Supporting Information

Designing P-Chirogenic 1,2-Diphosphinobenzenes at both P-Centers using P(III)-Phosphinites

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General Experimental Methods. All reactions were carried out under inert atmosphere. Solvents were dried and purified by conventional methods prior to use. Tetrahydrofuran (THF) and toluene were distilled from sodium/benzophenone and stored under argon. Methanol was distilled from sodium and dichloromethane from CaH_2 under argon prior to use. *n*-Butyllithium, 1,2-dibromobenzene, bromo-3,5-di-*tert*-butylbenzene, $BH_3.SMe_2$, 1,4-diazabicyclo[2.2.2]octane (DABCO) and the chlorophosphines **14** (R = Ph, *c*-Hex, *i*-Pr, 1-Np, *o*-Tol, *p*-Tol, *p*-$CF_3C_6H_4$, 3,5-$(CH_3)_2C_6H_3$, 3,5-$(CF_3)_2C_6H_3$) were purchased from commercial sources and used without purification. *sec*-Phosphine-boranes **13** and *o*-bromophenylphosphine-boranes **10** were synthesized according to previously reported procedure.[1,2] The solution of HCl in toluene (0.2-0.4M) was obtained by bubling HCl gas in toluene and titrated by acidimetry before use. The (2*S*, 4*R*, 5*S*)-(-)-3,4-dimethyl-2,5-diphenyl-1,3,2-oxazaphospholidine-2-borane (-)-**9** and its enantiomer (2*R*, 4*S*, 5*R*)-(+)-**9a**, were prepared from (+)- or (-)-ephedrine, respectively as previously described.[2] The aminophosphine-boranes (R_p)-(-)-**16a** (R^2 = *o*-An),[3] and (R_p)-(-)-**16b** (R^2 = *o*-Tol)[3] were prepared from (-)-**9** prepared from the (+)-ephedrine according to the published procedure.[3] The aminophosphine-borane (S_p)-(+)-**16d** (R^2 = *o*-biPh) was prepared from (+)-**9** prepared from the (-)-ephedrine according to similar procedure.[3,4] The *o*-bromophenylphosphine **10a (**R^1 = Ph), *(S)*-**10b** (R^1 = *o*-An), (*S*)-**10c** (R^1 = Fc) and (*R*)-**10d** (R^1 = *i*-Pr), were synthesized according to previously reported procedure.[1] The (*R*)-(+)-di-μ-chlorobis[2[1-(dimethylamino)ethyl]phenyl-C,N]dipalladium was prepared from (*R*)-(+)-1-phenylethyl amine according to literature procedures.[5] For HPLC, hexane and 2-propanol were of chromatographic grade and used without purification. Reactions were monitored by thin-layer chromatography (TLC) using 0.25 mm precoated silica gel plates. Flash chromatography was performed with the indicated solvents using silica gel 60 (60AAC, 35-70 μm). The ^1H, ^{13}C, ^{31}P and ^{19}F NMR spectra were recorded on 500 or 300 MHz spectrometers at ambient temperature using TMS as internal reference for ^1H, ^{13}C NMR, phosphoric acid (85%) and $CFCl_3$ as external references for ^{31}P- and ^{19}F-NMR, respectively. Data are reported as s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br.s = broad signal, coupling constant(s) in Hertz, integration. HPLC analyses were performed on a chromatograph equipped with a UV detector at λ = 210 and 254 nm. Infrared spectra were recorded on FT-IR instrument. Melting points were measured on a Kofler melting points apparatus and are uncorrected. Optical rotation values were determined at 20 °C on a polarimeter at 589 nm (sodium lamp). Mass spectroscopies were performed under (ESI) conditions with a micro-Q-TOF or Orbitrap detector. Elemental analyses were measured with a precision superior to 0.3% on a CHNS-O instrument apparatus. X-Ray analyses were performed at the Université de Bourgogne, and the data were collected at 115 K on a Bruker Nonius Apex II CCD system using graphite-monochromated Mo-Kα radiation. Using Olex2[6] the structures were solved with the ShelXT structure solution program,[7] using the direct methods solution method. The model was refined with version 2014/7 of ShelXL using Least Squares minimisation.[8] Crystallographic data and structures refinement details for DP*B (*S*)-**12a**, (*R*)-**12j** and (*S*,*S*)-**12p** were reported below.

I. Synthesis of (R_p)-*N*-methyl-*N*-[(1*S*,2*R*)(1-hydroxy-2-methyl-1-phenyl-2-propyl)]amino-(3,5-di-*t*-butylphenyl)phenyl phosphine-borane 16c

The aminophosphine-borane (*R*)-**16c** (R^3 = 3,5-di-*t*-BuC_6H_3) was prepared from the complex (-)-**9** prepared from the (+)-ephedrine according to the published procedure.[3,4]

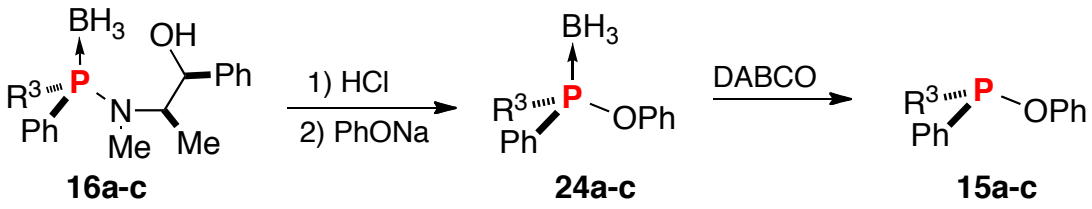
To a solution of borane complex (-)-**9** (0.70 g, 2.48 mmol) in THF (3 mL) was added at -78 °C under argon a solution of 3,5-di-*tert*-butylphenyllithium in THF, previously prepared by mixing in THF (2 mL) at -78 °C, 3,5-di-*tert*-butyl-1-bromobenzene (1.00 g, 3.72 mmol) and *tert*-butyllithium (1.6 M in pentane, 1.2 mL, 3.72 mmol). The resulting solution was allowed to stir at room temperature overnight. After quenching with water, the mixture was extracted with dichloromethane (3 x 10 mL) and the organic phases were dried over $MgSO_4$. The solvent was evaporated under vacuum to give a residue which was purified by chromatography on column (silica gel) using dichloromethane as eluent.

Yield = 63% (0.74 g); White solid; R_f 0.36 (dichloromethane); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.19 (d, *J* = 6.8 Hz, 3H), 1.21 (s, 18H), 1.75 (d, *J* = 4.3 Hz, 1H), 2.37 (d, *J* = 8.0 Hz, 3H), 4.22-4.30 (m, 1H), 4.74-4.78 (m, 1H), 7.09-7.40 (m, 13H), 7.43-7.44 (m, 1H); ^{31}P NMR (121.5 MHz, $CDCl_3$) δ +71.6-72.2 (m); HRMS (ESI) calcd for $C_{30}H_{43}OBNPNa$ $[M+Na]^+$: 498.3073, found 498.3059.

II. Synthesis of the P(III)-chirogenic phosphinites 15

The P(III)-chirogenic phosphinites **15a-e** were prepared from their borane-complexes **24a-e** by decomplexation using DABCO, according to a described procedure[9] (Scheme SI.1 and SI.2).

II.1. P(III)-chirogenic phenyl phosphinites 15a-c



Scheme SI.1

II.1.1 Preparation of the P-chirogenic phenylphosphinite-boranes 24a-c

The phenylphosphinite-boranes **24a-c** were prepared from the corresponding aminophosphine-boranes (*R*)-**16a**, (*R*)-**16b** and (*R*)-**16c** according to a procedure described (Scheme SI.1).[3]

Typical procedure: A freshly titrated toluene solution of dry HCl (12 mmol) was added to the aminophosphine-borane **16a-c** (2 mmol) and the mixture was stirred at room temperature during one hour. The ephedrine hydrochloride was filtered off using a Millipore 4 µm filter, and the resulting solution of chlorophosphine-borane was cooled to -78 °C. Phenate (2.4 mmol), previously prepared by reaction of phenol (2.4 mmol) with NaH (2.6 mmol) in THF (3 mL) at 0 °C during one hour, was added and the resulting mixture was stirred at room temperature overnight. After hydrolysis (10 mL H_2O) the mixture was extracted with dichloromethane (3 x 10 mL) and the combined organic phases were dried over $MgSO_4$. The solvent was removed under vacuum and the resulting crude product was purified by chromatography on column of silica gel.

II.1.1.1. (*R*)-Phenyl-*o*-anisylphenylphosphinite-borane 24a

The purification was achieved using a mixture of petroleum ether/ethyl acetate in 2:1 ratio as eluent. White solid; Yield = 86% (0.554 g); R_f 0.42 (petroleum ether/ethyl acetate 2:1); $[\alpha]_D$ = +25.4 (c 0.3, $CHCl_3$); IR (neat): 3063, 2939, 2381, 1968, 1897, 1822, 1587, 1475, 1251, 1159, 914 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 3.54 (s, 3H), 6.86 (dd, *J* = 4.2, 8.3 Hz, 1H), 6.92-7.03 (m, 4H), 7.11-7.16 (m, 2H), 7.33-7.48 (m, 4H), 7.74-7.81 (m, 2H), 7.86 (ddd, *J* = 1.7, 7.6, 12.8 Hz, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 55.5, 111.7 (d, *J* = 4.8 Hz), 119.2 (d, *J* = 61.0 Hz), 121.0 (d, *J* = 11.8 Hz), 121.3 (d, *J* = 4.1 Hz), 124.5 (d, *J* = 1.0 Hz), 128.2 (d, *J* = 11.2 Hz), 129.2, 131.3 (d, *J* = 11.7 Hz), 131.5 (d, *J* = 2.0 Hz), 132.3 (d, *J* = 66.3 Hz), 134.5 (d, *J* = 12.5 Hz), 134.6, 152.5 (d, *J* = 5.6 Hz), 161.1 (d, *J* = 2.6 Hz); ^{31}P NMR (121.5 MHz, $CDCl_3$) δ +108.1-108.8 (m); Anal calcd for $C_{19}H_{20}PO_2B$: C 70.84, H 6.26; found: C 70.58, H 6.42; HRMS (ESI) calcd for $C_{19}H_{20}O_2PBNa$ $[M+Na]^+$: 345.1190, found 345.1206. The enantiomeric excess (99% ee) was determined by HPLC analysis on chiralcel OD-H, flow 0.3 $mL.min^{-1}$ with a mixture hexane/2-propanol in 98:2 ratio as eluent: t_R (*R*) = 27.8 min, t_R (*S*) = 30.7 min.

II.1.1.2. (*R*)-Phenyl-phenyl-*o*-tolylphosphinite-borane 24b

The purification was achieved by chromatography on column (silica gel) using a mixture of petroleum ether/ethyl acetate in 2:1 ratio as eluent. Colorless oil; Yield = 80% (0.490 g); R_f 0.45 (petroleum ether/ethyl acetate 3:1); $[\alpha]_D$ = +12.5 (c 0.3, $CHCl_3$); IR (neat): 3058, 2930, 2391, 1947, 1592, 1489, 1438, 1196, 1165, 1082, 914, 896, 775, 743, 726, 620 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.26 (s, 3H), 6.90-6.94 (m, 2H), 7.00-7.07 (m, 1H), 7.14-7.21 (m, 3H), 7.27-7.32 (m, 1H), 7.39-7.48 (m, 4H), 7.64-7.71 (m, 2H), 7.94 (ddd, *J* = 1.3, 7.7, 13.2 Hz, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 21.5 (d, *J* = 4.1 Hz), 121.1 (d, *J* = 4.8 Hz), 124.5 (d, *J* = 1.0 Hz), 126.0 (d, *J* = 12.4 Hz), 128.8 (d, *J* = 11.4 Hz), 129.4, 129.6, 131.3 (d, *J* = 11.4 Hz), 131.9 (d, *J* = 64.5 Hz), 131.9 (d, *J* = 8.4 Hz), 132.0 (d, *J* = 2.4 Hz), 132.7 (d, *J* = 2.4 Hz), 134.1 (d, *J* = 16.2 Hz), 142.0 (d, *J* = 7.5 Hz), 152.3 (d, *J* = 3.8 Hz); ^{31}P NMR (121.5 MHz, $CDCl_3$) δ +111.6-112.2 (m); HRMS (ESI) calcd for $C_{19}H_{20}OPBNa$ $[M+Na]^+$: 329.1240, found 329.1243. The enantiomeric excess (98% ee) was determined by HPLC analysis on Lux 5µ cellulose-2, flow 0.7 $mL.min^{-1}$ using a mixture hexane/2-propanol in 97:3 ratio as eluent: t_R (*R*) = 8.5 min, t_R (*S*) = 9.5 min.

II.1.1.3. (*R*)-Phenyl-(3,5-di-*tert*-butylphenyl)phenylphosphinite-borane 24c

The purification was achieved using a mixture of petroleum ether/ethyl acetate in 3:1 ratio as eluent. White solid; Yield = 78% (0.631 g); R_f 0.61 (petroleum ether/ethyl acetate 3:1); $[\alpha]_D$ = +3.3 (c 0.3, $CHCl_3$); IR (neat): 2967, 2404, 2381, 1590, 1489, 1437, 1423, 1363, 1247, 1196, 1145, 1061, 906, 759, 723, 704, 687 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.33 (s, 18H), 7.01-7.05 (m, 1H), 7.11-7.14 (m, 1H), 7.22-7.26 (m, 3H), 7.50-7.58 (m, 3H), 7.61-7.62 (m, 1H), 7.65 (d, *J* = 1.8 Hz, 1H), 7.69 (d, *J* = 1.8 Hz, 1H), 7.84-7.91 (m, 2H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 31.3, 35.1, 121.4 (d, *J* = 4.3 Hz), 124.6, 125.8 (d, *J* = 11.5 Hz), 126.4 (d, *J* = 1.8 Hz), 128.6 (d, *J* = 10.0 Hz), 129.4, 130.3 (d, *J* = 63.1 Hz), 131.6 (d, *J* = 11.5 Hz), 132.0 (d, *J* = 2.0 Hz), 132.1 (d, *J* = 63.1 Hz), 151.3 (d, *J* = 10.6 Hz), 152.5 (d, *J* = 5.1 Hz); ^{31}P NMR (121.5 MHz, $CDCl_3$) δ +110.4-111.0 (m); Anal calcd for $C_{26}H_{34}POB$: C 77.23, H 8.48; found: C 77.03, H 8.64; HRMS (ESI) calcd for $C_{26}H_{34}OPBNa$ $[M+Na]^+$: 427.2337, found 427.2338. The enantiomeric excess (99% ee) was

determined by HPLC analysis on Lux 5µ cellulose-2, flow 0.4 mL.min^{-1} using a mixture hexane/2-propanol 99:1 as eluent: t_R (*R*) = 12.5 min, t_R (*S*) = 14.7 min.

II.1.2. Decomplexation in P-chirogenic phenyl-phosphinites 15a-c

Typical procedure: To a solution of phenyl phosphinite-boranes **24a-c** (1.0 mmol) in toluene (3 mL) was added DABCO (4.0 mmol). The resulting solution was stirred under argon at room temperature overnight and the solvent was removed under vacuum. The residue was purified by flash chromatography on silica gel using a mixture of petroleum ether/ethyl acetate in 5:1 ratio as eluent.

II.1.2.1. (*R*)-Phenyl-*o*-anisylphenylphosphinite 15a

Colorless oil; Yield = 86% (0.265 g); R_f 0.42 (petroleum ether/ethyl acetate 5:1); $[\alpha]_D$ = +63.5 (c 0.3, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.24 (s, 3H), 6.51 (ddd, *J* = 0.8, 4.8, 8.2 Hz, 1H), 6.92 (tt, *J* = 1.0, 7.3 Hz, 1H), 7.00-7.05 (m, 1H), 7.11-7.21 (m, 6H), 7.33-7.36 (m, 2H), 7.88-7.97 (m, 3H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 55.6, 110.5, 119.0 (d, *J* = 10.0 Hz), 121.3, 122.3, 128.3 (d, *J* = 7.3 Hz), 128.9 (d, *J* = 18.5 Hz), 129.5, 129.7 (2s), 130.8, 131.1, 131.3, 140.2 (d, *J* = 17.9 Hz), 157.6 (d, *J* = 10.7 Hz), 160.1 (d, *J* = 17.9 Hz); ^{31}P NMR (121.5 MHz, $CDCl_3$) δ +103.9 (s); HRMS (ESI) calcd for $C_{19}H_{17}O_2PNa$ $[M+Na]^+$: 331.0858, found 331.0845. The enantiomeric excess (99% ee) was determined by HPLC analysis of the borane complex **24a** after complexation with BH_3.DMS, on chiralcel OD-H, flow 0.3 mL.min^{-1} using a mixture hexane/2-propanol in 98:2 ratio as eluent: t_R (*R*) = 27.8 min, t_R (*S*) = 30.7 min.

II.1.2.2. (*R*)-Phenyl-phenyl-*o*-tolylphosphinite 15b

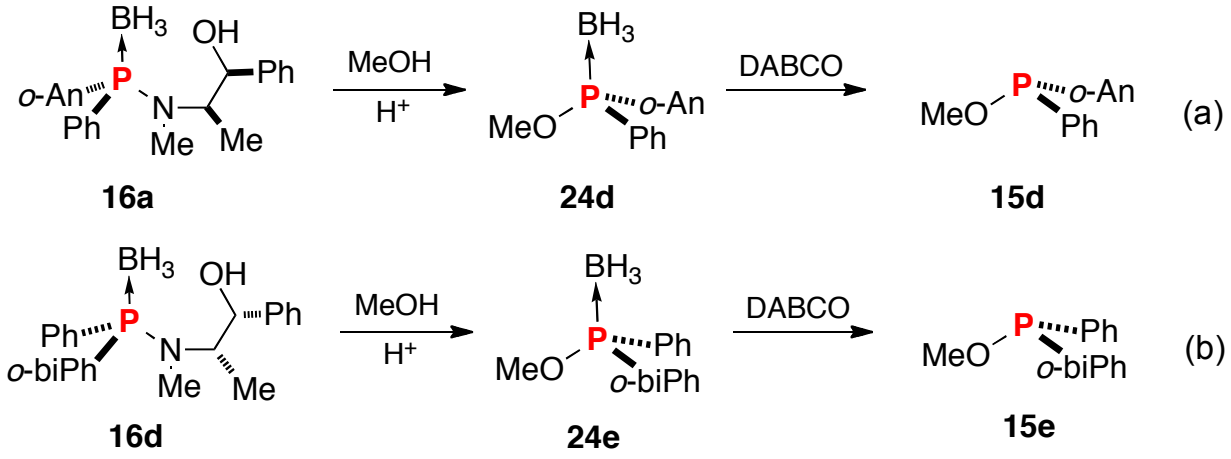
Colorless oil; Yield = 84% (0.245 g); R_f 0.55 (petroleum ether/ethyl acetate 5:1); $[\alpha]_D$ = +29.7 (c 0.3, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.39 (d, *J* = 1.2 Hz, 3H), 6.91 (tt, *J* = 1.0, 7.5 Hz, 1H), 7.01-7.06 (m, 1H), 7.11-7.21 (m, 7H), 7.24-7.31 (m, 2H), 7.69-7.74 (m, 2H), 7.93-7.98 (m, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 20.5 (d, *J* = 22.2 Hz), 118.8 (d, *J* = 11.5 Hz), 122.5, 126.1 (d, *J* = 2.6 Hz), 128.5 (d, *J* = 6.9 Hz), 129.5, 129.6, 129.7 (d, *J* = 7.6 Hz), 129.9, 130.3 (d, *J* = 4.1 Hz), 131.5 (d, *J* = 21.4 Hz), 138.5 (d, *J* = 17.6 Hz), 139.6 (d, *J* = 17.6 Hz), 140.5 (d, *J* = 26.4 Hz), 157.5 (d, *J* = 8.8 Hz); ^{31}P NMR (121.5 MHz, $CDCl_3$) δ +106.2 (s); HRMS (ESI) calcd for $C_{19}H_{17}O_2PNa$ $[M+O+Na]^+$: 331.0858, found 331.0825. The enantiomeric excess (98% ee) was determined by HPLC analysis of the borane complex **24b** after complexation with BH_3.DMS, on Lux 5µ cellulose-2, flow 0.7 mL.min^{-1} using a mixture hexane/2-propanol in 97:3 ratio as eluent: t_R (*R*) = 8.5 min, t_R (*S*) = 9.5 min.

II.1.2.3. (*R*)-Phenyl-(3,5-di-*tert*-butylphenyl)phenylphosphinite 15c

Colorless oil; Yield = 86% (0.336 g); R_f 0.57 (petroleum ether/ethyl acetate 5:1); $[\alpha]_D$ = +20.3 (c 0.3, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.32 (s, 18H), 7.01-7.06 (m, 1H), 7.15-7.19 (m, 2H), 7.26-7.32 (m, 2H), 7.40-7.47 (m, 6H), 7.59-7.65 (m, 2H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 31.4, 35.0, 119.1 (d, *J* = 11.1 Hz), 122.4, 124.1, 124.9, 125.1, 128.4 (d, *J* = 7.4 Hz), 129.5 (d, *J* = 7.4 Hz), 130.4, 130.6, 139.4 (d, *J* = 16.2 Hz), 141.1 (d, *J* = 16.2 Hz), 150.7 (d, *J* = 8.1 Hz), 157.6 (d, *J* = 8.1 Hz); ^{31}P NMR (121.5 MHz, $CDCl_3$) δ +113.6 (s); HRMS (ESI) calcd for $C_{26}H_{31}OPNa$ $[M+Na]^+$: 413.2005, found 413.2002. The

enantiomeric excess (99% ee) was determined by HPLC analysis of the borane complex **24c** obtained by complexation with BH_3.DMS, on Lux 5µ cellulose-2, flow 0.4 mL.min^{-1}, using a mixture hexane/2-propanol in 99:1 ratio as eluent: t_R (*R*) = 12.5 min, t_R (*S*) = 14.7 min.

II.2. P(III)-Chirogenic methyl phosphinites 15d,e



Scheme SI.2

II.2.1 Preparation of the P-chirogenic methyl phosphinite-boranes 24d,e

The methyl phosphinite-boranes **24d,e** was prepared from aminophosphine-boranes (R_p)-**16a** and (S_p)-**16d**, respectively, by methanolysis in acidic conditions according to a procedure described (Scheme SI.2).[10]

Typical procedure: To a solution of aminophosphine-borane **16a** (or **16d**) (0.57 mmol) in MeOH (6 mL) was added dropwise at 0 °C sulfuric acid (0.04 mL, 0.68 mmol). After stirring at room temperature overnight, water was added and the solution was extracted with CH_2Cl_2 (3 x 10 mL). Organic phases were washed with saturated $NaHCO_3$ solution (10 mL) and dried over $MgSO_4$. Solvents were removed and the residue was purified by chromatography on column (silica gel) using a mixture of petroleum ether/ethyl acetate in 3:1 ratio as eluent.

II.2.1.1. (*S*)-Methyl-*o*-anisylphenylphosphinite-borane 24d[10,11]

Yield = 75% (0.11 g); Colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.58 (d, *J* = 12.1 Hz, 3H), 6.91-6.95 (m, 2H), 7.11-7.17 (m, 1H), 7.22-7.44 (m, 7H), 7.51-7.63(m, 2H), 8.06-8.13 (m, 1H); ^{31}P NMR (121.5 MHz, CD_2Cl_2) δ +108.2-108.8 (m).

II.2.1.2. (*R*)-Methyl-*o*-biphenylphenylphosphinite-borane 24e[11]

Yield = 85% (0.15 g); White solid; ^{1}H NMR (300 MHz, CD_2Cl_2) δ 3.55 (s, 3H), 3.66 (d, *J* = 12.0 Hz, 3H), 6.79 (dd, *J* = 4.4, 8.3 Hz, 1H), 7.00 (tdd, *J* = 1.0, 2.0, 7.5 Hz, 1H), 7.31-7.45 (m, 4H), 7.63-7.76 (m, 3H); ^{31}P NMR (121.5 MHz, CD_2Cl_2) δ + 105.6-107.2 (m).

II.2.1.3. Decomplexation in P-chirogenic methyl phosphinites 15d,e

General procedure

To a solution of methyl phosphinite-borane **15d** (or **15e**) (1.0 mmol) in toluene (3 mL) was added DABCO (4.0 mmol). The resulting solution was stirred under argon at room temperature overnight and the solvent was removed under vacuum. The residue was purified by flash chromatography on alumina using a mixture of petroleum ether/ethyl acetate in 10:1 ratio as eluent.

II.2.2.3.1. (*S*)-Methyl-*o*-anisylphenylphosphinite 15d

Yield = 81% (0.20 g); Colorless oil; R_f 0.56 (petroleum ether/ethyl acetate 10:1; alumina); $[\alpha]_D$ = -149.0 (c 0.4, $CHCl_3$); ^{1}H NMR (300 MHz, CD_2Cl_2) δ 3.69 (d, *J* = 14.0 Hz, 3H), 3.77 (s, 3H), 6.89 (dd, *J* = 4.5, 8.2 Hz, 1H), 7.07 (td, *J* = 0.7, 7.4 Hz, 1H), 7.36-7.39 (m, 4H), 7.48-7.56 (m, 3H); ^{13}C NMR (75.5 MHz, CD_2Cl_2) δ 55.4, 56.9 (d, *J* = 22.8 Hz), 110.4, 121.0, 128.0 (d, *J* = 7.4 Hz), 128.9 (d, *J* = 3.5 Hz), 129.2, 129.9 (d, *J* = 21.3 Hz), 130.3, 130.6 (d, *J* = 21.8 Hz), 141.3 (d, *J* = 20.6 Hz), 160.0 (d, *J* = 17.7 Hz); ^{31}P NMR (121.5 MHz, CD_2Cl_2) δ +107.5 (s); HRMS (ESI) calcd for $C_{14}H_{15}O_2PNa$ $[M+Na]^+$: 269.0702, found 269.0698; The enantiomeric excess (99% ee) was determined by HPLC analysis on Chiralpak IB, flow 0.5 $mL.min^{-1}$, using a mixture hexane/2-propanol in 98:2 ratio as eluent: t_R (*S*) = 8.8 min, t_R (*R*) = 9.4 min.

II.2.2.3.1. (*R*)-Methyl-*o*-biphenylphenylphosphinite 15e

Yield = 90% (0.26 g); Colorless oil; R_f 0.58 (petroleum ether/ethyl acetate 10:1; alumina); $[\alpha]_D$ = +187.0 (c 0.6, $CHCl_3$); ^{1}H NMR (300 MHz, CD_2Cl_2) δ 3.57 (d, *J* = 12.1 Hz, 3H), 7.22-7.37 (m, 11H), 7.45-7.90 (m, 2H), 7.75-7.77 (m, 1H,); ^{13}C NMR (75.5 MHz, CD_2Cl_2) δ 56.5 (d, *J*= 22.9 Hz), 127.3, 127.8, 128.1 (d, *J* = 6.9 Hz), 129.0, 129.2 (d, *J* = 2.9 Hz), 129.3, 129.8 (d, *J* = 3.5 Hz), 131.1 (d, *J* = 22.3 Hz), 139.9 (d, *J* = 24.0 Hz), 141.0 (d, *J* = 5.3 Hz), 141.4 (d, *J* = 20.1 Hz), 145.9 (d, *J* = 26.7 Hz); ^{31}P NMR (121.5 MHz, CD_2Cl_2) δ +108.9 (s); HRMS (ESI) calcd for $C_{19}H_{17}OPNa$ $[M+Na]^+$: 315.0909, found 315.0902; The enantiomeric excess (99% ee) was determined by HPLC analysis on Chiralpak IB, flow 0.5 $mL.min^{-1}$, with a mixture hexane/2-propanol in 99:1 ratio as eluent: t_R (*S*) = 8.3 min, t_R (*R*) = 8.8 min.

III. Synthesis of P(III)-chirogenic 1,2-diphosphinobenzenes 12a-k according to route A

III.1. General procedure:

To a solution of *o*-bromophenylphosphine **10a** (or **10b**,**c**) (0.54 mmol) in THF (2 mL) was added at -78 °C under argon *n*-BuLi (1.6 M in hexane) (0.37 mL, 0.59 mmol) and the resulting solution was stirred at this temperature during one hour. At this time, chlorophosphine **14** (0.65 mmol) was added at -78 °C and the solution was stirred at room temperature overnight. After quenching with water, the mixture was extracted with dichloromethane (3 x 5 mL) and the organic phases were dried over $MgSO_4$. The solvent was evaporated under vacuum giving a residue which was purified either by chromatographic column on silica gel or recrystallization (or both).

III.2. (*S*)-1-(*o*-Anisylphenylphosphino)-2-(diphenylphosphino)benzene 12a[12]

This compound was synthesized using the (*S*)-*o*-anisyl-(*o*-bromophenyl)phenylphosphine **10b** and the chlorodiphenylphosphine **14a** (R' = Ph). The purification was achieved using a mixture of petroleum

ether/dichloromethane in 3:1 ratio, as eluent. Analytical pure sample was obtained by recrystallization in dichloromethane/methyl alcohol. White solid; Yield = 70% (0.180 g); R_f 0.18 (petroleum ether/dichloromethane 3:1); $[\alpha]_D$ = +52.6 (c 0.3, $CHCl_3$); IR (neat): 3048, 1581, 1571, 1469, 1431, 1299, 1272, 1240, 1180, 1160, 1129, 1090, 1069, 1022, 793, 743, 719 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 3.57 (s, 3H), 6.56 (ddd, *J* = 1.7, 4.4, 7.4 Hz, 1H), 6.67-6.75 (m, 2H), 6.90-7.00 (m, 2H), 7.04-7.22 (m, 18H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 55.6, 110.2 (d, *J* = 1.5 Hz), 120.8, 125.9 (dd, *J* = 6.7, 13.9 Hz), 128.1, 128.2, 128.3, 129.0, 130.0, 133.6, 133.7, 133.8, 133.9, 134.0, 134.1, 134.2, 134.3, 136.5 (dd, *J* = 4.9, 11.0 Hz), 137.4 (dd, *J* = 5.1, 12.1 Hz), 143.3 (dd, *J* = 10.7, 21.7 Hz), 143.6 (dd, *J* = 9.5, 32.5 Hz), 161.0 (d, *J* = 15.3 Hz); ^{31}P NMR (121.5 MHz, $CDCl_3$) δ -14.0 (d, *J* = 164.8 Hz), -23.6 (d, *J* = 164.8 Hz); HRMS (ESI) calcd for $C_{31}H_{26}OP_2Na$ $[M+Na]^+$: 499.1351, found 499.1375. The enantiomeric excess (99% ee) was determined by HPLC analysis on chiralpak AD, flow 0.2 $mL.min^{-1}$, using a mixture hexane/2-propanol in 99:1 ratio, as eluent: t_R (*S*) = 44.5 min, t_R (*R*)= 61.9 min.

III.3. (*S*)-1-(*o*-Anisylphenylphosphino)-2-[di-(1-naphtyl)phosphino]benzene 12b

This compound was synthesized using the (*S*)-*o*-anisyl-(*o*-bromophenyl)phenylphosphine **10b** and the chlorodi(1-naphtyl)phosphine **14b** (R' = 1-Np). The purification was achieved using a mixture of petroleum ether/dichloromethane in 2:1 ratio as eluent. White solid; Yield = 44% (0.137 g); R_f 0.38 (petroleum ether/dichloromethane 2:1); $[\alpha]_D$ = +51.0 (c 0.3, $CHCl_3$); IR (neat): 3048, 1581, 1570, 1469, 1431, 1299, 1270, 1240, 1180, 1129, 1090, 1022, 793, 743, 718 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 3.61 (s, 3H), 6.74-7.01 (m, 6H), 7.10-7.45 (m, 15H), 7.74-7.87 (m, 4H), 8.06-8.11 (m, 1H), 8.34 (dd, *J* = 4.0, 7.9 Hz, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 55.6, 110.2, 120.9, 125.5, 125.7 (d, *J* = 5.8 Hz), 125.9 (d, *J* = 2.2 Hz), 126.0 (d, *J* = 2.5 Hz), 126.2 (dd, *J* = 8.3, 14.4 Hz), 126.6, 126.8 (d, *J* = 1.1 Hz), 127.0, 128.2 (d, *J* = 7.1 Hz), 128.3, 128.4, 129.1 (d, *J* = 5.6 Hz), 129.2 (d, *J* = 3.4 Hz), 130.0, 131.1 (2s), 134.6, 134.8, 135.0 (d, *J* = 6.5 Hz), 135.4 (dd, *J* = 20.3, 23.5 Hz), 136.4 (d, *J* = 11.4 Hz), 141.5 (dd, *J* = 7.1, 33.5 Hz), 144.5 (dd, *J* = 9.1, 33.5 Hz), 161.0 (d, *J* = 15.3 Hz); ^{31}P NMR (121.5 MHz, $CDCl_3$) δ -23.4 (d, *J* = 176.0 Hz), -30.4 (d, *J* = 176.0 Hz); Anal calcd for $C_{39}H_{30}P_2O$: C 81.24, H 5.24; found: C 81.11, H 5.33; HRMS (ESI) calcd for $C_{39}H_{30}OP_2Na$ $[M+Na]^+$: 599.1664, found 599.1656. The enantiomeric excess (99% ee) was determined by HPLC analysis on Lux 5µ Cellulose 2, flow 0.7 $mL.min^{-1}$, using a mixture hexane/2-propanol in 98:2 ratio as eluent: t_R (*S*) = 9.3 min, t_R (*R*) = 11.9 min.

III.4. (*S*)-1-(*o*-Anisylphenylphosphino)-2-[di-(*o*-tolyl)phosphino]benzene 12c

This compound was synthesized using the (*S*)-*o*-anisyl-(*o*-bromophenyl)phenylphosphine **10b** and the chloro-di-(*o*-tolyl)phosphine **14c** (R' = *o*-Tol). The purification was achieved using a mixture of toluene/petroleum ether in 3:1 ratio as eluent and recrystallization in dichloromethane/methyl alcohol. White solid; Yield = 37% (0.101 g); R_f 0.39 (toluene/petroleum ether 3:1); $[\alpha]_D$ = +73.0 (c 0.2, $CHCl_3$); IR (neat): 3050, 2929, 2834, 1573, 1469, 1429, 1272, 1241, 1130, 1108, 1070, 1025, 745 cm^{-1}; ^1H NMR (300 MHz, C_6D_6) δ 2.38 (s, 3H), 2.54 (s, 3H), 3.23 (s, 3H), 6.56 (dd, *J* = 4.2, 7.8 Hz, 1H), 6.82-6.85 (m, 1H), 7.01-7.26 (m, 14H), 7.27-7.30 (m, 2H), 7.38-7.39 (m, 1H), 7.53-7.55 (m, 1H); ^{13}C NMR (75.5 MHz, C_6D_6) δ 21.1 (d, *J* = 21.1 Hz), 21.3 (d, *J* = 21.1 Hz), 54.9, 126.0 (d, *J* = 5.7 Hz), 126.9 (dd, *J* = 6.9, 16.0 Hz),

128.1, 128.2, 128.3 (d, *J* = 3.1 Hz), 128.5 (d, *J* = 6.9 Hz), 129.1 (d, *J* = 4.6 Hz), 129.8, 130.2 (2d, *J* = 5.1 Hz; *J* = 4.7 Hz), 133.7, 133.9, 134.0 (d, *J* = 6.9 Hz), 134.1 (d, *J* = 7.0 Hz), 134.2, 134.4, 134.6, 136.1-136.3 (m), 137.5 (dd, *J* = 4.7,13.6 Hz), 142.7 (2dd, *J* = 9.9, 34.0 Hz; *J* = 15.2, 26.7 Hz), 155.7 (dd, *J* = 11.1, 32.8 Hz), 162.2 (d, *J* = 15.3 Hz); ^{31}P NMR (121 MHz, C_6D_6) δ -22.0 (d, *J* = 172.5 Hz), -26.3 (d, *J* = 172.5 Hz); Anal calcd for $C_{33}H_{30}P_2O$: C 78.56, H 5.99; found: C 78.53, H 6.09; HRMS (ESI) calcd for $C_{33}H_{31}OP_2$ $[M+H]^+$: 505.1845, found 505.1841. The enantiomeric excess (99% ee) was determined by HPLC analysis on Lux 5µ Cellulose 2, flow 0.5 mL.min^{-1}, using a mixture hexane/2-propanol in 98:2 ratio as eluent: t_R (*S*) = 8.2 min, t_R (*R*) = 9.6 min.

III.5. (*S*)-1-(*o*-Anisylphenylphosphino)-2-[di-(*p*-tolyl)phosphino]benzene 12d

This compound was synthesized using the (*S*)-*o*-anisyl-(*o*-bromophenyl)phenylphosphine **10b** and the chloro-di-(*p*-tolyl)phosphine **14d** (R' = *p*-Tol). The purification was achieved using a mixture of toluene/petroleum ether in 2:1 ratio as eluent. White solid; Yield = 52% (0.141 g); R_f 0.17 (toluene/petroleum ether 2:1); $[\alpha]_D$ = +58.0 (c 0.3, $CHCl_3$); IR (neat): 3046, 2963, 2919, 1572, 1496, 1470, 1429, 1396, 1260, 1240, 1184, 1090, 1020, 803, 750, 696 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.32-2.33 (2s, 6H), 3.67 (s, 3H), 6.62 (ddd, *J* = 1.7, 4.3, 7.4 Hz, 1H), 6.76-6.84 (m, 2H), 6.99-7.31 (m, 18H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 20.2, 20.3, 54.5, 109.1 (d, *J* = 1.3 Hz), 119.7, 125.0 (dd, *J* = 6.5, 13.9 Hz), 127.0, 127.1, 127.6, 127.8, 127.9 (d, *J* = 3.0 Hz), 128.0 (d, *J* = 2.7 Hz), 128.8, 132.6 (d, *J* = 7.6 Hz), 132.7-133.2 (m), 135.6 (dd, *J* = 4.8, 11.5 Hz), 136.9), 137.0, 142.2 (dd, *J* = 10.1, 31.6 Hz), 143.2 (dd, *J* = 11.2, 32.4 Hz), 160.0 (d, *J* = 15.4 Hz); ^{31}P NMR (121.5 MHz, $CDCl_3$) δ -15.4 (d, *J* = 162.8 Hz), -24.1 (d, *J* = 162.8 Hz); Anal calcd for $C_{33}H_{30}P_2O$: C 78.56, H 5.99; found: C 78.35, H 6.22; HRMS (ESI) calcd for $C_{33}H_{30}OP_2Na$ $[M+Na]^+$: 527.1664, found 527.1687. The enantiomeric excess (99% ee) was determined by HPLC analysis on Lux 5µ Cellulose 2, flow 0.5 mL.min^{-1}, using a mixture hexane/2-propanol in 90:10 ratio as eluent: t_R (*S*) = 8.0 min, t_R (*R*) = 10.9 min.

III.6. (*S*)-1-(*o*-Anisylphenylphosphino)-2-[di-(*p*-trifluoromethylphenyl)phosphino]benzene 12e

This compound was synthesized using the (*S*)-*o*-anisyl-(*o*-bromophenyl)phenylphosphine **10b** and the chloro-di-(*p*-trifluoromethylphenyl)phosphine **14e** (R' = *p*-$CF_3C_6H_4$). The purification was achieved using a mixture of toluene/petroleum ether 2:1, as eluent. White solid; Yield = 58% (0.192 g); R_f 0.56 (toluene/petroleum ether 2:1); $[\alpha]_D$ = +52.9 (c 0.3, $CHCl_3$); IR (neat): 3050, 2933, 1431, 1397, 1320, 1242, 1163, 1120, 1105, 1059, 1015, 830, 750, 696 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.57 (s, 3H), 6.48-6.52 (m, 1H), 6.65-6.74 (m, 2H), 6.90-7.01 (m, 2H), 7.06-7.25 (m, 12H), 7.35 (d, *J* = 7.8 Hz, 2H), 7.41 (d, *J* = 7.8 Hz, 2H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 55.6, 120.9, 124.0 (2q, *J* = 272.4 Hz), 124.9-125.1 (m), 128.2, 128.4 (d, *J* = 7.3 Hz), 128.7, 129.1, 129.3, 129.6, 130.4, 130.5 (q, *J* = 32.4 Hz), 133.9-134.2 (m), 134.5, 135.6 (dd, *J* = 4.5, 10.1 Hz), 140.8 (d, *J* = 9.8 Hz), 141.3-141.8 (m), 144.2 (dd, *J* = 10.5, 32.8 Hz), 161.0 (d, *J* = 15.4 Hz); ^{31}P NMR (121.5 MHz, $CDCl_3$) δ -14.5 (d, *J* = 164.5 Hz), -24.0 (d, *J* = 164.5 Hz); ^{19}F NMR (282.4 MHz, $CDCl_3$) δ -62.8 (2s); Anal calcd for $C_{33}H_{24}P_2OF_6$: C 64.71, H 3.95; found: C 64.87, H 4.05; HRMS (ESI) calcd for $C_{33}H_{24}OF_6P_2Na$ $[M+Na]^+$: 635.1099, found 635.1103. The enantiomeric excess

(99% ee) was determined by HPLC analysis on Lux 5µ Cellulose 2, flow 0.3 mL.min^{-1}, using a mixture hexane/2-propanol in 90:10 ratio as eluent: t_R (*S*) = 11.3 min, t_R (*R*) = 13.1 min.

III.7. (*S*)-1-(*o*-Anisylphenylphosphino)-2-[di-(*m*-xylyl)phosphino]benzene 12f

This compound was synthesized using the (*S*)-*o*-anisyl-(*o*-bromophenyl)phenylphosphine **10b** and the chloro-di-(*m*-xylyl)phosphine **14f** (R' = *m*-Xyl). The purification was achieved using a mixture of petroleum ether/dichloromethane in a ratio 2:1 as eluent. White solid; Yield = 61% (0.175 g); R_f 0.27 (petroleum ether/dichloromethane 2:1); $[\alpha]_D$ = +21.5 (c 0.3, $CHCl_3$); IR (neat): 3050, 1579, 1570, 1431, 1298, 1270, 1240, 1180, 1129, 1089, 1022, 792, 743, 719 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.22 (s, 6H), 2.25 (s, 6H), 3.70 (s, 3H), 6.66 (ddd, *J* = 1.6, 4.3, 7.2 Hz, 1H), 6.80-6.91 (m, 8H), 7.04-7.08 (m, 1H), 7.14-7.16 (m, 1H), 7.22-7.31 (m, 8H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 21.3, 21.4, 55.6, 110.2, 120.7, 126.2 (dd, *J* = 6.8, 14.6 Hz), 128.0 (d, *J* = 6.8 Hz), 128.2, 128.6, 128.8, 129.9, 130.0 (d, *J* = 6.8 Hz), 131.6 (d, *J* = 13.8 Hz), 131.8 (d, *J* = 14.1 Hz), 133.9 (dd, *J* = 6.5, 15.0 Hz), 134.0, 134.2 (d, *J* = 4.2 Hz), 137.0 (dd, *J* = 5.2, 12.1 Hz), 137.1 (dd, *J* = 1.5, 6.3 Hz), 137.2 (dd, *J* = 1.7, 6.2 Hz), 137.4 (d, *J* = 7.1 Hz), 143.5 (dd, *J* = 10.0, 31.9 Hz), 144.1 (dd, *J* = 12.0, 32.8 Hz), 161.0 (d, *J* = 14.6 Hz); ^{31}P NMR (121.5 MHz, $CDCl_3$) δ -14.1 (d, *J* = 167.5 Hz), -24.2 (d, *J* = 167.5 Hz); HRMS (ESI) calcd for $C_{35}H_{34}OP_2Na$ $[M+Na]^+$: 555.1977, found 555.1979. The enantiomeric excess (99% ee) was determined by HPLC analysis on Lux 5µ Cellulose 2, flow 0.7 mL.min^{-1}, using a mixture hexane/2-propanol in 90:10 ratio as eluent: t_R (*S*) = 5.5 min, t_R (*R*) = 7.1 min.

III.8. (*S*)-1-(*o*-Anisylphenylphosphino)-2-[di-(3,5-di-trifluoromethylphenyl)phosphino]benzene 12g

This compound was synthesized using the (*S*)-*o*-anisyl-(*o*-bromophenyl)phenylphosphine **10b** and the chloro-di-(3,5-di-trifluoromethylphenyl)phosphine **14g** (R' = 3,5-$(CF_3)_2C_6H_3$). The purification was achieved using a mixture of petroleum ether/dichloromethane in 2:1 ratio as eluent. White solid; Yield = 44% (0.178 g); R_f 0.58 (petroleum ether/dichloromethane 2:1); $[\alpha]_D$ = +29.7 (c 0.3, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.75 (s, 3H), 6.56 (ddd, *J* = 1.6, 4.8, 6.7 Hz, 1H), 6.78 (t, *J*= 7.4 Hz, 1H), 6.87 (dd, *J* = 4.8, 7.9 Hz, 1H), 7.02-7.05 (m, 1H), 7.13-7.16 (m, 1H), 7.21-7.33 (m, 6H), 7.39-7.42 (m, 2H), 7.54 (d, *J* = 6.3 Hz, 2H), 7.63 (d, *J* = 6.3 Hz, 2H), 7.82 (d, *J* = 17.5 Hz, 2H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 55.6, 110.3 (d, *J* = 1.4 Hz), 121.0, 122.9 (q, *J* = 4.1 Hz), 123.0 (2q, *J* = 273.6 Hz), 124.2 (dd, *J* = 7.0, 11.7 Hz), 126.2 (d, *J* = 6.2 Hz), 128.5 (d, *J* = 7.7 Hz), 129.0, 129.7, 130.5, 130.7, 131.8 (qd, *J* = 5.9, 33.5 Hz), 131.9 (qd, *J* = 5.9, 33.5 Hz), 133.2 (dd, *J* = 3.5, 9.8 Hz), 133.3 (dd, *J* = 3.5, 9.8 Hz), 133.8 (d, *J* = 6.3 Hz), 134.2, 134.3, 134.5, 135.1 (dd, *J* = 4.9, 9.4 Hz), 138.7 (dd, *J* = 9.0, 31.7 Hz), 139.6 (t, *J* = 7.9 Hz), 139.8 (t, *J* = 7.9 Hz), 144.9 (dd, *J* = 11.2, 35.8 Hz), 161.0 (d, *J* = 17.7 Hz); ^{31}P NMR (121.5 MHz, $CDCl_3$) δ -14.5 (d, *J* = 162.7 Hz), -23.1 (d, *J* = 162.7 Hz); ^{19}F NMR (470.5 MHz, $CDCl_3$) δ -63.0 (s), -63.1 (s); HRMS (ESI) calcd for $C_{35}H_{22}OF_{12}P_2Na$ $[M+Na]^+$: 771.0847, found 771.0839. The enantiomeric excess (99% ee) was achieved by HPLC analysis on Lux 5µ Cellulose 2, flow 0.5 mL.min^{-1}, using a mixture hexane/2-propanol in 98:2 ratio as eluent: t_R (*S*) = 6.5 min, t_R (*R*) = 7.9 min.

III.9. (*S*)-1-(*o*-Anisylphenylphosphino)-2-(di-cyclohexylphosphino)benzene 12h

This compound was synthesized using the (*S*)-*o*-anisyl-(*o*-bromophenyl)phenylphosphine **10b** and the chloro-dicyclohexylphosphine **14h** (R' = *c*-Hex). The purification was achieved using a mixture of petroleum ether/ethyl acetate in 3:1 ratio as eluent. White solid; Yield = 47% (0.124 g); R_f 0.62 (petroleum ether/ethyl acetate 3:1); $[\alpha]_D$ = +57.1 (c 0.3, $CHCl_3$); IR (neat): 2922, 2847, 1582, 1571, 1471, 1445, 1430, 1241, 1041, 836, 752, 695 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.00-1.20 (m, 10H), 1.48-1.79 (m, 12H), 3.62 (s, 3H), 6.54 (ddd, *J* = 1.5, 3.6, 7.2 Hz, 1H), 6.73-6.85 (m, 3H), 7.09-7.7.27 (m, 9H), 7.43-7.47 (m, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 26.4 (d, *J* = 8.6 Hz), 27.0-27.5 (m), 28.8 (d, *J* = 7.8 Hz), 29.1 (d, *J* = 10.5 Hz), 34.0 (dd, *J* = 5.4, 14.7 Hz), 34.9 (dd, *J* = 4.3, 15.4 Hz), 55.6, 110.1, 120.8, 127.5 (dd, *J* = 9.1, 17.7 Hz), 127.8, 128.0-128.1 (m), 128.6, 129.7, 132.4 (dd, *J* = 2.2, 6.2 Hz), 133.4 (d, *J* = 7.5 Hz), 134.2, 134.3, 134.6, 137.3 (dd, *J* = 3.8, 15.2 Hz), 141.7 (dd, *J* = 17.0, 31.2 Hz), 146.2 (dd, *J* = 8.2, 32.4 Hz), 160.8 (d, *J* = 15.8 Hz); ^{31}P NMR (121.5 MHz, $CDCl_3$) δ -12.2 (d, *J* = 167.8 Hz), -23.2 (d, *J* = 167.8 Hz); Anal calcd for $C_{31}H_{38}P_2O$: C 76.21, H 7.84; found: C 76.51, H 8.13; HRMS (ESI) calcd for $C_{31}H_{38}OP_2Na$ $[M+Na]^+$: 511.2290, found 511.2295. The enantiomeric excess (99% ee) was determined by HPLC analysis on Lux 5µ Cellulose 2, flow 0.5 $mL.min^{-1}$, using a mixture hexane/2-propanol in 98:2 ratio as eluent: t_R (*S*) = 7.6 min, t_R (*R*) = 10.7 min.

III.10. (*S*)-1-(*o*-Anisylphenylphosphino)-2-(di-isopropylphosphino)benzene 12i

This compound was synthesized using the (*S*)-*o*-anisyl-(*o*-bromophenyl)phenylphosphine **10b** and the chloro-(di-*i*-propyl)phosphine **14i**. The purification was achieved using a mixture of petroleum ether/ethyl acetate in 3:1 ratio as eluent. Colorless sticky oil; Yield = 43% (0.095 g); R_f 0.63 (petroleum ether/ethyl acetate 3:1); $[\alpha]_D$ = +85.0 (c 0.5 $CHCl_3$); IR (neat): 2948, 2864, 1572, 1461, 1429, 1271, 1240, 1180, 1104, 1070, 1025, 879, 746 cm^{-1}; ^1H NMR (300 MHz, C_6D_6) δ 0.90 (dd, *J* = 7.2, 12.0 Hz, 3H), 1.12 (dd, *J* = 7.2, 10.8 Hz, 3H), 1.24 (dd, *J* = 7.2, 13.8 Hz, 3H), 1.36 (dd, *J* = 7.2, 14.4 Hz, 3H), 2.12-2.18 (m, 2H), 3.30 (s, 3H), 6.61 (dd, *J* = 4.4, 8.1 Hz, 1H), 6.86 (t, *J* = 7.4 Hz, 1H), 7.06-7.11 (m, 2H), 7.18-7.24 (m, 5H), 7.31-7.33 (m, 1H), 7.46-7.48 (m, 1H), 7.57-7.60 (m, 2H); ^{13}C NMR (75.5 MHz, C_6D_6) δ 19.2 (d, *J* = 9.3 Hz), 19.5 (d, *J* = 12.5 Hz), 20.1 (d, *J* = 18.7), 20.2 (dd, *J* = 1.9, 18.6 Hz), 24.3 (dd, *J* = 5.6, 15.7 Hz), 25.0 (dd, *J* = 4.5, 16.6 Hz), 54.9, 110.1, 121.0, 128.1, 128.2, 128.3, 128.8, 129.7, 132.2 (d, *J* = 2.3 Hz), 132.3 (d, *J* = 2.8 Hz), 133.4 (d, *J* = 7.8 Hz), 134.6, 134.9, 135.0, 138.2 (dd, *J* = 4.9, 14.7 Hz), 142.1 (d, *J* = 19.4 Hz), 142.3 (d, *J* = 18.8 Hz), 147.1 (dd, *J* = 11.2, 32.7 Hz), 161.2 (d, *J* = 15.1 Hz); ^{31}P NMR (121.5 MHz, C_6D_6) δ -3.7 (d, *J* = 165.0 Hz), -20.7 (d, *J* = 165.0 Hz); HRMS (ESI) calcd for $C_{25}H_{30}OP_2Na$ $[M+Na]^+$: 431.1664, found 431.1682. The enantiomeric excess (99% ee) was achieved by HPLC analysis on Lux 5µ Cellulose 2, flow 0.3 $mL.min^{-1}$, using a mixture hexane/2-propanol in 98:2 ratio: t_R (*S*) = 12.8 min, t_R (*R*) = 14.7 min.

III.11. (*R*)-1-(Ferrocenylphenylphosphino)-2-(diphenylphosphino)benzene 12j

This compound was synthesized using the (*R*)-(*o*-bromophenyl)ferrocenylphenylphosphine **10c** and the chlorodiphenylphosphine **14a** (R' = Ph). The purification was achieved using a mixture of toluene/ petroleum ether in 1:1 ratio and by recrystallization in dichloromethane/acetone. Orange solid; Yield = 56% (0.167 g); R_f 0.34 (toluene/petroleum ether 1:1); $[\alpha]_D$ = -55.5 (c 0.2, $CHCl_3$); IR (neat): 3048, 1585, 1567, 1478, 1433, 1307, 1193, 1158, 1106, 1069, 1025, 1000, 888 cm^{-1}; ^1H NMR (300 MHz, C_6D_6) δ 4.04

(br.s, 1H), 4.19 (br.s, 5H), 4.22 (br.s, 1H), 4.26 (br.s, 1H), 4.37 (br.s, 1H), 7.04-7.18 (m, 11H), 7.30-7.34 (m, 3H), 7.54-7.56 (m, 5H); ^{13}C NMR (75.5 MHz, C_6D_6) δ 69.4, 70.6, 71.2 (d, *J* = 5.3 Hz), 72.7 (d, *J* = 5.4 Hz), 73.8 (d, *J* = 24.1 Hz), 77.4 (d, *J* = 11.1 Hz), 128.1, 128.2 (2s), 128.3, 128.5 (d, *J* = 5.8 Hz), 128.8 (d, *J* = 6.3 Hz), 133.6, 133.7, 133.8, 134.2, 134.4 (2s), 134.5, 137.4 (dd, *J* = 4.0, 12.5 Hz), 138.6 (dd, *J* = 7.9, 14.0 Hz), 139.1 (d, *J* = 9.8 Hz), 142.9 (dd, *J* = 12.3, 30.8 Hz), 146.9 (dd, *J* = 13.7, 32.3 Hz); ^{31}P NMR (121.5 MHz, C_6D_6) δ -13.6 (d, *J* = 155.5 Hz), -24.6 (d, *J* = 155.5 Hz); HRMS (ESI) calcd for $C_{34}H_{28}FeP_2Na$ $[M+Na]^+$: 577.0908, found 577.0935. The enantiomeric excess (99% ee) was determined by HPLC analysis on Lux 5µ Cellulose 2, low 1.0 mL.min^{-1}, using a mixture hexane/2-propanol in 98:2 ratio: t_R (*S*) = 5.5 min, t_R (*R*) = 7.9 min.

III.12. (*R*)-1-(Phenyl-*i*-propylphosphino)-2-(diphenylphosphino)benzene 12k

This compound was synthesized using the (*R*)-(*o*-bromophenyl)phenyl(*i*-propyl)phosphine **10d** and the chlorodiphenylphosphine **14**a (R' = Ph). The purification was achieved using a mixture of petroleum ether/toluene in 2:1 ratio and by recrystallization in methanol. White solid; Yield = 54% (0.120 g); R_f 0.39 (petroleum ether/toluene 2:1); $[\alpha]_D$ = +61.7 (c 0.3, $CHCl_3$); IR (neat): 3050, 2962, 2923, 2864, 1477, 1433, 1381, 1363, 1305, 1270, 1229, 1181, 1155, 1091, 1069, 1025, 999, 745, 695, 648 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.07 (ddd, *J* = 2.6, 6.8, 13.6 Hz, 3H), 1.11 (ddd, *J* = 2.9, 6.8, 12.8 Hz, 3H), 2.48-2.55 (m, 1H), 6.94-6.97 (m, 1H), 7.07-7.35 (m, 16H), 7.38 (td, *J* = 1.3, 7.5 Hz, 1H), 7.66-7.68 (m, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 19.5 (dd, *J* = 3.4, 18.4 Hz), 19.7 (dd, *J* = 3.4, 16.2 Hz), 25.9 (dd, *J* = 4.6, 7.1 Hz), 127.9, 128.0, 128.1, 128.2 (2s), 128.3, 128.4, 128.7, 128.9, 131.9 (d, *J* = 5.1 Hz), 133.3 (d, *J* = 3.4 Hz), 133.4 (d, *J* = 3.7 Hz), 133.9 (d, *J* = 6.1 Hz), 134.0 (t, *J* = 4.1 Hz), 134.2 (t, *J* = 4.4 Hz), 136.9 (d, *J* = 9.5 Hz), 137.7 (d, *J* = 11.8 Hz), 138.0 (dd, *J* = 5.3, 10.2 Hz), 143.5 (dd, *J* = 6.5, 22.8 Hz), 144.8 (dd, *J* = 3.9, 25.0 Hz); ^{31}P NMR (121.5 MHz, $CDCl_3$) δ -13.1 (d, *J* = 155.8 Hz), -14.2 (d, *J* = 155.8 Hz); HRMS (ESI) calcd for $C_{27}H_{27}P_2$ $[M+H]^+$: 413.1582, found 413.1586. The enantiomeric excess (98% ee) was determined by HPLC analysis on Lux 5µ Cellulose 2 of the dithiophosphine derivative (obtained by reaction of sulfur with **12k** one night at room temperature under stirring in DCM), flow 0.8 mL.min^{-1}, using a mixture hexane/2-propanol in 80:20 ratio: t_R (*R*) = 16.2 min, t_R (*S*) = 18.2 min.

