Supporting Information for

Manganese(III)-mediated phosphinoyl radical reaction for stereoselective synthesis of phosphinoylated tetrahydronaphathalenes

Xiang-Qiang Pan,[a] Lu Wang,[a] Jian-Ping Zou*[a] and Wei Zhang*[b]

[a] *Key Laboratory of Organic Synthesis of Jiangsu Province, College of Chemistry and Chemical Engineering, Suzhou University, 199 Renai Street, Suzhou, Jiangsu 215123, China*

[b] *Department of Chemistry, University of Massachusetts Boston, 100 Morrissey Boulevard, Boston, MA 02125, USA*

E-mail: jpzou@suda.edu.cn (J. P. Zou); E-mail: wei2.zhang@umb.edu (W. Zhang)

Table of contents

General information

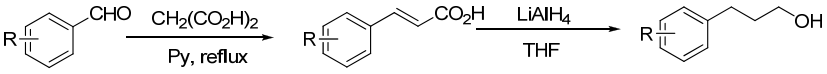
All reactions were carried out under air. Solvents were dried by the standard procedures. ^{1}H and ^{13}C NMR spectra were determined in $CDCl_3$ on a Varian-Inova 300MHz or 400 MHz spectrometer and chemical shifts were reported in ppm from internal TMS(δ). High resolution mass spectra were recorded on a MicroMass-TOF machine (EI). Column chromatography was performed with 200-300 mesh silica gel using flash column techniques. All of the reagents were used directly as obtained commercially unless otherwise noted.

Manganese triacetate, [1] (*E*)-5-aryl-2-pentenoic acid methyl ester [2] and 2-arylethyl styrene [3] were prepared according to the reported procedures.

---

1. W. J. De Klein, in Organic Syntheses by oxidation with metal compounds, Eds. W. J. Mijs and C. R. H. I. De. Jonge. **1986,** Plenum Press, New York.
2. a) R. F. Nystrom, W. G. Brown, *J. Am. Chem. Soc.*, **1947**, *69*, 2548; b) J. Kang, G. J. Lim, S. K. Yoon, M. Y. Kim, *J. Org. Chem.*, **1995**, *60*, 564; c) Q. W. Zhang, R. M. Mohan, L. Cook, S. Kazanis, D. Peisach. *J. Org. Chem.*, **1993,** *58*, 7640.
3. a) H. Saumen, M. Biswajit, S. Debarshi, B. Sukanta, *Tetrahedron Lett.*, **2008**, *49*, 4057; b) X. Zhang, S. Sarkar, R. C. Larock *J. Org. Chem.* **2006**, *71*, 236.

Preparation of 3-aryl-propan-1-ols



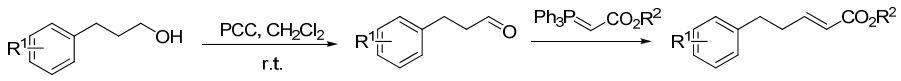
R= H, *p*-CH_3, *p*-OCH_3, *p*-Br, *o*-Br

Typical procedure for the preparation of 3-phenyl-propan-1-ol

To a rapidly stirred suspension of $LiAlH_4$ (2.9g, 75 mmol, 3 equiv) in 20 mL of THF was added over 30 min a solution of cinnamate acid (3.7g, 25mmol) in 10 mL of THF at 0^{o}C. After addition was complete, refluxing was continued for an additional 2 h, and then the mixture was cooled to room temperature, poured into ice water which was then poured into a solution of 5% HCl over ice and extracted once with ethyl ether (20 mL) and twice with 20 mL portions of EtOAc. The combined organic extract was washed with a saturated solution of $NaHCO_3$ (30 mL) and brine (30 mL) and dried over anhydrous $MgSO_4$. Evaporation followed by flash column chromatographic purification afforded pure 3-phenyl-propan-1-ol (2.0 g, 60%) as an oil.

Other 3-aryl-propan-1-ols could be prepared from the substituted cinnamate acids, which were derived from their corresponding substituted benzaldehydes and malonic acid by standard procedure.

Preparation of ethyl *trans*-5-aryl-2-pentenoates

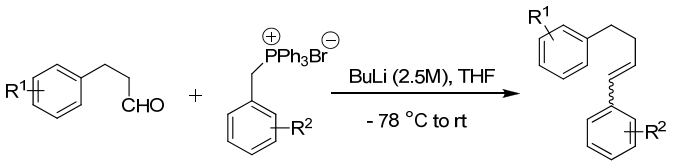


R^1= H, *p*-CH_3, *p*-OCH_3, *p*-Br, *o*-Br
R^2 = Me, Et

Typical procedure for the preparation of ethyl *trans*-5-phenyl-2-pentenoate

Pyridinium chlorochromate (2.85 g, 13.2 mmol) was added to 3-phenylpropan-1-ol (1.2 g, 8.8 mmol) in dichloromethane (25 mL). The mixture was well stirred for 2 h. When the oxidation was complete, the reaction mixture was diluted with diethyl ether and filtered through Florisil. Removal of the solvent gave the pure 3-phenylpropanal (0.968 g, 82%) as a colorless oil. Ethyl (triphenylphosphorany1idene) acetate (2.96 g, 8.5 mmol) was added to 3-phenylpropanal (0.950 g, 7.1 mmol) in dichloromethane (20 mL) at room temperature. The mixture was stirred for 1 h at the same temperature,.diluted with H_2O and extracted with ethyl acetate. The combined extracts were washed with water and brine, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel eluted with 1:3 ethyl ether/hexane to give ethyl *trans*-5-phenyl-2-pentenoate(1.29 g, 89%) as a colorless oil.

Preparation of 1,4-diaryl-l-butenes



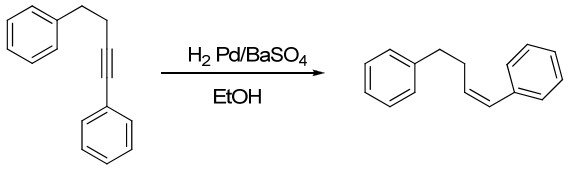
Typical procedure for the preparation of 1,4-diphenyl-l-butene

A suspension of benzyl triphenylphosphonium bromide (4.8 g, 11 mmol) in 10 mL of THF was added *n*-BuLi (5 mL, 2.5 M hexane solution) under nitrogen at -78˚C. The resulting solution was stirred at 0˚C for 20 min and then 3-phenyl-propionaldehyde (1.34g, 10 mmol) in 5 mL of THF was slowly added. After the mixture was stirred at 0˚C for 30 min, the temperature was slowly raised to room temperature, Reaction was monitored by TLC. After completion, it was quenched with aqueous NH_4Cl solution (10 mL) and extracted with ether (3×20mL). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, concentrated and purified by flash

column chromatography over silica-gel eluted with petroleum ether/acetic acetate(10/1) to afford *E/Z* mixture of 1,4-diphenyl-l-butene (1.5g, 70%).

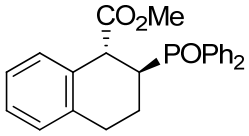
Other 1,4-diaryl-l-butenes could be prepared from the substituted benzyl triphenylphosphonium bromides, which were derived from their corresponding substituted benzyl bromides and Ph_3P by standard procedure.

Preparation of *cis*-1,4-diphenyl-l-butene



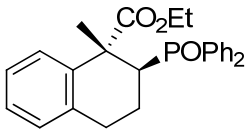
To a solution of 1,4-diphenyl-1-butyne (0.5 g, 2.42 mmol) in absolute ethanol (30 ml) was added Lindlar catalyst (0.05 g), the flask was evacuated, purged with hydrogen three times, and the mixture was stirred under hydrogen atmosphere for 12 h. The reaction was filtered over celite, washed with DCM twice (2×10mL). Evaporation followed by flash column chromatograph on silica gel eluted with 10:1 petroleum ether/acetic acetate to afford *cis*-1,4-diphenyl-l-butene (0.42 g, 85%) as an oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.32-7.19 (m, 10H), 6.47 (d, J = 12.3Hz, 1H), 5.78-5.71 (m, 1H), 2.85-2.79 (m, 2H), 2.73-2.67 (m, 2H).

Methyl 2-(diphenylphosphoryl)-1,2,3,4-tetrahydronaphthalene-1-carboxylate (8a)



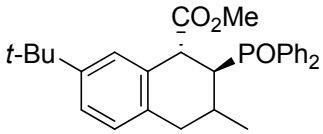
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82-7.92 (m, 4H), 7.49-7.52 (m, 6H), 7.06-7.23 (m, 4H), 4.27 (dd, J= 8.5, 15.3 Hz, 1H), 3.38-3.51 (m, 1H), 3.27(s, 3H), 2.75-2.90 (m, 2H), 2.01-2.10(m, 1H), 1.75-1.88 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 174.9, 137.8, 132.6, 132.2(d, J = 9.3 Hz), 131.7(d, J = 8.6 Hz), 129.6, 129.4(d, J = 11.3 Hz), 129.2, 129.1, 127.7, 127.2, 52.8, 44.1, 37.0(d, J = 72.1 Hz), 29.7(d, J = 13.2 Hz), 22.4; ^{31}P NMR(122 MHz, $CDCl_3$): δ 34.5. HRMS (M^+): *m/z* (%), calcd for $C_{24}H_{23}O_3P$ 390.1385, found 390.1380(M^+, 19.42).

Ethyl 2-(diphenylphosphoryl)-1-methyl-1,2,3,4-tetrahydronaphthalene-1-carboxylate (8b)



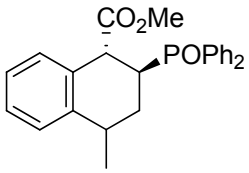
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72-7.78 (m, 2H), 7.63-7.68 (m, 2H), 7.36-7.48 (m, 6H), 7.17-7.23 (m, 3H), 6.91 (d, J = 6.6Hz, 1H), 3.82-3.90 (m, 2H), 2.93-2.99 (m, 1H), 2.70-2.77 (m, 1H), 2.50 (td, J = 8.3, 13.6Hz, 1H), 1.90-1.99 (m, 2H), 1.27 (d, J = 7.0 Hz, 3H), 1.16 (t, J = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 175.0 (d, J = 6.8 Hz), 141.3, 134.1 (d, J = 61.1 Hz), 133.2 (d, J = 63.4 Hz), 132.5, 132.0, 131.6 (d, J = 9.1Hz), 131.3 (d, J = 8.3 Hz), 129.1, 128.9 (d, J = 21.7Hz), 126.6, 61.2, 39.4, 39.2 (d, J = 70.3 Hz), 34.0 (d, J = 8.5Hz), 29.8, 15.5, 14.5. HRMS (M^+): *m/z* (%), calcd for $C_{26}H_{27}O_3P$ 418.1698, found 420.1853(M^++2H, 3.04).

Methyl 7-*tert*-butyl-2-(diphenylphosphoryl)-3-methyl-1,2,3,4-tetrahydronaphthalene-1-carboxylate (8d)



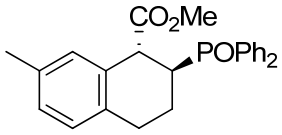
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88-8.02 (m, 4H), 7.46-7.54 (m, 6H), 7.23(s, 1H), 7.16 (d, J = 7.8 Hz, 1H), 6.97 (d, J = 7.9 Hz, 1H), 4.45 (dd, J = 9.6, 14.4 Hz, 1H), 3.44-3.48 (m, 1H), 3.10 (s, 3H), 3.02-3.06 (m, 1H), 2.50-2.56 (m, 2H), 1.24 (s, 9H), 0.94 (d, J = 6.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 175.1, 149.8, 132.5 (d, J = 1.7 Hz), 132.2 (d, J = 15.4 Hz), 132.2, 131.5 (d, J = 8.8 Hz), 130.1, 129.5 (d, J = 11.3Hz), 128.9 (d, J = 11.4Hz), 125.5, 124.8, 52.5 (d, J = 1.6 Hz), 41.1 (d, J = 70.9 Hz), 38.1 (d, J = 13.7 Hz), 34.9, 31.9, 28.2, 21.8, 16.2; ^{31}P NMR (122 MHz, $CDCl_3$): δ 32.2. HRMS (M^+): m/z (%), calcd. for $C_{29}H_{33}O_3P$ 460.2167, found 460.2171(M^+, 6.65).

Methyl 2-(diphenylphosphoryl)-4-methyl-1,2,3,4-tetrahydronaphthalene-1-carboxylate (8e)



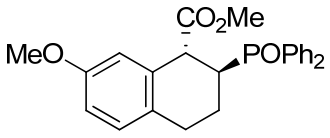
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70-7.80 (m. 4H), 7.39-7.44 (m, 6H), 7.01-7.19 (m, 4H), 4.16-4.22 (m. 1H), 3.54-3.56 (m, 1H), 3.17 (s, 1.2H), 3.13 (s, 1.8H), 2.85-2.95 (m, 1H), 1.84-1.97 (m, 1H), 1.49-1.73 (m, 1H), 1.30(d, J = 6.8 Hz, 1.8H), 1.18 (d, J = 6.8 Hz, 1.2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 174.8, 174.7, 142.4, 142.3, 132.4, 132.4, 132.3, 132.2, 132.1, 131.6, 131.6, 131.5, 131.5, 129.3 (d, J = 17.9 Hz), 129.3, 129.0, 128.9(d, J = 21.0 Hz), 128.7, 127.7 (d, J = 15.5 Hz), 127.0 (d, J = 11.5 Hz), 125.9, 52.7, 52.6 (d, J = 1.26 Hz), 44.6, 43.4, 32.9, 32.8, 32.7 (d, J = 2.2Hz), 31.5, 31.3, 30.0 (d, J = 41.1 Hz), 28.1, 22.8, 20.0. HRMS (M^+): m/z (%), calcd. for $C_{25}H_{25}O_3P$ 404.1541, found 404.1536(M^+, 11.13).

Methyl 2-(diphenylphosphoryl)-7-methyl-1,2,3,4-tetrahydronaphthalene-1-carboxylate (8f)



^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85-7.87 (m, 4H), 7.47-7.52 (m, 6H), 7.02(s, 1H), 6.94 (t, J = 8.2 Hz, 2H), 4.23 (dd, J = 8.6, 15.2Hz, 1H), 3.46-3.37 (m, 1H), 3.28(s, 3H), 2.72-2.84 (m, 2H), 2.23 (s, 3H), 2.01-2.08 (m, 1H), 1.74-1.80 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 174.6, 136.2, 134.3, 132.1 (d, J = 4.4 Hz), 132.0(d, J = 4.0 Hz), 131.9 (d, J = 2.7Hz), 131.8 (d, J = 4.4 Hz), 131.4 (d, J = 8.5 Hz), 129.1 (d, J = 1.9Hz), 128.8 (d, J = 10.6 Hz), 128.4 (d, J = 35.2 Hz), 52.4, 43.7, 36.7 (d, J = 72.5 Hz), 29.0 (d, J = 12.4 Hz), 22.2, 21.3. HRMS (M^+): m/z (%), calcd for $C_{25}H_{25}O_3P$ 404.1541, found 404.1543(M^+, 8.84).

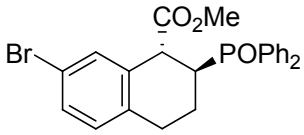
Methyl 2-(diphenylphosphoryl)-7-methoxy-1,2,3,4-tetrahydronaphthalene-1-carboxylate (8g)



^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82-7.91 (m, 4H), 7.46-7.51(m, 6H), 6.97 (d, J = 8.3Hz, 1H), 6.77 (s, 1H), 6.69 (d, J = 8.3Hz, 1H), 4.24 (dd, J = 8.6, 15.2Hz, 1H), 3.70 (s, 3H), 3.37-3.42 (m, 1H), 3.27 (s, 3H), 2.74-2.77 (m, 2H), 2.00-2.06 (m, 1H), 1.76-1.80 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): 174.7 (d, J =2.9 Hz), 158.6, 133.4 (d, J = 8.1 Hz), 132.5 (d, J = 2.5 Hz), 132.4 (d, J = 2.5 Hz), 132.2 (d, J = 9.1 Hz), 131.7 (d, J = 9.6 Hz), 131.3 (d, J = 6.7 Hz), 130.4, 131.0 (d, J = 244.5 Hz), 129.9, 129.4 (d, J = 11.4 Hz), 129.0 (d, J = 11.4 Hz), 113.8 (d, J = 4.0 Hz), 55.8, 52.8, 44.2, 37.0 (d, J = 72.1 Hz), 29.0 (d, J = 12.7 Hz), 22.6. HRMS (M^+): m/z (%), calcd for $C_{25}H_{25}O_4P$ 420.1490,

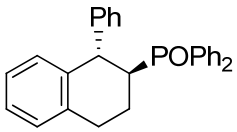
found 420.1489(M^+, 3.04).

Methyl 7-bromo-2-(diphenylphosphoryl)-1,2,3,4-tetrahydronaphthalene-1-carboxylate (8h)



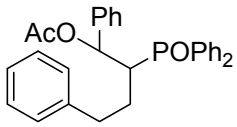
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.92-7.83 (m, 4H), 7.48-7.54 (m, 6H), 7.22 (d, J = 6.7Hz, 1H), 7.11 (t, J = 6.1Hz, 1H), 7.06 (d, J = 6.8Hz, 1H), 4.28 (dd, J = 8.1, 15.4Hz, 1H), 3.42-3.47 (m, 1H), 3.28(s, 3H), 2.77-2.90 (m, 2H), 2.03-2.11 (m, 1H), 1.79-1.85 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 175.0(d, J = 3.3Hz), 137.9, 132.7, 132.6, 132.5 (d, J = 2.4 Hz), 132.3 (d, J = 9.2 Hz), 131.8 (d, J = 8.6Hz), 129.5 (d, J = 11.3 Hz), 129.4 (d, J = 40.5 Hz), 129.1 (d, J = 11.5 Hz), 127.4 (d, J = 37.7 Hz), 52.9, 44.1, 37.1 (d, J = 72.0 Hz), 29.8 (d, J = 11.5 Hz), 22.5. HRMS (M^+): m/z (%), calcd for $C_{24}H_{22}BrO_3P$ 468.0490, found 390.1397(M^+-Br^-, 11.54).

1-Phenyl-2-(diphenylphosphoryl)-1,2,3,4-tetrahydronaphthalene (15a)



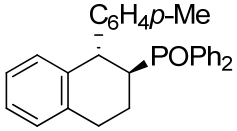
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74-7.79 (m, 2H), 7.56-7.60 (m, 2H), 7.40-7.44 (m, 3H), 7.29-7.33 (m, 1H), 7.21-7.23 (m, 2H), 7.00-7.05 (m, 2H), 6.92-6.95 (m, 4H), 6.78-6.80 (m, 2H), 6.71 (d, J = 7.7Hz, 1H), 4.59 (dd, J = 6.7, 14.5Hz, 1H), 2.81-3.01 (m, 3H), 2.00 (dt, J = 6.0, 12.0 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 147.2 (d, J = 4.7 Hz), 138.9 (d, J = 5.5 Hz), 137.1, 134.0 (d, J = 19.2 Hz), 131.9 (d, J = 29.0Hz), 131.5 (d, J = 5.4 Hz), 131.1, 129.6, 129.3 (d, J = 10.9 Hz), 129.0 (d, J = 14.1Hz), 128.9, 128.8, 126.8 (d, J = 4.9 Hz), 126.5, 44.1, 42.3 (d, J = 70.0 Hz), 29.4 (d, J = 8.6 Hz), 22.2; ^{31}P NMR (122 MHz, $CDCl_3$): δ 34.5. HRMS (M^+): m/z (%), calcd for $C_{28}H_{25}OP$ 408.1643, found 408.1640(M^+, 5.25).

2-(Diphenylphosphoryl)-1,4-diphenylbutyl acetate (16a)



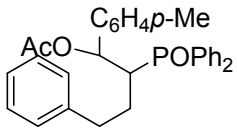
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85-7.90 (m, 2H), 7.66-7.79 (m, 3H), 7.37-7.49 (m, 5H), 7.19-7.39 (m, 5H), 7.05-7.08 (m, 3H), 6.54-6.57 (m, 2H), 6.27 (dd, J = 3.1, 9.0 Hz, 1H), 2.93-3.00 (m, 1H), 2.04-2.12 (m, 4H), 1.93 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.8, 141.4, 140.1 (d, J = 10.4Hz), 132.2, 131.7 (d, J = 8.4Hz), 131.5 (d, J = 8.7Hz), 129.3 (d, J = 2.6 Hz), 129.1 (d, J = 2.8 Hz), 129.0, 128.8 (d, J = 3.6 Hz), 128.4 (d, J = 62.2 Hz), 126.5, 126.3, 72.6, 44.7 (d, J = 67.3 Hz), 35.5 (d, J = 7.2 Hz), 26.1, 21.4. HRMS(ESI): m/z, calcd for $C_{30}H_{30}O_3P$ 469.1927, found 469.1928 ($M+H^+$).

