

# Supporting Information for Manuscript

## Rhodium-Catalyzed Double [2+2+2] Cycloaddition of 1,4-Bis(diphenylphosphinoyl)buta-1,3-diyne with Tethered Diynes: A Modular, Highly Versatile Single-Pot Synthesis of NU-BIPHEP Biaryl Diphosphines

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**General Comments.** All manipulations involving air-sensitive materials were carried out using standard Schlenk line techniques under an atmosphere of nitrogen or argon in oven-dried glassware. Dichloromethane was distilled from calcium hydride and THF and toluene from sodium under an atmosphere of nitrogen. 1,6-heptadiyne, 1,7-octadiyne, bispropargylether, ethyl trifluoropyruvate, allylbenzene, acetophenone, 1-acetylnaphthylene, silver tetrafluoroborate, silver hexafluoroantimonate, (*S,S*)-1,2-diphenylethylenediamine and *rac*-BINAP were purchased from commercial suppliers and used without further purification.  $[\text{RhCl}(\text{COD})]_2$ ,<sup>1</sup>  $[(\text{cycloocta-1,5-diene})\text{PtCl}_2]$ ,<sup>2</sup>  $[\text{RuCl}_2(\text{nbd})(\text{py})_2]$ ,<sup>3</sup> *N*-acryloyl oxazolidinone,<sup>4</sup> diprop-2-ynyl-malonic acid dimethyl ester,<sup>5</sup> *N,N*-diprop-2-ynyl-toluenesulfonamide<sup>6</sup> and allylbenzene derivatives<sup>7</sup> were prepared as previously described.  $^1\text{H}$  and  $^{13}\text{C}\{\text{H}\}$  NMR spectra were recorded on a JEOL LAMBDA 500 or a Bruker AMX 300 instrument. Optical rotations were measured on a Optical Activity PolAAr 2001 digital polarimeter with a sodium lamp and are reported as follows:  $[\alpha]_D^{20}$  (*c* g/100 mL, solvent). Thin-layer chromatography (TLC) was carried out on aluminum sheets pre-coated with silica gel 60F 254 and column chromatography was performed using Merck Kieselgel 60. Gas chromatography was performed on a Shimadzu 2010 series gas chromatograph equipped with a split-mode capillary injection system and flame ionization detection using a Supelco Beta DEX column. Analytical high performance liquid chromatography (HPLC) was performed on an Agilent 110 Series HPLC equipped with a variable wavelength detector using a Daicel Chiralcel OD-H column. Enantiomeric excesses were calculated from the HPLC and GC profiles.

### Synthesis of 1,4-bis(diphenylphosphinoyl)buta-1,3-diyne (2)

1,4-Bis(diphenylphosphino)buta-1,3-diyne (2.70 g, 6.46 mmol) was dissolved in chloroform (100 mL) hydrogen peroxide (35% aq. solution, 2.8 mL, 29.1 mmol) added dropwise and the resulting mixture refluxed for 30 min. The solution was allowed to cool, washed with water (6 x 30 mL) and the organic layer dried over  $\text{MgSO}_4$ , filtered and the solvent removed *in vacuo* to yield the product as a spectroscopically pure beige powder (2.85 g,

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<sup>3</sup> Akotsi, O. M.; Metera, K.; Reid, R. D.; McDonald, R.; Bergens, S. H. *Chirality* **2000**, 12, 514.

<sup>4</sup> Evans, D. A.; Miller, S.; Lectka, T.; von Matt, P. *J. Am. Chem. Soc.* **1999**, 121, 7559.

<sup>5</sup> Llerena, D.; Buisine, O.; Aubert, C.; Malacria, A. *Tetrahedron* **1998**, 54, 9373.

<sup>6</sup> Greau, S.; Radetich, B.; RajanBabu, T. V. *J. Am. Chem. Soc.* **2000**, 122, 5879.

<sup>7</sup> Doherty, S.; Knight, J. G.; Smyth, C. H.; Harrington, R. W.; Clegg, W. *Organometallics* **2007**, 26, in the press.

98%).  $^{31}\text{P}\{\text{H}\}$  NMR (202.5 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 9.8;  $^1\text{H}$  NMR (500.0 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 7.77 (dd,  $J$  = 14.1, 7.1 Hz, 8H,  $\text{C}_6\text{H}_5$  *o*-H), 7.56 (dt,  $J$  = 7.3, 1.3 Hz, 4H,  $\text{C}_6\text{H}_5$  *p*-H), 7.47 (dt,  $J$  = 7.5, 3.4 Hz, 4H,  $\text{C}_6\text{H}_5$  *m*-H);  $^{13}\text{C}\{\text{H}\}$  NMR (125.8 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 132.9 (d,  $J$  = 10.1 Hz,  $\text{C}_6\text{H}_5$  *p*-C), 130.9 (d,  $J$  = 123 Hz, *Q*), 130.9 (d,  $J$  = 11.6 Hz,  $\text{C}_6\text{H}_5$  *o*-C), 128.8 (d,  $J$  = 14.0 Hz,  $\text{C}_6\text{H}_5$  *m*-C), 85.4 (dd,  $J$  = 28, 6.4 Hz,  $\text{C}\equiv\text{CP}$ ), 78.9 (dd,  $J$  = 150, 2.1 Hz,  $\text{C}\equiv\text{CP}$ ).

### A Typical Procedure for the Rhodium-Catalyzed [2+2+2] Cycloadditions

Synthesis of 3,3'-bis(diphenylphosphinoyl)-5,6,7,8,5',6',7',8'-octahydro[2,2']binaphthalene (**3a**) as a representative example. A flame-dried Schlenk flask was charged with  $[\text{RhCl}(\text{COD})]_2$  (0.037 g, 0.075 mmol),  $\text{AgBF}_4$  (0.029 g, 0.15 mmol), *rac*-BINAP (0.093 g, 0.15 mmol) and  $\text{CH}_2\text{Cl}_2$  (25 mL). 1,4-Bis(diphenylphosphinoyl)buta-1,3-diyne (0.675 g, 1.5 mmol) and 1,7-octadiyne (0.48 mL, 3.6 mmol) were added and the resulting solution stirred at room temperature for 16 hr. After this time, diethyl ether (40 mL) was added followed by water (40 mL). The organic layer was removed and the aqueous phase extracted with diethyl ether (2 x 30 mL). The organic phases were combined, dried over  $\text{MgSO}_4$ , filtered and the solvent removed *in vacuo* to leave a crude brown solid which was purified by column chromatography eluting with ethyl acetate/acetone (2:1) to yield the product as an off-white solid (0.944 g, 95%).  $^{31}\text{P}\{\text{H}\}$  NMR (202.5 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 28.4;  $^1\text{H}$  NMR (500.0 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 7.73 (dd,  $J$  = 11.4, 7.5 Hz, 4H,  $\text{C}_6\text{H}_5$  *o*-H), 7.64 (dd,  $J$  = 11.6, 7.4 Hz, 4H,  $\text{C}_6\text{H}_5$  *o*-H) 7.48 (m, 2H,  $\text{C}_6\text{H}_5$  *p*-H), 7.43 (m, 4H,  $\text{C}_6\text{H}_5$  *m*-H), 7.29-7.23 (m, 6H,  $\text{C}_6\text{H}_5$  *m/p*-H), 6.83 (d,  $J$  = 14.4 Hz, 2H,  $\text{C}_6\text{H}_2$  H3), 6.66 (d,  $J$  = 4.4 Hz, 2H,  $\text{C}_6\text{H}_2$  H6), 2.54-2.42 (m, 4H,  $\text{C}_4\text{H}_8$ ), 2.39-2.34 (m, 4H,  $\text{C}_4\text{H}_8$ ), 1.66 (br s, 8H,  $\text{C}_4\text{H}_8$ );  $^{13}\text{C}\{\text{H}\}$  NMR (75.5 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 141.3 (d,  $J$  = 13.4 Hz, *Q*), 140.1 (*Q*), 135.7 (d,  $J$  = 12.5 Hz, *Q*), 135.4 (d,  $J$  = 104 Hz, *Q*), 134.7 (d,  $J$  = 13.4 Hz,  $\text{C}_6\text{H}_2$  C3), 133.9 (d,  $J$  = 104 Hz, *Q*), 133.7 (d,  $J$  = 11.5 Hz,  $\text{C}_6\text{H}_2$  C6), 132.1 (d,  $J$  = 10.6 Hz,  $\text{C}_6\text{H}_5$  *o*-C), 131.9 (d,  $J$  = 10.6 Hz,  $\text{C}_6\text{H}_5$  *o*-C), 131.2 ( $\text{C}_6\text{H}_5$  *p*-C), 130.6 ( $\text{C}_6\text{H}_5$  *p*-C), 128.3 (d,  $J$  = 12.5 Hz,  $\text{C}_6\text{H}_5$  *m*-C), 127.8 (d,  $J$  = 103 Hz, *Q*), 127.7 (d,  $J$  = 12.5 Hz,  $\text{C}_6\text{H}_5$  *m*-C), 29.1 ( $\text{C}_4\text{H}_8$ ), 29.0 ( $\text{C}_4\text{H}_8$ ), 23.0 ( $\text{C}_4\text{H}_8$ ), 22.7 ( $\text{C}_4\text{H}_8$ ); LRMS (ESI $^+$ )  $m/z$  663 [ $\text{M}+\text{H}]^+$ ; HRMS (ESI $^+$ ) exact mass calcd for  $\text{C}_{44}\text{H}_{41}\text{P}_2\text{O}_2$  [ $\text{M}+\text{H}]^+$  requires  $m/z$  663.2582, found  $m/z$  663.2560. Anal. Calcd for  $\text{C}_{44}\text{H}_{40}\text{O}_2\text{P}_2$ : C, 79.74; H, 6.08. Found: C, 79.91; H, 6.12.

### Synthesis of 6,6'-bis(diphenylphosphinoyl)-2,3,2',3'-tetrahydro-1*H*,1'*H*-[5,5']biindene (3b)

Compound **3b** was prepared according to the procedure described above for **3a** on the same scale and isolated as an analytically and spectroscopically pure off-white solid in 93% yield (0.884 g) after purification by column chromatography.  $^{31}\text{P}\{\text{H}\}$  NMR (202.5 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 28.7;  $^1\text{H}$  NMR (500.0 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 7.75 (dd,  $J$  = 11.5, 7.0 Hz, 4H,  $\text{C}_6\text{H}_5$  *o*-H), 7.68 (dd,  $J$  = 11.8, 6.8 Hz, 4H,  $\text{C}_6\text{H}_5$  *o*-H), 7.49-7.41 (m, 6H,  $\text{C}_6\text{H}_5$  *m/p*-H), 7.29-7.22 (m, 6H,  $\text{C}_6\text{H}_5$  *m/p*-H), 6.98 (d,  $J$  = 13.9 Hz, 2H,  $\text{C}_6\text{H}_2$  H3), 6.79 (d,  $J$  = 3.9 Hz, 2H,  $\text{C}_6\text{H}_2$  H6), 2.68 (m, 4H,  $\text{C}_4\text{H}_8$ ), 2.56 (m, 4H,  $\text{C}_3\text{H}_6$ ), 1.98-1.90 (m, 4H,  $\text{C}_3\text{H}_6$ );  $^{13}\text{C}\{\text{H}\}$  NMR (125.8 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 147.2 (*Q*), 143.1 (m, *Q*), 142.8 (d,  $J$  = 13.4 Hz, *Q*), 135.6 (d,  $J$  = 103 Hz, *Q*), 134.0 (d,  $J$  = 103 Hz, *Q*), 132.2 (d,  $J$  = 9.6 Hz,  $\text{C}_6\text{H}_5$  *o*-C), 131.9 (d,  $J$  = 9.4 Hz,  $\text{C}_6\text{H}_5$  *o*-C), 131.1 ( $\text{C}_6\text{H}_5$  *p*-C), 130.5 ( $\text{C}_6\text{H}_5$  *p*-C), 129.5 (d,  $J$  = 12.6 Hz,  $\text{C}_6\text{H}_2$  C3), 129.1 (d,  $J$  = 11.0 Hz,  $\text{C}_6\text{H}_2$  C6), 128.9 (d,  $J$  = 104 Hz, *Q*), 128.3 (d,  $J$  = 12.0 Hz,  $\text{C}_6\text{H}_5$  *m*-C), 127.7 (d,  $J$  = 12.1 Hz,  $\text{C}_6\text{H}_5$  *m*-C), 32.7 ( $\text{C}_3\text{H}_6$ ), 32.4 ( $\text{C}_3\text{H}_6$ ), 25.0 ( $\text{C}_3\text{H}_6$ ); LRMS (ESI $^+$ )  $m/z$  635 [M+H] $^+$ ; HRMS (ESI $^+$ ) exact mass calcd for  $\text{C}_{42}\text{H}_{37}\text{P}_2\text{O}_2$  [M+H] $^+$  requires  $m/z$  635.2269, found  $m/z$  635.2243. Anal. Calcd for  $\text{C}_{42}\text{H}_{36}\text{O}_2\text{P}_2$ : C, 79.48; H, 5.72. Found: C, 79.77; H, 6.01.

### Synthesis of 6,6'-bis(diphenylphosphinoyl)-1,3,1',3'-tetrahydro[5,5']biisobenzofuran (3c)

Compound **3c** was prepared according to the procedure described above for **3a**, on the same scale, and isolated as an off-white solid in 90% yield (0.861 g) after purification by column chromatography.  $^{31}\text{P}\{\text{H}\}$  NMR (202.5 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 28.6;  $^1\text{H}$  NMR (500.0 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 7.73-7.67 (m, 8H,  $\text{C}_6\text{H}_5$  *o*-H), 7.50 (m, 2H,  $\text{C}_6\text{H}_5$  *p*-H), 7.45 (m, 4H,  $\text{C}_6\text{H}_5$  *m*-H), 7.35-7.28 (m, 6H,  $\text{C}_6\text{H}_5$  *m/p*-H), 6.99 (d,  $J$  = 13.7 Hz, 2H,  $\text{C}_6\text{H}_2$  H3), 6.81 (d,  $J$  = 13.7 Hz, 2H,  $\text{C}_6\text{H}_2$  H6), 4.95 (AB,  $J_{\text{AB}}$  = 12.9 Hz, 2H,  $\text{CH}_2$ ), 4.89 (AB,  $J_{\text{AB}}$  = 12.9 Hz, 2H,  $\text{CH}_2$ ), 4.85 (AB,  $J_{\text{AB}}$  = 13.9 Hz, 2H,  $\text{CH}_2$ ), 4.79 (AB,  $J_{\text{AB}}$  = 13.9 Hz, 2H,  $\text{CH}_2$ );  $^{13}\text{C}\{\text{H}\}$  NMR (125.8 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 143.6 (m, *Q*), 141.9 (d,  $J$  = 2.5 Hz, *Q*), 138.1 (d,  $J$  = 13.7 Hz, *Q*), 134.5 (d,  $J$  = 103 Hz, *Q*), 132.9 (d,  $J$  = 104 Hz, *Q*), 132.1 (d,  $J$  = 9.7 Hz,  $\text{C}_6\text{H}_5$  *o*-C), 131.6 (d,  $J$  = 9.4 Hz,  $\text{C}_6\text{H}_5$  *o*-C), 131.4 (d,  $J$  = 2.7 Hz,  $\text{C}_6\text{H}_5$  *p*-C), 131.0 (d,  $J$  = 103 Hz, *Q*), 130.9 (d,  $J$  = 2.7 Hz,  $\text{C}_6\text{H}_5$  *p*-C), 128.4 (d,  $J$  = 12.0 Hz,  $\text{C}_6\text{H}_5$  *m*-C), 127.9 (d,  $J$  = 12.3 Hz,  $\text{C}_6\text{H}_5$  *m*-C), 125.9 (d,  $J$  = 13.4 Hz,  $\text{C}_6\text{H}_2$  C3), 125.4 (d,  $J$  = 10.5 Hz,  $\text{C}_6\text{H}_2$  C6), 73.3 ( $\text{CH}_2$ ), 73.2 ( $\text{CH}_2$ ); LRMS (ESI $^+$ )  $m/z$  639 [M+H] $^+$ ; HRMS (ESI $^+$ ) exact mass calcd for  $\text{C}_{40}\text{H}_{33}\text{P}_2\text{O}_4$  [M+H] $^+$  requires  $m/z$  639.1854, found  $m/z$  639.1828. Anal. Calcd for  $\text{C}_{40}\text{H}_{32}\text{O}_4\text{P}_2$ : C, 75.23; H, 5.05. Found: C, 75.44; H, 5.23.

## Synthesis of 6,6-bis(diphenylphosphinoyl)-1,3,1',3'-tetrahydro[5,5']biindenyl-2,2,2',2'-tetracarboxylate (3d)

Compound **3c** was prepared according to the procedure described above for **3a**, on the same scale, and isolated as an off-white solid in 96% yield (1.25 g) after purification by column chromatography.  $^{31}\text{P}\{\text{H}\}$  NMR (202.5 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 28.3;  $^1\text{H}$  NMR (500.0 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 7.69 (dd,  $J = 11.6, 7.2$  Hz, 4H,  $\text{C}_6\text{H}_5$  *o*-H), 7.62 (dd,  $J = 11.8, 7.1$  Hz, 4H,  $\text{C}_6\text{H}_5$  *o*-H), 7.49 (m, 2H,  $\text{C}_6\text{H}_5$  *p*-H), 7.44 (m, 4H,  $\text{C}_6\text{H}_5$  *m*-H), 7.29 (m, 2H  $\text{C}_6\text{H}_5$  *p*-H), 7.25 (m, 4H,  $\text{C}_6\text{H}_5$  *m*-H), 6.93 (d,  $J = 13.8$  Hz, 2H,  $\text{C}_6\text{H}_2$  H3), 6.70 (d,  $J = 3.6$  Hz, 2H,  $\text{C}_6\text{H}_2$  H6), 3.77 (s, 6H,  $\text{CH}_3$ ), 3.68 (s, 6H,  $\text{CH}_3$ ), 3.43 (AB,  $J_{\text{AB}} = 16.8$  Hz, 2H,  $\text{CH}_2$ ), 3.37 (AB,  $J_{\text{AB}} = 16.8$  Hz, 2H,  $\text{CH}_2$ ), 3.31 (AB,  $J_{\text{AB}} = 17.4$  Hz, 2H,  $\text{CH}_2$ ), 3.27 (AB,  $J_{\text{AB}} = 17.4$  Hz, 2H,  $\text{CH}_2$ );  $^{13}\text{C}\{\text{H}\}$  NMR (125.8 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 171.8 ( $\text{C}=\text{O}$ ), 171.5 ( $\text{C}=\text{O}$ ), 143.4 (m,  $Q$ ), 142.9 ( $Q$ ), 138.8 (d,  $J = 13.4$  Hz,  $Q$ ), 134.8 (d,  $J = 103$  Hz,  $Q$ ), 133.2 (d,  $J = 103$  Hz,  $Q$ ), 132.2 (d,  $J = 9.5$  Hz,  $\text{C}_6\text{H}_5$  *o*-C), 131.8 (d,  $J = 8.6$  Hz,  $\text{C}_6\text{H}_5$  *o*-C), 131.4 ( $\text{C}_6\text{H}_5$  *p*-C), 130.8 ( $\text{C}_6\text{H}_5$  *p*-C), 130.5 (d,  $J = 103$  Hz,  $Q$ ), 129.3 (d,  $J = 12.4$  Hz,  $\text{C}_6\text{H}_2$  C3), 128.9 (d,  $J = 10.5$  Hz,  $\text{C}_6\text{H}_2$  C6), 128.5 (d,  $J = 11.5$  Hz,  $\text{C}_6\text{H}_5$  *m*-C), 127.9 (d,  $J = 12.4$  Hz,  $\text{C}_6\text{H}_5$  *m*-C), 60.0 ( $\text{C}_3\text{H}_4$   $Q$ ), 53.1 (2 x  $\text{CH}_3$ ), 40.6 ( $\text{CH}_2$ ), 40.4 ( $\text{CH}_2$ ); LRMS (ESI $^+$ )  $m/z$  867 [ $\text{M}+\text{H}]^+$ ; HRMS (ESI $^+$ ) exact mass calcd for  $\text{C}_{50}\text{H}_{45}\text{P}_2\text{O}_{10}$  [ $\text{M}+\text{H}]^+$  requires  $m/z$  867.2488, found  $m/z$  867.2484. Anal. Calcd for  $\text{C}_{50}\text{H}_{44}\text{O}_{10}\text{P}_2$ : C, 69.28; H, 5.12. Found: C, 69.46; H, 5.19.

## Synthesis of 6,6'-bis(diphenylphosphinoyl)-2,2'-bis(4-methyl)benzenesulfonyl)-2,3,2',3'-tetrahydro-1*H*,1'*H*-[5,5']biisoindole (3e)

A flame-dried Schlenk flask was charged with  $[\text{RhCl}(\text{COD})]_2$  (0.037 g, 0.075 mmol),  $\text{AgBF}_4$  (0.029 g, 0.15 mmol), *rac*-BINAP (0.093 g, 0.15 mmol), 1,4-bis(diphenylphosphinoyl)buta-1,3-diyne (0.675 g, 1.5 mmol) and  $\text{CH}_2\text{Cl}_2$  (25 mL). A solution of *N,N*-diprop-2-ynyl-toluenesulfonamide (0.889 g, 3.6 mmol) in dichloromethane (20 mL) was added over 6 hrs using a syringe pump. The resulting mixture was stirred for a further 12 h after which time diethyl ether (40 mL) was added followed by water (40 mL). The organic layer was removed and the aqueous phase extracted with diethyl ether (2 x 30 mL). The organic phases were combined, dried over  $\text{MgSO}_4$ , filtered and the solvent removed *in vacuo* to leave a crude brown solid which was purified by column chromatography eluting with ethyl acetate/acetone (5:1) to yield the product as an off-white solid in 93% yield (1.39 g).  $^{31}\text{P}\{\text{H}\}$  NMR (202.5 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 27.8;  $^1\text{H}$  NMR (500.0 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 7.72 (d,  $J = 8.2$  Hz, 4H,

$C_6H_4$ ), 7.63-7.51 (m, 10H,  $C_6H_5$  *o/p*-H), 7.44-7.41 (m, 4H,  $C_6H_5$  *m*-H), 7.35 (d,  $J$  = 8.1 Hz, 4H,  $C_6H_4$ ), 7.21-7.19 (m, 2H,  $C_6H_5$  *p*-H), 7.09-7.05 (m, 4H,  $C_6H_5$  *m*-H), 6.86 (d,  $J$  = 13.7 Hz, 2H,  $C_6H_2$  H3), 6.65 (d,  $J$  = 3.3 Hz, 2H,  $C_6H_2$  H6), 4.47 (AB,  $J_{AB}$  = 13.3 Hz, 2H,  $CH_2$ ), 4.38 (AB,  $J_{AB}$  = 14.2 Hz, 2H,  $CH_2$ ), 4.31 (AB,  $J_{AB}$  = 13.3 Hz, 2H,  $CH_2$ ), 4.20 (AB,  $J_{AB}$  = 14.2 Hz, 2H,  $CH_2$ ), 2.41 (s, 6H,  $C_6H_4CH_3$ );  $^{13}C\{^1H\}$  NMR (125.8 MHz,  $CDCl_3$ ,  $\delta$ ): 144.1 ( $Q$ ), 143.5 (m,  $Q$ ), 138.9 (m,  $Q$ ), 135.4 (d,  $J$  = 13.9 Hz,  $Q$ ), 134.3 (d,  $J$  = 104 Hz,  $Q$ ), 133.5 ( $Q$ ), 132.6 (d,  $J$  = 104 Hz,  $Q$ ), 132.1 (d,  $J$  = 9.7 Hz,  $C_6H_5$  *o*-C), 131.9 (d,  $J$  = 103 Hz,  $Q$ ), 131.8 ( $C_6H_5$  *p*-C), 131.6 (d,  $J$  = 9.4 Hz,  $C_6H_5$  *o*-C), 131.1, ( $C_6H_5$  *p*-C), 130.0 ( $C_6H_4$ ), 128.6 (d,  $J$  = 12.0 Hz,  $C_6H_5$  *m*-C), 127.9 (d,  $J$  = 12.1 Hz,  $C_6H_5$  *m*-C), 127.7 ( $C_6H_4$ ), 127.6 (d,  $J$  = 13.3 Hz,  $C_6H_2$  C3), 126.8 (d,  $J$  = 10.5 Hz,  $C_6H_2$  C6), 53.6 ( $CH_2$ ), 53.5 ( $CH_2$ ), 21.6 ( $CH_3$ ); LRMS (ESI $^+$ )  $m/z$  945 [M+H] $^+$ ; HRMS (ESI $^+$ ) exact mass calcd for  $C_{54}H_{47}N_2P_2O_6S_2$  [M+H] $^+$  requires  $m/z$  945.2351, found  $m/z$  945.2314. Anal. Calcd for  $C_{54}H_{46}N_2O_6P_2S_2$ : C, 68.63; H, 4.91; N, 2.96. Found: C, 68.79; H, 5.11; N, 3.12.

### General Procedure for Reduction of Phosphine Oxides **3a-e**

Reduction of 3,3'-bis(diphenylphosphanyl)-5,6,7,8,5',6',7',8'-octahydro[2,2']binaphthalene (**3a**) as a representative example. A flame-dried Schlenk flask was charged with phosphine oxide **3a** (0.95 g, 1.44 mmol), THF (15 mL), toluene (15 mL) and triethylphosphite (2.5 mL, 14.4 mmol). Trichlorosilane (4.4 mL, 43.1 mmol) was added dropwise and the mixture was heated at 100 °C for 48 hr. After this time, the mixture was diluted with diethyl ether (40 mL), cooled to 0 °C and 20% aq NaOH (60 mL) was added slowly. After heating at 60 °C for 1hr, with vigorous stirring, the mixture was cooled to room temperature, filtered through celite, the organic layer removed and the aqueous phase extracted with diethyl ether (3 x 30 mL). The organic fractions were combined, dried over  $MgSO_4$ , filtered and the solvent removed *in vacuo* to afford **4a** as a spectroscopically pure white solid in 95% yield (0.642 g). X-ray quality crystals of **4a** were obtained by slow diffusion of a chloroform solution layered with methanol.  $M_p$  = 254-259 °C.  $^{31}P\{^1H\}$  NMR (202.5 MHz,  $CDCl_3$ ,  $\delta$ ): -14.3;  $^1H$  NMR (500.0 MHz,  $CDCl_3$ ,  $\delta$ ): 7.31 (m, 10H,  $C_6H_5$ ), 7.25-7.22 (m, 10H,  $C_6H_5$ ), 6.78 (br s, 2H,  $C_6H_2$  H6), 6.54 (br s, 2H,  $C_6H_2$  H3), 2.62 (br m, 4H,  $C_4H_8$ ), 2.51 (AB t,  $J_{AB}$  = 17.3,  $J$  = 6.0 Hz, 2H,  $C_4H_8$ ), 2.40 (AB t,  $J_{AB}$  = 17.3,  $J$  = 5.8 Hz, 2H,  $C_4H_8$ ), 1.76-1.68 (m, 8H,  $C_4H_8$ );  $^{13}C\{^1H\}$  NMR (125.8 MHz,  $CDCl_3$ ,  $\delta$ ): 144.5 (m,  $Q$ ), 138.7 (m,  $Q$ ), 138.2 (m,  $Q$ ), 137.0 ( $Q$ ), 136.2 ( $Q$ ), 134.4 (m,  $C_6H_2$  C6), 134.1 (m,  $C_6H_5$  *o*-C), 133.5 (m,  $C_6H_5$  *o*-C), 132.9 (m,

*Q*), 131.9 (m, C<sub>6</sub>H<sub>2</sub> C3), 128.2 (C<sub>6</sub>H<sub>5</sub>), 128.1 (m, 2 x C<sub>6</sub>H<sub>5</sub>), 127.7 (C<sub>6</sub>H<sub>5</sub>), 29.1 (C<sub>4</sub>H<sub>8</sub>), 28.9 (C<sub>4</sub>H<sub>8</sub>), 23.1 (C<sub>4</sub>H<sub>8</sub>), 23.0 (C<sub>4</sub>H<sub>8</sub>); LRMS (ESI<sup>+</sup>) *m/z* 631 [M+H]<sup>+</sup>; HRMS (ESI<sup>+</sup>) exact mass calcd for C<sub>44</sub>H<sub>41</sub>P<sub>2</sub> [M+H]<sup>+</sup> requires *m/z* 631.2684, found *m/z* 631.2670. Anal. Calcd for C<sub>44</sub>H<sub>40</sub>P<sub>2</sub>: C, 83.79; H, 6.39. Found: C, 84.08; H, 6.66.

### Synthesis of 6,6'-bis(diphenylphosphanyl)-2,3,2',3'-tetrahydro-1*H*,1'*H*-[5,5']biindene (4b)

Compound **4b** was prepared according to the procedure described above for **4a** on the same scale and isolated as an off-white solid in 87% yield (0.754 g) after purification by column chromatography. An analytically and spectroscopically pure sample was obtained by slow diffusion of a chloroform solution layered with methanol at room temperature. <sup>31</sup>P{<sup>1</sup>H} NMR (202.5 MHz, CDCl<sub>3</sub>,  $\delta$ ): -13.5; <sup>1</sup>H NMR (500.0 MHz, CDCl<sub>3</sub>,  $\delta$ ): 7.31-7.23 (m, 20H, C<sub>6</sub>H<sub>5</sub>), 6.97 (br s, 2H, C<sub>6</sub>H<sub>2</sub> H6), 6.71 (br s, 2H, C<sub>6</sub>H<sub>2</sub> H3), 2.82 (t, *J* = 7.4 Hz, 4H, C<sub>3</sub>H<sub>6</sub>), 2.74 (AB t, *J*<sub>AB</sub> = 16.2 Hz, *J* = 7.5 Hz, 2H, CH<sub>2</sub>), 2.67 (AB, *J*<sub>AB</sub> = 16.0 Hz, *J* = 7.5 Hz, 2H, CH<sub>2</sub>) 2.05-1.99 (m, 4H, C<sub>3</sub>H<sub>6</sub>); <sup>13</sup>C{<sup>1</sup>H} NMR (125.8 MHz, CDCl<sub>3</sub>,  $\delta$ ): 146.0 (m, *Q*), 144.4 (*Q*), 143.4 (*Q*), 138.7 (m, *Q*), 138.3 (m, *Q*), 134.1 (m, C<sub>6</sub>H<sub>5</sub> *o*-C), 133.7 (m, *Q*), 133.5 (m, C<sub>6</sub>H<sub>5</sub> *o*-C), 129.5 (m, C<sub>6</sub>H<sub>2</sub> C6), 128.1 (m, 3x C<sub>6</sub>H<sub>5</sub>), 127.7 (C<sub>6</sub>H<sub>5</sub>), 127.2 (m, C<sub>6</sub>H<sub>2</sub> C3), 32.8 (C<sub>3</sub>H<sub>6</sub>), 32.7 (C<sub>3</sub>H<sub>6</sub>), 25.3 (C<sub>3</sub>H<sub>6</sub>); LRMS (ESI<sup>+</sup>) *m/z* 603 [M+H]<sup>+</sup>; HRMS (ESI<sup>+</sup>) exact mass calcd for C<sub>42</sub>H<sub>37</sub>P<sub>2</sub> [M+H]<sup>+</sup> requires *m/z* 603.2371, found *m/z* 603.2382. Anal. Calcd for C<sub>42</sub>H<sub>36</sub>P<sub>2</sub>: C, 83.70; H, 6.02. Found: C, 83.89; H, 6.19.

