

Supporting Information

Asymmetric synthesis of α -alkenyl homoallylic primary amines via 1,2-addition of Grignard reagent to α,β -unsaturated phosphonyl imines

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1. General information

All the reactions were carried out in oven-dried glasswares under an atmosphere of dry argon, unless otherwise stated. All commercially available reagents were used without further purification. Ether, toluene, THF, 2-MeTHF used for the reaction were distilled using benzophenone-sodium under nitrogen prior to use. DCM used for the reaction was distilled using calcium hydride under nitrogen prior to use. ^1H NMR, ^{13}C NMR, ^{31}P NMR spectra (TMS used as internal standard) were recorded at 400 MHz, 100 MHz, 162 MHz respectively in CDCl_3 with JMTC-400/54/55. High resolution mass spectra for all the new compounds were done by the Bruker APEX IV instruments. Optical rotation values were taken using AUTOPOL IV automatic polarimeter. Analytical thin-layer chromatography (TLC) was performed using 0.25 mm precoated silica gel plates and the compounds were visualized with UV light ($\lambda = 254$ nm) Compounds were purified using flash column chromatography (forced flow) on silica gel (SiO_2) 60 Å (32-63 μm) particle size.

2. General procedure for synthesis of α,β -unsaturated imines

An oven dried and argon flushed reaction vial was charged in succession with cinnamaldehyde (1.5 mmol), phosphoramidate (1.0 mmol), triethylamine (2.0 mmol) in DCM (8.0 mL). The mixture was cooled in an ice bath, then titanium chloride (0.5 mmol in a 1 mol/L DCM solution) was added dropwise during 30 min. After addition, the ice bath was removed and the whole solution was kept at rt 48 h later, the mixture was poured into a pad of celite, washing the pad with 100 mL DCM. After concentrated under reduced pressure, the residue was purified via column chromatography with ethyl acetate and petroleum ether (from 1:10 to 1:2 v/v) as eluent to give the product **3**.

3a. pale yellow solid: mp 70-71 °C, $[\alpha]_{\text{D}}^{25} = -26.0$ ($c = 1.08$, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ 9.01 (dd, $J = 33.2, 8.8$ Hz, 1H), 7.60 (dd, $J = 7.6, 1.2$ Hz, 2H), 7.44-7.25 (m, 14 H), 7.13 (ddd, $J = 11.2, 8.8, 2.0$ Hz, 1H), 4.25 (qd, $J = 6.0, 3.6$ Hz, 2H), 3.25-3.06 (m, 2H), 1.22 (dd, $J = 8.8, 7.2$ Hz, 6H), 1.07 (d, $J = 6.4$ Hz, 3H), 0.89 (d, $J = 6.4$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 174.7 (d, $J = 7.2$ Hz), 148.9,

141.9 (d, $J = 5.3$ Hz), 140.7 (d, $J = 6.4$ Hz), 135.2 (d, $J = 1.3$ Hz), 130.4, 129.4, 129.1, 128.6, 128.5, 128.2, 128.0, 127.8, 127.6, 67.7 (d, $J = 11.1$ Hz), 67.1 (d, $J = 11.4$ Hz), 46.7 (d, $J = 4.9$ Hz), 45.9 (d, $J = 4.5$ Hz), 21.2 (d, $J = 1.6$ Hz), 21.1 (d, $J = 1.2$ Hz), 20.9 (d, $J = 1.8$ Hz); ^{31}P NMR (162 MHz, CDCl_3) δ 24.0; HRMS-(ESI) m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{29}\text{H}_{35}\text{N}_3\text{OP}$, 472.2518; found, 472.2510.

3b. pale yellow solid: mp 74-76 °C, $[\alpha]_{\text{D}}^{25} = -53.1$ ($c = 0.89$, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ 8.99 (dd, $J = 33.2, 8.8$ Hz, 1H), 7.54 (dt, $J = 8.8, 1.6$ Hz, 2H), 7.46-7.44 (m, 2H), 7.31-7.24 (m, 11H), 7.10 (ddd, $J = 11.2, 8.8, 2.4$ Hz, 1H), 4.25 (qd, $J = 6.4, 4.0$ Hz, 2H), 3.22-3.06 (m, 2H), 1.21 (dd, $J = 8.4, 7.2$ Hz, 6H), 1.06 (d, $J = 6.4$ Hz, 3H), 0.88 (d, $J = 6.8$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 174.2 (d, $J = 7.2$ Hz), 147.2, 141.9 (d, $J = 5.1$ Hz), 140.7 (d, $J = 6.2$ Hz), 134.1 (d, $J = 1.2$ Hz), 132.3, 130.0, 129.6, 129.5, 128.6, 128.5, 128.0, 127.8, 127.7, 127.6, 124.6, 67.7 (d, $J = 11.1$ Hz), 67.1 (d, $J = 11.3$ Hz), 46.8 (d, $J = 4.9$ Hz), 45.9 (d, $J = 4.5$ Hz), 21.2, 21.1 (d, $J = 1.2$ Hz), 20.9 (d, $J = 1.8$ Hz); ^{31}P NMR (162 MHz, CDCl_3) δ 23.8; HRMS-(ESI) m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{29}\text{H}_{34}\text{BrN}_3\text{OP}$, 550.1623; found, 550.1612.

3c. pale yellow solid: mp 57-59 °C, $[\alpha]_{\text{D}}^{25} = -45.6$ ($c = 1.21$, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ 8.91 (d, $J = 31.6$ Hz, 1H), 7.96-7.94 (m, 2H), 7.48-7.25 (m, 14H), 4.29-4.24 (m, 2H), 3.29-3.10 (m, 2H), 1.21 (dd, $J = 11.6, 6.8$ Hz, 6H), 1.04 (d, $J = 6.4$ Hz, 3H), 0.89 (d, $J = 6.4$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 169.7 (d, $J = 4.8$ Hz), 142.5 (d, $J = 4.1$ Hz), 142.4, 141.5 (d, $J = 6.0$ Hz), 133.5 (d, $J = 1.3$ Hz), 132.4, 132.1, 130.9, 130.6, 128.8, 128.7, 128.6, 128.0, 127.8, 127.7, 127.5, 67.7 (d, $J = 12.0$ Hz), 66.6 (d, $J = 11.9$ Hz), 46.6 (d, $J = 5.4$ Hz), 46.0 (d, $J = 4.6$ Hz), 21.7 (d, $J = 1.9$ Hz), 21.2 (d, $J = 2.2$ Hz), 21.1 (d, $J = 1.6$ Hz); ^{31}P NMR (162 MHz, CDCl_3) δ 23.0; HRMS-(ESI) m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{29}\text{H}_{34}\text{ClN}_3\text{OP}$, 506.2128; found, 506.2144.

3d. pale yellow solid: mp 66-67 °C, $[\alpha]_{\text{D}}^{25} = -38.5$ ($c = 0.68$, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ 9.04 (dd, $J = 33.2, 8.8$ Hz, 1H), 7.69-7.63 (m, 2H), 7.33-7.18 (m, 13H), 7.07 (ddd, $J = 11.2, 8.8, 2.0$ Hz, 1H), 4.26 (qd, $J = 6.0, 3.6$ Hz, 2H), 3.24-3.05 (m, 2H), 2.44 (s, 3H), 1.21 (dd, $J = 6.4$ Hz, 6H), 1.07 (d, $J = 6.8$ Hz, 3H), 0.89 (d, $J = 6.4$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 174.9 (d, $J = 7.2$ Hz), 145.4, 142.0 (d, $J = 5.1$ Hz), 140.8 (d, $J = 6.2$ Hz), 133.9, 132.1 (d, $J = 1.4$ Hz), 131.6, 131.3 (d, $J = 2.2$

Hz), 130.9, 129.0, 128.6, 128.5, 128.0, 127.8 (d, $J = 4.5$ Hz), 127.7, 127.2, 126.4, 125.6, 125.2, 123.1, 67.7 (d, $J = 11.2$ Hz), 67.1 (d, $J = 11.3$ Hz), 46.8 (d, $J = 5.1$ Hz), 45.9 (d, $J = 4.5$ Hz), 21.2, 21.0 (d, $J = 1.7$ Hz); ^{31}P NMR (162 MHz, CDCl_3) δ 24.1; HRMS-(ESI) m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{30}\text{H}_{37}\text{N}_3\text{OP}$, 486.2674; found, 486.2672.

3e. white solid: mp 64-65 °C, $[\alpha]_{\text{D}}^{25} = -42.0$ ($c = 0.60$, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ 9.00 (dd, $J = 33.2, 9.2$ Hz, 1H), 7.48 (d, $J = 8.4$ Hz, 2H), 7.34-7.20 (m, 13H), 7.08 (ddd, $J = 16.0, 9.2, 2.4$ Hz, 1H), 4.25 (qd, $J = 6.0, 3.6$ Hz, 2H), 3.22-3.07 (m, 2H), 2.37 (s, 3H), 1.21 (dd, $J = 8.8, 7.2$ Hz, 6H), 1.07 (d, $J = 6.8$ Hz, 3H), 0.89 (d, $J = 6.8$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 174.9 (d, $J = 7.1$ Hz), 149.0, 141.9 (d, $J = 5.3$ Hz), 140.8 (d, $J = 6.4$ Hz), 132.5 (d, $J = 1.1$ Hz), 129.8, 128.6, 128.5, 128.4, 128.2, 128.1, 128.0, 127.8 (d, $J = 0.8$ Hz), 127.6, 67.7 (d, $J = 11.1$ Hz), 67.1 (d, $J = 11.4$ Hz), 46.7 (d, $J = 4.9$ Hz), 45.9 (d, $J = 4.5$ Hz), 21.6, 21.2 (d, $J = 1.9$ Hz), 21.1 (d, $J = 1.2$ Hz), 20.9 (d, $J = 1.6$ Hz); ^{31}P NMR (162 MHz, CDCl_3) δ 24.1; HRMS-(ESI) m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{30}\text{H}_{37}\text{N}_3\text{OP}$, 486.2674; found, 486.2669.

3f. pale yellow solid: mp 61-62 °C, $[\alpha]_{\text{D}}^{25} = -12.2$ ($c = 0.97$, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ 9.01 (dd, $J = 33.6, 9.2$ Hz, 1H), 7.75 (d, $J = 16.0$ Hz, 1H), 7.62 (dd, $J = 8.0, 1.6$ Hz, 1H), 7.37-7.24 (m, 11H), 7.18 (ddd, $J = 11.2, 9.2, 2.4$ Hz, 1H), 6.98 (t, $J = 7.6$ Hz, 1H), 6.93 (d, $J = 8.4$ Hz, 1H), 4.25 (qd, $J = 6.4, 2.4$ Hz, 2H), 3.90 (s, 3H), 3.22-3.06 (m, 2H), 1.22 (dd, $J = 7.2, 8.4$ Hz, 6H), 1.07 (d, $J = 6.4$ Hz, 3H), 0.89 (d, $J = 6.4$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 175.7 (d, $J = 7.2$ Hz), 158.1, 144.4, 141.8 (d, $J = 5.6$ Hz), 140.7 (d, $J = 7$ Hz), 131.8, 129.6, 129.3, 128.6, 128.5, 128.4, 128.0, 127.8, 127.7, 124.1 (d, $J = 1.4$ Hz), 120.9, 111.3, 67.7 (d, $J = 11.1$ Hz), 67.1 (d, $J = 11.2$ Hz), 55.7, 46.7 (d, $J = 4.8$ Hz), 45.9 (d, $J = 4.5$ Hz), 21.2 (d, $J = 1.9$ Hz), 21.1 (d, $J = 1.3$ Hz), 20.9 (d, $J = 1.6$ Hz); ^{31}P NMR (162 MHz, CDCl_3) δ 24.2; HRMS-(ESI) m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{30}\text{H}_{37}\text{N}_3\text{O}_2\text{P}$, 502.2623; found, 502.2611.

3g. yellow solid: mp 63-65 °C, $[\alpha]_{\text{D}}^{25} = -10.4$ ($c = 0.47$, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ 8.97 (dd, $J = 33.2, 9.2$ Hz, 1H), 7.56-7.54 (m, 2H), 7.33-7.27 (m, 11H), 6.99 (ddd, $J = 11.2, 9.2, 2.4$ Hz, 1H), 6.96-6.92 (m, 2H), 4.25 (qd, $J = 6.0, 3.2$ Hz, 2H), 3.85 (s, 3H), 3.22-3.06 (m, 2H), 1.21 (dd, $J = 7.2$ Hz, 6H), 1.07 (d, $J = 6.4$ Hz, 3H), 0.89 (d, $J = 6.8$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 175.2 (d, $J = 7.1$

Hz), 161.6, 149.1, 141.7 (d, $J = 5.5$ Hz), 140.7 (d, $J = 6.4$ Hz), 129.9, 128.6, 128.5, 128.0, 127.8, 127.7, 127.1, 126.8, 114.5, 67.7 (d, $J = 11.1$ Hz), 67.1 (d, $J = 11.2$ Hz), 55.5, 46.7 (d, $J = 4.6$ Hz), 45.9 (d, $J = 4.3$ Hz), 21.2, 21.1, 20.9; ^{31}P NMR (162 MHz, CDCl_3) δ 24.3; HRMS-(ESI) m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{30}\text{H}_{37}\text{N}_3\text{O}_2\text{P}$, 502.2623; found, 502.2629.

