# Synthesis of a Phosphapyracene via Metal-Mediated Cyclization: Structural and Reactivity Effects of Acenaphthene Precursors

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# Supporting Information

1. Additional Experimental Information
2. NMR Spectra
3. Details of the X-ray Crystallographic Studies

## 1. Additional Experimental Information

**6-bromo-5-acenaphthoic acid (9)**. This known compound was prepared by a modified literature method.[1,2] A brown solution of 5,6-dibromoacenaphthene (5.011 g, 16 mmol) in 200 mL of THF was cooled to –78 °C under $N_2$, and *n*-BuLi (9.64 mL, 19 mmol, 1.2 equiv, 2 M in cyclohexane) was slowly added. After complete addition, the resulting yellow mixture was stirred for about 20 min at –78 °C. Excess dry ice pellets were dropped through the neck of the Schlenk flask against the $N_2$ flow, turning the mixture to milky white. It was stirred until it warmed up to room temperature, then acidified to pH 6 with $H_2SO_4$ (conc or 1 M), and extracted with $Et_2O$ (2 x 50 mL). The combined organic layers were extracted with 1 M NaOH (2 x 50 mL). The combined aqueous extracts were acidified with conc HCl, yielding an off-white precipitate, which was filtered and recrystallized from EtOH to give an off-white solid. Yield = 2.83 g (64%). This reaction was also run with 10.44 g of dibromoacenaphthene to give 4.88 g of the acid (55% yield).

$^1$H NMR (acetone-$d_6$): δ 7.81 (d, $J$ = 7, 1H), 7.70 (d, $J$ = 7, 1H), 7.41 (dt, $J$ = 7, 1, 1H), 7.30 (dt, $J$ = 7, 1, 1H), 3.41 (m, 4H). $^{13}$C{$^1$H} NMR (acetone-$d_6$): δ 170.3, 149.5, 147.1, 140.8, 134.4, 130.0, 128.9, 127.1, 121.4, 119.7, 114.1, 30.3, 29.7.

**Bromo alcohol 10** Carboxylic acid **9** was converted to an acid chloride using $SOCl_2$ or oxalyl chloride by analogy to related procedures,[3] then reduced to alcohol **10**. The thionyl chloride method was preferred. Under $N_2$, $SOCl_2$ (0.299 mL, 4.51 mmol, 11 equiv) was added via syringe to a Schlenk tube containing 6-bromo-5-acenaphthoic acid (0.100 g, 0.361 mmol) at room temperature. The bromoacenaphthoic acid was insoluble at room temperature but the mixture turned dark as it was slowly heated up to reflux for 1-3 h. It was then cooled to room temperature and the excess $SOCl_2$ was removed *in vacuo* to give an off-white solid, which was

dissolved in 20-25 mL of $Et_2O$ to give a yellow solution. $LiAlH_4$ (0.014 g, 0.36 mmol, 1 equiv) was added. The solution was heated gently to reflux for 5-8 h. Workup involved addition of 5-10 mL of $H_2O$ at room temperature, extraction with $Et_2O$ (2 x 50 mL), drying with $MgSO_4$, filtration and solvent removal *in vacuo*. The yellow solid was purified by recrystallization from $CH_2Cl_2$ layered with petroleum ether. Yield: 0.084 g (0.32 mmol, 88%). This reaction was also scaled up successfully: 4.88 g of acid gave 2.76 g of alcohol (64% yield).

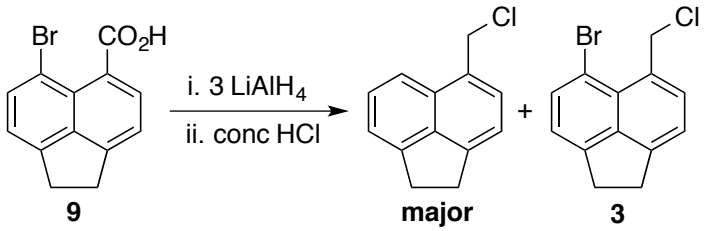
Anal. Calcd. for $C_{13}H_{11}BrO$: C, 59.34; H, 4.21; Found C, 59.04; H, 4.98. HRMS m/z calcd for $C_{13}H_{11}BrO$: 261.9993. Found: m/z 261.9996. $^1H$ NMR ($CDCl_3$): δ 7.75 (d, *J* = 7, 1H), 7.57 (d, *J* = 7, 1H), 7.28 (d, *J* = 7, 1H), 7.13 (d, *J* = 7, 1H), 5.34 (d, *J* = 2, 2H), 3.39-3.33 (m, 4H), 2.39 (br, OH, 1H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 147.8, 147.2, 142.0, 134.4, 132.9, 132.2, 129.0, 120.6, 120.3, 113.4, 64.1, 30.3, 30.2.

**Benzyl Chloride 3 via Alcohol 10** Under $N_2$, a solution of alcohol **10** (0.600 g, 2.28 mmol) in ca. 50 mL of $CH_2Cl_2$ was treated with $NEt_3$ (0.477 mL, 3.42 mmol, 1.5 equiv). The mixture was cooled to 0 °C and methanesulfonyl chloride (0.194 mL, 2.51 mmol, 1.1 equiv) was added via syringe. The mixture was stirred until it reached room temperature, and then overnight. The workup involved addition of 10 mL of aqueous $NH_4Cl$ solution, extraction using $CH_2Cl_2$ (2 x 10 mL), drying with $MgSO_4$ and removing the solvent *in vacuo*. The resulting light yellow solid was purified via recrystallization from $Et_2O$. Yield = 0.438 g (1.56 mmol, 68%); similarly, 2 g of alcohol **10** gave 1.70 g of **3** (79% yield). Note: when this reaction was followed by $^1H$ NMR spectroscopy in $CD_2Cl_2$, the $CH_2$ signal for the mesylate intermediate was observed at δ 6.01; it was soon replaced by the analogous signal for the product (δ 5.45).

**Reduction of Carboxylic Acid 9 to Alcohol 10 Using Oxalyl Chloride and $LiAlH_4$, Instead of $SOCl_2/LiAlH_4$** Under $N_2$, oxalyl chloride (0.037 mL, 0.43 mmol, 1.2 equiv) was added via

syringe to a suspension of 6-bromo-5-acenaphthoic acid (0.100 g, 0.361 mmol) in 10 mL of $CH_2Cl_2$ at room temperature. Addition of DMF (2 drops) resulted in rapid gas evolution; then the mixture turned light yellow. The solution was stirred for 20 min and then the solvent was removed *in vacuo* to give an off-white solid, which was dissolved in 20-25 mL of $Et_2O$. To the clear solution, $LiAlH_4$ (0.014 g, 0.36 mmol, 1 equiv) was added and the mixture was heated to reflux for 5-8 h. Workup of the reaction mixture involved addition of 5-10 mL of $H_2O$ at room temperature, extraction with $Et_2O$ (2x 50 mL), drying with $MgSO_4$, filtration and solvent removal *in vacuo*. The white solid was purified via recrystallization from $CH_2Cl_2$ layered with petroleum ether. Yield: 0.038 g (0.144 mmol, 40%).

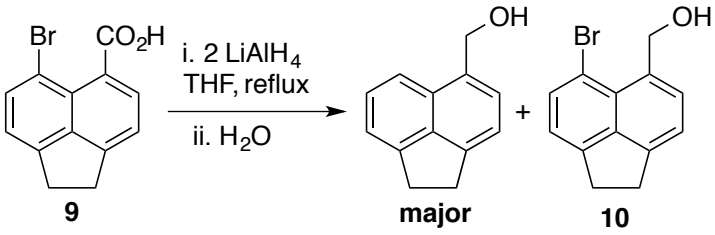
Attempts to reduce acid **9** directly, without converting it to the acid chloride, led to dehalogenation.




**Attempted reduction of 6-Br-5-acenaphthoic acid with $LiAlH_4$** Under $N_2$, the carboxylic acid **9** (421 mg, 1.52 mmol) was dissolved in 15 mL of dry THF. A gray suspension of 3 equiv of $LiAlH_4$ (173 mg, 4.56 mmol) in 5 mL of dry THF was added to the carboxylic acid solution with a pipet under $N_2$ flow. Bubbles were observed immediately after addition. The mixture was stirred at room temperature overnight. Workup: 4 mL of conc HCl was added dropwise to the reaction flask at 0 °C. 2×50 mL of ether was used to extract the product. The organic layer was collected and dried with $MgSO_4$. After removing the solvent under reduced pressure, 332 mg (108% yield) of deep green solid was obtained. $^1$H NMR spectroscopy showed a mixture of the

debrominated benzyl chloride and the desired bromo-benzyl chloride **3** in an approximate ratio of 1:0.18.

$^1$H NMR ($CDCl_3$): δ 7.82 (d, *J* = 8, 1H), 7.55 (dd, *J* = 8, 7, 1H), 7.46 (d, *J* = 7, 1H), 7.34 (d, *J* = 7, 1H), 7.23 (d, *J* = 7, 1H), 5.02 (2H, benzyl), 3.44-3.34 (m, 4H, ace $CH_2$).




Under $N_2$, the carboxylic acid **9** (247 mg, 0.89 mmol) was dissolved in 10 mL of dry THF. A gray suspension of 2 equiv of $LiAlH_4$ (68 mg, 1.78 mmol) in 3 mL of dry THF was added to the carboxylic acid solution with a pipet under $N_2$ flow. Bubbles were observed immediately after addition. The mixture was heated to reflux at 75 °C overnight. Workup: 6 mL of distilled water was added dropwise to the reaction flask at 0 °C. 2×30 mL of ether was used to extract the product. The organic layer was collected and then washed with 50 mL of aqueous $NH_4Cl$. After drying with $MgSO_4$ and concentrating the solution, 148 mg (90% yield) of white solid was obtained. $^1$H NMR spectroscopy confirmed the formation of the debrominated alcohol, plus ca. 5% of the desired bromo-benzyl alcohol **10** and 8% of unidentified impurities.

$^1$H NMR ($CDCl_3$): δ 7.82 (d, *J* = 8, 1H), 7.51 (dd, *J* = 8, 7, 1H), 7.45 (d, *J* = 7, 1H), 7.32 (d, *J* = 7, 1H), 7.24 (d, *J* = 7, 1H), 5.09 (d, *J* = 6, 2H benzyl), 3.42-3.39 (m, 4H, ace $CH_2$), 1.62 (t, *J* = 6, 1H).

The product debrominated alcohol and benzyl chloride derivatives are known compounds and were identified by comparison of their $^1$H NMR spectra ($CDCl_3$) to the literature data (Honda, H. JP2002205967, **2002**.)

**Arbuzov Reaction: Formation of Phosphine Oxide 13** Under $N_2$, benzyl chloride **3** (0.466 g, 1.66 mmol, 1 equiv) was placed in a 50 mL round bottom flask. Diisopropyl phenylphosphonite (0.19 mL, 0.8 mmol, 0.5 equiv) was added via syringe. The reaction mixture was placed in a short-path distillation apparatus and heated to 50 °C, then slowly heated to 150 °C in increments of 10 °C every 10-15 min. The benzyl chloride **3** appeared to sublime up the walls of the flask, so it was occasionally washed down with aliquots of an additional 0.19 mL of the phosphonite (a total of 0.38 mL, 1.6 mmol, 1 equiv was used, resulting in full conversion of **3**). The temperature was held at 150 °C for 1 h. Then, the apparatus was placed under vacuum at 150 °C for 30 min to remove volatile materials. The involatile residue was recrystallized from warm petroleum ether or toluene/petroleum ether in a refrigerator to give colorless blocks (0.65 g, 72% yield). A second recrystallization from warm petroleum ether gave analytically pure material, while X-ray quality crystals were obtained from toluene/petroleum ether.

Anal. calcd for $C_{22}H_{22}BrO_2P$: C, 61.55; H, 5.17. Found: C, 61.67; H, 5.01. HRMS m/z calcd for $C_{22}H_{22}BrO_2P$: 429.0619. Found: m/z 429.0625. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 39.0. $^1H$ NMR ($CDCl_3$): δ 7.67 (m, 3H), 7.45-7.41 (m, 3H), 7.34-7.33 (m, 1H), 7.22-7.21 (m, 1H), 7.02-7.01 (m, 1H), 4.63-4.57 (t, $J$ = 16, 1H), 4.48-4.44 (m, 1H), 4.24-4.17 (t, $J$ = 16, 1H), 3.34-3.30 (m, 4H), 1.15-1.07 (dd, m, 6H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 146.7, 146.1 (d, $J$ = 4), 141.4, 134.5, 133.6 (d, $J$ = 7), 132.4, 132.04, 132.0, 131.7 (d, $J$ = 3), 131.4, 129.0 (d, $J$ = 4), 128.0 (d, $J$ = 12), 124.0 (d, $J$ = 10), 119.9, 119.8 (d, $J$ = 4), 114.3 (d, $J$ = 2), 69.7 (d, $J$ = 7), 36.0 (d, $J$ = 96), 30.0, 29.8, 24.2 (d, $J$ = 3), 23.9 (d, $J$ = 5).

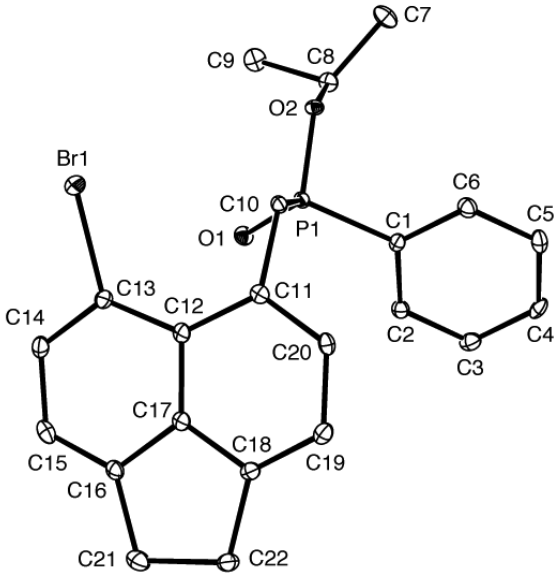


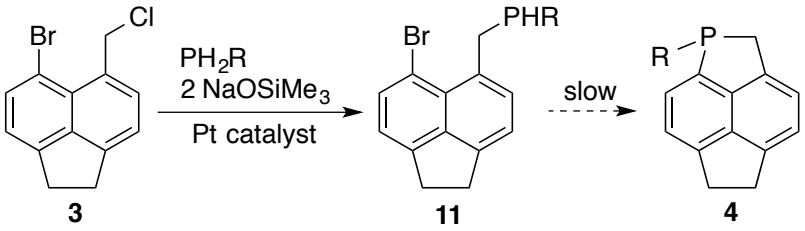

**Figure S1** ORTEP diagram of Arbuzov product **13**.

**Secondary Phosphine Ph-11 from Reduction of Phosphine Oxide 13** To a $LiAlH_4$ slurry (0.079 g or 0.22 g, 2.1 mmol or 5.8 mmol, 6 equiv) in 10-20 mL of THF, $Me_3SiCl$ (0.27 mL or 0.74 mL, 2.1 mmol or 5.8 mmol, 6 equiv) was added via syringe; the mixture was cooled to –78 °C and stirred for 1 h. The gray solution was then stirred at room temperature for 30 min before cooling to –40 °C. To this mixture, a solution of Arbuzov product **13** (0.15 g or 0.41 g, 0.35 mmol or 0.96 mmol, 1 equiv) in 10-20 mL of THF was added via cannula. The mixture was stirred and allowed to reach room temperature overnight. Workup involved adding 30-50 mL of degassed water, extracting with dry $Et_2O$ (2 x 30 mL), combining the organic layers, drying with $MgSO_4$ and removing the solvent *in vacuo*. Although this method gave secondary phosphine **Ph-11**, the primary phosphine $PH_2Ph$ and other unidentified impurities were also formed.

**[Pt((*R,R*)-Me-DuPhos)(Ph)(PHPh($CH_2$Ar))][OTf] (17) Using AgOTf** We originally prepared this cation using AgOTf, but the $NH_4PF_6$ procedure (experimental section) gave higher-purity product more conveniently.

In the glove box, AgOTf (42 mg, 0.16 mmol) and Pt((*R,R*)-Me-DuPhos)(Ph)(Cl) (101 mg, 0.16 mmol, 1 equiv) were dissolved in 1 mL of THF separately in two vials. The two solutions were mixed together and white precipitate formed immediately. After stirring for 5 min, the mixture was filtered through Celite to remove the precipitate. The filtrate was added to a solution of secondary phosphine **Ph-11** (65 mg, 0.18 mmol, 1.1 equiv) in 1 mL of THF. The color turned deep red immediately. Several more filtrations didn't help to remove the color and the solution was still yellow/brown. After concentrating the THF solution to about 1 mL, 2 mL of pentane was added and beige product precipitated (67 mg, 34% yield). The $^{31}$P NMR spectrum showed the product was formed, but some impurity peaks were present. In a similar procedure, the reaction mixture was protected from light using aluminum foil. However, it was still difficult to remove colored impurities and the product was beige.

**Screening Pt-Catalyzed Tandem Phosphination/Cyclization of Benzyl Chloride 3**




**General procedure**: A solution of benzyl chloride **3** (15 mg, 0.05 mmol) in ca. 0.2 mL of THF was added to a mixture of $PH_2Ph$ (6 mg, 0.05 mmol), $NaOSiMe_3$ (12 mg, 0.10 mmol, 2 equiv) and Pt((*R,R*)-Me-DuPhos)(Ph)(Cl) (2 mg, $3x10^{-3}$ mmol, 6 mol %) in 0.3 mL of THF. The reaction was monitored by $^{31}$P NMR spectroscopy.

Similar experiments were carried out using other primary phosphines, including commercially available $PH_2Cy$, *o*-$C_6H_4(PH_2)_2$, and $H_2PCH_2CH_2PH_2$, as well as $FcCH_2PH_2$ and 1,1'-$Fc(PH_2)_2$, which were prepared by the literature procedures. (See: (a) Goodwin, N. J.; Henderson, W.; Nicholson, B. K.; Fawcett, J.; Russell, D. R. *J. Chem. Soc., Dalton Trans.* **1999**, 1785-1793. (b) Burk, M. J.; Gross, M. F. *Tetrahedron Lett.* **1994**, *35*, 9363-9366.)

We also tested the solvent toluene, the base KOtBu, and other catalyst precursors, including Pt((*R,R*)-*i*-Pr-DuPhos)(Ph)(Cl), Pt((*R,R*)-*i*-Pr-DuPhos)(Me)(Cl), Pt((*R,R*)-Me-BPE)(Ph)(Cl), Pt((*R,R*)-Me-BPE)(Me)(Cl), and Pt((*R,R*)-Ph-BPE)(Me)(Cl) (see Guino-o, M. A.; Zureick, A. H.; Blank, N. F.; Anderson, B. J.; Chapp, T. W.; Kim, Y.; Glueck, D. S.; Rheingold, A. L. *Organometallics* **2012**, *31*, 6900-6910.) As described briefly in the text, the main product of these catalytic reactions was the secondary phosphine **Ph-11** and its assumed analogues with other R groups.

**Ph-PyraPhos(O) (16)** As described in the experimental section, deprotection of Ph-PyraPhos($BH_3$) gave a small amount of phosphine oxide **16**, which was isolated by washing the silica plug with methanol quickly (isopropanol can also elute the phosphine oxide). Removal of methanol under vacuum gave a light yellow solid, which was characterized by NMR and mass spectrometry.

HRMS (m/z): calcd for $C_{19}H_{16}OP$ $(MH)^+$, 291.0939, found, 291.0938. We could not obtain satisfactory elemental analyses for this compound even after recrystallization by vapor diffusion of pentane into a $CH_2Cl_2$ solution. For example: Anal. Calcd for $C_{19}H_{15}OP$: C, 78.61; H, 5.21. Found: C, 74.80; H, 4.61. Also found C, 76.67; H, 4.62. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 51.3; $^{31}P\{^1H\}$ NMR (THF): δ 46.4. $^1H$ NMR ($CDCl_3$): δ 7.84 (dd, $J_{P\text{-}H}$ = 10, $J_{H\text{-}H}$ = 7, 1H), 7.58-7.54 (m, 2H), 7.50-7.43 (m, 2H), 7.41-7.36 (m, 4H), 3.73 (ABX, $J_{AB}$ = 18, $J_{AX}$ = 18, 1H, benzyl), 3.62 (ABX,

$J_{AB}$ = 18, $J_{AX}$ = 6, 1H, benzyl), 3.55-3.47 (m, 4H, ace H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 150.4 (d, *J* = 2, Ar, quat), 143.8 (d, *J* = 1, Ar, quat), 138.0 (d, *J* = 17, Ar, quat), 137.9 (d, *J* = 33, Ar, quat), 134.5 (d, *J* = 99, Ar, quat), 132.0 (d, *J* = 3, Ar), 130.6 (d, *J* = 11, Ar), 129.6 (d, *J* = 8, Ar), 129.0 (d, *J* = 7, Ar, quat), 128.8 (d, *J* = 12, Ar), 127.8 (d, *J* = 102, Ar, quat), 125.1 (d, *J* = 12, Ar), 121.5 (d, *J* = 12, Ar), 121.2 (d, *J* = 1, Ar), 35.9 (d, *J* = 77, benzyl $CH_2$), 32.1 (d, *J* = 1, ace-$CH_2$), 31.2 (ace-$CH_2$).

**Oxidation of Ph-PyraPhos Ph-4 in air also gave phosphine oxide 16.** Under $N_2$, Ph-PyraPhos (**Ph-4**, 13 mg, 0.047 mmol) was dissolved in 1 mL of THF and transferred to a NMR tube with a rubber septum. The NMR tube was then heated at 60 °C with a vent needle in the septum to allow air exchange. $^{31}P$ NMR monitoring showed formation of the phosphine oxide after 6 d.

**Formation of Ph-PyraPhos(O) (16) via Its Hydrogen Peroxide Adduct 16•0.5$H_2O_2$** A solution of Ph-PyraPhos (**Ph-4**, 28 mg, 0.11 mmol) in 1 mL of THF was transferred to a NMR tube with a rubber septum. Concentrated aqueous $H_2O_2$ (30 weight % in $H_2O$, 0.2 mL, 1.7 mmol $H_2O_2$) was added dropwise via syringe. The reaction was exothermic. After the NMR tube was shaken briefly, the $^{31}P$ NMR spectrum showed that oxidation had occurred (δ 52.2). Thirty min later, small crystals came out and the solution was allowed to sit overnight (in another repeated reaction, crystals formed after overnight standing). The next day, the crystals were separated (approximately 10 mg, 30% yield) and the X-ray single crystal analysis showed that two PyraPhos oxide molecules co-crystallized with one $H_2O_2$ molecule, which was also observed by $^{1}H$ NMR spectroscopy (δ 8.33 (broad), $CDCl_3$). To remove the $H_2O_2$, molecular sieves were added to a $CH_2Cl_2$ solution of the crystals. After two d, the solution was decanted and removal of the solvent gave oxide **16**.[4]

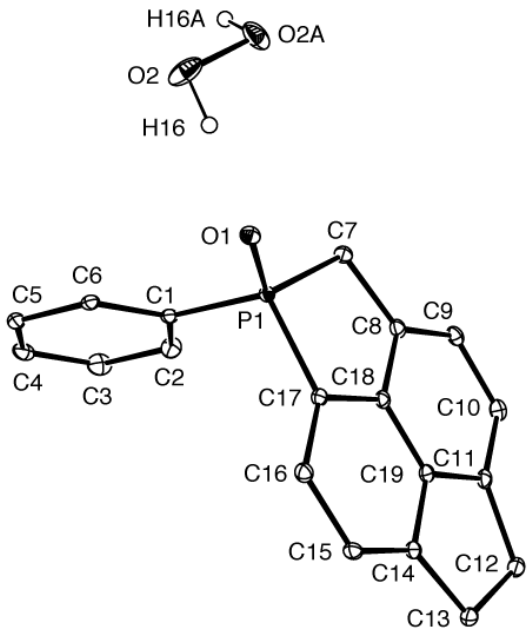



**Figure S2**. ORTEP diagram of Ph-PyraPhos(O)•0.5$H_2O_2$ (**16**•0.5$H_2O_2$), showing one of the hydrogen bonding interactions. Selected distances (Å) and angles (deg): O2–O1 2.694; O1-H16 1.798; O2–H16–O1 176.05 (H16 was located and refined).

Note: In a similar reaction with 28 mg of Ph-PyraPhos, after addition of $H_2O_2$, a few crystals formed immediately. However, after standing overnight, no more crystals came out. The mixture was then added to 10 mL of $CH_2Cl_2$ and dried with anhydrous $MgSO_4$. After filtration, activated molecular sieves were added to the solution to remove $H_2O_2$. After three d, the solution was decanted and the solvent was removed to give 14 mg of white solid (47% yield). The crude product was dissolved in a small amount of $CH_2Cl_2$ and loaded onto a short silica column (5 cm long). Five mL of $CH_2Cl_2$ was first used to flush the column to remove any impurities. Then 5 mL of THF was used to wash the phosphine oxide off the column. Removal of THF gave 13 mg

of white solid (44% yield). The $^{31}P$ NMR spectrum showed a clean singlet for **16**. However, the $^{1}H$ NMR spectrum showed a few impurities were present.

We could not obtain satisfactory elemental analysis for the **16•0.5$H_2O_2$** adduct, even with crystals from the same batch used for X-ray analysis. Anal. Calcd for $C_{19}H_{15}OP{\cdot}0.5H_2O_2$: C, 74.26; H, 5.25. Found: C, 73.44; H, 4.79. $^{31}P\{^{1}H\}$ NMR ($CDCl_3$): δ 52.3. $^{1}H$ NMR ($CDCl_3$): δ 8.33 (broad, 1H, $H_2O_2$), 7.85 (dd, $J_{P\text{-}H}$ = 10, $J_{H\text{-}H}$ = 7, 1H), 7.61-7.54 (m, 2H), 7.52-7.44 (m, 2H), 7.44-7.36 (m, 4H), 3.76 (ABX, $J_{AB}$ = 18, $J_{AX}$ = 18, 1H, benzyl), 3.63 (ABX, $J_{AB}$ = 18, $J_{AX}$ = 6, 1H, benzyl), 3.58-3.45 (m, 4H, ace H).

**Cyclization of Pt-Phosphido Complex Ph-8, Generated by Deprotonation of the Cation [Pt((*R*,*R*)-Me-DuPhos)(Ph)(PH(Ph)($CH_2$Ar))][$PF_6$] (17)** The reaction was repeated by the procedure described in the experimental section multiple times on different scales. However, the rate and the ratio of the two diastereomers of the product **18** were not consistent or reproducible. Starting with 100 mg of Pt complex **17**, the reaction was done in 1 week and the diastereomer ratio was about 1.4:1 with 46% yield. In another reaction with 1.042 g of **17**, the reaction took 2 weeks and the diastereomer ratio was 1.4:1. For small-scale reactions starting with 20 mg of **17**, the reaction was in one case done in 2 days giving 5:1 diastereomer ratio, and in another case took about two weeks giving 2:1 diastereomer ratio. The reaction was also conducted at 45 °C with 20 mg of **17**. After 27 h, no phosphido complex **Ph-8** could be seen in the $^{31}P$ NMR spectrum, while the color of the solution was light yellow. It took 3 days until the solution became colorless. After workup, 14 mg (76% yield) of white solid was obtained and the diastereomer ratio was 1.7:1.

**Isolation of Highly Diastereoenriched [Pt((*R*,*R*)-Me-DuPhos)(Ph)(*R*-Ph-PyraPhos)][$PF_6$] (18a) by Recrystallization and Its Use to Prepare Highly Diastereoenriched [Pt((*S*,*S*)-Me-**

**DuPhos)(Ph)(*R*-Ph-PyraPhos)][$PF_6$] (18b')** Approximately 700 mg of **18a-b** (diastereomer ratio = 1.4:1) was recrystallized multiple times via vapor diffusion of ether into THF solution at room temperature to give 90 mg of the major diastereomer **18a** (dr = 98:2). In these recrystallizations, after removal of the mother liquor via pipet, crystals which were enriched in **18a** were collected. The sticky solid formed at the bottom of the vials (enriched in the minor diastereomer **18b**) was dissolved in $CH_2Cl_2$ and separated. The process was repeated multiple times until the crystals collected were almost diastereopure.

In the glove box, a solution of tetraoctylammonium bromide (99 mg, 0.18 mmol, 2 equiv) in 2 mL of THF was added to a solution of enriched **18a** (90 mg, 0.09 mmol) in 2 mL of THF. The $^{31}P$ NMR spectrum showed a mixture of Ph-PyraPhos (**Ph-4**, 51%), Ph-PyraPhos(O) (**16**, 40%), remaining cation **18a** (10%) and Pt((*R,R*)-Me-DuPhos)(Ph)(Br) (**19**). Then 0.2 mL of $BH_3$-THF (1 M in THF, 0.2 mmol, 2.1 equiv) was added to the mixture, to give Ph-PyraPhos($BH_3$) (**14**). The THF was removed under vacuum and the residue was dissolved in the minimum amount of $CH_2Cl_2$ and loaded on a silica column. Pentane/ethyl acetate (20:1) was used as eluent for chromatography, yielding a co-eluting mixture of phosphine borane **14**, an unidentified Pt(Me-Duphos) complex ($^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 78.8 ($J_{Pt-P}$ = 2346), 77.1 ($J_{Pt-P}$ = 2434)), and [$NOct_4$][Br]. After removal of the solvent from the eluent, the residue was extracted with pentane/ethyl acetate (20:1) to separate the less soluble tetraoctylammonium bromide salt. Then four more columns were conducted to partially separate borane adduct **14** from the unidentified Pt(Me-Duphos) complex. A total of 9 mg (35% crude yield) of solid was collected which contained about 20% of the Pt complex ($^{31}P$ NMR integration). This impurity was eventually removed when using silica gel chromatography to purify **18b'**, which was much more polar than the Pt complex (see below).

The crude phosphine-borane **14** (9 mg, 0.03 mmol) was dissolved in 8 mL of toluene and piperazinomethyl polystyrene (1% DVB, 100-200 mesh, Matrix Innovation, 23 mg, 2.7 mmol/g, 0.062 mmol, 2 equiv) was added to the solution. After stirring at 60 °C under $N_2$ for 2 d, the toluene was removed under vacuum. In the glove box, the residue was extracted with degassed dry $CH_2Cl_2$ and the solution was passed through a silica plug (5 cm long) to remove any phosphine oxide. Removal of $CH_2Cl_2$ gave Ph-PyraPhos **Ph-4** as a white solid (4 mg, 47%).

In the glove box, Ph-PyraPhos **Ph-4** (4 mg, 0.01 mmol) was dissolved in about 0.3 mL of THF. A mixture of Pt((*S,S*)-Me-DuPhos)(Ph)(Cl) (9 mg, 0.01 mmol) and $NH_4PF_6$ (3 mg, 0.02 mmol) in 1 mL of THF was prepared and added to the Ph-PyraPhos solution portion by portion. The $^{31}P$ NMR spectrum was checked during the addition to ensure the exact stoichiometry. White precipitate, which formed during the addition, was filtered off through a Celite plug. The THF was removed under vacuum and the residue was extracted with $CH_2Cl_2$. Removal of $CH_2Cl_2$ gave 11 mg of white solid, which was further purified with silica gel chromatography (2:1 ethyl acetate/pentane as eluant, $R_f$ = 0.3 in ethyl acetate). 4 mg (28% yield) of the cation **18b'** was collected; the $^{31}P$ NMR spectrum showed it was highly enriched, with the ratio **18a'/18b'** = 3/97. The overall yield of this reaction from **18a** to **18b'** was 4%.

**Generation of [Pt((*R,R*)-Me-DuPhos)(Ph)(Ph-PyraPhos)][$PF_6$] (18a-b) by Complexation of Racemic Ph-PyraPhos** A solution of racemic Ph-PyraPhos (**Ph-4**, 9 mg, 0.03 mmol) in about 0.3 mL of $CDCl_3$ was added to a mixture of Pt((*R,R*)-Me-DuPhos)(Ph)(Cl) (20 mg, 0.03 mmol) and $NH_4PF_6$ (11 mg, 0.07 mmol) in 1 mL of $CDCl_3$. The $^{31}P$ NMR spectrum showed generation of a 1:1 mixture of diastereomers of cation **18**, plus about 11% of unreacted Pt((*R,R*)-Me-DuPhos)(Ph)(Cl), presumably due to inexact stoichiometry on this small scale.

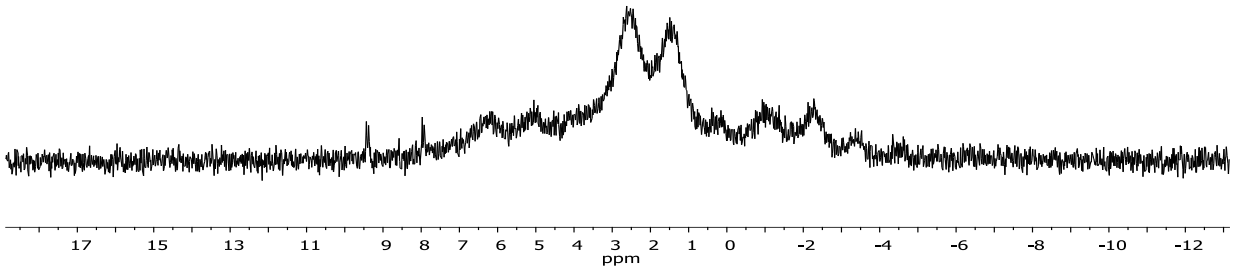
**Kinetic Resolution in Complexation of Racemic Ph-PyraPhos to Pt((*R*,*R*)-Me-DuPhos)(Ph)(Cl)** A mixture of Pt((*R*,*R*)-Me-DuPhos)(Ph)(Cl) (19 mg, 0.03 mmol, 1 equiv) and $NH_4PF_6$ (7 mg, 0.04 mmol, 1.33 equiv) in 1 mL of $CDCl_3$ was slowly added to a solution of racemic Ph-PyraPhos **Ph-4** (17 mg, 0.06 mmol, 2 equiv) solution in about 0.5 mL of $CDCl_3$. The $^{31}P$ NMR spectrum showed generation of a 1.3:1 mixture of **18b** (*S*-Ph-PyraPhos complex) and **18a** (*R*-Ph-PyraPhos complex) plus extra Ph-PyraPhos. The ratio didn't change after two weeks at room temperature, or after heating at 60 °C for 3 d. These experiments demonstrated low-selectivity kinetic resolution in binding **Ph-4** to the $[Pt(Me\text{-}DuPhos)(Ph)]^+$ group.

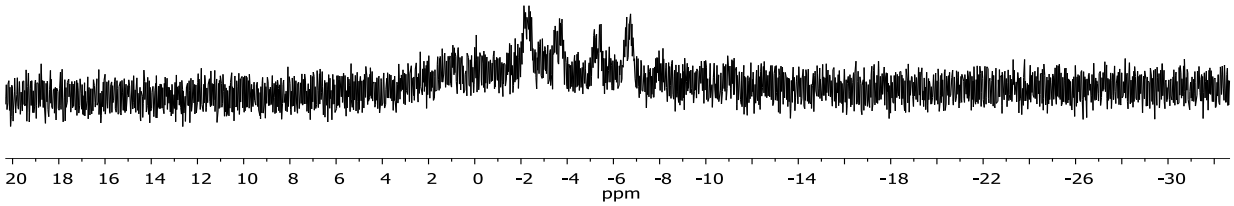
**Intermediates in the Reaction of Pt((*R*,*R*)-Me-DuPhos)(Ph)(PPh($CH_2$Ar)) (Ph-8) with AgOTf** As described in the experimental section, this reaction gave long-lived intermediates with distinctive broad $^{31}P$ NMR signals near 0 ppm. Two closely related sets of spectra were observed over multiple experiments; these may arise from the same intermediate, or from structurally related complexes. In most cases, we observed broad $^{31}P$ NMR signals which were consistent with the fragment Pt(Me-DuPhos)(Ph)(PPh($CH_2$Ar)(X)), in which unidentified modification of the phosphido group has occurred. $^{31}P\{^1H\}$ NMR (THF): δ 60.7 (br d, J ~ 270, $J_{Pt\text{-}P}$ = 2240), 59.5 (br, $J_{Pt\text{-}P}$ = 1700), 1.8 (br d, J ~ 270, $J_{Pt\text{-}P}$ ~ 1800). In a few cases, we observed a similar broad spectrum, which differed slightly in the chemical shift and appearance of the upfield signal, which now showed a four-line pattern tentatively assigned to a Pt-Ag $\mu$-phosphido complex as a mixture of two diastereomers, although we could not identify the expected Pt satellites on the upfield peak, or the analogous expected signal of the minor diastereomer. $^{31}P\{^1H\}$ NMR (THF): δ 61.5 (br d, J ~ 270, $J_{Pt\text{-}P}$ = 2250, b), 60.7 (br d, J ~ 260, $J_{Pt\text{-}P}$ = 2240, a), 60.0 (br, $J_{Pt\text{-}P}$ ~ 1710, a), 59.6 (br, $J_{Pt\text{-}P}$ ~ 1700, b), –1.8 (br d, J ~ 280, $J_{Ag\text{-}P}$ ~ 650, 570, a). The ratio a/b was about 2:1. We cannot tell if these spectra are due to the same intermediate,

and did not attempt to carry out further structural characterization of this material, or of the precipitate formed.

As described in the experimental section, these intermediates decomposed over the course of a few days to form a mixture of Pt complexes. The major product, cyclometalated complex **21** was usually formed first, but the ratio of this product, Ph-PyraPhos complex **18**, and unidentified **22** was not consistent over several runs, perhaps for the same reason that the rate and selectivity of formation of **18** from **Ph-8** in the absence of AgOTf was also inconsistent.

**Figure S3** Portions of the $^{31}P\{^{1}H\}$ NMR spectra (THF) of the intermediate(s) formed by addition of [Pt((*R*,*R*)-Me-Duphos)(Ph)(PHPh($CH_2$Ar))][$PF_6$] (**17**), $NaOSiMe_3$ and AgOTf. Top: broad doublet signal; bottom: 4-line pattern

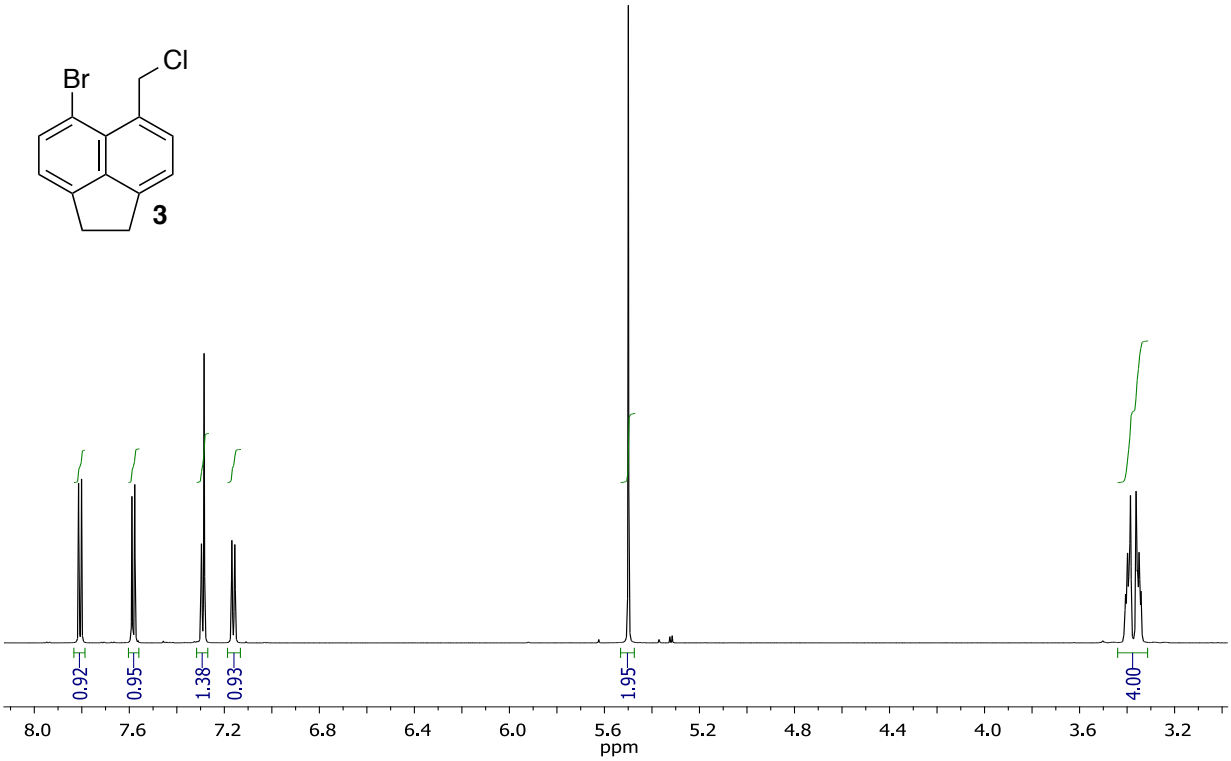


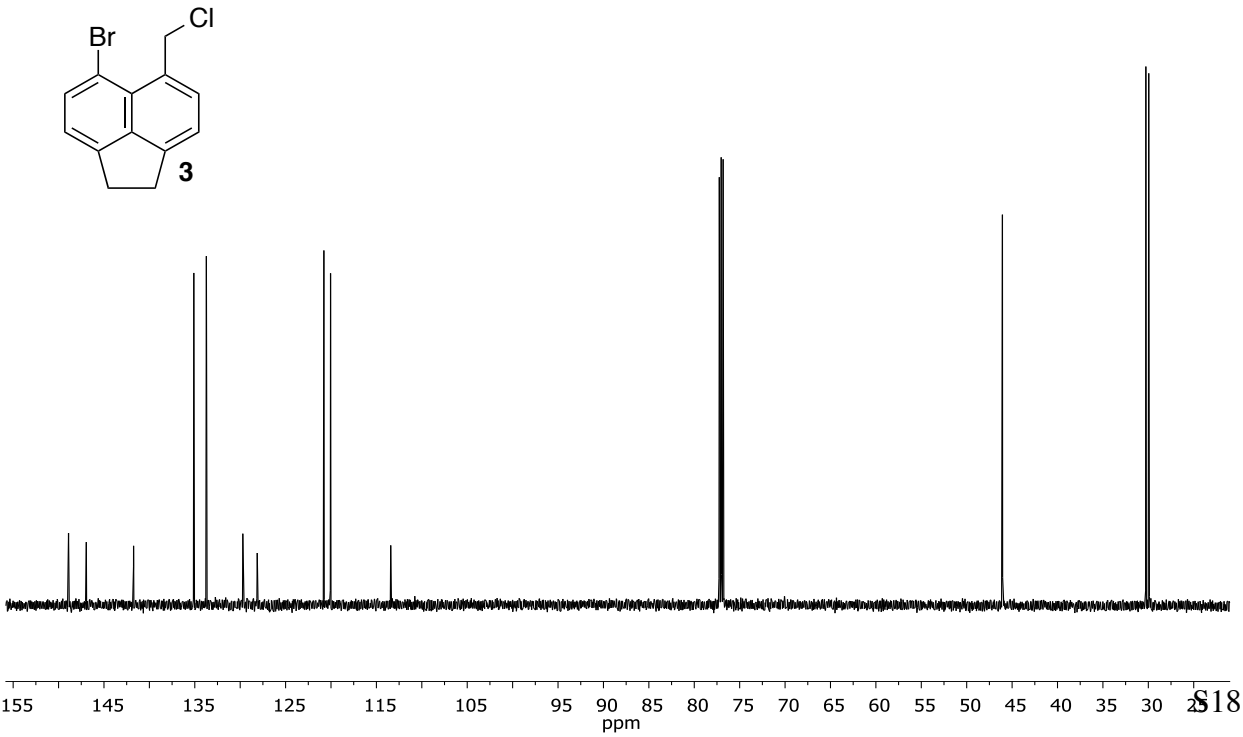


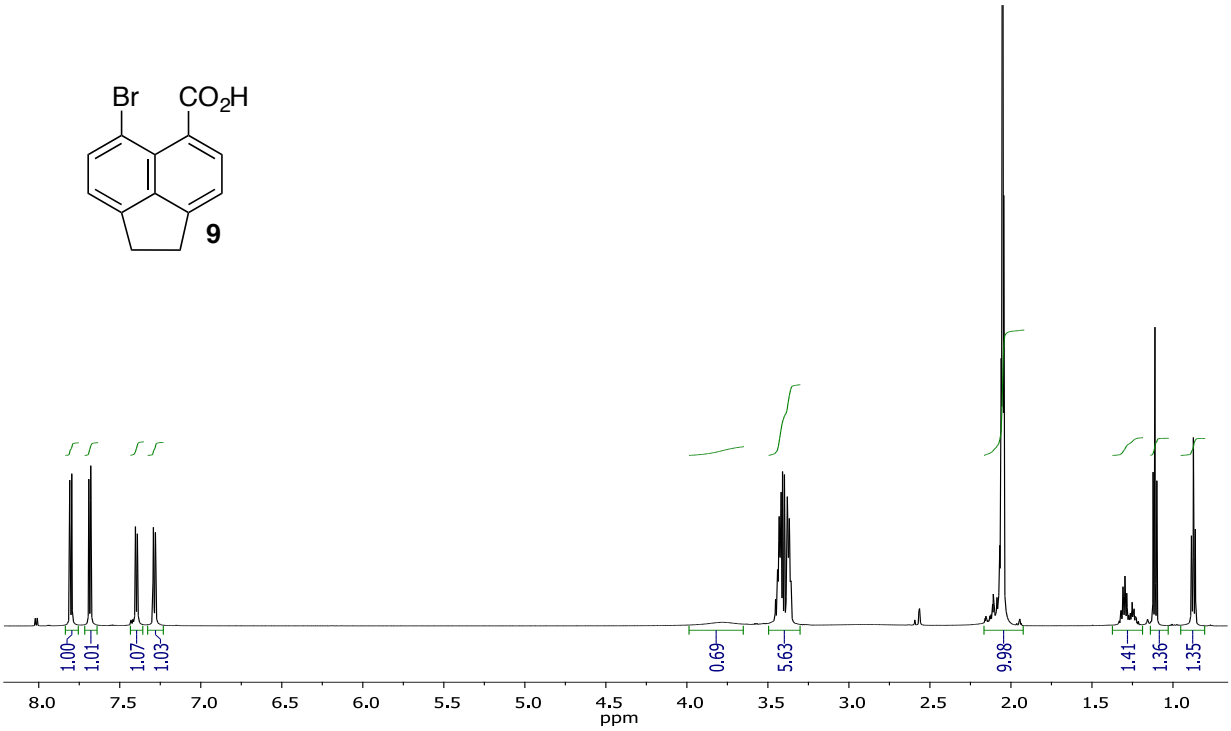

**Pt((*R*,*R*)-Me-Duphos)(*trans*-stilbene) was synthesized by a modified literature method.[5]** To a stirring slurry of Pt((*R*,*R*)-Me-Duphos)$Cl_2$ (80 mg, 0.14 mmol) and *trans*-stilbene (30 mg, 0.17 mmol, 1.2 equiv) in THF (4 mL) was added a solution of $NaBH(OMe)_3$ (54 mg, 0.42 mmol, 3 equiv) in THF (2 mL). The reaction mixture immediately turned brown. After stirring at room temperature for 3 d, it was filtered through a Celite plug to give a clear light brown solution. After the solvent was removed under vacuum, the brown residue was extracted with toluene (8 mL) and filtered; removing the toluene from the filtrate under vacuum gave 91 mg (95% crude yield) of brown solid. The $^{31}P$ NMR spectrum in toluene showed a clean 4:1 mixture of two diastereomers. The crude product was used directly in the next step without further purification.