### Synthesis of 6,6'-bis(diphenylphosphanyl)-1,3,1',3'-tetrahydro[5,5']biisobenzofuran (4c)

Compound **4b** was prepared according to the procedure described above for **4a** on the same scale and isolated as an off-white solid in 86% yield (0.75 g) after purification by column chromatography. An analytically and spectroscopically pure sample was obtained by slow diffusion of a chloroform solution layered with methanol at room temperature. <sup>31</sup>P{<sup>1</sup>H} NMR (202.5 MHz, CDCl<sub>3</sub>,  $\delta$ ): -12.7; <sup>1</sup>H NMR (500.0 MHz, CDCl<sub>3</sub>,  $\delta$ ): 7.29 (m, 12H, C<sub>6</sub>H<sub>5</sub>), 7.25-7.21 (m, 8H, C<sub>6</sub>H<sub>5</sub>), 6.94 (br s, 2H, C<sub>6</sub>H<sub>2</sub> H3), 6.58 (br s, 2H, C<sub>6</sub>H<sub>2</sub> H6), 5.02 (br s, 4H, CH<sub>2</sub>), 4.93 (d, *J* = 12.5 Hz, 2H, CH<sub>2</sub>), 4.81 (d, *J* = 12.5 Hz, 2H, CH<sub>2</sub>); <sup>13</sup>C{<sup>1</sup>H} NMR (125.8 MHz, CDCl<sub>3</sub>,  $\delta$ ): 146.0 (m, *Q*), 139.3 (*Q*), 138.7 (*Q*), 137.5 (m, *Q*), 137.1 (m, *Q*), 136.4 (m, *Q*), 134.2 (m, C<sub>6</sub>H<sub>5</sub>), 133.5 (m, C<sub>6</sub>H<sub>5</sub>), 128.6 (C<sub>6</sub>H<sub>5</sub>), 128.3 (m, C<sub>6</sub>H<sub>5</sub>), 128.2 (m, 2 x C<sub>6</sub>H<sub>5</sub>), 125.8 (C<sub>6</sub>H<sub>2</sub> C6), 123.6 (m, C<sub>6</sub>H<sub>2</sub> C3), 73.5 (CH<sub>2</sub>), 73.3 (CH<sub>2</sub>);

LRMS (ESI<sup>+</sup>) *m/z* 607 [M+H]<sup>+</sup>; HRMS (ESI<sup>+</sup>) exact mass calcd for C<sub>40</sub>H<sub>33</sub>P<sub>2</sub>O<sub>2</sub> [M+H]<sup>+</sup> requires *m/z* 607.1956, found *m/z* 607.1942. Anal. Calcd for C<sub>40</sub>H<sub>32</sub>P<sub>2</sub>: C, 79.20; H, 5.32. Found: C, 79.18; H, 5.44.

### Synthesis of 6,6-bis(diphenylphosphanyl)-1,3,1',3'-tetrahydro[5,5']biindenyl-2,2,2',2'-tetracarboxylate (4d)

Compound **4d** was prepared according to the procedure described above for **4a**, on the same scale, and isolated as an off-white solid in 94% yield (1.13 g) after purification by column chromatography. An analytically and spectroscopically pure sample was obtained by slow diffusion of a chloroform solution layered with methanol at room temperature. mp = 238-241 °C. <sup>31</sup>P{<sup>1</sup>H} NMR (202.5 MHz, CDCl<sub>3</sub>,  $\delta$ ): -12.5; <sup>1</sup>H NMR (500.0 MHz, CDCl<sub>3</sub>,  $\delta$ ): 7.33-7.28 (m, 10H, C<sub>6</sub>H<sub>5</sub>), 7.26-7.22 (m, 10H, C<sub>6</sub>H<sub>5</sub>), 6.91 (br s, 2H, C<sub>6</sub>H<sub>2</sub>H<sub>6</sub>), 6.52 (br s, 2H, C<sub>6</sub>H<sub>2</sub>H<sub>3</sub>), 3.77 (s, 6H, CH<sub>3</sub>), 3.73 (s, 6H, CH<sub>3</sub>), 3.55 (AB,  $J_{AB}$  = 16.9 Hz, 2H, CH<sub>2</sub>), 3.53 (AB,  $J_{AB}$  = 16.9 Hz, 2H, CH<sub>2</sub>), 3.41 (AB,  $J_{AB}$  = 17.0 Hz, 2H, CH<sub>2</sub>), 3.35 (AB,  $J_{AB}$  = 17.0 Hz, 2H, CH<sub>2</sub>); <sup>13</sup>C{<sup>1</sup>H} NMR (125.8 MHz, CDCl<sub>3</sub>,  $\delta$ ): 172.1 (C=O), 171.8 (C=O), 145.7 (m, Q), 139.7 (Q), 139.2 (Q), 137.8 (m, Q), 137.4 (m, Q), 135.6 (m, Q), 134.3 (m, C<sub>6</sub>H<sub>5</sub>), 133.4 (m, C<sub>6</sub>H<sub>5</sub>), 128.7 (C<sub>6</sub>H<sub>2</sub>C<sub>6</sub>), 128.4 (C<sub>6</sub>H<sub>5</sub>), 128.1 (m, 2x C<sub>6</sub>H<sub>5</sub>), 127.9 (C<sub>6</sub>H<sub>5</sub>), 126.8 (m, C<sub>6</sub>H<sub>2</sub>C<sub>3</sub>), 59.8 (C<sub>3</sub>H<sub>4</sub> Q), 52.8 (CH<sub>3</sub>), 52.7 (CH<sub>3</sub>), 40.4 (CH<sub>2</sub>), 40.3 (CH<sub>2</sub>); LRMS (ESI<sup>+</sup>) *m/z* 835 [M+H]<sup>+</sup>; HRMS (ESI<sup>+</sup>) exact mass calcd for C<sub>50</sub>H<sub>45</sub>P<sub>2</sub>O<sub>8</sub> [M+H]<sup>+</sup> requires *m/z* 835.2590, found *m/z* 835.2569. Anal. Calcd for C<sub>50</sub>H<sub>44</sub>O<sub>8</sub>P<sub>2</sub>: C, 71.94; H, 5.31. Found: C, 72.17; H, 5.54.

### Synthesis of 6,6'-bis(diphenylphosphanyl)-2,2'-bis(4-methylbenzenesulfonyl)-2,3,2',3'-tetrahydro-1H,1'H-[5,5']biisoindole (4e)

Compound **4e** was prepared according to the procedure described above for **4a** on the same scale and isolated as an off-white solid in 90% yield (1.25 g) after purification by column chromatography. An analytically and spectroscopically pure sample was obtained by slow diffusion of a dichloromethane solution layered with methanol at room temperature. <sup>31</sup>P{<sup>1</sup>H} NMR (202.5 MHz, CDCl<sub>3</sub>,  $\delta$ ): -12.5; <sup>1</sup>H NMR (500.0 MHz, CDCl<sub>3</sub>,  $\delta$ ): 7.72 (d,  $J$  = 8.2 Hz, 4H, C<sub>6</sub>H<sub>4</sub>), 7.32 (d,  $J$  = 8.1 Hz, 4H, C<sub>6</sub>H<sub>4</sub>), 7.30-7.16 (m, 20H, C<sub>6</sub>H<sub>5</sub>), 6.82 (br s, 2H, C<sub>6</sub>H<sub>6</sub>), 6.38 (br s, 2H, C<sub>6</sub>H<sub>2</sub>H<sub>3</sub>), 4.48 (AB,  $J_{AB}$  = 13.7 Hz, 2H, CH<sub>2</sub>), 4.46 (AB-,  $J_{AB}$  = 13.7 Hz, 2H, CH<sub>2</sub>), 4.39 (AB,  $J_{AB}$  = 13.6 Hz, 2H, CH<sub>2</sub>), 4.23 (AB,  $J_{AB}$  = 13.6 Hz, 2H, CH<sub>2</sub>), 2.42 (s, 6H, C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>); <sup>13</sup>C{<sup>1</sup>H} NMR (125.8

MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 145.8 (m,  $Q$ ), 143.7 ( $Q$ ), 137.3 (m,  $Q$ ), 136.9 (m,  $Q$ ), 136.6 (m,  $Q$ ), 136.2 ( $Q$ ), 135.9 ( $Q$ ), 134.2 (m,  $\text{C}_6\text{H}_5$  *o*-C), 133.8 (m,  $Q$ ), 133.5 (m,  $\text{C}_6\text{H}_5$  *o*-C), 129.8 ( $\text{C}_6\text{H}_4$ ), 129.0 ( $\text{C}_6\text{H}_5$  *p*-C), 128.5 ( $\text{C}_6\text{H}_5$  *p*-C), 128.4 (m,  $\text{C}_6\text{H}_5$  *m*-C), 128.3 (m,  $\text{C}_6\text{H}_5$  *m*-C), 127.6 ( $\text{C}_6\text{H}_4$ ), 127.4 ( $\text{C}_6\text{H}_2$  C6), 125.1 (m,  $\text{C}_6\text{H}_2$  C6), 53.5 ( $\text{CH}_2$ ), 53.4 ( $\text{CH}_2$ ), 21.5 ( $\text{CH}_3$ ); LRMS (ESI $^+$ )  $m/z$  913 [M+H] $^+$ ; HRMS (ESI $^+$ ) exact mass calcd for  $\text{C}_{54}\text{H}_{47}\text{N}_2\text{P}_2\text{O}_4\text{S}_2$  [M+H] $^+$  requires  $m/z$  913.2453, found  $m/z$  913.2454. Anal. Calcd for  $\text{C}_{54}\text{H}_{46}\text{N}_2\text{O}_4\text{P}_2\text{S}_2$ : C, 71.04; H, 5.08; N, 3.07. Found: C, 71.48; H, 5.37; N, 3.33.

**Attempted cycloaddition between 2,8-decadiyne and 2. Synthesis and characterization of mono cycloaddition adduct 5.**

A flame-dried Schlenk flask was charged with  $[\text{RhCl}(\text{COD})]_2$  (0.0123 g, 0.025 mmol),  $\text{AgBF}_4$  (0.0098 g, 0.05 mmol), *rac*-BINAP (0.031 g, 0.05 mmol) and chlorobenzene (8 mL). 1,4-Bis(diphenylphosphinoyl)buta-1,3-diyne (0.225 g, 0.5 mmol) and 2,8-decadiyne (0.161 g, 1.2 mmol) were added and the resulting solution stirred at 100 °C for 16 hr. After this time, diethyl ether (10 mL) was added followed by water (10 mL). The organic layer was removed and the aqueous phase extracted with diethyl ether (2 x 10 mL). The organic phases were combined, dried over  $\text{MgSO}_4$ , filtered and the solvent removed *in vacuo* to leave a crude brown solid which was purified by column chromatography eluting with ethyl acetate/acetone (4:1) to yield the product as a pale brown solid (0.263 g, 90%). X-ray quality crystals of **5** were obtained by slow diffusion of a dichloromethane solution layered with hexane. mp 217-220 °C.  $^{31}\text{P}\{\text{H}\}$  NMR (202.5 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 32.3, 7.4;  $^1\text{H}$  NMR (500.0 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 7.61-7.54 (m, 8H,  $\text{C}_6\text{H}_5$  *o*-H), 7.47 (dt,  $J$  = 7.4, 1.3 Hz, 2H,  $\text{C}_6\text{H}_5$  *p*-H), 7.39 (dt,  $J$  = 7.5, 1.3 Hz, 2H,  $\text{C}_6\text{H}_5$  *p*-H), 7.35 (dt,  $J$  = 7.7, 3.4 Hz, 4H,  $\text{C}_6\text{H}_5$  *m*-H), 7.26 (dt,  $J$  = 7.7, 3.0 Hz, 4H,  $\text{C}_6\text{H}_5$  *m*-H), 2.66 (br d,  $J$  = 14.8 Hz, 4H,  $\text{C}_4\text{H}_8$ ), 2.38 (s, 3H,  $\text{CH}_3$ ), 2.24 (s, 3H,  $\text{CH}_3$ ), 1.79 (br, 4H,  $\text{C}_4\text{H}_8$ );  $^{13}\text{C}\{\text{H}\}$  NMR (125.8 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 142.2 (d,  $J$  = 7.0 Hz,  $Q$ ), 141.1 (d,  $J$  = 9.2 Hz,  $Q$ ), 140.7 (d,  $J$  = 10.4 Hz,  $Q$ ), 140.2 ( $Q$ ), 134.5 (d,  $J$  = 105 Hz,  $Q$ ), 132.9 (d,  $J$  = 122 Hz,  $Q$ ), 131.9 ( $\text{C}_6\text{H}_5$  *p*-C), 131.6 (d,  $J$  = 10.1 Hz,  $\text{C}_6\text{H}_5$  *o*-C), 131.5 ( $\text{C}_6\text{H}_5$  *p*-C), 131.0 (d,  $J$  = 11.1 Hz,  $\text{C}_6\text{H}_5$  *o*-C), 129.2 (d,  $J$  = 101 Hz,  $Q$ ), 128.5 (d,  $J$  = 12.5 Hz,  $\text{C}_6\text{H}_5$  *m*-C), 128.3 (d,  $J$  = 13.5 Hz,  $\text{C}_6\text{H}_5$  *m*-C), 120.5 (dd,  $J$  = 8.1, 3.7 Hz,  $\text{CC}\equiv\text{C}$ ), 103.4 (dd,  $J$  = 30, 6.2 Hz,  $\text{C}\equiv\text{CP}$ ), 95.4 (d,  $J$  = 170 Hz,  $\text{C}\equiv\text{CP}$ ), 28.4 ( $\text{C}_4\text{H}_8$ ), 28.1 ( $\text{C}_4\text{H}_8$ ), 22.4 ( $\text{C}_4\text{H}_8$ ), 22.3 ( $\text{C}_4\text{H}_8$ ), 18.9 (d,  $J$  = 5.1 Hz,  $\text{CH}_3$ ), 17.4 ( $\text{CH}_3$ ); LRMS (ESI $^+$ )

*m/z* 585 [M+H]<sup>+</sup>; HRMS (ESI<sup>+</sup>) exact mass calcd for C<sub>38</sub>H<sub>34</sub>P<sub>2</sub>O<sub>2</sub> [M+H]<sup>+</sup> requires *m/z* 585.2112, found *m/z* 585.2143. Anal. Calcd for C<sub>58</sub>H<sub>34</sub>O<sub>2</sub>P<sub>2</sub>: C, 78.07; H, 5.86. Found: C, 78.52; H, 5.73.

### **Dichloro[3,3'-bis(diphenylphosphanyl)-5,6,7,8,5',6',7',8'-octahydro[2,2']binaphthalene]platinum (6a)**

A solution of [(cycloocta-1,5-diene)PtCl<sub>2</sub>] (0.147 g, 0.392 mmol) in dichloromethane (6 mL) was treated with a dichloromethane solution (5 mL) of **4a** (0.247 g, 0.392 mmol) and the resulting yellow solution stirred vigorously for 16 hr. The reaction mixture was filtered, the solvent removed *in vacuo* and the resulting yellow solid triturated with hexane. Crystallization by slow diffusion of a dichloromethane solution layered with hexane at room temperature gave **6a** as deep yellow needles in 93% yield (0.330 g). <sup>31</sup>P{<sup>1</sup>H} NMR (202.5 MHz, CD<sub>2</sub>Cl<sub>2</sub>,  $\delta$ ): 7.3 ( $J_{P-Pt}$  = 3648 Hz); <sup>1</sup>H NMR (500.0 MHz, CD<sub>2</sub>Cl<sub>2</sub>,  $\delta$ ): 7.74 (m, 4H, C<sub>6</sub>H<sub>5</sub> *o*-H), 7.65 (m, 4H, C<sub>6</sub>H<sub>5</sub> *o*-H), 7.47 (m, 2H, C<sub>6</sub>H<sub>5</sub> *p*-H), 7.42 (m, 4H, C<sub>6</sub>H<sub>5</sub> *m*-H), 7.38 (m, 2H, C<sub>6</sub>H<sub>5</sub> *p*-H), 7.26 (m, 4H, C<sub>6</sub>H<sub>5</sub> *m*-H), 6.69 (d,  $J$  = 11.7 Hz, 2H, C<sub>6</sub>H<sub>2</sub> H3), 6.22 (d,  $J$  = 3.5 Hz, 2H, C<sub>6</sub>H<sub>2</sub> H6), 2.52-2.33 (m, 8H, C<sub>4</sub>H<sub>8</sub>), 1.66-1.59 (m, 8H, C<sub>4</sub>H<sub>8</sub>); <sup>13</sup>C{<sup>1</sup>H} NMR (125.8 MHz, CD<sub>2</sub>Cl<sub>2</sub>,  $\delta$ ): 141.0 (m,  $Q$ ), 140.3 (m,  $Q$ ), 136.6 (m,  $Q$ ), 136.1 (m, C<sub>6</sub>H<sub>5</sub> *o*-C), 135.1 (m, C<sub>6</sub>H<sub>5</sub> *o*-C), 134.1 (m, C<sub>6</sub>H<sub>2</sub> C6), 133.4 (m, C<sub>6</sub>H<sub>2</sub> C3), 131.2 (C<sub>6</sub>H<sub>5</sub> *p*-C), 130.8 (C<sub>6</sub>H<sub>5</sub> *p*-C), 128.3 (m,  $Q$ ), 127.8 (m, C<sub>6</sub>H<sub>5</sub> *m*-C), 127.7 (m,  $Q$ ), 127.3 (m, C<sub>6</sub>H<sub>5</sub> *m*-C), 125.0 (m,  $Q$ ), 29.1 (C<sub>4</sub>H<sub>8</sub>), 28.8 (C<sub>4</sub>H<sub>8</sub>), 22.7 (C<sub>4</sub>H<sub>8</sub>), 22.6 (C<sub>4</sub>H<sub>8</sub>); LRMS (EI<sup>+</sup>) *m/z* 895 [M]<sup>+</sup>; HRMS (EI<sup>+</sup>) exact mass calcd for C<sub>44</sub>H<sub>40</sub>P<sub>2</sub>Cl<sub>2</sub>Pt [M]<sup>+</sup> requires *m/z* 895.163019, found *m/z* 895.159058. Anal. Calcd for C<sub>44</sub>H<sub>40</sub>Cl<sub>2</sub>P<sub>2</sub>Pt: C, 58.93; H, 4.50. Found: C, 59.22; H, 4.76.

### **$\delta$ -[{3,3'-bis(diphenylphosphanyl)-5,6,7,8,5',6',7',8'-octahydro[2,2']binaphthalene}platinum{(S)-BINOL}] (δ-7a)**

A solution of (S)-BINOL (0.072 g, 0.251 mmol) in THF (8 mL) was added slowly to a rapidly stirred solution of freshly sublimed sodium *tert*-butoxide (0.053 g, 0.552 mmol) in THF (8 mL). After stirring for 20 min, the resulting solution was transferred *via* cannula to a suspension of **6a** (0.225 g, 0.251 mmol) in toluene (10 mL), which resulted in an immediate appearance of a deep yellow coloration. The reaction was stirred for 2 hr during which time the suspension dissolved to give a dark yellow solution. The solvent was removed *in vacuo* and the remaining yellow solid dissolved in chloroform (7 mL) and filtered to remove sodium chloride. The solvent was removed *in vacuo* and the solid triturated with hexane to afford the desired product as a 1:1 mixture of

diastereoisomers. Thermolysis of this mixture in toluene at 90 °C for 3 days resulted in diastereointerconversion and near quantitative precipitation of the thermodynamically favored diastereopure  $\delta$ -[(**4a**)Pt{(S)-BINOL}] ( $\delta$ -**7a**) as a deep yellow microcrystalline solid, which was isolated by filtration. The isolated solid was dissolved in chloroform and hexane added to precipitate the product as a spectroscopically and analytically pure solid in 90% yield (0.251 g).  $^{31}\text{P}\{\text{H}\}$  NMR (202.5 MHz,  $\text{CDCl}_3$ ,  $\delta$ ):  $\delta$ -diastereoisomer (major): 1.8 ( $J_{\text{P-Pt}} = 3690$  Hz),  $\lambda$ -diastereoisomer (minor): 2.8 ( $J_{\text{P-Pt}} = 3661$  Hz);  $^1\text{H}$  NMR (500.0 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 7.79 (dd,  $J = 11.3, 8.0$  Hz, 4H,  $\text{C}_6\text{H}_5$  *o*-H), 7.70 (d,  $J = 8.0$  Hz, 2H,  $\text{C}_{20}\text{H}_{12}$ ), 7.61 (dd,  $J = 10.9, 8.1$  Hz, 4H,  $\text{C}_6\text{H}_5$  *o*-H), 7.49 (d,  $J = 8.7$  Hz, 2H,  $\text{C}_{20}\text{H}_{12}$ ), 7.34 (t,  $J = 7.5$  Hz, 2H,  $\text{C}_6\text{H}_5$  *p*-H), 7.29 (t,  $J = 7.5$  Hz, 2H,  $\text{C}_6\text{H}_5$  *p*-H), 7.22-7.15 (m, 8H,  $\text{C}_6\text{H}_5$  *m*-H), 7.11-7.08 (m, 2H,  $\text{C}_{20}\text{H}_{12}$ ), 7.02-6.99 (m, 4H,  $\text{C}_{20}\text{H}_{12}$ ), 6.78 (d,  $J = 8.7$  Hz, 2H,  $\text{C}_{20}\text{H}_{12}$ ), 6.37 (d,  $J = 12.1$  Hz, 2H,  $\text{C}_6\text{H}_2$  H3), 6.21 (d,  $J = 3.0$  Hz, 2H,  $\text{C}_6\text{H}_2$  H6), 2.53-2.48 (m, 2H,  $\text{C}_4\text{H}_8$ ), 2.33 (m, 6H,  $\text{C}_4\text{H}_8$ ), 1.66-1.55 (m, 8H,  $\text{C}_4\text{H}_8$ );  $^{13}\text{C}\{\text{H}\}$  NMR (125.8 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 160.1 (C-O), 140.1 (m,  $Q$ ), 140.0 ( $Q$ ), 136.2 (m,  $Q$ ), 135.7 (m,  $Q$  and  $\text{C}_6\text{H}_5$  *o*-C), 135.1 (m,  $\text{C}_6\text{H}_5$  *o*-C), 133.7 (m,  $\text{C}_6\text{H}_2$  C6), 132.4 (m,  $\text{C}_6\text{H}_2$  C3), 130.6 ( $\text{C}_{20}\text{H}_{12}$ ), 130.5 ( $\text{C}_6\text{H}_5$  *p*-C), 128.1 ( $\text{C}_6\text{H}_5$  *p*-C), 127.6 (m,  $\text{C}_6\text{H}_5$  *m*-C), 127.4 ( $Q$ ), 127.3 (m,  $\text{C}_6\text{H}_5$  *m*-C), 126.8 ( $\text{C}_{20}\text{H}_{12}$ ), 126.7 (m,  $Q$ ), 126.4 ( $\text{C}_{20}\text{H}_{12}$ ), 126.2 (m,  $Q$ ), 125.4 ( $\text{C}_{20}\text{H}_{12}$ ), 125.2 (m,  $Q$ ), 124.1 ( $\text{C}_{20}\text{H}_{12}$ ), 121.2 ( $Q$ ), 120.3 ( $\text{C}_{20}\text{H}_{12}$ ), 28.9 ( $\text{C}_4\text{H}_8$ ), 28.7 ( $\text{C}_4\text{H}_8$ ), 22.7 ( $\text{C}_4\text{H}_8$ ), 22.6 ( $\text{C}_4\text{H}_8$ ); LRMS (EI $^+$ )  $m/z$  1109 [M] $^+$ ; HRMS (EI $^+$ ) exact mass calcd for  $\text{C}_{64}\text{H}_{52}\text{P}_2\text{O}_2\text{Pt}$  [M] $^+$  requires  $m/z$  1109.309043, found  $m/z$  1109.307434. Anal. Calcd for  $\text{C}_{64}\text{H}_{52}\text{O}_2\text{P}_2\text{Pt}$ : C, 69.24; H, 4.72. Found: C, 69.56; H, 5.03.  $[\alpha]_D = -439$  ( $c = 1.0$ ,  $\text{CH}_2\text{Cl}_2$ ).

### **$\delta$ -Dichloro[3,3'-bis(diphenylphosphanyl)-5,6,7,8,5',6',7',8'-octahydro[2,2']binaphthalene]platinum ( $\delta$ -**6a**)**

A solution of diastereopure  $\delta$ -**6a** (0.202 g, 0.182 mmol) in dichloromethane (7 mL) was cooled to -20 °C and treated with a diethyl ether solution of HCl (0.4 mL, 0.400 mmol, 1.0 M solution in diethyl ether). Addition of HCl resulted in an immediate color change from deep yellow to near colorless. After 10 min the solution was filtered, the solvent removed under vacuum and the resulting residue triturated with diethyl ether (6 x 5 mL) and hexane (4 x 5 mL). Crystallization of the product by slow diffusion of a dichloromethane solution layered with hexane at -20 °C gave enantiopure  $\delta$ -**5a** in 98% yield (0.160 g).  $^{31}\text{P}\{\text{H}\}$  NMR (202.5 MHz,  $\text{CD}_2\text{Cl}_2$ ,  $\delta$ ): 7.3 ( $J_{\text{P-Pt}} = 3648$  Hz);  $^1\text{H}$  NMR (500.0 MHz,  $\text{CD}_2\text{Cl}_2$ ,  $\delta$ ): 7.74 (m, 4H,  $\text{C}_6\text{H}_5$  *o*-H), 7.65 (m, 4H,  $\text{C}_6\text{H}_5$  *o*-H), 7.47 (m, 2H,

$C_6H_5$  *p*-H), 7.42 (m, 4H,  $C_6H_5$  *m*-H), 7.38 (m, 2H,  $C_6H_5$  *p*-H), 7.26 (m, 4H,  $C_6H_5$  *m*-H), 6.69 (d,  $J$  = 11.7 Hz, 2H,  $C_6H_2$  H3), 6.22 (d,  $J$  = 3.5 Hz, 2H,  $C_6H_2$  H6), 2.52-2.33 (m, 8H,  $C_4H_8$ ), 1.66-1.59 (m, 8H,  $C_4H_8$ ); LRMS (EI<sup>+</sup>) *m/z* 895 [M]<sup>+</sup>; HRMS (EI<sup>+</sup>) exact mass calcd for  $C_{44}H_{40}P_2Cl_2Pt$  [M]<sup>+</sup> requires *m/z* 895.163019, found *m/z* 895.159058.  $[\alpha]_D$  = -150.4 (*c* = 1.0,  $CH_2Cl_2$ ).

**Synthesis of *trans*-[RuCl<sub>2</sub>{3,3'-bis(diphenylphosphanyl)-5,6,7,8,5',6',7',8'-octahydro[2,2']binaphthalene}{(S,S)-DPEN}] (11a)**

A solution of [RuCl<sub>2</sub>(nbd)(py)<sub>2</sub>] 0.134 g, 0.317 mmol) in dichloromethane (10 mL) was treated with a dichloromethane solution (4 mL) 3,3'-bis(diphenylphosphanyl)-5,6,7,8,5',6',7',8'-octahydro[2,2']binaphthalene (0.200 g, 0.317 mmol) and stirred overnight, during which time a deep yellow solid precipitated. A solution of (S,S)-DPEN (0.067 g, 0.317 mmol) in dichloromethane (4 mL) was added dropwise via cannula transfer and the resulting mixture stirred at room temperature for a further 3 hr, during which time the precipitate slowly dissolved to give a clear homogenous intense amber solution. The solvent was removed and the resulting solid triturated with hexane (2 x 5 mL) to afford the desired product as a near 1:1 mixture of diastereoisomers in 92% yield (0.296 g). A spectroscopically and analytically pure solid was obtained by crystallization from a concentrated dichloromethane solution layered with hexane. <sup>31</sup>P{<sup>1</sup>H} NMR (202.5 MHz,  $CDCl_3$ ,  $\delta$ ): 44.4 (Dia A) and 44.3 (Dia B); <sup>1</sup>H NMR (500.0 MHz,  $CD_2Cl_2$ ,  $\delta$ ): 7.86 (m, 8H,  $C_6H_5$ ), 7.67-7.60 (m, 8H,  $C_6H_5$ ), 7.29 (t,  $J$  = 7.5 Hz, 8H,  $C_6H_5$ ), 7.24-7.20 (m, 4H,  $C_6H_5$ ), 7.19-7.14 (m, 8H,  $C_6H_5$ ), 7.13-7.04 (m, 20H,  $C_6H_5$  and  $C_6H_2$ ), 7.00 (t,  $J$  = 7.7 Hz, 8H,  $C_6H_5$ ), 6.92 (m, 4H,  $C_6H_2$ ), 4.49 (m, 2H,  $CHNH_2$ ), 4.32 (m, 2H,  $CHNH_2$ ), 4.00 (br t,  $J$  = 9.4 Hz, 2H,  $NH_2$ ), 3.36 (br d,  $J$  = 8.6 Hz, 2H,  $NH_2$ ), 3.20 (br t,  $J$  = 9.6 Hz, 2H,  $NH_2$ ), 3.08 (br t,  $J$  = 8.5 Hz, 2H,  $NH_2$ ), 2.78-2.67 (m, 4H,  $C_4H_8$ ), 2.57-2.40 (m, 8H,  $C_4H_8$ ), 2.33-2.25 (m, 4H,  $C_4H_8$ ), 1.76-1.69 (m, 16H,  $C_4H_8$ ); <sup>13</sup>C{<sup>1</sup>H} NMR (125.8 MHz,  $CD_2Cl_2$ ,  $\delta$ ): 144.1 (m, 2 x *Q*), 142.3 (*Q*), 142.2 (m, *Q*), 140.0 (m, *Q*), 139.7 (*Q*), 139.6 (*Q*), 138.7 (*Q*), 138.3 (m, 2x  $C_6H_5$ ), 138.2 (m,  $C_6H_5$  and 2x  $C_6H_2$ ), 137.8 (m, *Q*), 137.4 (m, *Q*), 136.4 (m,  $C_6H_5$  and  $C_6H_2$ ), 136.2 ( $C_6H_5$  and  $C_6H_2$ ), 131.3 (*Q*), 130.9 (*Q*), 130.8 ( $C_6H_5$ ), 130.7 ( $C_6H_5$ ), 130.5 ( $C_6H_5$ ), 130.2 (m, *Q*), 130.0 ( $C_6H_5$ ), 129.9 (m,  $C_6H_5$ ), 129.8 ( $C_6H_5$ ), 129.7 (m, 2 x  $C_6H_5$ ), 129.4 (*Q*), 129.1 ( $C_6H_5$ ), 128.9 ( $C_6H_5$ ), 128.2 (m, 3x  $C_6H_5$ ), 65.2 ( $CHNH_2$ ), 64.7 ( $CHNH_2$ ), 31.2 ( $C_4H_8$ ), 31.1 ( $C_4H_8$ ), 30.7 ( $C_4H_8$ ), 30.6 ( $C_4H_8$ ), 25.2 ( $C_4H_8$ ), 25.1 ( $C_4H_8$ ), 25.0 ( $C_4H_8$ ), 24.9 ( $C_4H_8$ ); LRMS (EI<sup>+</sup>) *m/z* 1014 [M]<sup>+</sup>; HRMS (EI<sup>+</sup>) exact mass calcd

for  $C_{58}H_{56}N_2P_2Cl_2Ru$   $[M]^+$  requires  $m/z$  1014.233930, found  $m/z$  1014.238800. Anal. Calcd for  $C_{58}H_{56}Cl_2N_2P_2Ru$ : C, 68.63; H, 5.56; N, 2.76. Found: C, 69.01; H, 5.77, N, 2.98.

