Supporting Information

Asymmetric Synthesis of Functionalized 2,3-Dihydrobenzofurans by using Salicyl *N*-Phosphonyl Imines Facilitated by Group-Assisted Purification (GAP) Chemistry

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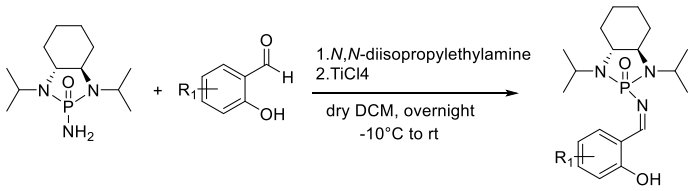
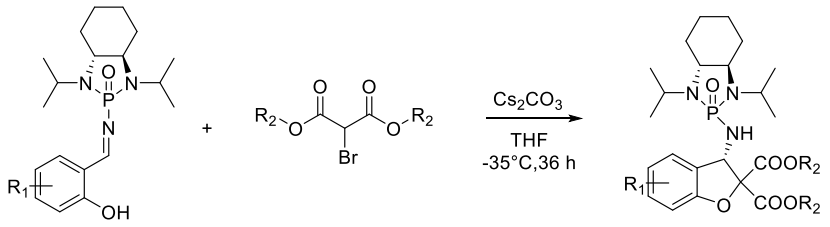
EXPERIMENTAL SECTION

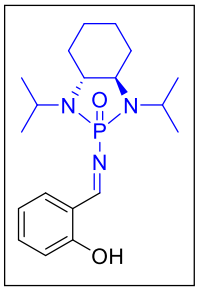
General Aspects. All commercially available chemicals were used as received without further purification. Solvents were obtained as follows: ether, dichloromethane, tetrahydrofuran, and toluene were delivered from an Innovation Technology solvent system. All reactions were carried out in a flame-dried flask under nitrogen gas. The ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ on a 400 MHz instrument with TMS as the internal standard. Chemical shifts (δ) were reported in ppm with respect to TMS. Data are represented as follows: chemical shift, mutiplicity (s = singlet, d = doublet, t = triplet, m = multiplet), coupling constant (J, Hz), and integration. ^{31}P NMR spectra were referenced to external H_3PO_4 (0.00 ppm). Shifts in ^{19}F NMR spectra were reported based on an external hexafluorobenzene reference. HRMS analyses were carried out using a TOF-MS instrument with an ESI source.

General synthesis of salicyl *N*-phosphonyl imine (1a-1n): Into an oven-dried round bottom flask, flushed and protected by argon, phosphoramide (1g, 3.85 mmol) and salicylaldehyde (5.78 mmol) were dissolved in 40 ml dry dichloromethane. After 5 minutes, the mixture was cooled to -10^{o} C, followed by drop-wise addition of diisopropylethylamine (11.56 mmol) and $TiCl_4$ in DCM (1M, 3.08 mmol). The reaction stirred at -10^{o}C for 30 minutes and room temperature overnight. Next, the mixture was concentrated to 5 ml by rotary evaporation in vacuo. The resultatnt solution was passed through a pad of silica gel, eluted with Hexanes: Ethyl acetate (v/v 7:3 to 3:7) to provide salicyl *N*-phosphonyl imine as a yellow solid.

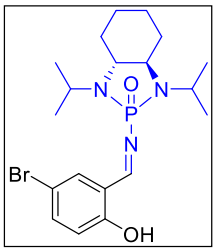


Synthesis and characterization of 2,3-dihydrobenzofuran (3a-3t): Into an oven-dried round bottom flask, flushed and protected by argon, salicyl N-phosphonyl imine (1 mmol) was dissolved in freshly dried THF. The reaction was cooled to -35^{o}C and after 5 minutes Cs_2CO_3 (2 mmol) was added, and reaction stirred at same temperature for 20 minutes. Next, dialkyl bromo malonate (2 mmol) dissolved in 1 ml dry THF was added drop wise, and reaction stirred at -35^{o}C for 36 hours. Reaction was quenched by addition of 5 ml water and extracted with Ethyl acetate. Organic layer was extracted with brine and dried over Na_2SO_4. After that, the solution was concentrated before addition of hexanes and stirring the reaction overnight to precipitate the product. Solid Pure product was obtained by filtration and washing the solid product few times with hexanes.

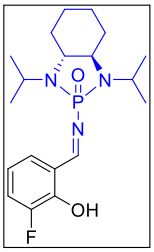




(3aR,7aR)-2-((2-hydroxybenzylidene)amino)-1,3-diisopropyloctahydrobenzo[d][1,3,2]diazaphosphole 2-oxide **(1a).** Yellow solid, 0.981 g, 70% yield; $[\alpha]_D^{25}$ +10.6 (c 0.45, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 9.09 (d, J = 29.0 Hz, 1H), 7.45 – 7.36 (m, 2H), 7.00 – 6.88 (m, 2H), 3.46 – 3.26 (m, 2H), 3.11 – 3.02 (m, 1H), 2.90 (td, J = 10.4, 3.1 Hz, 1H), 2.14 – 1.92 (m, 2H), 1.80 (d, J = 6.4 Hz, 2H), 1.40 – 1.27 (m, 3H), 1.27 – 1.14 (m, 10H), 1.09 (d, J = 6.7 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.50 (s), 175.44 (s), 162.84 (d, J = 1.9 Hz), 135.04 (s), 133.94 (s), 119.28 (s), 117.62 (s), 60.01 (d, J = 2.5 Hz), 59.92 (d, J = 2.4 Hz), 45.09 (d, J = 3.3 Hz), 44.49 (d, J = 3.6 Hz), 29.85 (d, J = 9.7 Hz), 29.57 (d, J = 9.5 Hz), 24.41 – 24.31 (m), 21.98 (d, J = 3.7 Hz), 21.21 (s), 21.19 (s), 20.85 (s), 20.38 (d, J = 1.5 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 21.81. ; HRMS (TOF ES+) m/z calcd for $C_{19}H_{30}N_3O_2P$ $[(M + H)^+]$, 364.207; found, 364.216

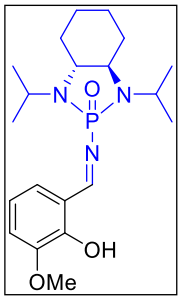


(3aR,7aR)-2-((5-bromo-2-hydroxybenzylidene)amino)-diisopropyloctahydrobenzo[d][1,3,2]diazaphosphole 2-oxide **(1b).**Yellow solid, 1.16 g, 68% yield; $[\alpha]_D^{25}$ +16 (c 0.45, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 9.01 (d, J = 28.4 Hz, 1H), 7.52 (d, J = 2.5 Hz, 1H), 7.47 (dd, J = 8.8, 2.4 Hz, 1H), 6.88 (d, J = 8.9 Hz, 1H), 3.46 – 3.28 (m, 2H), 3.16 – 3.01 (m, 1H), 2.96 – 2.79 (m, 1H), 2.11 – 2.03 (m, 2H), 1.82 (d, J = 7.2 Hz, 2H), 1.44 – 1.30 (m, 3H), 1.27 – 1.16 (m, 10H), 1.09 (d, J = 6.7 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.70 (d, J = 6.1 Hz), 161.93 (d, J = 1.9 Hz), 137.60 (s), 135.68 (s), 120.46 (d, J = 20.0 Hz), 119.76 (s), 110.68 (d, J = 1.3 Hz), 60.03 (d, J = 6.9 Hz), 59.94 (d, J = 7.2 Hz), 45.18 (d, J = 3.2 Hz), 44.54 (d, J = 3.5 Hz), 29.78 (d, J = 9.7 Hz), 29.55 (d, J = 9.4 Hz), 24.34 (s), 21.97 (s), 21.94 (s), 21.19 (d, J = 2.8 Hz), 20.85 (d, J = 1.3 Hz), 20.45 (d, J = 1.5 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 21.44. ; HRMS (TOF ES+) m/z calcd for $C_{19}H_{29}BrN_3O_2P$ $[(M + H)^+]$, 443.118; found, 442.127

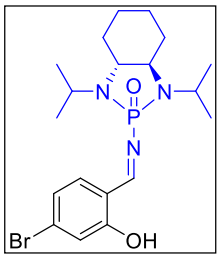


(3aR,7aR)-2-((3-fluoro-2-hydroxybenzylidene)amino)-1,3diisopropyloctahydrobenzo[d][1,3,2]diazaphosphole 2-oxide **(1c).** Yellow solid, 0.941 g, 64% yield;

$[\alpha]_D^{25}$ -10.7 (c 0.40, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 9.07 (dd, J = 27.3, 1.2 Hz, 1H), 7.24 – 7.16 (m, 2H), 6.90 – 6.75 (m, 1H), 3.48 – 3.27 (m, 2H), 3.12 – 3.01 (m, 1H), 2.98 – 2.87 (m, 1H), 2.06 (t, J = 10.6 Hz, 2H), 1.81 (d, J = 7.1 Hz, 2H), 1.34 (td, J = 11.8, 6.3 Hz, 4H), 1.26 – 1.16 (m, 10H), 1.09 (dd, J = 14.7, 6.7 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.46 (dd, J = 5.8, 2.8 Hz), 152.75 (dd, J = 13.0, 1.9 Hz), 150.40 (d, J = 0.8 Hz), 128.72 (d, J = 3.6 Hz), 120.79 (d, J = 17.5 Hz), 120.57 (d, J = 4.2 Hz), 118.15 (d, J = 6.3 Hz), 60.10 (d, J = 6.2 Hz), 60.01 (d, J = 6.1 Hz), 45.12 (d, J = 3.4 Hz), 44.55 (d, J = 3.7 Hz), 29.82 (d, J = 9.7 Hz), 29.55 (d, J = 9.4 Hz), 24.34 (d, J = 1.1 Hz), 22.06 (s), 22.03 (s), 21.23 (d, J = 2.7 Hz), 20.85 (d, J = 1.5 Hz), 20.45 (d, J = 1.5 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 21.75 ; HRMS (TOF ES+) m/z calcd for $C_{19}H_{29}FN_3O_2P$ [$(M + H)^+$], 382.198; found, 382.206

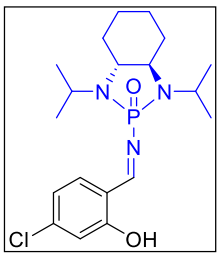


(3aR,7aR)-2-((2-hydroxy-3-methoxybenzylidene)amino)-1,3-diisopropyloctahydrobenzo[d][1,3,2]diazaphosphole 2-oxide **(1d).**Yellow solid, 0.951 g, 68% yield; $[\alpha]_D^{25}$ -12.5 (c 0.40, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 9.06 (d, J = 27.2 Hz, 1H), 7.04 (d, J = 7.9 Hz, 1H), 7.01 – 6.95 (m, 1H), 6.84 (t, J = 7.9 Hz, 1H), 3.90 (s, 3H), 3.49 – 3.27 (m, 2H), 3.12 – 3.02 (m, 1H), 2.93 (dd, J = 13.4, 6.2 Hz, 1H), 2.08 (d, J = 18.5 Hz, 2H), 1.81 (d, J = 8.4 Hz, 2H), 1.43 – 1.28 (m, 3H), 1.26 – 1.17 (m, 10H), 1.11 (d, J = 6.7 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.15 (d, J = 6.2 Hz), 157.37 (s), 152.34 (s), 152.33 (s), 123.26 (s), 118.62 (s), 115.74 (s), 60.03 (d, J = 1.6 Hz), 59.94 (d, J = 1.6 Hz), 55.96 (s), 45.10 (d, J = 3.3 Hz), 44.51 (d, J = 3.6 Hz), 29.85 (d, J = 9.8 Hz), 29.55 (d, J = 9.4 Hz), 24.36 (dd, J = 2.2, 1.3 Hz), 22.00 (s), 21.96 (s), 21.19 (d, J = 2.7 Hz), 20.88 (d, J = 1.3 Hz), 20.40 (d, J = 1.3 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) 20.90 ; HRMS (TOF ES+) m/z calcd for $C_{20}H_{32}N_3O_3P$ [$(M + H)^+$], 394.218 ; found, 394.226

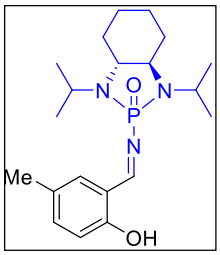


(3aR,7aR)-2-((4-bromo-2-hydroxybenzylidene)amino)-1,3-diisopropyloctahydrobenzo[d][1,3,2]diazaphosphole 2-oxide **(1e).**Yellow solid, 1.14 g, 67% yield; $[\alpha]_D^{25}$ -12.5(c 0.4, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 9.02 (d, J = 28.0 Hz, 1H), 7.24 (d, J = 8.3 Hz, 1H), 7.13 (d, J = 1.7 Hz, 1H), 7.03 (dd, J = 8.3, 1.8 Hz, 1H), 3.45 – 3.27 (m, 2H), 3.11 – 3.01 (m, 1H), 2.94 – 2.83 (m, 1H), 2.04 (d, J = 10.7 Hz, 2H), 1.80 (d, J = 6.2 Hz, 2H), 1.42 – 1.29 (m, 3H), 1.21 (dd, J = 14.3, 6.9 Hz, 11H), 1.08 (d, J = 6.7 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.31 (d, J = 6.0 Hz), 163.92 (s), 134.74 (s), 129.92 (s), 122.70 (s), 121.21 (d, J = 0.8 Hz), 118.00 (d, J = 19.5 Hz), 60.04 (d, J = 2.2 Hz), 59.95 (d, J = 2.0 Hz), 45.12 (d, J = 3.3 Hz), 44.49 (d, J = 3.7 Hz), 29.82 (d, J = 9.8 Hz), 29.51 (d, J = 9.5 Hz), 24.36 – 24.30 (m), 22.01 (s), 21.97 (s), 21.17 (d, J = 2.8 Hz), 20.85 (d, J = 1.4 Hz), 20.39 (d, J = 1.5 Hz); ^{31}P NMR

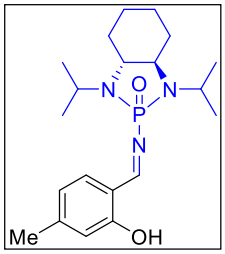
(162 MHz, $CDCl_3$) 21.29 ; HRMS (TOF ES+) m/z calcd for $C_{19}H_{29}BrN_3O_2P$ [(M + H)$^+$], 442.118; found, 442.127



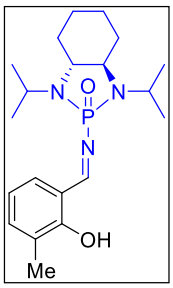
(3aR,7aR)-2-((4-chloro-2-hydroxybenzylidene)amino)-1,3-diisopropyloctahydrobenzo[d][1,3,2]diazaphosphole 2-oxide **(1f).**Yellow solid, 1.04 g, 68% yield; $[\alpha]_D^{25}$ +8.88 (c 0.45, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ ^{1}H NMR (400 MHz, CHLOROFORM-D) δ 9.03 (d, J = 28.0 Hz, 1H), 7.32 (d, J = 8.3 Hz, 1H), 6.96 (d, J = 2.0 Hz, 1H), 6.87 (dd, J = 8.3, 1.9 Hz, 1H), 3.44 – 3.26 (m, 2H), 3.11 – 3.01 (m, 1H), 2.95 – 2.83 (m, 1H), 2.12 – 1.98 (m, 2H), 1.80 (d, J = 6.4 Hz, 2H), 1.42 – 1.25 (m, 3H), 1.26 – 1.12 (m, 11H), 1.09 (d, J = 6.7 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.12 (d, J = 5.9 Hz), 164.11 (d, J = 1.9 Hz), 141.26 (s), 134.71 (s), 119.85 (s), 118.10 (d, J = 0.7 Hz), 117.71 (d, J = 19.6 Hz), 60.04 (d, J = 2.2 Hz), 59.95 (d, J = 2.0 Hz), 45.12 (d, J = 3.3 Hz), 44.49 (d, J = 3.6 Hz), 29.83 (d, J = 9.7 Hz), 29.52 (d, J = 9.5 Hz), 25.34 – 23.53 (m), 22.01 (s), 21.97 (s), 21.17 (d, J = 2.8 Hz), 20.86 (d, J = 1.4 Hz), 20.39 (d, J = 1.5 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) 21.33 ; HRMS (TOF ES+) m/z calcd for $C_{19}H_{29}ClN_3O_2P$ [(M + H)$^+$], 398.168; found, 398.177



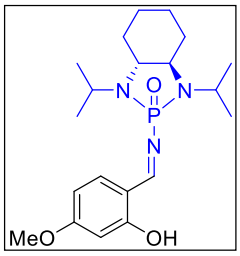
(3aR,7aR)-2-((2-hydroxy-5-methylbenzylidene)amino)-1,3-diisopropyloctahydrobenzo[d][1,3,2]diazaphosphole 2-oxide **(1g).**Yellow solid, 1.03 g, 71% yield; $[\alpha]_D^{25}$ +16.6 (c 0.45, $CHCl_3$); ^{1}H NMR (400 MHz, CDCl3) δ 9.05 (d, J = 29.1 Hz, 1H), 7.24 – 7.17 (m, 2H), 6.87 (d, J = 8.2 Hz, 1H), 3.46 – 3.26 (m, 2H), 3.13 – 3.01 (m, 1H), 2.88 (td, J = 10.0, 3.1 Hz, 1H), 2.28 (s, 3H), 2.15 (s, 1H), 2.04 (dd, J = 11.0, 6.2 Hz, 2H), 1.80 (d, J = 6.7 Hz, 2H), 1.35 (dd, J = 13.6, 5.5 Hz, 3H), 1.26 – 1.15 (m, 10H), 1.09 (d, J = 6.7 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.37 (d, J = 6.4 Hz), 160.69 (d, J = 2.2 Hz), 136.09 (s), 133.68 (s), 128.43 (d, J = 1.1 Hz), 118.89 (d, J = 20.1 Hz), 117.41 (d, J = 1.2 Hz), 60.00 (d, J = 1.6 Hz), 59.91 (d, J = 1.5 Hz), 45.09 (d, J = 3.6 Hz), 44.50 (d, J = 3.8 Hz), 29.83 (d, J = 9.8 Hz), 29.58 (d, J = 9.5 Hz), 24.64 – 23.72 (m), 21.95 (s), 21.91 (s), 21.19 (d, J = 3.0 Hz), 20.85 (d, J = 1.8 Hz), 20.39 (s), 20.37 (s); ^{31}P NMR (162 MHz, $CDCl_3$) 22.02 ; HRMS (TOF ES+) m/z calcd for $C_{20}H_{32}N_3O_2P$ [(M + H)$^+$], 378.223; found, 378.231



(3aR,7aR)-2-((2-hydroxy-4-methylbenzylidene)amino)-1,3-diisopropyloctahydrobenzo[d][1,3,2]diazaphosphole 2-oxide **(1h).**Yellow solid, 0.932 g, 64% yield; $[\alpha]_D^{25}$ +17 (c 0.3, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 9.01 (d, J = 28.9 Hz, 1H), 7.26 (d, J = 8.3 Hz, 1H), 6.73 (s, 1H), 6.70 (d, J = 7.9 Hz, 1H), 3.45 – 3.23 (m, 2H), 3.09 – 2.98 (m, 1H), 2.86 (td, J = 10.2, 3.1 Hz, 1H), 2.30 (s, 3H), 2.09 – 1.98 (m, 2H), 1.77 (d, J = 6.0 Hz, 2H), 1.23 – 1.15 (m, 10H), 1.06 (d, J = 6.7 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.90 (d, J = 6.2 Hz), 163.04 (d, J = 1.9 Hz), 146.67 (s), 133.76 (s), 120.56 (s), 117.86 (d, J = 0.8 Hz), 117.01 (d, J = 20.0 Hz), 59.97 (d, J = 4.6 Hz), 59.88 (d, J = 4.5 Hz), 45.04 (d, J = 3.3 Hz), 44.44 (d, J = 3.6 Hz), 29.83 (d, J = 9.8 Hz), 29.54 (d, J = 9.4 Hz), 24.34 (dd, J = 2.0, 1.3 Hz), 22.13 (s), 21.93 (s), 21.90 (s), 21.15 (d, J = 2.8 Hz), 20.83 (d, J = 1.4 Hz), 20.32 (d, J = 1.5 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) 22.01 ; HRMS (TOF ES+) m/z calcd for $C_{20}H_{32}N_3O_2P$ [(M + H)$^+$], 378.223; found, 378.231

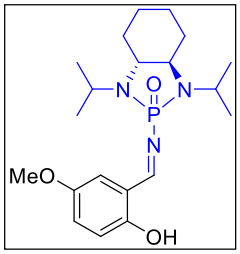


(3aR,7aR)-2-((2-hydroxy-3-methylbenzylidene)amino)-1,3-diisopropyloctahydrobenzo[d][1,3,2]diazaphosphole 2-oxide **(1i).**Yellow solid, 0.902 g, 62% yield; $[\alpha]_D^{25}$ +2.9 (c 0.55 $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 9.09 (d, J = 28.9 Hz, 1H), 7.26 (d, J = 7.5 Hz, 2H), 6.82 (t, J = 7.5 Hz, 1H), 3.47 – 3.24 (m, 2H), 3.12 – 3.00 (m, 1H), 2.92 (dd, J = 12.9, 6.1 Hz, 1H), 2.25 (s, 3H), 2.04 (d, J = 10.6 Hz, 2H), 1.80 (d, J = 7.1 Hz, 2H), 1.33 (q, J = 10.2 Hz, 3H), 1.25 – 1.16 (m, 10H), 1.10 (d, J = 6.6 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.86 (d, J = 6.2 Hz), 161.35 (d, J = 1.9 Hz), 135.94 (s), 131.61 (s), 126.61 (d, J = 0.7 Hz), 118.76 (s), 118.50 (d, J = 19.7 Hz), 60.07 (s), 59.99 (d, J = 2.2 Hz), 59.91 (s), 45.07 (d, J = 3.4 Hz), 44.48 (d, J = 3.7 Hz), 29.88 (d, J = 9.8 Hz), 29.55 (d, J = 9.4 Hz), 24.37 (t, J = 1.3 Hz), 22.06 (s), 22.02 (s), 21.18 (d, J = 2.6 Hz), 20.87 (d, J = 1.5 Hz), 20.41 (d, J = 1.5 Hz).; ^{31}P NMR (162 MHz, $CDCl_3$) 21.73 ; HRMS (TOF ES+) m/z calcd for $C_{20}H_{32}N_3O_2P$ [(M + H)$^+$], 378.223; found, 378.231

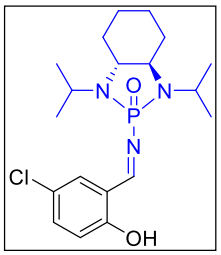


(3aR,7aR)-2-((2-hydroxy-4-methoxybenzylidene)amino)-1,3-diisopropyloctahydrobenzo[d][1,3,2]diazaphosphole 2-oxide **(1j).**Yellow solid, 0.971 g, 64% yield; $[\alpha]_D^{25}$ -16.7 (c 0.65, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 8.83 (d, J = 25.6 Hz, 1H), 7.23 (d, J = 8.7 Hz, 1H), 6.41 (dd, J = 8.7, 2.4 Hz, 1H), 6.35 (d, J = 1.8 Hz, 1H), 3.81 (s, 3H), 3.48 – 3.27 (m, 2H), 3.15 – 2.97 (m, 1H), 2.94 – 2.83 (m, 1H), 2.03 (dd, J = 7.4, 5.3 Hz, 2H), 1.80 (d, J = 4.6 Hz, 2H), 1.34 (dd, J = 11.6, 4.6 Hz, 3H), 1.26 – 1.17 (m, 10H), 1.10 (d, J = 6.7 Hz, 3H); ^{13}C NMR (101 MHz, $_{CDCl3}$) δ 171.91 (d, J = 4.6 Hz), 168.74 (s), 166.24 (s), 135.38 (s), 113.22 (d, J = 18.1 Hz), 108.36 (s), 101.26 (s), 60.03 (s), 59.93 (d, J = 2.6 Hz), 59.82 (s), 55.63 (s), 45.06 (d, J = 3.2 Hz), 44.47 (d, J = 3.6 Hz), 29.86 (d, J = 9.7 Hz), 29.48 (d, J = 9.6 Hz), 24.35 (dd, J = 3.0, 1.2 Hz), 21.91 (d, J = 3.8 Hz), 21.16 (d, J = 2.7 Hz), 20.86 (d, J = 1.4 Hz),

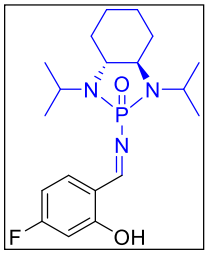
20.32 (d, J = 1.4 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) 21.01 ; HRMS (TOF ES+) m/z calcd for $C_{20}H_{32}N_3O_3P$ [(M + H)$^+$], 394.218; found, 394.226



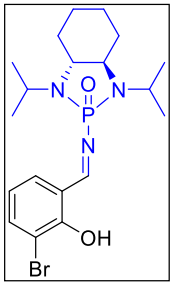
(3aR,7aR)-2-((2-hydroxy-5-methoxybenzylidene)amino)-1,3-diisopropyloctahydrobenzo[d][1,3,2]diazaphosphole 2-oxide **(1k).**Yellow solid, 1.06 g, 70% yield; $[\alpha]_D^{25}$ +18 (c 0.3, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.06 (d, J = 29.0 Hz, 1H), 7.03 (dd, J = 9.0, 3.1 Hz, 1H), 6.91 (d, J = 9.0 Hz, 2H), 3.77 (s, 3H), 3.48 – 3.22 (m, 2H), 3.13 – 3.01 (m, 1H), 2.91 (t, J = 8.0 Hz, 1H), 2.05 (d, J = 8.8 Hz, 2H), 1.81 (d, J = 5.6 Hz, 2H), 1.41 – 1.29 (m, 3H), 1.28 – 1.16 (m, 10H), 1.10 (d, J = 6.7 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.15 (d, J = 6.2 Hz), 157.37 (s), 152.34 (d, J = 1.0 Hz), 123.26 (s), 118.62 (s), 115.74 (s), 100.00 (s), 60.03 (d, J = 1.6 Hz), 59.94 (d, J = 1.6 Hz), 55.96 (s), 45.10 (d, J = 3.3 Hz), 44.51 (d, J = 3.6 Hz), 29.85 (d, J = 9.8 Hz), 29.55 (d, J = 9.4 Hz), 24.36 (dd, J = 2.2, 1.3 Hz), 22.00 (s), 21.96 (s), 21.19 (d, J = 2.7 Hz), 20.88 (d, J = 1.3 Hz), 20.40 (d, J = 1.3 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) 21.98 ; HRMS (TOF ES+) m/z calcd $C_{20}H_{32}N_3O_3P$ [(M + H)$^+$], 394.218; found, 392.226



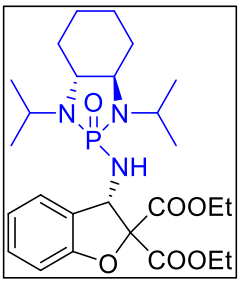
(3aR,7aR)-2-((5-chloro-2-hydroxybenzylidene)amino)-1,3-diisopropyloctahydrobenzo[d][1,3,2]diazaphosphole 2-oxide **(1l).**Yellow solid, 0.935 g, 61% yield; $[\alpha]_D^{25}$ -25.6 (c 2.2, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.99 (d, J = 28.5 Hz, 1H), 7.36 (d, J = 2.5 Hz, 1H), 7.31 (dd, J = 8.8, 2.5 Hz, 1H), 6.89 (d, J = 8.8 Hz, 1H), 3.50 – 3.22 (m, 2H), 3.17 – 2.95 (m, 1H), 2.84 (dd, J = 13.3, 6.1 Hz, 1H), 2.08 – 2.00 (m, 2H), 1.80 (d, J = 6.3 Hz, 2H), 1.33 (t, J = 9.5 Hz, 3H), 1.20 (t, J = 6.4 Hz, 10H), 1.07 (d, J = 6.7 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.79 (d, J = 6.2 Hz), 161.42 (d, J = 1.9 Hz), 134.80 (s), 132.59 (s), 123.86 (d, J = 1.2 Hz), 119.80 (d, J = 20.3 Hz), 119.32 (d, J = 0.8 Hz), 60.01 (d, J = 6.4 Hz), 59.91 (d, J = 6.8 Hz), 45.15 (d, J = 3.2 Hz), 44.52 (d, J = 3.5 Hz), 29.76 (d, J = 9.7 Hz), 29.53 (d, J = 9.4 Hz), 24.32 (s), 21.96 (s), 21.93 (s), 21.17 (d, J = 2.7 Hz), 20.83 (d, J = 1.2 Hz), 20.43 (d, J = 1.4 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) 21.51 ; HRMS (TOF ES+) m/z calcd $C_{19}H_{29}ClN_3O_2P$ [(M + H)$^+$], 398.168; found, 398.177



(3aR,7aR)-2-((4-fluoro-2-hydroxybenzylidene)amino)-1,3-diisopropyloctahydrobenzo[d][1,3,2]diazaphosphole 2-oxide **(1m).**Yellow solid, 0.912 g, 62% yield; $[\alpha]_D^{25}$ 23.7 (c 0.35 $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 8.99 (d, J = 28.8 Hz, 1H), 7.14 – 7.01 (m, 2H), 6.87 (dd, J = 8.7, 4.3 Hz, 1H), 3.45 – 3.20 (m, 2H), 3.09 – 2.94 (m, 1H), 2.83 (dd, J = 13.1, 6.0 Hz, 1H), 2.02 (s, 2H), 1.76 (d, J = 6.1 Hz, 2H), 1.30 (t, J = 9.3 Hz, 3H), 1.17 (dd, J = 9.4, 4.8 Hz, 10H), 1.05 (d, J = 6.6 Hz, 3H) ; ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.12 (dd, J = 6.2, 2.7 Hz), 158.95 (d, J = 1.6 Hz), 155.44 (dd, J = 238.2, 1.3 Hz), 122.36 (d, J = 23.6 Hz), 118.95 – 118.68 (m), 118.59 (d, J = 7.0 Hz), 118.26 (d, J = 22.7 Hz), 59.98 (d, J = 3.7 Hz), 59.89 (d, J = 3.9 Hz), 45.10 (d, J = 3.3 Hz), 44.47 (d, J = 3.5 Hz), 29.77 (d, J = 9.7 Hz), 29.49 (d, J = 9.4 Hz), 24.30 (s), 21.96 (s), 21.93 (s), 21.14 (d, J = 2.7 Hz), 20.81 (d, J = 1.1 Hz), 20.37 (d, J = 1.4 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) 21.67 ; HRMS (TOF ES+) m/z calcd $C_{19}H_{29}FN_3O_2P$ $[(M + H)^+]$, 382.198; found, 382.206

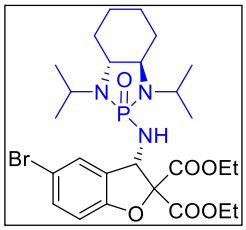


(3aR,7aR)-2-((3-bromo-2-hydroxybenzylidene)amino)-1,3-diisopropyloctahydrobenzo[d][1,3,2]diazaphosphole 2-oxide **(1n).**Yellow solid, 1.10 g, 65% yield; $[\alpha]_D^{25}$ -35.3 (c 0.3 $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 9.03 (d, J = 26.4 Hz, 1H), 7.68 (d, J = 7.8 Hz, 1H), 7.46 – 7.34 (m, 1H), 6.80 (td, J = 7.8, 1.0 Hz, 1H), 3.36 (ddt, J = 20.3, 13.6, 6.8 Hz, 2H), 3.20 – 2.84 (m, 2H), 2.06 (t, J = 13.2 Hz, 2H) , 1.83 (d, J = 7.5 Hz, 2H), 1.46 – 1.27 (m, 3H), 1.21 (dt, J = 13.4, 7.2 Hz, 10H), 1.12 (d, J = 6.7 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.28 (d, J = 5.4 Hz), 161.20 (d, J = 2.2 Hz), 138.30 (s), 133.15 (s), 119.56 (s), 112.23 (d, J = 1.5 Hz), 100.00 (s), 60.12 (d, J = 6.2 Hz), 60.03 (d, J = 6.4 Hz), 45.12 (d, J = 3.6 Hz), 44.56 (d, J = 3.9 Hz), 29.85 (d, J = 9.8 Hz), 29.45 (d, J = 9.5 Hz), 24.35 (s), 22.18 (d, J = 4.0 Hz), 21.21 (s), 21.18 (s), 20.87 (d, J = 2.0 Hz), 20.56 (d, J = 1.8 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) 20.21 ; HRMS (TOF ES+) m/z calcd $C_{19}H_{29}BrN_3O_2P$ $[(M + H)^+]$, 442.118; found, 442.127

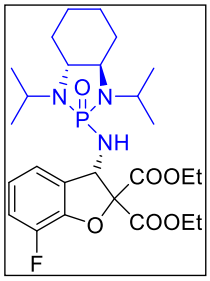


Diethyl (3S)-3-((1,3-diisopropyl-2-oxidooctahydrobenzo[d][1,3,2]diazaphosphol-2-yl)amino)benzofuran-2,2(3H)-dicarboxylate **(3a).**White solid, 0.417 g, 81% yield; $[\alpha]_D^{25}$ +1.6 (c 1, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, J = 7.5 Hz, 1H), 7.18 (dd, J = 11.3, 4.2 Hz, 1H), 6.94 (td, J = 7.5, 0.7 Hz, 1H), 6.88 (d, J = 8.1 Hz, 1H), 5.80 (dd, J = 11.2, 9.0 Hz, 1H), 4.39 – 4.31 (m, 1H), 4.27 (q, J = 7.1 Hz, 2H), 4.17 (dq, J = 10.8, 7.1 Hz, 1H), 3.70 – 3.49 (m, 2H), 2.94 (td, J = 10.9, 3.0 Hz, 1H), 2.85 – 2.68 (m, 2H), 2.04 (d, J = 7.9 Hz, 2H), 1.76 – 1.64 (m, 2H), 1.26 (ddd, J = 10.9, 8.0, 5.5 Hz, 13H), 1.17 (d, J = 6.9 Hz, 6H), 1.07 (d, J = 7.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.93 (s), 165.98 (s), 157.37 (s), 129.90 (s), 128.34 (d, J = 1.8 Hz), 125.15 (s), 122.34 (s), 110.66 (s), 91.88 (d, J = 7.1 Hz), 62.62 (s),

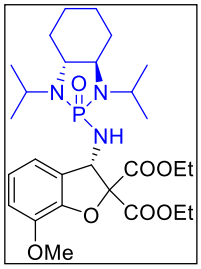
62.43 (s), 60.71 (d, J = 1.3 Hz), 59.65 (d, J = 11.4 Hz), 59.00 (d, J = 9.9 Hz), 44.17 (d, J = 3.4 Hz), 43.79 (d, J = 4.2 Hz), 31.96 (d, J = 11.9 Hz), 31.23 (d, J = 10.2 Hz), 24.49 (s), 24.41 (s), 24.36 (t, J = 1.6 Hz), 23.78 (d, J = 4.8 Hz), 20.14 (d, J = 1.5 Hz), 19.47 (s), 14.08 (s), 14.06 (s); ^{31}P NMR (162 MHz, $CDCl_3$) 23.50, 22.53 ; HRMS (TOF ES+) m/z calcd $C_{26}H_{40}N_3O_6P$ [(M + H)$^+$], 522.590; found, 522.275



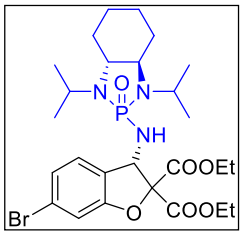
diethyl (3S)-5-bromo-3-((1,3-diisopropyl-2-oxidooctahydrobenzo[d][1,3,2]diazaphosphol-2-yl)amino)benzofuran-2,2(3H)-dicarboxylate **(3b).**White solid, 0.527 g, 88% yield; $[\alpha]_D^{25}$ -44.8 (c 1.6, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, J = 1.4 Hz, 1H), 7.24 (dd, J = 8.4, 1.7 Hz, 1H), 6.74 (d, J = 8.5 Hz, 1H), 5.76 (dd, J = 11.2, 8.9 Hz, 1H), 4.35 – 4.27 (m, 1H), 4.24 (q, J = 7.1 Hz, 2H), 4.14 (dq, J = 10.8, 7.1 Hz, 1H), 3.64 – 3.43 (m, 2H), 2.95 – 2.86 (m, 1H), 2.75 (dd, J = 11.1, 9.0 Hz, 1H), 2.66 (dd, J = 14.2, 5.9 Hz, 1H), 2.00 (d, J = 10.4 Hz, 2H), 1.74 – 1.62 (m, 2H), 1.13 (d, J = 6.9 Hz, 6H), 1.07 (d, J = 7.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.48 (s), 165.57 (s), 156.42 (s), 132.61 (s), 130.97 (d, J = 1.7 Hz), 128.27 (s), 114.27 (s), 112.28 (s), 92.23 (d, J = 7.3 Hz), 62.75 (s), 62.61 (s), 60.49 (d, J = 1.7 Hz), 59.55 (d, J = 11.6 Hz), 58.94 (d, J = 10.0 Hz), 44.25 (d, J = 3.8 Hz), 43.78 (d, J = 4.3 Hz), 31.94 (d, J = 12.0 Hz), 31.12 (d, J = 10.6 Hz), 24.44 (d, J = 8.5 Hz), 24.31 (d, J = 1.5 Hz), 23.60 (d, J = 4.9 Hz), 21.08 (s), 19.97 (d, J = 1.7 Hz), 19.42 (s), 14.05 (s), 14.01 (s); ^{31}P NMR (162 MHz, $CDCl_3$) 23.35, 22.15 ; HRMS (TOF ES+) m/z calcd $C_{26}H_{39}BrN_3O_6P$ [(M + H)$^+$], 600.180; found, 602.183



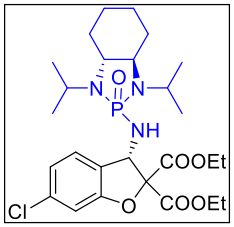
diethyl (3S)-3-((1,3-diisopropyl-2-oxidooctahydrobenzo[d][1,3,2]diazaphosphol-2-yl)amino)-7-fluorobenzofuran-2,2(3H)-dicarboxylate **(3c).**White solid, 0.442 g, 82% yield; $[\alpha]_D^{25}$ 4.6 (c 1.8, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 (d, J = 7.4 Hz, 1H), 6.98 – 6.91 (m, 1H), 6.90 – 6.84 (m, 1H), 5.83 (dd, J = 11.3, 9.0 Hz, 1H), 4.40 – 4.29 (m, 2H), 4.30 – 4.24 (m, 2H), 4.17 (dq, J = 10.8, 7.2 Hz, 1H), 3.68 – 3.48 (m, 2H), 2.89 (ddd, J = 28.4, 15.8, 6.6 Hz, 2H), 2.70 (dd, J = 14.0, 6.1 Hz, 1H), 2.01 (t, J = 9.4 Hz, 2H), 1.79 – 1.61 (m, 2H), 1.25 (ddd, J = 17.5, 9.7, 7.0 Hz, 14H), 1.16 (d, J = 6.8 Hz, 6H), 1.05 (d, J = 7.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.40 (s), 165.47 (s), 147.26 (d, J = 248.6 Hz), 144.14 (d, J = 11.1 Hz), 131.98 (s), 122.96 (dd, J = 14.1, 5.4 Hz), 120.64 (dd, J = 39.2, 3.6 Hz), 116.98 (d, J = 16.5 Hz), 92.52 (d, J = 7.0 Hz), 62.78 (s), 62.64 (s), 61.01 (s), 59.61 (d, J = 11.4 Hz), 59.02 (d, J = 9.9 Hz), 44.17 (d, J = 3.2 Hz), 43.78 (d, J = 4.1 Hz), 31.90 (d, J = 11.8 Hz), 31.17 (d, J = 10.4 Hz), 24.45 (s), 24.36 (d, J = 1.0 Hz), 24.32 (d, J = 1.8 Hz), 23.71 (d, J = 4.8 Hz), 20.09 (d, J = 1.4 Hz), 19.48 (s), 14.04 (s), 14.03 (s); ^{31}P NMR (162 MHz, $CDCl_3$) 23.35, 22.36 ; HRMS (TOF ES+) m/z calcd $C_{26}H_{39}FN_3O_6P$ [(M + H)$^+$], 540.26; found, 540.265



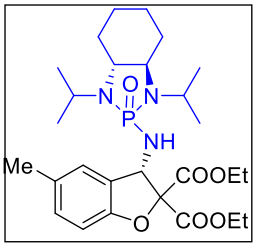
diethyl (3S)-3-((1,3-diisopropyl-2-oxidooctahydrobenzo[d][1,3,2]diazaphosphol-2-yl)amino)-7-methoxybenzofuran-2,2(3H)-dicarboxylate **(3d).**White solid, 0.474 g, 86% yield; $[\alpha]_D^{25}$ -14.5 (c 0.6, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.00 (d, J = 7.5 Hz, 1H), 6.86 (t, J = 7.8 Hz, 1H), 6.74 (d, J = 8.1 Hz, 1H), 5.79 (dd, J = 11.2, 9.1 Hz, 1H), 4. 31 (dd, J = 10.8, 7.1 Hz, 1H), 4.28 – 4.19 (m, 2H), 4.13 (tt, J = 10.7, 7.3 Hz, 1H), 3.80 (s, 3H), 3.67 – 3.46 (m, 2H), 2.96 – 2.85 (m, 1H), 2.85 – 2.76 (m, 1H), 2.69 (dd, J = 14.0, 6.1 Hz, 1H), 2.06 – 1.97 (m, 2H), 1.72 – 1.64 (m, 2H), 1.14 (dd, J = 6.8, 3.5 Hz, 6H), 1.03 (d, J = 6.9 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.82 (s), 165.77 (s), 145.83 (s), 144.67 (s), 129.46 (d, J = 2.0 Hz), 122.99 (s), 116.92 (s), 112.83 (s), 92.05 (d, J = 7.1 Hz), 62.54 (s), 62.38 (s), 61.19 (d, J = 1.8 Hz), 59.65 (d, J = 11.4 Hz), 59.02 (d, J = 10.0 Hz), 56.03 (s), 44.11 (d, J = 3.8 Hz), 43.79 (d, J = 4.4 Hz), 31.92 (d, J = 12.0 Hz), 31.16 (d, J = 10.4 Hz), 24.42 (d, J = 8.6 Hz), 24.32 (s), 23.69 (d, J = 4.9 Hz), 20.22 (d, J = 1.9 Hz), 19.48 (s), 14.06 (s), 14.04 (s); ^{31}P NMR (162 MHz, $CDCl_3$) 23.31, 22.43 ; HRMS (TOF ES+) m/z calcd $C_{27}H_{42}N_3O_7P$ $[(M + H)^+]$, 552.28; found, 522.285



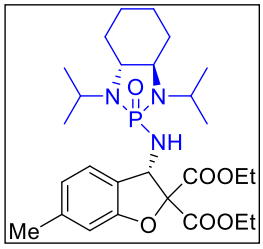
diethyl (3S)-6-bromo-3-((1,3-diisopropyl-2-oxidooctahydrobenzo[d][1,3,2]diazaphosphol-2-yl)amino)benzofuran-2,2(3H)-dicarboxylate **(3e).**White solid, 0.509 g, 85% yield; $[\alpha]_D^{25}$ -2.6 (c 1, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.29 (d, J = 8.0 Hz, 1H), 7.06 (dd, J = 8.0, 1.6 Hz, 1H), 7.02 (d, J = 1.6 Hz, 1H), 5.73 (dd, J = 11.2, 8.8 Hz, 1H), 4.38 – 4.30 (m, 1H), 4.26 (q, J = 7.1 Hz, 2H), 4.16 (dq, J = 10.8, 7.1 Hz, 1H), 3.64 – 3.46 (m, 2H), 2.91 (td, J = 11.0, 3.0 Hz, 1H), 2.79 (dd, J = 11.0, 9.4 Hz, 1H), 2.68 (dd, J = 14.0, 6.1 Hz, 1H), 2.00 (d, J = 6.8 Hz, 2H), 1.75 – 1.65 (m, 2H), 1.30 – 1.24 (m, 7H), 1.23 – 1.19 (m, 5H), 1.15 (d, J = 6.8 Hz, 6H), 1.05 (d, J = 7.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.53 (s), 165.62 (s), 158.20 (s), 127.79 (d, J = 1.5 Hz), 126.36 (s), 125.51 (s), 122.95 (s), 114.24 (s), 92.23 (d, J = 7.2 Hz), 62.79 (s), 62.65 (s), 60.29 (d, J = 1.6 Hz), 59.60 (d, J = 11.3 Hz), 59.02 (d, J = 9.9 Hz), 44.20 (d, J = 3.3 Hz), 43.78 (d, J = 4.1 Hz), 31.87 (d, J = 11.8 Hz), 31.13 (d, J = 10.4 Hz), 24.45 (s), 24.36 (s), 24.33 (t, J = 1.3 Hz), 23.66 (d, J = 4.8 Hz), 20.08 (d, J = 1.4 Hz), 19.52 (s), 14.05 (s), 14.05 (s); ^{31}P NMR (162 MHz, $CDCl_3$) 23.33, 22.43 ; HRMS (TOF ES+) m/z calcd $C_{26}H_{39}BrN_3O_6P$ $[(M + H)^+]$, 600.18; found, 602.183



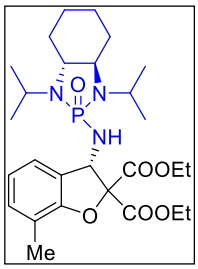
***diethyl (3S)-6-chloro-3-((1,3-diisopropyl-2-oxidooctahydrobenzo[d][1,3,2]diazaphosphol-2-yl)amino)benzofuran-2,2(3H)-dicarboxylate* (3f).** White solid, 0.499 g, 90% yield; $[\alpha]_D^{25}$ -4.7 (c 0.7, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.32 (d, J = 8.0 Hz, 1H), 6.88 (dd, J = 8.0, 1.8 Hz, 1H), 6.84 (d, J = 1.7 Hz, 1H), 5.72 (dd, J = 11.2, 8.8 Hz, 1H), 4.36 – 4.28 (m, 1H), 4.24 (q, J = 7.1 Hz, 2H), 4.18 – 4.08 (m, 1H), 3.59 – 3.45 (m, 2H), 2.95 – 2.84 (m, 1H), 2.76 (dd, J = 11.1, 9.4 Hz, 1H), 2.66 (dd, J = 14.0, 6.0 Hz, 1H), 1.97 (d, J = 12.8 Hz, 3H), 1.73 – 1.63 (m, 2H), 1.28 – 1.16 (m, 13H), 1.13 (d, J = 6.8 Hz, 6H), 1.03 (d, J = 7.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.52 (s), 165.60 (s), 158.08 (s), 135.22 (s), 127.22 (d, J = 1.6 Hz), 125.91 (s), 122.58 (s), 111.34 (s), 92.34 (d, J = 7.2 Hz), 62.76 (s), 62.62 (s), 60.19 (d, J = 1.4 Hz), 59.58 (, J = 11.3 Hz), 59.00 (d, J = 9.9 Hz), 44.15 (d, J = 3.3 Hz), 43.76 (d, J = 3.9 Hz), 31.85 (d, J = 11.8 Hz), 31.10 (d, J = 10.4 Hz), 24.41 (s), 24.33 (s), 24.30 (s), 23.63 (d, J = 4.8 Hz), 20.06 (d, J = 1.4 Hz), 19.49 (s), 14.02 (s); ^{31}P NMR (162 MHz, $CDCl_3$) 23.32, 22.42 ; HRMS (TOF ES+) m/z calcd $C_{26}H_{39}ClN_3O_6P$ [(M + H)$^+$], 556.23; found, 556.235



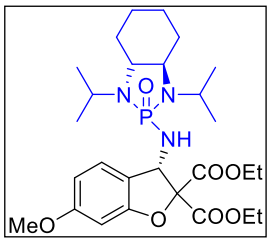
***diethyl (3S)-3-((1,3-diisopropyl-2-oxidooctahydrobenzo[d][1,3,2]diazaphosphol-2-yl)amino)-5-methylbenzofuran-2,2(3H)-dicarboxylate* (3g).** White solid, 0.439 g, 82% yield; $[\alpha]_D^{25}$ +10 (c 1.05, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.21 – 7.18 (m, 1H), 6.95 (ddd, J = 8.2, 1.2, 0.7 Hz, 1H), 6.75 (d, J = 8.2 Hz, 1H), 5.75 (dd, J = 11.2, 8.9 Hz, 1H), 4.37 – 4.29 (m, 1H), 4.25 (q, J = 7.2 Hz, 2H), 4.15 (dq, J = 10.8, 7.1 Hz, 1H), 3.72 – 3.45 (m, 2H), 2.96 – 2.88 (m, 1H), 2.75 – 2.65 (m, 2H), 2.23 (s, 3H), 2.00 (dd, J = 6.4, 3.7 Hz, 2H), 1.74 – 1.65 (m, 2H), 1.30 – 1.20 (m, 12H), 1.15 (dd, J = 6.8, 2.4 Hz, 6H), 1.06 (d, J = 7.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.99 (s), 166.00 (s), 155.27 (s), 131.72 (s), 130.27 (s), 128.39 (d, J = 1.7 Hz), 125.51 (s), 110.20 (s), 92.13 (d, J = 7.3 Hz), 62.54 (s), 62.34 (s), 60.73 (d, J = 0.9 Hz), 59.55 (d, J = 11.5 Hz), 58.92 (d, J = 9.9 Hz), 44.13 (d, J = 3.3 Hz), 43.77 (d, J = 4.1 Hz), 32.01 (d, J = 11.9 Hz), 31.25 (d, J = 10.3 Hz), 24.47 (d, J = 8.6 Hz), 24.35 (d, J = 1.5 Hz), 24.33 (s), 23.71 (dd, J = 11.4, 4.3 Hz), 20.87 (s), 19.99 (d, J = 1.5 Hz), 19.41 (s), 14.07 (s), 14.05 (s); ^{31}P NMR (162 MHz, $CDCl_3$) 23.60, 22.51 ; HRMS (TOF ES+) m/z calcd $C_{27}H_{42}N_3O_6P$ [(M + H)$^+$], 536.28; found, 536.290



***diethyl (3S)-3-((1,3-diisopropyl-2-oxidooctahydrobenzo[d][1,3,2]diazaphosphol-2-yl)amino)-6-methylbenzofuran-2,2(3H)-dicarboxylate* (3h).** White solid, 0.492 g, 92% yield; $[\alpha]_D^{25}$ +2.7 (c 1.4, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.25 (d, J = 7.6 Hz, 1H), 6.73 (d, J = 7.7 Hz, 1H), 6.68 (s, 1H), 5.74 (dd, J = 10.9, 9.3 Hz, 1H), 4.39 – 4.29 (m, 1H), 4.25 (q, J = 7.1 Hz, 2H), 4.15 (dq, J = 10.8, 7.1 Hz, 1H), 3.69 – 3.44 (m, 2H), 2.98 – 2.86 (m, 1H), 2.79 – 2.66 (m, 2H), 2.26 (s, 3H), 2.00 (d, J = 11.7 Hz, 2H), 1.80 – 1.59 (m, 2H), 1.30 – 1.21 (m, 11H), 1.16 (d, J = 6.8 Hz, 6H), 1.06 (d, J = 7.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.02 (s), 166.04 (s), 157.65 (s), 140.31 (s), 125.32 (d, J = 1.8 Hz), 124.71 (s), 123.14 (s), 111.18 (s), 92.12 (d, J = 7.1 Hz), 62.55 (s), 62.36 (s), 60.56 (d, J = 1.2 Hz), 59.63 (d, J = 11.4 Hz), 58.99 (d, J = 10.0 Hz), 44.16 (d, J = 3.2 Hz), 43.77 (d, J = 4.1 Hz), 31.94 (d, J = 11.8 Hz), 31.23 (d, J = 10.3 Hz), 24.45 (d, J = 8.6 Hz), 24.36 (d, J = 2.2 Hz), 24.34 (s), 23.78 (d, J = 4.7 Hz), 21.63 (s), 20.16 (d, J = 1.4 Hz), 19.48 (s), 14.07 (s); ^{31}P NMR (162 MHz, $CDCl_3$) 23.50, 22.50 ; HRMS (TOF ES+) m/z calcd $C_{27}H_{42}N_3O_6P$ $[(M + H)^+]$, 536.28; found, 526.290

