Supporting Information

Atroposelective Synthesis of PINAP via Dynamic Kinetic Asymmetric Transformation

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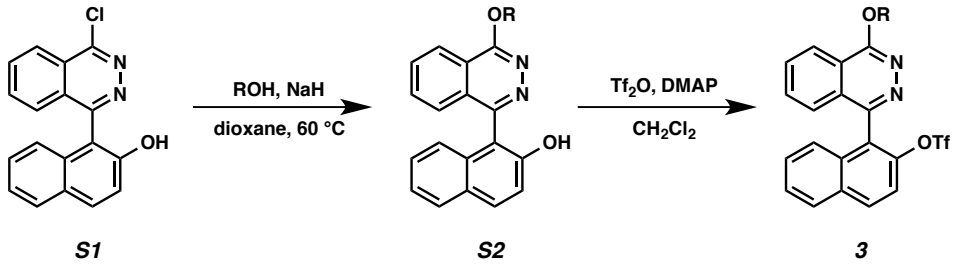
Materials and Methods.

Unless otherwise stated, reactions were performed in flame-dried glassware under an argon or nitrogen atmosphere using dry, deoxygenated solvents. Reaction progress was monitored by thin-layer chromatography (TLC). THF, Et_2O, CH_2Cl_2, toluene, benzene, CH_3CN, and dioxane were dried by passage through an activated alumina column under argon. Purified water was obtained using a Barnstead NANOpure Infinity UV/UF system. Brine solutions are saturated aqueous solutions of sodium chloride. Commercially available reagents were purchased from Sigma-Aldrich, Acros Organics, Strem, or Alfa Aesar and used as received unless otherwise stated. Reaction temperatures were controlled by an IKAmag temperature modulator unless otherwise indicated. Glove box manipulations were performed under a N_2 atmosphere. TLC was performed using E. Merck silica gel 60 F254 precoated glass plates (0.25 mm) and visualized by UV fluorescence quenching, *p*-anisaldehyde, or PMA (phosphomolybdic acid) staining. Silicycle Silia*Flash* P60 Academic Silica gel (particle size 0.040-0.064 mm) was used for flash column chromatography. ^{1}H NMR spectra were recorded on a Varian Inova 500 MHz spectrometer and are reported relative to residual $CHCl_3$ (δ 7.26 ppm). ^{13}C NMR spectra are recorded on a Varian Inova 500 MHz spectrometer (125MHz) and are reported relative to $CHCl_3$ (δ 77.16 ppm). Data for ^{1}H NMR are reported as follows: s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, sept = septuplet, m = multiplet, br s = broad singlet, br d= broad doublet, app = apparent. IR spectra were obtained using a Perkin Elmer Paragon 1000 spectrometer using thin films deposited on NaCl plates and reported in frequency of absorption (cm^{-1}). Optical rotations were measured with a Jasco P-2000 polarimeter operating on the sodium D-line (589 nm), using a 100 mm path-length cell and are reported as: $[\alpha]_D^T$ (concentration in g/100 mL, solvent). Analytical HPLC was performed with an Agilent 1100 Series HPLC utilizing a Chiralpak (AD-H or AS) or Chiralcel (OD-H, OJ-H, or OB-H) columns (4.6 mm x 25 cm) obtained from Daicel Chemical Industries, Ltd. Analytical SFC was performed with a Mettler SFC supercritical CO_2 analytical chromatography system utilizing Chiralpak (AD-H, AS-H or IC) or Chiralcel (OD-H, OJ-H, or OB-H) columns (4.5 mm x 25 cm) obtained from Daicel Chemical Industries, Ltd. High resolution mass spectra (HRMS) were obtained from the Caltech Mass Spectral Facility using JEOL JMS-600H High Resolution Mass Spectrometer in fast atom bombardment (FAB+) or electron

ionization (EI+) mode, or Agilent 6200 Series TOF with an Agilent G1978A Multimode source in electrospray ionization (ESI+), atmospheric pressure chemical ionization (APCI+), or mixed ionization mode (MM: ESI-APCI+).

Triflate substrates **3i–3k** were prepared by known methods.[1] All the data from PINAP **4i**–**4k** were confirmed by reported data.[1]

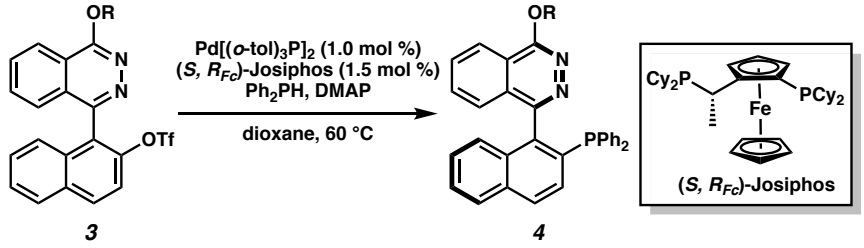
General Procedure for Synthesis of Triflate Substrates



To a solution of NaH (4.00 mmol, 2.00 equiv) in dioxane (8.00 mL) was added alcohol (2.10 mmol, 1.05 equiv) in dioxane (2.00 mL) dropwise. The reaction mixture was stirred for 15 min at 23 °C and then **S1** (2.00 mmol, 1.00 equiv) was added portionwise. The solution was stirred for 18 h at 60 °C then diluted with EtOAc (10.0 mL) and water (20.0 mL). The aqueous phase was extracted with EtOAc (3 x 10.0 mL). The combined organic phases were washed with brine, dried over $MgSO_4$ and concentrated *in vacuo*. The residue was used in the next step without further purification.

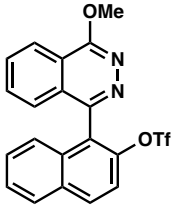
To a solution of crude mixture of **S2** (2.00 mmol, 1.00 equiv) and DMAP (4.00 mmol, 2.00 equiv) in CH_2Cl_2 (20.0 mL) was added Tf_2O (2.00 mmol, 1.00 equiv) dropwise at 0 °C. The reaction mixture was stirred at 23 °C until **S2** was fully consumed by TLC analysis. The reaction mixture was diluted with CH_2Cl_2 (10.0 mL) and water (10.0 mL). The aqueous phase was extracted with CH_2Cl_2 (3 x 6.00 mL). The combined organic phases were washed with brine, dried over $MgSO_4$ and concentrated *in vacuo*. The residue was purified by flash column chromatography (1:4 EtOAc:hexanes) on silica gel to give the corresponding triflate substrates.

General Procedure of PINAP from Triflates via Dynamic Kinetic Asymmetric Transformation



This reaction was performed in a nitrogen-filled glovebox. $Pd[(o\text{-tol})_3P]_2$ (10.8 mg, 0.0151 mmol) and (*S, R_{Fc}*)-Josiphos (13.7 mg, 0.0226 mmol) in dioxane (0.302 mL) were pre-stirred in a vial until all the solids were dissolved. To a solution of triflates **3** (0.211 mmol, 1.00 equiv) in dioxane (1.06 mL) was added DMAP (0.844 mmol, 4.00 equiv) and pre-stirred $Pd[(o\text{-tol})_3P]_2$ and (*S, R_{Fc}*)-Josiphos (0.05 M in dioxane; 0.00211 mmol, 0.01 equiv) at 23 °C. The mixture was placed in a reaction well preheated to 60 °C. A solution of Ph_2PH (1.00 M in dioxane; 0.317 mmol, 1.50 equiv) was added to the reaction mixture in 20 uL portions every 30 minutes manually. After completion of the addition (8 hours), the reaction was stirred for further 7 hours at which point complete consumption of the starting material was observed. The reaction was cooled, removed from the glovebox and dilulted with EtOAc (1.50 mL) and water (2.00 mL). The aqueous phase was extracted with EtOAc (3 x 1.50 mL). The combined organic phases were washed with brine, dried with $MgSO_4$ and concentrated. The crude material was purified by flash column chromatography on silica gel to afford the corresponding PINAP **4**.

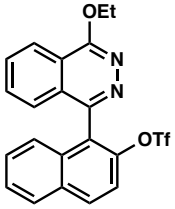
Spectroscopic Data



3a

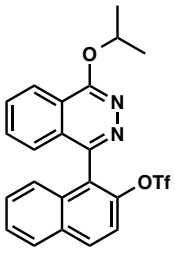
452 mg, 52% (2-step yield); R_f = 0.29 (1:4 EtOAc:hexanes); ^1H NMR (500 MHz, $CDCl_3$) δ 8.35 (dd, *J* = 8.2, 1.0 Hz, 1H), 8.12 (d, *J* = 9.1 Hz, 1H), 8.00 (d, *J* = 8.2 Hz,

1H), 7.87 (ddd, *J* = 8.2, 7.0, 1.1 Hz, 1H), 7.70 (ddd, *J* = 8.4, 7.1, 1.3 Hz, 1H), 7.62 (d, *J* = 9.1 Hz, 1H), 7.58 (ddd, *J* = 8.2, 6.8, 1.3 Hz, 1H), 7.42 (ddd, *J* = 8.2, 6.7, 1.3 Hz, 1H), 7.36 (d, *J* = 8.5 Hz, 1H), 7.31 (dt, *J* = 8.4, 1.0 Hz, 1H), 4.41 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.9, 151.1, 145.6, 133.6, 132.7, 132.6, 132.4, 131.9, 129.2, 128.4, 128.1, 127.4, 126.7, 126.6, 125.7, 123.5, 119.9, 119.6, 117.1, 55.3; IR (Neat Film NaCl) 3063, 2945, 1668, 1581, 1541, 1496, 1457, 1420, 1364, 1247, 1213, 1139, 952, 834 cm^{-1}; HRMS (MM: ESI-APCI+) *m/z* calc'd for $C_{20}H_{14}F_3N_2O_4S$ $[M+H]^+$: 435.0621; found: 435.0625.



3b

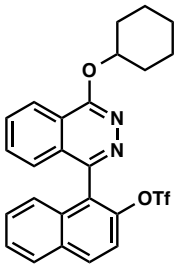
430 mg, 48% (2-step yield); R_f = 0.33 (1:4 EtOAc:hexanes); ^{1}H NMR (500 MHz, Chloroform-d) δ 8.38 (dd, *J* = 8.2, 1.2 Hz, 1H), 8.12 (d, *J* = 9.1 Hz, 1H), 7.99 (d, *J* = 8.3 Hz, 1H), 7.87 (ddd, *J* = 8.2, 6.9, 1.2 Hz, 1H), 7.69 (ddd, *J* = 8.4, 7.1, 1.3 Hz, 1H), 7.61 (d, *J* = 9.0 Hz, 1H), 7.57 (ddd, *J* = 8.2, 6.7, 1.4 Hz, 1H), 7.42 (ddd, *J* = 8.1, 6.7, 1.3 Hz, 1H), 7.37 (d, *J* = 8.5 Hz, 1H), 7.29 (dd, *J* = 8.3, 1.0 Hz, 1H), 4.88 (qd, *J* = 7.0, 3.9 Hz, 2H), 1.62 (td, *J* = 7.1, 1.6 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.6, 150.7, 145.6, 133.6, 132.7, 132.5, 132.3, 131.8, 129.2, 128.4, 128.1, 127.4, 126.7, 126.6, 125.6, 123.6, 120.0, 119.6, 117.1, 63.9, 14.7; IR (Neat Film NaCl) 3066, 2984, 1582, 1540, 1495, 1422, 1381, 1342, 1214, 1140, 1073, 1024, 956, 941, 834 cm^{-1}; HRMS (MM: ESI-APCI+) *m/z* calc'd for $C_{21}H_{16}F_3N_2O_4S$ $[M+H]^+$: 449.0777; found: 449.0780.



3c

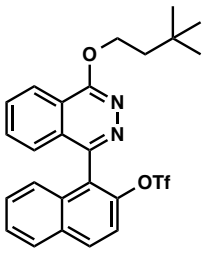
342 mg, 37% (2-step yield); R_f = 0.35 (1:4 EtOAc:hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.37 (dd, *J* = 8.2, 1.0 Hz, 1H), 8.13 (d, *J* = 9.1 Hz, 1H), 8.00 (d, *J* = 8.3 Hz,

1H), 7.87 (ddd, *J* = 8.2, 7.0, 1.2 Hz, 1H), 7.69 (ddd, *J* = 8.4, 7.1, 1.3 Hz, 1H), 7.62 (d, *J* = 9.1 Hz, 1H), 7.58 (ddd, *J* = 8.2, 6.7, 1.3 Hz, 1H), 7.43 (ddd, *J* = 8.1, 6.7, 1.3 Hz, 1H), 7.40 – 7.35 (m, 1H), 7.30 (dt, *J* = 8.3, 0.9 Hz, 1H), 5.94 (hept, *J* = 6.2 Hz, 1H), 1.60 (d, *J* = 6.1 Hz, 3H), 1.58 (d, *J* = 6.2 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.3, 150.2, 145.7, 133.5, 132.7, 132.5, 132.4, 132.0, 129.3, 128.5, 128.2, 127.4, 126.6, 126.4, 125.7, 123.7, 120.4, 119.7, 71.1, 22.3, 22.1; IR (Neat Film NaCl) 2981, 1582, 1493, 1417, 1322, 1212, 1140, 1106, 958, 942, 833, 748 cm^{-1}; HRMS (MM: ESI-APCI+) *m/z* calc'd for $C_{22}H_{17}F_3N_2O_4S$ $[M+H]^+$: 463.0934; found: 463.0964.



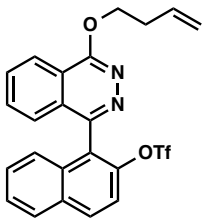
3d

362 mg, 36% (2-step yield); R_f = 0.43 (1:4 EtOAc:hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.37 (d, *J* = 8.2 Hz, 1H), 8.11 (dd, *J* = 9.1, 1.6 Hz, 1H), 7.99 (d, *J* = 8.3 Hz, 1H), 7.85 (ddd, *J* = 8.4, 7.1, 1.3 Hz, 1H), 7.67 (td, *J* = 7.7, 7.0, 1.4 Hz, 1H), 7.61 (dd, *J* = 9.1, 2.0 Hz, 1H), 7.57 (ddd, *J* = 8.2, 6.2, 1.9 Hz, 1H), 7.44 – 7.37 (m, 2H), 7.27 (d, *J* = 8.3 Hz, 1H), 5.72 (tt, *J* = 8.7, 3.7 Hz, 1H), 2.25 (d, *J* = 12.3 Hz, 2H), 1.90 (ddt, *J* = 13.9, 8.9, 4.5 Hz, 2H), 1.85 – 1.74 (m, 2H), 1.66 (td, *J* = 8.5, 7.7, 4.2 Hz, 1H), 1.57 (dtt, *J* = 13.5, 10.2, 3.4 Hz, 2H), 1.45 (ddt, *J* = 13.3, 10.1, 3.5 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.2, 150.3, 145.6, 133.6, 132.7, 132.3, 132.1, 131.7, 129.3, 128.4, 128.1, 127.3, 126.9, 126.7, 125.5, 123.7, 120.3, 119.7, 75.4, 32.0, 31.8, 25.9, 24.1; IR (Neat Film NaCl) 2937, 2858, 1582, 1537, 1493, 1418, 1362, 1342, 1214, 1140, 959, 944, 834 cm^{-1}; HRMS (MM: ESI-APCI+) *m/z* calc'd for $C_{25}H_{22}F_3N_2O_4S$ $[M+H]^+$: 503.1247; found: 503.1248.



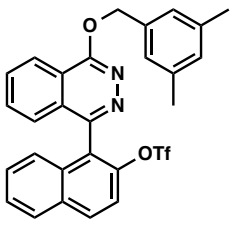
3e

494 mg, 49% (2-step yield); R_f = 0.33 (1:4 EtOAc:hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.35 (d, *J* = 8.2 Hz, 1H), 8.12 (d, *J* = 9.1 Hz, 1H), 8.00 (d, *J* = 8.2 Hz, 1H), 7.86 (ddd, *J* = 8.2, 7.0, 1.1 Hz, 1H), 7.69 (ddd, *J* = 8.3, 7.1, 1.2 Hz, 1H), 7.62 (d, *J* = 9.1 Hz, 1H), 7.57 (ddd, *J* = 8.2, 6.6, 1.3 Hz, 1H), 7.42 (ddd, *J* = 8.1, 6.6, 1.2 Hz, 1H), 7.39 – 7.35 (m, 1H), 7.29 (d, *J* = 8.3 Hz, 1H), 4.88 (t, *J* = 7.2 Hz, 2H), 1.96 (t, *J* = 7.2 Hz, 2H), 1.10 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.7, 150.7, 145.6, 133.6, 132.7, 132.4, 132.3, 131.8, 129.2, 128.4, 128.1, 127.4, 126.6, 125.6, 123.5, 120.0, 119.6, 117.1, 110.2, 65.8, 42.5, 30.0; IR (Neat Film NaCl) 2958, 1582, 1538, 1495, 1422, 1360, 1214, 1141, 1073, 953, 834, 620 cm^{-1}; HRMS (MM: ESI-APCI+) *m/z* calc'd for $C_{25}H_{23}F_3N_2O_4S$ $[M+H]^+$: 505.1403; found: 505.1436.