1-(4-MethylPhenyl)-2-(diphenylphosphoryl)-1,2,3,4-tetrahydronaphthalene (15b)



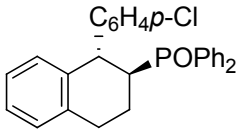
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.78-7.82 (m, 2H), 7.58-7.62 (m, 2H), 7.42-7.48 (m, 3H), 7.36 (t, J = 7.3 Hz, 1H), 7.22-7.26 (m, 2H), 7.04-7.07 (m, 2H), 6.96-6.99 (m, 1H), 6.78 (d, J =7.6 Hz, 2H), 6.76-6.77 (m, 1H), 6.72 (d, J = 7.9 Hz, 2H), 4.60 (dd, J = 6.9, 14.0 Hz, 1H), 2.85-3.05 (m, 3H), 2.19 (s, 3H), 2.00-2.07 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 139.1 (d, J = 6.7Hz), 137.1, 136.2 (d, J = 1.6Hz), 132.0 (d, J = 4.1Hz), 131.6, 131.5, 131.4, 131.2, 131.0, 129.5, 129.1 (d, J = 12.0 Hz), 128.7 (d, J = 6.7 Hz), 126.6 (d, J = 33.1 Hz), 43.9, 42.6 (d, J = 69.4 Hz), 29.5 (d, J = 9.5 Hz), 22.4, 21.5. HRMS (M^+): m/z (%), calcd for $C_{29}H_{27}OP$ 422.1800, found 422.1804 (M^+, 6.83).

2-(Diphenylphosphoryl)-4-phenyl-1-*p*-tolylbutyl acetate (16b)



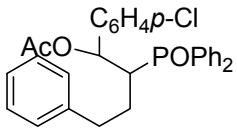
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.78-7.83 (m, 2H), 7.69-7.74 (m, 2H), 7.39-7.49 (m, 7H), 7.15 (d, J = 8.1 Hz, 2H), 7.11-7.13 (m, 2H), 7.06 (d, J = 8.0 Hz, 2H), 6.65-6.67 (m, 2H), 6.32 (dd, J = 3.3, 8.7 Hz, 1H), 2.77-2.81 (m, 1H), 2.34 (s, 3H), 2.10-2.23 (m, 4H), 1.96 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 169.8, 141.6, 138.1, 132.2 (d, J = 2.7 Hz), 132.0 (d, J = 2.7 Hz), 131.7 (d, J = 8.5 Hz), 131.5 (d, J = 8.8 Hz), 129.7, 129.3 (d, J = 73.0 Hz), 129.2 (d, J = 3.2 Hz), 129.1 (d, J = 3.2 Hz), 128.9 (d, J = 6.0 Hz), 126.4 (d, J = 2.9 Hz), 72.8, 44.7 (d, J = 67.5 Hz), 35.5 (d, J = 7.2 Hz), 26.4, 21.7, 21.5; ^{31}P NMR (122 MHz, $CDCl_3$): δ 33.6. HRMS (M^+): m/z (%), calcd for $C_{31}H_{31}O_3P$ 482.2011, found 482.2010 (M^+, 4.9).

1-(4--Chlorophenyl)-2-(diphenylphosphoryl)-1,2,3,4-tetrahydronaphthalene (15c)



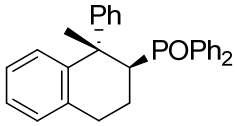
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79-7.83 (m, 2H), 7.53-7.58 (m, 2H), 7.36-7.46 (m, 4H), 7.22-7.27 (m, 2H), 6.96-7.08 (m, 3H), 6.89 (d, J = 8.3 Hz, 2H), 6.78 (d, J = 8.3 Hz, 2H), 6.70 (d, J = 7.7 Hz, 1H), 4.66 (dd, J = 8.1, 13.5 Hz, 1H), 2.86-3.01 (m, 3H), 1.98-2.04 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 144.8 (d, J = 4.1Hz), 138.4 (d, J = 7.8 Hz), 136.5, 133.5 (d, J = 12.3 Hz), 132.3 (d, J = 11.5 Hz), 131.7 (d, J = 2.4 Hz), 131.1 (d, J = 2.6 Hz), 131.0 (d, J = 1.8 Hz), 130.8 (d, J = 2.2 Hz), 130.8, 129.8 (d, J = 110.6 Hz), 128.8 (d, J = 5.7 Hz), 128.5 (d, J = 11.4 Hz), 126.4 (d, J = 16.0 Hz), 43.6, 42.3 (d. J = 71.2 Hz), 29.3 (d, J = 10.9 Hz), 22.5. HRMS (M^+): m/z (%), calcd for $C_{28}H_{24}ClOP$ 442.1253, found 442.1250 (M^+, 3.87).

1-(4-Chlorophenyl)-2-(diphenylphosphoryl)-4-phenylbutyl acetate(16c)



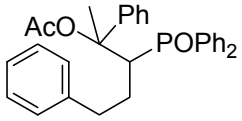
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.78-7.84 (m, 2H), 7.62-7.72 (m, 2H), 7.30-7.54 (m, 8H), 7.14-7.18 (m, 5H), 6.63-6.70 (m, 2H), 6.26-6.43 (m, 1H), 2.74-2.84 (m, 1H), 2.64-2.80 (m, 2H), 2.04-2.12 (m, 2H), 1.96 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 169.8, 141.2, 134.3, 132.6, 132.3 (d, J = 17.9 Hz), 131.6 (d, J = 25.1 Hz), 129.5, 129.3 (d, J = 29.6 Hz), 129.0 (d, J = 15.1 Hz), 128.8, 128.2, 126.6, 72.6, 35.2, 30.9 (d, J = 94.7 Hz), 26.6, 21.4. HRMS(ESI): m/z, calcd for $C_{30}H_{29}ClO_3P$ 503.1537, found 503.1545 ($M+H^+$).

1-Phenyl-1-methyl-2-(diphenylphosphoryl)-1,2,3,4-tetrahydronaphthalene (15d)



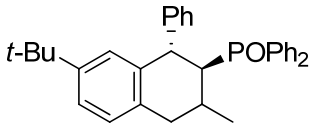
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55-7.70 (m, 4H), 7.39-7.48 (m, 4H), 7.25-7.34 (m, 5H), 7.14-7.18 (m, 2H), 6.96-7.01 (m, 2H), 6.72-6.80 (m, 2H), 3.46 (t, J = 8.6 Hz, 1H), 2.82-2.85 (m, 1H), 2.53-2.57 (m, 1H), 2.14-2.33 (m, 2H), 1.26(s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 158.5(d, J = 6.5Hz), 140.4, 132.2, 131.9, 131.5 (d, J = 9.1 Hz), 131.3, 131.2, 131.1(d, J = 8.5 Hz), 130.9, 129.1 (d, J = 11.5 Hz), 128.7(d, J = 21 Hz), 128.4, 127.8, 126.6, 48.2, 33.7 (d, J = 13.9Hz), 32.6, 29.9.

3-(Diphenylphosphoryl)-2,5-diphenylpentan-2-yl acetate (16d)



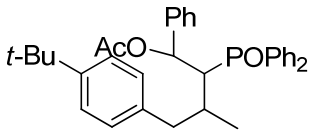
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85-7.89 (m, 2H), 7.48-7.52 (m, 6H), 7.23-7.33 (m, 4H), 7.07-7.16 (m, 6H), 6.60 (d, J = 6.5 Hz, 2H), 2.85 (d, J = 11.0Hz, 1H), 2.33 (s, 3H), 1.96-2.17 (m, 4H), 1.80(s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 168.9, 141.4, 131.8 (d, J = 7.5 Hz), 131.0 (d, J = 4.7 Hz), 130.7, 128.6, 128.5, 128.4, 128.3, 128.2, 127.0 (d, J = 150.4 Hz), 125.9, 69.5, 37.6, 29.1, 22.2, 21.7.

1-Phenyl-2-(diphenylphosphoryl)-3-methyl-7-*tert*-butyl-1,2,3,4-tetrahydronaphthalene (15f)



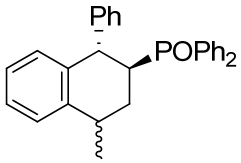
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84-7.88 (m, 2H), 7.44-7.46 (m, 5H), 7.11-7.20 (m, 4H), 6.84-7.02 (m, 6H), 6.70 (s, 1H), 4.71 (t, J = 10.6 Hz, 1H), 3.03-3.11 (m, 2H), 2.71-2.75 (m, 1H), 2.33-2.35 (m, 1H), 1.10 (s, 9H), 1.08 (d, J = 7.4Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 148.8, 145.6, 134.3 (d, J = 96.1 Hz), 132.1, 131.3 (d, J = 2.3 Hz), 130.9 (d, J = 8.4 Hz), 130.5 (d, J = 8.4 Hz), 129.9, 128.7 (d, J = 11.3 Hz), 128.4 (d, J = 88.9 Hz), 128.1, 127.7 (d, J = 52.6 Hz), 126.9 (d, J = 109.4 Hz), 123.2, 46.1 (d, J = 70.4 Hz), 42.7, 37.6 (d, J = 11.5 Hz), 34.4, 31.4, 28.5, 16.5. HRMS (M^+): m/z (%), calcd for $C_{33}H_{35}OP$ 478.2426, found 478.2423 (M^+, 7.65).

4-(4-*tert*-Butylphenyl)-2-(diphenylphosphoryl)-3-methyl-1-phenylbutyl acetate (16f)



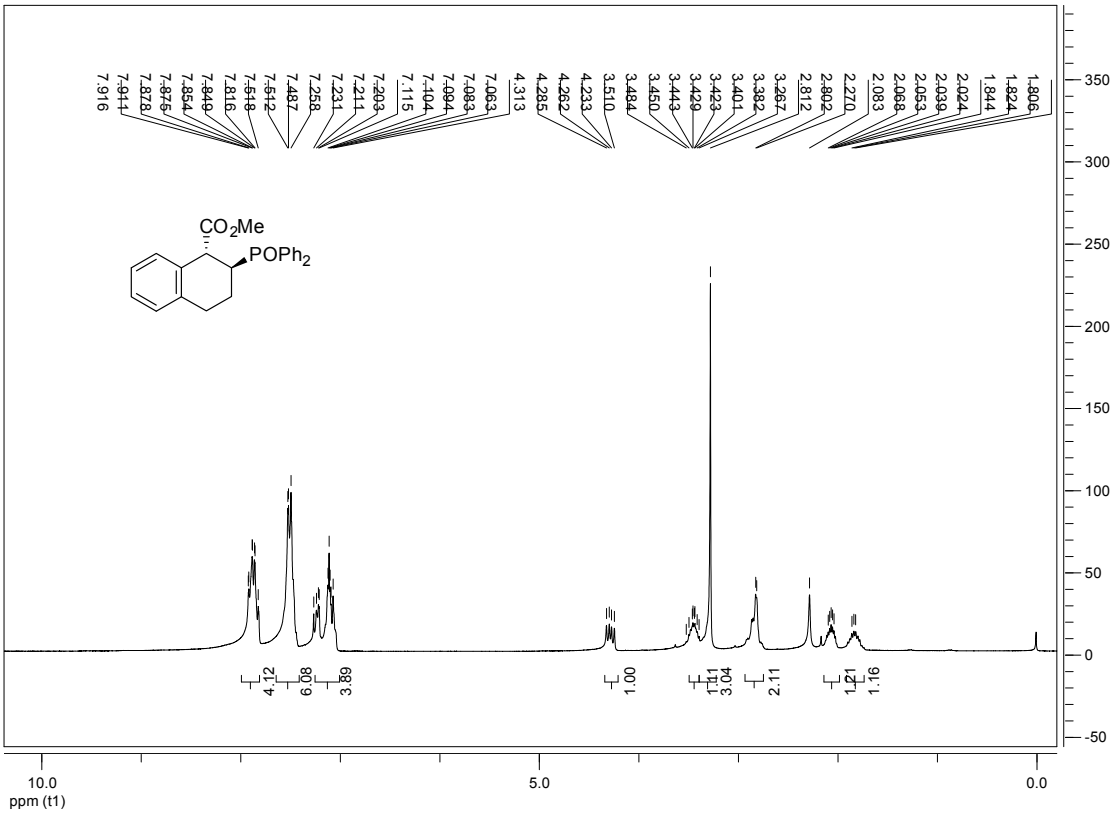
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.36-7.49 (m, 8H), 7.10-7.22 (m, 5H), 6.92-7.07 (m, 6H), 6.37 (dd, J = 5.8, 9.2 Hz, 1H), 3.04 (t, J = 9.7 Hz, 1H), 2.90 (dd, J_1 = 9.4, 12.9 Hz, 1H), 2.62 (dd, J_1 = 6.7, 13.2 Hz, 1H), 2.24-2.30 (m, 1H), 2.11 (s, 3H), 1.40 (s, 9H), 1.20 (d, J = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.7, 149.9, 139.2, 138.5, 131.9, 131.4 (d, J = 8.2 Hz), 131.0, 130.7 (d, J = 8.3 Hz), 130.2, 129.1 (d, J = 11.3 Hz), 128.6 (d, J = 19.7 Hz), 128.5, 125.9, 75.3 (d, J = 5.2 Hz), 44.6 (d, J = 68.2 Hz), 43.7 (d, J = 12.0 Hz), 35.7, 32.2, 31.7, 22.3, 17.9. HRMS (ESI): m/z, calcd for $C_{35}H_{39}O_3P$ 538.2637, found $C_{35}H_{40}O_3P$ 539.2717 ($M+H^+$).

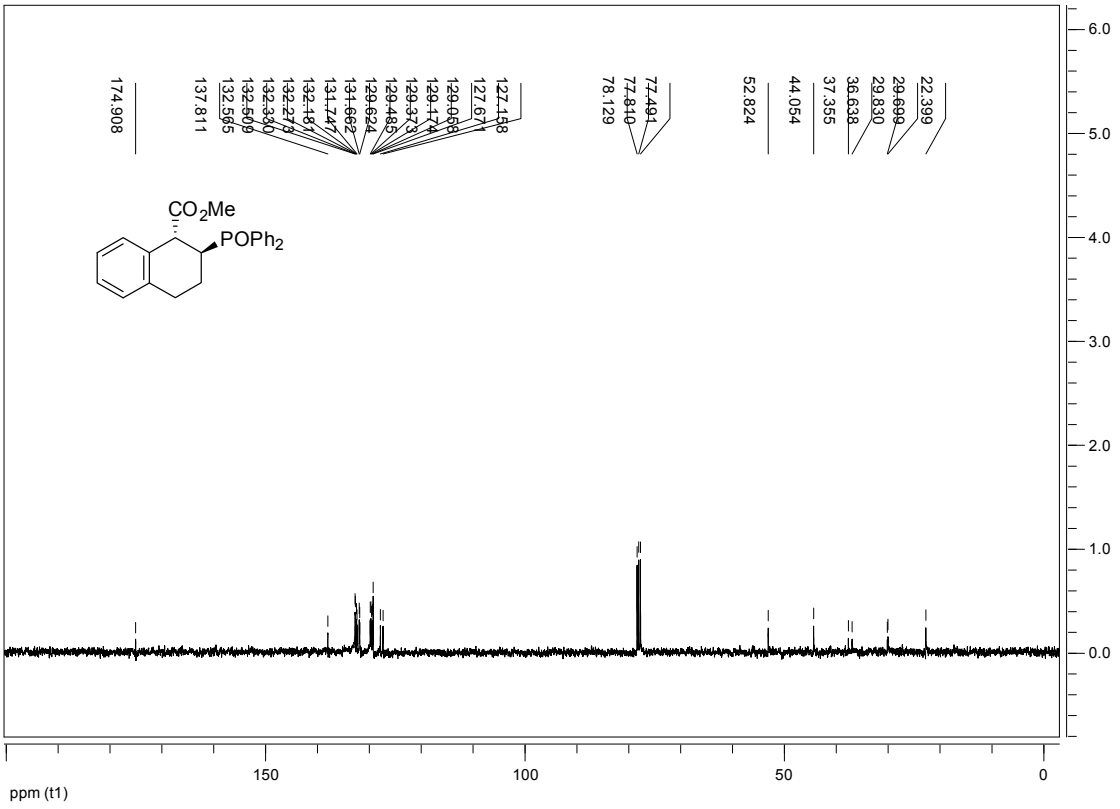
1-Phenyl-2-(diphenylphosphoryl)-4-methyl-1,2,3,4-tetrahydronaphthalene (15g)



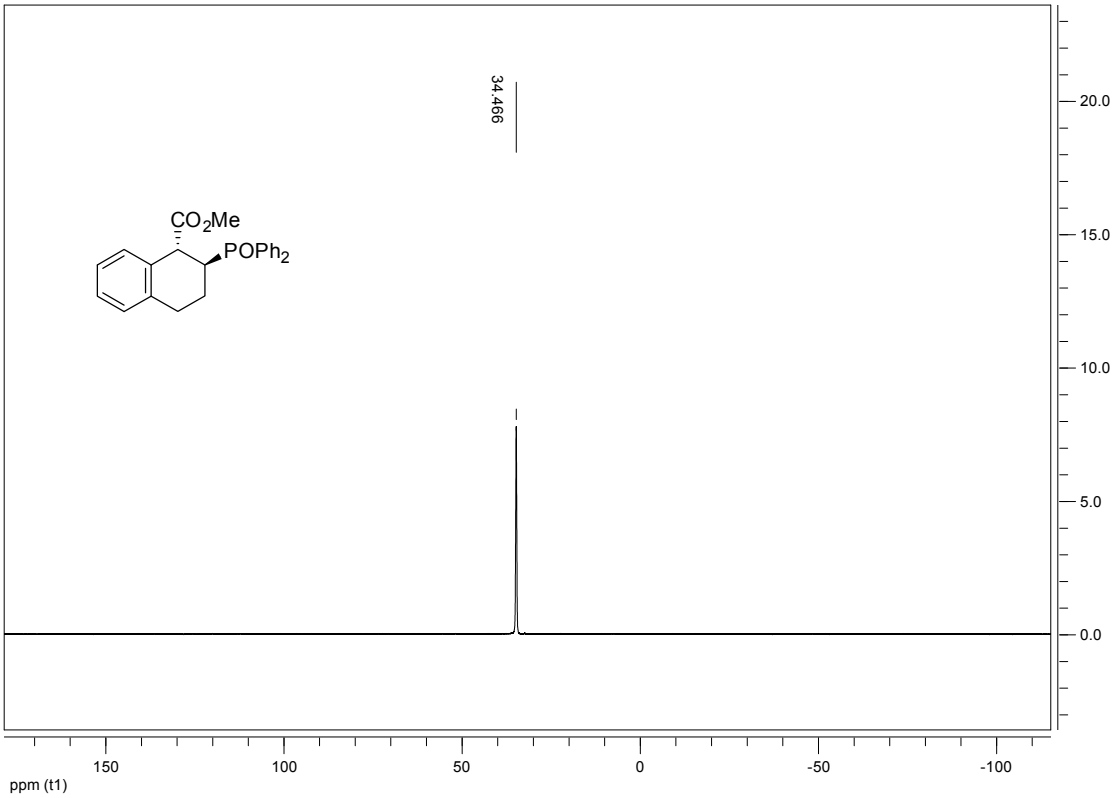
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.77-7.81 (m, 2H), 7.44-7.61 (m, 5H), 7.08-7.30 (m, 5H), 6.69-6.96 (m, 7H), 4.76 (dd, J = 9.6, 14.9 Hz, 0.6H), 4.63 (dd, J = 7.7, 13.3 Hz, 0.4H), 3.13-3.16 (m, 2H), 1.79-1.90 (m, 2H), 1.42 (d, J = 6.9 Hz, 1.2H), 1.33 (d, J = 6.5 Hz, 1.8H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.7, 146.4 (d, J = 4.5 Hz), 141.8, 141.3, 140.0 (d, J = 9.5 Hz), 138.3 (d, J = 7.7 Hz), 134.1 (d, J = 12.6 Hz), 133.7 (d, J = 33.6 Hz), 133.1 (d, J = 12.8 Hz), 132.7 (d, J = 33.8 Hz), 131.9, 131.3, 131.2, 131.1, 131.0, 130.9, 129.8, 129.6, 129.2 (d, J = 3.8 Hz), 129.1 (d, J = 3.9 Hz), 128.7, 128.6, 128.3 (d, J = 27.9 Hz), 126.6 (d, J = 8.8 Hz), 126.5, 126.4, 125.7, 44.7 (d, J = 81.0 Hz), 42.3 (d, J = 71.5 Hz), 38.5, 37.8, 33.6 (d, J = 13.4 Hz), 33.0, 31.9 (d, J = 9.1 Hz), 29.2, 23.4, 21.0. HRMS (ESI): m/z, calcd for $C_{29}H_{27}OP$ 422.1800, found 423.1872 ($M+H^+$). HPLC: 55:45.

