Supporting Information

Asymmetric Hydrogenation of Heteroaromatic Compounds Mediated by Iridium-(*P-OP*) Complexes

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Experimental Section

All syntheses were carried out using chemicals as purchased from commercial sources unless otherwise cited. All manipulations and reactions were performed under inert atmosphere, in either a glove box or with standard Schlenk-type techniques. Glassware was dried *in vacuo* before use with a hot air gun. All solvents were dried by using a Solvent Purification System (SPS). Silica gel 60 (230-400 mesh) was used for column chromatography. NMR spectra were recorded in $CDCl_3$ unless otherwise cited using a 400 MHz spectrometer. ^{1}H-NMR and ^{13}C-NMR chemical shifts were quoted in ppm relative to residual solvent peaks, whereas $^{31}P\{^{1}H\}$-NMR chemical shifts were quoted in ppm relative to 85% phosphoric acid in water. Mass spectra were obtained by electrospray ionization (ESI, HRMS). Optical rotations were measured in dry THF, $CHCl_3$ or CH_2Cl_2. Melting points were determined in open capillaries and were uncorrected. Enantiomeric excesses were determined by HPLC on a chromatograph with an UV detector.

1. General synthetic procedure for the preparation of cationic iridium complexes derived from phosphine-phosphinite ligands.

$[\{Ir(\mu\text{-}Cl)(cod)\}_2]$ was dissolved in CH_2Cl_2 (1.0 mL) and a solution of the corresponding *P-OP* ligand in CH_2Cl_2 (2.0 mL) was added. After 10 min, NaBArF was added and the resulting mixture was stirred at room temperature for 30 min. After filtration of the formed salts through a 0.2 μm filter, the resulting filtrate was purified by flash cromatography on SiO_2 (hexanes/CH_2Cl_2 1:1) to give the corresponding cationic complexes [Ir(cod)(*P-OP*)]BArF as red powders.

[Ir(cod)(2a)]BArF (4a). The reaction between $[\{Ir(\mu\text{-}Cl)(cod)\}_2]$ and **2a** was carried out following the general procedure starting from **2a** (9 mg, 0.018 mmol) and $[\{Ir(\mu\text{-}Cl)(cod)\}_2]$ (6 mg, 0.009 mmol). $^{31}P\{^{1}H\}$-NMR (162 MHz, CD_2Cl_2) δ 92.0 (d, J = 44.2 Hz, P-O), 14.0 (d, J = 44.2 Hz, P-C) (see Figure 1). The resulting iridium complex was not further purified and allowed to react with NaBArF (16 mg, 0.018 mmol) following the general procedure. Complex **4a** was obtained as an intense red solid (19 mg, 65%

yield). $[\alpha]_D^{28}$ = −43.4 (*c* = 1.40, CH_2Cl_2); ^{1}H-NMR (400 MHz, CD_2Cl_2) δ 7.89-7.12 (m, 35H), 6.55-6.50 (m, 2H), 4.98-4.96 (m, 1H), 4.61-4.59 (m, 1H), 4.55 (d, *J* = 16.0 Hz, 1H), 4.23-4.12 (m, 2H), 4.04-4.02 (m, 1H), 3.29-3.20 (m, 5H), 2.56-2.41 (m, 4H), 2.32-2.27 (m, 2H), 2.14-2.09 (m, 2H); DEPTQ 135 (100 MHz, CD_2Cl_2) δ 161.7 (q, *J* = 49.5 Hz, C), 135.8 (CH), 135.7 (CH), 134.8 (CH), 134.1 (C), 133.45 (C), 133.39 (CH), 133.25 (CH), 133.22 (CH), 133.19 (CH), 132.82 (CH), 132.80 (CH), 132.5 (C), 132.3 (CH), 132.2 (CH), 132.0 (C), 131.9 (CH), 131.8 (CH), 131.38 (CH), 131.35 (CH), 129.7 (CH), 129.62 (CH), 129.58 (CH), 129.5 (CH), 129.43 (C), 129.36 (CH), 129.26 (CH), 129.1 (C), 129.03 (C), 129.00 (C), 128.97 (C), 128.9 (C), 128.8 (CH), 128.72 (CH), 128.69 (C), 128.66 (C), 128.4 (CH), 128.3 (CH), 124.6 (q, *J* = 270.8 Hz, C), 117.5-117.4 (m, CH), 95.0 (d, *J* = 13.0 Hz, CH), 92.9 (d, *J* = 9.2 Hz, CH), 92.7 (d, *J* = 9.5 Hz, CH), 83.6 (d, *J* = 10.7 Hz, CH), 73.8 (dd, *J* = 3.6 Hz, *J* = 3.6 Hz, CH), 72.2 (dd, *J* = 8.9 Hz, *J* = 8.9 Hz, CH_2), 58.8 (CH_3), 41.4 (d, *J* = 35.8 Hz, CH), 32.4 (CH_2), 31.9 (CH_2), 30.0 (CH_2), 29.4 (CH_2); ^{31}P{^{1}H}-NMR (162 MHz, CD_2Cl_2) δ 102.9 (d, *J* = 30.5 Hz, P-O), 12.0 (d, *J* = 30.5 Hz, P-C); ^{11}B{^{1}H}-NMR (128 MHz, CD_2Cl_2) δ −6.7; ^{19}F{^{1}H}-NMR (376 MHz, CD_2Cl_2) δ −62.9; MS HR-ESI [found 833.2396, $C_{42}H_{44}O_2P_2{}^{191}Ir$ $(M-BArF)^+$ requires 833.2423].

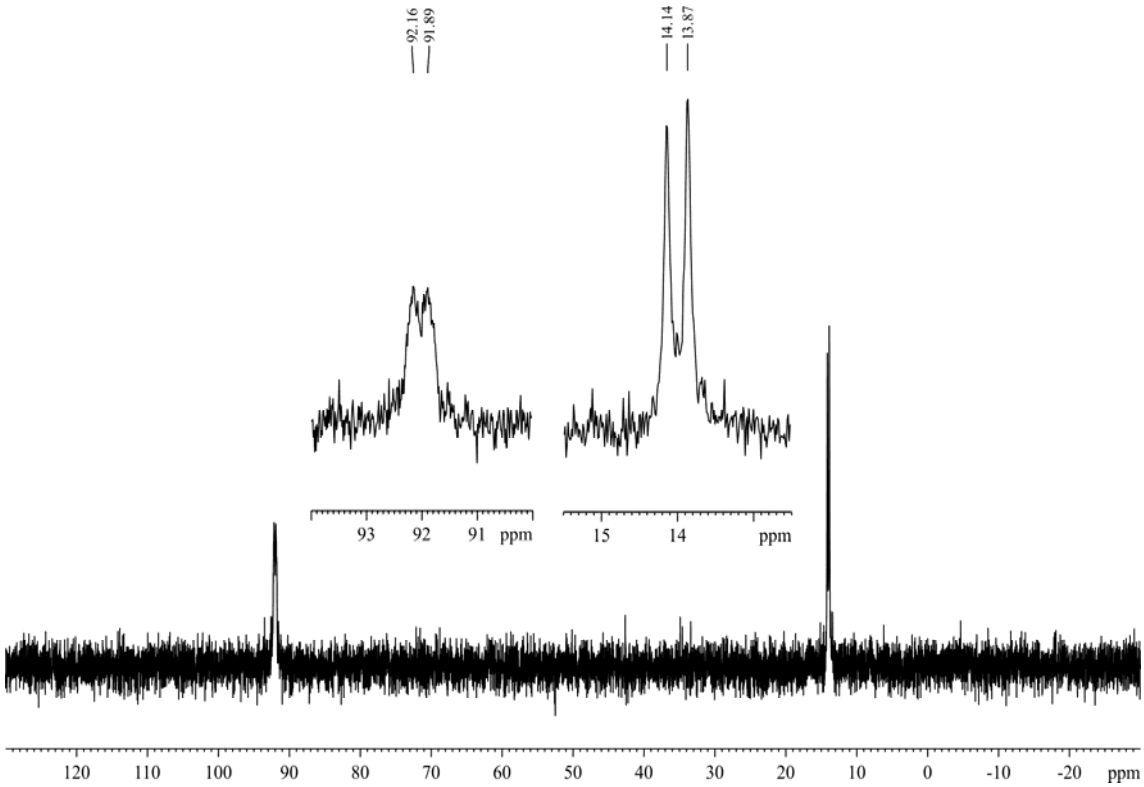


Figure 1

[Ir(cod)(2b)]BArF (4b). The reaction between [{Ir(μ-Cl)(cod)}$_2$] and **2b** was carried out following the general procedure starting from **2b** (14 mg, 0.018 mmol) and [{Ir(μ-Cl)(cod)}$_2$] (6 mg, 0.009 mmol). ^{31}P{^{1}H}-NMR (162 MHz, CD_2Cl_2) δ 91.1 (bs, P-O), 13.2 (d, J = 44.4 Hz, P-C) (see Figure 2). The resulting iridium complex was not further purified and allowed to react with NaBArF (16 mg, 0.018 mmol) following the general procedure. Complex **4b** was obtained as an intense red solid (31 mg, 90% yield). $[\alpha]_D^{28}$ = −32.2 (c = 1.63, CH_2Cl_2); ^{1}H-NMR (400 MHz, CD_2Cl_2) δ 8.01-7.97 (m, 2H), 7.81-7.63 (m, 12H), 7.63-7.15 (m, 36H), 6.65-6.61 (m, 2H), 5.05 (bs, 1H), 4.72 (d, J = 15.8 Hz, 1H), 4.59 (bs, 1H), 4.28-4.20 (m, 1H), 4.07 (bs, 2H), 3.22-3.18 (m, 1H), 2.90 (dd, J = 9.0 Hz, J = 9.0 Hz, 1H), 2.60-2.39 (m, 4H), 2.32-2.28 (m, 2H), 2.13-2.08 (m, 2H); DEPTQ 135 (100 MHz, CD_2Cl_2) δ 161.8 (q, J = 49.8 Hz, C), 143.1 (C), 136.1 (CH), 136.0 (CH), 134.8 (CH), 133.8 (C), 133.25 (CH), 133.23 (CH), 133.15 (CH), 133.11 (C), 133.0 (CH), 132.94 (CH), 132.92 (CH), 132.5 (C), 132.4 (CH), 132.3 (CH), 132.00 (C), 131.97 (C), 131.90 (CH), 131.88 (CH), 131.44 (CH), 131.42 (CH), 130.0 (C), 129.8 (CH), 129.7 (CH), 129.6 (CH), 129.5 (CH), 129.4 (C), 129.3 (CH), 129.09 (C), 129.06 (C), 129.04 (C), 129.01 (C), 128.79 (CH), 128.75 (C), 128.72 (C), 128.68 (CH), 128.61 (CH), 128.55 (CH), 128.4 (CH), 128.2 (CH), 128.0 (CH), 127.9 (CH), 127.4 (CH), 124.6 (q, J = 272.0 Hz, C), 117.6-117.4 (m, CH), 95.3 (d, J = 13.0 Hz, CH), 93.2 (d, J = 9.1 Hz, CH), 93.0 (d, J = 9.3 Hz, CH), 87.7 (C), 83.5 (d, J = 11.0 Hz, CH), 74.6 (dd, J = 3.5 Hz, J = 3.5 Hz, CH), 63.3 (dd, J = 8.9 Hz, J = 8.9 Hz, CH_2), 42.3 (d, J = 35.8 Hz, CH), 32.6 (CH_2), 32.1 (CH_2), 29.8 (CH_2), 29.1 (CH_2); ^{31}P{^{1}H}-NMR (162 MHz, CD_2Cl_2) δ 103.6 (d, J = 30.0 Hz, P-O), 12.6 (d, J = 30.0 Hz, P-C); ^{11}B{^{1}H}-NMR (128 MHz, CD_2Cl_2) δ −6.7; ^{19}F{^{1}H}-NMR (376 MHz, CD_2Cl_2) δ −62.9; MS HR-ESI [found 1063.3408, $C_{60}H_{56}O_2P_2{}^{193}Ir$ $(M-BArF)^+$ requires 1063.3385].