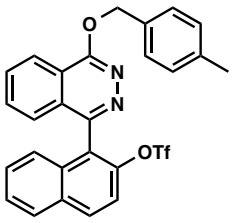
3f

493 mg, 52% (2-step yield); R_f = 0.33 (1:4 EtOAc:hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.38 – 8.34 (m, 1H), 8.12 (d, *J* = 9.1 Hz, 1H), 8.00 (d, *J* = 8.2 Hz, 1H), 7.87 (ddd, *J* = 8.3, 7.0, 1.1 Hz, 1H), 7.69 (ddd, *J* = 8.4, 7.0, 1.3 Hz, 1H), 7.61 (d, *J* = 9.1 Hz, 1H), 7.57 (ddd, *J* = 8.2, 6.7, 1.3 Hz, 1H), 7.42 (ddd, *J* = 8.1, 6.7, 1.2 Hz, 1H), 7.38 – 7.35 (m, 1H), 7.30 (dd, *J* = 8.3, 1.1 Hz, 1H), 6.04 (ddt, *J* = 17.1, 10.3, 6.7 Hz, 1H), 5.28 (dq, *J* = 17.2, 1.7 Hz, 1H), 5.17 (dq, *J* = 10.3, 1.4 Hz, 1H), 4.94 – 4.83 (m, 2H), 2.78 (dddd, *J* = 8.1, 6.6, 5.2, 1.4 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.6, 150.9, 145.6, 134.6, 133.6, 132.7, 132.5, 132.3, 131.8, 129.2, 128.4, 128.1, 127.4, 126.7, 126.6, 125.6, 123.5, 119.9, 119.6, 117.3, 117.1, 67.0, 33.6; IR (Neat Film NaCl) 1581, 1538, 1494, 1421, 1349, 1213, 1139, 954, 833 cm^{-1}; HRMS (MM: ESI-APCI+) *m/z* calc'd for $C_{23}H_{18}F_3N_2O_4S$ $[M+H]^+$: 475.0934; found: 475.0956.



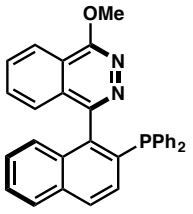
3g

377 mg, 35% (2-step yield); R_f = 0.38 (1:4 EtOAc:hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.40 (dt, *J* = 8.2, 1.0 Hz, 1H), 8.13 (d, *J* = 9.1 Hz, 1H), 8.00 (dt, *J* = 8.3, 0.9 Hz, 1H), 7.86 (ddd, *J* = 8.3, 7.1, 1.2 Hz, 1H), 7.70 (ddd, *J* = 8.3, 7.1, 1.2 Hz, 1H), 7.63 (d, *J* = 9.1 Hz, 1H), 7.58 (ddd, *J* = 8.2, 6.6, 1.3 Hz, 1H), 7.43 (ddd, *J* = 7.9, 6.6, 1.3 Hz, 1H), 7.39 (dd, *J* = 8.6, 1.2 Hz, 1H), 7.31 (dt, *J* = 8.4, 1.0 Hz, 1H), 7.04 (s, 1H), 5.80 (d, *J* = 2.3 Hz, 2H), 2.39 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.6, 151.1, 145.6, 138.3, 136.7, 133.6, 132.7, 132.6, 132.3, 131.8, 130.1, 129.3, 128.4, 128.1, 127.4, 126.7, 126.6, 126.6, 125.6, 123.7, 119.9, 119.7, 117.1, 69.8, 21.4; IR (Neat Film NaCl) 2917, 1581, 1494, 1418, 1343, 1213, 1140, 956, 835 cm^{-1}; HRMS (MM: ESI-APCI+) *m/z* calc'd for $C_{28}H_{22}F_3N_2O_4S$ $[M+H]^+$: 539.1247; found: 539.1252.



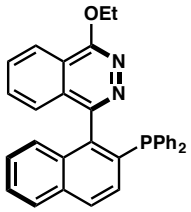
3h

713 mg, 68% (2-step yield); R_f = 0.37 (1:4 EtOAc:hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.38 (dt, *J* = 8.2, 1.0 Hz, 1H), 8.13 (d, *J* = 9.1 Hz, 1H), 8.01 (dt, *J* = 8.3, 0.9 Hz, 1H), 7.85 (ddd, *J* = 8.3, 7.0, 1.2 Hz, 1H), 7.70 (ddd, *J* = 8.4, 7.1, 1.3 Hz, 1H), 7.62 (dd, *J* = 9.1, 1.1 Hz, 1H), 7.58 (ddd, *J* = 8.1, 6.8, 1.3 Hz, 1H), 7.57 – 7.52 (m, 2H), 7.43 (ddd, *J* = 8.1, 6.8, 1.3 Hz, 1H), 7.37 (dt, J = 8.6, 1.0 Hz, 1H), 7.31 (dt, *J* = 8.3, 1.0 Hz, 1H), 7.27 (d, *J* = 7.2 Hz, 2H), 5.81 (d, *J* = 7.1 Hz, 2H), 2.41 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.5, 151.1, 145.5, 138.3, 133.7, 133.5, 132.6, 132.3, 131.9, 129.4, 129.2, 128.90, 128.4, 128.1, 127.4, 126.7, 126.6, 125.6, 123.6, 119.8, 119.6, 119.6, 117.0, 69.6, 21.4; IR (Neat Film NaCl) 3058, 1581, 1538, 1494, 1422, 1342, 1248, 1266, 1140, 1072, 953, 834, 776 cm^{-1}; HRMS (MM: ESI-APCI+) *m/z* calc'd for $C_{27}H_{19}F_3N_2O_4S$ $[M+H]^+$: 525.1090; found: 525.1096.



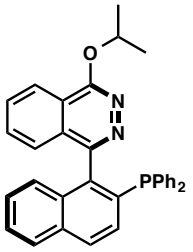
4a

79 mg, 80% yield, 96% ee; $[\alpha]_D^{25}$ +124.5 (*c* 0.51, $CHCl_3$); R_f = 0.42 (1:2 EtOAc:hexanes); ^1H NMR (500 MHz, $CDCl_3$) δ 8.27 (dt, *J* = 8.3, 1.0 Hz, 1H), 7.91 (dd, *J* = 8.6, 0.8 Hz, 1H), 7.90 – 7.87 (m, 1H), 7.74 (ddd, *J* = 8.2, 7.1, 1.1 Hz, 1H), 7.49 (ddd, *J* = 8.2, 6.8, 1.2 Hz, 1H), 7.46 – 7.42 (m, 2H), 7.29 (ddd, *J* = 8.2, 6.8, 1.3 Hz, 1H), 7.27 – 7.14 (m, 11H), 7.07 (dt, *J* = 8.2, 0.9 Hz, 1H), 4.36 (s, 3H); (Due to the C–P coupling, the ^{13}C NMR contained extra peaks. See the attached spectrum); ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.4, 156.8, 156.8, 141.5, 141.3, 137.5, 137.4, 137.3, 137.2, 136.0, 135.9, 134.0, 133.9, 133.7, 133.3, 133.2, 133.1, 131.8, 131.7, 130.3, 130.0, 129.9, 129.3, 128.7, 128.4, 128.4, 128.2, 128.1, 127.1, 126.9, 126.7, 126.7, 126.1, 123.2, 119.6, 55.1; ^{31}P NMR (121 MHz, $CDCl_3$) δ -14.3; IR (Neat Film NaCl) 3053, 1582, 1538, 1495, 1456, 1362, 1112, 1018, 744 cm^{-1}; HRMS (MM: ESI-APCI+) *m/z* calc'd for $C_{31}H_{23}N_2OP$ $[M+H]^+$: 471.1621; found: 471.1674; SFC conditions: 35% IPA, 2.5mL/min, Chiralcel OD-H column, t_R (min): major = 5.81, minor = 5.16.



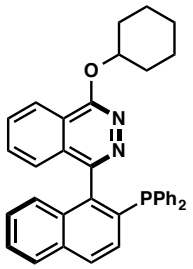
4b

75 mg, 73% yield, 94% ee; $[\alpha]_D^{25}$ +150.3 (*c* 0.47, $CHCl_3$); R_f = 0.54 (1:2 EtOAc:hexanes); ^1H NMR (500 MHz, $CDCl_3$) δ 8.30 (dd, *J* = 8.2, 1.0 Hz, 1H), 7.91 (d, *J* = 8.6 Hz, 1H), 7.89 (d, *J* = 7.8 Hz, 1H), 7.74 (ddd, *J* = 8.2, 7.1, 1.1 Hz, 1H), 7.49 (ddd, *J* = 8.1, 6.8, 1.3 Hz, 1H), 7.47 – 7.41 (m, 2H), 7.29 (ddd, *J* = 8.2, 6.8, 1.3 Hz, 1H), 7.27 – 7.13 (m, 11H), 7.07 (d, *J* = 8.2 Hz, 1H), 4.83 (qt, *J* = 7.1, 2.1 Hz, 2H), 1.60 (t, *J* = 7.1 Hz, 3H); (Due to the C–P coupling, the ^{13}C NMR contained extra peaks. See the attached spectrum); ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.2, 156.5, 156.5, 141.6, 141.3, 137.6, 137.5, 137.3, 137.2, 136.0, 135.9, 134.0, 133.8, 133.7, 133.3, 133.2, 133.1, 131.8, 131.5, 130.3, 130.0, 129.9, 129.2, 128.6, 128.4, 128.4, 128.2, 128.1, 127.1, 126.8, 126.8, 126.7, 126.1, 123.3, 119.6, 63.5, 14.9; ^{31}P NMR (121 MHz, $CDCl_3$) δ -14.2; IR (Neat Film NaCl) 3053, 2980, 1583, 1538, 1494, 1418, 1378, 1342, 1165, 1110, 1023, 818, 744 cm^{-1}; HRMS (MM: ESI-APCI+) *m/z* calc'd for $C_{32}H_{25}N_2OP$ $[M+H]^+$: 485.1777; found: 485.1800; SFC conditions: 30% MeOH, 2.5mL/min, Chiralpak AD-H column, t_R (min): major = 2.60, minor = 3.09.



4c

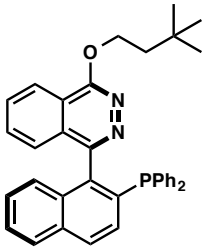
74 mg, 70% yield, 82% ee; $[\alpha]_D^{25}$ +131.7 (*c* 0.57, $CHCl_3$); R_f = 0.54 (1:2 EtOAc:hexanes); ^1H NMR (500 MHz, $CDCl_3$) δ 8.29 (dt, *J* = 8.1, 1.0 Hz, 1H), 7.90 (t, *J* = 9.0 Hz, 2H), 7.73 (ddd, *J* = 8.2, 7.1, 1.1 Hz, 1H), 7.52 – 7.42 (m, 3H), 7.30 (ddd, *J* = 8.4, 6.6, 1.2 Hz, 1H), 7.28 – 7.15 (m, 11H), 7.08 (dt, *J* = 8.1, 0.9 Hz, 1H), 5.88 (p, *J* = 6.2 Hz, 1H), 1.58 (d, *J* = 5.7 Hz, 3H), 1.56 (d, *J* = 5.7 Hz, 3H); (Due to the C–P coupling, the ^{13}C NMR contained extra peaks. See the attached spectrum); ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.7, 156.0, 156.0, 141.6, 141.3, 137.6, 137.5, 137.3, 137.2, 136.0, 135.9, 134.0, 133.8, 133.7, 133.4, 133.2, 133.2, 133.1, 131.7, 131.4, 130.2, 130.0, 129.2, 128.6, 128.4, 128.4, 128.4, 128.4, 128.2, 128.1, 127.0, 126.8, 126.0, 123.4, 120.0, 70.1, 22.4, 22.3; ^{31}P NMR (121 MHz, $CDCl_3$) δ -13.9; IR (Neat Film NaCl) 3053, 2978, 1584, 1489, 1413, 1383, 1315, 1106, 744 cm^{-1}; HRMS (MM: ESI-APCI+) *m/z* calc'd for $C_{33}H_{27}N_2OP$ $[M+H]^+$: 499.1934; found: 499.1960; SFC conditions: 40% MeOH, 2.5mL/min, Chiralpak AD-H column, t_R (min): major = 1.94, minor = 2.22.



4d

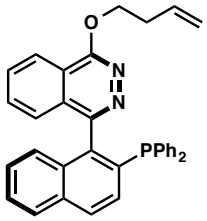
76 mg, 67% yield, 95% ee; $[\alpha]_D^{25}$ +91.0 (*c* 0.57, $CHCl_3$); R_f = 0.61 (1:2 EtOAc:hexanes); ^1H NMR (500 MHz, $CDCl_3$) δ 8.29 (dt, *J* = 8.2, 1.0 Hz, 1H), 7.89 (ddd, *J* = 9.4, 8.2, 0.8 Hz, 2H), 7.73 (ddd, *J* = 8.3, 7.0, 1.2 Hz, 1H), 7.49 (ddd, *J* = 8.1, 6.7, 1.3 Hz, 1H), 7.46 – 7.41 (m, 2H), 7.29 (ddd, *J* = 8.2, 6.7, 1.3 Hz, 1H), 7.26 – 7.14 (m, 11H), 7.07 (dt, *J* = 8.3, 0.9 Hz, 1H), 5.67 (tt, *J* = 8.9, 3.8 Hz, 1H), 2.30 – 2.18 (m, 2H), 1.88 (ddtd, *J* = 9.3, 7.9, 5.4, 4.0 Hz, 2H), 1.76 (qdt, *J* = 9.9, 6.1, 3.7 Hz, 2H),

1.64 (tt, *J* = 9.1, 4.9 Hz, 1H), 1.54 (qq, *J* = 10.2, 3.5 Hz, 2H), 1.42 (ddt, *J* = 13.4, 10.2, 3.5 Hz, 1H); (Due to the C–P coupling, the ^{13}C NMR contained extra peaks. See the attached spectrum); ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.6, 156.0, 155.9, 141.6, 141.4, 137.6, 137.5, 137.3, 137.2, 136.0, 135.9, 134.0, 133.9, 133.7, 133.4, 133.2, 131.7, 131.4, 130.3, 130.0, 129.2, 128.6, 128.4, 128.4, 128.4, 128.4, 128.2, 128.1, 127.0, 126.8, 126.8, 126.8, 126.0, 123.4, 120.0, 74.8, 32.0, 31.9, 25.9, 24.1, 24.0; ^{31}P NMR (121 MHz, $CDCl_3$) δ -13.9; IR (Neat Film NaCl) 3051, 2933, 2856, 1582, 1538, 1490, 1432, 1413, 1361, 1341, 1311, 1263, 1215, 1165, 1113, 1068, 1046, 1019, 744 cm^{-1}; HRMS (MM: ESI-APCI+) *m/z* calc'd for $C_{36}H_{31}N_2OP$ $[M+H]^+$: 539.2247; found: 539.2268; SFC conditions: 25% MeOH, 2.5mL/min, Chiralcel OD-H column, t_R (min): major = 7.58, minor = 8.13.



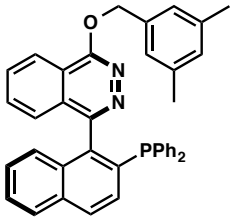
4e

65 mg, 57% yield, 95% ee; $[\alpha]_D^{25}$ +101.2 (*c* 0.42, $CHCl_3$); R_f = 0.62 (1:2 EtOAc:hexanes); ^1H NMR (500 MHz, $CDCl_3$) δ 8.27 (dt, *J* = 8.2, 1.0 Hz, 1H), 7.91 (d, *J* = 8.5 Hz, 1H), 7.89 (d, *J* = 8.4 Hz, 1H), 7.73 (ddt, *J* = 8.7, 7.1, 1.4 Hz, 1H), 7.49 (ddt, *J* = 8.5, 6.9, 1.5 Hz, 1H), 7.46 – 7.40 (m, 2H), 7.29 (ddd, *J* = 8.2, 6.7, 1.3 Hz, 1H), 7.27 – 7.14 (m, 11H), 7.06 (d, *J* = 8.2 Hz, 1H), 4.87 – 4.77 (m, 2H), 1.94 (td, *J* = 7.1, 1.9 Hz, 2H), 1.09 (s, 9H); (Due to the C–P coupling, the ^{13}C NMR contained extra peaks. See the attached spectrum); ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.3, 156.5, 156.4, 141.6, 141.3, 137.6, 137.5, 137.3, 137.2, 136.0, 135.9, 134.0, 133.9, 133.7, 133.3, 133.2, 133.1, 131.7, 131.6, 130.3, 129.9, 129.2, 128.7, 128.4, 128.4, 128.2, 128.1, 127.1, 126.8, 126.8, 126.7, 126.1, 123.2, 119.7, 77.2, 65.4, 42.5, 30.1; ^{31}P NMR (121 MHz, $CDCl_3$) δ -14.2; IR (Neat Film NaCl) 3051, 2956, 1418, 1386, 1114, 743 cm^{-1}; HRMS (MM: ESI-APCI+) *m/z* calc'd for $C_{36}H_{33}N_2OP$ $[M+H]^+$: 541.2403; found: 541.2409; SFC conditions: 35% IPA, 2.5mL/min, Chiralcel OD-H column, t_R (min): major = 4.33, minor = 4.84.



4f

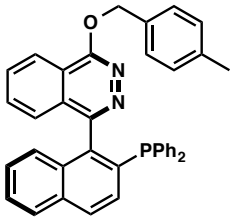
72 mg, 67% yield, 94% ee; $[\alpha]_D^{25}$ +117.9 (*c* 0.52, $CHCl_3$); R_f = 0.62 (1:2 EtOAc:hexanes); ^1H NMR (500 MHz, $CDCl_3$) δ 8.28 (d, *J* = 8.2 Hz, 1H), 7.91 (d, *J* = 8.6 Hz, 1H), 7.89 (d, *J* = 8.2 Hz, 1H), 7.75 (ddd, *J* = 8.3, 7.1, 1.2 Hz, 1H), 7.52 – 7.41 (m, 3H), 7.30 (ddd, *J* = 8.3, 6.8, 1.3 Hz, 1H), 7.26 – 7.14 (m, 11H), 7.08 (dt, *J* = 8.4, 0.9 Hz, 1H), 6.04 (ddt, *J* = 17.0, 10.3, 6.7 Hz, 1H), 5.28 (dq, *J* = 17.2, 1.7 Hz, 1H), 5.17 (dt, *J* = 10.5, 1.6 Hz, 1H), 4.88 – 4.77 (m, 2H), 2.75 (qt, *J* = 6.8, 1.3 Hz, 2H); (Due to the C–P coupling, the ^{13}C NMR contained extra peaks. See the attached spectrum); ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.1, 156.7, 156.6, 141.5, 141.2, 137.6, 137.5, 137.2, 137.2, 136.0, 135.9, 134.9, 134.0, 133.8, 133.7, 133.3, 133.2, 133.2, 133.1, 131.9, 131.6, 130.3, 130.0, 130.0, 129.3, 128.7, 128.4, 128.4, 128.2, 128.1, 127.1, 126.9, 126.7, 126.7, 126.1, 123.2, 119.6, 117.2, 77.2, 66.7, 33.7; ^{31}P NMR (121 MHz, $CDCl_3$) δ -14.2; IR (Neat Film NaCl) 2096, 1642, 1417, 1348, 1113, 1020, 818, 744 cm^{-1}; HRMS (MM: ESI-APCI+) *m/z* calc'd for $C_{34}H_{27}N_2OP$ $[M+H]^+$: 511.1934; found: 511.1954; SFC conditions: 35% MeOH, 2.5mL/min, Chiralpak AD-H column, t_R (min): major = 3.00, minor = 3.66.