IV. Synthesis of P(III)-chirogenic 1,2-diphosphinobenzenes 12a,l-q according to route B

IV.1. General procedure:

To a solution of *o*-bromophenyldiphenylphosphine **10** (0.59 mmol) in THF (3 mL) was added at -78 °C under argon *n*-BuLi (1.6 M in hexane) (0.65 mmol) and the resulting solution was stirred at this temperature during one hour. At this time, a solution of P(III)-chirogenic phosphinite **15a-e** (0.59 mmol) in THF (2 mL) was added dropwise at -78 °C and the mixture was stirred at room temperature overnight. After quenching with water, the mixture was extracted with dichloromethane (3 x 5 mL) and the organic phases were dried over $MgSO_4$. The solvent was evaporated under vacuum to give a residue which was purified by chromatographic column on silica gel.

IV.2. (*S*)-1-(Phenyl-*o*-tolylphosphino)-1-(diphenylphosphino)benzene 12l

This compound was synthesized using the (*o*-bromophenyl)diphenylphosphine **10a** and the (*R*)-phenyl-phenyl-*o*-tolylphosphinite **15b**. The purification was achieved using a mixture of petroleum ether/toluene 1:1 ratio as eluent. Colorless sticky solid; Yield = 54% (0.147 g); R_f 0.43 (petroleum ether/toluene 1:1); $[\alpha]_D$ = +33.0 (c 0.3, $CHCl_3$); IR (neat): 3051, 1584, 1477, 1433, 1269, 1068, 998, 739, 693 cm^{-1}; ^1H NMR (300 MHz, C_6D_6) δ 2.45 (d, *J* = 0.8 Hz), 7.00-7.07 (m, 3H), 7.08-7.19 (m, 12H), 7.30-7.32 (m, 1H), 7.36-7.38 (m, 1H), 7.43-7.48 (m, 6H); ^{13}C NMR (75.5 MHz, C_6D_6) δ 21.2 (d, *J* = 22.6 Hz), 126.0, 128.3, 128.4 (m), 128.5, 128.6 (d, *J* = 7.3 Hz), 129.2 (d, *J* = 6.2 Hz), 130.2 (d, *J* = 4.5 Hz), 133.7, 133.8, 134.0, 134.1, 134.2 (d, *J* = 18.7 Hz), 134.3, 134.4, 134.5, 136.7 (dd, *J* = 5.6, 13.3 Hz), 137.0 (dd, *J* = 5.6, 13.3 Hz), 137.7 (dd, *J* = 6.1, 12.8 Hz), 138.0 (dd, *J* = 6.1, 12.8 Hz), 142.4 (d, *J* = 26.2 Hz), 143.8 (dd, *J* = 11.7, 32.9 Hz), 144.4 (dd, *J* = 12.2, 33.2 Hz); ^{31}P NMR (121.5 MHz, C_6D_6) δ -12.7 (d, *J* = 154.0 Hz), -19.8 (d, *J* = 154.0 Hz); HRMS (ESI) calcd for $C_{31}H_{26}P_2Na$ $[M+Na]^+$: 483.1402, found 483.1423. The enantiomeric excess (99% ee) was determined by HPLC analysis on Lux 5µ Cellulose 2, flow 0.2 mL.min^{-1}, using a mixture hexane/2-propanol in 98:2 ratio as eluent: t_R (*S*) = 19.5 min, t_R (*R*) = 20.8 min.

IV.3. (*S*)-1-(Di-(3,5-di-*tert*-butylphenyl)phosphino)-2-(diphenylphosphino)benzene 12m

This compound was synthesized using the (*o*-bromophenyl)diphenylphosphine **10a** and the (*R*)-phenyl-(3,5-di-*tert*-butylphenyl)phenylphosphinite **15c**. The purification was achieved using a mixture of petroleum ether/dichloromethane in 2:1 ratio as eluent. White solid; Yield = 45% (0.148 g); R_f 0.31 (petroleum ether/methylene chloride 2:1); $[\alpha]_D$ = +1.7 (c 0.3 $CHCl_3$); IR (neat): 3051, 2960, 2867, 1583, 1476, 1433, 1361, 1248, 1134, 1092, 999, 874, 742, 694 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.13 (s, 18H), 6.95-7.00 (m, 4H), 7.07-7.19 (m, 17H), 7.23 (t, *J* = 1.8 Hz, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 31.4, 34.8, 122.4, 128.1-128.3 (m), 128.5 (d, *J* = 1.7 Hz), 128.9, 133.7 (d, *J* = 1.6 Hz), 133.8-134.1 (m), 135.5 (dd, *J* = 4.9, 9.0 Hz), 137.3 (dd, *J* = 4.8, 10.6 Hz), 137.5 (dd, *J* = 4.4, 10.2 Hz), 137.8 (dd, *J* = 4.8, 9.9 Hz), 143.6 (dd, *J* = 7.3, 28.3 Hz), 144.6 (dd, *J* = 7.9, 28.3 Hz), 150.4 (d, *J* = 6.2 Hz); ^{31}P NMR (121.5 MHz, $CDCl_3$) δ -12.5 (d, *J* = 158.7 Hz), -14.3 (d, *J* = 158.7 Hz); Anal calcd for $C_{38}H_{40}P_2$: C 81.69, H 7.22; found: C 81.91, H 7.13; HRMS (ESI) calcd for $C_{38}H_{41}P_2$ $[M+H]^+$: 559.2678, found 559.2683. The enantiomeric excess (99% ee) was determined by HPLC analysis on Lux 5µ Cellulose 2, flow 0.2 mL.min^{-1}, using a mixture hexane/2-propanol in 99:1 ratio: t_R (*S*) = 17.3 min, t_R (*R*) = 19.0 min.

IV.4. (*S*)-1-(*o*-Anisylphenylphosphino)-2-(diphenylphosphino)-benzene 12a[12]

This compound was synthesised using the *o*-bromophenyldiphenylphosphine **10a** and the (*R*)-phenyl-(*o*-anisyl)phenylphosphinite **15a**. The purification was achieved using a mixture of petroleum ether/dichloromethane in 3:1 ratio as eluent. Analytical pure sample for X-ray analysis was obtained by recrystallization in dichloromethane/methyl alcohol. White solid; Yield = 65%; R_f 0.18 (petroleum ether/dichloromethane 3:1); $[\alpha]_D$ = +52.6 (c 0.3, $CHCl_3$); IR (neat): 3048, 1581, 1571, 1469, 1431, 1299, 1272, 1240, 1180, 1160, 1129, 1090, 1069, 1022, 793, 743, 719 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 3.57 (s, 3H), 6.56 (ddd, *J* = 1.7, 4.4, 7.4 Hz, 1H), 6.67-6.75 (m, 2H), 6.90-7.00 (m, 2H), 7.04-7.22 (m, 18H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 55.6, 110.2 (d, *J* = 1.5 Hz), 120.8, 125.9 (dd, *J* = 6.7, 13.9 Hz), 128.1, 128.2, 128.3, 129.0, 130.0, 133.6, 133.7, 133.8, 133.9, 134.0, 134.1, 134.2, 134.3, 136.5 (dd, *J* = 4.9, 11.0 Hz),

137.4 (dd, *J* = 5.1, 12.1 Hz), 143.3 (dd, *J* = 10.7, 21.7 Hz), 143.6 (dd, *J* = 9.5, 32.5 Hz), 161.0 (d, *J* = 15.3 Hz); ^{31}P NMR (121.5 MHz, $CDCl_3$) δ -14.0 (d, *J* = 164.8 Hz), -23.6 (d, *J* = 164.8 Hz); HRMS (ESI) calcd for $C_{31}H_{26}OP_2Na$ $[M+Na]^+$: 499.1351, found 499.1375. The enantiomeric excess (99% ee) was determined by HPLC analysis on Lux 5µ cellulose-2, flow 1.0 mL.min^{-1}, using a mixture hexane/2-propanol in 90:10 ratio: t_R (*S*) = 4.2 min, t_R (*R*) = 5.3 min.

IV.5. (*R*)-1-(*o*-Anisylphenylphosphino)-2-(diphenylphosphino)-benzene 12a[12]

This compound was synthesized starting from the *o*-bromophenyldiphenylphosphine **10a** and using the (*S*)-methyl-(*o*-anisyl)phenylphosphinite **15d**. The purification was achieved as procedure described for (*S*)-**12a**. White solid; Yield = 55%; $[\alpha]_D$ = -51.8 (c 0.3, $CHCl_3$). All other analyses were similar to those reported before. The enantiomeric excess (99% ee) was determined by HPLC analysis on lux 5µ cellulose-2, flow 1.0 mL.min^{-1}, using a mixture hexane/2-propanol in 90:10 ratio: t_R (*S*) = 4.2 min, t_R (*R*) = 5.3 min.

IV.6. (*S*)-1-[(*o*-Biphenyl)phenylphosphino]-2-(diphenylphosphino)benzene 12n

This compound was synthesized starting from the *o*-bromophenyldiphenylphosphine **10a** and using the methyl (*R*)-(*o*-biphenyl)phenylphosphinite **15e**. The purification was achieved using a mixture of petroleum ether/ethyl acetate in 6:1 ratio as eluent. White solid; Yield = 33%; R_f 0.54 (petroleum ether/ethyl acetate 6:1); $[\alpha]_D$ = +34.3 (c 0.3, $CHCl_3$); IR (neat): 3052, 1584, 1476, 1433, 1270, 1069, 999, 740, 693 cm^{-1}; ^{1}H NMR (300 MHz, CD_2Cl_2) δ 7.00 (ddd, *J* = 1.1, 3.6, 4.7 Hz, 1H), 7.05-7.08 (m, 3H), 7.11-7.14 (m, 3H), 7.18-7.22 (m, 3H), 7.23-7.34 (m, 17H), 7.39 (td, *J* = 1.2, 7.5 Hz, 1H); ^{13}C NMR (75.5 MHz, CD_2Cl_2) δ 127.0, 127.2, 127.5, 128.2-128.3 (m), 128.6 (d, *J* = 13.4 Hz), 129.1, 129.5 (d, *J*= 3.3 Hz), 130.0 (d, *J* = 5.0 Hz), 133.4 (d, *J* = 5.1 Hz), 133.6 (d, *J* = 5.1 Hz), 134.0 (d, *J* = 7.6 Hz), 134.1, 134.2, 134.6 (d, *J* = 6.0 Hz), 134.9, 135.5 (dd, *J* = 6.3, 14.7 Hz), 137.0 (dd, *J* = 5.5, 13.0 Hz), 137.5-137.7 (m), 141.9 (d, *J* = 6.1 Hz), 142.8 (dd, *J* = 10.8, 31.7 Hz), 145.0 (dd, *J* = 12.0, 33.5 Hz), 147.9 (d, *J* = 28.5 Hz); ^{31}P NMR (121.5 MHz, CD_2Cl_2) δ -14.7 (d, *J* = 155.5 Hz), -18.8 (d, *J* = 155.5 Hz); HRMS (ESI) calcd for $C_{36}H_{28}P_2Na$ $[M+Na]^+$: 545.1558, found 545.1561. The enantiomeric excess (99% ee) was determined by HPLC analysis on lux 5µ cellulose-2, flow 0.5 mL.min^{-1}, using a mixture hexane/2-propanol in 98:2 ratio as eluent: t_R (*S*) 7.8 min, t_R (*R*) 8.6 min.

IV.7. (1*S*,2*S*)-1-(*o*-Anisylphenylphosphino)-2-[(*o*-biphenyl)phenylphosphino]benzene 12o

To a solution of (*S*)-(*o*-anisyl)-(2-bromophenyl)phenylphosphine **10b** (0.22 g, 0.59 mmol) in THF (3 mL) was added at -78 °C under argon *n*-BuLi (1.6 M in hexane; 0.41 mL, 0.65 mmol) and the resulting solution was stirred at this temperature during 1 hour. At this time, a solution of methyl (*R*)-(*o*-biphenyl)phenylphosphinite **15e** (0.21 g, 0.71 mmol) in THF (2 mL) was added dropwise at -78 °C and the mixture was stirred at room temperature overnight. After quenching with water, the mixture was extracted with dichloromethane (3 x 5 mL) and the organic phases were dried over $MgSO_4$. The solvent was evaporated under vacuum to afford a residue which was purified by chromatographic column on silica gel using a mixture of petroleum ether/ethyl acetate in 4:1 ratio as eluent.

White solid; Yield = 35%; R_f 0.49 (petroleum ether/ethyl acetate 4:1); $[\alpha]_D$ = +72.0 (c 0.3 $CHCl_3$); IR (neat): 3051, 2931, 2833, 1575, 1460, 1428, 1271, 1240, 1179, 1160, 1125, 1071, 1023, 743, 695 cm^{-1}; ^1H NMR (300 MHz, C_6D_6) δ 3.12 (s, 3H), 6.43 (dd, *J* = 4.5, 7.8 Hz, 1H), 6.64 (br.t, *J* = 7.3 Hz, 1H), 6.85-7.10 (m, 15H), 7.21-7.30 (m, 8H), 7.45-7.47 (m, 2H); ^{13}C NMR (75.5 MHz, C_6D_6) δ 54.9, 110.2, 120.8, 126.8, 127.1, 128.0-128.2 (m), 128.4, 128.6, 128.8, 129.6, 129.7 (d, *J* = 7.1 Hz), 130.2 (d, *J* = 5.0 Hz), 134.0-134.2 (m), 134.4, 134.6, 134.8, 136.7 (dd, *J* = 6.0, 16.2 Hz), 137.4 (dd, *J* = 6.0, 14.8 Hz), 138.3 (dd, *J* = 7.9, 16.2 Hz), 142.0 (d, *J* = 6.1 Hz), 143.4 (dd, *J* = 12.1, 32.3 Hz), 144.9 (dd, *J* = 14.1, 34.3 Hz), 148.2 (d, *J* = 28.2 Hz), 161.1 (d, *J* = 14.1 Hz); ^{31}P NMR (121.5 MHz, C_6D_6) δ -17.1 (d, *J* = 163.0 Hz), -23.0 (d, *J* = 163.0 Hz); HRMS (ESI) calcd for $C_{37}H_{31}OP_2$ $[M+H]^+$: 553.1845, found 553.1840.

IV.8. (1*S*,2*S*)-1,2-bis(*o*-Anisylphenylphosphino)benzene 12p

To a solution of (*S*)-*o*-anisyl-(2-bromophenyl)phenylphosphine **10b** (0.22 g, 0.59 mmol) in THF (3 mL) was added at -78 °C under argon *n*-BuLi (1.6 M in hexane; 0.41 mL, 0.65 mmol) and the resulting solution was stirred at this temperature during 1 hour. At this time, a solution of (*R*)-phenyl-*o*-anisylphenylphosphinite **15a** (0.18 g, 0.59 mmol) in THF (2 mL) was added dropwise at -78 °C and the mixture was stirred at room temperature overnight. After quenching with water, the mixture was extracted with methylene chloride (3 x 5 mL) and the organic phases were dried over $MgSO_4$. The solvent was evaporated under vacuum to afford a residue which was purified by chromatographic column on silica gel using a mixture of dichloromethane/petroleum ether in 2:1 ratio as eluent and by recrystallization in dichloromethane/methyl alcohol.

White solid; Yield = 52% (0.155 g); R_f 0.39 (methylene chloride/petroleum ether 2:1); $[\alpha]_D$ = +116.2 (c 0.4, $CHCl_3$); IR (neat): 3055, 2937, 2832, 1571, 1469, 1429, 1295, 1270, 1239, 1178, 1157, 1130, 1093, 1069, 1039, 1023, 1012, 792, 745, 730, 690 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 3.57 (s, 6H), 6.69-6.72 (m, 2H), 6.80-6.84 (m, 4H), 6.99-7.02 (m, 2H), 7.24-7.32 (m, 14H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 55.5, 110.2, 120.8, 126.6 (t, *J* = 3.6 Hz), 128.1 (3s), 128.9, 129.8, 133.5 (t, *J* = 3.2 Hz), 133.9, 134.0, 134.1, 134.2, 136.9 (t, *J* = 3.9 Hz), 143.3 (t, *J* = 11.9 Hz), 161.0 (d, *J* = 6.9 Hz); ^{31}P NMR (121.5 MHz, $CDCl_3$) δ -23.4 (s); Anal calcd for $C_{32}H_{28}P_2O_2$: C 75.88, H 5.57; found: C 75.83, H 5.60; HRMS (ESI) calcd for $C_{32}H_{29}O_2P_2$ $[M+H]^+$: 507.1637, found 507.1637. The enantiomeric excess (99% ee) was determined by ^{31}P NMR using the (+)-di-μ-chlorobis{2[1-(dimethylamino)ethyl]phenyl-C,N}dipalladium as chiral reagent.[5]

IV.9. (1*R*,2*S*)-1-(Phenyl-*i*-propylphosphino)-2-[(*o*-biphenyl)phenylphosphino]benzene 12q

To a solution of (*R*)-isopropyl-(2-bromophenyl)-phenylphosphine **10d** (0.18 g, 0.59 mmol) in THF (3 mL) was added at -78 °C under argon *n*-BuLi (1.6 M in hexane, 0.41 mL, 0.65 mmol) and the resulting solution was stirred at this temperature during 1 hour. A solution of (*R*)-phenyl-*o*-anisylphenylphosphinite **15a** (0.18 g, 0.59 mmol) in THF (2 mL) was then added dropwise at -78 °C and the mixture was stirred at room temperature overnight. After quenching with water, the mixture was extracted with dichloromethane (3 x 5 mL) and the organic phases were dried over $MgSO_4$. The solvent was evaporated under vacuum to afford a residue which was purified by chromatographic column on silica gel using a mixture of dichloromethane/petroleum ether in 2:1 ratio as eluent.

White sticky solid; Yield = 56% (0.146 g); R_f 0.44 (petroleum ether/methylene chloride 1:2); $[\alpha]_D$ = +85.0 (c 0.2 $CHCl_3$); IR (neat): 2954, 1575, 1461, 1429, 1271, 1239, 1179, 1129, 1070, 1023, 745, 695 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 6.81 (td, *J* = 6.8, 15.4 Hz, 6H), 2.47-2.57 (m, 1H), 3.61 (s, 3H), 6.47 (ddd, *J* = 1.5, 3.8, 7.2 Hz, 1H), 6.65 (t, *J* = 7.4 Hz, 1H), 6.79 (ddd, *J* = 0.7, 4.7, 8.2 Hz, 1H), 6.89-6.92 (m, 1H), 7.14-7.24 (m, 5H), 7.30-7.39 (m, 8H), 7.61-7.64 (m, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 19.5, 19.7, 25.6 (dd, *J* = 8.1, 10.7 Hz), 55.6, 110.1 (d, *J* = 1.4 Hz), 120.7, 126.0 (dd, *J* = 5.2, 13.7 Hz), 127.8 (d, *J* = 7.2 Hz), 128.0, 128.2 (2s), 128.8 (d, *J* = 17.2 Hz), 129.8, 131.7 (d, *J* = 6.4 Hz), 133.3 (d, *J* = 19.2 Hz), 134.0, 134.0 (d, *J* = 7.2 Hz), 134.2, 134.4, 137.3 (dd, *J* = 7.3, 13.8 Hz), 138.3 (d, *J*= 2.9 Hz), 143.8 (dd, *J* = 13.9, 31.6 Hz), 144.9 (d, *J* = 10.1 Hz), 160.9 (d, *J* = 13.5 Hz); ^{31}P NMR (121.5 MHz, $CDCl_3$) δ -13.5 (d, *J* = 163.2 Hz), -24.6 (d, *J* = 163.2 Hz); HRMS (ESI) calcd for $C_{28}H_{29}OP_2[M+H]^+$: 443.1688, found 443.1667. The enantiomeric excess (99% ee) was determined by HPLC analysis on Chiralpak AD, flow 0.2 $mL.min^{-1}$, using a mixture hexane/2-propanol in 98:2 ratio as eluent: t_R (*RS*) = 24.5 min, t_R (S*S*) = 27.5 min.

V. Comparative study of the ligands in asymmetric reactions by metal-based complexes

V.1. Typical procedure for the asymmetric hydrogenation

A solution of [Rh(COD)(DP*B **12**)]BF_4 (0.005 mmol, 1%) and substrate **18** (or **20**) (0.5 mmol) in dry solvent (7.5 mL) was introduced in a stainless steel autoclave. The autoclave was closed, purged with hydrogen and then pressurized with hydrogen. After 16h of stirring at room temperature, the pressure was released to atmospheric pressure and the solution was transferred to a round bottom flask. The solvent was removed on a rotary evaporator to give a residue, which was purified by column chromatography on silica gel to afford the hydrogenated product. The enantiomeric excess was determined by HPLC on chiral column.

Methyl 2-acetamido-3-phenylpropionate **19.** ^1H NMR (300 MHz, $CDCl_3$): δ 7.20 (m, 5H, C*H* $_{arom}$), 6.11 (br s, 1H, N*H*$COCH_3$), 4.87(m, 1H, C*H*CO_2CH_3), 3.64 (s, 3H, CO_2C*H*$_3$), 3.07 (m, 2H, C*H*$_2$Ph), 1.97 (s, 3H, COC*H*$_3$). The enantiomeric excess was determined by HPLC analysis on Chiralcel OD-H, flow 1 $mL.min^{-1}$, hexane/2-propanol 95:5 ratio, λ = 254 nm: t_R *(R)* = 21.4 min, t_R *(S)* = 34.7 min.

Dimethyl 2-methylsuccinate **21**. ^1H NMR (300 MHz, $CDCl_3$): δ 3.62 (s, 3H, CO_2C*H*$_3$), 3.60 (s, 3H, CO_2C*H*$_3$), 2.85 (m, 1H, C*H*$_2CO_2CH_3$), 2.66 (dd, 1H, *J*= 16.5, 8.1 Hz, C*H*$_2CO_2CH_3$), 2.31 (dd, 1H, *J*= 16.5, 3 Hz, C*H*$_2CO_2CH_3$), 1.14 (d, 3H, *J*= 7.1 Hz, CHC*H*$_3$). The enantiomeric excess was determined by HPLC analysis on Chiralcel OD-H, flow 1 $mL.min^{-1}$, hexane/2-propanol 95:5 ratio, λ = 205 and 230 nm: t_R *(R)* = 6.4 min, t_R *(S)* = 11 min.

V.2. Typical procedure for allylic alkylation of dimethyl malonate:

To a Schlenk tube containing the DP*B ligand **12** (0.02 mmol), [Pd(C_3H_5)Cl_2] (0.01 mmol) and substrate **22** (0.5 mmol) was added toluene or CH_2Cl_2 (4 mL). The mixture was stirred 30 min at room temperature. Dimethylmalonate (0.12 mL, 1.0 mmol) followed by *N*,*O*-bis(trimethylsilyl)acetamide (0.24 mL, 1.0 mmol) and a pitch of potassium acetate, were added. After 1 h, the reaction was diluted with diethyl ether

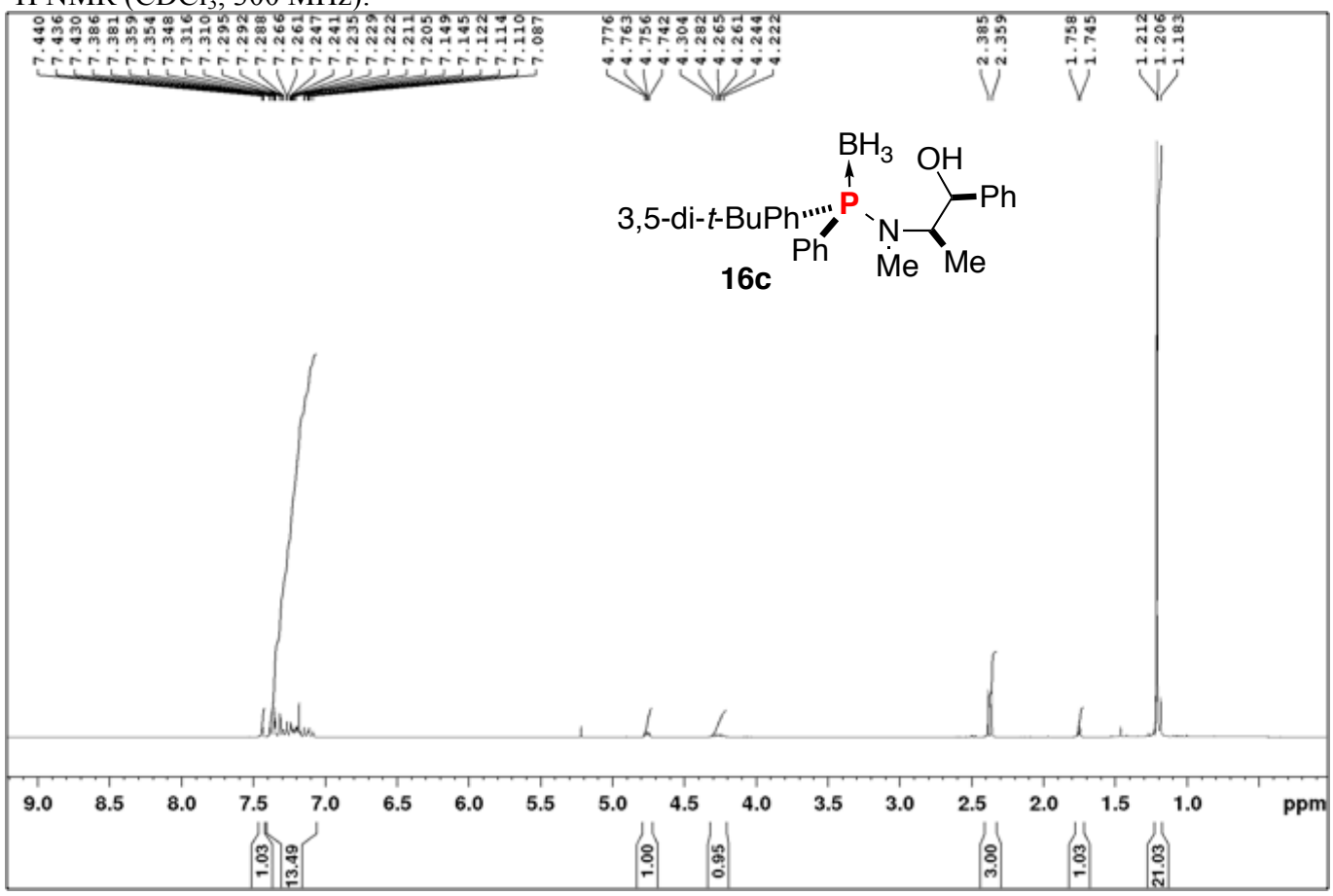
and washed with saturated NH_4Cl solution. The organic phase was dried over $MgSO_4$, filtered and concentrated in vacuo to give a residue which was purified by chromatography on silica gel using a mixture petroleum ether/ethyl acetate 5:1 as eluent.

(E)-Methyl-2-methoxycarbonyl-3,5-diphenylpent-4-enoate **23**. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.56 (s, 3H), 3.75 (s, 3H), 4.02 (d, J = 10.9 Hz, 1H), 4.27 (dd, J = 8.8, 10.8 Hz, 1H), 6.40 (dd, J = 8.6, 15.7 Hz, 1H), 6.54 (d, J = 15.7 Hz, 1H), 7.10-7.40 (m, 10H). The enantiomeric excess was determined by HPLC analysis on Chiralpak IA, flow 1.0 mL.min^{-1}, hexane/2-propanol 90:10 ratio, λ = 254 nm, t_R (*R*) = 8.6 min, t_R (*S*) = 10.4 min.

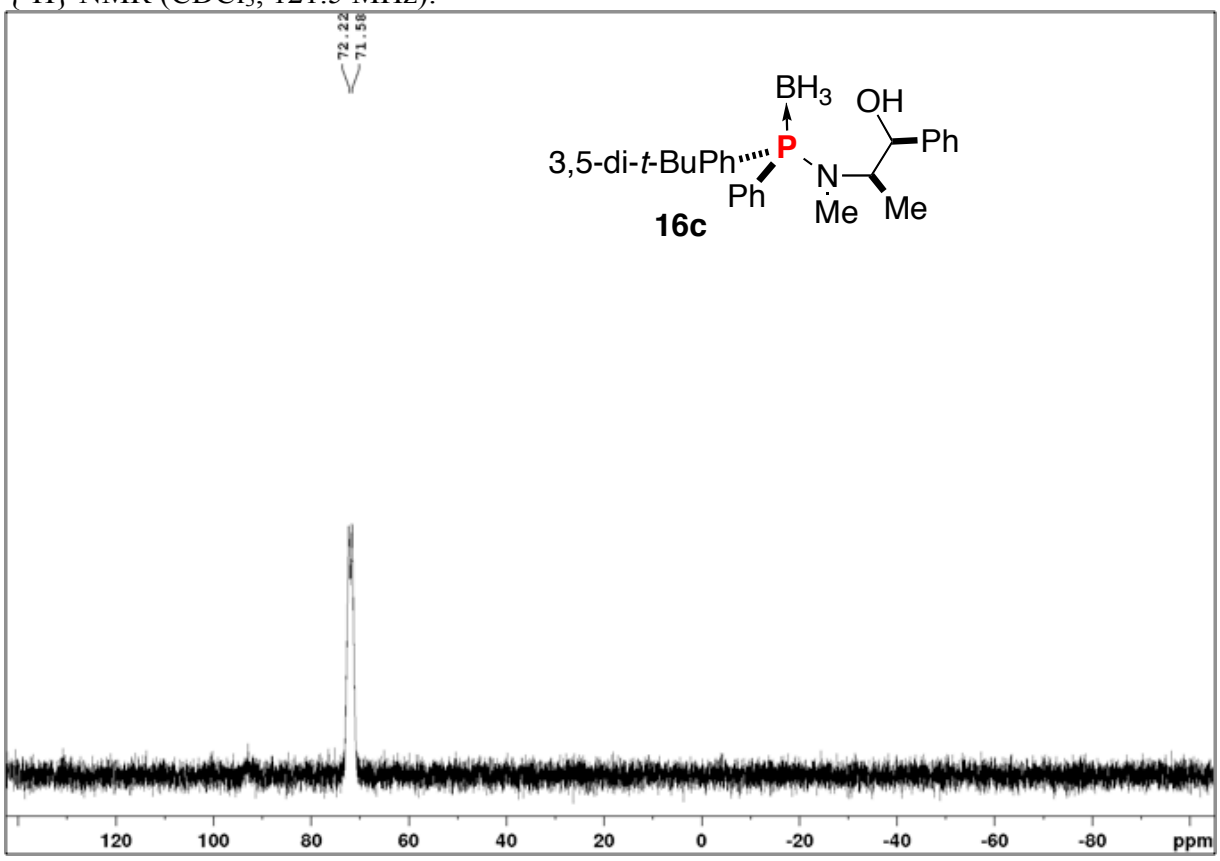
VI. ^{1}H, ^{13}C, ^{31}P and ^{19}F NMR spectra

(R_p)-*N*-methyl-*N*-[(1*S*,2*R*)(1-hydroxy-2-methyl-1-phenyl-2-propyl)]amino-(3,5-di-*tert*-butylphenyl)phenyl phosphine-borane **16c**

^{1}H NMR ($CDCl_3$, 300 MHz):

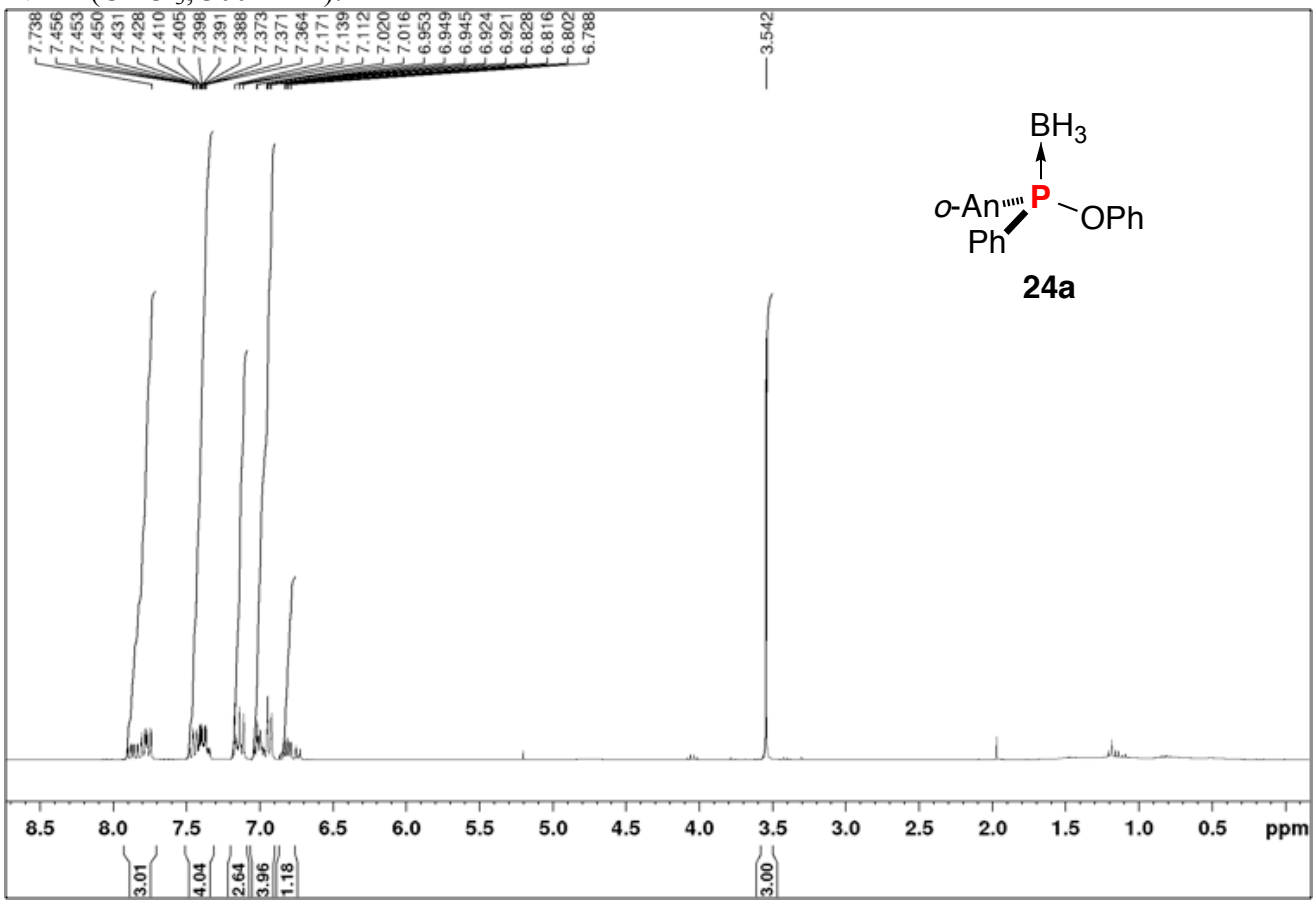


$^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 121.5 MHz):

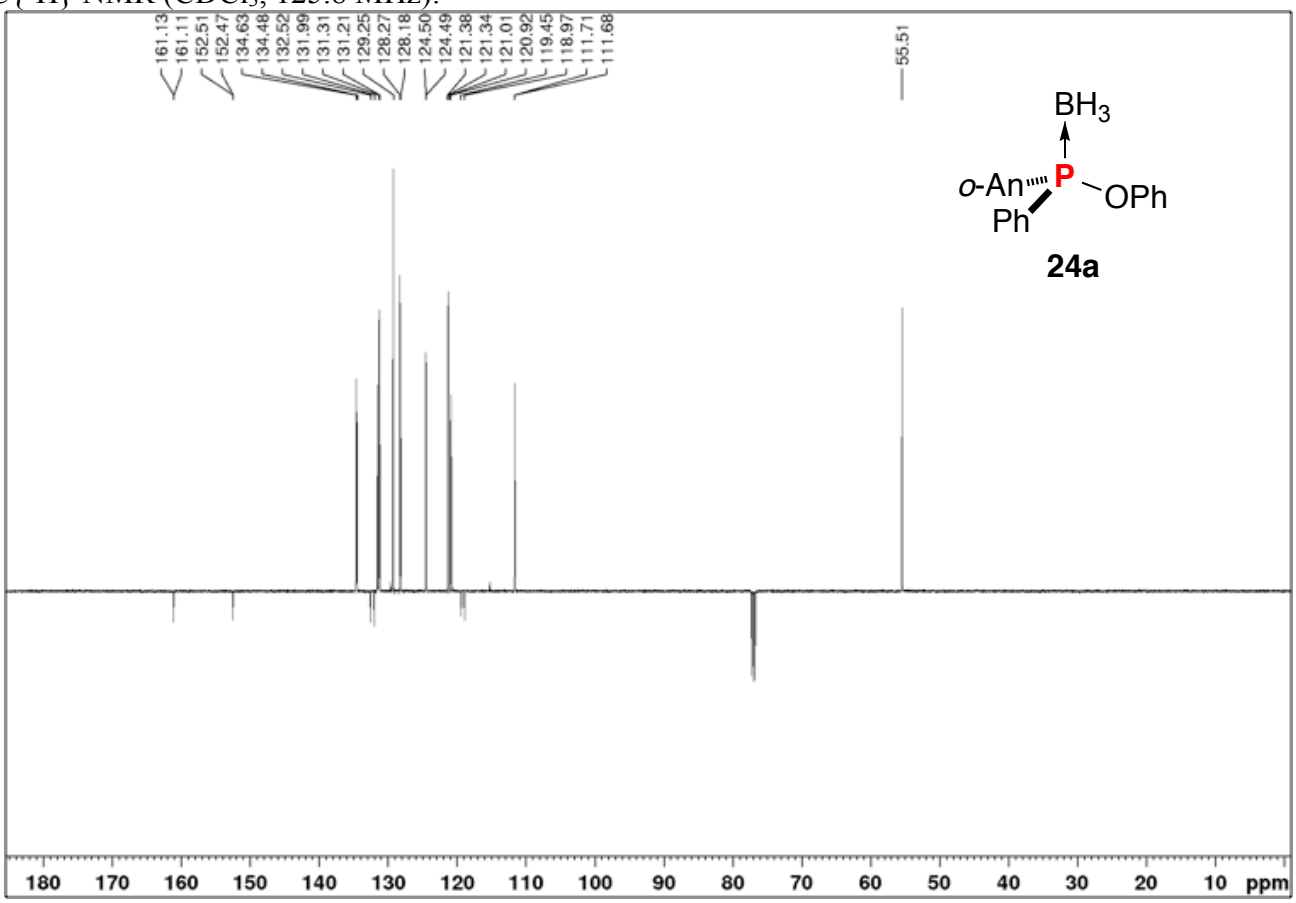


(*R*)-Phenyl-*o*-anisylphenylphosphinite-borane **24a**

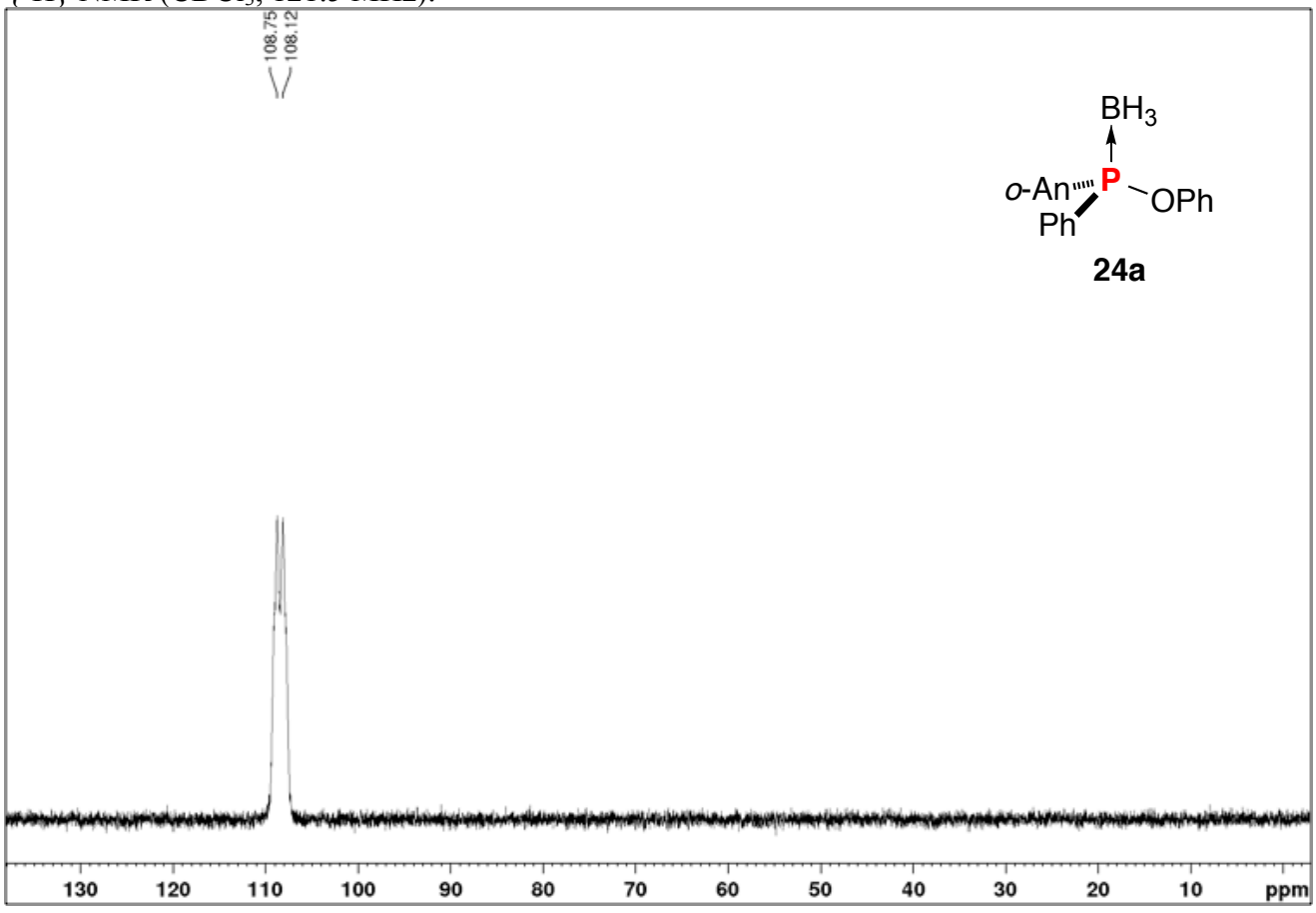
^{1}H NMR ($CDCl_3$, 300 MHz):



$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125.8 MHz):

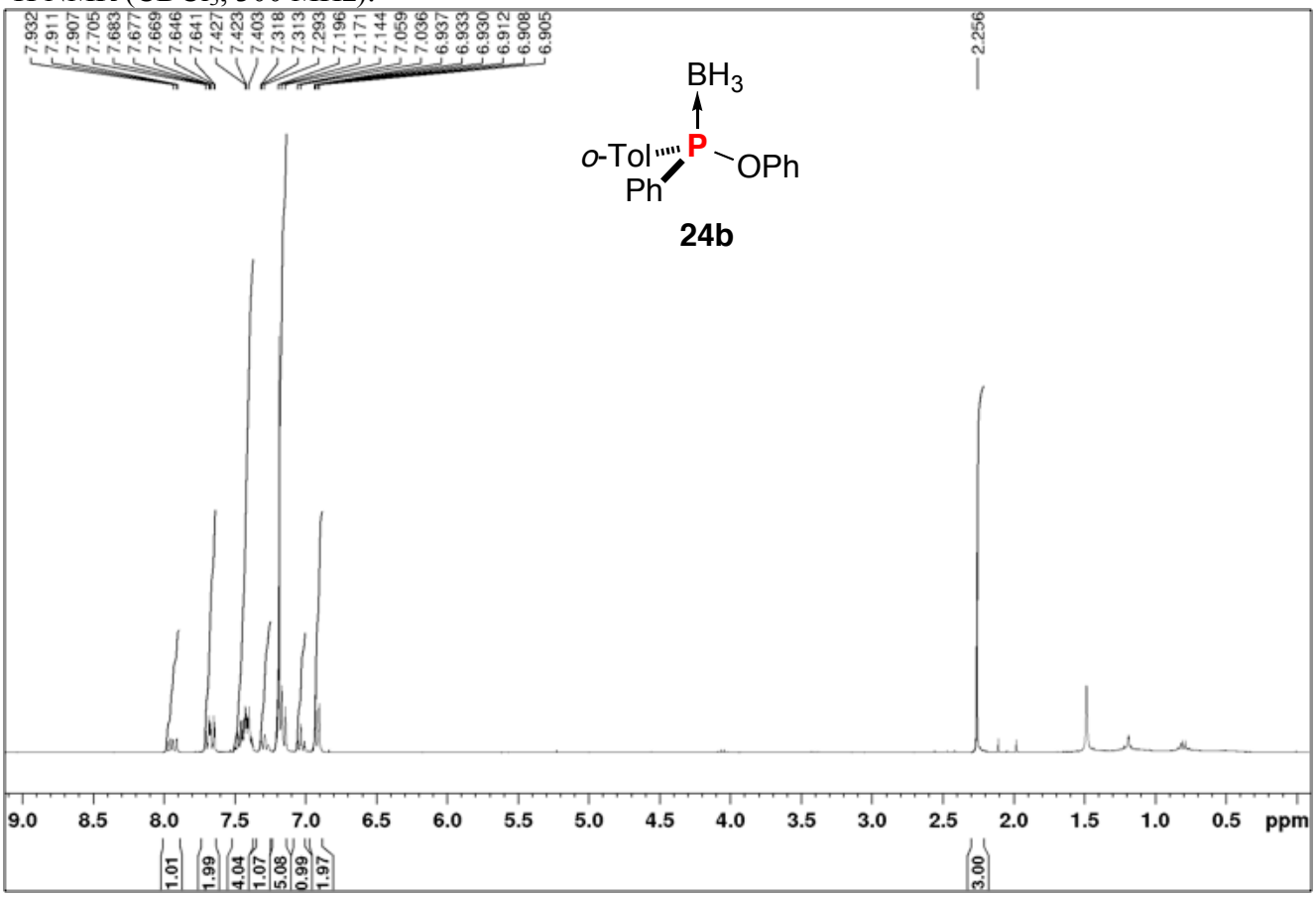


$^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 121.5 MHz):

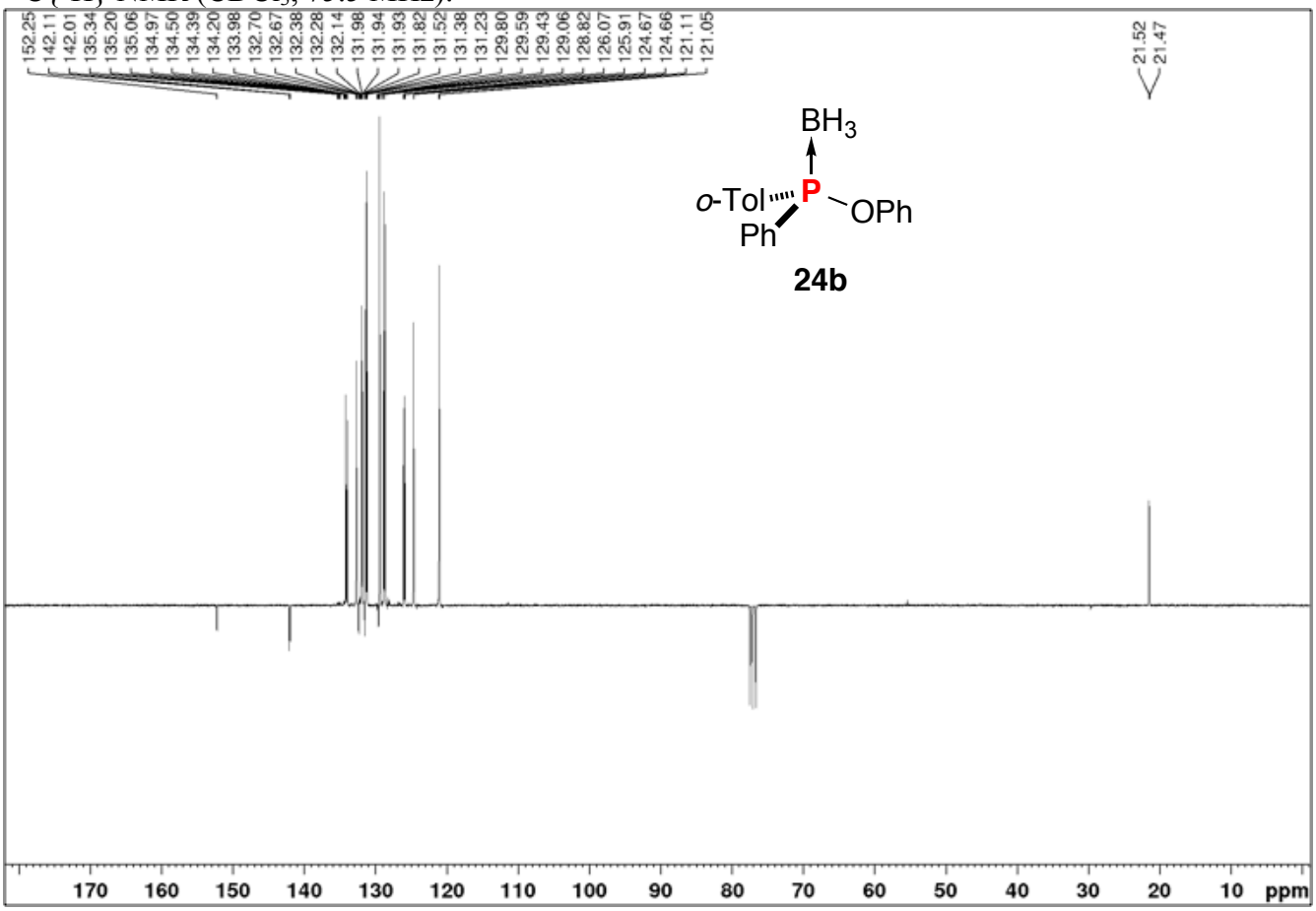


(*R*)-Phenyl-phenyl-*o*-tolylphosphinite-borane **24b**

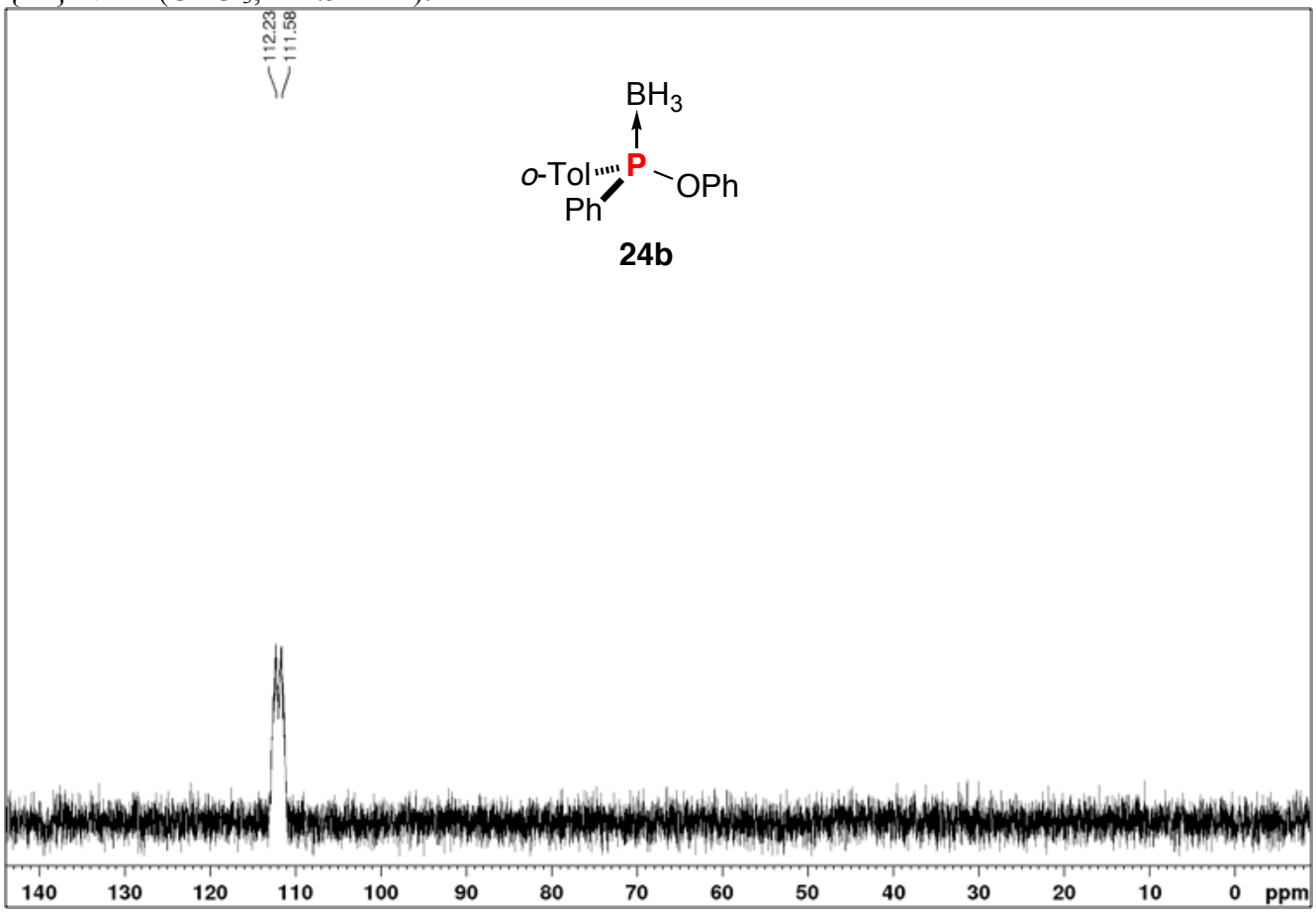
^{1}H NMR ($CDCl_3$, 300 MHz):



^{13}C{^{1}H} NMR ($CDCl_3$, 75.5 MHz):

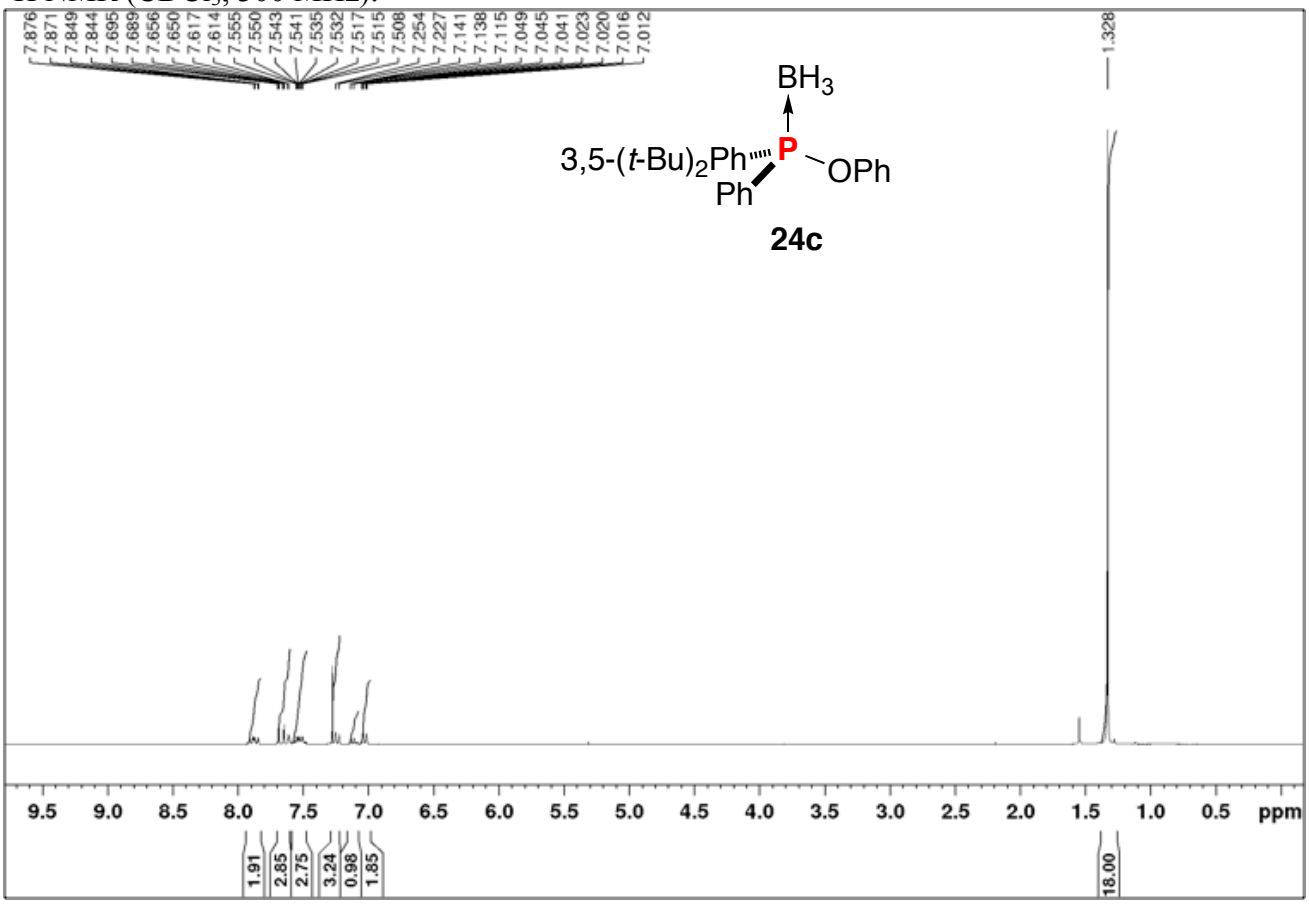


$^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 121.5 MHz):