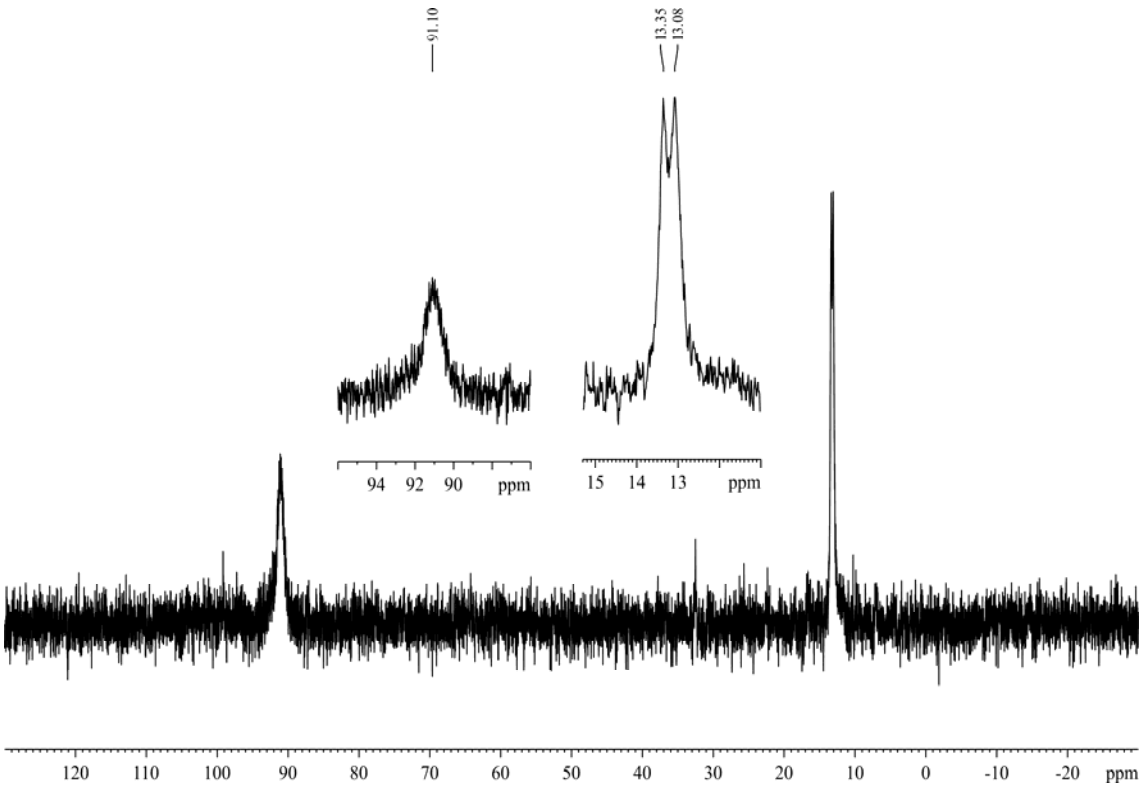


Figure 2

2. General synthetic procedure for the preparation of neutral iridium complexes derived from phosphine-phosphite ligands.

Method A. *In situ* preparation of the complexes: [{Ir(μ-Cl)(cod)}$_2$] was dissolved in THF-d_8 (300 μL) and a solution of the corresponding *P-OP* ligand in THF-d_8 (300 μL) was added. After 15 min stirring, the reaction mixture was *in situ* analyzed to characterize iridium complexes [Ir(Cl)(cod)(*P-OP*)].

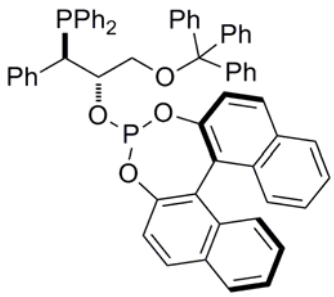
[Ir(Cl)(cod)(3)] (5). Iridium complex **5** was prepared following the general procedure (method A), starting from **3** (17.5 mg, 0.0310 mmol) and [{Ir(μ-Cl)(cod)}$_2$] (10.4 mg, 0.0155 mmol). ^{1}H-NMR (400 MHz, THF-d_8) δ 7.80-7.20 (m, 18H), 7.10-6.90 (m, 6H), 4.53 (dd, J = 13.3 Hz, J = 3.9 Hz, 1H), 3.88-3.85 (m, 2H), 3.33-3.11 (m, 7H), 2.86-2.76 (m, 2H), 2.44-2.39 (m, 2H), 1.80-1.72 (m, 2H), 1.37-1.33 (m, 2H); ^{13}C{^{1}H}-NMR (100 MHz, THF-d_8) δ 150.5 (C), 150.4 (C), 150.2 (C), 150.0 (C), 138.0 (CH), 137.9 (CH), 135.82 (C), 135.76 (C), 133.24 (CH), 133.17 (CH), 130.41 (CH), 130.39 (CH), 130.3 (CH), 130.2 (CH), 130.0 (C), 129.9 (C), 129.73 (CH), 129.71 (CH), 129.6 (C), 129.5 (CH), 129.4 (CH), 128.8 (CH), 128.6 (C), 128.0 (C), 127.4 (CH), 127.2 (CH), 127.1

(CH), 126.6 (CH), 126.53 (CH), 126.50 (CH), 125.4 (CH), 125.0 (CH), 123.4 (CH), 121.34 (CH), 121.31 (CH), 76.6 (CH), 73.6 (d, J = 7.8 Hz, CH_2), 73.1 (CH), 70.3 (CH), 57.7 (CH_3), 45.8 (d, J = 30.5 Hz, CH), 37.4 (CH_2), 27.6 (CH_2); $^{31}P\{^1H\}$-NMR (162 MHz, THF-d_8) δ 108.0 (d, J = 58.1 Hz, P-O), 13.7 (d, J = 58.1 Hz, P-C); MS HR-ESI [found 863.2164, $C_{42}H_{42}O_4P_2{}^{191}Ir$ $(M-Cl)^+$ requires 863.2148].

Method B. Preparation of the neutral iodo complex [Ir(I)(cod)(3)] (6). [{Ir(μ-Cl)(cod)}$_2$] (11.4 mg, 0.0170 mmol) was dissolved in CH_2Cl_2 (1.0 mL) and a solution of the corresponding *P-OP* ligand **3** (19.2 mg, 0.0340 mmol) in CH_2Cl_2 (2.0 mL) was added. After 15 min, the solvent was evaporated to dryness and the residue dissolved in dry acetone (2.0 mL). This solution was then transferred to a sealed tube, which contained an acetone solution (4.0 mL) of LiI (0.227 g, 1.70 mmol). The reaction mixture was stirred at reflux for 24 h while a yellow solid was precipitated. The solid was filtered, washed with dry acetone (3 x 2.0 mL) and dried *in vacuo*. The solid was dissolved in CH_2Cl_2 and precipitated by slow addition of hexanes, producing the corresponding neutral iridium complexes **6** as a yellow powder (16.3 mg, 48% yield). $[\alpha]_D{}^{28}$ = −385.4 (*c* 0.26, CH_2Cl_2); ^{1}H-NMR (400 MHz, CD_2Cl_2) δ 7.79 (bs, 2H), 7.66-7.54 (m, 5H), 7.48-7.33 (m, 9H), 7.23-7.20 (m, 2H), 7.05-6.56 (m, 6H), 4.41 (dd, J = 12.6 Hz, J = 4.4 Hz, 1H), 4.02 (bs, 1H), 3.31 (ddd, J = 10.7 Hz, J = 7.0 Hz, J = 1.8 Hz, 1H), 3.20 (s, 3H), 3.13 (ddd, J = 10.7 Hz, J = 5.1 Hz, J = 2.0 Hz, 1H), 2.80 (bs, 2H), 2.53-2.48 (m, 2H), 2.09-2.01 (m, 2H), 1.64-1.58 (m, 2H); DEPTQ 135 (100 MHz, CD_2Cl_2) δ 150.6 (C), 150.5 (C), 149.7 (C), 149.6 (C), 137.6 (CH), 133.3 (CH), 133.2 (CH), 130.54 (CH), 130.51 (CH), 130.46 (CH), 130.22 (CH), 130.20 (CH), 129.8 (CH), 129.69 (C), 129.64 (CH), 129.4 (C), 129.2 (CH), 129.0 (C), 128.4 (C), 127.6 (CH), 127.2 (CH), 127.1 (CH), 126.8 (CH), 126.7 (CH), 126.6 (CH), 125.6 (CH), 125.5 (CH), 123.1 (CH), 121.4 (CH), 121.3 (CH), 79.0 (bs, CH), 73.4 (dd, J = 7.5 Hz, J = 7.5 Hz, CH_2), 58.6 (CH_3), 45.9 (d, J = 29.6 Hz, CH), 29.1 (CH_2); $^{31}P\{^1H\}$-NMR (162 MHz, CD_2Cl_2) δ 105.3 (d, J = 57.9 Hz, P-O), 9.5 (d, J = 57.9 Hz, P-C); MS HR-ESI [found 865.2219, $C_{42}H_{42}O_4P_2{}^{193}Ir$ $(M-I)^+$ requires 865.2188].

3. General synthetic procedure for *P-OP* ligands.

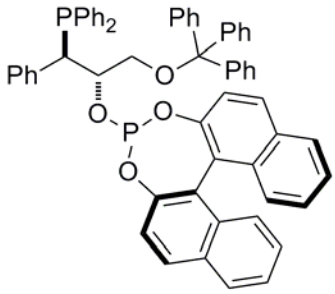
The *P-OP* ligands **2a**, **2b**, **3**, **11a**, and **11c** have been previously described and characterized.[1] *P-OP* ligands **11b** and **11d** were synthesized *via* a simplified experimental procedure with respect to the one reported in reference 1: The phosphine-borane complexes (1.0 mmol) and 1,4-diazabyciclo[2.2.2]octane (2.2 mmol) were loaded into a dried Schlenk flask, which was quickly purged by doing four fast vacuum/argon cycles. Toluene (15.0 mL) was added and the flask was dipped into a 60 ºC oil bath. After 2h, it was allowed to cool down to r.t. Then, a solution of the adequate chlorophosphite (1.1 mmol) in toluene (5.0 mL) was added dropwise *via* cannula onto the reaction mixture. The resulting mixture was stirred overnight at r.t. The reaction mixture was introduced in the glove box and filtered through a very short pad of previously dried and deoxygenated silica gel. The pad was washed with 10.0 mL of toluene. The filtrate was concentrated *in vacuo* and then purified by a short silica gel chromatography in the glovebox to give the corresponding phosphine-phosphites as white solids.



Compound 11b. Phosphine-phosphite **11b** was synthesized following the general procedure, starting from the corresponding phosphine-borane adduct[1] (0.600 g, 1.01 mmol), DABCO (0.255 g, 2.23 mmol), and (*S*)-(binaphthalene-2,2'-diyl)chlorophosphite (0.391 g, 1.11 mmol). The product was obtained as a white solid (0.434 g, 48% yield) after chromatography with silica gel (hexanes/Et_2O 67:33). M.p. 111.8–120.6 °C; $[\alpha]_D^{25}$ = +95.0 (*c* = 0.40, THF); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.95-7.90 (m, 2H), 7.84-7.82 (m, 1H), 7.67-7.63 (m, 2H), 7.52-7.16 (m, 29H), 7.08-6.94 (m, 7H), 6.77-6.74 (m, 1H), 4.77-4.70 (m, 1H), 3.82 (dd, *J* = 4.6 Hz, *J* = 4.6 Hz, 1H), 3.14 (dd, *J* = 9.9 Hz, *J* = 5.3 Hz, 1H), 3.07 (dd, *J* = 9.9 Hz, *J* = 7.0 Hz, 1H); DEPTQ 135 (100 MHz, $CDCl_3$) δ 148.04 (C), 148.00 (C), 147.7 (C), 143.6 (C), 136.5 (C), 136.4 (C), 136.3 (C), 136.2 (C), 134.7 (CH), 134.4 (CH), 133.4 (CH), 133.2 (CH), 132.8 (C), 132.5 (C), 131.4 (C), 131.0 (C), 130.8 (CH), 130.7 (CH), 130.0 (CH), 129.6 (CH),

[1] (a) Fernández-Pérez, H.; Pericas, M. A.; Vidal-Ferran, A. *Adv. Synth. Catal.* **2008**, *350*, 1984. (b) Fernández-Pérez, H.; Donald, S. M. A.; Munslow, I. J.; Benet-Buchholz, J.; Maseras, F.; Vidal-Ferran, A. *Chem. Eur. J.* **2010**, *16*, 6495.

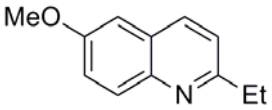
129.2 (CH), 128.74 (CH), 128.67 (CH), 128.3 (CH), 128.2 (CH), 128.1 (CH), 127.84 (CH), 127.81 (CH), 127.73 (CH), 127.66 (CH), 127.1 (CH), 127.0 (CH), 126.5 (CH), 126.0 (CH), 125.8 (CH), 124.8 (CH), 124.6 (CH), 124.44 (CH), 124.39 (C), 122.8 (C), 122.3 (CH), 122.1 (CH), 87.4 (C), 76.0 (dd, J = 18.2 Hz, J = 18.2 Hz, CH), 65.8 (CH_2), 48.3 (dd, J = 15.8 Hz, J = 4.3 Hz, CH); $^{31}P\{^1H\}$-NMR (162 MHz, $CDCl_3$) δ 156.2 (d, J = 18.2 Hz, P-O), −7.1 (d, J = 18.2 Hz, P-C); MS HR-ESI [found 893.2954; $C_{60}H_{47}O_4P_2$ $(M+H)^+$ requires 893.2950].