3h. red solid: mp 67-68 °C, $[\alpha]_{\text{D}}^{25} = -33.4$ ($c = 1.15$, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ 8.94 (dd, $J = 33.6, 9.2$ Hz, 1H), 7.44 (d, $J = 8.8$ Hz, 2H), 7.31-7.21 (m, 11H), 6.94 (ddd, $J = 15.6, 9.2, 2.0$ Hz, 1H), 6.64 (d, $J = 8.8$ Hz, 2H), 4.23 (qd, $J = 6.4, 3.6$ Hz, 2H), 3.20-3.06 (m, 2H), 2.98 (s, 6H), 1.21 (dd, $J = 7.2$ Hz, 6H), 1.05 (d, $J = 6.8$ Hz, 3H), 0.88 (d, $J = 6.8$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 175.4 (d, $J = 6.9$ Hz), 151.9, 150.2, 141.8 (d, $J = 5.6$ Hz), 140.8 (d, $J = 6.4$ Hz), 130.0, 128.5, 128.4, 127.9, 127.8, 127.7 (d, $J = 0.9$ Hz), 124.4, 124.0, 123.0 (d, $J = 1.2$ Hz), 111.9, 67.7 (d, $J = 11.0$ Hz), 67.2 (d, $J = 11.0$ Hz), 46.7 (d, $J = 4.8$ Hz), 45.9 (d, $J = 4.4$ Hz), 40.2, 21.2 (d, $J = 1.8$ Hz), 21.1 (d, $J = 1.2$ Hz), 21.0 (d, $J = 2.8$ Hz), 20.8 (d, $J = 1.6$ Hz); ^{31}P NMR (162 MHz, CDCl_3) δ 24.7; HRMS-(ESI) m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{31}\text{H}_{40}\text{N}_4\text{OP}$, 515.2940; found, 515.2934.

3i. pale yellow solid: mp 74-75 °C, $[\alpha]_{\text{D}}^{25} = -45.3$ ($c = 1.65$, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ 9.07 (dd, $J = 33.6, 9.2$ Hz, 1H), 7.98 (s, 1H), 7.89-7.83 (m, 3H), 7.77 (dd, $J = 8.8, 1.6$ Hz, 1H), 7.54-7.50 (m, 3H), 7.34-7.24 (m, 11H), 4.27 (qd, $J = 6.0, 3.6$ Hz, 2H), 3.25-3.09 (m, 2H), 1.24 (dd, $J = 8.8, 6.8$ Hz, 6H), 1.09 (d, $J = 6.4$ Hz, 3H), 0.91 (d, $J = 6.8$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 174.7 (d, $J = 7.2$ Hz), 148.9, 141.9 (d, $J = 5.3$ Hz), 140.8 (d, $J = 6.3$ Hz), 134.3, 133.5, 132.7 (d, $J = 1.4$ Hz), 129.9, 129.6, 129.3, 128.9, 128.7, 128.6, 128.5, 128.0, 127.9, 127.8 (d, $J = 1.5$ Hz), 127.7, 127.4, 126.9, 123.7, 67.7 (d, $J = 11.2$ Hz), 67.1 (d, $J = 11.3$ Hz), 46.8 (d, $J = 5.0$ Hz), 45.9 (d, $J = 4.5$ Hz), 21.2 (d, $J = 1.8$ Hz), 21.1 (d, $J = 1.3$ Hz), 20.9 (d, $J = 1.7$ Hz); ^{31}P NMR (162 MHz, CDCl_3) δ 24.0; HRMS-(ESI) m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{33}\text{H}_{37}\text{N}_3\text{OP}$, 522.2674; found, 522.2683.

3j. brown solid: mp 64-65 °C, $[\alpha]_{\text{D}}^{25} = -52.6$ ($c = 1.40$, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ 8.91 (dd, $J = 33.2, 9.2$ Hz, 1H), 7.51 (d, $J = 1.6$ Hz, 1H), 7.31-7.22 (m, 10H), 7.11 (d, $J = 15.6$ Hz, 1H), 6.98 (ddd, $J = 11.2, 8.8, 2.0$ Hz, 1H), 6.65 (d, $J = 3.2$

Hz, 1H), 6.47 (dd, $J = 3.2, 1.6$ Hz, 1H), 4.22 (qd, $J = 6.0, 4.0$ Hz, 2H), 3.20-3.04 (m, 2H), 1.19 (dd, $J = 8.8, 7.2$ Hz, 6H), 1.04 (d, $J = 6.4$ Hz, 3H), 0.86 (d, $J = 6.8$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 152.6, 144.0 (d, $J = 5.4$ Hz), 143.0 (d, $J = 2.8$ Hz), 141.9, 134.1, 131.4 (d, $J = 3.8$ Hz), 128.6 (d, $J = 4.6$ Hz), 127.7, 127.6, 127.5, 126.7, 118.6, 118.4, 111.3, 107.7, 66.3 (d, $J = 15.1$ Hz), 65.1 (d, $J = 12.8$ Hz), 53.3, 46.1 (d, $J = 4.7$ Hz), 45.1 (d, $J = 5.6$ Hz), 22.9 (d, $J = 1.6$ Hz), 22.3 (d, $J = 5.2$ Hz), 20.8, 20.6 (d, $J = 3.1$ Hz); ^{31}P NMR (162 MHz, CDCl_3) δ 24.0; HRMS-(ESI) m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{27}\text{H}_{33}\text{N}_3\text{O}_2\text{P}$, 462.2310; found, 462.2207.

3k. pale yellow solid: mp 67-69 °C, $[\alpha]_{\text{D}}^{25} = -26.8$ ($c = 0.64$, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ 8.94 (dd, $J = 33.6, 9.2$ Hz, 1H), 7.70 (s, 1H), 7.47-7.46 (m, 1H), 7.31-7.24 (m, 12H), 6.83 (ddd, $J = 11.2, 8.8, 2.0$ Hz, 1H), 6.69 (d, $J = 1.6$, 1H), 4.24 (qd, $J = 6.4, 3.6$ Hz, 2H), 3.23-3.04 (m, 2H), 1.21 (dd, $J = 8.8, 7.2$ Hz, 6H), 1.06 (d, $J = 6.8$ Hz, 3H), 0.88 (d, $J = 6.4$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 174.6 (d, $J = 7.2$ Hz), 144.7, 144.4, 141.8 (d, $J = 5.4$ Hz), 140.7 (d, $J = 6.4$ Hz), 138.5, 129.4, 129.1, 128.6, 128.5, 128.0, 127.8 (d, $J = 1.1$ Hz), 127.6, 123.7 (d, $J = 1.4$ Hz), 107.6, 67.7 (d, $J = 11.1$ Hz), 67.1 (d, $J = 11.4$ Hz), 46.7 (d, $J = 5.0$ Hz), 45.9 (d, $J = 4.6$ Hz), 21.2 (d, $J = 1.9$ Hz), 21.1 (d, $J = 2.1$ Hz), 20.9 (d, $J = 1.8$ Hz); ^{31}P NMR (162 MHz, CDCl_3) δ 24.1; HRMS-(ESI) m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{27}\text{H}_{33}\text{N}_3\text{O}_2\text{P}$, 462.2310; found, 462.2318

3. General procedure for nucleophilic addition of α,β -unsaturated imines

Into a reaction vial under argon, allylmagnesium bromide (0.5 mmol) was taken followed by THF (4.0 mL). Reaction mixture was then cooled to -78 °C using dry ice-acetone bath for 5 min. At the same time, α,β -unsaturated imines (0.2 mmol, dissolved in 4.0 mL of THF) properly sealed with a rubber septum in dry argon atmosphere, was cooled to -78 °C in the same dry ice-acetone bath for 5 min. Then the imines were added dropwise *via* a cannula at -78 °C and stirring was continued for 36 h at the same temperature. After confirming the consumption of imine, the reaction mixture was quenched with saturated Ammonium chloride (4.0 mL) and the organic layer was extracted with ethyl acetate. The organic layers were dried over anhydrous Na_2SO_4 , filtered and concentrated under reduced pressure. The crude product was

purified using flash column chromatography on silica gel using EtOAc/Hexanes (1:2, v/v) as the eluent to afford adduct **5**.

5a. colorless oil: $[\alpha]_D^{25} = -16.2$ ($c = 1.89$, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ 7.44-7.18 (m, 15H), 6.70 (d, $J = 16.0$ Hz, 1H), 6.32 (dd, $J = 16.0, 6.4$ Hz, 1H), 5.96-5.86 (m, 1H), 5.21-5.16 (m, 2H), 4.31-4.13 (m, 3H), 3.56-3.45 (m, 2H), 2.69-2.49 (m, 3H), 1.21 (d, $J = 6.4$ Hz, 3H), 1.10 (d, $J = 6.4$ Hz, 3H), 0.84 (dd, $J = 6.4, 2.0$ Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 143.9 (d, $J = 5.5$ Hz), 143.0 (d, $J = 2.9$ Hz), 137.0, 134.2, 132.7 (d, $J = 3.7$ Hz), 129.8, 128.7, 128.6, 127.7 (d, $J = 6.6$ Hz), 127.6, 126.8, 126.4, 118.6, 66.3 (d, $J = 15.0$ Hz), 65.2 (d, $J = 12.8$ Hz), 53.6, 46.2 (d, $J = 4.7$ Hz), 45.1 (d, $J = 5.6$ Hz), 42.3 (d, $J = 5.6$ Hz), 23.0 (d, $J = 1.4$ Hz), 22.4 (d, $J = 5.0$ Hz), 20.8, 20.7 (d, $J = 3.1$ Hz); ^{31}P NMR (162 MHz, CDCl_3) δ 23.0; HRMS-(ESI) m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{32}\text{H}_{41}\text{N}_3\text{OP}$, 514.2987; found, 514.2998

5b. colorless oil: $[\alpha]_D^{25} = -11.4$ ($c = 0.88$, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ 7.43-7.20 (m, 14H), 6.61 (d, $J = 15.6$ Hz, 1H), 6.30 (dd, $J = 15.6, 6.4$ Hz, 1H), 5.93-5.82 (m, 1H), 5.20-5.16 (m, 2H), 4.29-4.10 (m, 3H), 3.52-3.45 (m, 2H), 2.62-2.47 (m, 3H), 1.17 (d, $J = 6.4$ Hz, 3H), 1.07 (d, $J = 6.8$ Hz, 3H), 0.81 (dd, $J = 8.8, 6.8$ Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 144.0 (d, $J = 5.3$ Hz), 143.0 (d, $J = 2.6$ Hz), 135.9, 134.1, 133.6 (d, $J = 3.5$ Hz), 131.8, 128.6 (d, $J = 4.0$ Hz), 127.9, 127.8, 127.7, 127.5, 126.7, 121.2, 118.7, 66.3 (d, $J = 15.0$ Hz), 65.1 (d, $J = 12.8$ Hz), 53.6, 46.1 (d, $J = 4.7$ Hz), 45.1 (d, $J = 5.7$ Hz), 42.1 (d, $J = 5.8$ Hz), 22.9 (d, $J = 1.5$ Hz), 22.4 (d, $J = 5.0$ Hz), 20.8, 20.7 (d, $J = 3.1$ Hz); ^{31}P NMR (162 MHz, CDCl_3) δ 22.8; HRMS-(ESI) m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{32}\text{H}_{40}\text{BrN}_3\text{OP}$, 592.2092; found, 592.2084.

5c. colorless oil: $[\alpha]_D^{25} = -5.9$ ($c = 0.88$, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ 7.61 (d, $J = 7.2$ Hz, 2H), 7.51 (d, $J = 7.2$ Hz, 2H), 7.36-7.25 (m, 11H), 6.83 (s, 1H), 5.89-5.78 (m, 1H), 5.21-5.10 (m, 2H), 4.50-4.42 (m, 1H), 4.16-4.09 (m, 2H), 3.53-3.44 (m, 2H), 2.83 (t, $J = 9.2$ Hz, 1H), 2.64-2.55 (m, 2H), 1.06 (dd, $J = 6.8, 2.8$ Hz, 6H), 0.83 (d, $J = 6.8$ Hz, 3H), 0.72 (d, $J = 6.8$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 144.4, 143.4, 136.6, 134.5, 134.1, 129.3, 128.6, 128.3, 128.0, 127.7, 127.5, 127.2, 126.4, 125.9, 118.2, 66.3 (d, $J = 15.8$ Hz), 64.7 (d, $J = 13.3$ Hz), 59.7, 46.0,

45.3 (d, $J = 5.4$ Hz), 40.0 (d, $J = 8.0$ Hz), 22.8, 22.6 (d, $J = 4.8$ Hz), 20.9; ^{31}P NMR (162 MHz, CDCl_3) δ 21.3; HRMS-(ESI) m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{32}\text{H}_{40}\text{ClN}_3\text{OP}$, 548.2598; found, 548.2611.