### General Procedure for Platinum-Catalyzed Carbonyl-Ene Reactions between Allylbenzene Derivatives 8a-e and Ethyl Trifluoropyruvate

A flame-dried Schlenk flask charged with enantiopure **δ-6a** (0.018 g, 0.02 mmol),  $AgSbF_6$  (0.015 g, 0.044 mmol) and dichloromethane (2.0 ml) was stirred at room temperature for 20 mins, after which time ethyl trifluoropyruvate (80.0  $\mu$ l, 0.6 mmol) was added followed by allylbenzene (53.0  $\mu$ l, 0.4 mmol). The resulting mixture was stirred for a further 60 min after which time the solution was flushed through a short plug of silica with dichloromethane, the solvent removed, and the resulting residue purified by column chromatography to afford **9a** as a spectroscopically pure colorless oil. Enantiomeric excess determined by GC using a Supelco Beta DEX column (injection temp. 170 °C; column conditions 140 °C for 45 min ramp to 180 °C at 3 °C/min, pressure 21 psi): major (*R*)-enantiomer  $t_r$  = 35.4 min, minor (*S*)-enantiomer  $t_r$  = 37.7 min, 99%. Absolute stereochemistry assigned by comparison of the sign of the optical rotation with a sample prepared with  $[\{(R)\text{-BINAP}\}\text{PtCl}_2]$ .<sup>8</sup>

#### Ethyl *E*-2-(trifluoromethyl)-2-hydroxy-5-*p*-tolylpent-4-enoate (9b).

A sample was isolated as a colourless oil after purification by column chromatography.  $[\alpha]_D$  = +47.9 ( $c$  1.22,  $CH_2Cl_2$ );  $^1H$  NMR (300.0 MHz,  $CDCl_3$ ,  $\delta$ ): 7.23 (d,  $J$  = 8.0 Hz, 2H,  $C_6H_4$ ), 7.12 (d,  $J$  = 8.0 Hz, 2H,  $C_6H_4$ ), 6.51 (d,  $J$  = 15.8 Hz, 1H,  $C_6H_4CH=$ ), 6.10-6.00 (m, 1H,  $=CHCH_2$ ), 4.29-4.27 (m, 2H,  $OCH_2CH_3$ ), 3.94 (s, 1H, OH), 2.92-2.78 (m, 2H,  $=CHCH_2$ ), 2.34 (s, 3H,  $CH_3C_6H_4$ ), 1.33 (t,  $J$  = 7.1 Hz, 3H,  $OCH_2CH_3$ );  $^{13}C\{^1H\}$  NMR (75.5 MHz,  $CDCl_3$ ,  $\delta$ ): 169.3 ( $C=O$ ), 137.6 ( $C_6H_4$ ), 135.5 ( $C_6H_4CH=$ ), 134.2 ( $C_6H_4$ ), 129.2 ( $C_6H_4$ ), 126.2 ( $C_6H_4$ ), 123.5 (q,  $J_{C-F}$  = 286.1 Hz,  $CF_3$ ), 119.6 ( $=CHCH_2$ ), 77.9 (q,  $J_{C-F}$  = 29.0 Hz,  $CCF_3$ ), 63.7 ( $OCH_2CH_3$ ), 35.8 ( $=CHCH_2$ ), 21.0 ( $CH_3C_6H_4$ ), 14.0 ( $OCH_2CH_3$ ); LRMS (EI)  $m/z$  302  $[M]^+$ ; HRMS (EI) exact mass calcd for  $C_{15}H_{17}O_3F_3$   $[M]^+$  requires  $m/z$  302.112979, found  $m/z$  302.114487. Enantiomeric excess determined by GC using

<sup>8</sup> Mikami, K.; Aikawa, K.; Kainuma, S.; Kawakami, Y.; Saito, T.; Sayo, N.; Kumobayahi, H. *Tetrahedron: Asymmetry* **2004**, 15, 3885.

a SUPELCO BETA DEX column (injection temp 170°C; column conditions 140°C for 45 min ramp to 180°C at 3°C/min, hold for 15 min): major (*R*)-enantiomer  $t_r$  = 51.7 min, minor (*S*)-enantiomer  $t_r$  = 52.9 min; 99% ee. Absolute stereochemistry assigned by analogy.

**Ethyl *E*-2-(trifluoromethyl)-2-hydroxy-5-(2-chlorophenyl)pent-4-enoate (9c).**

A sample was isolated as a colourless oil after purification by column chromatography.  $[\alpha]_D$  = +5.6 (*c* 1.0,  $\text{CH}_2\text{Cl}_2$ );  $^1\text{H}$  NMR (300.0 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 7.48 (m, 1H,  $\text{C}_6\text{H}_4$ ), 7.35-7.32 (m, 1H,  $\text{C}_6\text{H}_4$ ), 7.24-7.15 (m, 2H,  $\text{C}_6\text{H}_4$ ), 6.92 (d,  $J$  = 15.8 Hz, 1H,  $\text{C}_6\text{H}_4\text{CH} =$ ), 6.16-6.06 (m, 1H,  $=\text{CHCH}_2$ ), 4.36 (q,  $J$  = 7.1 Hz, 2H,  $\text{OCH}_2\text{CH}_3$ ), 3.98 (br d,  $J$  = 0.9 Hz, 1H, OH), 2.98-2.83 (m, 2H,  $=\text{CHCH}_2$ ), 1.35 (t,  $J$  = 7.1 Hz, 3H,  $\text{OCH}_2\text{CH}_3$ );  $^{13}\text{C}\{^1\text{H}\}$  NMR (75.5 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 169.3 ( $\text{C}=\text{O}$ ), 135.1 ( $\text{C}_6\text{H}_4$ ), 133.0 ( $\text{C}_6\text{H}_4$ ), 131.8 ( $\text{C}_6\text{H}_4\text{CH} =$ ), 129.7 ( $\text{C}_6\text{H}_4$ ), 128.8 ( $\text{C}_6\text{H}_4$ ), 127.2 ( $\text{C}_6\text{H}_4$ ), 126.9 ( $\text{C}_6\text{H}_4$ ), 123.9 ( $=\text{CHCH}_2$ ), 123.5 (q,  $J_{\text{C}-\text{F}}$  = 286.1 Hz,  $\text{CF}_3$ ), 77.9 (q,  $J_{\text{C}-\text{F}}$  = 29.0 Hz,  $\text{CCF}_3$ ), 63.9 ( $\text{OCH}_2\text{CH}_3$ ), 35.8 ( $=\text{CHCH}_2$ ), 13.9 ( $\text{OCH}_2\text{CH}_3$ ); LRMS (EI)  $m/z$  322 [ $\text{M}]^+$ ; HRMS (EI) exact mass calcd for  $\text{C}_{14}\text{H}_{14}\text{O}_3\text{F}_3\text{Cl}$  [ $\text{M}]^+$  requires  $m/z$  322.058357, found  $m/z$  322.057823. Enantiomeric excess determined by GC using a SUPELCO BETA DEX column (injection temp 170°C; column conditions 140°C for 45 min ramp to 180°C at 3°C/min, hold for 40 min): major (*R*)-enantiomer  $t_r$  = 56.2 min, minor (*S*)-enantiomer  $t_r$  = 57.2 min; 91% ee. Absolute stereochemistry assigned by analogy.

**Ethyl *E*-2-(trifluoromethyl)-2-hydroxy-5-(3-chlorophenyl)pent-4-enoate (9d).**

A sample was isolated as a colourless oil after purification by column chromatography.  $[\alpha]_D$  = +46.4 (*c* 1.0,  $\text{CH}_2\text{Cl}_2$ );  $^1\text{H}$  NMR (300.0 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 7.31 (br s, 1H,  $\text{C}_6\text{H}_4$ ), 7.24-7.17 (m, 3H,  $\text{C}_6\text{H}_4$ ), 6.48 (d,  $J$  = 15.9 Hz, 1H,  $\text{C}_6\text{H}_4\text{CH} =$ ), 6.17-6.07 (m, 1H,  $=\text{CHCH}_2$ ), 4.40-4.32 (m, 2H,  $\text{OCH}_2\text{CH}_3$ ), 3.99 (br d,  $J$  = 0.7 Hz, 1H, OH), 2.93-2.79 (m, 2H,  $=\text{CHCH}_2$ ), 1.32 (t,  $J$  = 7.1 Hz, 3H,  $\text{OCH}_2\text{CH}_3$ );  $^{13}\text{C}\{^1\text{H}\}$  NMR (75.5 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 169.2 ( $\text{C}=\text{O}$ ), 138.8 ( $\text{C}_6\text{H}_4$ ), 134.7 ( $\text{C}_6\text{H}_4$ ), 134.2 ( $\text{C}_6\text{H}_4\text{CH} =$ ), 129.8 ( $\text{C}_6\text{H}_4$ ), 127.7 ( $\text{C}_6\text{H}_4$ ), 126.4 ( $\text{C}_6\text{H}_4$ ), 124.5 ( $\text{C}_6\text{H}_4$ ), 123.4 (q,  $J_{\text{C}-\text{F}}$  = 286.0 Hz,  $\text{CF}_3$ ), 122.5 ( $=\text{CHCH}_2$ ), 77.8 (q,  $J_{\text{C}-\text{F}}$  = 29.1 Hz,  $\text{CCF}_3$ ), 63.8 ( $\text{OCH}_2\text{CH}_3$ ), 35.6 ( $=\text{CHCH}_2$ ), 13.9 ( $\text{OCH}_2\text{CH}_3$ ); LRMS (EI)  $m/z$  322 [ $\text{M}]^+$ ; HRMS (EI) exact mass calcd for  $\text{C}_{14}\text{H}_{14}\text{O}_3\text{F}_3\text{Cl}$  [ $\text{M}]^+$  requires  $m/z$  322.058357, found  $m/z$  322.057274. Enantiomeric excess determined by GC using a SUPELCO

BETA DEX column (injection temp 170°C; column conditions 140°C for 45 min ramp to 180°C at 3°C/min, hold for 40 min): major (*R*)-enantiomer  $t_r$  = 58.8 min, minor (*S*)-enantiomer  $t_r$  = 59.4 min; 98% ee. Absolute stereochemistry assigned by analogy.

**Ethyl *E*-2-(trifluoromethyl)-2-hydroxy-5-(4-chlorophenyl)pent-4-enoate (9e).**

A sample was isolated as a crystalline solid after purification by column chromatography.  $[\alpha]_D$  = +33.6 ( $c$  1.0,  $\text{CH}_2\text{Cl}_2$ );  $^1\text{H}$  NMR (300.0 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 7.23-7.16 (m, 4H,  $\text{C}_6\text{H}_4$ ), 6.43 (d,  $J$  = 15.9 Hz, 1H,  $\text{C}_6\text{H}_4\text{CH} =$ ), 6.08-5.97 (m, 1H,  $=\text{CHCH}_2$ ), 4.34-4.24 (m, 2H,  $\text{OCH}_2\text{CH}_3$ ), 3.95 (s, 1H, OH), 2.86-2.73 (m, 2H,  $=\text{CHCH}_2$ ), 1.25 (t,  $J$  = 7.1 Hz, 3H,  $\text{OCH}_2\text{CH}_3$ );  $^{13}\text{C}\{\text{H}\}$  NMR (75.5 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 169.2 ( $\text{C}=\text{O}$ ), 135.4 ( $\text{C}_6\text{H}_4$ ), 134.3 ( $\text{C}_6\text{H}_4\text{CH} =$ ), 133.6 ( $\text{C}_6\text{H}_4$ ), 128.8 ( $\text{C}_6\text{H}_4$ ), 127.5 ( $\text{C}_6\text{H}_4$ ), 123.4 (q,  $J_{\text{C}-\text{F}} = 286.0$  Hz,  $\text{CF}_3$ ), 121.6 ( $=\text{CHCH}_2$ ), 77.8 (q,  $J_{\text{C}-\text{F}} = 29.1$  Hz,  $\text{CCF}_3$ ), 63.7 ( $\text{OCH}_2\text{CH}_3$ ), 35.7 ( $=\text{CHCH}_2$ ), 13.9 ( $\text{OCH}_2\text{CH}_3$ ); LRMS (EI)  $m/z$  322 [ $\text{M}]^+$ ; HRMS (EI) exact mass calcd for  $\text{C}_{14}\text{H}_{14}\text{O}_3\text{F}_3\text{Cl}$  [ $\text{M}]^+$  requires  $m/z$  322.058357, found  $m/z$  322.057198. Enantiomeric excess determined by GC using a SUPELCO BETA DEX column (injection temp 170°C; column conditions 140°C for 45 min ramp to 180°C at 3°C/min, hold for 40 min): major (*R*)-enantiomer  $t_r$  = 60.2 min, minor (*S*)-enantiomer  $t_r$  = 60.8 min; 99% ee. Absolute stereochemistry assigned by analogy.

**Ethyl *E*-2-(trifluoromethyl)-2-hydroxy-5-(4-nitrophenyl)pent-4-enoate (9f).**

A sample was isolated as a pale brown crystalline solid after purification by column chromatography.  $[\alpha]_D$  = +54.2 ( $c$  1.0,  $\text{CH}_2\text{Cl}_2$ );  $^1\text{H}$  NMR (300.0 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 8.16 (d,  $J$  = 8.8 Hz, 2H,  $\text{C}_6\text{H}_4$ ), 7.45 (d,  $J$  = 8.7 Hz, 2H,  $\text{C}_6\text{H}_4$ ), 6.60 (d,  $J$  = 15.9 Hz, 1H,  $\text{C}_6\text{H}_4\text{CH} =$ ), 6.34-6.24 (m, 1H,  $=\text{CHCH}_2$ ), 4.37 (q,  $J$  = 7.1 Hz, 2H,  $\text{OCH}_2\text{CH}_3$ ), 3.97 (s, 1H, OH), 2.92-2.88 (m, 2H,  $=\text{CHCH}_2$ ), 1.32 (t,  $J$  = 7.1 Hz, 3H,  $\text{OCH}_2\text{CH}_3$ );  $^{13}\text{C}\{\text{H}\}$  NMR (75.5 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 169.1 ( $\text{C}=\text{O}$ ), 147.4 ( $\text{C}_6\text{H}_4$ ), 143.1 ( $\text{C}_6\text{H}_4$ ), 133.5 ( $\text{C}_6\text{H}_4\text{CH} =$ ), 126.9 ( $\text{C}_6\text{H}_4$ ), 126.0 ( $=\text{CHCH}_2$ ), 124.0 ( $\text{C}_6\text{H}_4$ ), 123.4 (q,  $J_{\text{C}-\text{F}} = 286$  Hz,  $\text{CF}_3$ ), 77.6 (q,  $J_{\text{C}-\text{F}} = 29$  Hz,  $\text{CCF}_3$ ), 63.9 ( $\text{OCH}_2\text{CH}_3$ ), 35.7 ( $=\text{CHCH}_2$ ), 14.0 ( $\text{OCH}_2\text{CH}_3$ ); LRMS (EI)  $m/z$  333 [ $\text{M}]^+$ ; HRMS (EI) exact mass calcd for  $\text{C}_{14}\text{H}_{14}\text{NO}_5\text{F}_3$  [ $\text{M}]^+$  requires  $m/z$  333.082408, found  $m/z$  333.080917; Enantiomeric excess determined by GC using a SUPELCO BETA DEX column (injection temp 170°C; column conditions 140°C for 45 min ramp to 180°C at 3°C/min, hold for 75

min): major (*R*)-enantiomer  $t_r = 106.7$  min, minor (*S*)-enantiomer  $t_r = 108.0$  min; >99% ee. Absolute stereochemistry assigned by analogy.

### **General Procedure for Enantioselective Diels-Alder Reaction between Cyclopentadiene and *N*-Acryloyl oxazolidinone**

A flame-dried Schlenk flask charged with enantiopure **δ-6a** (0.014 g, 0.016 mmol), AgSbF<sub>6</sub> (0.012 mg, 0.0352 mmol) and CH<sub>2</sub>Cl<sub>2</sub> (3.0 ml) was stirred at room temperature for 20 mins, after which time *N*-acryloyl oxazolidinone (0.023 g, 0.16 mmol) was added. The resulting catalyst solution was cooled to -78 °C and freshly distilled cyclopentadiene added (0.066 mL, 0.8 mmol). After stirring at -60 °C for 20 h the reaction mixture was quenched with (S,S)-DPEN and the crude product purified by column chromatography over silica gel (60-200 mesh, 30% ethyl acetate/hexane). The *endo/exo* ratio was obtained from <sup>1</sup>H NMR spectroscopy and the enantiomeric excess was calculated from the HPLC profile (1 mL/min flow rate, hexane:2-propanol = 90:10). The retention times of the *endo* and *exo* isomers were 18.80 min (*exo*<sub>1</sub>), 20.59 min (*exo*<sub>2</sub>), 22.68 min (*endo*<sub>2S</sub>), 24.57 min (*endo*<sub>2R</sub>). The absolute configuration of the *endo* cycloadduct was assigned by comparison with the retention times of samples prepared from (*R*)- and [{(S)-BINAP}PtCl<sub>2</sub>].

### **General Experimental Procedure for the Asymmetric Hydrogenation of Acetophenone**

A flame dried Schlenk flask was charged with propan-2-ol (10 mL), acetophenone (0.206 g, 1.72 mmol) and catalyst (0.0017 g, 0.00172 mmol) and the resulting mixture degassed by three successive freeze-thaw cycles. A solution of *t*-BuOK in propan-2-ol (0.026 mL, 0.0258 mmol, 1M solution) was added and the resulting solution transferred to a 50 mL Parr stainless steel bench-top reactor. The vessel was pressurized to 10 atm with hydrogen and left to stand for 10 seconds before releasing the gas through an outlet valve. After repeating this sequence six times, the reactor was pressurized to *ca.* 10 atm and the solution stirred vigorously at 20-22°C for 12 hours. The pressure was released and the resulting mixture was filtered through a short silica plug, diluted with diethyl ether and analyzed by chiral GC (Supelco Beta DEX column, 0.25 mm i.d. x 25 m).

### **Hydrogenation of 1-acetylnaphthylene**

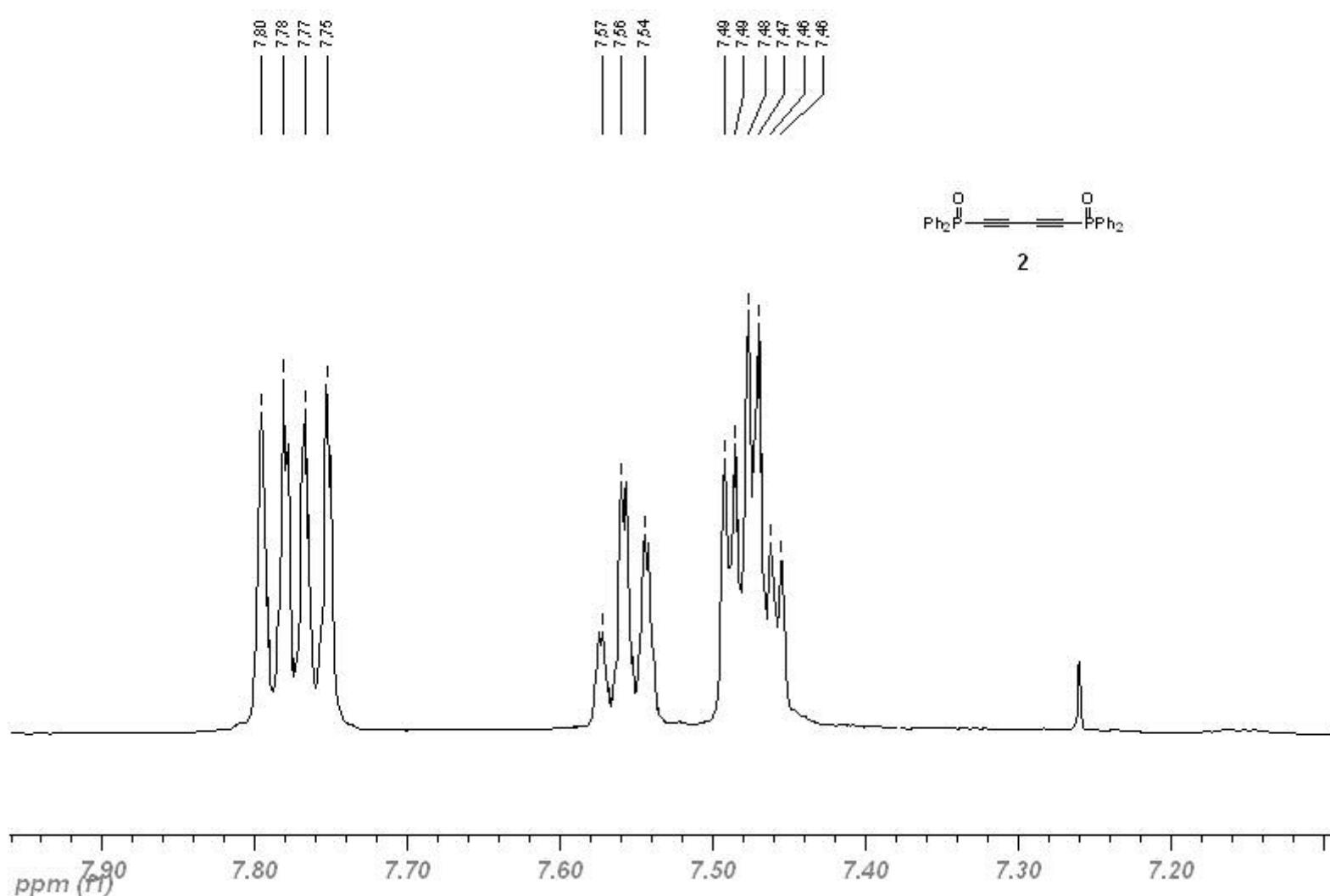
The same procedure as described above for acetophenone was used. The reaction mixture was analyzed by GC to determine the % conversion and % ee. The stereochemistry was assigned by comparing the optical rotation with literature data.

### **GC Analysis of Reduction Products**

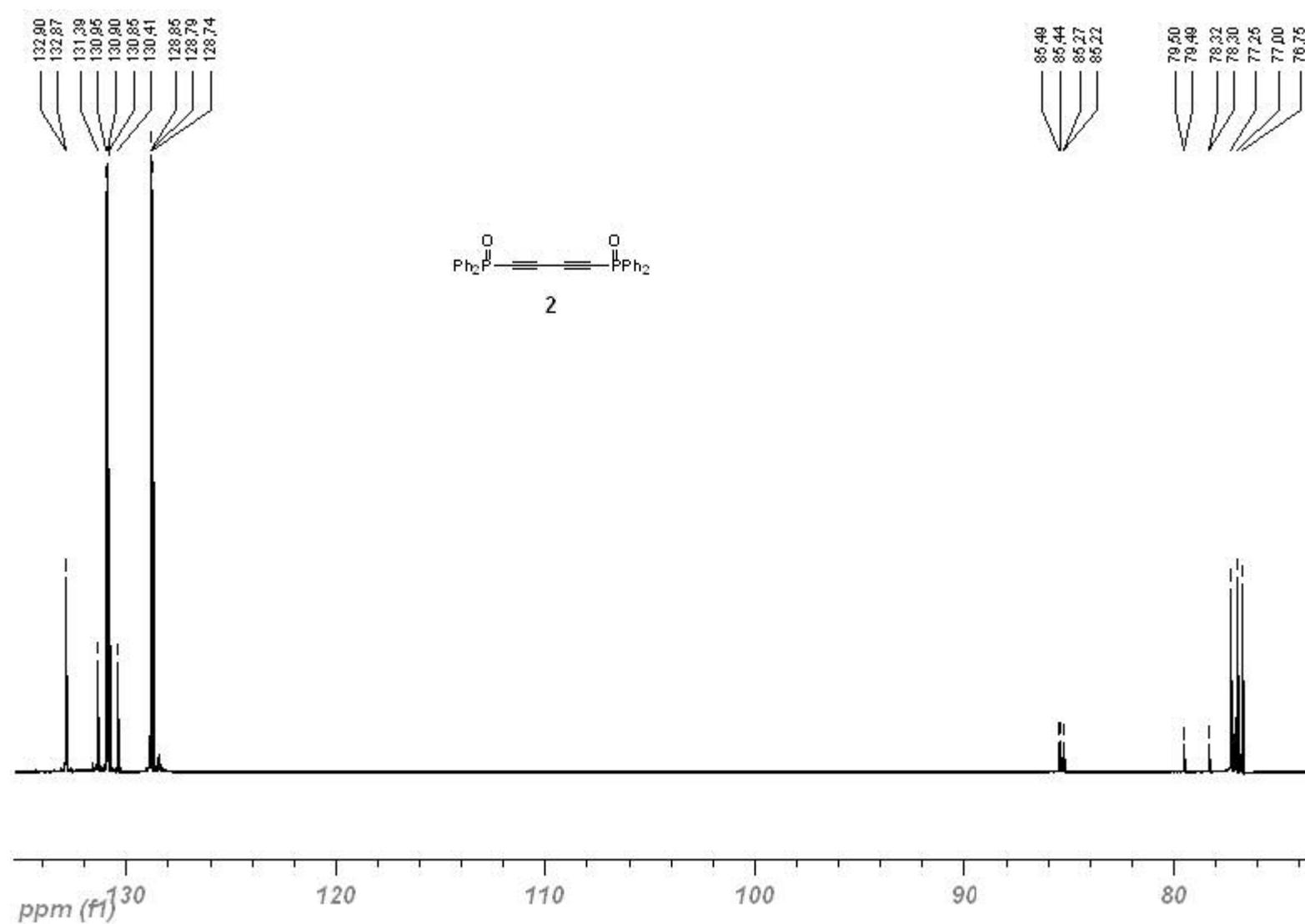
**(S)-1-phenylethanol:** (Supelco Beta DEX, injection temp 200 °C, column conditions 35 °C for 5 min, ramp to 115 °C at 5 °C/min, hold for 20 min, ramp to 170 °C at 5 °C/min, hold for 10 min, pressure 18.9 psi):  $t_R$  of *R*-enantiomer 26.1 min; *S*-enantiomer 27.2 min.

**(S)-1-(1'-naphthyl)ethanol:** (Supelco Beta DEX, injection temp 200 °C, column conditions 140 °C for 5 min, ramp to 170 °C at 5 °C/min, hold for 80 min, pressure 23.3 psi):  $t_R$  of *S*-enantiomer 44.4 min;  $t_R$  of *R*-enantiomer 45.8 min.

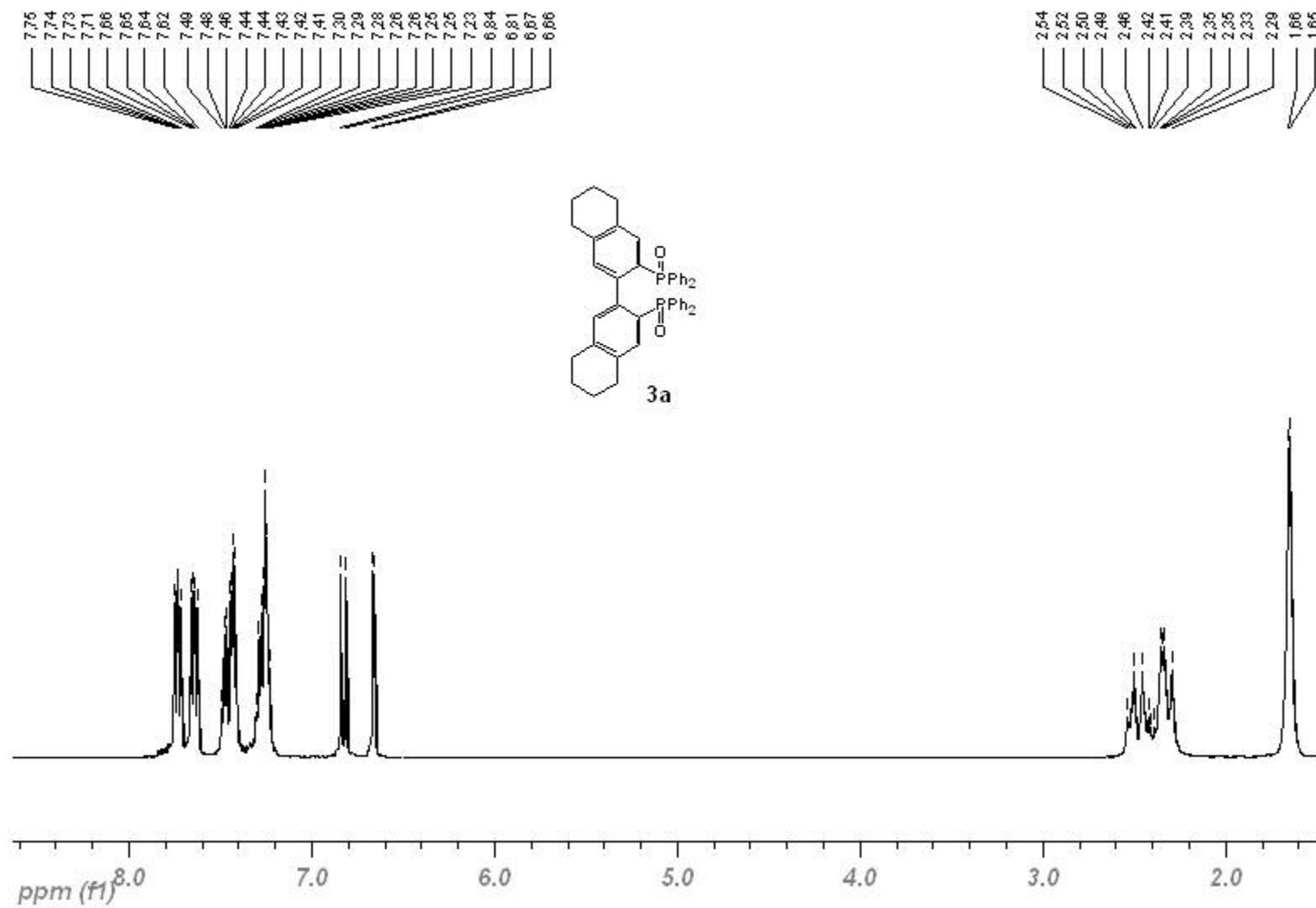
<sup>1</sup>H NMR Spectrum of 1,4-bis(diphenylphosphinoyl)buta-1,3-diyne (2)