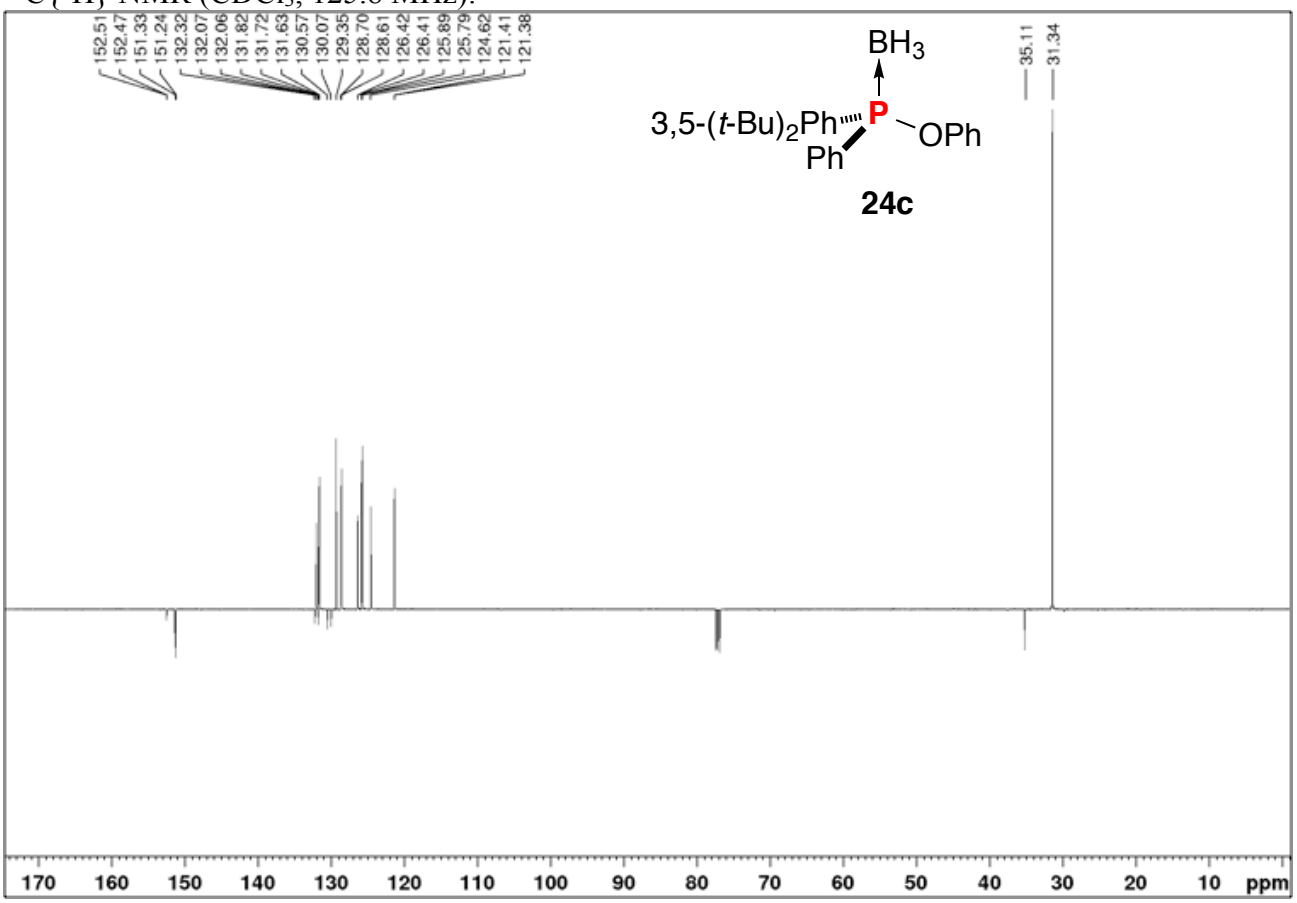


(*R*)-Phenyl-(3,5-di-*tert*-butylphenyl)phenylphosphinite-borane **24c**

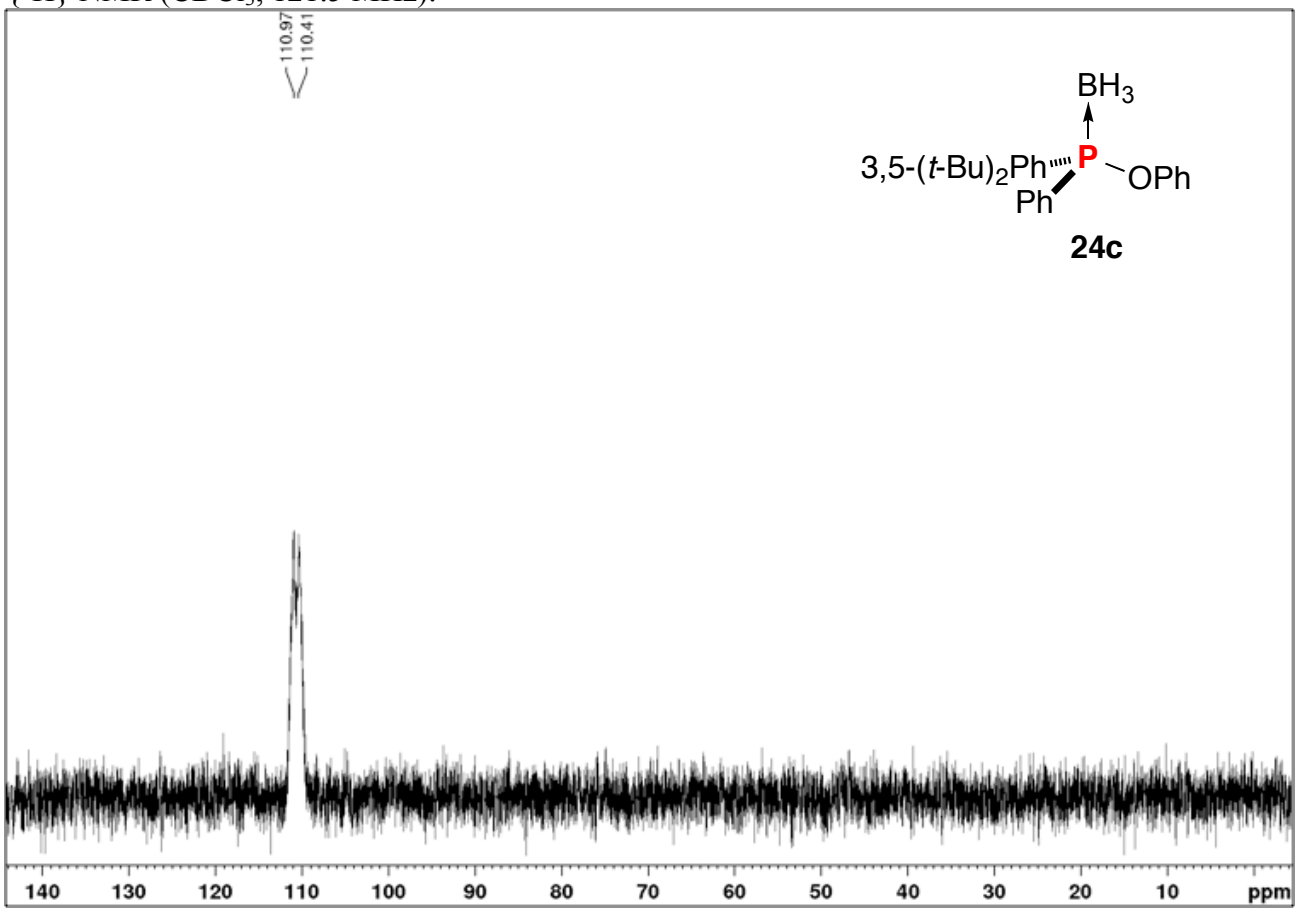
^{1}H NMR ($CDCl_3$, 300 MHz):



$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125.8 MHz):

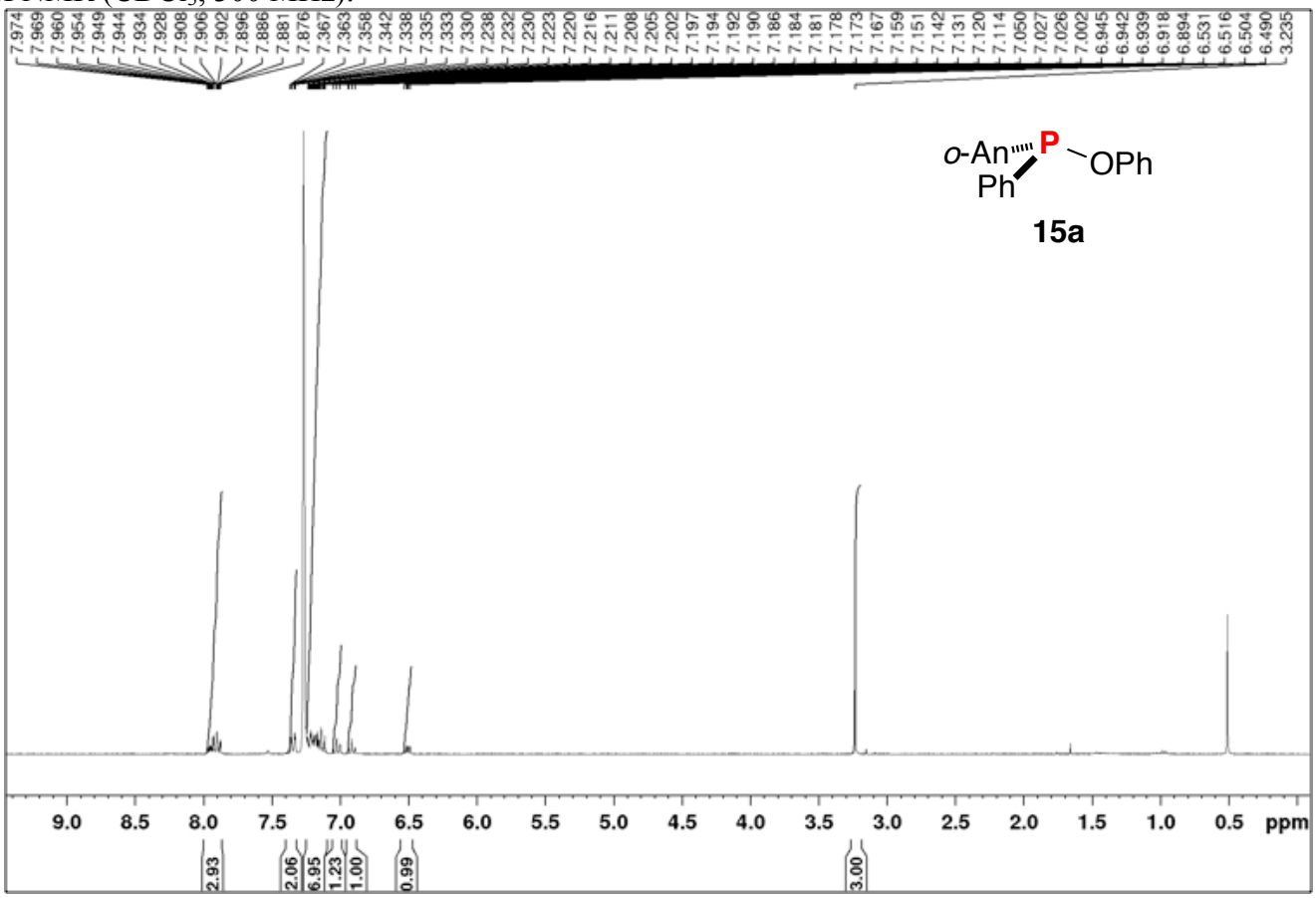


$^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 121.5 MHz):

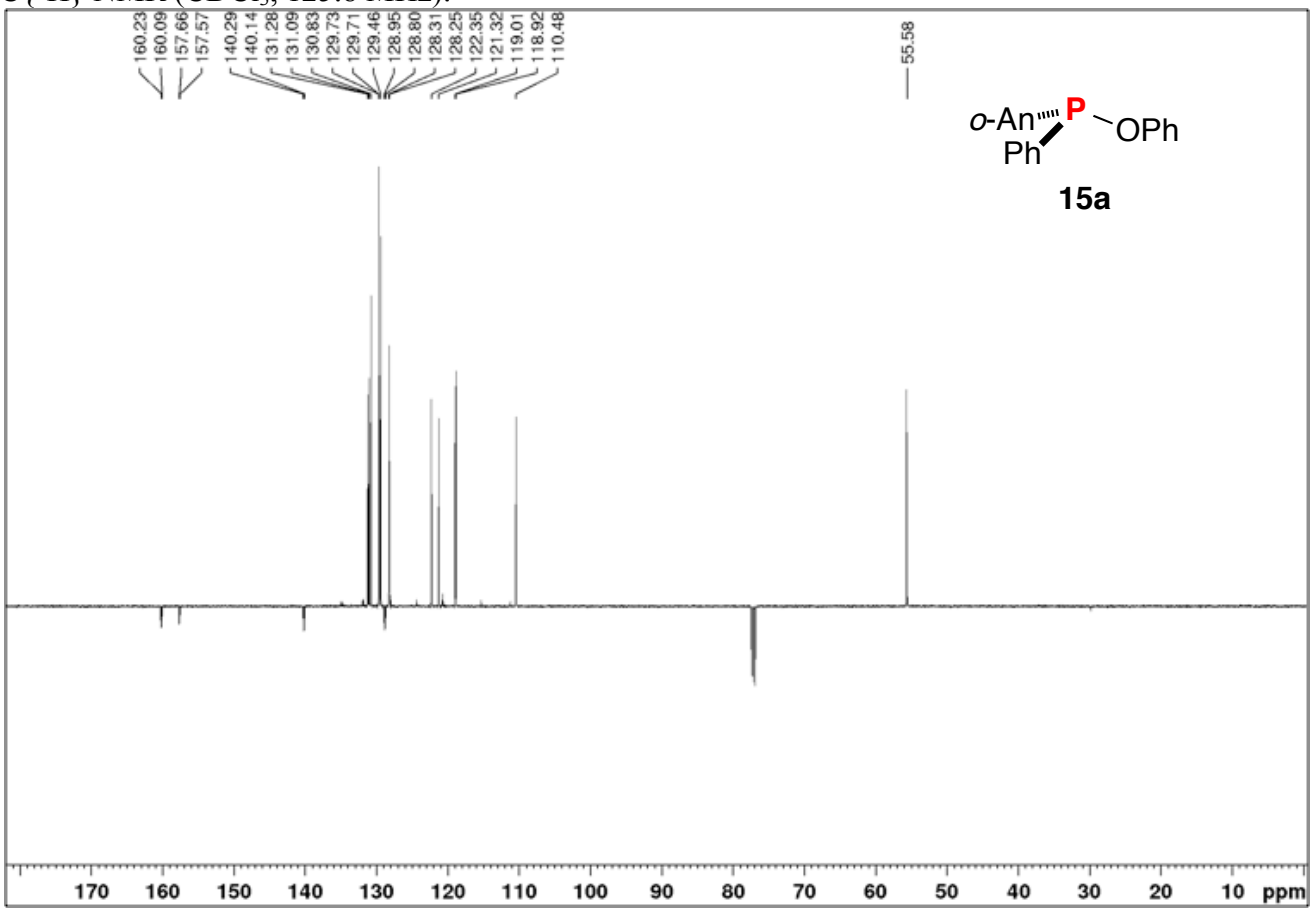


(*R*)-Phenyl-*o*-anisylphenylphosphinite **15a**

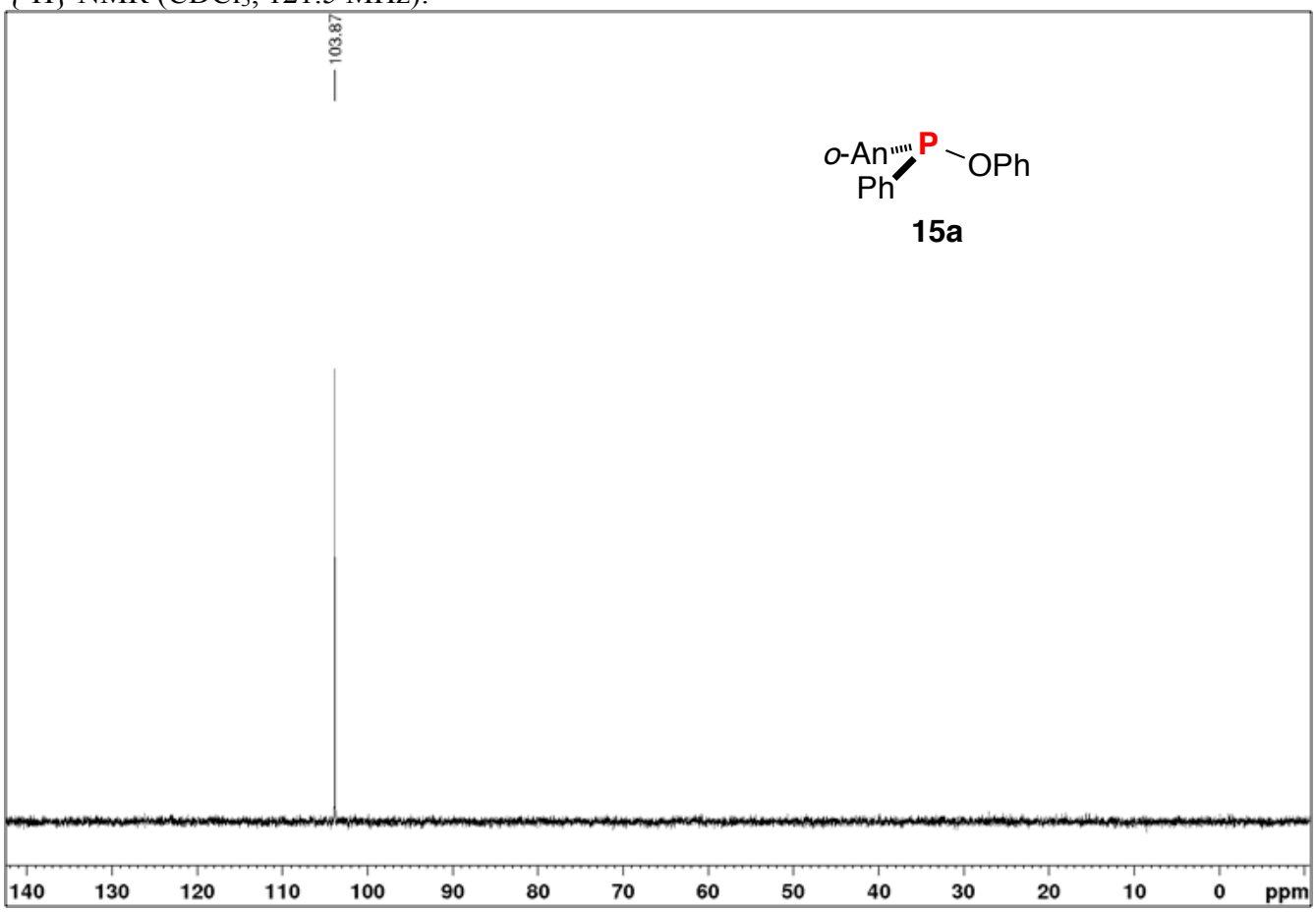
^{1}H NMR ($CDCl_3$, 300 MHz):



^{13}C{^{1}H} NMR ($CDCl_3$, 125.8 MHz):

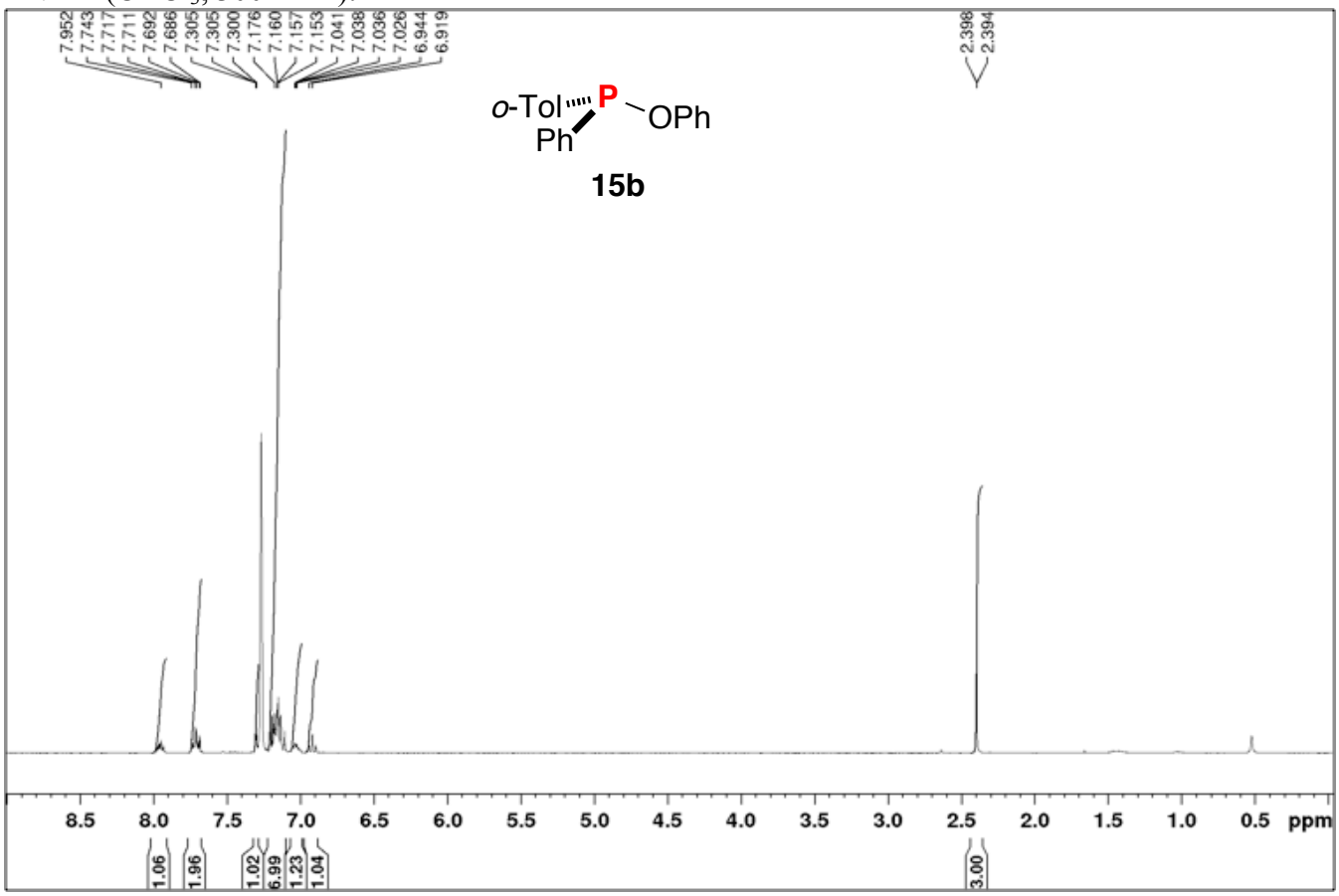


$^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 121.5 MHz):

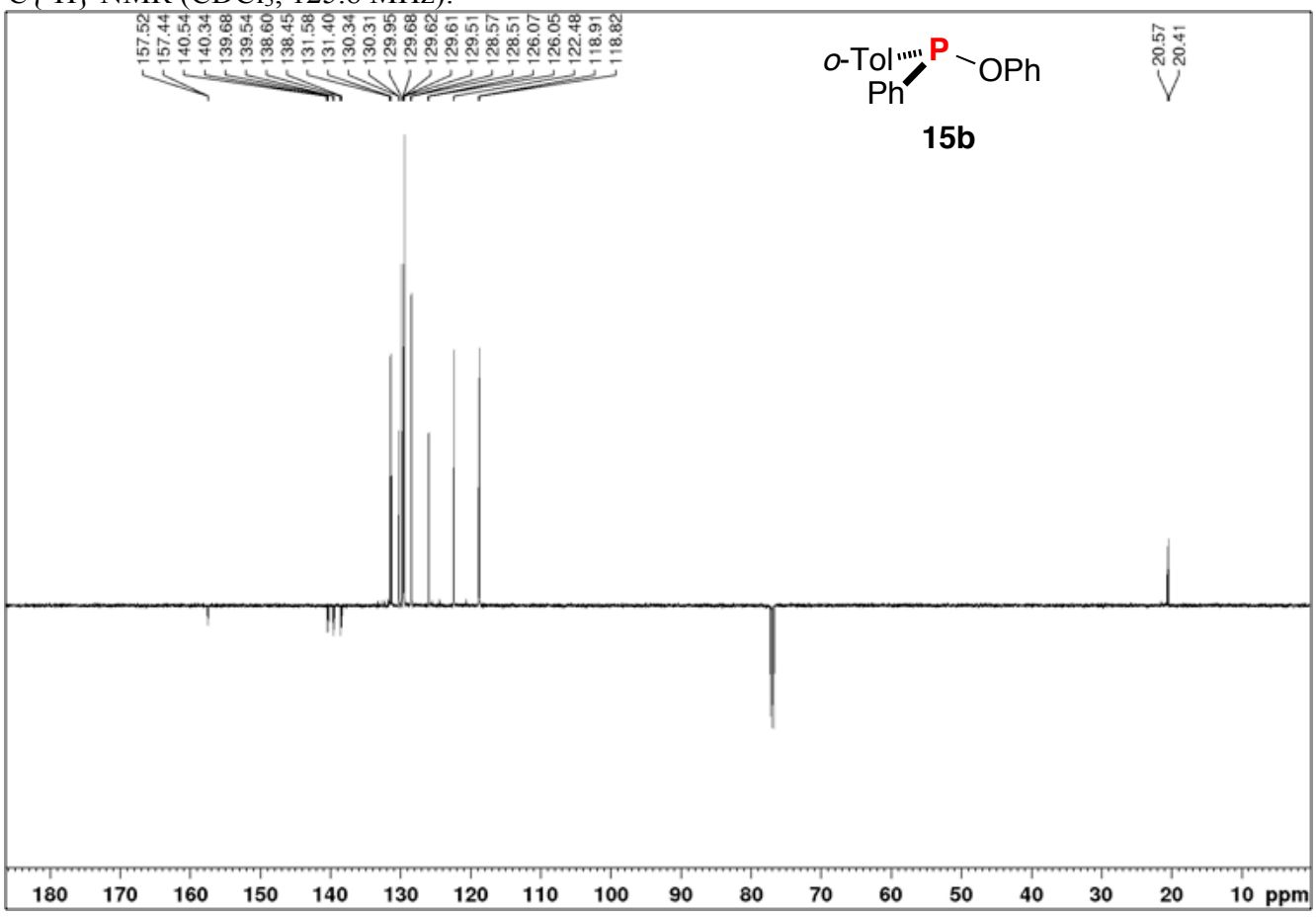


(*R*)-Phenyl-phenyl-*o*-tolylphosphinite **15b**

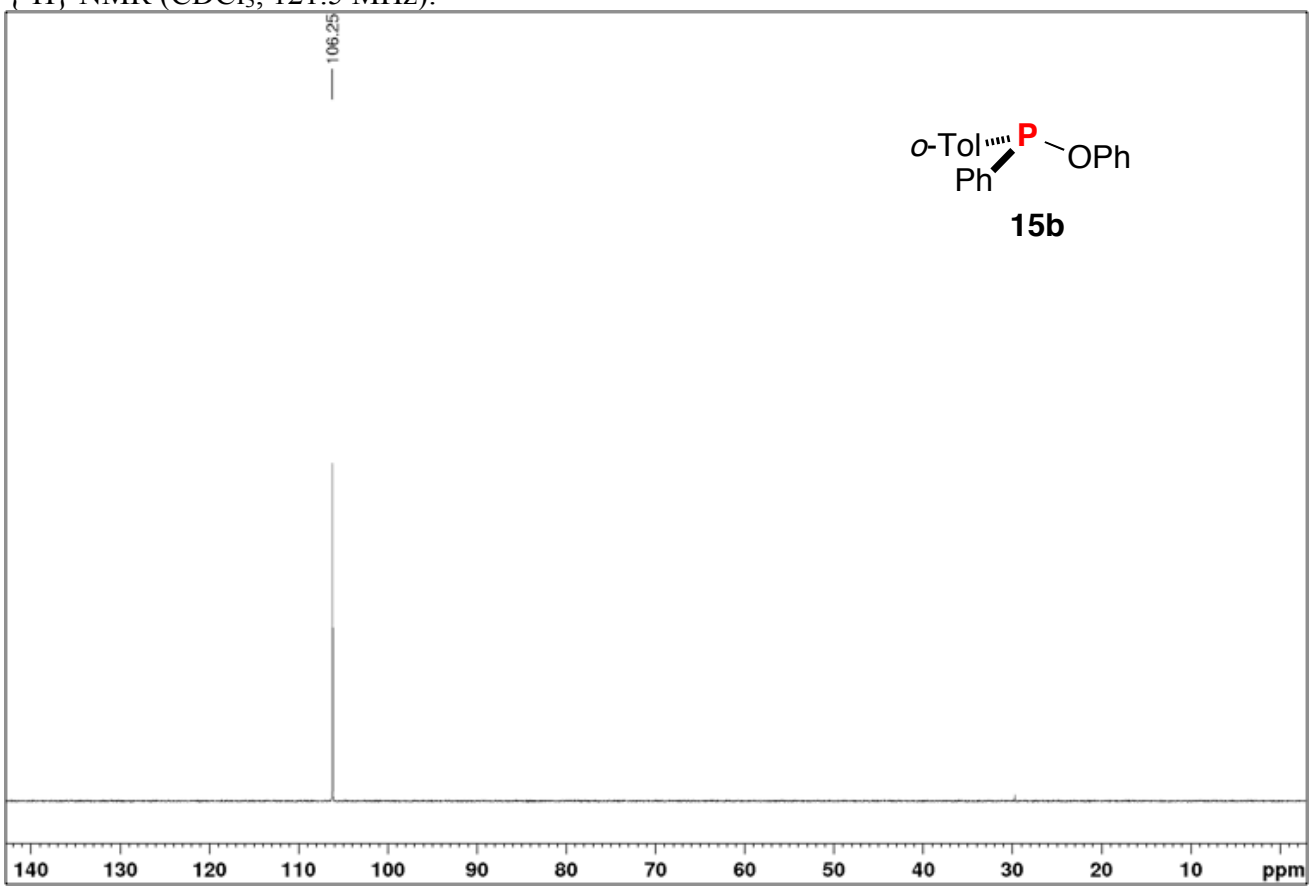
^{1}H NMR ($CDCl_3$, 300 MHz):



$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125.8 MHz):

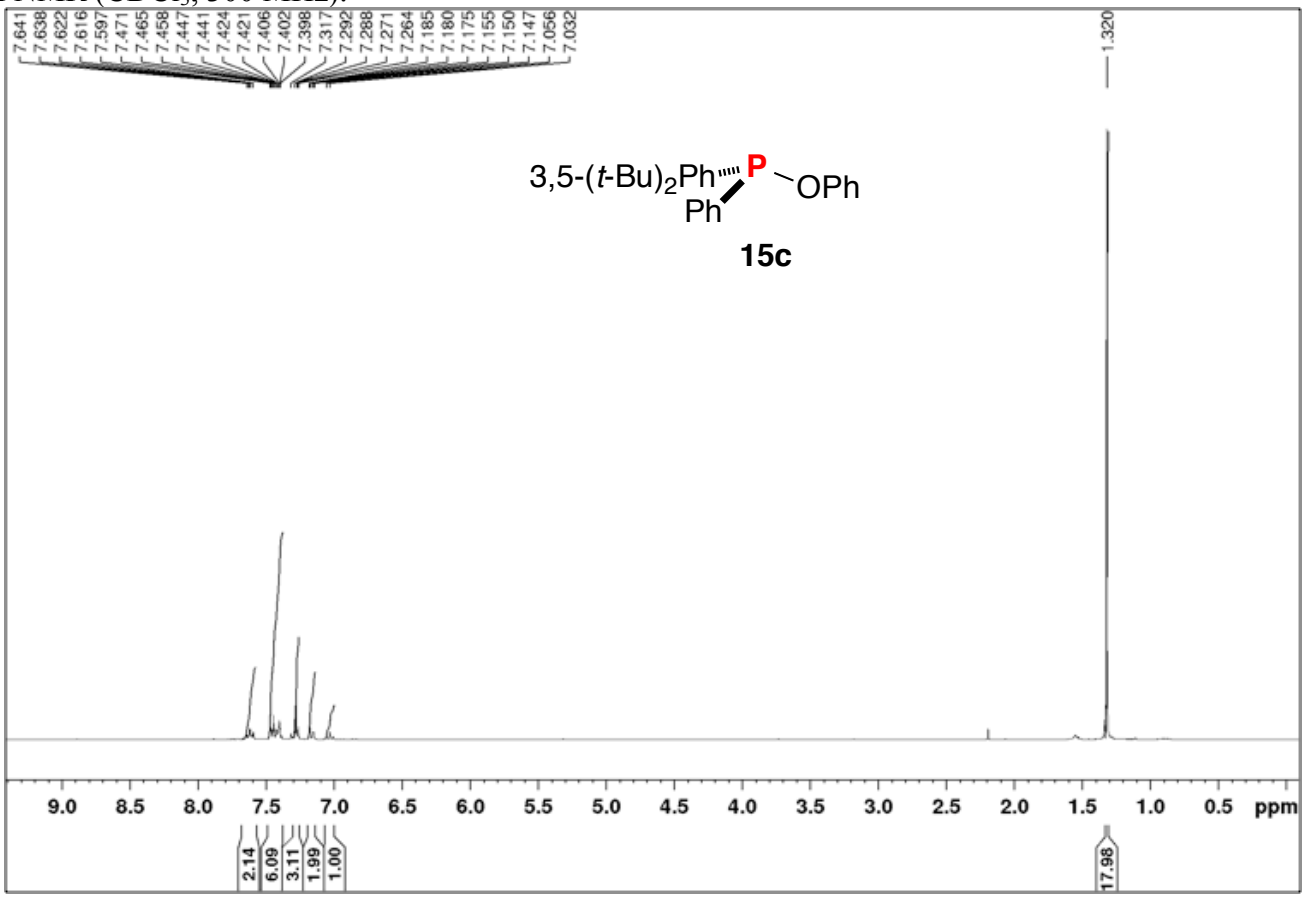


$^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 121.5 MHz):

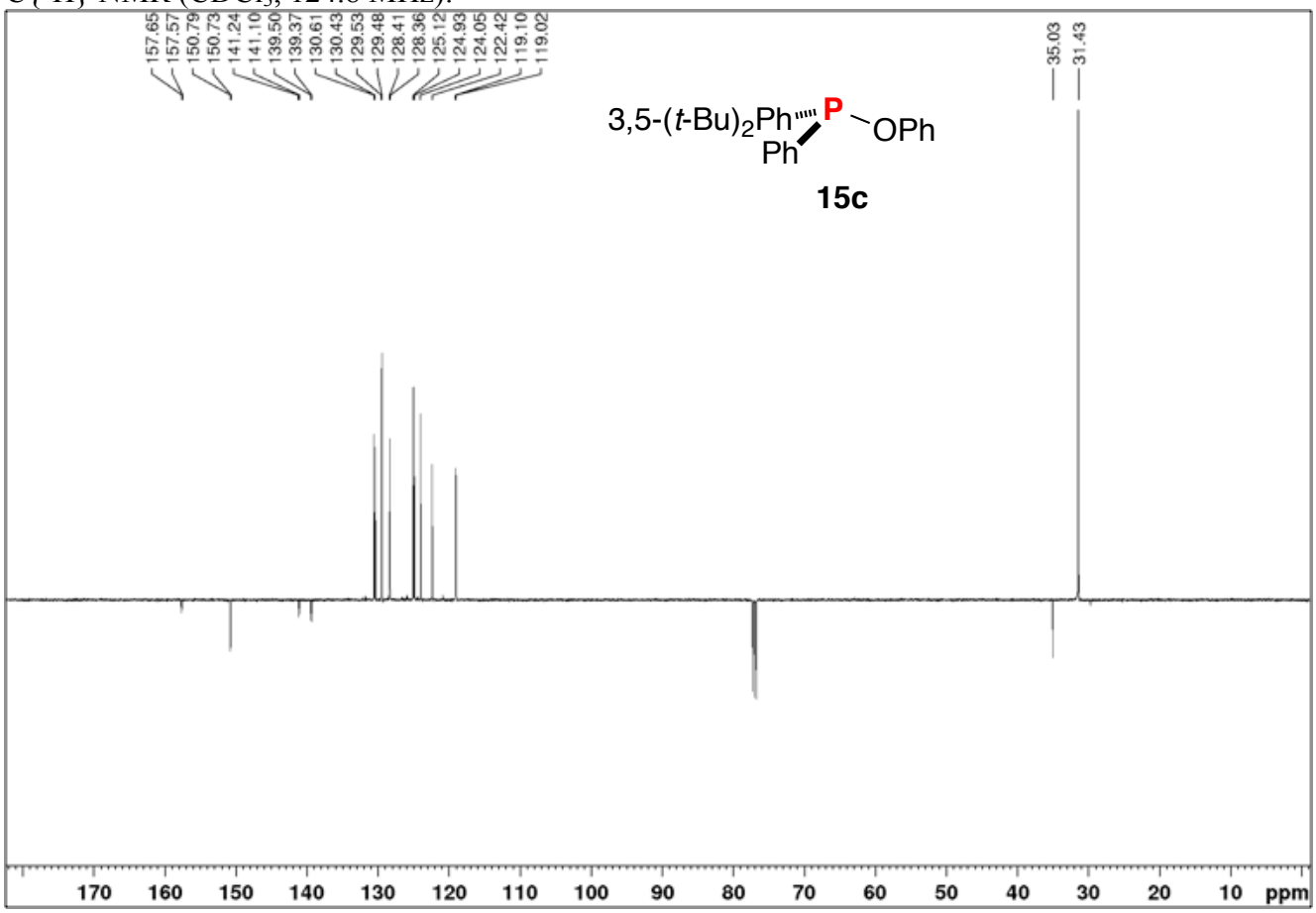


(*R*)-Phenyl-(3,5-di-*tert*-butylphenyl)phenylphosphinite **15c**

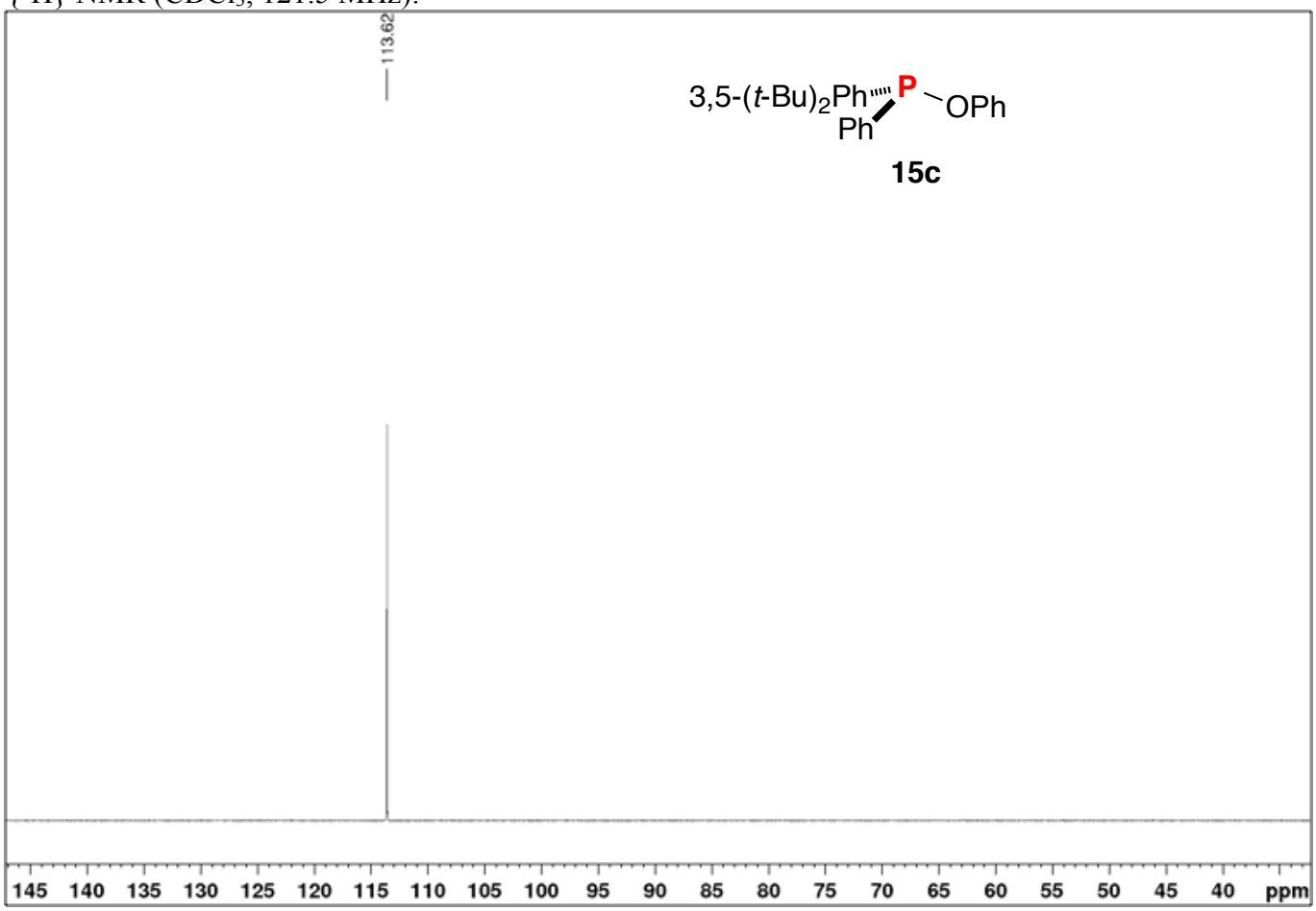
^{1}H NMR ($CDCl_3$, 300 MHz):



^{13}C{^{1}H} NMR ($CDCl_3$, 124.8 MHz):

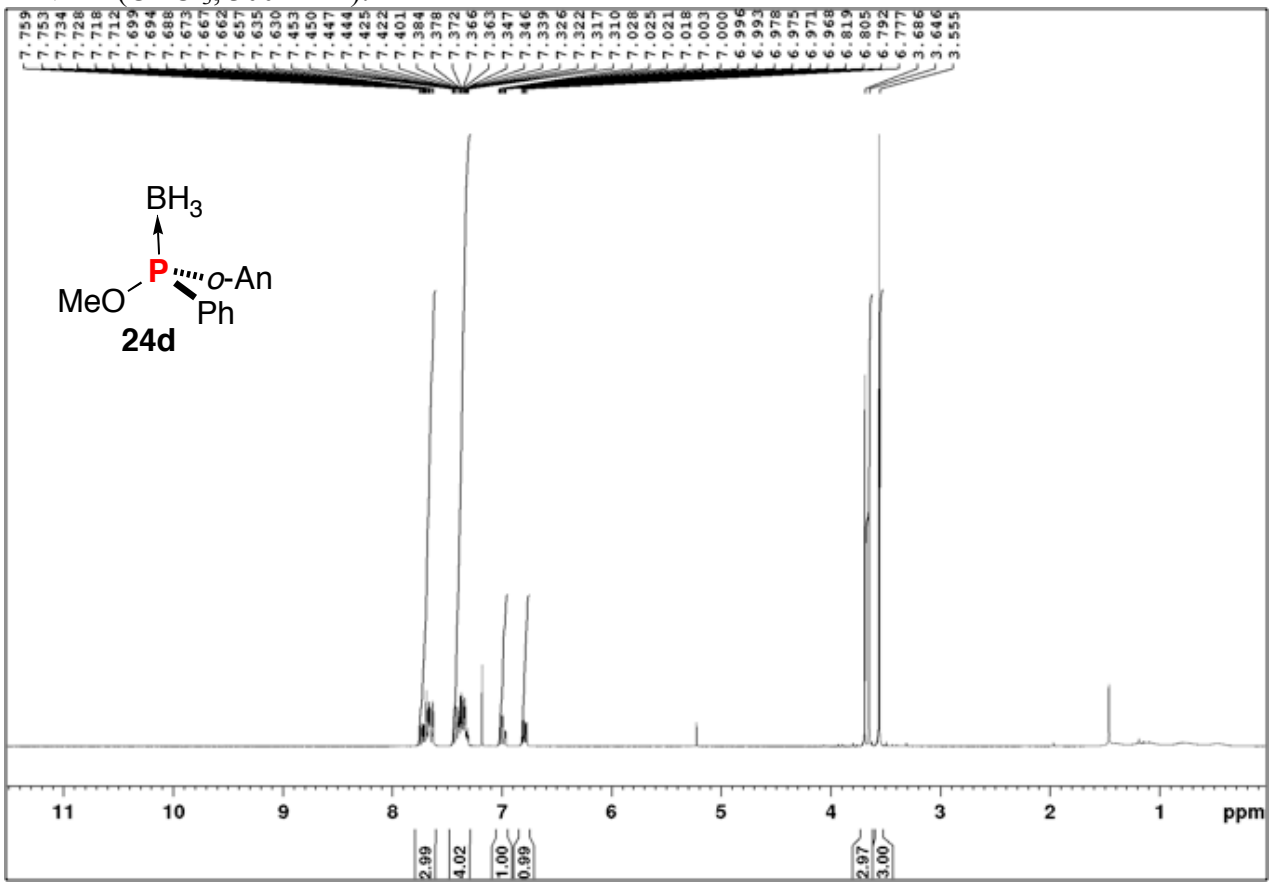


$^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 121.5 MHz):

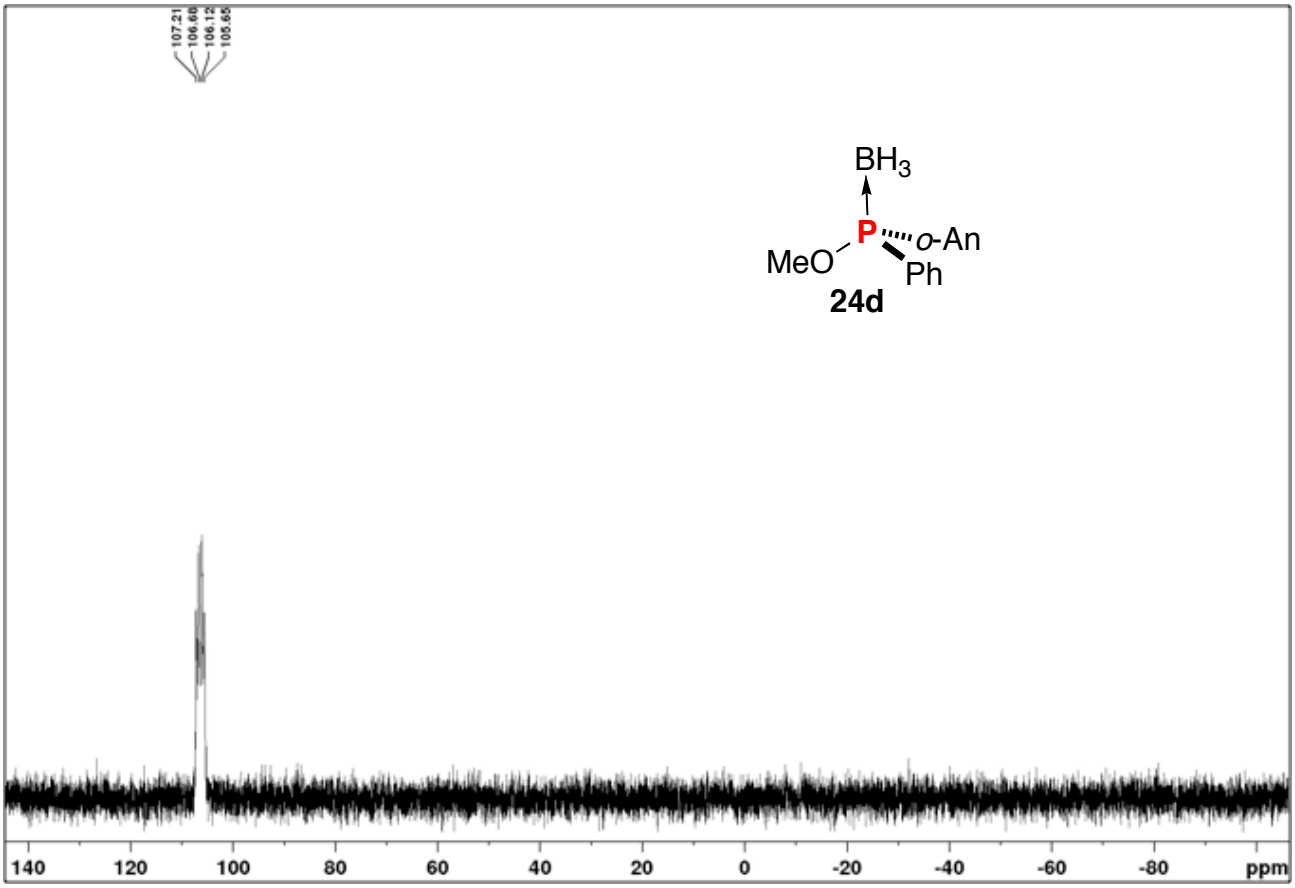


(*S*)-Methyl-*o*-anisylphenylphosphinite-borane **24d**

^{1}H NMR ($CDCl_3$, 300 MHz):

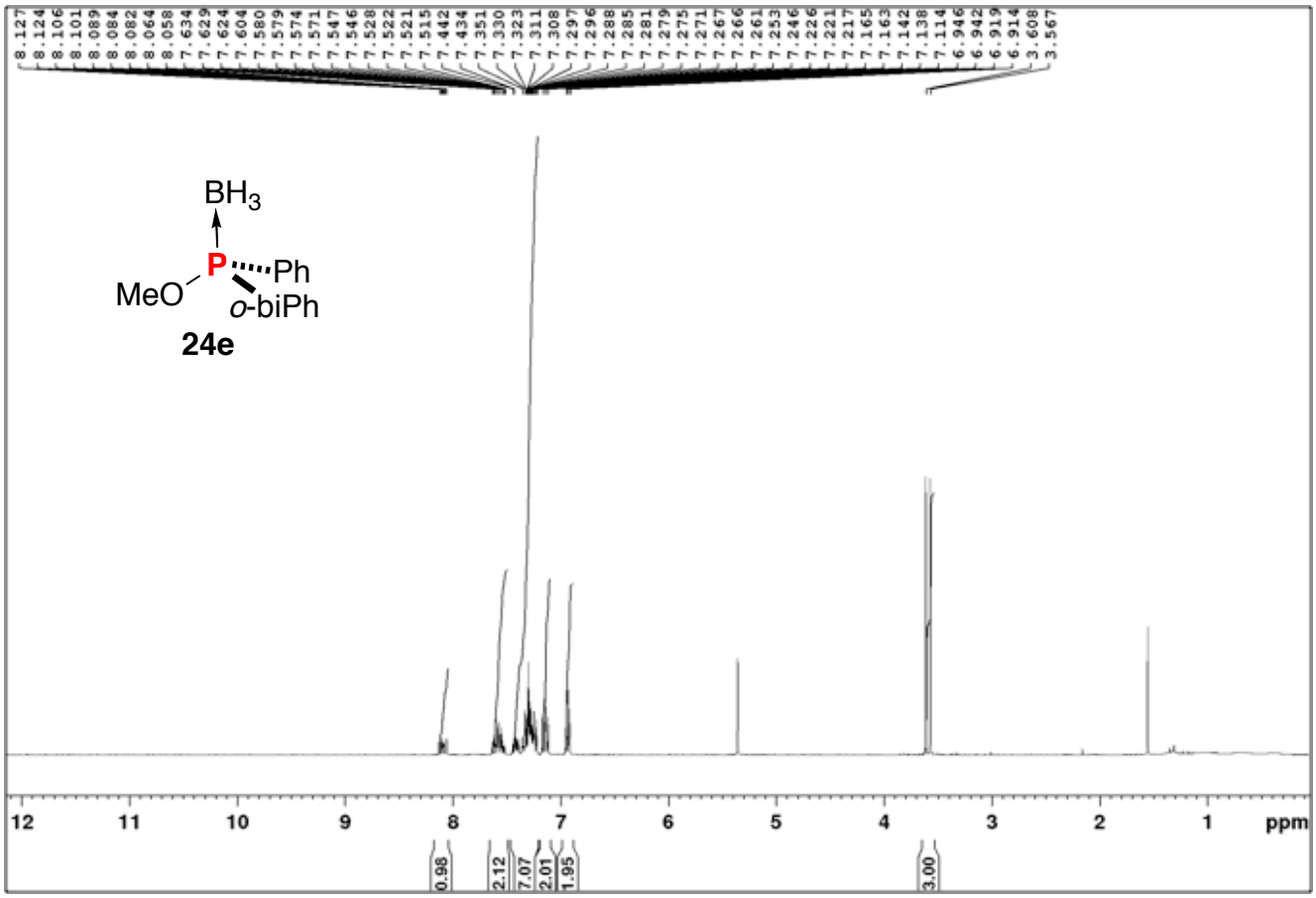


$^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 121.5 MHz):

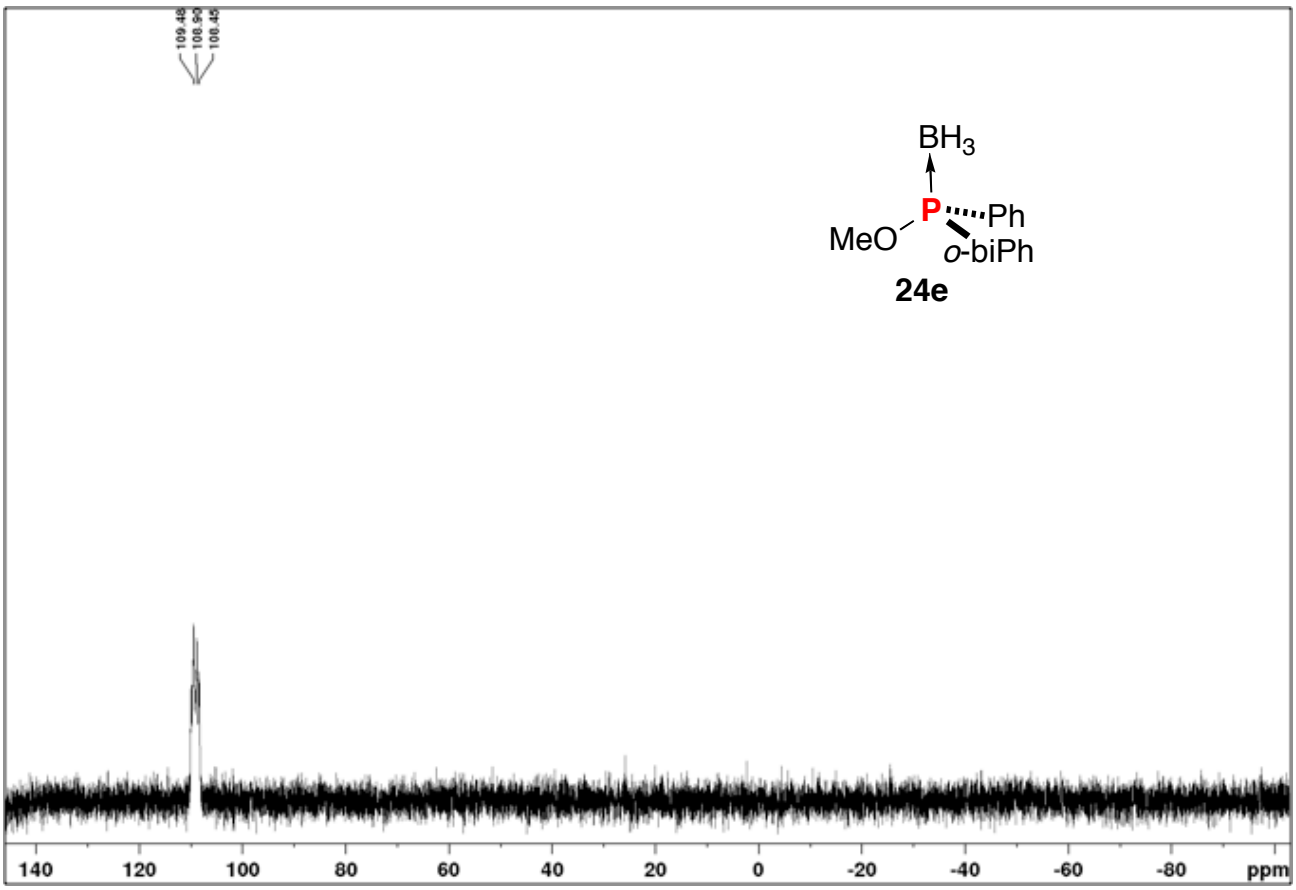


(*R*)-Phenyl-*o*-biphenylphenylphosphinite-borane **24e**

^{1}H NMR (CD_2Cl_2, 300 MHz):

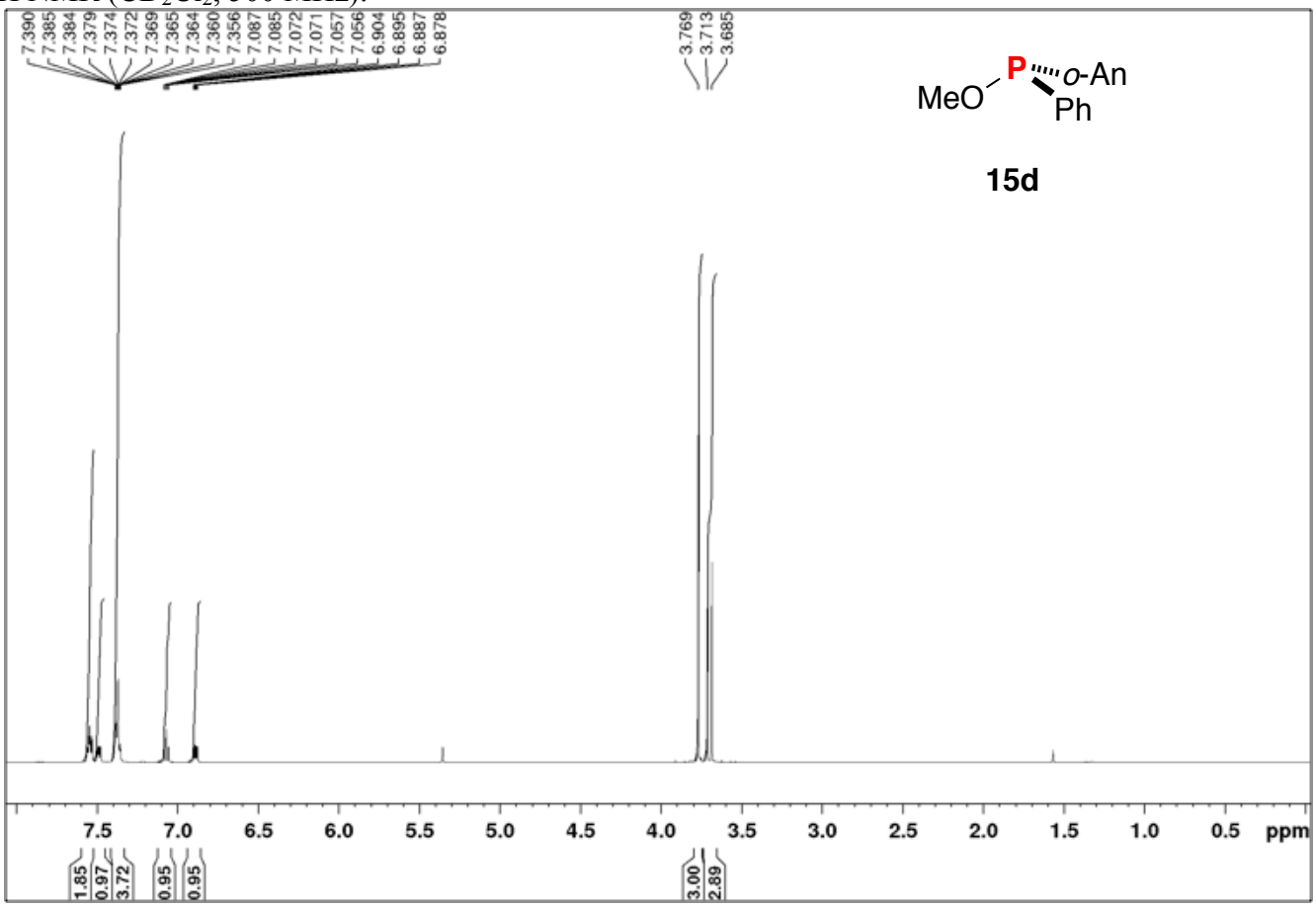


$^{31}P\{^{1}H\}$ NMR (C_2D_2, 121.5 MHz):