5d. colorless oil: $[\alpha]_{\text{D}}^{25} = -4.7$ ($c = 1.10$, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ 7.44 (d, $J = 7.2$ Hz, 2H), 7.33-7.23 (m, 12H), 7.19 (t, $J = 7.2$ Hz, 2H), 6.60 (s, 1H), 5.87-5.77 (m, 1H), 5.18-5.11 (m, 2H), 4.19-4.12 (m, 3H), 3.57-3.47 (m, 2H), 2.78 (t, $J = 10.0$ Hz, 1H), 2.66-2.45 (m, 2H), 1.94 (s, 3H), 1.21 (d, $J = 6.8$ Hz, 3H), 1.07 (d, $J = 6.8$ Hz, 3H), 0.83 (dd, $J = 12.4, 6.8$ Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 144.1 (d, $J = 5.3$ Hz), 143.1 (d, $J = 2.7$ Hz), 139.3 (d, $J = 2.7$ Hz), 137.9, 134.5, 129.0, 128.6 (d, $J = 4.1$ Hz), 128.2, 127.7, 127.6, 127.5, 126.7, 126.4 (d, $J = 5.3$ Hz), 117.9, 66.3 (d, $J = 15.1$ Hz), 65.1 (d, $J = 12.8$ Hz), 59.1, 46.1 (d, $J = 4.7$ Hz), 45.1 (d, $J = 5.7$ Hz), 40.2 (d, $J = 6.2$ Hz), 23.0 (d, $J = 1.3$ Hz), 22.6 (d, $J = 5.3$ Hz), 20.8, 20.6 (d, $J = 3.3$ Hz), 14.8; ^{31}P NMR (162 MHz, CDCl_3) δ 23.0; HRMS-(ESI) m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{33}\text{H}_{43}\text{N}_3\text{OP}$, 528.3144; found, 528.3153.

5e. colorless oil: $[\alpha]_{\text{D}}^{25} = -4.3$ ($c = 1.12$, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ 7.41 (s, 2H), 7.33-7.25 (m, 10H), 7.11 (dd, $J = 7.6, 2.4$ Hz, 2H), 6.65 (dd, $J = 16.0, 2.4$ Hz, 1H), 6.25 (dq, $J = 6.0, 3.2$ Hz, 1H), 5.94-5.84 (m, 1H), 5.20-5.15 (m, 2H), 4.24-4.11 (m, 3H), 3.53-3.48 (m, 2H), 2.64-2.51 (m, 3H), 2.31 (d, $J = 3.2$ Hz, 3H), 1.20 (dd, $J = 6.4, 3.2$ Hz, 3H), 1.08 (dd, $J = 6.4, 3.2$ Hz, 3H), 0.83 (dd, $J = 6.8, 3.2$ Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 143.9 (d, $J = 5.7$ Hz), 143.0 (d, $J = 2.7$ Hz), 137.3, 134.3 (d, $J = 8.4$ Hz), 131.6 (d, $J = 3.8$ Hz), 129.6, 129.4, 128.6 (d, $J = 5.1$ Hz), 127.7 (d, $J = 7.4$ Hz), 127.6, 126.8, 126.3, 118.5, 66.3 (d, $J = 14.9$ Hz), 65.2 (d, $J = 12.9$ Hz), 53.6, 46.2 (d, $J = 4.6$ Hz), 45.1 (d, $J = 5.7$ Hz), 42.4 (d, $J = 5.6$ Hz), 23.0, 22.4 (d, $J = 5.1$ Hz), 21.3, 20.8, 20.6 (d, $J = 3.0$ Hz); ^{31}P NMR (162 MHz, CDCl_3) δ 23.1; HRMS-(ESI) m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{33}\text{H}_{43}\text{N}_3\text{OP}$, 528.3144; found, 528.3148.

5f. colorless oil: $[\alpha]_{\text{D}}^{25} = -15.2$ ($c = 0.98$, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ 7.43 (dd, $J = 7.6, 5.2$ Hz, 2H), 7.33-7.17 (m, 9H), 7.04 (d, $J = 16.0$ Hz, 2H), 6.90 (t, $J = 7.6$ Hz, 1H), 6.84 (d, $J = 8.4$ Hz, 1H), 6.31 (dd, $J = 16.0, 6.0$ Hz, 1H), 5.97-5.86 (m, 1H), 5.20-5.15 (m, 2H), 4.31-4.24 (m, 1H), 4.19 (t, $J = 4.8$ Hz, 1H), 4.15 (dd, $J = 10.0, 4.8$ Hz, 1H), 3.78 (s, 3H), 3.57-3.46 (m, 2H), 2.68-2.48 (m, 3H), 1.22 (d, $J = 6.8$

Hz, 3H), 1.06 (d, $J = 6.8$ Hz, 3H), 0.84 (dd, $J = 6.4$ Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 156.7, 143.9 (d, $J = 5.7$ Hz), 143.1 (d, $J = 3.1$ Hz), 134.4, 133.2 (d, $J = 4.0$ Hz), 128.6, 128.5, 127.7, 127.6, 126.9, 126.7, 126.1, 124.4, 120.7, 118.4, 110.8, 66.3 (d, $J = 15.0$ Hz), 65.3 (d, $J = 12.8$ Hz), 55.4, 53.8, 46.2 (d, $J = 4.6$ Hz), 45.1 (d, $J = 5.7$ Hz), 42.5 (d, $J = 5.3$ Hz), 23.1 (d, $J = 1.4$ Hz), 22.2 (d, $J = 5.3$ Hz), 20.8, 20.6 (d, $J = 3.2$ Hz); ^{31}P NMR (162 MHz, CDCl_3) δ 23.2; HRMS-(ESI) m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{33}\text{H}_{43}\text{N}_3\text{O}_2\text{P}$, 544.3093; found, 544.3090.

5g. colorless oil: $[\alpha]_{\text{D}}^{25} = -13.8$ ($c = 1.33$, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ 7.41 (d, $J = 6.8$ Hz, 2H), 7.33-7.25 (m, 11H), 6.85-6.82 (m, 2H), 6.61 (d, $J = 16.0$ Hz, 1H), 6.16 (dd, $J = 15.6$, 6.4 Hz, 1H), 5.93-5.84 (m, 1H), 5.20-5.15 (m, 2H), 4.23-4.10 (m, 3H), 3.78 (s, 3H), 3.53-3.47 (m, 2H), 2.63-2.46 (m, 3H), 1.20 (d, $J = 6.8$ Hz, 3H), 1.08 (d, $J = 6.8$ Hz, 3H), 0.82 (dd, $J = 6.8$, 2.8 Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 159.2, 143.9 (d, $J = 5.7$ Hz), 143.0 (d, $J = 2.7$ Hz), 134.4, 130.5 (d, $J = 3.6$ Hz), 129.8, 129.2, 128.6 (d, $J = 4.6$ Hz), 127.7, 127.6, 127.5, 126.8, 118.4, 114.1, 66.3 (d, $J = 14.9$ Hz), 65.2 (d, $J = 12.8$ Hz), 55.4, 53.6, 46.1 (d, $J = 4.4$ Hz), 45.1 (d, $J = 5.6$ Hz), 42.4 (d, $J = 5.5$ Hz), 23.0, 22.4 (d, $J = 5.1$ Hz), 20.8, 20.6 (d, $J = 3.0$ Hz); ^{31}P NMR (162 MHz, CDCl_3) δ 23.1; HRMS-(ESI) m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{33}\text{H}_{43}\text{N}_3\text{O}_2\text{P}$, 544.3093; found, 544.3071.

5h. pale yellow oil: $[\alpha]_{\text{D}}^{25} = -29.0$ ($c = 0.92$, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ 7.41 (d, $J = 6.8$ Hz, 2H), 7.34-7.25 (m, 10H), 6.67-6.65 (m, 2H), 6.58 (d, $J = 16.0$ Hz, 1H), 6.09 (dd, $J = 15.6$, 6.4 Hz, 1H), 5.96-5.85 (m, 1H), 5.19-5.13 (m, 2H), 4.24-4.10 (m, 3H), 3.55-3.46 (m, 2H), 2.93 (s, 6H), 2.64-2.48 (m, 3H), 1.22 (d, $J = 6.8$ Hz, 3H), 1.08 (d, $J = 6.8$ Hz, 3H), 0.84 (dd, $J = 6.8$, 2.8 Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 150.1, 143.9 (d, $J = 5.8$ Hz), 143.1 (d, $J = 3.2$ Hz), 134.6, 129.6, 128.6, 128.5, 128.2 (d, $J = 4.0$ Hz), 127.7, 127.6, 127.3, 126.9, 125.5, 118.2, 112.5, 66.3 (d, $J = 14.8$ Hz), 65.3 (d, $J = 12.7$ Hz), 53.7, 46.2 (d, $J = 5.4$ Hz), 45.1 (d, $J = 5.7$ Hz), 40.6, 23.0 (d, $J = 1.4$ Hz), 22.4 (d, $J = 5.2$ Hz), 20.8, 20.6 (d, $J = 3.2$ Hz); ^{31}P NMR (162 MHz, CDCl_3) δ 23.2; HRMS-(ESI) m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{33}\text{H}_{43}\text{N}_3\text{O}_2\text{P}$, 557.3409; found, 557.3403.

5i. colorless oil: $[\alpha]_{\text{D}}^{25} = -29.0$ ($c = 0.92$, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ

7.78 (dd, $J = 7.6, 2.0$ Hz, 3H), 7.72 (s, 1H), 7.60 (dd, $J = 8.4, 1.6$ Hz, 1H), 7.46-7.24 (m, 12H), 6.86 (d, $J = 16.0$ Hz, 1H), 6.45 (dd, $J = 16.0, 6.4$ Hz, 1H), 6.00-5.89 (m, 1H), 5.24-5.19 (m, 2H), 4.37-4.14 (m, 3H), 3.59-3.46 (m, 2H), 2.71-2.53 (m, 3H), 1.21 (d, $J = 6.8$ Hz, 3H), 1.11 (d, $J = 6.8$ Hz, 3H), 0.85 (dd, $J = 6.4, 3.2$ Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 144.0 (d, $J = 5.5$ Hz), 143.0 (d, $J = 2.9$ Hz), 134.4, 134.3, 133.7, 133.1 (d, $J = 3.7$ Hz), 133.0, 129.9, 128.6 (d, $J = 6.3$ Hz), 128.3, 128.0, 127.8, 127.7, 127.6, 126.8, 126.4, 126.3, 125.9, 123.6, 118.6, 66.3 (d, $J = 15.0$ Hz), 65.2 (d, $J = 12.7$ Hz), 53.7, 46.2 (d, $J = 4.7$ Hz), 45.2 (d, $J = 5.7$ Hz), 42.3 (d, $J = 5.9$ Hz), 23.0 (d, $J = 1.4$ Hz), 22.4 (d, $J = 5.2$ Hz), 20.8, 20.7 (d, $J = 3.1$ Hz); ^{31}P NMR (162 MHz, CDCl_3) δ 23.0; HRMS-(ESI) m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{36}\text{H}_{43}\text{N}_3\text{OP}$, 564.3144; found, 564.3145.

5j. pale yellow oil: $[\alpha]_{\text{D}}^{25} = -4.0$ ($c = 1.24$, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ 7.42 (d, $J = 7.2$ Hz, 1H), 7.34-7.23 (m, 9H), 6.50 (dd, $J = 16.0, 1.6$ Hz, 1H), 6.33 (dd, $J = 3.2, 1.6$ Hz, 1H), 6.26 (dd, $J = 16.0, 6.4$ Hz, 1H), 6.18 (d, $J = 3.2$ Hz, 1H), 5.93-5.83 (m, 1H), 5.19-5.15 (m, 2H), 4.24-4.09 (m, 3H), 3.54-3.44 (m, 2H), 2.63-2.45 (m, 3H), 1.17 (d, $J = 6.8$ Hz, 3H), 1.07 (d, $J = 6.8$ Hz, 3H), 0.81 (dd, $J = 6.8$ Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 152.6, 144.0 (d, $J = 5.4$ Hz), 143.0 (d, $J = 2.8$ Hz), 141.9, 134.1, 131.4 (d, $J = 3.8$ Hz), 128.6 (d, $J = 4.6$ Hz), 127.7, 127.6, 127.5, 126.7, 118.6, 118.4, 111.3, 107.7, 66.3 (d, $J = 15.1$ Hz), 65.1 (d, $J = 12.8$ Hz), 53.3, 46.1 (d, $J = 4.7$ Hz), 45.1 (d, $J = 5.6$ Hz), 42.1 (d, $J = 4.7$ Hz), 22.9 (d, $J = 1.6$ Hz), 22.3 (d, $J = 5.2$ Hz), 20.8, 20.6 (d, $J = 3.1$ Hz); ^{31}P NMR (162 MHz, CDCl_3) δ 23.0; HRMS-(ESI) m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{36}\text{H}_{43}\text{N}_3\text{OP}$, 504.2780; found, 504.2782.