Compound 11d. Phosphine-phosphite **11d** was synthesized following the general procedure, starting from the corresponding phosphine-borane adduct[1] (0.800 g, 1.35 mmol), DABCO (0.340 g, 2.97 mmol), and (*R*)-(binaphthalene-2,2'-diyl)chlorophosphite (0.537 g, 1.49 mmol). The product was obtained as a white solid (0.697 g, 58% yield) after chromatography with silica gel (hexanes/Et_2O 75:25). M.p. 171.4–176.7 °C; $[\alpha]_D^{25}$ = −275.3 (c = 1.30, THF); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.91-7.82 (m, 4H), 7.68-7.64 (m, 2H), 7.42-7.02 (m, 36H), 4.77-4.70 (m, 1H), 3.73 (dd, J = 4.9 Hz, J = 4.9 Hz, 1H), 3.06 (dd, J = 9.9 Hz, J = 4.4 Hz, 1H), 2.92 (dd, J = 9.9 Hz, J = 8.4 Hz, 1H); $^{13}C\{^1H\}$-NMR (100 MHz, $CDCl_3$) δ 148.45 (C), 148.41 (C), 147.77 (C), 147.75 (C), 143.8 (C), 136.9 (C), 136.8 (C), 136.5 (C), 136.4 (C), 135.9 (C), 135.8 (C), 134.7 (CH), 134.5 (CH), 133.4 (C), 133.2 (C), 131.4 (C), 131.2 (C), 130.5 (CH), 130.4 (CH), 129.9 (CH), 129.7 (CH), 129.3 (CH), 128.80 (CH), 128.75 (CH), 128.2 (CH), 128.0 (CH), 127.81 (CH), 127.77 (CH), 127.7 (CH), 127.1 (CH), 127.0 (CH), 126.9 (CH), 126.6 (CH), 126.0 (CH), 125.8 (CH), 124.8 (CH), 124.6 (CH), 124.4 (C), 124.3 (C), 123.0 (CH), 122.9 (CH), 122.81 (C), 122.80 (C), 122.0 (CH), 87.6 (C), 76.4 (dd, J = 20.3 Hz, J = 20.3 Hz, CH), 66.2 (d, J = 2.6 Hz, CH_2), 48.3 (dd, J = 16.4 Hz, J = 5.7 Hz, CH); $^{31}P\{^1H\}$-NMR (162 MHz, $CDCl_3$) δ 157.1 (d, J = 3.1 Hz, P-O), −7.1 (bs, P-C); MS HR-ESI [found 893.2936; $C_{60}H_{47}O_4P_2$ $(M+H)^+$ requires 893.2950].

4. Preparation of hydrogenation substrates.

Substrates **9a**, **9e**, **9f**, **9g**, **9i** and **9j** are commercially available. Compounds **7**[2] and **9**[3] were prepared following the references indicated for each case. Spectroscopic data for these compounds were in agreement with the reported ones (**7**,[2] **9b**,[4] **9c**,[5] and **9d**[6]).



Compound (9h). Compound **9h** was synthesized following the previous reported[3] experimental procedure starting from commercially available **9g**. It was obtained as yellow oil (98% yield). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.97-7.92 (m, 2H), 7.34-7.31 (m, 1H), 7.27-7.24 (m, 1H), 7.04-7.03 (m, 1H), 3.90 (s, 3H), 2.96 (q, J = 7.6 Hz, 2H), 1.38 (t, J = 7.6 Hz, 3H); DEPTQ 135 (100 MHz, $CDCl_3$) δ 161.5 (C), 157.2 (C), 143.9 (C), 135.2 (CH), 130.2 (CH), 127.5 (C), 121.8 (CH), 121.0 (CH), 105.2 (CH), 55.5 (CH_3), 32.0 (CH_2), 14.1 (CH_3); MS HR-ESI [found 188.1070, $C_{12}H_{14}NO$ $(M+H)^+$ requires 188.1075].

5. General procedure for the Ir-mediated asymmetric hydrogenations.

Method A. *In situ* preparation of the catalyst: A solution of the required amount of iridium precursor ([{Ir(μ-Cl)(cod)}$_2$]) (0.005 mmol) and the *P-OP* ligand (0.011 mmol) in the corresponding dry and deoxygenated solvent (5.0 mL) were loaded into an autoclave under N_2 atmosphere, in which the substrate (1 mmol), NaBArF or additives (if necessary) were placed beforehand. The autoclave was purged three times with H_2 (at a pressure not higher than the selected one) and finally, the autoclave was pressurized with H_2 to the desired pressure. The reaction mixture was stirred at the desired temperature for the stated reaction time. The autoclave was subsequently depressurized, the reaction mixture passed through a short pad of SiO_2 and further eluted with EtOAc. The resulting solution was evaporated *in vacuo* and the conversion

[2] Gautier, F.-M.; Jones, S.; Martin, S. J. *Org. Biomol. Chem.* **2009**, *7*, 229.
[3] Compounds **9b-d** were prepared following the experimental procedure described in reference: Qian, B.; Guo, S.; Shao, J.; Zhu, Q.; Yang, L.; Xia, C.; Huang, H. *J. Am. Chem. Soc.* **2010**, *132*, 3650.
[4] Vieira, P. C.; Kubo, I. *Phytochem.* **1990**, *29*, 813.
[5] O'Byrne, A.; Evans, P. *Tetrahedron* **2008**, *64*, 8067.
[6] Lewis, J. C.; Bergman, R. G.; Ellman, J. A. *J. Am. Chem. Soc.* **2007**, *129*, 5332.

was determined by ^{1}H-NMR and enantioselectivities were determined by chiral HPLC chromatography.

Method B. Pre-formed catalyst: A solution of the required amount of [Ir(cod)(*P*-*OP*)]BArF or [Ir(I)(cod)(*P*-*OP*)] in the corresponding dry and deoxygenated solvent (5.0 mL) was loaded into an autoclave under N_2 atmosphere, in which the substrate (1 mmol) and additives (if necessary) were placed beforehand. The autoclave was purged three times with H_2 (at a pressure not higher than the selected one) and finally, the autoclave was pressurized with H_2 to the desired pressure. The reaction mixture was stirred at the desired temperature for the stated reaction time. The autoclave was subsequently depressurized, the reaction mixture passed through a short pad of SiO_2 and further eluted with EtOAc. The resulting solution was evaporated *in vacuo* and the conversion was determined by ^{1}H-NMR and enantioselectivities were determined by chiral HPLC chromatography.

6. Determination of enantiomeric excesses.

Hydrogenated product of 7.[7] HPLC (Chiracel® OD-H [Chiral Technologies], 25 x 0.46 cm, 98:2 hexane/*i*-PrOH, 0.5 ml/min, λ = 254 nm): t_R(*S*) = 18.2 min, t_R(*R*) = 21.7 min.

Hydrogenated product of 9a.[8] HPLC (Chiracel® OJ-H [Chiral Technologies], 25 x 0.46 cm, 95:5 hexane/*i*-PrOH, 0.5 ml/min, λ = 254 nm): t_R(*S*) = 22.6 min, t_R(*R*) = 25.2 min.

Hydrogenated product of 9b.[8] HPLC (Chiracel® OJ-H [Chiral Technologies], 25 x 0.46 cm, 95:5 hexane/*i*-PrOH, 0.5 ml/min, λ = 254 nm): t_R(*S*) = 16.5 min, t_R(*R*) = 20.7 min.

Hydrogenated product of 9c.[8] HPLC (Chiracel® OJ-H [Chiral Technologies], 25 x 0.46 cm, 95:5 hexane/*i*-PrOH, 0.5 ml/min, λ = 254 nm): t_R(*S*)= 12.9 min, t_R(*R*)= 14.9 min.

Hydrogenated product of 9d.[9] HPLC (Chiracel® OJ-H [Chiral Technologies], 25 x 0.46 cm, 95:5 hexane/*i*-PrOH, 0.5 ml/min, λ = 254 nm): t_{R1} = 13.4 min, t_{R2} = 17.6 min.

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[7] Imamoto, T.; Iwadate, N.; Yoshida, K. *Org. Lett.* **2006**, *8*, 2289.
[8] Wang, W.-B.; Lu, S.-M.; Yang, P.-Y.; Han, X.-W.; Zhou, Y.-G. *J. Am. Chem. Soc.* **2003**, *125*, 10536.

Hydrogenated product of 9e.[8] HPLC (Chiracel® OJ-H [Chiral Technologies], 25 x 0.46 cm, 94:6 hexane/*i*-PrOH, 1.0 ml/min, λ = 254 nm): $t_R(S)$ = 8.6 min, $t_R(R)$ = 9.0 min.

Hydrogenated product of 9f.[8] HPLC (Chiracel® OJ-H [Chiral Technologies], 25 x 0.46 cm, 90:10 hexane/*i*-PrOH, 0.5 ml/min, λ = 254 nm): $t_R(S)$ = 24.3 min, $t_R(R)$ = 30.9 min.

Hydrogenated product of 9g.[8] HPLC (Chiracel® OJ-H [Chiral Technologies], 25 x 0.46 cm, 90:10 hexane/*i*-PrOH, 0.5 ml/min, λ = 254 nm): $t_R(S)$ = 34.9 min, $t_R(R)$ = 44.7 min.

Hydrogenated product of 9h. HPLC (Chiracel® OJ-H [Chiral Technologies], 25 x 0.46 cm, 90:10 hexane/*i*-PrOH, 0.5 ml/min, λ = 254 nm): $t_R(-)$ = 30.4 min, $t_R(+)$ = 36.7 min.

Hydrogenated product of 9i.[10] HPLC (Chiracel® OD-H [Chiral Technologies], 25 x 0.46 cm, 90:10 hexane/*i*-PrOH, 1.0 ml/min, λ = 254 nm): $t_R(S)$ = 9.9 min, $t_R(R)$ = 13.3 min.

Hydrogenated product of 9j.[11] HPLC (Chiracel® OD-H [Chiral Technologies], 25 x 0.46 cm, 60:40:0.1 hexane/*i*-PrOH/$NHEt_2$, 0.5 ml/min, λ = 254 nm): $t_R(R)$ = 13.3 min, $t_R(S)$ = 15.6 min.

7. Determination of the absolute configurations.

The absolute configurations of the hydrogenated products were established by comparison with reported elution orders in the references in section 6.

8. Characterization of the hydrogenated compounds.

Hydrogenated compounds of substrates **7**, **9a**, **9b**, **9c**, **9d**, **9e**, **9f**, **9g**, **9i** and **9j** have previously been studied. Spectroscopic data were in agreement with the reported ones in the references in section 6.

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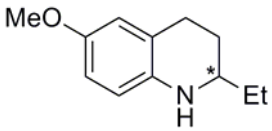
[9] Mrsic, N.; Lefort, L.; Boogers, J. A. F.; Minnaard, A. J.; Feringa, B. L.; de Vries, J. G. *Adv. Synth. Catal.* **2008**, *350*, 1081.

[10] Tadaoka, H.; Cartigny, D.; Nagano, T.; Gosavi, T.; Ayad, T.; Genet, J.-P.; Ohshima, T.; Ratovelomanana-Vidal, V.; Mashima, K. *Chem. Eur. J.* **2009**, *15*, 9990.

[11] Tang, W.; Xu, L.; Fan, Q.-H.; Wang, J.; Fan, B.; Zhou, Z.; Lam, K.-h.; Chan, A. S. C. *Angew. Chem. Int. Ed.* **2009**, *48*, 9135.



Hydrogenated product of 9h. $[\alpha]_D^{27}$ = −32.1 (*c* 0.19, $CHCl_3$); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 6.62-6.58 (m, 2H), 6.47 (d, *J* = 8.4 Hz, 1H), 3.74 (s, 3H), 3.34 (bs, 1H), 3.14-3.08 (m, 1H), 2.88-2.69 (m, 2H), 2.01-1.94 (m, 1H), 1.64-1.50 (m, 3H), 1.00 (t, *J* = 7.5 Hz, 3H); DEPTQ 135 (100 MHz, $CDCl_3$) δ 151.8 (C), 138.8 (C), 122.8 (C), 115.3 (CH), 114.6 (CH), 112.9 (CH), 55.8 (CH_3), 53.4 (CH), 29.3 (CH_2), 27.8 (CH_2), 26.8 (CH_2), 10.1 (CH_3); MS HR-ESI [found 192.1387, $C_{12}H_{18}NO$ $(M+H)^+$ requires 192.1388].

9. Initial screening and screening of additives in the asymmetric hydrogenation of test substrates using neutral iridium complexes derived from *P-OP* ligands.