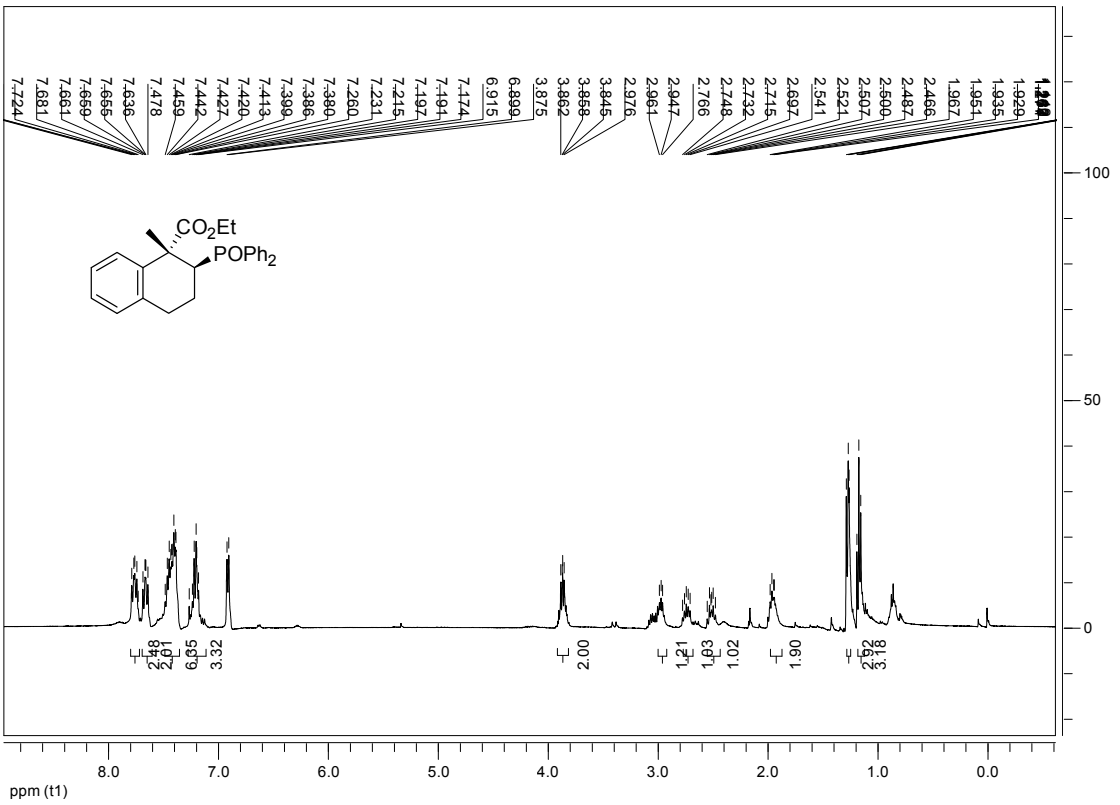
NMR Spectra


7.916
7.911
7.878
7.875
7.854
7.849
7.816
7.518
7.512
7.487
7.258
7.231
7.211
7.203
7.115
7.104
7.094
7.083
7.063
4.313
4.285
4.262
4.233
3.510
3.484
3.450
3.443
3.429
3.423
3.401
3.382
3.267
2.812
2.802
2.270
2.083
2.068
2.053
2.039
2.024
1.844
1.824
1.806
CO2Me
POPh2
4.12
6.08
3.89
1.00
1.11
3.04
2.11
1.21
1.16
10.0
5.0
0.0
ppm (t1)

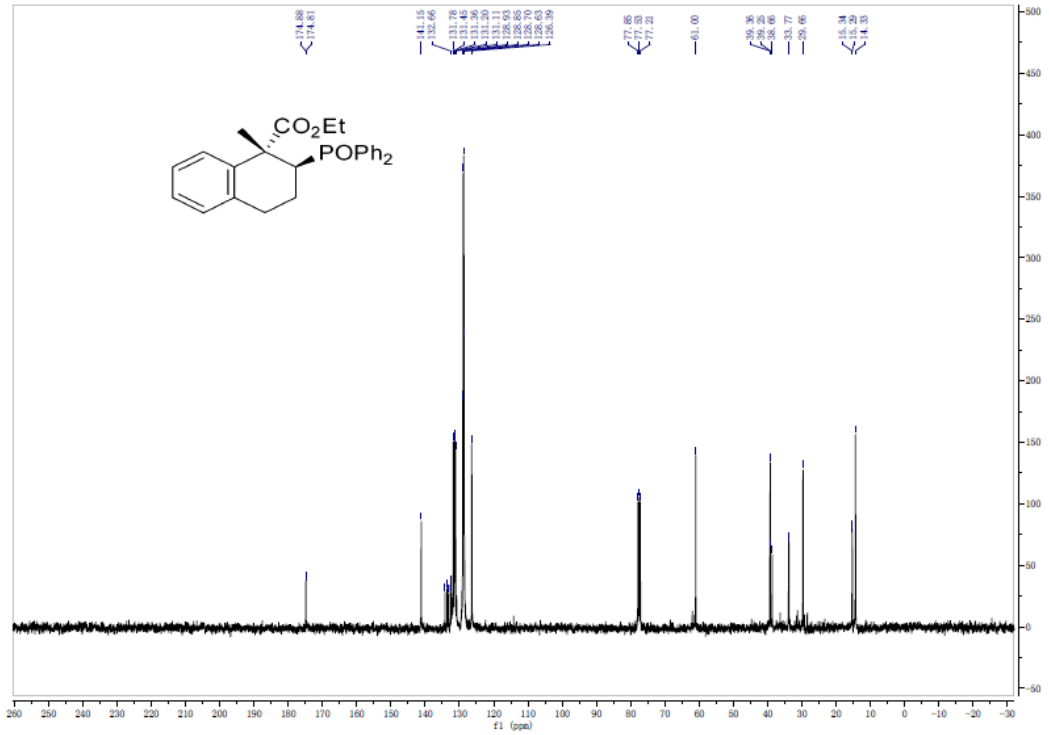

174.908
137.811
132.585
132.509
132.330
132.273
132.181
131.747
131.662
129.624
129.485
129.373
129.174
129.068
127.671
127.158
78.129
77.491
77.810
52.824
44.054
37.355
36.638
29.830
29.699
22.399
CO2Me
POPh2
150
100
50
0
ppm (t1)