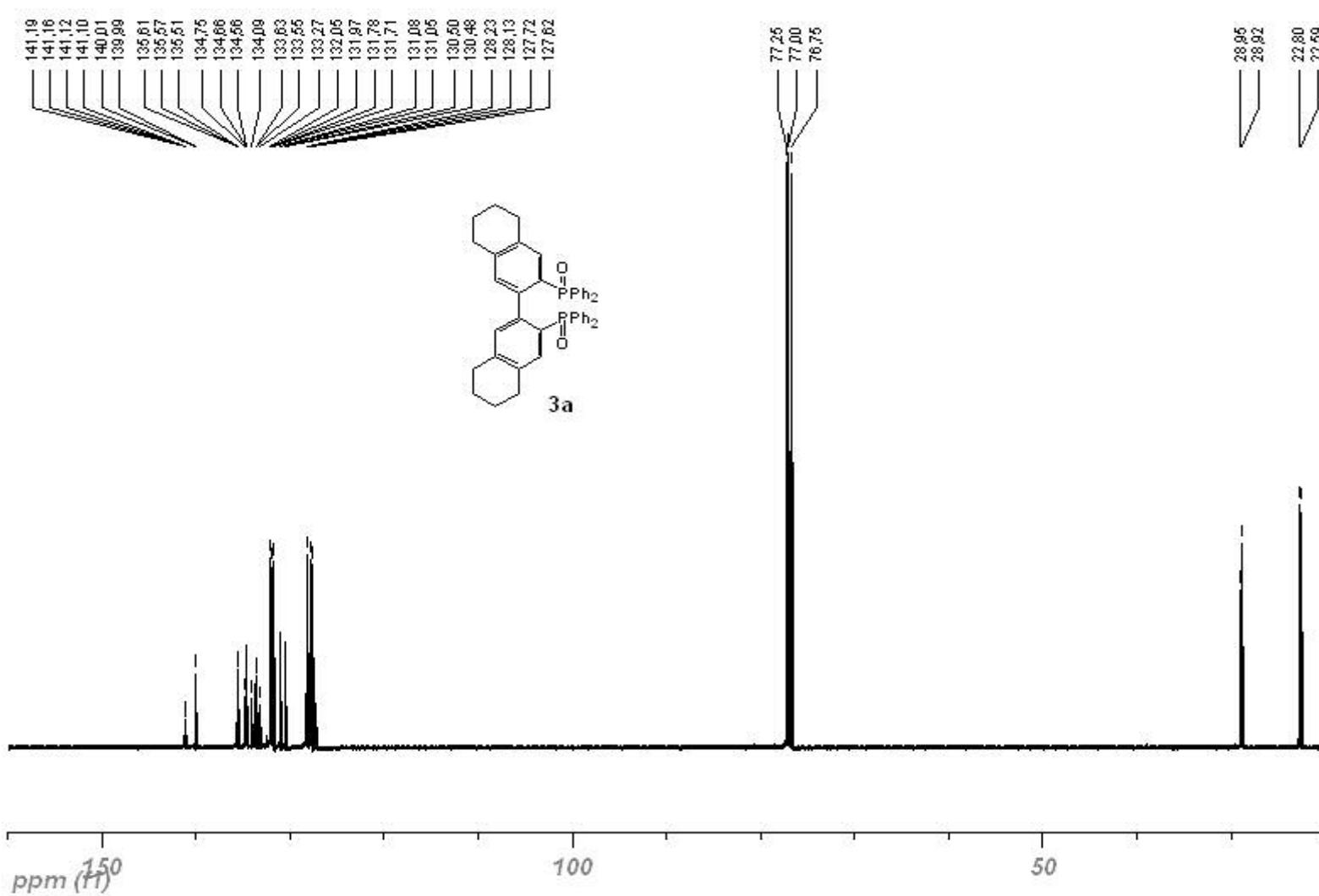
<sup>13</sup>C NMR Spectrum of 1,4-bis(diphenylphosphinoyl)buta-1,3-diyne (2)



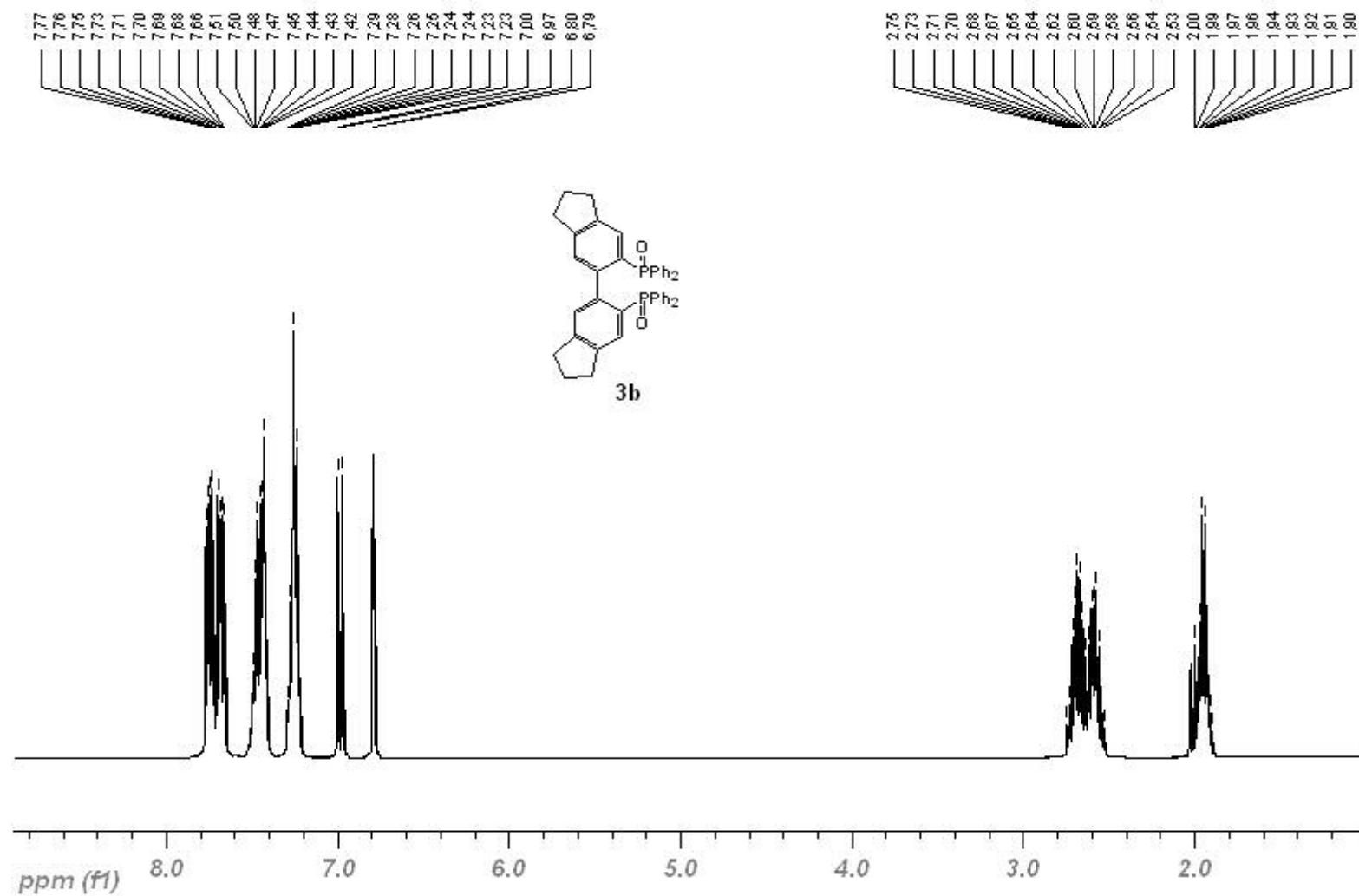
<sup>1</sup>H NMR Spectrum of 3,3'-bis(diphenylphosphinoyl)-5,6,7,8,5',6',7',8'-octahydro[2,2']binaphthalene (3a)



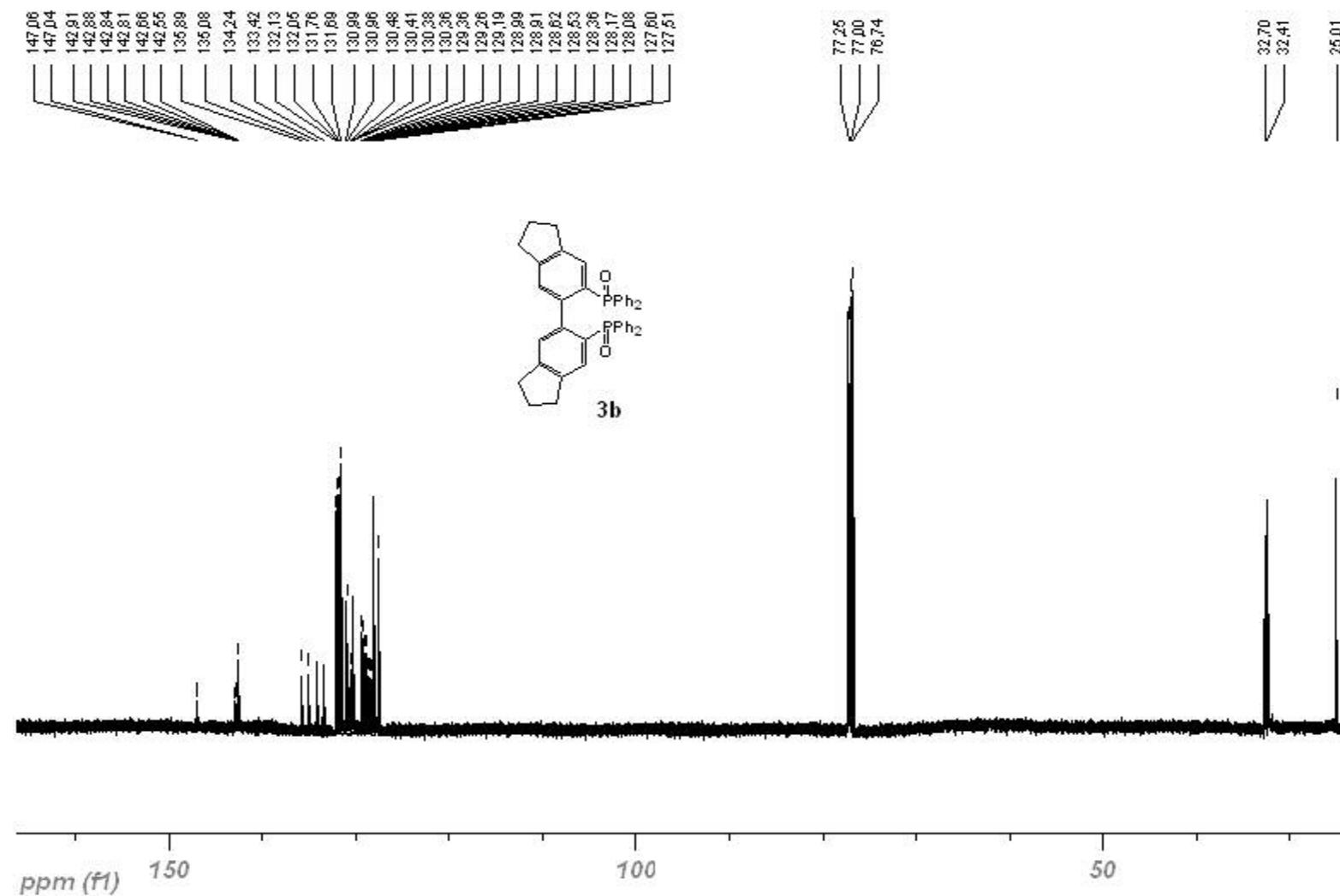
<sup>13</sup>C NMR Spectrum of 3,3'-bis(diphenylphosphinoyl)-5,6,7,8,5',6',7',8'-octahydro[2,2']binaphthalene (3a)



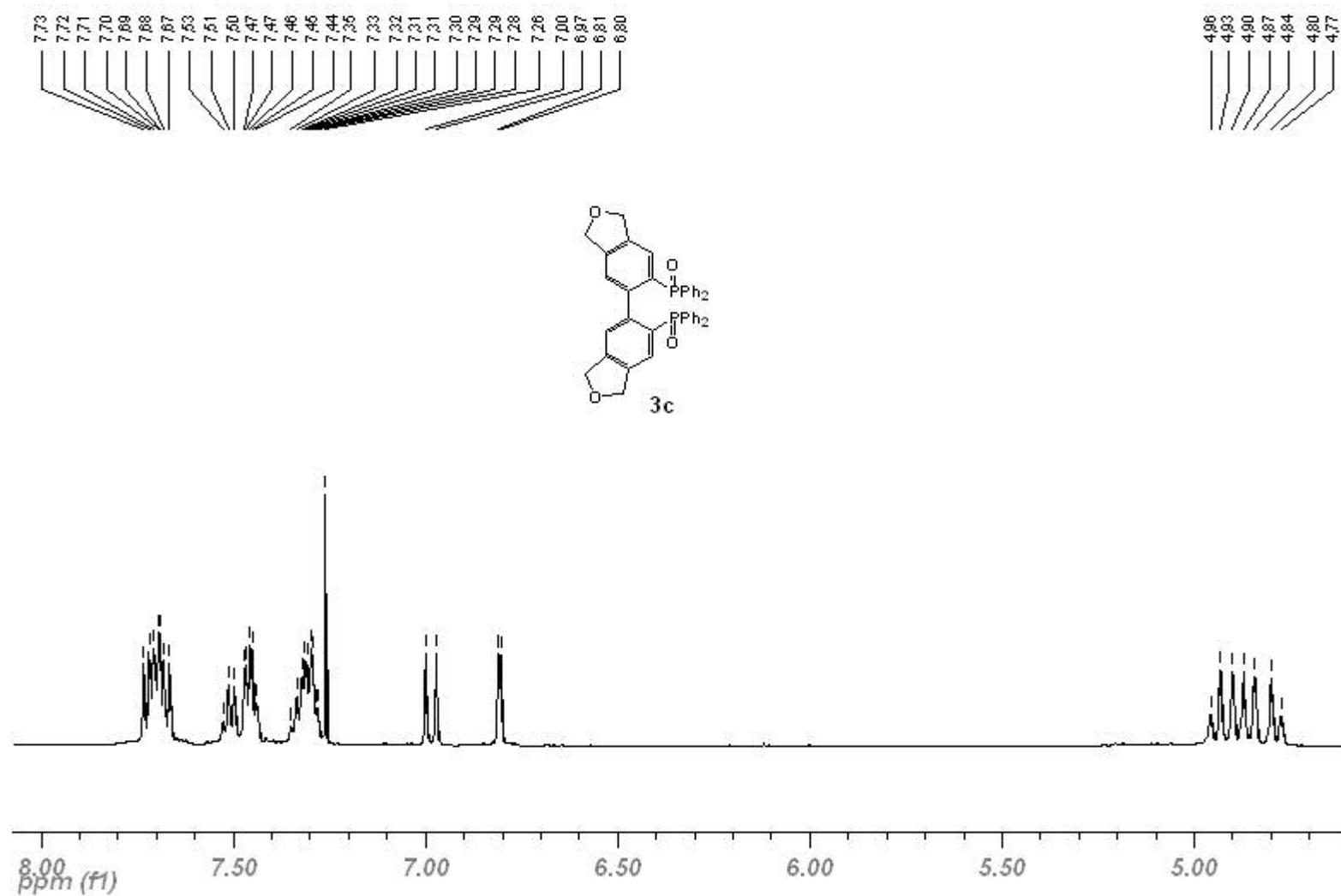
<sup>1</sup>H NMR Spectrum of 6,6'-bis(diphenylphosphinoyl)-2,3,2',3'-tetrahydro-1*H*,1'*H*-[5,5']biindene (3b)



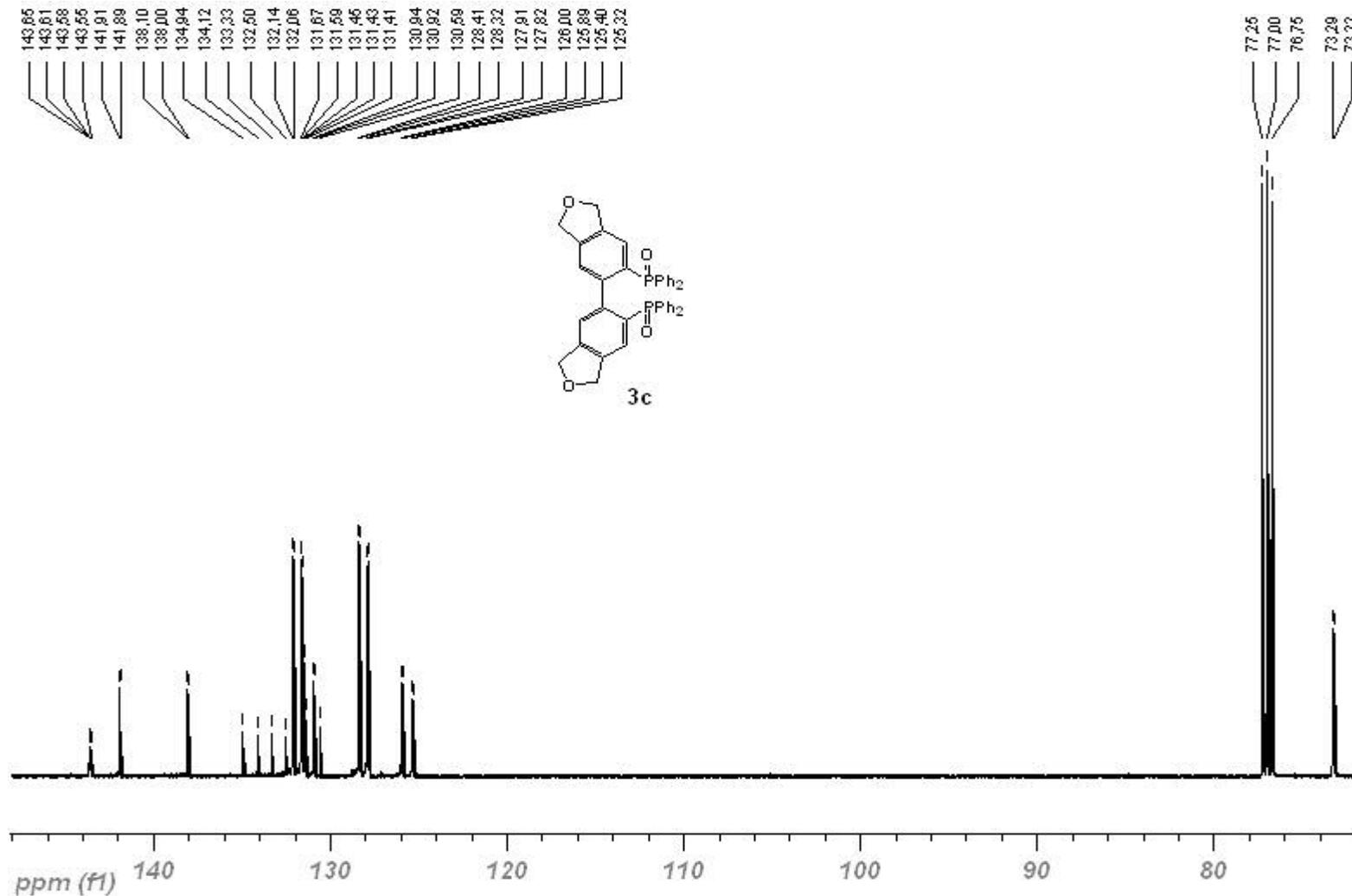
<sup>13</sup>C NMR Spectrum of 6,6'-bis(diphenylphosphinoyl)-2,3,2',3'-tetrahydro-1H,1'H-[5,5']biindene (3b)



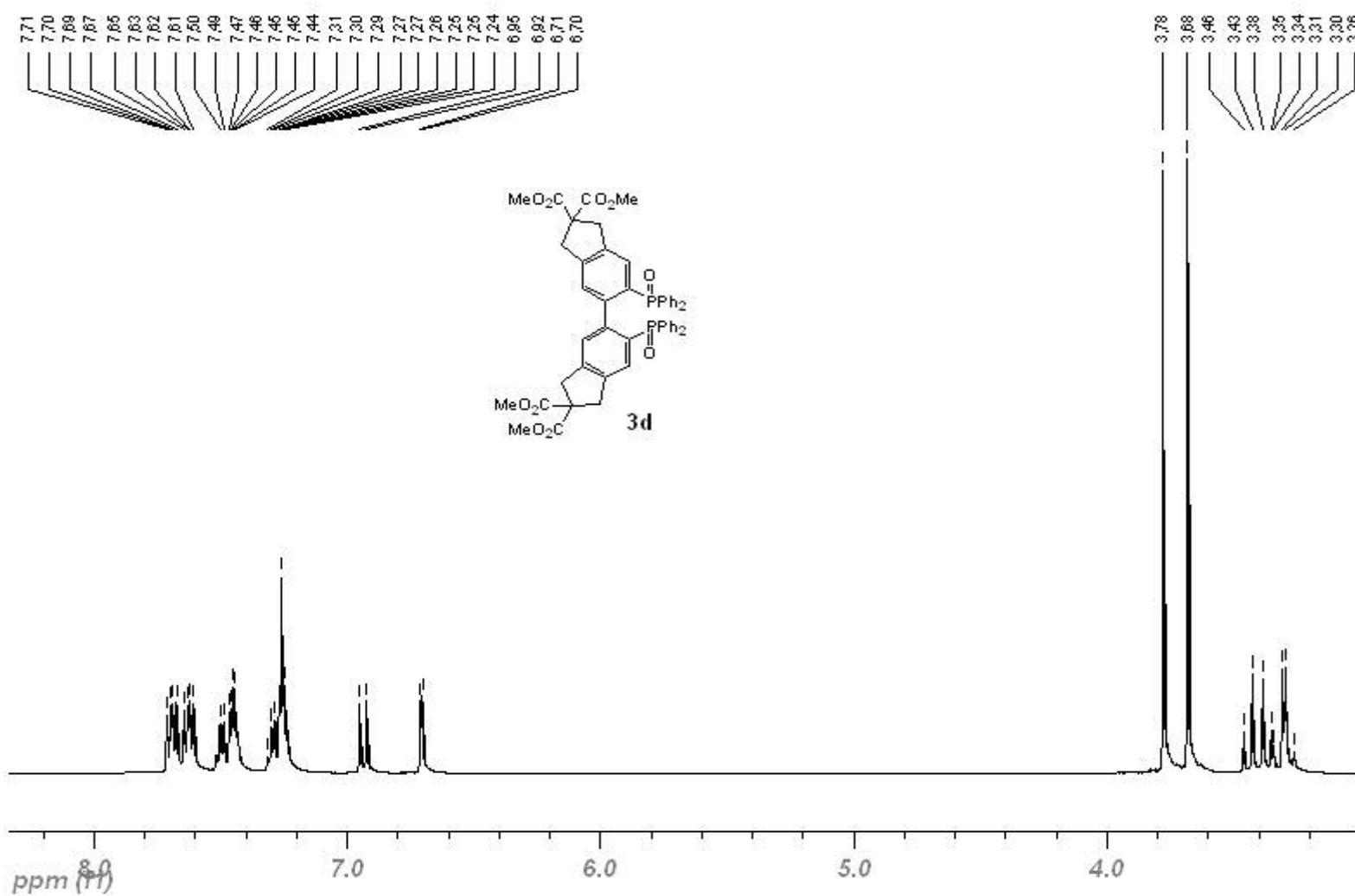
<sup>1</sup>H NMR Spectrum of 6,6'-bis(diphenylphosphinoyl)-1,3,1',3'-tetrahydro[5,5']biisobenzofuran (3c)



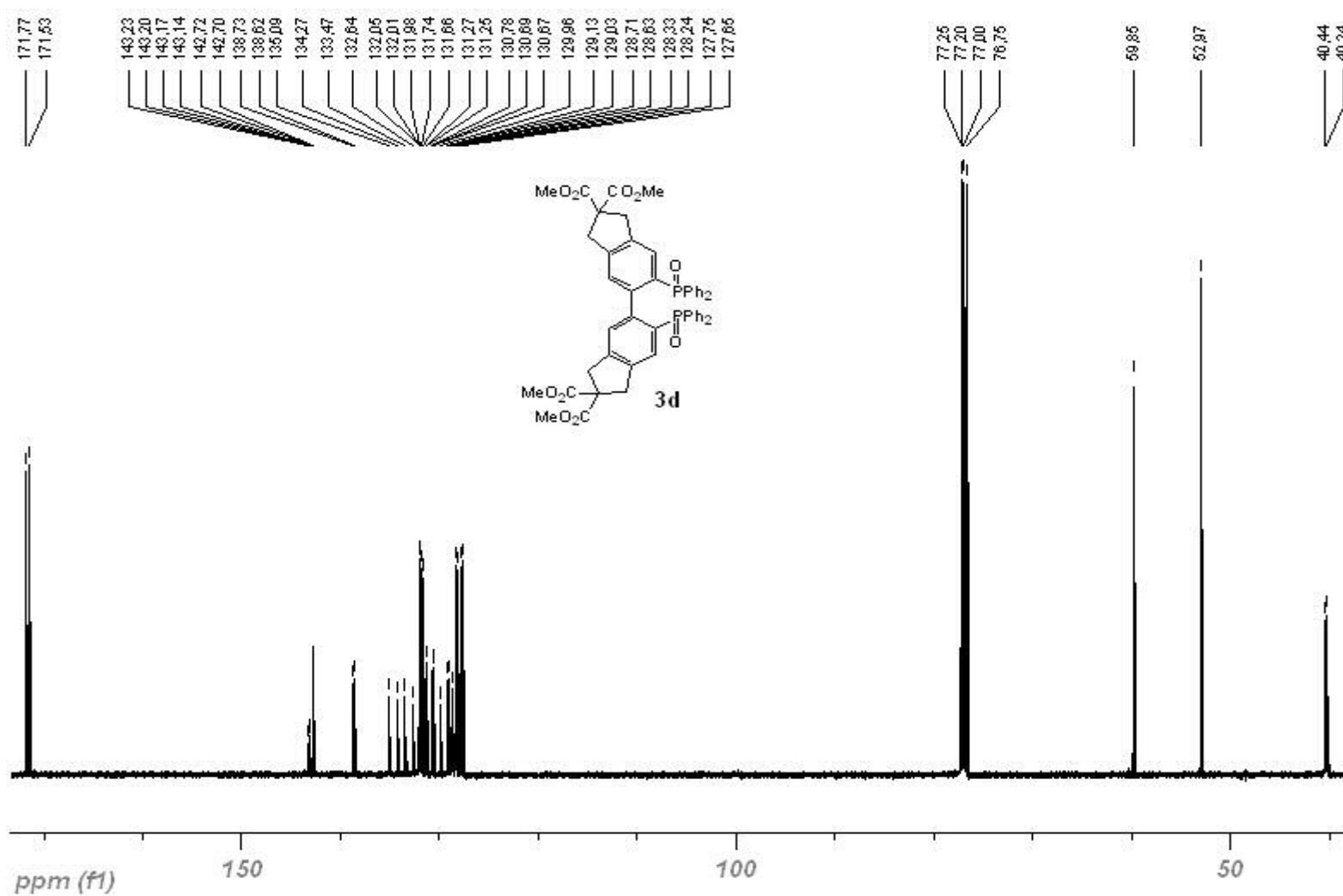
<sup>13</sup>C NMR Spectrum of 6,6'-bis(diphenylphosphinoyl)-1,3,1',3'-tetrahydro[5,5']biisobenzofuran (3c)



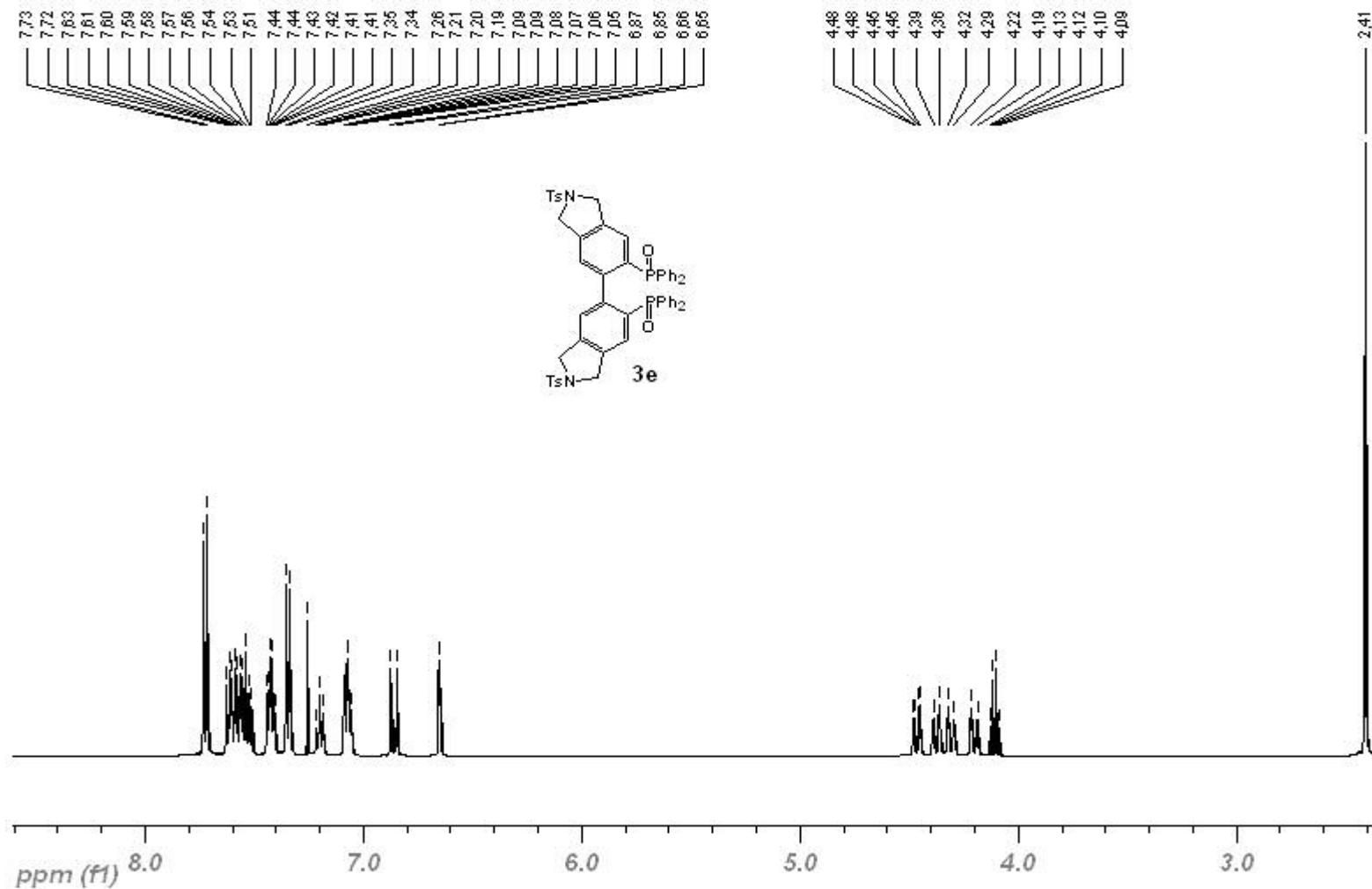
<sup>1</sup>H NMR Spectrum of 6,6-bis(diphenylphosphinoyl)-1,3,1',3'-tetrahydro[5,5']biindenyl-2,2,2',2'-tetracarboxylate (3d)