5k. pale yellow oil: $[\alpha]_{\text{D}}^{25} = -4.4$ ($c = 1.06$, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ 7.42-7.23 (m, 12H), 6.55-6.50 (m, 2H), 6.02 (dd, $J = 13.6, 6.4$ Hz, 1H), 5.93-5.82 (m, 1H), 5.19-5.15 (m, 2H), 4.20-4.09 (m, 3H), 3.53-3.44 (m, 2H), 2.53-2.44 (m, 3H), 1.18 (d, $J = 6.8$ Hz, 3H), 1.08 (d, $J = 6.8$ Hz, 3H), 0.82 (dd, $J = 6.8, 4.8$ Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 144.0 (d, $J = 5.6$ Hz), 143.6, 143.0 (d, $J = 2.9$ Hz), 140.4, 134.3, 132.3 (d, $J = 3.6$ Hz), 128.6 (d, $J = 2.7$ Hz), 127.7, 127.6, 127.5, 126.7, 123.8, 119.5, 118.5, 107.6, 66.3 (d, $J = 15.0$ Hz), 65.1 (d, $J = 12.7$ Hz), 53.5, 46.1 (d, $J = 4.8$ Hz), 45.1 (d, $J = 5.7$ Hz), 42.2 (d, $J = 5.9$ Hz), 22.9 (d, $J = 1.5$ Hz), 22.4 (d, $J = 5.2$

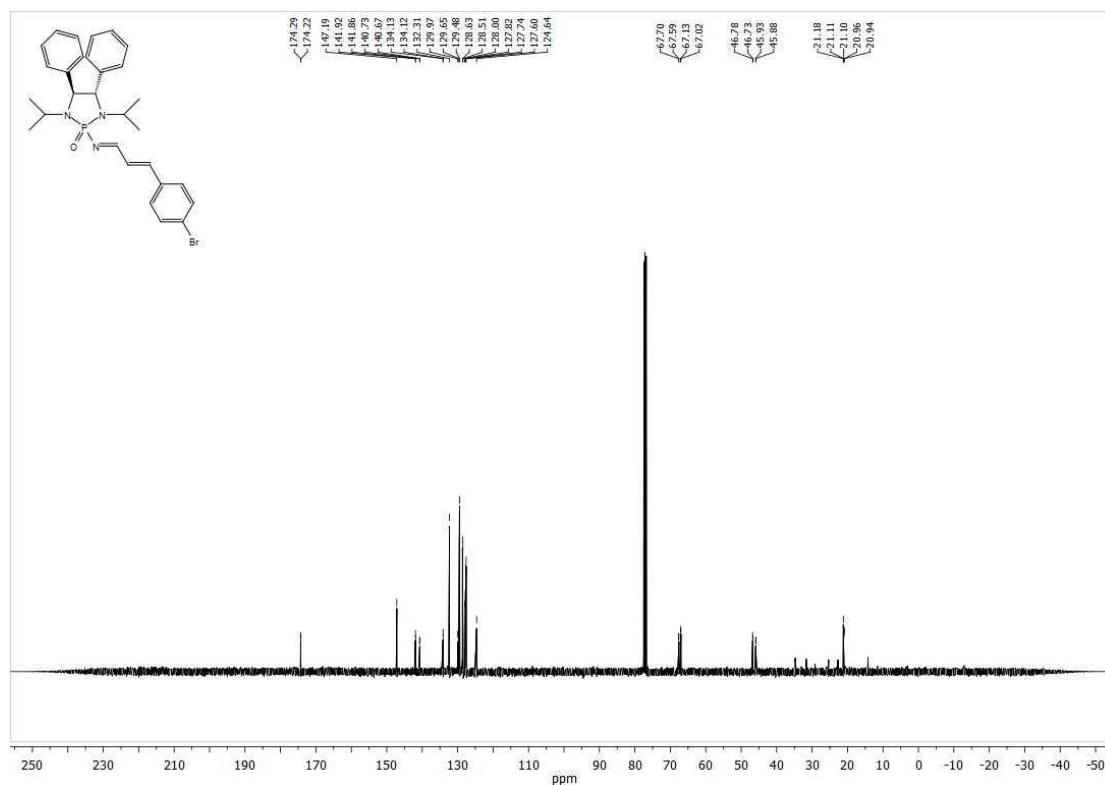
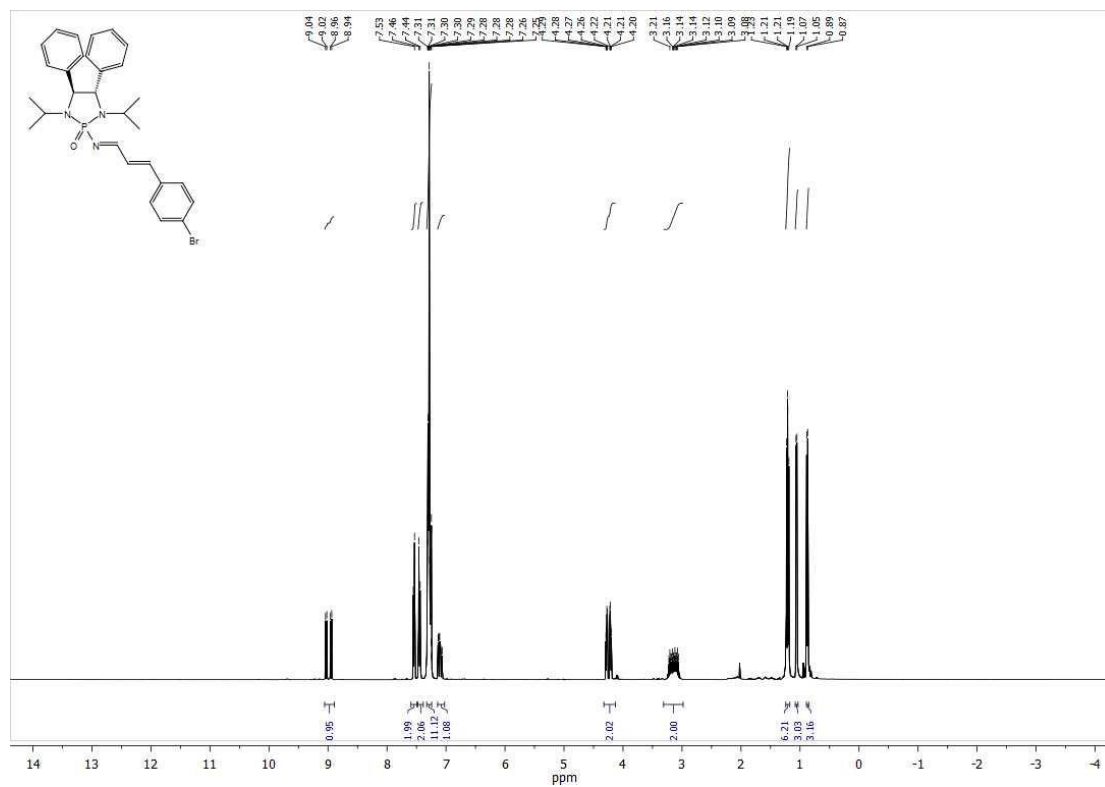
Hz), 20.7, 20.6 (d, $J = 3.0$ Hz); ^{31}P NMR (162 MHz, CDCl_3) δ 23.1; HRMS-(ESI) m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{30}\text{H}_{39}\text{N}_3\text{O}_2\text{P}$, 504.2780; found, 504.2777.

4. General procedure for cleavage of auxiliary

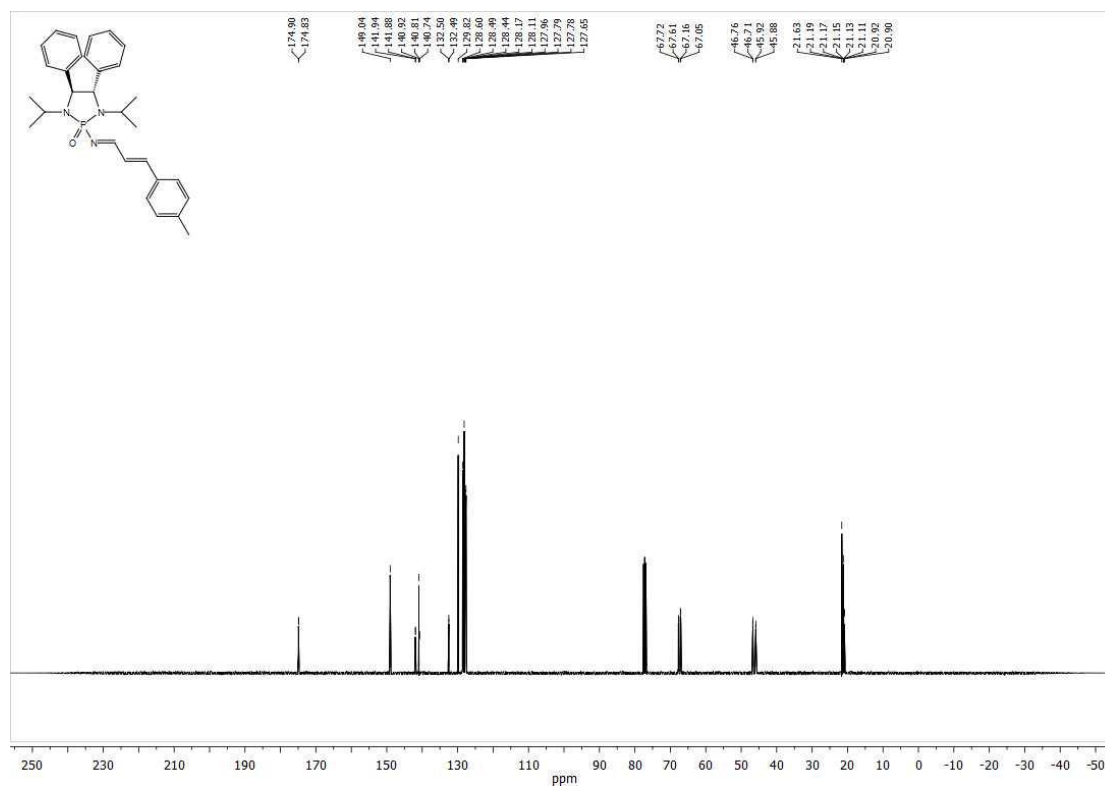
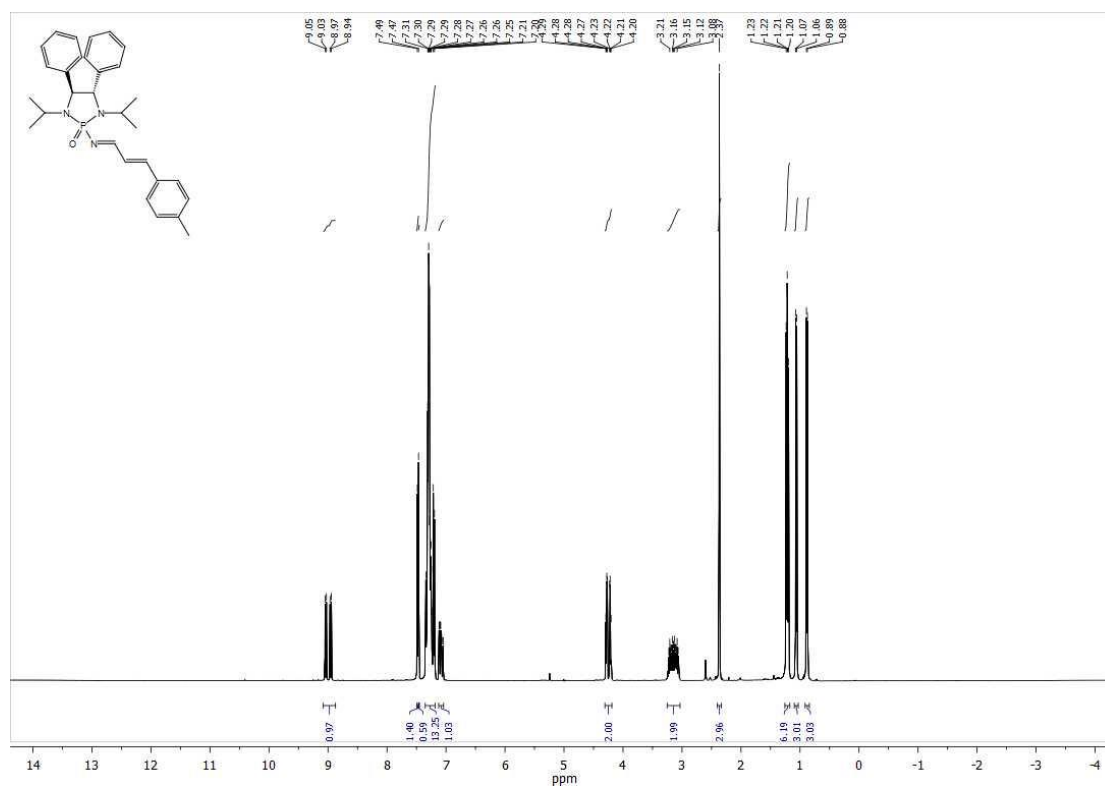
Compound **5a** (0.5 ml) was dissolved in methanol (4.0 mL), concentrated hydrochloric acid (4.0 mL) was added dropwise during 5min by syringe. When the auxiliary was confirmed to be completely cleaved by crude ^{31}P NMR (normally 4 days was needed), solvent was removed under vacuum. The residue was dissolved in DCM/water (10.0 mL/10.0 mL), The aqueous phase was washed by DCM (4×20.0 mL), and then evaporated under vacuum to give free amine as a white solid **6** with 53% isolated yield.