4g

73 mg, 60% yield, 94% ee; $[\alpha]_D^{25}$ +40.1 (*c* 0.31, $CHCl_3$); R_f = 0.56 (1:2 EtOAc:hexanes); ^1H NMR (300 MHz, $CDCl_3$) δ 8.32 (d, *J* = 8.2 Hz, 1H), 7.91 (t, *J* = 7.8 Hz, 2H), 7.73 (ddd, *J* = 8.3, 7.1, 1.3 Hz, 1H), 7.54 – 7.41 (m, 3H), 7.35 – 7.13 (m, 14H), 7.12 – 7.03 (m, 2H), 5.74 (d, *J* = 5.4 Hz, 2H), 2.39 (s, 6H); (Due to the C–P coupling, the ^{13}C NMR contained extra peaks. See the attached spectrum); ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.1, 156.9, 156.8, 141.5, 141.1, 138.3, 137.5, 137.4, 137.3, 137.1, 136.9, 136.0, 135.9, 134.1, 133.8, 133.7, 133.4, 133.2, 133.1, 133.1, 131.9,

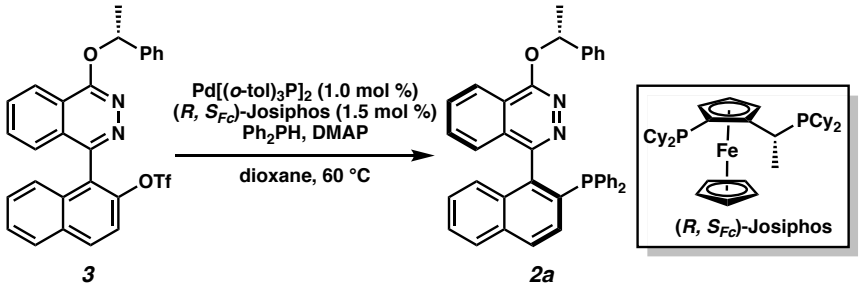
131.6, 130.3, 130.0, 130.0, 129.3, 128.7, 128.5, 128.4, 128.4, 128.2, 128.1, 127.1, 126.9, 126.7, 126.7, 126.6, 126.6, 126.1, 123.4, 119.6, 69.5, 21.5; ^{31}P NMR (121 MHz, $CDCl_3$) δ -14.2; IR (Neat Film NaCl) 3052, 2917, 1608, 1582, 1538, 1492, 1480, 1432, 1414, 1386, 1345, 1264, 1165, 1113, 1019, 962, 851, 818, 777, 743 cm^{-1}; HRMS (MM: ESI-APCI+) *m/z* calc'd for $C_{39}H_{31}N_2OP$ $[M+H]^+$: 575.2247; found: 575.2293; SFC conditions: 40% MeOH, 2.5mL/min, Chiralcel OD-H column, t_R (min): major = 5.77, minor = 6.82.



4h

85 mg, 72% yield, 94% ee; $[\alpha]_D^{25}$ +118.5 (*c* 0.33, $CHCl_3$); R_f = 0.61 (1:2 EtOAc:hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.29 (dt, *J* = 8.2, 1.7 Hz, 1H), 7.91 (dd, *J* = 8.6, 2.5 Hz, 1H), 7.88 (dd, *J* = 8.2, 1.1 Hz, 1H), 7.71 (ddd, *J* = 8.2, 7.0, 1.2 Hz, 1H), 7.52 (dd, *J* = 8.2, 2.6 Hz, 2H), 7.48 (ddd, *J* = 8.2, 6.7, 1.3 Hz, 1H), 7.43 (dddd, *J* = 9.2, 6.0, 3.4, 1.8 Hz, 2H), 7.32 – 7.13 (m, 14H), 7.10 – 7.06 (m, 1H), 5.76 (q, *J* = 12.1 Hz, 2H), 2.40 (s, 3H); (Due to the C–P coupling, the ^{13}C NMR contained extra peaks. See the attached spectrum); ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.1, 156.9, 156.8, 141.4, 141.2, 138.1, 137.5, 137.4, 137.2, 137.1, 136.0, 135.9, 134.0, 133.9, 133.7, 133.4, 133.2, 133.1, 131.9, 131.6, 130.3, 130.0, 130.0, 129.4, 129.4, 129.3, 128.9, 128.7, 128.4, 128.4, 128.4, 128.4, 128.3, 128.1, 127.1, 126.9, 126.7, 126.7, 126.1, 123.3, 119.6, 69.3, 21.4; ^{31}P NMR (121 MHz, $CDCl_3$) δ -14.2; IR (Neat Film NaCl) 3051, 1583, 1492, 1416, 1345, 1163, 1112, 1019, 744 cm^{-1}; HRMS (MM: ESI-APCI+) *m/z* calc'd for $C_{38}H_{29}N_2OP$ $[M+H]^+$: 561.2090; found: 561.2090; SFC conditions: 40% MeOH, 2.5mL/min, Chiralpak AD-H column, t_R (min): major = 3.43, minor = 5.21.

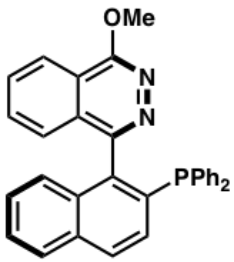
A gram scale example

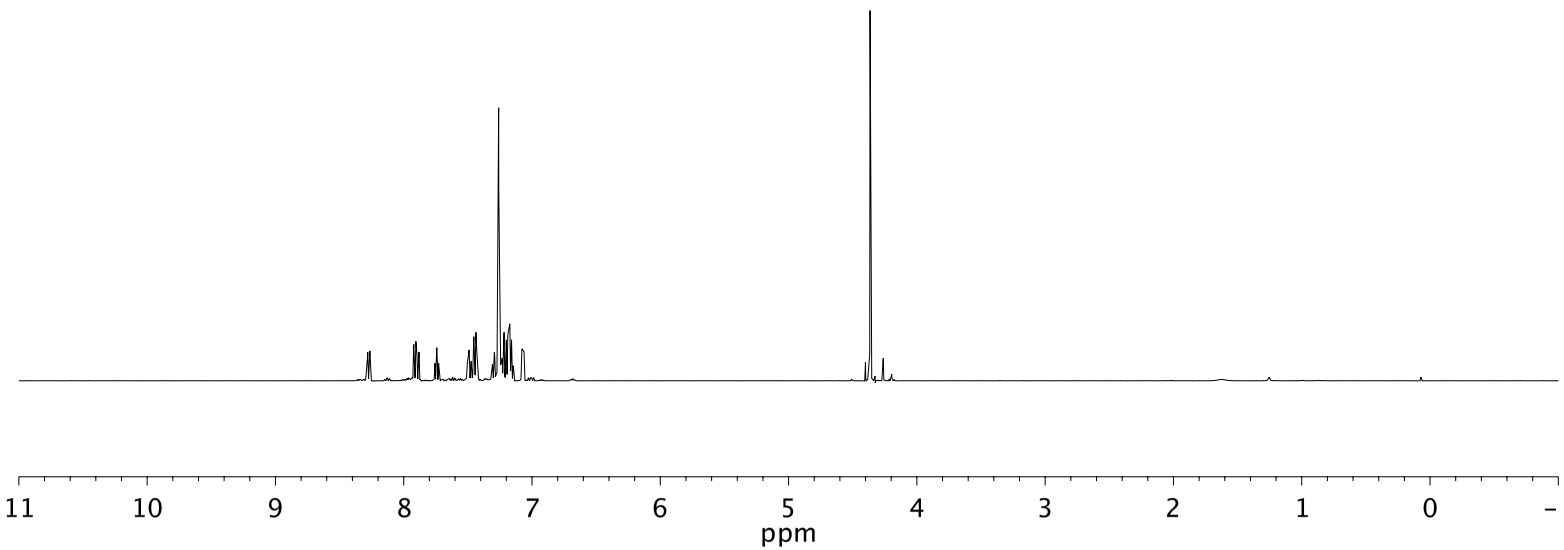


3 *2a*

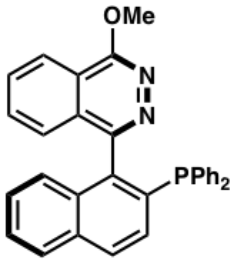
This reaction was performed in a nitrogen-filled glovebox. Pd[(*o*-tol)$_3$P]$_2$ (17.9 mg, 0.0250 mmol) and (*R, S*$_{Fc}$)-Josiphos (22.7 mg, 0.0375 mmol) in dioxane (0.50 mL) were pre-stirred in a vial until all the solids were dissolved. To a solution of triflates **3** (1.24g, 2.36 mmol, 1.00 equiv) in dioxane (12.0 mL) was added DMAP (1.16g, 9.46 mmol, 4.00 equiv) and pre-stirred Pd[(*o*-tol)$_3$P]$_2$ and (*R, S*$_{Fc}$)-Josiphos (0.05 M in dioxane; 0.47 mL, 0.0236 mmol, 0.01 equiv) at 23 °C. The mixture was placed in a reaction well preheated to 60 °C. A solution of Ph_2PH (1.00 M in dioxane; 3.54 mL, 3.54 mmol, 1.50 equiv) was added to the reaction mixture in 0.22 mL portions every 30 minutes manually. After completion of the addition (8 hours), the reaction was stirred for further 7 hours at which point complete consumption of the starting material was observed. The reaction was cooled, removed from the glovebox and dilulted with EtOAc (15.0 mL) and water (20.0 mL). The aqueous phase was extracted with EtOAc (3 x 15.0 mL). The combined organic phases were washed with brine, dried with $MgSO_4$ and concentrated. The crude material was purified by flash column chromatography on silica gel (0.94 g, 71% yield, 88% de), and then recrystallized to afford PINAP **2a** (0.75 g, 57% yield, 99% de). All the other spectra data were identical to the reported data. (ref. 1)

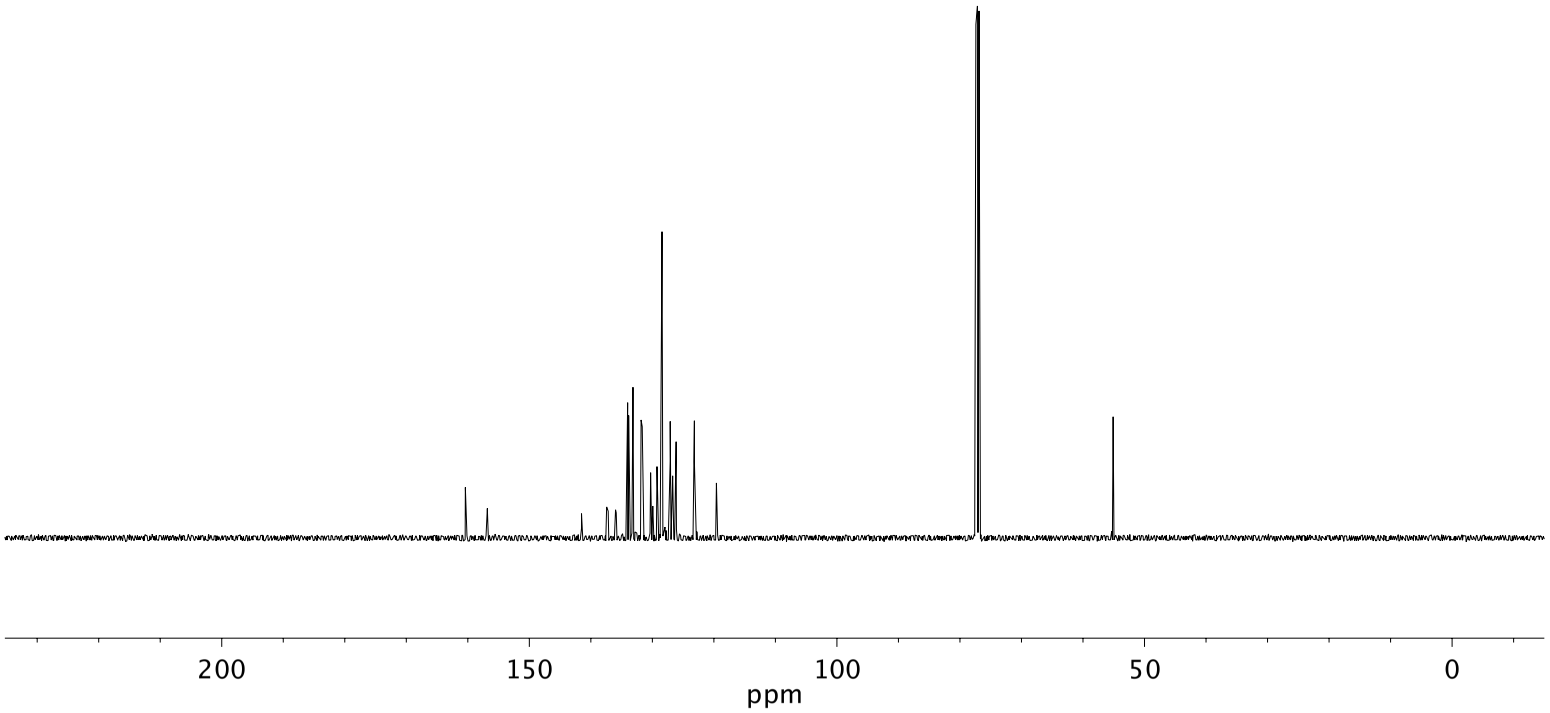
[1] a) T. F. Knöpfel, P. Aschwanden, T. Ichikawa, T. Watanabe, E. M. Carreira, *Angew. Chem., Int., Ed.* **2004**, *43*, 5971–5973. b) S. Fujimori, T. F. Knöpfel, P. Zarotti, T. Ichikawa, D. Boyall, E. M. Carreira, *Bull. Chem. Soc. Jpn.* **2007**, *80*, 1635–1657.



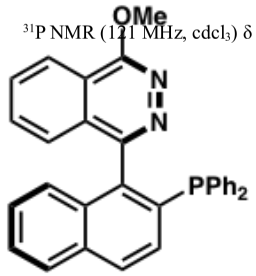


^{1}H NMR (500 MHz, $CDCl_3$) of compound **4a**.



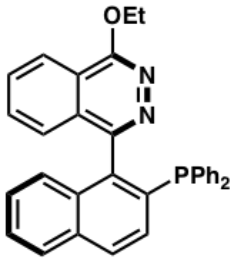


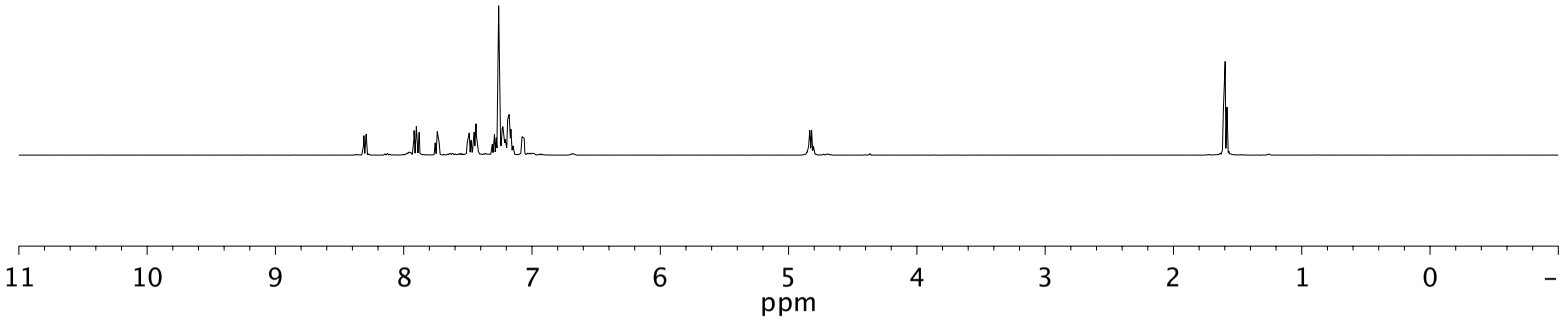
^{13}C NMR (126 MHz, $CDCl_3$) of compound **4a**.



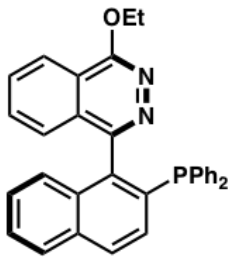
^{31}P NMR (121 MHz, cdcl$_3$) δ -14.26.