# 2. NMR Spectra

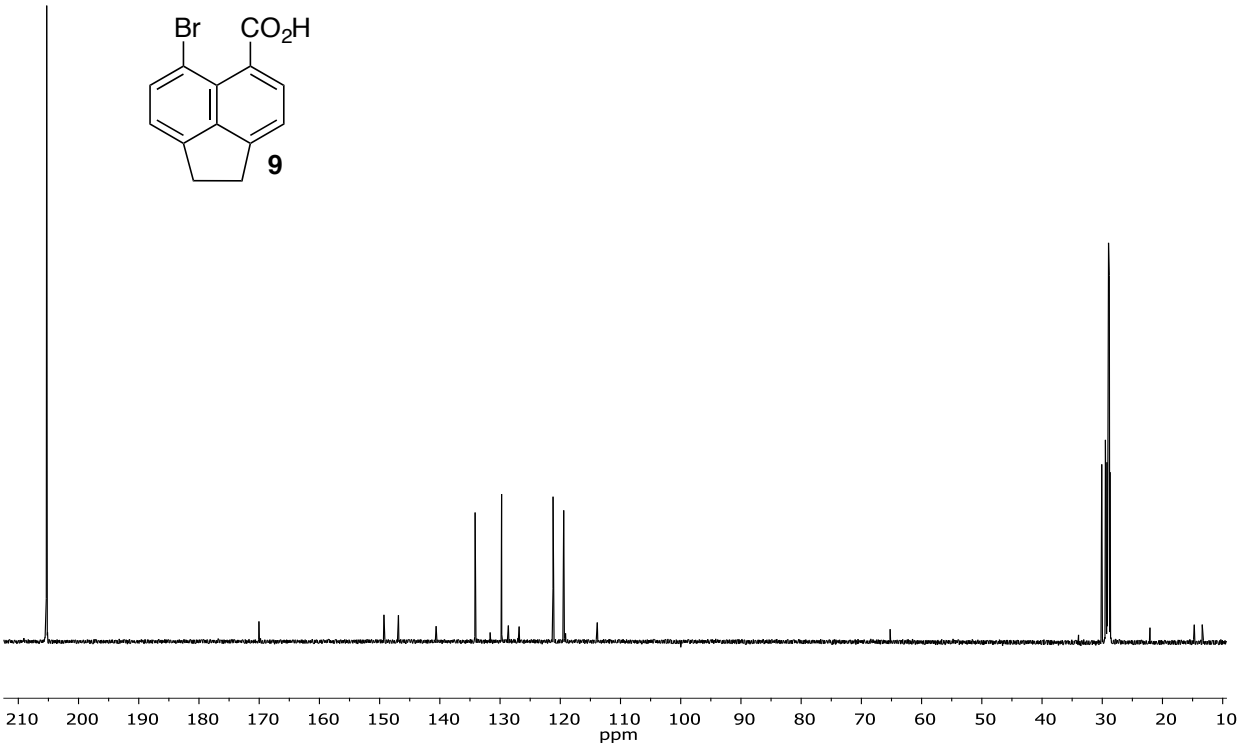
NMR spectra are included in the order $^{31}P\{^{1}H\}$ (where appropriate), $^{1}H$, $^{13}C\{^{1}H\}$.

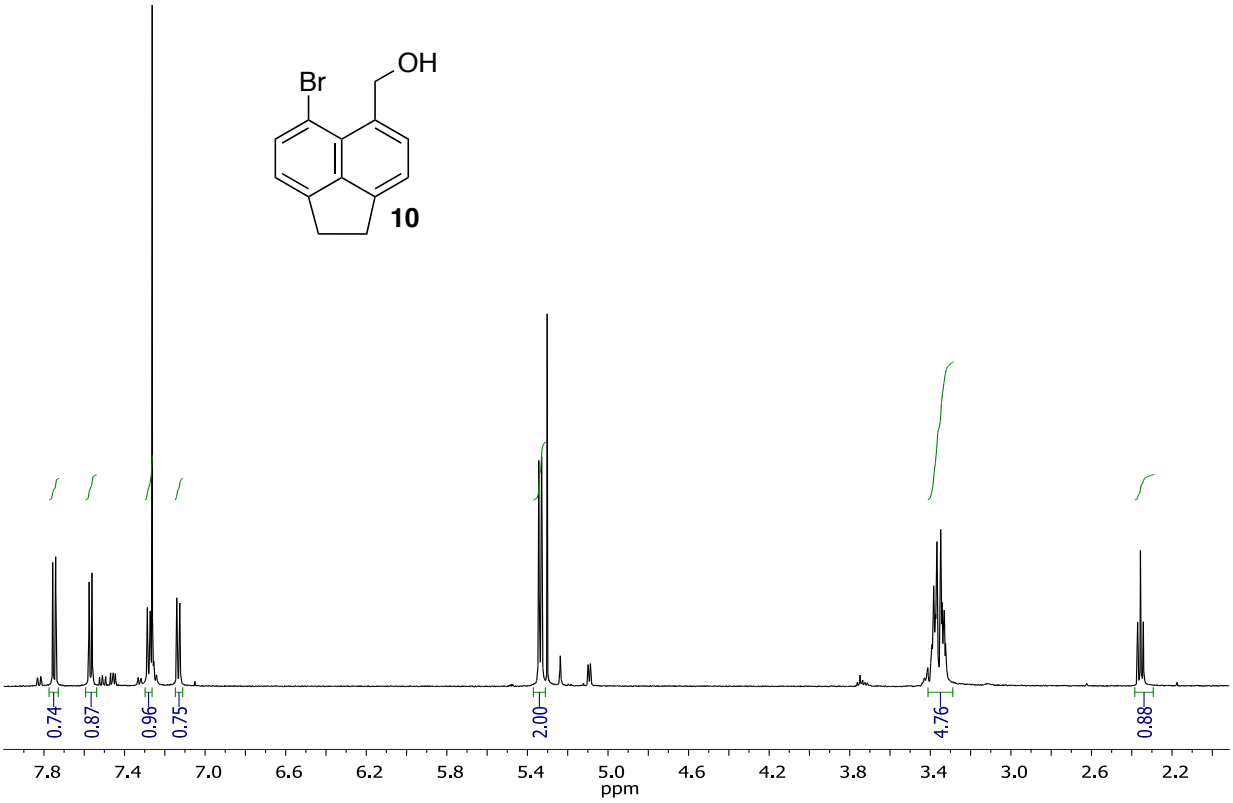





$^{1}H$ and $^{13}C$ NMR spectra for **9** in acetone-$d_6$

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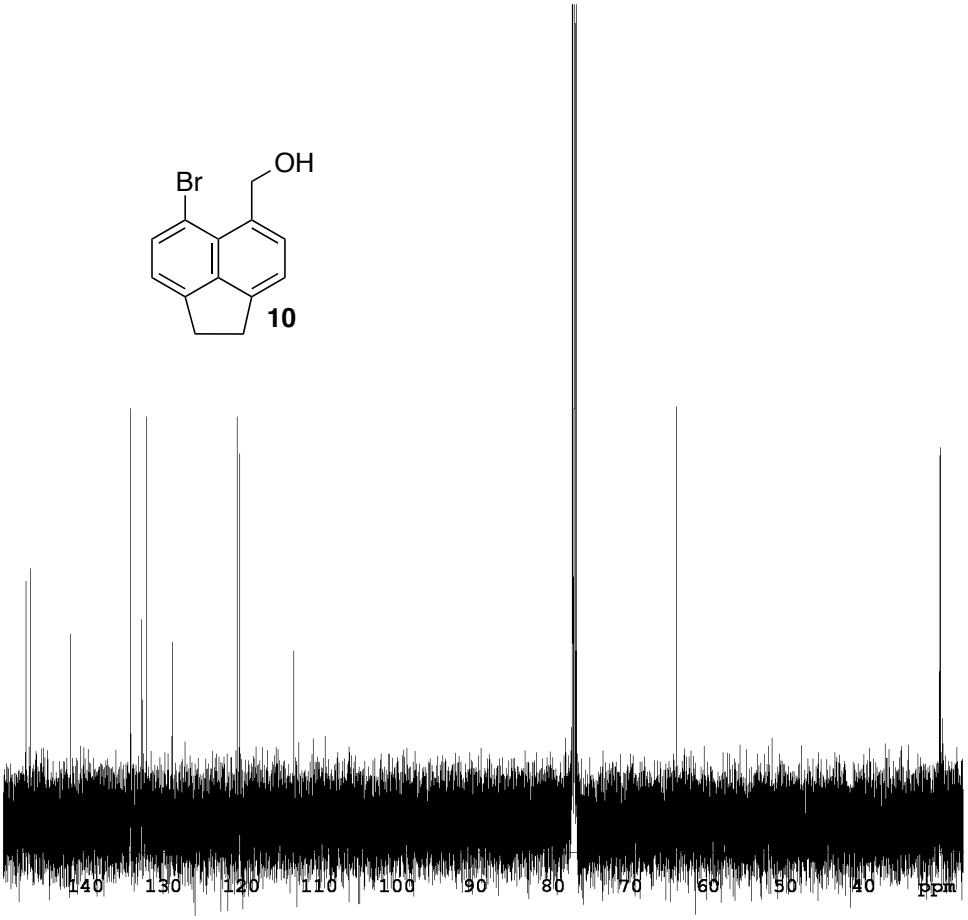
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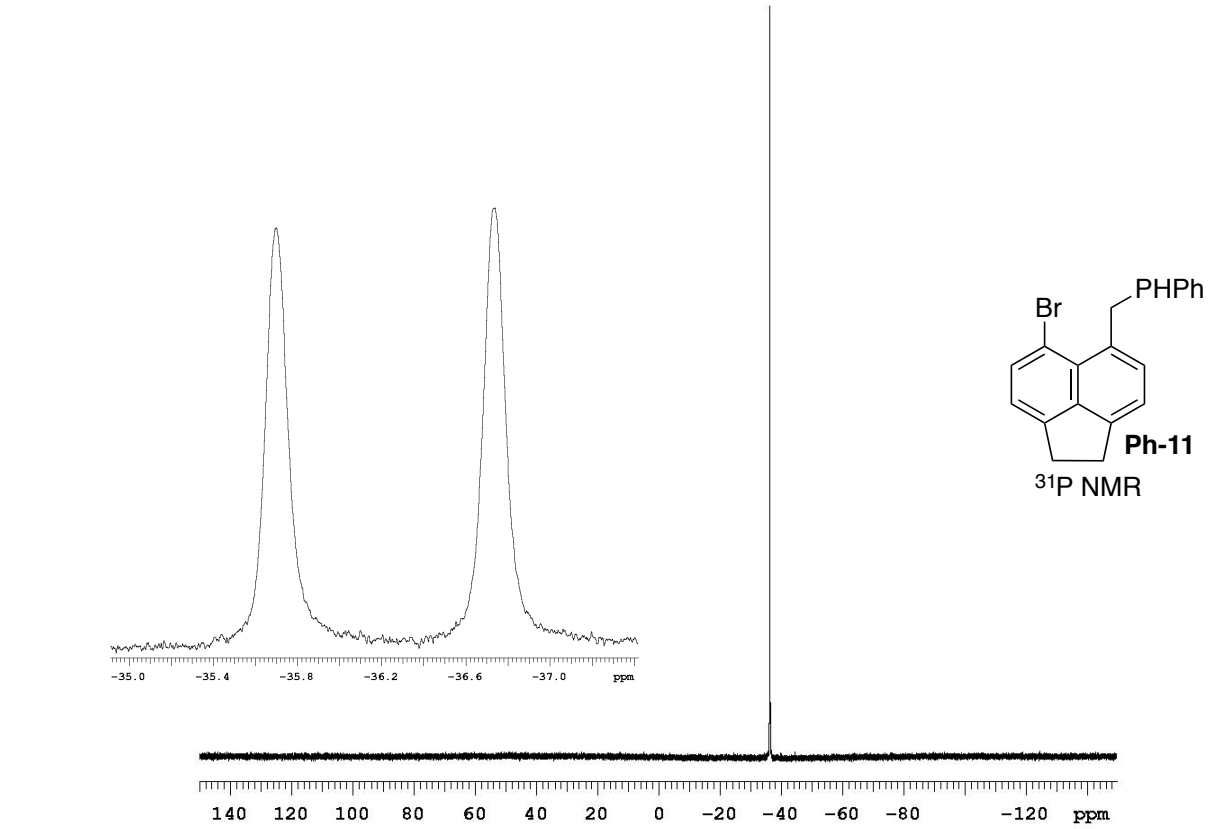
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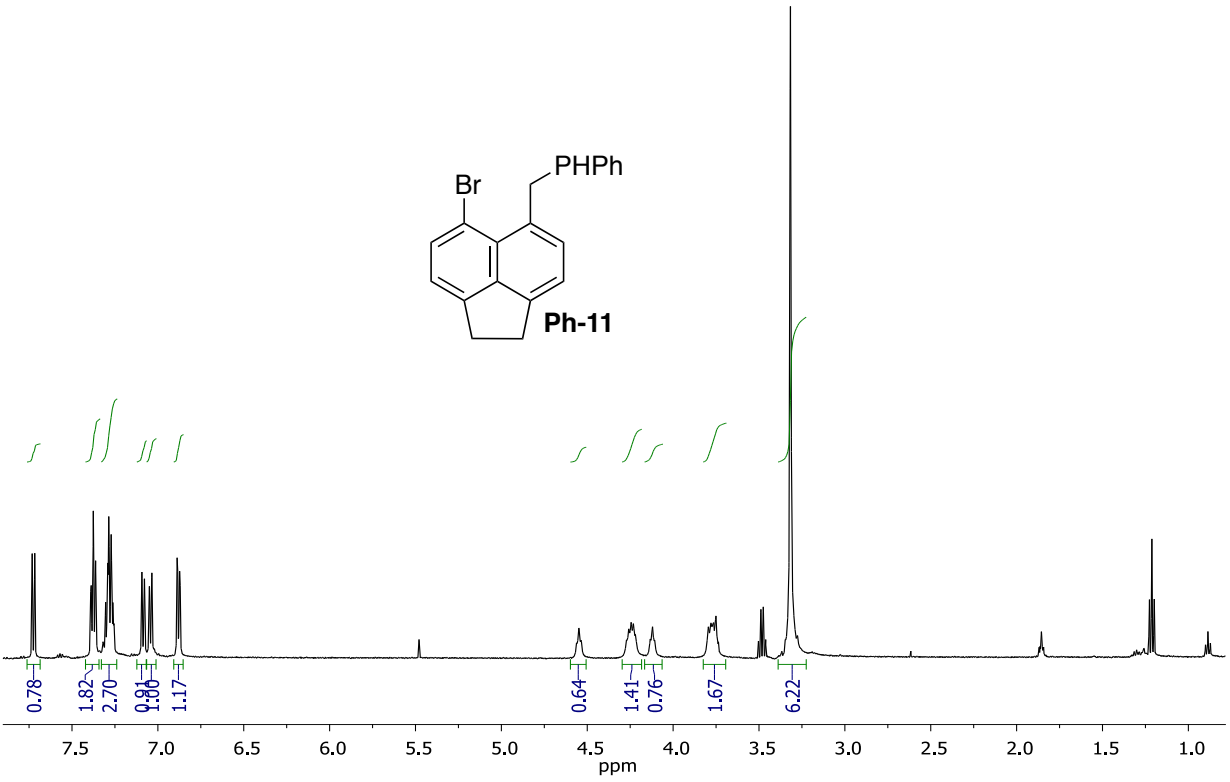
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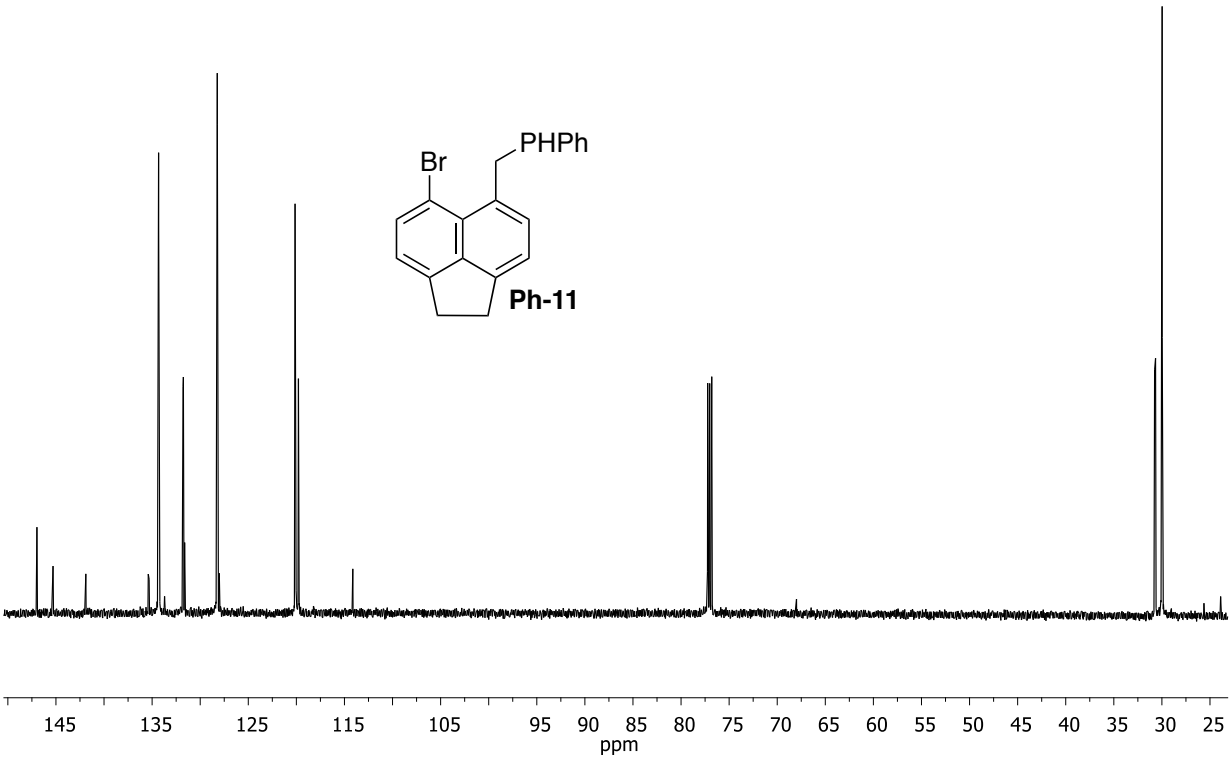
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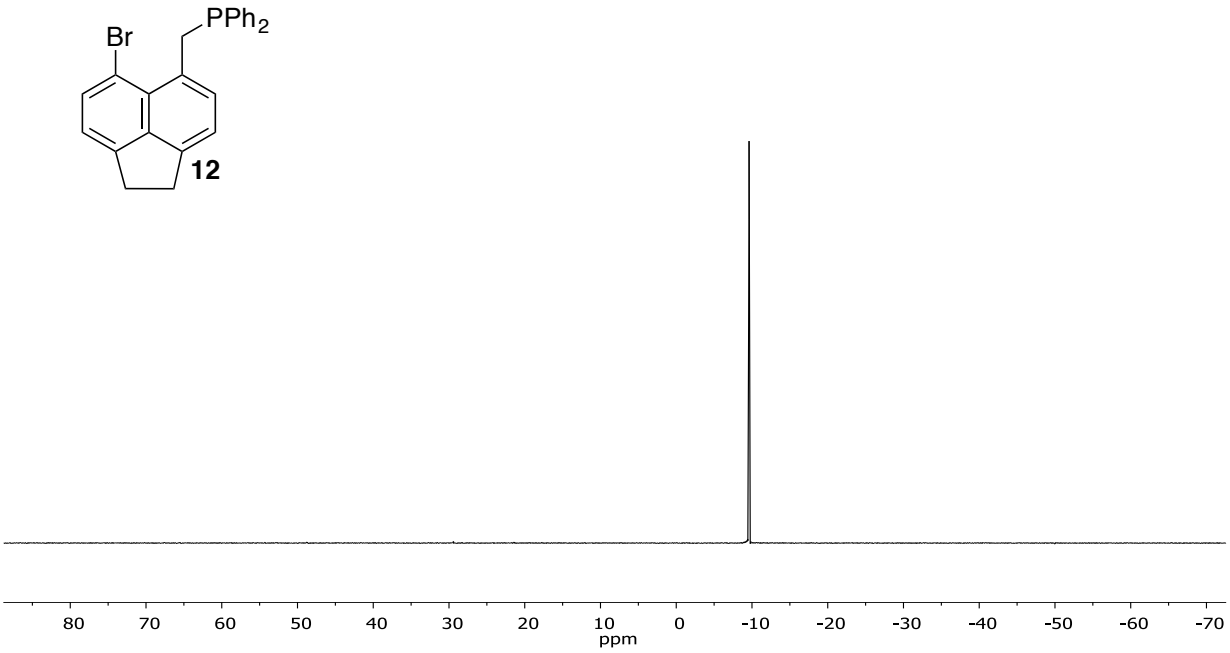
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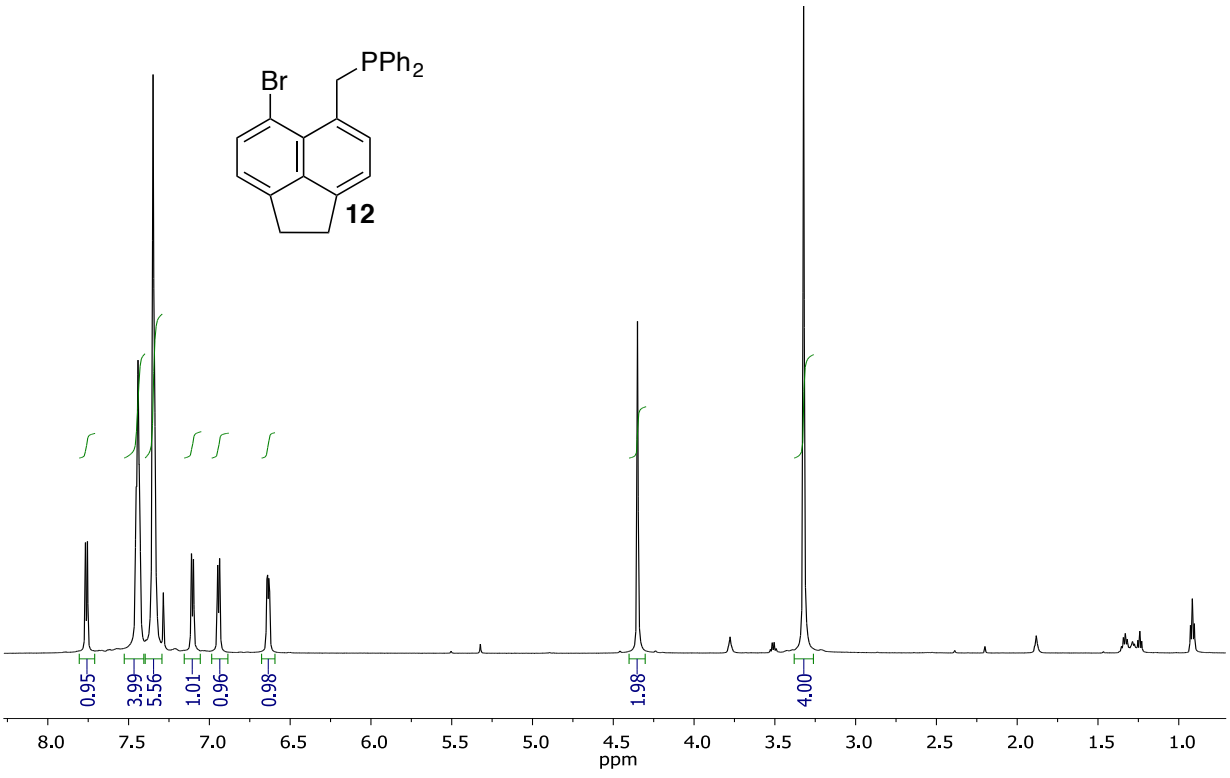
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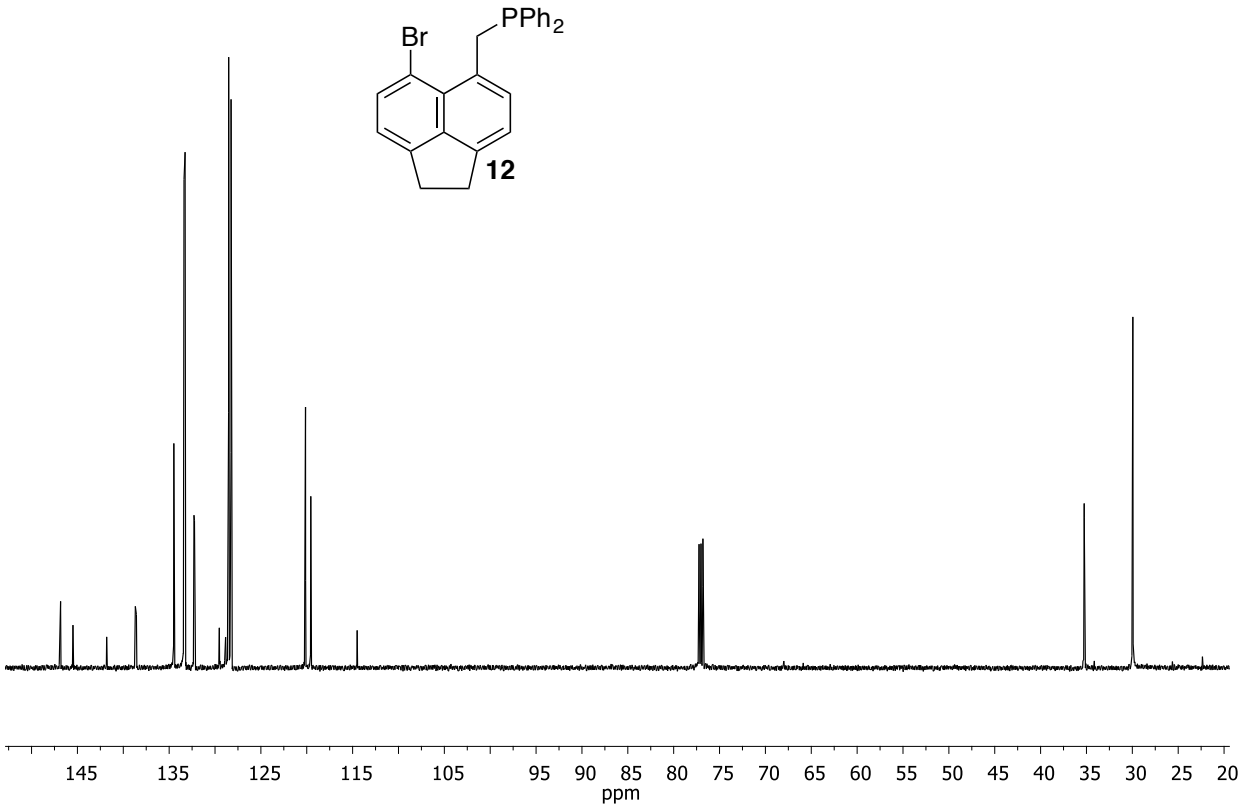
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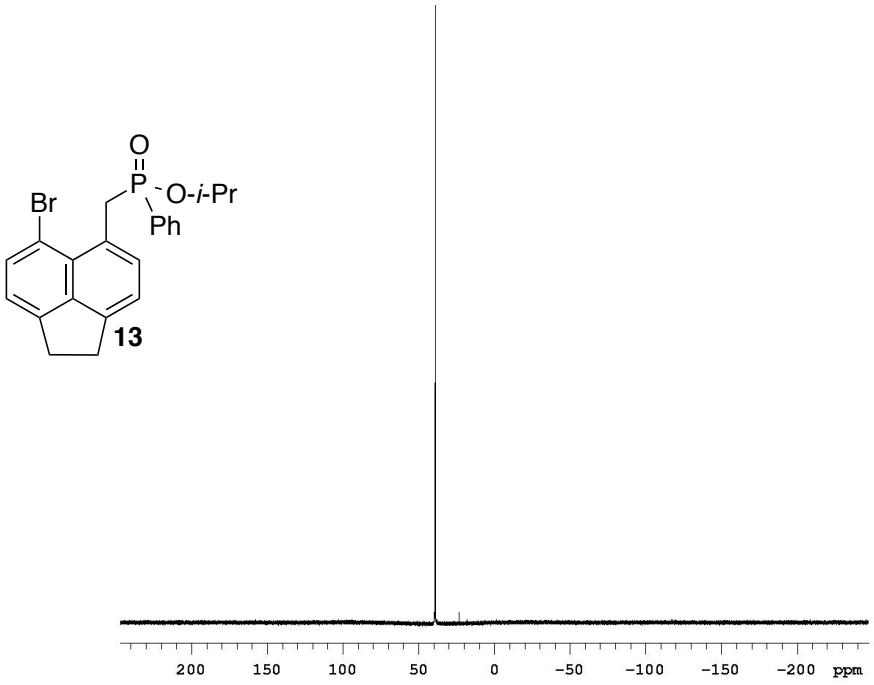
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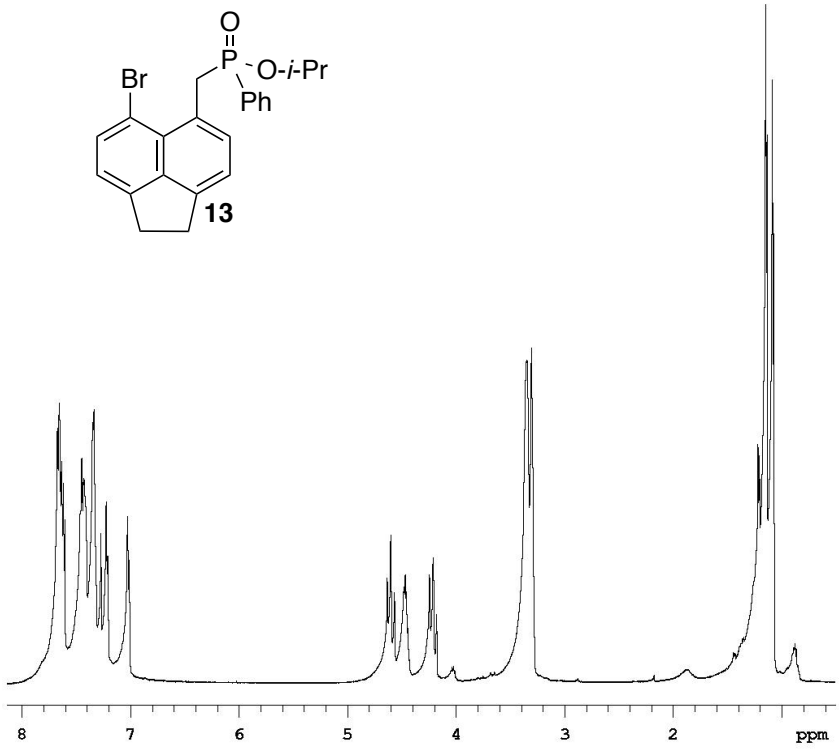
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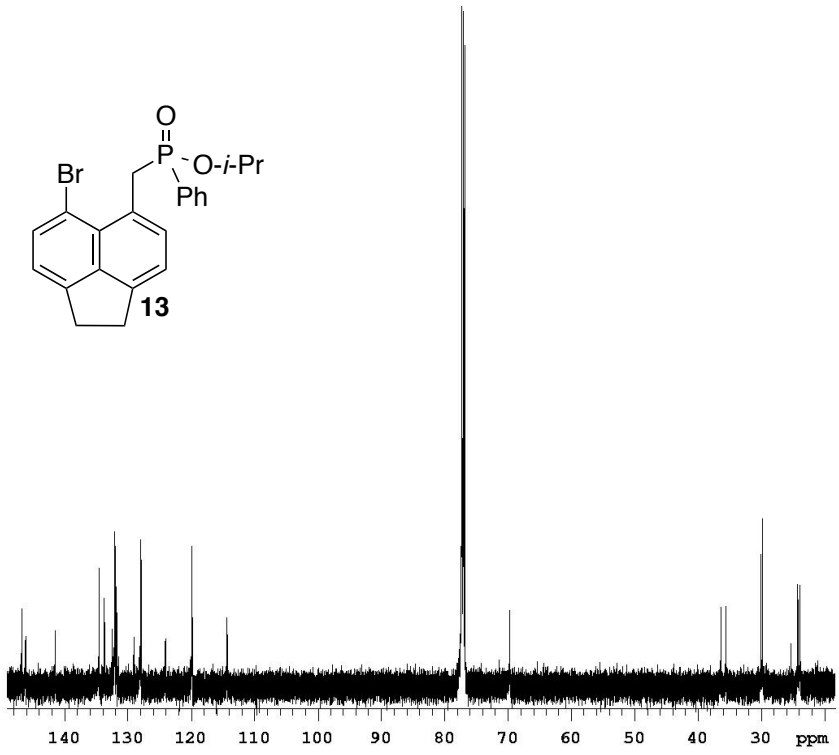
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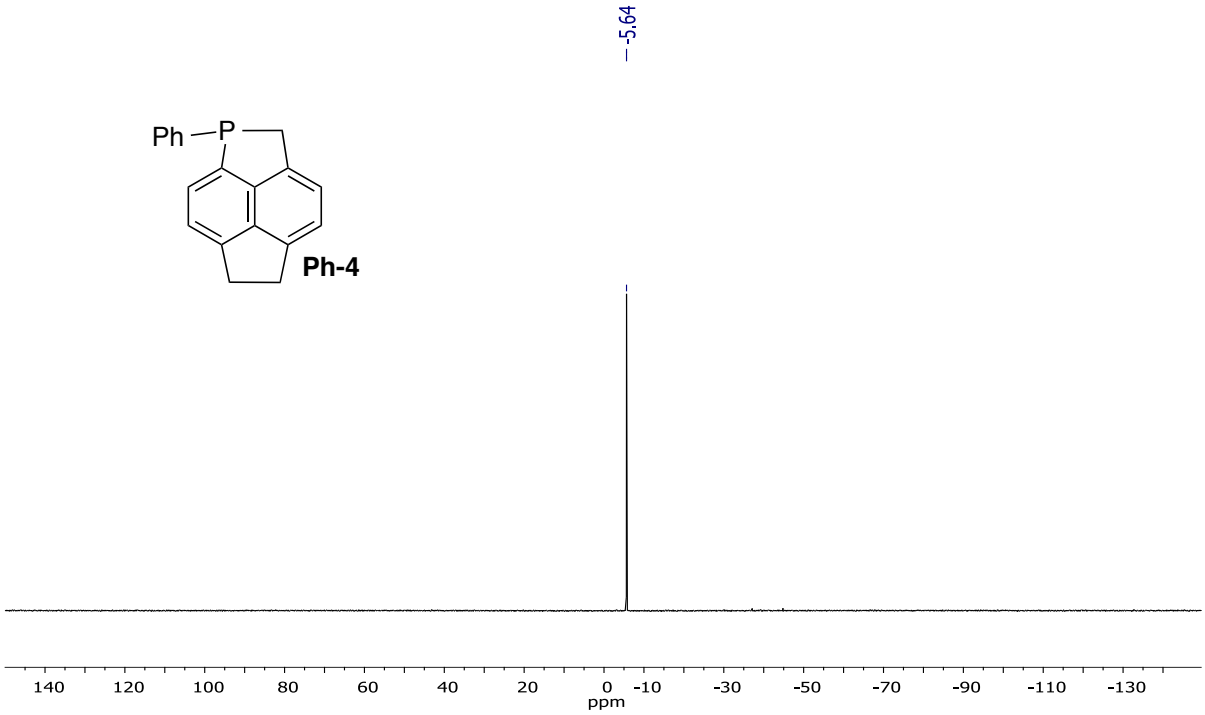
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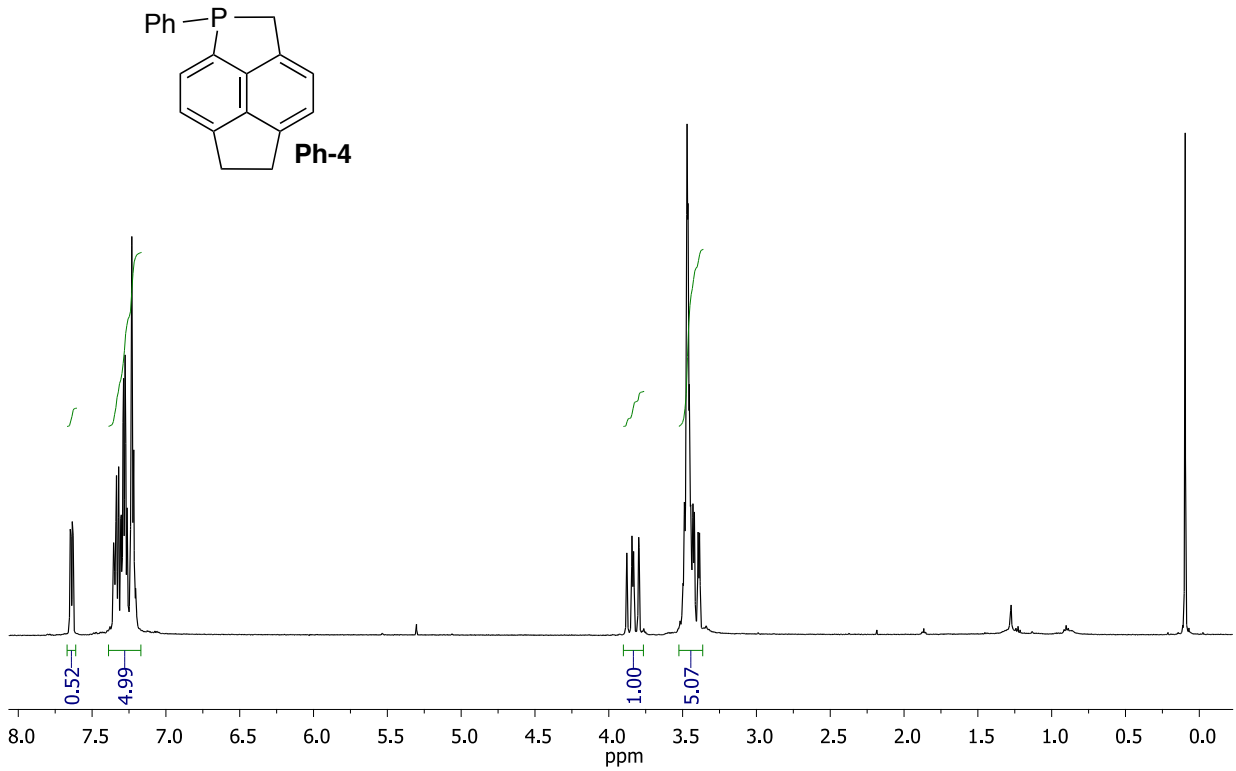
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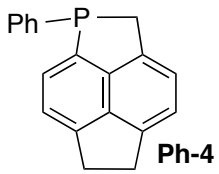
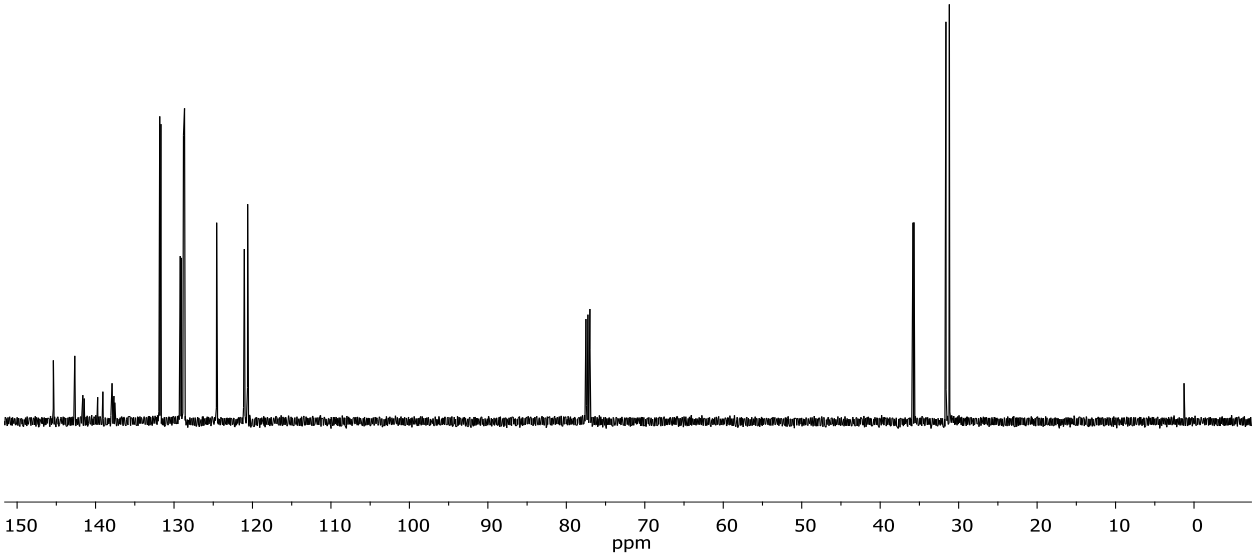
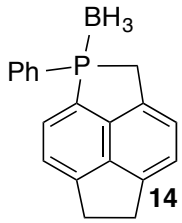