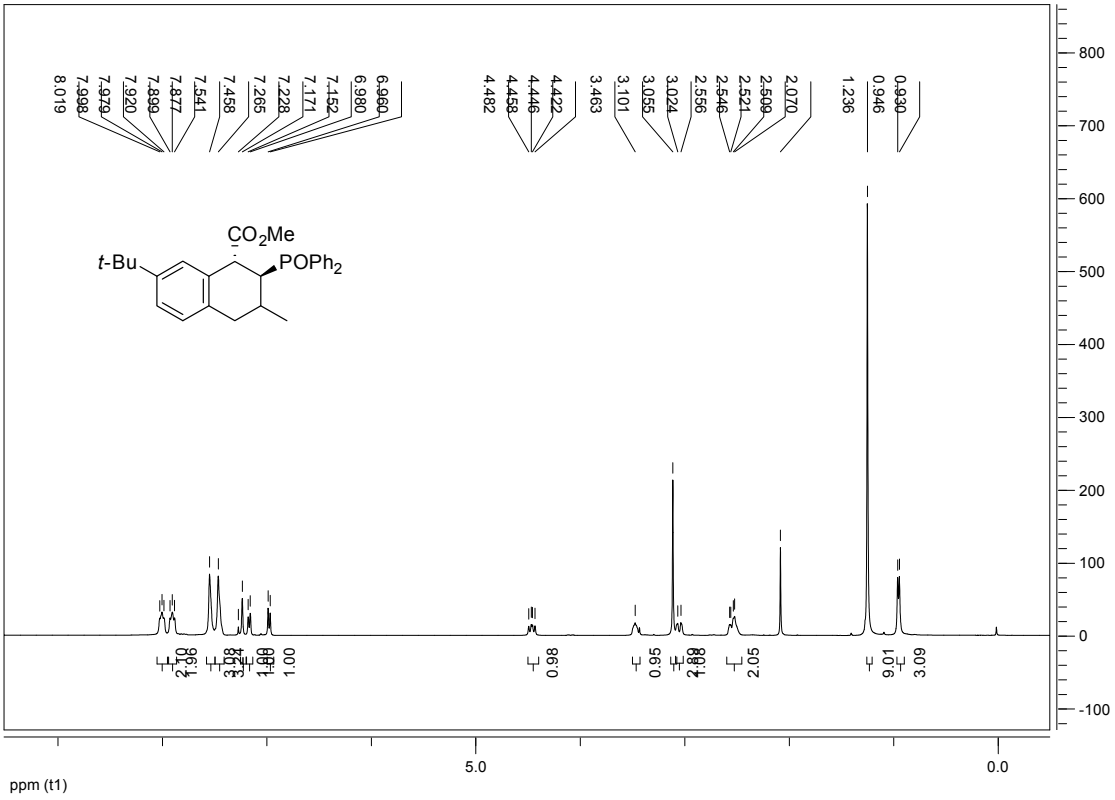
^{31}P NMR for 8a

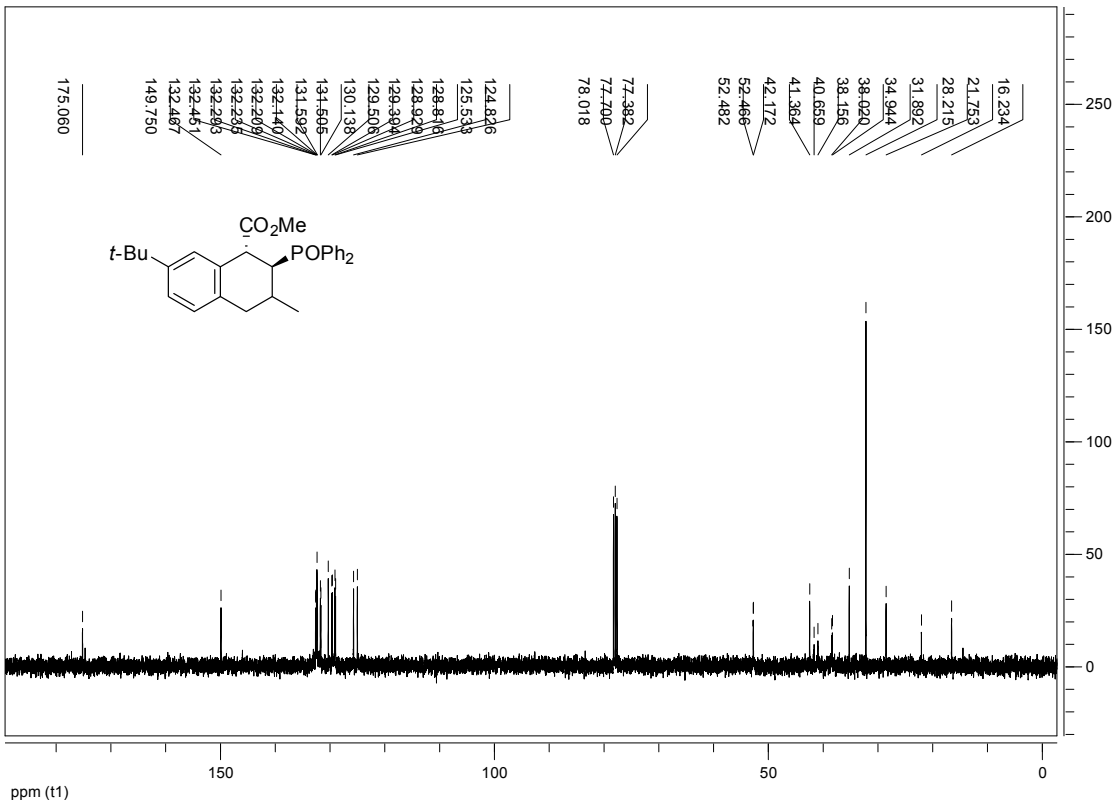




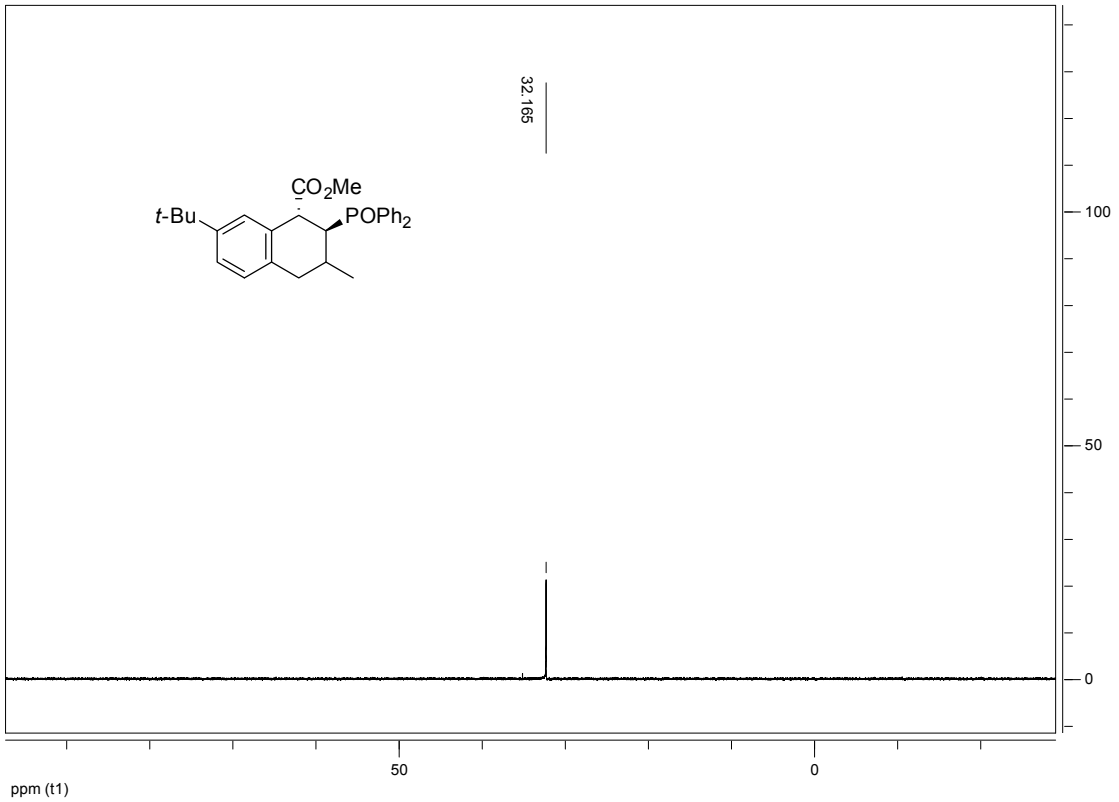
^{13}C NMR for 8b

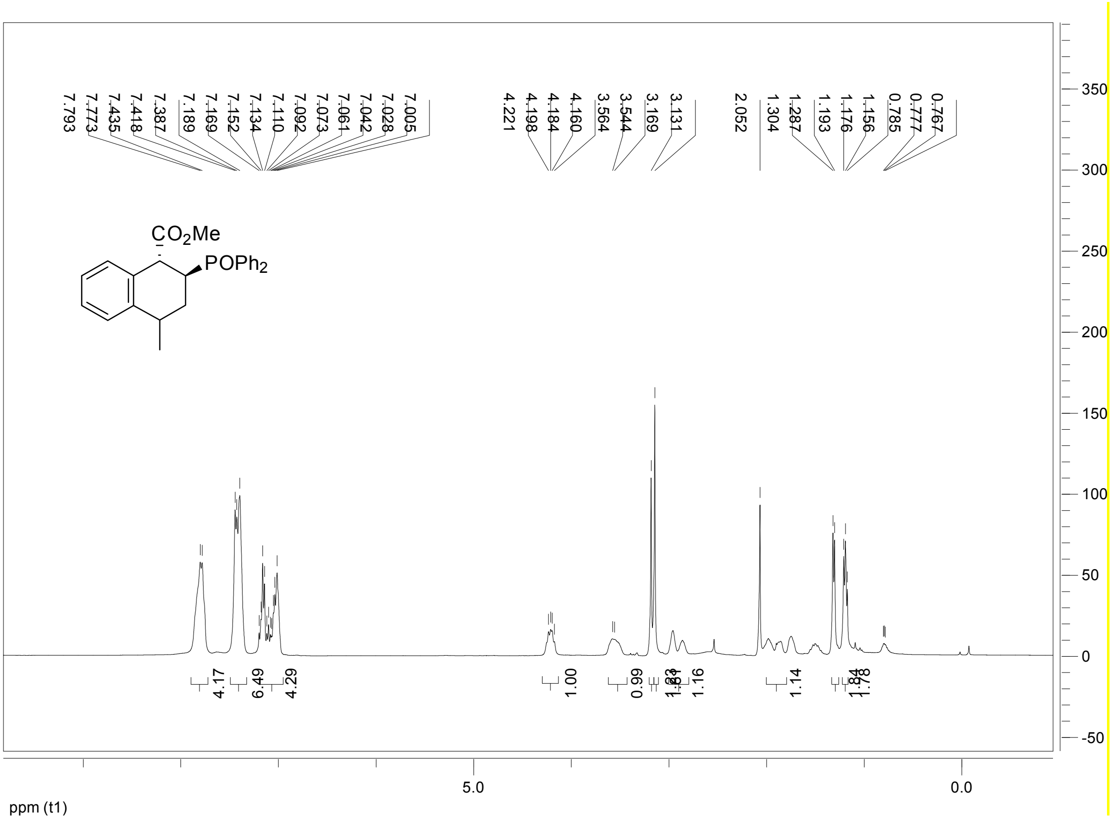


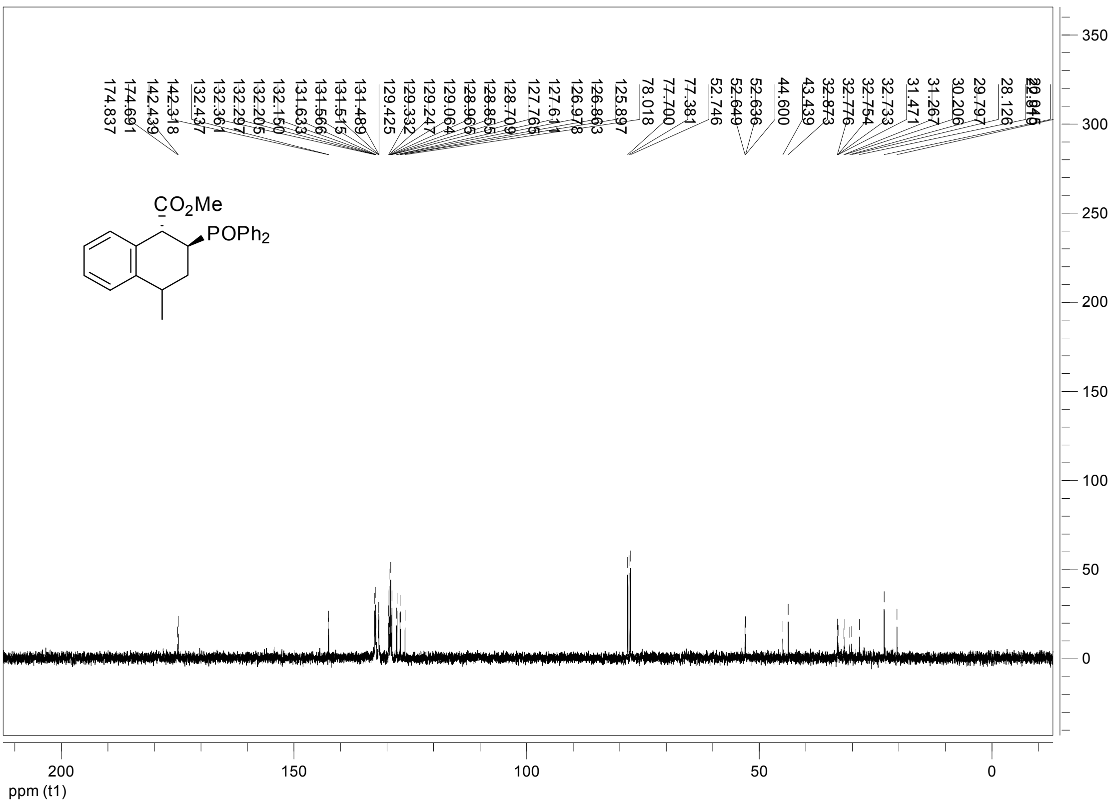


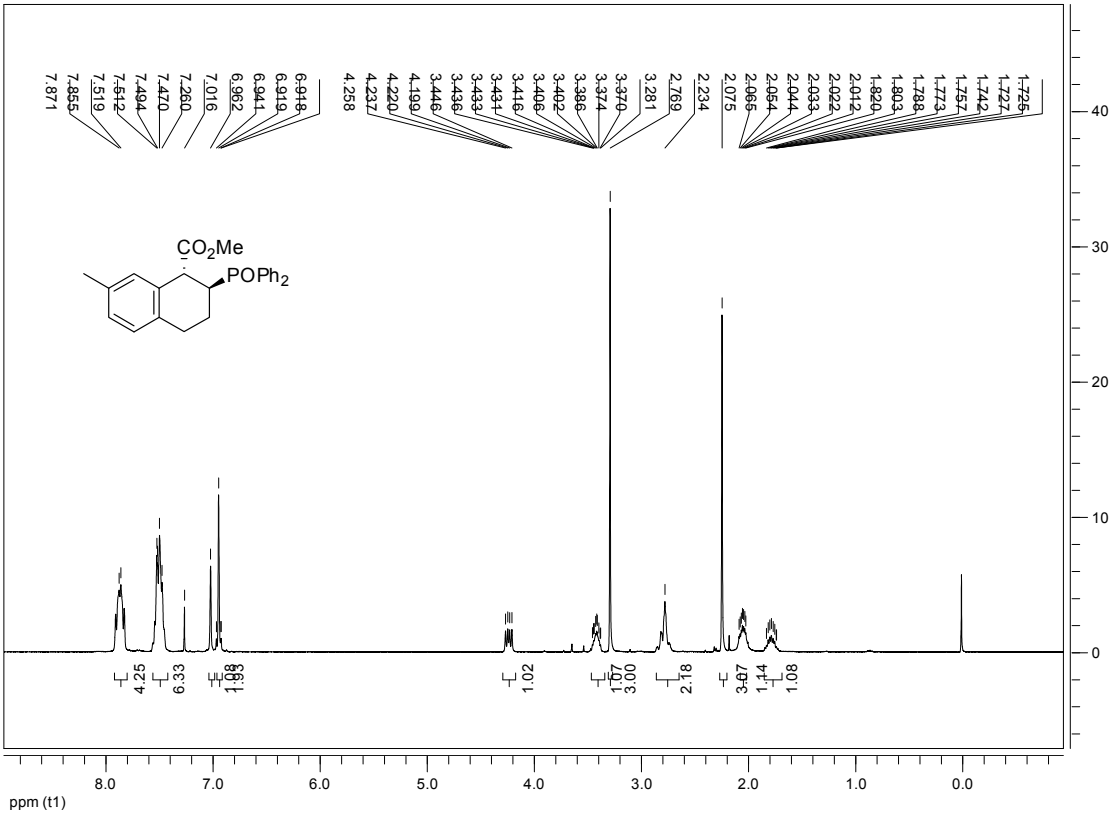


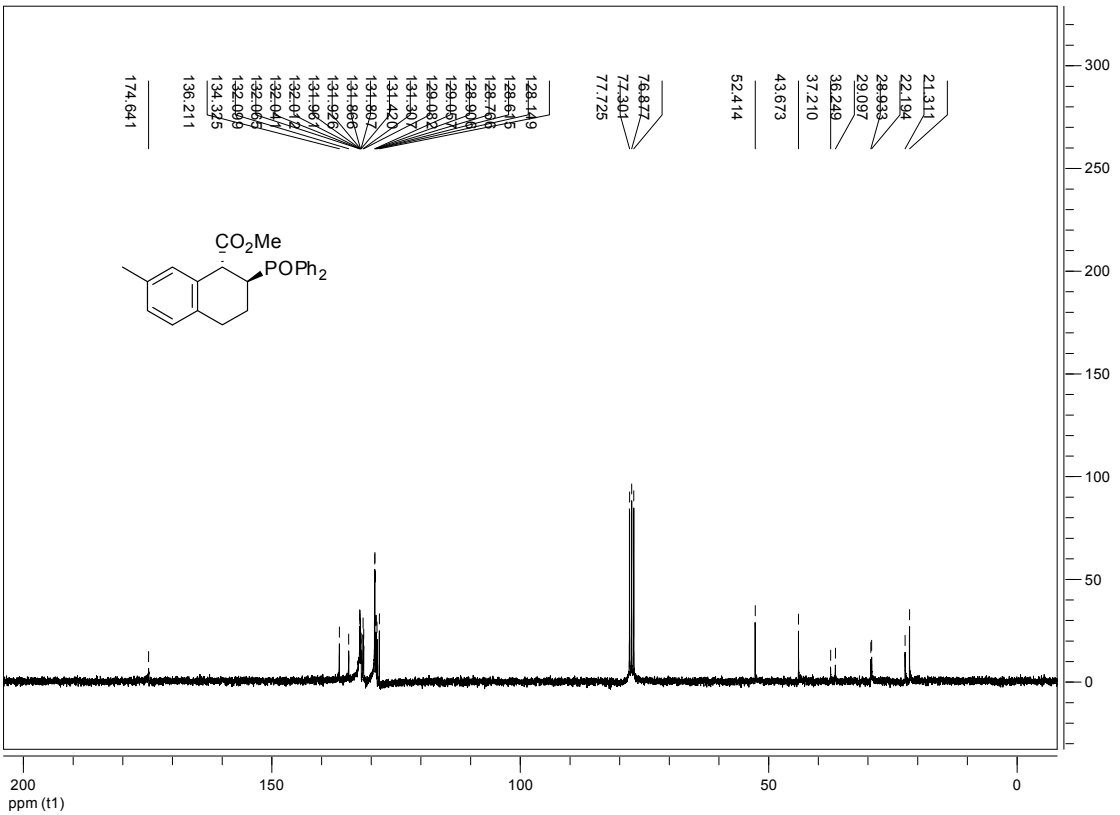
^{31}P NMR for 8d

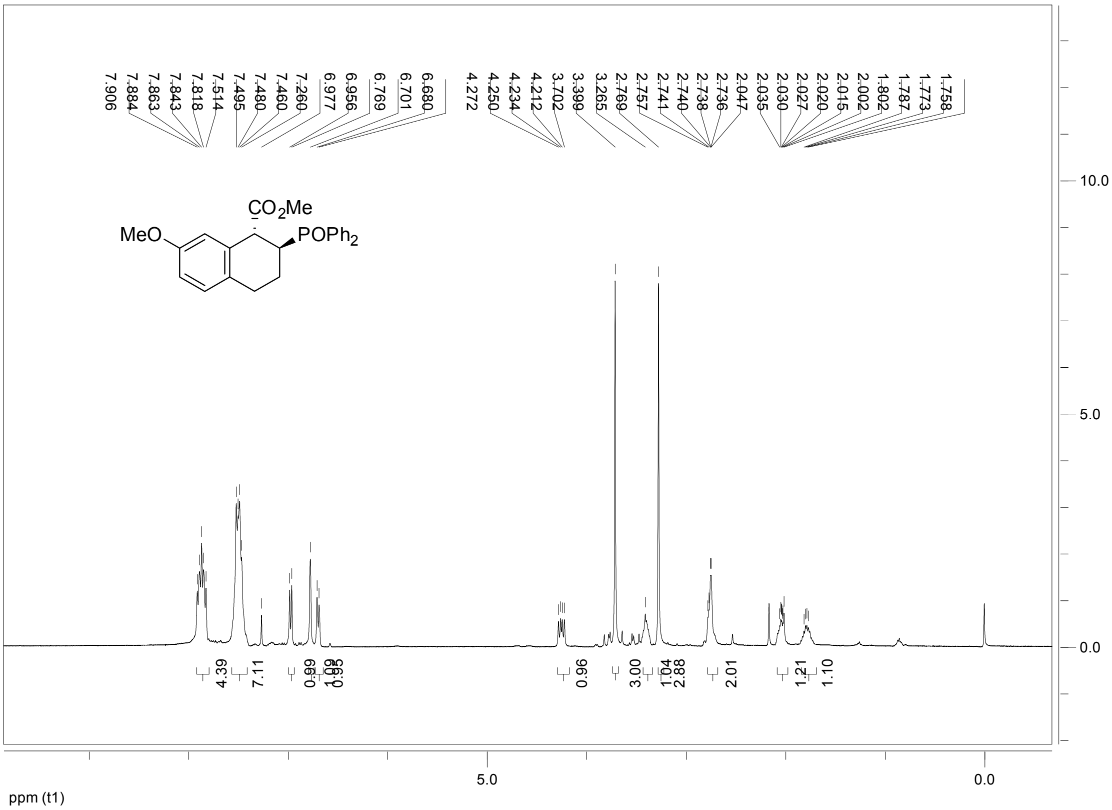


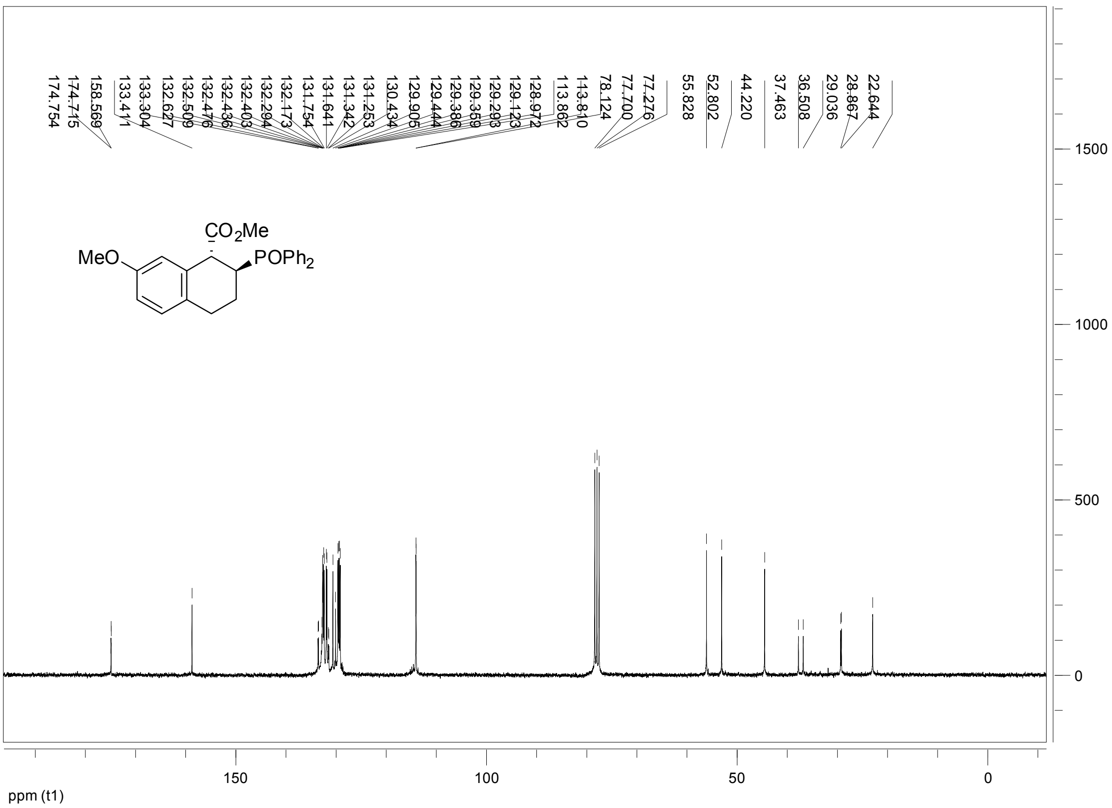


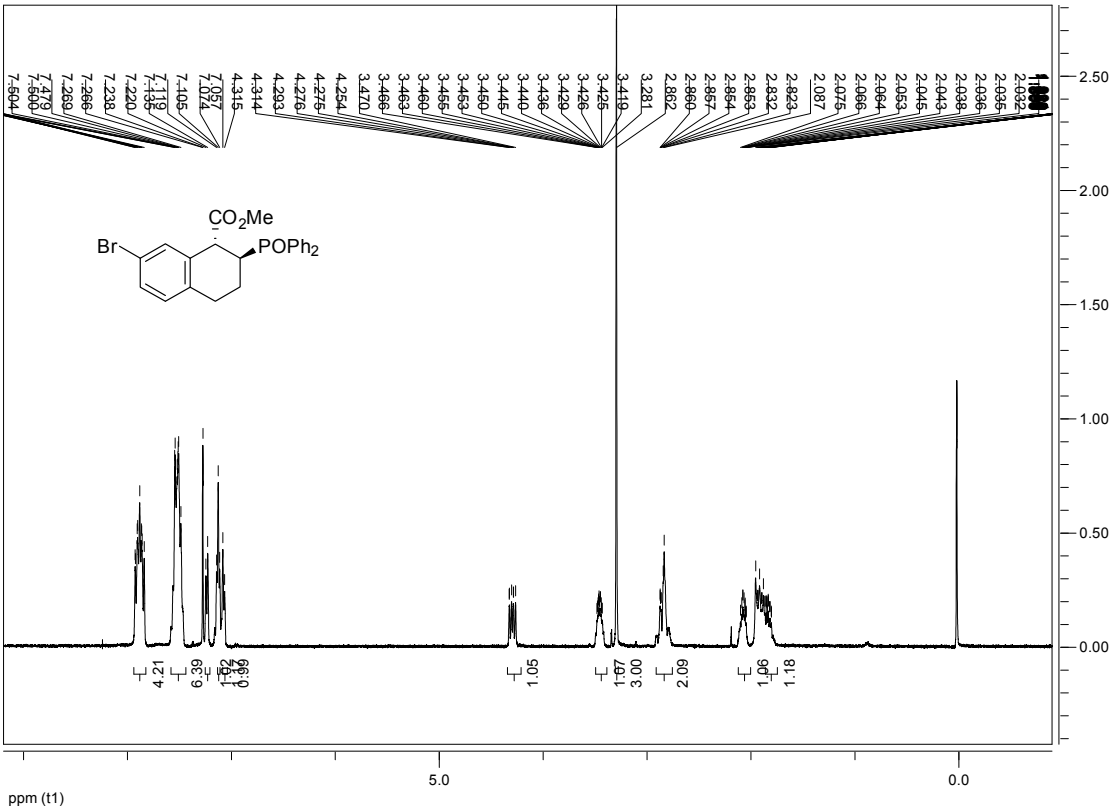


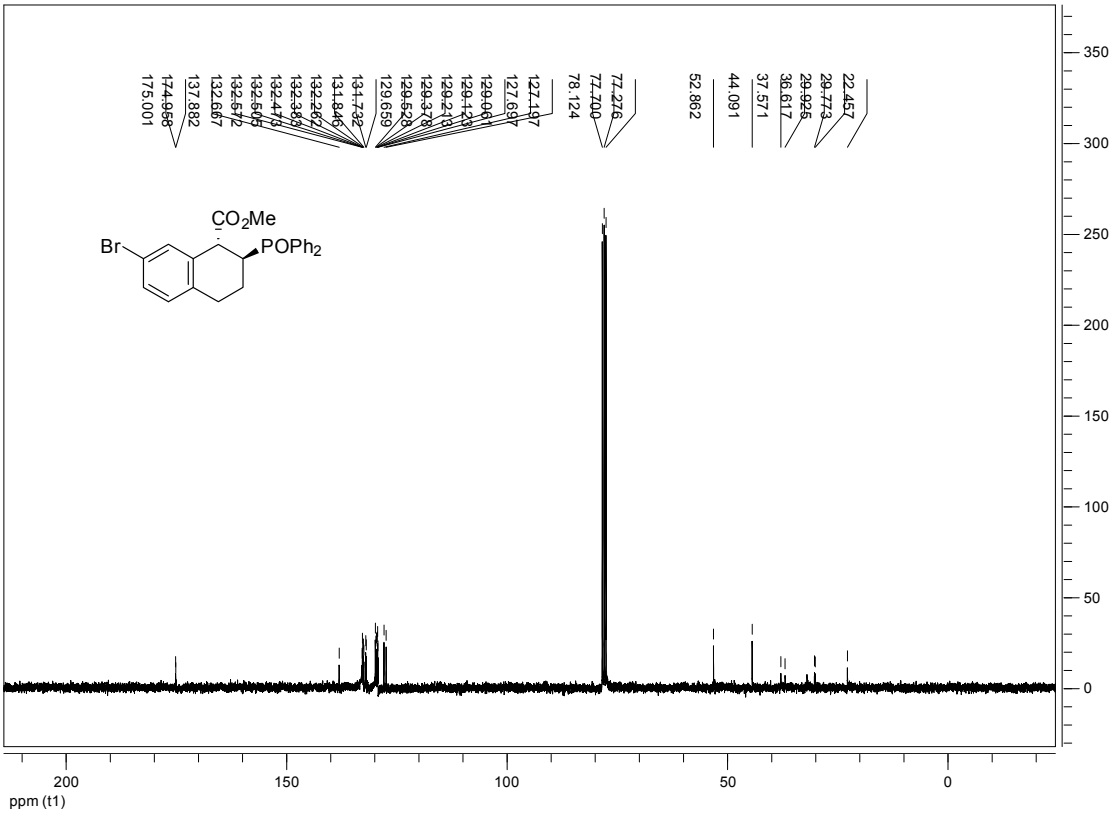

7.871
7.855
7.519
7.512
7.494
7.470
7.260
7.016
6.962
6.941
6.919
6.918
4.258
4.237
4.220
4.199
3.446
3.436
3.433
3.431
3.416
3.406
3.402
3.386
3.374
3.370
3.281
2.769
2.234
2.075
2.066
2.054
2.044
2.033
2.022
2.012
1.820
1.803
1.788
1.773
1.757
1.742
1.727
1.725
CO2Me
POPh2
4.25
3.33
1.02
3.00
2.18
3.67
1.14
1.08
ppm (t1)


174.641
136.211
134.375
132.099
132.065
132.047
132.012
131.961
131.926
131.866
131.807
131.420
131.307
129.083
129.057
128.906
128.768
128.615
128.149
77.725
77.301
76.877
52.414
43.673
37.210
36.249
29.097
28.933
22.194
21.311
CO2Me
POPh2
ppm (t1)