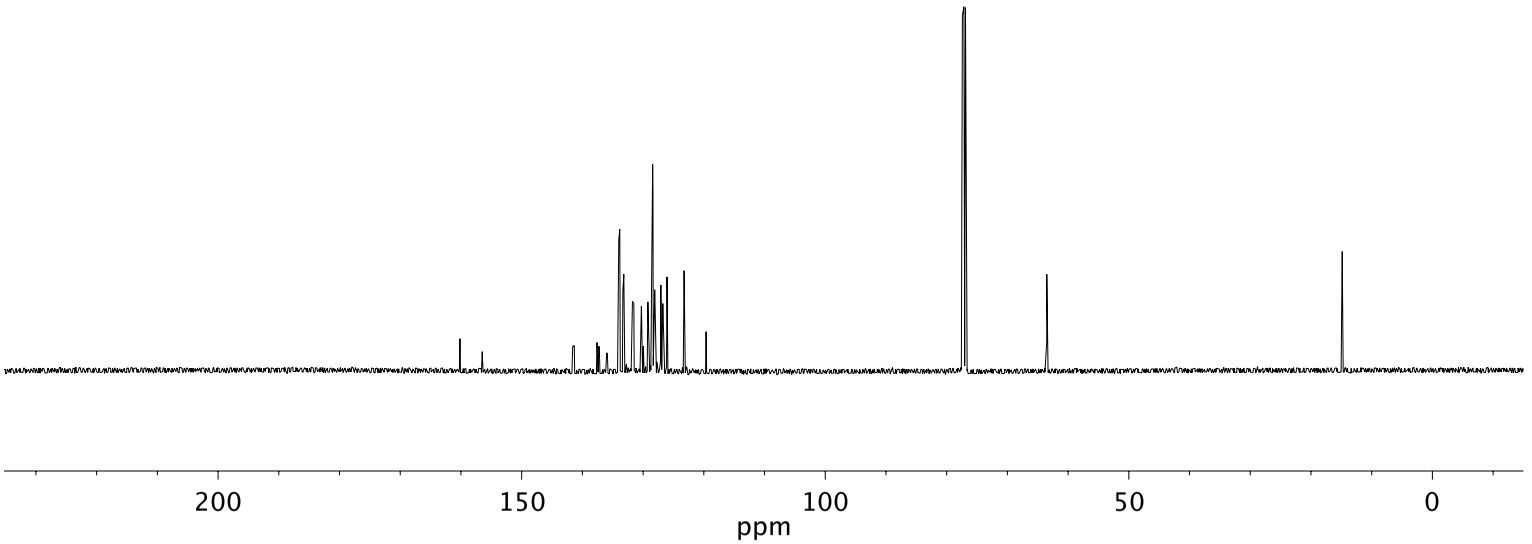
^{31}P NMR (121 MHz, $CDCl_3$) of compound **4a**.



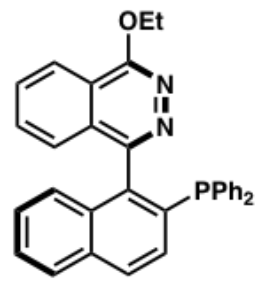


^{1}H NMR (500 MHz, $CDCl_3$) of compound **4b**.

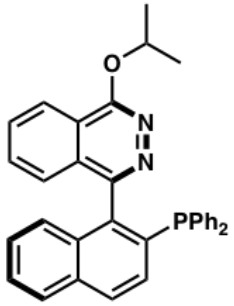


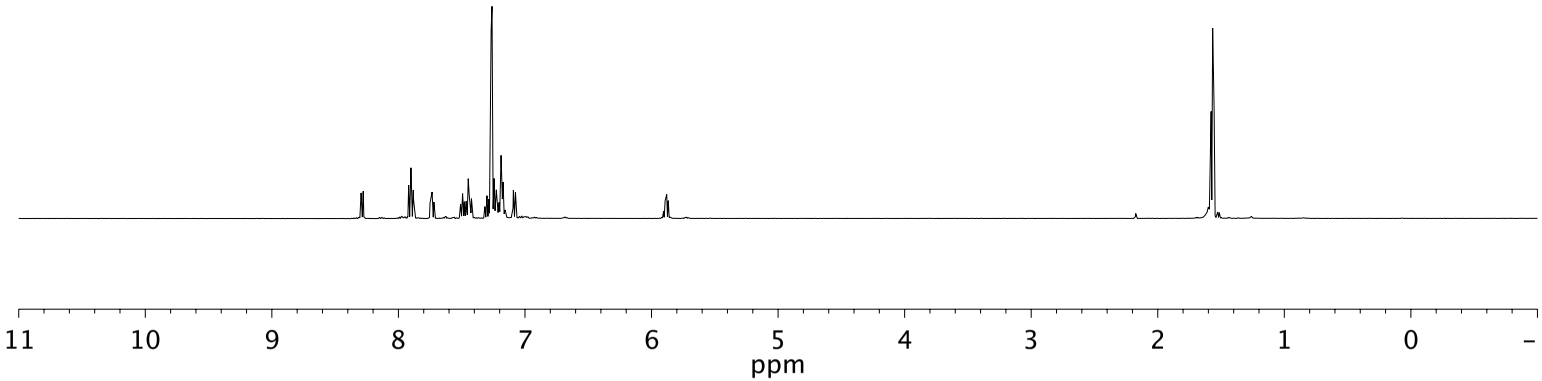


^{13}C NMR (126 MHz, $CDCl_3$) of compound **4b**.

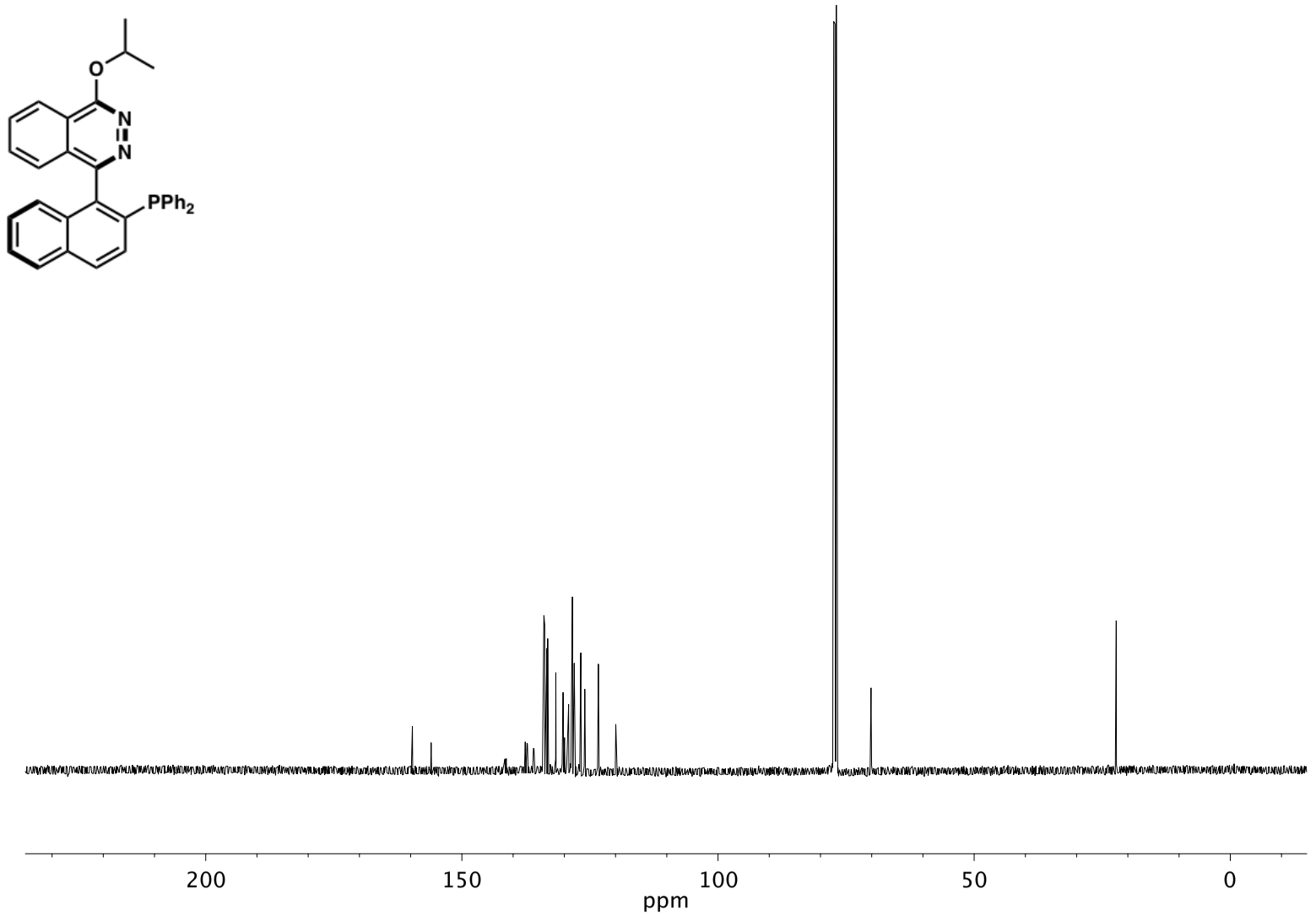


^{31}P NMR (121 MHz, $CDCl_3$) of compound **4b**.

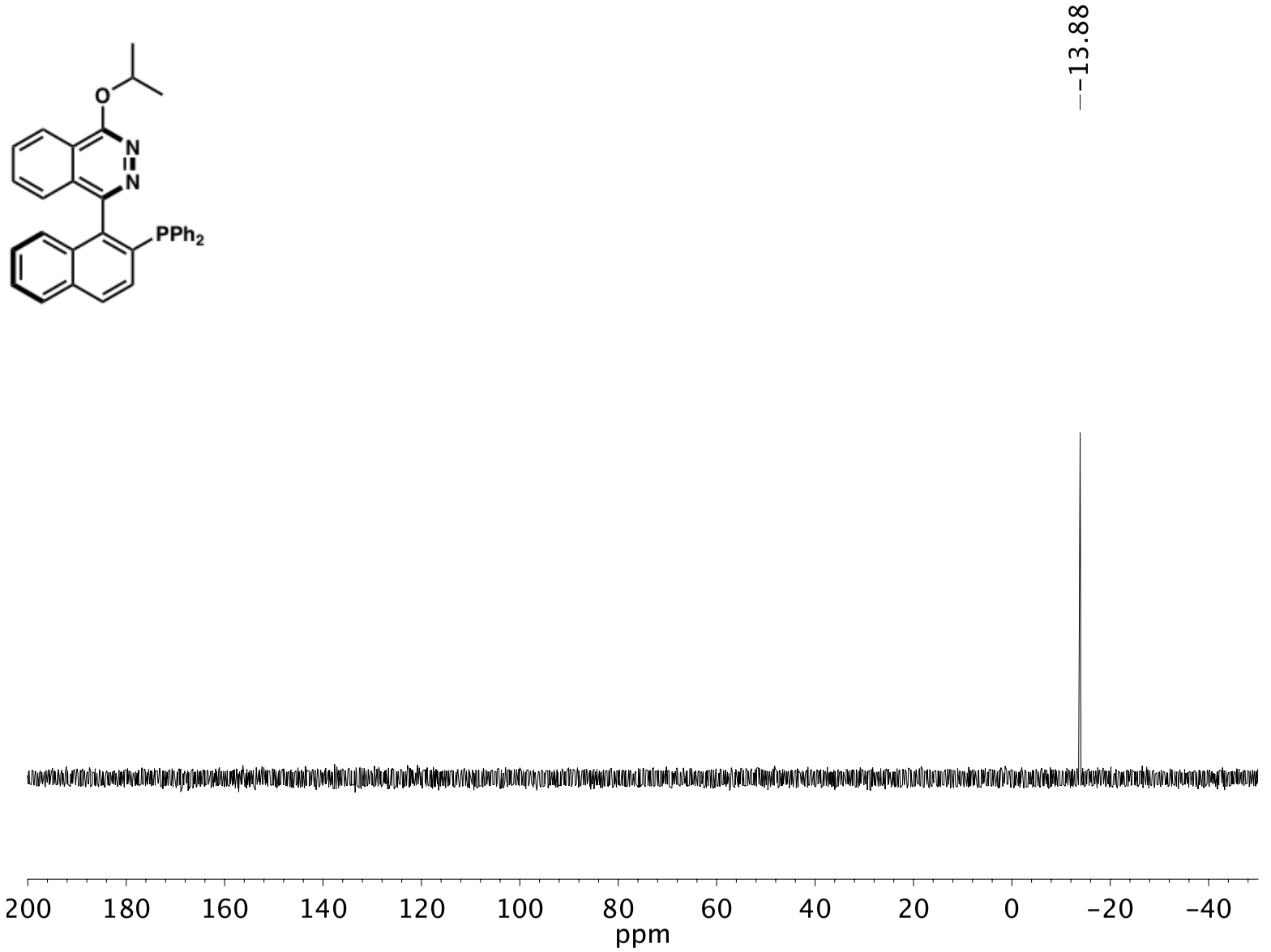




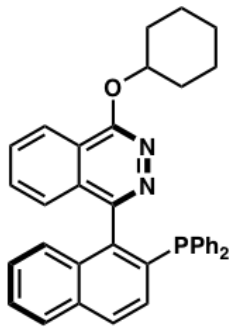
^{1}H NMR (500 MHz, $CDCl_3$) of compound **4c**.

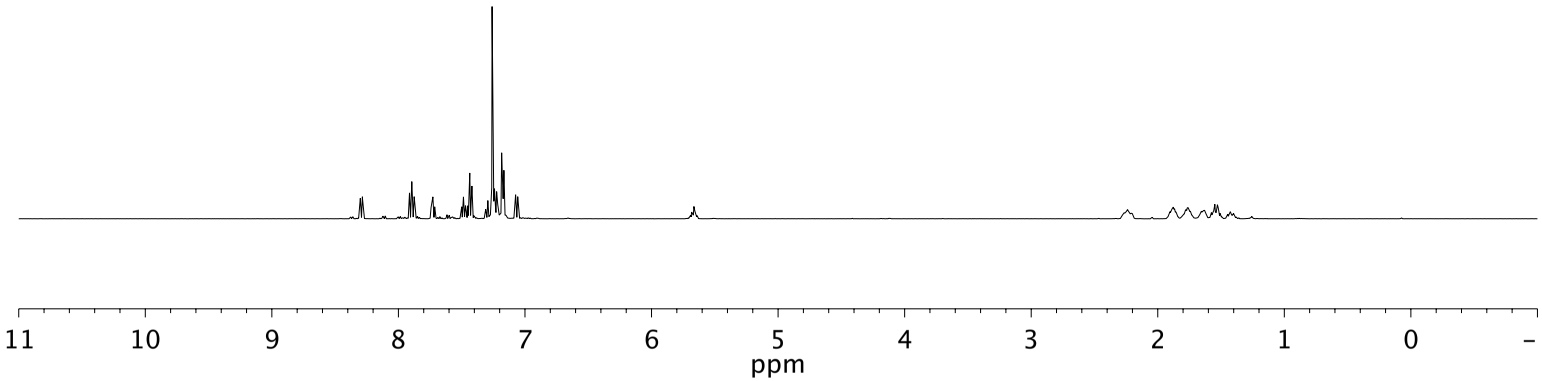


^{13}C NMR (126 MHz, $CDCl_3$) of compound **4c**.

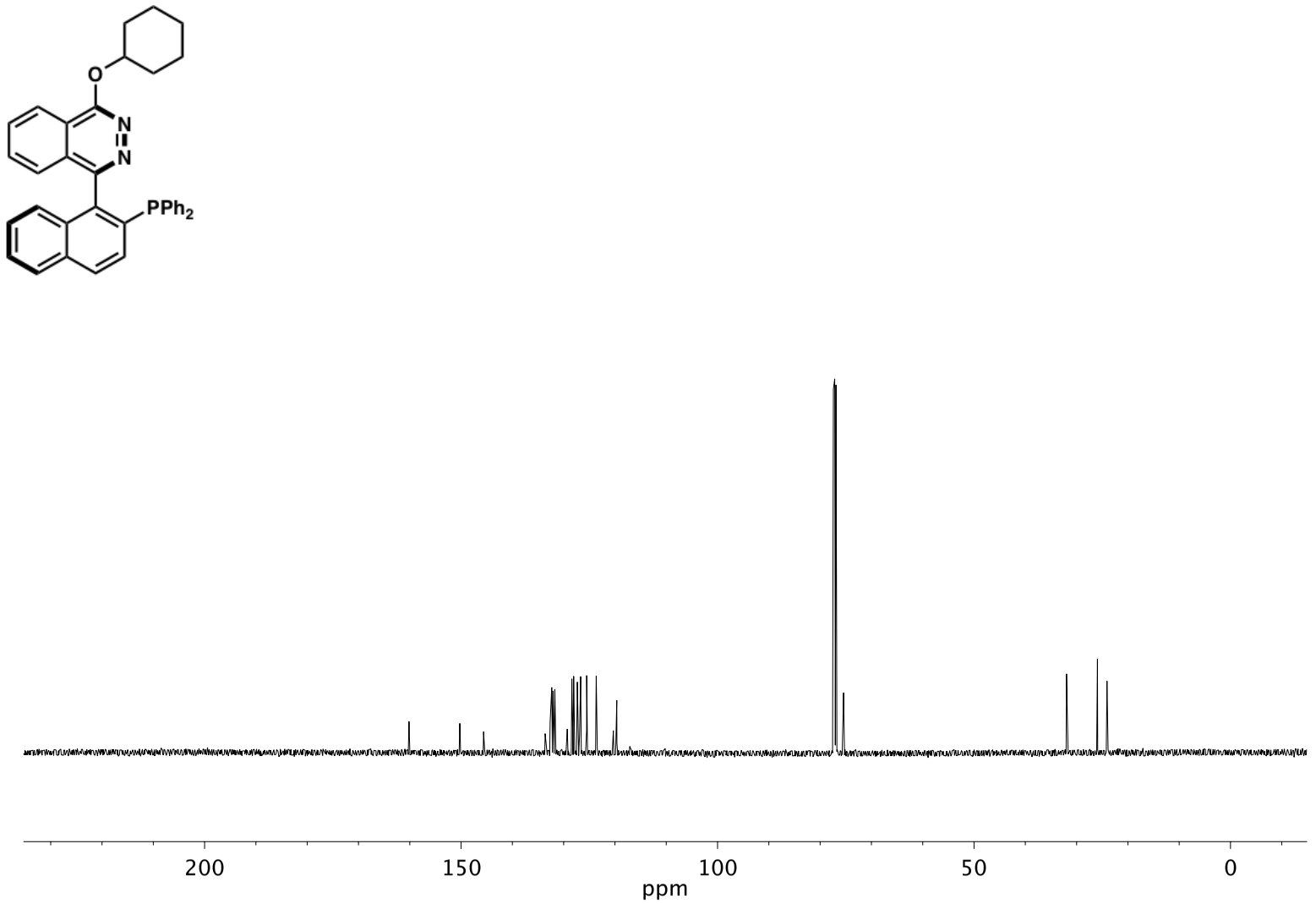


^{31}P NMR (121 MHz, $CDCl_3$) of compound **4c**.