(S,E)-1-phenylhexa-1,5-dien-3-aminium chloride (6). White solid: ^1H NMR (400 MHz, DMSO) δ 8.55 (bs, 3H), 7.22-7.40 (m, 5H), 6.70 (d, $J = 15.6$ Hz, 1H), 6.22 (q, $J = 15.6$ Hz, 1H), 5.75-5.78 (m, 1H), 5.08-5.17 (m, 2H), 3.88 (dd, $J = 12.4, 8.0$ Hz, 1H), 2.60-2.63 (m, 1H), 2.47-2.50 (m, 1H); ^{13}C NMR (100 MHz, DMSO) δ 135.7, 133.4, 133.0, 128.8, 128.2, 126.2, 125.6, 118.8, 52.3, 37.2

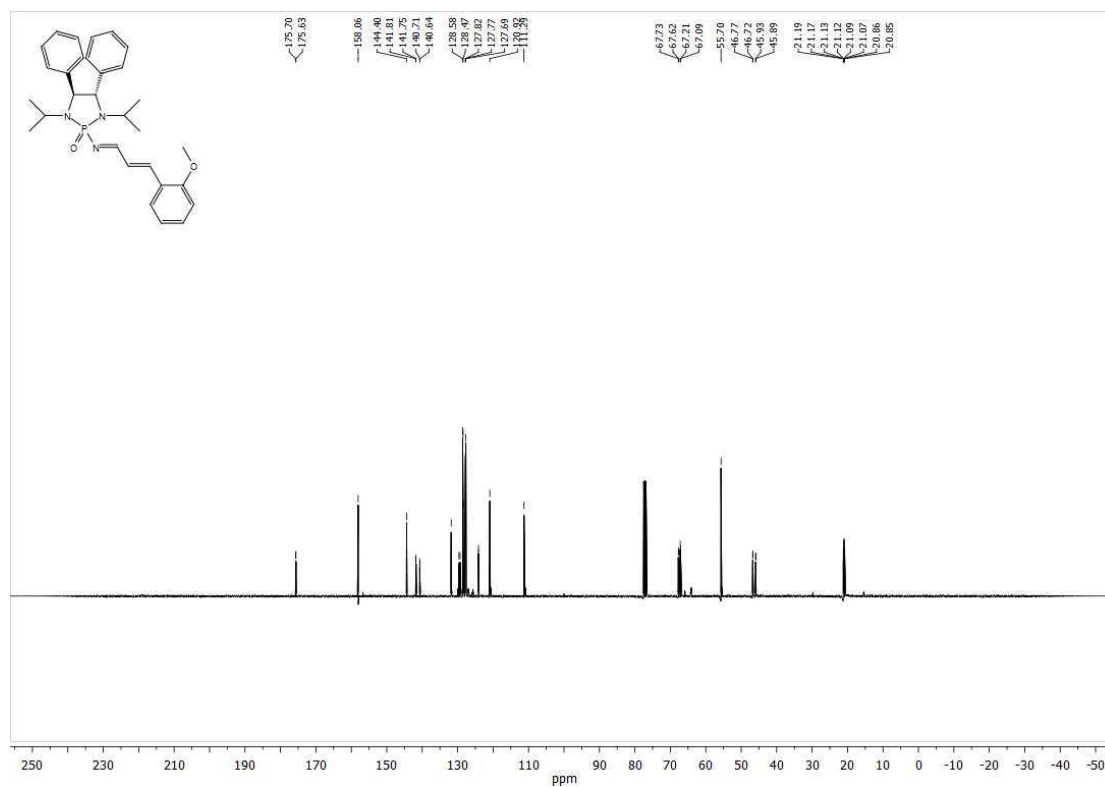
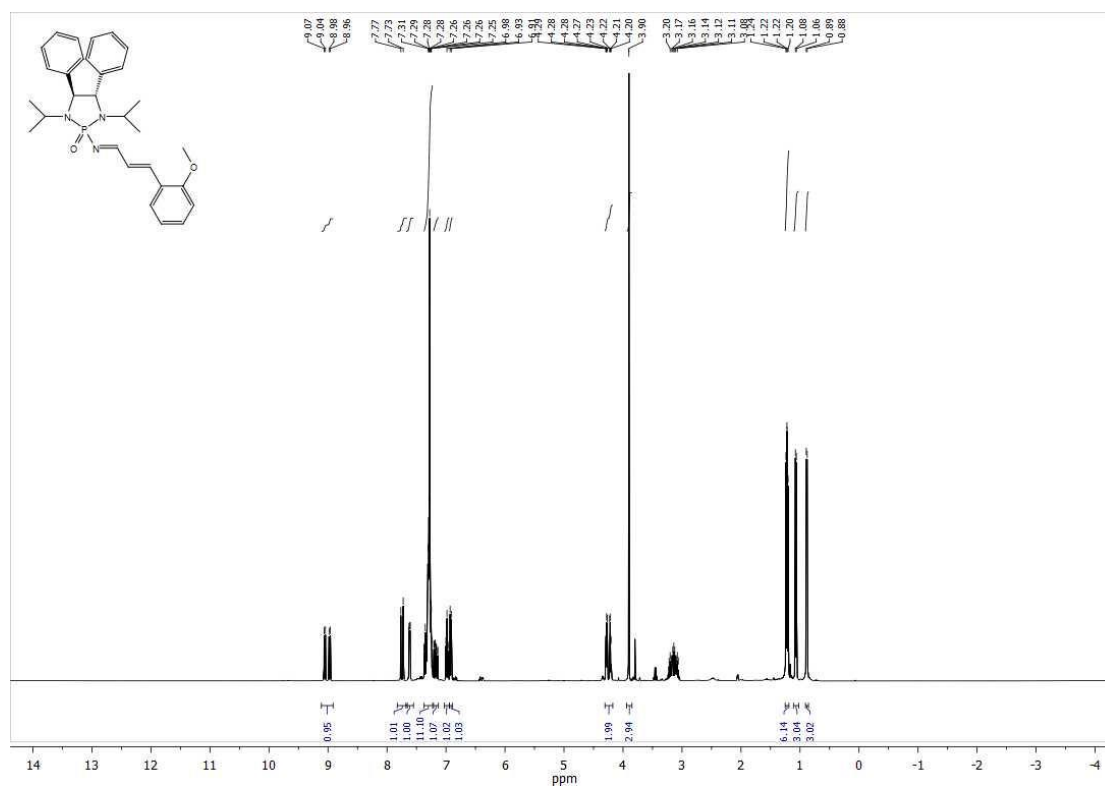
^1H NMR (400 MHz, CDCl_3) and ^{13}C NMR (100 MHz, CDCl_3) spectrum of 3b



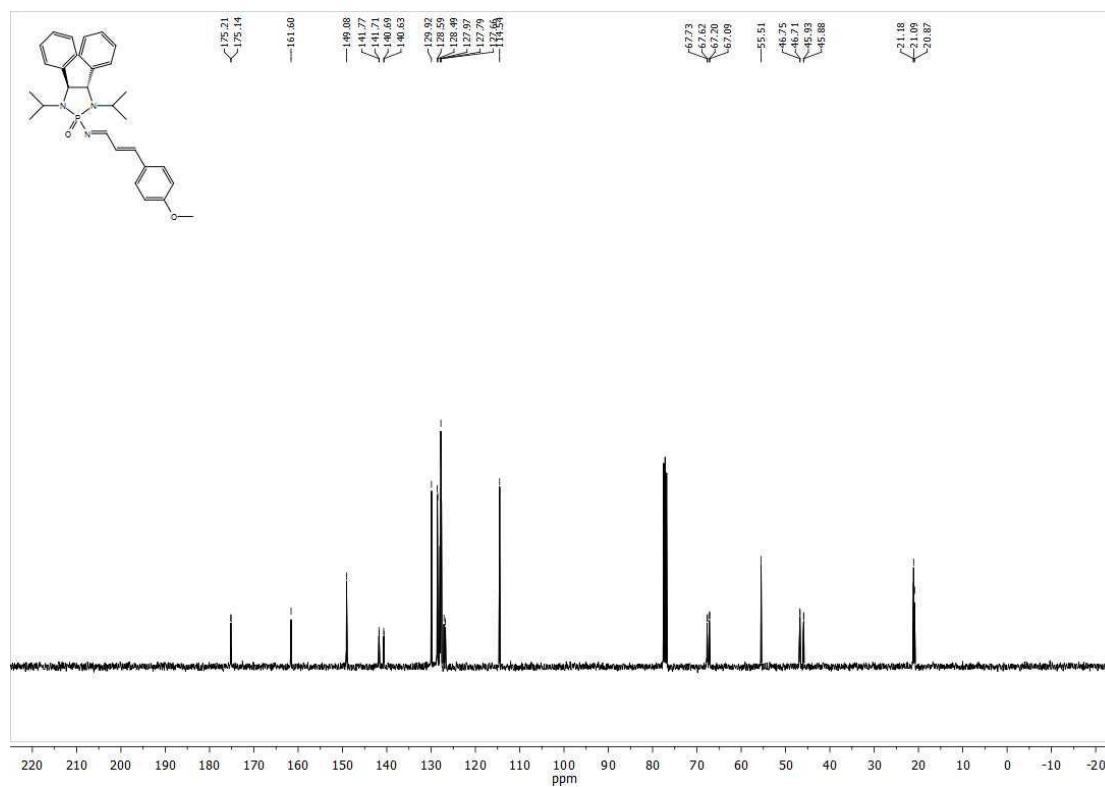
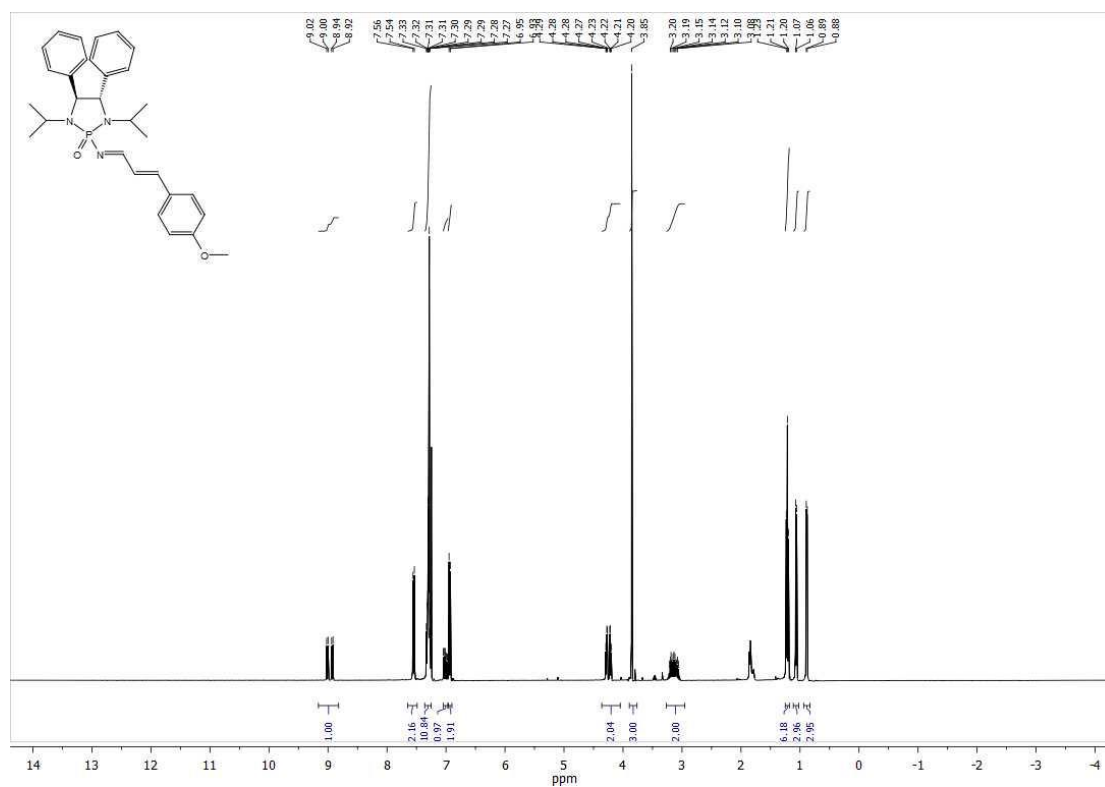
¹H NMR (400 MHz, CDCl₃) and ¹³C NMR (100 MHz, CDCl₃) spectrum of 3e



