Supporting Information

Asymmetric hydrogenation of di-, tri- and tetrasubstituted minimally functionalized olefins and cyclic β-enamides with easily accessible Ir-P,oxazoline catalysts

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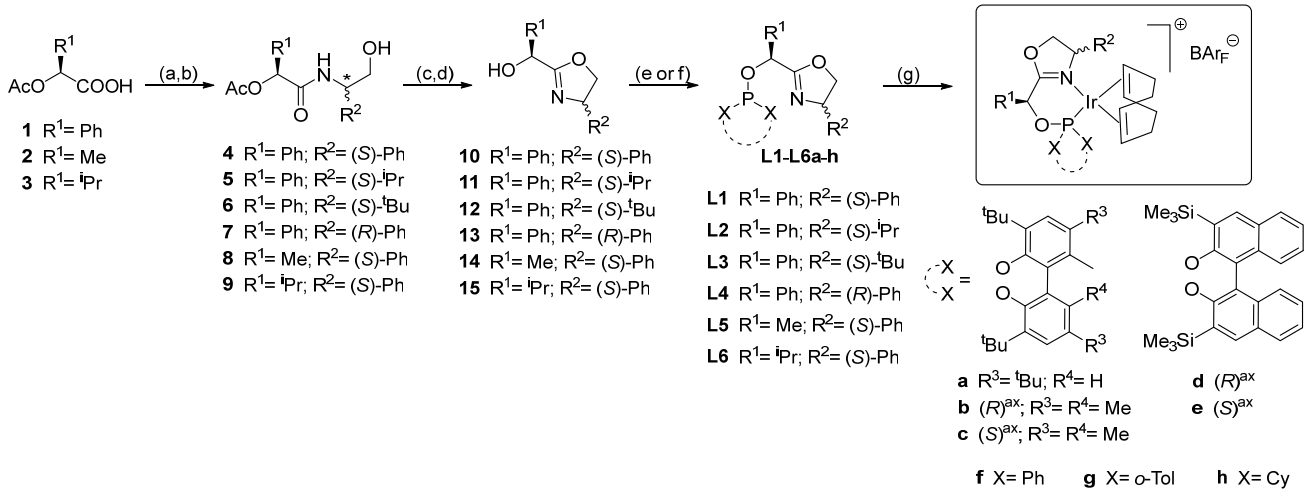
1. General considerations

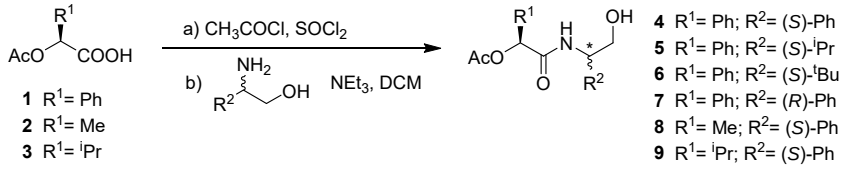
All reactions were carried out using standard Schlenk techniques under an argon atmosphere. Solvents were purified and dried by standard procedures. Phosphorochloridites were easily prepared in one-step from the corresponding biaryls.[1] ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded using a 400 MHz spectrometer. Chemical shifts are relative to that of $SiMe_4$ (^{1}H and ^{13}C) as internal standard or H_3PO_4 (^{31}P) as external standard. ^{1}H, ^{13}C, and ^{31}P assignments were made on the basis of ^{1}H-^{1}H gCOSY and ^{1}H-^{13}C gHSQC. Acetyl acid chlorides **1-3**,[2] acetoxyoxazolines **6-7**[2a] and hydroxyl-oxazolines **11-13**[2a,3] were prepared as previously described.

2. Preparation of [Ir(cod)(L1-L6a-h)]BAr$_F$ complexes



Scheme S1. Synthesis of [Ir(cod)(**L1-L6a-h**)]BAr$_F$ complexes. (a) $SOCl_2$, DCM, rt, 2 h; (b) aminoalcohol, NEt_3, DCM, rt, 5 h; (c) DAST, K_2CO_3, DCM, -78 ºC to rt for 3 h; (d) NaOH (aq), EtOH, 0 ºC, 2 h; (e) $ClP(OR)_2$, Py, toluene, 16 h; (f) $ClPR_2$, NEt_3, DMAP, toluene, rt, 30 min; (g) $[Ir(\mu\text{-}Cl)(cod)]_2$, DCM, reflux, 1 h then NaBAr$_F$, H_2O, rt, 30 min.

2.1. Preparation of intermediate compounds 4-8

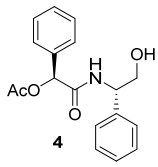


Scheme S2. Synthesis of intermediates **4-8**.

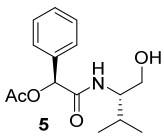
In a flame-dried round-bottom Schlenk, thionyl chloride (13 mL) and the corresponding acetyl acid (11.0 mmol) were added. The resulting solution was stirred and heated at reflux for 3 h. After this time, the reaction mixture was cooled to rt, and excess thionyl chloride was removed under high vacuum, to furnish the corresponding acetyl acid chloride which was successively been used without further purification.

In a flame-dried round-bottom Schlenk flask under an inert atmosphere of argon, the appropriate amino alcohol (10.0 mmol, 1.0 equiv) and NEt_3 (2.78 mL, 20.0 mmol, 2.0 equiv) were dissolved in CH_2Cl_2 (16 mL). The mixture was cooled to 0 °C, and a solution of the corresponding acetyl acid chloride (10 mmol, 1.0 equiv) in dry CH_2Cl_2 (14 mL) was added dropwise over 10 min. The resulting reaction mixture was allowed to warm to rt, stirred for 5 h and then washed with aq HCl (1 M; 2 × 20 mL). The combined aq phases were extracted with CH_2Cl_2 (20 mL), and the combined organic layers washed with sat. aq NaCl (2 × 20 mL). Drying over $MgSO_4$ followed by removal of the solvent *in vacuo* afforded **4-9** as crude product. Pure compounds **4-9** were obtained by recrystallization.

(S)-2-(((S)-2-Hydroxy-1-phenylethyl)amino)-2-oxo-1-phenylethyl acetate 4. 2.66 g (85% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ= 2.03 (bs, 1H, OH), 2.11 (s, 3H, CH_3, OAc), 3.79 (m, 2H, CH_2-O), 4.99 (m, 1H, CH-N), 6.05 (s, 1H, CH), 6.90 (bs, 1H, NH), 7.17-7.37 (m, 10H, CH=). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 21.0 (CH_3, OAc), 55.5 (CH-N), 66.1 (CH_2-O), 75.6 (CH), 126.6 (CH=), 127.4 (CH=), 127.7 (CH=), 127.9 (CH=), 128.8 (CH=), 128.9 (CH=), 129.0 (CH=), 135.2 (C), 138.5 (C), 168.8 (C=O), 169.4 (C=O).

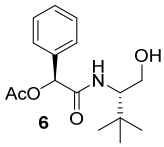


(S)-2-(((S)-1-Hydroxy-3-methylbutan-2-yl)amino)-2-oxo-1-phenylethyl acetate 5. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.90 (d, 3H, CH_3, ^{i}Pr, $^3J_{H-H}$= 8.0 Hz), 0.96 (d, 3H, CH_3, ^{i}Pr, $^3J_{H-H}$= 8.0 Hz), 1.95 (m, 1H, CH, ^{i}Pr), 2.19 (s, 3H, CH_3, OAc), 3.72 (m, 3H, CH_2-O, CH-N), 6.08 (s, 1H, CH), 6.35 (bs, 1H, NH), 7.29-7.56 (m, 5H, CH=). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 19.0 (CH_3, ^{i}Pr), 19.7

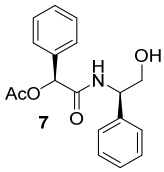


(CH_3, ^iPr), 21.2 (CH_3, OAc), 29.2 (CH, ^iPr), 57.1 (CH-N), 63.6 (CH_2-O), 75.9 (CH), 127.5 (CH=), 129.0 (CH=), 129.2 (CH=), 135.0 (C), 168.7 (C=O), 169.8 (C=O).

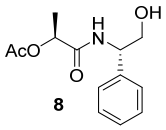
(S)-2-(((S)-1-Hydroxy-3,3-dimethylbutan-2-yl)amino)-2-oxo-1-phenylethyl acetate 6. 2.00 g (64% yield). Spectroscopic data are in agreement with the reported values.[2a] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.94 (s, 9H, CH_3, ^tBu), 2.20 (s, 3H, CH_3, OAc), 3.60 (m, 1H, CH-O), 3.80 (m, 2H, CH-O, CH-N), 6.10 (s, 1H, CH-O), 6.34 (bs, 1H, NH), 7.34-7.47 (m, 5H, CH=).



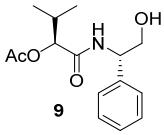
(S)-2-(((R)-2-Hydroxy-1-phenylethyl)amino)-2-oxo-1-phenylethyl acetate 7. 2.04 g (70% yield). Spectroscopic data are in agreement with the reported values.[2a] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.19 (s, 3H, CH_3, OAc), 3.92 (m, 2H, CH_2-O), 5.08 (m, 1H, CH-N), 6.09 (s, 1H, CH), 6.76 (bs, 1H, NH), 7.18-7.48 (m, 10H, CH=).



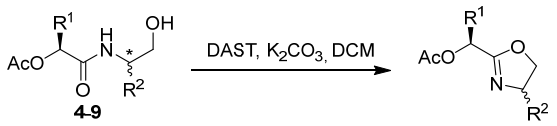
(S)-1-(((S)-2-Hydroxy-1-phenylethyl)amino)-1-oxopropan-2-yl acetate 8. 2.0 g (90% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.45 (d, 3H, CH_3, $^3J_{H-H}$= 6.8 Hz), 2.10 (s, 3H, CH_3, OAc), 3.79 (m, 2H, CH_2-O), 5.04 (m, 1H, CH-N), 5.20 (q, 1H, CH, $^3J_{H-H}$= 6.8 Hz), 7.26-7.40 (m, 5H, CH=). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 17.7 (CH_3), 20.9 (CH_3, OAc), 55.0 (CH-N), 65.3 (CH_2-O), 70.5 (CH-O), 126.5 (CH=), 127.6 (CH=), 128.6 (CH=), 138.9 (C), 169.9 (C=O), 171.0 (C=O).



(S)-1-(((S)-2-Hydroxy-1-phenylethyl)amino)-3-methyl-1-oxobutan-2-yl acetate 9. 2.51 g (90% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.88 (m, 6H, CH_3, ^iPr), 2.07 (s, 3H, CH_3, OAc), 2.19 (m, 1H, CH, ^iPr), 3.58 (m, 1H, CH-O), 3.66 (m, 1H, CH-O), 4.95 (m, 2H, CH, CH-N), 7.07 (d, 1H, CH=, $^3J_{H-H}$= 7.2 Hz), 7.21-7.29 (m, 4H, CH=). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 17.1 (CH_3, ^iPr), 18.6 (CH_3, ^iPr), 20.7 (CH_3, OAc), 30.6 (CH, ^iPr), 55.0 (CH-N), 65.3 (CH_2-O), 78.2 (CH-O), 126.6 (CH=), 127.5 (CH=), 128.6 (CH=), 139.1 (C), 169.8 (C=O), 170.4 (C=O).



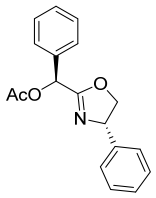
2.2. Preparation of acetate-oxazolines



Scheme S3. Synthesis of acetate-oxazolines.

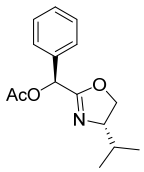
In a flame-dried, round-bottomed Schlenk flask under an inert atmosphere of argon, the appropriate acetyl hydroxyl-amide **4-9** (10.0 mmol) was dissolved in dry CH_2Cl_2 (100 mL). The solution was cooled to –78 °C and diethylaminosulfur trifluoride (DAST) was added dropwise (1.44 mL, 11.0 mmol, 1.1 equiv) over 5 min. After the addition, the reaction mixture was stirred at –78 °C for 1 h. Then, K_2CO_3 (2.07 g, 15 mmol, 1.5 equiv) was added in one portion and the reaction was allowed to warm to rt. Subsequently, the reaction mixture was poured into sat. aq $NaHCO_3$ (200 mL) and the organic layer was collected. The aqueous layer was extracted once more with CH_2Cl_2 (200 mL) and the combined organic layers were dried over $MgSO_4$. Removal of the solvent *in vacuo* afforded the corresponding crude acetoxyoxazoline as a brown or yellow oil. Purification by flash column chromatography (EtOAc–PE, 1:2) afforded the desired pure acetoxyoxazoline.

(S)-Phenyl((S)-4-phenyl-4,5-dihydrooxazol-2-yl)methyl acetate. 2.25 g (90% yield). ^{1}H



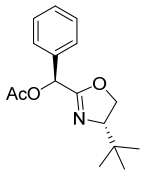
NMR (400 MHz, $CDCl_3$): δ= 2.06 (s, 3H, CH_3, OAc), 4.13 (pt, 1H, CH-O_{ox}, J_{H-H}= 8.2 Hz), 4.59 (dd, 1H, CH-O_{ox}, $^3J_{H-H}$= 10.1 Hz, $^2J_{H-H}$= 8.5 Hz), 5.24 (t, 1H, CH-N, $^3J_{H-H}$= 8.1 Hz), 6.35 (s, 1H, CH-O), 7.15-7.54 (m, 10H, CH=). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 20.9 (CH_3, OAc), 69.5 (CH-N), 70.9 (CH), 75.6 (CH_2-O), 126.5 (CH=), 126.7 (CH=), 127.6 (CH=), 128.7 (CH=), 129.2 (CH=), 129.2 (CH=), 135.1 (C), 141.8 (C), 165.4 (C=N), 169.9 (C=O).

(S)-((S)-4-Isopropyl-4,5-dihydrooxazol-2-yl)(phenyl)methyl acetate. 1.74 g (75%



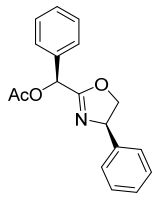
yield). Spectroscopic data are in agreement with the reported values.[3] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.83 (d, 3H, CH_3, ^{i}Pr, $^3J_{H-H}$= 6.8 Hz), 0.89 (d, 3H, CH_3, ^{i}Pr, $^3J_{H-H}$= 6.8 Hz), 1.75 (m, 1H, CH, ^{i}Pr), 2.16 (s, 3H, CH_3, OAc), 4.00 (m, 2H, CH_2-O_{ox}), 4.20 (m, 1H, CH-N), 6.27 (s, 1H, CH-O), 7.35 (m, 3H, CH=), 7.48 (m, 2H, CH=).

(S)-((S)-4-(tert-Butyl)-4,5-dihydrooxazol-2-yl)(phenyl)methyl acetate. 1.18 g (67%



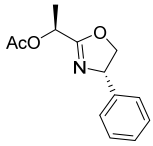
yield). Spectroscopic data are in agreement with the reported values.[2a] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.83 (s, 9H, CH_3, ^{t}Bu), 2.16 (s, 3H, CH_3, OAc), 3.88 (m, 1H, CH), 4.15 (m, 2H, CH), 6.27 (s, 1H, CH-O), 7.35 (m, 3H, CH=), 7.49 (m, 2H, CH=).

(S)-Phenyl-((R)-4-phenyl-4,5-dihydrooxazol-2-yl)methyl acetate. 1.34 g (65% yield).



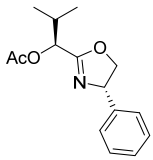
Spectroscopic data are in agreement with the reported values.[2a] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.20 (s, 3H, CH_3, OAc), 4.08 (pt, 1H, CH-O_{ox}, J_{H-H}= 8.8 Hz), 4.50 (dd, 1H, CH-O_{ox}, $^2J_{H-H}$= 10.0 Hz, $^3J_{H-H}$= 8.4 Hz), 5.23 (t, 1H, CH-N, $^3J_{H-H}$= 8.4 Hz), 6.35 (s, 1H, CH-O), 7.18-7.58 (m, 10H, CH=).

(S)-1-((S)-4-Phenyl-4,5-dihydrooxazol-2-yl)ethyl acetate. 1.49 g (80% yield). ^{1}H NMR



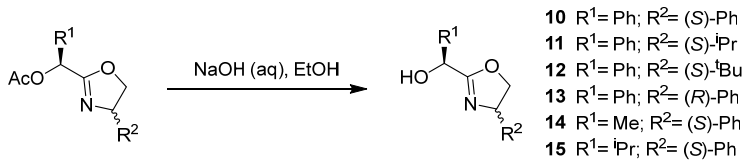
(400 MHz, $CDCl_3$): δ = 1.57 (d, 3H, CH_3, $^3J_{H-H}$= 6.8 Hz), 2.13 (s, 3H, CH_3, OAc), 4.14 (pt, 1H, CH-O_{ox}, J_{H-H}= 8.0 Hz), 4.58 (dd, 1H, CH-O_{ox}, $^2J_{H-H}$= 10.0 Hz, $^3J_{H-H}$= 8.4 Hz), 5.21 (m, 1H, CH-N), 5.52 (q, 1H, CH, $^3J_{H-H}$= 6.8 Hz), 7.19-7.36 (m, 5H, CH=). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 18.0 (CH_3), 20.9 (CH_3, OAc), 65.3 (CH-O), 69.5 (CH-N), 75.4 (CH_2-O), 126.6 (CH=), 127.6 (CH=), 128.7 (CH=), 141.9 (C), 166.9 (C=N), 170.1 (C=O).

(S)-2-Methyl-1-((S)-4-phenyl-4,5-dihydrooxazol-2-yl)propyl acetate. 1.99 g (85%



yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.03 (m, 6H, CH_3, ^{i}Pr), 2.10 (s, 3H, CH_3, OAc), 2.22 (m, 1H, CH, ^{i}Pr), 4.06 (pt, 1H, CH-O_{ox}, J_{H-H}= 8.0 Hz), 4.57 (dd, 1H, CH-O_{ox}, $^2J_{H-H}$= 10.0 Hz, $^3J_{H-H}$= 8.4 Hz), 5.17 (m, 2H, CH-O, CH-N), 7.14-7.29 (m, 5H, CH=). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 17.4 (CH_3, ^{i}Pr), 18.6 (CH_3, ^{i}Pr), 20.7 (CH_3, OAc), 30.6 (CH, ^{i}Pr), 69.4 (CH-O), 73.3 (CH-N), 75.0 (CH_2-O), 126.6 (CH=), 127.5 (CH=), 128.6 (CH=), 142.0 (C), 165.6 (C=N), 170.4 (C=O).

2.3. Preparation of hydroxyl-oxazolines 10-15

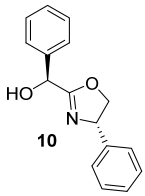


Scheme S4. Synthesis of hydroxyl-oxazolines **10-15**.

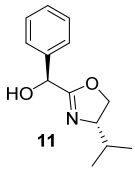
In a round-bottomed flask, the appropriate acetoxyoxazoline (5.0 mmol) was dissolved in MeOH (30 mL). The solution was cooled to 0 °C and aq NaOH solution (1 M; 15 mL, 3.0 equiv) was added dropwise. The reaction mixture was stirred at 0 °C for 3 h and allowed to warm to rt. The mixture was then extracted with CH_2Cl_2 (2 × 50 mL), and the combined organic layers were washed with sat. aq NaCl (2 × 50 mL).

After drying over $MgSO_4$ and evaporation of the solvent crude of the corresponding hydroxy-oxazoline was obtained as a yellow solid or oil. Recrystallization with ethyl acetate afforded the desired pure product **10-15**.

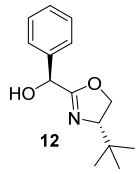
(S)-Phenyl((S)-4-phenyl-4,5-dihydrooxazol-2-yl)methanol 10. 1.87 g (97% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.18 (pt, 1H, CH-O_{ox}, J_{H-H}= 8.4 Hz), 4.62 (dd, 1H, CH-O_{ox}, $^2J_{H-H}$= 10.0 Hz, $^3J_{H-H}$= 8.4 Hz), 5.14 (t, 1H, CH-N, $^3J_{H-H}$= 9.2 Hz), 5.33 (s, 1H, CH-O), 7.18-7.45 (m, 10H, CH=). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 68.8 (CH-N), 69.7 (CH-O), 76.3 (CH_2-O), 126.7 (CH=), 126.8 (CH=), 126.9 (CH=), 127.9 (CH=), 128.0 (CH=), 128.6 (CH=), 128.8 (CH=), 129.0 (CH=), 139.3 (C), 141.7 (C), 170.0 (C=N).



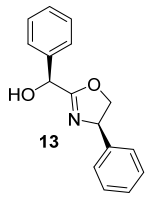
(S)-((S)-4-Isopropyl-4,5-dihydrooxazol-2-yl)(phenyl)methanol 11. 1.34 g (92% yield). Spectroscopic data are in agreement with the reported values.[3] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.89 (d, 3H, CH_3, ^{i}Pr, $^3J_{H-H}$= 6.8 Hz), 0.98 (d, 3H, CH_3, ^{i}Pr, $^3J_{H-H}$= 6.8 Hz), 1.76 (m, 1H, CH, ^{i}Pr), 3.75 (bs, 1H, OH), 3.90 (m, 1H, CH-O_{ox}), 4.08 (pt, 1H, CH-O_{ox}, J_{H-H}= 8.4 Hz), 4.29 (t, 1H, CH-N, $^3J_{H-H}$= 8.4Hz), 5.28 (s, 1H, CH-O), 7.28-7.39 (m, 3H, CH=), 7.44-7.46 (m, 2H, CH=).



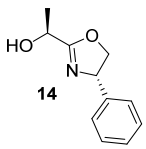
(S)-((S)-4-(tert-Butyl)-4,5-dihydrooxazol-2-yl)(phenyl)methanol 12. 0.95 g (95% yield). Spectroscopic data are in agreement with the reported values.[2a] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.90 (s, 9H, CH_3, ^{t}Bu), 3.88 (m, 2H, CH-N, OH), 4.15 (m, 2H, CH_2-O_{ox}), 5.30 (s, 1H, CH-O), 7.35 (m, 3H, CH=), 7.46 (m, 2H, CH=).



(S)-Phenyl-((R)-4-phenyl-4,5-dihydrooxazol-2-yl)methanol 13. 1.07 g (93% yield). Spectroscopic data are in agreement with the reported values.[2a] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.76 (bs, 1H, OH), 4.14 (pt, 1H, CH-O_{ox}, J_{H-H}= 8.8 Hz), 4.75 (dd, 1H, CH-O_{ox}, $^2J_{H-H}$= 10.0 Hz, $^3J_{H-H}$= 8.4 Hz), 5.26 (t, 1H, CH-N, $^3J_{H-H}$= 8.4 Hz), 5.38 (s, 1H, CH-O), 7.18 (m, 2H, CH=), 7.29-7.42 (m, 6H, CH=), 7.50 (m, 2H, CH=).

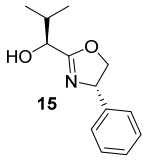


(S)-1-((S)-4-Phenyl-4,5-dihydrooxazol-2-yl)ethan-1-ol 14. 1.16 g (95% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.47 (d, 3H, CH_3, $^3J_{H-H}$= 6.8 Hz), 3.45 (bs, 1H, OH), 4.21 (pt, 1H, CH-O_{Ox}, J_{H-H}= 8.4 Hz), 4.45 (m, 1H, CH-O), 4.72 (dd, 1H, CH-O_{ox}, $^2J_{H-H}$= 10.0 Hz, $^3J_{H-H}$= 8.4 Hz), 5.21 (t, 1H, CH-N, $^3J_{H-H}$= 9.2 Hz), 7.23-7.38 (m, 5H, CH=). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 21.0 (CH_3),

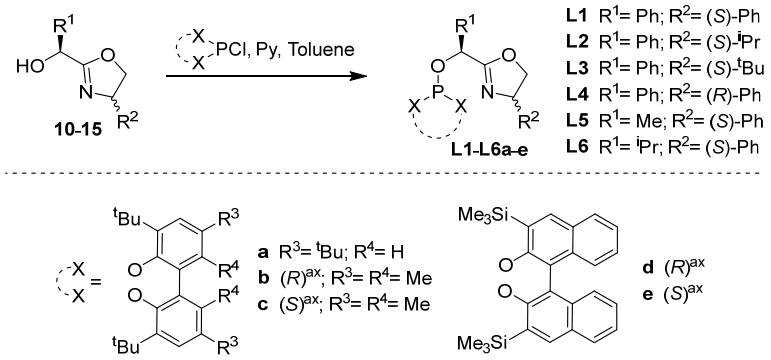


63.7 (CH-O), 69.1 (CH-N), 76.1 (CH_2-O), 126.7 (CH=), 128.0 (CH=), 129.0 (CH=), 141.8 (C), 171.5 (C=N).

(S)-2-Methyl-1-((S)-4-phenyl-4,5-dihydrooxazol-2-yl)propan-1-ol 15. 1.64 g (98% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.96 (d, 3H, CH_3, ^{i}Pr, $^3J_{H-H}$= 6.4 Hz), 1.06 (d, 3H, CH^3, ^{i}Pr, $^3J_{H-H}$= 6.4 Hz), 2.08 (m, 1H, CH, ^{i}Pr), 2.94 (bs, 1H, OH), 4.22 (m, 2H, CH-O_{ox}, CH-O), 4.73 (t, 1H, CH-N, $^3J_{H-H}$= 8.4 Hz), 5.21 (pt, 1H, CH-O_{ox}, J_{H-H}= 8.4 Hz), 7.24-7.38 (m, 5H, CH=). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 16.5 (CH_3, ^{i}Pr), 18.8 (CH_3, ^{i}Pr), 32.5 (CH, ^{i}Pr), 68.9 (CH_2-O), 72.2 (CH-N), 76.1 (CH-O), 126.7 (CH=), 127.9 (CH=), 129.0 (CH=), 141.7 (C), 171.0 (C=N).



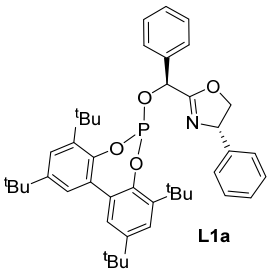
2.4. Preparation of phosphite-oxazoline ligands L1-L6a-e



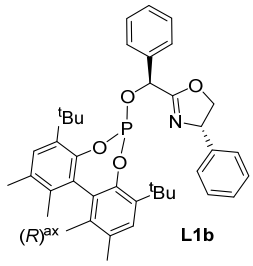
Scheme S5. Synthesis of phosphite-oxazolines **L1-L6a-e**.

To a solution of *in situ* generated phosphochloridite (1.1 mmol) in dry toluene (6 mL), pyridine (0.16 mL, 2.0 mmol) was added. Then, this solution was placed in a -78 ºC bath. After 2 min at that temperature, a solution of the corresponding hydroxyl-oxazoline (1.0 mmol) and pyridine (0.16 mL, 2.0 mmol) in toluene (6 mL) was added dropwise at -78 °C. The mixture was left to warm to room temperature and stirred overnight at this temperature. The precipitate formed was filtered under argon and the solvent was evaporated under vacuum. The residue was purified by flash chromatography (under argon, using neutral alumina and dry toluene as eluent system (1% NEt_3)) to afford the corresponding phosphite-oxazoline **L1-L6a-e** as white solids.

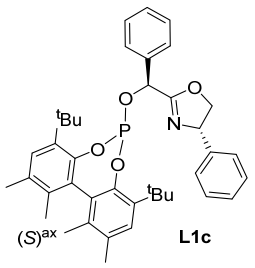
L1a: Yield: 339.0 mg (49%). ^{31}P NMR (161.9 MHz, C_6D_6): δ = 139.2 (s); ^{1}H NMR (400 MHz, C_6D_6): δ = 1.20 (s, 18H, CH_3, ^{t}Bu), 1.27 (s, 9H, CH_3, ^{t}Bu), 1.49 (s, 9H, CH_3, ^{t}Bu), 3.64 (pt, 1H, CH-O_{ox}, J_{H-H}= 8.8 Hz), 4.07 (pt, 1H, CH-O_{ox}, J_{H-H}= 8.4 Hz), 4.90 (pt, 1H, CH-N, J_{H-H}= 8.8 Hz), 6.08 (d, 1H, CH-OP, $^3J_{H-P}$= 10.0 Hz), 6.89-7.11 (m, 8H, CH=), 7.27 (d, 1H, CH=, $^4J_{H-H}$= 2.0 Hz), 7.29 (d, 1H, CH=, $^4J_{H-H}$= 2.8 Hz), 7.39 (d, 2H, CH=, $^3J_{H-H}$= 7.2 Hz), 7.49 (d, 1H, CH=, $^4J_{H-H}$= 2.4 Hz), 7.57 (d, 1H, CH=, $^4J_{H-H}$= 2.8 Hz). ^{13}C NMR (100.6 MHz, C_6D_6): δ = 30.7 (CH_3, ^{t}Bu), 30.9 (CH_3, ^{t}Bu), 31.0 (CH_3, ^{t}Bu), 31.2 (CH_3, ^{t}Bu), 34.3 (C, ^{t}Bu), 35.1 (C, ^{t}Bu), 35.3 (C, ^{t}Bu), 69.3 (CH-N), 73.1 (CH-OP), 74.6 (CH_2-O_{ox}), 124.0-146.6 (aromatic carbons), 166.1 (C=N). TOF-MS (ESI+): m/z = 714.3682 calcd. for $C_{44}H_{54}NNaO_4P$ $[M+Na]^+$: 714.3683



L1b: Yield: 394 mg (62%). ^{31}P NMR (161.9 MHz, C_6D_6): δ = 133.0 (s). ^{1}H NMR (400 MHz, C_6D_6): δ = 1.4 (s, 9H, CH_3, ^{t}Bu), 1.51 (s, 9H, CH_3, ^{t}Bu), 1.69 (s, 3H, CH_3), 1.83 (s, 3H, CH_3), 2.06 (s, 3H, CH_3), 2.12 (s, 3H, CH_3), 3.66 (pt, 1H, CH-O, J_{H-H}= 8.4 Hz), 4.17 (dd, 1H, CH-O, $^2J_{H-H}$= 10.0 Hz, $^3J_{H-H}$= 8.4 Hz), 4.95 (dd, 1H, CH-N, $^3J_{H-H}$= 10.0 Hz, $^3J_{H-H}$= 8.4 Hz), 5.74 (d, 1H, CH-OP, $^3J_{H-P}$= 9.2 Hz), 6.9 (m, 2H, CH=), 6.96-7.15 (m, 4H, CH=), 7.19 (s, 1H, CH=), 7.23 (s, 1H, CH=), 7.47-7.50 (m, 2H, CH=). ^{13}C NMR (100.6 MHz, C_6D_6): δ = 16.8 (CH_3), 17.1 (CH_3), 20.7 (CH_3), 20.8 (CH_3), 31.7 (CH_3, ^{t}Bu), 31.8 (d, CH_3, ^{t}Bu, J_{C-P}= 2.3 Hz), 35.1 (C, ^{t}Bu), 35.2 (C, ^{t}Bu), 70.1 (CH-N), 73.9 (d, CH-OP, J_{C-P}= 2.3 Hz), 75.3 (CH_2-O), 126.0-146.5 (aromatic carbons), 167.0 (C=N). MS HR-ESI [found 658.3061 $C_{40}H_{46}NO_4P$ $(M+Na)^+$ requires 658.3057].

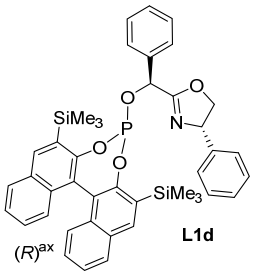


L1c: Yield: 149 mg (67%). ^{31}P NMR (161.9 MHz, C_6D_6): δ = 135.7 (s). ^{1}H NMR (400 MHz, C_6D_6): δ = 1.42 (s, 9H, CH_3, ^{t}Bu), 1.54 (s, 9H, CH_3, ^{t}Bu), 1.69 (s, 3H, CH_3), 1.77 (s, 3H, CH_3), 2.04 (s, 3H, CH_3), 2.09 (s, 3H, CH_3), 3.63 (pt, 1H, CH-O, J_{H-H}= 8.0 Hz), 4.05 (dd, 1H, CH-O, $^2J_{H-H}$= 10.0 Hz, $^3J_{H-H}$= 8.8 Hz), 4.90 (dd, 1H, CH-N, $^3J_{H-H}$= 10.0 Hz, $^3J_{H-H}$= 8.4 Hz), 5.93 (d, 1H, CH-OP, $^3J_{H-P}$= 8.8 Hz), 6.92 (m, 2H, CH=), 6.96-7.15 (m, 6H, CH=), 7.18 (s, 1H, CH=), 7.26 (s, 1H, CH=), 7.53 (d, 2H, CH=, $^3J_{H-H}$= 7.6 Hz). ^{13}C NMR (100.6 MHz, C_6D_6): δ = 16.9 (CH_3), 17.1 (CH_3), 20.7



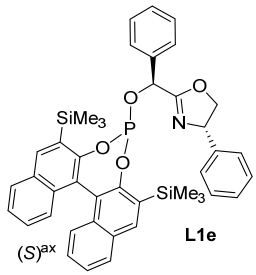
(CH_3), 20.8 (CH_3), 31.6 (d, CH_3, ^{t}Bu, J_{C-P}= 4.6 Hz), 32.0 (CH_3, ^{t}Bu), 35.1 (C, ^{t}Bu), 35.4 (C, ^{t}Bu), 70.1 (CH-N), 74.1 (d, CH-OP, J_{C-P}= 7.6 Hz), 75.4 (CH_2-O), 126.0-146.2 (aromatic carbons), 166.6 (C=N). MS HR-ESI [found 468.2067 $C_{28}H_{32}NO_2P$ $(M+Na)^+$ requires 468.2063].

L1d: Yield: 398.7 mg (56%). ^{31}P NMR (161.9 MHz, C_6D_6): δ = 139.8 (s); ^{1}H NMR



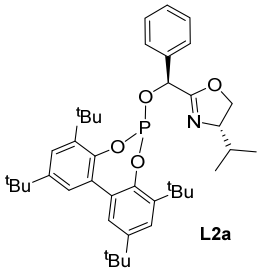
(400 MHz, C_6D_6): δ = 0.33 (s, 9H, CH_3, $SiMe_3$), 0.48 (s, 9H, CH_3, $SiMe_3$), 3.68 (pt, 1H, CH-O_{ox}, J_{H-H}= 8.0 Hz), 4.07 (dd, 1H, CH-O_{ox}, $^2J_{H-H}$= 10.0 Hz; $^3J_{H-H}$= 8.0 Hz), 4.92 (dd, 1H, CH-N, $^2J_{H-H}$= 10.0 Hz, $^3J_{H-H}$= 8.8 Hz), 5.95 (d, 1H, CH-OP, $^3J_{H-P}$= 9.6 Hz), 6.83 (m, 3H, CH=), 6.92-7.06 (m, 6H, CH=), 7.09-7.18 (m, 3H, CH=), 7.24 (m, 2H, CH=), 7.33 (d, 1H, CH=, $^3J_{H-H}$= 8.4 Hz), 7.69 (d, 1H, CH=, $^3J_{H-H}$= 8.4 Hz), 7.73 (d, 1H, CH=, $^3J_{H-H}$= 8.0 Hz), 8.04 (s, 1H, CH=), 8.13 (s, 1H, CH=). ^{13}C NMR (100.6 MHz, C_6D_6): δ = -0.3 (CH_3, $SiMe_3$), -0.2 (CH_3, $SiMe_3$), 69.3 (CH-N), 72.9 (CH-OP), 74.6 (CH_2-O_{ox}), 122.1-152.2 (aromatic carbons), 165.8 (C=N). TOF-MS (ESI+): m/z = 734.2278 calcd. For $C_{42}H_{42}NNaO_4PSi_2$ $[M+Na]^+$: 734.2282.

L1e: Yield: 484.1 mg (68%). ^{31}P NMR (161.9 MHz, C_6D_6): δ = 140.7 (s); ^{1}H NMR



(400 MHz, C_6D_6): δ = 0.32 (s, 9H, CH_3, $SiMe_3$), 0.56 (s, 9H, CH_3, $SiMe_3$), 3.59 (pt, 1H, CH-O_{ox}, J_{H-H}= 8.4 Hz), 4.05 (dd, 1H, CH-O_{ox}, $^2J_{H-H}$= 10.0 Hz; $^3J_{H-H}$= 8.8 Hz), 4.83 (dd, 1H, CH-N, $^2J_{H-H}$= 9.6 Hz, $^3J_{H-H}$= 7.6 Hz), 5.93 (d, 1H, CH-OP, $^3J_{H-P}$= 9.6 Hz), 6.80-7.05 (m, 7H, CH=), 7.09 (m, 4H, CH=), 7.26 (d, 1H, CH=, $^3J_{H-H}$= 8.8 Hz), 7.35 (m, 3H, CH=), 7.66 (d, 1H, CH=, $^3J_{H-H}$= 7.6 Hz), 7.71 (d, 1H, CH=, $^3J_{H-H}$= 8.0 Hz), 8.06 (s, 1H, CH=), 8.22 (s, 1H, CH=). ^{13}C NMR (100.6 MHz, C_6D_6): δ = -0.4 (CH_3, $SiMe_3$), 0.0 (CH_3, $SiMe_3$), 69.2 (CH-N), 73.6 (CH-OP), 74.5 (CH_2-O_{ox}), 122.6-152.3 (aromatic carbons), 165.3 (C=N). TOF-MS (ESI+): m/z = 734.2281, calcd. for $C_{42}H_{42}NNaO_4PSi_2$ $[M+Na]^+$: 734.2282.

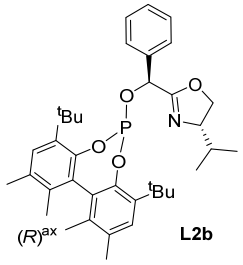
L2a: Yield: 395.5 mg (52%). ^{31}P NMR (161.9 MHz, C_6D_6): δ = 139.2 (s); ^{1}H NMR



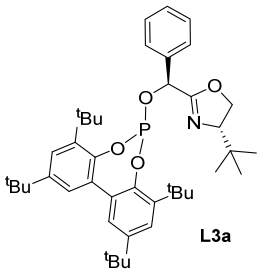
(400 MHz, C_6D_6): δ = 0.55 (d, 3H, CH_3, ^{i}Pr, $^3J_{H-H}$= 6.4 Hz), 0.76 (d, 3H, CH_3, ^{i}Pr, $^3J_{H-H}$= 6.4 Hz), 1.28 (s, 9H, CH_3, ^{t}Bu), 1.29 (s, 9H, CH_3, ^{t}Bu), 1.34 (s, 9H, CH_3, ^{t}Bu), 1.35 (m, 1H, CH, ^{i}Pr), 1.54 (s, 9H, CH_3, ^{t}Bu), 3.64 (pt, 1H, CH-O_{ox}, J_{H-H}= 8.4 Hz), 3.62 (m, 1H, CH-N), 3.85 (dd, 1H, CH-O_{ox}, $^2J_{H-H}$= 9.2 Hz, $^3J_{H-H}$= 8.0 Hz),

6.04 (d, 1H, CH-OP, $^3J_{H-P}$= 10.0 Hz), 6.99-7.15 (m, 3H, CH=), 7.27 (d, 1H, CH=, $^4J_{H-H}$= 2.8 Hz), 7.29 (d, 1H, CH=, $^4J_{H-H}$= 2.4 Hz), 7.38 (m, 2H, CH=), 7.51 (d, 1H, CH=, $^4J_{H-H}$= 2.8 Hz), 7.59 (d, 1H, CH=, $^4J_{H-H}$= 2.4 Hz). ^{13}C NMR (100.6 MHz, C_6D_6): δ = 18.8 (CH_3, ^{i}Pr), 19.2 (CH_3, ^{i}Pr), 31.4 (CH_3, ^{t}Bu), 31.7 (CH_3, ^{t}Bu), 31.8 (CH_3, ^{t}Bu), 31.9 (CH_3, ^{t}Bu), 33.4 (CH, ^{i}Pr), 35.0 (C, ^{t}Bu), 35.8 (C, ^{t}Bu), 35.9 (C, ^{t}Bu), 71.1 (CH_2-O_{ox}), 72.9 (CH-N), 73.9 (CH-OP), 124.7-147.2 (aromatic carbons), 165.2 (C=N). TOF-MS (ESI+): m/z = 680.3839 calcd. For $C_{41}H_{56}NNaO_4P$ $[M+Na]^+$: 680.3839.

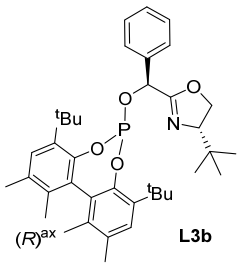
L2b: Yield: 409 mg (68%). ^{31}P NMR (161.9 MHz, C_6D_6): δ = 133.6 (s). ^{1}H NMR (400 MHz, C_6D_6): δ = 0.53 (d, 3H, CH_3, ^{i}Pr, $^3J_{H-H}$= 6.8 Hz), 0.74 (d, 3H, CH_3, ^{i}Pr, $^3J_{H-H}$= 6.8 Hz), 1.35 (m, 1H, CH, ^{i}Pr), 1.38 (s, 9H, CH_3, ^{t}Bu), 1.50 (s, 9H, CH_3, ^{t}Bu), 1.68 (s, 3H, CH_3), 1.81 (s, 3H, CH_3), 2.05 (s, 3H, CH_3), 2.12 (s, 3H, CH_3), 3.51 (pt, 1H, CH-O, J_{H-H}= 8.0 Hz), 3.63 (m, 1H, CH-N), 3.85 (pt, 1H, CH-O, J_{H-H}= 8.8 Hz), 6.65 (d, 1H, CH-OP, $^3J_{H-P}$= 9.2 Hz), 6.99-7.14 (m, 3H, CH=), 7.17 (s, 1H, CH=), 7.20 (s, 1H, CH=), 7.39 (s, 1H, CH=), 7.41 (s, 1H, CH=). ^{13}C NMR (100.6 MHz, C_6D_6): δ = 16.8 (CH_3), 17.1 (CH_3), 18.8 (CH_3, ^{i}Pr), 19.2 (CH_3, ^{i}Pr), 20.7 (CH_3), 20.8 (CH_3), 31.8 (d, CH_3, ^{t}Bu, J_{C-P}= 4.6 Hz), 32.0 (CH_3, ^{t}Bu), 33.4 (CH, ^{i}Pr), 35.1 (C, ^{t}Bu), 35.2 (C, ^{t}Bu), 71.0 (CH_2-O), 72.8 (CH-N), 74.0 (CH-OP), 126.0-146.4 (aromatic carbons), 165.4 (C=N). MS HR-ESI [found 624.3216$C_{37}H_{48}NO_4P$ $(M+Na)^+$ requires 624.3213].



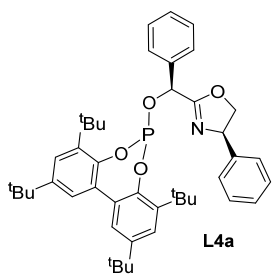
L3a: Yield: 436 mg (67%). ^{31}P NMR (161.9 MHz, C_6D_6): δ = 139.4 (s); ^{1}H NMR (400 MHz, C_6D_6): δ = 0.61 (s, 9H, CH_3, ^{t}Bu), 1.28 (s, 9H, CH_3, ^{t}Bu), 1.29 (s, 9H, CH_3, ^{t}Bu), 1.37 (s, 9H, CH_3, ^{t}Bu), 1.55 (s, 9H, CH_3, ^{t}Bu), 3.69 (m, 2H, CH-O_{ox}, CH-N), 3.88 (dd, 1H, CH-O_{ox}, $^2J_{H-H}$= 9.2 Hz, $^3J_{H-H}$= 7.6 Hz), 6.07 (d, 1H, CH-OP, $^3J_{H-P}$= 9.6 Hz), 6.99-7.15 (m, 3H, CH=), 7.27 (d, 1H, CH=, $^4J_{H-H}$= 2.4 Hz), 7.31 (d, 1H, CH=, $^4J_{H-H}$= 2.4 Hz), 7.41 (m, 2H, CH=), 7.52 (d, 1H, CH=, $^4J_{H-H}$= 2.4 Hz), 7.60 (d, 1H, CH=, $^4J_{H-H}$= 2.4 Hz). ^{13}C NMR (100.6 MHz, C_6D_6): δ = 26.0 (CH_3, ^{t}Bu), 31.4 (CH_3, ^{t}Bu), 31.6 (CH_3, ^{t}Bu), 31.7 (CH_3, ^{t}Bu), 31.9 (CH_3, ^{t}Bu), 34.2 (C, ^{t}Bu), 35.0 (C, ^{t}Bu), 35.1 (C, ^{t}Bu), 35.8 (C, ^{t}Bu), 35.9 (C, ^{t}Bu), 69.2 (CH_2-O_{ox}), 74.0 (CH-OP), 76.1 (CH-N), 124.7-147.3 (aromatic carbons), 165.2 (C=N). TOF-MS (ESI+): m/z = 694.3995 calcd. for $C_{42}H_{58}NNaO_4P$ $[M+Na]^+$: 694.3996.



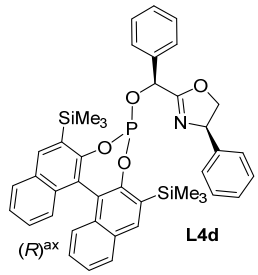
L3b: Yield: 412 mg (67%). ^{31}P NMR (161.9 MHz, C6D6): δ = 134.2 (s). ^{1}H NMR (400 MHz, C_6D_6): δ = 0.61 (s, 9H, CH_3, ^{t}Bu), 1.41 (s, 9H, CH_3, ^{t}Bu), 1.49 (s, 9H, CH_3, ^{t}Bu), 1.68 (s, 3H, CH_3), 1.80 (s, 3H, CH_3), 2.05 (s, 3H, CH_3), 2.12 (s, 3H, CH_3), 3.69 (m, 2H, CH-O, CH-N), 3.91 (m, 1H, CH-O), 5.70 (d, 1H, CH-OP, $^3J_{H-P}$= 9.6 Hz), 6.99-7.15 (m, 3H, CH=), 7.18 (s, 1H, CH=), 7.20 (s, 1H, CH=), 7.41 (s, 1H, CH=), 7.44 (s, 1H, CH=). ^{13}C NMR (100.6 MHz, C_6D_6): δ = 16.8 (CH_3), 17.1 (CH_3), 20.7 (CH_3), 20.8 (CH_3), 26.1 (CH_3, ^{t}Bu), 31.7 (d, CH_3, ^{t}Bu, J_{C-P}= 5.3 Hz), 31.9 (CH_3, ^{t}Bu), 34.2 (C, ^{t}Bu), 35.1 (C, ^{t}Bu), 35.2 (C, ^{t}Bu), 69.2 (CH_2-O), 74.0 (d, CH-OP, J_{C-P}= 4.6 Hz), 76.2 (CH-N), 126.0-146.4 (aromatic carbons), 165.4 (C=N). MS HR-ESI [found 638.3372 $C_{38}H_{50}NO_4P$ $(M+Na)^+$ requires 638.3370].



L4a: Yield: 420.3 mg (60%). ^{31}P NMR (161.9 MHz, C_6D_6): δ = 139.2 (s); ^{1}H NMR (400 MHz, C_6D_6): δ = 1.29 (s, 9H, CH_3, ^{t}Bu), 1.30 (s, 9H, CH_3, ^{t}Bu), 1.33 (s, 9H, CH_3, ^{t}Bu), 1.52 (s, 9H, CH_3, ^{t}Bu), 3.62 (pt, 1H, CH-O_{ox}, J_{H-H}= 8.4 Hz), 3.99 (dd, 1H, CH-O_{ox}, $^2J_{H-H}$= 10.4 Hz, $^3J_{H-H}$= 8.4 Hz), 4.92 (pt, 1H, CH-N, J_{H-H}= 10.0 Hz), 6.01 (d, 1H, CH-OP, $^3J_{H-P}$= 9.6 Hz), 6.99-7.14 (m, 8H, CH=), 7.32 (m, 2H, CH=), 7.39 (m, 2H, CH=), 7.53 (d, 1H, CH=, $^4J_{H-H}$= 2.4 Hz), 7.60 (d, 1H, CH=, $^4J_{H-H}$= 2.0 Hz). ^{13}C NMR (100.6 MHz, C_6D_6): δ = 31.4 (CH_3, ^{t}Bu), 31.5 (CH_3, ^{t}Bu), 31.6 (CH_3, ^{t}Bu), 31.9 (CH_3, ^{t}Bu), 35.0 (C, ^{t}Bu), 35.9 (C, ^{t}Bu), 36.0 (C, ^{t}Bu), 70.0 (CH-N), 73.8 (CH-OP), 75.3 (CH_2-O_{ox}), 124.7-147.3 (aromatic carbons), 167.0 (C=N). TOF-MS (ESI+): m/z = 694.3995 calcd. for $C_{42}H_{58}NNaO_4P$ $[M+Na]^+$: 694.3996.

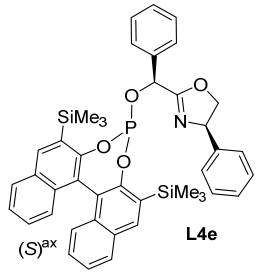


L4d: Yield: 440.1 mg (65%). ^{31}P NMR (161.9 MHz, C_6D_6): δ = 137.9 (s); ^{1}H NMR (400 MHz, C_6D_6): δ = 0.30 (s, 9H, CH_3, $SiMe_3$), 0.50 (s, 9H, CH_3, $SiMe_3$), 3.61 (pt, 1H, CH-O_{ox}, J_{H-H}= 8.4 Hz), 3.92 (dd, 1H, CH-O_{ox}, $^2J_{H-H}$= 10.0 Hz; $^3J_{H-H}$= 8.0 Hz), 4.92 (m, 1H, CH-N), 5.70 (d, 1H, CH-OP, $^3J_{H-P}$= 9.2 Hz), 6.86 (m, 2H, CH=), 6.98-7.06 (m, 6H, CH=), 7.10-7.24 (m, 6H, CH=), 7.26 (d, 1H, CH=, $^3J_{H-H}$= 8.8 Hz), 7.42 (d, 1H, CH=, $^3J_{H-H}$= 8.8 Hz), 7.70 (d, 1H, CH=, $^3J_{H-H}$= 8.4 Hz), 7.77 (d, 1H, CH=, $^3J_{H-H}$= 8.0 Hz), 8.04 (s, 1H, CH=), 8.13 (s, 1H, CH=). ^{13}C NMR (100.6 MHz, C_6D_6): δ = 0.3 (d, CH_3, $SiMe_3$, J_{C-P}= 3.1 Hz), 0.4 (CH_3,



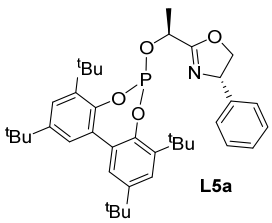
SiMe$_3$), 69.7 (CH-N), 73.5 (d, CH-OP, J_{C-P}= 5.33 Hz), 75.4 (CH$_2$-O$_{ox}$), 123.3-153.0 (aromatic carbons), 166.8 (C=N). TOF-MS (ESI+): m/z = 734.2280 calcd. for $C_{42}H_{42}NNaO_4PSi_2$ $[M+Na]^+$: 734.2282.

L4e: Yield: 498.6 mg (71%). ^{31}P NMR (161.9 MHz, C_6D_6): δ = 143.1 (s); ^{1}H NMR



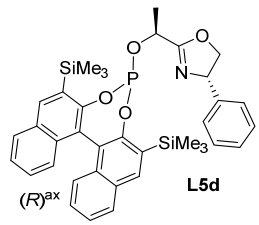
(400 MHz, C_6D_6): δ = 0.33 (s, 9H, CH$_3$, SiMe$_3$), 0.50 (s, 9H, CH$_3$, SiMe$_3$), 3.52 (dd, 1H, CH-O$_{ox}$, $^2J_{H-H}$= 9.2 Hz; $^3J_{H-H}$= 8.4 Hz), 3.91 (dd, 1H, CH-O$_{ox}$, $^2J_{H-H}$= 10.0 Hz; $^3J_{H-H}$= 8.4 Hz), 4.74 (pt, 1H, CH-N, J_{H-H}= 10.0 Hz), 5.87 (d, 1H, CH-OP, $^3J_{H-P}$= 8.8 Hz), 6.83-7.17 (m, 12H, CH=), 7.27 (d, 1H, CH=, $^3J_{H-H}$= 8.4 Hz), 7.36 (d, 1H, CH=, $^3J_{H-H}$= 8.4 Hz), 7.41 (m, 2H, CH=), 7.67 (d, 1H, CH=, $^3J_{H-H}$= 8.0 Hz), 7.77 (d, 1H, CH=, $^3J_{H-H}$= 8.0 Hz), 8.06 (s, 1H, CH=), 8.19 (s, 1H, CH=). ^{13}C NMR (100.6 MHz, C_6D_6): δ = 0.7 (d, CH$_3$, SiMe$_3$, J_{C-P}= 4.52 Hz), 1.0 (CH$_3$, SiMe$_3$), 70.4 (CH-N), 74.5 (CH-OP), 75.3 (CH$_2$-O$_{ox}$), 125.9-153.4 (aromatic carbons), 166.6 (C=N). TOF-MS (ESI+): m/z = 734.2281 calcd. For $C_{42}H_{42}NNaO_4PSi_2$ $[M+Na]^+$: 734.2282.

L5a: Yield: 445.3 mg (65%). ^{31}P NMR (161.9 MHz, C_6D_6): δ = 144.6 (s); ^{1}H NMR



(400 MHz, C_6D_6): δ = 1.25 (s, 9H, CH$_3$, ^{t}Bu), 1.27 (s, 9H, CH$_3$, ^{t}Bu), 1.45 (d, 3H, CH$_3$, 3J_{H-H}= 6.4 Hz), 1.59 (s, 9H, CH$_3$, ^{t}Bu), 1.60 (s, 9H, CH$_3$, ^{t}Bu), 3.77 (pt, 1H, CH-O$_{ox}$, J_{H-H}= 8.8 Hz), 4.14 (dd, 1H, CH-O$_{ox}$, $^2J_{H-H}$= 10.4 Hz, $^3J_{H-H}$= 8.4 Hz), 4.92 (pt, 1H, CH-N, J_{H-H}= 10.0 Hz), 5.18 (m, 1H, CH-OP), 6.99-7.14 (m, 5H, CH=), 7.33 (m, 2H, CH=), 7.60 (m, 2H, CH=). ^{13}C NMR (100.6 MHz, C_6D_6): δ = 20.7 (d, CH$_3$, $^3J_{C-P}$= 3.01 Hz), 31.8 (CH$_3$, ^{t}Bu), 31.9 (CH$_3$, ^{t}Bu), 32.0 (CH$_3$, ^{t}Bu), 32.1 (CH$_3$, ^{t}Bu), 35.0 (C, ^{t}Bu), 36.0 (C, ^{t}Bu), 36.1 (C, ^{t}Bu), 67.9 (d, CH-OP, $^2J_{C-P}$= 9.95 Hz), 70.2 (CH-N), 75.3 (CH$_2$-O$_{ox}$), 124.7-147.2 (aromatic carbons), 167.6 (C=N). TOF-MS (ESI+): m/z = 652.3525 calcd. For $C_{39}H_{52}NNaO_4P$ $[M+Na]^+$: 652.3526.

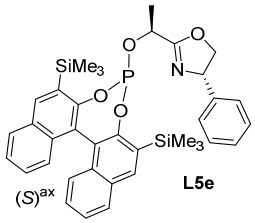
L5d: Yield: 398 mg (58%). ^{31}P NMR (161.9 MHz, C_6D_6): δ = 142.7 (s); ^{1}H NMR (400



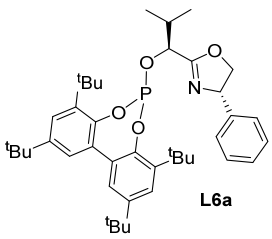
MHz, C_6D_6): δ = 0.54 (s, 9H, CH$_3$, SiMe$_3$), 0.55 (s, 9H, CH$_3$, SiMe$_3$), 1.27 (d, 3H, CH$_3$, 3J_{H-H}= 6.8 Hz), 3.76 (pt, 1H, CH-O$_{ox}$, J_{H-H}= 8.8 Hz), 4.15 (dd, 1H, CH-O$_{ox}$, $^2J_{H-H}$= 10.0 Hz; $^3J_{H-H}$= 8.8 Hz), 4.91 (pt, 1H, CH-N, J_{H-H}= 9.2 Hz), 5.13 (m, 1H, CH-OP), 6.86 (m, 2H, CH=), 6.99-7.15 (m, 7H, CH=), 7.27 (d, 1H, CH=,

$^3J_{H-H}$= 8.4 Hz), 7.36 (d, 1H, CH=, $^3J_{H-H}$= 8.0 Hz), 7.70 (d, 2H, CH=, $^3J_{H-H}$= 8.4 Hz), 8.13 (s, 1H, CH=), 8.15 (s, 1H, CH=). ^{13}C NMR (100.6 MHz, C_6D_6): δ = 0.4 (d, CH_3, $SiMe_3$, J_{C-P}= 5.33 Hz), 0.8 (CH_3, $SiMe_3$), 20.4 (d, CH_3, $^3J_{C-P}$= 1.06 Hz), 67.3 (CH-OP), 70.2 (CH-N), 75.2 (CH_2-O_{ox}), 123.3-152.9 (aromatic carbons), 167.3 (C=N). TOF-MS (ESI+): m/z = 672.2124 calcd. For $C_{37}H_{40}NNaO_4PSi_2$ $[M+Na]^+$: 672.2126.

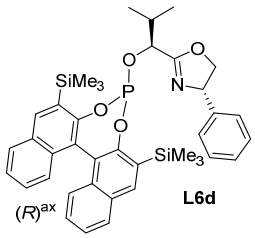
L5e: Yield: 405 mg (59%). ^{31}P NMR (161.9 MHz, C_6D_6): δ = 144.7 (s); ^{1}H NMR (400 MHz, C_6D_6): δ = 0.55 (s, 9H, CH_3, $SiMe_3$), 0.56 (s, 9H, CH_3, $SiMe_3$), 1.51 (d, 3H, CH_3, 3J_{H-H}= 6.8 Hz), 3.67 (pt, 1H, CH-O_{ox}, J_{H-H}= 8.4 Hz), 4.01 (dd, 1H, CH-O_{ox}, $^2J_{H-H}$= 10.0 Hz; $^3J_{H-H}$= 8.4 Hz), 4.85 (dd, 1H, CH-N, $^2J_{H-H}$= 10.0 Hz, $^3J_{H-H}$= 8.4 Hz), 5.05 (m, 1H, CH-OP), 6.86 (m, 2H, CH=), 6.86 (m, 2H, CH=), 6.99-7.15 (m, 7H, CH=), 7.27 (d, 1H, CH=, $^3J_{H-H}$= 8.4 Hz), 7.34 (d, 1H, CH=, $^3J_{H-H}$= 8.0 Hz), 7.70 (pt, 2H, CH=, J_{H-H}= 7.6 Hz), 8.12 (s, 1H, CH=), 8.16 (s, 1H, CH=). ^{13}C NMR (100.6 MHz, C_6D_6): δ = 0.5 (d, CH_3, $SiMe_3$, J_{C-P}= 4.52 Hz), 0.8 (CH_3, $SiMe_3$), 21.5 (d, CH_3, $^3J_{C-P}$= 3.02 Hz), 68.7 (d, CH-OP, $^2J_{C-P}$= 6.16 Hz), 70.0 (CH-N), 75.2 (CH_2-O_{ox}), 122.6-153.0 (aromatic carbons), 166.9 (C=N). TOF-MS (ESI+): m/z = 672.2125 calcd. for $C_{37}H_{40}NNaO_4PSi_2$ $[M+Na]^+$: 672.2126.



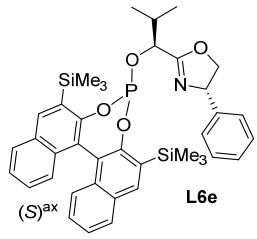
L6a: Yield: 429 mg (60%). ^{31}P NMR (161.9 MHz, C_6D_6): δ = 146.2 (s); ^{1}H NMR (400 MHz, C_6D_6): δ = 0.95 (d, 3H, CH_3, ^{i}Pr, $^3J_{H-H}$= 7.2 Hz), 1.00 (d, 3H, CH_3, ^{i}Pr, $^3J_{H-H}$= 7.2 Hz), 1.26 (s, 18H, CH_3, ^{t}Bu), 1.59 (s, 9H, CH_3, ^{t}Bu), 1.62 (s, 9H, CH_3, ^{t}Bu), 2.26 (m, 1H, CH, ^{i}Pr), 3.775 (pt, 1H, CH-O_{ox}, J_{H-H}= 8.8 Hz), 4.15 (dd, 1H, CH-O_{ox}, $^2J_{H-H}$= 10.0 Hz, $^3J_{H-H}$= 8.0 Hz), 4.97 (m, 2H, CH-N, CH-OP), 6.98-7.14 (m, 5H, CH=), 7.32 (m, 2H, CH=), 7.58 (m, 2H, CH=). ^{13}C NMR (100.6 MHz, C_6D_6): δ = 18.6 (CH_3, ^{i}Pr), 18.7 (CH_3, ^{i}Pr), 31.7 (CH_3, ^{t}Bu), 31.8 (CH_3, ^{t}Bu), 31.9 (CH_3, ^{t}Bu), 32.0 (CH_3, ^{t}Bu), 32.7 (d, CH, ^{i}Pr, $^3J_{C-P}$= 2.3 Hz), 35.0 (C, ^{t}Bu), 35.1 (C, ^{t}Bu), 36.0 (C, ^{t}Bu), 36.1 (C, ^{t}Bu), 70.2 (CH-N), 75.0 (CH_2-O_{ox}), 76.3 (d, CH-OP, $^2J_{C-P}$= 8.34 Hz), 124.6-147.2 (aromatic carbons), 166.1 (C=N). TOF-MS (ESI+): m/z = 680.3842 calcd. for $C_{41}H_{56}NNaO_4P$ $[M+Na]^+$: 680.3839.



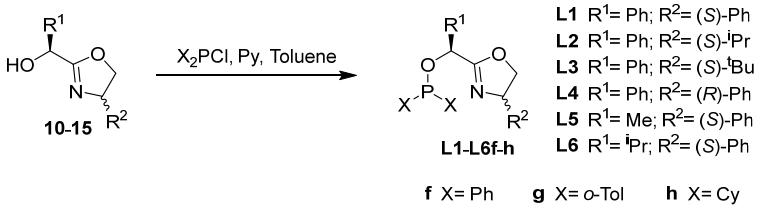
L6d: Yield: 480.3 mg (68%). ^{31}P NMR (161.9 MHz, C_6D_6): δ = 149.0 (s); ^{1}H NMR (400 MHz, C_6D_6): δ = 0.56 (s, 9H, CH_3, $SiMe_3$), 0.60 (s, 9H, CH_3, $SiMe_3$), 0.72 (d, 3H, CH_3, ^{i}Pr, $^{3}J_{H-H}$= 6.8 Hz), 0.82 (d, 3H, CH_3, ^{i}Pr, $^{3}J_{H-H}$= 6.8 Hz), 2.20 (m, 1H, CH, ^{i}Pr), 3.80 (pt, 1H, CH-O_{ox}, J_{H-H}= 8.8 Hz), 4.22 (dd, 1H, CH-O_{ox}, $^{2}J_{H-H}$= 10.4 Hz; $^{3}J_{H-H}$= 8.8 Hz), 4.77 (dd, 1H, CH-OP, $^{3}J_{H-P}$= 9.6 Hz; $^{3}J_{H-H}$= 6.8 Hz), 5.03 (pt, 1H, CH-N, J_{H-H}= 10.4 Hz), 6.86 (m, 2H, CH=), 6.99-7.15 (m, 7H, CH=), 7.28 (d, 1H, CH=, $^{3}J_{H-H}$= 8.8 Hz), 7.33 (d, 1H, CH=, $^{3}J_{H-H}$= 8.4 Hz), 7.71 (t, 2H, CH=, $^{3}J_{H-H}$= 7.2 Hz), 8.12 (s, 1H, CH=), 8.18 (s, 1H, CH=). ^{13}C NMR (100.6 MHz, C_6D_6): δ = 0.5 (d, CH_3, $SiMe_3$, J_{C-P}= 3.82 Hz), 0.8 (CH_3, $SiMe_3$), 18.4 (CH_3, ^{i}Pr), 18.6 (CH_3, ^{i}Pr), 32.6 (CH, ^{i}Pr), 70.3 (CH-N), 75.2 (CH_2-O_{ox}), 75.8 (CH-OP), 123.3-153.0 (aromatic carbons), 165.9 (C=N). TOF-MS (ESI+): m/z = 700.2441 calcd. for $C_{39}H_{44}NNaO_4PSi_2$ $[M+Na]^+$: 700.2439.



L6e: Yield: 481 mg (69%). ^{31}P NMR (161.9 MHz, C_6D_6): δ = 147.3 (s); ^{1}H NMR (400 MHz, C_6D_6): δ = 0.56 (s, 9H, CH_3, $SiMe_3$), 0.60 (s, 9H, CH_3, $SiMe_3$), 0.93 (d, 3H, CH_3, ^{i}Pr, $^{3}J_{H-H}$= 6.8 Hz), 1.06 (d, 3H, CH_3, ^{i}Pr, $^{3}J_{H-H}$= 6.8 Hz), 2.33 (m, 1H, CH, ^{i}Pr), 3.52 (pt, 1H, CH-O_{ox}, J_{H-H}= 8.8 Hz), 3.81 (dd, 1H, CH-O_{ox}, $^{2}J_{H-H}$= 10.4 Hz; $^{3}J_{H-H}$= 8.4 Hz), 4.05 (pt, 1H, CH-N, J_{H-H}= 9.2 Hz), 4.96 (pt, 1H, CH-OP, J_{H-H}= 7.6 Hz), 6.83 (m, 2H, CH=), 6.96-7.15 (m, 7H, CH=), 7.24 (d, 1H, CH=, $^{3}J_{H-H}$= 8.8 Hz), 7.30 (d, 1H, CH=, $^{3}J_{H-H}$= 8.4 Hz), 7.69 (t, 2H, CH=, $^{3}J_{H-H}$= 8.8 Hz), 8.18 (s, 2H, CH=). ^{13}C NMR (100.6 MHz, C_6D_6): δ = 0.5 (d, CH_3, $SiMe_3$, J_{C-P}= 4.60 Hz), 0.8 (CH_3, $SiMe_3$), 18.7 (CH_3, ^{i}Pr), 19.5 (CH_3, ^{i}Pr), 32.7 (d, CH, ^{i}Pr, $^{3}J_{H-P}$= 4.62 Hz), 69.7 (CH-N), 74.7 (CH_2-O_{ox}), 77.0 (CH-OP), 123.2-153.1 (aromatic carbons), 165.2 (C=N). TOF-MS (ESI+): m/z = 700.2438 calcd. For $C_{39}H_{44}NNaO_4PSi_2$ $[M+Na]^+$: 700.2439.



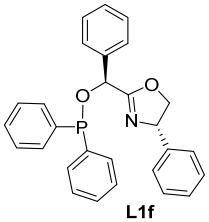
2.5. Preparation of phosphinite-oxazoline ligands L1-L6f-h



Scheme S6. Synthesis of phosphinite-oxazolines **L1-L6f-h**.

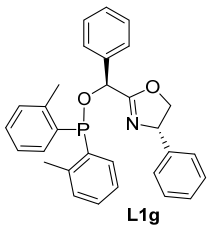
The corresponding hydroxyl-oxazoline compound (0.5 mmol) and DMAP (6.7 mg, 0.055 mmol) were dissolved in toluene (1 ml), and triethylamine was added (0.09 ml, 0.65 mmol) at rt, followed by the addition of the corresponding chlorophosphine (0.55 mmol) via syringe. The reaction was stirred for 20 min at rt. The solvent was removed *in vacuo* and the product was purified by flash chromatography on alumina (toluene/NEt_3= 100/1) to afford the corresponding phosphinite-oxazoline **L1-L6f-h** as a colorless oil.

L1f: Yield: 425 mg (67%); ^{31}P NMR (161.9 MHz, C_6D_6): δ = 116.5 (s). ^{1}H NMR (400 MHz, C_6D_6): δ = 3.64 (pt, 1H, CH-O, J_{H-H}= 7.6 Hz), 3.87 (dd, 1H, CH-O, $^{2}J_{H-H}$= 10.0 Hz, $^{3}J_{H-H}$= 8.0 Hz), 4.82 (dd, 1H, CH-N, $^{2}J_{H-H}$= 10.0 Hz, $^{3}J_{H-H}$= 8.0 Hz), 5.86 (d, 1H, CH-OP, $^{3}J_{H-P}$= 8.4 Hz), 6.95-7.11 (m, 14H, CH=), 7.56 (dt, 2H, CH=, $^{3}J_{H-H}$= 8.0 Hz, $^{4}J_{H-H}$= 2.0 Hz), 7.62 (d, 2H, CH=, $^{3}J_{H-H}$= 7.2 Hz), 7.39 (t, 2H, CH=, $^{3}J_{H-H}$= 7.2 Hz). ^{13}C NMR (100.6 MHz, C_6D_6): δ= 69.4 (CH-N), 74.6 (CH_2-O), 77.2 (CH-OP), 125.3-142.6 (aromatic carbons), 166.6 (C=N). MS HR-ESI [found 460.1439, $C_{40}H_{46}NO_4P$ $(M-Na)^+$ requires 460.1437].



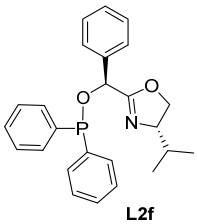
L1f

L1g: Yield: 121 mg (58%). ^{31}P NMR (161.9 MHz, C_6D_6): δ = 105.0 (s). ^{1}H NMR (400 MHz, C_6D_6): δ = 2.31 (s, 3H, CH_3), 2.44 (s, 3H, CH_3), 3.59 (m, 1H, CH-O), 3.87 (m, 1H, CH-O), 4.82 (m, 1H, CH-N), 5.92 (d, 1H, CH-OP, $^{3}J_{H-P}$= 8.4 Hz), 6.88 (m, 1H, CH=), 6.95-7.15 (m, 14H, CH=), 7.63 (d, 1H, CH=, $^{3}J_{H-H}$= 8.4 Hz), 7.72 (m, 1H, CH=), 8.09 (m, 1H, CH=). ^{13}C NMR (100.6 MHz, C_6D_6): δ = 20.2 (d, CH_3, J_{C-P}= 9.1 Hz), 20.4 (d, CH_3, J_{C-P}= 9.1 Hz) 69.3 (CH-N), 74.4 (CH_2-O), 77.6 (d, CH-OP, J_{C-P}= 24.4 Hz), 125.9-142.6 (aromatic carbons), 166.8 (C=N). MS HR-ESI [found 488.1754 $C_{26}H_{28}NO_2P$ $(M+Na)^+$ requires 488.1750].



L1g

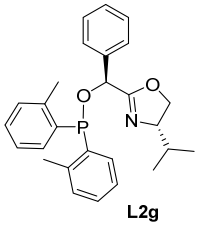
L2f: Yield: 116 mg (58%). ^{31}P NMR (161.9 MHz, C_6D_6): δ = 116.5 (s). ^{1}H NMR (400 MHz, C_6D_6): δ = 0.63 (d, 3H, CH_3, ^{i}Pr, $^{3}J_{H-H}$= 6.8 Hz), 0.77 (d, 3H, CH_3, ^{i}Pr, $^{3}J_{H-H}$= 6.8 Hz), 1.37 (m, 1H, CH, ^{i}Pr), 3.49 (pt, 1H, CH-O, J_{H-H}= 6.6 Hz), 3.54-.65 (m, 2H, CH-O, CH-N), 5.80 (d, 1H, CH-OP, $^{3}J_{H-P}$= 8.6 Hz), 6.99-7.18 (m, 9H, CH=), 7.55-7.63 (m, 3H, CH=), 7.79-7.84 (m, 2H, CH=). ^{13}C NMR (100.6 MHz, C_6D_6): δ = 18.3 (CH3, ^{i}Pr), 32.7 (CH, ^{i}Pr), 70.1 (CH-N), 71.9 (CH_2-O), 77.3 (d, CH-OP, $^{3}J_{C-P}$= 23.1



L2f

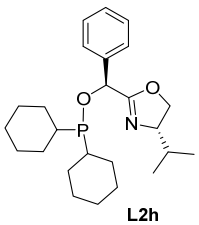
Hz), 125.4-142.3 (aromatic carbons), 165.0 (C=N). MS HR-ESI [found 426.1597 $C_{25}H_{26}NO_2P$ $(M+Na)^+$ requires 426.1593].

L2g: Yield: 121 mg (56%). ^{31}P NMR (161.9 MHz, C_6D_6): δ = 104.9 (s). ^1H NMR (400 MHz, C_6D_6): δ = 0.60 (d, 1H, CH_3, ^iPr, $^3J_{H-H}$= 6.7 Hz), 0.75 (d, 1H, CH_3, ^iPr, $^3J_{H-H}$= 6.7 Hz), 2.25 (s, 3H, CH_3), 1.31-1.39 (m, 1H, CH, ^iPr), 2.39 (s, 3H, CH_3), 3.44 (pt, 1H, CH-O, $^3J_{H-H}$= 7.5 Hz), 3.48-3.63 (m, 2H, CH-O, CH-N), 5.78 (d, 1H, CH-OP, $^3J_{H-P}$= 8.6 Hz), 6.82-7.12 (m, 9H, CH=), 7.55 (d, 2H, CH=, $^3J_{H-H}$= 7.8 Hz), 7.58-7.65 (m, 1H, CH=), 7.97-8.07 (m, 1H, CH=). ^{13}C NMR (100.6 MHz, C_6D_6): δ = 18.5 (CH_3, ^iPr), 20.5 (CH_3), 20.7 (CH_3), 32.7 (CH, ^iPr), 70.1 (CH-N), 72.1 (CH_2-O), 77.9 (d, CH-OP, $^2J_{C-P}$= 24.2 Hz), 126.1-141.3 (aromatic carbons), 165.1 (C=N). MS HR-ESI [found 454.1911 $C_{27}H_{30}NO_2P$ $(M+Na)^+$ requires 454.1906].



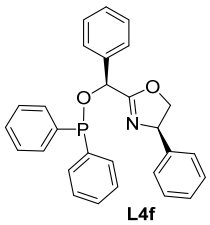
L2g

L2h: Yield: 170 mg (82%). ^{31}P NMR (161.9 MHz, C_6D_6): δ = 154.06 (s). ^1H NMR (400 MHz, C_6D_6): δ = 0.66 (d, 3H, CH_3, ^iPr, $^3J_{H-H}$= 6.7 Hz), 0.81 (d, 3H, CH_3, iPr, $^3J_{H-H}$= 6.7 Hz), 0.93-1.11 (m, 4H, CH_2, Cy), 1.17-1.33 (m, 4H, CH_2, Cy), 1.35-1.50 (m, 3H, CH_2, Cy, CH, ^iPr), 1.48-1.68 (m, 6H, CH_2, Cy), 1.72-1.76 (m, 4H, CH_2, CH, Cy), 2.11-2.15 (m, 1H, CH_2, Cy), 3.52 (pt, 1H, CH-O, J_{H-H}= 7.7 Hz), 3.61-3.70 (m, 1H, CH-O), 3.72-3.79 (m, 1H, CH-N), 5.53 (d, 1H, CH-OP, $^3J_{C-P}$= 8.8 Hz), 6.98-7.05 (m, 1H, CH=), 7.07-7.14 (m, 2H, CH=), 7.56-7.61 (m, 2H, CH=). ^{13}C NMR (100.6 MHz, C_6D_6): δ = 18.2 (CH_3, ^iPr), 18.3 (CH_3, ^iPr), 26.3-27.2 (CH_2, Cy), 27.9 (CH_2, Cy), 28.1 (CH_2, Cy), 28.2 (CH_2, Cy), 32.7 (CH, ^iPr), 37.9 (d, CH, Cy, $^1J_{C-P}$= 2.5 Hz), 38.1 (d, CH, Cy, $^1J_{C-P}$= 4.5 Hz), 69.9 (CH-N), 72.0 (CH_2-O), 79.5 (d, CH-OP, $^2J_{C-P}$= 23.6 Hz), 127.2-139.3 (aromatic carbons), 165.4 (C=N). MS HR-ESI [found 438.2535 $C_{25}H_{38}NO_2P$ $(M+Na)^+$ requires 438.2532].



L2h

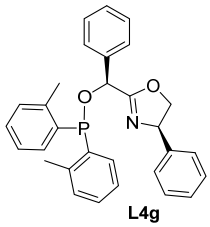
L4f: Yield: 118 mg (54%). ^{31}P NMR (161.9 MHz, C_6D_6): δ = 116.6 (s). ^1H NMR (400 MHz, C_6D_6): δ = 3.59 (t, 1H, CH-O, J_{H-H}= 8.6 Hz), 3.90-3.98 (m, 1H, CH-O), 4.83 (pt, 1H, CH-N, J_{H-H}= 9.6 Hz), 5.98 (d, 1H, CH-OP, $^3J_{H-P}$= 8.7 Hz), 6.96-7.19 (m, 14H, CH=), 7.56-7.64 (m, 2H, C=H), 7.65-7.72 (m, 2H, C=H), 7.76-7.84 (m, 2H, C=H). ^{13}C NMR (100.6 MHz, C_6D_6): δ = 69.5 (CH-N), 74.6 (CH_2-O), 77.4 (d, CH-OP, $^2J_{C-}$



L4f

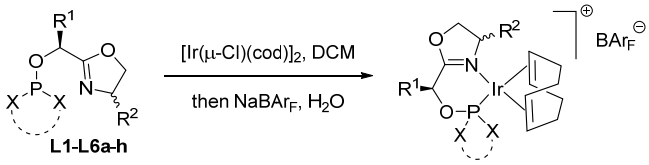
$_P$= 23.1 Hz), 125.3-142.4 (aromatic carbons), 166.5 (C=N). MS HR-ESI [found 460.1439 $C_{28}H_{24}NO_2P$ $(M+Na)^+$ requires 460.1437].

L4g: Yield: 155 mg (67%). ^{31}P NMR (161.9 MHz, C_6D_6): δ = 105.2 (s). ^{1}H NMR (400 MHz, C_6D_6): δ = 2.33 (s, 3H, CH_3, *o*-Tol), 2.41 (s, 3H, CH_3, *o*-Tol), 3.57 (pt, 1H, CH-O, J_{H-H}= 8.6 Hz), 3.90-3.95 (m, 1H, CH-O), 4.80 (pt, 1H, CH-N, J_{H-H}= 9.6 Hz), 5.97 (d, 1H, CH-OP, $^3J_{H-P}$= 8.8 Hz), 6.75-7.25 (m, 15H, C=H), 7.51-7.74 (m, 2H, CH=), 8.02-8.07 (m, 1H, C=H). ^{13}C NMR (100.6 MHz, C_6D_6): δ = 20.2 (CH_3, *o*-Tol), 20.5 (CH_3, *o*-Tol), 69.5 (CH-N), 74.5 (CH_2-O), 77.8 (d, CH-OP, $^2J_{C-P}$= 24.6 Hz), 125.3-142.4 (aromatic carbons), 166.4 (C=N). MS HR-ESI [found 488.1749 $C_{30}H_{28}NO_2P$ $(M+Na)^+$ requires 488.1750].



L4h: Yield: 120 mg (54%). ^{31}P NMR (161.9 MHz, C_6D_6): δ = 154.0 (s). ^{1}H NMR (400 MHz, C_6D_6): δ = 1.00-1.14 (m, 4H, CH_2, Cy), 1.17-1.28 (m, 4H, CH_2, Cy), 1.31-1.40 (m, 2H, CH_2, Cy), 1.45-1.52 (m, 2H, CH_2, Cy), 1.59-1.66 (m, 4H, CH_2, Cy), 1.69-1.72 (m, 2H, CH_2, Cy), 1.77-1.84 (m, 3H, CH_2, CH, Cy), 2.17-2.21 (m, 1H, CH_2, Cy), 3.74 (pt, 1H, CH-O, J_{H-H}= 8.6 Hz), 4.00 (dd, 1H, CH-O, $^2J_{H-H}$= 10.1 Hz, $^3J_{H-H}$= 8.4 Hz), 4.86 (pt, 1H, CH-N, J_{H-H}= 9.6 Hz), 5.79 (d, 1H, CH-OP, $^3J_{H-P}$= 8.6 Hz), 7.02-7.10 (m, 3H, C=H), 7.11-7.21 (m, 2H, CH=), 7.21-7.24 (m, 3H, CH=), 7.71 (dd, 2H, CH=, $^3J_{H-H}$= 7.9 Hz, $^4J_{H-H}$= 0.9 Hz). ^{13}C NMR (100.6 MHz, C_6D_6): δ = 26.3-27.0 (CH_2, Cy), 27.9 (CH_2, Cy), 28.1 (CH_2, Cy), 28.2 (CH_2, Cy), 28.3 (CH_2, Cy), 38.0 (d, CH, $^1J_{C-P}$= 11.3 Hz), 38.2 (d, CH, $^1J_{C-P}$=13.2 Hz), 69.4 (CH-N), 74.5 (CH_2-O), 79.6 (d, CH-OP, $^2J_{C-P}$= 23.4 Hz), 126.7-142.6 (aromatic carbons), 167.0 (C=N). MS HR-ESI [found 472.2378 $C_{28}H_{36}NO_2P$ $(M+Na)^+$ requires 472.2376].

2.6. Preparation of [Ir(cod)(L1-L6a-h)]BAr$_F$

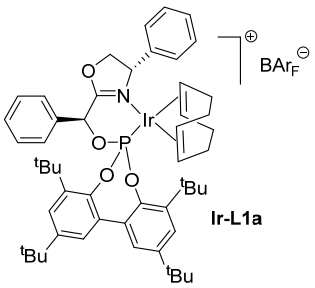


Scheme S7. Synthesis of [Ir(cod)(**L1-L6a-h**)]BAr$_F$.

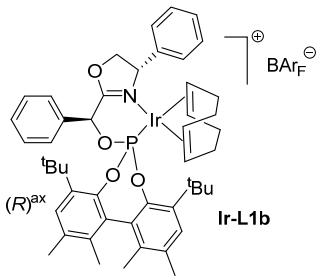
The corresponding ligand (0.074 mmol) was dissolved in CH_2Cl_2 (5 mL) and [Ir(μ-Cl)(cod)]$_2$ (25.0 mg, 0.037 mmol) was added. The reaction mixture was heated to reflux at 40 °C for 1 h. After 5 min at rt, NaBAr$_F$ (77.2 mg, 0.080 mmol) and water (5 mL)

were added and the reaction mixture was stirred vigorously for 30 min at rt. The phases were separated and the aqueous phase was extracted twice with CH_2Cl_2. The combined organic phases were dried with $MgSO_4$ filtered through a plug of Celite and the solvent was evaporated to give the product as an orange solid.

[Ir(cod)(L1a)]BAr$_F$: Yield: 63 mg (92%). ^{31}P NMR (161.9 MHz, $CDCl_3$): δ = 102.4 (s). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.29 (s, 9H, CH_3, ^{t}Bu), 1.32 (s, 9H, CH_3, ^{t}Bu), 1.34 (s, 9H, CH_3, ^{t}Bu), 1.44 (s, 9H, CH_3, ^{t}Bu), 1.80-2.00 (m, 7H, CH_2, cod), 2.12 (m, 1H, CH_2, cod), 3.30 (m, 1H, CH=, cod), 3.60 (m, 1H, CH=, cod), 4.55 (dd, 1H, CH-O, $^2J_{H-H}$= 12.0 Hz, $^3J_{H-H}$= 4.0 Hz), 4.80 (pt, 1H, CH-O, J_{H-H}= 8.0 Hz), 4.90 (m, 1H, CH=, cod), 5.19 (dd, 1H, CH-N, $^2J_{H-H}$= 12.0 Hz, $^3J_{H-H}$= 4.0 Hz), 5.33 (m, 1H, CH=, cod), 6.33 (d, 1H, CH-OP, $^3J_{H-P}$= 16.0 Hz), 7.13 (d, 1H, CH=, $^4J_{H-H}$= 2.6 Hz), 7.18 (m, 3H, CH=), 7.42-7.52 (m, 12H, CH=), 7.61 (m, 2H, CH=), 7.72 (m, 8H, CH=). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 28.7 (CH_2, cod), 28.9 (CH_2, cod), 31.2 (CH_2, cod), 31.4 (CH_3, ^{t}Bu), 31.6 (CH_2, cod), 31.7 (CH_3, ^{t}Bu), 32.0 (CH_2, cod), 34.7 (C, ^{t}Bu), 34.8 (C, ^{t}Bu), 35.3 (C, ^{t}Bu), 35.4 (C, ^{t}Bu), 62.9 (CH=, cod), 65.8 (CH=, cod), 71.2 (CH-N), 74.8 (CH-OP), 79.4 (CH_2-O), 103.5 (d, CH=, cod, J_{C-P}= 18.0 Hz), 104.4 (d, CH=, cod, J_{C-P}= 16.0 Hz), 117.4-149.2 (aromatic carbons), 161.6 (q, C-B, BAr$_F$, $^1J_{C-B}$= 50.3 Hz), 173.6 (C=N). MS HR-ESI [found 992.4362, $C_{52}H_{66}IrNO_4P$ (M-BAr$_F$)$^+$ requires 992.4359].

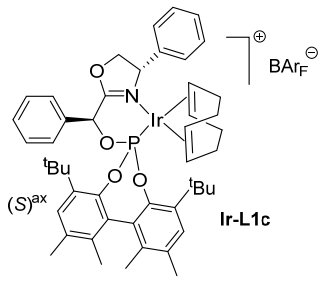


[Ir(cod)(L1b)]BAr$_F$: Yield: 61 mg (91%). ^{31}P NMR (161.9 MHz, $CDCl_3$): δ = 100.7 (s). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.05 (s, 9H, CH_3, ^{t}Bu), 1.25 (s, 9H, CH_3, ^{t}Bu), 1.74 (s, 3H, CH_3), 1.76 (s, 3H, CH_3), 1.89 (m, 3H, CH_2, cod), 2.10 (m, 1H, CH_2, cod), 2.18 (s, 3H, CH_3), 2.19 (m, 1H, CH_2, cod), 2.26 (s, 3H, CH_3), 2.30-2.47 (m, 3H, CH_2, cod), 2.85 (m, 1H, CH=, cod), 4.03 (m, 1H, CH=, cod), 4.55 (m, 1H, CH-O), 4.67 (pt, 1H, CH-O, J_{H-H}= 9.6 Hz), 4.95 (m, 2H, CH-N and CH=, cod), 5.66 (m, 1H, CH=, cod), 6.01 (d, 1H, CH-OP, $^3J_{H-P}$= 14.8 Hz), 7.09-7.28 (m, 4H, CH=), 7.47-7.54 (m, 10H, CH=), 7.77 (m, 10H, CH=). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 16.4 (CH_3), 16.5 (CH_3), 20.2 (CH_3), 20.3 (CH_3), 26.3 (CH_2, cod), 29.9 (CH_2, cod), 31.3 (CH_3, ^{t}Bu), 31.4 (CH_2, cod), 32.2 (CH_3, ^{t}Bu), 35.1 (C, ^{t}Bu), 34.6 (d, CH_2, cod, J_{C-P}= 5.3 Hz), 34.8 (C, ^{t}Bu), 61.5 (CH=, cod),

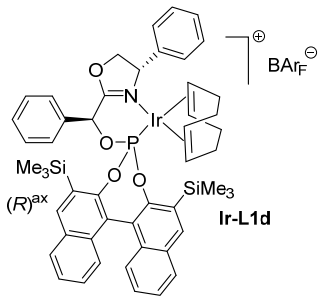


66.7 (CH=, cod), 70.5 (CH-N), 76.0 (CH-OP), 78.7 (CH_2-O), 100.1 (d, CH=, cod, J_{C-P}= 18.3 Hz), 103.6 (d, CH=, cod, J_{C-P}= 13.8 Hz), 117.4-143.5 (aromatic carbons), 161.6 (q, C-B, BAr_F, $^1J_{C-B}$= 49.7 Hz), 170.8 (d, C=N, $^3J_{C-P}$= 7.6 Hz). MS HR-ESI [found 936.3735, $C_{48}H_{58}IrNO_4P$ $(M-BAr_F)^+$ requires 936.3733].

[Ir(cod)(L1c)]BAr$_F$: Yield: 55 mg (94%). ^{31}P NMR (161.9 MHz, $CDCl_3$): δ = 101.9 (s). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.23 (s, 9H, CH_3, ^{t}Bu), 1.62 (s, 9H, CH_3, ^{t}Bu), 1.70 (m, 2H, CH_2, cod), 1.78 (s, 3H, CH_3), 1.83 (s, 3H, CH_3), 1.80-1.99 (m, 5H, CH_2, cod), 2.05 (m, 1H, CH_2, cod), 2.24 (s, 3H, CH_3), 2.30 (s, 3H, CH_3), 2.75 (m, 1H, CH=, cod), 3.97 (m, 1H, CH=, cod), 4.51 (m, 1H, CH-O), 4.86 (m, 1H, CH=, cod), 4.85 (pt, 1H, CH-O, J_{H-H}= 10.0 Hz), 5.05 (m, 1H, CH=, cod), 5.13 (m, 1H, CH-N), 6.45 (d, 1H, CH-OP, $^3J_{H-P}$= 9.2 Hz), 7.11-7.17 (m, 3H, CH=), 7.26 (m, 1H, CH=), 7.31 (m, 1H, CH=), 7.34-7.46 (m, 6H, CH=), 7.52 (s, 5H, CH=), 7.72 (s, 8H, CH=). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 16.5 (CH_3), 16.6 (CH_3), 20.2 (CH_3), 20.4 (CH_3), 27.4 (CH_2, cod), 30.2 (CH_2, cod), 30.6 (CH_2, cod), 31.2 (CH_3, ^{t}Bu), 32.5 (CH_3, ^{t}Bu), 33.3 (d, CH_2, cod, J_{C-P}= 5.0 Hz), 34.6 (C, ^{t}Bu), 35.1 (C, ^{t}Bu), 61.0 (CH=, cod), 69.7 (CH=, cod), 71.7 (CH-N), 74.1 (d, CH-OP, $^2J_{C-P}$= 8.3 Hz), 79.9 (CH_2-O), 103.5 (d, CH=, cod, J_{C-P}= 16.8 Hz), 104.3 (d, CH=, cod, J_{C-P}= 13.8 Hz), 117.4-143.6 (aromatic carbons), 161.7 (q, C-B, BAr_F, $^1J_{C-B}$= 49.7 Hz), 174.8 (C=N). MS HR-ESI [found 766.2429, $C_{38}H_{40}IrNO_2P$ $(M-BAr_F)^+$ requires 766.2426].

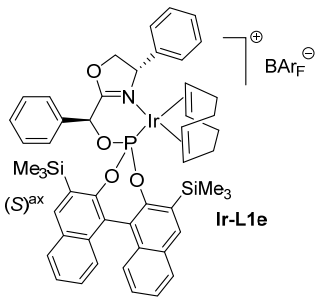


[Ir(cod)(L1d)]BAr$_F$: Yield: 64 mg (92%). ^{31}P NMR (161.9 MHz, $CDCl_3$): δ = 107.2 (s). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.37 (s, 9H, CH_3, $SiMe_3$), 0.49 (s, 9H, CH_3, $SiMe_3$), 1.53 (m, 2H, CH_2, cod), 1.63 (m, 1H, CH_2, cod), 1.76 (m, 1H, CH_2, cod), 1.94 (m, 1H, CH_2, cod), 2.09 (m, 1H, CH_2, cod), 2.15 (m, 1H, CH_2, cod), 2.37 (m, 1H, CH_2, cod), 3.11 (m, 1H, CH=, cod), 4.07 (m, 1H, CH=, cod), 4.42 (m, 1H, CH-O), 4.76 (m, 1H, CH-O), 4.98 (m, 1H, CH=, cod), 5.43 (m, 1H, CH-N), 5.82 (m, 1H, CH=, cod), 6.00 (m, 1H, CH-OP), 6.95 (m, 2H, CH=), 7.22 (m, 5H, CH=), 7.33-7.52 (m, 10H, CH=), 7.71 (m, 8H, CH=), 7.93 (m, 5H, CH=), 8.13 (m, 2H, CH=). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 0.2 (CH_3, $SiMe_3$), 1.4 (CH_3, $SiMe_3$), 26.4 (CH_2, cod), 29.4 (CH_2, cod), 31.4 (CH_2, cod),

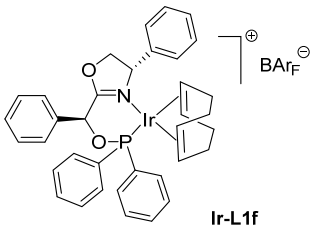


34.7 (CH_2, cod), 61.4 (CH=, cod), 67.0 (CH=, cod), 71.5 (CH-N), 74.4 (CH-OP), 80.3 (CH_2-O), 102.3 (d, CH=, cod, J_{C-P}= 15.9 Hz), 106.5 (d, CH=, cod, J_{C-P}= 16.2 Hz), 117.4-150.1 (aromatic carbons), 161.6 (q, C-B, BAr_F, $^1J_{C-B}$= 49.7 Hz), 172.8 (C=N). MS HR-ESI [found 1012.2961, C50H54IrNO4PSi2 $(M-BAr_F)^+$ requires 1012.2958].

[Ir(cod)(L1e)]BAr_F: Yield: 65 mg (94%). ^{31}P NMR (161.9 MHz, $CDCl_3$): δ = 108.3 (s). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.35 (s, 9H, CH_3, $SiMe_3$), 0.62 (s, 9H, CH_3, $SiMe_3$), 1.55 (m, 1H, CH_2, cod), 1.62 (m, 1H, CH_2, cod), 1.75 (m, 1H, CH_2, cod), 1.89 (m, 2H, CH_2, cod), 1.99 (m, 3H, CH_2, cod), 2.99 (m, 1H, CH=, cod), 3.99 (m, 1H, CH=, cod), 4.50 (dd, 1H, CH-O, $^2J_{H-H}$= 12.0 Hz, $^3J_{H-H}$= 4.0 Hz), 4.89 (m, 2H, CH-O and CH=, cod), 5.19 (m, 1H, CH=, cod), 5.32 (m, 1H, CH-N), 6.48 (d, 1H, CH-OP, $^3J_{H-H}$= 12.0 Hz), 6.99 (d, 1H, CH=, $^3J_{H-H}$= 8.0 Hz), 7.03 (d, 1H, CH=, $^3J_{H-H}$= 8.0 Hz), 7.25 (m, 3H, CH=), 7.37-7.53 (m, 14H, CH=), 7.73 (m, 9H, CH=), 6.92 (d, 1H, CH=, $^3J_{H-H}$= 8.0 Hz), 7.99 (d, 1H, CH=, $^3J_{H-H}$= 8.0 Hz), 8.04 (s, 1H, CH=), 8.21 (s, 1H, CH=). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 0.0 (CH_3, $SiMe_3$), 1.2 (CH_3, $SiMe_3$), 27.3 (CH_2, cod), 30.2 (CH_2, cod), 30.5 (CH_2, cod), 33.4 (CH_2, cod), 61.8 (CH=, cod), 69.8 (CH=, cod), 71.8 (CH-N), 74.6 (d, CH-OP, $^2J_{C-P}$= 6.0 Hz), 79.6 (CH_2-O), 104.4 (d, CH=, cod, J_{C-P}= 17.1 Hz), 106.0 (d, CH=, cod, J_{C-P}= 14.0 Hz), 117.4-150.2 (aromatic carbons), 161.7 (q, C-B, BAr_F, $^1J_{C-B}$= 49.3 Hz), 174.3 (d, C=N, $^3J_{C-P}$= 5.0 Hz). MS HR-ESI [found 1012.2960, $C_{50}H_{54}IrNO_4PSi_2$ $(M-BAr_F)^+$ requires 1012.2958].

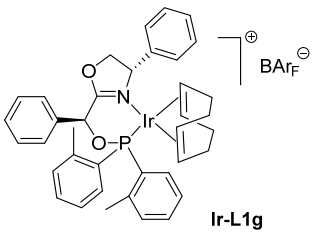


[Ir(cod)(L1f)]BAr_F: This compound was further purified by flash chromatography using neutral silica and dichloromethane as eluent. Yield: 50 mg (42%). ^{31}P NMR (161.9 MHz, $CDCl_3$): δ = 111.2 (s). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.56-1.73 (m, 2H, CH_2, cod), 1.77-1.86 (m, 1H, CH_2, cod), 1.92-2.01 (m, 1H, CH_2, cod), 2.10-2.15 (m, 2H, CH_2, cod), 2.25-2.36 (m, 2H, CH_2, cod), 2.48 (m, 1H, CH=, cod), 3.21 (m, 1H, CH=, cod), 4.33 (dd, 1H, CH-O, $^2J_{H-H}$= 9.4 Hz, $^3J_{H-H}$= 6.3 Hz), 4.70 (t, 1H, CH-O, J_{H-H}= 9.9 Hz), 5.10 (m, 1H, CH=, cod), 5.24 (dd, 1H, CH-N, $^3J_{H-H}$= 10.3 Hz, $^3J_{H-H}$= 6.3 Hz), 5.32 (m, 1H, CH=, cod), 6.00 (d, 1H, CH-OP, $^3J_{H-H}$= 21.3 Hz), 6.51 (dd, 2H, CH=, $^3J_{H-H}$= 11.7 Hz, $^3J_{H-H}$= 7.4 Hz), 6.74 (d, 2H, CH=, $^3J_{H-H}$= 7.3 Hz), 7.10-7.14 (m, 4H, CH=), 7.24-7.32 (m, 2H, CH=), 7.36-7.48 (m, 6H,

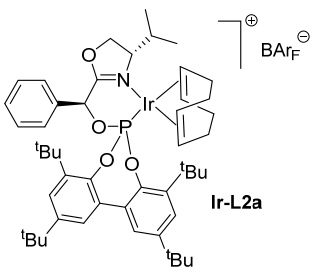


CH=), 7.49-7.69 (m, 14H, CH=), 7.97 (d, 2H, CH=, $^3J_{H-H}$= 6.5 Hz). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 27.4 (CH_2, cod), 30.3 (CH_2, cod), 30.9 (CH_2, cod), 34.0 (CH_2, cod), 61.2 (CH=, cod), 65.5 (CH=, cod), 69.3 (CH-N), 76.8 (CH-OP), 77.8 (CH_2-O), 97.4 (d, CH=, cod, J_{C-P}= 12.9 Hz), 98.7 (d, CH=, cod, J_{C-P}= 11.6 Hz), 117.5-137.6 (aromatic carbons), 161.7 (q, C-B, BAr_F, $^1J_{C-B}$= 49.8 Hz), 170.4 (d, C=N, $^3J_{C-P}$= 9.7 Hz) . MS HR-ESI [found 738.2109, $C_{36}H_{36}IrNO_2P$ $(M-BAr_F)^+$ requires 738.2107].

[Ir(cod)(L1g)]BAr$_F$: This compound was further purified by flash chromatography using neutral silica and dichloromethane as eluent. Yield: 56 mg (46%). Major isomer (55%): ^{31}P NMR (161.9 MHz, $CDCl_3$): δ = 115.8 (b). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.55-2.60 (m, 8H, CH_2, cod), 2.23 (s, 3H, CH_3, *o*-Tol), 2.31 (m, 1H, CH=, cod), 2.60 (s, 3H, CH_3, *o*-Tol), 3.15 (m, 1H, CH=, cod), 4.29 (m,1H, CH-O), 4.62 (m, 1H, CH-O), 4.91 (m, 1H, CH=, cod), 5.34 (m, 1H, CH-N), 5.58 (m, 2H, CH=, cod and CH-OP), 6.93-8.14 (m, 32H, CH=). ^{13}C (100.6 MHz, $CDCl_3$): δ = 21.4-22.7 (CH_3, *o*-Tol), 26.4-35.0 (CH_2, cod), 62.9 (CH=, cod), 65.9 (CH=, cod), 70.2 (CH-N), 75.3 (CH-OP), 77.7 (CH_2-O), 117.4-142.6 (aromatic carbons), 161.8 (q, C-B, BAr_F, $^1J_{C-B}$= 49.9 Hz), 170.0 (C=N). Minor isomer (45%): ^{31}P NMR (161.9 MHz, $CDCl_3$): δ = 115.8 (b). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.55-2.60 (m, 15H, CH_2, cod, CH_3, *o*-Tol and CH=, cod), 2.87 (m, 1H, CH=, cod), 4.36 (m, 1H, CH-O), 4.72 (m, 1H, CH-O), 4.95 (m, 1H, CH=, cod), 5.34 (m, 1H, CH-N), 5.58 (m, 1H, CH=, cod), 5.86 (m, 1H, CH-OP), 6.93-8.14 (m, 32H, CH=). ^{13}C (100.6 MHz, $CDCl_3$): δ = 21.4-22.7 (CH_3, *o*-Tol), 26.4-35.0 (CH_2, cod), 62.9 (CH=, cod), 65.9 (CH=, cod), 69.6 (CH-N), 75.3 (CH-OP), 78.3 (CH_2-O), 117.4-142.6 (aromatic carbons), 161.8 (q, C-B, BAr_F, $^1J_{C-B}$= 49.9 Hz), 174.0 (C=N). MS HR-ESI [found 766.2423, $C_{38}H_{40}IrNO_2P$ $(M-BAr_F)^+$ requires 766.2420].

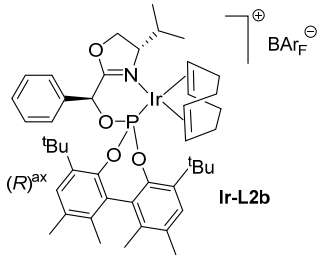


[Ir(cod)(L2a)]BAr$_F$: Yield: 63 mg (92%). ^{31}P NMR (161.9 MHz, $CDCl_3$): δ = 101.7 (s). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.90 (m, 6H, CH_3, ^{i}Pr), 1.04 (s, 9H, CH_3, ^{t}Bu), 1.29 (s, 9H, CH_3, ^{t}Bu), 1.36 (s, 9H, CH_3, ^{t}Bu), 1.57 (s, 9H, CH_3, ^{t}Bu), 1.71 (m, 2H, CH_2, cod), 2.05 (m, 1H, CH, ^{i}Pr), 2.06 (m, 3H, CH_2, cod), 2.26 (m, 1H, CH_2, cod), 2.39 (m, 2H, CH_2, cod), 3.29 (m, 1H,



CH=, cod), 3.85 (m, 1H, CH=, cod), 4.07 (m, 1H, CH-N), 4.21 (pt, 1H, CH-O, J_{H-H}= 9.6 Hz), 4.58 (dd, 1H, CH-O, $^2J_{H-H}$= 10.4 Hz, $^3J_{H-H}$= 3.2 Hz), 5.03 (m, 1H, CH=, cod), 5.59 (m, 1H, CH=, cod), 5.93 (d, 1H, CH-OP, $^3J_{H-P}$= 17.6 Hz), 7.08 (d, 1H, CH=, $^4J_{H-H}$= 2.4 Hz), 7.15 (d, 1H, CH=, $^4J_{H-H}$= 2.0 Hz), 7.38 (d, 1H, CH=, $^4J_{H-H}$= 2.4 Hz), 7.51 (m, 7H, CH=), 7.56 (d, 1H, CH=, $^4J_{H-H}$= 2.0 Hz), 7.70 (m, 10H, CH=). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 14.5 (CH_3, ^{i}Pr), 18.8 (CH_3, ^{i}Pr), 26.0 (CH_2, cod), 29.7 (CH_2, cod), 30.9 (CH_3, ^{t}Bu), 31.0 (CH, ^{i}Pr), 31.3 (CH_3, ^{t}Bu), 31.4 (CH_3, ^{t}Bu), 31.8 (CH_2, cod), 32.2 (CH_3, ^{t}Bu), 34.6 (C, ^{t}Bu), 34.7 (C, ^{t}Bu), 34.9 (C, ^{t}Bu), 35.2 (d, CH_2, cod, J_{C-P}= 7.08 Hz), 35.6 (C, ^{t}Bu), 64.2 (CH=, cod), 66.5 (CH=, cod), 70.7 (CH-N), 70.8 (CH_2-O), 76.2 (CH-OP), 98.7 (d, CH=, cod, J_{C-P}= 19.1 Hz), 104.7 (d, CH=, cod, J_{C-P}= 13.8 Hz), 117.4-149.1 (aromatic carbons), 161.8 (q, C-B, BAr_F, $^1J_{C-B}$= 49.7 Hz), 169.7 (C=N). MS HR-ESI [found 958.4517, $C_{49}H_{68}IrNO_4P$ $(M-BAr_F)^+$ requires 958.4515].

[Ir(cod)(L2b)]BAr_F: Yield: 59 mg (90%). ^{31}P NMR (161.9 MHz, $CDCl_3$): δ = 101.0 (s). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.91 (m, 6H, CH_3, ^{i}Pr), 0.98 (s, 9H, CH_3, ^{t}Bu), 1.58 (s, 9H, CH_3, ^{t}Bu), 1.73 (s, 3H, CH_3), 1.74 (s, 3H, CH_3), 1.75 (m, 2H, CH_2, cod), 2.09 (m, 1H, CH, ^{i}Pr), 2.09-2.16 (m, 4H, CH_2, cod), 2.17 (s, 3H, CH_3), 2.28 (s, 3H, CH_3), 2.43 (m, 2H, CH_2, cod), 3.24 (m, 1H, CH=, cod), 4.05 (m, 1H, CH=, cod), 4.06 (m, 1H, CH-N), 4.16 (pt, 1H, CH-O, J_{H-H}= 9.2 Hz), 4.55 (dd, 1H, CH-O, $^2J_{H-H}$= 10.0 Hz, $^3J_{H-H}$= 2.8 Hz), 4.87 (m, 1H, CH=, cod), 5.59 (m, 1H, CH=, cod), 5.83 (d, 1H, CH-OP, $^3J_{H-P}$= 12.8 Hz), 7.06 (s, 1H, CH=), 7.26 (s, 2H, CH=), 7.46 (m, 2H, CH=), 7.52 (s, 4H, CH=), 7.63 (m, 2H, CH=), 7.71 (s, 8H, CH=). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 14.6 (CH_3, ^{i}Pr), 16.4 (CH_3), 16.5 (CH_3), 18.8 (CH_3, ^{i}Pr), 20.2 (CH_3), 20.3 (CH_3), 25.4 (CH_2, cod), 29.1 (CH_2, cod), 31.0 (CH, ^{i}Pr), 31.3 (CH_3, ^{t}Bu), 32.4 (CH_3, ^{t}Bu), 32.6 (CH_2, cod), 34.4 (C, ^{t}Bu), 34.8 (C, ^{t}Bu), 35.9 (d, CH_2, cod, J_{C-P}= 5.4 Hz), 63.3 (CH=, cod), 67.4 (CH=, cod), 70.4 (CH-N), 70.7 (CH_2-O), 76.0 (CH-OP), 97.1 (d, CH=, cod, J_{C-P}= 19.9 Hz), 104.3 (d, CH=, cod, J_{C-P}= 13.8 Hz), 117.4-143.9 (aromatic carbons), 161.6 (q, C-B, BAr_F, $^1J_{C-B}$= 49.7 Hz), 169.0 (d, C=N, $^3J_{C-P}$= 8.3 Hz). MS HR-ESI [found 902.3892, $C_{45}H_{60}IrNO_4P$ $(M-BAr_F)^+$ requires 902.3889].

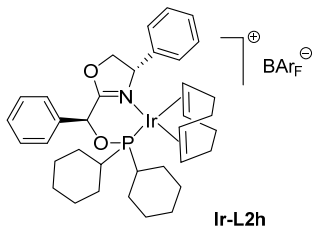


[Ir(cod)(L2f)]BAr$_F$: This compound was further purified by flash chromatography using neutral silica and dichloromethane as eluent. Yield: 64 mg (55%). Major isomer (74%): ^{31}P NMR (161.9 MHz, $CDCl_3$): δ = 110.7 (s). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.21 (d, 3H, CH_3, ^{i}Pr, $^3J_{H-H}$= 6.6 Hz), 0.83 (d, 3H, CH_3, ^{i}Pr, $^3J_{H-H}$= 7.0 Hz), 1.22-1.74 (m, 2H, CH_2, cod), 1.81-1.96 (m, 1H, CH_2, cod), 1.95-2.10 (m, 2H, CH_2, cod, CH, ^{i}Pr), 2.15-2.28 (m, 2H, CH_2, cod), 2.41-2.52 (m, 2H, CH_2, cod), 2.61 (m, CH=, cod), 3.50 (m, CH=, cod), 4.11 (m, 1H, CH-N), 4.29 (pt, 1H, CH-O, J_{H-H}= 9.7 Hz), 4.50 (m, 1H, CH-O), 5.08 (m, 1H, CH=, cod), 5.33 (m, 1H, CH=, cod), 5.91 (d, 1H, CH-OP, $^3J_{H-P}$= 21.0 Hz), 6.61-6.66 (m, 2H, CH=), 7.22-7.25 (m, 2H, CH=), 7.31-7.38 (m, 2H, CH=), 7.52 (s, 4H, CH=), 7.55-7.63 (m, 5H, CH=), 7.71 (s, 8H, CH=), 7.89-7.93 (m, 2H, CH=), 8.00 (d, 2H, CH=, $^3J_{H-H}$= 6.8 Hz). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 13.1 (CH_3, ^{i}Pr), 18.3 (CH_3, ^{i}Pr), 26.8 (CH_2, cod), 29.6 (CH_2, cod), 31.5 (CH_2, cod), 32.3 (CH, ^{i}Pr), 35.3 (CH_2, cod), 61.8 (CH=, cod), 65.3 (CH=, cod), 70.1 (CH-N), 70.4 (CH_2-O), 76.5 (d, CH-OP, $^2J_{C-P}$= 4.6 Hz), 97.8 (d, CH=, cod, J_{C-P}= 12.0 Hz), 98.0 (d, CH=, cod, J_{C-P}= 12.5 Hz), 117.5-134.8 (aromatic carbons), 161.7 (q, C-B, BAr$_F$, $^2J_{C-B}$= 49.9 Hz), 168.9 (d, C=N, J_{C-P}= 10.2 Hz). Minor isomer (26%): ^{31}P NMR (161.9 MHz, $CDCl_3$): δ = 109.8 (s). ^{1}H NMR (400 MHz, $CDCl_3$): δ =0.38 (d, 3H, CH_3, ^{i}Pr, $^3J_{H-H}$= 6.8 Hz), 0.84 (d, 3H, CH_3, ^{i}Pr, $^3J_{H-H}$= 6.9 Hz), 1.24-1.72 (m, 2H, CH_2, cod), 1.80-1.95 (m, 1H, CH_2, cod), 1.97-2.11 (m, 2H, CH_2, cod, CH, ^{i}Pr), 2.16-2.29 (m, 2H, CH_2, cod), 2.41-2.52 (m, 2H, CH_2, cod), 2.86 (m, CH=, cod), 3.67 (m, CH=, cod), 4.07 (m, 1H, CH=, cod), 4.11 (m, 1H, CH-N), 4.29 (m, 1H, CH-O), 4.45 (m, 1H, CH-O), 5.01 (m, 1H, CH=, cod), 6.04 (d, 1H, CH-OP, $^3J_{H-P}$= 8.7 Hz), 6.61-6.66 (m, 2H, CH=), 7.22-7.25 (m, 2H, CH=), 7.31-7.38 (m, 2H, CH=), 7.52 (s, 4H, CH=), 7.55-7.63 (m, 5H, CH=), 7.71 (s, 8H, CH=), 7.89-8.03 (m, 4H, CH=). MS HR-ESI [found 704.2272, $C_{33}H_{38}IrNO_2P$ (M-BAr$_F$)$^+$ requires 704.2269].

[Ir(cod)(L2g)]BAr$_F$: This compound was further purified by flash chromatography using neutral silica and dichloromethane as eluent. Yield: 45 mg (38%). Major isomer (63%): ^{31}P NMR (161.9 MHz, CD_2Cl_2, 233 K): δ = 117.3 (s). ^{1}H NMR (400 MHz, CD_2Cl_2, 233 K): δ = 0.35 (b, 3H, CH_3, ^{i}Pr), 0.89 (b, 3H, CH_3, ^{i}Pr), 1.28-2.60 (m, 8H, CH_2, cod and CH, ^{i}Pr), 2.24 (m, 1H, CH=,

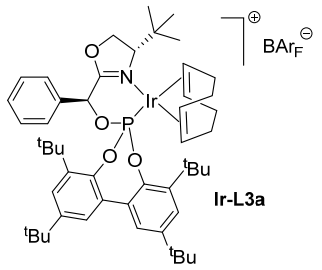
cod), 2.57 (s, 3H, CH_3, *o*-Tol), 2.73 (s, 3H. CH_3, *o*-Tol), 3.36 (m, 1H, CH=, cod), 4.14 (m, 1H, CH-O), 4.40 (b, 1H, CH-O), 4.46 (b, 1H, CH-N), 4.83 (m, 1H, CH=, cod), 5.60 (m, 1H, CH=, cod), 5.30 (b, 1H, CH-OP), 6.64-8.65 (m, 25H, CH=). ^{13}C NMR (100.6 MHz, CD_2Cl_2, rt): δ = 18.2 (CH_3, ^{i}Pr), 18.6 (CH_3, ^{i}Pr), 22.4 (CH_3, *o*-Tol), 25.6-36.5 (CH_2, cod and CH, ^{i}Pr), 63.3 (CH=, cod), 65.4 (CH=, cod), 70.3 (CH_2-O), 71.3 (CH-N), 75.1 (CH-OP), 95.7 (b, CH=, cod), 99.3 (b, CH=, cod), 117.4-142.7 (aromatic carbons), 171.9 (q, C-B, BAr_F, $^1J_{C\text{-}B}$= 49.8 Hz), 167.8 (C=N). Minor isomer (37%): ^{31}P NMR (161.9 MHz, CD_2Cl_2, 233 K): δ = 119.2 (s). ^{1}H NMR (400 MHz, CD_2Cl_2, 233 K): δ = 0.23 (b, 3H, CH_3, ^{i}Pr), 0.82 (b, 3H, CH_3, ^{i}Pr), 1.28-2.60 (m, 8H, CH_2, cod and CH, ^{i}Pr), 2.07 (s, 3H, CH_3, *o*-Tol), 2.12 (s, 3H. CH_3, *o*-Tol), 2.31 (m, 1H, CH=, cod), 3.22 (m, 1H, CH=, cod), 4.14 (m, 1H, CH-O), 4.34 (b, 1H, CH-O), 4.46 (b, 1H, CH-N), 5.02 (m, 1H, CH=, cod), 5.36 (m, 1H, CH=, cod), 6.01 (b, 1H, CH-OP), 6.56-8.61 (m, 25H, CH=). ^{13}C NMR (100.6 MHz, CD_2Cl_2, rt): δ = 13.0 (CH_3, ^{i}Pr), 13.8 (CH_3, ^{i}Pr), 22.0 (CH_3, *o*-Tol), 22.7 (CH_3, *o*-Tol), 25.6-36.5 (CH_2, cod and CH, ^{i}Pr), 63.3 (CH=, cod), 65.4 (CH=, cod), 70.7 (CH_2-O), 70.9 (CH-N), 75.1 (CH-OP), 95.7 (b, CH=, cod), 99.7 (b, CH=, cod), 117.4-142.7 (aromatic carbons), 171.9 (q, C-B, BAr_F, $^1J_{C\text{-}B}$= 49.8 Hz), 171.9 (C=N). MS HR-ESI [found 732.2585, $C_{35}H_{42}IrNO_2P$ $(M\text{-}BAr_F)^+$ requires 732.2582].

[Ir(cod)(L2h)]BAr$_F$: This compound was further purified by flash chromatography using neutral silica and dichloromethane as eluent. Yield: 65 mg (55%). ^{31}P NMR (161.9 MHz, $CDCl_3$): δ = 131.0 (s). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.25 (m, 1H, CH_2, Cy), 0.71-0.95 (m, 3H, CH_2, Cy), 0.75 (d, 3H, CH_3, ^{i}Pr, $^3J_{H\text{-}H}$= 6.6 Hz), 0.89 (d, 3H, CH_3, ^{i}Pr, $^3J_{H\text{-}H}$= 7.0 Hz), 0.96-1.36 (m, 10H, CH_2, Cy), 1.42-1.76 (m, 7H, CH_2, Cy, cod), 1.82-2.04 (m, 5H, CH_2, Cy, cod), 2.05-2.13 (m, 1H, CH, iPr), 2.20-2.38 (m, 4H, CH_2, CH, cod, Cy), 3.28 (m, CH=, cod), 3.78 (m, CH=, cod), 3.98 (m, CH-N), 4.19 (pt, CH-O, $J_{H\text{-}H}$= 9.6 Hz), 4.51 (dd, 1H, CH-O, $^2J_{H\text{-}H}$= 9.6 Hz, $^3J_{H\text{-}H}$= 3.2 Hz), 4.68 (m, CH=, cod), 5.07 (m, 1H, CH=, cod), 5.68 (d, 1H, CH-OP, $^3J_{H\text{-}P}$= 24.0 Hz), 7.34-7.40 (m, 4H, CH=), 7.41-7.43 (s, 2H, CH=), 7.56-7.68 (s, 11H, CH=). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 14.4 (CH_3, ^{i}Pr), 19.3 (CH_3, ^{i}Pr), 25.5-31.9 (CH_2, cod, Cy), 35.6 (CH, ^{i}Pr), 39.0 (d, CH, Cy, $^1J_{C\text{-}P}$= 30.3 Hz), 41.8 (d, CH, Cy, $^1J_{C\text{-}P}$= 34.4 Hz), 61.1 (CH=, cod), 61.5 (CH=, cod), 69.5 (CH-N), 70.5 (CH_2-O), 76.3 (d,

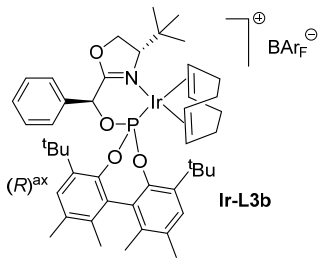


$^2J_{C\text{-}P}$= 5.9 Hz), 93.2 (d, CH=, cod, $J_{C\text{-}P}$= 11.7 Hz), 95.2 (d, CH=, cod, $J_{C\text{-}P}$= 11.2 Hz), 117.4-134.8 (aromatic carbons), 161.6 (q, C-B, BAr_F, $^1J_{C\text{-}B}$= 49.9 Hz), 169.8 (C=N). MS HR-ESI [found 716.3206, $C_{33}H_{50}IrNO_2P$ $(M\text{-}BAr_F)^+$ requires 716.3203].

[Ir(cod)(L3a)]BAr$_F$: Yield: 64 mg (94%). ^{31}P NMR (161.9 MHz, $CDCl_3$): δ = 103.2 (s). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.93 (s, 9H, CH_3, ^{t}Bu), 1.12 (s, 9H, CH_3, ^{t}Bu), 1.33 (s, 9H, CH_3, ^{t}Bu), 1.34 (s, 9H, CH_3, ^{t}Bu), 1.55 (s, 9H, CH_3, ^{t}Bu), 1.70 (m, 2H, CH_2, cod), 2.02 (m, 2H, CH_2, cod), 2.33 (m, 2H, CH_2, cod), 2.43 (m, 1H, CH_2, cod), 2.59 (m, 1H, CH_2, cod), 3.81 (m, 1H, CH=, cod), 4.04 (m, 1H, CH-N), 4.35 (pt, 1H, CH-O, $J_{H\text{-}H}$= 8.8 Hz), 4.72 (dd, 1H, CH-O, $^2J_{H\text{-}H}$= 10.0 Hz, $^3J_{H\text{-}H}$= 2.4 Hz), 5.00 (m, 1H, CH=, cod), 5.71 (m, 1H, CH=, cod), 5.83 (d, 1H, CH-OP, $^3J_{H\text{-}P}$= 20.8 Hz), 7.04 (d, 1H, CH=, $^4J_{H\text{-}H}$= 2.4 Hz), 7.17 (d, 2H, CH=, $^3J_{H\text{-}H}$= 7.6 Hz), 7.22 (d, 1H, CH=, $^4J_{H\text{-}H}$= 2.0 Hz), 7.29 (d, 1H, CH=, $^4J_{H\text{-}H}$= 2.0 Hz), 7.41 (t, 2H, CH=, $^3J_{H\text{-}H}$= 7.6 Hz), 7.47-7.52 (m, 4H, CH=), 7.71 (s, 8H, CH=). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 23.9 (CH_2, cod), 25.6 (CH_3, ^{t}Bu), 27.9 (CH_2, cod), 29.7 (CH_2, cod), 30.1 (CH_3, ^{t}Bu), 31.1 (CH_3, ^{t}Bu), 31.2 (CH_3, ^{t}Bu), 33.6 (CH_2, cod), 34.7 (C, ^{t}Bu), 34.8 (C, ^{t}Bu), 35.6 (C, ^{t}Bu), 36.9 (d, CH_2, cod, $J_{C\text{-}P}$= 6.8 Hz), 63.3 (CH=, cod), 67.4 (CH=, cod), 72.1 (CH_2-O), 74.5 (CH-N), 75.0 (CH-OP), 97.5 (d, CH=, cod, $J_{C\text{-}P}$= 22.2 Hz), 104.8 (d, CH=, cod, $J_{C\text{-}P}$= 12.1 Hz), 117.4-148.7 (aromatic carbons), 161.6 (q, C-B, BAr_F, $^1J_{C\text{-}B}$= 49.7 Hz), 169.6 (d, C=N, $^3J_{C\text{-}P}$= 7.6 Hz). MS HR-ESI [found 972.4675, $C_{50}H_{70}IrNO_4P$ $(M\text{-}BAr_F)^+$ requires 972.4672].

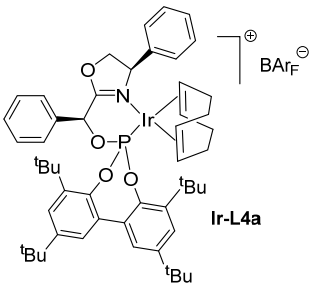


[Ir(cod)(L3b)]BAr$_F$: Yield: 60 mg (92%). ^{31}P NMR (161.9 MHz, $CDCl_3$): δ = 102.9 (s). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.95 (s, 9H, CH_3, ^{t}Bu), 1.11 (s, 9H, CH_3, ^{t}Bu), 1.58 (s, 9H, CH_3, ^{t}Bu), 1.65 (s, 3H, CH_3), 1.65 (m, 1H, CH_2, cod), 1.73 (m, 1H, CH_2, cod), 1.80 (s, 3H, CH_3), 1.99 (m, 1H, CH_2, cod), 2.15 (m, 1H, CH_2, cod), 2.23 (s, 3H, CH_3), 2.25 (s, 3H, CH_3), 2.26 (m, 1H, CH_2, cod), 2.43 (m, 2H, CH_2, cod), 2.54 (m, 1H, CH_2, cod), 3.98 (m, 1H, CH-N), 4.07 (m, 1H, CH=, cod), 4.16 (m, 1H, CH=, cod), 4.25 (pt, 1H, CH-O, $J_{H\text{-}H}$= 9.6 Hz), 4.64 (dd, 1H, CH-O, $^2J_{H\text{-}H}$= 10.0 Hz, $^3J_{H\text{-}H}$= 2.4 Hz), 4.92 (m, 1H, CH=, cod), 5.63 (m, 1H, CH=, cod), 5.74 (d, 1H, CH-OP, $^3J_{H\text{-}P}$= 12.4 Hz), 6.99 (s, 1H, CH=), 7.21 (s, 1H, CH=), 7.32 (m, 2H, CH=), 7.40-7.49 (m, 1H, CH=), 7.52 (s, 6H,

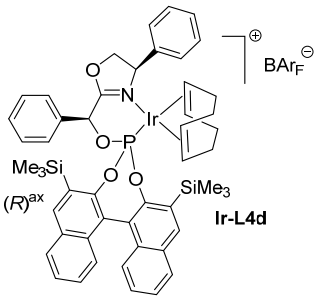


CH=), 7.71 (s, 8H, CH=). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 16.5 (CH_3), 16.6 (CH_3), 20.1 (CH_3), 20.3 (CH_3), 23.8 (CH_2, cod), 26.0 (CH_3, ^{t}Bu), 28.0 (CH_2, cod), 30.9 (CH_3, ^{t}Bu), 32.2 (CH_3, ^{t}Bu), 33.9 (CH_2, cod), 34.3 (C, ^{t}Bu), 34.6 (C, ^{t}Bu), 35.1 (C, ^{t}Bu), 37.0 (d, CH_2, cod, $J_{C\text{-}P}$= 7.6 Hz), 65.5 (CH=, cod), 66.9 (CH=, cod), 71.9 (CH_2-O), 74.7 (CH-N), 75.2 (d, CH-OP, $J_{C\text{-}P}$= 4.6 Hz), 95.5 (d, CH=, cod, $J_{C\text{-}P}$= 22.1 Hz), 103.5 (d, CH=, cod, $J_{C\text{-}P}$= 12.3 Hz), 117.4-145.1 (aromatic carbons), 161.6 (q, C-B, BAr_F, $^1J_{C\text{-}B}$= 49.7 Hz), 169.8 (d, C=N, $^3J_{C\text{-}P}$= 7.64 Hz). MS HR-ESI [found 916.4049, $C_{46}H_{62}IrNO_4P$ (M-BAr_F)$^+$ requires 916.4046].

[Ir(cod)(L4a)]BAr$_F$: Yield: 61 mg (92%). ^{31}P NMR (161.9 MHz, $CDCl_3$): δ = 101.5 (s). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.26 (s, 9H, CH_3, ^{t}Bu), 1.32 (s, 9H, CH_3, ^{t}Bu), 1.33 (s, 9H, CH_3, ^{t}Bu), 1.52 (s, 9H, CH_3, ^{t}Bu), 1.75-2.1 (m, 8H, CH_2, cod), 3.28 (m, 1H, CH=, cod), 3.61 (m, 1H, CH=, cod), 4.50 (dd, 1H, CH-O, $^2J_{H\text{-}H}$= 9.2 Hz, $^3J_{H\text{-}H}$= 3.6 Hz), 4.77 (pt, 1H, CH-O, $J_{H\text{-}H}$= 10.0 Hz), 5.13 (m, 1H, CH=, cod), 5.18 (m, 1H, CH-N), 5.26 (m, 1H, CH=, cod), 6.22 (d, 1H, CH-OP, $^3J_{H\text{-}P}$= 8.4 Hz), 6.97 (d, 1H, CH=, $^3J_{H\text{-}H}$= 7.6 Hz), 7.13 (m, 3H, CH=), 7.36-7.52 (m, 10H, CH=), 7.60 (d, 1H, CH=, $^3J_{H\text{-}H}$= 6.4 Hz), 7.72 (m, 9H, CH=). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 28.3 (CH_2, cod), 29.1 (CH_2, cod), 29.7 (CH_2, cod), 31.2 (CH_3, ^{t}Bu), 31.4 (CH_3, ^{t}Bu), 31.6 (CH_3, ^{t}Bu), 31.7 (CH_2, cod), 34.7 (C, ^{t}Bu), 35.3 (C, ^{t}Bu), 35.4 (C, ^{t}Bu), 63.5 (CH=, cod), 66.2 (CH=, cod), 70.8 (CH-N), 74.6 (CH-OP), 79.5 (CH_2-O), 103.4 (d, CH=, cod, $J_{C\text{-}P}$= 15.3 Hz), 104.9 (d, CH=, cod, $J_{C\text{-}P}$= 12.2 Hz), 117.4-149.0 (aromatic carbons), 161.6 (q, C-B, BAr_F, $^1J_{C\text{-}B}$= 50.5 Hz), 172.5 (C=N). MS HR-ESI [found 992.4361, $C_{52}H_{66}IrNO_4P$ (M-BAr_F)$^+$ requires 992.4359].

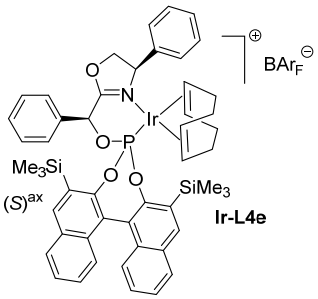


[Ir(cod)(L4d)]BAr$_F$: Yield: 62 mg (94%). ^{31}P NMR (161.9 MHz, $CDCl_3$): δ = 107.2 (s). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.30 (s, 9H, CH_3, $SiMe_3$), 0.66 (s, 9H, CH_3, $SiMe_3$), 1.56 (m, 1H, CH_2, cod), 1.69 (m, 1H, CH_2, cod), 1.96-2.17 (m, 6H, CH_2, cod), 3.08 (m, 1H, CH=, cod), 3.85 (m, 1H, CH=, cod), 4.41 (dd, 1H, CH-O, $^2J_{H\text{-}H}$= 8.8 Hz, $^3J_{H\text{-}H}$= 3.2 Hz), 4.80 (pt, 1H, CH-O, $J_{H\text{-}H}$= 9.2 Hz), 4.93 (m, 1H, CH=, cod), 5.10 (m, 1H, CH=, cod), 5.33 (m, 1H, CH-N), 5.97 (d, 1H, CH-OP, $^3J_{H\text{-}P}$= 4.4 Hz), 6.91 (d, 2H, CH=, $^3J_{H\text{-}H}$= 7.6 Hz), 6.96 (d, 1H, CH=, $^3J_{H\text{-}H}$= 8.8 Hz), 7.07 (d, 1H, CH=, $^3J_{H\text{-}H}$= 8.0 Hz), 7.22-

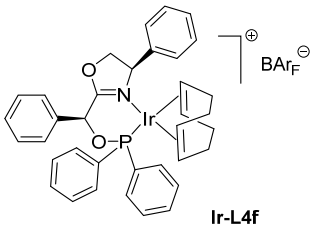


7.56 (m, 14H, CH=), 7.62 (d, 1H, CH=, $^3J_{H-H}$= 6.0 Hz), 7.71 (s, 8H, CH=), 7.89 (d, 1H, CH=, $^3J_{H-H}$= 8.0 Hz), 8.00 (d, 1H, CH=, $^3J_{H-H}$= 8.0 Hz), 8.03 (s, 1H, CH=), 8.22(s, 1H, CH=). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 0.1 (CH_3, $SiMe_3$), 1.2 (CH_3, $SiMe_3$), 26.1 (CH_2, cod), 28.9 (CH_2, cod), 32.1 (CH_2, cod), 35.0 (CH_2, cod), 61.4 (CH=, cod), 66.8 (CH=, cod), 72.5 (CH-N), 74.6 (CH-OP), 78.6 (CH_2-O), 103.3 (d, CH=, cod, J_{C-P}= 18.3 Hz), 104.9 (d, CH=, cod, J_{C-P}= 13.7 Hz), 117.4-150.2 (aromatic carbons), 161.6 (q, C-B, BAr_F, $^1J_{C-B}$= 49.7 Hz), 172.0 (d, C=N, $^3J_{C-P}$= 7.6 Hz). MS HR-ESI [found 1012.2960, $C_{50}H_{54}IrNO_4PSi2$ $(M-BAr_F)^+$ requires 1012.2958].

[Ir(cod)(L4e)]BAr$_F$: Yield: 64 mg (96%). ^{31}P NMR (161.9 MHz, $CDCl_3$): δ = 105.8 (s). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.48 (s, 9H, CH_3, $SiMe_3$), 0.71 (s, 9H, CH_3, $SiMe_3$), 1.91 (m, 1H, CH_2, cod), 2.04 (m, 1H, CH_2, cod), 2.37 (m, 4H, CH_2, cod), 2.49 (m, 1H, CH_2, cod), 2.51 (m, 1H, CH_2, cod), 3.11 (m, 1H, CH=, cod), 4.27 (m, 1H, CH=, cod), 4.75 (m, 1H, CH-O), 5.00 (pt, 1H, CH-O, J_{H-H}= 10.0 Hz), 5.40 (m, 1H, CH-N), 5.75 (m, 1H, CH=, cod), 5.81 (m, 1H, CH=, cod), 6.66 (d, 1H, CH-OP, $^3J_{H-P}$= 6.8 Hz), 7.19 (t, 2H, CH=, $^3J_{H-H}$= 9.6 Hz), 7.32 (d, 2H, CH=, $^3J_{H-H}$= 6.8 Hz), 7.48 (m, 3H, CH=), 7.62-7.79 (m, 13H, CH=), 7.98 (s, 8H, CH=), 8.11 (d, 1H, CH=, $^3J_{H-H}$= 8.0 Hz), 8.18 (d, 1H, CH=, $^3J_{H-H}$= 8.0 Hz), 8.25 (s, 1H, CH=), 8.34 (s, 1H, CH=). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 0.5 (CH_3, $SiMe_3$), 0.6 (CH_3, $SiMe_3$), 26.4 (CH_2, cod), 30.1 (CH_2, cod), 30.6 (CH_2, cod), 34.3 (d, CH_2, cod, J_{C-P}= 7.4 Hz), 61.3 (CH=, cod), 68.6 (CH=, cod), 69.8 (CH-N), 74.6 (CH-OP), 78.8 (CH_2-O), 102.5 (d, CH=, cod, J_{C-P}= 18.3 Hz), 107.5 (d, CH=, cod, J_{C-P}= 14.4 Hz), 117.5-149.9 (aromatic carbons), 161.6 (q, C-B, BAr_F, $^1J_{C-B}$= 49.7 Hz), 172.4 (C=N). MS HR-ESI [found 1012.2962, $C_{50}H_{54}IrNO_4PSi_2$ $(M-BAr_F)^+$ requires 1012.2958].