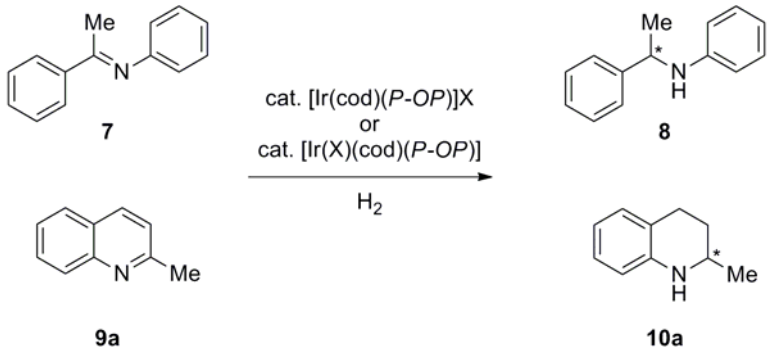


Table 1. Asymmetric hydrogenation of *C=N* bonds mediated by [Ir(cod)(*P-OP*)]X or [Ir(X)(cod)(*P-OP*)] complexes[a]

Entry	Ir-pre-catalyst	Substrate	Solvent	Pressure (bar)	Conv. (%)[b]	ee (%)[c] (config.)[d]
1	1 mol % **4a**	**7**	MeOH	50	80	23 (*S*)
2	2 mol % **5** (*in situ*)	**7**	DCM	50	>99	19 (*R*)
3	2 mol % **6**	**7**	DCM	50	>99	21 (*R*)
4	1 mol % **4a**	**9a**	THF	80	17	15 (*R*)
5	1 mol % **5** (*in situ*)	**9a**	Toluene	80	21	11 (*S*)
6	1 mol % **5** (*in situ*)	**9a**	THF	80	64	*rac*
7	1 mol % **6**	**9a**	Toluene	80	65	17 (*S*)
8	1 mol % **6**	**9a**	THF	80	>99	6 (*S*)

[a] All reactions were run at room temperature for 20 h. [b] Conversion was determined by ^{1}H-NMR. [c] Enantiomeric excess was determined by HPLC. [d] The absolute configuration was assigned by comparison with published data.

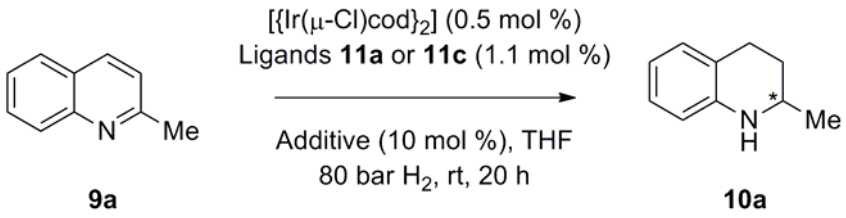


Table 2. Ir-catalyzed asymmetric hydrogenation of 2-methylquinoline **9a**

Entry	Ligand	Additive	Conv. (%)[a]	ee (%)[b] (config.)[c]
1	**11a**	-	69	62 (*R*)
2	**11a**	NBS	83	11 (*R*)
3	**11a**	I_2	>99	7 (*R*)
4	**11a**	MeOH	48	64 (*R*)
5	**11c**	-	87	83 (*S*)
6	**11c**	HCl	>99	84 (*S*)
7	**11c**	*p*-toluenesulfonic acid	88	81 (*S*)
8	**11c**	TFA	67	85 (*S*)
9	**11c**	Triflic acid	82	81 (*S*)
10	**11c**	(1*R*)-(+)-camphorsulfonic acid	62	83 (*S*)
11	**11c**	(1*R*)-(−)-camphorsulfonic acid	74	82 (*S*)
12	**11c**	I_2	>99	18 (*S*)

[a] Conversion was determined by ^{1}H-NMR. [b] Enantiomeric excess was determined by HPLC. [c] The absolute configuration was assigned on the comparison with published data.

10. X-ray structure determination.

Crystals of **6** were grown by slow diffusion of diethyl ether into solutions of **6** in dichloromethane. The measured crystals were prepared under inert conditions and immersed in perfluoropolyether as protecting oil for manipulation.

Data collection: were made on a diffractometer equipped with an APPEX 2 4K CCD area detector, a FR591 rotating anode with MoK_α radiation, Montel mirrors as monochromator and a low temperature device (T = −173 °C). Full-sphere data collection was used with ω and φ scans.

Programs used: Data collection APEX-2,[12] data reduction Bruker Saint[13] V/.60A and absorption correction SADABS.[14]

Structure Solution and Refinement: SHELXTL[15] was used. The crystal data parameters are listed in Table .

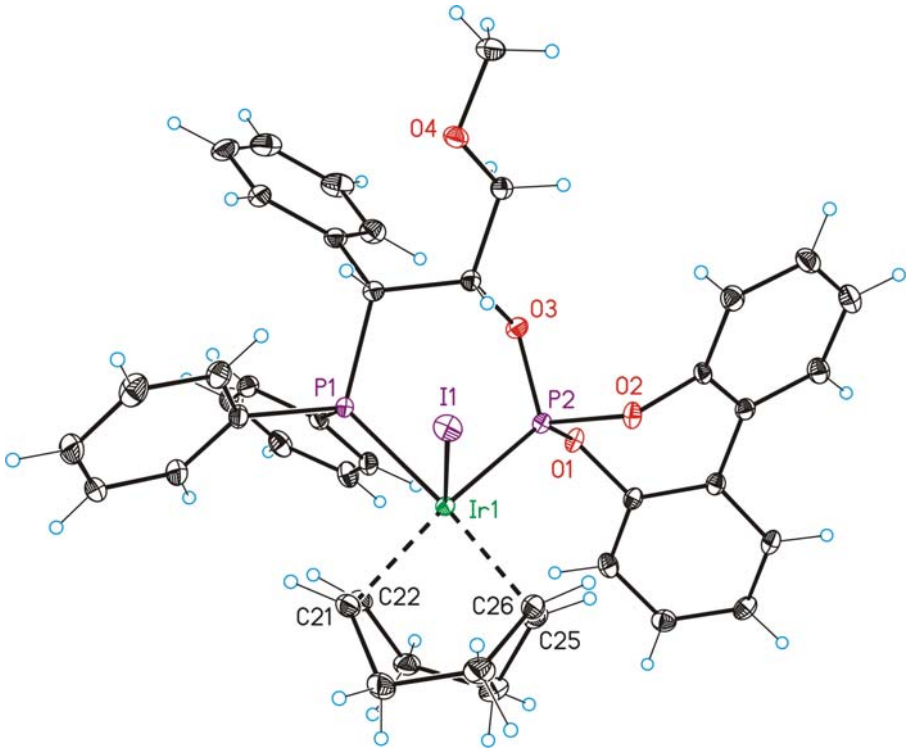


Figure 3. Ortep-Plot (thermal ellipsoids shown at 50 % probability level) of compound **6**

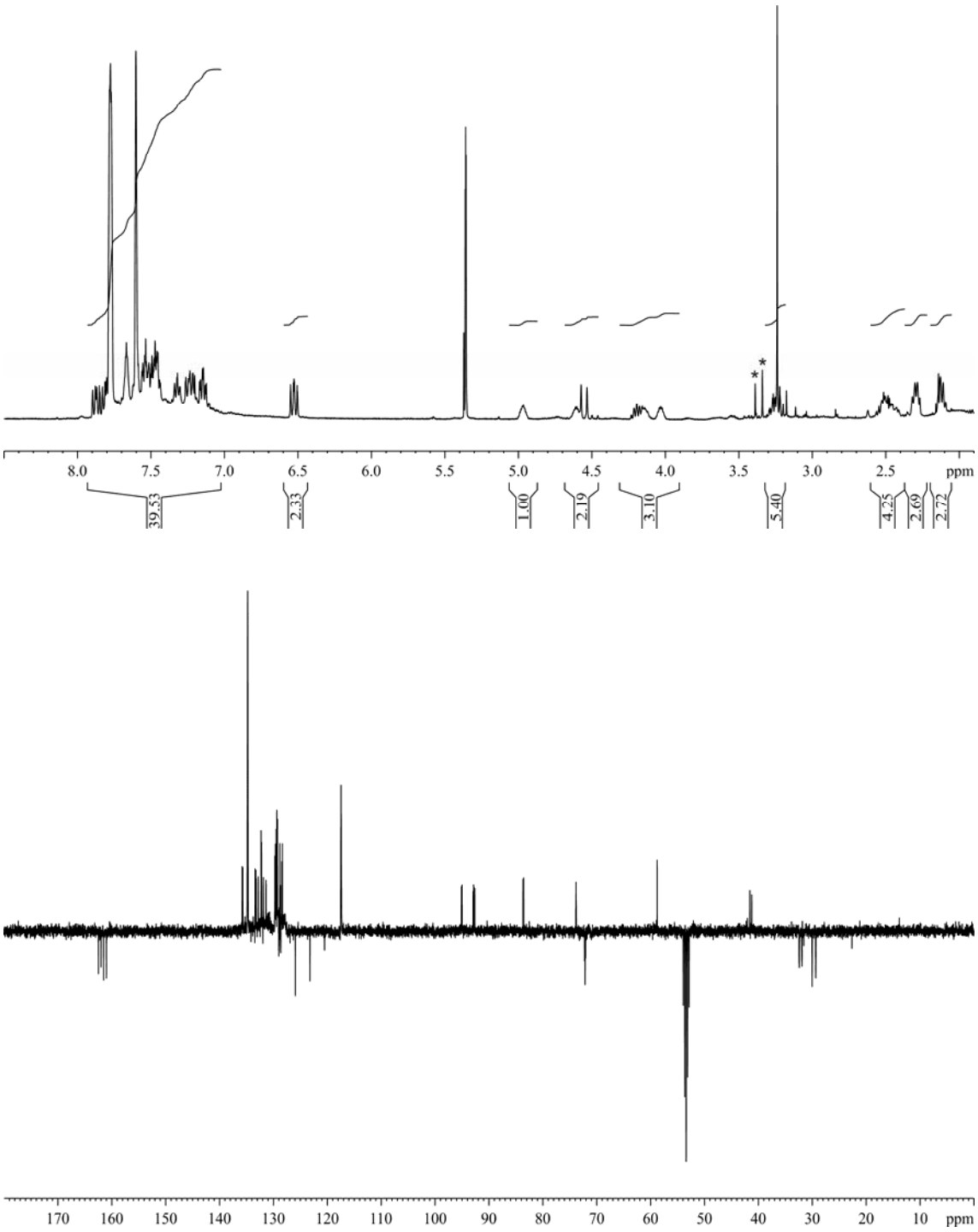
[12] Data collection with APEX II v2009.1-02. Bruker (2007). Bruker AXS Inc., Madison, Wisconsin, USA.
[13] Data reduction with Bruker SAINT V7.60A. Bruker (2007). Bruker AXS Inc., Madison, Wisconsin, USA.
[14] SADABS: V2008/1 Bruker (2001). Bruker AXS Inc., Madison, Wisconsin, USA. Blessing, Acta Cryst. (1995) A51 33-38.
[15] Sheldrick, G.M. *Acta Cryst*. **2008** A64, 112-122. SHELXTL V6.14.

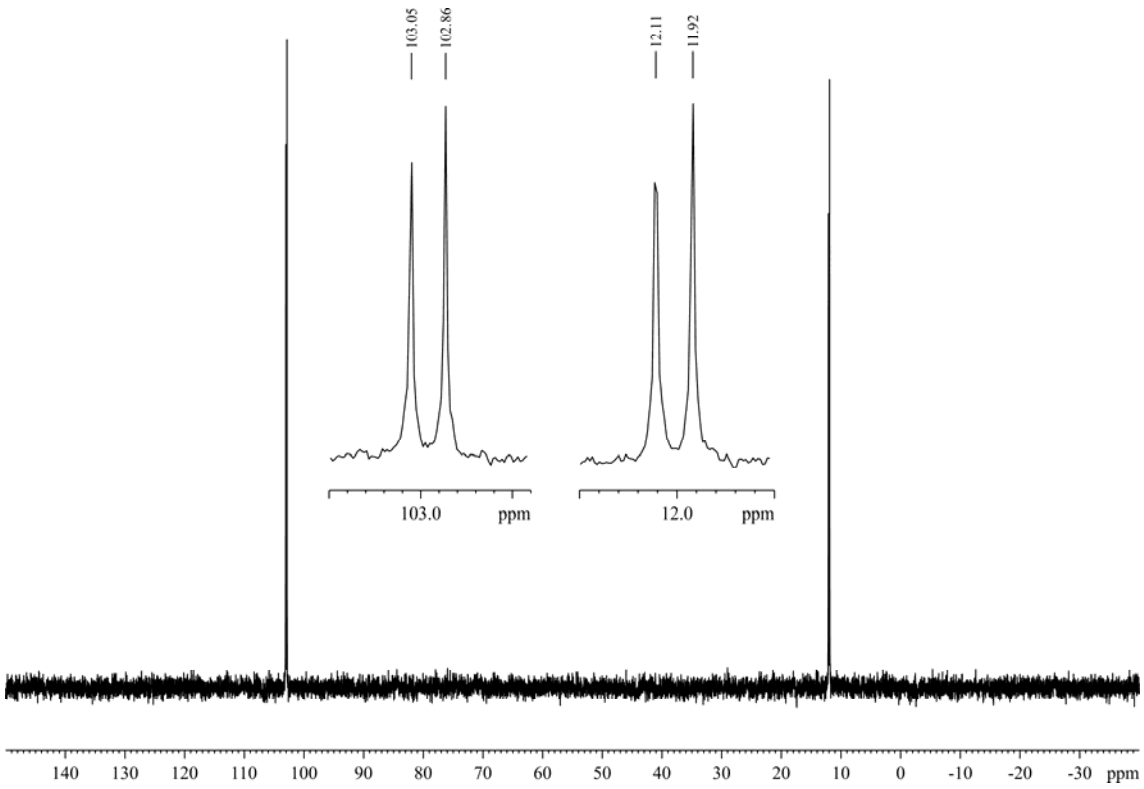
Table 3. Crystal data for compound **6**

