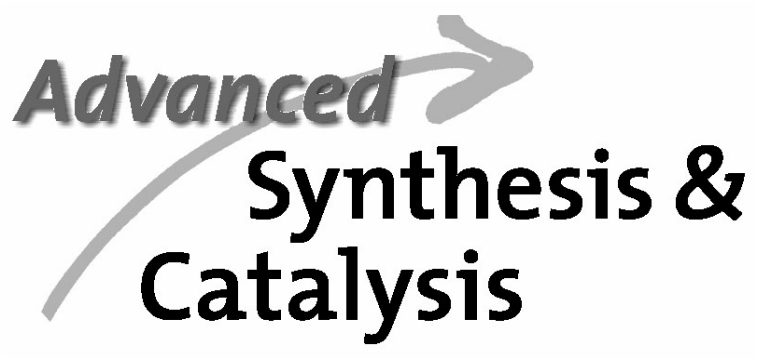


Supporting Information

Electronic Supporting Information for Manuscript

Electron-Rich, Bicyclic Biaryl-Like KITPHOS Monophosphines via [4+2] Cycloaddition Between 1-Alkynylphosphine Oxides and Anthracene: Highly Efficient Ligands for Palladium Catalysed C-N and C-C Bond Formation.

Simon Doherty, Julian G. Knight, Catherine H. Smyth and Graeme A. Jorgenson

Contents

Experimental Section

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. Chloroform was distilled from calcium hydride, methanol from magnesium methoxide, THF from Na/benzophenone and toluene from sodium under an atmosphere of nitrogen. All amines were purchased from commercial suppliers and purified by passing through a short column of alumina immediately prior to use. Phenylacetylene, 2-ethynylanisole, chlorodicyclohexylphosphine, anthracene, aryl halides and boronic acids were purchased from commercial suppliers and used without further purification. 2-ethynyl-*N*,*N*-dimethylaniline[1] were prepared as previously described. ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra were recorded on a JEOL LAMBDA 500 or a Bruker AMX 300 instrument. 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.

Synthesis of (Dicyclohexylphosphinoylethynyl)benzene (4a).[2] To a solution of phenylacetylene (0.46 mL, 4.19 mmol) in THF (20 mL) cooled to -78 °C was added BuLi (1.76 mL, 2.38 M, 4.19 mmol). The reaction was allowed to warm to 0 °C, stirred for 20 min and then cooled to -78 °C. Chlorodicyclohexylphosphine (0.9 mL, 4.07 mmol) was added dropwise and the solution allowed to warm to room temperature and stirred for a further 2.5 h. The reaction was then cooled to 0 °C and hydrogen peroxide (35% aq. solution, 1.53 mL, 5.46 mmol). The solution was allowed to warm to room temperature and stirred for 30 min. Water (20 mL) was added and the product extracted with diethyl ether (3 x 20 mL). The combined organics were dried over $MgSO_4$ and the solvent removed in vacuo to leave a yellow solid. Purification by column chromatography eluting with CH_2Cl_2/ethylacetate (2:3) gave the desired product as a pale yellow solid in 92% yield (1.20 g). $^{31}P\{^{1}H\}$ NMR (202.5 MHz, $CDCl_3$, *d*): 36.3; ^{1}H NMR (300.0 MHz, $CDCl_3$, *d*): 7.54-7.52 (m, 2H, C_6H_5), 7.42 (m, 3H, C_6H_5), 2.07-1.85 (m, 10H, C_6H_{11}), 1.73 (br, 2H,

[1] (a) D. Yue, T. Yao, R. C. Larock, *J. Org. Chem.* **2006**, *71*, 62. (b) H. Li, J. L. Petersen, K. K. Wang, *J. Org. Chem.* **2003**, *68*, 5512.
[2] B. Heller, A. Gutnov, C. Fischer, H.-J. Drexler, A. Spannenberg, D. Redkin, C. Sundermann, B. Sundermann, *Chem. Eur. J.* **2007**, *13*, 1117.

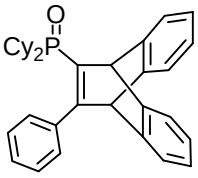
C_6H_{11}), 1.57-1.51 (m, 4H, C_6H_{11}), 1.27-1.24 (m, 6H, C_6H_{11}); $^{13}C\{^1H\}$ NMR (75.8 MHz, $CDCl_3$, *d*): 132.4 (C_6H_5 *o*-C), 130.1 (C_6H_5 *p*-C), 128.5 (C_6H_5 *m*-C), 120.8 (d, *J* = 2.9 Hz, C_6H_5 *Q*), 103.2 (d, *J* = 21 Hz, *C*=CP), 82.0 (d, *J* = 136 Hz, C=*C*P), 37.4 (d, *J* = 79 Hz, C_6H_{11}), 26.5 (d, *J* = 7.4 Hz, C_6H_{11}), 26.3 (d, *J* = 7.0 Hz, C_6H_{11}), 26.1 (d, *J* = 2.9 Hz, C_6H_{11}), 26.0 (C_6H_{11}), 25.0 (d, *J* = 2.9 Hz, C_6H_{11}); LRMS (ESI^+) *m*/*z* 315 $[M+H]^+$; HRMS (ESI^+) exact mass calcd for $C_{20}H_{28}OP$ $[M+H]^+$ requires m/z 315.1878, found *m*/*z* 315.1879. Anal. Calcd for $C_{20}H_{27}OP$: C, 76.40; H, 8.66. Found: C, 76.77; H, 8.92.

Synthesis of 2-(Dicyclohexylphosphinoylethynyl)anisole (4b). Compound **4b** was prepared according to the procedure described above for **4a** on the same scale and isolated as an off-white crystalline solid in 91% yield (1.27 g) after purification by column chromatography eluting with CH_2Cl_2/ethyl acetate (1:1). $^{31}P\{^1H\}$ NMR (202.5 MHz, $CDCl_3$, *d*): 35.5; ^1H NMR (500.0 MHz, $CDCl_3$, *d*): 7.43 (d, *J* = 7.6 Hz, 1H, $C_6H_4OCH_3$), 7.33 (t, *J* = 7.9 Hz, 1H, $C_6H_4OCH_3$), 6.90-6.83 (m, 2H, $C_6H_4OCH_3$), 3.82 (s, 3H, OCH_3), 1.99-1.82 (m, 10H, C_6H_{11}), 1.71 (br, 2H, C_6H_{11}), 1.56 (br, 4H, C_6H_{11}), 1.25 (br, 6H, C_6H_{11}); $^{13}C\{^1H\}$ NMR (125.8 MHz, $CDCl_3$, *d*): 161.2 ($C_6H_4OCH_3$ *Q*), 133.9 ($C_6H_4OCH_3$, *o*-C), 131.6 ($C_6H_4OCH_3$, *p*-C), 120.3 ($C_6H_4OCH_3$, *m*-C), 110.6 ($C_6H_4OCH_3$, *m*-C), 109.7 (d, *J* = 3.6 Hz, $C_6H_4OCH_3$ *Q*), 99.6 (d, *J* = 23 Hz, *C*=CP), 85.3 (d, *J* = 133 Hz, C=*C*P), 55.6 (OCH_3), 36.7 (d, *J* = 79 Hz, C_6H_{11}), 26.2 (d, *J* = 12.5 Hz, C_6H_{11}), 26.1 (d, *J* = 13.7 Hz, C_6H_{11}), 25.8 (C_6H_{11}), 25.6 (d, *J* = 3.0 Hz, C_6H_{11}), 24.5 (d, *J* = 3.2 Hz, C_6H_{11}); LRMS (ESI^+) *m*/*z* 345 $[M+H]^+$; HRMS (ESI^+) exact mass calcd for $C_{21}H_{30}O_2P$ $[M+H]^+$ requires m/z 345.1983, found *m*/*z* 345.1983. Anal. Calcd for $C_{21}H_{29}O_2P$: C, 73.23 H, 8.49. Found: C, 73.54; H, 8.71.

Synthesis of 2-(Dicyclohexylphosphinoylethynyl)-*N*,*N*-dimethylaniline (4c). Compound **4c** was prepared according to the procedure described above for **4a** on the same scale and isolated as a pale brown oil in 93% yield (1.29 g) after purification by column chromatography eluting with CH_2Cl_2/ethyl acetate (2:3). $^{31}P\{^1H\}$ NMR (202.5 MHz, $CDCl_3$, *d*): 34.9; ^1H NMR (500.0 MHz, $CDCl_3$, *d*): 7.46 (d, *J* = 9.0 Hz, 1H, $C_6H_4N(CH_3)_2$), 7.30 (t, *J* = 7.0 Hz, 1H, $C_6H_4N(CH_3)_2$), 6.91-6.83 (m, 2H, $C_6H_4N(CH_3)_2$), 2.96 (s, 6H, $N(CH_3)_2$), 2.07 (br, 2H, C_6H_{11}), 1.98 (br, 2H, C_6H_{11}), 1.87 (br, 6H, C_6H_{11}), 1.74 (br, 2H, C_6H_{11}), 1.57 (br, 4H, C_6H_{11}), 1.28 (br, 6H, C_6H_{11}); $^{13}C\{^1H\}$ NMR (125.8 MHz, $CDCl_3$, *d*): 154.8 ($C_6H_4N(CH_3)_2$ *Q*), 134.5 ($C_6H_4N(CH_3)_2$, *o*-C), 130.3 ($C_6H_4N(CH_3)_2$, *p*-C), 119.0 ($C_6H_4N(CH_3)_2$, *m*-C), 116.0 ($C_6H_4N(CH_3)_2$, *m*-C),

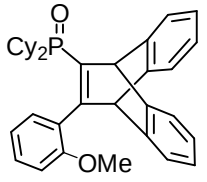
110.3 (d, *J* = 3.3 Hz, $C_6H_4OCH_3$ *Q*), 103.2 (d, *J* = 23 Hz, *C*=CP), 84.5 (d, *J* = 139 Hz, C=*C*P), 42.5 ($N(CH_3)_2$), 36.0 (d, *J* = 79 Hz, C_6H_{11}), 25.4 (d, *J* = 10.1 Hz, C_6H_{11}), 25.3 (d, *J* = 9.7 Hz, C_6H_{11}), 25.0 (C_6H_{11}), 24.8 (d, *J* = 2.6 Hz, C_6H_{11}), 23.9 (d, *J* = 2.7 Hz, C_6H_{11}); LRMS (ESI^+) *m*/*z* 358 $[M+H]^+$; HRMS (ESI^+) exact mass calcd for $C_{22}H_{33}PON$ $[M+H]^+$ requires m/z 358.2300, found *m*/*z* 358.2284. Anal. Calcd for $C_{22}H_{32}NOP$: C, 73.92 H, 9.02; N, 3.92 Found: C, 74.28; H, 9.11; N, 4.03.

Synthesis of 2-(dicyclohexylphosphinoyl)-12-phenyl-9,10-dihydro-9,10-ethenoanthracene (5a). 1-Alkynylphosphine oxide **4a** (1.25 g, 4.00 mmol) and anthracene (1.07 g, 6.00 mmol) were mixed in a flask which was gradually heated to 220 °C using a Wood's metal bath. The temperature was then lowered to 200 °C and the mixture heated for a further 12 h. The resulting dark solid residue was purified by column chromatography eluting with CH_2Cl_2/ethyl acetate (3:2) to afford **5a** as an off-white solid in 80% yield (1.57 g).



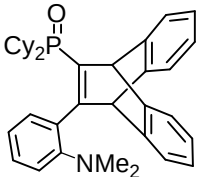
$^{31}P\{^1H\}$ NMR (202.5 MHz, $CDCl_3$, *d*): 47.2; ^1H NMR (500.0 MHz, $CDCl_3$, *d*): 7.40 (d, *J* = 6.4 Hz, 2H, C_6H_4), 7.33-7.31 (m, 5H, C_6H_4, C_6H_5 *o*/*p*-H), 7.08-7.05 (m, 2H, C_6H_5 *m*-H), 7.03-7.01 (m, 4H, C_6H_4), 5.60 (d, *J* = 6.8 Hz, 1H, bridgehead C*H*), 5.23 (d, *J* = 2.3 Hz, 1H, bridgehead C*H*), 2.23 (br, 2H, C_6H_{11}), 1.85-1.81 (m, 2H, C_6H_{11}), 1.71 (m, 2H, C_6H_{11}), 1.57-1.52 (m, 4H, C_6H_{11}), 1.32-1.19 (m, 6H, C_6H_{11}), 1.11-1.08 (m, 4H, C_6H_{11}), 1.00-0.95 (m, 2H, C_6H_{11}); $^{13}C\{^1H\}$ NMR (125.8 MHz, $CDCl_3$, *d*): 163.8 (d, *J* = 5.0 Hz, *C*=CP), 144.5 (C_6H_4 *Q*), 144.2 (C_6H_4 *Q*), 139.2 (C_6H_5 *Q*), 136.4 (d, *J* = 80 Hz, C=*C*P), 127.9 (C_6H_5 *p*-C), 127.8 (C_6H_5 *o*-C), 126.7 (C_6H_5 *m*-C), 125.0 (C_6H_4), 124.9 (C_6H_4), 123.5 (C_6H_4), 123.1 (C_6H_4), 61.4 (d, *J* = 8.9 Hz, bridgehead *C*H), 52.5 (d, *J* = 8.4 Hz, bridgehead *C*H), 37.0 (d, *J* = 67.9 Hz, C_6H_{11}), 26.4 (C_6H_{11}), 26.3 (C_6H_{11}), 25.7 (C_6H_{11}), 25.6 (C_6H_{11}), 25.3 (C_6H_{11}); LRMS (ESI^+) *m*/*z* 493 $[M+H]^+$; HRMS (ESI^+) exact mass calcd for $C_{34}H_{38}PO$ $[M+H]^+$ requires m/z 493.2660, found *m*/*z* 493.2643. Anal. Calcd for $C_{34}H_{37}OP$: C, 82.89; H, 7.57. Found: C, 83.21; H, 7.93.

Synthesis of 11-(dicyclohexylphosphinoyl)-12-(2-methoxyphenyl)-9,10-dihydro-9,10-ethenoanthracene (5b). Compound **5b** was prepared according to the procedure described above for **5a** on the same scale and isolated as an analytically pure off-white solid in 83% yield (1.73 g) after purification by column chromatography eluting with CH_2Cl_2/ethyl acetate (1:1). $^{31}P\{^1H\}$ NMR (202.5



MHz, $CDCl_3$, *d*): 47.3; ^{1}H NMR (500.0 MHz, $CDCl_3$, *d*): 7.38-7.29 (m, 4H, C_6H_4), 7.30 (t, *J* = 7.9 Hz, 1H, $C_6H_4OCH_3$ *p*-H), 7.01-6.98 (m, 4H, C_6H_4), 6.89-6.85 (m, 2H, $C_6H_4OCH_3$ *m*-H), 6.76 (d, *J* = 7.4 Hz, 1H, $C_6H_4OCH_3$ *o*-H), 5.67 (d, *J* = 6.9 Hz, 1H, bridgehead C*H*), 5.16 (d, *J* = 2.9 Hz, 1H, bridgehead C*H*), 3.67 (s, 3H, OCH_3), 1.87-1.52 (br m, 10H, C_6H_{11}), 1.30-0.99 (br m, 12H, C_6H_{11}); ^{13}C{^{1}H} NMR (125.8 MHz, $CDCl_3$, *d*): 161.9 (d, *J* = 6.1 Hz, *C*=CP), 156.7 ($C_6H_4OCH_3$ *Q*), 145.6 (C_6H_4 *Q*), 145.4 (C_6H_4 *Q*), 144.2 (br, C_6H_4 *Q*), 143.9 (C_6H_4 *Q*), 136.8 (d, *J* = 81 Hz, C=*C*P), 129.5 ($C_6H_4OCH_3$ *p*-C), 129.0 (d, *J* = 1.6 Hz, $C_6H_4OCH_3$ *o*-C), 127.8 (d, *J* = 3.4 Hz, $C_6H_4OCH_3$ *Q*), 124.6 (br, C_6H_4), 124.5 (br, C_6H_4), 124.4 (br, C_6H_4), 123.2 (br, C_6H_4), 119.7 ($C_6H_4OCH_3$ *m*-C), 110.2 ($C_6H_4OCH_3$ *m*-C), 60.3 (d, *J* = 9.1 Hz, bridgehead *C*H), 54.6 (OCH_3), 52.3 (d, *J* = 7.8 Hz, bridgehead *C*H), 38.1 (d, J = 66 Hz, C_6H_{11}), 36.7 (d, J = 67 Hz, C_6H_{11}), 26.5 (br, C_6H_{11}), 26.4 (br, C_6H_{11}), 26.0 (br, C_6H_{11}), 25.7 (br, C_6H_{11}), 25.1 (br, C_6H_{11}); LRMS (ESI$^+$) *m/z* 523 $[M+H]^+$; HRMS (ESI$^+$) exact mass calcd for $C_{35}H_{40}O_2P$ $[M+H]^+$ requires m/z 523.2766, found *m/z* 523.2766. Anal. Calcd for $C_{35}H_{39}O_2P$: C, 80.43; H, 7.52. Found: C, 80.76; H, 7.82.