**Ph-4**

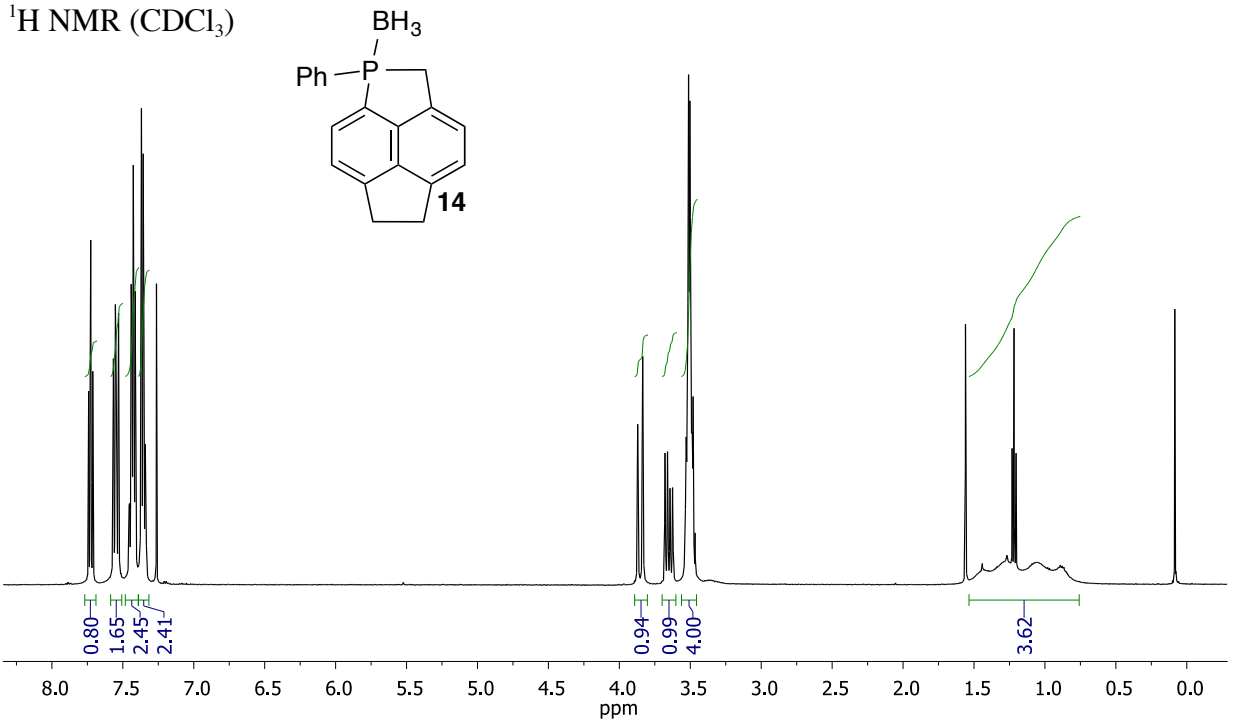



$^{31}P\{^{1}H\}$ NMR ($CDCl_3$)




**14**

$^{1}$H NMR ($CDCl_3$)

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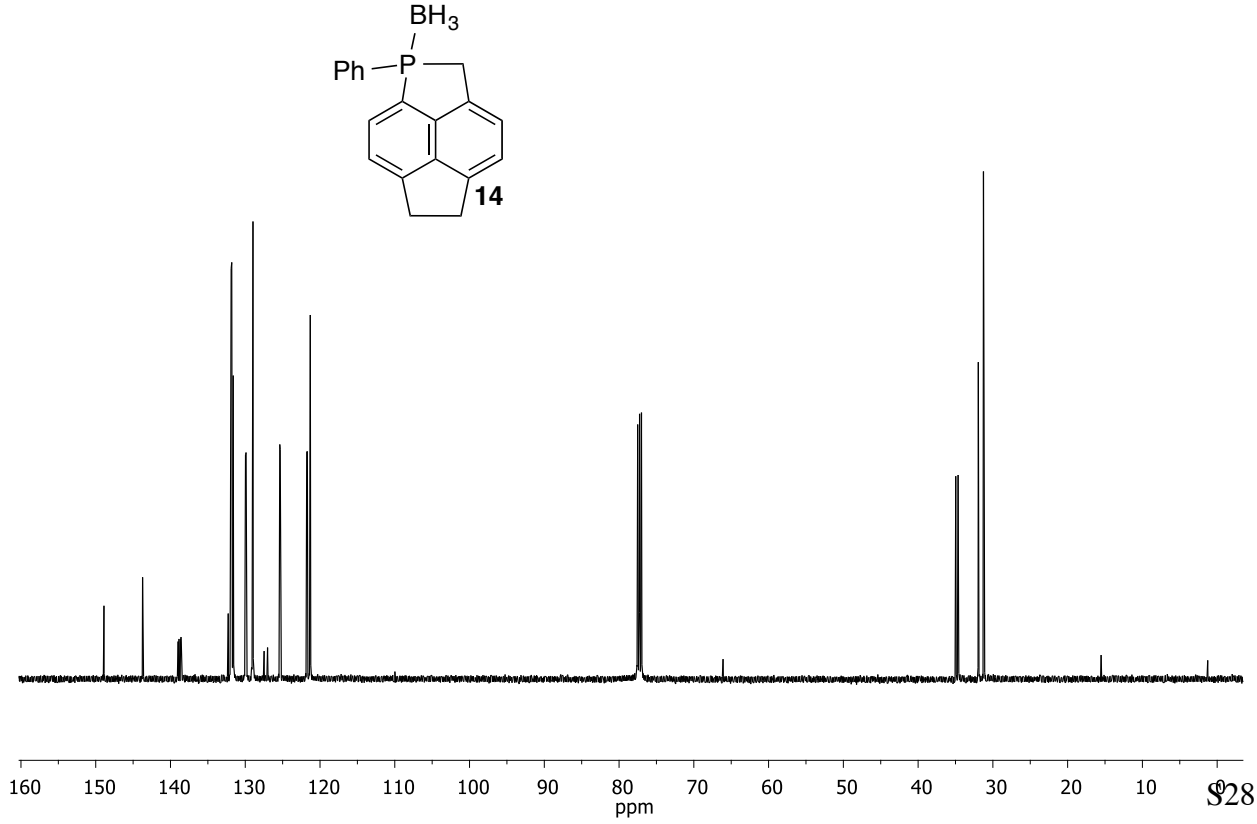

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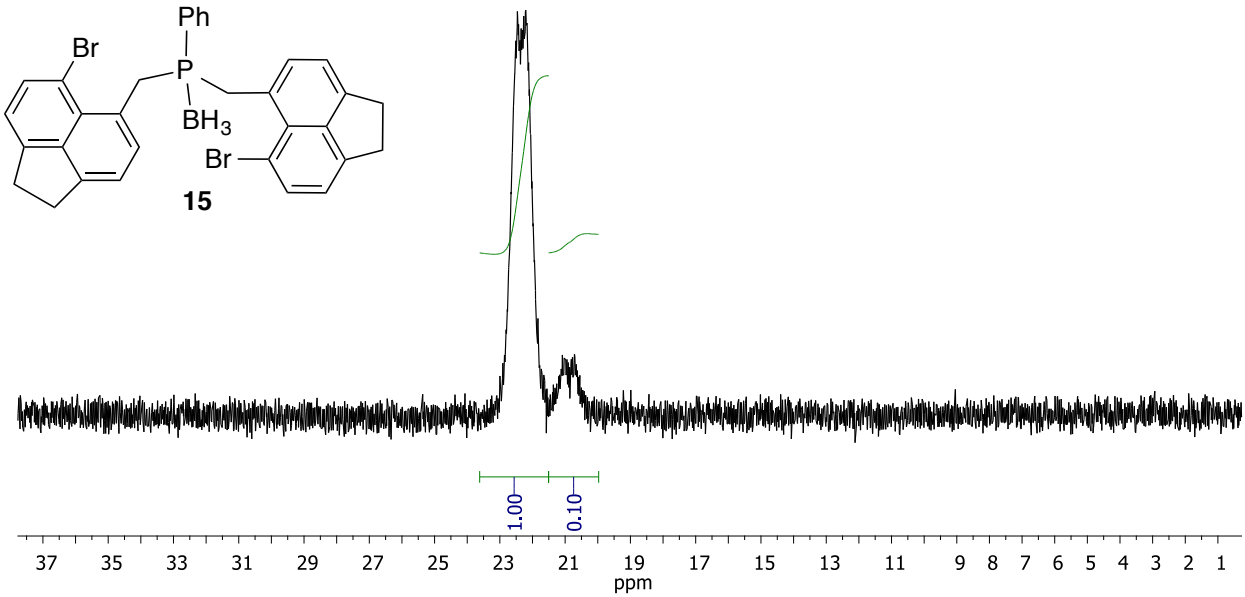


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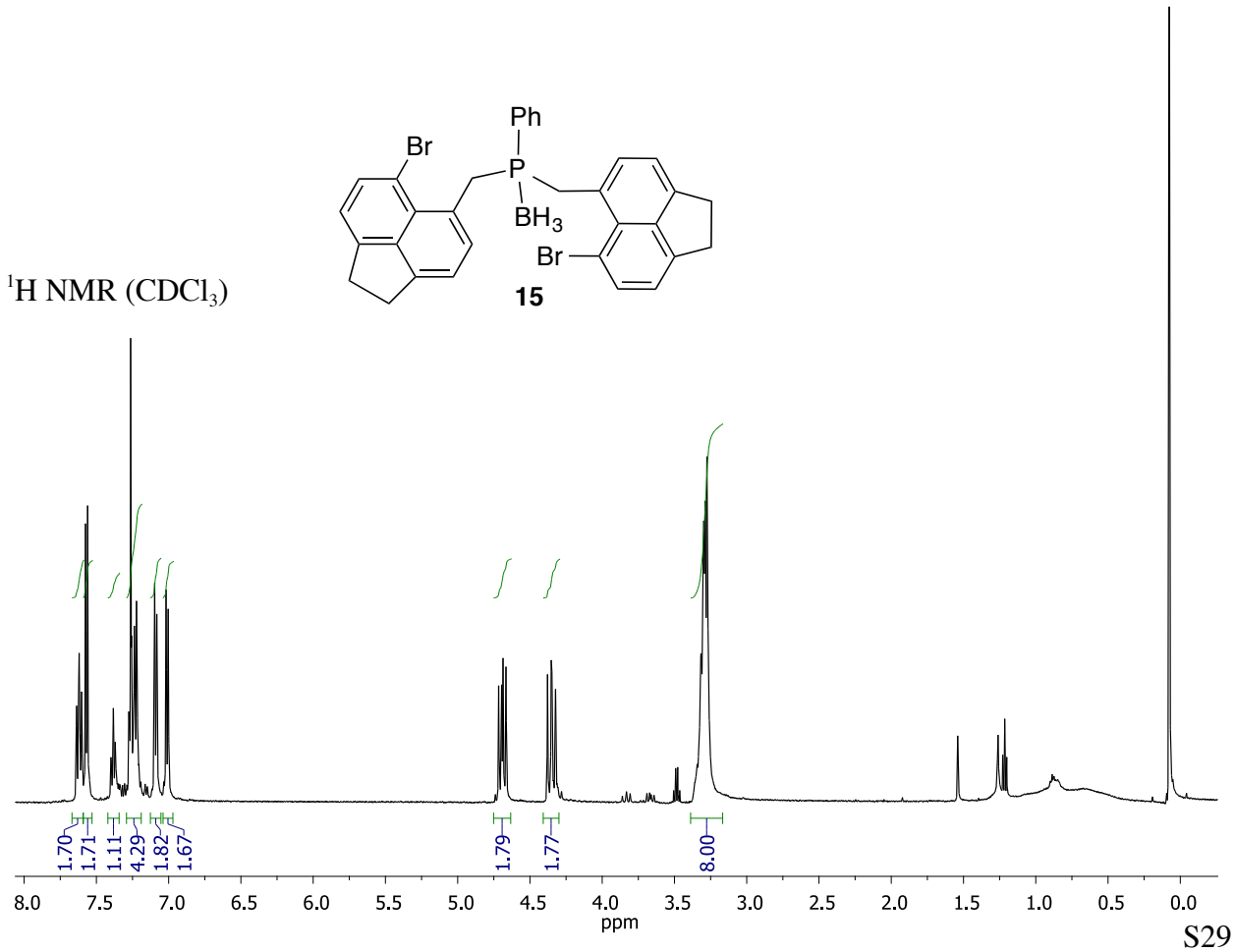

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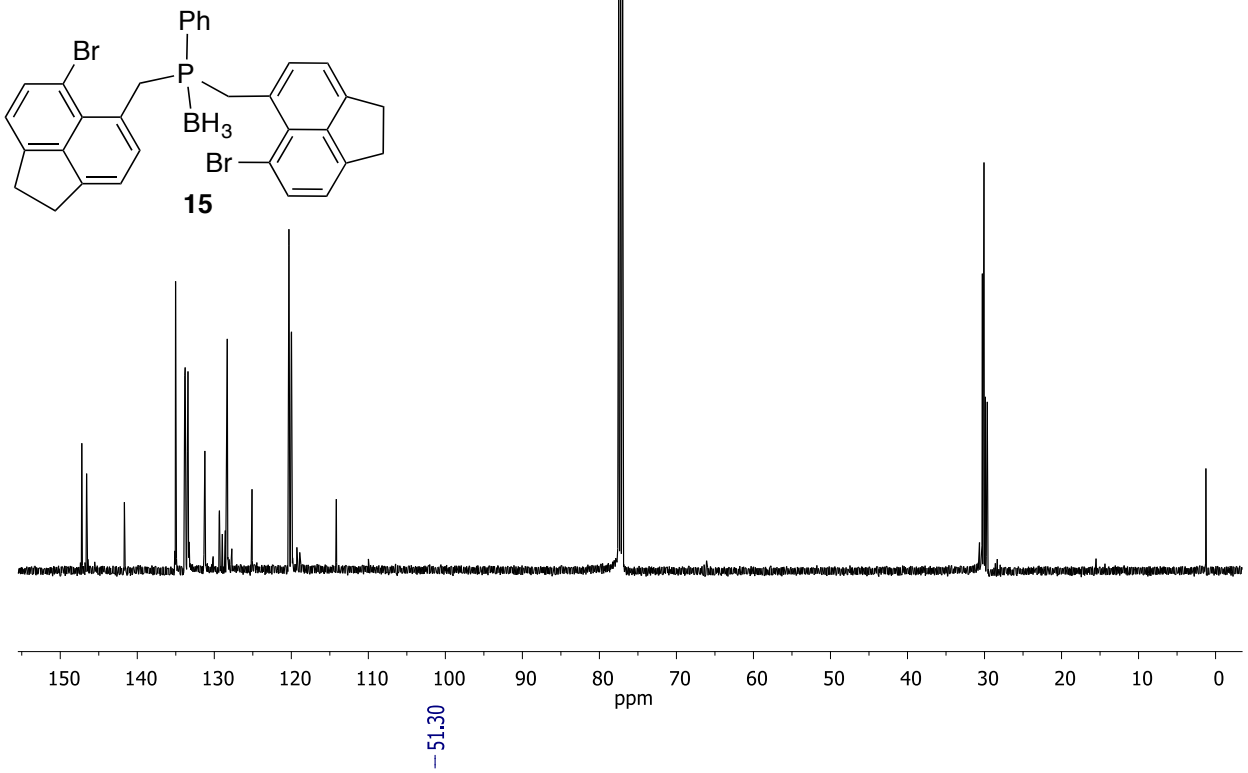


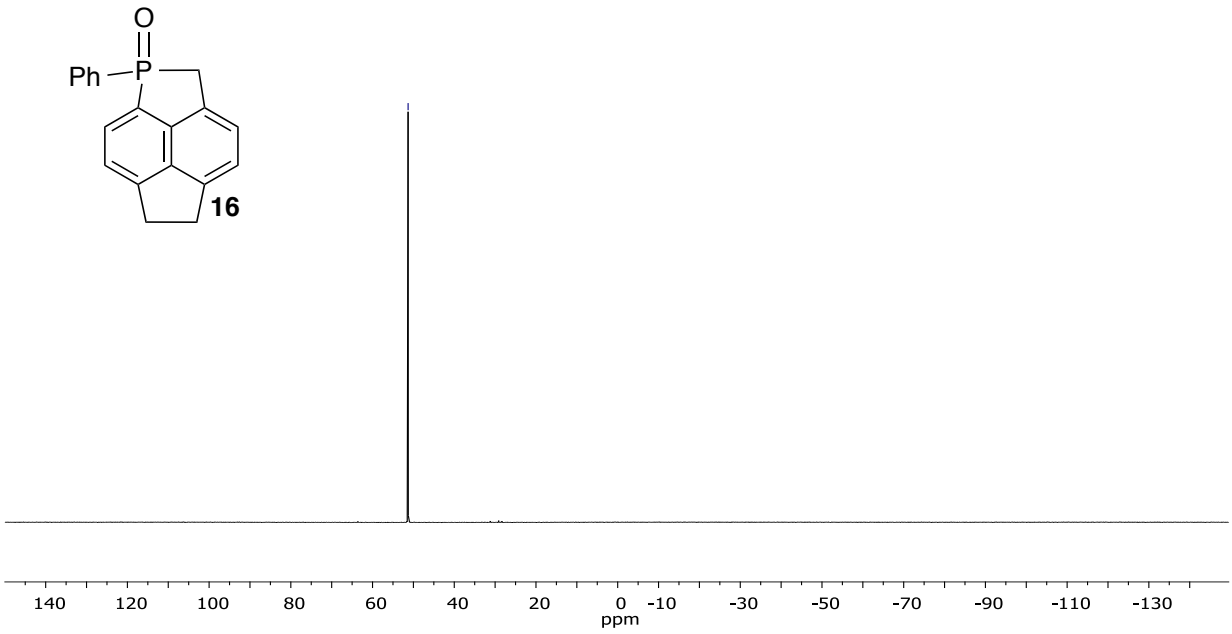

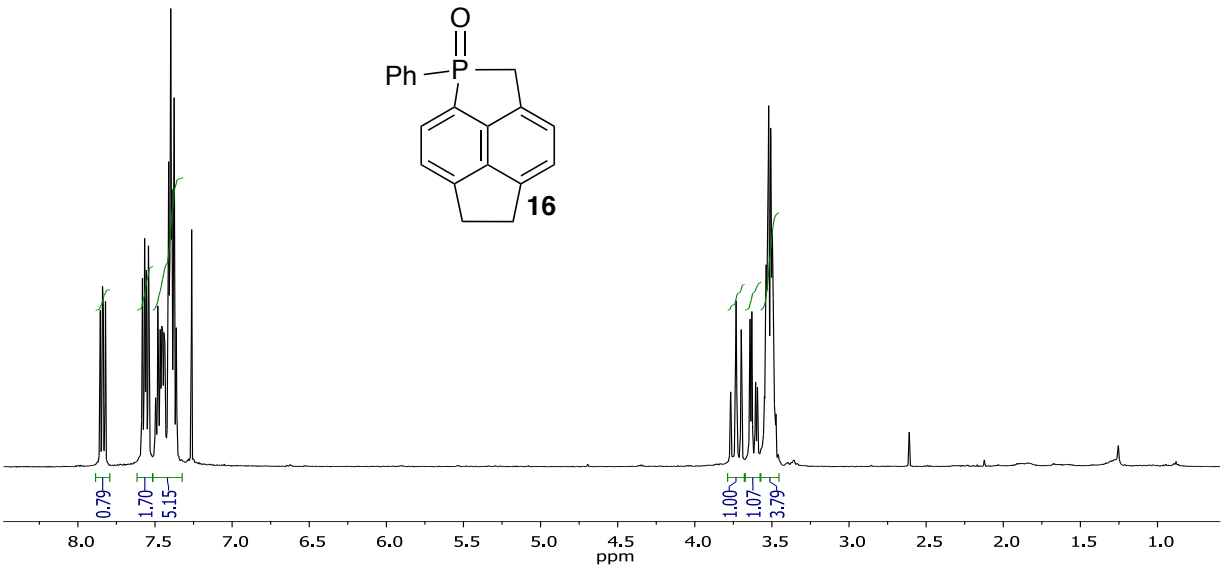
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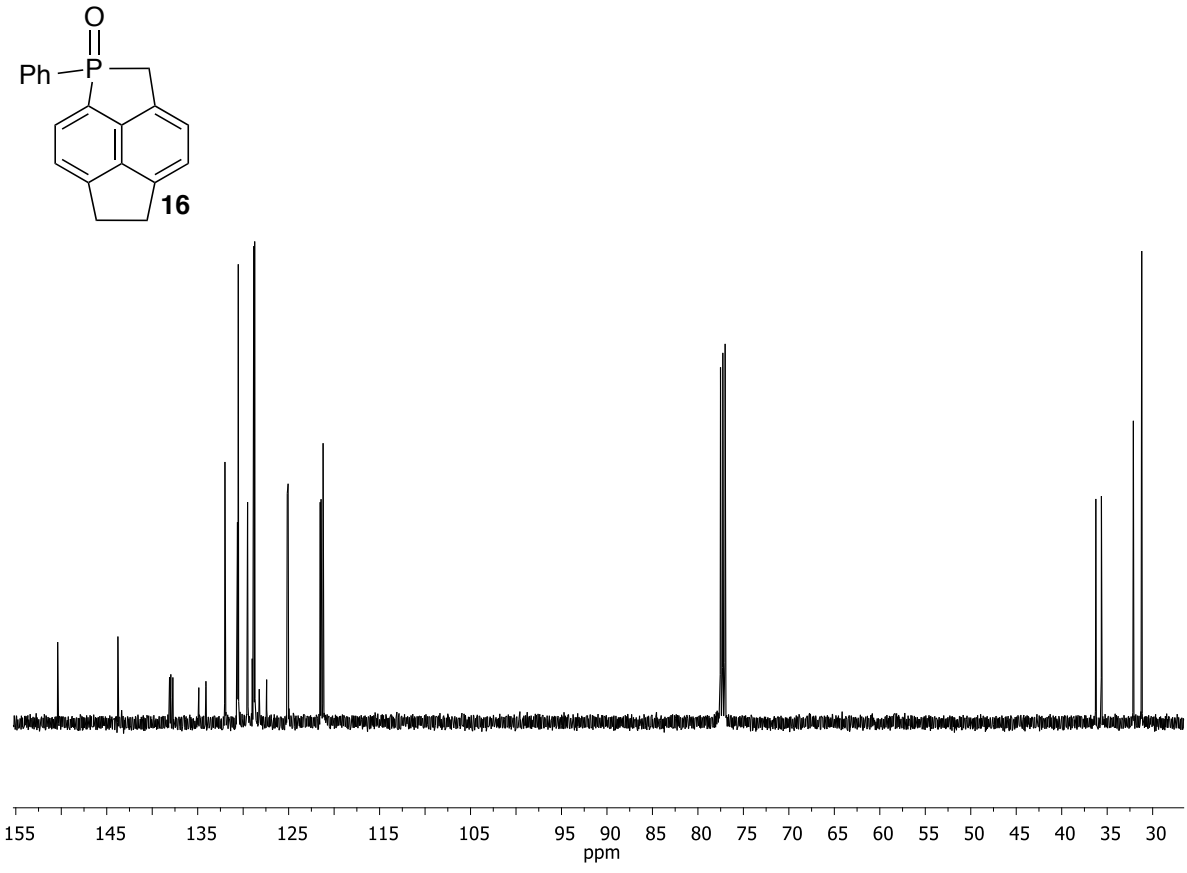
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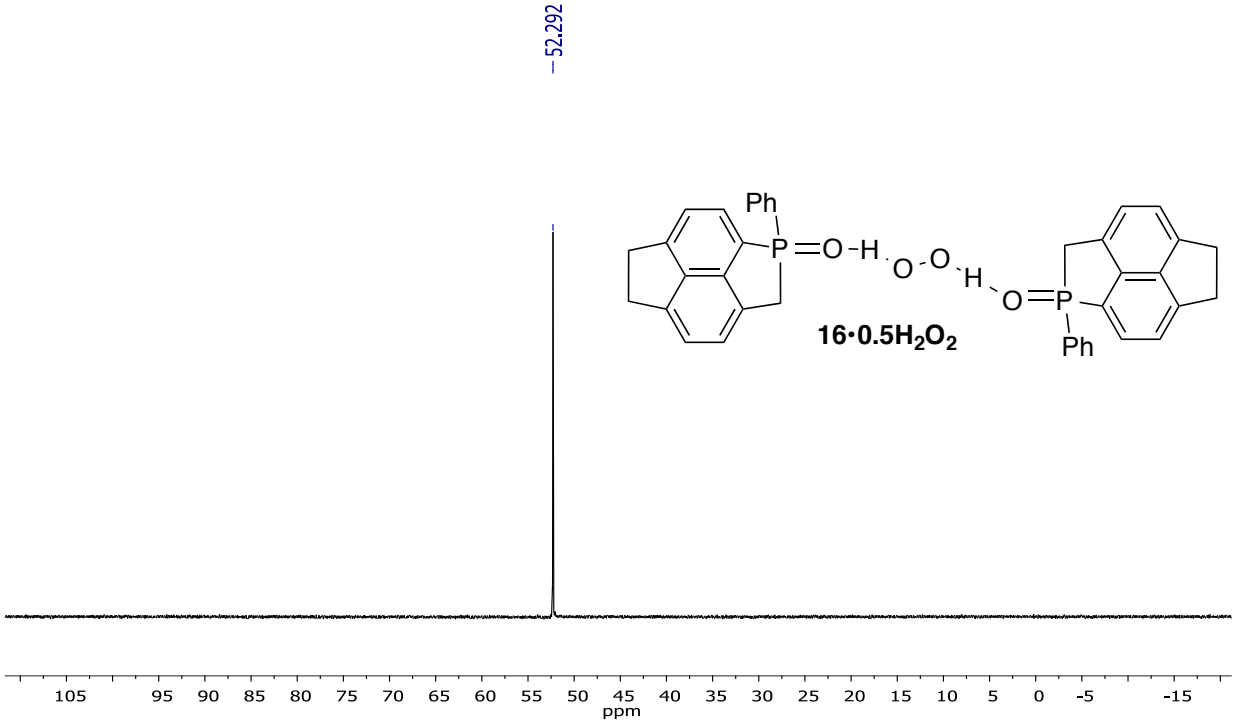
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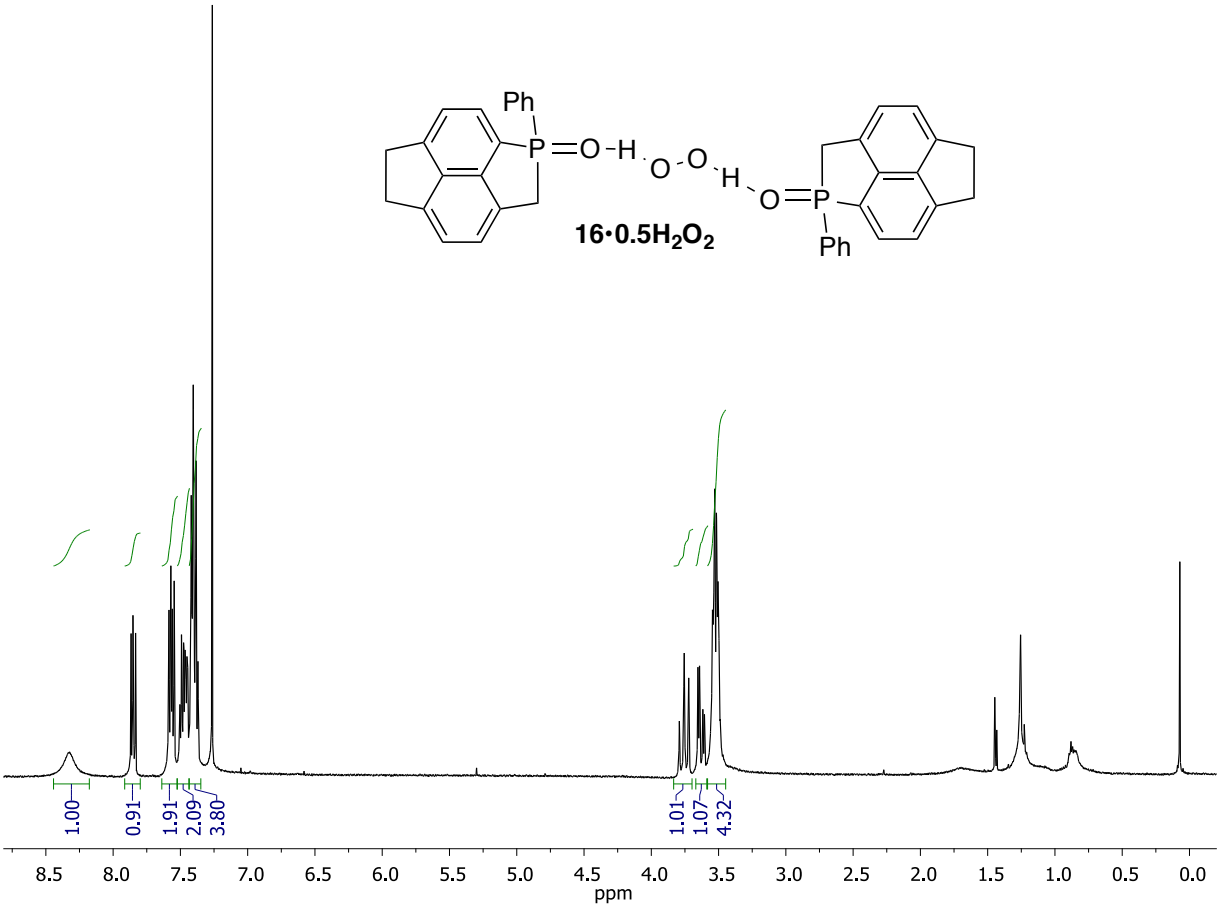
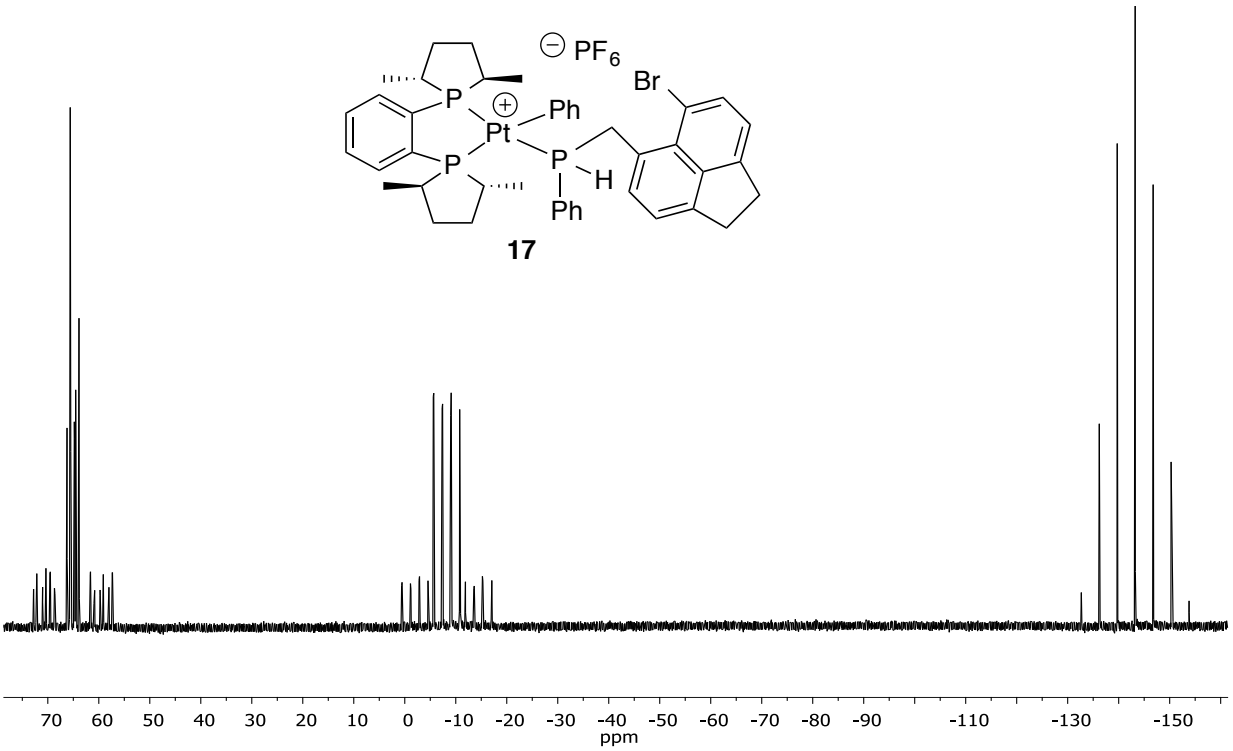
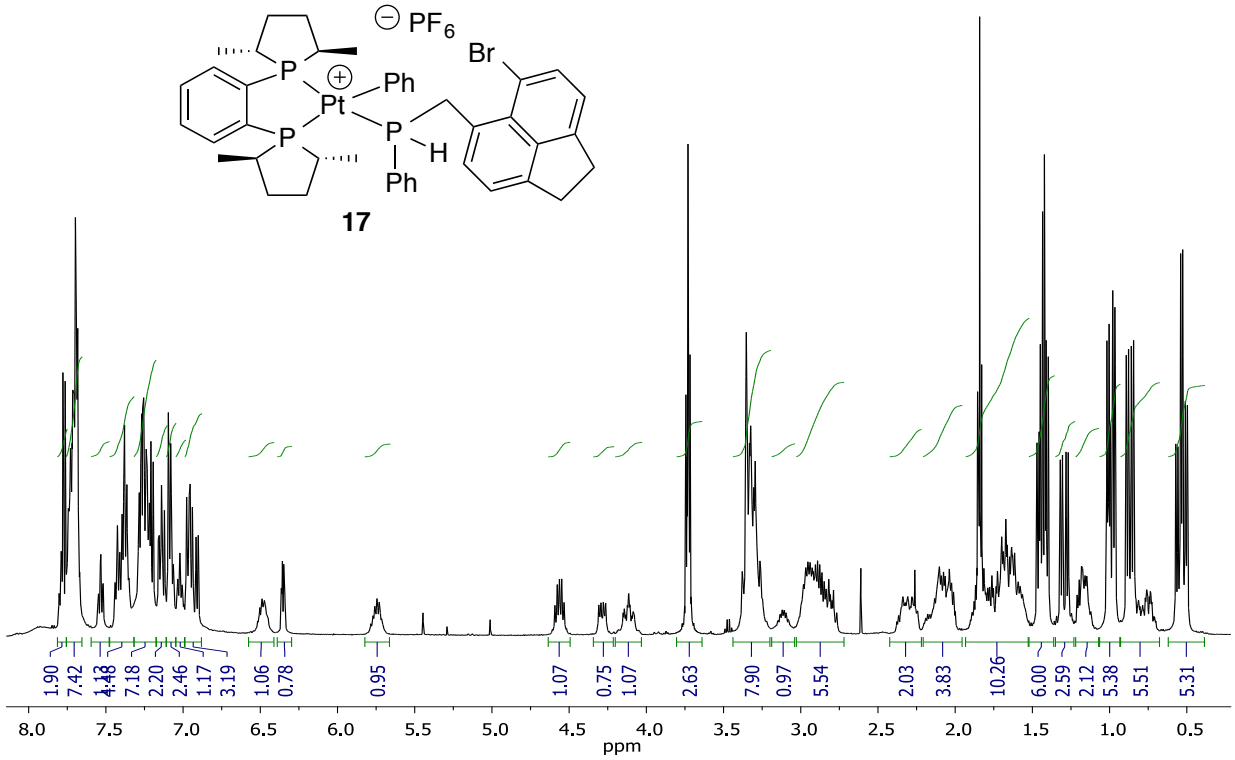
16·0.5H2O2
105
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
-5
-15
ppm


Ph
P
O
H
O
O
H
O
P
Ph
16·0.5H2O2
1.00
0.91
1.91
2.09
3.80
1.01
1.07
4.32
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm


PF6
Br
Ph
Pt
P
P
P
H
Ph
70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -110 -130 -150
ppm

**17**


PF6
Br
Ph
Pt
P
P
P
H
Ph
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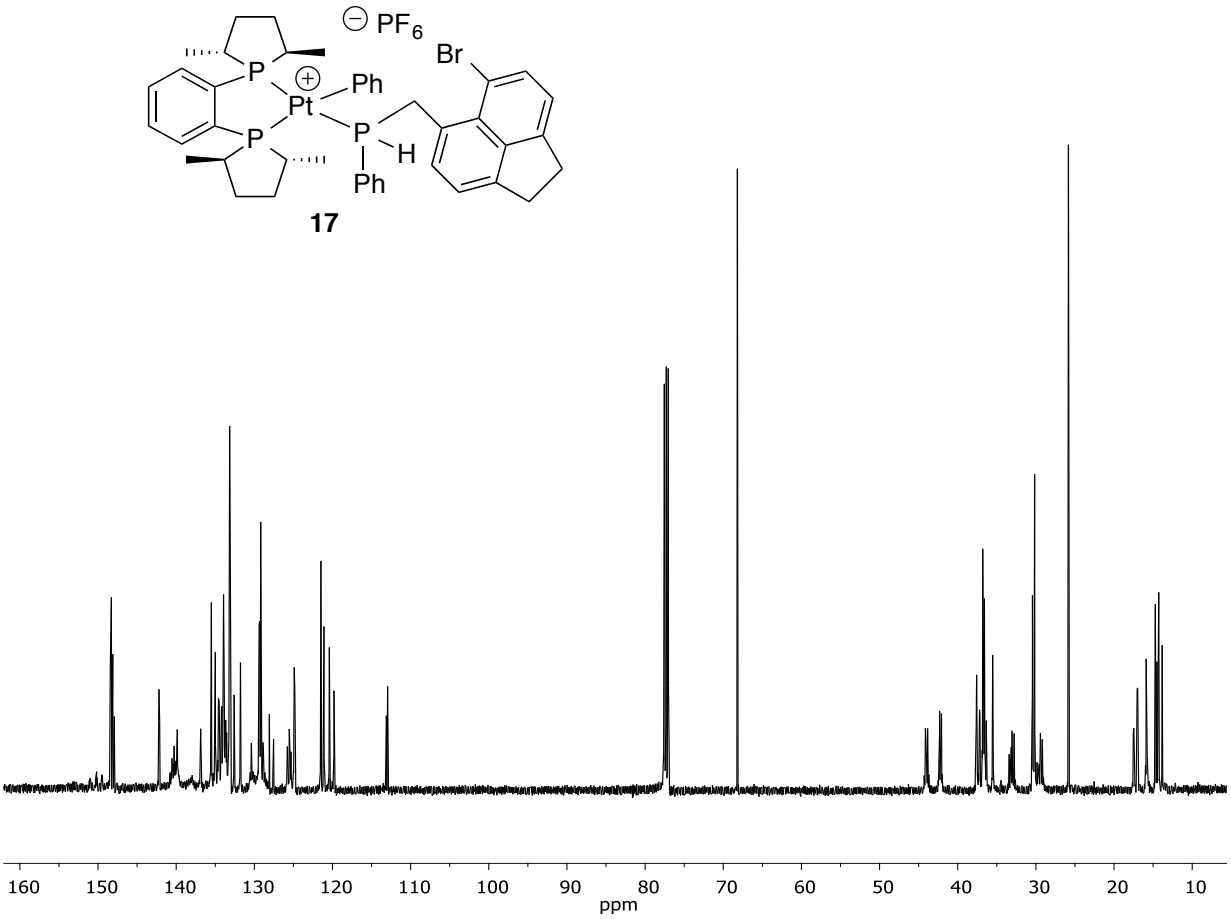
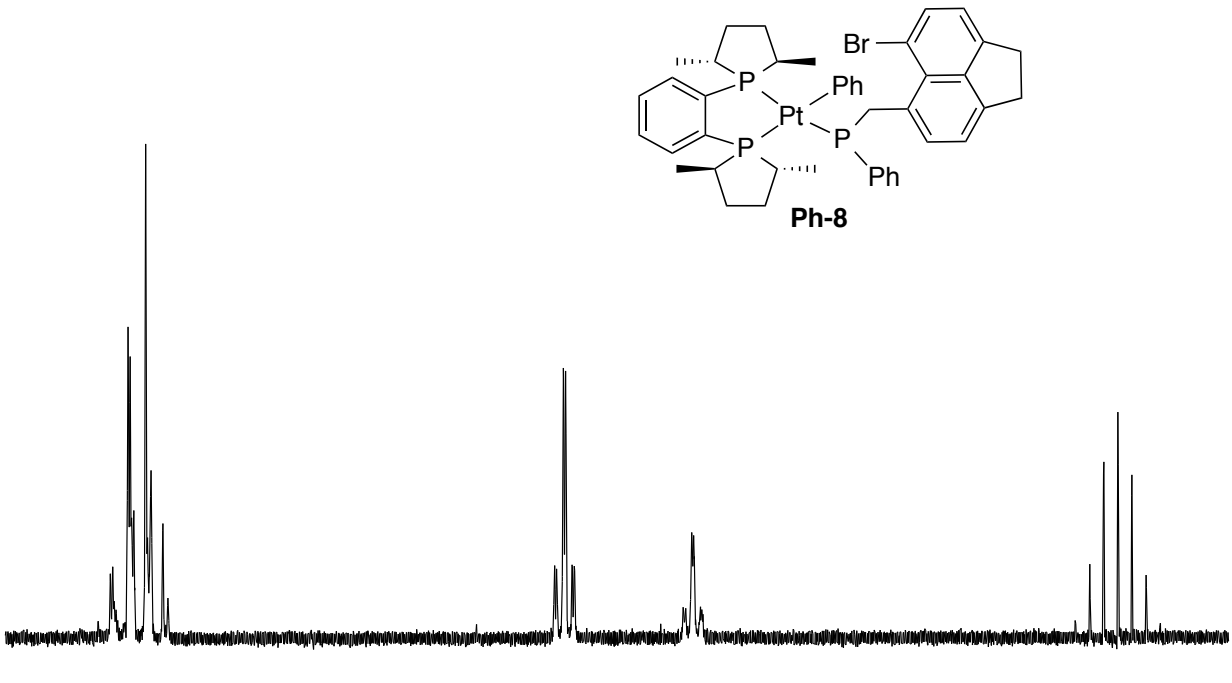
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
ppm