Compound	**6**
Formula	$C_{42}H_{42}I_1Ir_1O_4P_2$
Formula weight	991.80
Crystal size (mm^3)	0.60 x 0.10 x 0.05
Crystal color	yellow
Temp (K)	100
Crystal system	orthorhombic
Space group	$P2_12_12_1$
A (Å)	9.3274(6)
B (Å)	14.2183(9)
C (Å)	27.2235(14)
α (deg)	90
β (deg)	90
γ (deg)	90
V ($Å^3$)	3610.4(4)
Z	4
ρ (g/cm^3)	1.825
μ (mm^{-1})	4.685
θ_{max} (deg)	35.10
Reflec. measured	40449
Unique reflections	13923 [R_{int}=0.0366]
Absorpt. correct.	SADABS (Bruker)
Trans. min/max	0.81/0.98
Parameters	452
R1/wR2 [I>2σ(I)]	0.0272/0.598
R1/wR2 [all data]	0.0314/0.674
Goodness-of-fit (F^2)	1.090
Abs. Conf: Flack (std)	-0.008(3)
Peak/hole ($e/Å^3$)	2.303/-1.976

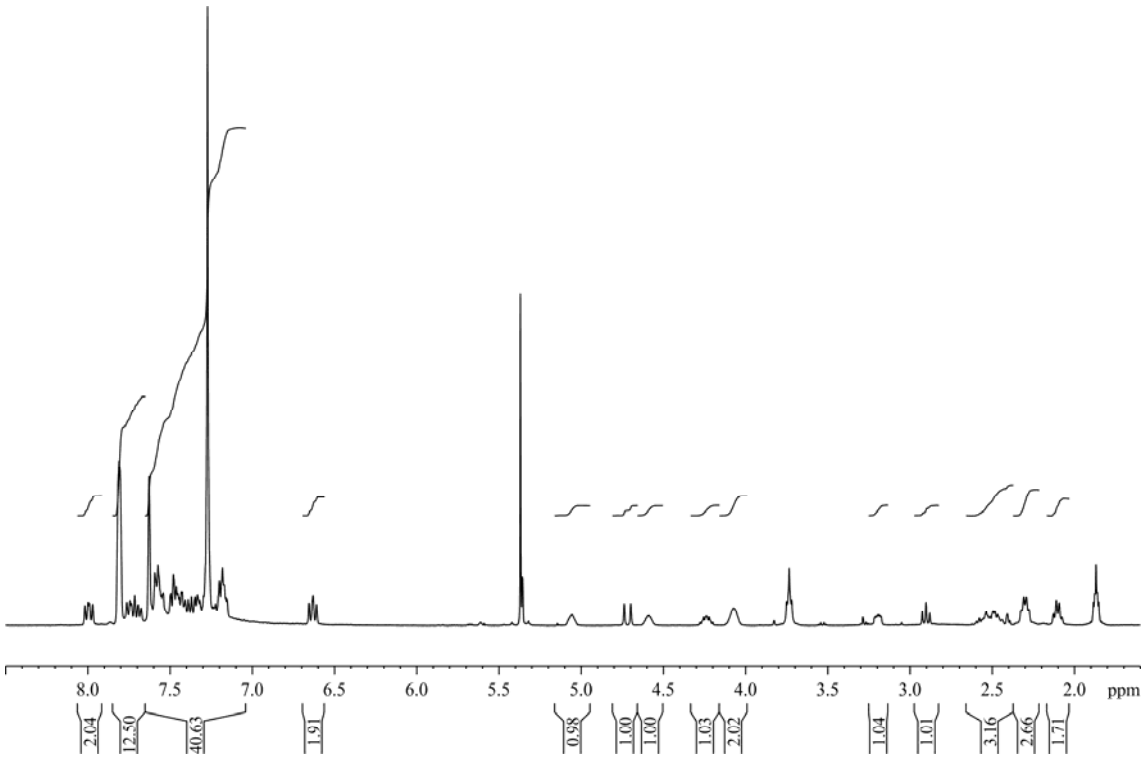
11. NMR spectra.

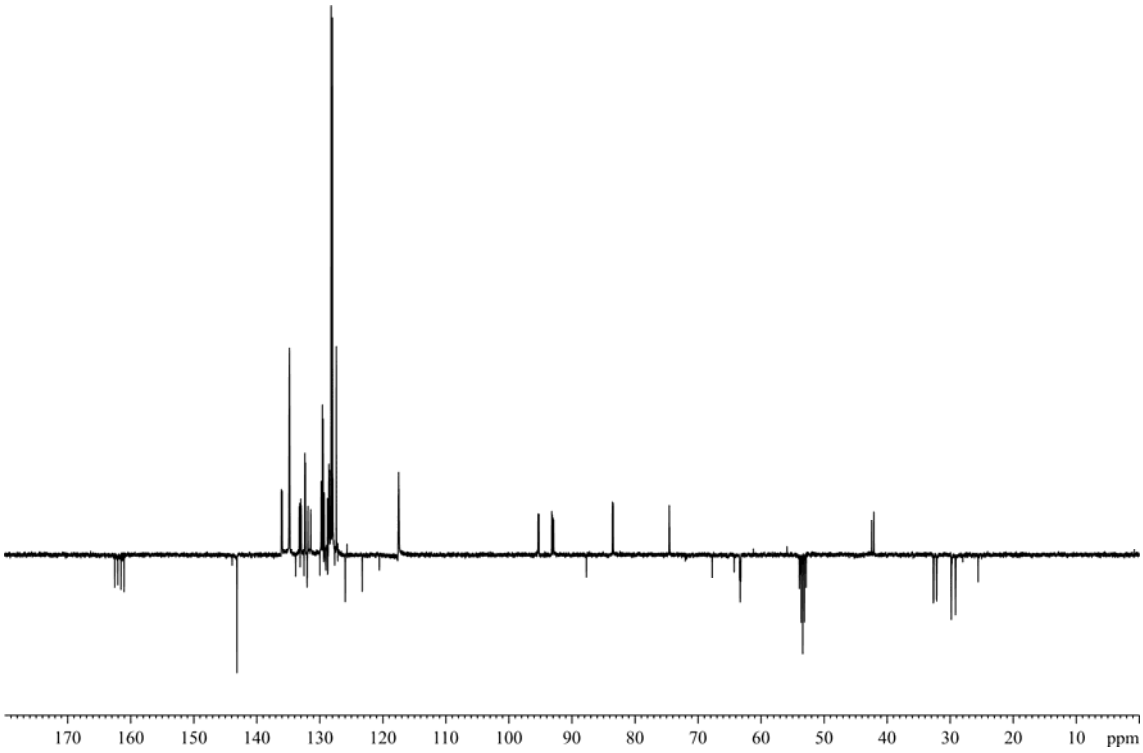
^{1}H, DEPTQ 135, and $^{31}P\{^{1}H\}$-NMR (CD_2Cl_2) spectra of compound **4a**

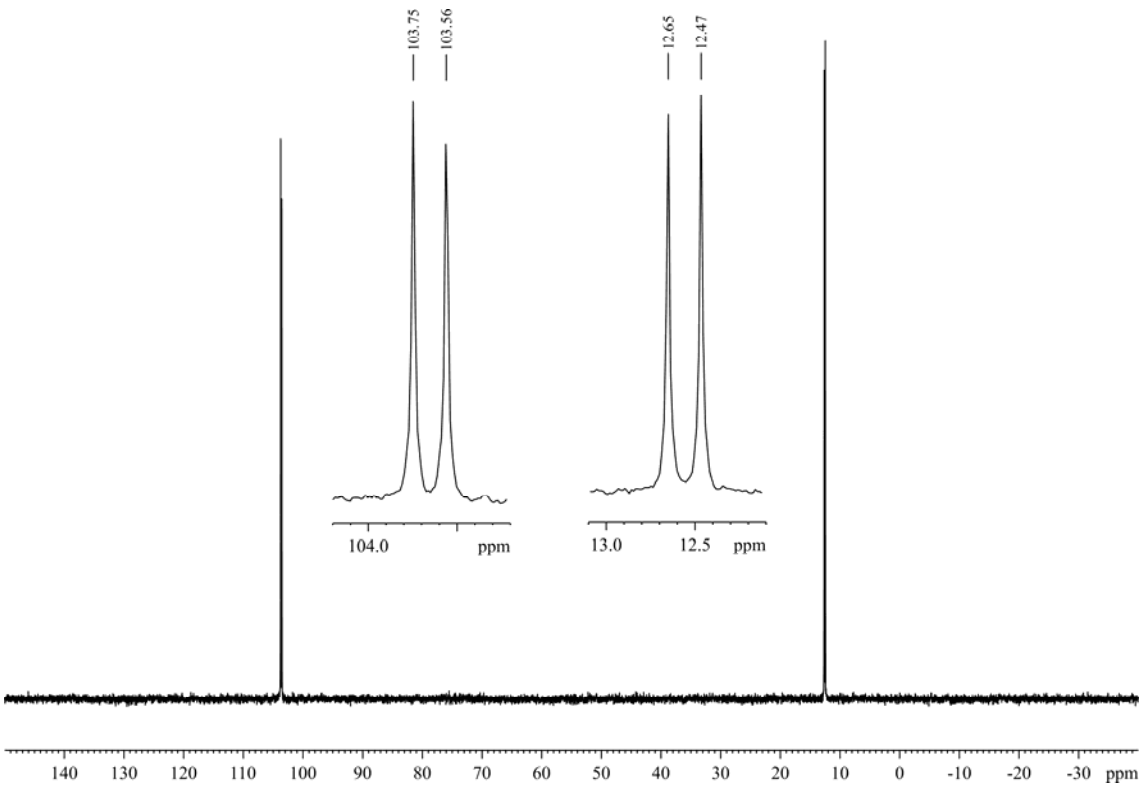




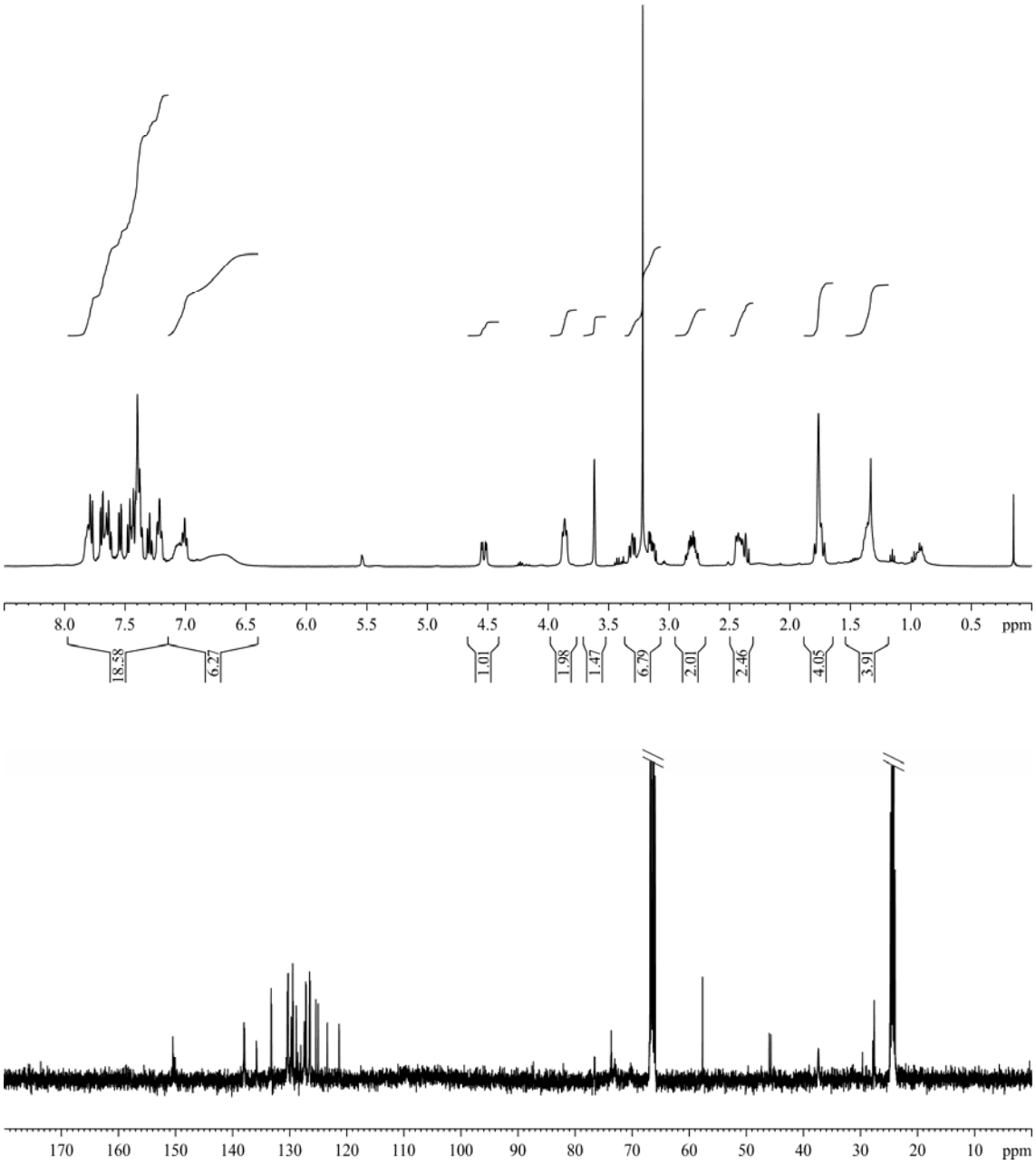
^{1}H, DEPTQ 135, and $^{31}P\{^{1}H\}$-NMR (CD_2Cl_2) spectra of compound **4b**

