Electronic Supplementary Material (ESI) for Dalton Transactions.


# Sterically Hindered Ortho-Substituted Phosphatriptycenes as Configurationally Stable P-Chirogenic Triarylphosphines

Lei Hu,[a,b] Damien Mahaut,[a] Nikolay Tumanov,[a] Johan Wouters,[a] Laurent Collard,[b]

Raphaël Robiette,*[,b] Guillaume Berionni*[,a]

a University of Namur, Department of Chemistry, Namur Institute of Structured Matter. Rue de Bruxelles 61, 5000 Namur, Belgium

b Université catholique de Louvain, Institute of Condensed Matter and Nanosciences. Place Louis Pasteur 1 box L4.01.02, 1348 Louvain-la-Neuve, Belgium

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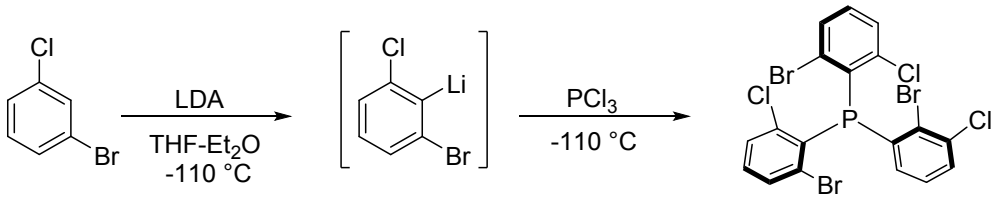
## 1. General Experimental procedures

### 1.1 General information

Commercial reagents were used as received from Sigma Aldrich, ABCR, TCI, FluoroChem (> 97% purity), and used without further purification. Unless otherwise noted, all reactions were carried out using purified and dried solvents in a Schlenk flask or in a high-performance glovebox under an inert atmosphere (Argon or Nitrogen). Dichloromethane (DCM), diethyl ether ($Et_2O$), tetrahydrofuran (THF), and toluene were dried over a Pure Solv$^{TM}$ solvent purification system. Thin layer chromatography was performed using Merck aluminum roll silica gel 60-F254 monitored by UV light at 254 nm. Flash chromatography was performed using silica gel Silica Flash® 40-63 micron (230-400 mesh). TLC detection was accomplished by irradiation with a UV lamp at 265 or 313 nm. $^{1}H$ and $^{13}C$ nuclear magnetic resonance (NMR) spectra were obtained on a JEOL ECX 400 MHz or 500 MHz in $CDCl_3$ or $CD_2Cl_2$ or $CD_3CN$. The chemical shifts ($\delta$) reported are given in parts per million (ppm). The signal splitting patterns were described as s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublet, dt = doublet of triplet, td = triplet of doublet, tt = triplet of triplet, ddd = doublet of doublet of doublet, bs= broad, and m = multiplet, with coupling constants (*J*) in hertz (Hz). Chemical shifts (δ) are reported in ppm and referenced indirectly to residual solvent signals. Infrared (IR): The IR spectra were acquired on a Perkin-Elmer Spectrum II FT-IR System UATR mounted with a diamond crystal on neat compounds. Selected absorption bands are reported by wavenumber ($cm^{-1}$). The spectra were measured between wavenumbers of 4000-450 $cm^{-1}$. High resolution mass spectra (HRMS) were recorded on a *Thermo Orbitrap Exactive* device and performed by the Molecular Structural Analysis (ASM) technological platform of the Université catholique de Louvain (UCLouvain). 2-Br-3-$CF_3$-benzaldehyde,[1] diarylmethanol compound **21**,[2] and 9-phosphatriptycene[3] were prepared according to literature procedures.