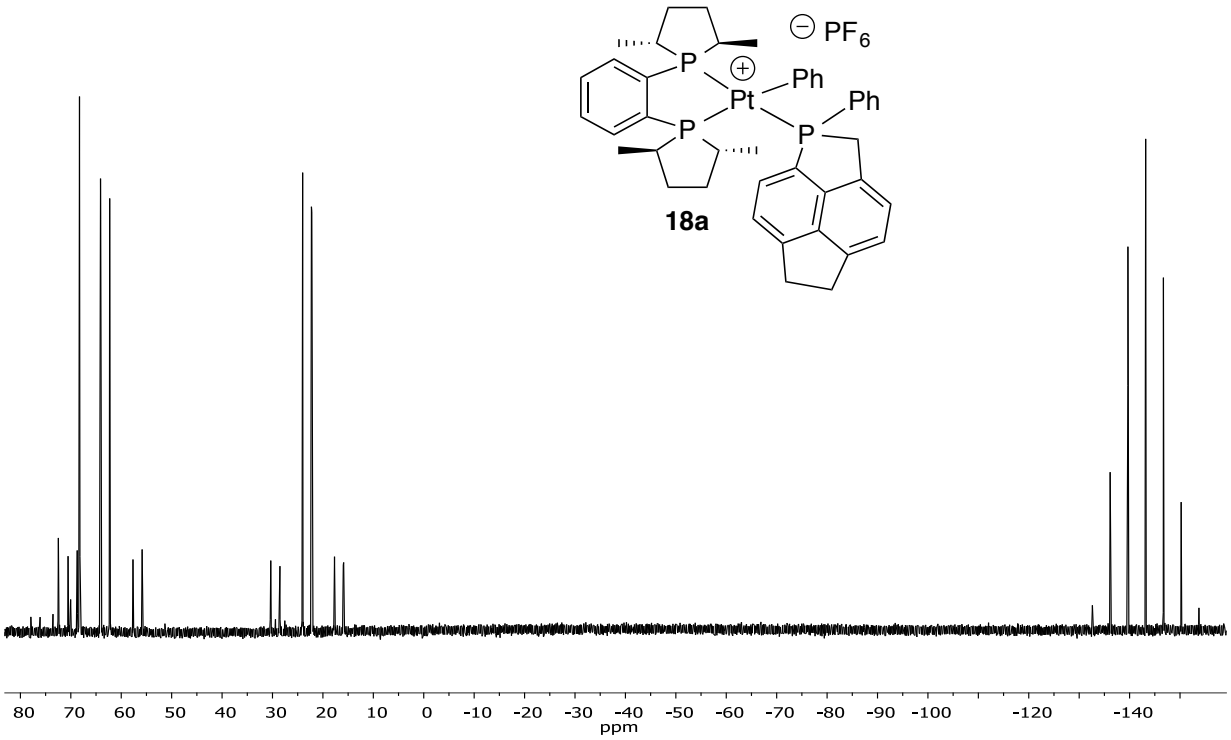
**17**

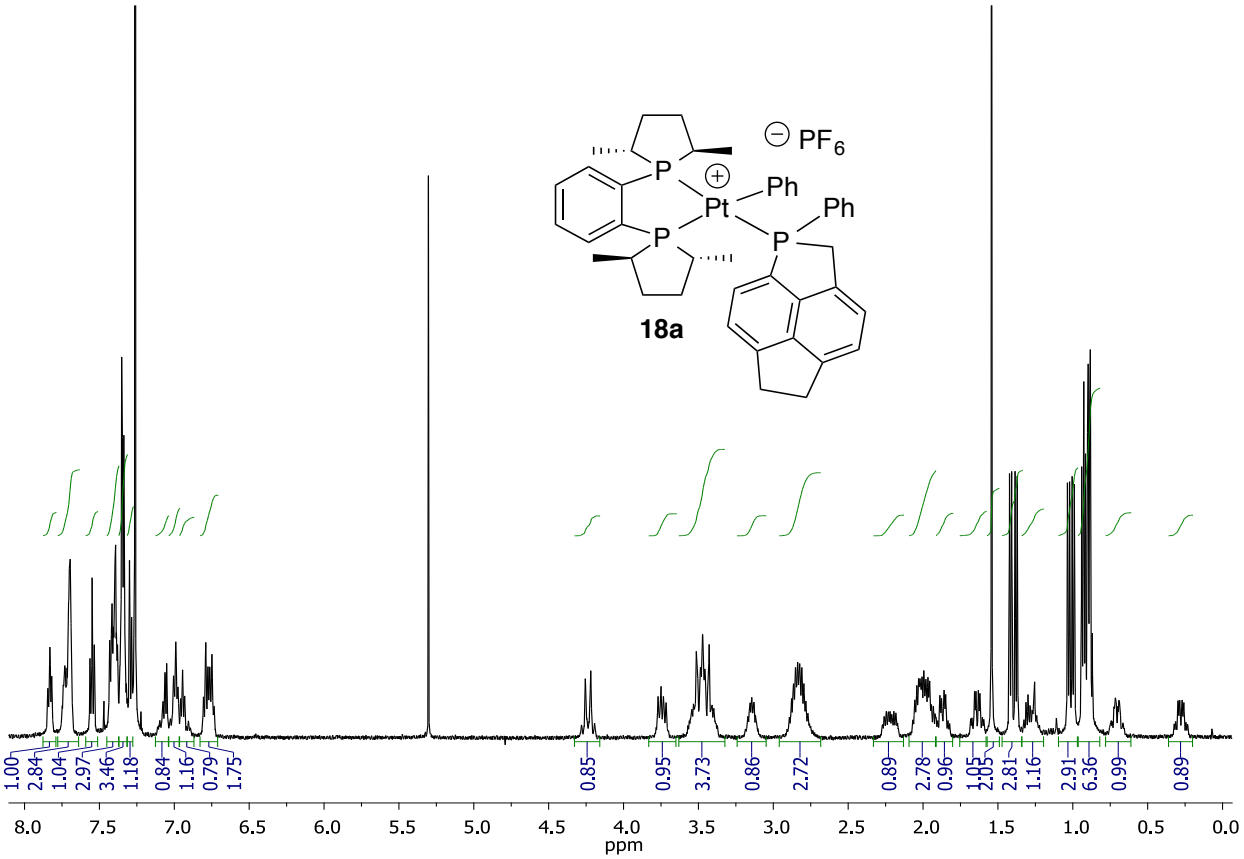

PF6
Br
P
Pt
Ph
P
H
Ph
P
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

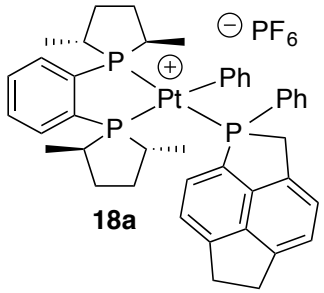
**17**


Br
P
Ph
Pt
P
P
Ph
80
70
60
50
40
30
20
10
0
-10
-30
-50
-70
-90
-110
-130
-150
ppm

**Ph-8**

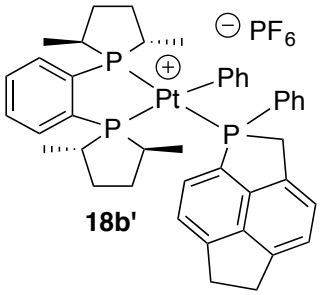

PF6
P
Pt
Ph
Ph
P
P
18a
80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -120 -140
ppm


PF6
P
Pt
Ph
Ph
P
P
18a
1.00 2.84 1.04 2.97 3.46 1.18 0.84 1.16 0.79 1.75
0.85 0.95 3.73 0.86 2.72 0.89 2.78 0.96 1.05 2.05 2.81 1.16 2.91 6.36 0.99 0.89
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm


PF6
P
Pt
Ph
Ph
P
P

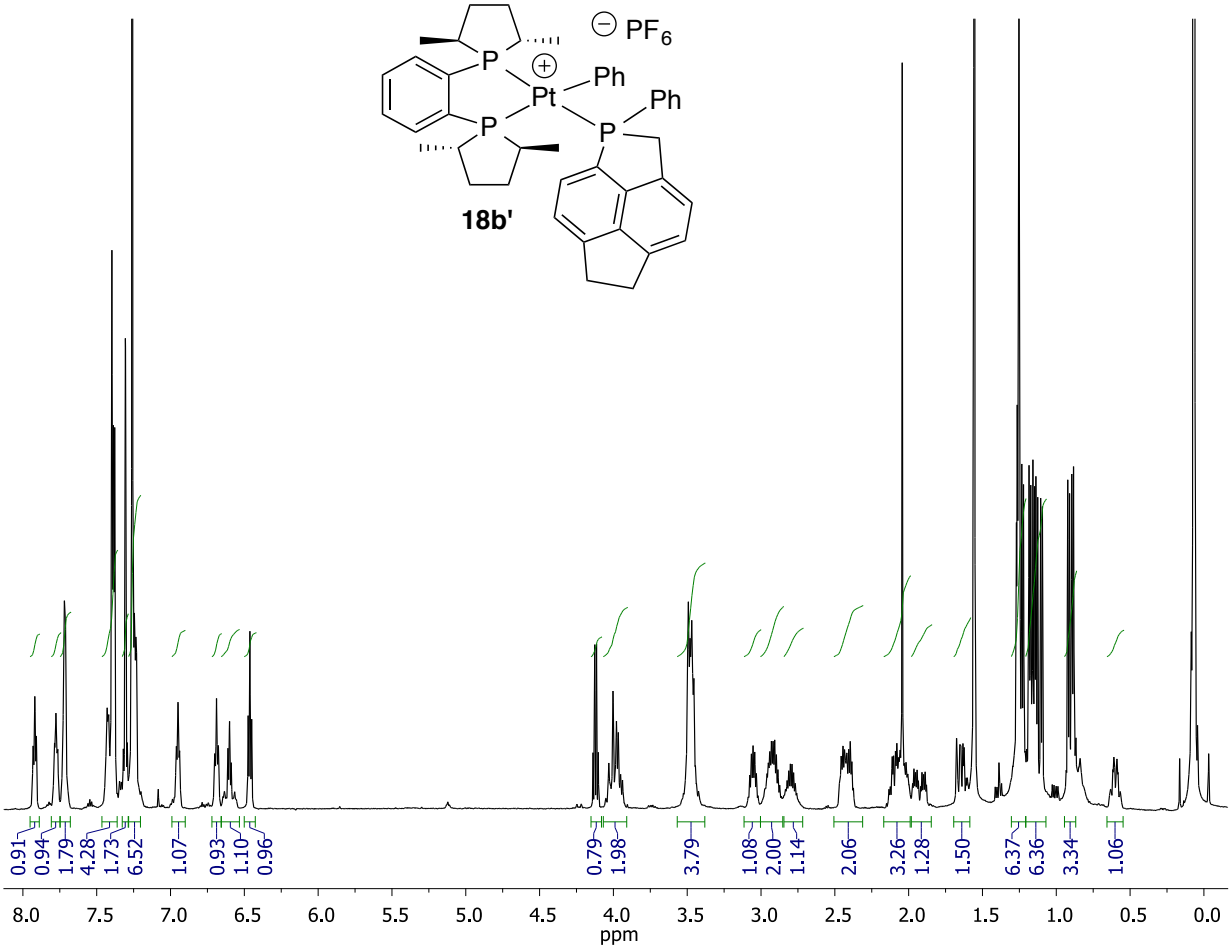
**18a**

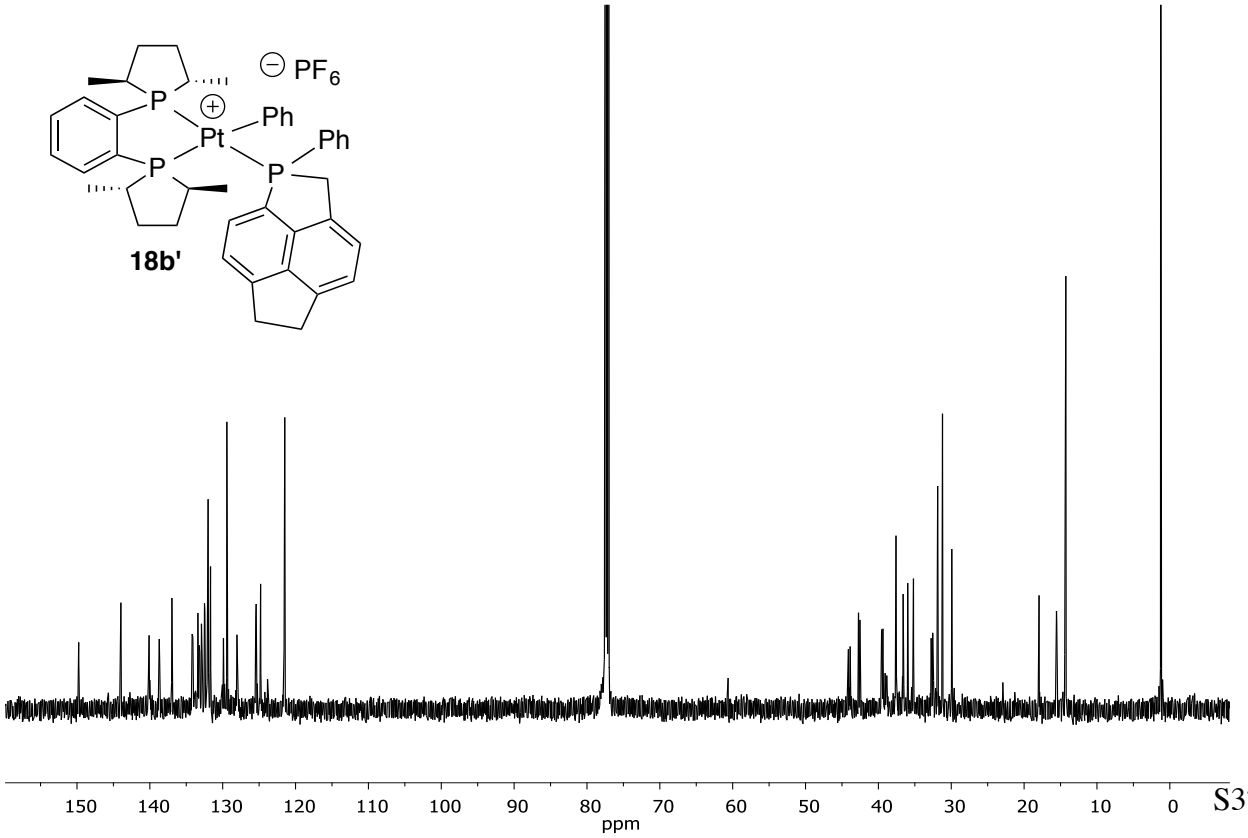

150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

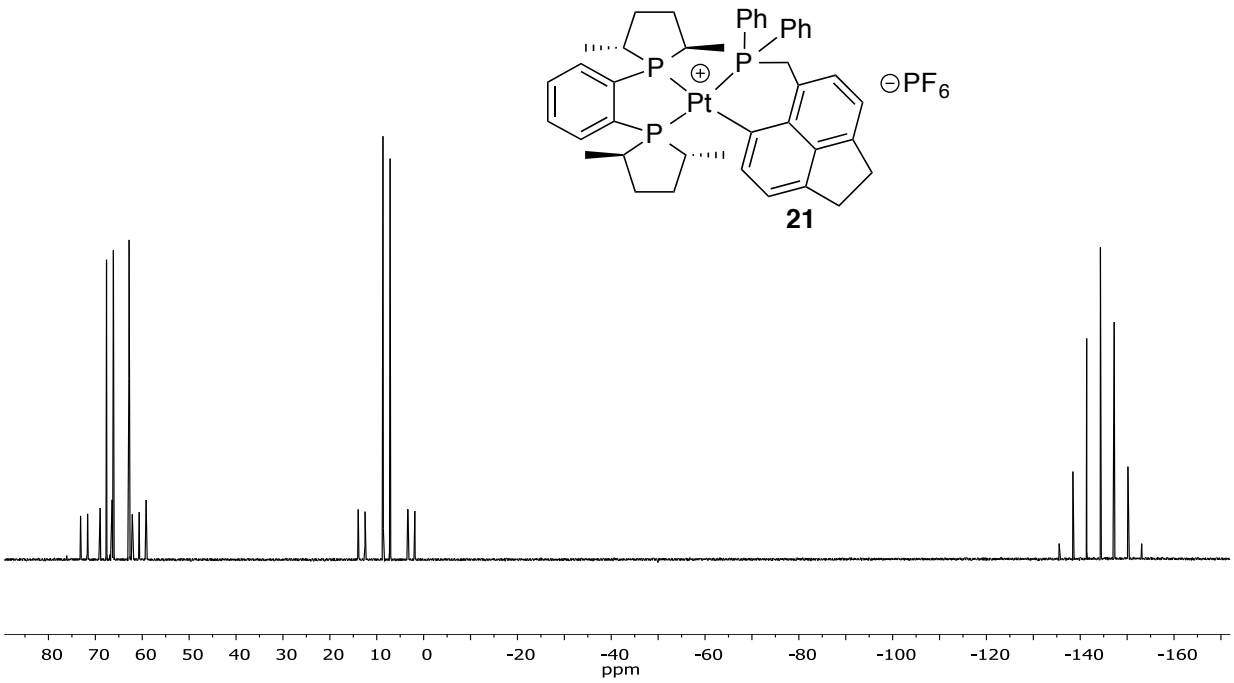

PF6
P
Pt
Ph
Ph
P
P

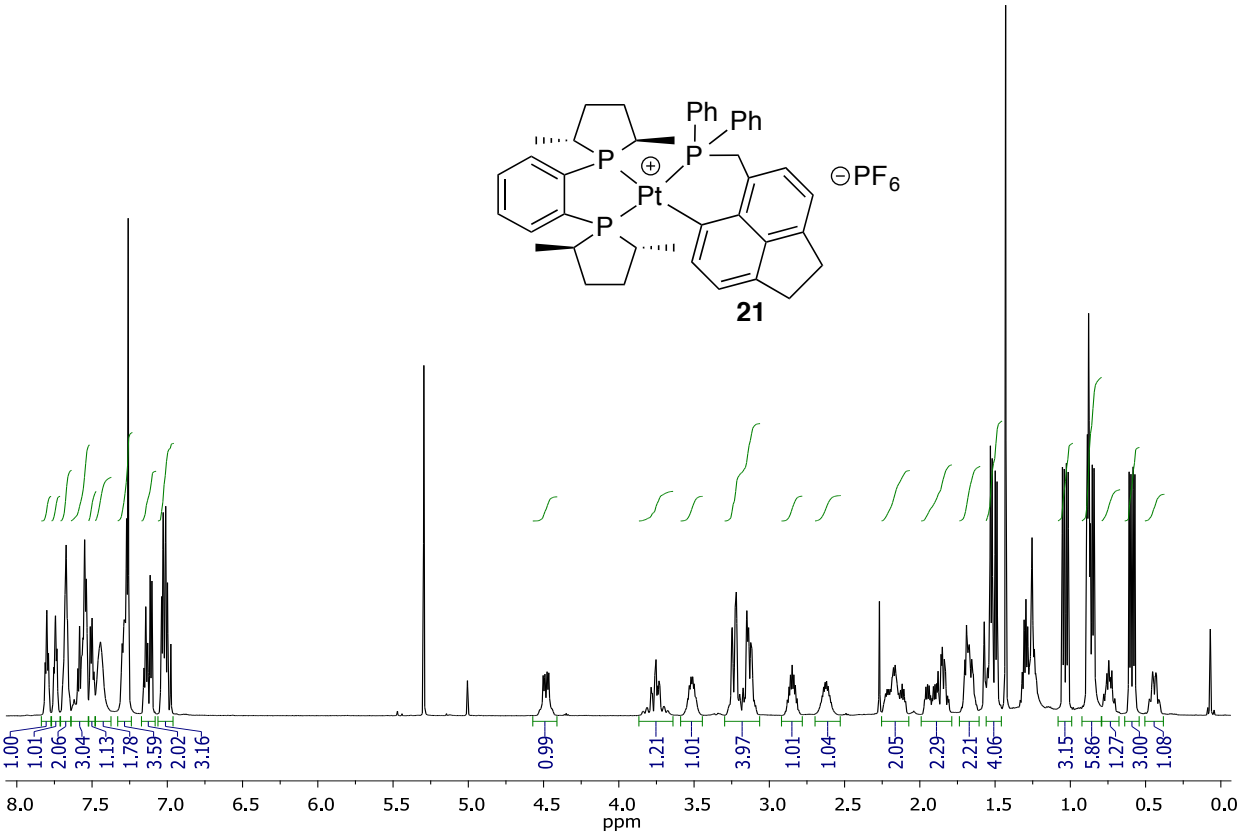
**18b'**


80
70
60
50
40
30
20
10
0
-10
-30
ppm
-50
-70
-90
-110
-130
-150


PF6
P
Pt
Ph
Ph
P
P
18b'
0.91
0.94
1.79
4.28
1.73
6.52
1.07
0.93
1.10
0.96
0.79
1.98
3.79
1.08
2.00
1.14
2.06
3.26
1.28
1.50
6.37
6.36
3.34
1.06
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

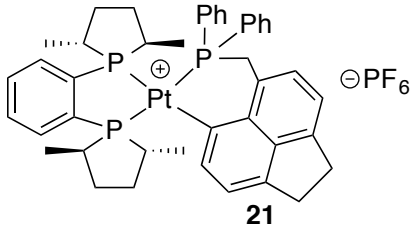

PF6
P
Pt
Ph
Ph
P
P
18b'
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm




The $^{1}$H NMR sample contained $CH_2Cl_2$.

The $^{13}C$ NMR sample contained THF.




**21**

# 3. X-Ray Crystallographic Data

These compounds are identified with an internal code (GLUxxx), a name/formula, the number in the manuscript (**in bold**), and the CCDC deposit number.

1. GLU298 5-Br-6-$CH_2Cl$-acenaphthene (**3**, CCDC 1047184)

2. GLU301 1-Br-8-$CH_2Cl$-naphthalene (**1**, CCDC 1047185)

3. GLU308 5-Br-6-$CH_2P(O)(O\text{-}i\text{-}Pr)(Ph)$-acenaphthene (**13**, CCDC 1047186)

4. GLU314 5-Br-6-$CH_2PHPh$-acenaphthene (**Ph-11**, CCDC 1047187)

5. GLU388 [Pt((*R*,*R*)-Me-DuPhos)(Ph)(*R*-Ph-PyraPhos)][$PF_6$] (**18a**, CCDC 1047188)

6. GLU391 Ph-PyraPhos($BH_3$) (**14**, CCDC 1047189)

7. GLU395 [Pt((*R*,*R*)-Me-DuPhos)(Ph)(*R*-Ph-PyraPhos)][$PF_6$]•THF (**18a•THF**, CCDC 1047190)

8. GLU395a $PhP(CH_2Ar)_2(BH_3)$ (**15**, CCDC 1047191)

9. GLU397 Ph-PyraPhos(O)•$0.5H_2O_2$ (**16•0.5$H_2O_2$**, CCDC 1047192)

10. GLU421 [Pt((*R*,*R*)-Me-DuPhos)($\kappa^2$-(P,C)-5-$PPh_2CH_2$-6-$C_{12}H_8$)][$PF_6$] (**21**, CCDC 1047193)

Table 1. Crystal data and structure refinement for 5-bromo-6-(chloromethyl)-acenaphthene, glu298.

| | | |
|---|---|---|
| Identification code | glu298 | |
| Empirical formula | C13 H10 Br Cl | |
| Formula weight | 281.57 | |
| Temperature | 100(2) K | |
| Wavelength | 1.54178 Å | |
| Crystal system | Orthorhombic | |
| Space group | Pna2(1) | |
| Unit cell dimensions | a = 16.0522(6) Å | α= 90° |
| | b = 14.3181(6) Å | β= 90° |
| | c = 4.6148(3) Å | γ = 90° |
| Volume | 1060.65(9) $Å^3$ | |
| Z | 4 | |
| Density (calculated) | 1.763 $g/cm^3$ | |
| Absorption coefficient | 7.247 $mm^{-1}$ | |
| F(000) | 560 | |
| Crystal size | 0.41 x 0.10 x 0.04 $mm^3$ | |
| Crystal color, habit | Colorless needle | |
| Theta range for data collection | 6.18 to 65.10° | |
| Index ranges | -18<=h<=18, -16<=k<=16, -5<=l<=3 | |
| Reflections collected | 3251 | |
| Independent reflections | 1310 [R(int) = 0.0504] | |
| Completeness to theta = 65.00° | 96.1 % | |
| Absorption correction | Multi-scan | |
| Max. and min. transmission | 0.7603 and 0.1551 | |
| Refinement method | Full-matrix least-squares on $F^2$ | |
| Data / restraints / parameters | 1310 / 1 / 137 | |
| Goodness-of-fit on $F^2$ | 1.006 | |
| Final R indices [I>2sigma(I)] | R1 = 0.0363, wR2 = 0.0809 | |
| R indices (all data) | R1 = 0.0505, wR2 = 0.0867 | |
| Absolute structure parameter | 0.10(5) | |
| Extinction coefficient | 0.0013(3) | |
| Largest diff. peak and hole | 0.442 and -0.422 e $Å^{-3}$ | |

Table 2. Atomic coordinates (x $10^4$) and equivalent isotropic displacement parameters ($Å^2$x $10^3$) for 5-bromo-6-(chloromethyl)-acenaphthene, glu298. U(eq) is defined as one third of the trace of the orthogonalized $U^{ij}$ tensor.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| Br(1) | 5081(1) | 8878(1) | 5246(4) | 29(1) |
| Cl(1) | 3890(1) | 6777(1) | 4997(6) | 24(1) |
| C(1) | 4765(4) | 6823(4) | 2532(16) | 20(2) |
| C(2) | 5555(4) | 6535(4) | 4053(14) | 16(2) |
| C(3) | 5819(4) | 5635(4) | 3574(16) | 20(1) |
| C(4) | 6529(4) | 5227(4) | 4920(20) | 22(2) |
| C(5) | 6980(4) | 5760(4) | 6764(16) | 19(2) |
| C(6) | 7744(4) | 5542(4) | 8536(16) | 22(2) |
| C(7) | 6032(3) | 7113(4) | 5966(14) | 14(2) |
| C(8) | 6724(4) | 6694(4) | 7289(16) | 17(1) |
| C(9) | 7264(4) | 7128(4) | 9266(15) | 24(2) |
| C(10) | 7106(3) | 8032(4) | 10050(20) | 21(1) |
| C(11) | 6436(4) | 8490(4) | 8768(17) | 23(2) |
| C(12) | 5919(4) | 8072(4) | 6801(16) | 20(2) |
| C(13) | 7954(3) | 6465(4) | 10130(30) | 21(1) |

Table 3. Bond lengths [Å] and angles [deg] for 5-bromo-6-(chloromethyl)-acenaphthene, glu298.

| | | | |
|---|---|---|---|
| Br(1)-C(12) | 1.912(6) | C(6)-C(13) | 1.548(9) |
| Cl(1)-C(1) | 1.809(7) | C(7)-C(8) | 1.403(9) |
| C(1)-C(2) | 1.508(9) | C(7)-C(12) | 1.438(8) |
| C(2)-C(3) | 1.374(8) | C(8)-C(9) | 1.404(9) |
| C(2)-C(7) | 1.431(8) | C(9)-C(10) | 1.368(8) |
| C(3)-C(4) | 1.424(9) | C(9)-C(13) | 1.512(8) |
| C(4)-C(5) | 1.352(10) | C(10)-C(11) | 1.392(9) |
| C(5)-C(8) | 1.421(8) | C(11)-C(12) | 1.368(9) |
| C(5)-C(6) | 1.506(9) | | |

| | | | |
|---|---|---|---|
| C(2)-C(1)-Cl(1) | 110.5(5) | C(7)-C(8)-C(9) | 125.7(6) |
| C(3)-C(2)-C(7) | 118.5(6) | C(7)-C(8)-C(5) | 123.9(6) |
| C(3)-C(2)-C(1) | 116.2(5) | C(9)-C(8)-C(5) | 110.4(6) |
| C(7)-C(2)-C(1) | 125.3(5) | C(10)-C(9)-C(8) | 118.4(6) |
| C(2)-C(3)-C(4) | 124.1(6) | C(10)-C(9)-C(13) | 131.4(6) |
| C(5)-C(4)-C(3) | 118.1(5) | C(8)-C(9)-C(13) | 110.2(6) |
| C(4)-C(5)-C(8) | 119.0(6) | C(9)-C(10)-C(11) | 118.6(7) |
| C(4)-C(5)-C(6) | 131.3(5) | C(12)-C(11)-C(10) | 123.0(6) |
| C(8)-C(5)-C(6) | 109.7(5) | C(11)-C(12)-C(7) | 121.3(6) |
| C(5)-C(6)-C(13) | 105.0(5) | C(11)-C(12)-Br(1) | 114.3(4) |
| C(8)-C(7)-C(2) | 116.4(5) | C(7)-C(12)-Br(1) | 124.4(5) |
| C(8)-C(7)-C(12) | 113.0(6) | C(9)-C(13)-C(6) | 104.6(6) |
| C(2)-C(7)-C(12) | 130.6(5) | | |

Table 4. Anisotropic displacement parameters ($Å^2 \times 10^3$) for 5-bromo-6-(chloromethyl)-acenaphthene, glu298. The anisotropic displacement factor exponent takes the form: $-2\pi^2[ h^2 a^{*2} U^{11} + ... + 2 h k a^* b^* U^{12}]$

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{23}$ | $U^{13}$ | $U^{12}$ |
|---|---|---|---|---|---|---|
| Br(1) | 29(1) | 19(1) | 39(1) | 0(1) | -2(1) | 5(1) |
| Cl(1) | 20(1) | 27(1) | 25(1) | 3(1) | -1(1) | 0(1) |
| C(1) | 26(3) | 21(3) | 12(4) | -4(3) | 5(3) | 1(2) |
| C(2) | 14(3) | 22(3) | 11(4) | 4(2) | 3(2) | -2(3) |
| C(3) | 17(3) | 22(3) | 21(4) | -3(3) | 7(3) | -7(2) |
| C(4) | 24(3) | 17(2) | 25(4) | -2(4) | 8(4) | 0(2) |
| C(5) | 16(3) | 16(3) | 23(4) | 2(3) | 8(3) | -1(2) |
| C(6) | 30(4) | 15(3) | 20(4) | -3(3) | 5(3) | 1(2) |
| C(7) | 20(3) | 14(3) | 9(4) | 2(2) | 9(2) | -2(2) |
| C(8) | 16(3) | 16(3) | 19(4) | -3(3) | 11(3) | -6(2) |
| C(9) | 23(3) | 23(3) | 26(5) | 3(3) | 6(3) | -7(2) |
| C(10) | 26(3) | 23(3) | 15(3) | 3(4) | 1(5) | -9(2) |
| C(11) | 24(3) | 14(3) | 31(4) | -6(3) | 6(3) | -3(3) |
| C(12) | 24(3) | 14(3) | 21(4) | 8(3) | -1(3) | 4(2) |
| C(13) | 21(2) | 26(3) | 14(3) | -2(5) | 1(5) | -3(2) |

Table 5. Hydrogen coordinates (x $10^4$) and isotropic displacement parameters ($Å^2$ x $10^3$) for 5-bromo-6-(chloromethyl)-acenaphthene, glu298.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| H(1A) | 4662 | 6401 | 871 | 23 |
| H(1B) | 4827 | 7466 | 1773 | 23 |
| H(3) | 5508 | 5262 | 2260 | 24 |
| H(4) | 6682 | 4598 | 4539 | 26 |
| H(6A) | 8211 | 5348 | 7271 | 26 |
| H(6B) | 7628 | 5036 | 9942 | 26 |
| H(10) | 7446 | 8341 | 11435 | 26 |
| H(11) | 6333 | 9122 | 9283 | 27 |
| H(13A) | 7962 | 6370 | 12253 | 25 |
| H(13B) | 8503 | 6707 | 9506 | 25 |

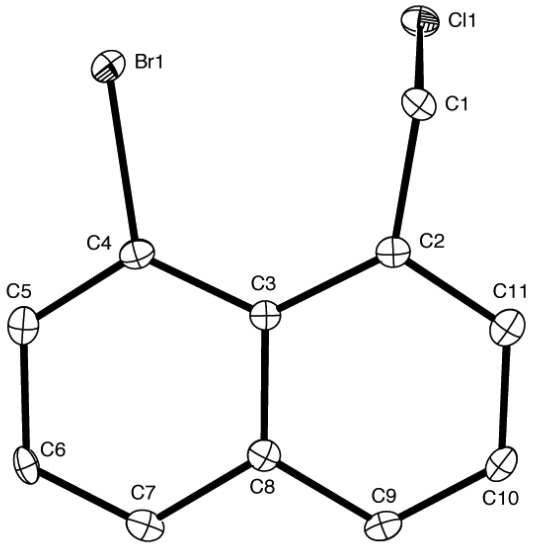



**Figure S4**. ORTEP diagram of 1-bromo-8-(chloromethyl)naphthalene, glu301 (one of the two molecules in the unit cell)

Table 1. Crystal data and structure refinement for 1-bromo-8-(chloromethyl)naphthalene, glu301.

| | | |
|---|---|---|
| Identification code | glu301 | |
| Empirical formula | C11 H8 Br Cl | |
| Formula weight | 255.53 | |
| Temperature | 100(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Monoclinic | |
| Space group | P2(1)/c | |
| Unit cell dimensions | a = 8.0594(3) Å | α= 90° |
| | b = 28.0000(10) Å | β= 90.1380(10)° |
| | c = 8.3318(3) Å | γ = 90° |
| Volume | 1880.18(12) $Å^3$ | |
| Z, Z' | 8, 2 | |
| Density (calculated) | 1.805 $g/cm^3$ | |
| Absorption coefficient | 4.599 $mm^{-1}$ | |
| F(000) | 1008 | |
| Crystal size | 0.41 x 0.33 x 0.30 $mm^3$ | |
| Crystal color, habit | Colorless block | |
| Theta range for data collection | 2.53 to 26.47° | |
| Index ranges | -10<=h<=10, -34<=k<=35, -10<=l<=10 | |
| Reflections collected | 15297 | |
| Independent reflections | 3403 [R(int) = 0.0220] | |
| Completeness to theta = 25.00° | 98.5 % | |
| Absorption correction | Multi-scan | |
| Max. and min. transmission | 0.3391 and 0.2543 | |
| Refinement method | Full-matrix least-squares on $F^2$ | |
| Data / restraints / parameters | 3403 / 0 / 235 | |
| Goodness-of-fit on $F^2$ | 1.041 | |
| Final R indices [I>2sigma(I)] | R1 = 0.0250, wR2 = 0.0609 | |
| R indices (all data) | R1 = 0.0289, wR2 = 0.0627 | |
| Largest diff. peak and hole | 1.097 and -0.326 e $Å^{-3}$ | |

Table 2. Atomic coordinates (x $10^4$) and equivalent isotropic displacement parameters ($Å^2$ x $10^3$) for 1-bromo-8-(chloromethyl)naphthalene, glu301. U(eq) is defined as one third of the trace of the orthogonalized $U^{ij}$ tensor.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| Br(1) | 4865(1) | 1417(1) | -1368(1) | 22(1) |
| Br(1') | 3865(1) | -1076(1) | 7354(1) | 21(1) |
| Cl(1') | 2818(1) | -33(1) | 9277(1) | 22(1) |
| Cl(1) | 6881(1) | 2483(1) | -709(1) | 21(1) |
| C(1) | 4942(3) | 2537(1) | -1815(3) | 17(1) |
| C(1') | 4138(3) | 46(1) | 7537(3) | 17(1) |
| C(2') | 3138(3) | 64(1) | 6010(3) | 15(1) |
| C(2) | 3465(3) | 2555(1) | -717(3) | 16(1) |
| C(3) | 2544(3) | 2150(1) | -129(3) | 14(1) |
| C(3') | 2593(3) | -344(1) | 5096(3) | 13(1) |
| C(4) | 2906(3) | 1652(1) | -357(3) | 17(1) |
| C(4') | 2850(3) | -841(1) | 5434(3) | 16(1) |
| C(5') | 2332(3) | -1198(1) | 4421(3) | 19(1) |
| C(5) | 1873(4) | 1298(1) | 176(3) | 21(1) |
| C(6') | 1504(3) | -1088(1) | 2974(4) | 20(1) |
| C(6) | 376(3) | 1407(1) | 1007(3) | 17(1) |
| C(7) | 28(3) | 1871(1) | 1319(3) | 20(1) |
| C(7') | 1168(3) | -623(1) | 2615(3) | 18(1) |
| C(8) | 1072(3) | 2245(1) | 777(3) | 16(1) |
| C(8') | 1691(3) | -249(1) | 3632(3) | 15(1) |
| C(9) | 618(3) | 2722(1) | 1157(3) | 19(1) |
| C(9') | 1317(3) | 228(1) | 3177(3) | 17(1) |
| C(10) | 1550(3) | 3095(1) | 625(3) | 20(1) |
| C(10') | 1844(3) | 603(1) | 4076(3) | 19(1) |
| C(11) | 2957(3) | 3011(1) | -327(3) | 20(1) |
| C(11') | 2760(3) | 517(1) | 5483(3) | 18(1) |

Table 3. Bond lengths [Å] and angles [deg] for 1-bromo-8-(chloromethyl)naphthalene, glu301.

| | | | |
|---|---|---|---|
| Br(1)-C(4) | 1.908(3) | C(4)-C(5) | 1.370(4) |
| Br(1')-C(4') | 1.913(2) | C(4')-C(5') | 1.373(4) |
| Cl(1')-C(1') | 1.814(3) | C(5')-C(6') | 1.411(4) |
| Cl(1)-C(1) | 1.818(2) | C(5)-C(6) | 1.425(4) |
| C(1)-C(2) | 1.503(4) | C(6')-C(7') | 1.363(4) |
| C(1')-C(2') | 1.505(3) | C(6)-C(7) | 1.356(4) |
| C(2')-C(11') | 1.376(4) | C(7)-C(8) | 1.418(4) |
| C(2')-C(3') | 1.439(3) | C(7')-C(8') | 1.412(4) |
| C(2)-C(11) | 1.381(4) | C(8)-C(9) | 1.421(4) |
| C(2)-C(3) | 1.442(4) | C(8')-C(9') | 1.420(4) |
| C(3)-C(8) | 1.433(4) | C(9)-C(10) | 1.362(4) |
| C(3)-C(4) | 1.437(4) | C(9')-C(10') | 1.359(4) |
| C(3')-C(4') | 1.435(3) | C(10)-C(11) | 1.405(4) |
| C(3')-C(8') | 1.443(3) | C(10')-C(11') | 1.405(4) |

| | | | |
|---|---|---|---|
| C(2)-C(1)-Cl(1) | 112.03(18) | C(2')-C(3')-C(8') | 117.0(2) |
| C(2')-C(1')-Cl(1') | 111.44(18) | C(5)-C(4)-C(3) | 122.4(3) |
| C(11')-C(2')-C(3') | 119.6(2) | C(5)-C(4)-Br(1) | 113.5(2) |
| C(11')-C(2')-C(1') | 114.7(2) | C(3)-C(4)-Br(1) | 124.1(2) |
| C(3')-C(2')-C(1') | 125.7(2) | C(5')-C(4')-C(3') | 122.9(2) |
| C(11)-C(2)-C(3) | 119.6(3) | C(5')-C(4')-Br(1') | 113.07(19) |
| C(11)-C(2)-C(1) | 114.2(2) | C(3')-C(4')-Br(1') | 124.03(19) |
| C(3)-C(2)-C(1) | 126.2(2) | C(4')-C(5')-C(6') | 120.7(2) |
| C(8)-C(3)-C(4) | 114.8(2) | C(4)-C(5)-C(6) | 121.2(3) |
| C(8)-C(3)-C(2) | 117.4(2) | C(7')-C(6')-C(5') | 119.2(2) |
| C(4)-C(3)-C(2) | 127.8(3) | C(7)-C(6)-C(5) | 118.3(2) |
| C(4')-C(3')-C(2') | 128.4(2) | C(6)-C(7)-C(8) | 121.6(3) |
| C(4')-C(3')-C(8') | 114.6(2) | C(6')-C(7')-C(8') | 121.3(2) |

| | | | |
|---|---|---|---|
| C(7)-C(8)-C(9) | 118.0(3) | C(10)-C(9)-C(8) | 120.4(3) |
| C(7)-C(8)-C(3) | 121.5(2) | C(10')-C(9')-C(8') | 121.0(2) |
| C(9)-C(8)-C(3) | 120.5(2) | C(9)-C(10)-C(11) | 120.1(3) |
| C(7')-C(8')-C(9') | 118.4(2) | C(9')-C(10')-C(11') | 119.3(2) |
| C(7')-C(8')-C(3') | 121.3(2) | C(2)-C(11)-C(10) | 121.9(3) |
| C(9')-C(8')-C(3') | 120.3(2) | C(2')-C(11')-C(10') | 122.8(2) |

Table 4. Anisotropic displacement parameters ($Å^2$ x $10^3$) for 1-bromo-8-(chloromethyl)naphthalene, glu301. The anisotropic displacement factor exponent takes the form: $-2\pi^2[ h^2 a^{*2} U^{11} + ... + 2 h k a^* b^* U^{12}]$

