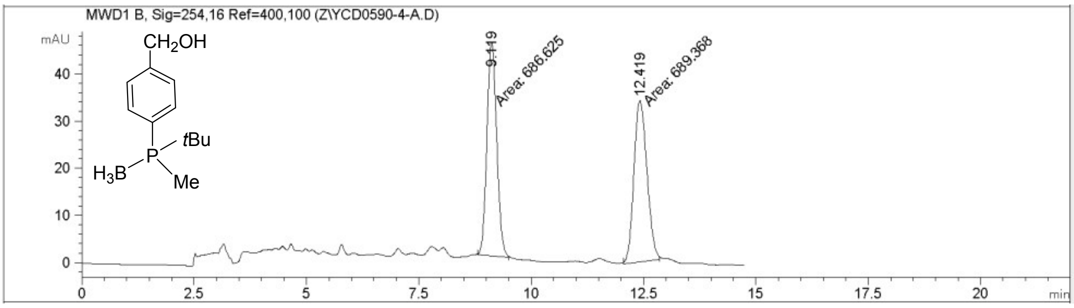
Condition: Daicel Chiralcel OD-H, *n*-hexane/*i*-PrOH = 95/5, UV = 250 nm, flow rate: 0.8 mL/min, retention time: t (minor) = 7.872 min, t (major) = 8.778 min, ee = 93%.



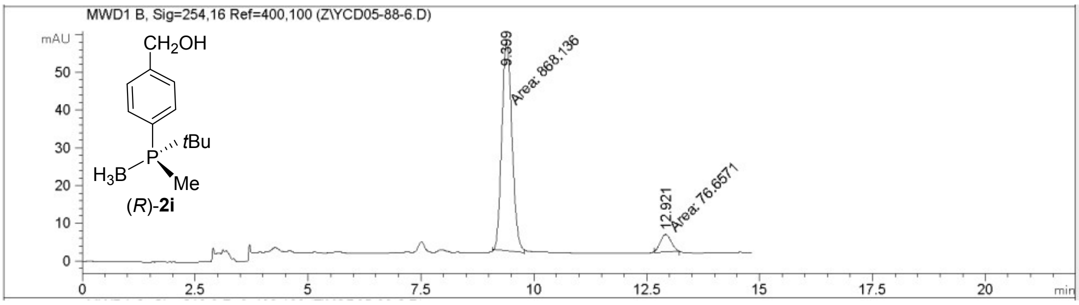
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.872	VV	0.1703	580.03973	51.13816	3.6508
2	8.778	VB	0.2049	1.53080e4	1152.85278	96.3492

Chiral HPLC chromatographic analysis of (*R*)-**2i**

Condition: Daicel Chiralcel OD-H, *n*-hexane/*i*-PrOH = 90/10, UV = 254 nm, flow rate: 1.0 mL/min, retention time: t (major) = 9.399 min, t (minor) = 12.921 min, ee = 84%.



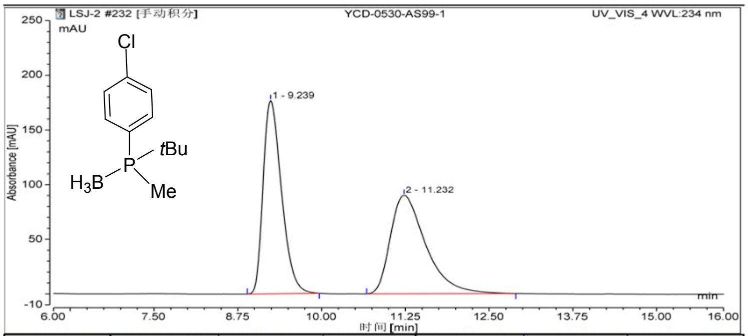
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.119	MM	0.2525	686.62518	45.32128	49.9003
2	12.419	MM	0.3361	689.36816	34.18288	50.0997



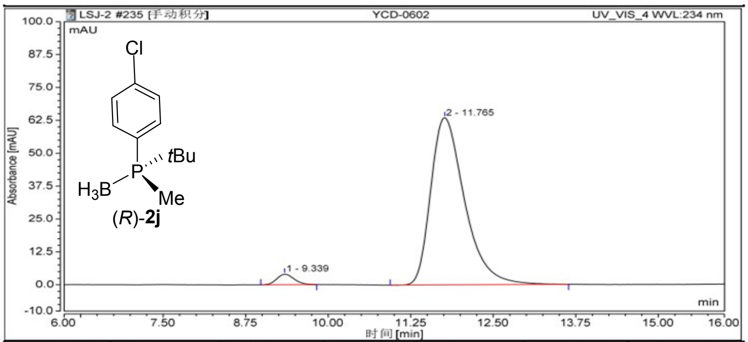
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.399	MM	0.2610	868.13562	55.44395	91.8864
2	12.921	MM	0.2772	76.65712	4.60930	8.1136

Chiral HPLC chromatographic analysis of (*R*)-**2j**

Condition: Daicel Chiralcel AS-H, *n*-hexane/*i*-PrOH = 99/1, UV = 234 nm, flow rate: 1.0 mL/min, retention time: t (minor) = 9.339 min, t (major) = 11.765 min, ee = 94%.



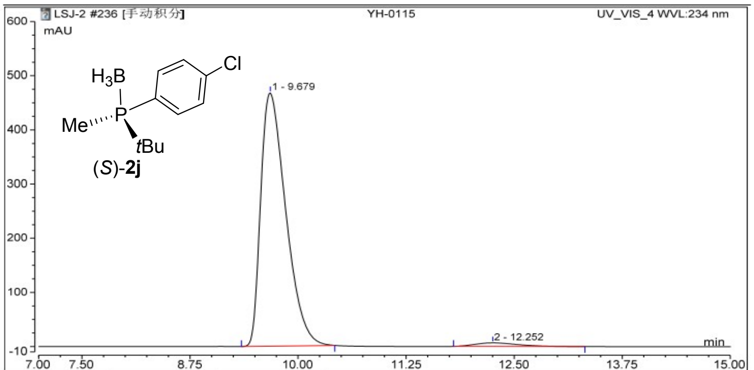
peak.number	retention_time min	peak.area mAU*min	peak.height mAU	peak.rel_area %	peak.rel_height %	peak.amount n.a.
1	9.239	56.152	176.720	50.45	66.25	n.a.
2	11.232	55.143	90.022	49.55	33.75	n.a.



peak.number	retention_time min	peak.area mAU*min	peak.height mAU	peak.rel_area %	peak.rel_height %	peak.amount n.a.
1	9.339	1.218	4.006	3.12	5.93	n.a.
2	11.765	37.761	63.534	96.88	94.07	n.a.

Chiral HPLC chromatographic analysis of (*S*)-**2j**

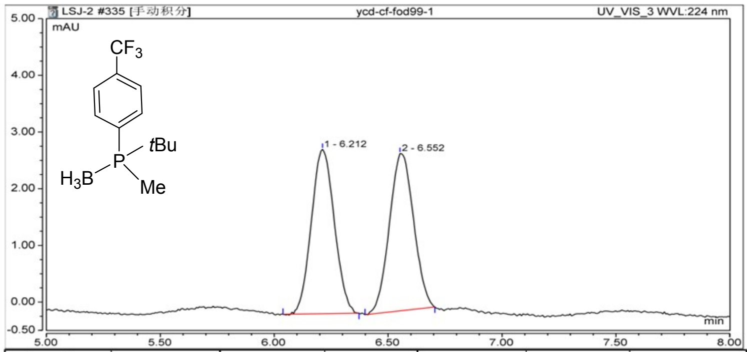
Condition: Daicel Chiralcel AS-H, *n*-hexane/*i*-PrOH = 99/1, UV = 234 nm, flow rate: 1.0 mL/min, retention time: t (major) = 9.679 min, t (minor) = 12.252 min, ee = 95%.



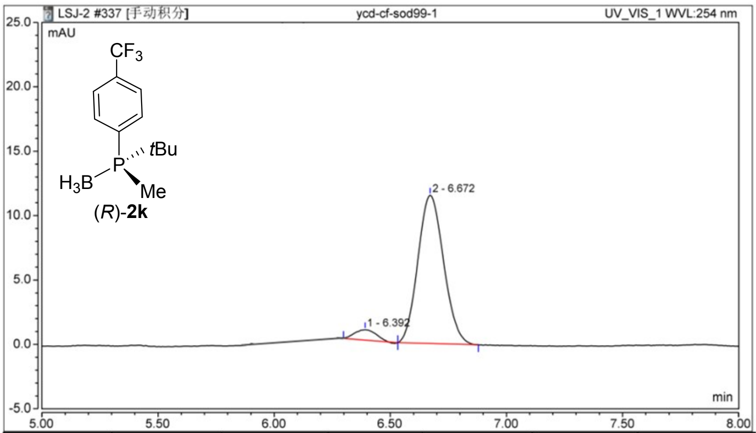
peak.number	retention_time min	peak.area mAU*min	peak.height mAU	peak.rel_area %	peak.rel_height %	peak.amount n.a.
1	9.679	157.168	467.626	97.65	98.60	n.a.
2	12.252	3.786	6.628	2.35	1.40	n.a.

Chiral HPLC chromatographic analysis of (*R*)-**2k**

Condition: Daicel Chiralcel AS-H, *n*-hexane/*i*-PrOH = 99/1, UV = 254 nm, flow rate: 1.0 mL/min, retention time: t (minor) = 6.392 min, t (major) = 6.672 min, ee = 89%.