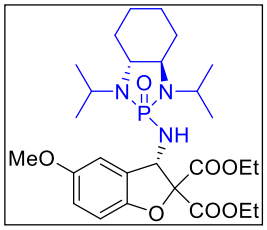


***diethyl (3S)-3-((1,3-diisopropyl-2-oxidooctahydrobenzo[d][1,3,2]diazaphosphol-2-yl)amino)-7-methylbenzofuran-2,2(3H)-dicarboxylate* (3i).** White solid, 0.497 g, 93% yield; $[\alpha]_D^{25}$ +12.57 (c 1.05, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.21 (d, J = 7.3 Hz, 1H), 6.97 (d, J = 7.4 Hz, 1H), 5.77 (dd, J = 11.1, 9.2 Hz, 1H), 4.38 – 4.29 (m, 1H), 4.28 – 4.20 (m, 2H), 4.19 – 4.11 (m, 1H), 3.59 (dtt, J = 41.6, 13.7, 6.8 Hz, 2H), 2.99 – 2.82 (m, 1H), 2.82 – 2.61 (m, 2H), 2.21 (s, 3H), 2.00 (d, J = 12.3 Hz, 2H), 1.77 – 1.63 (m, 2H), 1.30 – 1.20 (m, 12H), 1.16 (d, J = 6.8 Hz, 7H), 1.05 (d, J = 7.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.11 (s), 166.10 (s), 155.88 (s), 131.10 (s), 127.62 (d, J = 1.7 Hz), 122.39 (s), 122.16 (s), 120.77 (s), 91.74 (d, J = 7.0 Hz), 62.50 (s), 62.29 (s), 61.02 (d, J = 1.1 Hz), 59.63 (d, J = 11.4 Hz), 58.98 (d, J = 9.9 Hz), 44.13 (d, J = 3.3 Hz), 43.79 (d, J = 4.0 Hz), 31.96 (d, J = 11.9 Hz), 31.23 (d, J = 10.3 Hz), 24.44 (d, J = 8.6 Hz), 24.36 (d, J = 1.5 Hz), 24.36 (s), 23.77 (d, J = 4.7 Hz), 20.17 (d, J = 1.4 Hz), 19.45 (s), 15.06 (s), 14.06 (s), 14.05 (s); ^{31}P NMR (162 MHz, $CDCl_3$) 23.47, 22.45 ; HRMS (TOF ES+) m/z calcd $C_{27}H_{42}N_3O_6P$ $[(M + H)^+]$, 536.28; found, 536.290

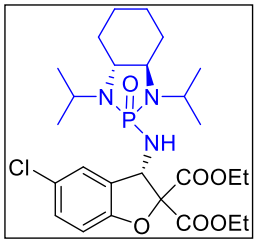


***diethyl (3S)-3-((1,3-diisopropyl-2-oxidooctahydrobenzo[d][1,3,2]diazaphosphol-2-yl)amino)-6-methoxybenzofuran-2,2(3H)-dicarboxylate* (3j).** White solid, 0.468 g, 85% yield; $[\alpha]_D^{25}$ +7 (c 1.05, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.26 (d, J = 8.3 Hz, 1H), 6.51 – 6.42 (m, 2H), 5.71 (dd, J = 11.2, 8.7 Hz, 1H), 4.33 (dq, J = 10.8, 7.1 Hz, 1H), 4.25 (q, J = 7.1 Hz, 2H), 4.15 (dq, J = 10.8, 7.1 Hz, 1H), 3.71 (s, 3H), 3.67 – 3.44 (m, 2H), 2.98 – 2.84 (m, 1H), 2.70 (t, J = 10.0 Hz, 2H), 1.99 (d, J = 9.5 Hz, 2H), 1.74 – 1.65 (m, 2H), 1.24 (ddd, J = 18.7, 9.5, 5.5 Hz, 11H), 1.15 (dd, J = 6.8, 1.9 Hz, 5H), 1.05 (d, J = 7.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.92 (s), 165.90 (s), 161.59 (s), 158.76 (s), 125.49 (s), 120.19 (d, J = 1.7 Hz), 108.47 (s), 96.67 (s), 92.73 (d, J = 7.3 Hz), 62.60 (s), 62.42 (s), 60.24 (d, J = 1.1 Hz), 59.67 (d,

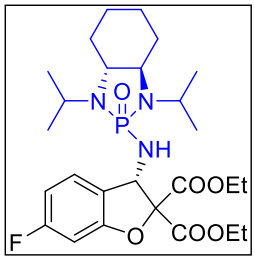
J = 11.3 Hz), 59.00 (d, J = 9.9 Hz), 55.56 (s), 44.12 (d, J = 3.4 Hz), 43.80 (d, J = 4.1 Hz), 31.92 (d, J = 11.9 Hz), 31.15 (d, J = 10.2 Hz), 24.44 (d, J = 8.5 Hz), 24.35 (d, J = 1.4 Hz), 24.35 (s), 23.67 (d, J = 4.7 Hz), 20.22 (d, J = 1.4 Hz), 19.49 (s), 14.06 (s); ^{31}P NMR (162 MHz, $CDCl_3$) 23.51, 22.53 ; HRMS (TOF ES+) m/z calcd $C_{27}H_{42}N_3O_7P$ [(M + H)$^+$], 552.28; found, 552.285



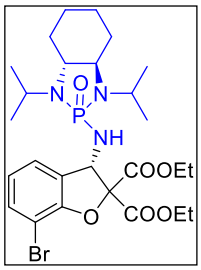
***diethyl (3S)-3-((1,3-diisopropyl-2-oxidooctahydrobenzo[d][1,3,2]diazaphosphol-2-yl)amino)-5-methoxybenzofuran-2,2(3H)-dicarboxylate* (3k).** White solid, 0.441 g, 80% yield; $[\alpha]_D^{25}$ -17.4 (c 0.55, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.03 (d, J = 2.6 Hz, 1H), 6.80 (dd, J = 8.7, 6.3 Hz, 1H), 6.75 – 6.66 (m, 1H), 5.75 (dd, J = 11.2, 8.5 Hz, 1H), 4.40 – 4.30 (m, 1H), 4.31 – 4.22 (m, 2H), 4.21 – 4.12 (m, 1H), 3.70 (d, J = 2.0 Hz, 3H), 3.68 – 3.44 (m, 2H), 2.93 (td, J = 10.9, 2.9 Hz, 1H), 2.87 – 2.76 (m, 1H), 2.70 (dd, J = 14.1, 6.0 Hz, 1H), 2.01 (d, J = 9.0 Hz, 2H), 1.74 – 1.67 (m, 2H), 1.34 – 1.22 (m, 12H), 1.17 (dd, J = 6.8, 4.0 Hz, 6H), 1.06 (d, J = 7.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ ^{13}C NMR (101 MHz, CHLOROFORM-D) δ 167.06 (s), 166.03 (s), 155.41 (s), 129.23 (s), 116.13 (s), 111.02 (s), 110.00 (s), 92.23 (d, J = 7.4 Hz), 62.61 (s), 62.43 (s), 60.95 (s), 59.64 (d, J = 11.2 Hz), 58.98 (d, J = 9.9 Hz), 55.96 (s), 44.17 (d, J = 3.0 Hz), 43.80 (d, J = 4.1 Hz), 31.91 (d, J = 11.7 Hz), 31.12 (d, J = 10.4 Hz), 24.51 (s), 24.42 (s), 24.36 (s), 23.62 (d, J = 4.6 Hz), 20.14 (s), 19.48 (s), 14.08 (s), 14.06 (s); ^{31}P NMR (162 MHz, $CDCl_3$) 23.48, 22.58 ; HRMS (TOF ES+) m/z calcd $C_{27}H_{42}N_3O_7P$ [(M + H)$^+$], 552.28; found, 552.285



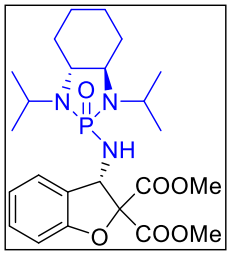
***diethyl (3S)-5-chloro-3-((1,3-diisopropyl-2-oxidooctahydrobenzo[d][1,3,2]diazaphosphol-2-yl)amino)benzofuran-2,2(3H)-dicarboxylate* (3l).** White solid, 0.522 g, 94% yield; $[\alpha]_D^{25}$ -32.2 (c 0.77, 00); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, J = 2.1 Hz, 1H), 7.19 – 7.08 (m, 1H), 6.82 (d, J = 8.5 Hz, 1H), 5.79 (dd, J = 11.2, 8.9 Hz, 1H), 4.39 – 4.32 (m, 1H), 4.29 (q, J = 7.1 Hz, 2H), 4.18 (dq, J = 10.8, 7.2 Hz, 1H), 3.68 – 3.48 (m, 2H), 3.00 – 2.87 (m, 1H), 2.86 – 2.76 (m, 1H), 2.70 (dd, J = 14.1, 6.1 Hz, 1H), 2.04 (d, J = 11.0 Hz, 2H), 1.82 – 1.65 (m, 2H), 1.28 (dt, J = 9.4, 7.1 Hz, 12H), 1.17 (d, J = 6.8 Hz, 6H), 1.11 (d, J = 7.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.06 (s), 166.03 (s), 155.41 (s), 129.23 (s), 116.13 (s), 111.02 (s), 110.00 (s), 92.23 (d, J = 7.4 Hz), 62.61 (s), 62.43 (s), 60.95 (s), 59.64 (d, J = 11.2 Hz), 58.98 (d, J = 9.9 Hz), 55.96 (s), 44.17 (d, J = 3.0 Hz), 43.80 (d, J = 4.1 Hz), 31.91 (d, J = 11.7 Hz), 31.12 (d, J = 10.4 Hz), 24.51 (s), 24.42 (s), 24.36 (s), 23.62 (d, J = 4.6 Hz), 20.14 (s), 19.48 (s), 14.08 (s), 14.06 (s); ^{31}P NMR (162 MHz, $CDCl_3$) 23.39; HRMS (TOF ES+) m/z calcd $C_{26}H_{39}ClN_3O_6P$ [(M + H)$^+$], 556.23; found, 556.235



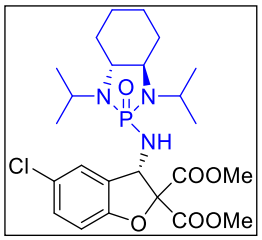
***diethyl (3S)-3-((1,3-diisopropyl-2-oxidooctahydrobenzo[d][1,3,2]diazaphosphol-2-yl)amino)-6-fluorobenzofuran-2,2(3H)-dicarboxylate* (3m).** White solid, 0.463 g, 86% yield; $[\alpha]_D^{25}$ +6 (c 0.95, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.13 (dd, J = 7.8, 2.6 Hz, 1H), 6.86 (td, J = 8.7, 2.7 Hz, 1H), 6.80 (dd, J = 8.8, 4.1 Hz, 1H), 5.77 (dd, J = 11.2, 8.8 Hz, 1H), 4.38 – 4.30 (m, 1H), 4.27 (q, J = 7.1 Hz, 2H), 4.16 (dq, J = 10.8, 7.1 Hz, 1H), 3.76 – 3.38 (m, 2H), 3.01 – 2.87 (m, 1H), 2.83 (dd, J = 10.9, 9.5 Hz, 1H), 2.76 – 2.64 (m, 1H), 2.06 – 1.99 (m, 2H), 1.76 – 1.64 (m, 2H), 1.31 – 1.19 (m, 12H), 1.16 (d, J = 6.8 Hz, 6H), 1.08 (d, J = 7.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.73 (s), 165.79 (s), 158.45 (d, J = 239.8 Hz), 153.14 (d, J = 1.5 Hz), 129.97 (dd, J = 8.3, 1.4 Hz), 116.34 (d, J = 24.6 Hz), 112.76 – 112.50 (m), 112.22 (d, J = 25.7 Hz), 111.15 (d, J = 8.4 Hz), 92.38 (d, J = 7.2 Hz), 62.73 (s), 62.57 (s), 60.70 (s), 59.60 (d, J = 11.3 Hz), 59.02 (d, J = 9.9 Hz), 44.23 (d, J = 3.2 Hz), 43.80 (d, J = 3.9 Hz), 31.90 (d, J = 11.8 Hz), 31.14 (d, J = 10.4 Hz), 24.38 (s), 24.31 (d, J = 2.4 Hz), 23.64 (d, J = 4.8 Hz), 20.05 (d, J = 1.2 Hz), 19.46 (s), 14.05 (s), 14.02 (s).; ^{31}P NMR (162 MHz, $CDCl_3$) 23.30; HRMS (TOF ES+) m/z calcd $C_{26}H_{39}FN_3O_6P$ $[(M + H)^+]$, 540.26; found, 540.265



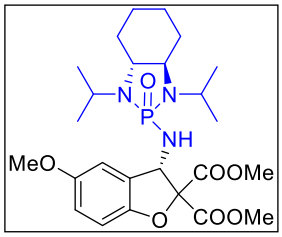
***diethyl (3S)-7-bromo-3-((1,3-diisopropyl-2-oxidooctahydrobenzo[d][1,3,2]diazaphosphol-2-yl) amino)benzofuran-2,2(3H)-dicarboxylate* (3n).**
White solid, 0.509 g, 85% yield; $[\alpha]_D^{25}$ -5.1 (c 0.7, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 4.30 – 4.24 (m, 2H), 4.17 (dq, J = 10.8, 7.2 Hz, 1H), 3.66 – 3.49 (m, 2H), 2.89 (ddd, J = 28.4, 15.8, 6.6 Hz, 2H), 2.70 (dd, J = 14.0, 6.1 Hz, 1H), 2.01 (dd, J = 15.4, 7.0 Hz, 2H), 1.82 – 1.62 (m, 2H), 1.25 (ddd, J = 17.5, 9.7, 7.0 Hz, 12H), 1.16 (d, J = 6.8 Hz, 6H), 1.05 (d, J = 7.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.52 (s), 165.60 (s), 158.08 (s), 135.22 (s), 127.22 (d, J = 1.6 Hz), 125.91 (s), 122.58 (s), 111.34 (s), 92.34 (d, J = 7.2 Hz), 62.76 (s), 62.62 (s), 60.19 (d, J = 1.4 Hz), 59.58 (d, J = 11.3 Hz), 59.00 (d, J = 9.9 Hz), 44.15 (d, J = 3.3 Hz), 43.76 (d, J = 3.9 Hz), 31.85 (d, J = 11.8 Hz), 31.10 (d, J = 10.4 Hz), 24.41 (s), 24.33 (s), 24.30 (s), 23.63 (d, J = 4.8 Hz), 20.06 (d, J = 1.4 Hz), 19.49 (s), 14.02 (s); ^{31}P NMR (162 MHz, $CDCl_3$) 23.33, 22.43; HRMS (TOF ES+) m/z calcd $C_{26}H_{39}BrN_3O_6P$ $[(M + H)^+]$, 600.18; found, 600.185



***dimethyl (3S)-3-((1,3-diisopropyl-2-oxidooctahydrobenzo[d][1,3,2]diazaphosphol-2-yl)amino)benzofuran-2,2(3H)-dicarboxylate* (3o).** White solid, 0.400 g, 81% yield; $[\alpha]_D^{25}$ +8.3 (c 0.55, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, J = 7.5 Hz, 1H), 7.21 (t, J = 7.8 Hz, 1H), 6.97 (t, J = 7.4 Hz, 1H), 6.91 (d, J = 8.1 Hz, 1H), 5.87 – 5.78 (m, 1H), 3.83 (d, J = 1.7 Hz, 3H), 3.81 (d, J = 1.6 Hz, 2H), 3.72 – 3.50 (m, 2H), 2.97 (dd, J = 14.5, 5.7 Hz, 1H), 2.77 (t, J = 9.5 Hz, 2H), 2.07 (d, J = 10.8 Hz, 2H), 1.79 – 1.66 (m, 2H) , 1.30 (ddd, J = 18.8, 15.0, 7.1 Hz, 8H), 1.20 (dd, J = 6.7, 3.8 Hz, 6H), 1.10 (d, J = 6.9 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.39 (s), 166.34 (s), 157.30 (s), 130.04 (s), 128.04 (s), 125.10 (s), 122.50 (s), 110.77 (s), 92.04 (d, J = 6.8 Hz), 60.95 (d, J = 1.2 Hz), 59.66 (d, J = 11.6 Hz), 59.10 (d, J = 9.9 Hz), 53.49 (s), 53.23 (s), 44.31 (s), 43.82 (d, J = 4.3 Hz), 31.89 (d, J = 12.1 Hz), 31.31 (d, J = 10.2 Hz), 24.40 (s), 24.36 (s), 24.31 (s), 23.86 (d, J = 4.5 Hz), 20.20 (d, J = 1.4 Hz), 19.46 (s); ^{31}P NMR (162 MHz, $CDCl_3$) 23.59, 22.59; HRMS (TOF ES+) m/z calcd $C_{24}H_{36}N_3O_6P$ [(M + H)$^+$], 494.23; found, 494.243

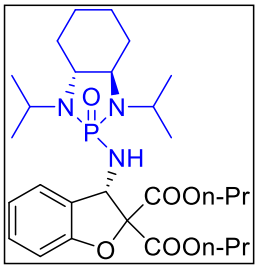


***dimethyl (3S)-5-chloro-3-((1,3-diisopropyl-2-oxidooctahydrobenzo[d][1,3,2]diazaphosphol-2-yl)amino)benzofuran-2,2(3H)-dicarboxylate* (3p).**
White solid, 0.463 g, 88% yield; $[\alpha]_D^{25}$ +29.6 (c 0.6, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) 7.41 – 7.36 (m, 1H), 7.16 (dd, J = 8.6, 2.3 Hz, 1H), 6.83 (d, J = 8.6 Hz, 1H), 5.81 (dd, J = 11.2, 9.0 Hz, 1H), 3.83 (s, 3H), 3.81 (s, 3H), 3.02 – 2.88 (m, 1H), 2.80 – 2.67 (m, 2H), 2.05 (d, J = 10.7 Hz, 2H), 1.79 – 1.65 (m, 2H), 1.41 – 1.21 (m, 8H), 1.18 (dd, J = 6.8, 3.6 Hz, 6H), 1.12 (d, J = 7.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.02 (s), 166.01 (s), 155.83 (s), 130.22 (d, J = 1.8 Hz), 129.90 (s), 127.41 (s), 125.34 (s), 111.85 (s), 92.47 (d, J = 6.9 Hz), 60.83 (d, J = 1.4 Hz), 59.63 (d, J = 11.5 Hz), 59.04 (d, J = 9.9 Hz), 53.59 (s), 53.36 (s), 44.33 (d, J = 3.3 Hz), 43.81 (d, J = 4.0 Hz), 31.95 (d, J = 12.0 Hz), 31.21 (d, J = 10.4 Hz), 24.43 (s), 24.36 (s), 24.34 (s), 23.71 (d, J = 4.7 Hz), 20.06 (d, J = 1.5 Hz), 19.45 (s); ^{31}P NMR (162 MHz, $CDCl_3$) 23.44; HRMS (TOF ES+) m/z calcd $C_{24}H_{35}ClN_3O_6P$ [(M + H)$^+$], 528.20; found, ?528.204

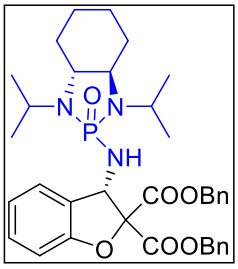


***dimethyl (3S)-3-((1,3-diisopropyl-2-oxidooctahydrobenzo[d][1,3,2]diazaphosphol-2-yl)amino)-5-methoxybenzofuran-2,2(3H)-dicarboxylate* (3q).** White solid, 0.465 g, 89% yield; $[\alpha]_D^{25}$ -9.7 (c 0.4,

$CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.02 (d, J = 2.6 Hz, 1H), 6.81 (d, J = 8.8 Hz, 1H), 6.73 (dd, J = 8.8, 2.7 Hz, 1H), 5.77 (dd, J = 11.2, 8.7 Hz, 1H), 3.81 (dd, J = 1.9, 0.7 Hz, 2H), 3.72 (s, 1H), 2.99 – 2.89 (m, 1H), 2.75 (ddd, J = 16.4, 11.1, 6.1 Hz, 1H), 2.10 – 1.97 (m, 1H), 1.80 – 1.66 (m, 1H), 1.44 – 1.27 (m, 1H), 1.26 – 1.22 (m, 1H), 1.19 (d, J = 6.8 Hz, 2H), 1.08 (d, J = 7.0 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.52 (s), 166.38 (s), 155.51 (s), 151.07 (s), 128.98 (d, J = 2.1 Hz), 116.16 (s), 111.12 (s), 110.01 (s), 92.37 (d, J = 7.2 Hz), 61.18 (d, J = 1.7 Hz), 59.69 (d, J = 11.5 Hz), 58.93 (t, J = 17.6 Hz), 55.97 (s), 53.49 (s), 53.23 (s), 44.21 (d, J = 3.7 Hz), 43.80 (d, J = 4.4 Hz), 31.91 (d, J = 11.9 Hz), 31.19 (d, J = 10.4 Hz), 24.47 (s), 24.39 (s), 24.34 (s), 23.71 (d, J = 4.8 Hz), 20.19 (d, J = 2.0 Hz), 19.47 (s).; ^{31}P NMR (162 MHz, $CDCl_3$) 23.59, 22.63; HRMS (TOF ES+) m/z calcd $C_{25}H_{38}N_3O_7P$ [$(M + H)^+$], 524.24; found, 524.254



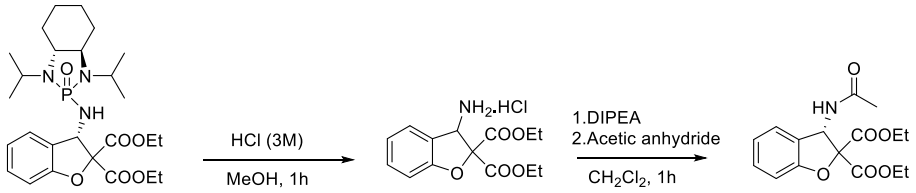
***dipropyl (3S)-3-((1,3-diisopropyl-2-oxidooctahydrobenzo[d][1,3,2]diazaphosphol-2-yl)amino)benzofuran-2,2(3H)-dicarboxylate* (3r).**
White solid, 0.390 g, 71% yield; $[\alpha]_D^{25}$ +5 (c 0.9, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, J = 7.4 Hz, 1H), 7.18 (t, J = 7.7 Hz, 1H), 6.94 (t, J = 7.5 Hz, 1H), 6.89 (d, J = 8.1 Hz, 1H), 5.81 (dd, J = 11.1, 9.0 Hz, 1H), 4.25 (dt, J = 10.6, 6.7 Hz, 1H), 4.17 (qt, J = 10.6, 5.3 Hz, 2H), 4.07 (dt, J = 10.7, 6.6 Hz, 1H), 3.74 – 3.47 (m, 2H), 3.01 – 2.89 (m, 1H), 2.84 – 2.67 (m, 2H), 2.02 (d, J = 9.9 Hz, 2H), 1.81 – 1.58 (m, 6H), 1.43 – 1.27 (m, 3H), 1.24 (d, J = 6.8 Hz, 4H), 1.18 (d, J = 6.8 Hz, 6H), 1.07 (d, J = 7.0 Hz, 3H), 0.89 (td, J = 7.4, 4.4 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.10 (s), 166.03 (s), 157.43 (s), 129.91 (s), 128.42 (s), 125.19 (s), 122.33 (s), 110.65 (s), 92.09 (d, J = 7.0 Hz), 68.19 (s), 67.93 (s), 60.75 (s), 59.64 (d, J = 11.4 Hz), 58.99 (d, J = 9.8 Hz), 44.15 (d, J = 2.7 Hz), 43.82 (d, J = 3.8 Hz), 31.98 (d, J = 12.0 Hz), 31.26 (d, J = 10.4 Hz), 24.51 (s), 24.38 (s), 23.81 (d, J = 4.7 Hz), 21.86 (s), 20.15 (s), 19.48 (s), 10.31 (s), 10.27 (s); ^{31}P NMR (162 MHz, $CDCl_3$) 23.52, 22.53; HRMS (TOF ES+) m/z calcd $C_{28}H_{44}N_3O_6P$ [$(M + H)^+$], 550.30; found, 550.306



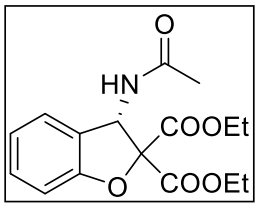
***Dibenzyl (3S)-3-((1,3-diisopropyl-2-oxidooctahydrobenzo[d][1,3,2]diazaphosphol-2-yl)amino)benzofuran-2,2(3H)-dicarboxylate* (3s).** White solid, 0.374 g, 58% yield; $[\alpha]_D^{25}$ -16.2 (c 1.6, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.36 (m, 1H), 7.32 – 7.14 (m, 10H), 6.97 (t, J = 7.5 Hz, 1H), 6.91 (dd, J = 8.2, 4.1 Hz, 1H), 5.89 (dd, J = 11.2, 9.1 Hz, 1H), 5.28 (ddd, J = 28.8, 14.4, 9.9 Hz, 2H), 5.18 – 5.04 (m, 2H), 3.71 – 3.32 (m, 2H), 2.93 (ddd, J = 12.3, 7.0, 3.3 Hz, 1H), 2.88 – 2.60 (m, 2H), 2.00 (d, J = 7.8 Hz, 2H), 1.71 (d, J = 9.5 Hz, 2H), 1.34 (dt, J = 20.2, 9.8 Hz, 3H), 1.25 (s, 1H), 1.22 (d, J = 6.7 Hz, 3H), 1.12 – 0.99 (m, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.78 (s), 165.63 (d, J = 16.7 Hz), 157.44 (d, J = 3.3 Hz), 134.95 (s), 134.62 (s), 128.75 (s), 128.61 (s), 128.54 (d, J = 1.3 Hz), 128.39 (s), 128.38 (s), 128.32 (s), 128.25 (s), 128.20 (s), 128.12 (s), 125.64 (s), 125.24 (s), 122.37 (d, J = 16.8 Hz), 110.81 (d, J = 14.6 Hz), 92.37 (d, J = 6.2 Hz), 92.12 (d, J = 7.2 Hz), 68.16 (s), 67.96 (s), 67.85 (s), 60.99 (d, J = 1.8 Hz), 60.44 (d, J

= 5.5 Hz), 59.65 (s), 59.53 (s), 59.08 (d, J = 10.1 Hz), 44.13 (d, J = 3.8 Hz), 43.85 (d, J = 4.4 Hz), 31.86 (d, J = 12.0 Hz), 31.21 (d, J = 10.4 Hz), 24.40 (d, J = 8.9 Hz), 23.70 (d, J = 4.9 Hz), 22.99 (d, J = 6.7 Hz), 20.22 (d, J = 1.8 Hz), 19.81 (d, J = 2.4 Hz), 19.64 (s), 19.50 (s).; ^{31}P NMR (162 MHz, $CDCl_3$) 23.42, 22.55; HRMS (TOF ES+) m/z calcd $C_{36}H_{44}N_3O_6P$ [$(M + H)^+$], 646.30; found, 646.306

Synthesis and characterization of deprotected 2,3-dihydrobenzofuran (5a): Into 25 ml round bottom flask, 104 mg (0.2 mmol) of 3a was dissolved in 4 ml methanol followed by addition of 1.6 mmol HCl (3M) at 0^o C. After 30 minutes, reaction warmed to room temperature and stirred for 1 hour. Then, all volatiles were evaporated to result 4a as a white solid, which was directly dissolved in 6 ml dry dichloromethane. The reaction cooled to 0^{o}C, and diisopropylethylamine (0.6 mmol) and acetic anhydride (0.6 mmol) were added. After 30 minutes of stirring at the same temperature, the reaction warmed to room temperature and was kept for 2 hours. The crude product was subjected directly to column chromatography using ethyl acetate/ hexanes 5/10) to separate the product as a white solid.



Diethyl (S)-3-acetamidobenzofuran-2,2(3H)-dicarboxylate **(5a).**



White solid, 0.038 g, *62*% yield; $[\alpha]_D^{25}$ +118.2 (1.3, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 – 7.20 (m, 1H), 7.01 – 6.91 (m, 1H), 6.54 (d, J = 9.8 Hz, 1H), 5.95 (d, J = 9.8 Hz, 1H), 4.39 – 4.16 (m, 2H), 1.94 (s, 1H), 1.27 (td, J = 7.1, 2.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.92 (s), 166.01 (s), 165.70 (s), 158.07 (s), 130.68 (s), 125.30 (s), 124.95 (s), 122.86 (s), 110.92 (s), 91.44 (s), 62.91 (s), 62.69 (s), 55.50 (s), 23.26 (s), 14.11 (s), 13.99 (s); HRMS (TOF ES+) m/z calcd $C_{16}H_{19}NO_6$ [$(M + H)^+$], 322.12; found, 322.128

X-Ray Structure of Products 3a

General Data Collection

Data were collected on a Rigaku XtaLAB Synergy-*i* Kappa diffractometer equipped with a PhotonJet-*i* X-ray source operated at 50 W (50kV, 1 mA) to generate Cu Kα radiation (λ = 1.54178 Å) and a HyPix-6000HE HPC detector. Crystals were transferred from the vial and placed on a glass slide in type NVH immersion oil by Cargille. A Zeiss Stemi 305 microscope was used to identify a suitable specimen for X-ray diffraction from a representative sample of the material. The crystal and a small amount of the oil were collected on a MiTeGen 50 micron MicroLoop and transferred to the instrument where it was placed under a cold nitrogen stream (Oxford 700 series) maintained at 100K throughout the duration of the experiment. The sample was optically centered with the aid of a video camera to ensure that no translations were observed as the crystal was rotated through all positions.

A unit cell collection was then carried out. After it was determined that the unit cell was not present in the CCDC database, a data collection strategy was calculated by *CrysAlis*^{Pro}[1]. The crystal was measured for size, morphology, and color. These values are reported in the accompanying Li21_05_tables file.

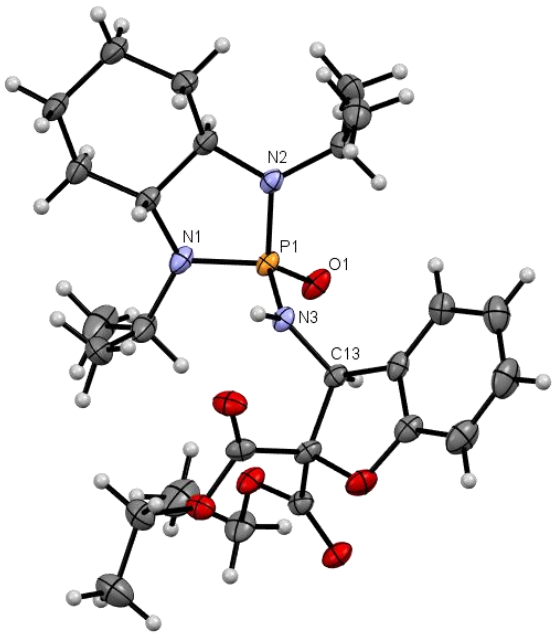
Refinement Details

After data collection, the unit cell was re-determined using a subset of the full data collection. Intensity data were corrected for Lorentz, polarization, and background effects using the *CrysAlis*^{Pro}[1]. A numerical absorption correction was applied based on a Gaussian integration over a multifaceted crystal and followed by a semi-empirical correction for adsorption applied using the program *SCALE3 ABSPACK*[2]. The programs *SHELXT*[3] was used for the initial

structure solution and *SHELXL*[4] was used for refinement of the structure. Both of these programs were utilized within the OLEX2 software[5]. The interstitial chloroform molecule was positionally disordered and modeled over three sites using the SUMP command to restrain the total occupancy of the three orientations to a total value of 1. To help maintain reasonable ADP and bond length values, SIMU, RIGU, and free variable DFIX restraints were applied to the disordered sites. Hydrogen atoms bound to carbon and nitrogen atoms were located in the difference Fourier map and were geometrically constrained using the appropriate AFIX commands.

References:

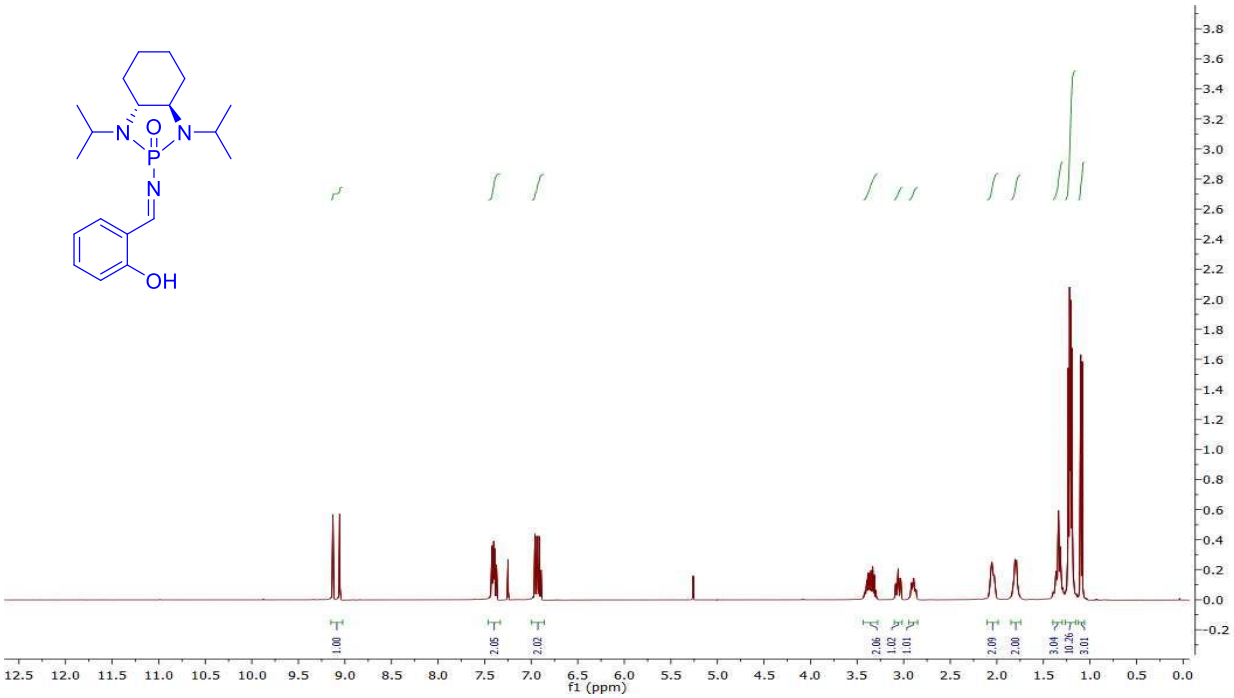
1. CrysAlis^{Pro} (2018) Oxford Diffraction Ltd.
2. SCALE3 ABSPACK (2005) Oxford Diffraction Ltd.
3. Sheldrick, G. M. (2015) *Acta Crystallogr*., C**71**, 3-8.
4. Sheldrick, G. M. (2015) *Acta Crystallogr*., A**71**, 3-8.
5. Dolomanov, O. V.; Bourhis, . L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann. H. (2009) *J. Appl. Cryst*. **42**, 339-341.



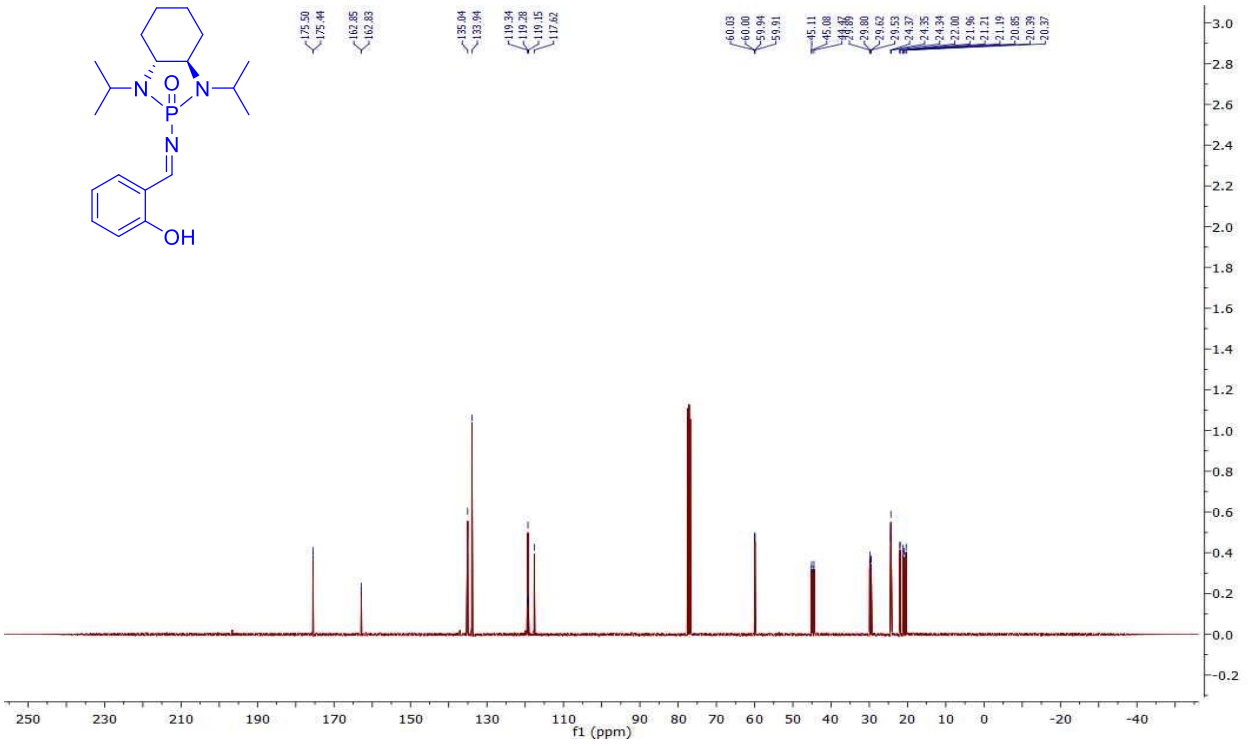
The thermal ellipsoids are represented at 50% probability. Carbon, hydrogen, nitrogen, oxygen and phosphorus atoms are represented by gray, white, light blue, red and light orange ellipsoids, respectively. The interstitial chloroform molecule was omitted for clarity.

Crystal used for single crystal X-ray diffraction experiment.

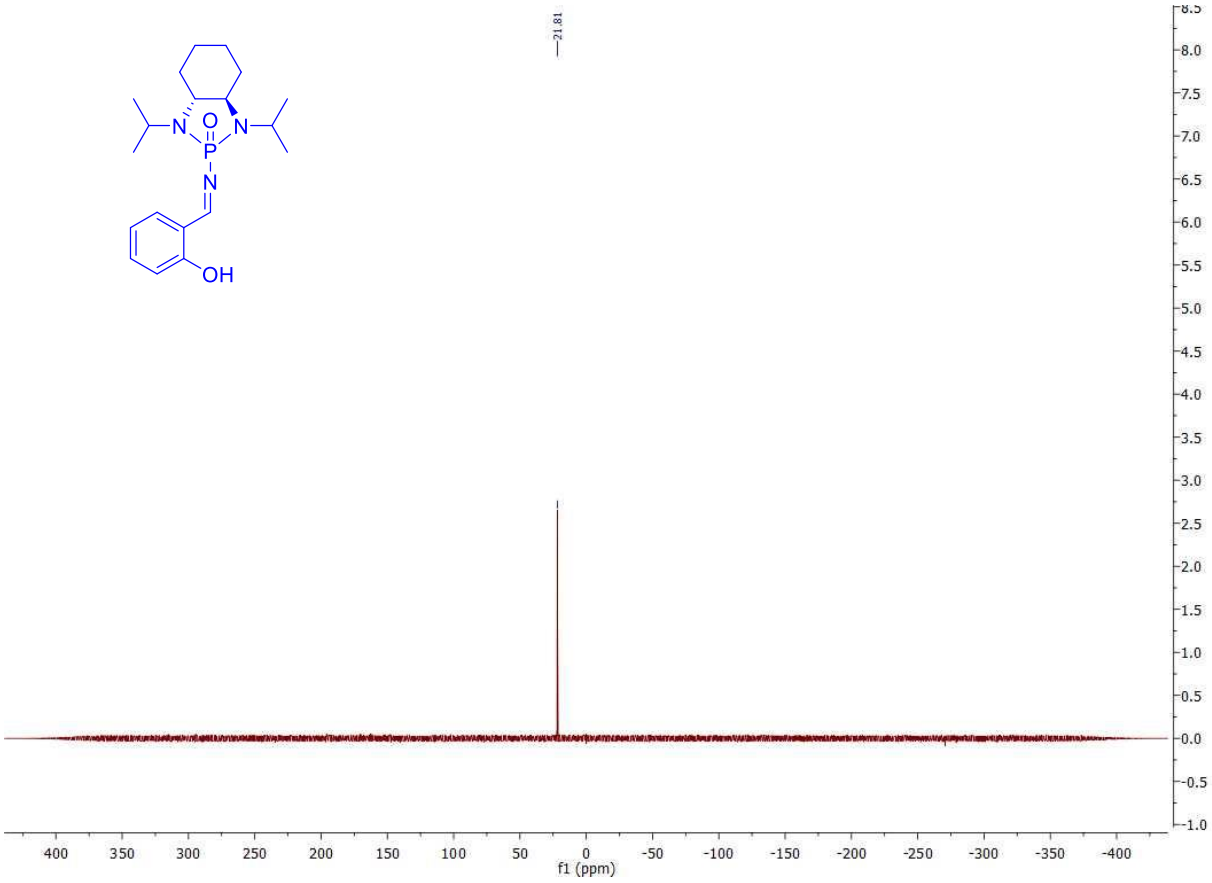
Copies of NMRs of compounds 1a-1n



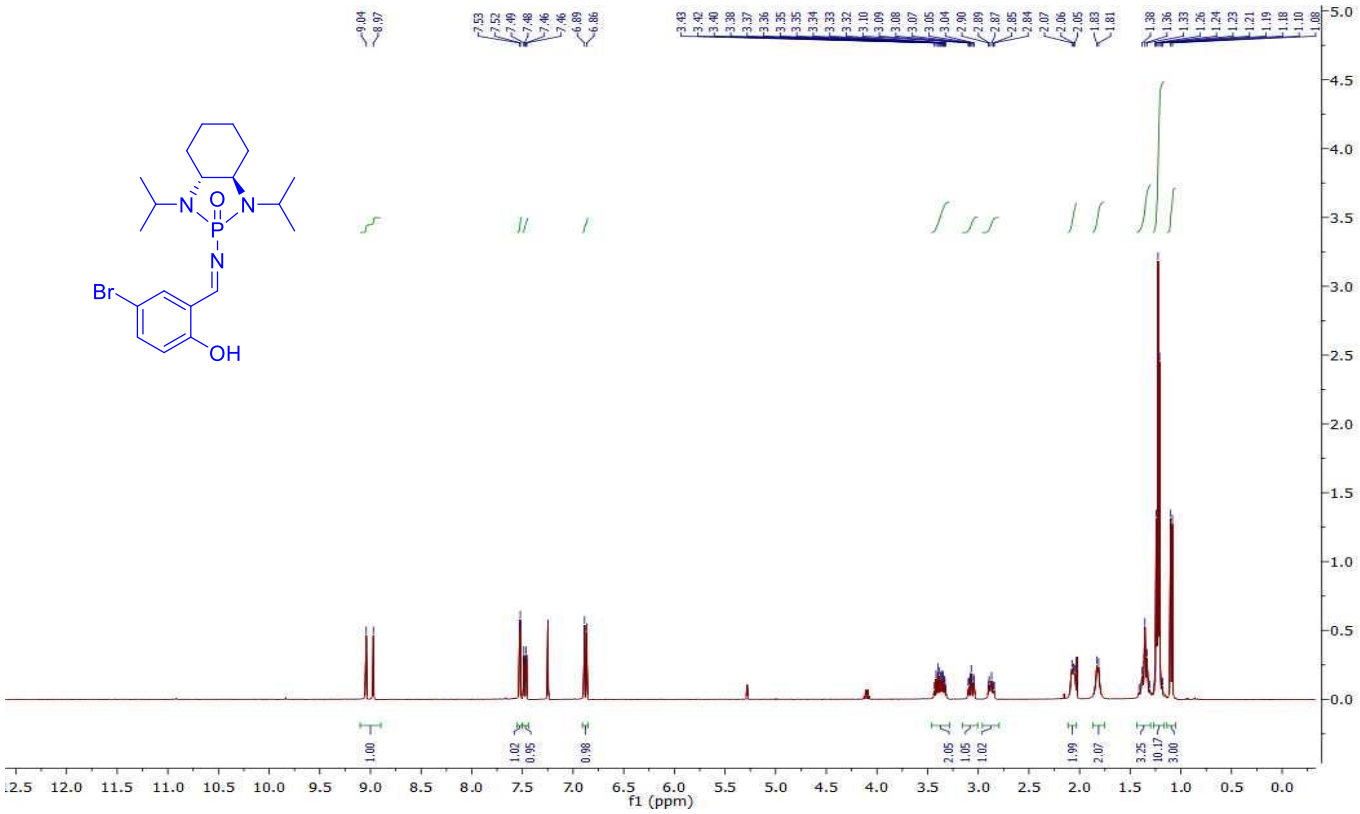
^{1}H NMR of imine **1a** ($CDCl_3$, 400 Hz)



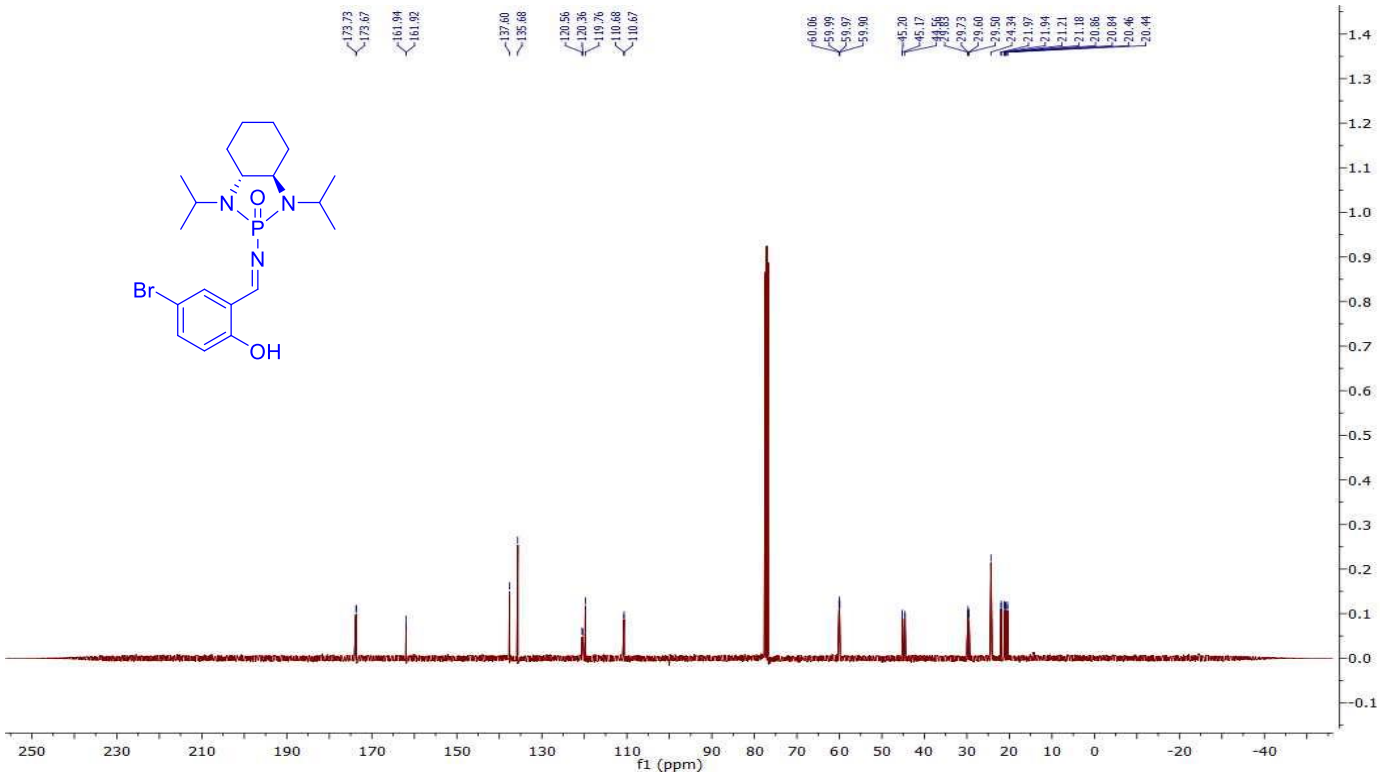
^{13}C NMR of imine **1a** ($CDCl_3$, 100 Hz)



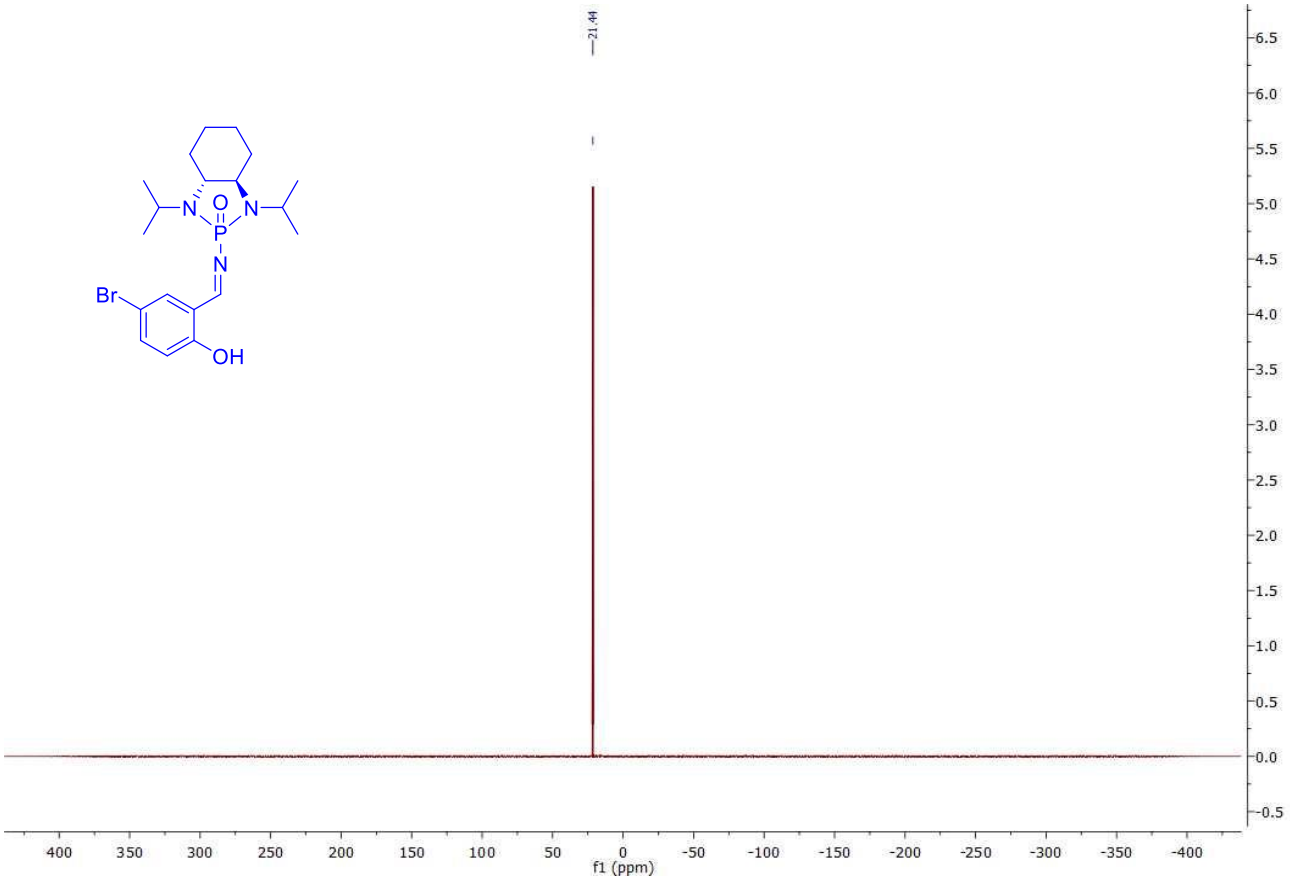
^{31}P NMR of imine **1a** ($CDCl_3$, 162 Hz)



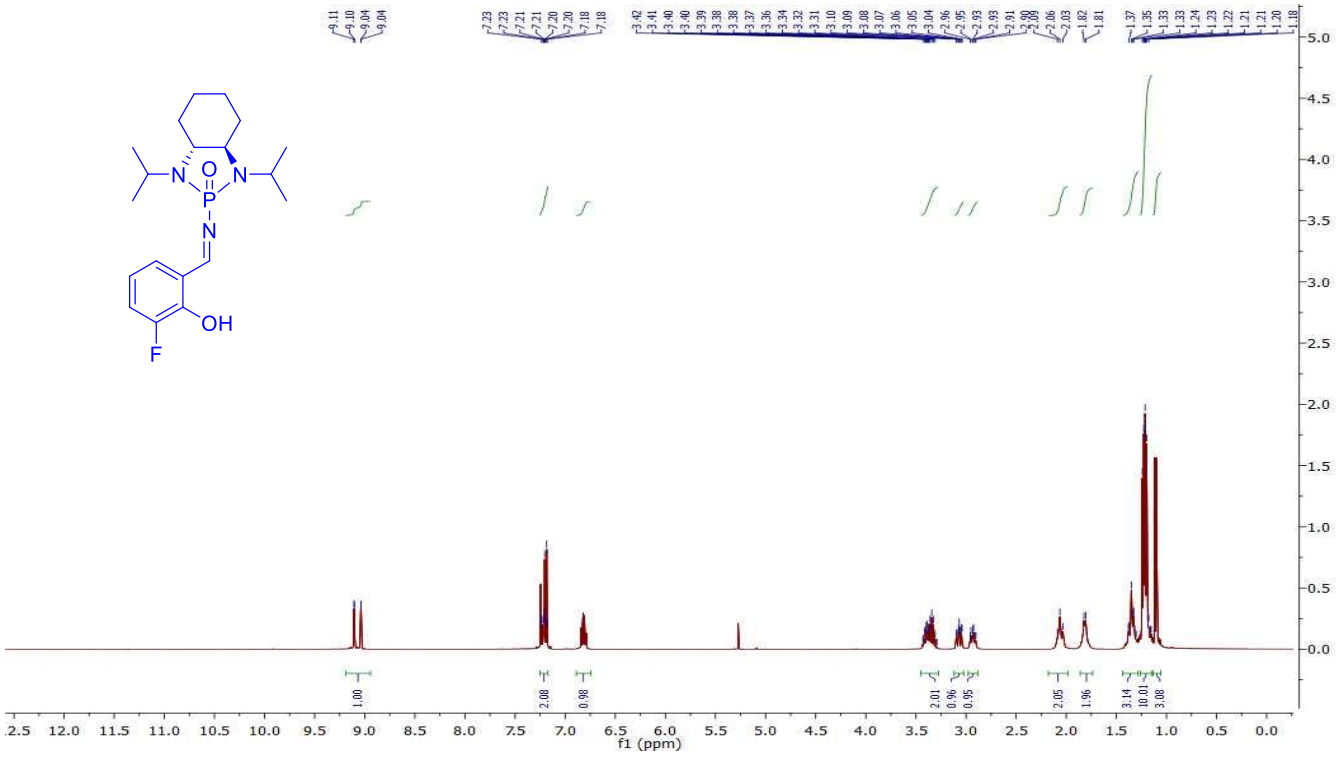
^{1}H NMR of imine **1b** ($CDCl_3$, 400 Hz)