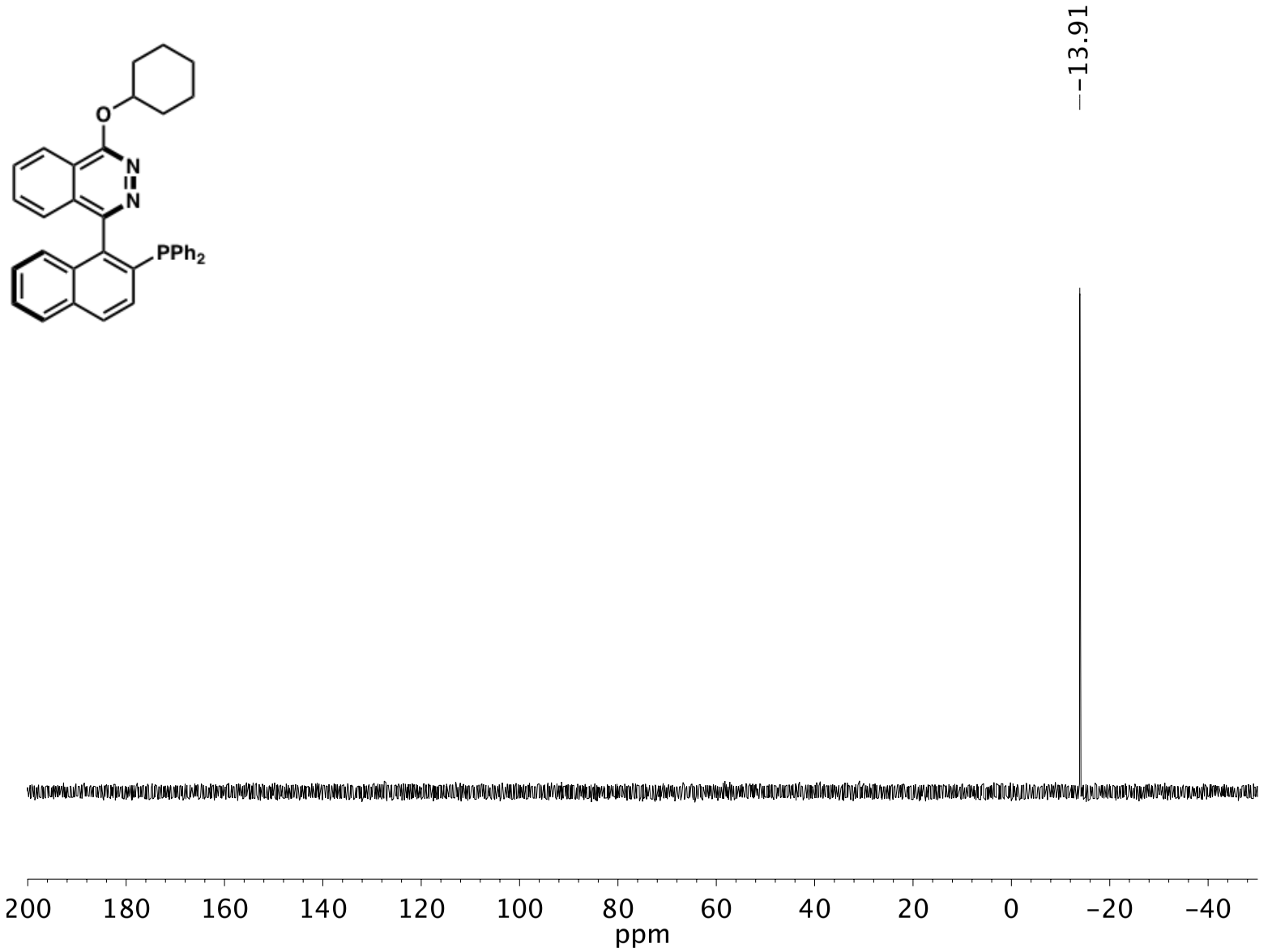




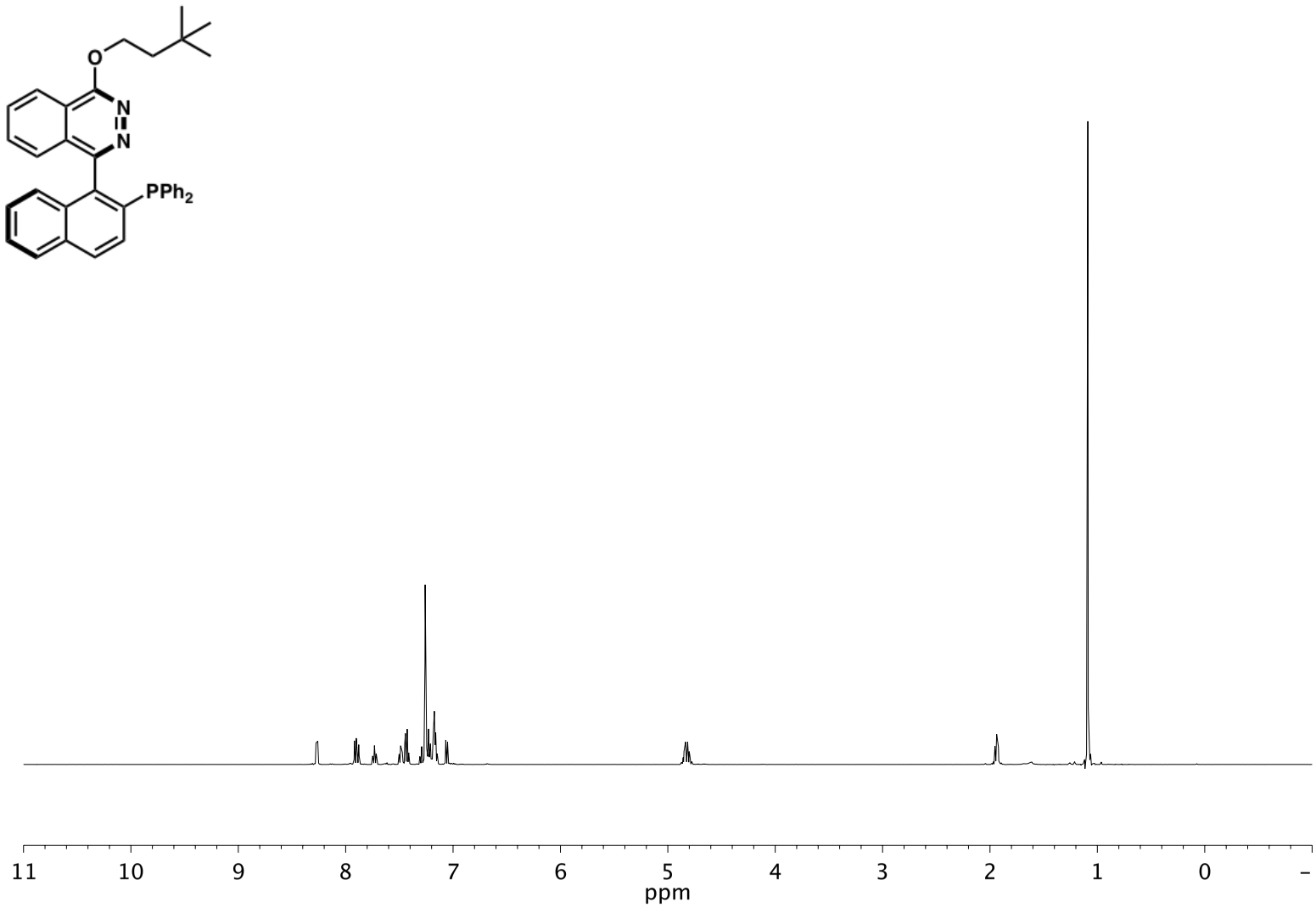
^{1}H NMR (500 MHz, $CDCl_3$) of compound **4d**.



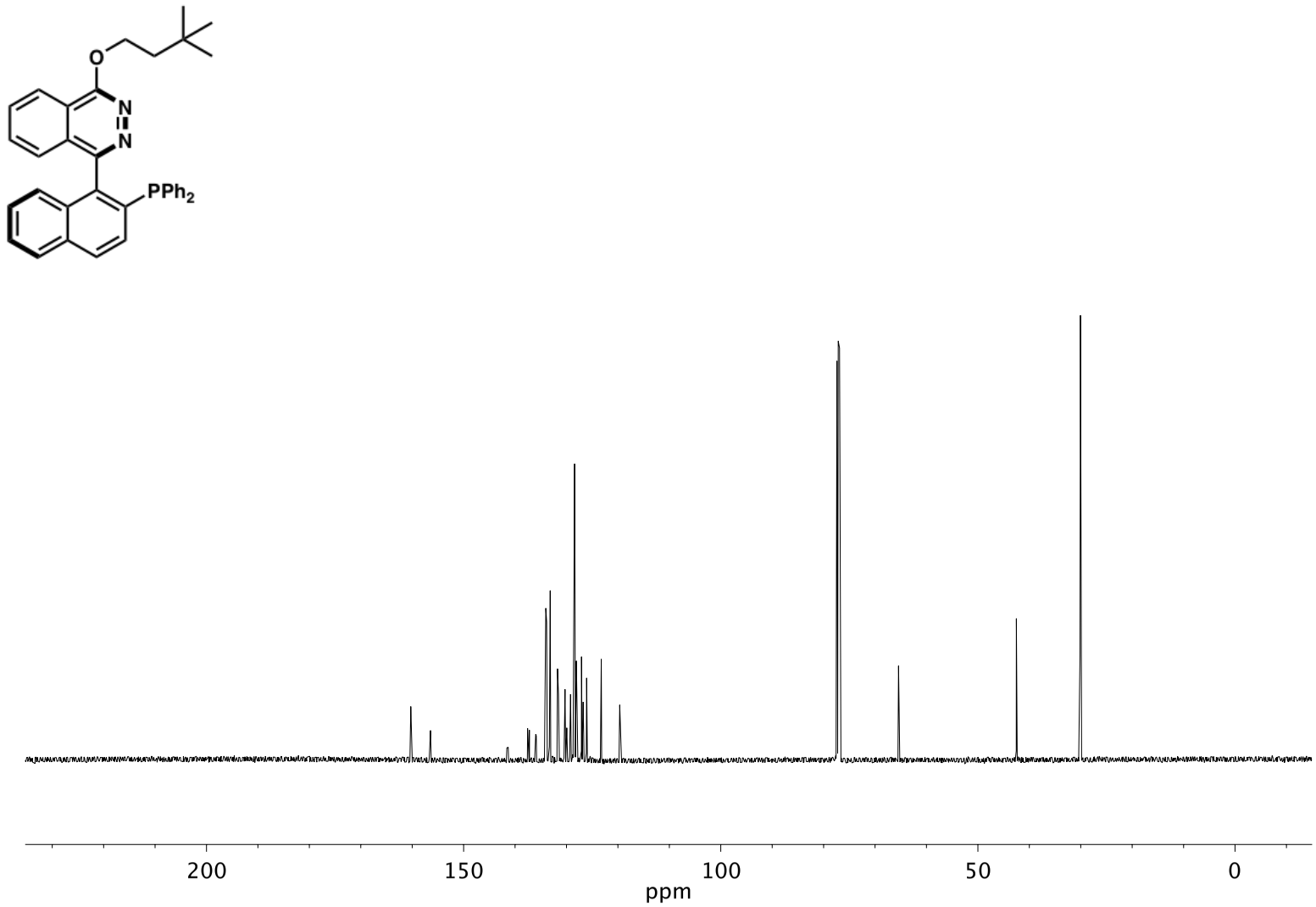
^{13}C NMR (126 MHz, $CDCl_3$) of compound **4d**.



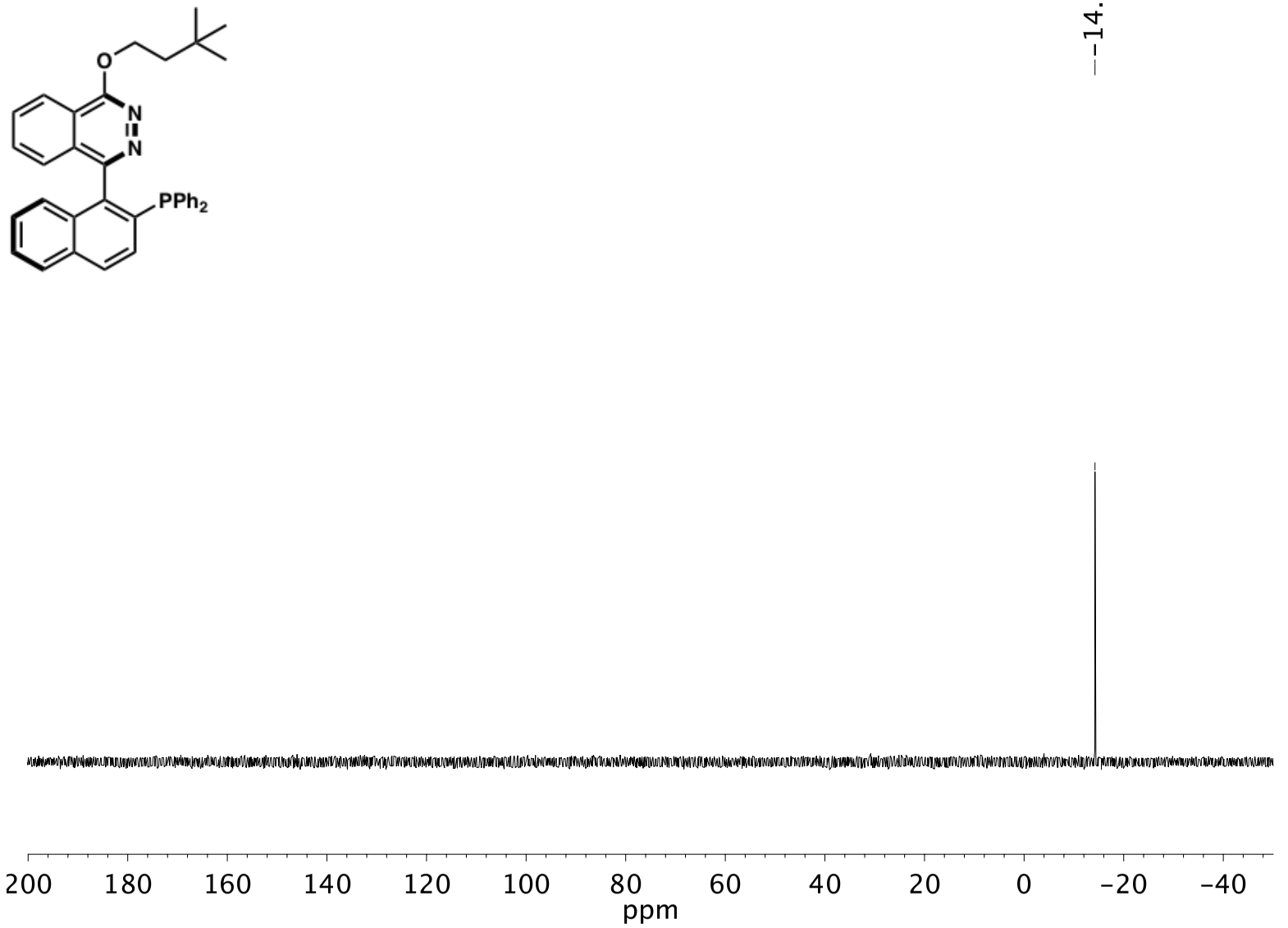
^{31}P NMR (121 MHz, $CDCl_3$) of compound **4d**.



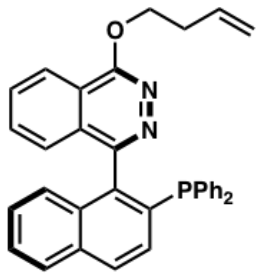
^{1}H NMR (500 MHz, $CDCl_3$) of compound **4e**.

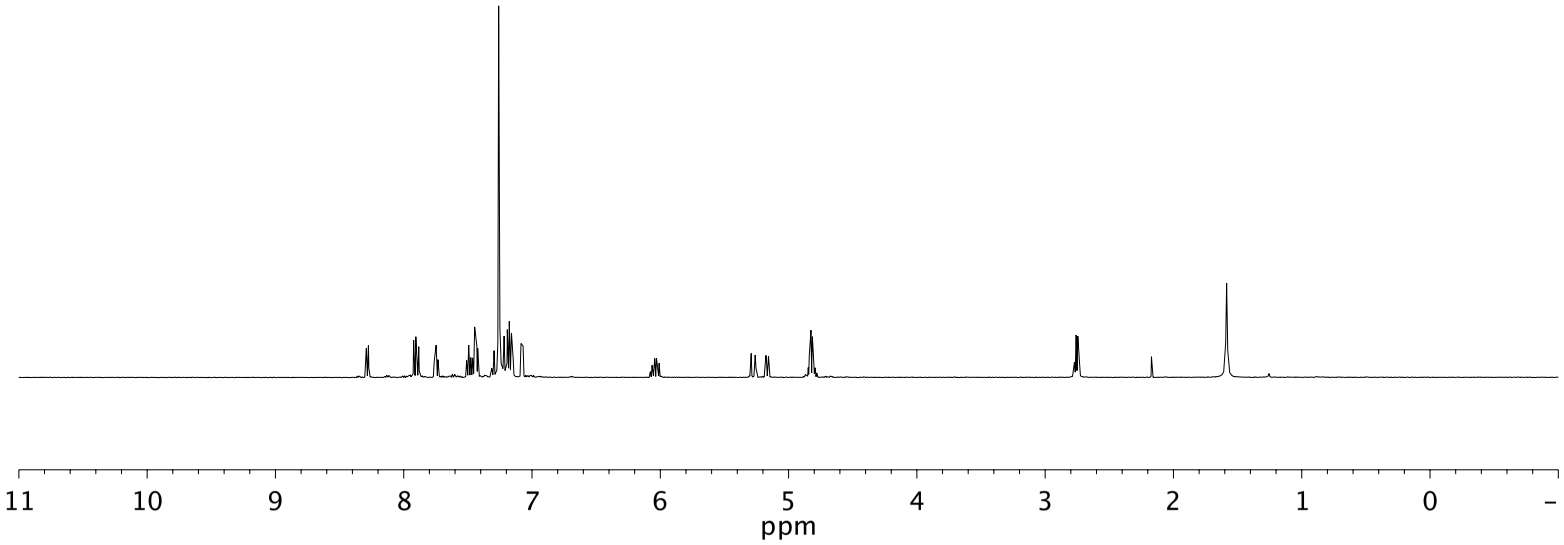


^{13}C NMR (126 MHz, $CDCl_3$) of compound **4e**.