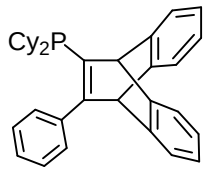
Synthesis of 11-(dicyclohexylphosphinoyl)-12-(2-dimethylaminophenyl)-9,10-dihydro-9,10-ethenoanthracene (5c). Compound **5c** was prepared according to the procedure described above for **5a**



on the same scale and isolated as an analytically pure pale brown solid in 24% yield after purification by column chromatography eluting with CH_2Cl_2/ethyl acetate (2:3). ^{31}P{^{1}H} NMR (202.5 MHz, $CDCl_3$, *d*): 45.5; ^{1}H NMR (500.0 MHz, $CDCl_3$, *d*): 7.38 (d, *J* = 6.6 Hz, 1H, C_6H_4), 7.33 (d, *J* = 6.9 Hz, 2H, C_6H_4), 7.24 (t, *J* = 7.7 Hz, 1H, $C_6H_4N(CH_3)_2$ *o*-H), 7.19 (d, *J* = 7.0 Hz, 1H, C_6H_4), 7.05-7.01 (m, 3H, 2 x C_6H_4, $C_6H_4N(CH_3)_2$ *m*-H), 6.99-6.93 (m, 3H, 2 x C_6H_4, $C_6H_4N(CH_3)_2$ *p*-H), 6.87 (t, *J* = 7.4 Hz, 1H, $C_6H_4N(CH_3)_2$ *m*-H), 5.38 (d, *J* = 6.9 Hz, 1H, bridgehead C*H*), 5.25 (d, *J* = 2.6 Hz, 1H, bridgehead C*H*), 2.39 (s, 6H, $N(CH_3)_2$), 2.05-2.01 (m, 1H, C_6H_{11}), 1.94-1.74 (m, 6H, C_6H_{11}), 1.67 (m, 1H, C_6H_{11}), 1.61-1.56 (m, 4H, C_6H_{11}), 1.26-1.04 (m, 10H, C_6H_{11}); ^{13}C{^{1}H} NMR (125.8 MHz, $CDCl_3$, *d*): 167.3 (d, *J* = 3.6 Hz, *C*=CP), 151.6 ($C_6H_4N(CH_3)_2$ *Q*), 145.8 (C_6H_4 *Q*), 145.4 (C_6H_4 *Q*), 145.1 (C_6H_4 *Q*), 143.3 (C_6H_4 *Q*), 133.8 (d, *J* = 81 Hz, C=*C*P), 132.6 (d, *J* = 3.0 Hz, $C_6H_4N(CH_3)_2$ *Q*), 130.6 ($C_6H_4N(CH_3)_2$ *p*-C), 128.7 ($C_6H_4N(CH_3)_2$ *o*-C), 124.8 (2 x C_6H_4), 124.6 (C_6H_4), 124.5 (C_6H_4), 123.4 (C_6H_4), 123.4 (C_6H_4), 122.8 (C_6H_4), 122.6 (C_6H_4), 121.0 ($C_6H_4N(CH_3)_2$

m-C), 117.8 ($C_6H_4N(CH_3)_2$ *m*-C), 61.0 (d, *J* = 9.0 Hz, bridgehead *C*H), 52.6 (d, *J* = 10.1 Hz, bridgehead *C*H), 44.0 ($N(CH_3)_2$), 37.5 (d, *J* = 68 Hz, C_6H_{11}), 36.7 (d, J = 69 Hz, C_6H_{11}), 26.9 (C_6H_{11}), 26.8 (C_6H_{11}), 26.7 (d, *J* = 4.1 Hz, C_6H_{11}), 26.6 (d, *J* = 4.1 Hz, C_6H_{11}), 26.5 (C_6H_{11}), 26.4 (C_6H_{11}), 26.0 (C_6H_{11}), 25.8 (C_6H_{11}), 25.7 (C_6H_{11}), 25.4 (C_6H_{11}); LRMS (ESI^+) *m*/*z* 536 $[M+H]^+$; HRMS (ESI^+) exact mass calcd for $C_{36}H_{43}ONP$ $[M+H]^+$ requires m/z 536.3082, found *m*/*z* 536.3052. Anal. Calcd for $C_{36}H_{42}NOP$: C, 80.71; H, 7.91; N, 2.61. Found: C, 80.98; H, 8.09; N, 2.77.

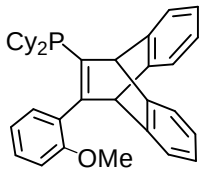
Reduction of 11-(dicyclohexylphosphinoyl)-12-phenyl-9,10-dihydro-9,10-ethenoanthracene (5a). A flame-dried Schlenk flask was charged with **5a** (0.70 g, 1.34 mmol), toluene (25 mL), and



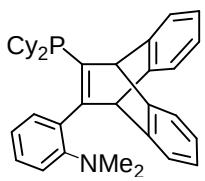
triethylamine (7.5 mL, 53.6 mmol). Trichlorosilane (1.35 mL, 13.4 mmol) was added slowly and the mixture heated at 110 °C for 3 days. The reaction mixture was diluted with diethyl ether (20 mL) and added slowly to a mixture of ice (10 g) and 20 % aq NaOH (20 mL). After stirring vigorously at room temperature for 30 min, the organic layer was removed and the aqueous phase extracted with diethyl ether (3 x 30 mL). The organic fractions were combined, washed with sat. $NaHCO_3$ (2 x 20 mL), water (2 x 20 mL) and brine (2 x 20 mL), dried over $MgSO_4$, filtered and the solvent removed *in vacuo*. The product was purified by column chromatography eluting with hexane/ethyl acetate (9:1) to afford **6a** as a spectroscopically pure white solid in 69% yield (0.44 g). An analytically pure sample that was also suitable for a singe crystal X-ray study was obtained by slow diffusion of a chloroform solution layered with methanol at room temperature. $^{31}P\{^1H\}$ NMR (202.5 MHz, $CDCl_3$, *d*): -12.8; ^1H NMR (500.0 MHz, $CDCl_3$, *d*): 7.35-7.31 (m, 6H, C_6H_4, C_6H_5 *m*-H), 7.26 (t, *J* = 7.2 Hz, 1H, C_6H_5 *p*-H), 7.19 (d, *J* = 7.4 Hz, 2H, C_6H_5 *o*-H), 7.02-6.97 (m, 4H, C_6H_4), 5.54 (s, 1H, bridgehead C*H*), 5.31 (d, *J* = 2.0 Hz, 1H, bridgehead C*H*), 1.99 (t, *J* = 10.6 Hz, 2H, C_6H_{11}), 1.76-1.70 (m, 4H, C_6H_{11}), 1.62 (d, *J* = 10.6 Hz, 2H, C_6H_{11}), 1.54 (d, *J* = 11.0 Hz, 2H, C_6H_{11}), 1.33-1.26 (m, 2H, C_6H_{11}), 1.21-1.18 (m, 2H, C_6H_{11}), 1.08-0.98 (m, 8H, C_6H_{11}); $^{13}C\{^1H\}$ NMR (125.8 MHz, $CDCl_3$, *d*): 163.0 (d, *J* = 26 Hz, *C*=CP), 145.8 (C_6H_4 *Q*), 144.9 (C_6H_4 *Q*), 141.3 (d, *J* = 29 Hz, C=*C*P), 140.0 (C_6H_5 *Q*), 128.1 (d, *J* = 3.3 Hz, C_6H_5 *o*-C), 127.7 (C_6H_5 *m*-C), 127.1 (C_6H_5 *p*-C), 124.6 (C_6H_4), 124.5 (C_6H_4), 122.9 (C_6H_4), 122.7 (C_6H_4), 59.7 (d, *J* = 6.1 Hz, bridgehead *C*H), 54.2 (d, *J* = 6.3 Hz, bridgehead *C*H), 34.4 (d, *J* = 11.9 Hz, C_6H_{11}), 30.6 (d, *J* = 16.6 Hz, C_6H_{11}), 30.3 (d, *J* = 9.4 Hz, C_6H_{11}), 27.3 (d, *J* = 11.6 Hz, C_6H_{11}), 27.0 (d, *J* =

8.3 Hz, C_6H_{11}), 26.3 (C_6H_{11}); LRMS (ESI^+) *m*/*z* 477 $[M+H]^+$; HRMS (ESI^+) exact mass calcd for $C_{34}H_{38}P$ $[M+H]^+$ requires m/z 477.2711, found *m*/*z* 477.2680. Anal. Calcd for $C_{34}H_{37}P.0.25CHCl_3$: C, 81.22; H, 7.41. Found: C, 80.78; H, 7.70.

Reduction of 11-(dicyclohexylphosphinoyl)-12-(2-methoxyphenyl)-9,10-dihydro-9,10-ethenoanthracene (5b). Compound **5b** was reduced according to the procedure described above for **5a** on the same scale to afford **6b** as an off-white solid in 67 % yield (0.455 g) after purification by column chromatography eluting with hexane/ethyl acetate (85:15). An analytically and spectroscopically pure sample was obtained by slow diffusion of a chloroform solution layered with methanol at room temperature. $^{31}P\{^1H\}$ NMR (202.5 MHz, $CDCl_3$, *d*): -13.1; ^1H NMR (500.0 MHz, $CDCl_3$, *d*): 7.32-7.30 (m, 2H, C_6H_4), 7.27-7.24 (m, 3H, C_6H_4, C_6H_5 *p*-H), 6.99-6.97 (m, 4H, C_6H_4, C_6H_5 *m*-H), 6.89-6.85 (m, 3H, C_6H_4, C_6H_5 *o*-H), 5.48 (s, 1H, bridgehead C*H*), 5.20 (s, 1H, bridgehead C*H*), 3.67 (s, 3H, OCH_3), 1.96 (br, 2H, C_6H_{11}), 1.69-1.56 (br m, 10H, C_6H_{11}), 1.28 (m, 4H, C_6H_{11}), 1.07 (br, 6H, C_6H_{11}); $^{13}C\{^1H\}$ NMR (125.8 MHz, $CDCl_3$, *d*): 162.6 (d, *J* = 28.0 Hz, *C*=CP), 157.7 ($C_6H_4OCH_3$ *Q*), 145.8 (br, C_6H_4 *Q*), 145.6 (br, C_6H_4 *Q*), 141.2 (d, *J* = 28.0 Hz, C=*C*P), 131.2 (d, *J* = 4.7 Hz, $C_6H_4OCH_3$ *o*-C), 129.1 (d, *J* = 5.8 Hz, $C_6H_4OCH_3$ *Q*), 128.7 (C_6H_5 *p*-C), 124.3 (C_6H_4), 124.1 (C_6H_4), 123.1 (C_6H_4), 122.6 (C_6H_4), 119.9 ($C_6H_4OCH_3$ *m*-C), 110.6 ($C_6H_4OCH_3$ *m*-C), 58.8 (d, *J* = 5.8 Hz, bridgehead *C*H), 54.9 (OCH_3), 54.0 (d, *J* = 6.3 Hz, bridgehead *C*H), 34.2 (br, C_6H_{11}), 30.3 (br, C_6H_{11}), 30.1 (br, C_6H_{11}), 27.3 (d, *J* = 11.5 Hz, C_6H_{11}), 27.1 (d, *J* = 7.8 Hz, C_6H_{11}), 26.4 (C_6H_{11}); LRMS (ESI^+) *m*/*z* 507 $[M+H]^+$; HRMS (ESI^+) exact mass calcd for $C_{35}H_{40}OP$ $[M+H]^+$ requires m/z 507.2817, found *m*/*z* 507.2778. Anal. Calcd for $C_{35}H_{39}OP$: C, 82.97; H, 7.76. Found: C, 83.06; H, 7.91.



Reduction of 11-(dicyclohexylphosphinoyl)-12-(2-dimethylaminophenyl)-9,10-dihydro-9,10-ethenoanthracene (5c). Compound **5c** was reduced according to the procedure described above for **5a** on the same scale to afford **6c** as an off-white solid in 65% yield (0.452 g) after purification by column chromatography eluting with dichloromethane/hexane (2:1). An analytically pure sample was obtained by slow diffusion of a chloroform solution layered with methanol at room temperature. $^{31}P\{^1H\}$ NMR (202.5 MHz,



$CDCl_3$, *d*): -13.9; ^{1}H NMR (500.0 MHz, $CDCl_3$, *d*): 7.35 (br, 1H, C_6H_4), 7.31 (br d, *J* = 7.9 Hz, 2H, C_6H_4), 7.23 (t, *J* = 8.4 Hz, 1H, $C_6H_4N(CH_3)_2$ *p*-H), 7.13 (br, 1H, C_6H_4), 7.06 (br d, *J* = 8.0 Hz, 1H, $C_6H_4N(CH_3)_2$ *m*-H), 7.01-6.93 (br m, 3H, C_6H_4), 6.91-6.88 (br, 1H, C_6H_4), 6.89 (t, *J* = 7.3 Hz, 1H, $C_6H_4N(CH_3)_2$ *m*-H), 6.84 (br d, *J* = 7.5 Hz, 1H, $C_6H_4N(CH_3)_2$ *o*-H), 5.53 (s, 1H, bridgehead C*H*), 5.28 (d, *J* = 2.4 Hz, 1H, bridgehead C*H*), 2.35 (s, 6H, $N(CH_3)_2$), 2.05-1.91 (br m, 2H, C_6H_{11}), 1.78-1.64 (br m, 6H, C_6H_{11}), 1.54 (br, 1H, C_6H_{11}), 1.42-1.08 (br m, 12H, C_6H_{11}), 0.88 (br, 1H, C_6H_{11}); ^{13}C{^{1}H} NMR (125.8 MHz, $CDCl_3$, *d*): 165.2 (d, *J* = 28 Hz, *C*=CP), 152.4 ($C_6H_4N(CH_3)_2$ *Q*), 146.9 (C_6H_4 *Q*), 146.2 (C_6H_4 *Q*), 145.5 (C_6H_4 *Q*), 144.7 (C_6H_4 *Q*), 139.3 (d, *J* = 29 Hz, C=*C*P), 133.7 (d, *J* = 4.4 Hz, $C_6H_4N(CH_3)_2$ *Q*), 131.9 (d, *J* = 5.0 Hz, $C_6H_4N(CH_3)_2$ *o*-C), 128.4 ($C_6H_4N(CH_3)_2$ *p*-C), 124.4 (2 x C_6H_4), 124.2 (br, 2 x C_6H_4), 123.1 (2 x C_6H_4), 122.4 (br, 2 x C_6H_4), 121.2 ($C_6H_4N(CH_3)_2$ *m*-C), 118.2 ($C_6H_4N(CH_3)_2$ *m*-C), 59.2 (d, *J* = 6.3 Hz, bridgehead *C*H), 54.0 (d, *J* = 5.9 Hz, bridgehead *C*H), 43.8 ($N(CH_3)_2$), 35.2 (br d, *J* = 54.0 Hz, C_6H_{11}), 31.1 (br, C_6H_{11}), 30.7 (br, C_6H_{11}), 27.4 (br, C_6H_{11}), 27.2 (br, C_6H_{11}), 26.4 (C_6H_{11}); LRMS (ESI^+) *m*/*z* 520 $[M+H]^+$; HRMS (ESI^+) exact mass calcd for $C_{36}H_{43}NP$ $[M+H]^+$ requires m/z 520.3133, found *m*/*z* 520.3087. Anal. Calcd for $C_{36}H_{42}NP$: C, 83.20; H, 8.14; N, 2.69. Found: C, 83.52; H, 8.33; N, 2.97.