### 1.2 General procedure and characterization data for bis-(2-bromo-6-chlorophenyl)-(2-bromo-3-chlorophenyl)-phosphine 13a




**13a** 41%

Under an argon atmosphere, a 2.5 M solution of *n*-BuLi (17.0 mL, 42.56 mmol, 1.0 equiv) in hexane was added dropwise to a solution of diisopropylamine (6.0 mL, 42.56 mmol, 1.0 equiv.) in THF-ether (1:1, 40 mL) at -110 °C. After stirring for 30 min, a solution of 1-bromo-3-chloro-benzene (5.0 mL, 42.56 mmol, 1.0 equiv) in THF-ether (1:1, 15 mL) was added dropwise and stirred for 2 additional hours at the same temperature. Then, a solution of $PCl_3$ (1.1 mL, 12.8 mmol, 0.3 equiv) in 10 mL of THF-ether (1:1) was added dropwise to the reaction mixture. After maintaining the temperature at -110 °C for 2 hours, the resulting solution was allowed to warm up to room temperature overnight. The reaction mixture was quenched with a saturated solution of $NH_4Cl$ (80 mL) and the subsequent aqueous layer was extracted three times with EtOAc (80 mL). The gathered organic layers were washed with brine, dried over $MgSO_4$ and concentrated under reduced pressure. The resulting crude product was purified by flash chromatography on silica gel (cyclohexane: AcOEt = 20:1) to provide **13a** as a colourless solid (3.1 g, 5.2 mmol, 41%). Crystals suitable for X-ray diffraction analysis were obtained by slow evaporation of a saturated solution of the phosphine **13a** in AcOEt.

$^1$H NMR (400 MHz, $CDCl_3$) δ 7.57 (ddd, *J* = 8.0, 3.2, 1.2 Hz, 1H), 7.53 (ddd, *J* = 7.9, 3.1, 1.2 Hz, 1H), 7.46 (dt, *J* = 7.9, 1.5 Hz, 1H), 7.37 (dt, *J* = 8.0, 1.1 Hz, 1H), 7.32 (dt, *J* = 8.0, 1.3 Hz, 1H), 7.18 (t, *J* = 8.0 Hz, 1H), 7.16 – 7.09 (m, 2H), 6.98 – 6.95 (m, 1H).

$^{13}$C NMR (100 MHz, $CDCl_3$) δ 141.26 (d, *J* = 9.0 Hz), 141.07 (d, *J* = 8.5 Hz), 139.28, 139.13, 135.32 (d, *J* = 3.2 Hz), 134.42 (d, *J* = 6.7 Hz), 134.16 (d, *J* = 10.3 Hz), 132.86 (d, *J* = 2.4 Hz), 132.74 (d, *J* = 2.0 Hz), 132.49 (s), 132.12 (d, *J* = 2.8 Hz), 131.58 (s), 131.39 (d, *J* = 2.4 Hz), 131.07 (s), 130.97 (s), 130.62 (s), 130.51 (d, *J* = 1.1 Hz), 128.02 (d, *J* = 0.7 Hz).

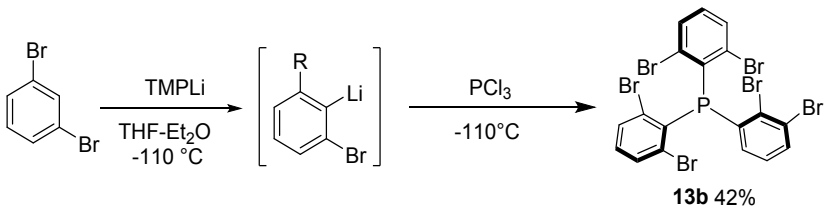
$^{31}$P NMR (161 MHz, $CDCl_3$): δ 13.85.