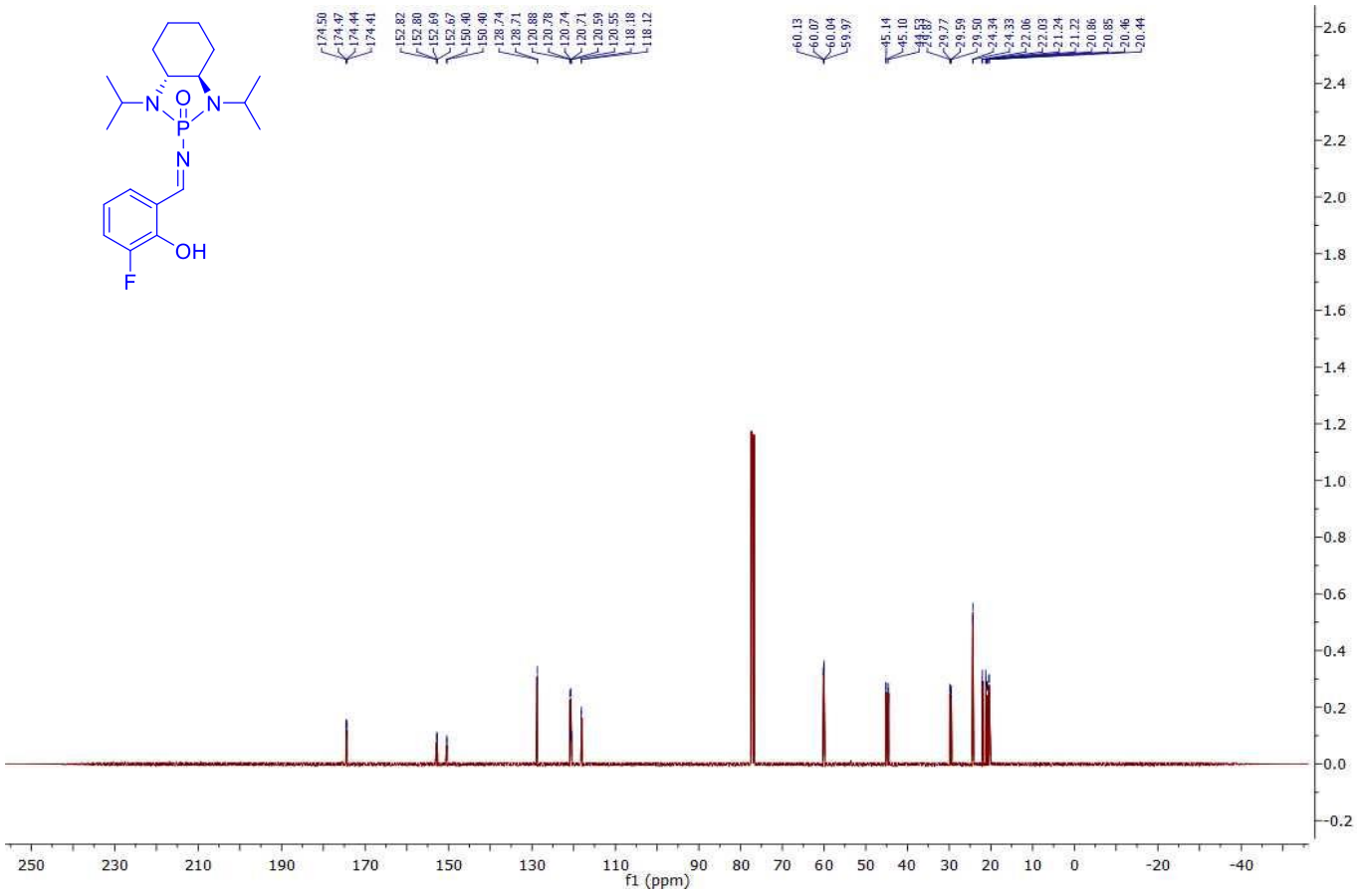
^{13}C NMR of imine **1b** ($CDCl_3$, 100 Hz)



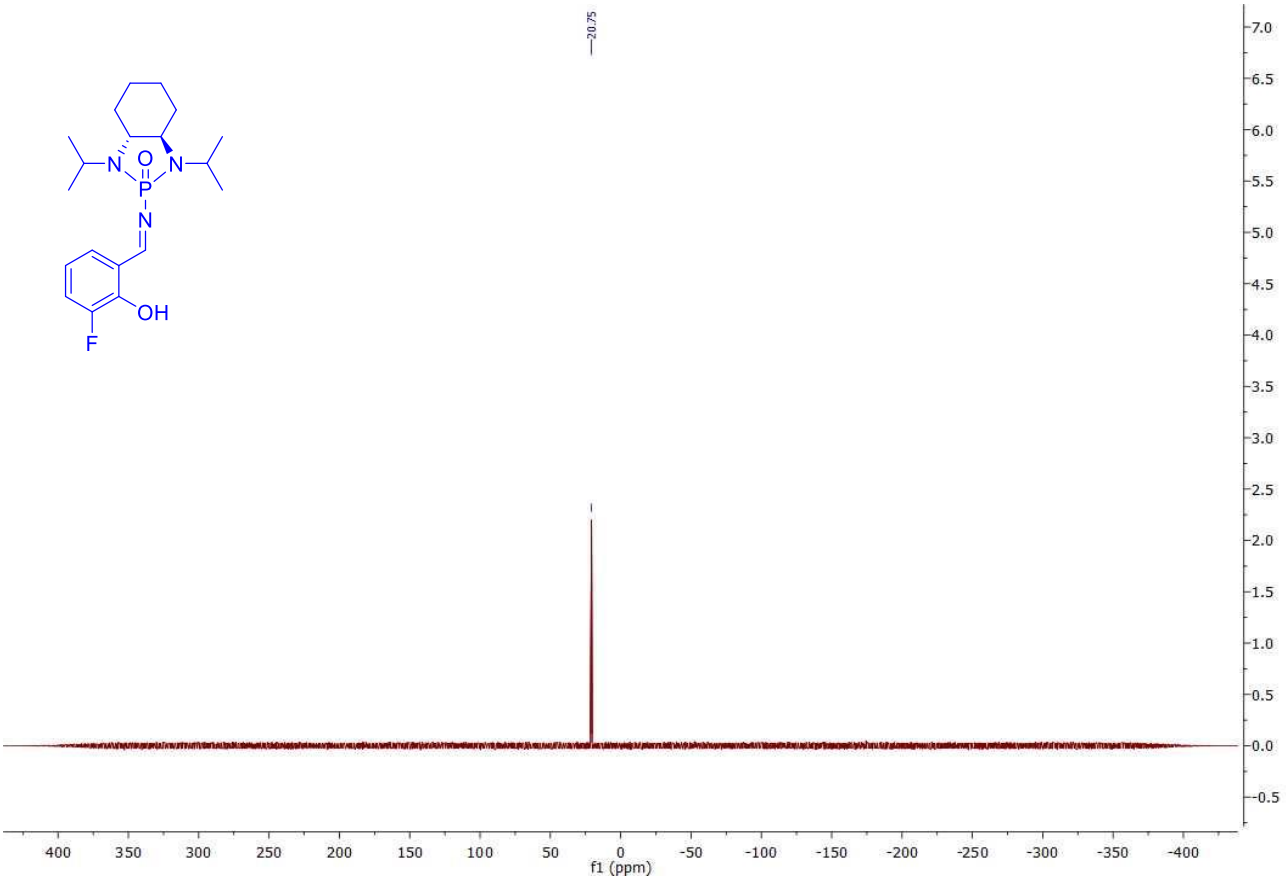
^{31}P NMR of imine **1b** ($CDCl_3$, 162 Hz)



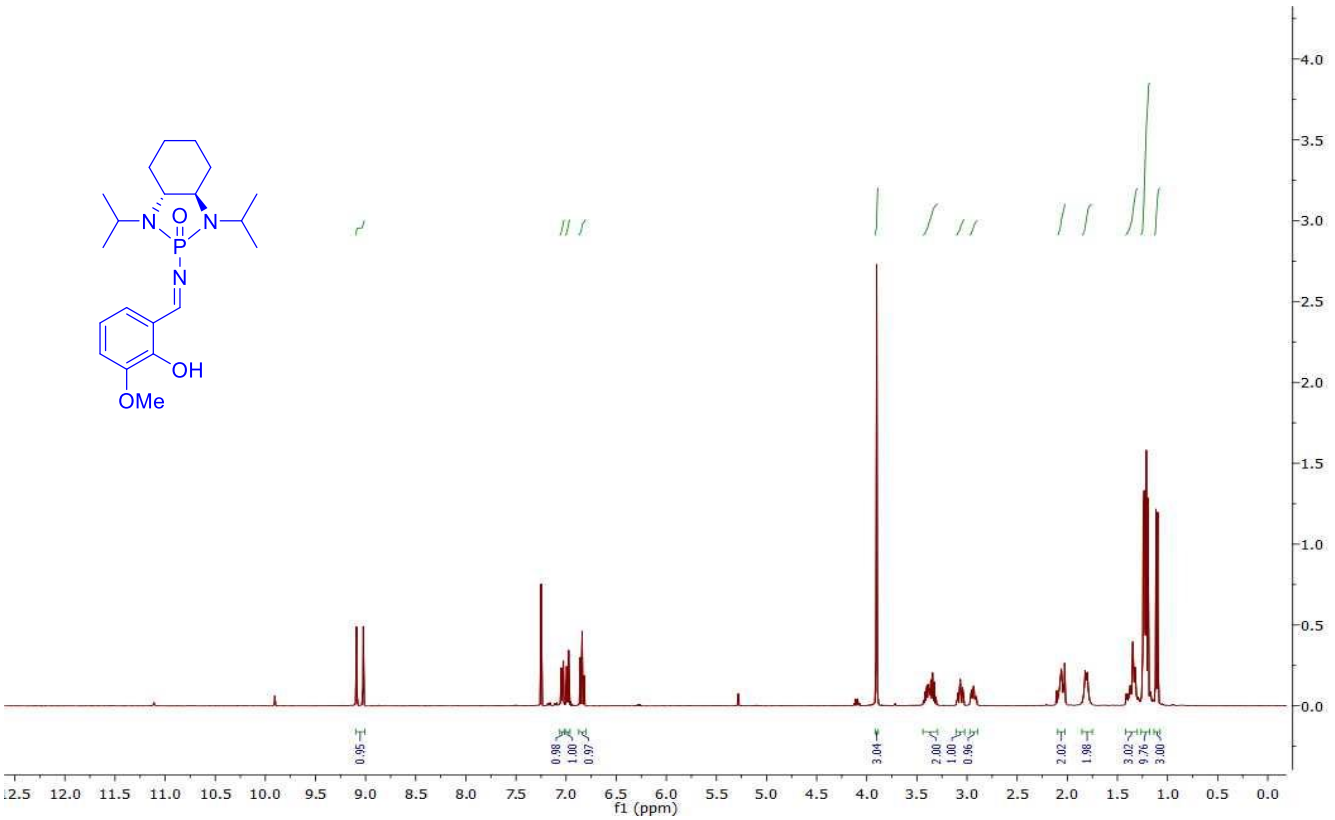
^{1}H NMR of imine **1c** ($CDCl_3$, 400 Hz)



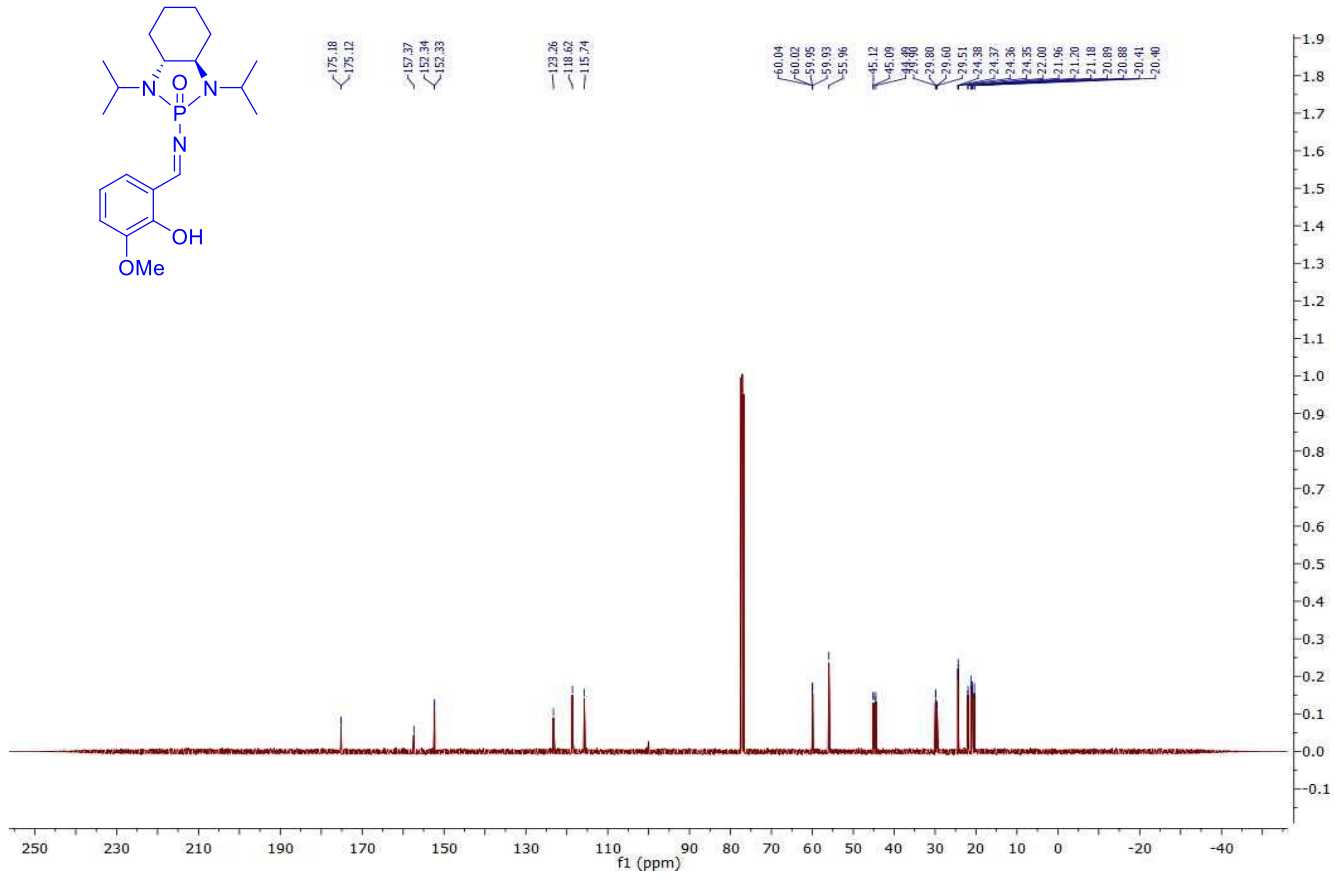
^{13}C NMR of imine **1c** ($CDCl_3$, 100 Hz)



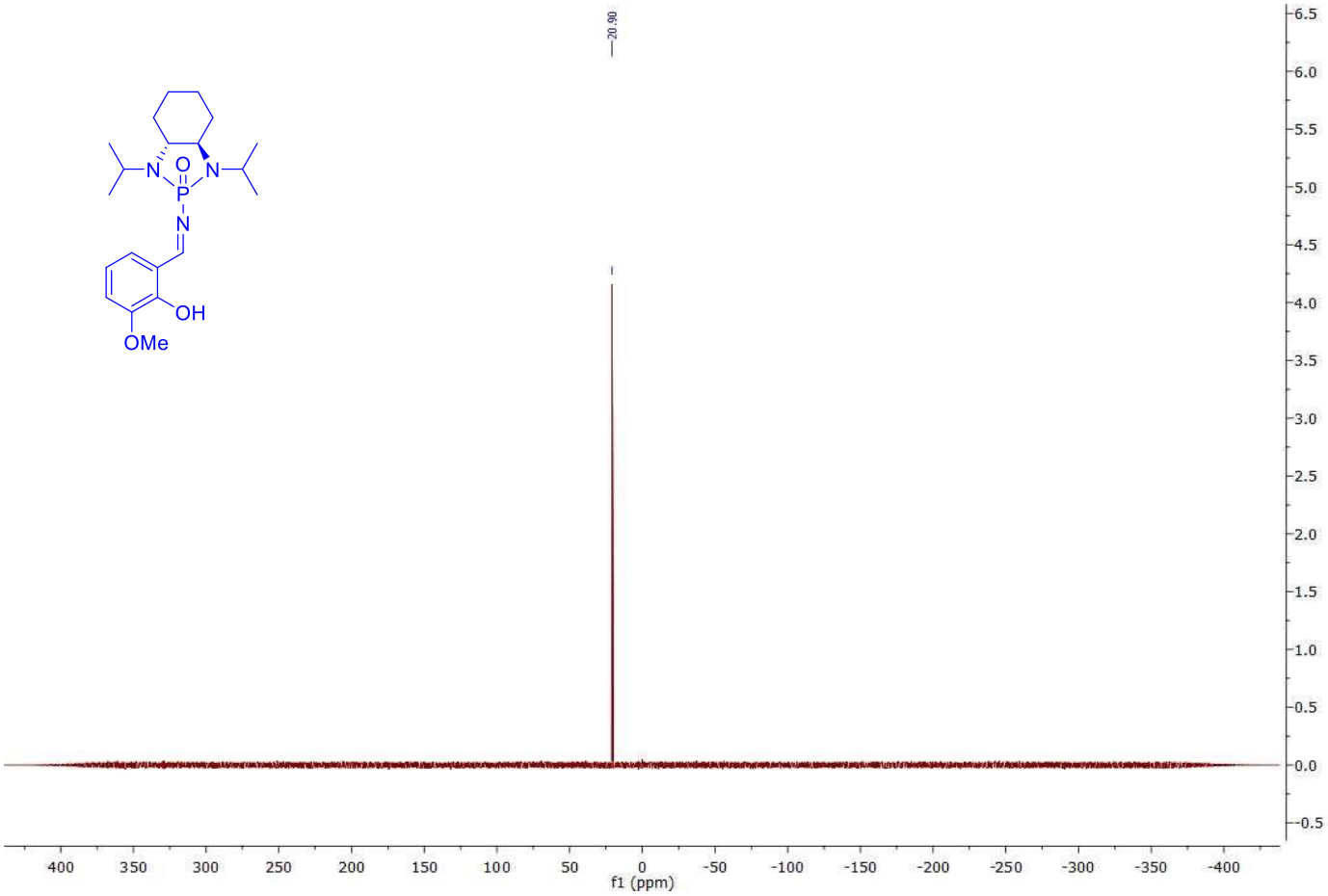
^{31}P NMR of imine **1c** ($CDCl_3$, 162 Hz)



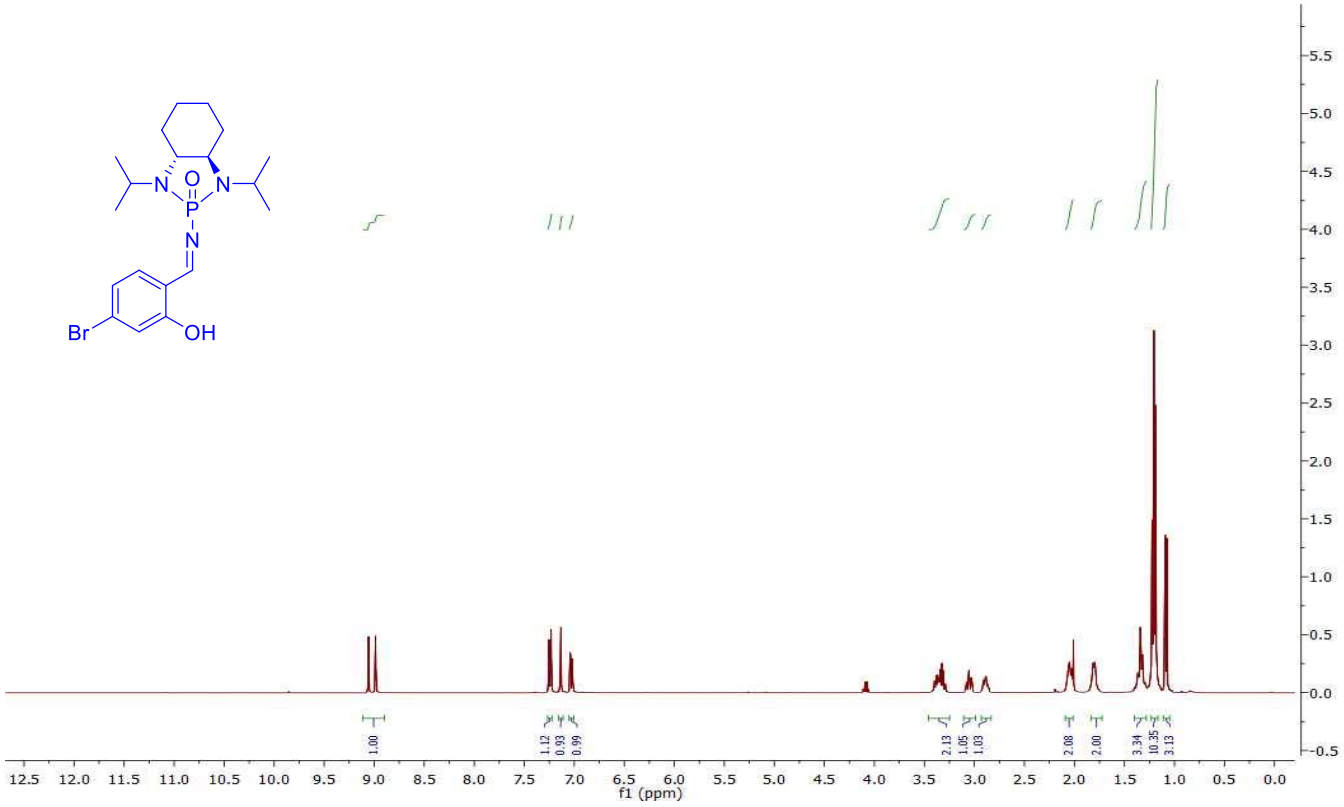
^{1}H NMR of imine **1d** ($CDCl_3$, 400 Hz)



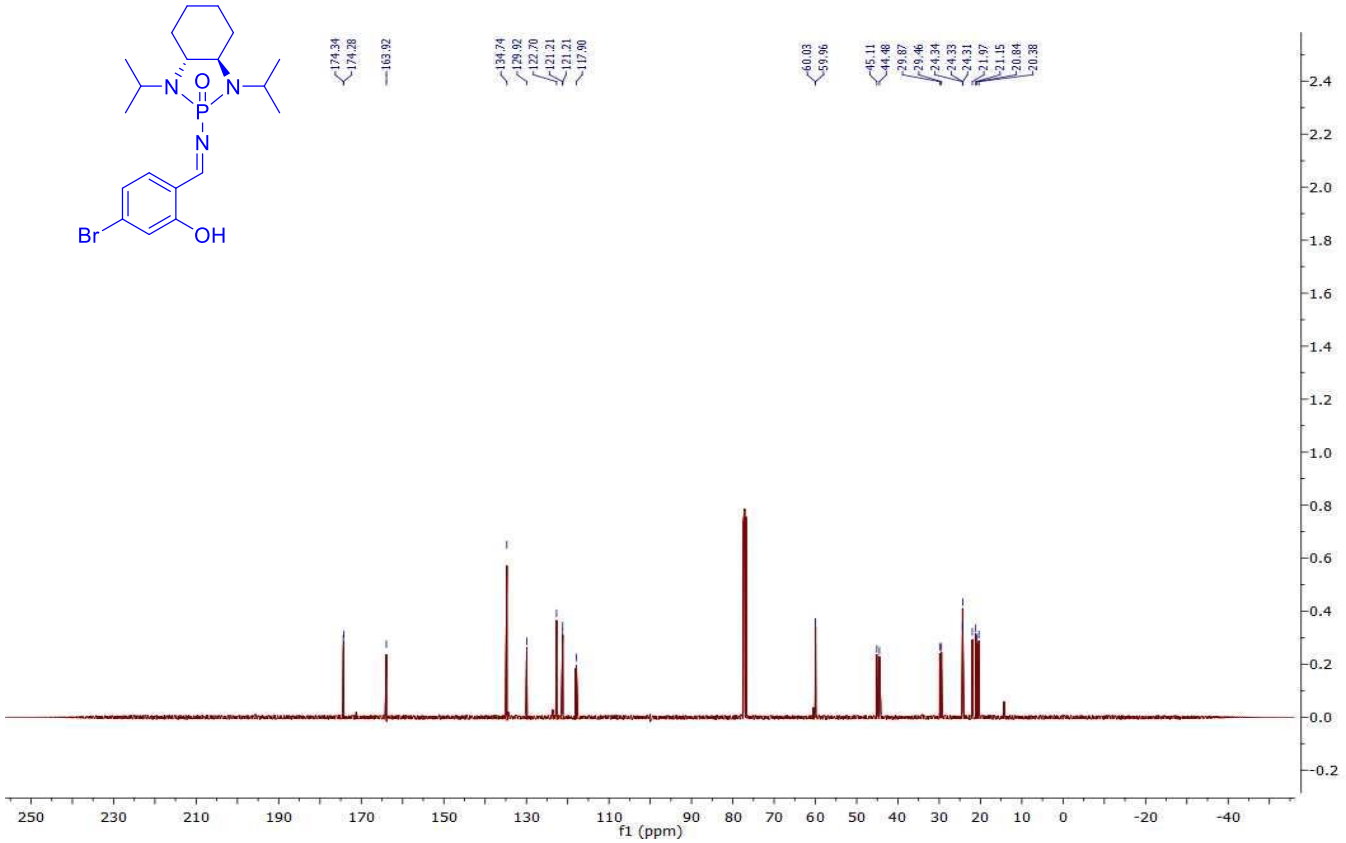
^{13}C NMR of imine **1d** ($CDCl_3$, 100 Hz)



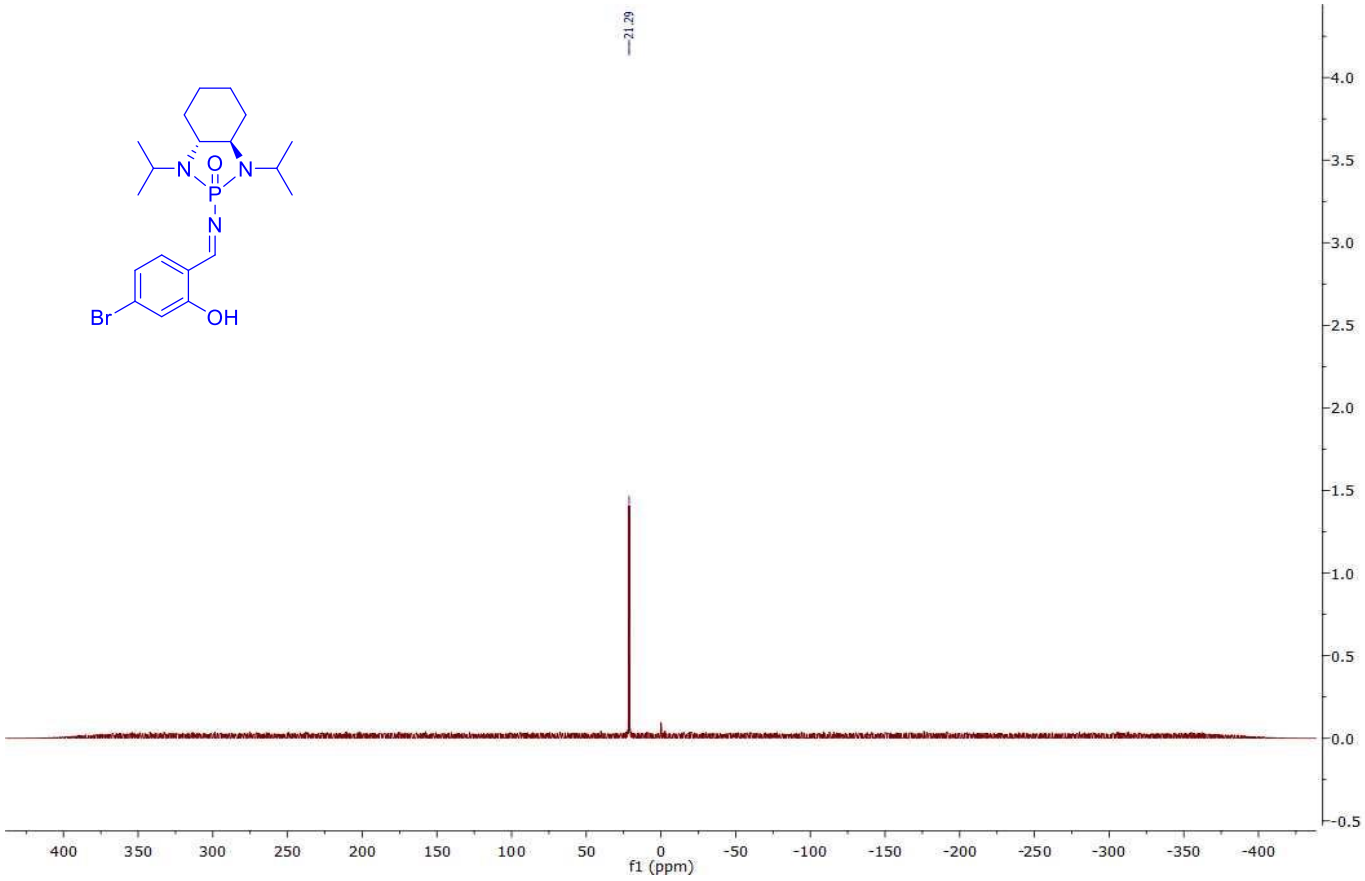
^{31}P NMR of imine **1d** ($CDCl_3$, 162 Hz)



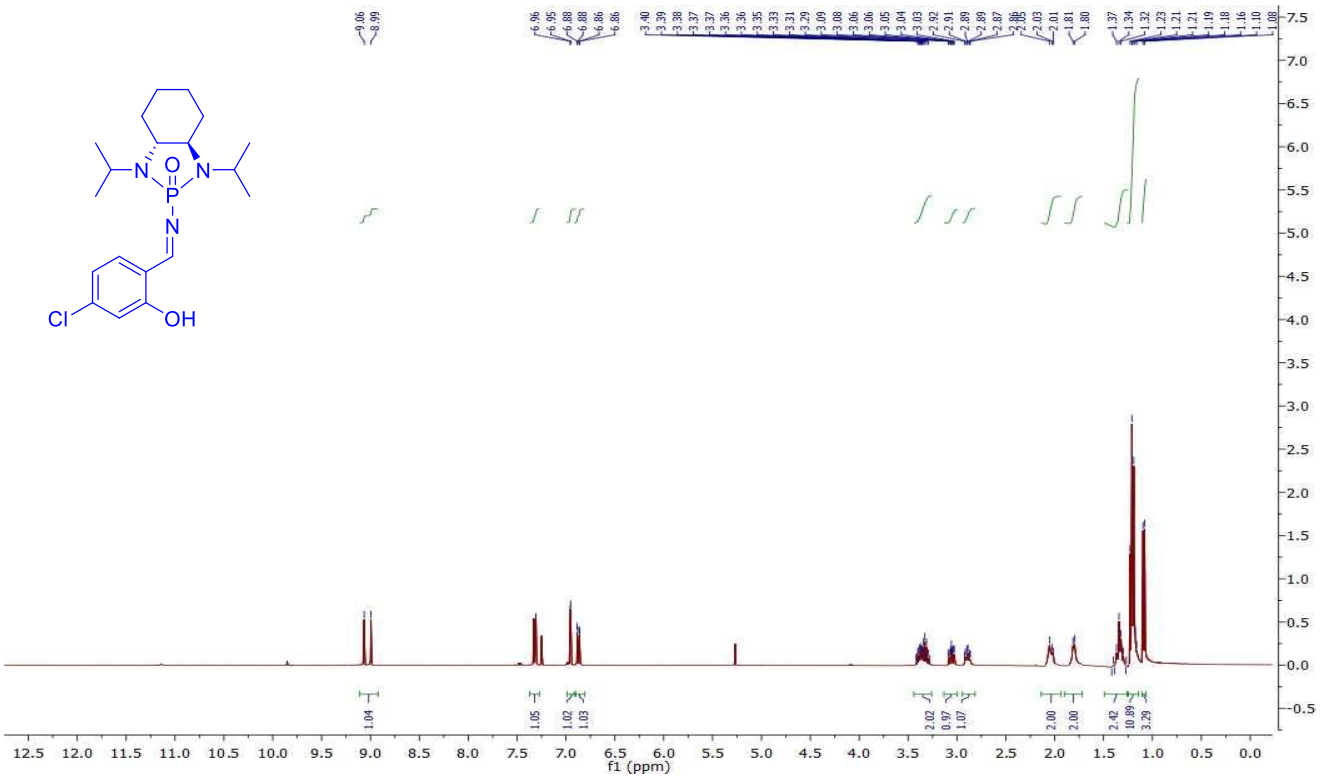
^{1}H NMR of imine **1e** ($CDCl_3$, 400 Hz)



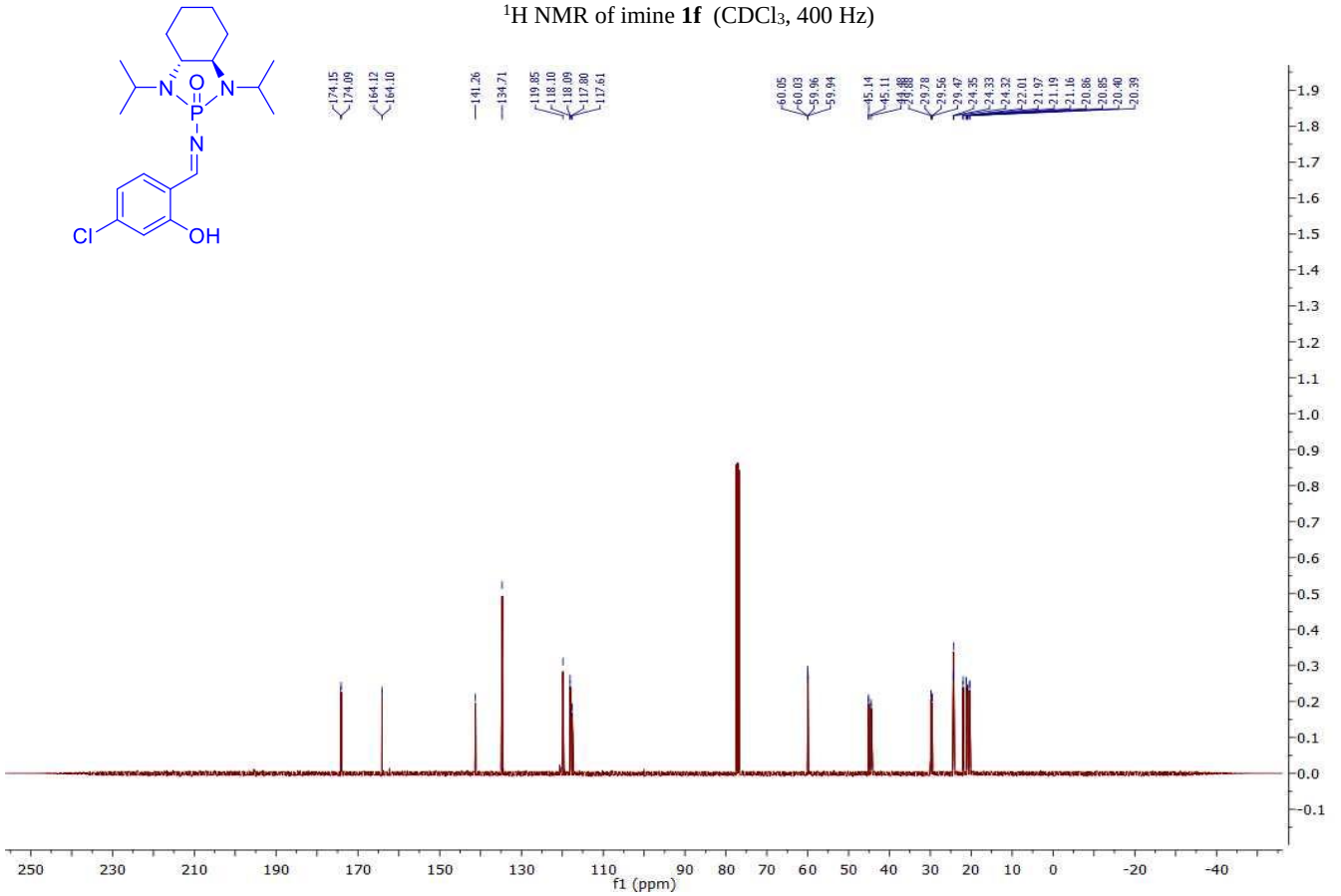
^{13}C NMR of imine **1e** ($CDCl_3$, 100 Hz)



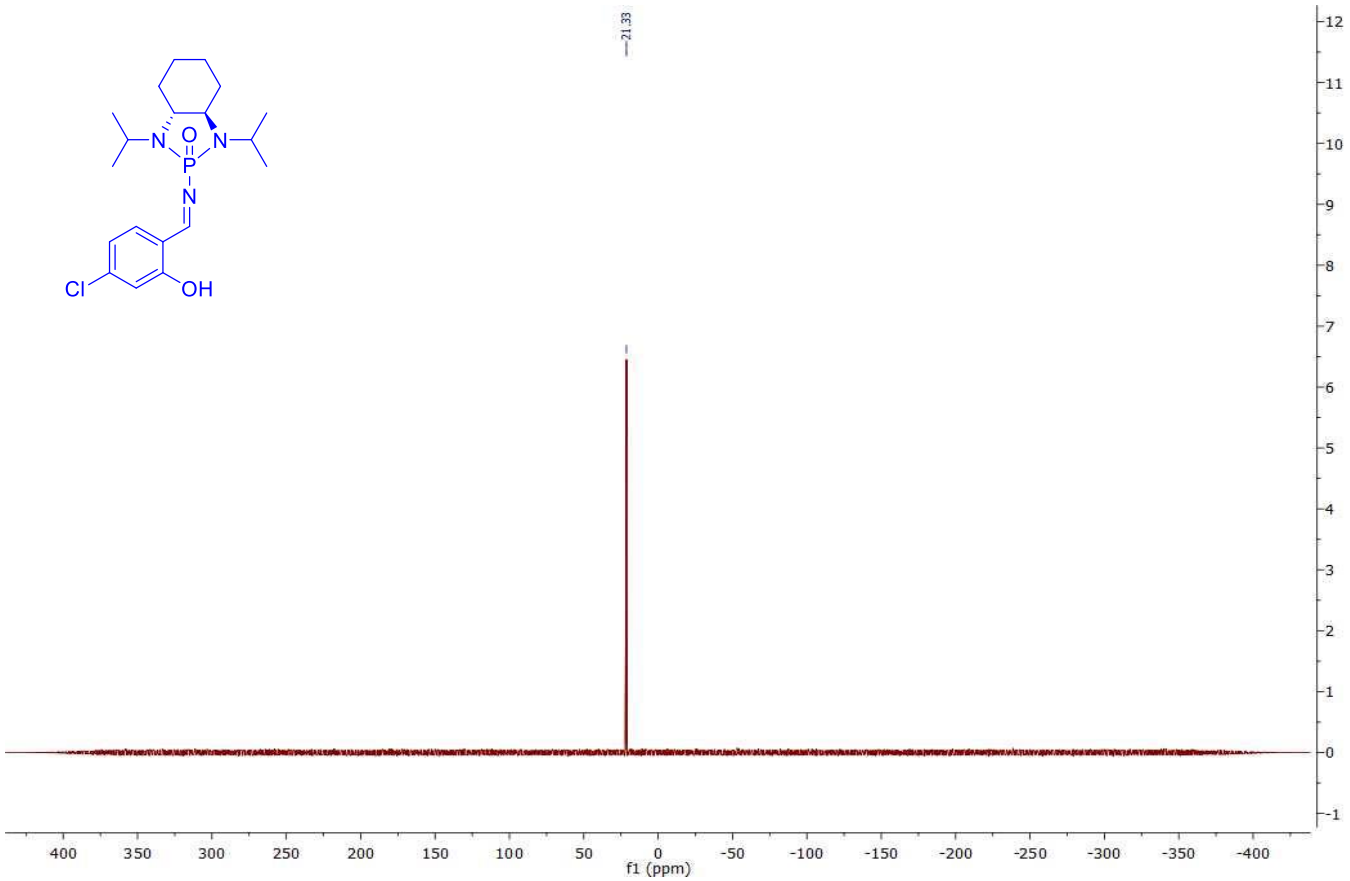
^{31}P NMR of imine **1e** ($CDCl_3$, 162 Hz)



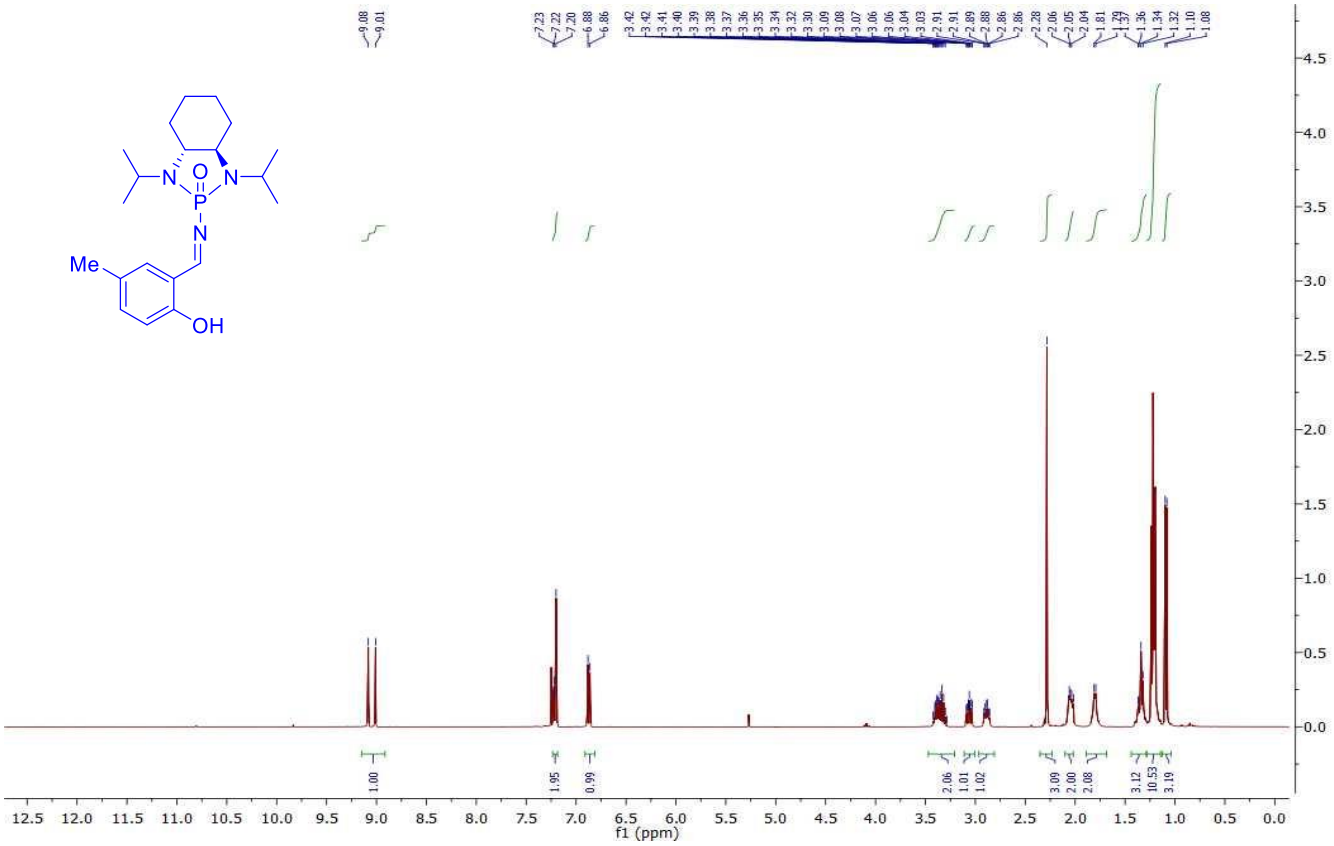
^{1}H NMR of imine **1f** ($CDCl_3$, 400 Hz)



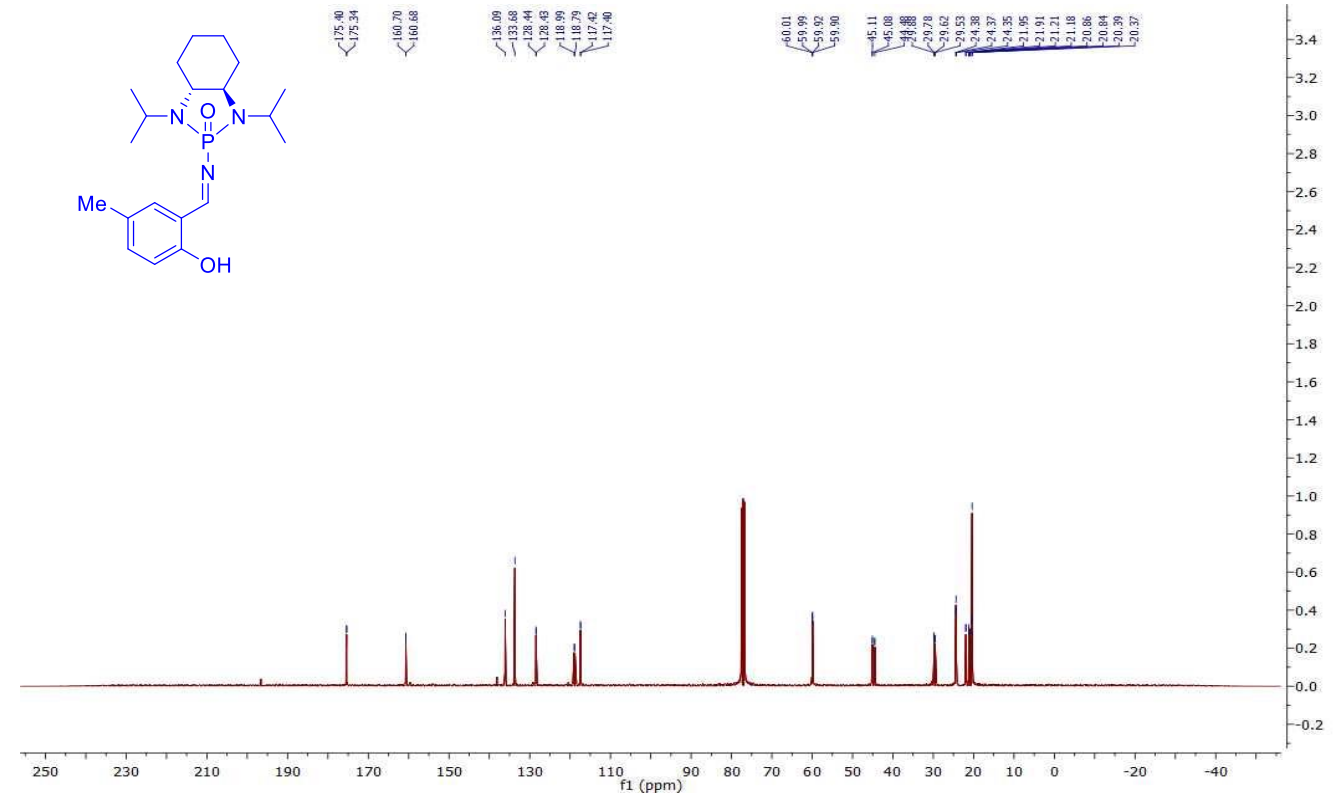
^{13}C NMR of imine **1f** ($CDCl_3$, 100 Hz)



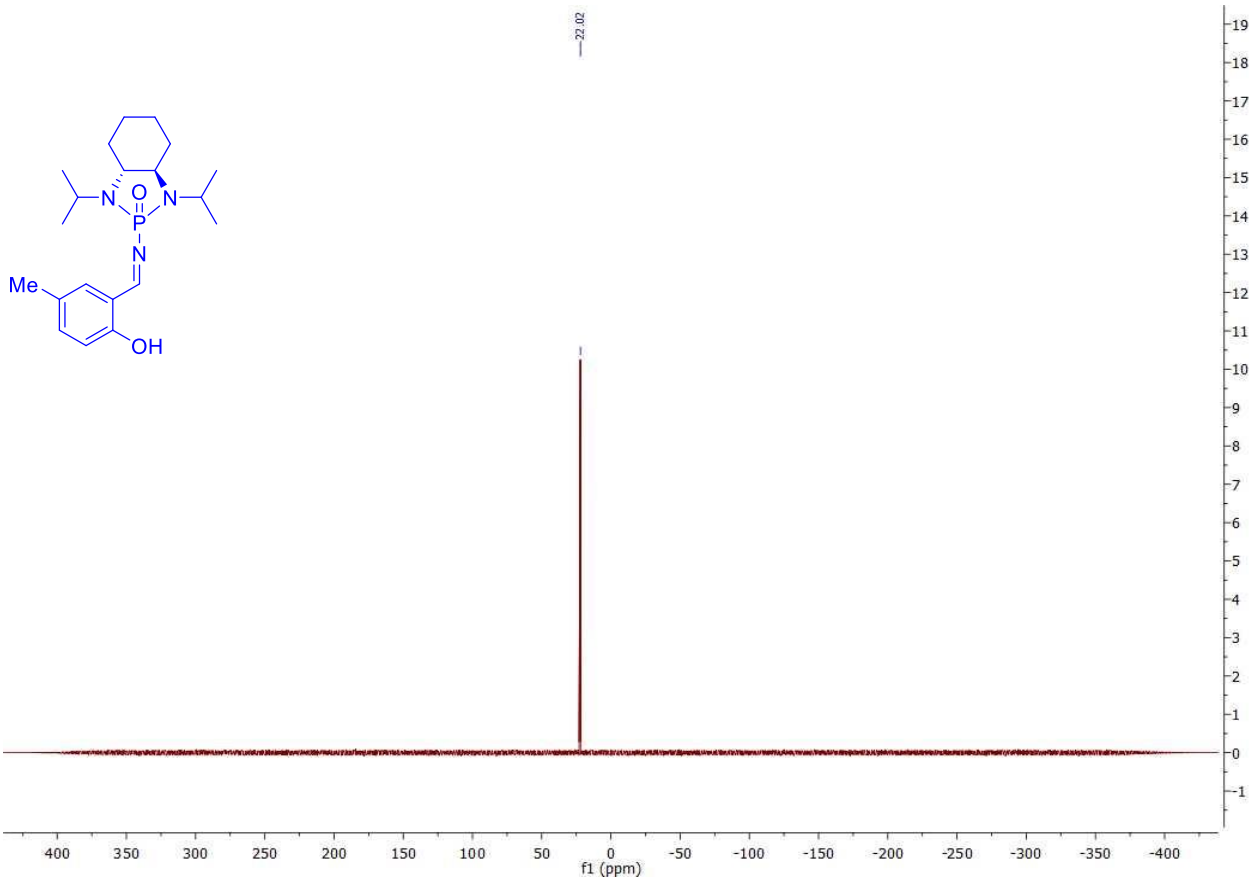
^{31}P NMR of imine **1f** ($CDCl_3$, 162 Hz)