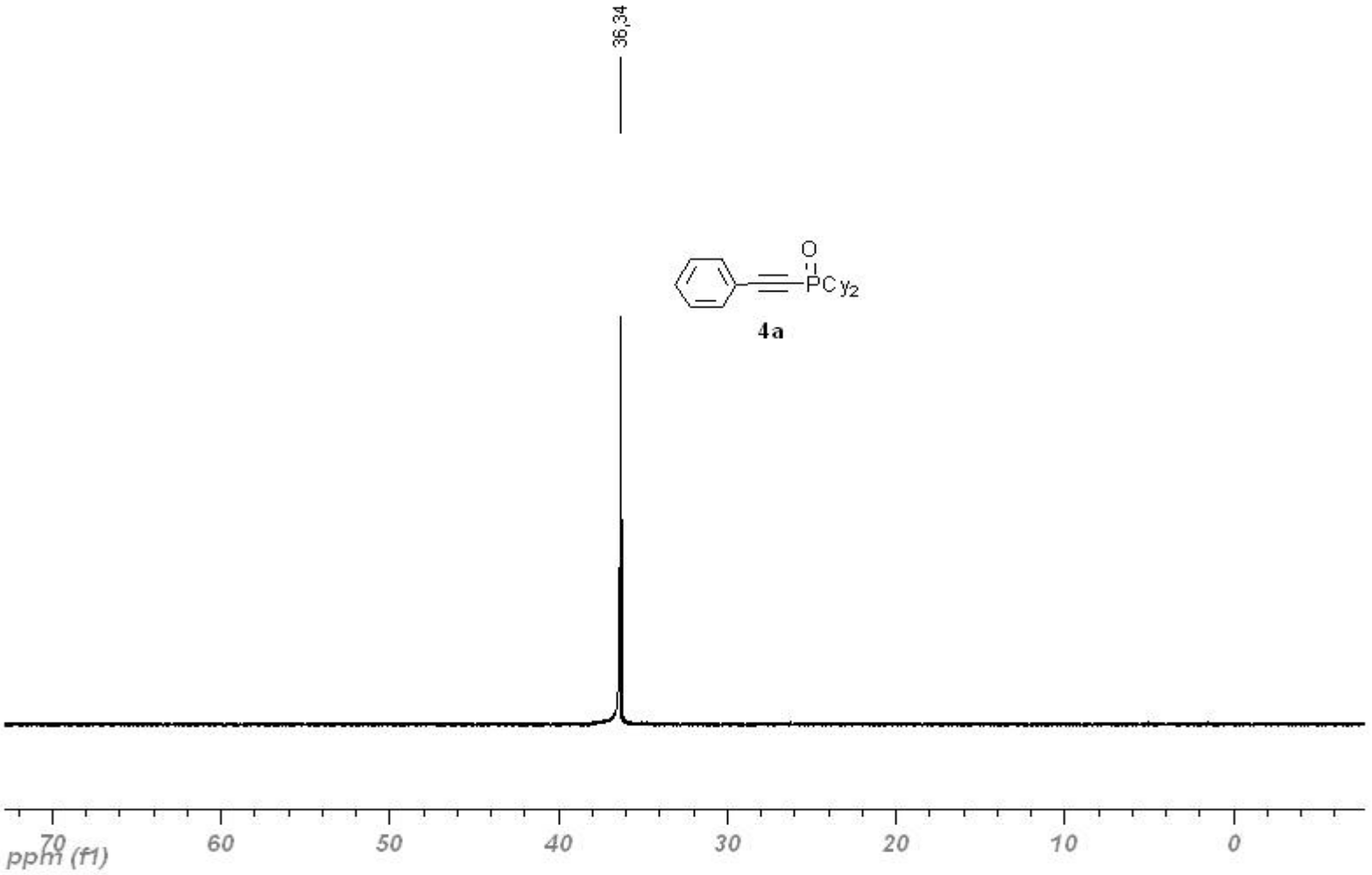
General Procedure for the Amination of Aryl Halides. A flame-dried Schlenk flask was charged with tris(dibenzylideneacetone)palladium (4.6 mg, 0.005 mmol), **6a** (11.9 mg, 0.025 mmol), sodium *tert*-butoxide (134 mg, 1.40 mmol) and toluene (2.0 mL) under nitrogen. Aryl halide (1.00 mmol) and amine (1.10 mmol) were added and the resulting red solution heated at the appropriate temperature with rapid stirring until reaction was complete, as judged by GC analysis. The reaction mixture was allowed to cool to room temperature, diluted with diethyl ether, passed through celite and the solvent removed to leave a yellow solid. Known products were characterised by NMR spectroscopy and mass spectrometry and unknown products by NMR spectroscopy, mass spectrometry and high resolution mass spectrometry (HRMS).

General Procedure for the Suzuki-Miyaura Coupling of Aryl Chlorides in THF Using KF as Base. A flame-dried Schlenk flask was charged with $Pd(OAc)_2$ (2.2 mg, 0.01 mmol), **6a** (11.9 mg, 0.025 mmol), potassium fluoride (177 mg, 3.00 mmol), boronic acid (1.50 mmol) and THF (2.0 mL) under nitrogen.

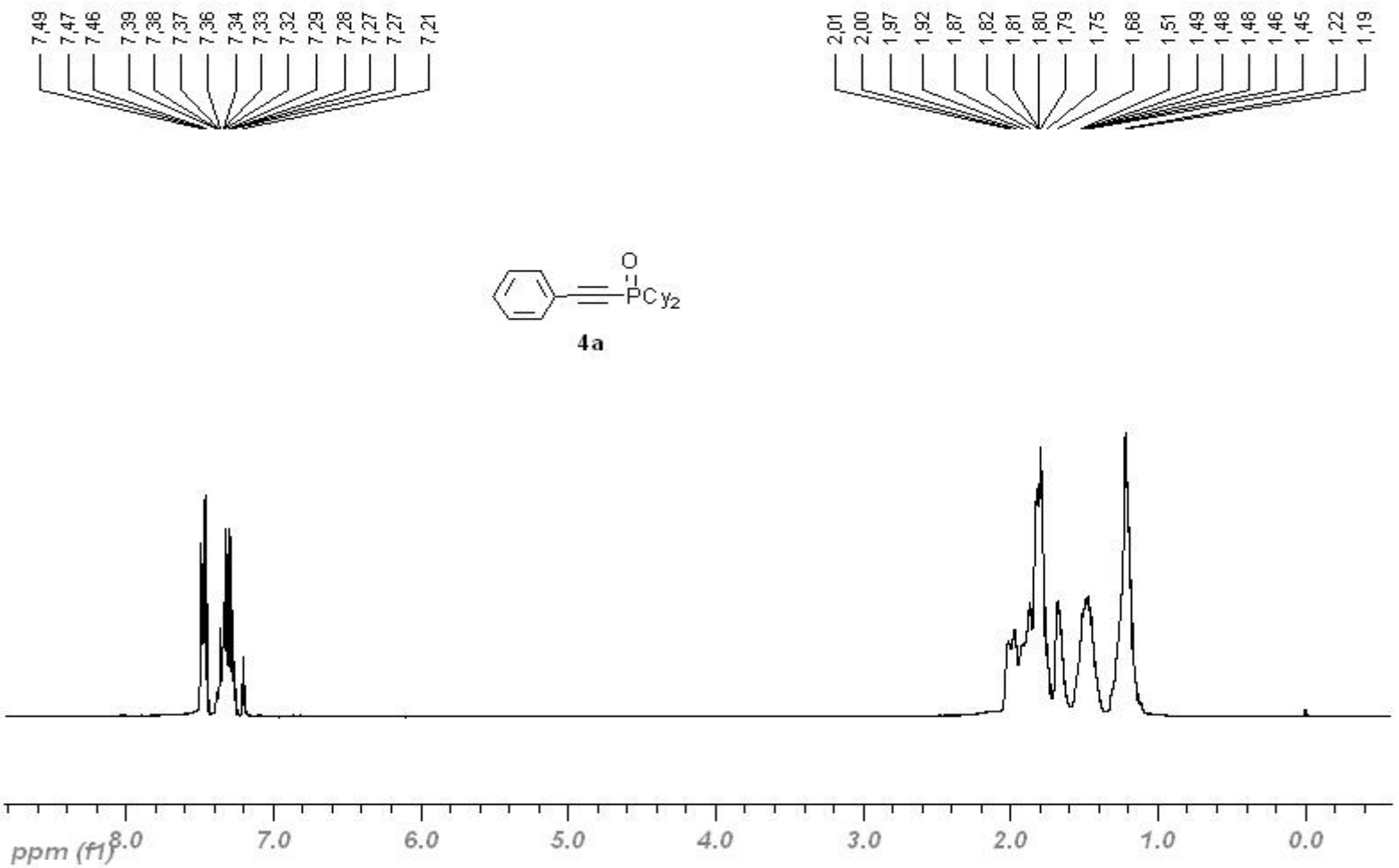
Aryl chloride (1.00 mmol) was added and the resulting mixture heated at the appropriate temperature (40-60 °C) with rapid stirring until reaction was complete, as judged by GC analysis. The reaction mixture was allowed to cool to room temperature, diethyl ether (2 mL) and water (2 mL) were added, and the organic layer was passed through a short silica plug and the solvent removed to leave a yellow solid. Known products were characterised by NMR spectroscopy and mass spectrometry and unknown products by NMR spectroscopy, mass spectrometry and high resolution mass spectrometry (HRMS).

General Procedure for the Suzuki-Miyaura Coupling of Aryl Chlorides in Toluene Using K_3PO_4 as Base. A flame-dried Schlenk flask was charged with $Pd(OAc)_2$ (2.2 mg, 0.01 mmol), KITPHOS (11.9 mg, 0.025 mmol), potassium phosphate (424 mg, 2.00 mmol), boronic acid (1.50 mmol) and toluene (2.0 mL) under nitrogen. Aryl chloride (1.00 mmol) was added and the resulting mixture heated at the required temperature with rapid stirring until reaction was complete, as judged by GC analysis. The reaction mixture was allowed to cool to room temperature, diethyl ether (2 mL) and water (2 mL) were added, and the organic layer was passed through a short silica plug and the solvent removed to leave a yellow solid. Known products were characterised by NMR spectroscopy and mass spectrometry and unknown products by NMR spectroscopy, mass spectrometry and high resolution mass spectrometry (HRMS).

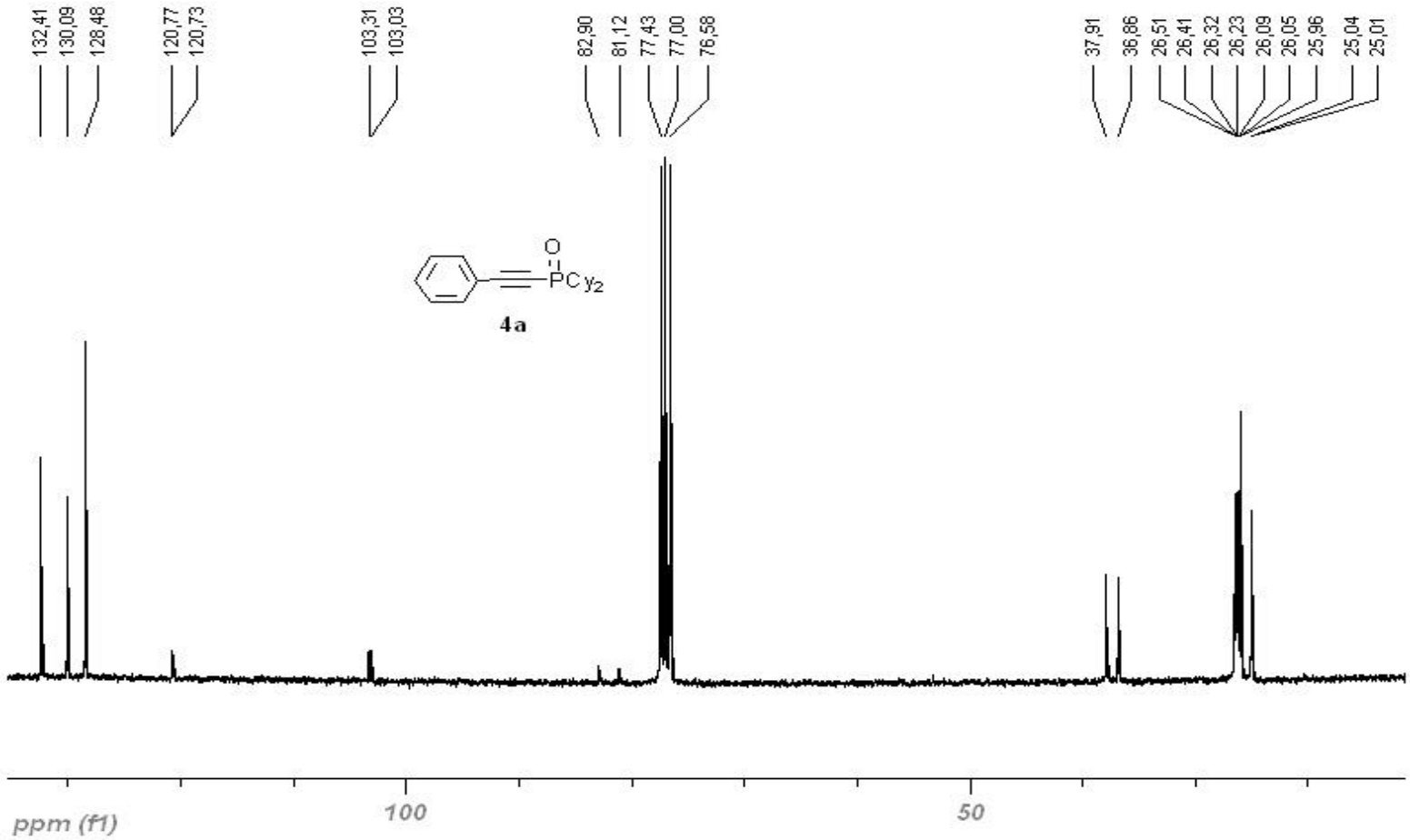
$^{31}P\{^{1}H\}$ NMR Spectrum of (Dicyclohexylphosphinoylethynyl)benzene (4a)



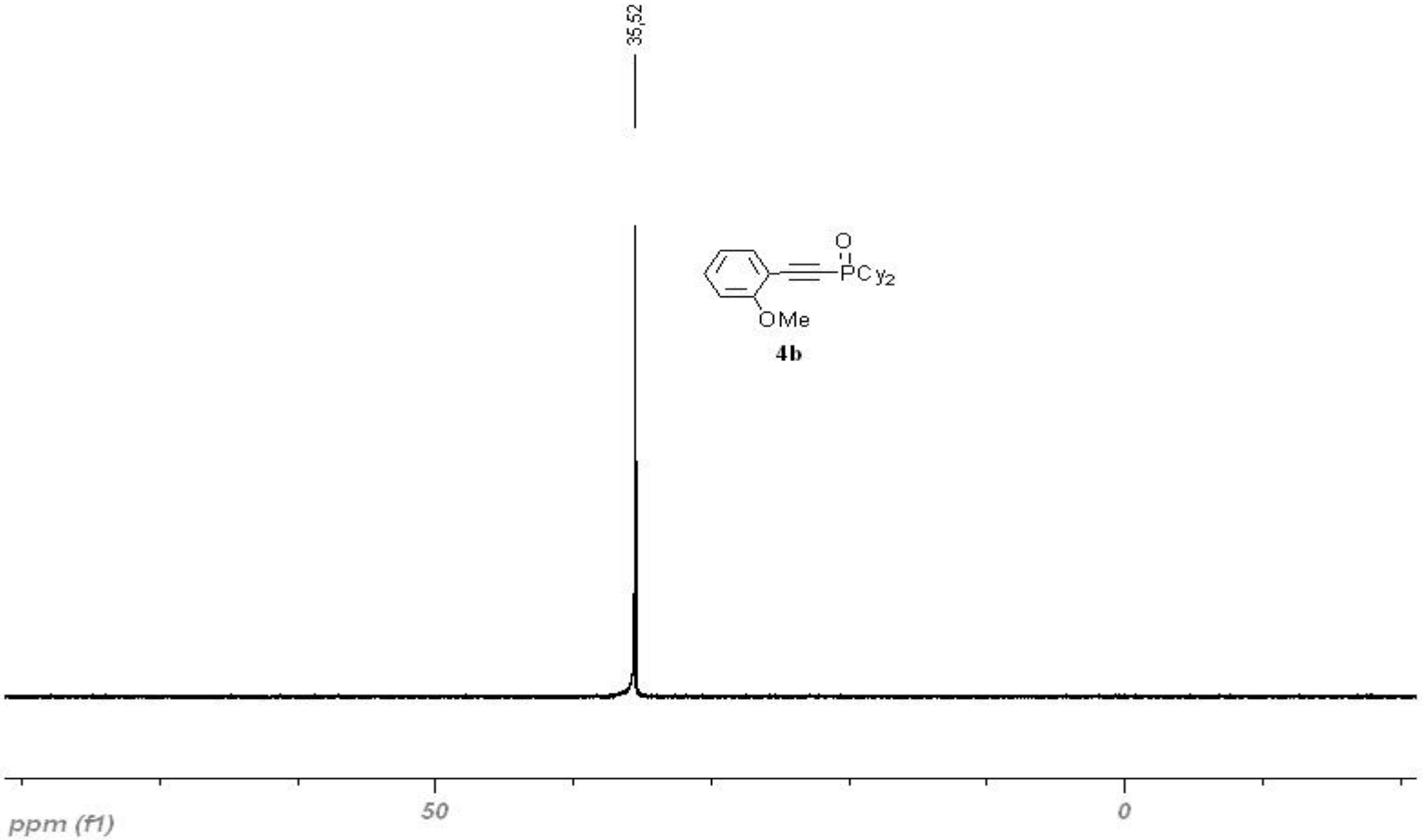
^{1}H NMR Spectrum of (Dicyclohexylphosphinoylethynyl)benzene (4a)