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{23}$ | $U^{13}$ | $U^{12}$ |
|---|---|---|---|---|---|---|
| Br(1) | 21(1) | 18(1) | 28(1) | -4(1) | 4(1) | 3(1) |
| Br(1') | 24(1) | 18(1) | 21(1) | 4(1) | -1(1) | 2(1) |
| Cl(1') | 23(1) | 30(1) | 14(1) | 0(1) | 3(1) | 4(1) |
| Cl(1) | 15(1) | 28(1) | 21(1) | -1(1) | -1(1) | -1(1) |
| C(1) | 15(1) | 21(1) | 16(1) | 3(1) | -1(1) | -2(1) |
| C(1') | 16(1) | 19(1) | 16(1) | -1(1) | 3(1) | -2(1) |
| C(2') | 11(1) | 22(1) | 12(1) | 1(1) | 4(1) | 0(1) |
| C(2) | 14(1) | 20(1) | 13(1) | 0(1) | -3(1) | 1(1) |
| C(3) | 14(1) | 17(1) | 10(1) | 1(1) | -2(1) | 1(1) |
| C(3') | 10(1) | 17(1) | 13(1) | 1(1) | 6(1) | 0(1) |
| C(4) | 16(1) | 21(1) | 15(1) | -1(1) | -1(1) | 3(1) |
| C(4') | 13(1) | 20(1) | 15(1) | 3(1) | 3(1) | 0(1) |
| C(5') | 20(1) | 15(1) | 23(2) | 3(1) | 7(1) | -3(1) |
| C(5) | 24(1) | 17(1) | 22(1) | 0(1) | -4(1) | -1(1) |
| C(6') | 19(1) | 20(1) | 21(1) | -5(1) | 4(1) | -5(1) |
| C(6) | 21(1) | 14(1) | 17(1) | 6(1) | -3(1) | -6(1) |
| C(7) | 16(1) | 26(1) | 16(1) | 4(1) | -1(1) | 0(1) |
| C(7') | 15(1) | 24(1) | 16(1) | -1(1) | 2(1) | -3(1) |
| C(8) | 16(1) | 19(1) | 13(1) | 2(1) | -4(1) | 1(1) |
| C(8') | 11(1) | 19(1) | 15(1) | 1(1) | 5(1) | -1(1) |
| C(9) | 17(1) | 23(1) | 17(1) | -3(1) | -1(1) | 5(1) |
| C(9') | 15(1) | 23(1) | 15(1) | 3(1) | 2(1) | 1(1) |
| C(10) | 22(1) | 15(1) | 23(2) | -2(1) | -2(1) | 5(1) |
| C(10') | 18(1) | 18(1) | 21(1) | 3(1) | 6(1) | 4(1) |
| C(11) | 21(1) | 20(1) | 19(1) | -2(1) | -6(1) | 2(1) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C(11') | 18(1) | 17(1) | 19(1) | -2(1) | 3(1) | -1(1) |

Table 5. Hydrogen coordinates (x $10^4$) and isotropic displacement parameters ($Å^2$ x $10^3$) for 1-bromo-8-(chloromethyl)naphthalene, glu301.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| H(1A) | 4970 | 2831 | -2473 | 21 |
| H(1B) | 4826 | 2261 | -2551 | 21 |
| H(1'A) | 4775 | 347 | 7652 | 20 |
| H(1'B) | 4940 | -221 | 7479 | 20 |
| H(5'A) | 2534 | -1522 | 4697 | 23 |
| H(5A) | 2159 | 973 | -11 | 25 |
| H(6'A) | 1184 | -1336 | 2257 | 24 |
| H(6A) | -358 | 1160 | 1335 | 21 |
| H(7A) | -939 | 1948 | 1915 | 23 |
| H(7'A) | 570 | -550 | 1662 | 22 |
| H(9A) | -342 | 2781 | 1787 | 23 |
| H(9'A) | 690 | 285 | 2229 | 21 |
| H(10A) | 1249 | 3413 | 897 | 24 |
| H(10B) | 1596 | 921 | 3758 | 23 |
| H(11A) | 3576 | 3276 | -714 | 24 |
| H(11B) | 3134 | 782 | 6097 | 22 |

Table 1. Crystal data and structure refinement for glu308, 1-Br-8-$CH_2PPh(O)(O$-*i*-Pr)-acenaphthene.

| | | |
|---|---|---|
| Identification code | glu308 | |
| Empirical formula | C22 H22 Br O2 P | |
| Formula weight | 429.28 | |
| Temperature | 100(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Orthorhombic | |
| Crystal color, habit | Colorless block | |
| Space group | Pna2(1) | |
| Unit cell dimensions | a = 18.9410(7) Å | α= 90° |
| | b = 17.6865(6) Å | β= 90° |
| | c = 5.6269(2) Å | γ = 90° |
| Volume | 1885.01(12) $Å^3$ | |
| Z | 4 | |
| Density (calculated) | 1.513 $g/cm^3$ | |
| Absorption coefficient | 2.279 $mm^{-1}$ | |
| F(000) | 880 | |
| Crystal size | 0.34 x 0.30 x 0.26 $mm^3$ | |
| Theta range for data collection | 1.58 to 25.41° | |
| Index ranges | -22<=h<=21, -20<=k<=21, -6<=l<=6 | |
| Reflections collected | 9974 | |
| Independent reflections | 3251 [R(int) = 0.0271] | |
| Completeness to theta = 25.00° | 99.8 % | |
| Absorption correction | Semi-empirical from equivalents | |
| Max. and min. transmission | 0.849 and 0.678 | |
| Refinement method | Full-matrix least-squares on $F^2$ | |
| Data / restraints / parameters | 3251 / 1 / 235 | |
| Goodness-of-fit on $F^2$ | 1.031 | |
| Final R indices [I>2sigma(I)] | R1 = 0.0262, wR2 = 0.0615 | |
| R indices (all data) | R1 = 0.0289, wR2 = 0.0629 | |
| Absolute structure parameter | 0.003(7) | |
| Largest diff. peak and hole | 0.308 and -0.413 e $Å^{-3}$ | |

Table 2. Atomic coordinates (x $10^4$) and equivalent isotropic displacement parameters ($Å^2$ x $10^3$) for glu308, 1-Br-8-$CH_2$PPh(O)(O-*i*-Pr)-acenaphthene. U(eq) is defined as one third of the trace of the orthogonalized $U^{ij}$ tensor.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| Br(1) | 3076(1) | 7166(1) | 5080(1) | 29(1) |
| P(1) | 1000(1) | 7745(1) | 6169(1) | 13(1) |
| O(1) | 1172(1) | 7868(1) | 3640(4) | 18(1) |
| O(2) | 723(1) | 6918(1) | 6814(3) | 14(1) |
| C(1) | 300(1) | 8370(2) | 7114(5) | 14(1) |
| C(2) | 118(1) | 8971(2) | 5662(4) | 16(1) |
| C(3) | -424(1) | 9459(2) | 6308(5) | 20(1) |
| C(4) | -789(2) | 9337(2) | 8384(5) | 19(1) |
| C(5) | -614(1) | 8743(2) | 9867(6) | 20(1) |
| C(6) | -61(1) | 8259(2) | 9241(5) | 19(1) |
| C(7) | -309(2) | 6155(2) | 7144(5) | 24(1) |
| C(8) | 138(1) | 6602(2) | 5415(5) | 17(1) |
| C(9) | 435(2) | 6131(2) | 3426(5) | 24(1) |
| C(10) | 1730(1) | 7838(1) | 8203(5) | 13(1) |
| C(11) | 2087(1) | 8589(2) | 7743(4) | 13(1) |
| C(12) | 2583(1) | 8723(2) | 5863(5) | 14(1) |
| C(13) | 2970(1) | 8220(2) | 4381(5) | 17(1) |
| C(14) | 3363(2) | 8465(2) | 2477(5) | 18(1) |
| C(15) | 3438(1) | 9235(2) | 1943(5) | 20(1) |
| C(16) | 3141(1) | 9753(2) | 3424(5) | 16(1) |
| C(17) | 2724(1) | 9495(1) | 5336(5) | 14(1) |
| C(18) | 2447(1) | 10105(2) | 6654(5) | 15(1) |
| C(19) | 2020(1) | 9961(2) | 8544(5) | 18(1) |
| C(20) | 1841(1) | 9199(2) | 9045(5) | 16(1) |
| C(21) | 3156(2) | 10609(2) | 3429(5) | 23(1) |

| | | | | |
|---|---|---|---|---|
| C(22) | 2698(2) | 10843(2) | 5572(5) | 20(1) |

Table 3. Bond lengths [Å] and angles [deg] for glu308, 1-Br-8-$CH_2$PPh(O)(O-*i*-Pr)-acenaphthene.

| | | | |
|---|---|---|---|
| Br(1)-C(13) | 1.915(3) | C(11)-C(20) | 1.385(4) |
| P(1)-O(1) | 1.476(2) | C(11)-C(12) | 1.434(4) |
| P(1)-O(2) | 1.5947(19) | C(12)-C(13) | 1.423(4) |
| P(1)-C(10) | 1.802(3) | C(12)-C(17) | 1.423(4) |
| P(1)-C(1) | 1.806(3) | C(13)-C(14) | 1.376(4) |
| O(2)-C(8) | 1.469(3) | C(14)-C(15) | 1.401(4) |
| C(1)-C(2) | 1.385(4) | C(15)-C(16) | 1.362(4) |
| C(1)-C(6) | 1.393(4) | C(16)-C(17) | 1.411(4) |
| C(2)-C(3) | 1.389(4) | C(16)-C(21) | 1.513(4) |
| C(3)-C(4) | 1.374(4) | C(17)-C(18) | 1.411(4) |
| C(4)-C(5) | 1.383(4) | C(18)-C(19) | 1.360(4) |
| C(5)-C(6) | 1.397(4) | C(18)-C(22) | 1.516(4) |
| C(7)-C(8) | 1.513(4) | C(19)-C(20) | 1.419(4) |
| C(8)-C(9) | 1.505(4) | C(21)-C(22) | 1.543(4) |
| C(10)-C(11) | 1.512(4) | | |

| | | | |
|---|---|---|---|
| O(1)-P(1)-O(2) | 115.28(11) | C(1)-C(2)-C(3) | 120.5(3) |
| O(1)-P(1)-C(10) | 115.44(13) | C(4)-C(3)-C(2) | 119.7(3) |
| O(2)-P(1)-C(10) | 101.10(11) | C(3)-C(4)-C(5) | 120.8(3) |
| O(1)-P(1)-C(1) | 110.82(13) | C(4)-C(5)-C(6) | 119.6(3) |
| O(2)-P(1)-C(1) | 104.60(11) | C(1)-C(6)-C(5) | 119.9(3) |
| C(10)-P(1)-C(1) | 108.65(12) | O(2)-C(8)-C(9) | 109.1(2) |
| C(8)-O(2)-P(1) | 118.39(16) | O(2)-C(8)-C(7) | 106.1(2) |
| C(2)-C(1)-C(6) | 119.5(2) | C(9)-C(8)-C(7) | 113.4(2) |
| C(2)-C(1)-P(1) | 118.7(2) | C(11)-C(10)-P(1) | 108.34(17) |
| C(6)-C(1)-P(1) | 121.8(2) | C(20)-C(11)-C(12) | 118.8(3) |

| | | | |
|---|---|---|---|
| C(20)-C(11)-C(10) | 116.3(2) | C(17)-C(16)-C(21) | 109.5(2) |
| C(12)-C(11)-C(10) | 124.4(2) | C(16)-C(17)-C(18) | 111.1(2) |
| C(13)-C(12)-C(17) | 112.4(2) | C(16)-C(17)-C(12) | 125.1(3) |
| C(13)-C(12)-C(11) | 131.8(3) | C(18)-C(17)-C(12) | 123.7(3) |
| C(17)-C(12)-C(11) | 115.8(2) | C(19)-C(18)-C(17) | 119.2(3) |
| C(14)-C(13)-C(12) | 122.6(3) | C(19)-C(18)-C(22) | 131.4(3) |
| C(14)-C(13)-Br(1) | 114.2(2) | C(17)-C(18)-C(22) | 109.3(2) |
| C(12)-C(13)-Br(1) | 122.83(19) | C(18)-C(19)-C(20) | 118.5(3) |
| C(13)-C(14)-C(15) | 121.9(3) | C(11)-C(20)-C(19) | 123.7(3) |
| C(16)-C(15)-C(14) | 118.8(3) | C(16)-C(21)-C(22) | 105.0(2) |
| C(15)-C(16)-C(17) | 118.7(3) | C(18)-C(22)-C(21) | 105.0(2) |
| C(15)-C(16)-C(21) | 131.8(3) | | |

Table 4. Anisotropic displacement parameters ($Å^2$ x $10^3$) for glu308, 1-Br-8-$CH_2$PPh(O)(O-*i*-Pr)-acenaphthene. The anisotropic displacement factor exponent takes the form: $-2\pi^2[ h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{23}$ | $U^{13}$ | $U^{12}$ |
|---|---|---|---|---|---|---|
| Br(1) | 34(1) | 15(1) | 36(1) | 0(1) | 17(1) | 3(1) |
| P(1) | 11(1) | 14(1) | 13(1) | 1(1) | 1(1) | 0(1) |
| O(1) | 20(1) | 20(1) | 14(1) | 2(1) | 0(1) | 0(1) |
| O(2) | 14(1) | 11(1) | 16(1) | 0(1) | -2(1) | -2(1) |
| C(1) | 9(1) | 14(2) | 18(1) | -4(1) | -1(1) | -1(1) |
| C(2) | 13(1) | 17(2) | 19(2) | 1(1) | 0(1) | 0(1) |
| C(3) | 20(2) | 16(2) | 26(2) | 1(1) | -2(1) | 1(1) |
| C(4) | 11(1) | 16(2) | 30(2) | -8(1) | -2(1) | 4(1) |
| C(5) | 14(1) | 26(2) | 19(1) | -4(1) | 4(1) | -1(1) |
| C(6) | 15(2) | 21(2) | 21(1) | 2(1) | 1(1) | 0(1) |
| C(7) | 21(2) | 30(2) | 22(2) | 3(1) | -1(1) | -11(1) |
| C(8) | 11(1) | 20(2) | 21(2) | 2(1) | -4(1) | -1(1) |
| C(9) | 24(2) | 27(2) | 22(2) | -4(1) | -3(1) | -4(1) |
| C(10) | 12(1) | 14(2) | 14(1) | -1(1) | 2(1) | -1(1) |
| C(11) | 9(1) | 17(2) | 14(1) | 2(1) | -5(1) | 0(1) |
| C(12) | 8(1) | 18(2) | 17(1) | 0(1) | -3(1) | 0(1) |
| C(13) | 13(1) | 15(2) | 22(2) | 2(1) | 1(1) | 2(1) |
| C(14) | 15(2) | 20(2) | 18(1) | -4(1) | 3(1) | 1(1) |
| C(15) | 13(2) | 28(2) | 18(1) | 4(1) | 1(1) | -2(1) |
| C(16) | 10(1) | 18(2) | 19(1) | 1(1) | -1(1) | -1(1) |
| C(17) | 9(1) | 16(1) | 17(1) | 3(1) | -3(1) | 1(1) |
| C(18) | 11(1) | 13(2) | 21(2) | -1(1) | -3(1) | 0(1) |
| C(19) | 16(2) | 17(2) | 20(2) | -4(1) | -1(1) | 2(1) |
| C(20) | 10(2) | 22(2) | 15(1) | -1(1) | 1(1) | -1(1) |
| C(21) | 24(2) | 21(2) | 23(2) | 6(1) | 1(1) | -3(1) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C(22) | 18(2) | 13(2) | 30(2) | 0(1) | 0(1) | -1(1) |

Table 5. Hydrogen coordinates (x $10^4$) and isotropic displacement parameters (Å$^2$ x $10^3$) for glu308, 1-Br-8-$CH_2$PPh(O)(O-*i*-Pr)-acenaphthene.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| H(2A) | 360 | 9049 | 4245 | 19 |
| H(3A) | -539 | 9867 | 5339 | 24 |
| H(4A) | -1158 | 9658 | 8796 | 23 |
| H(5A) | -862 | 8665 | 11271 | 24 |
| H(6A) | 65 | 7863 | 10243 | 23 |
| H(7A) | -482 | 6485 | 8365 | 36 |
| H(7B) | -28 | 5763 | 7849 | 36 |
| H(7C) | -700 | 5933 | 6314 | 36 |
| H(8A) | -144 | 7016 | 4748 | 21 |
| H(9A) | 713 | 6445 | 2395 | 36 |
| H(9B) | 56 | 5909 | 2538 | 36 |
| H(9C) | 727 | 5738 | 4075 | 36 |
| H(10A) | 1561 | 7817 | 9829 | 16 |
| H(10B) | 2062 | 7428 | 7967 | 16 |
| H(14A) | 3586 | 8110 | 1516 | 22 |
| H(15A) | 3687 | 9388 | 602 | 24 |
| H(19A) | 1850 | 10353 | 9486 | 21 |
| H(20A) | 1541 | 9103 | 10319 | 19 |
| H(21A) | 2962 | 10808 | 1962 | 27 |
| H(21B) | 3636 | 10793 | 3611 | 27 |
| H(22A) | 2973 | 11130 | 6710 | 25 |
| H(22B) | 2300 | 11147 | 5059 | 25 |

Sample GLU314 code reference mage302

Data collected on July 5, 2009

A colorless crystal of sample GLU314 (mag-e302) was mounted on a Cryoloop with Paratone-N oil. Data were collected on a Bruker APEX II CCD systems using Mo K alpha radiation in a nitrogen gas stream at 100(2) K using phi and omega scans. Crystal-to-detector distance was 60 mm and exposure time was 10 seconds per frame using a scan width of 0.5°. Indexing and unit cell refinement indicated a primitive, monoclinic lattice with space group of $P2_1$. The data were integrated using the Bruker SHELXTL software program and scaled using the SADABS software program. Solution by direct methods (SHELXS) and all non-hydrogen atoms were refined anisotropically by full-matrix least-squares (SHELXL-97). Structural solution indicated a racemic twin (roughly BASF value of 0.472 ). Hydrogen atom on P1 was found from a Fourier difference map and was set using a DFIX command. Attempts to solve structure under a triclinic space group P1 indicated either error message of wrong structure – try racemic twin. Best solution was found using $P2_1$ with twin command.

Table 1. Crystal data and structure refinement for 5-Br-6-$CH_2$PHPh-acenaphthene, GLU314.

| | | |
|---|---|---|
| Identification code | glu314 | |
| Empirical formula | C19 H16 Br P | |
| Formula weight | 355.20 | |
| Temperature | 100(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Monoclinic | |
| Crystal color/habit | colorless/block | |
| Space group | P2(1) | |
| Unit cell dimensions | a = 10.217(3) Å | α= 90° |
| | b = 6.9781(19) Å | β= 101.873(3)° |
| | c = 10.816(3) Å | γ = 90° |
| Volume | 754.6(4) $Å^3$ | |
| Z | 2 | |
| Density (calculated) | 1.563 $Mg/m^3$ | |
| Absorption coefficient | 2.820 $mm^{-1}$ | |
| F(000) | 360 | |
| Crystal size | 0.25 x 0.20 x 0.10 $mm^3$ | |
| Theta range for data collection | 1.92 to 27.93°. | |
| Index ranges | -13<=h<=13, -8<=k<=9, -14<=l<=13 | |
| Reflections collected | 11849 | |
| Independent reflections | 3365 [R(int) = 0.0711] | |
| Completeness to theta = 25.00° | 100.0 % | |
| Absorption correction | multi-scan | |
| Max. and min. transmission | 0.7657 and 0.5391 | |
| Refinement method | Full-matrix least-squares on $F^2$ | |
| Data / restraints / parameters | 3365 / 2 / 194 | |
| Goodness-of-fit on $F^2$ | 1.003 | |
| Final R indices [I>2sigma(I)] | R1 = 0.0391, wR2 = 0.0852 | |
| R indices (all data) | R1 = 0.0482, wR2 = 0.0888 | |
| Absolute structure parameter | 0.00(19) – found racemic twin | |
| Largest diff. peak and hole | 0.767 and -0.666 e.$Å^{-3}$ | |

Table 2. Atomic coordinates (x $10^4$) and equivalent isotropic displacement parameters ($Å^2$ x $10^3$) for 5-Br-6-$CH_2$PHPh-acenaphthene, GLU314. U(eq) is defined as one third of the trace of the orthogonalized $U^{ij}$ tensor.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| Br(1) | 4980(1) | 7580(1) | 2658(1) | 26(1) |
| P(1) | 6589(1) | 4361(2) | 4937(1) | 24(1) |
| C(1) | 6602(4) | 3248(5) | 2389(3) | 19(1) |
| C(2) | 7358(4) | 1651(6) | 2267(4) | 22(1) |
| C(3) | 8111(4) | 1433(6) | 1307(4) | 22(1) |
| C(4) | 8087(3) | 2861(7) | 459(3) | 22(1) |
| C(5) | 7339(4) | 4525(6) | 573(3) | 20(1) |
| C(6) | 6608(3) | 4813(6) | 1535(3) | 20(1) |
| C(7) | 5957(4) | 6642(6) | 1449(4) | 21(1) |
| C(8) | 6014(4) | 7913(6) | 503(3) | 25(1) |
| C(9) | 6738(3) | 7541(9) | -444(3) | 24(1) |
| C(10) | 7410(4) | 5845(6) | -399(3) | 22(1) |
| C(11) | 8255(4) | 5023(6) | -1255(4) | 26(1) |
| C(12) | 8734(4) | 3054(7) | -673(4) | 32(1) |
| C(13) | 5798(4) | 3217(6) | 3420(3) | 21(1) |
| C(14) | 7915(3) | 2650(8) | 5562(3) | 21(1) |
| C(15) | 9237(4) | 3273(6) | 5976(3) | 25(1) |
| C(16) | 10211(4) | 2022(6) | 6577(4) | 28(1) |
| C(17) | 9893(4) | 141(7) | 6755(4) | 29(1) |
| C(18) | 8590(4) | -508(7) | 6345(4) | 28(1) |
| C(19) | 7612(4) | 773(6) | 5764(4) | 26(1) |

Table 3. Bond lengths [Å] and angles [deg] for 5-Br-6-$CH_2$PHPh-acenaphthene, GLU314.

| | | | |
|---|---|---|---|
| Br(1)-C(7) | 1.916(4) | C(9)-H(9A) | 0.9500 |
| P(1)-C(14) | 1.827(5) | C(10)-C(11) | 1.504(5) |
| P(1)-C(13) | 1.854(4) | C(11)-C(12) | 1.548(6) |
| P(1)-H(1) | 1.285(19) | C(11)-H(11A) | 0.9900 |
| C(1)-C(2) | 1.378(5) | C(11)-H(11B) | 0.9900 |
| C(1)-C(6) | 1.432(5) | C(12)-H(12A) | 0.9900 |
| C(1)-C(13) | 1.515(5) | C(12)-H(12B) | 0.9900 |
| C(2)-C(3) | 1.422(5) | C(13)-H(13A) | 0.9900 |
| C(2)-H(2A) | 0.9500 | C(13)-H(13B) | 0.9900 |
| C(3)-C(4) | 1.350(6) | C(14)-C(19) | 1.373(7) |
| C(3)-H(3A) | 0.9500 | C(14)-C(15) | 1.402(5) |
| C(4)-C(5) | 1.410(6) | C(15)-C(16) | 1.382(5) |
| C(4)-C(12) | 1.513(5) | C(15)-H(15A) | 0.9500 |
| C(5)-C(10) | 1.411(6) | C(16)-C(17) | 1.376(6) |
| C(5)-C(6) | 1.414(5) | C(16)-H(16A) | 0.9500 |
| C(6)-C(7) | 1.433(5) | C(17)-C(18) | 1.389(6) |
| C(7)-C(8) | 1.364(6) | C(17)-H(17A) | 0.9500 |
| C(8)-C(9) | 1.406(5) | C(18)-C(19) | 1.390(6) |
| C(8)-H(8A) | 0.9500 | C(18)-H(18A) | 0.9500 |
| C(9)-C(10) | 1.364(7) | C(19)-H(19A) | 0.9500 |

| | | | |
|---|---|---|---|
| C(14)-P(1)-C(13) | 101.60(17) | C(1)-C(2)-H(2A) | 118.2 |
| C(14)-P(1)-H(1) | 98(2) | C(3)-C(2)-H(2A) | 118.2 |
| C(13)-P(1)-H(1) | 103.0(19) | C(4)-C(3)-C(2) | 118.7(4) |
| C(2)-C(1)-C(6) | 118.6(3) | C(4)-C(3)-H(3A) | 120.7 |
| C(2)-C(1)-C(13) | 117.3(3) | C(2)-C(3)-H(3A) | 120.7 |
| C(6)-C(1)-C(13) | 124.1(3) | C(3)-C(4)-C(5) | 118.9(3) |
| C(1)-C(2)-C(3) | 123.7(4) | C(3)-C(4)-C(12) | 131.7(4) |

| | | | |
|---|---|---|---|
| C(5)-C(4)-C(12) | 109.4(4) | C(4)-C(12)-H(12B) | 110.8 |
| C(4)-C(5)-C(10) | 111.2(3) | C(11)-C(12)-H(12B) | 110.8 |
| C(4)-C(5)-C(6) | 124.0(4) | H(12A)-C(12)-H(12B) | 108.9 |
| C(10)-C(5)-C(6) | 124.8(4) | C(1)-C(13)-P(1) | 116.2(2) |
| C(5)-C(6)-C(1) | 116.1(4) | C(1)-C(13)-H(13A) | 108.2 |
| C(5)-C(6)-C(7) | 112.8(4) | P(1)-C(13)-H(13A) | 108.2 |
| C(1)-C(6)-C(7) | 131.1(3) | C(1)-C(13)-H(13B) | 108.2 |
| C(8)-C(7)-C(6) | 122.5(4) | P(1)-C(13)-H(13B) | 108.2 |
| C(8)-C(7)-Br(1) | 113.5(3) | H(13A)-C(13)-H(13B) | 107.4 |
| C(6)-C(7)-Br(1) | 124.1(3) | C(19)-C(14)-C(15) | 118.6(4) |
| C(7)-C(8)-C(9) | 122.4(4) | C(19)-C(14)-P(1) | 120.5(3) |
| C(7)-C(8)-H(8A) | 118.8 | C(15)-C(14)-P(1) | 120.5(4) |
| C(9)-C(8)-H(8A) | 118.8 | C(16)-C(15)-C(14) | 120.5(4) |
| C(10)-C(9)-C(8) | 118.1(4) | C(16)-C(15)-H(15A) | 119.7 |
| C(10)-C(9)-H(9A) | 121.0 | C(14)-C(15)-H(15A) | 119.7 |
| C(8)-C(9)-H(9A) | 121.0 | C(17)-C(16)-C(15) | 120.0(4) |
| C(9)-C(10)-C(5) | 119.4(3) | C(17)-C(16)-H(16A) | 120.0 |
| C(9)-C(10)-C(11) | 131.1(4) | C(15)-C(16)-H(16A) | 120.0 |
| C(5)-C(10)-C(11) | 109.5(4) | C(16)-C(17)-C(18) | 120.3(4) |
| C(10)-C(11)-C(12) | 105.2(3) | C(16)-C(17)-H(17A) | 119.8 |
| C(10)-C(11)-H(11A) | 110.7 | C(18)-C(17)-H(17A) | 119.8 |
| C(12)-C(11)-H(11A) | 110.7 | C(19)-C(18)-C(17) | 119.1(4) |
| C(10)-C(11)-H(11B) | 110.7 | C(19)-C(18)-H(18A) | 120.4 |
| C(12)-C(11)-H(11B) | 110.7 | C(17)-C(18)-H(18A) | 120.4 |
| H(11A)-C(11)-H(11B) | 108.8 | C(14)-C(19)-C(18) | 121.4(4) |
| C(4)-C(12)-C(11) | 104.7(3) | C(14)-C(19)-H(19A) | 119.3 |
| C(4)-C(12)-H(12A) | 110.8 | C(18)-C(19)-H(19A) | 119.3 |
| C(11)-C(12)-H(12A) | 110.8 | | |

Table 4. Anisotropic displacement parameters ($Å^2$ x $10^3$) for 5-Br-6-$CH_2$PHPh-acenaphthene, GLU314. The anisotropic displacement factor exponent takes the form: $-2\pi^2[ h^2a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12} ]$

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{23}$ | $U^{13}$ | $U^{12}$ |
|---|---|---|---|---|---|---|
| Br(1) | 22(1) | 31(1) | 24(1) | 1(1) | 5(1) | 6(1) |
| P(1) | 23(1) | 31(1) | 16(1) | -2(1) | -1(1) | 6(1) |
| C(1) | 11(2) | 29(2) | 14(2) | -5(1) | -5(1) | -5(2) |
| C(2) | 15(2) | 28(2) | 20(2) | 0(2) | -3(2) | -3(2) |
| C(3) | 12(2) | 27(2) | 24(2) | -6(2) | 1(2) | -3(2) |
| C(4) | 14(2) | 36(3) | 17(2) | -7(2) | 1(1) | -4(2) |
| C(5) | 12(2) | 31(2) | 16(2) | -7(2) | -3(2) | -5(2) |
| C(6) | 10(2) | 30(2) | 17(2) | -3(2) | -3(1) | -4(2) |
| C(7) | 18(2) | 32(2) | 14(2) | -4(2) | 0(2) | 0(2) |
| C(8) | 17(2) | 32(3) | 20(2) | 0(2) | -5(1) | -3(2) |
| C(9) | 20(2) | 35(2) | 13(2) | 3(3) | -2(1) | -5(3) |
| C(10) | 14(2) | 38(2) | 12(2) | -3(2) | -4(1) | -4(2) |
| C(11) | 17(2) | 41(3) | 19(2) | -2(2) | 2(2) | -5(2) |
| C(12) | 24(2) | 48(3) | 26(2) | -7(2) | 6(2) | -1(2) |
| C(13) | 16(2) | 29(2) | 16(2) | 2(2) | 0(1) | -1(2) |
| C(14) | 20(2) | 30(2) | 11(1) | -3(2) | 1(1) | 1(2) |
| C(15) | 25(2) | 33(2) | 16(2) | -1(2) | 3(2) | 3(2) |
| C(16) | 17(2) | 46(3) | 18(2) | -5(2) | -1(2) | 2(2) |
| C(17) | 23(2) | 41(3) | 20(2) | 1(2) | -3(2) | 14(2) |
| C(18) | 35(2) | 31(2) | 17(2) | 1(2) | 2(2) | 4(2) |
| C(19) | 21(2) | 35(2) | 21(2) | -3(2) | 3(2) | 1(2) |

Table 5. Hydrogen coordinates (x $10^4$) and isotropic displacement parameters ($Å^2$ x $10^3$) for 5-Br-6-$CH_2$PHPh-acenaphthene, GLU314.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| H(1) | 7330(40) | 5660(50) | 4600(40) | 36 |
| H(2A) | 7376 | 637 | 2857 | 26 |
| H(3A) | 8621 | 307 | 1263 | 26 |
| H(8A) | 5546 | 9093 | 484 | 29 |
| H(9A) | 6760 | 8445 | -1096 | 28 |
| H(11A) | 9028 | 5868 | -1282 | 32 |
| H(11B) | 7723 | 4867 | -2123 | 32 |
| H(12A) | 8442 | 2009 | -1286 | 39 |
| H(12B) | 9721 | 3020 | -411 | 39 |
| H(13A) | 5601 | 1865 | 3591 | 25 |
| H(13B) | 4932 | 3862 | 3096 | 25 |
| H(15A) | 9465 | 4566 | 5843 | 29 |
| H(16A) | 11102 | 2461 | 6867 | 33 |
| H(17A) | 10567 | -719 | 7160 | 35 |
| H(18A) | 8370 | -1809 | 6461 | 34 |
| H(19A) | 6717 | 340 | 5500 | 31 |

Table 1. Crystal data and structure refinement for [Pt(*R*,*R*)-Me-DuPhos)(Ph)(Ph-PyraPhos)][$PF_6$], glu388.

| | | |
|---|---|---|
| Identification code | glu388 | |
| Empirical formula | C43 H48 F6 P4 Pt | |
| Formula weight | 997.78 | |
| Temperature | 100(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Orthorhombic | |
| Space group | P2(1)2(1)2(1) | |
| Unit cell dimensions | a = 12.5232(4) Å | α= 90° |
| | b = 15.3824(5) Å | β= 90° |
| | c = 20.9494(6) Å | γ = 90° |
| Volume | 4035.6(2) $Å^3$ | |
| Z | 4 | |
| Density (calculated) | 1.642 $g/cm^3$ | |
| Absorption coefficient | 3.694 $mm^{-1}$ | |
| F(000) | 1992 | |
| Crystal size | 0.38 x 0.36 x 0.32 $mm^3$ | |
| Theta range for data collection | 2.31 to 26.43° | |
| Index ranges | -14<=h<=15, -19<=k<=19, -22<=l<=26 | |
| Reflections collected | 50401 | |
| Independent reflections | 8283 [R(int) = 0.0513] | |
| Completeness to theta = 25.00° | 99.9 % | |
| Absorption correction | Multi-scan | |
| Max. and min. transmission | 0.3844 and 0.3342 | |
| Refinement method | Full-matrix least-squares on $F^2$ | |
| Data / restraints / parameters | 8283 / 0 / 488 | |
| Goodness-of-fit on $F^2$ | 0.911 | |
| Final R indices [I>2sigma(I)] | R1 = 0.0198, wR2 = 0.0387 | |
| R indices (all data) | R1 = 0.0226, wR2 = 0.0394 | |
| Absolute structure parameter | 0.000(3) | |
| Extinction coefficient | 0.00025(3) | |
| Largest diff. peak and hole | 0.454 and -0.341 e $Å^{-3}$ | |

Table 2. Atomic coordinates (x $10^4$) and equivalent isotropic displacement parameters ($Å^2$ x $10^3$) for [Pt(*R*,*R*)-Me-DuPhos)(Ph)(Ph-PyraPhos)][$PF_6$], glu388. U(eq) is defined as one third of the trace of the orthogonalized $U^{ij}$ tensor.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| Pt(1) | 7586(1) | 1512(1) | 6837(1) | 9(1) |
| P(1) | 7974(1) | 1819(1) | 5795(1) | 11(1) |
| P(2) | 7204(1) | 2951(1) | 6941(1) | 11(1) |
| P(3) | 8103(1) | 79(1) | 6915(1) | 12(1) |
| F(1) | 6524(2) | 2910(1) | 2701(1) | 39(1) |
| F(2) | 8417(2) | 3818(2) | 3467(1) | 38(1) |
| F(3) | 8322(2) | 2826(2) | 2679(1) | 43(1) |
| F(4) | 7506(2) | 4122(1) | 2558(1) | 37(1) |
| F(5) | 7447(2) | 2604(1) | 3603(1) | 34(1) |
| F(6) | 6626(2) | 3909(2) | 3488(1) | 44(1) |
| C(1) | 7701(2) | 2971(2) | 5657(1) | 11(1) |
| C(2) | 7819(2) | 3357(2) | 5052(1) | 15(1) |
| C(3) | 7591(2) | 4227(2) | 4967(1) | 18(1) |
| C(4) | 7256(2) | 4722(2) | 5481(1) | 18(1) |
| C(5) | 7151(2) | 4357(2) | 6077(1) | 15(1) |
| C(6) | 7364(2) | 3476(2) | 6166(1) | 12(1) |
| C(7) | 5913(2) | 3280(2) | 7288(1) | 15(1) |
| C(8) | 5047(2) | 3486(2) | 6807(2) | 23(1) |
| C(9) | 6200(3) | 3999(2) | 7773(2) | 21(1) |
| C(10) | 7286(3) | 3774(2) | 8054(1) | 22(1) |
| C(11) | 8049(2) | 3569(2) | 7502(1) | 18(1) |
| C(12) | 9098(2) | 3127(2) | 7667(2) | 22(1) |
| C(13) | 9273(2) | 1554(2) | 5429(2) | 25(1) |
| C(14) | 10107(3) | 2259(3) | 5447(2) | 51(1) |
| C(15) | 8999(3) | 1187(3) | 4772(2) | 46(1) |

| | | | | |
|---|---|---|---|---|
| C(16) | 7979(3) | 659(2) | 4846(2) | 42(1) |
| C(17) | 7167(3) | 1223(2) | 5193(1) | 22(1) |
| C(18) | 6202(3) | 743(3) | 5465(2) | 45(1) |
| C(19) | 6862(2) | 1288(2) | 7718(1) | 12(1) |
| C(20) | 7321(3) | 1335(2) | 8321(1) | 16(1) |
| C(21) | 6725(3) | 1222(2) | 8873(2) | 22(1) |
| C(22) | 5644(3) | 1045(2) | 8840(2) | 21(1) |
| C(23) | 5161(2) | 991(2) | 8246(2) | 20(1) |
| C(24) | 5760(2) | 1114(2) | 7697(1) | 15(1) |
| C(25) | 6950(2) | -683(2) | 6925(1) | 17(1) |
| C(26) | 7217(2) | -1403(2) | 6460(1) | 13(1) |
| C(27) | 6657(2) | -2139(2) | 6319(2) | 18(1) |
| C(28) | 7072(3) | -2780(2) | 5882(2) | 19(1) |
| C(29) | 8042(3) | -2665(2) | 5609(2) | 19(1) |
| C(30) | 8747(3) | -3187(2) | 5153(2) | 27(1) |
| C(31) | 9810(3) | -2672(2) | 5112(2) | 28(1) |
| C(32) | 9644(2) | -1861(2) | 5499(2) | 18(1) |
| C(33) | 10258(2) | -1157(2) | 5660(1) | 15(1) |
| C(34) | 9862(2) | -499(2) | 6076(1) | 14(1) |
| C(35) | 8845(2) | -554(2) | 6326(1) | 12(1) |
| C(36) | 8217(2) | -1277(2) | 6172(1) | 12(1) |
| C(37) | 8613(2) | -1911(2) | 5757(1) | 15(1) |
| C(38) | 8883(2) | -58(2) | 7638(1) | 14(1) |
| C(39) | 9729(2) | 507(2) | 7738(2) | 20(1) |
| C(40) | 10339(2) | 458(2) | 8284(2) | 27(1) |
| C(41) | 10097(3) | -169(3) | 8739(2) | 30(1) |
| C(42) | 9267(3) | -734(2) | 8638(2) | 30(1) |
| C(43) | 8667(2) | -689(2) | 8090(2) | 22(1) |
| P(4) | 7470(1) | 3364(1) | 3080(1) | 20(1) |

Table 3. Bond lengths [Å] and angles [deg] for [Pt(*R*,*R*)-Me-DuPhos)(Ph)(Ph-PyraPhos)][$PF_6$], glu388.