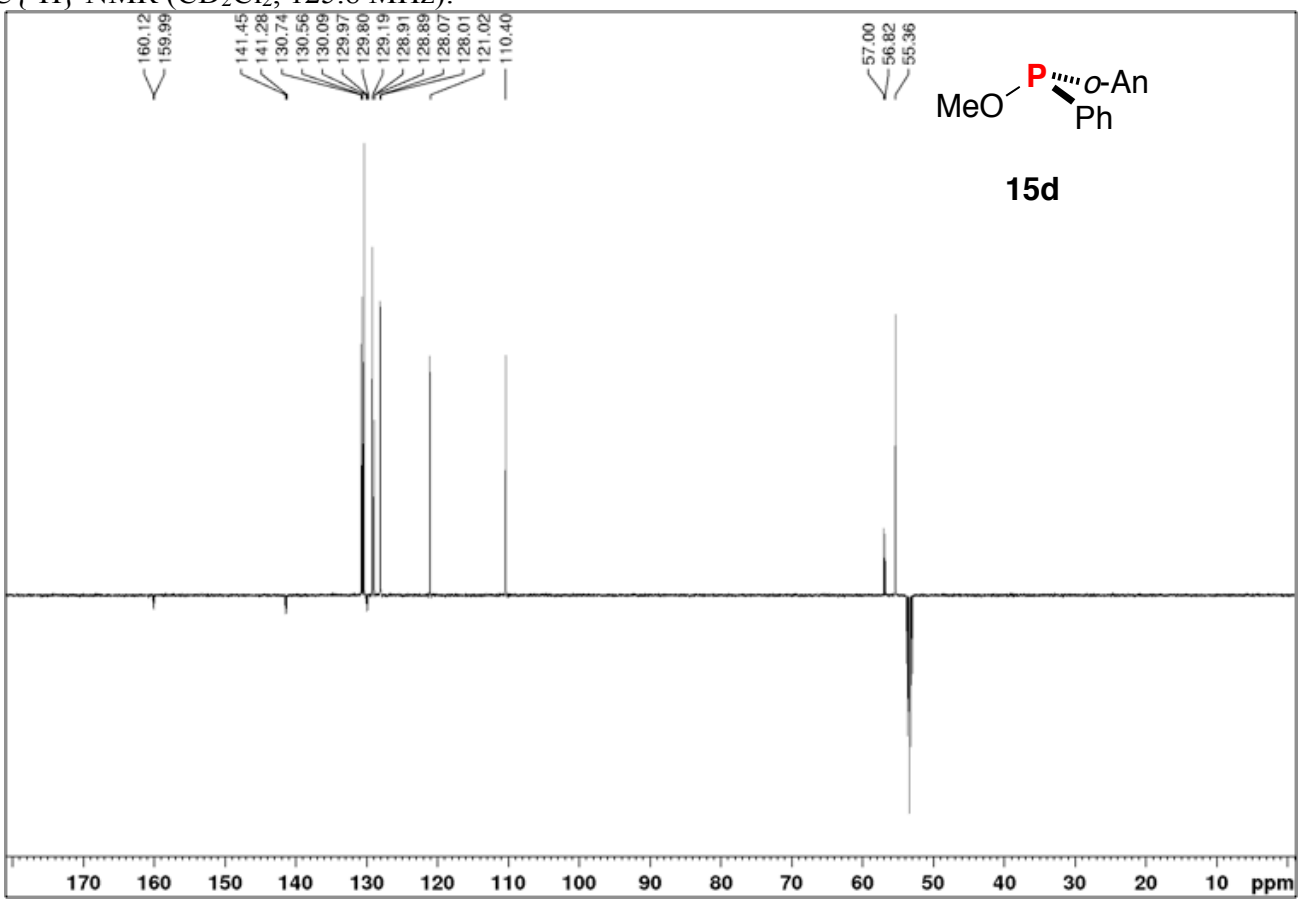


(*S*)-Methyl-*o*-anisylphenylphosphinite **15d**

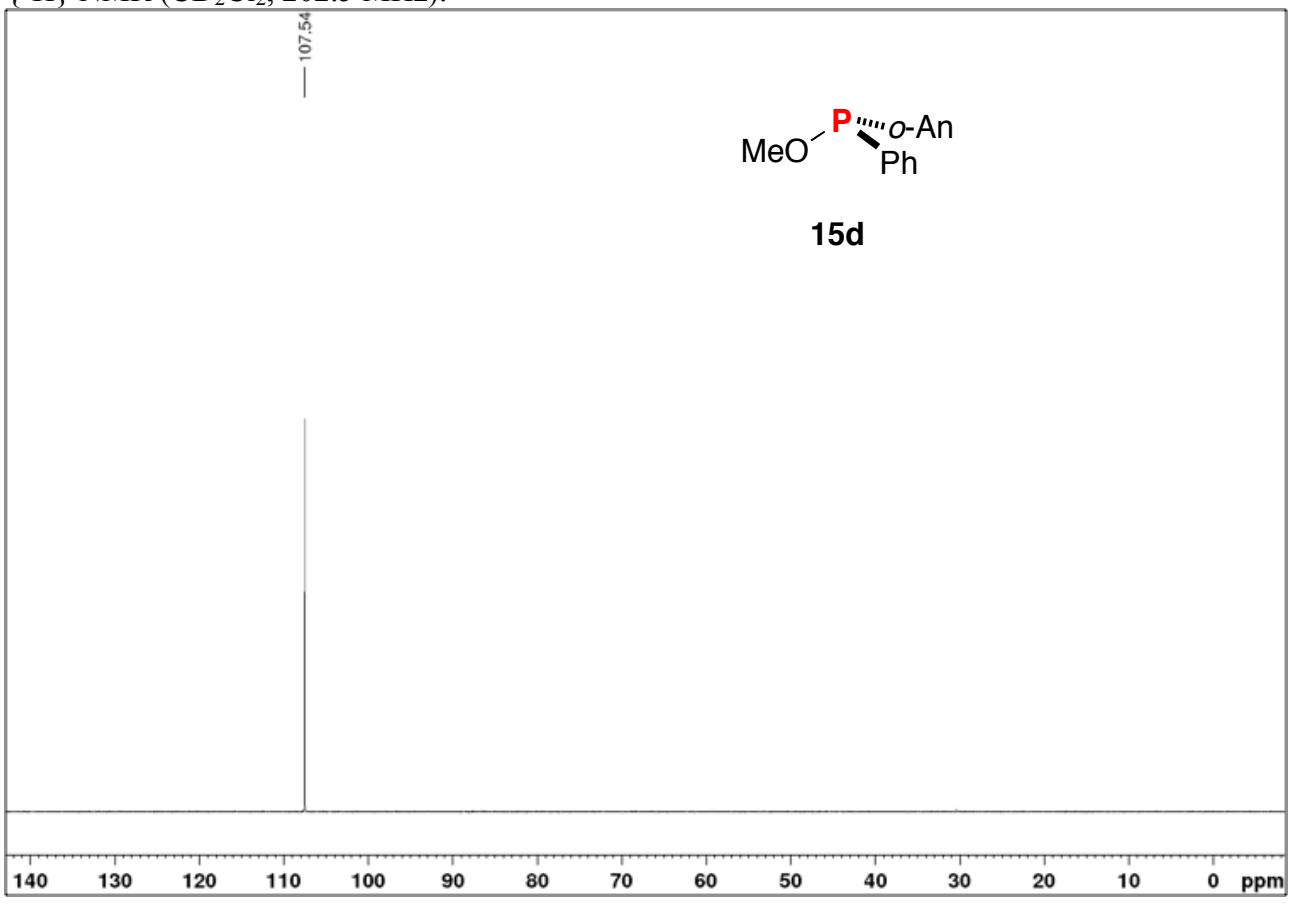
^{1}H NMR (CD_2Cl_2, 500 MHz):



$^{13}C\{^{1}H\}$ NMR (CD_2Cl_2, 125.8 MHz):

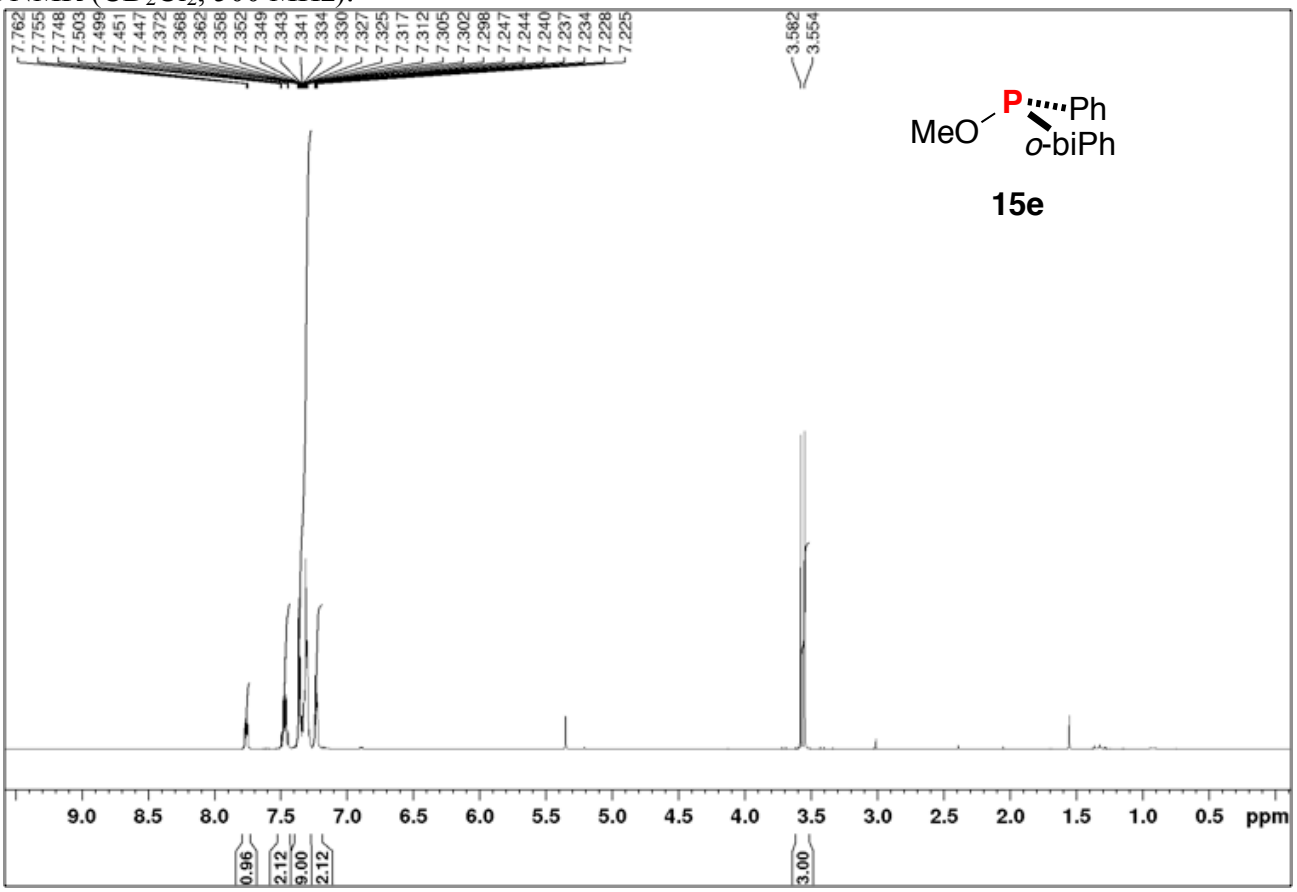


$^{31}P\{^{1}H\}$ NMR (CD_2Cl_2, 202.5 MHz):

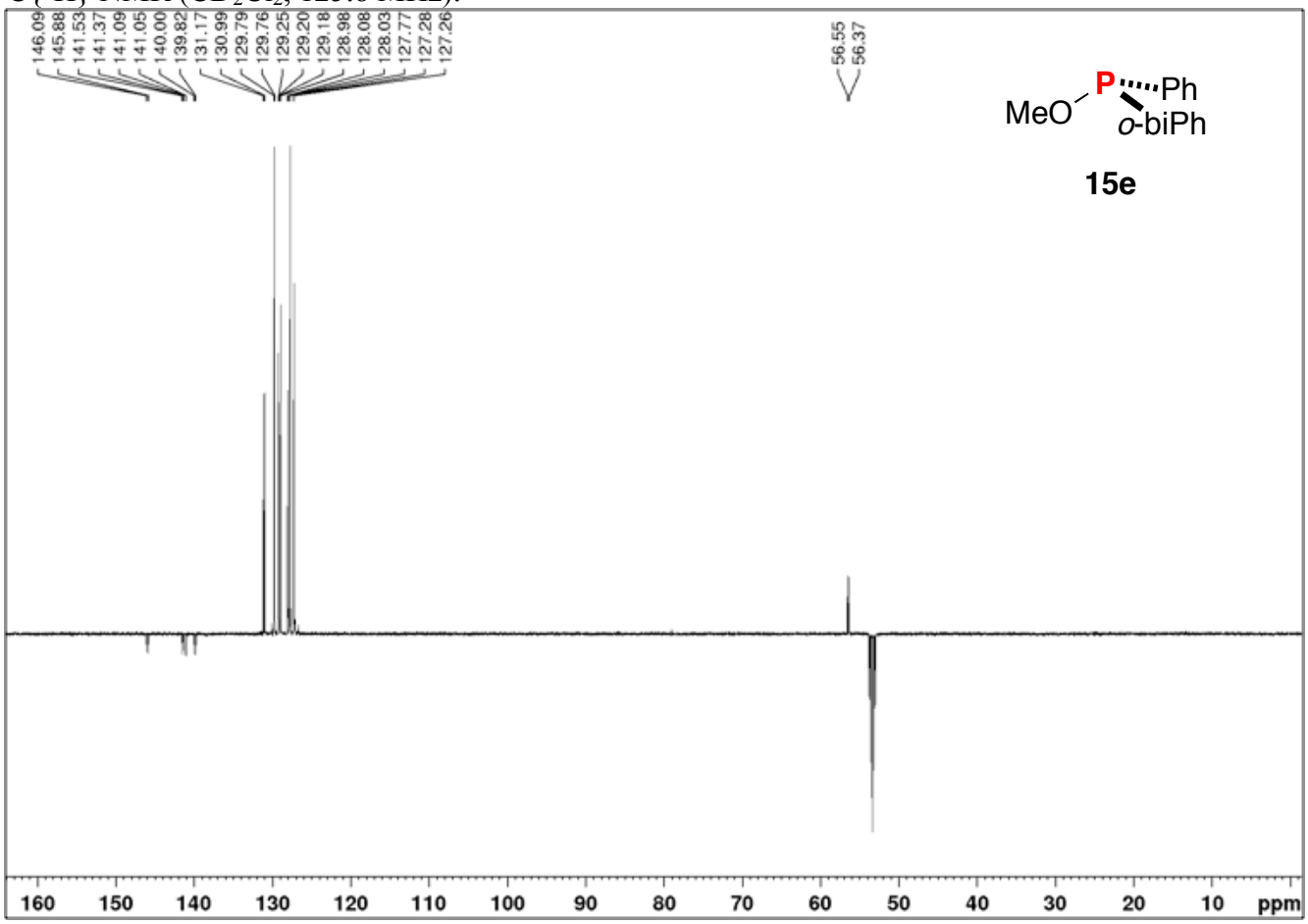


(*R*)-Phenyl-*o*-biphenylphenylphosphinite **15e**

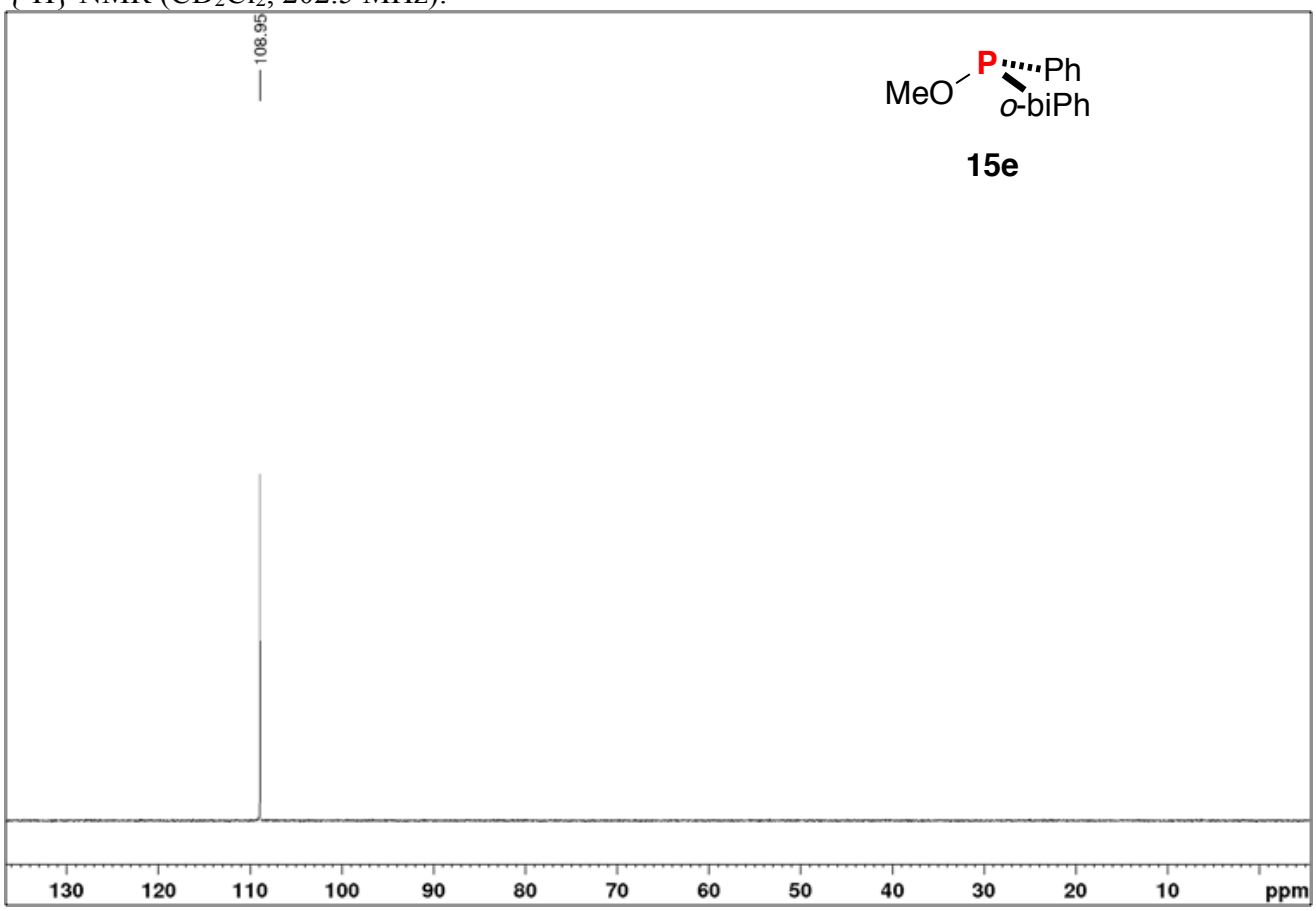
^{1}H NMR (CD_2Cl_2, 500 MHz):



^{13}C{^{1}H} NMR (CD_2Cl_2, 125.8 MHz):

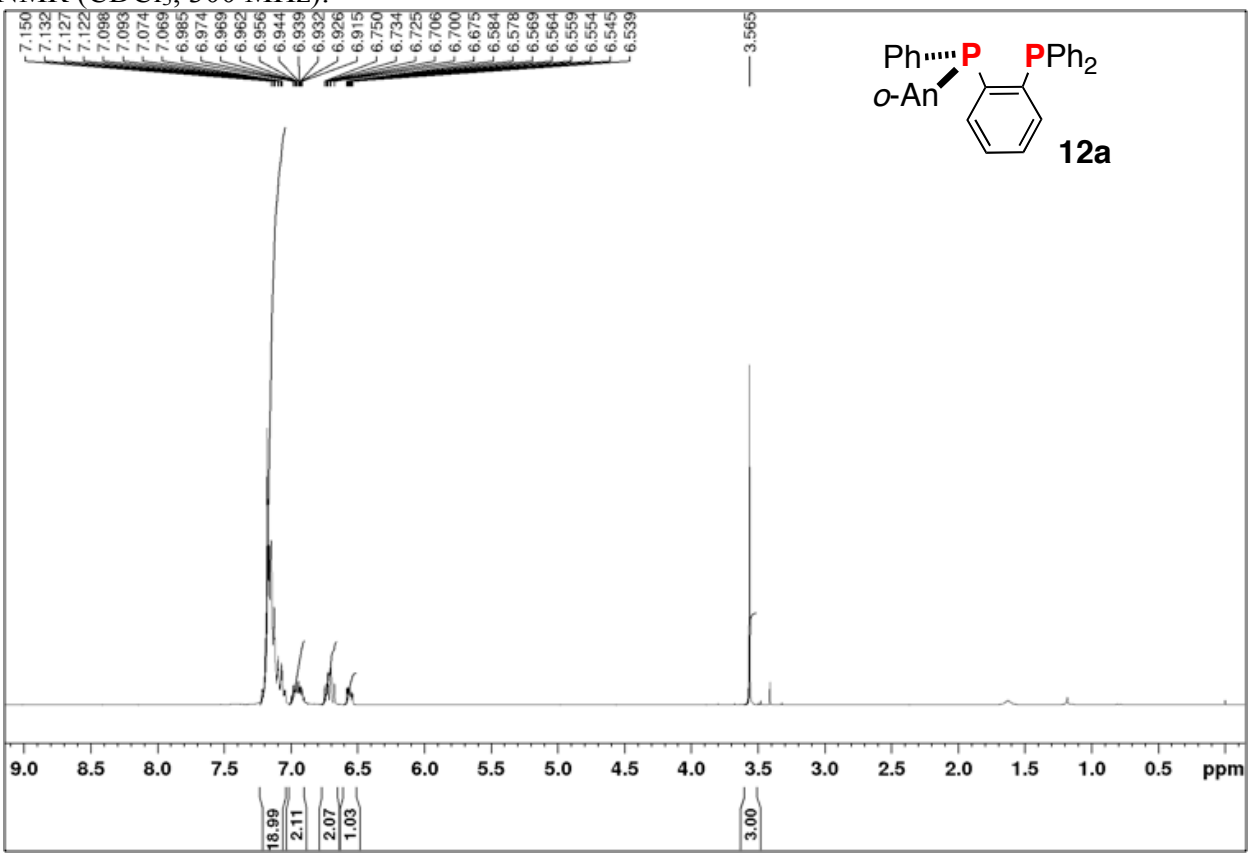


$^{31}P\{^{1}H\}$ NMR (CD_2Cl_2, 202.5 MHz):

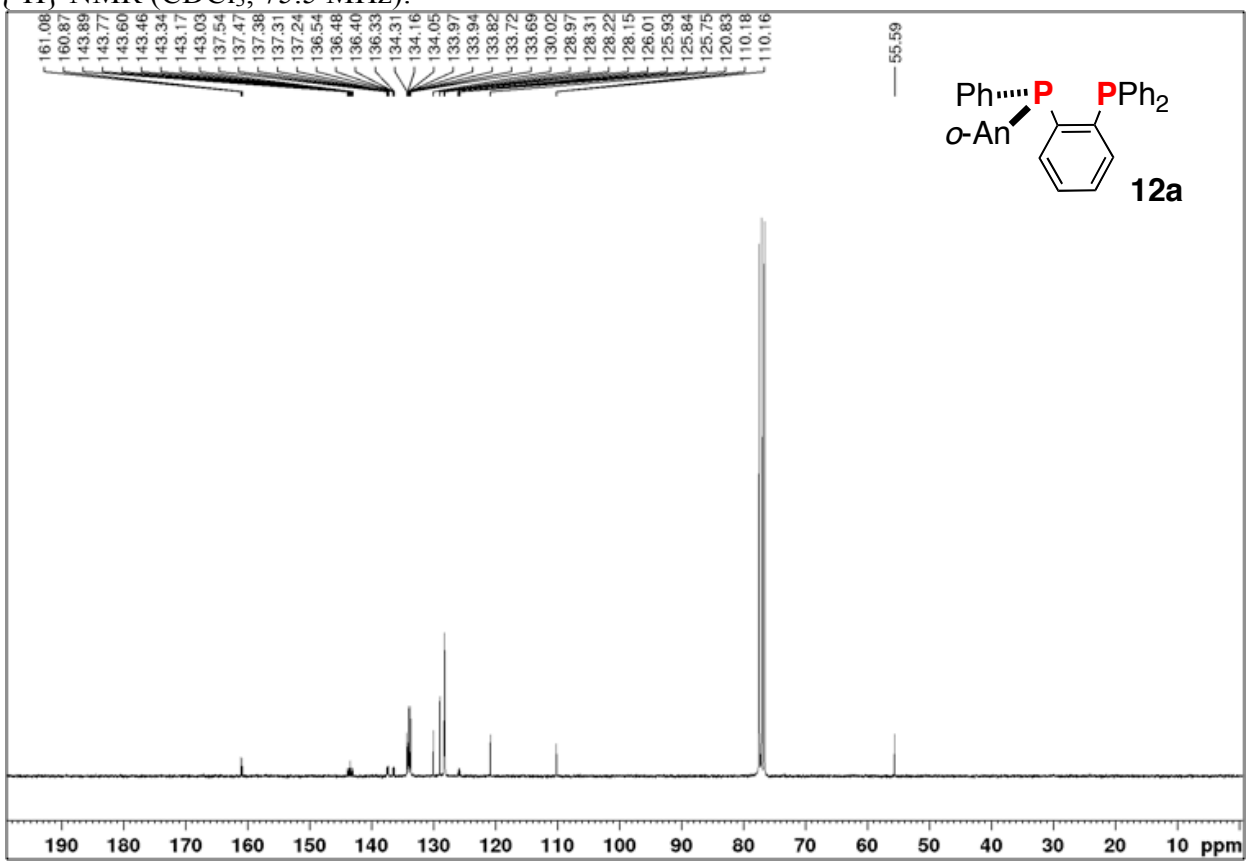


(*S*)-1-(*o*-Anisylphenylphosphino)-2-(diphenylphosphino)benzene **12a**

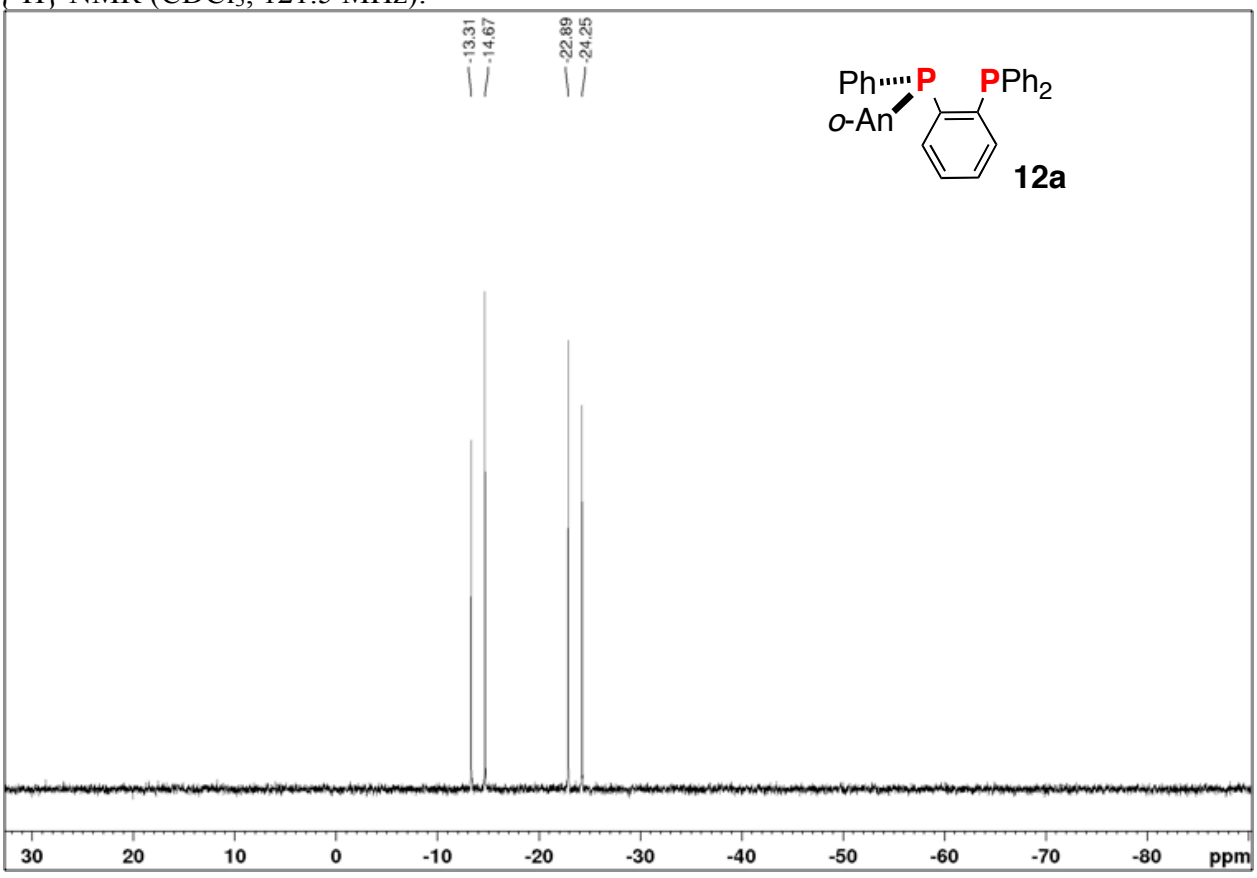
^{1}H NMR ($CDCl_3$, 300 MHz):



$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 75.5 MHz):

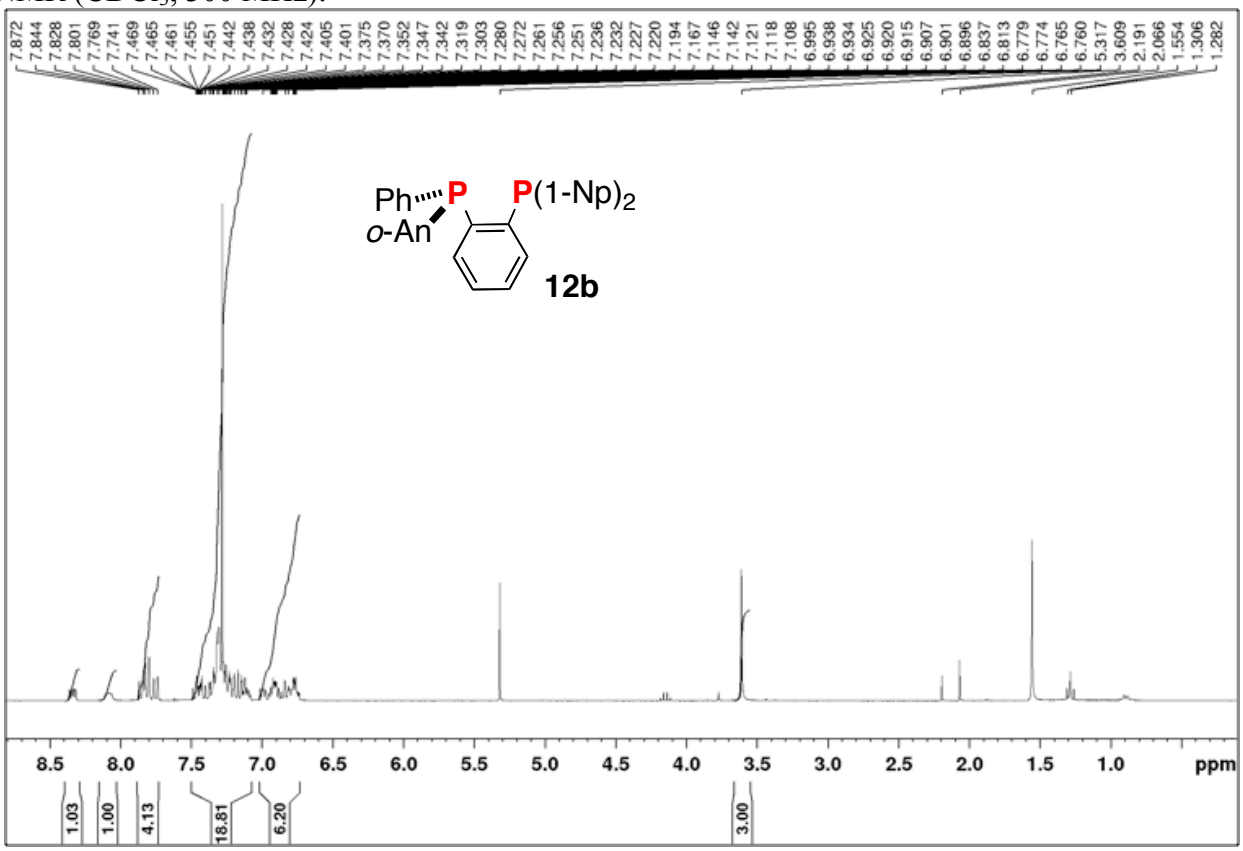


$^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 121.5 MHz):

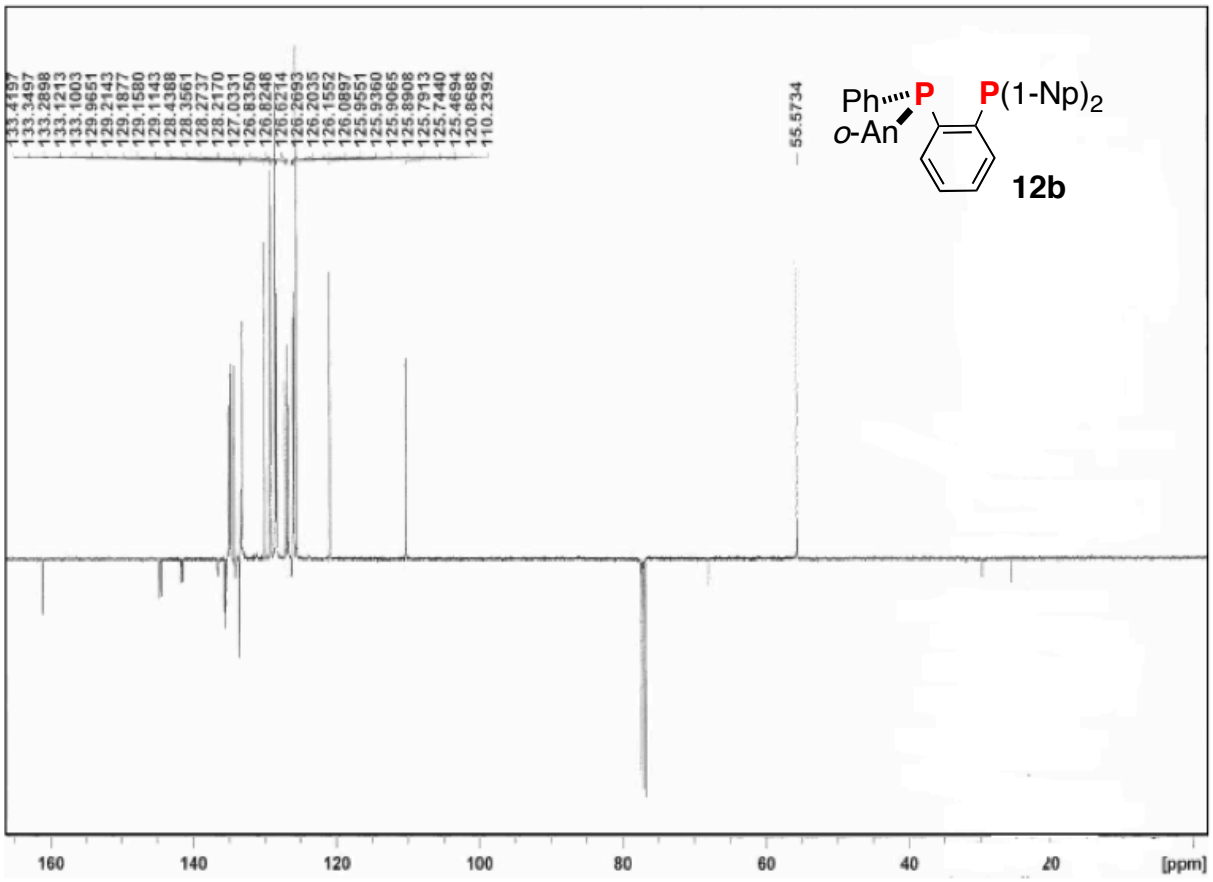


(*S*)-1-(*o*-Anisylphenylphosphino)-2-[di-(1-naphtyl)phosphino]benzene **12b**

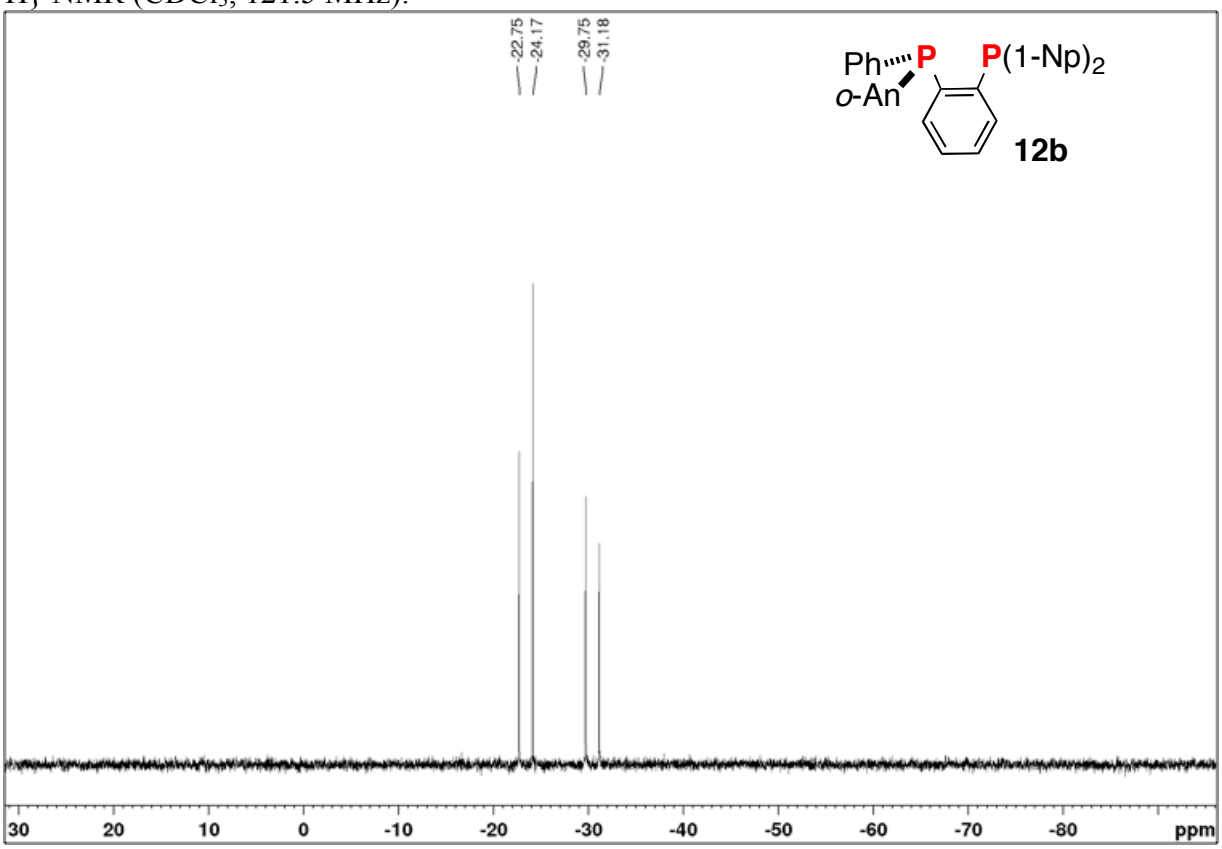
^{1}H NMR ($CDCl_3$, 300 MHz):



^{13}C{^{1}H}NMR ($CDCl_3$, 75.5 MHz):

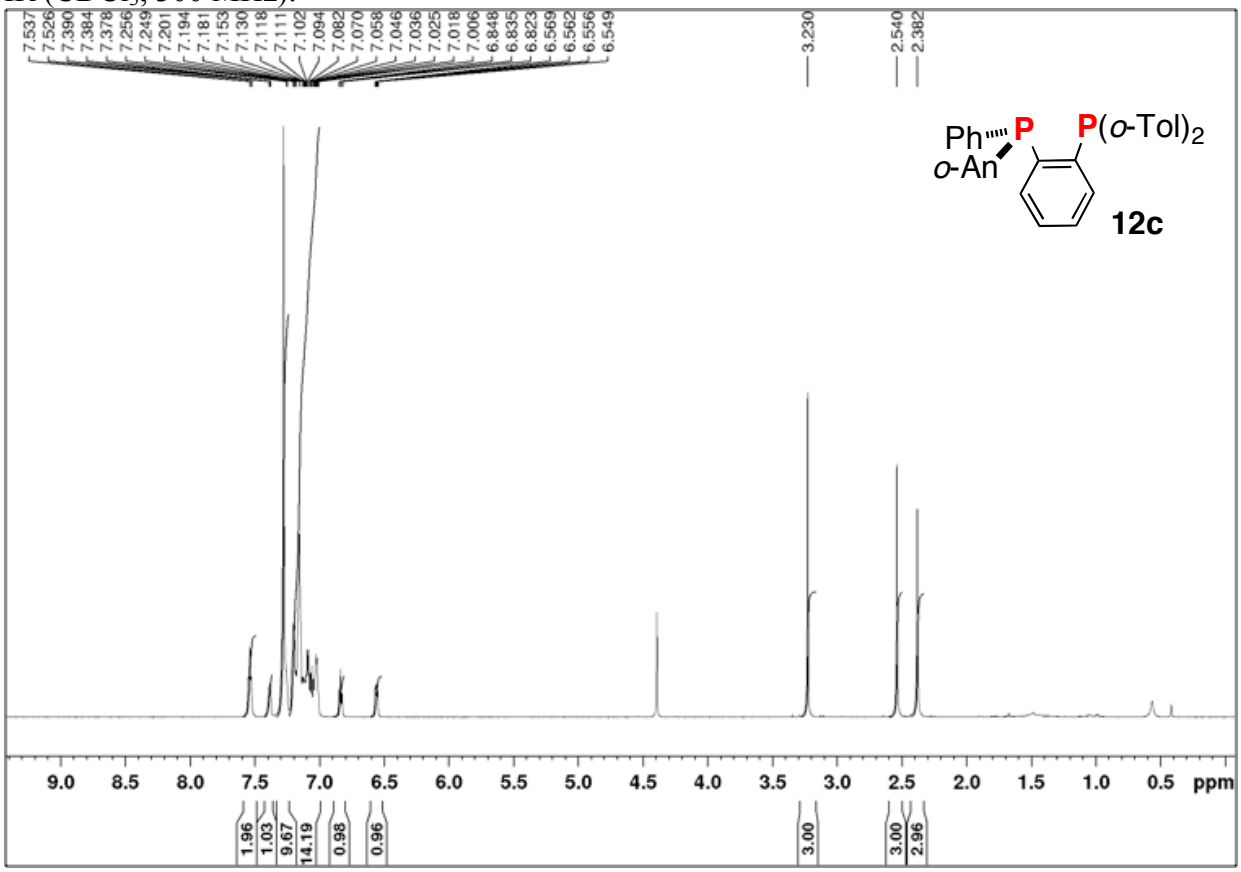


$^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 121.5 MHz):

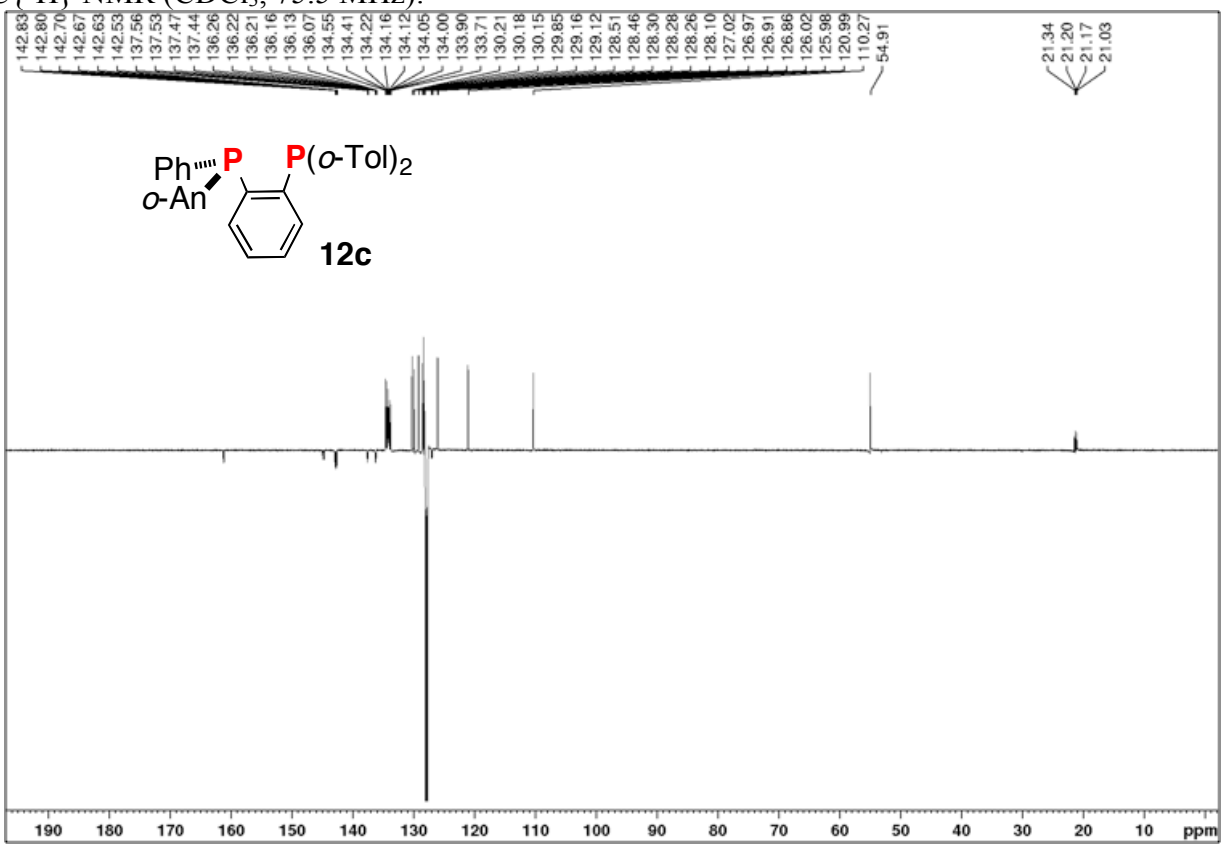


(*S*)-1-(*o*-Anisylphenylphosphino)-2-[di-(*o*-tolyl)phosphino]benzene **12c**

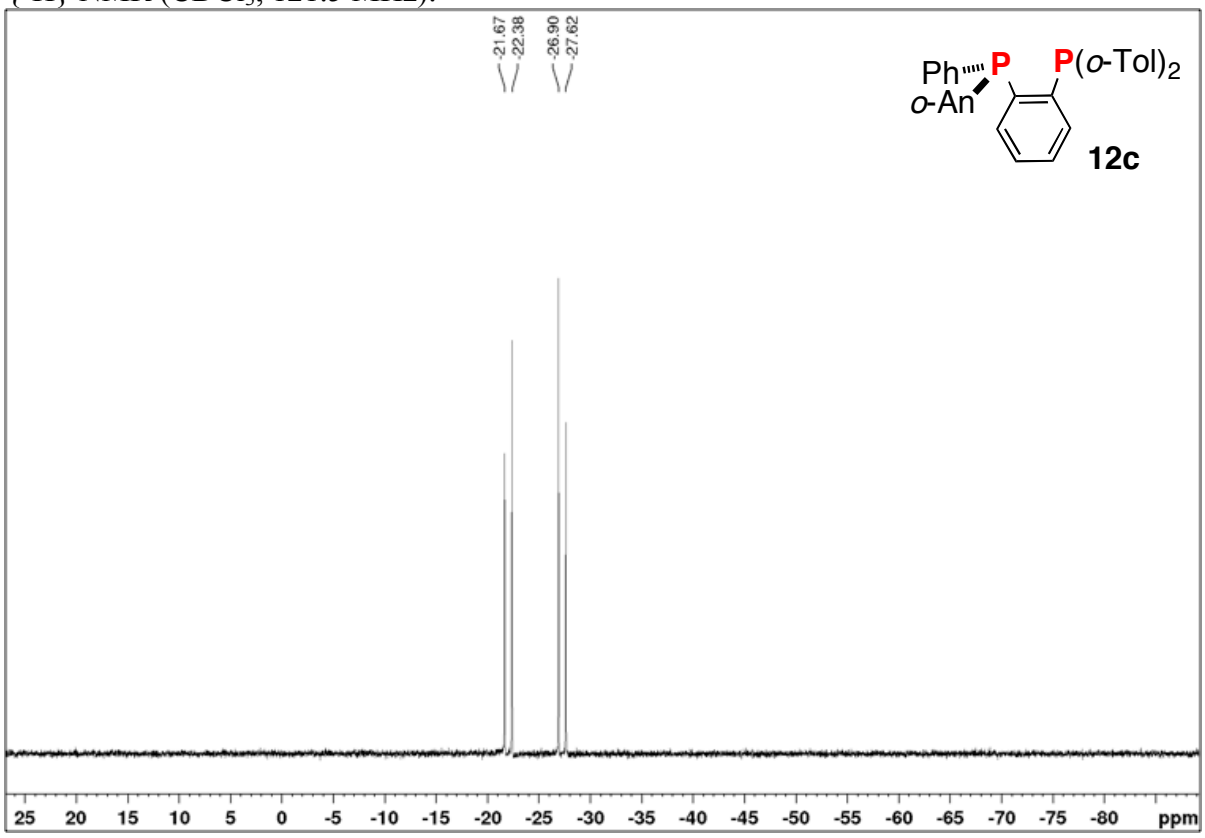
^{1}H NMR ($CDCl_3$, 300 MHz):



$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 75.5 MHz):

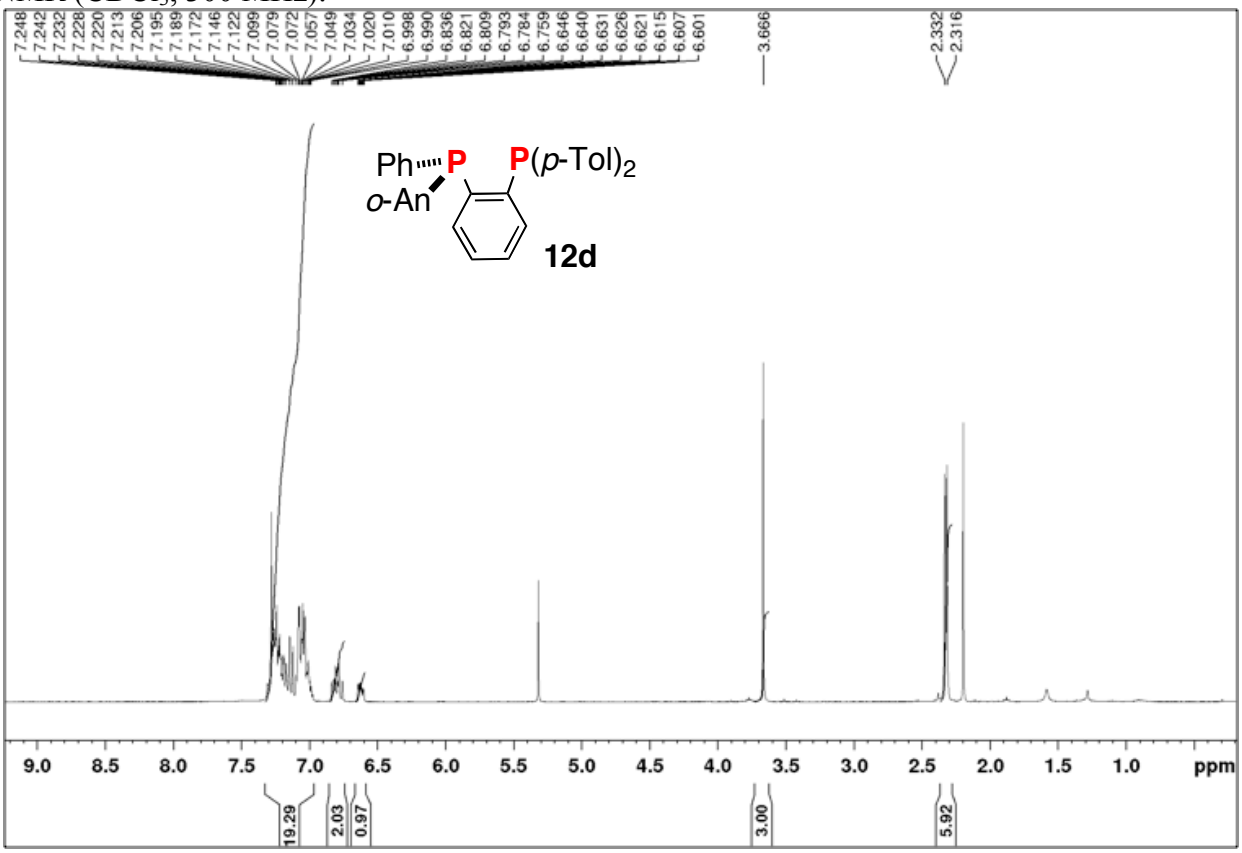


$^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 121.5 MHz):