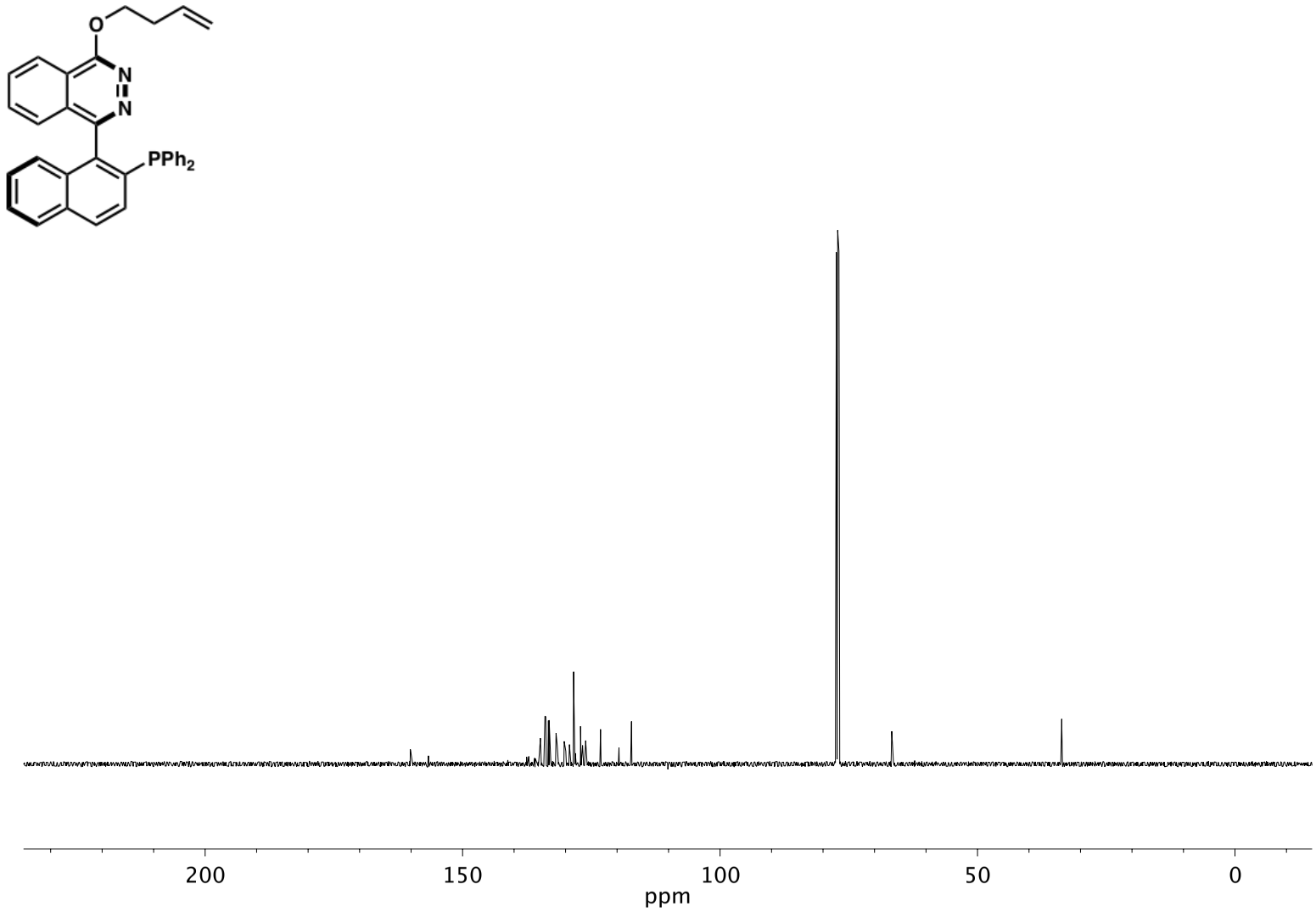


^{31}P NMR (121 MHz, $CDCl_3$) of compound **4e**.

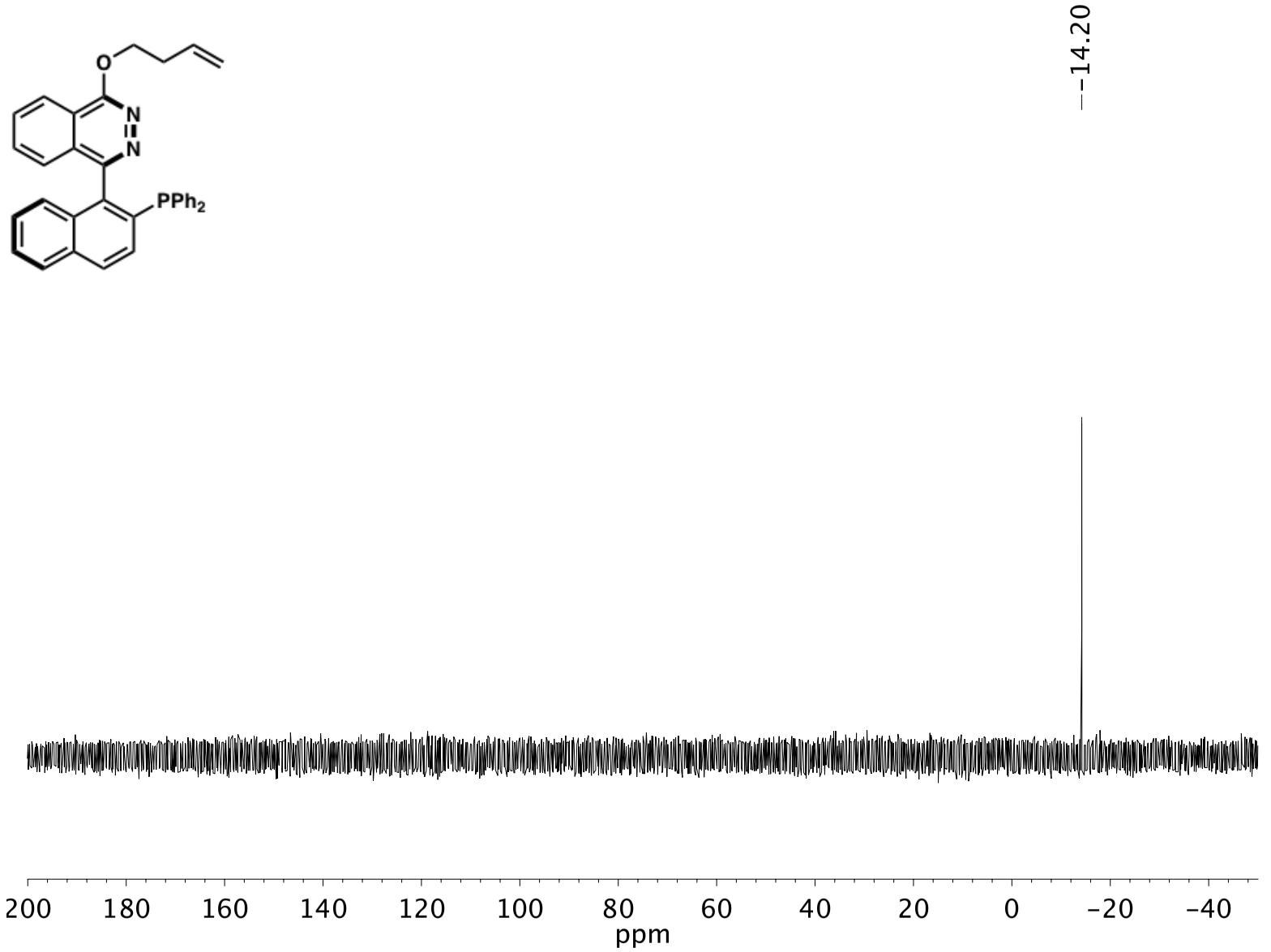




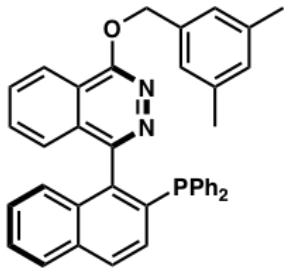
^{1}H NMR (500 MHz, $CDCl_3$) of compound **4f**.

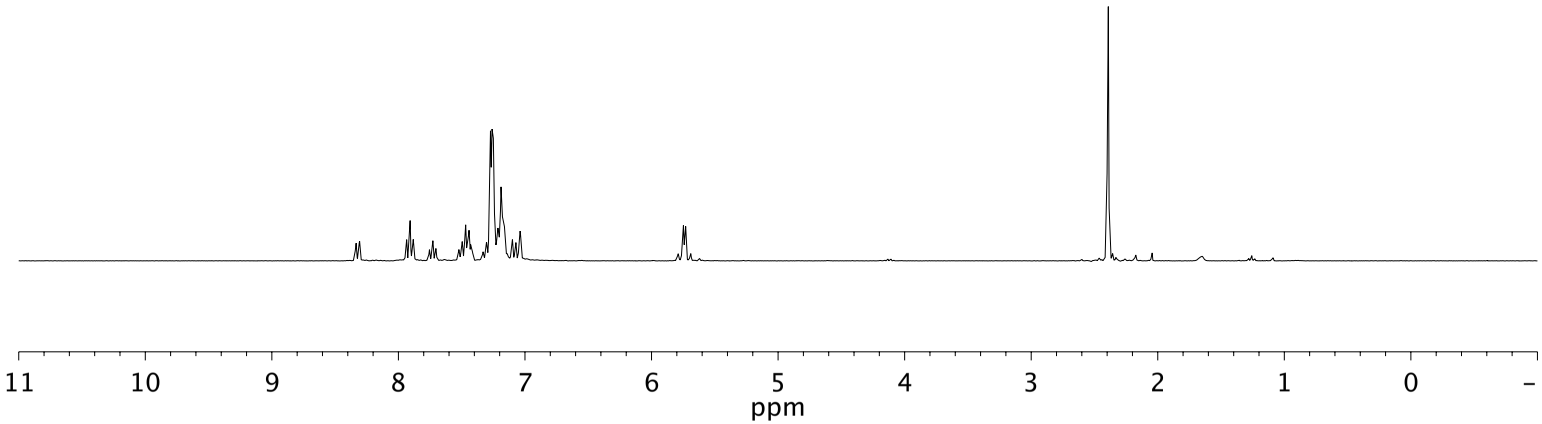


^{13}C NMR (126 MHz, $CDCl_3$) of compound **4f**.

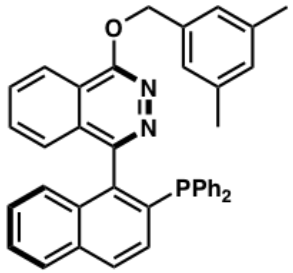


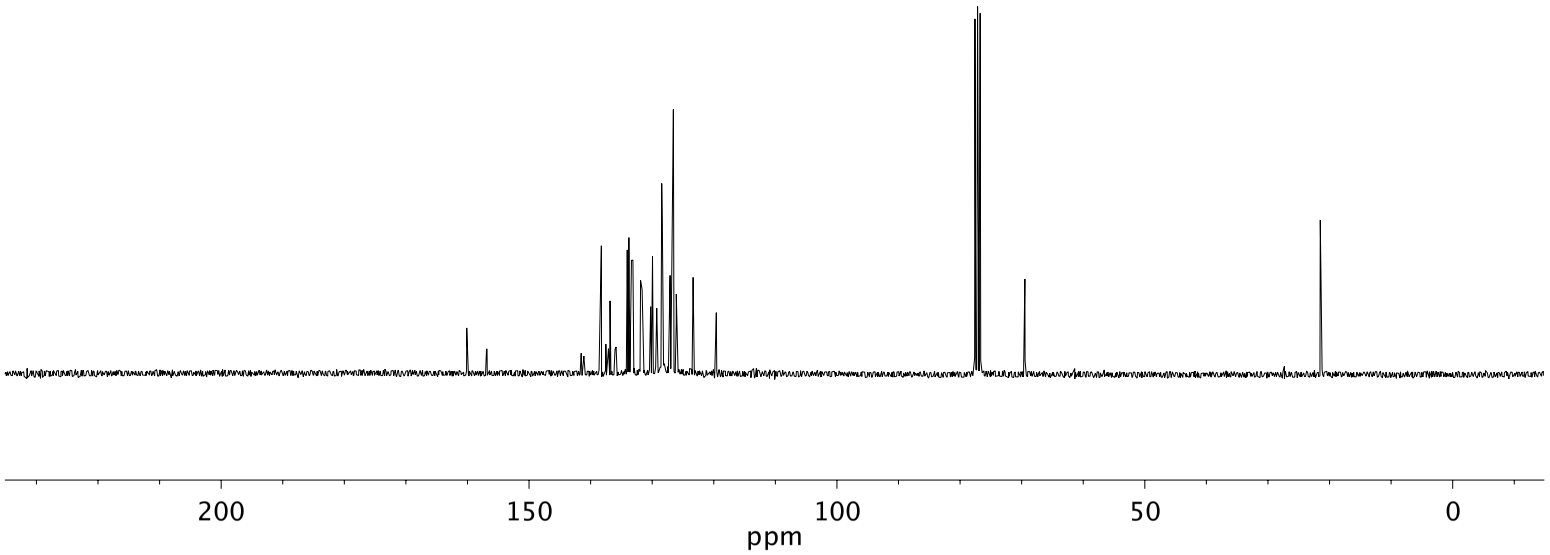
^{31}P NMR (121 MHz, $CDCl_3$) of compound **4f**.



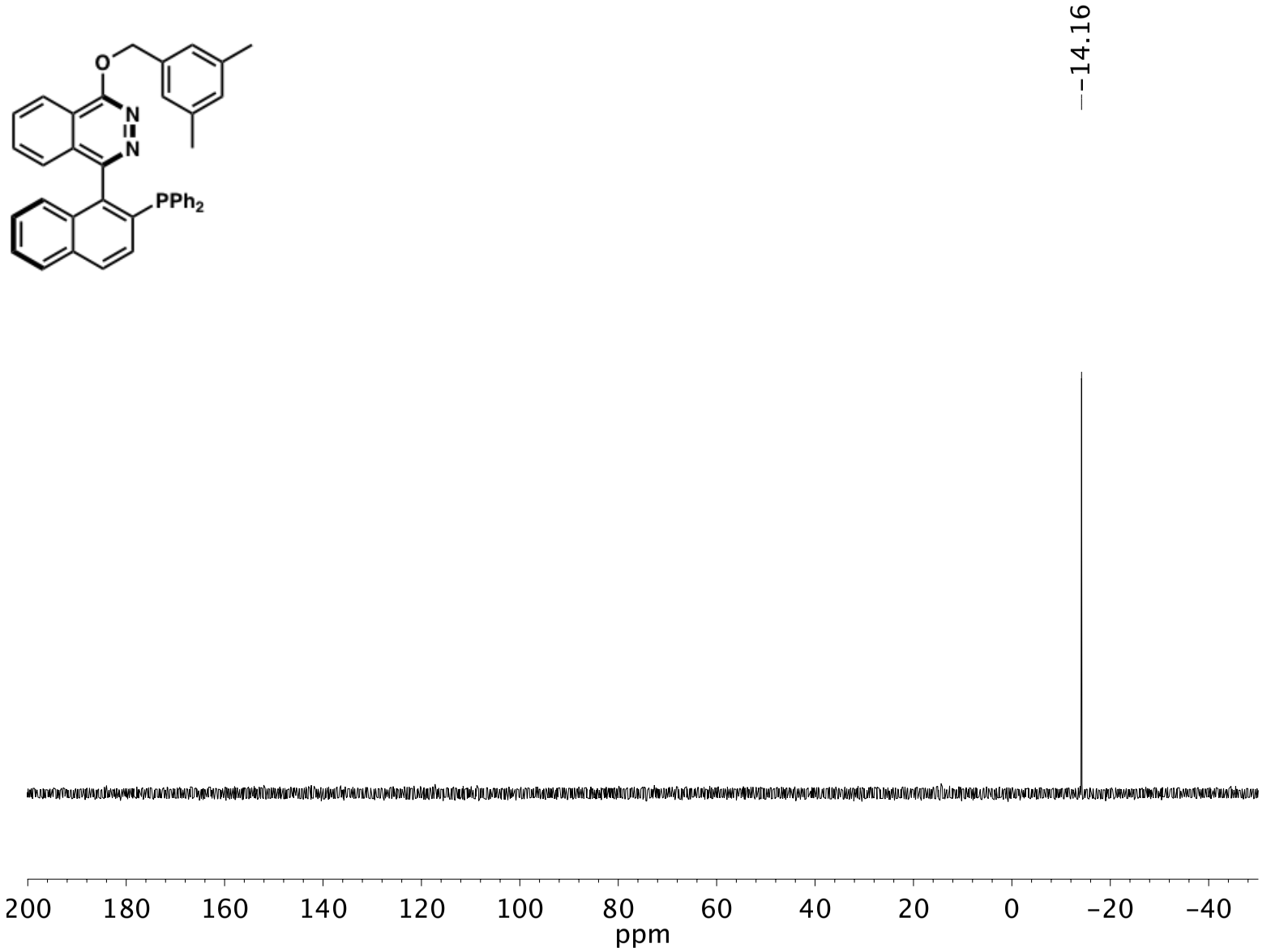


^{1}H NMR (500 MHz, $CDCl_3$) of compound **4g**.