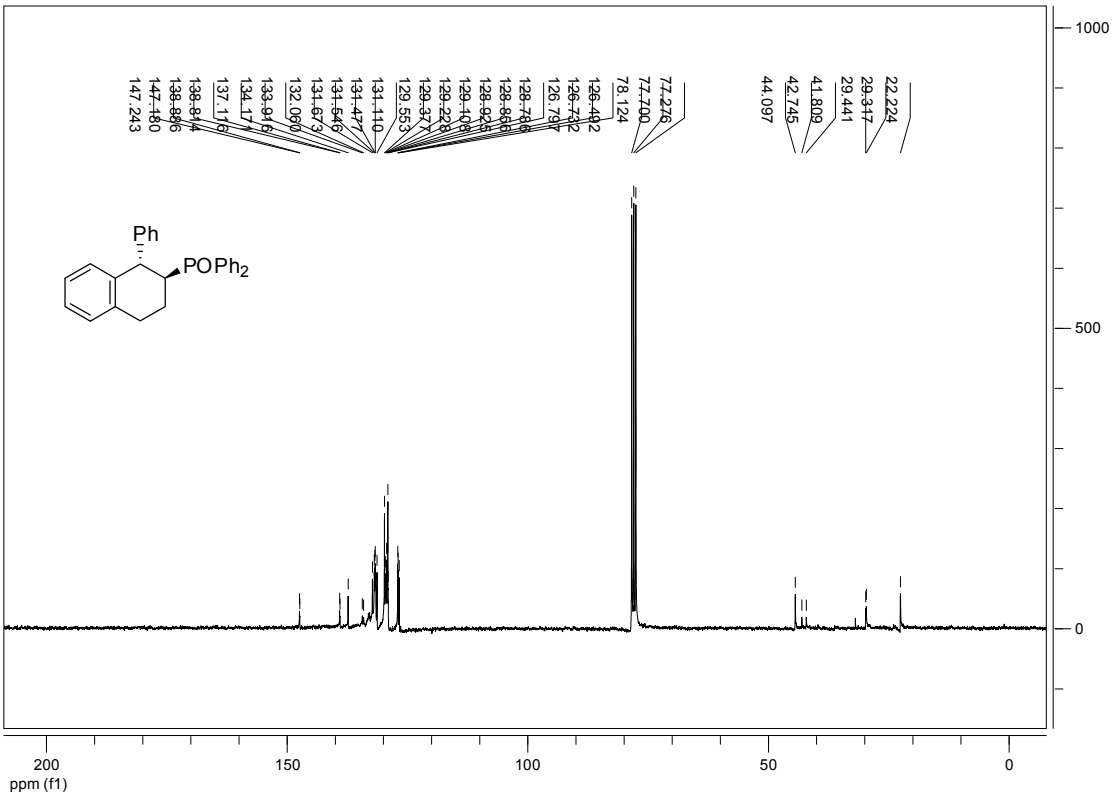

7.906
7.884
7.863
7.843
7.818
7.514
7.495
7.480
7.460
7.260
6.977
6.956
6.769
6.701
6.680
4.272
4.250
4.234
4.212
3.702
3.399
3.265
2.769
2.757
2.741
2.740
2.738
2.736
2.047
2.035
2.030
2.027
2.020
2.015
2.002
1.802
1.787
1.773
1.758
MeO
CO2Me
POPh2
10.0
5.0
0.0
4.39
7.11
0.99
1.00
0.95
0.96
3.00
1.04
2.88
2.01
1.21
1.10
5.0
0.0
ppm (t1)

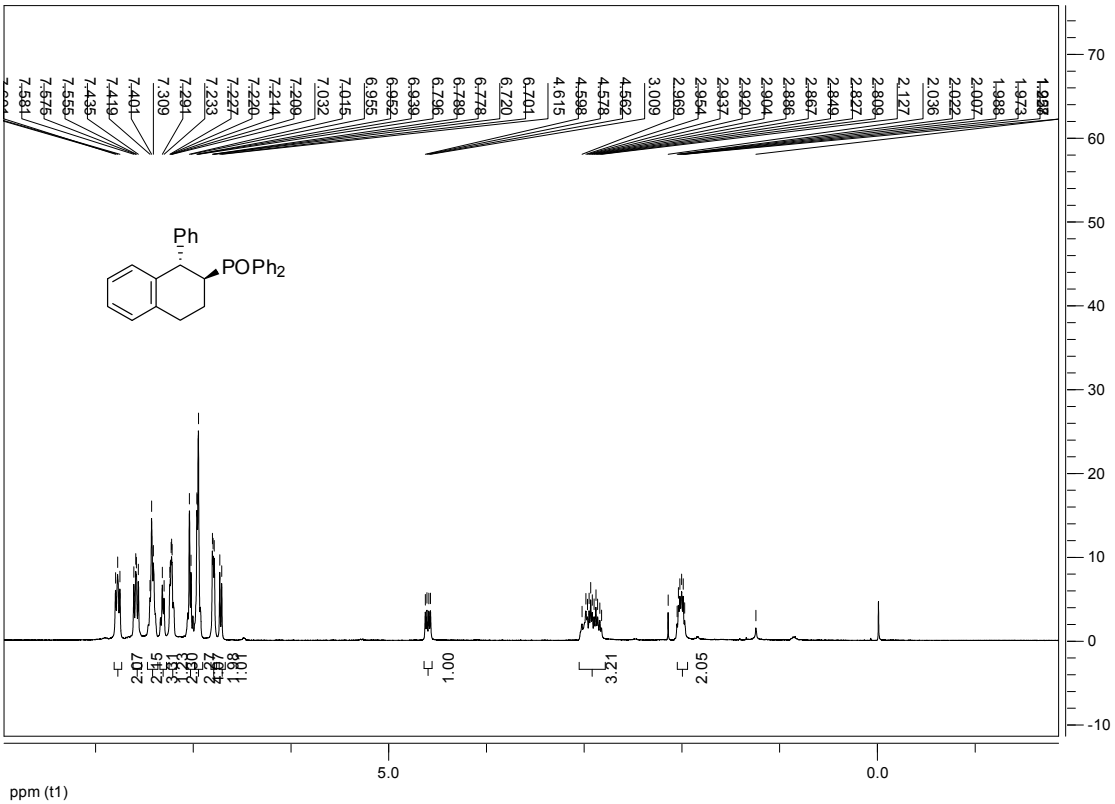

174.754
174.715
158.569
133.411
133.304
132.627
132.509
132.476
132.436
132.403
132.294
132.173
131.754
131.641
131.342
131.263
130.434
129.905
129.444
129.386
129.369
129.293
129.123
128.972
113.862
113.810
78.124
77.700
77.276
55.828
52.802
44.220
37.463
36.508
29.036
28.867
22.644
MeO
CO2Me
POPh2
1500
1000
500
0
150
100
50
0
ppm (t1)


CO2Me
Br
POPh2
ppm (t1)

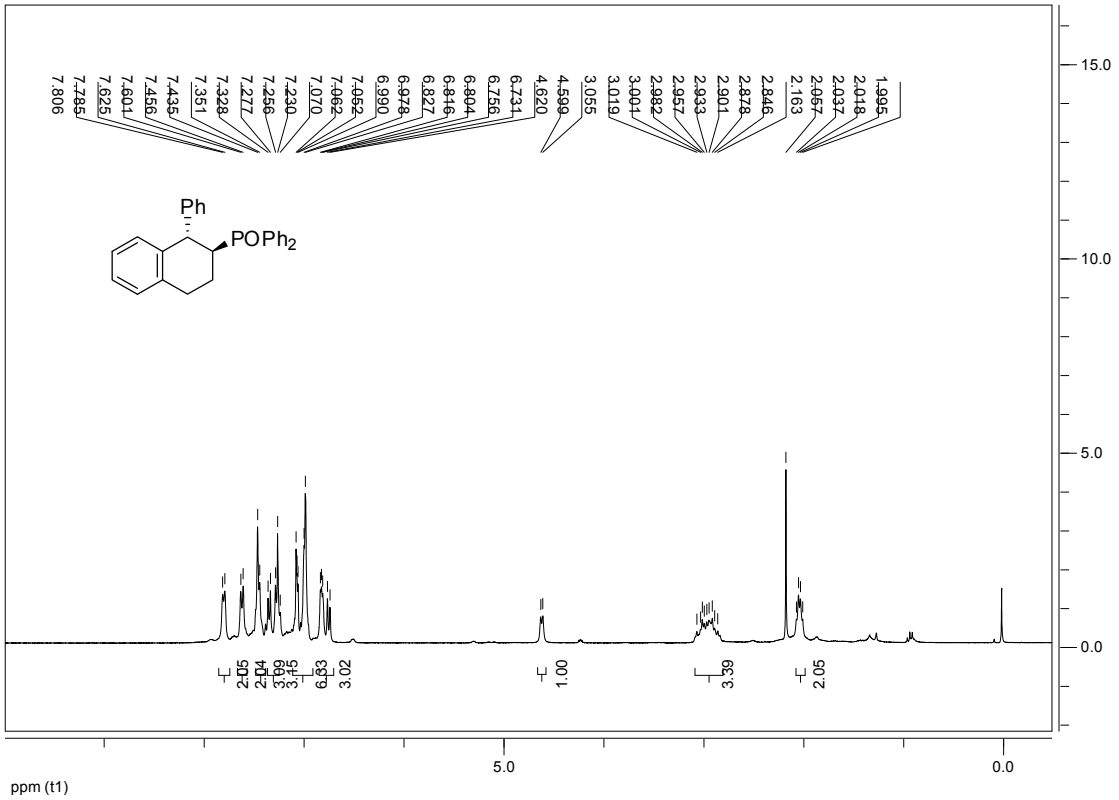

CO2Me
Br
POPh2
ppm (t1)