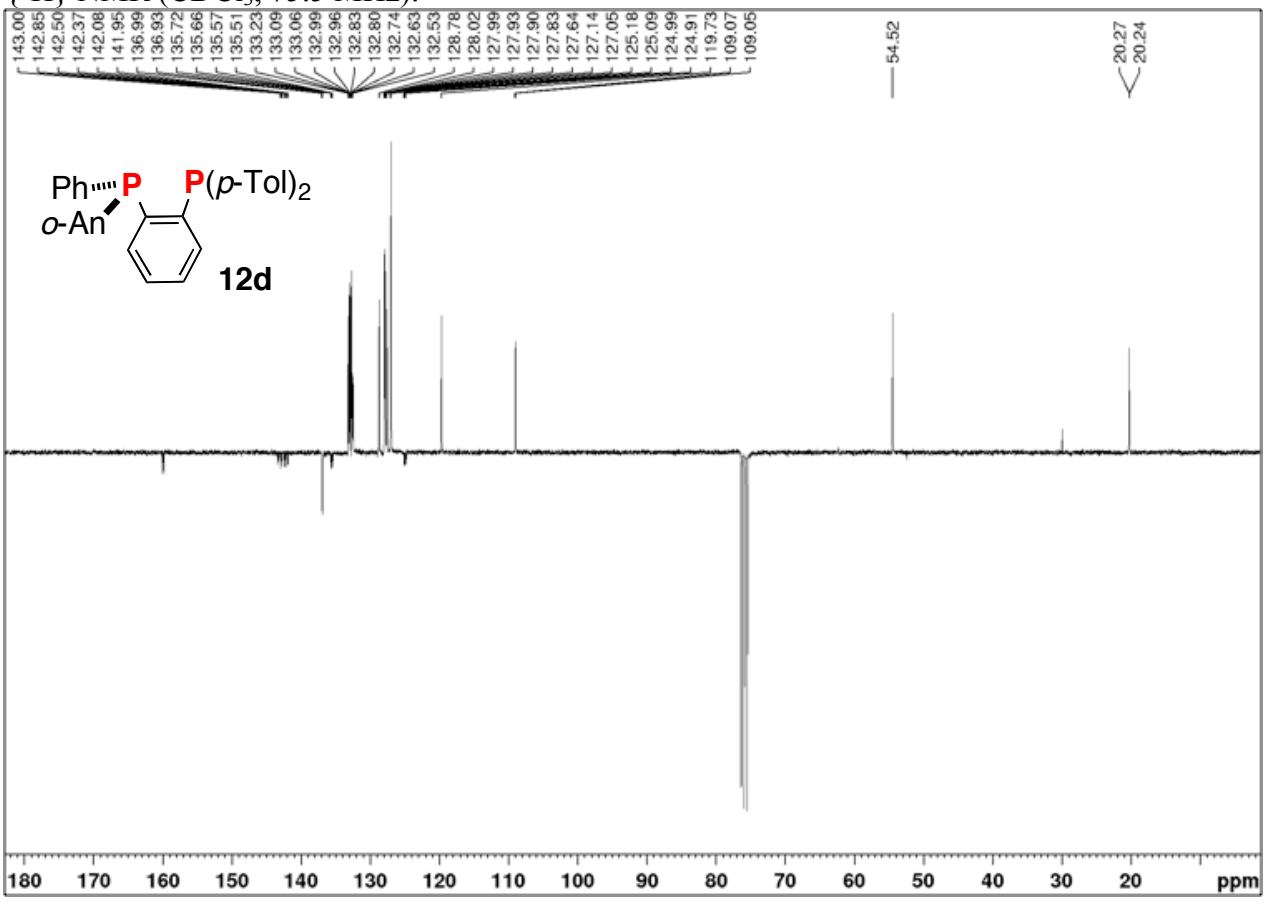


(*S*)-1-(*o*-Anisylphenylphosphino)-2-[di-(*p*-tolyl)phosphino]benzene **12d**

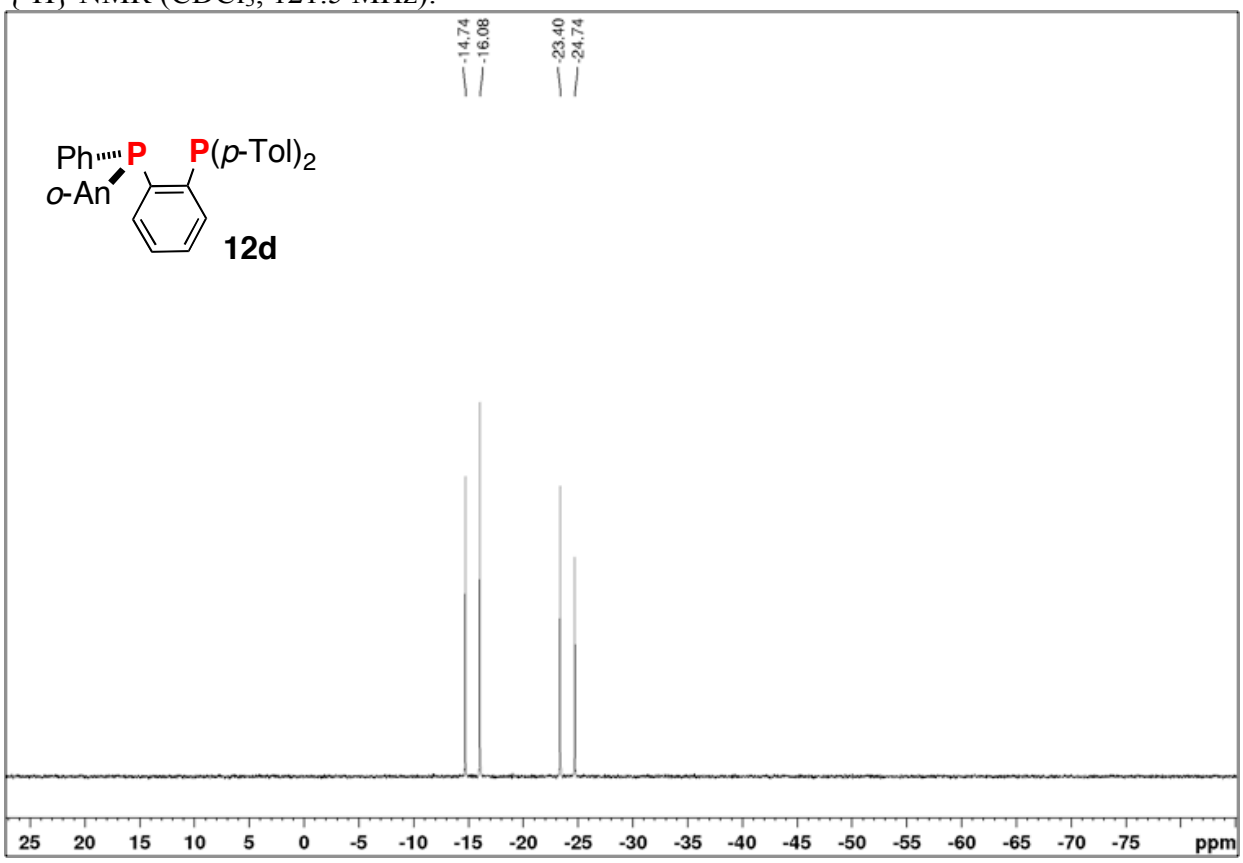
^{1}H NMR ($CDCl_3$, 300 MHz):



^{13}C{^{1}H} NMR ($CDCl_3$, 75.5 MHz):

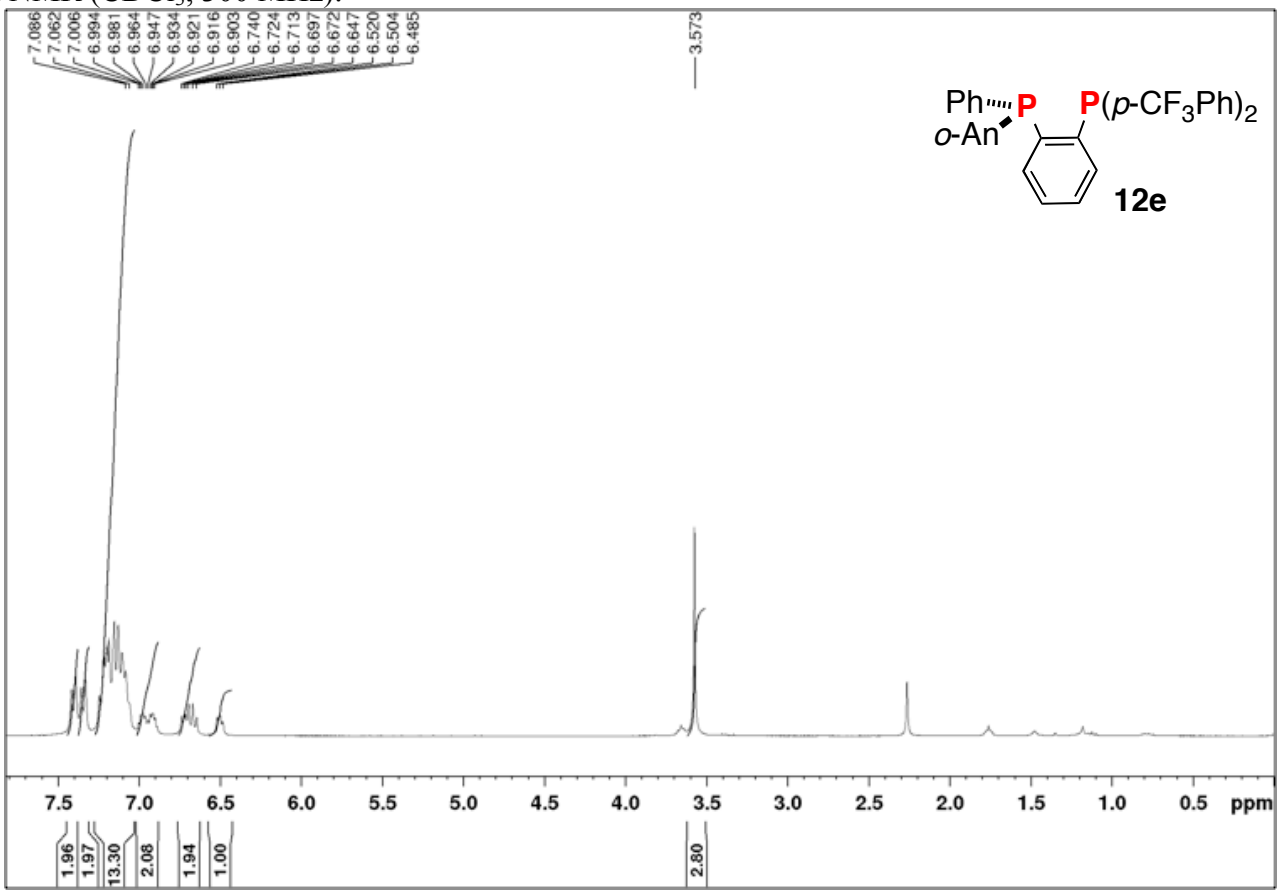


$^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 121.5 MHz):

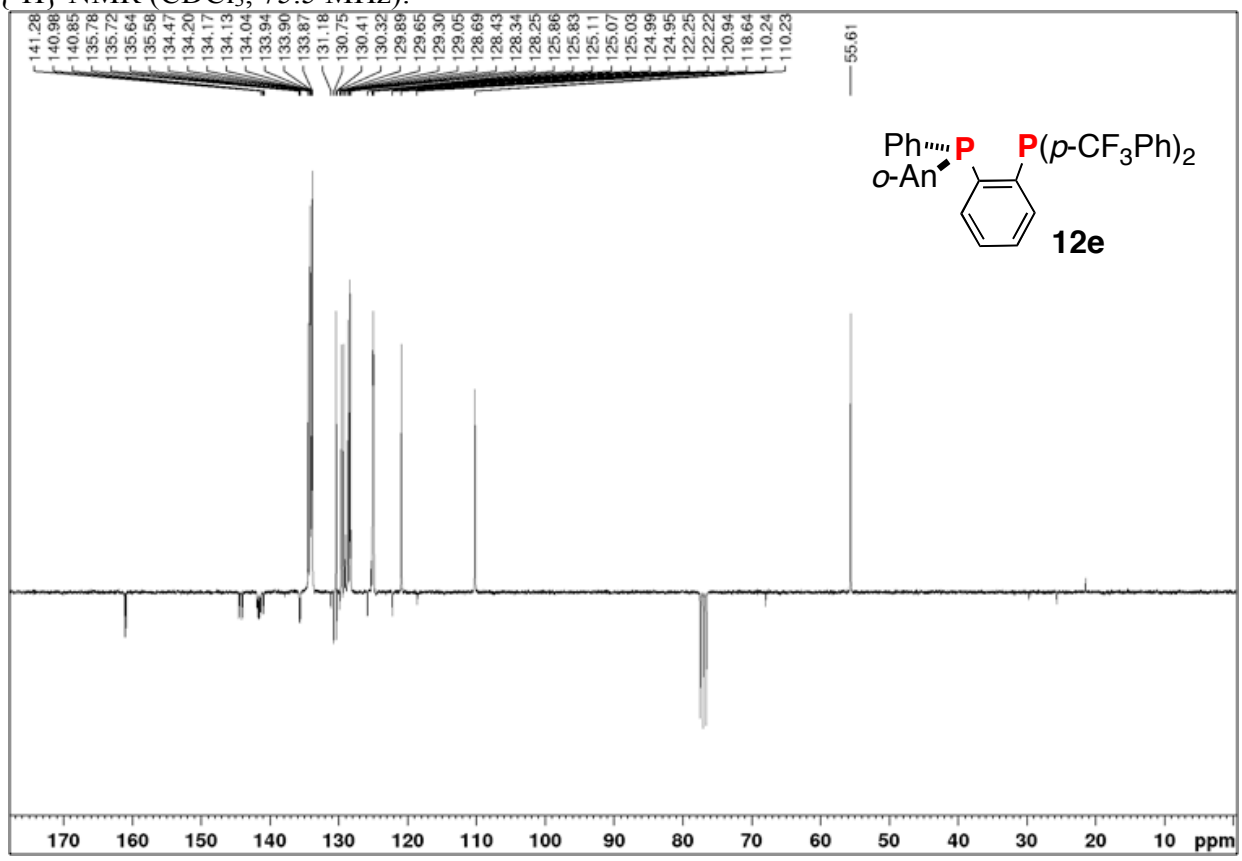


(*S*)-1-(*o*-Anisylphenylphosphino)-2-[di-(*p*-trifluoromethylphenyl)phosphino]benzene **12e**

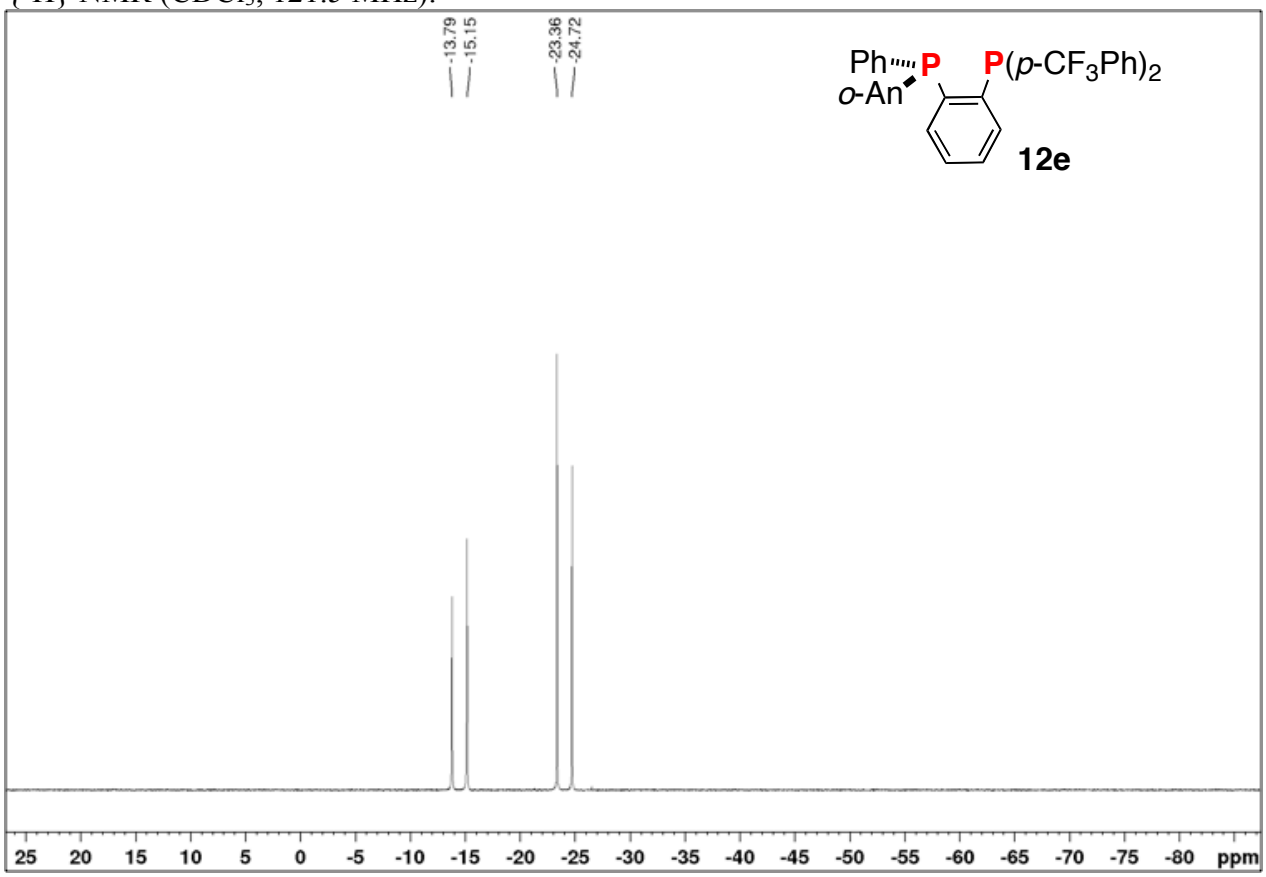
^{1}H NMR ($CDCl_3$, 300 MHz):



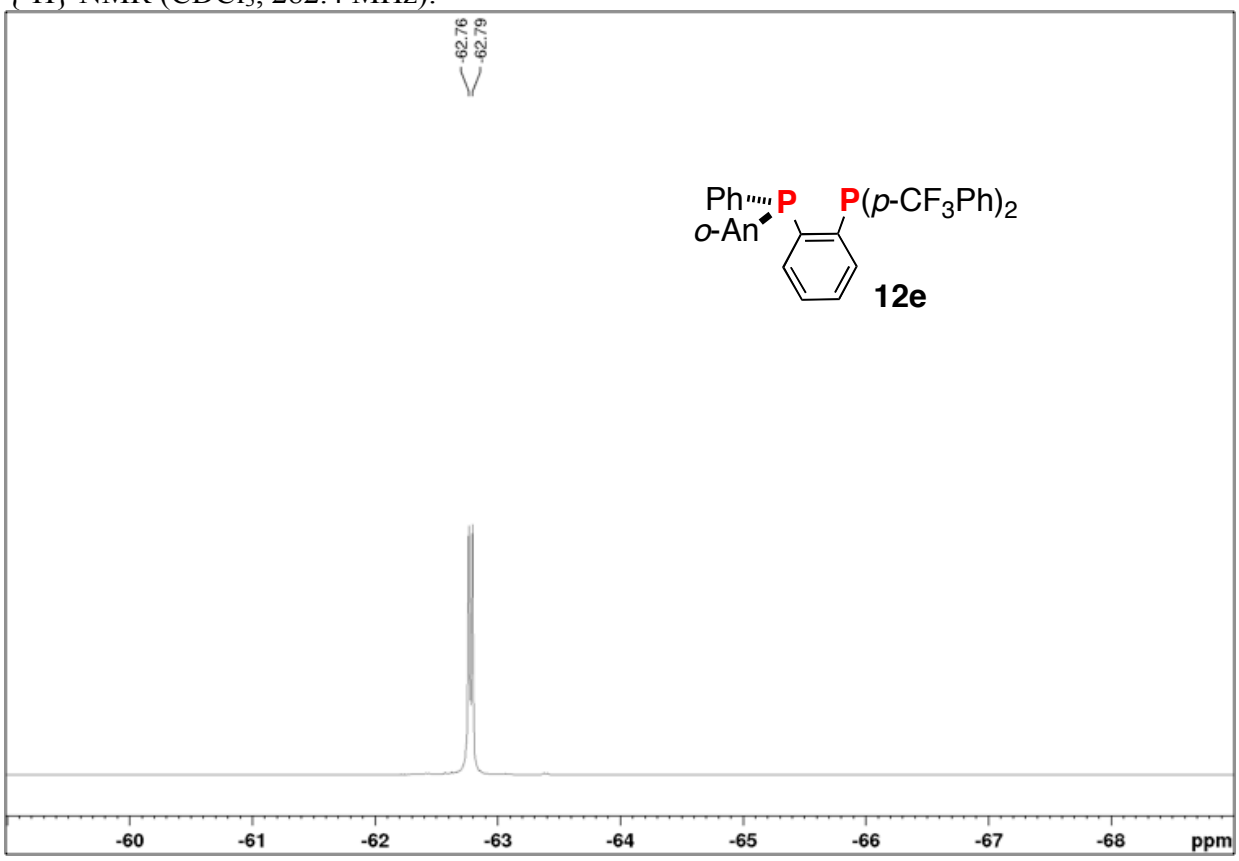
$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 75.5 MHz):



$^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 121.5 MHz):

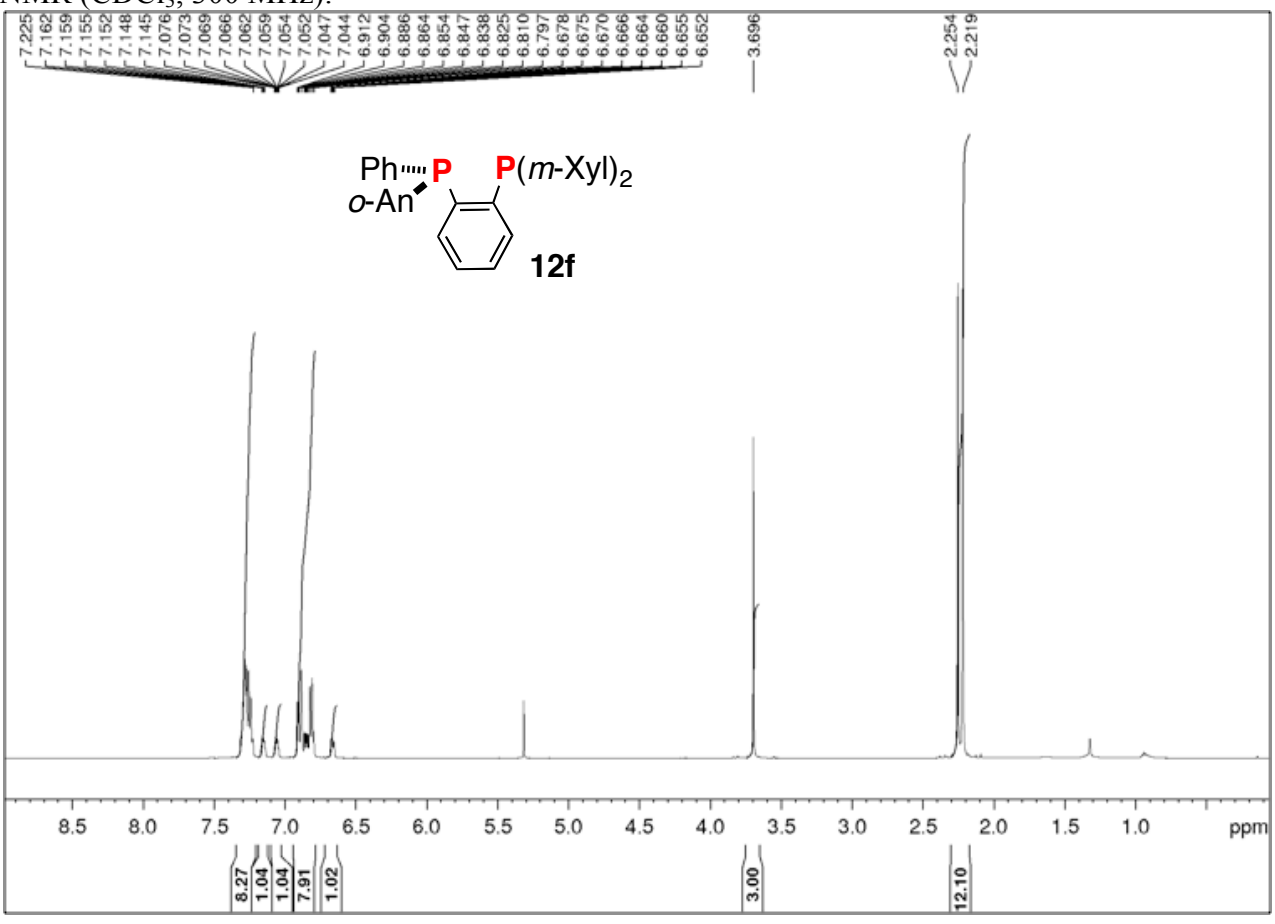


$^{19}F\{^{1}H\}$ NMR ($CDCl_3$, 282.4 MHz):

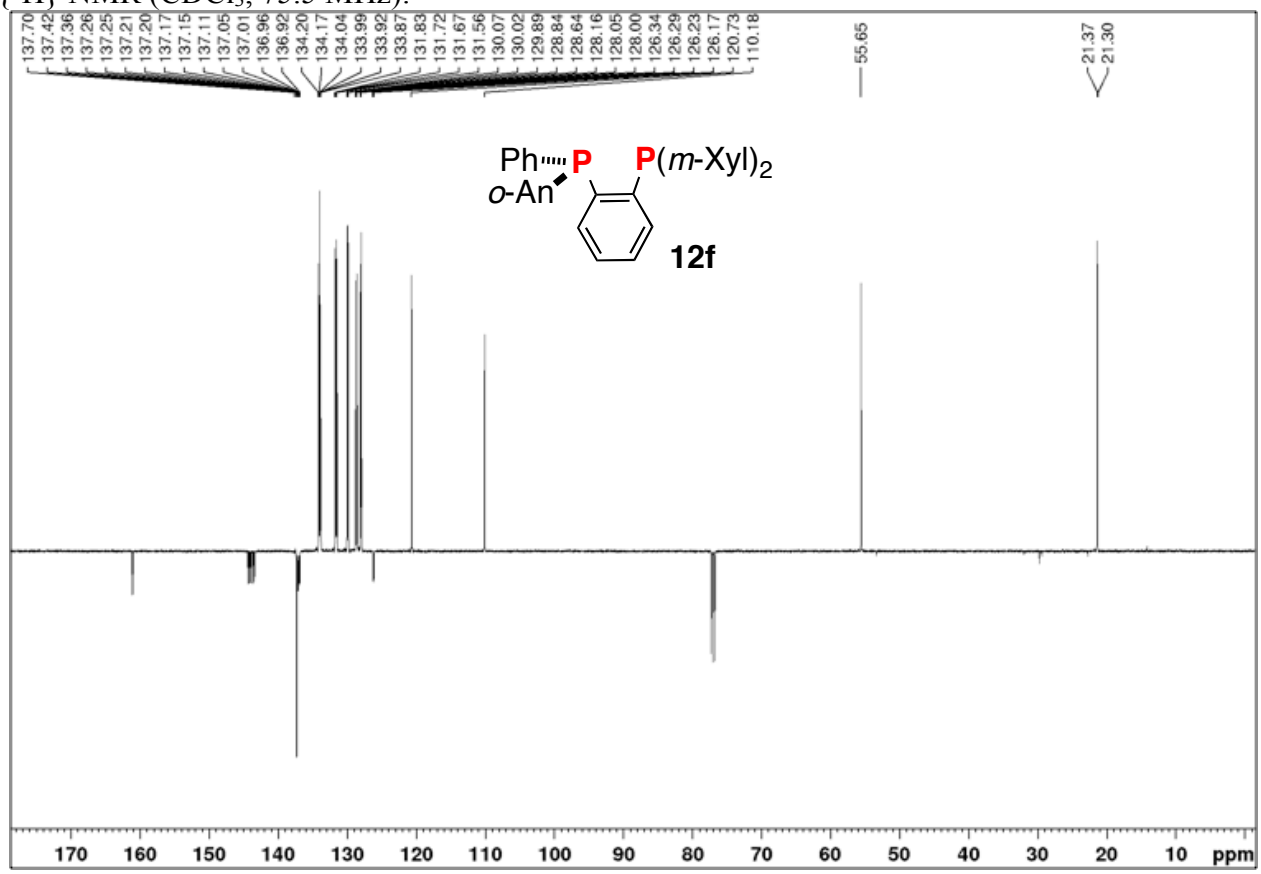


(*S*)-1-(*o*-Anisylphenylphosphino)-2-[di-(*m*-xylyl)phosphino]benzene **12f**

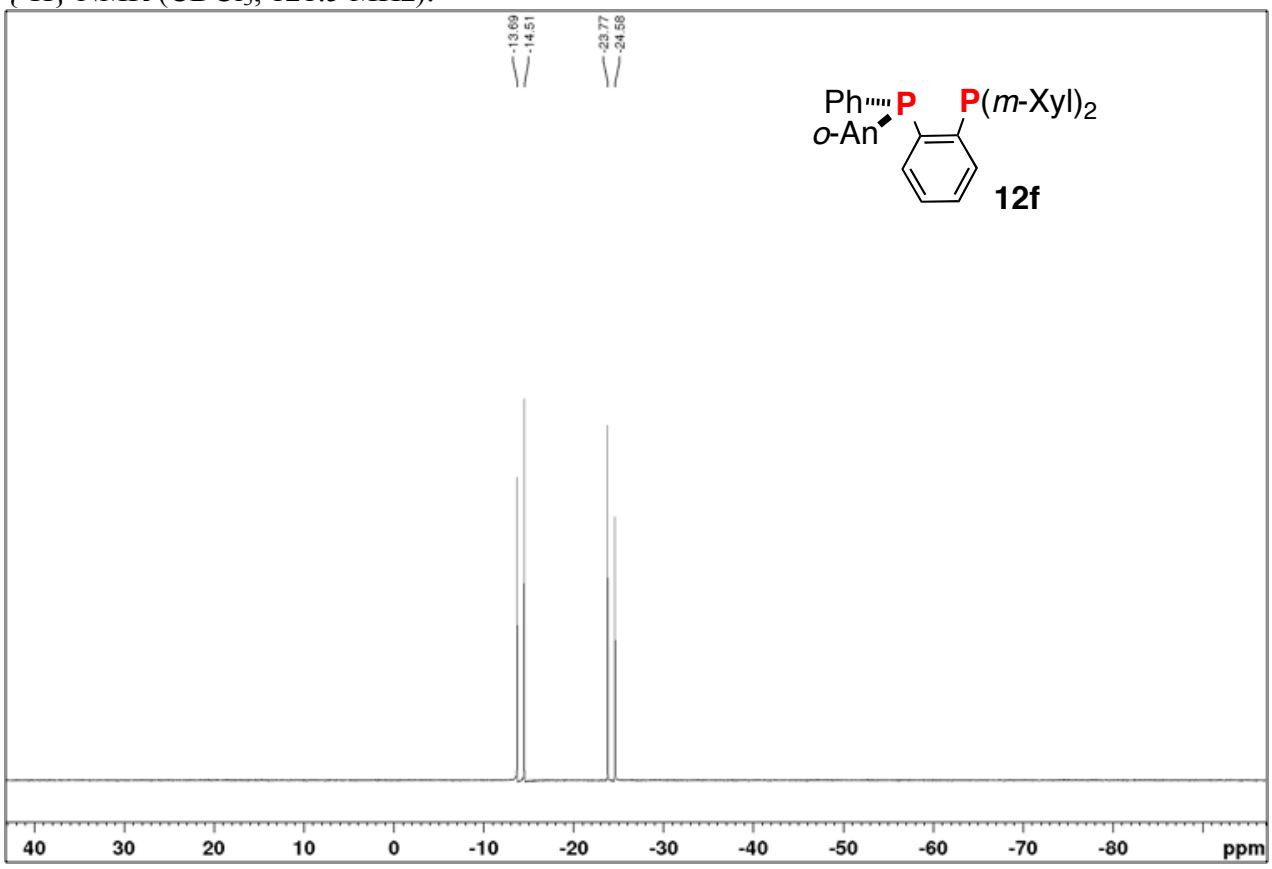
^{1}H NMR ($CDCl_3$, 300 MHz):



$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 75.5 MHz):

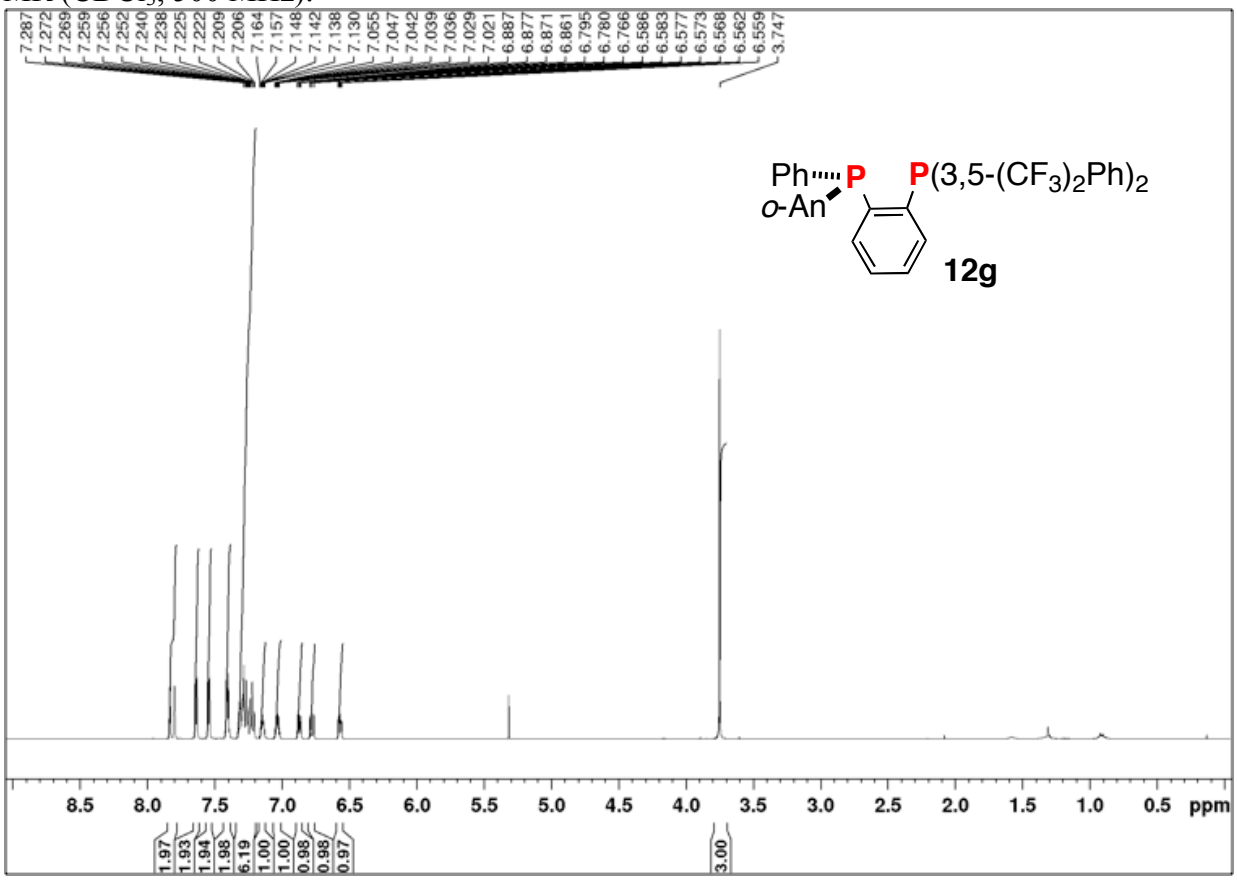


$^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 121.5 MHz):

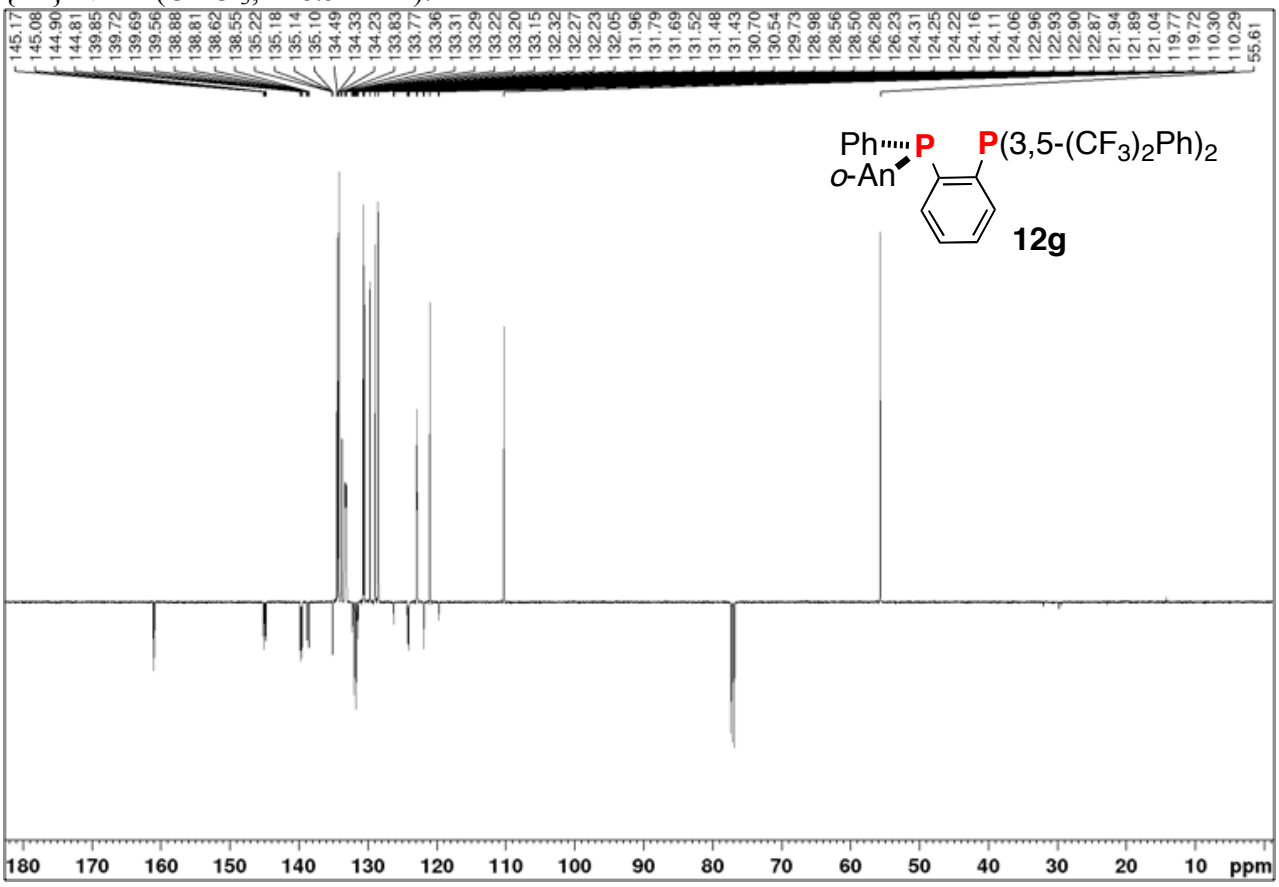


(*S*)-1-(*o*-Anisylphenylphosphino)-2-[di-(3,5-di-trifluoromethylphenyl)phosphino]benzene **12g**

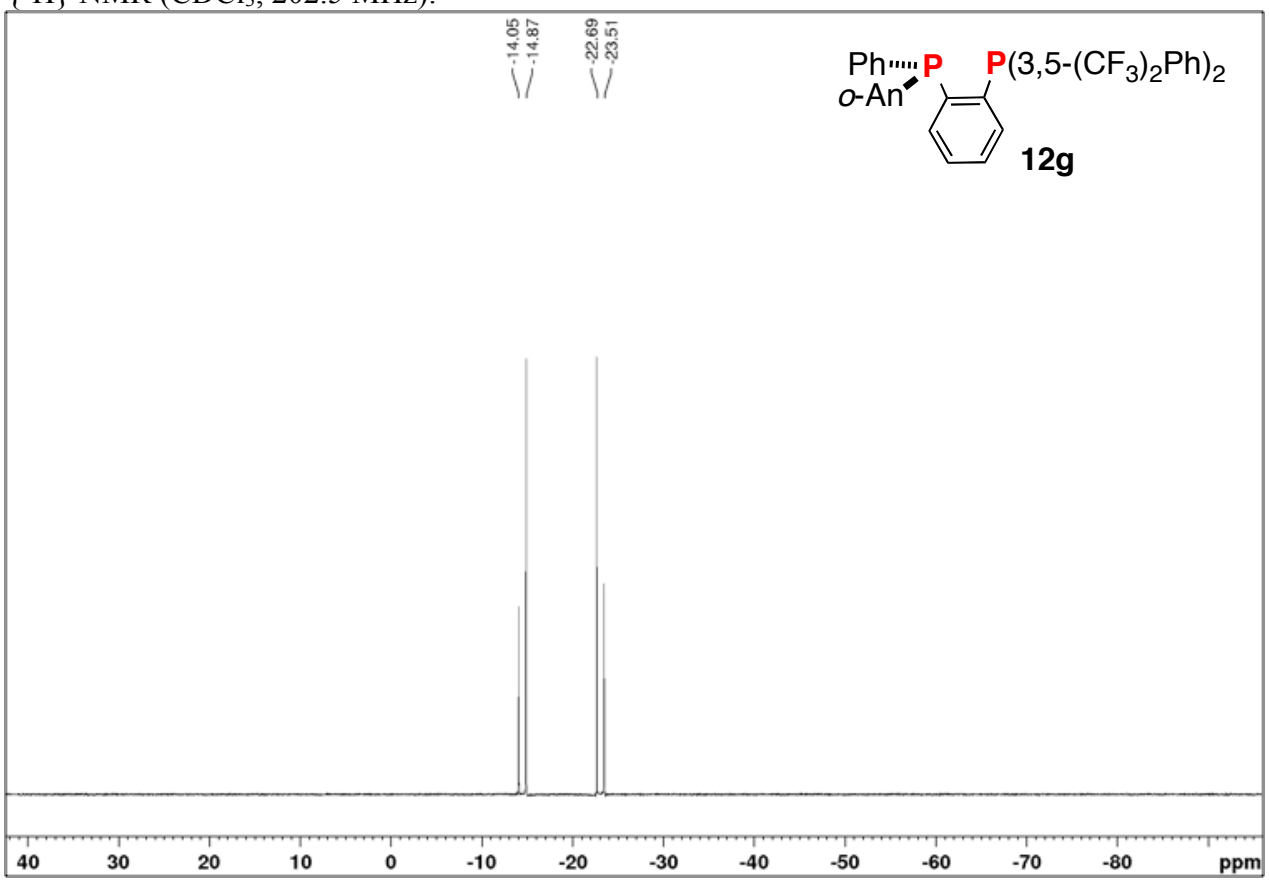
^{1}H NMR ($CDCl_3$, 500 MHz):



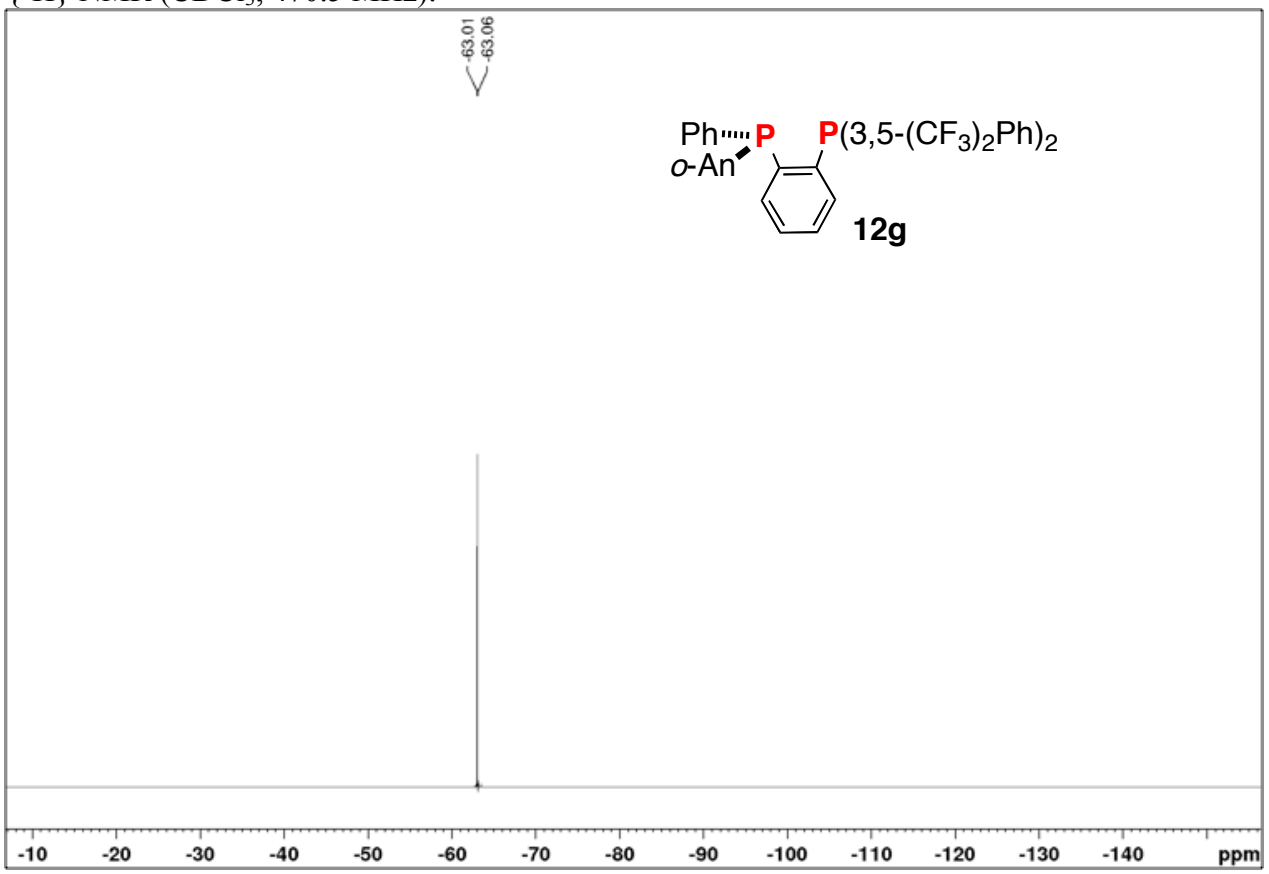
^{13}C{^{1}H} NMR ($CDCl_3$, 128.5 MHz):



$^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 202.5 MHz):

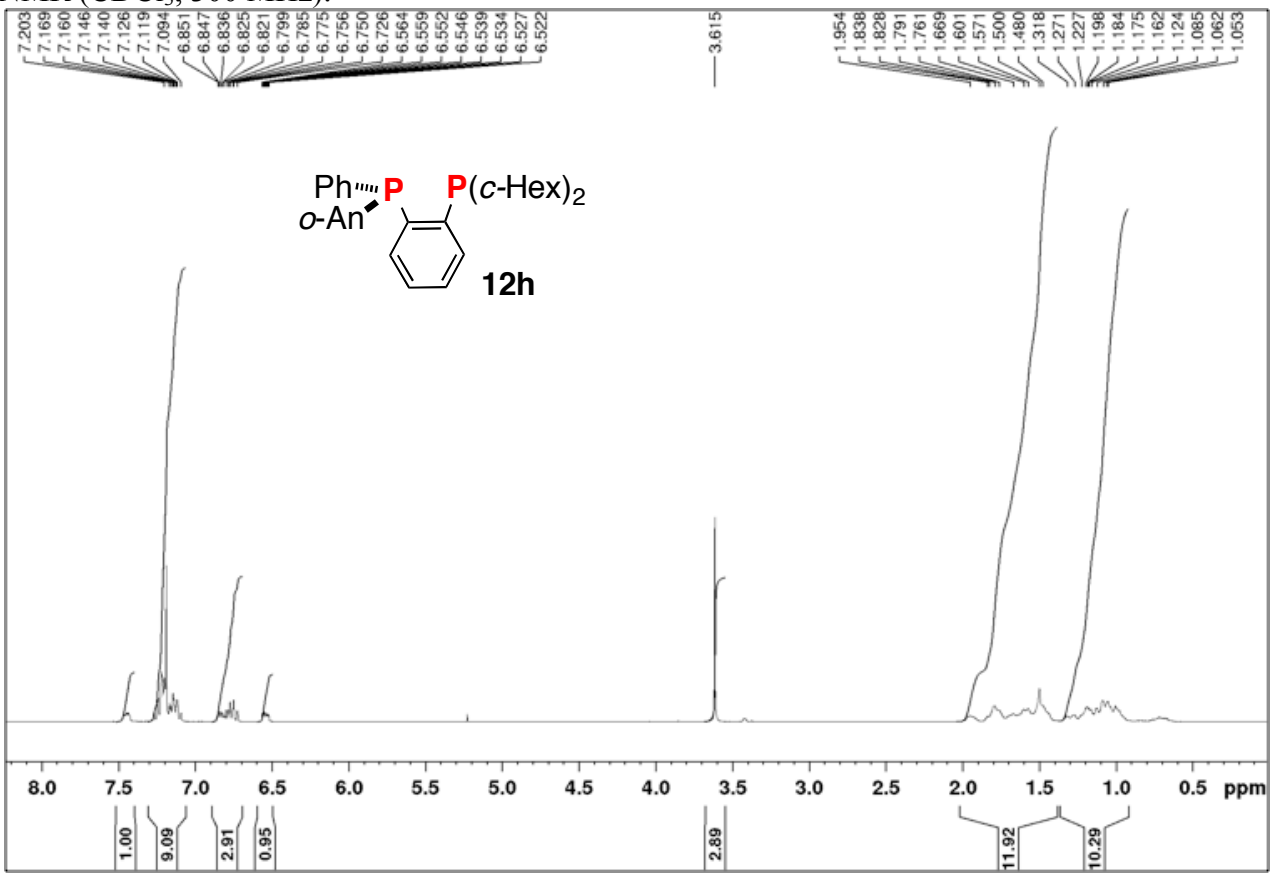


$^{19}F\{^{1}H\}$ NMR ($CDCl_3$, 470.5 MHz):

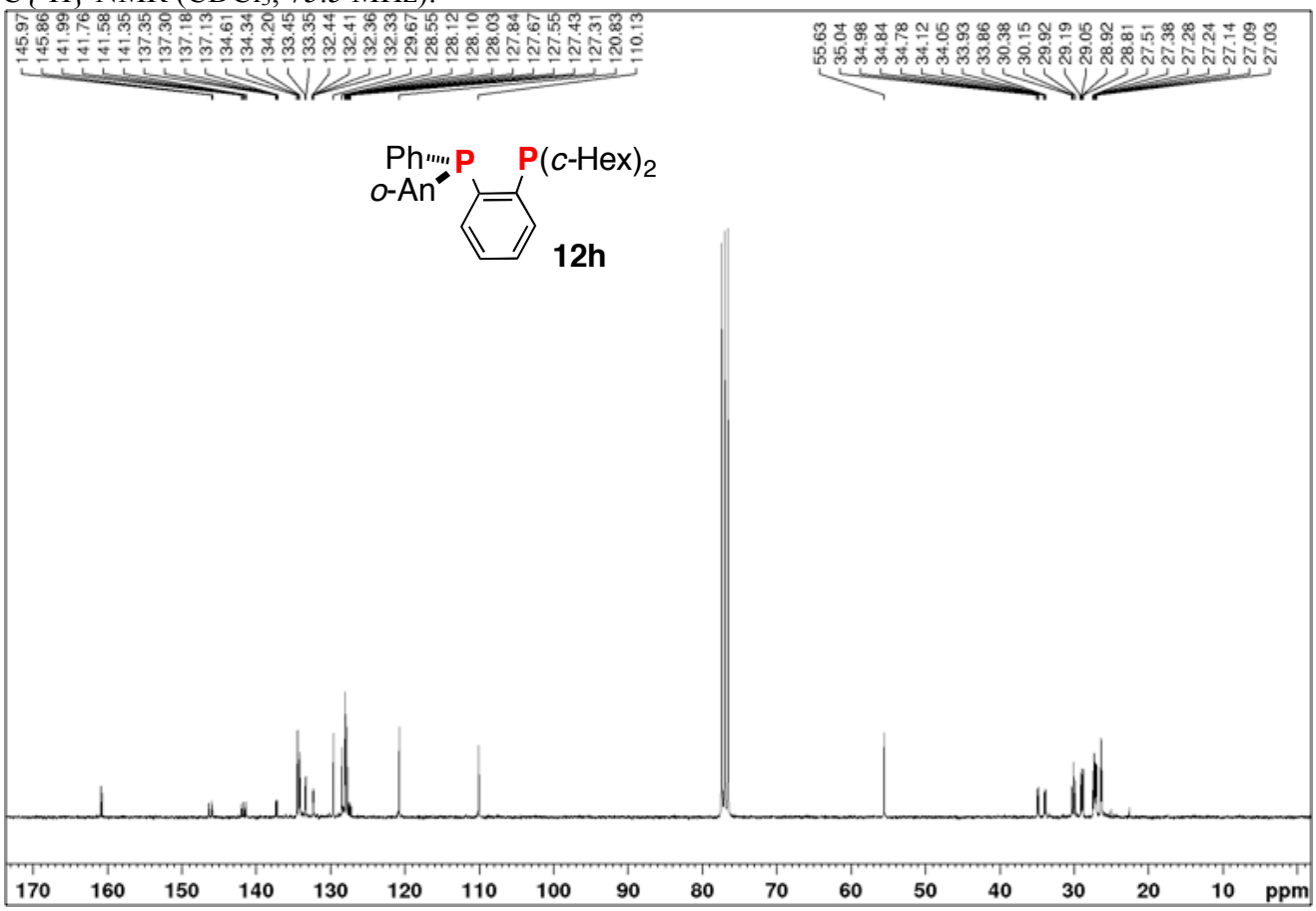


(*S*)-1-(*o*-Anisylphenylphosphino)-2-(di-cyclohexylphosphino)benzene **12h**

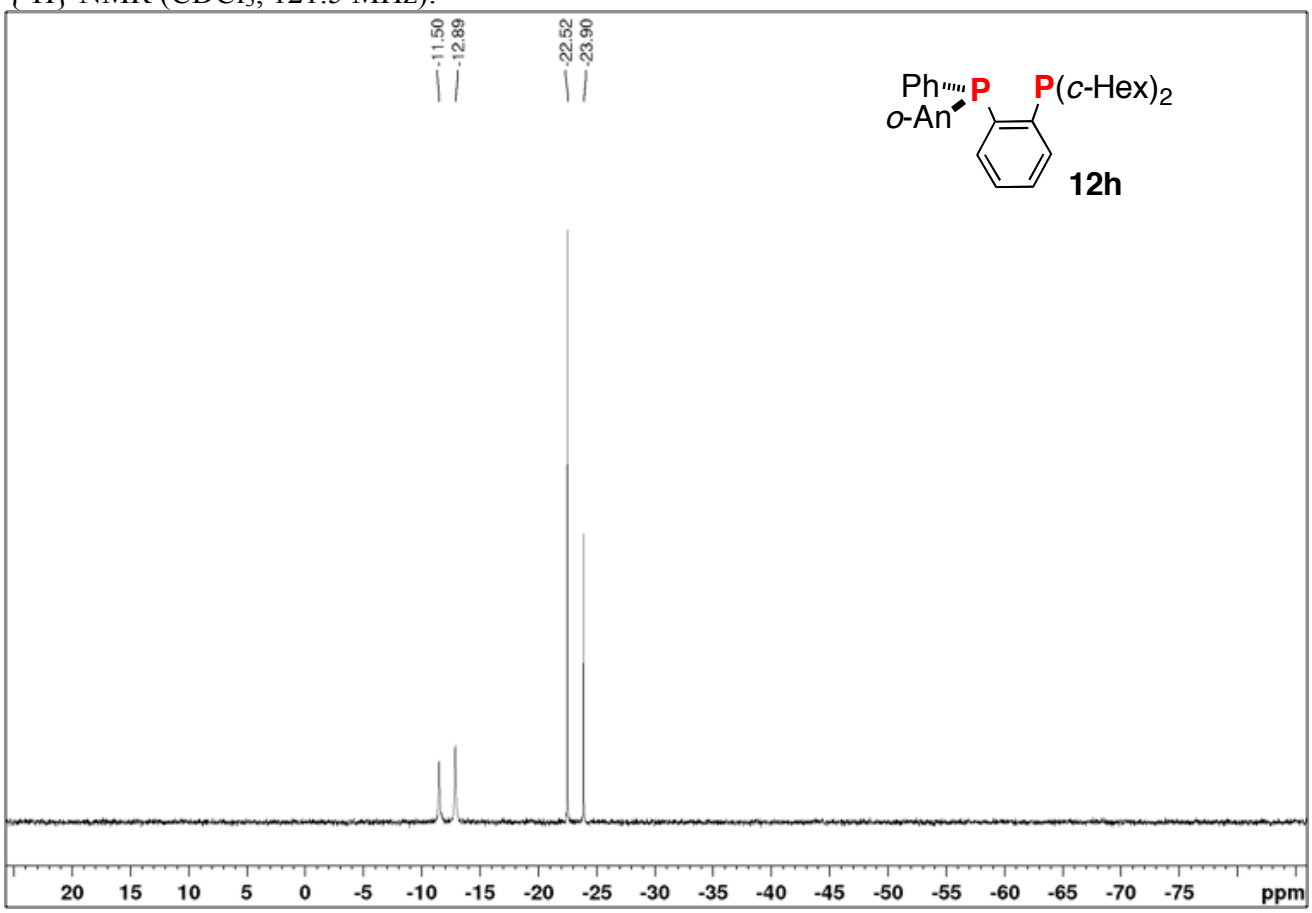
^{1}H NMR ($CDCl_3$, 300 MHz):



^{13}C{^{1}H} NMR ($CDCl_3$, 75.5 MHz):

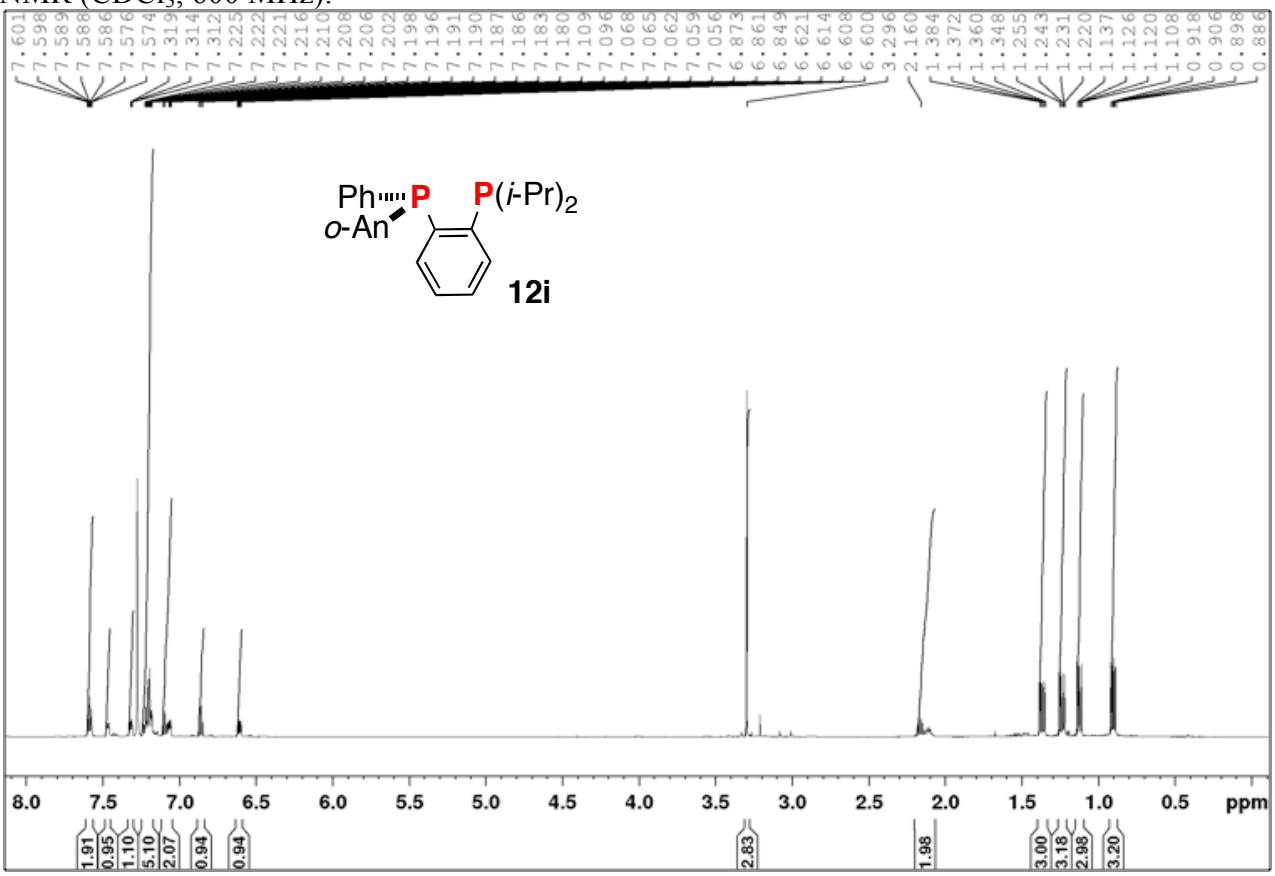


$^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 121.5 MHz):