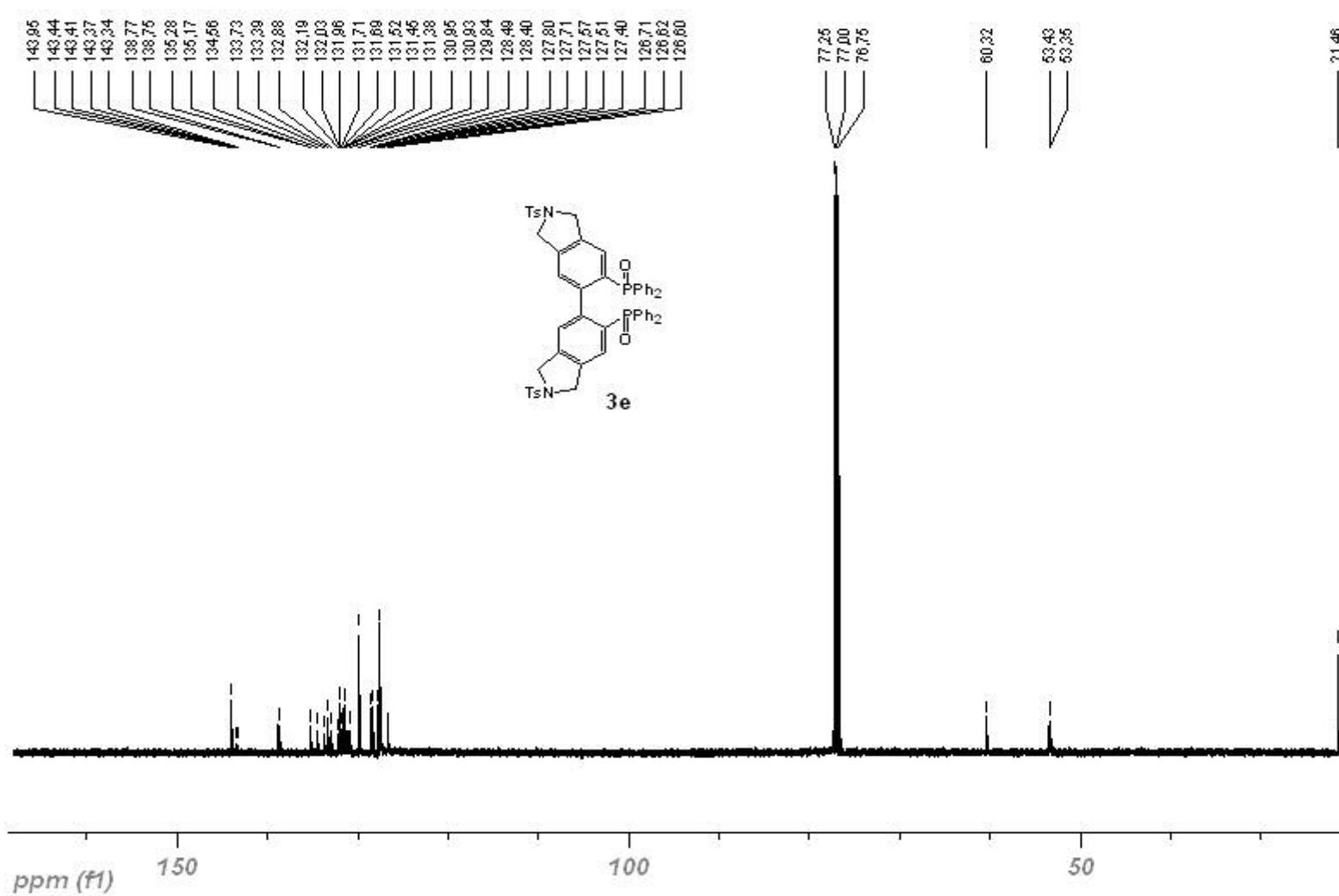
<sup>13</sup>C NMR Spectrum of 6,6-bis(diphenylphosphinoyl)-1,3,1',3'-tetrahydro[5,5']biindenyl-2,2,2',2'-tetracarboxylate (3d)



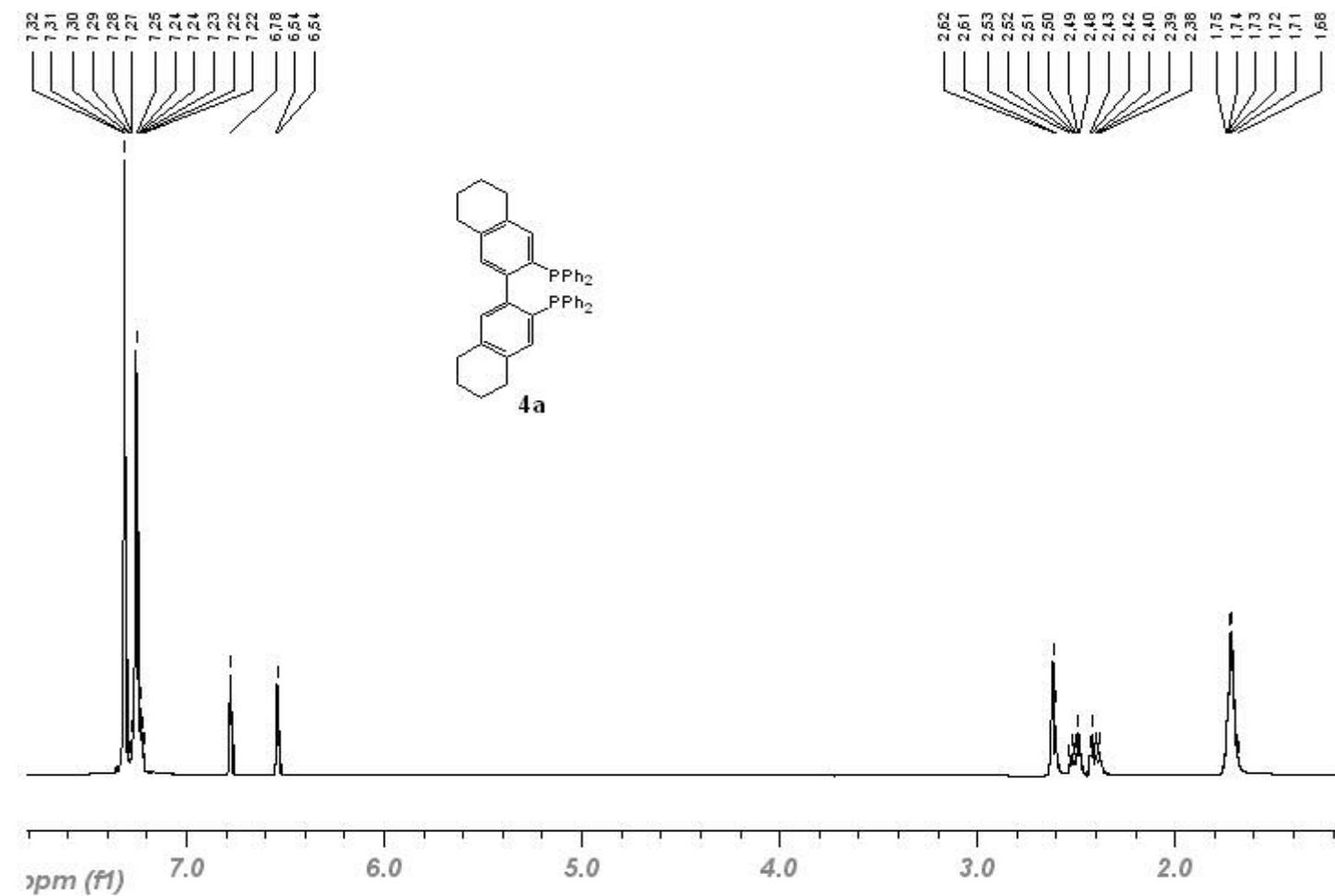
<sup>1</sup>H NMR Spectrum of 6,6'-bis(diphenylphosphinoyl)-2,2'-bis(4-methyl)benzenesulfonyl)-2,3,2',3'-tetrahydro-1*H*,1*H*-[5,5']biisoindole (3e)



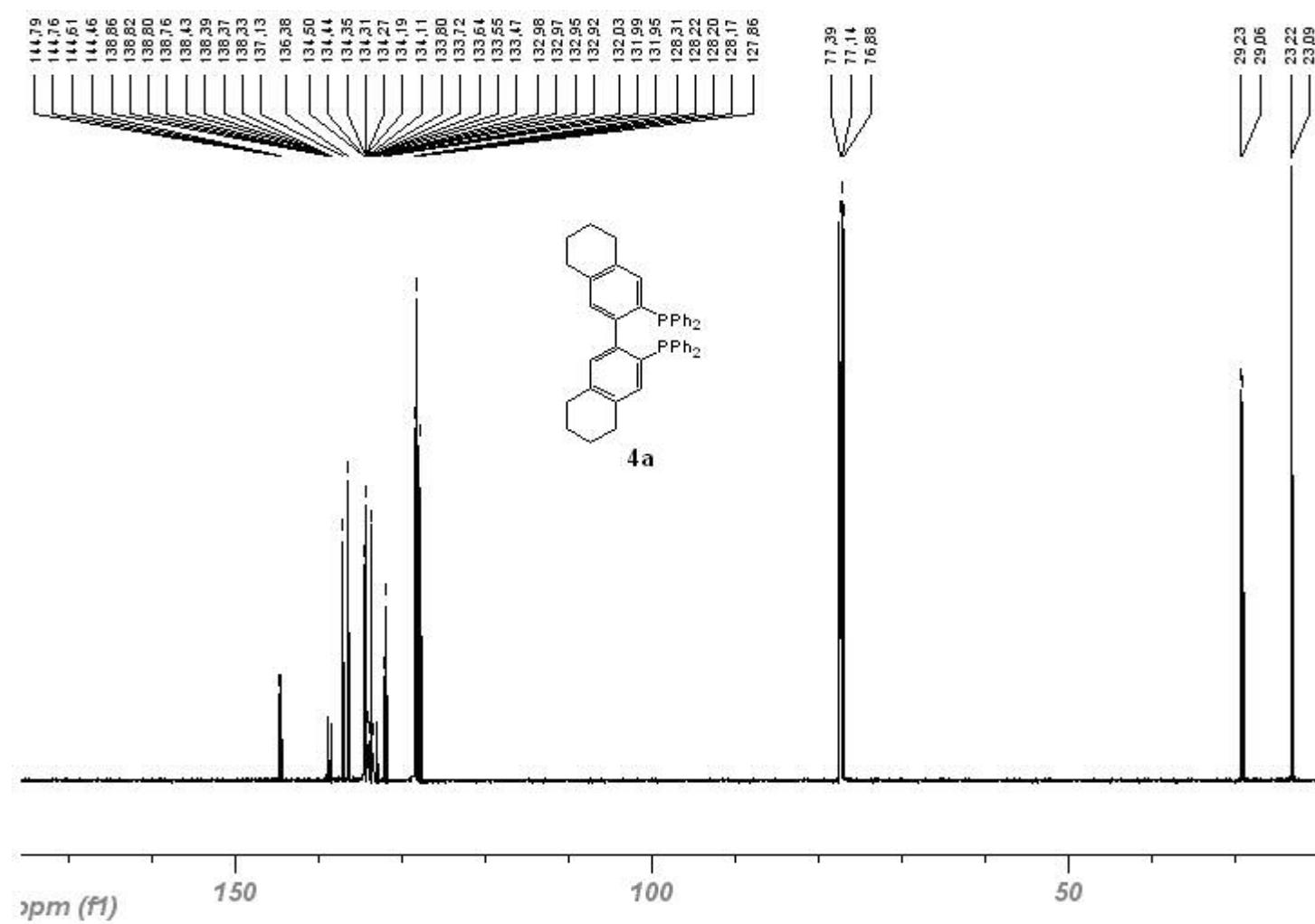
<sup>13</sup>C NMR Spectrum of 6,6'-bis(diphenylphosphinoyl)-2,2'-bis(4-methyl)benzenesulfonyl)-2,3,2',3'-tetrahydro-1H,1'H-[5,5']biisoindole (3e)



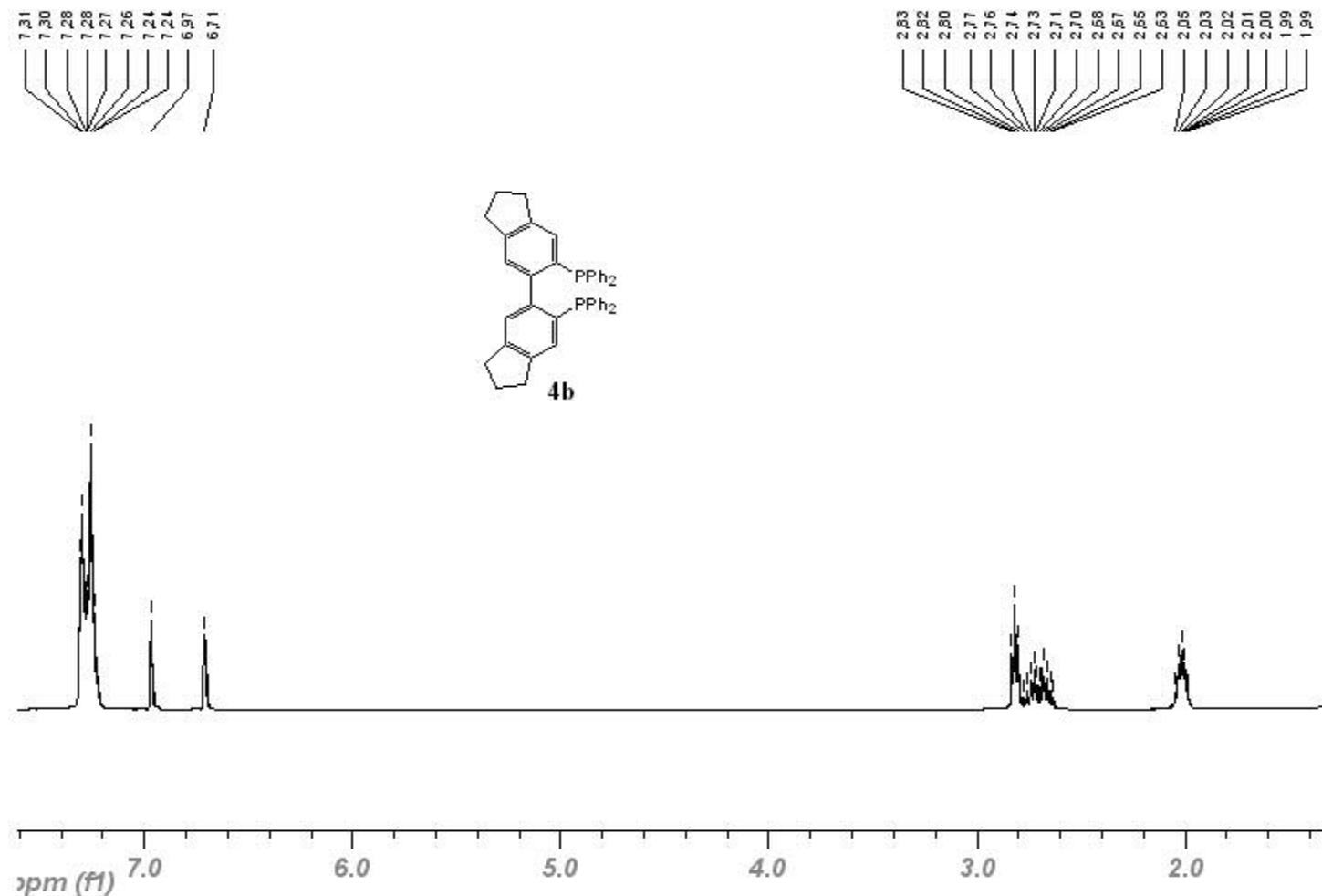
<sup>1</sup>H NMR Spectrum of 3,3'-bis(diphenylphosphanyl)-5,6,7,8,5',6',7',8'-octahydro[2,2']binaphthalene (4a)



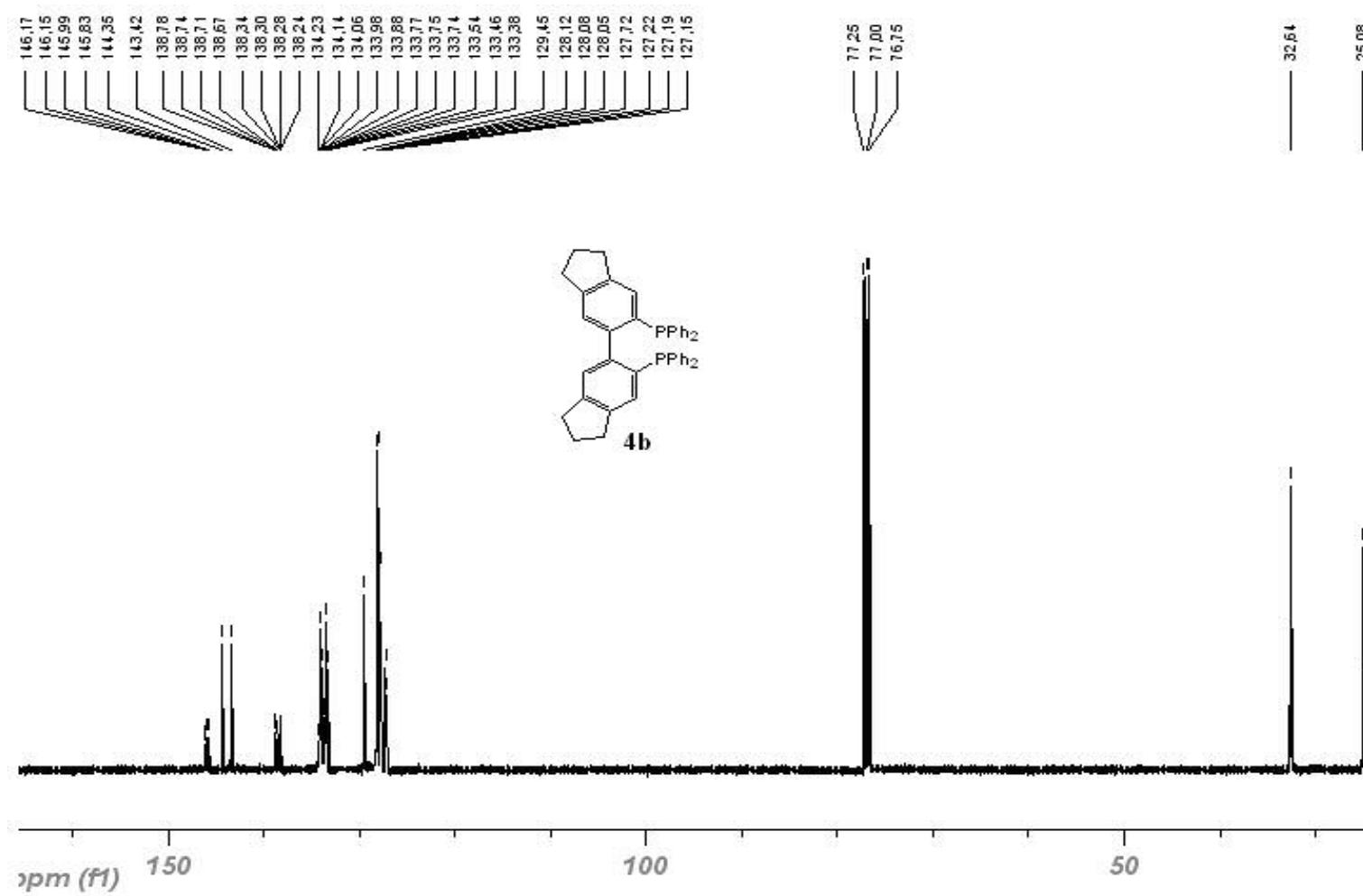
<sup>13</sup>C NMR Spectrum of 3,3'-bis(diphenylphosphanyl)-5,6,7,8,5',6',7',8'-octahydro[2,2']binaphthalene (4a)



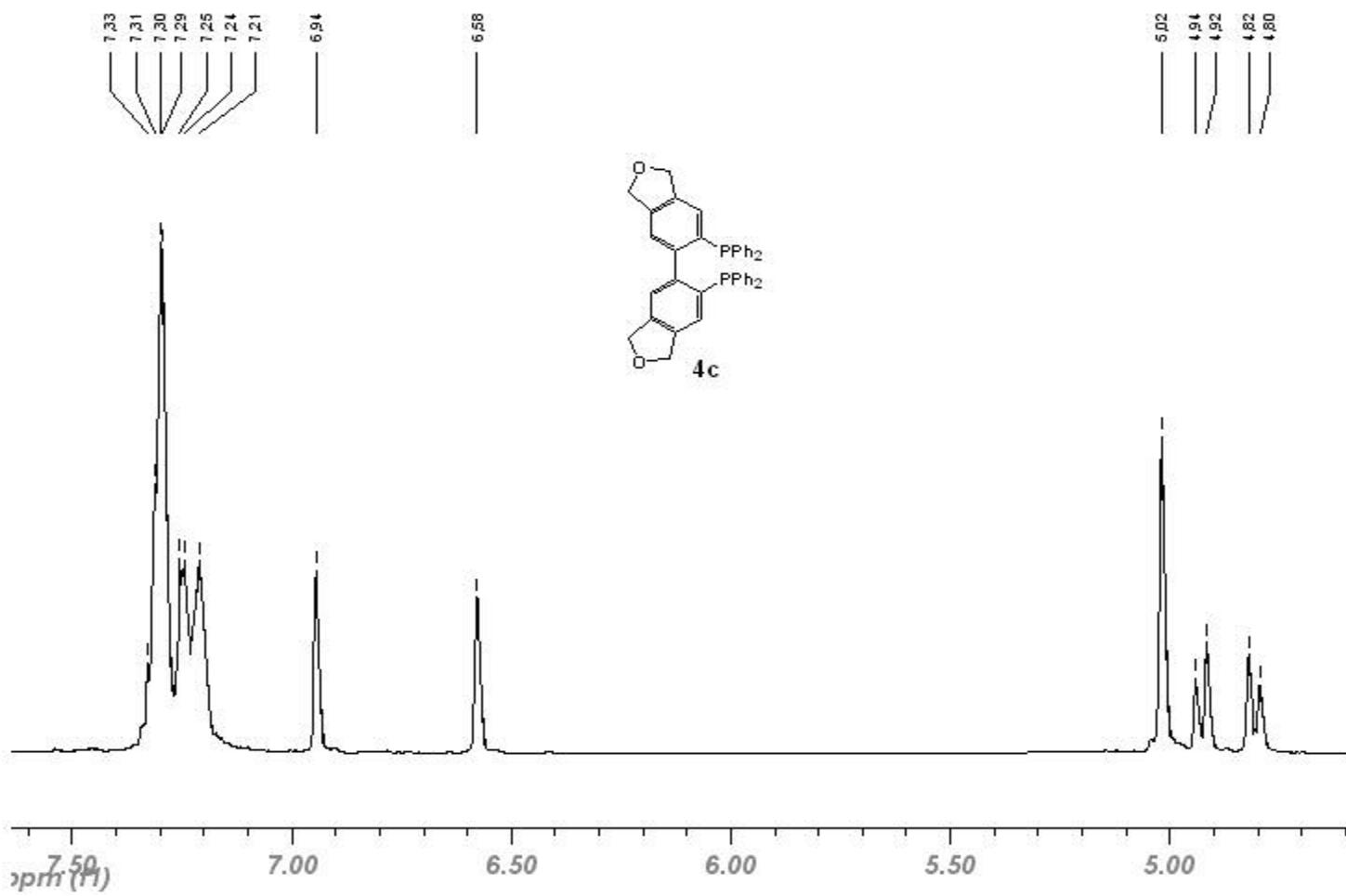
<sup>1</sup>H NMR Spectrum of 6,6'-bis(diphenylphosphanyl)-2,3,2',3'-tetrahydro-1*H*,1*H*-[5,5']biindene (4b)



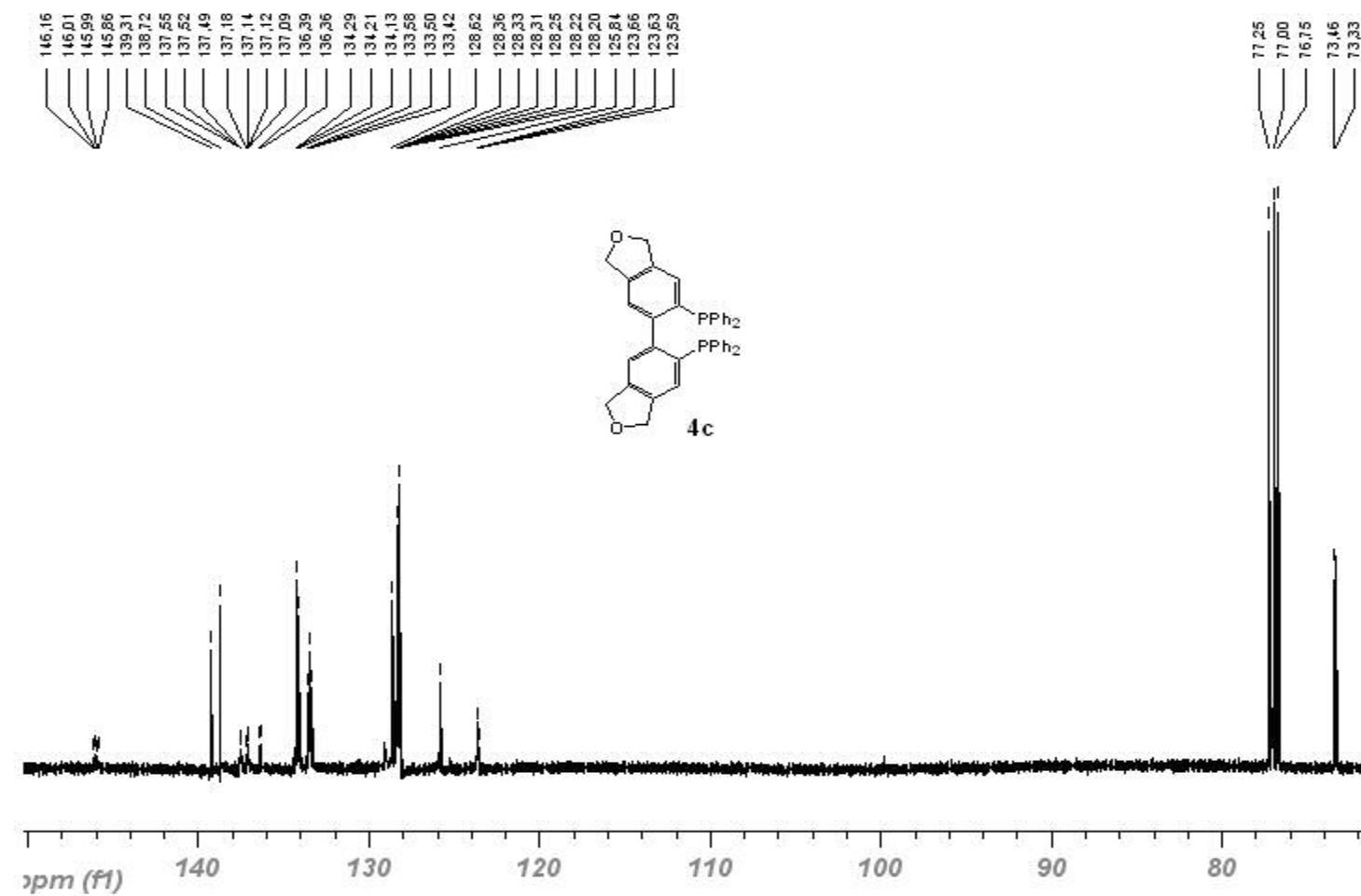
<sup>13</sup>C NMR Spectrum of 6,6'-bis(diphenylphosphanyl)-2,3,2',3'-tetrahydro-1H,1'H-[5,5']biindene (4b)



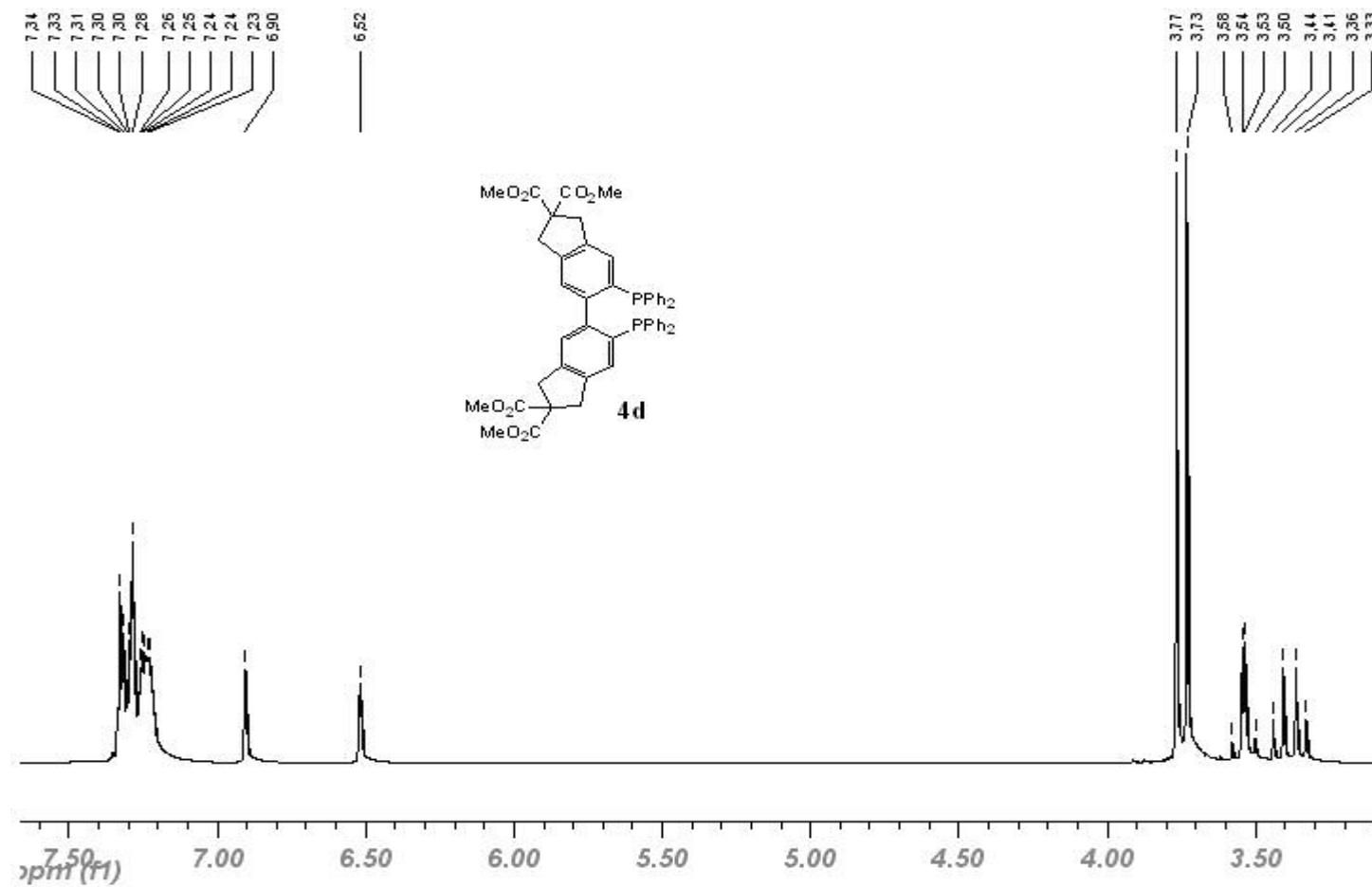
<sup>1</sup>H NMR Spectrum of 6,6'-bis(diphenylphosphanyl)-1,3,1',3'-tetrahydro[5,5']biisobenzofuran (4c)