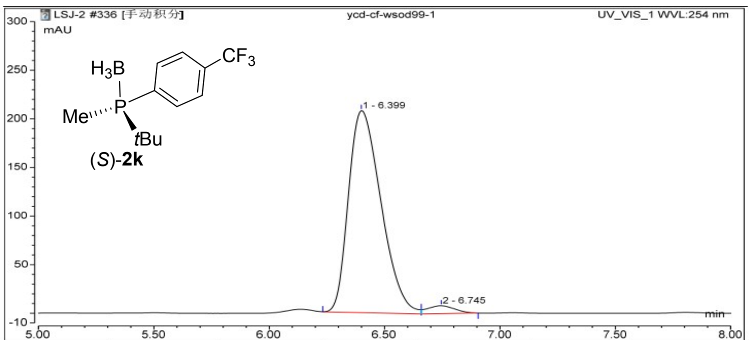
peak.number	retention_time min	peak.area mAU*min	peak.height mAU	peak.rel_area %	peak.rel_height %	peak.amount n.a.
1	6.212	0.339	2.901	49.76	51.11	n.a.
2	6.552	0.342	2.775	50.24	48.89	n.a.



peak.number	retention_time min	peak.area mAU*min	peak.height mAU	peak.rel_area %	peak.rel_height %	peak.amount n.a.
1	6.392	0.085	0.802	5.42	6.51	n.a.
2	6.672	1.476	11.513	94.58	93.49	n.a.

Chiral HPLC chromatographic analysis of (*S*)-**2k**

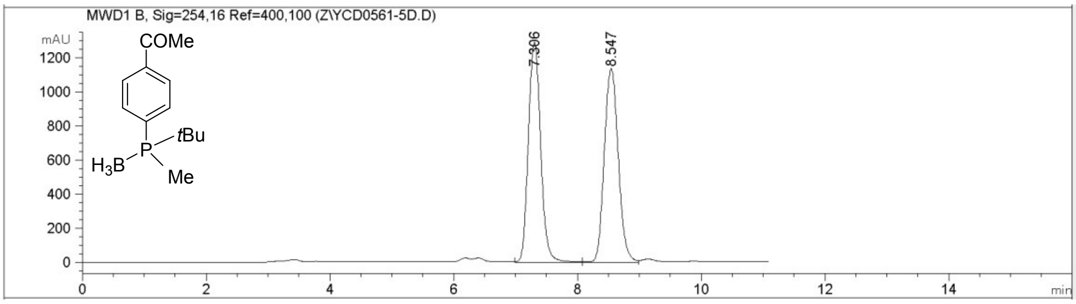
Condition: Daicel Chiralcel AS-H, *n*-hexane/*i*-PrOH = 99/1, UV = 254 nm, flow rate: 1.0 mL/min, retention time: t (major) = 6.399 min, t (minor) = 6.745 min, ee = 94%.



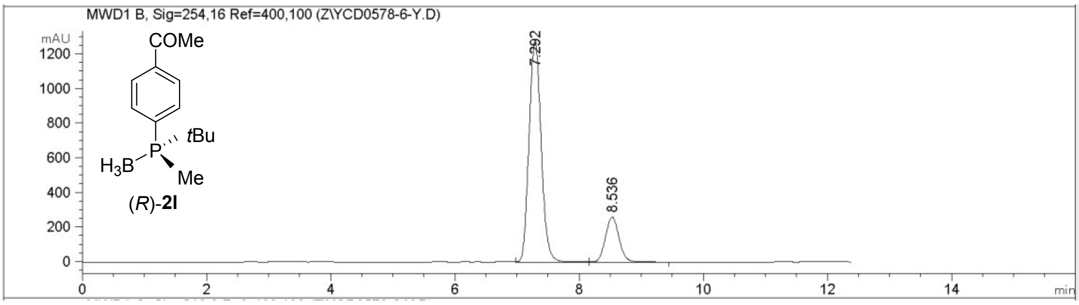
peak.number	retention_time min	peak.area mAU*min	peak.height mAU	peak.rel_area %	peak.rel_height %	peak.amount n.a.
1	6.399	33.938	207.884	96.81	96.26	n.a.
2	6.745	1.118	8.072	3.19	3.74	n.a.

Chiral HPLC chromatographic analysis of (*R*)-**2l**

Condition: Daicel Chiralcel OD-H, *n*-hexane/*i*-PrOH = 90/10, UV = 254 nm, flow rate: 1.0 mL/min, retention time: t (major) = 7.292 min, t (minor) = 8.536 min, ee = 63%.



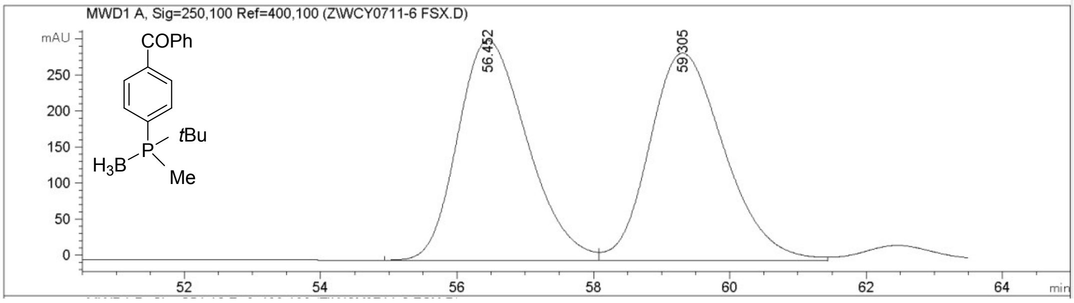
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.306	VV	0.2173	1.78369e4	1290.30762	50.0311
2	8.547	VV	0.2489	1.78147e4	1136.46375	49.9689



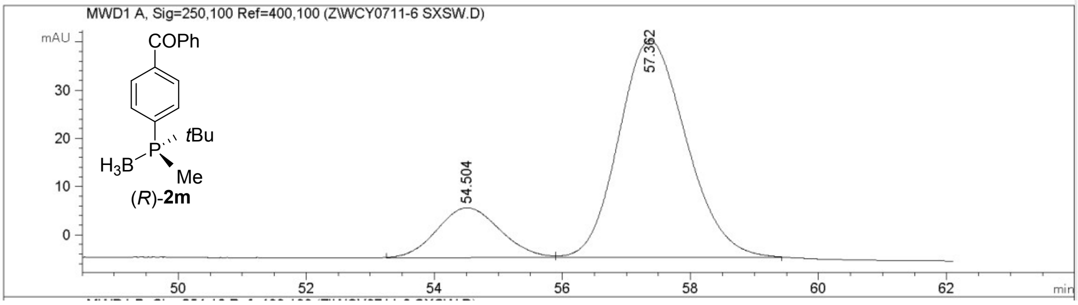
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.292	VV	0.2148	1.73500e4	1274.82043	81.5114
2	8.536	VB	0.2391	3935.37378	259.18015	18.4886

Chiral HPLC chromatographic analysis of (*R*)-**2m**

Condition: Daicel Chiralcel OD-H, *n*-hexane/*i*-PrOH = 98/2, UV = 250 nm, flow rate = 1.0 mL/min, retention time: t (minor) = 54.504 min, t (major) = 57.362 min, ee = 65%.



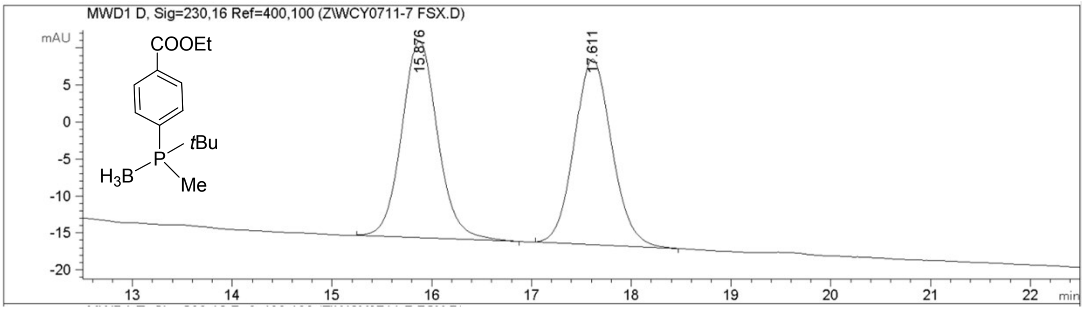
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	56.452	BV	1.0689	2.16603e4	305.59460	49.6648
2	59.305	VB	1.1507	2.19528e4	288.19479	50.3352



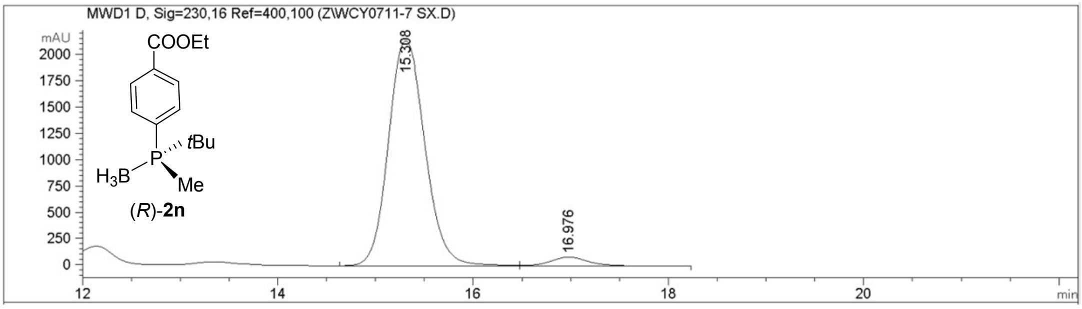
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	54.504	BV	0.8122	710.31201	10.35647	17.6685
2	57.362	VB	1.0115	3309.91113	45.03048	82.3315

Chiral HPLC chromatographic analysis of (*R*)-**2n**

Condition: Daicel Chiralcel OD-H, *n*-hexane/*i*-PrOH = 98/2, UV = 230 nm, flow rate: 0.8 mL/min, retention time: t (major) = 15.308 min, t (minor) = 16.976 min, ee = 92%.