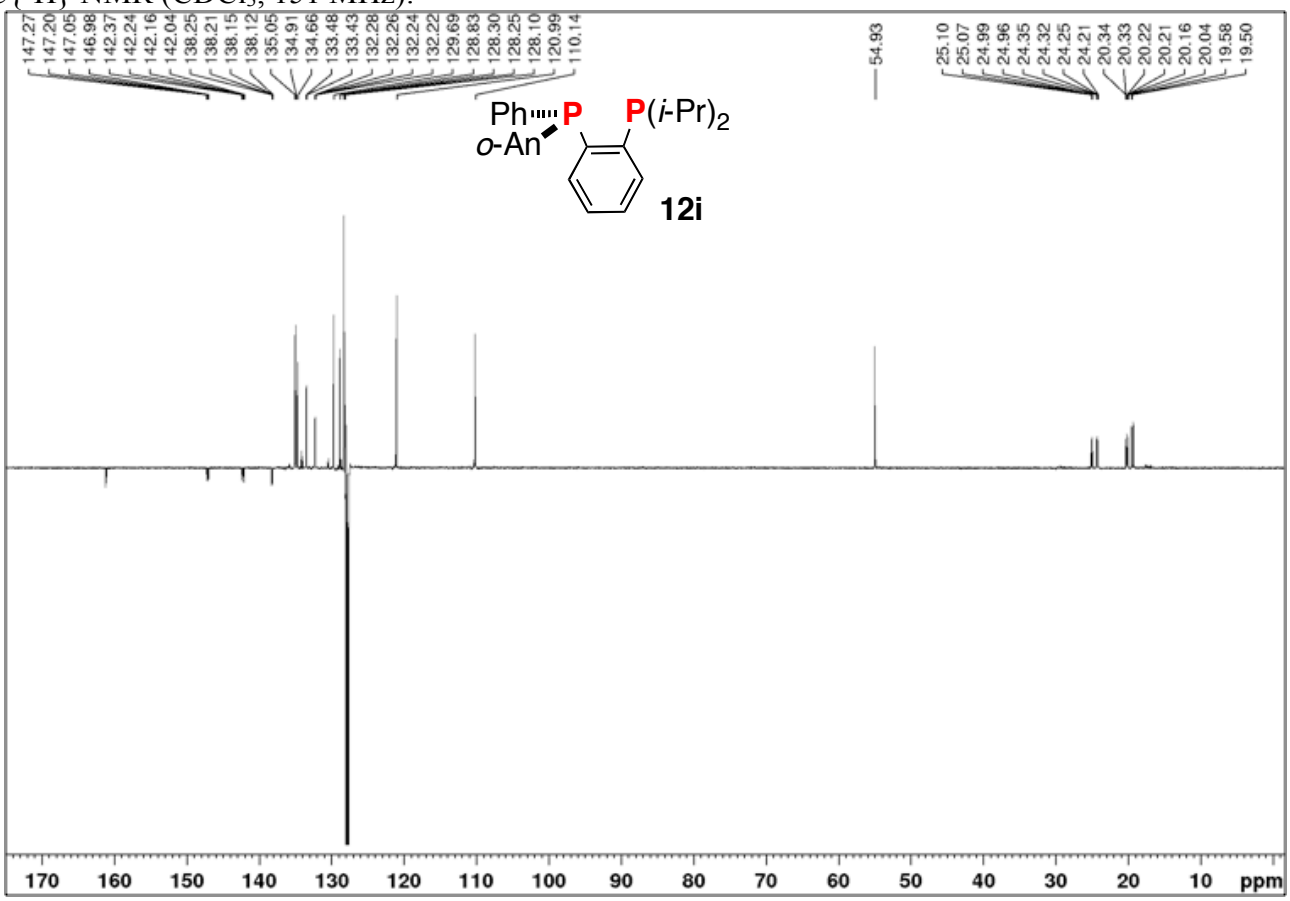


(*S*)-1-(*o*-Anisylphenylphosphino)-2-(di-isopropylphosphino)benzene **12i**

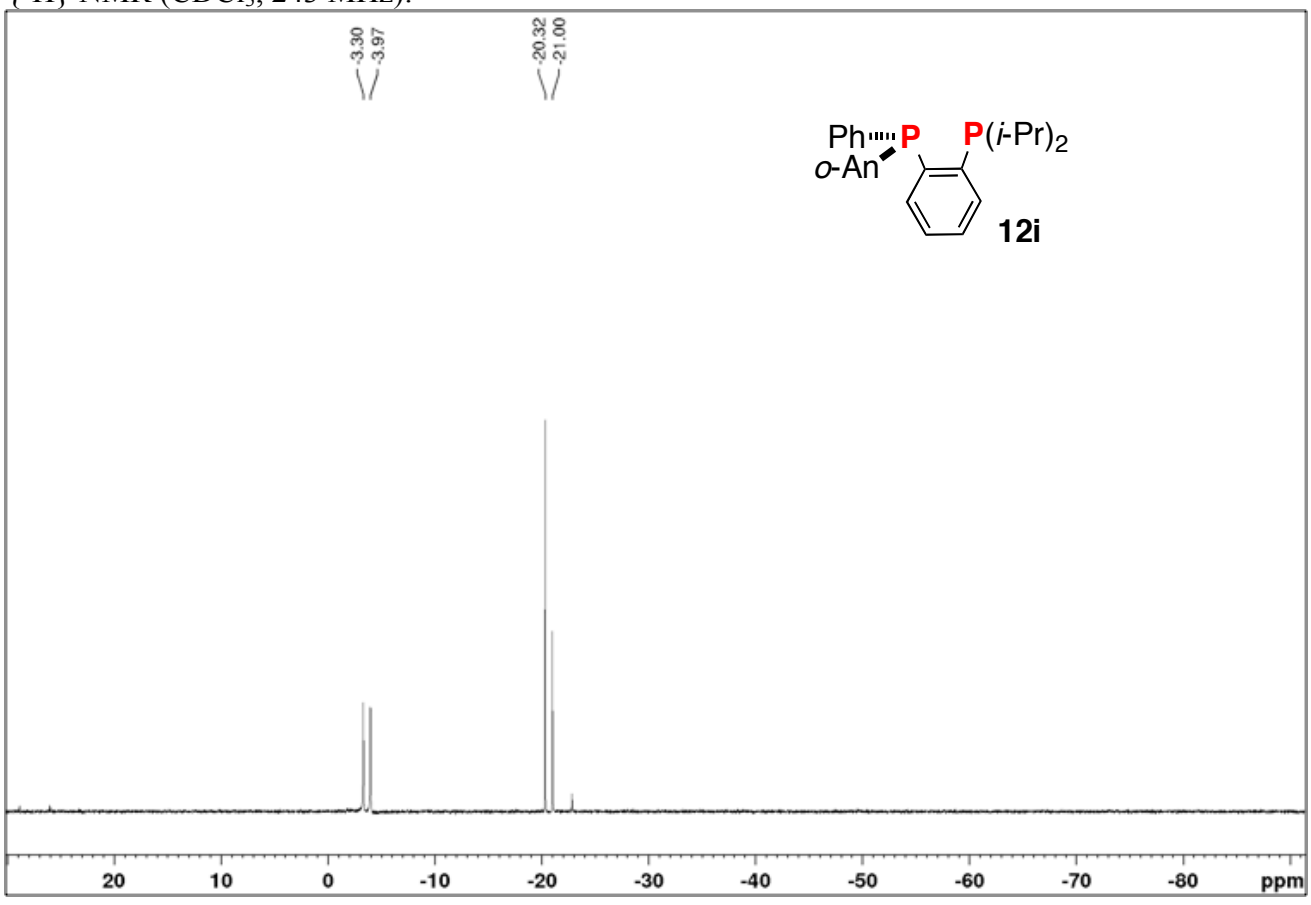
^{1}H NMR ($CDCl_3$, 600 MHz):



$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 151 MHz):

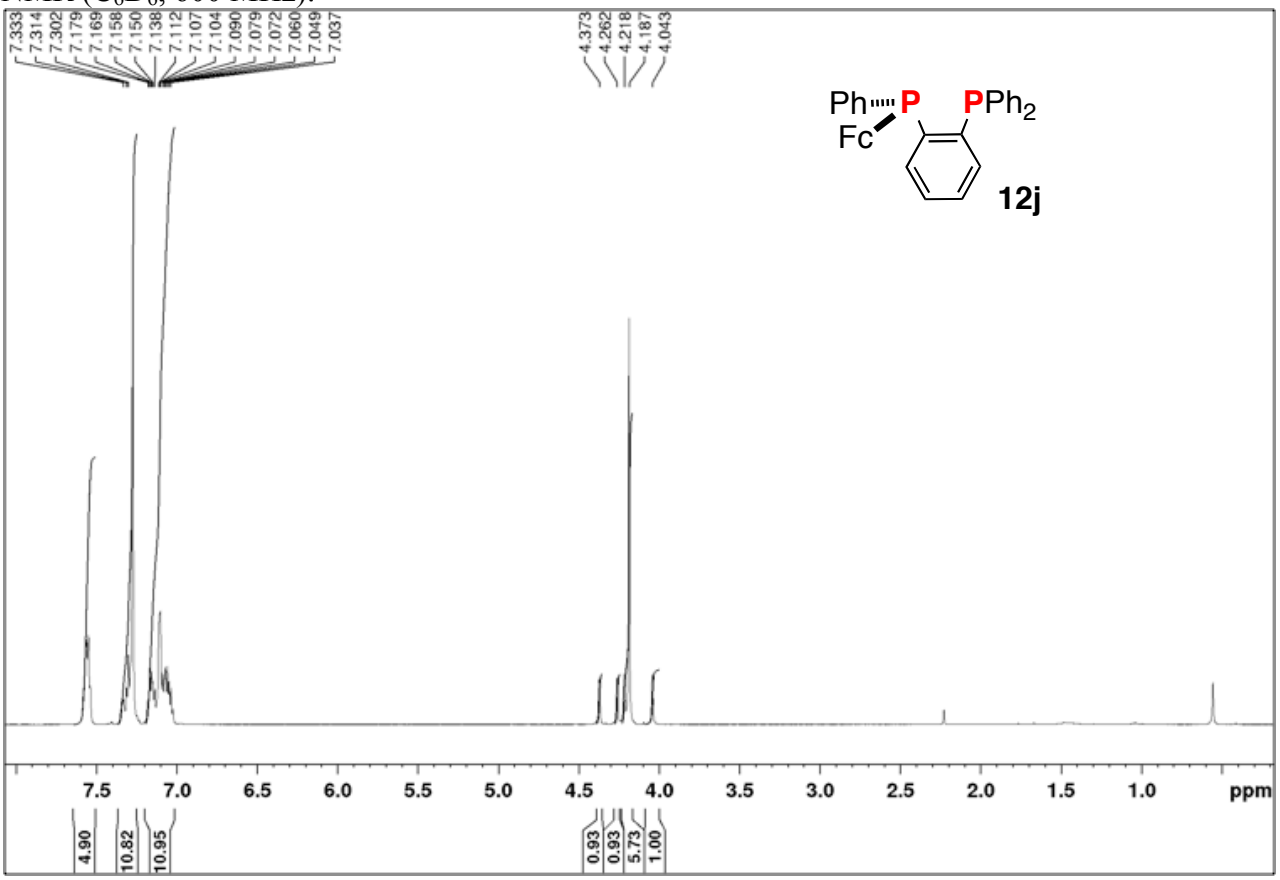


$^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 243 MHz):

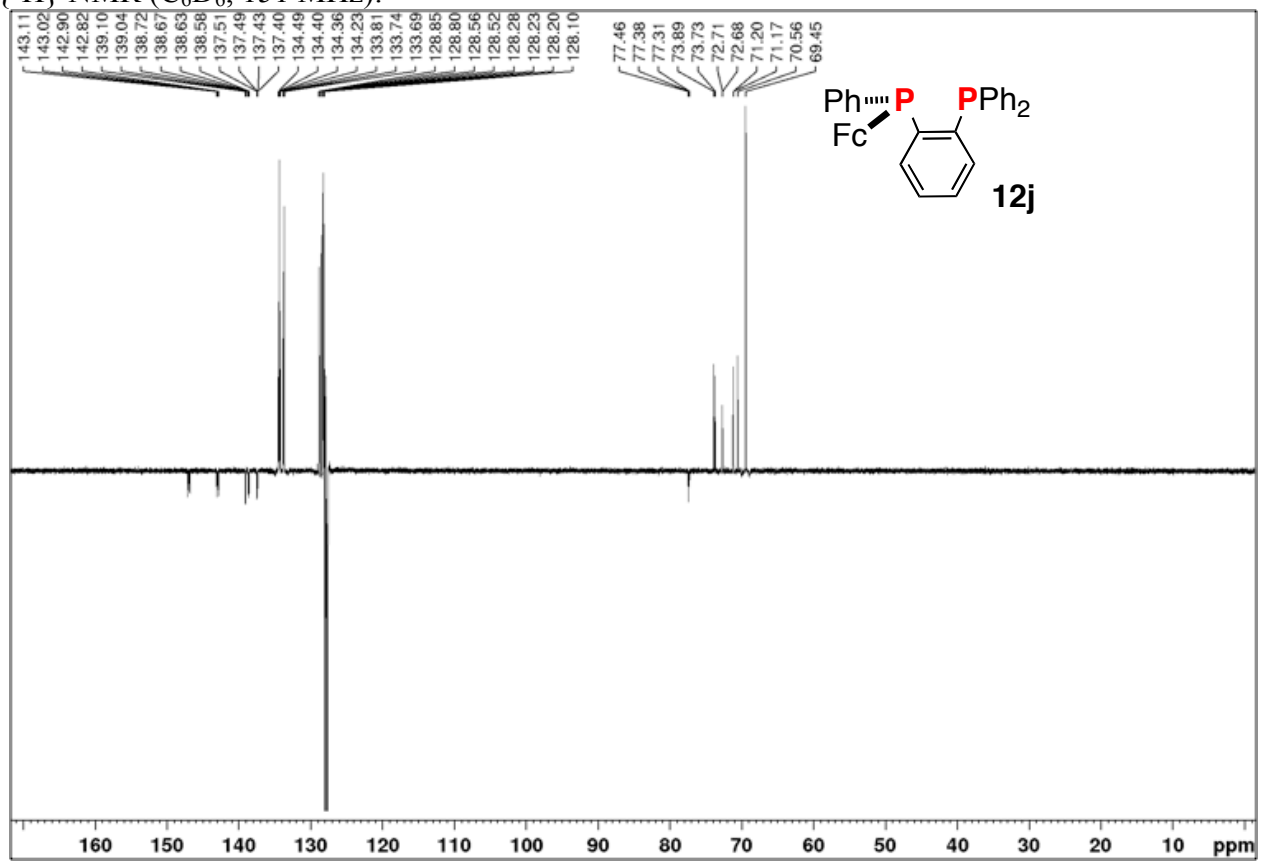


(*R*)-1-(Ferrocenylphenylphosphino)-2-(diphenylphosphino)benzene **12j**

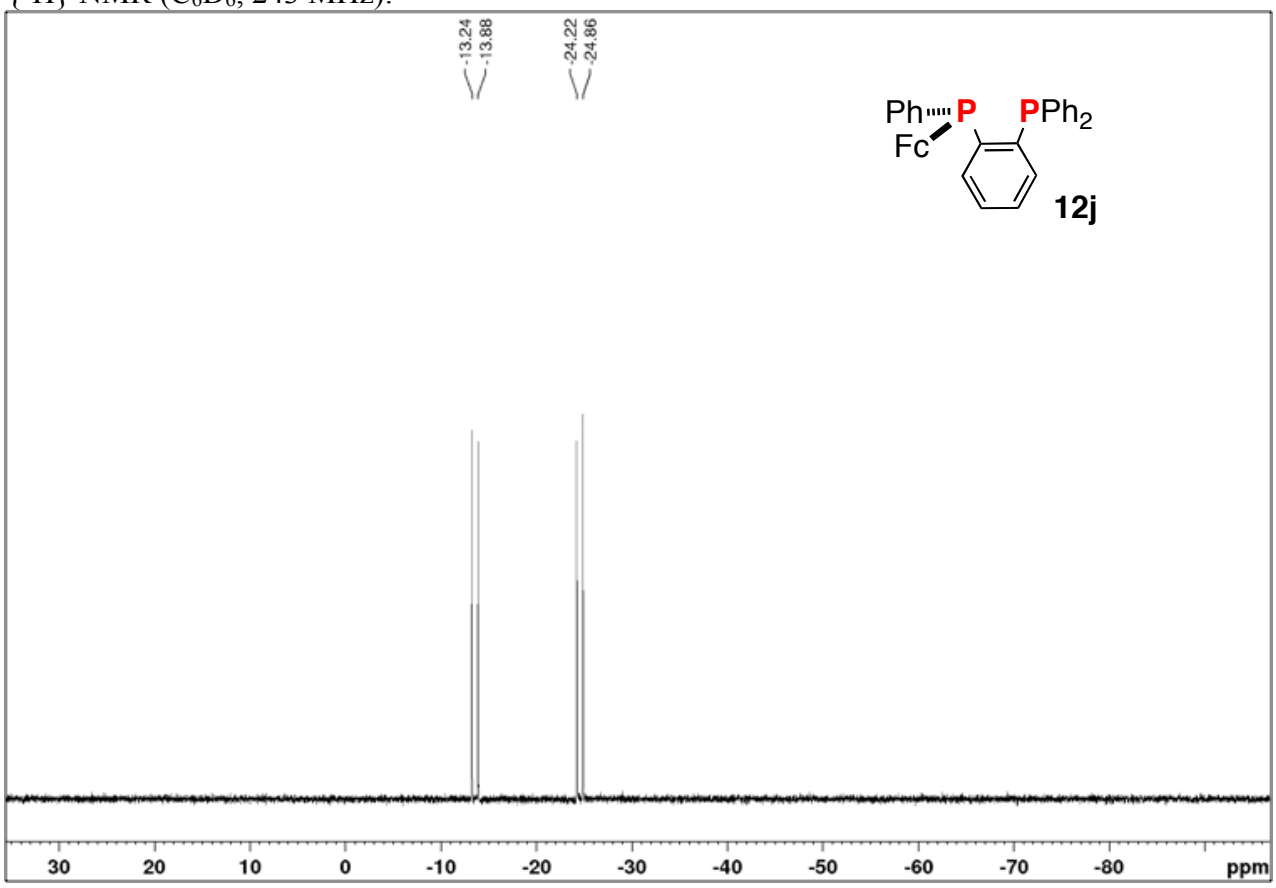
^{1}H NMR (C_6D_6, 600 MHz):



^{13}C{^{1}H} NMR (C_6D_6, 151 MHz):

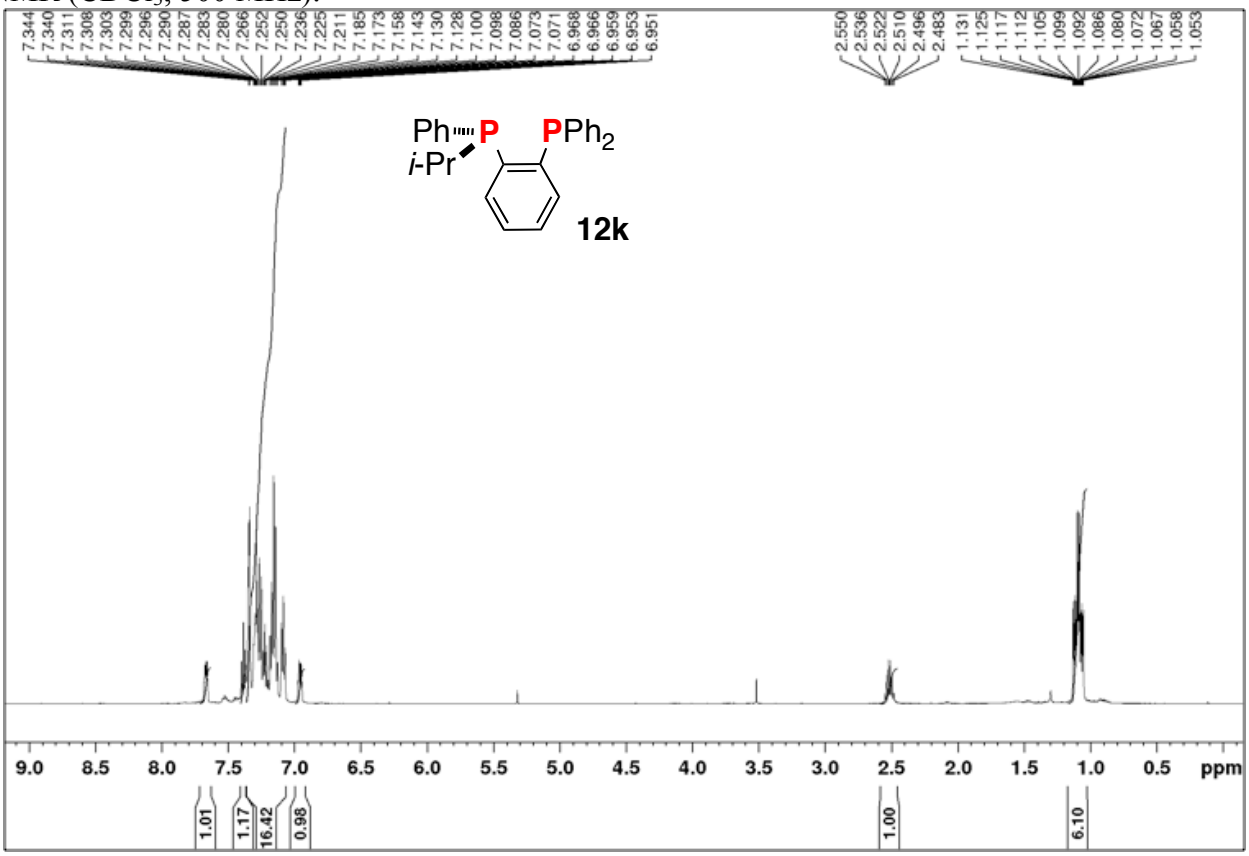


$^{31}P\{^{1}H\}$ NMR (C_6D_6, 243 MHz):

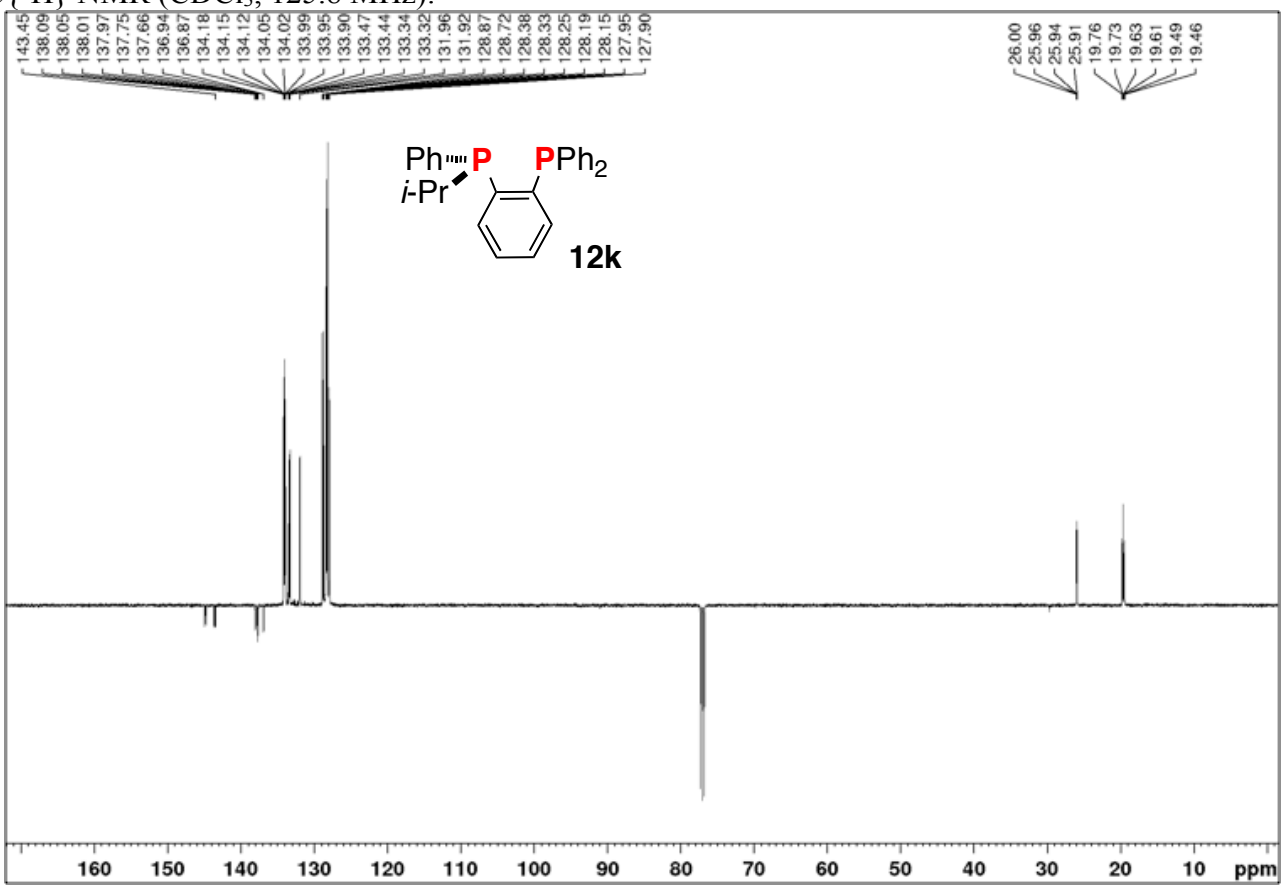


(*R*)-1-(Phenyl-*i*-propylphosphino)-2-(diphenylphosphino)benzene **12k**

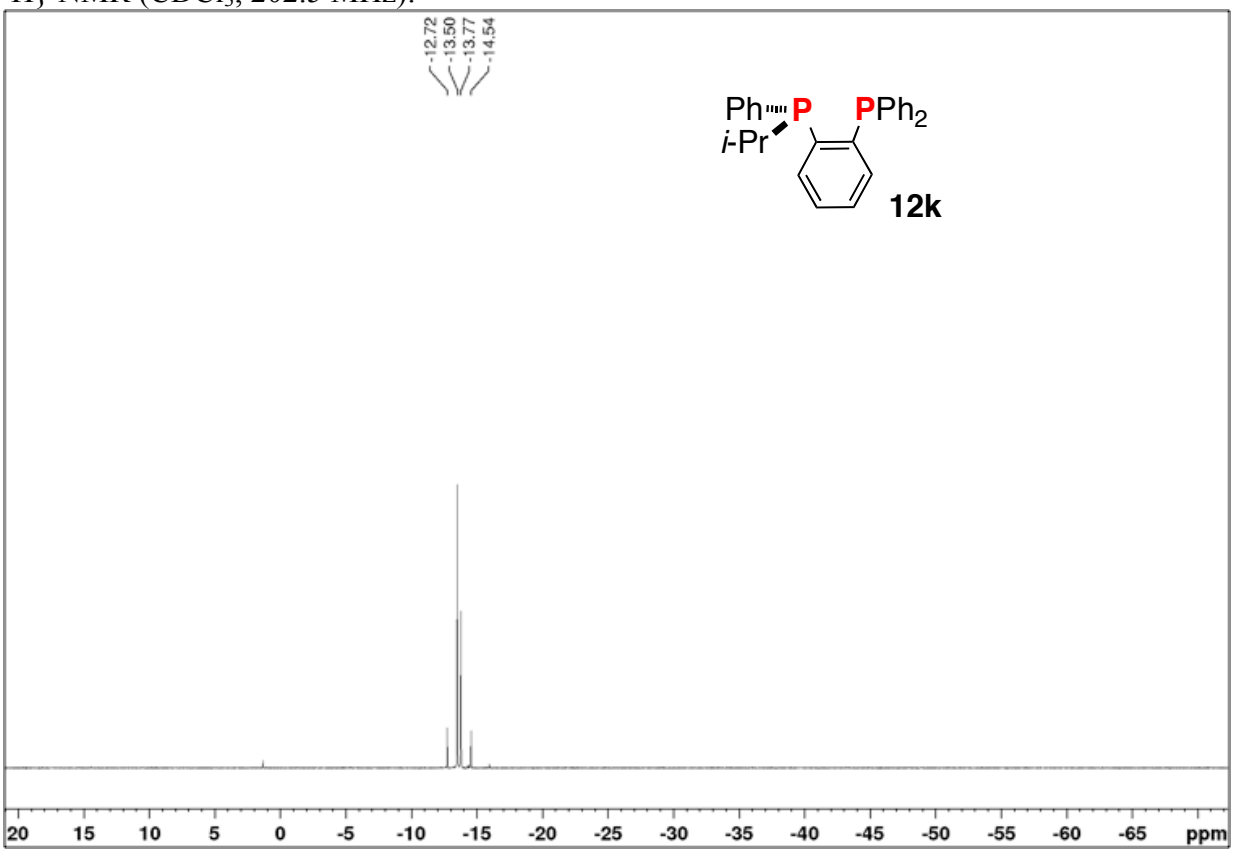
^{1}H NMR ($CDCl_3$, 500 MHz):



$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125.8 MHz):

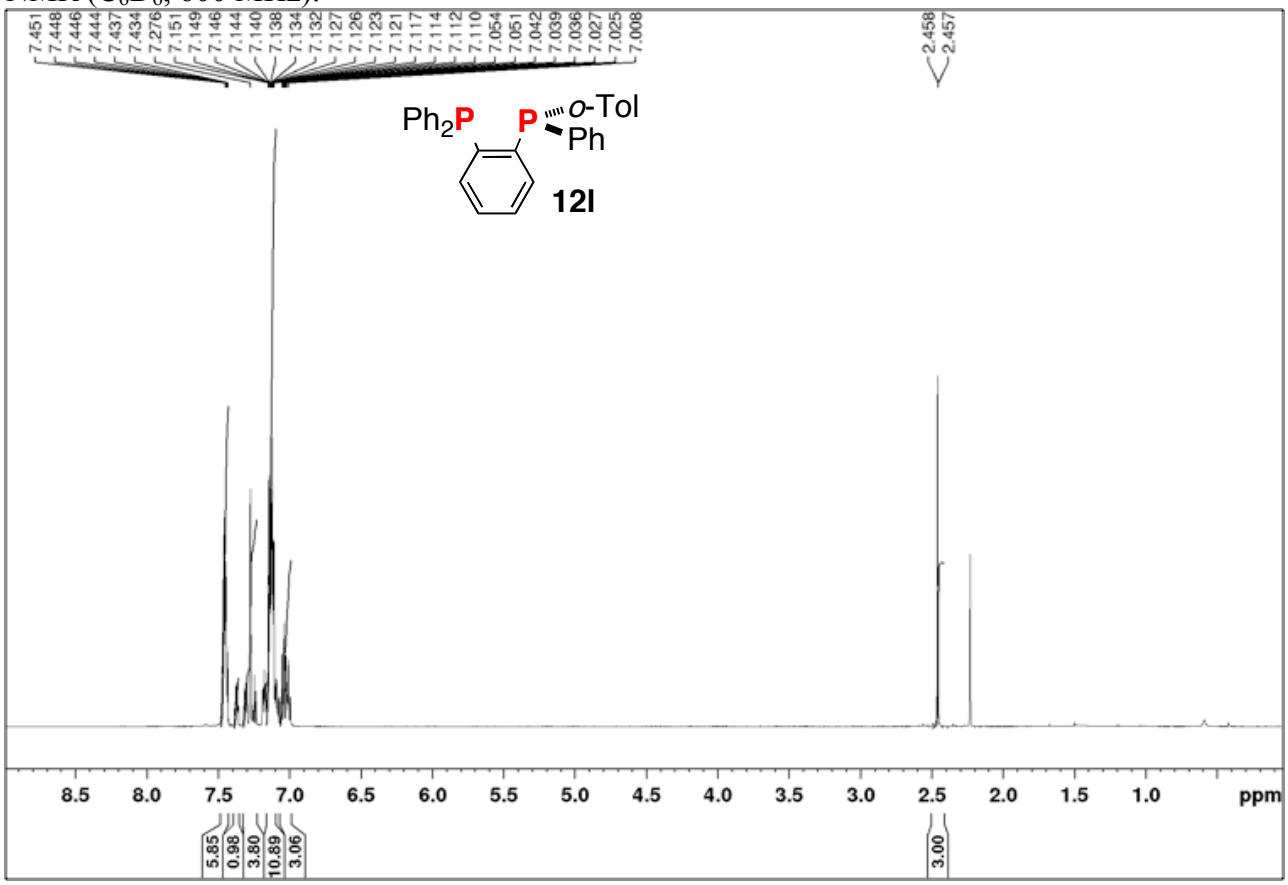


$^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 202.5 MHz):

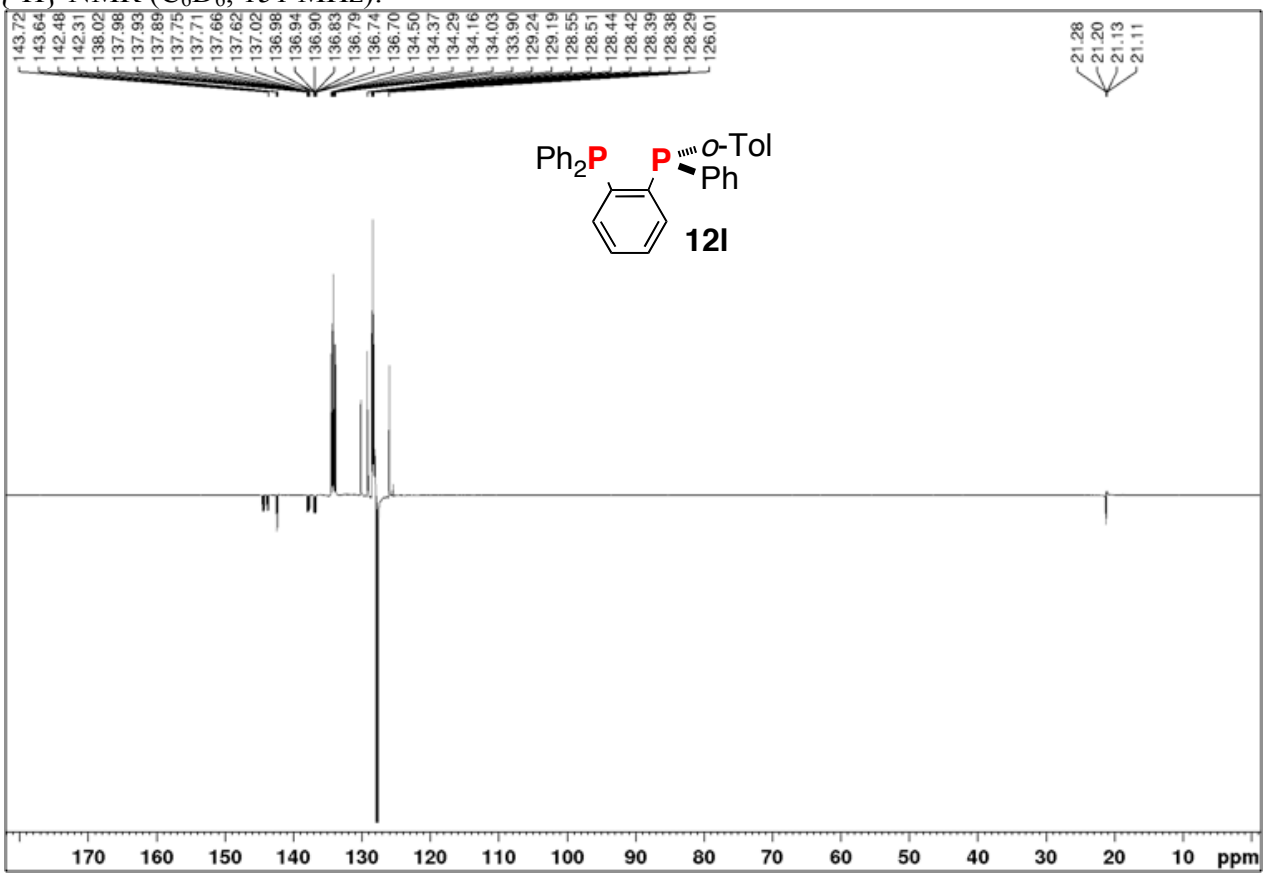


(*S*)-1-(Phenyl-*o*-tolylphosphino)-2-(diphenylphosphino)benzene **12l**

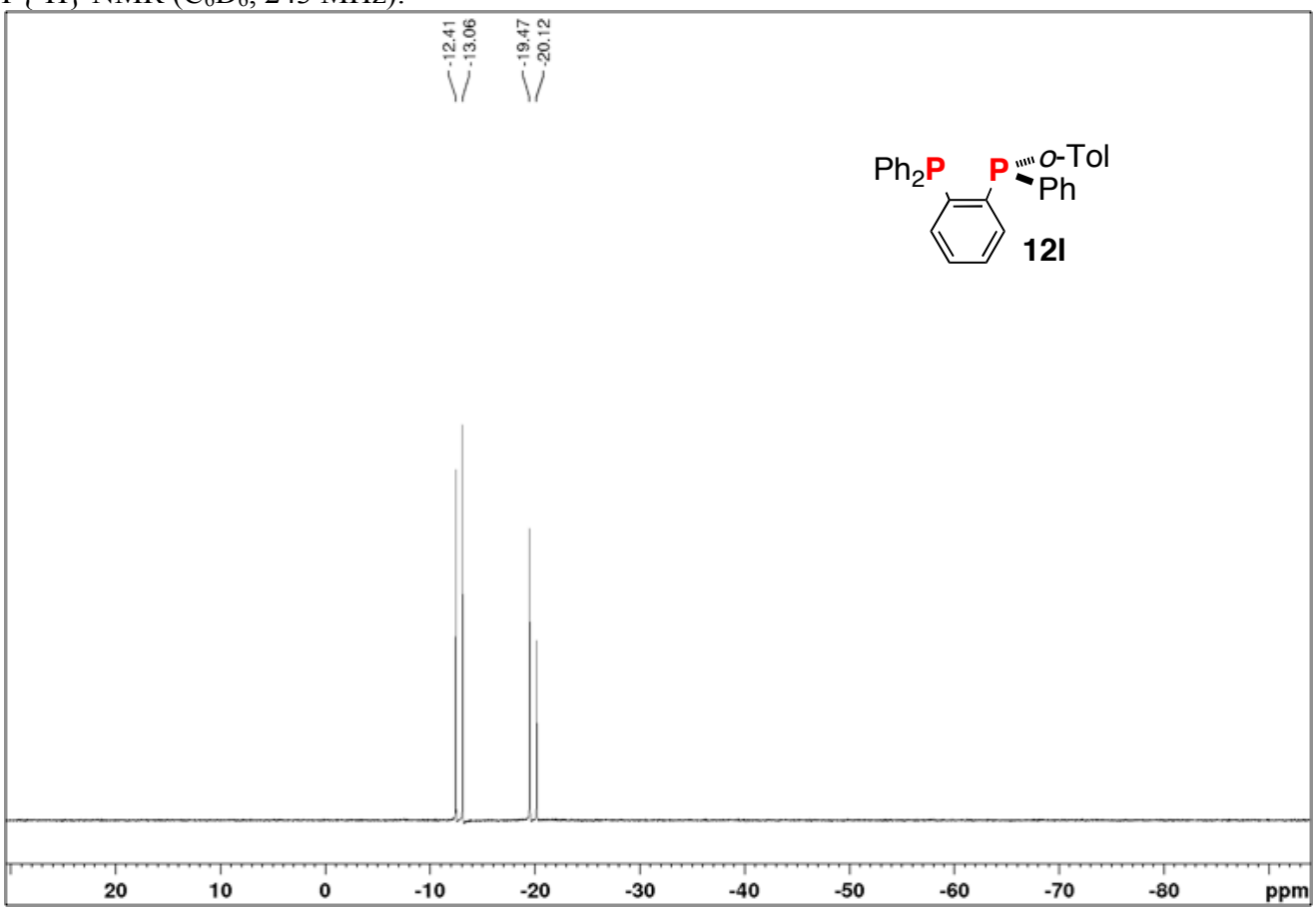
^{1}H NMR (C_6D_6, 600 MHz):



^{13}C{^{1}H} NMR (C_6D_6, 151 MHz):

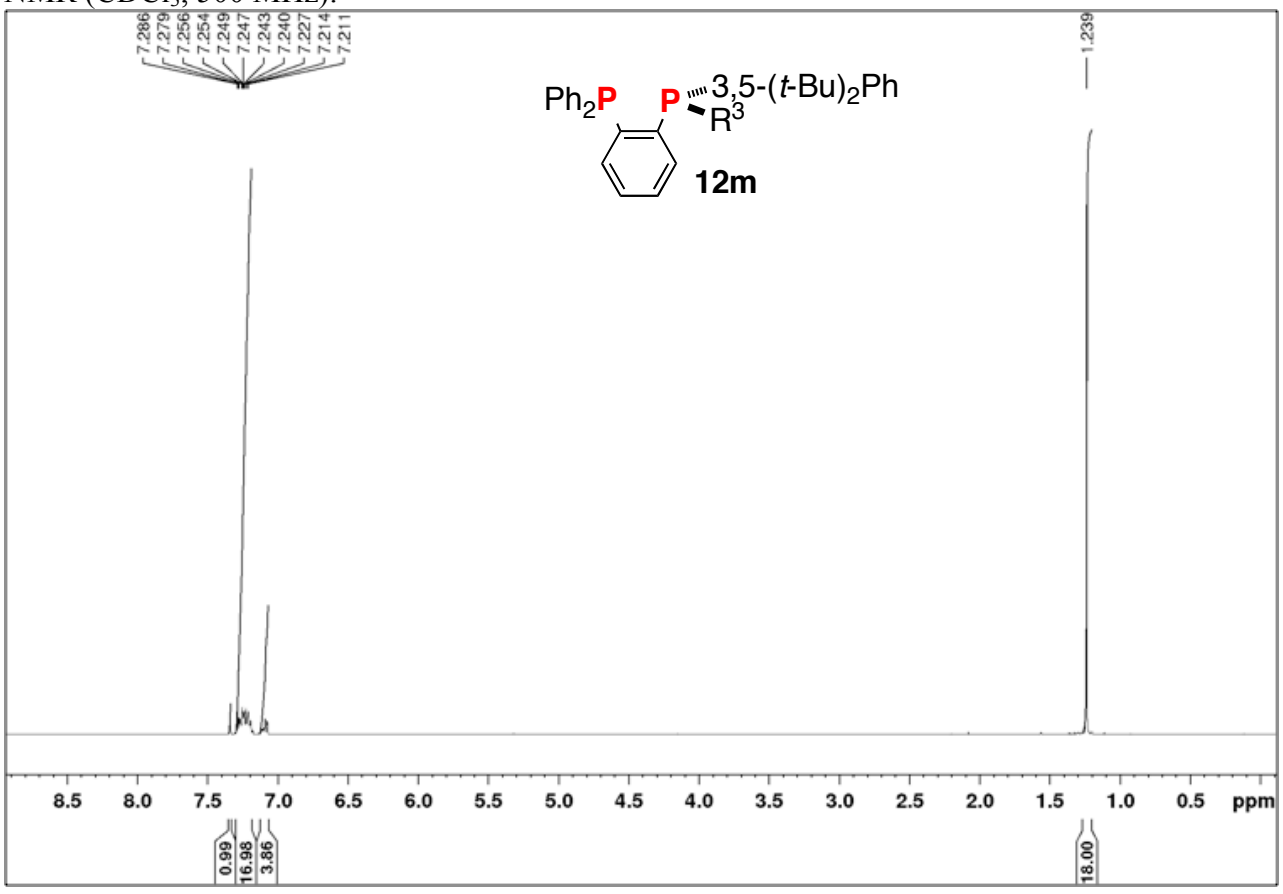


$^{31}P\{^{1}H\}$ NMR (C_6D_6, 243 MHz):

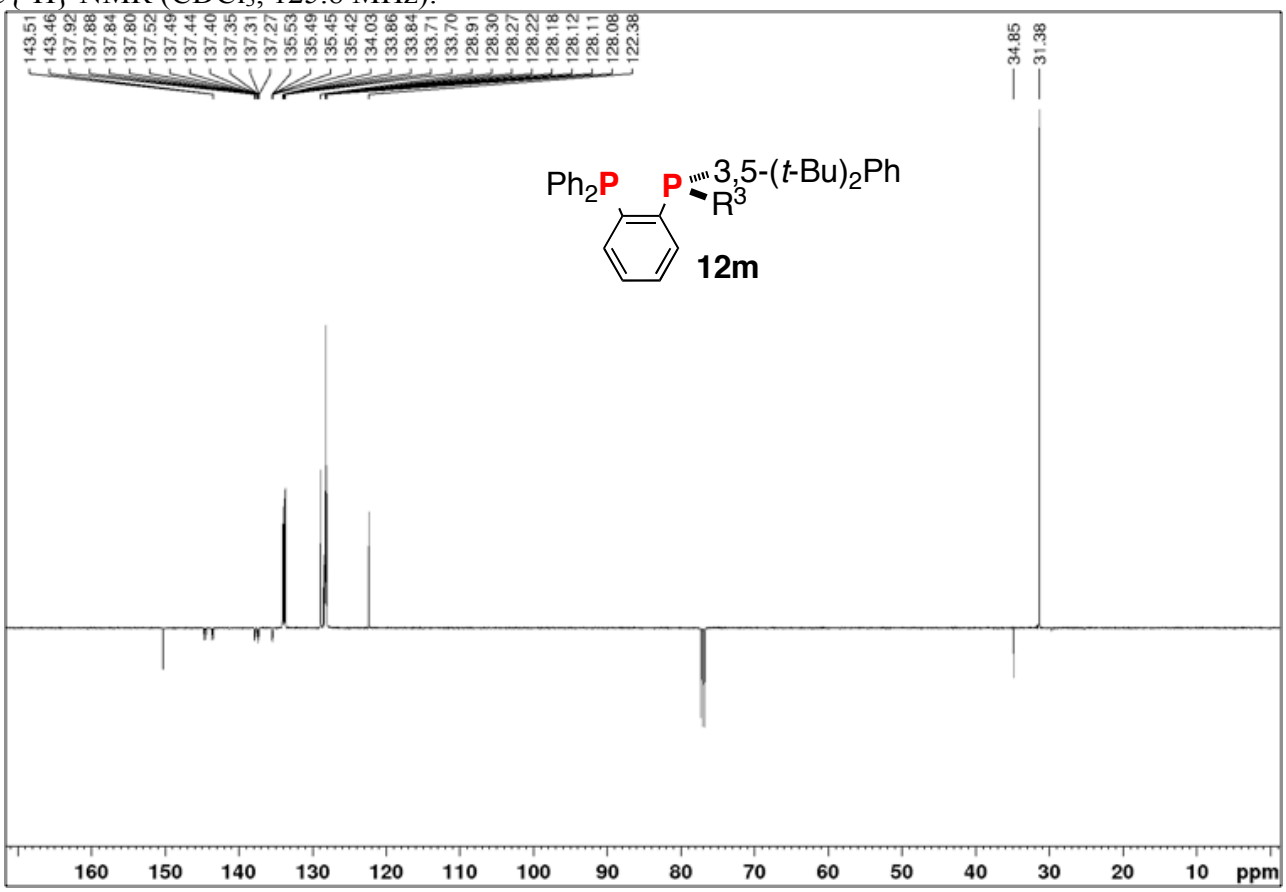


(*S*)-1-(3,5-Di-*tert*-butylphenyl)phenylphosphino)-2-(diphenylphosphino)benzene **12m**

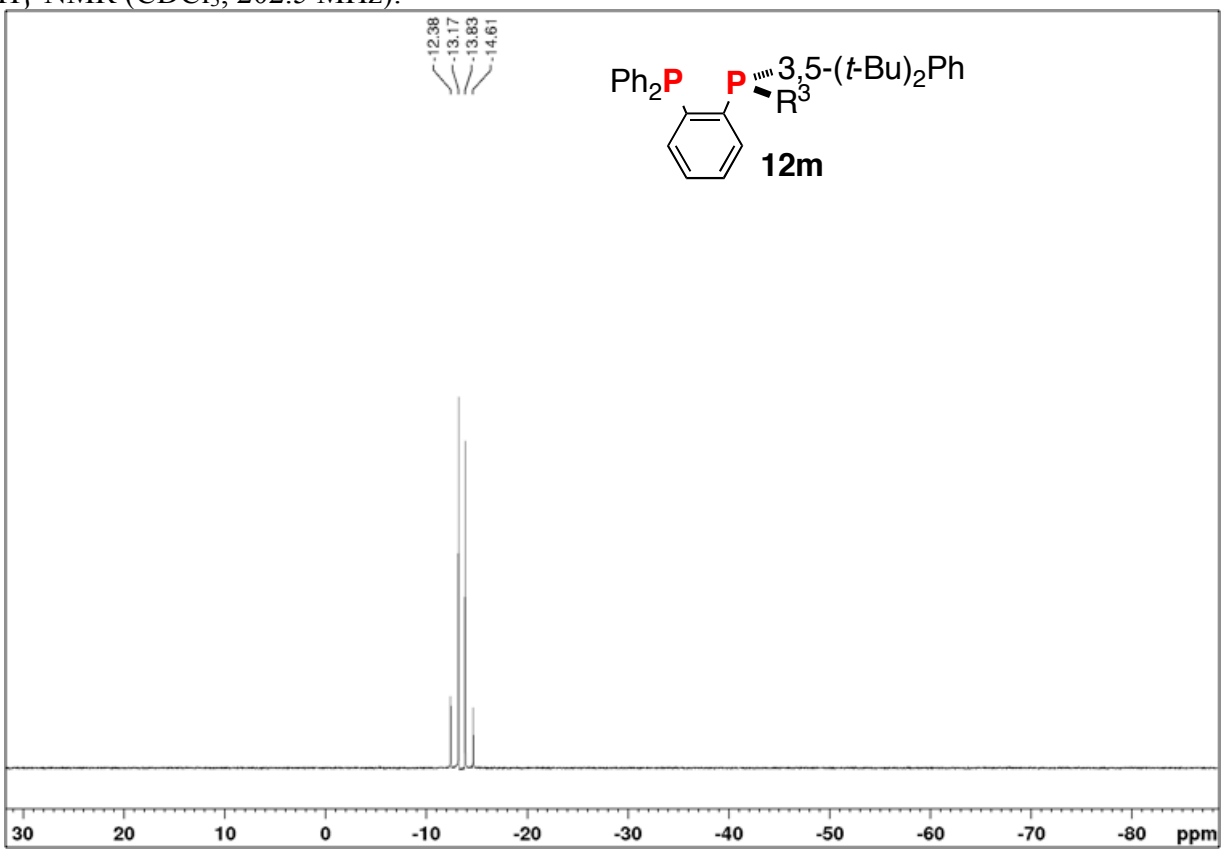
^{1}H NMR ($CDCl_3$, 500 MHz):



$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125.8 MHz):

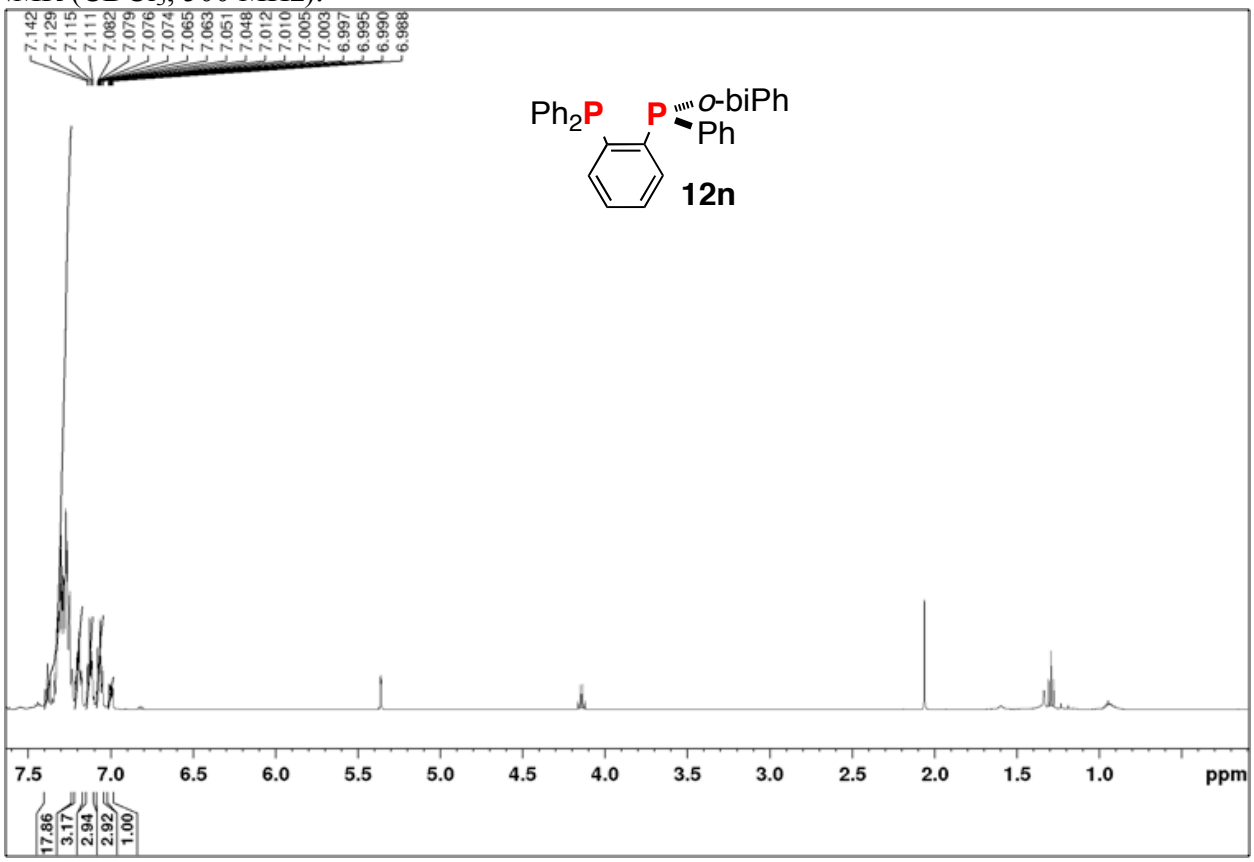


$^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 202.5 MHz):