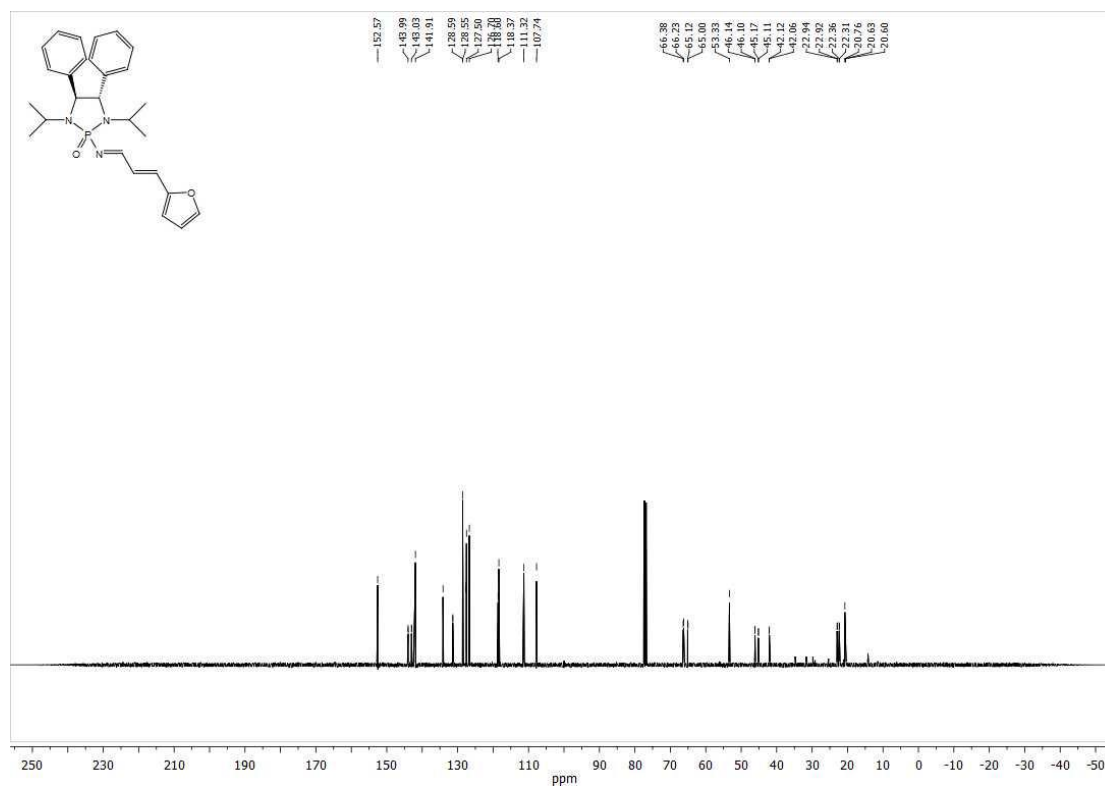
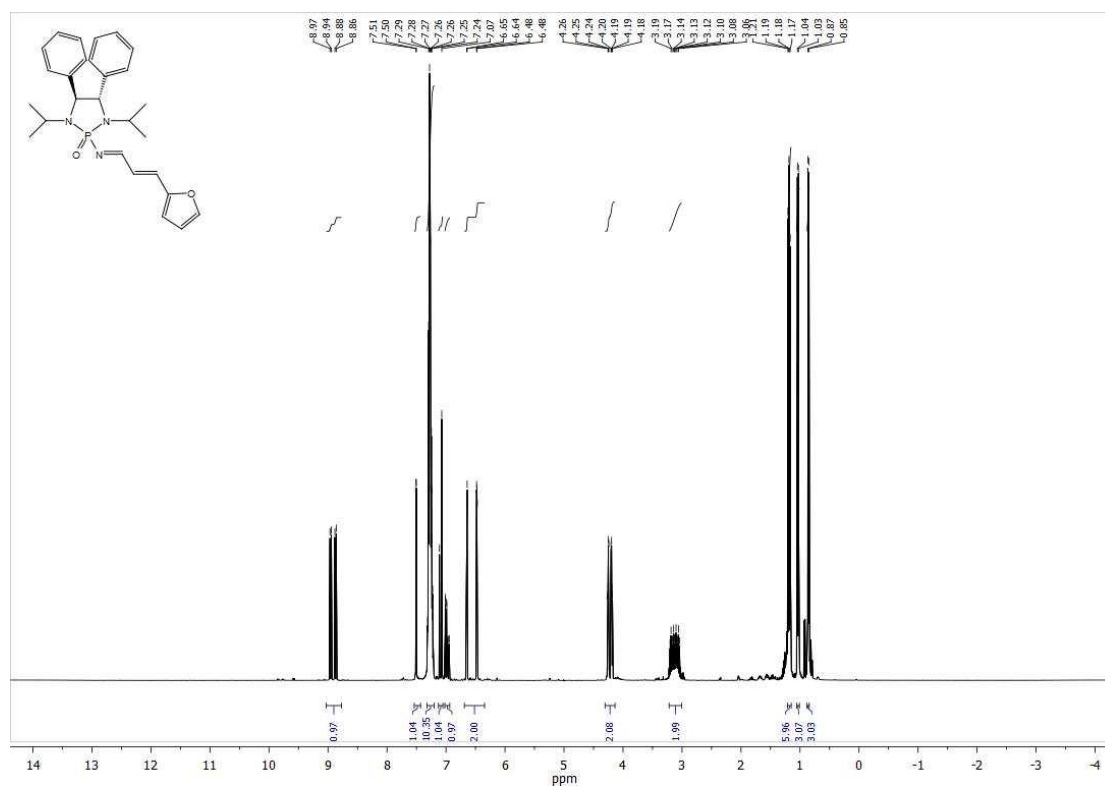
^1H NMR (400 MHz, CDCl_3) and ^{13}C NMR (100 MHz, CDCl_3) spectrum of 3f



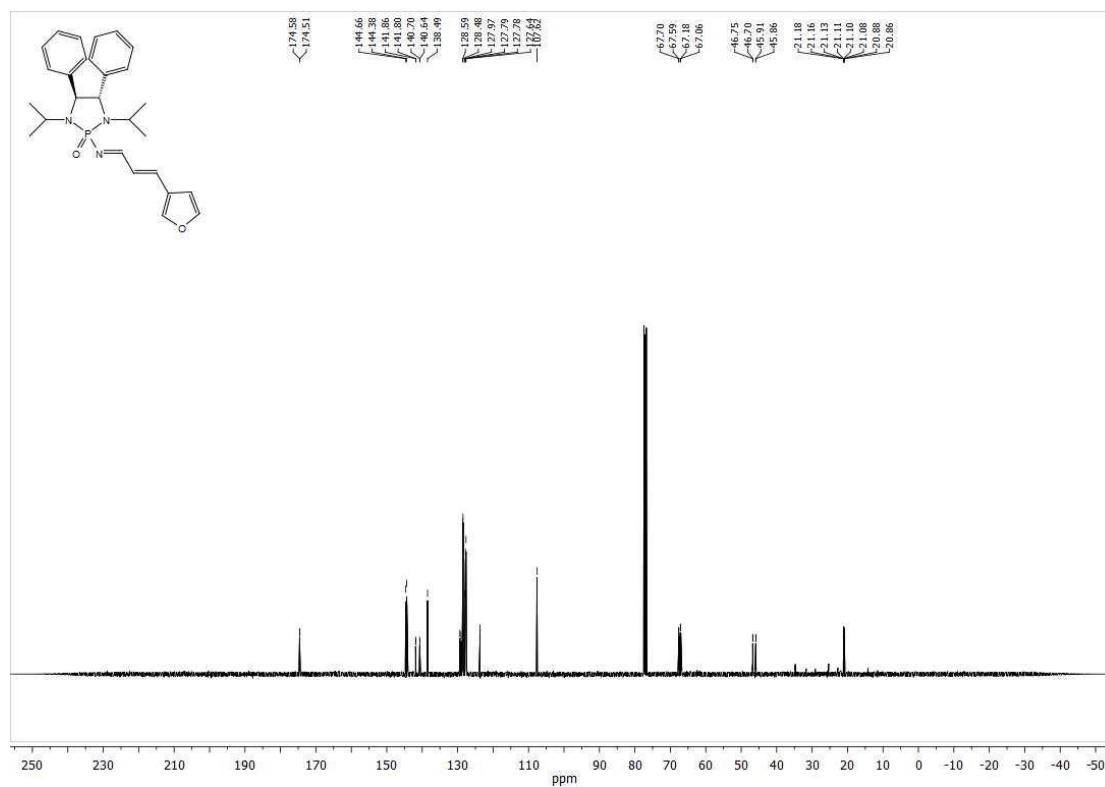
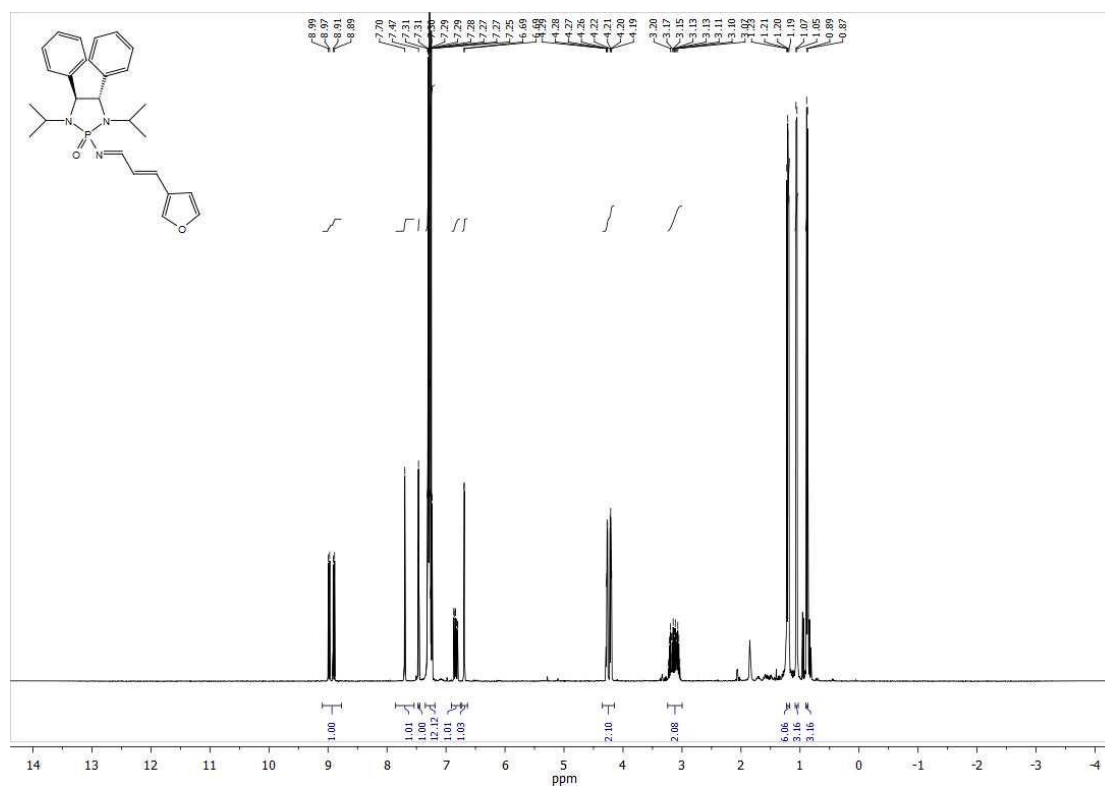
¹H NMR (400 MHz, CDCl₃) and ¹³C NMR (100 MHz, CDCl₃) spectrum of 3g



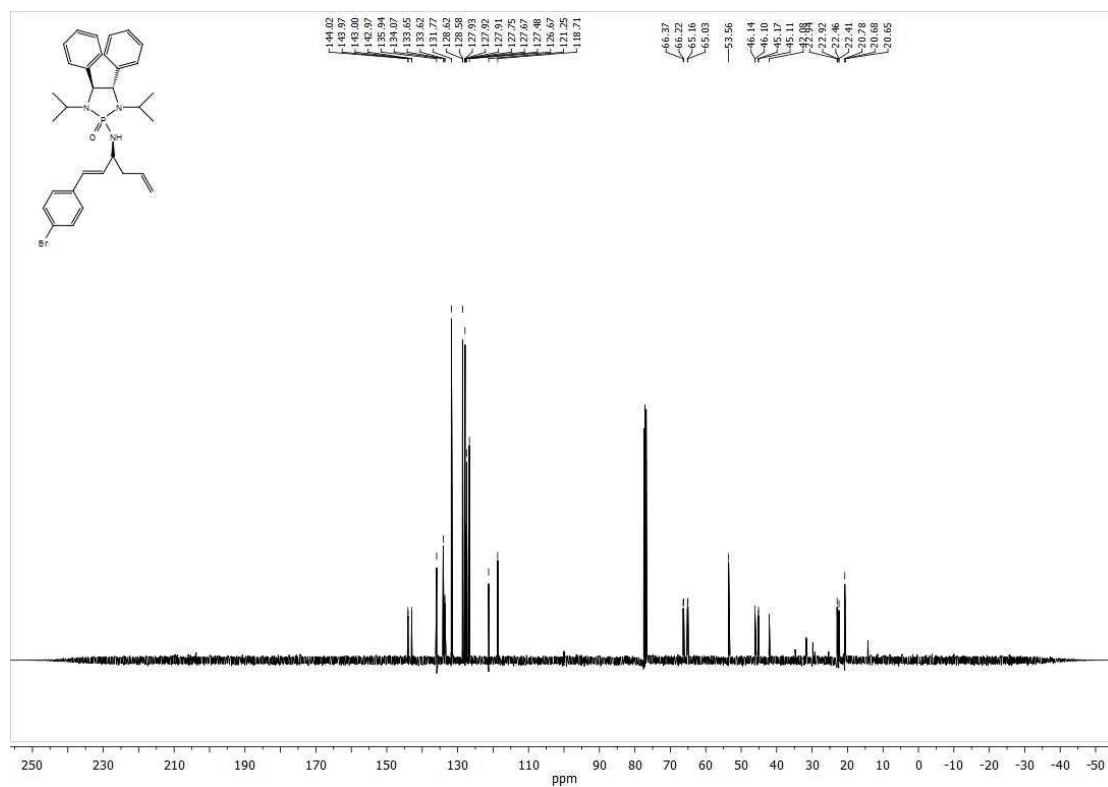
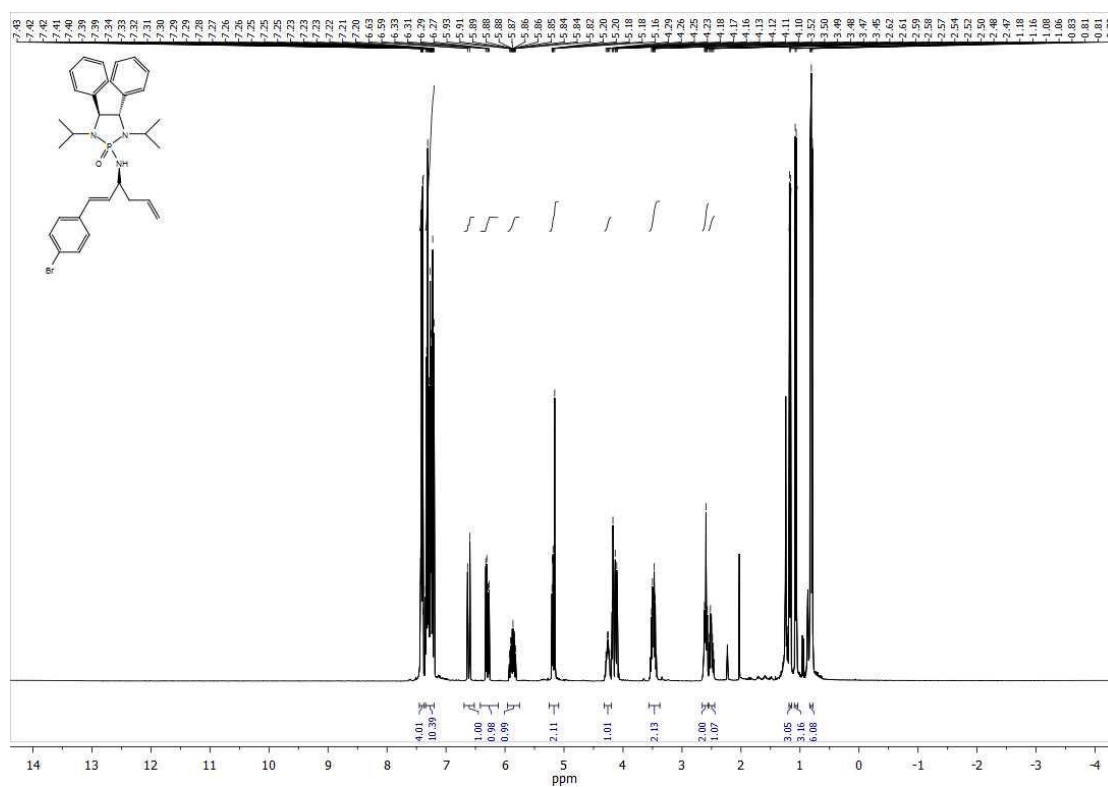
^1H NMR (400 MHz, CDCl_3) and ^{13}C NMR (100 MHz, CDCl_3) spectrum of 3j