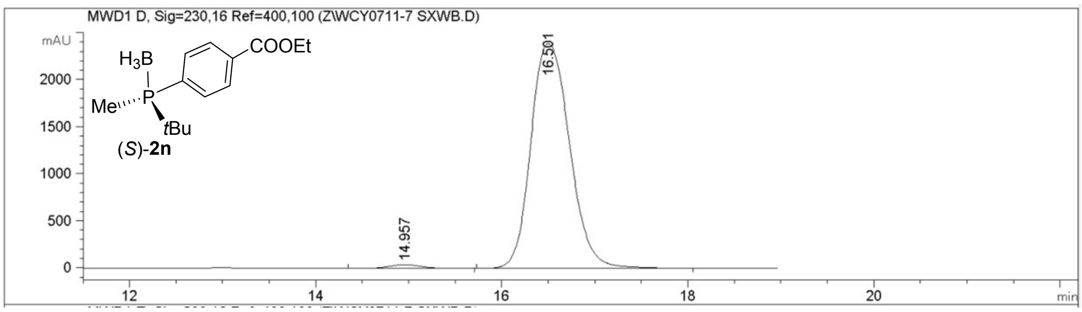
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.876	BB	0.3852	664.83820	26.63724	50.2941
2	17.611	BB	0.4033	657.06366	25.10902	49.7059



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.308	BV	0.4053	5.55358e4	2136.49756	95.9750
2	16.976	VBA	0.4180	2329.07520	84.37858	4.0250

Chiral HPLC chromatographic analysis of (*S*)-**2n**

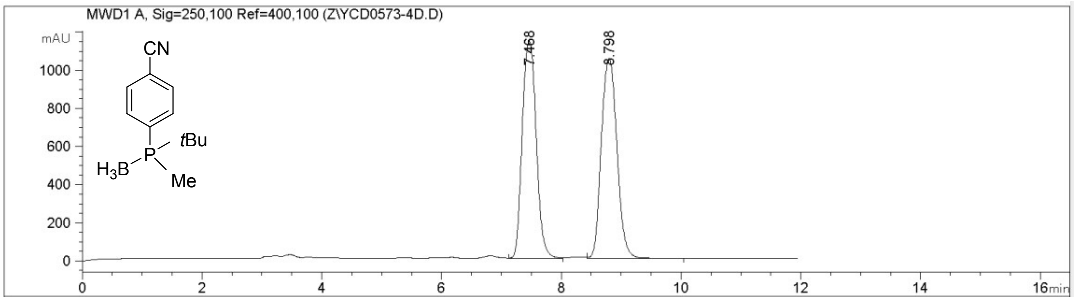
Condition: Daicel Chiralcel OD-H, *n*-hexane/*i*-PrOH = 98/2, UV = 230 nm, flow rate: 0.8 mL/min, retention time: t (minor)= 14.957 min, t (major) = 16.501 min, ee = 97%.



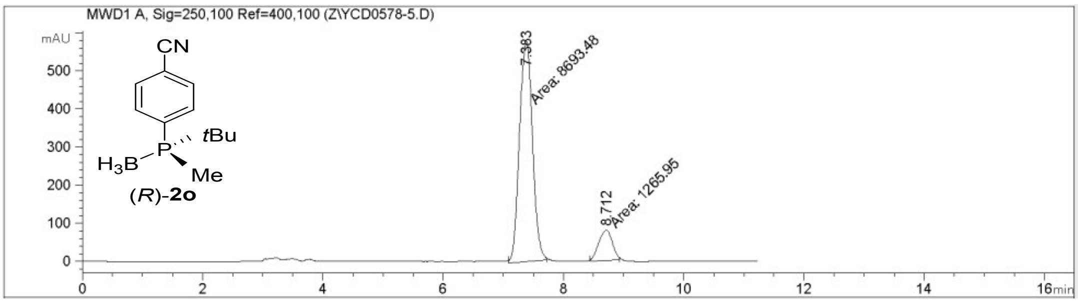
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.957	BB	0.3703	964.50848	40.14457	1.3745
2	16.501	BB	0.4558	6.92074e4	2390.02808	98.6255

Chiral HPLC chromatographic analysis of (*R*)-**2o**

Condition: Daicel Chiralcel OD-H, *n*-hexane/*i*-PrOH = 90/10, UV = 250 nm, flow rate: 1.0 mL/min, retention time: t (major) = 7.383 min, t (minor) = 8.712 min, ee = 74%.



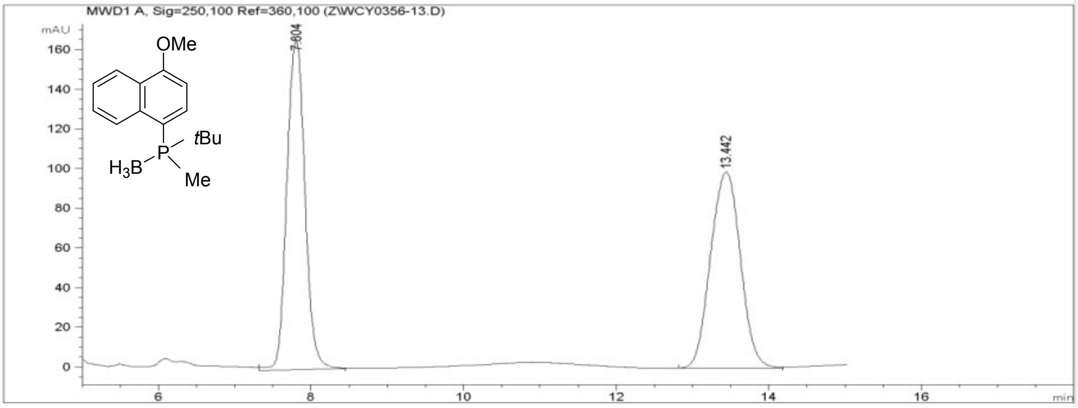
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.468	VV	0.2641	1.85677e4	1139.59644	49.4247
2	8.798	VB	0.2932	1.89999e4	1049.40784	50.5753



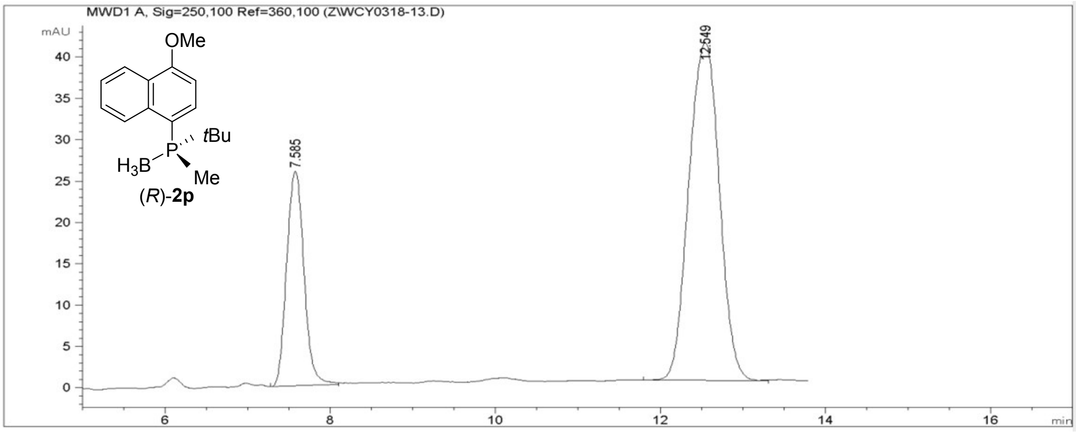
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.383	MM	0.2504	8693.47656	578.62793	87.2889
2	8.712	MM	0.2651	1265.95020	79.58189	12.7111

Chiral HPLC chromatographic analysis of (*R*)-**2p**

Condition: Daicel Chiralcel OD-H, *n*-hexane/*i*-PrOH = 98/2, UV = 250 nm, flow rate: 1 mL/min, retention time: t (minor) = 7.585 min, t (major) = 12.549 min, ee = 46%.