New ^{13}CNMR spectrum for 15a

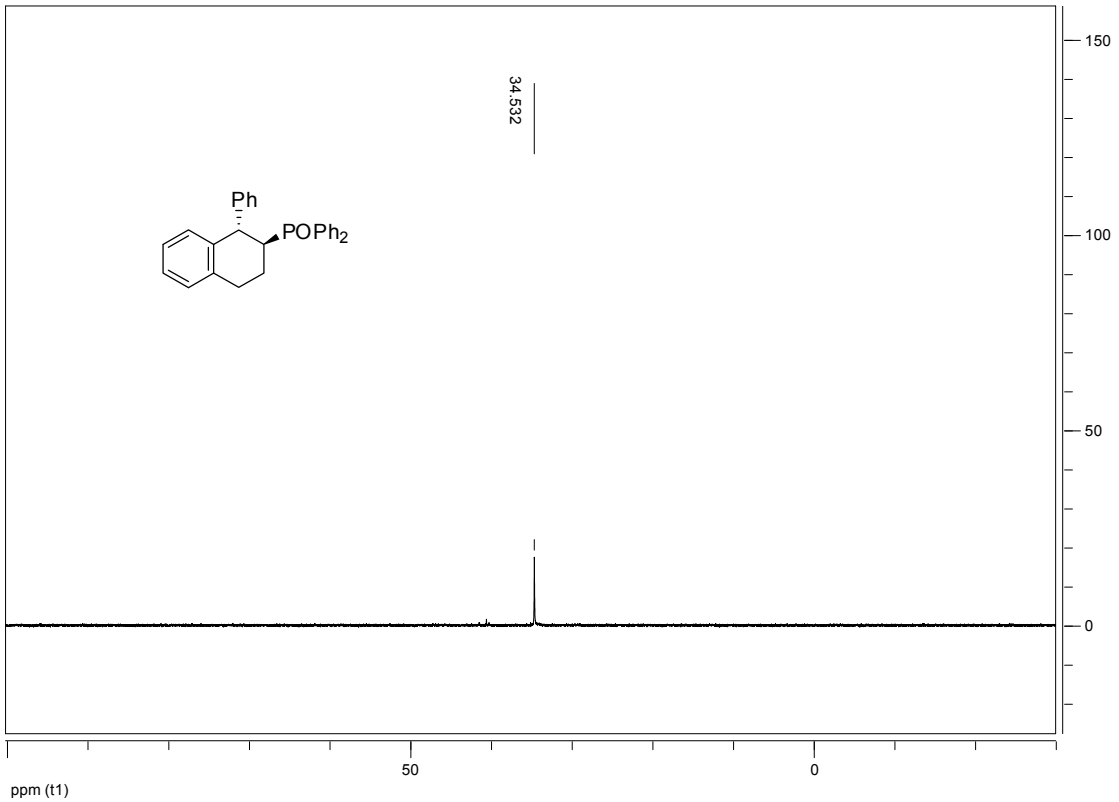


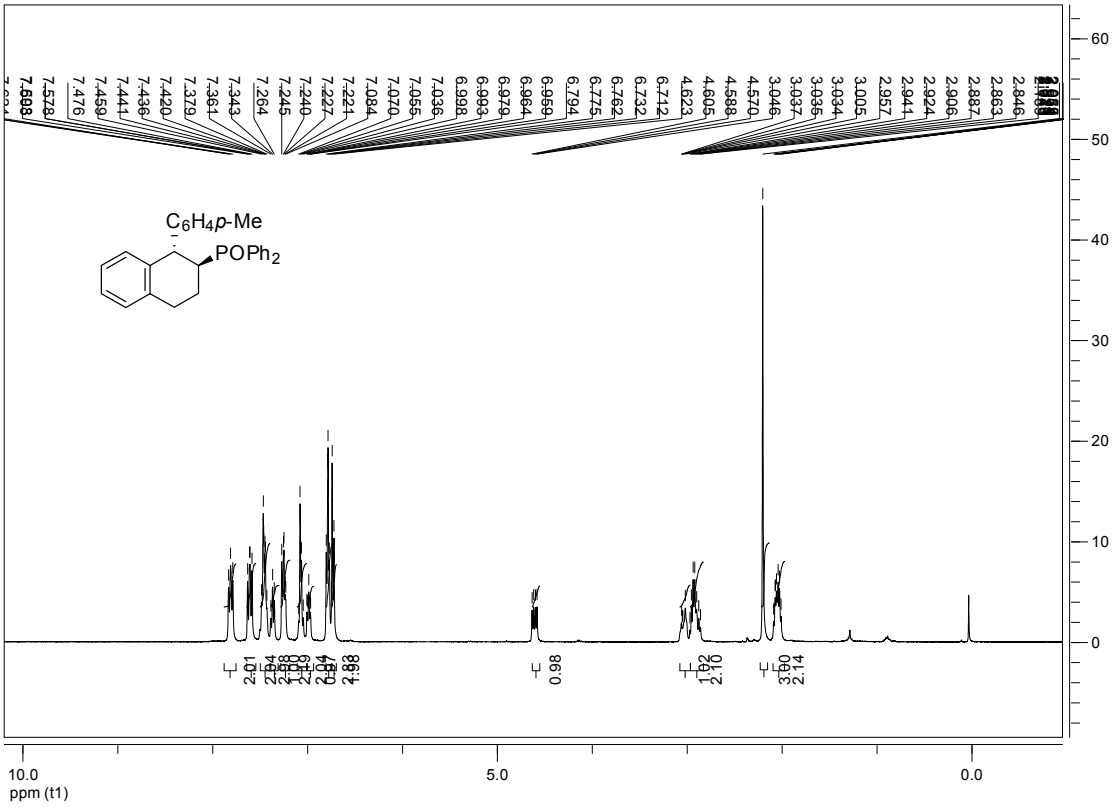


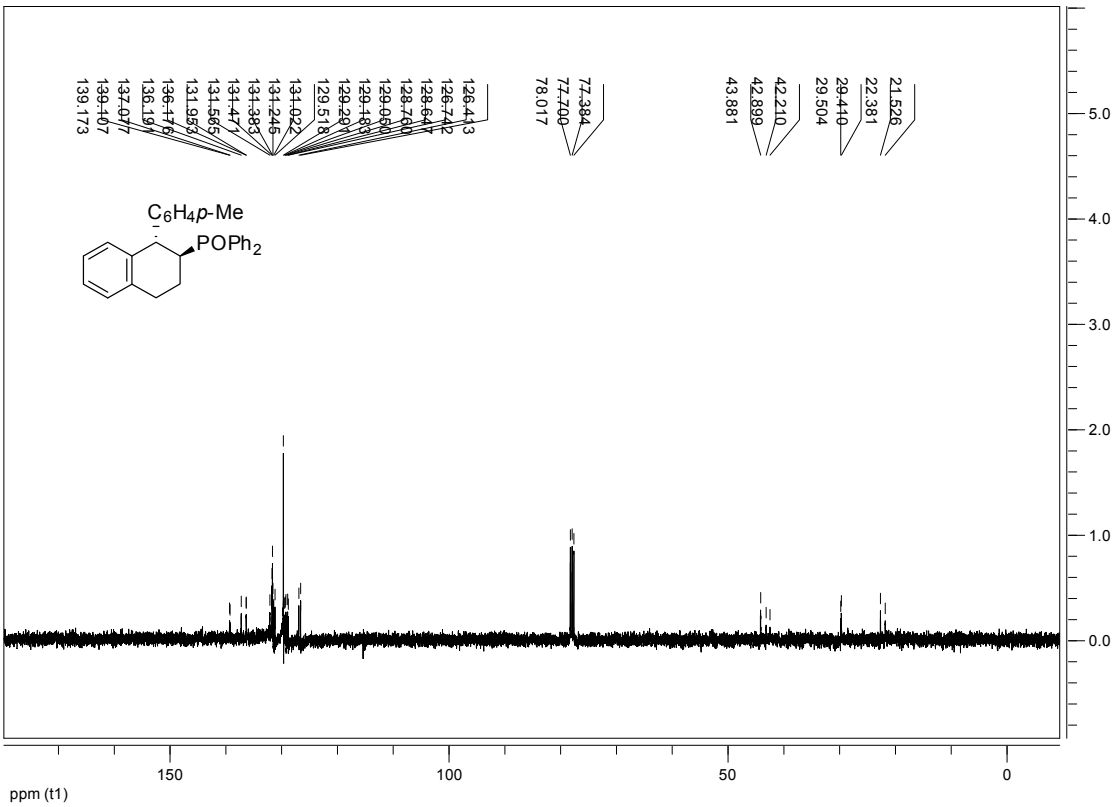
^{31}P-decoupled proton NMR for 15a

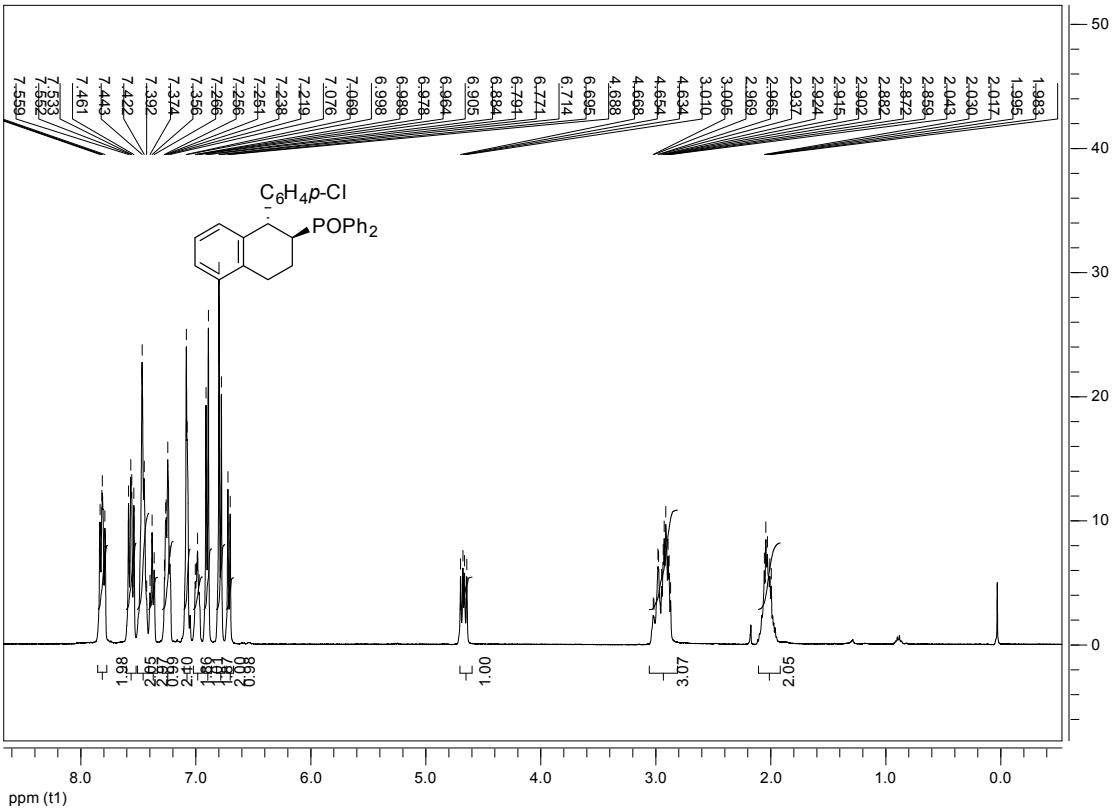


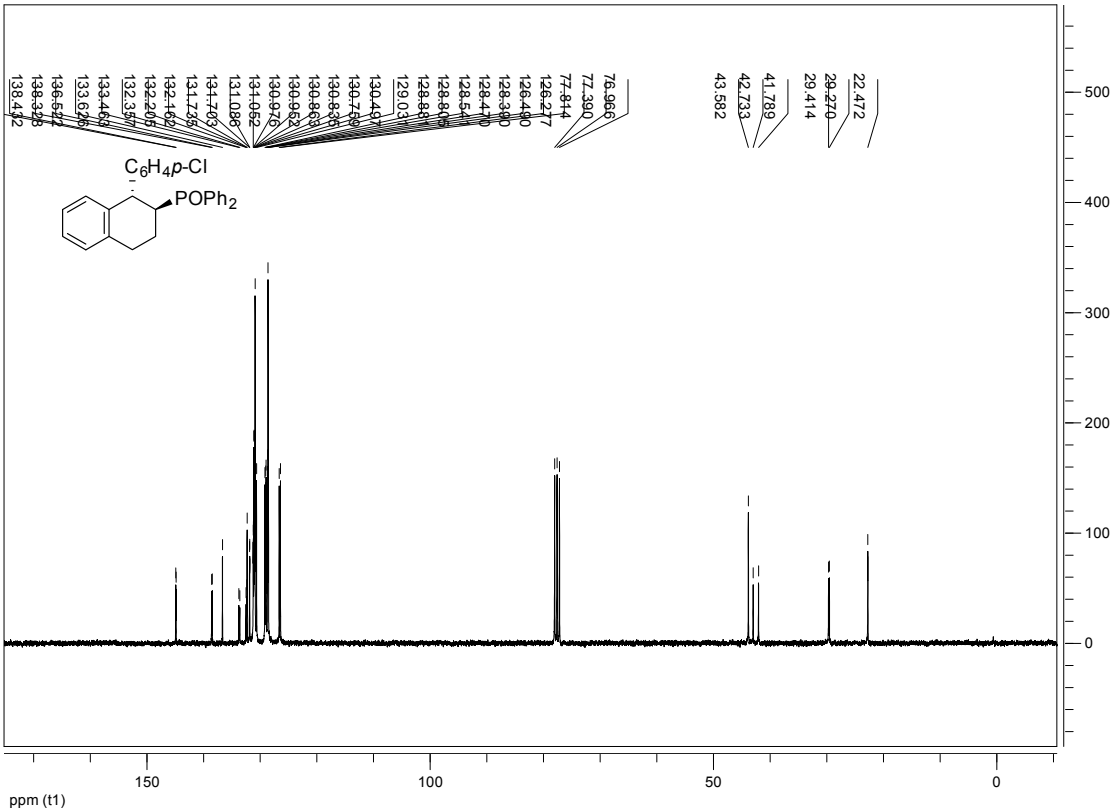
^{31}P NMR for 15a

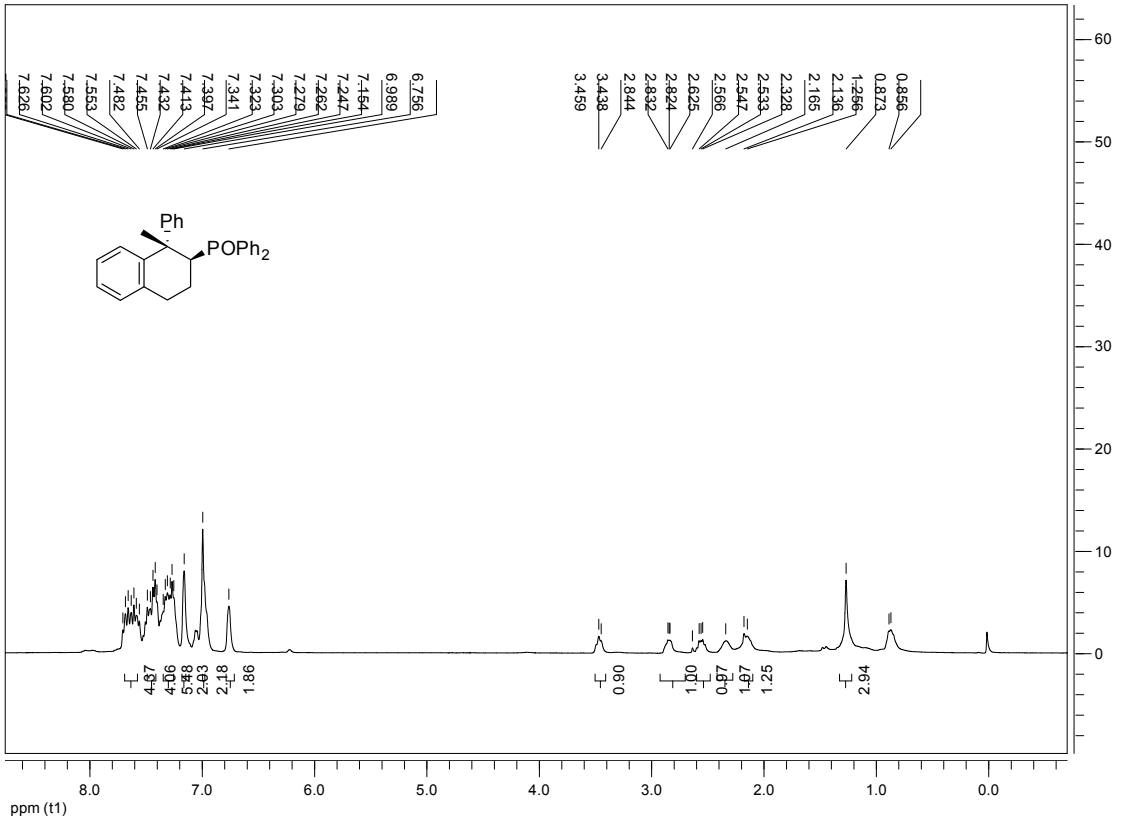


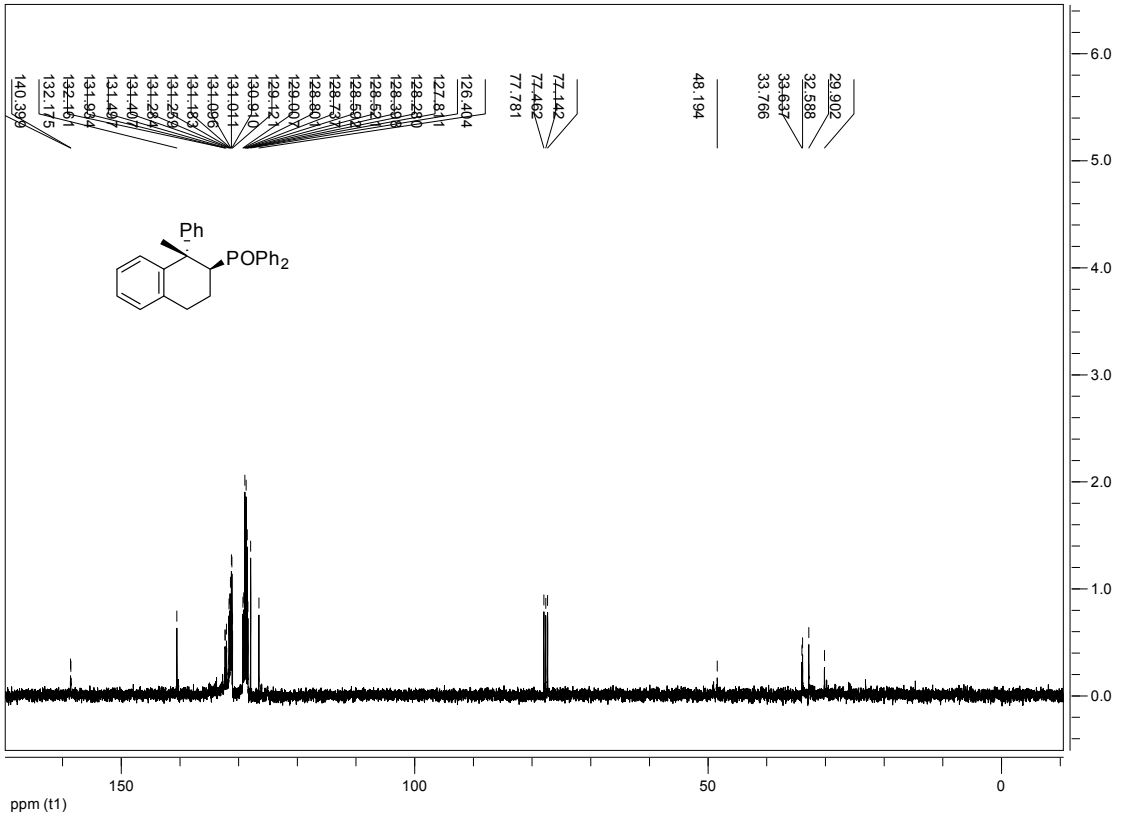

C6H4p-Me
POPh2
10.0
5.0
0.0
ppm (t1)

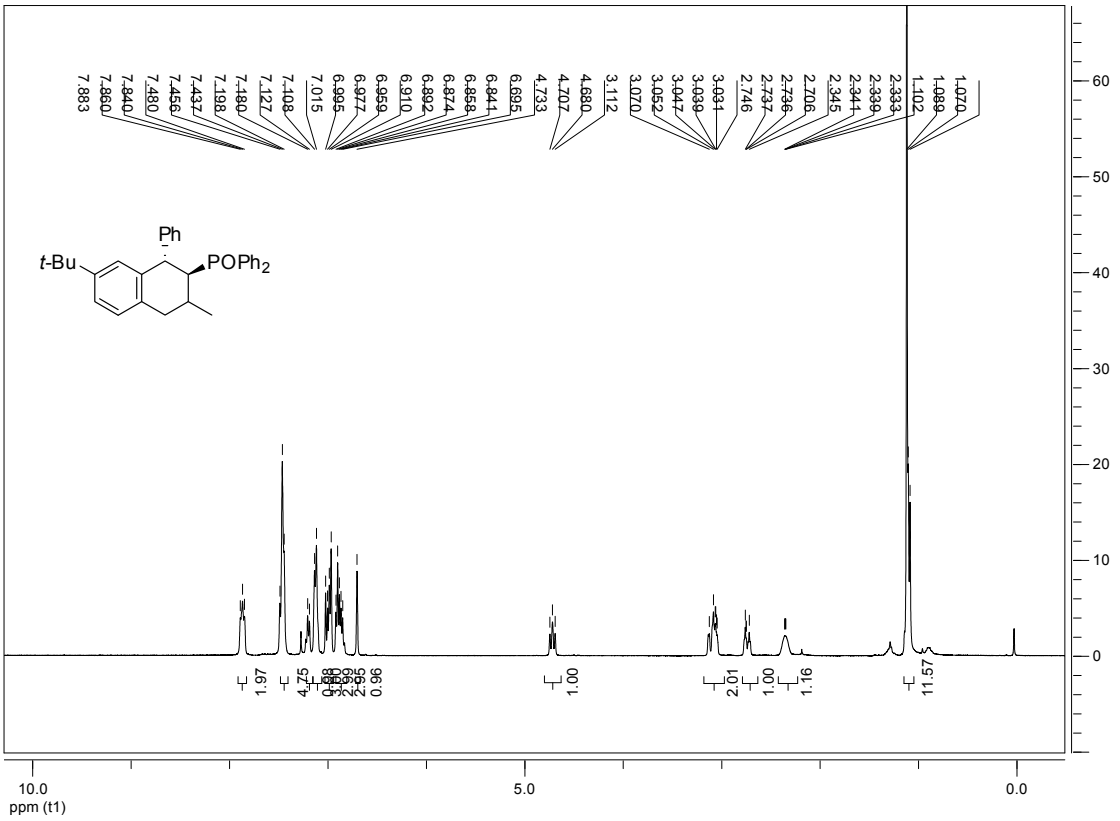

C6H4p-Me
POPh2
150
100
50
0
ppm (t1)

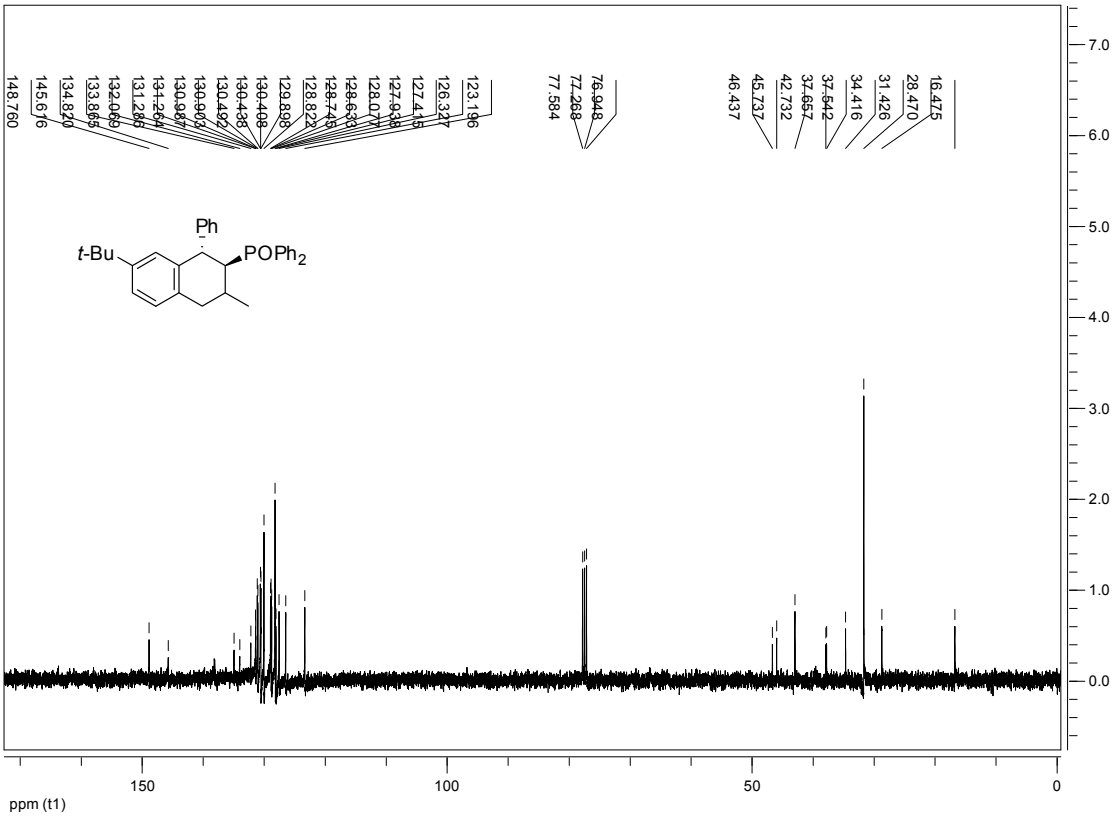

C6H4p-Cl
POPh2
ppm (t1)

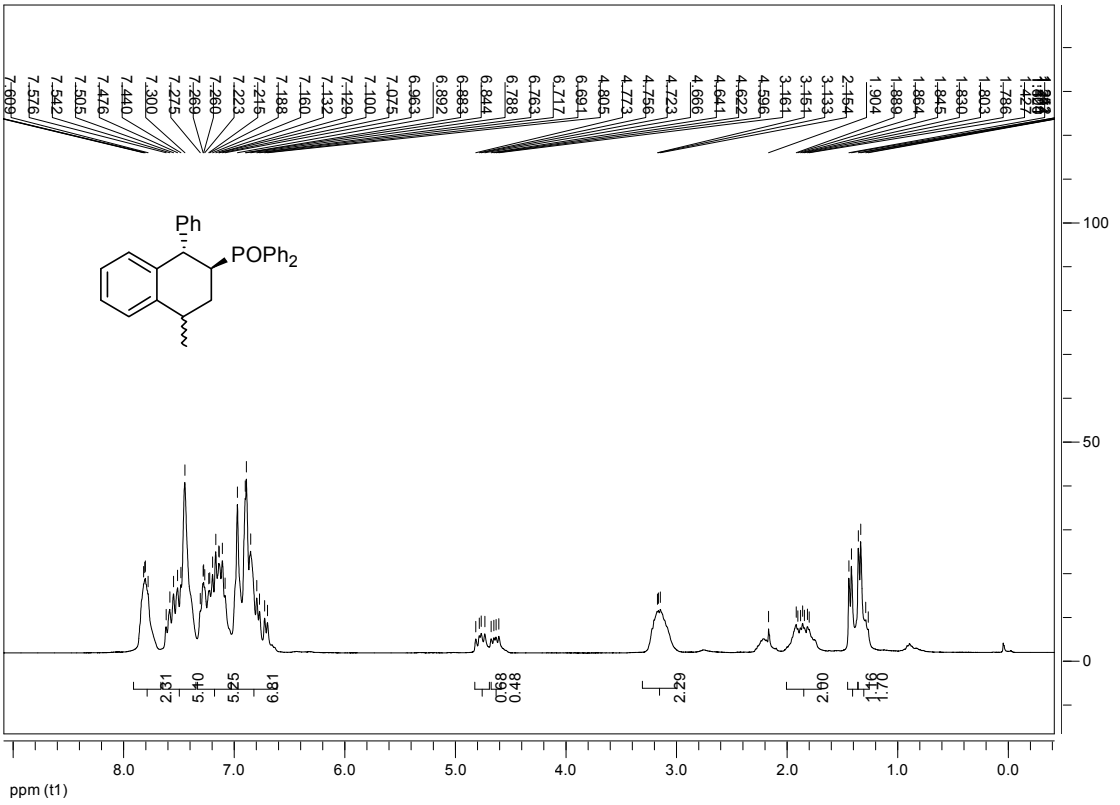

C6H4p-Cl
POPh2
ppm (t1)

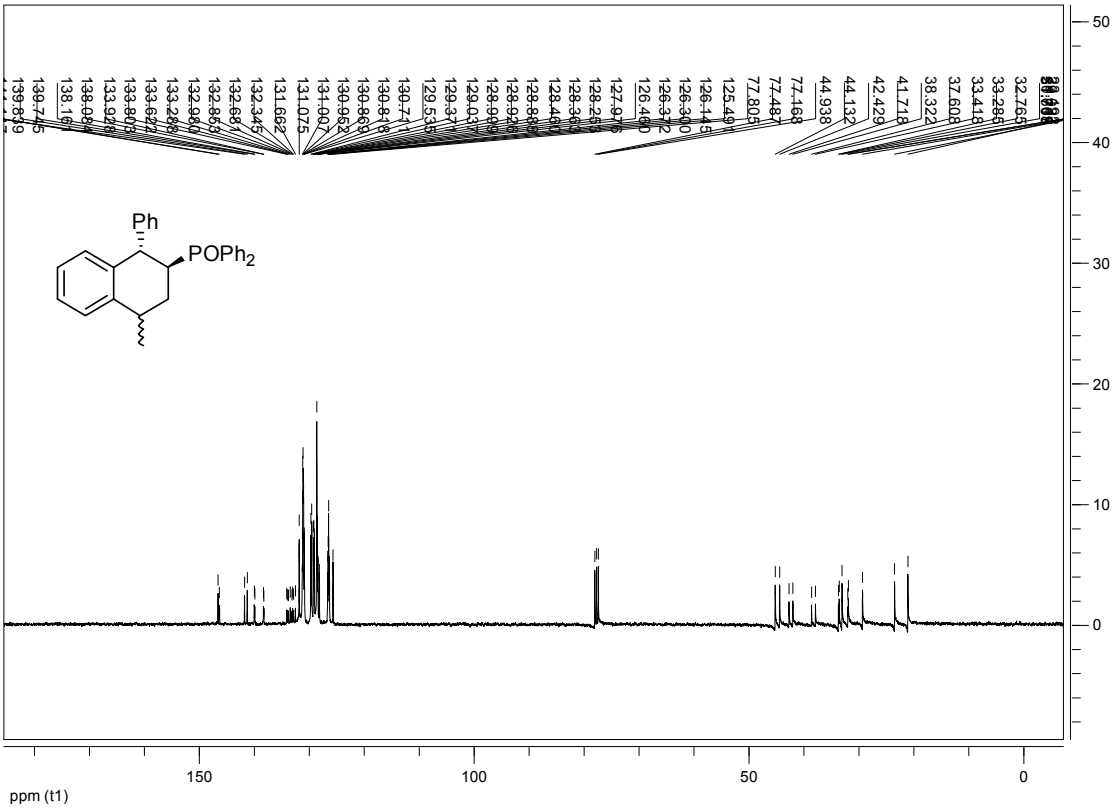

7.626
7.602
7.580
7.553
7.482
7.455
7.432
7.413
7.397
7.341
7.323
7.303
7.279
7.262
7.247
7.154
6.989
6.756
3.459
3.438
2.844
2.832
2.824
2.625
2.566
2.547
2.533
2.328
2.165
2.136
1.266
0.873
0.856
Ph
POPh2
ppm (t1)