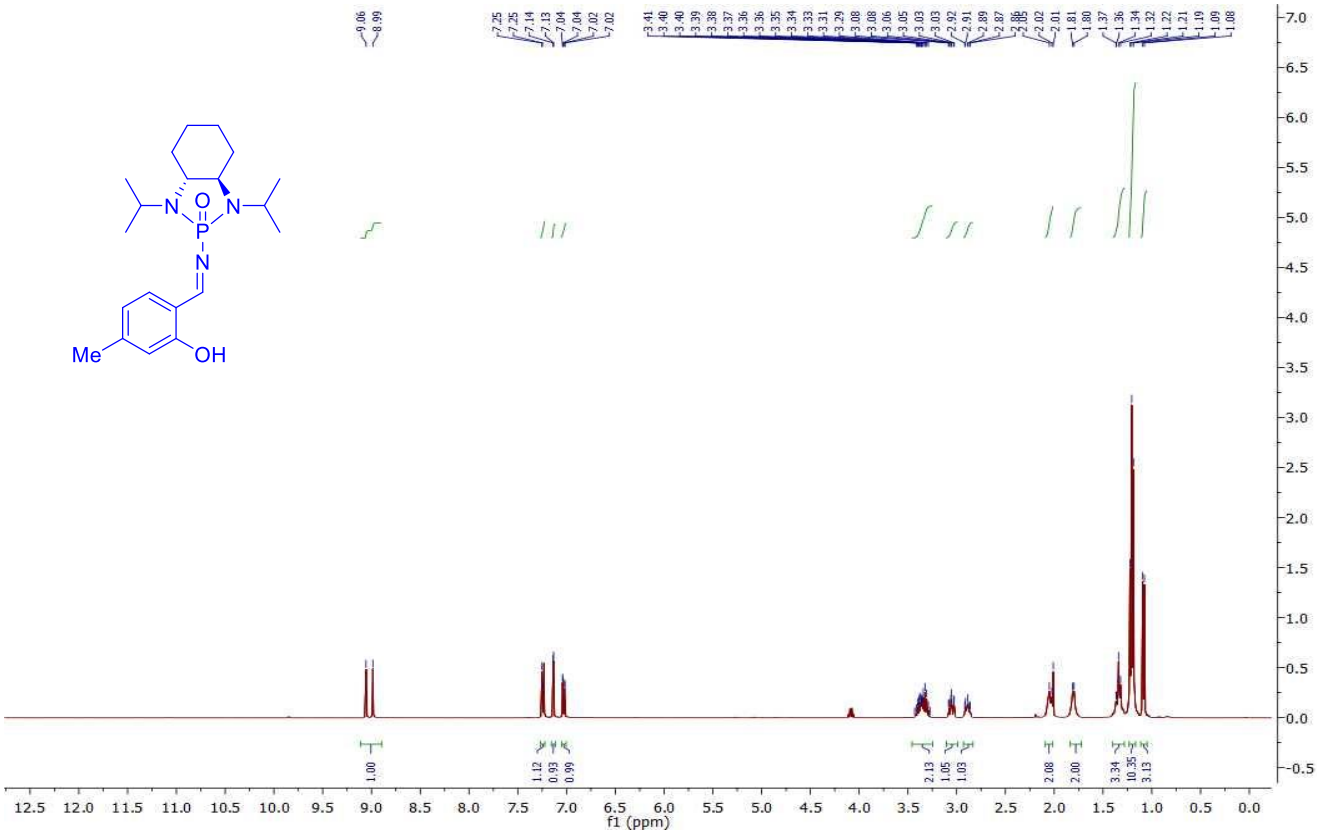
^{1}H NMR of imine **1g** ($CDCl_3$, 400 Hz)



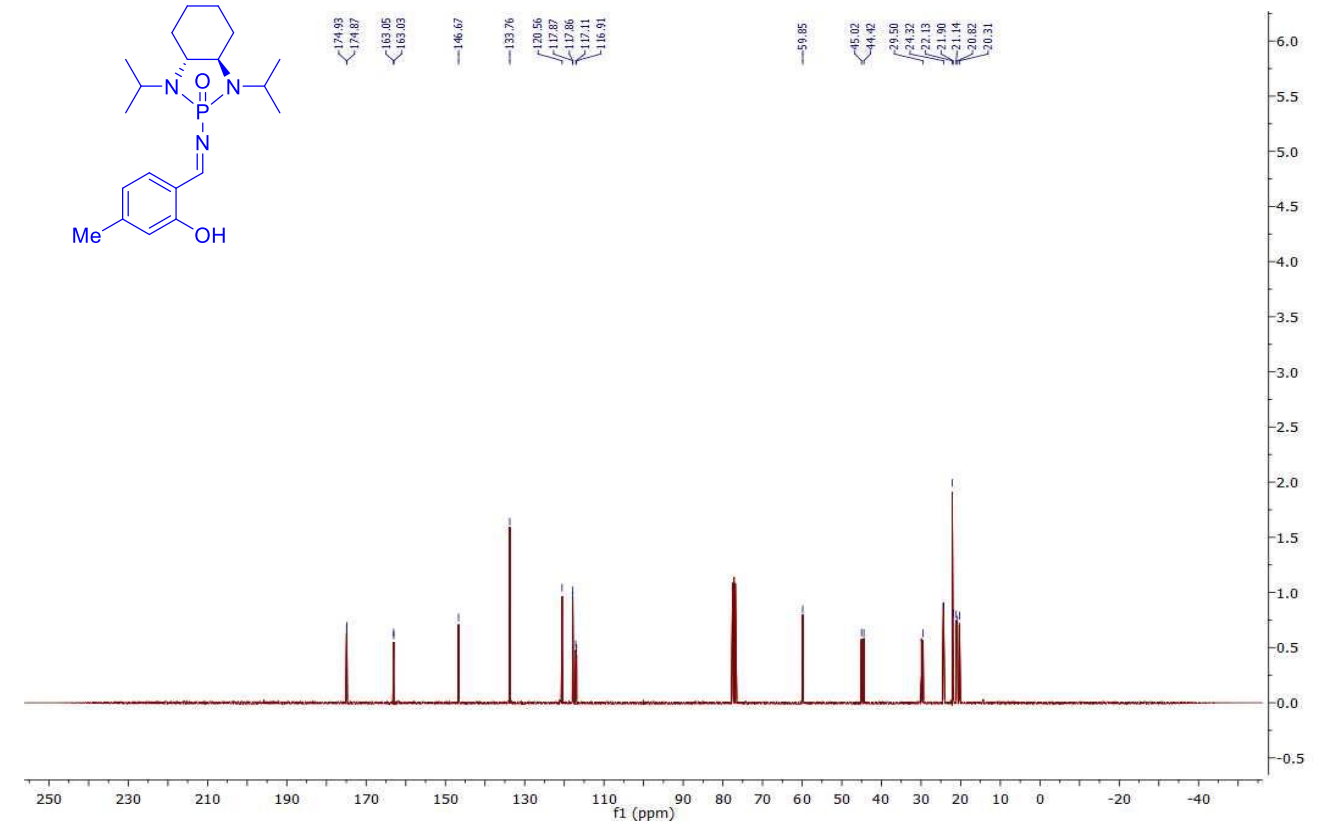
^{13}C NMR of imine **1g** ($CDCl_3$, 100 Hz)



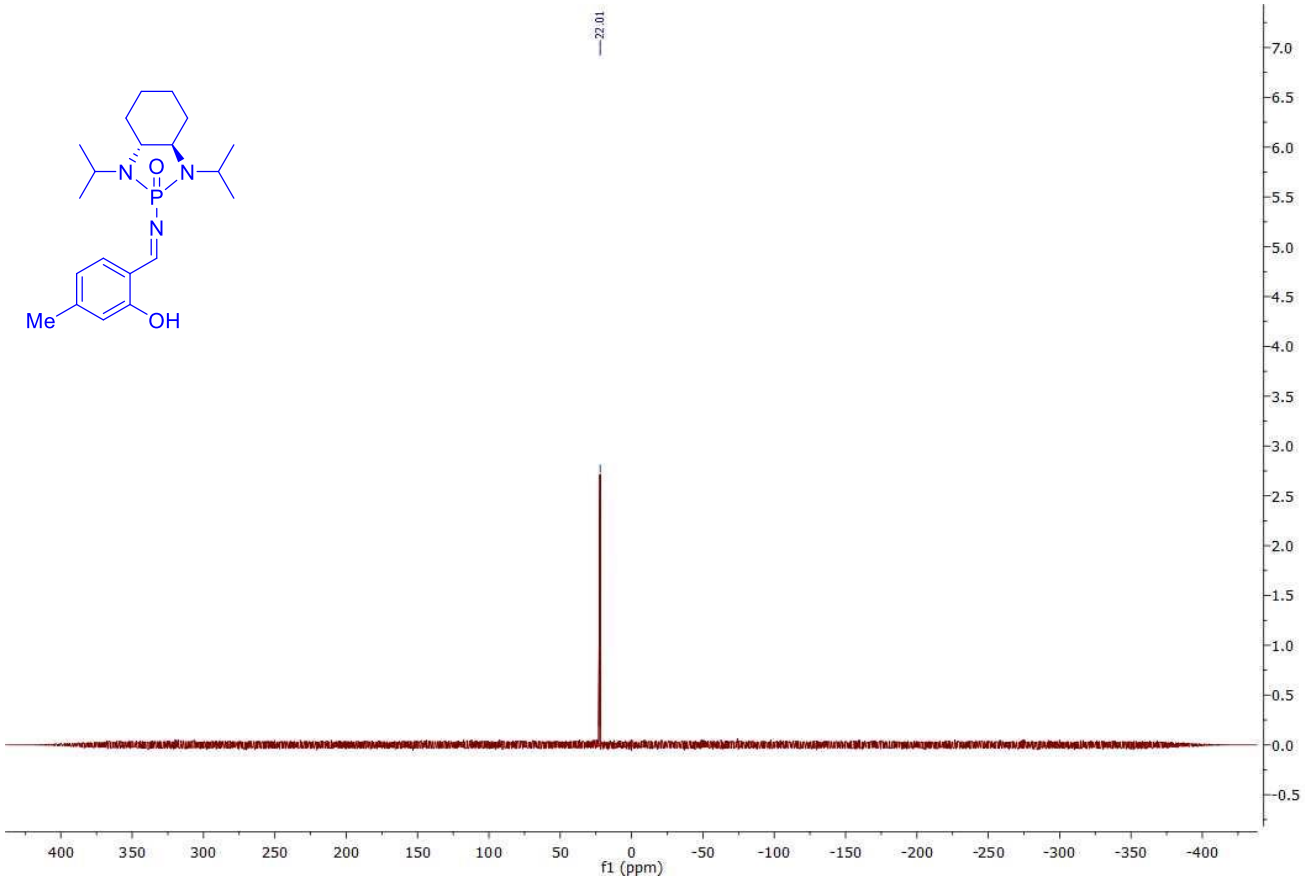
^{31}P NMR of imine **1g** ($CDCl_3$, 162 Hz)



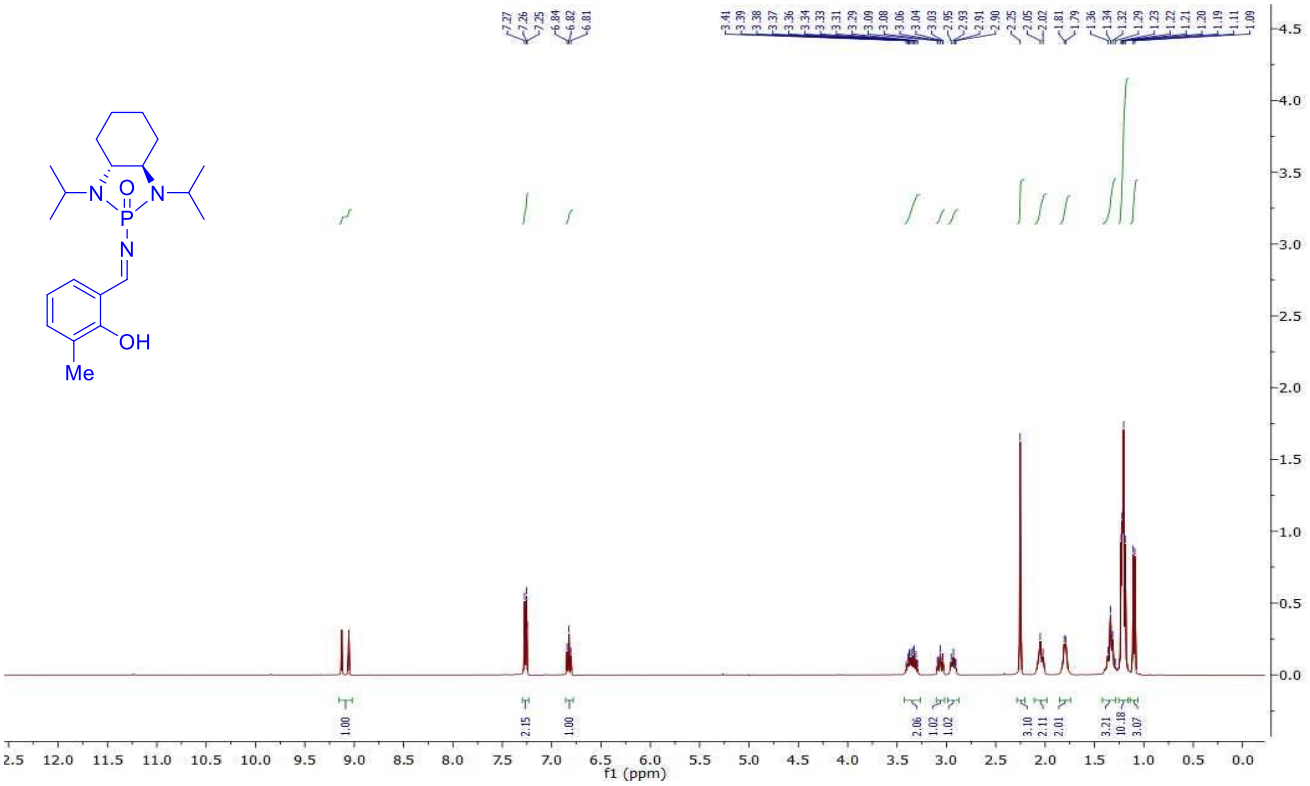
^{1}H NMR of imine **1h** ($CDCl_3$, 400 Hz)



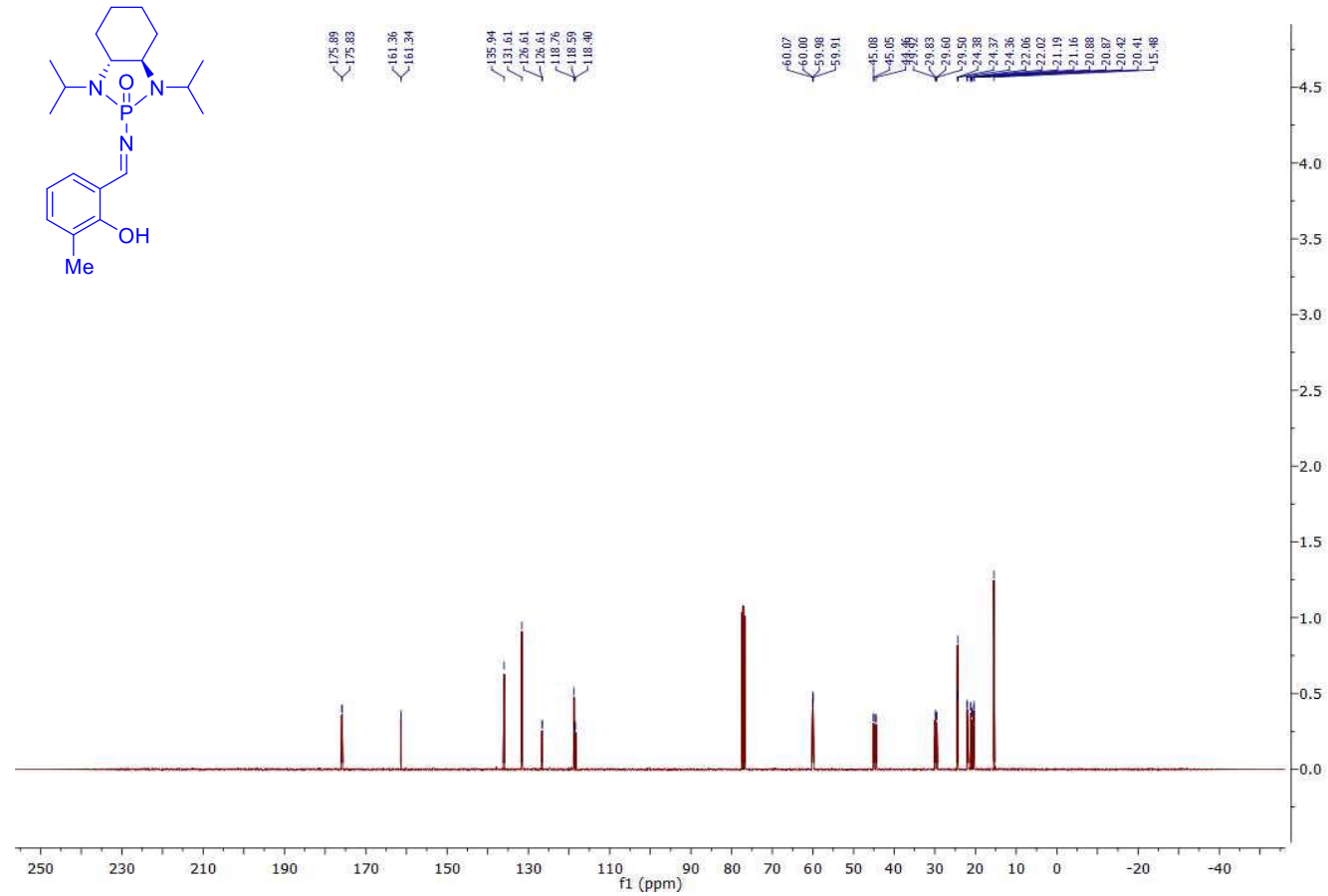
^{13}C NMR of imine **1h** ($CDCl_3$, 100 Hz)



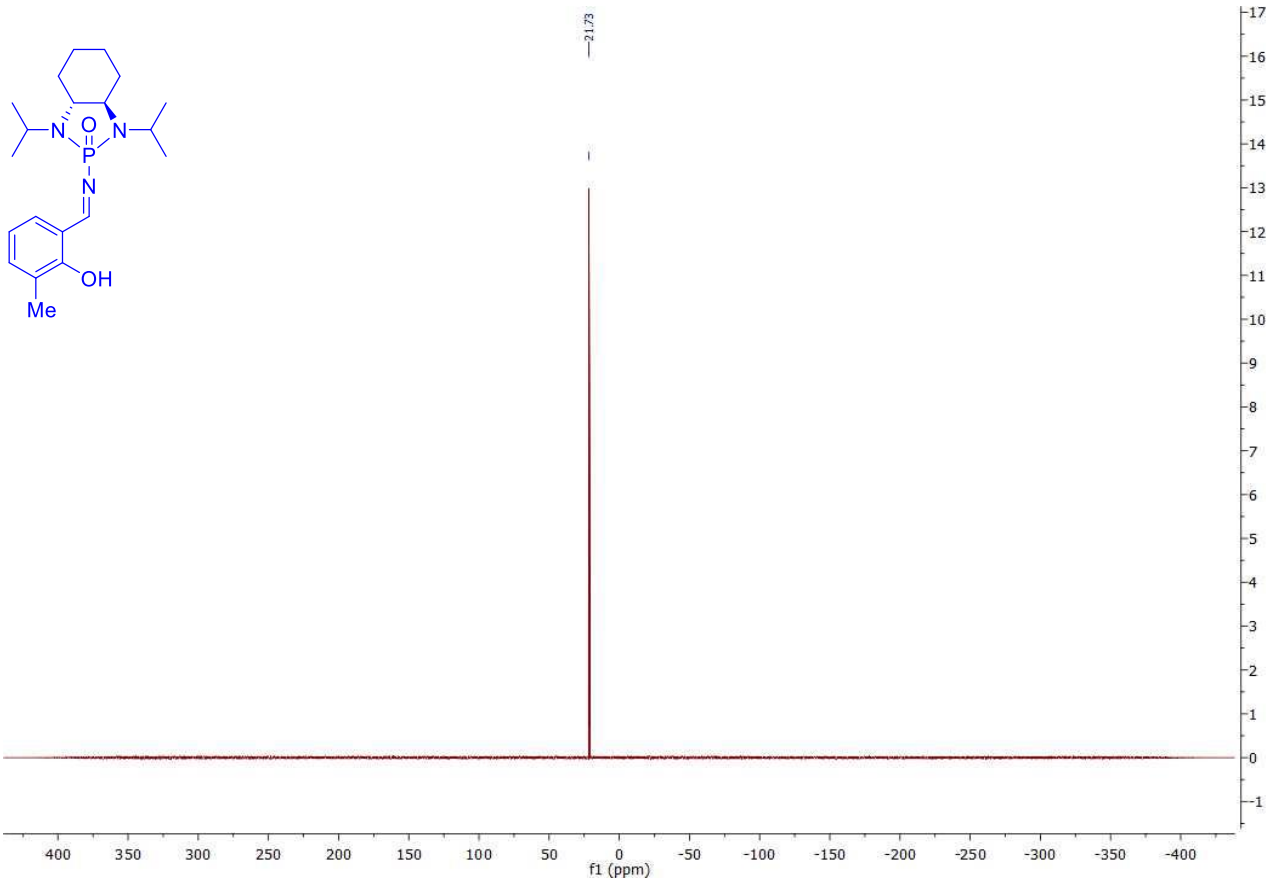
^{31}P NMR of imine **1h** ($CDCl_3$, 162 Hz)



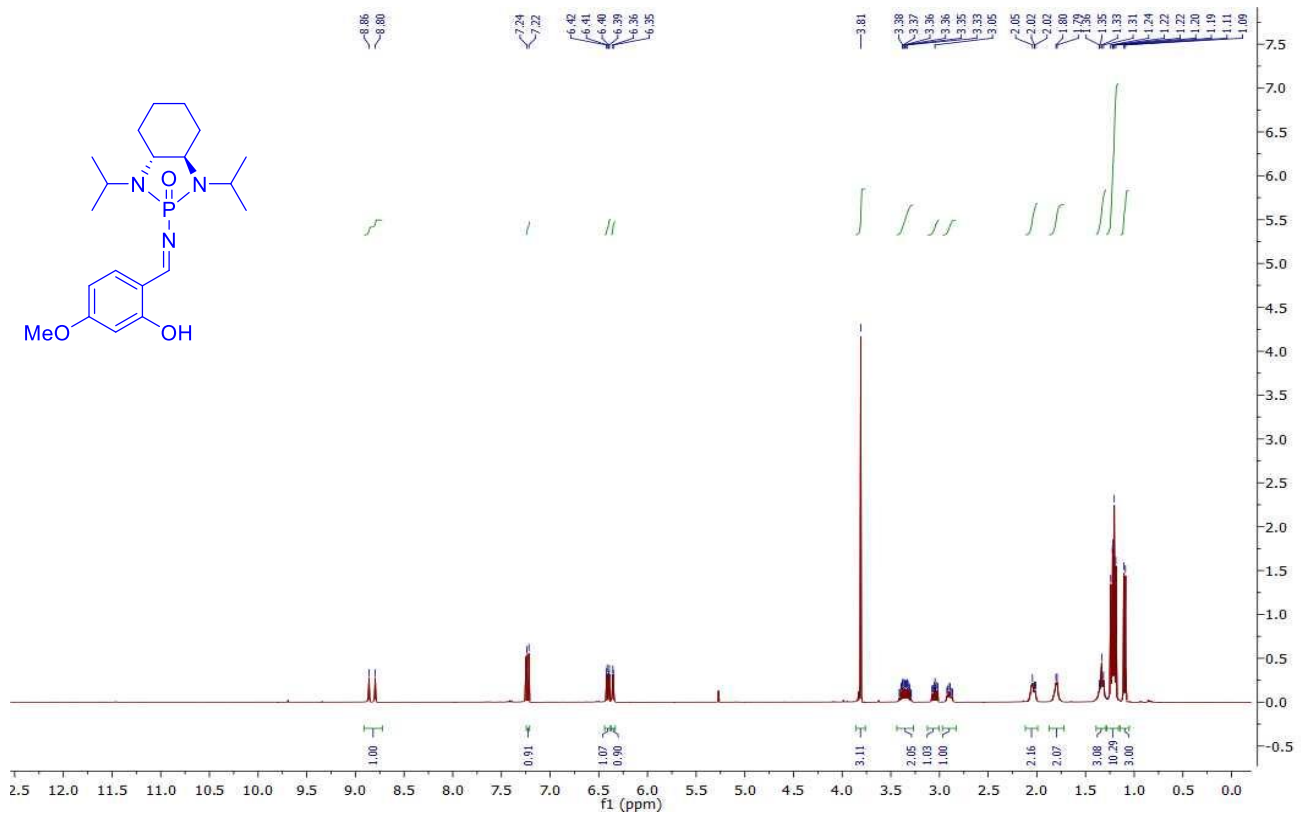
^{1}H NMR of imine **1i** ($CDCl_3$, 400 Hz)



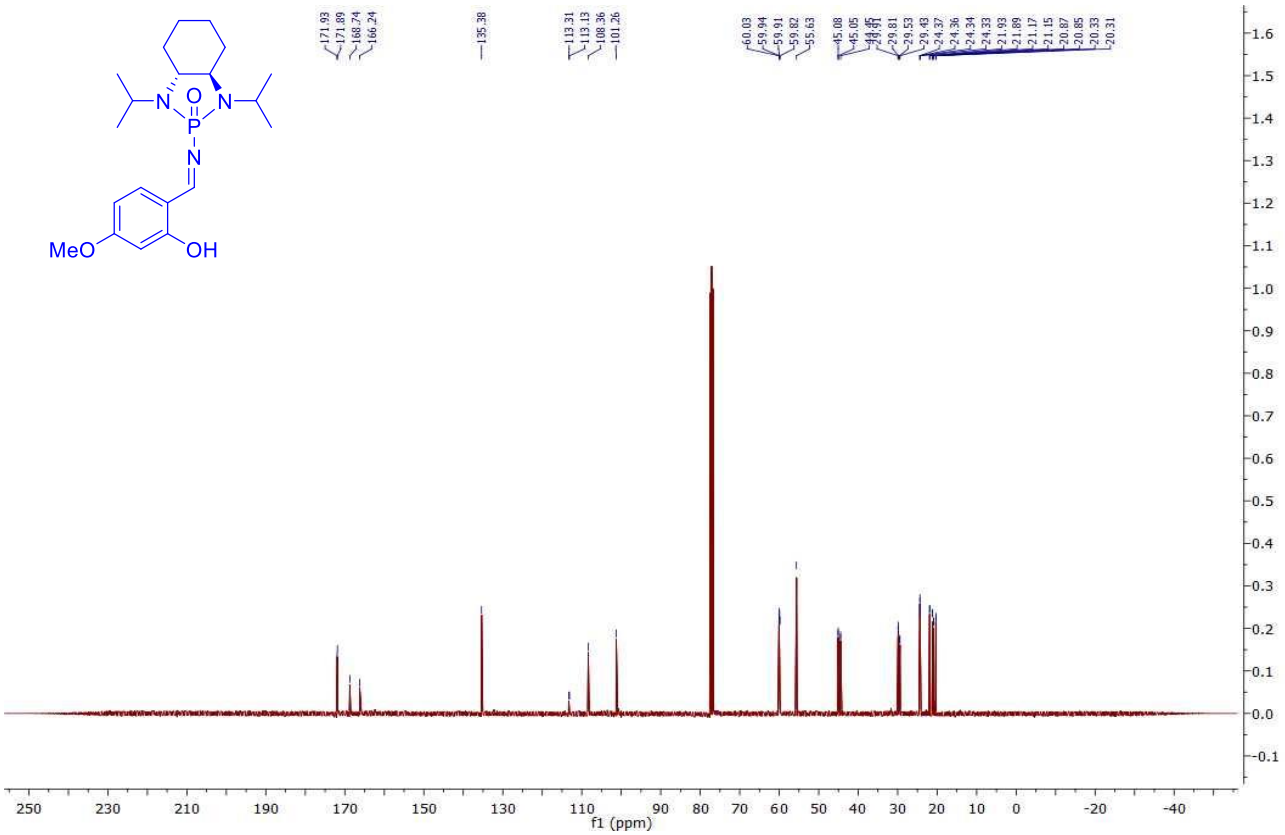
^{3}C NMR of imine **1i** ($CDCl_3$, 100 Hz)



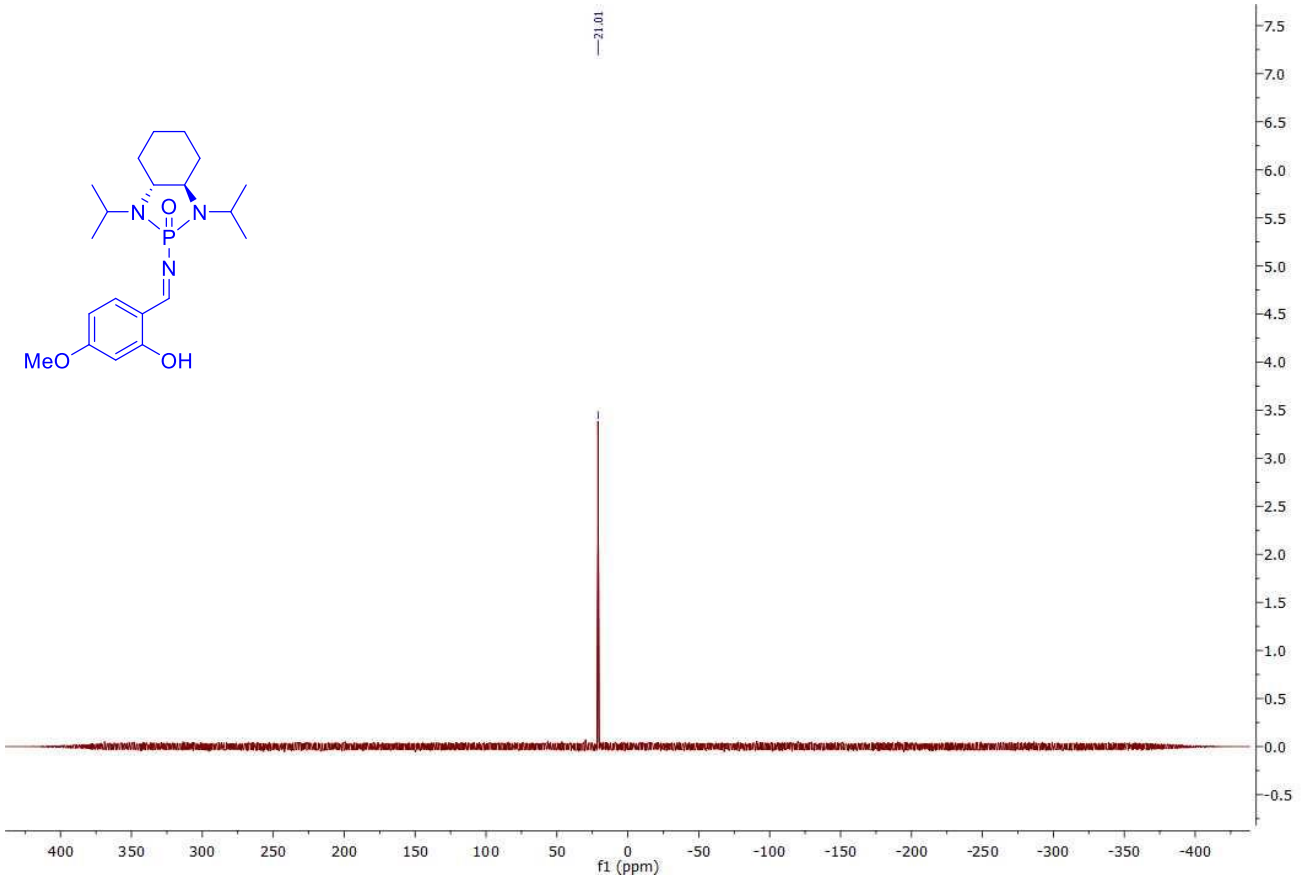
^{31}P NMR of imine **1i** ($CDCl_3$, 162 Hz)



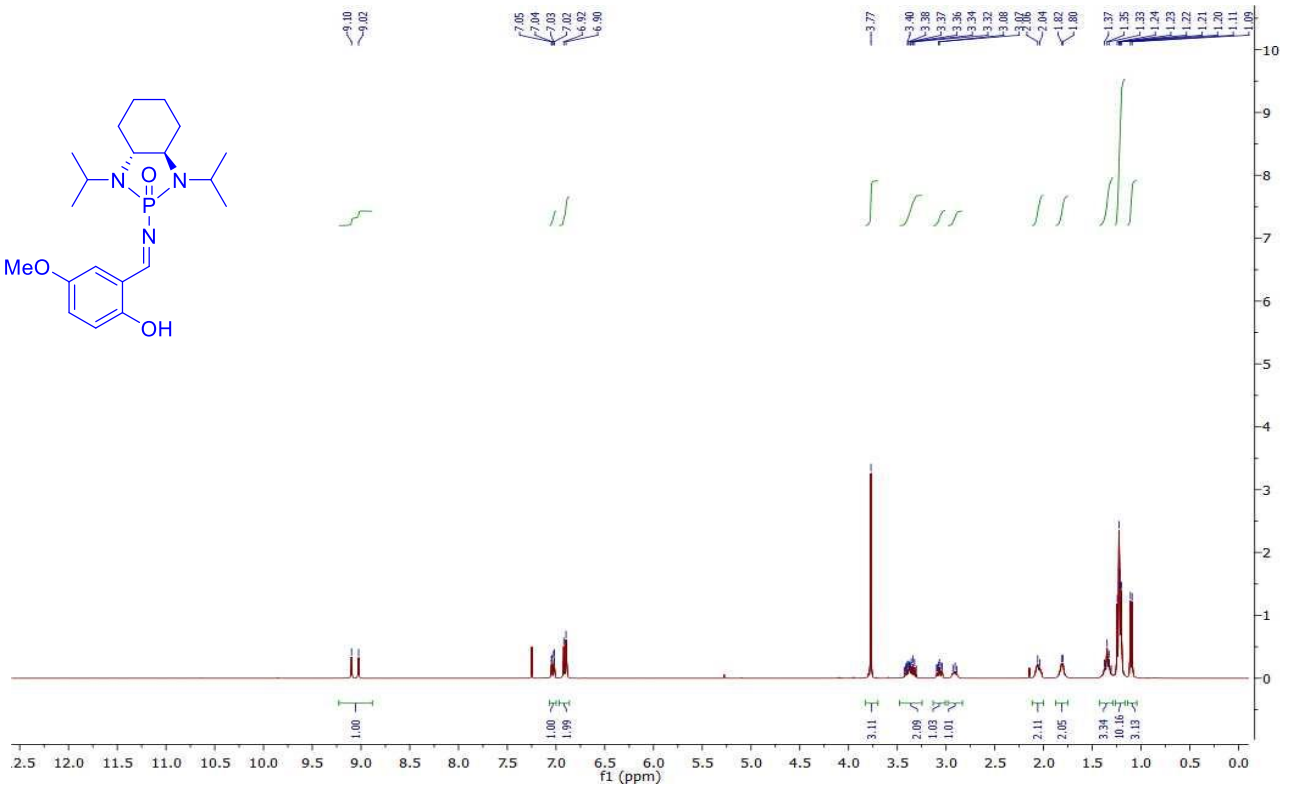
^{1}H NMR of imine **1j** ($CDCl_3$, 400 Hz)



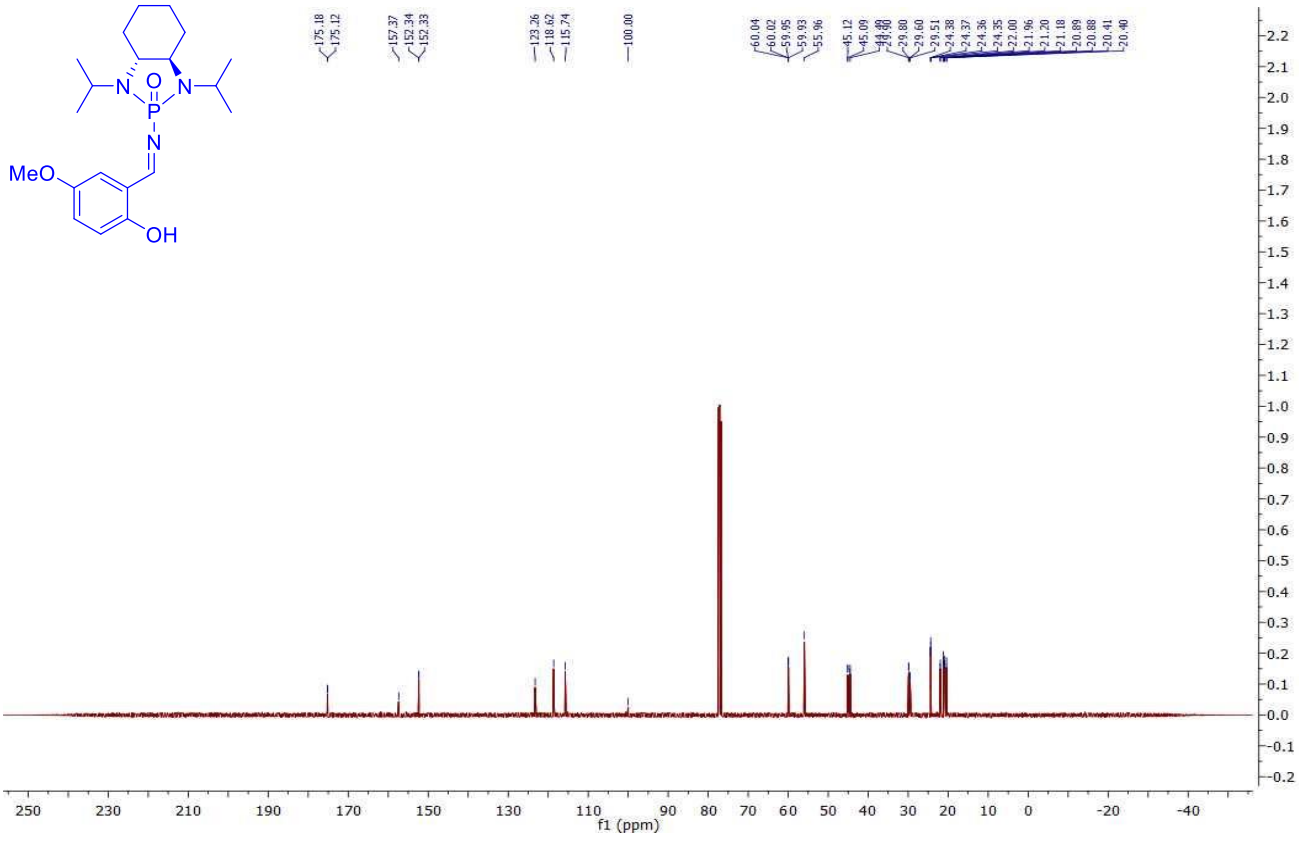
^{3}C NMR of imine **1j** ($CDCl_3$, 100 Hz)



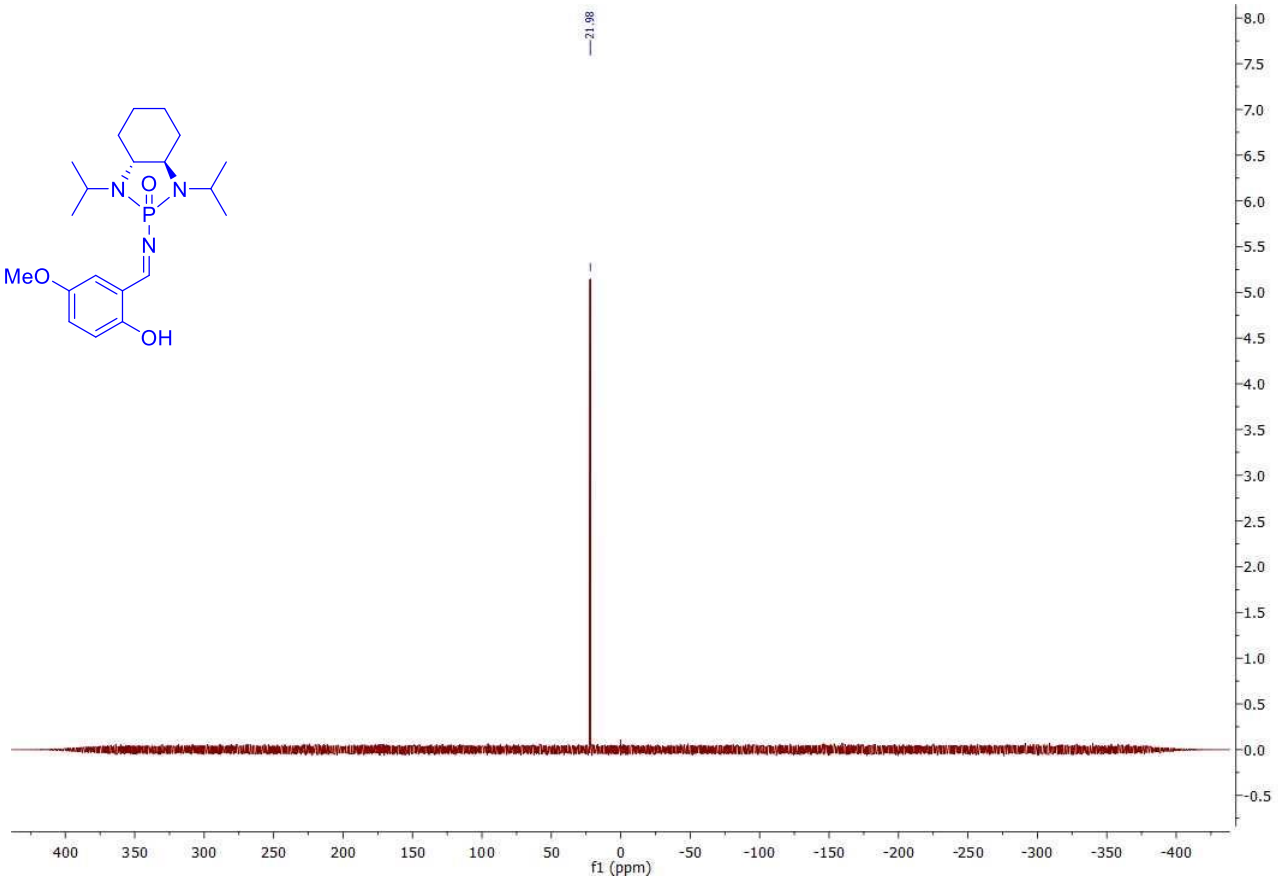
^{31}P NMR of imine **1j** ($CDCl_3$, 162 Hz)



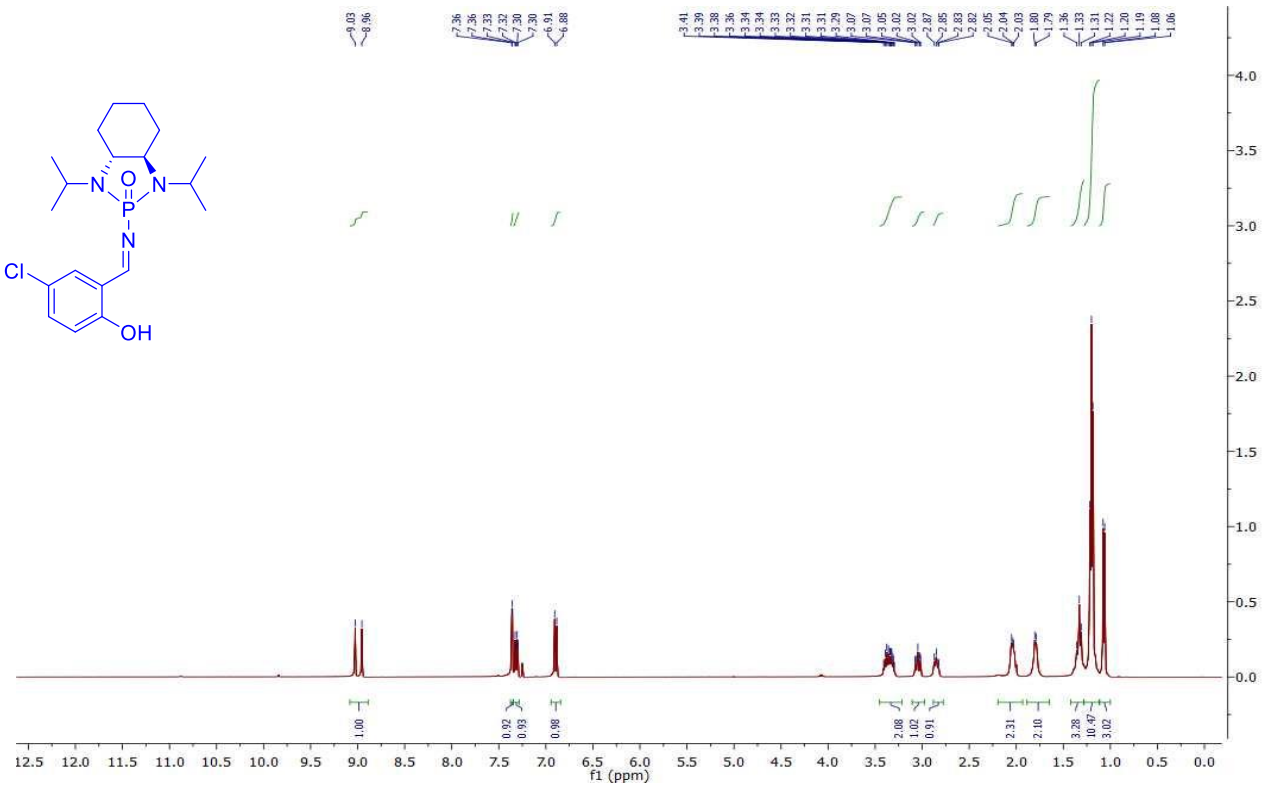
^{1}H NMR of imine **1k** ($CDCl_3$, 400 Hz)



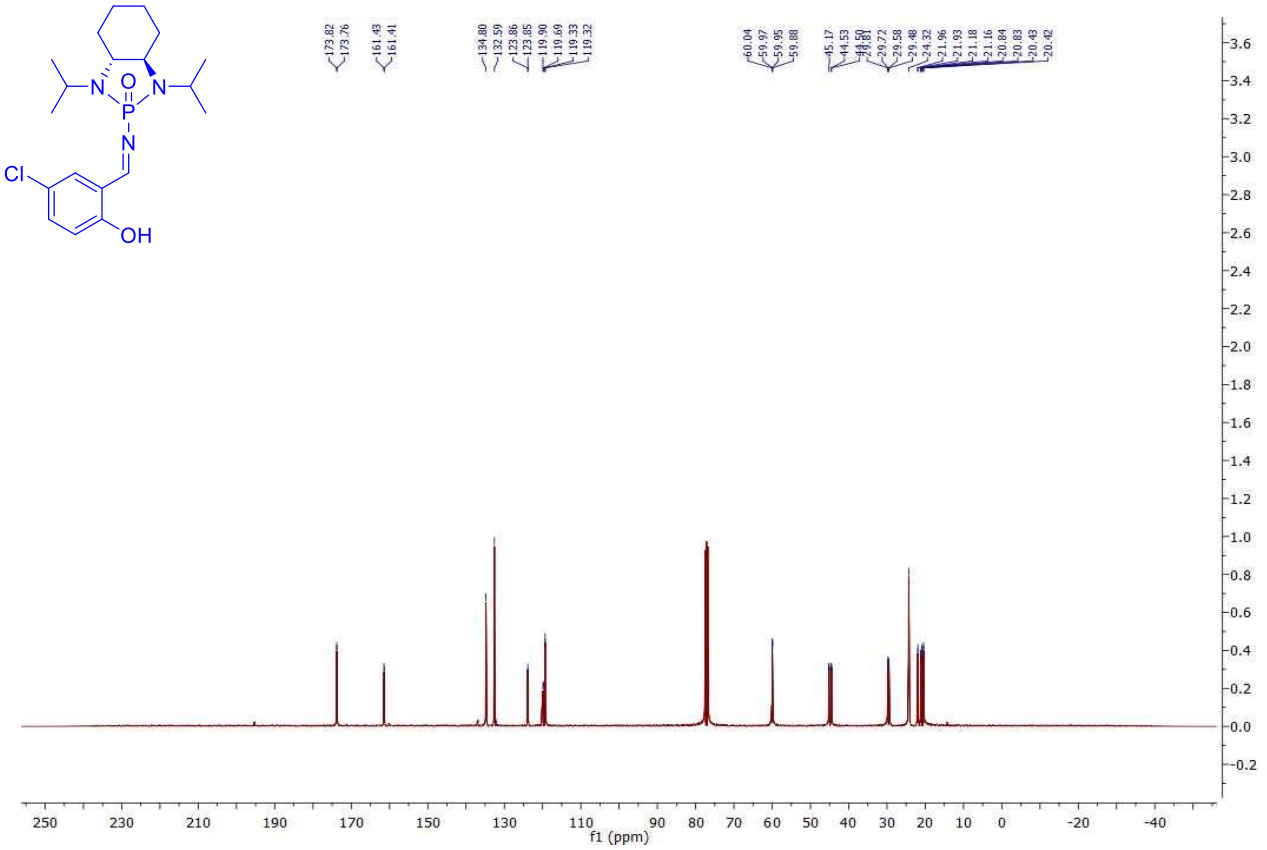
^{3}C NMR of imine **1k** ($CDCl_3$, 100 Hz)



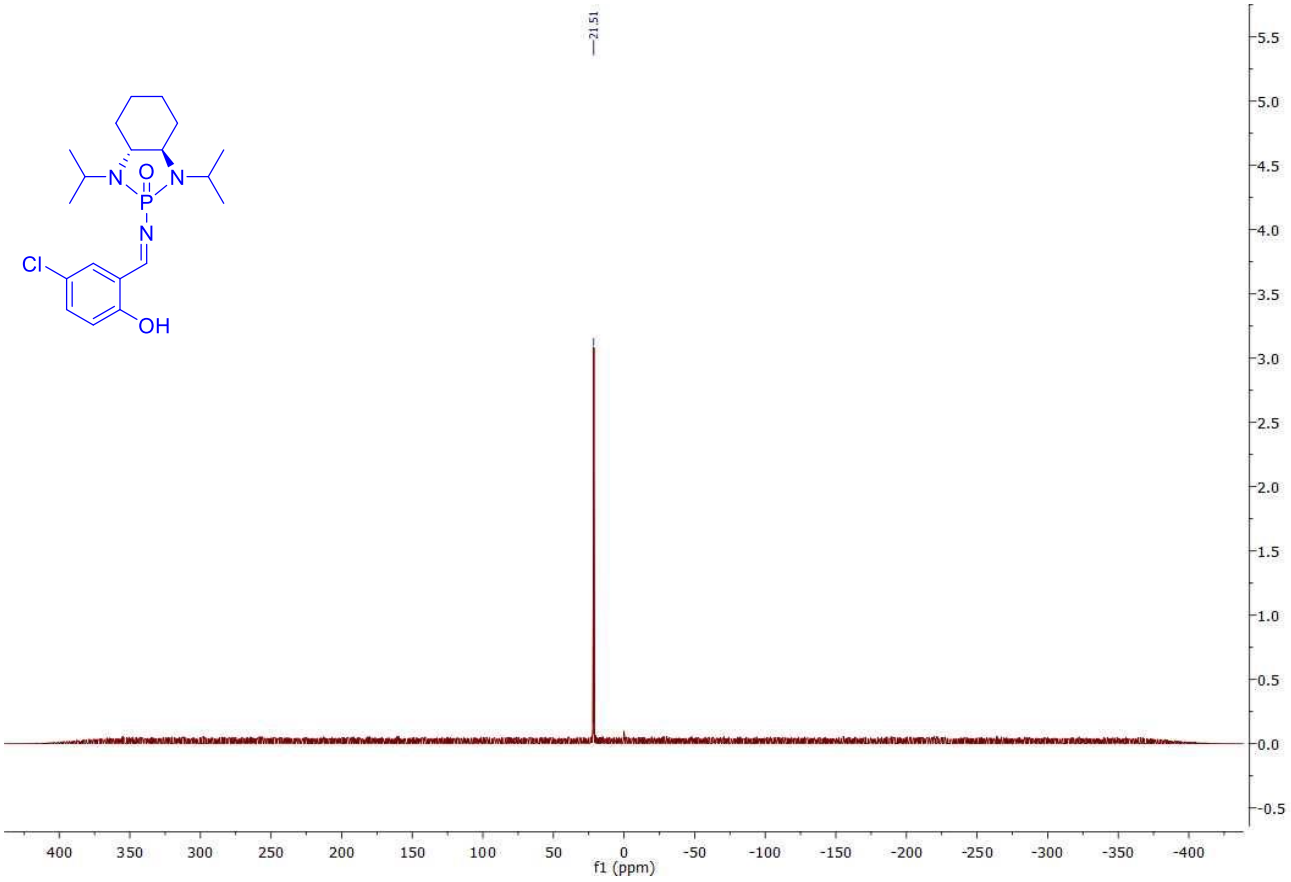
^{31}P NMR of imine **1k** ($CDCl_3$, 162 Hz)