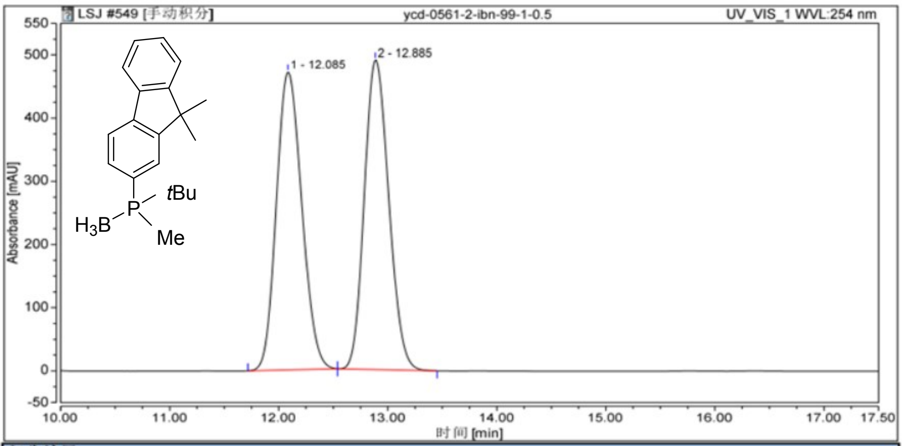
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.804	VB	0.2622	2737.16406	166.10471	50.4405
2	13.442	BV	0.4397	2689.35889	98.75276	49.5595



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.585	MM	0.2464	388.42853	26.27163	26.8371
2	12.549	MM	0.4311	1058.92957	40.94217	73.1629

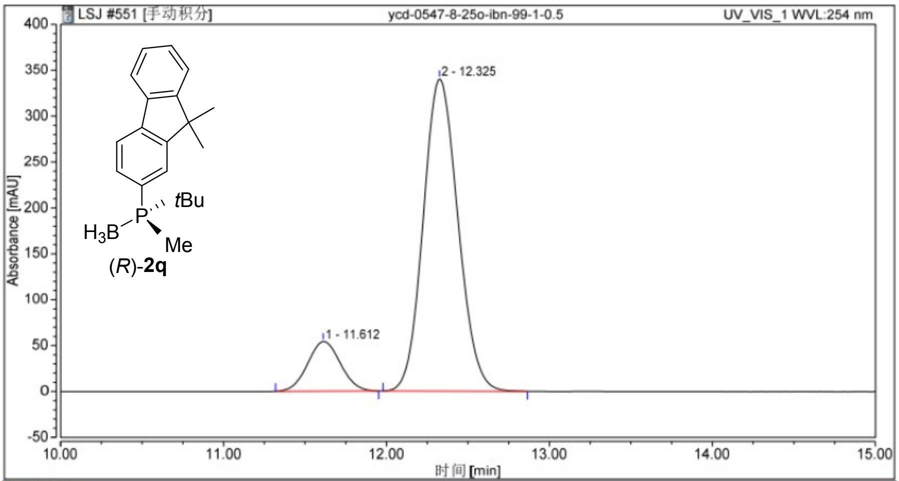
Chiral HPLC chromatographic analysis of (*R*)-**2q**

Condition: Daicel Chiralcel IBN-H, *n*-hexane/*i*-PrOH = 99/1, UV = 254 nm, flow rate: 0.5 mL/min, retention time: t (minor) = 11.612 min, t (major) = 12.325 min, ee = 74%.



积分结果

序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		12.085	127.314	471.545	50.02	49.04	n.a.
2		12.885	127.214	489.931	49.98	50.96	n.a.
总和:			**254.528**	**961.476**	**100.00**	**100.00**	

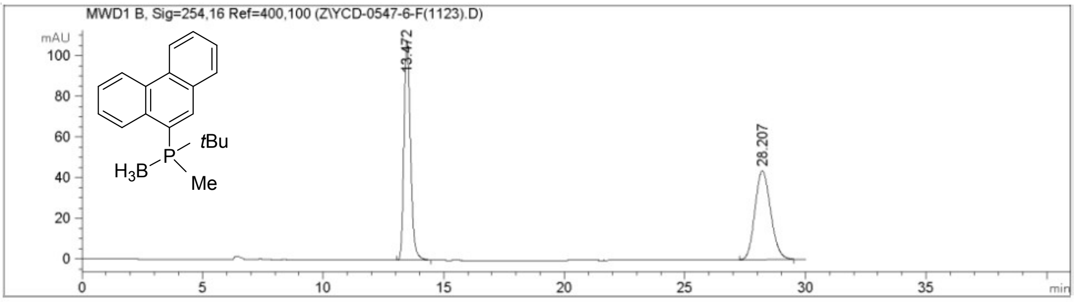


积分结果

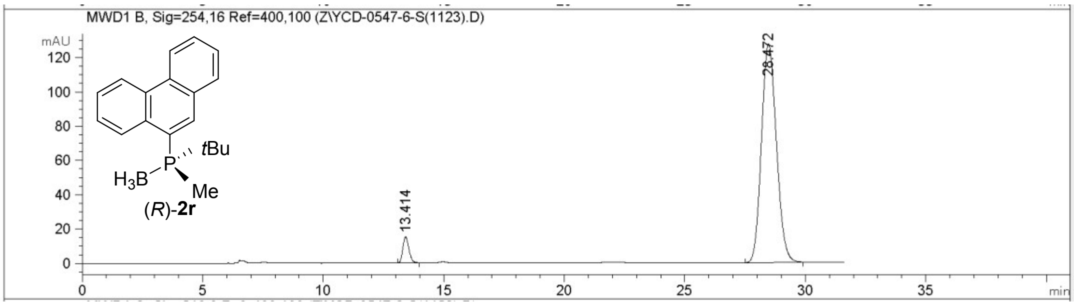
序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		11.612	12.628	54.116	13.06	13.72	n.a.
2		12.325	84.070	340.380	86.94	86.28	n.a.
总和:			**96.698**	**394.496**	**100.00**	**100.00**	

Chiral HPLC chromatographic analysis of (*R*)-**2r**

Condition: Daicel Chiralcel AS-H, *n*-hexane/*i*-PrOH = 90/10, UV = 254 nm, flow rate: 1.0 mL/min, retention time: t (minor) = 13.414 min, t (major) = 28.472 min, ee = 91%.



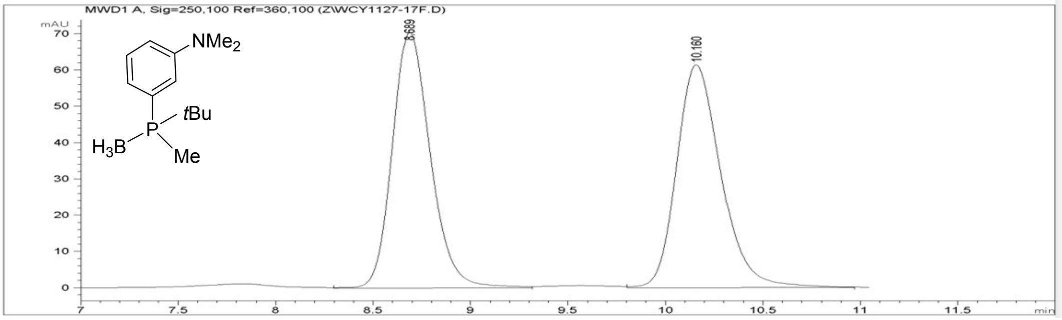
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.472	BB	0.2857	2014.30762	107.95863	50.4901
2	28.207	BB	0.7027	1975.20361	43.75396	49.5099



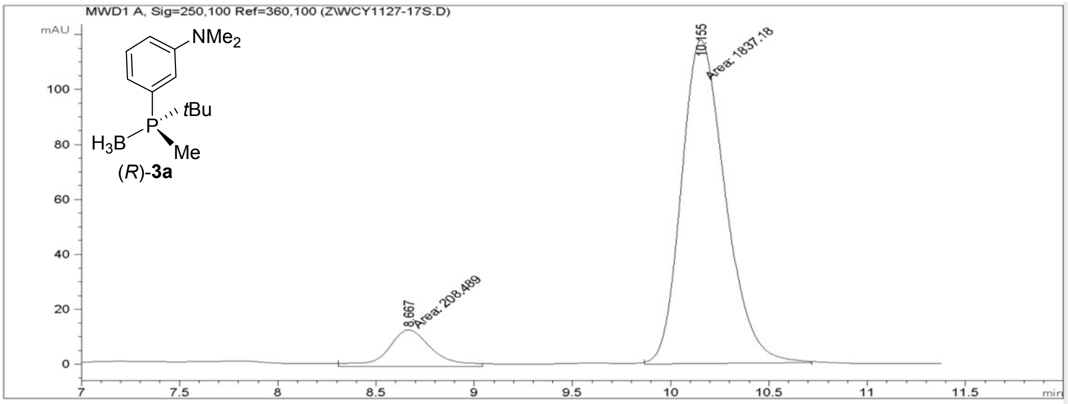
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.414	BB	0.2684	264.03180	15.21731	4.5899
2	28.472	BB	0.6664	5488.38379	127.44125	95.4101

Chiral HPLC chromatographic analysis of (*R*)-**3a**

Condition: Daicel Chiralcel OD-H, *n*-hexane/*i*-PrOH = 98/2, UV = 250 nm, flow rate: 0.8 mL/min, retention time: t (minor) = 8.667 min, t (major) = 10.155 min, ee = 80%.



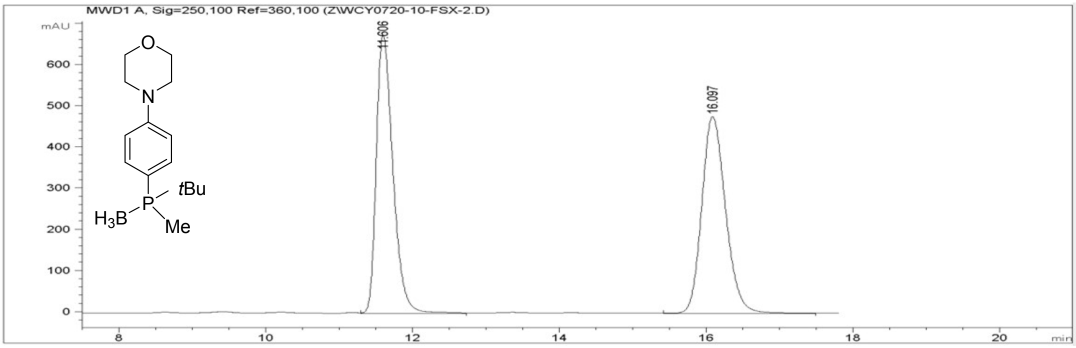
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.689	VB	0.2075	951.84967	70.50359	49.4794
2	10.160	VB	0.2447	971.87811	61.37379	50.5206