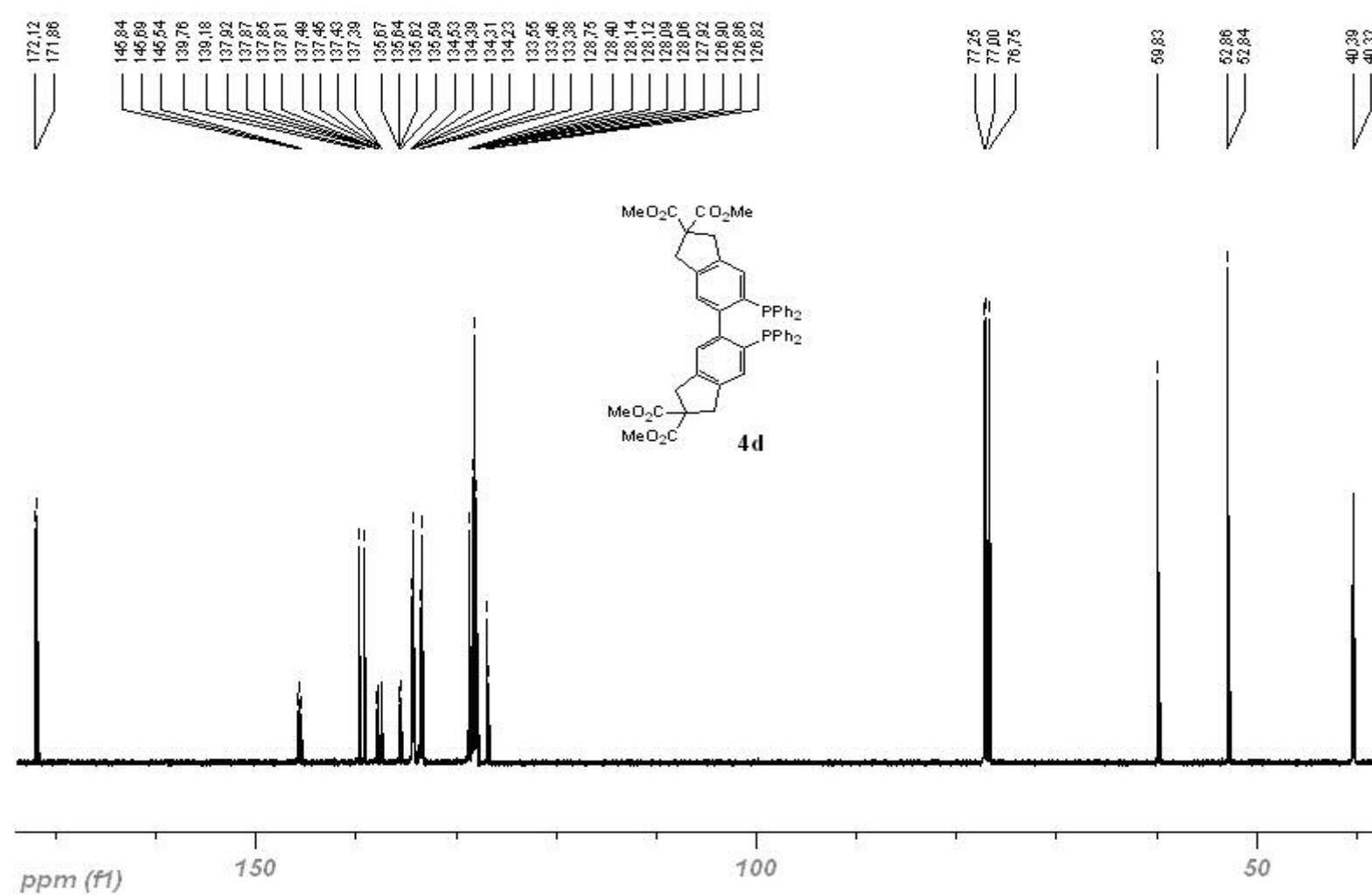
<sup>13</sup>C NMR Spectrum of 6,6'-bis(diphenylphosphanyl)-1,3,1',3'-tetrahydro[5,5']biisobenzofuran (4c)



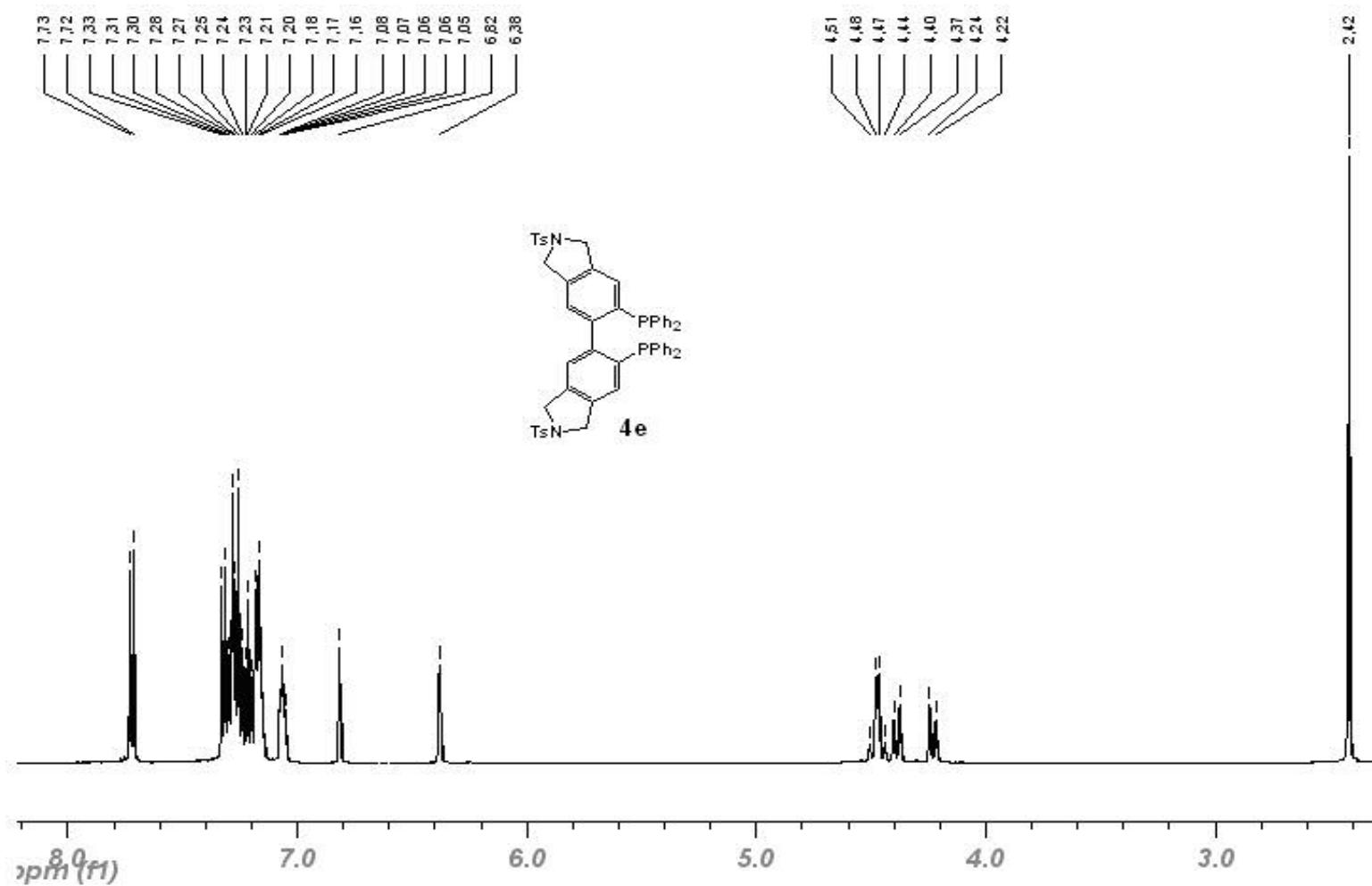
<sup>1</sup>H NMR Spectrum of 6,6-bis(diphenylphosphanyl)-1,3,1',3'-tetrahydro[5,5']biindenyl-2,2,2',2'-tetracarboxylate (4d)



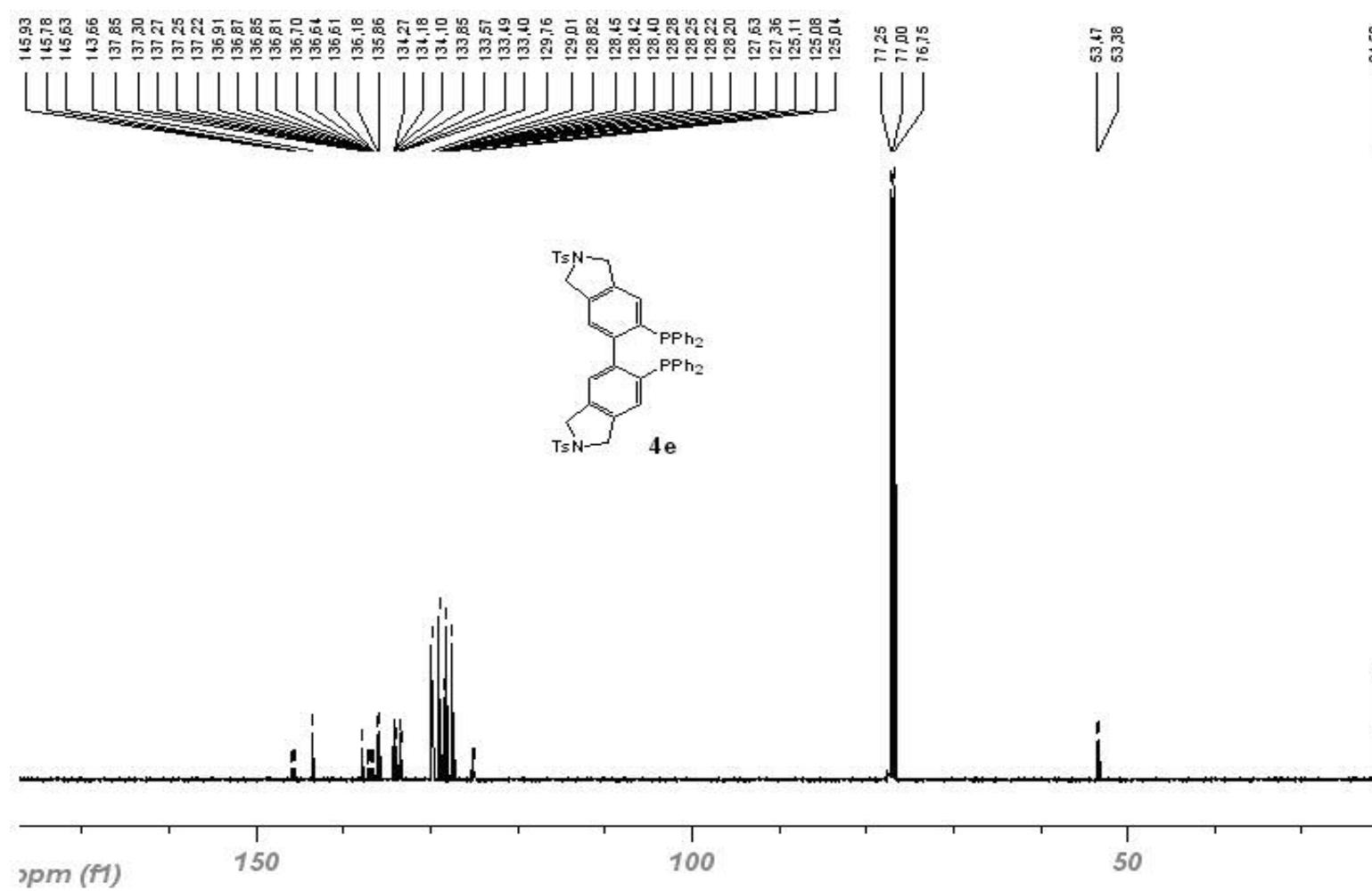
<sup>13</sup>C NMR Spectrum of 6,6-bis(diphenylphosphanyl)-1,3,1',3'-tetrahydro[5,5']biindenyl-2,2,2',2'-tetracarboxylate (4d)



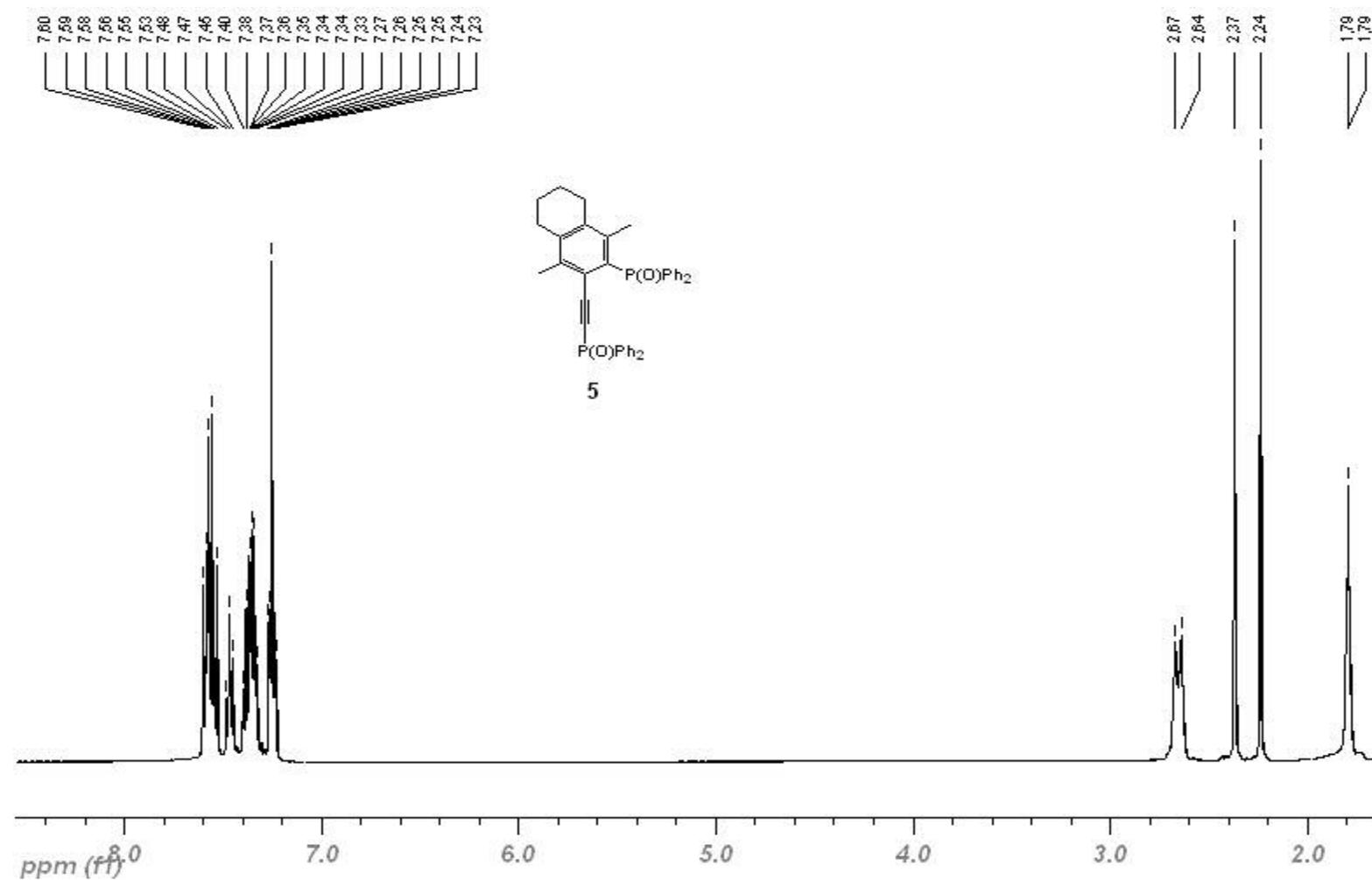
<sup>1</sup>H NMR Spectrum of 6,6'-bis(diphenylphosphanyl)-2,2'-bis(4-methyl)benzenesulfonyl)-2,3,2',3'-tetrahydro-1*H*,1*H*-[5,5']biisoindole (4e)



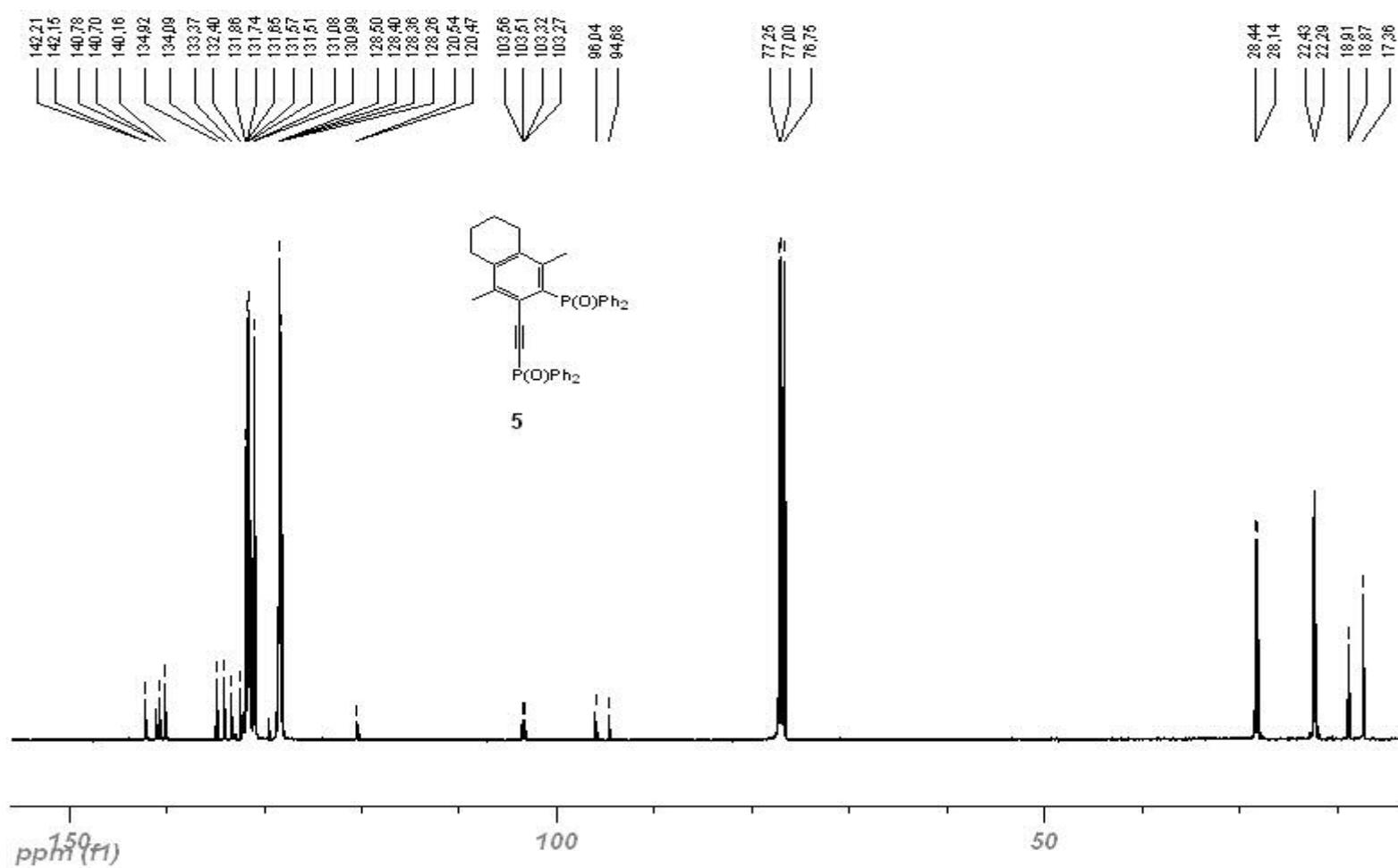
<sup>13</sup>C NMR Spectrum of 6,6'-bis(diphenylphosphanyl)-2,2'-bis(4-methyl)benzenesulfonyl)-2,3,2',3'-tetrahydro-1*H*,1*H*-[5,5']biisoindole (4e)



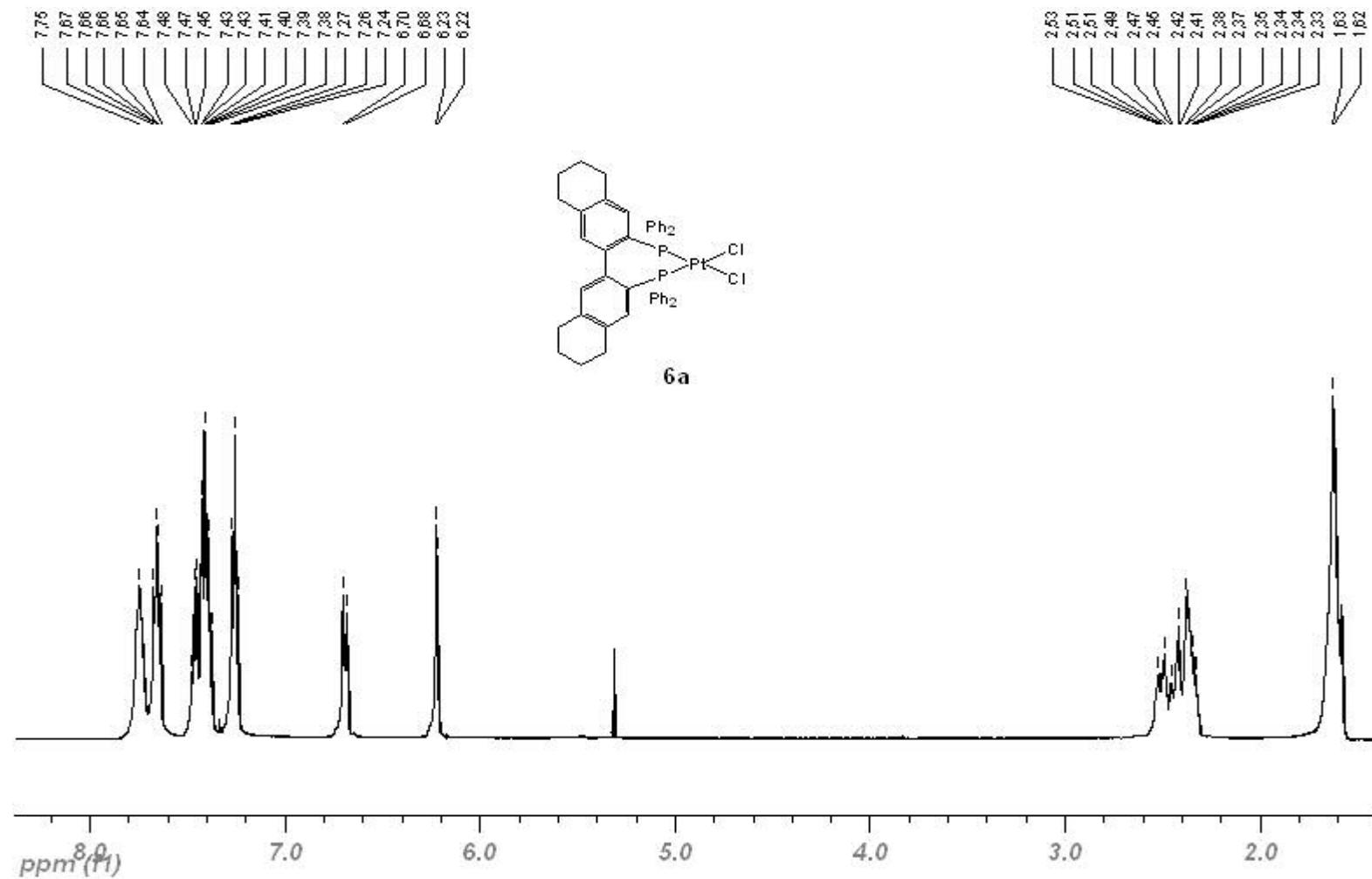
<sup>1</sup>H NMR Spectrum of Mono Cycloaddition Adduct 5



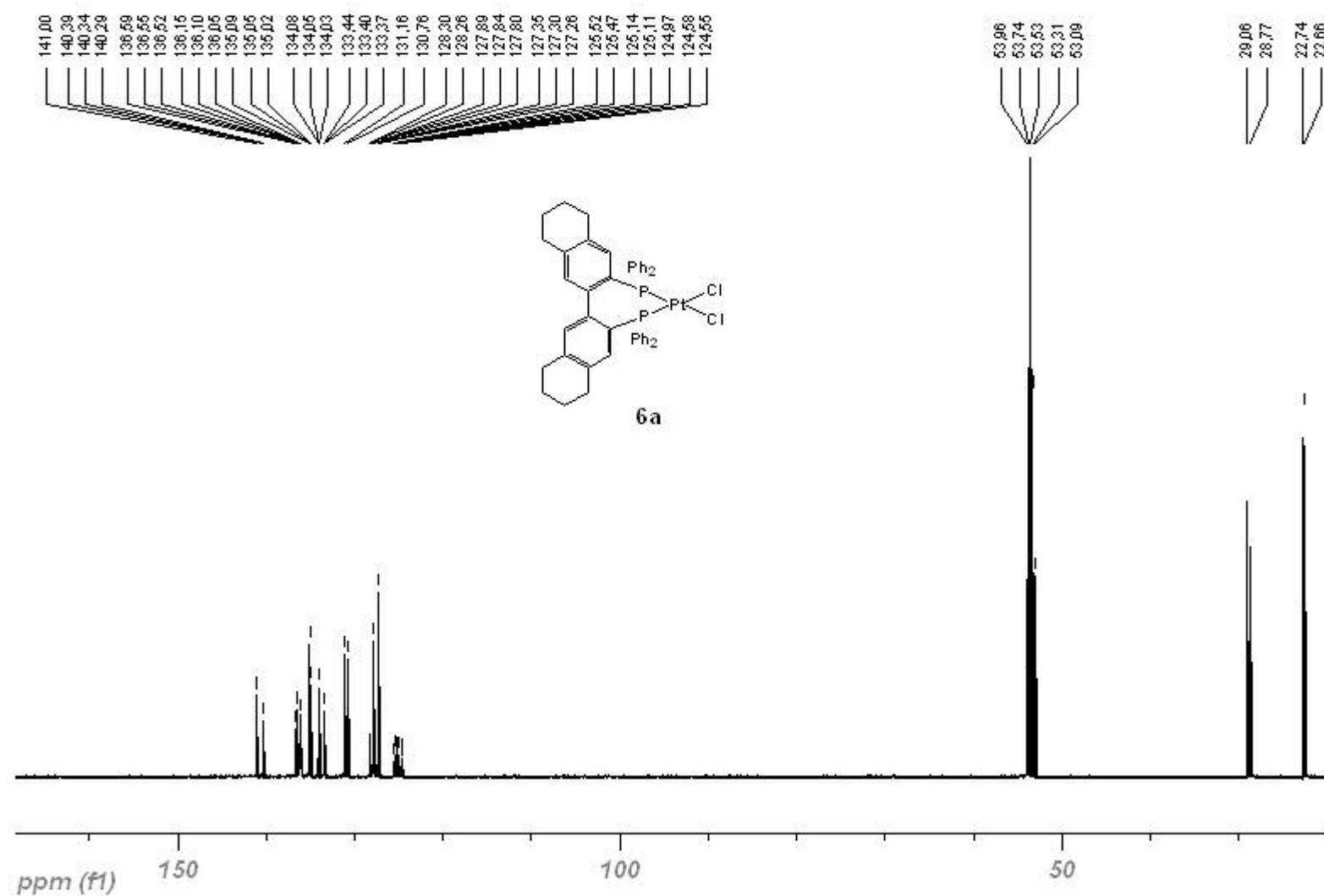
<sup>13</sup>C NMR Spectrum of Mono Cycloaddition Adduct 5



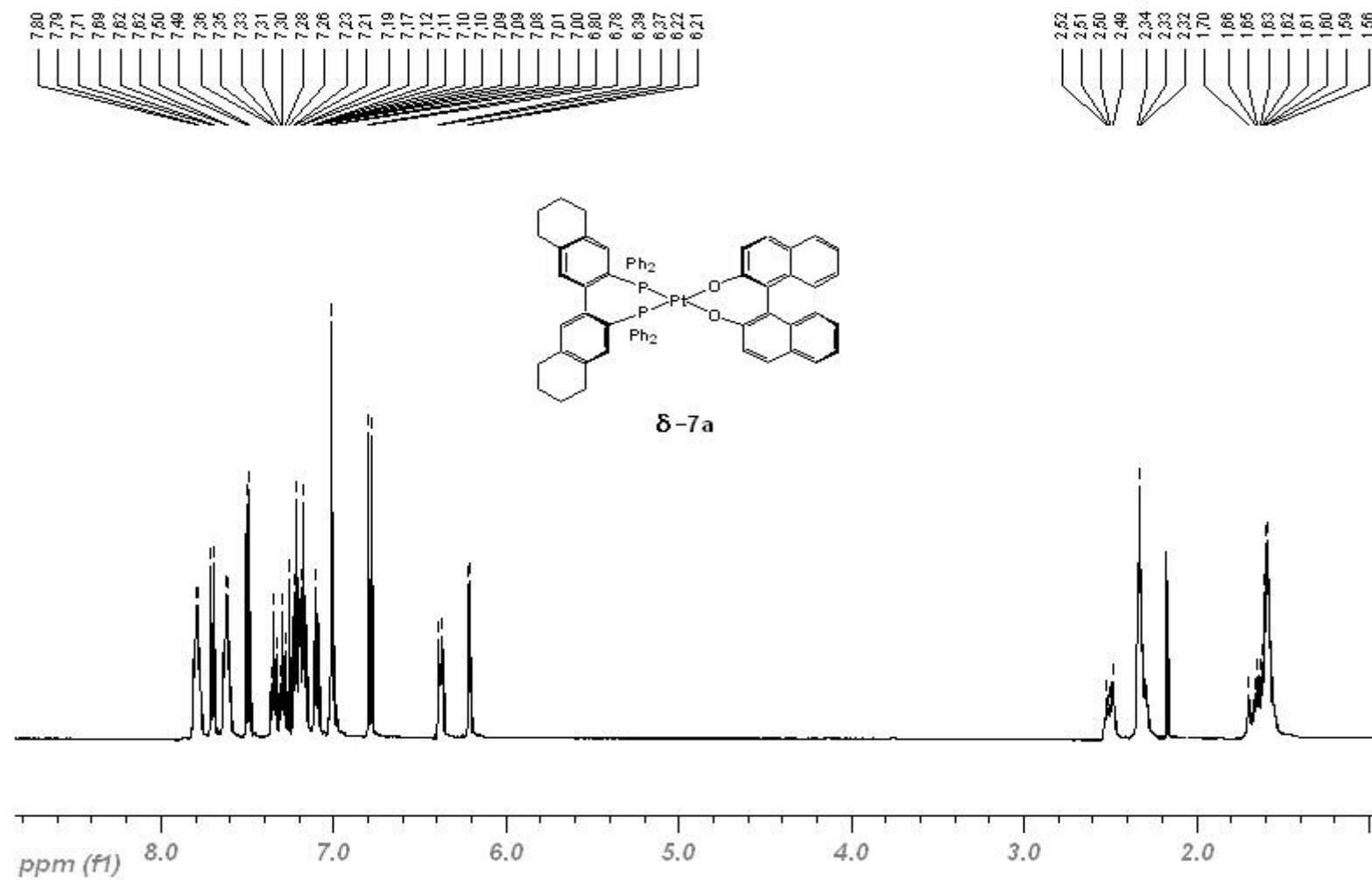
**<sup>1</sup>H NMR Spectrum of Dichloro[3,3'-bis(diphenylphosphanyl)-5,6,7,8,5',6',7',8'-octahydro[2,2']binaphthalene]platinum (6a)**