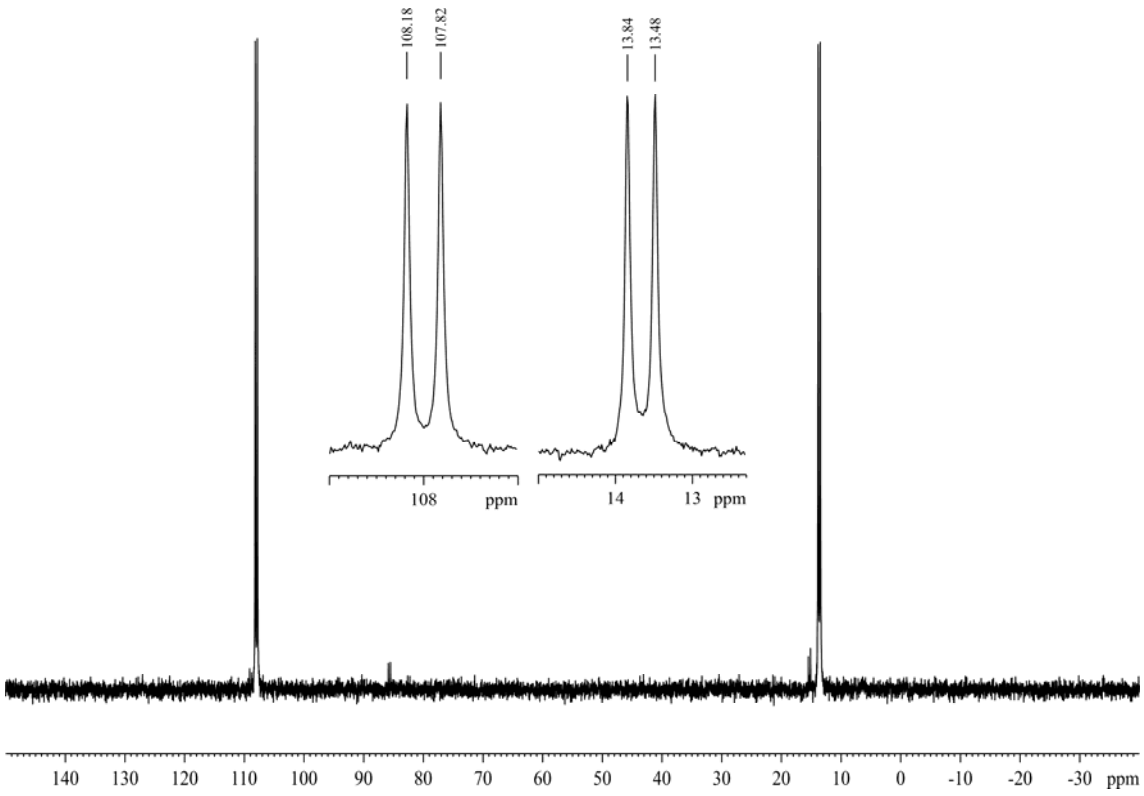



170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

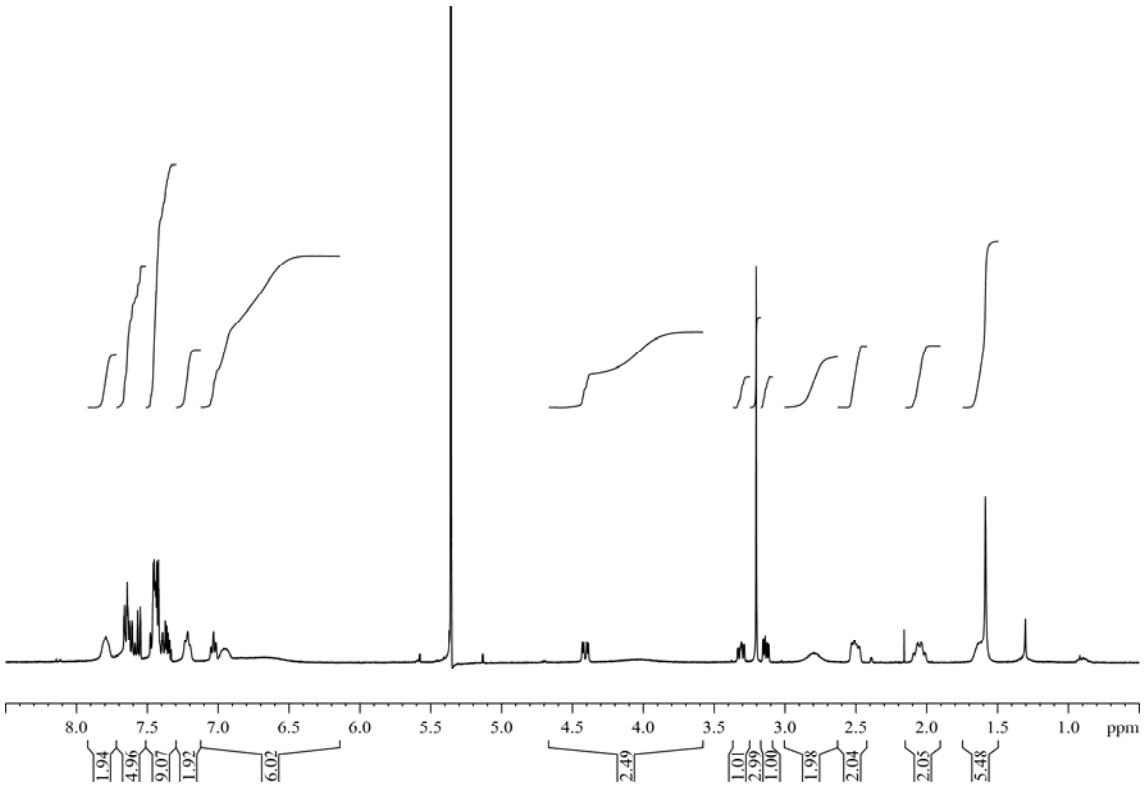

103.75
103.56
12.65
12.47
104.0 ppm
13.0 12.5 ppm
140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 ppm

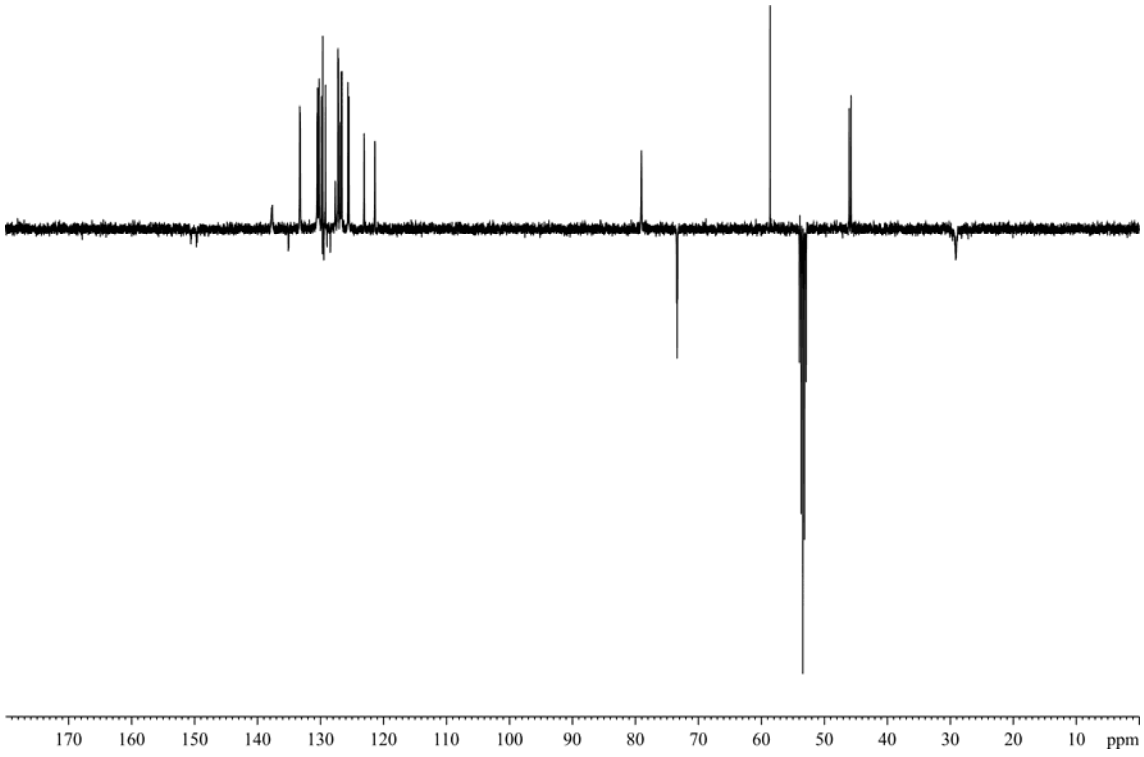
^{1}H, $^{13}C\{^{1}H\}$, and $^{31}P\{^{1}H\}$-NMR (THF-d_8) spectra of compound **5**