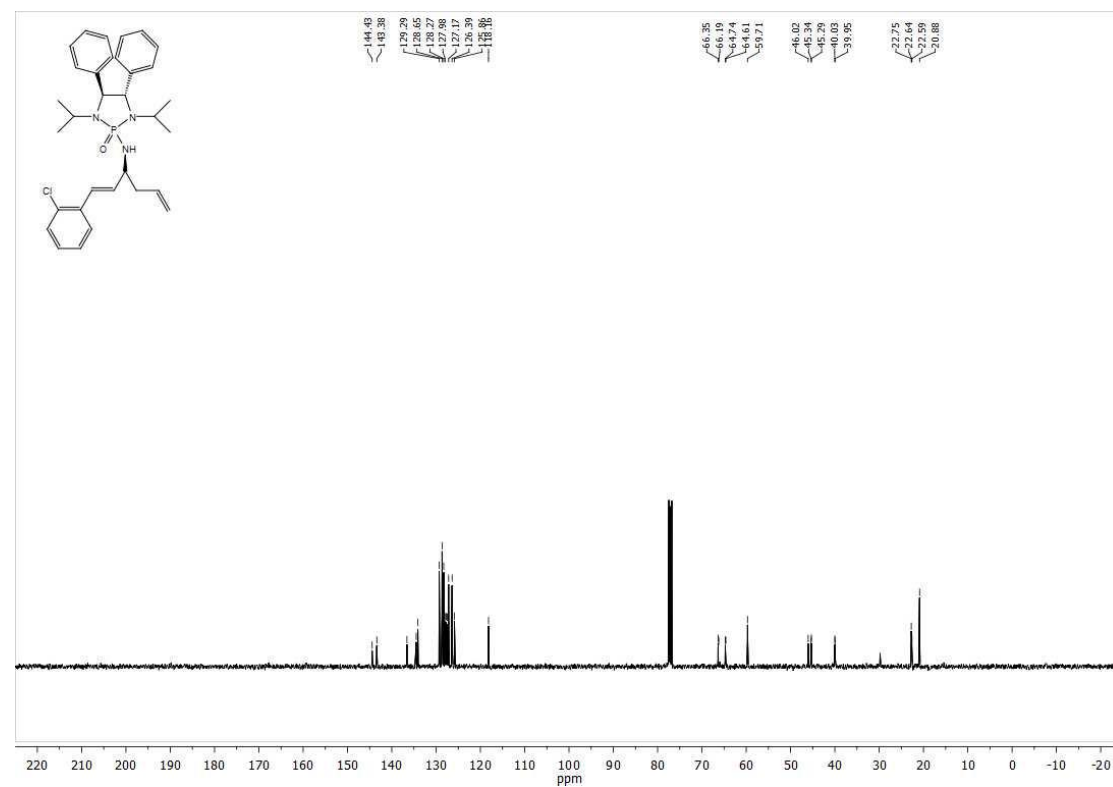
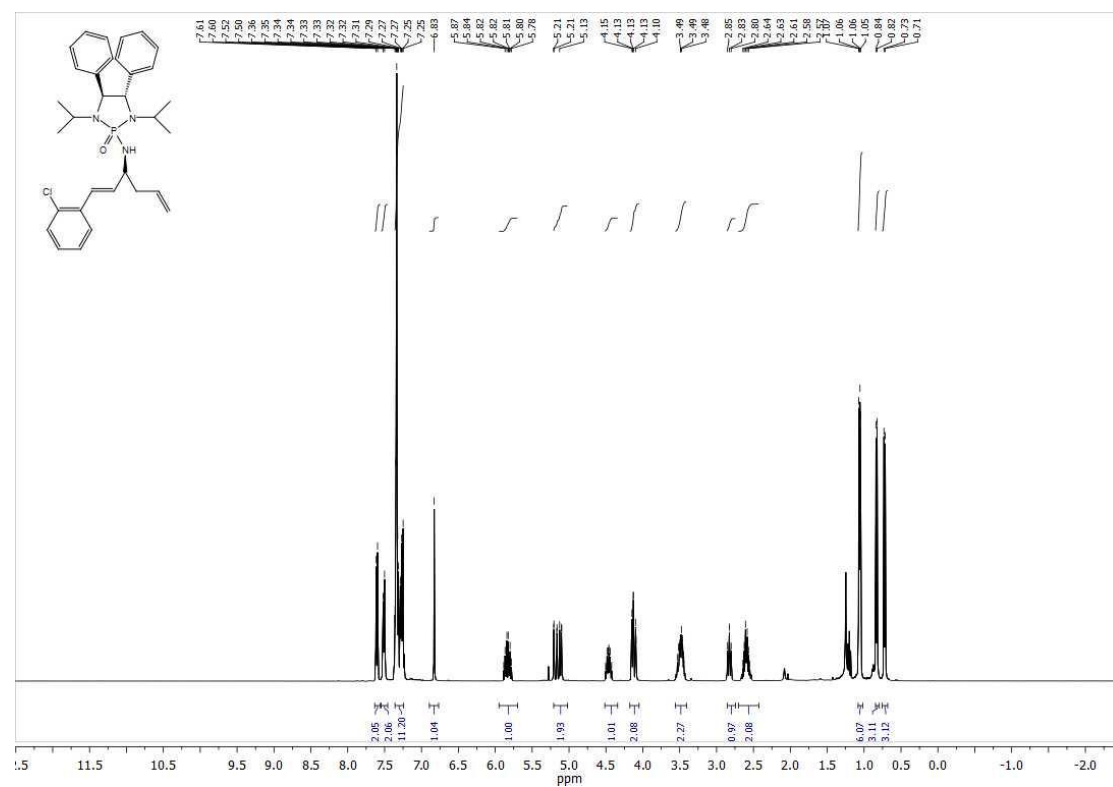
^1H NMR (400 MHz, CDCl_3) and ^{13}C NMR (100 MHz, CDCl_3) spectrum of 3k



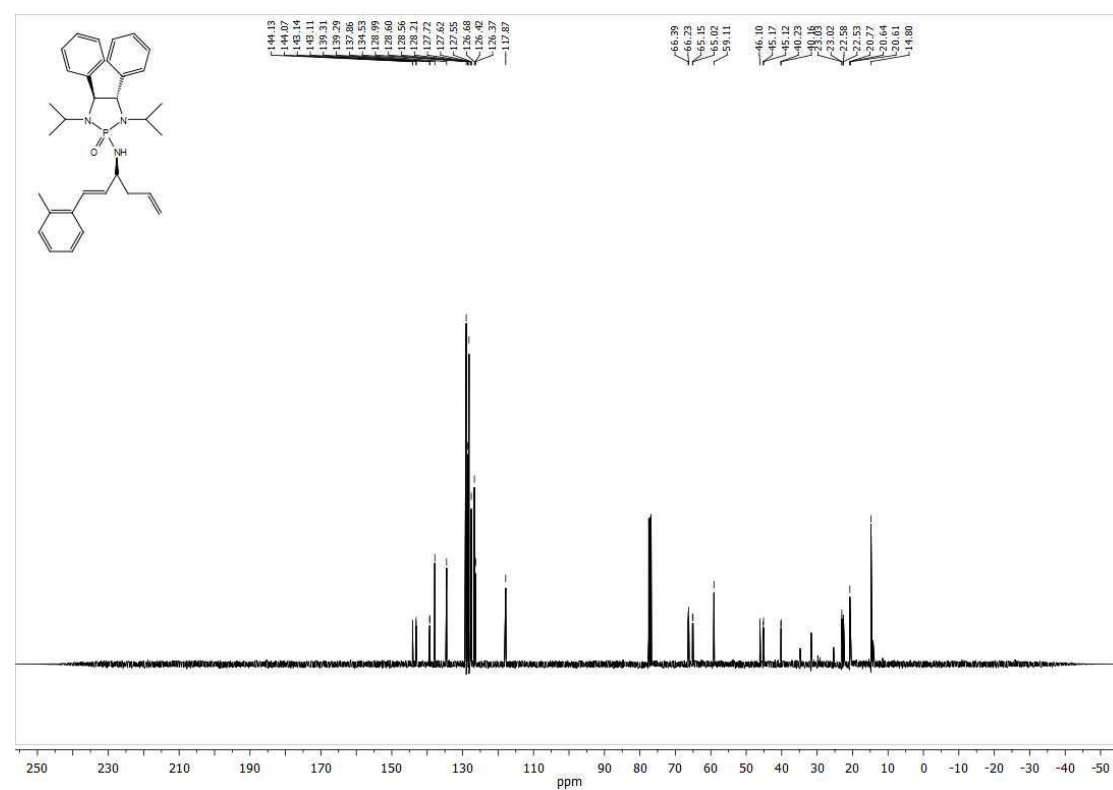
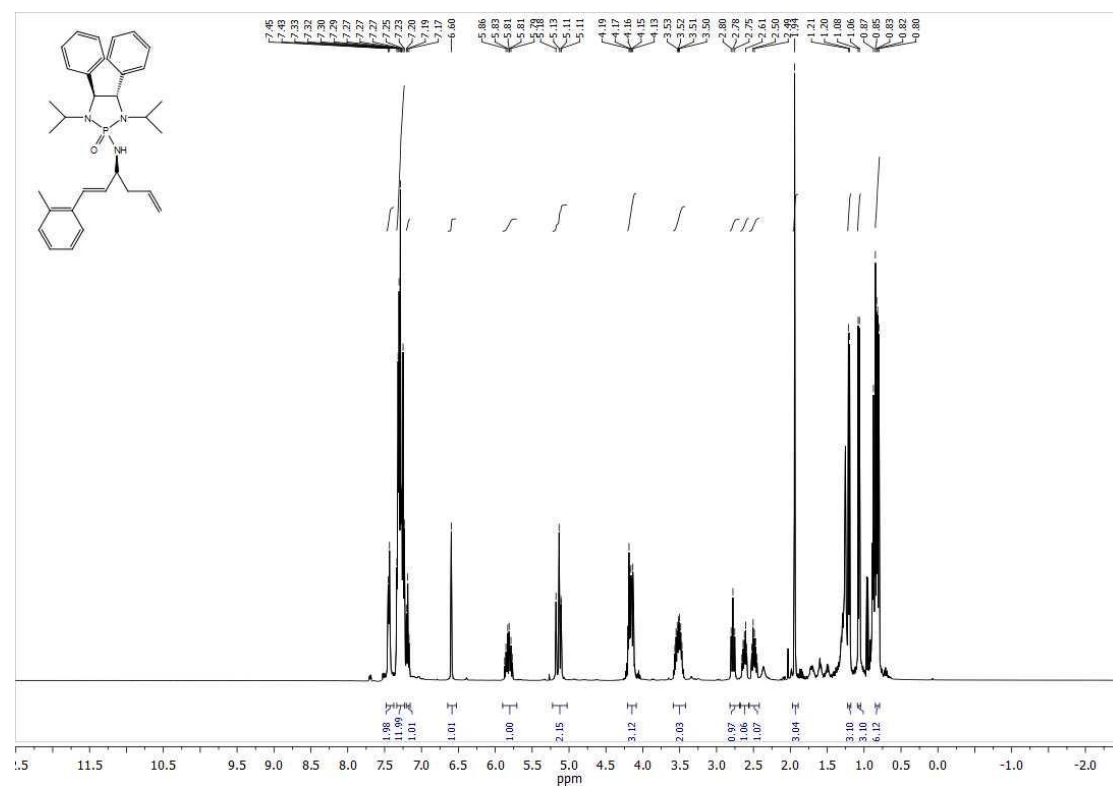
^1H NMR (400 MHz, CDCl_3) and ^{13}C NMR (100 MHz, CDCl_3) spectrum of 5b