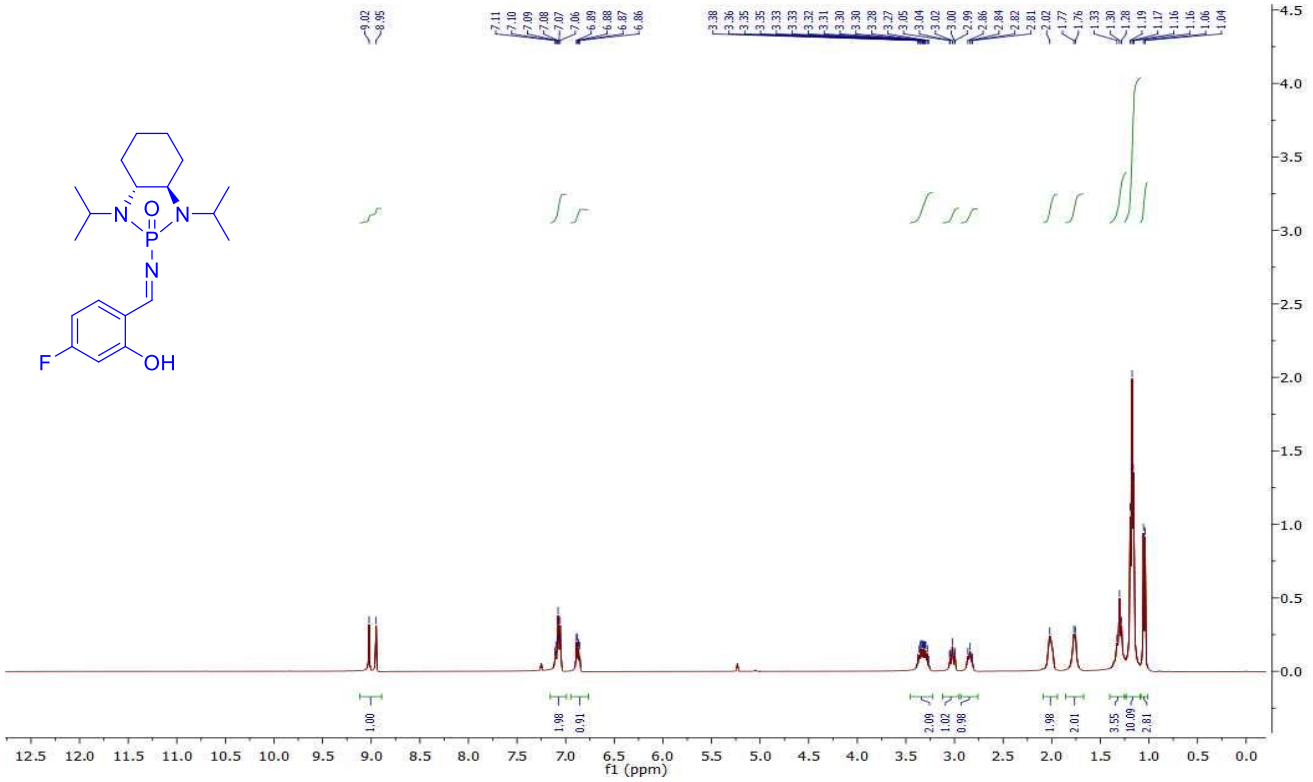
^{1}H NMR of imine **1l** ($CDCl_3$, 400 Hz)



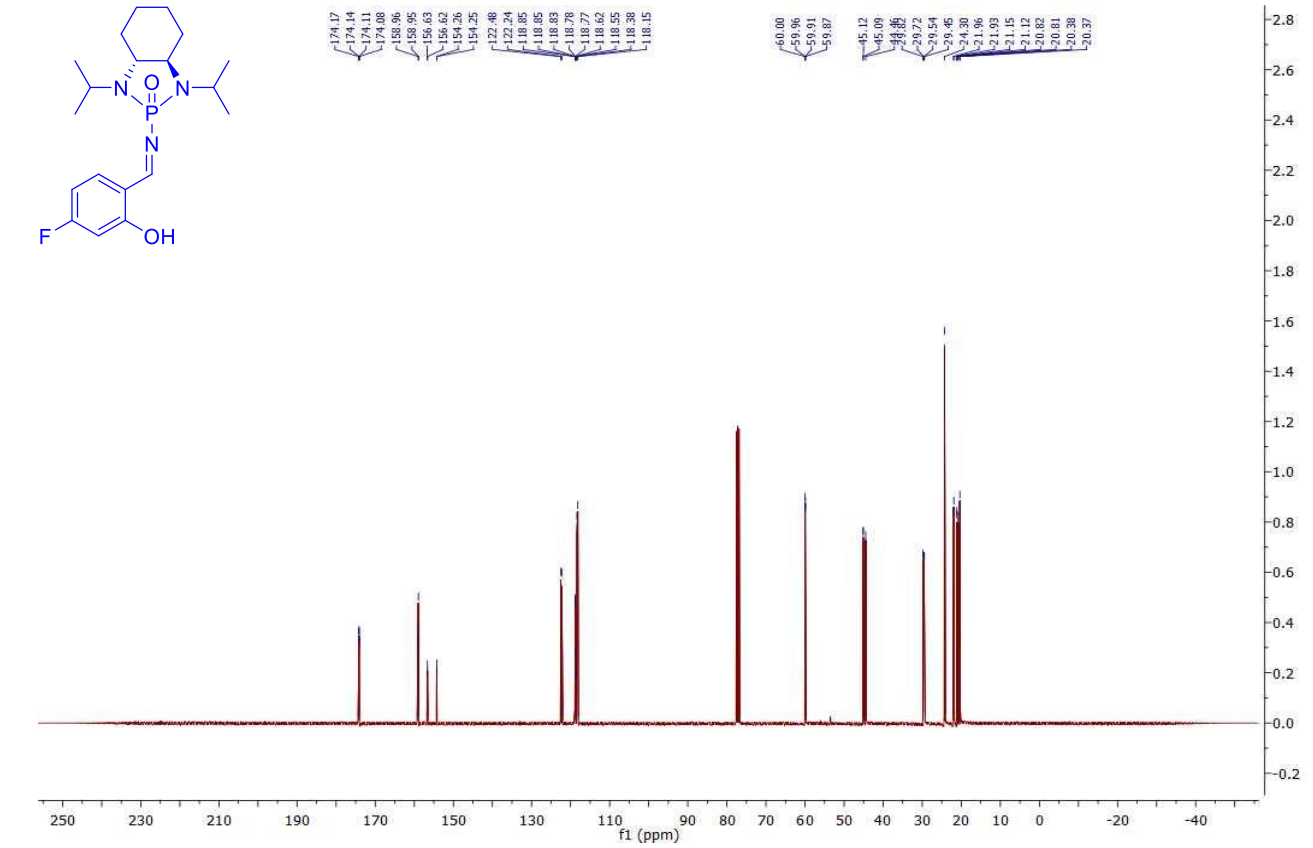
^{3}C NMR of imine **1l** ($CDCl_3$, 100 Hz)



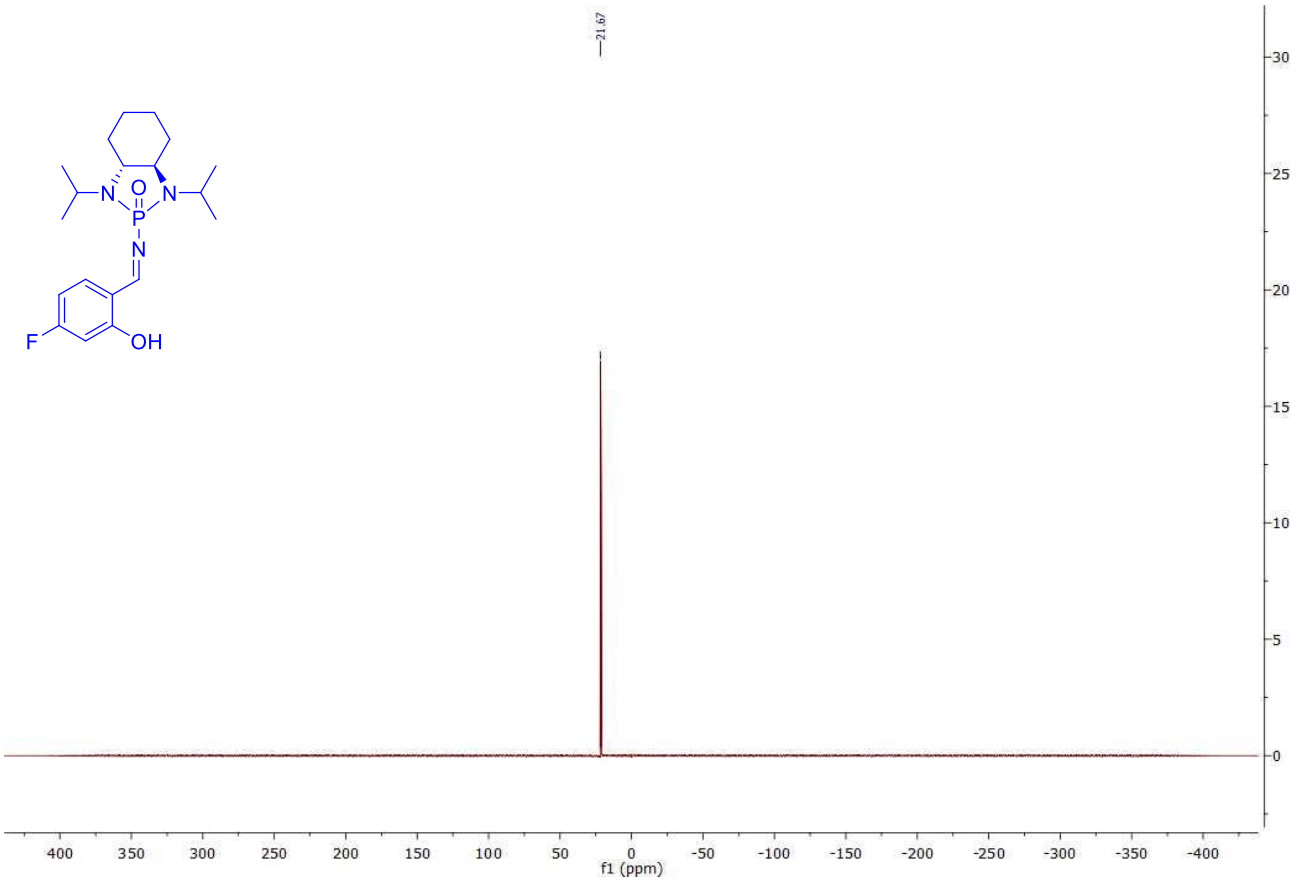
^{31}P NMR of imine **1l** ($CDCl_3$, 162 Hz)



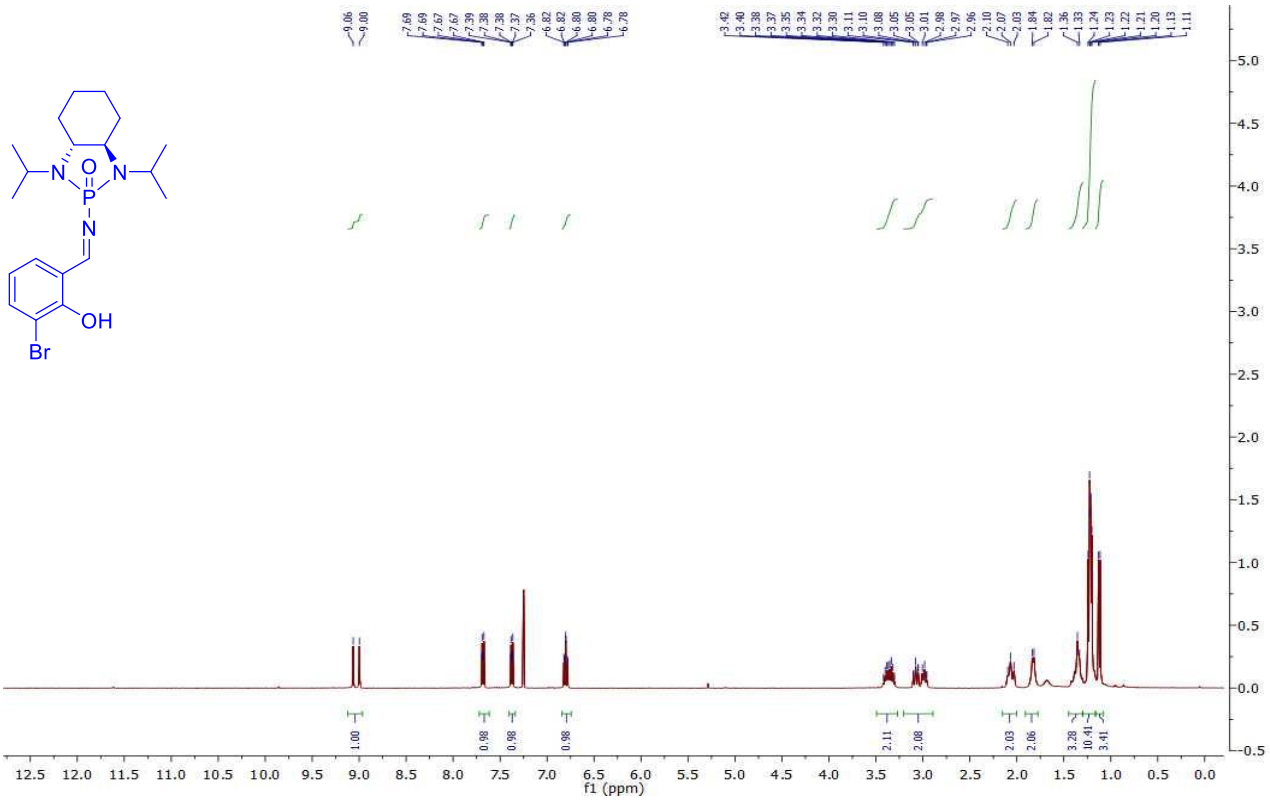
^{1}H NMR of imine **1m** ($CDCl_3$, 400 Hz)



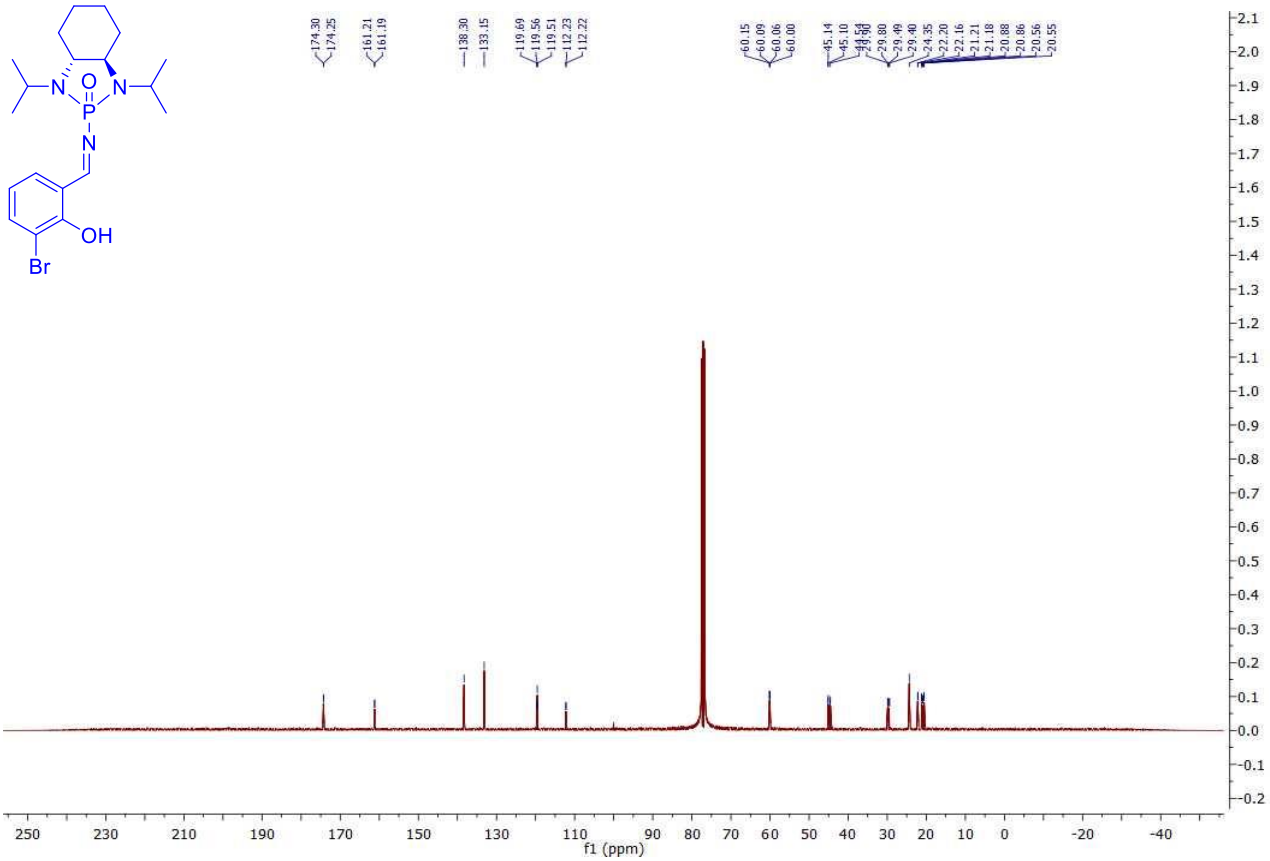
^{3}C NMR of imine **1m** ($CDCl_3$, 100 Hz)



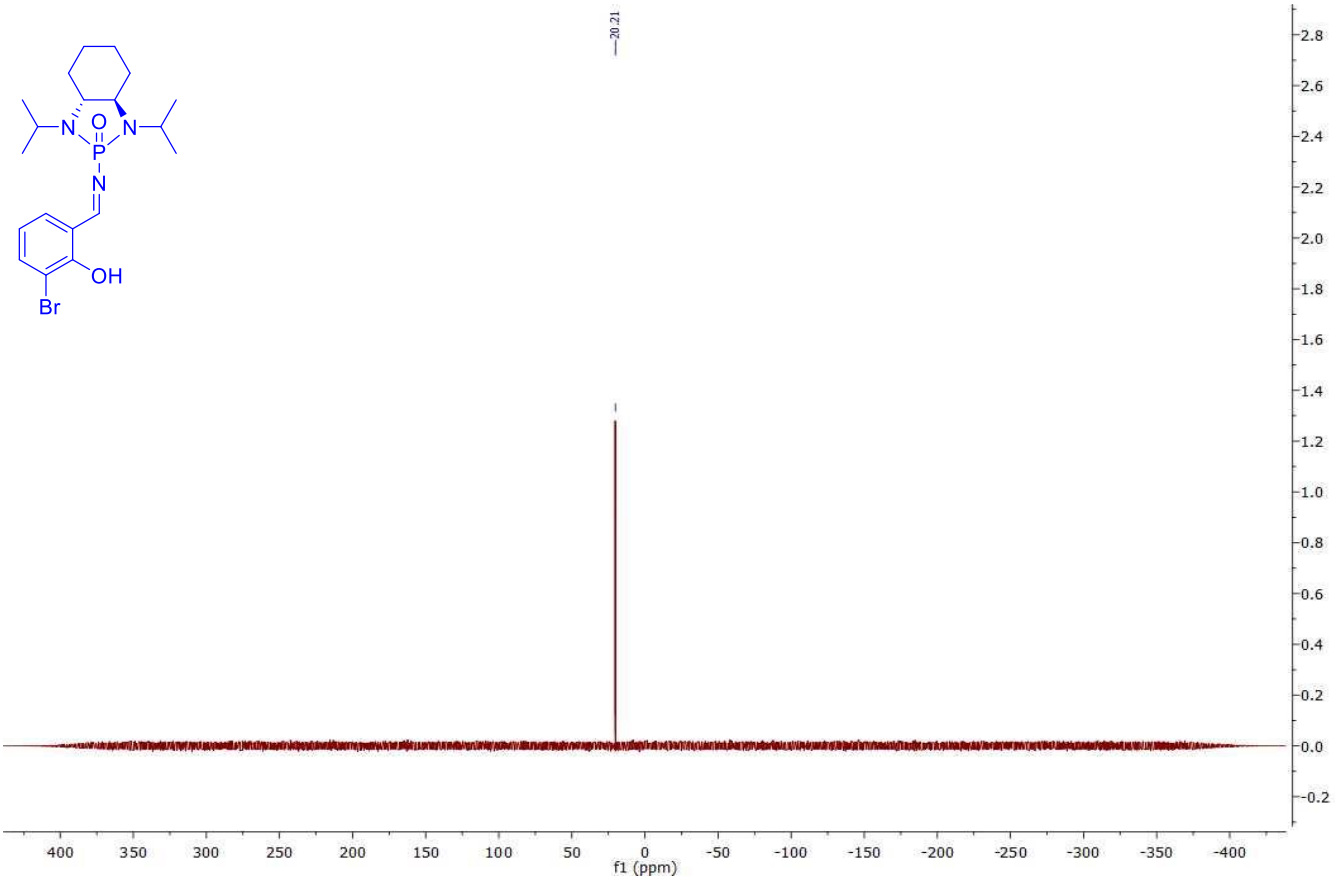
^{31}P NMR of imine **1m** ($CDCl_3$, 162 Hz)



^{1}H NMR of imine **1n** ($CDCl_3$, 400 Hz)

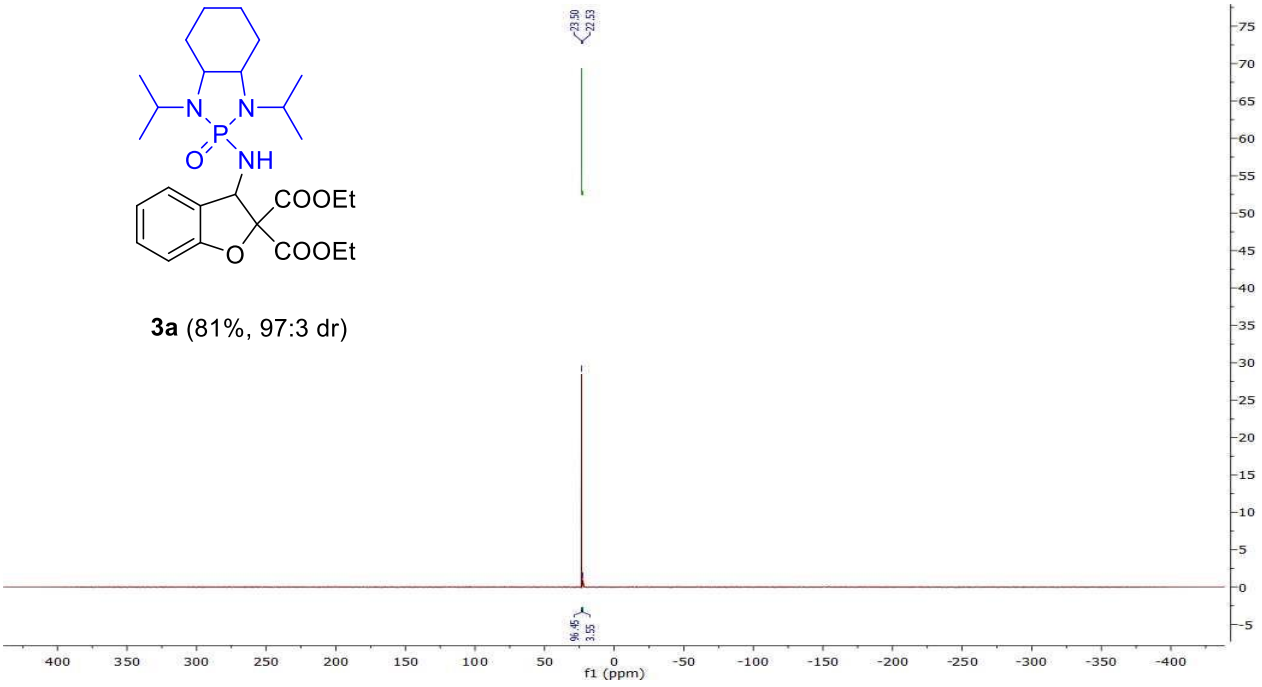


^{3}C NMR of imine **1n** ($CDCl_3$, 100 Hz)



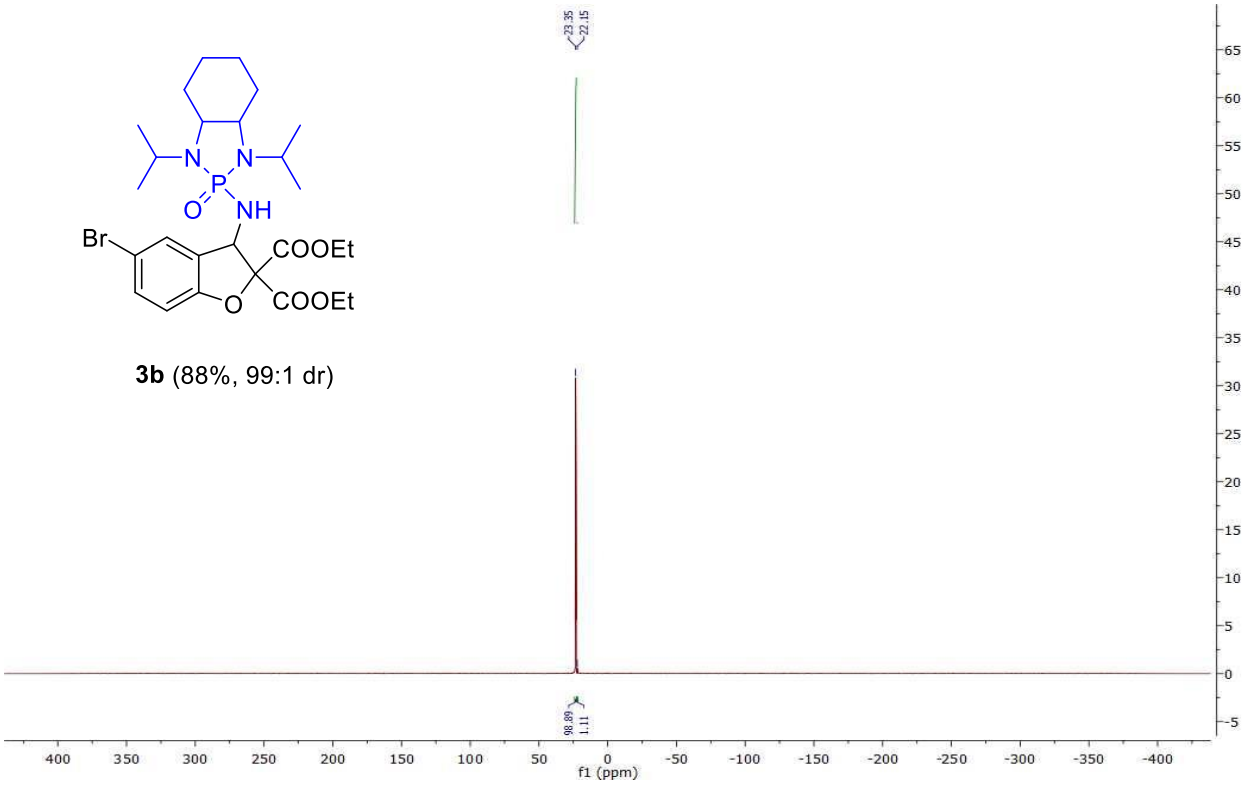
^{31}P NMR of imine **1n** ($CDCl_3$, 162 Hz)

Evaluation of dr from ^{31}P NMR analysis of 3a-3r



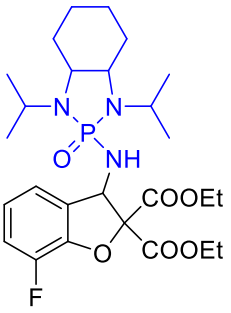
3a (81%, 97:3 dr)

^{31}P NMR of 2,3-dihydrobenzofuran **3a** ($CDCl_3$, 162 Hz)



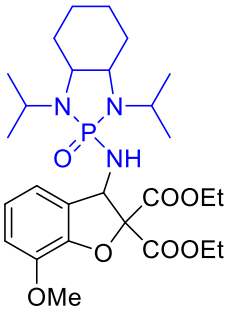
3b (88%, 99:1 dr)

^{31}P NMR of 2,3-dihydrobenzofuran **3b** ($CDCl_3$, 162 Hz)



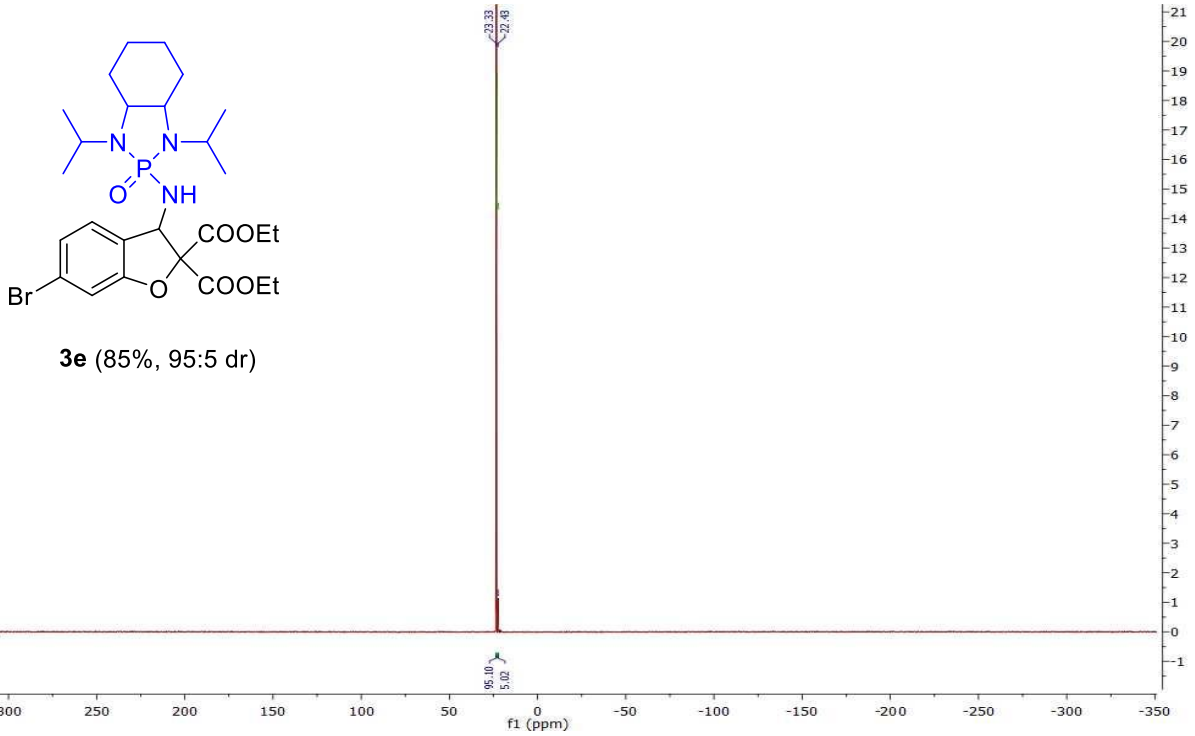
3c (82%, 96:4 dr)

^{31}P NMR of 2,3-dihydrobenzofuran **3c** ($CDCl_3$, 162 Hz)



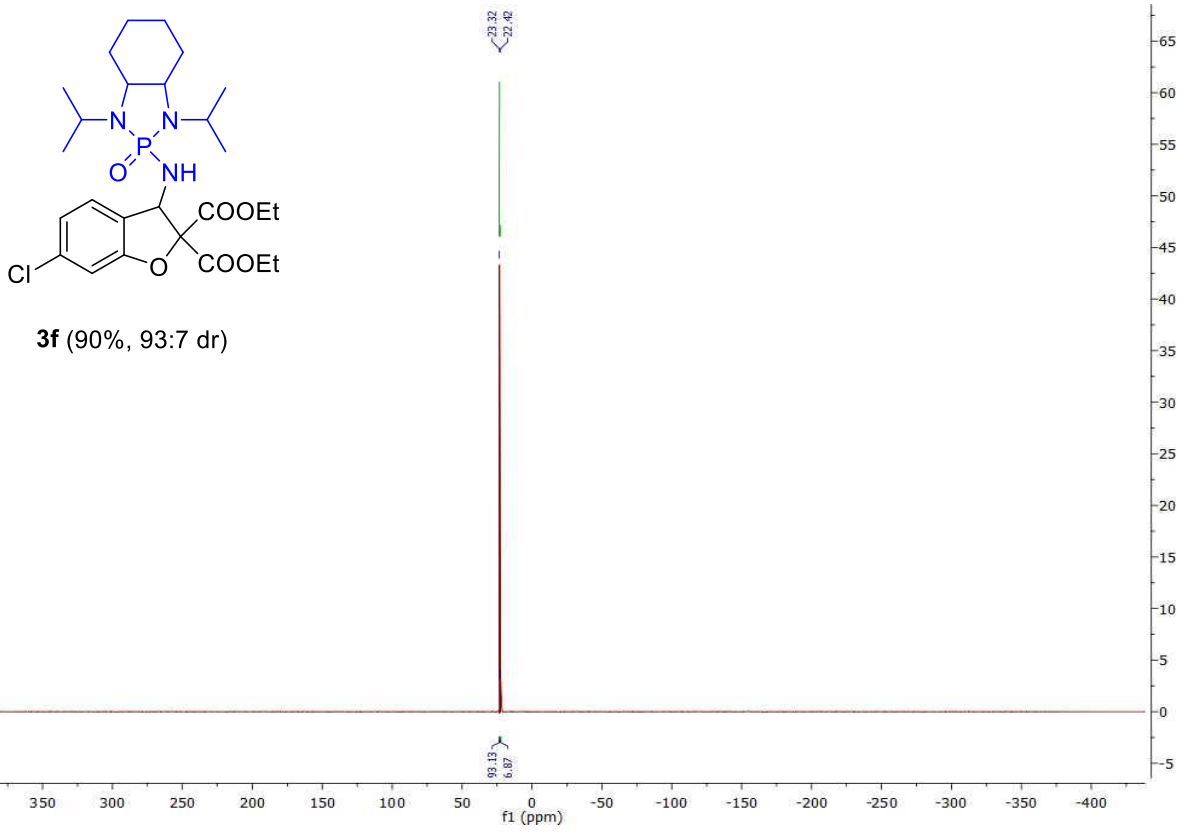
3d (86%, 96:4 dr)

^{31}P NMR of 2,3-dihydrobenzofuran **3d** ($CDCl_3$, 162 Hz)



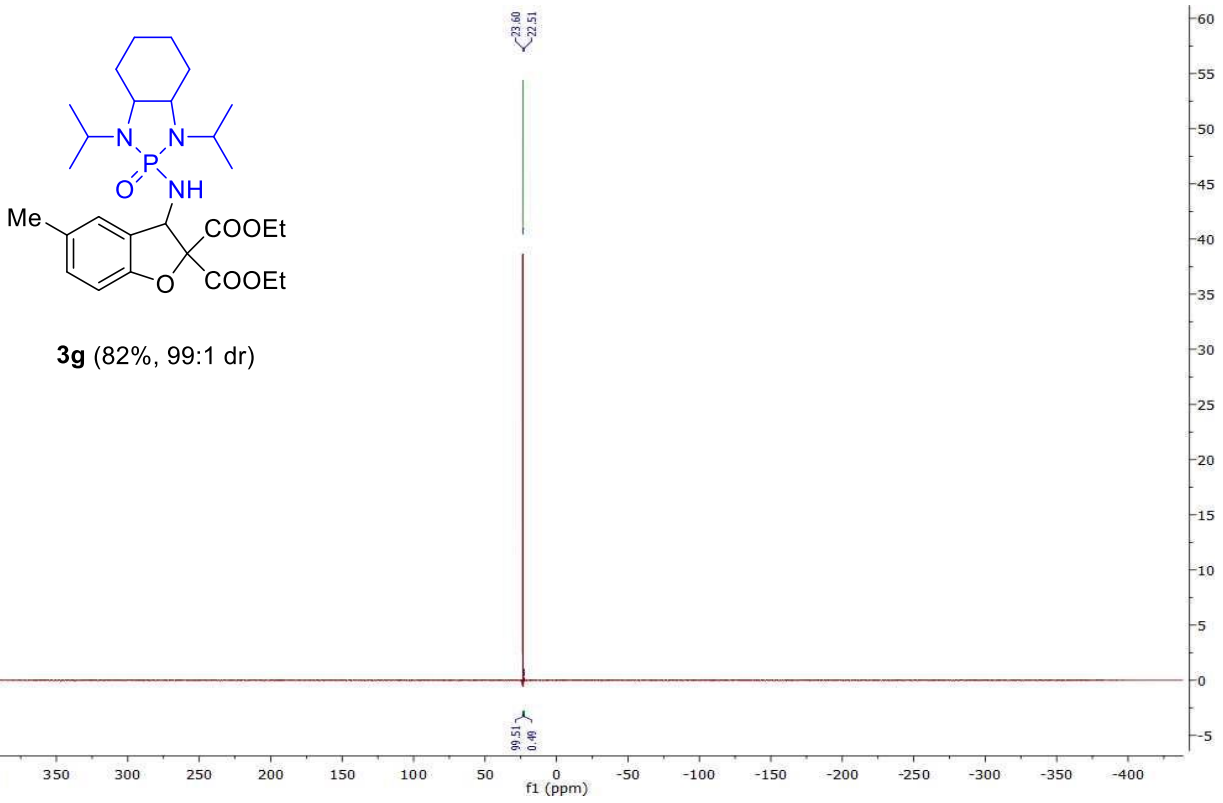
3e (85%, 95:5 dr)

^{31}P NMR of 2,3-dihydrobenzofuran **3e** ($CDCl_3$, 162 Hz)



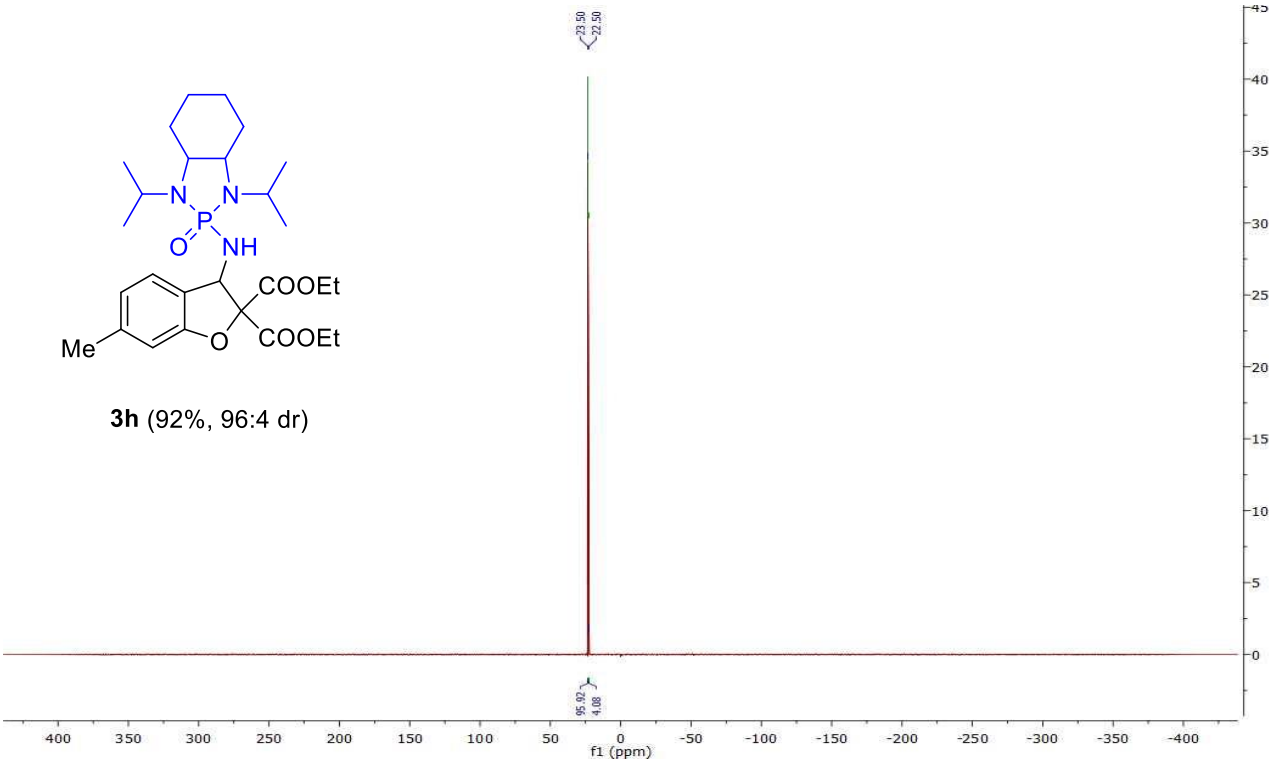
3f (90%, 93:7 dr)

^{31}P NMR of 2,3-dihydrobenzofuran **3f** ($CDCl_3$, 162 Hz)



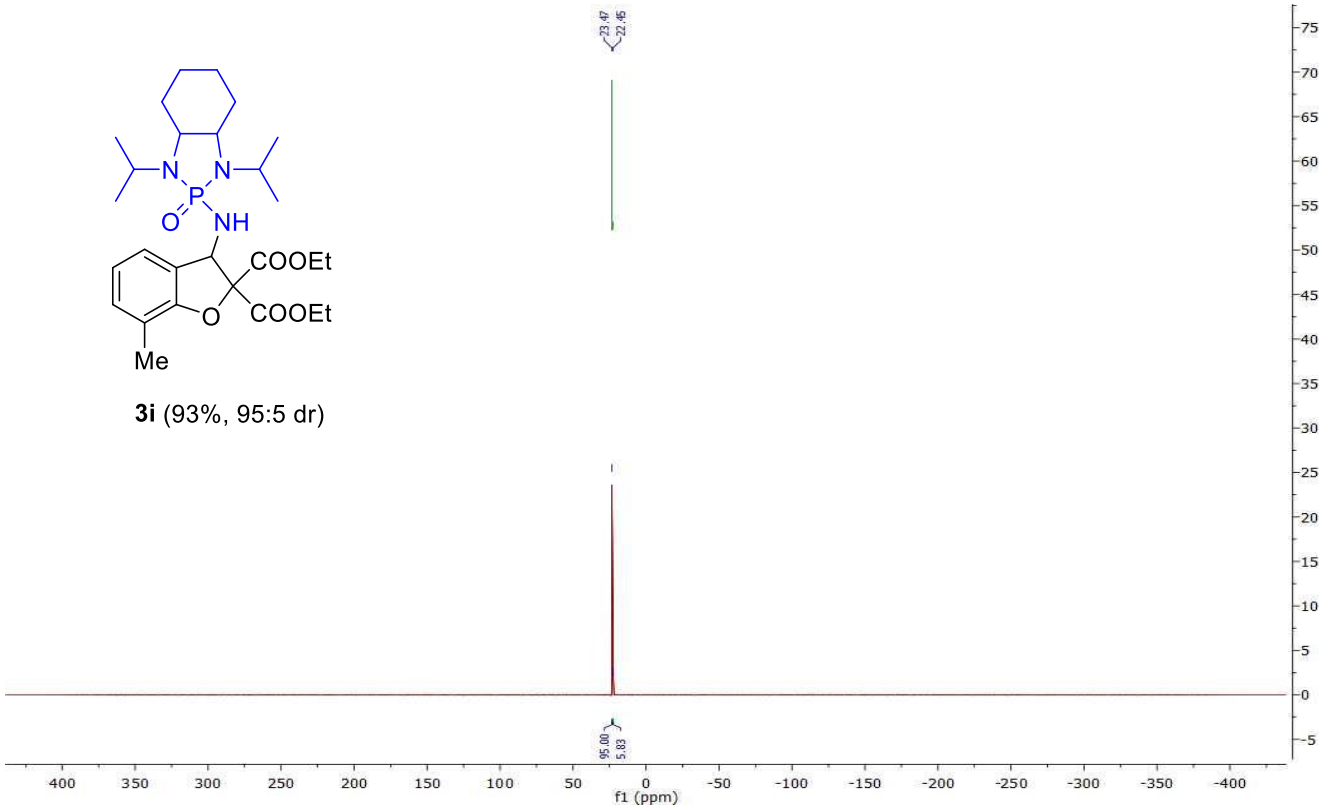
3g (82%, 99:1 dr)

^{31}P NMR of 2,3-dihydrobenzofuran **3g** ($CDCl_3$, 162 Hz)



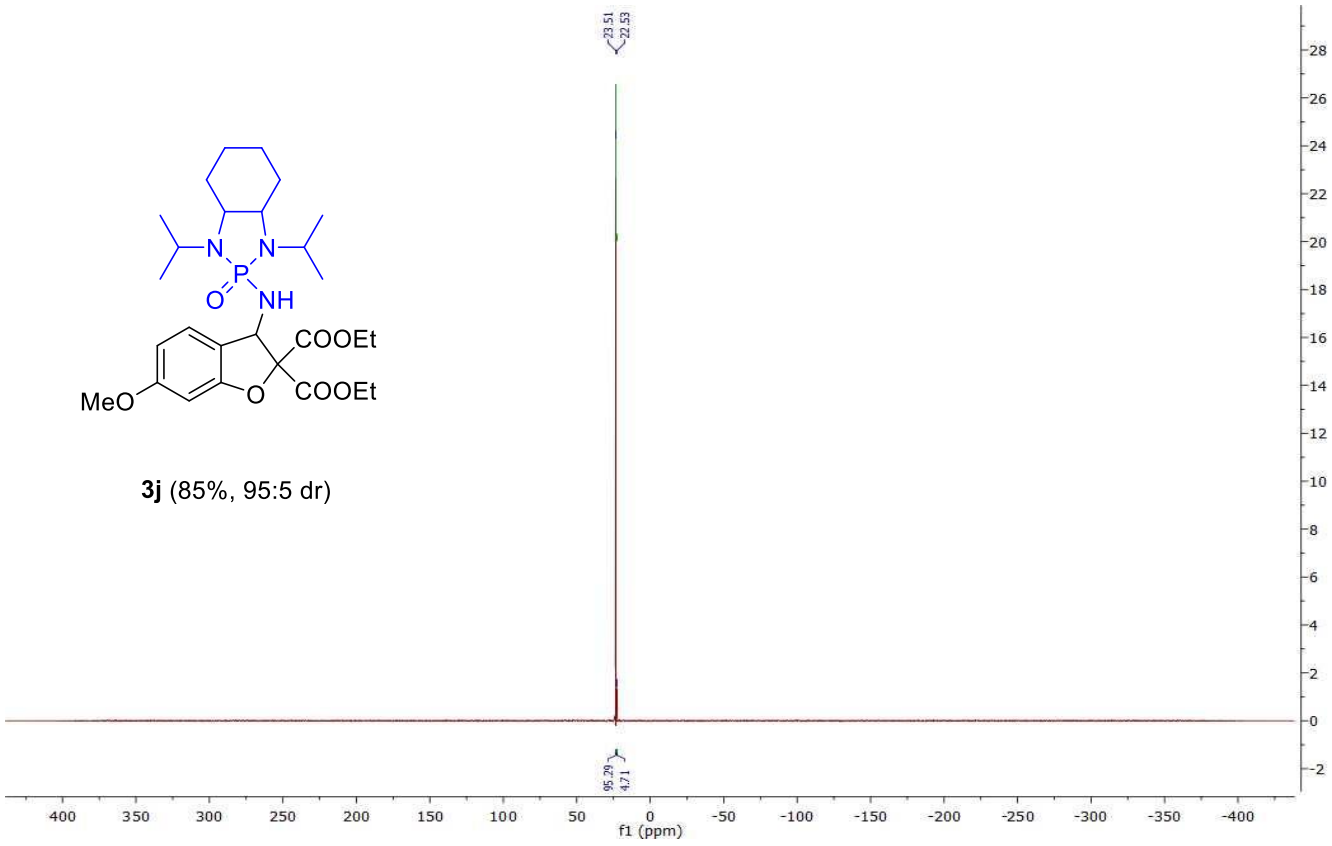
3h (92%, 96:4 dr)

^{31}P NMR of 2,3-dihydrobenzofuran **3h** ($CDCl_3$, 162 Hz)



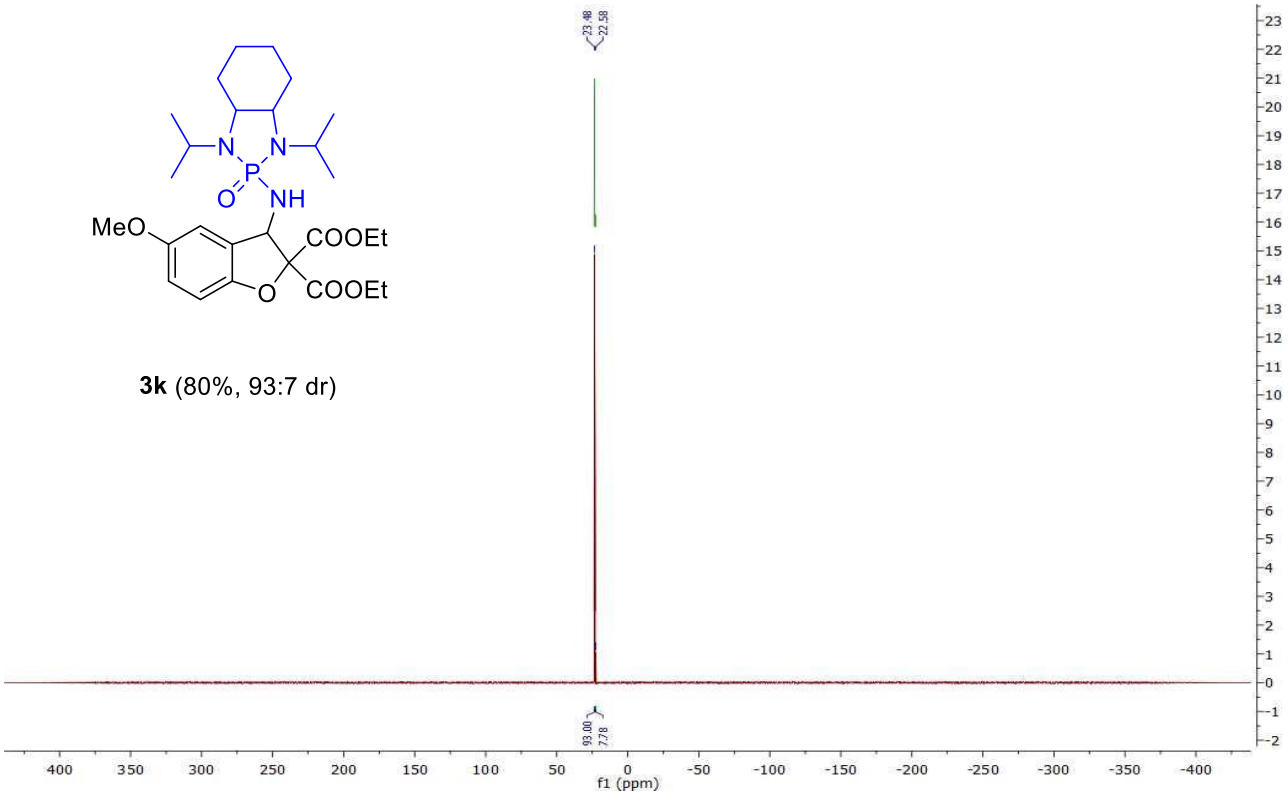
3i (93%, 95:5 dr)

^{31}P NMR of 2,3-dihydrobenzofuran **3i** ($CDCl_3$, 162 Hz)



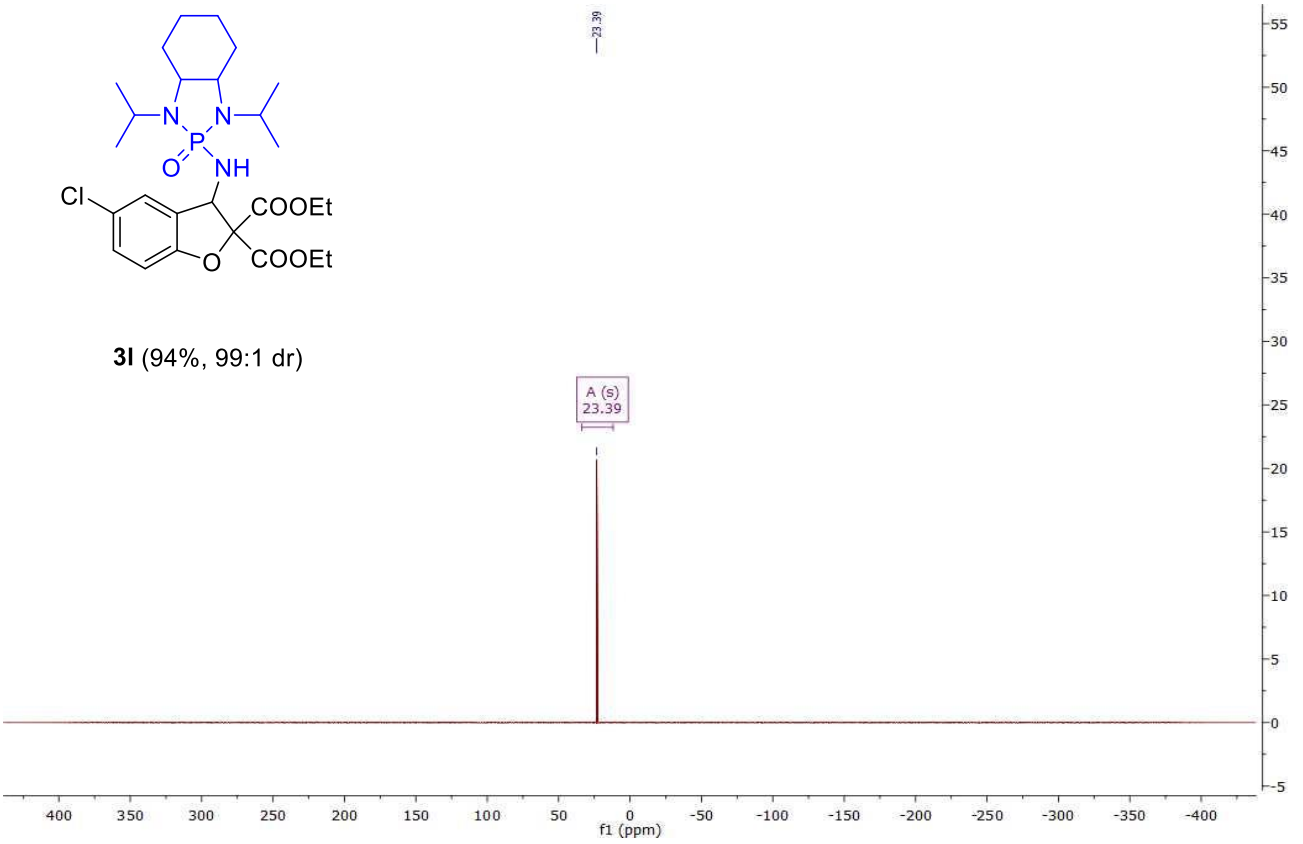
3j (85%, 95:5 dr)