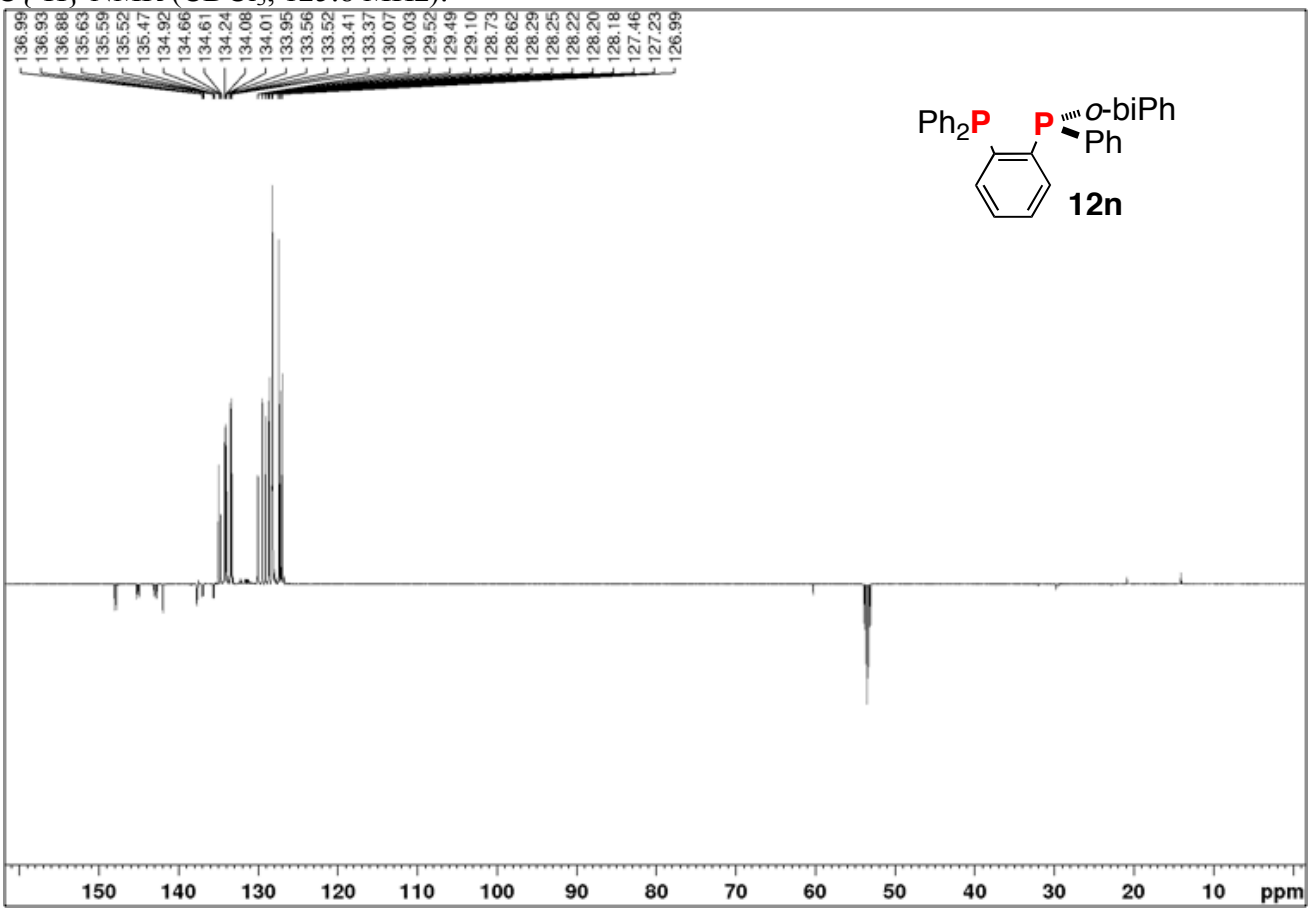


(*S*)-1-[(*o*-Biphenyl)phenylphosphino]-2-(diphenylphosphino)benzene **12n**

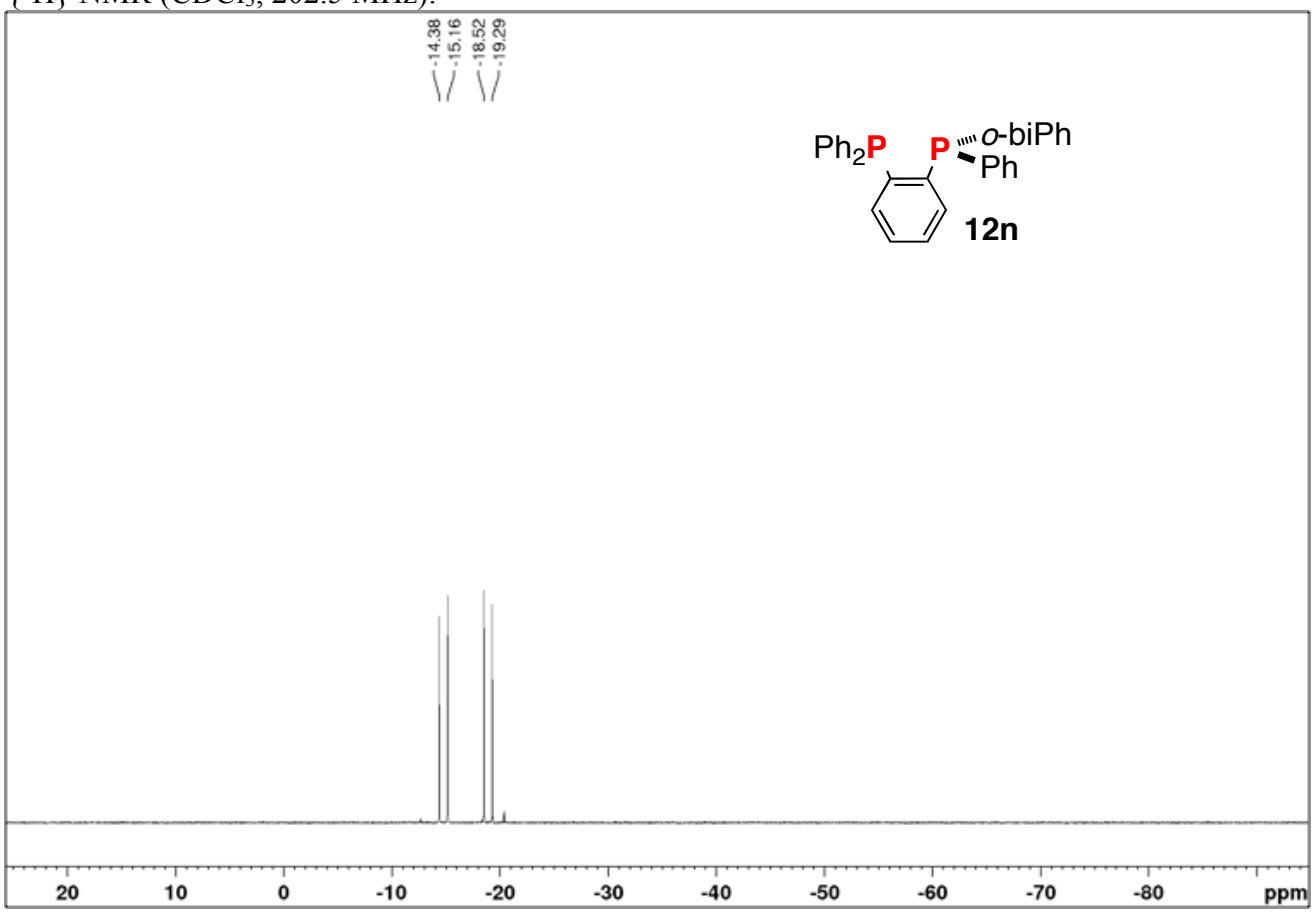
^{1}H NMR ($CDCl_3$, 500 MHz):



^{13}C{^{1}H} NMR ($CDCl_3$, 125.8 MHz):

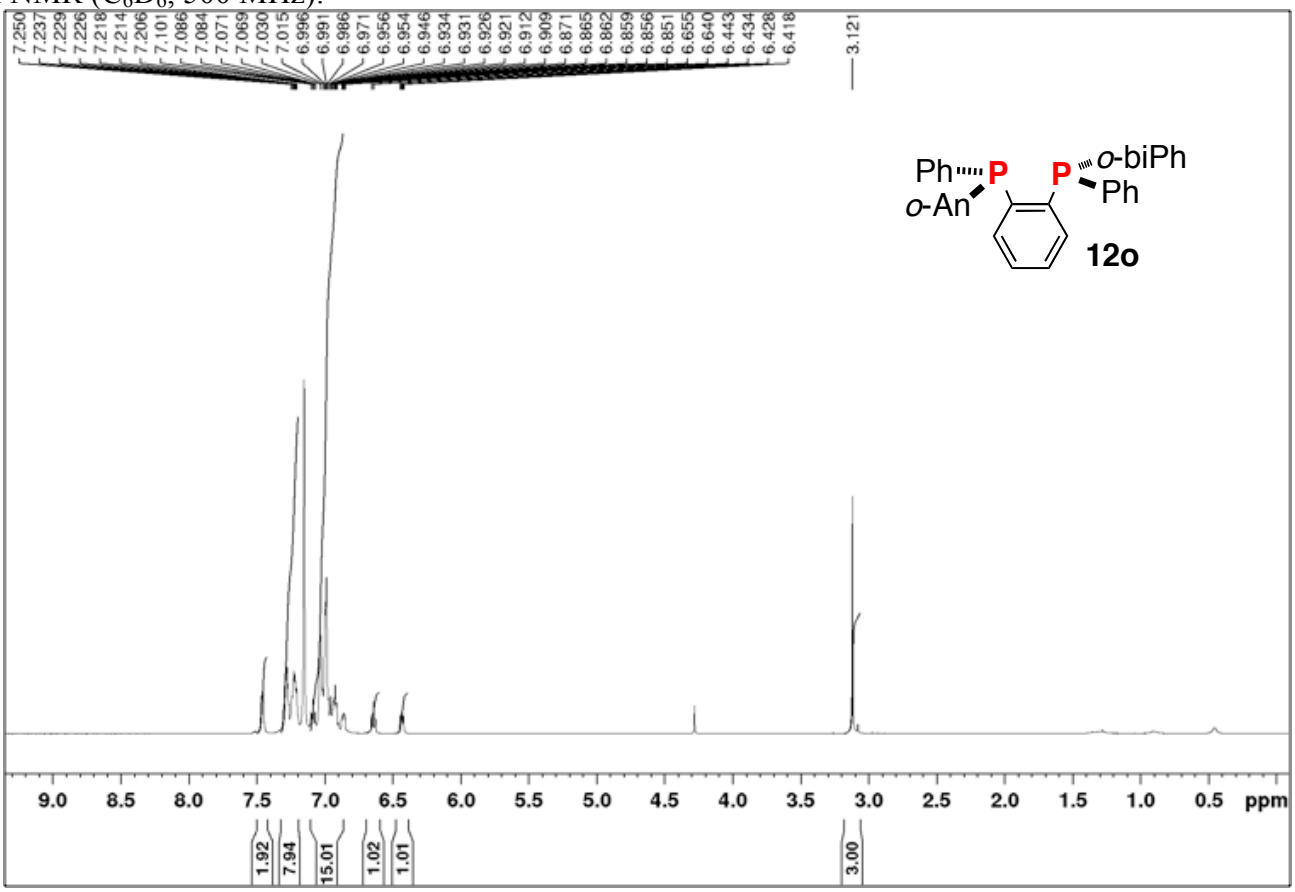


$^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 202.5 MHz):

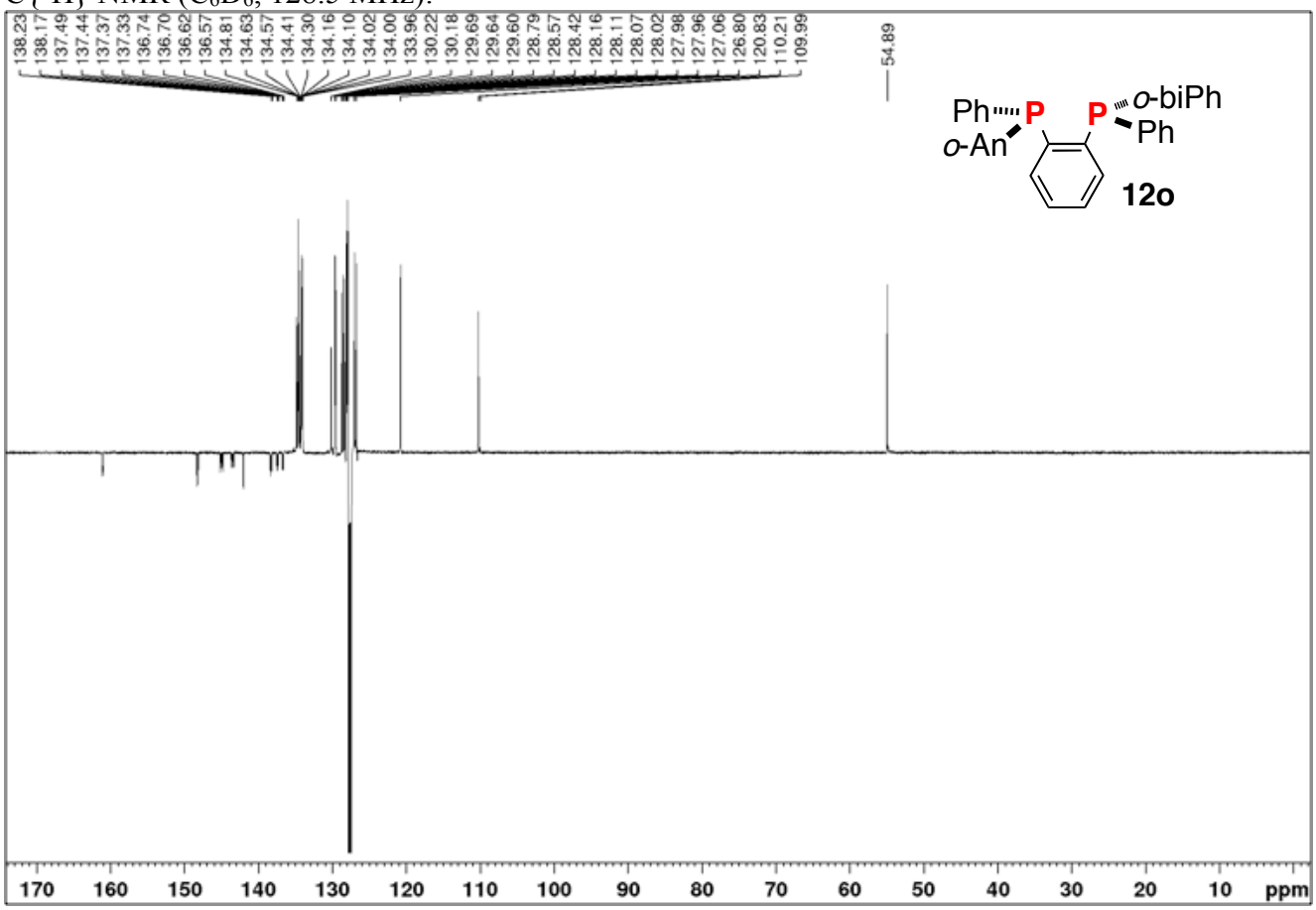


(1*S*,2*S*)-1-(*o*-Anisylphenylphosphino)-2-[(*o*-biphenyl)phenylphosphino]benzene **12o**

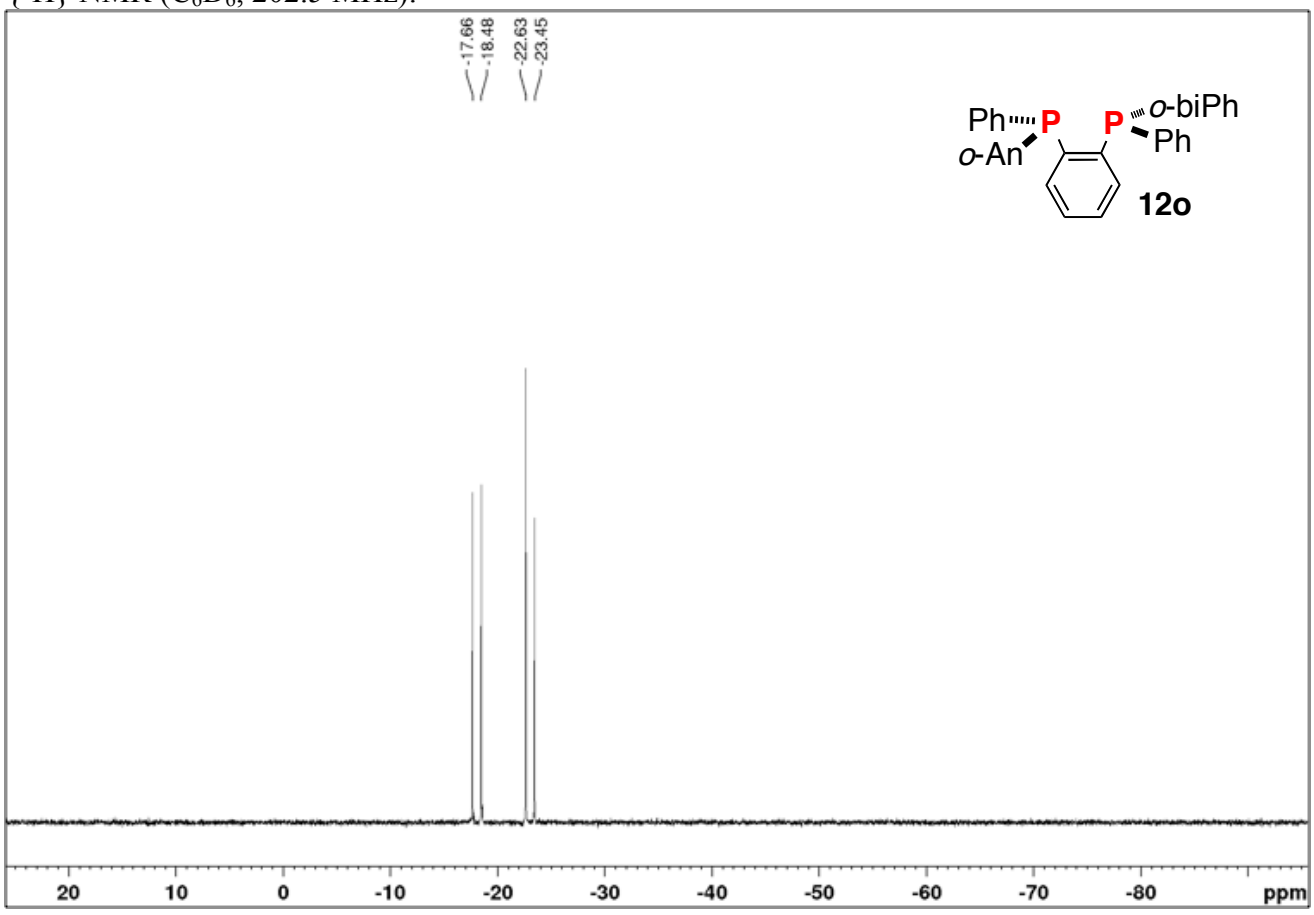
^{1}H NMR (C_6D_6, 500 MHz):



$^{13}C\{^{1}H\}$ NMR (C_6D_6, 128.5 MHz):

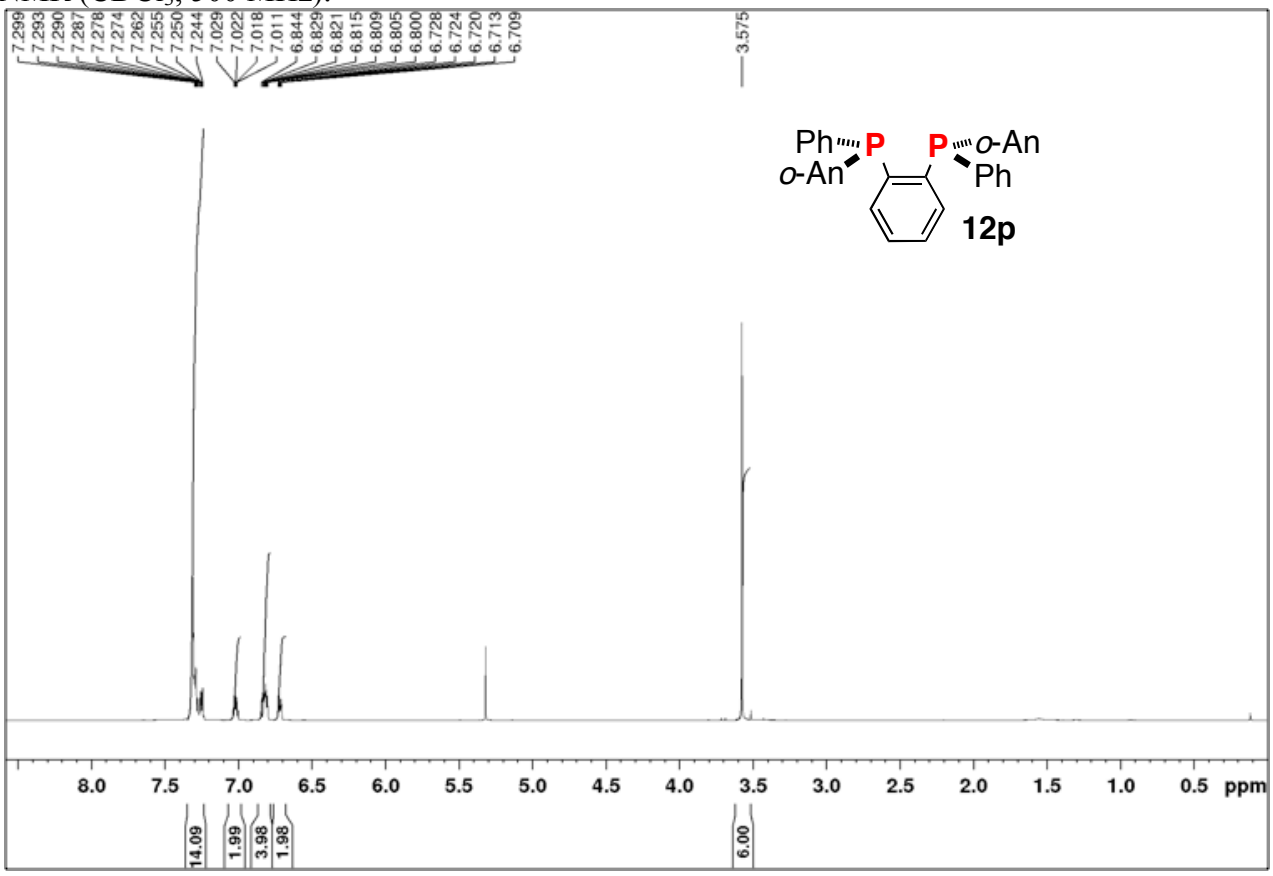


$^{31}P\{^{1}H\}$ NMR (C_6D_6, 202.5 MHz):

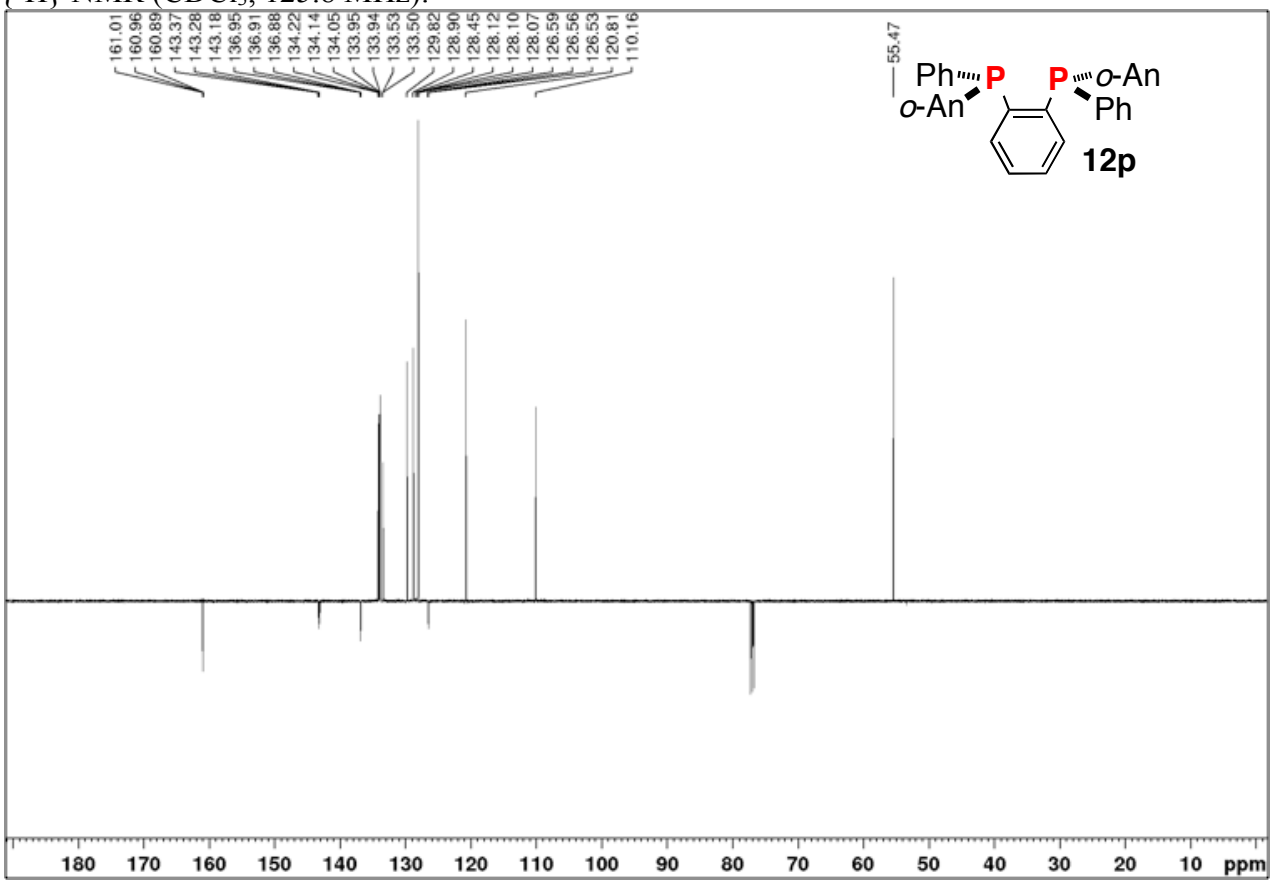


(1*S*,2*S*)-1,2-Bis(*o*-anisylphenylphosphino)benzene **12p**

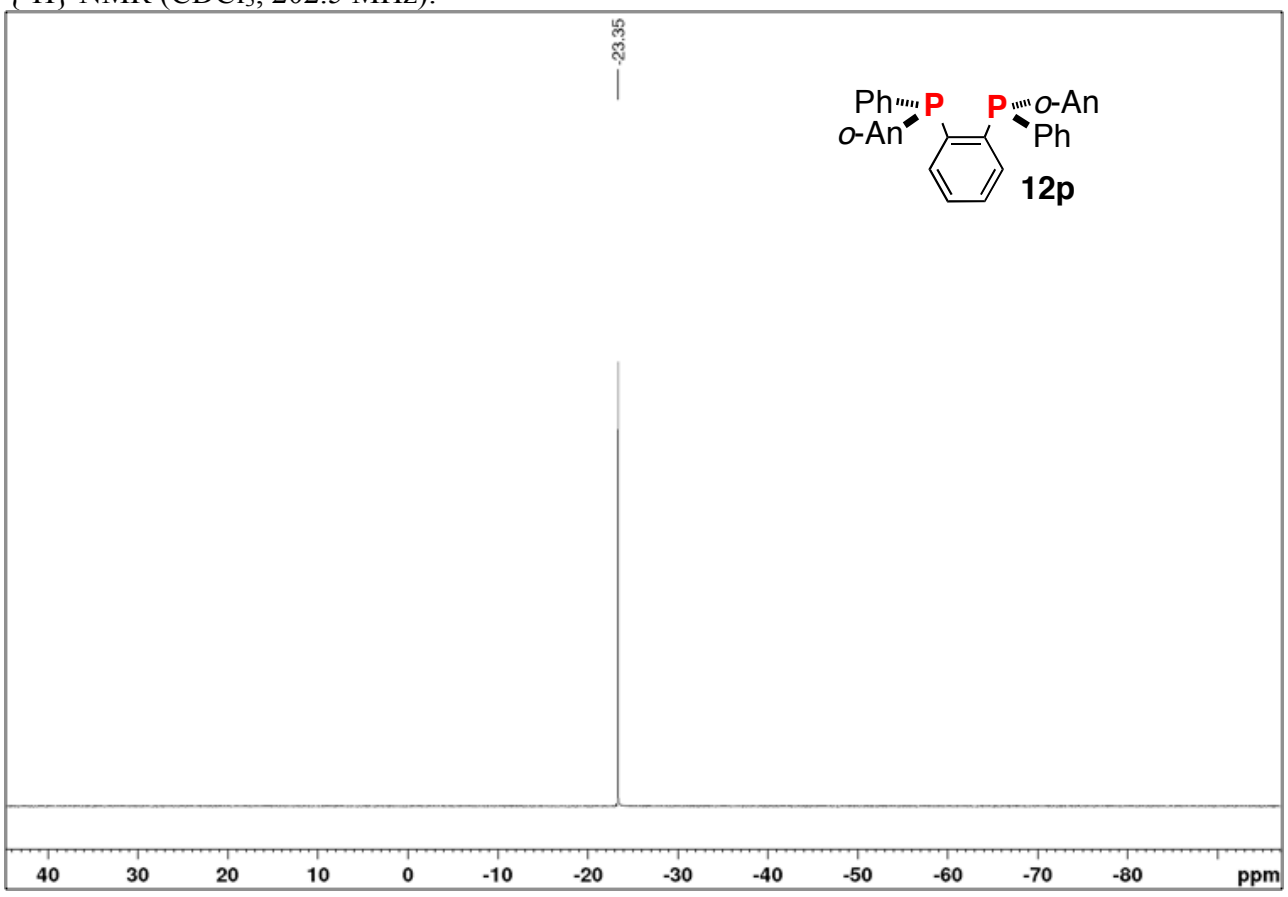
^{1}H NMR ($CDCl_3$, 500 MHz):



^{13}C{^{1}H} NMR ($CDCl_3$, 125.8 MHz):

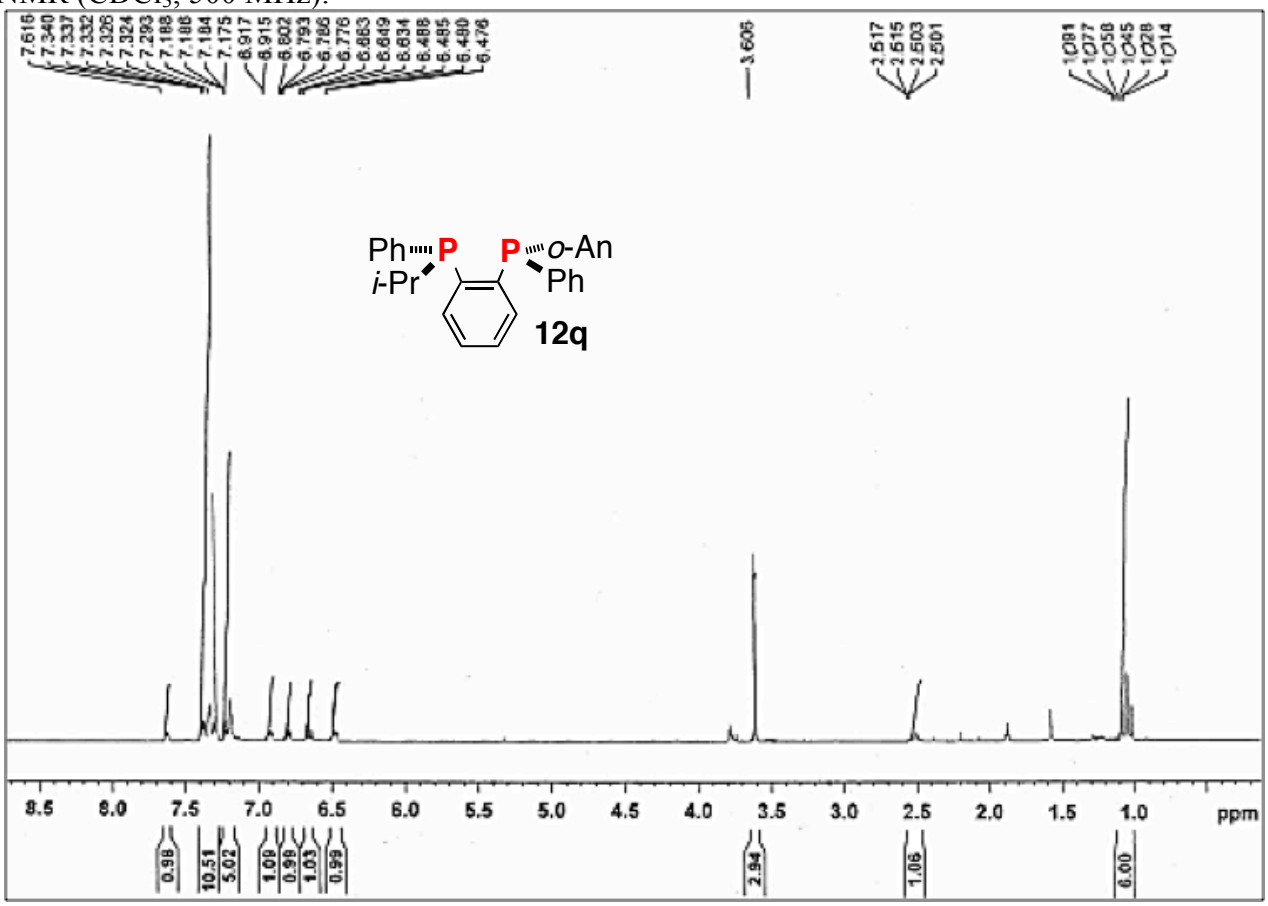


$^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 202.5 MHz):

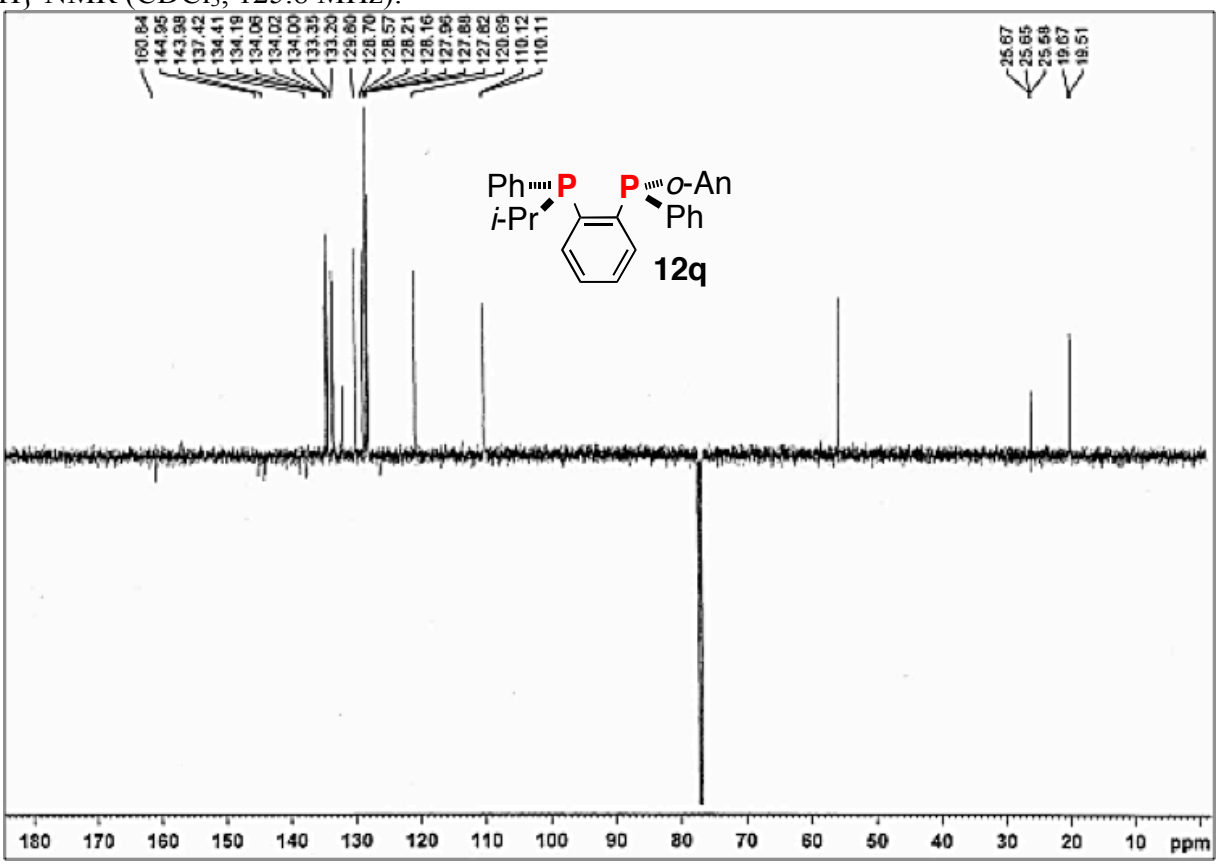


(1*R*,2*S*)-1-(Phenyl-*i*-propylphosphino)-2-[(*o*-anisylphenylphosphino]benzene **12q**

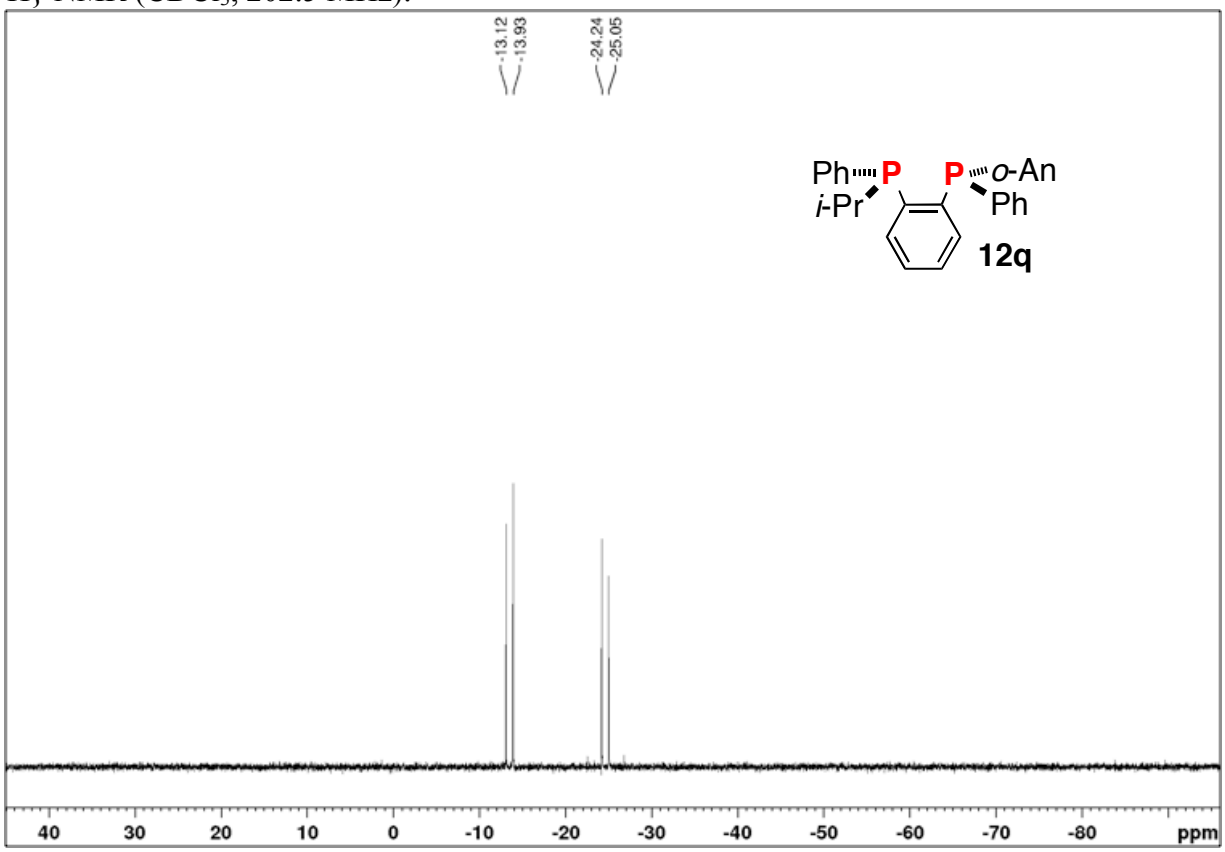
^{1}H NMR ($CDCl_3$, 500 MHz):



$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125.8 MHz):



$^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 202.5 MHz):



VII. References

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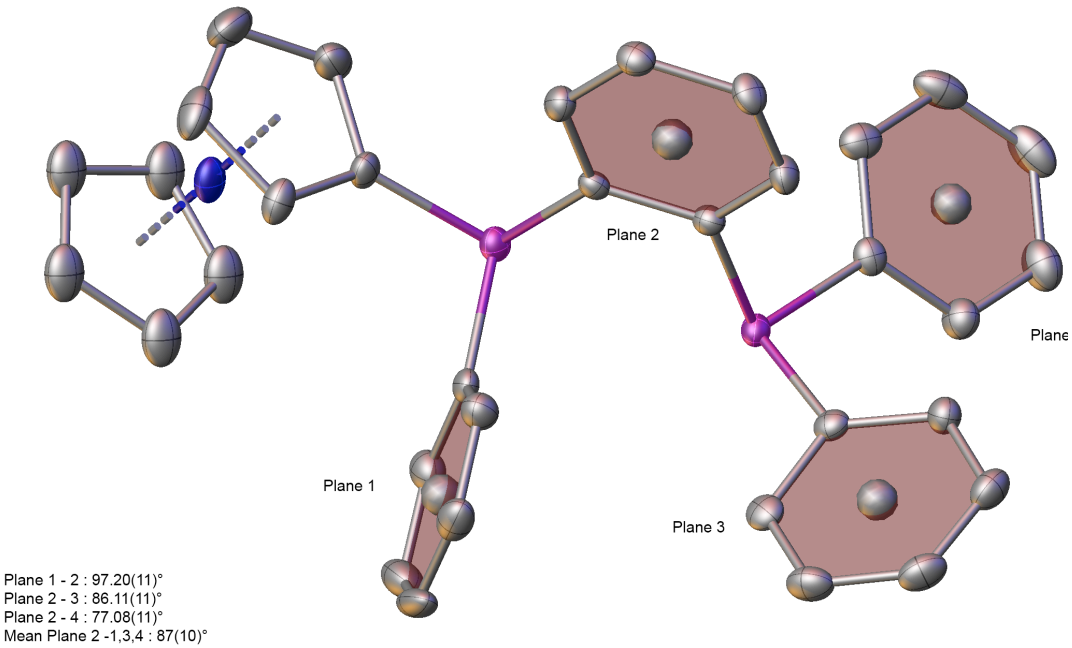
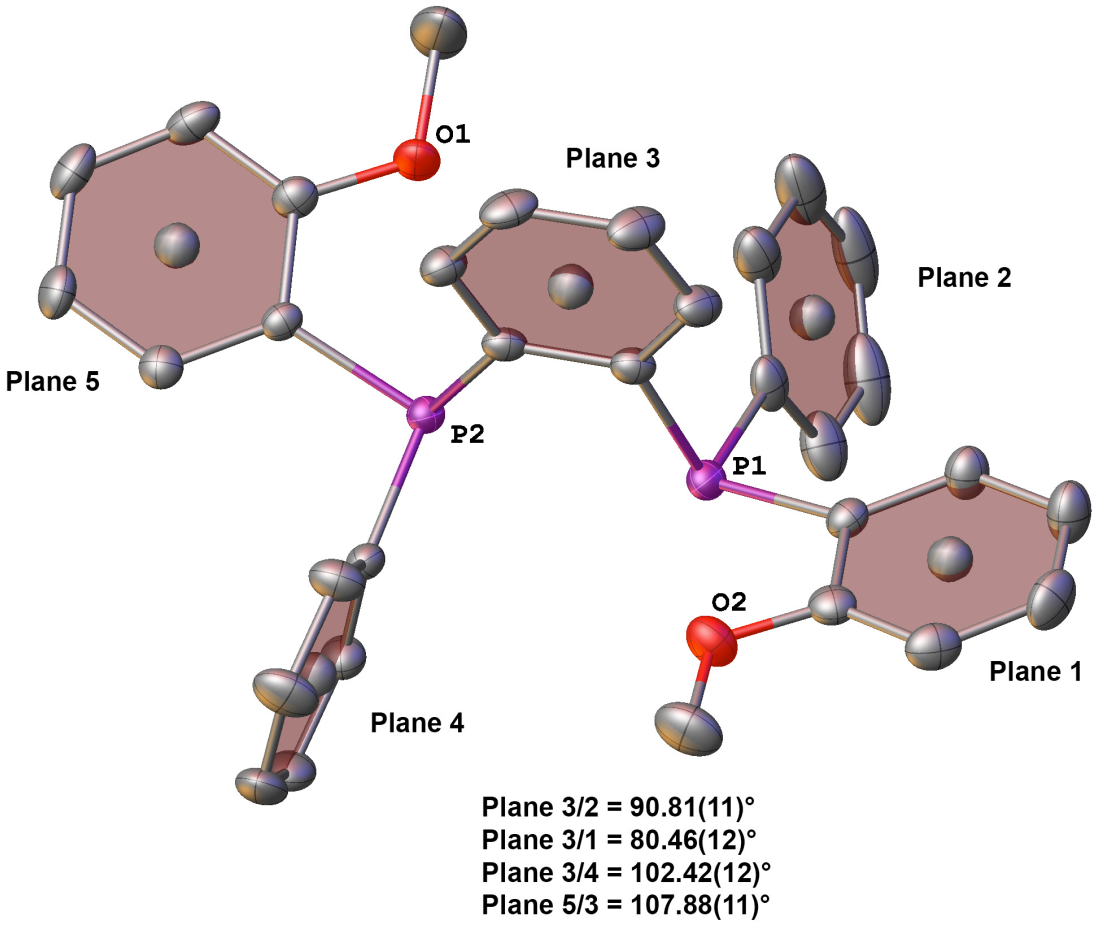
VIII. X-ray structures of compounds (*R*)-12a, (*R*)-12j and (*S*,*S*)-12p

VIII.1. View of the aromatic planes in compound (*R*)-12j



VIII.2. View of the aromatic planes in compound (*S*,*S*)-12p



VIII.3. X-ray data for compounds (*S*)-12a, (*R*)-12j and (*S*,*S*)-12p

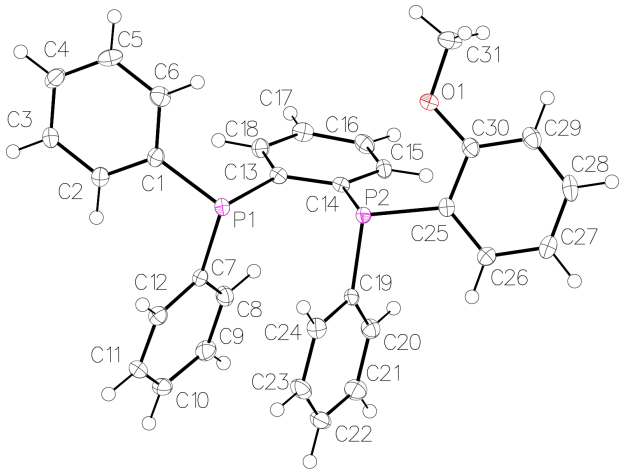
X-Ray data

Compound 12a

Olex2

Internal reference: 09afa16

Summary



Crystal Data: $C_{31}H_{26}OP_2$, $M_r =$ 476.46, monoclinic, $P2_1$ (No. 4), a = 9.4876(4) Å, b = 8.0486(3) Å, c = 16.3501(7) Å, $\beta =$ 104.642(2)°, $\alpha = \gamma =$ 90°, $V =$ 1207.98(9) Å^3, $T =$ 115(2) K, $Z =$ 2, $Z' =$1, μ(MoK$_\alpha$) = 0.203, 5286 reflections measured, 5286 unique (Rint = .) which were used in all calculations. The final wR_2 was 0.0808 (all data) and R_1 was 0.0354 ($I > 2\sigma(I)$).

Experimental: Single clear light colourless prism-shaped crystals of (**Compound 12a**) were recrystallised from a mixture of DCM and methanol by slow evaporation. A suitable crystal (0.25×0.25×0.20) mm^3 was selected and mounted on a glass fibre with grease on a Nonius Kappa Apex II diffractometer. The crystal was kept at $T =$ 115(2) K during data collection. Using **Olex2** [1], the structure was solved with the **ShelXS** [2] structure solution program, using the Direct Methods solution method. The model was refined with version 2014/7 of **ShelXL** [3] using Least Squares minimisation.

Compound	**12a**
Formula	$C_{31}H_{26}OP_2$
$D_{calc.}/gcm^{-3}$	1.310
μ/mm^{-1}	0.203
Formula Weight	476.46
Colour	clear light colourless
Shape	prism
Size/mm^3	0.25×0.25×0.20
T/K	115(2)
Crystal System	monoclinic
Flack Parameter	0.13(10)
Hooft Parameter	0.12(2)
Space Group	$P2_1$
a/Å	9.4876(4)
b/Å	8.0486(3)
c/Å	16.3501(7)
α/°	90
β/°	104.642(2)
γ/°	90
V/Å^3	1207.98(9)
Z	2
Z'	1
Wavelength/Å	0.71073
Radiation type	MoK$_\alpha$
Θ_{min}/°	2.219
Θ_{max}/°	27.467
Measured Refl.	5286
Independent Refl.	5286
Reflections Used	5169
Rint	.
Parameters	309
Restraints	1
Largest Peak	0.222
Deepest Hole	-0.214
GooF	1.045
wR_2 (all data)	0.0808
wR_2	0.0794
R_1 (all data)	0.0368
R_1	0.0354

Experimental Extended

A clear light colourless prism-shaped crystal with dimensions 0.25×0.25×0.20 mm^3 was mounted on a glass fibre with grease. X-ray diffraction data were collected using a Nonius Kappa Apex II diffractometer equipped with a Oxford Cryosystems low-temperature device, operating at $T = 115(2)$ K. Data were measured using ϕ and ω scans using MoK_α radiation (X-ray tube, 50 kV, 32 mA). The total number of runs and images was based on the strategy calculation from the program Collect (Nonius BV, 1997-2000).The maximum resolution achieved was $\Theta = 27.467°$ Cell parameters were retrieved using the **SCALEPACK** [4] software and refined using **DENZO** [4] on 2670 reflections, 51% % of the observed reflections. Data reduction was performed using the **DENZO** [4] software which corrects for Lorentz polarisation. The final completeness is 99.60% out to 27.467 in Θ. No absorption correction was performed. The absorption coefficient μ of this material is 0.203 at this wavelength ($\lambda = 0.71073$). The structure was solved in the space group $P2_1$ (# 4) by Direct Methods using the **ShelXS** [2] structure solution program and refined by Least Squares using version 2014/7 of **ShelXL** [3]. All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated geometrically and refined using the riding model.

_refine_special_details: Refined as a 2-component inversion twin.

There is a single molecule in the asymmetric unit, which is represented by the reported sum formula. In other words: Z is 2 and Z' is 1. The Flack parameter was refined to 0.13(10). Determination of absolute structure using Bayesian statistics on Bijvoet differences using the Olex2 results in 0.12(2). Note: The Flack parameter is used to determine chirality of the crystal studied, the value should be near 0, a value of 1 means that the stereochemistry is wrong and the model should be inverted. A value of 0.5 means that the crystal consists of a racemic mixture of the two enantiomers.

Reflection Statistics

Total reflections (after filtering)	5295
Unique reflections	5286
Completeness	0.956
Mean I/σ	25.01
hkl_{max} collected	(12, 10, 21)
hkl_{min} collected	(-12, -9, -21)
hkl_{max} used	(11, 10, 21)
hkl_{min} used	(-12, -9, 0)
Lim d_{max} collected	100.0
Lim d_{min} collected	0.36
d_{max} used	9.18
d_{min} used	0.77
Friedel pairs	2339
Friedel pairs merged	0
Inconsistent equivalents	0
R_{int}	0.0
R_{sigma}	0.0309
Intensity transformed	0
Omitted reflections	0
Omitted by user (OMIT hkl)	0
Multiplicity	(5295,)
Maximum multiplicity	1
Removed systematic absences	9
Filtered off (SHEL/OMIT)	0

Table 1: Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for **Compound 12a**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij}.

Atom	x	y	z	U(eq)
C1	4922(3)	1480(4)	6153.5(17)	15.6(5)
C2	3777(3)	549(4)	6307.5(18)	20.8(6)
C3	2694(3)	−78(4)	5640.7(19)	23.5(7)

C4	2723(3)	221(4)	4810.6(18)	22.3(6)
C5	3868(3)	1123(4)	4648.3(17)	20.8(6)
C6	4949(3)	1761(4)	5310.8(18)	19.6(6)
C7	5986(3)	1673(4)	7959.9(16)	15.3(5)
C8	6887(3)	499(4)	8468.1(17)	18.9(6)
C9	6574(3)	−66(4)	9205.5(18)	21.6(6)
C10	5353(3)	499(4)	9438.6(17)	20.4(6)
C11	4458(3)	1681(4)	8946.5(18)	21.1(6)
C12	4791(3)	2282(4)	8219.1(17)	17.5(6)
C13	7982(3)	1422(3)	6937.3(16)	14.1(5)
C14	9334(3)	2226(3)	7223.1(16)	13.3(5)
C15	10 620(3)	1313(4)	7310.2(17)	16.0(5)
C16	10 560(3)	−369(4)	7105.8(17)	18.4(6)
C17	9223(3)	−1145(4)	6783.5(18)	18.4(6)
C18	7948(3)	−255(4)	6703.7(17)	17.3(6)
C19	9051(3)	4452(4)	8509.2(15)	14.5(5)
C20	9785(3)	3401(4)	9158.1(18)	18.7(6)
C21	9430(3)	3380(4)	9932.8(19)	23.1(6)
C22	8317(3)	4370(4)	10 063.7(18)	23.2(6)
C23	7570(3)	5415(4)	9423.7(19)	22.6(6)
C24	7937(3)	5459(4)	8652.9(18)	19.0(6)
C25	11 232(3)	5126(3)	7605.4(17)	14.6(5)
C26	12 045(3)	5865(3)	8347.8(17)	17.1(6)
C27	13 366(3)	6667(4)	8379.4(18)	20.1(6)
C28	13 894(3)	6718(4)	7663(2)	22.5(6)
C29	13 122(3)	5976(4)	6916.0(19)	20.7(6)
C30	11 800(3)	5199(4)	6885.8(17)	16.7(5)
C31	11 449(3)	4477(5)	5424.3(18)	29.2(7)
O1	10 944(2)	4473(3)	6179.0(12)	21.1(4)
P1	6310.2(7)	2540.0(9)	6979.2(4)	13.44(14)
P2	9327.9(7)	4472.9(9)	7440.7(4)	12.31(14)

Table 2: Anisotropic Displacement Parameters ($\times 10^4$) **Compound 12a**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a*{}^2 \times U_{11} + ... + 2hka* \times b* \times U_{12}]$

Atom	$\mathbf{U}_{11}$	$\mathbf{U}_{22}$	$\mathbf{U}_{33}$	$\mathbf{U}_{23}$	$\mathbf{U}_{13}$	$\mathbf{U}_{12}$
C1	13.7(13)	14.3(14)	17.7(12)	−0.2(10)	2(1)	1.7(10)
C2	17.2(13)	26.7(16)	18.1(13)	−0.4(12)	4.0(11)	−4.3(12)
C3	16.2(13)	32.0(19)	23.3(14)	−5.9(12)	6.9(11)	−7.9(12)
C4	19.2(14)	26.0(16)	18.6(13)	−6.4(12)	−1.0(11)	2.0(12)
C5	30.1(16)	18.3(15)	13.1(12)	0.7(10)	3.6(11)	3.5(12)
C6	23.3(15)	15.9(14)	20.9(13)	1.9(11)	7.9(11)	−1.8(12)
C7	14.0(13)	16.7(14)	14.7(11)	−2.6(10)	2.8(10)	−4.0(11)
C8	14.5(13)	22.3(15)	20.2(13)	1.9(11)	4.7(10)	1.3(11)
C9	20.7(15)	23.9(17)	18.3(13)	4.1(11)	1.5(11)	0.7(12)
C10	23.0(14)	24.1(16)	14.6(12)	0.2(11)	5.8(11)	−4.6(12)
C11	17.4(14)	29.0(17)	18.7(13)	−4.6(12)	8.2(11)	−2.3(13)
C12	17.3(13)	16.9(16)	17.5(13)	−0.4(11)	3.1(10)	1.3(11)
C13	14.6(12)	13.8(13)	14.2(11)	1.4(10)	4.4(10)	1.3(10)
C14	14.6(12)	14.1(14)	12.3(11)	0.4(9)	5.2(9)	0.5(10)
C15	12.2(12)	17.7(14)	17.9(12)	1.0(11)	3.9(10)	−0.8(11)

C16	17.3(13)	19.0(15)	20.7(13)	3.3(12)	7.9(10)	5.4(12)
C17	23.9(15)	13.0(13)	19.4(13)	0.7(10)	7.4(11)	1.2(11)
C18	16.7(13)	16.5(15)	18.7(12)	−0.4(10)	4.6(10)	−2.7(11)
C19	13.5(12)	15.8(13)	15.3(11)	−2.6(11)	5.6(9)	−4.5(12)
C20	17.7(14)	19.3(15)	19.5(13)	1.2(11)	5.2(11)	0.7(11)
C21	26.1(16)	23.0(16)	20.6(14)	4.3(12)	6.7(12)	−0.8(13)
C22	26.0(14)	26.7(16)	20.6(13)	−4.4(13)	12.8(11)	−6.2(14)
C23	22.4(15)	21.9(16)	27.3(15)	−5.7(13)	13.3(12)	0.8(13)
C24	18.7(13)	16.9(14)	21.5(13)	−0.3(11)	5.2(11)	0.6(12)
C25	12.8(12)	13.7(13)	17.1(12)	1(1)	3.4(10)	−0.1(10)
C26	17.8(14)	16.1(14)	16.7(12)	0.3(10)	3.1(10)	−0.1(11)
C27	17.0(14)	17.6(15)	22.7(13)	0.5(12)	−0.5(11)	−2.0(12)
C28	11.9(13)	22.1(16)	32.6(16)	6.5(13)	3.9(12)	−1.1(12)
C29	16.8(14)	22.4(16)	23.7(14)	6.1(12)	6.4(11)	2.4(12)
C30	14.1(13)	17.1(14)	18.8(13)	2.9(11)	4.1(10)	3.0(11)
C31	28.8(16)	43.5(19)	17.6(13)	−1.9(15)	10.2(12)	0.9(17)
O1	18.2(9)	31.4(11)	15.1(9)	−2.9(9)	6.8(7)	−3.6(10)
P1	11.3(3)	14.1(3)	14.9(3)	0.3(3)	3.3(2)	−0.6(3)
P2	11.9(3)	12.3(3)	12.8(3)	0.1(3)	3.1(2)	−0.5(3)

Table 3: Bond Lengths in Å for **Compound 12a**.

Atoms	**Length/Å**	**Atoms**	**Length/Å**
C1 –C2	1.394(4)	C15–C16	1.392(4)
C1 –C6	1.403(4)	C16–C17	1.392(4)
C1 –P1	1.840(3)	C17–C18	1.383(4)
C2 –C3	1.390(4)	C19–C20	1.397(4)
C3 –C4	1.385(4)	C19–C24	1.398(4)
C4 –C5	1.387(5)	C19–P2	1.831(3)
C5 –C6	1.388(4)	C20–C21	1.390(4)
C7 –C8	1.398(4)	C21–C22	1.382(4)
C7 –C12	1.396(4)	C22–C23	1.389(4)
C7 –P1	1.845(3)	C23–C24	1.390(4)
C8 –C9	1.389(4)	C25–C26	1.396(4)
C9 –C10	1.384(4)	C25–C30	1.414(4)
C10–C11	1.388(4)	C25–P2	1.835(3)
C11–C12	1.392(4)	C26–C27	1.399(4)
C13–C14	1.407(4)	C27–C28	1.385(4)
C13–C18	1.401(4)	C28–C29	1.391(4)
C13–P1	1.840(3)	C29–C30	1.391(4)
C14–C15	1.400(4)	C30–O1	1.364(3)
C14–P2	1.844(3)	C31–O1	1.432(3)

Table 4: Bond Angles in ° for **Compound 12a**.