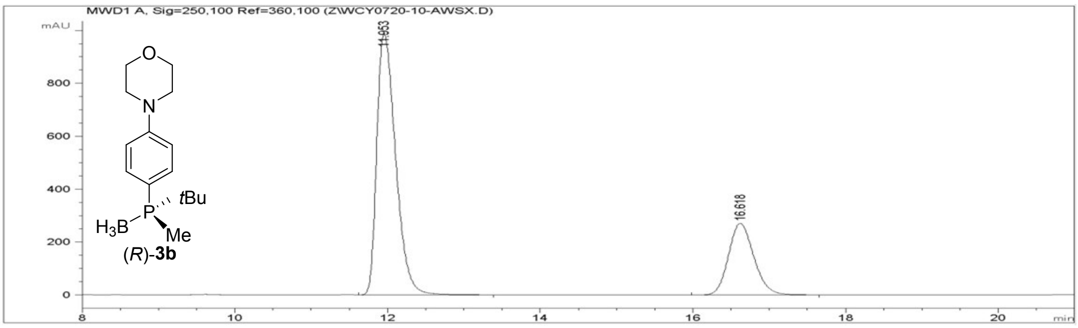
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.667	MM	0.2614	208.48915	13.29100	10.1917
2	10.155	MM	0.2600	1837.17725	117.78152	89.8083

Chiral HPLC chromatographic analysis of (*R*)-**3b**

Condition: Daicel Chiralcel OD-H, *n*-hexane/*i*-PrOH = 90/10, UV = 250 nm, flow rate: 1.0 mL/min, retention time: t (major) = 11.953 min, t (minor) = 16.618 min, ee = 46%.



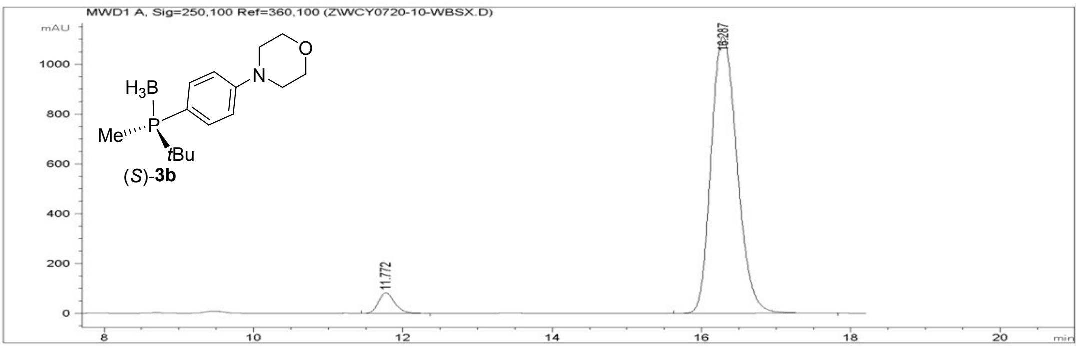
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.606	VV	0.2441	1.06681e4	675.93866	49.7857
2	16.097	VV	0.3490	1.07599e4	477.22977	50.2143



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.953	VB	0.2657	1.68999e4	987.07568	73.0724
2	16.618	VB	0.3566	6227.70654	270.53220	26.9276

Chiral HPLC chromatographic analysis of (*S*)-**3b**

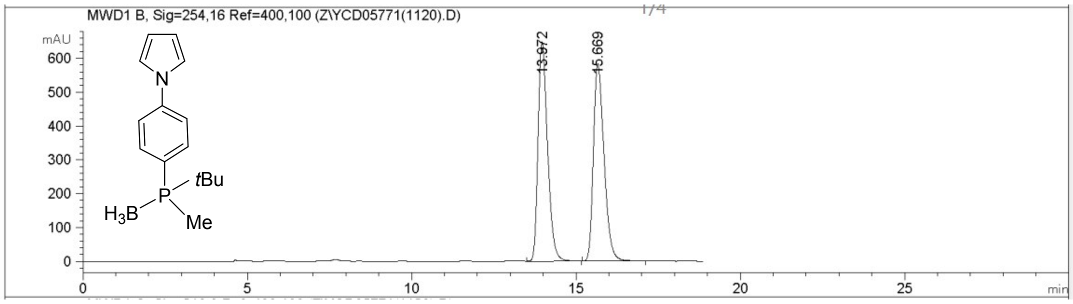
Condition: Daicel Chiralcel OD-H, *n*-hexane/*i*-PrOH = 90/10, UV = 250 nm, flow rate: 1.0 mL/min, retention time: t (minor) = 11.772 min, t (major) = 16.287 min, ee = 91%.



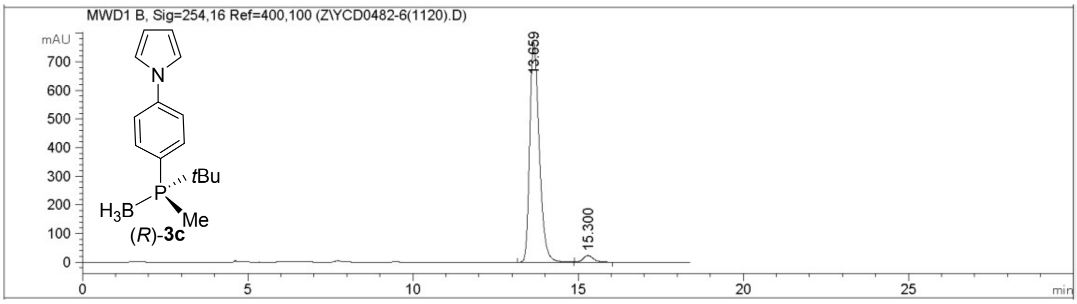
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.772	VB	0.2353	1256.51868	82.66304	4.4697
2	16.287	VB	0.3820	2.68556e4	1110.85352	95.5303

Chiral HPLC chromatographic analysis of (*R*)-**3c**

Condition: Daicel Chiralcel OD-H, *n*-hexane/*i*-PrOH = 98/2, UV = 254 nm, flow rate: 0.8 mL/min, retention time: t (major) =13.659 min, t (minor) = 15.300 min, ee = 94%.



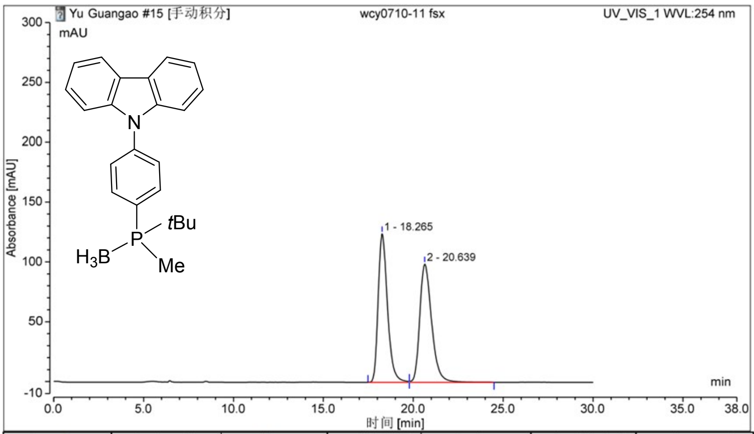
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.972	VB	0.3092	1.30541e4	647.54486	49.8619
2	15.669	BB	0.3465	1.31264e4	583.34375	50.1381



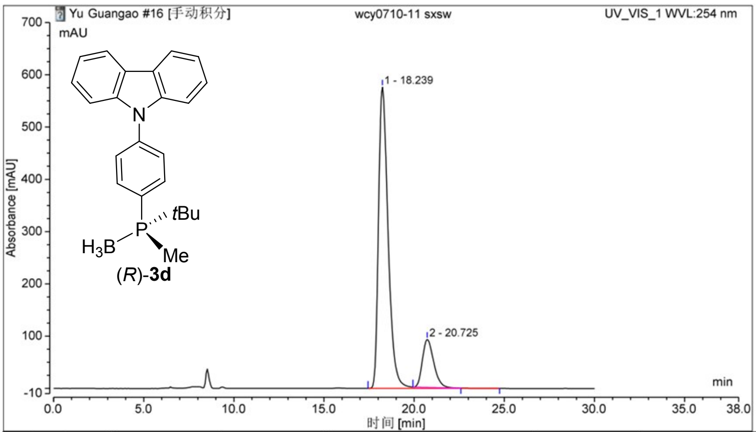
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.659	BB	0.3100	1.55394e4	768.12622	96.8499
2	15.300	BB	0.3310	505.42291	23.30959	3.1501

Chiral HPLC chromatographic analysis of (*R*)-**3d**

Condition: Daicel Chiralcel AS-H, *n*-hexane/*i*-PrOH = 98/2, UV = 254 nm, flow rate: 0.5 mL/min, retention time: t (major) = 18.239 min, t (minor) = 20.275 min, ee = 69%.



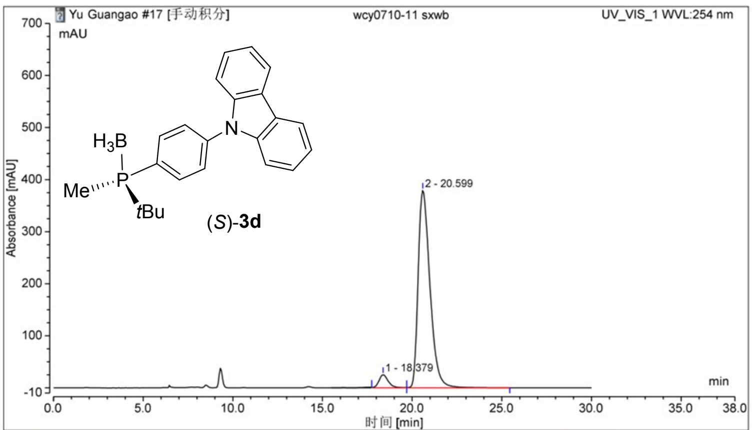
peak.number	retention_time min	peak.area mAU*min	peak.height mAU	peak.rel_area %	peak.rel_height %	peak.amount n.a.
1	18.265	74.927	124.257	49.74	55.68	n.a.
2	20.639	75.714	98.922	50.26	44.32	n.a.



peak.number	retention_time min	peak.area mAU*min	peak.height mAU	peak.rel_area %	peak.rel_height %	peak.amount n.a.
1	18.239	359.122	576.490	84.34	86.28	n.a.
2	20.725	66.699	91.708	15.66	13.72	n.a.