^{31}P NMR of 2,3-dihydrobenzofuran **3j** ($CDCl_3$, 162 Hz)



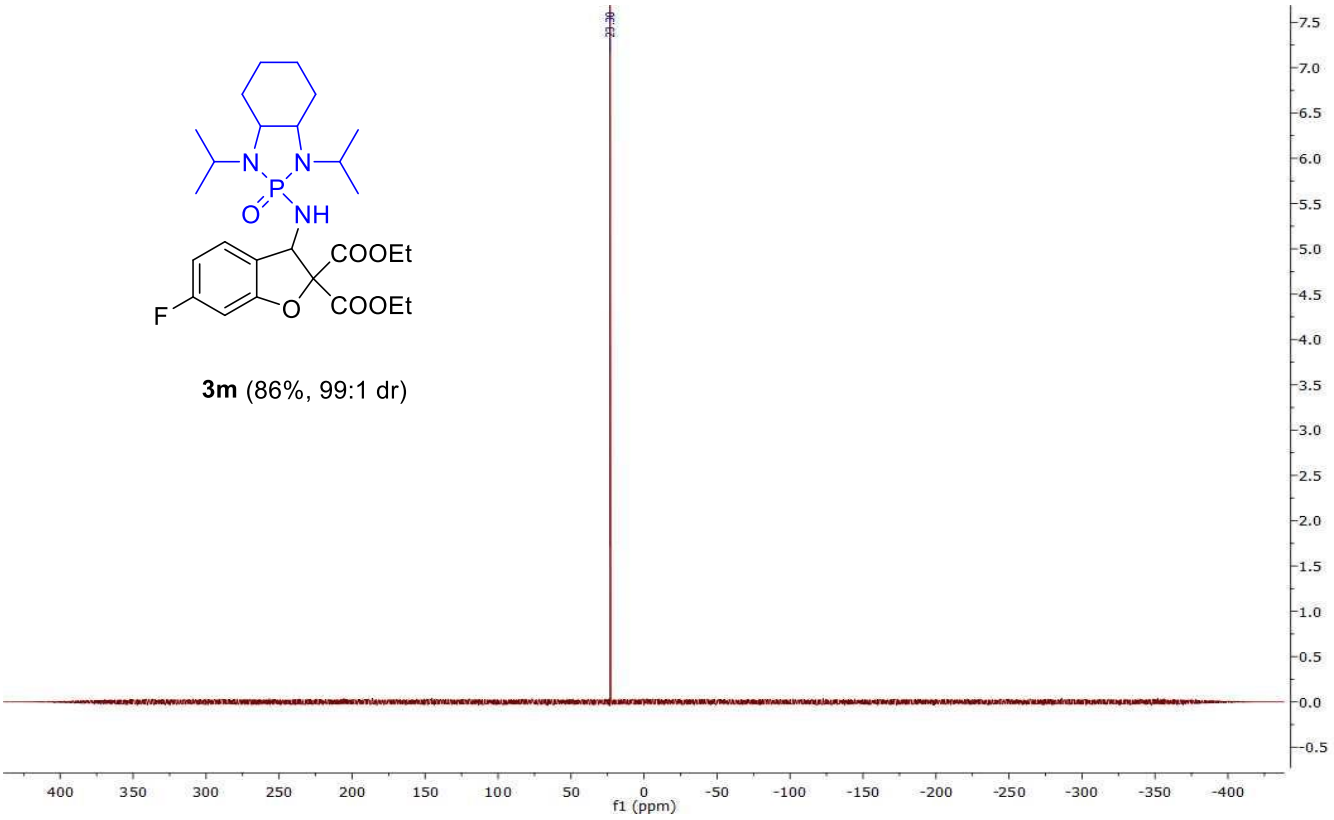
3k (80%, 93:7 dr)

^{31}P NMR of 2,3-dihydrobenzofuran **3k** ($CDCl_3$, 162 Hz)



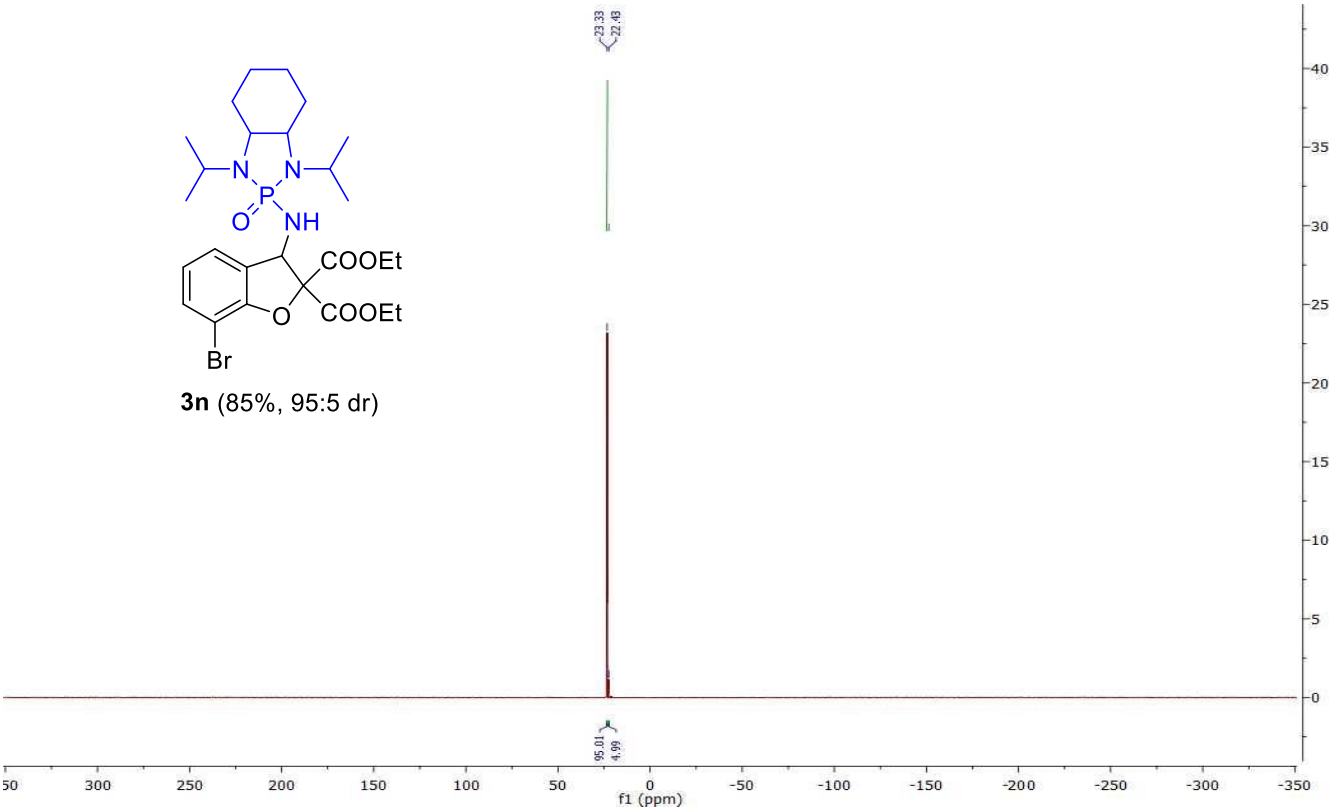
3l (94%, 99:1 dr)

^{31}P NMR of 2,3-dihydrobenzofuran **3l** ($CDCl_3$, 162 Hz)



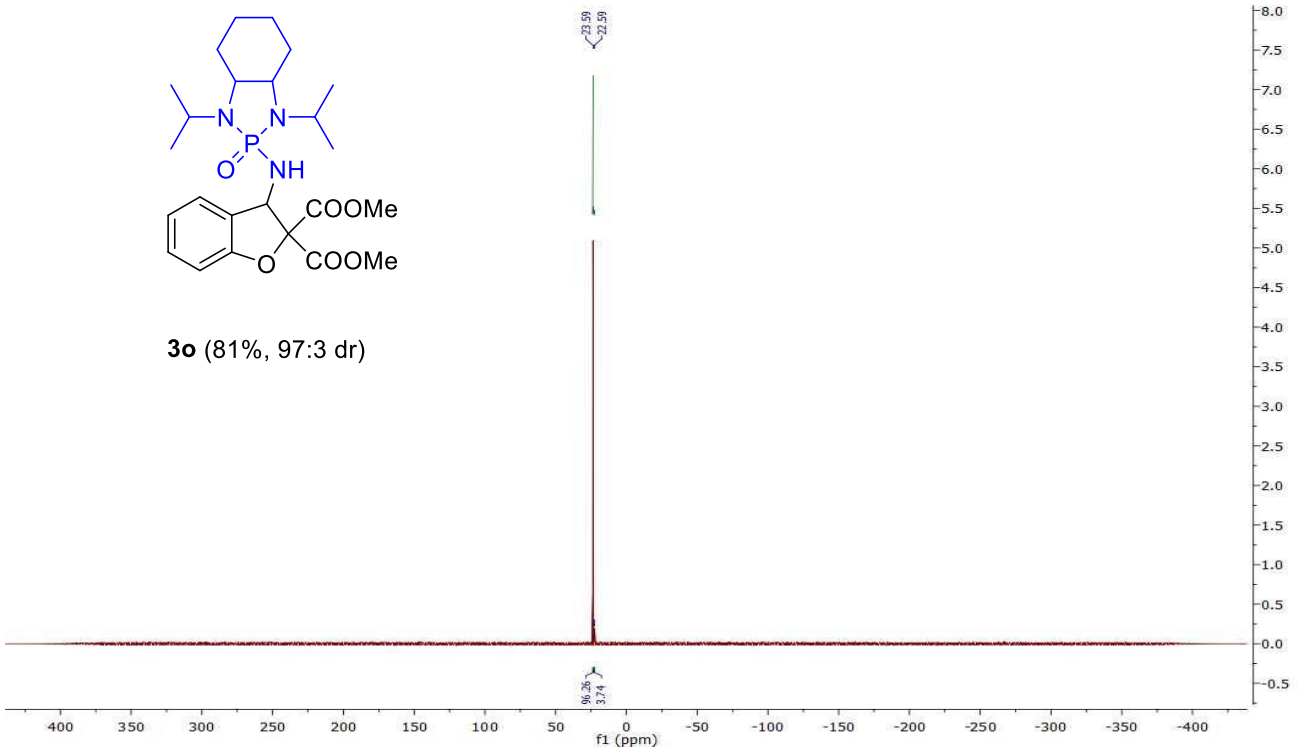
3m (86%, 99:1 dr)

^{31}P NMR of 2,3-dihydrobenzofuran **3m** ($CDCl_3$, 162 Hz)



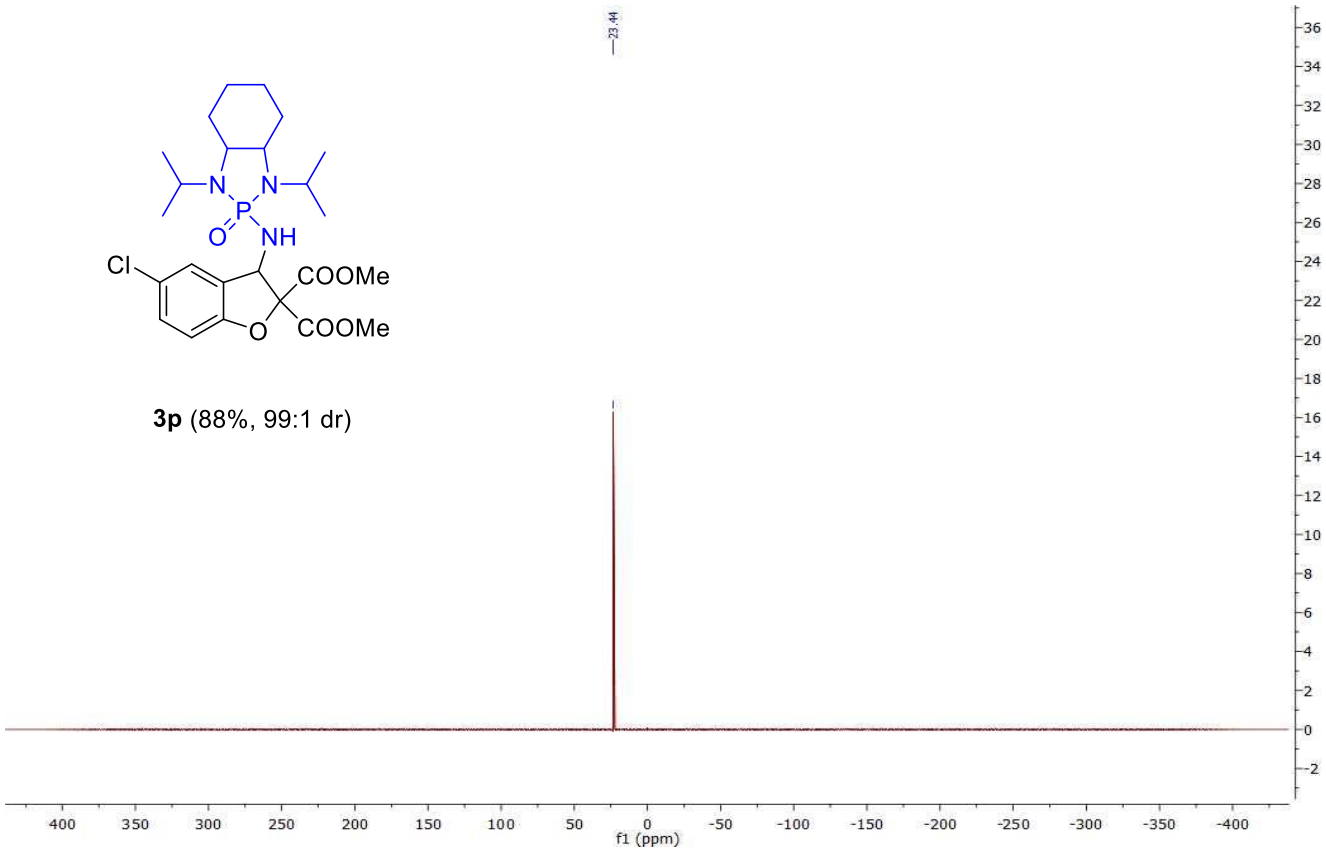
3n (85%, 95:5 dr)

^{31}P NMR of 2,3-dihydrobenzofuran **3n** ($CDCl_3$, 162 Hz)



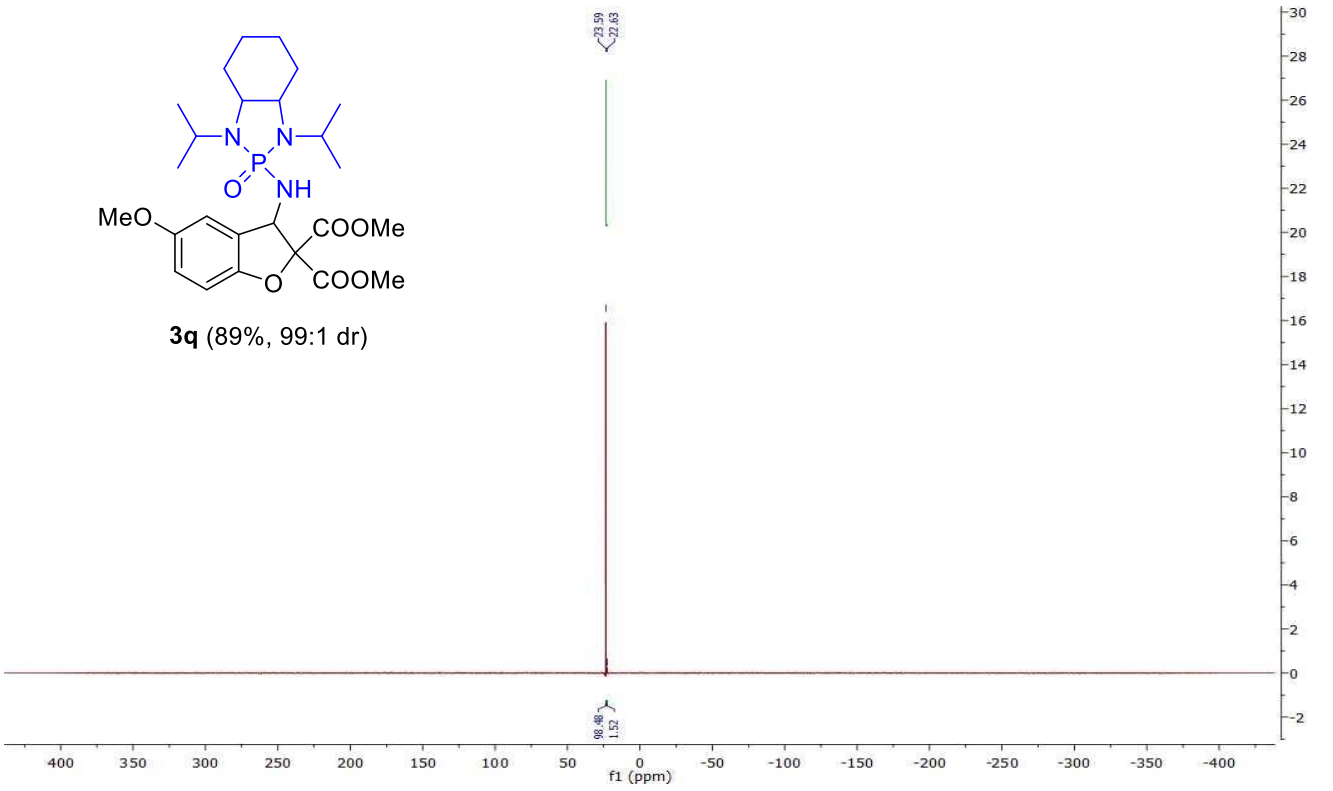
3o (81%, 97:3 dr)

^{31}P NMR of 2,3-dihydrobenzofuran **3o** ($CDCl_3$, 162 Hz)

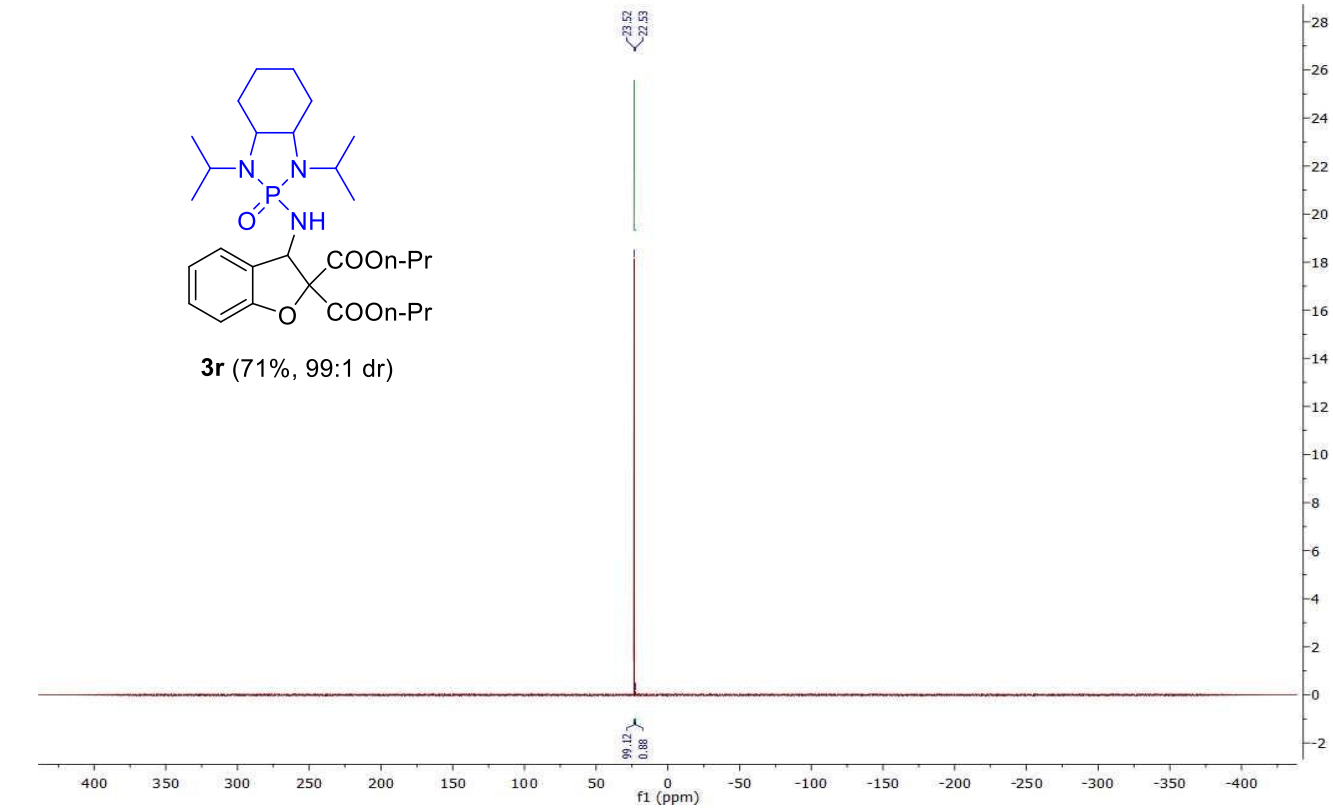


3p (88%, 99:1 dr)

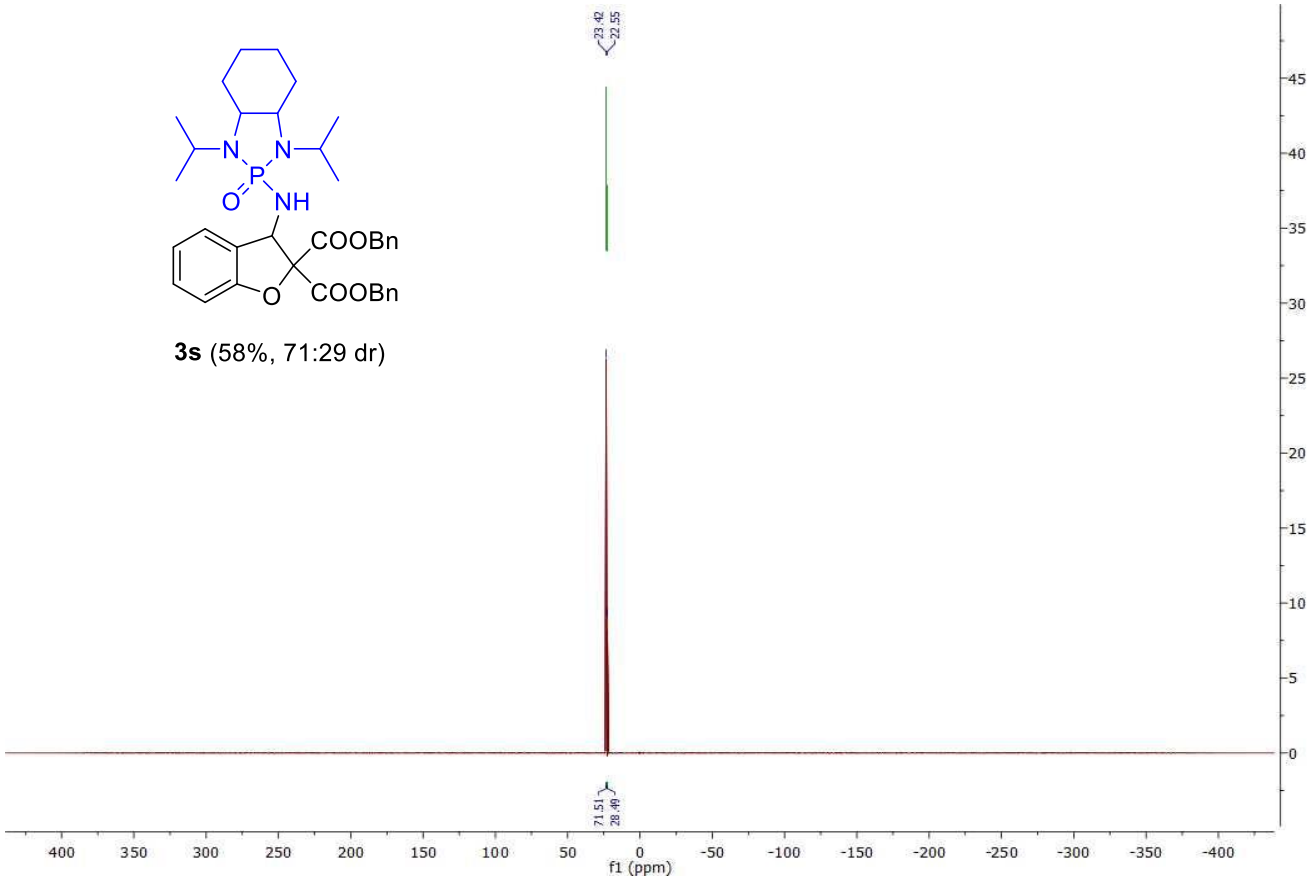
^{31}P NMR of 2,3-dihydrobenzofuran **3p** ($CDCl_3$, 162 Hz)



^{31}P NMR of 2,3-dihydrobenzofuran **3q** ($CDCl_3$, 162 Hz)



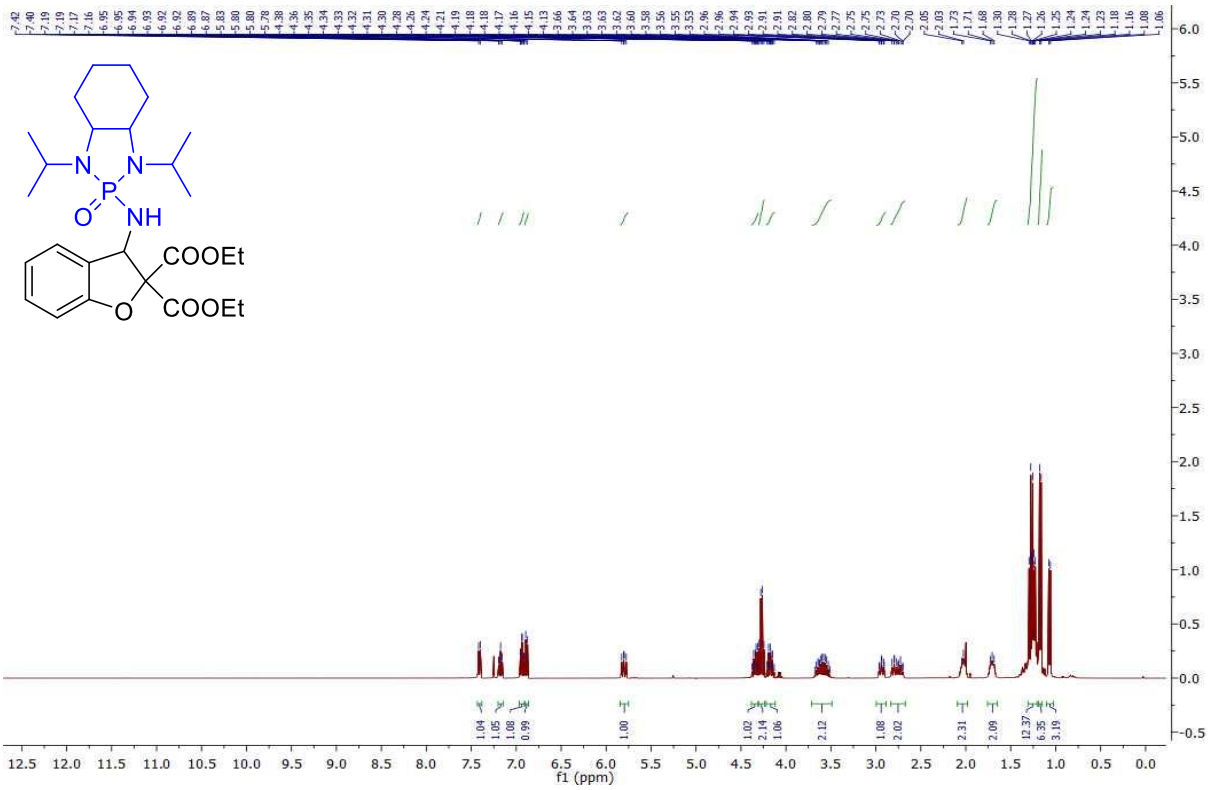
^{31}P NMR of 2,3-dihydrobenzofuran **3r** ($CDCl_3$, 162 Hz)



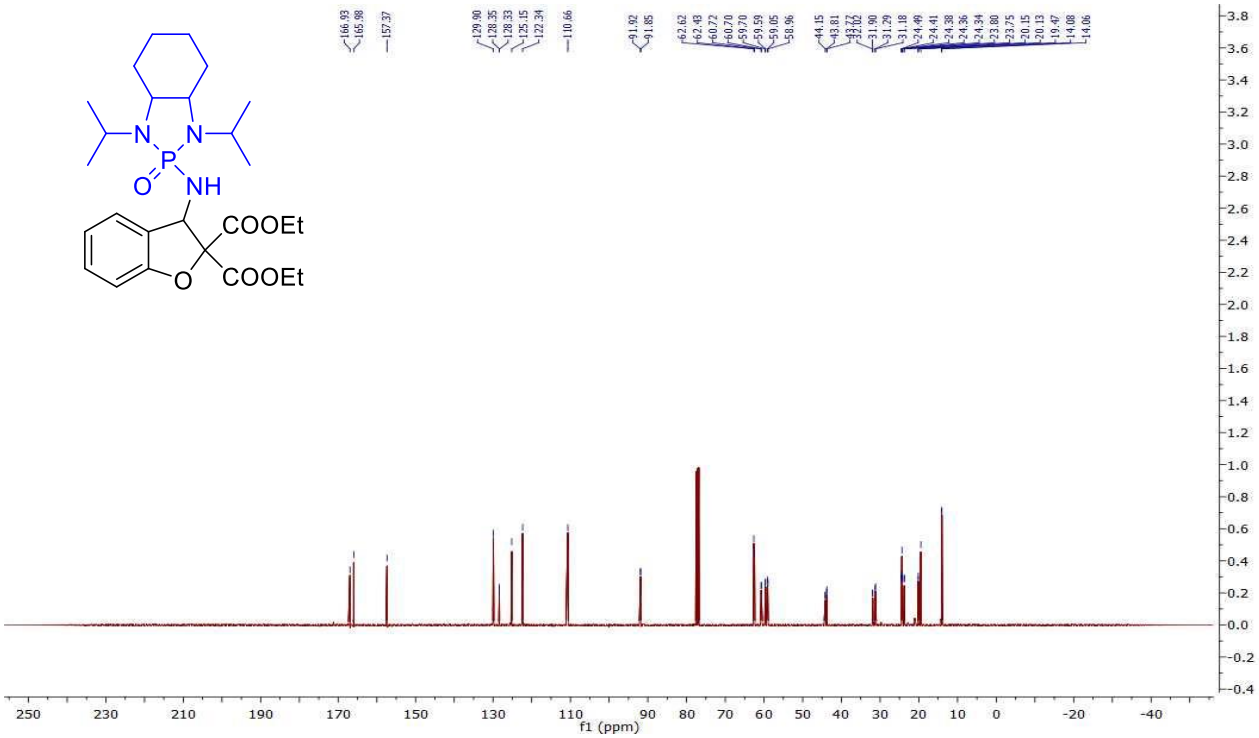
3s (58%, 71:29 dr)

^{31}P NMR of 2,3-dihydrobenzofuran **3s** ($CDCl_3$, 162 Hz)

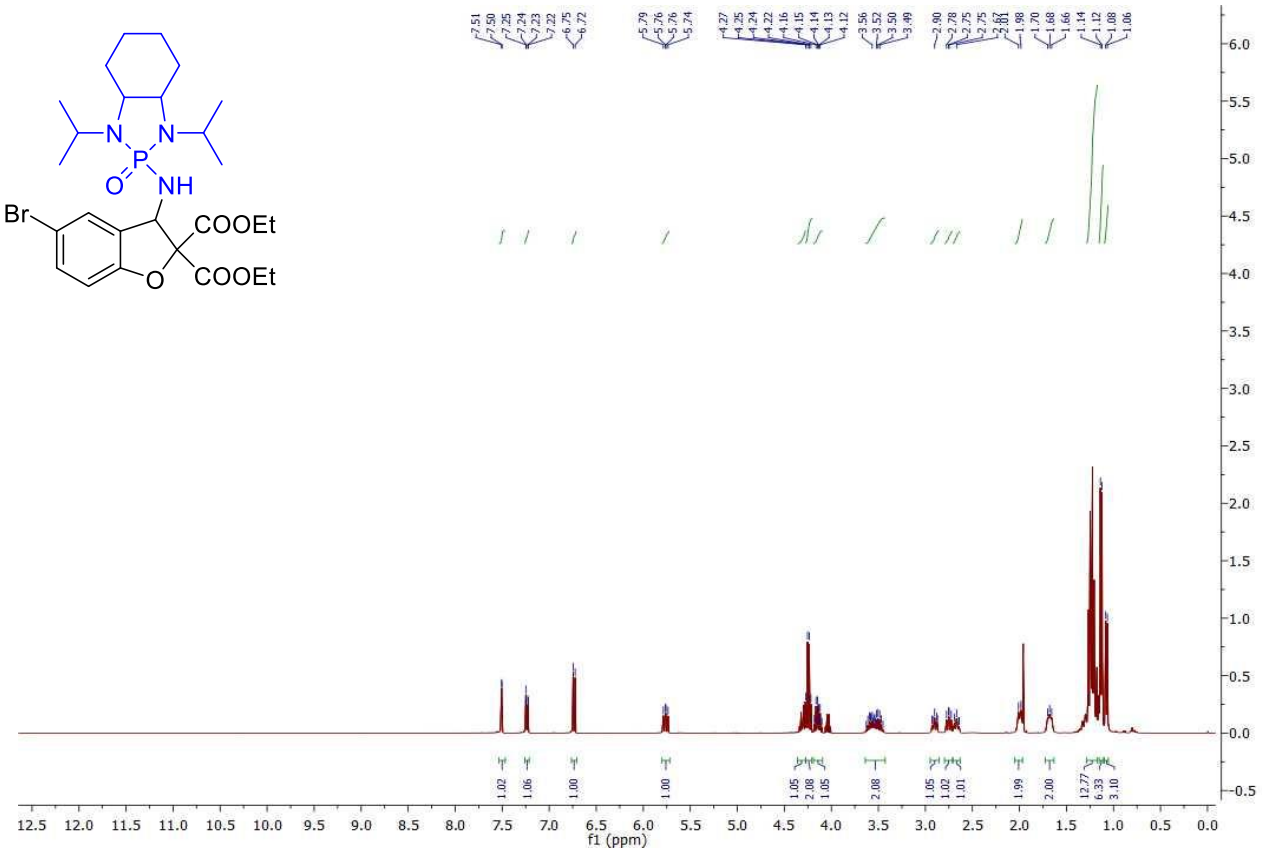
Copies of ^{1}H, ^{13}C NMR Spectra for Compounds 3a-3r



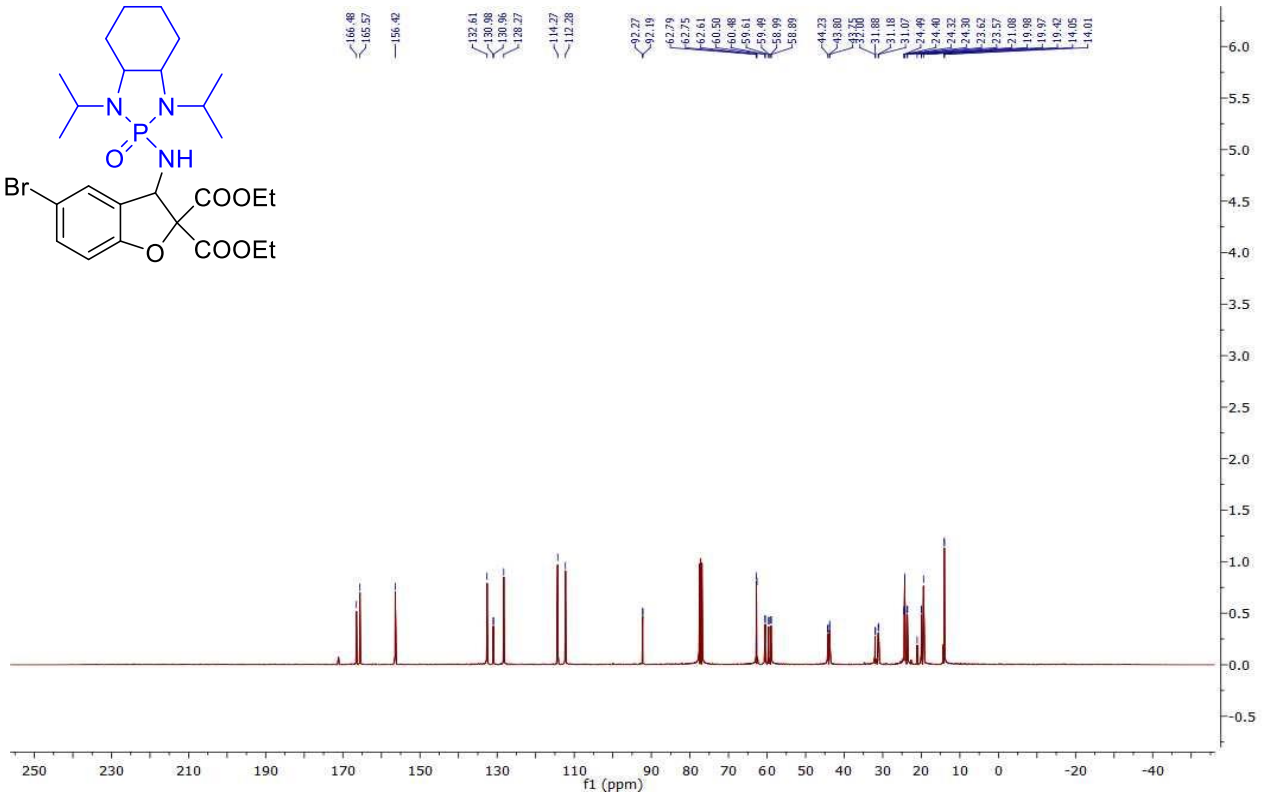
^{1}H NMR of 2,3-dihydrobenzofuran **3a** ($CDCl_3$, 400 Hz)



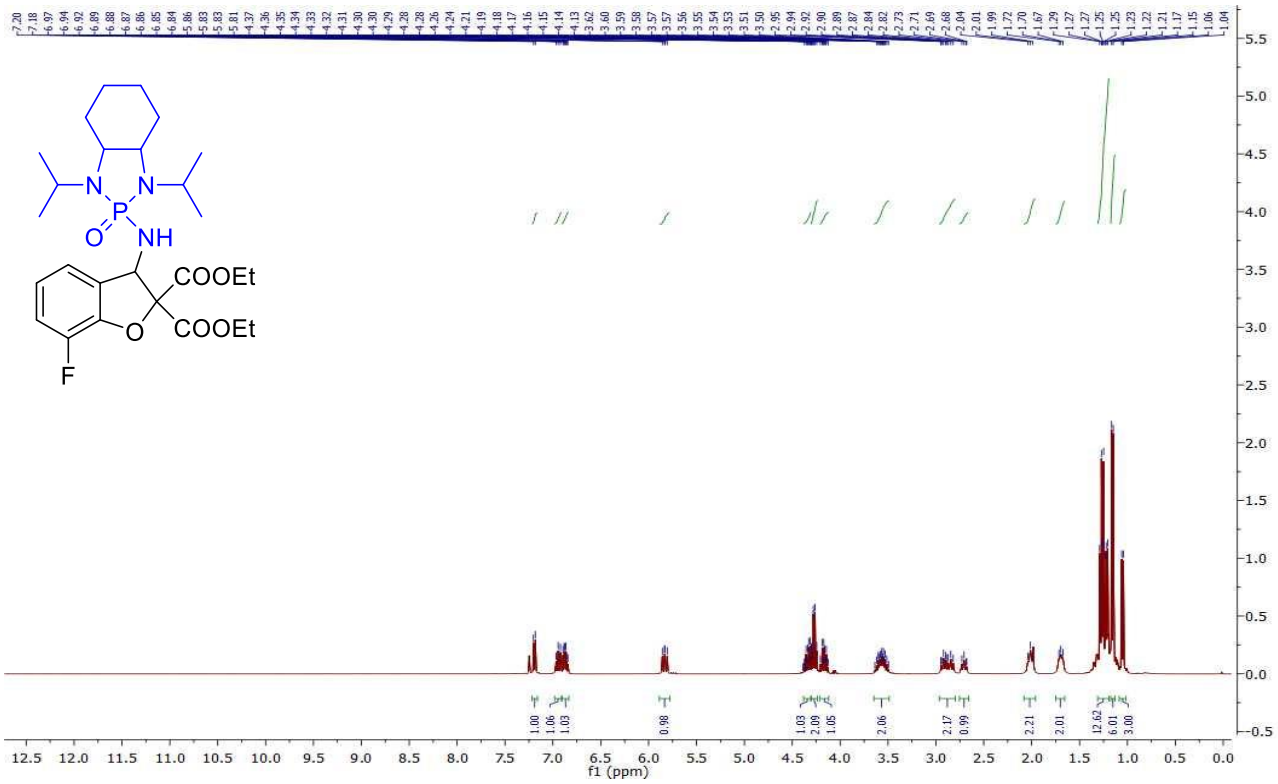
^{13}C NMR of 2,3-dihydrobenzofuran **3a** ($CDCl_3$, 100 Hz)



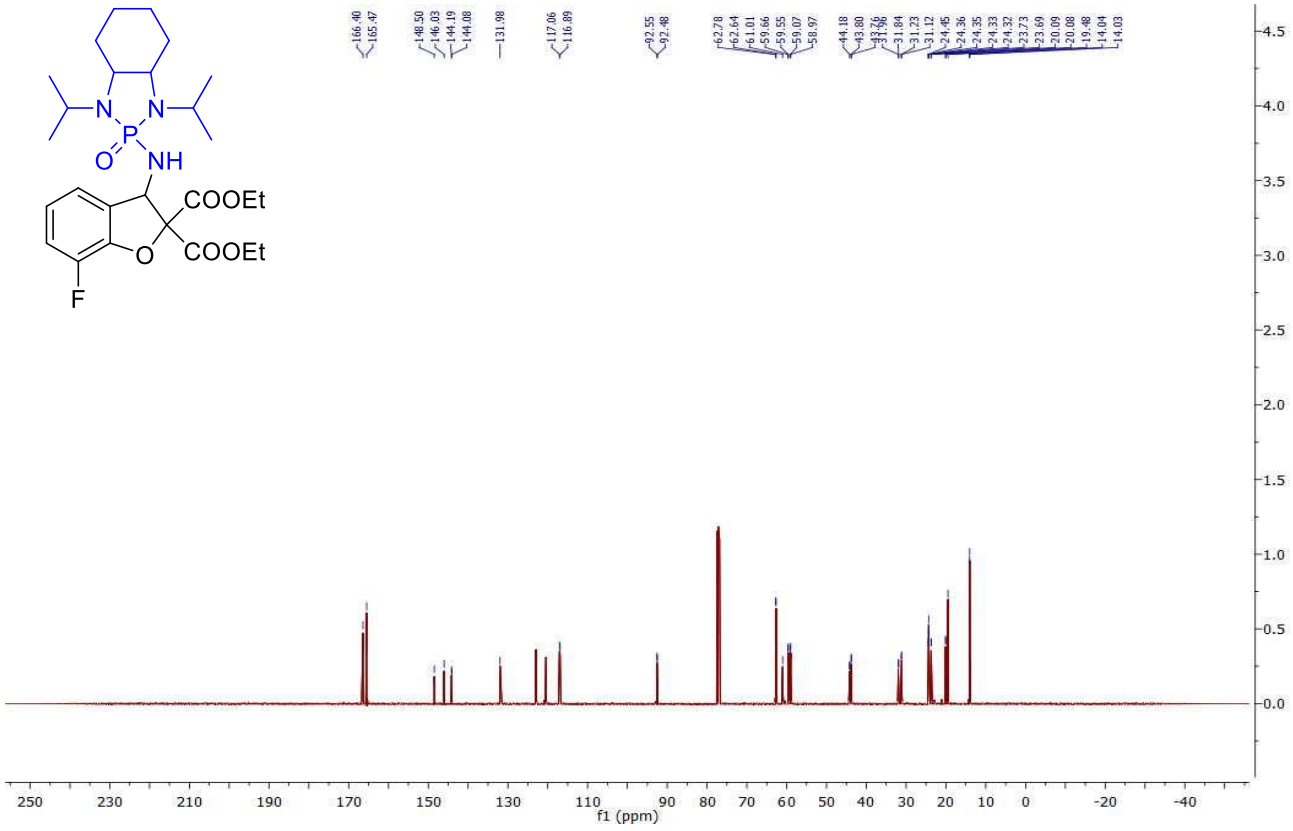
^{1}H NMR of 2,3-dihydrobenzofuran **3b** ($CDCl_3$, 400 Hz)



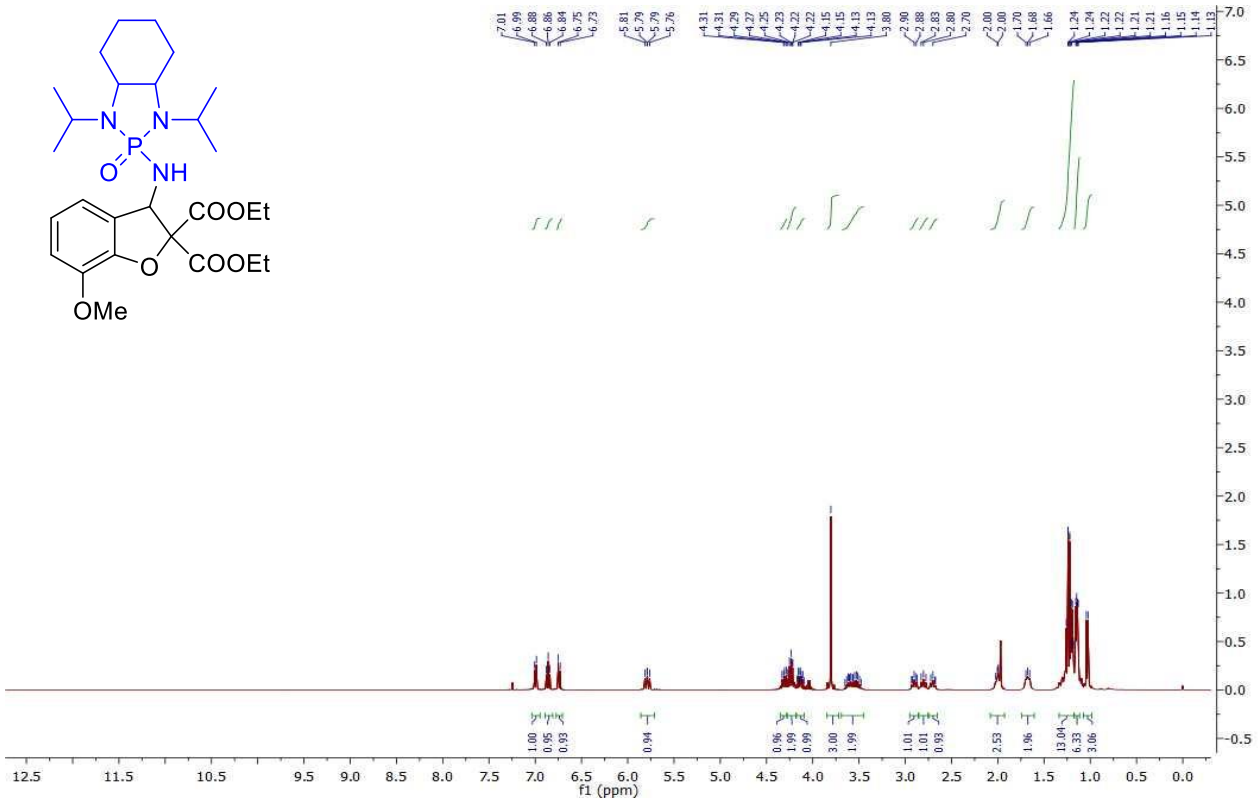
^{13}C NMR of 2,3-dihydrobenzofuran **3b** ($CDCl_3$, 100 Hz)



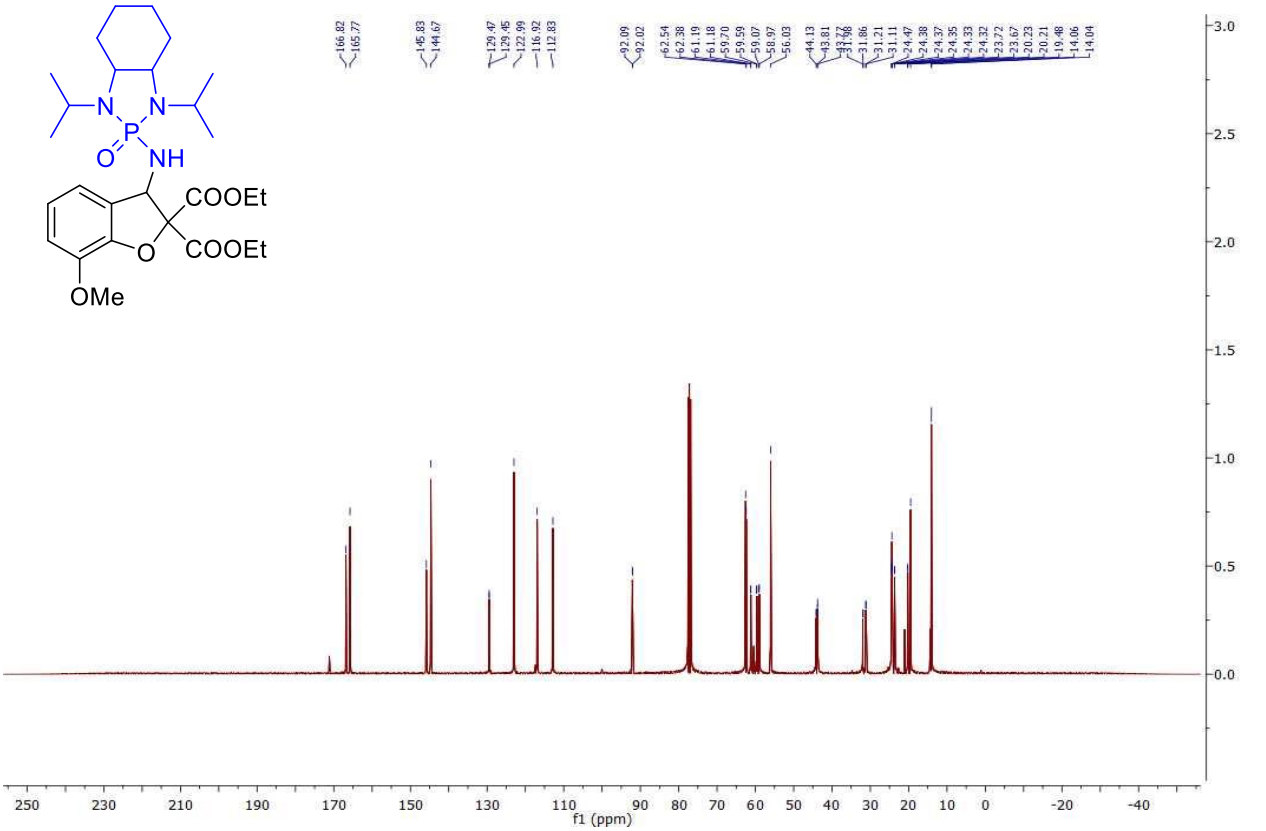
^{1}H NMR of 2,3-dihydrobenzofuran **3c** ($CDCl_3$, 400 Hz)