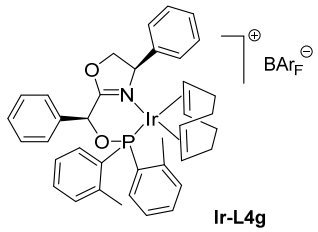


[Ir(cod)(L4f)]BAr$_F$: This compound was further purified by flash chromatography using neutral silica and dichloromethane as eluent. Yield: 48 mg (40%). Major isomer (78%): ^{31}P NMR (161.9 MHz, $CDCl_3$): δ = 111.1 (s). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.67-1.90 (m, 2H, CH_2, cod), 2.04-2.12 (m, 4H, CH_2, cod), 2.27-2.36 (m, 2H, CH_2, cod), 2.95 (m, 1H, CH=, cod), 3.36 (m, CH=, cod), 4.38 (m, 1H, CH-O), 4.78 (m, 1H, CH-O), 5.01 (m, 1H, CH=, cod),



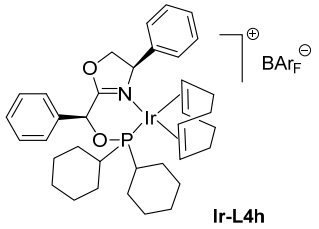
5.27 (m, 1H, CH-N), 5.34 (m, 1H, CH=, cod), 6.10 (d, 1H, CH-OP, $^{3}J_{C\text{-}P}$= 9.0 Hz), 6.91 (d, 2H, CH=, $^{3}J_{H\text{-}H}$= 7.5 Hz), 7.19-7.27 (m, CH=, 3H), 7.30-7.40 (m, 4H, CH=), 7.43-7.50 (m, 7H, CH=), 7.53 (s, 4H, CH=), 7.59-7.64 (m, 4H, CH=), 7.73 (s, 8H, CH=). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 27.5 (CH_2, cod), 29.7 (CH_2, cod), 30.5 (CH_2, cod), 33.6 (CH_2, cod), 62.6 (CH=, cod), 65.5 (CH=, cod), 69.1 (CH-N), 77.2 (CH-OP), 78.6 (CH_2-O), 99.0 (d, CH=, cod, $J_{C\text{-}P}$= 11.9 Hz), 100.3 (d, CH=, cod, $J_{C\text{-}P}$= 12.0 Hz), 117.4-137.8 (aromatic carbons), 161.6 (q, C-B, BAr_F, $^{1}J_{C\text{-}B}$= 49.6 Hz), 173.5 (C=N). Minor isomer (22%): ^{31}P NMR (161.9 MHz, $CDCl_3$): δ = 111.2 (s). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.66-1.92 (m, 4H, CH_2, cod), 2.04-2.12 (m, 2H, CH_2, cod), 2.27-2.36 (m, 2H, CH_2, cod), 2.61 (m, 1H, CH=, cod), 3.31 (m, CH=, cod), 4.43 (m, 1H, CH-O), 4.78 (m, 1H, CH-O), 5.20 (m, 1H, CH=, cod), 5.27 (m, 1H, CH-N), 5.40 (m, 1H, CH=, cod), 6.10 (m, 1H, CH-OP), 6.57-6.62 (m, 2H, CH=), 6.83 (d, 2H, CH=, $^{3}J_{H\text{-}H}$= 7.3 Hz), 7.19-7.27 (m, CH=, 2H), 7.30-7.40 (m, 3H, CH=), 7.43-7.50 (m, 6H, CH=), 7.53 (s, 4H, CH=), 7.59-7.64 (m, 4H, CH=), 7.73 (s, 8H, CH=), 8.07 (d, 1H, CH=, $^{3}J_{H\text{-}H}$= 7.0 Hz). MS HR-ESI [found 738.2111, $C_{36}H_{36}IrNO_2P$ $(M\text{-}BAr_F)^+$ requires 738.2107].

[Ir(cod)(L4g)]BAr$_F$: This compound was further purified by flash chromatography using neutral silica and dichloromethane as eluent. Yield: 52 mg (43%). Major isomer (57%): ^{31}P NMR (161.9 MHz, CD_2Cl_2): δ = 116.4 (b). ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 1.58-2.63 (m, 8H, CH_2, cod), 2.28 (s, 3H, CH_3, *o*-Tol), 2.42 (m, 1H, CH=, cod), 2.64 (s, 3H, CH_3, *o*-Tol), 3.21 (m, 1H, CH=, cod), 4.39 (m,1H, CH-O), 4.67 (m, 1H, CH-O), 4.95 (m, 1H, CH=, cod), 5.38 (m, 1H, CH-N), 5.66 (m, 2H, CH=, cod and CH-OP), 6.75-8.12 (m, 32H, CH=). ^{13}C (100.6 MHz, CD_2Cl_2): δ = 21.3-22.6 (CH_3, *o*-Tol), 25.9-35.2 (CH_2, cod), 63.0 (CH=, cod), 64.7 (CH=, cod), 70.2 (CH-N), 75.1 (CH-OP), 77.9 (CH_2-O), 117.5-142.7 (aromatic carbons), 161.7 (q, C-B, BAr_F, $^{1}J_{C\text{-}B}$= 49.9 Hz), 170.6 (C=N). Minor isomer (43%): ^{31}P NMR (161.9 MHz, CD_2Cl_2): δ = 116.4 (b). ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 1.58-2.63 (m, 15H, CH_2, cod, CH_3, *o*-Tol and CH=, cod), 2.96 (m, 1H, CH=, cod), 4.42 (m, 1H, CH-O), 4.79 (m, 1H, CH-O), 5.01 (m, 1H, CH=, cod), 5.38 (m, 1H, CH-N), 5.48 (m, 1H, CH=, cod), 5.93 (m, 1H, CH-OP), 6.75-8.12 (m, 32H, CH=). ^{13}C (100.6 MHz, CD_2Cl_2): δ = 21.3-22.6 (CH_3, *o*-Tol), 25.9-35.2 (CH_2, cod), 63.0 (CH=, cod), 64.7 (CH=, cod), 69.6 (CH-N), 75.1 (CH-OP), 78.7 (CH_2-O), 117.5-142.7

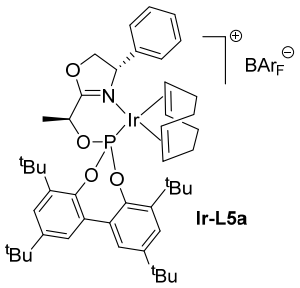


(aromatic carbons), 161.7 (q, C-B, BAr_F, $^1J_{C-B}$= 49.9 Hz), 173.3 (C=N). MS HR-ESI [found 766.2423, $C_{38}H_{40}IrNO_2P$ $(M-BAr_F)^+$ requires 766.2420].

[Ir(cod)(L4h)]BAr$_F$: This compound was further purified by flash chromatography using neutral silica and dichloromethane as eluent. Yield: 66 mg (55%). ^{31}P NMR (161.9 MHz, $CDCl_3$): δ = 132.6 (s). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.83-0.94 (m, 2H, CH_2, Cy), 1.06-1.52 (m, 12H, CH_2, cod, Cy), 1.65-1.94 (m, 10H, CH_2, cod, Cy), 2.10-2.41 (m, 6H, CH_2, CH, cod, Cy), 3.53 (m, 1H, CH=, cod), 3.67 (m, 1H, CH=, cod), 4.61 (dd, 1H, CH-O, $^2J_{H-H}$= 9.7 Hz, $^3J_{H-H}$= 4.9 Hz), 4.76 (pt, 1H, CH-O, J_{H-H}= 9.7 Hz), 5.04-5.16 (m, 2H, CH=, cod), 5.19 (dd, 1H, CH-N, $^3J_{H-H}$= 9.7 Hz, $^3J_{H-H}$= 4.9 Hz), 5.80 (d, 1H, CH-OP, $^3J_{C-P}$= 9.3 Hz), 7.17-7.20 (m, 1H, CH=), 7.40-7.45 (m, 2H, CH=), 7.46-7.50 (m, 2H, CH=), 7.55 (s, 3H, CH=), 7.75 (s, 6H, CH=). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 25.6-26.9 (CH_2), 28.6 (CH_2), 28.7 (CH_2), 29.7 (CH_2), 30.1 (CH_2), 30.8 (CH_2), 34.2 (CH_2), 40.71 (d, CH, Cy, J_{C-P}= 36.3 Hz), 39.2 (d, CH, Cy, J_{C-P}= 27.0 Hz), 60.6 (CH=, cod), 62.6 (CH=, cod), 68.6 (CH-N), 77.1 (d, CH-OP, $^2J_{C-P}$= 3.1 Hz), 78.2 (CH_2-O), 95.8 (d, CH=, cod, J_{C-P}= 12.0 Hz), 96.9 (d, CH=, cod, J_{C-P}= 11.2 Hz), 117.4-137.7 (aromatic carbons), 161.7 (q, C-B, BAr_F, $^1J_{C-B}$= 49.8 Hz), 173.7 (C=N). MS HR-ESI [found 750.3049, $C_{36}H_{48}IrNO_2P$ $(M-BAr_F)^+$ requires 750.3046].

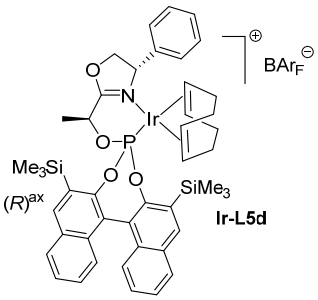


[Ir(cod)(L5a)]BAr$_F$: Yield: 64 mg (96%). ^{31}P NMR (161.9 MHz, $CDCl_3$): δ = 103.4 (s). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.35 (s, 9H, CH_3, ^{t}Bu), 1.37 (s, 9H, CH_3, ^{t}Bu), 1.48 (s, 9H, CH_3, ^{t}Bu), 1.61 (s, 9H, CH_3, ^{t}Bu), 1.74 (d, 3H, CH_3, $^3J_{H-H}$= 6.8 Hz), 1.75-2.06 (m, 8H, CH_2, cod), 3.17 (m, 1H, CH=, cod), 3.76 (m, 1H, CH=, cod), 4.58 (dd, 1H, CH-O, $^2J_{H-H}$= 9.2 Hz, $^3J_{H-H}$= 4.0 Hz), 4.71 (m, 1H, CH=, cod), 4.90 (pt, 1H, CH-O, J_{H-H}= 9.2 Hz), 5.17 (m, 1H, CH-N), 5.18 (m, 1H, CH=, cod), 5.55 (m, 1H, CH-OP), 7.17 (m, 4H, CH=), 7.40 (m, 3H, CH=), 7.53 (m, 6H, CH=), 7.32 (s, 8H, CH=). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 17.1 (d, CH_3, $^3J_{C-P}$= 9.9 Hz), 28.2 (CH_2, cod), 29.4 (CH_2, cod), 31.2 (CH_2, cod), 31.2 (CH_3, ^{t}Bu), 31.3 (CH_3, ^{t}Bu), 32.1 (CH_3, ^{t}Bu), 32.5 (CH_2, cod), 34.7 (C, ^{t}Bu), 34.8 (C, ^{t}Bu), 35.4 (C, ^{t}Bu), 35.6 (C, ^{t}Bu), 62.0 (CH=, cod), 67.5 (CH=, cod), 69.2 (CH-OP), 71.4 (CH-N), 79.4 (CH_2-O), 103.9 (CH=, cod) 117.4-149.3 (aromatic

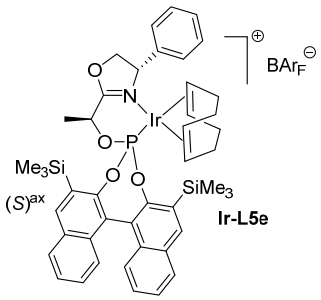


carbons), 161.6 (q, C-B, BAr_F, $^1J_{C-B}$= 49.7 Hz), 174.4 (C=N). MS HR-ESI [found 930.4205, $C_{47}H_{64}IrNO_4P$ $(M-BAr_F)^+$ requires 930.4202].

[Ir(cod)(L5d)]BAr_F: Yield: 63 mg (94%). ^{31}P NMR (161.9 MHz, $CDCl_3$): δ = 107.2 (s). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.48 (s, 9H, CH_3, $SiMe_3$), 0.51 (s, 9H, CH_3, $SiMe_3$), 1.62 (d, 3H, CH_3, $^3J_{H-H}$= 6.4 Hz), 1.63 (m, 2H, CH_2, cod), 1.72 (m, 1H, CH_2, cod), 1.92 (m, 2H, CH_2, cod), 2.05 (m, 1H, CH_2, cod), 2.17 (m, 1H, CH_2, cod), 2.34 (m, 1H, CH_2, cod), 3.14 (m, 1H, CH=, cod), 4.03 (m, 1H, CH=, cod), 4.44 (dd, 1H, CH-O, $^2J_{H-H}$= 9.6 Hz, $^3J_{H-H}$= 4.8 Hz), 4.84 (m, 2H, CH-O, CH=, cod), 5.20 (m, 1H, CH-OP), 5.38 (m, 1H, CH-N), 5.75 (m, 1H, CH=, cod), 6.98 (d, 1H, CH=, $^3J_{H-H}$= 8.4 Hz), 7.04 (d, 1H, CH=, $^3J_{H-H}$= 8.8 Hz), 7.11 (d, 2H, CH=, $^3J_{H-H}$= 8.4 Hz), 7.26 (t, 3H, CH=, $^3J_{H-H}$= 6.4 Hz), 7.44-7.52 (m, 8H, CH=), 7.71 (s, 8H, CH=), 7.93 (d, 1H, CH=, $^3J_{H-H}$= 8.0 Hz), 7.96 (d, 1H, CH=, $^3J_{H-H}$= 8.0 Hz), 8.10 (s, 1H, CH=), 8.13 (s, 1H, CH=). ^{13}C (100.6 MHz, $CDCl_3$): δ = 0.2 (CH_3, $SiMe_3$), 1.3 (CH_3, $SiMe_3$), 19.3 (d, CH_3, $^3J_{C-P}$= 6.8 Hz), 26.3 (CH_2, cod), 29.4 (CH_2, cod), 31.4 (CH_2, cod), 34.7 (CH_2, cod), 60.9 (CH=, cod), 66.4 (CH=, cod), 68.2 (CH-OP), 71.2 (CH-N), 78.4 (CH_2-O), 101.8 (d, CH=, cod, J_{C-P}= 18.3 Hz), 106.7 (d, CH=, cod, J_{C-P}= 15.3 Hz), 117.4-150.3 (aromatic carbons), 161.6 (q, C-B, BAr_F, $^1J_{C-B}$= 50.5 Hz), 173.4 (d, C=N, $^3J_{C-P}$= 7.6 Hz). MS HR-ESI [found 950.2804, $C_{45}H_{52}IrNO_4PSi_2$ $(M-BAr_F)^+$ requires 950.2802].

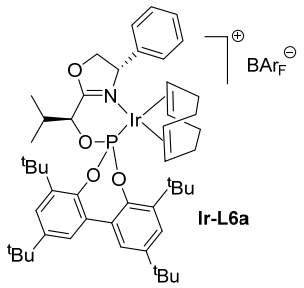


[Ir(cod)(L5e)]BAr_F: Yield: 61 mg (92%). ^{31}P NMR (161.9 MHz, $CDCl_3$): δ = 109.1 (s). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.50 (s, 9H, CH_3, $SiMe_3$), 0.64 (s, 9H, CH_3, $SiMe_3$), 1.66 (m, 1H, CH_2, cod), 1.73 (d, 3H, CH_3, $^3J_{H-H}$= 6.8 Hz), 1.81 (m, 1H, CH_2, cod), 1.92 (m, 5H, CH_2, cod), 2.06 (m, 1H, CH_2, cod), 3.05 (m, 1H, CH=, cod), 3.97 (m, 1H, CH=, cod), 4.60 (dd, 1H, CH-O, $^2J_{H-H}$= 9.2 Hz, $^3J_{H-H}$= 4.0 Hz), 4.91 (m, 2H, CH-O, CH=, cod), 5.18 (m, 1H, CH=, cod), 5.28 (m, 1H, CH-N), 5.47 (m, 1H, CH-OP), 6.96 (d, 1H, CH=, $^3J_{H-H}$= 8.8 Hz), 7.03 (d, 1H, CH=, $^3J_{H-H}$= 8.4 Hz), 7.18 (m, 2H, CH=), 7.25 (m, 2H, CH=), 7.46-7.52 (m, 6H, CH=), 7.72 (s, 9H, CH=), 7.95 (d, 1H, CH=, $^3J_{H-H}$= 8.0 Hz), 7.97 (d, 1H, CH=, $^3J_{H-H}$= 8.0 Hz), 8.13 (s, 1H, CH=), 8.18 (s, 1H, CH=). ^{13}C (100.6 MHz, $CDCl_3$): δ = 0.0 (CH_3, $SiMe_3$), 1.2 (CH_3, $SiMe_3$), 18.2 (d, CH_3, $^3J_{C-P}$= 7.6 Hz),

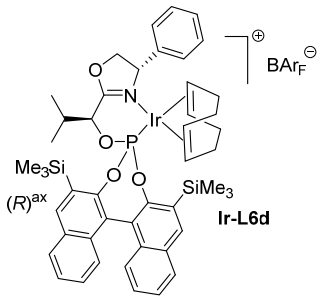


27.5 (CH_2, cod), 29.7 (CH_2, cod), 29.8 (CH_2, cod), 33.2 (CH_2, cod), 60.7 (CH=, cod), 69.2 (CH=, cod), 69.8 (CH-OP), 71.3 (CH-N), 79.2 (CH_2-O), 104.6 (d, CH=, cod, $J_{C\text{-}P}$= 17.5 Hz), 105.7 (d, CH=, cod, $J_{C\text{-}P}$= 14.4 Hz), 117.4-150.6 (aromatic carbons), 161.6 (q, C-B, BAr_F, $^1J_{C\text{-}B}$= 49.7 Hz), 174.2 (C=N). MS HR-ESI [found 950.2805, $C_{45}H_{52}IrNO_4PSi_2$ $(M\text{-}BAr_F)^+$ requires 950.2802].

[Ir(cod)(L6a)]BAr$_F$: Yield: 65 mg (96%). ^{31}P NMR (161.9 MHz, $CDCl_3$): δ = 104.1 (s). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.57 (d, 3H, CH_3, ^{i}Pr, $^3J_{H\text{-}H}$= 6.8 Hz), 0.89 (d, 3H, CH_3, ^{i}Pr, $^3J_{H\text{-}H}$= 6.8 Hz), 1.35 (s, 18H, CH_3, ^{t}Bu), 1.59 (s, 9H, CH_3, ^{t}Bu), 1.67 (s, 9H, CH_3, ^{t}Bu), 1.70 (m, 3H, CH_2, cod) 1.89 (m, 1H, CH_2, cod), 2.17 (m, 3H, CH_2, cod), 2.30 (m, 1H, CH_2, cod), 2.40 (m, 1H, CH, ^{i}Pr), 3.97 (m, 2H, CH=, cod), 4.48 (dd, 1H, CH-O, $^2J_{H\text{-}H}$= 8.8 Hz, $^3J_{H\text{-}H}$= 4.4 Hz), 4.63 (m, 1H, CH=, cod), 4.84 (pt, 1H, CH-O, $J_{H\text{-}H}$= 9.6 Hz), 4.90 (m, 1H, CH-OP), 5.34 (dd, 1H, CH-N, $^2J_{H\text{-}H}$= 9.6 Hz, $^3J_{H\text{-}H}$= 4.4 Hz), 5.65 (m, 1H, CH=, cod), 7.14-7.25 (m, 3H, CH=), 7.405-7.52 (m, 9H, CH=), 7.71 (s, 8H, CH=). ^{13}C (100.6 MHz, $CDCl_3$): δ = 15.8 (CH_3, ^{i}Pr), 17.6 (CH_3, ^{i}Pr), 26.1 (CH_2, cod), 29.4 (CH_2, cod), 31.1 (CH_2, cod), 31.2 (CH_3, ^{t}Bu), 31.3 (CH_3, ^{t}Bu), 31.4 (CH_3, ^{t}Bu), 34.5 (CH_2, cod), 34.6 (CH, ^{i}Pr), 34.7 (C, ^{t}Bu), 34.8 (C, ^{t}Bu), 35.3 (C, ^{t}Bu), 35.6 (C, ^{t}Bu), 63.9 (CH=, cod), 64.0 (CH=, cod), 70.4 (CH-N), 75.9 (CH-OP), 78.9 (CH_2-O), 101.4 (d, CH=, cod, $J_{C\text{-}P}$= 18.3 Hz), 105.4 (d, CH=, cod, $J_{C\text{-}P}$= 14.4 Hz), 117.4-149.1 (aromatic carbons), 161.6 (q, C-B, BAr_F, $^1J_{C\text{-}B}$= 50.5 Hz), 173.0 (C=N). MS HR-ESI [found 958.4518, $C_{49}H_{68}IrNO_4P$ $(M\text{-}BAr_F)^+$ requires 958.4515].

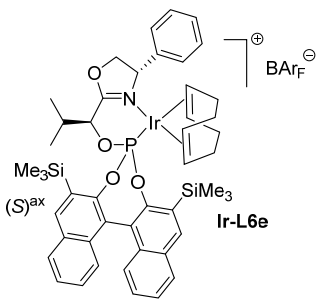


[Ir(cod)(L6d)]BAr$_F$: Yield: 64 mg (95%). ^{31}P NMR (161.9 MHz, $CDCl_3$): δ = 108.8 (s). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.28 (d, 3H, CH_3, ^{i}Pr, $^3J_{H\text{-}H}$= 6.8 Hz), 0.55 (s, 18H, CH_3, $SiMe_3$), 0.84 (d, 3H, CH_3, ^{i}Pr, $^3J_{H\text{-}H}$= 7.2 Hz), 1.64 (m, 4H, CH_2, cod), 2.08 (m, 2H, CH_2, cod), 2.20 (m, 1H, CH_2, cod), 2.35 (m, 1H, CH_2, cod), 2.40 (m, 1H, CH, ^{i}Pr), 3.52 (m, 1H, CH=, cod), 4.08 (m, 1H, CH=, cod), 4.47 (dd, 1H, CH-O, $^2J_{H\text{-}H}$= 9.2 Hz, $^3J_{H\text{-}H}$= 4.4 Hz), 4.75 (m, 1H, CH=, cod), 4.87 (m, 2H, CH-O, CH-OP), 5.38 (m, 1H, CH-N), 5.85 (m, 1H, CH=, cod), 6.98 (t, 2H, CH=, $^3J_{H\text{-}H}$= 9.2 Hz), 7.11 (m, 2H, CH=), 7.25 (m, 3H, CH=), 7.45-7.52 (m, 8H, CH=), 7.71 (s, 8H, CH=), 7.94 (m, 2H, CH=), 8.11 (s, 1H,



CH=), 8.14 (s, 1H, CH=). ^{13}C (100.6 MHz, $CDCl_3$): δ = 0.1 (CH_3, $SiMe_3$), 1.0 (CH_3, $SiMe_3$), 15.8 (CH_3, ^{i}Pr), 17.8 (CH_3, iPr), 25.9 (CH_2, cod), 29.2 (CH_2, cod), 30.6 (d, CH, ^{i}Pr, $^{3}J_{C\text{-}P}$= 6.8 Hz), 31.7 (CH_2, cod), 35.0 (CH_2, cod), 61.2 (CH=, cod), 65.5 (CH=, cod), 70.5 (CH-N), 75.2 (CH-OP), 78.4 (CH_2-O), 101.7 (d, CH=, cod, $J_{C\text{-}P}$= 19.1 Hz), 106.7 (d, CH=, cod, $J_{C\text{-}P}$= 13.6 Hz), 117.4-151.1 (aromatic carbons), 161.6 (q, C-B, BAr_F, $^{1}J_{C\text{-}B}$= 50.4 Hz), 173.4 (C=N). MS HR-ESI [found 978.3119, $C_{47}H_{56}IrNO_4PSi_2$ $(M\text{-}BAr_F)^+$ requires 978.3115].

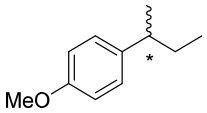
[Ir(cod)(L6e)]BAr$_F$: Yield: 63 mg (93%). ^{31}P NMR (161.9 MHz, $CDCl_3$): δ = 108.9 (s). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.51 (s, 9H, CH_3, $SiMe_3$), 0.64 (s, 9H, CH_3, $SiMe_3$), 0.95 (d, 3H, CH_3, ^{i}Pr, $^{3}J_{H\text{-}H}$= 6.4 Hz), 1.00 (d, 3H, CH_3, ^{i}Pr, $^{3}J_{H\text{-}H}$= 6.4 Hz), 1.85 (m, 5H, CH_2, cod), 2.00 (m, 2H, CH_2, cod), 2.14 (m, 1H, CH_2, cod), 2.45 (m, 1H, CH, ^{i}Pr), 3.33 (m, 1H, CH=, cod), 4.02 (m, 1H, CH=, cod), 4.62 (dd, 1H, CH-O, $^{2}J_{H\text{-}H}$= 9.2 Hz, $^{3}J_{H\text{-}H}$= 4.4 Hz), 4.92 (m, 3H, CH=, cod, CH-O, CH-OP), 5.29 (m, 2H, CH-N, CH=, cod), 6.99 (m, 2H, CH=), 7.26 (m, 4H, CH=), 7.42-7.53 (m, 9H, CH=), 7.73 (s, 8H, CH=), 7.96 (m, 2H, CH=), 8.13 (s, 1H, CH=), 8.16 (s, 1H, CH=). ^{13}C (100.6 MHz, $CDCl_3$): δ = 0.1 (CH_3, $SiMe_3$), 1.0 (CH_3, $SiMe_3$), 18.3 (CH_3, ^{i}Pr), 18.3 (CH_3, ^{i}Pr), 28.1 (CH_2, cod), 29.3 (CH_2, cod), 31.4 (CH_2, cod), 32.2 (d, CH, ^{i}Pr, $^{3}J_{C\text{-}P}$= 6.1 Hz), 32.6 (CH_2, cod), 60.6 (CH=, cod), 69.1 (CH=, cod), 71.0 (CH-N), 78.2 (CH_2-O), 78.6 (CH-OP), 104.6 (d, CH=, cod, $J_{C\text{-}P}$= 16.9 Hz), 105.4 (d, CH=, cod, $J_{C\text{-}P}$= 14.6 Hz), 117.4-150.2 (aromatic carbons), 161.6 (q, C-B, BAr_F, $^{1}J_{C\text{-}B}$= 49.7 Hz), 173.6 (d, C=N, $^{3}J_{C\text{-}P}$= 6.1 Hz). MS HR-ESI [found 978.3118, $C_{47}H_{56}IrNO_4PSi_2$ $(M\text{-}BAr_F)^+$ requires 978.3115].



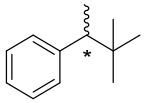
3. General procedure for the asymmetric hydrogenation. Characterization details and methods for enantiomeric excess determination of hydrogenated products

The alkene (0.5 mmol) and Ir complex (1 mol%) were dissolved in CH_2Cl_2 (2 mL) in a high-pressure autoclave, which was purged four times with hydrogen. The apparatus was pressurized to the desired pressure and, after the required reaction time, the autoclave was depressurized and the solvent evaporated off. The residue was dissolved in Et_2O (1.5 mL) and filtered through a short Celite plug.

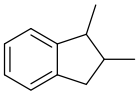
1-(sec-Butyl)-4-methoxybenzene.[4] Enantiomeric excess determined by GC using Chiradex B-DM column (100 kPa H_2, 60 °C for 30 min, 3 °C/min until 175 °C). t_R 44.4 min (*S*); t_R 44.7 min (*R*). ^{1}H NMR ($CDCl_3$), δ: 0.81 (t, 3H, *J*= 7.5 Hz), 1.21 (d, 3H, *J*= 6.6 Hz), 1.55 (m, 2H), 2.53 (m, 1H), 3.79 (s, 3H), 6.84 (m, 2H), 7.10 (m, 2H).



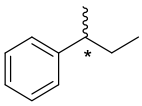
(3,3-Dimethylbutan-2-yl)benzene.[4] Enantiomeric excess determined by GC using Chiradex B-DM column (100 kPa H_2, 60 °C for 30 min, 3 °C/min until 175 °C). t_R 36.0 min (*S*); t_R 37.5 min (*R*). ^{1}H NMR ($CDCl_3$), δ: 0.83 (s, 9H), 1.24 (d, 3H, *J*= 6.8 Hz), 2.54 (q, 1H, *J*= 6.8 Hz), 7.1-7.3 (m, 5H).



1,2-Dimethyl-2,3-dihydro-1*H*-indene.[5] Enantiomeric excess determined by GC using Chiraldex β-DM (100 kPa H_2, Isotherm at 90 ºC). t_R 11.7 (*R,R*); t_R 12.6 (*S,S*). ^{1}H NMR (400 MHz, $CDCl_3$): δ= 0.96 (d, 3H, CH_3, *J*= 6.8 Hz), 1.12 (d, 3H, CH_3, J= 7.1 Hz), 2.51-2.61 (m, 2H, CH_2), 2.94-2.98 (m, 1H, CH), 3.12-3.16 (m, 1H, CH), 7.10-7.19 (m, 4H, CH=).



sec-Butylbenzene.[6] Enantiomeric excess determined by GC using Chiradex B-DM column (100 kPa H_2, 50 °C for 30 min, 2 °C/min until 175 °C). t_R 27.5 min (*S*); t_R 27.8 min (*R*). ^{1}H NMR ($CDCl_3$), δ: 0.80 (t, 3H, *J*= 7.6 Hz), 1.22 (d, 3H, *J*= 6.4 Hz), 1.61 (m, 2H), 2.60 (m, 1H), 7.18 (m, 3H), 7.33 (m, 2H).



Propane-1,2-diyldibenzene.[4] Enantiomeric excess determined by HPLC using Chiracel OJ-H column (hexane/2-propanol=99/1, 0.5 mL/min, 254 nm). t_R 12.6 min (*R*); t_R 17.5 min (*S*). ^{1}H NMR ($CDCl_3$), δ: 1.24 (d, 3H, *J*= 6.8 Hz), 2.75 (m, 1H), 2.96 (m, 2H), 7.08 (m, 2H), 7.1-7.4 (m, 8H).

1-Benzyl-2,3-dihydro-1H-indene.[7] Enantiomeric excess determined by HPLC using Chiracel OJ-H column (hexane/2-propanol=95/5, 0.5 mL/min, 210 nm). t_R 11.6 min (*S*); t_R 13.2 min (*R*). ^{1}H NMR ($CDCl_3$), δ: 1.80 (m, 1H), 2.20 (m, 1H), 2.74 (dd, 1H, *J*= 13.6 Hz, *J*= 9.2 Hz), 2.87 (m, 2H), 3.20 (dd, 1H, *J*= 13.6 Hz, *J*= 5.6 Hz), 3.51 (m, 1H), 7.1-7.4 (m, 9H)

Ethyl 3-phenylbutanoate.[4] Enantiomeric excess determined by HPLC using Chiracel IB column (hexane/2-propanol=99.5/0.5, 1 mL/min, 254 nm). t_R 10.6 min (*R*); t_R 18.5 min (*S*). ^{1}H NMR ($CDCl_3$), δ: 1.16 (t, 3H, *J*= 7.2 Hz), 1.30 (d, 3H, *J*= 6.8 Hz), 2.54 (m, 2H), 3.28 (m, 1H), 4.08 (q, 2H, *J*= 7.2 Hz), 7.2-7.4 (m, 5H).

Ethyl 3-(p-tolyl)butanoate.[8] Enantiomeric excess determined by HPLC using Chiracel IB column (hexane/2-propanol=99.5/0.5, 0.5 mL/min, 254 nm). t_R 12.3 min (*R*); t_R 13.0 min (*S*). ^{1}H NMR ($CDCl_3$), δ: 1.18 (t, 3H, *J*= 7.2 Hz), 1.28 (d, 3H, *J*= 6.0 Hz), 2.31 (s, 3H), 2.56 (m, 2H), 3.25 (m, 1H), 4.08 (q, 2H, *J*= 7.2 Hz), 7.12 (m, 4H).

Ethyl 3-(4-methoxyphenyl)butanoate.[8] Enantiomeric excess determined by HPLC using Chiracel IB column (hexane/2-propanol=99.5/0.5, 0.5 mL/min, 254 nm). t_R 18.5 min (*R*); t_R 19.5 min (*S*). ^{1}H NMR ($CDCl_3$), δ: 1.19 (t, 3H, *J*= 7.2 Hz), 1.26 (d, 3H, *J*= 6.4 Hz), 2.54 (m, 2H), 3.24 (m, 1H), 3.29 (s, 3H), 4.07 (q, 2H, *J*= 7.2 Hz), 6.83 (m, 2H), 7.15 (m, 2H).

Ethyl 3-phenylpentanoate.[8] Enantiomeric excess determined by HPLC using Chiracel IC column (hexane/2-propanol=99.5/0.5, 0.5 mL/min, 254 nm). t_R 11.6 min (*R*); t_R 12.0 min (*S*). ^{1}H NMR ($CDCl_3$), δ: 0.79 (t, 3H, *J*= 7.2 Hz), 1.13 (t, 3H, *J*= 7.2 Hz), 1.53 (d, 3H, *J*= 6.0 Hz), 1.62 (m, 2H), 2.60 (m, 2H), 2.99 (m, 1H), 4.03 (q, 2H, *J*= 7.2 Hz), 7.21 (m, 2H), 7.34 (m, 3H).

Ethyl 4-methyl-3-phenylpentanoate.[9] Enantiomeric excess determined by HPLC using Chiracel OD-H column (hexane/2-propanol=99/1, 0.5 mL/min, 254 nm). t_R 11.0 min (*R*); t_R 18.8 min (*S*). ^{1}H NMR ($CDCl_3$), δ: 0.77 (d, 3H, *J*= 6.0 Hz), 0.97 (d, 3H, *J*= 6.0 Hz), 1.06 (t, 3H, *J*= 6.8 Hz), 1.86 (m, 1H), 2.60 (m, 1H), 2.80 (m, 1H), 2.88 (m, 1H), 3.96 (q, 2H, *J*= 6.8 Hz), 7.1-7.3 (m, 5H).

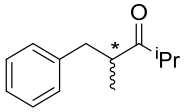
Ethyl 3-cyclohexyl-3-phenylpropanoate.[10] Enantiomeric excess determined by HPLC using Chiracel OD-H column (hexane/2-propanol=99/1, 0.5 mL/min, 254 nm). t_R 10.4 min (*R*); t_R 17.9 min (*S*). ^{1}H NMR ($CDCl_3$), δ: 0.90 (m, 1H), 0.93 (m, 1H), 1.06 (t, 3H, *J*= 7.2 Hz), 1.12 (m, 1H), 1.24 (m, 2H), 1.42 (m, 2H), 1.60 (m, 2H), 1.72 (m, 1H), 1.80 (m, 1H), 2.54 (m, 1H), 2.78 (m, 1H), 2.89 (m, 1H), 3.92 (q, 2H, *J*= 7.2 Hz), 7.1-7.3 (m, 5H).

3-Methyl-4-phenylbutan-2-one.[11] Enantiomeric excess determined by HPLC using Chiracel OJ-H column (hexane/2-propanol=97/3, 1 mL/min, 220 nm). t_R 8.4 min (*S*); t_R 9.1 min (*R*). ^{1}H NMR ($CDCl_3$), δ: 1.09 (d, 3H, *J*= 6.8 Hz), 2.09 (s, 3H), 2.56 (m, 1H), 2.83 (m, 1H), 3.01 (m, 1H), 7.1-7.3 (m, 5H).

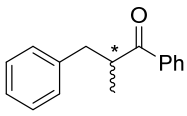
4-(4-Methoxyphenyl)-3-methylbutan-2-one.[11] Enantiomeric excess determined by HPLC using Chiracel OJ-H column (hexane/2-propanol=95/5, 0.5 mL/min, 220 nm). t_R 39.5 min (*S*); t_R 44.5 min (*R*). ^{1}H NMR ($CDCl_3$), δ: 1.07 (d, 3H, *J*= 6.8 Hz), 2.08 (s, 3H), 2.52 (dd, 1H, *J*= 7.4 Hz, *J*= 13.4 Hz), 2.78 (m, 1H), 2.93 (dd, 1H, *J*= 6.8 Hz, *J*= 13.4 Hz), 3.77 (s, 3H), 6.82 (m, 2H), 7.0-7.3 (m, 2H).

2-Methyl-1-phenylpentan-3-one.[11] Enantiomeric excess determined by HPLC using Chiracel OJ-H column (hexane/2-propanol=99/1, 0.5 mL/min, 220 nm). t_R 15.2 min (*S*); t_R 16.2 min (*R*). ^{1}H NMR ($CDCl_3$), δ: 0.96 (t, 3H, *J*= 7.2 Hz), 1.08 (d, 3H, *J*= 6.8 Hz), 2.21 (m, 1H), 2.43 (m, 1H), 2.57 (dd, 1H, *J*= 7.0 Hz, *J*= 13.4 Hz), 2.83 (m, 1H), 2.92 (dd, 1H, *J*= 6.8 Hz, *J*= 13.4 Hz), 7.1-7.3 (m, 5H).

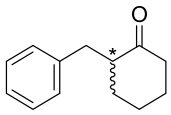
2,4-Dimethyl-1-phenylpentan-3-one.[12] Enantiomeric excess determined by GC using Lipodex-E column (100 kPa H_2, 90 °C isotherm). t_R 26.2 (*R*); t_R 27.9 min (*S*). ^{1}H NMR ($CDCl_3$), δ: 0.87 (d, 3H, *J*= 6.8 Hz), 1.01 (d, 3H, *J*= 6.8 Hz), 1.08 (d, 1H, *J*= 6.8 Hz), 2.51 (m, 2H), 2.97 (m, 2H), 7.1-7.5 (m, 5H).



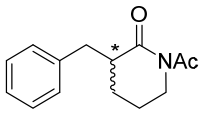
2-Methyl-1,3-diphenylpropan-1-one.[11] Enantiomeric excess determined by HPLC using Chiracel OJ column (hexane/2-propanol=99/1, 0.5 mL/min, 220 nm). t_R 12.9 min (*S*); t_R 13.6 min (*R*). ^{1}H NMR ($CDCl_3$), δ: 1.21 (d, 3H, *J*= 6.8 Hz), 2.69 (dd, 1H, *J*= 13.2 Hz, *J*= 7.2 Hz), 3.18 (dd, 1H, *J*= 13.2 Hz, *J*= 6.4 Hz), 3.74 (m, 1H), 7.1-8.0 (m, 10H).



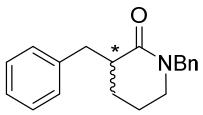
2-Benzylcyclohexanone.[11] Enantiomeric excess determined by HPLC using Chiracel OJ-H column (hexane/2-propanol=97/3, 1 mL/min, 210 nm). t_R 8.4 min (*S*); t_R 9.1 min (*R*). ^{1}H NMR ($CDCl_3$), δ: 1.35 (m, 1H), 1.63 (m, 2H), 1.83 (m, 1H), 2.04 (m, 2H), 2.44 (m, 4H), 3.24 (dd, 1H, *J* = 14.0 Hz, *J*= 4.6 Hz), 7.18 (m, 3H), 7.28 (m, 2H).



1-Acetyl-3-benzylpiperidin-2-one. Enantiomeric excess determined by HPLC using Chiracel OJ-H column (hexane/2-propanol=80/20, 0.5 mL/min, 210 nm). t_R 21.5 min (*S*); t_R 23.6 min (*R*). ^{1}H NMR ($CDCl_3$), δ: 1.47 (m, 1H), 1.71 (m, 1H), 1.82 (m, 2H), 2.54 (s, 3H), 2.72 (m, 2H), 3.38 (m, 1H), 3.62 (m, 1H), 3.84 (m, 1H), 7.1-7.3 (m, 5H).



1,3-dibenzylpiperidin-2-one.[13] Enantiomeric excess determined by HPLC using Chiracel OJ-H column (hexane/2-propanol=80/20, 0.5 mL/min, 220 nm). t_R 14.4 min (-); t_R 22.3 min (+). ^{1}H NMR ($CDCl_3$), δ: 1.51 (m, 1H), 1.69 (m, 3H), 2.64 (m, 1H), 2.75 (dd, 1H, *J*= 13.2 Hz, *J*= 10 Hz), 3.17 (m, 2H), 3.45 (dd, 1H, *J*= 13.2 Hz, *J*= 3.6 Hz), 4.61 (s, 2H), 7.2-7.4 (m, 10H).



1-benzyl-3-(cyclohexylmethyl)piperidin-2-one. Enantiomeric excess determined by HPLC using Chiracel IA column (hexane/2-propanol=90/10, 0.5 mL/min, 210 nm). t_R 16.3 min (*S*); t_R 19.1 min (*R*). ^{1}H NMR ($CDCl_3$), δ: 0.85 (m, 1H), 0.92 (m, 1H), 1.0-1.4 (m, 5H), 1.43 (m, 1H), 1.64 (m, 5H), 1.81 (m, 1H), 1.92 (m, 2H), 2.41 (m, 1H), 3.18 (m, 1H), 4.42 (m, 2H), 7.2-7.3 (m, 5H).

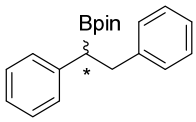
2,2'-(1-Phenylethane-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane).[14]

Enantiomeric excess were determined after oxidation of the pinacolborane derivative to the corresponding diol using NaOH (3N, 2.0 mL) and H_2O_2 (30%, 1.5 mL). Enantiomeric excess determined by HPLC using Chiracel OD-H column (hexane/2-propanol=95/5, 0.5 mL/min, 254 nm). t_R 38.2 min (*R*); t_R 42.3 min (*S*). ^{1}H NMR ($CDCl_3$), δ: 1.10 (dd, 1H, *J*= 5.4 Hz, *J*= 16.0 Hz), 1.17 (s, 6H), 1.20 (s, 6H), 1.21 (s, 12H), 1.38 (dd, 1H, *J*= 11.2 Hz, *J*= 16.0 Hz), 2.53 (dd, 1H, *J*= 5.4 Hz, *J*= 11.2 Hz), 7.1-7.3 (m, 5H).

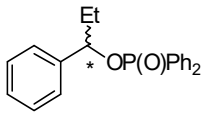
2,2'-(1-(4-Fluorophenyl)ethane-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane).[14] Enantiomeric excess were determined after oxidation of the pinacolborane derivative to the corresponding diol using NaOH (3N, 2.0 mL) and H_2O_2 (30%, 1.5 mL). Enantiomeric excess determined by HPLC using Chiracel OD-H column (hexane/2-propanol=95/5, 0.5 mL/min, 254 nm). t_R 33.4 min (*R*); t_R 35.7 min (*S*). ^{1}H NMR ($CDCl_3$), δ: 1.07 (dd, 1H, *J*= 16.0 Hz, *J*= 5.8 Hz), 1.17 (s, 6H), 1.19 (s, 6H), 1.21 (s, 12H), 1.33 (dd, 1H, *J*= 16.0 Hz, *J*= 10.8 Hz), 2.46 (dd, 1H, *J*= 10.8 Hz, *J*= 5.8 Hz), 3.78 (s, 3H), 6.8-7.4 (m, 4H).

2,2'-(1-(4-Methoxyphenyl)ethane-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane).[14] Enantiomeric excess were determined after oxidation of the pinacolborane derivative to the corresponding diol using NaOH (3N, 2.0 mL) and H_2O_2 (30%, 1.5 mL). Enantiomeric excess determined by HPLC using Chiracel OD-H column (hexane/2-propanol=90/10, 0.5 mL/min, 254 nm). t_R 54.5 min (*R*); t_R 57.4 min (*S*). ^{1}H NMR ($CDCl_3$), δ: 1.07 (dd, 1H, *J*= 16.0 Hz, *J*= 5.8 Hz), 1.17 (s, 6H), 1.19 (s, 6H), 1.21 (s, 12H), 1.33 (dd, 1H, *J*= 16.0 Hz, *J*= 10.8 Hz), 2.46 (dd, 1H, *J*= 10.8 Hz, *J*= 5.8 Hz), 3.78 (s, 3H), 6.8-7.4 (m, 4H).

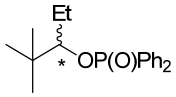
2-(1,2-Diphenylethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane.[15] Enantiomeric excess determined by HPLC using Chiracel OJ-H column (hexane/2-propanol=99/1, 0.5 mL/min, 254 nm). t_R 9.5 min (-); t_R 12.9 min (+). ^{1}H NMR ($CDCl_3$), δ: 1.12 (s, 6H), 1.13 (s, 6H), 2.71 (dd, 1H, *J*= 6.8 Hz, *J*= 10.0 Hz), 2.98 (dd, 1H, *J*= 7.0 Hz, *J*= 13.6 Hz), 3.17 (dd, 1H, *J*= 9.6 Hz, *J*= 13.6 Hz), 7.1-7.4 (m, 10H).



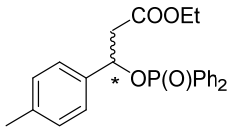
1-Phenylpropyl diphenylphosphinate.[16] Enantiomeric excess determined by HPLC using Chiralcel AD (hexane/2-propanol=90/10, 0.5 mL/min, 220 nm). t_R = 25.8 min (*R*); t_R 35.3 min (*S*). ^{1}H NMR ($CDCl_3$), δ: 0.87(dt, 3H, *J* = 7.2, 2.4 Hz), 1.98 (m, 1H), 2.12 (m, 1H), 5.30 (m, 1H), 7.2-7.3 (m, 7H), 7.4-7.7 (m, 6H), 7.8-7.9 (m, 2H).



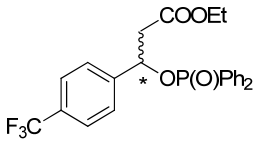
2,2-Dimethylpentan-3-yl diphenylphosphinate.[16] Enantiomeric excess determined by HPLC using Chiralcel IA (hexane/2-propanol=95/5, 0.5 mL/min, 220 nm). t_R = 26.5 min (*R*); t_R 28.8 min (*S*). ^{1}H NMR ($CDCl_3$), δ: 0.70 (t, 3H, *J*= 7.2 Hz), 0.90 (s, 3H), 1.14 (m, 2H), 1.01 (s, 9H), 1.55 (m, 2H), 4.26 (m, 1H), 7.3-7.8 (m, 10H)



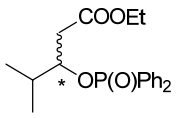
Ethyl 3-((diphenylphosphoryl)oxy)-3-(p-tolyl)propanoate.[16] Enantiomeric excess determined by HPLC using Chiralcel OD (hexane/2-propanol=90/10, 0.5 mL/min, 220 nm). t_R = 17.5 min (*R*); t_R 21.9 min (*S*). ^{1}H NMR ($CDCl_3$), δ: 0.85 (t, 3H, *J* = 7.2 Hz), 1.85 (m, 1H), 2.08 (m, 1H),3.95 (m, 2H), 5.34 (m, 1H), 7.2-7.9 (m, 14H).



Ethyl 3-((diphenylphosphoryl)oxy)-3-(4-(trifluoromethyl)phenyl)propanoate.[16] Enantiomeric excess determined by HPLC using Chiralcel OD-H (hexane/2-propanol=90/10, 0.5 mL/min, 220 nm). t_R = 17.2 min (*R*); t_R 21.2 min (*S*). ^{1}H NMR ($CDCl_3$), δ: 1.13 (t, 3H, *J* = 7.2 Hz), 2.89 (dd, 1H, *J* = 6.4 Hz, *J*= 15.6 Hz), 3.20 (dd, 1H, *J* = 6.4 Hz, *J*= 15.6 Hz), 4.00 (m, 2H), 5.82 (br, 1H), 7.3-7.8 (m, 14H)

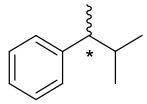


Ethyl 3-((diphenylphosphoryl)oxy)-4-methylpentanoate.[16] Enantiomeric excess determined by HPLC using Chiralcel OD-H (hexane/2-propanol=95/5, 0.5 mL/min, 220 nm). t_R = 52.0 min (*R*); t_R 53.8 min (*S*). ^{1}H NMR ($CDCl_3$), δ: 0.92 (dd, 3H, *J*= 8.0 Hz, *J*= 6.8 Hz), 1.14 (t, 3H, *J*= 7.2

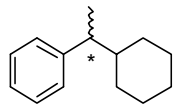


Hz), 2.07 (m, 1H), 2.56 (dd, 1H, *J*= 15.4 Hz, J= 5.2 Hz), 2.75 (dd, 1H, *J*= 15.2 Hz, *J*= 7.2 Hz), 3.93 (m, 2H), 4.73 (m, 1H), 7.4 - 7.7 (m, 10H).

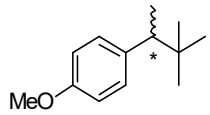
(3-Methylbutan-2-yl)benzene.[4] Enantiomeric excess determined by GC using Chiradex B-DM column (100 kPa H_2, 60 °C for 30 min, 3 °C/min until 175 °C). t_R 22.4 min (*S*); t_R 24.0 min (*R*). ^{1}H NMR ($CDCl_3$), δ: 0.76 (d, 3H, *J*= 7.6 Hz), 0.92 (d, 3H, *J*= 7.6 Hz), 1.23 (d, 3H, *J*= 6.8 Hz), 1.79 (m, 1H), 2.42 (m, 1H), 7.1-7.3 (m, 5H).



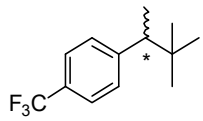
(1-Cyclohexylethyl)benzene.[17] Enantiomeric excess determined by GC using Chiradex B-DM column (100 kPa H_2, 60 °C for 30 min, 3 °C/min until 175 °C). t_R 53.6 min (*S*); t_R 54.0 min (*R*). ^{1}H NMR ($CDCl_3$), δ: 0.76 (m, 1H), 0.93 (m, 1H), 1.09 (m, 1H), 1.21 (d, 3H, *J*= 6.8 Hz), 1.23 (m, 1H), 1.39 (m, 2H), 1.59 (m, 2H), 1.71 (m, 1H), 1.83 (m, 1H), 2.40 (m, 2H), 7.1-7.3 (m, 5H).



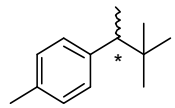
1-(3,3-Dimethylbutan-2-yl)-4-methoxybenzene. [18] Enantiomeric excess determined by GC using Chiradex B-DM column (100 kPa H_2, 60 °C for 30 min, 3 °C/min until 175 °C). t_R 53.4 min (*S*); t_R 53.8 min (*R*). ^{1}H NMR ($CDCl_3$), δ: 0.78 (s, 9H), 1.16 (d, 3H, *J*= 6.8 Hz), 2.42 (q, 1H, *J*= 6.8 Hz), 3.71 (s, 3H), 6.72 (d, 2H, *J*= 7.2 Hz), 6.94 (d, 2H, *J*= 7.2 Hz).



1-(3,3-Dimethylbutan-2-yl)-4-(trifluoromethyl)benzene.[18] Enantiomeric excess determined by GC using Chiradex B-DM column (100 kPa H_2, 60 °C for 30 min, 3 °C/min until 175 °C). t_R 41.1 min (*S*); t_R 42.0 min (*R*). ^{1}H NMR ($CDCl_3$), δ: 0.83 (s, 9H), 1.14 (d, 3H, *J*= 6.8 Hz), 2.44 (q, 1H, *J*= 6.8 Hz), 7.27 (d, 2H, *J*= 7.2 Hz), 7.53 (d, 2H, *J*= 7.2 Hz).



1-(3,3-Dimethylbutan-2-yl)-4-methylbenzene.[18] Enantiomeric excess determined by GC using Chiradex B-DM column (100 kPa H_2, 60 °C for 30 min, 3 °C/min until 175 °C). t_R 39.3 min (*S*); t_R 39.7 min (*R*). ^{1}H NMR ($CDCl_3$), δ: 0.82 (s, 9H), 1.23 (d, 3H, *J*= 6.8 Hz), 2.33 (s, 3H), 2.43 (q, 1H, *J*= 6.8 Hz), 7.06 (m, 5H).



1-(3,3-Dimethylbutan-2-yl)-3-methylbenzene.[18] Enantiomeric excess determined by GC using Chiradex B-DM column (100 kPa H_2, 60 °C for 30 min, 3 °C/min until 175 °C). t_R 41.7 min (*S*); t_R 42.5 min (*R*). ^{1}H NMR ($CDCl_3$), δ: 0.79 (s, 9H), 1.18 (d, 3H, *J*= 6.8 Hz), 2.26 (s, 3H), 2.44 (q, 1H, *J*= 6.8 Hz), 6.92 (m, 3H), 7.06 (m, 1H).

1-(3,3-Dimethylbutan-2-yl)-2-methylbenzene.[18] Enantiomeric excess determined by GC using Chiradex B-DM column (100 kPa H_2, 60 °C for 30 min, 3 °C/min until 175 °C). t_R 39.8 min (*S*); t_R 40.5 min (*R*). ^{1}H NMR ($CDCl_3$), δ: 0.83 (s, 9H), 1.23 (d, 3H, *J*= 6.8 Hz), 2.37 (s, 3H), 2.93 (q, 1H, *J*= 6.8 Hz), 6.9-7.2 (m, 5H).

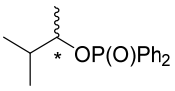
1-(3,3-Dimethylbutan-2-yl)naphthalene.[18] Enantiomeric excess determined by GC using Chiradex B-DM column (100 kPa H_2, 60 °C for 30 min, 3 °C/min until 175 °C). t_R 60.7 min (*S*); t_R 61.0 min (*R*). ^{1}H NMR ($CDCl_3$), δ: 0.91 (s, 9H), 1.25 (d, 3H, *J*= 6.8 Hz), 2.81 (q, 1H, *J*= 6.8 Hz), 6.8-7.0 (m, 2H), 7.3-8.2 (m, 5H).

2-(3,3-Dimethylbutan-2-yl)pyridine.[4] Enantiomeric excess determined by GC using Chiral β-Dex column (120 kPa H_2, 60 °C for 60 min, 3 °C/min until 150 °C). t_R 69.3 min (-); t_R 69.8 min (+). ^{1}H NMR ($CDCl_3$), δ: 0.93 (s, 9H), 1.12 (d, 3H, *J*= 7.2 Hz), 3.79 (q, 1H, *J*= 7.2 Hz), 7.02 (m, 1H), 7.40 (m, 1H), 7.58 (m, 1H), 8.43 (m, 1H).

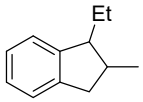
2-(sec-Butyl)pyridine.[17] Enantiomeric excess determined by GC using Chiral β-Dex column (120 kPa H_2, 500 °C for 60 min, 3 °C/min until 150 °C). t_R 52.5 min (-); t_R 52.8 min (+). ^{1}H NMR ($CDCl_3$), δ: 0.84 (t, 3H *J*= 7.0 Hz), 1.28 (d, 3H, *J*= 6.8 Hz), 1.63 (m, 1H), 1.76 (m, 1H), 2.78 (m, 1H), 7.04 (m, 2H), 7.59 (m, 1H), 8.54 (d, 1H, *J*= 4.0 Hz).

1-Phenylethyl diphenylphosphinate.[19] Enantiomeric excess determined by HPLC using Chiralcel AD (hexane/2-propanol=90/10, 0.5 mL/min, 220 nm). t_R = 29.7 min (*R*); t_R 33.6 min (*S*). ^{1}H NMR ($CDCl_3$), δ: 1.81 (dd, 3H, *J* = 7.2 Hz, *J* = 2.4 Hz). 5.60 (m, 1H), 7.18 (m, 3H), 7.31 (m, 2H), 7.42 (m, 4H), 7.52 (m, 2H), 7.82 (m, 4H).

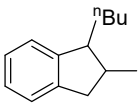
3-Methylbutan-2-yl diphenylphosphinate.[19] Enantiomeric excess determined by HPLC using Chiralcel IC (hexane/2-propanol=90/10, 0.5 mL/min, 220 nm). t_R = 42.5 min (*R*); t_R 47.0 min (*S*). ^{1}H NMR ($CDCl_3$), δ: 0.92 (dd, 3H, *J*= 0.8 Hz, *J*= 6.8 Hz), 0.94 (dd, 3H, *J*= 0.8 Hz, *J*= 6.8 Hz), 1.22 (dd, 3H, *J*= 0.8 Hz, *J*= 6.4 Hz), 1.90 (m, 1H), 4.40 (m, 1H), 7.4 - 7.8 (m, 10H).



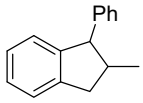
1-Ethyl-2-methyl-2,3-dihydro-1*H*-indene.[5] Enantiomeric excess determined by GC using Hydrodex β-3P (100 kPa H_2, Isotherm at 90 ºC). t_R 18.0 (*R,R*); t_R 18.9 (*S,S*). ^{1}H NMR (400 MHz, $CDCl_3$): δ= 0.94 (d, 3H, CH_3, *J*= 6.9 Hz), 1.01 (t, 3H, CH_3, Et, *J*= 7.4 Hz), 1.49-1.68 (m, 2H, CH_2, Et), 2.51-2.66 (m, 2H, CH_2), 2.87-2.96 (m, 2H, CH), 7.10-7.20 (m, 4H, CH=).



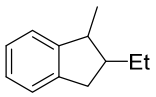
1-Butyl-2-methyl-2,3-dihydro-1*H*-indene.[20] Enantiomeric excess determined by GC using Chiraldex β-DM (100 kPa H_2, Isotherm at 120 ºC). t_R 12.8 (*R,R*); t_R 13.3 (*S,S*). ^{1}H NMR (400 MHz, $CDCl_3$): δ= 0.91 – 0.95 (m, 6H, CH_3), 1.36-1.40 (m, 4H, CH_2, ^{n}Bu), 1.53-1.57 (m, 2H, CH_2, ^{n}Bu), 2.51-2.65 (m, 2H, CH_2), 2.90-3.00 (m, 2H, CH), 7.11-7.20 (m, 4H, CH=).



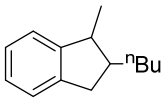
2-Methyl-1-phenyl-2,3-dihydro-1*H*-indene.[5] Enantiomeric excess determined by GC using Chiraldex β-DM (100 kPa H_2, Isotherm at 150 ºC). t_R 13.6 (*S,R*); t_R 14.6 (*R,S*). ^{1}H NMR (400 MHz, $CDCl_3$): δ= 0.70 (d, 3H, CH_3, *J*= 7.0 Hz), 2.68 (dd, 1H, CH_2, *J*= 15.4 Hz, *J*= 7.4 Hz), 2.83 (m, 1H, CH), 3.05 (dd, 1H, CH_2, *J*= 15.4 Hz, *J*= 7.4 Hz), 4.37 (d, 1H, CH-Ph, *J*= 7.9 Hz), 6.98 (m, 2H, CH=), 7.14-7.33 (m, 7H, CH=).



2-Ethyl-1-methyl-2,3-dihydro-1*H*-indene[21]: Enantiomeric excess determined by GC using Chiraldex β-DM (100 kPa H_2, Isotherm at 90 ºC). t_R 18.9 (*R,R*); t_R 19.9 (*S,S*). ^{1}H NMR (400 MHz, $CDCl_3$): δ= 0.95 (t, 3H, CH_3, Et, *J*= 8.0 Hz), 1.04 (d, 3H, CH_3, *J*= 7.5 Hz), 1.42 (m, 1H, CH_2, Et), 1.53 (m, 1H, CH_2, Et), 2.30 (m, 1H, CH_2), 2.60 (dd, 1H, CH_2, *J*= 9.4 Hz, *J*= 15.4 Hz), 2.90 (dd, 1H, CH, *J*= 7.5 Hz, *J*= 15.4 Hz), 3.16 (m, 1H, CH), 7.08-7.18 (m, 4H, CH=).



2-Butyl-1-methyl-2,3-dihydro-1*H*-indene.[5] Enantiomeric excess determined by GC using Chiraldex β-DM (100 kPa H_2, 90 ºC, 45 min – 5 ºC/min – 175 ºC). t_R 53.2 (*R,R*); t_R 53.8 (*S,S*). ^{1}H NMR (400 MHz, $CDCl_3$): δ= 0.93 (m, 3H, CH_3, ^{n}Bu), 1.03 (d, 3H, CH_3, *J*= 7.0 Hz), 1.30-1.45 (m, 5H, CH_2, ^{n}Bu), 1.69-1.74 (1H, m, CH_2, ^{n}Bu), 1.85-1.95 (m, 1H, CH_2), 2.51 (dd, 1H, CH_2, *J*= 9.2 Hz, *J*= 15.7 Hz), 2.76



(qd, 1H, CH, *J*= 6.6 Hz, *J*= 7.0 Hz), 3.05 (dd, 1H, CH, *J*= 7.7 Hz, *J*= 15.6 Hz), 7.11-7.19 (m, 4H, CH=).

1,2-Dimethyl-1,2,3,4-tetrahydronaphthalene.[5] Enantiomeric excess determined by GC using Chiraldex β-DM (100 kPa H_2, Isotherm at 90 ºC). t_R 28.1 (*R,R*); t_R 33.7 (*S,S*). ^{1}H NMR (400 MHz, $CDCl_3$): δ= 0.99 (d, 3H, CH_3, *J*= 6.9 Hz), 1.11 (d, 3H, CH_3, *J*= 7.2 Hz), 1.64 (dq, 2H, CH_2, *J*= 6.4 Hz, *J*= 2.0 Hz), 1.98 (m, 1H, CH), 2.82 (m, 3H, CH, CH_2), 7.08-7.16 (m, 4H, CH=).

1-Methyl-4-(3-methylbutan-2-yl)benzene.[22] Enantiomeric excess determined by GC using Chiraldex β-DM (100 kPa H_2, 60 ºC, 30 min – 3 ºC/min – 175 ºC). t_R 38.7 (*S*); t_R 40.0 (*R*). ^{1}H NMR (400 MHz, $CDCl_3$): δ= 0.78 (d, 3H, CH_3, *J*= 6.7 Hz), 0.92 (d, 3H, CH_3, *J*= 6.7 Hz), 1.21 (d, 3H, CH_3, *J*= 7.1 Hz), 1.68 (m, 1H, CH), 2.32 (s, 3H, CH_3), 2.39 (q, 1H, CH, *J*= 7.2 Hz), 7.05 (d, 2H, CH=, *J*= 7.9 Hz), 7.09 (d, 2H, CH=, *J*= 7.9 Hz).

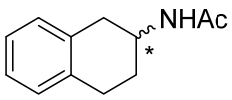
1-Methoxy-4-(3-methylbutan-2-yl)benzene.[22] Enantiomeric excess determined by GC using Chiraldex β-DM (100 kPa H_2, 60 ºC, 30 min – 3 ºC/min – 175 ºC). t_R 50.7 (*S*); t_R 51.3 (*R*). ^{1}H NMR (400 MHz, $CDCl_3$): δ= 0.74 (d, 3H, CH_3, *J*= 6.7 Hz), 0.91 (d, 3H, CH_3, *J*= 6.7 Hz), 1.20 (d, 3H, CH_3, *J*= 7.1 Hz), 1,71 (m, 1H, CH), 2.38 (m, 1H, CH), 3.78 (s, 3H, CH_3-O), 7.02-7.09 (m, 4H, CH=).

1-Methyl-3-(3-methylbutan-2-yl)benzene. Enantiomeric excess determined by GC using Hydrodex β-3P (100 kPa H_2, 50 ºC, 30 min – 3 ºC/min – 170 ºC). t_R 43.2 (*S*); t_R 43.5 (*R*). ^{1}H NMR (400 MHz, $CDCl_3$): δ= 0.76 (d, 3H, CH_3, *J*= 6.7 Hz), 0.92 (d, 3H, CH_3, *J*= 6.7 Hz), 1.23 (d, 3H, CH_3, *J*= 7.0 Hz), 1.78 (m, 1H, CH), 2.33 (s, 3H, CH_3), 2.39 (m, 1H, CH), 6.98 (m, 3H, CH=), 7.17 (m, 1H, CH=). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ= 18.9 (CH_3), 20.3 (CH_3), 21.4 (CH_3), 21.7 (CH_3), 34.5 (CH), 47.0 (CH), 124.8 (CH=), 126.5 (CH=), 128.0 (CH=), 128.6 (CH=), 137.5 (C), 147.3 (C).

1-Methoxy-2-(3-methylbutan-2-yl)benzene. Enantiomeric excess determined by GC using Chiraldex β-DM (100 kPa H_2, 60 ºC, 30 min – 3 ºC/min – 175 ºC). t_R 48.7 (*S*); t_R 49.1 (*R*). ^{1}H NMR (400 MHz, $CDCl_3$): δ= 0.77 (d, 3H, CH_3, *J*= 6.7 Hz), 0.92 (d, 3H, CH_3, *J*= 6.7 Hz), 1.21 (d, 3H, CH_3, *J*= 7.0 Hz), 1.76 (m, 1H, CH), 2.39 (m, 1H, CH), 3.8 (s, 3H, CH_3-O), 6.72 (m, 3H, CH=), 7.18

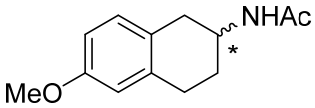
(m, 1H, CH=). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ= 18.6 (CH_3), 20.2 (CH_3), 21.1 (CH_3), 34.4 (CH), 46.9 (CH), 55.1 (CH_3-O), 110.6 (CH=), 113.7 (CH=), 120.2 (CH=), 129.0 (CH=), 148.9 (C), 159.4 (C).

***N*-(1,2,3,4-Tetrahydronaphthalen-2-yl)acetamide.**[23] Enantiomeric excess determined



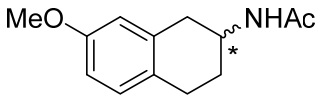
by HPLC using Chiralcel OJ-H column (80% hexane/2-propanol, flow 1 mL/min). t_R 5.7 min (*R*); t_R 6.6 min (*S*). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.70-1.85 (m, 1H, CH_2), 1.98 (s, 3H, CH_3, NAc), 2.0-2.1 (m, 1H, CH_2), 2.64 (dd, 1H, CH_2, $^2J_{H-H}$= 16.0 Hz, $^3J_{H-H}$= 8.0 Hz), 2.83-2.91 (m, 2H, CH_2), 3.11 (dd, 1H, CH_2, $^2J_{H-H}$= 16.0 Hz, $^3J_{H-H}$= 8.0 Hz), 4.28 (m, 1H, CH-N), 5.62 (bs, 1H, NH), 7.04-7.14 (m, 4H, CH=).

***N*-(6-Methoxy-1,2,3,4-tetrahydronaphthalen-2-yl)acetamide**.[23] Enantiomeric excess



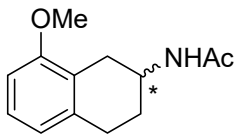
determined by HPLC using Chiralcel OJ-H column (80% hexane/2-propanol, flow 1 mL/min). t_R 8.4 min (*R*); t_R 11.2 min (*S*). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.79 (m, 1H, CH_2), 1.98 (s, 3H, CH_3, NAc), 2.03 (m, 1H, CH_2), 2.57 (dd, 1H, CH_2, $^2J_{H-H}$= 16.0 Hz, $^3J_{H-H}$ = 8.0 Hz), 2.85 (m, 2H, CH_2), 3.05 (dd, 1H, CH_2, $^2J_{H-H}$= 16.0 Hz, $^3J_{H-H}$ = 8.0 Hz), 3.78 (s, 3H, CH_3, OMe), 4.28 (m, 1H, CH-N), 5.51 (bs, 1H, NH), 6.64 (d, 1H, CH=, $^3J_{H-H}$ = 8.0 Hz), 6.77 (dd, 1H, CH=, $^3J_{H-H}$ = 8.0 Hz, $^4J_{H-H}$= 2.6 Hz), 6.97 (d, 1H, CH=, $^3J_{H-H}$ = 8.0 Hz).

***N*-(7-Methoxy-1,2,3,4-tetrahydronaphthalen-2-yl)acetamide**.[24] Enantiomeric excess



determined by HPLC using Chiralcel OJ-H column (80% hexane/2-propanol, flow 1 mL/min). t_R 7.7 min (*R*); t_R 10.9 min (*S*). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.80 (m, 1H, CH_2), 1.98 (s, 3H, CH_3, NAc), 2.00 (m, 1H, CH_2), 2.63 (dd, 1H, CH_2, $^2J_{H-H}$= 16.0 Hz, $^3J_{H-H}$= 8.0 Hz), 2.80 (m, 2H, CH_2), 3.10 (dd, 1H, CH_2, $^2J_{H-H}$= 16.0 Hz, $^3J_{H-H}$= 8.0 Hz), 3.78 (s, 3H, CH_3, OMe), 4.29 (m, 1H, CH-N), 5.58 (bs, 1H, NH), 6.59 (d, 1H, CH=, $^4J_{H-H}$= 2.6 Hz), 6.72 (dd, 1H, CH=, $^3J_{H-H}$ = 8.0 Hz, $^4J_{H-H}$ = 2.6 Hz), 7.01 (d, 1H, CH=, $^3J_{H-H}$ = 8.0 Hz).

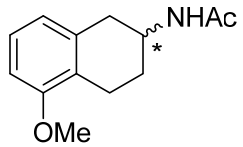
***N*-(8-Methoxy-1,2,3,4-tetrahydronaphthalen-2-yl)acetamide**.[23] Enantiomeric excess



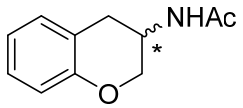
determined by HPLC using Chiralcel OJ-H column (80% hexane/2-propanol, flow 1 mL/min). t_R 6.7 min (*S*); t_R 7.6 min (*R*). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.78 (m, 1H, CH_2), 1.99 (s, 3H,

CH_3, NAc), 2.01 (m, 1H, CH_2), 2.43 (dd, 1H, CH_2, $^2J_{H-H}$= 16.0 Hz, $^3J_{H-H}$ = 8.0 Hz), 2.84 (m, 2H, CH_2), 3.07 (dd, 1H, CH_2, $^2J_{H-H}$= 16.0 Hz, $^3J_{H-H}$ = 8.0 Hz), 3.80 (s, 3H, CH_3, OMe), 4.26 (m, 1H, CH-N), 5.51 (bs, 1H, NH), 6.67 (d, 1H, CH=, $^3J_{H-H}$ = 8.0 Hz), 6.72 (d, 1H, CH=, $^3J_{H-H}$ = 8.0 Hz), 7.12 (t, 1H, CH=, $^3J_{H-H}$ = 8.0 Hz).

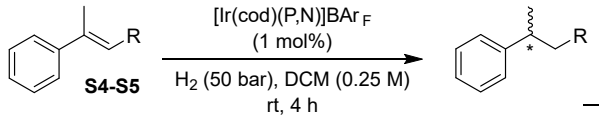
***N*-(5-Methoxy-1,2,3,4-tetrahydronaphthalen-2-yl)acetamide**.[25] Enantiomeric excess determined by HPLC using Chiralcel OJ-H column (80% hexane/2-propanol, flow 1 mL/min). t_R 6.9 min (*R*); t_R 7.7 min (*S*). ^{1}H NMR (400 MHz, $CDCl_3$): δ= 1.79 (m, 1H, CH_2), 1.98 (s, 3H, CH_3, NAc), 2.01 (m, 1H, CH_2), 2.65 (dd, 1H, CH_2, $^2J_{H-H}$= 16.0 Hz, $^3J_{H-H}$ = 8.0 Hz), 2.77 (m, 2H, CH_2), 3.09 (dd, 1H, CH_2, $^2J_{H-H}$= 16.0 Hz, $^3J_{H-H}$ = 8.0 Hz), 3.82 (s, 3H, CH_3, OMe), 4.28 (m, 1H, CH-N), 5.54 (bs, 1H, NH), 6.67 (d, 2H, CH=, $^3J_{H-H}$ = 8.0 Hz), 7.11 (t, 1H, CH=, $^3J_{H-H}$ = 8.0 Hz).



***N*-(Chroman-3-yl)acetamide.**[26] Enantiomeric excess determined by HPLC using Chiralcel OD-H column (95% hexane/2-propanol, flow 1 mL/min). t_R 37.4 min (*R*); t_R 40.1 min (*S*). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.96 (s, 3H, CH_3, NAc), 2.75 (m, 1H, CH-O), 3.12 (m, 1H, CH-O), 4.08 (m, 1H, CH_2), 4.18 (m, 1H, CH_2), 4.49 (m, 1H, CH-N), 5.89 (bs, 1H, NH), 6.85 (d, 1H, CH=, $^3J_{H-H}$= 8.0 Hz), 6.91 (t, 1H, CH=, $^3J_{H-H}$= 8.0 Hz), 7.05 (d, 1H, CH=, $^3J_{H-H}$= 8.0 Hz), 7.14 (t, 1H, CH=, $^3J_{H-H}$= 8.0 Hz).



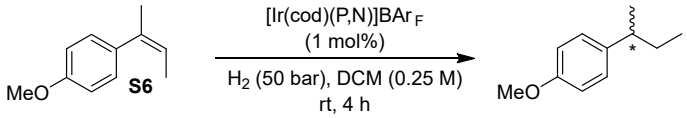
4. Complete series of results for the asymmetric hydrogenation of unfunctionalized olefins S4-S57 and cyclic β-enamide S58 using [Ir(cod)(L1-L6a-h)]BAr$_F$



		L4e		L5d	
	R	% Conv	% ee	% Conv	%ee
S4	Me	100	92 (*S*)	100	97 (*R*)
S5	Ph	100	95 (*S*)	100	99 (*R*)

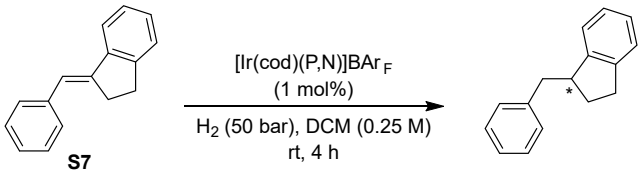
Figure S1. Asymmetric hydrogenation of substrates **S4-S5** using [Ir(cod)(L)]BAr$_F$ (L=**L5d** and **L4e**)

Table S1. Asymmetric hydrogenation of S6 using [Ir(cod)(L1-L6a-h)]BAr$_F$



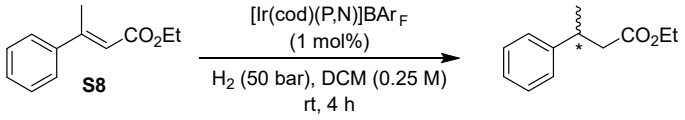
Entry	L	%Conv	%ee	Entry	L	%Conv	%ee
1	**L1a**	100	21 (*S*)	14	**L3b**	60	25 (*S*)
2	**L1b**	100	91 (*S*)	15	**L4a**	100	71 (*R*)
3	**L1c**	100	44 (*R*)	16	**L4d**	100	33 (*R*)
4	**L1d**	100	86 (*S*)	17	**L4e**	100	91 (*R*)
5	**L1e**	100	41 (*R*)	18	**L4f**	100	71 (*S*)
6	**L1f**	100	53 (*S*)	19	**L4g**	100	66 (*S*)
7	**L1g**	100	50 (*S*)	20	**L4h**	100	80 (*S*)
8	**L2a**	100	33 (*S*)	21	**L5a**	100	5 (*S*)
9	**L2b**	100	92 (*S*)	22	**L5d**	100	80 (*S*)
10	**L2f**	100	71 (*S*)	23	**L5e**	100	45 (*R*)
11	**L2g**	100	82 (*S*)	24	**L6a**	100	70 (*S*)
12	**L2h**	100	10 (*R*)	25	**L6d**	100	78 (*S*)
13	**L3a**	60	37 (*S*)	26	**L6e**	100	8 (*S*)

Table S2. Asymmetric hydrogenation of trisubstituted exocyclic olefin S7 [Ir(cod)(L1-L6a-h)]BAr$_F$

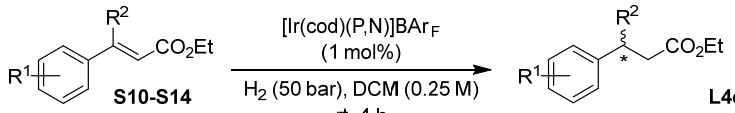


Entry	L	%Conv	%ee
1	**L1a**	100	54 (*R*)
2	**L1b**	100	96 (*R*)
3	**L1e**	100	2 (*R*)
4	**L1f**	100	21 (*R*)
5	**L1g**	100	29 (*R*)
6	**L2a**	100	51 (*R*)
7	**L2b**	100	91 (*R*)
8	**L2f**	100	43 (*R*)
9	**L2g**	100	64 (*R*)
10	**L2h**	100	61(*R*)
11	**L3b**	100	46 (*R*)
12	**L4a**	100	50 (*S*)
13	**L4c**	100	93 (*S*)
14	**L4d**	100	14 (*S*)
15	**L4f**	100	31 (*S*)
16	**L4g**	100	49 (*S*)
17	**L4h**	100	53 (*S*)
18	**L5d**	100	89 (*R*)
19	**L5e**	100	1 (*S*)
20	**L6d**	100	86 (*R*)

Table S3. Asymmetric hydrogenation of α,β-unsaturated ester S8 using [Ir(cod)(L1-L6a-h)]BAr$_F$



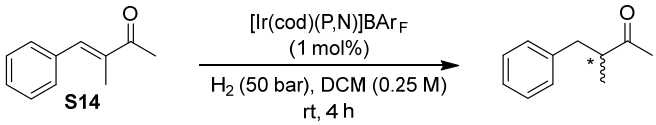
Entry	L	%Conv	%ee	Entry	L	%Conv	%ee
1	**L1a**	100	92 (*R*)	14	**L3b**	100	21 (*R*)
2	**L1b**	100	87 (*R*)	15	**L4a**	100	81 (*S*)
3	**L1c**	100	74 (*R*)	16	**L4d**	100	75 (*S*)
4	**L1d**	100	79 (*R*)	17	**L4e**	100	94 (*S*)
5	**L1e**	100	68 (*R*)	18	**L4f**	100	35 (*S*)
6	**L1f**	100	78 (*R*)	19	**L4g**	100	72 (*S*)
7	**L1g**	100	90 (*R*)	20	**L4h**	100	75 (*S*)
8	**L2a**	100	90 (*R*)	21	**L5a**	100	93 (*R*)
9	**L2b**	100	87 (*R*)	22	**L5d**	100	98 (*R*)
10	**L2f**	100	73 (R)	23	**L5e**	100	65 (*R*)
11	**L2g**	100	87 (R)	24	**L6a**	100	79 (*R*)
12	**L2h**	100	61 (R)	25	**L6d**	100	81 (*R*)
13	**L3a**	100	19 (*R*)	26	**L6e**	100	65 (*R*)



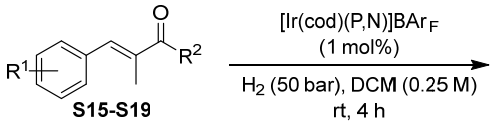
			L4e		L5d	
	R^1	R^2	% Conv	% ee	% Conv	%ee
S9	*p*-Me	Me	100	94 (*S*)	100	98 (*R*)
S10	*p*-OMe	Me	100	94 (*S*)	100	99 (*R*)
S11	H	Et	100	95 (*S*)	100	98 (*R*)
S12	H	^{i}Pr	100	96 (*S*)	100	99 (*R*)
S13	H	Cy	100	97 (*S*)	100	99 (*R*)

Figure S2. Asymmetric hydrogenation of α,β-unsaturated esters **S9-S13** using [Ir(cod)(L)]BAr$_F$ (L=**L5d** and **L4e**)[a]

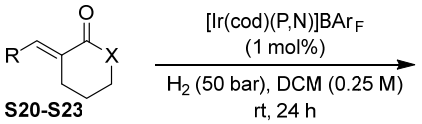
Table S4. Asymmetric hydrogenation of α,β-unsaturated enone S14 using [Ir(cod)(L1-L6a-h)]BAr$_F$



Entry	L	%Conv	%ee	Entry	L	%Conv	%ee
1	**L1a**	100	61 (*S*)	14	**L3b**	100	49 (*R*)
2	**L1b**	100	88 (*R*)	15	**L4a**	100	24 (*S*)
3	**L1c**	100	93 (*S*)	16	**L4d**	100	40 (*S*)
4	**L1d**	100	40 (*R*)	17	**L4e**	100	97 (*S*)
5	**L1e**	100	85 (*S*)	18	**L4f**	100	40 (*S*)
6	**L1f**	100	8 (*R*)	19	**L4g**	100	9 (*S*)
7	**L1g**	100	10 (*R*)	20	**L4h**	100	44 (*S*)
8	**L2a**	100	52 (*S*)	21	**L5a**	100	71 (*S*)
9	**L2b**	100	90 (*R*)	22	**L5d**	100	96 (*R*)
10	**L2f**	100	41 (*S*)	23	**L5e**	100	84 (*S*)
11	**L2g**	100	68 (*R*)	24	**L6a**	100	59 (*S*)
12	**L2h**	100	25 (*S*)	25	**L6d**	100	89 (*R*)
13	**L3a**	100	18 (*S*)	26	**L6e**	100	86 (*S*)



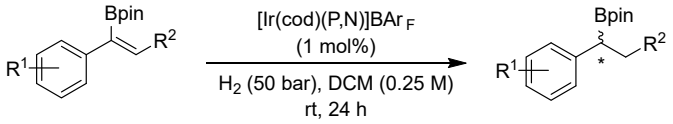
	R^1	R^2	L4e % Conv	L4e % ee	L5d % Conv	L5d % ee
S15	*p*-Me	Me	100	95 (*S*)	100	95 (*R*)
S16	*p*-OMe	Me	100	97 (*S*)	100	94 (*R*)
S17	H	Et	100	97 (*S*)	100	95 (*R*)
S18	H	^{i}Pr	100	96 (*S*)	100	96 (*R*)
S19	H	Ph	100	97 (*S*)	100	96 (*R*)



	R	X	L4e % Conv	L4e % ee	L5d % Conv	L5d % ee
S20	Ph	CH_2	100	98 (*S*)	100	95 (*R*)
S21	Ph	NAc	59	>99 (*R*)	48	>99 (*S*)
S22	Ph	NBn	77	>99 (*R*)	83	>99 (*S*)
S23	Cy	NBn	60	99 (*R*)	51	>99 (*S*)

Figure S3. Asymmetric hydrogenation of α,β-unsaturated enones **S16-S20** and lactames **S21-S23** using [Ir(cod)(L)]BAr$_F$ (L=**L5d** and **L4e**).

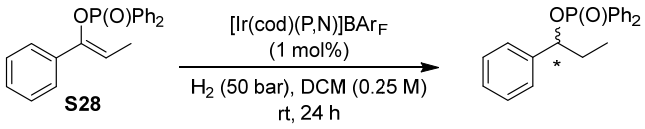
Table S5. Asymmetric hydrogenation of vinyl boronates S24-S27 using [Ir(cod)(L1-L6a-h)]BAr$_F$



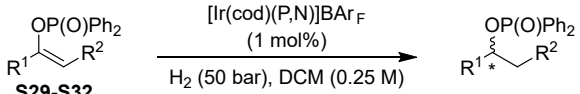
S24 R^1= H; R^2= Bpin
S25 R^1= 4-F-C_6H_3; R^2= Bpin
S26 R^1= 4-OMe-C_6H_3; R^2= Bpin
S27 R^1= H; R^2= Ph

		S24		**S25**		**S26**		**S27**	
Entry	L	%Conv	%ee	%Conv	%ee	%Conv	%ee	%Conv	%ee
1	**L1a**	100	92 (*S*)	100	91 (*S*)	100	92 (*S*)	99	93 (+)
2	**L1d**	100	99 (*S*)	100	99 (*S*)	100	98 (*S*)	100	>99 (+)
3	**L1e**	100	32 (*S*)	100	29 (*S*)	100	31 (*S*)	98	32 (+)
4	**L1f**	100	84 (*S*)	100	85 (*S*)	100	86 (*S*)	42	83 (+)
5	**L1g**	100	90 (*S*)	100	90 (*S*)	100	91 (*S*)	46	92 (+)
6	**L2a**	100	87 (*S*)	100	85 (*S*)	100	87 (*S*)	100	87 (+)
7	**L2b**	100	92 (*S*)	100	91 (*S*)	100	89 (*S*)	100	90 (+)
8	**L2f**	100	81 (*S*)	100	72 (*S*)	100	83 (*S*)	49	86 (+)
9	**L2g**	100	92 (*S*)	100	91 (*S*)	100	92 (*S*)	68	94 (+)
10	**L2h**	100	30 (*S*)	100	28 (*S*)	100	31 (*S*)	36	36 (+)
11	**L3b**	100	81 (*S*)	100	81 (*S*)	100	80 (*S*)	49	84 (+)
12	**L4a**	100	90 (*R*)	100	92 (*R*)	100	90 (*R*)	100	89 (-)
13	**L4d**	100	62 (*R*)	100	59 (*R*)	100	61 (*R*)	100	63 (-)
14	**L4e**	100	98 (*R*)	100	97 (*R*)	100	98 (*R*)	100	98 (-)
15	**L4f**	100	96 (*R*)	100	94 (*R*)	100	94 (*R*)	84	94 (-)
16	**L4g**	100	86 (*R*)	100	83 (*R*)	100	87 (*R*)	81	83 (-)
17	**L4h**	100	90 (*R*)	100	92 (*R*)	100	89 (*R*)	46	91 (-)
18	**L5d**	100	97 (*S*)	100	95 (*S*)	100	96 (*S*)	100	93 (+)
19	**L5e**	100	23 (*S*)	100	22 (*S*)	100	25 (*S*)	100	43 (+)
20	**L6d**	100	91 (*S*)	100	89 (*S*)	100	90 (*S*)	68	88 (+)

Table S6. Asymmetric hydrogenation of enol phosphonate S28 using [Ir(cod)(L1-L6a-h)]BAr$_F$



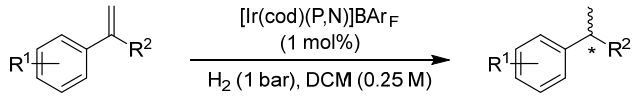
Entry	L	%Conv	%ee	Entry	L	%Conv	%ee
1	**L1a**	100	95 (*R*)	14	**L3b**	68	87 (*R*)
2	**L1b**	100	98 (*R*)	15	**L4a**	100	83 (*S*)
3	**L1c**	100	18 (*S*)	16	**L4d**	100	8 (*R*)
4	**L1d**	100	95 (*R*)	17	**L4e**	100	96 (*S*)
5	**L1e**	100	26 (*S*)	18	**L4f**	62	95 (*S*)
6	**L1f**	74	93 (*R*)	19	**L4g**	45	96 (*S*)
7	**L1g**	68	98 (*R*)	20	**L4h**	55	65 (*S*)
8	**L2a**	100	92 (*R*)	21	**L5a**	100	83 (*R*)
9	**L2b**	100	93 (*R*)	22	**L5d**	100	81 (*R*)
10	**L2f**	73	67 (*R*)	23	**L5e**	100	60 (*R*)
11	**L2g**	56	92 (*R*)	24	**L6a**	100	89 (*R*)
12	**L2h**	35	17 (*S*)	25	**L6d**	100	92 (*R*)
13	**L3a**	77	88 (*R*)	26	**L6e**	100	15 (*R*)



			L1b		L4e	
	R^1	R^2	% Conv	% ee	% Conv	%ee
S29	^{t}Bu	Me	100	98 (*R*)	100	96 (*S*)
S30	4-Me-C_6H_4	CO_2Et	100	96 (*R*)	100	97 (*S*)
S31	4-CF_3-C_6H_4	CO_2Et	100	98 (*R*)	100	96 (*S*)
S32	^{i}Pr	CO_2Et	100	97 (*R*)	100	95 (*S*)

Figure S4. Asymmetric hydrogenation of enol phosphonates **S29-S32** using [Ir(cod)(L)]BAr$_F$ (L=**L1b** and **L4e**)

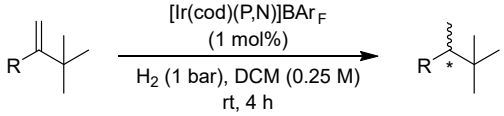
Table S7. Asymmetric hydrogenation of disubstituted olefins S33-S35 using [Ir(cod)(L1-L6a-h)]BAr$_F$

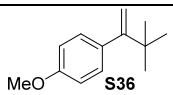
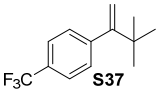
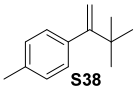
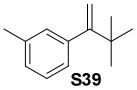
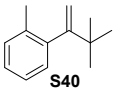
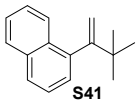
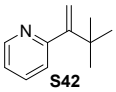
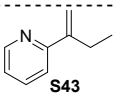
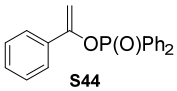
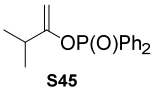


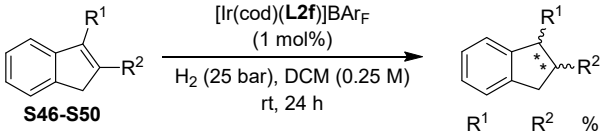
S33 R^1= 4-OMe; R^2= Et
S34 R^1= H; R^2= ^{i}Pr
S35 R^1= H; R^2= Cy

		S33		S34		S35	
Entry	L	%Conv	%ee	%Conv	%ee	%Conv	%ee
1	**L1a**	100	48 (*S*)	100	62 (*S*)	100	39 (*S*)
2	**L1d**	100	86 (*S*)	100	92 (*S*)	100	88 (*S*)
3	**L1e**	100	21 (*R*)	100	3 (*R*)	100	3 (*R*)
4	**L1f**	100	41 (*S*)	100	50 (*S*)	100	51 (*S*)
5	**L1g**	100	55 (*S*)	100	47 (*S*)	100	60 (*S*)
6	**L2a**	100	43 (*S*)	100	51 (*S*)	100	48 (*S*)
7	**L2b**	100	78 (*S*)	100	86 (*S*)	100	83 (*S*)
8	**L2f**	100	50 (*S*)	100	52 (*S*)	100	43 (*S*)
9	**L2g**	100	28 (*S*)	100	33 (*S*)	100	26 (*S*)
10	**L2h**	100	11 (*S*)	100	9 (*S*)	100	10(*S*)
11	**L3b**	100	19 (*S*)	100	26 (*S*)	100	26 (*S*)
12	**L4a**	100	54 (*R*)	100	84 (*R*)	100	80 (*R*)
13	**L4d**	100	22 (*R*)	100	36 (*R*)	100	51 (*R*)
14	**L4e**	100	83 (*R*)	100	70 (*R*)	100	66 (*R*)
15	**L4f**	100	50 (*R*)	100	48 (*R*)	100	49 (*R*)
16	**L4g**	100	53 (*R*)	100	53 (*R*)	100	50 (*R*)
17	**L4h**	100	55 (*R*)	100	58 (*R*)	100	48 (*R*)
18	**L5d**	100	76 (*S*)	100	77 (*S*)	100	82 (*S*)
19	**L5e**	100	32 (*R*)	100	28 (*R*)	100	11 (*R*)
20	**L6d**	100	84 (*S*)	100	81 (*S*)	100	83 (*S*)

Table S8. Asymmetric hydrogenation of 1,1'-(hetero)aryl-*tert*-butyl alkenes S36-S43 and enol phosphonates S44-S45 using [Ir(cod)(L)]BAr$_F$ (L=L1a and L4a)



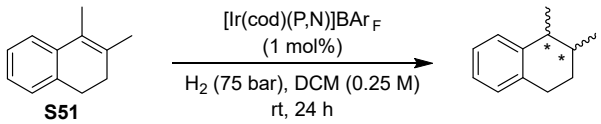
Entry	Substrate	L1a		L4a	
		%Conv	%ee	%Conv	%ee
1	 S36	100	95 (*S*)	100	97 (*R*)
2	 S37	100	96 (*S*)	100	97 (*R*)
3	 S38	100	96 (*S*)	100	98 (*R*)
4	 S39	100	96 (*S*)	100	96 (*R*)
5	 S40	100	97 (*S*)	100	>99 (*R*)
6	 S41	100	96 (*S*)	100	98 (*R*)
7	 S42	100	95 (*S*)	100	97 (*R*)
		L1b		**L4e**	
Entry	Substrate	%Conv	%ee	%Conv	%ee
8	 S43	100	88 (*S*)	100	80 (*R*)
9	 S44	100	95 (*R*)	100	92 (*S*)
10	 S45	100	94 (*R*)	100	93 (*S*)



	R^1	R^2	% Conv	% ee
S46	Et	Me	100	97 (*S*,*S*)
S47	^{n}Bu	Me	100	98 (*S*,*S*)
S48	Ph	Me	100	94 (*R*,*S*)
S49	Me	Et	100	92 (*S*,*S*)
S50	Me	^{n}Bu	100	93 (*S*,*S*)

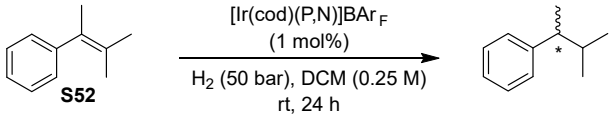
Figure S5. Asymmetric hydrogenation of indenes **S46-S50** using [Ir(cod)(L)]BAr$_F$ (L=**L1b** and **L4e**)

Table S9. Asymmetric hydrogenation of dihydronapthalene S51 using [Ir(cod)(L1-L6a-h)]BAr$_F$



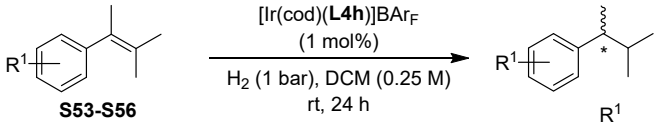
Entry	L	%Conv	%ee
1	**L2f**	100	81 (*S*,*S*)
2	**L2g**	100	90 (*S*,*S*)
3	**L2h**	100	71 (*S*,*S*)
4	**L4f**	100	77 (*R*,*R*)
5	**L4g**	100	75 (*R*,*R*)
6	**L4h**	100	66 (*R*,*R*)

Table S10. Asymmetric hydrogenation of acyclic tetrasubstituted substrate S52 using [Ir(cod)(L1-L6a-h)]BAr$_F$



Entry	L	%Conv	%ee	Entry	L	%Conv	%ee
1	**L1a**	80	28 (*S*)	15	**L4a**	50	41 (*R*)
2	**L1b**	20	2 (*S*)	16	**L4d**	40	13 (*R*)
3	**L1c**	65	1 (*S*)	17	**L4e**	35	36 (*R*)
4	**L1d**	25	2 (*S*)	18	**L4f**	65	12 (*S*)
5	**L1e**	70	4 (*R*)	19	**L4g**	100	26 (*S*)
6	**L1f**	85	1 (*R*)	20	**L4h**	100	91 (*S*)
7	**L1g**	75	2 (*R*)	21	**L5a**	70	36 (*S*)
8	**L2a**	75	15 (*S*)	22	**L5d**	40	28 (*S*)
9	**L2b**	25	3 (*R*)	23	**L5e**	40	11 (*S*)
10	**L2f**	100	25 (*R*)	24	**L6a**	80	37 (*S*)
11	**L2g**	95	8 (*R*)	25	**L6d**	40	30 (*S*)
12	**L2h**	98	38 (*R*)	26	**L6e**	50	13 (*S*)
13	**L3a**	5	4 (*R*)	27[a]	**L4h**	100	97 (*S*)
14	**L3b**	5	8 (*R*)	28[b]	**L4h**	100	97 (*S*)

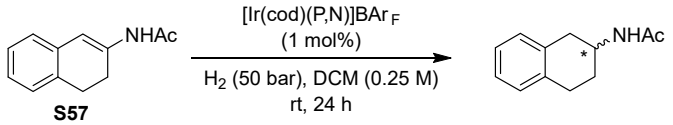
[a] Reaction carried out at 25 bar H_2. [b] Reaction carried out at 1 bar H_2



	R^1	% Conv	% ee
S53	4-Me	100	97 (*S*)
S54	4-OMe	100	96 (*S*)
S55	3-Me	100	98 (*S*)
S56	2-OMe	100	97 (*S*)

Figure S6. Asymmetric hydrogenation of acyclic tetrasubstituted substrates **S53-S56** using [Ir(cod)(**L4h**)]BAr$_F$

Table S11. Asymmetric hydrogenation of cyclic β-enamide S57 using [Ir(cod)(L1-L6a-h)]BAr$_F$



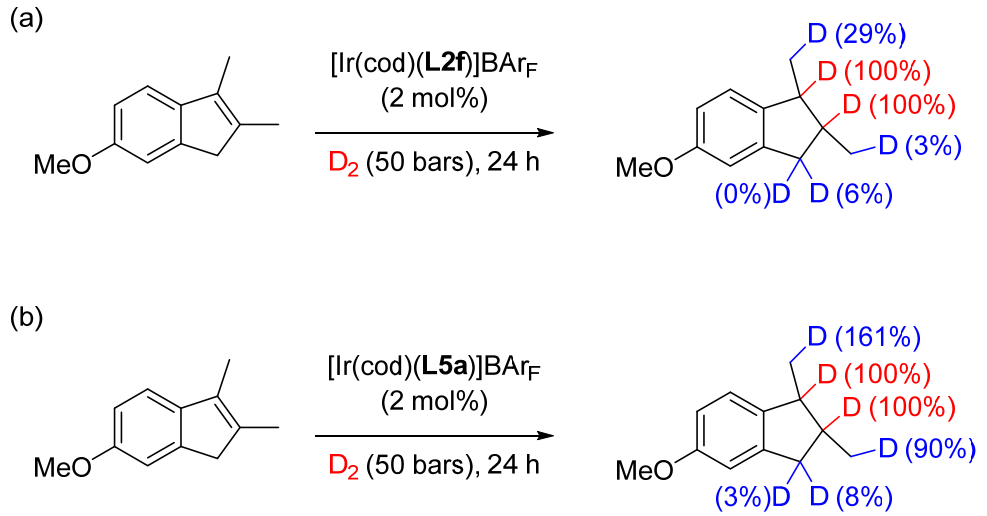
Entry	L	%Conv	%ee	Entry	L	%Conv	%ee
1	**L1a**	100	20 (*R*)	14	**L3b**	100	40 (*S*)
2	**L1b**	100	85 (*S*)	15	**L4a**	100	18 (S)
3	**L1c**	100	51 (*R*)	16	**L4d**	100	66 (S)
4	**L1d**	100	85 (*S*)	17	**L4e**	100	97 (*R*)
5	**L1e**	100	53 (*R*)	18	**L4f**	100	13 (*R*)
6	**L1f**	100	19 (*S*)	19	**L4g**	100	41 (*R*)
7	**L1g**	100	37 (*S*)	20	**L4h**	100	55 (*R*)
8	**L2a**	100	32 (*R*)	21	**L5a**	100	36 (*R*)
9	**L2b**	100	91 (*S*)	22	**L5d**	100	94 (*S*)
10	**L2f**	100	47 (*S*)	23	**L5e**	100	58 (*R*)
11	**L2g**	100	64 (*S*)	24	**L6a**	100	34 (*R*)
12	**L2h**	100	65 (*S*)	25	**L6d**	100	92 (*S*)
13	**L3a**	100	16 (*R*)	26	**L6e**	100	60 (*R*)

5. Deuterium labeling experiments

In order to find out a plausible explanation for the different behavior in the hydrogenation of tetrasubstituted olefins when using phosphite- or phosphinite-based catalysts precursors, we performed preliminary deuteration experiments using 6-methoxy-2,3-dimethyl-1*H*-indene as substrate. We selected this substrate because the ^{1}H-NMR signal of the methoxy group can be easily use as internal standard to measure the incorporation of deuterium to the different substrate sites.

For both ligand types, the results indicated the addition of deuterium not only at the expected positions (direct incorporation to the double bond, shown in red) but also at other sites (shown in blue), being as expected the allylic position the most favorable one, which is in agreement with a competing isomerization pathway. However, the isomerization degree is much more pronounced using Ir-phosphite-oxazoline catalyst precursor, which fully accounts for the lower enantioselectivities achieved using this type of catalysts.

As expected, the mass spectral data of the corresponding deuterated product catalyzed by [Ir(cod)(**L5a**)]BAr$_F$ clearly showed species with more than two incorporated deuteriums (see below).



Scheme S8. Deuterium labeling experiments of 6-methoxy-2,3-dimethyl-1*H*-indene with D_2 (50 bar) using (a) [Ir(cod)(**L2f**)]BAr$_F$ and (b) [Ir(cod)(**L5a**)]BAr$_F$ catalyst precursors. The percentage of incorporation of deuterium atoms is shown in parentheses. The results of the direct addition to the double bond are shown in red and those for the indirect addition of deuterium due to the isomerization process are shown in blue.

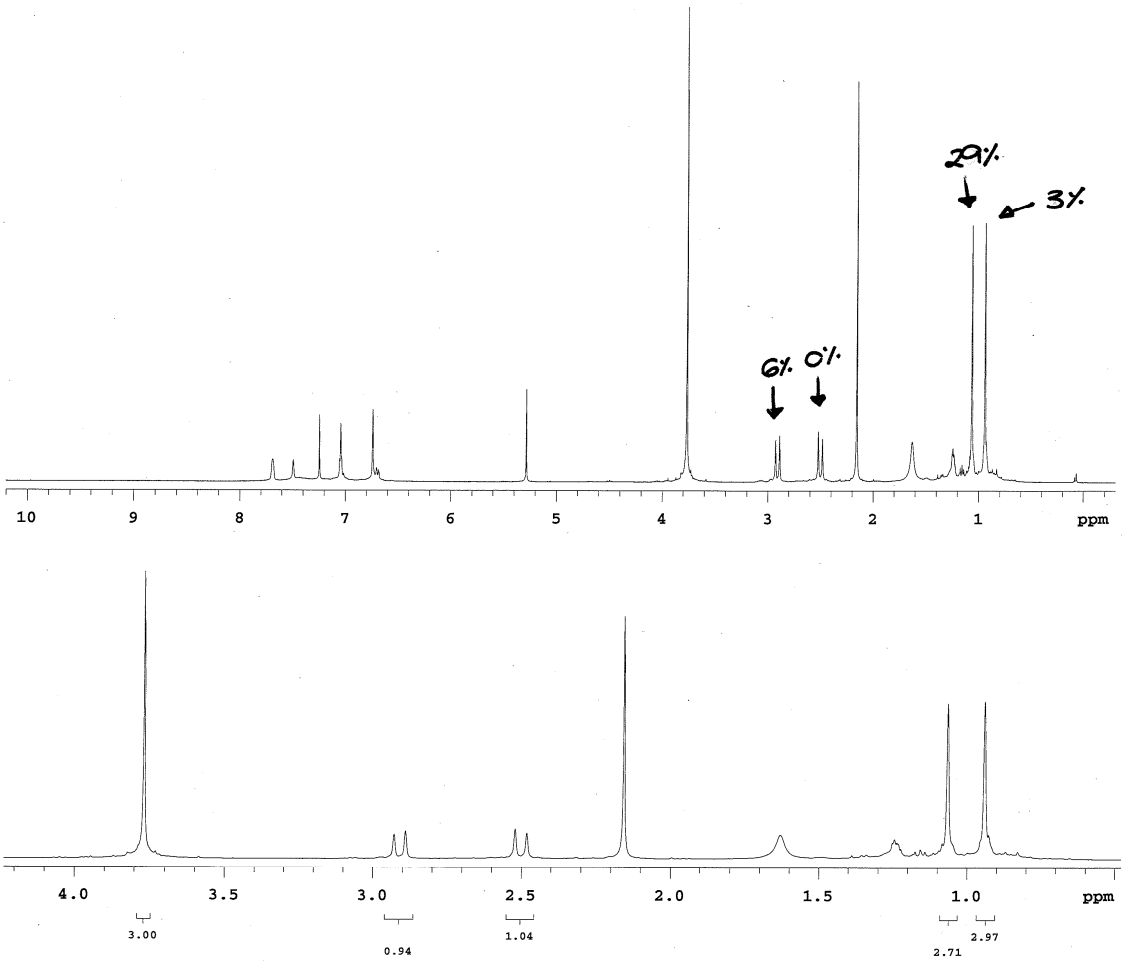


Figure S7. ^{1}H NMR of the reaction of 6-methoxy-2,3-dimethyl-1*H*-indene with D_2 (50 bar) using Ir-**L2f** catalyst precursor after 24 h.

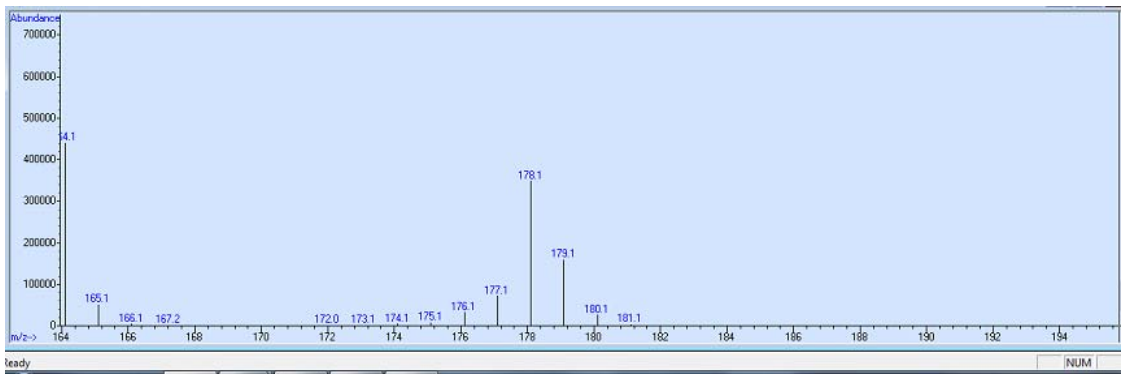


Figure S8. Mass spectrum of the reaction of 6-methoxy-2,3-dimethyl-1*H*-indene with D_2 (50 bar) using Ir-**L2f** catalyst precursor after 24 h.

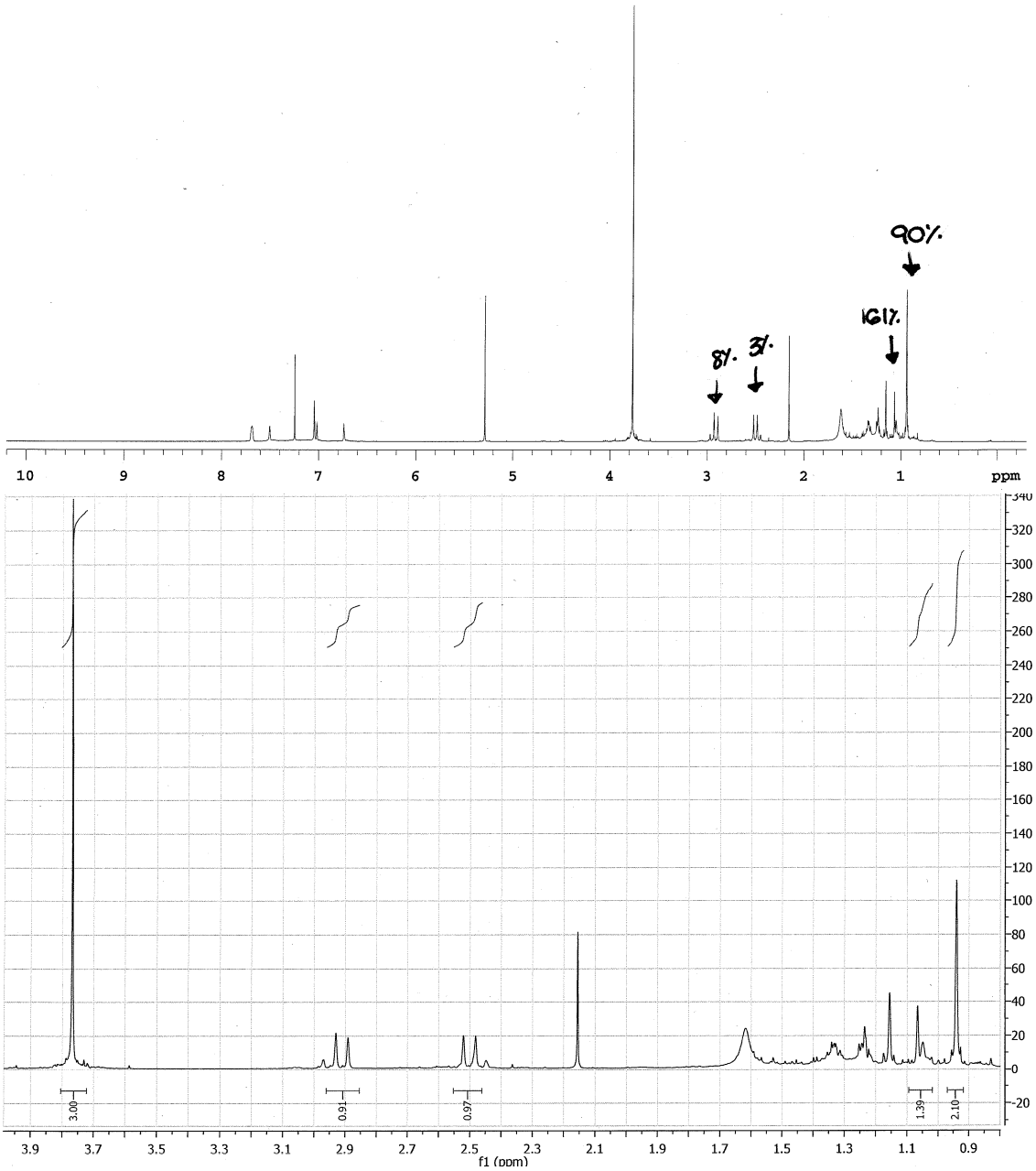


Figure S9. ^{1}H NMR of the reaction of 6-methoxy-2,3-dimethyl-1*H*-indene with D_2 (50 bars) using Ir-**L5a** catalyst precursor after 24 h.

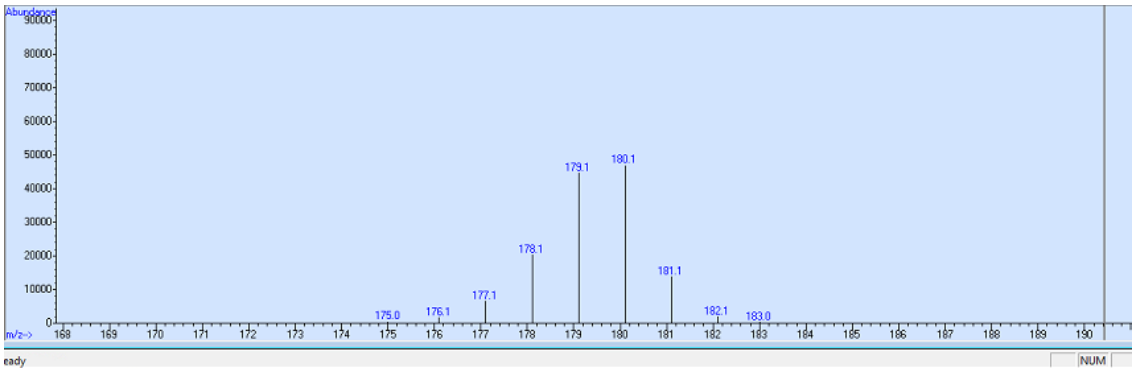


Figure S10. Mass spectrum of the reaction of 6-methoxy-2,3-dimethyl-1*H*-indene with D_2 (50 bars) using Ir- **L5a** catalyst precursor after 24 h.