Chiral HPLC chromatographic analysis of (*S*)-**3d**

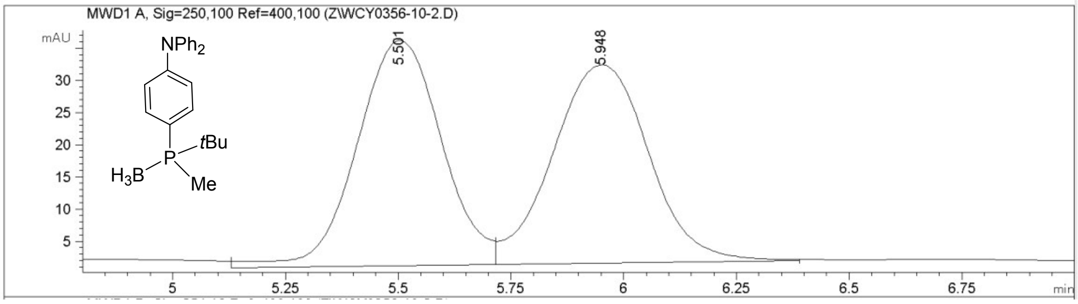
Condition: Daicel Chiralcel AS-H, *n*-hexane/*i*-PrOH = 98/2, UV = 254 nm, flow rate: 0.5 mL/min, retention time: t (minor) = 18.379 min, t (major) = 20.599 min, ee = 90%.



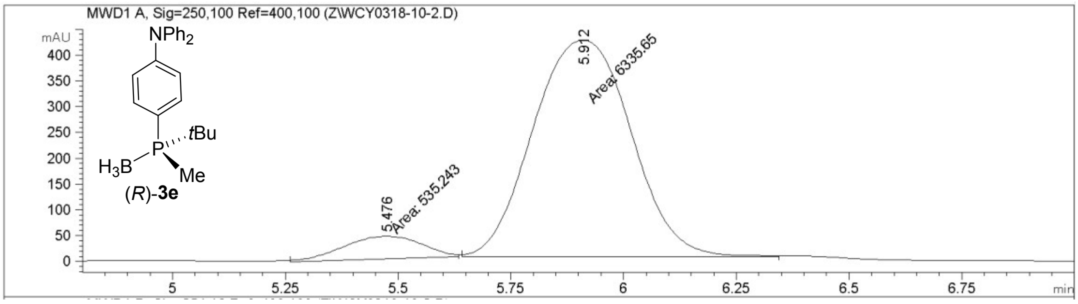
peak.number	retention_time min	peak.area mAU*min	peak.height mAU	peak.rel_area %	peak.rel_height %	peak.amount n.a.
1	18.379	15.424	25.311	5.05	6.25	n.a.
2	20.599	289.765	379.467	94.95	93.75	n.a.

Chiral HPLC chromatographic analysis of (*R*)-**3e**

Condition: Daicel Chiralcel OD-H, *n*-hexane/*i*-PrOH = 98/2, UV = 250 nm, flow rate: 1.0 mL/min, retention time: t (minor) = 5.476 min, t (major) = 5.912 min, ee = 84%.



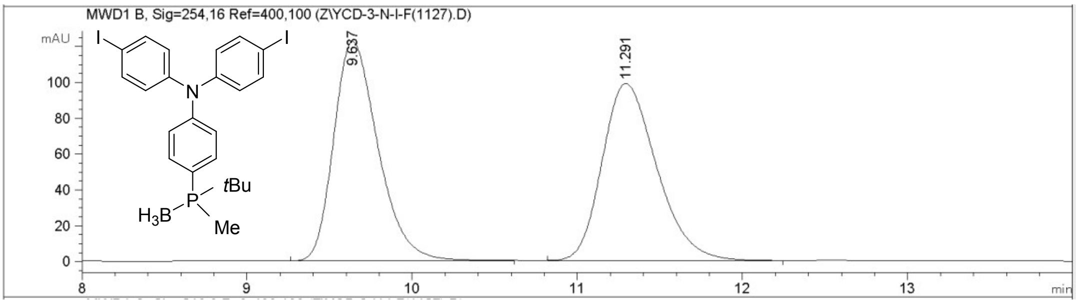
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.501	VV	0.2049	459.19754	35.03112	50.1799
2	5.948	VB	0.2327	455.90411	30.79701	49.8201



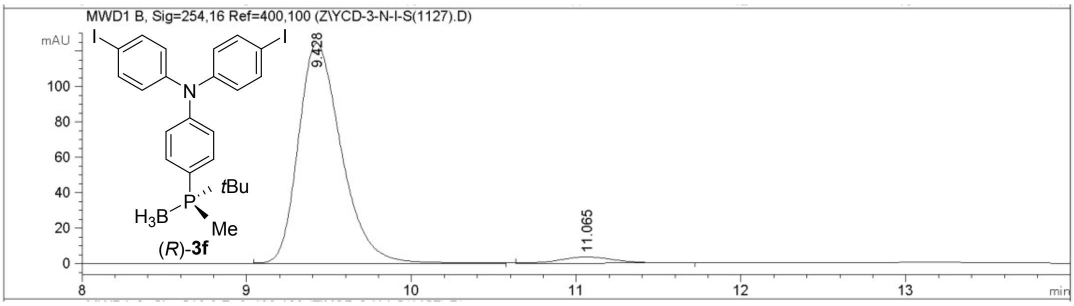
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.476	MM	0.2041	535.24298	43.70932	7.7900
2	5.912	MM	0.2519	6335.65332	419.17145	92.2100

Chiral HPLC chromatographic analysis of (*R*)-**3f**

Condition: Daicel Chiralcel OD-H, *n*-hexane/*i*-PrOH = 90/10, UV = 254 nm, flow rate: 1.0 mL/min, retention time: t (major) = 9.428 min, t (minor) = 11.065 min, ee = 94%.



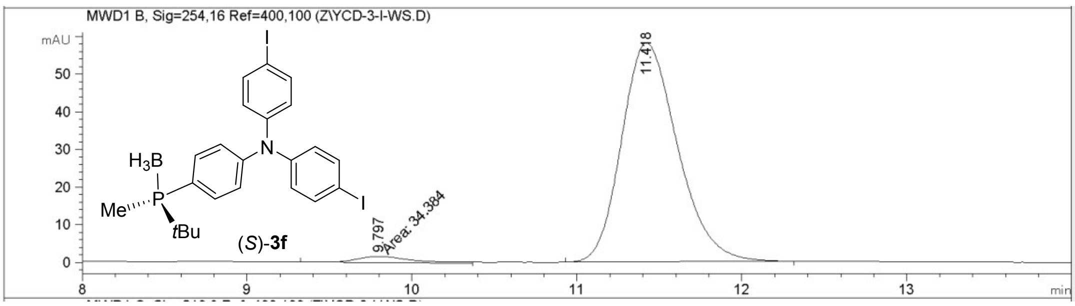
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.637	BB	0.2880	2291.81104	122.62823	50.1904
2	11.291	BB	0.3562	2274.42212	98.93695	49.8096



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.428	BB	0.2757	2232.09448	124.19257	96.7876
2	11.065	BB	0.3213	74.08373	3.41209	3.2124

Chiral HPLC chromatographic analysis of (*S*)-**3f**

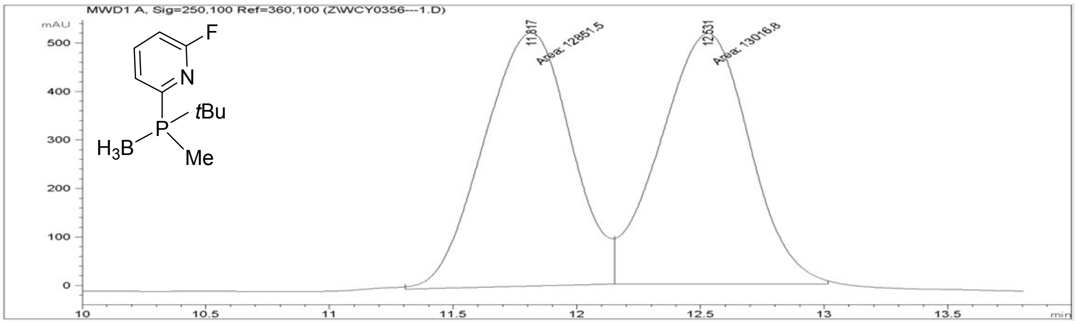
Condition: Daicel Chiralcel OD-H, *n*-hexane/*i*-PrOH = 90/10, UV = 254 nm, flow rate: 1.0 mL/min, retention time: t (minor) = 9.797 min, t (major) = 11.418 min, ee = 95%.