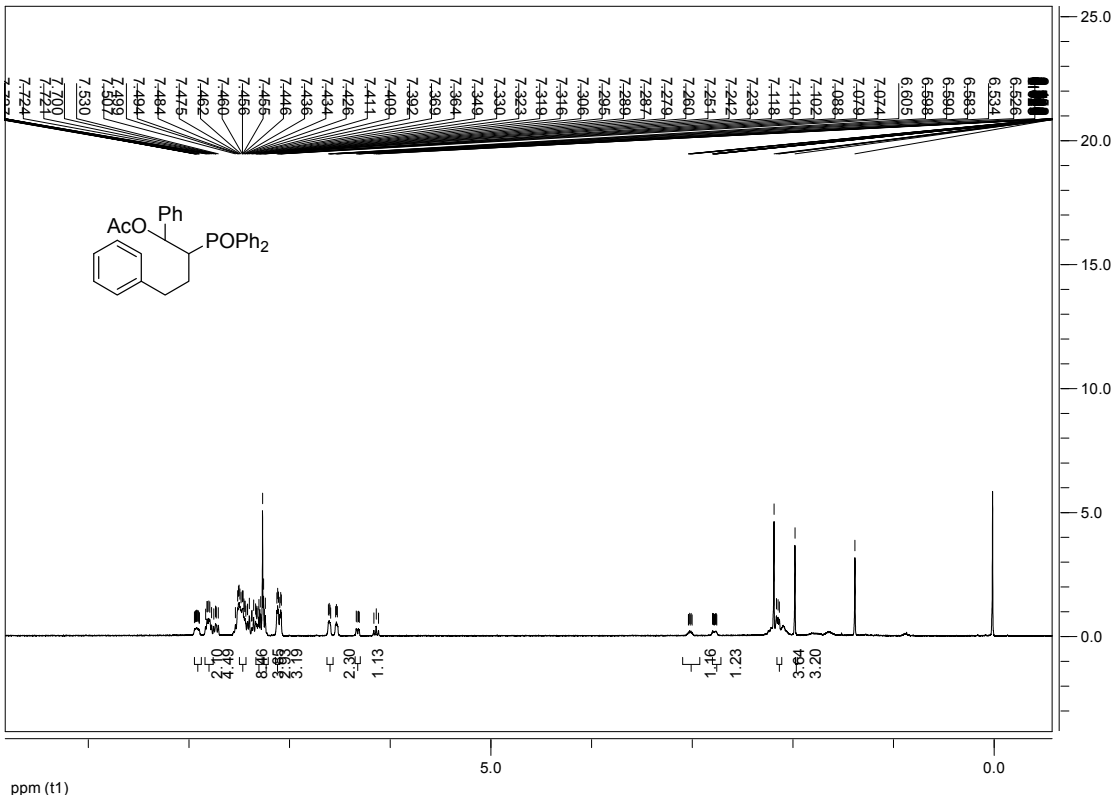

140.398
132.175
132.101
131.924
131.497
131.407
131.284
131.259
131.183
131.096
131.011
130.910
129.121
129.007
128.801
128.732
128.592
128.521
128.398
128.280
127.811
126.404
77.781
77.462
77.142
48.194
33.766
33.637
32.588
29.902
Ph
POPh2
ppm (t1)

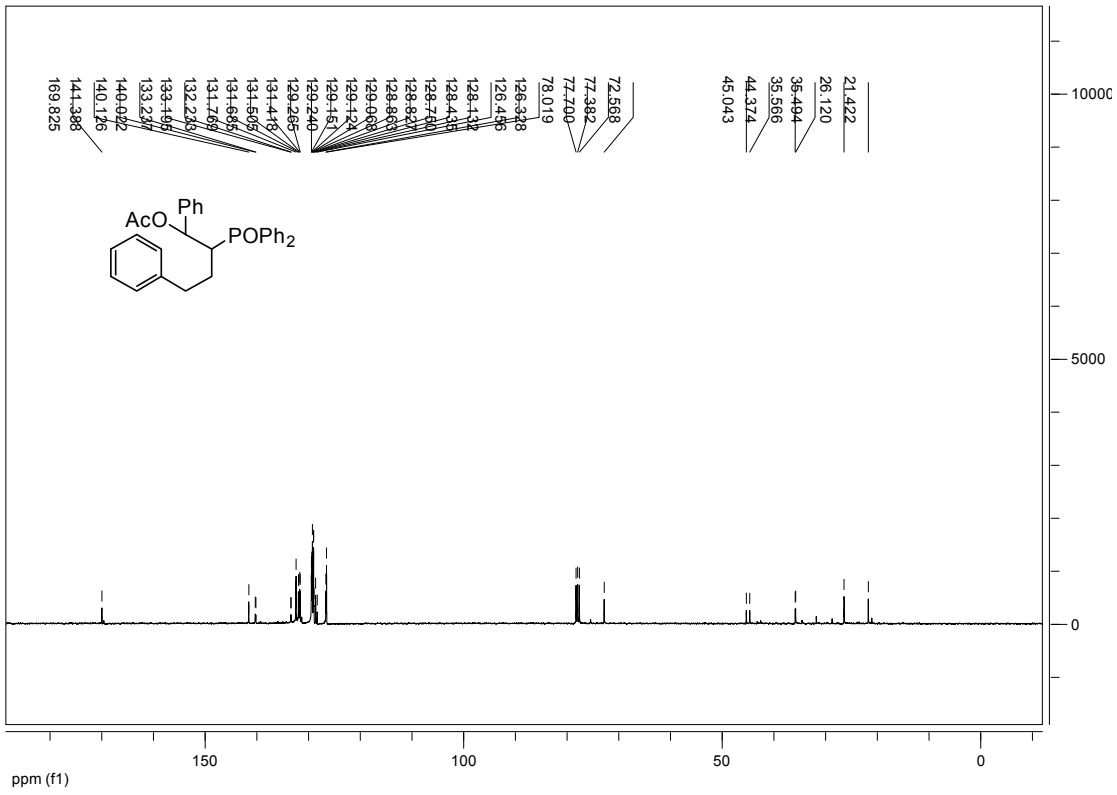

7.883
7.860
7.840
7.480
7.456
7.437
7.198
7.180
7.127
7.108
7.015
6.995
6.977
6.959
6.910
6.892
6.874
6.858
6.841
6.695
4.733
4.707
4.680
3.112
3.070
3.052
3.047
3.039
3.031
2.746
2.737
2.736
2.706
2.345
2.341
2.339
2.333
1.102
1.089
1.070
Ph
t-Bu
POPh2
1.97
4.75
96.0
1.00
2.01
1.00
1.16
11.57
10.0
ppm (t1)
5.0
0.0

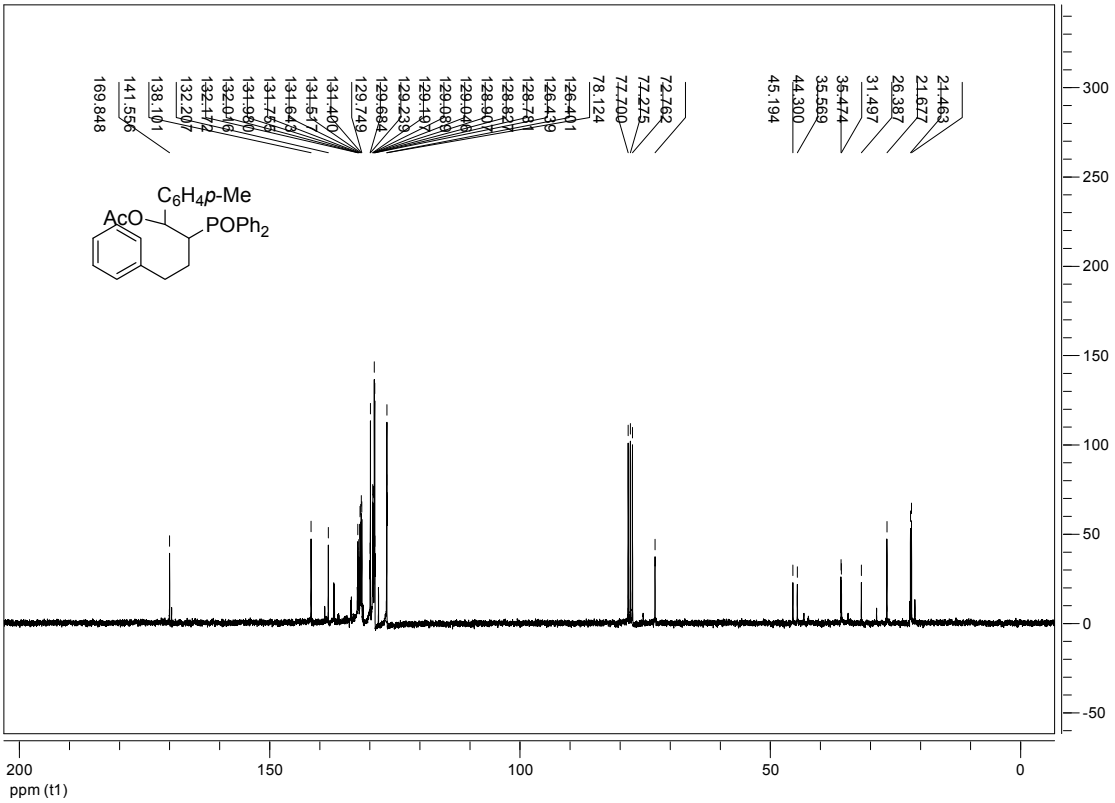

148.760
145.676
134.820
133.865
132.060
131.286
131.264
130.987
130.903
130.492
130.438
130.409
129.898
128.822
128.745
128.633
128.074
127.938
127.415
126.327
123.196
77.584
76.948
46.437
45.737
42.732
37.657
37.542
34.416
31.426
28.470
16.475
Ph
t-Bu
POPh2
150
100
50
0
ppm (t1)

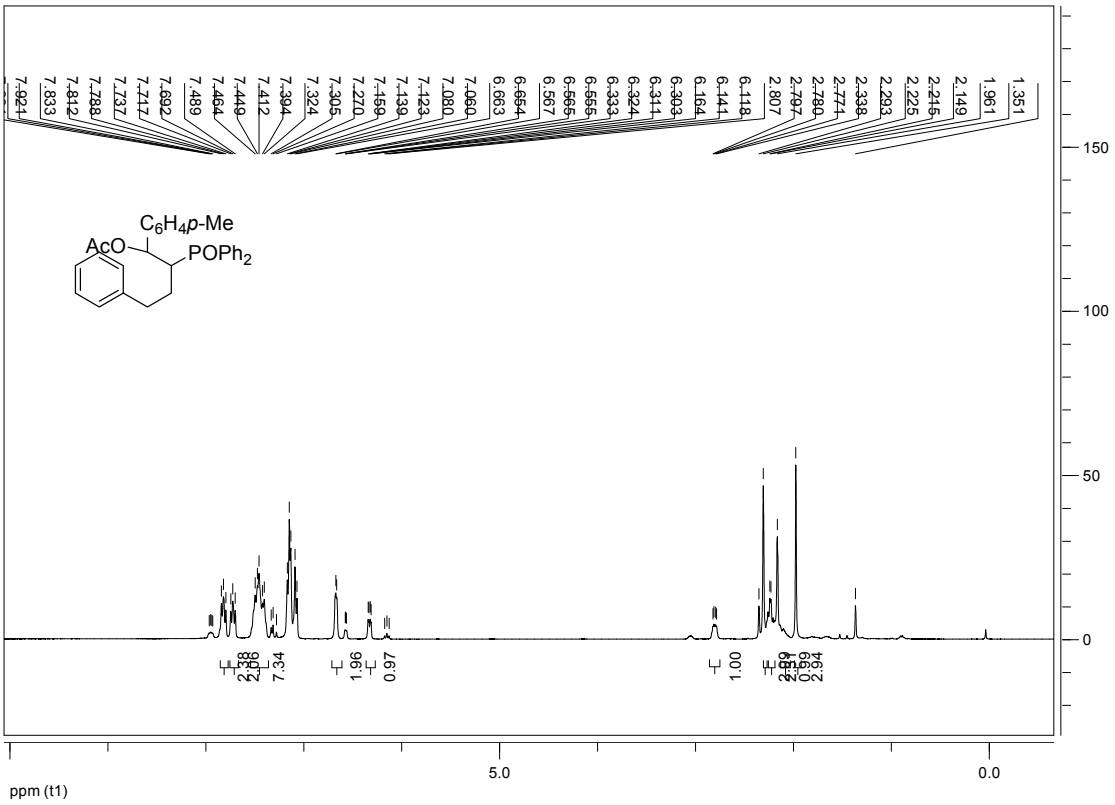

Ph
POPh2
ppm (t1)


Ph
POPh2
ppm (t1)

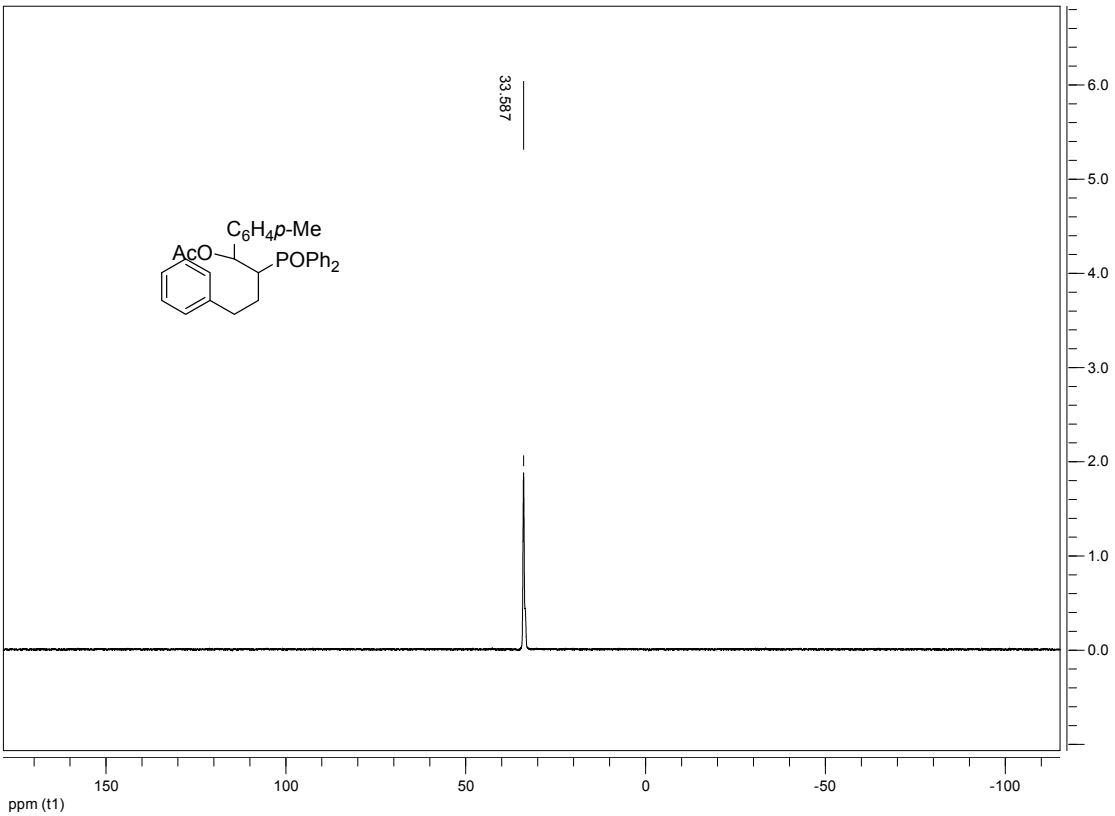

AcO
Ph
POPh2
25.0
20.0
15.0
10.0
5.0
0.0
5.0
0.0
ppm (t1)

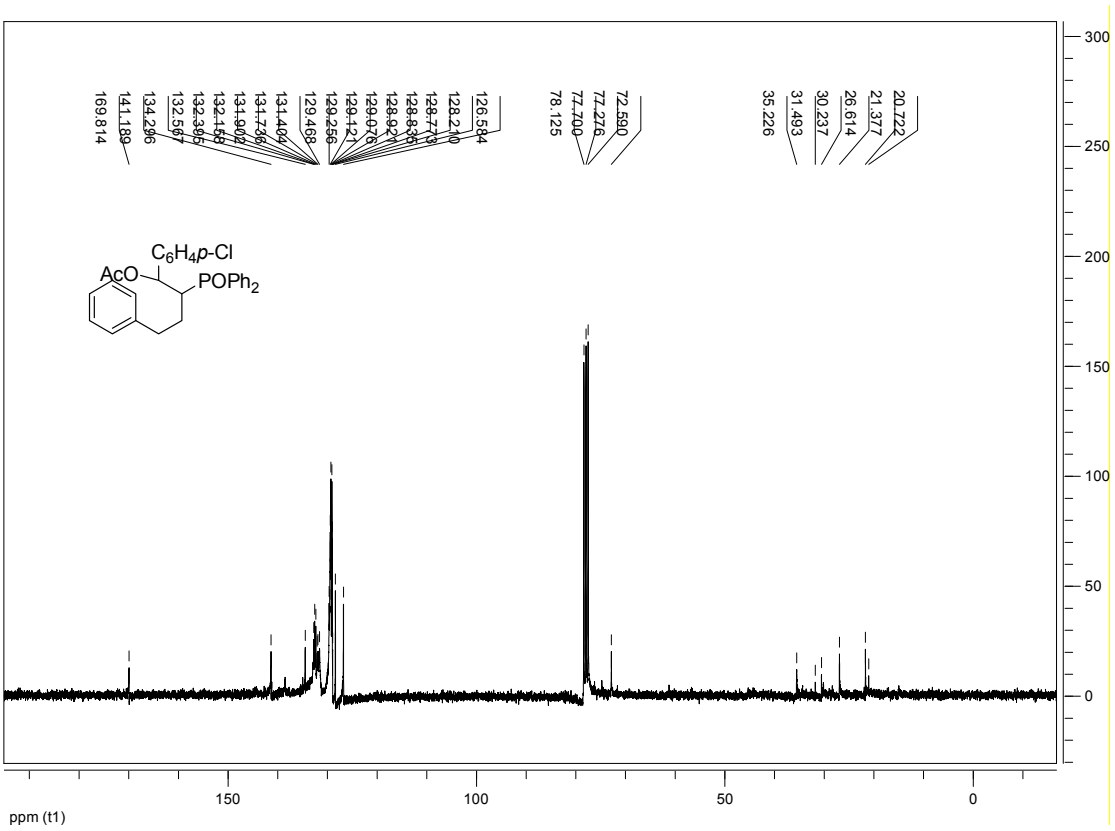

AcO
Ph
POPh2
10000
5000
0
150
100
50
0
ppm (f1)

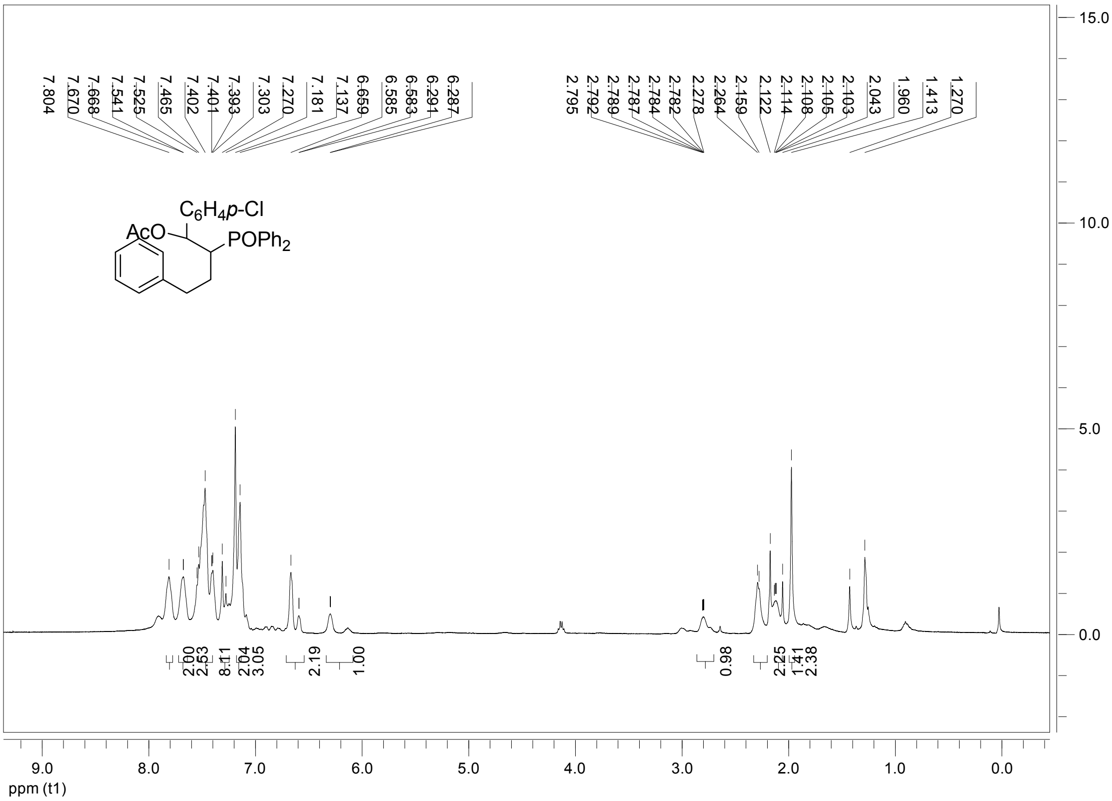

169.848
141.556
138.101
132.207
132.172
132.016
131.980
131.755
131.643
131.517
131.400
129.749
129.684
129.233
129.197
129.083
129.048
128.901
128.827
128.781
126.439
126.401
78.124
77.700
77.275
72.762
45.194
44.300
35.569
35.474
31.497
26.387
21.677
21.463
C6H4p-Me
AcO
POPh2
300
250
200
150
100
50
0
-50
200
150
100
50
0
ppm (t1)