| | | | |
|---|---|---|---|
| Pt(1)-C(19) | 2.086(3) | C(10)-C(11) | 1.533(4) |
| Pt(1)-P(2) | 2.2747(7) | C(11)-C(12) | 1.519(4) |
| Pt(1)-P(1) | 2.2859(7) | C(13)-C(14) | 1.506(5) |
| Pt(1)-P(3) | 2.3030(7) | C(13)-C(15) | 1.527(5) |
| P(1)-C(1) | 1.828(3) | C(15)-C(16) | 1.521(5) |
| P(1)-C(13) | 1.844(3) | C(16)-C(17) | 1.521(5) |
| P(1)-C(17) | 1.859(3) | C(17)-C(18) | 1.527(5) |
| P(2)-C(6) | 1.824(3) | C(19)-C(20) | 1.388(4) |
| P(2)-C(11) | 1.844(3) | C(19)-C(24) | 1.406(4) |
| P(2)-C(7) | 1.845(3) | C(20)-C(21) | 1.388(4) |
| P(3)-C(38) | 1.815(3) | C(21)-C(22) | 1.383(5) |
| P(3)-C(35) | 1.825(3) | C(22)-C(23) | 1.384(4) |
| P(3)-C(25) | 1.861(3) | C(23)-C(24) | 1.387(4) |
| F(1)-P(4) | 1.589(2) | C(25)-C(26) | 1.513(4) |
| F(2)-P(4) | 1.597(2) | C(26)-C(27) | 1.365(4) |
| F(3)-P(4) | 1.590(2) | C(26)-C(36) | 1.403(4) |
| F(4)-P(4) | 1.5979(17) | C(27)-C(28) | 1.442(4) |
| F(5)-P(4) | 1.6038(17) | C(28)-C(29) | 1.354(4) |
| F(6)-P(4) | 1.597(2) | C(29)-C(37) | 1.398(4) |
| C(1)-C(6) | 1.387(4) | C(29)-C(30) | 1.529(4) |
| C(1)-C(2) | 1.407(4) | C(30)-C(31) | 1.552(4) |
| C(2)-C(3) | 1.380(4) | C(31)-C(32) | 1.502(4) |
| C(3)-C(4) | 1.383(4) | C(32)-C(33) | 1.370(4) |
| C(4)-C(5) | 1.375(4) | C(32)-C(37) | 1.402(4) |
| C(5)-C(6) | 1.394(4) | C(33)-C(34) | 1.425(4) |
| C(7)-C(8) | 1.514(4) | C(34)-C(35) | 1.379(4) |
| C(7)-C(9) | 1.544(4) | C(35)-C(36) | 1.400(4) |
| C(9)-C(10) | 1.523(4) | C(36)-C(37) | 1.398(4) |

| | | | |
|---|---|---|---|
| C(38)-C(43) | 1.383(4) | C(40)-C(41) | 1.390(5) |
| C(38)-C(39) | 1.386(4) | C(41)-C(42) | 1.371(5) |
| C(39)-C(40) | 1.377(4) | C(42)-C(43) | 1.374(4) |

| | | | |
|---|---|---|---|
| C(19)-Pt(1)-P(2) | 89.16(8) | C(2)-C(1)-P(1) | 122.2(2) |
| C(19)-Pt(1)-P(1) | 166.38(8) | C(3)-C(2)-C(1) | 120.2(3) |
| P(2)-Pt(1)-P(1) | 86.27(3) | C(2)-C(3)-C(4) | 119.8(3) |
| C(19)-Pt(1)-P(3) | 84.34(8) | C(5)-C(4)-C(3) | 120.7(3) |
| P(2)-Pt(1)-P(3) | 169.63(3) | C(4)-C(5)-C(6) | 120.1(3) |
| P(1)-Pt(1)-P(3) | 101.83(3) | C(1)-C(6)-C(5) | 120.0(2) |
| C(1)-P(1)-C(13) | 108.22(15) | C(1)-C(6)-P(2) | 118.1(2) |
| C(1)-P(1)-C(17) | 105.57(13) | C(5)-C(6)-P(2) | 122.0(2) |
| C(13)-P(1)-C(17) | 95.04(15) | C(8)-C(7)-C(9) | 117.0(3) |
| C(1)-P(1)-Pt(1) | 108.19(9) | C(8)-C(7)-P(2) | 115.0(2) |
| C(13)-P(1)-Pt(1) | 122.66(11) | C(9)-C(7)-P(2) | 104.6(2) |
| C(17)-P(1)-Pt(1) | 115.55(11) | C(10)-C(9)-C(7) | 107.4(2) |
| C(6)-P(2)-C(11) | 106.01(13) | C(9)-C(10)-C(11) | 108.2(2) |
| C(6)-P(2)-C(7) | 108.99(13) | C(12)-C(11)-C(10) | 117.3(3) |
| C(11)-P(2)-C(7) | 96.35(14) | C(12)-C(11)-P(2) | 114.2(2) |
| C(6)-P(2)-Pt(1) | 108.83(9) | C(10)-C(11)-P(2) | 103.2(2) |
| C(11)-P(2)-Pt(1) | 116.20(10) | C(14)-C(13)-C(15) | 116.5(3) |
| C(7)-P(2)-Pt(1) | 119.28(10) | C(14)-C(13)-P(1) | 116.2(3) |
| C(38)-P(3)-C(35) | 103.15(13) | C(15)-C(13)-P(1) | 105.0(2) |
| C(38)-P(3)-C(25) | 109.56(14) | C(16)-C(15)-C(13) | 107.1(3) |
| C(35)-P(3)-C(25) | 93.81(13) | C(15)-C(16)-C(17) | 107.8(3) |
| C(38)-P(3)-Pt(1) | 108.72(10) | C(16)-C(17)-C(18) | 115.6(3) |
| C(35)-P(3)-Pt(1) | 127.33(10) | C(16)-C(17)-P(1) | 104.0(2) |
| C(25)-P(3)-Pt(1) | 112.73(10) | C(18)-C(17)-P(1) | 114.5(2) |
| C(6)-C(1)-C(2) | 119.2(3) | C(20)-C(19)-C(24) | 116.5(3) |
| C(6)-C(1)-P(1) | 118.6(2) | C(20)-C(19)-Pt(1) | 127.9(2) |

| | | | |
|---|---|---|---|
| C(24)-C(19)-Pt(1) | 115.5(2) | C(35)-C(36)-C(26) | 120.8(3) |
| C(21)-C(20)-C(19) | 121.9(3) | C(36)-C(37)-C(29) | 122.3(3) |
| C(22)-C(21)-C(20) | 120.6(3) | C(36)-C(37)-C(32) | 122.0(3) |
| C(21)-C(22)-C(23) | 119.0(3) | C(29)-C(37)-C(32) | 115.5(3) |
| C(22)-C(23)-C(24) | 120.1(3) | C(43)-C(38)-C(39) | 119.1(3) |
| C(23)-C(24)-C(19) | 122.0(3) | C(43)-C(38)-P(3) | 123.2(3) |
| C(26)-C(25)-P(3) | 106.39(19) | C(39)-C(38)-P(3) | 117.7(2) |
| C(27)-C(26)-C(36) | 118.7(3) | C(40)-C(39)-C(38) | 121.0(3) |
| C(27)-C(26)-C(25) | 129.3(3) | C(39)-C(40)-C(41) | 119.2(3) |
| C(36)-C(26)-C(25) | 111.9(3) | C(42)-C(41)-C(40) | 119.9(3) |
| C(26)-C(27)-C(28) | 121.3(3) | C(41)-C(42)-C(43) | 120.8(3) |
| C(29)-C(28)-C(27) | 120.1(3) | C(42)-C(43)-C(38) | 120.0(3) |
| C(28)-C(29)-C(37) | 118.3(3) | F(1)-P(4)-F(3) | 90.43(11) |
| C(28)-C(29)-C(30) | 135.5(3) | F(1)-P(4)-F(6) | 90.22(13) |
| C(37)-C(29)-C(30) | 106.2(3) | F(3)-P(4)-F(6) | 179.33(13) |
| C(29)-C(30)-C(31) | 105.2(3) | F(1)-P(4)-F(2) | 179.43(13) |
| C(32)-C(31)-C(30) | 106.0(3) | F(3)-P(4)-F(2) | 89.90(12) |
| C(33)-C(32)-C(37) | 117.7(3) | F(6)-P(4)-F(2) | 89.44(11) |
| C(33)-C(32)-C(31) | 135.4(3) | F(1)-P(4)-F(4) | 90.02(12) |
| C(37)-C(32)-C(31) | 106.8(3) | F(3)-P(4)-F(4) | 89.99(12) |
| C(32)-C(33)-C(34) | 121.1(3) | F(6)-P(4)-F(4) | 90.15(12) |
| C(35)-C(34)-C(33) | 120.7(3) | F(2)-P(4)-F(4) | 90.44(12) |
| C(34)-C(35)-C(36) | 118.7(3) | F(1)-P(4)-F(5) | 90.41(12) |
| C(34)-C(35)-P(3) | 133.9(2) | F(3)-P(4)-F(5) | 89.65(12) |
| C(36)-C(35)-P(3) | 107.1(2) | F(6)-P(4)-F(5) | 90.21(12) |
| C(37)-C(36)-C(35) | 119.9(3) | F(2)-P(4)-F(5) | 89.13(12) |
| C(37)-C(36)-C(26) | 119.2(3) | F(4)-P(4)-F(5) | 179.44(14) |

Table 4. Anisotropic displacement parameters ($Å^2$ x $10^3$) for [Pt(*R*,*R*)-Me-DuPhos)(Ph)(Ph-PyraPhos)][$PF_6$], glu388. The anisotropic displacement factor exponent takes the form: $-2\pi^2[ h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{23}$ | $U^{13}$ | $U^{12}$ |
|---|---|---|---|---|---|---|
| Pt(1) | 10(1) | 9(1) | 9(1) | -1(1) | 1(1) | 0(1) |
| P(1) | 13(1) | 11(1) | 10(1) | -1(1) | 1(1) | 2(1) |
| P(2) | 13(1) | 10(1) | 10(1) | -1(1) | 2(1) | 0(1) |
| P(3) | 13(1) | 10(1) | 13(1) | -1(1) | 2(1) | -1(1) |
| F(1) | 41(1) | 32(1) | 44(2) | 4(1) | -21(1) | -13(1) |
| F(2) | 35(1) | 46(2) | 33(1) | -8(1) | -9(1) | -13(1) |
| F(3) | 46(2) | 60(2) | 23(1) | -10(1) | 3(1) | 28(1) |
| F(4) | 45(1) | 28(1) | 37(1) | 11(1) | -6(1) | -4(1) |
| F(5) | 48(1) | 30(1) | 24(1) | 5(1) | -7(1) | -2(1) |
| F(6) | 40(1) | 46(2) | 45(2) | -10(1) | 11(1) | 19(1) |
| C(1) | 7(2) | 13(1) | 13(1) | 0(1) | 2(1) | 2(1) |
| C(2) | 15(2) | 18(2) | 11(1) | -2(1) | -1(1) | 2(1) |
| C(3) | 17(2) | 21(2) | 16(1) | 3(1) | 0(2) | -1(2) |
| C(4) | 21(2) | 12(1) | 22(2) | 4(1) | -3(1) | 4(1) |
| C(5) | 16(2) | 14(2) | 16(2) | -3(1) | 3(1) | 1(1) |
| C(6) | 10(1) | 14(1) | 13(1) | 0(1) | -1(1) | -5(2) |
| C(7) | 18(2) | 10(2) | 17(2) | -1(1) | 9(1) | 5(1) |
| C(8) | 16(2) | 26(2) | 27(2) | -4(2) | 6(2) | 4(2) |
| C(9) | 28(2) | 20(2) | 16(2) | -5(1) | 8(2) | 6(2) |
| C(10) | 35(2) | 16(1) | 16(2) | -5(1) | 4(2) | 0(1) |
| C(11) | 26(2) | 14(2) | 14(2) | 1(1) | 1(1) | -6(2) |
| C(12) | 20(2) | 25(2) | 23(2) | -2(2) | -4(2) | -7(2) |
| C(13) | 25(2) | 25(2) | 25(2) | 10(2) | 14(1) | 14(2) |
| C(14) | 19(2) | 47(3) | 88(3) | 35(3) | 20(2) | 8(2) |
| C(15) | 70(3) | 48(3) | 20(2) | 5(2) | 22(2) | 41(2) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C(16) | 82(3) | 24(2) | 20(2) | -9(2) | -16(2) | 26(2) |
| C(17) | 38(2) | 14(2) | 16(2) | -2(1) | -8(2) | -1(2) |
| C(18) | 56(3) | 40(3) | 40(2) | 12(2) | -31(2) | -31(2) |
| C(19) | 16(2) | 7(2) | 13(2) | 1(1) | 5(1) | 2(1) |
| C(20) | 16(2) | 15(2) | 18(2) | 2(1) | 0(1) | 6(1) |
| C(21) | 38(2) | 16(2) | 13(2) | 2(1) | 3(2) | 9(2) |
| C(22) | 28(2) | 15(2) | 19(2) | 8(1) | 12(2) | 4(2) |
| C(23) | 19(2) | 13(2) | 28(2) | -1(2) | 11(2) | -1(1) |
| C(24) | 19(2) | 12(2) | 14(2) | 0(1) | 0(1) | 0(1) |
| C(25) | 15(2) | 17(2) | 20(2) | 1(1) | 5(1) | -5(1) |
| C(26) | 14(2) | 13(2) | 12(2) | 1(1) | 0(1) | 3(1) |
| C(27) | 17(2) | 15(2) | 22(2) | 3(1) | 1(2) | -2(1) |
| C(28) | 16(2) | 17(2) | 24(2) | -3(2) | -2(2) | -4(1) |
| C(29) | 27(2) | 11(2) | 18(2) | -2(1) | 4(2) | 1(1) |
| C(30) | 35(2) | 17(2) | 30(2) | -8(2) | 9(2) | 0(2) |
| C(31) | 33(2) | 21(2) | 29(2) | -4(2) | 13(2) | 1(2) |
| C(32) | 22(2) | 16(2) | 15(2) | 3(1) | 3(1) | 4(1) |
| C(33) | 15(2) | 18(2) | 11(2) | 6(1) | 5(1) | 4(1) |
| C(34) | 18(2) | 13(2) | 12(2) | 6(1) | 2(1) | 2(1) |
| C(35) | 14(2) | 12(2) | 11(2) | 5(1) | -1(1) | 1(1) |
| C(36) | 16(2) | 11(2) | 10(2) | 3(1) | -2(1) | 1(1) |
| C(37) | 18(2) | 11(2) | 17(2) | 3(1) | 0(1) | 1(1) |
| C(38) | 15(2) | 17(2) | 12(2) | 1(1) | 4(1) | 7(1) |
| C(39) | 18(2) | 25(2) | 17(2) | 6(2) | 1(1) | 3(2) |
| C(40) | 15(2) | 41(2) | 24(2) | 0(2) | -1(2) | 1(2) |
| C(41) | 23(2) | 56(3) | 12(2) | 1(2) | -3(2) | 12(2) |
| C(42) | 35(2) | 36(2) | 17(2) | 10(2) | 5(2) | 9(2) |
| C(43) | 23(2) | 22(2) | 21(2) | 2(2) | 4(2) | 5(1) |
| P(4) | 20(1) | 20(1) | 20(1) | -3(1) | -1(1) | 3(1) |

Table 5. Hydrogen coordinates (x $10^4$) and isotropic displacement parameters ($Å^2$ x $10^3$) for [Pt(*R*,*R*)-Me-DuPhos)(Ph)(Ph-PyraPhos)][$PF_6$], glu388.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| H(2A) | 8056 | 3018 | 4701 | 18 |
| H(3A) | 7664 | 4486 | 4558 | 21 |
| H(4A) | 7096 | 5321 | 5421 | 22 |
| H(5A) | 6934 | 4706 | 6428 | 18 |
| H(7A) | 5651 | 2773 | 7543 | 18 |
| H(8A) | 4390 | 3646 | 7032 | 35 |
| H(8B) | 4913 | 2974 | 6541 | 35 |
| H(8C) | 5277 | 3971 | 6537 | 35 |
| H(9A) | 6229 | 4572 | 7557 | 26 |
| H(9B) | 5655 | 4027 | 8115 | 26 |
| H(10A) | 7223 | 3263 | 8339 | 27 |
| H(10B) | 7563 | 4269 | 8306 | 27 |
| H(11A) | 8228 | 4133 | 7291 | 21 |
| H(12A) | 9501 | 3493 | 7964 | 34 |
| H(12B) | 9516 | 3040 | 7276 | 34 |
| H(12C) | 8953 | 2563 | 7866 | 34 |
| H(13A) | 9571 | 1059 | 5681 | 30 |
| H(14A) | 10761 | 2051 | 5241 | 77 |
| H(14B) | 10260 | 2413 | 5891 | 77 |
| H(14C) | 9842 | 2773 | 5220 | 77 |
| H(15A) | 8890 | 1665 | 4462 | 55 |
| H(15B) | 9586 | 812 | 4615 | 55 |
| H(16A) | 8123 | 124 | 5094 | 51 |
| H(16B) | 7701 | 489 | 4421 | 51 |
| H(17A) | 6893 | 1660 | 4880 | 27 |

| | | | | |
|---|---|---|---|---|
| H(18A) | 5821 | 447 | 5119 | 68 |
| H(18B) | 5723 | 1160 | 5673 | 68 |
| H(18C) | 6443 | 313 | 5779 | 68 |
| H(20A) | 8065 | 1448 | 8356 | 19 |
| H(21A) | 7063 | 1268 | 9278 | 26 |
| H(22A) | 5239 | 961 | 9218 | 25 |
| H(23A) | 4419 | 869 | 8216 | 24 |
| H(24A) | 5415 | 1081 | 7294 | 18 |
| H(25A) | 6844 | -923 | 7359 | 20 |
| H(25B) | 6288 | -380 | 6793 | 20 |
| H(27A) | 5981 | -2232 | 6512 | 22 |
| H(28A) | 6664 | -3284 | 5785 | 23 |
| H(30A) | 8408 | -3234 | 4728 | 33 |
| H(30B) | 8872 | -3780 | 5322 | 33 |
| H(31A) | 10406 | -3020 | 5288 | 33 |
| H(31B) | 9976 | -2524 | 4663 | 33 |
| H(33A) | 10959 | -1106 | 5490 | 18 |
| H(34A) | 10302 | -18 | 6183 | 17 |
| H(39A) | 9891 | 934 | 7425 | 24 |
| H(40A) | 10917 | 847 | 8348 | 32 |
| H(41A) | 10507 | -206 | 9120 | 36 |
| H(42A) | 9105 | -1161 | 8950 | 35 |
| H(43A) | 8104 | -1092 | 8022 | 27 |

Table 1. Crystal data and structure refinement for Ph-PyraPhos($BH_3$), glu391.

| | | |
|---|---|---|
| Identification code | glu391 | |
| Empirical formula | C19 H18 B P | |
| Molecular formula | C19 H18 B P | |
| Formula weight | 288.11 | |
| Temperature | 100 K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Monoclinic | |
| Space group | C 1 2/c 1 | |
| Unit cell dimensions | a = 27.795(3) Å | α= 90°. |
| | b = 6.3966(7) Å | β= 91.000(7)°. |
| | c = 17.4407(17) Å | γ = 90°. |
| Volume | 3100.3(5) $Å^3$ | |
| Z | 8 | |
| Density (calculated) | 1.235 $Mg/m^3$ | |
| Absorption coefficient | 0.167 $mm^{-1}$ | |
| F(000) | 1216 | |
| Crystal size | 0.40 x 0.35 x 0.10 $mm^3$ | |
| Crystal color, habit | Colorless blade | |
| Theta range for data collection | 2.736 to 28.311°. | |
| Index ranges | -35<=h<=36, -8<=k<=7, -23<=l<=23 | |
| Reflections collected | 12047 | |
| Independent reflections | 3852 [R(int) = 0.0384] | |
| Completeness to theta = 26.000° | 99.9 % | |
| Absorption correction | Semi-empirical from equivalents | |
| Max. and min. transmission | 0.7457 and 0.6835 | |
| Refinement method | Full-matrix least-squares on $F^2$ | |
| Data / restraints / parameters | 3852 / 41 / 249 | |
| Goodness-of-fit on $F^2$ | 1.025 | |
| Final R indices [I>2sigma(I)] | R1 = 0.0438, wR2 = 0.1015 | |
| R indices (all data) | R1 = 0.0653, wR2 = 0.1123 | |
| Extinction coefficient | n/a | |
| Largest diff. peak and hole | 0.289 and -0.234 e.$Å^{-3}$ | |

Table 2. Atomic coordinates (x $10^4$) and equivalent isotropic displacement parameters ($Å^2$x $10^3$) for Ph-PyraPhos($BH_3$), glu391. U(eq) is defined as one third of the trace of the orthogonalized $U^{ij}$ tensor.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| P(1) | 4005(1) | 2608(1) | 8526(1) | 20(1) |
| C(1) | 3609(1) | 4491(3) | 8073(1) | 21(1) |
| C(2) | 3379(1) | 6269(3) | 8324(1) | 28(1) |
| C(3) | 3050(2) | 7385(9) | 7830(3) | 33(1) |
| C(4) | 2964(1) | 6715(3) | 7101(1) | 30(1) |
| C(5) | 2647(1) | 7447(3) | 6434(1) | 38(1) |
| C(6) | 2743(1) | 5882(5) | 5758(2) | 38(1) |
| C(7) | 3085(1) | 4260(3) | 6102(1) | 27(1) |
| C(8) | 3286(1) | 2452(4) | 5836(1) | 31(1) |
| C(9) | 3606(1) | 1265(5) | 6328(1) | 28(1) |
| C(10) | 3728(1) | 1929(3) | 7056(1) | 22(1) |
| C(11) | 3512(1) | 3782(3) | 7323(1) | 20(1) |
| C(12) | 3197(1) | 4880(4) | 6846(2) | 24(1) |
| C(13) | 4066(1) | 965(3) | 7650(1) | 24(1) |
| B(1) | 3744(3) | 1185(13) | 9399(5) | 26(1) |
| P(1M) | 3918(1) | 3137(4) | 8772(1) | 20(1) |
| C(1M) | 3769(2) | 2670(10) | 7763(4) | 21(1) |
| C(2M) | 3882(3) | 1144(14) | 7258(6) | 28(1) |
| C(3M) | 3685(6) | 1220(20) | 6483(9) | 33(1) |
| C(4M) | 3378(3) | 2723(13) | 6252(5) | 30(1) |
| C(5M) | 3107(3) | 3276(13) | 5525(6) | 38(1) |
| C(6M) | 2841(5) | 5310(20) | 5731(8) | 38(1) |
| C(7M) | 2945(3) | 5838(12) | 6542(4) | 27(1) |
| C(8M) | 2808(3) | 7326(16) | 7018(5) | 31(1) |
| C(9M) | 3011(10) | 7390(40) | 7812(9) | 28(1) |

| | | | | |
|---|---|---|---|---|
| C(10M) | 3316(3) | 5850(14) | 8059(5) | 22(1) |
| C(11M) | 3464(4) | 4249(15) | 7556(5) | 20(1) |
| C(12M) | 3270(5) | 4330(20) | 6820(7) | 24(1) |
| C(13M) | 3534(3) | 5462(12) | 8859(4) | 24(1) |
| B(1M) | 3797(15) | 940(70) | 9450(30) | 26(1) |
| C(14) | 4576(1) | 3844(2) | 8731(1) | 26(1) |
| C(15) | 4914(1) | 2742(3) | 9172(1) | 34(1) |
| C(16) | 5368(1) | 3566(3) | 9301(1) | 38(1) |
| C(17) | 5487(1) | 5473(3) | 9004(1) | 41(1) |
| C(18) | 5154(1) | 6590(3) | 8582(1) | 53(1) |
| C(19) | 4698(1) | 5779(3) | 8444(1) | 42(1) |

Table 3. Bond lengths [Å] and angles [deg] for Ph-PyraPhos($BH_3$), glu391.

| | | | |
|---|---|---|---|
| P(1)-C(1) | 1.8046(17) | C(13)-H(13B) | 0.9900 |
| P(1)-C(13) | 1.8647(19) | B(1)-H(1A) | 1.162(15) |
| P(1)-B(1) | 1.927(10) | B(1)-H(1B) | 1.161(16) |
| P(1)-C(14) | 1.8033(15) | B(1)-H(1C) | 1.182(16) |
| C(1)-C(2) | 1.379(3) | P(1M)-C(1M) | 1.826(7) |
| C(1)-C(11) | 1.407(2) | P(1M)-C(13M) | 1.838(8) |
| C(2)-H(2) | 0.9500 | P(1M)-B(1M) | 1.87(4) |
| C(2)-C(3) | 1.434(4) | P(1M)-C(14) | 1.887(3) |
| C(3)-H(3) | 0.9500 | C(1M)-C(2M) | 1.355(9) |
| C(3)-C(4) | 1.360(5) | C(1M)-C(11M) | 1.364(10) |
| C(4)-C(5) | 1.522(3) | C(2M)-H(2M) | 0.9500 |
| C(4)-C(12) | 1.415(3) | C(2M)-C(3M) | 1.450(13) |
| C(5)-H(5A) | 0.9900 | C(3M)-H(3M) | 0.9500 |
| C(5)-H(5B) | 0.9900 | C(3M)-C(4M) | 1.344(12) |
| C(5)-C(6) | 1.573(4) | C(4M)-C(5M) | 1.505(10) |
| C(6)-H(6B) | 0.9900 | C(4M)-C(12M) | 1.463(12) |
| C(6)-H(6A) | 0.9900 | C(5M)-H(5MA) | 0.9900 |
| C(6)-C(7) | 1.523(3) | C(5M)-H(5MB) | 0.9900 |
| C(7)-C(8) | 1.369(3) | C(5M)-C(6M) | 1.542(13) |
| C(7)-C(12) | 1.387(3) | C(6M)-H(6MA) | 0.9900 |
| C(8)-H(8) | 0.9500 | C(6M)-H(6MB) | 0.9900 |
| C(8)-C(9) | 1.441(3) | C(6M)-C(7M) | 1.479(13) |
| C(9)-H(9) | 0.9500 | C(7M)-C(8M) | 1.324(11) |
| C(9)-C(10) | 1.374(3) | C(7M)-C(12M) | 1.400(10) |
| C(10)-C(11) | 1.411(3) | C(8M)-H(8M) | 0.9500 |
| C(10)-C(13) | 1.519(2) | C(8M)-C(9M) | 1.487(16) |
| C(11)-C(12) | 1.387(3) | C(9M)-H(9M) | 0.9500 |
| C(13)-H(13A) | 0.9900 | C(9M)-C(10M) | 1.366(16) |

| | | | |
|---|---|---|---|
| C(10M)-C(11M) | 1.415(10) | C(1)-C(2)-C(3) | 121.0(3) |
| C(10M)-C(13M) | 1.531(9) | C(3)-C(2)-H(2) | 119.5 |
| C(11M)-C(12M) | 1.384(12) | C(2)-C(3)-H(3) | 119.9 |
| C(13M)-H(13C) | 0.9900 | C(4)-C(3)-C(2) | 120.3(3) |
| C(13M)-H(13D) | 0.9900 | C(4)-C(3)-H(3) | 119.9 |
| B(1M)-H(1MA) | 0.9800 | C(3)-C(4)-C(5) | 135.1(2) |
| B(1M)-H(1MB) | 0.9800 | C(3)-C(4)-C(12) | 118.8(2) |
| B(1M)-H(1MC) | 0.9800 | C(12)-C(4)-C(5) | 106.1(2) |
| C(14)-C(15) | 1.395(2) | C(4)-C(5)-H(5A) | 110.6 |
| C(14)-C(19) | 1.379(2) | C(4)-C(5)-H(5B) | 110.6 |
| C(15)-H(15) | 0.9500 | C(4)-C(5)-C(6) | 105.88(17) |
| C(15)-C(16) | 1.381(2) | H(5A)-C(5)-H(5B) | 108.7 |
| C(16)-H(16) | 0.9500 | C(6)-C(5)-H(5A) | 110.6 |
| C(16)-C(17) | 1.368(3) | C(6)-C(5)-H(5B) | 110.6 |
| C(17)-H(17) | 0.9500 | C(5)-C(6)-H(6B) | 110.9 |
| C(17)-C(18) | 1.373(3) | C(5)-C(6)-H(6A) | 110.9 |
| C(18)-H(18) | 0.9500 | H(6B)-C(6)-H(6A) | 108.9 |
| C(18)-C(19) | 1.388(2) | C(7)-C(6)-C(5) | 104.49(19) |
| C(19)-H(19) | 0.9500 | C(7)-C(6)-H(6B) | 110.9 |
| | | C(7)-C(6)-H(6A) | 110.9 |
| C(1)-P(1)-C(13) | 94.71(8) | C(8)-C(7)-C(6) | 134.2(2) |
| C(1)-P(1)-B(1) | 115.2(2) | C(8)-C(7)-C(12) | 118.20(18) |
| C(13)-P(1)-B(1) | 115.0(3) | C(12)-C(7)-C(6) | 107.6(2) |
| C(14)-P(1)-C(1) | 108.85(8) | C(7)-C(8)-H(8) | 120.2 |
| C(14)-P(1)-C(13) | 108.50(8) | C(7)-C(8)-C(9) | 119.6(2) |
| C(14)-P(1)-B(1) | 113.1(3) | C(9)-C(8)-H(8) | 120.2 |
| C(2)-C(1)-P(1) | 134.01(15) | C(8)-C(9)-H(9) | 119.1 |
| C(2)-C(1)-C(11) | 118.59(17) | C(10)-C(9)-C(8) | 121.7(3) |
| C(11)-C(1)-P(1) | 107.26(13) | C(10)-C(9)-H(9) | 119.1 |
| C(1)-C(2)-H(2) | 119.5 | C(9)-C(10)-C(11) | 117.7(2) |

| | | | |
|---|---|---|---|
| C(9)-C(10)-C(13) | 130.1(2) | C(1M)-C(2M)-C(3M) | 119.6(10) |
| C(11)-C(10)-C(13) | 112.19(15) | C(3M)-C(2M)-H(2M) | 120.2 |
| C(1)-C(11)-C(10) | 120.18(17) | C(2M)-C(3M)-H(3M) | 118.9 |
| C(12)-C(11)-C(1) | 120.15(19) | C(4M)-C(3M)-C(2M) | 122.1(13) |
| C(12)-C(11)-C(10) | 119.66(18) | C(4M)-C(3M)-H(3M) | 118.9 |
| C(7)-C(12)-C(4) | 115.75(19) | C(3M)-C(4M)-C(5M) | 136.6(10) |
| C(7)-C(12)-C(11) | 122.98(19) | C(3M)-C(4M)-C(12M) | 115.9(10) |
| C(11)-C(12)-C(4) | 121.3(2) | C(12M)-C(4M)-C(5M) | 107.4(7) |
| P(1)-C(13)-H(13A) | 110.7 | C(4M)-C(5M)-H(5MA) | 111.0 |
| P(1)-C(13)-H(13B) | 110.7 | C(4M)-C(5M)-H(5MB) | 111.0 |
| C(10)-C(13)-P(1) | 105.40(12) | C(4M)-C(5M)-C(6M) | 103.7(8) |
| C(10)-C(13)-H(13A) | 110.7 | H(5MA)-C(5M)-H(5MB) | 109.0 |
| C(10)-C(13)-H(13B) | 110.7 | C(6M)-C(5M)-H(5MA) | 111.0 |
| H(13A)-C(13)-H(13B) | 108.8 | C(6M)-C(5M)-H(5MB) | 111.0 |
| P(1)-B(1)-H(1A) | 104.9(10) | C(5M)-C(6M)-H(6MA) | 109.9 |
| P(1)-B(1)-H(1B) | 105.0(13) | C(5M)-C(6M)-H(6MB) | 109.9 |
| P(1)-B(1)-H(1C) | 106.5(11) | H(6MA)-C(6M)-H(6MB) | 108.3 |
| H(1A)-B(1)-H(1B) | 112.5(16) | C(7M)-C(6M)-C(5M) | 109.2(8) |
| H(1A)-B(1)-H(1C) | 112.7(14) | C(7M)-C(6M)-H(6MA) | 109.9 |
| H(1B)-B(1)-H(1C) | 114.2(16) | C(7M)-C(6M)-H(6MB) | 109.9 |
| C(1M)-P(1M)-C(13M) | 95.1(3) | C(8M)-C(7M)-C(6M) | 135.2(8) |
| C(1M)-P(1M)-B(1M) | 116.6(14) | C(8M)-C(7M)-C(12M) | 118.0(8) |
| C(1M)-P(1M)-C(14) | 101.8(2) | C(12M)-C(7M)-C(6M) | 106.8(8) |
| C(13M)-P(1M)-B(1M) | 116.4(14) | C(7M)-C(8M)-H(8M) | 120.1 |
| C(13M)-P(1M)-C(14) | 111.9(3) | C(7M)-C(8M)-C(9M) | 119.7(10) |
| B(1M)-P(1M)-C(14) | 112.9(12) | C(9M)-C(8M)-H(8M) | 120.1 |
| C(2M)-C(1M)-P(1M) | 133.9(6) | C(8M)-C(9M)-H(9M) | 120.1 |
| C(2M)-C(1M)-C(11M) | 120.7(8) | C(10M)-C(9M)-C(8M) | 119.8(14) |
| C(11M)-C(1M)-P(1M) | 105.3(5) | C(10M)-C(9M)-H(9M) | 120.1 |
| C(1M)-C(2M)-H(2M) | 120.2 | C(9M)-C(10M)-C(11M) | 120.8(10) |

| | | | |
|---|---|---|---|
| C(9M)-C(10M)-C(13M) | 129.7(9) | C(15)-C(14)-P(1M) | 120.14(14) |
| C(11M)-C(10M)-C(13M) | 109.4(7) | C(19)-C(14)-P(1) | 122.82(12) |
| C(1M)-C(11M)-C(10M) | 123.9(8) | C(19)-C(14)-P(1M) | 118.25(13) |
| C(1M)-C(11M)-C(12M) | 120.4(8) | C(19)-C(14)-C(15) | 119.07(14) |
| C(12M)-C(11M)-C(10M) | 115.7(8) | C(14)-C(15)-H(15) | 120.0 |
| C(7M)-C(12M)-C(4M) | 112.8(8) | C(16)-C(15)-C(14) | 120.08(16) |
| C(11M)-C(12M)-C(4M) | 121.2(8) | C(16)-C(15)-H(15) | 120.0 |
| C(11M)-C(12M)-C(7M) | 125.9(9) | C(15)-C(16)-H(16) | 119.8 |
| P(1M)-C(13M)-H(13C) | 110.5 | C(17)-C(16)-C(15) | 120.35(16) |
| P(1M)-C(13M)-H(13D) | 110.5 | C(17)-C(16)-H(16) | 119.8 |
| C(10M)-C(13M)-P(1M) | 106.1(5) | C(16)-C(17)-H(17) | 119.9 |
| C(10M)-C(13M)-H(13C) | 110.5 | C(16)-C(17)-C(18) | 120.10(16) |
| C(10M)-C(13M)-H(13D) | 110.5 | C(18)-C(17)-H(17) | 119.9 |
| H(13C)-C(13M)-H(13D) | 108.7 | C(17)-C(18)-H(18) | 119.9 |
| P(1M)-B(1M)-H(1MA) | 109.5 | C(17)-C(18)-C(19) | 120.24(18) |
| P(1M)-B(1M)-H(1MB) | 109.5 | C(19)-C(18)-H(18) | 119.9 |
| P(1M)-B(1M)-H(1MC) | 109.5 | C(14)-C(19)-C(18) | 120.14(16) |
| H(1MA)-B(1M)-H(1MB) | 109.5 | C(14)-C(19)-H(19) | 119.9 |
| H(1MA)-B(1M)-H(1MC) | 109.5 | C(18)-C(19)-H(19) | 119.9 |
| H(1MB)-B(1M)-H(1MC) | 109.5 | | |
| C(15)-C(14)-P(1) | 118.06(12) | | |

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for Ph-PyraPhos ($BH_3$), glu391. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{23}$ | $U^{13}$ | $U^{12}$ |
|---|---|---|---|---|---|---|
| P(1) | 18(1) | 19(1) | 21(1) | 2(1) | 0(1) | 2(1) |
| C(1) | 16(1) | 19(1) | 27(1) | 2(1) | -1(1) | 1(1) |
| C(2) | 22(1) | 22(1) | 39(1) | -5(1) | 0(1) | 2(1) |
| C(3) | 23(2) | 15(1) | 62(2) | -2(1) | -3(1) | 5(1) |
| C(4) | 16(1) | 25(1) | 50(1) | 12(1) | -5(1) | -3(1) |
| C(5) | 21(1) | 29(1) | 64(1) | 18(1) | -11(1) | -2(1) |
| C(6) | 17(1) | 54(2) | 42(1) | 26(1) | -7(1) | 1(1) |
| C(7) | 17(1) | 38(1) | 28(1) | 12(1) | -2(1) | -6(1) |
| C(8) | 26(1) | 44(1) | 23(1) | 6(1) | -3(1) | -6(1) |
| C(9) | 27(2) | 34(1) | 22(1) | -2(1) | 4(1) | 0(1) |
| C(10) | 21(1) | 24(1) | 20(1) | 3(1) | 1(1) | 1(1) |
| C(11) | 18(1) | 20(1) | 22(1) | 4(1) | -1(1) | -3(1) |
| C(12) | 13(1) | 24(2) | 33(1) | 10(1) | -2(1) | -2(1) |
| C(13) | 25(1) | 22(1) | 25(1) | -1(1) | 0(1) | 7(1) |
| B(1) | 24(2) | 27(3) | 26(2) | 3(2) | 1(1) | -1(2) |
| P(1M) | 18(1) | 19(1) | 21(1) | 2(1) | 0(1) | 2(1) |
| C(1M) | 16(1) | 19(1) | 27(1) | 2(1) | -1(1) | 1(1) |
| C(2M) | 22(1) | 22(1) | 39(1) | -5(1) | 0(1) | 2(1) |
| C(3M) | 23(2) | 15(1) | 62(2) | -2(1) | -3(1) | 5(1) |
| C(4M) | 16(1) | 25(1) | 50(1) | 12(1) | -5(1) | -3(1) |
| C(5M) | 21(1) | 29(1) | 64(1) | 18(1) | -11(1) | -2(1) |
| C(6M) | 17(1) | 54(2) | 42(1) | 26(1) | -7(1) | 1(1) |
| C(7M) | 17(1) | 38(1) | 28(1) | 12(1) | -2(1) | -6(1) |
| C(8M) | 26(1) | 44(1) | 23(1) | 6(1) | -3(1) | -6(1) |
| C(9M) | 27(2) | 34(1) | 22(1) | -2(1) | 4(1) | 0(1) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C(10M) | 21(1) | 24(1) | 20(1) | 3(1) | 1(1) | 1(1) |
| C(11M) | 18(1) | 20(1) | 22(1) | 4(1) | -1(1) | -3(1) |
| C(12M) | 13(1) | 24(2) | 33(1) | 10(1) | -2(1) | -2(1) |
| C(13M) | 25(1) | 22(1) | 25(1) | -1(1) | 0(1) | 7(1) |
| B(1M) | 24(2) | 27(3) | 26(2) | 3(2) | 1(1) | -1(2) |
| C(14) | 21(1) | 30(1) | 28(1) | 4(1) | -3(1) | -1(1) |
| C(15) | 28(1) | 36(1) | 38(1) | 7(1) | -6(1) | 4(1) |
| C(16) | 22(1) | 59(1) | 33(1) | 2(1) | -4(1) | 8(1) |
| C(17) | 21(1) | 66(1) | 37(1) | -2(1) | 0(1) | -9(1) |
| C(18) | 35(1) | 54(1) | 68(1) | 21(1) | -6(1) | -19(1) |
| C(19) | 28(1) | 44(1) | 56(1) | 23(1) | -10(1) | -8(1) |

Table 5. Hydrogen coordinates (x $10^4$) and isotropic displacement parameters ($Å^2$ x $10^3$) for Ph-PyraPhos($BH_3$), glu391.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| H(2) | 3440 | 6762 | 8830 | 33 |
| H(3) | 2892 | 8597 | 8014 | 40 |
| H(5A) | 2732 | 8891 | 6283 | 46 |
| H(5B) | 2304 | 7416 | 6575 | 46 |
| H(6B) | 2440 | 5219 | 5577 | 45 |
| H(6A) | 2893 | 6609 | 5321 | 45 |
| H(8) | 3214 | 1981 | 5331 | 37 |
| H(9) | 3737 | -9 | 6145 | 33 |
| H(13A) | 4402 | 987 | 7469 | 29 |
| H(13B) | 3974 | -500 | 7756 | 29 |
| H(1A) | 3376(6) | 530(30) | 9184(11) | 29(5) |
| H(1B) | 3702(8) | 2470(30) | 9862(12) | 44(6) |
| H(1C) | 4021(8) | -150(30) | 9568(12) | 38(7) |
| H(2M) | 4089 | 31 | 7411 | 33 |
| H(3M) | 3777 | 176 | 6128 | 40 |
| H(5MA) | 2876 | 2158 | 5380 | 46 |
| H(5MB) | 3330 | 3507 | 5098 | 46 |
| H(6MA) | 2948 | 6461 | 5395 | 45 |
| H(6MB) | 2490 | 5122 | 5650 | 45 |
| H(8M) | 2580 | 8347 | 6853 | 37 |
| H(9M) | 2929 | 8507 | 8146 | 33 |
| H(13C) | 3278 | 5214 | 9235 | 29 |
| H(13D) | 3727 | 6682 | 9029 | 29 |
| H(1MA) | 3853 | 1422 | 9979 | 38 |
| H(1MB) | 4013 | -227 | 9342 | 38 |

| | | | | |
|---|---|---|---|---|
| H(1MC) | 3462 | 488 | 9388 | 38 |
| H(15) | 4833 | 1424 | 9384 | 41 |
| H(16) | 5598 | 2805 | 9597 | 46 |
| H(17) | 5801 | 6024 | 9090 | 49 |
| H(18) | 5237 | 7924 | 8384 | 63 |
| H(19) | 4469 | 6558 | 8152 | 51 |

Table 1. Crystal data and structure refinement for [Pt(*R*,*R*)-Me-DuPhos)(Ph)((*R*)-Ph-PyraPhos)][$PF_6$]•THF, glu395.

| | | |
|---|---|---|
| Identification code | 18a.THF | |
| Empirical formula | C47 H56 F6 O P4 Pt | |
| Formula weight | 1069.88 | |
| Temperature | 100(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Orthorhombic | |
| Space group | P 21 21 21 | |
| Unit cell dimensions | a = 11.5207(4) Å | α= 90° |
| | b = 17.2787(5) Å | β= 90° |
| | c = 22.7156(7) Å | γ = 90° |
| Volume | 4521.8(2) $Å^3$ | |
| Z | 4 | |
| Density (calculated) | 1.572 $Mg/m^3$ | |
| Absorption coefficient | 3.305 $mm^{-1}$ | |
| F(000) | 2152 | |
| Crystal size | 0.300 x 0.240 x 0.090 $mm^3$ | |
| Theta range for data collection | 1.982 to 28.319° | |
| Index ranges | -13<=h<=15, -21<=k<=22, -19<=l<=30 | |
| Reflections collected | 43409 | |
| Independent reflections | 11027 [R(int) = 0.0493] | |
| Completeness to theta = 25.000° | 99.8 % | |
| Absorption correction | Semi-empirical from equivalents | |
| Max. and min. transmission | 0.666 and 0.394 | |
| Refinement method | Full-matrix least-squares on $F^2$ | |
| Data / restraints / parameters | 11027 / 195 / 597 | |
| Goodness-of-fit on $F^2$ | 1.023 | |
| Final R indices [I>2sigma(I)] | R1 = 0.0438, wR2 = 0.0684 | |
| R indices (all data) | R1 = 0.0462, wR2 = 0.0719 | |
| Absolute structure parameter | 0.000(4) | |

| | |
|---|---|
| Extinction coefficient | n/a |
| Largest diff. peak and hole | 1.412 and -1.456 e.Å$^{-3}$ |

Table 2. Atomic coordinates ( x $10^4$) and equivalent isotropic displacement parameters (Å$^2$ x $10^3$) for [Pt(*R*,*R*)-Me-DuPhos)(Ph)((*R*)-Ph-PyraPhos)][$PF_6$]•THF, glu395. U(eq) is defined as one third of the trace of the orthogonalized $U^{ij}$ tensor.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| Pt(1) | 2620(1) | 3674(1) | 8243(1) | 16(1) |
| P(1) | 2009(1) | 2456(1) | 8027(1) | 17(1) |
| P(2) | 3137(1) | 3187(1) | 9145(1) | 18(1) |
| P(3) | 2901(2) | 4981(1) | 8386(1) | 19(1) |
| P(3') | 3557(9) | 4915(5) | 8340(4) | 19(1) |
| P(4B) | 7871(5) | 4378(4) | 8503(3) | 68(2) |
| F(1B) | 7526(13) | 4997(6) | 8990(5) | 111(4) |
| F(2B) | 6590(6) | 4077(7) | 8383(5) | 75(4) |
| F(3B) | 7741(13) | 4946(7) | 7957(5) | 105(4) |
| F(4B) | 9165(6) | 4668(8) | 8598(5) | 136(6) |
| F(5B) | 8024(9) | 3740(6) | 9001(4) | 103(4) |
| F(6B) | 8316(8) | 3758(6) | 8038(4) | 79(3) |
| O(1) | 2184(6) | 8652(5) | 8983(4) | 88(3) |
| C(1) | -363(6) | 2171(5) | 8360(4) | 40(2) |
| C(2) | 443(5) | 2377(5) | 7851(3) | 27(2) |
| C(3) | 391(7) | 1838(5) | 7322(3) | 39(2) |
| C(4) | 1468(7) | 1988(5) | 6949(3) | 41(2) |
| C(5) | 2512(7) | 1928(4) | 7366(2) | 28(2) |
| C(6) | 3673(7) | 2187(5) | 7108(4) | 38(2) |
| C(7) | 2345(5) | 1830(3) | 8646(2) | 18(1) |
| C(8) | 2058(5) | 1032(4) | 8635(3) | 25(2) |

| | | | | |
|---|---|---|---|---|
| C(9) | 2328(7) | 568(4) | 9112(3) | 32(2) |
| C(10) | 2844(7) | 882(4) | 9597(3) | 32(2) |
| C(11) | 3102(6) | 1659(4) | 9626(3) | 26(2) |
| C(12) | 2861(5) | 2153(4) | 9148(3) | 18(1) |
| C(13) | 1377(8) | 3994(5) | 9781(4) | 56(3) |
| C(14) | 2486(8) | 3515(4) | 9842(3) | 38(2) |
| C(15) | 3460(8) | 3895(6) | 10188(3) | 55(3) |
| C(16) | 4570(8) | 3466(6) | 10055(3) | 54(3) |
| C(17) | 4651(6) | 3355(5) | 9391(3) | 36(2) |
| C(18) | 5532(6) | 2760(5) | 9172(5) | 52(3) |
| C(19) | 3642(7) | 5431(5) | 7752(4) | 35(2) |
| C(20) | 4727(7) | 5171(5) | 7617(4) | 42(2) |
| C(21) | 5286(7) | 5446(6) | 7120(5) | 57(3) |
| C(22) | 4755(7) | 5976(5) | 6745(5) | 51(2) |
| C(23) | 3664(7) | 6244(5) | 6888(4) | 43(2) |
| C(24) | 3123(7) | 5970(5) | 7391(3) | 36(2) |
| C(25) | 1468(7) | 5441(5) | 8539(4) | 47(2) |
| C(26) | 1562(7) | 5903(5) | 9073(4) | 45(2) |
| C(27) | 765(9) | 6307(6) | 9366(5) | 66(3) |
| C(28) | 1063(13) | 6735(7) | 9906(6) | 85(4) |
| C(29) | 2112(13) | 6752(6) | 10099(4) | 69(4) |
| C(30) | 2708(13) | 7154(6) | 10581(4) | 80(4) |
| C(31) | 4020(14) | 6897(7) | 10555(5) | 95(5) |
| C(32) | 4085(11) | 6371(6) | 10036(4) | 69(3) |
| C(33) | 4989(8) | 5944(6) | 9745(4) | 52(3) |
| C(34) | 4688(7) | 5501(5) | 9235(4) | 41(2) |
| C(35) | 3578(7) | 5466(5) | 9017(4) | 41(2) |
| C(36) | 2966(7) | 6332(5) | 9766(3) | 45(2) |
| C(37) | 2731(9) | 5891(5) | 9288(3) | 46(2) |
| C(38) | 835(6) | 4293(5) | 7403(4) | 36(2) |
| C(39) | 347(8) | 4619(5) | 6901(4) | 56(3) |