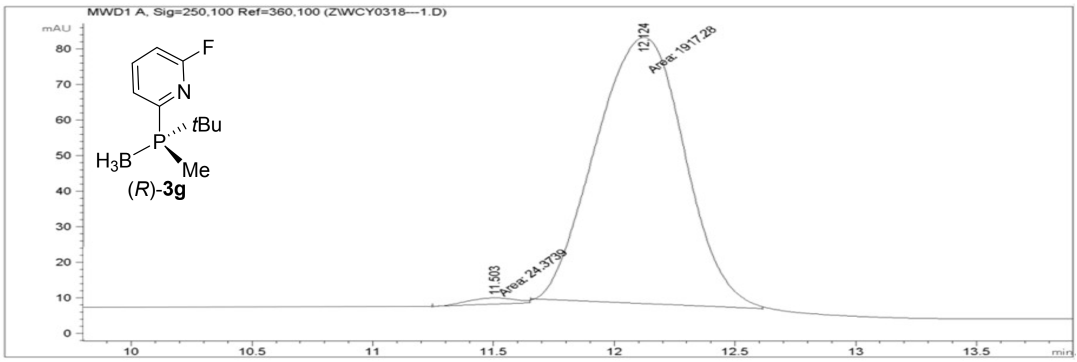
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.797	MM	0.3612	34.38400	1.58657	2.4392
2	11.418	BB	0.3653	1375.23950	58.27720	97.5608

Chiral HPLC chromatographic analysis of (*R*)-**3g**

Condition: Daicel Chiralcel AS-H, *n*-hexane/*i*-PrOH = 98/2, UV = 250 nm, flow rate: 1.0 mL/min, retention time: t (minor) = 11.503 min, t (major) = 12.124 min, ee = 97%.



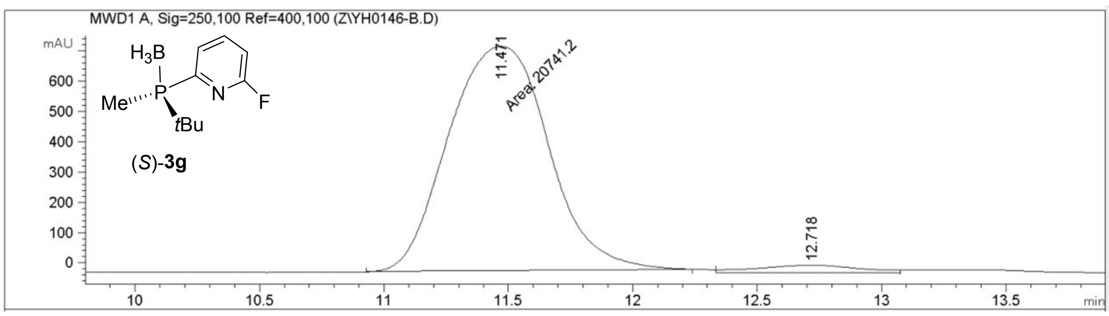
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.817	MM	0.4101	1.28515e4	522.30109	49.6805
2	12.531	MM	0.4201	1.30168e4	516.47839	50.3195



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.503	MM	0.2345	24.37392	1.73228	1.2553
2	12.124	MM	0.4272	1917.28198	74.80308	98.7447

Chiral HPLC chromatographic analysis of (*S*)-**3g**

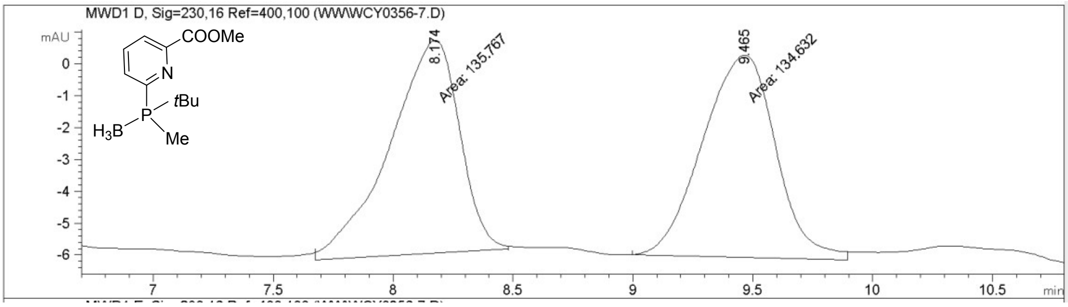
Condition: Daicel Chiralcel AS-H, *n*-hexane/*i*-PrOH = 98/2, UV = 250 nm, flow rate: 1.0 mL/min, retention time: t (major) = 11.471 min, t (minor) = 12.718 min, ee = 93%.



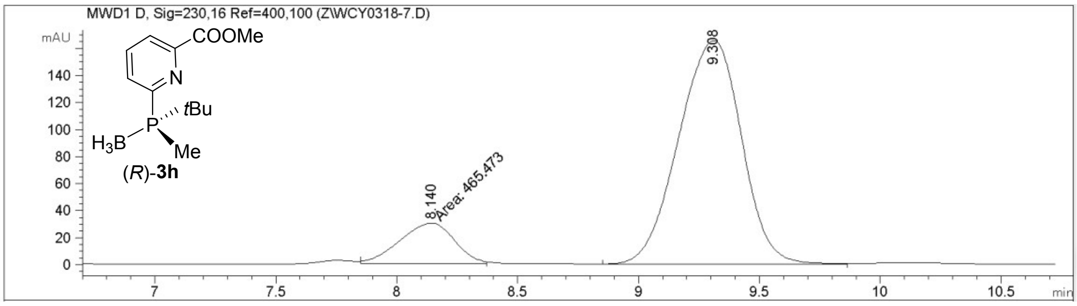
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.471	MM	0.4666	2.07412e4	740.90192	96.7001
2	12.718	VV	0.4179	707.80133	24.73396	3.2999

Chiral HPLC chromatographic analysis of (*R*)-**3h**

Condition: Daicel Chiralcel AS-H, *n*-hexane/*i*-PrOH = 95/5, UV = 230 nm, flow rate: 1.0 mL/min, retention time: t (minor) = 8.140 min, t (major) = 9.308 min, ee = 73%.



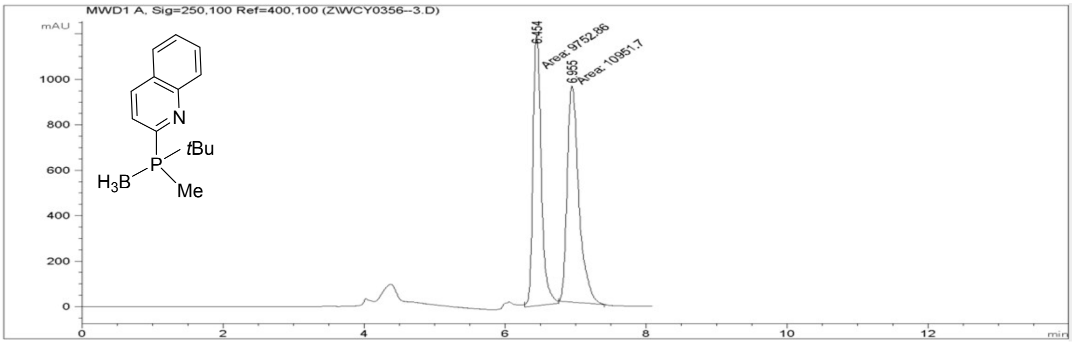
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.174	MM	0.3382	135.76715	6.69110	50.2099
2	9.465	MM	0.3538	134.63216	6.34185	49.7901



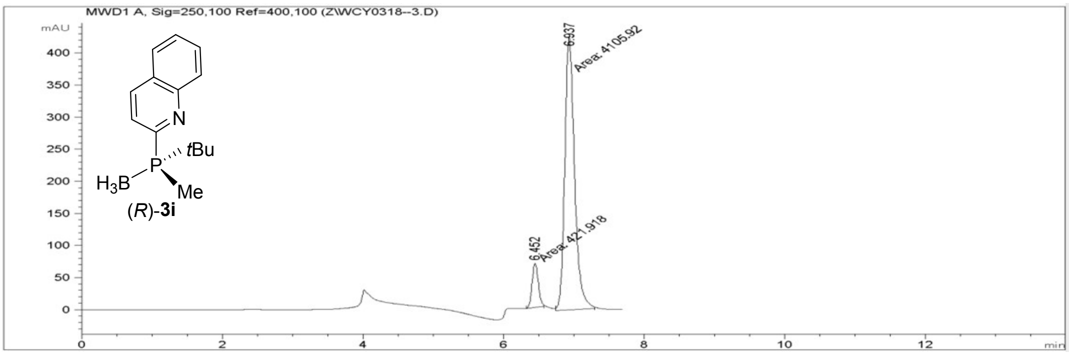
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.140	MM	0.2612	465.47260	29.70196	13.4696
2	9.308	BB	0.2891	2990.25122	165.27945	86.5304

Chiral HPLC chromatographic analysis of (*R*)-**3i**

Condition: Daicel Chiralcel AS-H, *n*-hexane/*i*-PrOH = 98/2, UV = 250 nm, flow rate: 0.8 mL/min, retention time: t (minor) = 6.452 min, t (major) = 6.937 min, ee = 81%.