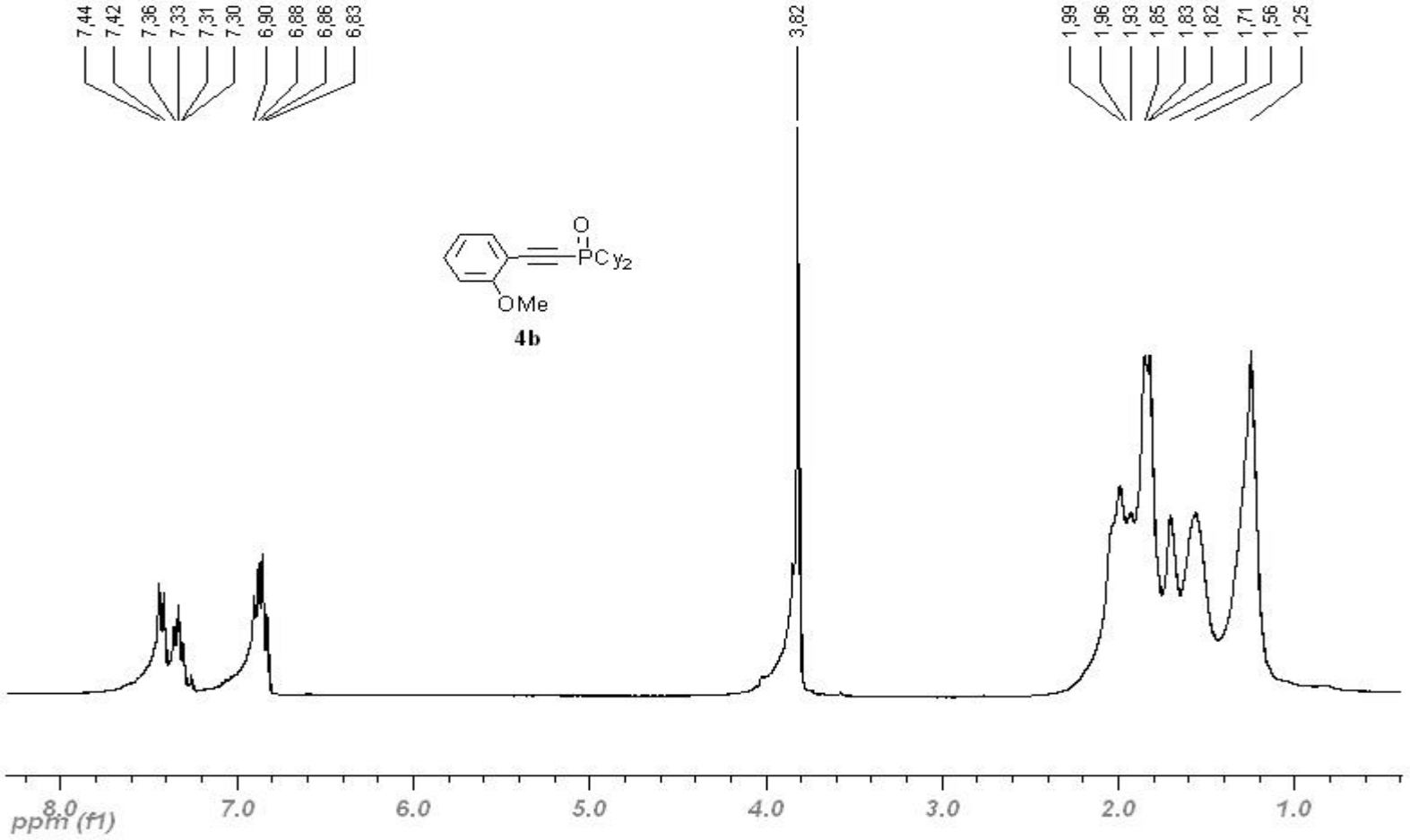
^{13}C {^{1}H} NMR Spectrum of (Dicyclohexylphosphinoylethynyl)benzene (4a)



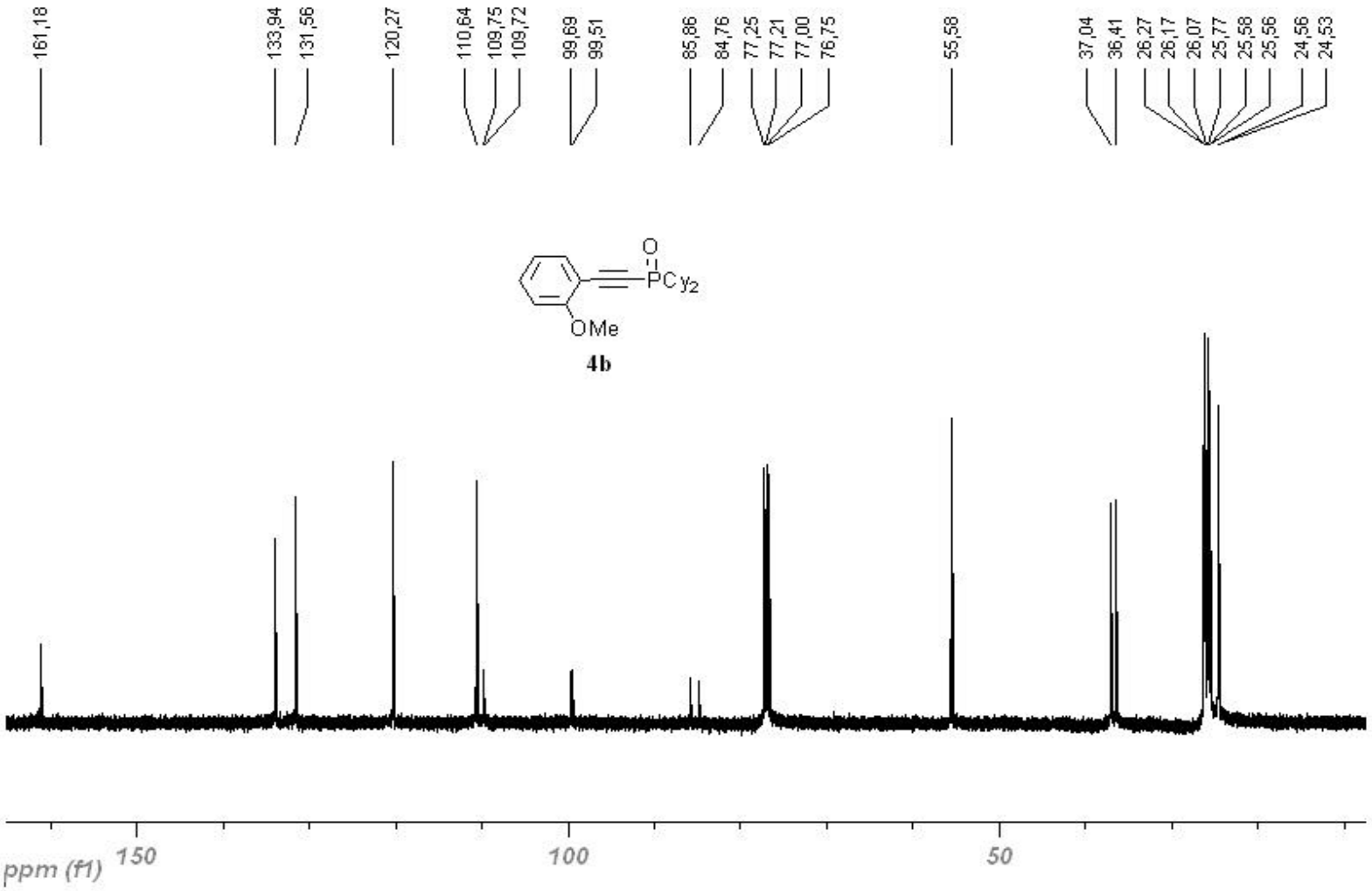
$^{31}P\{^{1}H\}$ NMR Spectrum of 2-(Dicyclohexylphosphinoylethynyl)anisole (4b).



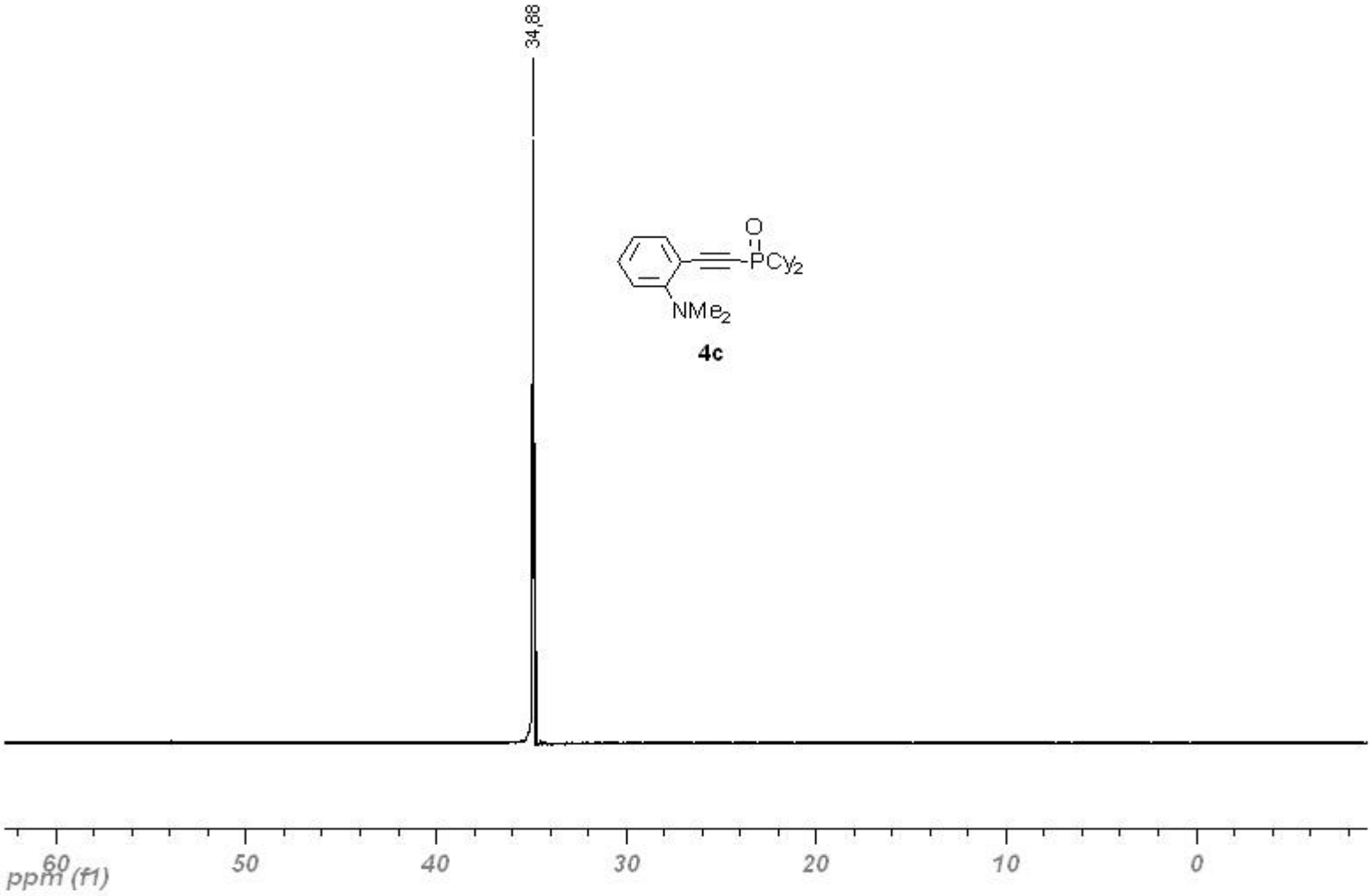
^{1}H NMR Spectrum of 2-(Dicyclohexylphosphinoylethynyl)anisole (4b).



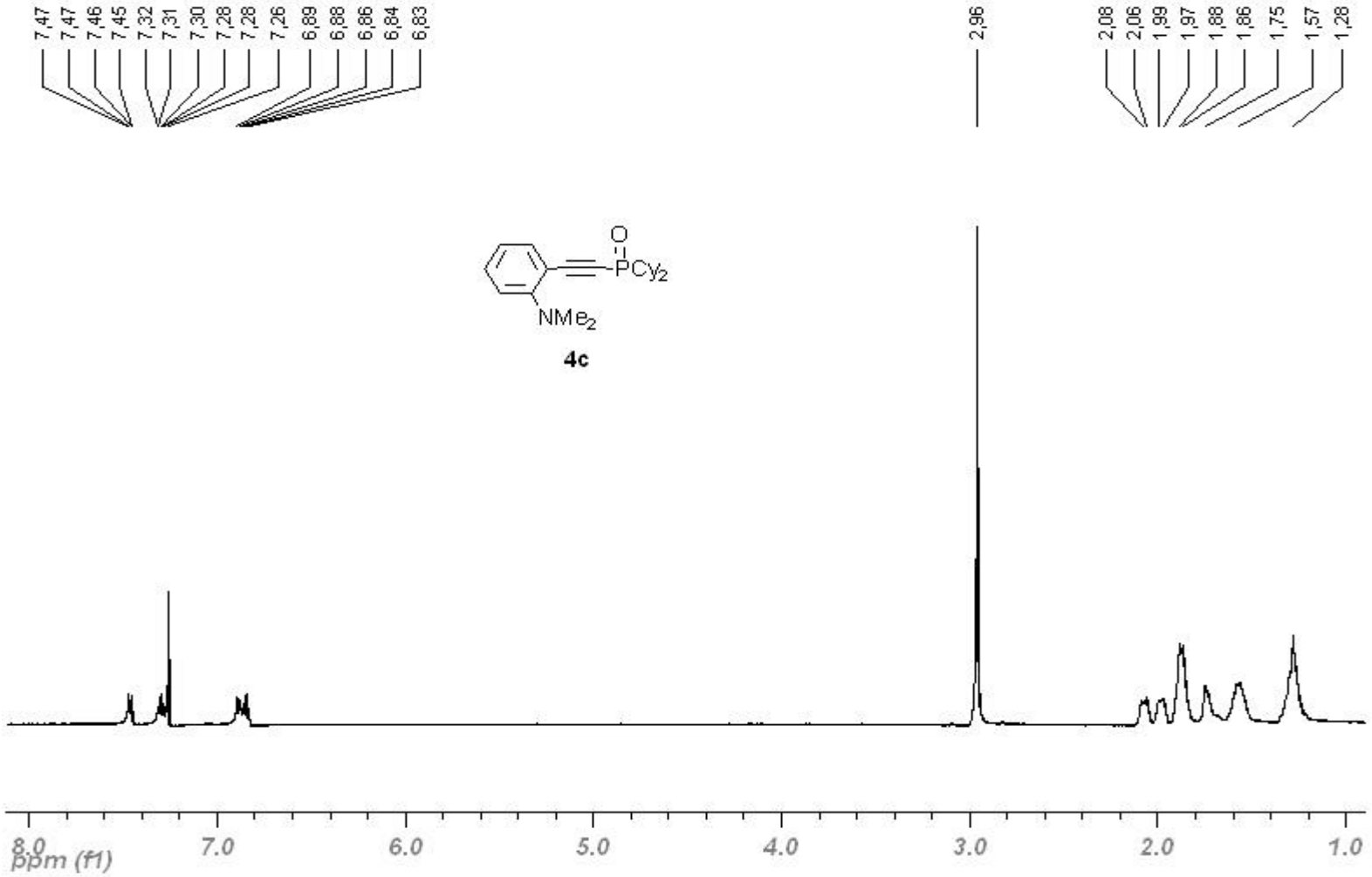
^{13}C {^{1}H} NMR Spectrum of 2-(Dicyclohexylphosphinoylethynyl)anisole (4b).



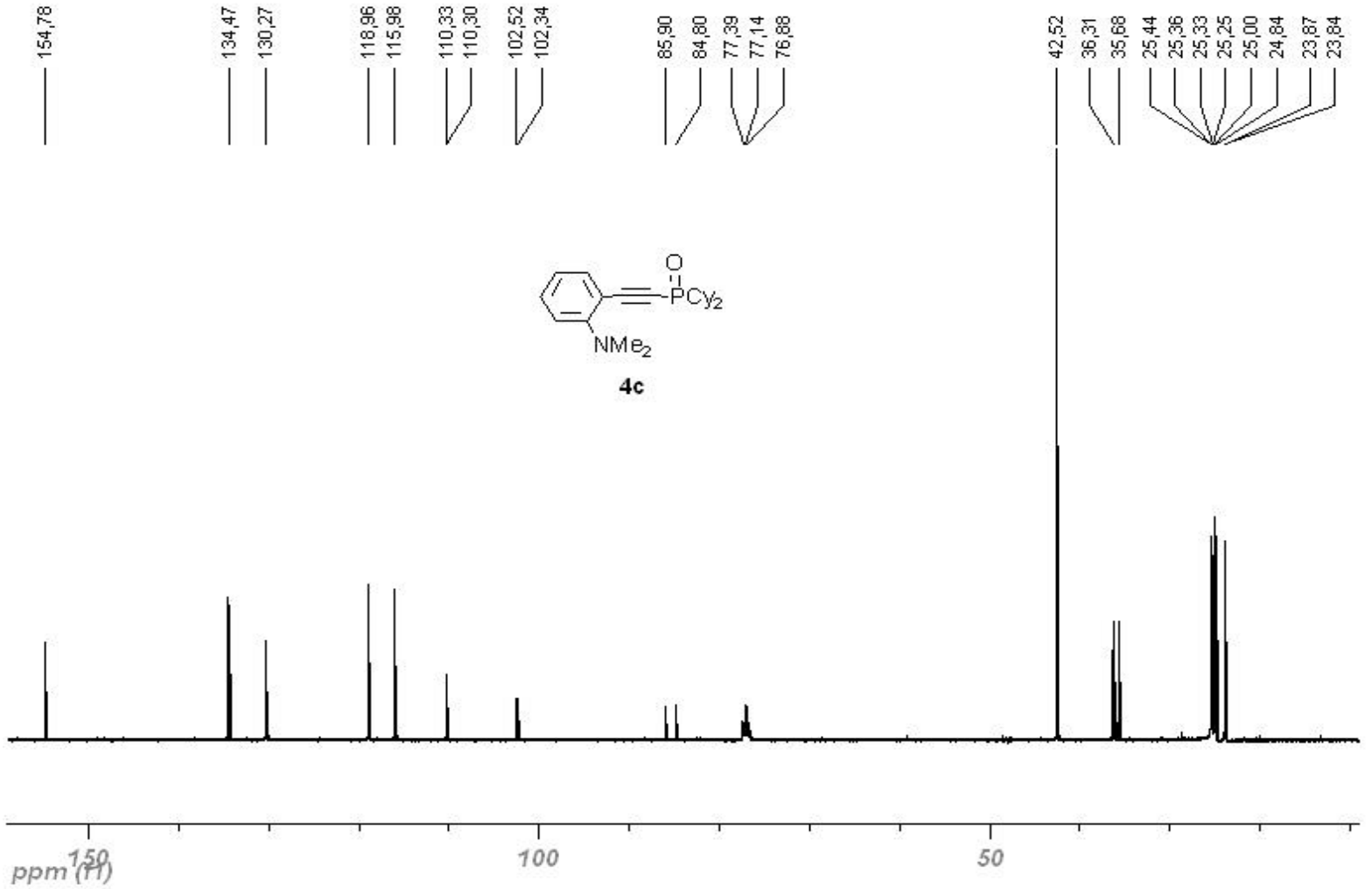
$^{31}P\{^{1}H\}$ NMR Spectrum of 2-(Dicyclohexylphosphinoylethynyl)-*N*,*N*-dimethylaniline (4c)