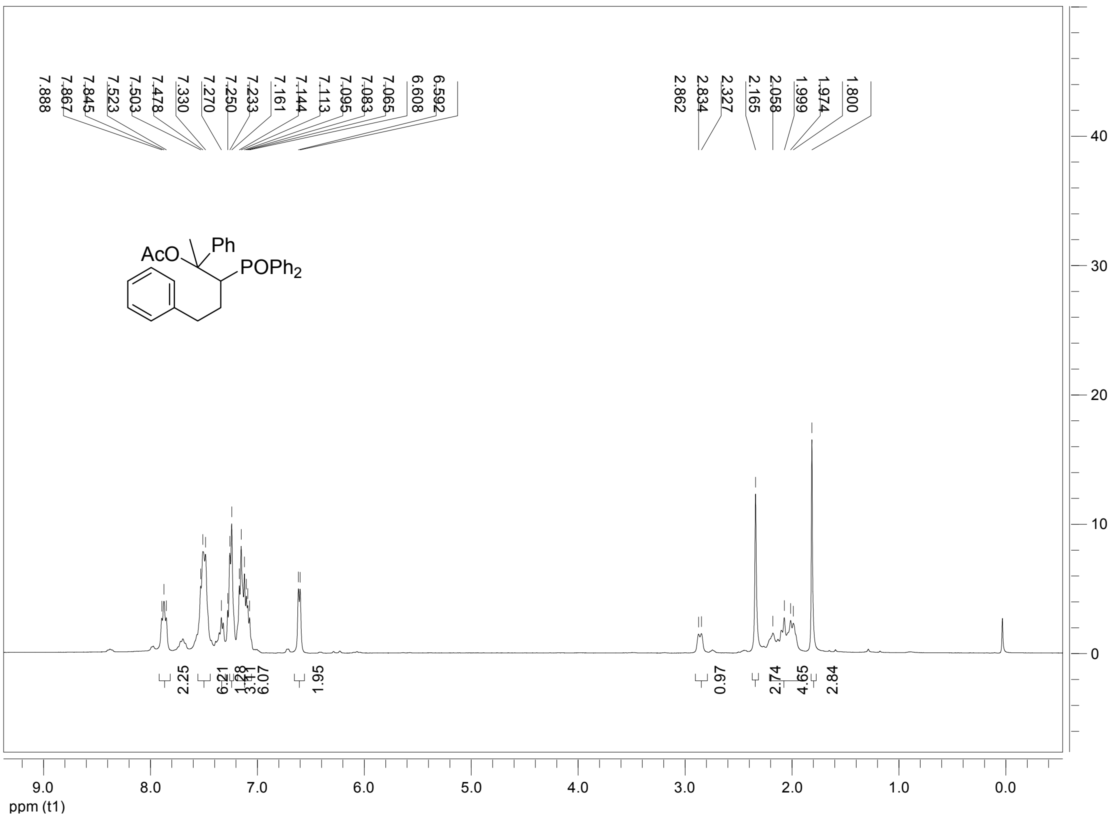

7.921
7.833
7.812
7.788
7.737
7.717
7.692
7.489
7.464
7.449
7.412
7.394
7.324
7.305
7.270
7.159
7.139
7.123
7.080
7.060
6.663
6.654
6.567
6.565
6.555
6.333
6.324
6.311
6.303
6.164
6.141
6.118
2.807
2.797
2.780
2.771
2.338
2.293
2.225
2.215
2.149
1.961
1.351
C6H4p-Me
AcO
POPh2
150
100
50
0
5.0
0.0
ppm (t1)

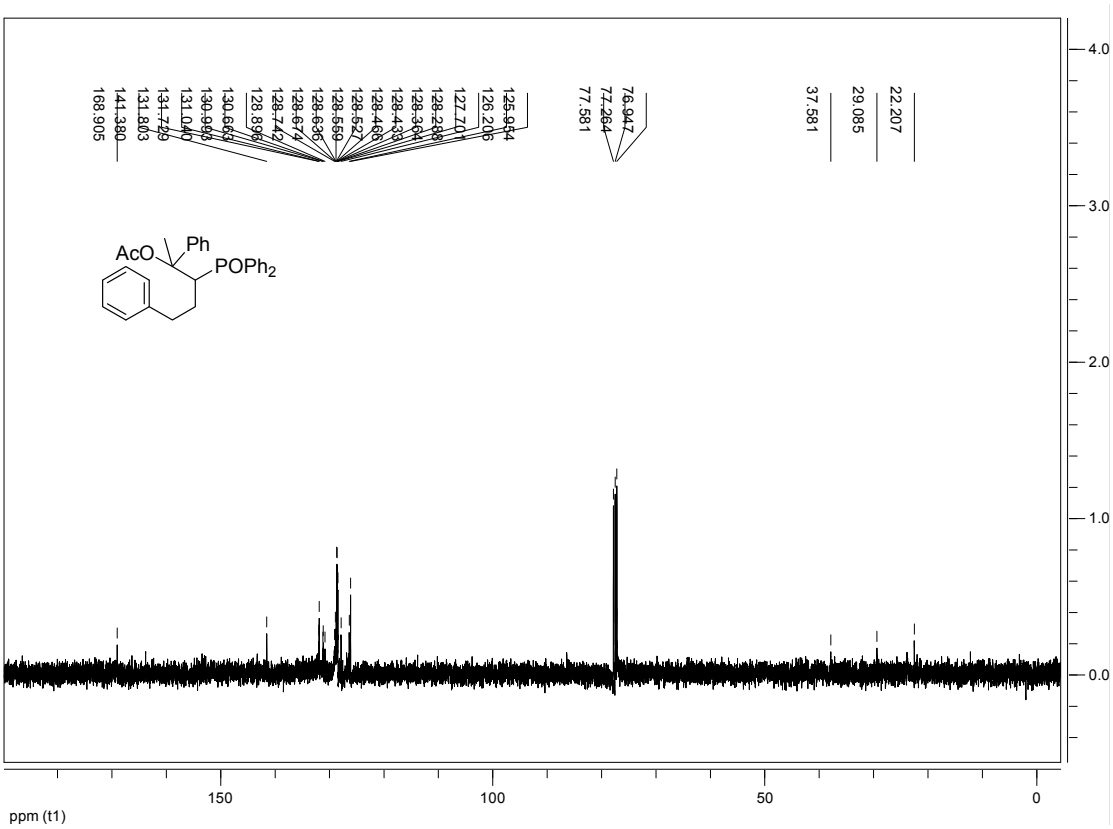
^{31}P NMR for 16b

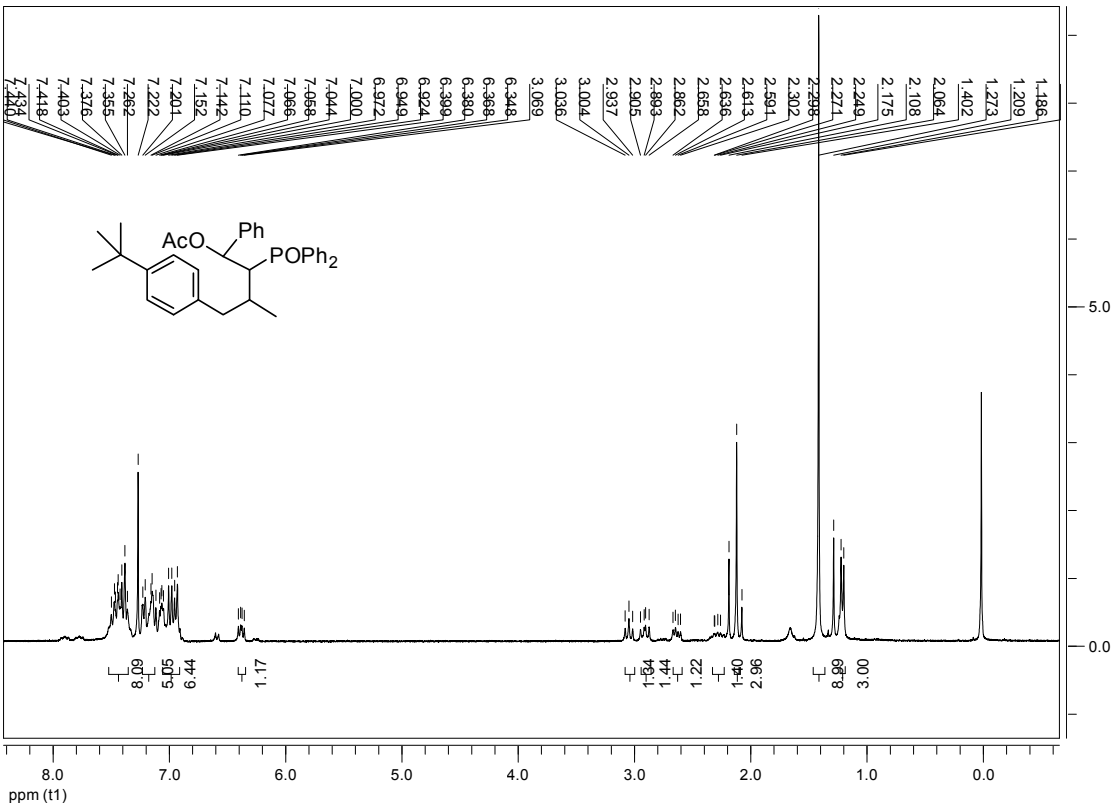


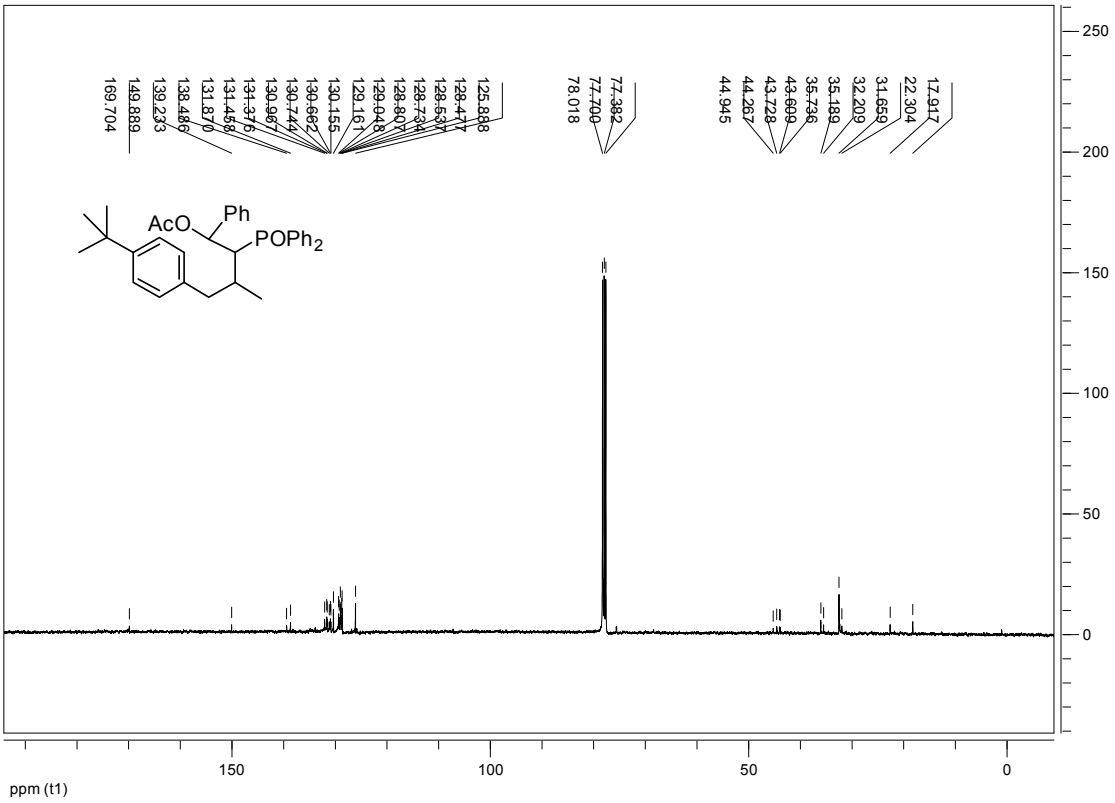



7.804 7.670 7.668 7.541 7.525 7.465 7.402 7.401 7.393 7.303 7.270 7.181 7.137 6.659 6.585 6.583 6.291 6.287
2.795 2.792 2.789 2.787 2.784 2.782 2.278 2.264 2.159 2.122 2.114 2.108 2.105 2.103 2.043 1.960 1.413 1.270
C6H4p-Cl
AcO
POPh2
2.00 2.53 8.11 2.04 3.05 2.19 1.00
0.98 2.25 1.41 2.38
15.0
10.0
5.0
0.0
9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0
ppm (t1)


7.888 7.867 7.845 7.523 7.503 7.478 7.330 7.270 7.250 7.233 7.161 7.144 7.113 7.095 7.083 7.065 6.608 6.592
2.862 2.834 2.327 2.165 2.058 1.999 1.974 1.800
AcO
Ph
POPh2
2.25 6.21 1.28 3.11 6.07 1.95
0.97 2.74 4.65 2.84
40
30
20
10
0
9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0
ppm (t1)

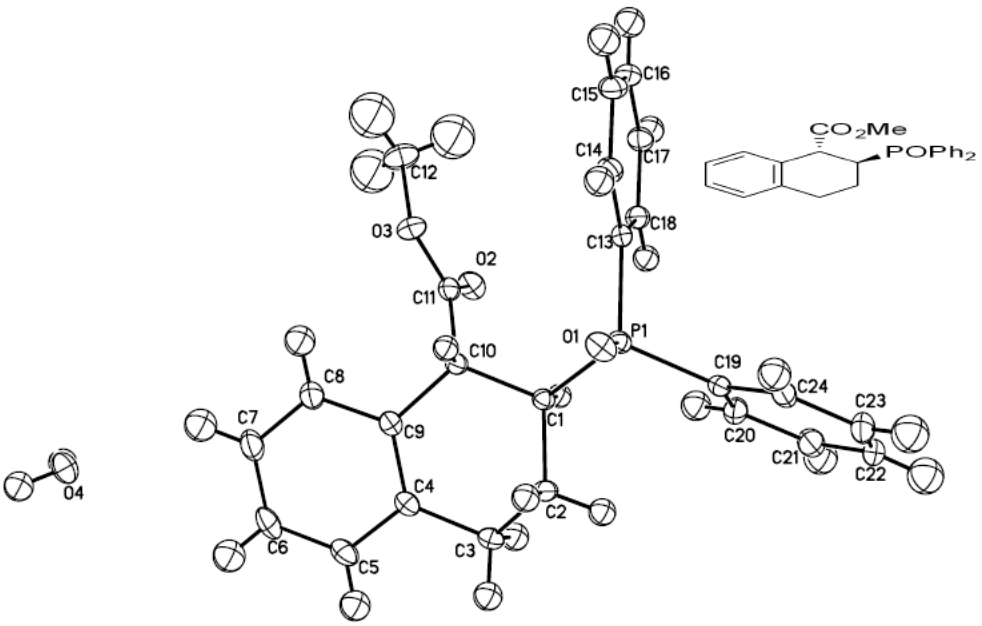

168.905
141.380
131.803
131.729
131.040
130.993
130.663
128.896
128.742
128.674
128.636
128.559
128.527
128.466
128.433
128.364
128.283
127.701
126.206
125.954
77.581
77.264
76.947
37.581
29.085
22.207
AcO
Ph
POPh2
4.0
3.0
2.0
1.0
0.0
150
100
50
0
ppm (t1)


7.434
7.418
7.403
7.376
7.355
7.262
7.222
7.201
7.152
7.142
7.110
7.077
7.066
7.058
7.044
7.000
6.972
6.949
6.924
6.399
6.380
6.368
6.348
3.069
3.036
3.004
2.937
2.905
2.893
2.862
2.658
2.636
2.613
2.591
2.302
2.298
2.271
2.249
2.175
2.108
2.064
1.402
1.273
1.209
1.186
AcO
Ph
POPh2
5.0
0.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)


169.704
149.889
139.233
138.486
131.870
131.458
131.376
130.967
130.744
130.662
130.155
129.161
129.048
128.807
128.734
128.537
128.417
125.888
78.018
77.700
77.382
44.945
44.267
43.728
43.609
35.736
35.189
32.209
31.659
22.304
17.917
AcO
Ph
POPh2
250
200
150
100
50
0
150
100
50
0
ppm (t1)

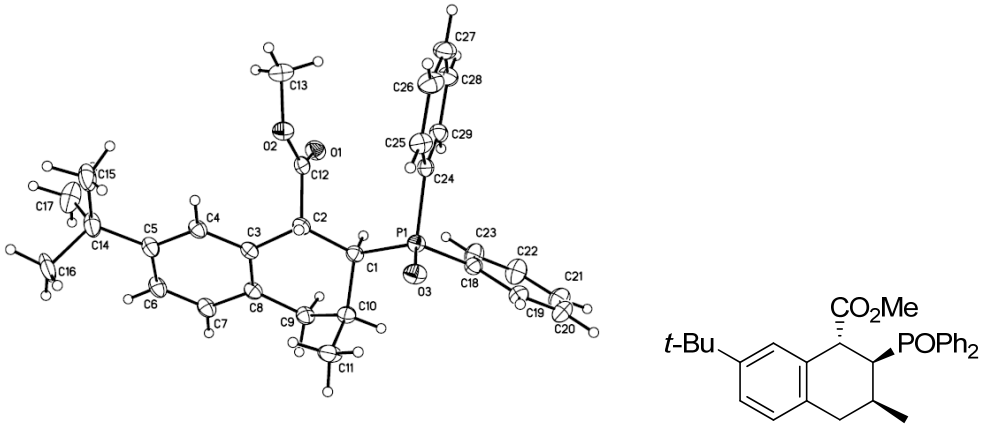
X-ray crystal structures

8a



$C_{24}H_{25}O_4P$, M = 408.41, triclinic, a = 8.735(3) Å, b = 11.975(4) Å, c = 12.478(5) Å, α = 61.480(5) °, β = 69.536(3)°, γ = 80.201(7)°, U = 1074.5(6) Å^3, T = 223(2) K, space group P -1, Z = 2, Dc = 1.262 g/cm^{-3}, Rigaku Saturn CCD diffractometer, μ(Mo-Kα) = 0.155 mm^{-1}, 9895 independent reflections (4850 observed), 270 parameters, R_{int} = 0.0379, R = 0.0465, wR(F2) = 0.0866, thermal ellipsoids probability level is 20%. CCDC 816923.

8d



$C_{29}H_{33}O_3P$, M = 460.52, monoclinic, a = 12.3944(14) Å, b = 15.6919(19) Å, c = 13.1793(16) Å, α = 90 °, β = 94.749(3)°, γ = 90°, U = 2554.5(5) Å^3, T = 223(2) K, space group P 21/n, Z = 4, Dc = 1.197 g/cm^{-3}, Rigaku Saturn CCD diffractometer, μ(Mo-Kα) = 0.135 mm^{-1}, 14357 independent reflections (5831 observed), 334 parameters, R_{int} = 0.0265, R = 0.0523, wR(F2) = 0.1312, thermal ellipsoids probability level is 25%. CCDC 824309.