–Atoms–	Angle/°	–Atoms–	Angle/°
C2 – C1 – C6	118.2(3)	C20– C19– C24	118.4(2)
C2 – C1 – P1	124.2(2)	C20– C19– P2	124.5(2)
C6 – C1 – P1	117.3(2)	C24– C19– P2	116.9(2)
C3 – C2 – C1	120.6(3)	C21– C20– C19	120.7(3)
C4 – C3 – C2	120.8(3)	C22– C21– C20	120.3(3)
C3 – C4 – C5	119.2(3)	C21– C22– C23	119.8(3)
C4 – C5 – C6	120.3(3)	C22– C23– C24	120.1(3)
C5 – C6 – C1	120.9(3)	C23– C24– C19	120.7(3)
C8 – C7 – P1	124.1(2)	C26– C25– C30	117.6(3)
C12– C7 – C8	118.6(3)	C26– C25– P2	123.8(2)
C12– C7 – P1	117.2(2)	C30– C25– P2	117.3(2)
C9 – C8 – C7	120.3(3)	C25– C26– C27	121.4(3)
C10– C9 – C8	120.6(3)	C28– C27– C26	119.6(3)
C9 – C10– C11	119.8(3)	C27– C28– C29	120.5(3)
C10– C11– C12	119.7(3)	C28– C29– C30	119.6(3)
C11– C12– C7	121.0(3)	C29– C30– C25	121.3(3)
C14– C13– P1	119.0(2)	O1 – C30– C25	114.6(2)
C18– C13– C14	119.3(3)	O1 – C30– C29	124.1(2)
C18– C13– P1	121.4(2)	C30– O1 – C31	118.1(2)
C13– C14– P2	117.9(2)	C1 – P1 – C7	102.51(12)
C15– C14– C13	119.4(3)	C13– P1 – C1	102.10(12)
C15– C14– P2	122.7(2)	C13– P1 – C7	100.49(12)
C16– C15– C14	120.3(3)	C19– P2 – C14	100.58(13)
C15– C16– C17	120.3(3)	C19– P2 – C25	103.63(12)
C18– C17– C16	119.7(3)	C25– P2 – C14	104.96(13)
C17– C18– C13	120.9(3)	– –	

Table 5: Torsion Angles in ° for **Compound 12a**.

–Atoms–	Angle/°
C1 –C2 –C3 –C4	−0.6(5)
C2 –C1 –C6 –C5	−0.3(4)
C2 –C1 –P1 –C7	11.4(3)
C2 –C1 –P1 –C13	115.2(3)
C2 –C3 –C4 –C5	1.6(5)
C3 –C4 –C5 –C6	−2.0(5)
C4 –C5 –C6 –C1	1.3(5)
C6 –C1 –C2 –C3	−0.1(4)
C6 –C1 –P1 –C7	−174.7(2)
C6 –C1 –P1 –C13	−70.9(2)
C7 –C8 –C9 –C10	1.3(4)
C8 –C7 –C12–C11	−3.0(4)
C8 –C7 –P1 –C1	105.6(3)
C8 –C7 –P1 –C13	0.6(3)
C8 –C9 –C10–C11	−2.1(4)
C9 –C10–C11–C12	0.3(5)

C10–C11–C12–C7	2.2(4)
C12–C7 –C8 –C9	1.3(4)
C12–C7 –P1 –C1	−76.7(2)
C12–C7 –P1 –C13	178.2(2)
C13–C14–C15–C16	0.8(4)
C13–C14–P2 –C19	82.6(2)
C13–C14–P2 –C25	−170.0(2)
C14–C13–C18–C17	2.7(4)
C14–C13–P1 –C1	155.6(2)
C14–C13–P1 –C7	−99.1(2)
C14–C15–C16–C17	2.4(4)
C15–C14–P2 –C19	−99.1(2)
C15–C14–P2 –C25	8.3(2)
C15–C16–C17–C18	−3.0(4)
C16–C17–C18–C13	0.5(4)
C18–C13–C14–C15	−3.3(4)
C18–C13–C14–P2	175.1(2)
C18–C13–P1 –C1	−30.5(2)
C18–C13–P1 –C7	74.8(2)
C19–C20–C21–C22	1.8(5)
C20–C19–C24–C23	0.1(4)
C20–C19–P2 –C14	44.6(3)
C20–C19–P2 –C25	−63.8(3)
C20–C21–C22–C23	−1.3(5)
C21–C22–C23–C24	0.3(5)
C22–C23–C24–C19	0.3(5)
C24–C19–C20–C21	−1.1(4)
C24–C19–P2 –C14	−129.4(2)
C24–C19–P2 –C25	122.2(2)
C25–C26–C27–C28	−0.7(4)
C25–C30–O1 –C31	−179.3(3)
C26–C25–C30–C29	0.1(4)
C26–C25–C30–O1	−179.2(3)
C26–C25–P2 –C14	−121.1(2)
C26–C25–P2 –C19	−16.0(3)
C26–C27–C28–C29	−0.1(5)
C27–C28–C29–C30	0.9(5)
C28–C29–C30–C25	−0.9(4)
C28–C29–C30–O1	178.3(3)
C29–C30–O1 –C31	1.4(4)
C30–C25–C26–C27	0.7(4)
C30–C25–P2 –C14	72.5(2)
C30–C25–P2 –C19	177.6(2)
P1 –C1 –C2 –C3	173.7(2)
P1 –C1 –C6 –C5	−174.5(2)
P1 –C7 –C8 –C9	178.9(2)
P1 –C7 –C12–C11	179.2(2)
P1 –C13–C14–C15	170.72(19)
P1 –C13–C14–P2	−10.9(3)
P1 –C13–C18–C17	−171.2(2)
P2 –C14–C15–C16	−177.5(2)
P2 –C19–C20–C21	−175.1(2)
P2 –C19–C24–C23	174.6(2)

P2	–C25–C26–C27	−165.7(2)
P2	–C25–C30–C29	167.4(2)
P2	–C25–C30–O1	−11.9(3)

Table 6: Hydrogen Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for **Compound 12a**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij}.

Atom	x	y	z	U(eq)
H2	3737	342	6873	25
H3	1926	−719	5756	28
H4	1966	−187	4358	27
H5	3913	1305	4081	25
H6	5717	2397	5192	24
H8	7716	86	8308	23
H9	7203	−847	9553	26
H10	5128	80	9934	24
H11	3622	2077	9105	25
H12	4197	3119	7894	21
H15	11 537	1844	7510	19
H16	11 436	−990	7187	22
H17	9187	−2279	6619	22
H18	7037	−789	6487	21
H20	10 533	2694	9069	22
H21	9956	2683	10 374	28
H22	8064	4337	10 590	28
H23	6807	6100	9513	27
H24	7425	6181	8219	23
H26	11 694	5823	8842	20
H27	13 898	7174	8889	24
H28	14 790	7264	7683	27
H29	13 495	6000	6429	25
H31A	10 756	3872	4978	44
H31B	12 405	3937	5536	44
H31C	11 533	5625	5243	44

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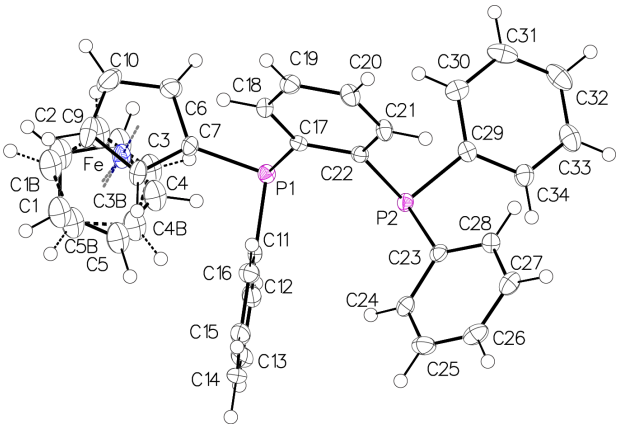
Compound 12j

Olex2

Internal Reference: 10jb489

Summary



Crystal Data: $C_{34}H_{28}P_2Fe$, $M_r =$ 554.35, monoclinic, $P2_1$ (No. 4), a = 12.3910(6) Å, b = 8.0519(4) Å, c = 14.1295(5) Å, $\beta =$ 107.842(2)°, $\alpha = \gamma =$ 90°, $V =$ 1341.92(11) Å^3, $T =$ 115 K, $Z =$ 2, $Z' =$1, μ(MoK$_\alpha$) = 0.703, 4103 reflections measured, 4103 unique (Rint = .) which were used in all calculations. The final wR_2 was 0.0712 (all data) and R_1 was 0.0320 ($I > 2\sigma(I)$).

Experimental: Single clear light orange prism-shaped crystals of (**Compound 12j**) were recrystallised from a mixture of DCM and acetone by slow evaporation. A suitable crystal (0.30×0.30×0.20) mm^3 was selected and mounted on a glass fibre with grease on a Nonius Kappa Apex II diffractometer. The crystal was kept at $T =$ 115 K during data collection. Using **Olex2** [1], the structure was solved with the **ShelXT** [2] structure solution program, using the direct methods solution method. The model was refined with version 2014/7 of **ShelXL** [3] using Least Squares minimisation.

Compound	**12j**
Formula	$C_{34}H_{28}P_2Fe$
$D_{calc.}/gcm^{-3}$	1.372
μ/mm^{-1}	0.703
Formula Weight	554.35
Colour	clear light orange
Shape	prism
Size/mm^3	0.30×0.30×0.20
T/K	115
Crystal System	monoclinic
Flack Parameter	0.05(2)
Hooft Parameter	0.086(10)
Space Group	$P2_1$
a/Å	12.3910(6)
b/Å	8.0519(4)
c/Å	14.1295(5)
α/°	90
β/°	107.842(2)
γ/°	90
V/Å^3	1341.92(11)
Z	2
Z'	1
Wavelength/Å	0.71073
Radiation type	MoK$_\alpha$
Θ_{min}/°	1.916
Θ_{max}/°	27.478
Measured Refl.	4103
Independent Refl.	4103
Reflections Used	4024
Rint	.
Parameters	308
Restraints	1
Largest Peak	0.388
Deepest Hole	-0.261
GooF	1.050
wR_2 (all data)	0.0712
wR_2	0.0702
R_1 (all data)	0.0332
R_1	0.0320

Experimental Extended

A clear light orange prism-shaped crystal with dimensions 0.30×0.30×0.20 mm^3 was mounted on a glass fibre with grease. X-ray diffraction data were collected using a Nonius Kappa Apex II diffractometer equipped with a Oxford Cryosystems low-temperature device, operating at $T = 115$ K. Data were measured using CCD rotation images using MoK_α radiation (X-ray tube, 50 kV, 32 mA). The total number of runs and images was based on the strategy calculation from the program Collect (Nonius BV, 1997-2000).The maximum resolution achieved was $\Theta = 27.478°$ Cell parameters were retrieved using the **SCALEPACK** [4] software and refined using **DENZO** [4] on 2879 reflections, 70% % of the observed reflections. Data reduction was performed using the **DENZO** [4] software which corrects for Lorentz polarisation. The final completeness is 99.30% out to 27.478 in Θ. No absorption correction was performed. The absorption coefficient μ of this material is 0.703 at this wavelength (λ= 0.71073). The structure was solved in the space group $P2_1$ (# 4) by direct methods using the **ShelXT** [2] structure solution program and refined by Least Squares using version 2014/7 of **ShelXL** [3]. All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated geometrically and refined using the riding model. One cyclopentadienyl was found disordered over two position 55%/45%.

_refine_special_details: Refined as a 2-component inversion twin.

There is a single molecule in the asymmetric unit, which is represented by the reported sum formula. In other words: Z is 2 and Z' is 1. The Flack parameter was refined to 0.05(2). Determination of absolute structure using Bayesian statistics on Bijvoet differences using the Olex2 results in 0.086(10). Note: The Flack parameter is used to determine chirality of the crystal studied, the value should be near 0, a value of 1 means that the stereochemistry is wrong and the model should be inverted. A value of 0.5 means that the crystal consists of a racemic mixture of the two enantiomers.

Reflection Statistics

Total reflections (after filtering)	4107
Unique reflections	4103
Completeness	0.667
Mean I/σ	26.24
hkl_{max} collected	(16, 10, 18)
hkl_{min} collected	(-16, -5, -18)
hkl_{max} used	(15, 10, 18)
hkl_{min} used	(-16, -5, 0)
Lim d_{max} collected	100.0
Lim d_{min} collected	0.36
d_{max} used	10.63
d_{min} used	0.77
Friedel pairs	835
Friedel pairs merged	0
Inconsistent equivalents	0
R_{int}	0.0
R_{sigma}	0.0289
Intensity transformed	0
Omitted reflections	0
Omitted by user (OMIT hkl)	0
Multiplicity	(4107,)
Maximum multiplicity	1
Removed systematic absences	4
Filtered off (SHEL/OMIT)	0

Table 1: Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for **Compound 12j**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij}.

Atom	x	y	z	U(eq)
C1	−4001(4)	2526(9)	4656(4)	32.5(7)
C2	−3757(4)	3215(8)	3819(4)	32.5(7)

C3	−2710(4)	2541(8)	3785(3)	32.5(7)
C4	−2308(4)	1435(8)	4600(4)	32.5(7)
C5	−3106(4)	1426(8)	5139(3)	32.5(7)
C1B	−3970(5)	3235(10)	3970(5)	32.5(7)
C2B	−3015(5)	3029(9)	3625(4)	32.5(7)
C3B	−2275(4)	1860(10)	4254(5)	32.5(7)
C4B	−2772(5)	1344(9)	4987(4)	32.5(7)
C5B	−3819(5)	2194(11)	4812(5)	32.5(7)
C6	−1158(3)	5417(5)	5277(3)	28.5(8)
C7	−1056(3)	4510(5)	6178(2)	19.0(7)
C8	−2042(3)	4879(5)	6465(2)	23.0(7)
C9	−2738(3)	5992(5)	5744(3)	32.1(9)
C10	−2181(4)	6323(6)	5027(3)	36.7(10)
C11	−403(2)	2088(5)	7676(2)	17.4(6)
C12	−807(3)	481(5)	7420(3)	25.3(7)
C13	−1258(3)	−437(5)	8043(3)	33.3(9)
C14	−1291(3)	243(5)	8936(3)	33.8(10)
C15	−887(3)	1830(5)	9202(3)	27.8(8)
C16	−446(3)	2753(5)	8575(2)	22.6(7)
C17	1079(2)	4769(4)	7631(2)	14.7(6)
C18	765(3)	6433(4)	7643(2)	18.7(7)
C19	1477(3)	7575(4)	8255(2)	20.0(7)
C20	2532(3)	7088(5)	8881(2)	20.8(7)
C21	2857(3)	5442(4)	8879(2)	19.1(7)
C22	2152(2)	4273(4)	8256(2)	15.3(6)
C23	3064(3)	1733(4)	9630(2)	17.2(7)
C24	2229(3)	1150(4)	10 036(2)	20.2(7)
C25	2470(3)	974(5)	11 053(3)	26.0(8)
C26	3541(3)	1328(5)	11 686(2)	26.4(8)
C27	4378(3)	1846(5)	11 292(2)	25.2(8)
C28	4139(3)	2065(5)	10 272(2)	19.9(6)
C29	3893(2)	2221(4)	7950(2)	17.4(6)
C30	3998(3)	3358(5)	7239(2)	22.5(7)
C31	4939(3)	3318(5)	6897(3)	30.4(8)
C32	5796(3)	2167(5)	7274(3)	31.8(9)
C33	5702(3)	1035(5)	7983(3)	30.3(9)
C34	4748(3)	1037(5)	8307(3)	22.9(7)
P1	159.6(6)	3218.9(11)	6792.7(6)	16.65(17)
P2	2579.2(6)	2073.3(11)	8278.9(6)	15.54(17)
Fe	−2489.5(4)	3829.6(9)	5077.6(3)	22.86(12)

Table 2: Anisotropic Displacement Parameters ($\times 10^4$) **Compound 12j**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a*{}^2 \times U_{11} + ... + 2hka* \times b* \times U_{12}]$

Atom	$\mathbf{U}_{11}$	$\mathbf{U}_{22}$	$\mathbf{U}_{33}$	$\mathbf{U}_{23}$	$\mathbf{U}_{13}$	$\mathbf{U}_{12}$
C1	25.5(12)	45.5(17)	22.4(12)	−10.8(11)	1.2(8)	−0.3(12)
C2	25.5(12)	45.5(17)	22.4(12)	−10.8(11)	1.2(8)	−0.3(12)
C3	25.5(12)	45.5(17)	22.4(12)	−10.8(11)	1.2(8)	−0.3(12)
C4	25.5(12)	45.5(17)	22.4(12)	−10.8(11)	1.2(8)	−0.3(12)
C5	25.5(12)	45.5(17)	22.4(12)	−10.8(11)	1.2(8)	−0.3(12)
C1B	25.5(12)	45.5(17)	22.4(12)	−10.8(11)	1.2(8)	−0.3(12)

C2B	25.5(12)	45.5(17)	22.4(12)	−10.8(11)	1.2(8)	−0.3(12)
C3B	25.5(12)	45.5(17)	22.4(12)	−10.8(11)	1.2(8)	−0.3(12)
C4B	25.5(12)	45.5(17)	22.4(12)	−10.8(11)	1.2(8)	−0.3(12)
C5B	25.5(12)	45.5(17)	22.4(12)	−10.8(11)	1.2(8)	−0.3(12)
C6	23.3(16)	36(2)	23.0(17)	8.7(17)	2.8(13)	−5.7(17)
C7	15.4(14)	24.9(18)	14.2(14)	3.0(13)	0.7(11)	0.7(14)
C8	19.6(15)	29(2)	17.8(15)	−2.0(15)	1.1(12)	6.4(15)
C9	22.5(17)	30(2)	36(2)	−3.2(17)	−2.4(15)	10.3(16)
C10	36(2)	33(2)	33(2)	13.4(19)	−1.6(16)	1.8(19)
C11	10.9(12)	19.5(16)	20.2(15)	3.6(14)	2.6(11)	2.4(13)
C12	18.9(15)	23.7(19)	33.2(18)	1.0(16)	7.7(13)	1.4(15)
C13	23.6(17)	25(2)	53(2)	8.3(19)	14.9(16)	−1.4(16)
C14	21.6(17)	34(2)	50(2)	26(2)	16.9(16)	4.0(17)
C15	21.2(16)	41(2)	23.1(16)	9.5(17)	9.8(13)	5.8(17)
C16	21.3(15)	25.0(19)	21.5(16)	1.9(14)	6.6(12)	−1.5(14)
C17	15.0(14)	15.2(16)	15.0(13)	0.5(12)	6.2(11)	−2.3(12)
C18	15.2(14)	20.0(17)	20.6(15)	1.8(14)	5.3(12)	2.2(13)
C19	22.5(15)	15.3(16)	23.4(16)	−1.0(13)	8.8(13)	0.2(13)
C20	17.8(14)	19.7(17)	24.0(16)	−6.8(15)	5.3(12)	−3.4(14)
C21	14.0(14)	20.3(18)	21.2(15)	−3.0(14)	2.5(12)	−0.8(13)
C22	15.7(13)	13.8(16)	17.7(13)	0.2(12)	7.0(11)	0.3(12)
C23	19.5(14)	13.6(17)	19.3(15)	2.1(13)	6.8(11)	3.8(13)
C24	20.9(15)	13.7(16)	26.6(17)	0.6(14)	8.3(13)	5.1(13)
C25	31.9(18)	23.6(19)	28.3(18)	5.0(15)	17.7(15)	1.8(16)
C26	37.4(19)	24.5(19)	18.1(16)	3.9(15)	9.7(14)	5.2(17)
C27	26.4(16)	24(2)	20.5(16)	2.0(15)	0.7(13)	3.6(16)
C28	17.2(14)	20.7(16)	21.4(15)	0.9(15)	5.1(11)	1.3(14)
C29	16.8(13)	19.0(17)	16.3(14)	−5.1(13)	5.0(11)	−1.1(14)
C30	28.9(16)	19.4(18)	18.5(14)	−2.0(14)	6.1(12)	−1.5(15)
C31	41(2)	30(2)	25.7(17)	−4.0(16)	18.5(15)	−12.3(18)
C32	29.6(17)	33(2)	41(2)	−14.4(19)	23.0(16)	−7.7(18)
C33	22.7(17)	32(2)	38(2)	−7.1(18)	12.3(15)	0.7(16)
C34	21.0(16)	22.7(19)	25.6(17)	−0.4(15)	8.1(13)	3.7(15)
P1	15.2(3)	19.5(4)	14.4(4)	−0.9(3)	3.3(3)	−0.7(3)
P2	13.5(3)	14.1(4)	17.3(4)	−0.5(3)	2.3(3)	0.3(3)
Fe	16.6(2)	34.2(3)	14.9(2)	−1.9(2)	0.60(15)	1.0(2)

Table 3: Bond Lengths in Å for **Compound 12j**.

Atoms	**Length/Å**	**Atoms**	**Length/Å**
C1 –C2	1.4200	C10–Fe	2.049(5)
C1 –C5	1.4200	C11–C12	1.395(5)
C1 –Fe	2.069(6)	C11–C16	1.394(4)
C2 –C3	1.4200	C11–P1	1.846(3)
C2 –Fe	2.040(6)	C12–C13	1.391(5)
C3 –C4	1.4200	C13–C14	1.387(6)
C3 –Fe	2.045(5)	C14–C15	1.382(6)
C4 –C5	1.4200	C15–C16	1.390(5)
C4 –Fe	2.077(6)	C17–C18	1.396(5)
C5 –Fe	2.092(6)	C17–C22	1.409(4)
C1B–C2B	1.4200	C17–P1	1.853(3)

C1B–C5B	1.4200	C18–C19	1.380(5)
C1B–Fe	2.069(7)	C19–C20	1.391(4)
C2B–C3B	1.4200	C20–C21	1.385(5)
C2B–Fe	2.057(6)	C21–C22	1.398(4)
C3B–C4B	1.4200	C22–P2	1.846(3)
C3B–Fe	2.032(7)	C23–C24	1.408(4)
C4B–C5B	1.4200	C23–C28	1.389(4)
C4B–Fe	2.029(8)	C23–P2	1.837(3)
C5B–Fe	2.052(8)	C24–C25	1.383(5)
C6 –C7	1.439(5)	C25–C26	1.384(5)
C6 –C10	1.411(6)	C26–C27	1.383(5)
C6 –Fe	2.037(4)	C27–C28	1.390(4)
C7 –C8	1.432(4)	C29–C30	1.395(5)
C7 –P1	1.817(3)	C29–C34	1.399(5)
C7 –Fe	2.045(3)	C29–P2	1.829(3)
C8 –C9	1.430(5)	C30–C31	1.392(5)
C8 –Fe	2.048(3)	C31–C32	1.387(6)
C9 –C10	1.416(6)	C32–C33	1.385(6)
C9 –Fe	2.047(4)	C33–C34	1.392(5)

Table 4: Bond Angles in ° for **Compound 12j**.

–Atoms–	**Angle/°**	**–Atoms–**	**Angle/°**
C2 –C1 –Fe	68.7(2)	C27 –C26–C25	119.4(3)
C5 –C1 –C2	108.0	C26 –C27–C28	120.5(3)
C5 –C1 –Fe	70.9(2)	C23 –C28–C27	120.7(3)
C1 –C2 –Fe	70.9(2)	C30 –C29–C34	118.7(3)
C3 –C2 –C1	108.0	C30 –C29–P2	120.9(2)
C3 –C2 –Fe	69.8(2)	C34 –C29–P2	119.9(3)
C2 –C3 –Fe	69.5(2)	C31 –C30–C29	120.5(3)
C4 –C3 –C2	108.0	C32 –C31–C30	120.4(3)
C4 –C3 –Fe	71.1(2)	C33 –C32–C31	119.6(3)
C3 –C4 –C5	108.0	C32 –C33–C34	120.4(4)
C3 –C4 –Fe	68.6(2)	C33 –C34–C29	120.5(3)
C5 –C4 –Fe	70.6(2)	C7 –P1 –C11	100.13(14)
C1 –C5 –Fe	69.2(2)	C7 –P1 –C17	100.22(15)
C4 –C5 –C1	108.0	C11 –P1 –C17	100.70(14)
C4 –C5 –Fe	69.5(2)	C23 –P2 –C22	99.31(14)
C2B–C1B–Fe	69.4(3)	C29 –P2 –C22	101.91(15)
C5B–C1B–C2B	108.0	C29 –P2 –C23	103.95(14)
C5B–C1B–Fe	69.2(3)	C2 –Fe –C1	40.43(11)
C1B–C2B–Fe	70.3(3)	C2 –Fe –C3	40.69(10)
C3B–C2B–C1B	108.0	C2 –Fe –C7	170.13(17)
C3B–C2B–Fe	68.7(3)	C2 –Fe –C8	147.60(17)
C2B–C3B–C4B	108.0	C2 –Fe –C9	115.04(18)
C2B–C3B–Fe	70.6(3)	C2 –Fe –C10	108.0(2)
C4B–C3B–Fe	69.4(3)	C3 –Fe –C1	67.90(14)
C3B–C4B–C5B	108.0	C3 –Fe –C8	170.68(18)
C3B–C4B–Fe	69.7(3)	C3 –Fe –C9	147.64(19)

C5B–C4B–Fe	70.5(3)	C3 –Fe –C10	116.2(2)
C1B–C5B–C4B	108.0	C3B–Fe –C2B	40.63(12)
C1B–C5B–Fe	70.5(3)	C3B–Fe –C5B	68.46(18)
C4B–C5B–Fe	68.8(3)	C3B–Fe –C6	109.0(2)
C7 –C6 –Fe	69.64(19)	C3B–Fe –C7	114.14(18)
C10 –C6 –C7	108.2(3)	C3B–Fe –C8	145.6(2)
C10 –C6 –Fe	70.3(2)	C3B–Fe –C9	172.6(2)
C6 –C7 –P1	123.3(3)	C3B–Fe –C10	133.3(3)
C6 –C7 –Fe	69.08(19)	C4B–Fe –C2B	68.42(16)
C8 –C7 –C6	107.1(3)	C4B–Fe –C3B	40.93(14)
C8 –C7 –P1	129.6(2)	C4B–Fe –C5B	40.72(15)
C8 –C7 –Fe	69.66(17)	C4B–Fe –C6	138.1(2)
P1 –C7 –Fe	127.6(2)	C4B–Fe –C7	113.9(2)
C7 –C8 –Fe	69.38(18)	C4B–Fe –C8	117.3(2)
C9 –C8 –C7	108.0(3)	C4B–Fe –C9	145.1(2)
C9 –C8 –Fe	69.5(2)	C4B–Fe –C10	174.1(2)
C8 –C9 –Fe	69.6(2)	C5B–Fe –C2B	67.99(16)
C10 –C9 –C8	107.9(3)	C6 –Fe –C1	168.94(19)
C10 –C9 –Fe	69.9(3)	C6 –Fe –C2	130.34(18)
C6 –C10 –C9	108.7(3)	C6 –Fe –C3	108.84(17)
C6 –C10 –Fe	69.3(2)	C6 –Fe –C2B	109.28(19)
C9 –C10 –Fe	69.7(2)	C6 –Fe –C5B	177.2(2)
C12 –C11 –P1	117.5(3)	C6 –Fe –C7	41.28(13)
C16 –C11 –C12	118.8(3)	C6 –Fe –C8	68.82(15)
C16 –C11 –P1	123.7(3)	C6 –Fe –C9	68.44(17)
C13 –C12 –C11	120.7(4)	C6 –Fe –C10	40.39(16)
C14 –C13 –C12	119.7(4)	C7 –Fe –C1	148.64(17)
C15 –C14 –C13	120.2(3)	C7 –Fe –C3	131.48(16)
C14 –C15 –C16	120.1(4)	C7 –Fe –C2B	141.10(19)
C15 –C16 –C11	120.5(4)	C7 –Fe –C5B	140.6(2)
C18 –C17 –C22	118.5(3)	C7 –Fe –C8	40.96(13)
C18 –C17 –P1	122.3(2)	C7 –Fe –C9	68.93(14)
C22 –C17 –P1	119.1(2)	C7 –Fe –C10	68.66(15)
C19 –C18 –C17	121.3(3)	C8 –Fe –C1	116.13(16)
C18 –C19 –C20	120.4(3)	C8 –Fe –C2B	173.6(2)
C21 –C20 –C19	119.1(3)	C8 –Fe –C5B	114.0(2)
C20 –C21 –C22	121.3(3)	C8 –Fe –C10	68.32(16)
C17 –C22 –P2	119.6(2)	C9 –Fe –C1	108.26(19)
C21 –C22 –C17	119.4(3)	C9 –Fe –C2B	132.8(2)
C21 –C22 –P2	121.0(2)	C9 –Fe –C5B	113.9(2)
C24 –C23 –P2	115.2(2)	C9 –Fe –C8	40.86(14)
C28 –C23 –C24	118.3(3)	C9 –Fe –C10	40.43(17)
C28 –C23 –P2	126.4(2)	C10 –Fe –C1	130.5(2)
C25 –C24 –C23	120.4(3)	C10 –Fe –C2B	106.1(2)
C24 –C25 –C26	120.6(3)	C10 –Fe –C5B	140.4(2)

Table 5: Torsion Angles in ° for **Compound 12j**.

–Atoms–				Angle/°
C1	–C2	–C3	–C4	0.0
C1	–C2	–C3	–Fe	−60.9(2)
C2	–C1	–C5	–C4	0.0
C2	–C1	–C5	–Fe	58.9(2)
C2	–C3	–C4	–C5	0.0
C2	–C3	–C4	–Fe	−59.9(2)
C3	–C4	–C5	–C1	0.0
C3	–C4	–C5	–Fe	−58.7(2)
C5	–C1	–C2	–C3	0.0
C5	–C1	–C2	–Fe	−60.3(2)
C1B	–C2B	–C3B	–C4B	0.0
C1B	–C2B	–C3B	–Fe	−59.6(3)
C2B	–C1B	–C5B	–C4B	0.0
C2B	–C1B	–C5B	–Fe	58.7(3)
C2B	–C3B	–C4B	–C5B	0.0
C2B	–C3B	–C4B	–Fe	−60.4(3)
C3B	–C4B	–C5B	–C1B	0.0
C3B	–C4B	–C5B	–Fe	−59.8(3)
C5B	–C1B	–C2B	–C3B	0.0
C5B	–C1B	–C2B	–Fe	−58.6(3)
C6	–C7	–C8	–C9	0.2(4)
C6	–C7	–C8	–Fe	59.2(2)
C6	–C7	–P1	–C11	−167.3(3)
C6	–C7	–P1	–C17	89.8(3)
C7	–C6	–C10	–C9	−0.8(5)
C7	–C6	–C10	–Fe	−59.5(3)
C7	–C8	–C9	–C10	−0.7(4)
C7	–C8	–C9	–Fe	58.9(2)
C8	–C7	–P1	–C11	14.7(4)
C8	–C7	–P1	–C17	−88.3(3)
C8	–C9	–C10	–C6	0.9(5)
C8	–C9	–C10	–Fe	59.4(3)
C10	–C6	–C7	–C8	0.3(4)
C10	–C6	–C7	–P1	−178.1(3)
C10	–C6	–C7	–Fe	59.9(3)
C11	–C12	–C13	–C14	−1.0(5)
C12	–C11	–C16	–C15	−0.2(5)
C12	–C11	–P1	–C7	99.7(3)
C12	–C11	–P1	–C17	−157.8(2)
C12	–C13	–C14	–C15	0.6(5)
C13	–C14	–C15	–C16	0.1(5)
C14	–C15	–C16	–C11	−0.2(5)
C16	–C11	–C12	–C13	0.8(5)
C16	–C11	–P1	–C7	−80.2(3)
C16	–C11	–P1	–C17	22.3(3)
C17	–C18	–C19	–C20	0.0(5)
C17	–C22	–P2	–C23	−130.6(2)
C17	–C22	–P2	–C29	122.9(2)
C18	–C17	–C22	–C21	1.2(4)

C18 –C17 –C22 –P2	178.6(2)
C18 –C17 –P1 –C7	−1.6(3)
C18 –C17 –P1 –C11	−104.0(3)
C18 –C19 –C20 –C21	0.0(5)
C19 –C20 –C21 –C22	0.7(5)
C20 –C21 –C22 –C17	−1.3(5)
C20 –C21 –C22 –P2	−178.7(3)
C21 –C22 –P2 –C23	46.8(3)
C21 –C22 –P2 –C29	−59.7(3)
C22 –C17 –C18 –C19	−0.6(5)
C22 –C17 –P1 –C7	−179.3(2)
C22 –C17 –P1 –C11	78.3(3)
C23 –C24 –C25 –C26	−1.6(5)
C24 –C23 –C28 –C27	−0.8(5)
C24 –C23 –P2 –C22	91.0(3)
C24 –C23 –P2 –C29	−164.2(3)
C24 –C25 –C26 –C27	−0.7(6)
C25 –C26 –C27 –C28	2.2(6)
C26 –C27 –C28 –C23	−1.4(6)
C28 –C23 –C24 –C25	2.3(5)
C28 –C23 –P2 –C22	−86.0(3)
C28 –C23 –P2 –C29	18.9(3)
C29 –C30 –C31 –C32	−1.3(5)
C30 –C29 –C34 –C33	2.1(5)
C30 –C29 –P2 –C22	−38.4(3)
C30 –C29 –P2 –C23	−141.2(3)
C30 –C31 –C32 –C33	1.1(6)
C31 –C32 –C33 –C34	0.8(6)
C32 –C33 –C34 –C29	−2.4(6)
C34 –C29 –C30 –C31	−0.3(5)
C34 –C29 –P2 –C22	150.5(3)
C34 –C29 –P2 –C23	47.6(3)
P1 –C7 –C8 –C9	178.5(3)
P1 –C7 –C8 –Fe	−122.5(3)
P1 –C11 –C12 –C13	−179.1(3)
P1 –C11 –C16 –C15	179.7(2)
P1 –C17 –C18 –C19	−178.3(2)
P1 –C17 –C22 –C21	179.0(2)
P1 –C17 –C22 –P2	−3.6(3)
P2 –C23 –C24 –C25	−174.9(3)
P2 –C23 –C28 –C27	176.0(3)
P2 –C29 –C30 –C31	−171.5(3)
P2 –C29 –C34 –C33	173.5(3)
Fe –C1 –C2 –C3	60.3(2)
Fe –C1 –C5 –C4	−58.9(2)
Fe –C2 –C3 –C4	60.9(2)
Fe –C3 –C4 –C5	59.9(2)
Fe –C4 –C5 –C1	58.7(2)
Fe –C1B–C2B–C3B	58.6(3)
Fe –C1B–C5B–C4B	−58.7(3)
Fe –C2B–C3B–C4B	59.6(3)
Fe –C3B–C4B–C5B	60.4(3)
Fe –C4B–C5B–C1B	59.8(3)

Fe	–C6	–C7	–C8	−59.6(2)
Fe	–C6	–C7	–P1	122.0(3)
Fe	–C6	–C10	–C9	58.7(3)
Fe	–C7	–C8	–C9	−59.0(3)
Fe	–C7	–P1	–C11	−79.2(2)
Fe	–C7	–P1	–C17	177.83(19)
Fe	–C8	–C9	–C10	−59.6(3)
Fe	–C9	–C10	–C6	−58.5(3)

Table 6: Hydrogen Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for **Compound 12j**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij}.

Atom	**x**	**y**	**z**	**U(eq)**
H1	−4650	2760	4857	39
H2	−4213	3991	3363	39
H3	−2344	2786	3301	39
H4	−1625	811	4758	39
H5	−3050	795	5720	39
H1B	−4598	3945	3688	39
H2B	−2893	3577	3071	39
H3B	−1571	1489	4194	39
H4B	−2459	567	5504	39
H5B	−4330	2085	5191	39
H6	−628	5406	4913	34
H8	−2206	4458	7034	28
H9	−3449	6432	5747	38
H10	−2451	7038	4469	44
H12	−774	8	6814	30
H13	−1543	−1524	7858	40
H14	−1593	−384	9366	41
H15	−910	2291	9814	33
H16	−172	3845	8760	27
H18	47	6786	7221	22
H19	1245	8701	8250	24
H20	3023	7873	9303	25
H21	3573	5101	9310	23
H24	1496	877	9608	24
H25	1895	606	11 320	31
H26	3701	1217	12 384	32
H27	5122	2053	11 721	30
H28	4717	2444	10 012	24
H30	3424	4166	6986	27
H31	4995	4083	6402	37
H32	6443	2154	7048	38
H33	6291	254	8249	36
H34	4678	229	8775	27

Table 7: Atomic Occupancies for all atoms that are not fully occupied in **Compound 12j**.

Atom	**Occu**	**Atom**	**Occu**	**Atom**	**Occu**
C1	0.55	H4	0.55	C3B	0.45
H1	0.55	C5	0.55	H3B	0.45
C2	0.55	H5	0.55	C4B	0.45
H2	0.55	C1B	0.45	H4B	0.45
C3	0.55	H1B	0.45	C5B	0.45
H3	0.55	C2B	0.45	H5B	0.45
C4	0.55	H2B	0.45		

References

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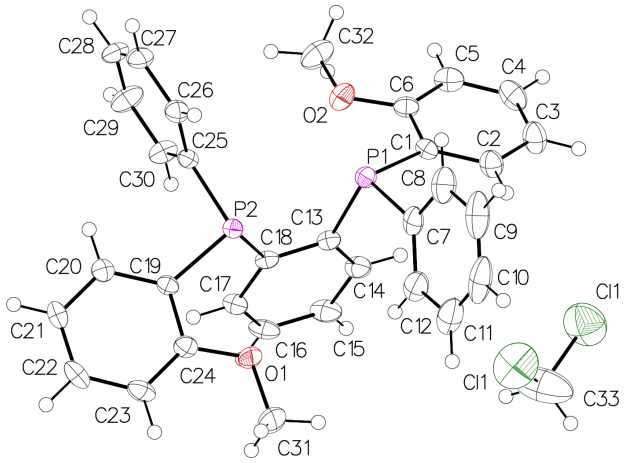
Compound 12p

Olex2

Internal reference: 10jb534

Summary



Crystal Data: $C_{65}H_{58}O_4P_4Cl_2$, $M_r =$ 1097.89, monoclinic, $C2$ (No. 5), a = 21.1345(7) Å, b = 7.5878(4) Å, c = 19.4577(8) Å, $\beta =$ 113.067(2)°, $\alpha = \gamma =$ 90°, $V =$ 2870.8(2) Å^3, $T =$ 115(2) K, $Z =$ 2, Z' =0.5, μ(MoK$_\alpha$) = 0.272, 5059 reflections measured, 5059 unique (Rint = .) which were used in all calculations. The final wR_2 was 0.0900 (all data) and R_1 was 0.0414 ($I > 2\sigma(I)$).

Experimental: Single clear light colourless prism-shaped crystals of (**Compound 12p**) were recrystallised from a mixture of DCM and methanol by slow evaporation. A suitable crystal (0.25×0.20×0.20) mm^3 was selected and mounted on a glass fibre with grease on a Nonius Kappa Apex II diffractometer. The crystal was kept at $T =$ 115(2) K during data collection. Using **Olex2** [1], the structure was solved with the **ShelXT** [2] structure solution program, using the direct methods solution method. The model was refined with version 2014/7 of **ShelXL** [3] using Least Squares minimisation.

Compound	**12p**
Formula	$C_{65}H_{58}O_4P_4Cl_2$
$D_{calc.}/gcm^{-3}$	1.270
μ/mm^{-1}	0.272
Formula Weight	1097.89
Colour	clear light colourless
Shape	prism
Size/mm^3	0.25×0.20×0.20
T/K	115(2)
Crystal System	monoclinic
Flack Parameter	0.13(10)
Hooft Parameter	0.07(3)
Space Group	$C2$
a/Å	21.1345(7)
b/Å	7.5878(4)
c/Å	19.4577(8)
α/°	90
β/°	113.067(2)
γ/°	90
V/Å^3	2870.8(2)
Z	2
Z'	0.5
Wavelength/Å	0.71073
Radiation type	MoK$_\alpha$
Θ_{min}/°	1.137
Θ_{max}/°	27.439
Measured Refl.	5059
Independent Refl.	5059
Reflections Used	4876
Rint	.
Parameters	312
Restraints	1
Largest Peak	0.368
Deepest Hole	-0.565
GooF	1.078
wR_2 (all data)	0.0900
wR_2	0.0870
R_1 (all data)	0.0444
R_1	0.0414

Experimental Extended

A clear light colourless prism-shaped crystal with dimensions 0.25×0.20×0.20 mm^3 was mounted on a glass fibre with grease. X-ray diffraction data were collected using a Nonius Kappa Apex II diffractometer equipped with a Oxford Cryosystems low-temperature device, operating at $T = 115(2)$ K. Data were measured using ϕ and ω scans ousing MoK_α radiation (X-ray tube, 50 kV, 32 mA). The total number of runs and images was based on the strategy calculation from the program Collect (Nonius BV, 1997-2000).The maximum resolution achieved was $\Theta = 27.439°$ Cell parameters were retrieved using the **SCALEPACK** [4] software and refined using **DENZO** [4] on 2798 reflections, 55% % of the observed reflections. Data reduction was performed using the **DENZO** [4] software which corrects for Lorentz polarisation. The final completeness is 99.00% out to 27.439 in Θ. No absorption correction was performed. The absorption coefficient μ of this material is 0.272 at this wavelength ($\lambda = 0.71073$). The structure was solved in the space group $C2$ (# 5) by direct methods using the **ShelXT** [2] structure solution program and refined by Least Squares using version 2014/7 of **ShelXL** [3]. All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated geometrically and refined using the riding model.

_refine_special_details: Refined as a 2-component inversion twin.

The value of Z' is 0.5. This means that only half of the formula unit is present in the asymmetric unit, with the other half consisting of symmetry equivalent atoms. The Flack parameter was refined to 0.13(10). Determination of absolute structure using Bayesian statistics on Bijvoet differences using the Olex2 results in 0.07(3). Note: The Flack parameter is used to determine chirality of the crystal studied, the value should be near 0, a value of 1 means that the stereochemistry is wrong and the model should be inverted. A value of 0.5 means that the crystal consists of a racemic mixture of the two enantiomers.

Reflection Statistics

Total reflections (after filtering)	5059
Unique reflections	5059
Completeness	0.772
Mean I/σ	22.03
hkl_{max} collected	(27, 9, 25)
hkl_{min} collected	(-27, -7, -25)
hkl_{max} used	(25, 9, 25)
hkl_{min} used	(-27, -7, 0)
Lim d_{max} collected	100.0
Lim d_{min} collected	0.36
d_{max} used	17.9
d_{min} used	0.77
Friedel pairs	1586
Friedel pairs merged	0
Inconsistent equivalents	0
R_{int}	0.0
R_{sigma}	0.0317
Intensity transformed	0
Omitted reflections	0
Omitted by user (OMIT hkl)	0
Multiplicity	(5059,)
Maximum multiplicity	1
Removed systematic absences	0
Filtered off (SHEL/OMIT)	0

Table 1: Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for **Compound 12p**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij}.

Atom	x	y	z	U(eq)
C1	3254.3(15)	3739(4)	4022.1(17)	21.0(7)
C2	3927.5(16)	3776(5)	4549.9(18)	28.9(8)
C3	4081.7(18)	3449(6)	5301(2)	36.5(9)

C4	3553(2)	3064(6)	5527.1(19)	35.6(9)
C5	2874.7(18)	3021(5)	5018(2)	30.1(8)
C6	2727.0(16)	3382(5)	4275.9(19)	24.3(7)
C7	3812.6(15)	4180(6)	2911.6(17)	27.9(8)
C8	4143.6(19)	2597(7)	2909(2)	39.4(10)
C9	4756(2)	2588(8)	2790(2)	52.6(15)
C10	5029.3(19)	4127(10)	2665(2)	56.7(15)
C11	4704(2)	5697(8)	2662(2)	50.9(14)
C12	4090.5(18)	5726(7)	2783(2)	37.7(10)
C13	2686.4(16)	6335(5)	2912.3(18)	21.2(7)
C14	2859.3(18)	7498(5)	3516.6(19)	27.6(8)
C15	2574.3(19)	9171(5)	3424.5(19)	32.9(8)
C16	2117.1(19)	9717(5)	2727(2)	29.7(8)
C17	1950.3(16)	8591(5)	2121.0(19)	24.5(7)
C18	2233.1(15)	6896(4)	2203.9(18)	19.6(6)
C19	1717.4(15)	6909(4)	616.8(17)	18.7(6)
C20	1050.4(16)	6845(5)	68.1(18)	22.8(7)
C21	858.8(16)	7907(5)	−565.8(19)	27.7(8)
C22	1331.7(17)	9035(5)	−660.5(19)	30.0(7)
C23	1996.9(16)	9146(5)	−113.3(19)	28.8(7)
C24	2182.2(15)	8099(5)	514.8(18)	23.1(7)
C25	1297.0(14)	4223(5)	1351.2(16)	20.4(6)
C26	1182.4(17)	2581(5)	1016(2)	27.2(7)
C27	584.6(19)	1625(5)	906(2)	33.0(8)
C28	104.4(18)	2346(6)	1144(2)	36.2(9)
C29	218.6(17)	3963(6)	1491(2)	39.0(9)
C30	810.5(17)	4911(5)	1595(2)	29.7(8)
C31	3306(2)	9354(8)	1051(3)	62.9(16)
C32	1513.5(18)	3102(7)	3944(3)	43.7(11)
C33	5000	9644(12)	5000	100(4)
O1	2823.0(11)	8089(4)	1082.1(13)	29
O2	2077.7(11)	3448(4)	3732.7(14)	31
P1	2985.1(4)	4037.8(12)	3010.0(4)	21
P2	2074.4(4)	5397.0(12)	1413.7(4)	18
Cl1	4954.1(8)	8389(3)	4241.1(9)	83

Table 2: Anisotropic Displacement Parameters ($\times 10^4$) **Compound 12p**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a*^2 \times U_{11} + ... + 2hka* \times b* \times U_{12}]$

Atom	$\mathbf{U}_{11}$	$\mathbf{U}_{22}$	$\mathbf{U}_{33}$	$\mathbf{U}_{23}$	$\mathbf{U}_{13}$	$\mathbf{U}_{12}$
C1	25.7(14)	17.9(18)	20.4(14)	1.2(13)	10.3(12)	1.8(12)
C2	28.7(15)	37(2)	21.9(16)	2.4(16)	10.7(13)	2.8(15)
C3	33.3(17)	51(3)	22.9(17)	4.7(18)	8.6(14)	5.1(17)
C4	50(2)	39(2)	18.7(17)	3.7(17)	14.5(15)	7.0(19)
C5	40.4(18)	29(2)	28.4(18)	−3.0(16)	21.0(15)	−2.8(16)
C6	28.9(15)	16.9(17)	27.9(17)	−2.4(15)	12.1(13)	−0.8(13)
C7	24.4(14)	45(2)	13.4(14)	−1.1(17)	6.0(11)	−0.4(16)
C8	35.1(19)	54(3)	24.3(19)	−10(2)	7.0(15)	5.2(18)
C9	35(2)	93(4)	25(2)	−14(3)	6.4(17)	21(2)
C10	26.2(17)	124(5)	19.2(17)	−6(3)	8.0(14)	1(3)
C11	30.0(19)	94(5)	29(2)	7(3)	11.6(16)	−12(2)

C12	30.4(17)	58(3)	24.9(18)	4.5(19)	10.6(15)	−7.0(18)
C13	23.9(14)	19.9(18)	22.5(16)	−1.7(14)	11.8(13)	−4.0(13)
C14	38.7(18)	23.3(19)	19.8(17)	−3.7(15)	10.6(14)	−7.2(15)
C15	55(2)	21.8(19)	25.5(17)	−6.2(17)	19.4(16)	−7.3(18)
C16	46(2)	14.2(17)	35(2)	−0.7(15)	22.7(16)	−0.4(15)
C17	31.1(15)	19.7(19)	24.2(16)	1.3(14)	12.6(13)	−0.5(13)
C18	23.1(14)	17.6(17)	21.8(15)	−1.8(14)	12.7(12)	−4.5(12)
C19	22.9(13)	17.6(17)	18.2(15)	1.1(13)	10.8(12)	0.8(12)
C20	23.4(14)	21.7(18)	24.3(16)	−1.1(15)	10.4(13)	1.8(13)
C21	26.3(15)	30(2)	23.2(17)	5.7(16)	5.4(13)	9.1(14)
C22	38.1(17)	29(2)	25.0(16)	10.7(18)	15.0(14)	13.6(17)
C23	34.4(16)	24.9(19)	35.3(18)	9.3(18)	22.6(14)	3.9(16)
C24	23.7(14)	24.4(19)	24.8(16)	1.7(14)	13.5(12)	0.5(13)
C25	23.1(13)	17.7(17)	19.2(14)	2.9(14)	6.9(11)	−1.3(13)
C26	30.0(16)	20.7(19)	27.7(18)	−0.8(15)	7.9(13)	−0.1(13)
C27	40.0(19)	19(2)	33(2)	−2.6(16)	6.8(16)	−7.9(15)
C28	31.4(17)	34(2)	38(2)	3.9(18)	8.3(16)	−16.8(16)
C29	31.4(17)	45(3)	49(2)	−8(2)	24.6(16)	−14.0(19)
C30	28.9(16)	28(2)	36.6(19)	−5.5(17)	17.2(15)	−7.5(14)
C31	30.3(19)	79(4)	67(3)	34(3)	6.4(19)	−21(2)
C32	31.1(18)	48(3)	59(3)	−9(2)	24.5(18)	−10.5(18)
C33	188(11)	49(6)	95(7)	0	89(8)	0
O1	22	35	30	7	11	−7
O2	25	38	32	−4	12	−5
P1	23	20	18	−1	7	−1
P2	19	17	17	0	8	0
Cl1	87	99	74	−17	43	−6

Table 3: Bond Lengths in Å for **Compound 12p**.

Atoms	**Length/Å**	**Atoms**	**Length/Å**
C1 –C2	1.391(4)	C17–C18	1.401(5)
C1 –C6	1.411(4)	C18–P2	1.835(3)
C1 –P1	1.837(3)	C19–C20	1.396(4)
C2 –C3	1.390(5)	C19–C24	1.405(4)
C3 –C4	1.383(5)	C19–P2	1.836(3)
C4 –C5	1.387(5)	C20–C21	1.394(5)
C5 –C6	1.380(5)	C21–C22	1.382(5)
C6 –O2	1.366(4)	C22–C23	1.394(5)
C7 –C8	1.391(6)	C23–C24	1.379(5)
C7 –C12	1.378(6)	C24–O1	1.372(4)
C7 –P1	1.836(3)	C25–C26	1.383(5)
C8 –C9	1.401(6)	C25–C30	1.392(4)
C9 –C10	1.366(8)	C25–P2	1.831(3)
C10–C11	1.375(8)	C26–C27	1.398(5)
C11–C12	1.406(5)	C27–C28	1.383(6)
C13–C14	1.400(5)	C28–C29	1.376(6)
C13–C18	1.402(4)	C29–C30	1.387(5)
C13–P1	1.838(4)	C31–O1	1.420(5)
C14–C15	1.386(5)	C32–O2	1.430(4)
C15–C16	1.385(5)	C33–Cl1[1]	1.727(5)

C16–C17	1.386(5)	C33–Cl1	1.727(5)

[1]1-x,+y,1-z

Table 4: Bond Angles in ° for **Compound 12p**.

–Atoms–	Angle/°	–Atoms–	Angle/°
C2 – C1 – C6	117.7(3)	C20 – C19– C24	117.8(3)
C2 – C1 – P1	125.9(2)	C20 – C19– P2	125.6(2)
C6 – C1 – P1	116.3(2)	C24 – C19– P2	116.2(2)
C3 – C2 – C1	121.6(3)	C21 – C20– C19	120.9(3)
C4 – C3 – C2	119.1(3)	C22 – C21– C20	120.1(3)
C3 – C4 – C5	121.0(3)	C21 – C22– C23	120.1(3)
C6 – C5 – C4	119.3(3)	C24 – C23– C22	119.6(3)
C5 – C6 – C1	121.2(3)	C23 – C24– C19	121.6(3)
O2 – C6 – C1	114.4(3)	O1 – C24– C19	114.0(3)
O2 – C6 – C5	124.3(3)	O1 – C24– C23	124.4(3)
C8 – C7 – P1	116.8(3)	C26 – C25– C30	118.8(3)
C12– C7 – C8	118.9(3)	C26 – C25– P2	117.2(2)
C12– C7 – P1	124.1(3)	C30 – C25– P2	123.9(3)
C7 – C8 – C9	120.3(5)	C25 – C26– C27	121.4(3)
C10– C9 – C8	120.5(5)	C28 – C27– C26	118.7(4)
C9 – C10– C11	119.7(4)	C29 – C28– C27	120.5(3)
C10– C11– C12	120.4(5)	C28 – C29– C30	120.6(4)
C7 – C12– C11	120.2(5)	C29 – C30– C25	120.0(4)
C14– C13– C18	119.2(3)	Cl1[1]– C33– Cl1	113.1(5)
C14– C13– P1	123.0(3)	C24 – O1 – C31	117.5(3)
C18– C13– P1	117.7(3)	C6 – O2 – C32	117.9(3)
C15– C14– C13	120.8(3)	C1 – P1 – C13	100.23(15)
C16– C15– C14	120.1(3)	C7 – P1 – C1	102.21(13)
C15– C16– C17	119.8(3)	C7 – P1 – C13	103.66(17)
C16– C17– C18	120.9(3)	C18 – P2 – C19	101.54(15)
C13– C18– P2	117.8(3)	C25 – P2 – C18	102.82(14)
C17– C18– C13	119.3(3)	C25 – P2 – C19	100.77(14)
C17– C18– P2	122.9(3)	– –	

[1]1-x,+y,1-z

Table 5: Torsion Angles in ° for **Compound 12p**.

–Atoms–	Angle/°
C1 –C2 –C3 –C4	0.5(6)
C1 –C6 –O2 –C32	−180.0(3)
C2 –C1 –C6 –C5	−2.2(5)
C2 –C1 –C6 –O2	177.1(3)
C2 –C1 –P1 –C7	4.7(4)
C2 –C1 –P1 –C13	−101.8(3)
C2 –C3 –C4 –C5	−0.8(7)
C3 –C4 –C5 –C6	−0.5(6)
C4 –C5 –C6 –C1	2.0(6)
C4 –C5 –C6 –O2	−177.2(4)

C5 –C6 –O2 –C32	−0.7(5)
C6 –C1 –C2 –C3	1.0(6)
C6 –C1 –P1 –C7	−173.1(3)
C6 –C1 –P1 –C13	80.4(3)
C7 –C8 –C9 –C10	−1.0(6)
C8 –C7 –C12–C11	−0.9(5)
C8 –C7 –P1 –C1	80.6(3)
C8 –C7 –P1 –C13	−175.5(3)
C8 –C9 –C10–C11	0.5(6)
C9 –C10–C11–C12	−0.3(6)
C10–C11–C12–C7	0.4(6)
C12–C7 –C8 –C9	1.1(5)
C12–C7 –P1 –C1	−104.7(3)
C12–C7 –P1 –C13	−0.9(3)
C13–C14–C15–C16	−0.6(5)
C13–C18–P2 –C19	−161.7(2)
C13–C18–P2 –C25	94.2(2)
C14–C13–C18–C17	−1.6(4)
C14–C13–C18–P2	175.2(2)
C14–C13–P1 –C1	17.1(3)
C14–C13–P1 –C7	−88.3(3)
C14–C15–C16–C17	−0.5(5)
C15–C16–C17–C18	0.6(5)
C16–C17–C18–C13	0.5(5)
C16–C17–C18–P2	−176.1(2)
C17–C18–P2 –C19	14.9(3)
C17–C18–P2 –C25	−89.1(3)
C18–C13–C14–C15	1.7(5)
C18–C13–P1 –C1	−159.2(2)
C18–C13–P1 –C7	95.5(2)
C19–C20–C21–C22	0.3(5)
C19–C24–O1 –C31	−175.1(4)
C20–C19–C24–C23	−1.6(5)
C20–C19–C24–O1	179.4(3)
C20–C19–P2 –C18	−115.6(3)
C20–C19–P2 –C25	−9.9(3)
C20–C21–C22–C23	−1.6(6)
C21–C22–C23–C24	1.2(6)
C22–C23–C24–C19	0.4(5)
C22–C23–C24–O1	179.3(3)
C23–C24–O1 –C31	6.0(6)
C24–C19–C20–C21	1.2(5)
C24–C19–P2 –C18	71.6(3)
C24–C19–P2 –C25	177.2(3)
C25–C26–C27–C28	−0.5(5)
C26–C25–C30–C29	−0.9(5)
C26–C25–P2 –C18	−156.1(3)
C26–C25–P2 –C19	99.3(3)
C26–C27–C28–C29	−0.8(6)
C27–C28–C29–C30	1.2(6)
C28–C29–C30–C25	−0.4(6)
C30–C25–C26–C27	1.3(5)
C30–C25–P2 –C18	26.3(3)

C30	–C25	–P2	–C19	−78.3(3)
P1	–C1	–C2	–C3	−176.8(3)
P1	–C1	–C6	–C5	175.7(3)
P1	–C1	–C6	–O2	−5.0(4)
P1	–C7	–C8	–C9	176.1(3)
P1	–C7	–C12	–C11	−175.4(3)
P1	–C13	–C14	–C15	−174.5(3)
P1	–C13	–C18	–C17	174.8(2)
P1	–C13	–C18	–P2	−8.5(3)
P2	–C19	–C20	–C21	−171.5(3)
P2	–C19	–C24	–C23	171.8(3)
P2	–C19	–C24	–O1	−7.2(4)
P2	–C25	–C26	–C27	−176.4(3)
P2	–C25	–C30	–C29	176.7(3)

[1] 1-x,+y,1-z

Table 6: Hydrogen Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters (Å$^2 \times 10^3$) for **Compound 12p**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij}.

Atom	x	y	z	U(eq)
H2	4290	4032	4393	35
H3	4544	3489	5655	44
H4	3655	2825	6039	43
H5	2516	2747	5178	36
H8	3954	1519	2987	47
H9	4983	1503	2797	63
H10	5443	4112	2581	68
H11	4894	6769	2578	61
H12	3867	6816	2777	45
H14	3176	7138	3996	33
H15	2693	9944	3840	39
H16	1919	10 860	2665	36
H17	1640	8974	1643	29
H20	723	6069	128	27
H21	402	7855	−933	33
H22	1203	9736	−1099	36
H23	2320	9936	−173	35
H26	1517	2091	858	33
H27	510	502	672	40
H28	−307	1721	1067	43
H29	−111	4435	1661	47
H30	884	6030	1833	36
H31A	3408	9138	609	94
H31B	3731	9257	1501	94
H31C	3114	10 540	1023	94
H32A	1081	3181	3503	66
H32B	1512	3972	4316	66
H32C	1561	1917	4159	66
H33B	5410	10 413	5149	120
H33A	4590	10 413	4851	120

Table 7: Atomic Occupancies for all atoms that are not fully occupied in **Compound 12p**.

Atom	**Occu**	**Atom**	**Occu**	**Atom**	**Occu**
H33B	0.5	H33A	0.5		

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