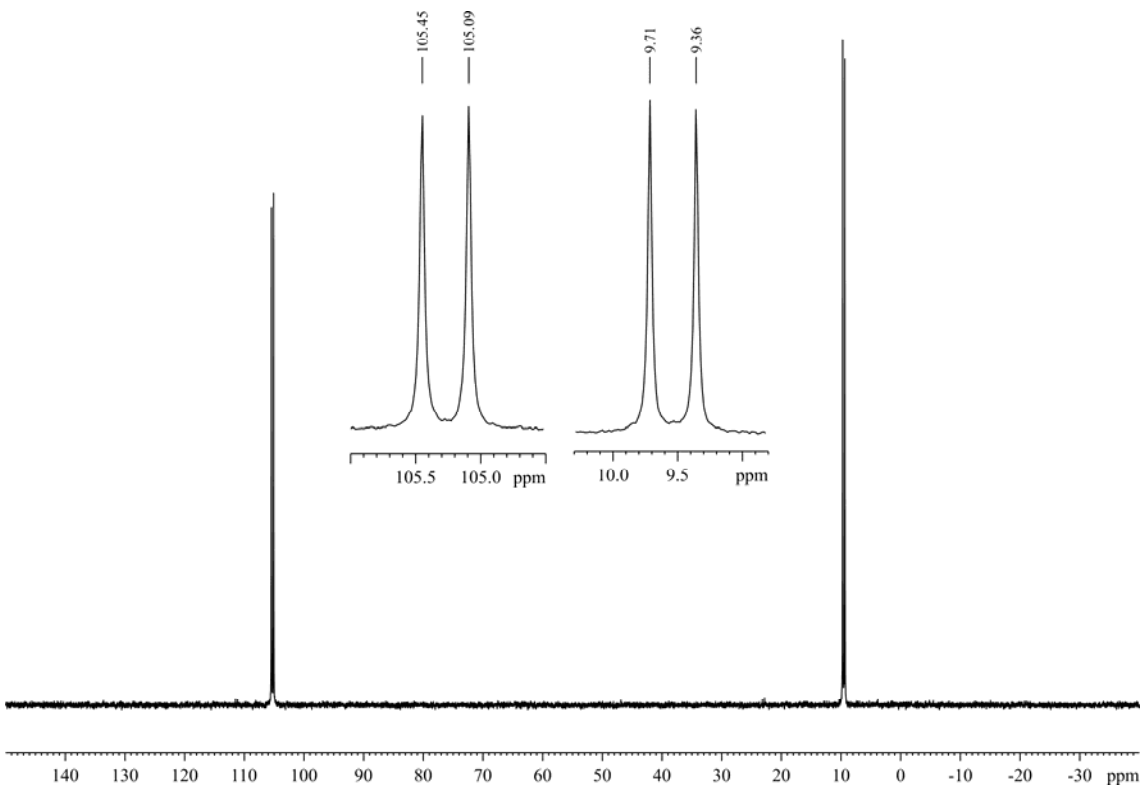




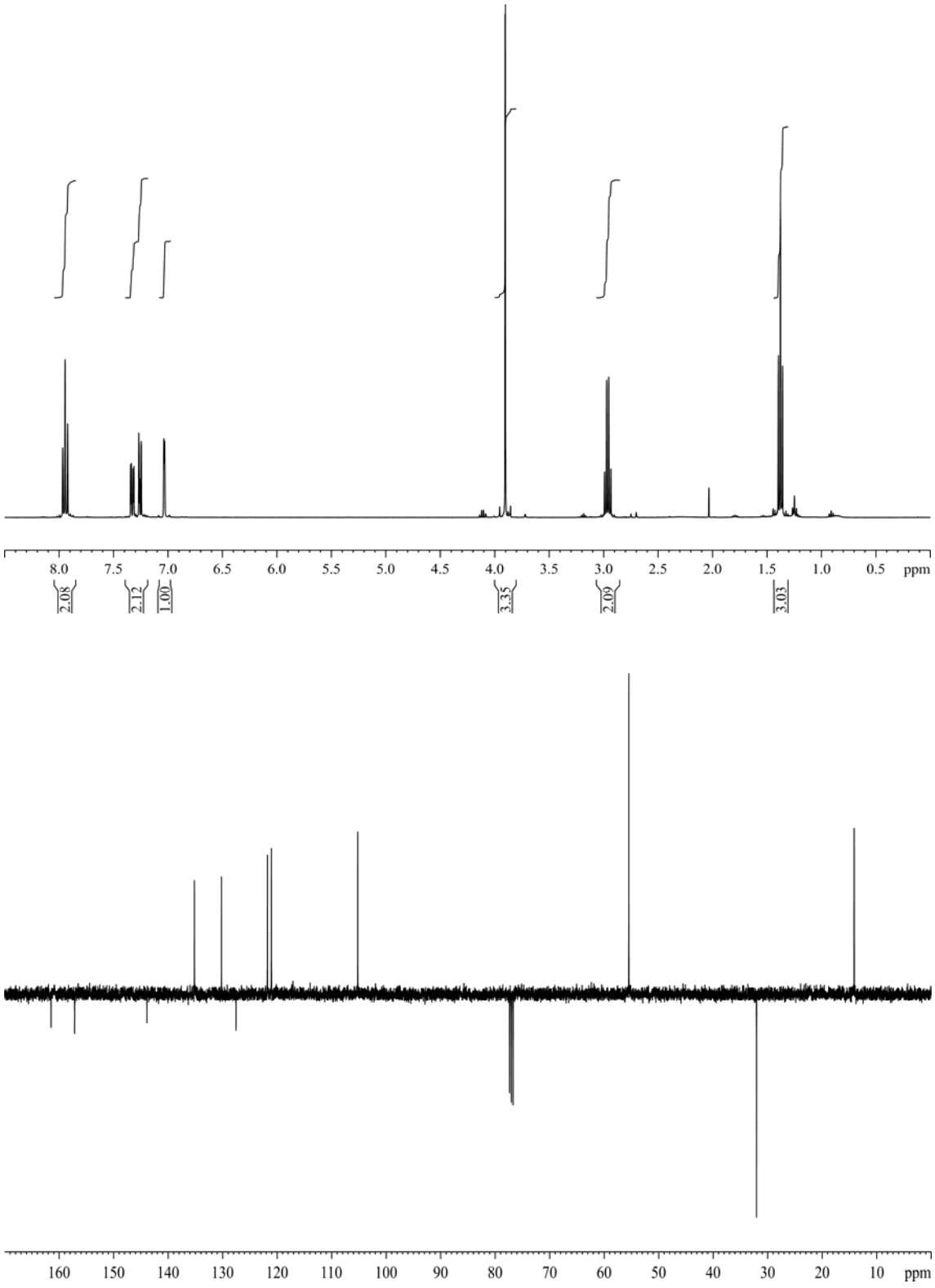
^{1}H, DEPTQ 135, and $^{31}P\{^{1}H\}$-NMR (CD_2Cl_2) spectra of compound **6**



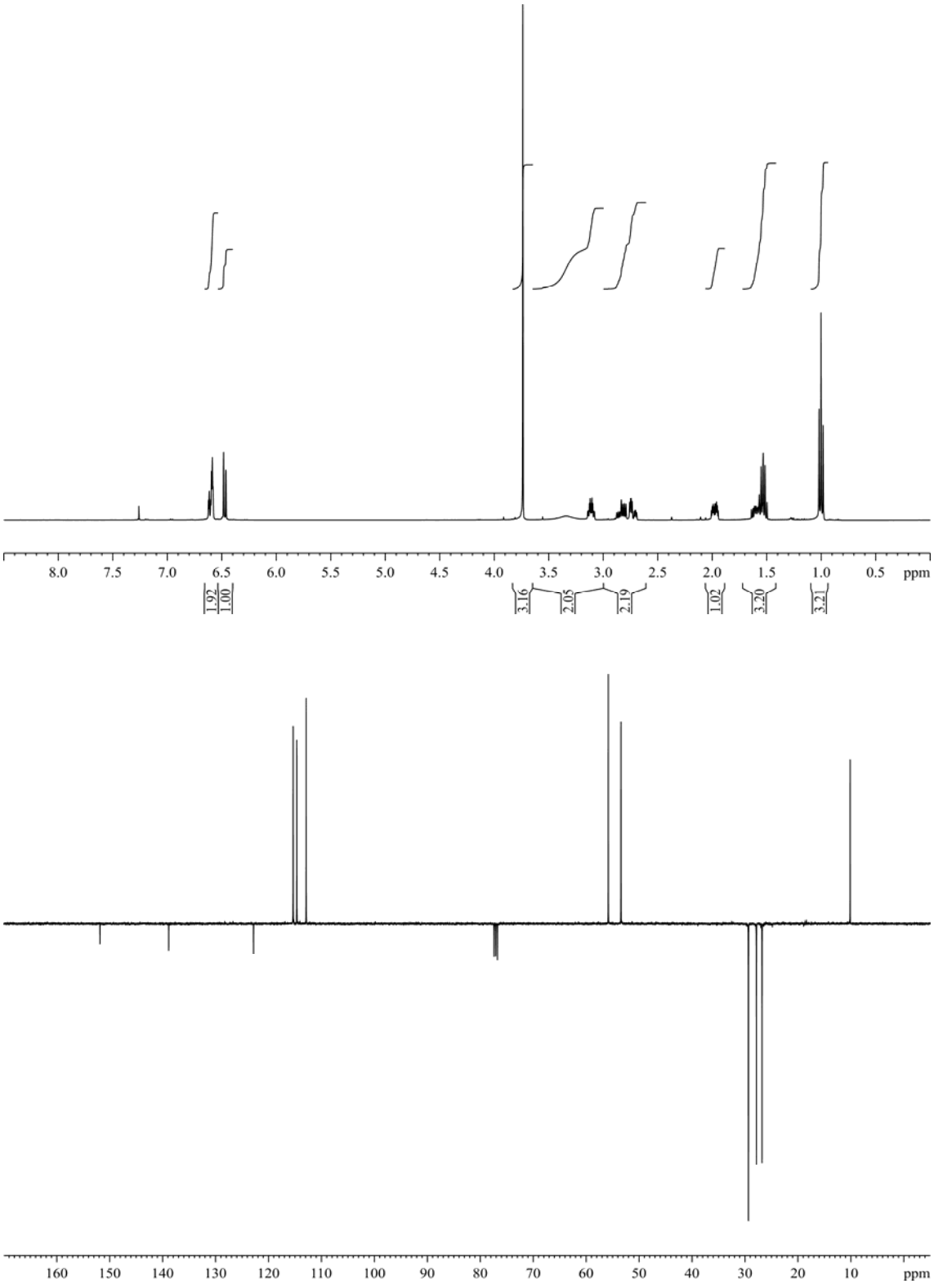

170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


105.45
105.09
9.71
9.36
105.5 105.0 ppm
10.0 9.5 ppm
140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 ppm

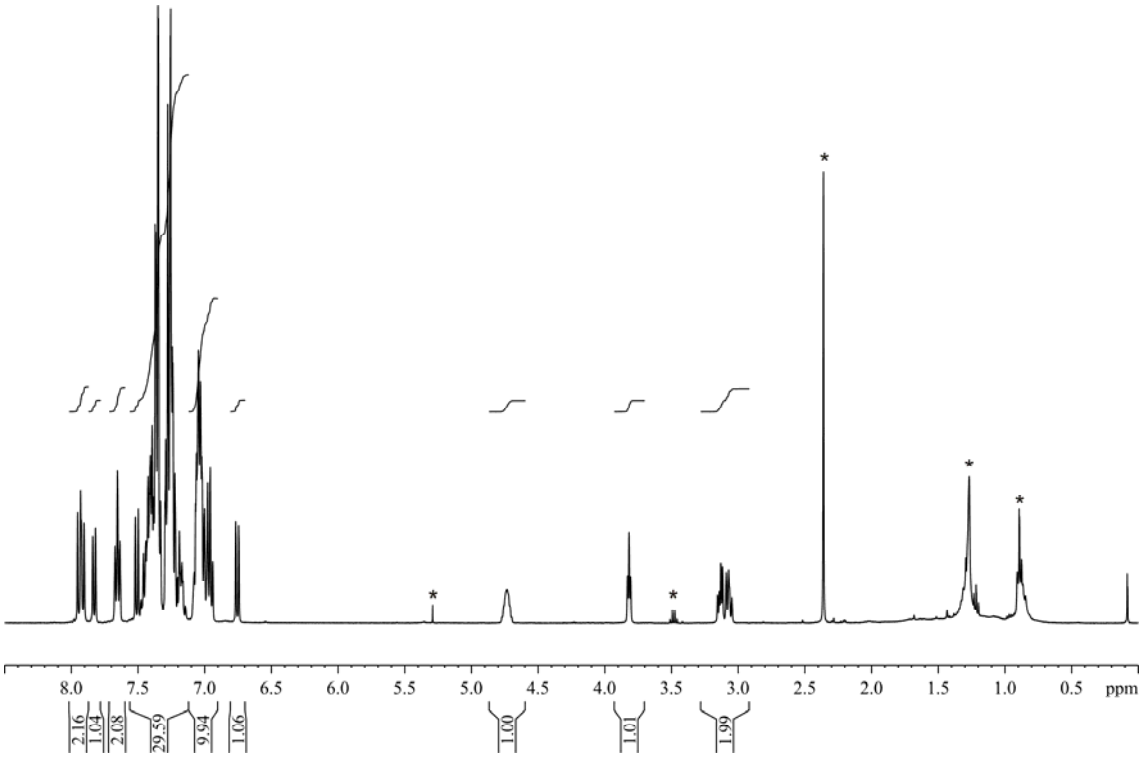
^{1}H and DEPTQ 135 NMR ($CDCl_3$) spectra of compound **9h**