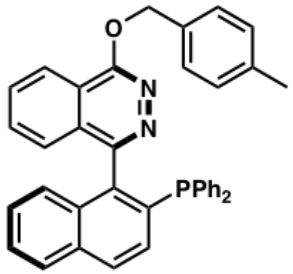


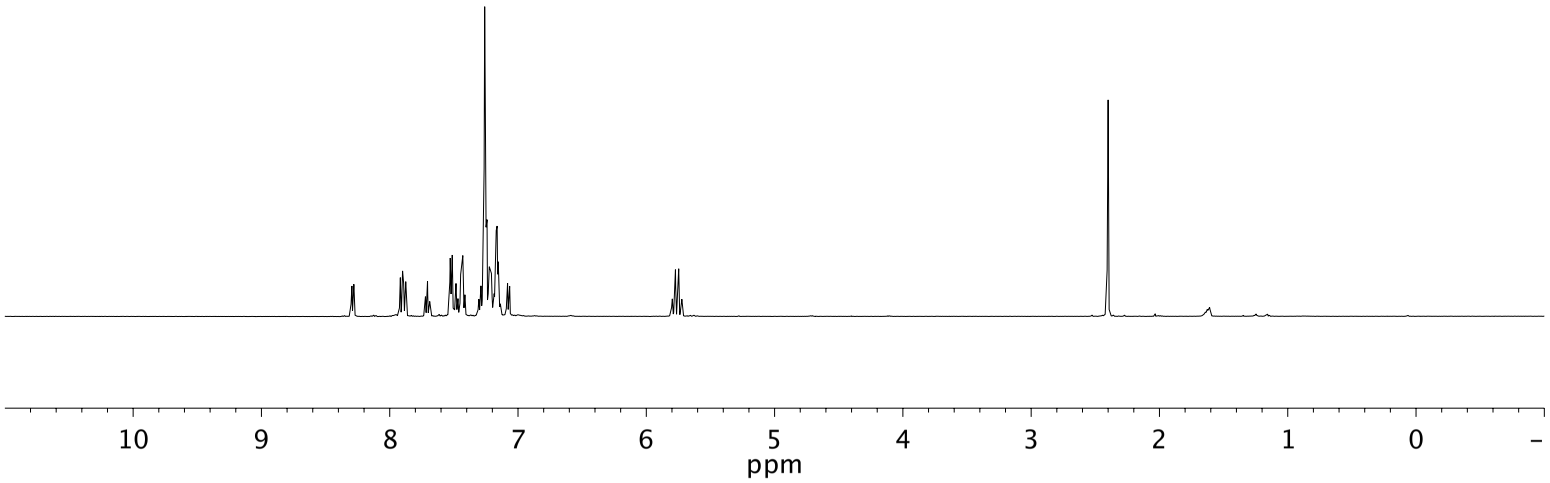


^{13}C NMR (126 MHz, $CDCl_3$) of compound **4g**.

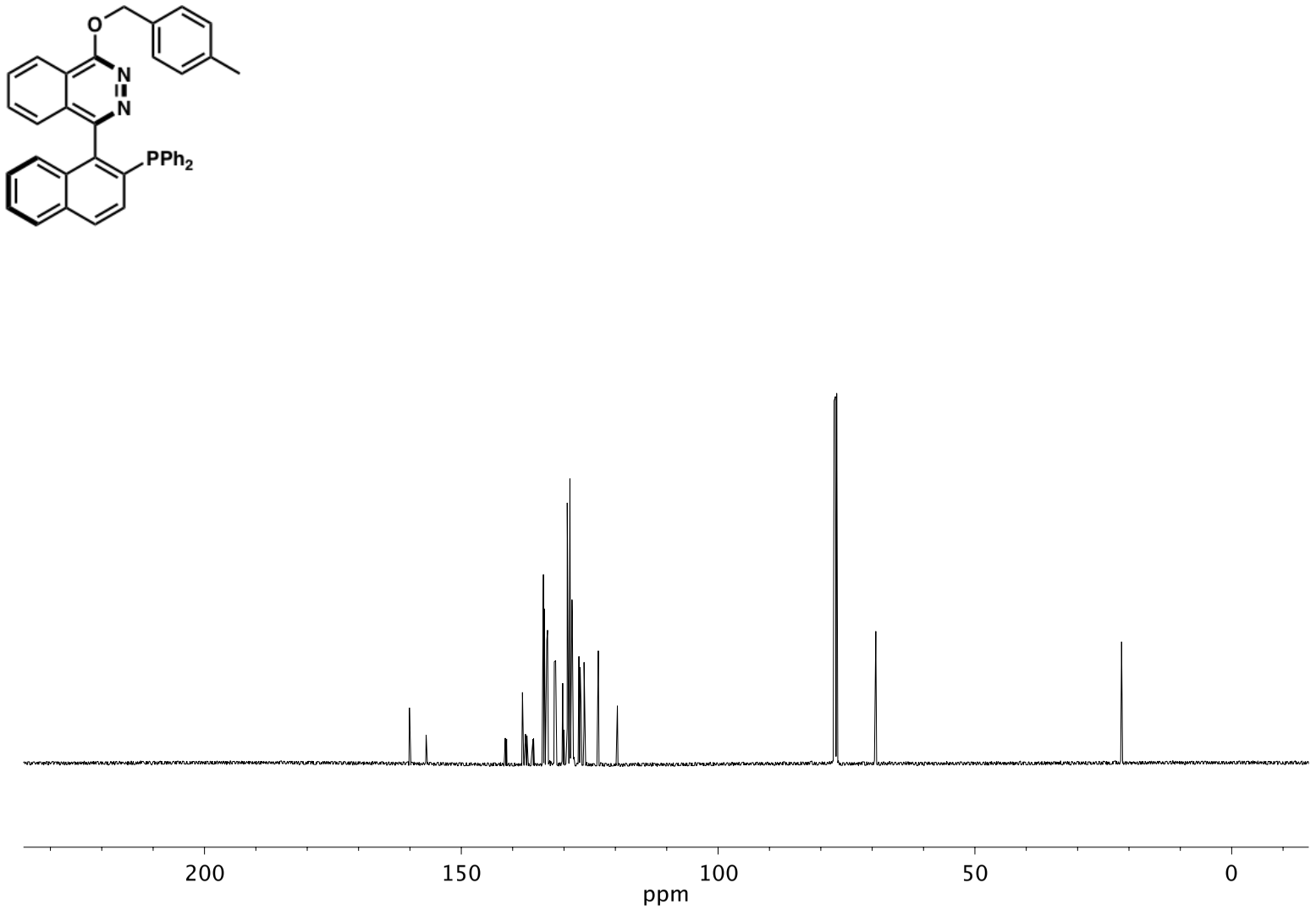


^{31}P NMR (121 MHz, $CDCl_3$) of compound **4g**.

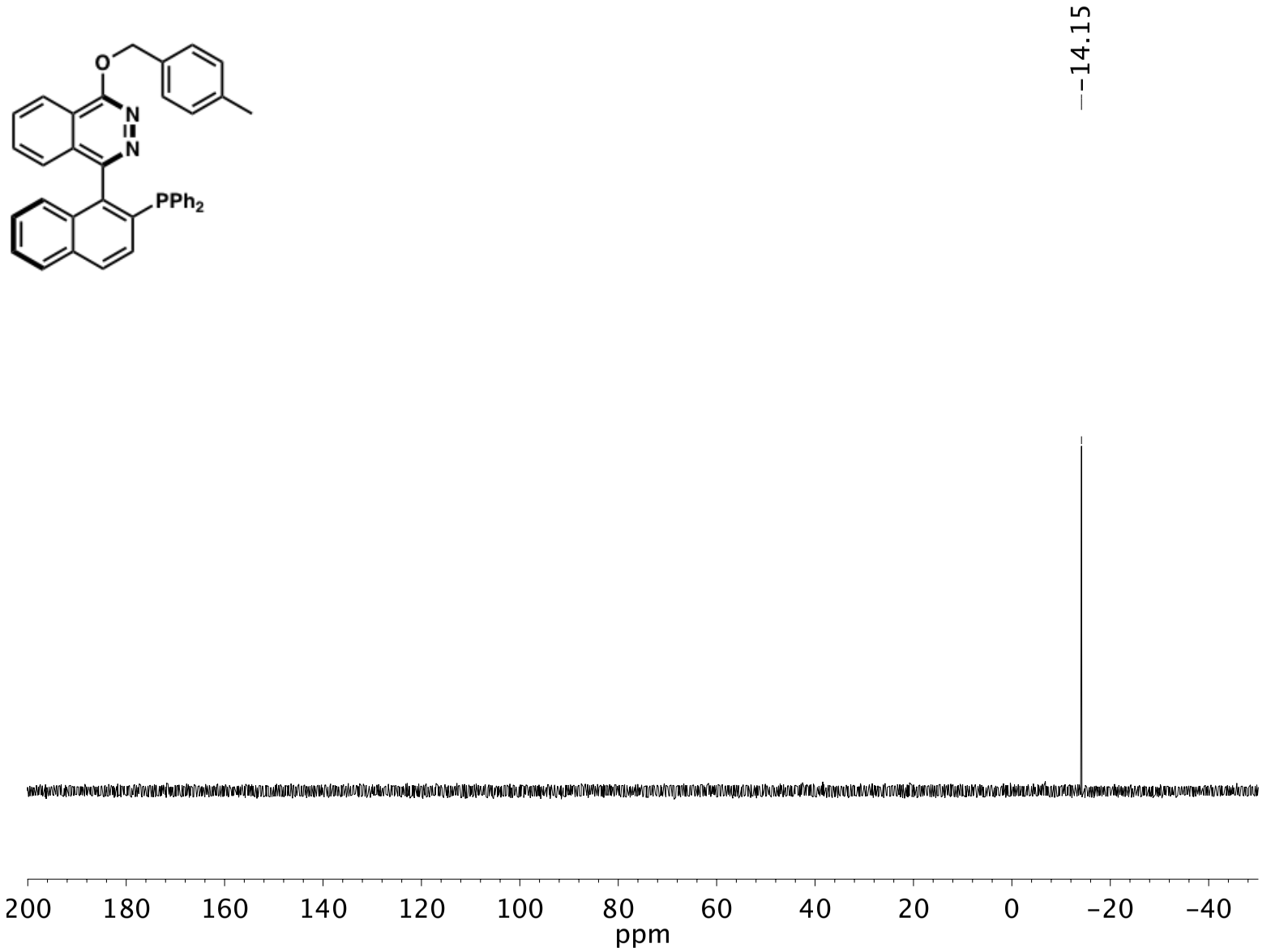




^{1}H NMR (500 MHz, $CDCl_3$) of compound **4h**.



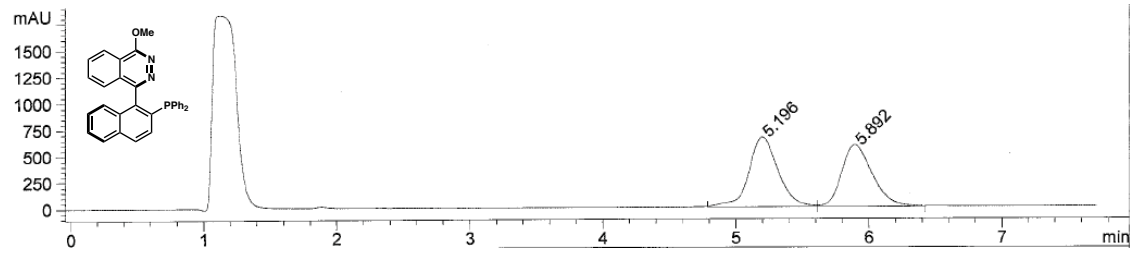
^{13}C NMR (126 MHz, $CDCl_3$) of compound **4h**.



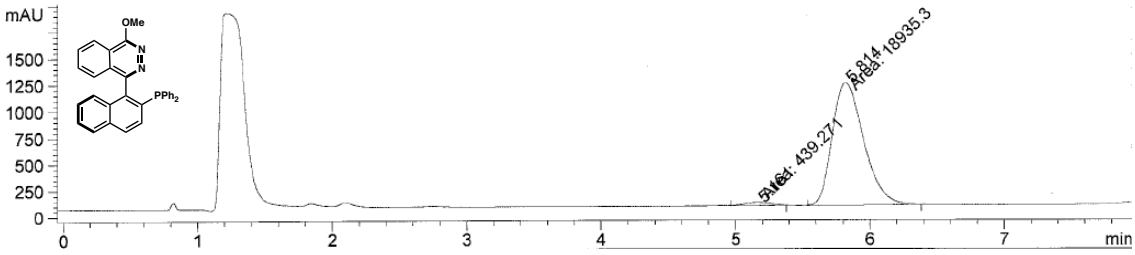
^{31}P NMR (121 MHz, $CDCl_3$) of compound **4h**.

Copies of SFC/HPLC spectra

(*R*)-1-(2-(diphenylphosphaneyl)naphthalen-1-yl)-4-methoxyphthalazine (**4a**)
SFC conditions: 35% IPA, 2.5mL/min, Chiralcel OD-H column, t_R (min): major = 5.81, minor = 5.16.

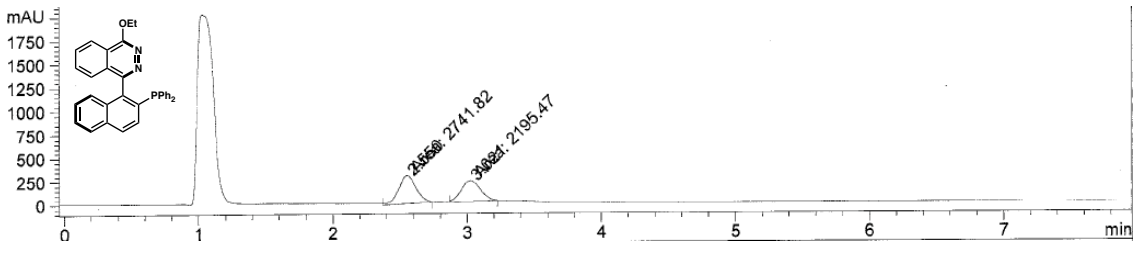


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.196	BV	0.2338	1.00925e4	662.16052	51.9047
2	5.892	VB	0.2468	9351.81543	583.98657	48.0953

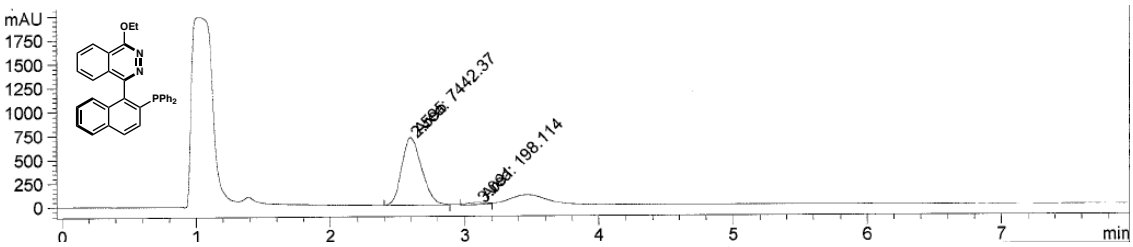


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	2.550	MM	0.1521	2741.81885	300.50073	55.5329
2	3.021	MM	0.1634	2195.46948	223.98593	44.4671

(*R*)-1-(2-(diphenylphosphaneyl)naphthalen-1-yl)-4-ethoxyphthalazine (**4b**)
SFC conditions: 30% MeOH, 2.5mL/min, Chiralpak AD-H column, t_R (min): major = 2.60, minor = 3.09.

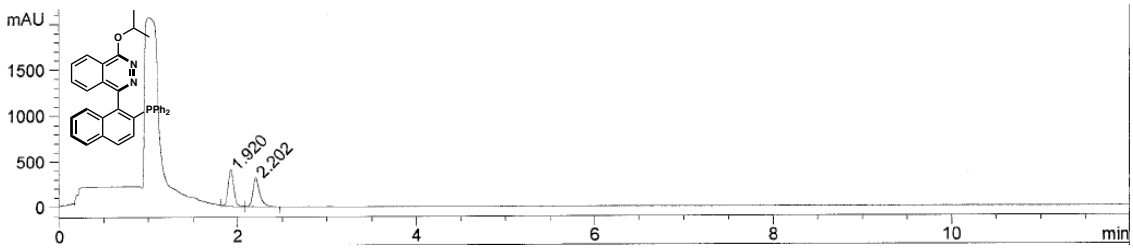


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	2.550	MM	0.1521	2741.81885	300.50073	55.5329
2	3.021	MM	0.1634	2195.46948	223.98593	44.4671

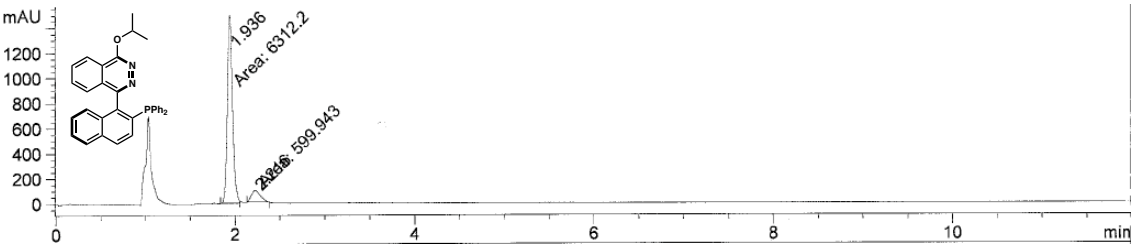


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	2.595	MM	0.1744	7442.37354	711.03772	97.4070
2	3.091	MM	0.1613	198.11423	20.46870	2.5930

(*R*)-1-(2-(diphenylphosphaneyl)naphthalen-1-yl)-4-isopropoxyphthalazine (**4c**)
SFC conditions: 40% MeOH, 2.5mL/min, Chiralpak AD-H column, t_R (min): major = 1.94, minor = 2.22.