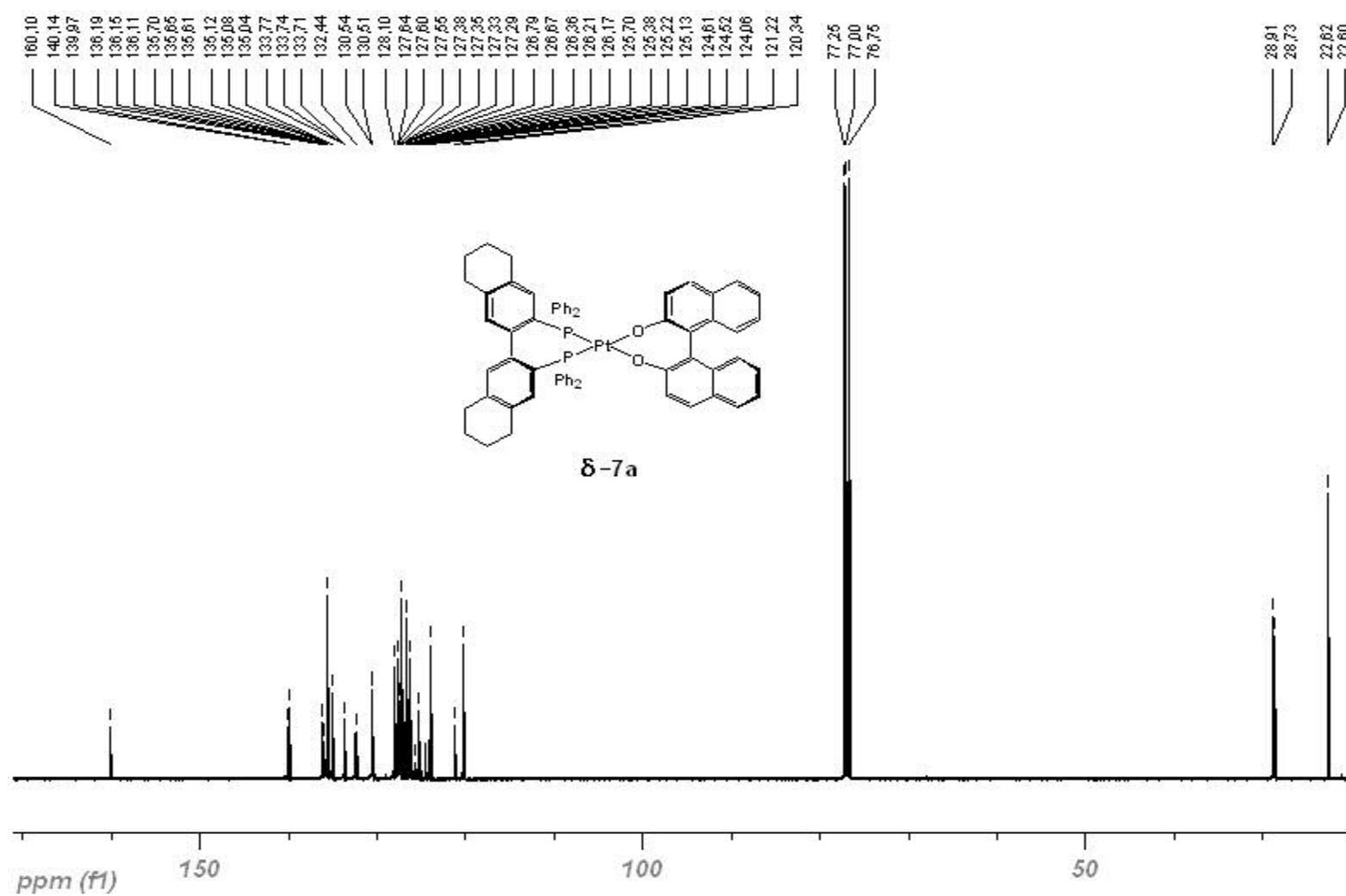
<sup>13</sup>C NMR Spectrum of Dichloro[3,3'-bis(diphenylphosphanyl)-5,6,7,8,5',6',7',8'-octahydro[2,2']binaphthalene]platinum (6a)



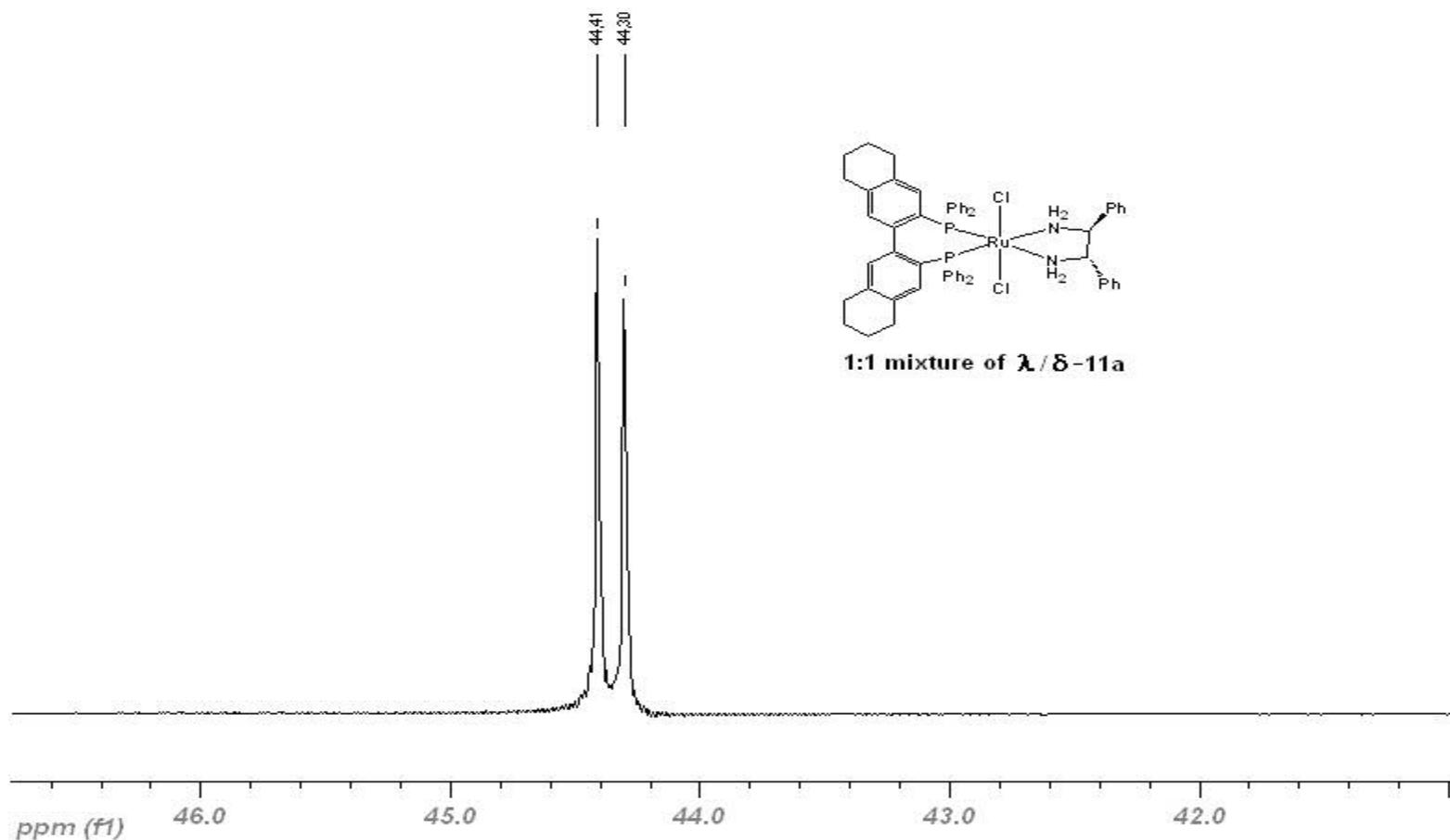
<sup>1</sup>H NMR Spectrum of  $\delta$ -[{3,3'-bis(diphenylphosphanyl)-5,6,7,8,5',6',7',8'-octahydro[2,2']binaphthalene}platinum{(S)-BINOL}] ( $\delta$ -7a)



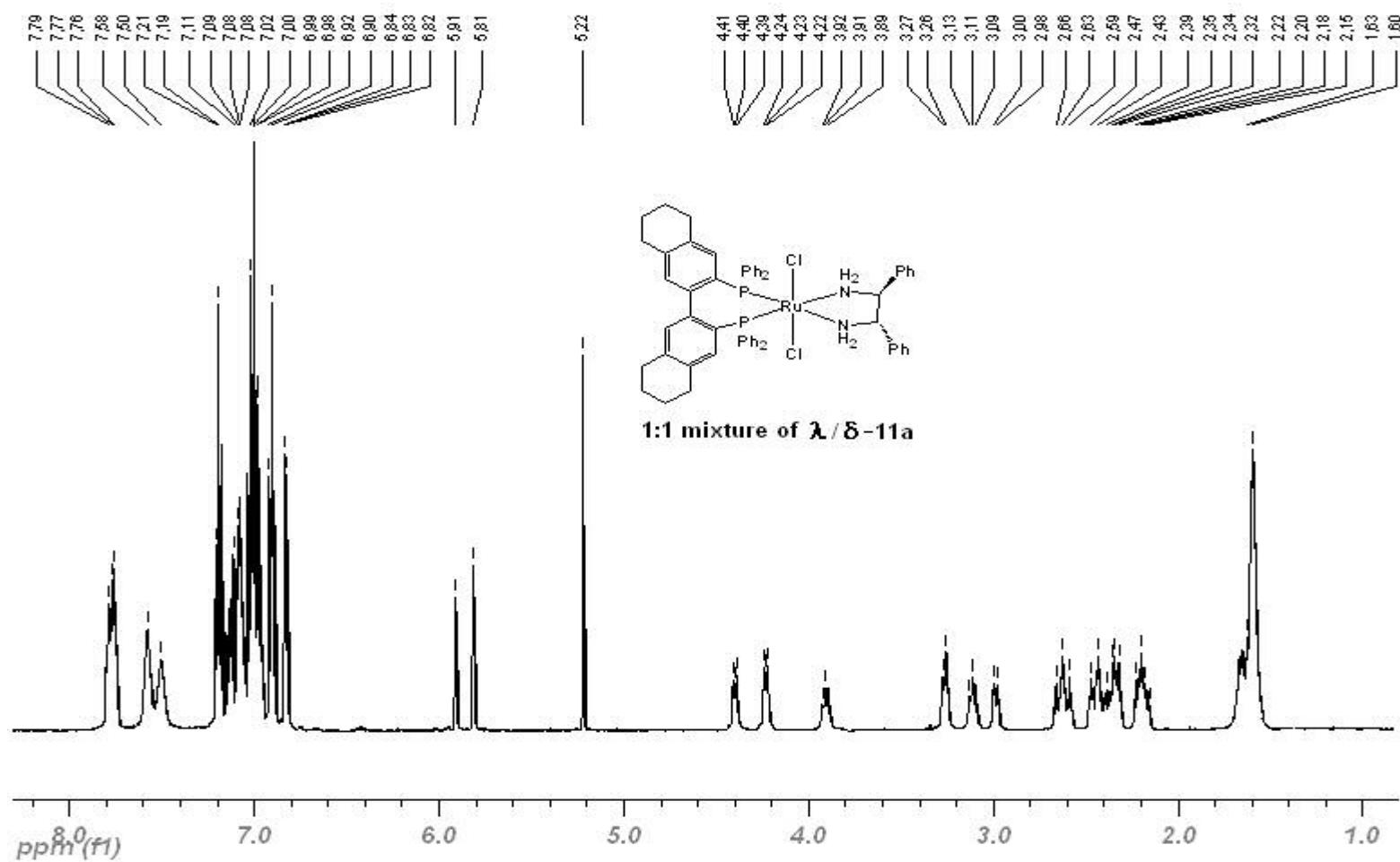
<sup>13</sup>C NMR Spectrum of  $\delta$ -[3,3'-bis(diphenylphosphanyl)-5,6,7,8,5',6',7',8'-octahydro[2,2']binaphthalene]platinum{(S)-BINOL}] ( $\delta$ -7a)



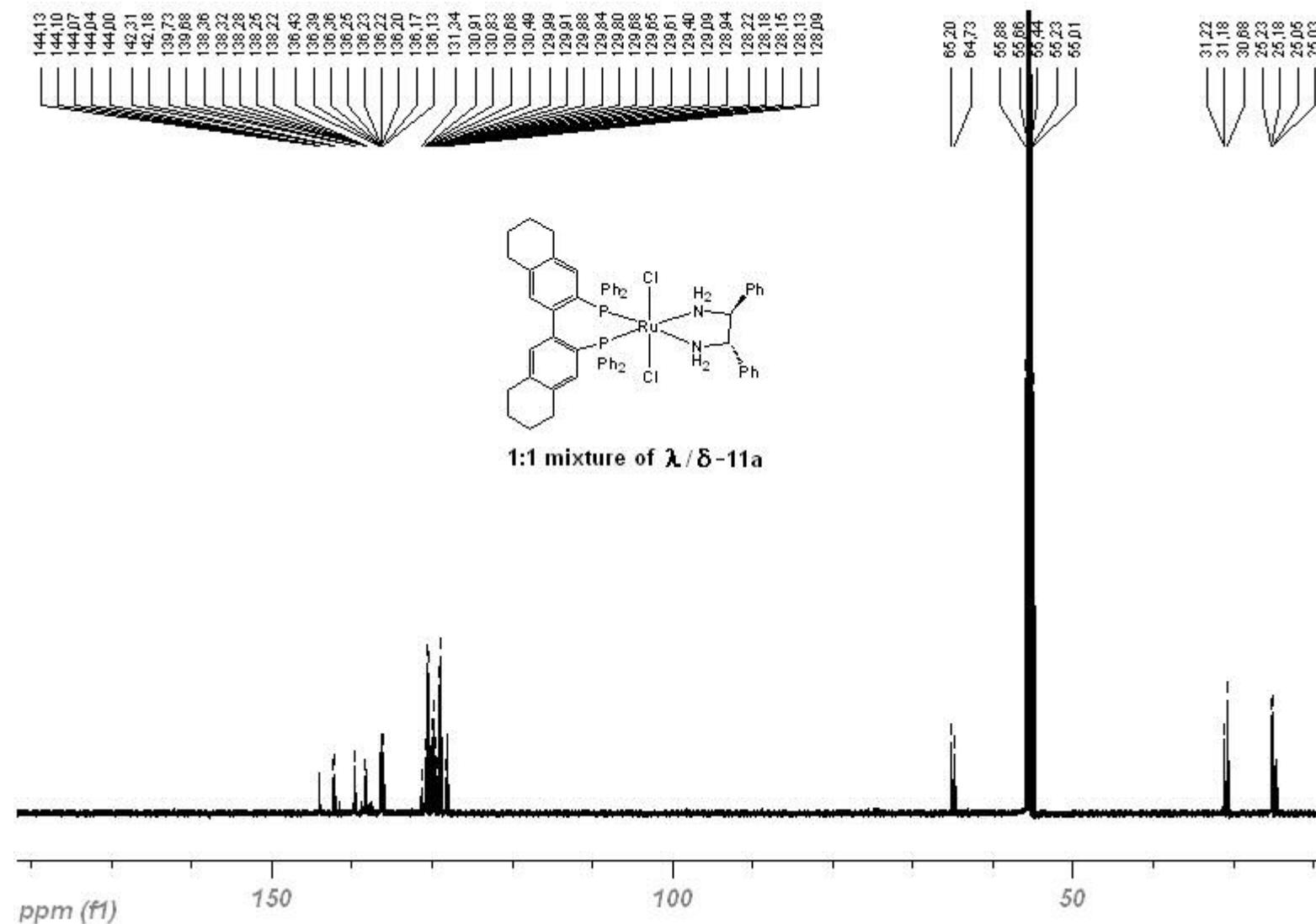
<sup>31</sup>P NMR Spectrum of *trans*-[RuCl<sub>2</sub>{3,3'-bis(diphenylphosphanyl)-5,6,7,8,5',6',7',8'-octahydro[2,2']binaphthalene}{(S,S)-DPEN}] (11a)



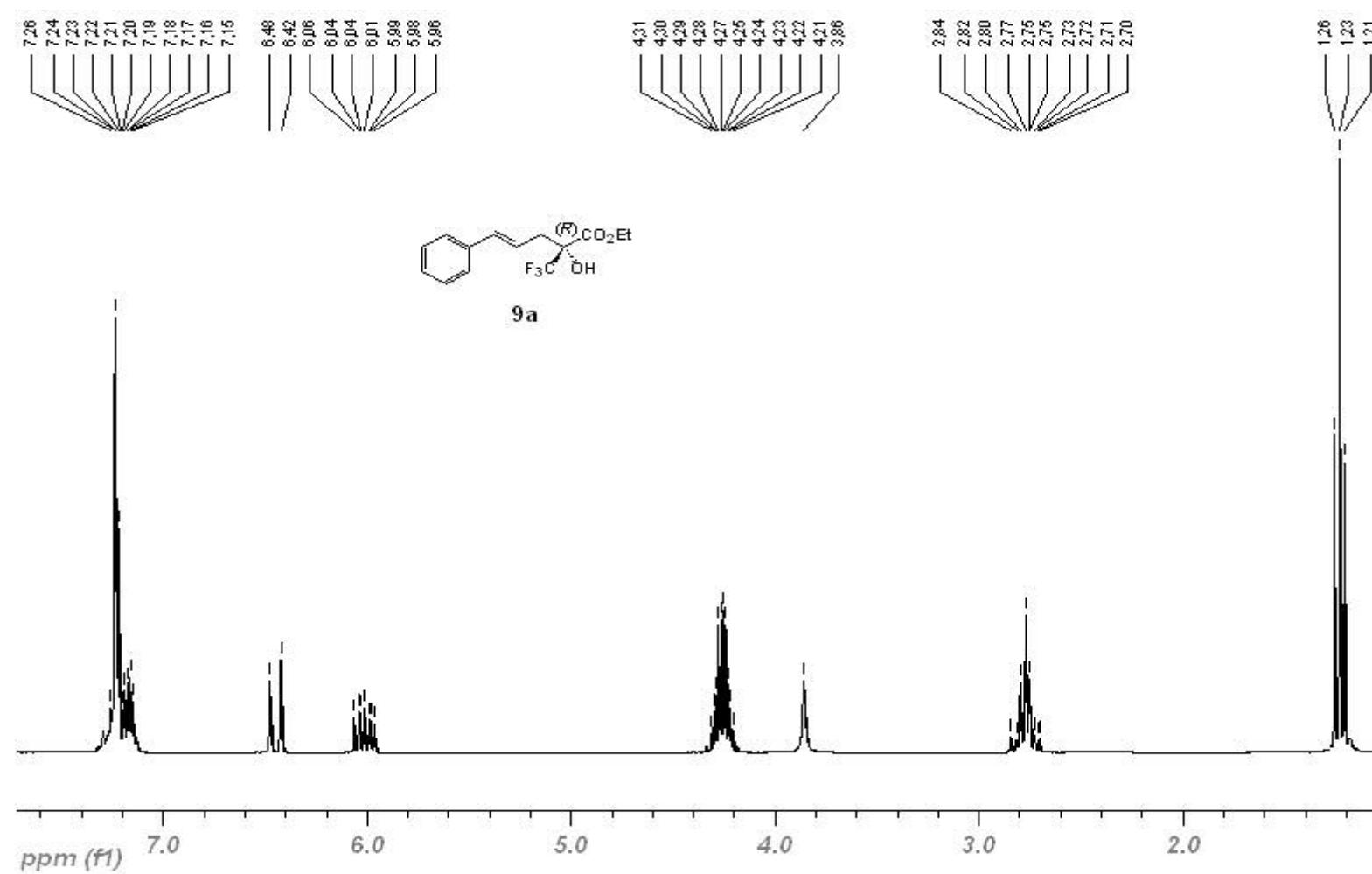
<sup>1</sup>H NMR Spectrum of *trans*-[RuCl<sub>2</sub>{3,3'-bis(diphenylphosphanyl)-5,6,7,8,5',6',7',8'-octahydro[2,2']binaphthalene}{(S,S)-DPEN}] (11a)



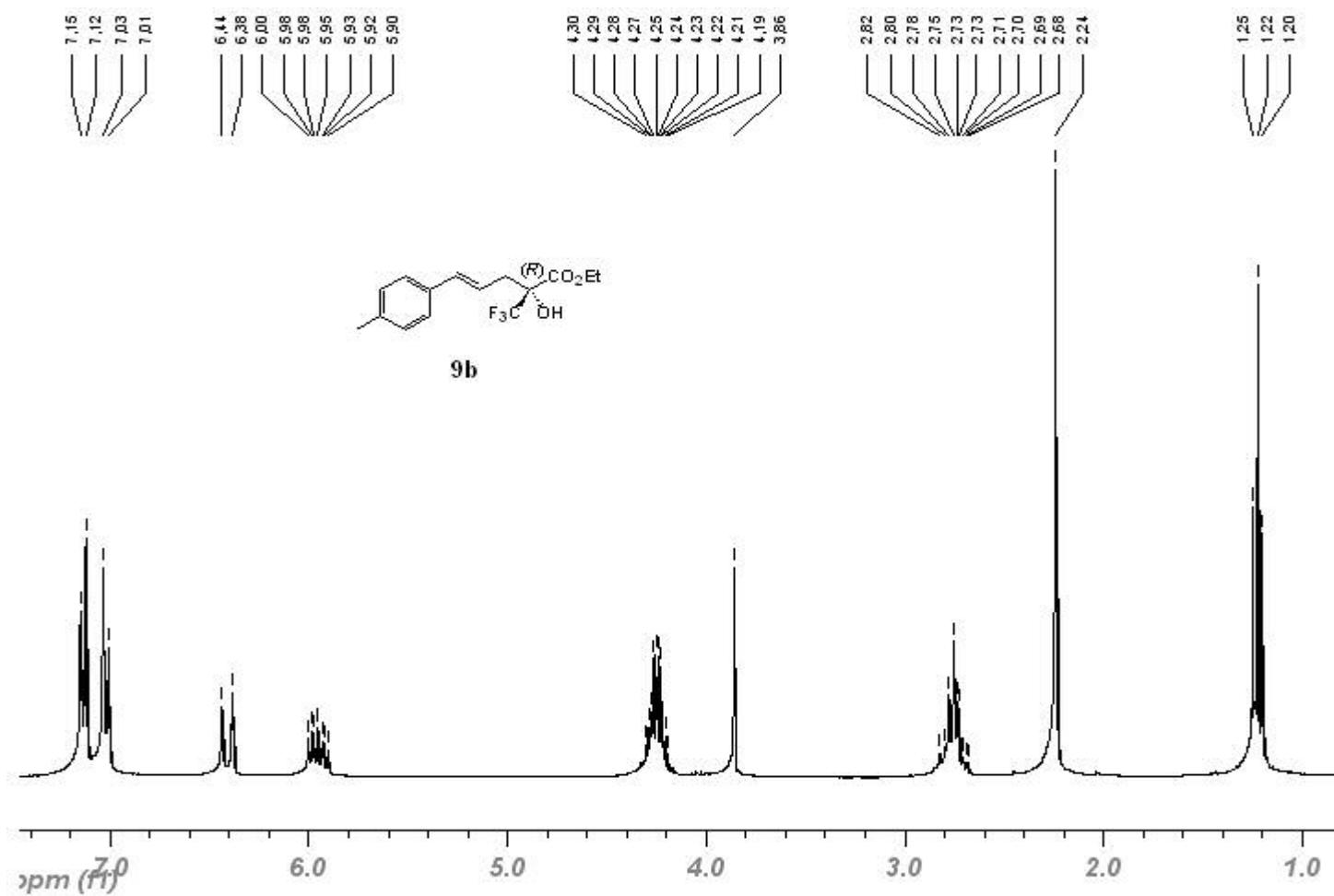
<sup>13</sup>C NMR Spectrum of *trans*-[RuCl<sub>2</sub>{3,3'-bis(diphenylphosphanyl)-5,6,7,8,5',6',7',8'-octahydro[2,2']binaphthalene}{(S,S)-DPEN}] (11a)



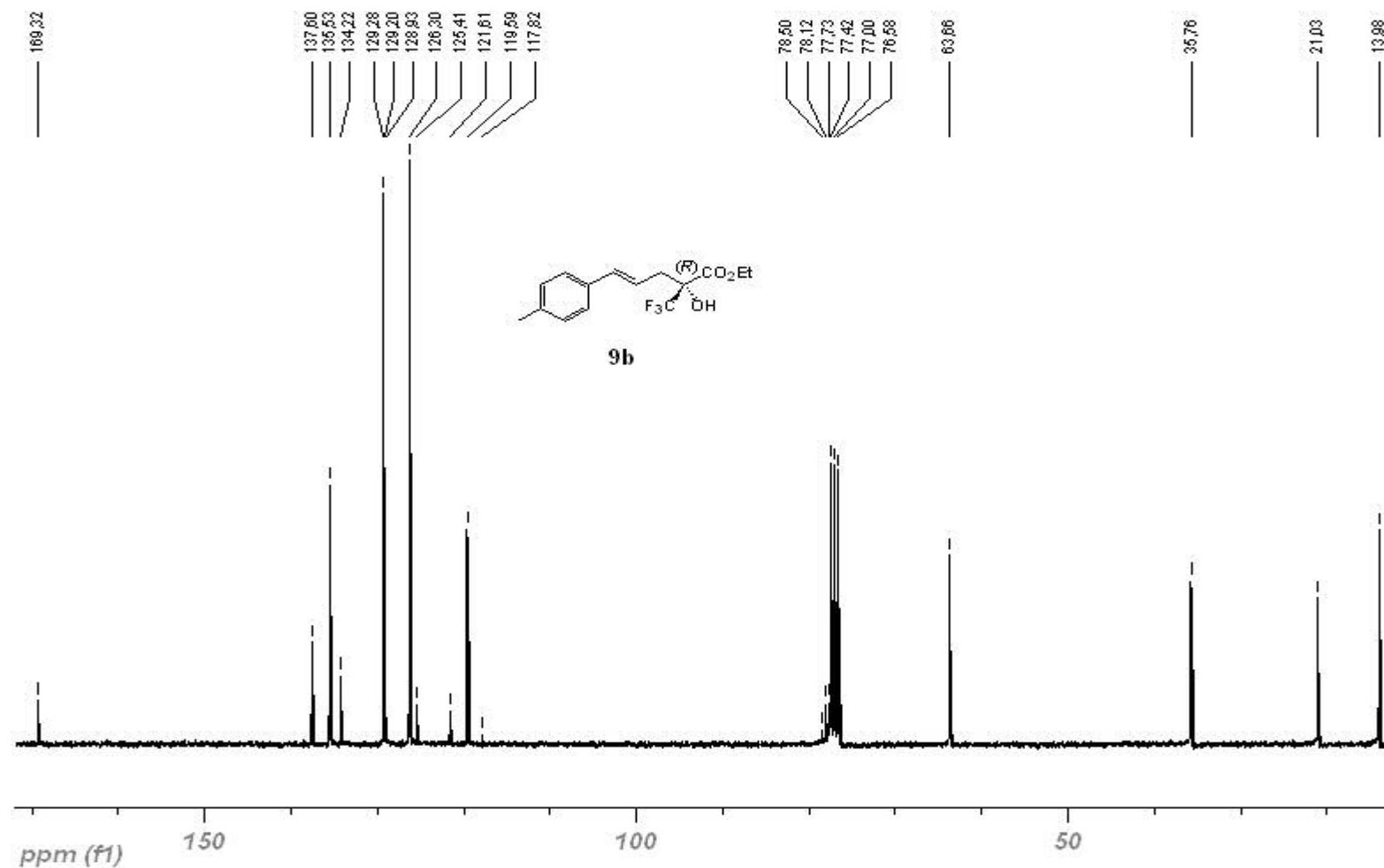
<sup>1</sup>H NMR Spectrum of Ethyl *E*-2-(trifluoromethyl)-2-hydroxy-5-phenylpent-4-enoate (9a)



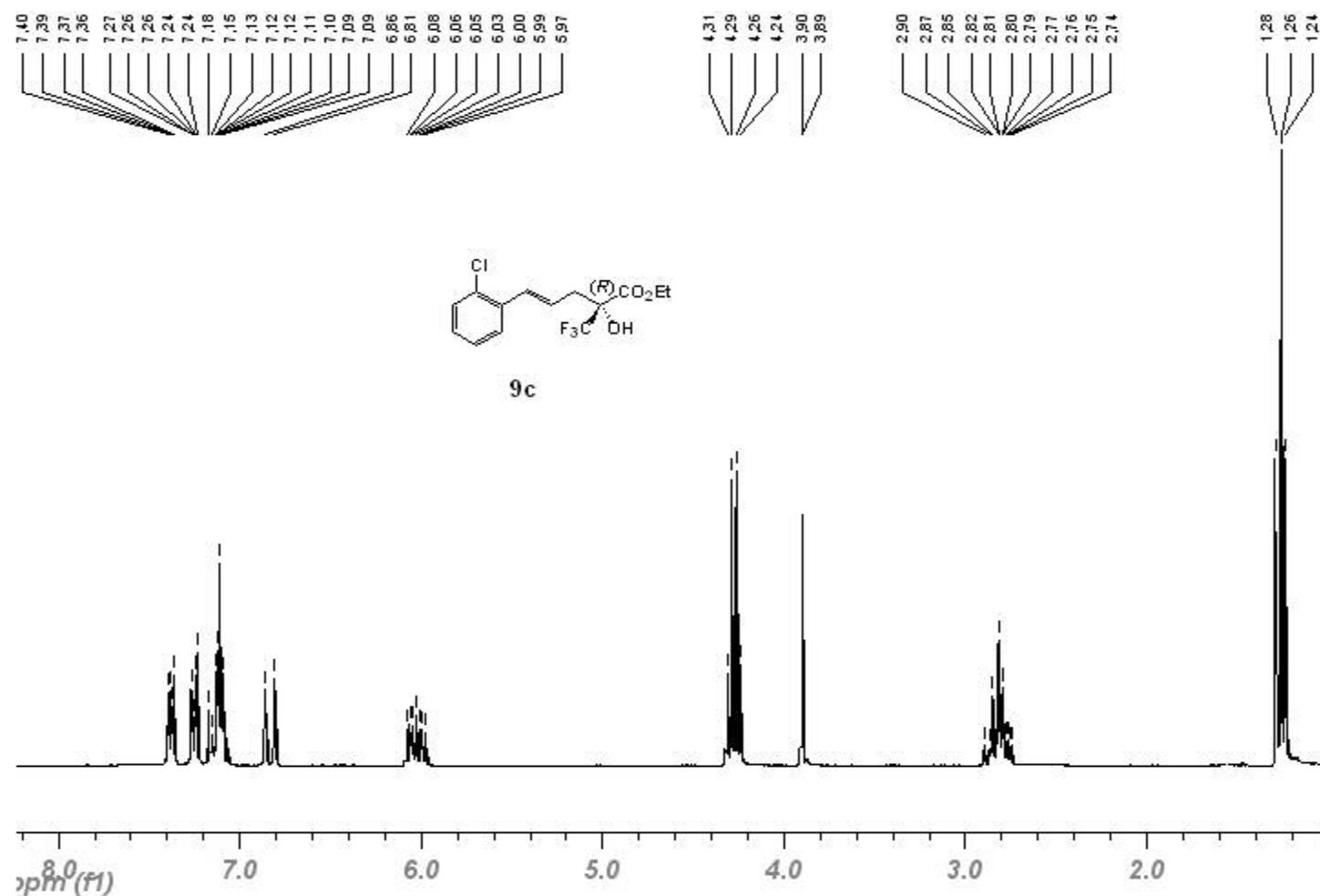
<sup>1</sup>H NMR Spectrum of Ethyl *E*-2-(trifluoromethyl)-2-hydroxy-5-*p*-tolylpent-4-enoate (9b)