6. Copies of NMR spectra of [Ir(cod)(L1-L6a-h)]BAr$_F$ complexes

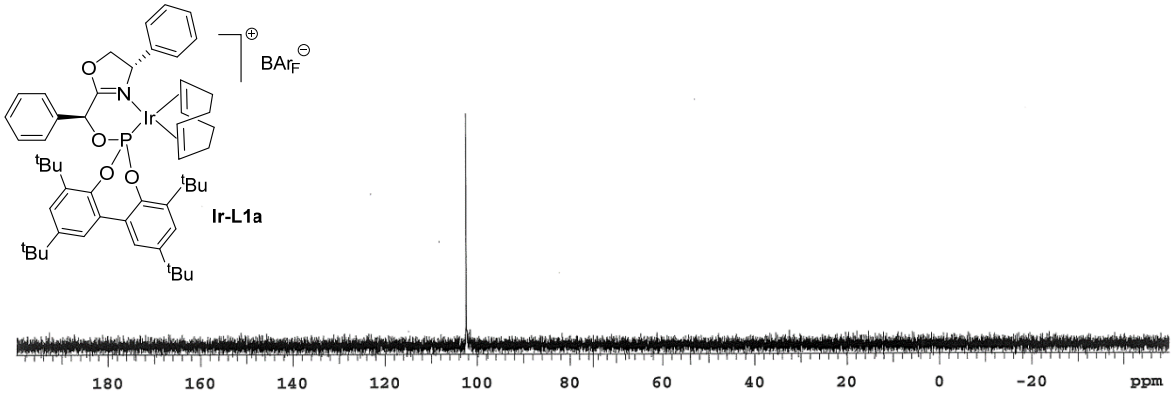


Figure S11. $^{31}P\{^1H\}$-NMR spectrum of [Ir(cod)(**L1a**)]BAr$_F$

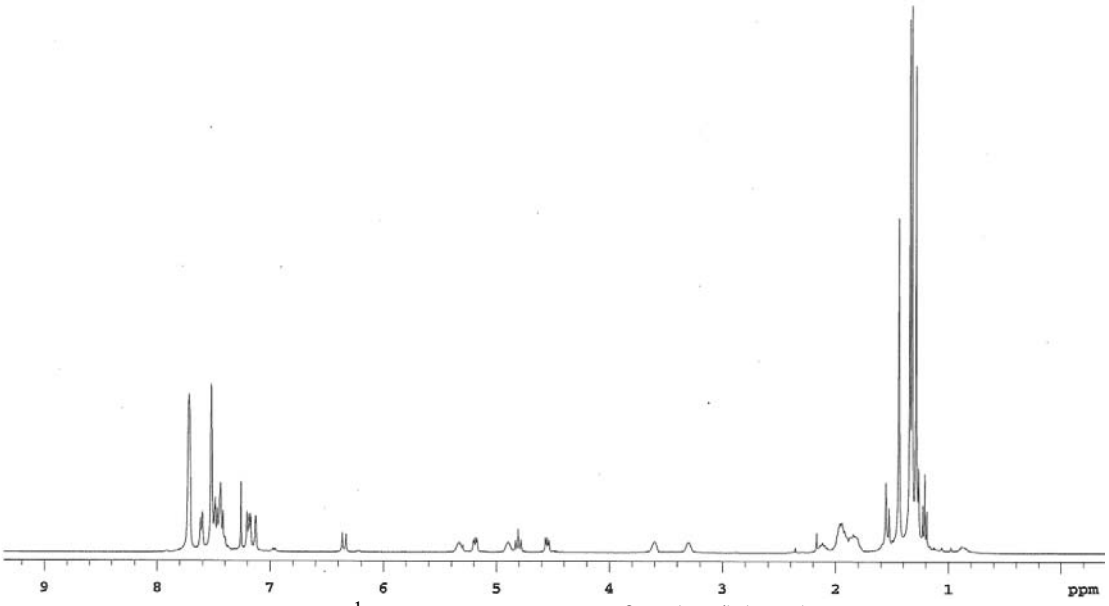


Figure S12. ^1H-NMR spectrum of [Ir(cod)(**L1a**)]BAr$_F$

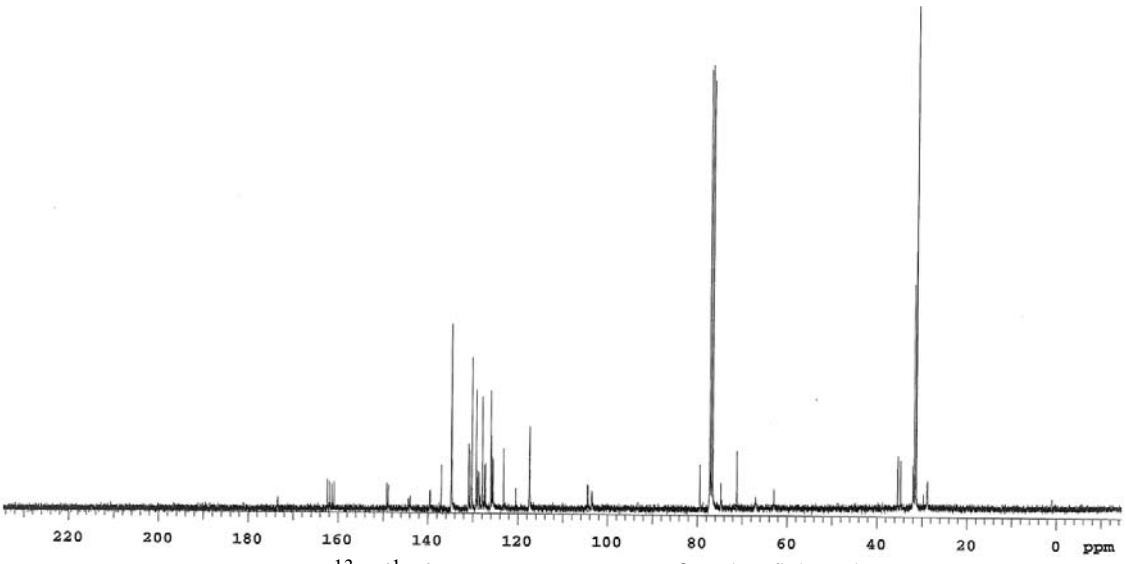


Figure S13. $^{13}C\{^1H\}$-NMR spectrum of [Ir(cod)(**L1a**)]BAr$_F$

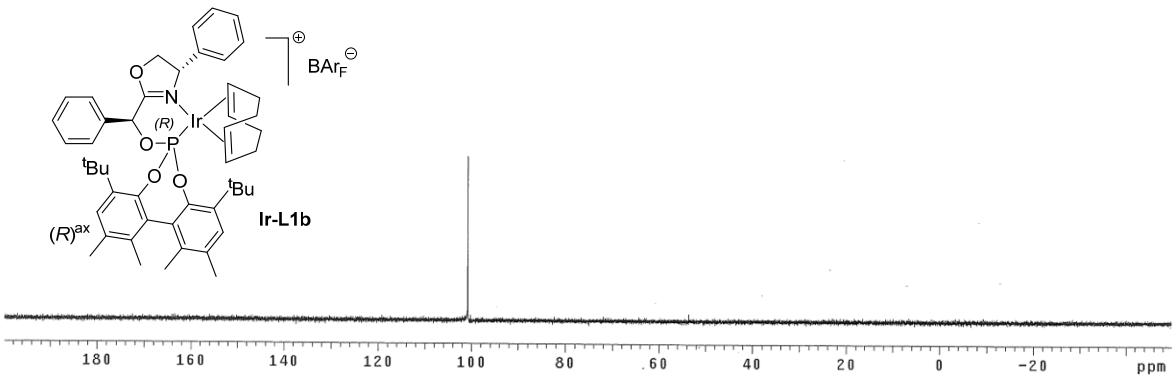


Figure S14. $^{31}P\{^{1}H\}$-NMR spectrum of [Ir(cod)(**L1b**)]BAr_F

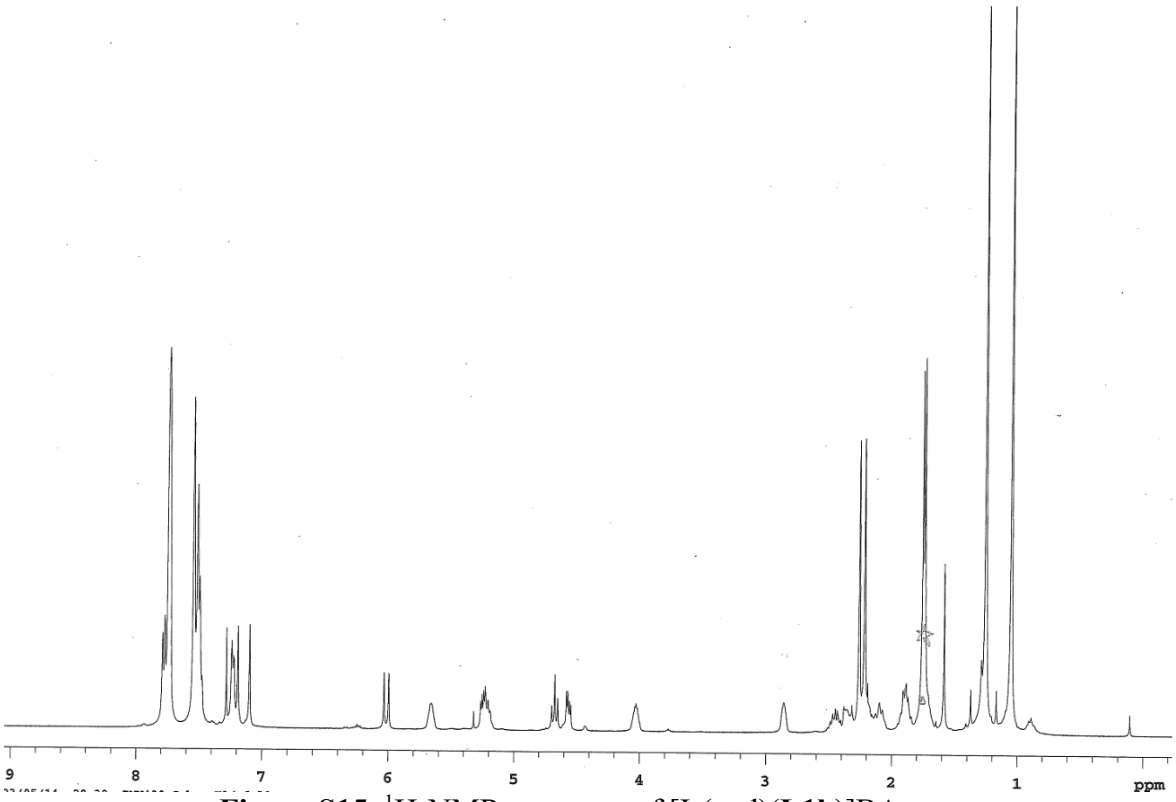


Figure S15. ^{1}H-NMR spectrum of [Ir(cod)(**L1b**)]BAr_F

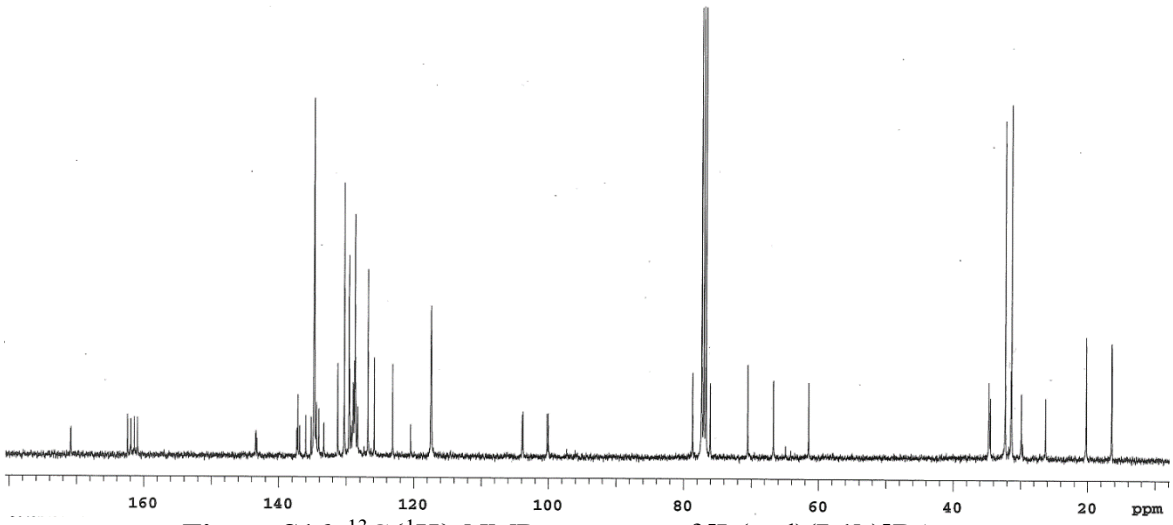


Figure S16. $^{13}C\{^{1}H\}$-NMR spectrum of [Ir(cod)(**L1b**)]BAr_F

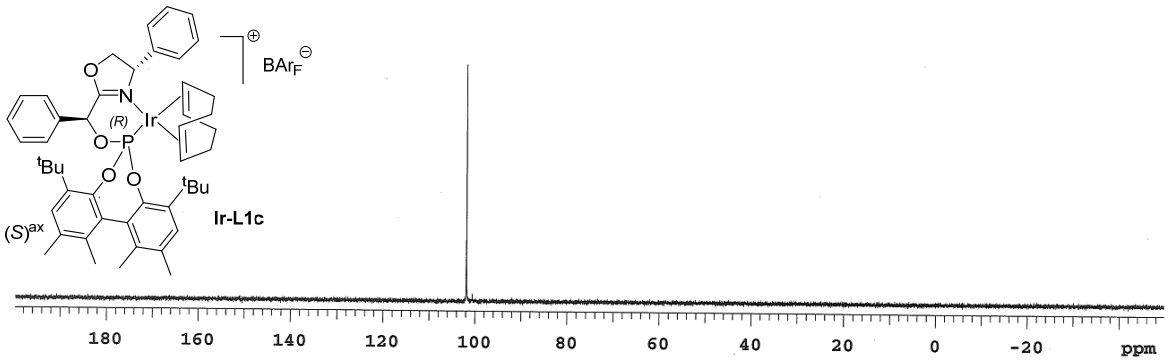


Figure S17. $^{31}P\{^{1}H\}$-NMR spectrum of [Ir(cod)(**L1c**)]BAr$_F$

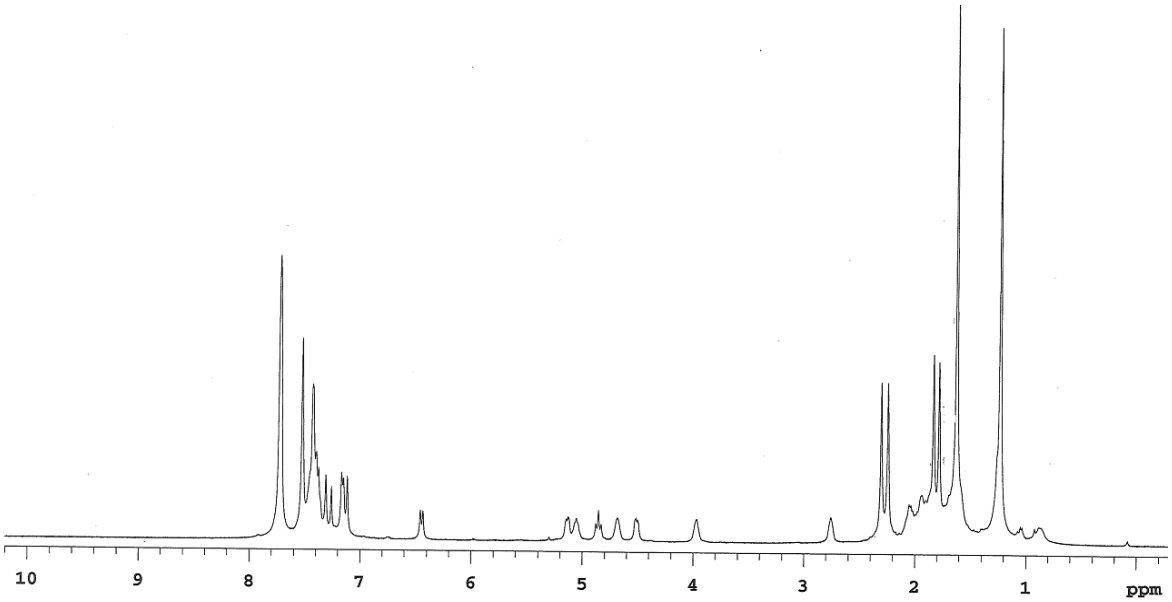


Figure S18. ^{1}H-NMR spectrum of [Ir(cod)(**L1c**)]BAr$_F$

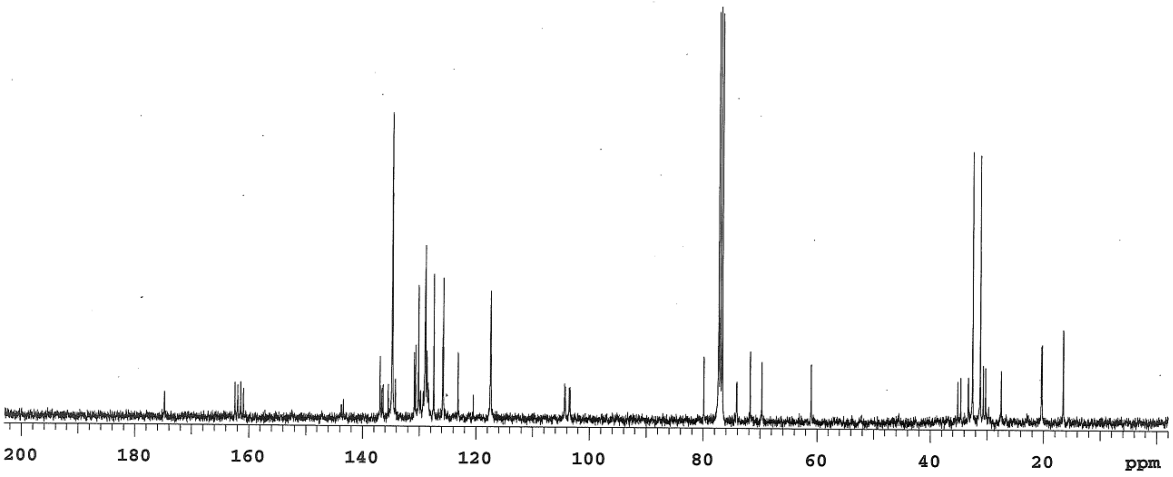


Figure S19. $^{13}C\{^{1}H\}$-NMR spectrum of [Ir(cod)(**L1c**)]BAr$_F$

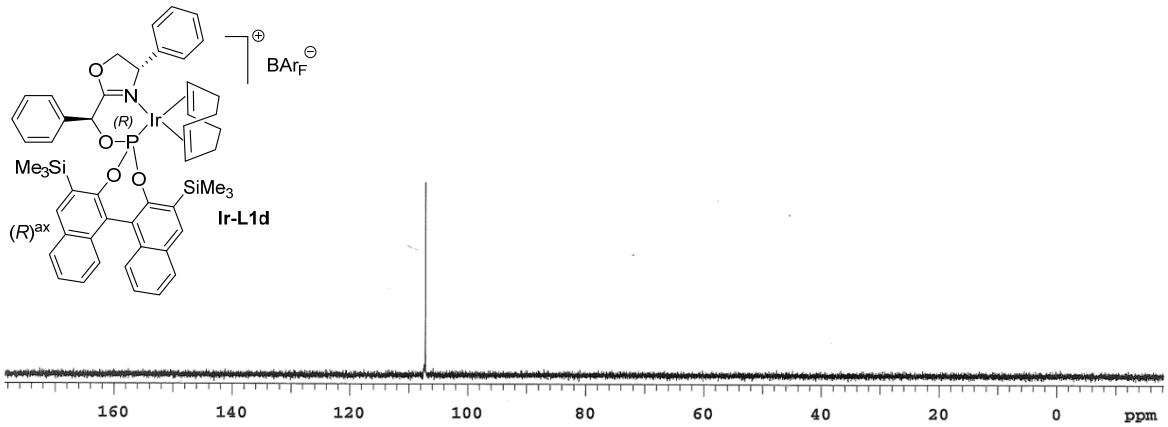


Figure S20. $^{31}P\{^{1}H\}$-NMR spectrum of [Ir(cod)(**L1d**)]BAr$_F$

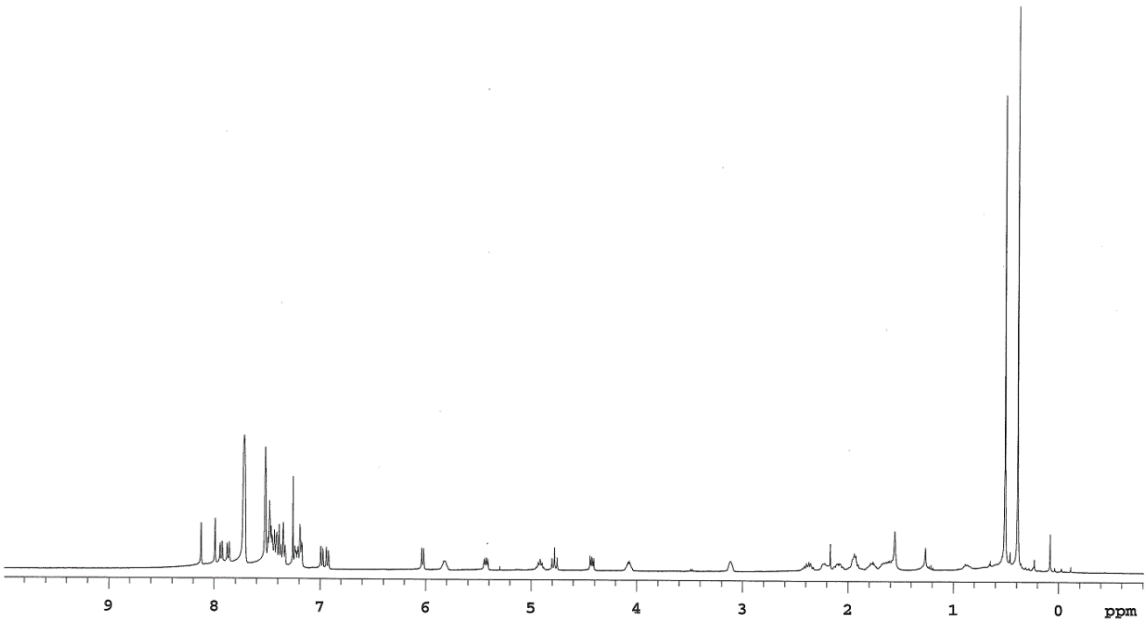


Figure S21. ^{1}H-NMR spectrum of [Ir(cod)(**L1d**)]BAr$_F$

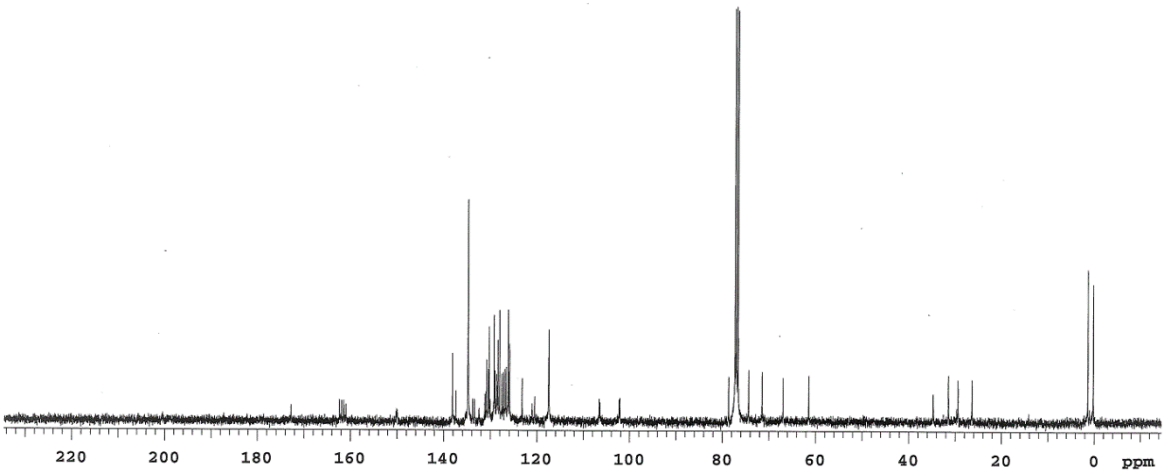


Figure S22. $^{13}C\{^{1}H\}$-NMR spectrum of [Ir(cod)(**L1d**)]BAr$_F$

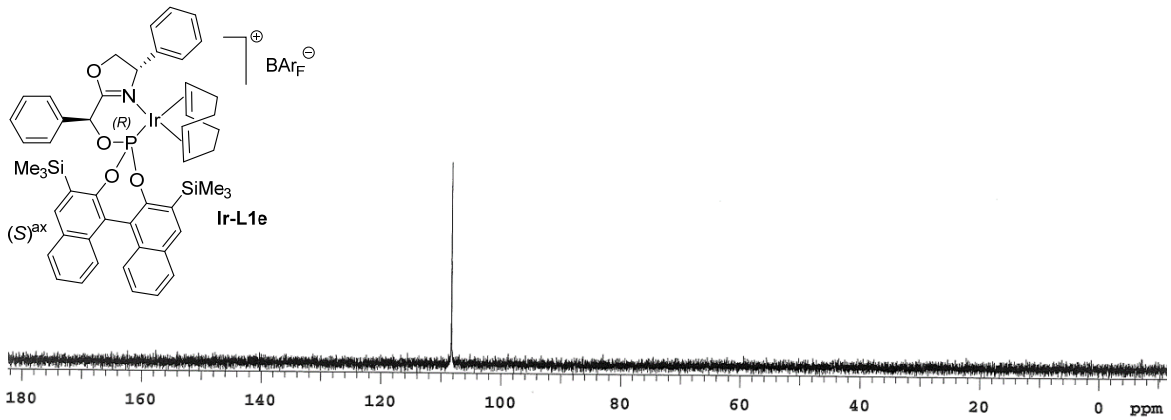


Figure S23. $^{31}P\{^{1}H\}$-NMR spectrum of [Ir(cod)(**L1e**)]BAr_F

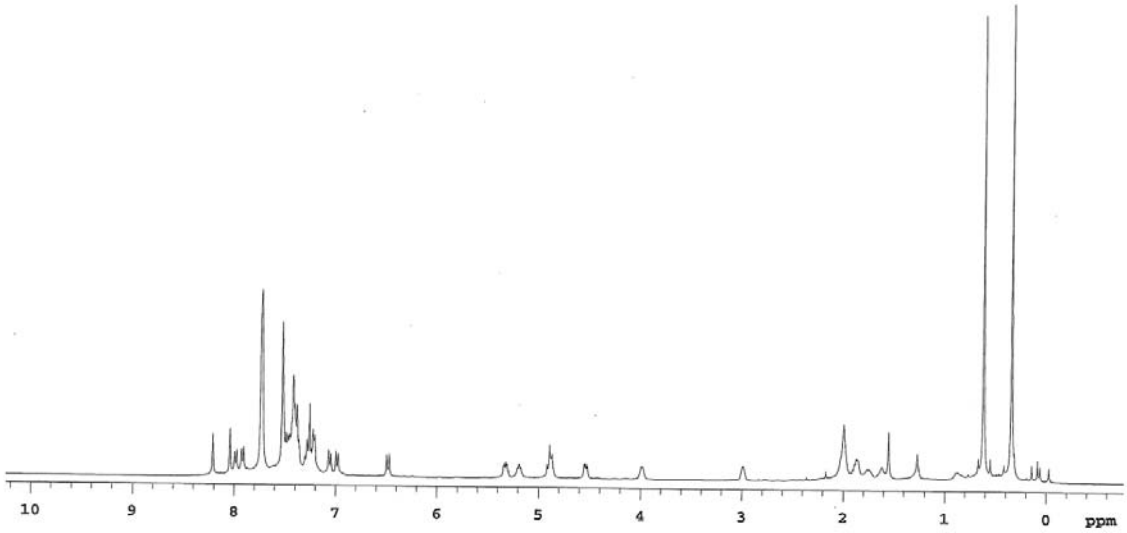


Figure S24. ^{1}H-NMR spectrum of [Ir(cod)(**L1e**)]BAr_F

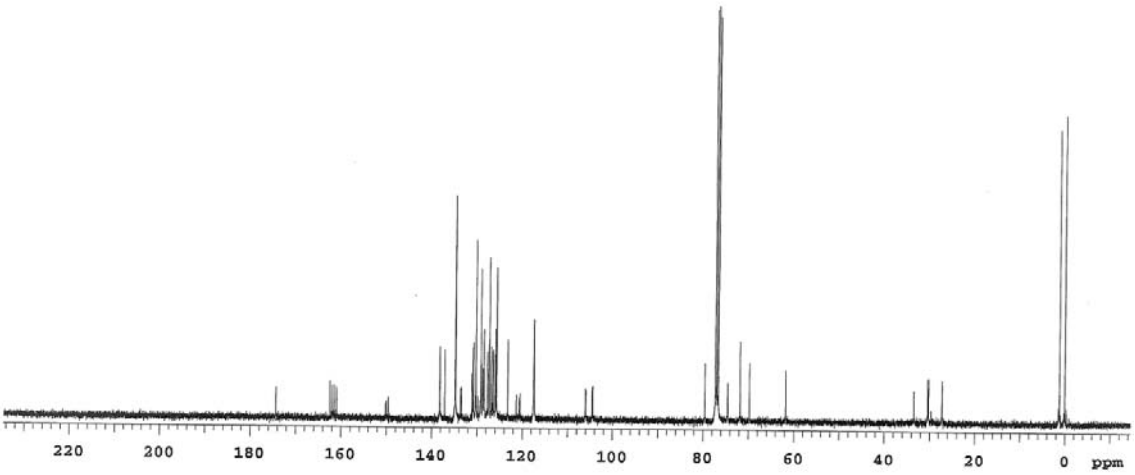


Figure S25. $^{13}C\{^{1}H\}$-NMR spectrum of [Ir(cod)(**L1e**)]BAr_F

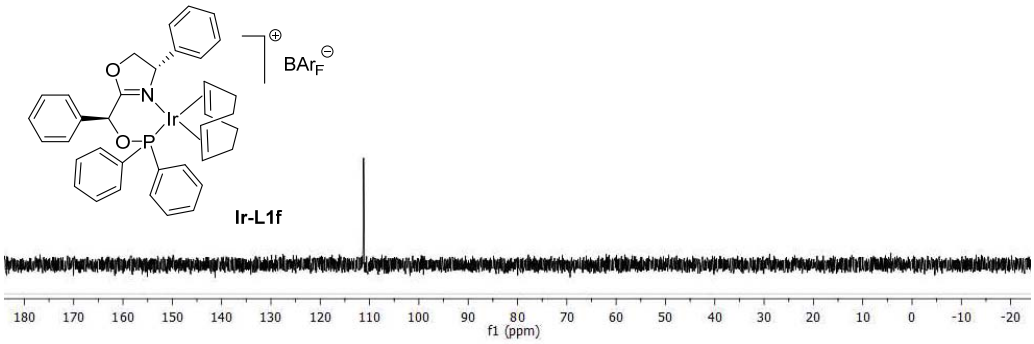


Figure S26. $^{31}P\{^{1}H\}$-NMR spectrum of [Ir(cod)(**L1f**)]BAr_F

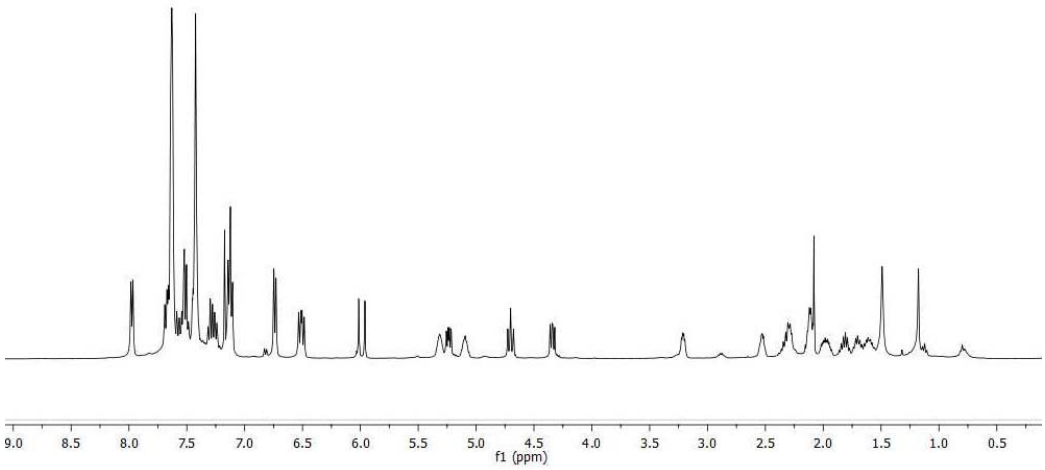


Figure S27. ^{1}H-NMR spectrum of [Ir(cod)(**L1f**)]BAr_F

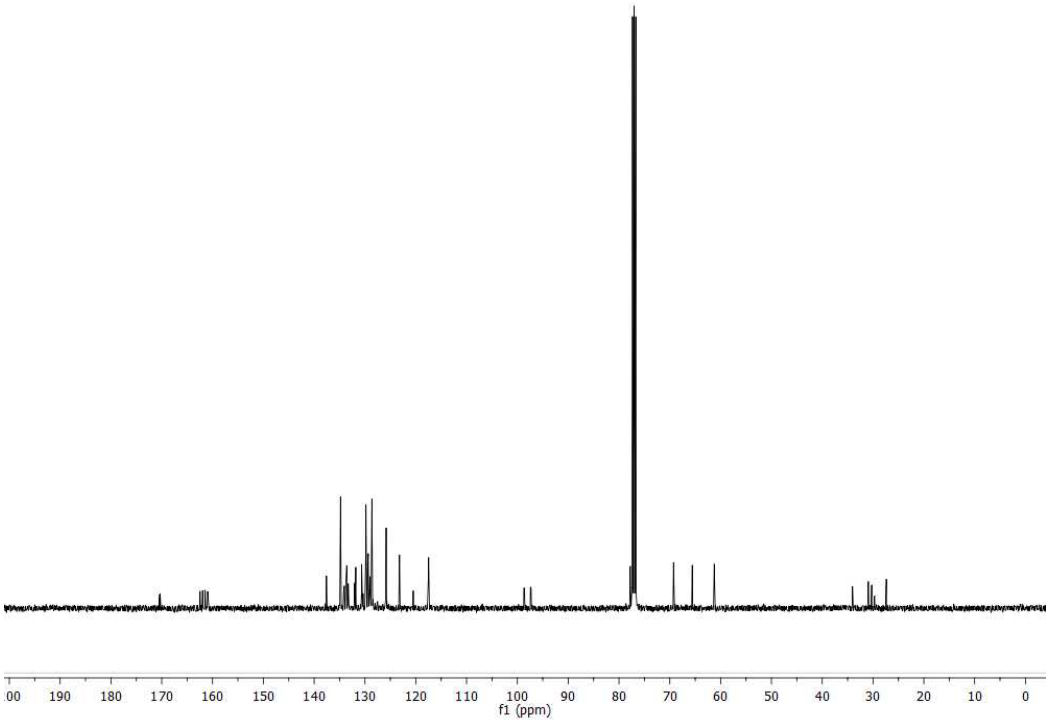


Figure S28. $^{13}C\{^{1}H\}$-NMR spectrum of [Ir(cod)(**L1f**)]BAr_F

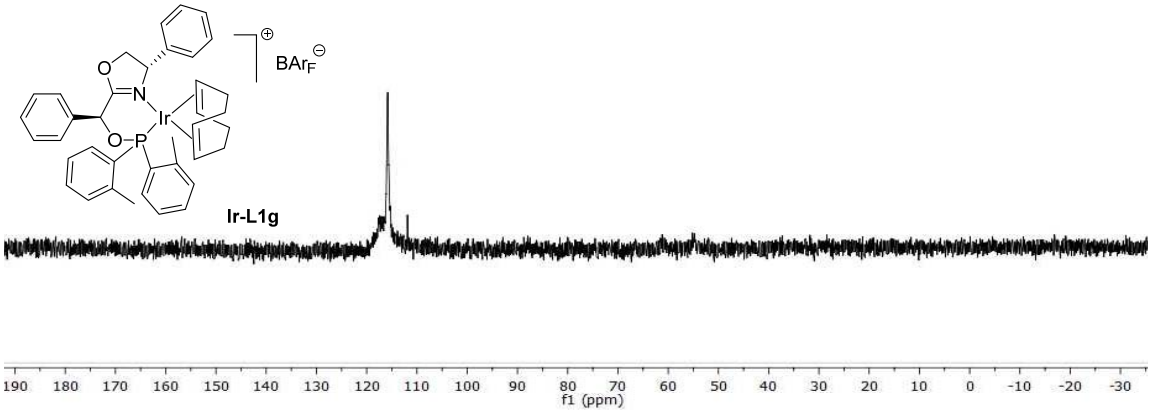


Figure S29. $^{31}P\{^{1}H\}$-NMR spectrum of [Ir(cod)(**L1g**)]BAr$_F$

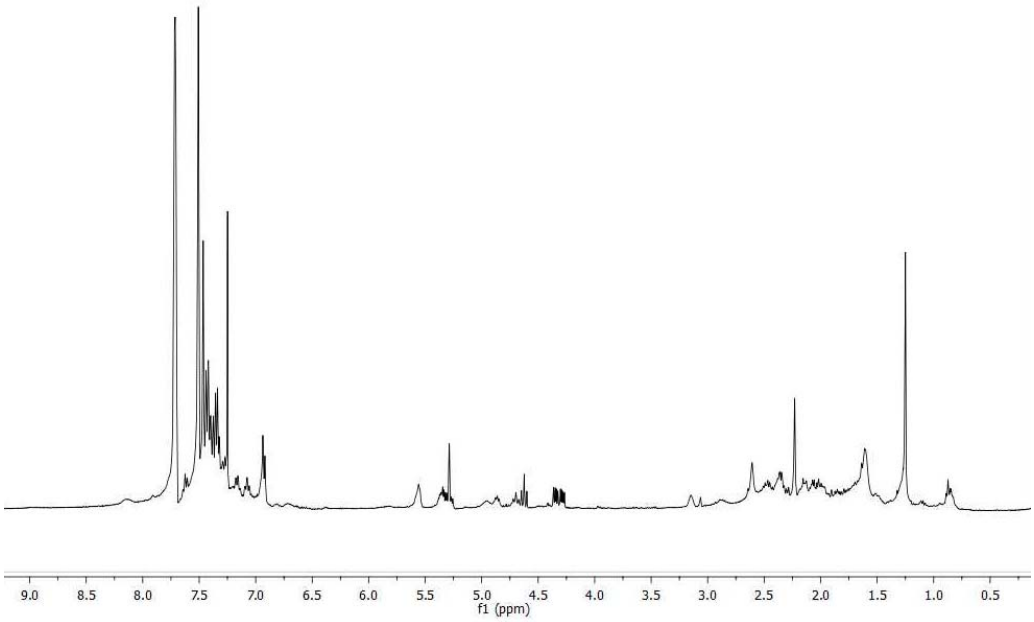


Figure S30. ^{1}H-NMR spectrum of [Ir(cod)(**L1g**)]BAr$_F$

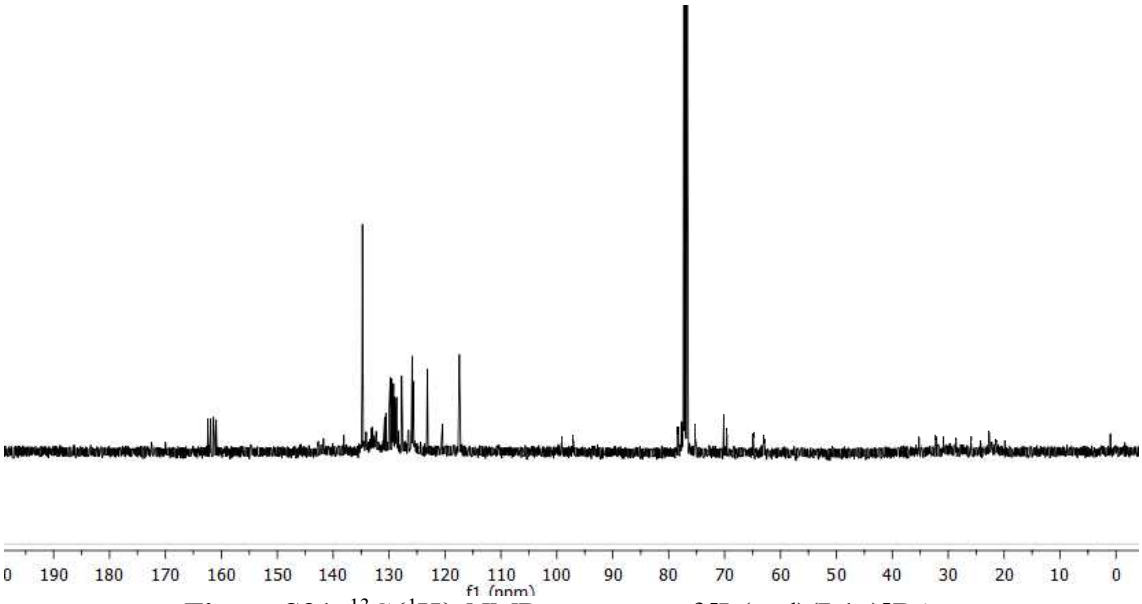


Figure S31. $^{13}C\{^{1}H\}$-NMR spectrum of [Ir(cod)(**L1g**)]BAr$_F$

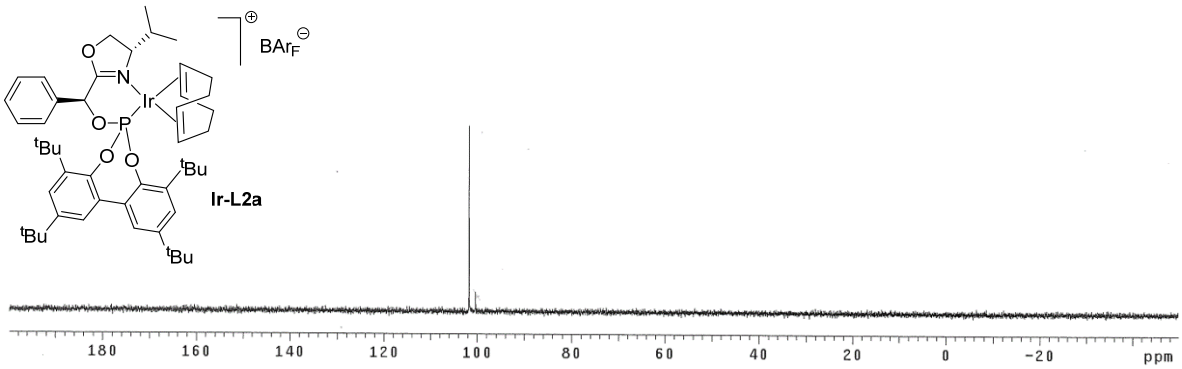


Figure S32. $^{31}P\{^{1}H\}$-NMR spectrum of [Ir(cod)(**L2a**)]BAr$_F$

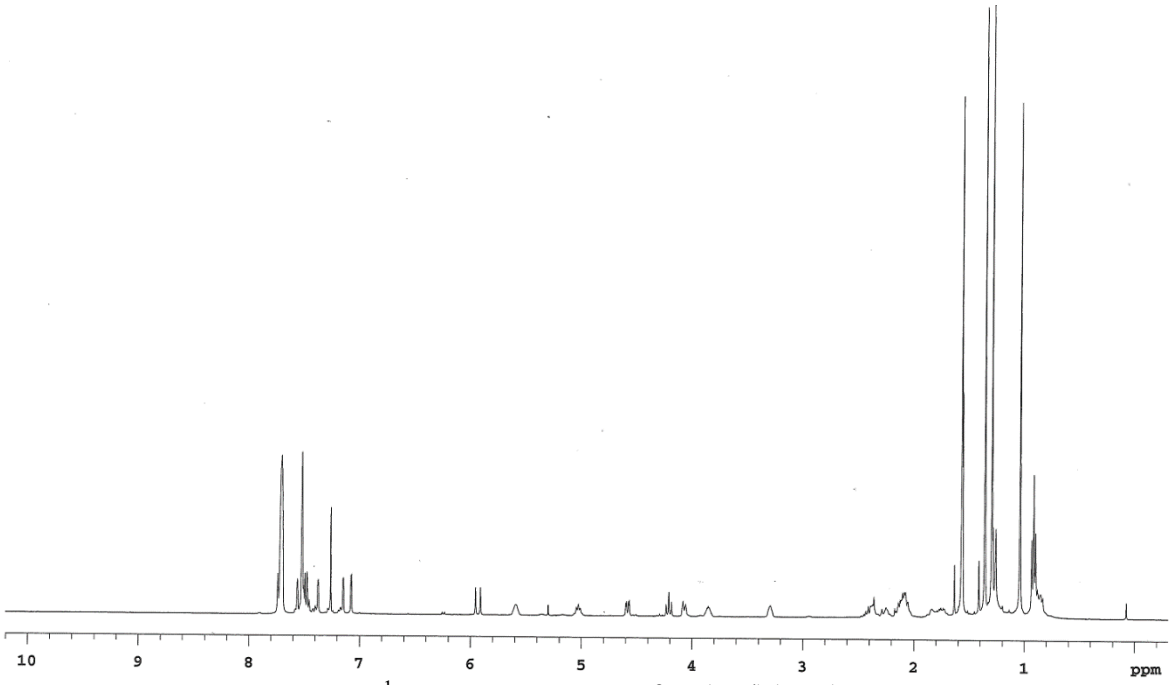


Figure S33. ^{1}H-NMR spectrum of [Ir(cod)(**L2a**)]BAr$_F$

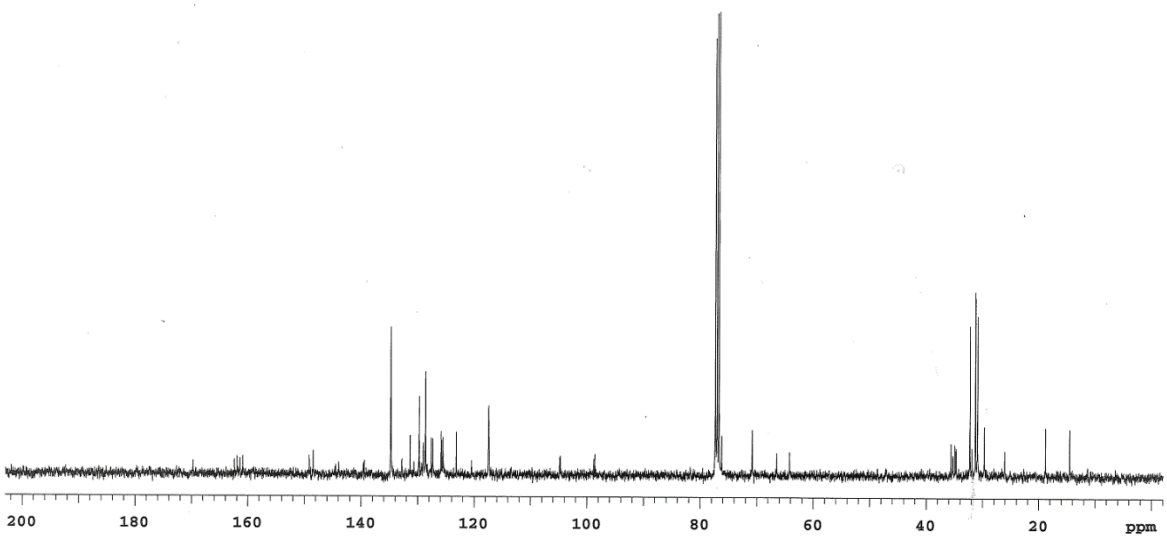


Figure S34. $^{13}C\{^{1}H\}$-NMR spectrum of [Ir(cod)(**L2a**)]BAr$_F$

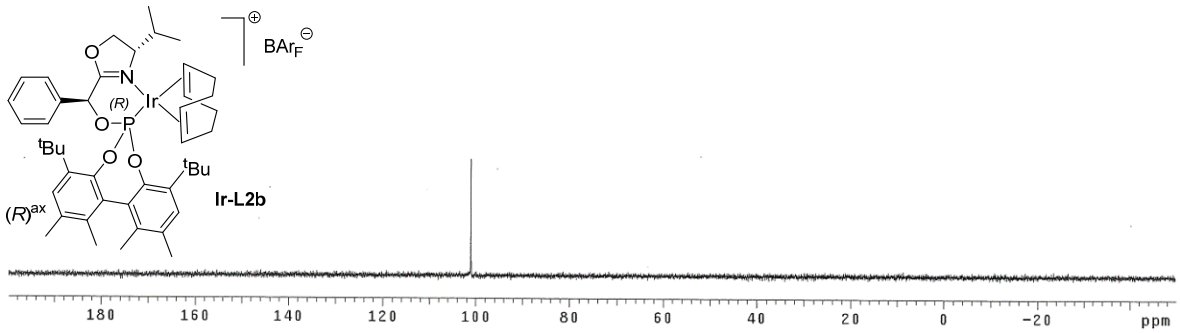


Figure S35. $^{31}P\{^{1}H\}$-NMR spectrum of [Ir(cod)(**L2b**)]BAr_F

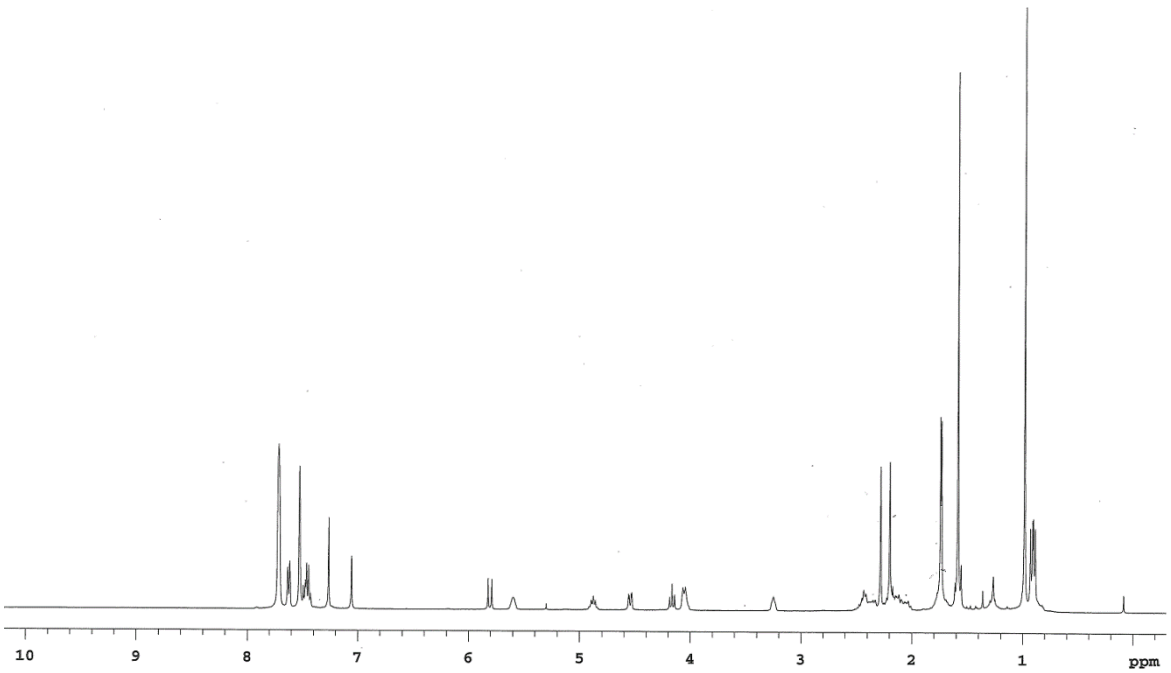


Figure S36. ^{1}H-NMR spectrum of [Ir(cod)(**L2b**)]BAr_F

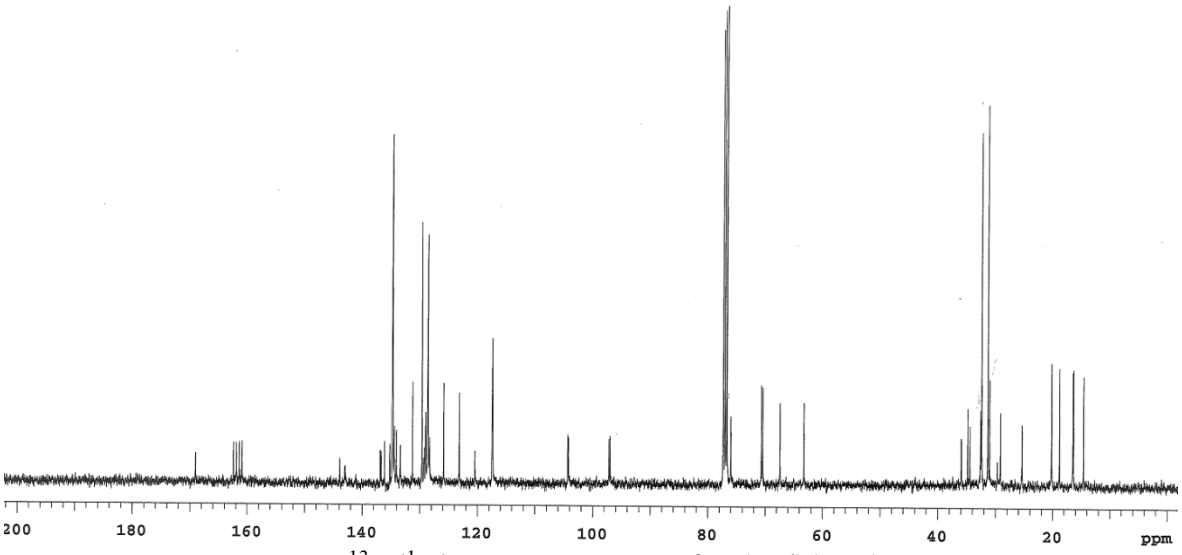


Figure S37. $^{13}C\{^{1}H\}$-NMR spectrum of [Ir(cod)(**L2b**)]BAr_F

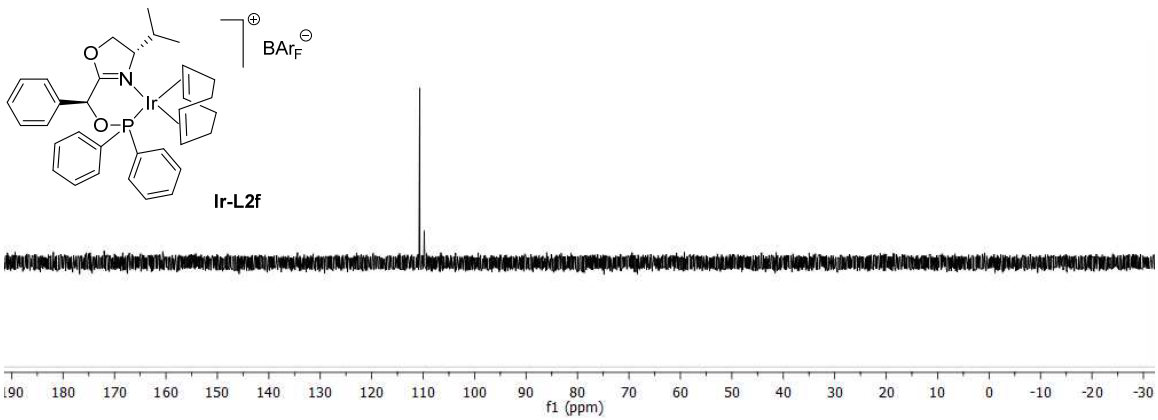


Figure S38. $^{31}P\{^1H\}$-NMR spectrum of [Ir(cod)(**L2f**)]BAr$_F$

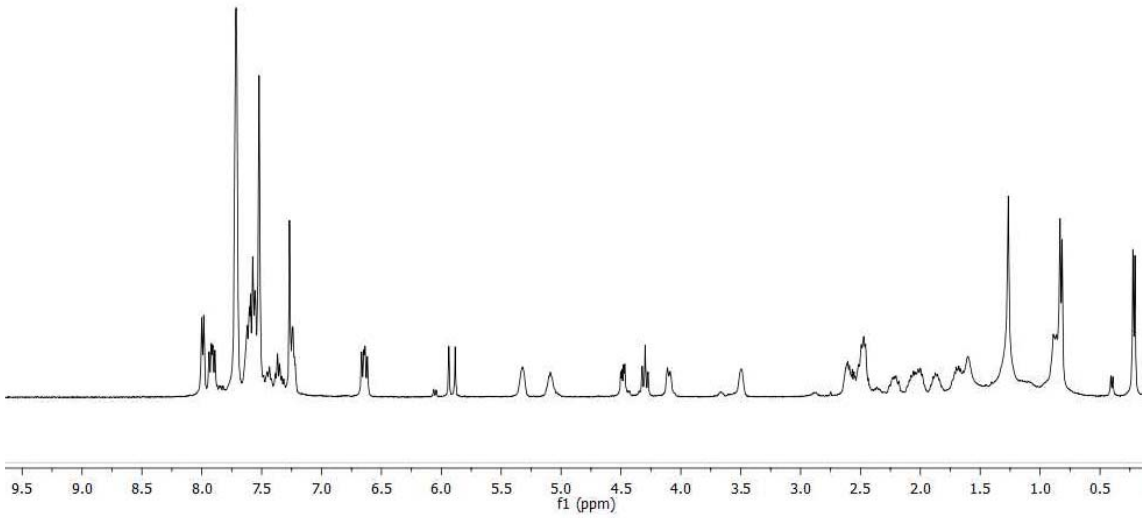


Figure S39. ^1H-NMR spectrum of [Ir(cod)(**L2f**)]BAr$_F$

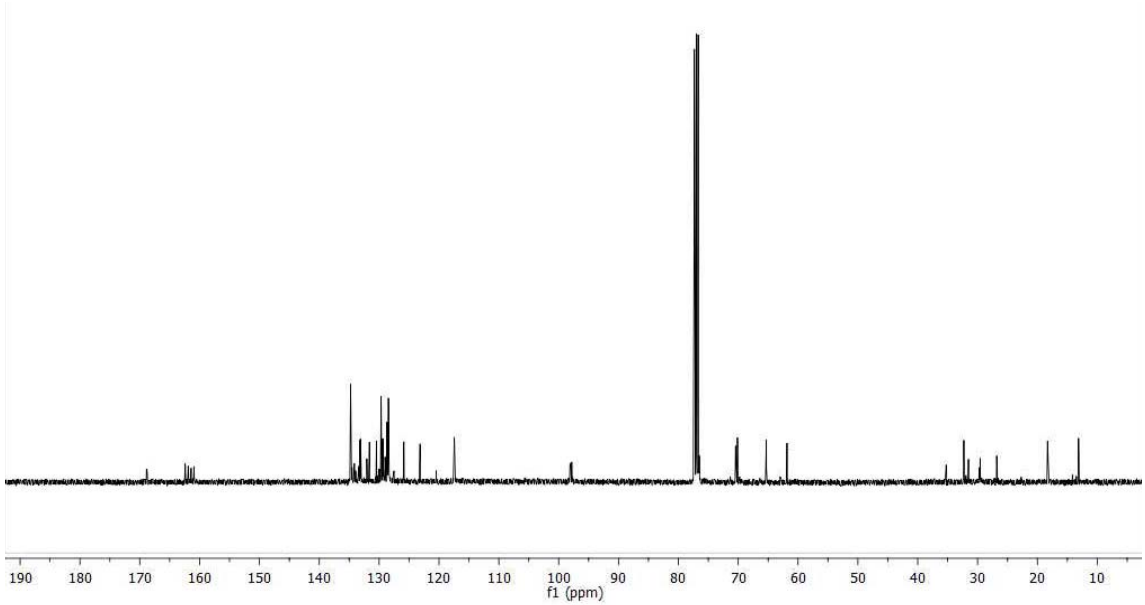


Figure S40. $^{13}C\{^1H\}$-NMR spectrum of [Ir(cod)(**L2f**)]BAr$_F$

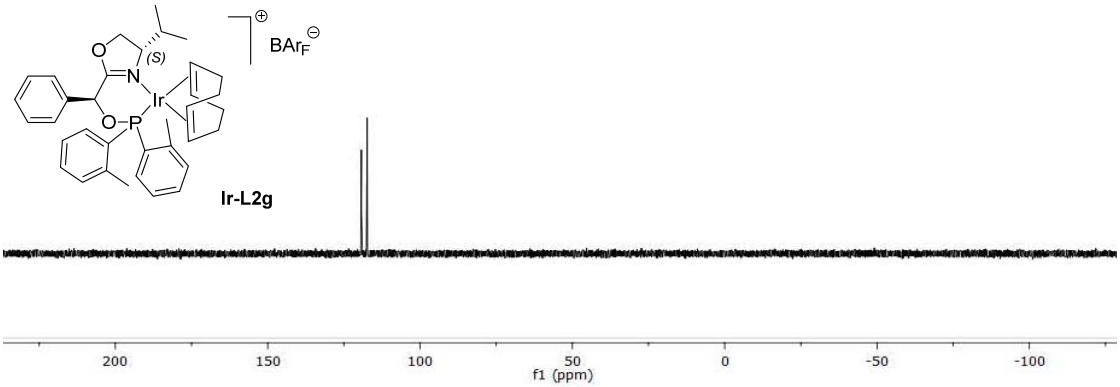


Figure S41. $^{31}P\{^{1}H\}$-NMR spectrum of [Ir(cod)(**L2g**)]BAr$_F$

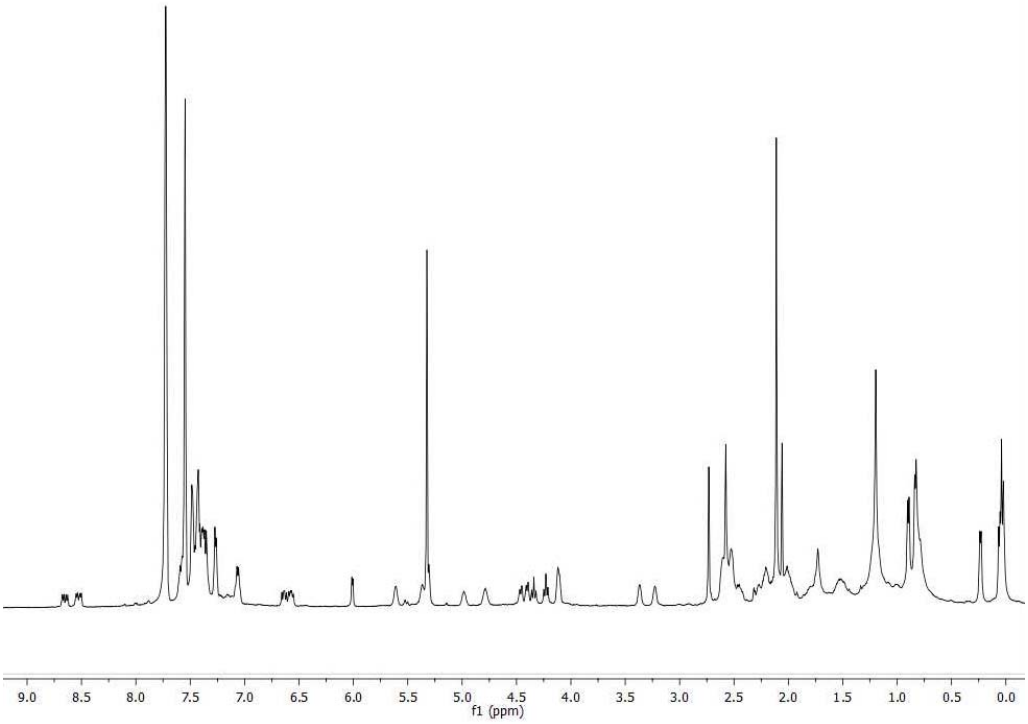


Figure S42. ^{1}H-NMR spectrum of [Ir(cod)(**L2g**)]BAr$_F$

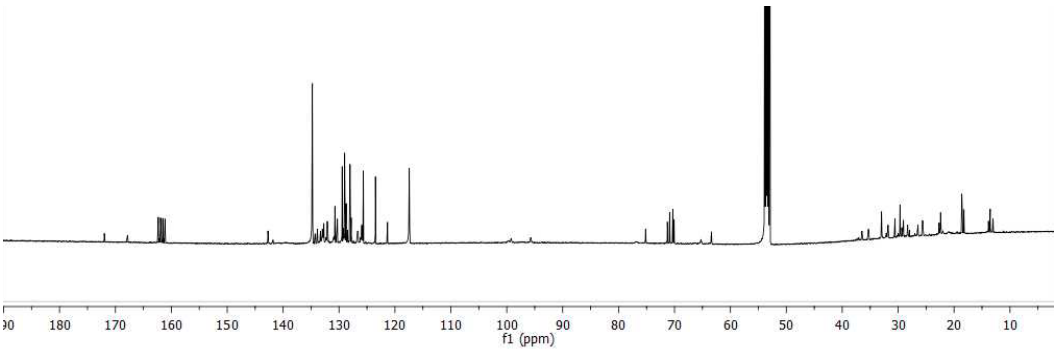


Figure S43. $^{13}C\{^{1}H\}$-NMR spectrum of [Ir(cod)(**L2g**)]BAr$_F$

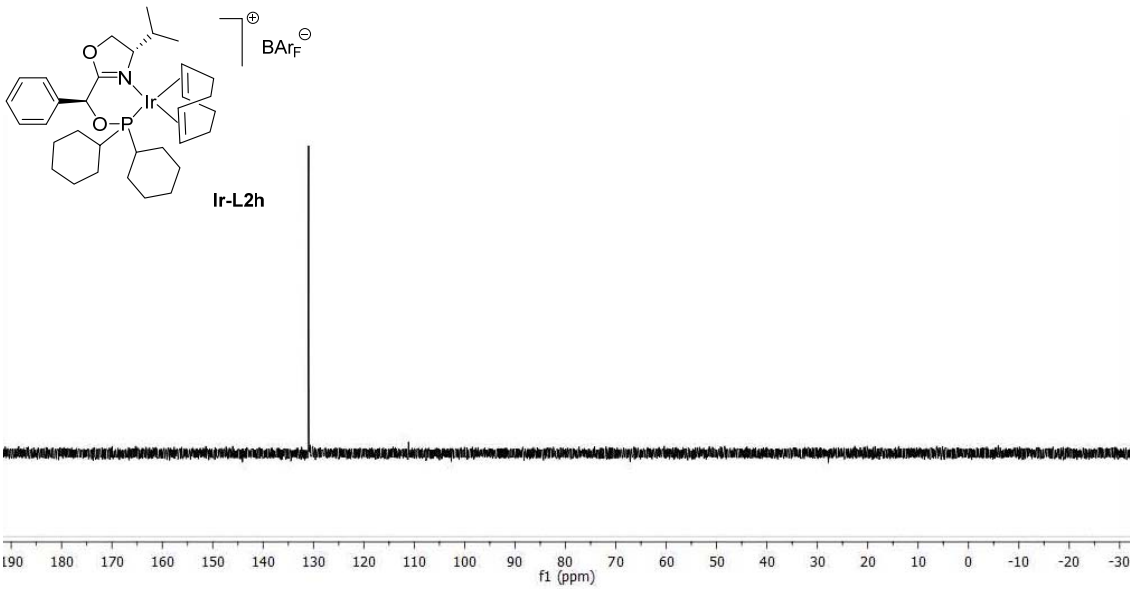


Figure S44. $^{31}P\{^{1}H\}$-NMR spectrum of [Ir(cod)(**L2h**)]BAr$_F$

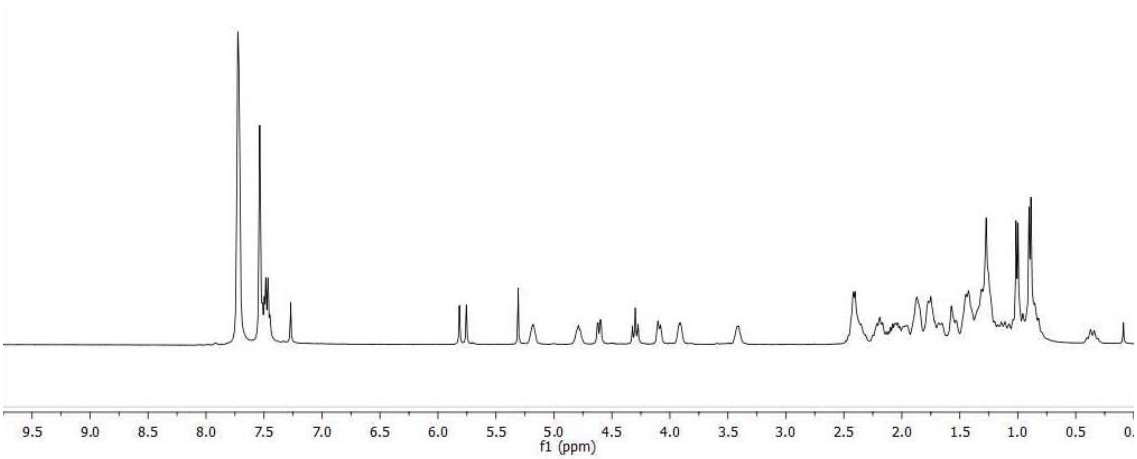


Figure S45. ^{1}H-NMR spectrum of [Ir(cod)(**L2h**)]BAr$_F$

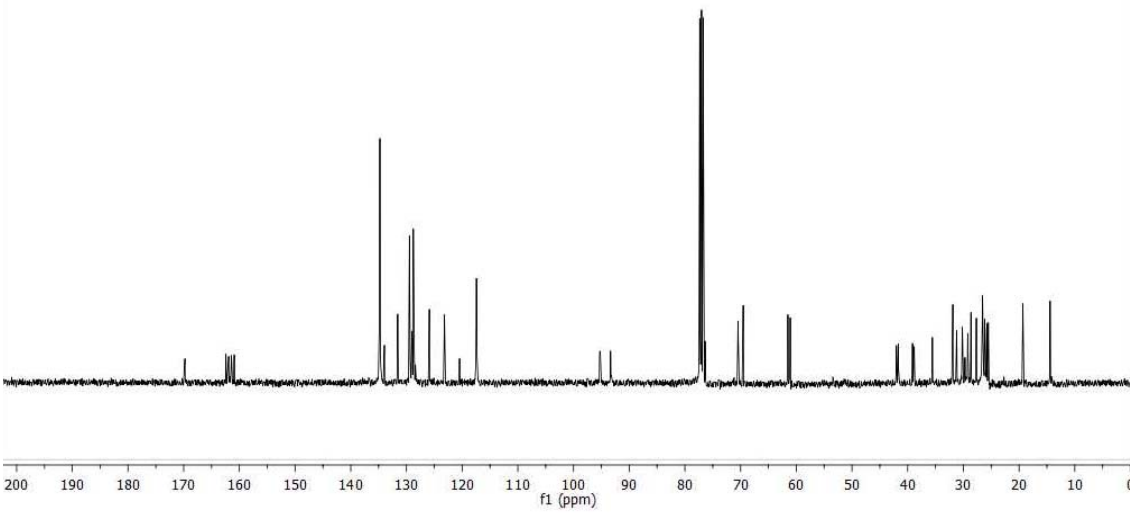


Figure S46. $^{13}C\{^{1}H\}$-NMR spectrum of [Ir(cod)(**L2h**)]BAr$_F$

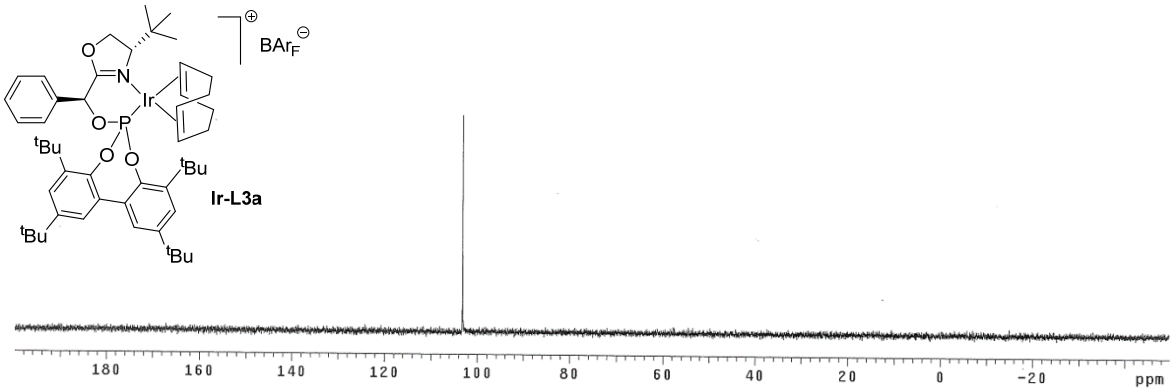


Figure S47. $^{31}P\{^{1}H\}$-NMR spectrum of [Ir(cod)(**L3a**)]BArF

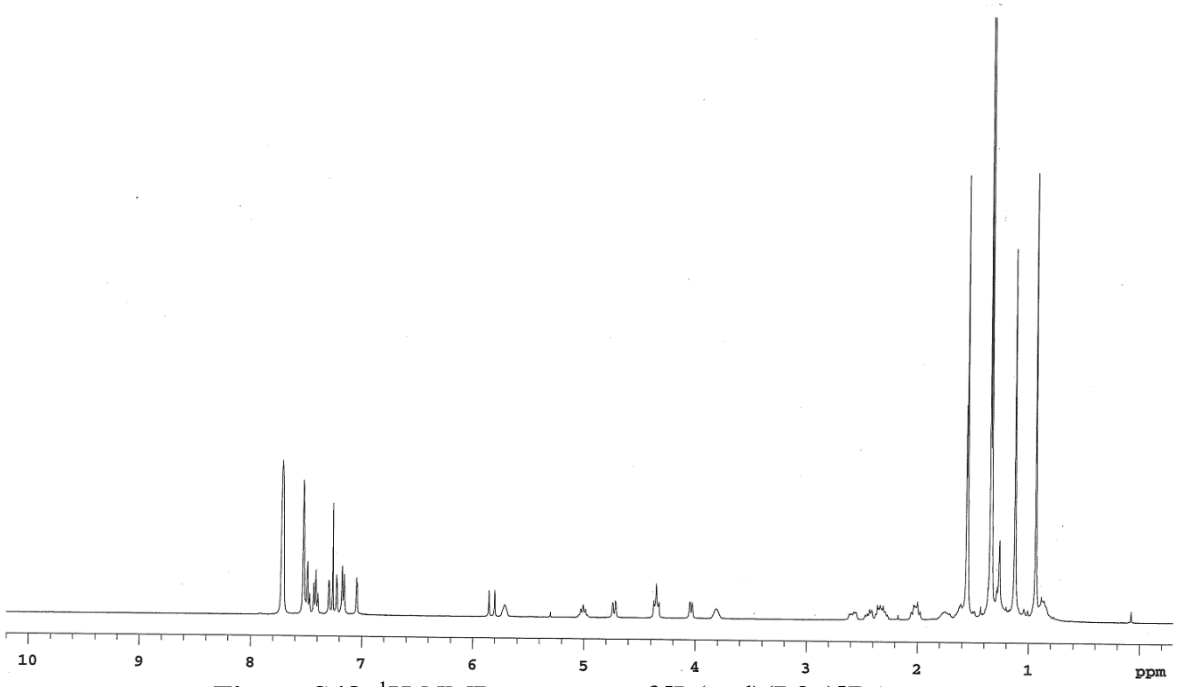


Figure S48. ^{1}H-NMR spectrum of [Ir(cod)(**L3a**)]BArF

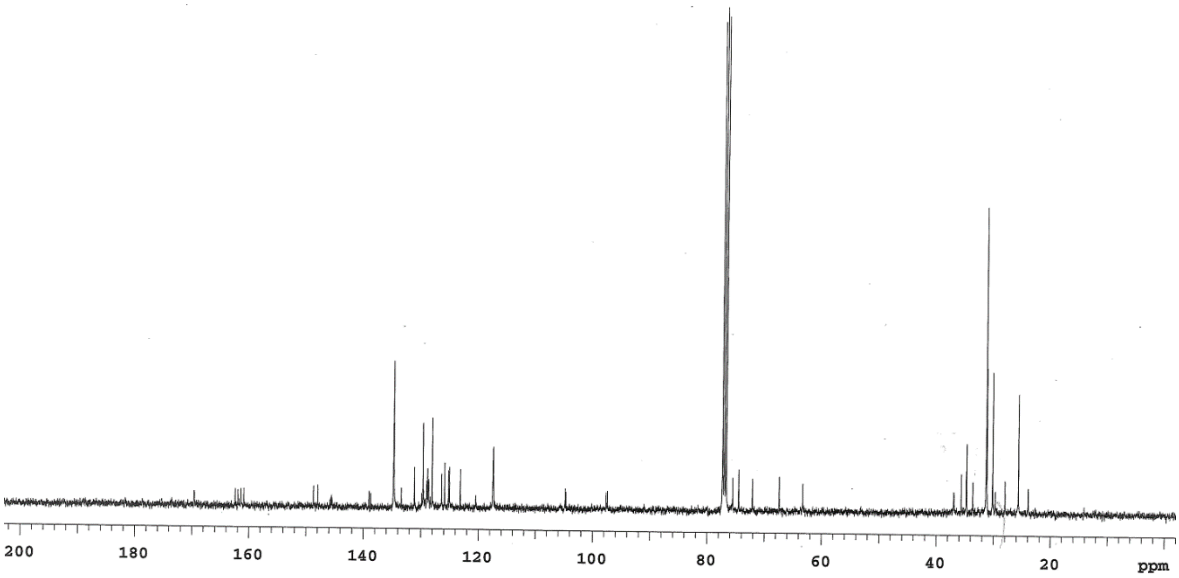


Figure S49. $^{13}C\{^{1}H\}$-NMR spectrum of [Ir(cod)(**L3a**)]BArF

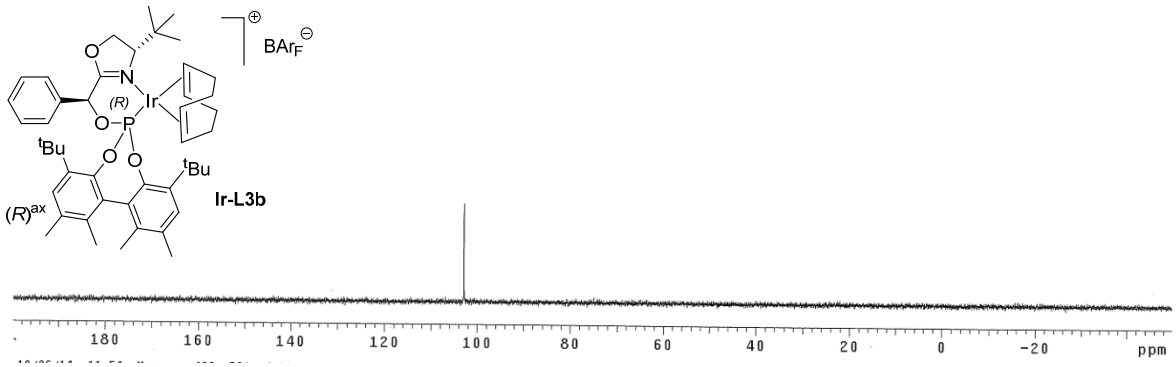


Figure S50. $^{31}P\{^{1}H\}$-NMR spectrum of [Ir(cod)(**L3b**)]BAr$_F$

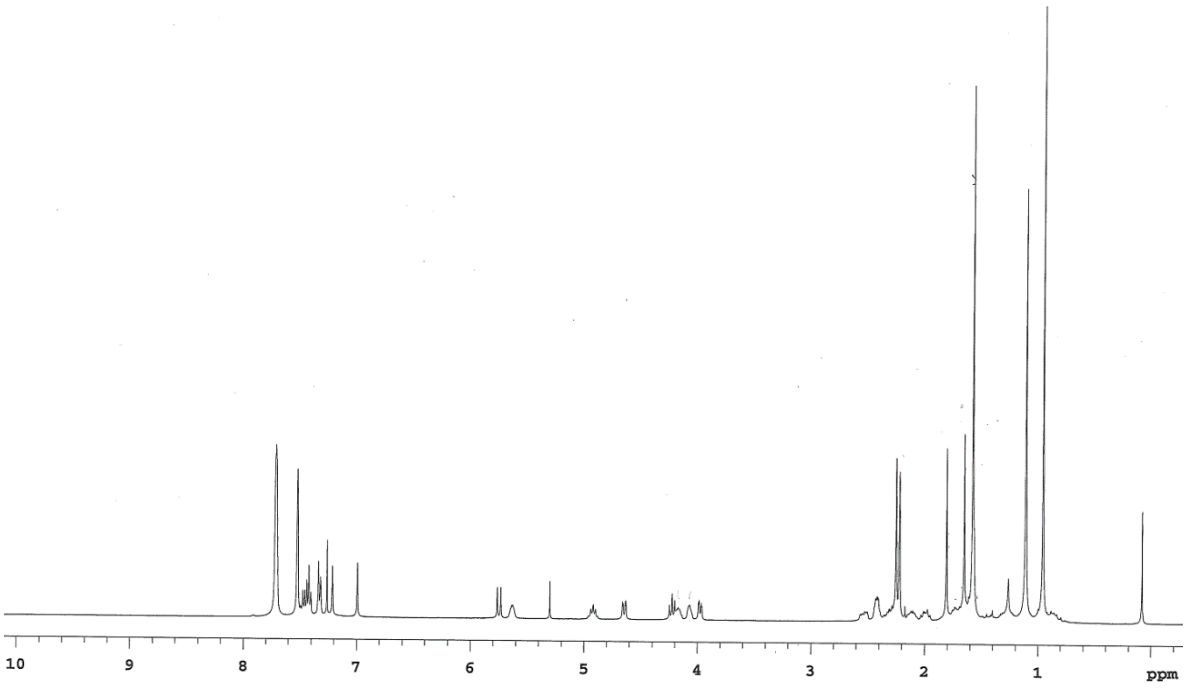


Figure S51. ^{1}H-NMR spectrum of [Ir(cod)(**L3b**)]BAr$_F$

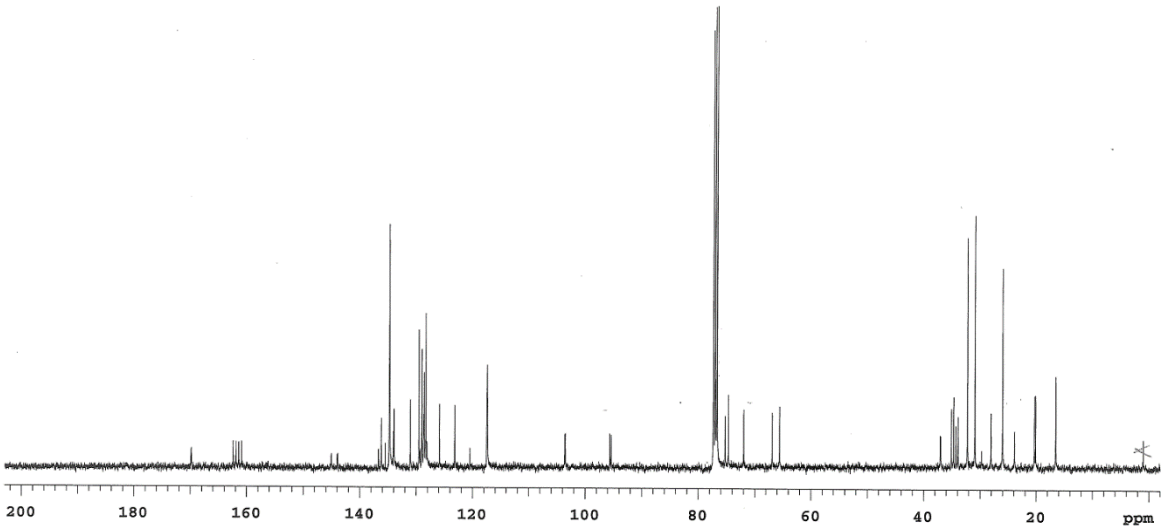


Figure S52. $^{13}C\{^{1}H\}$-NMR spectrum of [Ir(cod)(**L3b**)]BAr$_F$

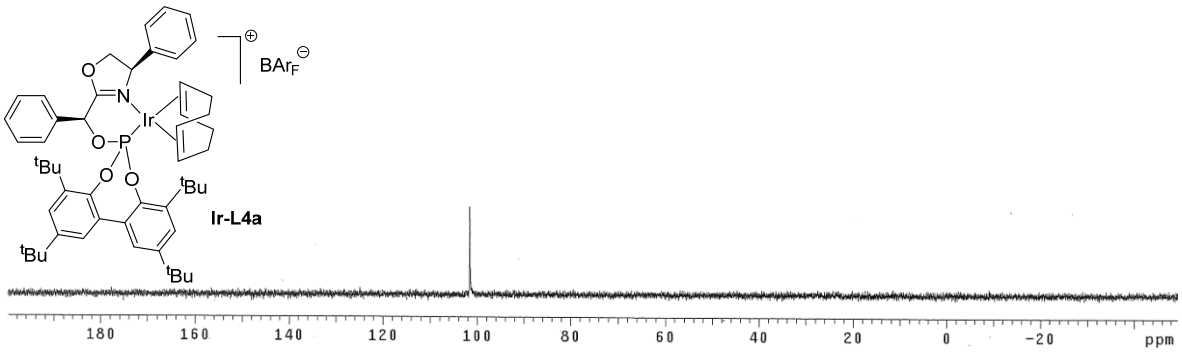


Figure S53. $^{31}P\{^{1}H\}$-NMR spectrum of [Ir(cod)(**L4a**)]BAr$_F$

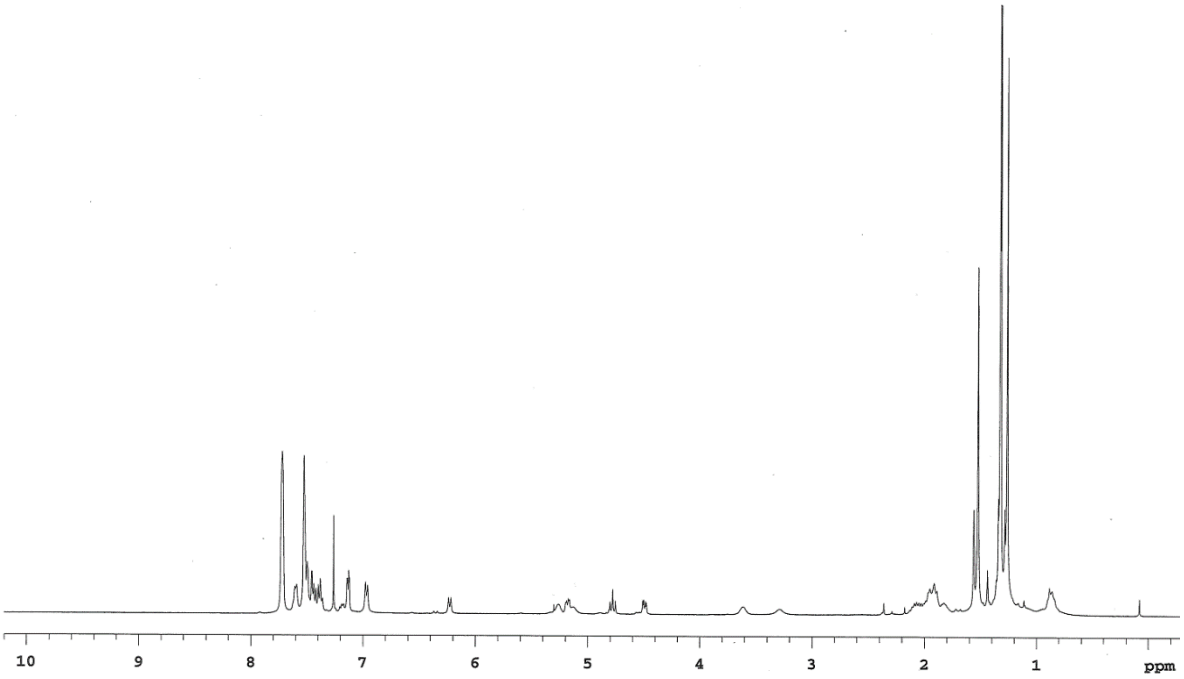


Figure S54. ^{1}H-NMR spectrum of [Ir(cod)(**L4a**)]BAr$_F$

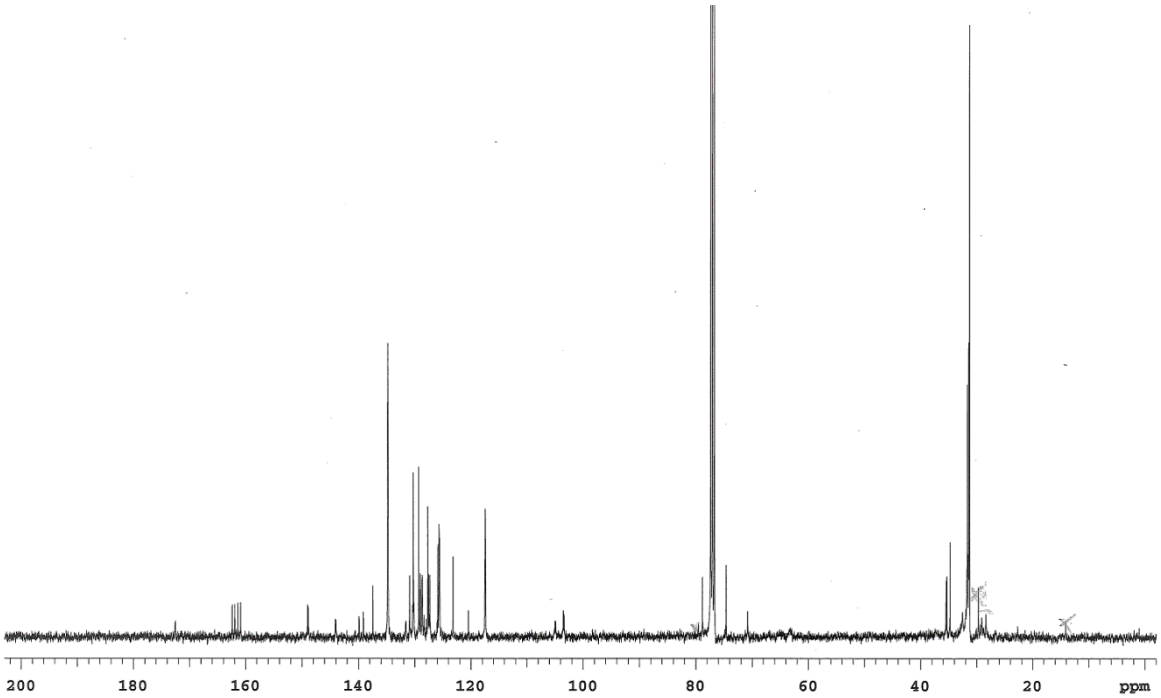


Figure S55. $^{13}C\{^{1}H\}$-NMR spectrum of [Ir(cod)(**L4a**)]BAr$_F$

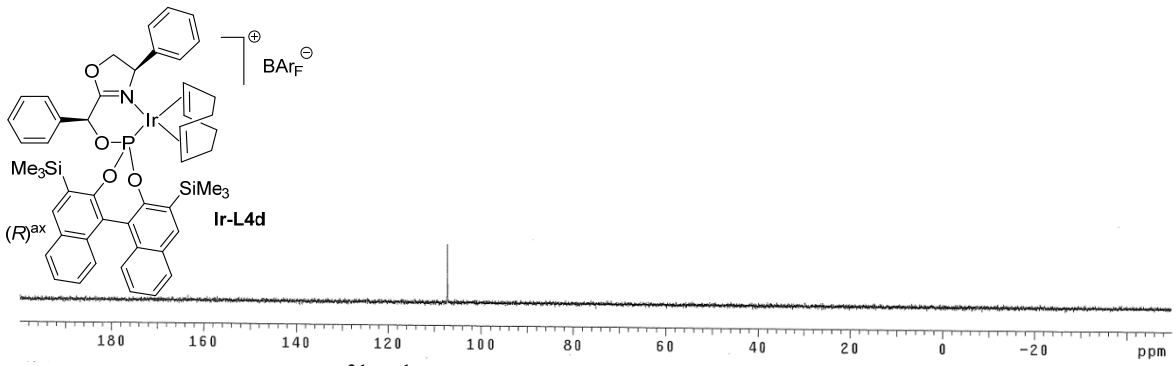


Figure S56. $^{31}P\{^{1}H\}$-NMR spectrum of [Ir(cod)(**L4d**)]BAr$_F$

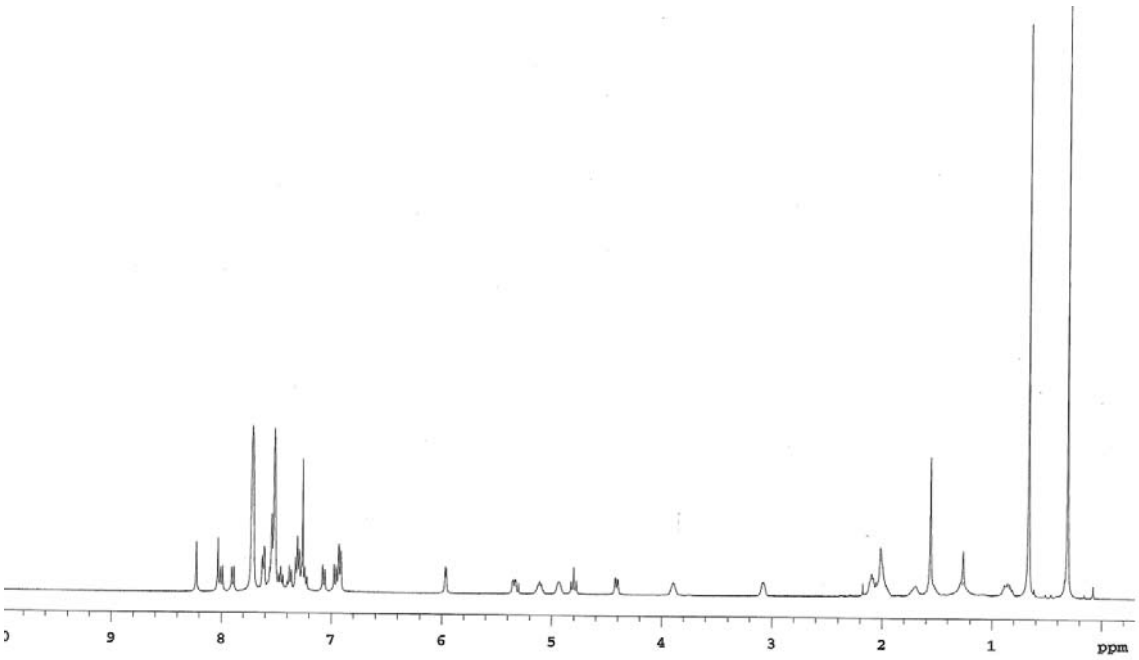


Figure S57. ^{1}H-NMR spectrum of [Ir(cod)(**L4d**)]BAr$_F$

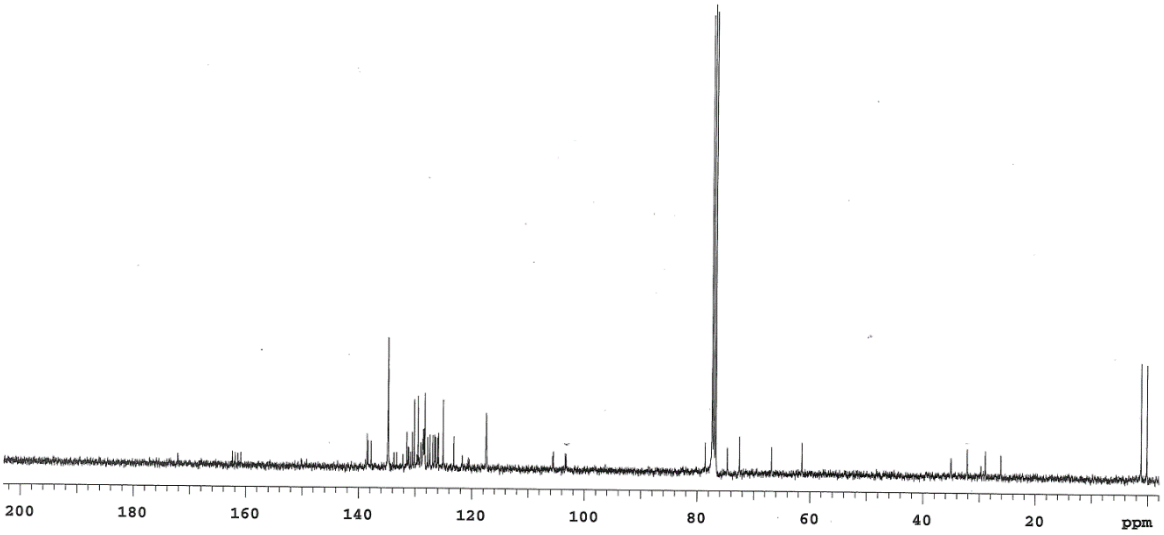


Figure S58. $^{13}C\{^{1}H\}$-NMR spectrum of [Ir(cod)(**L4d**)]BAr$_F$

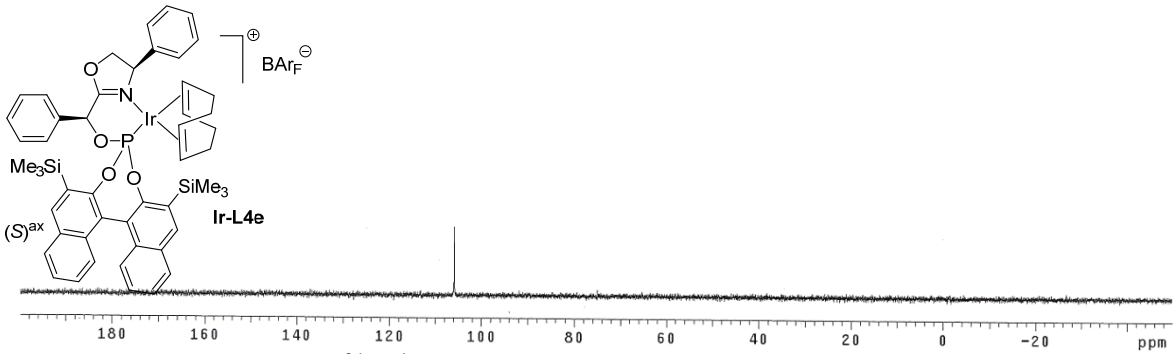


Figure S59. $^{31}P\{^{1}H\}$-NMR spectrum of [Ir(cod)(**L4d**)]BAr$_F$

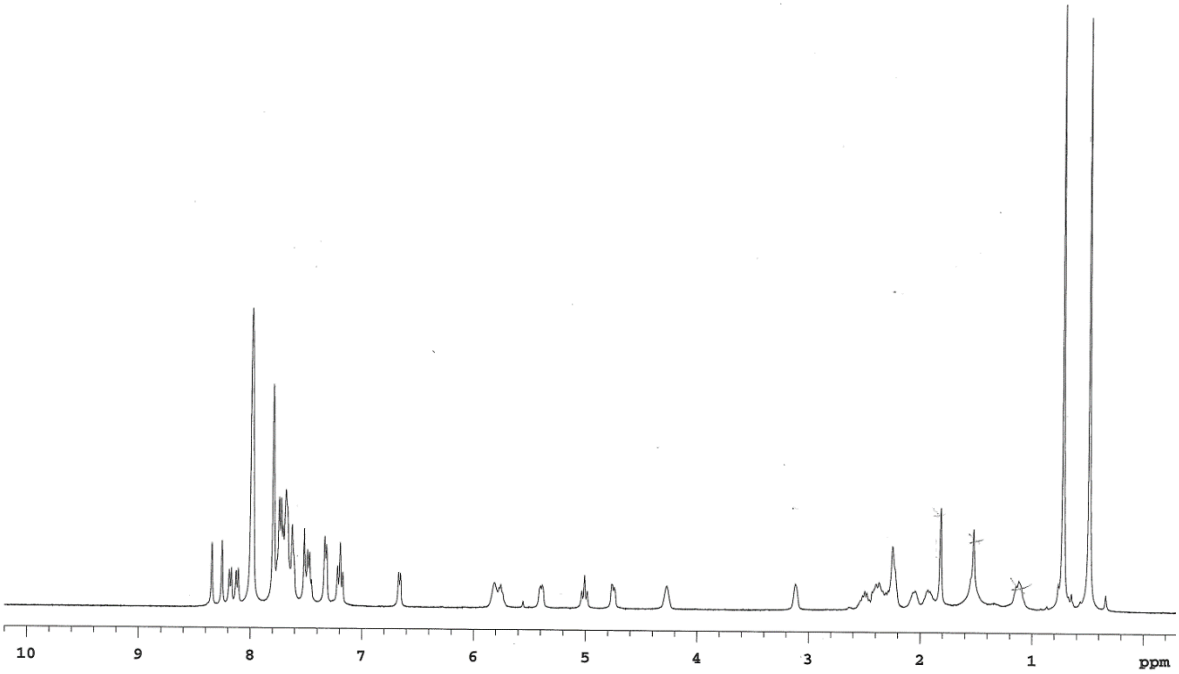


Figure S60. ^{1}H-NMR spectrum of [Ir(cod)(**L4d**)]BAr$_F$

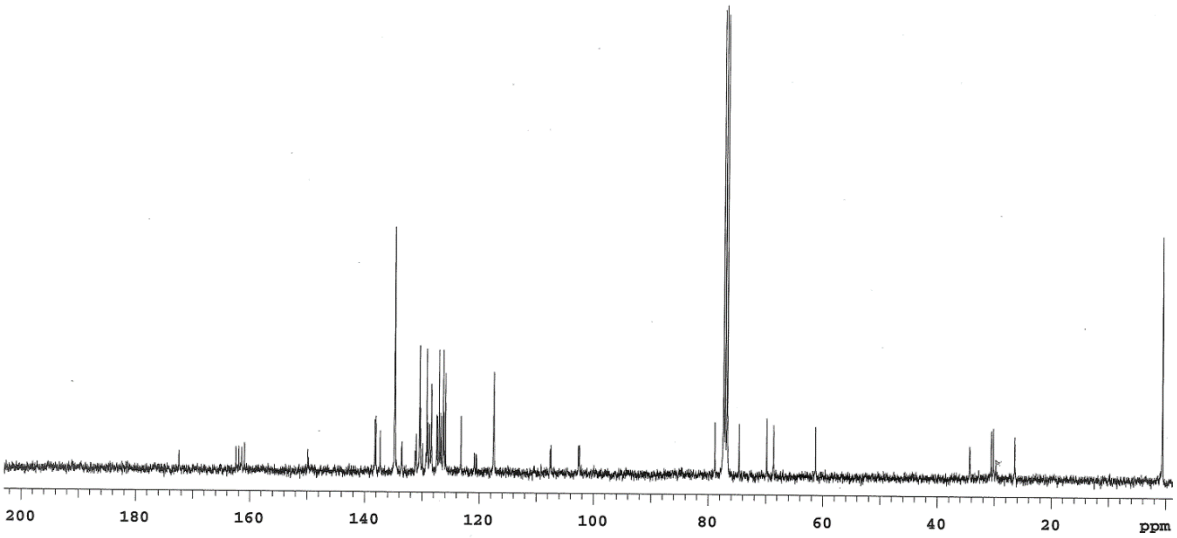


Figure S61. $^{13}C\{^{1}H\}$-NMR spectrum of [Ir(cod)(**L4d**)]BAr$_F$

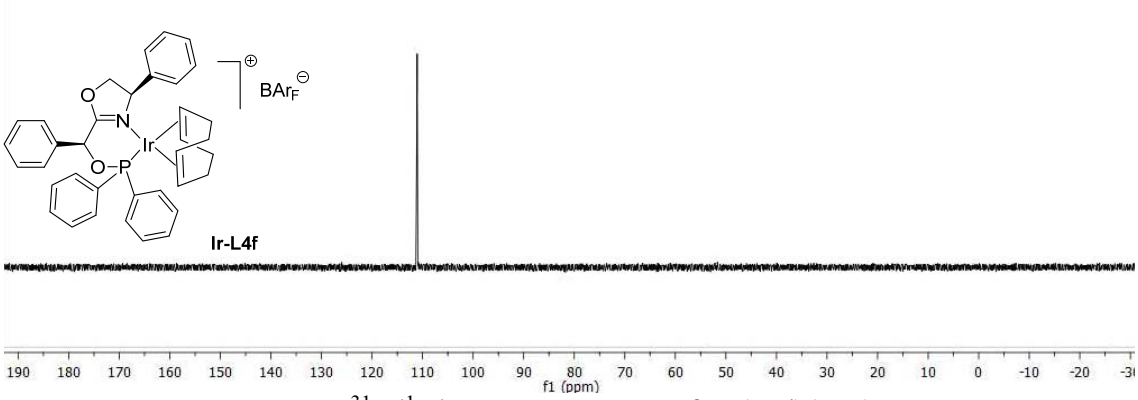


Figure S62. $^{31}P\{^{1}H\}$-NMR spectrum of [Ir(cod)(**L4f**)]BAr$_F$

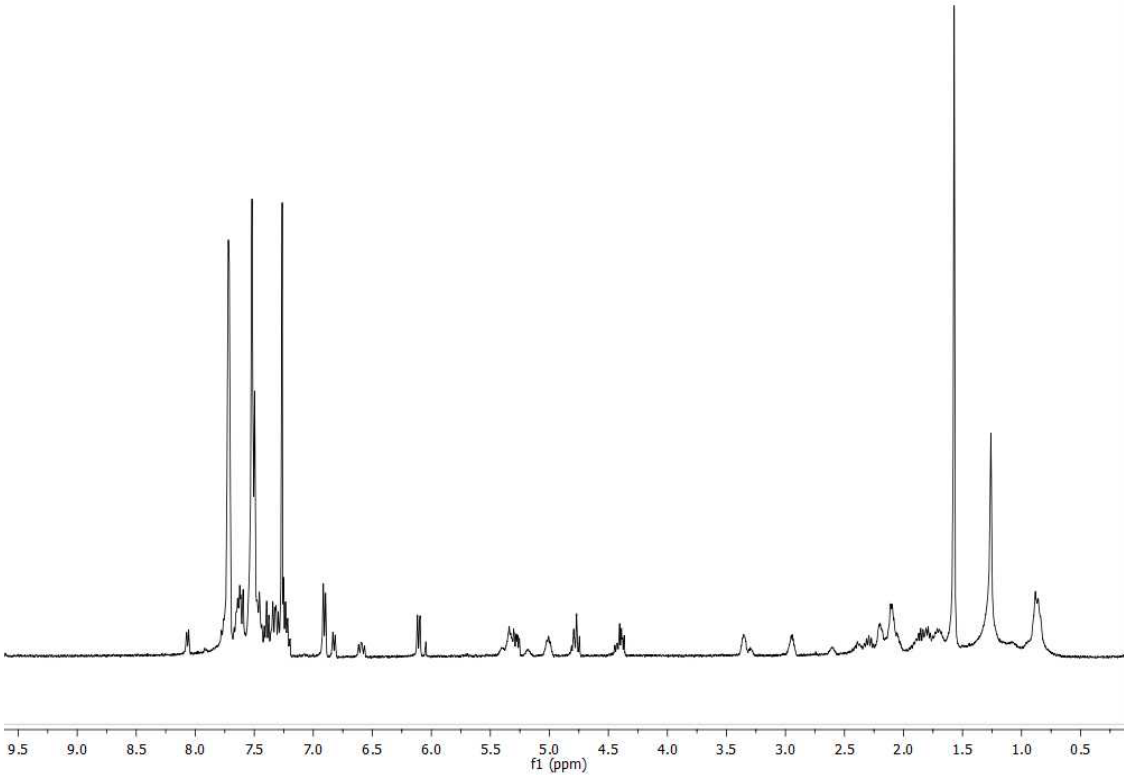


Figure S63. ^{1}H-NMR spectrum of [Ir(cod)(**L4f**)]BAr$_F$

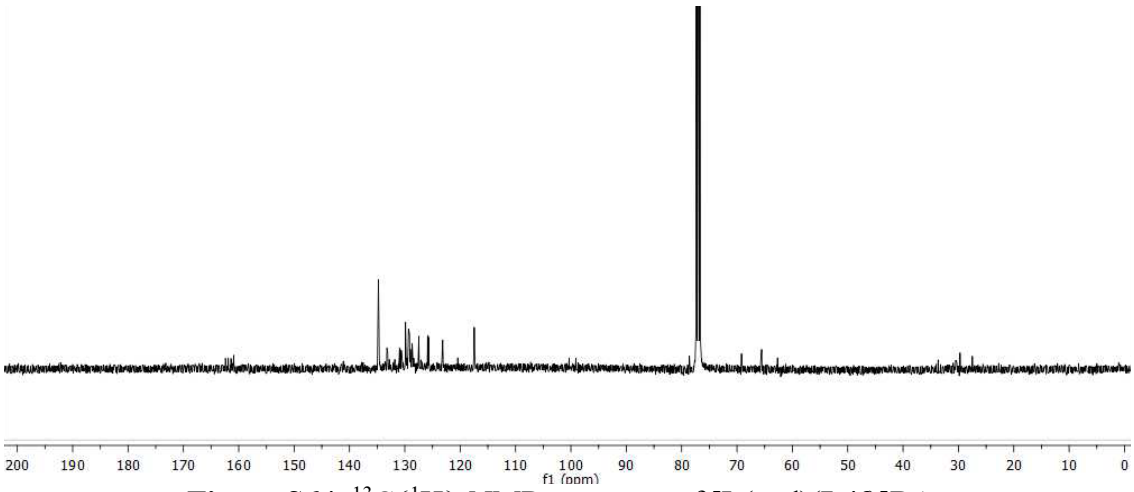


Figure S64. $^{13}C\{^{1}H\}$-NMR spectrum of [Ir(cod)(**L4f**)]BAr$_F$

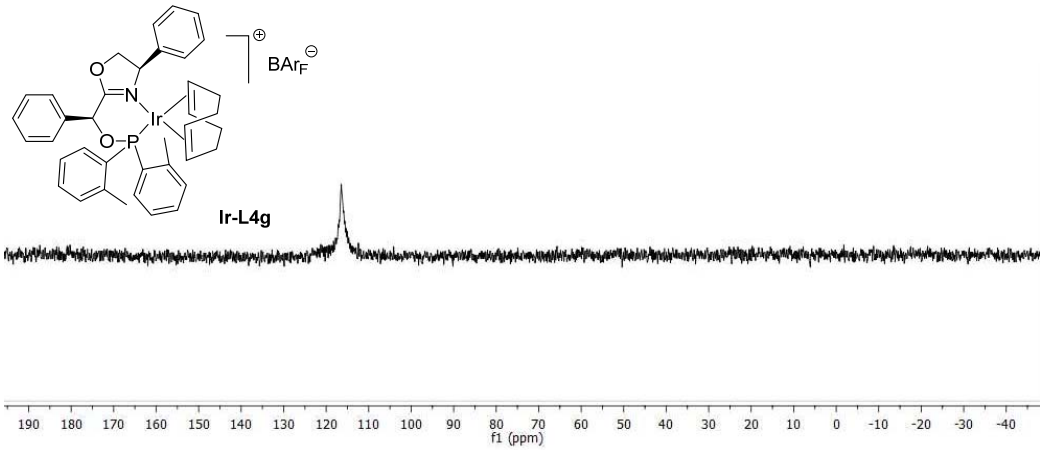


Figure S65. $^{31}P\{^{1}H\}$-NMR spectrum of [Ir(cod)(**L4g**)]BAr_F

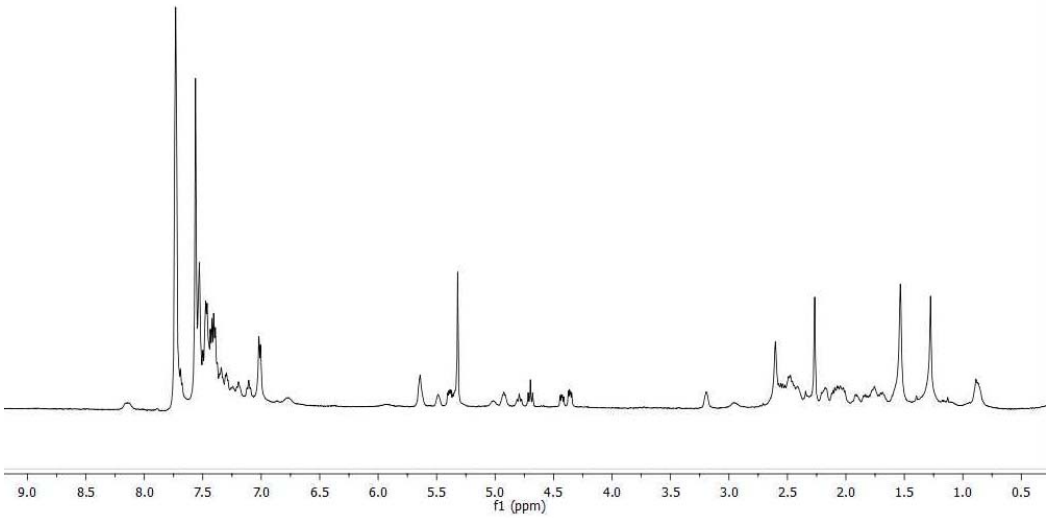


Figure S66. ^{1}H-NMR spectrum of [Ir(cod)(**L4g**)]BAr_F

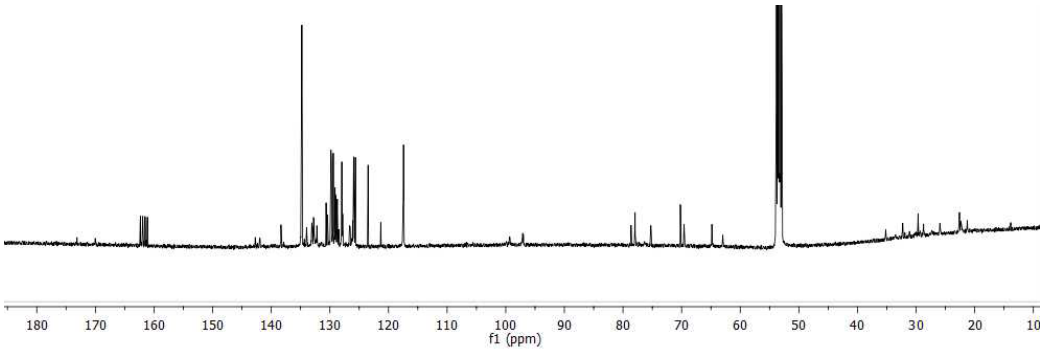


Figure S67. $^{13}C\{^{1}H\}$-NMR spectrum of [Ir(cod)(**L4g**)]BAr_F

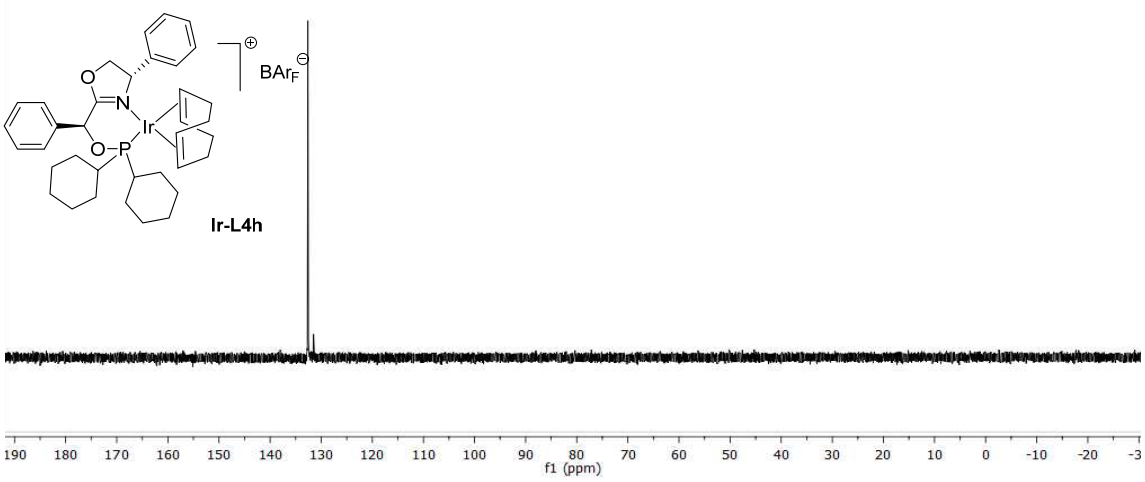


Figure S68. $^{31}P\{^{1}H\}$-NMR spectrum of [Ir(cod)(**L4h**)]BAr$_F$

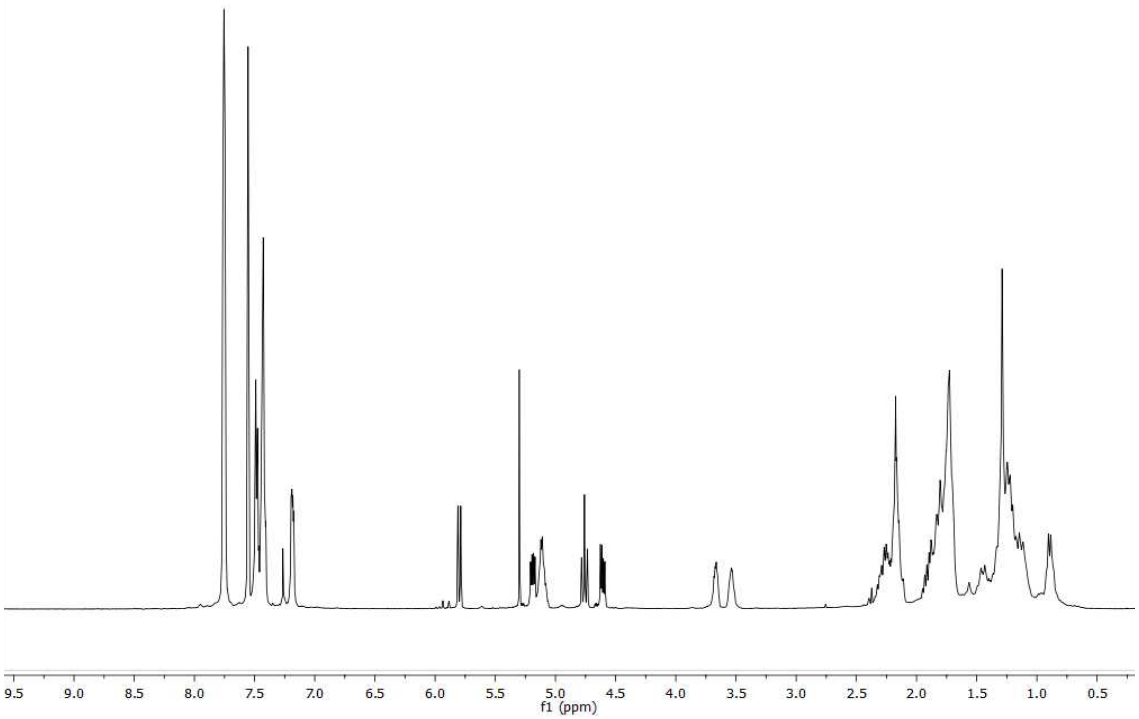


Figure S69. ^{1}H-NMR spectrum of [Ir(cod)(**L4h**)]BAr$_F$

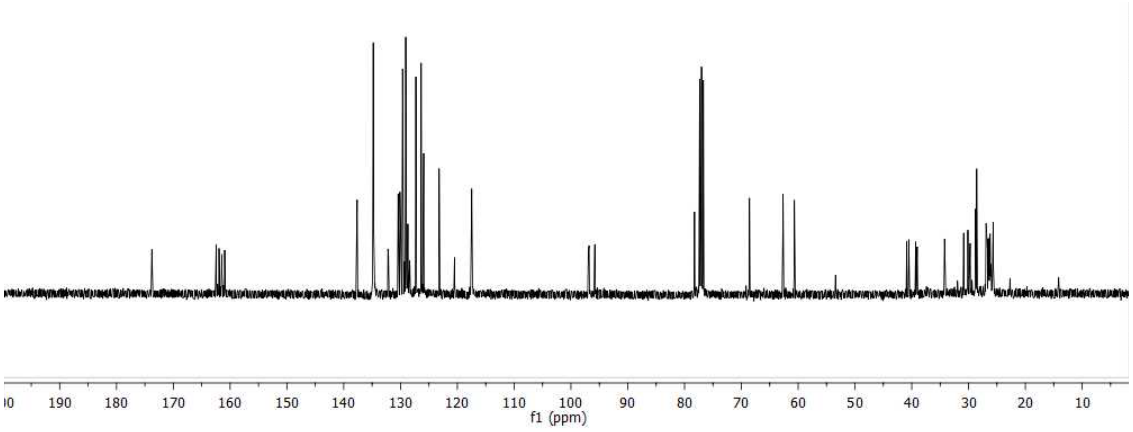


Figure S70. $^{13}C\{^{1}H\}$-NMR spectrum of [Ir(cod)(**L4h**)]BAr$_F$

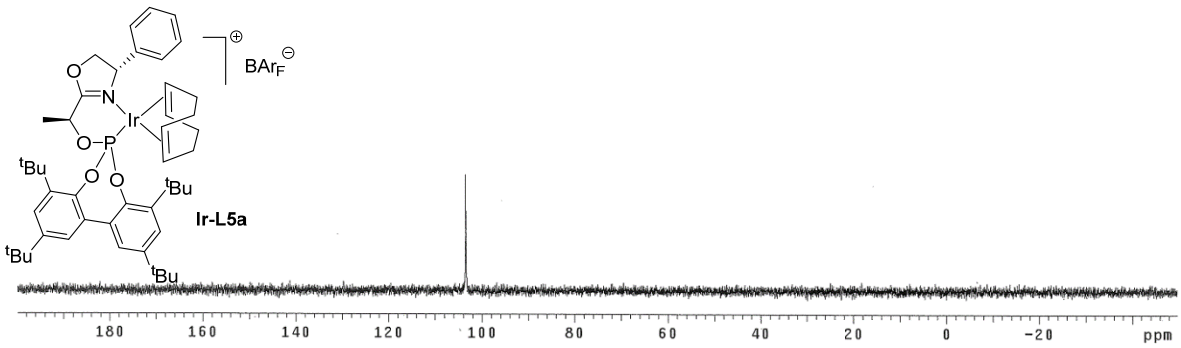


Figure S71. $^{31}P\{^{1}H\}$-NMR spectrum of [Ir(cod)(**L5a**)]BAr$_F$

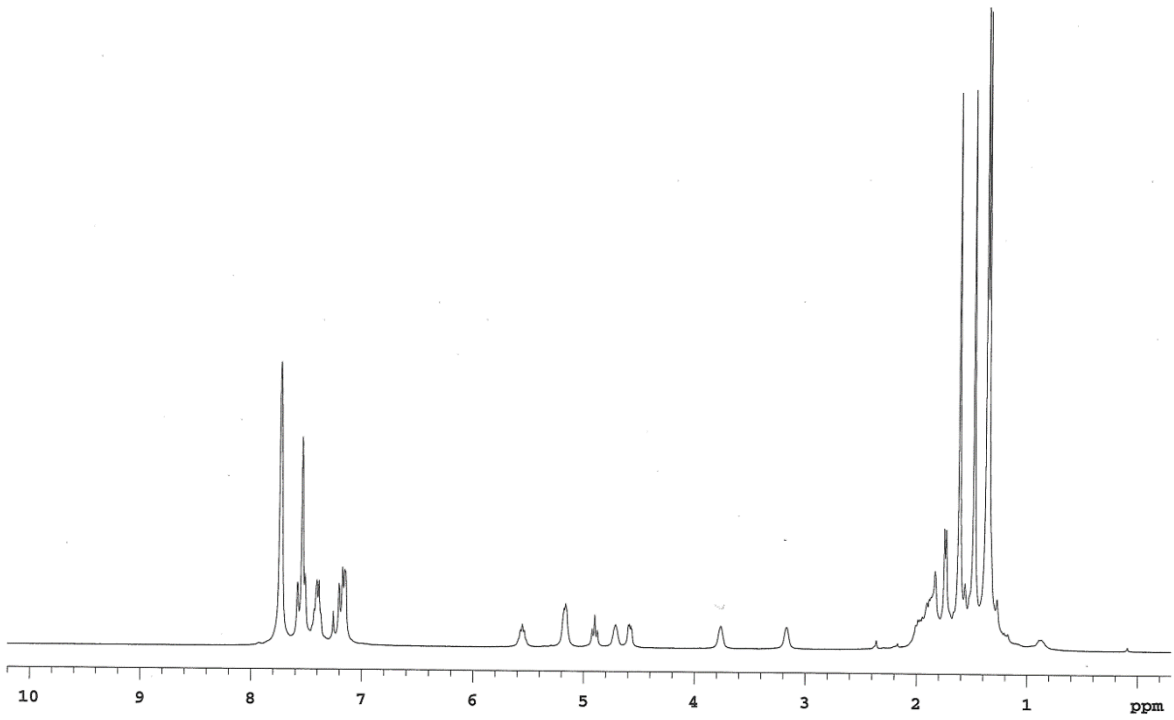


Figure S72. ^{1}H-NMR spectrum of [Ir(cod)(**L5a**)]BAr$_F$

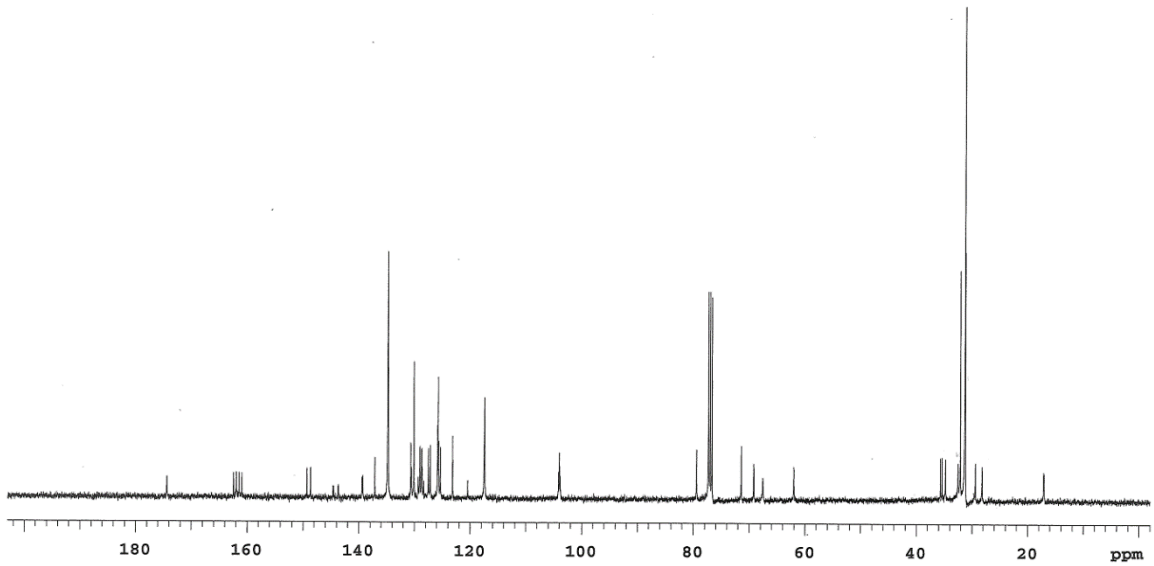


Figure S73. $^{13}C\{^{1}H\}$-NMR spectrum of [Ir(cod)(**L5a**)]BAr$_F$

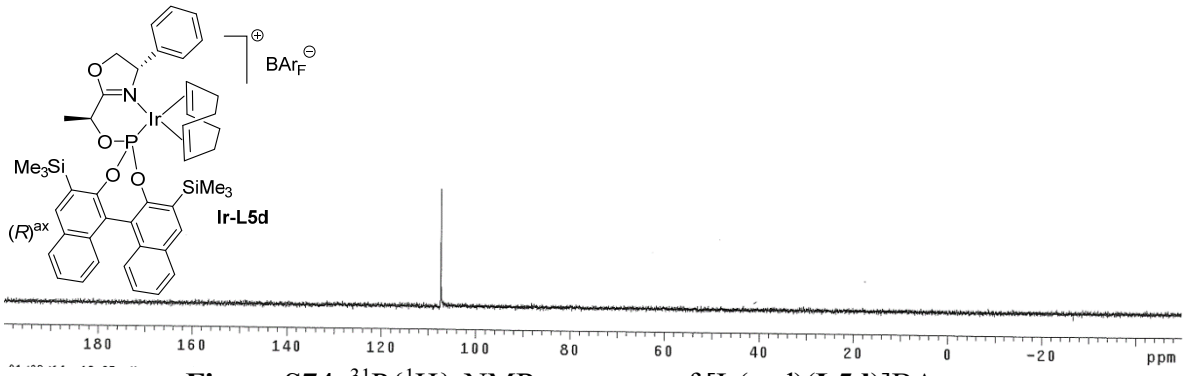


Figure S74. $^{31}P\{^1H\}$-NMR spectrum of [Ir(cod)(**L5d**)]BAr$_F$

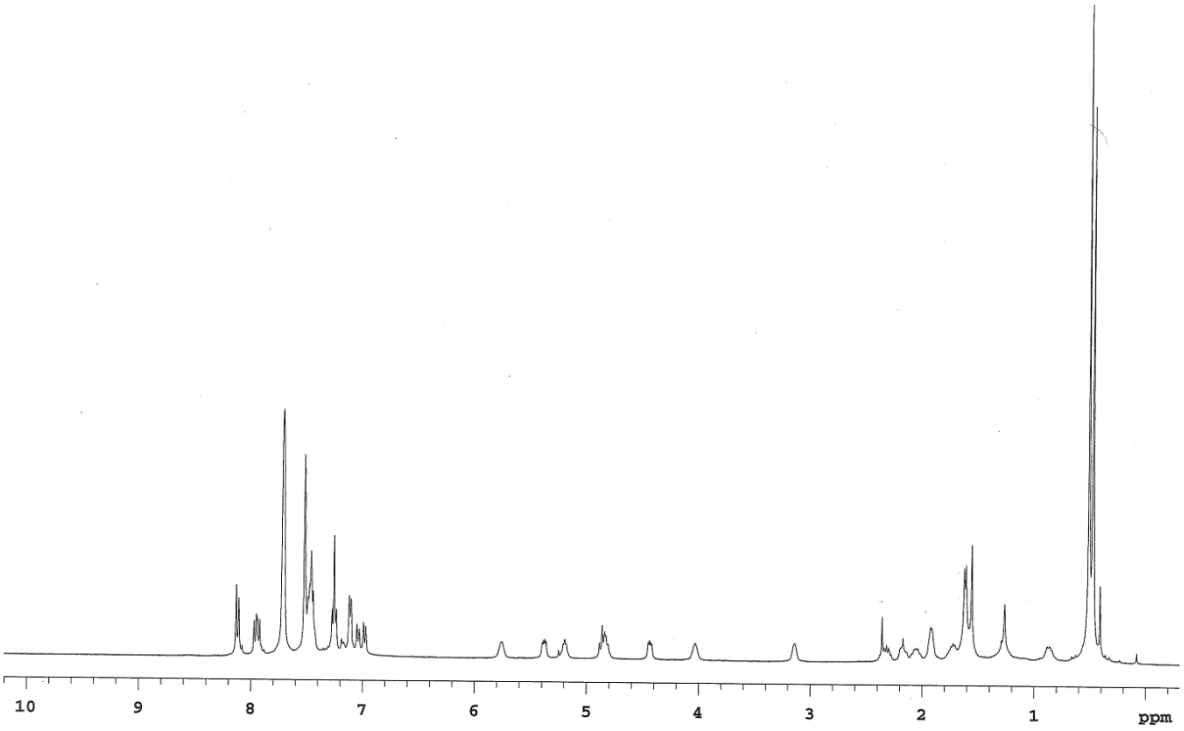


Figure S75. ^1H-NMR spectrum of [Ir(cod)(**L5d**)]BAr$_F$

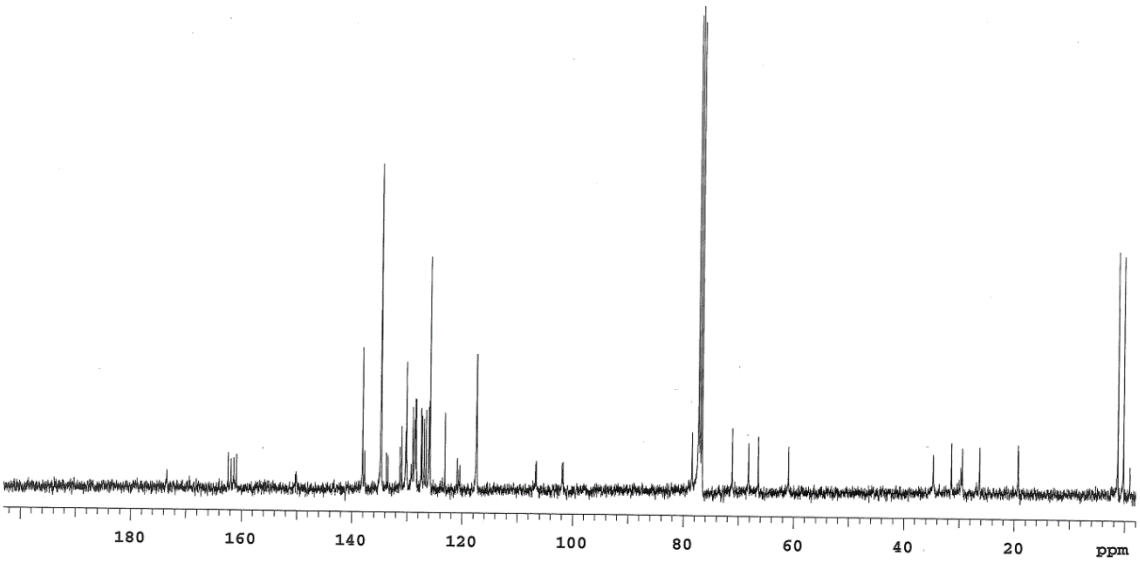


Figure S76. $^{13}C\{^1H\}$-NMR spectrum of [Ir(cod)(**L5d**)]BAr$_F$

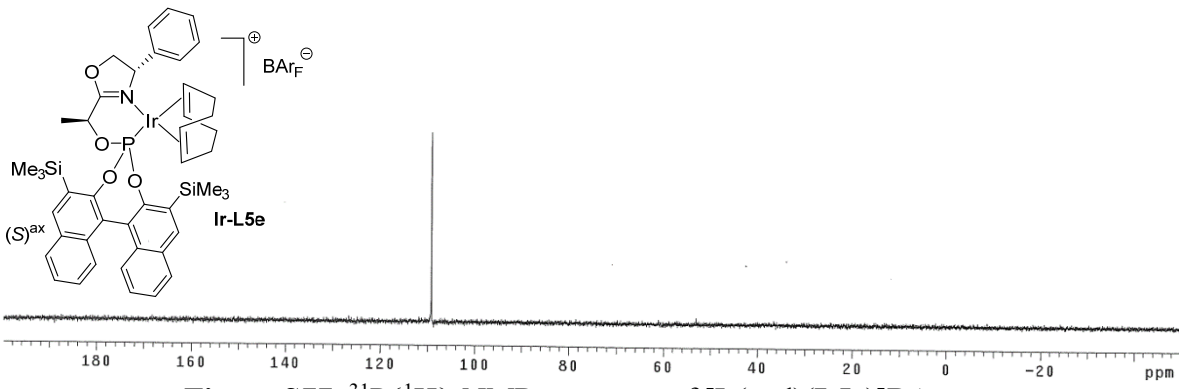


Figure S77. $^{31}P\{^1H\}$-NMR spectrum of [Ir(cod)(**L5e**)]BAr$_F$

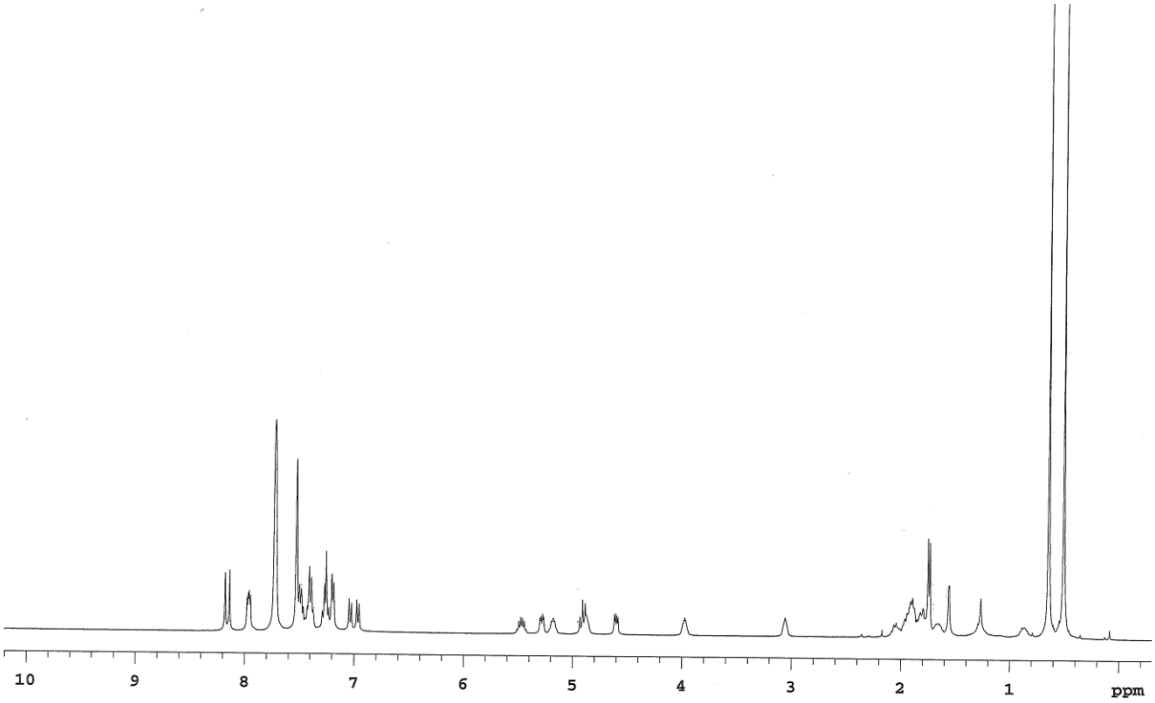


Figure S78. ^1H-NMR spectrum of [Ir(cod)(**L5e**)]BAr$_F$

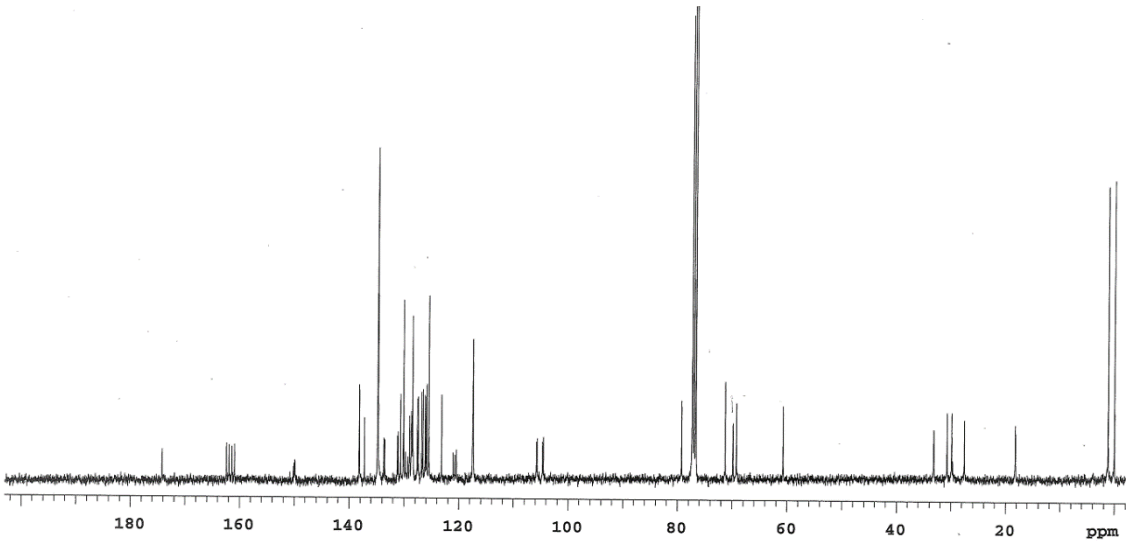


Figure S79. $^{13}C\{^1H\}$-NMR spectrum of [Ir(cod)(**L5e**)]BAr$_F$

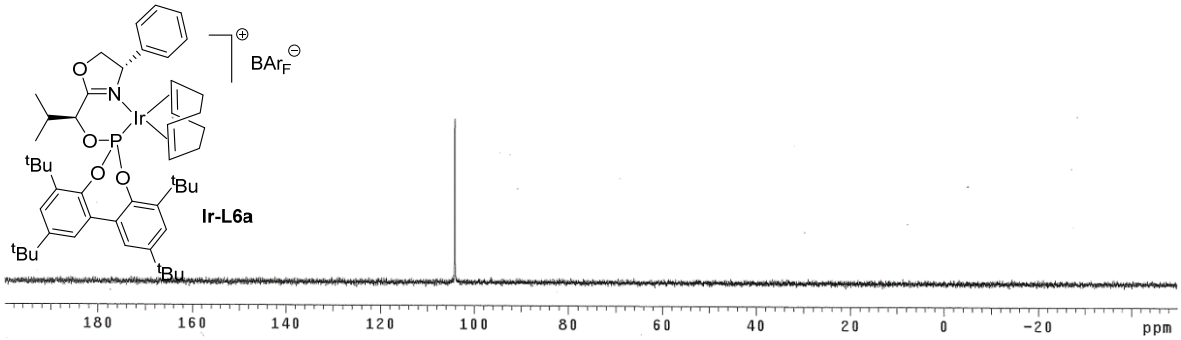


Figure S80. $^{31}P\{^{1}H\}$-NMR spectrum of [Ir(cod)(**L6a**)]BAr$_F$