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|---|---|---|---|---|
| C(40) | 1022(10) | 4729(6) | 6421(5) | 61(3) |
| C(41) | 2182(9) | 4520(5) | 6421(3) | 51(3) |
| C(42) | 2665(8) | 4184(4) | 6932(3) | 36(2) |
| C(48) | 2097(13) | 8221(10) | 8460(8) | 139(7) |
| C(43) | 2006(6) | 4060(4) | 7430(3) | 24(2) |
| C(47) | 3179(14) | 7989(10) | 8237(7) | 139(7) |
| C(46) | 3975(11) | 8181(11) | 8712(6) | 123(6) |
| C(45) | 3291(9) | 8507(7) | 9187(5) | 71(3) |
| P(4A) | 7943(6) | 4684(5) | 8525(3) | 68(2) |
| F(6A) | 8865(13) | 4026(9) | 8608(9) | 118(5) |
| F(4A) | 8595(14) | 5167(10) | 9007(7) | 113(5) |
| F(5A) | 7160(9) | 4319(8) | 9044(5) | 72(3) |
| F(2A) | 7139(15) | 4299(11) | 8059(7) | 122(5) |
| F(3A) | 8745(10) | 5101(7) | 8076(7) | 86(4) |
| F(1) | 7017(8) | 5386(7) | 8456(6) | 81(4) |

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Table 3. Bond lengths [Å] and angles [deg] for [Pt(*R*,*R*)-Me-DuPhos)(Ph)((*R*)-Ph-PyraPhos)][$PF_6$]•THF, glu395.

| | | | |
|---|---|---|---|
| Pt(1)-C(43) | 2.087(6) | C(4)-C(5) | 1.534(10) |
| Pt(1)-P(1) | 2.2726(17) | C(5)-C(6) | 1.528(10) |
| Pt(1)-P(2) | 2.2933(16) | C(7)-C(12) | 1.400(8) |
| Pt(1)-P(3) | 2.305(2) | C(7)-C(8) | 1.418(9) |
| Pt(1)-P(3') | 2.412(9) | C(8)-C(9) | 1.381(9) |
| P(1)-C(7) | 1.817(6) | C(9)-C(10) | 1.364(10) |
| P(1)-C(5) | 1.850(6) | C(10)-C(11) | 1.377(10) |
| P(1)-C(2) | 1.853(6) | C(11)-C(12) | 1.410(9) |
| P(2)-C(12) | 1.815(7) | C(13)-C(14) | 1.528(12) |
| P(2)-C(14) | 1.841(7) | C(14)-C(15) | 1.519(11) |
| P(2)-C(17) | 1.854(7) | C(15)-C(16) | 1.508(13) |
| P(3)-P(3') | 0.772(10) | C(16)-C(17) | 1.524(11) |
| P(3)-C(35) | 1.835(9) | C(17)-C(18) | 1.529(12) |
| P(3)-C(19) | 1.846(8) | C(19)-C(20) | 1.363(11) |
| P(3)-C(25) | 1.864(8) | C(19)-C(24) | 1.377(10) |
| P(3')-C(19) | 1.609(12) | C(20)-C(21) | 1.383(12) |
| P(3')-C(35) | 1.808(13) | C(21)-C(22) | 1.392(13) |
| P(4B)-F(4B) | 1.5878(12) | C(22)-C(23) | 1.378(11) |
| P(4B)-F(6B) | 1.5886(12) | C(23)-C(24) | 1.386(10) |
| P(4B)-F(2B) | 1.5887(12) | C(25)-C(26) | 1.457(12) |
| P(4B)-F(1B) | 1.5890(12) | C(26)-C(27) | 1.331(12) |
| P(4B)-F(3B) | 1.5893(12) | C(26)-C(37) | 1.432(13) |
| P(4B)-F(5B) | 1.5895(12) | C(27)-C(28) | 1.474(16) |
| O(1)-C(45) | 1.379(12) | C(28)-C(29) | 1.286(17) |
| O(1)-C(48) | 1.405(15) | C(29)-C(36) | 1.438(14) |
| C(1)-C(2) | 1.524(10) | C(29)-C(30) | 1.468(14) |
| C(2)-C(3) | 1.522(10) | C(30)-C(31) | 1.577(19) |
| C(3)-C(4) | 1.525(11) | C(31)-C(32) | 1.489(15) |

| | | | |
|---|---|---|---|
| C(32)-C(36) | 1.429(14) | P(3)-Pt(1)-P(3') | 18.7(2) |
| C(32)-C(33) | 1.438(15) | C(7)-P(1)-C(5) | 105.6(3) |
| C(33)-C(34) | 1.431(12) | C(7)-P(1)-C(2) | 109.3(3) |
| C(34)-C(35) | 1.373(11) | C(5)-P(1)-C(2) | 95.4(3) |
| C(35)-C(37) | 1.369(12) | C(7)-P(1)-Pt(1) | 108.5(2) |
| C(36)-C(37) | 1.352(11) | C(5)-P(1)-Pt(1) | 122.3(2) |
| C(38)-C(39) | 1.392(11) | C(2)-P(1)-Pt(1) | 114.6(3) |
| C(38)-C(43) | 1.410(10) | C(12)-P(2)-C(14) | 103.3(3) |
| C(39)-C(40) | 1.352(14) | C(12)-P(2)-C(17) | 108.6(3) |
| C(40)-C(41) | 1.385(14) | C(14)-P(2)-C(17) | 94.3(4) |
| C(41)-C(42) | 1.411(11) | C(12)-P(2)-Pt(1) | 108.5(2) |
| C(42)-C(43) | 1.379(9) | C(14)-P(2)-Pt(1) | 123.3(3) |
| C(48)-C(47) | 1.405(19) | C(17)-P(2)-Pt(1) | 117.1(3) |
| C(47)-C(46) | 1.454(19) | P(3')-P(3)-C(35) | 75.8(8) |
| C(46)-C(45) | 1.450(15) | P(3')-P(3)-C(19) | 60.3(8) |
| P(4A)-F(3A) | 1.554(11) | C(35)-P(3)-C(19) | 102.7(4) |
| P(4A)-F(2A) | 1.555(14) | P(3')-P(3)-C(25) | 162.8(8) |
| P(4A)-F(6A) | 1.568(13) | C(35)-P(3)-C(25) | 92.1(4) |
| P(4A)-F(4A) | 1.568(14) | C(19)-P(3)-C(25) | 112.0(4) |
| P(4A)-F(5A) | 1.613(10) | P(3')-P(3)-Pt(1) | 88.5(7) |
| P(4A)-F(1) | 1.622(12) | C(35)-P(3)-Pt(1) | 128.1(3) |
| | | C(19)-P(3)-Pt(1) | 111.6(3) |
| C(43)-Pt(1)-P(1) | 90.0(2) | C(25)-P(3)-Pt(1) | 108.6(3) |
| C(43)-Pt(1)-P(2) | 174.72(19) | P(3)-P(3')-C(19) | 95.1(9) |
| P(1)-Pt(1)-P(2) | 86.23(6) | P(3)-P(3')-C(35) | 79.7(8) |
| C(43)-Pt(1)-P(3) | 81.8(2) | C(19)-P(3')-C(35) | 114.5(6) |
| P(1)-Pt(1)-P(3) | 168.91(6) | P(3)-P(3')-Pt(1) | 72.8(7) |
| P(2)-Pt(1)-P(3) | 101.38(7) | C(19)-P(3')-Pt(1) | 116.4(5) |
| C(43)-Pt(1)-P(3') | 87.0(3) | C(35)-P(3')-Pt(1) | 123.5(6) |
| P(1)-Pt(1)-P(3') | 169.1(3) | F(4B)-P(4B)-F(6B) | 90.01(9) |
| P(2)-Pt(1)-P(3') | 97.4(2) | F(4B)-P(4B)-F(2B) | 177.7(7) |

| | | | |
|---|---|---|---|
| F(6B)-P(4B)-F(2B) | 88.0(7) | C(11)-C(12)-P(2) | 124.3(5) |
| F(4B)-P(4B)-F(1B) | 85.9(7) | C(15)-C(14)-C(13) | 115.6(7) |
| F(6B)-P(4B)-F(1B) | 175.5(7) | C(15)-C(14)-P(2) | 106.1(5) |
| F(2B)-P(4B)-F(1B) | 96.2(8) | C(13)-C(14)-P(2) | 115.4(5) |
| F(4B)-P(4B)-F(3B) | 89.97(9) | C(16)-C(15)-C(14) | 108.1(7) |
| F(6B)-P(4B)-F(3B) | 85.9(8) | C(15)-C(16)-C(17) | 108.1(7) |
| F(2B)-P(4B)-F(3B) | 88.9(7) | C(16)-C(17)-C(18) | 116.6(7) |
| F(1B)-P(4B)-F(3B) | 96.0(7) | C(16)-C(17)-P(2) | 105.1(6) |
| F(4B)-P(4B)-F(5B) | 91.0(7) | C(18)-C(17)-P(2) | 114.9(5) |
| F(6B)-P(4B)-F(5B) | 88.3(6) | C(20)-C(19)-C(24) | 119.1(8) |
| F(2B)-P(4B)-F(5B) | 89.92(9) | C(24)-C(19)-P(3') | 147.4(8) |
| F(1B)-P(4B)-F(5B) | 89.93(9) | C(20)-C(19)-P(3) | 117.4(6) |
| F(3B)-P(4B)-F(5B) | 174.1(7) | C(24)-C(19)-P(3) | 123.2(6) |
| C(45)-O(1)-C(48) | 104.7(9) | P(3')-C(19)-P(3) | 24.6(4) |
| C(3)-C(2)-C(1) | 115.6(6) | C(19)-C(20)-C(21) | 119.8(8) |
| C(3)-C(2)-P(1) | 104.7(5) | C(20)-C(21)-C(22) | 121.4(8) |
| C(1)-C(2)-P(1) | 116.5(5) | C(23)-C(22)-C(21) | 118.6(9) |
| C(2)-C(3)-C(4) | 107.6(6) | C(22)-C(23)-C(24) | 119.3(8) |
| C(3)-C(4)-C(5) | 106.4(6) | C(19)-C(24)-C(23) | 121.8(8) |
| C(6)-C(5)-C(4) | 115.4(6) | C(26)-C(25)-P(3) | 108.8(6) |
| C(6)-C(5)-P(1) | 116.2(5) | C(27)-C(26)-C(37) | 119.0(9) |
| C(4)-C(5)-P(1) | 102.9(5) | C(27)-C(26)-C(25) | 130.7(9) |
| C(12)-C(7)-C(8) | 120.1(6) | C(37)-C(26)-C(25) | 110.3(7) |
| C(12)-C(7)-P(1) | 118.8(4) | C(26)-C(27)-C(28) | 121.3(10) |
| C(8)-C(7)-P(1) | 121.1(4) | C(29)-C(28)-C(27) | 120.9(11) |
| C(9)-C(8)-C(7) | 119.8(6) | C(28)-C(29)-C(36) | 116.9(10) |
| C(10)-C(9)-C(8) | 120.1(7) | C(28)-C(29)-C(30) | 134.8(12) |
| C(9)-C(10)-C(11) | 121.3(7) | C(36)-C(29)-C(30) | 108.1(11) |
| C(10)-C(11)-C(12) | 120.8(7) | C(29)-C(30)-C(31) | 106.7(10) |
| C(7)-C(12)-C(11) | 117.9(6) | C(32)-C(31)-C(30) | 104.5(10) |
| C(7)-C(12)-P(2) | 117.7(4) | C(36)-C(32)-C(33) | 115.5(8) |

| | | | |
|---|---|---|---|
| C(36)-C(32)-C(31) | 108.9(11) | C(42)-C(43)-C(38) | 116.5(7) |
| C(33)-C(32)-C(31) | 135.5(11) | C(42)-C(43)-Pt(1) | 126.1(6) |
| C(34)-C(33)-C(32) | 118.2(8) | C(38)-C(43)-Pt(1) | 117.0(5) |
| C(35)-C(34)-C(33) | 122.8(9) | C(48)-C(47)-C(46) | 103.1(12) |
| C(37)-C(35)-C(34) | 118.6(9) | C(45)-C(46)-C(47) | 107.3(11) |
| C(37)-C(35)-P(3') | 131.0(8) | O(1)-C(45)-C(46) | 108.9(11) |
| C(34)-C(35)-P(3') | 110.0(8) | F(3A)-P(4A)-F(2A) | 96.1(10) |
| C(37)-C(35)-P(3) | 107.1(6) | F(3A)-P(4A)-F(6A) | 90.7(7) |
| C(34)-C(35)-P(3) | 134.3(8) | F(2A)-P(4A)-F(6A) | 100.1(12) |
| P(3')-C(35)-P(3) | 24.5(3) | F(3A)-P(4A)-F(4A) | 85.8(10) |
| C(37)-C(36)-C(32) | 123.5(9) | F(2A)-P(4A)-F(4A) | 171.0(12) |
| C(37)-C(36)-C(29) | 124.7(9) | F(6A)-P(4A)-F(4A) | 88.6(11) |
| C(32)-C(36)-C(29) | 111.5(9) | F(3A)-P(4A)-F(5A) | 173.7(10) |
| C(36)-C(37)-C(35) | 121.4(9) | F(2A)-P(4A)-F(5A) | 89.8(9) |
| C(36)-C(37)-C(26) | 117.0(9) | F(6A)-P(4A)-F(5A) | 90.4(9) |
| C(35)-C(37)-C(26) | 121.6(8) | F(4A)-P(4A)-F(5A) | 88.1(8) |
| C(39)-C(38)-C(43) | 122.6(8) | F(3A)-P(4A)-F(1) | 89.0(7) |
| C(40)-C(39)-C(38) | 119.0(9) | F(2A)-P(4A)-F(1) | 82.1(9) |
| C(39)-C(40)-C(41) | 121.2(8) | F(6A)-P(4A)-F(1) | 177.7(12) |
| C(40)-C(41)-C(42) | 119.2(8) | F(4A)-P(4A)-F(1) | 89.1(9) |
| C(43)-C(42)-C(41) | 121.5(8) | F(5A)-P(4A)-F(1) | 89.7(7) |
| C(47)-C(48)-O(1) | 113.1(12) | | |

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2$ x $10^3$) for [Pt(*R*,*R*)-Me-DuPhos)(Ph)((*R*)-Ph-PyraPhos)][$PF_6$]•THF, glu395. The anisotropic displacement factor exponent takes the form: $-2\pi^2[ h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12} ]$

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{23}$ | $U^{13}$ | $U^{12}$ |
|---|---|---|---|---|---|---|
| Pt(1) | 21(1) | 15(1) | 13(1) | 0(1) | -1(1) | 0(1) |
| P(1) | 20(1) | 17(1) | 14(1) | -1(1) | -2(1) | -4(1) |
| P(2) | 24(1) | 16(1) | 13(1) | -1(1) | -1(1) | -1(1) |
| P(3) | 19(1) | 17(1) | 20(1) | -2(1) | -2(1) | 0(1) |
| P(3') | 19(1) | 17(1) | 20(1) | -2(1) | -2(1) | 0(1) |
| P(4B) | 27(1) | 119(5) | 58(2) | 27(3) | 7(1) | -11(2) |
| F(1B) | 68(8) | 182(11) | 84(8) | -12(8) | 6(7) | 1(8) |
| F(2B) | 36(5) | 107(9) | 82(8) | 31(7) | -5(5) | -4(5) |
| F(3B) | 110(10) | 114(9) | 91(8) | 19(7) | -16(7) | -49(8) |
| F(4B) | 48(6) | 238(16) | 123(12) | -33(11) | 12(6) | -35(8) |
| F(5B) | 80(7) | 174(11) | 55(6) | 30(7) | 6(5) | 15(8) |
| F(6B) | 54(6) | 129(9) | 54(6) | 24(6) | 3(4) | 1(6) |
| O(1) | 55(4) | 57(5) | 152(8) | -42(5) | -4(4) | 9(4) |
| C(1) | 30(4) | 42(5) | 48(5) | 9(4) | 2(3) | -11(3) |
| C(2) | 22(3) | 33(5) | 27(4) | 10(3) | -10(3) | -8(3) |
| C(3) | 47(5) | 37(5) | 32(4) | 1(4) | -22(4) | -17(4) |
| C(4) | 57(5) | 44(6) | 23(4) | -5(4) | -6(3) | -15(4) |
| C(5) | 42(4) | 25(4) | 16(3) | -7(2) | 5(3) | -7(4) |
| C(6) | 45(4) | 37(5) | 32(4) | -4(4) | 17(3) | 2(4) |
| C(7) | 19(3) | 15(3) | 18(3) | -1(2) | -2(3) | 0(3) |
| C(8) | 29(4) | 21(4) | 25(3) | 2(3) | -1(3) | -1(3) |
| C(9) | 45(4) | 15(4) | 36(4) | 4(3) | 4(4) | 1(3) |
| C(10) | 49(5) | 16(4) | 32(4) | 11(3) | -6(3) | -1(3) |
| C(11) | 37(4) | 18(4) | 25(3) | 3(3) | -5(3) | 1(3) |
| C(12) | 21(3) | 20(4) | 14(3) | 1(2) | 1(2) | 2(3) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C(13) | 78(6) | 38(6) | 51(6) | 2(5) | 36(5) | -1(5) |
| C(14) | 66(5) | 27(4) | 22(3) | 0(3) | 18(4) | -8(4) |
| C(15) | 89(7) | 59(7) | 15(4) | -13(4) | 7(4) | -22(5) |
| C(16) | 78(6) | 56(7) | 27(4) | 3(4) | -21(4) | -23(5) |
| C(17) | 37(4) | 32(5) | 38(4) | 6(4) | -20(3) | -13(3) |
| C(18) | 26(4) | 44(6) | 87(7) | 6(5) | -17(4) | 0(4) |
| C(19) | 40(4) | 25(5) | 39(4) | 0(4) | -15(4) | -10(3) |
| C(20) | 42(5) | 30(5) | 54(5) | 15(4) | -7(4) | -14(4) |
| C(21) | 29(4) | 56(7) | 87(8) | 6(6) | 4(5) | -9(4) |
| C(22) | 45(4) | 52(6) | 55(5) | 11(5) | 8(5) | -22(4) |
| C(23) | 50(4) | 37(5) | 43(5) | 15(4) | -10(3) | -11(4) |
| C(24) | 44(4) | 29(5) | 34(4) | 8(4) | -2(3) | -4(3) |
| C(25) | 42(5) | 47(6) | 51(6) | 14(5) | 6(4) | 9(4) |
| C(26) | 54(5) | 24(5) | 57(6) | 0(4) | 3(4) | 5(4) |
| C(27) | 88(7) | 47(7) | 62(6) | 2(6) | -9(5) | 28(6) |
| C(28) | 126(11) | 64(9) | 64(8) | 9(7) | 8(8) | 39(8) |
| C(29) | 140(11) | 41(6) | 27(4) | -2(4) | -1(6) | 17(7) |
| C(30) | 156(13) | 43(6) | 41(5) | -6(4) | -5(8) | -13(8) |
| C(31) | 177(15) | 64(9) | 45(6) | 2(6) | -7(8) | -61(9) |
| C(32) | 140(10) | 33(6) | 32(5) | 7(5) | 7(6) | -47(7) |
| C(33) | 71(6) | 52(6) | 33(4) | 19(5) | -22(5) | -38(5) |
| C(34) | 38(4) | 49(6) | 37(5) | 12(4) | -13(4) | -27(4) |
| C(35) | 46(5) | 42(6) | 35(5) | 4(4) | -3(4) | -14(4) |
| C(36) | 75(5) | 22(4) | 39(4) | -11(4) | 3(4) | -13(5) |
| C(37) | 88(7) | 20(4) | 29(4) | 3(3) | 1(5) | 0(5) |
| C(38) | 40(4) | 27(5) | 42(5) | 15(4) | -9(4) | -3(3) |
| C(39) | 59(6) | 41(6) | 67(7) | 21(5) | -34(5) | -5(4) |
| C(40) | 96(8) | 35(6) | 53(6) | 19(5) | -41(6) | -12(5) |
| C(41) | 101(8) | 31(5) | 20(3) | 5(3) | 6(5) | -24(5) |
| C(42) | 58(5) | 25(4) | 26(3) | -4(3) | 7(4) | -15(4) |
| C(48) | 106(11) | 134(14) | 176(18) | -84(13) | -64(11) | 34(10) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C(43) | 34(4) | 25(4) | 14(3) | 3(3) | -6(3) | -6(3) |
| C(47) | 161(14) | 177(18) | 78(10) | -45(12) | -25(11) | 85(13) |
| C(46) | 63(8) | 230(20) | 77(9) | -17(11) | 19(7) | 30(10) |
| C(45) | 66(7) | 67(9) | 80(8) | 1(7) | 21(6) | 15(6) |
| P(4A) | 27(1) | 119(5) | 58(2) | 27(3) | 7(1) | -11(2) |
| F(6A) | 100(9) | 80(8) | 175(14) | 76(8) | 36(8) | 21(7) |
| F(4A) | 90(9) | 124(10) | 126(9) | 24(7) | -15(7) | -33(7) |
| F(5A) | 61(7) | 89(8) | 66(6) | 29(6) | 8(5) | -21(6) |
| F(2A) | 125(11) | 151(11) | 91(8) | 27(8) | -21(8) | -13(9) |
| F(3A) | 61(6) | 76(8) | 121(9) | 48(7) | 41(6) | 36(5) |
| F(1) | 38(5) | 104(8) | 100(9) | 48(6) | 21(5) | 5(5) |

Table 5. Hydrogen coordinates (x $10^4$) and isotropic displacement parameters ($Å^2$ x $10^3$) for [Pt(*R*,*R*)-Me-DuPhos)(Ph)((*R*)-Ph-PyraPhos)][$PF_6$]•THF, glu395.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| H(1A) | -1171 | 2204 | 8228 | 60 |
| H(1B) | -238 | 2534 | 8685 | 60 |
| H(1C) | -197 | 1643 | 8493 | 60 |
| H(2) | 195 | 2898 | 7708 | 33 |
| H(3A) | -319 | 1940 | 7089 | 46 |
| H(3B) | 375 | 1292 | 7453 | 46 |
| H(4A) | 1432 | 2509 | 6769 | 49 |
| H(4B) | 1530 | 1599 | 6630 | 49 |
| H(5) | 2594 | 1371 | 7478 | 33 |
| H(6A) | 3893 | 1839 | 6786 | 57 |
| H(6B) | 4270 | 2173 | 7415 | 57 |
| H(6C) | 3600 | 2716 | 6956 | 57 |
| H(8) | 1681 | 816 | 8302 | 30 |
| H(9) | 2155 | 31 | 9101 | 38 |
| H(10) | 3028 | 557 | 9922 | 39 |
| H(11) | 3446 | 1865 | 9972 | 32 |
| H(13A) | 977 | 4014 | 10161 | 83 |
| H(13B) | 867 | 3753 | 9488 | 83 |
| H(13C) | 1575 | 4520 | 9655 | 83 |
| H(14) | 2267 | 3037 | 10064 | 46 |
| H(15A) | 3537 | 4445 | 10073 | 65 |
| H(15B) | 3291 | 3872 | 10615 | 65 |
| H(16A) | 4569 | 2957 | 10255 | 64 |
| H(16B) | 5246 | 3767 | 10198 | 64 |
| H(17) | 4892 | 3866 | 9223 | 43 |

| | | | | |
|---|---|---|---|---|
| H(18A) | 6317 | 2929 | 9277 | 79 |
| H(18B) | 5471 | 2712 | 8743 | 79 |
| H(18C) | 5372 | 2258 | 9355 | 79 |
| H(20) | 5098 | 4801 | 7863 | 50 |
| H(21) | 6048 | 5269 | 7033 | 69 |
| H(22) | 5137 | 6149 | 6399 | 61 |
| H(23) | 3288 | 6613 | 6643 | 52 |
| H(24) | 2373 | 6158 | 7489 | 43 |
| H(25A) | 1240 | 5775 | 8204 | 56 |
| H(25B) | 867 | 5037 | 8589 | 56 |
| H(27) | -10 | 6320 | 9223 | 79 |
| H(28) | 471 | 7002 | 10115 | 102 |
| H(30A) | 2362 | 7009 | 10965 | 96 |
| H(30B) | 2642 | 7722 | 10532 | 96 |
| H(31A) | 4535 | 7350 | 10501 | 114 |
| H(31B) | 4247 | 6622 | 10920 | 114 |
| H(33) | 5764 | 5955 | 9887 | 62 |
| H(34) | 5282 | 5219 | 9039 | 50 |
| H(38) | 360 | 4225 | 7741 | 43 |
| H(39) | -449 | 4762 | 6894 | 67 |
| H(40) | 695 | 4954 | 6077 | 73 |
| H(41) | 2648 | 4601 | 6082 | 61 |
| H(42) | 3461 | 4040 | 6933 | 44 |
| H(48A) | 1617 | 7756 | 8535 | 166 |
| H(48B) | 1694 | 8538 | 8159 | 166 |
| H(47A) | 3375 | 8276 | 7873 | 167 |
| H(47B) | 3189 | 7427 | 8152 | 167 |
| H(46A) | 4387 | 7711 | 8848 | 148 |
| H(46B) | 4559 | 8561 | 8574 | 148 |
| H(45A) | 3260 | 8140 | 9521 | 85 |
| H(45B) | 3650 | 8994 | 9326 | 85 |

A colorless crystal of GW 1-103 part 3 was mounted on a Cryoloop with Paratone-N oil and data was collected at 100 K with a Bruker APEX II CCD using Mo K alpha radiation. Data was corrected for absorption with SADABS and structure was solved by direct methods. All non-hydrogen atoms were refined anisotropically by full matrix least squares on $F^2$ and all hydrogen atoms were placed in calculated positions with appropriate riding parameters.

Highest peak 1.13 at 0.1828 0.5550 0.2543 [ 0.24 A from H16A ]

Deepest hole -0.65 at 0.0818 0.4891 0.5801 [ 0.61 A from BR2 ]

Table 1. Crystal data and structure refinement for $PhP(CH_2Ar)_2(BH_3)$ (Ar = 5-bromo,6-acenaphthenyl), GLU395A.

| | | |
|---|---|---|
| Identification code | glu395a (GW 1-103 part 3) | |
| Empirical formula | C32 H28 B Br2 P | |
| Molecular formula | C32 H28 B Br2 P | |
| Formula weight | 614.14 | |
| Temperature | 100(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Monoclinic | |
| Space group | P2(1)/c | |
| Unit cell dimensions | a = 21.116(3) Å | α= 90°. |
| | b = 10.2016(12) Å | β= 91.709(4)°. |
| | c = 12.0731(13) Å | γ = 90°. |
| Volume | 2599.6(5) $Å^3$ | |
| Z | 4 | |
| Density (calculated) | 1.569 $Mg/m^3$ | |
| Absorption coefficient | 3.201 $mm^{-1}$ | |
| F(000) | 1240 | |
| Crystal size | 0.20 x 0.10 x 0.06 $mm^3$ | |
| Crystal color, habit | colourless BLOCK | |
| Theta range for data collection | 1.93 to 26.39°. | |
| Index ranges | -26<=h<=25, -12<=k<=12, -15<=l<=15 | |
| Reflections collected | 28486 | |
| Independent reflections | 5329 [R(int) = 0.0579] | |
| Completeness to theta = 25.00° | 100.0 % | |
| Absorption correction | multi-scan / sadabs | |
| Max. and min. transmission | 0.8311 and 0.5669 | |
| Refinement method | Full-matrix least-squares on $F^2$ | |
| Data / restraints / parameters | 5329 / 0 / 326 | |
| Goodness-of-fit on $F^2$ | 1.033 | |
| Final R indices [I>2sigma(I)] | R1 = 0.0420, wR2 = 0.0960 | |
| R indices (all data) | R1 = 0.0634, wR2 = 0.1042 | |
| Largest diff. peak and hole | 1.134 and -0.649 $e.Å^{-3}$ | |

Table 2. Atomic coordinates (x $10^4$) and equivalent isotropic displacement parameters ($Å^2$ x $10^3$) for $PhP(CH_2Ar)_2(BH_3)$ (Ar = 5-bromo,6-acenaphthenyl), GLU395A. U(eq) is defined as one third of the trace of the orthogonalized $U^{ij}$ tensor.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| P(1) | 2480(1) | 6234(1) | 6421(1) | 16(1) |
| B(1) | 2564(2) | 6287(4) | 4838(3) | 20(1) |
| Br(1) | 3453(1) | 9290(1) | 5436(1) | 25(1) |
| Br(2) | 935(1) | 5096(1) | 5378(1) | 28(1) |
| C(1) | 3136(2) | 7002(4) | 7216(3) | 18(1) |
| C(2) | 3783(2) | 6449(3) | 6961(3) | 17(1) |
| C(3) | 3962(2) | 5295(4) | 7484(3) | 19(1) |
| C(4) | 4548(2) | 4665(4) | 7388(3) | 19(1) |
| C(5) | 4992(2) | 5243(3) | 6748(3) | 17(1) |
| C(6) | 4823(2) | 6409(3) | 6171(3) | 15(1) |
| C(7) | 4224(2) | 7031(3) | 6238(3) | 16(1) |
| C(8) | 4183(2) | 8172(3) | 5542(3) | 19(1) |
| C(9) | 4663(2) | 8557(4) | 4881(3) | 22(1) |
| C(10) | 5244(2) | 7886(4) | 4846(3) | 21(1) |
| C(11) | 5325(2) | 6813(4) | 5506(3) | 18(1) |
| C(12) | 5877(2) | 5906(4) | 5655(3) | 21(1) |
| C(13) | 5659(2) | 4871(4) | 6505(3) | 22(1) |
| C(14) | 1772(2) | 7000(4) | 6996(3) | 19(1) |
| C(15) | 1492(2) | 8124(4) | 6340(3) | 18(1) |
| C(16) | 1625(2) | 9374(4) | 6707(3) | 23(1) |
| C(17) | 1410(2) | 10525(4) | 6174(3) | 24(1) |
| C(18) | 1061(2) | 10420(4) | 5205(3) | 21(1) |
| C(19) | 916(2) | 9151(3) | 4801(3) | 16(1) |
| C(20) | 1102(2) | 7976(4) | 5345(3) | 16(1) |
| C(21) | 860(2) | 6833(3) | 4797(3) | 19(1) |
| C(22) | 508(2) | 6896(4) | 3823(3) | 19(1) |
| C(23) | 357(2) | 8095(4) | 3303(3) | 21(1) |
| C(24) | 551(2) | 9221(4) | 3808(3) | 19(1) |
| C(25) | 453(2) | 10636(4) | 3489(3) | 25(1) |
| C(26) | 769(2) | 11434(4) | 4450(3) | 24(1) |
| C(27) | 2486(2) | 4596(4) | 6995(3) | 18(1) |

| | | | | |
|---|---|---|---|---|
| C(28) | 2309(2) | 4370(4) | 8085(3) | 24(1) |
| C(29) | 2378(2) | 3135(4) | 8548(3) | 30(1) |
| C(30) | 2622(2) | 2128(4) | 7942(4) | 34(1) |
| C(31) | 2801(2) | 2334(4) | 6860(4) | 30(1) |
| C(32) | 2725(2) | 3564(4) | 6385(3) | 23(1) |

Table 3. Bond lengths [Å] and angles [deg] for $PhP(CH_2Ar)_2(BH_3)$ (Ar = 5-bromo,6-acenaphthenyl), GLU395A.

| | | | |
|---|---|---|---|
| P(1)-C(27) | 1.808(4) | C(14)-H(14A) | 0.9900 |
| P(1)-C(1) | 1.837(4) | C(14)-H(14B) | 0.9900 |
| P(1)-C(14) | 1.842(4) | C(15)-C(16) | 1.376(5) |
| P(1)-B(1) | 1.925(4) | C(15)-C(20) | 1.444(5) |
| B(1)-H(1AA) | 0.9800 | C(16)-C(17) | 1.407(5) |
| B(1)-H(1AB) | 0.9800 | C(16)-H(16A) | 0.9500 |
| B(1)-H(1AC) | 0.9800 | C(17)-C(18) | 1.368(5) |
| Br(1)-C(8) | 1.918(4) | C(17)-H(17A) | 0.9500 |
| Br(2)-C(21) | 1.911(4) | C(18)-C(19) | 1.414(5) |
| C(1)-C(2) | 1.517(5) | C(18)-C(26) | 1.499(5) |
| C(1)-H(1A) | 0.9900 | C(19)-C(24) | 1.407(5) |
| C(1)-H(1B) | 0.9900 | C(19)-C(20) | 1.417(5) |
| C(2)-C(3) | 1.383(5) | C(20)-C(21) | 1.428(5) |
| C(2)-C(7) | 1.426(5) | C(21)-C(22) | 1.374(5) |
| C(3)-C(4) | 1.403(5) | C(22)-C(23) | 1.407(5) |
| C(3)-H(3A) | 0.9500 | C(22)-H(22A) | 0.9500 |
| C(4)-C(5) | 1.366(5) | C(23)-C(24) | 1.359(5) |
| C(4)-H(4A) | 0.9500 | C(23)-H(23A) | 0.9500 |
| C(5)-C(6) | 1.418(5) | C(24)-C(25) | 1.506(5) |
| C(5)-C(13) | 1.496(5) | C(25)-C(26) | 1.552(5) |
| C(6)-C(11) | 1.409(5) | C(25)-H(25A) | 0.9900 |
| C(6)-C(7) | 1.420(5) | C(25)-H(25B) | 0.9900 |
| C(7)-C(8) | 1.437(5) | C(26)-H(26A) | 0.9900 |
| C(8)-C(9) | 1.365(5) | C(26)-H(26B) | 0.9900 |
| C(9)-C(10) | 1.408(5) | C(27)-C(32) | 1.389(5) |
| C(9)-H(9A) | 0.9500 | C(27)-C(28) | 1.397(5) |
| C(10)-C(11) | 1.362(5) | C(28)-C(29) | 1.384(5) |
| C(10)-H(10A) | 0.9500 | C(28)-H(28A) | 0.9500 |
| C(11)-C(12) | 1.496(5) | C(29)-C(30) | 1.370(6) |
| C(12)-C(13) | 1.552(5) | C(29)-H(29A) | 0.9500 |
| C(12)-H(12A) | 0.9900 | C(30)-C(31) | 1.386(6) |
| C(12)-H(12B) | 0.9900 | C(30)-H(30A) | 0.9500 |
| C(13)-H(13A) | 0.9900 | C(31)-C(32) | 1.387(6) |
| C(13)-H(13B) | 0.9900 | C(31)-H(31A) | 0.9500 |
| C(14)-C(15) | 1.505(5) | C(32)-H(32A) | 0.9500 |

| | | | |
|---|---|---|---|
| C(27)-P(1)-C(1) | 101.40(16) | C(9)-C(8)-C(7) | 122.8(3) |
| C(27)-P(1)-C(14) | 104.07(17) | C(9)-C(8)-Br(1) | 113.5(3) |
| C(1)-P(1)-C(14) | 103.28(17) | C(7)-C(8)-Br(1) | 123.7(3) |
| C(27)-P(1)-B(1) | 114.03(19) | C(8)-C(9)-C(10) | 122.8(4) |
| C(1)-P(1)-B(1) | 114.62(18) | C(8)-C(9)-H(9A) | 118.6 |
| C(14)-P(1)-B(1) | 117.52(18) | C(10)-C(9)-H(9A) | 118.6 |
| P(1)-B(1)-H(1AA) | 109.5 | C(11)-C(10)-C(9) | 117.8(4) |
| P(1)-B(1)-H(1AB) | 109.5 | C(11)-C(10)-H(10A) | 121.1 |
| H(1AA)-B(1)-H(1AB) | 109.5 | C(9)-C(10)-H(10A) | 121.1 |
| P(1)-B(1)-H(1AC) | 109.5 | C(10)-C(11)-C(6) | 119.1(3) |
| H(1AA)-B(1)-H(1AC) | 109.5 | C(10)-C(11)-C(12) | 130.6(4) |
| H(1AB)-B(1)-H(1AC) | 109.5 | C(6)-C(11)-C(12) | 110.3(3) |
| C(2)-C(1)-P(1) | 113.8(2) | C(11)-C(12)-C(13) | 104.7(3) |
| C(2)-C(1)-H(1A) | 108.8 | C(11)-C(12)-H(12A) | 110.8 |
| P(1)-C(1)-H(1A) | 108.8 | C(13)-C(12)-H(12A) | 110.8 |
| C(2)-C(1)-H(1B) | 108.8 | C(11)-C(12)-H(12B) | 110.8 |
| P(1)-C(1)-H(1B) | 108.8 | C(13)-C(12)-H(12B) | 110.8 |
| H(1A)-C(1)-H(1B) | 107.7 | H(12A)-C(12)-H(12B) | 108.9 |
| C(3)-C(2)-C(7) | 117.3(3) | C(5)-C(13)-C(12) | 104.9(3) |
| C(3)-C(2)-C(1) | 117.3(3) | C(5)-C(13)-H(13A) | 110.8 |
| C(7)-C(2)-C(1) | 125.3(3) | C(12)-C(13)-H(13A) | 110.8 |
| C(2)-C(3)-C(4) | 125.6(4) | C(5)-C(13)-H(13B) | 110.8 |
| C(2)-C(3)-H(3A) | 117.2 | C(12)-C(13)-H(13B) | 110.8 |
| C(4)-C(3)-H(3A) | 117.2 | H(13A)-C(13)-H(13B) | 108.8 |
| C(5)-C(4)-C(3) | 118.2(3) | C(15)-C(14)-P(1) | 115.8(3) |
| C(5)-C(4)-H(4A) | 120.9 | C(15)-C(14)-H(14A) | 108.3 |
| C(3)-C(4)-H(4A) | 120.9 | P(1)-C(14)-H(14A) | 108.3 |
| C(4)-C(5)-C(6) | 118.2(3) | C(15)-C(14)-H(14B) | 108.3 |
| C(4)-C(5)-C(13) | 131.9(3) | P(1)-C(14)-H(14B) | 108.3 |
| C(6)-C(5)-C(13) | 109.9(3) | H(14A)-C(14)-H(14B) | 107.4 |
| C(11)-C(6)-C(5) | 110.1(3) | C(16)-C(15)-C(20) | 118.1(3) |
| C(11)-C(6)-C(7) | 126.0(3) | C(16)-C(15)-C(14) | 117.6(3) |
| C(5)-C(6)-C(7) | 123.9(3) | C(20)-C(15)-C(14) | 124.3(3) |
| C(6)-C(7)-C(2) | 116.6(3) | C(15)-C(16)-C(17) | 124.5(3) |
| C(6)-C(7)-C(8) | 111.6(3) | C(15)-C(16)-H(16A) | 117.8 |
| C(2)-C(7)-C(8) | 131.8(3) | C(17)-C(16)-H(16A) | 117.8 |

| | | | |
|---|---|---|---|
| C(18)-C(17)-C(16) | 118.9(3) | C(24)-C(25)-H(25B) | 110.7 |
| C(18)-C(17)-H(17A) | 120.5 | C(26)-C(25)-H(25B) | 110.7 |
| C(16)-C(17)-H(17A) | 120.5 | H(25A)-C(25)-H(25B) | 108.8 |
| C(17)-C(18)-C(19) | 118.2(3) | C(18)-C(26)-C(25) | 104.6(3) |
| C(17)-C(18)-C(26) | 131.8(3) | C(18)-C(26)-H(26A) | 110.8 |
| C(19)-C(18)-C(26) | 109.9(3) | C(25)-C(26)-H(26A) | 110.8 |
| C(24)-C(19)-C(18) | 110.8(3) | C(18)-C(26)-H(26B) | 110.8 |
| C(24)-C(19)-C(20) | 125.1(3) | C(25)-C(26)-H(26B) | 110.8 |
| C(18)-C(19)-C(20) | 124.1(3) | H(26A)-C(26)-H(26B) | 108.9 |
| C(19)-C(20)-C(21) | 112.7(3) | C(32)-C(27)-C(28) | 119.1(3) |
| C(19)-C(20)-C(15) | 116.1(3) | C(32)-C(27)-P(1) | 119.7(3) |
| C(21)-C(20)-C(15) | 131.1(3) | C(28)-C(27)-P(1) | 121.0(3) |
| C(22)-C(21)-C(20) | 122.3(3) | C(29)-C(28)-C(27) | 120.2(4) |
| C(22)-C(21)-Br(2) | 113.2(3) | C(29)-C(28)-H(28A) | 119.9 |
| C(20)-C(21)-Br(2) | 124.3(3) | C(27)-C(28)-H(28A) | 119.9 |
| C(21)-C(22)-C(23) | 122.2(3) | C(30)-C(29)-C(28) | 120.2(4) |
| C(21)-C(22)-H(22A) | 118.9 | C(30)-C(29)-H(29A) | 119.9 |
| C(23)-C(22)-H(22A) | 118.9 | C(28)-C(29)-H(29A) | 119.9 |
| C(24)-C(23)-C(22) | 118.2(3) | C(29)-C(30)-C(31) | 120.5(4) |
| C(24)-C(23)-H(23A) | 120.9 | C(29)-C(30)-H(30A) | 119.8 |
| C(22)-C(23)-H(23A) | 120.9 | C(31)-C(30)-H(30A) | 119.8 |
| C(23)-C(24)-C(19) | 119.3(3) | C(30)-C(31)-C(32) | 119.7(4) |
| C(23)-C(24)-C(25) | 131.1(3) | C(30)-C(31)-H(31A) | 120.2 |
| C(19)-C(24)-C(25) | 109.5(3) | C(32)-C(31)-H(31A) | 120.2 |
| C(24)-C(25)-C(26) | 105.0(3) | C(31)-C(32)-C(27) | 120.4(4) |
| C(24)-C(25)-H(25A) | 110.7 | C(31)-C(32)-H(32A) | 119.8 |
| C(26)-C(25)-H(25A) | 110.7 | C(27)-C(32)-H(32A) | 119.8 |