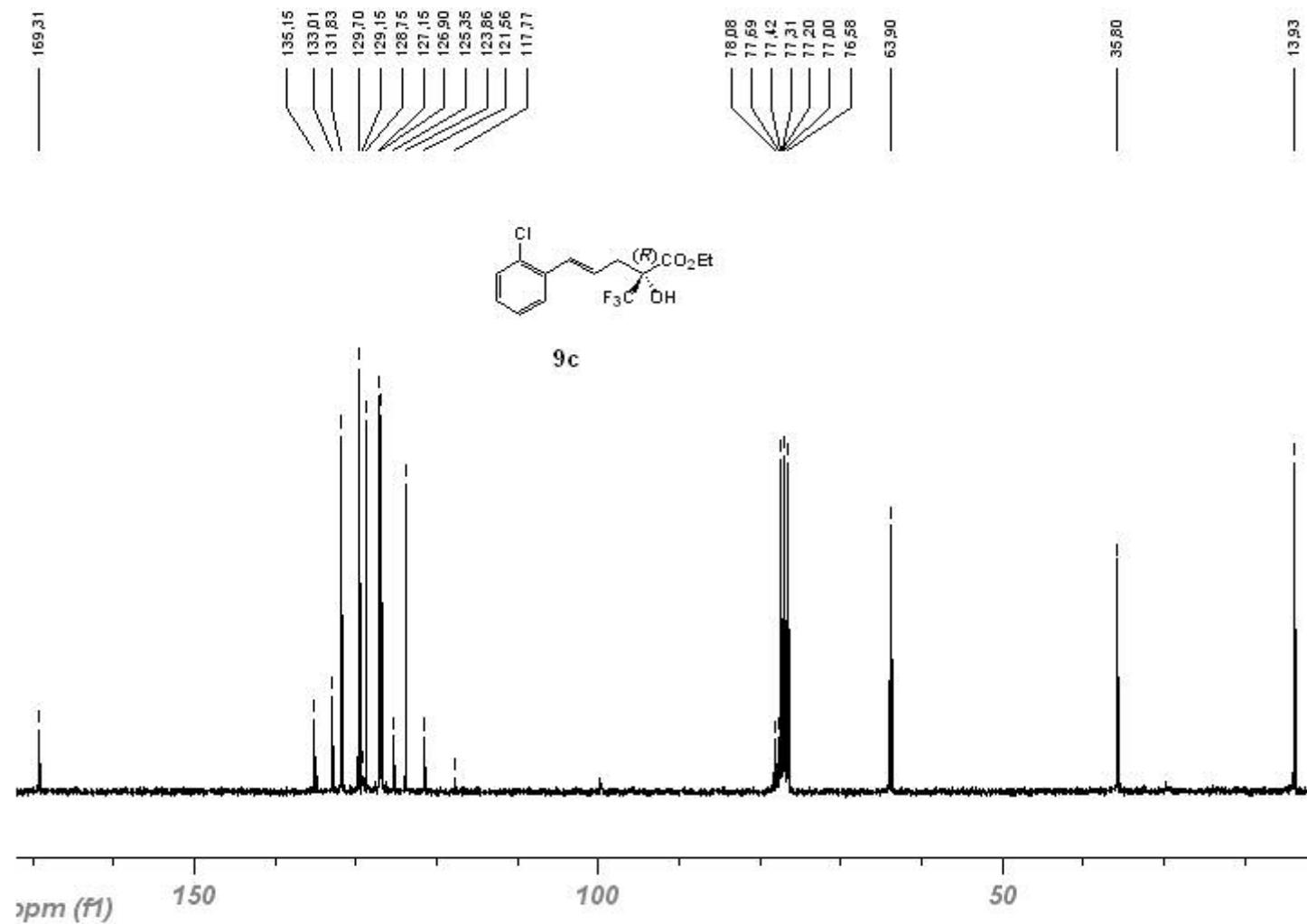
<sup>13</sup>C NMR Spectrum of Ethyl *E*-2-(trifluoromethyl)-2-hydroxy-5-*p*-tolylpent-4-enoate (9b)



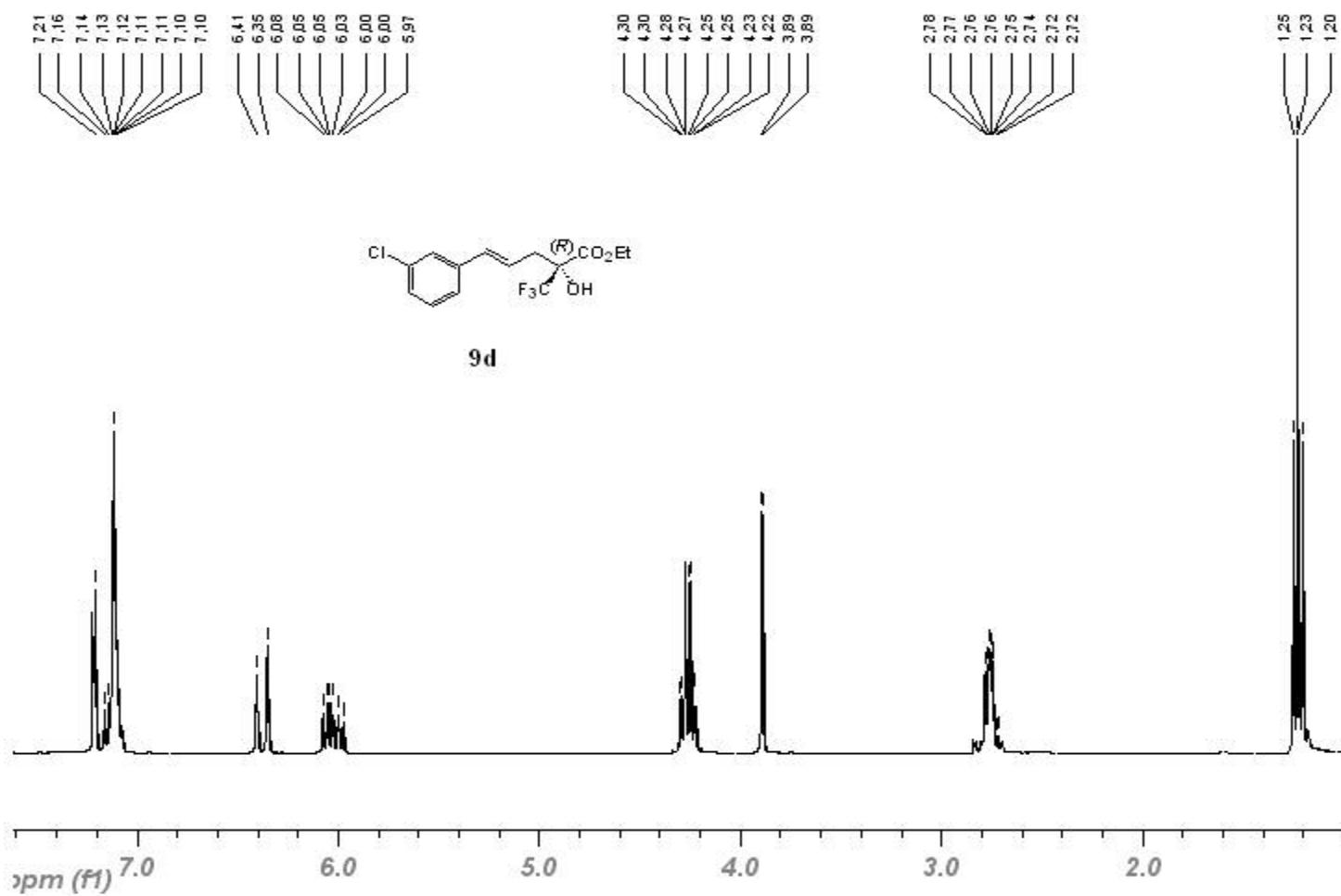
<sup>1</sup>H NMR Spectrum of Ethyl *E*-2-(trifluoromethyl)-2-hydroxy-5-(2-chlorophenyl)pent-4-enoate (9c)



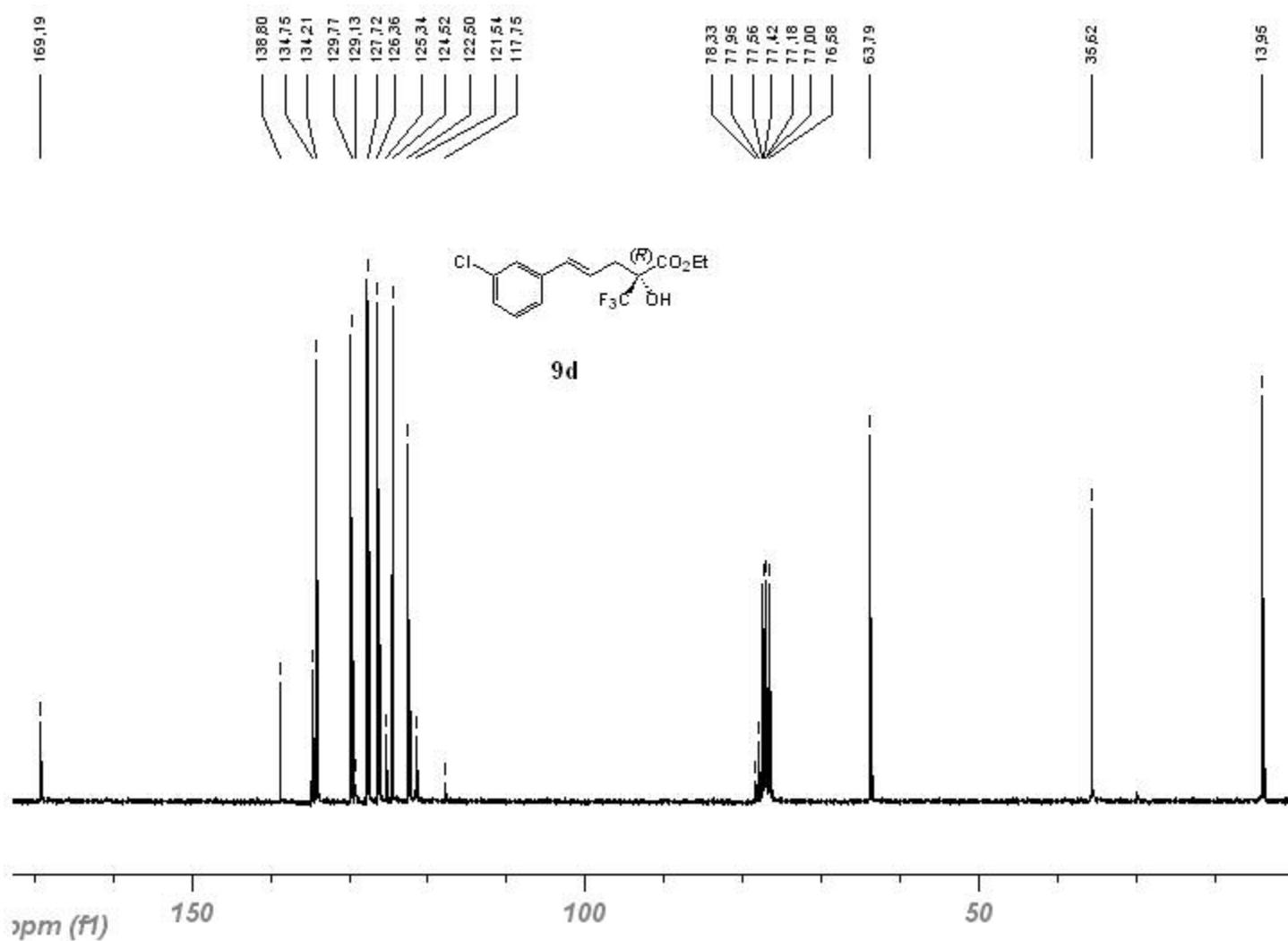
<sup>13</sup>C NMR Spectrum of Ethyl *E*-2-(trifluoromethyl)-2-hydroxy-5-(2-chlorophenyl)pent-4-enoate (9c)



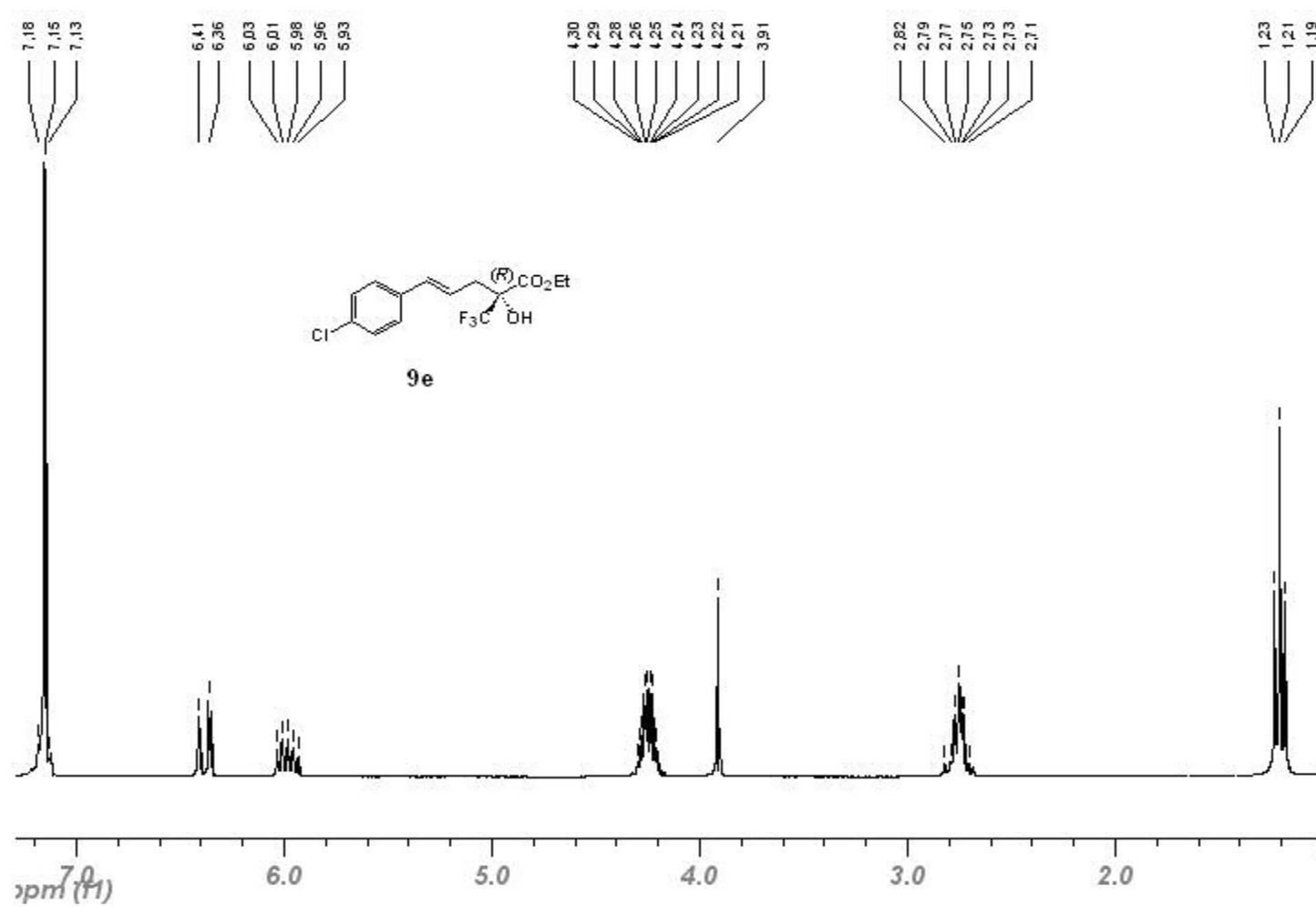
<sup>1</sup>H NMR Spectrum of Ethyl *E*-2-(trifluoromethyl)-2-hydroxy-5-(3-chlorophenyl)pent-4-enoate (9d)



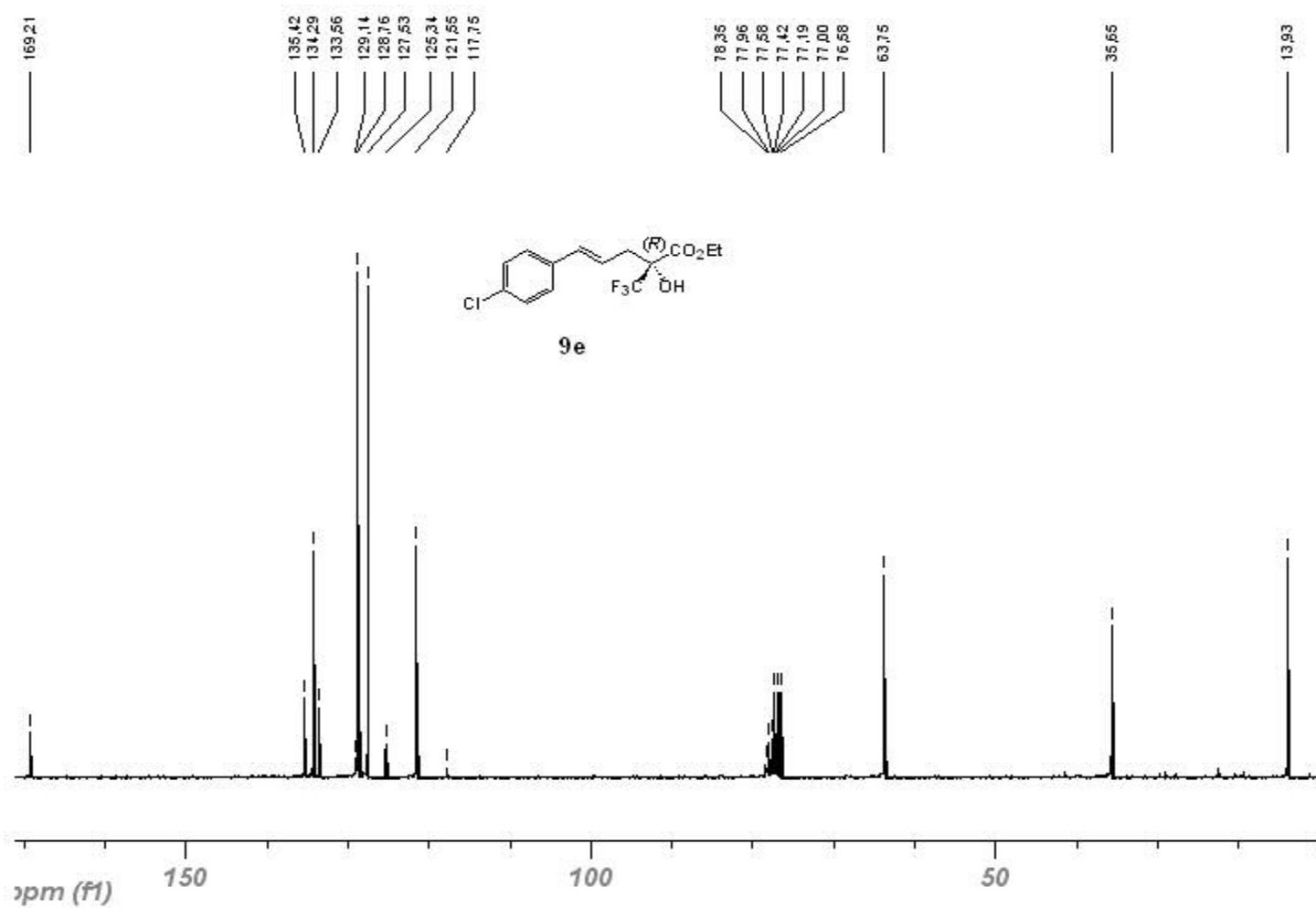
<sup>13</sup>C NMR Spectrum of Ethyl *E*-2-(trifluoromethyl)-2-hydroxy-5-(3-chlorophenyl)pent-4-enoate (9d)



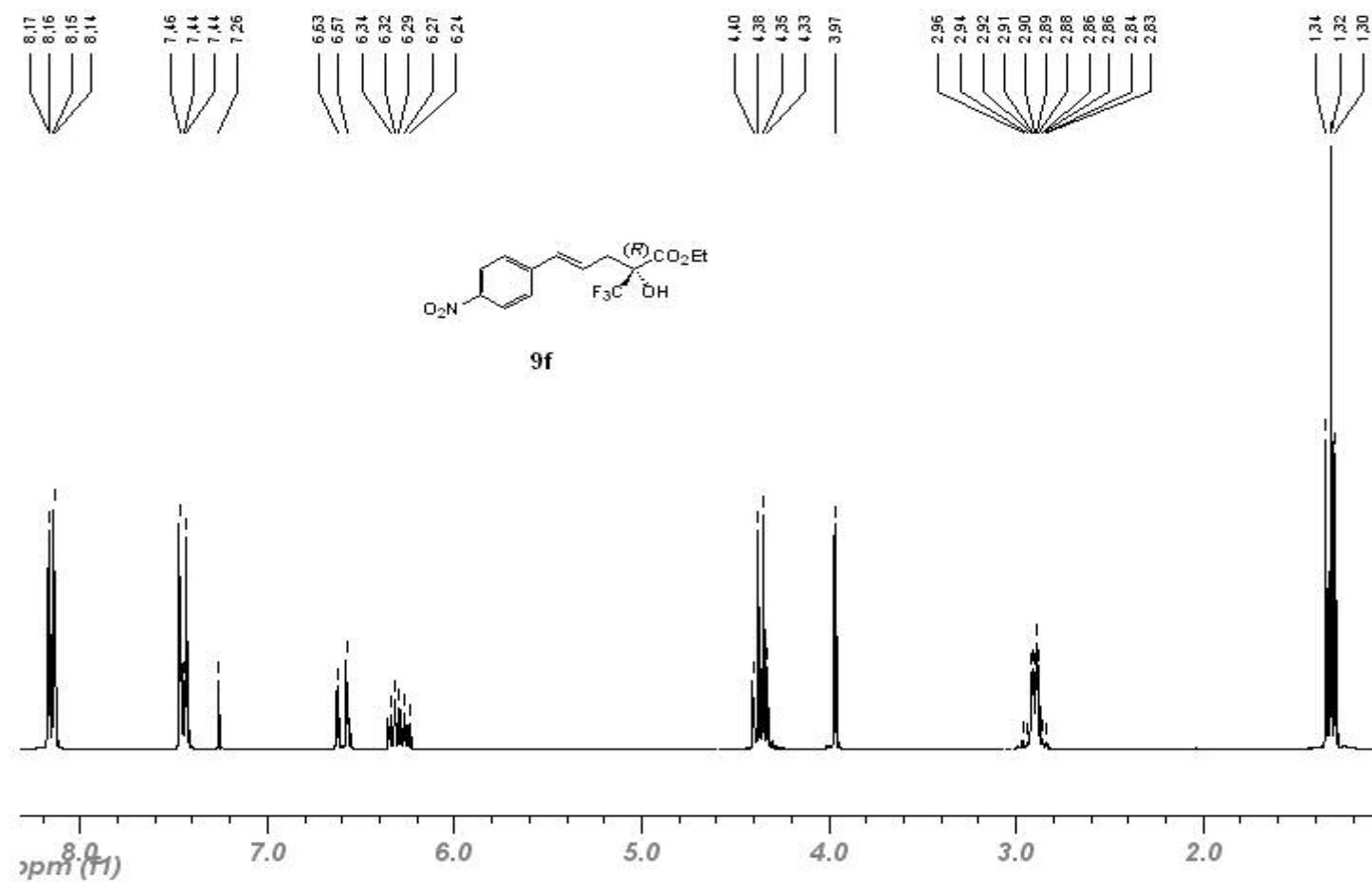
<sup>1</sup>H NMR Spectrum of Ethyl *E*-2-(trifluoromethyl)-2-hydroxy-5-(4-chlorophenyl)pent-4-enoate (9e)



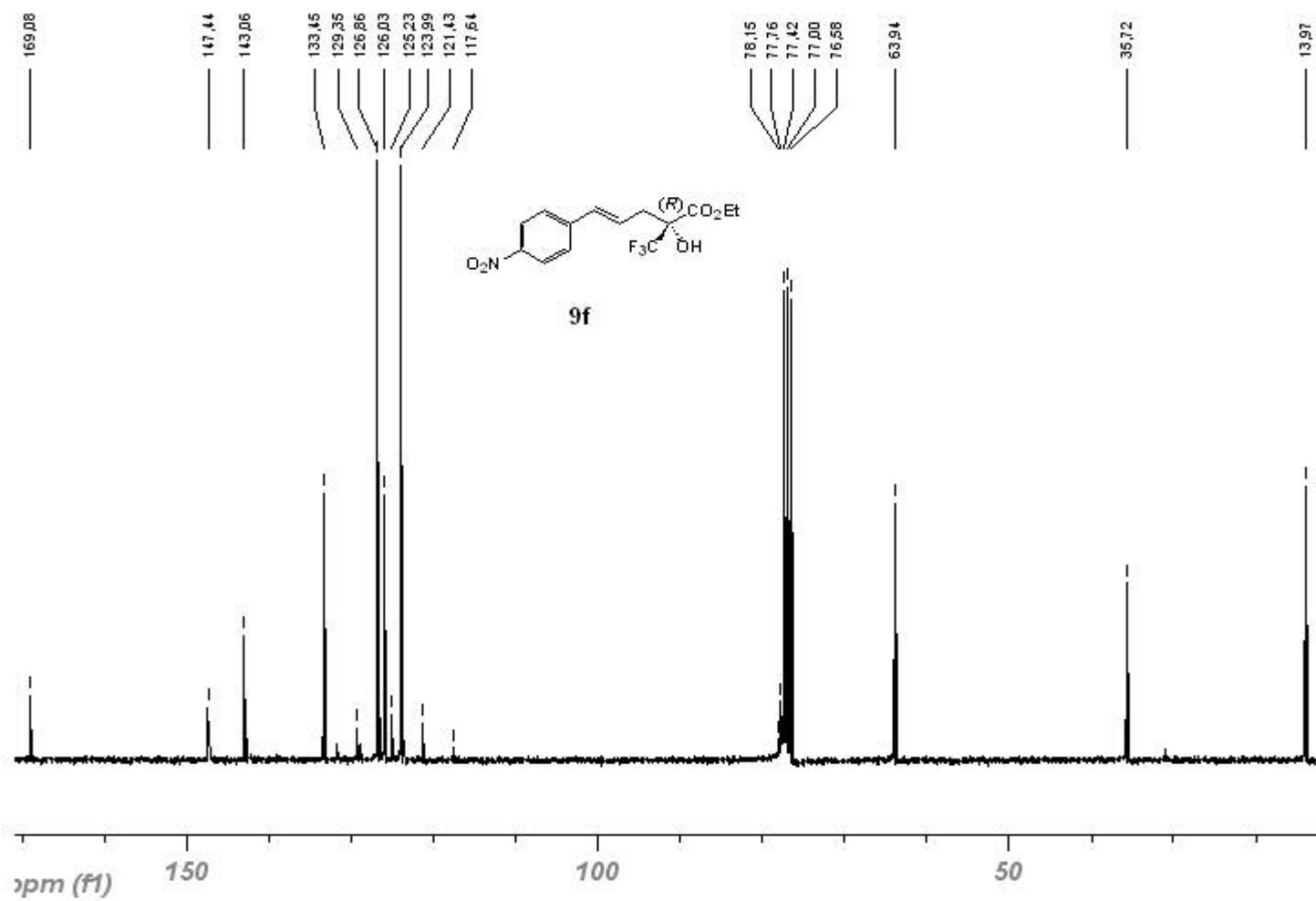
<sup>13</sup>C NMR Spectrum of Ethyl *E*-2-(trifluoromethyl)-2-hydroxy-5-(4-chlorophenyl)pent-4-enoate (9e)



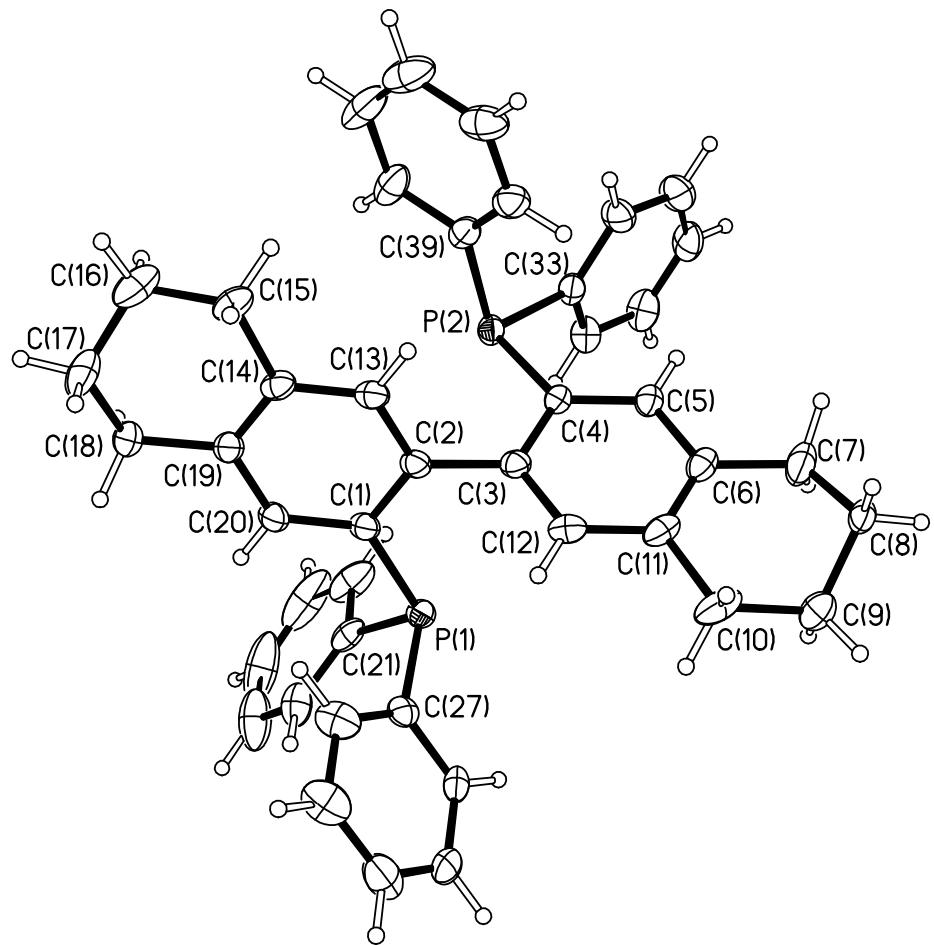
<sup>1</sup>H NMR Spectrum of Ethyl *E*-2-(trifluoromethyl)-2-hydroxy-5-(4-nitrophenyl)pent-4-enoate (9f)



<sup>13</sup>C NMR Spectrum of Ethyl *E*-2-(trifluoromethyl)-2-hydroxy-5-(4-nitrophenyl)pent-4-enoate (9f)



**Figure S1** Structure of one of the two crystallographically inequivalent molecules of **4a** with 40% probability ellipsoids. Chloroform molecule of crystallization omitted for clarity.



**Figure S2** Molecular structure of *rac*-dichloro[3,3'-bis(diphenylphosphanyl)-5,6,7,8,5',6',7',8'-octahydro[2,2']binaphthalene]platinum (*rac*-**6a**) with 40% probability ellipsoids. Hydrogen atoms have been omitted for clarity.