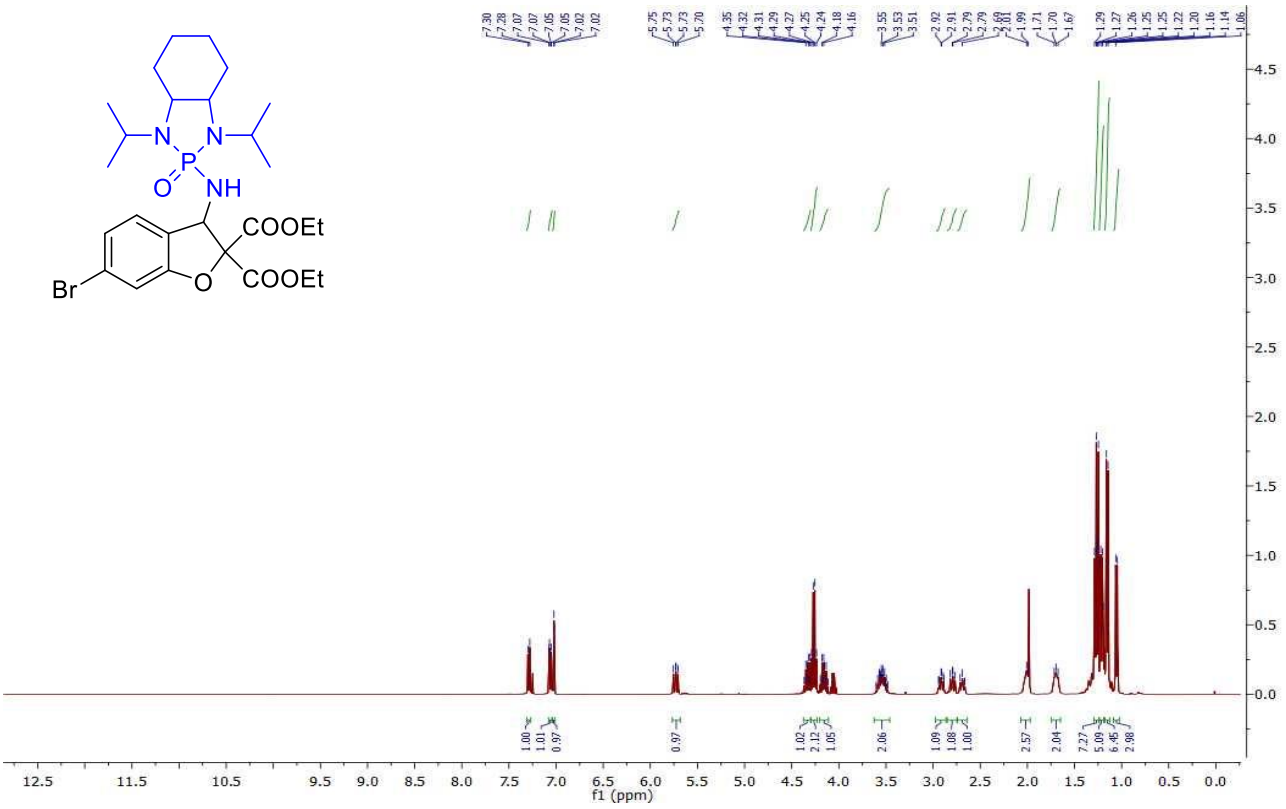
^{13}C NMR of 2,3-dihydrobenzofuran **3c** ($CDCl_3$, 100 Hz)



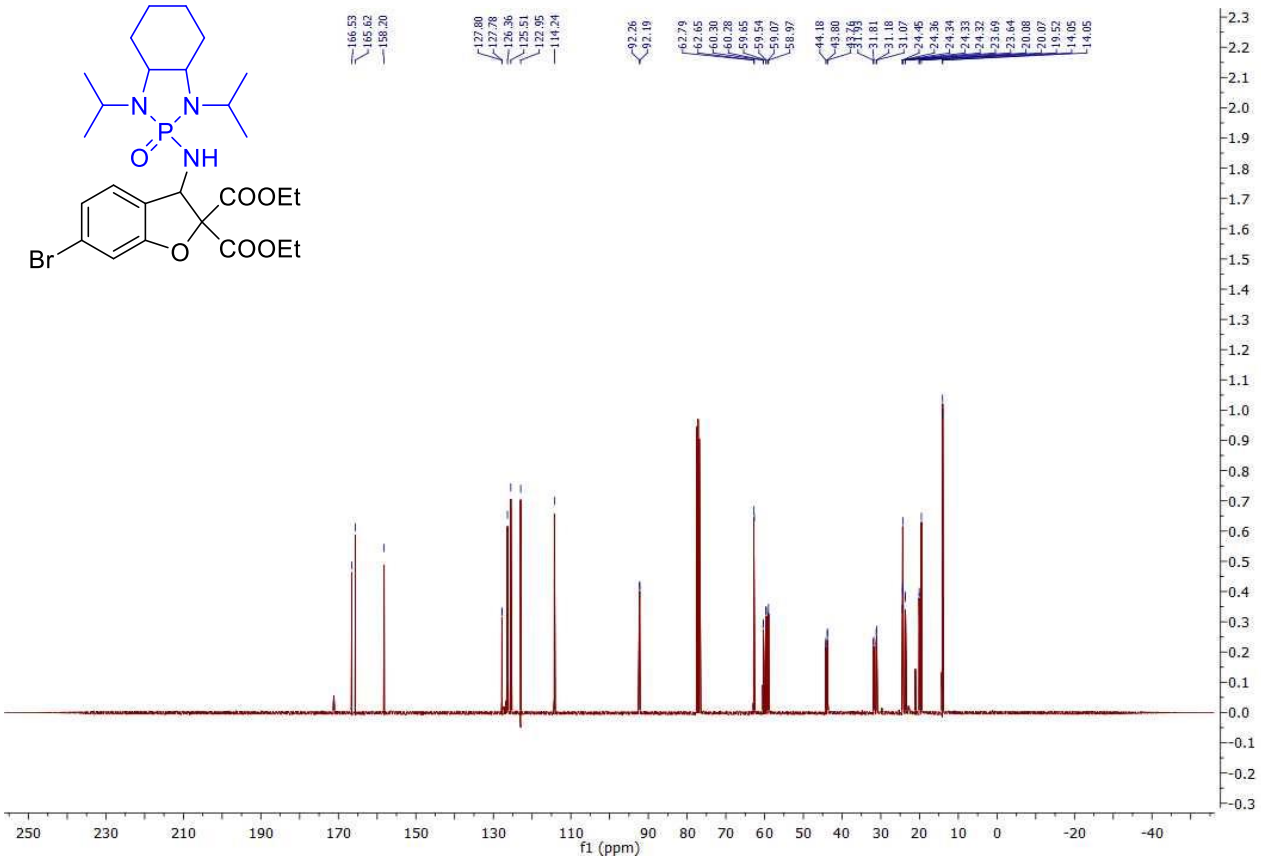
^{1}H NMR of 2,3-dihydrobenzofuran **3d** ($CDCl_3$, 400 Hz)



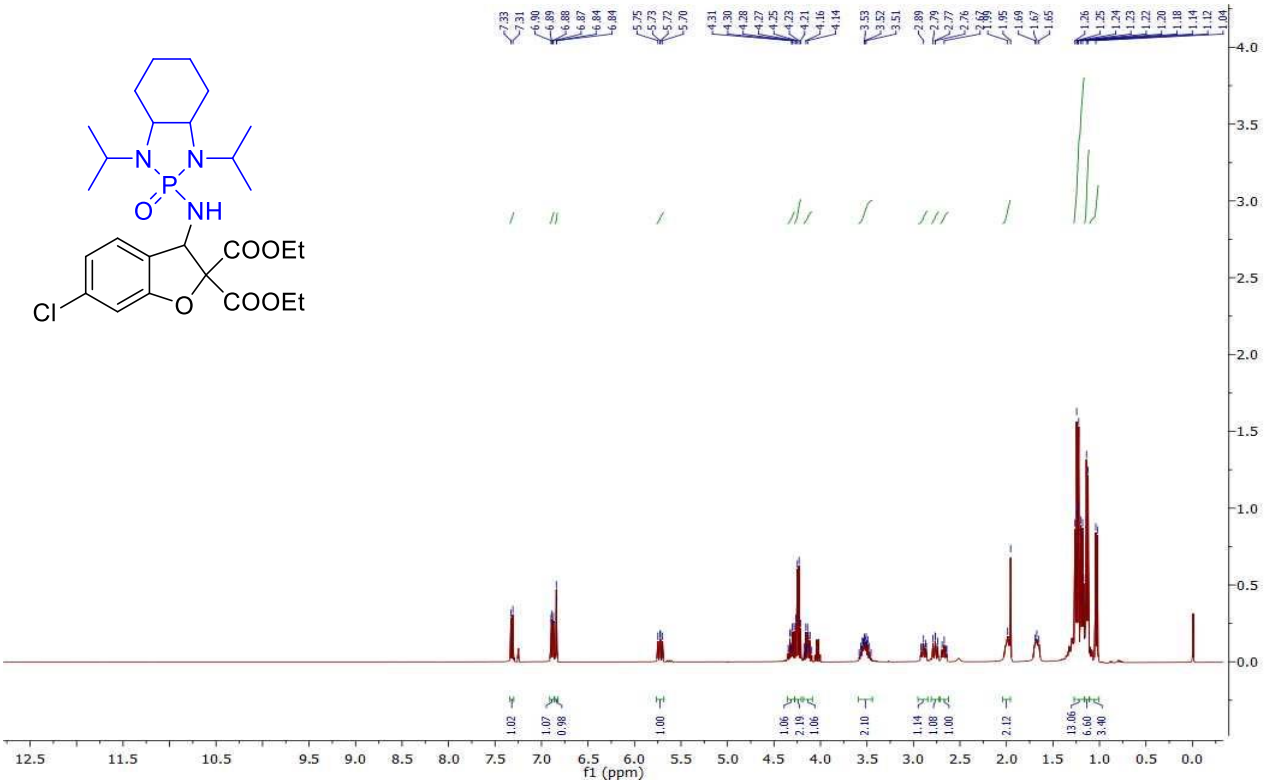
^{13}C NMR of 2,3-dihydrobenzofuran **3d** ($CDCl_3$, 100 Hz)



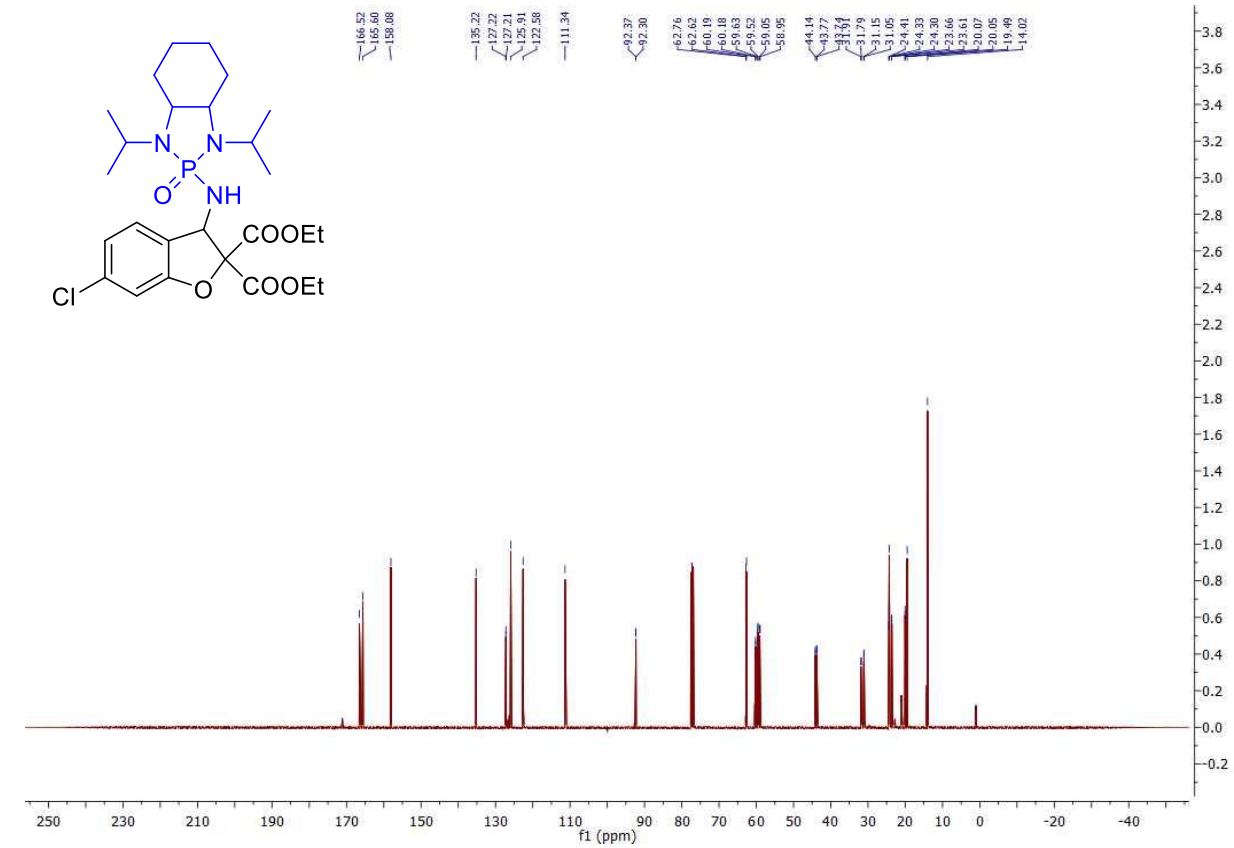
^{1}H NMR of 2,3-dihydrobenzofuran **3e** ($CDCl_3$, 400 Hz)



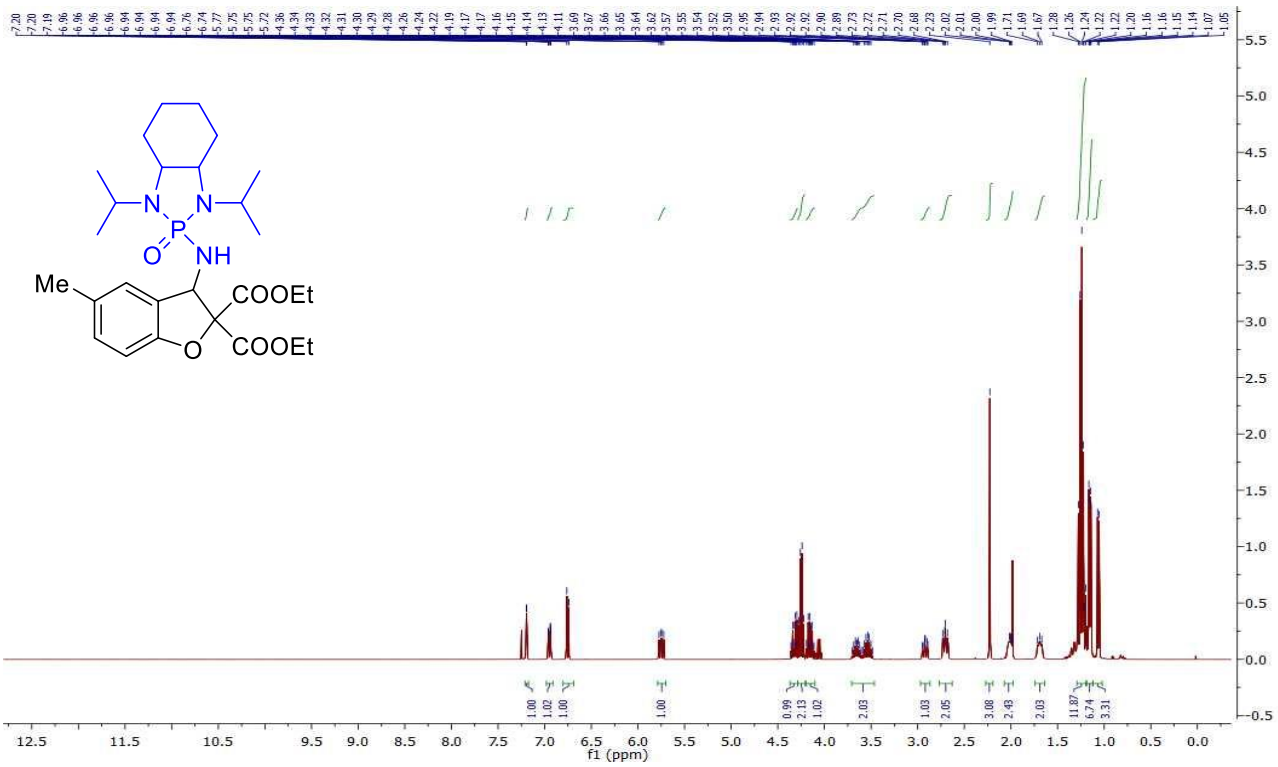
^{13}C NMR of 2,3-dihydrobenzofuran **3e** ($CDCl_3$, 100 Hz)



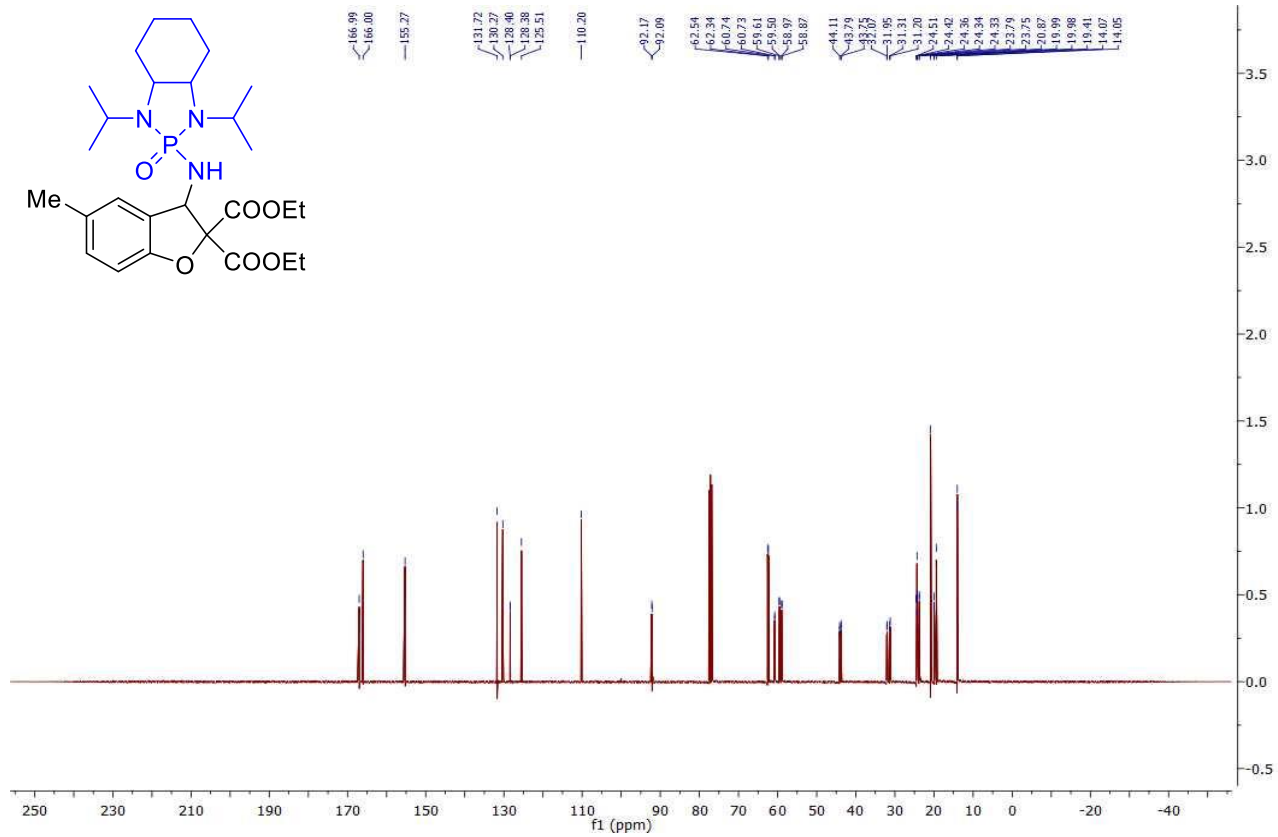
^{1}H NMR of 2,3-dihydrobenzofuran **3f** ($CDCl_3$, 400 Hz)



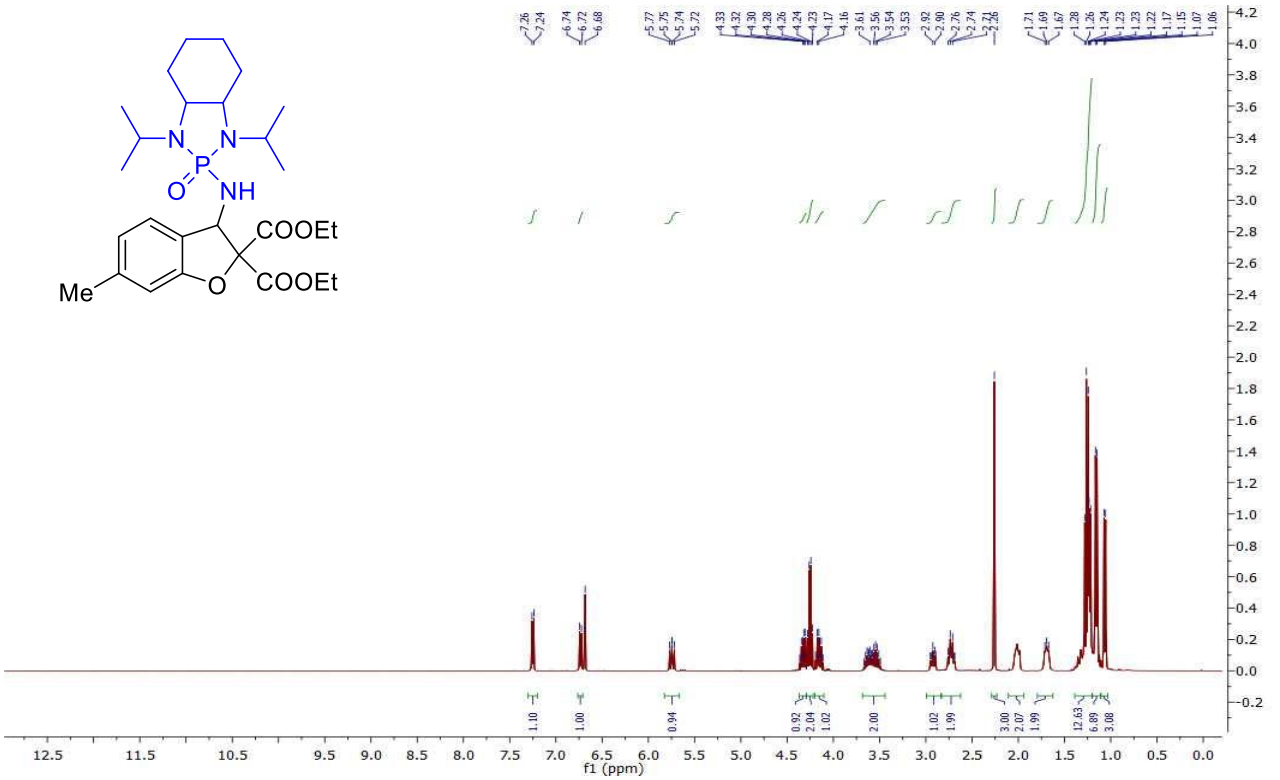
^{13}C NMR of 2,3-dihydrobenzofuran **3f** ($CDCl_3$, 100 Hz)



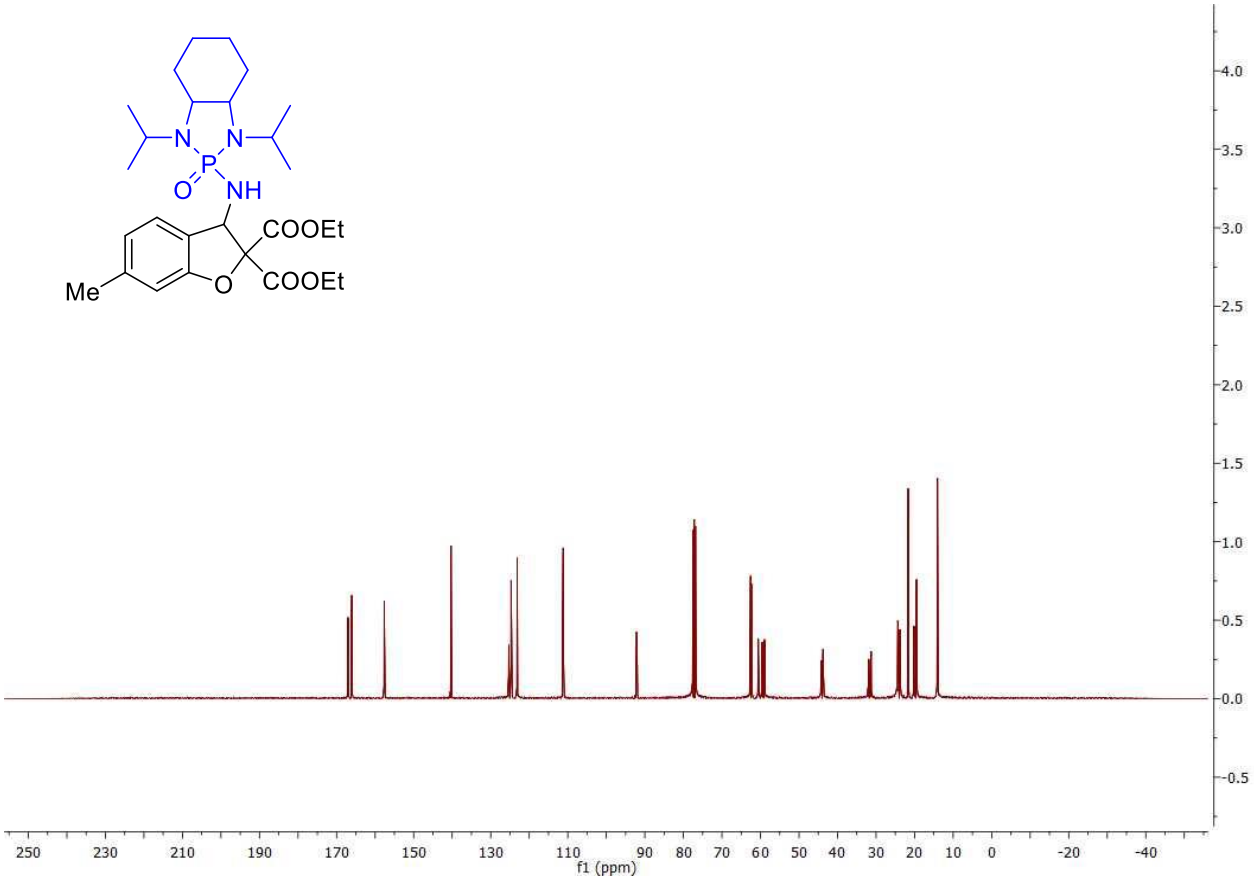
^{1}H NMR of 2,3-dihydrobenzofuran **3g** ($CDCl_3$, 400 Hz)



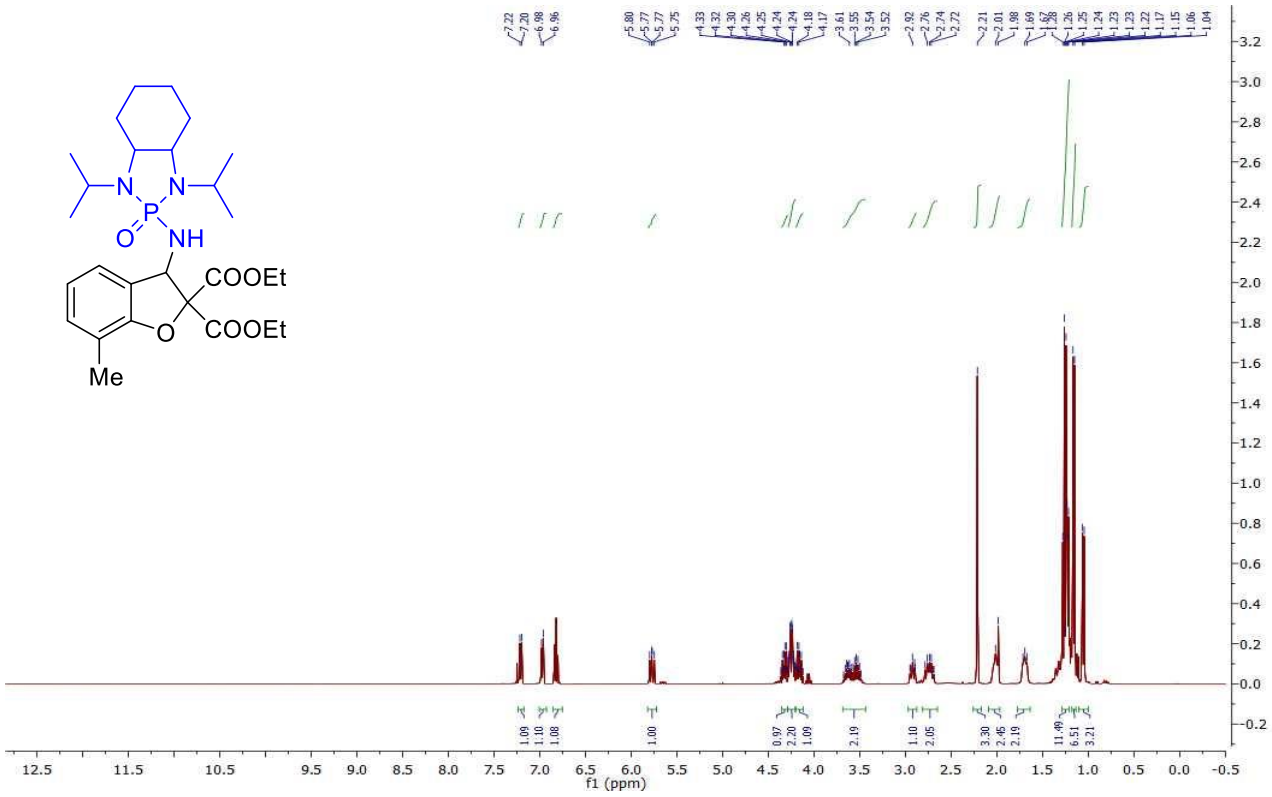
^{13}C NMR of 2,3-dihydrobenzofuran **3g** ($CDCl_3$, 100 Hz)



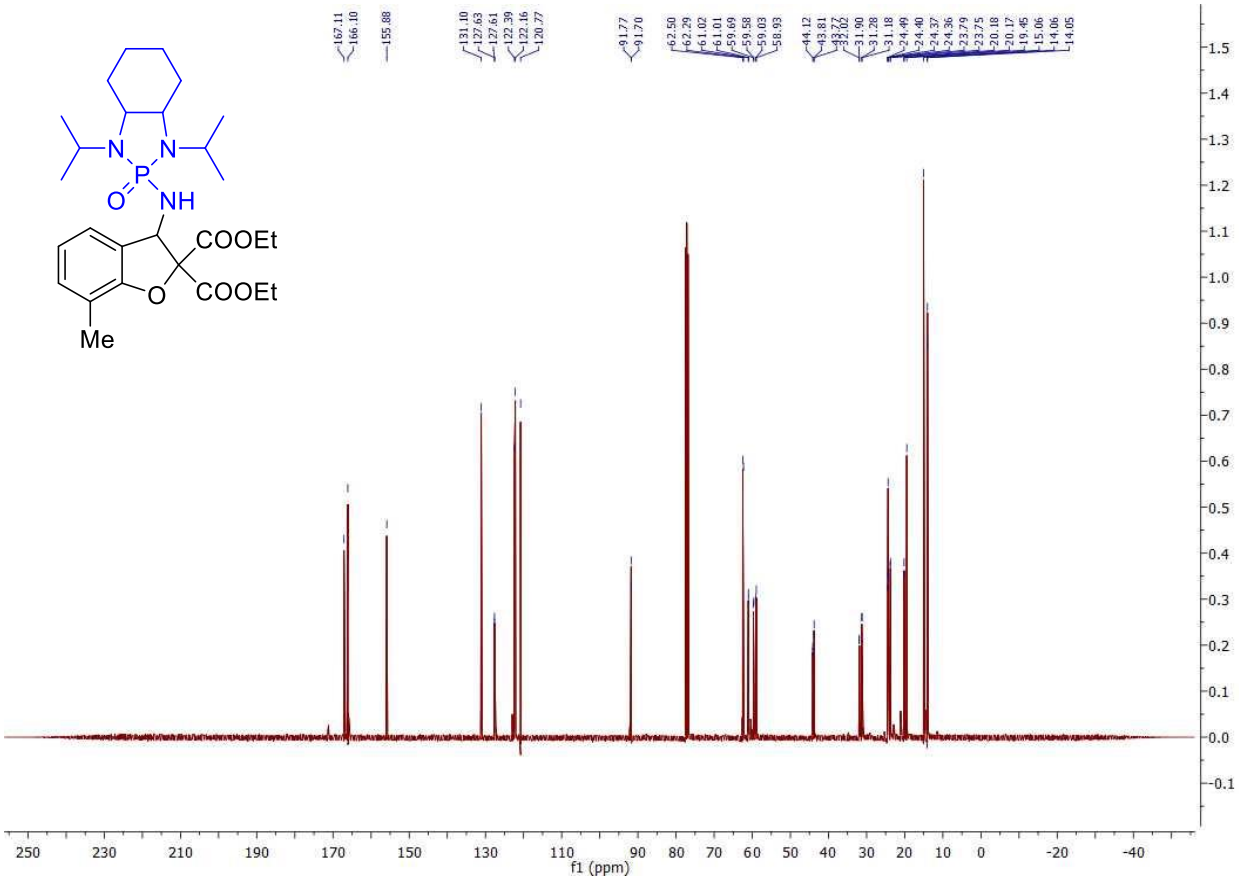
^{1}H NMR of 2,3-dihydrobenzofuran **3h** ($CDCl_3$, 400 Hz)



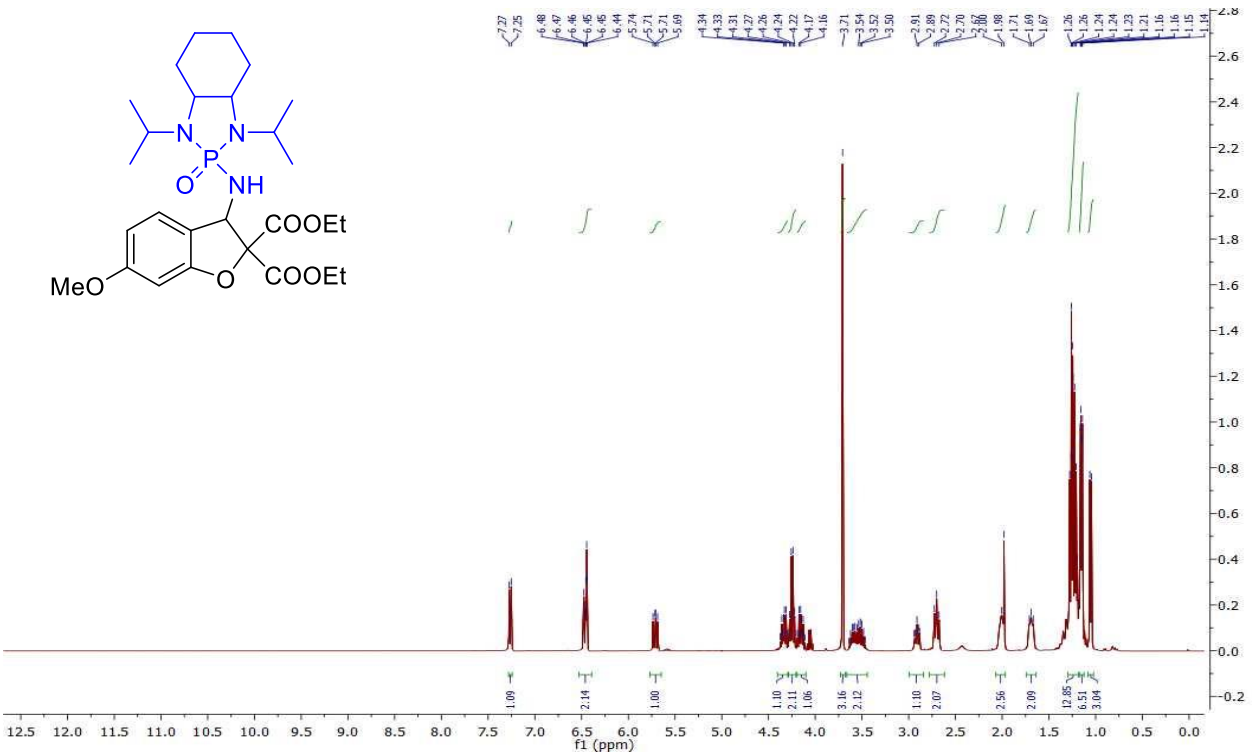
^{13}C NMR of 2,3-dihydrobenzofuran **3h** ($CDCl_3$, 100 Hz)



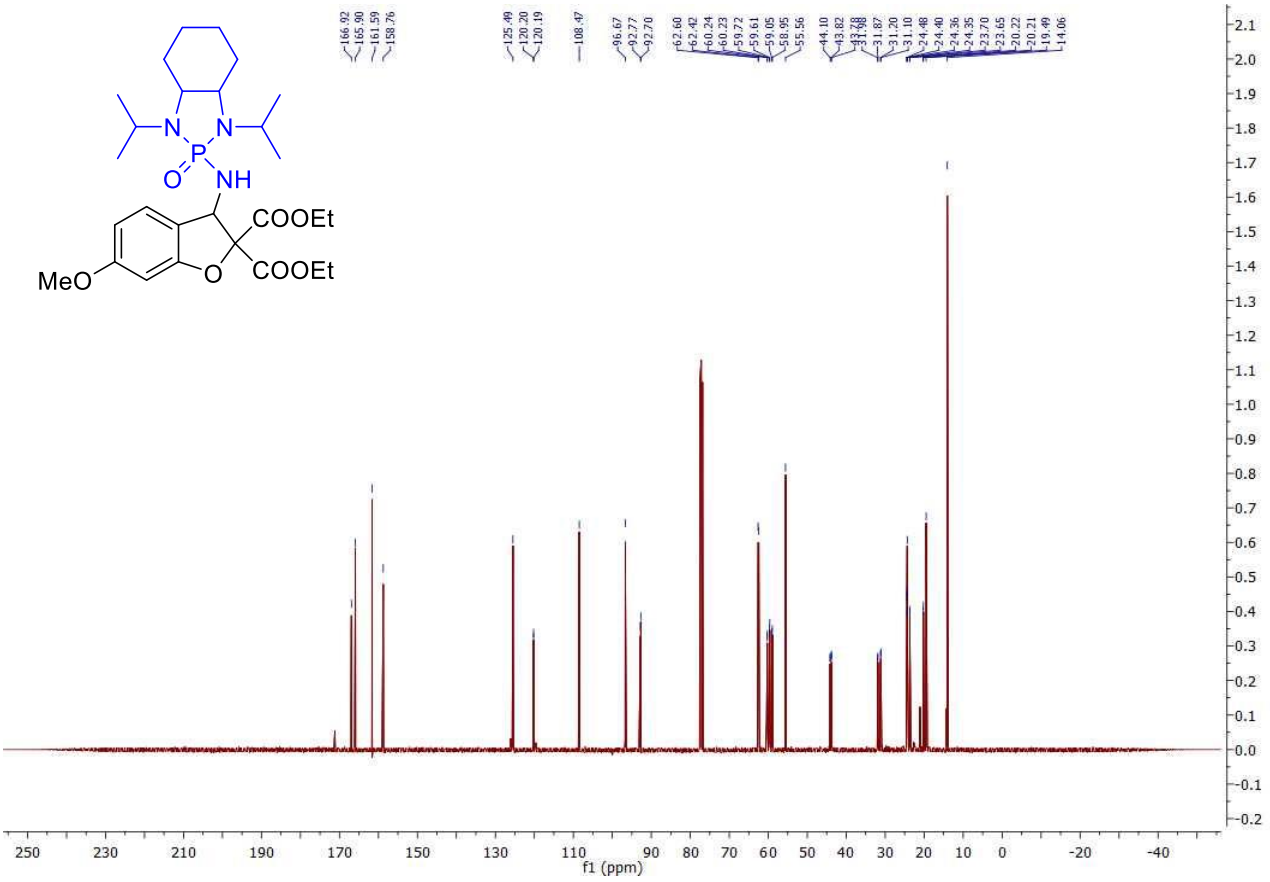
^{1}H NMR of 2,3-dihydrobenzofuran **3i** ($CDCl_3$, 400 Hz)



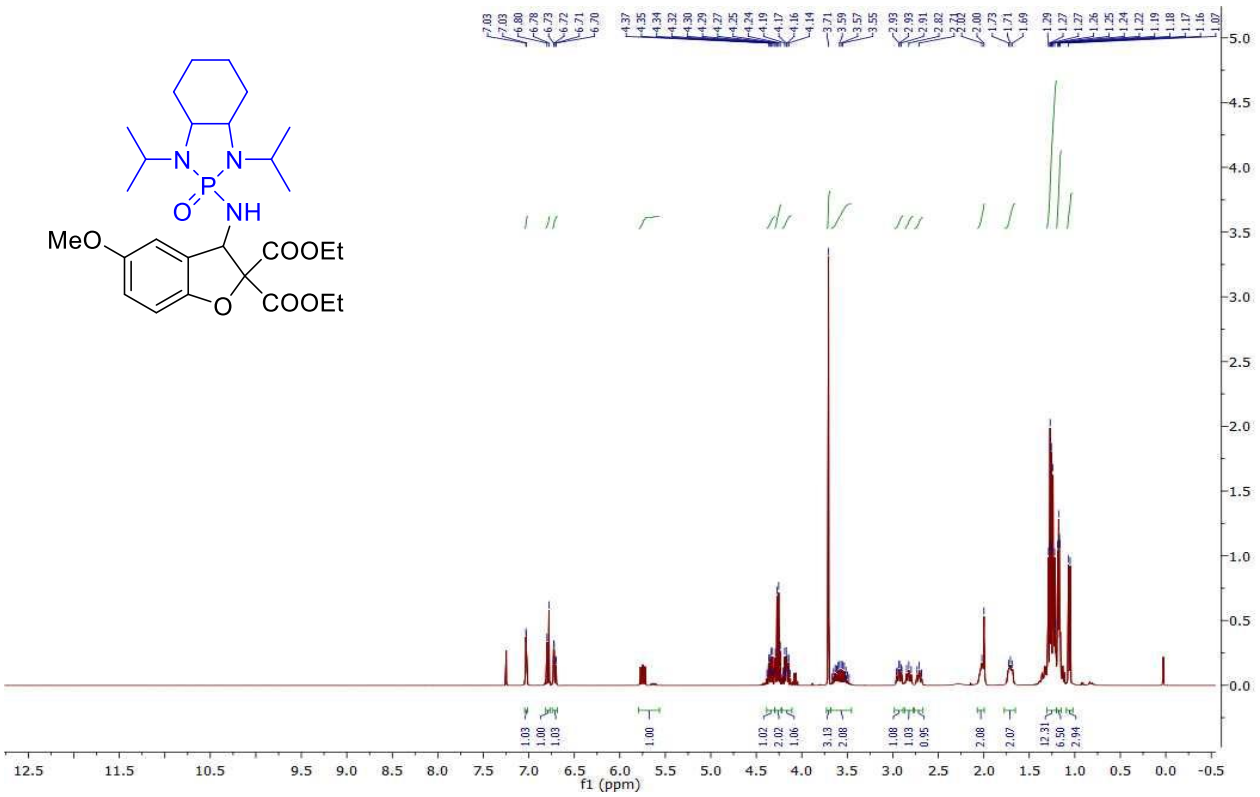
^{13}C NMR of 2,3-dihydrobenzofuran **3i** ($CDCl_3$, 100 Hz)



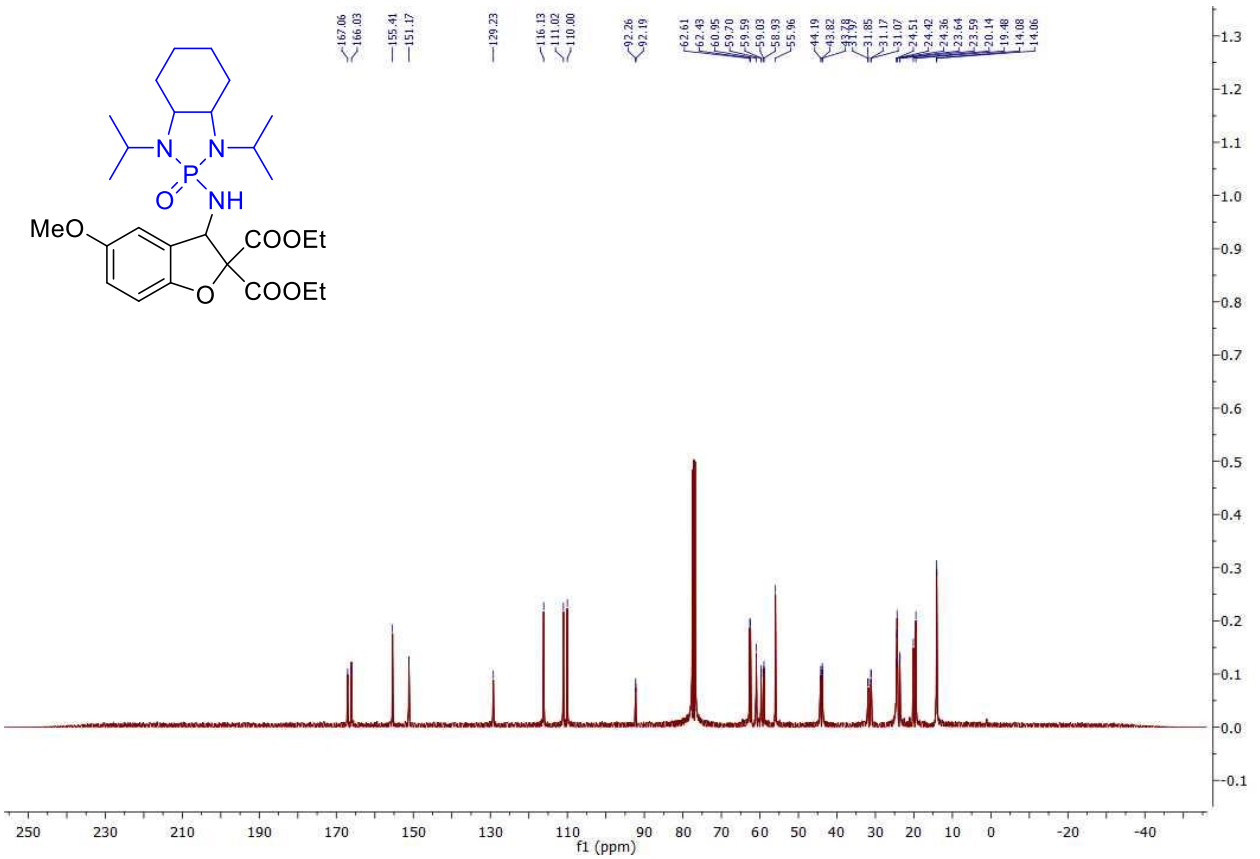
^{1}H NMR of 2,3-dihydrobenzofuran **3j** ($CDCl_3$, 400 Hz)



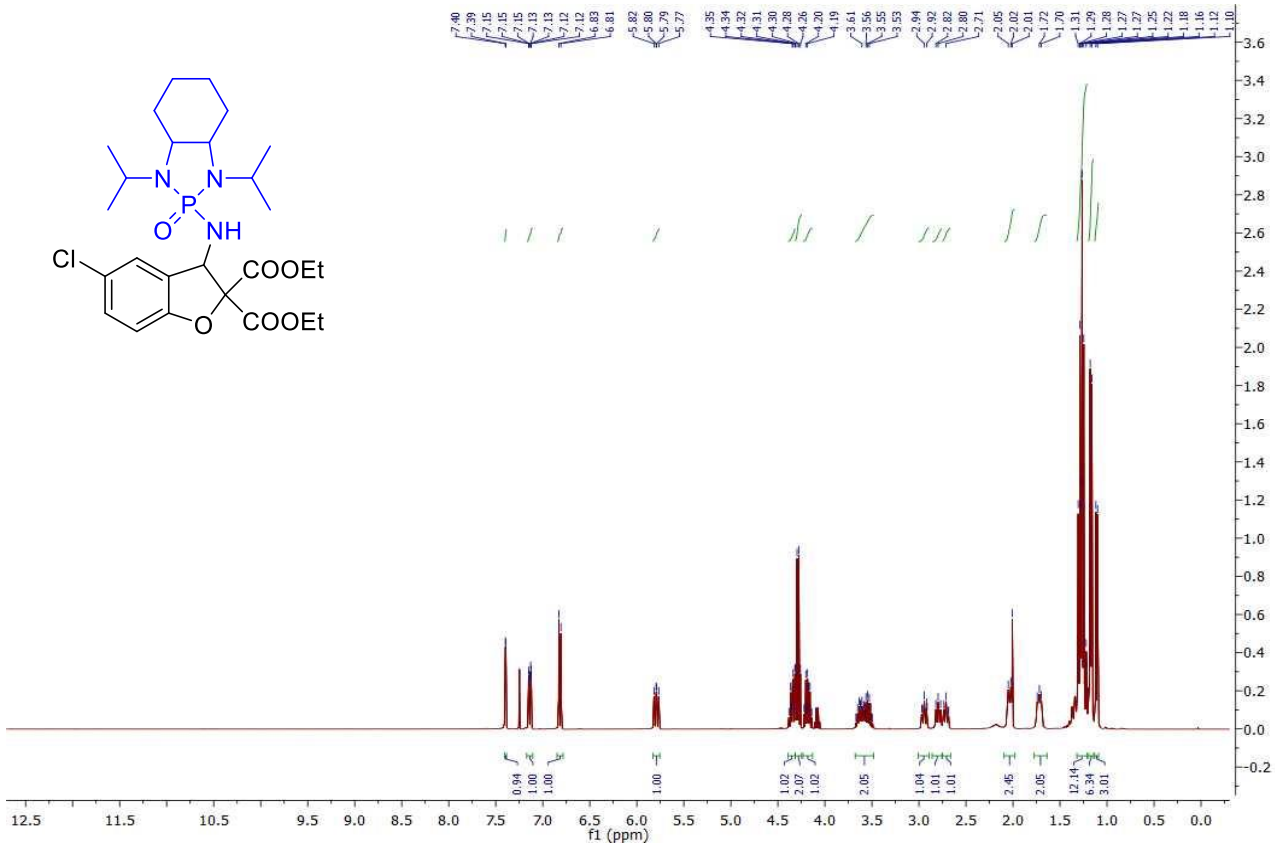
^{13}C NMR of 2,3-dihydrobenzofuran **3j** ($CDCl_3$, 100 Hz)



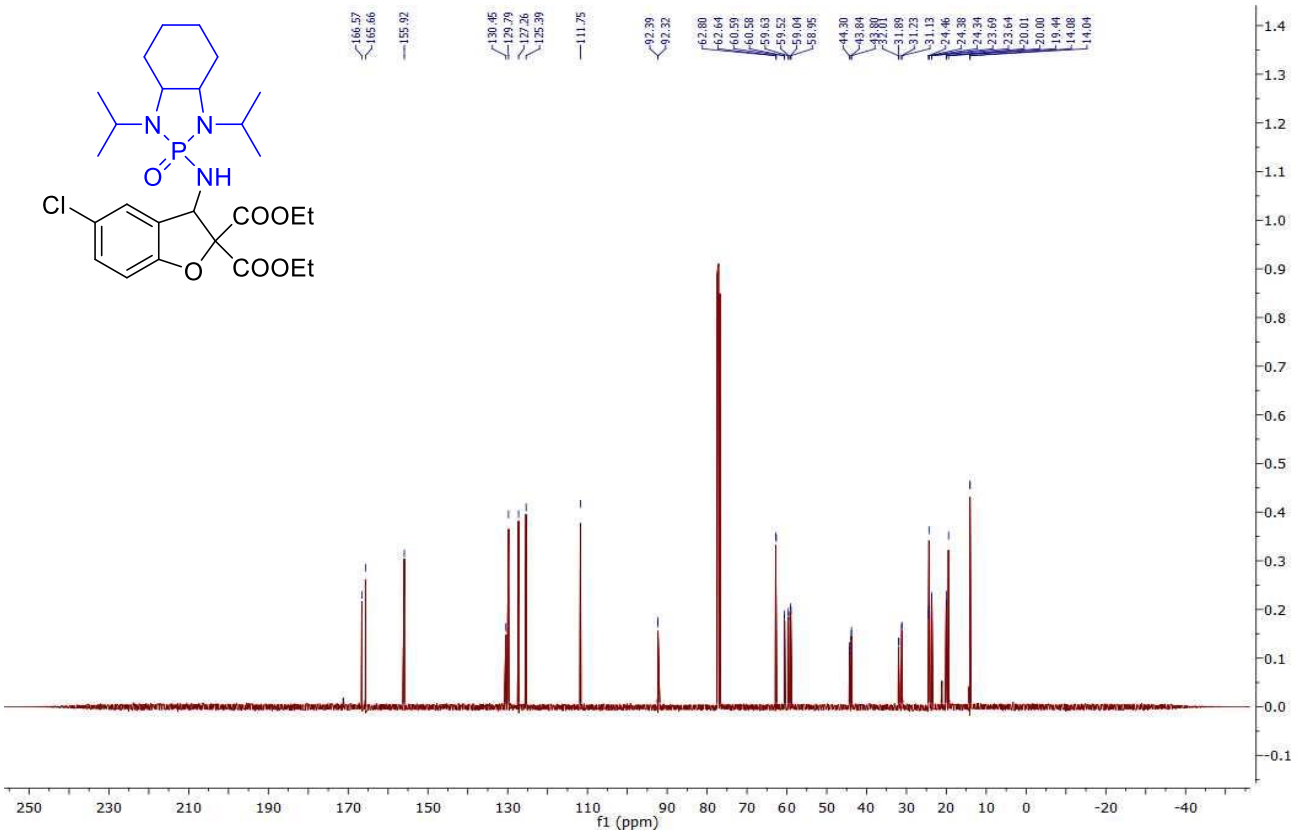
^{1}H NMR of 2,3-dihydrobenzofuran **3k** ($CDCl_3$, 400 Hz)