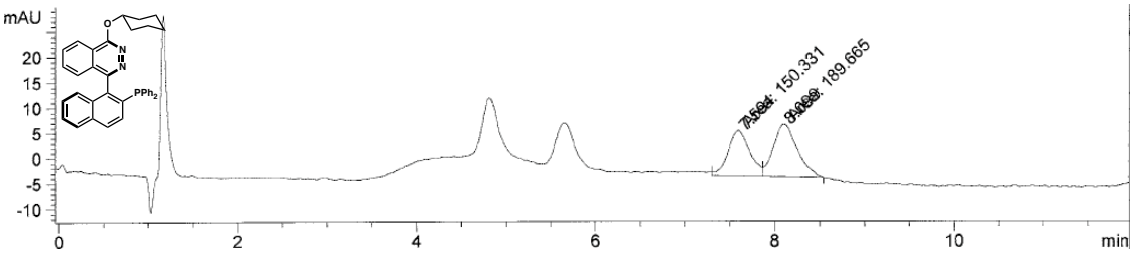


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	1.920	VV	0.0768	1785.10193	394.13144	51.5172
2	2.202	VB	0.0866	1679.95740	313.21683	48.4828

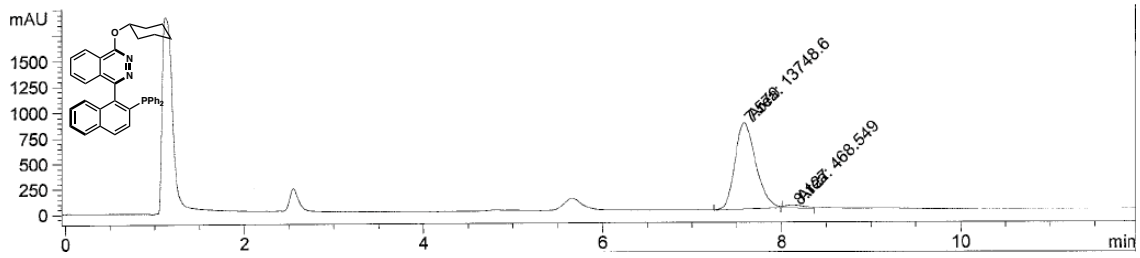


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	1.936	MM	0.0703	6312.20410	1497.13525	91.3204
2	2.216	MM	0.1102	599.94330	90.70389	8.6796

(*R*)-1-(cyclohexyloxy)-4-(2-(diphenylphosphaneyl)naphthalen-1-yl)phthalazine (**4d**)
SFC conditions: 25% MeOH, 2.5mL/min, Chiralcel OD-H column, t_R (min): major = 7.58, minor = 8.13.

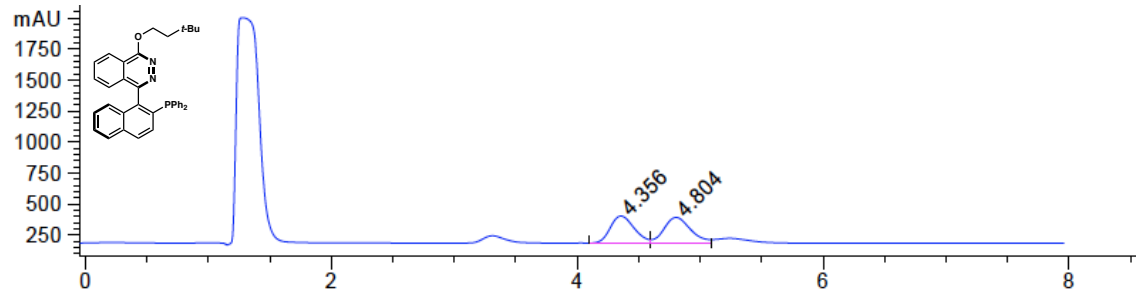


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.594	MF	0.2808	150.33107	8.92187	44.2155
2	8.099	FM	0.3050	189.66528	10.36333	55.7845

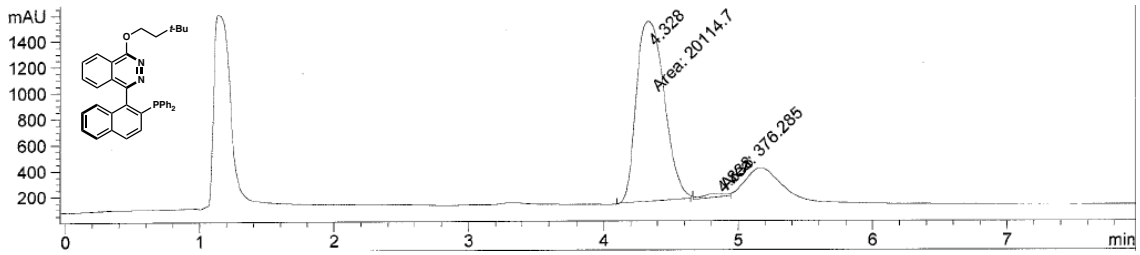


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.579	MM	0.2709	1.37486e4	845.92017	96.7044
2	8.127	MM	0.2481	468.54892	31.47503	3.2956

(*R*)-1-(3,3-dimethylbutoxy)-4-(2-(diphenylphosphaneyl)naphthalen-1-yl)phthalazine (**4e**) SFC conditions: 35% IPA, 2.5mL/min, Chiralcel OD-H column, t_R (min): major = 4.33, minor = 4.84.



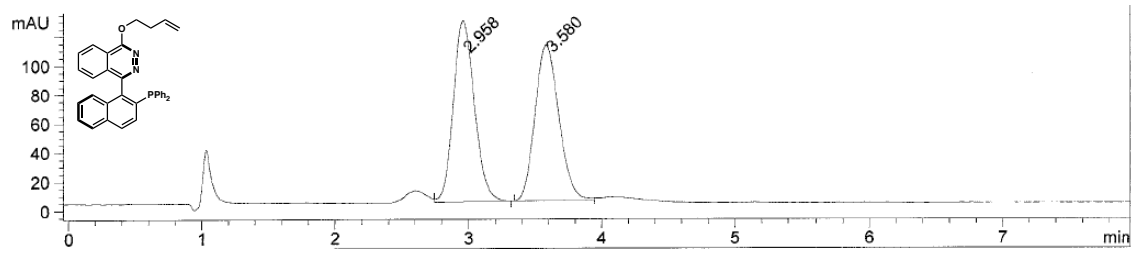
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.356	BV	0.2138	2953.75537	218.43739	48.5644
2	4.804	VV	0.2321	3128.38086	207.24126	51.4356



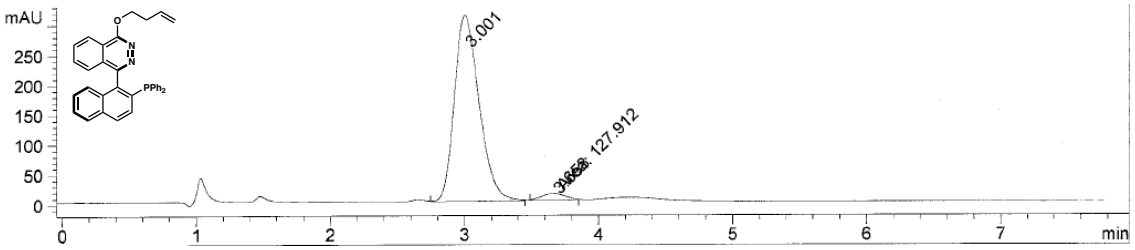
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.328	MM	0.2414	2.01147e4	1388.95361	98.1637
2	4.838	MM	0.1996	376.28491	31.41685	1.8363

(*R*)-1-(but-3-en-1-yloxy)-4-(2-(diphenylphosphaneyl)naphthalen-1-yl)phthalazine (**4f**) SFC conditions: 35% MeOH, 2.5mL/min, Chiralpak AD-H column, t_R (min): major =

3.00, minor = 3.66.



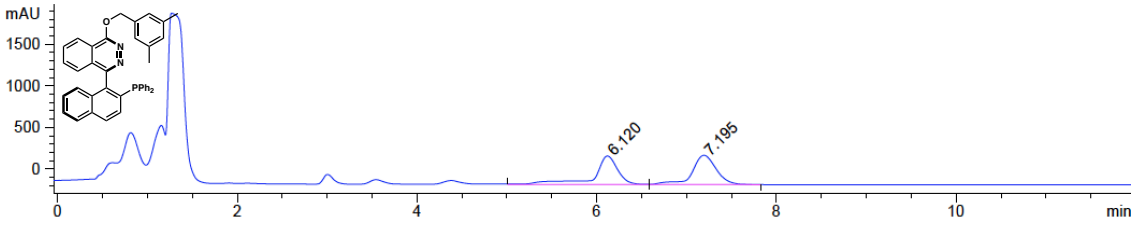
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	2.958	VB	0.1725	1371.77686	124.52699	50.7194
2	3.580	BB	0.1937	1332.85999	106.76146	49.2806



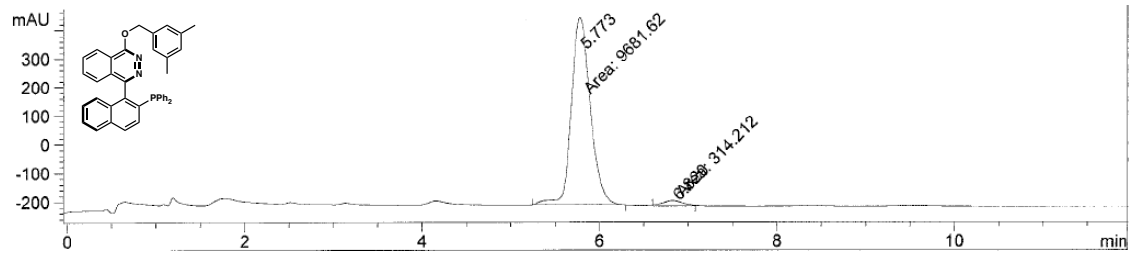
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.001	VV	0.2011	3975.26660	311.00824	96.8826
2	3.658	MM	0.1991	127.91221	10.70956	3.1174

(*R*)-1-((3,5-dimethylbenzyl)oxy)-4-(2-(diphenylphosphaneyl)naphthalen-1-yl)phthalazine (**4g**)

SFC conditions: 40% MeOH, 2.5mL/min, Chiralcel OD-H column, t_R (min): major = 5.77, minor = 6.82.



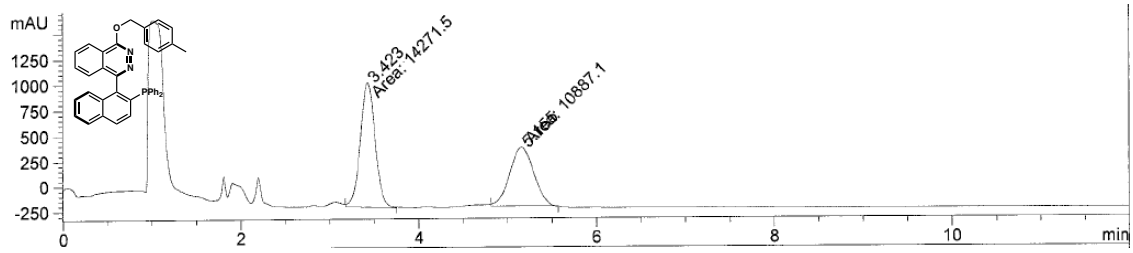
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.120	VV	0.2697	6394.47949	342.69516	49.3689
2	7.195	VV	0.2807	6557.97656	353.05951	50.6311



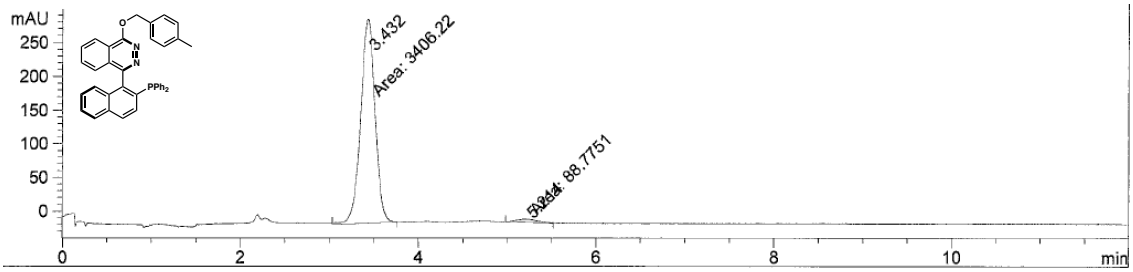
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.773	MM	0.2476	9681.61914	651.68408	96.8566
2	6.820	MM	0.2737	314.21243	19.13087	3.1434

(*R*)-1-(2-(diphenylphosphaneyl)naphthalen-1-yl)-4-((4-methylbenzyl)oxy)phthalazine (**4h**)

SFC conditions: 40% MeOH, 2.5mL/min, Chiralpak AD-H column, t_R (min): major = 3.43, minor = 5.21.



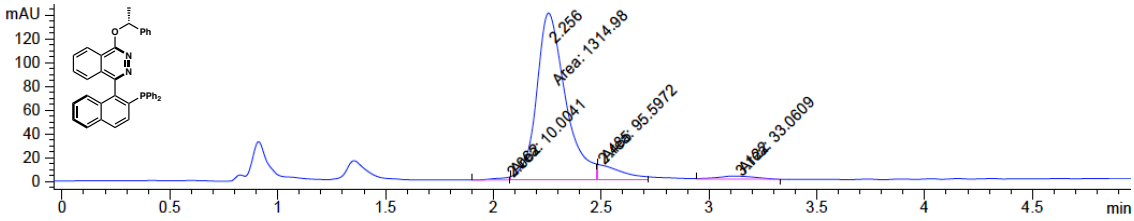
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.423	MM	0.1945	1.42715e4	1223.03918	56.7261
2	5.155	MM	0.3141	1.08871e4	577.68909	43.2739



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.432	MM	0.1881	3406.21655	301.85727	97.4599
2	5.214	MM	0.2921	88.77509	5.06575	2.5401

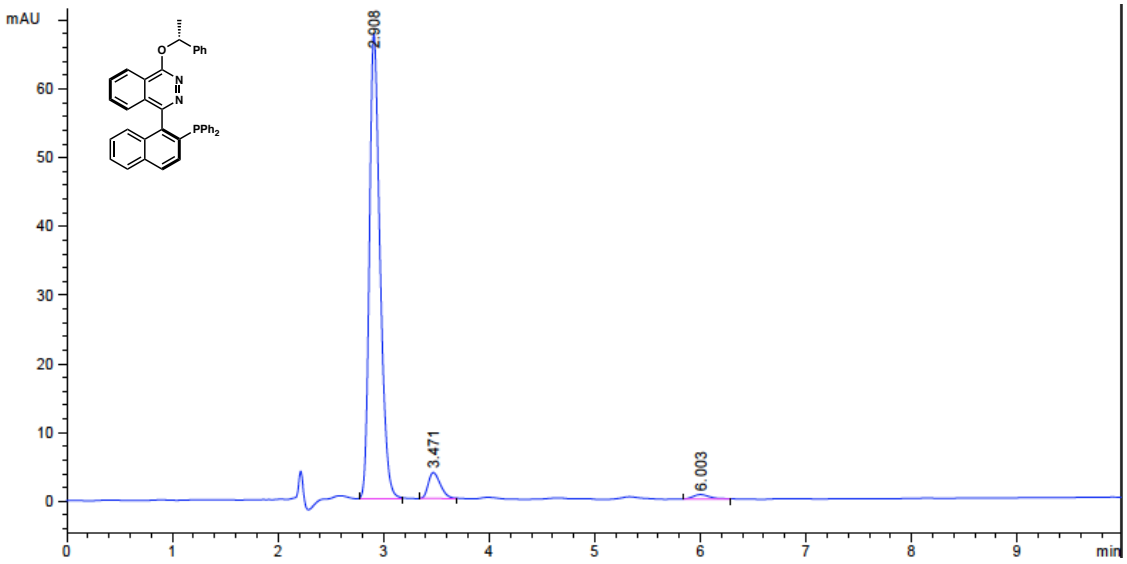
1-((*R*)-2-(diphenylphosphaneyl)naphthalen-1-yl)-4-((*R*)-1-phenylethoxy)phthalazine (**4i**)

SFC conditions: 40% IPA, 2.5 mL/min, Chiralpak OD-H column, tR (min): major = 2.26, minor = 3.12.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	2.062	MM	0.0871	10.00407	1.91379	0.6882
2	2.256	MM	0.1553	1314.98193	141.13321	90.4611
3	2.485	MM	0.1229	95.59724	12.96553	6.5764
4	3.122	MM	0.2031	33.06094	2.71275	2.2743

1-(2-(diphenylphosphaneyl)naphthalen-1-yl)-4-((*R*)-1-phenylethoxy)phthalazine (**2a**)
HPLC conditions: 5% IPA/hexane, 1.5 mL/min, Chiralpak OD-H column, tR (min): major = 2.91, minor = 3.47. (prior to crystallization)



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	2.908	BB	0.1061	471.78455	67.68509	92.6210
2	3.471	BB	0.1237	30.24422	3.78954	5.9376
3	6.003	BB	0.1750	7.34233	6.45293e-1	1.4415