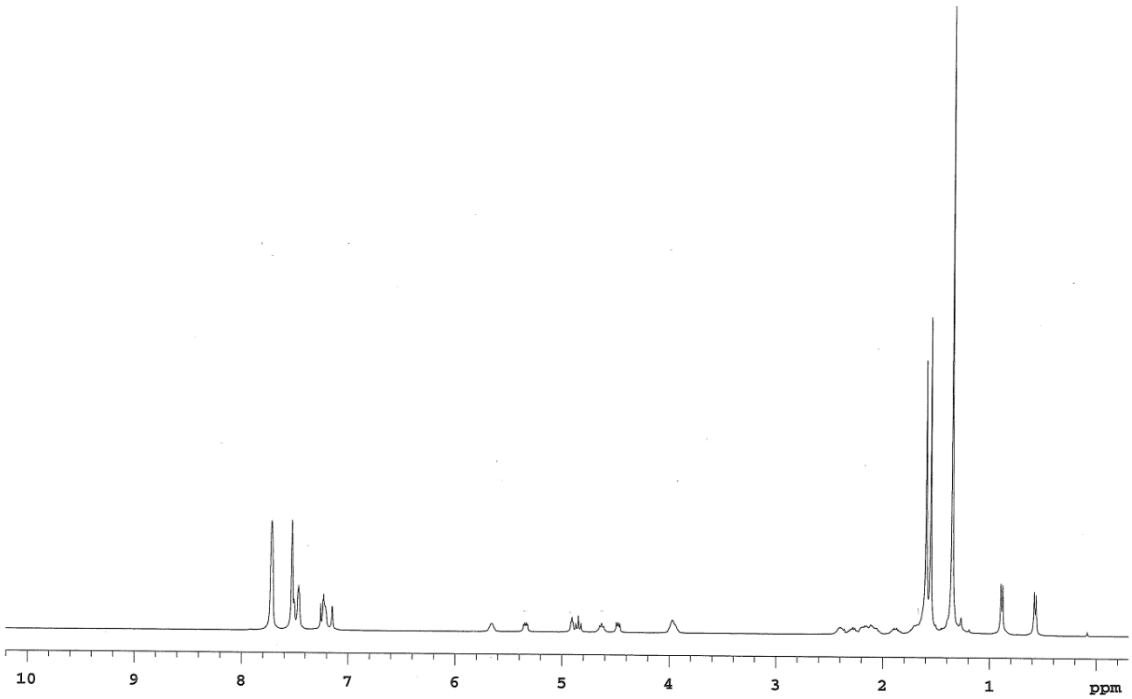


Figure S81. ^{1}H-NMR spectrum of [Ir(cod)(**L6a**)]BAr$_F$

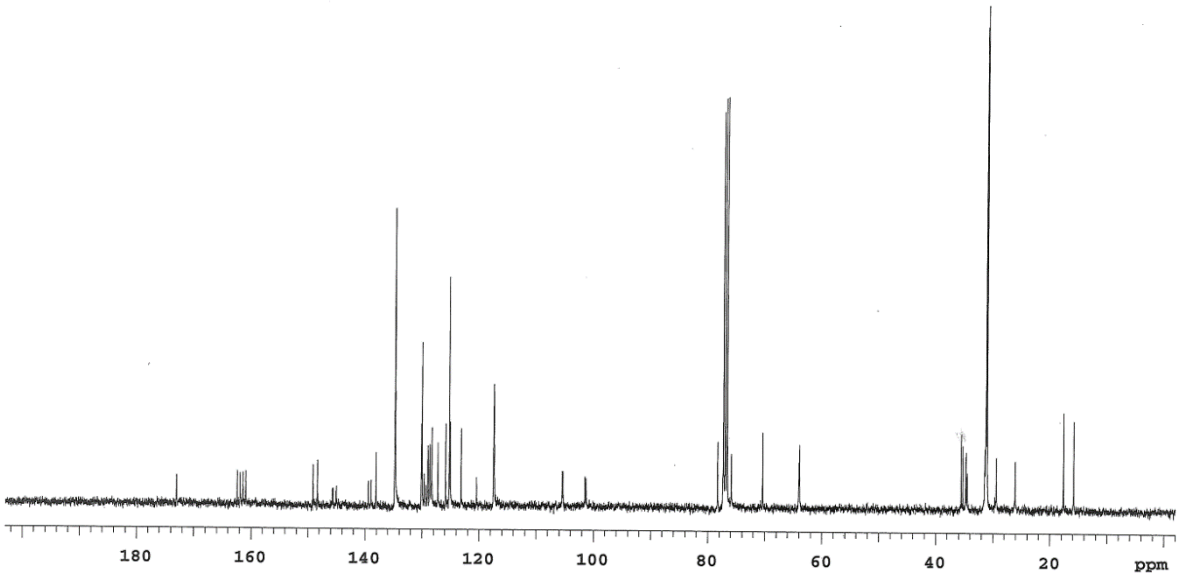


Figure 82. $^{13}C\{^{1}H\}$-NMR spectrum of [Ir(cod)(**L6a**)]BAr$_F$

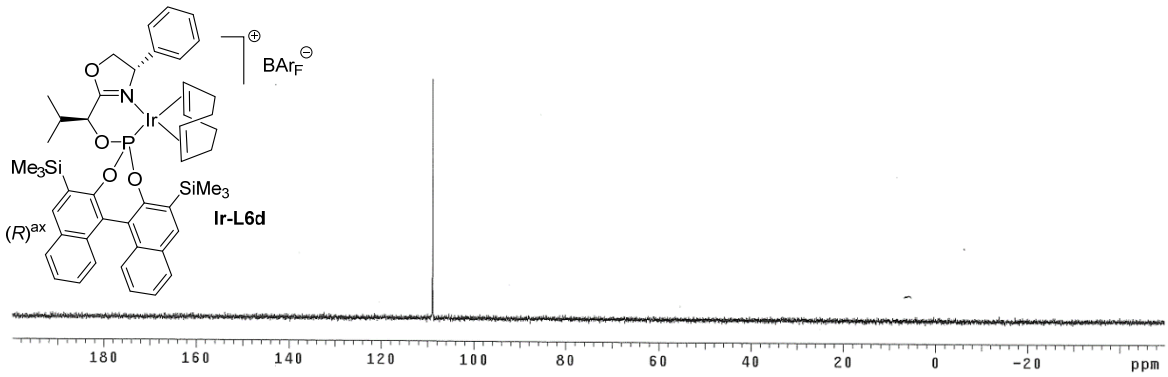


Figure S83. $^{31}P\{^{1}H\}$-NMR spectrum of [Ir(cod)(**L6d**)]BAr$_F$

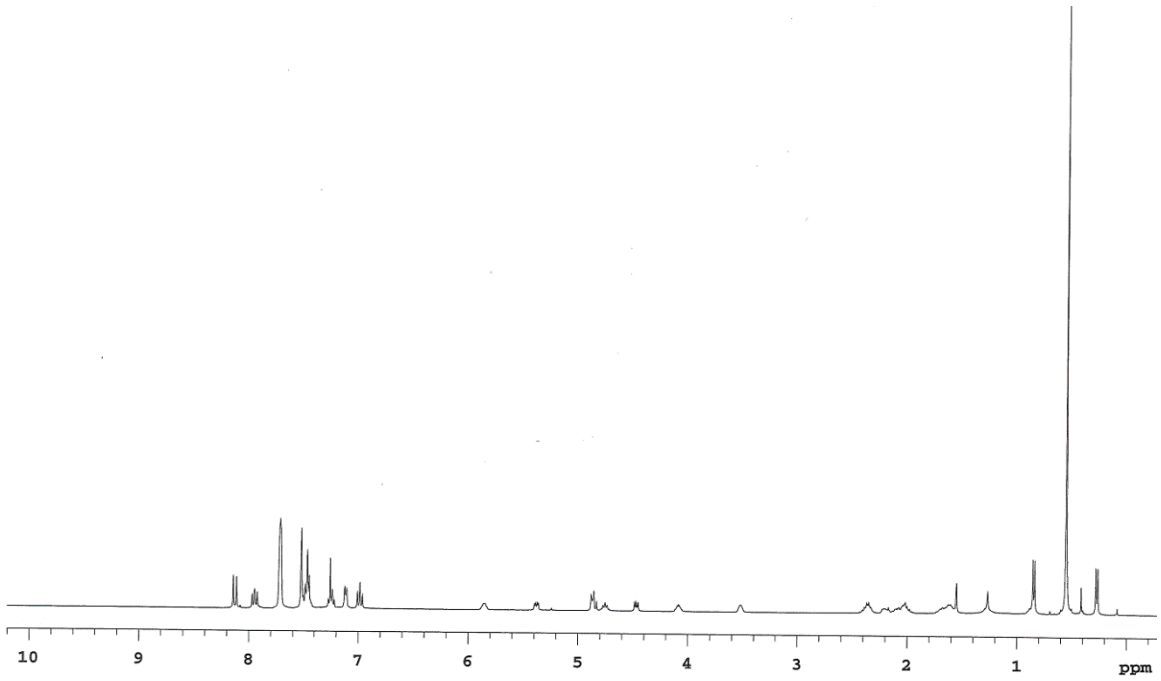


Figure S84. ^{1}H-NMR spectrum of [Ir(cod)(**L6d**)]BAr$_F$

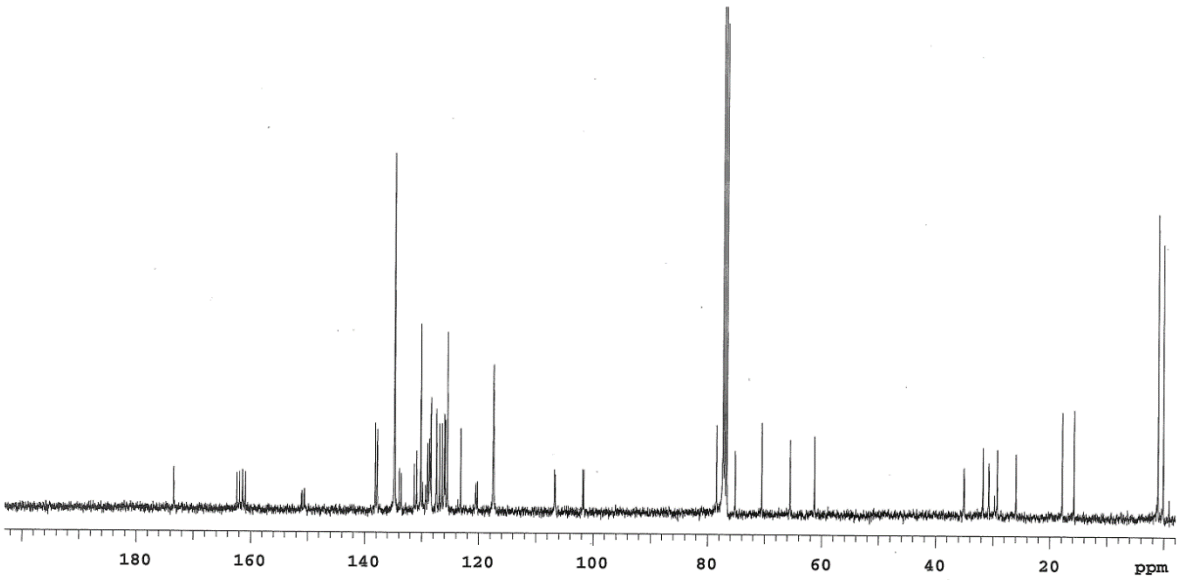


Figure S85. $^{13}C\{^{1}H\}$-NMR spectrum of [Ir(cod)(**L6d**)]BAr$_F$

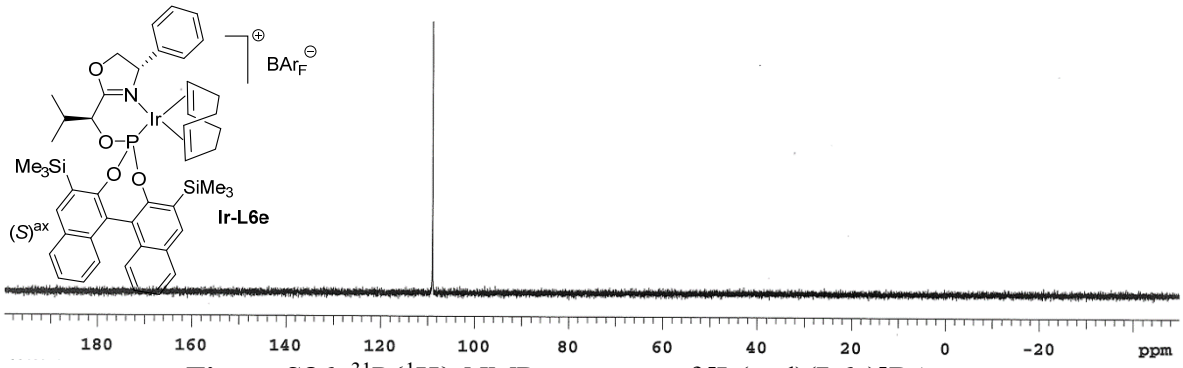


Figure S86. $^{31}P\{^1H\}$-NMR spectrum of [Ir(cod)(**L6e**)]BAr$_F$

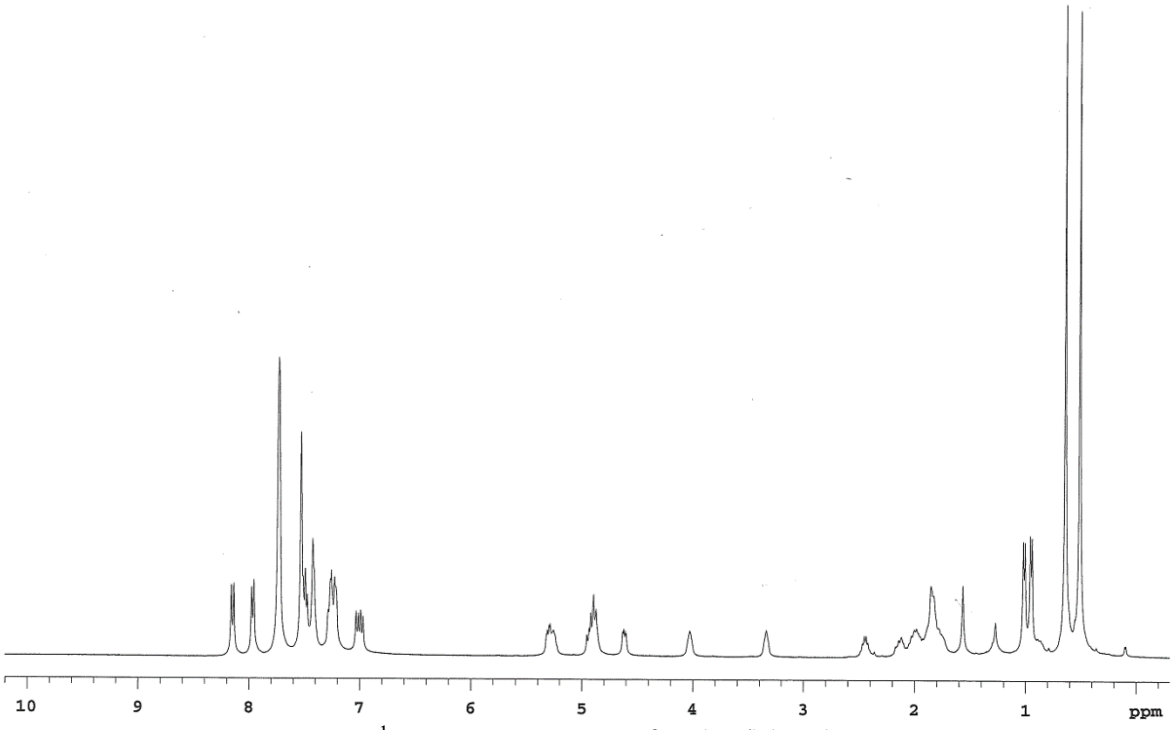


Figure S87. ^1H-NMR spectrum of [Ir(cod)(**L6e**)]BAr$_F$

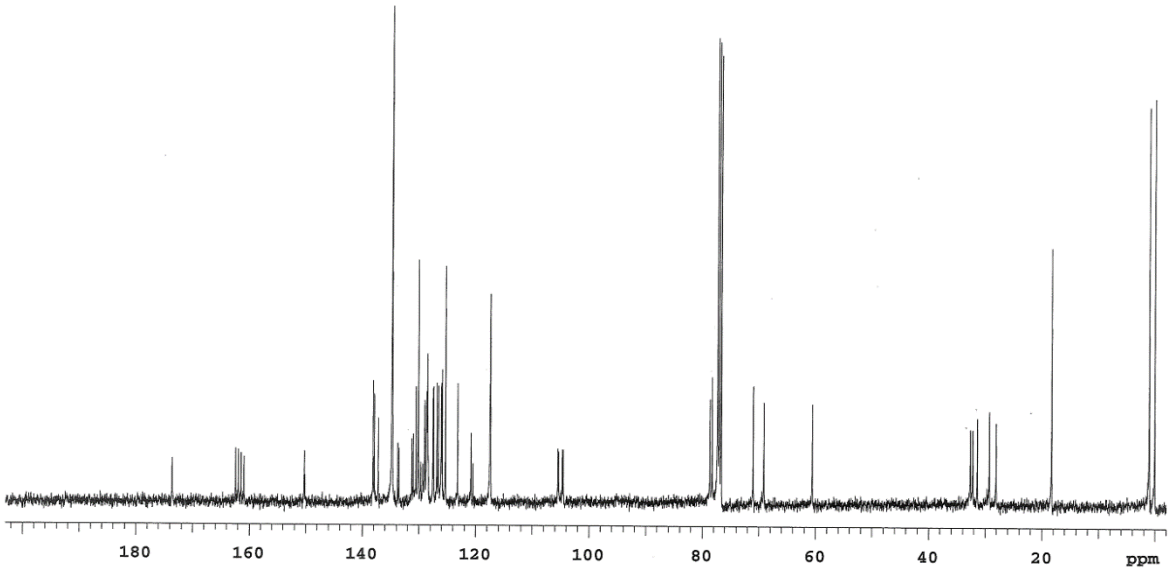


Figure S88. $^{13}C\{^1H\}$-NMR spectrum of [Ir(cod)(**L6e**)]BAr$_F$

7. Copies of NMR spectra of phosphite/phosphinite-oxazoline ligands L1-L6a-h

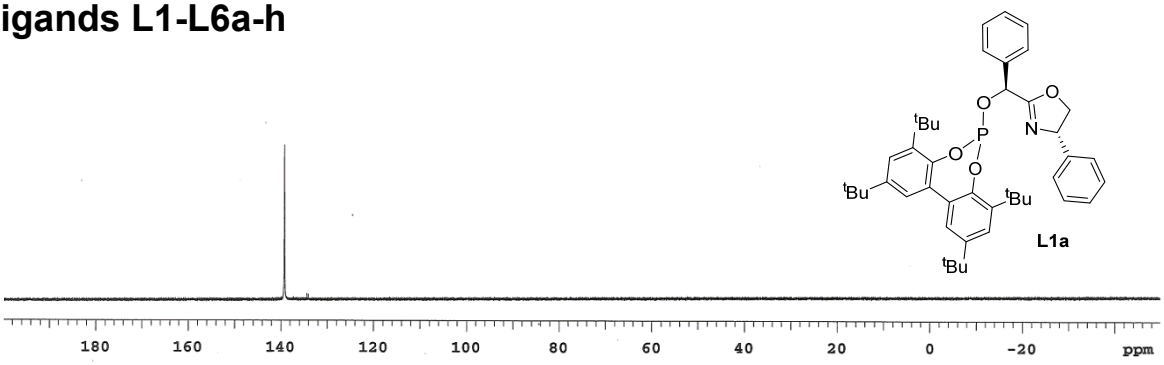


Figure S89. $^{31}P\{^{1}H\}$-NMR spectrum of **L1a**

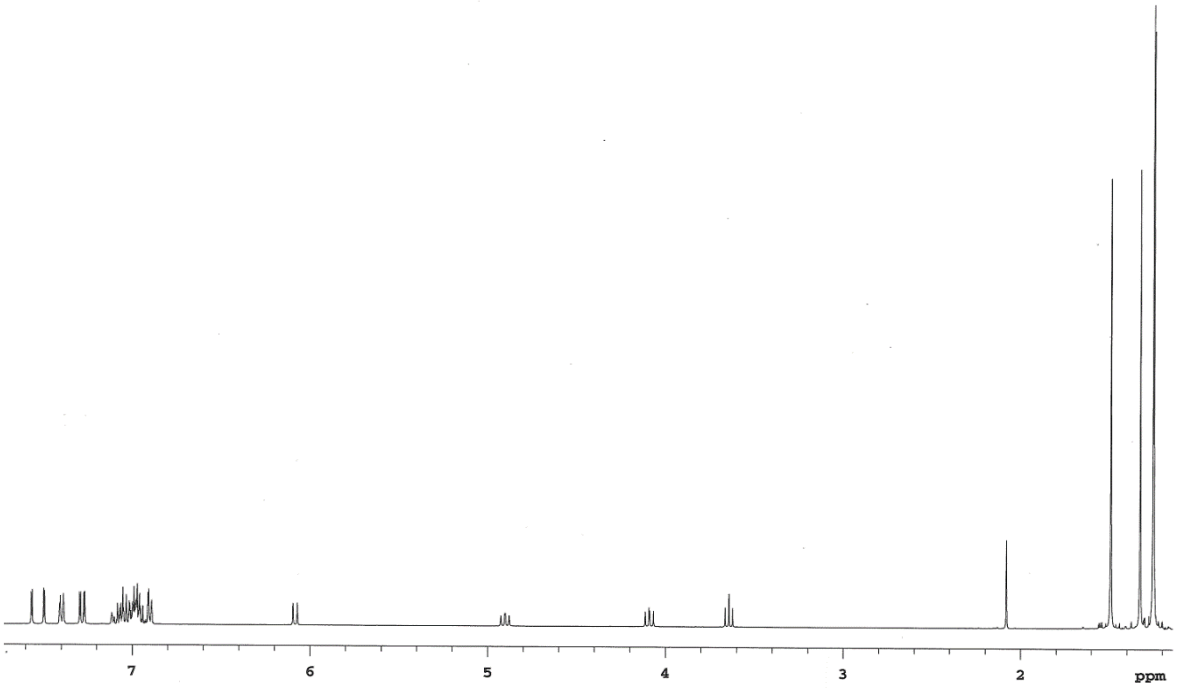


Figure S90. ^{1}H-NMR spectrum of **L1a**

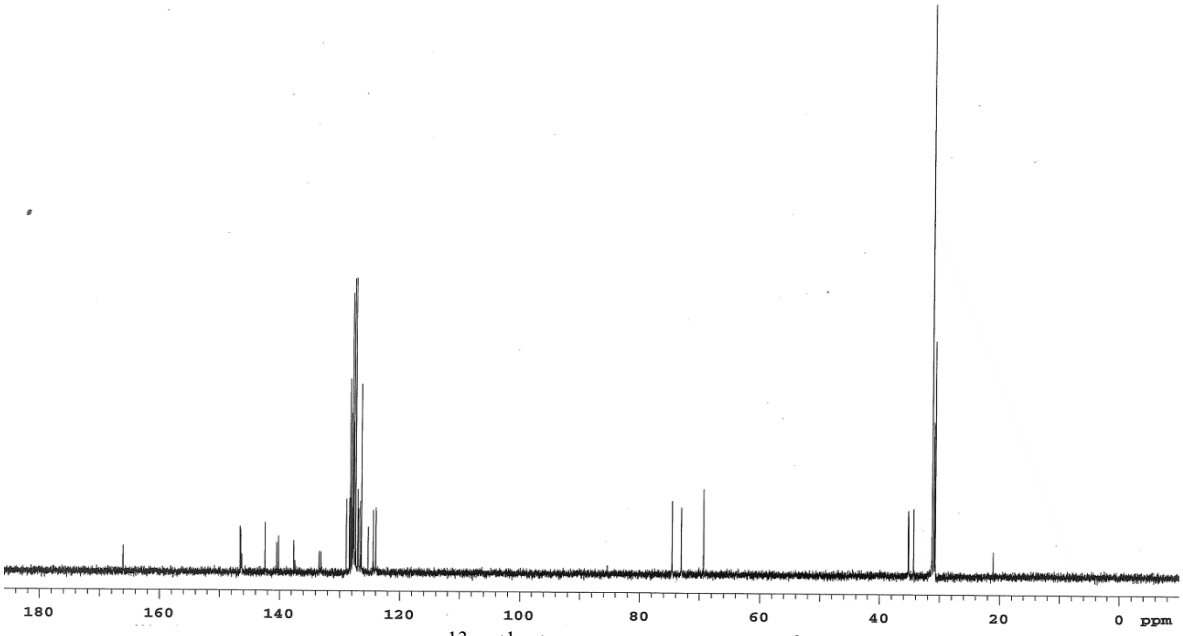


Figure S91. $^{13}C\{^{1}H\}$-NMR spectrum of **L1a**

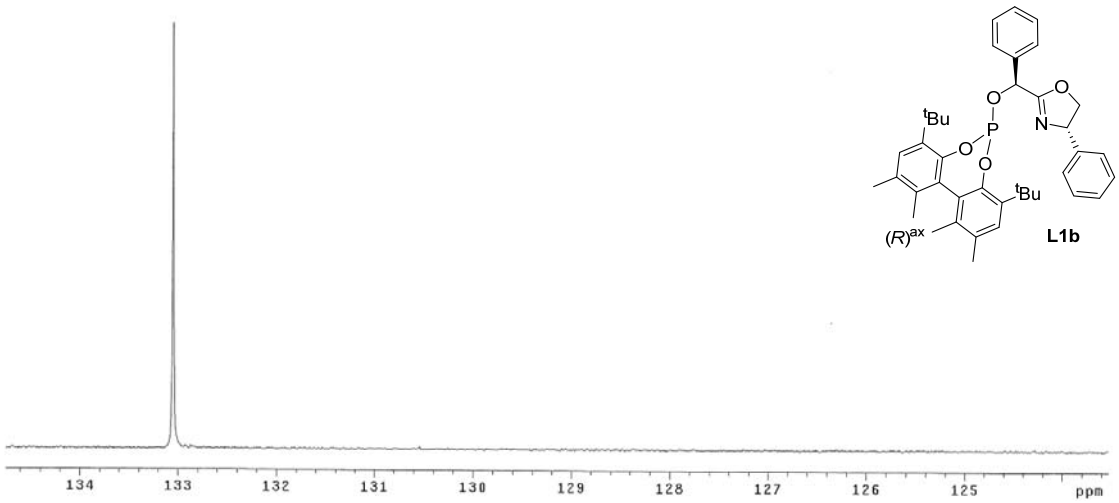


Figure S92. $^{31}P\{^{1}H\}$-NMR spectrum of **L1b**

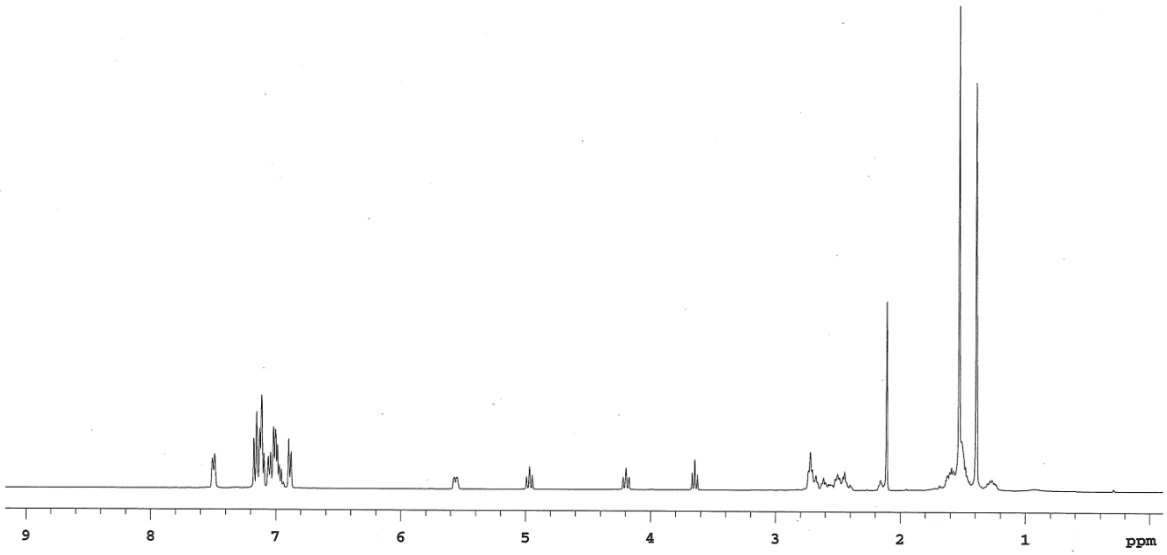


Figure S93. ^{1}H-NMR spectrum of **L1b**

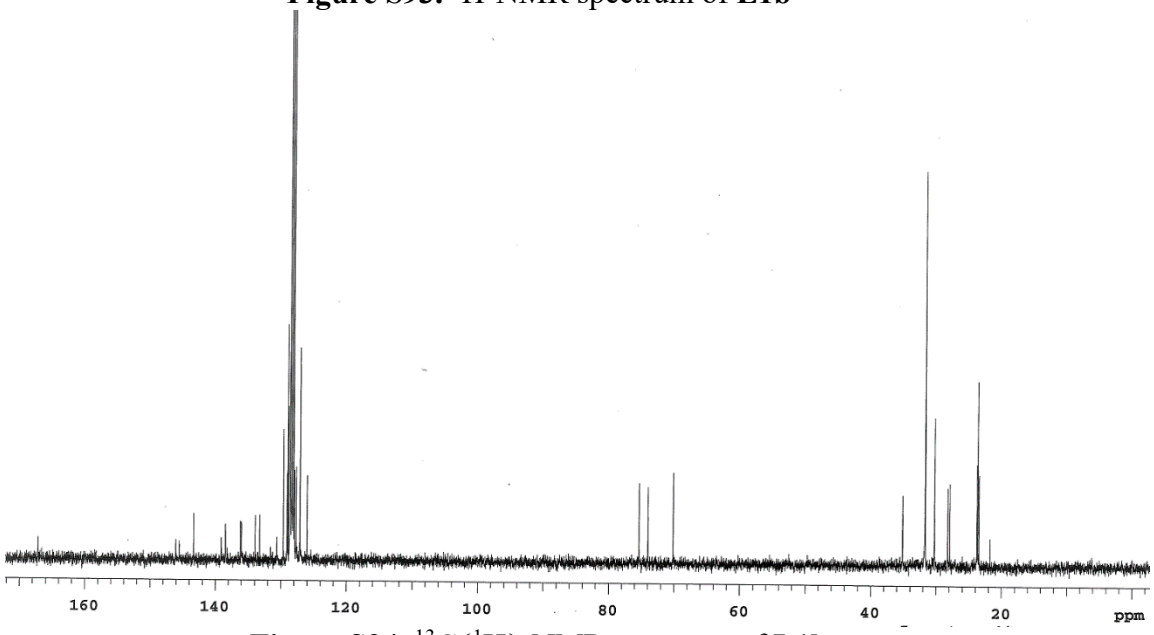


Figure S94. $^{13}C\{^{1}H\}$-NMR spectrum of **L1b**

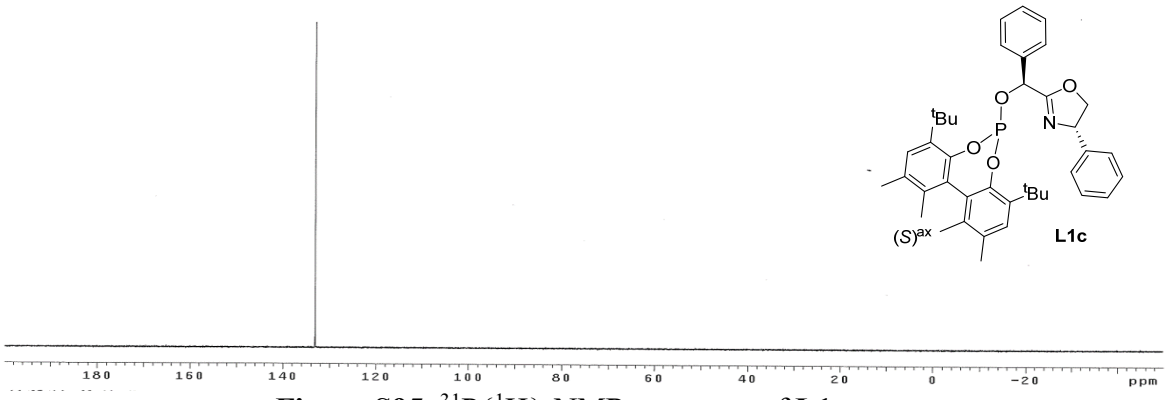


Figure S95. $^{31}P\{^{1}H\}$-NMR spectrum of **L1c**

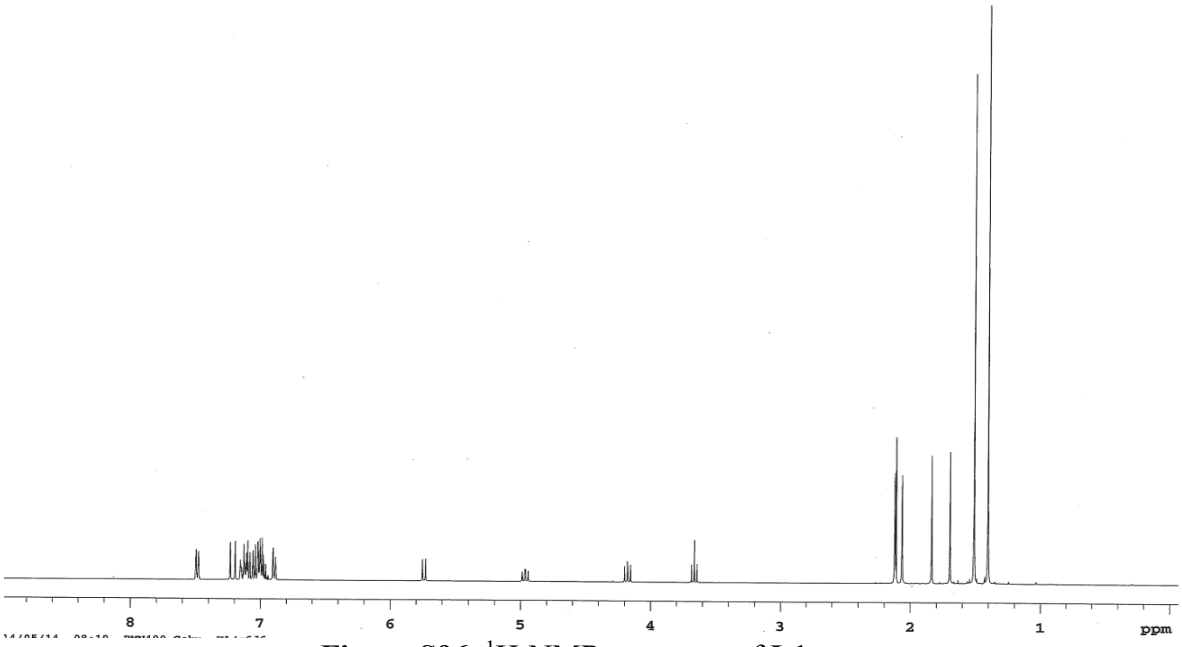


Figure S96. ^{1}H-NMR spectrum of **L1c**

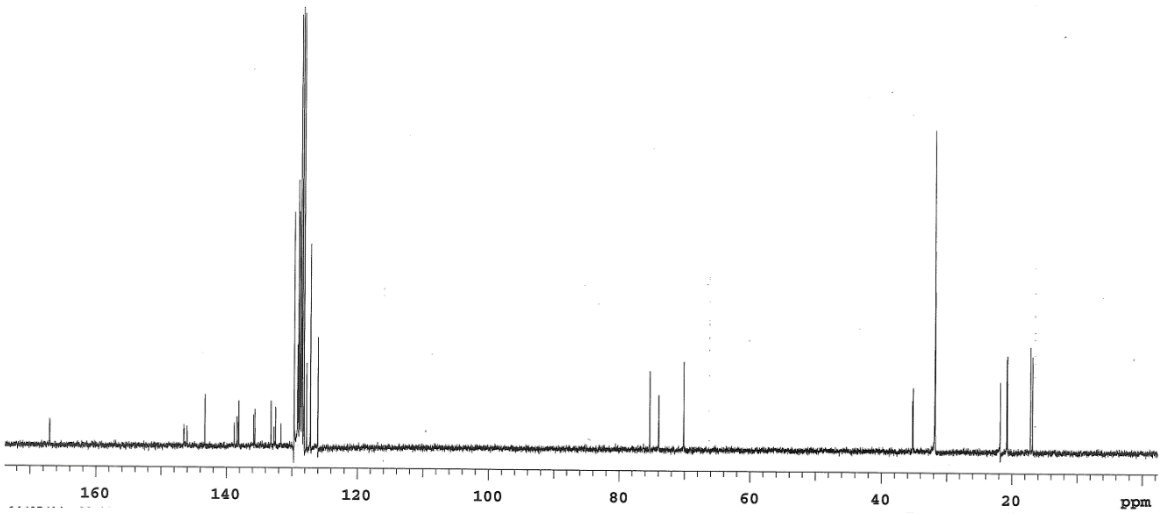


Figure S97. $^{13}C\{^{1}H\}$-NMR spectrum of **L1c**

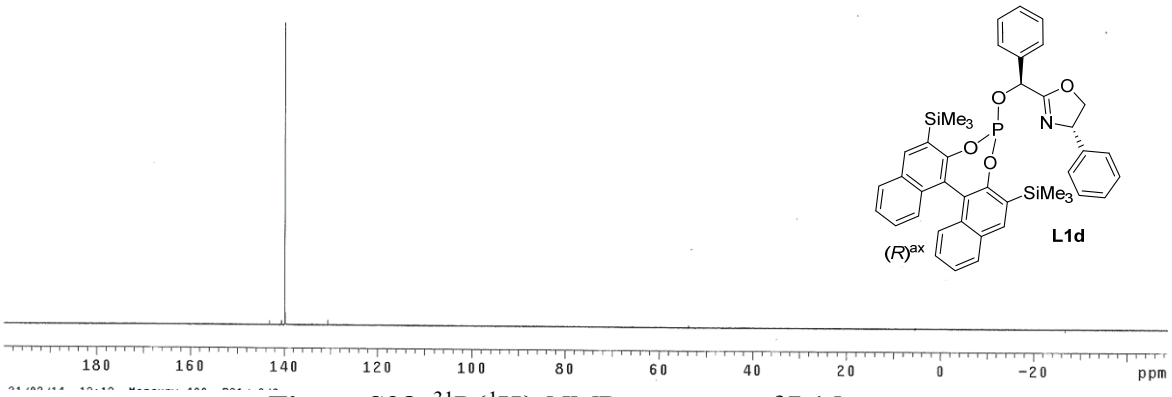


Figure S98. $^{31}P\{^{1}H\}$-NMR spectrum of **L1d**

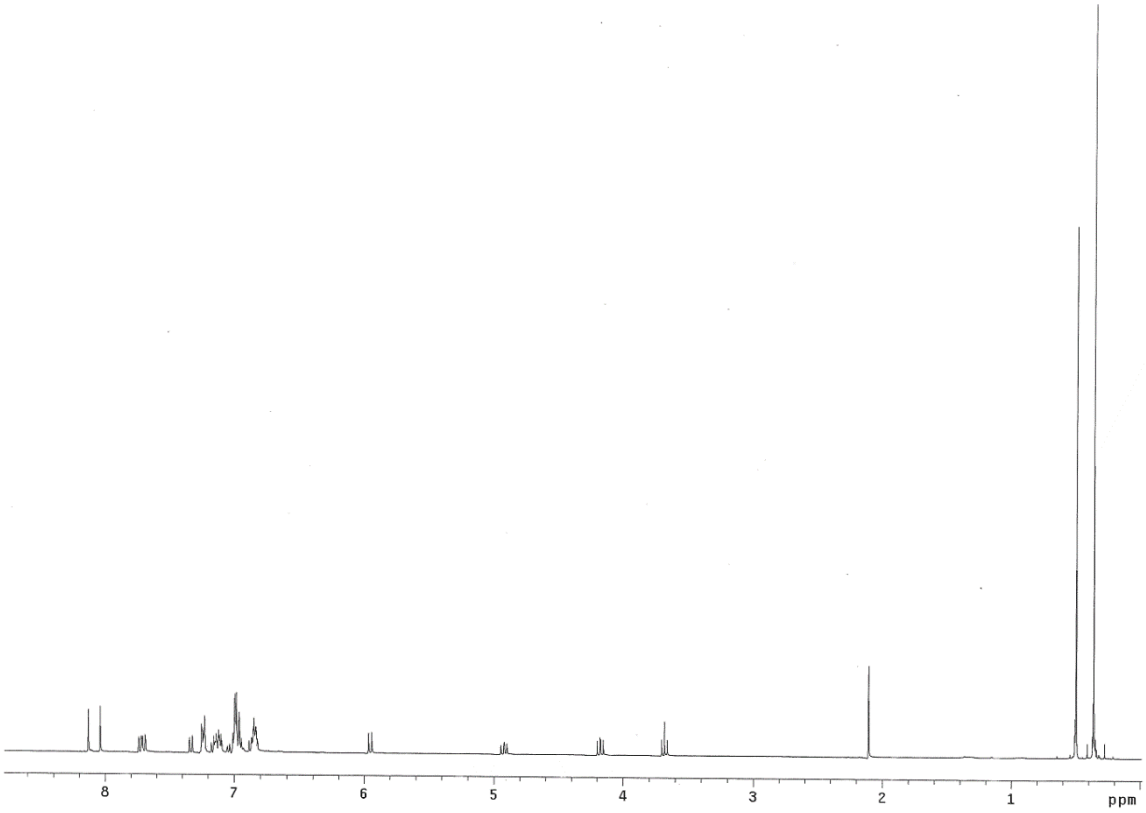


Figure S99. ^{1}H-NMR spectrum of **L1d**

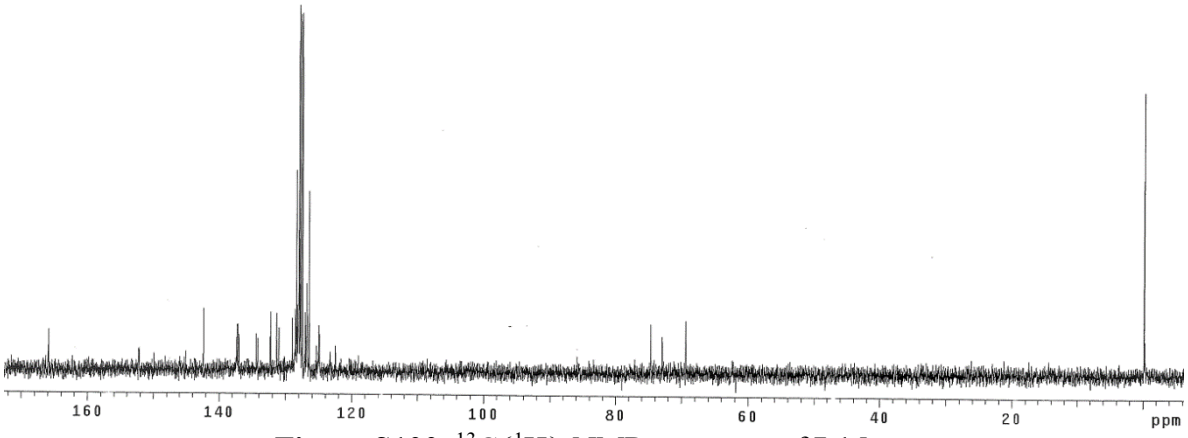


Figure S100. $^{13}C\{^{1}H\}$-NMR spectrum of **L1d**

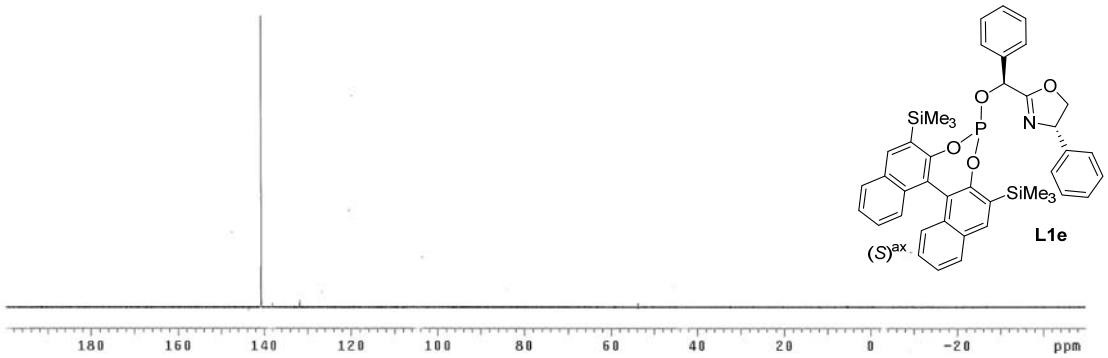


Figure S101. $^{31}P\{^{1}H\}$-NMR spectrum of **L1e**

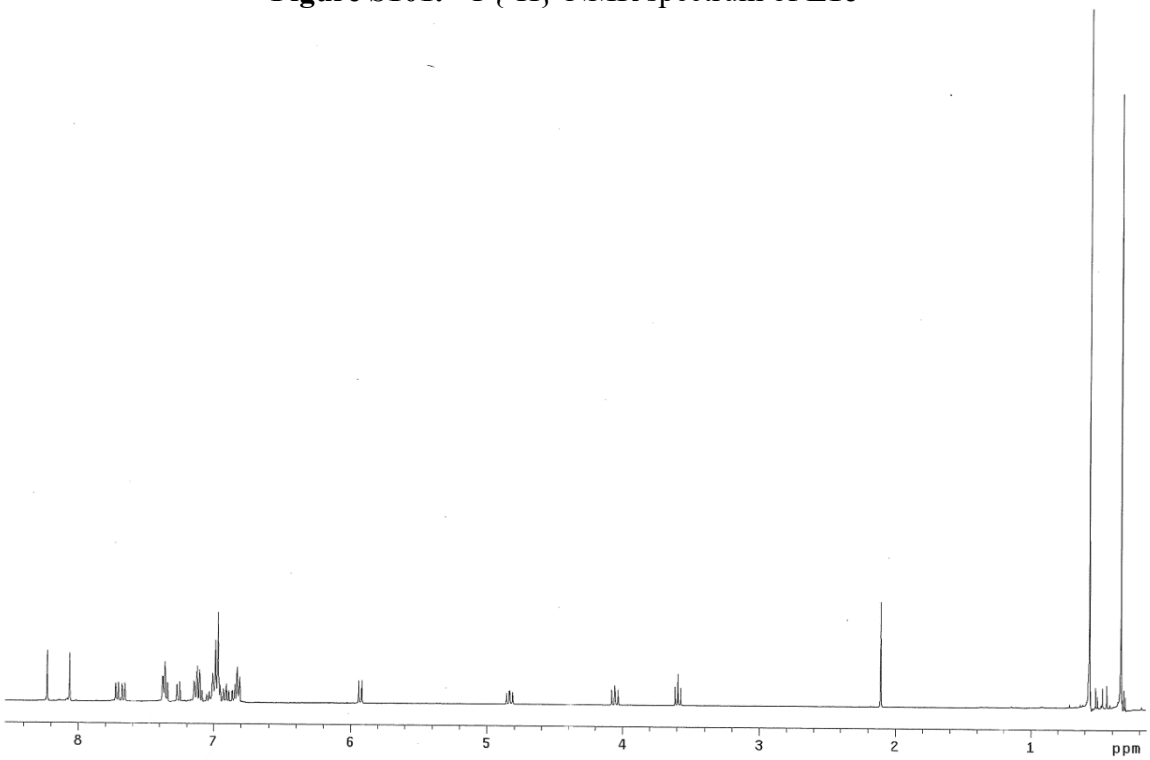


Figure S102. ^{1}H-NMR spectrum of **L1e**

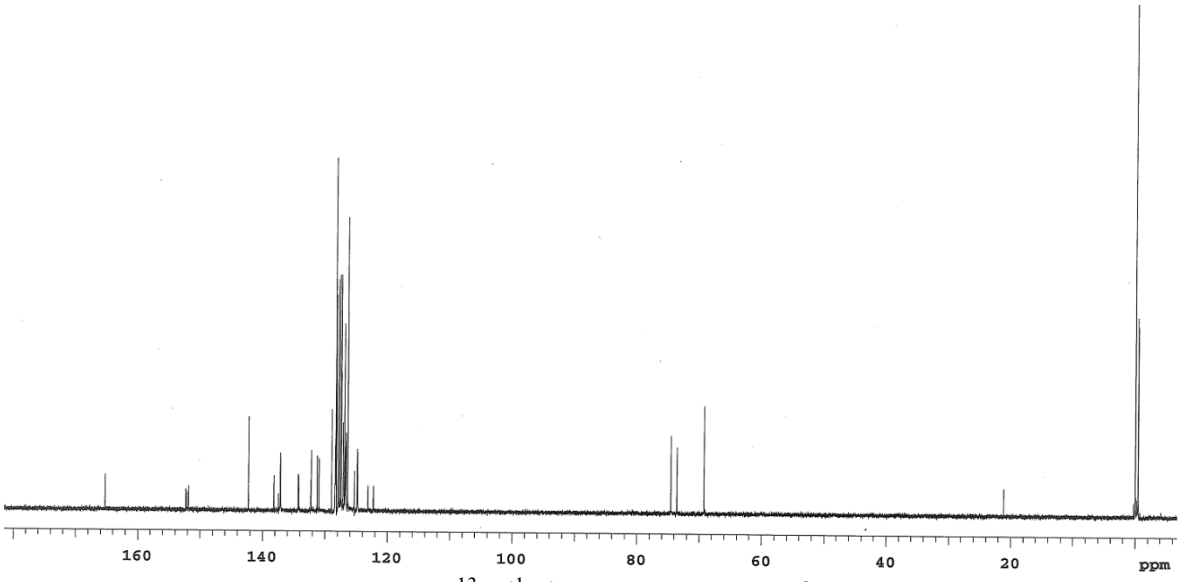


Figure S103. $^{13}C\{^{1}H\}$-NMR spectrum of **L1e**

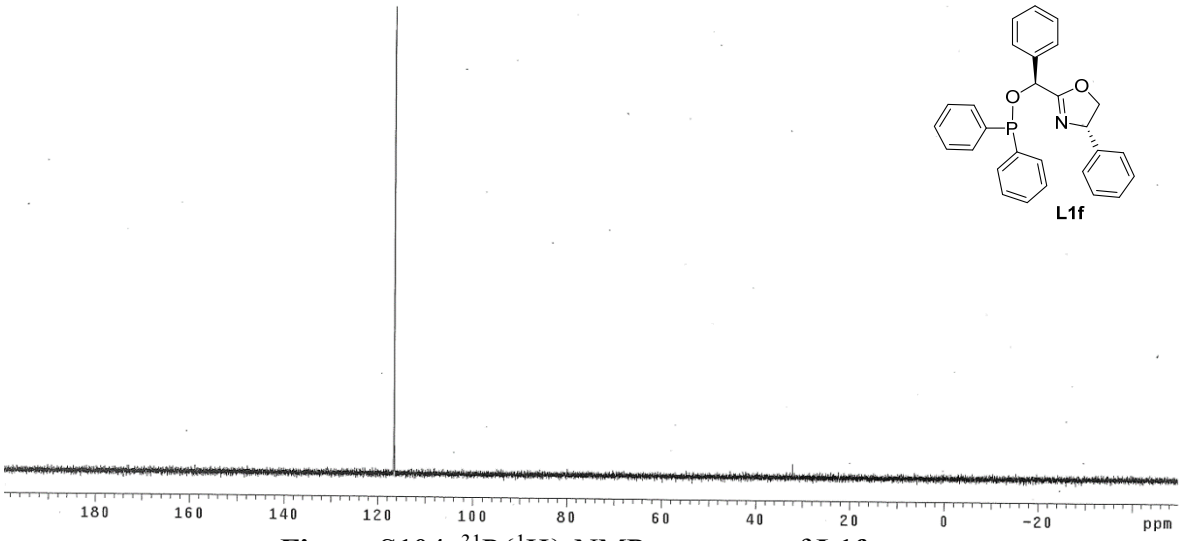


Figure S104. $^{31}P\{^{1}H\}$-NMR spectrum of **L1f**

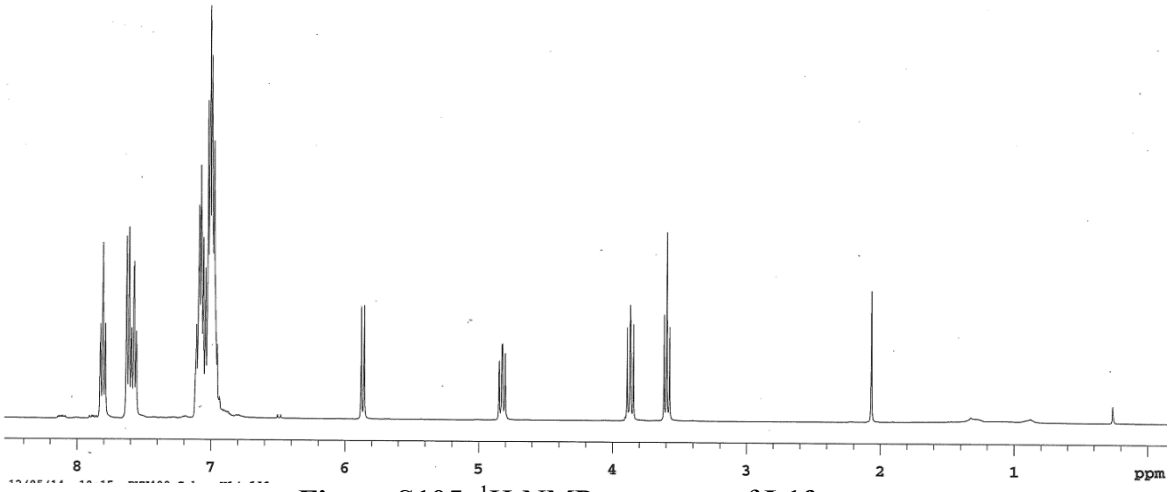


Figure S105. ^{1}H-NMR spectrum of **L1f**

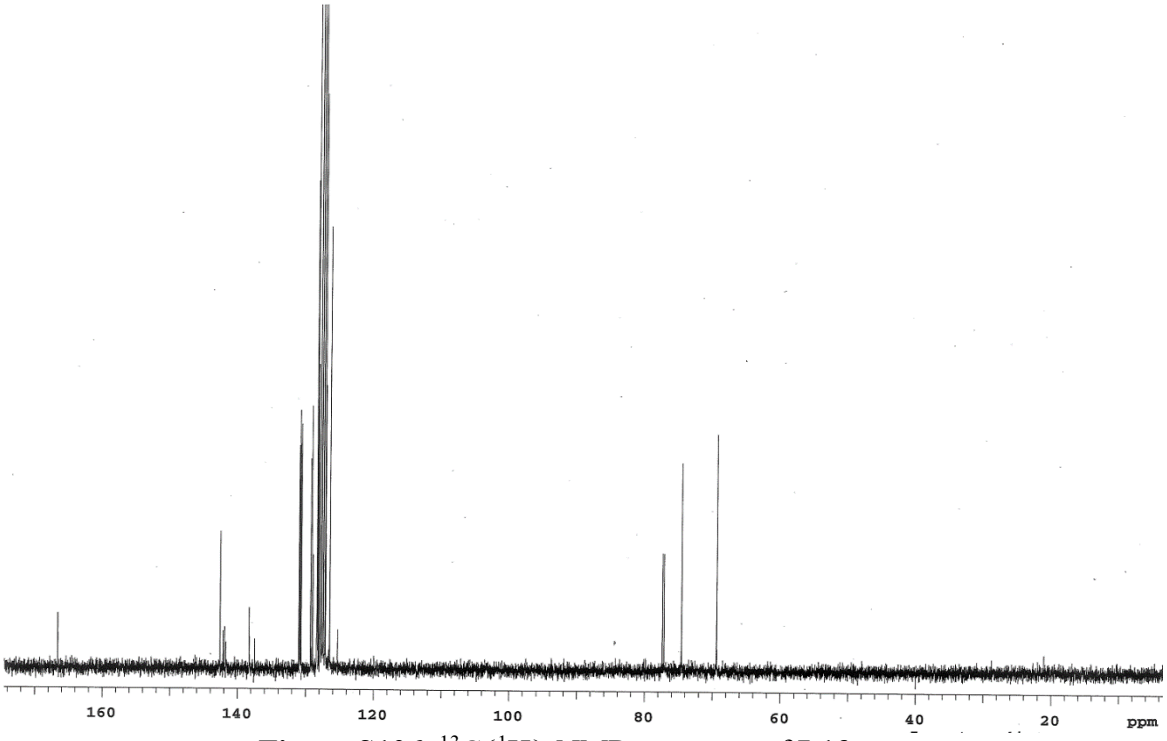


Figure S106. $^{13}C\{^{1}H\}$-NMR spectrum of **L1f**

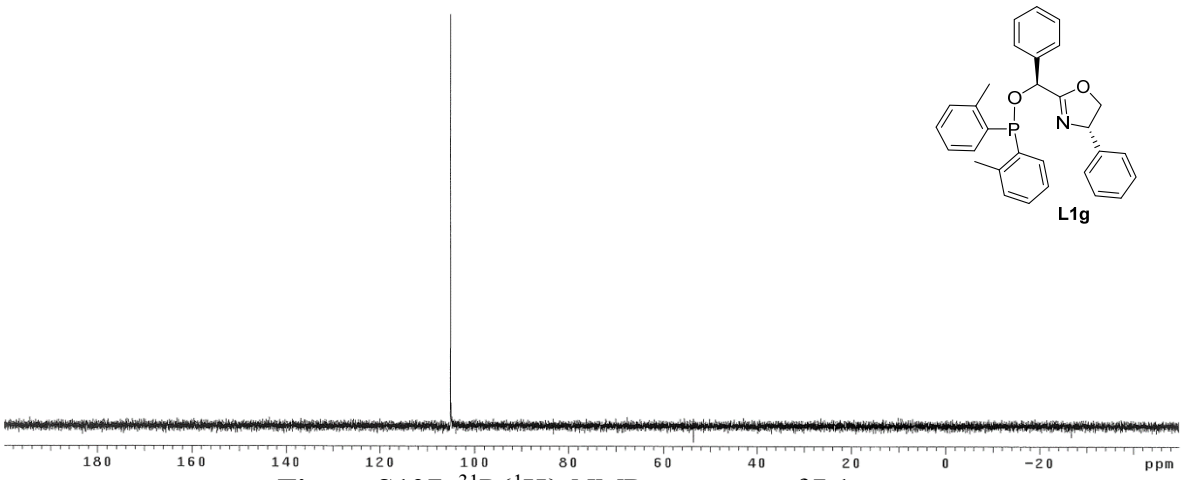


Figure S107. $^{31}P\{^{1}H\}$-NMR spectrum of **L1g**

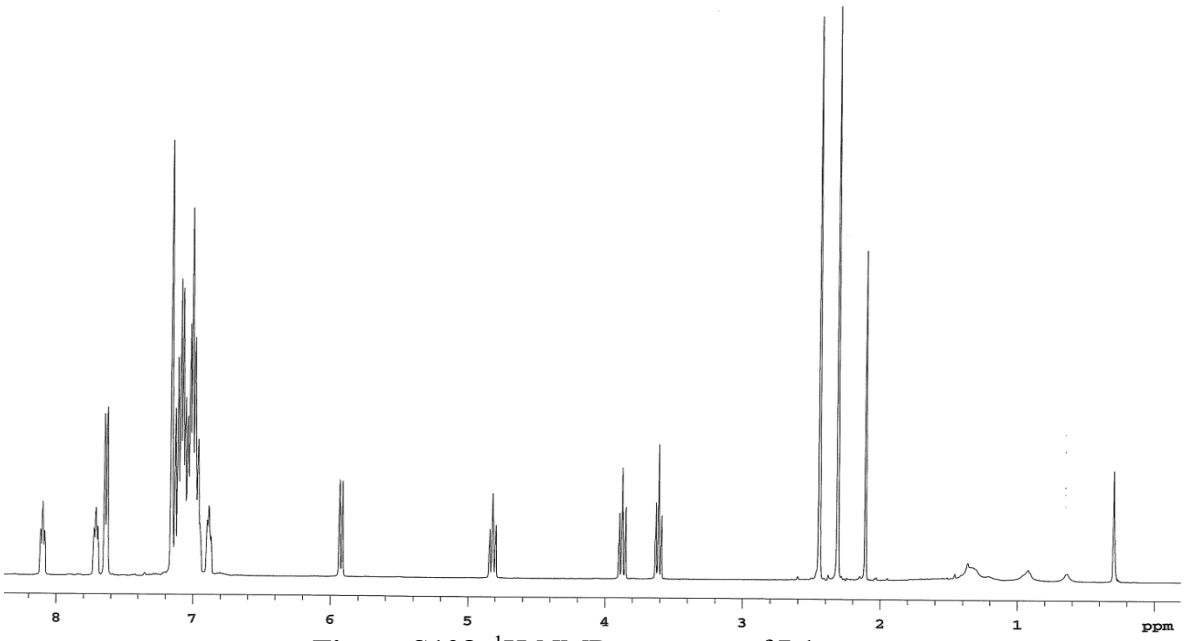


Figure S108. ^{1}H-NMR spectrum of **L1g**

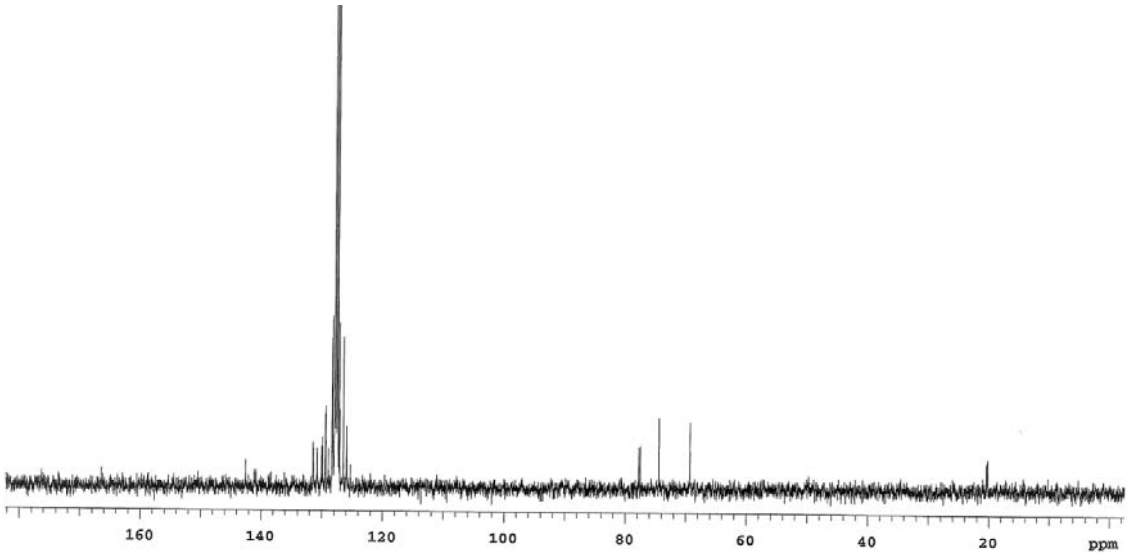


Figure S109. $^{13}C\{^{1}H\}$-NMR spectrum of **L1g**

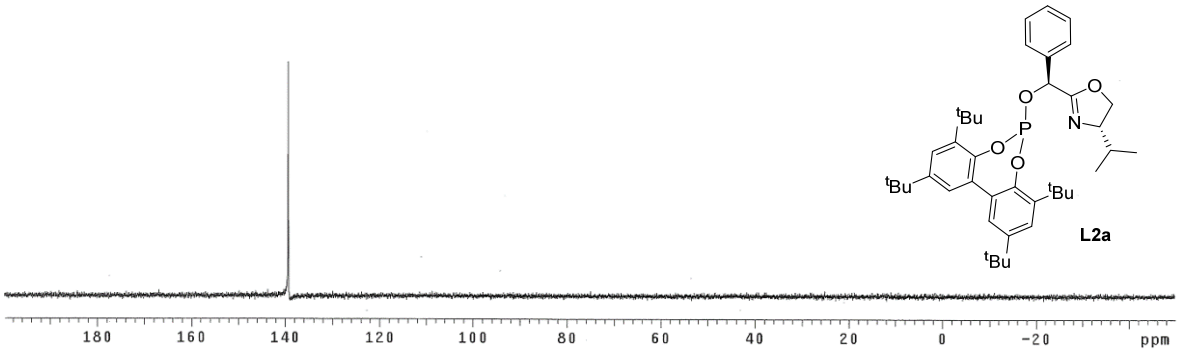


Figure S110. $^{31}P\{^{1}H\}$-NMR spectrum of **L2a**

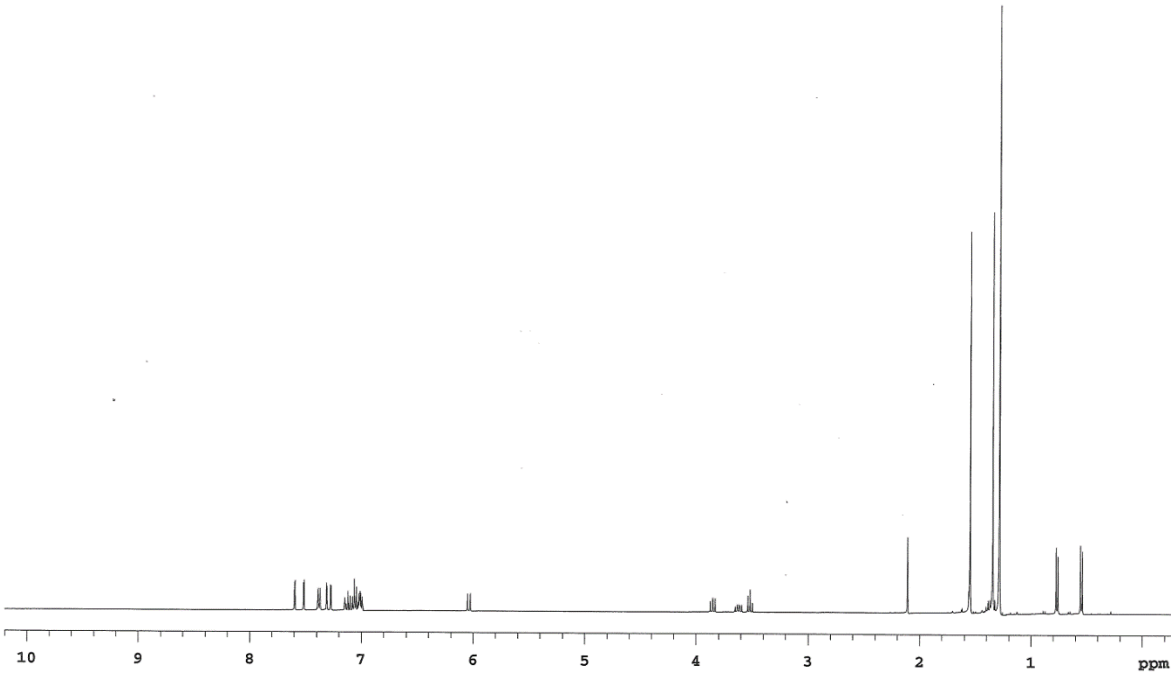


Figure S111. ^{1}H-NMR spectrum of **L2a**

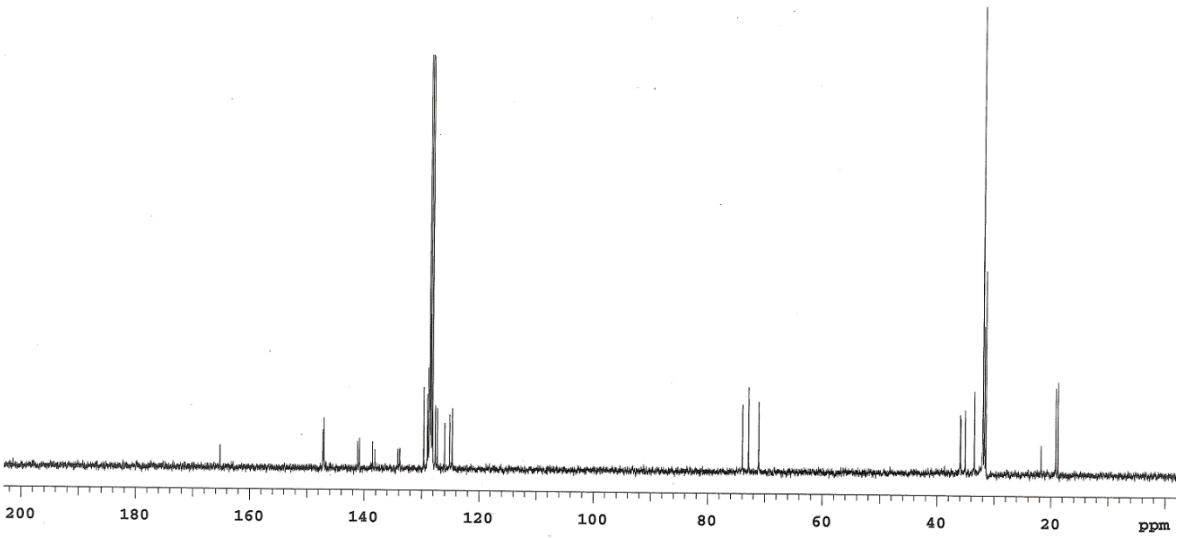


Figure S112. $^{13}C\{^{1}H\}$-NMR spectrum of **L2a**

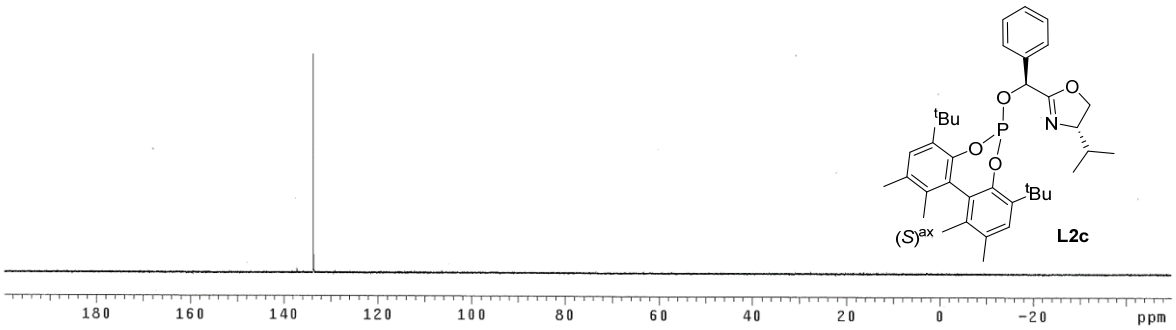


Figure S113. $^{31}P\{^{1}H\}$-NMR spectrum of **L2c**

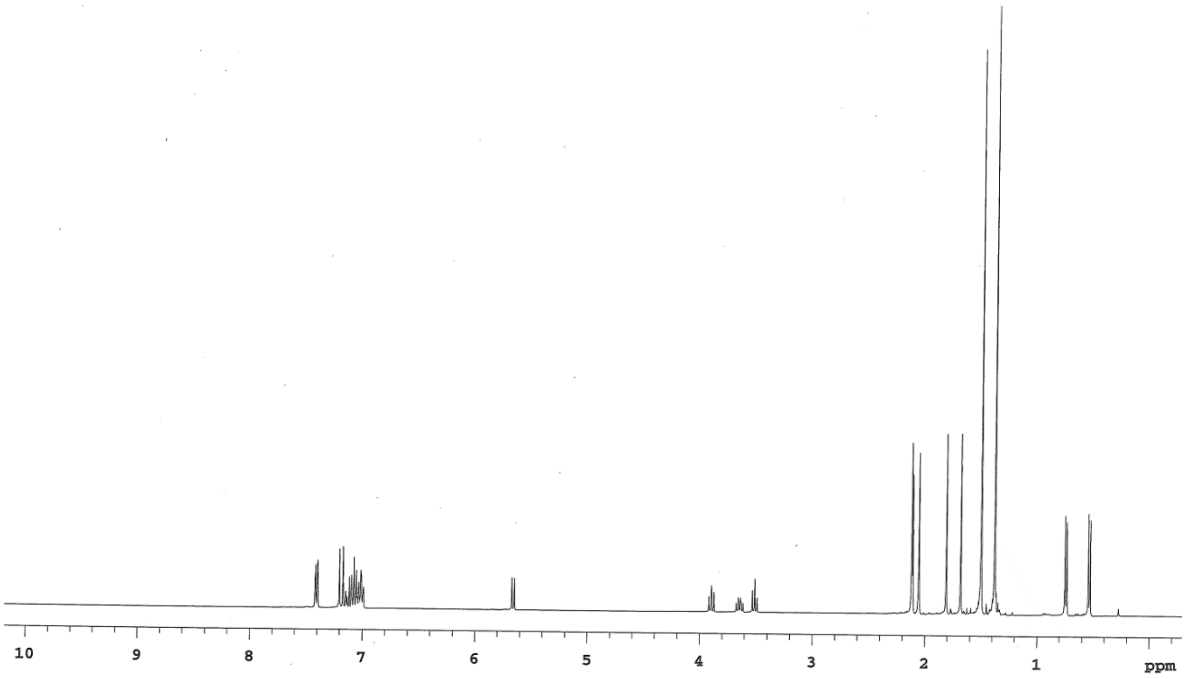


Figure S114. ^{1}H-NMR spectrum of **L2c**

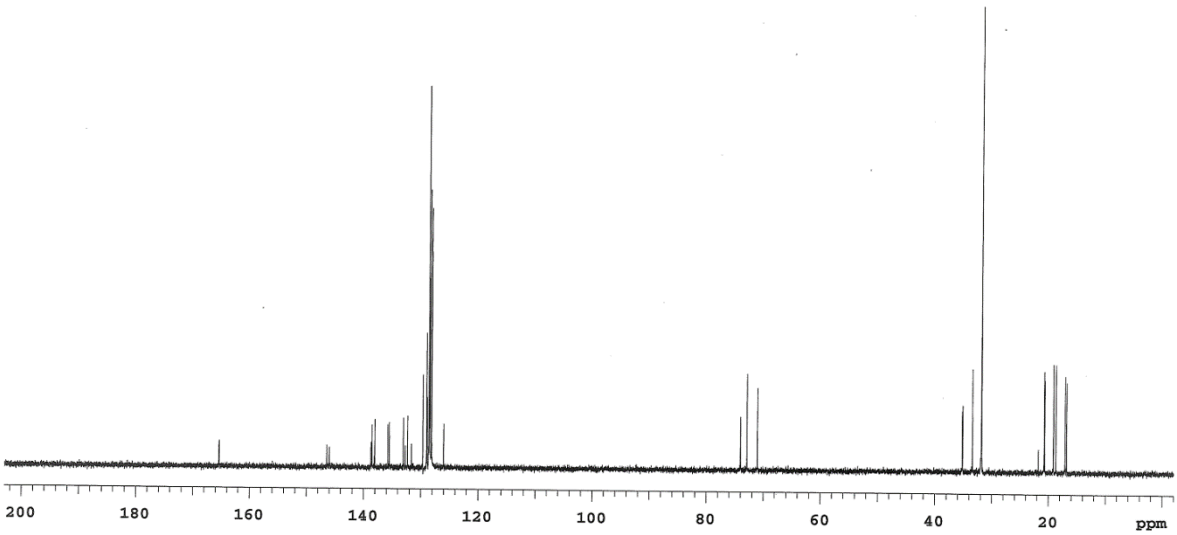


Figure S115. $^{13}C\{^{1}H\}$-NMR spectrum of **L2c**

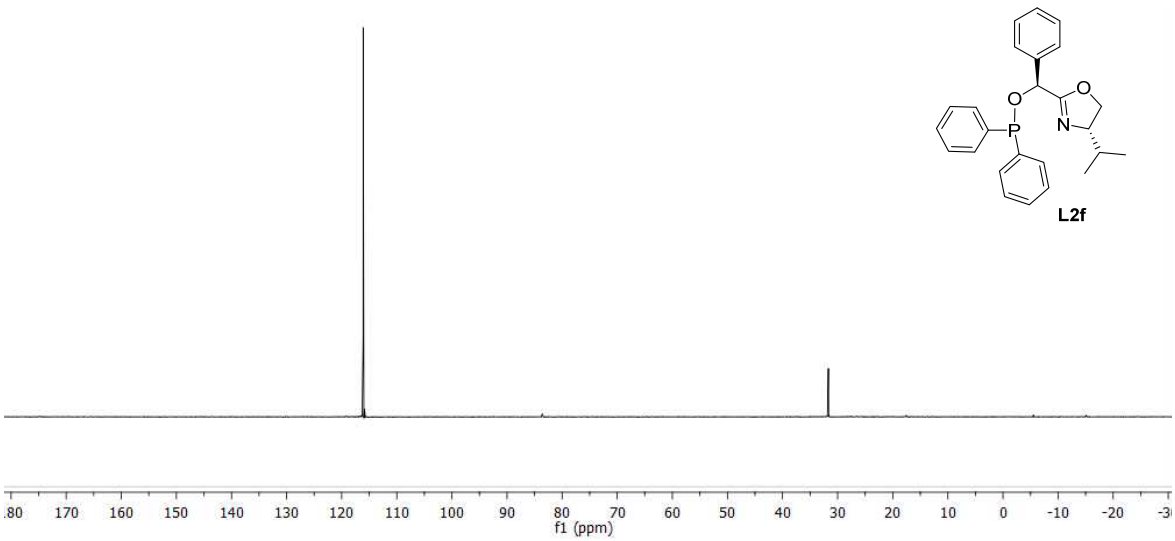


Figure S116. $^{31}P\{^{1}H\}$-NMR spectrum of **L2f**

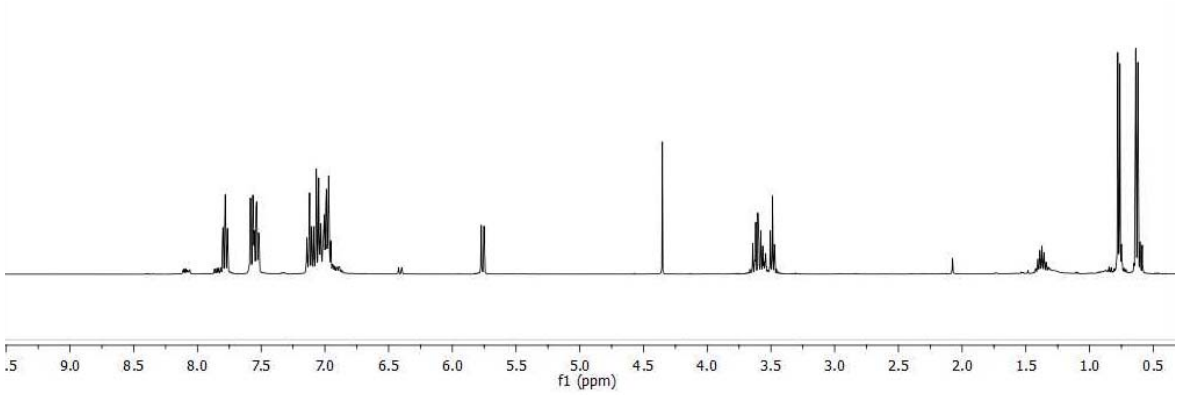


Figure S117. ^{1}H-NMR spectrum of **L2f**

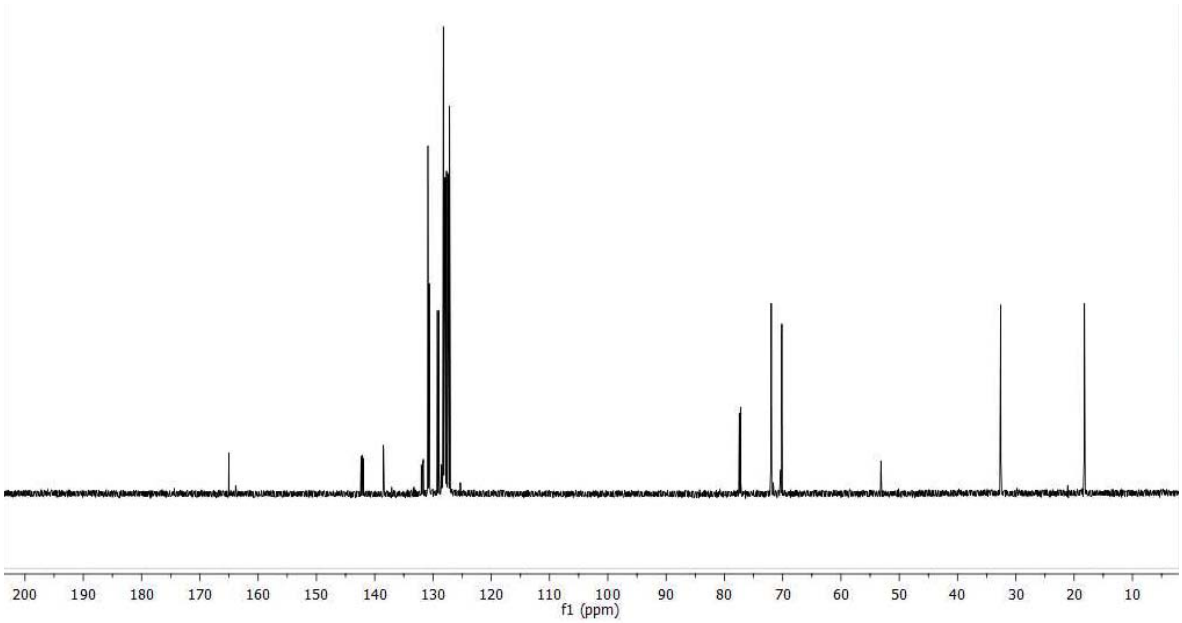


Figure S118. $^{13}C\{^{1}H\}$-NMR spectrum of **L2c**

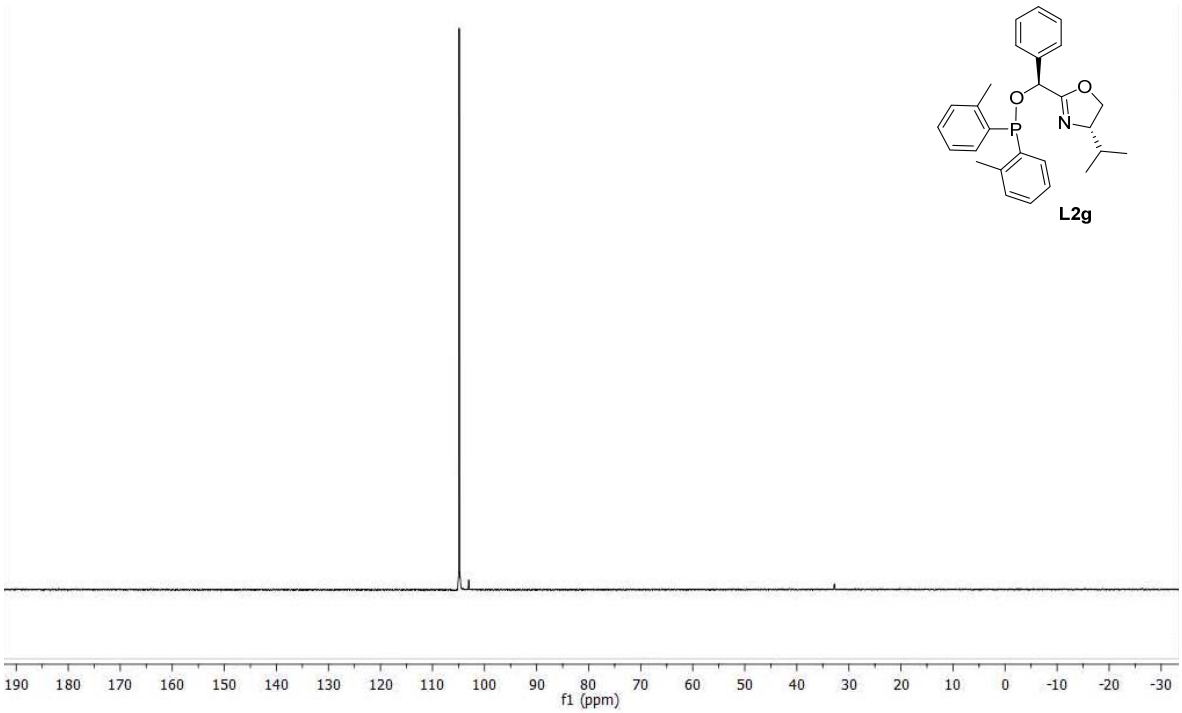


Figure S119. $^{31}P\{^{1}H\}$-NMR spectrum of **L2g**

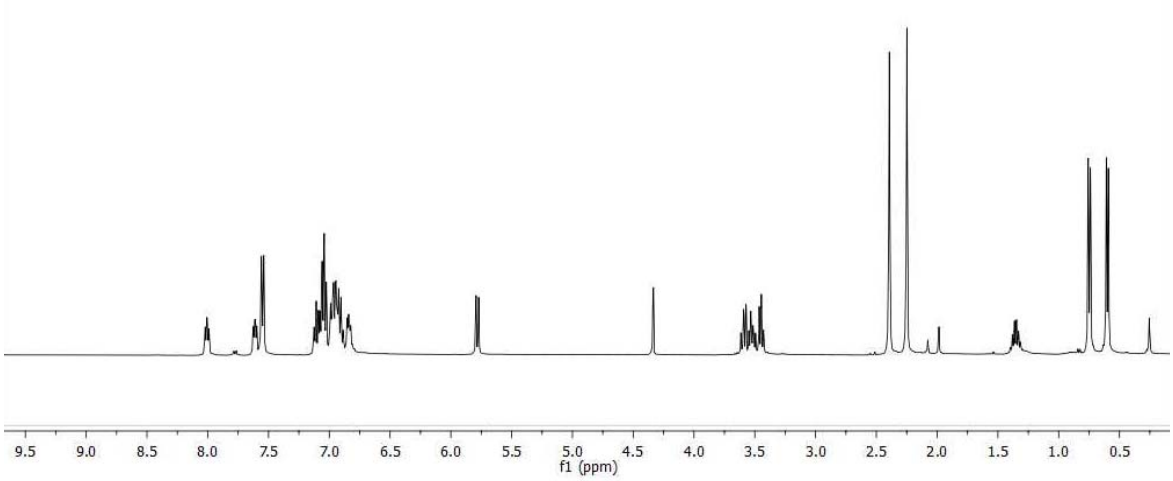


Figure S120. ^{1}H-NMR spectrum of **L2g**

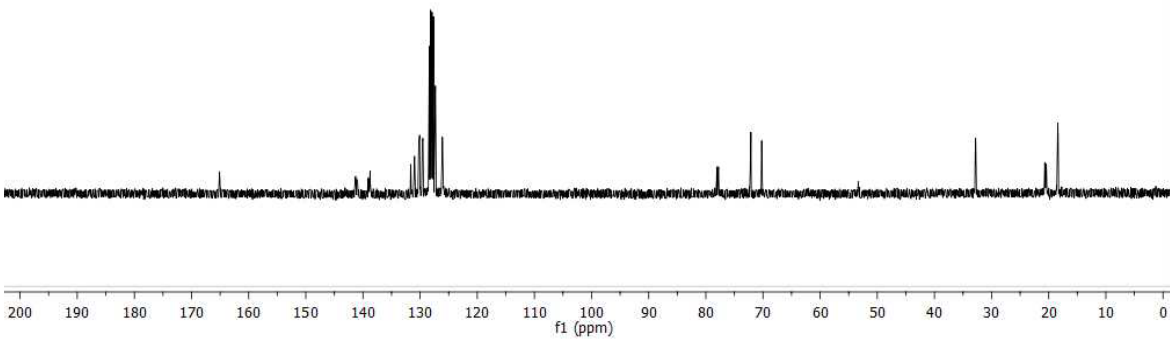


Figure S121. $^{13}C\{^{1}H\}$-NMR spectrum of **L2g**

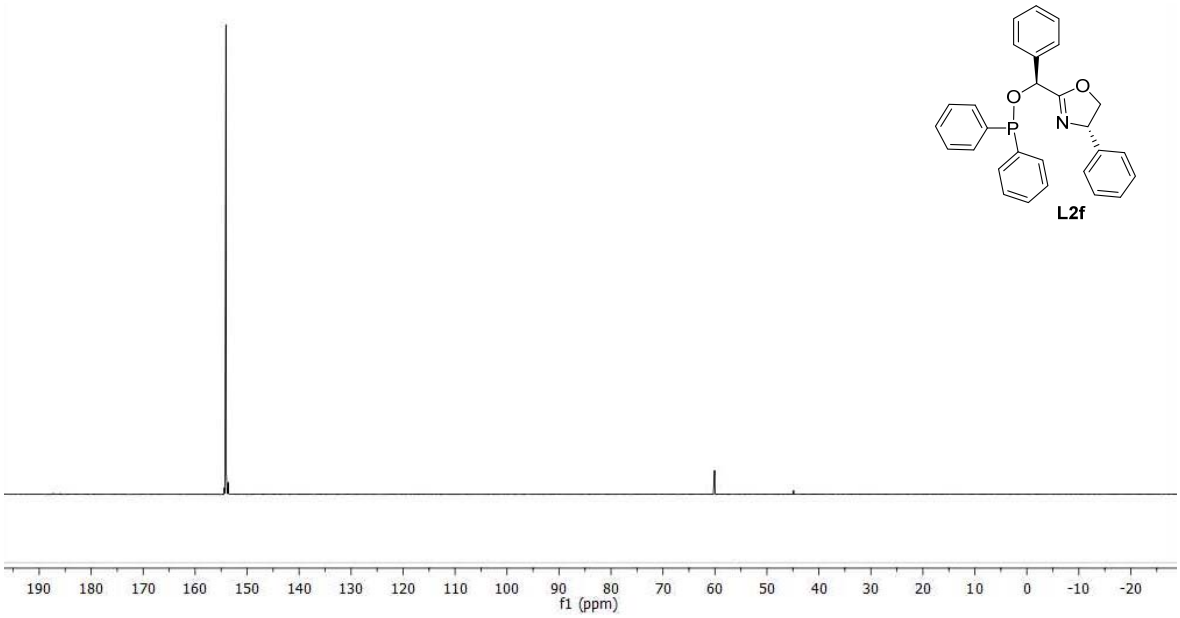


Figure S122. $^{31}P\{^{1}H\}$-NMR spectrum of **L2f**

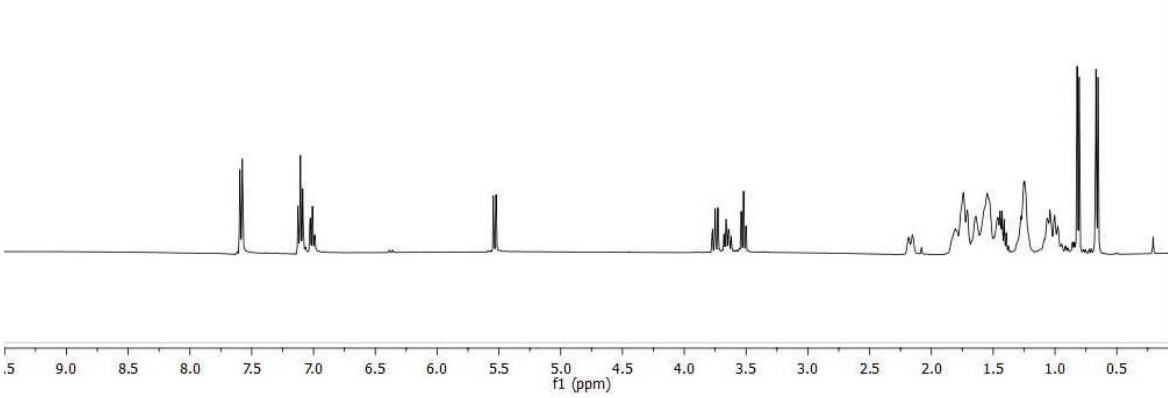


Figure S123. ^{1}H-NMR spectrum of **L2f**

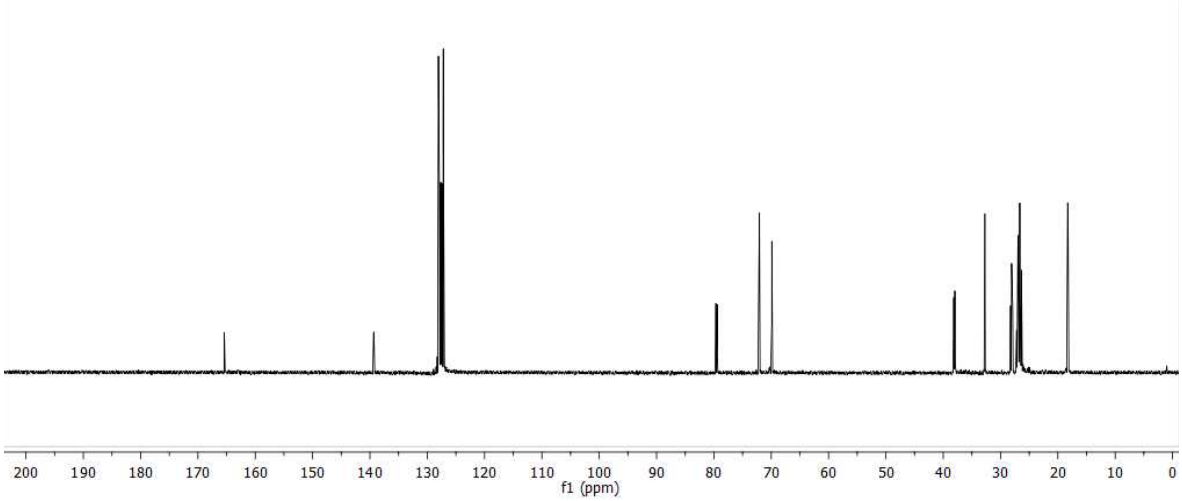


Figure S124. $^{13}C\{^{1}H\}$-NMR spectrum of **L2f**

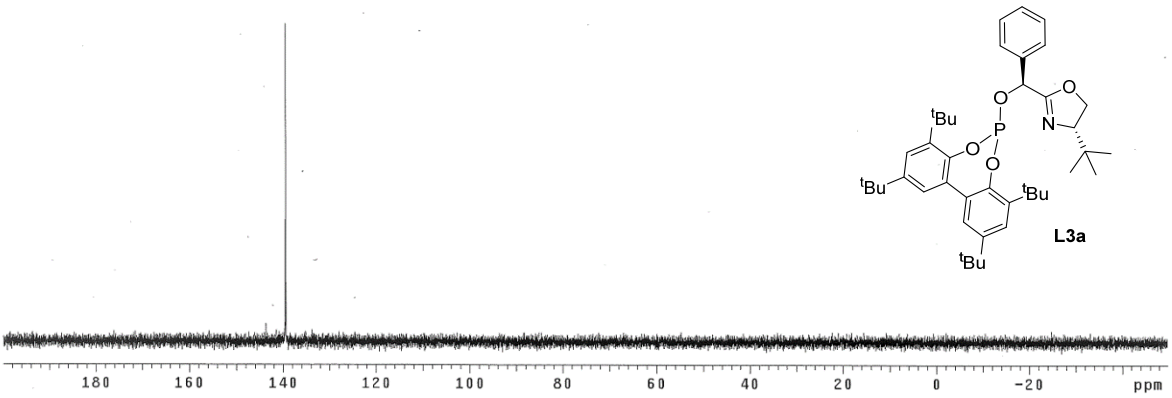


Figure S125. $^{31}P\{^{1}H\}$-NMR spectrum of **L3a**

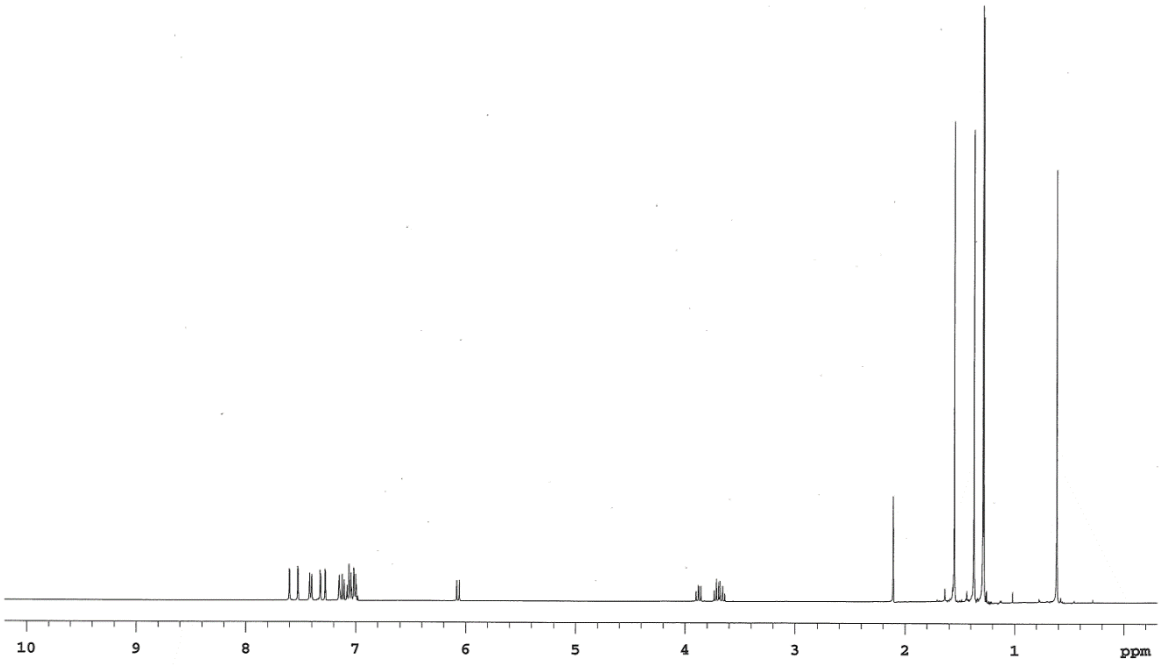


Figure S126. ^{1}H-NMR spectrum of **L3a**

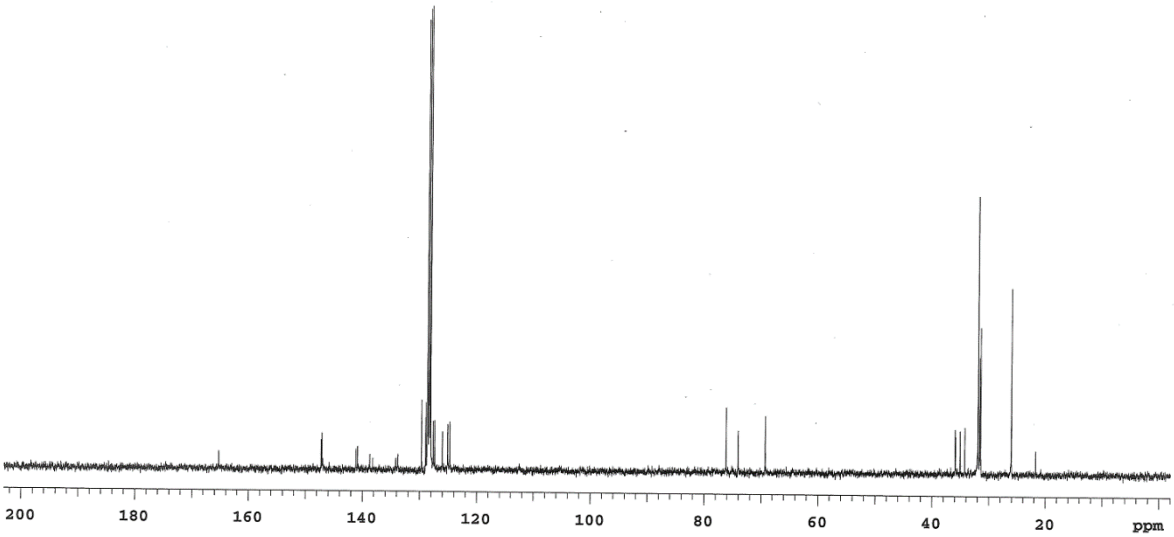


Figure S127. $^{13}C\{^{1}H\}$-NMR spectrum of **L3a**

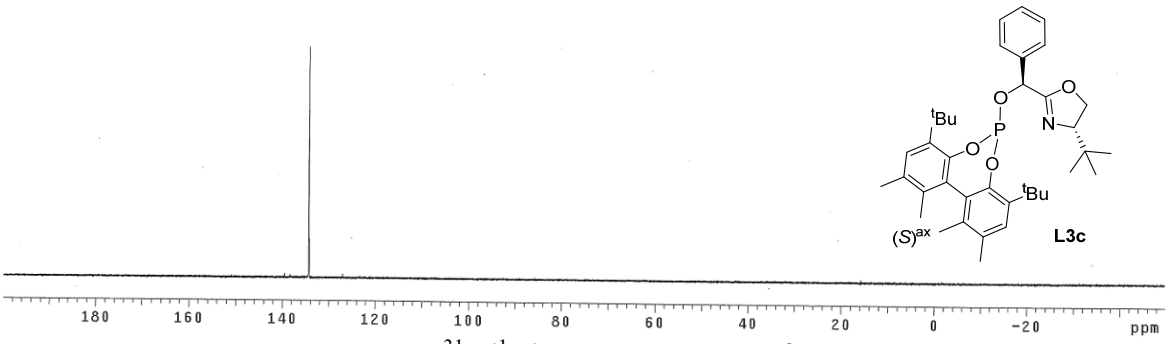


Figure S128. $^{31}P\{^{1}H\}$-NMR spectrum of **L3c**

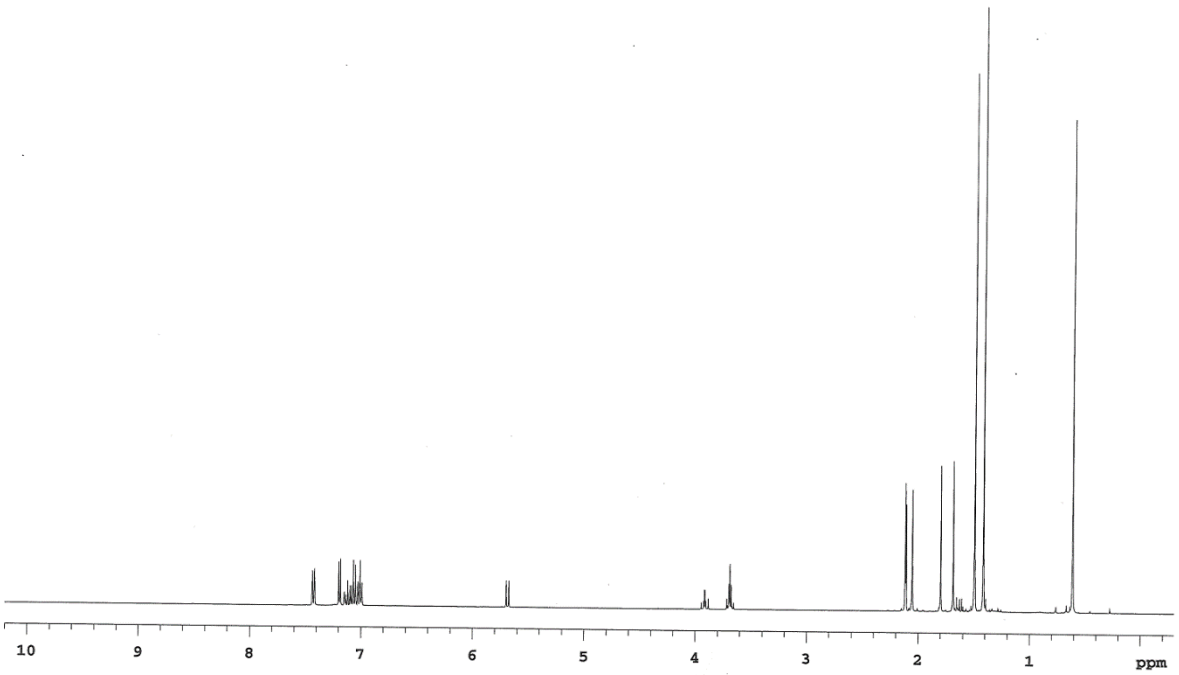


Figure S129. ^{1}H-NMR spectrum of **L3c**

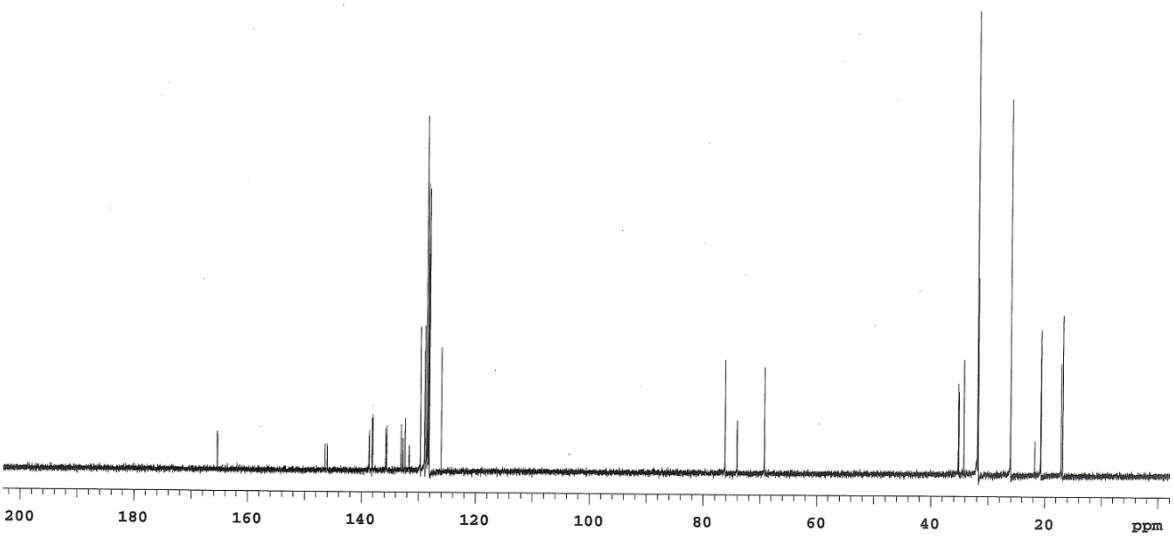


Figure S130. $^{13}C\{^{1}H\}$-NMR spectrum of **L3c**

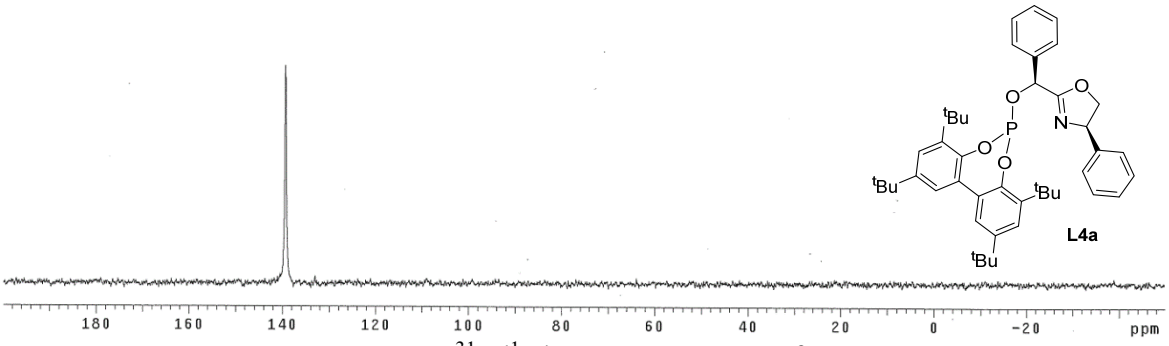


Figure S131. $^{31}P\{^{1}H\}$-NMR spectrum of **L4a**

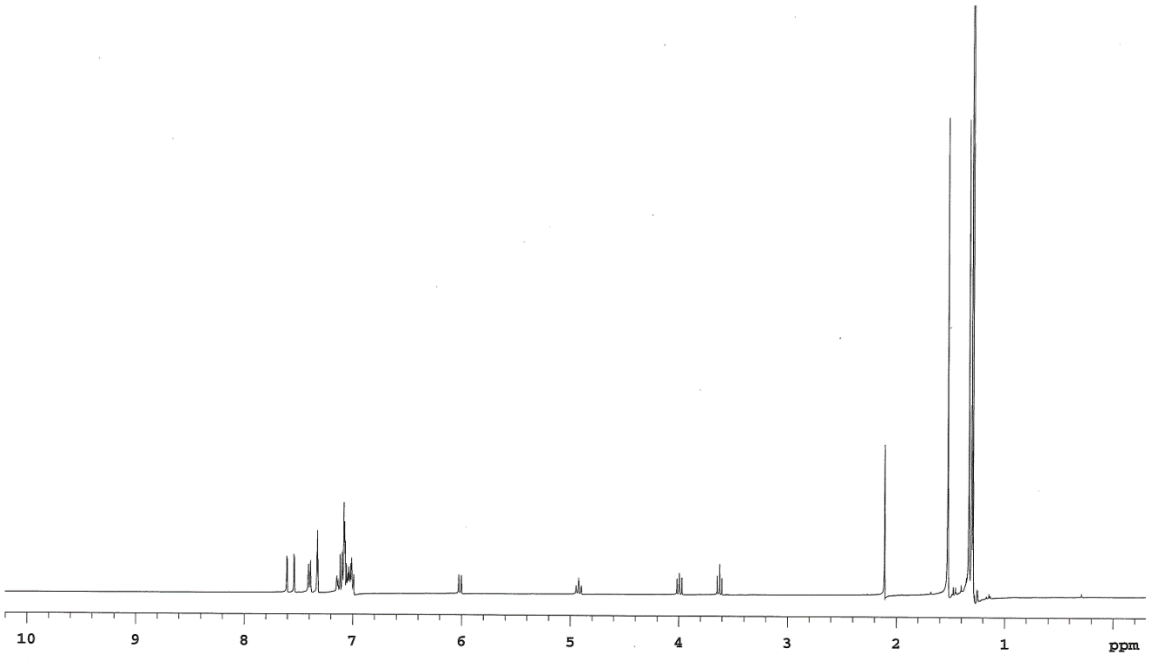


Figure S132. ^{1}H-NMR spectrum of **L4a**

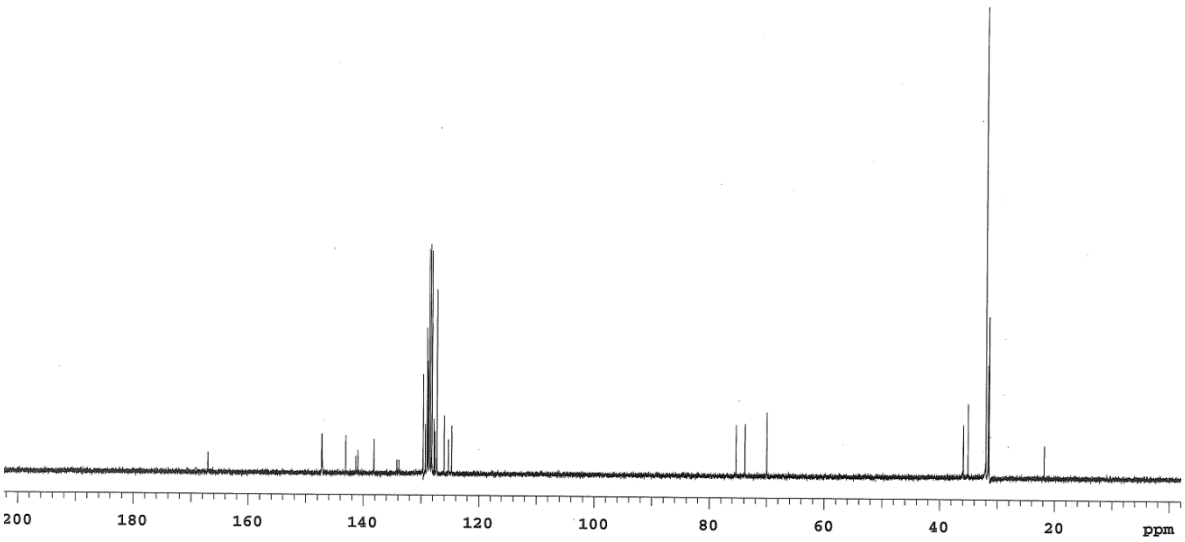


Figure S133. $^{13}C\{^{1}H\}$-NMR spectrum of **L4a**

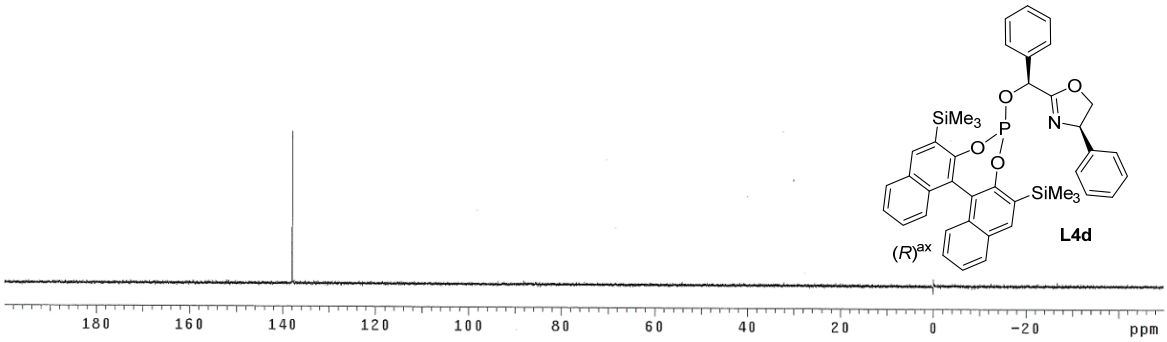


Figure S134. $^{31}P\{^{1}H\}$-NMR spectrum of **L4d**

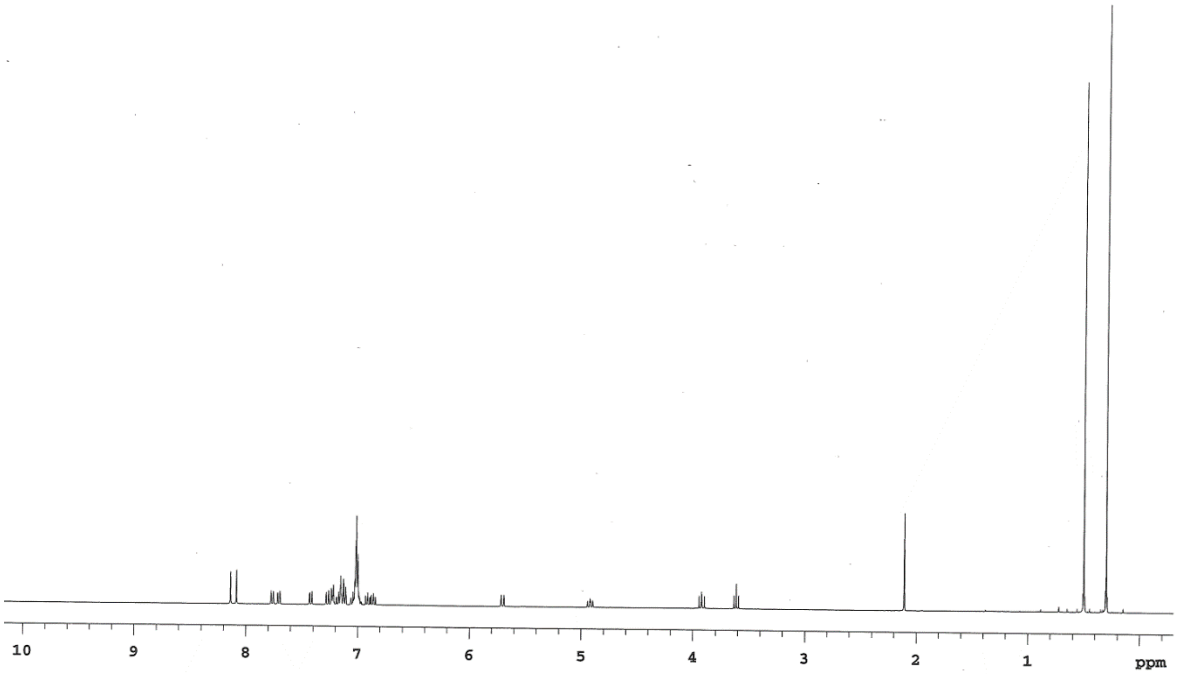


Figure S135. ^{1}H-NMR spectrum of **L4d**

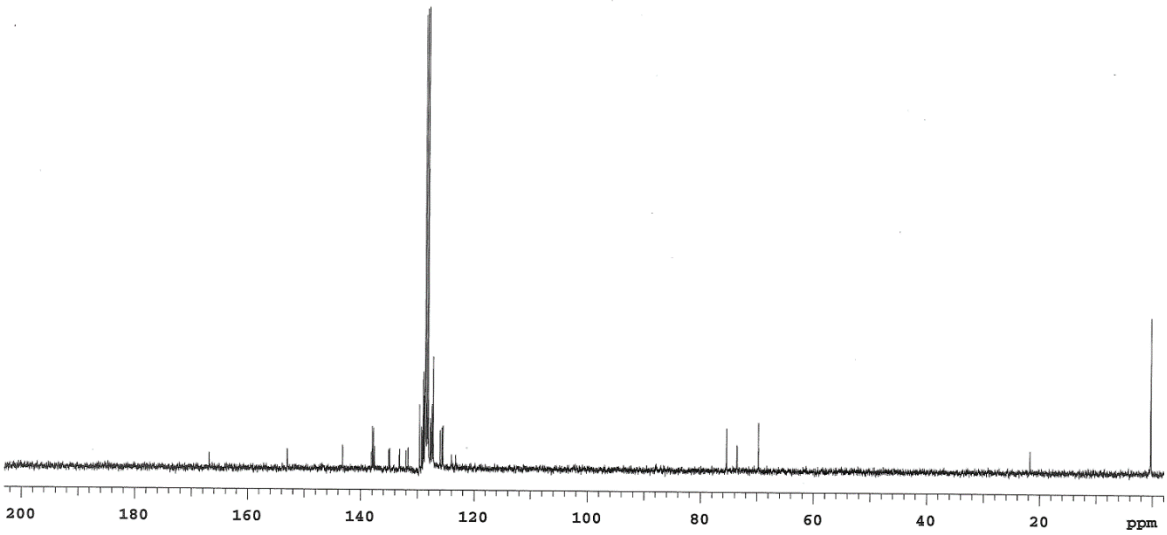


Figure S136. $^{13}C\{^{1}H\}$-NMR spectrum of **L4d**

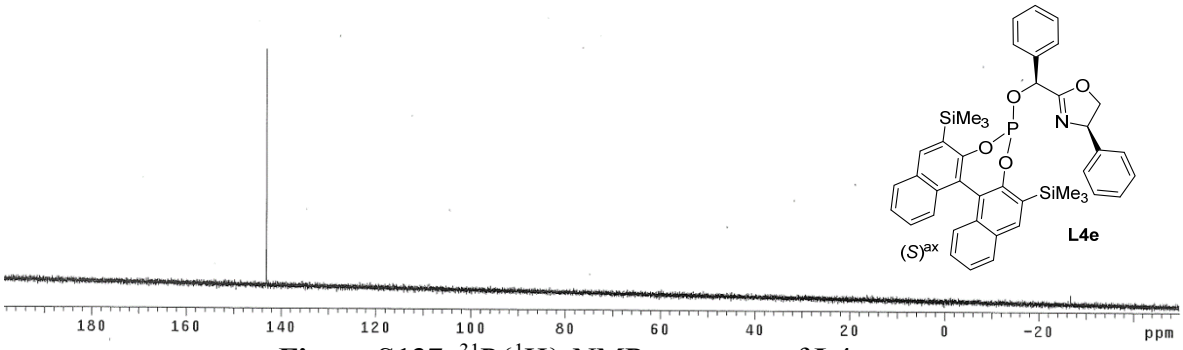


Figure S137. $^{31}P\{^{1}H\}$-NMR spectrum of **L4e**

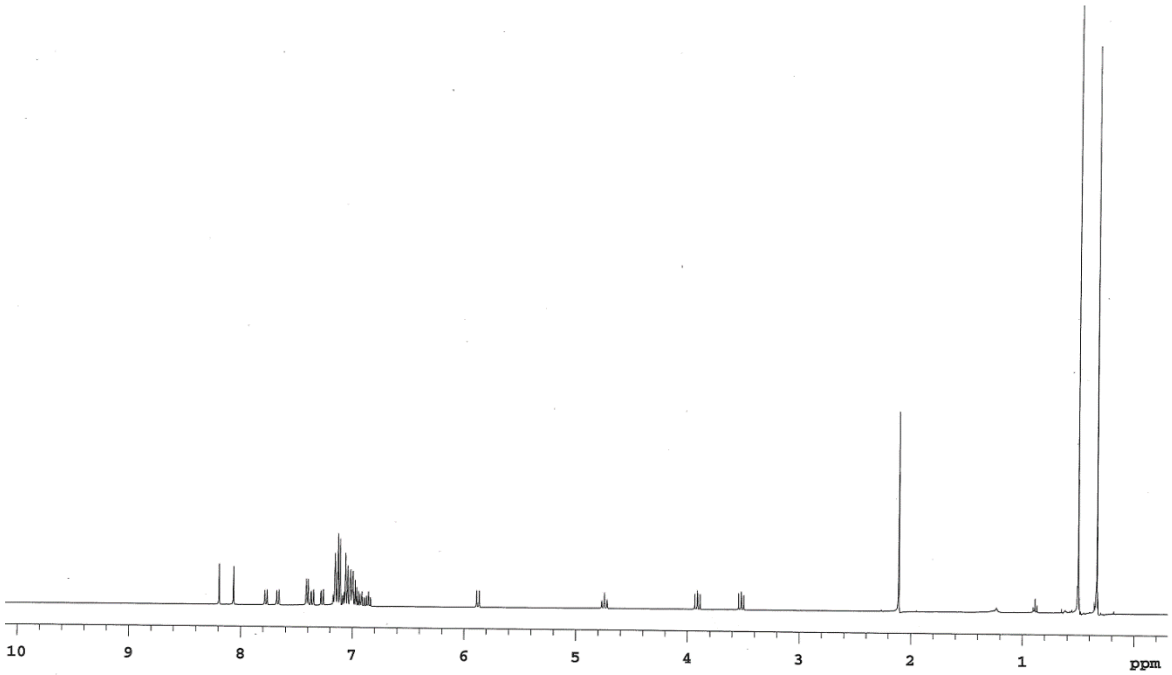


Figure S138. ^{1}H-NMR spectrum of **L4e**

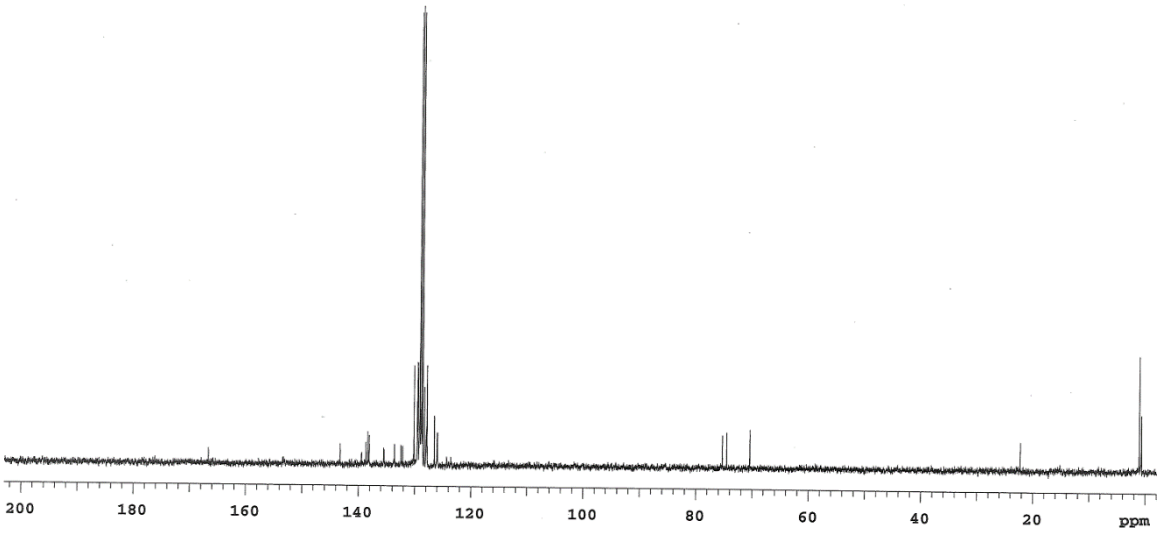


Figure S139. $^{13}C\{^{1}H\}$-NMR spectrum of **L4e**

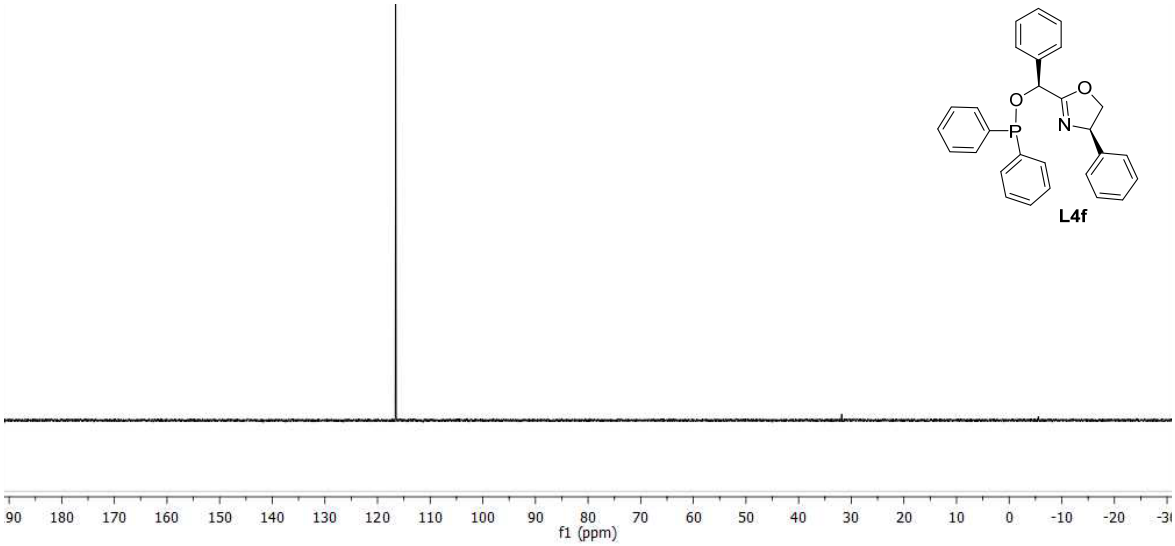


Figure S140. $^{31}P\{^{1}H\}$-NMR spectrum of **L4f**

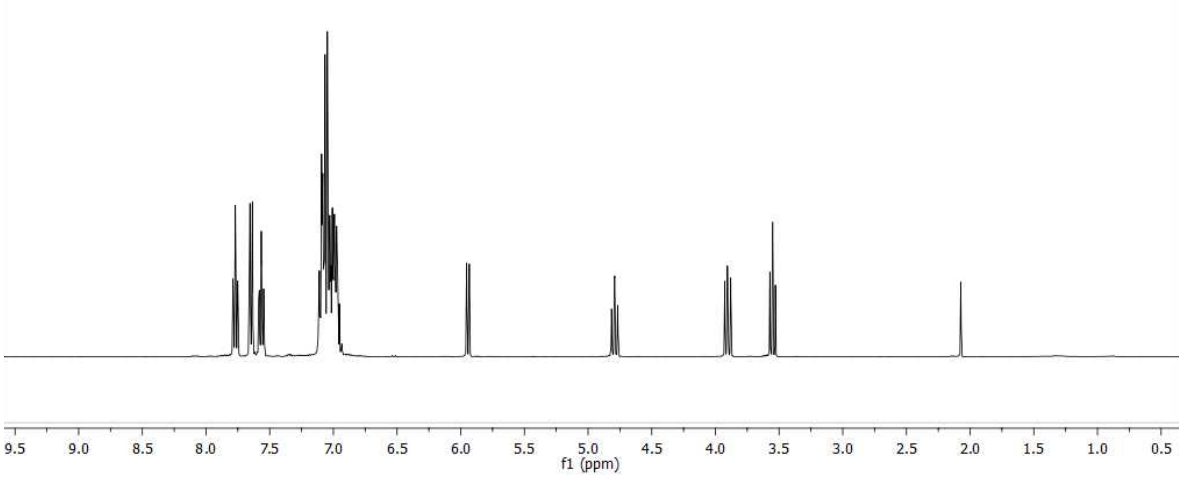


Figure S141. ^{1}H-NMR spectrum of **L4f**

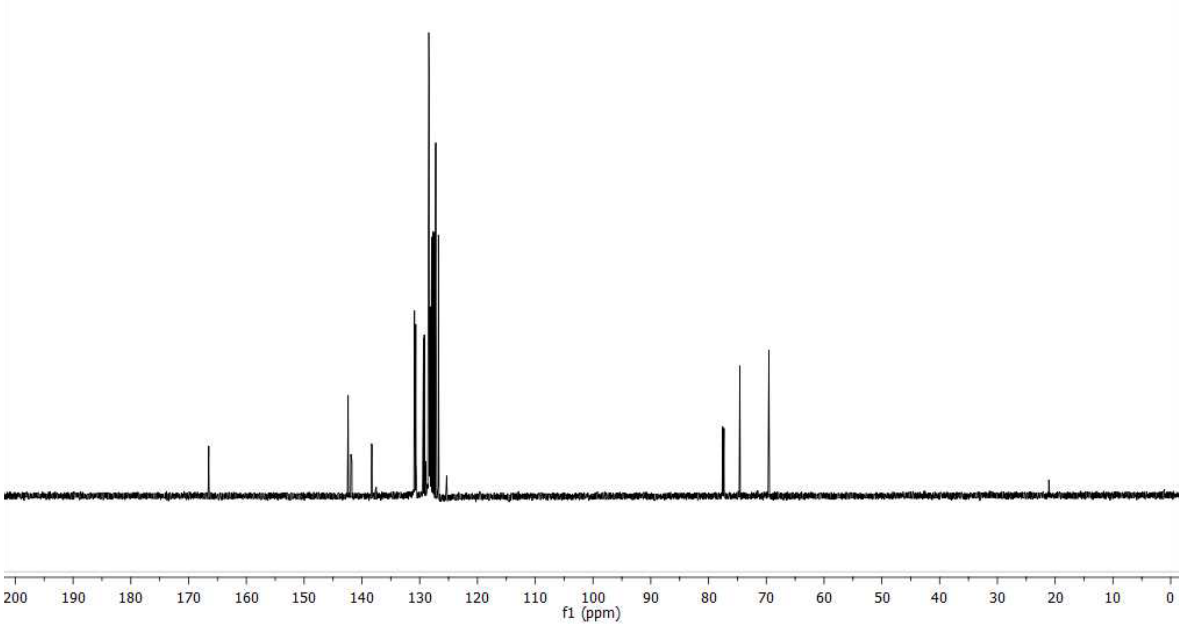


Figure S142. $^{13}C\{^{1}H\}$-NMR spectrum of **L4f**

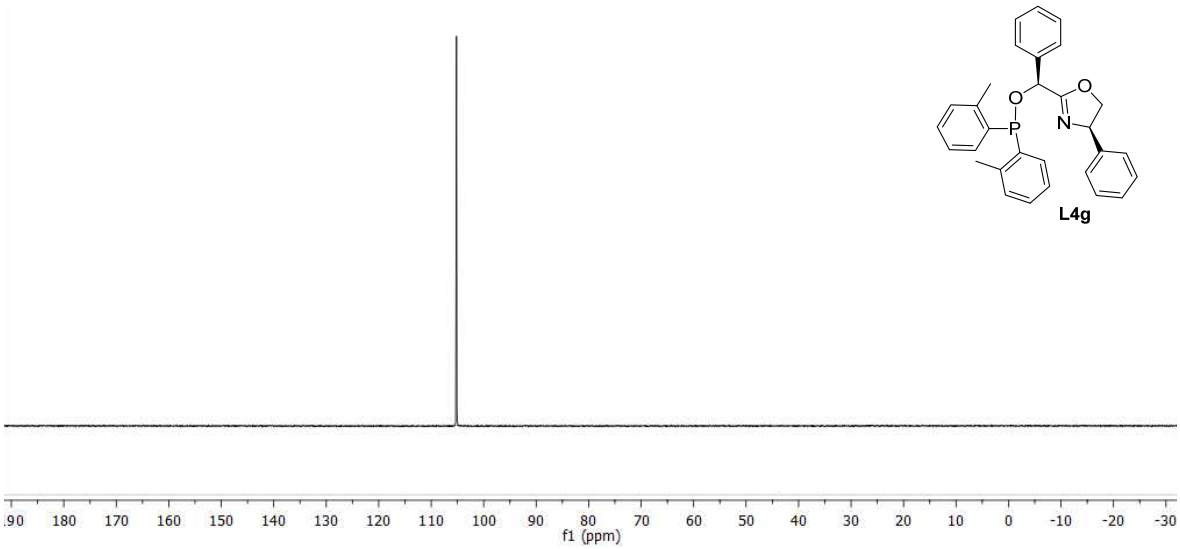


Figure S143. $^{31}P\{^{1}H\}$-NMR spectrum of **L4g**

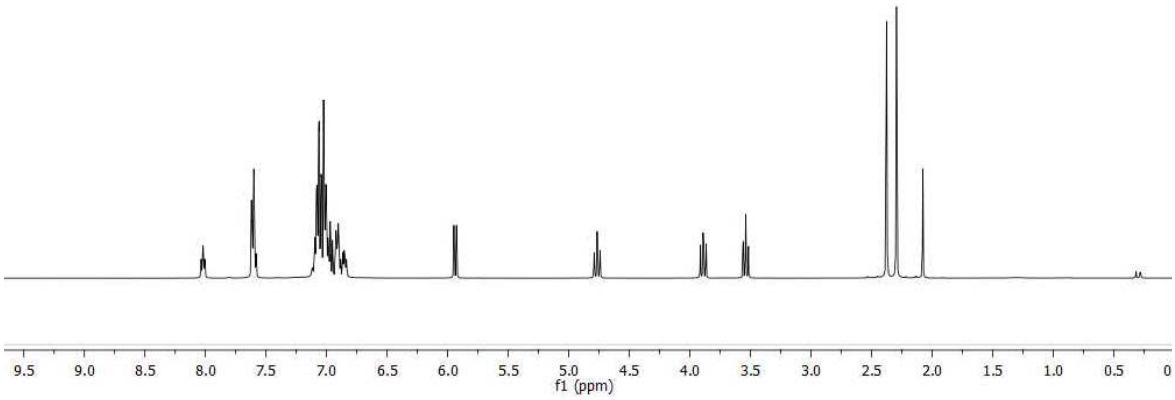


Figure S144. ^{1}H-NMR spectrum of **L4g**

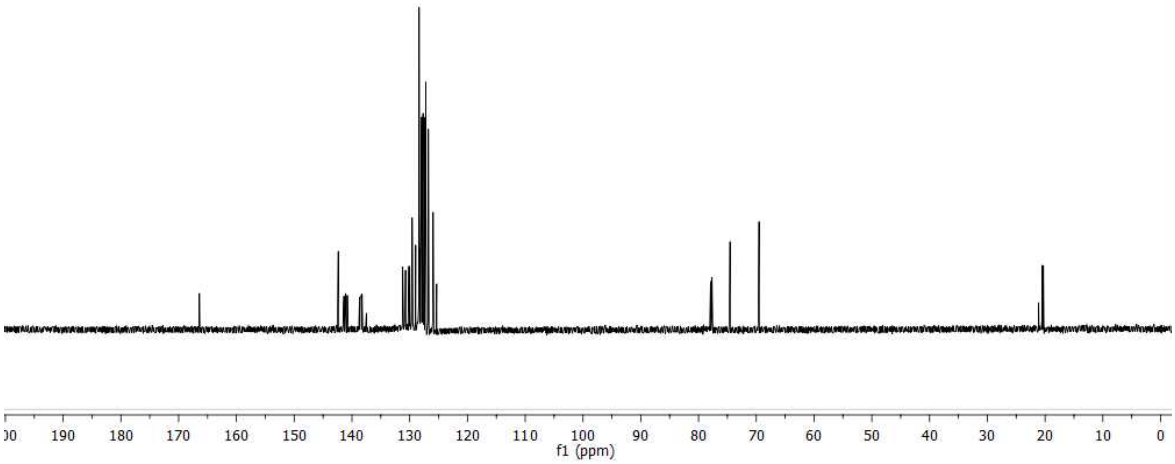


Figure S145. $^{13}C\{^{1}H\}$-NMR spectrum of **L4g**

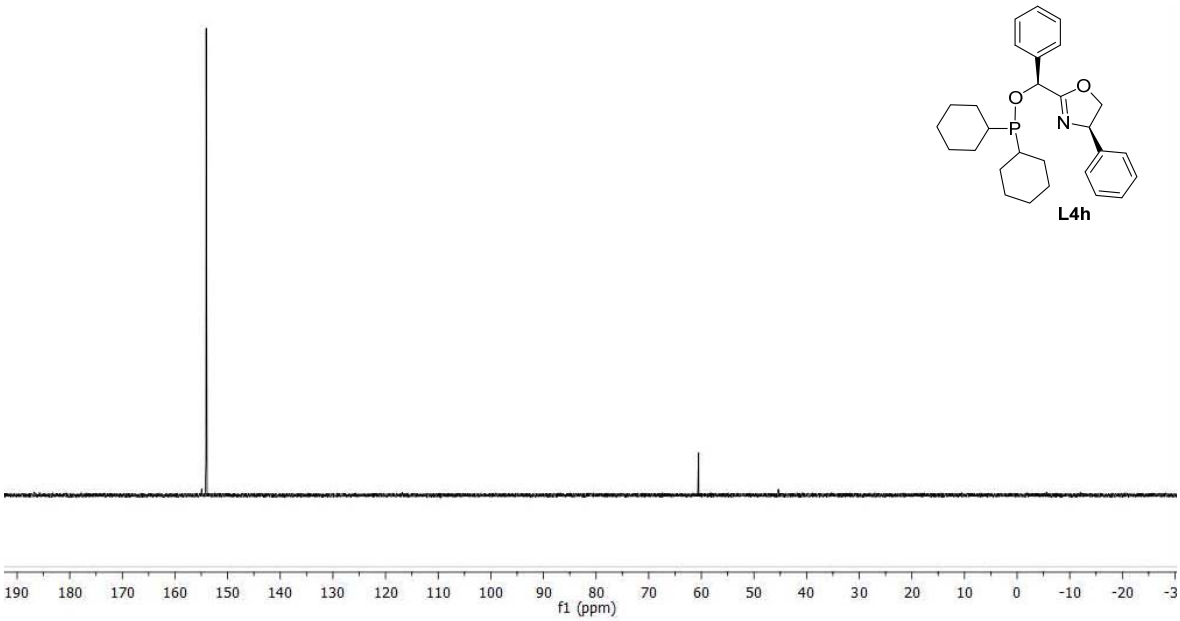


Figure S146. $^{31}P\{^{1}H\}$-NMR spectrum of **L4h**

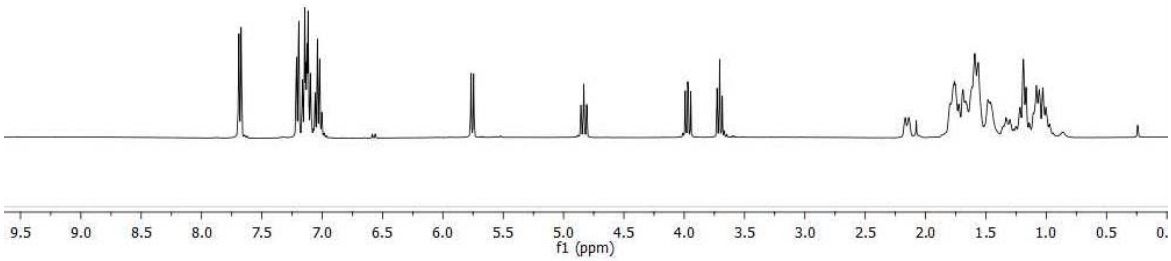


Figure S147. ^{1}H-NMR spectrum of **L4h**

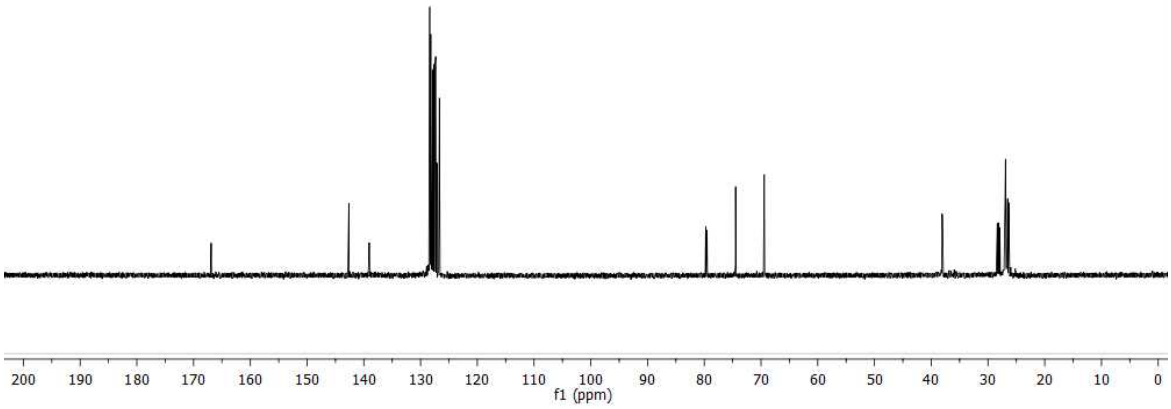


Figure S148. $^{13}C\{^{1}H\}$-NMR spectrum of **L4h**

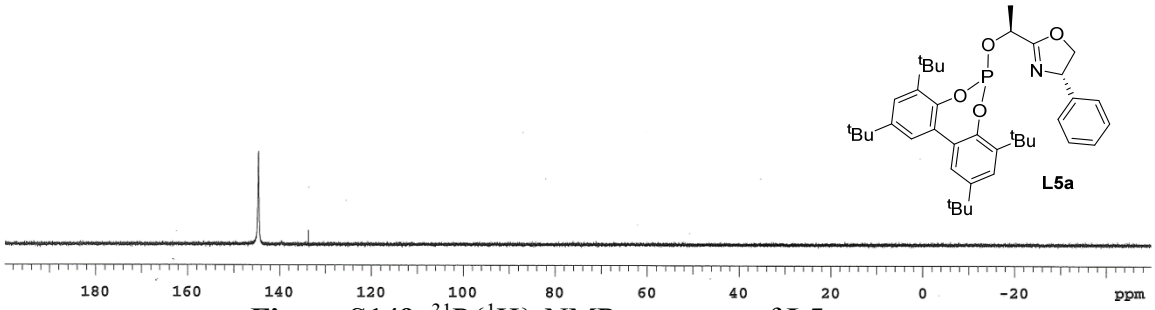


Figure S149. $^{31}P\{^{1}H\}$-NMR spectrum of **L5a**

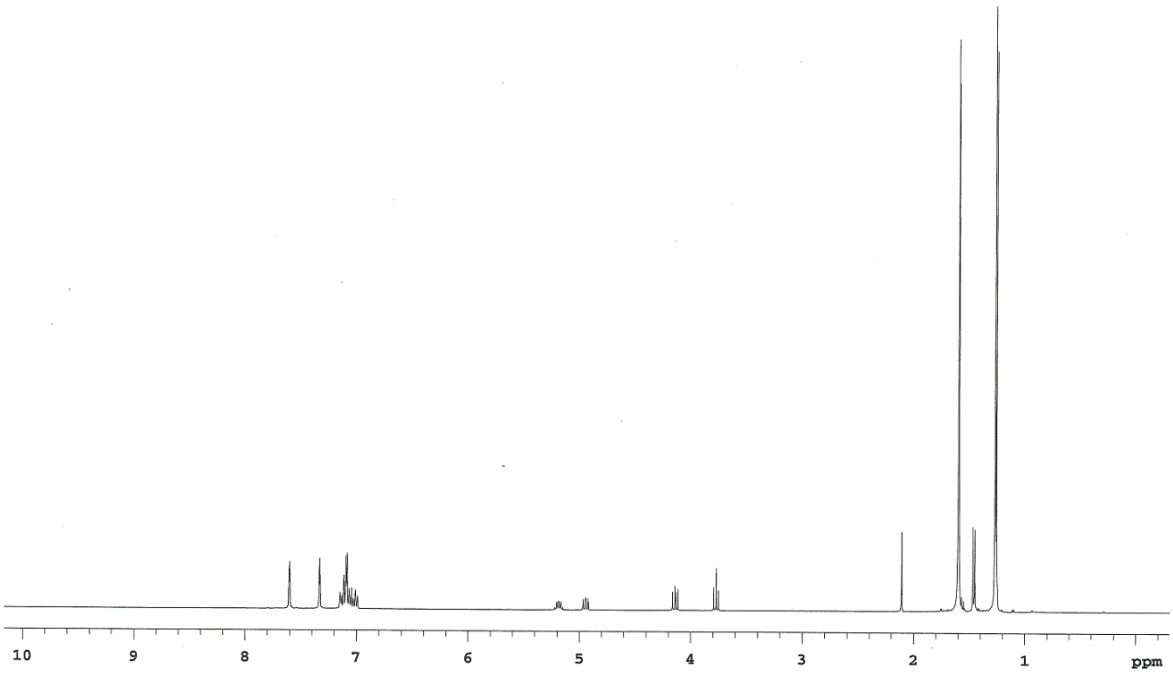


Figure S150. ^{1}H-NMR spectrum of **L5a**

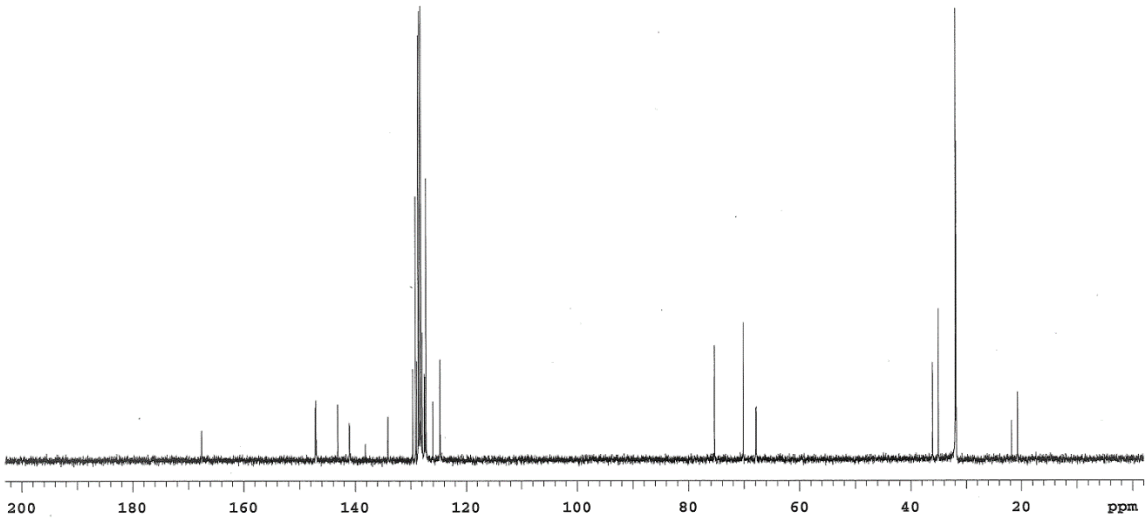


Figure S151. $^{13}C\{^{1}H\}$-NMR spectrum of **L5a**

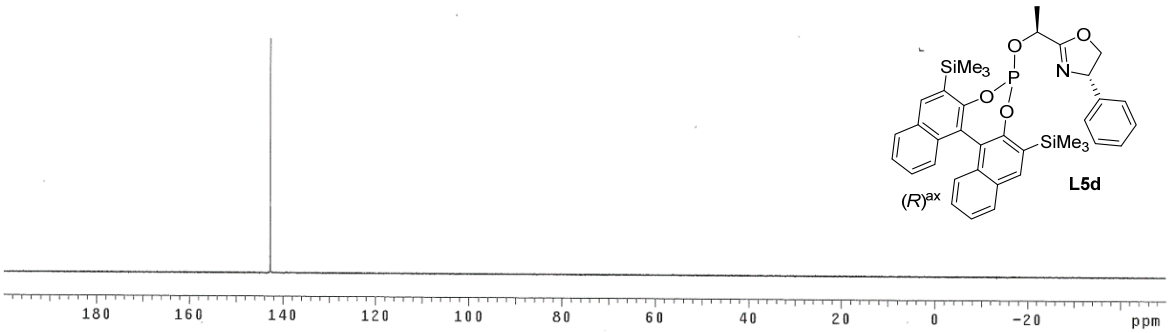


Figure S152. $^{31}P\{^{1}H\}$-NMR spectrum of **L5d**

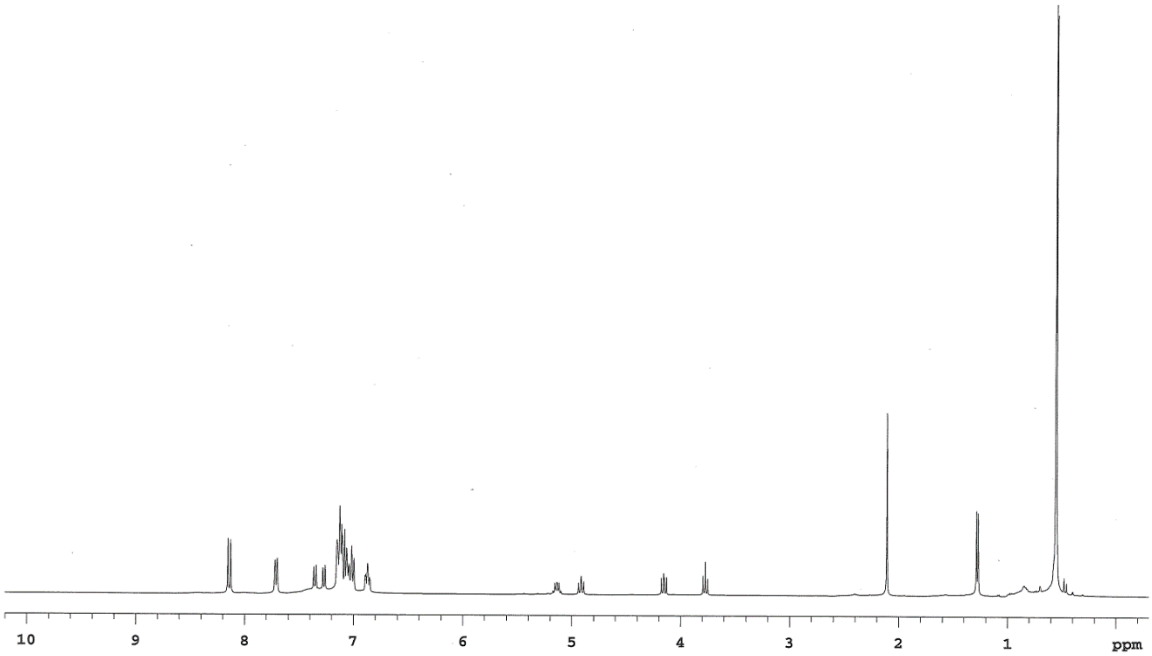


Figure S153. ^{1}H-NMR spectrum of **L5d**

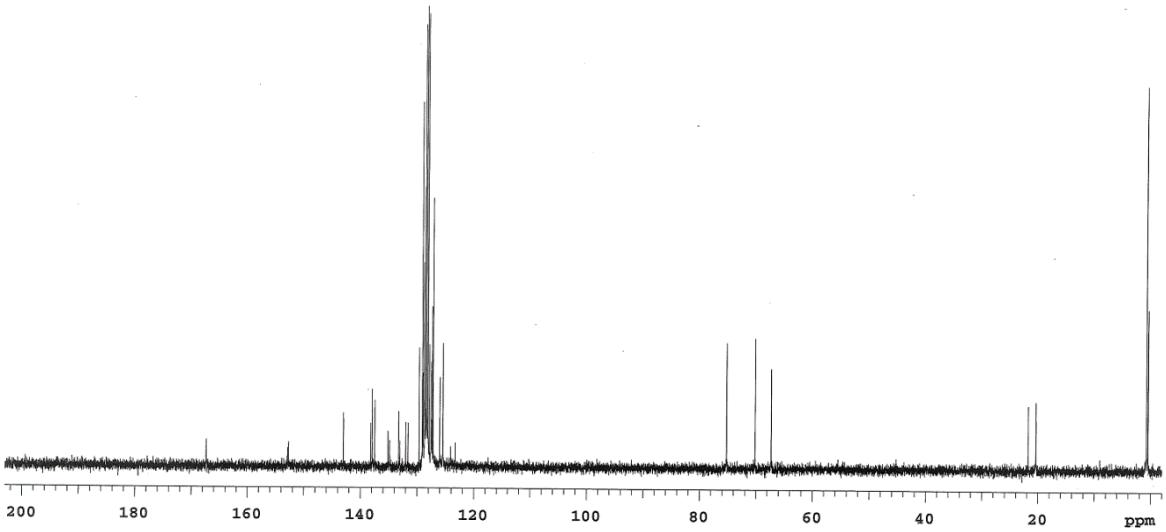


Figure S154. $^{13}C\{^{1}H\}$-NMR spectrum of **L5d**

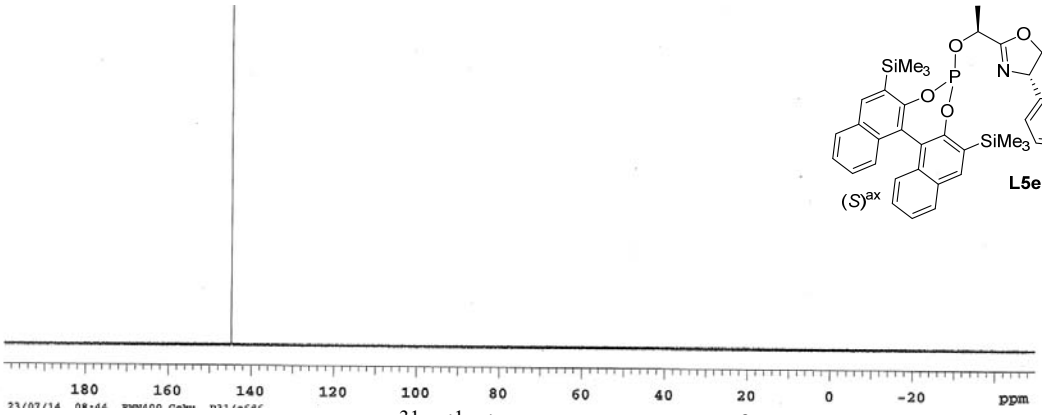


Figure S155. $^{31}P\{^{1}H\}$-NMR spectrum of **L5e**

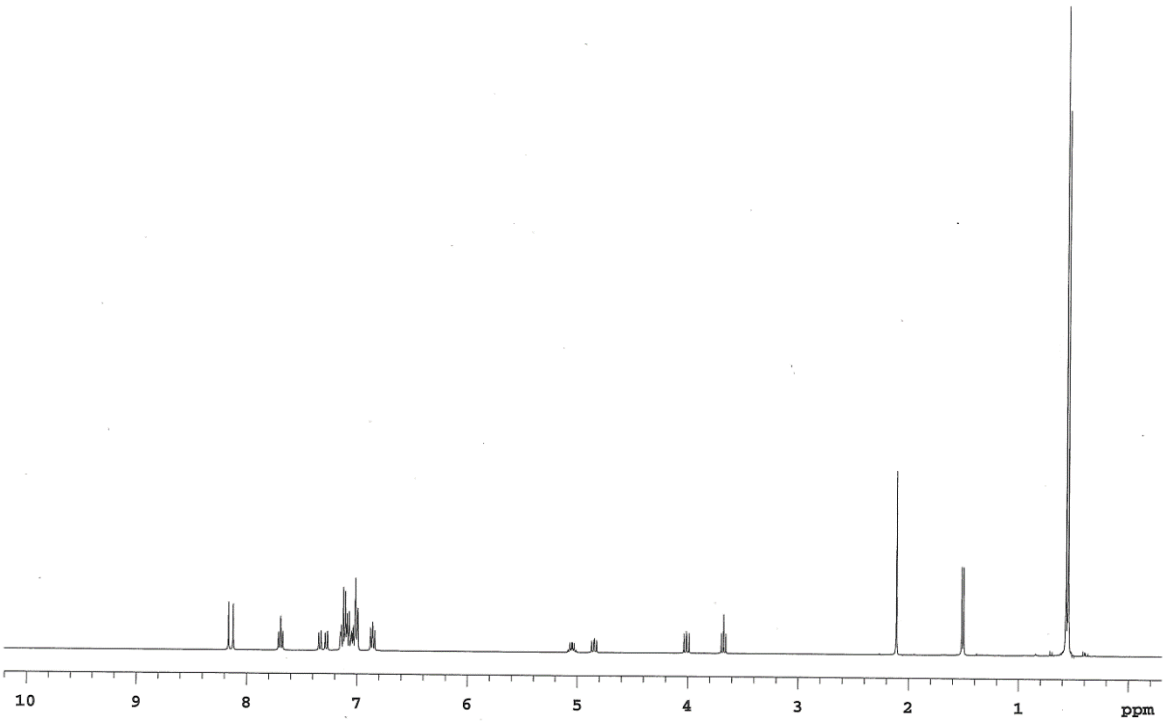


Figure S156. ^{1}H-NMR spectrum of **L5e**

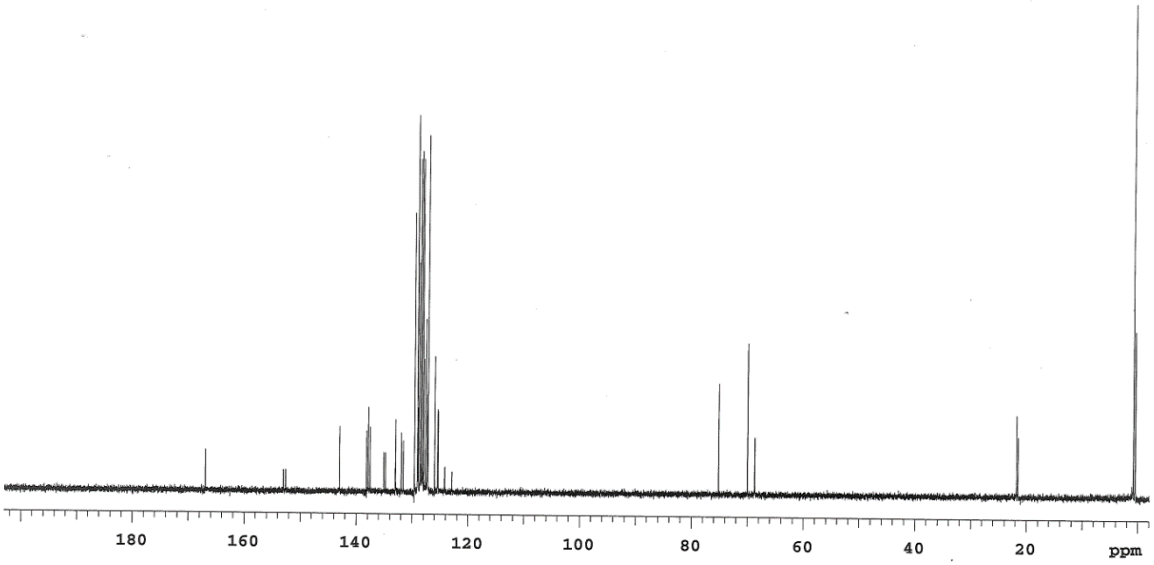


Figure S157. $^{13}C\{^{1}H\}$-NMR spectrum of **L5e**

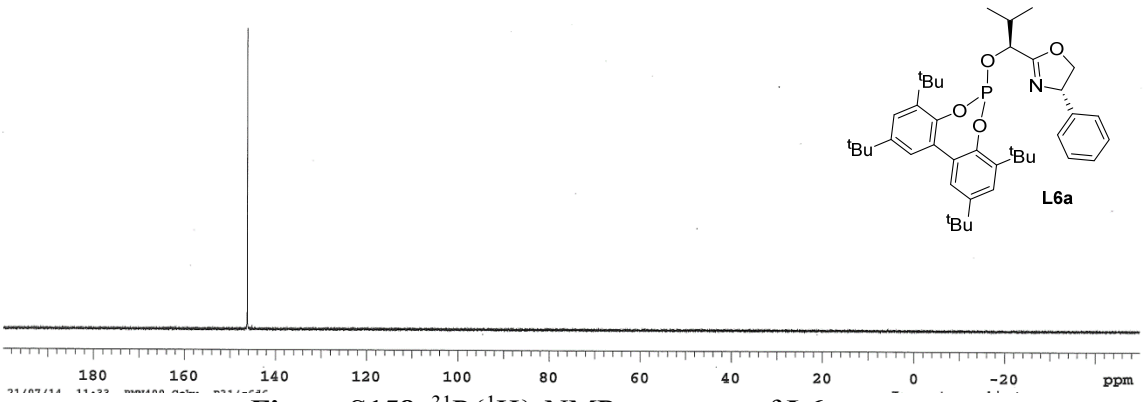


Figure S158. $^{31}P\{^{1}H\}$-NMR spectrum of **L6a**

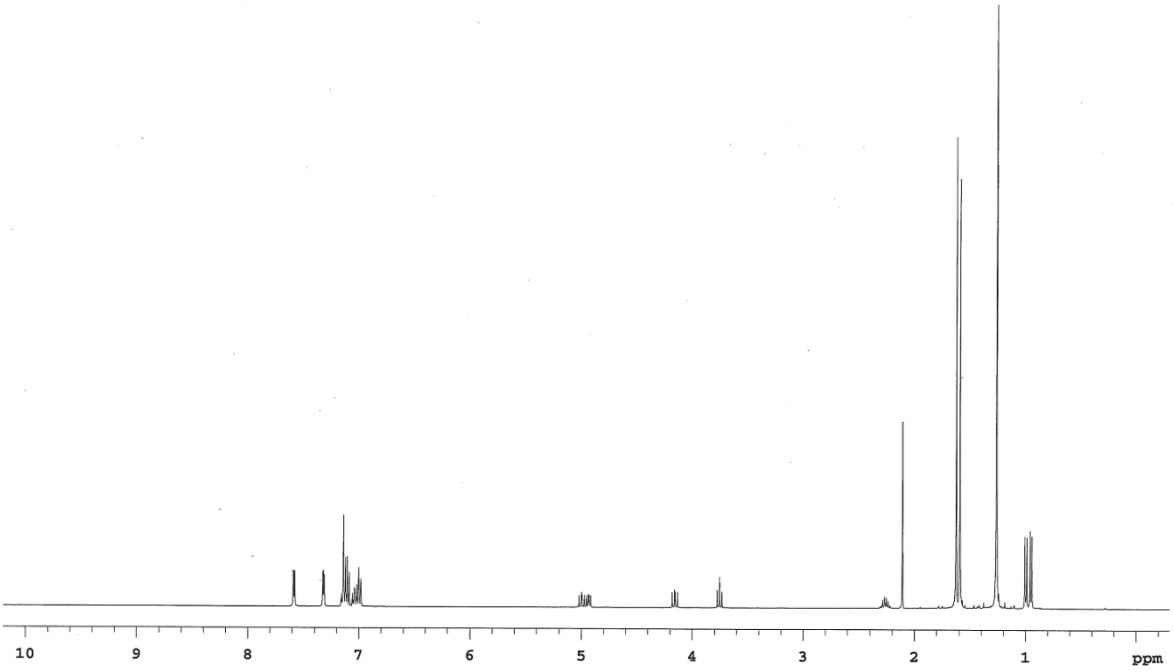


Figure S159. ^{1}H-NMR spectrum of **L6a**

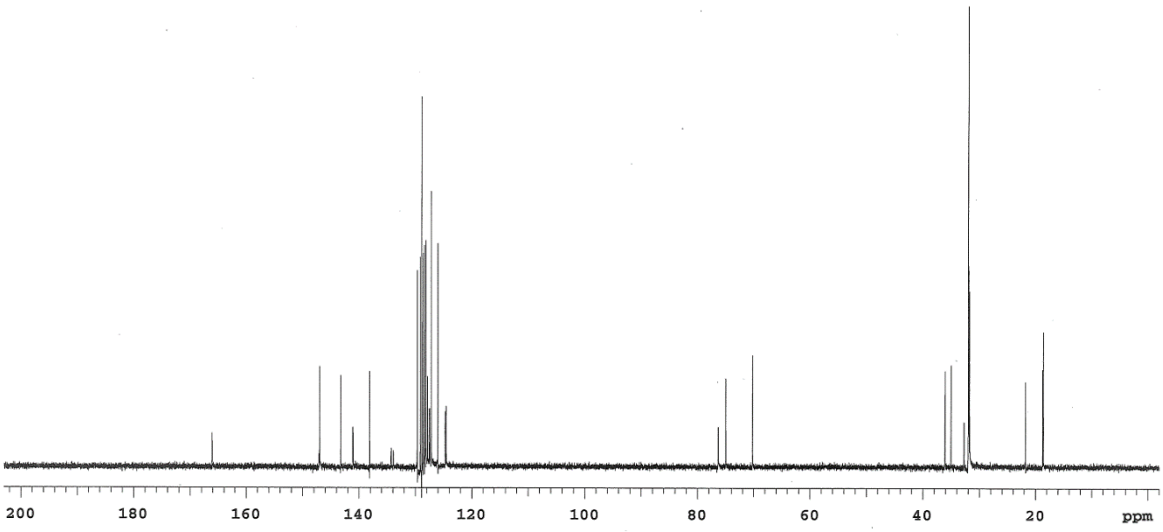


Figure S160. $^{13}C\{^{1}H\}$-NMR spectrum of **L6a**