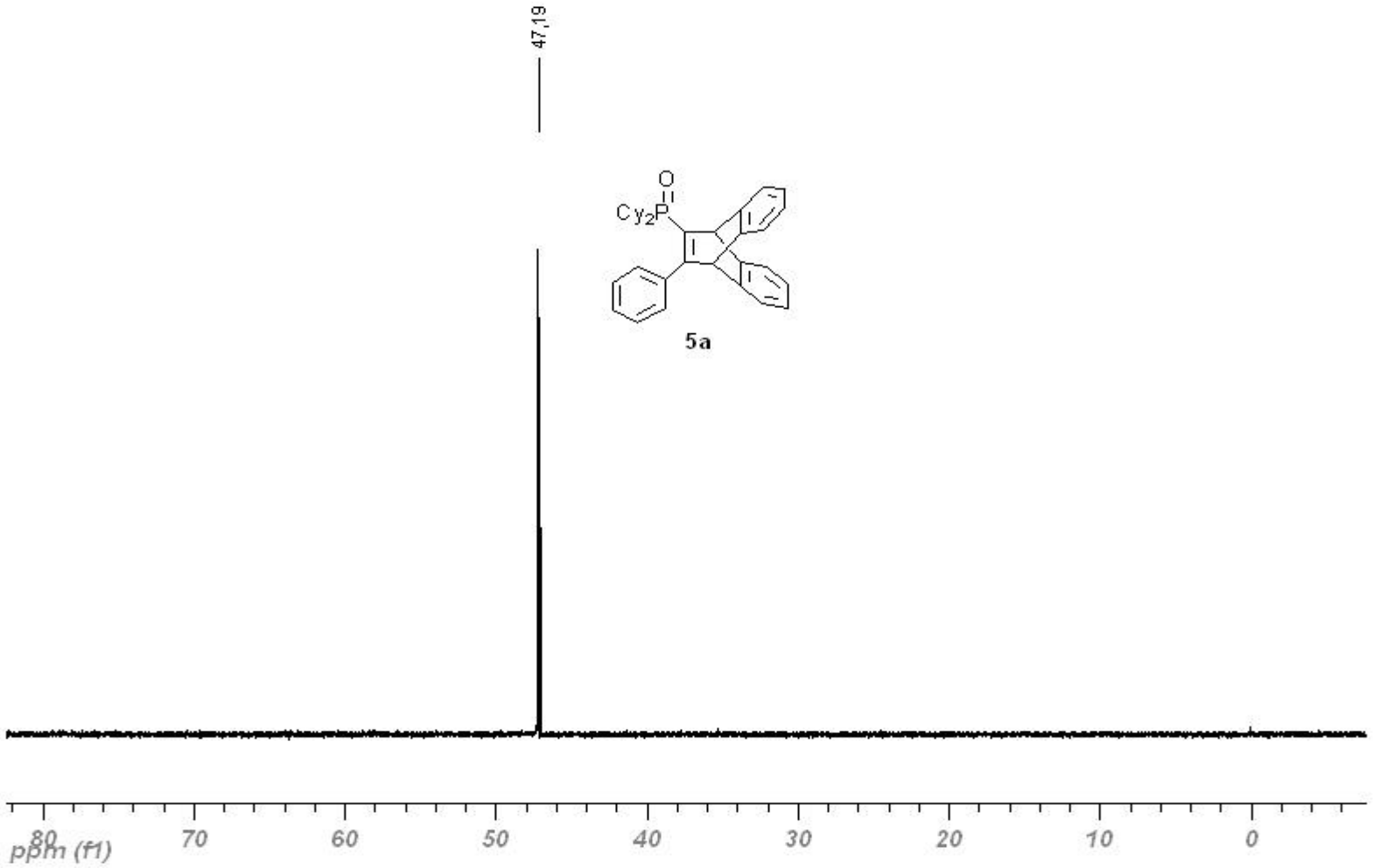
^{1}H NMR Spectrum of 2-(Dicyclohexylphosphinoylethynyl)-*N*,*N*-dimethylaniline (4c)



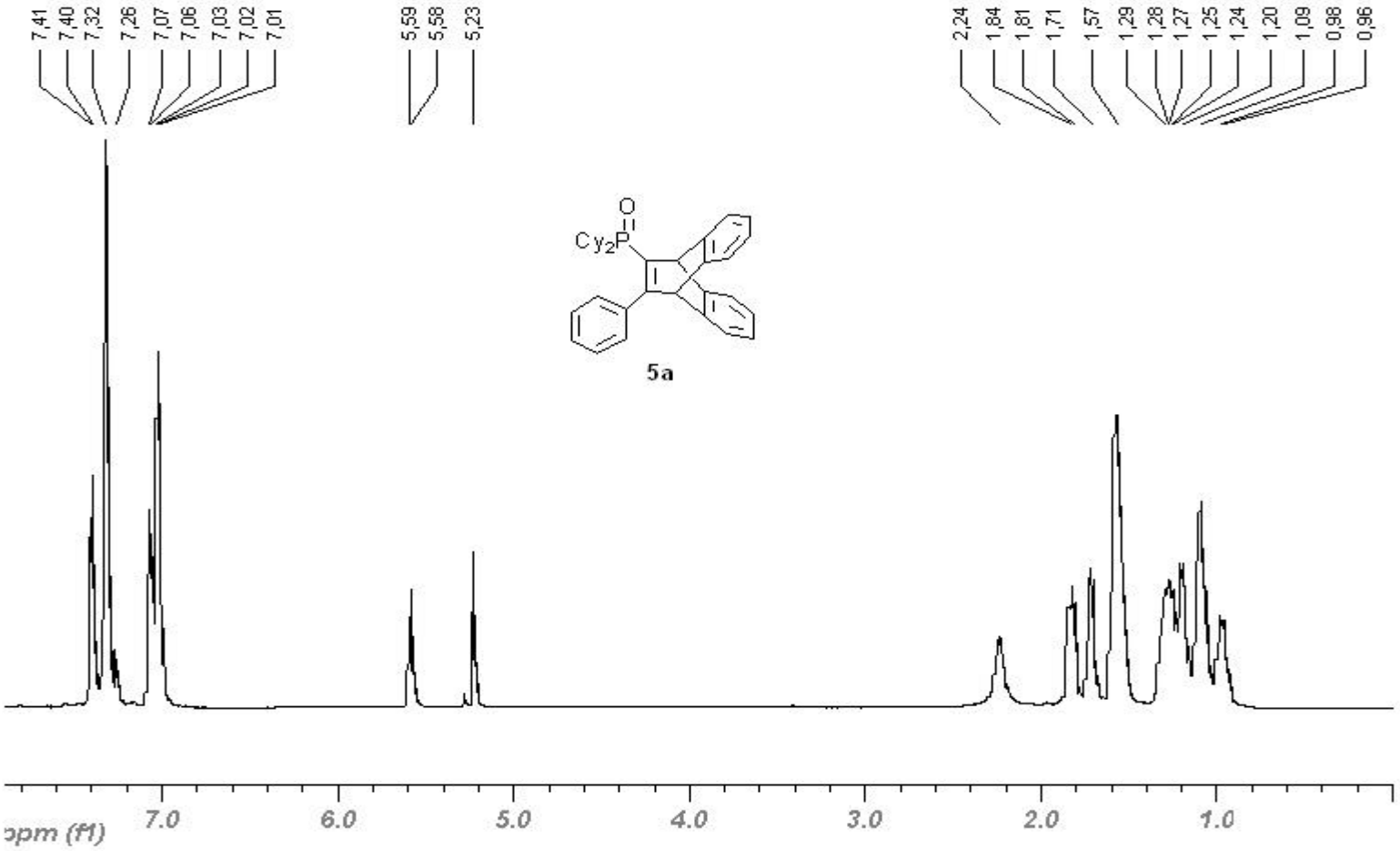
^{13}C {^{1}H} NMR Spectrum of 2-(Dicyclohexylphosphinoylethynyl)-*N*,*N*-dimethylaniline (4c)



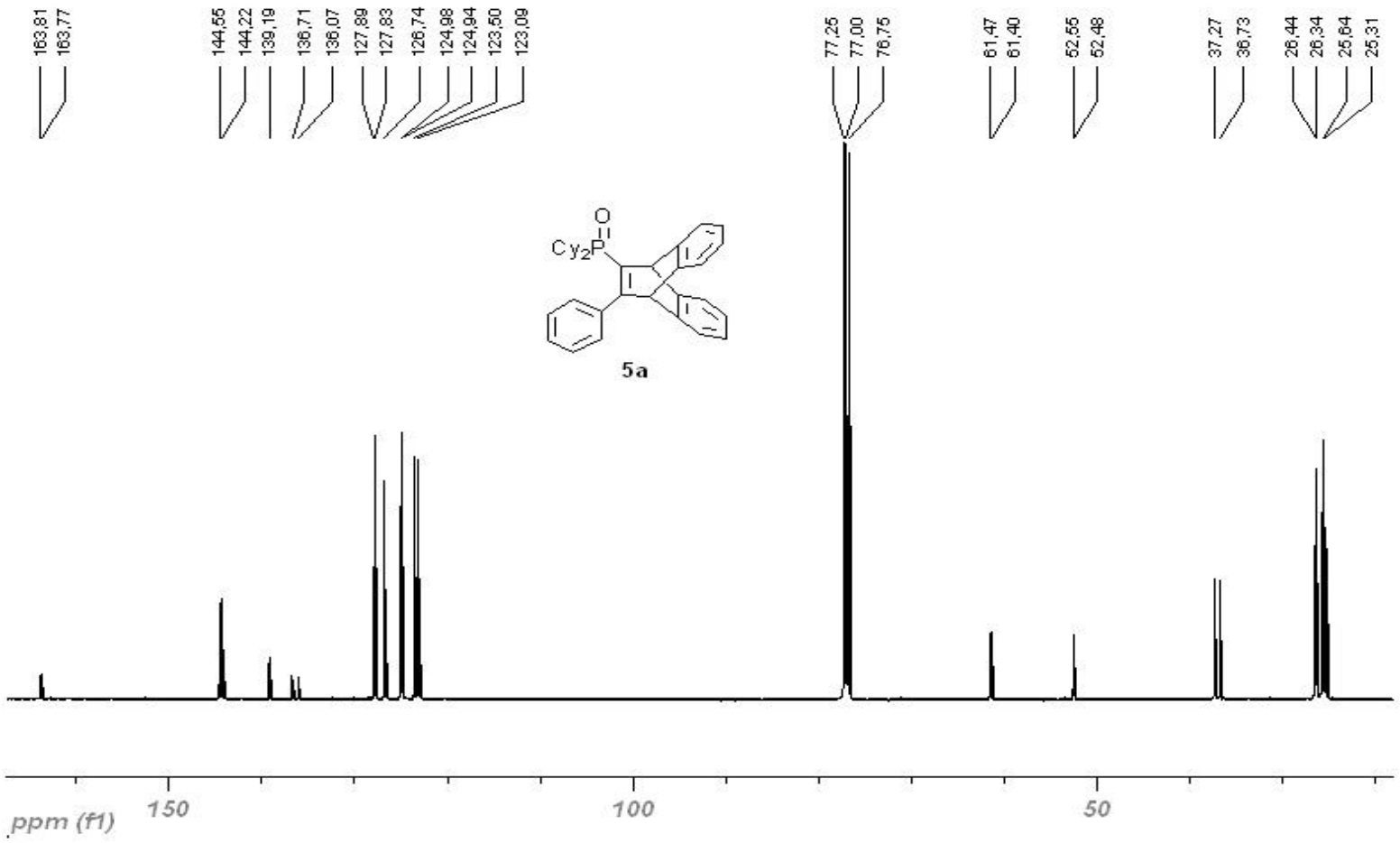
$^{31}P\{^{1}H\}$ NMR Spectrum of 2-(dicyclohexylphosphinoyl)-12-phenyl-9,10-dihydro-9,10-ethenoanthracene (5a)



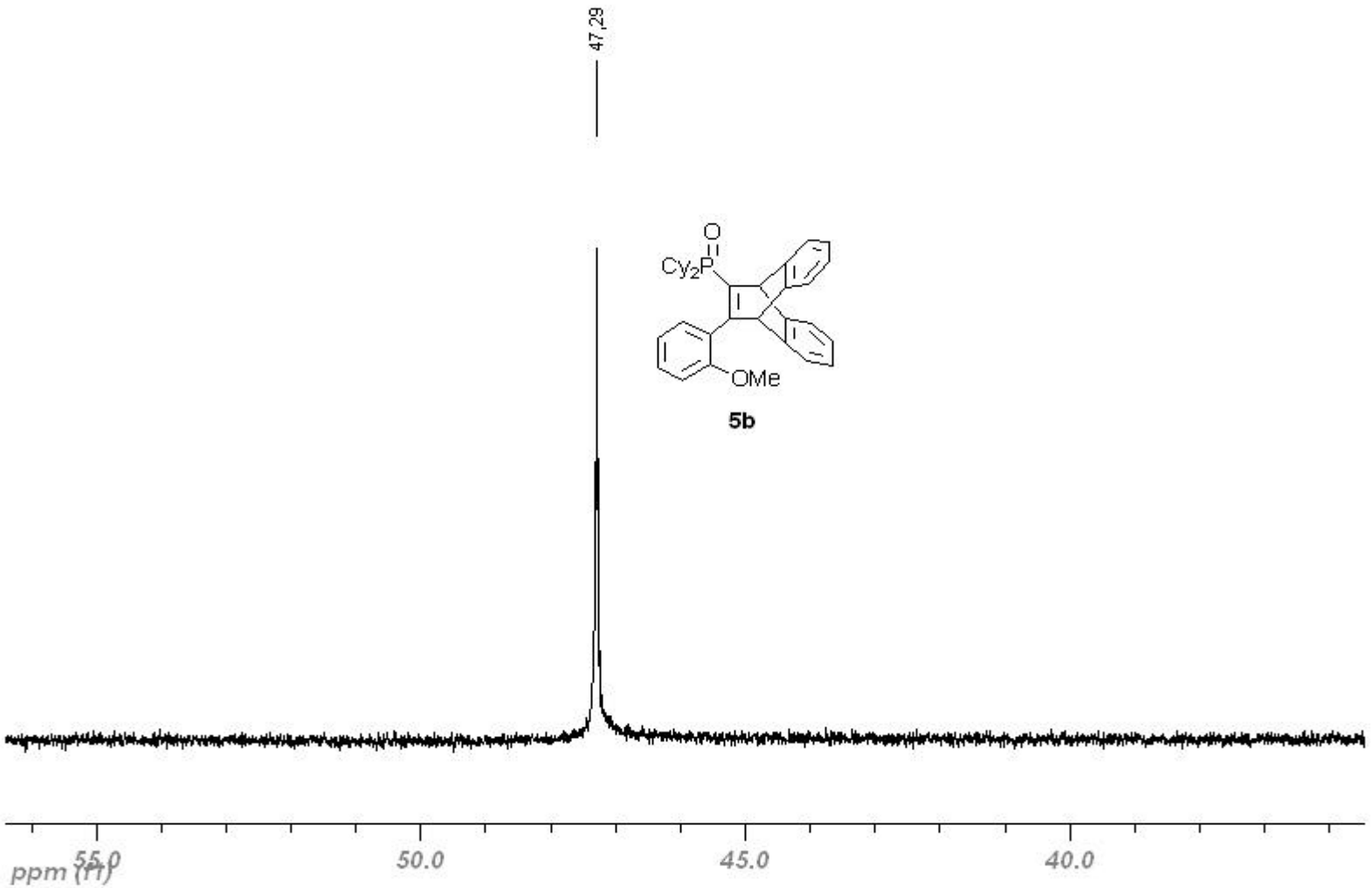
^{1}H NMR Spectrum of 2-(dicyclohexylphosphinoyl)-12-phenyl-9,10-dihydro-9,10-ethenoanthracene (5a)