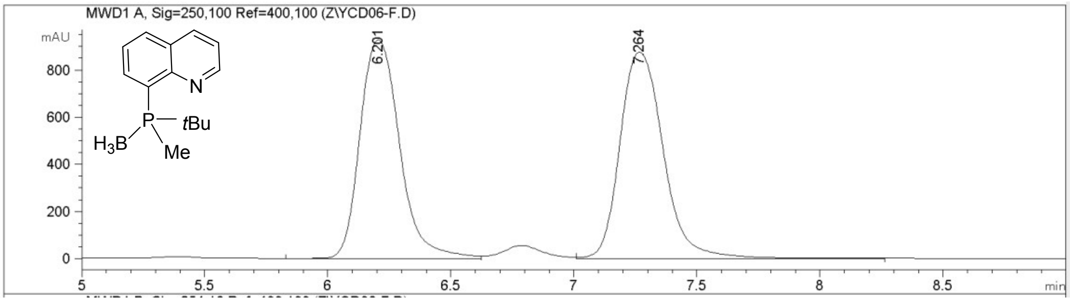
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.454	MM	0.1390	1.00071e4	1199.93201	49.5254
2	6.955	MM	0.1839	1.01989e4	924.26465	50.4746



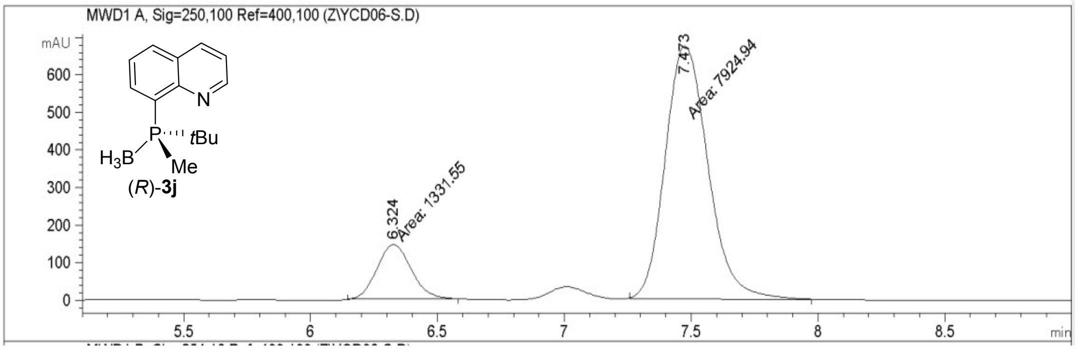
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.452	MM	0.1016	421.91812	69.22715	9.3183
2	6.937	MM	0.1604	4105.91650	426.71967	90.6817

Chiral HPLC chromatographic analysis of (*R*)-**3j**

Condition: Daicel Chiralcel OD-H, *n*-hexane/i-PrOH = 98/2, UV = 250 nm, flow rate: 1.0 mL/min, retention time: t (minor) = 6.324 min, t (major) = 7.473 min, ee = 71%.



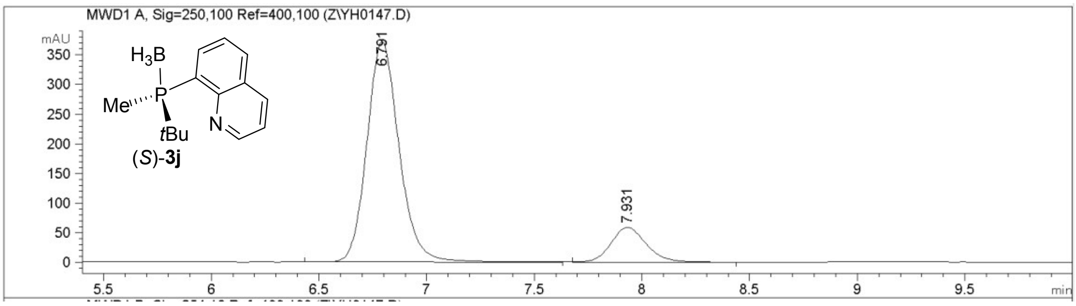
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.201	VV	0.1764	1.03656e4	927.12408	49.2435
2	7.264	VB	0.1923	1.06840e4	875.73108	50.7565



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.324	MM	0.1537	1331.55420	144.35512	14.3851
2	7.473	MM	0.1960	7924.94189	673.93359	85.6149

Chiral HPLC chromatographic analysis of (*S*)-**3j**

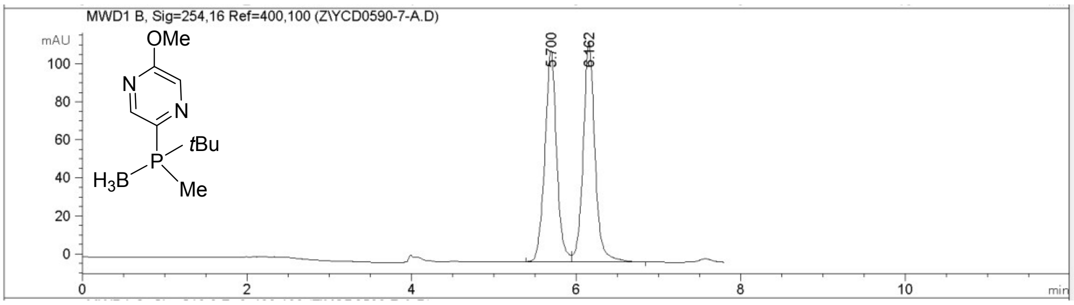
Condition: Daicel Chiralcel OD-H, *n*-hexane/*i*-PrOH = 98/2, UV = 250 nm, flow rate: 1.0 mL/min, retention time: t (major) = 6.791 min, t (minor) = 7.931 min, ee = 71%.



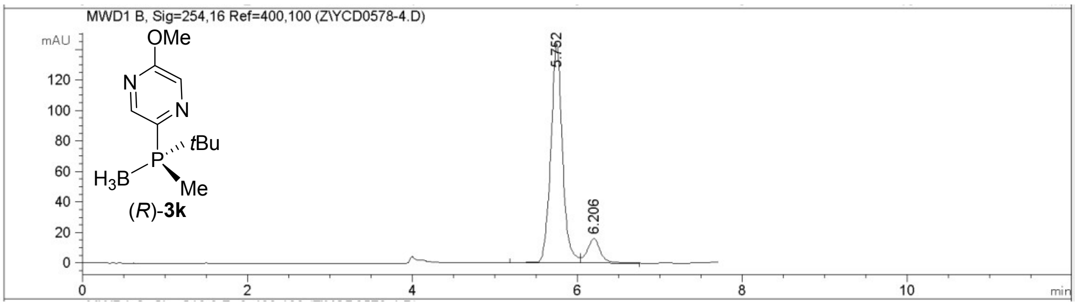
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.791	BB	0.1576	722.98175	70.54803	85.6130
2	7.931	BB	0.1728	121.49510	10.83360	14.3870

Chiral HPLC chromatographic analysis of (*R*)-**3k**

Condition: Daicel Chiralcel OD-H, *n*-hexane/*i*-PrOH = 98/2, UV = 254 nm, flow rate: 0.8 mL/min, retention time: t (major) = 5.752 min, t (minor) = 6.206 min, ee = 77%.



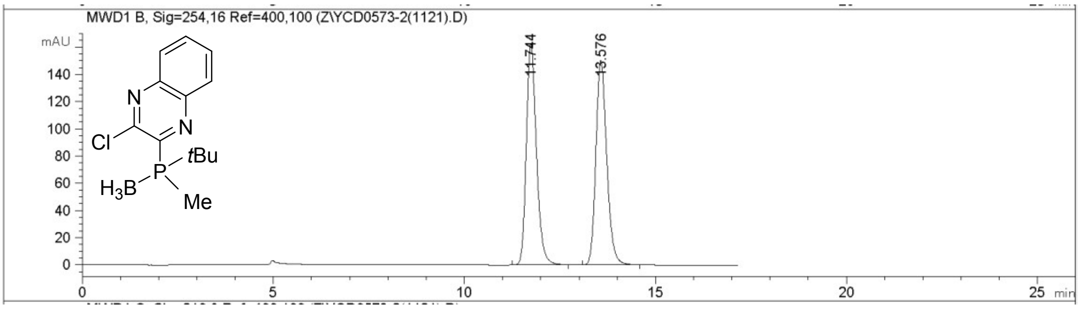
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.700	BV	0.1498	1101.96777	111.02318	49.0171
2	6.162	VB	0.1502	1146.15967	115.12369	50.9829



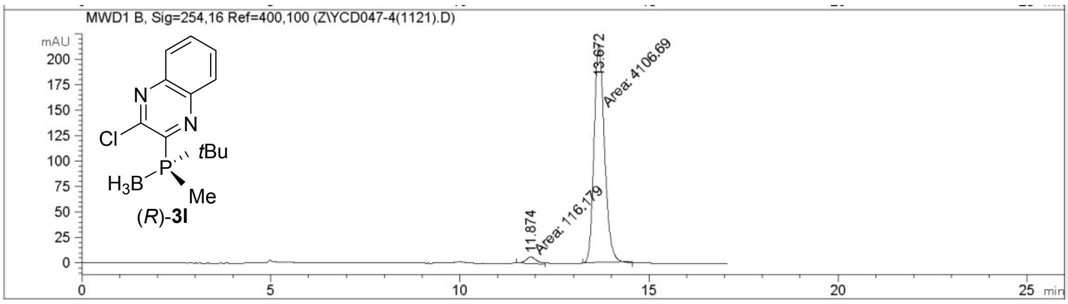
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.752	BV	0.1468	1417.11865	144.04102	88.7869
2	6.206	VB	0.1627	178.97156	16.22691	11.2131

Chiral HPLC chromatographic analysis of (*R*)-**3l**

Condition: Daicel Chiralcel OD-H, *n*-hexane/*i*-PrOH = 98/2, UV = 254 nm, flow rate: 0.8 mL/min, retention time: t (minor) = 11.874 min, t (major) = 13.672 min, ee = 94%.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.744	BB	0.2825	2982.82666	162.20386	50.0961
2	13.576	BB	0.3049	2971.38452	150.14647	49.9039



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.874	MM	0.3169	116.17851	6.10941	2.7512
2	13.672	MM	0.3198	4106.69238	214.00578	97.2488