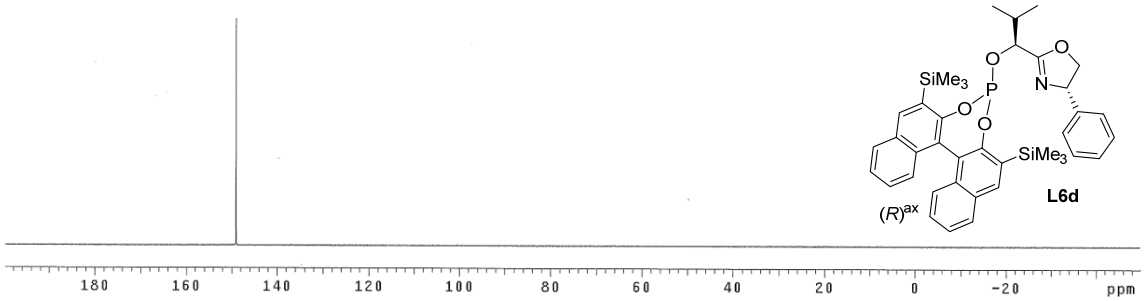


Figure S161. $^{31}P\{^{1}H\}$-NMR spectrum of **L6d**

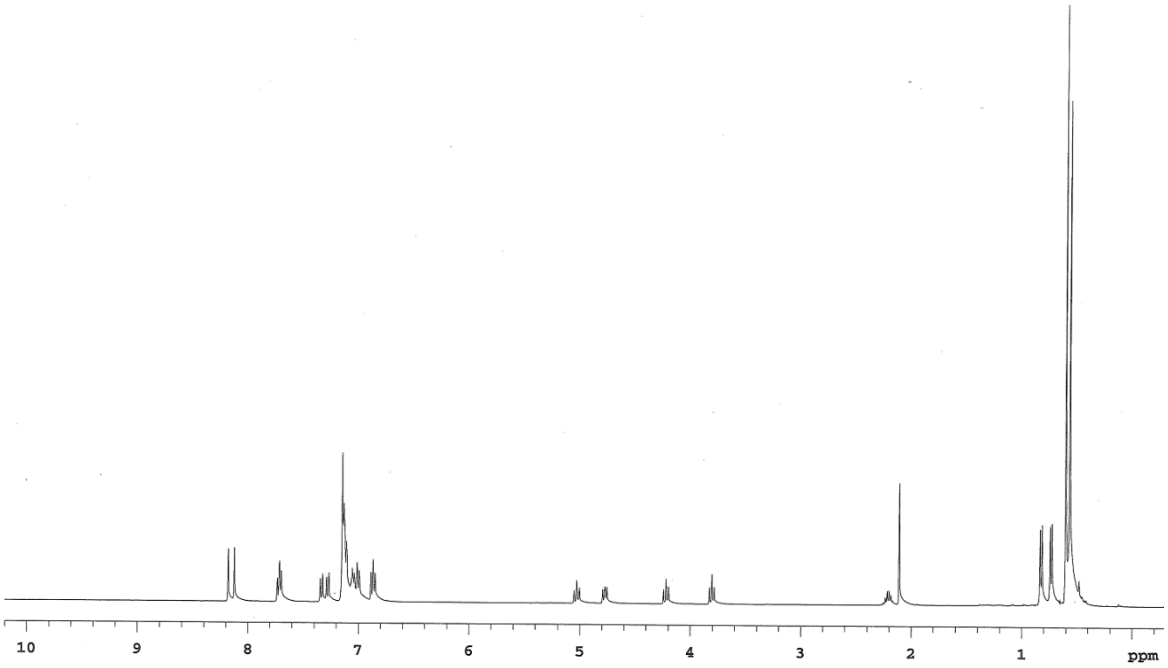


Figure S162. ^{1}H-NMR spectrum of **L6d**

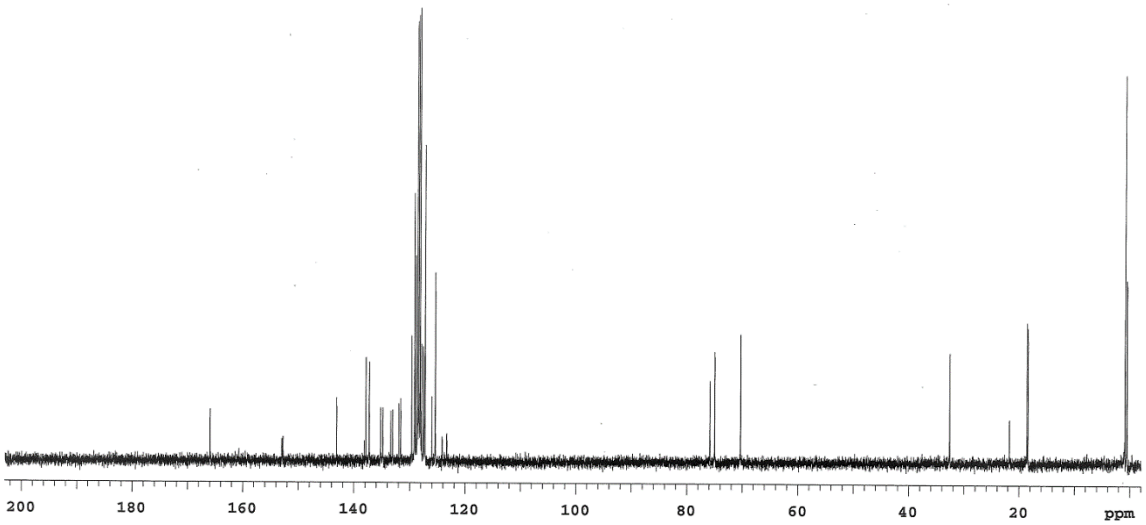


Figure S163. $^{13}C\{^{1}H\}$-NMR spectrum of **L6d**

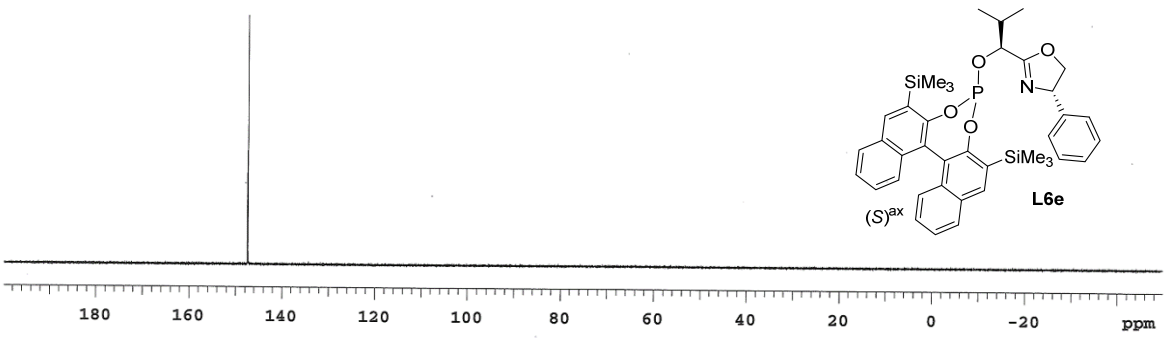


Figure S164. $^{31}P\{^{1}H\}$-NMR spectrum of **L6e**

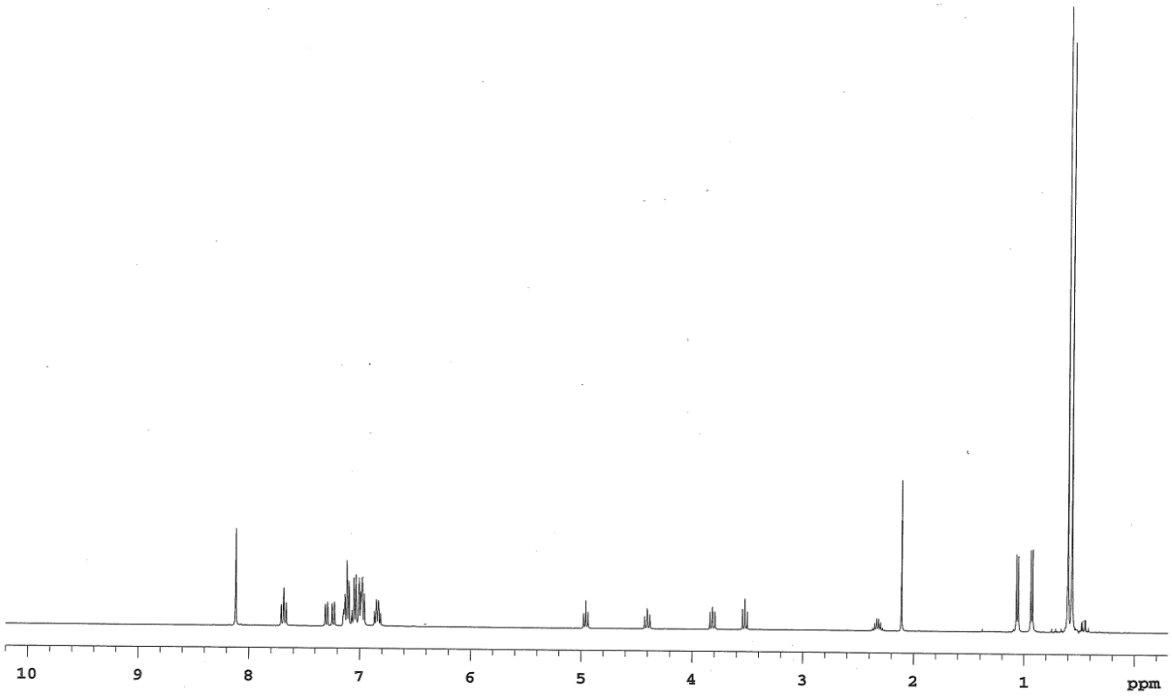


Figure S165. ^{1}H-NMR spectrum of **L6e**

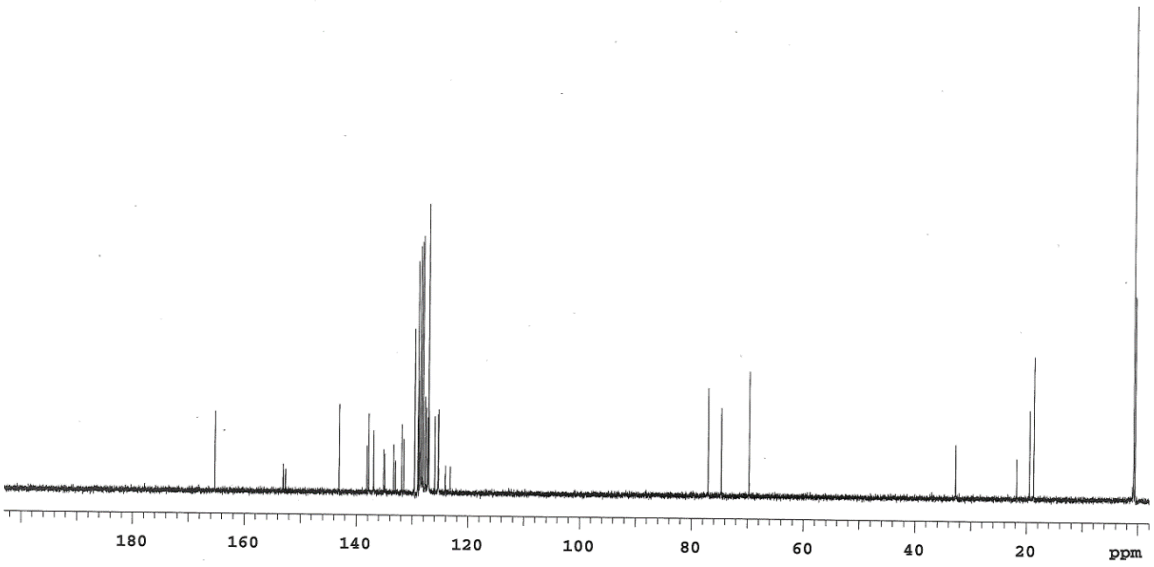


Figure S166. $^{13}C\{^{1}H\}$-NMR spectrum of **L6e**

8. Copies of NMR spectra of hydroxyl-amides 4-9 and hydroxyl-oxazolines 10-15

(S)-2-(((S)-2-Hydroxy-1-phenylethyl)amino)-2-oxo-1-phenylethyl acetate 4

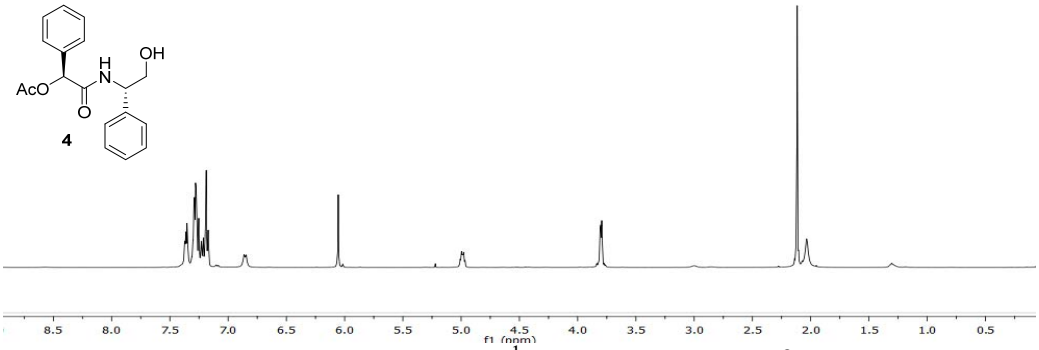


Figure S167. ^{1}H-NMR spectrum of **4**

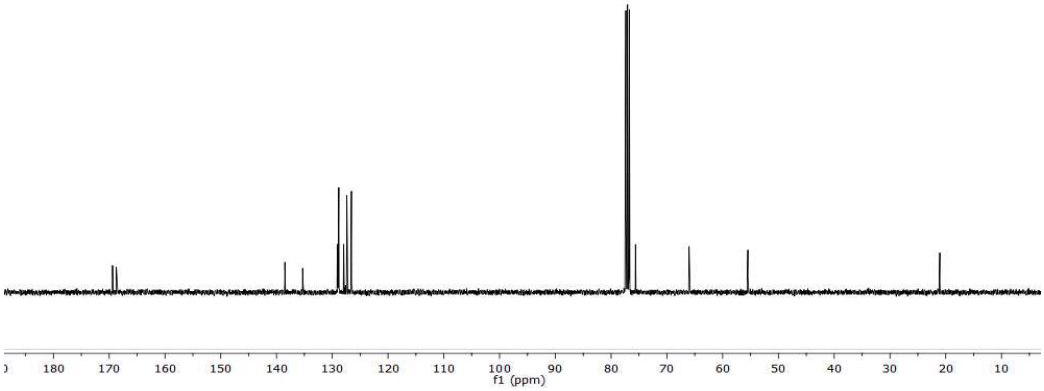


Figure S168. ^{13}C{^{1}H}-NMR spectrum of **4**

(S)-2-(((S)-1-Hydroxy-3-methylbutan-2-yl)amino)-2-oxo-1-phenylethyl acetate 5

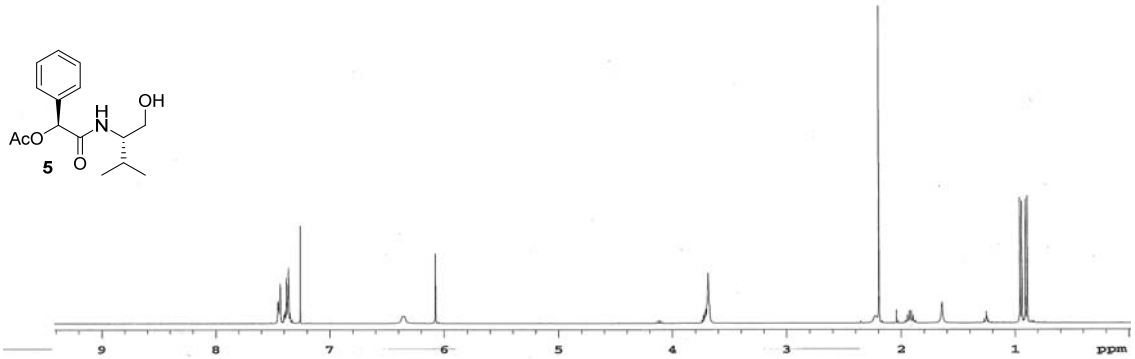


Figure S169. ^{1}H-NMR spectrum of **5**

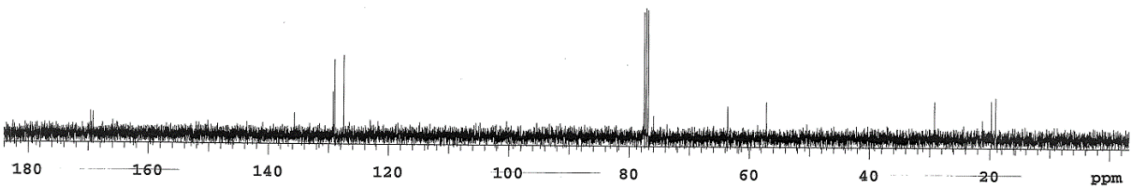


Figure S170. ^{13}C{^{1}H}-NMR spectrum of **5**

(S)-2-(((S)-1-Hydroxy-3,3-dimethylbutan-2-yl)amino)-2-oxo-1-phenylethyl acetate 6

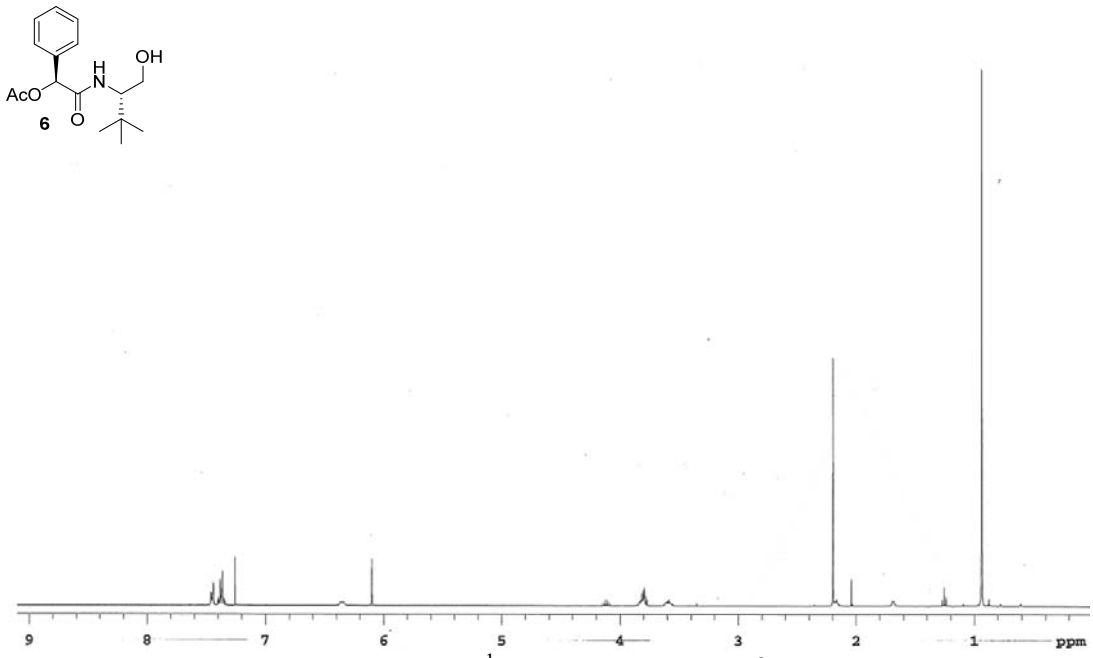


Figure S171. ^{1}H-NMR spectrum of **6**

(S)-2-(((R)-2-Hydroxy-1-phenylethyl)amino)-2-oxo-1-phenylethyl acetate 7

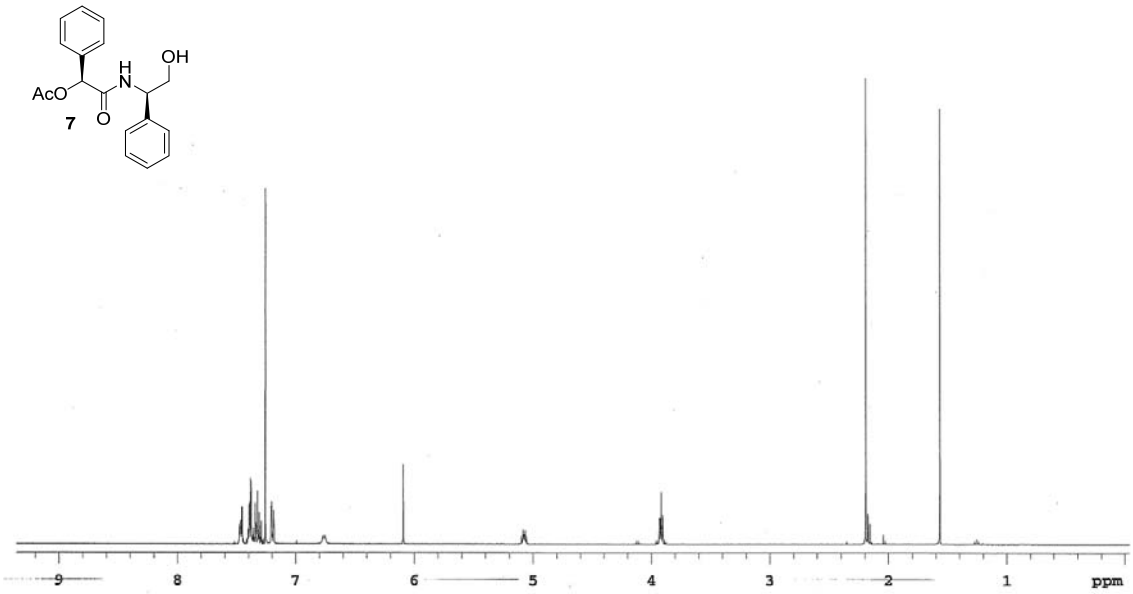


Figure S172. ^{1}H-NMR spectrum of **7**

(S)-1-(((S)-2-Hydroxy-1-phenylethyl)amino)-1-oxopropan-2-yl acetate 8

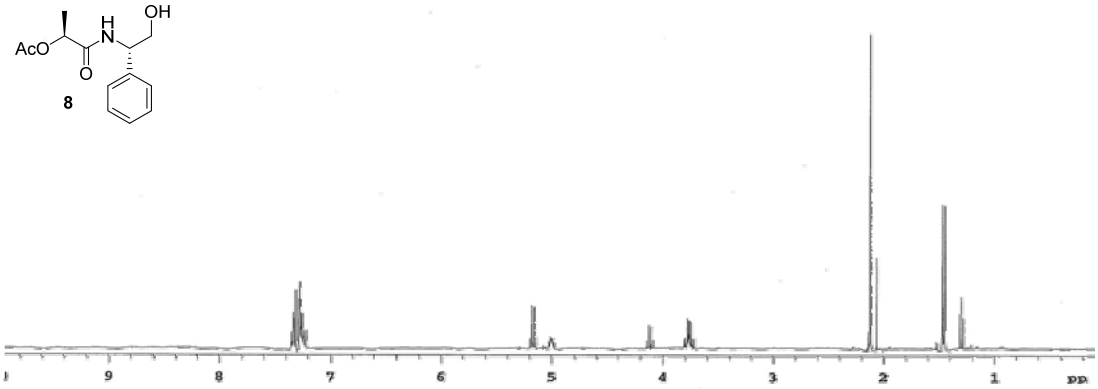


Figure S173. ^{1}H-NMR spectrum of **8**

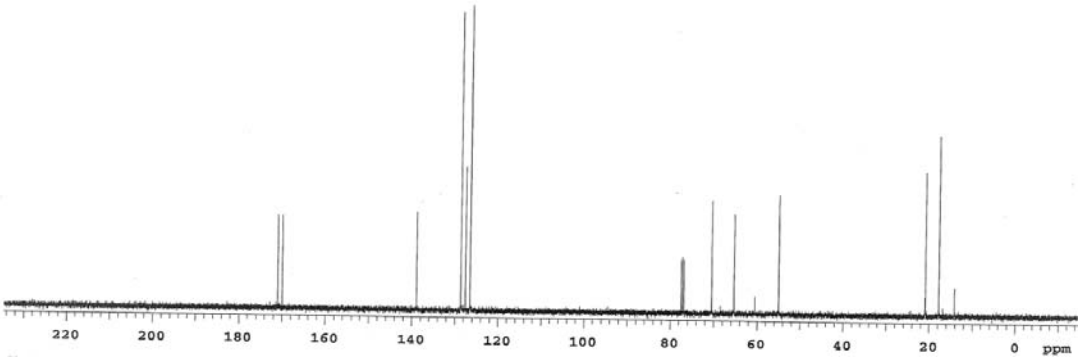


Figure S174. ^{13}C{^{1}H}-NMR spectrum of **8**

(S)-1-(((S)-2-Hydroxy-1-phenylethyl)amino)-3-methyl-1-oxobutan-2-yl acetate 9

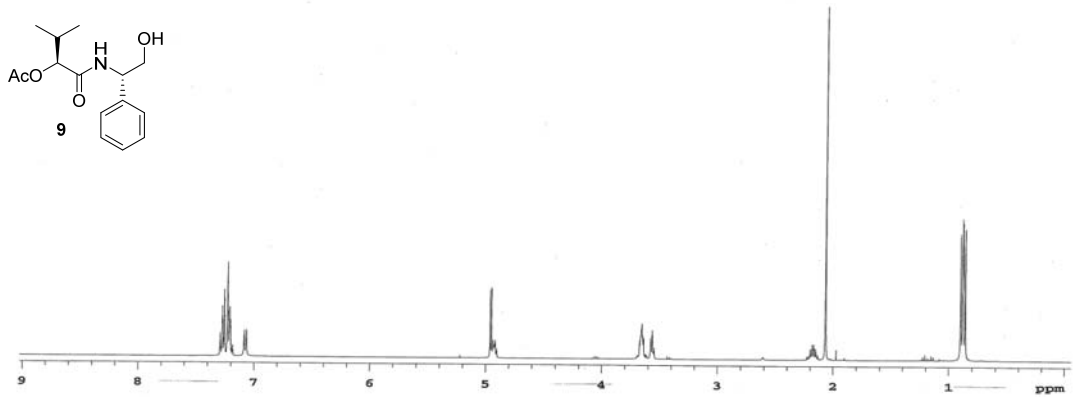


Figure S175. ^{1}H-NMR spectrum of **9**

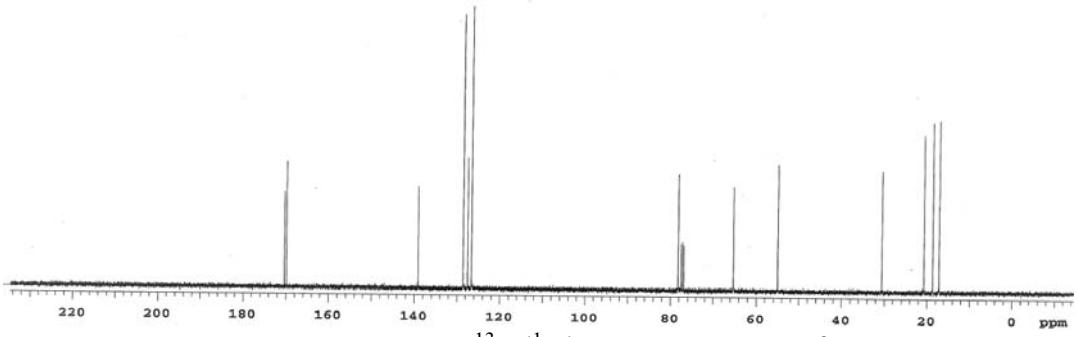


Figure S176. ^{13}C{^{1}H}-NMR spectrum of **9**

(S)-Phenyl-((S)-4-phenyl-4,5-dihydrooxazol-2-yl)methyl acetate

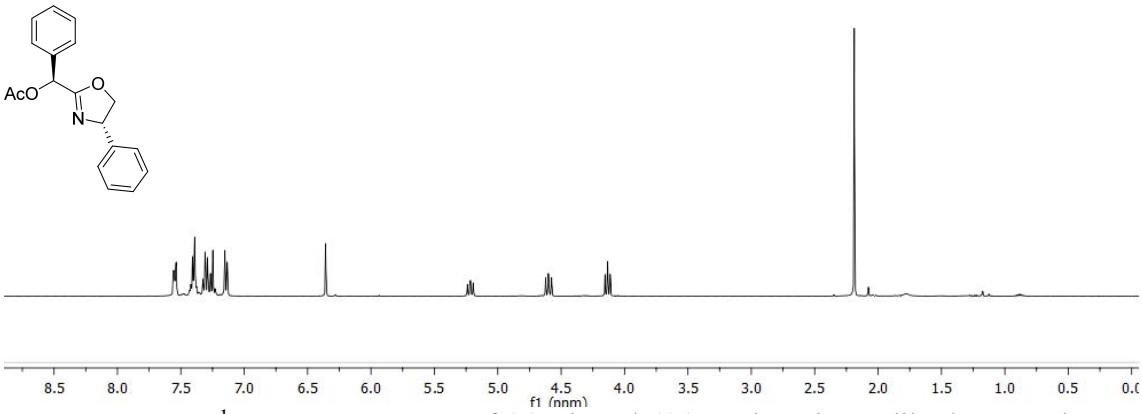


Figure S177. ^{1}H-NMR spectrum of (*S*)-phenyl-((*S*)-4-phenyl-4,5-dihydrooxazol-2-yl)methyl acetate

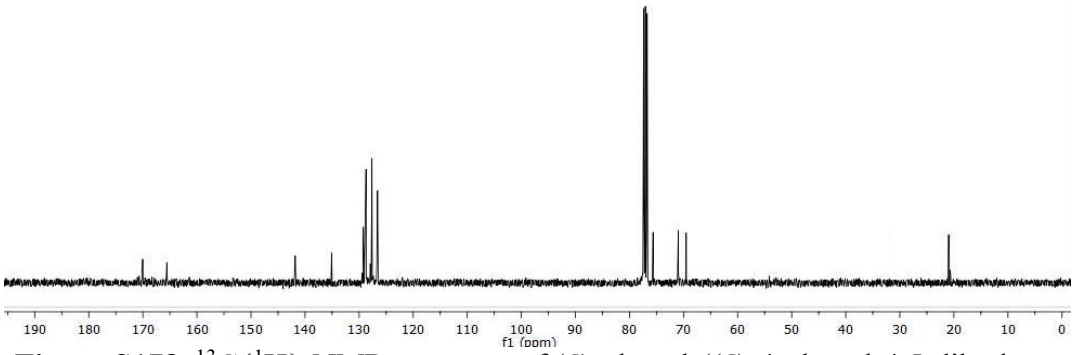


Figure S178. ^{13}C{^{1}H}-NMR spectrum of (*S*)-phenyl-((*S*)-4-phenyl-4,5-dihydrooxazol-2-yl)methyl acetate

(S)-((S)-4-Isopropyl-4,5-dihydrooxazol-2-yl)(phenyl)methyl acetate

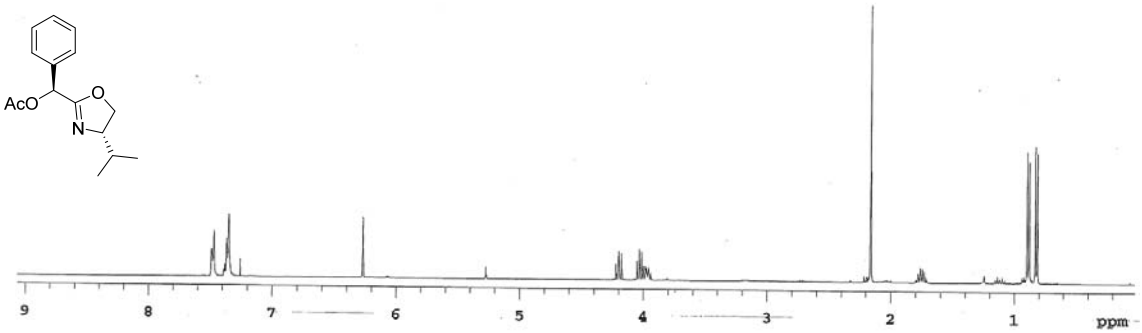


Figure S179. ^{1}H-NMR spectrum of (*S*)-((*S*)-4-isopropyl-4,5-dihydrooxazol-2-yl)(phenyl)methyl acetate

(S)-((S)-4-(tert-Butyl)-4,5-dihydrooxazol-2-yl)(phenyl)methyl acetate

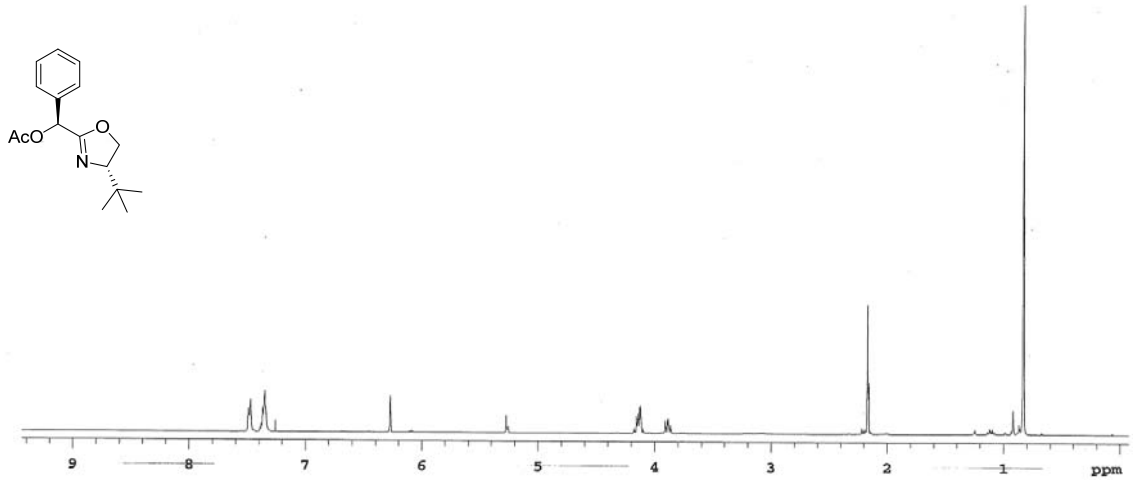


Figure S180. ^{1}H-NMR spectrum of (*S*)-((*S*)-4-(*tert*-Butyl)-4,5-dihydrooxazol-2-yl)(phenyl)methyl acetate

(S)-Phenyl-((R)-4-phenyl-4,5-dihydrooxazol-2-yl)methyl acetate

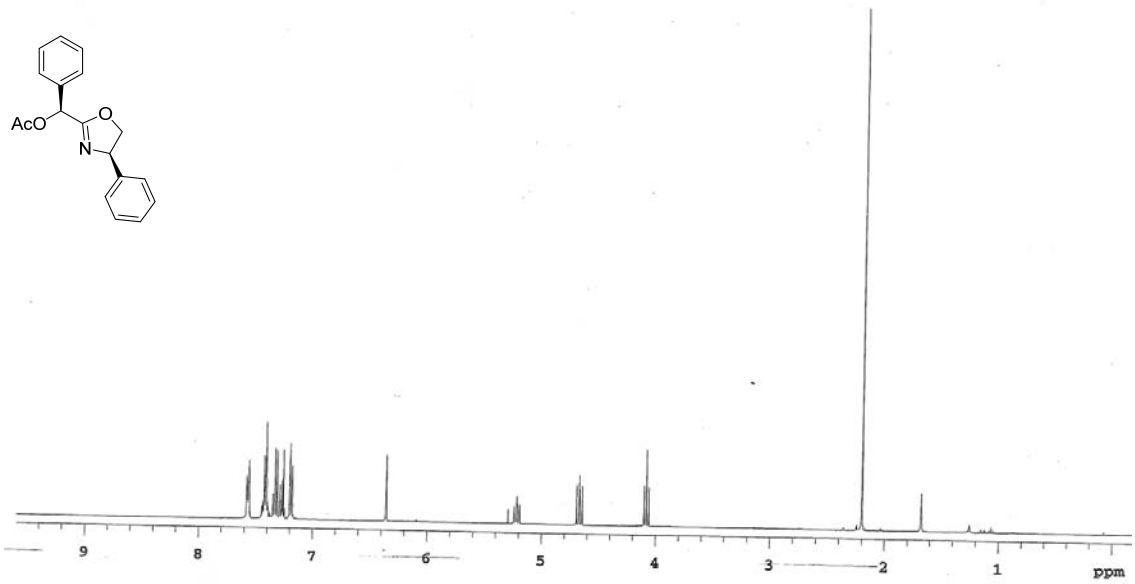


Figure S181. ^{1}H-NMR spectrum of (*S*)-phenyl-((*R*)-4-phenyl-4,5-dihydrooxazol-2-yl)methyl acetate

(S)-1-((S)-4-Phenyl-4,5-dihydrooxazol-2-yl)ethyl acetate

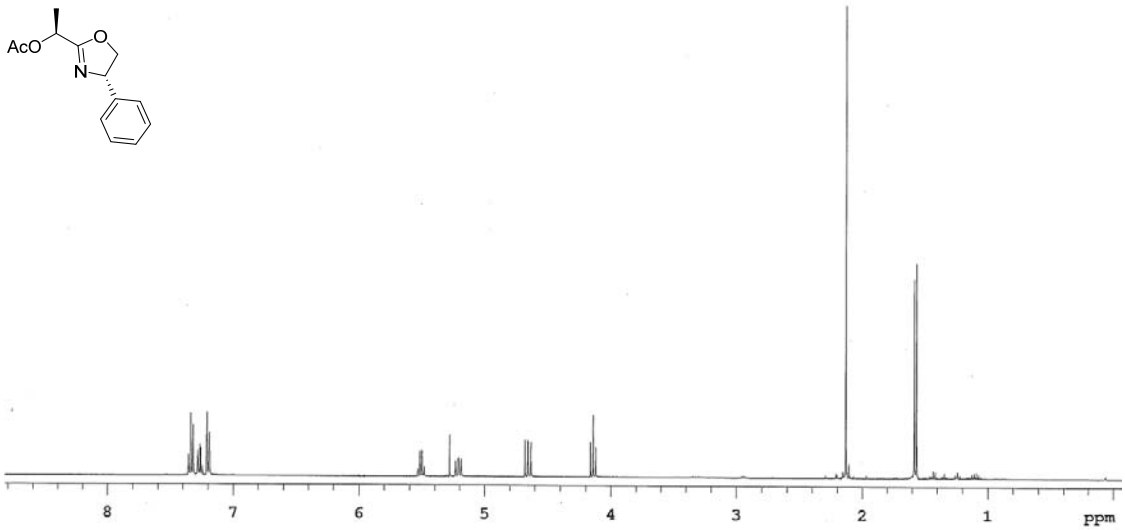


Figure S182. ^{1}H-NMR spectrum of (*S*)-1-((*S*)-4-Phenyl-4,5-dihydrooxazol-2-yl)ethyl acetate

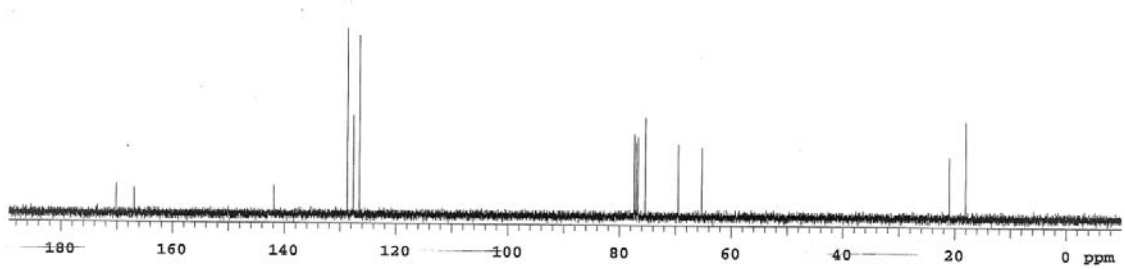


Figure S183. ^{13}C-{^{1}H}-NMR spectrum of (*S*)-1-((*S*)-4-Phenyl-4,5-dihydrooxazol-2-yl)ethyl acetate

(S)-2-Methyl-1-((S)-4-phenyl-4,5-dihydrooxazol-2-yl)propyl acetate

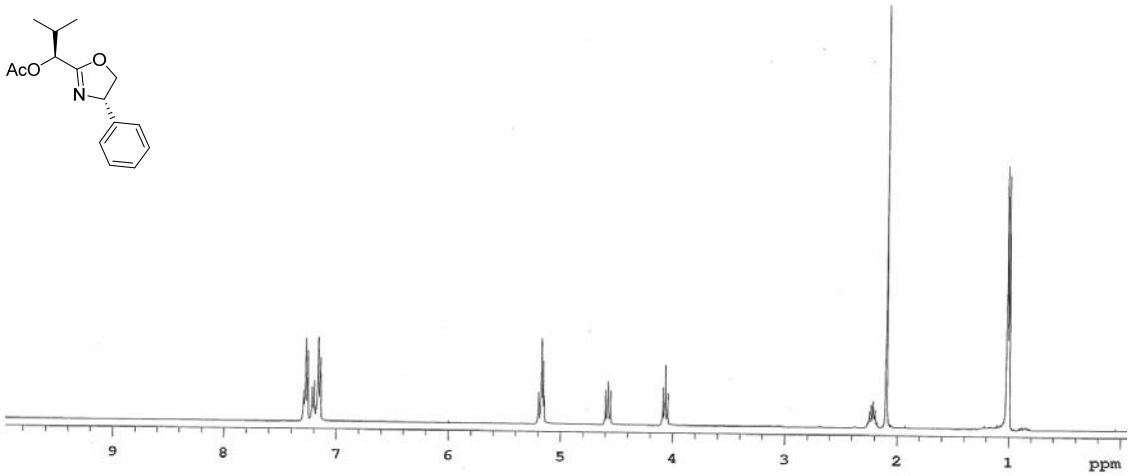


Figure S184. ^{1}H-NMR spectrum of (*S*)-2-methyl-1-((*S*)-4-phenyl-4,5-dihydrooxazol-2-yl)propyl acetate

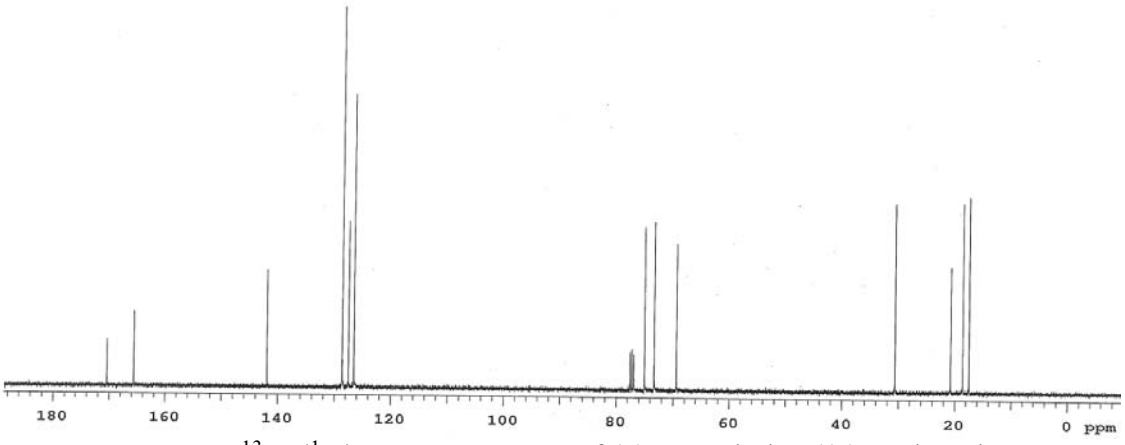


Figure S185. ^{13}C-{^{1}H}-NMR spectrum of (*S*)-2-methyl-1-((*S*)-4-phenyl-4,5-dihydrooxazol-2-yl)propyl acetate

(S)-Phenyl-((S)-4-phenyl-4,5-dihydrooxazol-2-yl)methanol 10

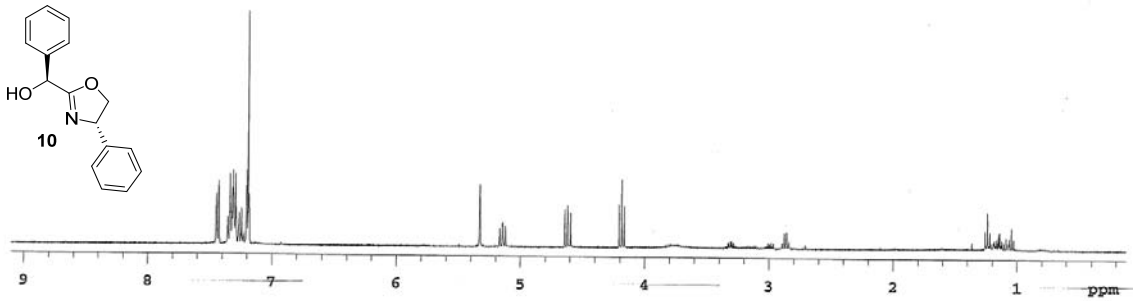


Figure S186. ^{1}H-NMR spectrum of **10**

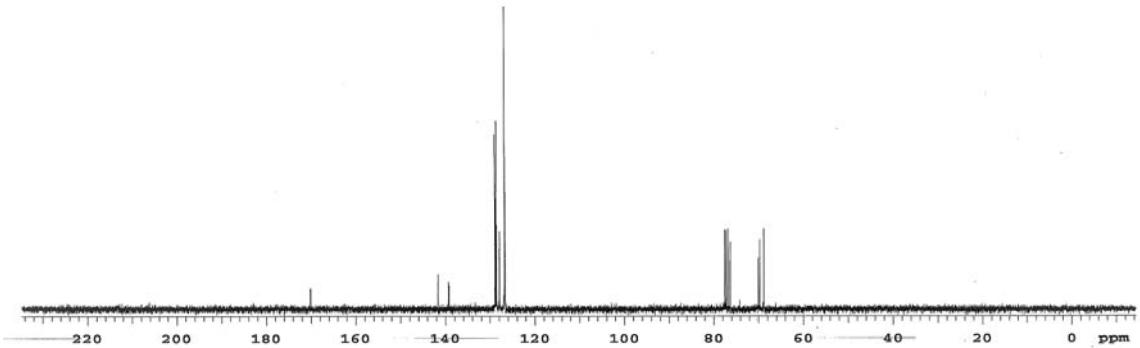


Figure S187. ^{13}C-{^{1}H}-NMR spectrum of **10**

(S)-((S)-4-Isopropyl-4,5-dihydrooxazol-2-yl)(phenyl)methanol 11

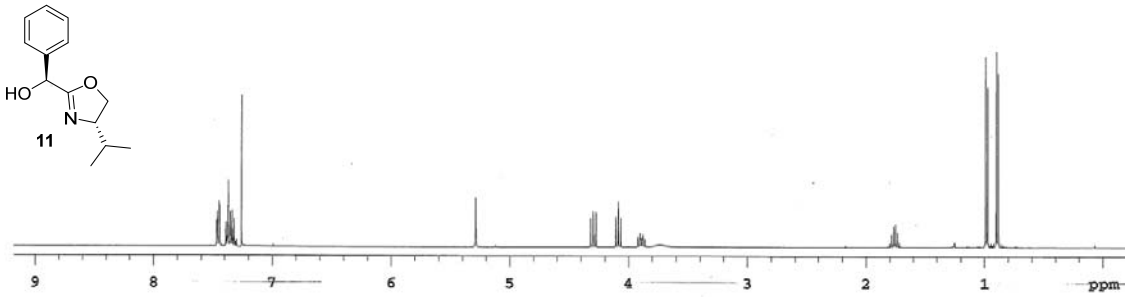


Figure S188. ^{1}H-NMR spectrum of **11**

(S)-((S)-4-(tert-Butyl)-4,5-dihydrooxazol-2-yl)(phenyl)methanol 12

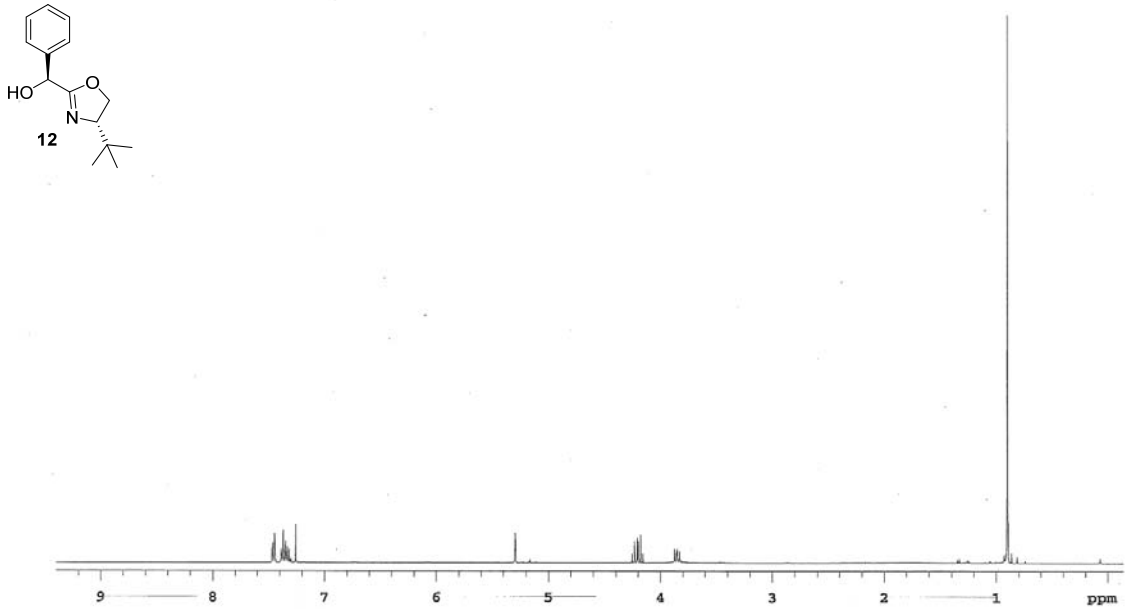


Figure S189. ^{1}H-NMR spectrum of **12**

(S)-Phenyl-((R)-4-phenyl-4,5-dihydrooxazol-2-yl)methanol 13

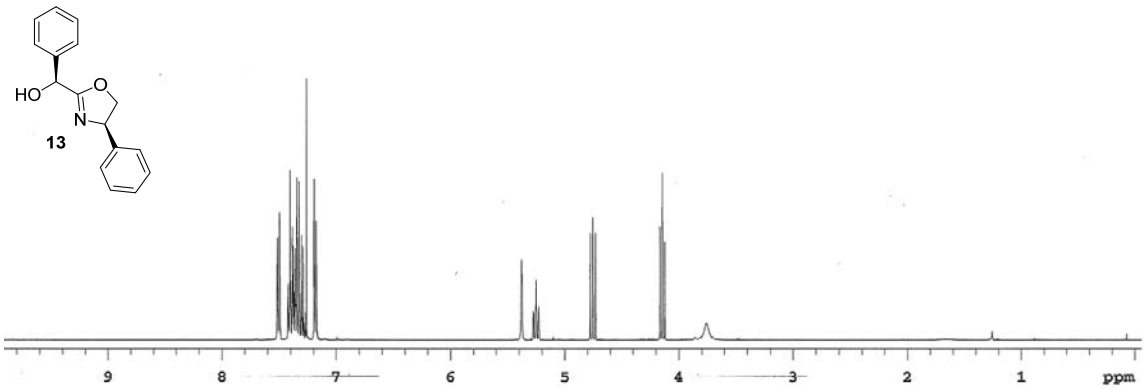


Figure S190. ^{1}H-NMR spectrum of **13**

(S)-1-((S)-4-Phenyl-4,5-dihydrooxazol-2-yl)ethan-1-ol 14

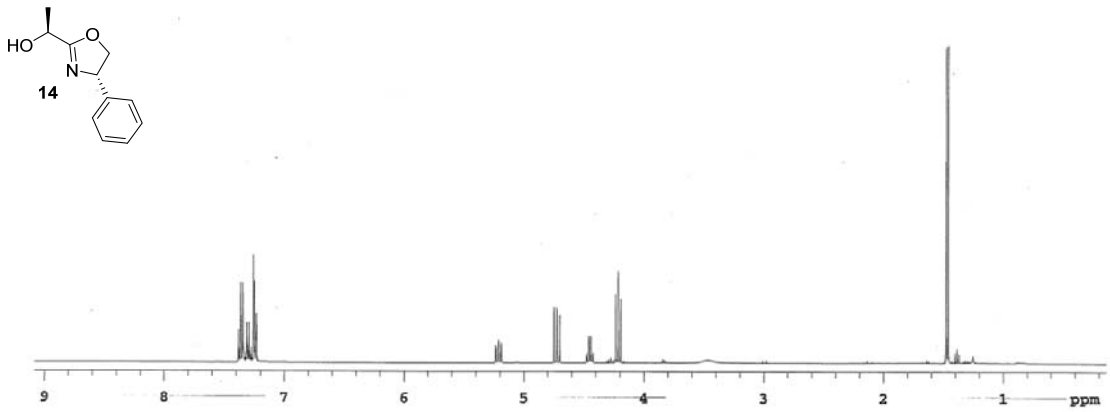


Figure S191. ^{1}H-NMR spectrum of **14**

(S)-2-Methyl-1-((S)-4-phenyl-4,5-dihydrooxazol-2-yl)propan-1-ol 15

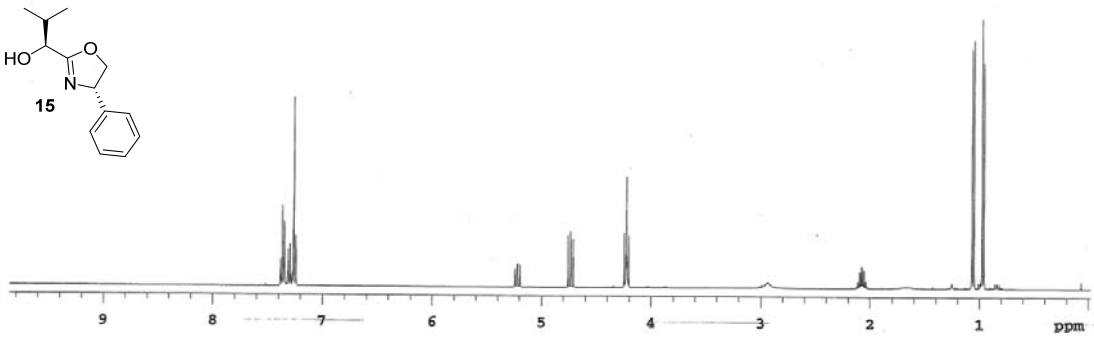


Figure S192. ^{1}H-NMR spectrum of **15**

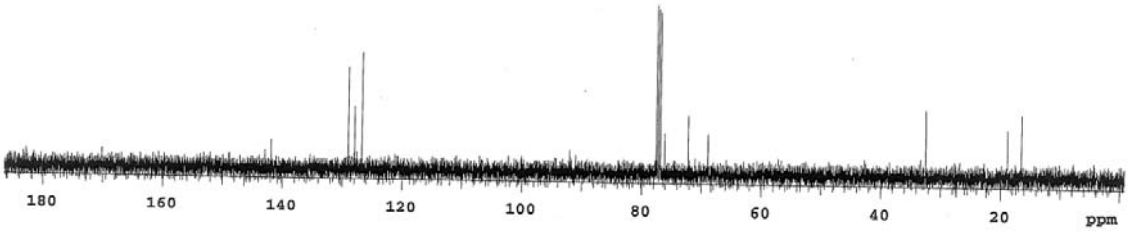


Figure S193. ^{13}C-{^{1}H}-NMR spectrum of **15**

9. Copies of NMR spectra and GC/HPLC spectra of hydrogenated compounds

(R)-1-(sec-Butyl)-4-methoxybenzene

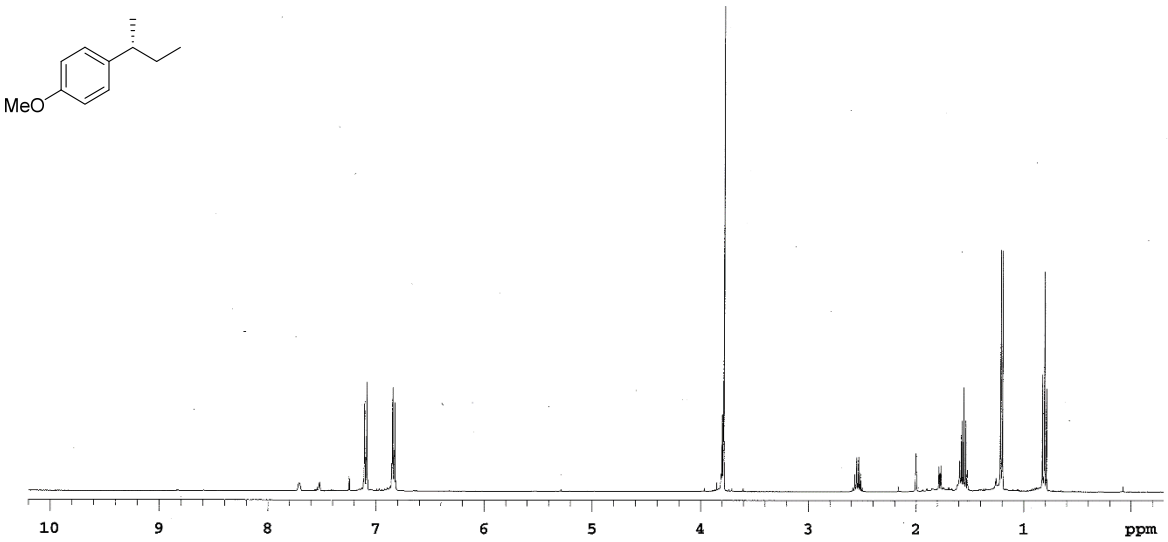


Figure S194. ^{1}H NMR of 1-(*sec*-butyl)-4-methoxybenzene

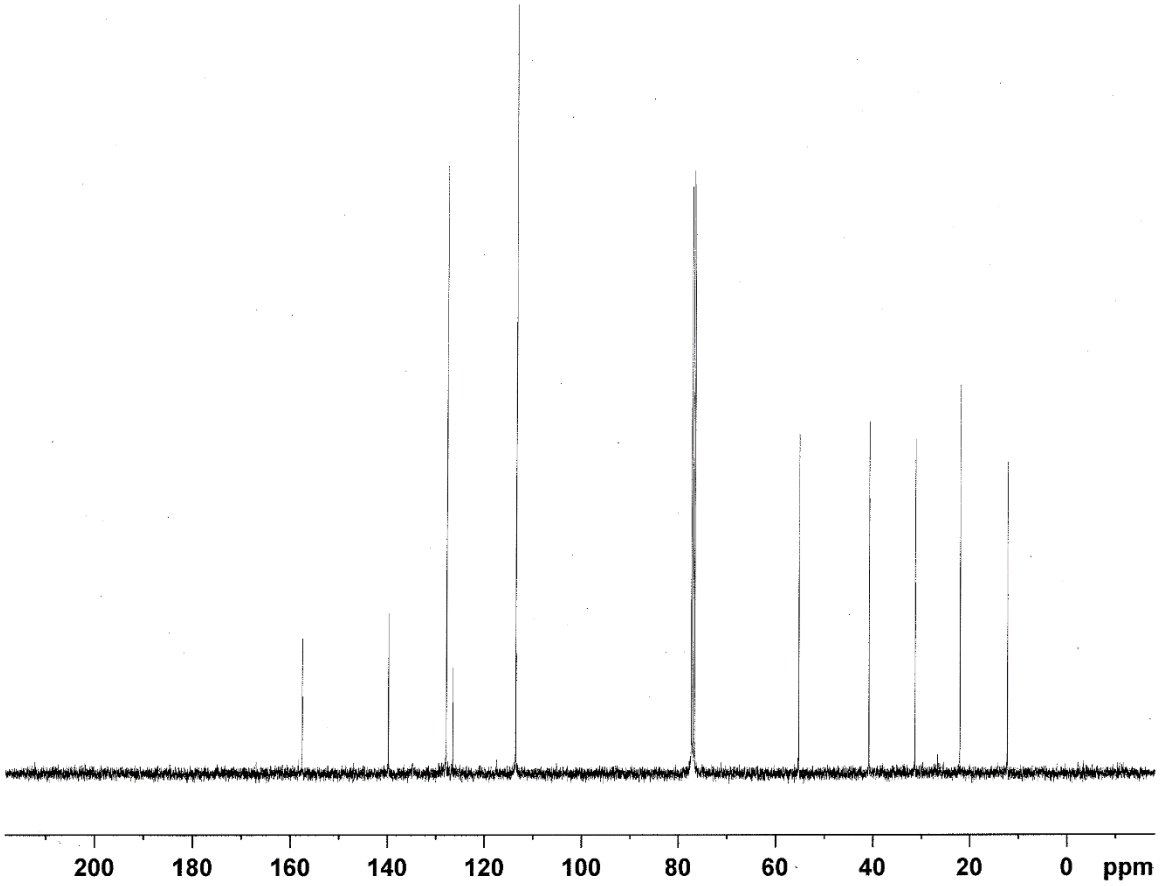
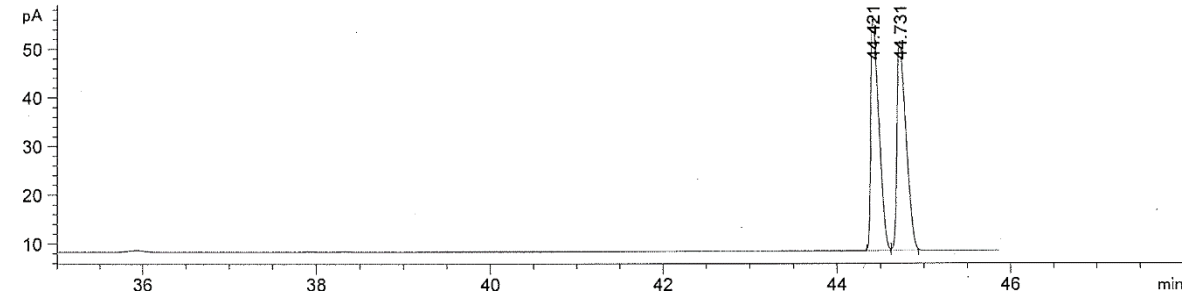


Figure S195. ^{13}C NMR of 1-(*sec*-butyl)-4-methoxybenzene

a)



b)

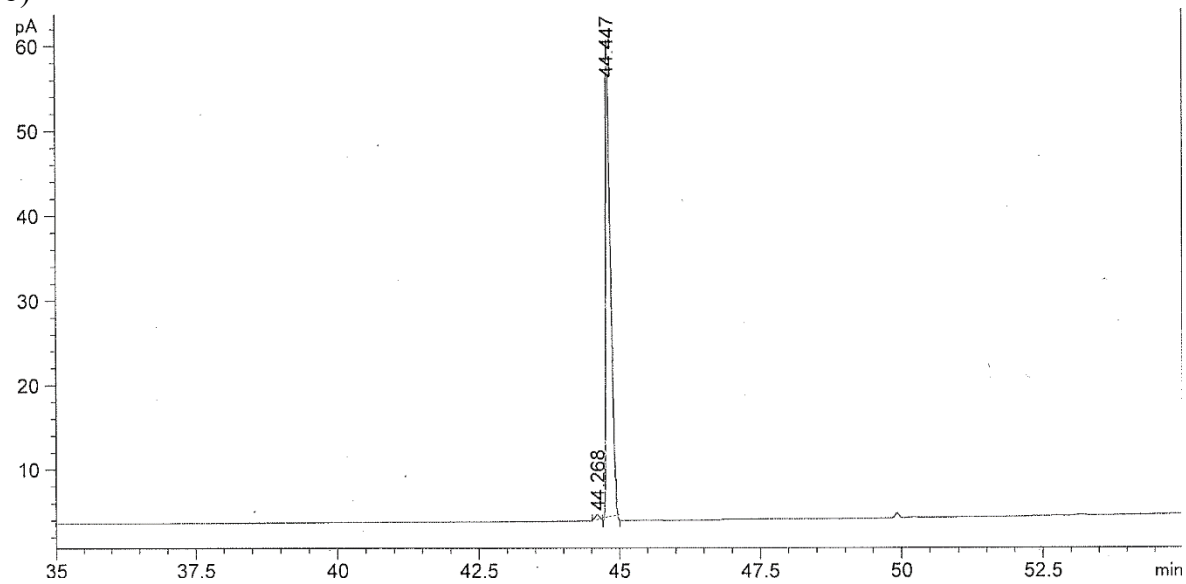


Figure S196. GC traces of (a) racemic and (b) enantioenriched product (98% (*R*) ee using Ir-**L5d** catalytic system; Table 1, substrate **S1**)

(S)-(3,3-Dimethylbutan-2-yl)benzene

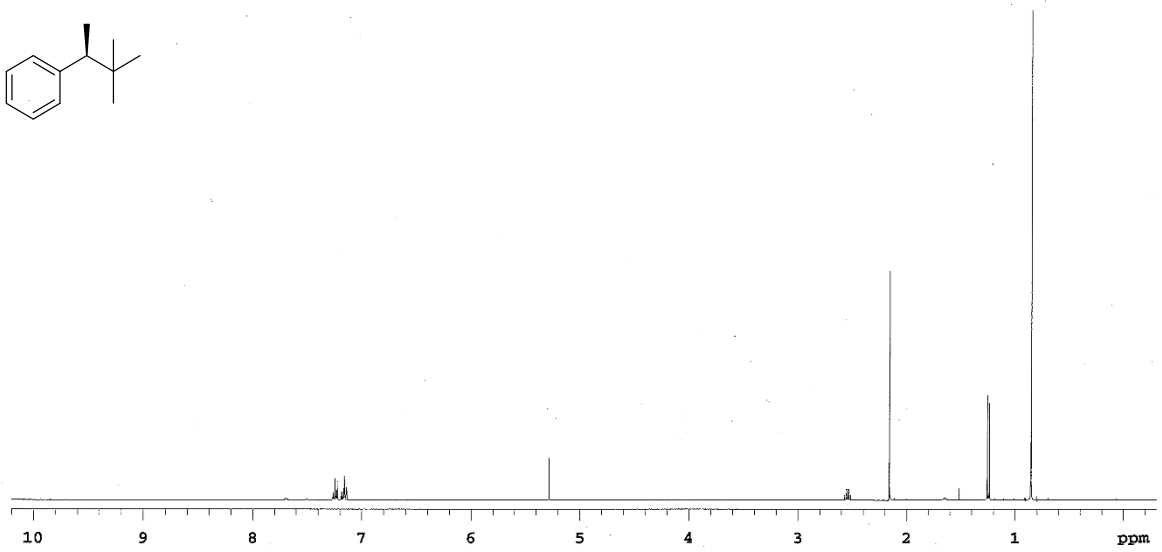


Figure S197. ^{1}H NMR of (3,3-dimethylbutan-2-yl)benzene

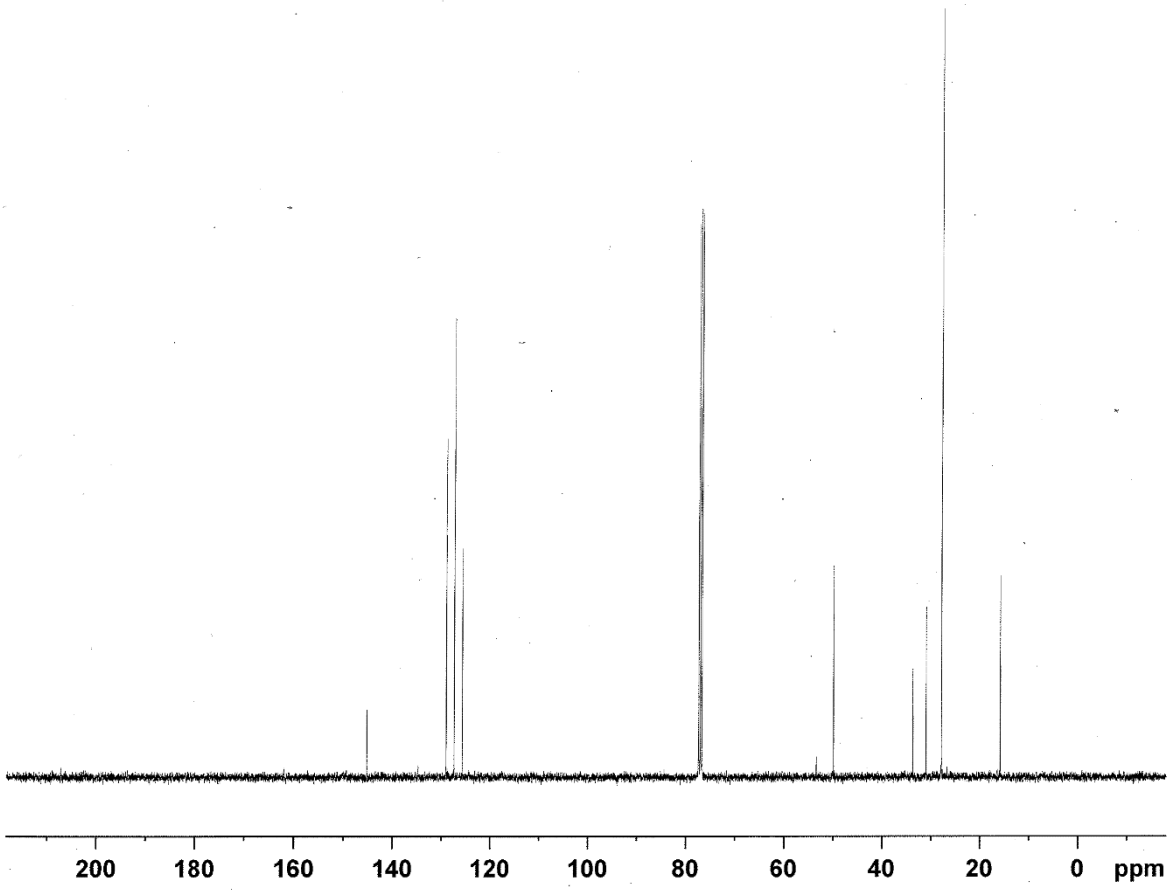
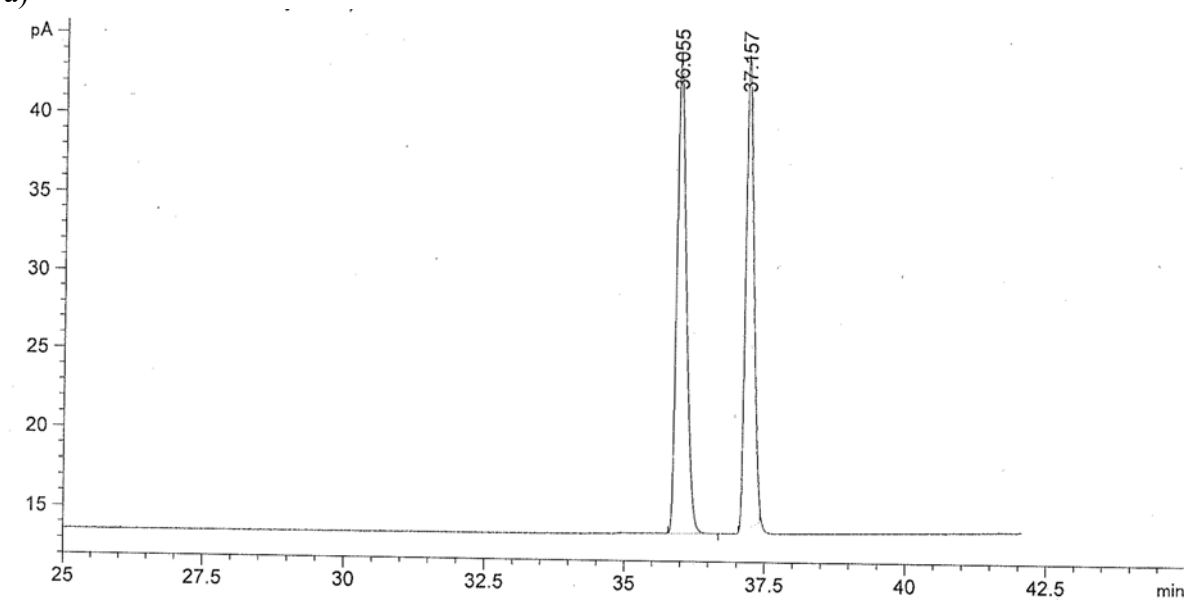


Figure S198. ^{13}C NMR of (3,3-dimethylbutan-2-yl)benzene

a)



b)

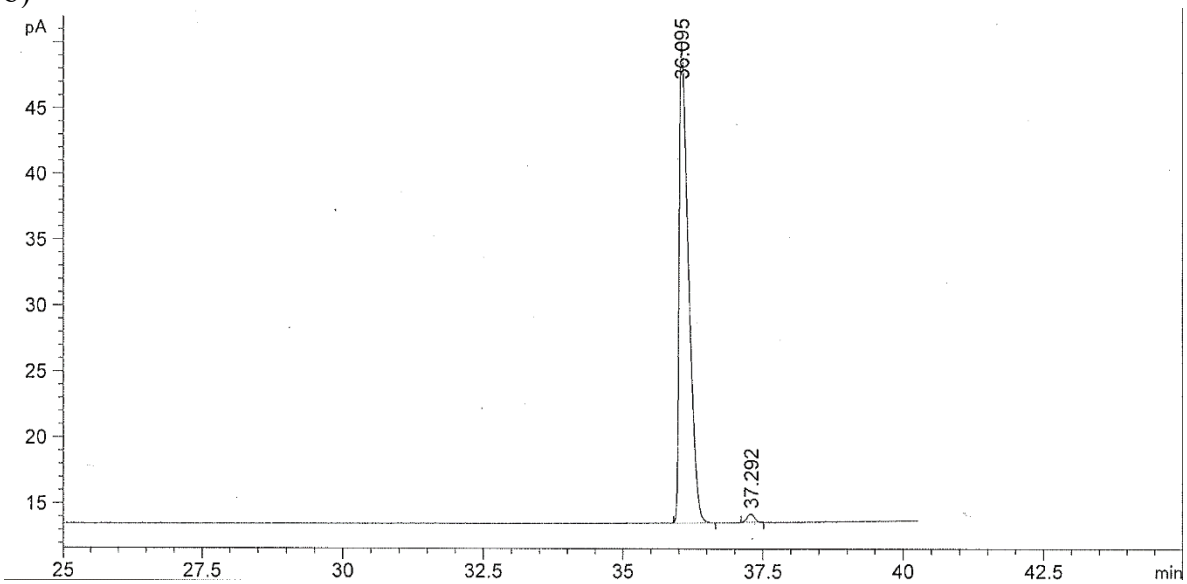
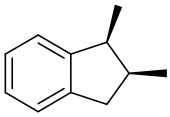


Figure S199. GC traces of (a) racemic and (b) enantioenriched product (97% (*S*) ee using Ir-**L3a** catalytic system; Table 1, substrate **S2**)

(S,S)-1,2-Dimethyl-2,3-dihydro-1H-indene



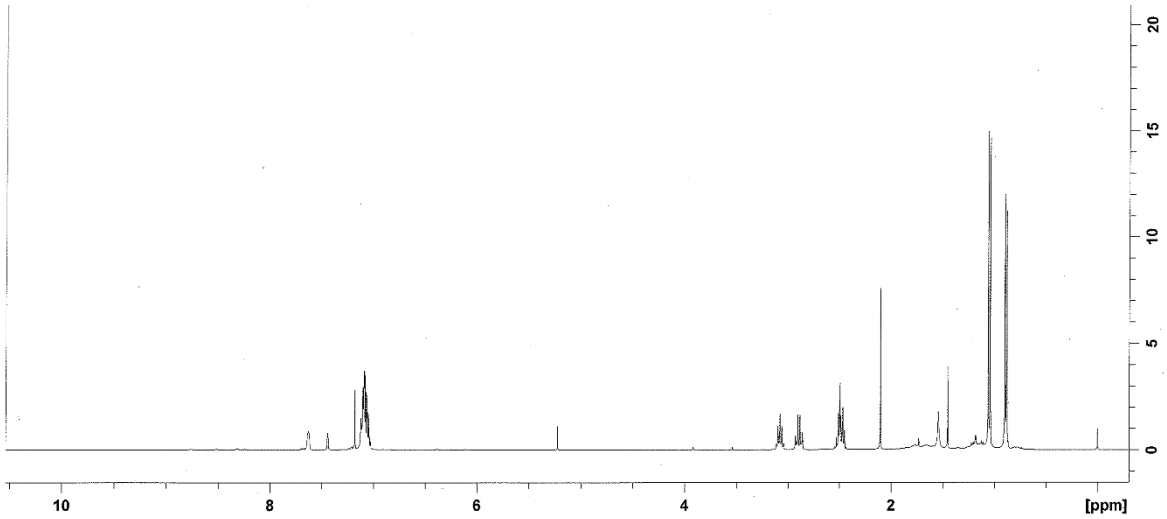


Figure S200. ^{1}H NMR of 1,2-dimethyl-2,3-dihydro-1*H*-indene

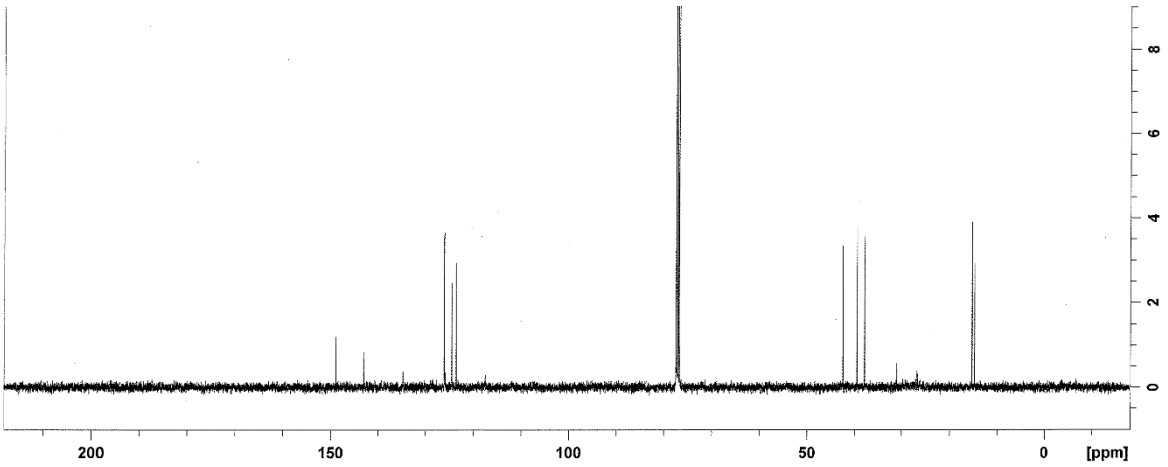
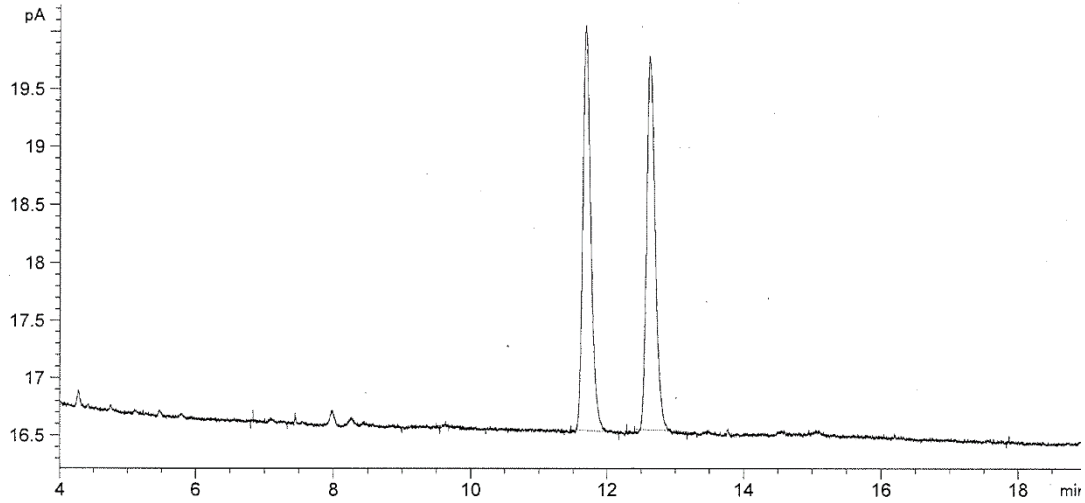


Figure S201. ^{13}C NMR of 1,2-dimethyl-2,3-dihydro-1*H*-indene

a)



b)

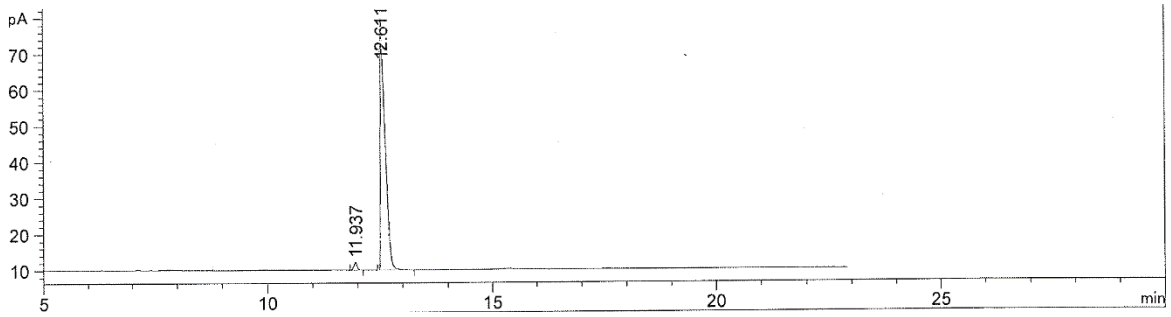


Figure S202. GC traces of (a) racemic and (b) enantioenriched product (97% (*S*,*S*) ee using Ir-**L2f** catalytic system; Table 1, substrate **S3**)

(R)-sec-Butylbenzene

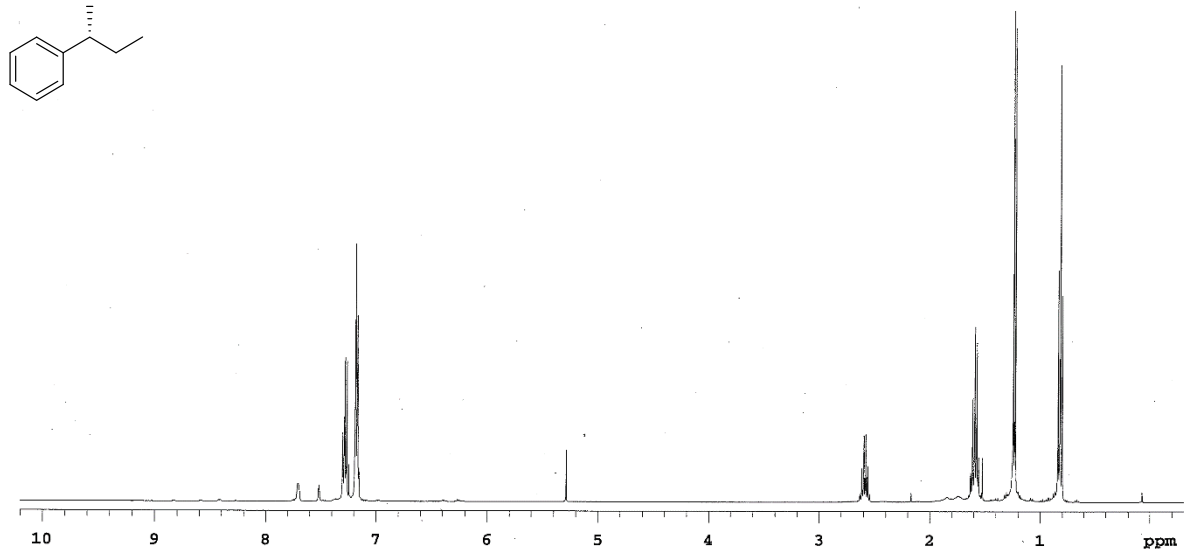


Figure S203. ^{1}H NMR of *sec*-butylbenzene

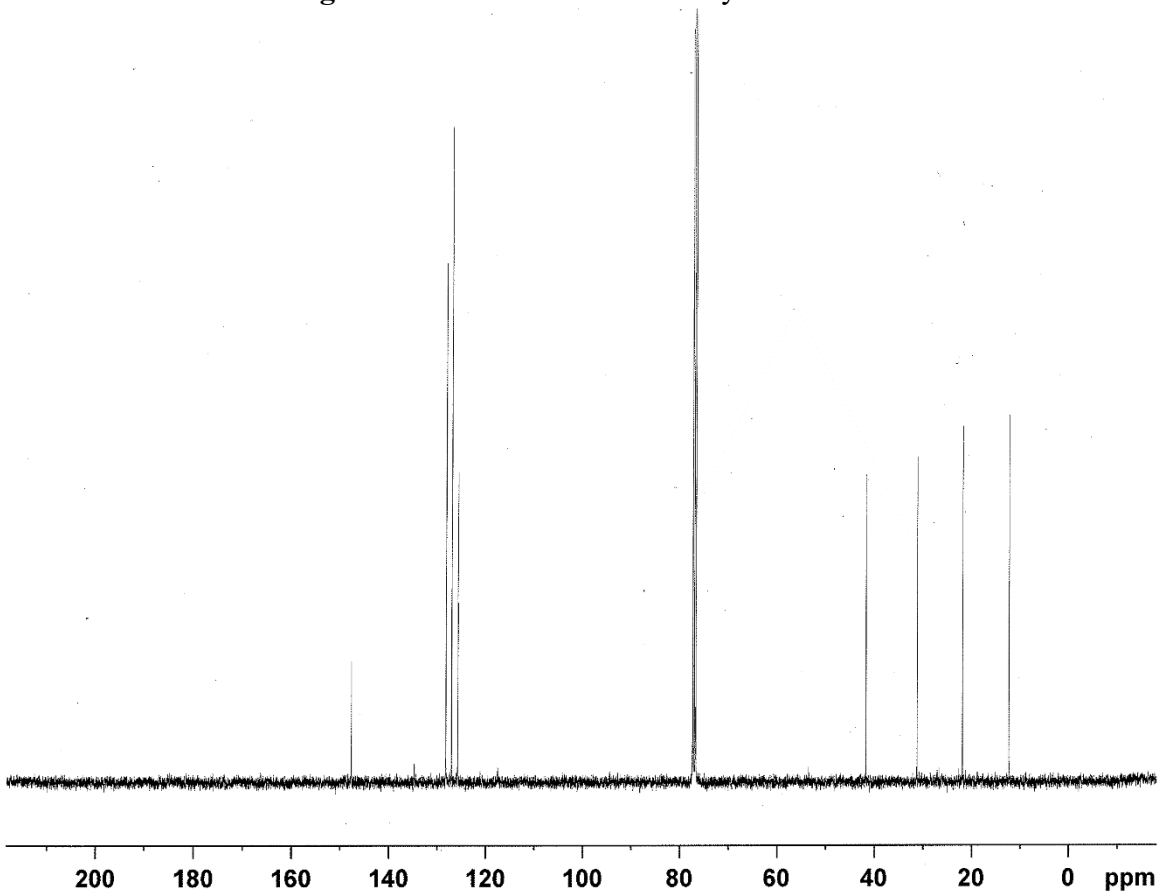
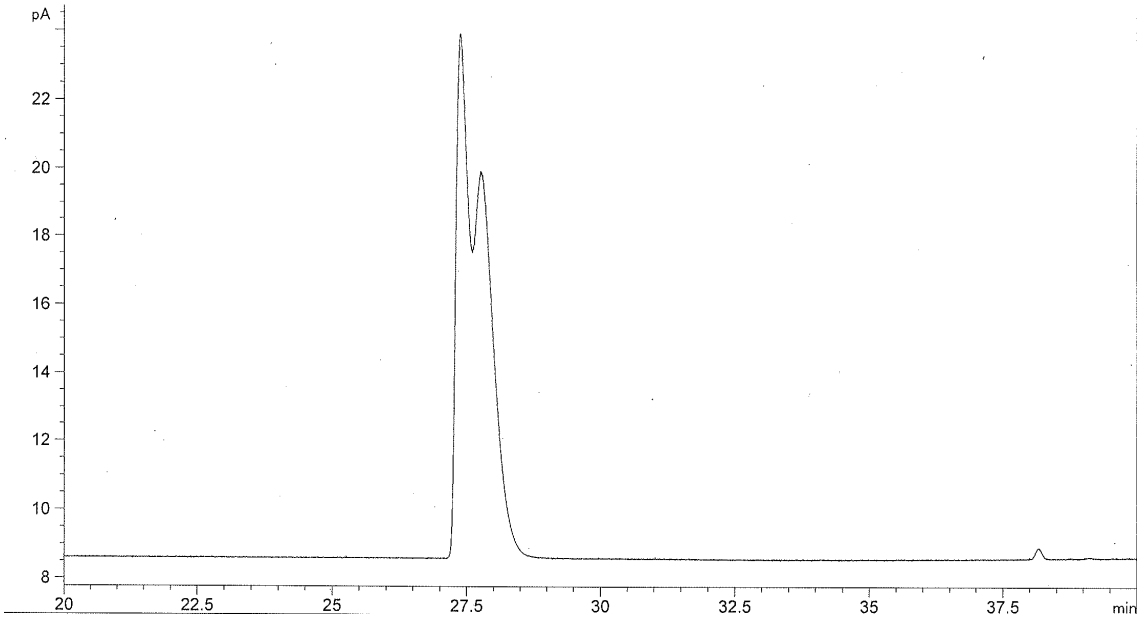


Figure S204. ^{13}C NMR of *sec*-butylbenzene

a)



b)

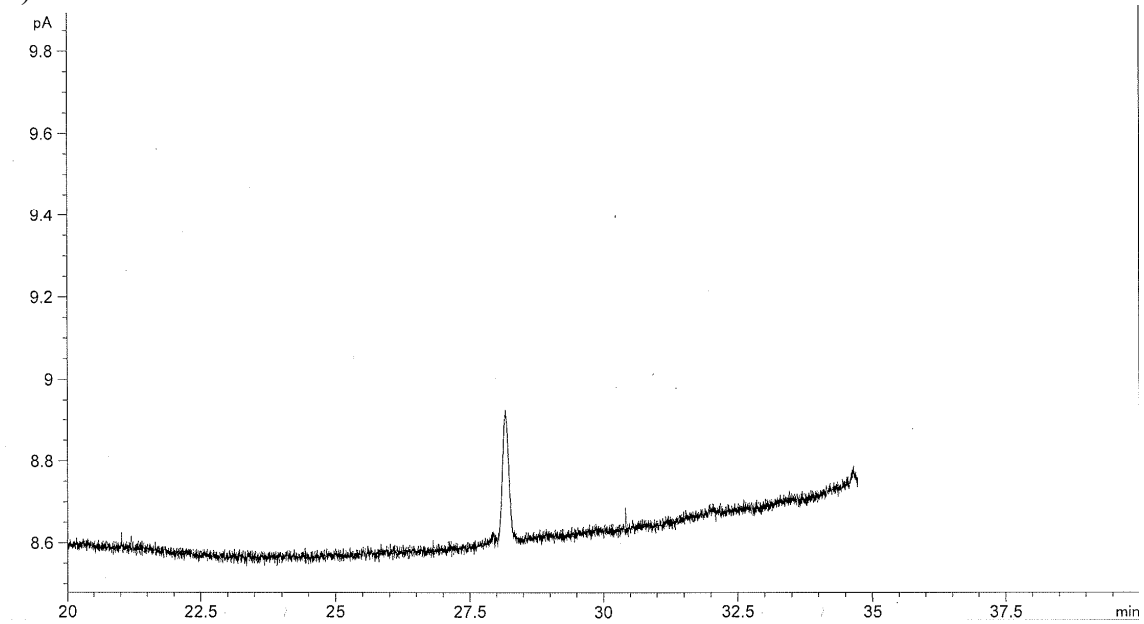


Figure S205. GC traces of (a) racemic and (b) enantioenriched product (97% (*R*) ee using Ir-**L5d** catalytic system; Table 1, substrate **S4**)

(R)-Propane-1,2-diyldibenzene

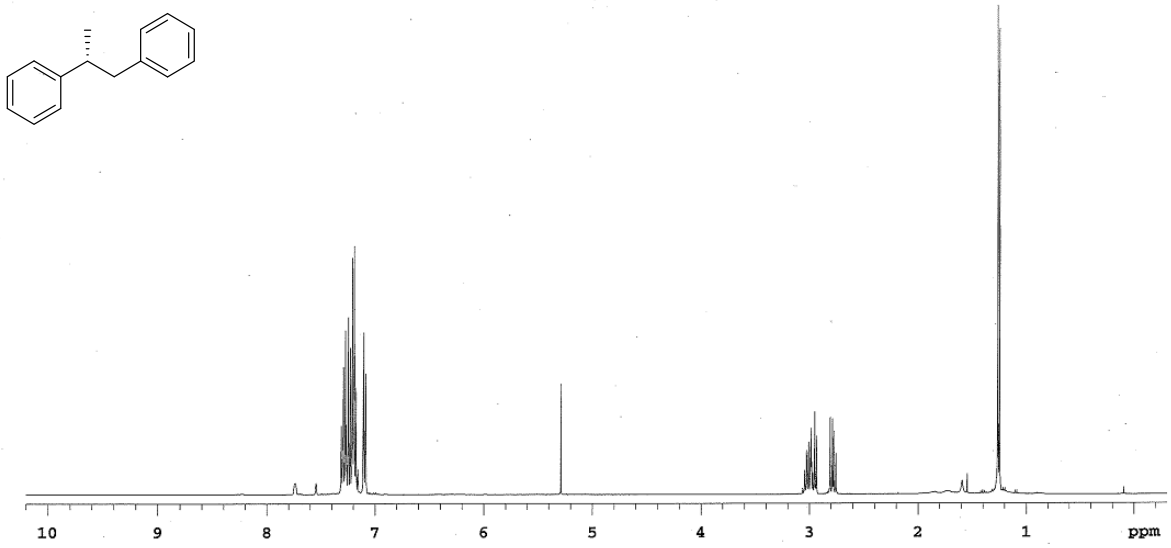


Figure S206. ^{1}H NMR of propane-1,2-diyldibenzene

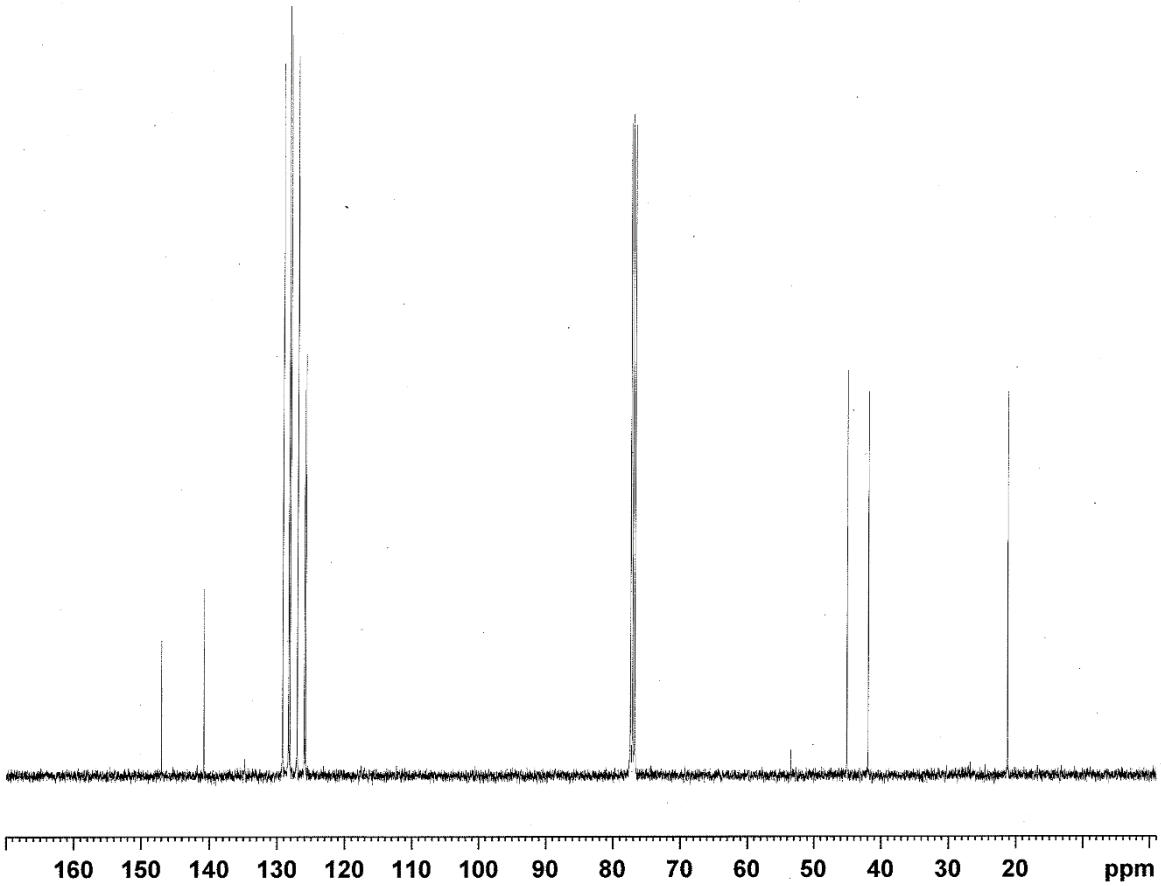
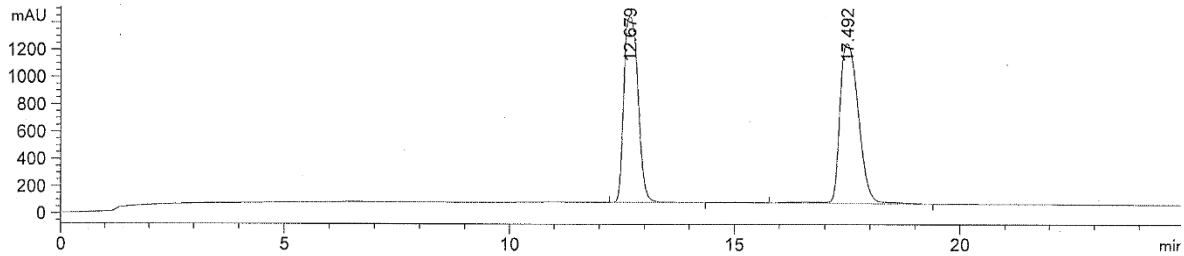


Figure S207. ^{13}C NMR of propane-1,2-diyldibenzene

a)



b)

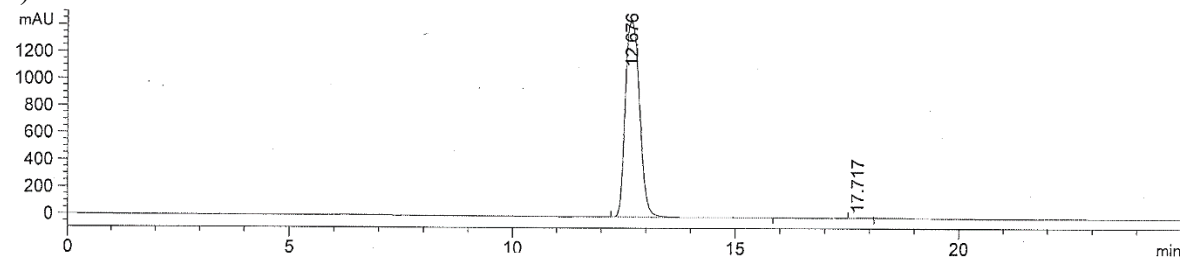


Figure S208. HPLC traces of (a) racemic and (b) enantioenriched product (99% (*R*) ee using Ir-**L5d** catalytic system; Figure 2, substrate **S5**)

(R)-1-Benzyl-2,3-dihydro-1H-indene

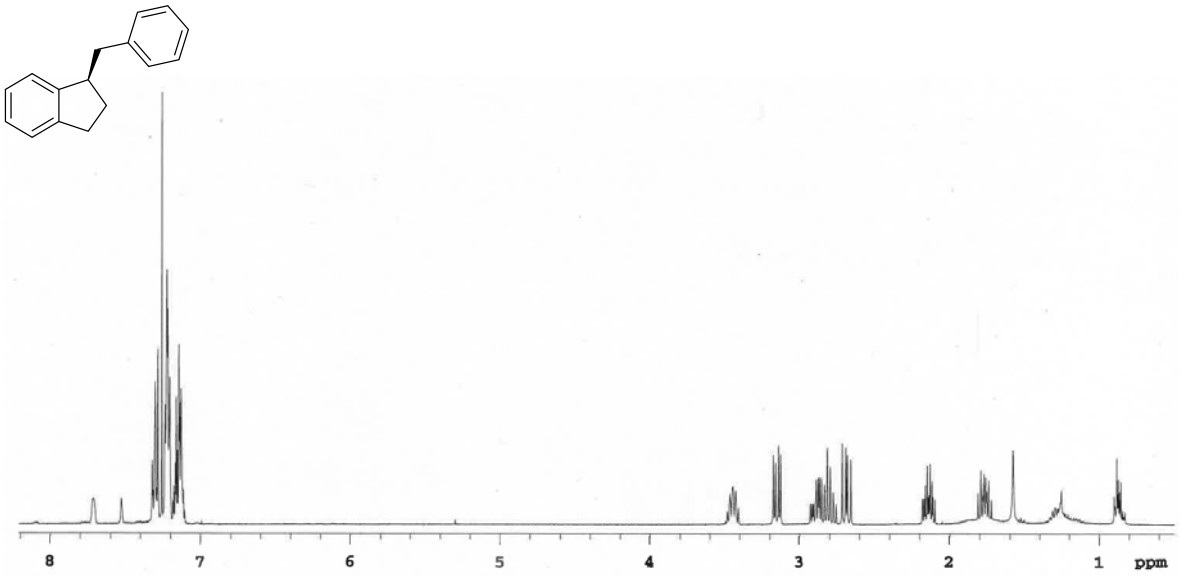


Figure S209. ^{1}H NMR of 1-benzyl-2,3-dihydro-1H-indene

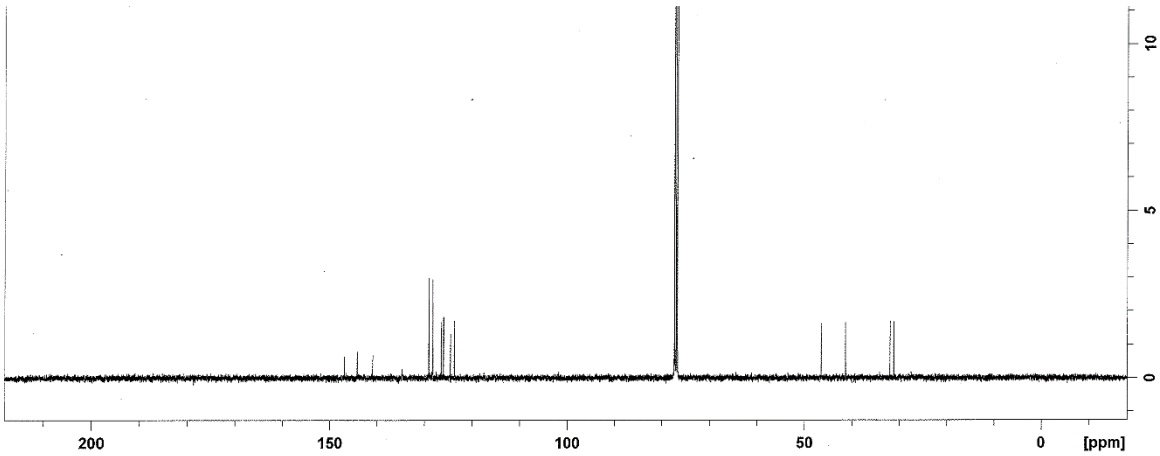
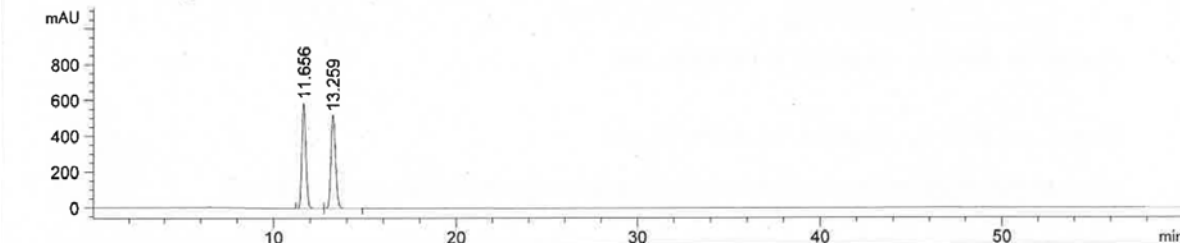


Figure S210. ^{1}H NMR of 1-benzyl-2,3-dihydro-1H-indene

a)



b)

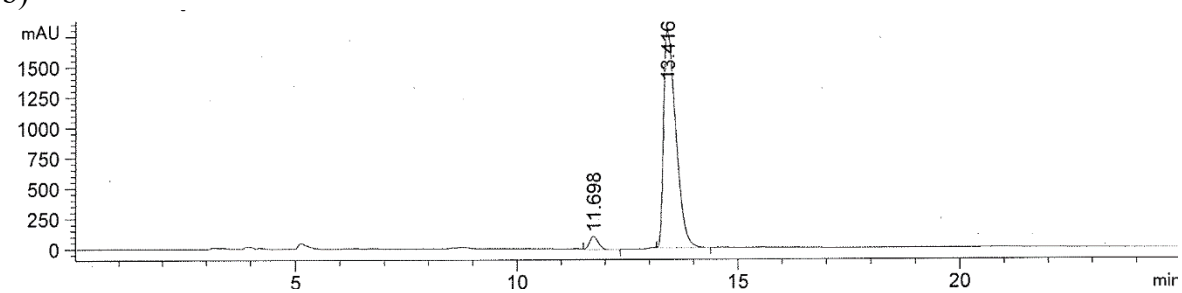


Figure S211. HPLC traces of (a) racemic and (b) enantioenriched product (96% (*R*) ee using Ir-**L1b** catalytic system; Figure 3, substrate **S7**)