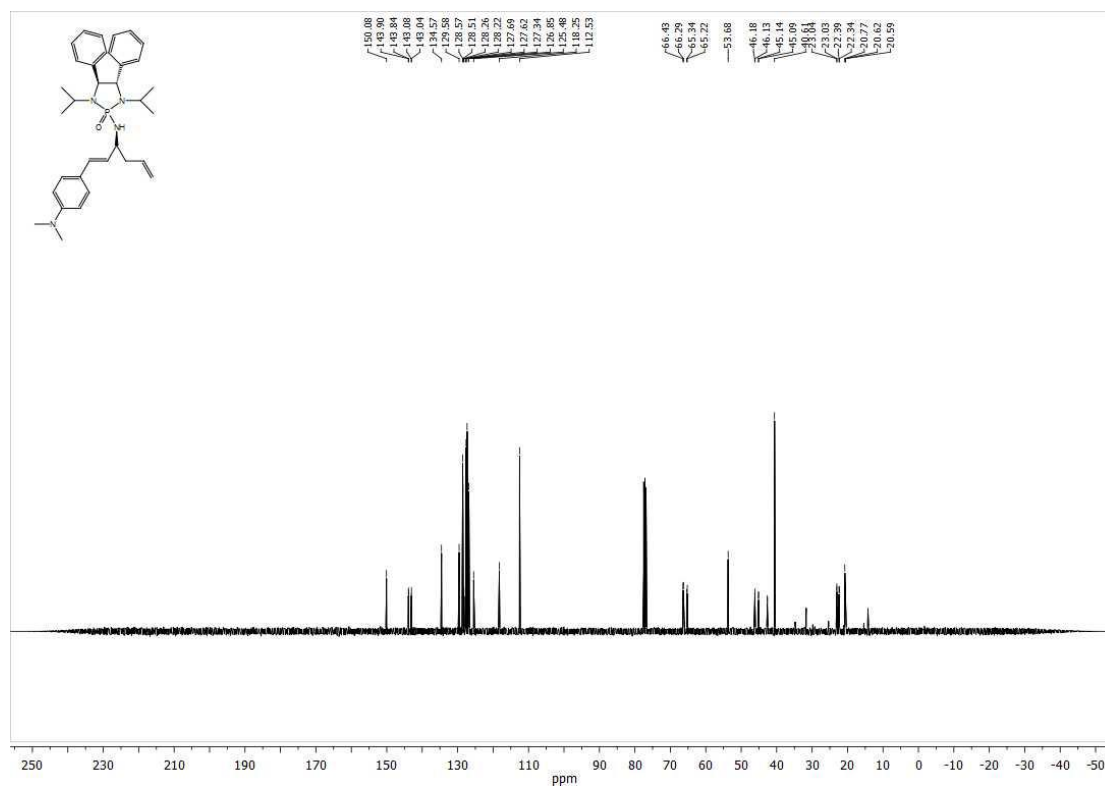
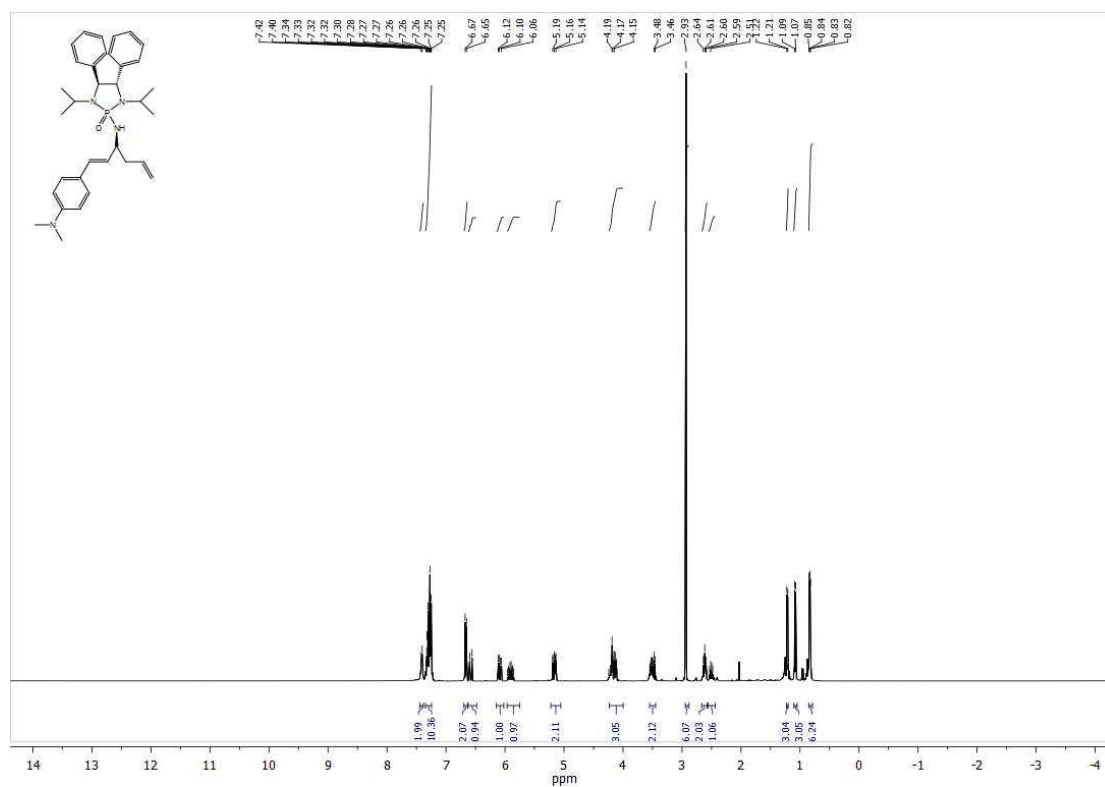
^1H NMR (400 MHz, CDCl_3) and ^{13}C NMR (100 MHz, CDCl_3) spectrum of **5c**



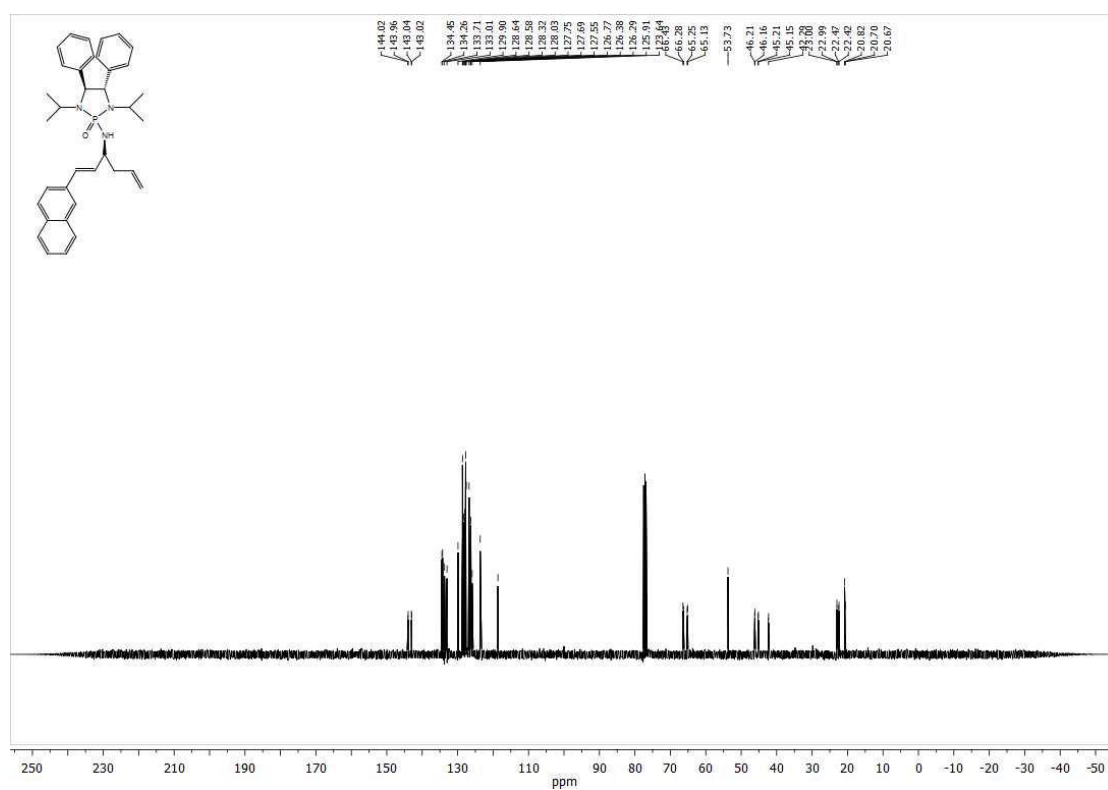
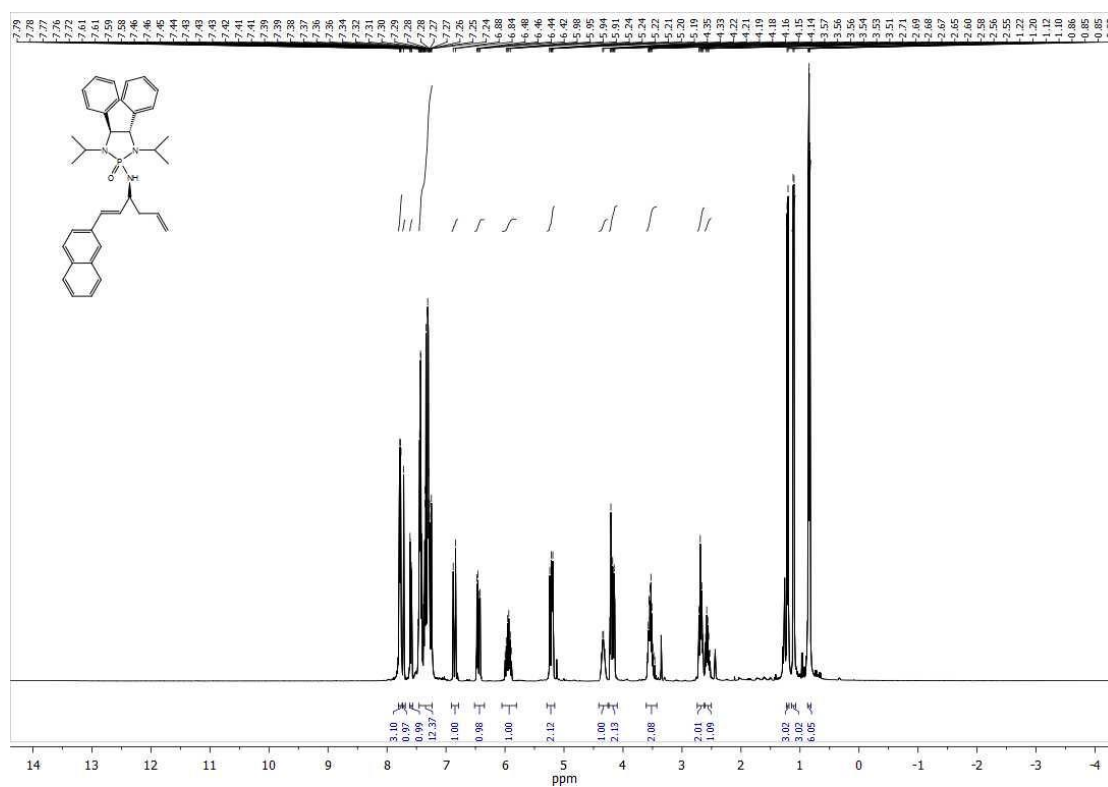
^1H NMR (400 MHz, CDCl_3) and ^{13}C NMR (100 MHz, CDCl_3) spectrum of 5d



^1H NMR (400 MHz, CDCl_3) and ^{13}C NMR (100 MHz, CDCl_3) spectrum of 5h



^1H NMR (400 MHz, CDCl_3) and ^{13}C NMR (100 MHz, CDCl_3) spectrum of 5i



^1H NMR (400 MHz, CDCl_3) and ^{13}C NMR (100 MHz, CDCl_3) spectrum of 5k