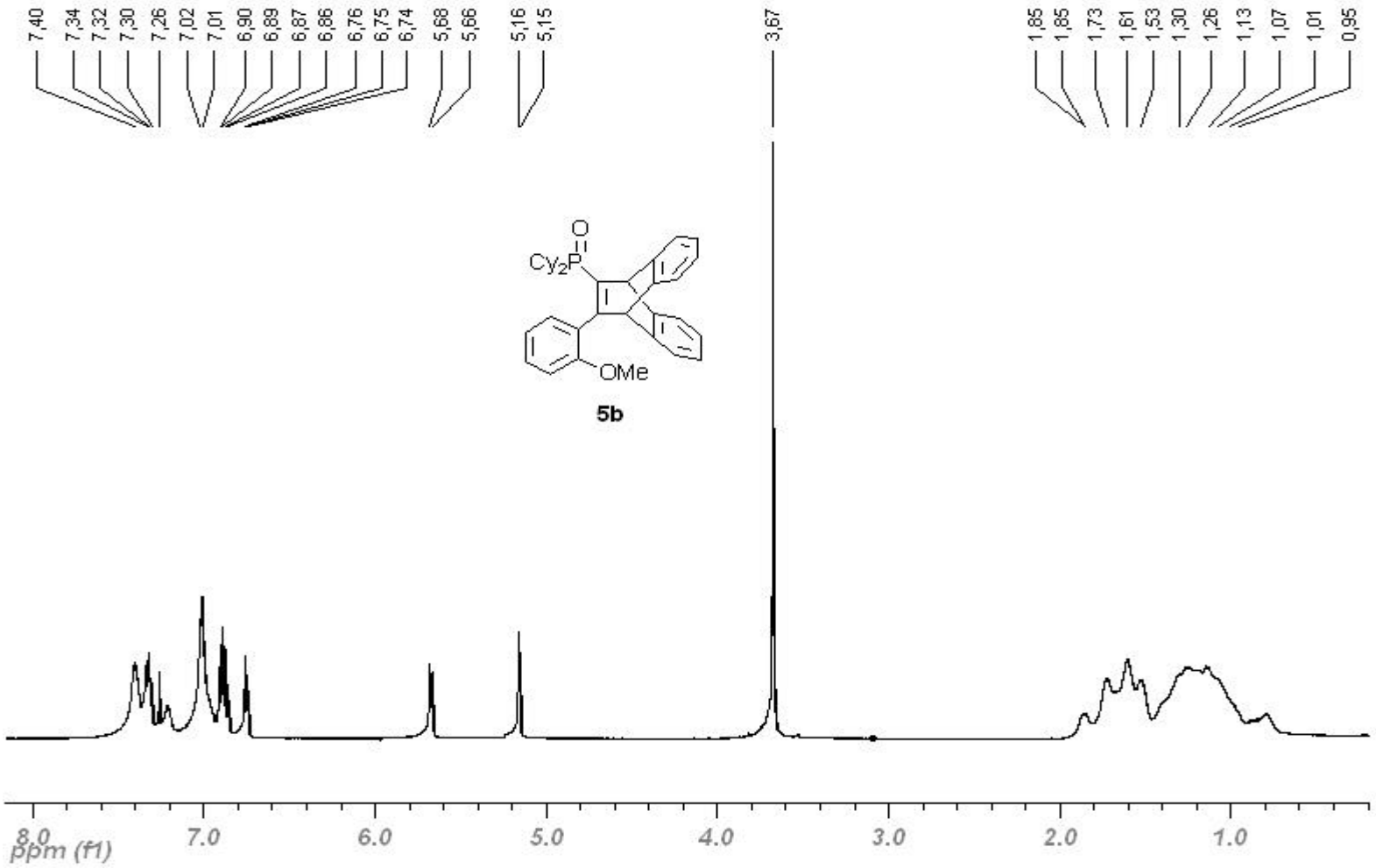
^{13}C {^{1}H} NMR Spectrum of 2-(dicyclohexylphosphinoyl)-12-phenyl-9,10-dihydro-9,10-ethenoanthracene (5a)



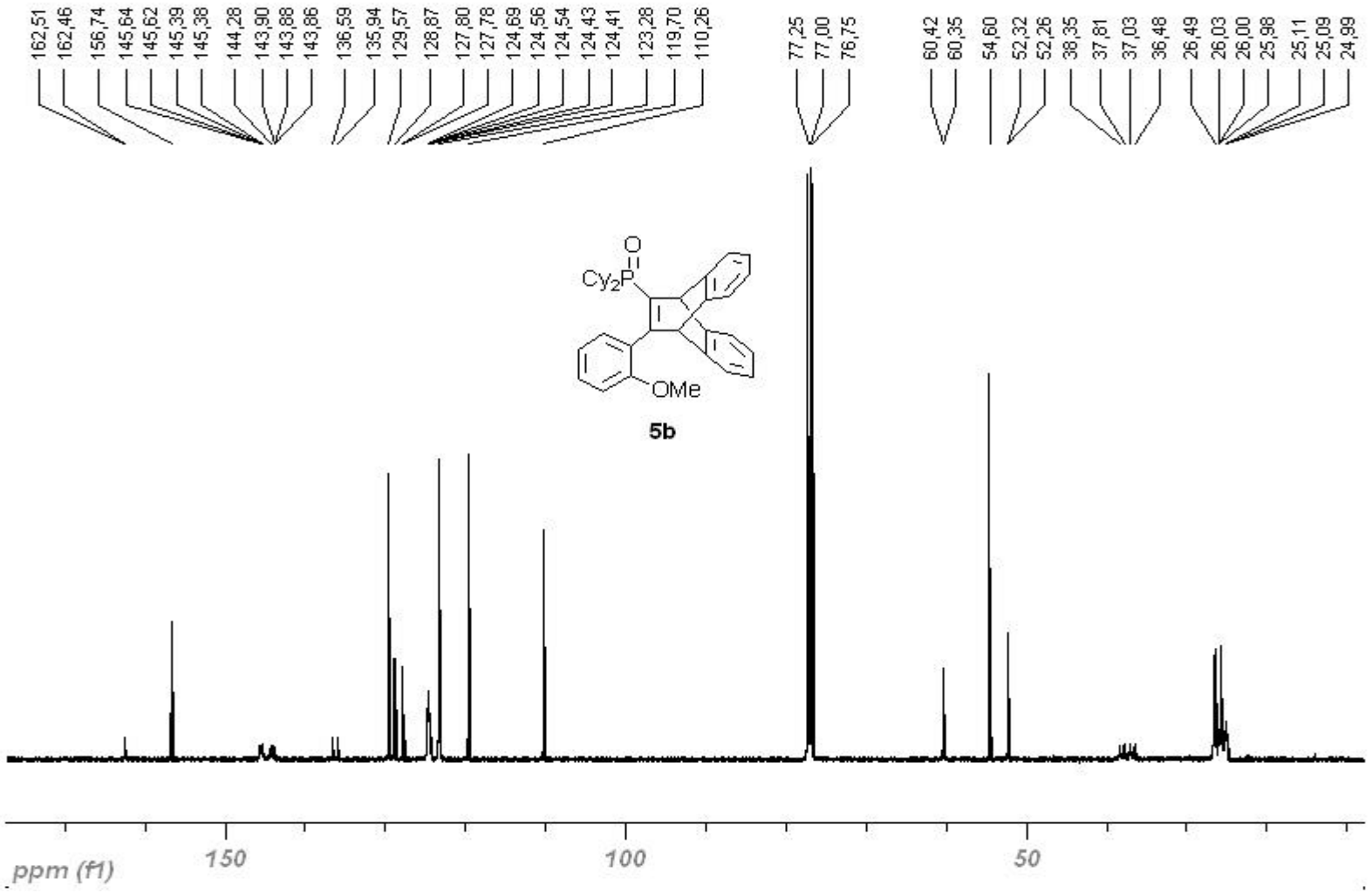
$^{31}P\{^{1}H\}$ NMR Spectrum of 11-(dicyclohexylphosphinoyl)-12-(2-methoxyphenyl)-9,10-dihydro-9,10-ethenoanthracene (5b)



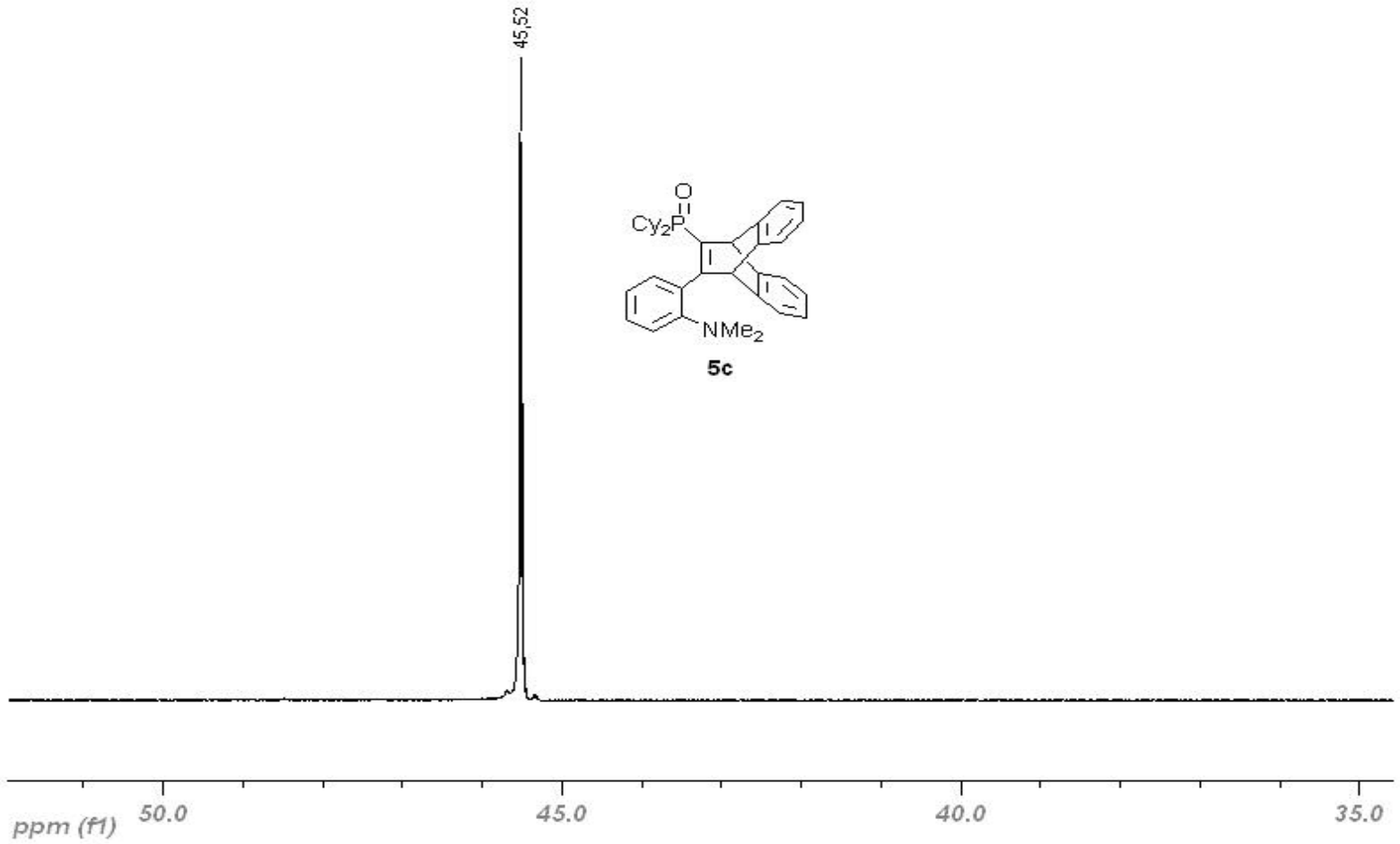
^{1}H NMR Spectrum of 11-(dicyclohexylphosphinoyl)-12-(2-methoxyphenyl)-9,10-dihydro-9,10-ethenoanthracene (5b)



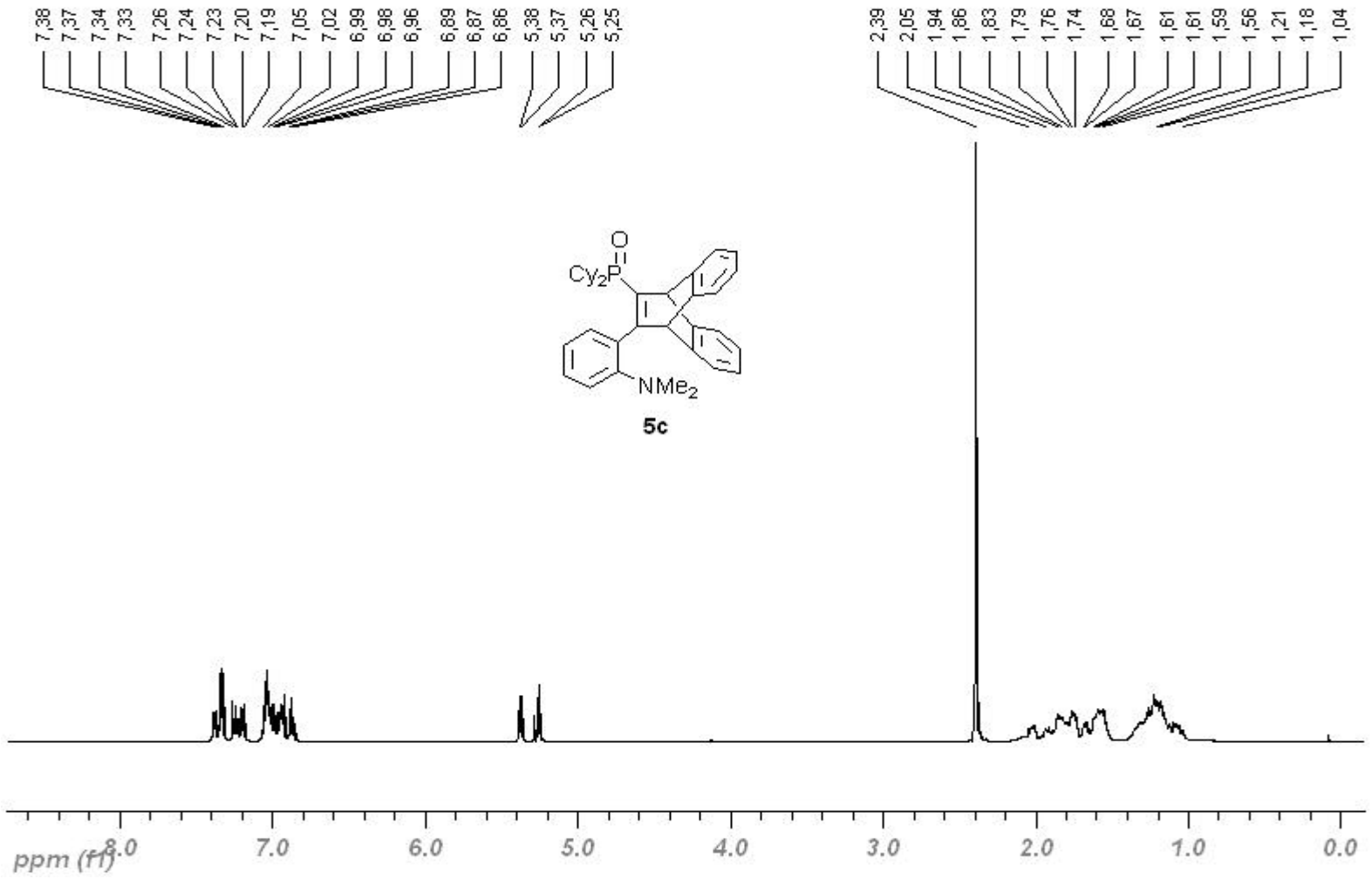
^{13}C {^{1}H} NMR Spectrum of 11-(dicyclohexylphosphinoyl)-12-(2-methoxyphenyl)-9,10-dihydro-9,10-ethenoanthracene (5b)