(R)-Ethyl 3-phenylbutanoate

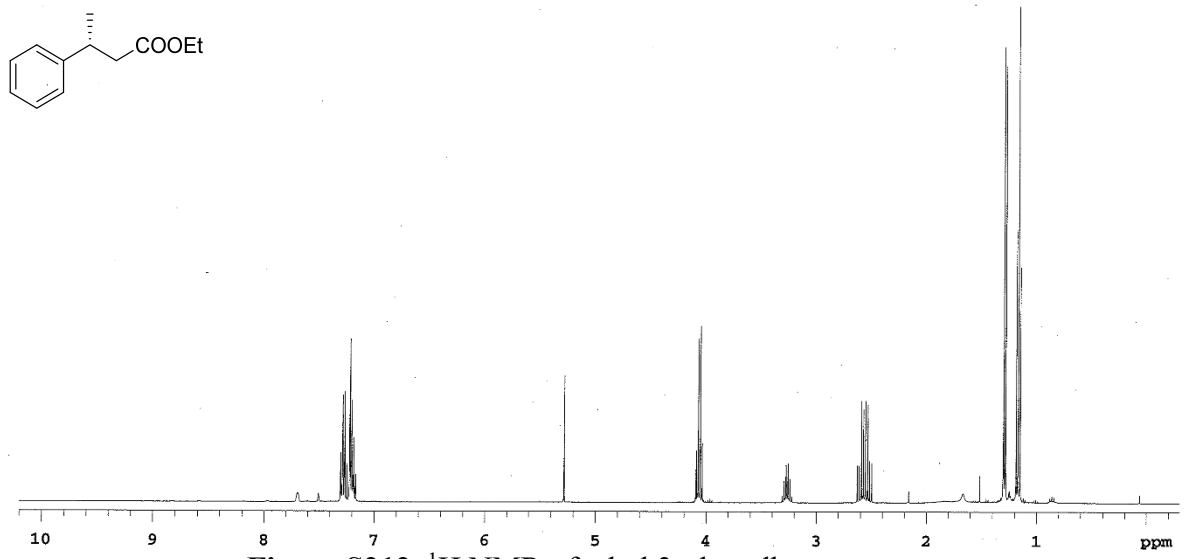


Figure S212. ^{1}H NMR of ethyl 3-phenylbutanoate

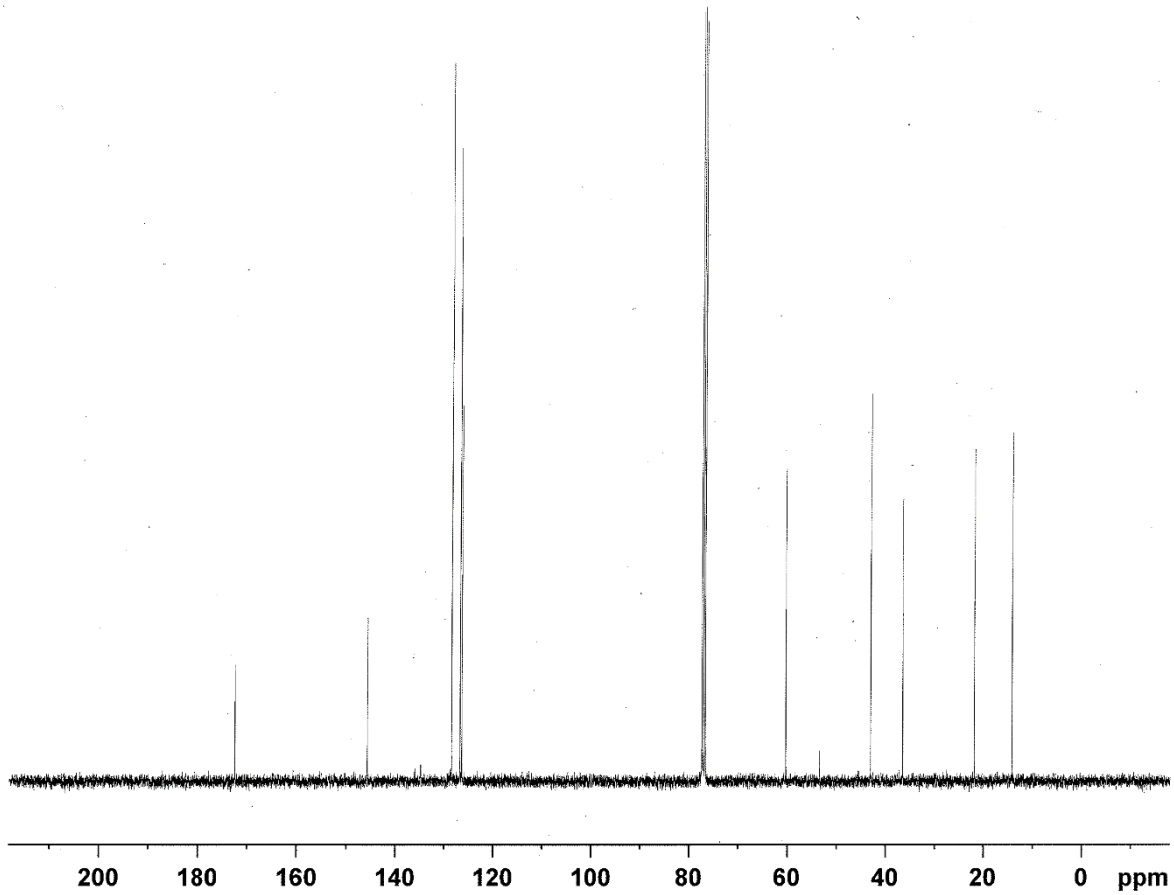
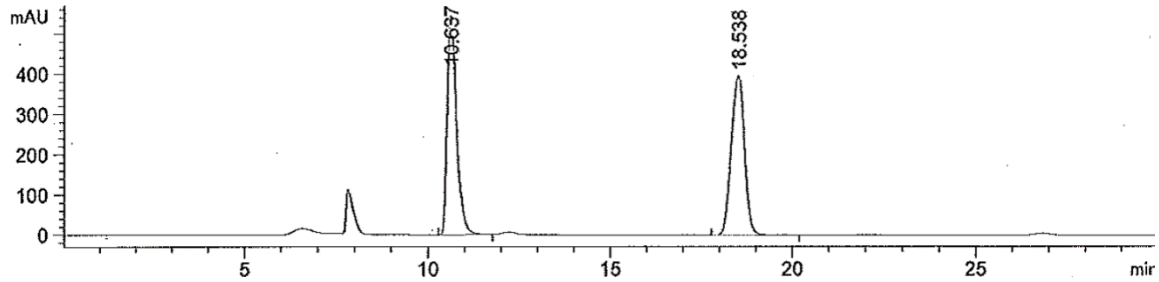


Figure S213. ^{13}C NMR of ethyl 3-phenylbutanoate

a)



b)

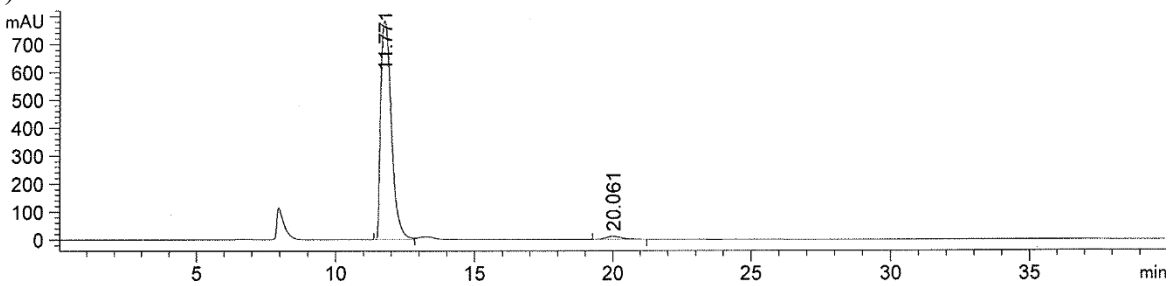


Figure S214. HPLC traces of (a) racemic and (b) enantioenriched product (98% (*R*) ee using Ir-**L5d** catalytic system; Figure 2, substrate **S8**)

(R)-Ethyl 3-(p-tolyl)butanoate

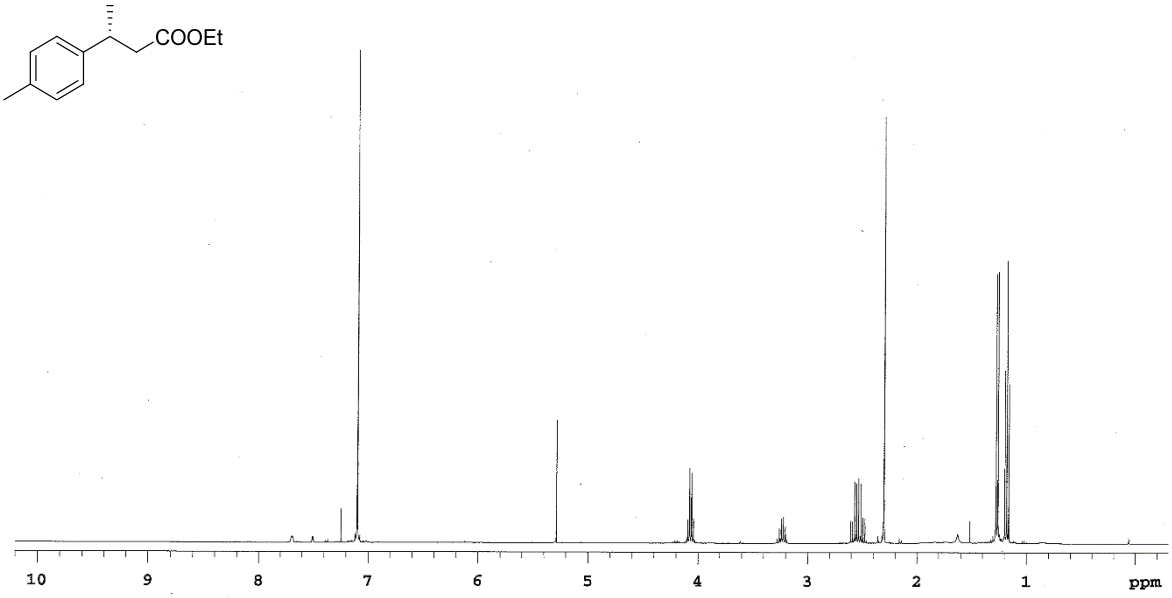


Figure S215. ^{1}H NMR of ethyl 3-(*p*-tolyl)butanoate

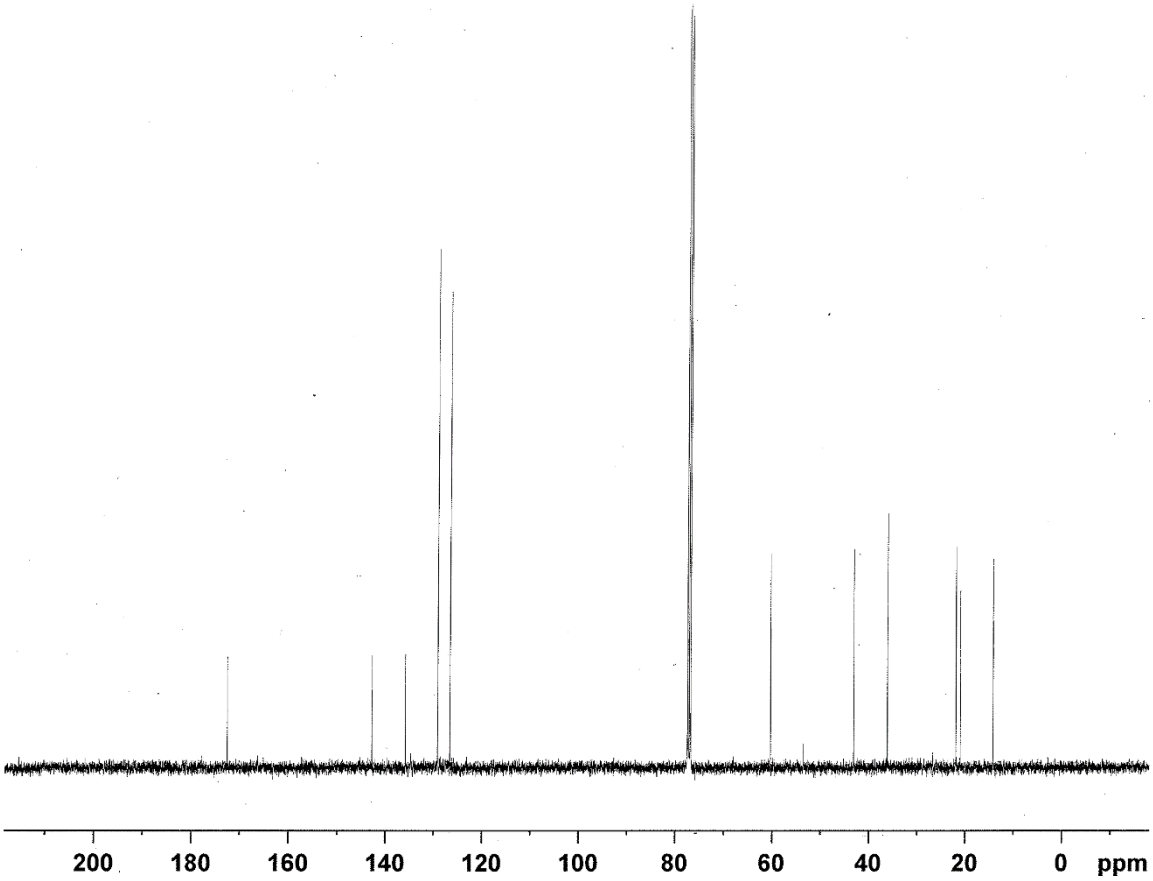
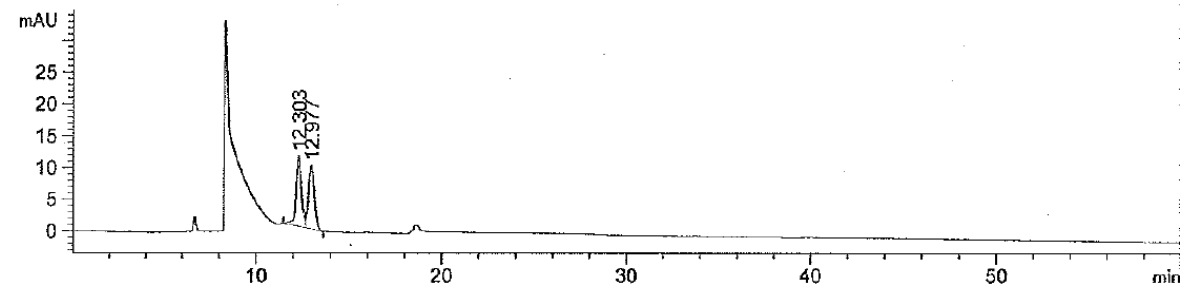


Figure S216. ^{13}C NMR of ethyl 3-(*p*-tolyl)butanoate

a)



b)

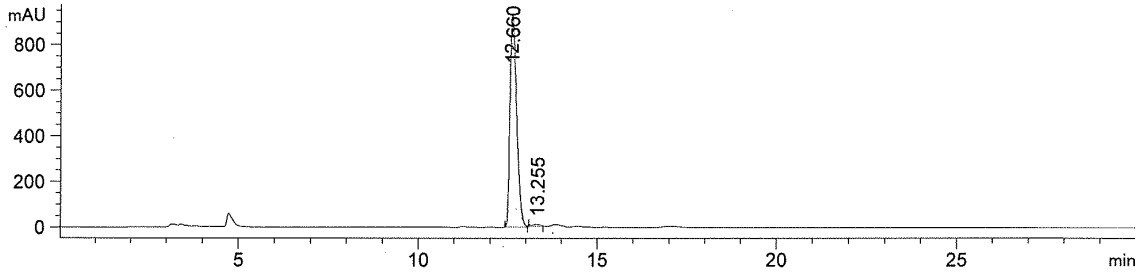


Figure S217. HPLC traces of (a) racemic and (b) enantioenriched product (98% (*R*) ee using Ir-**L5d** catalytic system; Figure 2, substrate **S9**)

(R)-Ethyl 3-(4-methoxyphenyl)butanoate

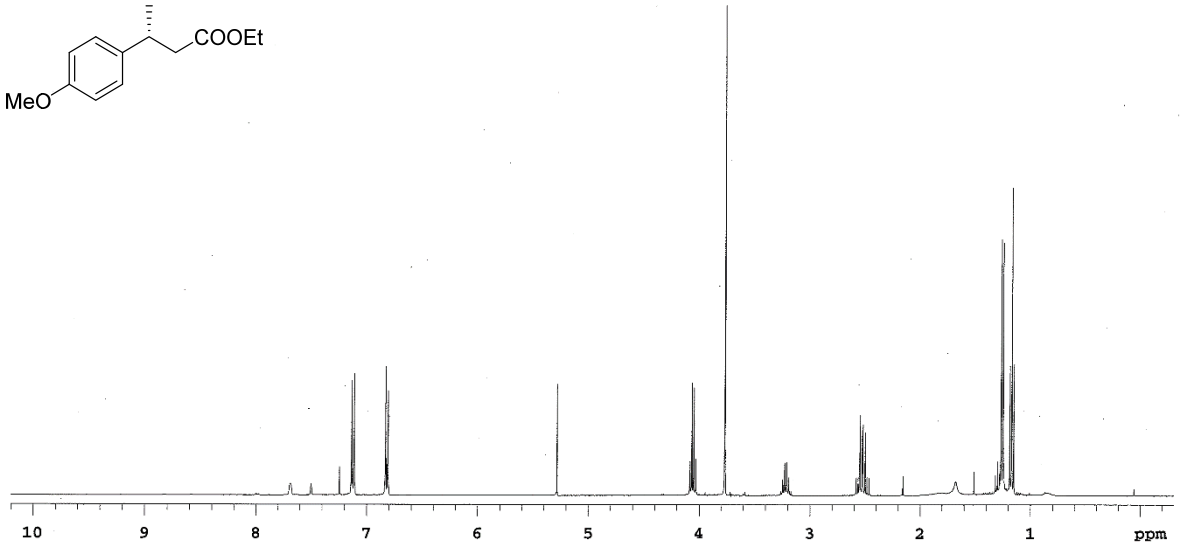


Figure S218. ^{1}H NMR of ethyl 3-(4-methoxyphenyl)butanoate

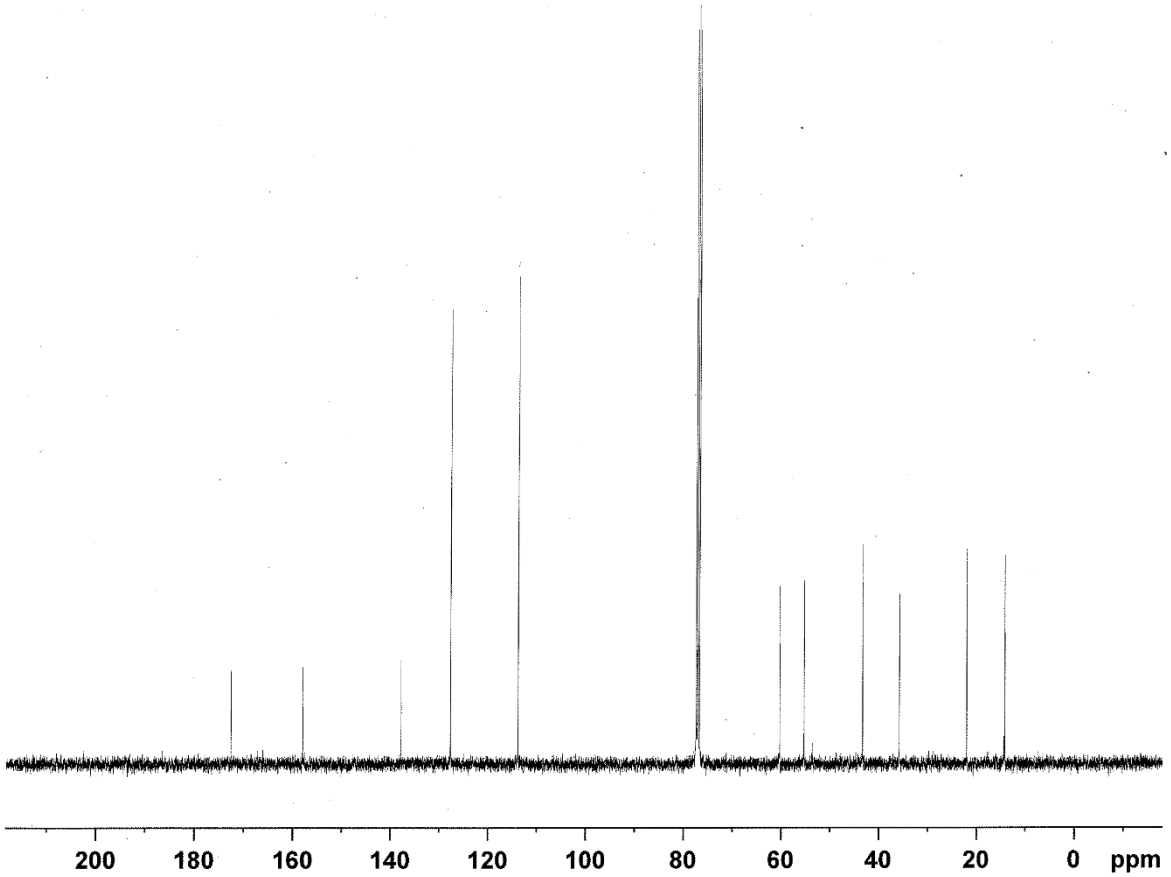
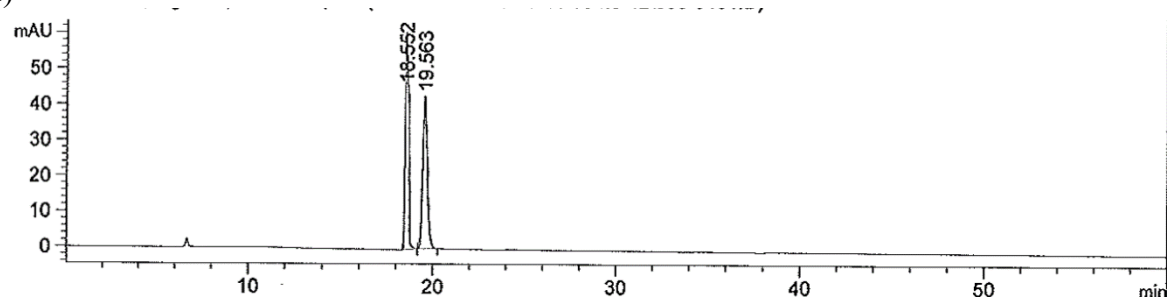


Figure S219. ^{13}C NMR of ethyl 3-(4-methoxyphenyl)butanoate

a)



b)

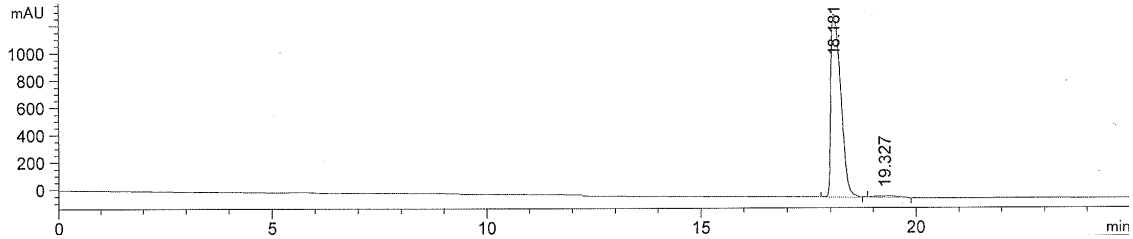


Figure S220. HPLC traces of (a) racemic and (b) enantioenriched product (99% (*R*) ee using Ir-**L5d** catalytic system; Figure 2, substrate **S10**)

(R)-Ethyl 3-phenylpentanoate

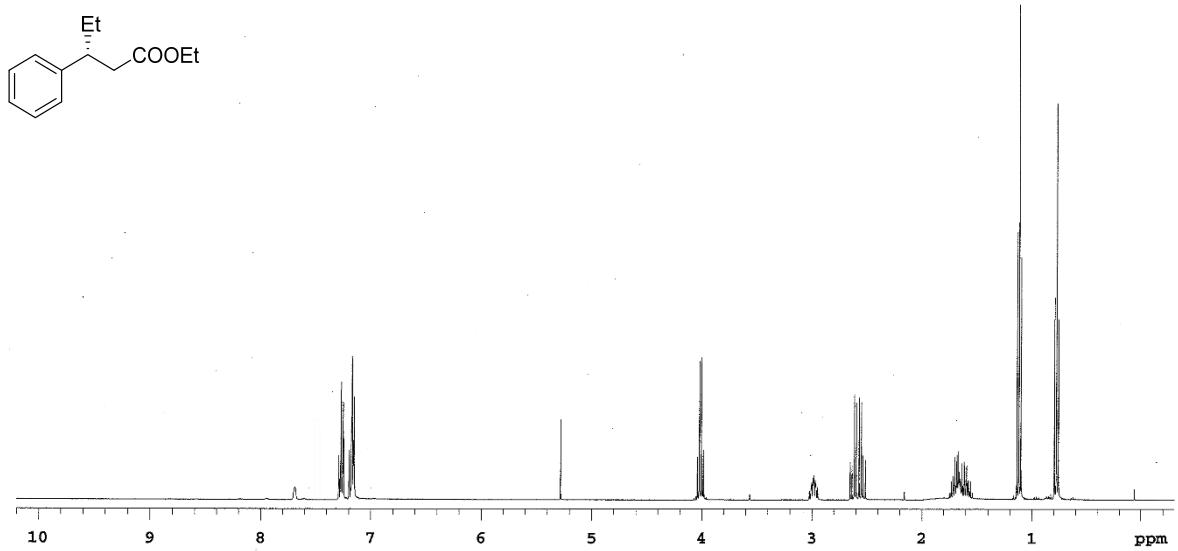


Figure S221. ^{1}H NMR of ethyl 3-phenylpentanoate

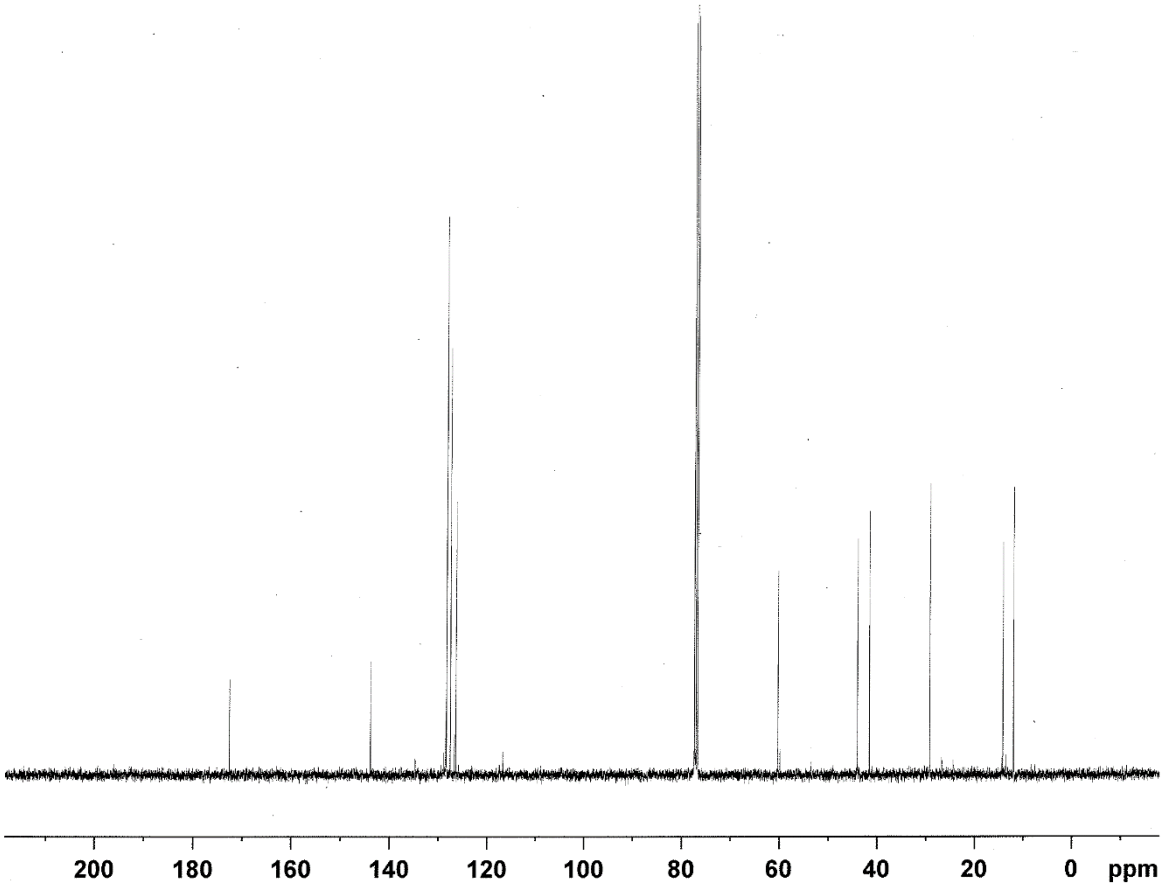
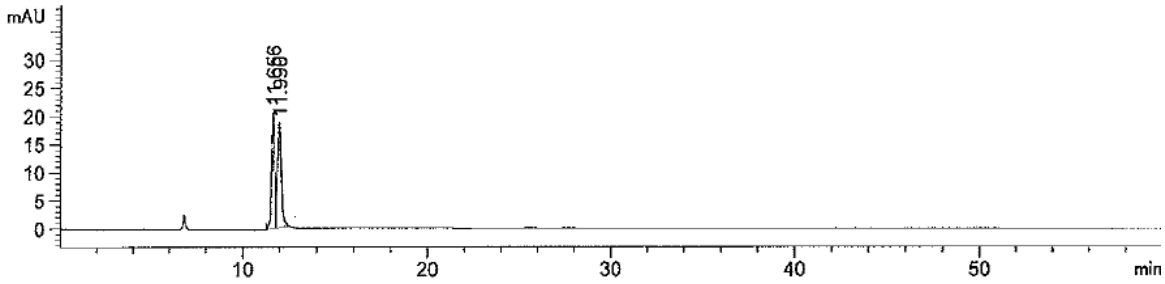


Figure S222. ^{13}C NMR of ethyl 3-phenylpentanoate

a)



b)

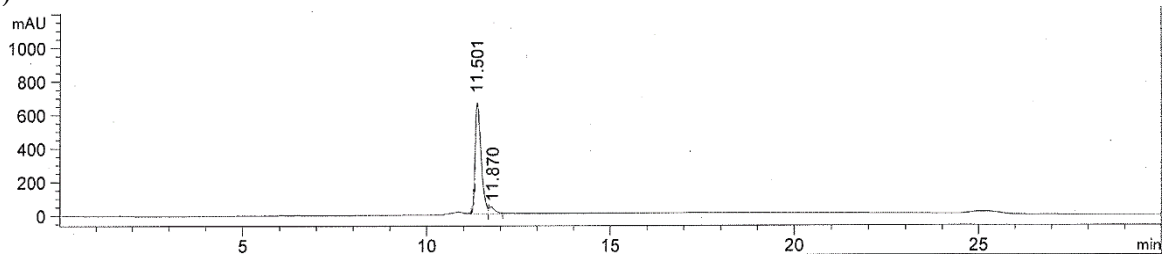


Figure S223. HPLC traces of (a) racemic and (b) enantioenriched product (98% (*R*) ee using Ir-**L5d** catalytic system; Figure 2, substrate **S11**)

(R)-Ethyl 4-methyl-3-phenylpentanoate

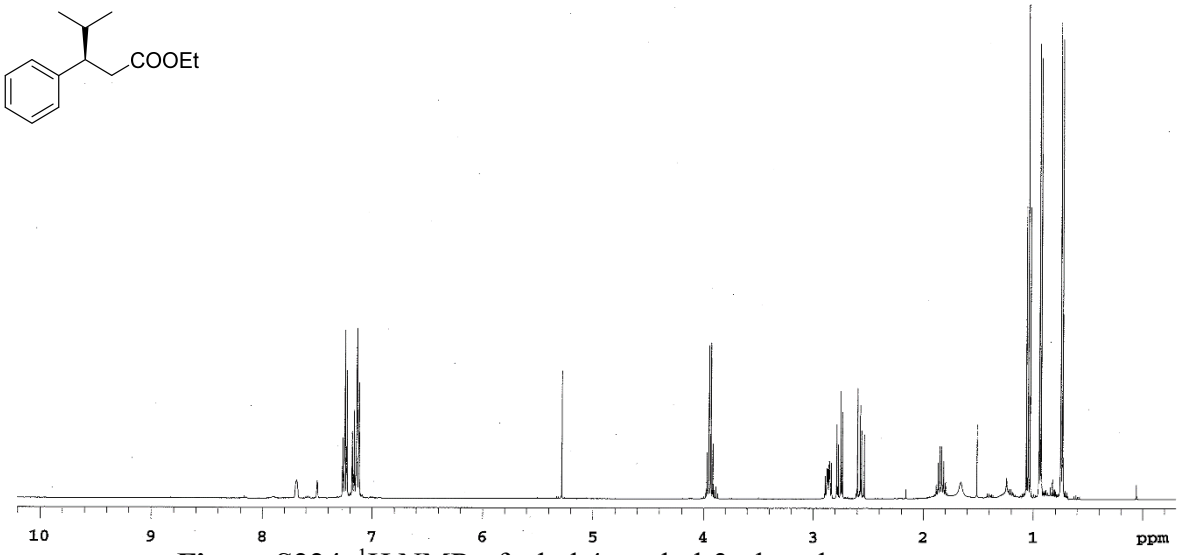


Figure S224. ^{1}H NMR of ethyl 4-methyl-3-phenylpentanoate

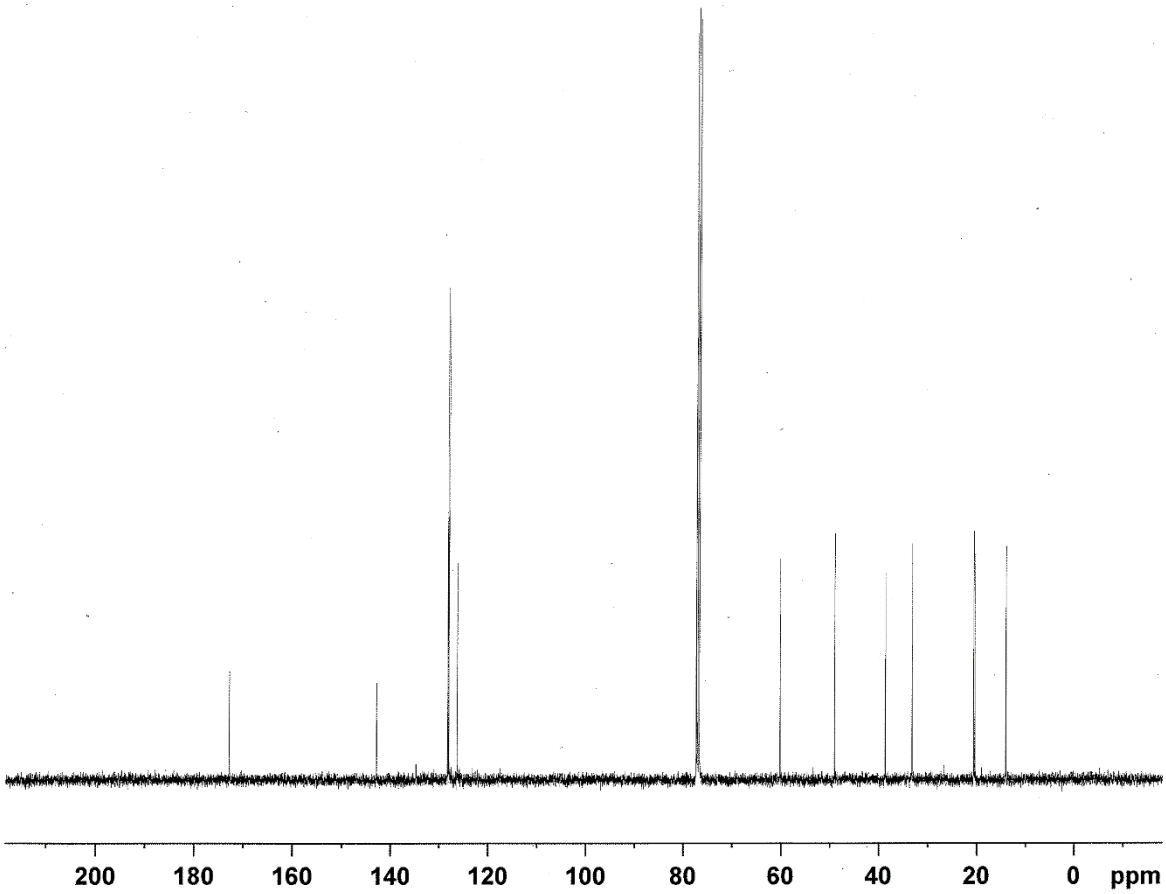
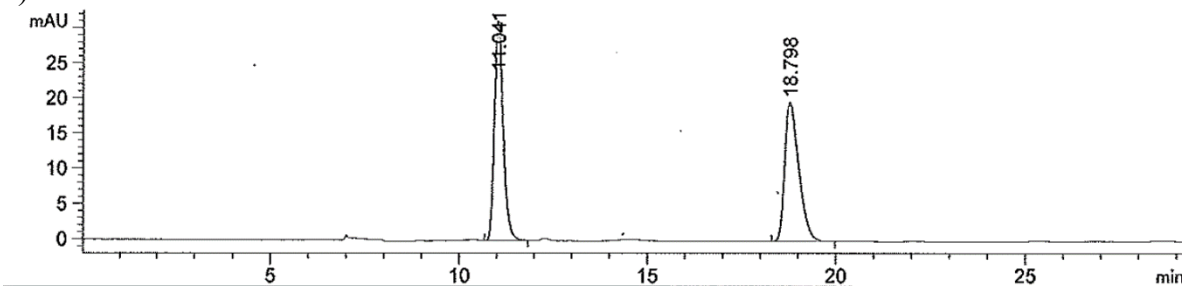


Figure S225. ^{13}C NMR of ethyl 4-methyl-3-phenylpentanoate

a)



b)

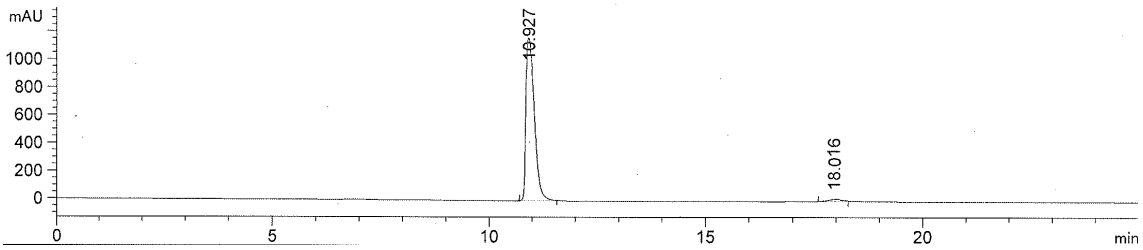


Figure S226. HPLC traces of (a) racemic and (b) enantioenriched product (99% (*R*) ee using Ir-**L5d** catalytic system; Figure 2, substrate **S12**)

(R)-Ethyl 3-cyclohexyl-3-phenylpropanoate

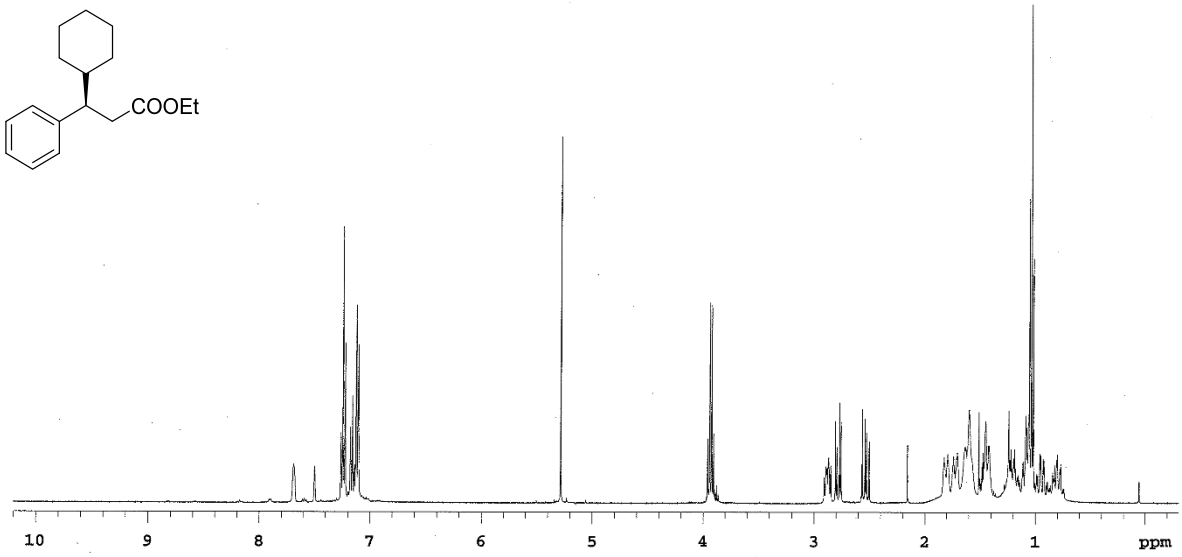


Figure S227. ^{1}H NMR of ethyl 3-cyclohexyl-3-phenylpropanoate

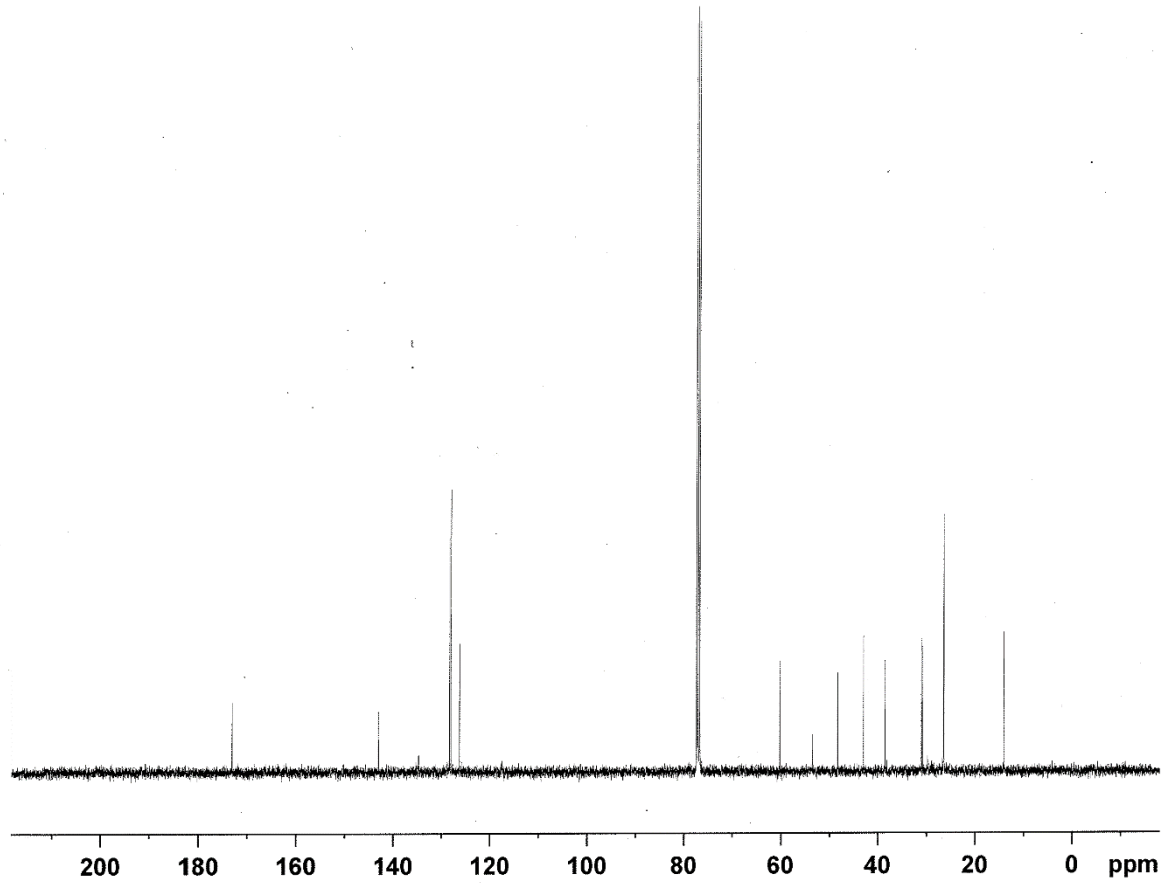
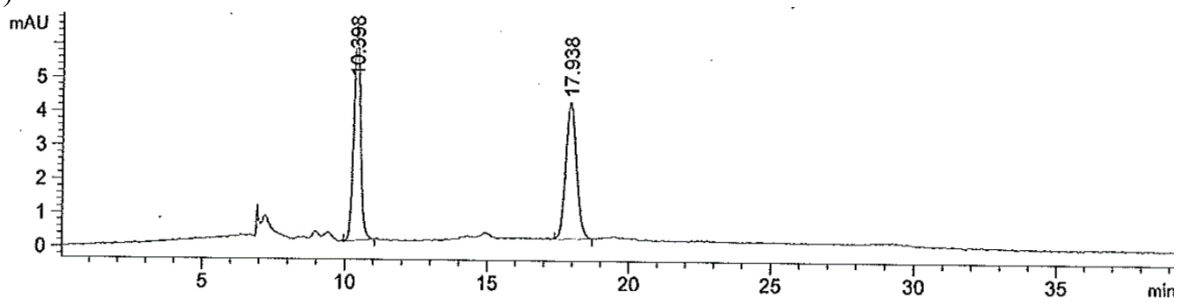


Figure S228. ^{13}C NMR of ethyl 3-cyclohexyl-3-phenylpropanoate

a)



b)

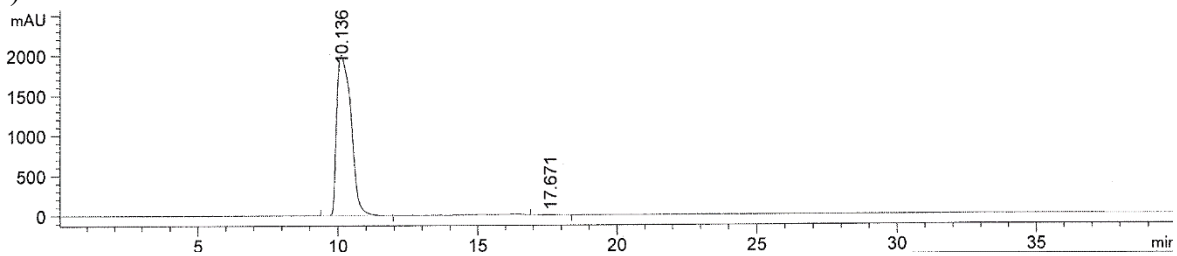


Figure S229. HPLC traces of (a) racemic and (b) enantioenriched product (99% (*R*) ee using Ir-**L5d** catalytic system; Figure 2, substrate **S13**)

(S)-3-Methyl-4-phenylbutan-2-one

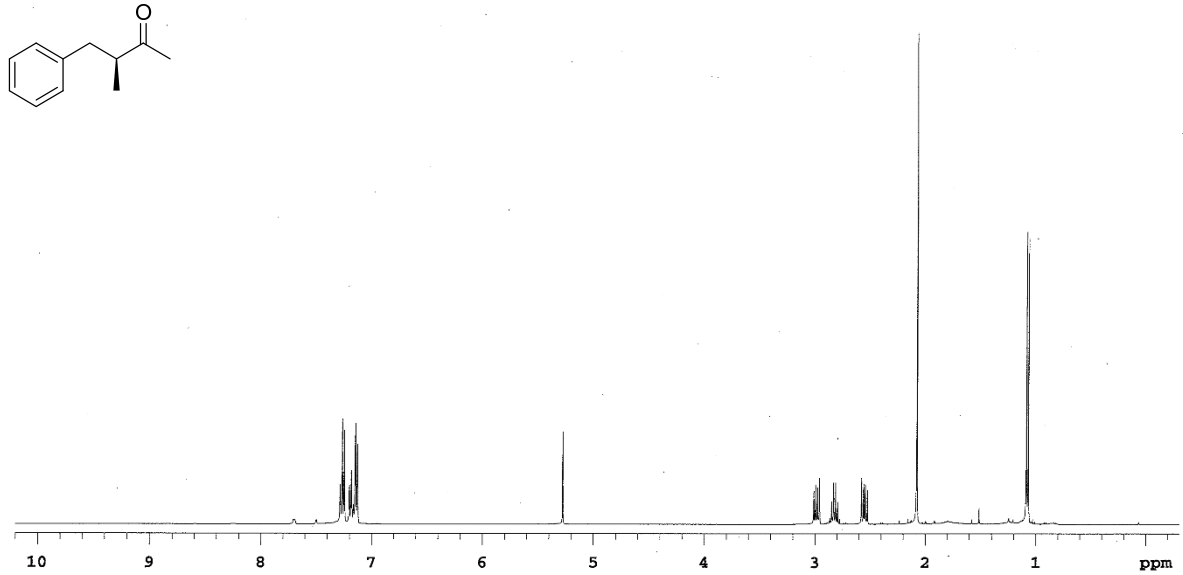


Figure S230. ^{1}H NMR of 3-methyl-4-phenylbutan-2-one

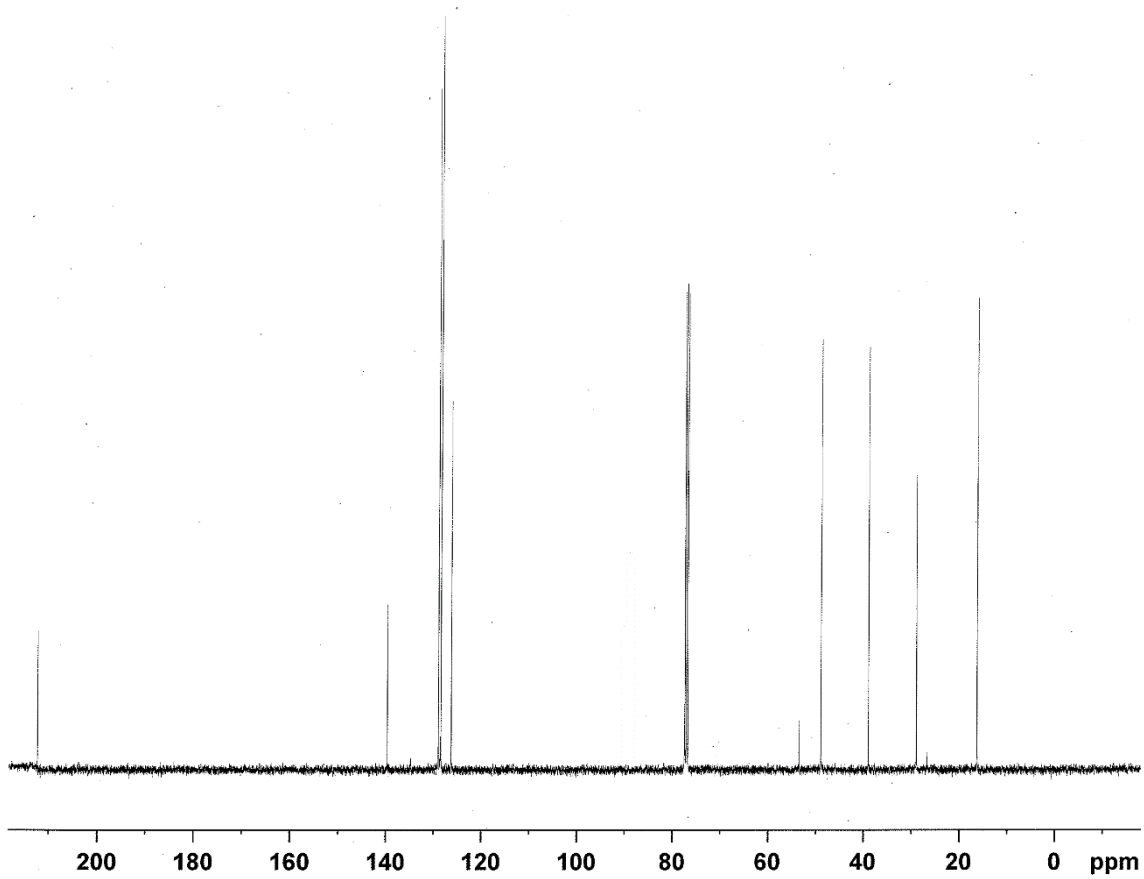
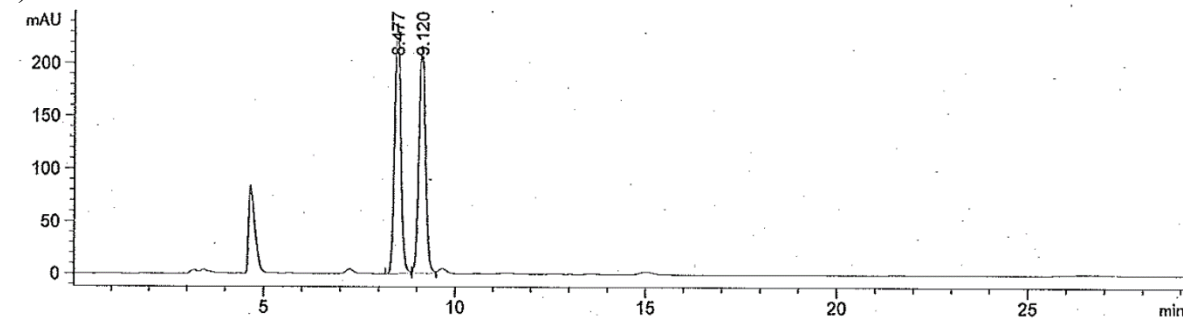


Figure S231. ^{13}C NMR of 3-methyl-4-phenylbutan-2-one

a)



b)

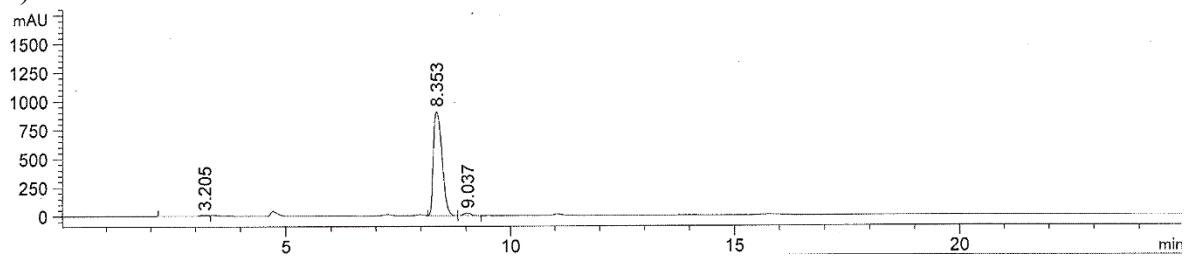


Figure S232. HPLC traces of (a) racemic and (b) enantioenriched product (97% (*S*) ee using Ir-**L4e** catalytic system; Figure 2, substrate **S14**)

(S)-4-(4-Methoxyphenyl)-3-methylbutan-2-one

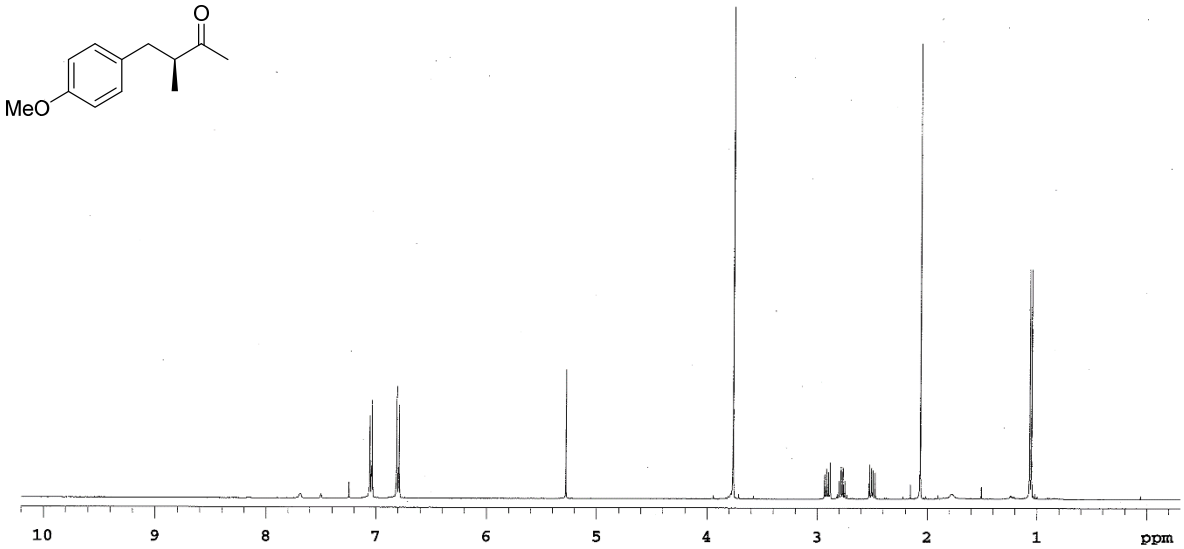


Figure S233. ^{1}H NMR of 4-(4-methoxyphenyl)-3-methylbutan-2-one

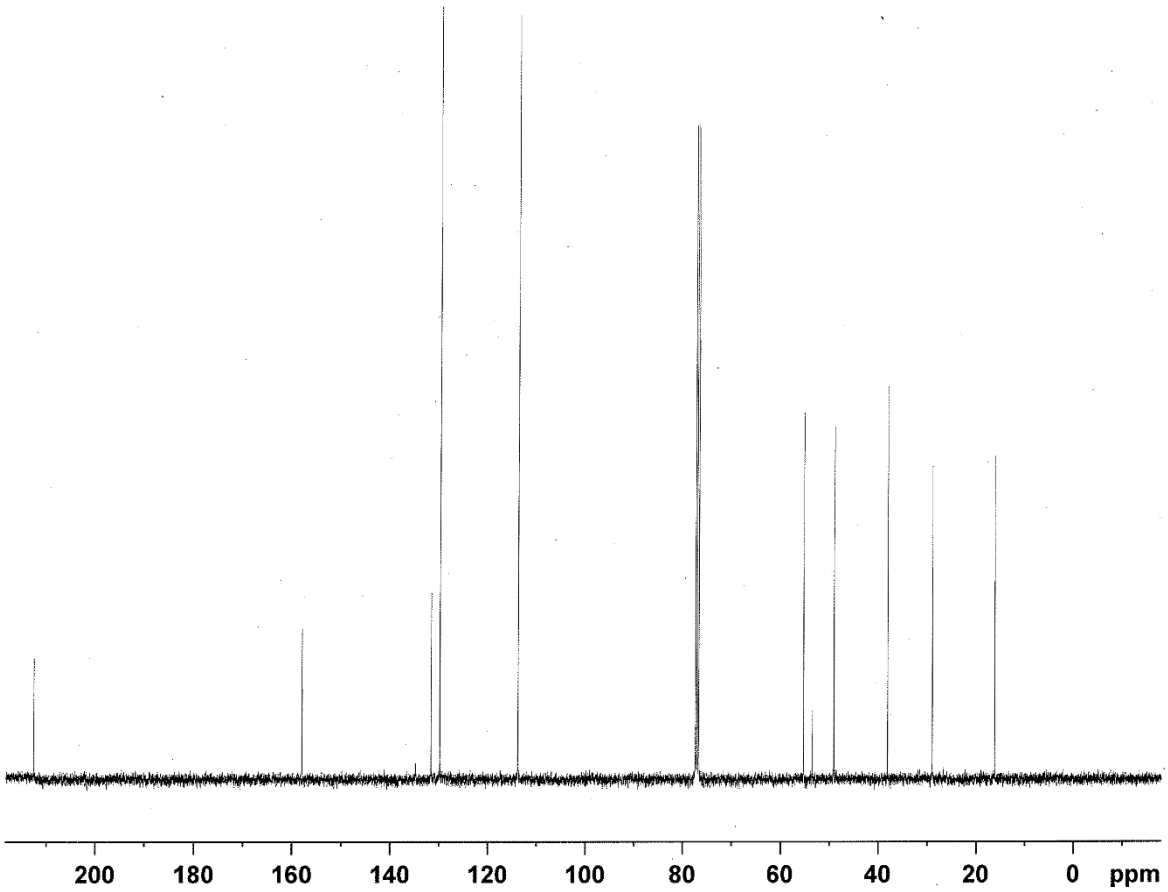
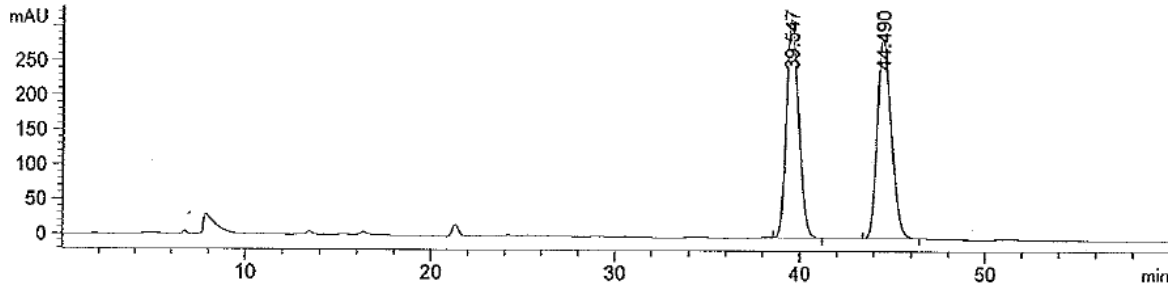


Figure S234. ^{13}C NMR of 4-(4-methoxyphenyl)-3-methylbutan-2-one

a)



b)

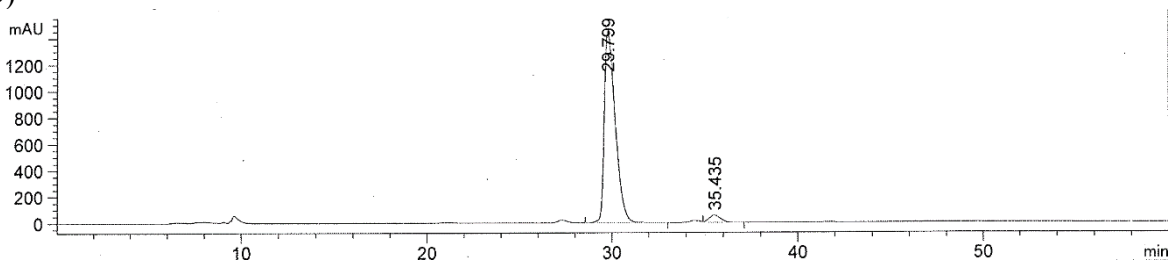


Figure S235. HPLC traces of (a) racemic and (b) enantioenriched product (97% (*S*) ee using Ir-**L4e** catalytic system; Figure 2, substrate **S16**)

(S)-2-Methyl-1-phenylpentan-3-one

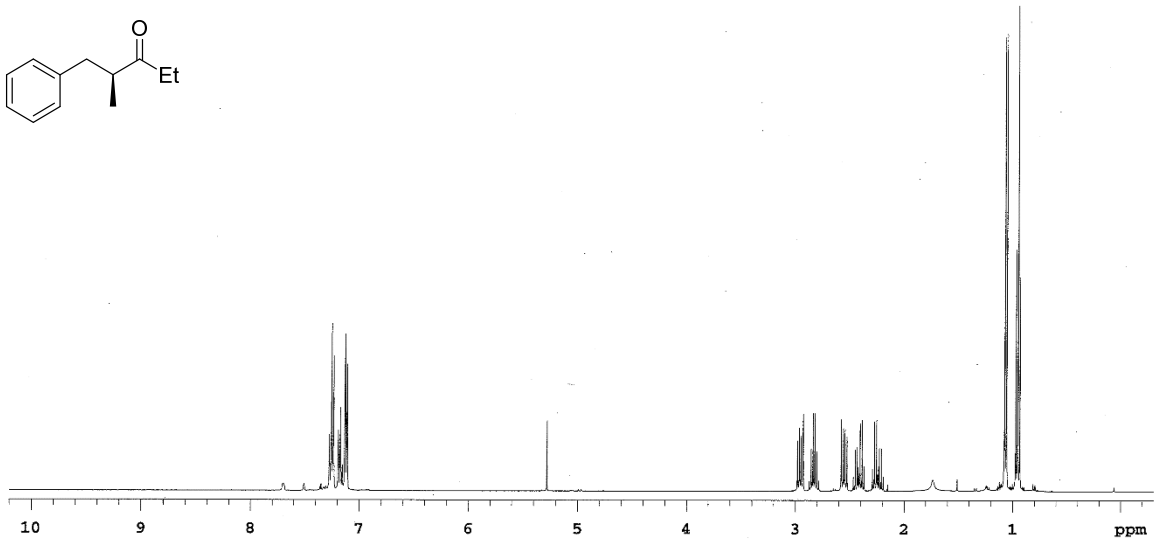


Figure S236. ^{1}H NMR of 2-methyl-1-phenylpentan-3-one

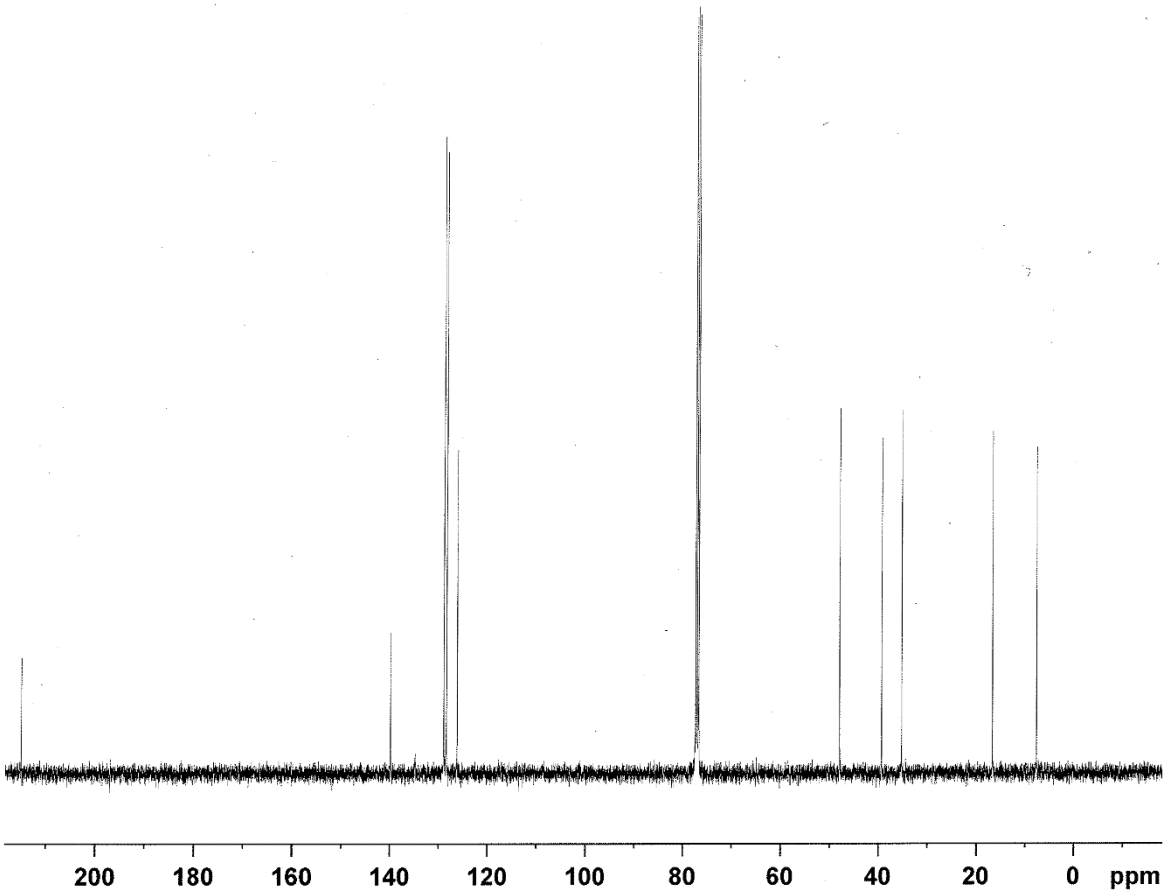
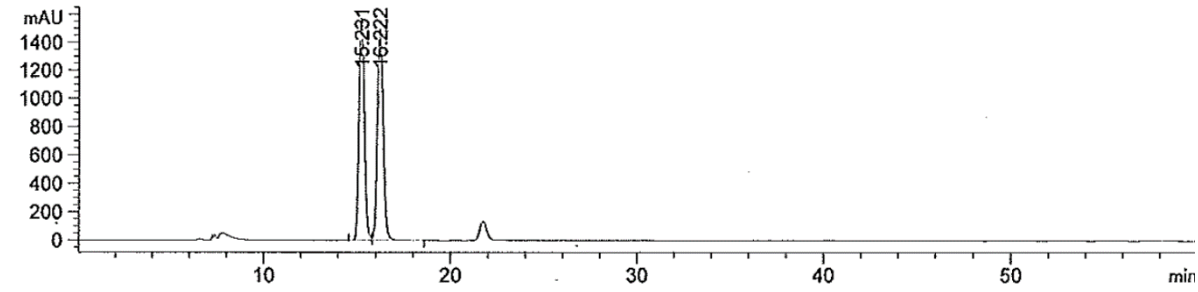


Figure S237. ^{13}C NMR of 2-methyl-1-phenylpentan-3-one

a)



b)

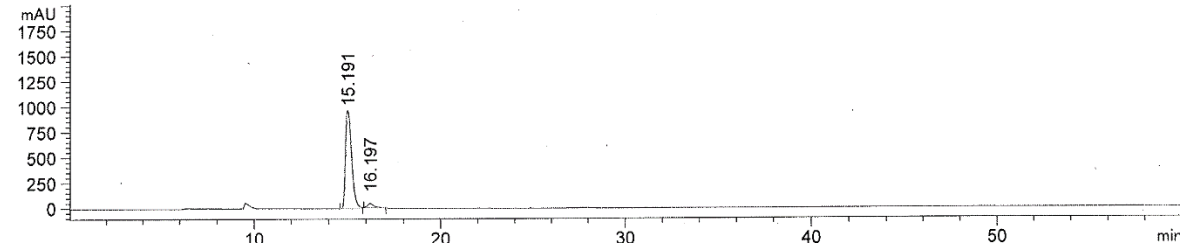


Figure S238. HPLC traces of (a) racemic and (b) enantioenriched product (97% (*S*) ee using Ir-**L4e** catalytic system; Figure 2, substrate **S17**)

(S)-2,4-Dimethyl-1-phenylpentan-3-one

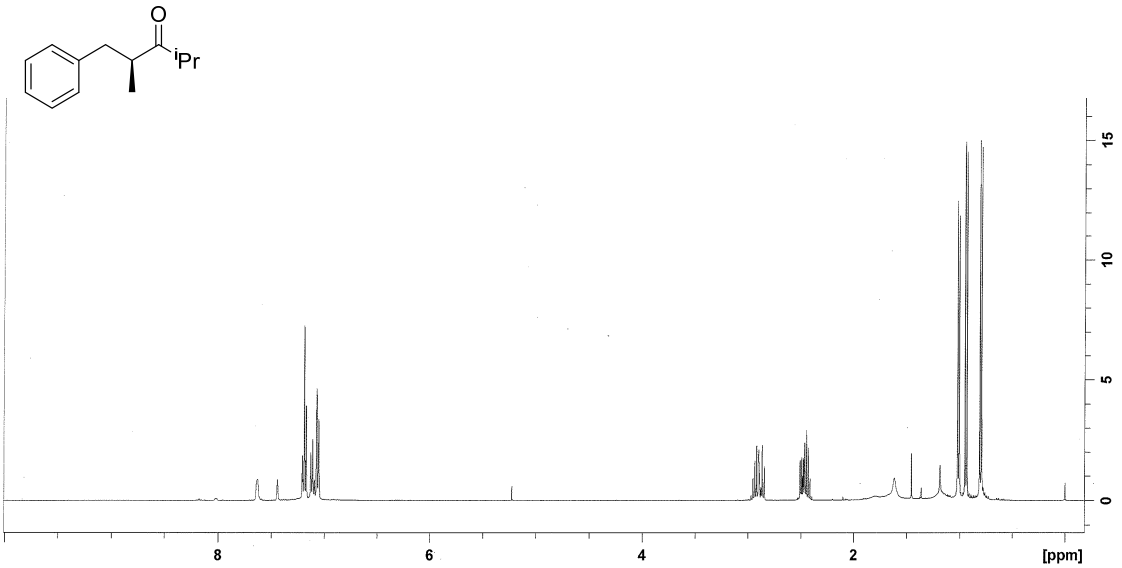


Figure S239. ^{1}H NMR of 2,4-dimethyl-1-phenylpentan-3-one

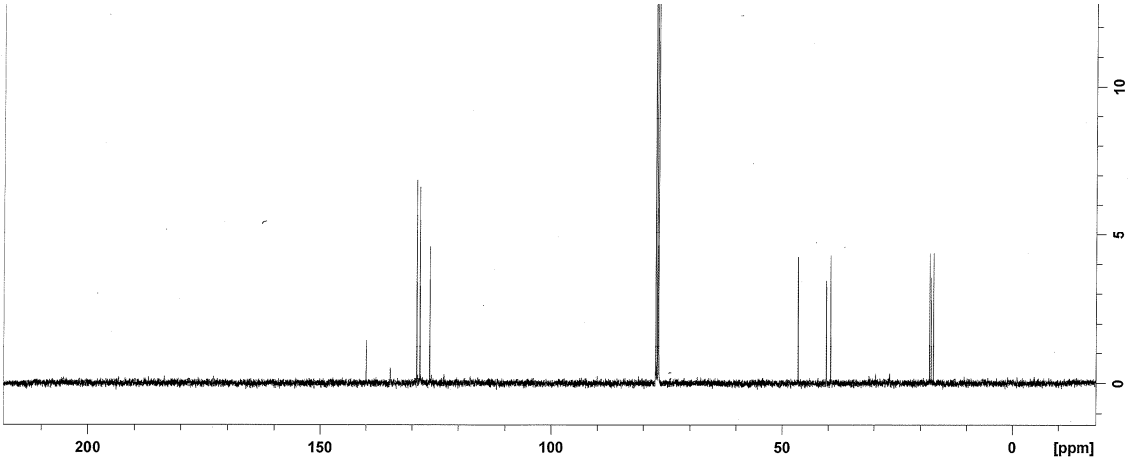
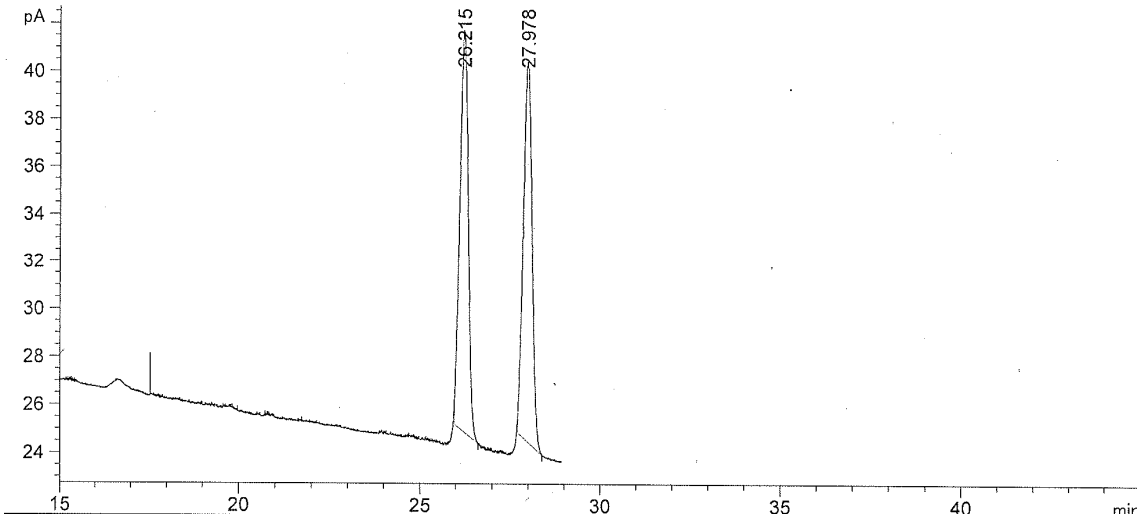


Figure S240. ^{13}C NMR of 2,4-dimethyl-1-phenylpentan-3-one

a)



b)

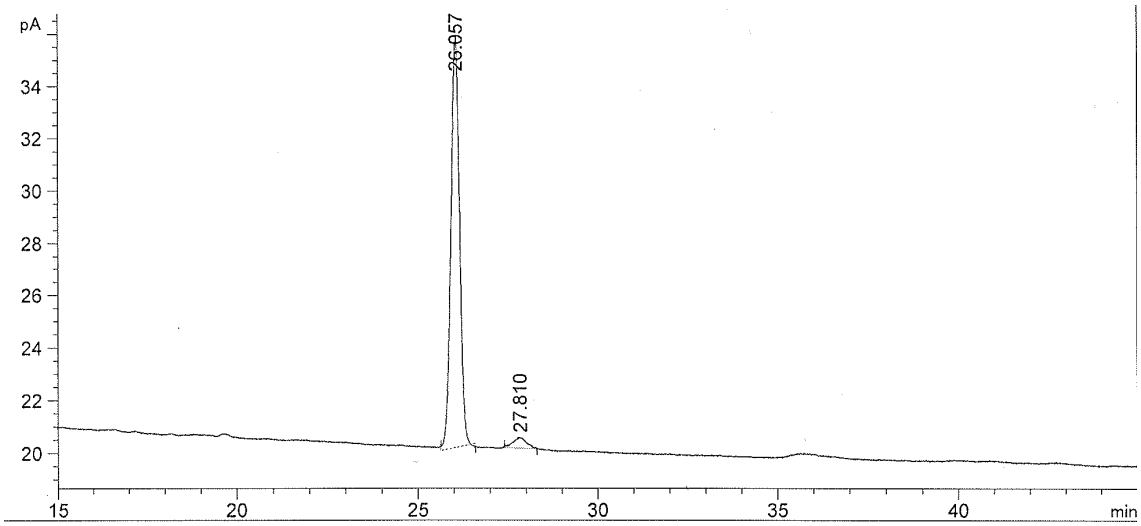


Figure S241. HPLC traces of (a) racemic and (b) enantioenriched product (96% (*R*) ee using Ir-**L5d** catalytic system; Figure 2, substrate **S18**)

(S)-2-Methyl-1,3-diphenylpropan-1-one

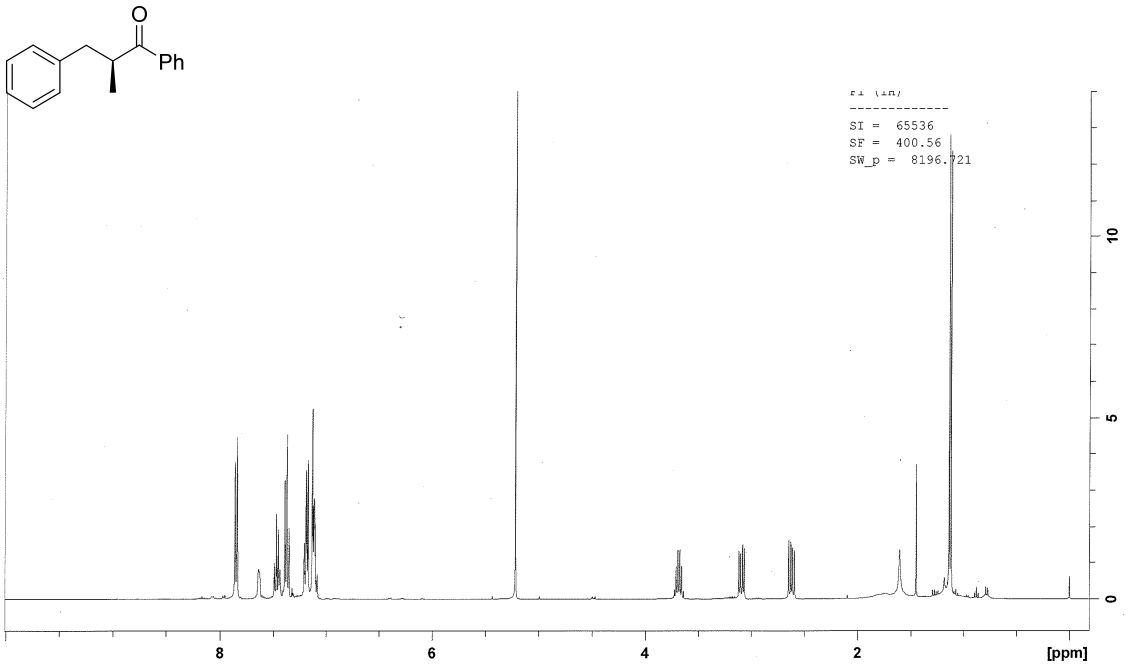


Figure S242. ^{1}H NMR of 2-methyl-1,3-diphenylpropan-1-one

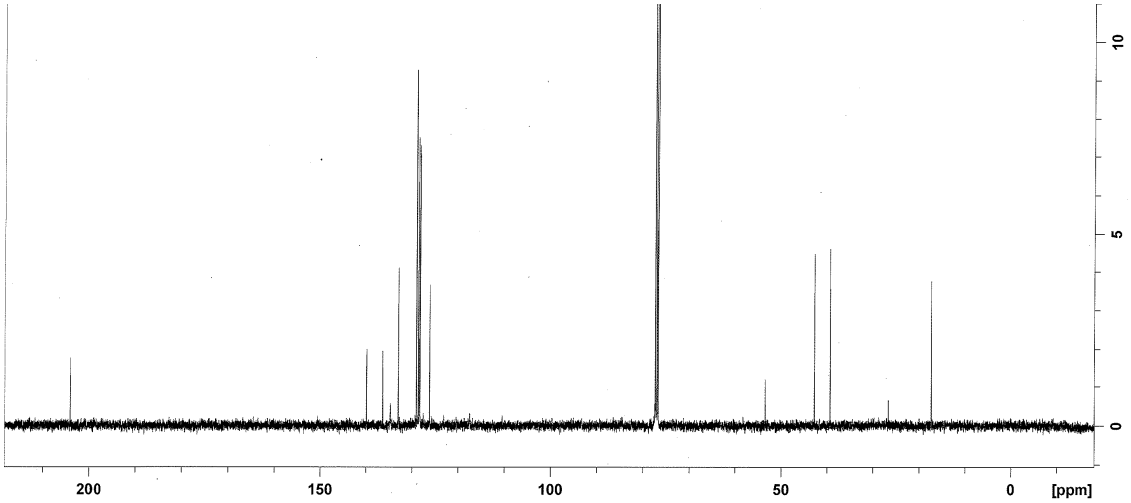
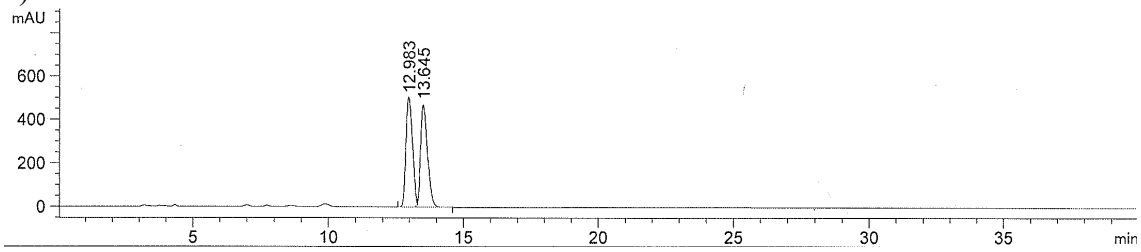


Figure S243. ^{13}C NMR of 2-methyl-1,3-diphenylpropan-1-one

a)



b)

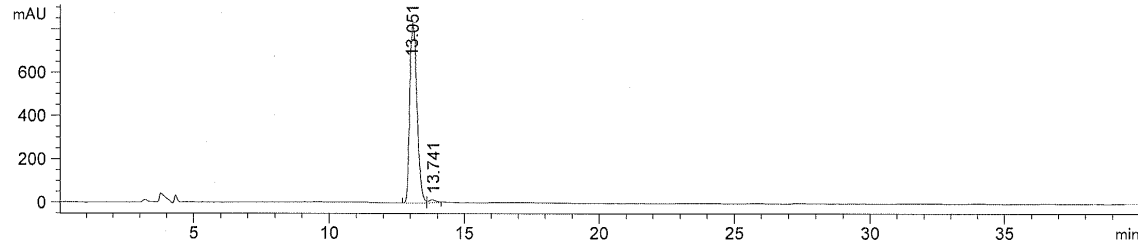


Figure S244. HPLC traces of (a) racemic and (b) enantioenriched product (97% (*S*) ee using Ir-**L4e** catalytic system; Figure 2, substrate **S19**)

(S)-2-Benzylcyclohexanone

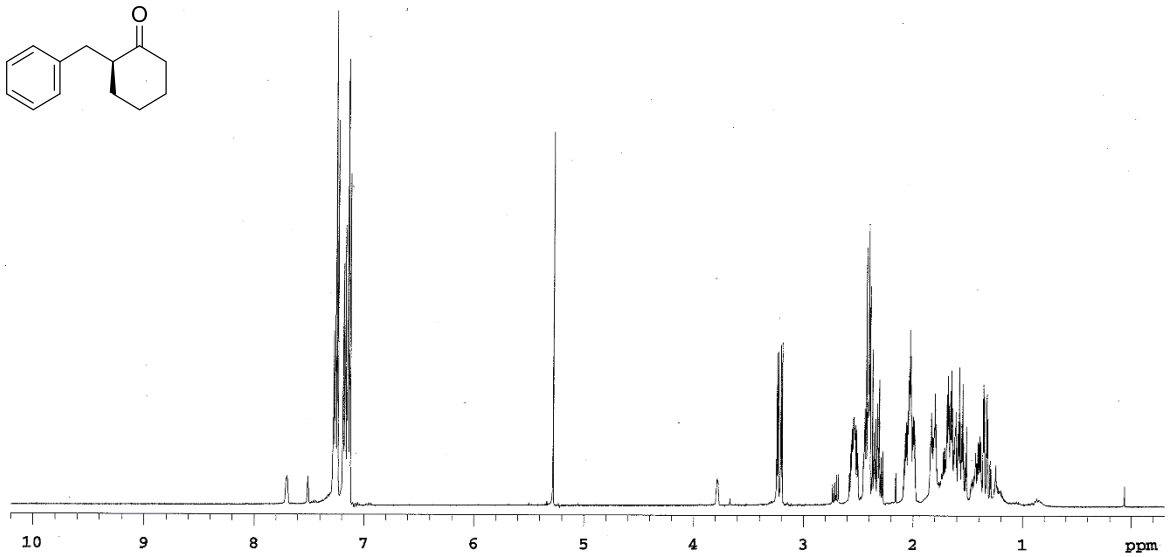


Figure S245. ^{1}H NMR of 2-benzylcyclohexanone

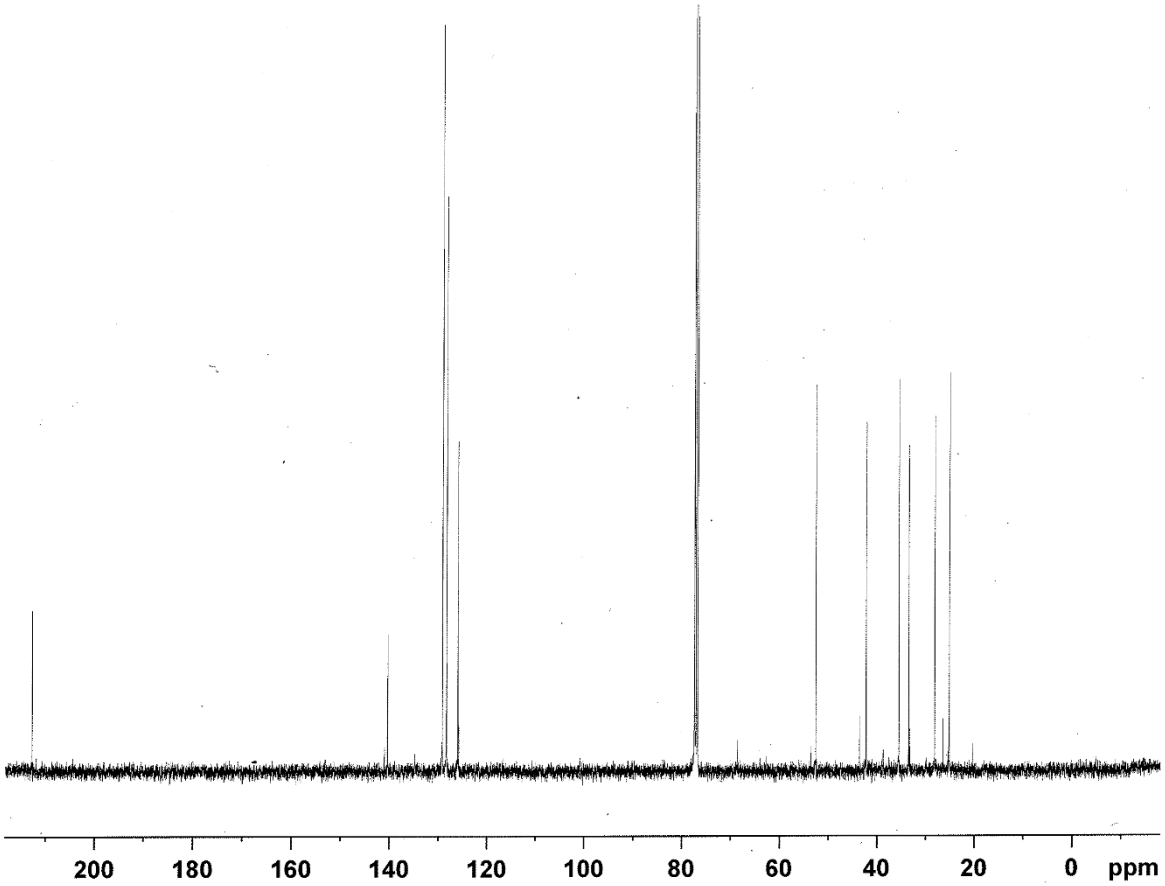
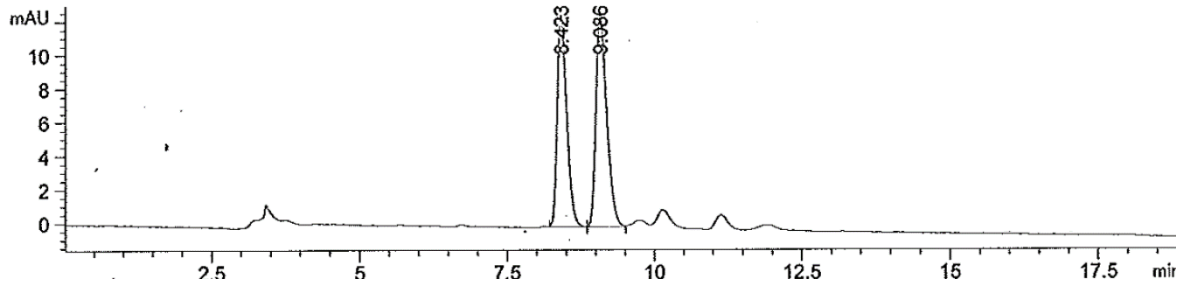


Figure S246. ^{13}C NMR of 2-benzylcyclohexanone

a)



b)

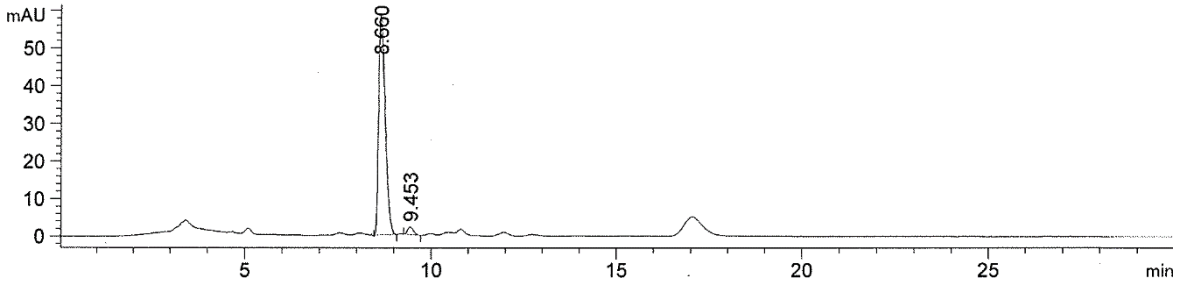


Figure S247. HPLC traces of (a) racemic and (b) enantioenriched product (98% (*S*) ee using Ir-**L4e** catalytic system; Figure 2, substrate **S20**)

(R)-1-Acetyl-3-benzylpiperidin-2-one

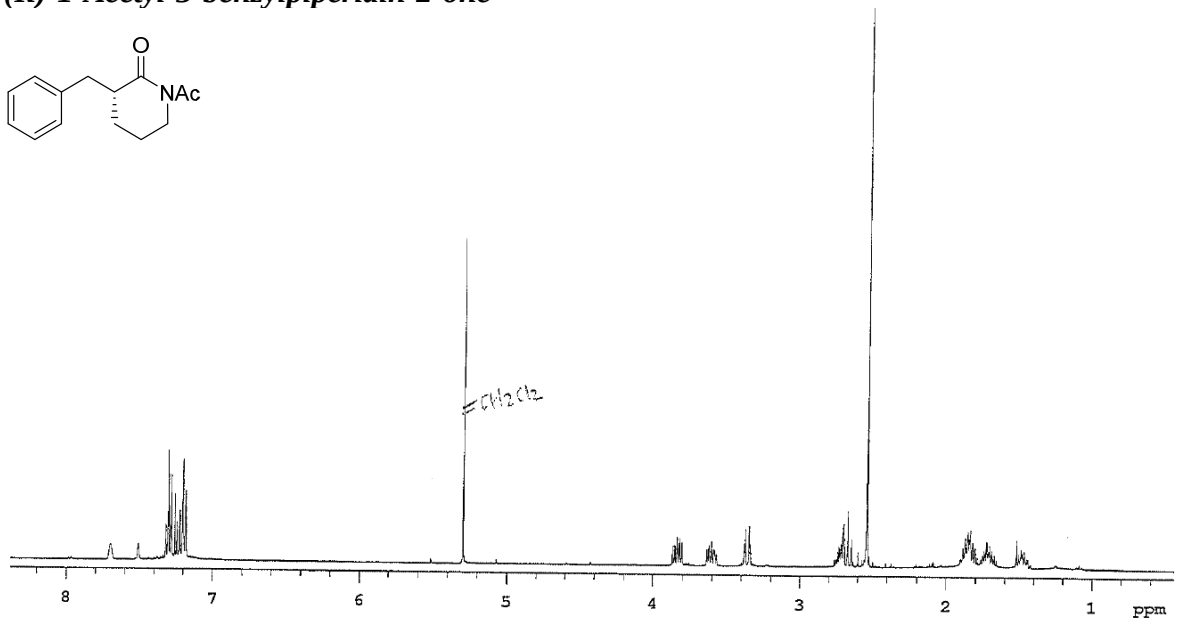


Figure S248. ^{1}H NMR of 1-acetyl-3-benzylpiperidin-2-one

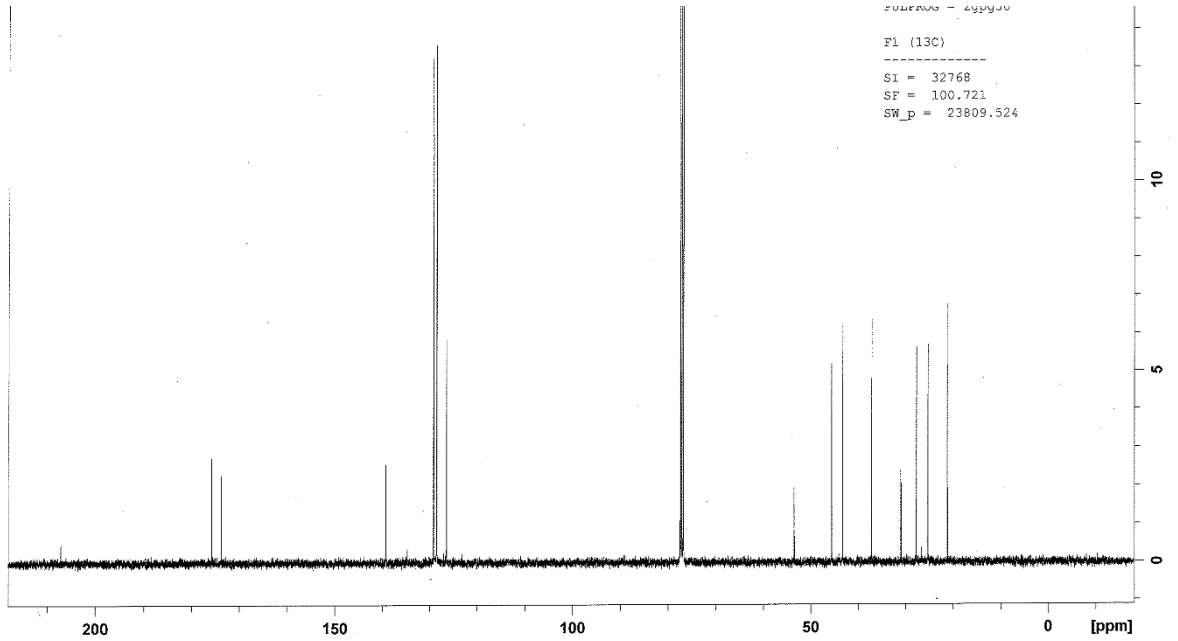
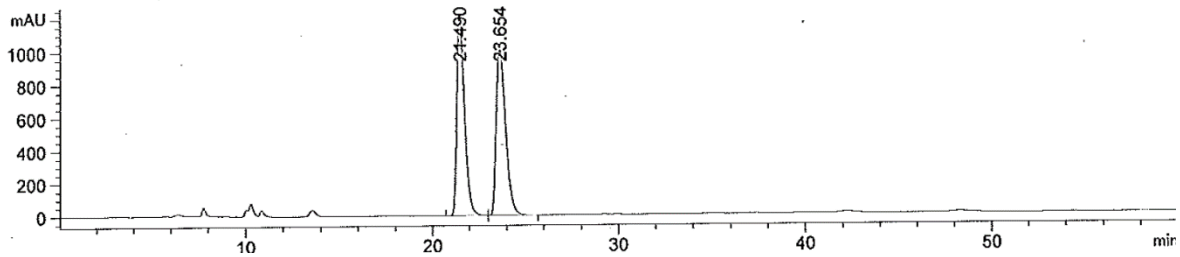


Figure S249. ^{13}C NMR of 1-acetyl-3-benzylpiperidin-2-one

a)



b)

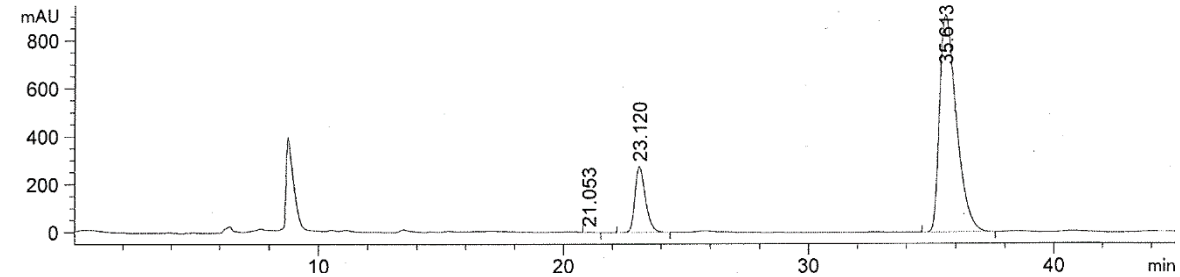


Figure S250. HPLC traces of (a) racemic and (b) enantioenriched product (>99% (*R*) ee using Ir-**L4e** catalytic system; Figure 2, substrate **S21**)

(R)-1,3-Dibenzylpiperidin-2-one

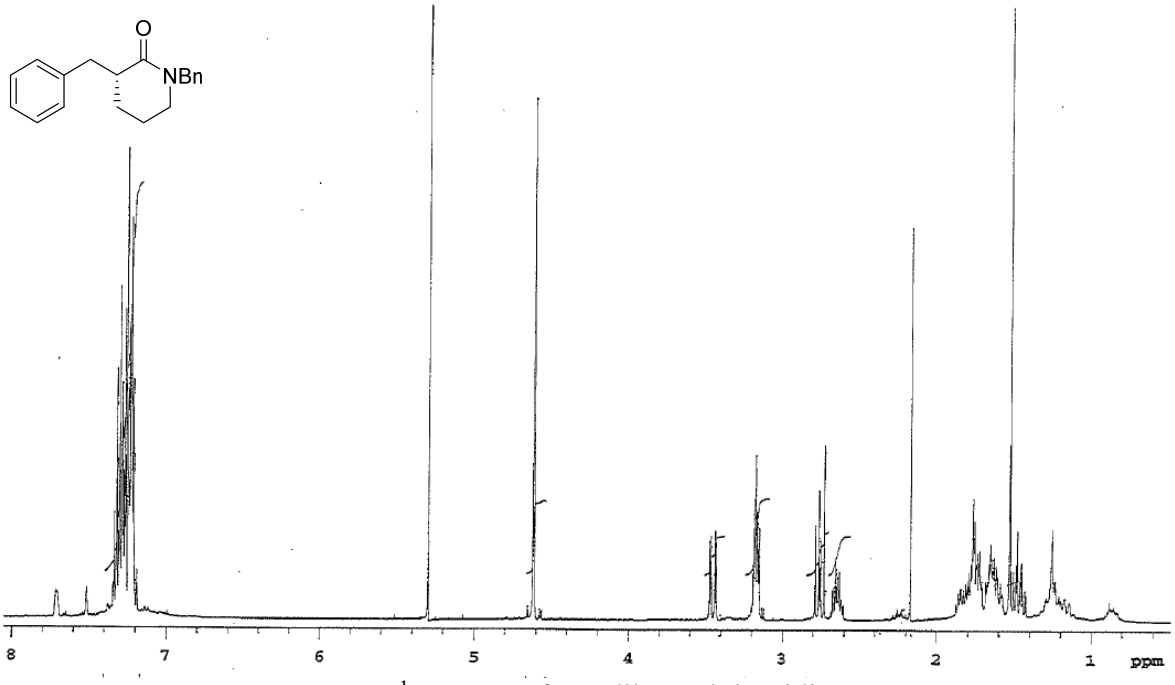


Figure S251. ^{1}H NMR of 1,3-dibenzylpiperidin-2-one

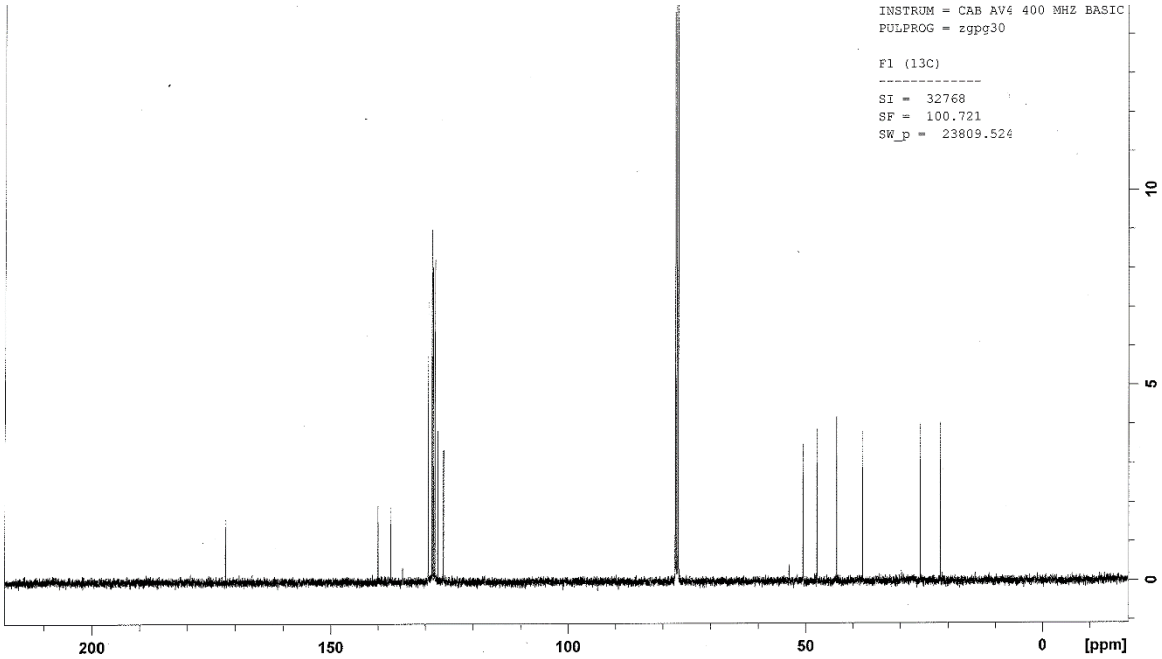
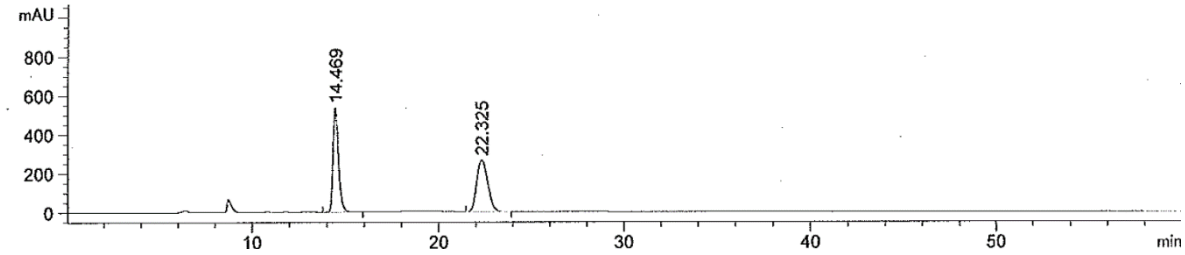


Figure S252. ^{13}C NMR of 1,3-dibenzylpiperidin-2-one

a)



b)

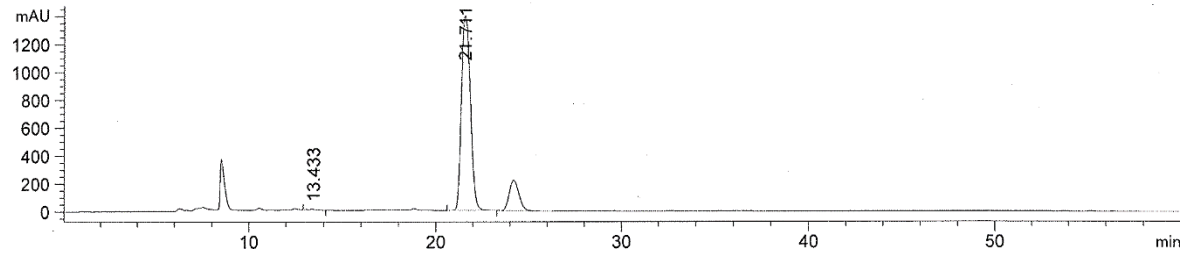


Figure S253. HPLC traces of (a) racemic and (b) enantioenriched product (>99% (+) ee using Ir-**L4e** catalytic system; Figure 2, substrate **S22**)

(S)-1-Benzyl-3-(cyclohexylmethyl)piperidin-2-one

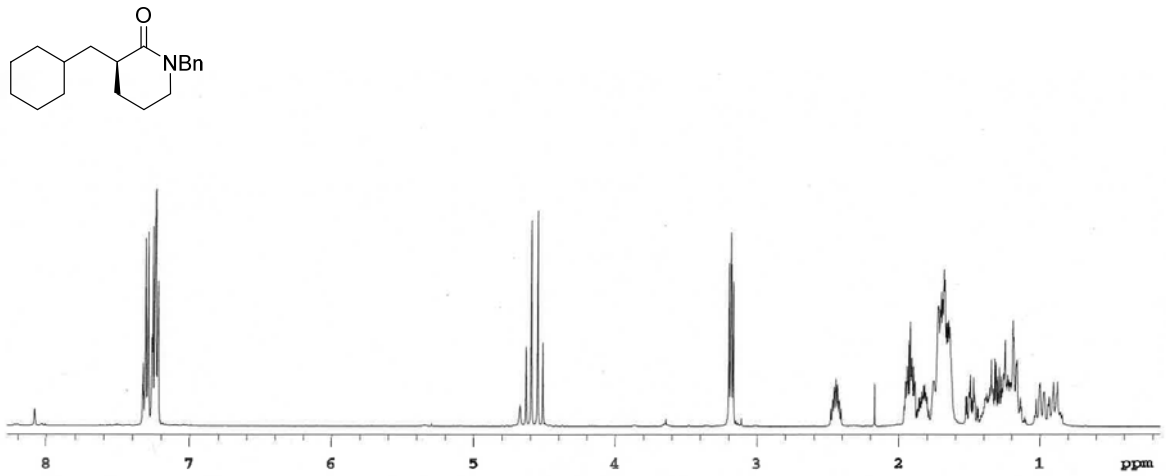


Figure S254. ^{1}H NMR of 1-benzyl-3-(cyclohexylmethyl)piperidin-2-one

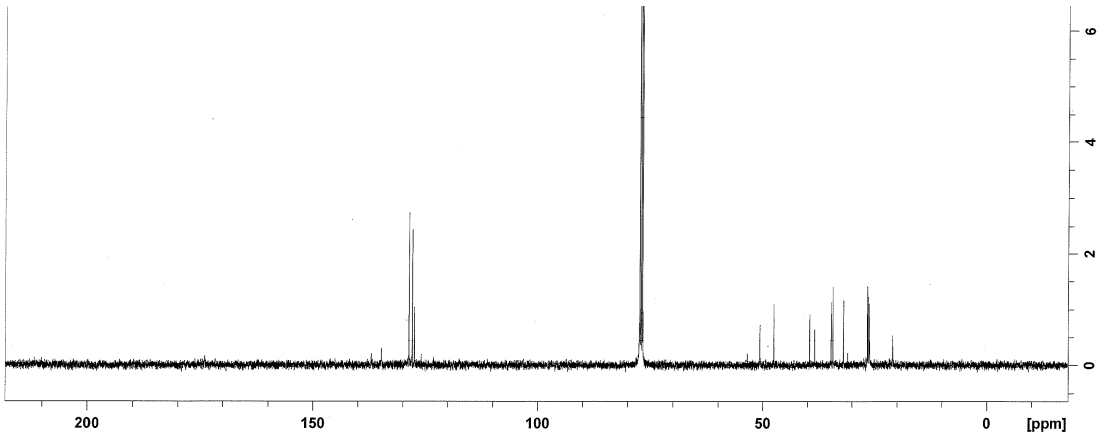
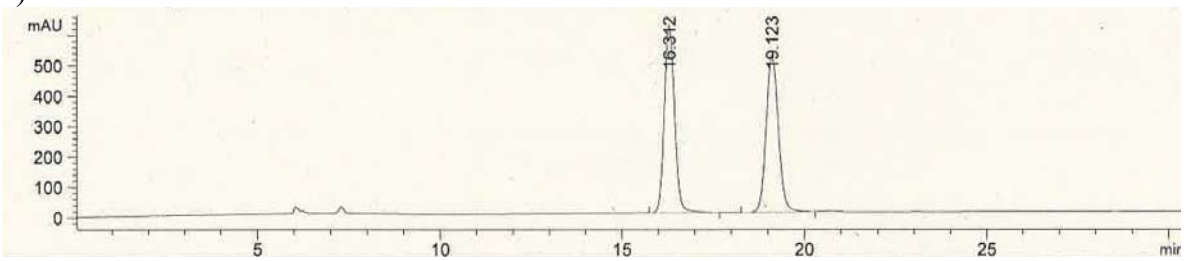


Figure S255. ^{13}C NMR of 1-benzyl-3-(cyclohexylmethyl)piperidin-2-one

a)



b)

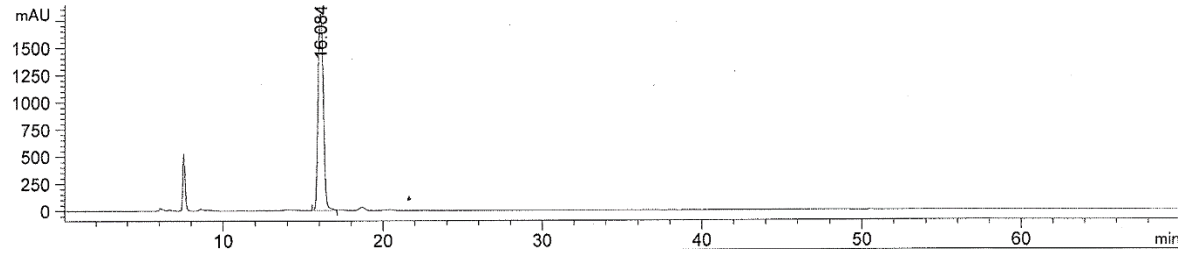


Figure S256. HPLC traces of (a) racemic and (b) enantioenriched product (>99% (*S*) ee using Ir-**L5d** catalytic system; Figure 2, substrate **S23**)

(S)-2,2'-(1-Phenylethane-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane)

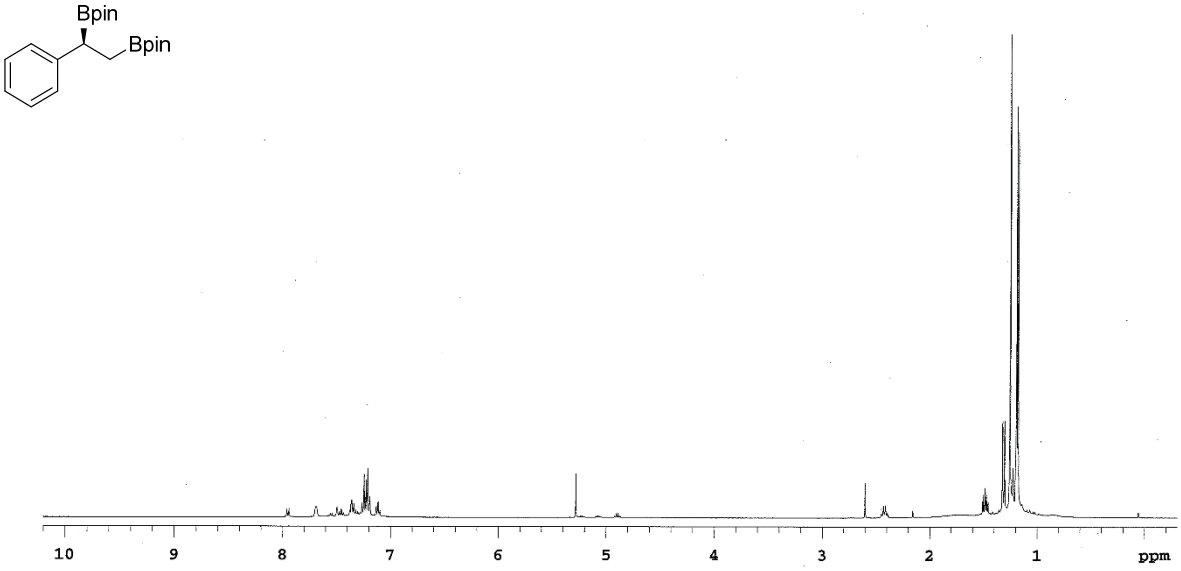


Figure S257. ^{1}H NMR of 2,2'-(1-phenylethane-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane)

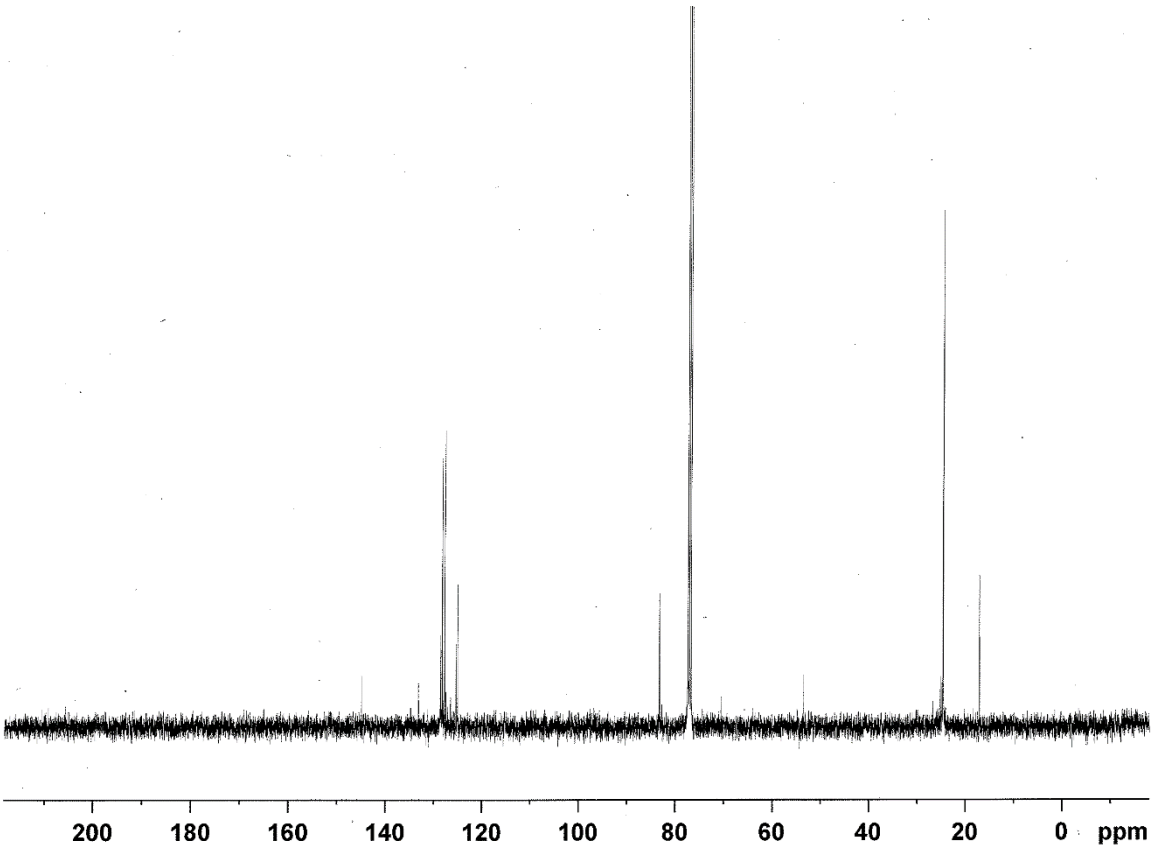
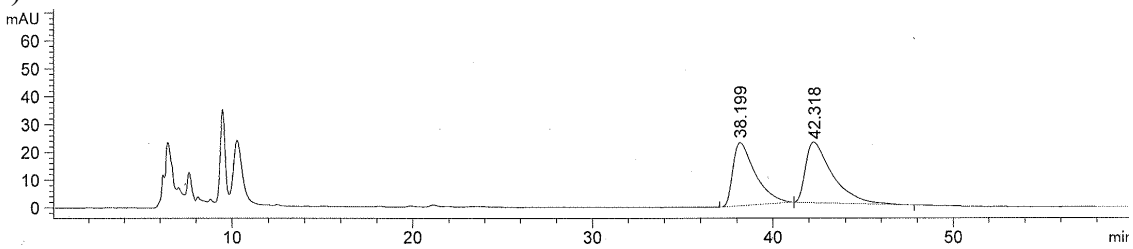


Figure S258. ^{13}C NMR of 2,2'-(1-phenylethane-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane)

a)



b)

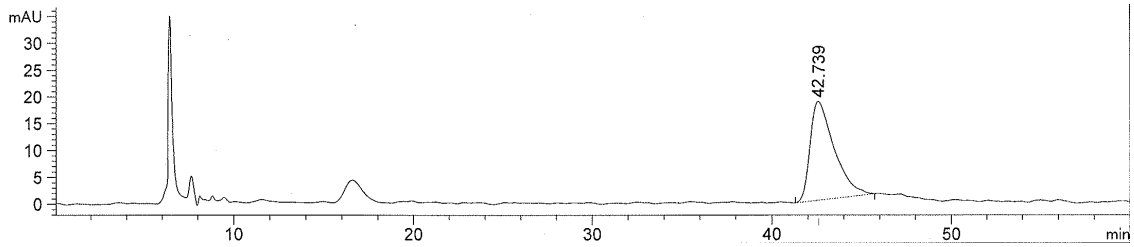


Figure S259. HPLC traces of (a) racemic and (b) enantioenriched product (99% (*S*) ee using Ir-**L1d** catalytic system; Figure 2, substrate **S24**)

(S)-2,2'-(1-(4-Fluorophenyl)ethane-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane)

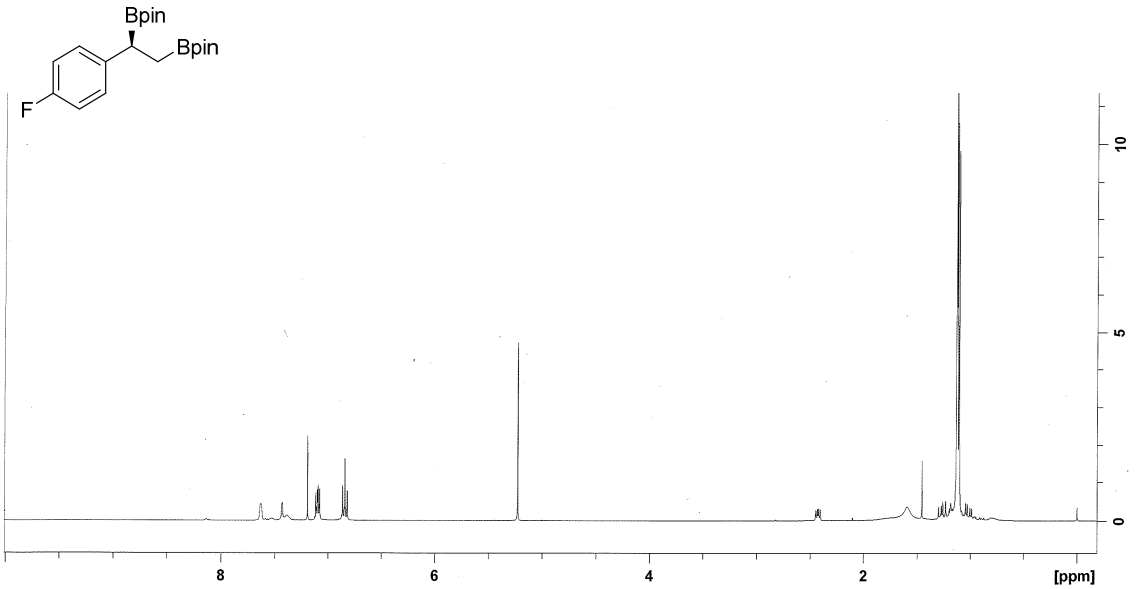


Figure S260. ^{1}H NMR of 2,2'-(1-(4-fluorophenyl)ethane-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane)

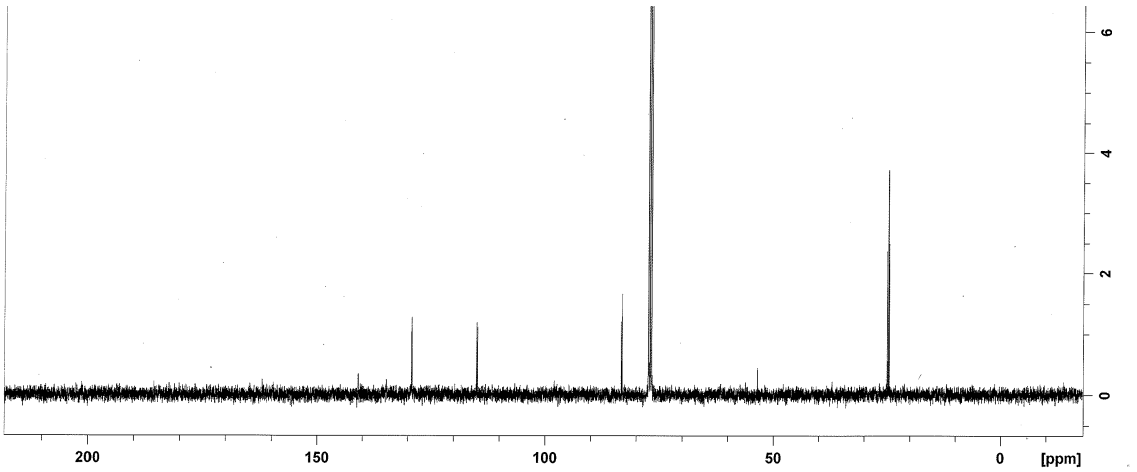
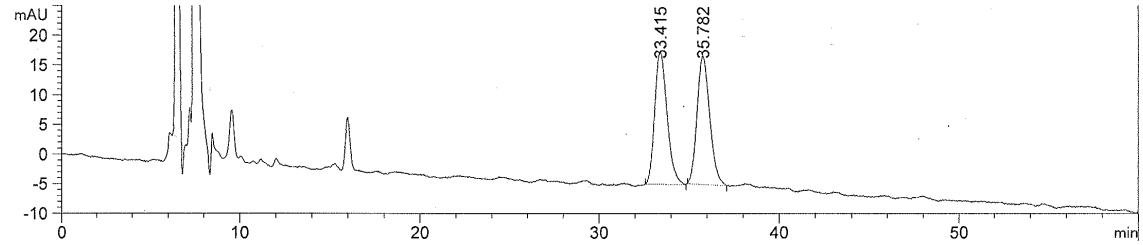


Figure S261. ^{1}H NMR of 2,2'-(1-(4-fluorophenyl)ethane-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane)

a)



b)

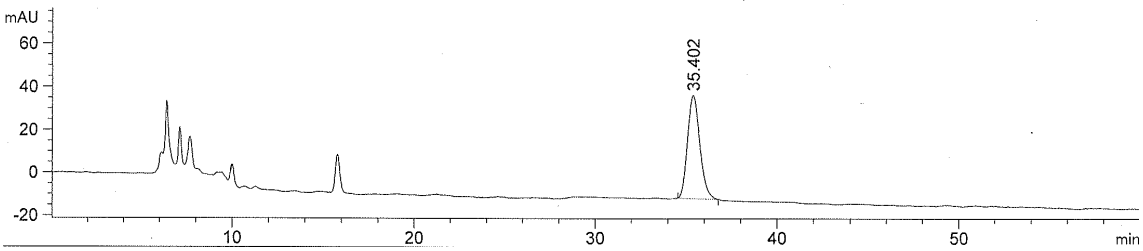


Figure S262. HPLC traces of (a) racemic and (b) enantioenriched product (99% (*S*) ee using Ir-**L1d** catalytic system; Figure 2, substrate **S25**)

(S)-2,2'-(1-(4-Methoxyphenyl)ethane-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane)

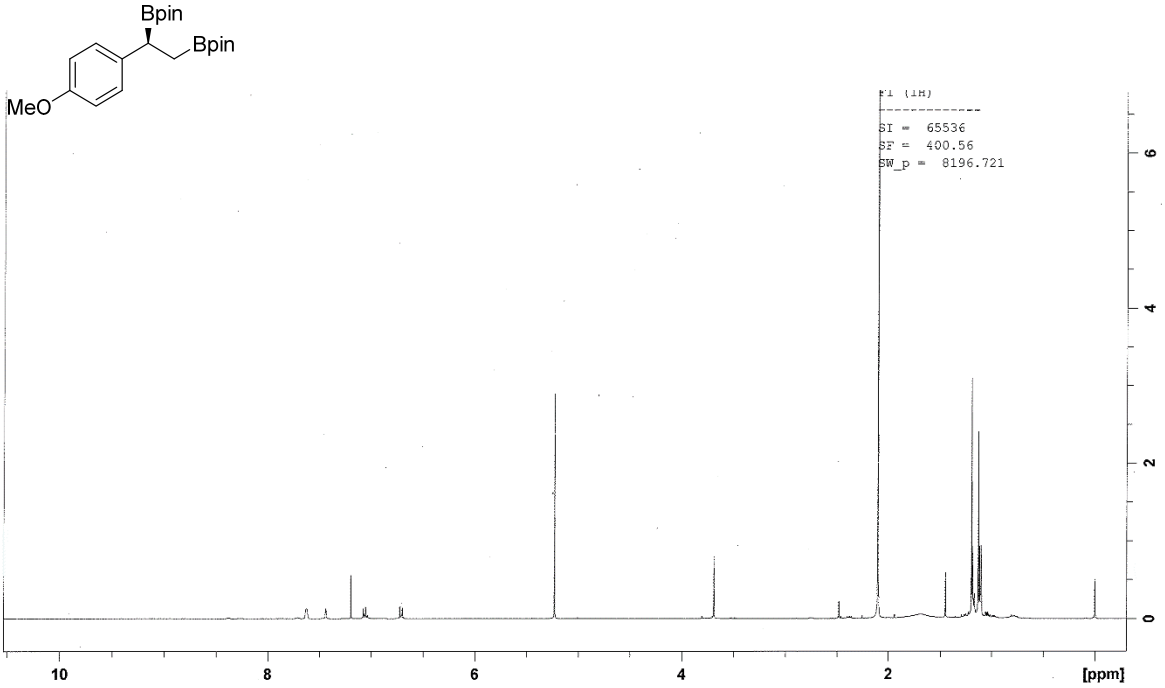


Figure S263. ^{1}H NMR of 2,2'-(1-(4-methoxyphenyl)ethane-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane)

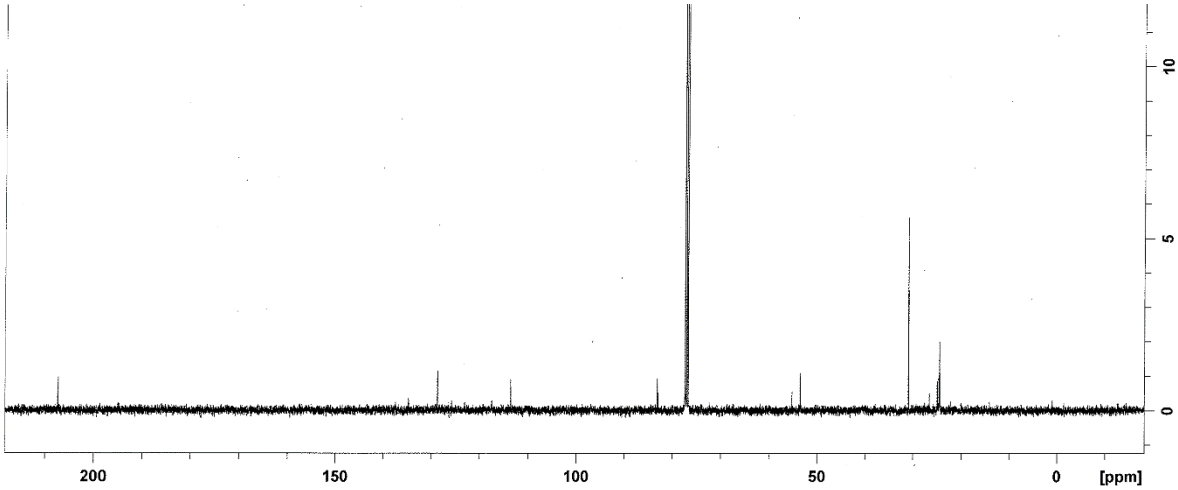
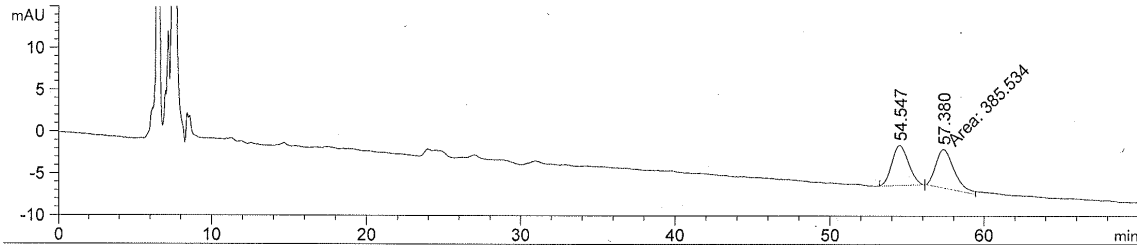


Figure S264. ^{13}C NMR of 2,2'-(1-(4-methoxyphenyl)ethane-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane)

a)



b)

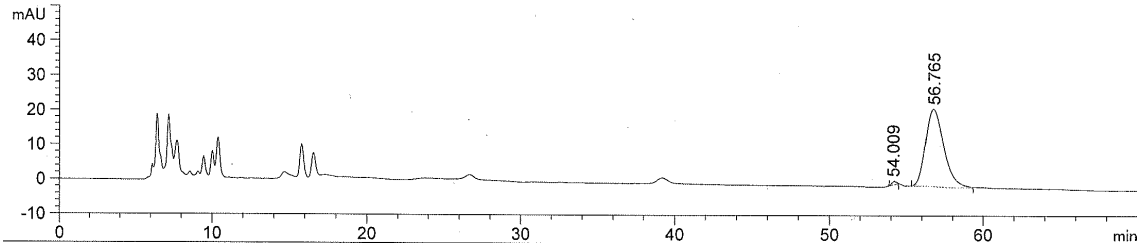


Figure S265. HPLC traces of (a) racemic and (b) enantioenriched product (98% (*S*) ee using Ir-**L1d** catalytic system; Figure 2, substrate **S26**)

(+)-2-(1,2-Diphenylethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

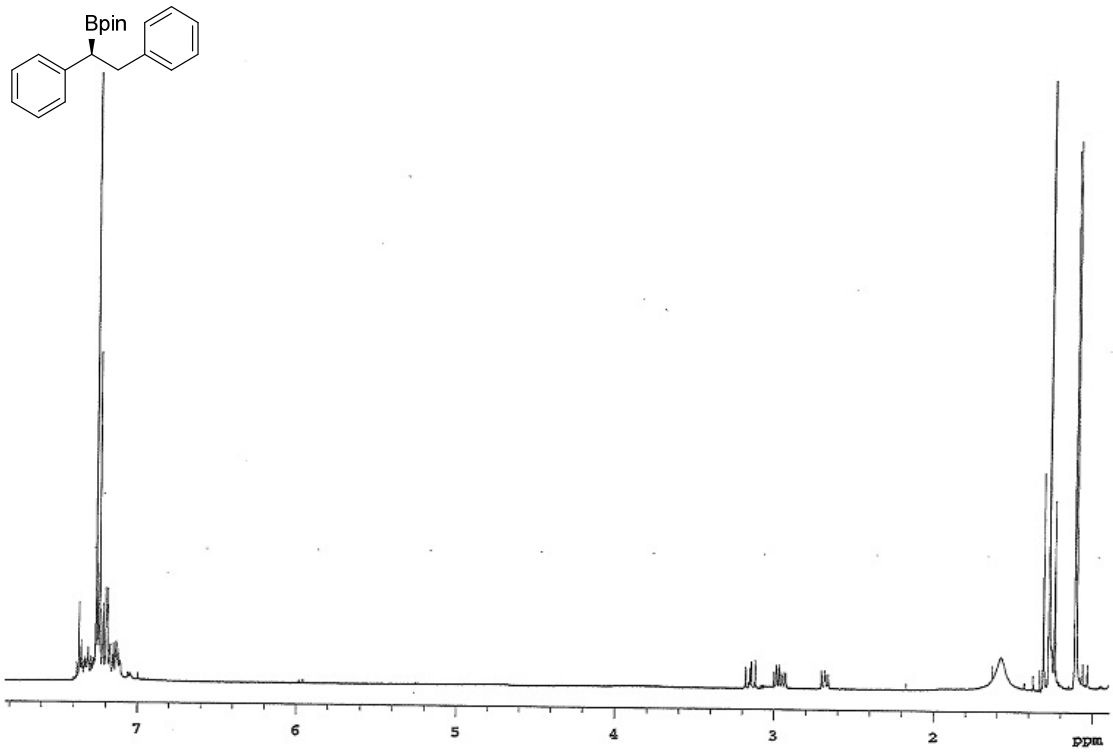


Figure S266. ^{1}H NMR of 2-(1,2-diphenylethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

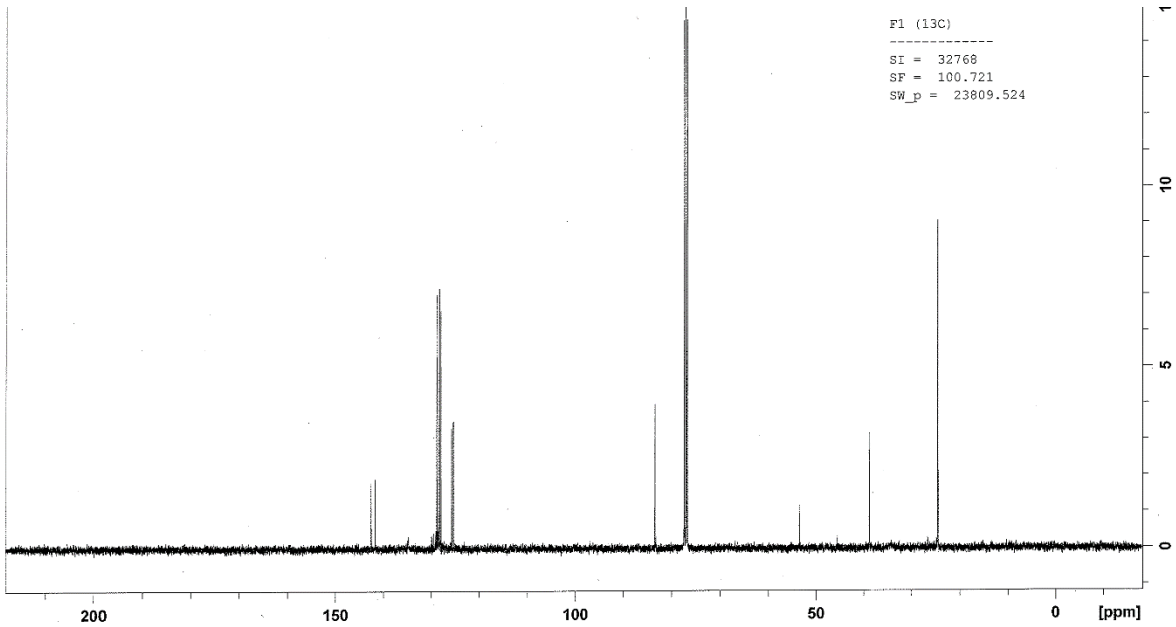
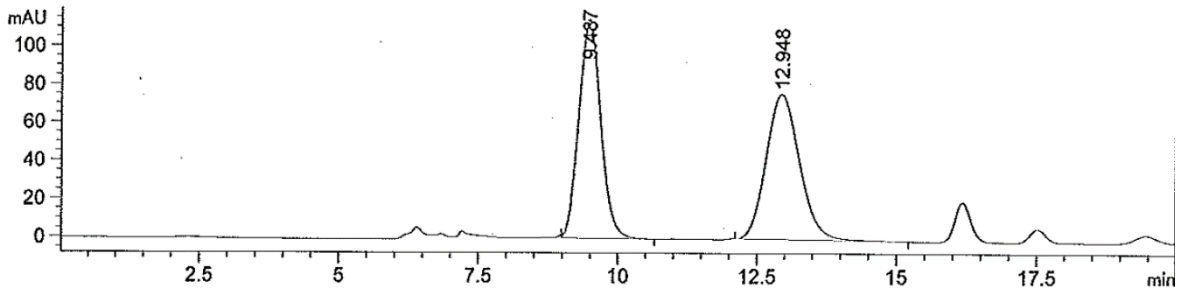


Figure S267. ^{13}C NMR of 2-(1,2-diphenylethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

a)



b)

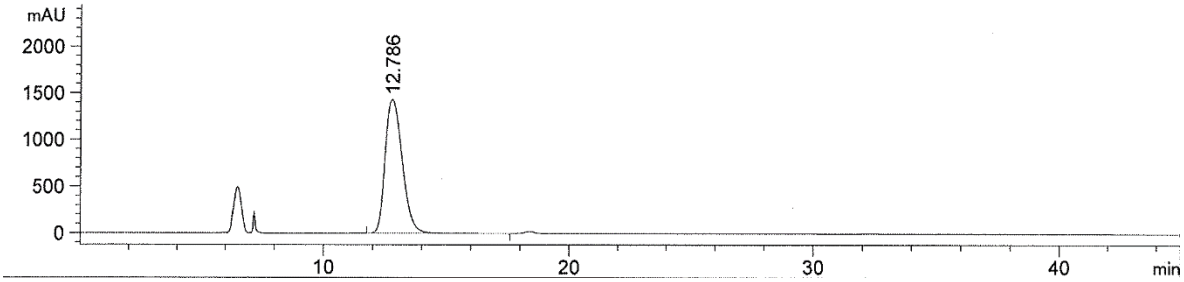


Figure S268. HPLC traces of (a) racemic and (b) enantioenriched product (>99% (+) ee using Ir-**L1d** catalytic system; Figure 2, substrate **S27**)

(R)-1-Phenylpropyl diphenylphosphinate

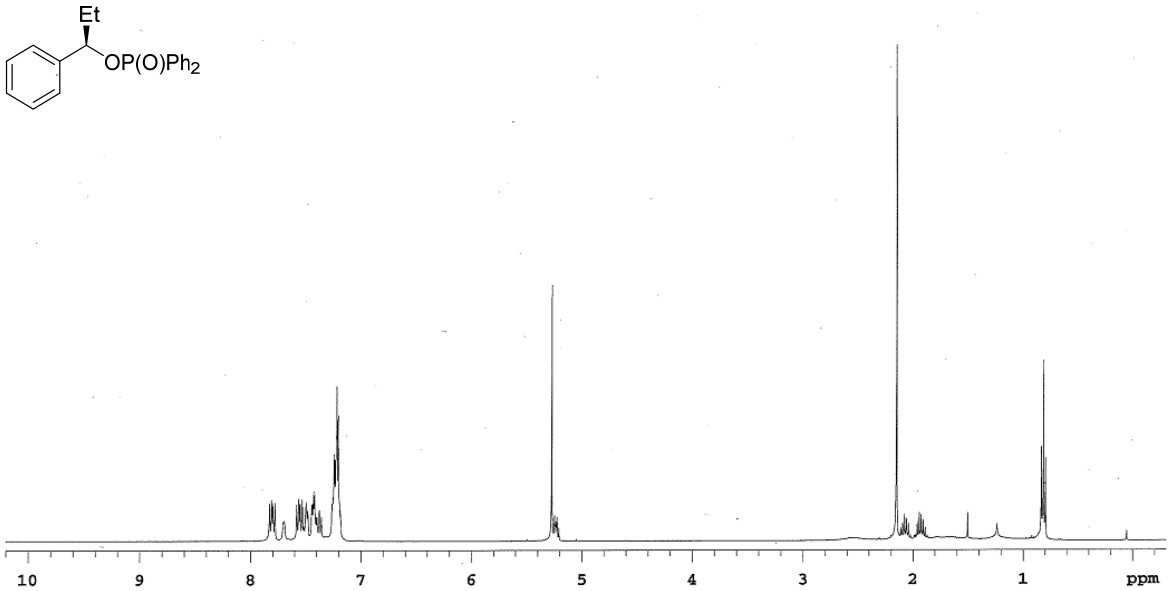


Figure S269. ^{1}H NMR of 1-phenylpropyl diphenylphosphinate

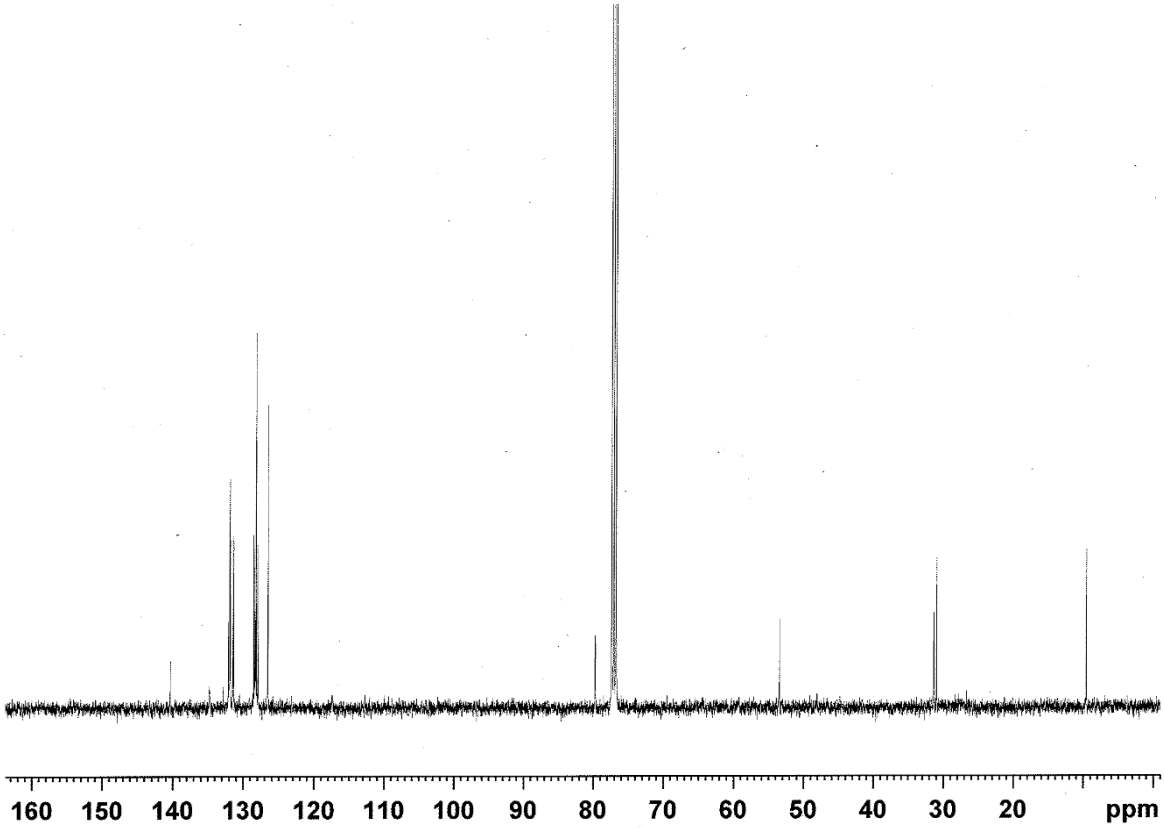
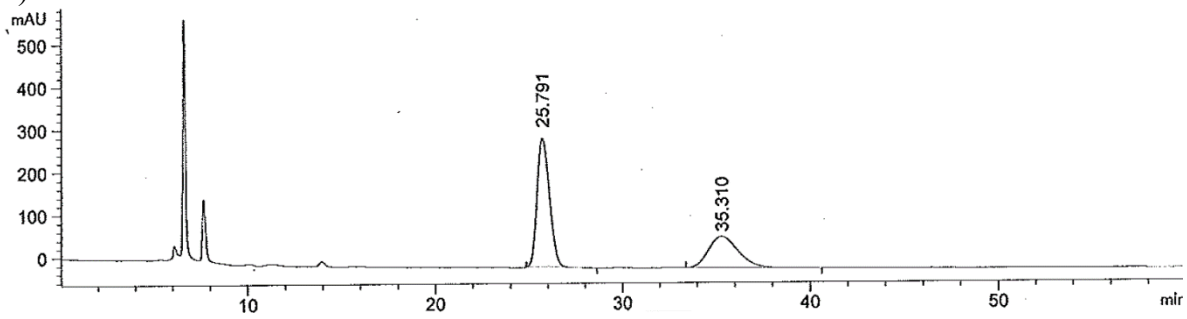


Figure S270. ^{13}C NMR of 1-phenylpropyl diphenylphosphinate

a)



b)

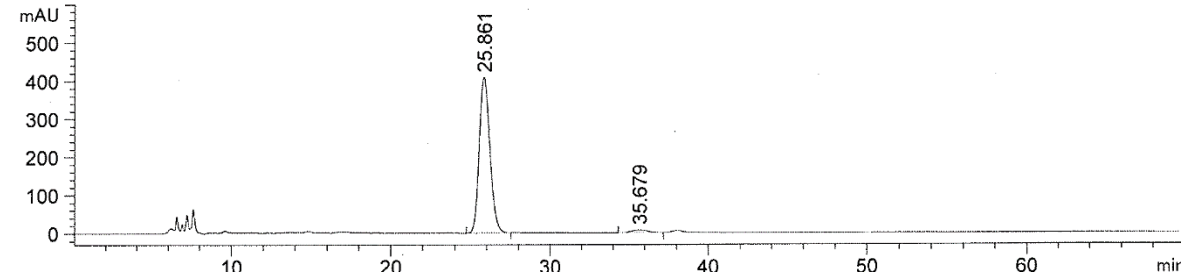
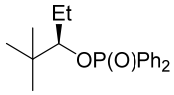


Figure S271. HPLC traces of (a) racemic and (b) enantioenriched product (98% (*R*) ee using Ir-**L1b** catalytic system; Figure 2, substrate **S28**)

(R)-2,2-Dimethylpentan-3-yl diphenylphosphinate



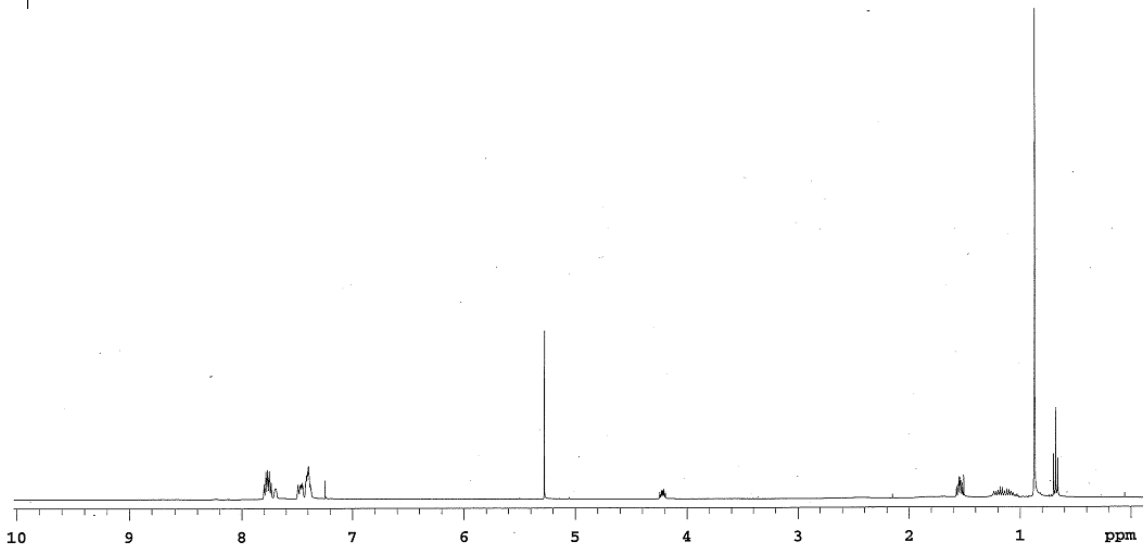


Figure S272. ^{1}H NMR of 2,2-dimethylpentan-3-yl diphenylphosphinate.