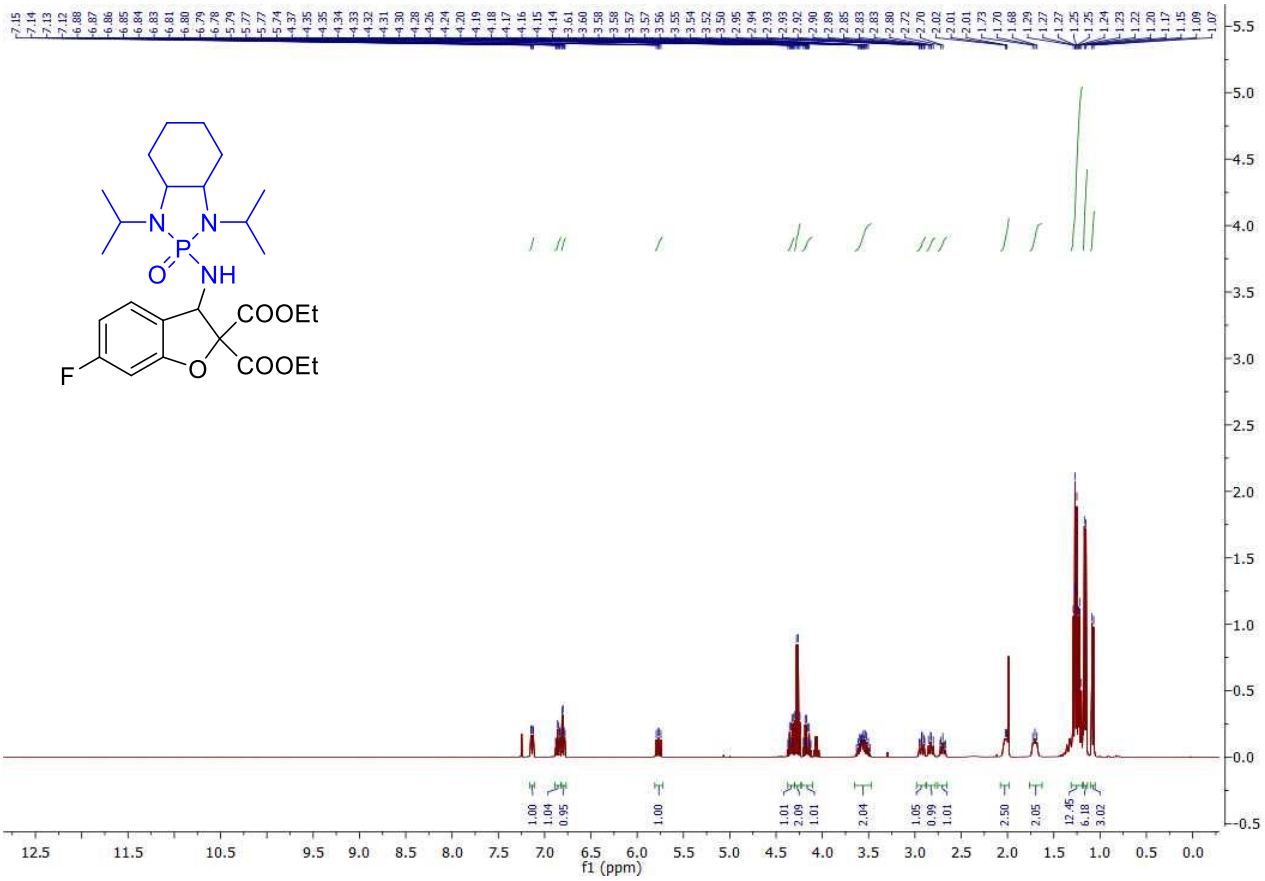
^{13}C NMR of 2,3-dihydrobenzofuran **3k** ($CDCl_3$, 100 Hz)



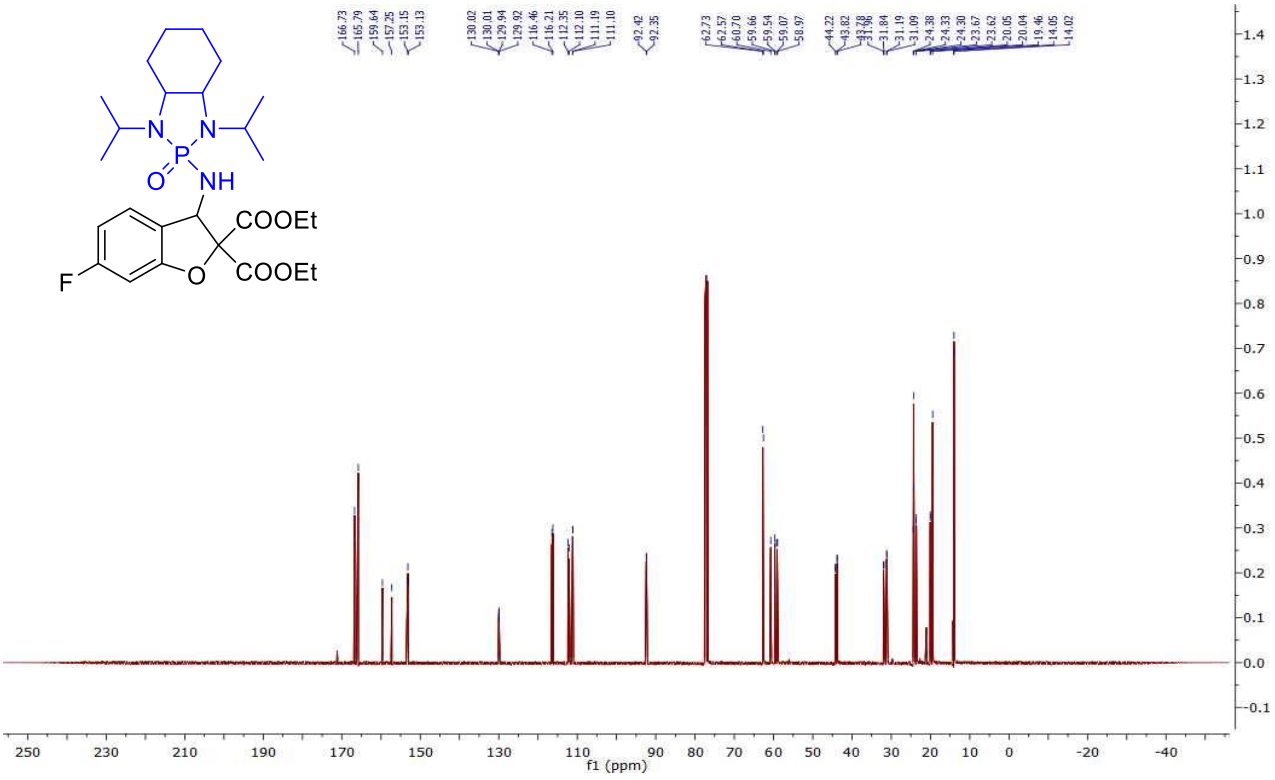
^{1}H NMR of 2,3-dihydrobenzofuran **3l** ($CDCl_3$, 400 Hz)



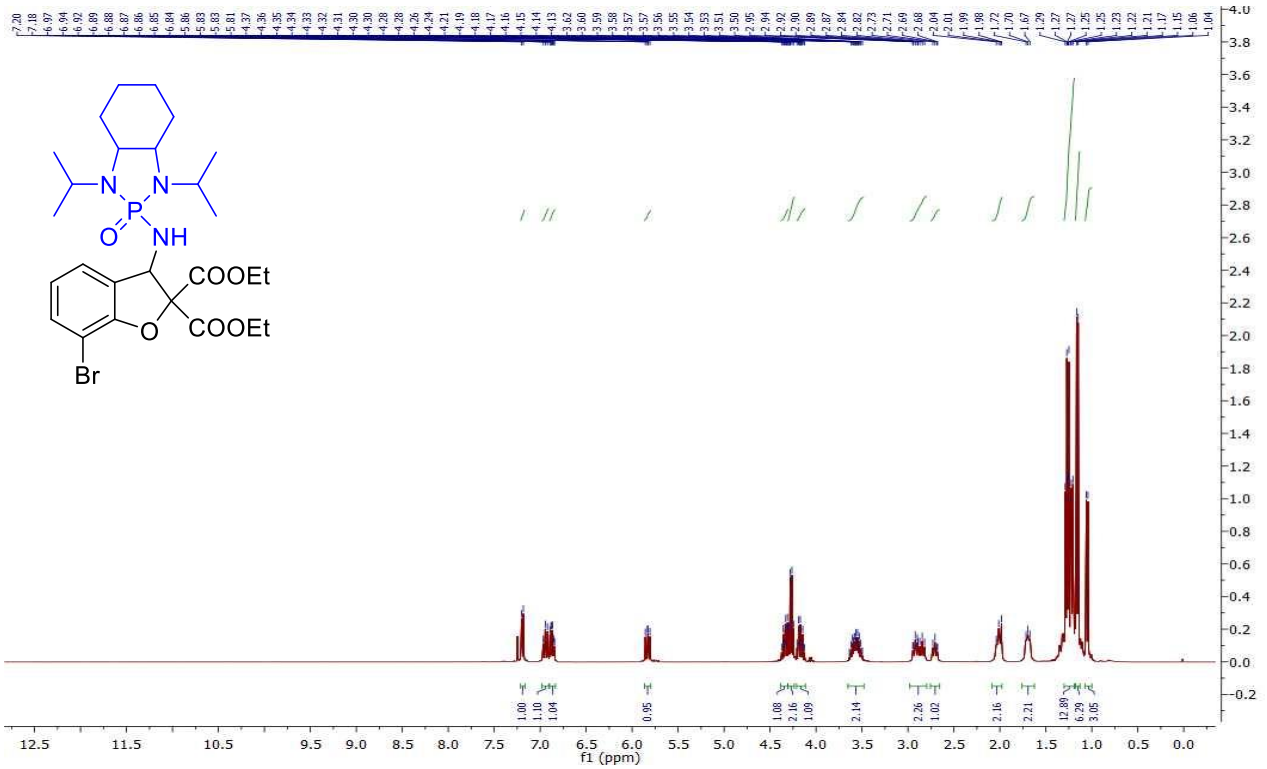
^{13}C NMR of 2,3-dihydrobenzofuran **3l** ($CDCl_3$, 100 Hz)



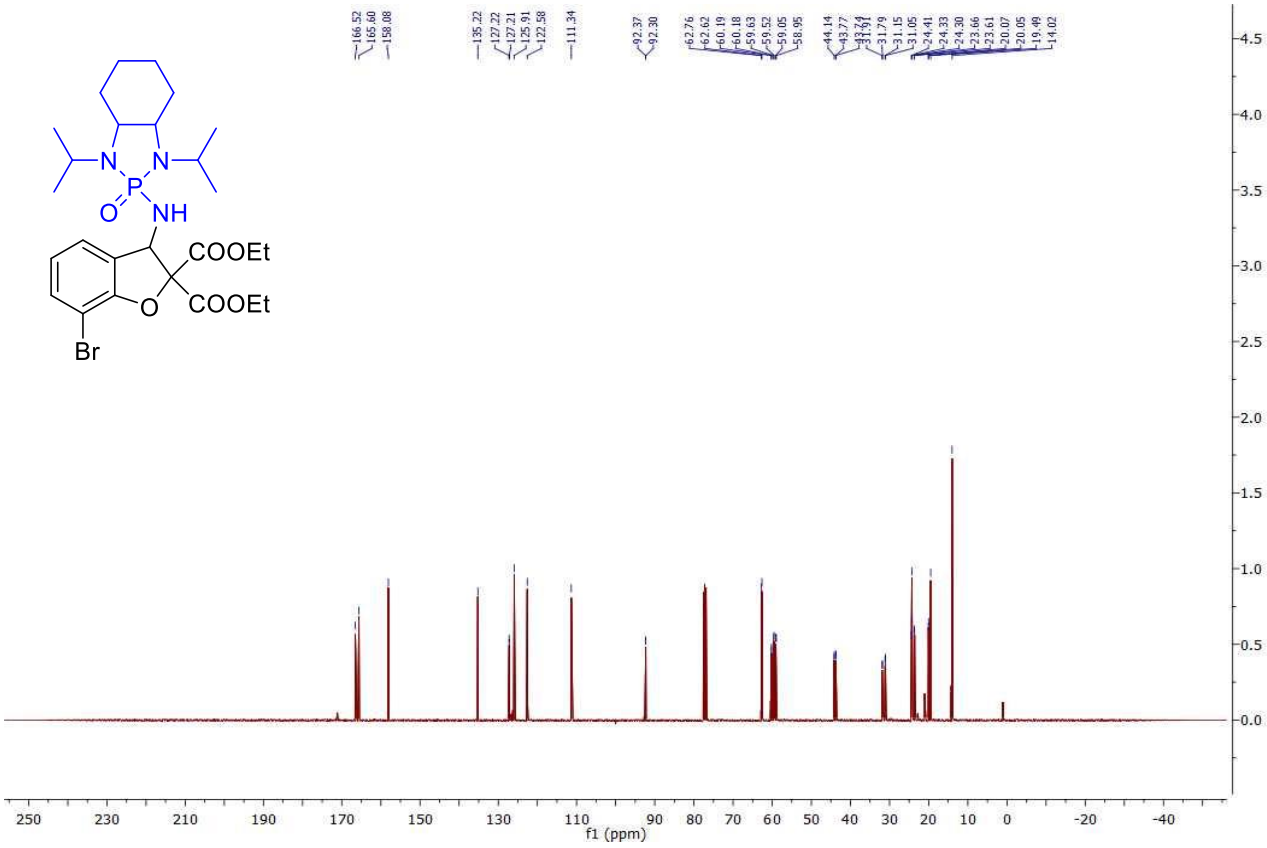
^{1}H NMR of 2,3-dihydrobenzofuran **3m** ($CDCl_3$, 400 Hz)



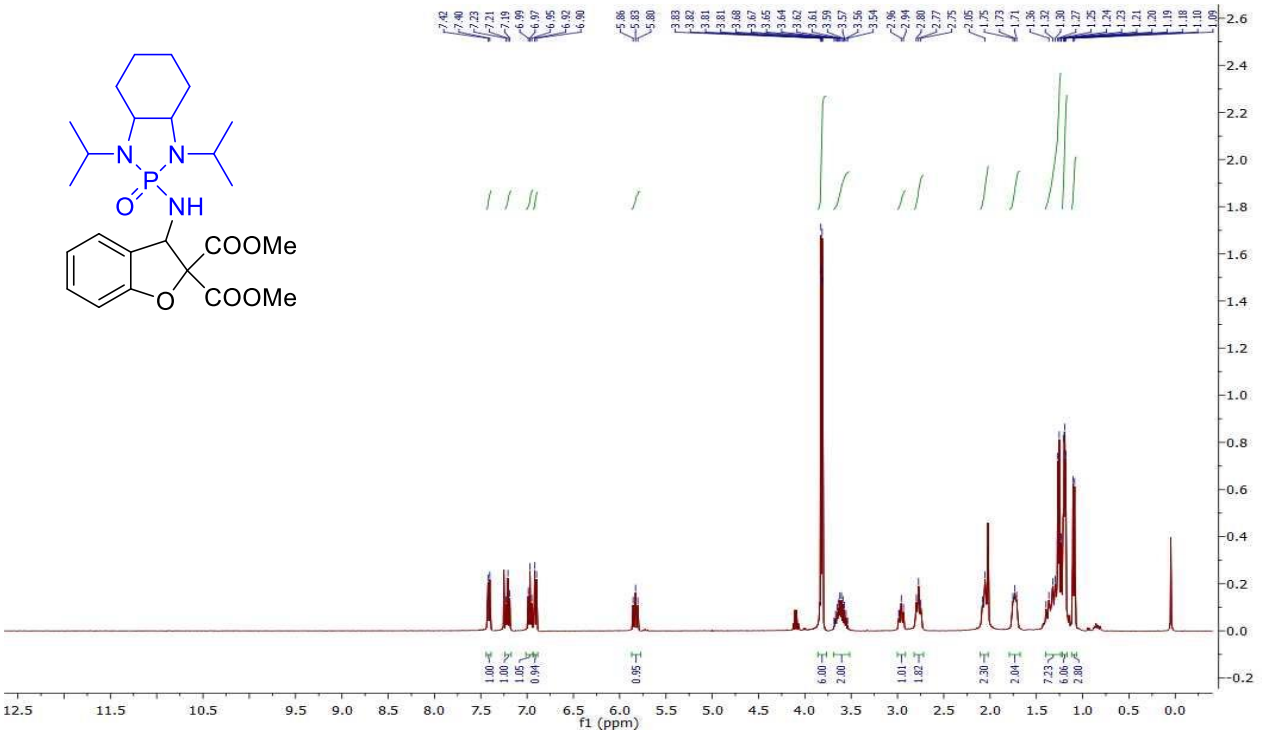
^{13}C NMR of 2,3-dihydrobenzofuran **3m** ($CDCl_3$, 100 Hz)



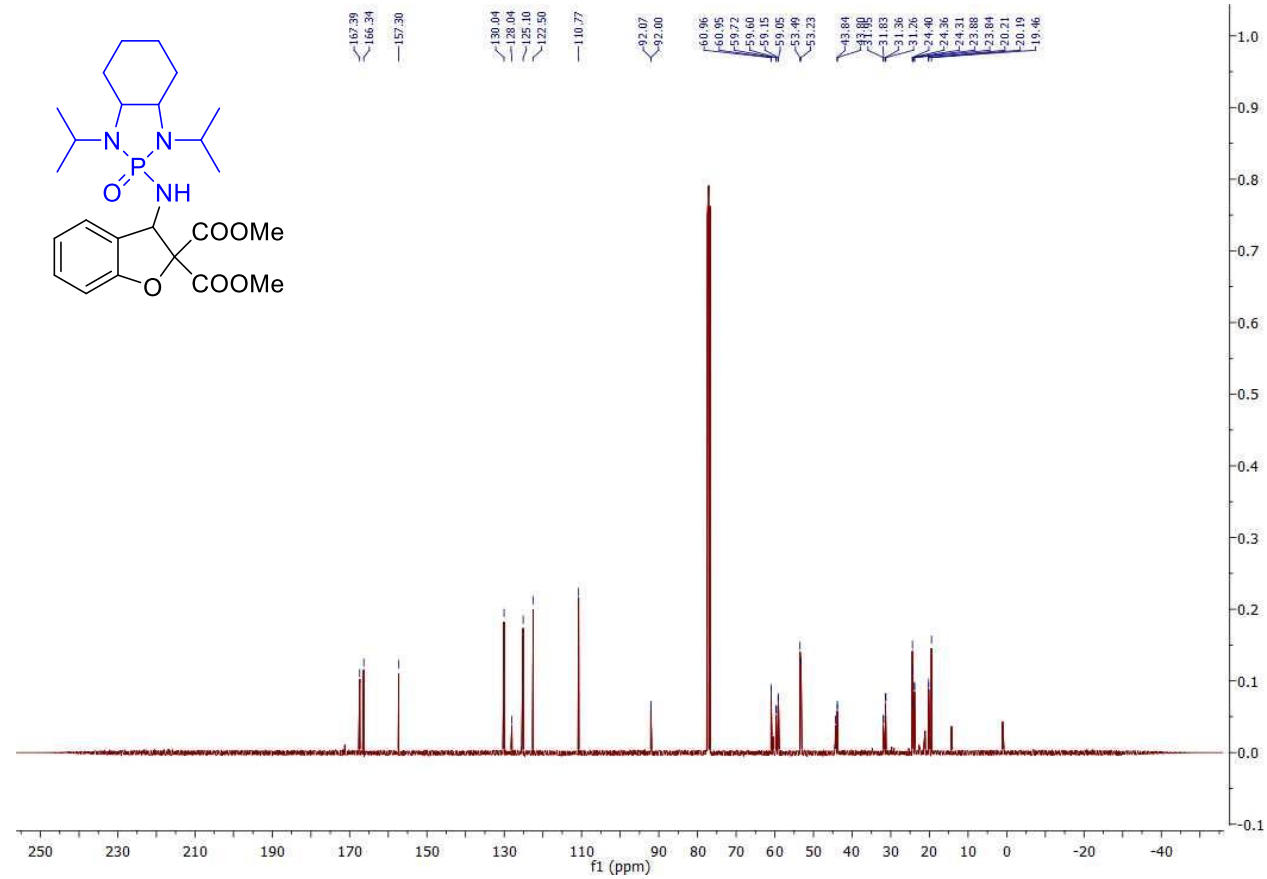
^{1}H NMR of 2,3-dihydrobenzofuran **3n** ($CDCl_3$, 400 Hz)



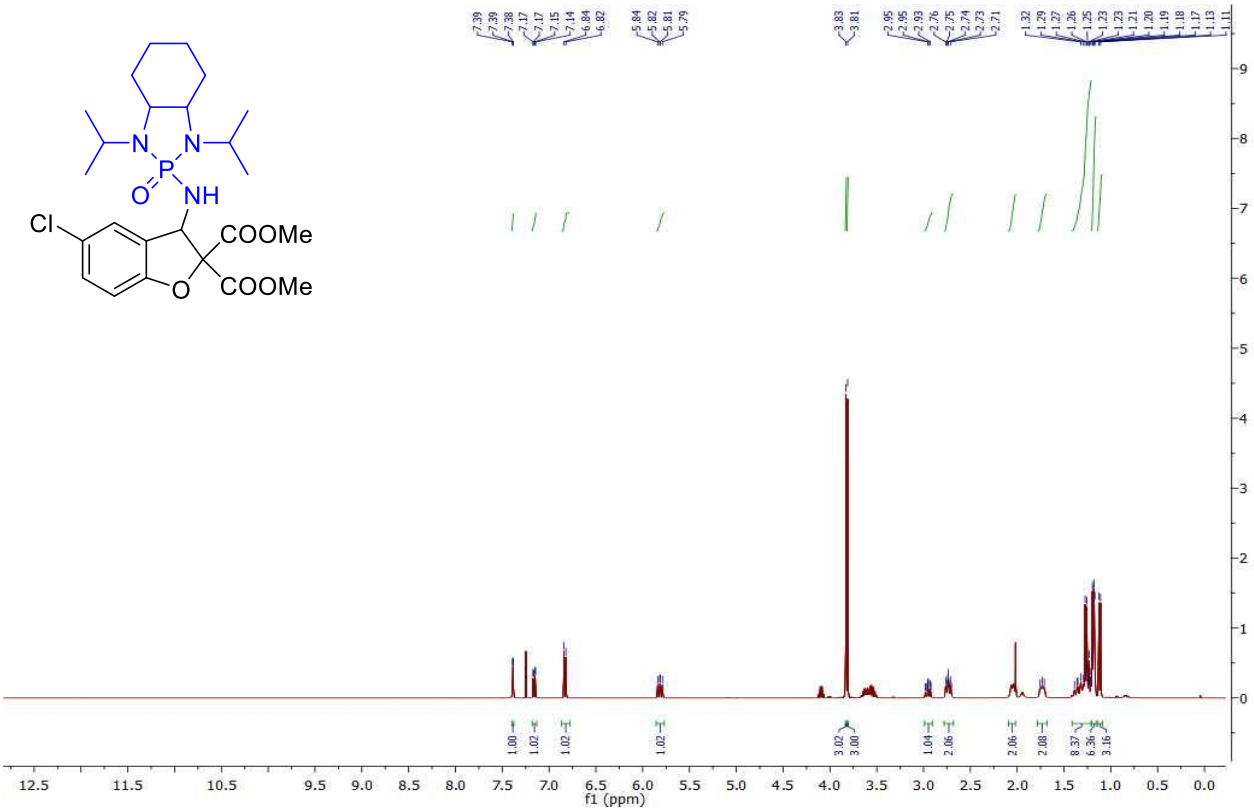
^{13}C NMR of 2,3-dihydrobenzofuran **3n** ($CDCl_3$, 100 Hz)



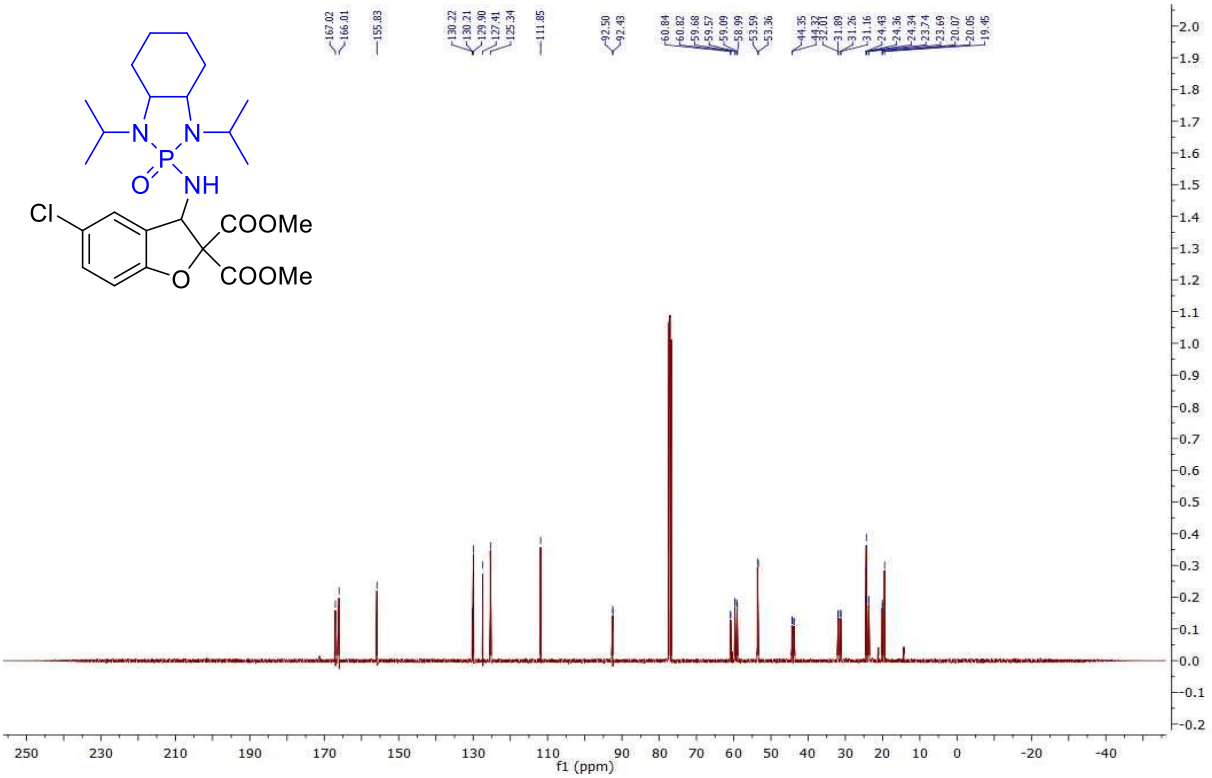
^{1}H NMR of 2,3-dihydrobenzofuran **3o** ($CDCl_3$, 400 Hz)



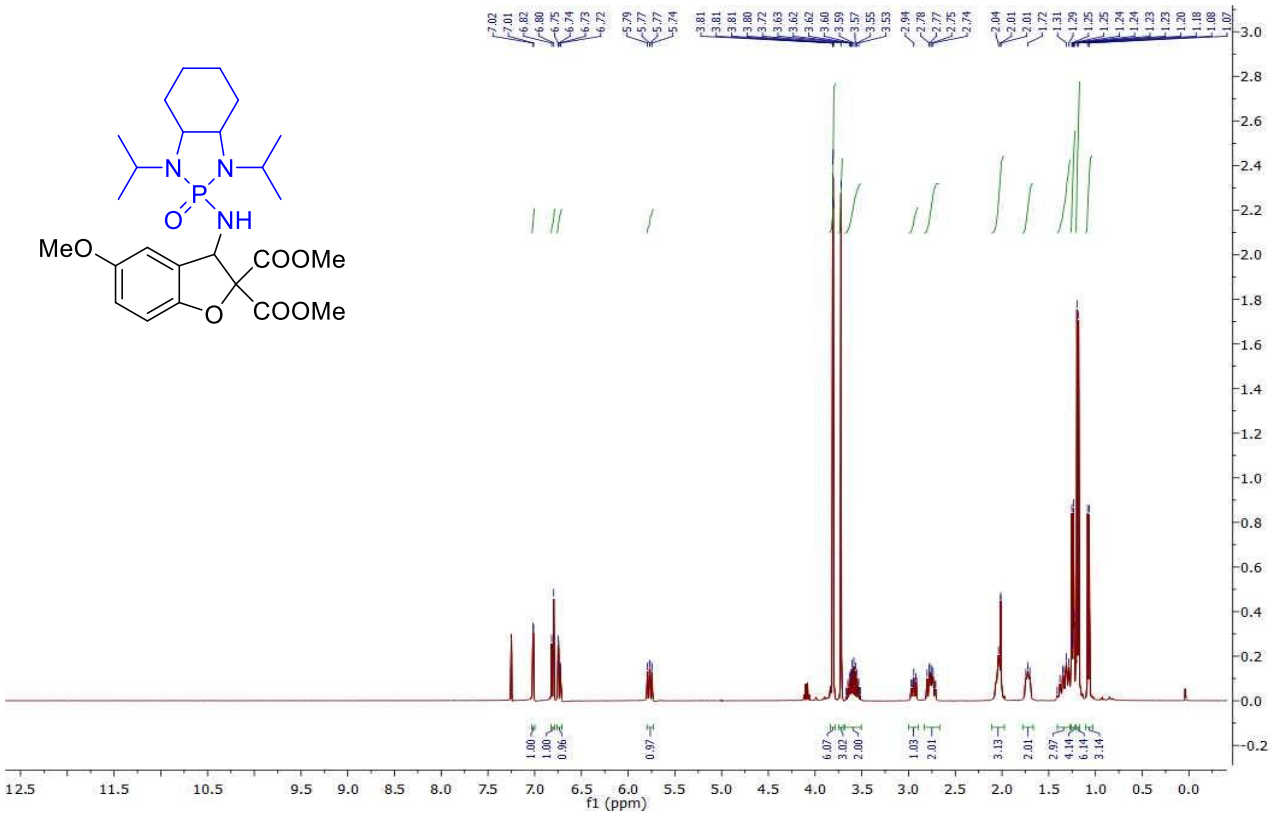
^{13}C NMR of 2,3-dihydrobenzofuran **3o** ($CDCl_3$, 100 Hz)



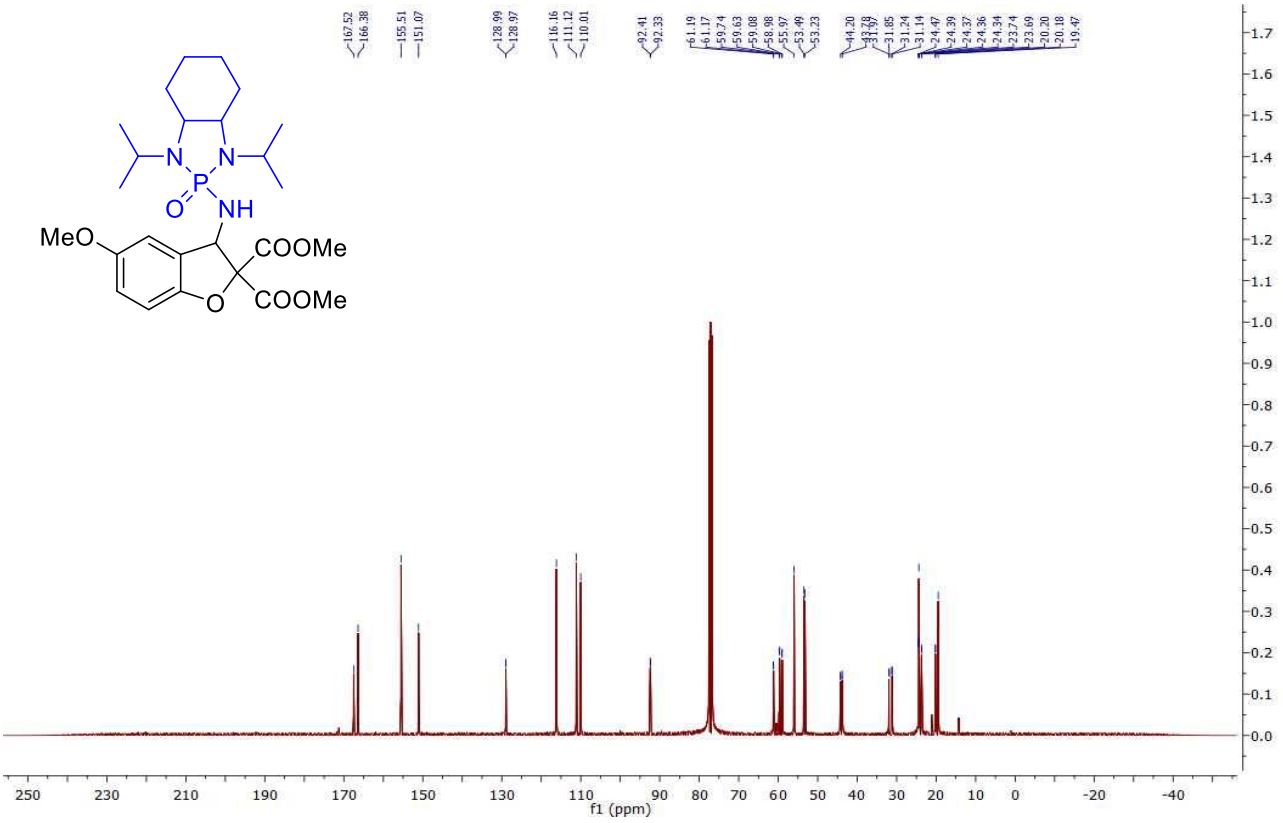
^{1}H NMR of 2,3-dihydrobenzofuran **3p** ($CDCl_3$, 400 Hz)



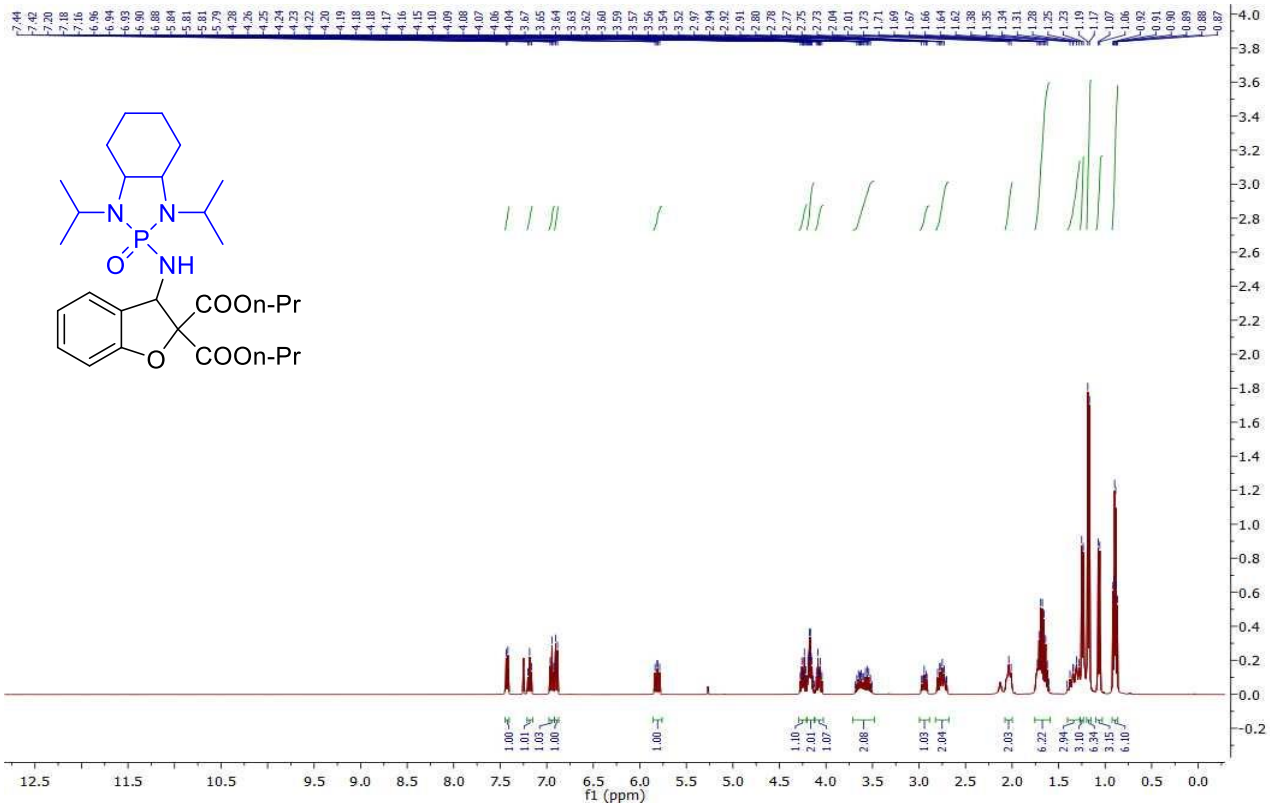
^{13}C NMR of 2,3-dihydrobenzofuran **3p** ($CDCl_3$, 100 Hz)



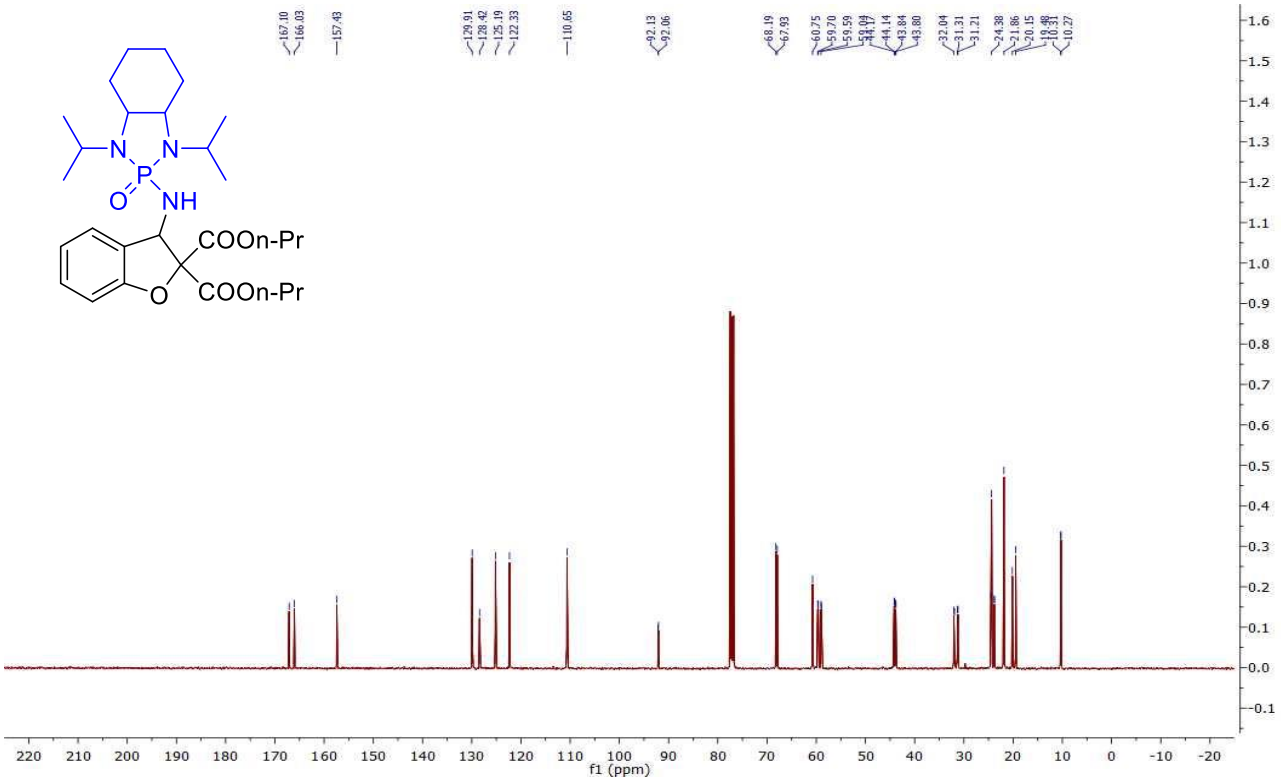
^{1}H NMR of 2,3-dihydrobenzofuran **3q** ($CDCl_3$, 400 Hz)



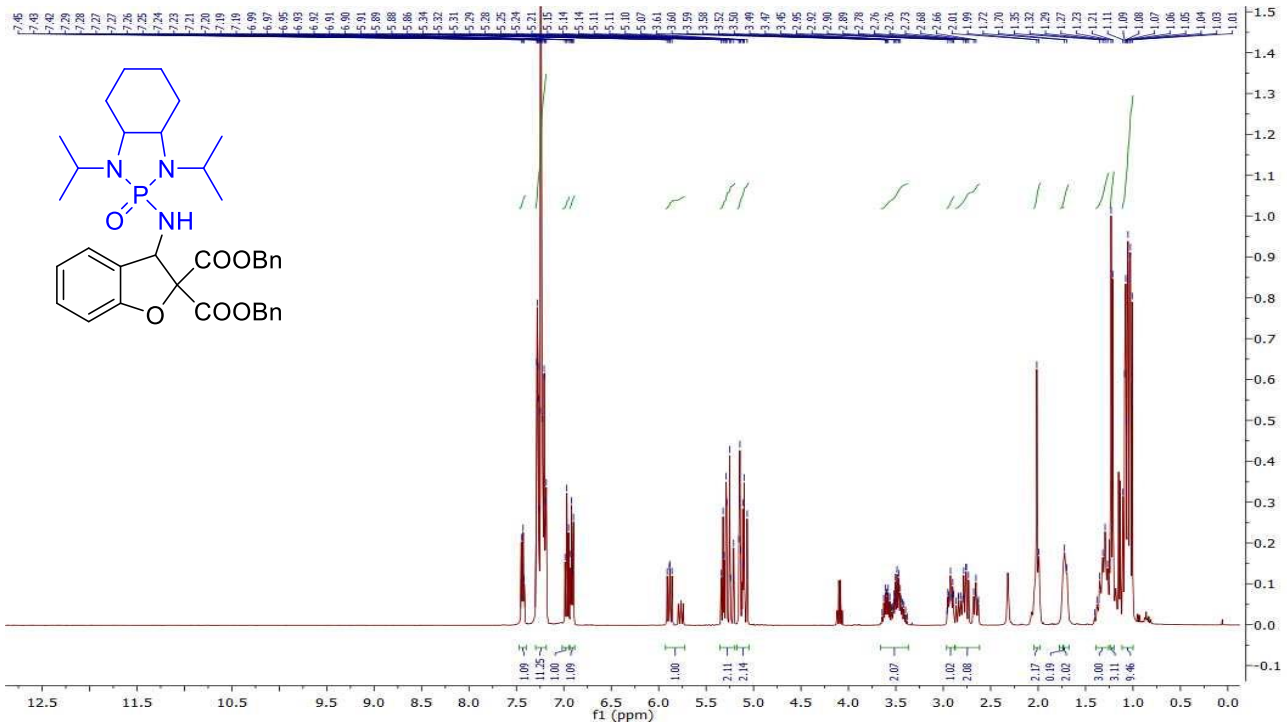
^{13}C NMR of 2,3-dihydrobenzofuran **3q** ($CDCl_3$, 100 Hz)



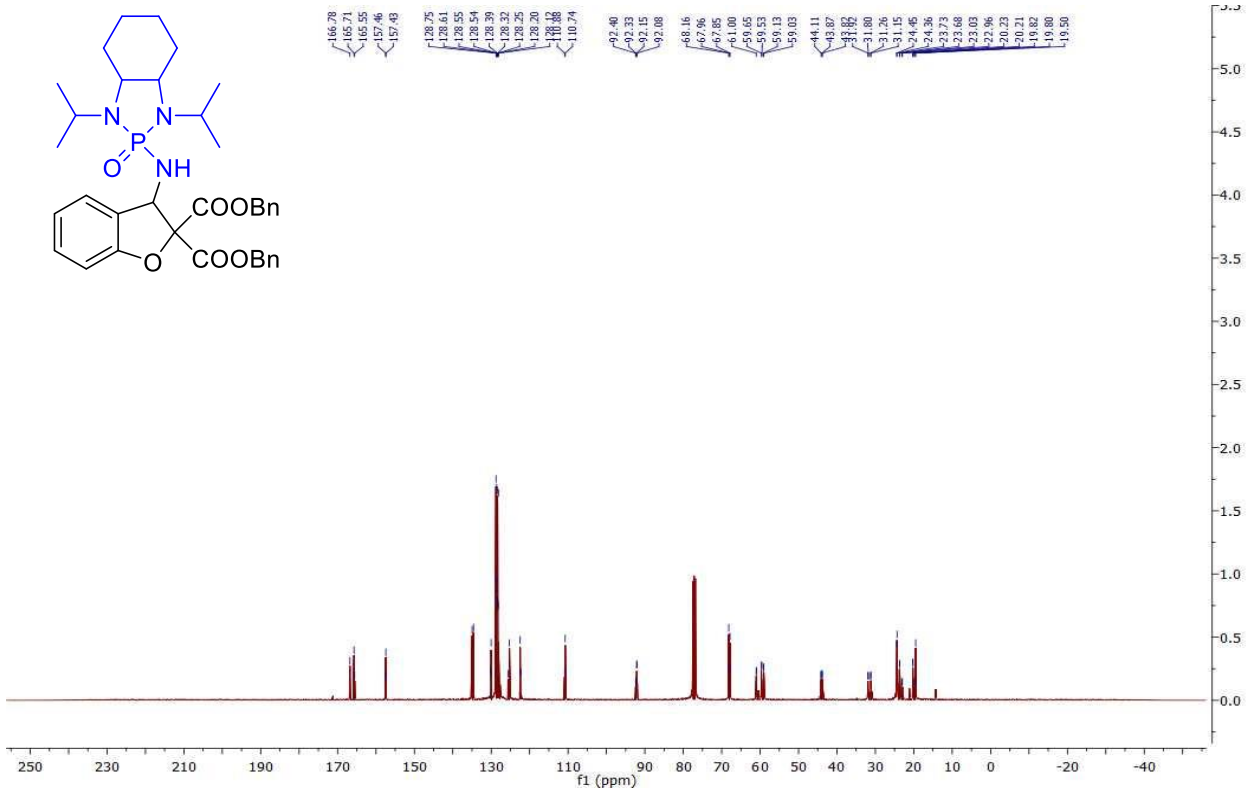
^{1}H NMR of 2,3-dihydrobenzofuran **3r** ($CDCl_3$, 400 Hz)



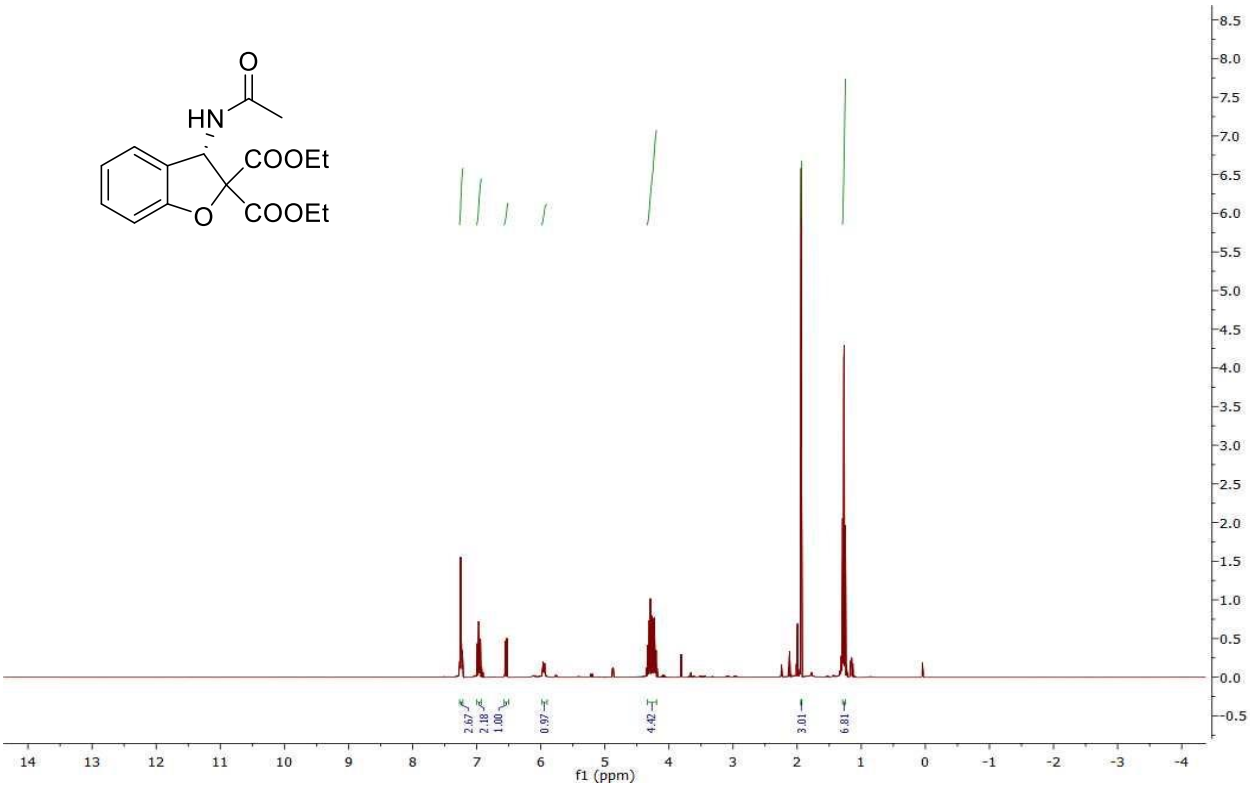
^{13}C NMR of 2,3-dihydrobenzofuran **3r** ($CDCl_3$, 100 Hz)



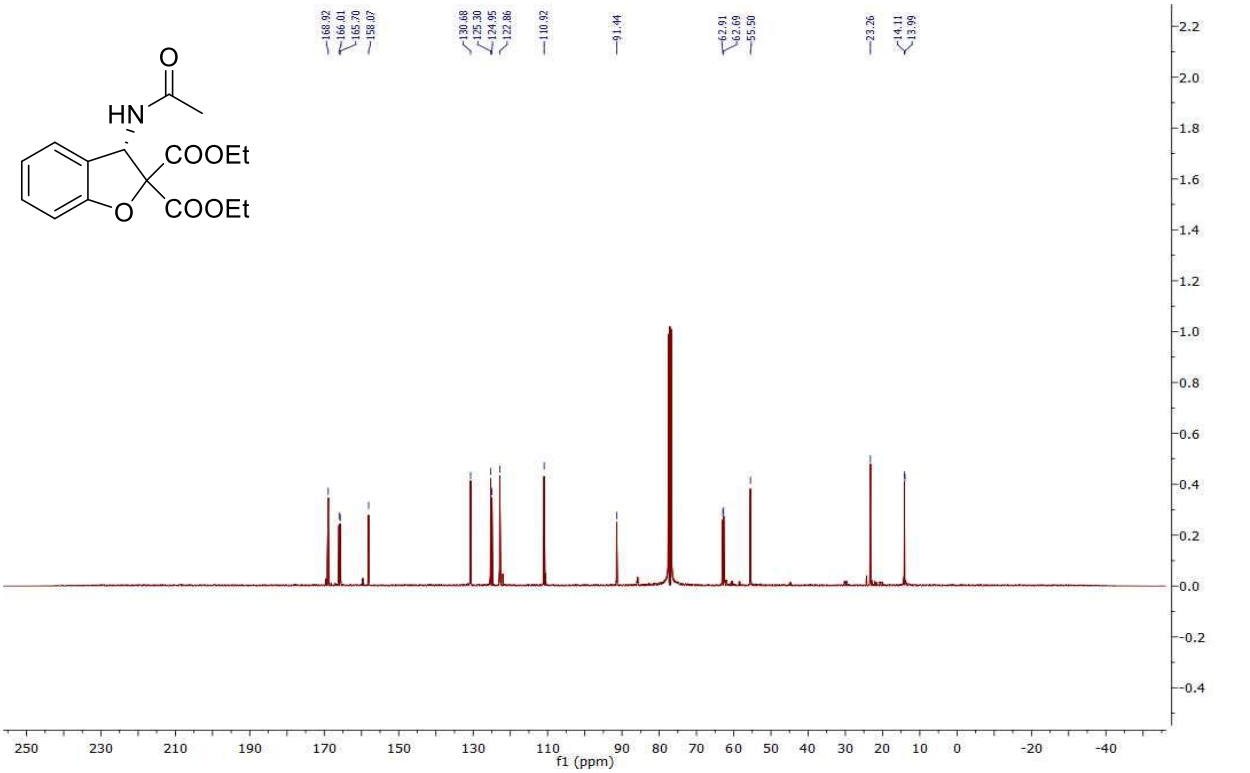
^{1}H NMR of 2,3-dihydrobenzofuran **3s** ($CDCl_3$, 400 Hz)



^{13}C NMR of 2,3-dihydrobenzofuran **3s** ($CDCl_3$, 100 Hz)



^{1}H NMR of 2,3-dihydrobenzofuran **5a** ($CDCl_3$, 400 Hz)



^{13}C NMR of 2,3-dihydrobenzofuran **5a** ($CDCl_3$, 100 Hz)