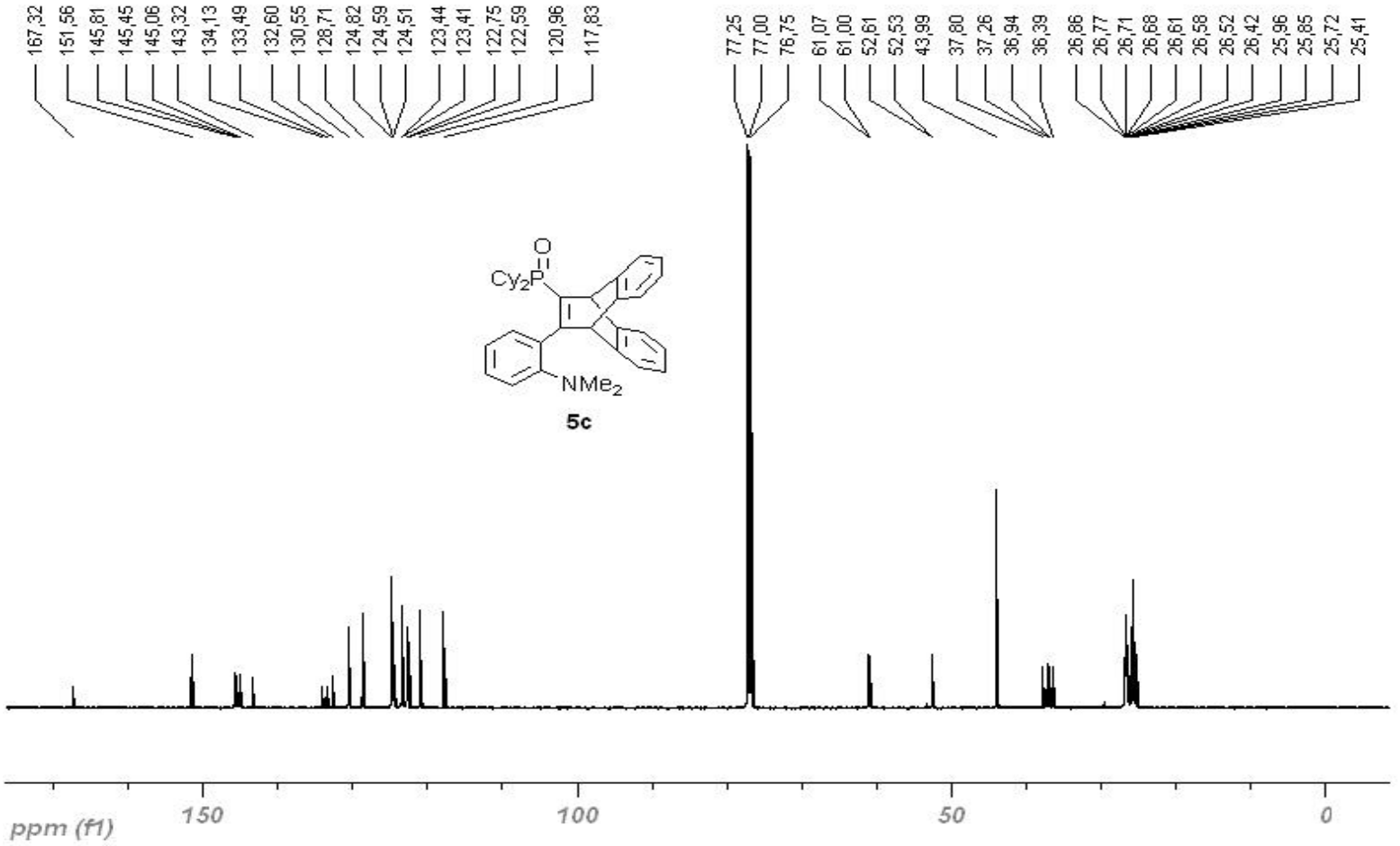
$^{31}P\{^{1}H\}$ NMR Spectrum of 11-(dicyclohexylphosphinoyl)-12-(2-dimethylaminophenyl)-9,10-dihydro-9,10-ethenoanthracene (5c)



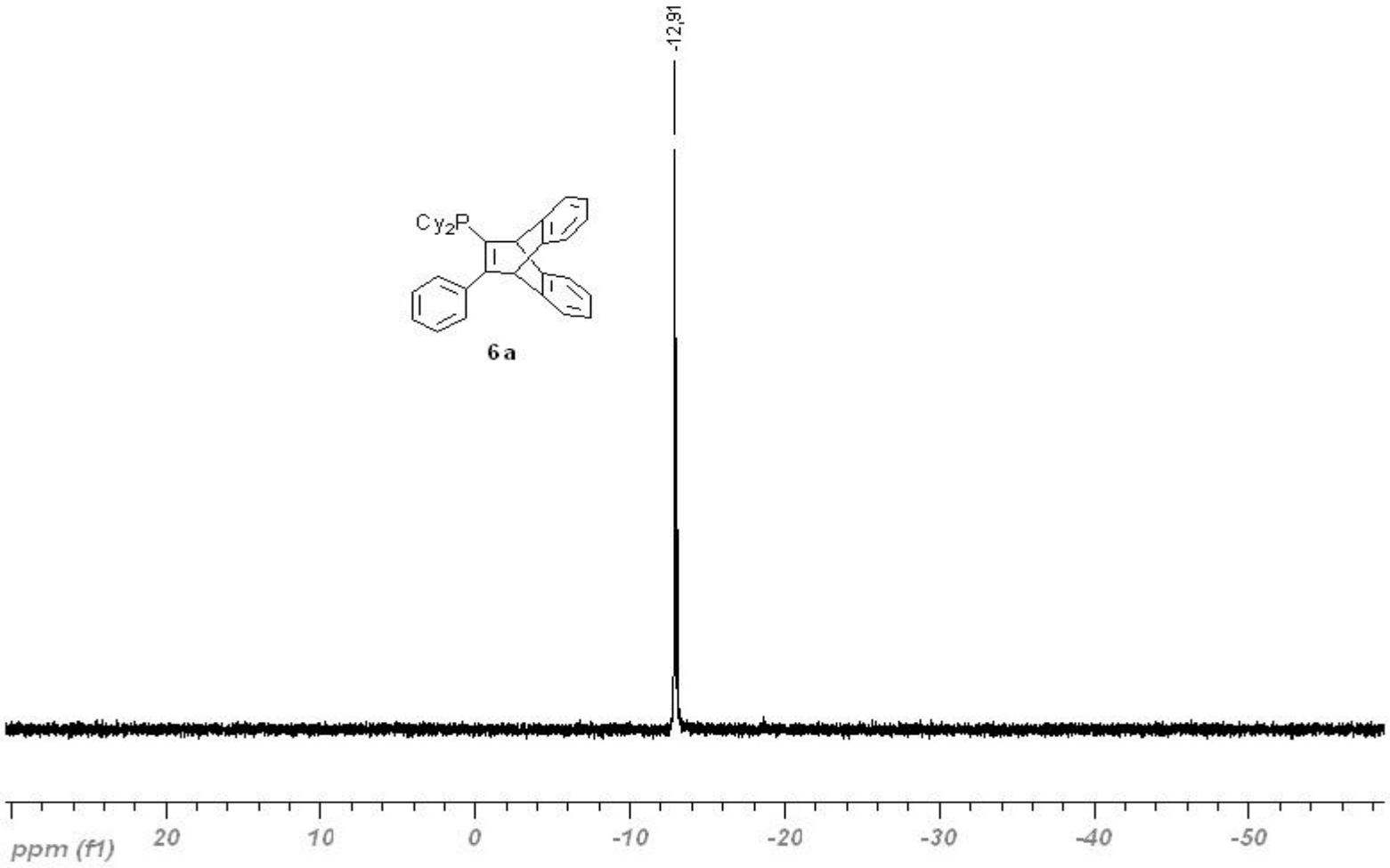
^{1}H NMR Spectrum of 11-(dicyclohexylphosphinoyl)-12-(2-dimethylaminophenyl)-9,10-dihydro-9,10-ethenoanthracene (5c)



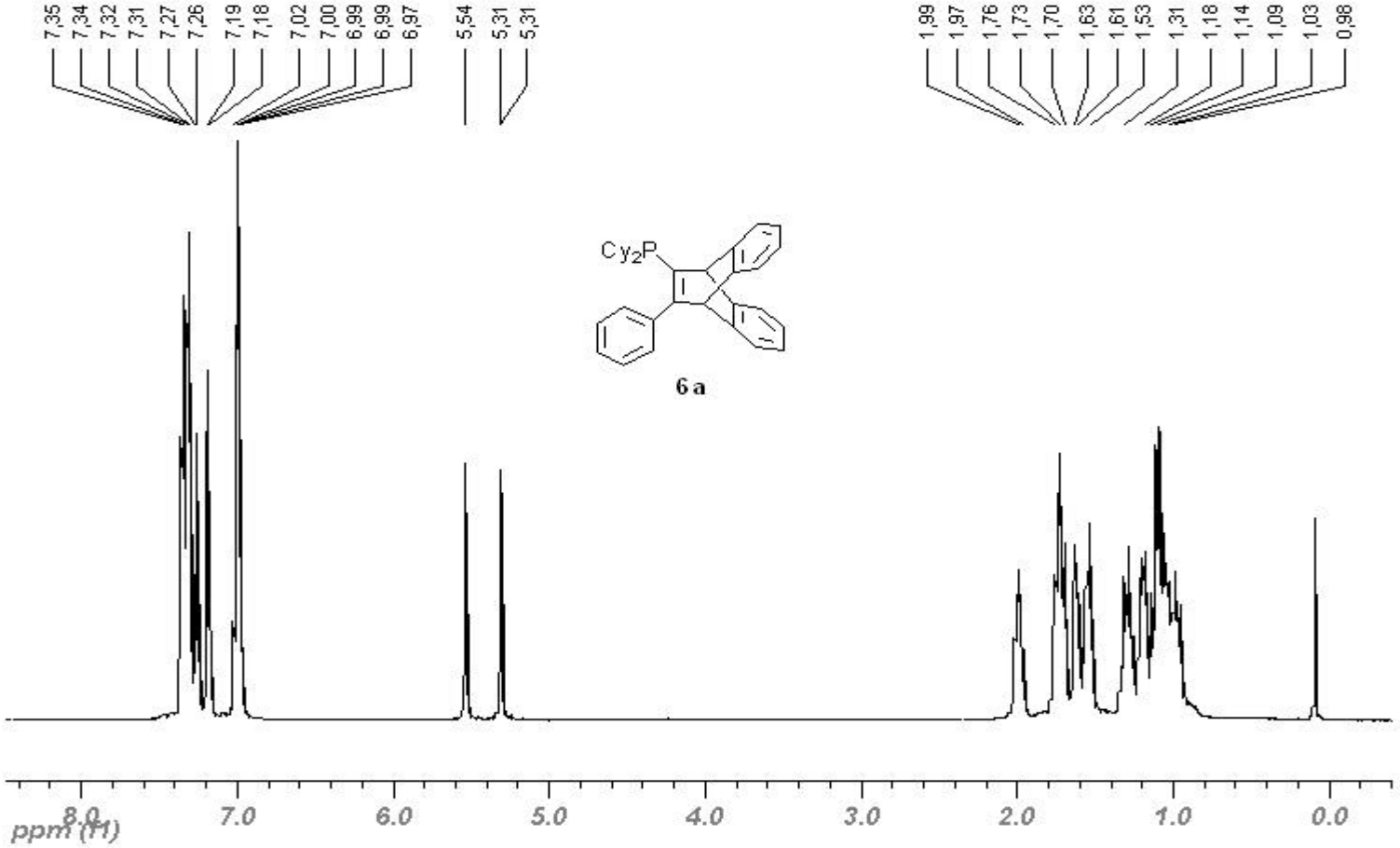
^{13}C {^{1}H} NMR Spectrum of 11-(dicyclohexylphosphinoyl)-12-(2-dimethylaminophenyl)-9,10-dihydro-9,10-ethenoanthracene (5c)



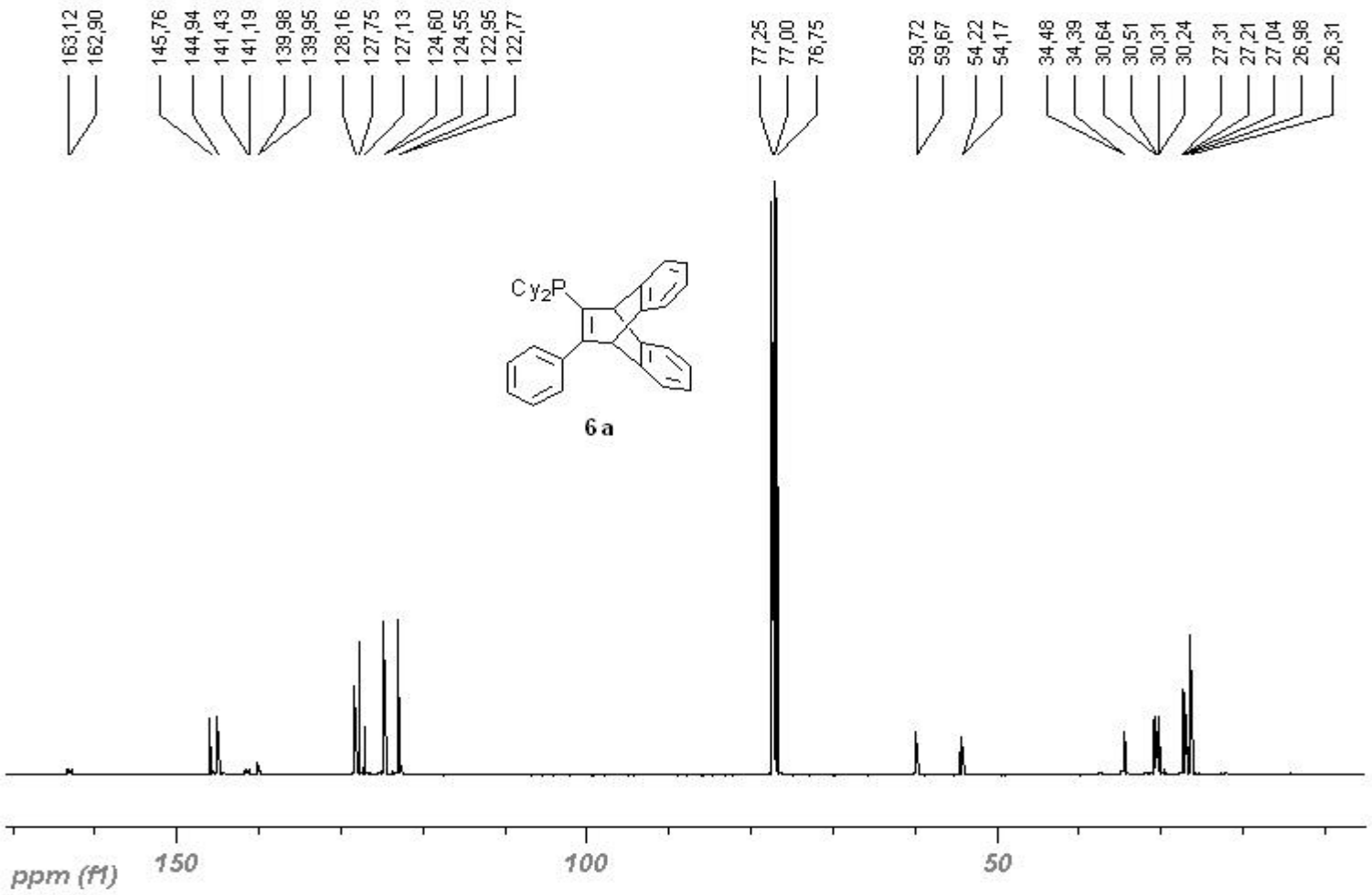
$^{31}P\{^{1}H\}$ NMR Spectrum of 2-(dicyclohexylphosphino)-12-phenyl-9,10-dihydro-9,10-ethenoanthracene (6a)



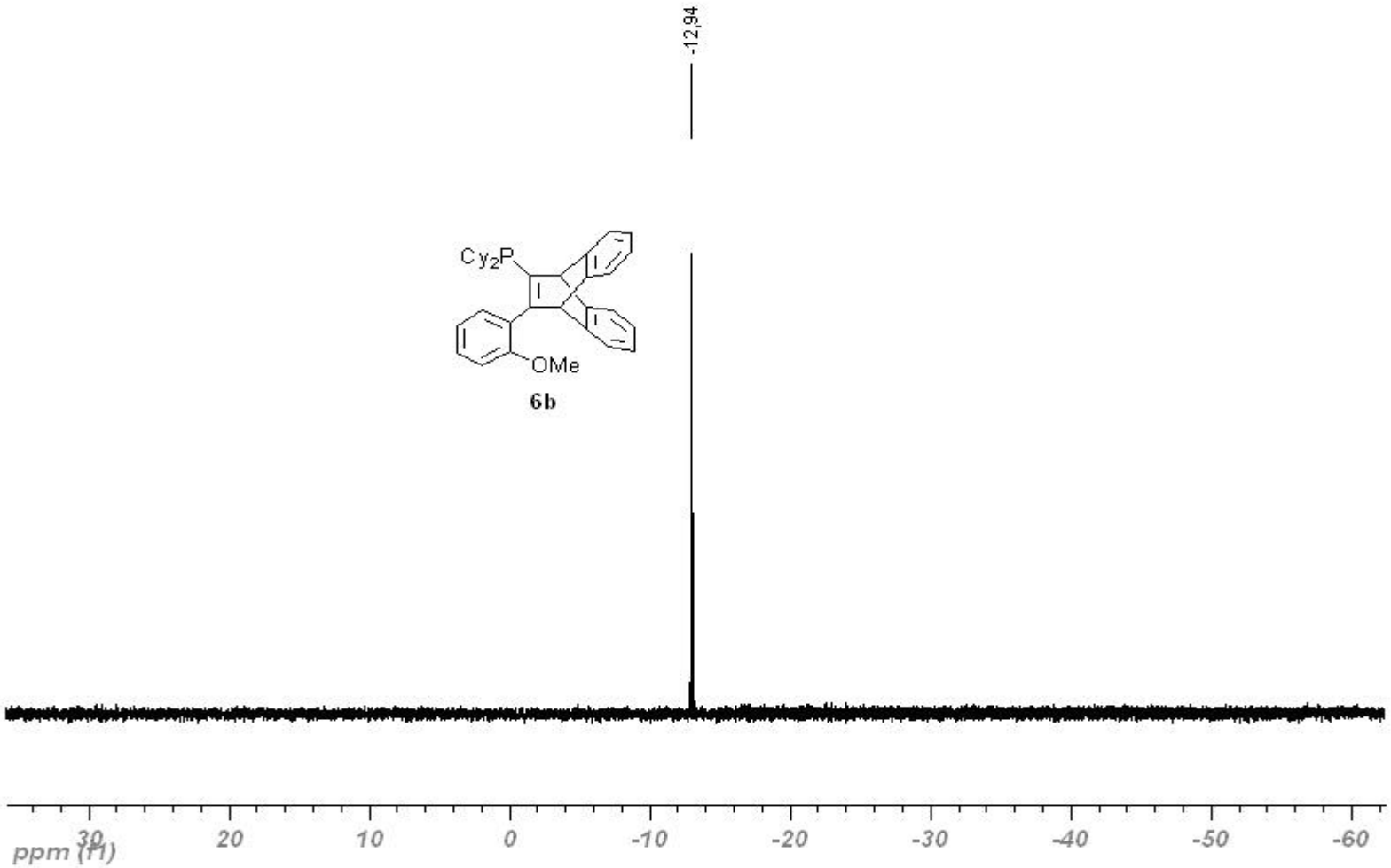
^{1}H NMR Spectrum of 2-(dicyclohexylphosphino)-12-phenyl-9,10-dihydro-9,10-ethenoanthracene (6a)