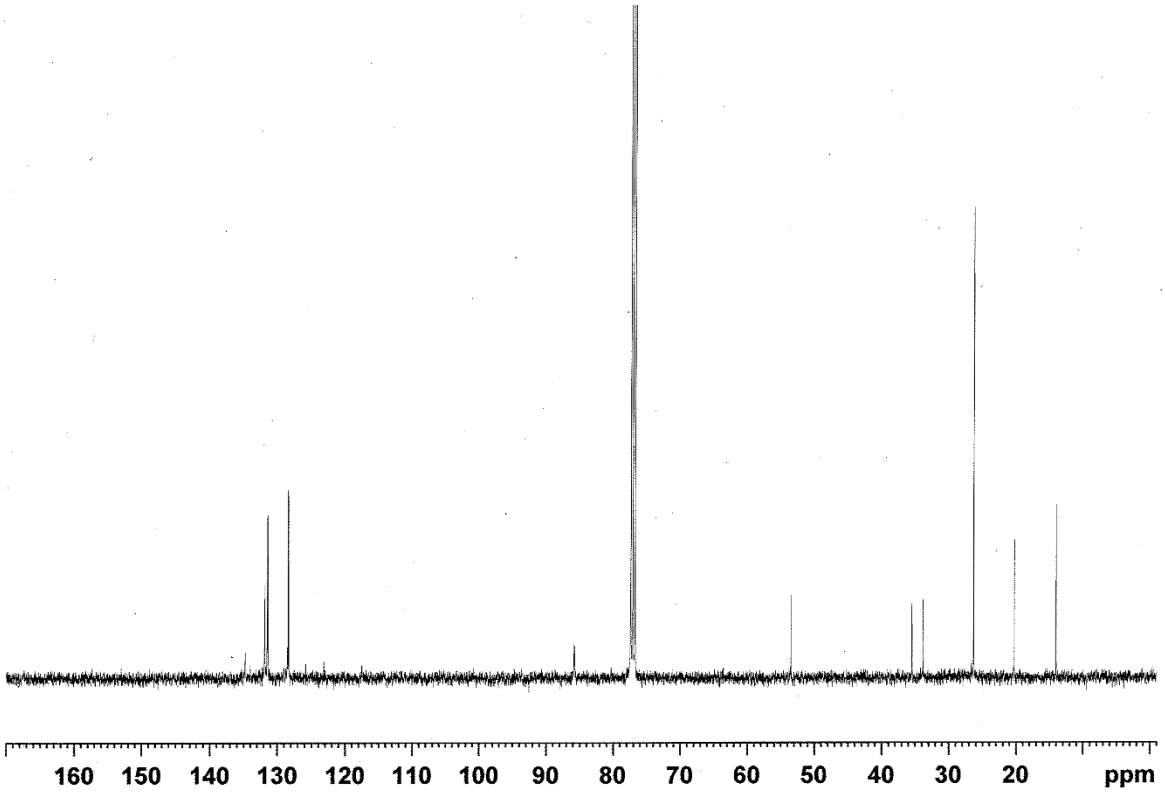


Figure S273. ^{13}C NMR of 2,2-dimethylpentan-3-yl diphenylphosphinate.

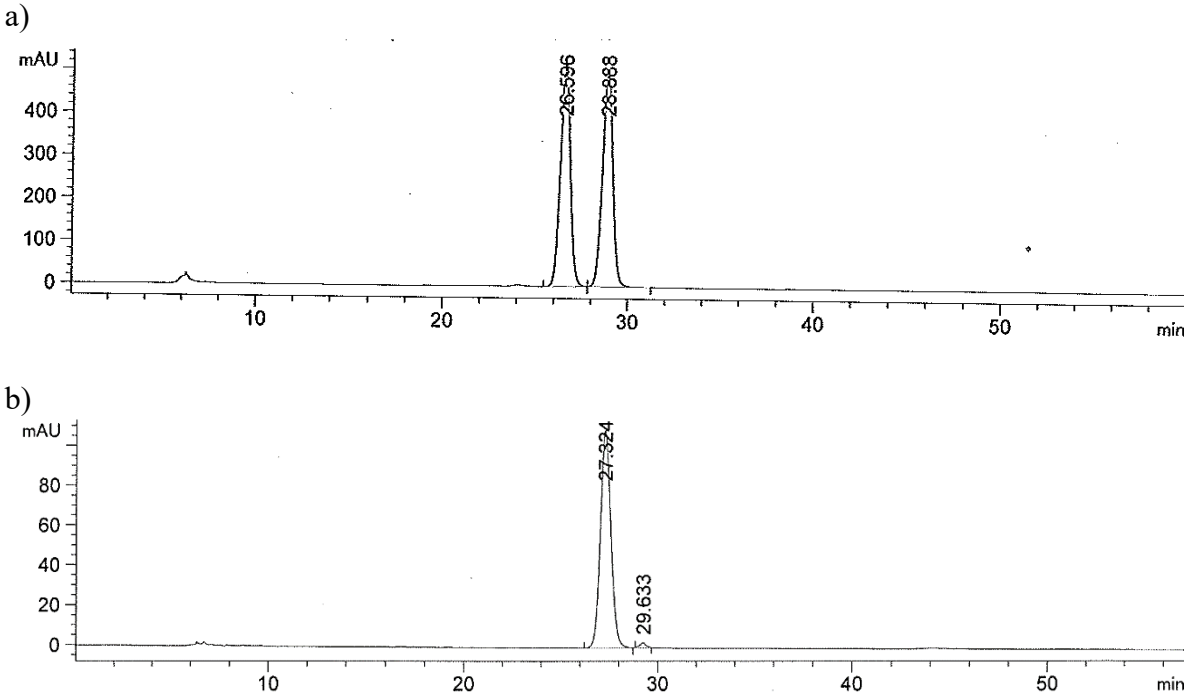
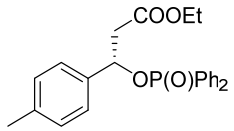


Figure S274. HPLC traces of (a) racemic and (b) enantioenriched product (98% (*R*) ee using Ir-**L1b** catalytic system; Figure 2, substrate **S29**)

(S)-Ethyl 3-((diphenylphosphoryl)oxy)-3-(p-tolyl)propanoate



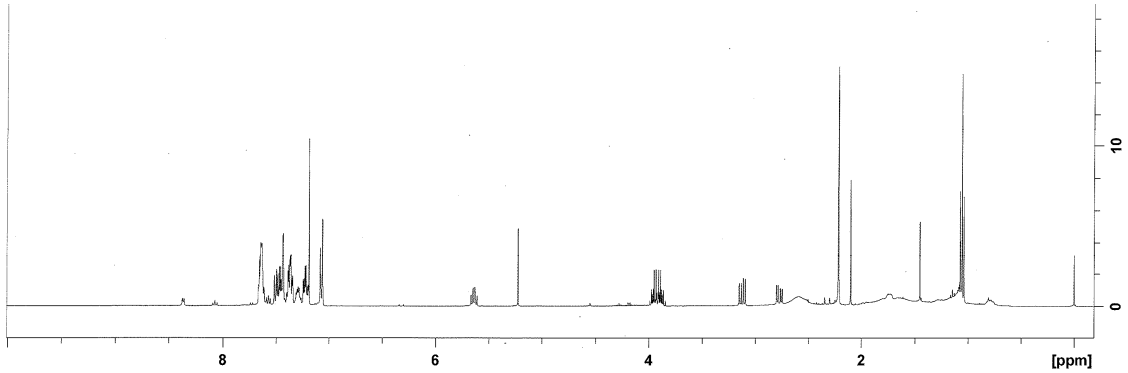


Figure S275. ^{1}H NMR of ethyl 3-((diphenylphosphoryl)oxy)-3-(*p*-tolyl)propanoate.

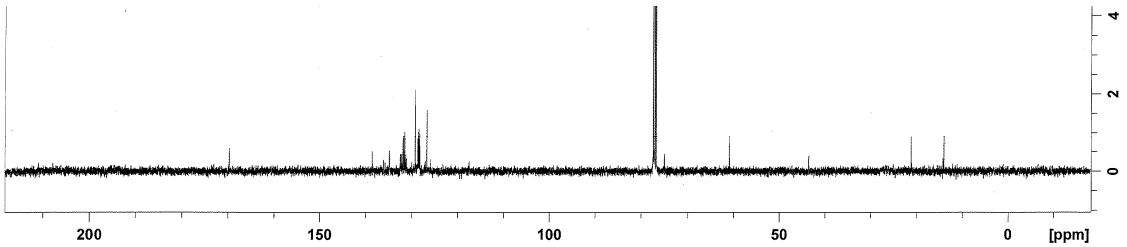
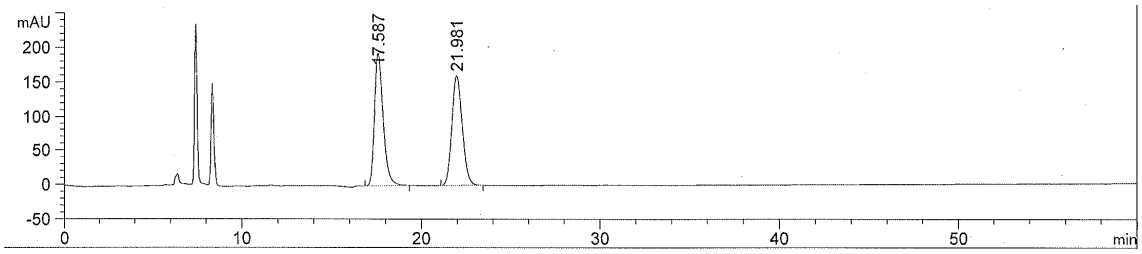


Figure S276. ^{1}H NMR of ethyl 3-((diphenylphosphoryl)oxy)-3-(*p*-tolyl)propanoate.

a)



b)

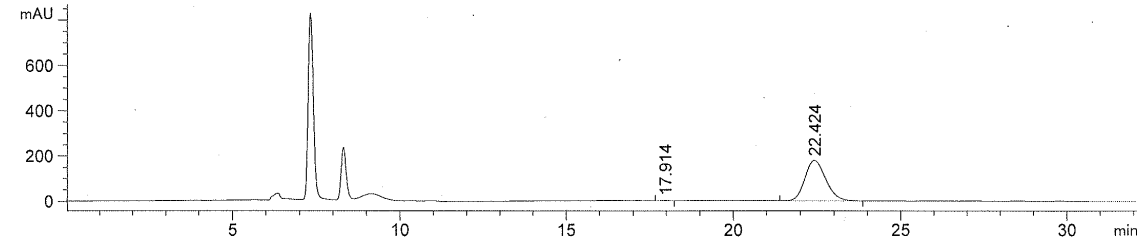


Figure S277. HPLC traces of (a) racemic and (b) enantioenriched product (97% (*S*) ee using Ir-**L4e** catalytic system; Figure 2, substrate **S30**)

(R)-Ethyl 3-((diphenylphosphoryl)oxy)-3-(4-(trifluoromethyl)phenyl)propanoate

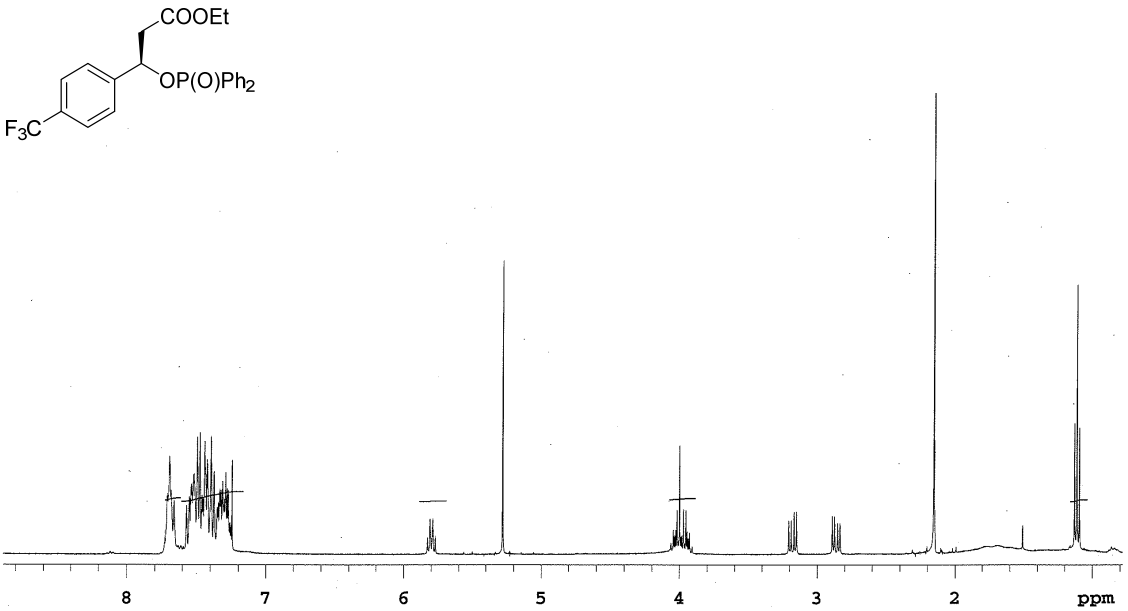


Figure S278. ^{1}H NMR of ethyl 3-((diphenylphosphoryl)oxy)-3-(4-(trifluoromethyl)phenyl)propanoate.

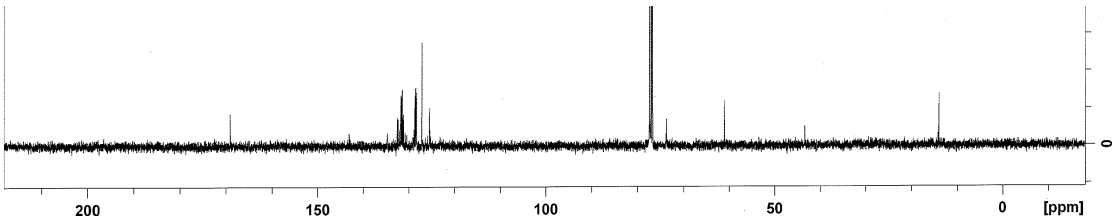
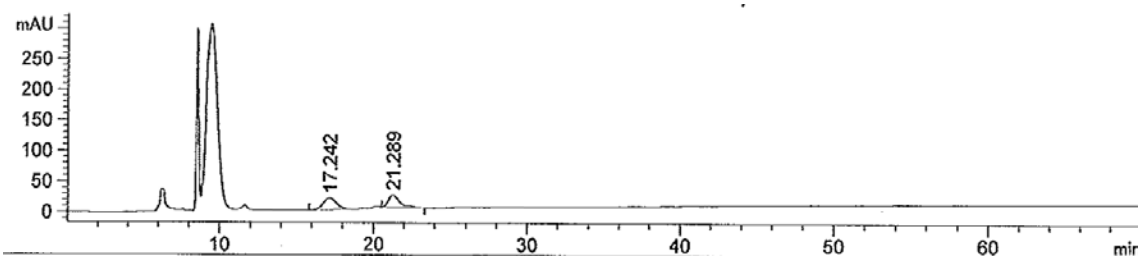


Figure S279. ^{13}C NMR of ethyl 3-((diphenylphosphoryl)oxy)-3-(4-(trifluoromethyl)phenyl)propanoate.

a)



b)

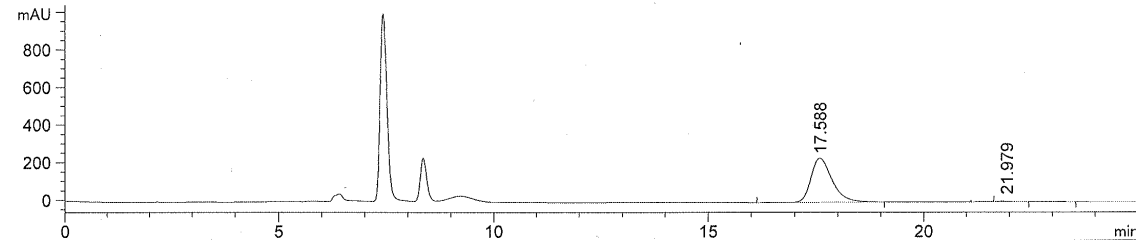


Figure S280. HPLC traces of (a) racemic and (b) enantioenriched product (98% (*R*) ee using Ir-**L1b** catalytic system; Figure 2, substrate **S31**)

(S)-Ethyl 3-((diphenylphosphoryl)oxy)-4-methylpentanoate

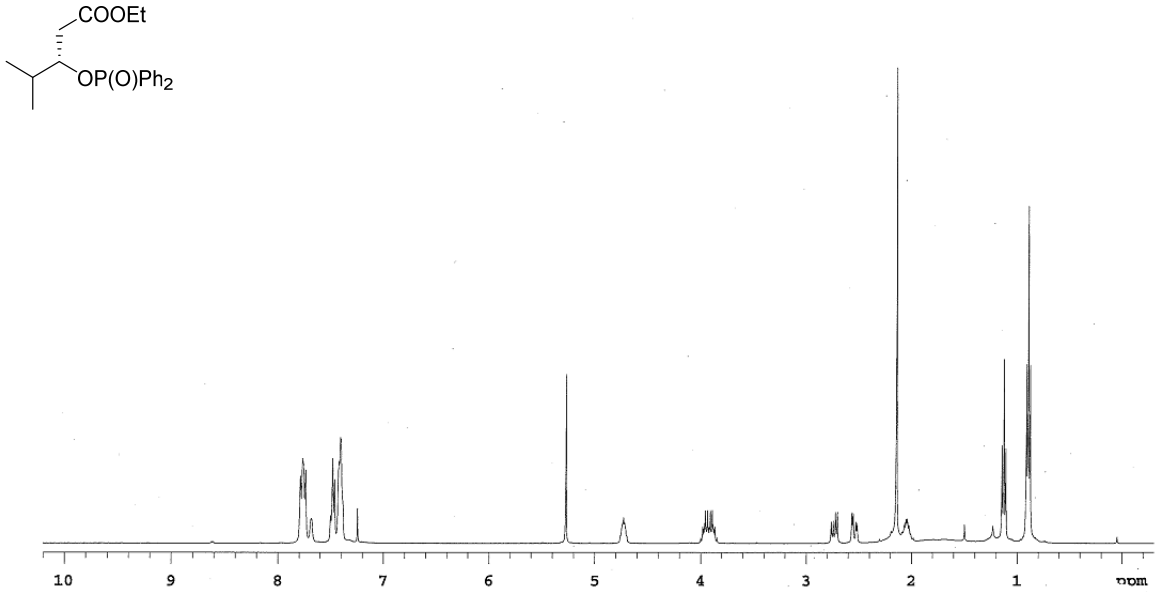


Figure S281. ^{1}H NMR of ethyl 3-((diphenylphosphoryl)oxy)-4-methylpentanoate.

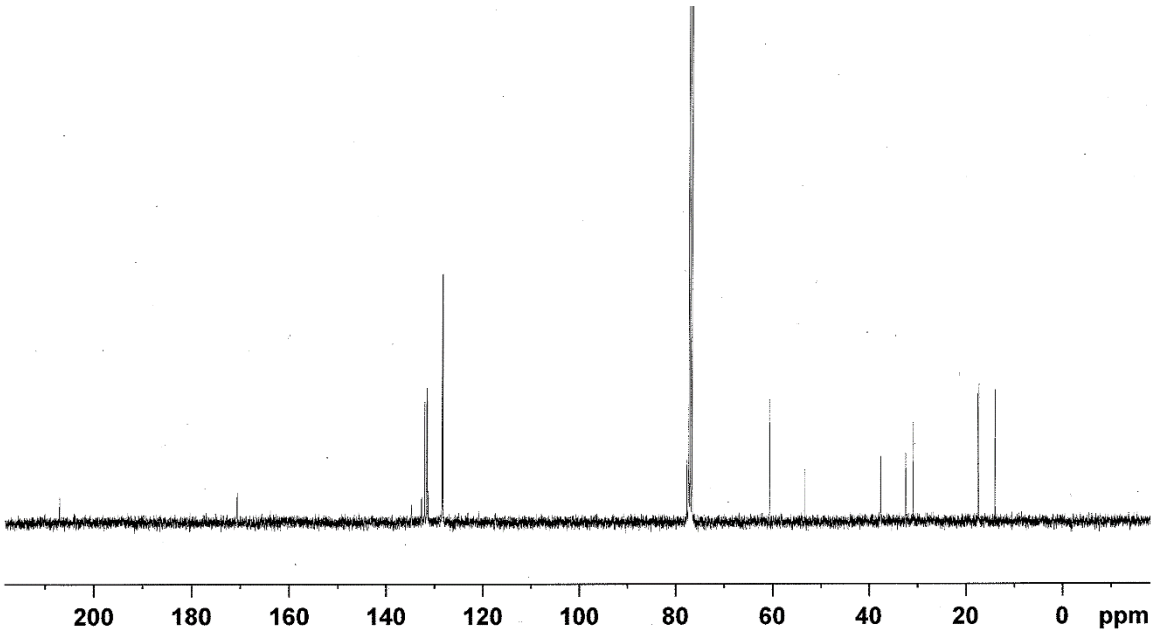
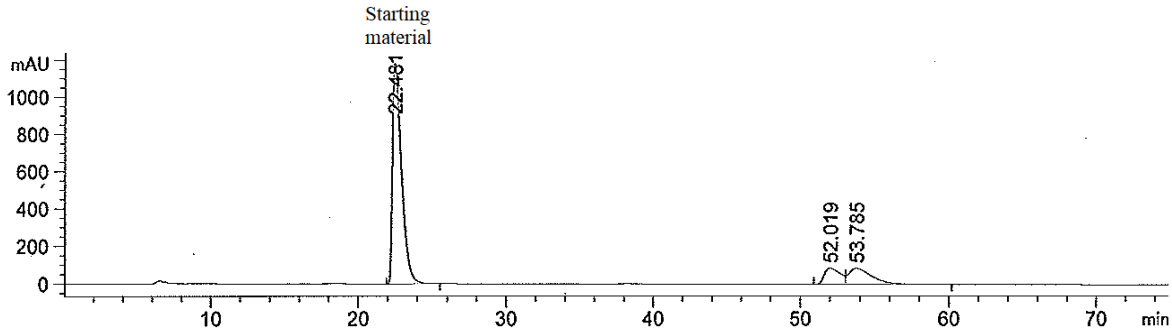


Figure S282. ^{13}C NMR of ethyl 3-((diphenylphosphoryl)oxy)-4-methylpentanoate.

a)



b)

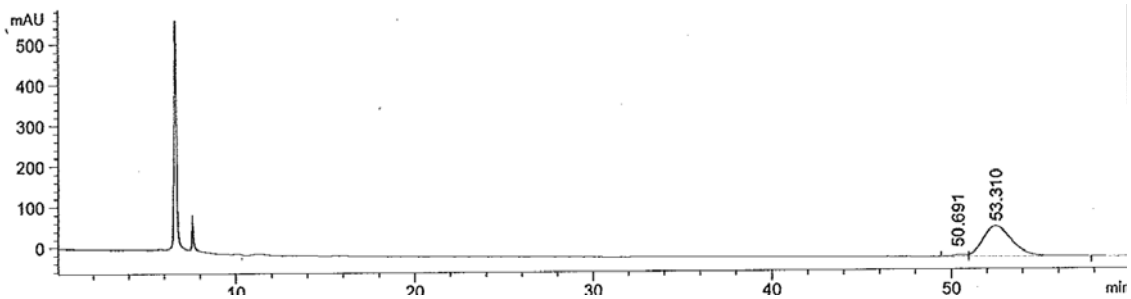


Figure S283. HPLC traces of (a) racemic and (b) enantioenriched product (95% (*S*) ee using Ir-**L4e** catalytic system; Figure 2, substrate **S32**)

(S)-(3-Methylbutan-2-yl)benzene

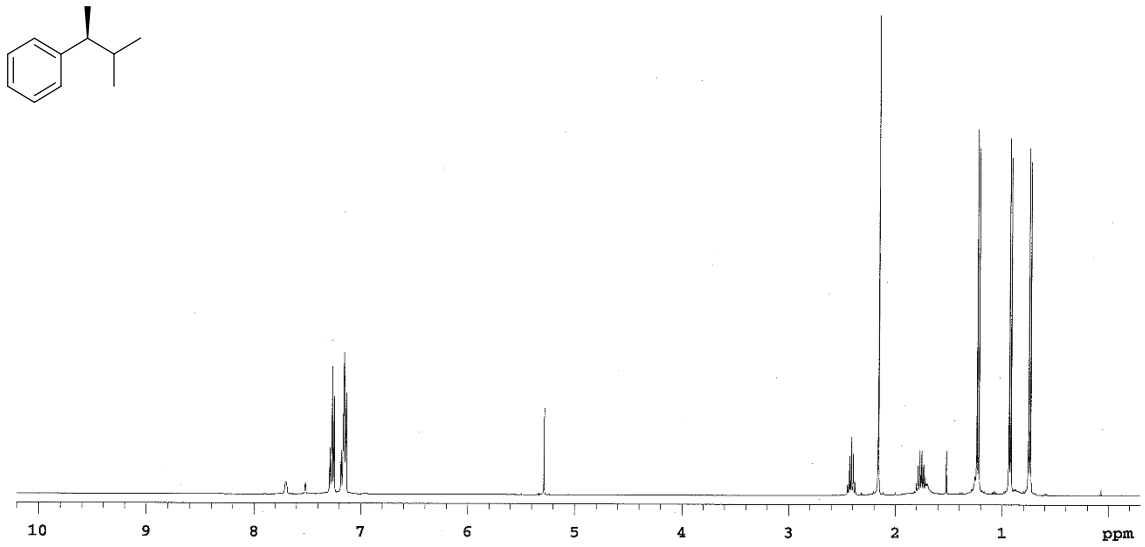


Figure S284. ^{1}H NMR of (3-methylbutan-2-yl)benzene.

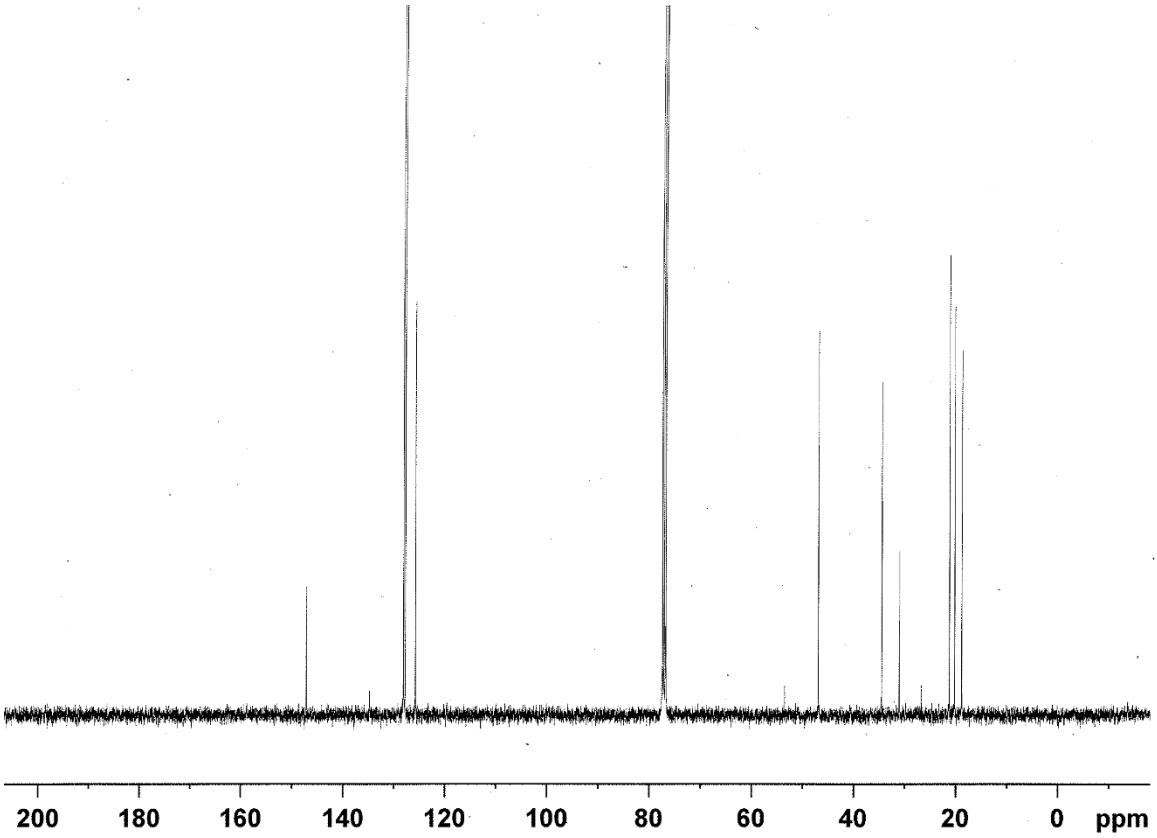
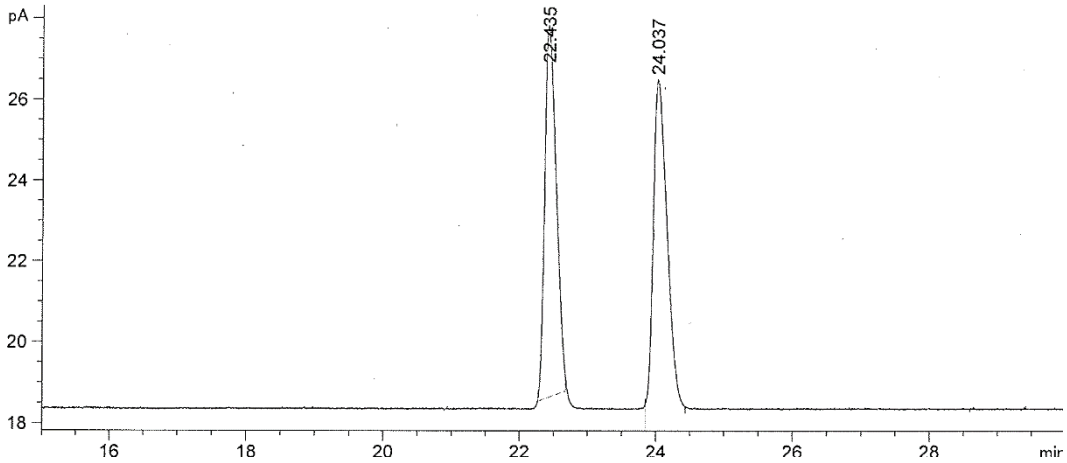


Figure S285. ^{13}C NMR of (3-methylbutan-2-yl)benzene.

a)



b)

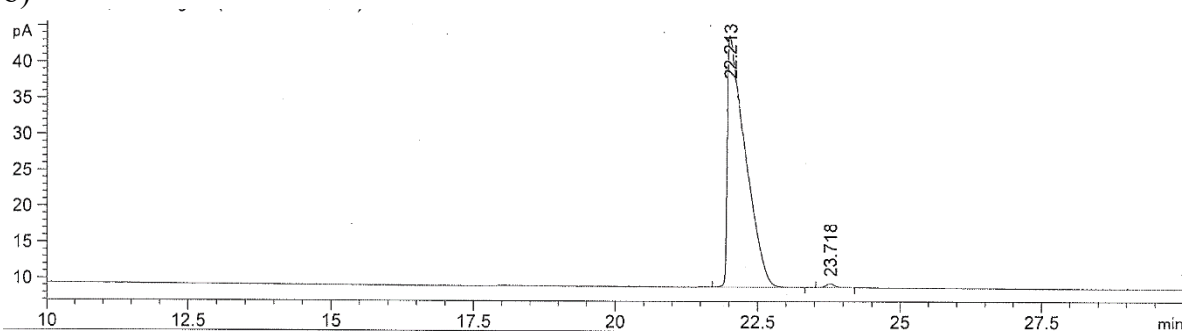
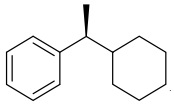


Figure S286. GC traces of (a) racemic and (b) enantioenriched product (92% (*S*) ee using Ir-**L1d** catalytic system; Figure 2, substrate **S34**)

(S)-(1-Cyclohexylethyl)benzene



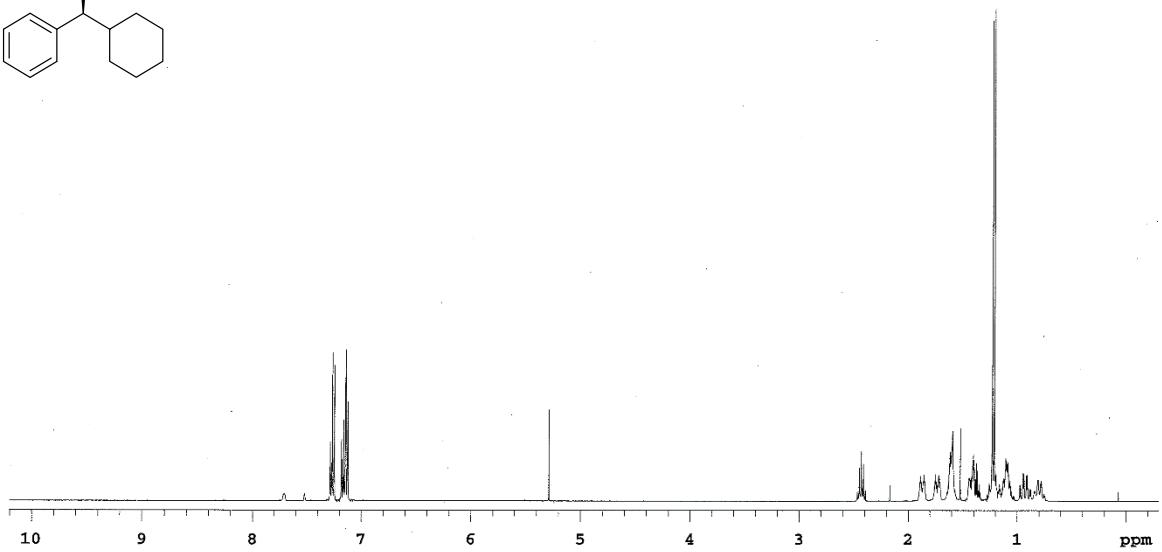


Figure S287. ^{1}H NMR of (1-cyclohexylethyl)benzene.

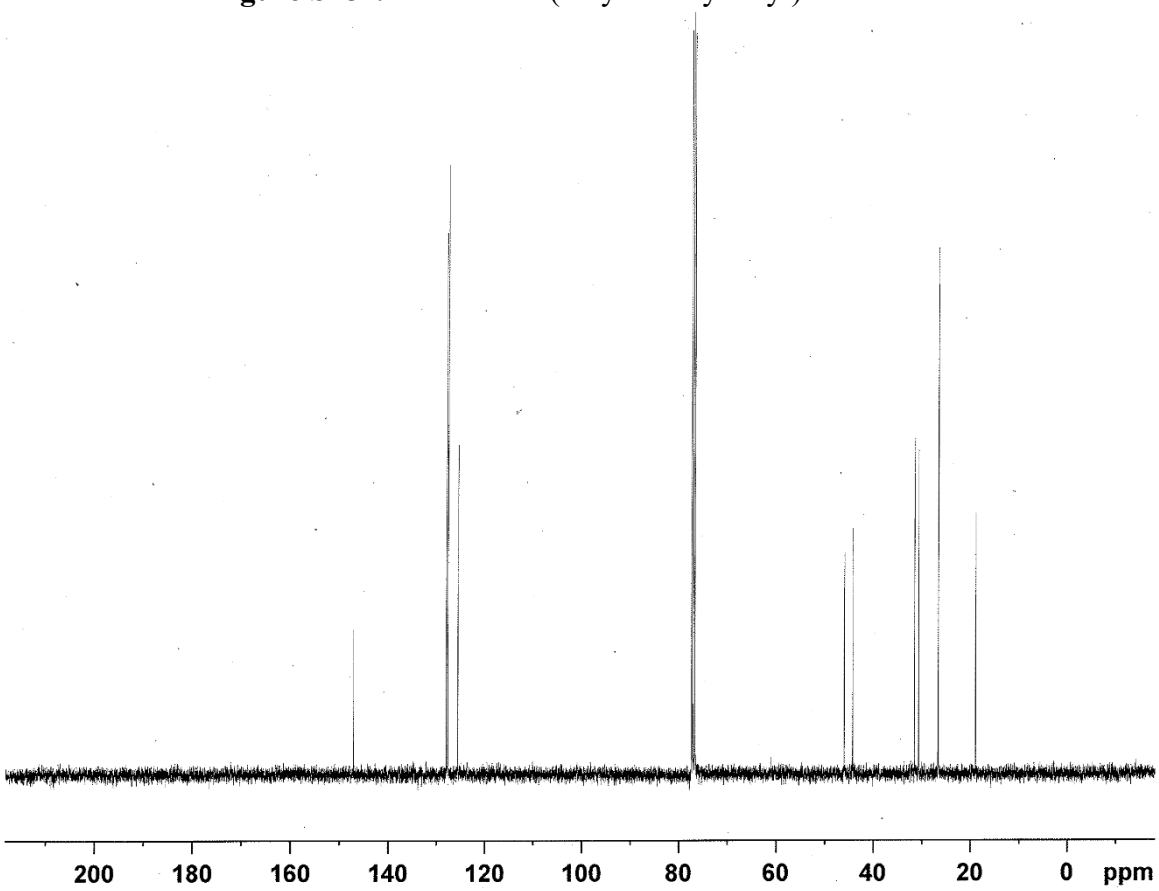
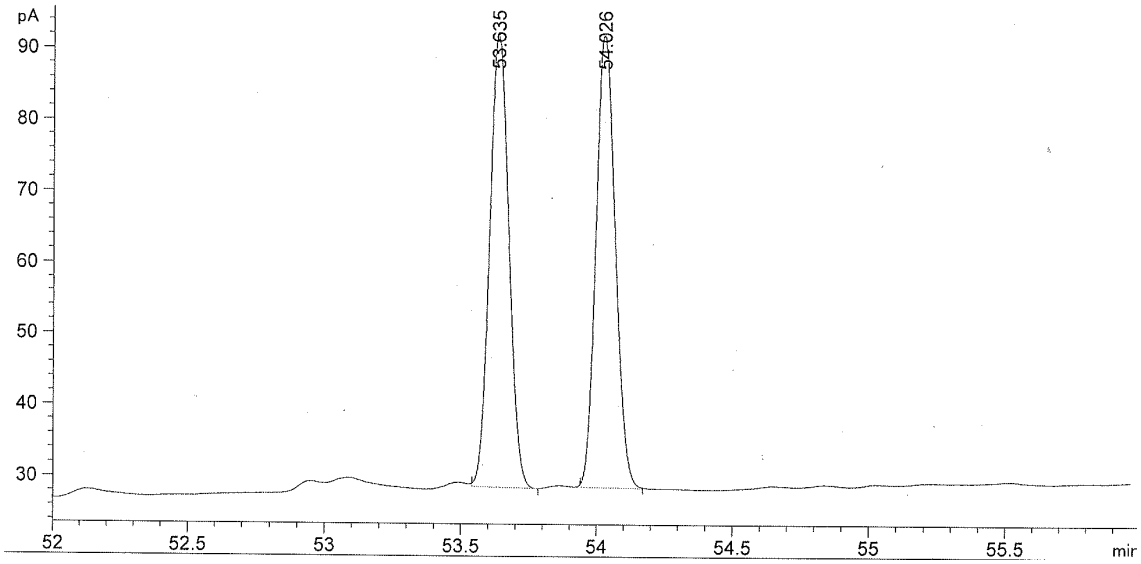


Figure S288. ^{13}C NMR of (1-cyclohexylethyl)benzene.

a)



b)

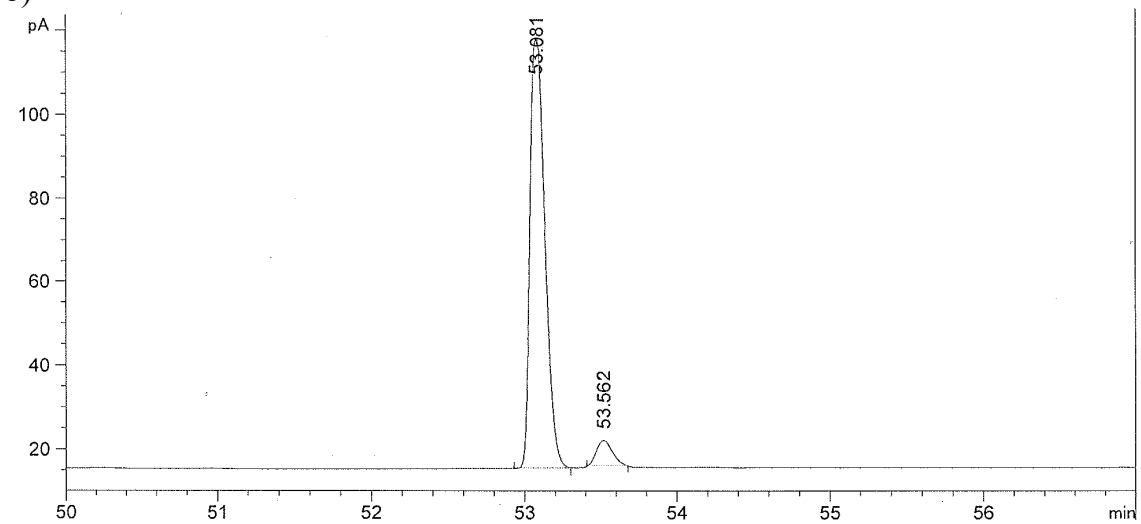


Figure S289. GC traces of (a) racemic and (b) enantioenriched product (88% (*S*) ee using Ir-**L1d** catalytic system; Figure 2, substrate **S35**)

(R)-1-(3,3-Dimethylbutan-2-yl)-4-methoxybenzene.

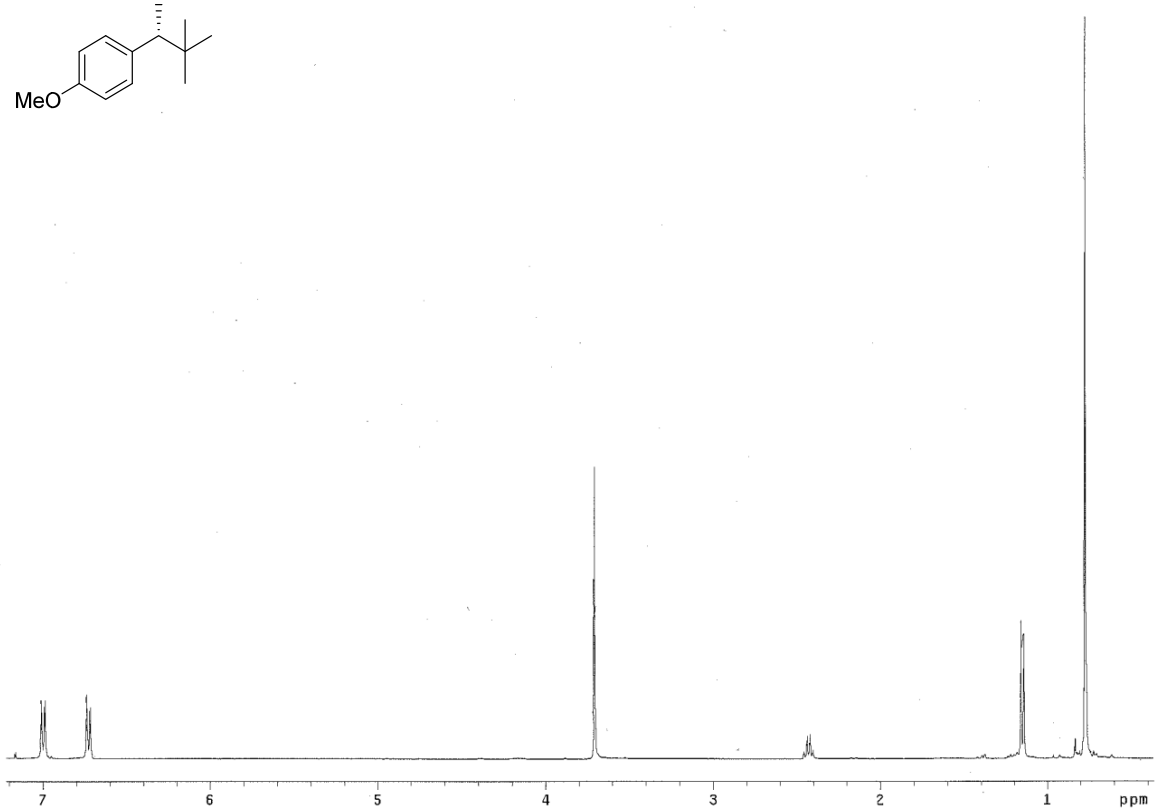


Figure S290. ^{1}H NMR of 1-(3,3-dimethylbutan-2-yl)-4-methoxybenzene.

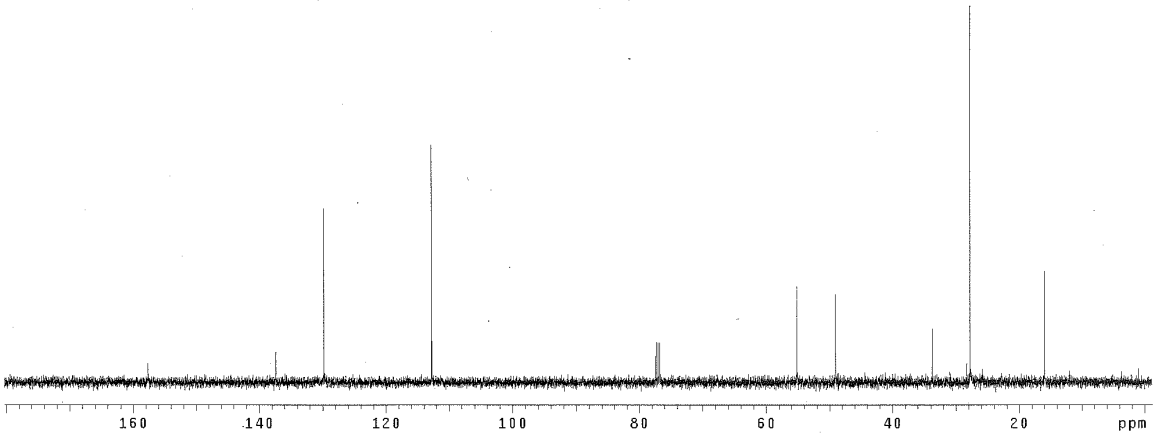
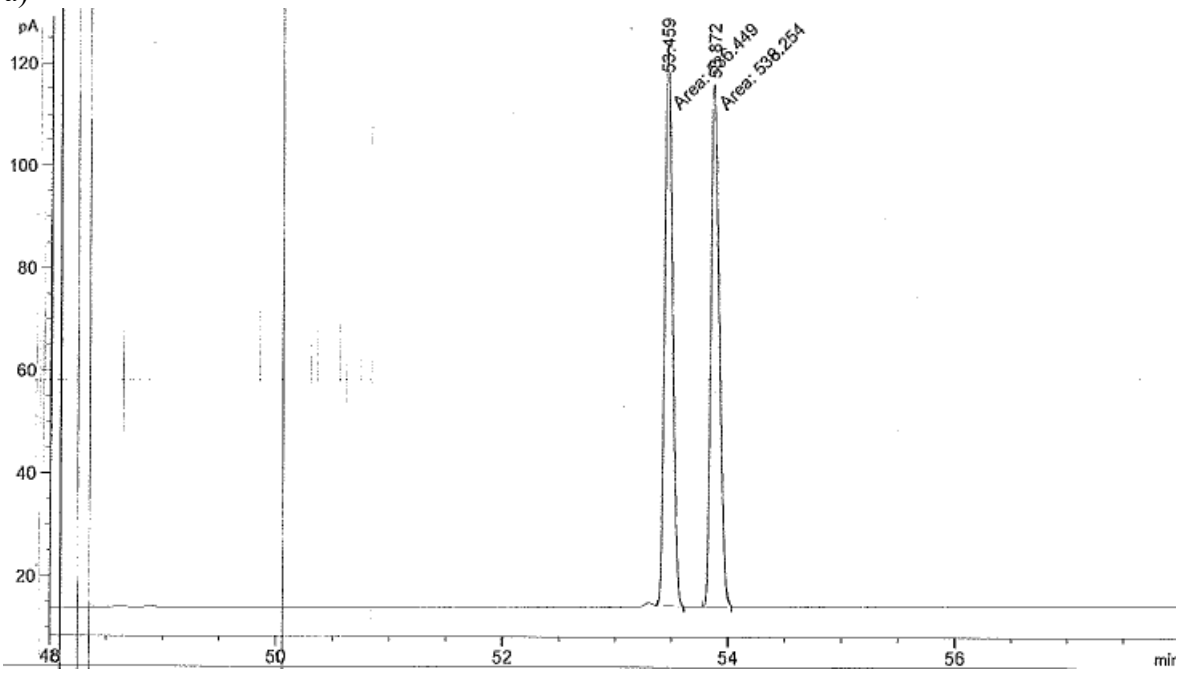


Figure S291. ^{13}C NMR of 1-(3,3-dimethylbutan-2-yl)-4-methoxybenzene.

a)



b)

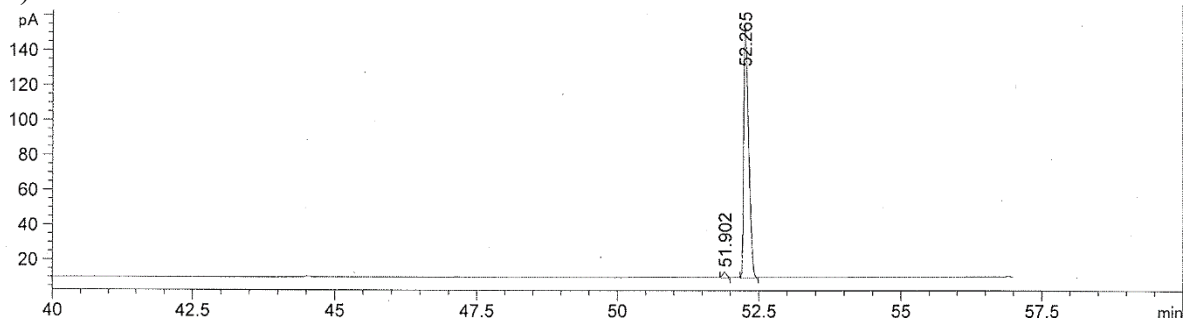


Figure S292. GC traces of (a) racemic and (b) enantioenriched product (97% (*R*) ee using Ir-**L4a** catalytic system; Figure 2, substrate **S36**)

(R)-1-(3,3-Dimethylbutan-2-yl)-4-(trifluoromethyl)benzene

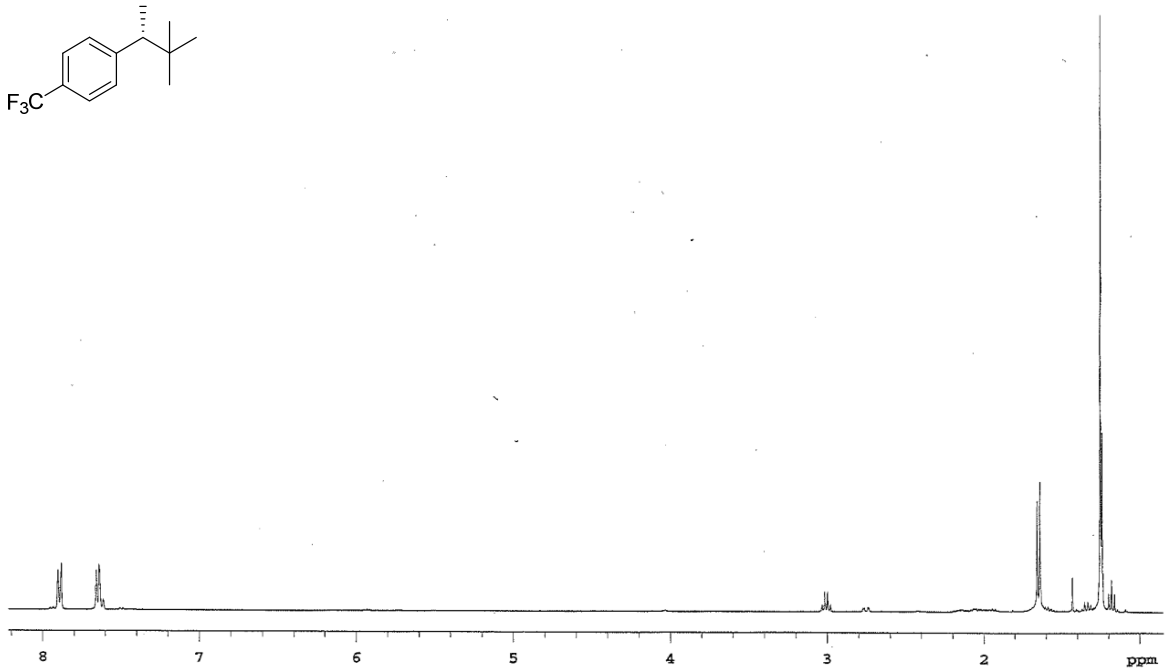


Figure S293. ^{1}H NMR of 1-(3,3-dimethylbutan-2-yl)-4-(trifluoromethyl)benzene.

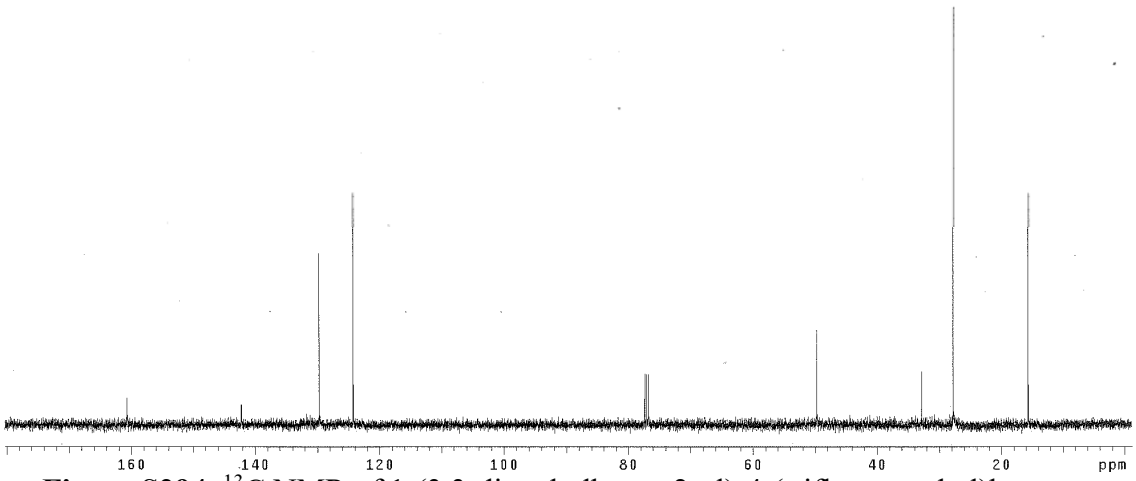
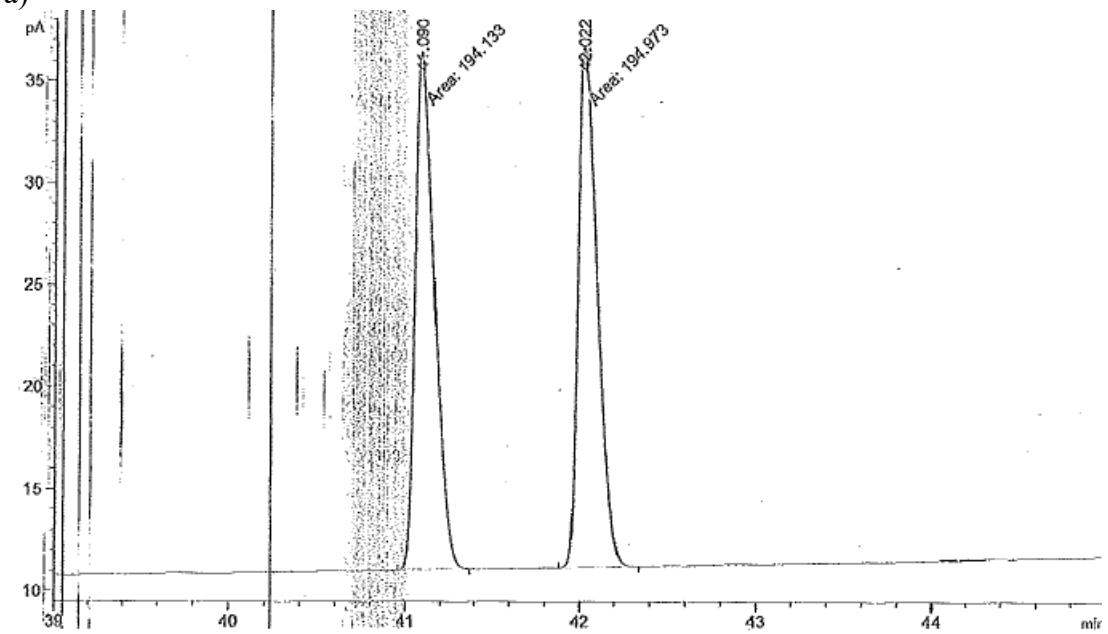


Figure S294. ^{13}C NMR of 1-(3,3-dimethylbutan-2-yl)-4-(trifluoromethyl)benzene.

a)



b)

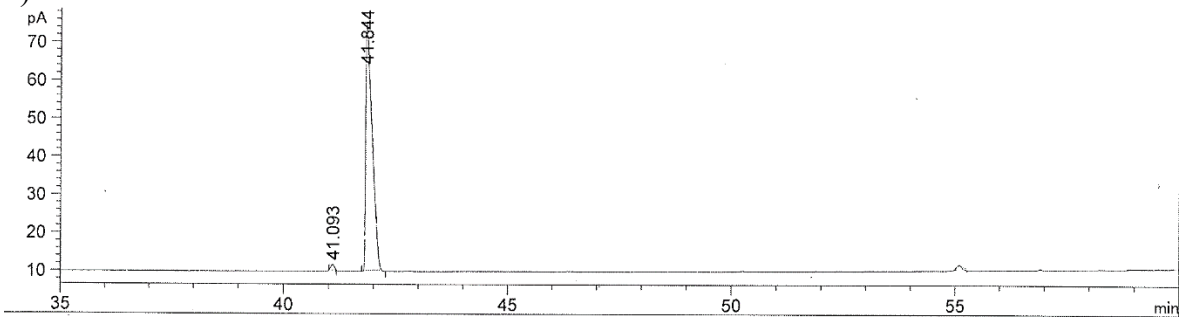


Figure S295. GC traces of (a) racemic and (b) enantioenriched product (97% (*R*) ee using Ir-**L4a** catalytic system; Figure 2, substrate **S37**)

(R)-1-(3,3-Dimethylbutan-2-yl)-4-methylbenzene

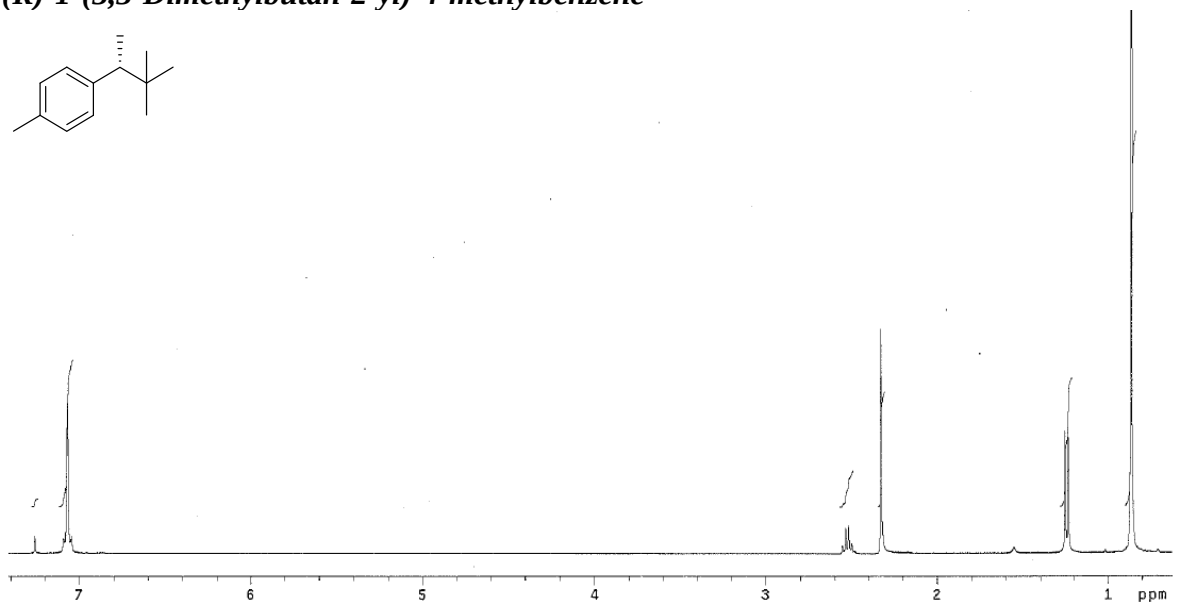


Figure S296. ^{1}H NMR of 1-(3,3-dimethylbutan-2-yl)-4-methylbenzene.

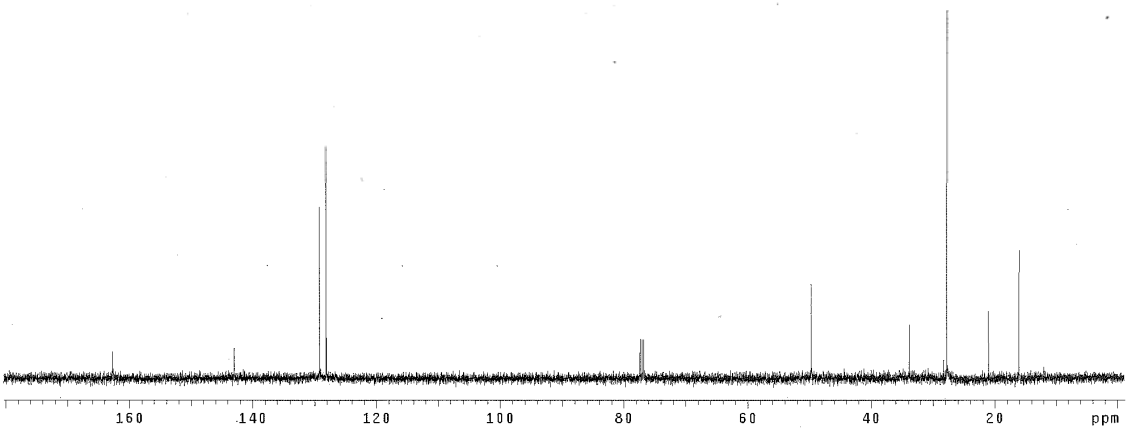
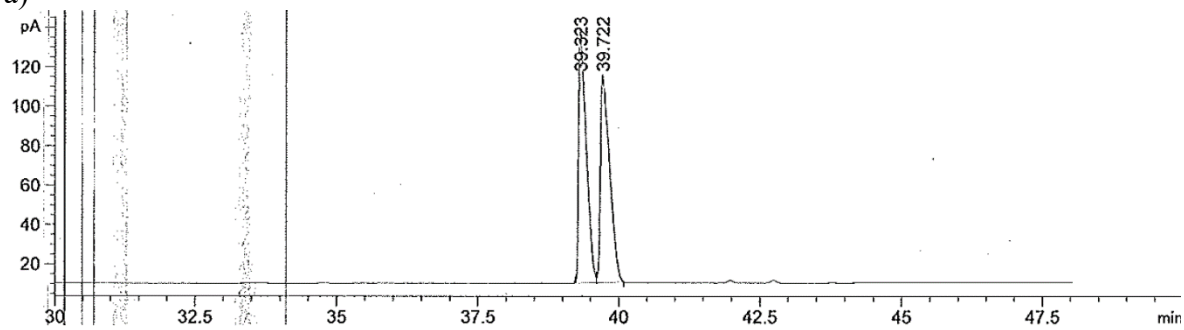


Figure S297. ^{13}C NMR of 1-(3,3-dimethylbutan-2-yl)-4-methylbenzene.

a)



b)

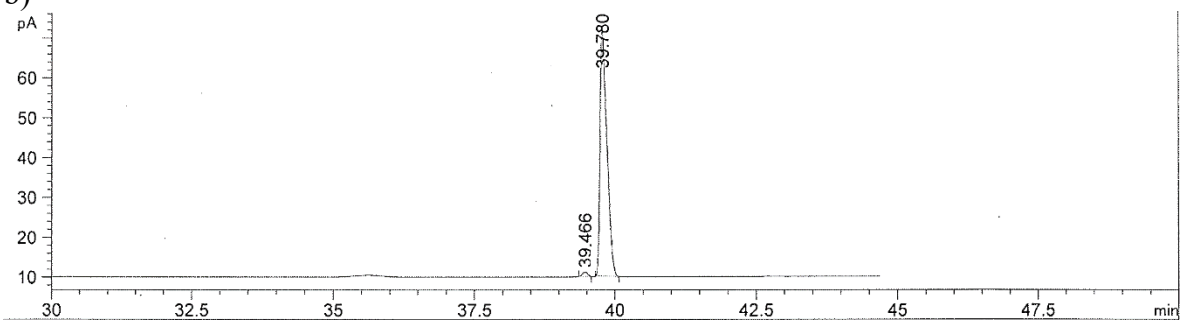


Figure S298. GC traces of (a) racemic and (b) enantioenriched product (98% (*R*) ee using Ir-**L4a** catalytic system; Figure 2, substrate **S38**)

(R)-1-(3,3-Dimethylbutan-2-yl)-3-methylbenzene

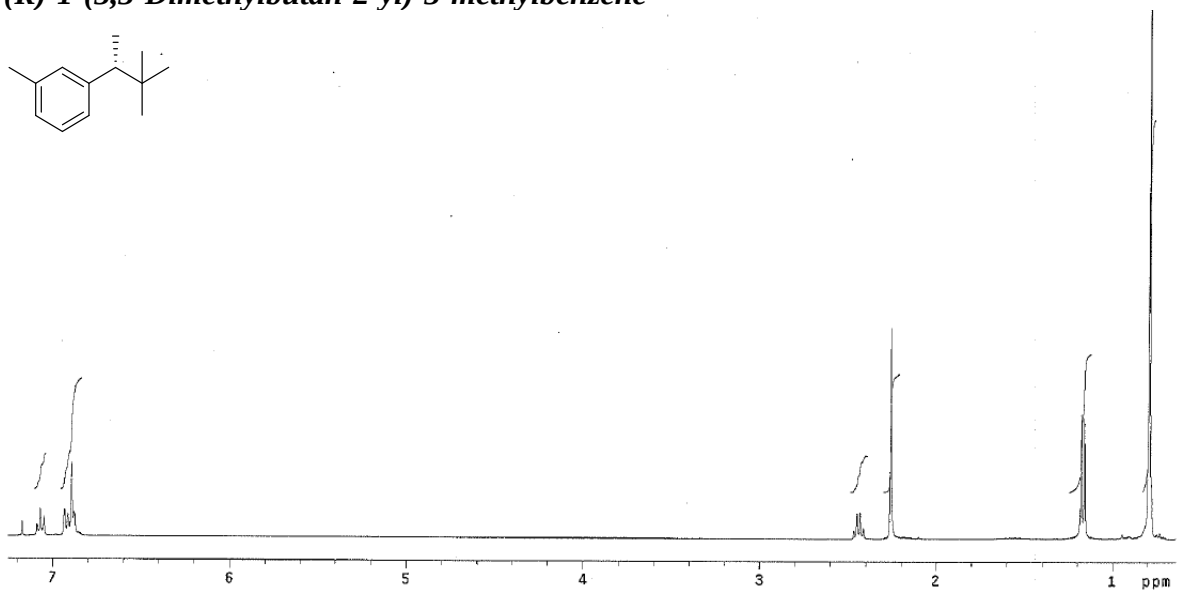


Figure S299. ^{1}H NMR of 1-(3,3-dimethylbutan-2-yl)-3-methylbenzene.

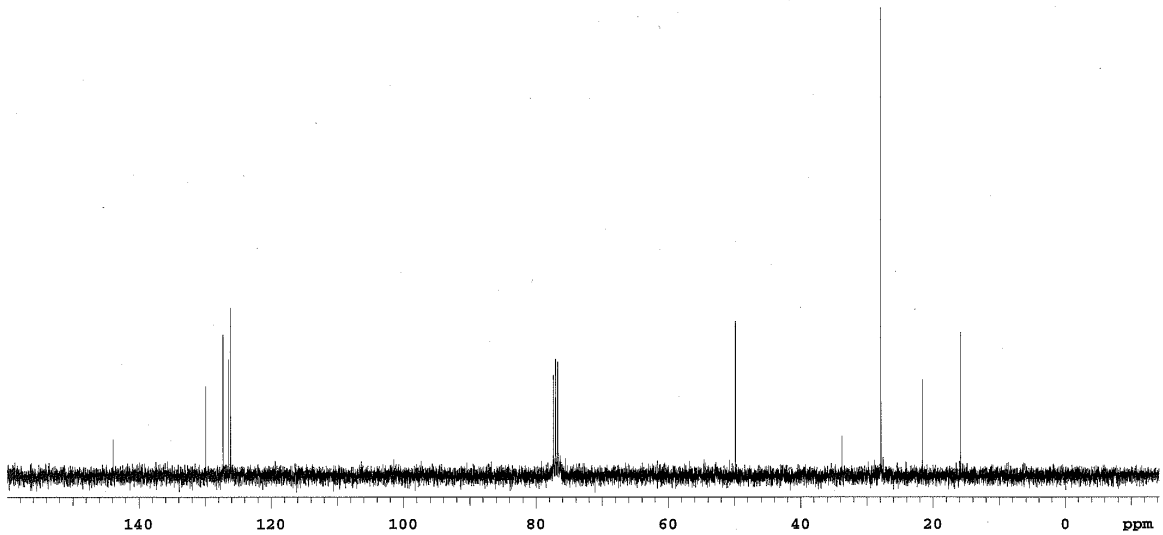
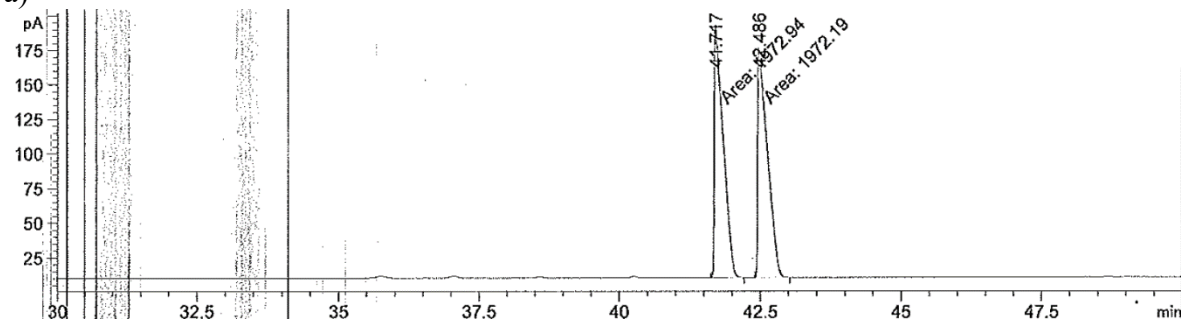


Figure S300. ^{13}C NMR of 1-(3,3-dimethylbutan-2-yl)-3-methylbenzene.

a)



b)

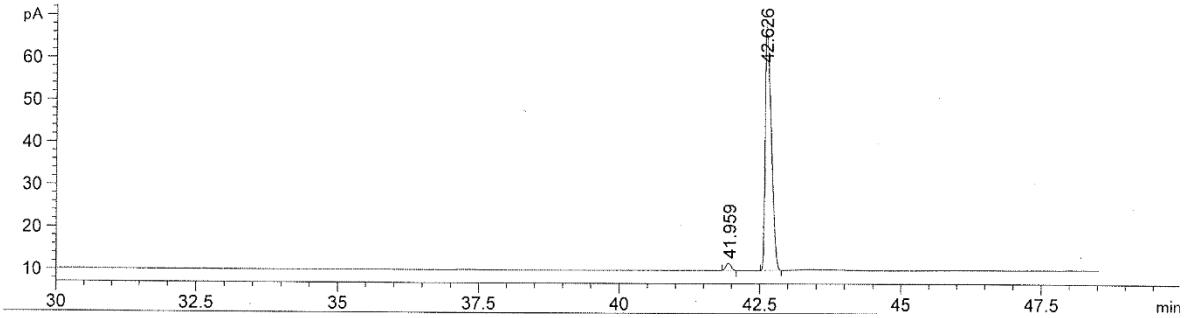


Figure 301. GC traces of (a) racemic and (b) enantioenriched product (96% (*R*) ee using Ir-**L4a** catalytic system; Figure 2, substrate **S39**)

(R)-1-(3,3-dimethylbutan-2-yl)-2-methylbenzene

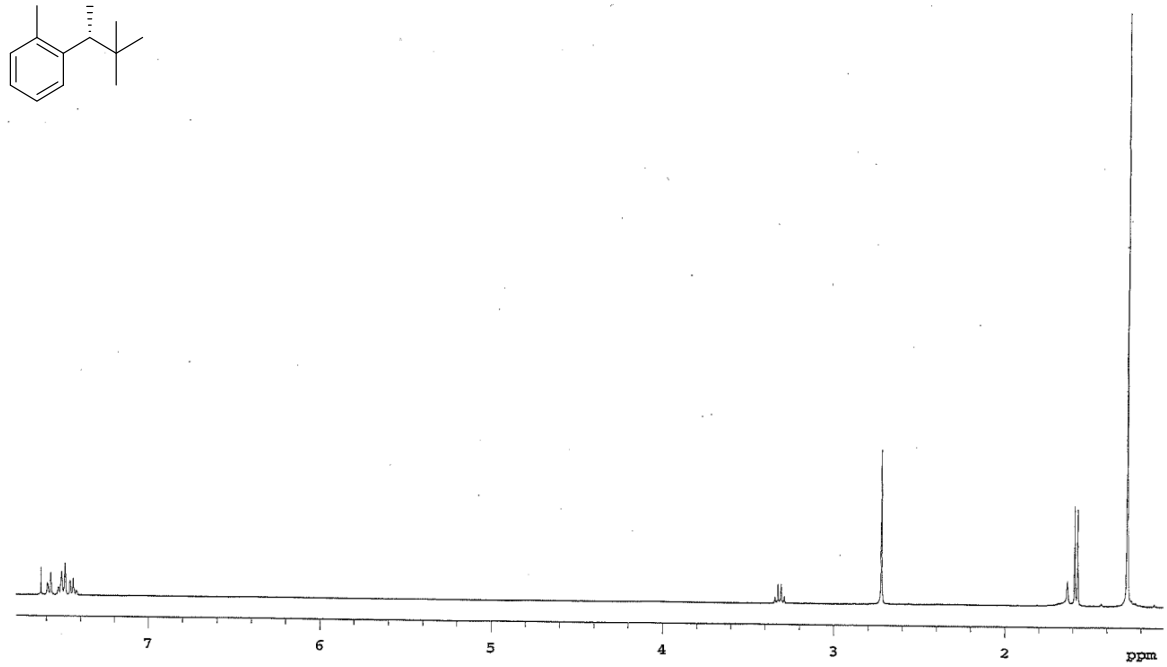


Figure S302. ^{1}H NMR of 1-(3,3-dimethylbutan-2-yl)-2-methylbenzene.

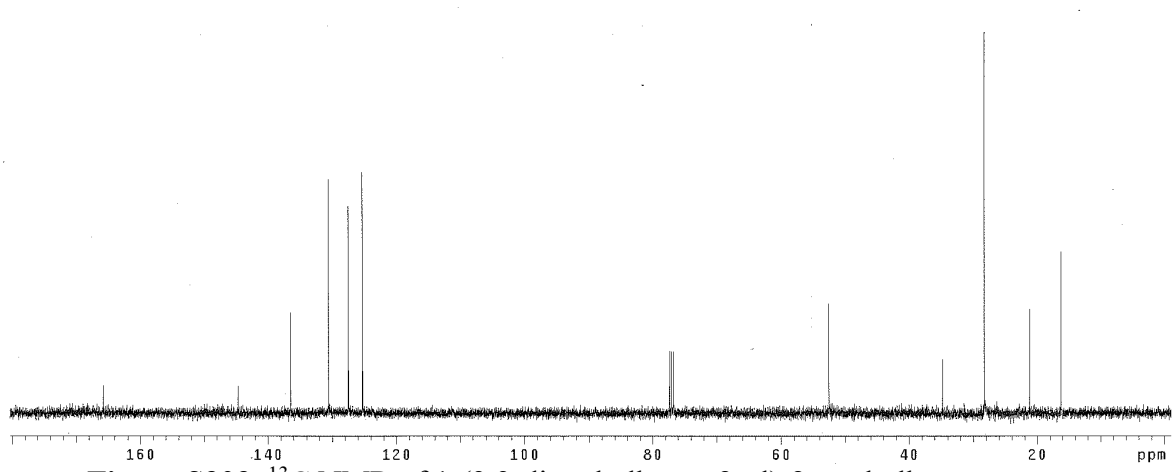
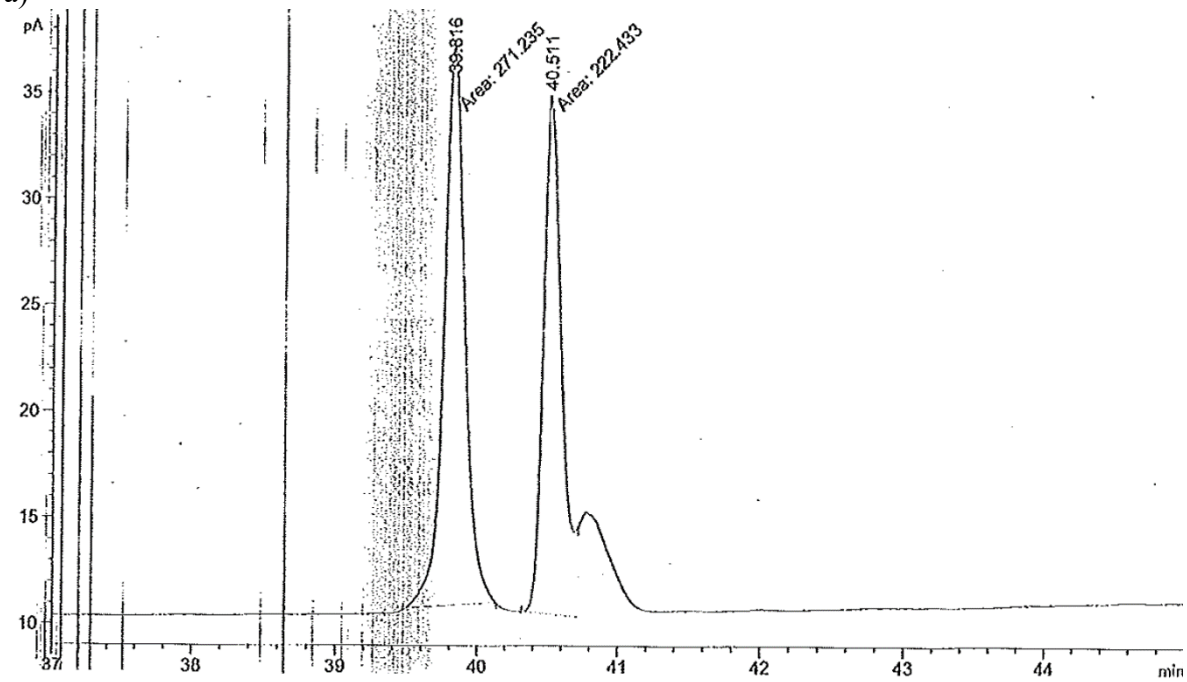


Figure S303. ^{13}C NMR of 1-(3,3-dimethylbutan-2-yl)-2-methylbenzene.

a)



b)

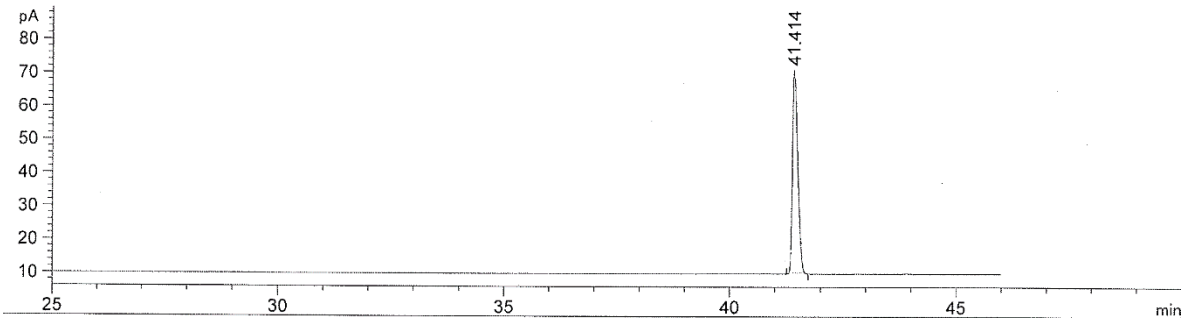


Figure S304. GC traces of (a) racemic and (b) enantioenriched product (>99% (*R*) ee using Ir-**L4a** catalytic system; Figure 2, substrate **S40**)

(R)-1-(3,3-Dimethylbutan-2-yl)naphthalene

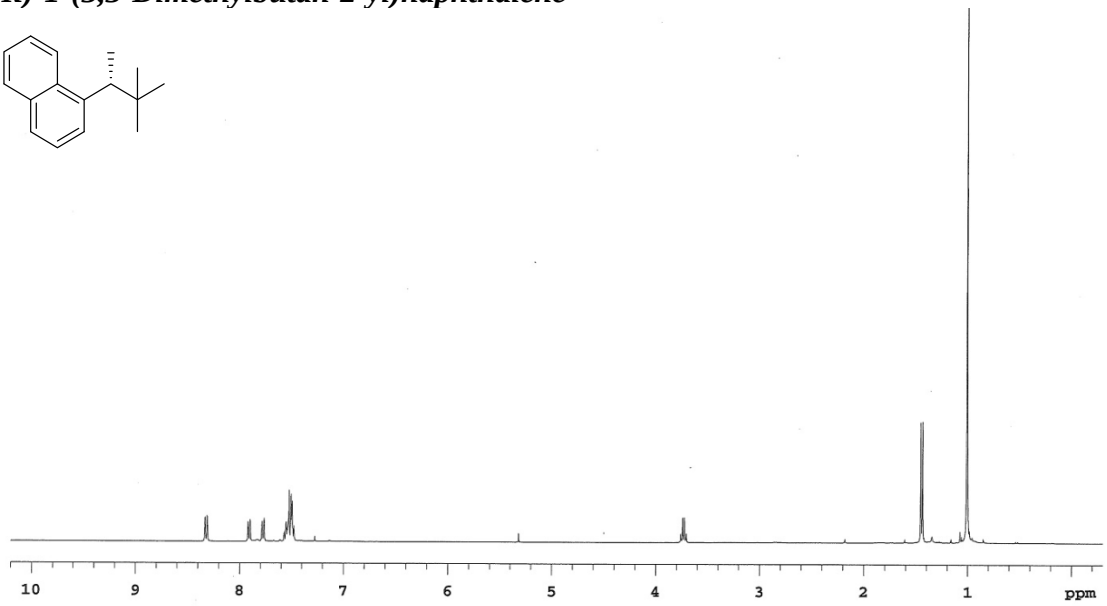


Figure S305. ^{1}H NMR of 1-(3,3-dimethylbutan-2-yl)-2-methylbenzene.

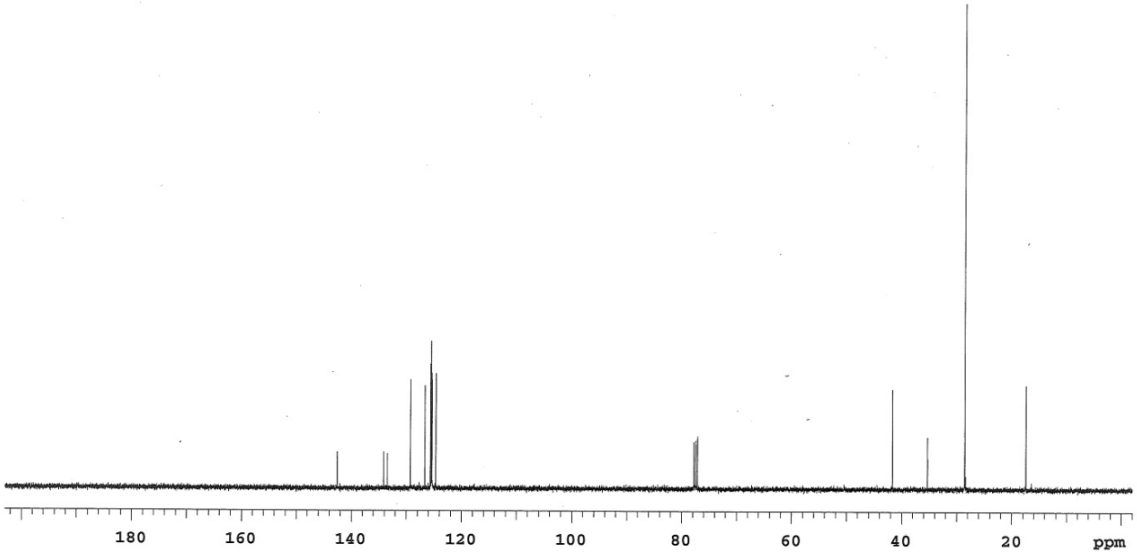
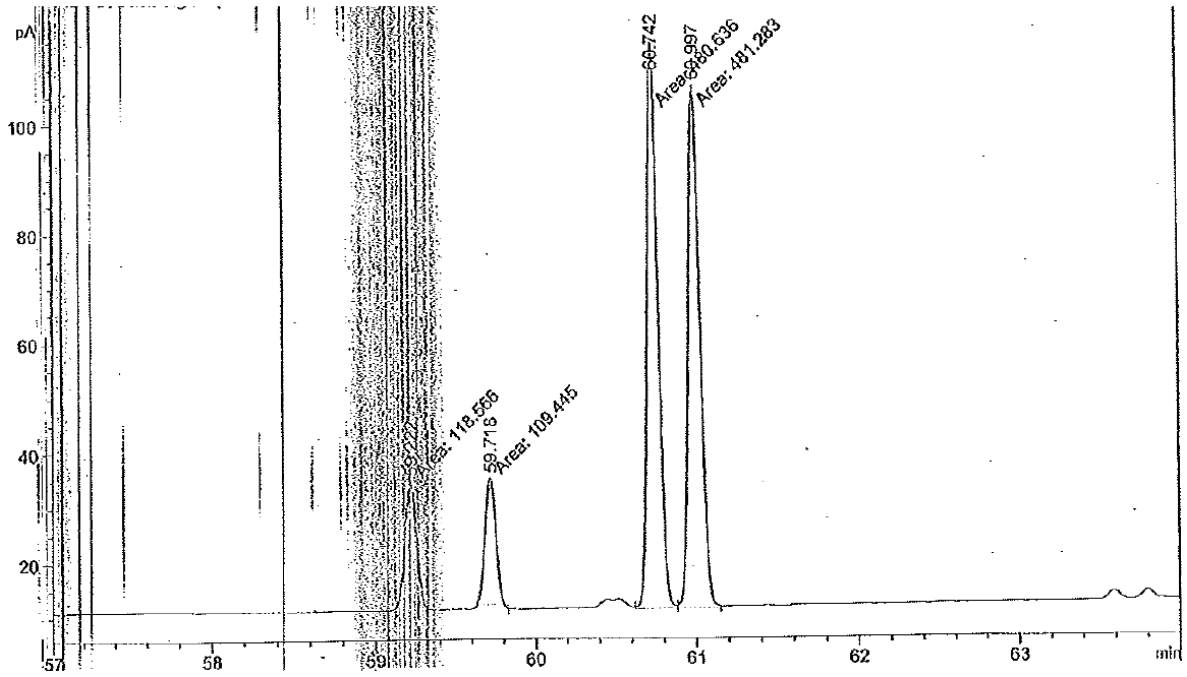


Figure S306. ^{13}C NMR of 1-(3,3-dimethylbutan-2-yl)-2-methylbenzene.

a)



b)

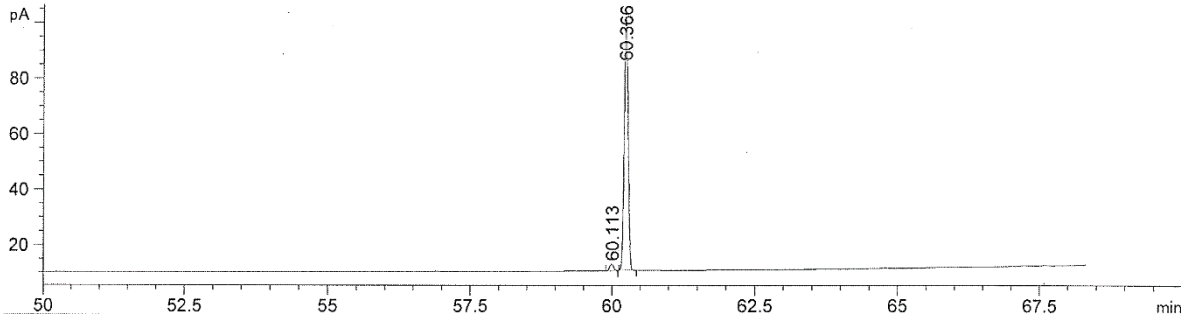


Figure S307. GC traces of (a) racemic and (b) enantioenriched product (98% (*R*) ee using Ir-**L4a** catalytic system; Figure 2, substrate **S41**)

(R)-2-(3,3-Dimethylbutan-2-yl)pyridine

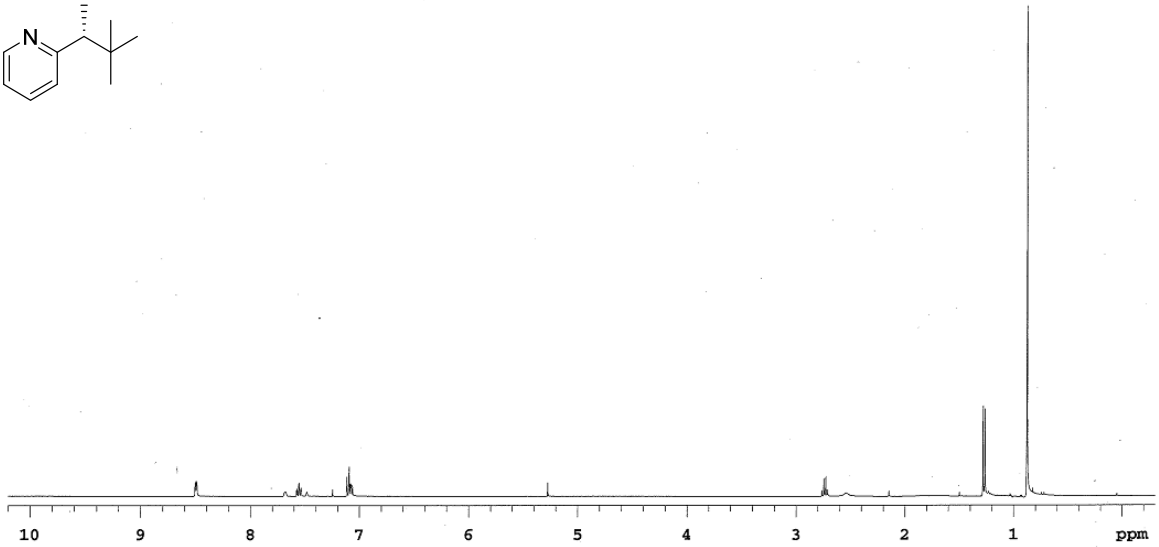


Figure S308. ^{1}H NMR of 2-(3,3-dimethylbutan-2-yl)pyridine.

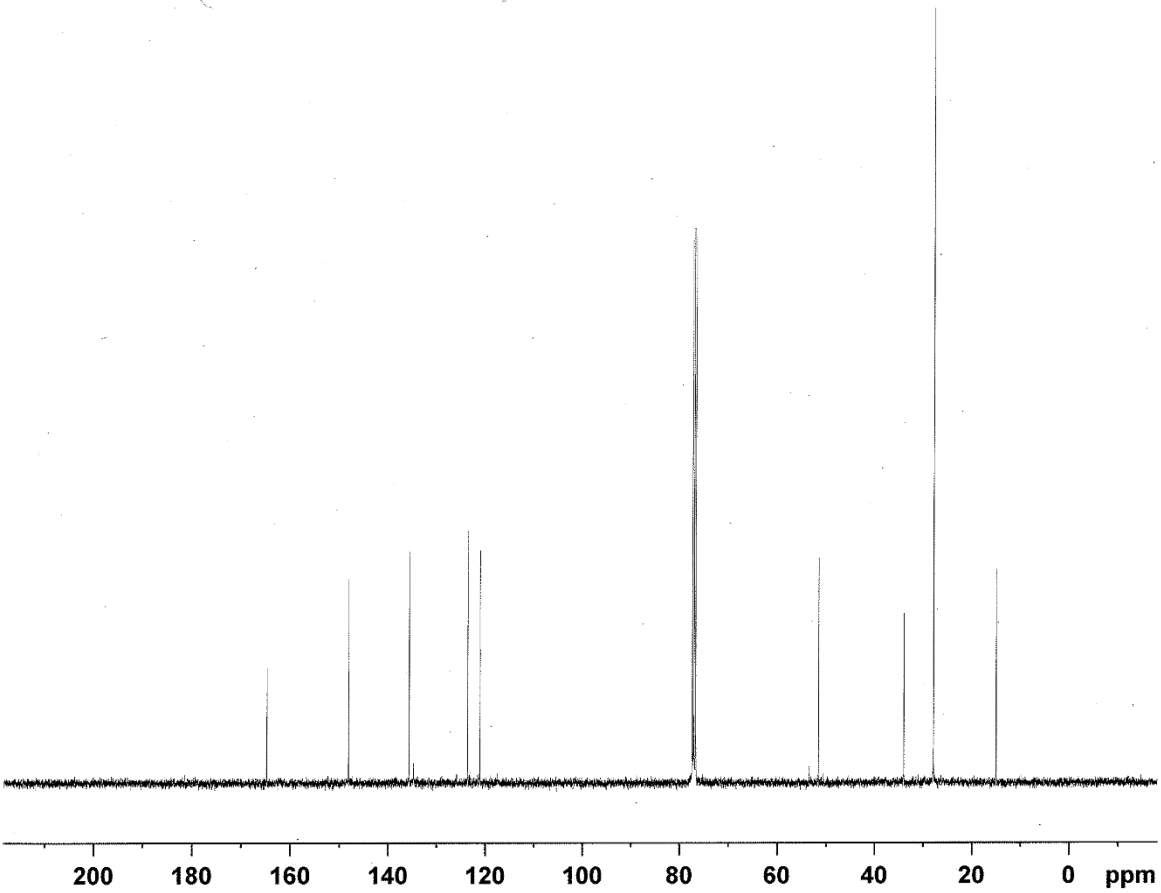


Figure S309. ^{13}C NMR of 2-(3,3-dimethylbutan-2-yl)pyridine.

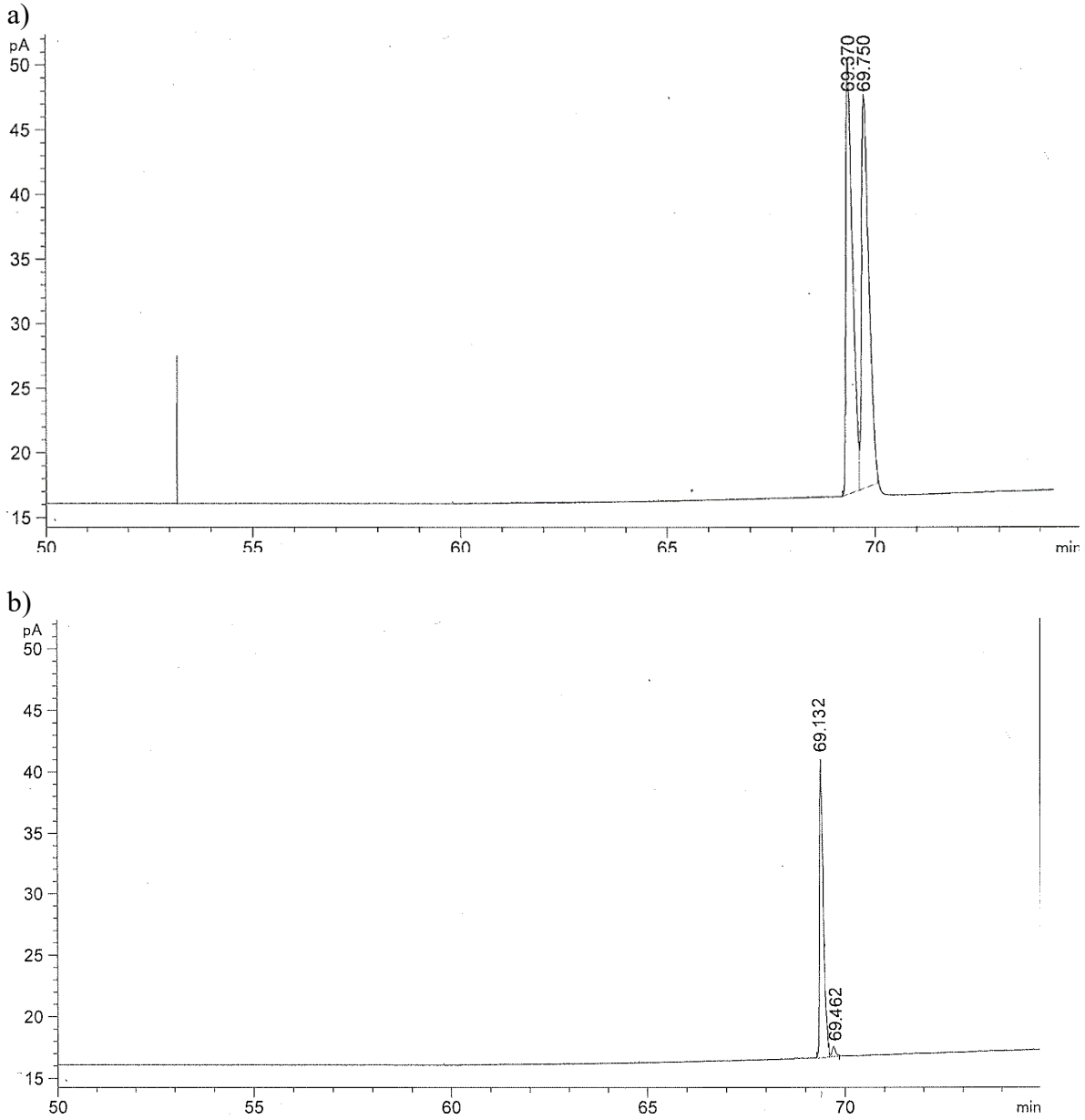
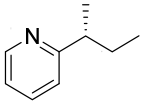


Figure S310. GC traces of (a) racemic and (b) enantioenriched product (97% (*R*) ee using Ir-**L4a** catalytic system; Figure 2, substrate **S42**)

(R)-2-(sec-Butyl)pyridine



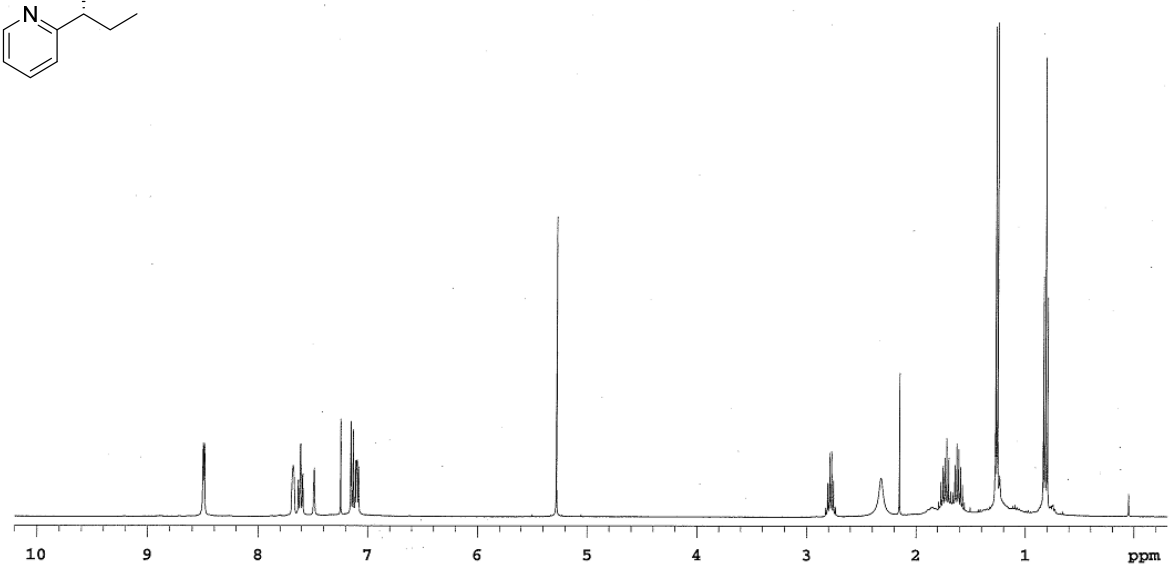


Figure S311. ^{1}H NMR of 2-(*sec*-butyl)pyridine.

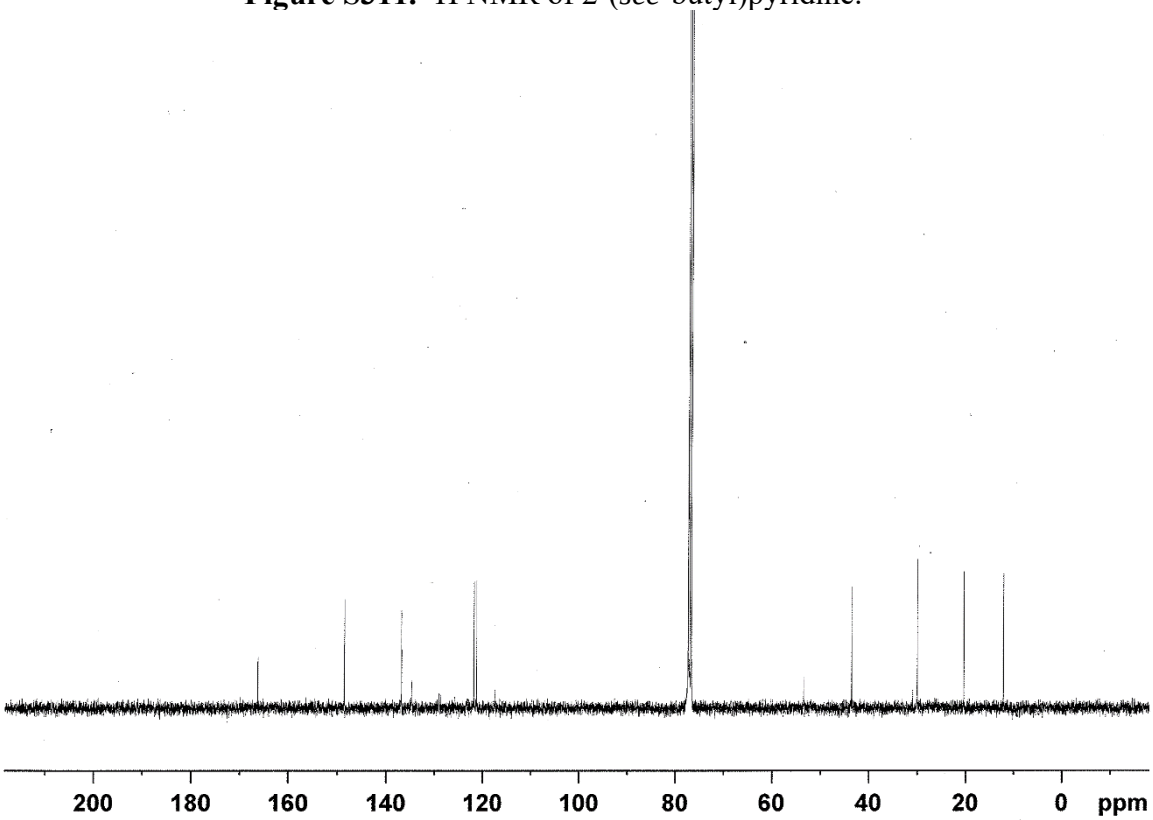
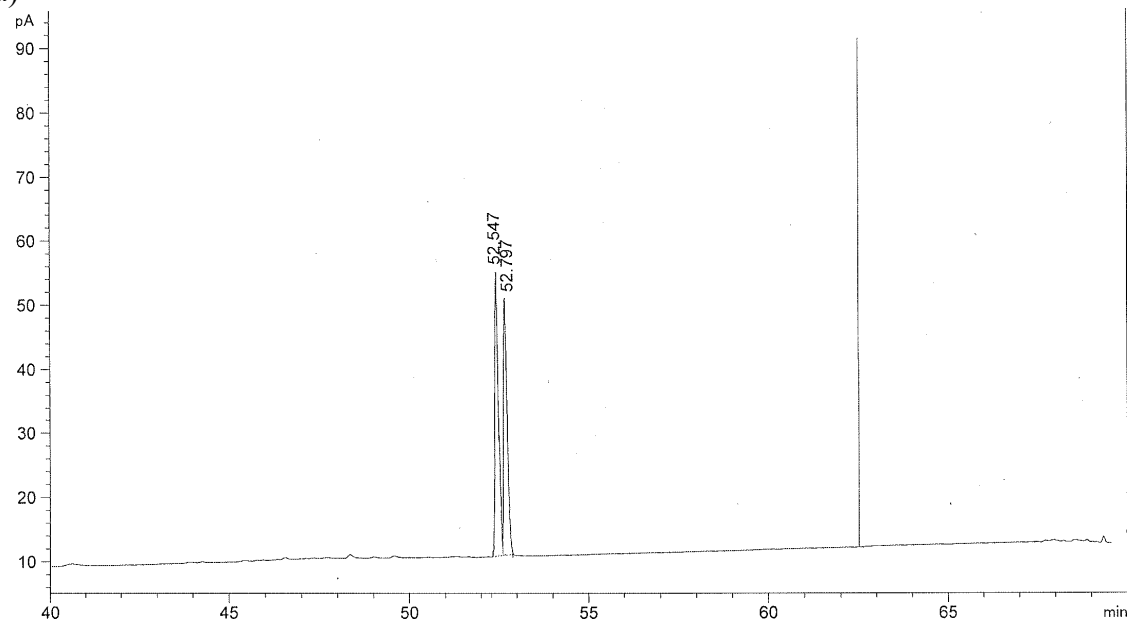


Figure S312. ^{13}C NMR of 2-(*sec*-butyl)pyridine.

a)



b)

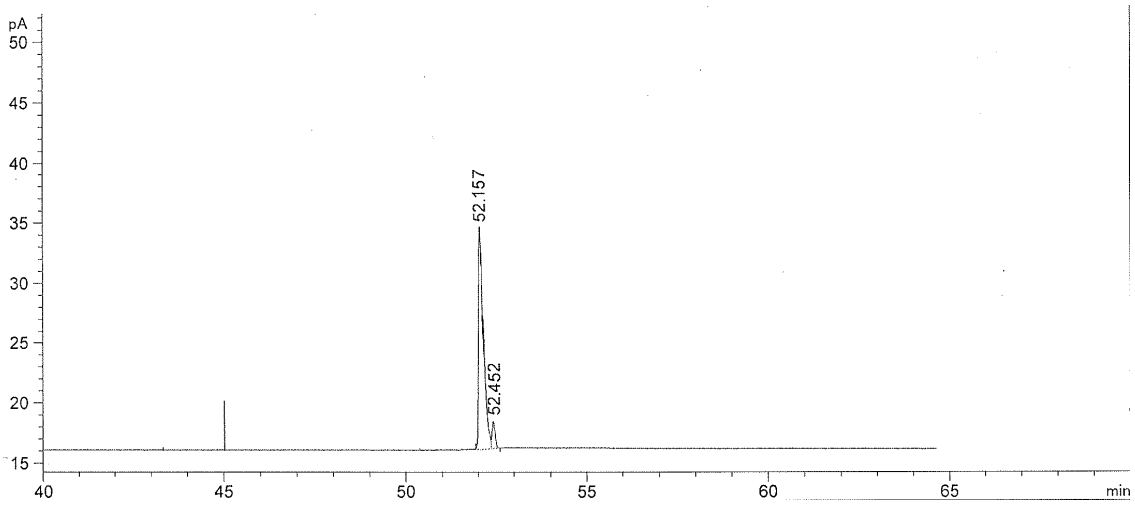


Figure S313. GC traces of (a) racemic and (b) enantioenriched product (80% (*R*) ee using Ir-**L4e** catalytic system; Figure 2, substrate **S43**)

(R)-1-Phenylethyl diphenylphosphinate

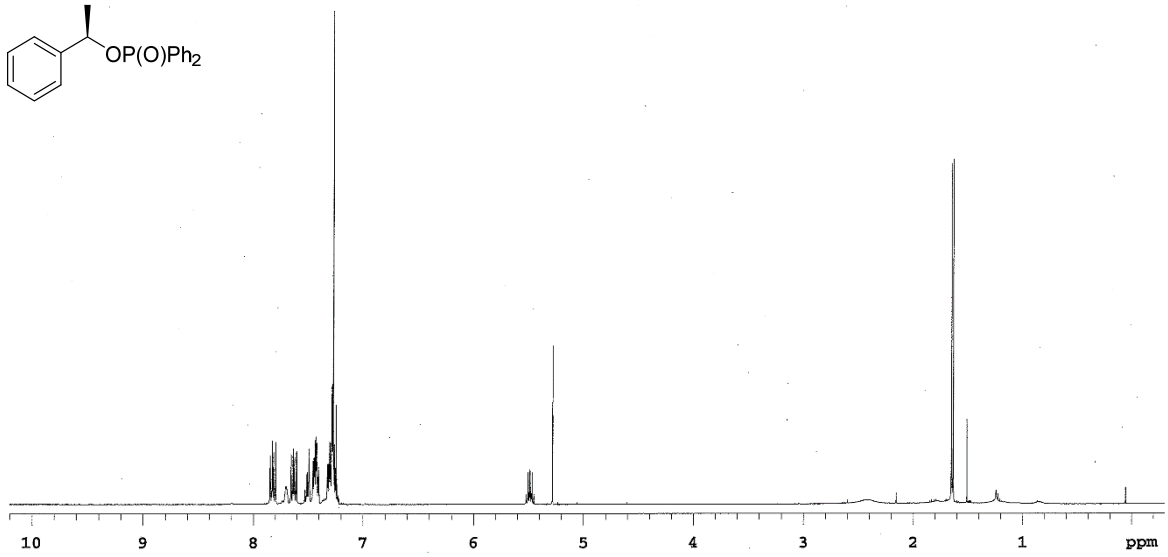


Figure S314. ^{1}H NMR of 1-phenylethyl diphenylphosphinate.

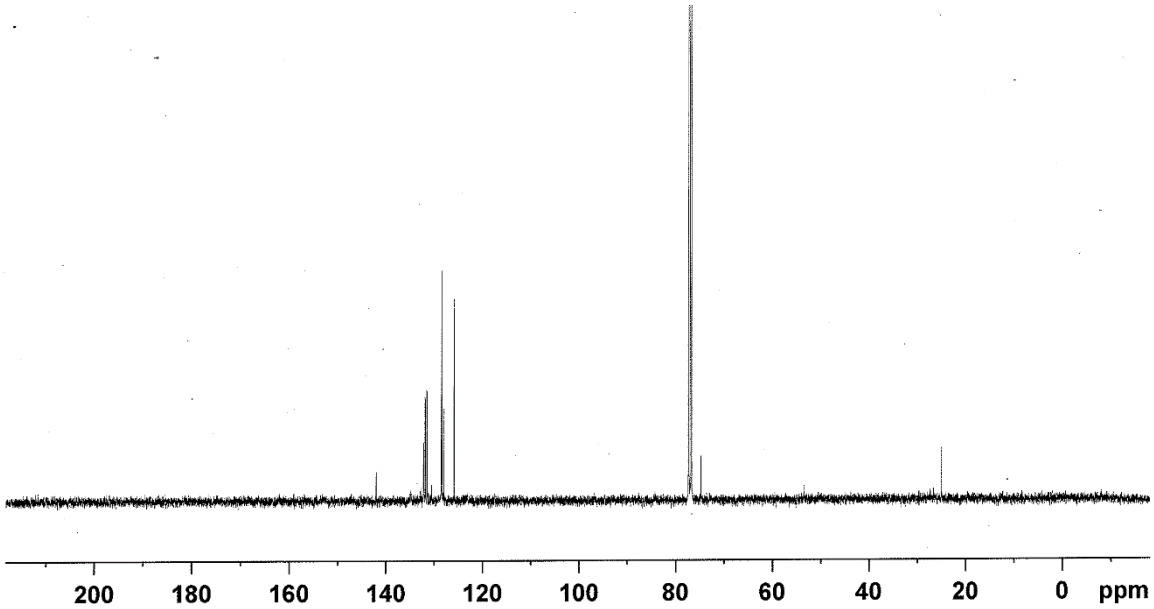
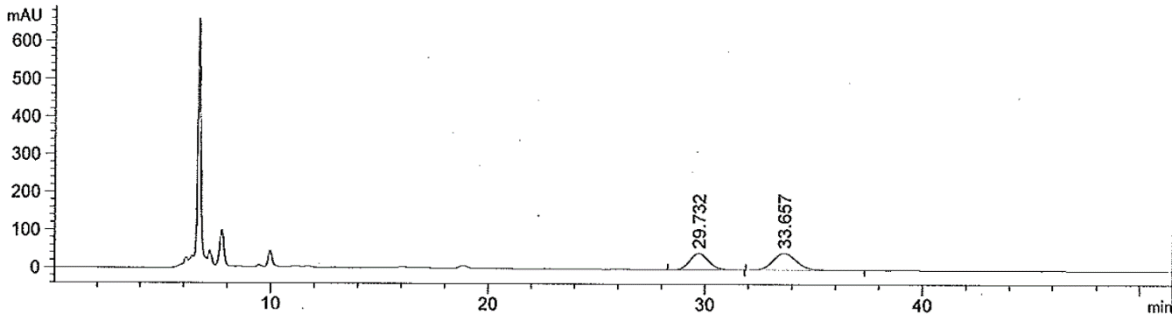


Figure S315. ^{13}C NMR of 1-phenylethyl diphenylphosphinate.

a)



b)

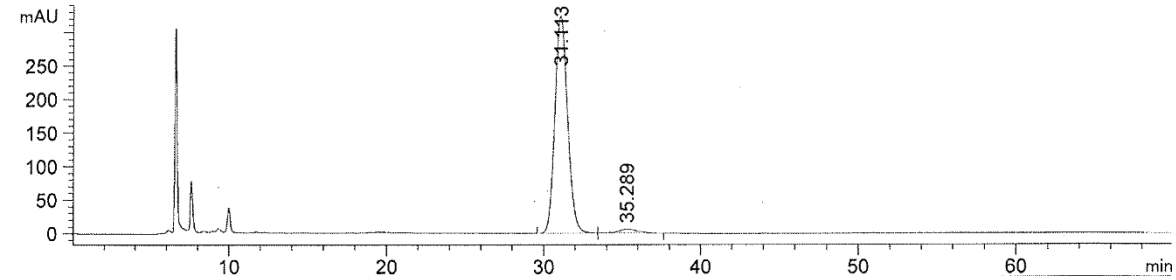


Figure S316. HPLC traces of (a) racemic and (b) enantioenriched product (95% (*R*) ee using Ir-**L1b** catalytic system; Figure 2, substrate **S44**)

(R)-3-Methylbutan-2-yl diphenylphosphinate

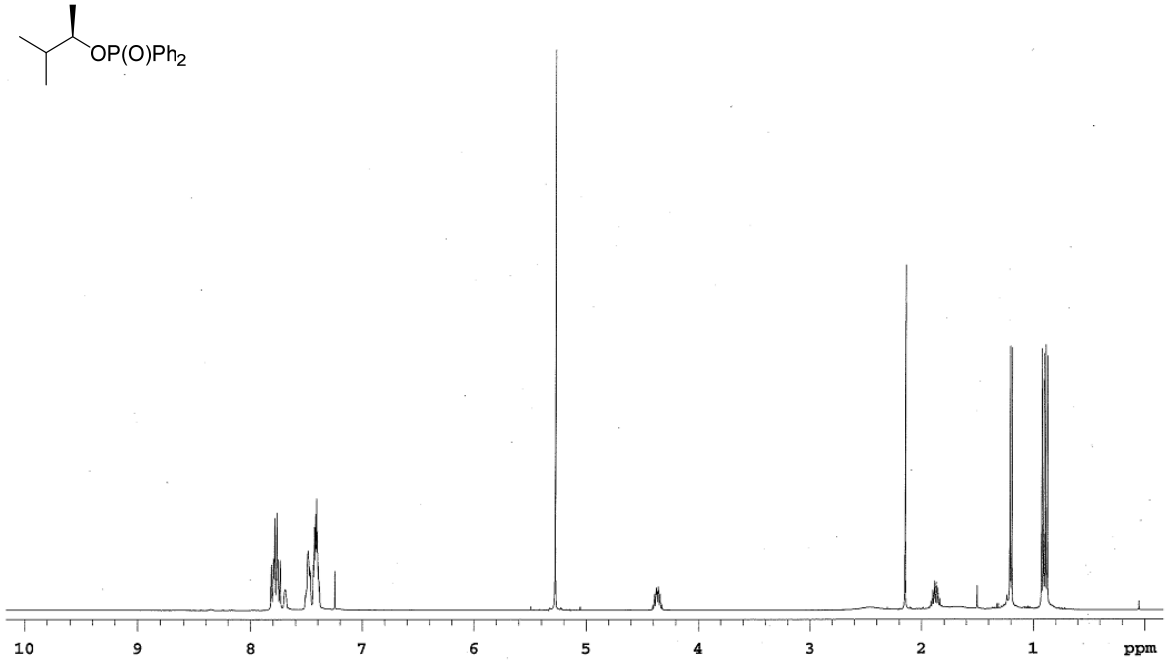


Figure S317. ^{1}H NMR of 3-methylbutan-2-yl diphenylphosphinate.