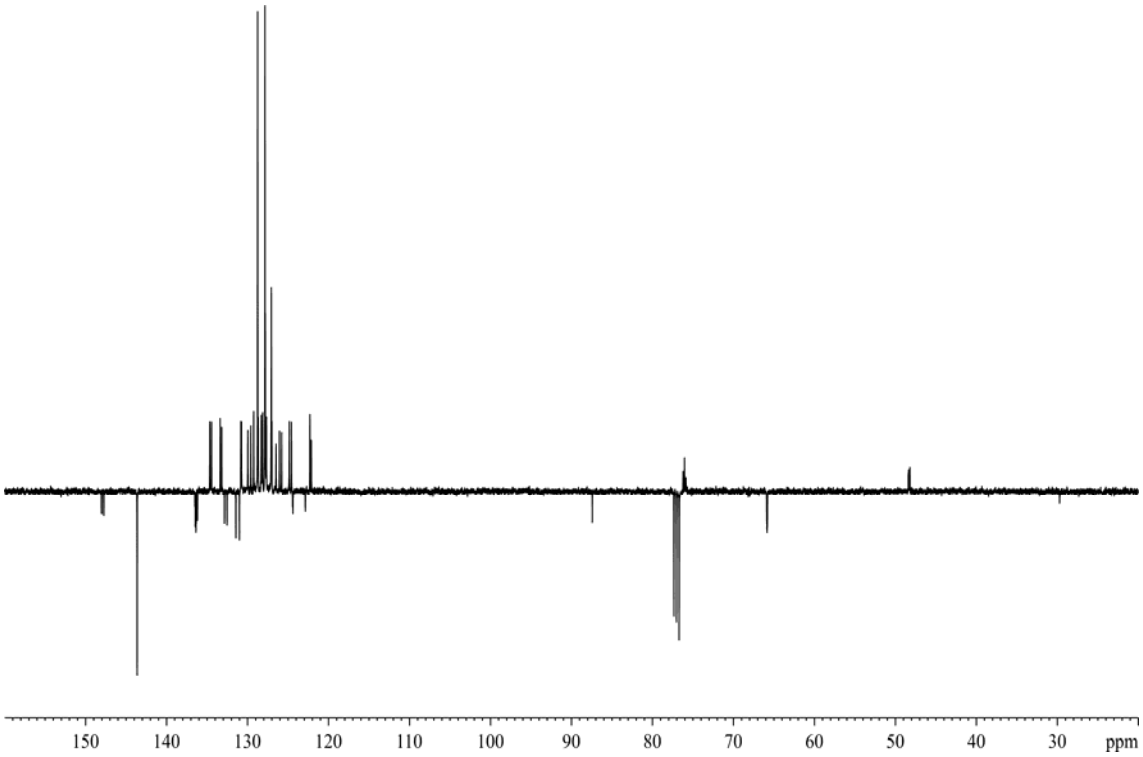


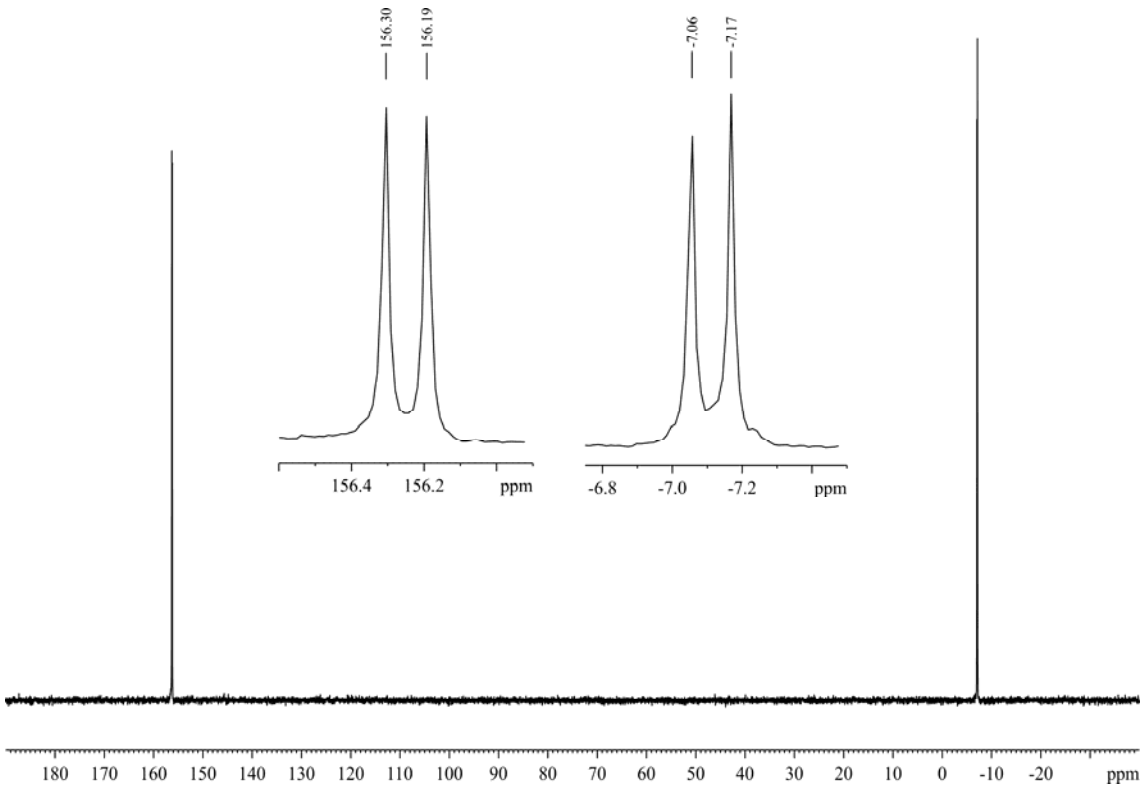
^{1}H and DEPTQ 135 NMR ($CDCl_3$) spectra of hydrogenated product of **9h**



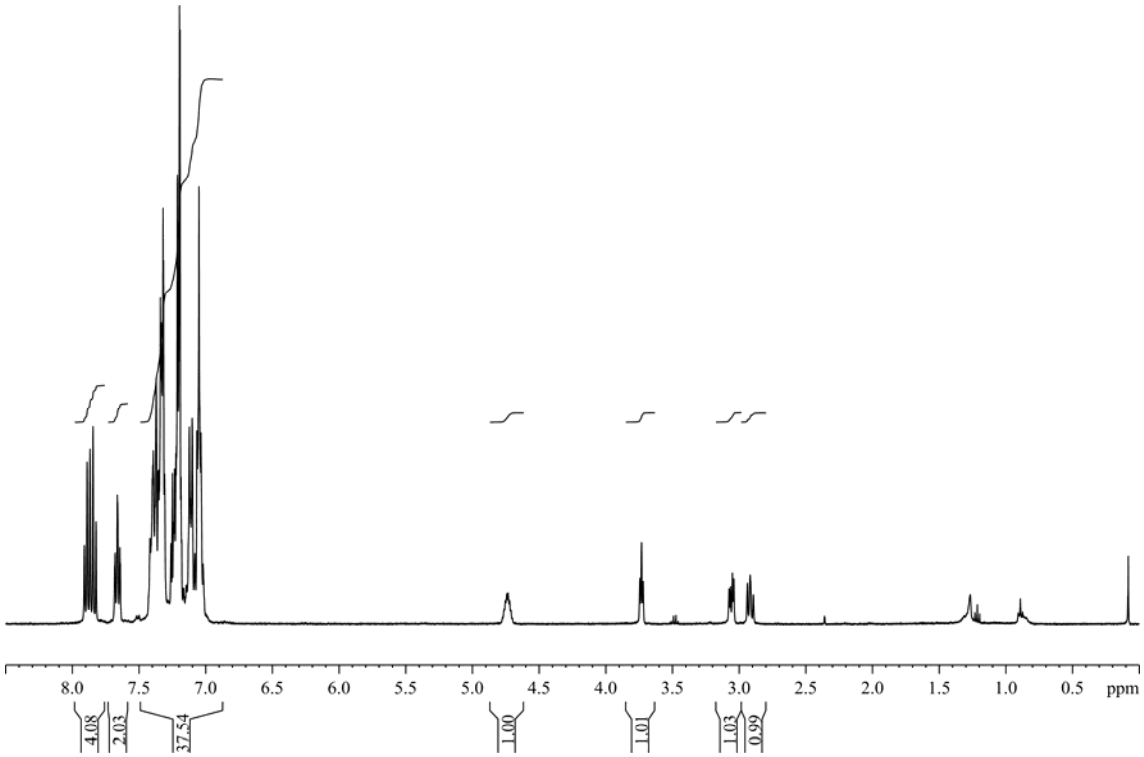
^{1}H, DEPTQ 135, and ^{31}P{^{1}H}-NMR ($CDCl_3$) spectra of compound **11b**

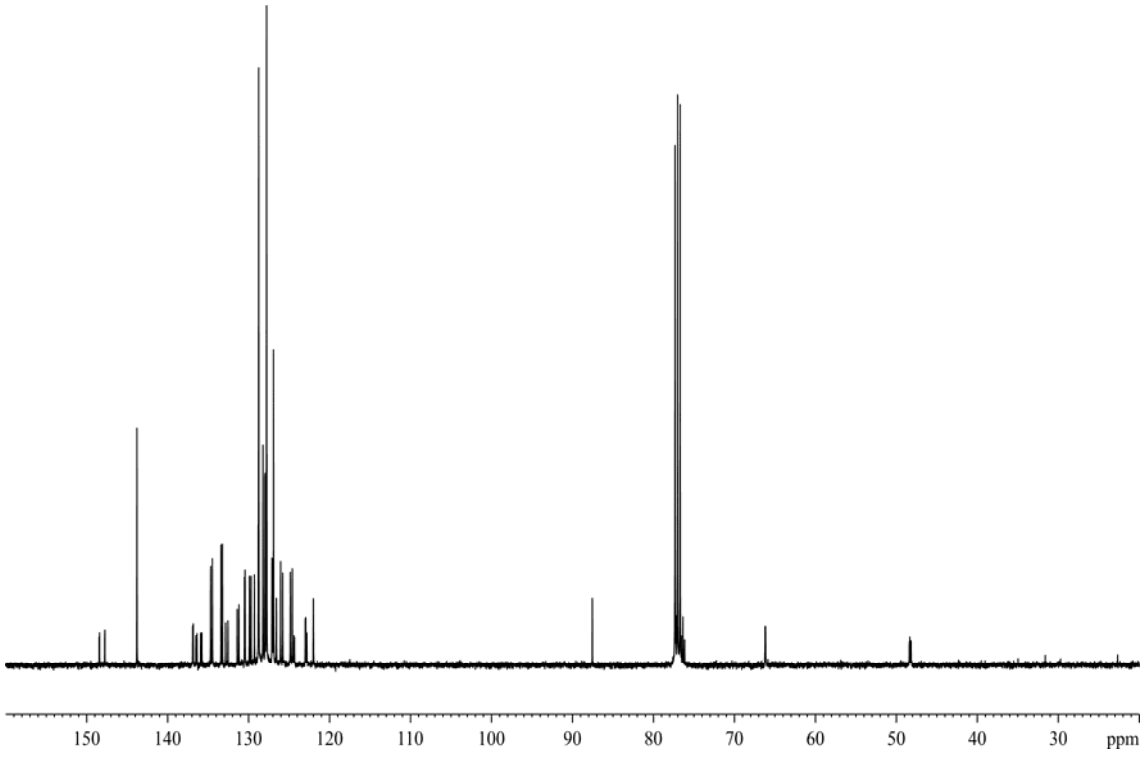






^{1}H, $^{13}C\{^{1}H\}$, and $^{31}P\{^{1}H\}$-NMR ($CDCl_3$) spectra of compound **11d**

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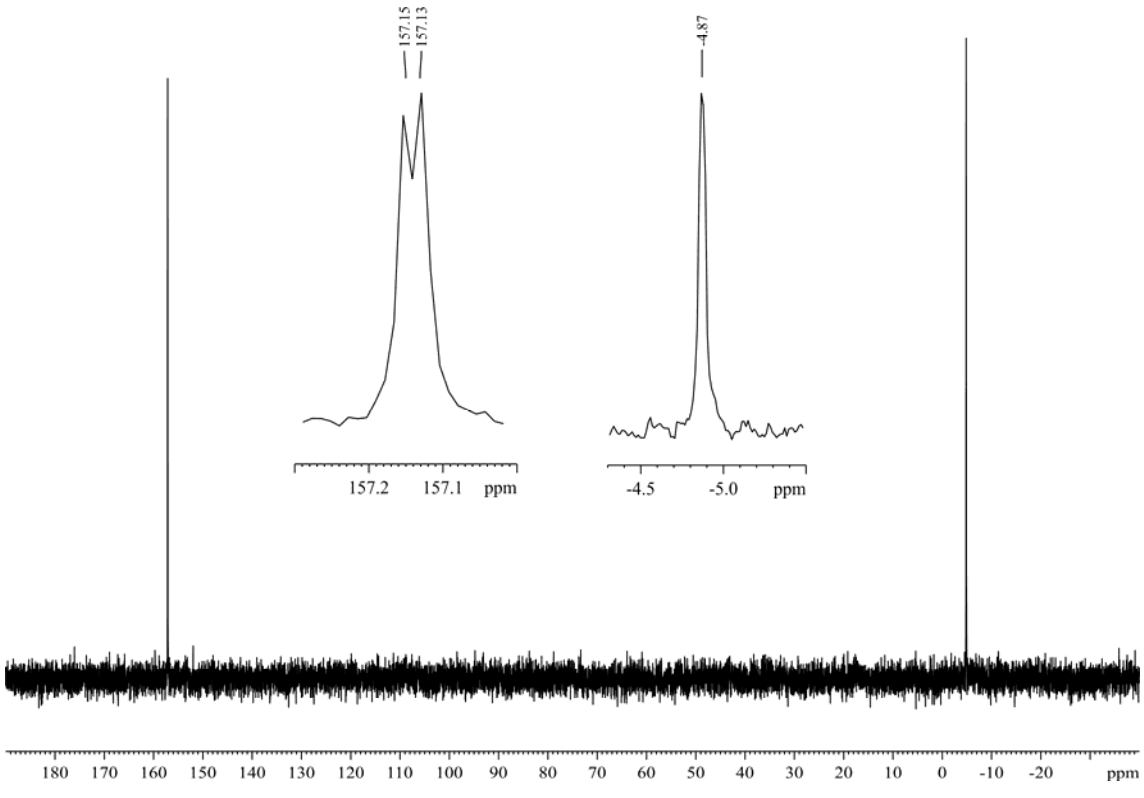
157.15
157.13
-4.87
157.2 157.1 ppm
-4.5 -5.0 ppm
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 ppm