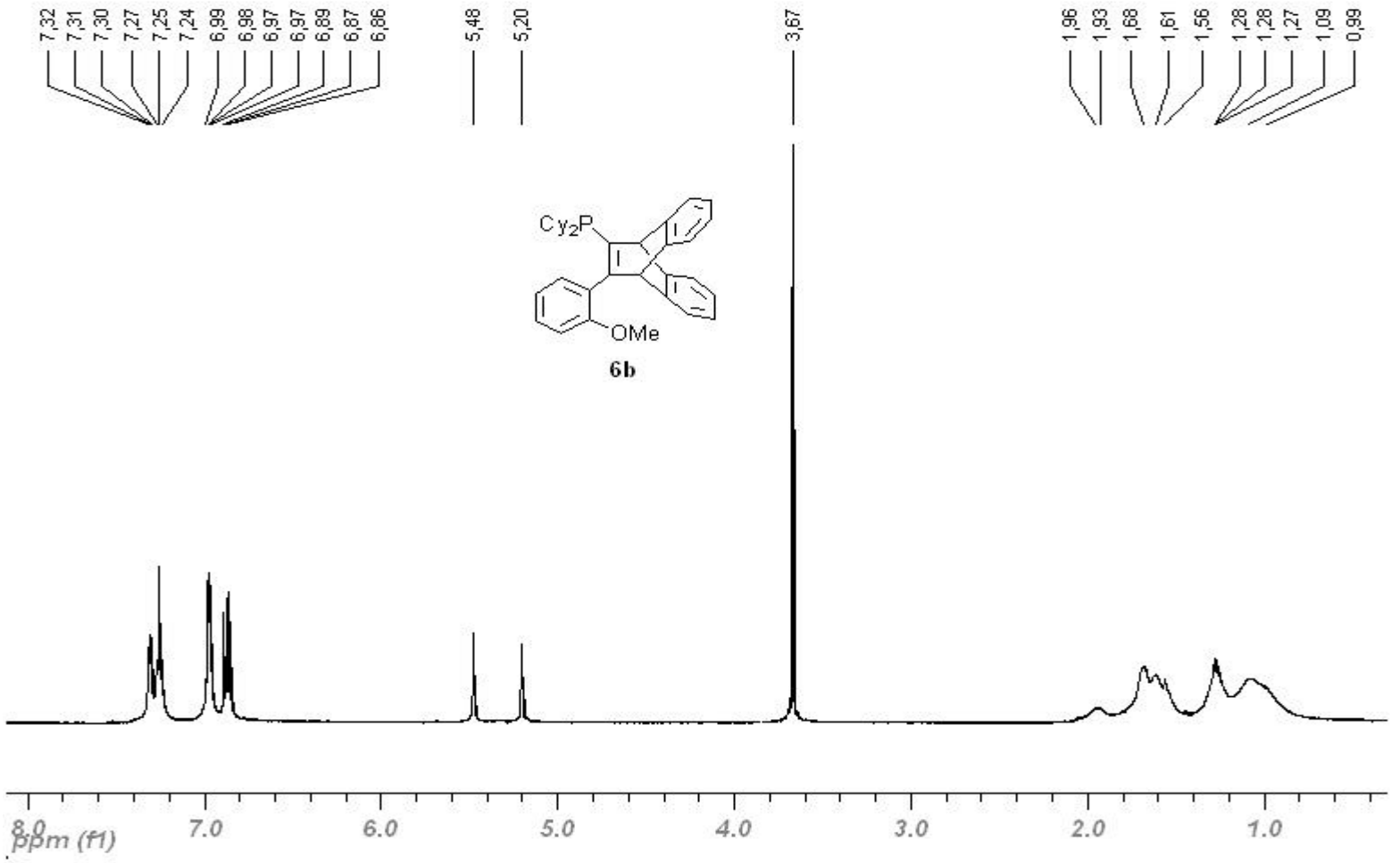
^{13}C {^{1}H} NMR Spectrum of 2-(dicyclohexylphosphino)-12-phenyl-9,10-dihydro-9,10-ethenoanthracene (6a)



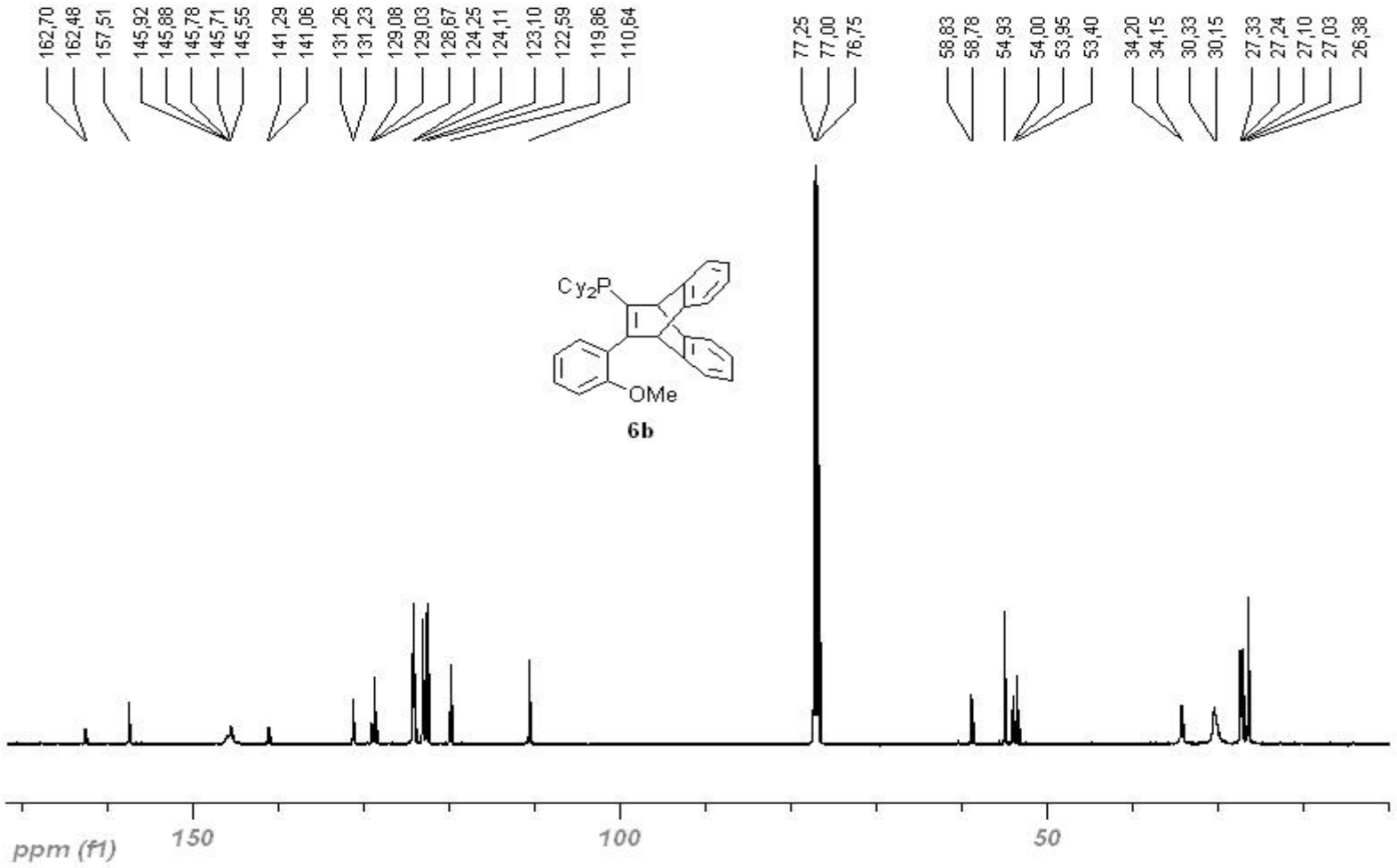
$^{31}P\{^{1}H\}$ NMR Spectrum of 11-(dicyclohexylphosphino)-12-(2-methoxyphenyl)-9,10-dihydro-9,10-ethenoanthracene (6b)



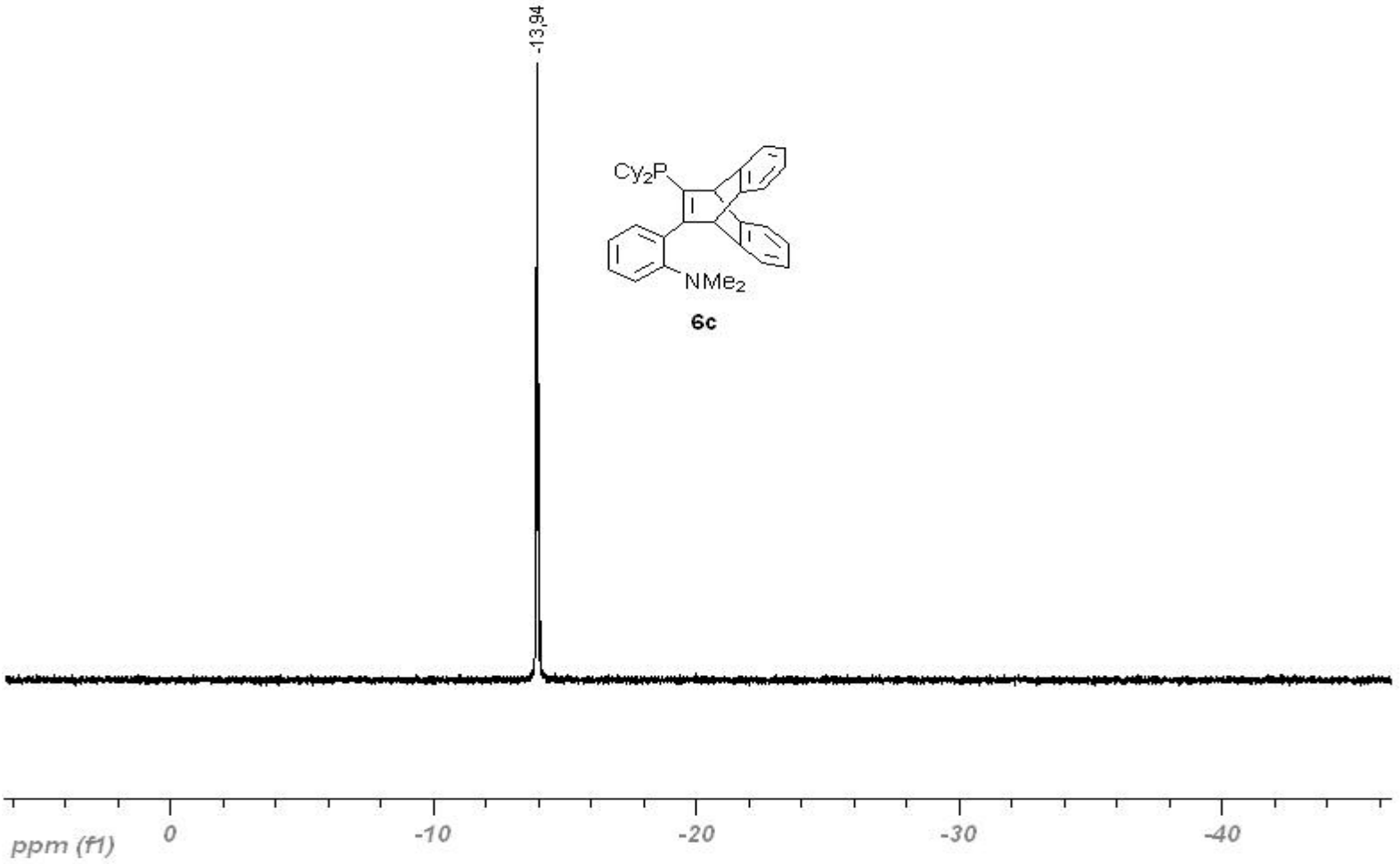
^{1}H NMR Spectrum of 11-(dicyclohexylphosphino)-12-(2-methoxyphenyl)-9,10-dihydro-9,10-ethenoanthracene (6b)



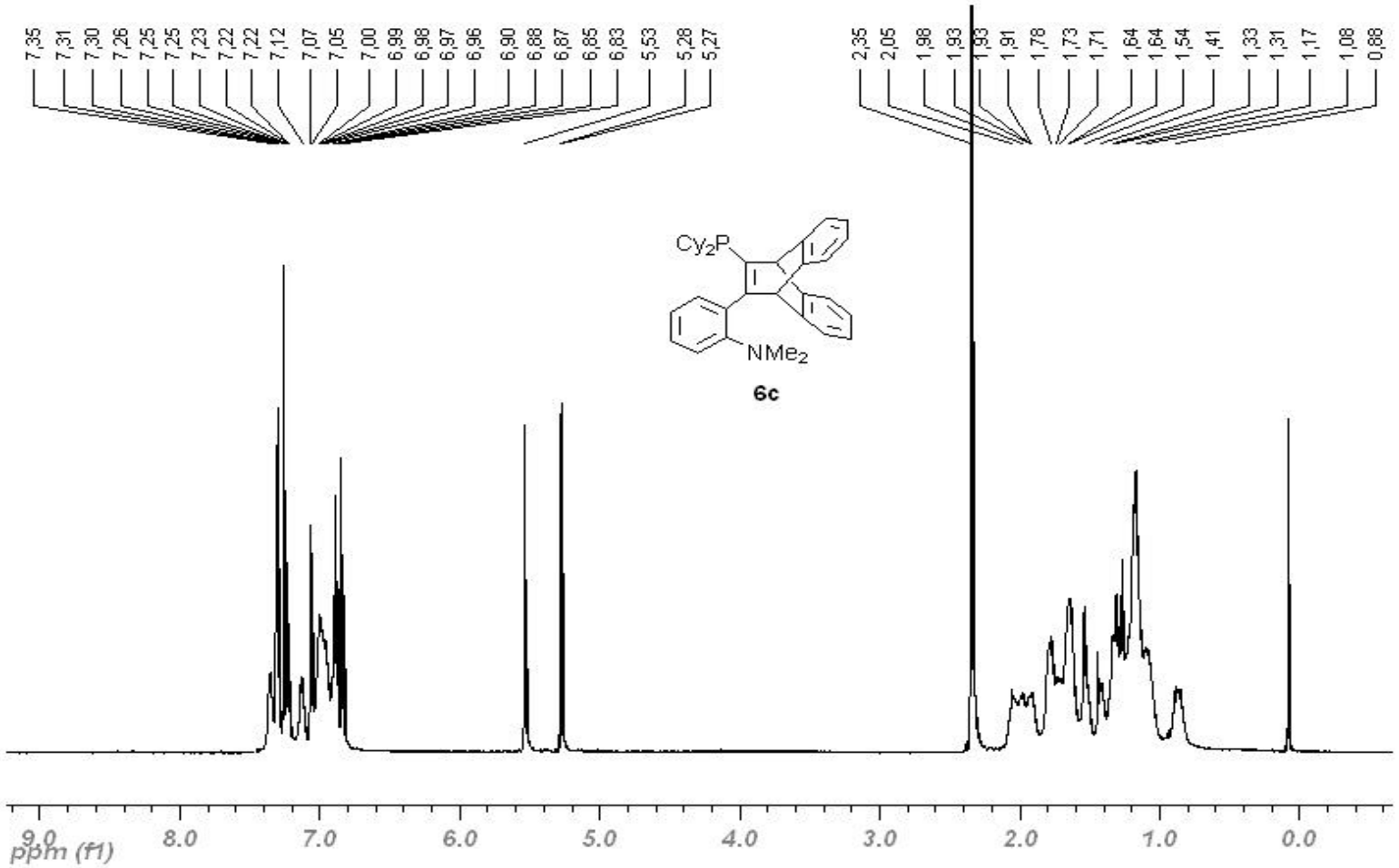
^{1}H NMR Spectrum of 11-(dicyclohexylphosphino)-12-(2-methoxyphenyl)-9,10-dihydro-9,10-ethenoanthracene (6b)



$^{31}P\{^{1}H\}$ NMR Spectrum of 11-(dicyclohexylphosphino)-12-(2-dimethylaminophenyl)-9,10-dihydro-9,10-ethenoanthracene (6c)



^{1}H NMR Spectrum of 11-(dicyclohexylphosphino)-12-(2-dimethylaminophenyl)-9,10-dihydro-9,10-ethenoanthracene (6c)



^{13}C {^{1}H} NMR Spectrum of 11-(dicyclohexylphosphino)-12-(2-dimethylaminophenyl)-9,10-dihydro-9,10-ethenoanthracene (6c)