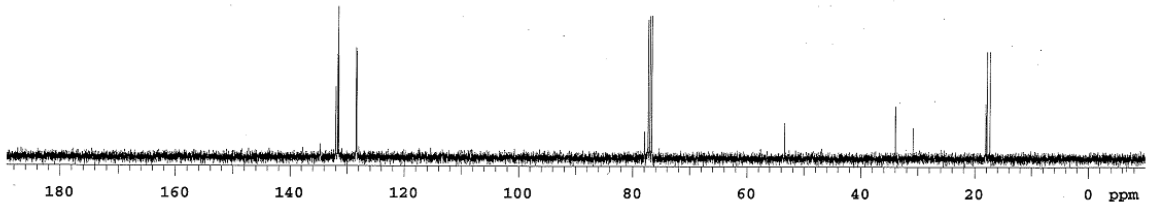
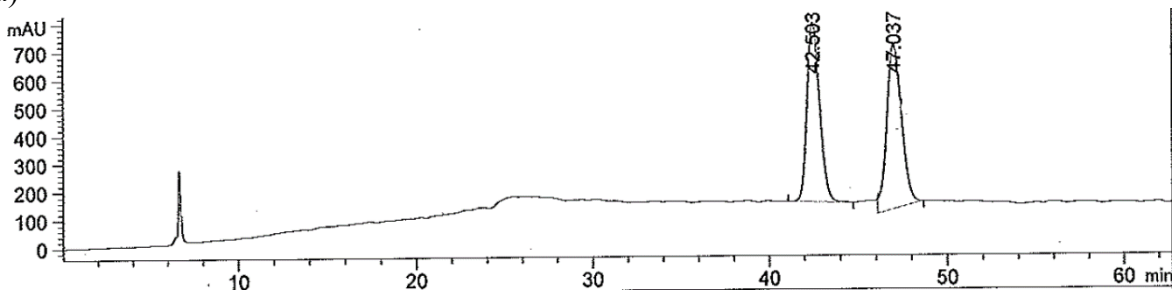


Figure S318. ^{13}C NMR of 3-methylbutan-2-yl diphenylphosphinate.

a)



b)

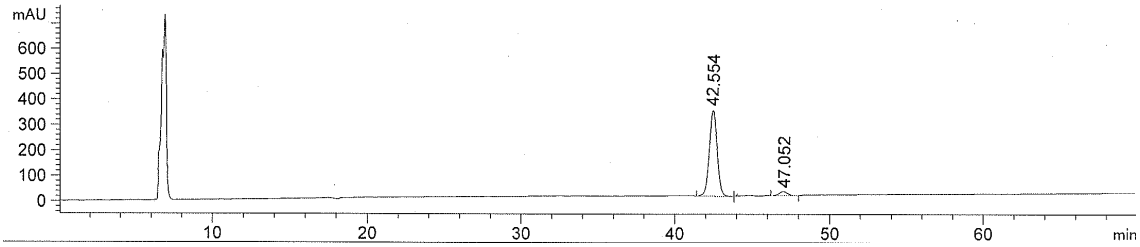


Figure S319. HPLC traces of (a) racemic and (b) enantioenriched product (94% (*R*) ee using Ir-**L1b** catalytic system; Figure 2, substrate **S45**)

(S,S)-1-Ethyl-2-methyl-2,3-dihydro-1H-indene

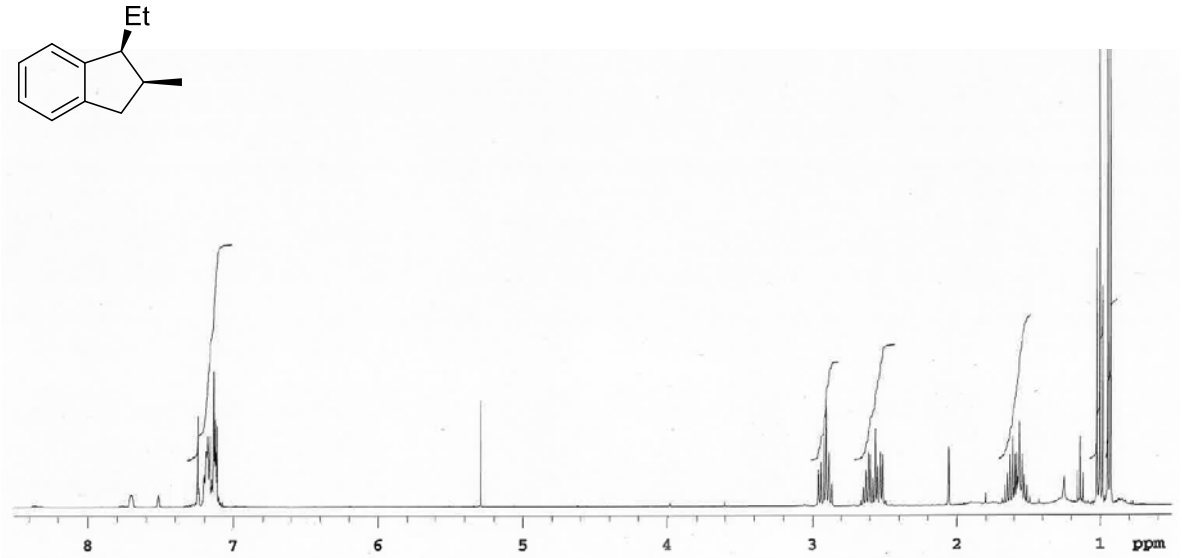


Figure S320. ^{1}H NMR of 1-ethyl-2-methyl-2,3-dihydro-1*H*-indene.

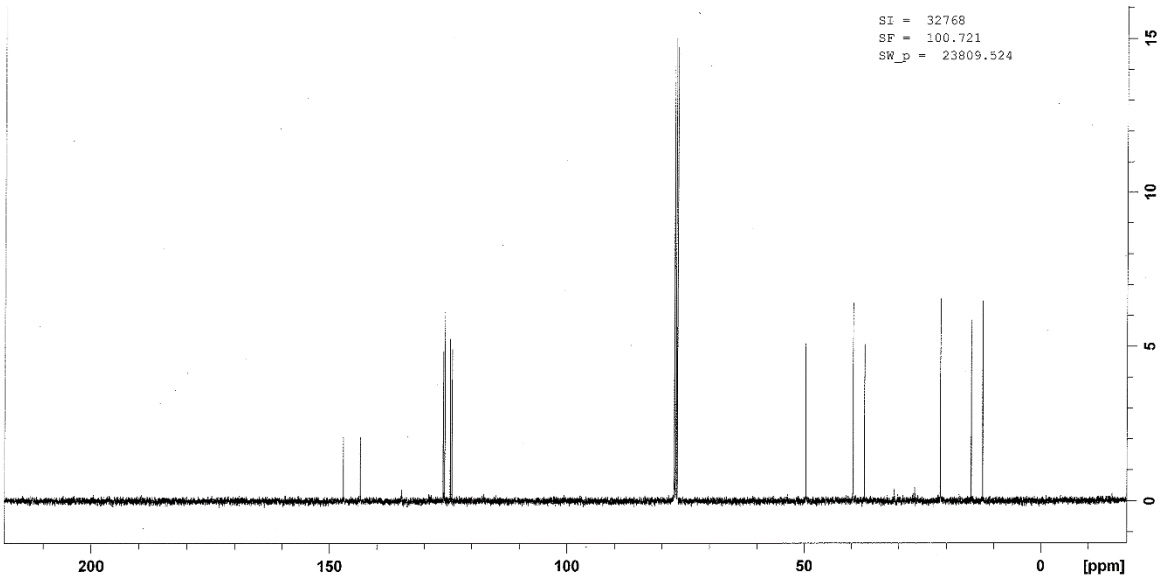
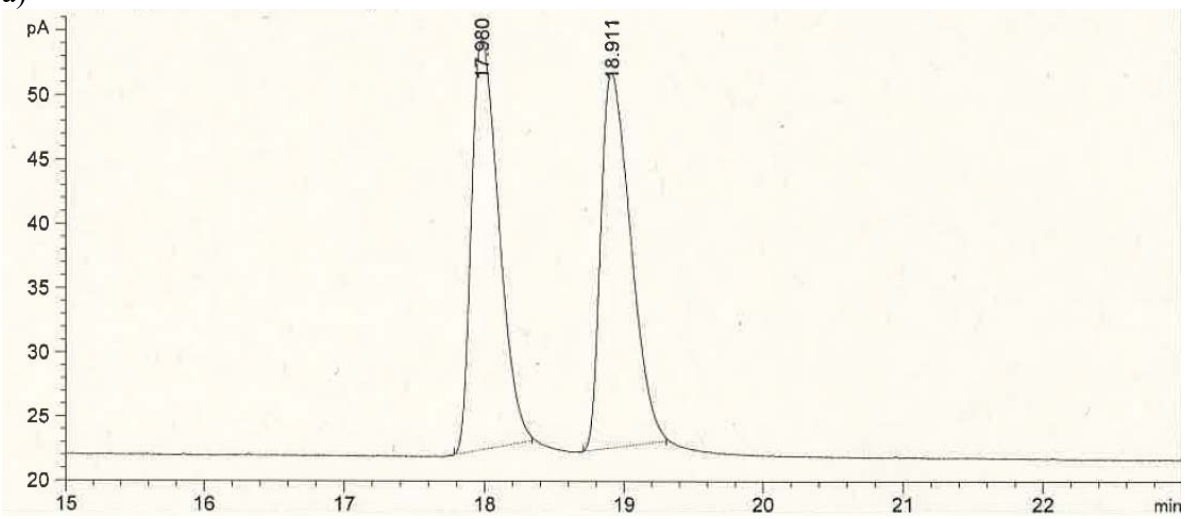


Figure S321. ^{13}C NMR of 1-ethyl-2-methyl-2,3-dihydro-1*H*-indene.

a)



b)

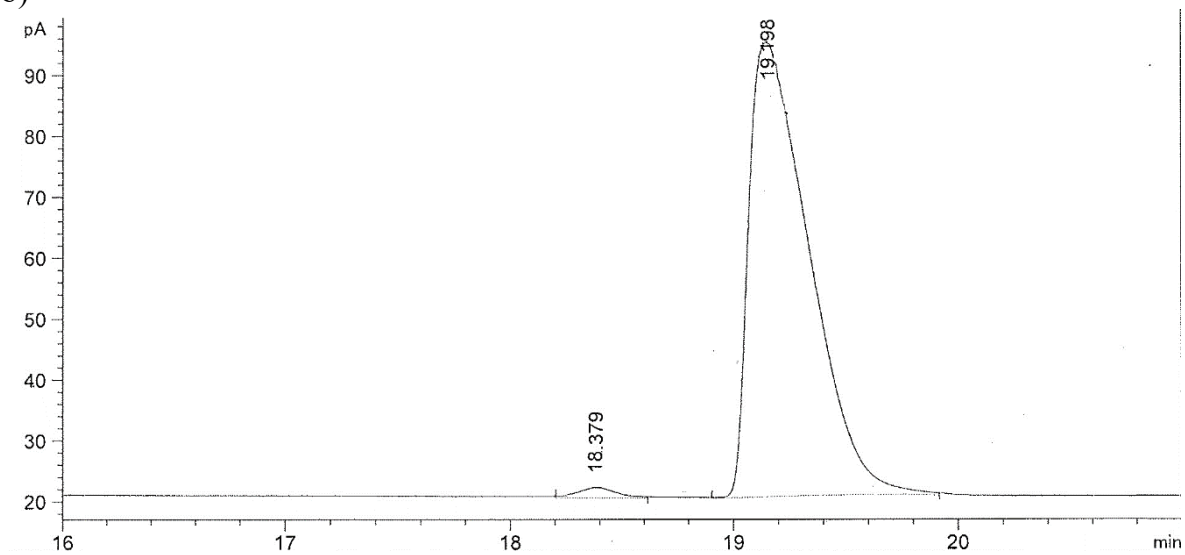


Figure S322. GC traces of (a) racemic and (b) enantioenriched product (97% (*S*,*S*) ee using Ir-**L2f** catalytic system; Figure 2, substrate **S46**)

(S,S)-1-Butyl-2-methyl-2,3-dihydro-1H-indene

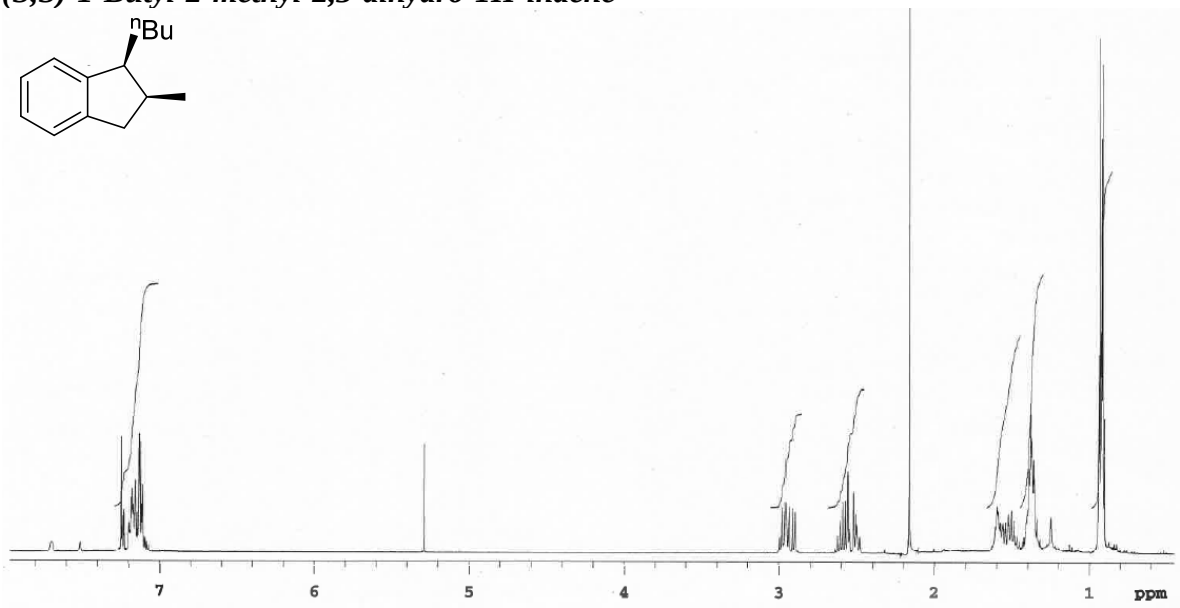


Figure S323. ^{1}H NMR of 1-butyl-2-methyl-2,3-dihydro-1*H*-indene.

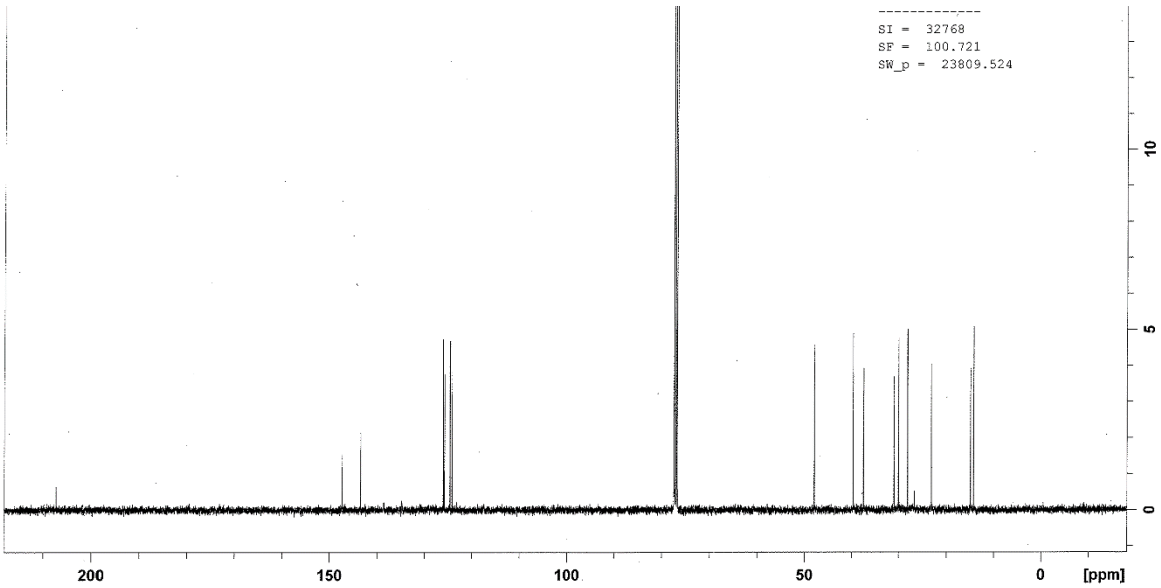
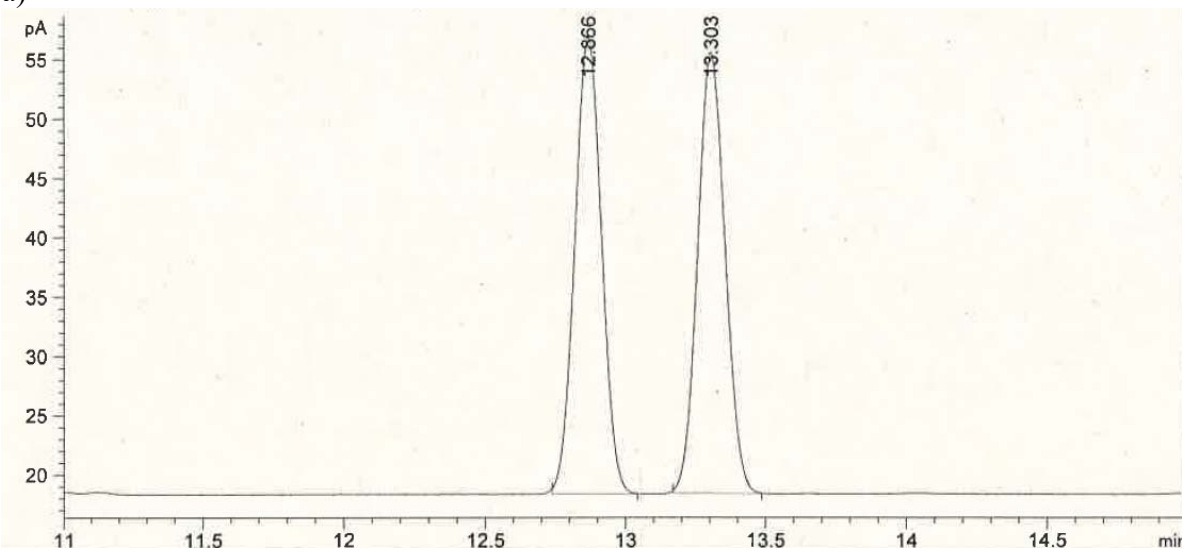


Figure S324. ^{1}H NMR of 1-butyl-2-methyl-2,3-dihydro-1*H*-indene.

a)



b)

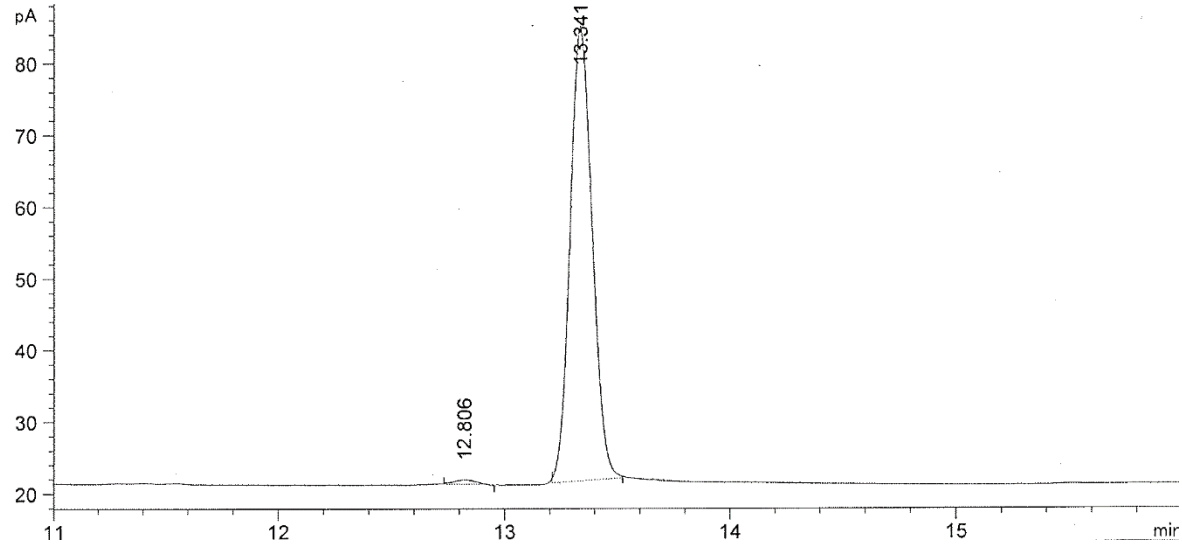


Figure S325. GC traces of (a) racemic and (b) enantioenriched product (98% (*S*,*S*) ee using Ir-**L2f** catalytic system; Figure 2, substrate **S47**)

(R,S)-2-Methyl-1-phenyl-2,3-dihydro-1H-indene

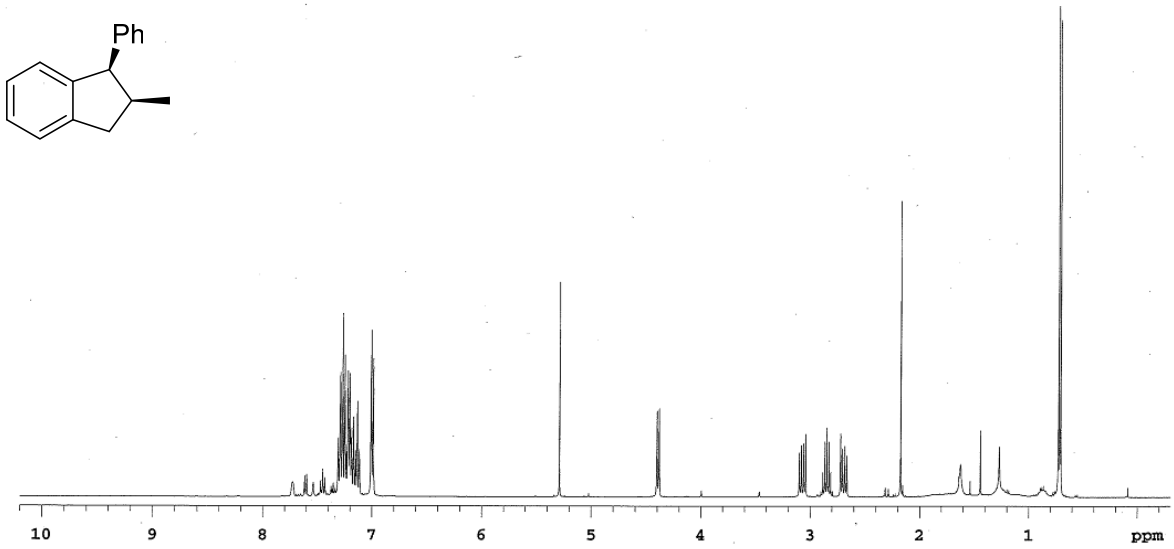


Figure S326. ^{1}H NMR of 2-methyl-1-phenyl-2,3-dihydro-1*H*-indene.

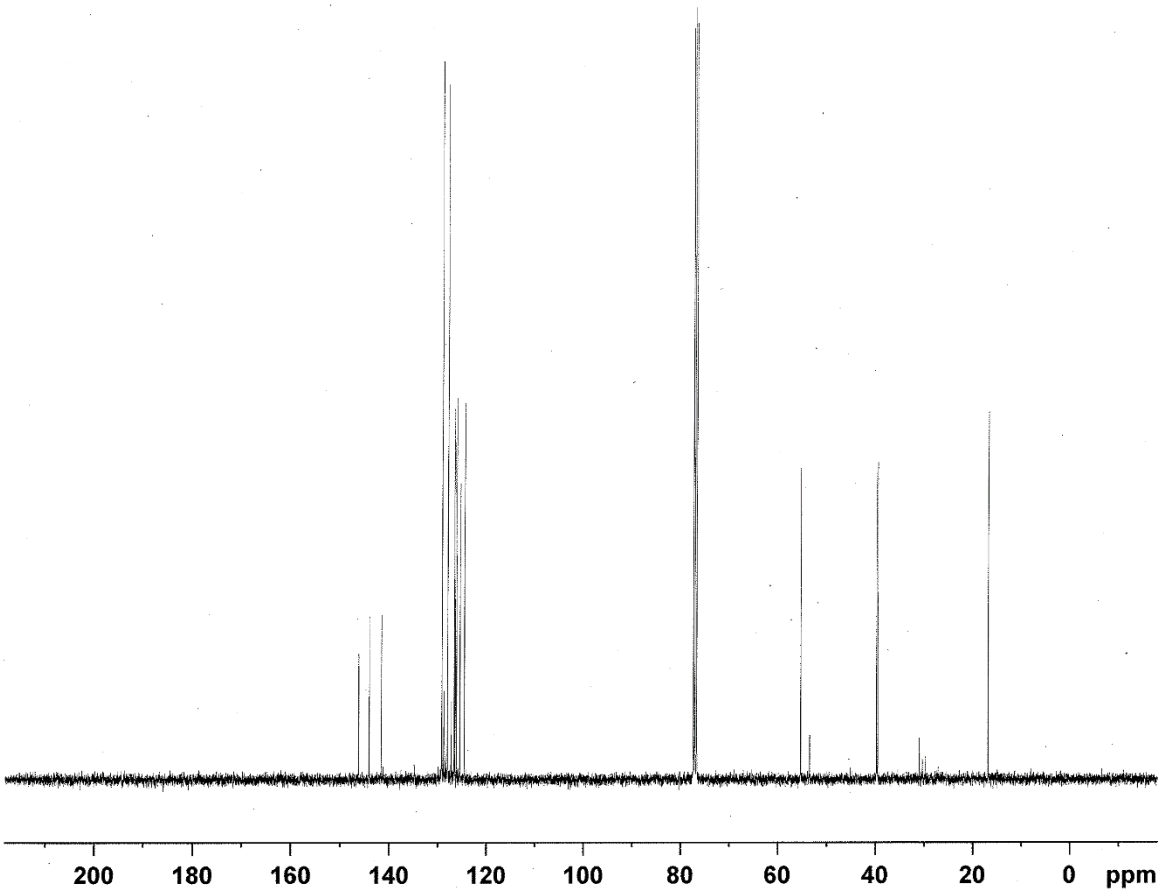
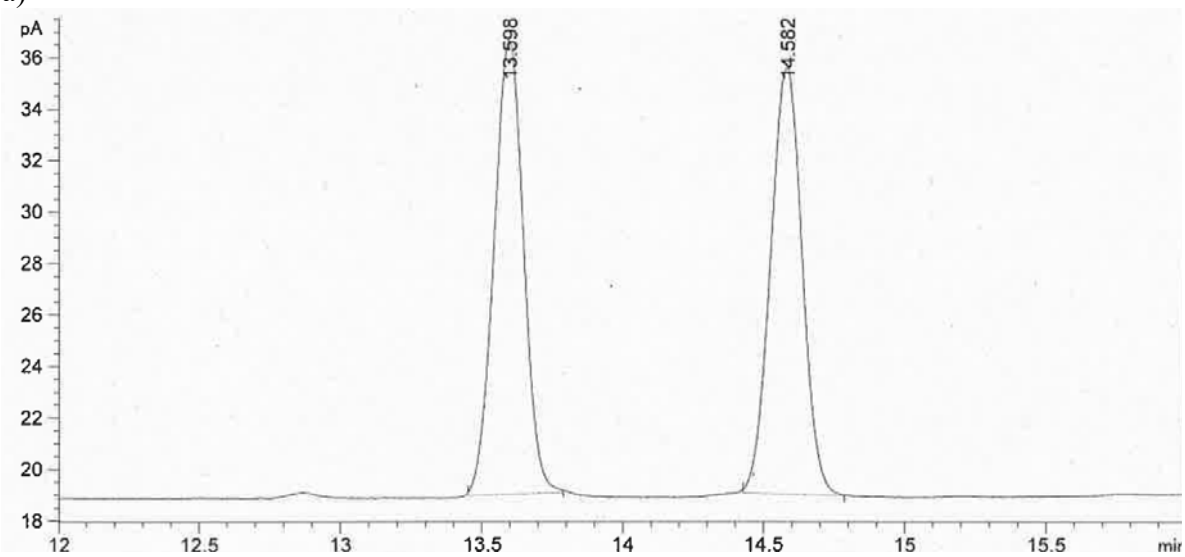


Figure S327. ^{13}C NMR of 2-methyl-1-phenyl-2,3-dihydro-1*H*-indene.

a)



b)

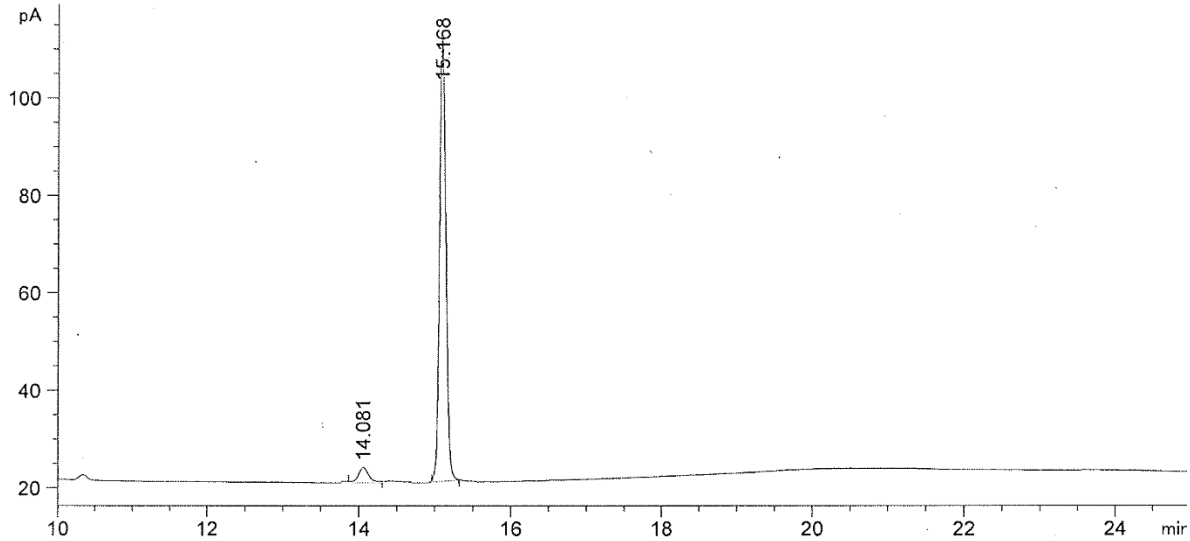


Figure S328. GC traces of (a) racemic and (b) enantioenriched product (94% (*R*,*S*) ee using Ir-**L2f** catalytic system; Figure 2, substrate **S48**)

(S,S)-2-Ethyl-1-methyl-2,3-dihydro-1H-indene

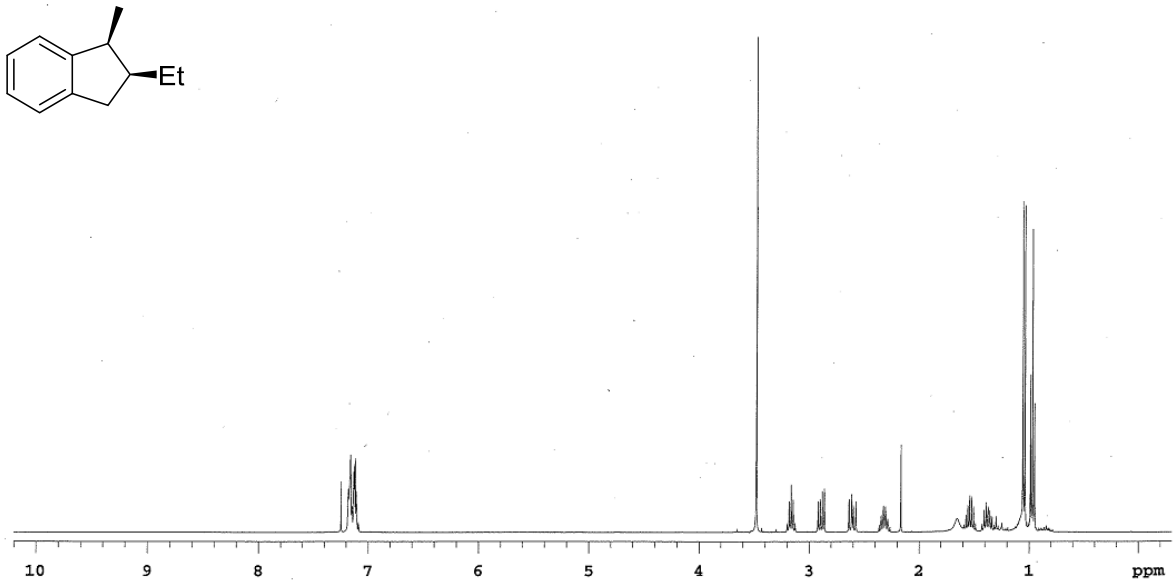


Figure S329. ^{1}H NMR of 2-ethyl-1-methyl-2,3-dihydro-1*H*-indene.

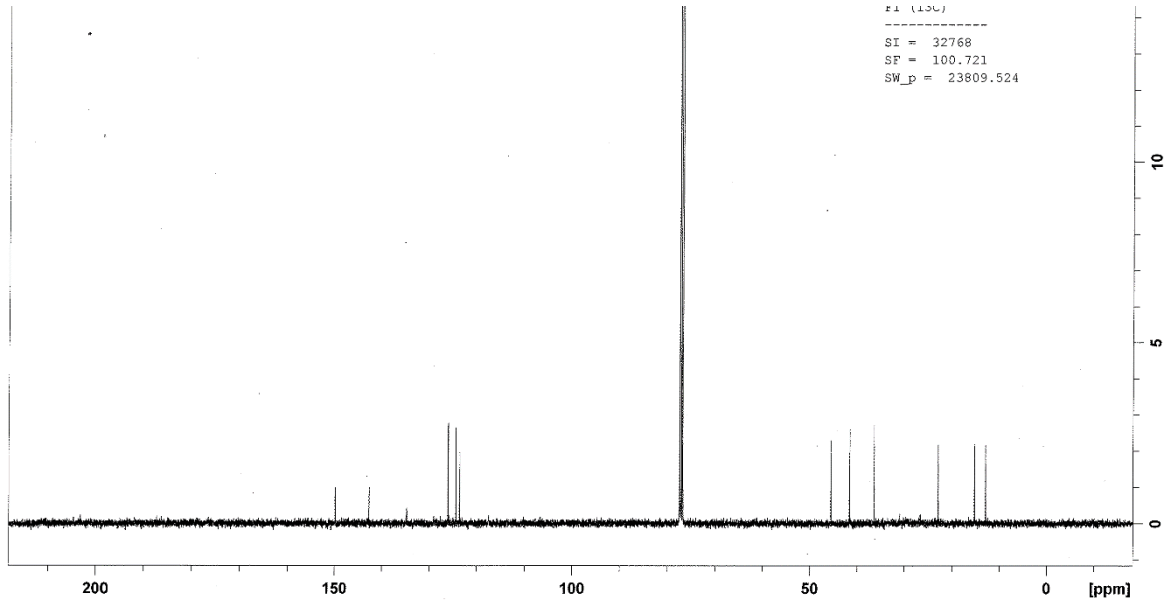
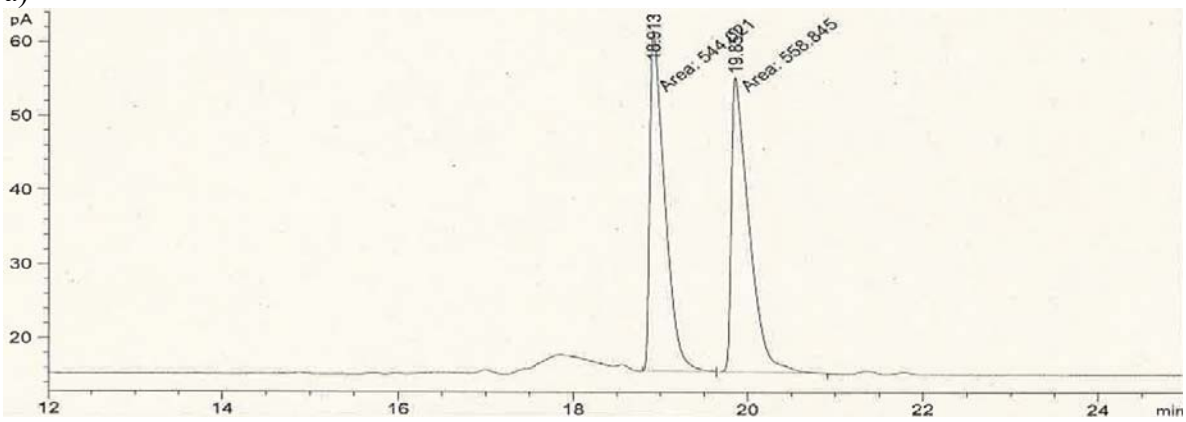


Figure S330. ^{13}C NMR of 2-ethyl-1-methyl-2,3-dihydro-1*H*-indene.

a)



b)

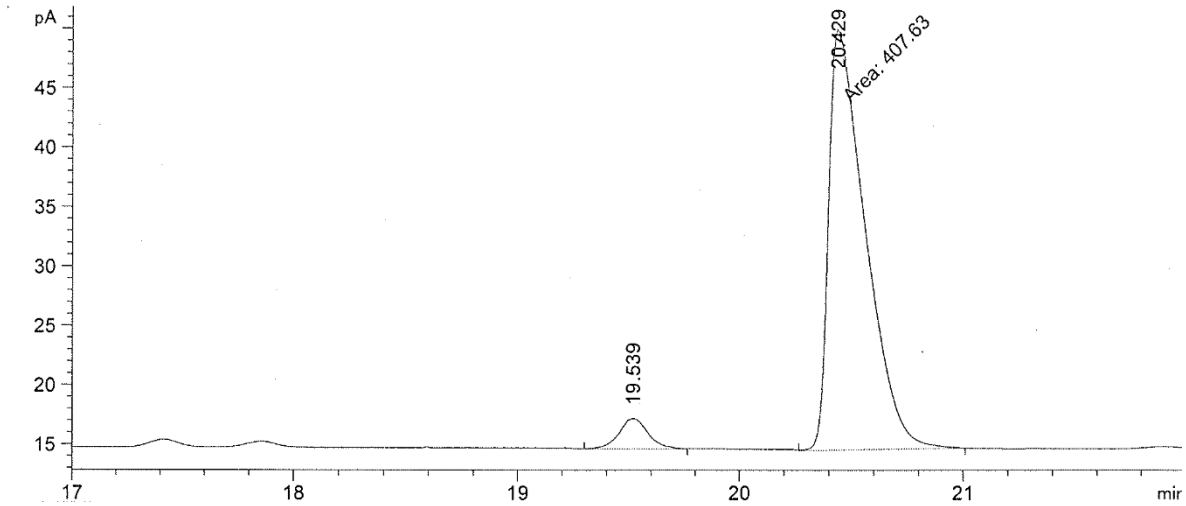


Figure S331. GC traces of (a) racemic and (b) enantioenriched product (92% (*S*,*S*) ee using Ir-**L2f** catalytic system; Figure 2, substrate **S49**)

(S,S)-2-Butyl-1-methyl-2,3-dihydro-1H-indene

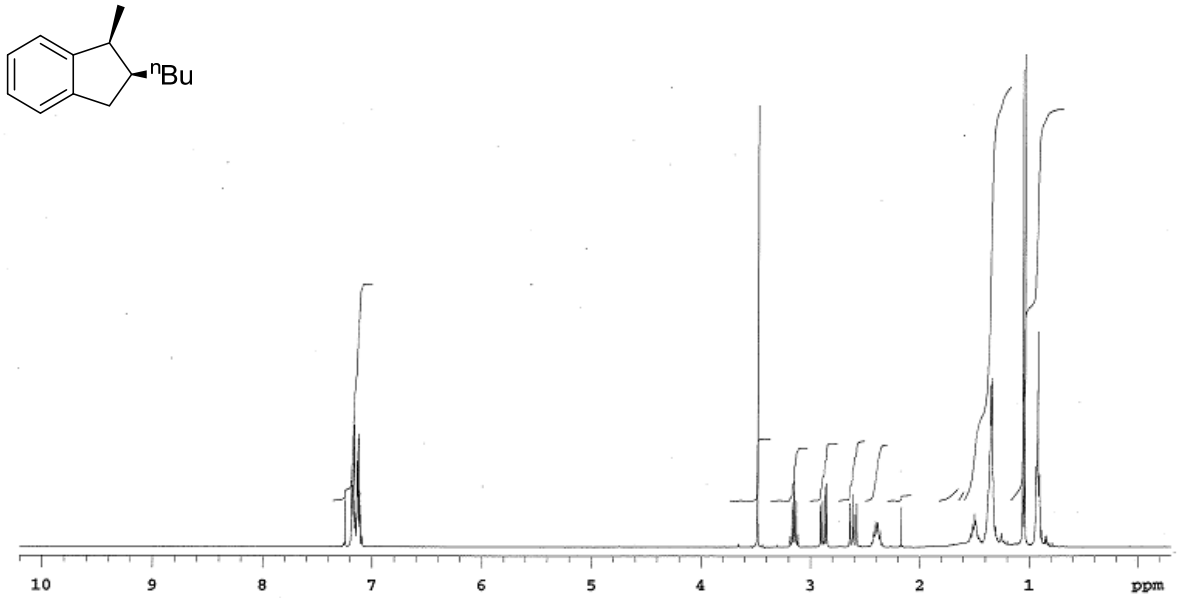


Figure S332. ^{1}H NMR of 2-butyl-1-methyl-2,3-dihydro-1*H*-indene.

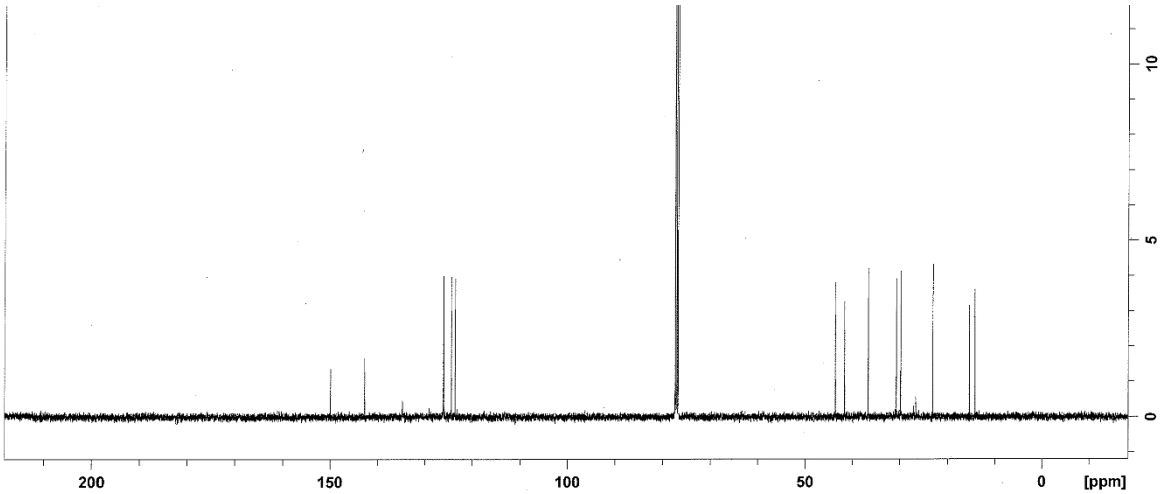
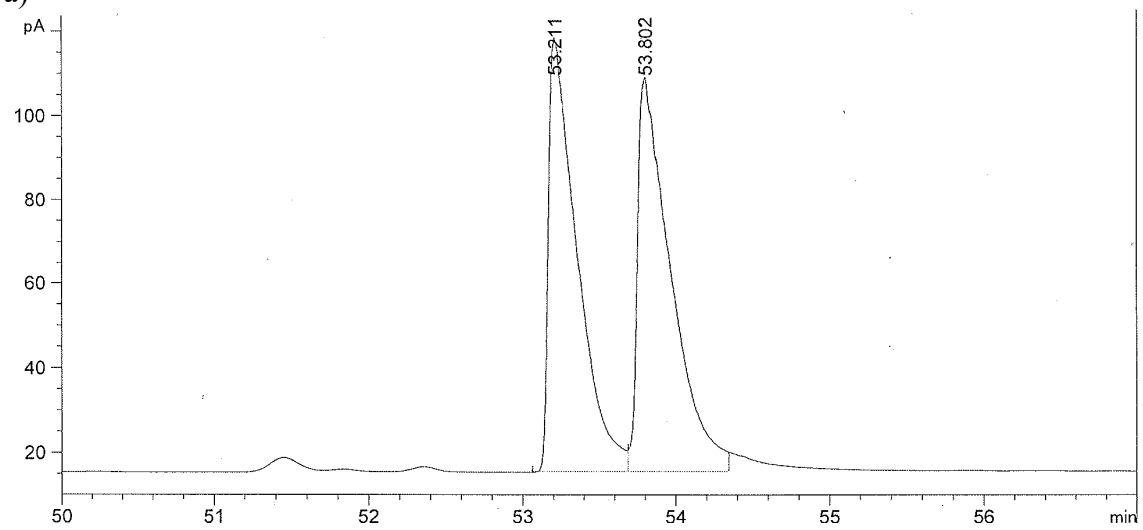


Figure S333. ^{13}C NMR of 2-butyl-1-methyl-2,3-dihydro-1*H*-indene.

a)



b)

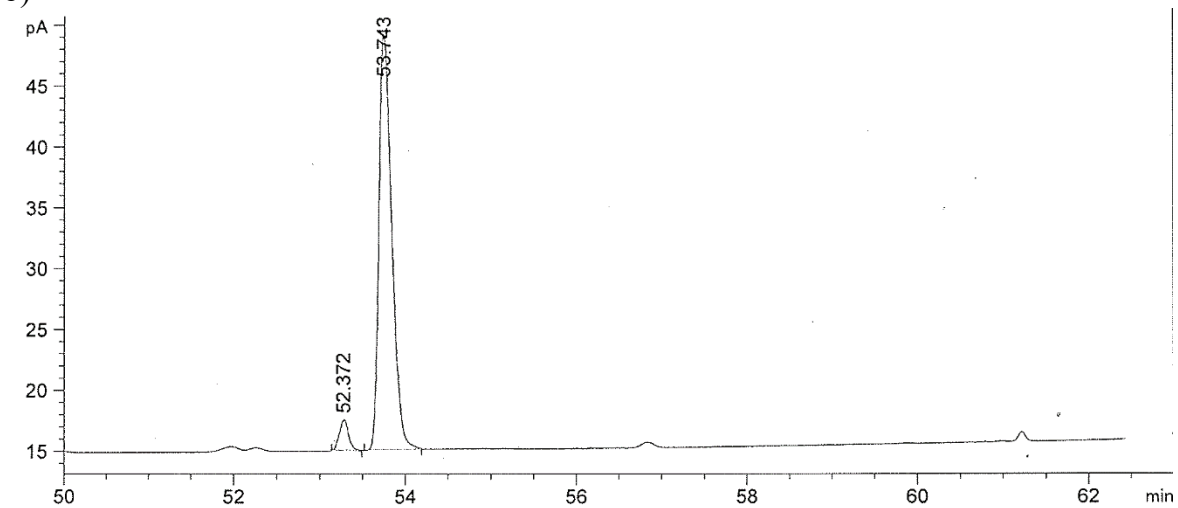


Figure S334. GC traces of (a) racemic and (b) enantioenriched product (93% (*S*,*S*) ee using Ir-**L2f** catalytic system; Figure 2, substrate **S50**)

(S,S)-1,2-Dimethyl-1,2,3,4-tetrahydronaphthalene

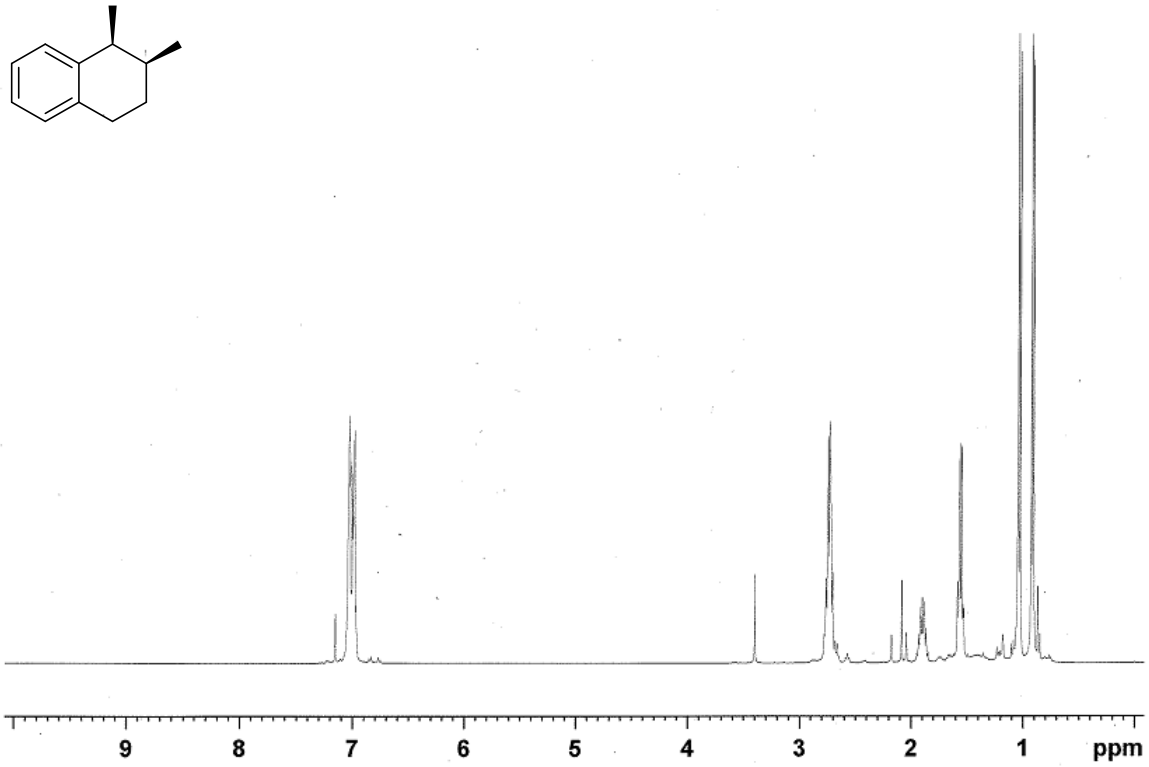


Figure S335. ^{1}H NMR of 1,2-dimethyl-1,2,3,4-tetrahydronaphthalene.

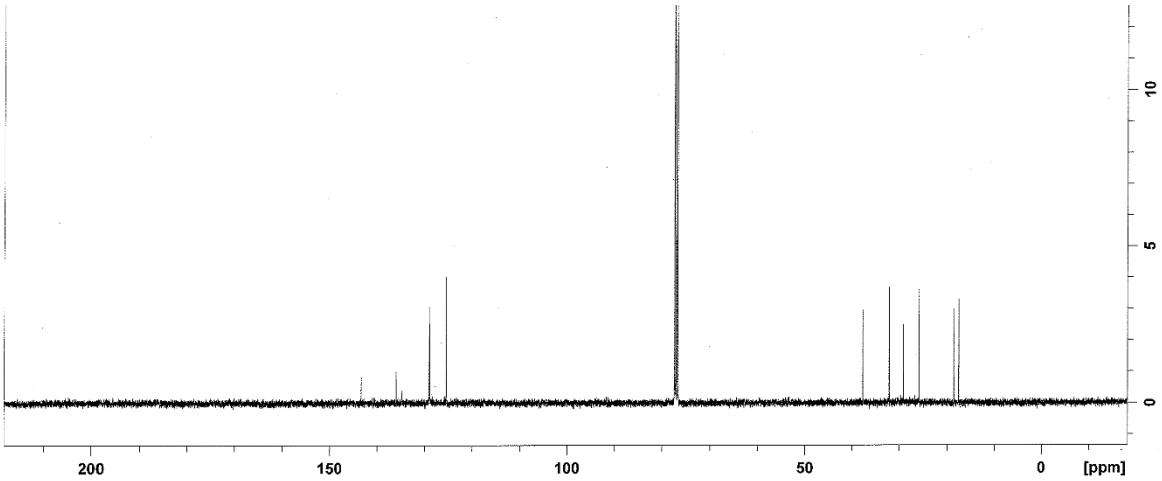
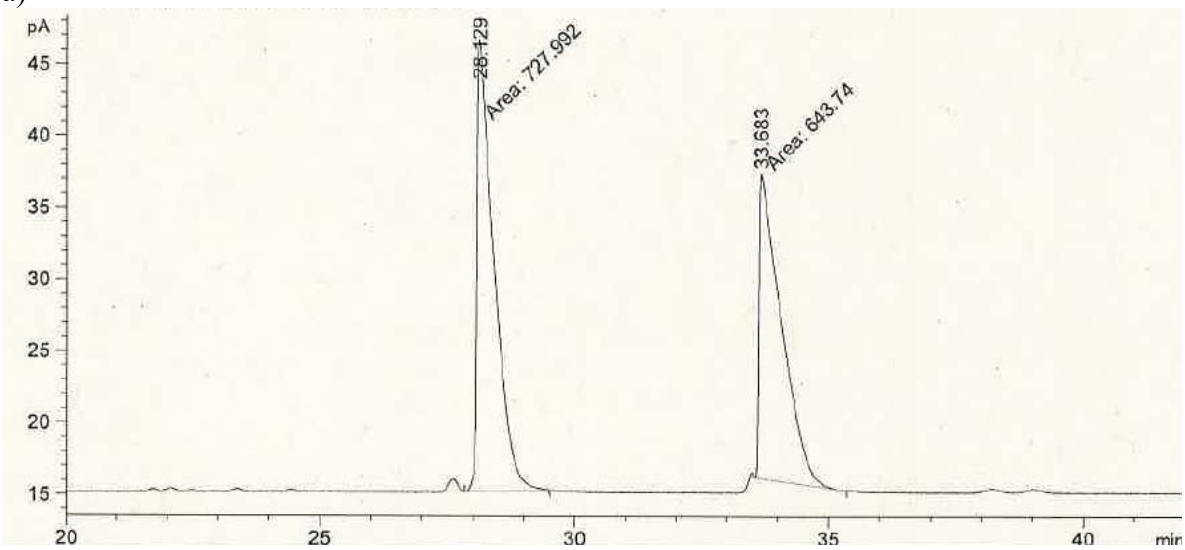


Figure S336. ^{13}C NMR of 1,2-dimethyl-1,2,3,4-tetrahydronaphthalene.

a)



b)

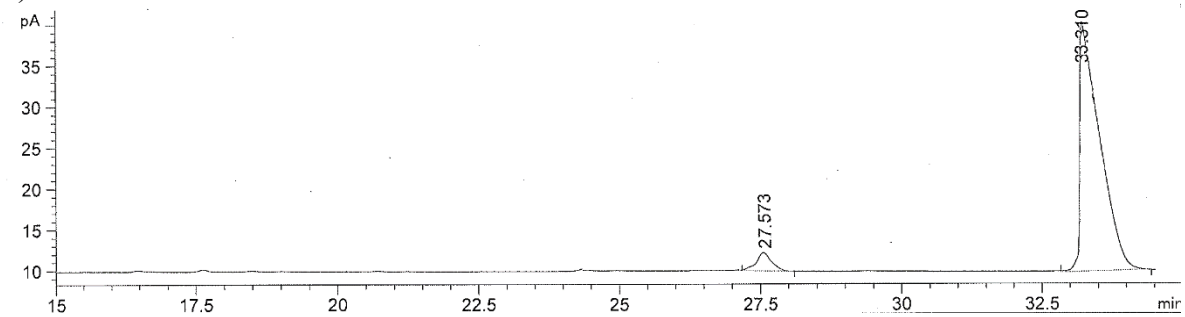


Figure S337. GC traces of (a) racemic and (b) enantioenriched product (90% (*S*,*S*) ee using Ir-**L2g** catalytic system; Figure 2, substrate **S51**)

(S)-1-Methyl-4-(3-methylbutan-2-yl)benzene

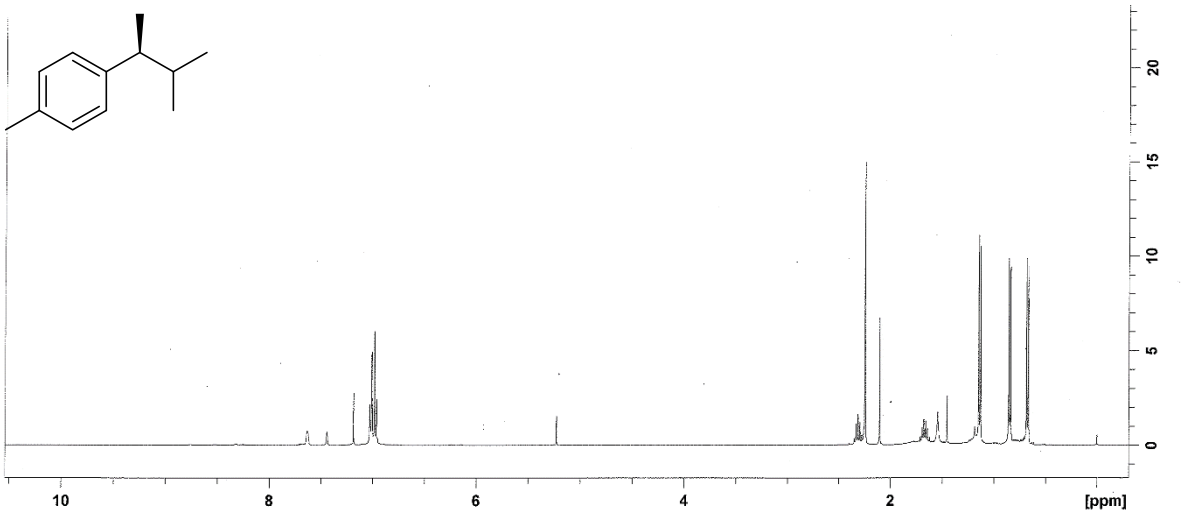


Figure S338. ^{1}H NMR of 1-methyl-4-(3-methylbutan-2-yl)benzene.

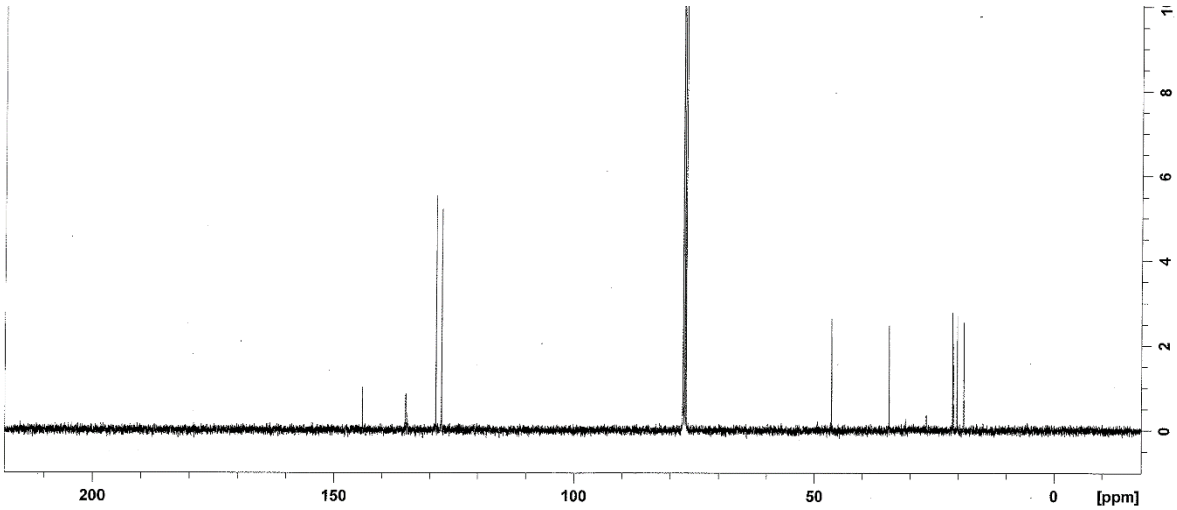
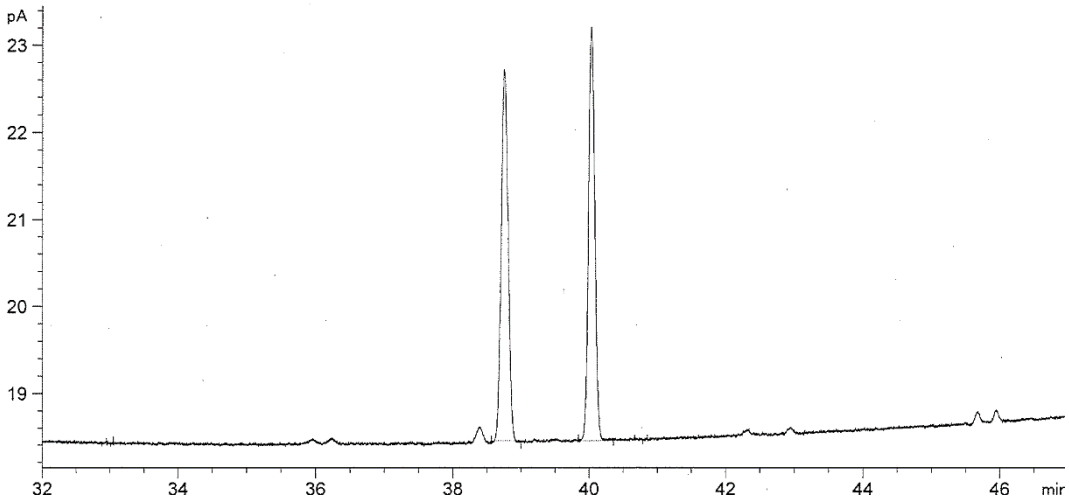


Figure S339. ^{13}C NMR of 1-methyl-4-(3-methylbutan-2-yl)benzene.

a)



b)

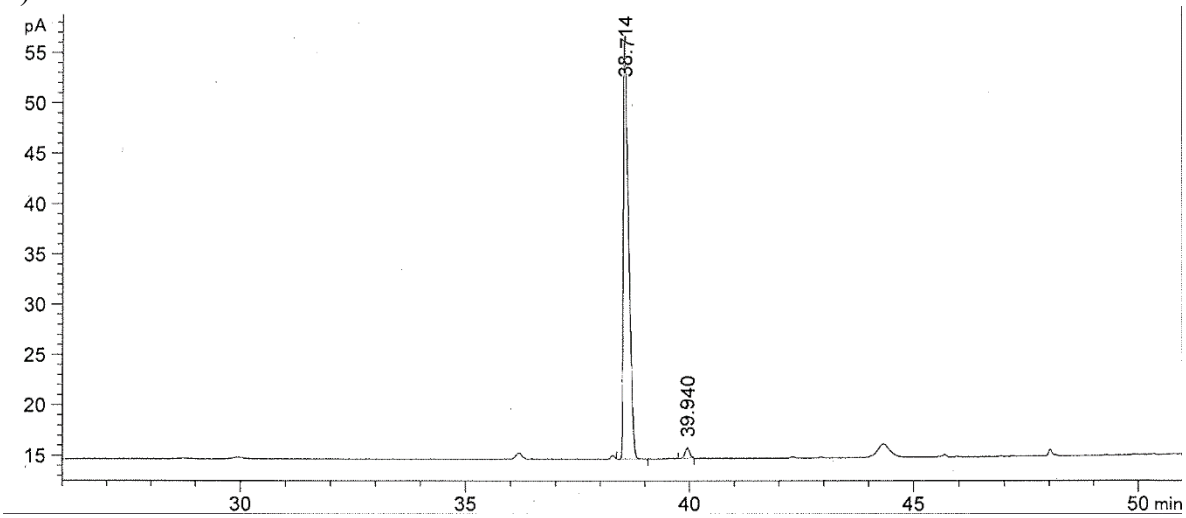


Figure S340. GC traces of (a) racemic and (b) enantioenriched product (97% (*S*) ee using Ir-**L4h** catalytic system; Figure 2, substrate **S53**)

(S)-1-Methoxy-4-(3-methylbutan-2-yl)benzene

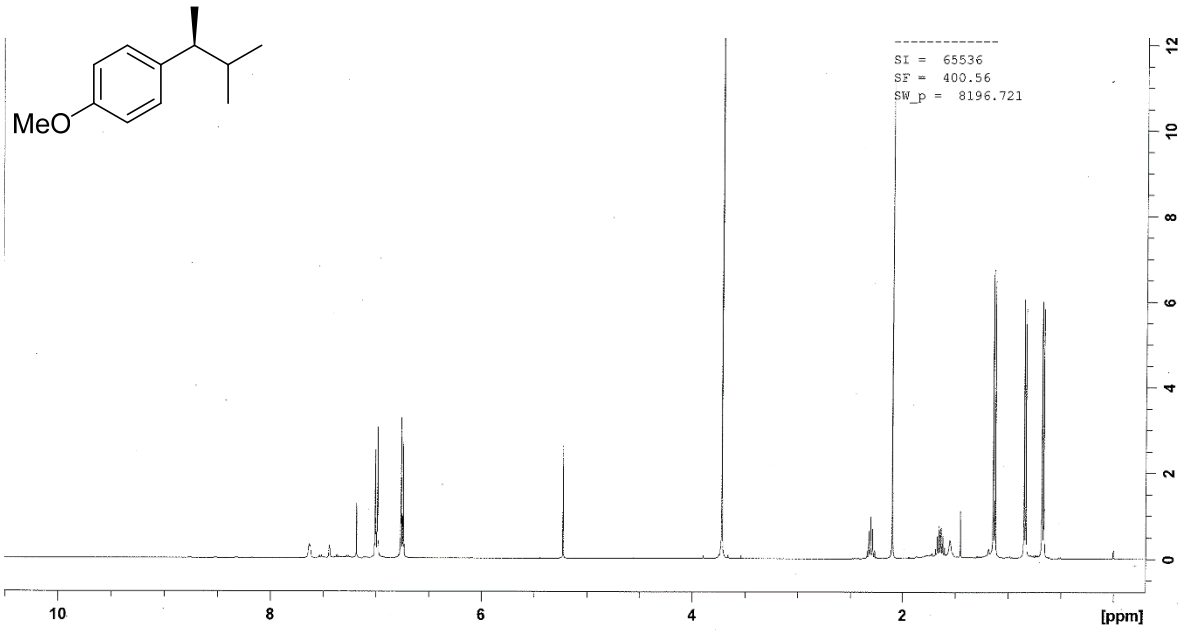


Figure S341. ^{1}H NMR of 1-methoxy-4-(3-methylbutan-2-yl)benzene.

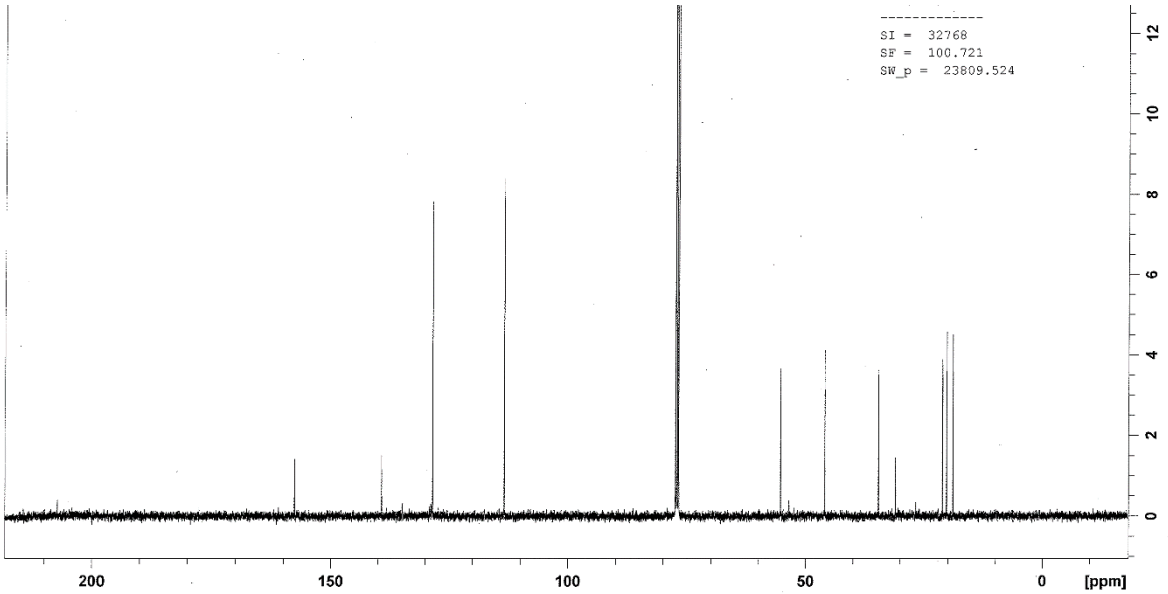
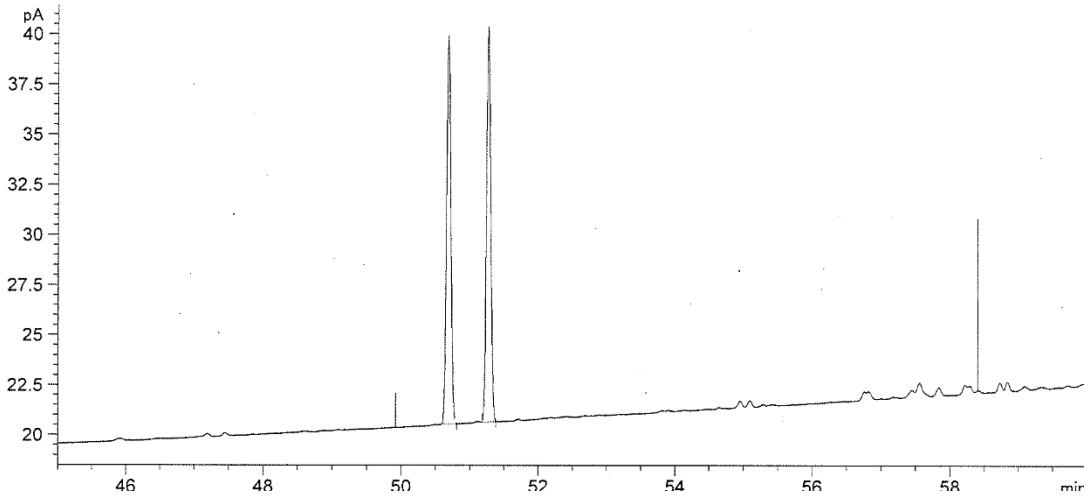


Figure S342. ^{1}H NMR of 1-methoxy-4-(3-methylbutan-2-yl)benzene.

a)



b)

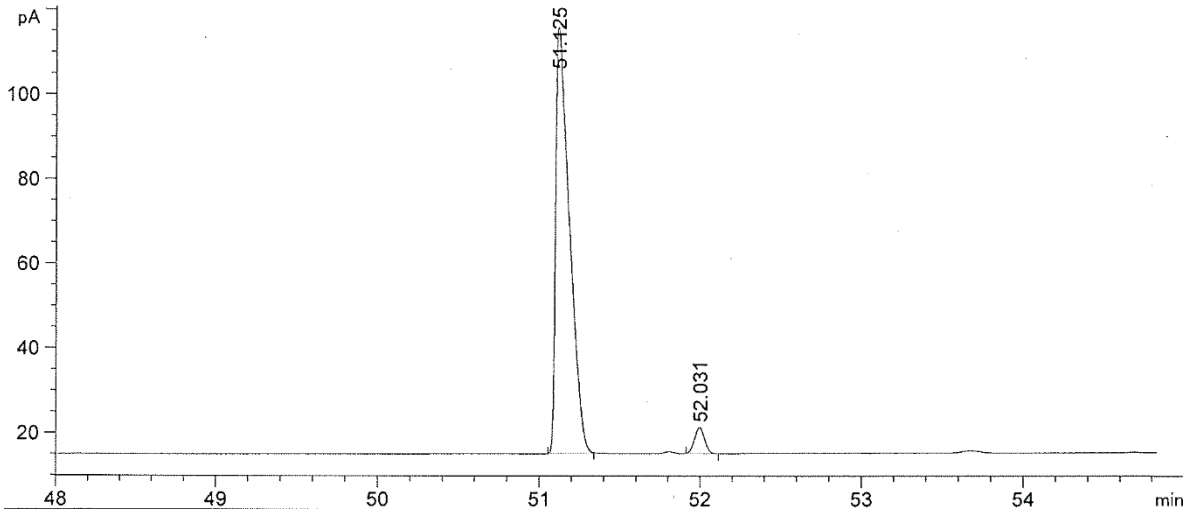


Figure S343. GC traces of (a) racemic and (b) enantioenriched product (96% (*S*) ee using Ir-**L4h** catalytic system; Figure 2, substrate **S54**)

(S)-1-Methyl-3-(3-methylbutan-2-yl)benzene

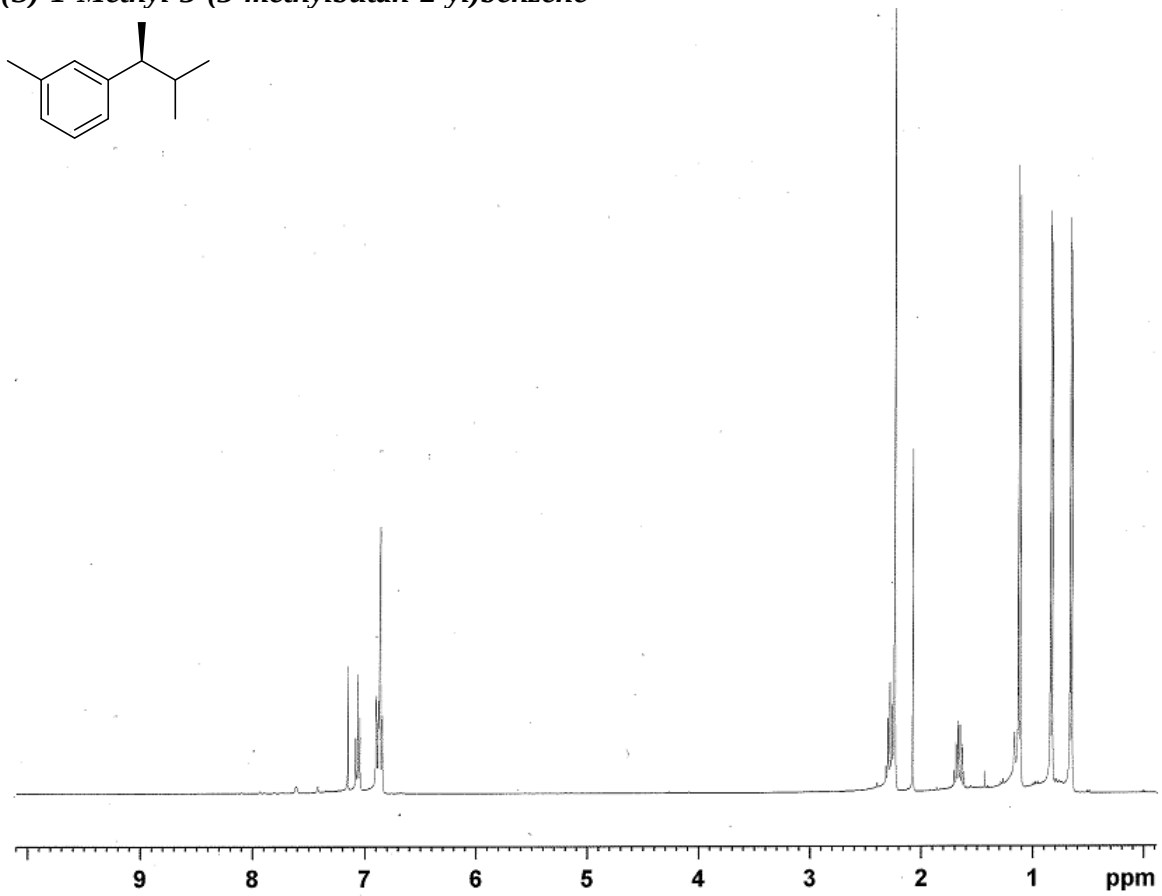


Figure S344. ^{1}H NMR of 1-methyl-3-(3-methylbutan-2-yl)benzene.

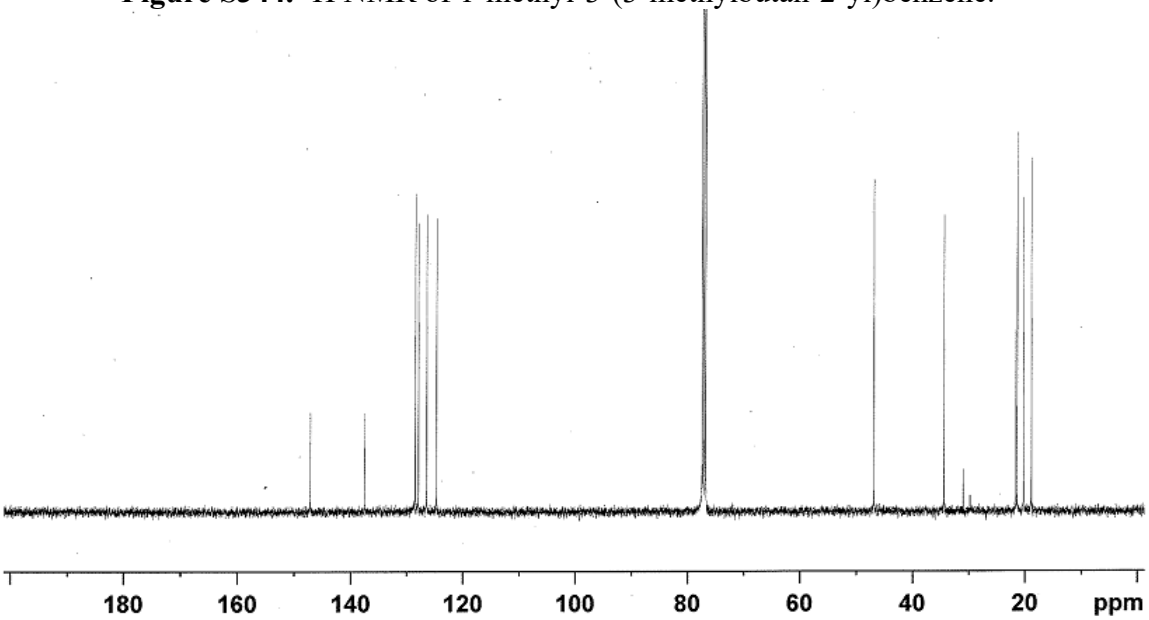
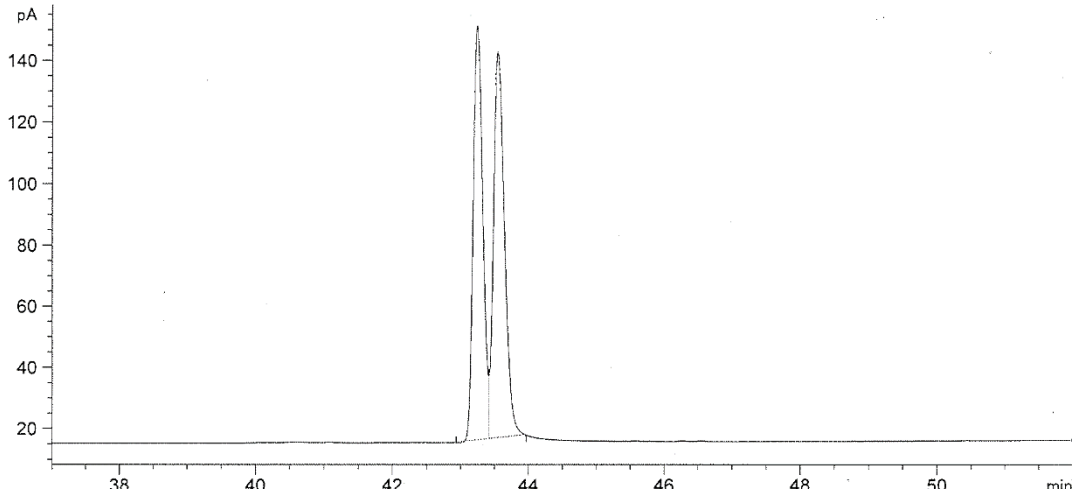


Figure S345. ^{13}C NMR of 1-methyl-3-(3-methylbutan-2-yl)benzene.

a)



b)

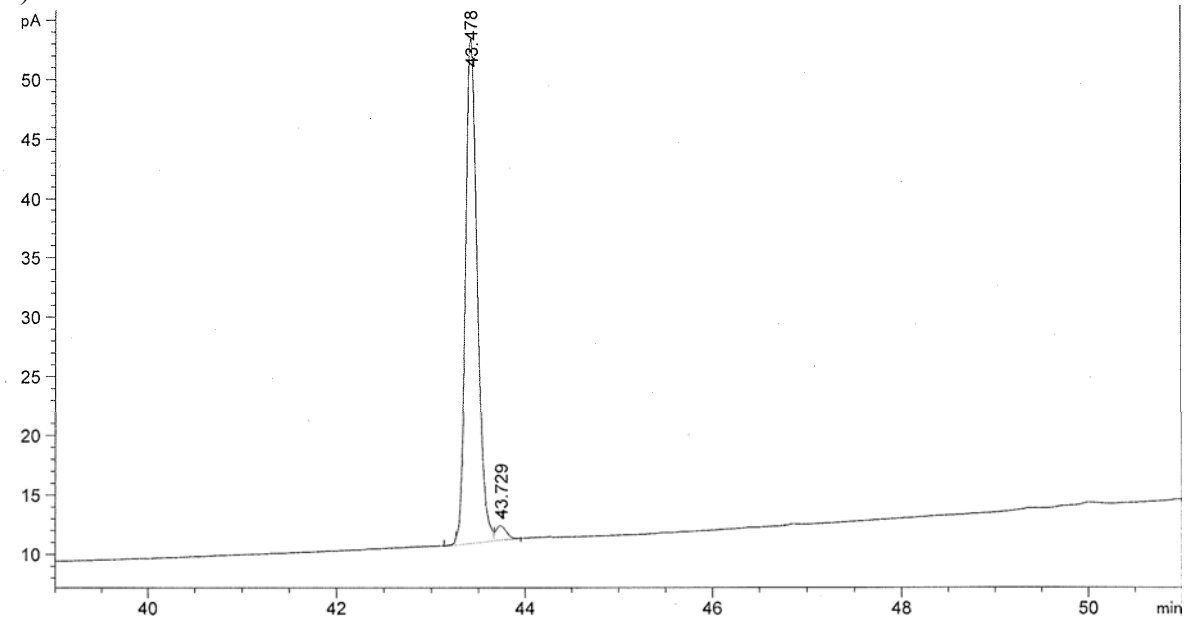


Figure S346. GC traces of (a) racemic and (b) enantioenriched product (98% (*S*) ee using Ir-**L4h** catalytic system; Figure 2, substrate **S55**)

(S)-1-Methoxy-2-(3-methylbutan-2-yl)benzene

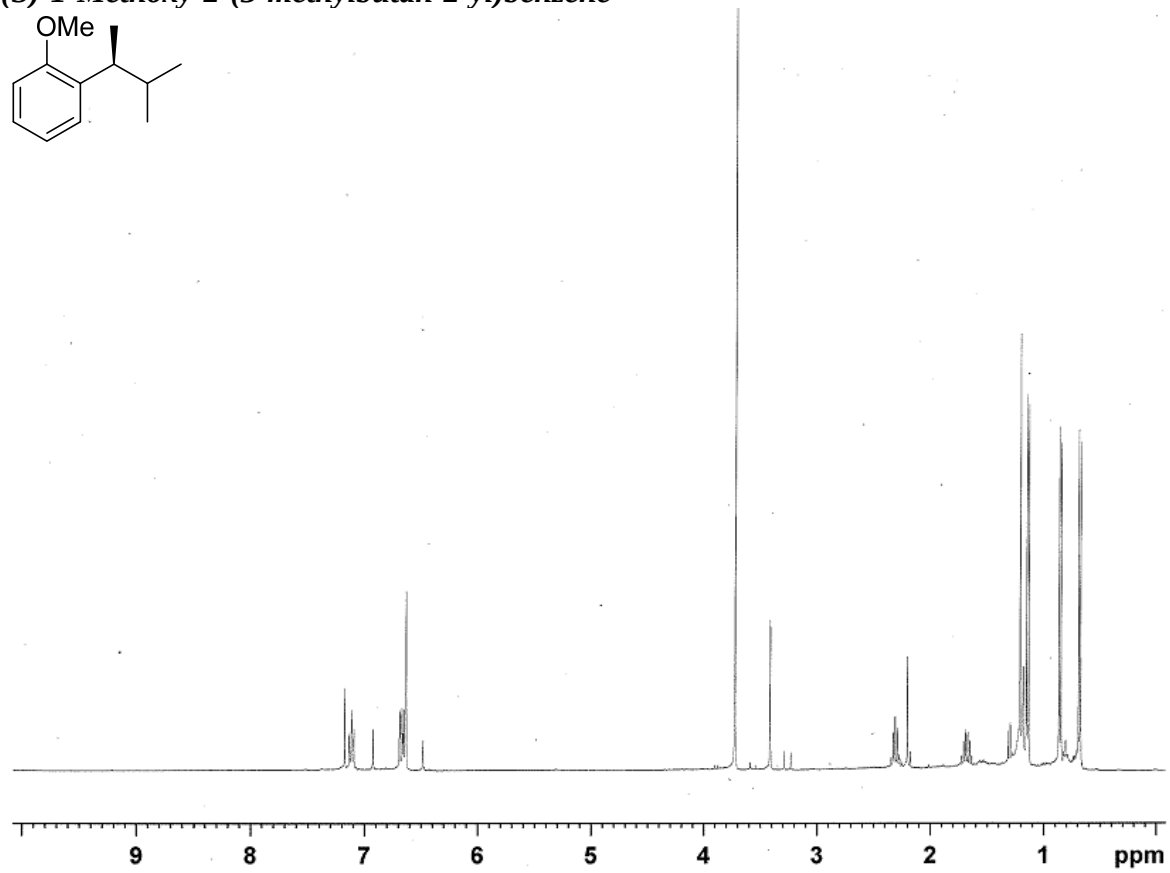


Figure S347. ^{1}H NMR of 1-methoxy-2-(3-methylbutan-2-yl)benzene.

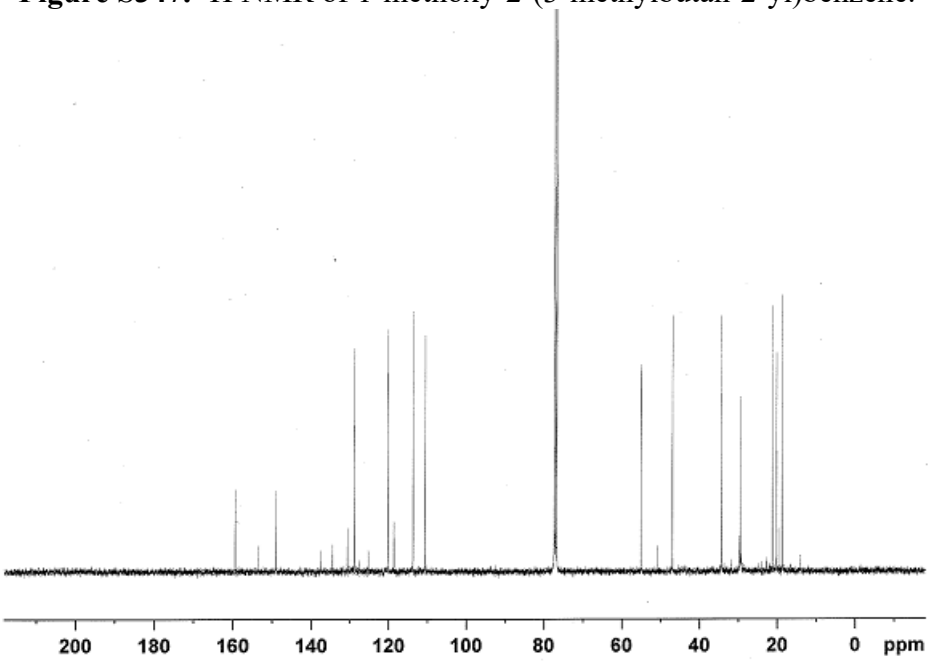
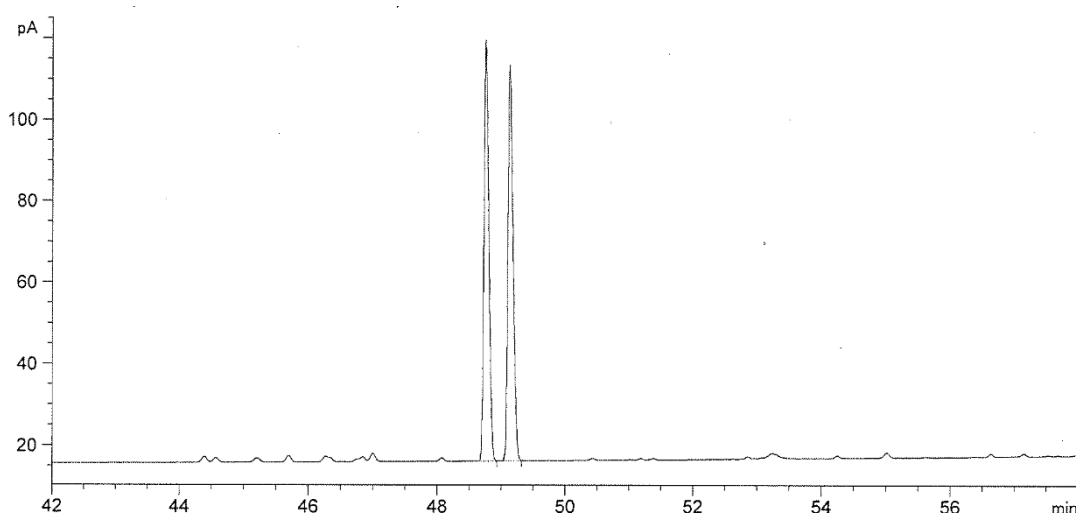


Figure S348. ^{13}C NMR of 1-methoxy-2-(3-methylbutan-2-yl)benzene.

a)



b)

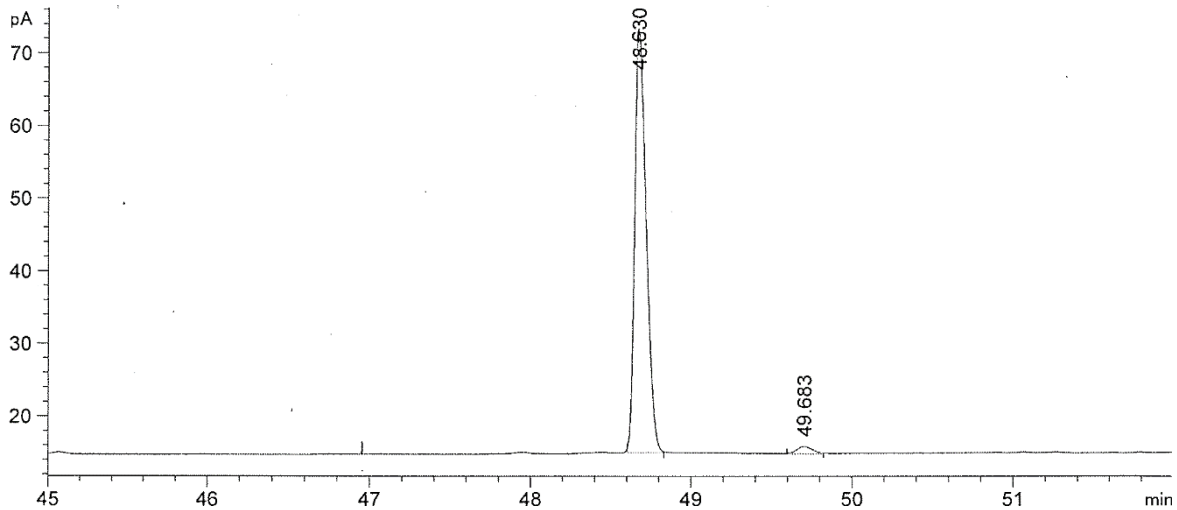


Figure S349. GC traces of (a) racemic and (b) enantioenriched product (97% (*S*) ee using Ir-**L4h** catalytic system; Figure 2, substrate **S56**)

(R)-N-(1,2,3,4-Tetrahydronaphthalen-2-yl)acetamide

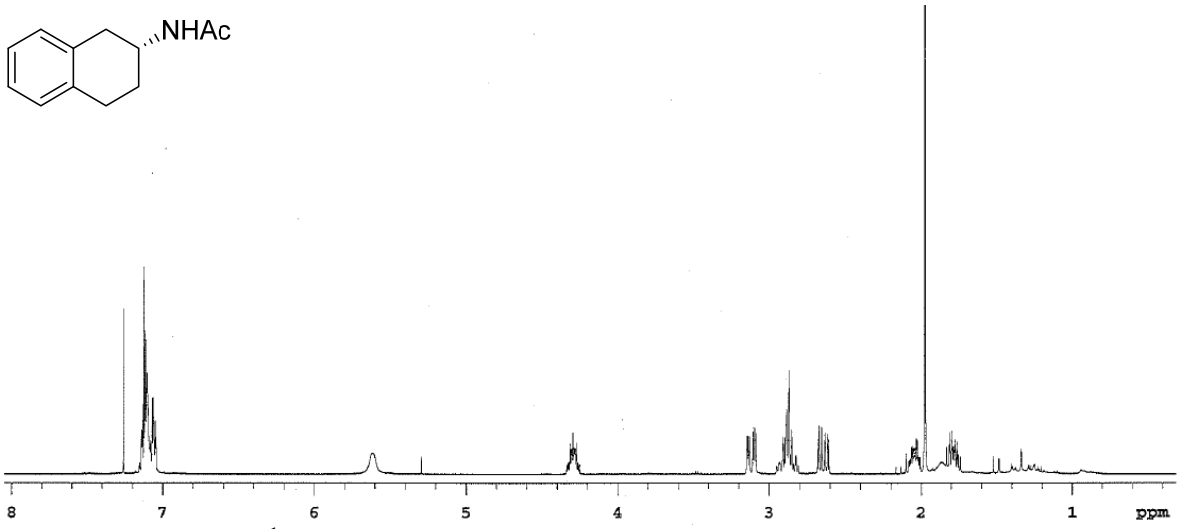


Figure S350. ^{1}H NMR of *N*-(1,2,3,4-tetrahydronaphthalen-2-yl)acetamide.

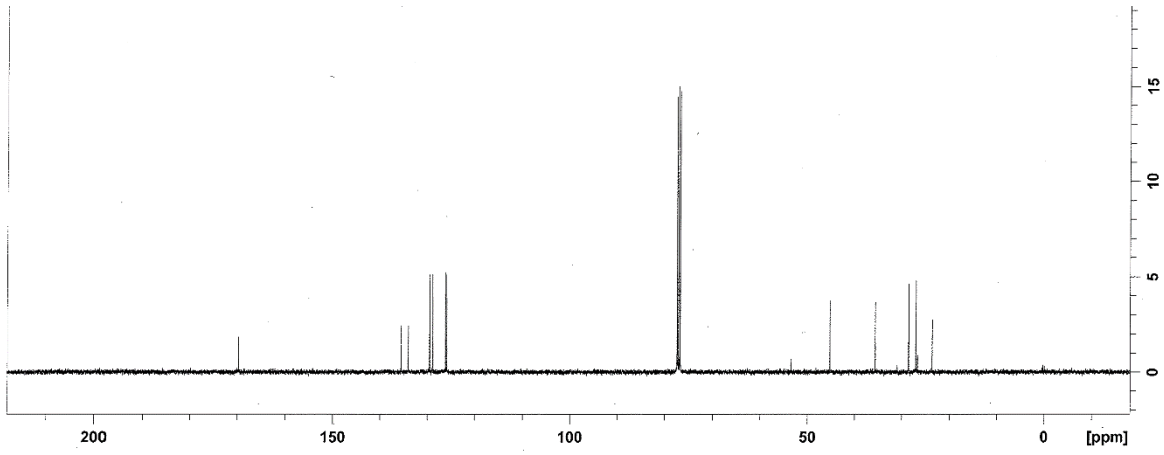
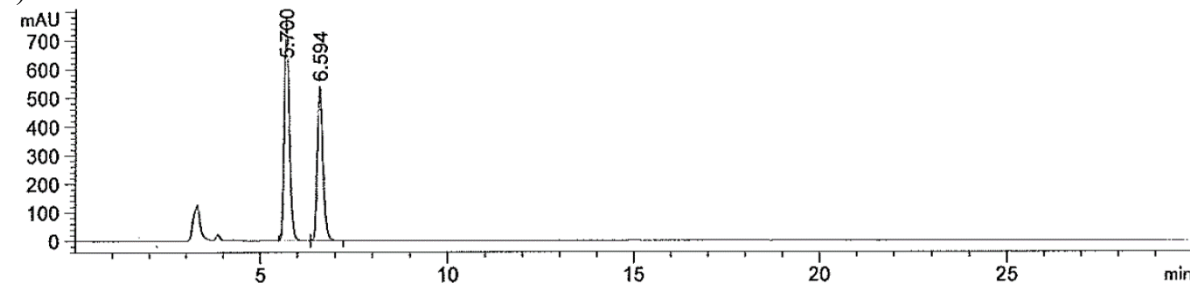


Figure S351. ^{13}C NMR of *N*-(1,2,3,4-tetrahydronaphthalen-2-yl)acetamide.

a)



b)

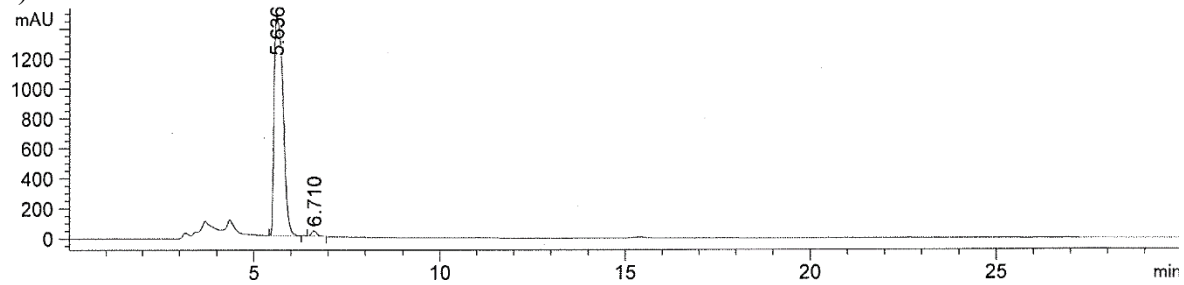


Figure S352. HPLC traces of (a) racemic and (b) enantioenriched product (97% (*R*) ee using Ir-**L4e** catalytic system; Figure 3, substrate **S57**)

(R)-N-(6-Methoxy-1,2,3,4-tetrahydronaphthalen-2-yl)acetamide

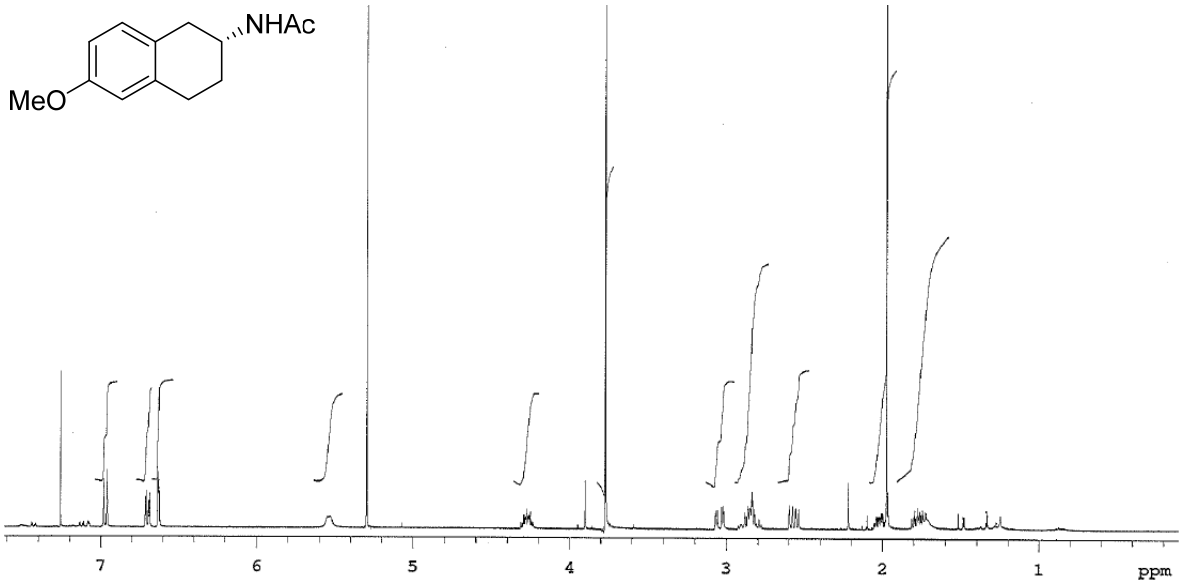


Figure S353. ^{1}H NMR of *N*-(6-methoxy-1,2,3,4-tetrahydronaphthalen-2-yl)acetamide.

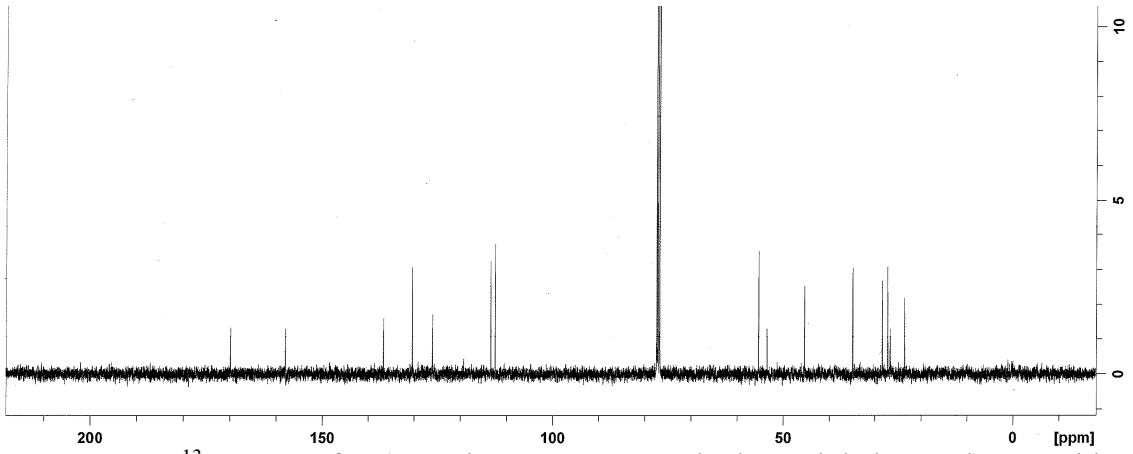
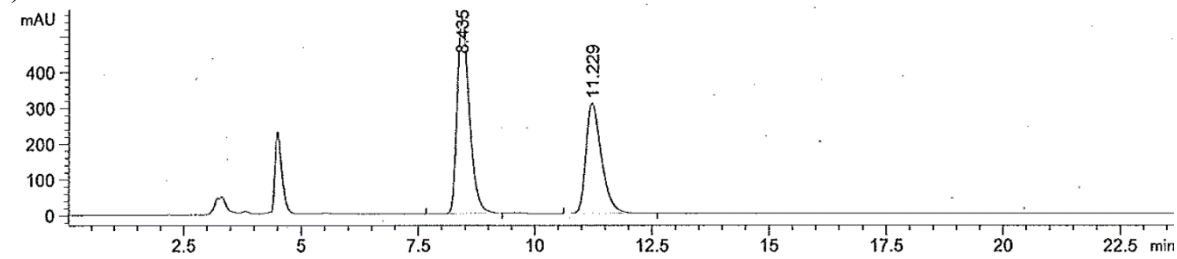


Figure S354. ^{13}C NMR of *N*-(6-methoxy-1,2,3,4-tetrahydronaphthalen-2-yl)acetamide.

a)



b)

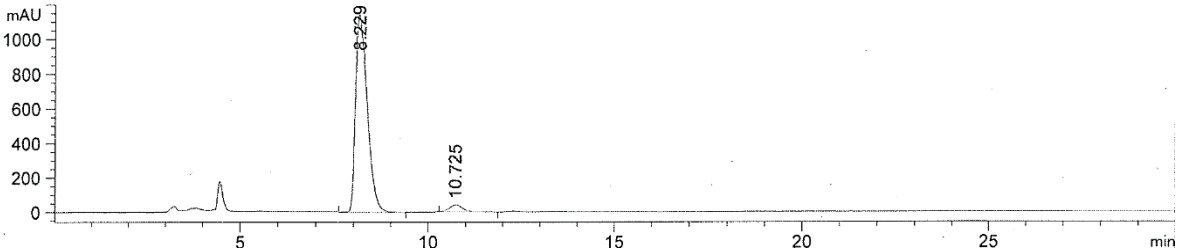


Figure S355. HPLC traces of (a) racemic and (b) enantioenriched product (95% (*R*) ee using Ir-**L4e** catalytic system; Figure 3, substrate **S58**)

(R)-N-(7-Methoxy-1,2,3,4-tetrahydronaphthalen-2-yl)acetamide

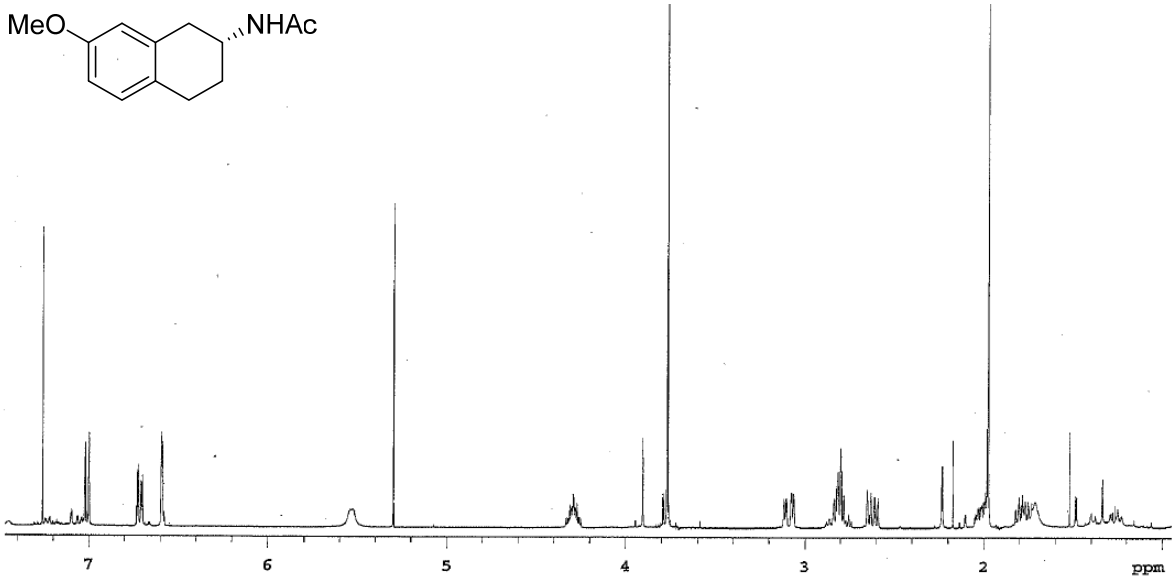


Figure S356. ^{1}H NMR of *N*-(7-methoxy-1,2,3,4-tetrahydronaphthalen-2-yl)acetamide.

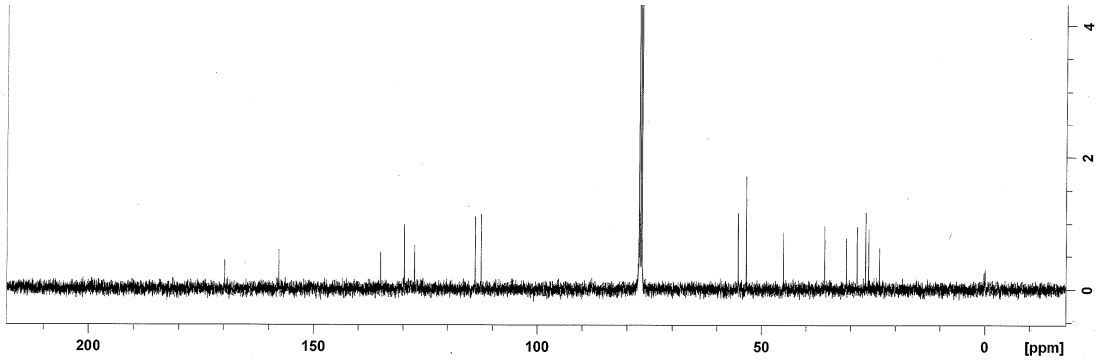


Figure S357. ^{13}C NMR of *N*-(7-methoxy-1,2,3,4-tetrahydronaphthalen-2-yl)acetamide.

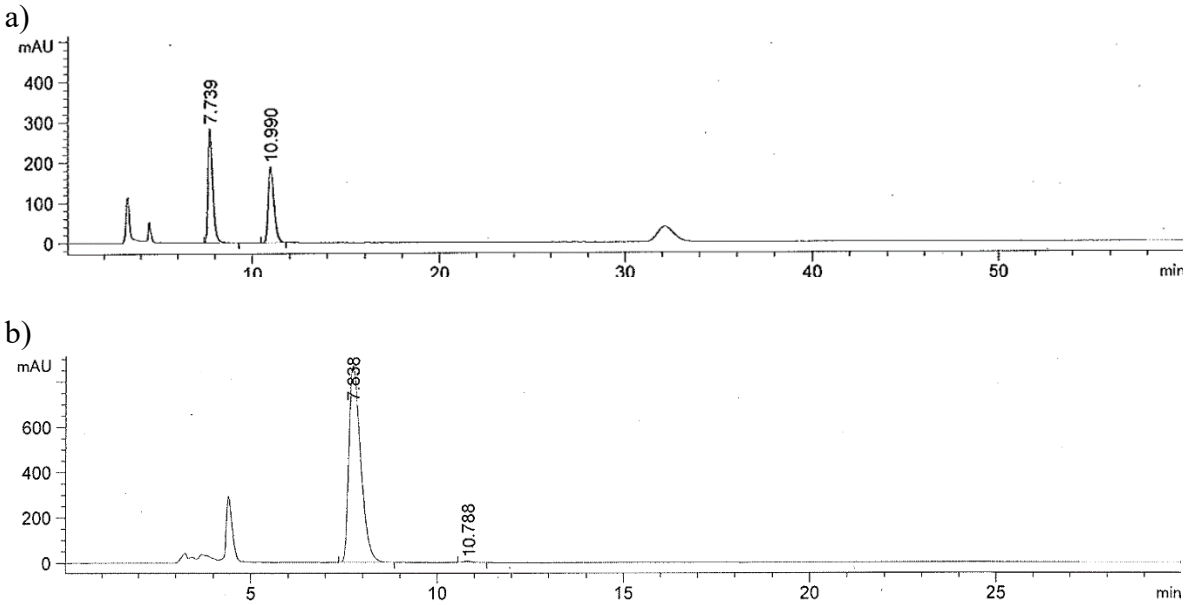


Figure S358. HPLC traces of (a) racemic and (b) enantioenriched product (99% (*R*) ee using Ir-**L4e** catalytic system; Figure 3, substrate **S59**)

(R)-N-(8-Methoxy-1,2,3,4-tetrahydronaphthalen-2-yl)acetamide

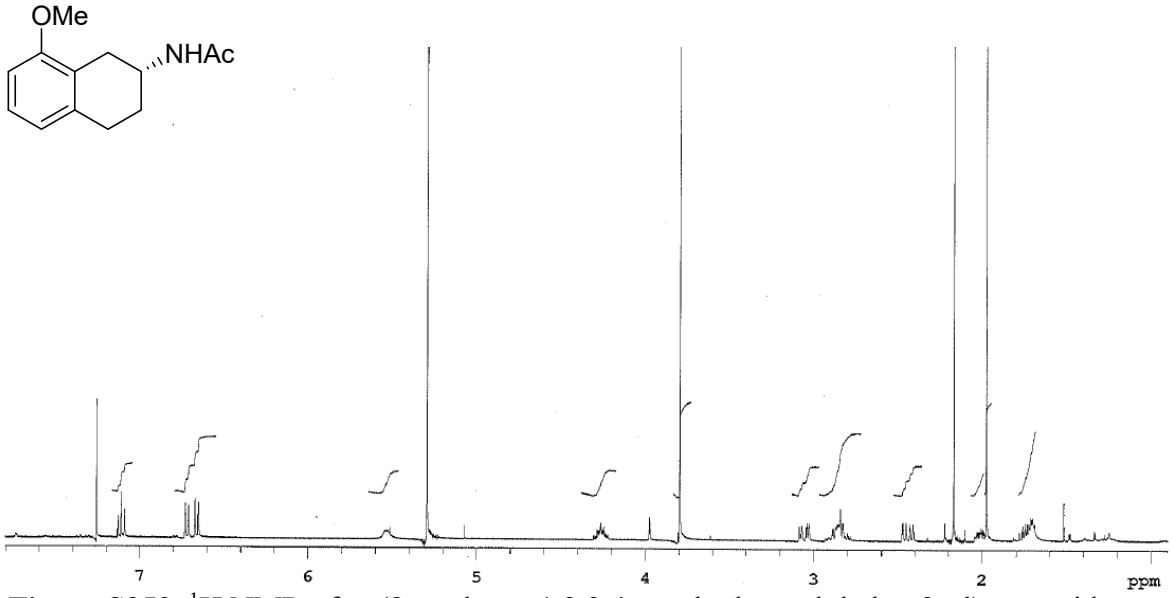


Figure S359. ^{1}H NMR of *N*-(8-methoxy-1,2,3,4-tetrahydronaphthalen-2-yl)acetamide.

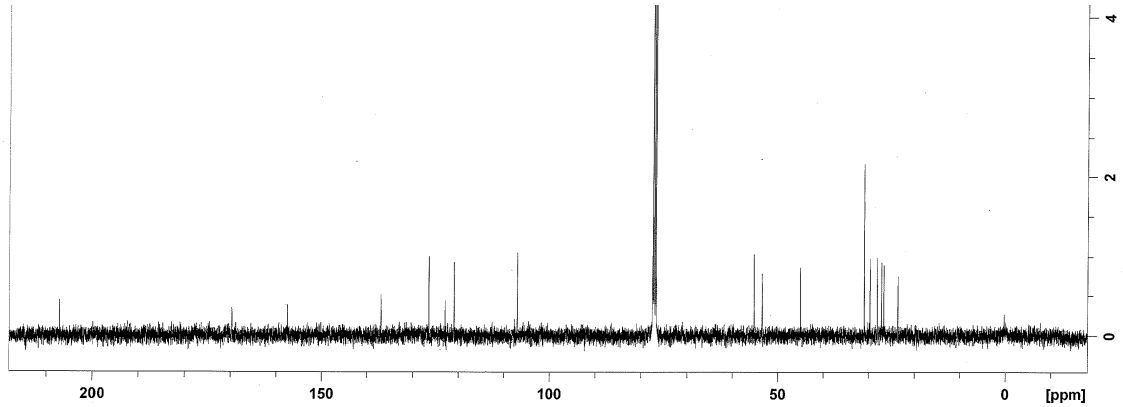
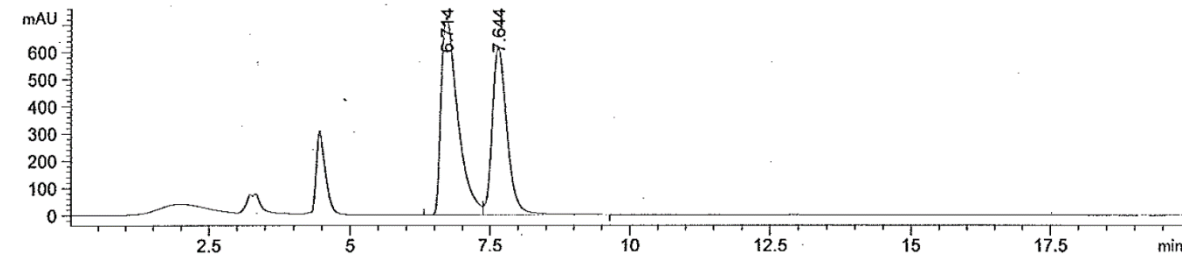


Figure S360. ^{13}C NMR of *N*-(8-methoxy-1,2,3,4-tetrahydronaphthalen-2-yl)acetamide.

a)



b)

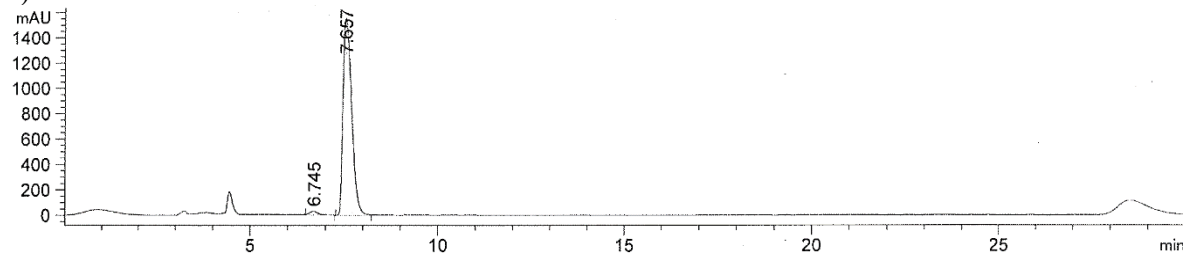


Figure S361. HPLC traces of (a) racemic and (b) enantioenriched product (98% (*R*) ee using Ir-**L4e** catalytic system; Figure 3, substrate **S60**)

(R)-N-(5-Methoxy-1,2,3,4-tetrahydronaphthalen-2-yl)acetamide

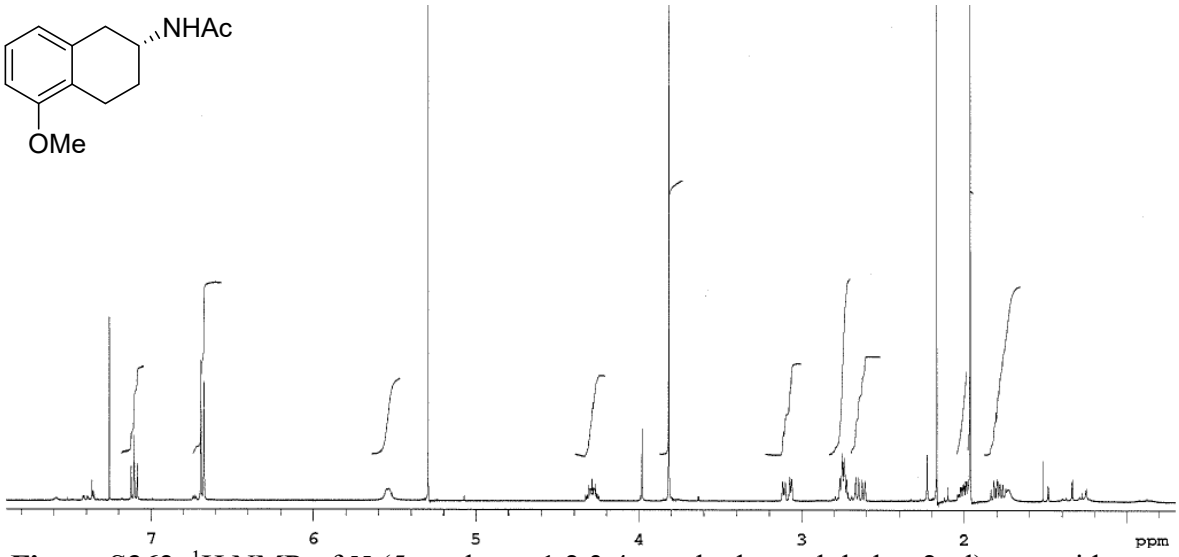


Figure S362. ^{1}H NMR of *N*-(5-methoxy-1,2,3,4-tetrahydronaphthalen-2-yl)acetamide.

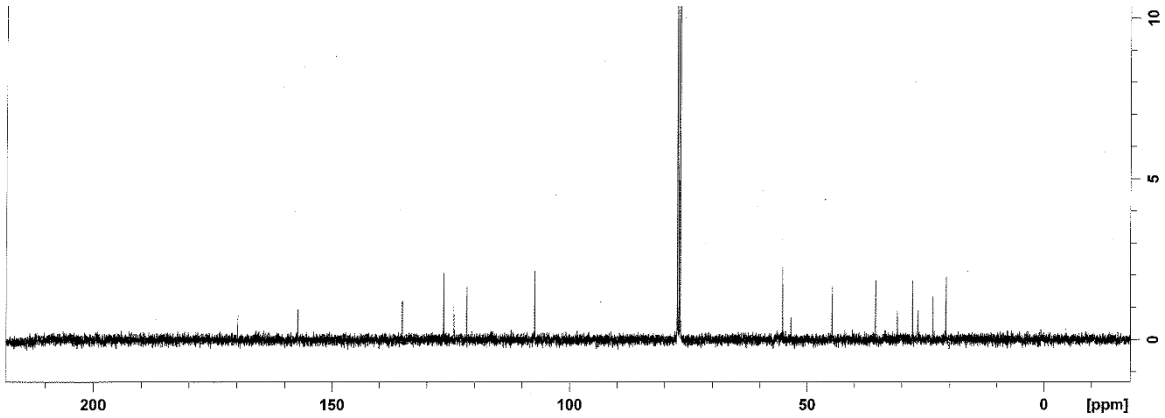
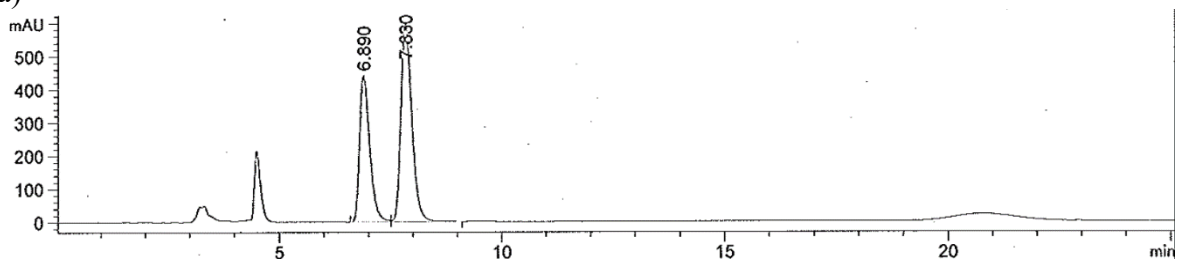


Figure S363. ^{13}C NMR of *N*-(5-methoxy-1,2,3,4-tetrahydronaphthalen-2-yl)acetamide.

a)



b)

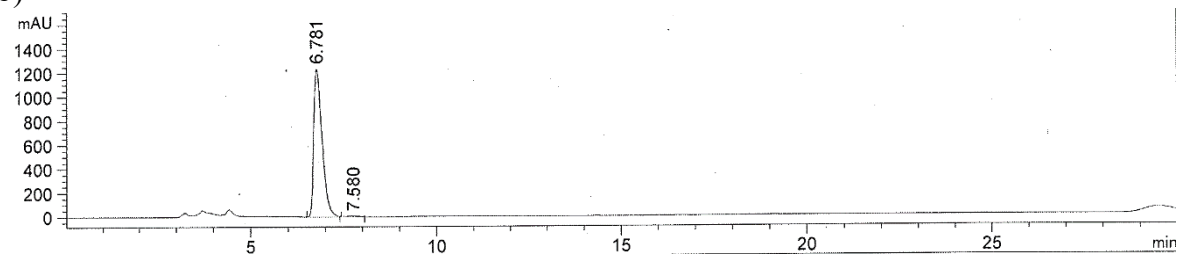


Figure S364. HPLC traces of (a) racemic and (b) enantioenriched product (99% (*R*) ee using Ir-**L4e** catalytic system; Figure 3, substrate **S61**)

(S)-N-(Chroman-3-yl)acetamide

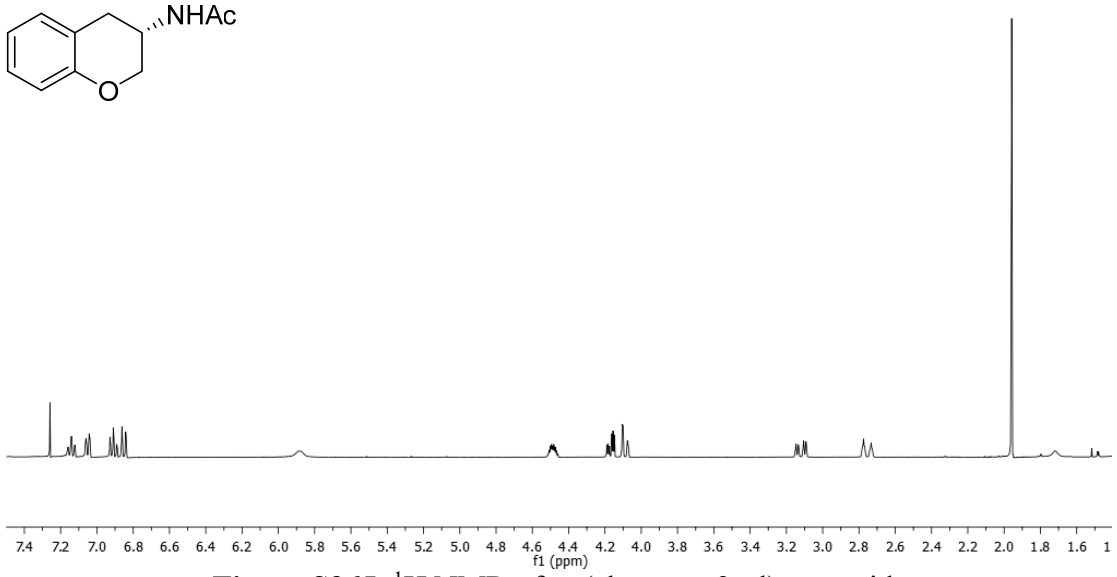


Figure S365. ^{1}H NMR of *N*-(chroman-3-yl)acetamide.

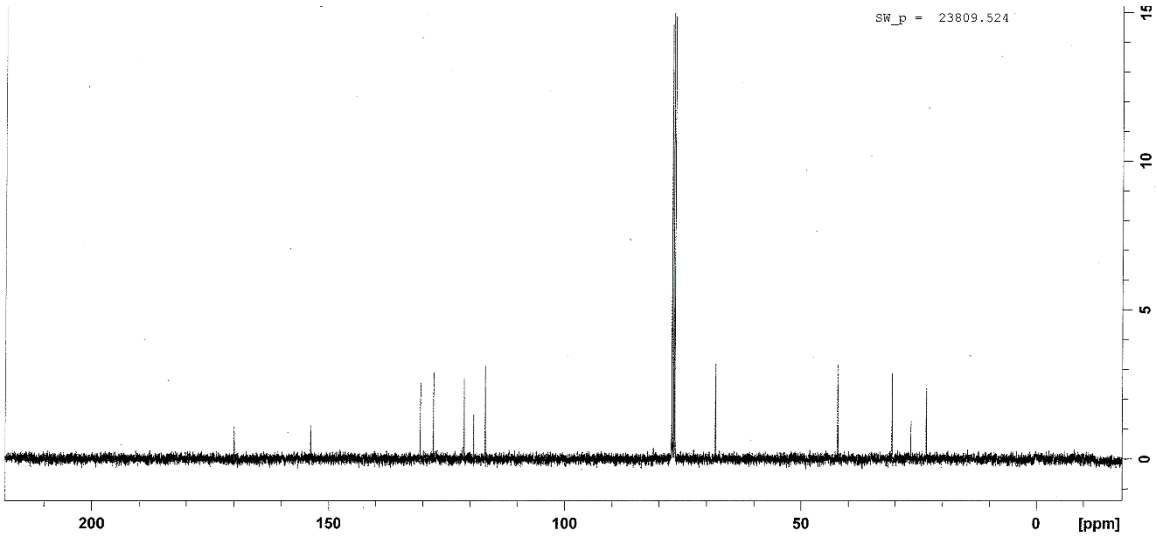
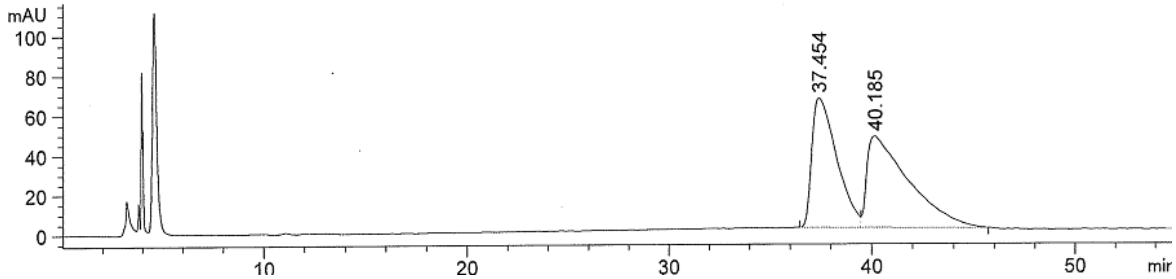


Figure S366. ^{13}C NMR of *N*-(chroman-3-yl)acetamide.

a)



b)

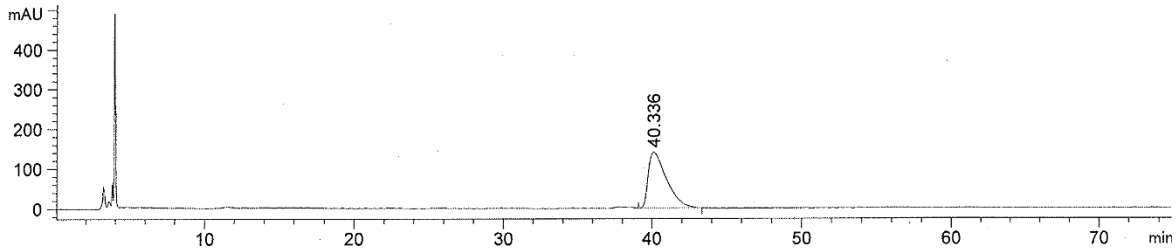


Figure S367. HPLC traces of (a) racemic and (b) enantioenriched product (97% (*S*) ee using Ir-**L5d** catalytic system; Figure 3, substrate **S62**)

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