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for $PhP(CH_2Ar)_2(BH_3)$ (Ar = 5-bromo,6-acenaphthenyl), GLU395A. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{23}$ | $U^{13}$ | $U^{12}$ |
|---|---|---|---|---|---|---|
| P(1) | 16(1) | 19(1) | 12(1) | 1(1) | -1(1) | 2(1) |
| B(1) | 19(2) | 28(2) | 13(2) | -1(2) | -2(2) | 0(2) |
| Br(1) | 29(1) | 20(1) | 27(1) | 2(1) | -3(1) | 7(1) |
| Br(2) | 30(1) | 18(1) | 34(1) | 3(1) | -3(1) | -2(1) |
| C(1) | 20(2) | 20(2) | 13(2) | -3(2) | -2(2) | 2(2) |
| C(2) | 21(2) | 18(2) | 12(2) | -4(2) | -4(1) | 2(2) |
| C(3) | 19(2) | 24(2) | 13(2) | 0(2) | -3(2) | -1(2) |
| C(4) | 23(2) | 18(2) | 16(2) | 4(2) | -6(2) | 4(2) |
| C(5) | 20(2) | 19(2) | 13(2) | -5(2) | -6(2) | 0(2) |
| C(6) | 20(2) | 13(2) | 12(2) | -5(1) | -2(1) | -2(1) |
| C(7) | 22(2) | 15(2) | 12(2) | -6(2) | -5(1) | -3(2) |
| C(8) | 22(2) | 15(2) | 18(2) | -5(2) | -8(2) | 4(2) |
| C(9) | 31(2) | 16(2) | 20(2) | 0(2) | -5(2) | -5(2) |
| C(10) | 25(2) | 18(2) | 19(2) | -1(2) | -2(2) | -9(2) |
| C(11) | 21(2) | 20(2) | 15(2) | -6(2) | -5(2) | -4(2) |
| C(12) | 19(2) | 23(2) | 22(2) | -6(2) | -2(2) | -3(2) |
| C(13) | 21(2) | 24(2) | 19(2) | -2(2) | -5(2) | 3(2) |
| C(14) | 17(2) | 24(2) | 16(2) | 0(2) | 1(2) | 1(2) |
| C(15) | 18(2) | 20(2) | 17(2) | 0(2) | 1(2) | 2(2) |
| C(16) | 23(2) | 26(2) | 21(2) | -3(2) | -3(2) | -1(2) |
| C(17) | 25(2) | 20(2) | 27(2) | -6(2) | 0(2) | -3(2) |
| C(18) | 20(2) | 19(2) | 22(2) | -2(2) | 3(2) | 1(2) |
| C(19) | 14(2) | 20(2) | 15(2) | 0(2) | 3(1) | 3(1) |
| C(20) | 13(2) | 19(2) | 16(2) | 2(2) | 3(1) | 3(1) |
| C(21) | 20(2) | 15(2) | 21(2) | 1(2) | 2(2) | 2(2) |
| C(22) | 20(2) | 20(2) | 18(2) | -4(2) | 1(2) | -3(2) |
| C(23) | 21(2) | 28(2) | 13(2) | -3(2) | -2(2) | 0(2) |
| C(24) | 19(2) | 24(2) | 16(2) | 4(2) | 4(2) | 4(2) |
| C(25) | 26(2) | 26(2) | 21(2) | 4(2) | 3(2) | 6(2) |
| C(26) | 25(2) | 19(2) | 28(2) | 2(2) | 3(2) | 5(2) |
| C(27) | 13(2) | 19(2) | 22(2) | 3(2) | -3(2) | 1(1) |
| C(28) | 19(2) | 29(2) | 24(2) | 7(2) | -3(2) | 4(2) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C(29) | 26(2) | 34(2) | 28(2) | 15(2) | -6(2) | -1(2) |
| C(30) | 28(2) | 25(2) | 46(3) | 14(2) | -17(2) | -7(2) |
| C(31) | 27(2) | 20(2) | 43(3) | -6(2) | -9(2) | -1(2) |
| C(32) | 24(2) | 21(2) | 24(2) | -2(2) | -6(2) | -3(2) |

Table 5. Hydrogen coordinates (x $10^4$) and isotropic displacement parameters ($Å^2$ x $10^3$) for $PhP(CH_2Ar)_2(BH_3)$ (Ar = 5-bromo,6-acenaphthenyl), GLU395A.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| H(1AA) | 3009 | 6157 | 4658 | 30 |
| H(1AB) | 2420 | 7141 | 4556 | 30 |
| H(1AC) | 2306 | 5592 | 4494 | 30 |
| H(1A) | 3136 | 7954 | 7060 | 21 |
| H(1B) | 3063 | 6887 | 8017 | 21 |
| H(3A) | 3662 | 4895 | 7949 | 23 |
| H(4A) | 4634 | 3860 | 7757 | 23 |
| H(9A) | 4601 | 9309 | 4427 | 27 |
| H(10A) | 5570 | 8172 | 4376 | 25 |
| H(12A) | 6255 | 6385 | 5943 | 26 |
| H(12B) | 5980 | 5485 | 4944 | 26 |
| H(13A) | 5676 | 3978 | 6187 | 26 |
| H(13B) | 5931 | 4899 | 7187 | 26 |
| H(14A) | 1442 | 6317 | 7066 | 23 |
| H(14B) | 1883 | 7318 | 7752 | 23 |
| H(16A) | 1878 | 9466 | 7366 | 28 |
| H(17A) | 1507 | 11361 | 6482 | 29 |
| H(22A) | 362 | 6104 | 3490 | 23 |
| H(23A) | 125 | 8116 | 2616 | 25 |
| H(25A) | -4 | 10843 | 3414 | 30 |
| H(25B) | 656 | 10832 | 2779 | 30 |
| H(26A) | 1097 | 12032 | 4168 | 28 |
| H(26B) | 450 | 11957 | 4841 | 28 |
| H(28A) | 2140 | 5065 | 8509 | 29 |
| H(29A) | 2256 | 2985 | 9288 | 36 |
| H(30A) | 2669 | 1284 | 8265 | 40 |
| H(31A) | 2974 | 1635 | 6446 | 36 |
| H(32A) | 2838 | 3701 | 5638 | 28 |

Table 1. Crystal data and structure refinement for Ph-PyraPhos(O)•0.5$H_2O_2$, glu397.

| | | |
|---|---|---|
| Identification code | glu397 | |
| Empirical formula | C19 H16 O2 P | |
| Formula weight | 307.29 | |
| Temperature | 100(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Monoclinic | |
| Space group | C 2/c | |
| Unit cell dimensions | a = 14.5181(6) Å | α= 90°. |
| | b = 9.0445(4) Å | β= 105.5400(10)°. |
| | c = 22.9130(9) Å | γ = 90°. |
| Volume | 2898.7(2) $Å^3$ | |
| Z | 8 | |
| Density (calculated) | 1.408 $Mg/m^3$ | |
| Absorption coefficient | 0.194 $mm^{-1}$ | |
| F(000) | 1288 | |
| Crystal size | 0.240 x 0.230 x 0.190 $mm^3$ | |
| Theta range for data collection | 1.845 to 27.873°. | |
| Index ranges | -19<=h<=19, -10<=k<=11, -30<=l<=28 | |
| Reflections collected | 29611 | |
| Independent reflections | 3460 [R(int) = 0.0602] | |
| Completeness to theta = 25.000° | 100.0 % | |
| Absorption correction | Multi-scan | |
| Refinement method | Full-matrix least-squares on $F^2$ | |
| Data / restraints / parameters | 3460 / 0 / 202 | |
| Goodness-of-fit on $F^2$ | 1.037 | |
| Final R indices [I>2sigma(I)] | R1 = 0.0368, wR2 = 0.0965 | |
| R indices (all data) | R1 = 0.0397, wR2 = 0.0987 | |
| Extinction coefficient | n/a | |
| Largest diff. peak and hole | 0.477 and -0.383 e.$Å^{-3}$ | |

Table 2. Atomic coordinates (x $10^4$) and equivalent isotropic displacement parameters ($Å^2$ x $10^3$) for Ph-PyraPhos(O)•0.5$H_2O_2$, glu397. U(eq) is defined as one third of the trace of the orthogonalized $U^{ij}$ tensor.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| P(1) | 576(1) | 5358(1) | 3748(1) | 11(1) |
| O(1) | 893(1) | 3806(1) | 3692(1) | 14(1) |
| O(2) | 521(1) | 2535(1) | 2590(1) | 33(1) |
| C(12) | -888(1) | 9204(2) | 5586(1) | 16(1) |
| C(11) | -1088(1) | 8365(1) | 4991(1) | 14(1) |
| C(19) | -242(1) | 7642(1) | 4974(1) | 12(1) |
| C(18) | -163(1) | 6800(1) | 4482(1) | 12(1) |
| C(17) | 720(1) | 6136(1) | 4490(1) | 12(1) |
| C(1) | 1167(1) | 6607(1) | 3355(1) | 12(1) |
| C(6) | 1990(1) | 6120(1) | 3208(1) | 13(1) |
| C(5) | 2482(1) | 7069(2) | 2919(1) | 16(1) |
| C(4) | 2151(1) | 8499(2) | 2778(1) | 19(1) |
| C(13) | 193(1) | 8888(2) | 5911(1) | 15(1) |
| C(14) | 532(1) | 7857(1) | 5486(1) | 13(1) |
| C(15) | 1389(1) | 7179(2) | 5498(1) | 15(1) |
| C(16) | 1484(1) | 6320(2) | 4995(1) | 14(1) |
| C(7) | -722(1) | 5699(2) | 3485(1) | 14(1) |
| C(8) | -959(1) | 6649(1) | 3971(1) | 14(1) |
| C(10) | -1869(1) | 8198(2) | 4500(1) | 16(1) |
| C(9) | -1801(1) | 7335(2) | 3987(1) | 15(1) |
| C(3) | 1336(1) | 8998(2) | 2924(1) | 22(1) |
| C(2) | 845(1) | 8052(2) | 3215(1) | 18(1) |

Table 3. Bond lengths [Å] and angles [deg] for Ph-PyraPhos(O)•0.5$H_2O_2$, glu397.

| | | | |
|---|---|---|---|
| P(1)-O(1) | 1.4937(9) | C(17)-C(16) | 1.3825(18) |
| P(1)-C(17) | 1.7982(13) | C(1)-C(2) | 1.3964(18) |
| P(1)-C(1) | 1.7999(13) | C(1)-C(6) | 1.3971(17) |
| P(1)-C(7) | 1.8445(13) | C(6)-C(5) | 1.3928(18) |
| O(2)-O(2)#1 | 1.457(2) | C(5)-C(4) | 1.387(2) |
| C(12)-C(11) | 1.5205(18) | C(4)-C(3) | 1.389(2) |
| C(12)-C(13) | 1.5731(19) | C(13)-C(14) | 1.5224(18) |
| C(11)-C(10) | 1.3755(19) | C(14)-C(15) | 1.3802(19) |
| C(11)-C(19) | 1.4016(18) | C(15)-C(16) | 1.4279(18) |
| C(19)-C(18) | 1.3885(18) | C(7)-C(8) | 1.5177(18) |
| C(19)-C(14) | 1.4041(18) | C(8)-C(9) | 1.3795(18) |
| C(18)-C(17) | 1.4121(17) | C(10)-C(9) | 1.4363(19) |
| C(18)-C(8) | 1.4147(18) | C(3)-C(2) | 1.3917(19) |

| | | | |
|---|---|---|---|
| O(1)-P(1)-C(17) | 119.26(6) | C(2)-C(1)-P(1) | 121.83(10) |
| O(1)-P(1)-C(1) | 110.34(6) | C(6)-C(1)-P(1) | 118.42(10) |
| C(17)-P(1)-C(1) | 106.06(6) | C(5)-C(6)-C(1) | 120.05(12) |
| O(1)-P(1)-C(7) | 116.13(6) | C(4)-C(5)-C(6) | 119.70(13) |
| C(17)-P(1)-C(7) | 95.38(6) | C(5)-C(4)-C(3) | 120.79(12) |
| C(1)-P(1)-C(7) | 108.29(6) | C(14)-C(13)-C(12) | 105.15(11) |
| C(11)-C(12)-C(13) | 105.06(10) | C(15)-C(14)-C(19) | 118.06(12) |
| C(10)-C(11)-C(19) | 117.56(12) | C(15)-C(14)-C(13) | 134.65(12) |
| C(10)-C(11)-C(12) | 134.95(12) | C(19)-C(14)-C(13) | 107.27(11) |
| C(19)-C(11)-C(12) | 107.48(11) | C(14)-C(15)-C(16) | 120.45(12) |
| C(18)-C(19)-C(11) | 122.80(12) | C(17)-C(16)-C(15) | 120.86(12) |
| C(18)-C(19)-C(14) | 122.17(12) | C(8)-C(7)-P(1) | 105.49(9) |
| C(11)-C(19)-C(14) | 115.01(12) | C(9)-C(8)-C(18) | 117.93(12) |
| C(19)-C(18)-C(17) | 119.72(12) | C(9)-C(8)-C(7) | 130.53(12) |
| C(19)-C(18)-C(8) | 119.84(12) | C(18)-C(8)-C(7) | 111.54(11) |
| C(17)-C(18)-C(8) | 120.42(12) | C(11)-C(10)-C(9) | 120.44(12) |
| C(16)-C(17)-C(18) | 118.71(12) | C(8)-C(9)-C(10) | 121.41(12) |
| C(16)-C(17)-P(1) | 134.67(10) | C(4)-C(3)-C(2) | 119.60(13) |
| C(18)-C(17)-P(1) | 106.26(9) | C(3)-C(2)-C(1) | 120.14(13) |
| C(2)-C(1)-C(6) | 119.72(12) | | |

Symmetry transformations used to generate equivalent atoms:

#1 -x,y,-z+1/2

Table 4. Anisotropic displacement parameters ($Å^2$x $10^3$) for Ph-PyraPhos(O)•0.5$H_2O_2$, glu397. The anisotropic displacement factor exponent takes the form: $-2\pi^2[ h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12} ]$

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{23}$ | $U^{13}$ | $U^{12}$ |
|---|---|---|---|---|---|---|
| P(1) | 11(1) | 11(1) | 10(1) | 0(1) | 3(1) | -1(1) |
| O(1) | 15(1) | 11(1) | 15(1) | 1(1) | 3(1) | -1(1) |
| O(2) | 34(1) | 41(1) | 21(1) | -7(1) | 2(1) | 21(1) |
| C(12) | 19(1) | 14(1) | 17(1) | -1(1) | 9(1) | -1(1) |
| C(11) | 15(1) | 13(1) | 16(1) | 2(1) | 8(1) | -2(1) |
| C(19) | 14(1) | 12(1) | 13(1) | 2(1) | 6(1) | -2(1) |
| C(18) | 12(1) | 13(1) | 12(1) | 2(1) | 4(1) | -2(1) |
| C(17) | 13(1) | 14(1) | 11(1) | 1(1) | 4(1) | -2(1) |
| C(1) | 14(1) | 12(1) | 9(1) | -1(1) | 3(1) | -3(1) |
| C(6) | 15(1) | 14(1) | 9(1) | -2(1) | 3(1) | -2(1) |
| C(5) | 16(1) | 22(1) | 10(1) | -3(1) | 5(1) | -7(1) |
| C(4) | 26(1) | 20(1) | 12(1) | 1(1) | 4(1) | -11(1) |
| C(13) | 18(1) | 15(1) | 14(1) | -1(1) | 7(1) | -3(1) |
| C(14) | 16(1) | 14(1) | 11(1) | 1(1) | 5(1) | -4(1) |
| C(15) | 13(1) | 19(1) | 10(1) | 0(1) | 1(1) | -3(1) |
| C(16) | 12(1) | 17(1) | 14(1) | 1(1) | 3(1) | 0(1) |
| C(7) | 11(1) | 19(1) | 12(1) | -1(1) | 1(1) | -1(1) |
| C(8) | 13(1) | 15(1) | 14(1) | 2(1) | 4(1) | -2(1) |
| C(10) | 13(1) | 17(1) | 19(1) | 4(1) | 6(1) | 1(1) |
| C(9) | 10(1) | 18(1) | 15(1) | 4(1) | 1(1) | -2(1) |
| C(3) | 30(1) | 14(1) | 21(1) | 4(1) | 6(1) | -2(1) |
| C(2) | 21(1) | 14(1) | 19(1) | 2(1) | 7(1) | 2(1) |

Table 5. Hydrogen coordinates ( x $10^4$) and isotropic displacement parameters ($Å^2$x $10^3$) for Ph-PyraPhos(O)•0.5$H_2O_2$, glu397.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| H(16) | 617(17) | 2950(30) | 2957(11) | 50 |
| H(12A) | -1304 | 8845 | 5835 | 19 |
| H(12B) | -999 | 10277 | 5514 | 19 |
| H(6A) | 2215 | 5140 | 3305 | 15 |
| H(5A) | 3042 | 6739 | 2818 | 19 |
| H(4A) | 2486 | 9144 | 2580 | 23 |
| H(13A) | 568 | 9817 | 5974 | 18 |
| H(13B) | 260 | 8411 | 6309 | 18 |
| H(15A) | 1919 | 7284 | 5844 | 17 |
| H(16A) | 2080 | 5869 | 5008 | 17 |
| H(7A) | -886 | 6223 | 3091 | 17 |
| H(7B) | -1080 | 4756 | 3437 | 17 |
| H(10A) | -2458 | 8656 | 4500 | 19 |
| H(9A) | -2347 | 7234 | 3651 | 18 |
| H(3A) | 1115 | 9980 | 2827 | 26 |
| H(2A) | 289 | 8390 | 3318 | 21 |

Table 1. Crystal data and structure refinement for [Pt((*R,R*)-Me-DuPhos)($\kappa^2$-(P,C)-5-$PPh_2CH_2$-6-$C_{12}H_8$)][$PF_6$], glu421.

| | | |
|---|---|---|
| Identification code | glu421 | |
| Empirical formula | C43 H48 F6 P4 Pt | |
| Formula weight | 997.78 | |
| Temperature | 100(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Orthorhombic | |
| Space group | P 21 21 21 | |
| Unit cell dimensions | a = 11.698(3) Å | α= 90°. |
| | b = 17.675(3) Å | β= 90°. |
| | c = 19.808(5) Å | γ = 90°. |
| Volume | 4095.7(15) $Å^3$ | |
| Z | 4 | |
| Density (calculated) | 1.618 $Mg/m^3$ | |
| Absorption coefficient | 3.640 $mm^{-1}$ | |
| F(000) | 1992 | |
| Crystal size | 0.472 x 0.271 x 0.232 $mm^3$ | |
| Theta range for data collection | 2.305 to 28.307°. | |
| Index ranges | -15<=h<=15, -23<=k<=20, -26<=l<=19 | |
| Reflections collected | 23377 | |
| Independent reflections | 9979 [R(int) = 0.0671] | |
| Completeness to theta = 25.000° | 99.8 % | |
| Absorption correction | Analytical | |
| Refinement method | Full-matrix least-squares on $F^2$ | |
| Data / restraints / parameters | 9979 / 0 / 491 | |
| Goodness-of-fit on $F^2$ | 0.888 | |
| Final R indices [I>2sigma(I)] | R1 = 0.0413, wR2 = 0.0803 | |
| R indices (all data) | R1 = 0.0524, wR2 = 0.0855 | |
| Absolute structure parameter | 0.003(6) | |
| Extinction coefficient | n/a | |
| Largest diff. peak and hole | 1.117 and -1.113 e.$Å^{-3}$ | |

Table 2. Atomic coordinates (x $10^4$) and equivalent isotropic displacement parameters ($Å^2$ x $10^3$) for [Pt((*R,R*)-Me-DuPhos)($\kappa^2$-(P,C)-5-$PPh_2CH_2$-6-$C_{12}H_8$)][$PF_6$], glu421. U(eq) is defined as one third of the trace of the orthogonalized $U^{ij}$ tensor.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| Pt(1) | 5646(1) | 4319(1) | 2297(1) | 11(1) |
| P(1) | 3753(2) | 4581(1) | 2462(1) | 13(1) |
| P(2) | 5851(2) | 4517(1) | 1148(1) | 12(1) |
| P(3) | 7522(2) | 3898(1) | 2232(1) | 16(1) |
| C(1) | 7840(7) | 3681(5) | 1350(4) | 16(2) |
| C(2) | 8829(8) | 3301(5) | 1160(4) | 20(2) |
| C(3) | 9060(8) | 3180(5) | 479(4) | 20(2) |
| C(4) | 8315(8) | 3466(5) | -5(4) | 22(2) |
| C(5) | 7360(8) | 3852(6) | 178(4) | 23(2) |
| C(6) | 7097(8) | 3985(5) | 864(4) | 16(2) |
| C(7) | 4707(7) | 4339(5) | 527(3) | 16(2) |
| C(8) | 4518(9) | 3529(5) | 322(4) | 24(2) |
| C(9) | 4899(8) | 4926(5) | -45(4) | 20(2) |
| C(10) | 5266(7) | 5670(6) | 297(3) | 21(2) |
| C(11) | 6124(7) | 5508(4) | 878(3) | 14(2) |
| C(12) | 6006(9) | 6086(5) | 1453(4) | 23(2) |
| C(13) | 8073(8) | 3084(5) | 2728(5) | 24(2) |
| C(14) | 7189(9) | 2604(5) | 3086(5) | 31(2) |
| C(15) | 8996(8) | 3414(6) | 3187(4) | 28(2) |
| C(16) | 9591(8) | 4059(5) | 2813(4) | 29(2) |
| C(17) | 8694(9) | 4572(5) | 2485(4) | 23(2) |
| C(18) | 9158(9) | 5057(5) | 1918(4) | 28(2) |
| C(19) | 5606(8) | 4167(4) | 3352(3) | 12(2) |
| C(20) | 6505(7) | 4483(5) | 3723(4) | 18(2) |
| C(21) | 6705(7) | 4336(6) | 4415(3) | 19(2) |
| C(22) | 6005(7) | 3854(5) | 4748(4) | 17(2) |
| C(23) | 5957(8) | 3591(5) | 5485(4) | 23(2) |
| C(24) | 5000(8) | 2984(5) | 5486(4) | 17(2) |
| C(25) | 4358(9) | 3108(4) | 4826(3) | 16(2) |
| C(26) | 5045(8) | 3558(5) | 4404(4) | 14(2) |

| | | | | |
|---|---|---|---|---|
| C(27) | 4779(7) | 3744(4) | 3724(4) | 12(2) |
| C(28) | 3657(7) | 3498(5) | 3514(3) | 14(2) |
| C(29) | 2968(8) | 3092(5) | 3938(4) | 17(2) |
| C(30) | 3322(8) | 2863(5) | 4592(4) | 18(2) |
| C(31) | 3161(8) | 3714(5) | 2829(4) | 20(2) |
| C(32) | 2809(7) | 4760(5) | 1754(4) | 15(2) |
| C(33) | 2249(7) | 4176(5) | 1419(4) | 19(2) |
| C(34) | 1649(7) | 4327(7) | 818(4) | 26(2) |
| C(35) | 1625(8) | 5035(6) | 551(4) | 26(2) |
| C(36) | 2164(7) | 5630(6) | 891(4) | 24(2) |
| C(37) | 2738(8) | 5497(5) | 1490(4) | 22(2) |
| C(38) | 3496(8) | 5384(5) | 3024(4) | 18(2) |
| C(39) | 2394(8) | 5557(6) | 3234(4) | 25(2) |
| C(40) | 2204(9) | 6185(6) | 3641(4) | 30(2) |
| C(41) | 3115(9) | 6653(6) | 3827(4) | 29(2) |
| C(42) | 4206(10) | 6494(5) | 3599(4) | 31(2) |
| C(43) | 4416(9) | 5858(5) | 3196(4) | 22(2) |
| P(4) | 8445(2) | 6860(2) | 3197(1) | 26(1) |
| F(1) | 8062(7) | 6567(4) | 2490(3) | 60(2) |
| F(2) | 8875(6) | 7639(3) | 2861(3) | 43(2) |
| F(3) | 9683(6) | 6509(4) | 3081(4) | 62(2) |
| F(4) | 8840(7) | 7173(4) | 3916(3) | 54(2) |
| F(5) | 8005(8) | 6105(4) | 3551(3) | 64(2) |
| F(6) | 7218(6) | 7241(4) | 3324(3) | 49(2) |

Table 3. Bond lengths [Å] and angles [deg] for [Pt((*R,R*)-Me-DuPhos)($\kappa^2$-(P,C)-5-$PPh_2CH_2$-6-$C_{12}H_8$)][$PF_6$], glu421.

| | | | |
|---|---|---|---|
| Pt(1)-C(19) | 2.107(6) | C(20)-C(21) | 1.416(10) |
| Pt(1)-P(1) | 2.286(2) | C(21)-C(22) | 1.353(12) |
| Pt(1)-P(2) | 2.3146(18) | C(22)-C(26) | 1.414(12) |
| Pt(1)-P(3) | 2.321(2) | C(22)-C(23) | 1.532(10) |
| P(1)-C(32) | 1.813(8) | C(23)-C(24) | 1.552(12) |
| P(1)-C(38) | 1.828(9) | C(24)-C(25) | 1.523(11) |
| P(1)-C(31) | 1.832(9) | C(25)-C(30) | 1.367(13) |
| P(2)-C(6) | 1.824(9) | C(25)-C(26) | 1.407(11) |
| P(2)-C(7) | 1.845(7) | C(26)-C(27) | 1.422(10) |
| P(2)-C(11) | 1.859(8) | C(27)-C(28) | 1.444(11) |
| P(3)-C(1) | 1.827(8) | C(28)-C(29) | 1.368(11) |
| P(3)-C(13) | 1.858(8) | C(28)-C(31) | 1.525(10) |
| P(3)-C(17) | 1.884(10) | C(29)-C(30) | 1.421(11) |
| C(1)-C(2) | 1.389(12) | C(32)-C(33) | 1.391(12) |
| C(1)-C(6) | 1.405(11) | C(32)-C(37) | 1.407(12) |
| C(2)-C(3) | 1.394(11) | C(33)-C(34) | 1.406(11) |
| C(3)-C(4) | 1.390(12) | C(34)-C(35) | 1.359(15) |
| C(4)-C(5) | 1.358(13) | C(35)-C(36) | 1.398(14) |
| C(5)-C(6) | 1.413(10) | C(36)-C(37) | 1.383(11) |
| C(7)-C(8) | 1.505(12) | C(38)-C(39) | 1.388(12) |
| C(7)-C(9) | 1.553(11) | C(38)-C(43) | 1.406(12) |
| C(9)-C(10) | 1.541(13) | C(39)-C(40) | 1.390(13) |
| C(10)-C(11) | 1.553(11) | C(40)-C(41) | 1.398(15) |
| C(11)-C(12) | 1.537(10) | C(41)-C(42) | 1.383(15) |
| C(13)-C(14) | 1.514(13) | C(42)-C(43) | 1.400(12) |
| C(13)-C(15) | 1.526(13) | P(4)-F(1) | 1.559(6) |
| C(15)-C(16) | 1.527(13) | P(4)-F(3) | 1.592(8) |
| C(16)-C(17) | 1.531(13) | P(4)-F(5) | 1.593(7) |
| C(17)-C(18) | 1.514(11) | P(4)-F(4) | 1.597(6) |
| C(19)-C(20) | 1.399(11) | P(4)-F(6) | 1.605(7) |
| C(19)-C(27) | 1.427(11) | P(4)-F(2) | 1.610(6) |
| | | | |
| C(19)-Pt(1)-P(1) | 82.1(2) | P(1)-Pt(1)-P(2) | 102.17(7) |
| C(19)-Pt(1)-P(2) | 175.1(3) | C(19)-Pt(1)-P(3) | 92.0(2) |

| | | | |
|---|---|---|---|
| P(1)-Pt(1)-P(3) | 171.44(7) | C(12)-C(11)-P(2) | 113.4(5) |
| P(2)-Pt(1)-P(3) | 84.06(7) | C(10)-C(11)-P(2) | 106.0(6) |
| C(32)-P(1)-C(38) | 103.7(4) | C(14)-C(13)-C(15) | 114.8(8) |
| C(32)-P(1)-C(31) | 102.8(4) | C(14)-C(13)-P(3) | 116.3(7) |
| C(38)-P(1)-C(31) | 110.3(4) | C(15)-C(13)-P(3) | 105.3(6) |
| C(32)-P(1)-Pt(1) | 120.9(3) | C(13)-C(15)-C(16) | 108.6(7) |
| C(38)-P(1)-Pt(1) | 113.8(3) | C(15)-C(16)-C(17) | 109.6(8) |
| C(31)-P(1)-Pt(1) | 104.7(3) | C(18)-C(17)-C(16) | 113.9(8) |
| C(6)-P(2)-C(7) | 106.6(4) | C(18)-C(17)-P(3) | 115.0(6) |
| C(6)-P(2)-C(11) | 105.0(4) | C(16)-C(17)-P(3) | 103.7(6) |
| C(7)-P(2)-C(11) | 95.4(4) | C(20)-C(19)-C(27) | 116.6(6) |
| C(6)-P(2)-Pt(1) | 108.0(3) | C(20)-C(19)-Pt(1) | 116.9(6) |
| C(7)-P(2)-Pt(1) | 123.7(2) | C(27)-C(19)-Pt(1) | 126.4(6) |
| C(11)-P(2)-Pt(1) | 116.3(2) | C(19)-C(20)-C(21) | 124.0(8) |
| C(1)-P(3)-C(13) | 105.8(4) | C(22)-C(21)-C(20) | 119.2(8) |
| C(1)-P(3)-C(17) | 103.8(4) | C(21)-C(22)-C(26) | 118.6(7) |
| C(13)-P(3)-C(17) | 95.5(4) | C(21)-C(22)-C(23) | 132.6(8) |
| C(1)-P(3)-Pt(1) | 108.2(3) | C(26)-C(22)-C(23) | 108.5(7) |
| C(13)-P(3)-Pt(1) | 123.2(3) | C(22)-C(23)-C(24) | 103.7(6) |
| C(17)-P(3)-Pt(1) | 118.1(3) | C(25)-C(24)-C(23) | 104.8(6) |
| C(2)-C(1)-C(6) | 121.0(7) | C(30)-C(25)-C(26) | 119.0(7) |
| C(2)-C(1)-P(3) | 122.0(6) | C(30)-C(25)-C(24) | 133.0(7) |
| C(6)-C(1)-P(3) | 116.7(6) | C(26)-C(25)-C(24) | 108.0(8) |
| C(1)-C(2)-C(3) | 119.9(8) | C(25)-C(26)-C(22) | 112.2(7) |
| C(4)-C(3)-C(2) | 119.3(8) | C(25)-C(26)-C(27) | 124.7(8) |
| C(5)-C(4)-C(3) | 121.0(8) | C(22)-C(26)-C(27) | 123.0(7) |
| C(4)-C(5)-C(6) | 121.3(8) | C(26)-C(27)-C(19) | 117.5(7) |
| C(1)-C(6)-C(5) | 117.4(8) | C(26)-C(27)-C(28) | 113.7(7) |
| C(1)-C(6)-P(2) | 118.7(6) | C(19)-C(27)-C(28) | 128.7(7) |
| C(5)-C(6)-P(2) | 123.9(7) | C(29)-C(28)-C(27) | 121.2(7) |
| C(8)-C(7)-C(9) | 117.4(6) | C(29)-C(28)-C(31) | 116.9(8) |
| C(8)-C(7)-P(2) | 116.7(6) | C(27)-C(28)-C(31) | 121.8(7) |
| C(9)-C(7)-P(2) | 105.5(6) | C(28)-C(29)-C(30) | 122.6(8) |
| C(10)-C(9)-C(7) | 106.9(6) | C(25)-C(30)-C(29) | 118.5(8) |
| C(9)-C(10)-C(11) | 110.4(7) | C(28)-C(31)-P(1) | 114.7(6) |
| C(12)-C(11)-C(10) | 111.7(7) | C(33)-C(32)-C(37) | 118.8(7) |

| | | | |
|---|---|---|---|
| C(33)-C(32)-P(1) | 121.9(7) | F(1)-P(4)-F(3) | 90.1(4) |
| C(37)-C(32)-P(1) | 119.0(7) | F(1)-P(4)-F(5) | 91.4(4) |
| C(32)-C(33)-C(34) | 119.9(9) | F(3)-P(4)-F(5) | 91.8(5) |
| C(35)-C(34)-C(33) | 120.9(9) | F(1)-P(4)-F(4) | 179.1(4) |
| C(34)-C(35)-C(36) | 119.7(8) | F(3)-P(4)-F(4) | 90.0(4) |
| C(37)-C(36)-C(35) | 120.3(9) | F(5)-P(4)-F(4) | 89.4(4) |
| C(36)-C(37)-C(32) | 120.4(9) | F(1)-P(4)-F(6) | 91.3(4) |
| C(39)-C(38)-C(43) | 120.5(8) | F(3)-P(4)-F(6) | 178.0(4) |
| C(39)-C(38)-P(1) | 120.4(7) | F(5)-P(4)-F(6) | 89.6(4) |
| C(43)-C(38)-P(1) | 118.9(7) | F(4)-P(4)-F(6) | 88.5(4) |
| C(38)-C(39)-C(40) | 119.9(9) | F(1)-P(4)-F(2) | 90.2(4) |
| C(39)-C(40)-C(41) | 120.2(9) | F(3)-P(4)-F(2) | 89.4(4) |
| C(42)-C(41)-C(40) | 119.8(8) | F(5)-P(4)-F(2) | 178.0(4) |
| C(41)-C(42)-C(43) | 120.8(9) | F(4)-P(4)-F(2) | 89.0(3) |
| C(42)-C(43)-C(38) | 118.8(9) | F(6)-P(4)-F(2) | 89.2(4) |

Table 4. Anisotropic displacement parameters ($Å^2$ x $10^3$) for [Pt((*R,R*)-Me-DuPhos)($\kappa^2$-(P,C)-5-$PPh_2CH_2$-6-$C_{12}H_8$)] [$PF_6$], glu421. The anisotropic displacement factor exponent takes the form: $-2\pi^2[ h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12} ]$

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{23}$ | $U^{13}$ | $U^{12}$ |
|---|---|---|---|---|---|---|
| Pt(1) | 12(1) | 11(1) | 10(1) | 2(1) | -1(1) | 0(1) |
| P(1) | 11(1) | 15(1) | 13(1) | 2(1) | -1(1) | -3(1) |
| P(2) | 13(1) | 11(1) | 11(1) | 2(1) | -1(1) | 0(1) |
| P(3) | 19(1) | 17(1) | 13(1) | 1(1) | -3(1) | 6(1) |
| C(1) | 14(5) | 16(4) | 18(4) | -5(3) | -2(3) | 2(3) |
| C(2) | 17(5) | 16(4) | 27(4) | -9(3) | -6(4) | 2(4) |
| C(3) | 14(5) | 21(5) | 26(4) | -9(3) | 3(3) | 5(4) |
| C(4) | 24(5) | 23(5) | 19(4) | -5(3) | 4(4) | 3(4) |
| C(5) | 21(5) | 31(5) | 17(4) | -6(4) | 1(3) | 5(4) |
| C(6) | 18(5) | 13(4) | 18(4) | -3(3) | 0(3) | 0(4) |
| C(7) | 16(4) | 24(4) | 9(3) | 2(3) | -2(3) | -2(4) |
| C(8) | 27(6) | 23(5) | 22(4) | -6(3) | 1(4) | 0(4) |
| C(9) | 16(5) | 30(5) | 13(3) | 4(3) | -2(3) | 6(4) |
| C(10) | 24(5) | 24(4) | 14(3) | 6(4) | -1(3) | -2(4) |
| C(11) | 15(4) | 13(4) | 13(3) | -1(3) | 4(3) | -2(3) |
| C(12) | 32(6) | 11(4) | 24(4) | -2(3) | 2(4) | -4(4) |
| C(13) | 27(5) | 16(4) | 29(4) | 6(4) | -2(5) | 7(4) |
| C(14) | 40(7) | 15(5) | 39(5) | 10(4) | -2(5) | -1(4) |
| C(15) | 23(6) | 38(6) | 23(4) | 15(4) | -10(4) | 1(4) |
| C(16) | 19(5) | 35(5) | 32(5) | 2(4) | -5(4) | 0(4) |
| C(17) | 28(5) | 23(5) | 17(4) | 1(3) | -1(3) | -1(4) |
| C(18) | 26(6) | 34(5) | 25(4) | -2(4) | 8(4) | -8(5) |
| C(19) | 11(4) | 13(4) | 13(3) | -2(2) | -3(3) | 3(4) |
| C(20) | 17(5) | 22(5) | 14(3) | 3(3) | 0(3) | -3(4) |
| C(21) | 14(4) | 28(4) | 16(3) | 0(4) | -6(3) | 9(4) |
| C(22) | 17(5) | 21(4) | 12(3) | -1(3) | -1(3) | 5(4) |
| C(23) | 29(6) | 27(5) | 14(4) | 1(3) | 1(3) | 5(4) |
| C(24) | 20(5) | 20(4) | 12(3) | 4(3) | 0(3) | 2(4) |
| C(25) | 21(4) | 16(4) | 11(3) | -2(3) | 6(4) | 7(4) |
| C(26) | 18(5) | 12(4) | 12(3) | 1(3) | 2(3) | 3(3) |
| C(27) | 12(4) | 12(4) | 12(3) | -2(3) | 1(3) | 0(3) |
| C(28) | 16(5) | 15(4) | 9(3) | -2(3) | 0(3) | 0(4) |
| C(29) | 17(5) | 16(4) | 16(4) | -1(3) | 6(3) | -3(4) |
| C(30) | 26(5) | 12(4) | 16(4) | 4(3) | 8(3) | 1(4) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C(31) | 17(5) | 27(5) | 18(4) | 5(3) | 1(3) | -5(4) |
| C(32) | 6(4) | 24(5) | 16(4) | 2(3) | 0(3) | 0(3) |
| C(33) | 17(5) | 25(5) | 16(3) | 2(3) | 1(3) | -5(4) |
| C(34) | 14(5) | 43(6) | 21(4) | -2(5) | -4(3) | -8(5) |
| C(35) | 20(5) | 42(6) | 16(4) | 4(4) | -4(4) | 9(4) |
| C(36) | 21(5) | 30(5) | 21(4) | 9(4) | 4(3) | 19(5) |
| C(37) | 20(5) | 22(5) | 23(4) | -1(3) | 5(3) | 7(4) |
| C(38) | 18(5) | 26(5) | 11(3) | 1(3) | 1(3) | 1(4) |
| C(39) | 21(5) | 34(6) | 21(4) | -2(4) | -4(3) | 7(4) |
| C(40) | 18(5) | 41(6) | 29(5) | -8(4) | 4(4) | 17(5) |
| C(41) | 37(6) | 27(5) | 24(4) | -14(4) | -8(4) | 11(5) |
| C(42) | 29(6) | 28(5) | 35(5) | -10(4) | -14(5) | 0(5) |
| C(43) | 17(5) | 23(5) | 29(4) | -6(3) | -8(4) | 2(4) |
| P(4) | 27(2) | 24(1) | 28(1) | 0(1) | -9(1) | -6(1) |
| F(1) | 67(5) | 72(5) | 41(4) | -21(3) | -13(3) | -12(4) |
| F(2) | 49(4) | 36(4) | 44(4) | 10(3) | 16(3) | 4(3) |
| F(3) | 48(5) | 59(5) | 79(5) | -6(4) | -22(4) | 26(4) |
| F(4) | 82(6) | 46(4) | 33(3) | -2(3) | -16(3) | -22(4) |
| F(5) | 100(7) | 28(4) | 63(4) | 1(3) | 7(4) | -21(4) |
| F(6) | 36(4) | 56(5) | 54(4) | 4(3) | 12(3) | 5(3) |

Table 5. Hydrogen coordinates (x $10^4$) and isotropic displacement parameters (Å$^2$ x $10^3$) for [Pt((*R,R*)-Me-DuPhos)(κ$^2$-(P,C)-5-$PPh_2CH_2$-6-$C_{12}H_8$)][$PF_6$], glu421.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| H(02) | 9347 | 3125 | 1495 | 24 |
| H(03) | 9720 | 2905 | 346 | 24 |
| H(04) | 8476 | 3390 | -470 | 26 |
| H(05) | 6860 | 4036 | -162 | 28 |
| H(07) | 3984 | 4497 | 755 | 20 |
| H(08A) | 5169 | 3354 | 51 | 36 |
| H(08B) | 3816 | 3491 | 53 | 36 |
| H(08C) | 4447 | 3213 | 726 | 36 |
| H(09A) | 5502 | 4749 | -358 | 23 |
| H(09B) | 4185 | 5002 | -305 | 23 |
| H(10A) | 4584 | 5931 | 480 | 25 |
| H(10B) | 5627 | 6007 | -40 | 25 |
| H(11) | 6918 | 5540 | 692 | 16 |
| H(12A) | 5226 | 6070 | 1633 | 34 |
| H(12B) | 6167 | 6595 | 1281 | 34 |
| H(12C) | 6550 | 5962 | 1813 | 34 |
| H(13) | 8473 | 2743 | 2401 | 29 |
| H(14A) | 6882 | 2884 | 3472 | 47 |
| H(14B) | 7545 | 2135 | 3244 | 47 |
| H(14C) | 6567 | 2483 | 2772 | 47 |
| H(15A) | 9558 | 3017 | 3306 | 34 |
| H(15B) | 8646 | 3605 | 3609 | 34 |
| H(16A) | 10104 | 3850 | 2463 | 34 |
| H(16B) | 10060 | 4356 | 3134 | 34 |
| H(17) | 8385 | 4916 | 2841 | 27 |
| H(18A) | 9498 | 4732 | 1571 | 42 |
| H(18B) | 9742 | 5401 | 2097 | 42 |
| H(18C) | 8534 | 5353 | 1720 | 42 |
| H(20) | 7012 | 4818 | 3496 | 21 |
| H(21) | 7323 | 4573 | 4643 | 23 |
| H(23A) | 5762 | 4016 | 5789 | 28 |
| H(23B) | 6697 | 3371 | 5627 | 28 |
| H(24B) | 5330 | 2468 | 5503 | 21 |

| | | | | |
|---|---|---|---|---|
| H(24A) | 4485 | 3052 | 5877 | 21 |
| H(29) | 2223 | 2958 | 3788 | 20 |
| H(30) | 2851 | 2546 | 4862 | 21 |
| H(31A) | 2324 | 3776 | 2877 | 24 |
| H(31B) | 3294 | 3292 | 2510 | 24 |
| H(33) | 2271 | 3677 | 1595 | 23 |
| H(34) | 1255 | 3928 | 596 | 31 |
| H(35) | 1244 | 5126 | 136 | 31 |
| H(36) | 2135 | 6127 | 710 | 29 |
| H(37) | 3087 | 5906 | 1723 | 26 |
| H(39) | 1772 | 5246 | 3100 | 30 |
| H(40) | 1453 | 6297 | 3794 | 35 |
| H(41) | 2985 | 7079 | 4109 | 35 |
| H(42) | 4820 | 6819 | 3718 | 37 |
| H(43) | 5167 | 5748 | 3042 | 27 |

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