HRMS (ESI$^+$): Calcd. for $C_{18}H_{10}Br_3Cl_3P$ $[M + H]^+$: 602.70845, found: 602.70836.

m.p.: 196-197 °C

**TLC: $R_f$** = 0.59 (cyclohexane: AcOEt = 5:1)

### 1.3 General procedure and characterization data for hexa-*ortho*-substituted phosphine 13b




**13b** 42%

Under an argon atmosphere, a 2.5 M solution of *n*BuLi (7.4 mL, 18.37 mmol, 1.1 equiv.) in hexane was added dropwise to a solution of 2,2,6,6-tetramethylpiperidine (3.1 mL, 18.37 mmol, 1.1 eq) in THF-ether (1:1, 15 mL) at –110 °C over 10 min. This freshly prepared solution of TMPLi was slowly added to a THF-ether (1:1, 60 mL) solution of 1,3-dibromobenzene (2.0 mL, 16.7 mmol, 1.0 equiv.) at -110 °C, and the reaction mixture was stirred for 3 h at this temperature. Then, neat $PCl_3$ (0.28 mL, 5.0 mmol, 0.3 eq.) was added dropwise to the reaction mixture and the reaction mixture was stirred for 3 additional hours at this temperature and then allowed to warm up to room temperature overnight. The reaction mixture was quenched with a saturated solution of $NH_4Cl$ (2 mL) and the solvents were removed under reduced pressure. The resulting crude product was purified by flash chromatography

on silica gel (cyclohexane: DCM = 10:1) to provide **13b** as a white solid (1.5 g, 2.1 mmol, 42%). Crystals suitable for X-ray diffraction analysis were obtained by slow evaporation of a saturated solution of the corresponding phosphine **13b** in AcOEt.

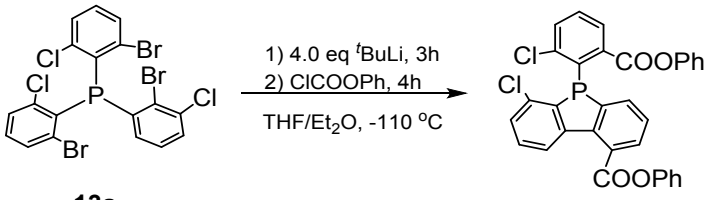
$^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.64 (ddd, *J* = 6.6, 2.8, 1.5 Hz, 1H), 7.58 (dd, *J* = 7.9, 2.2 Hz, 4H), 7.09 – 7.03 (m, 4H).

$^{13}$C NMR (100 MHz, $CDCl_3$) δ 139.37 (d, *J* = 15.5 Hz), 136.00 (d, *J* = 26.1 Hz), 134.55, 134.24, 134.00, 133.83, 133.51, 131.43, 131.38, 131.15, 128.34, 126.07.

$^{31}$P NMR (161 MHz, $CDCl_3$) δ 27.30.

**TLC: $R_f$** = 0.43 (cyclohexane: DCM = 20:1)

### 1.4 General procedure and characterization data for 9-phenyl-9-phosphafluorene derivative 15a




**13a** **15a** 47%

A 1.9 M solution of *t*BuLi (3.5 mL, 6.6 mmol, 4.0 equiv.) in hexane was added dropwise to a solution of the selected phosphine **13a** (1.00 g, 1.65 mmol, 1.0 equiv.) in THF/ $Et_2O$ (15 mL/15 mL) at –110 °C and the reaction mixture was stirred for 3 h at this temperature. A solution of phenyl chloroformate (0.2 mL in 3 mL of THF, 1.73 mmol, 1.05 equiv.) was added dropwise to the reaction mixture at –110 °C and the reaction mixture was stirred for 4 additional hours at this temperature and then allowed to warm up to room temperature overnight. The reaction mixture was quenched with a saturated solution of $NH_4Cl$ (2 mL) and the solvents were removed under reduced pressure. The resulting crude product was purified by flash chromatography on silica gel (cyclohexane: AcOEt = 15:1 to 7:1) to provide **15a** as a colourless solid (0.44 g, 0.78 mmol, 47%). Crystals suitable for X-ray diffraction analysis were obtained by slow evaporation of a saturated solution of the 9-phenyl-9-phosphafluorene compound **15a** in AcOEt.

$^{1}$H NMR (400 MHz, $CD_2Cl_2$) δ 8.21 (d, *J* = 8.0 Hz, 1H), 8.04 (ddd, *J* = 7.4, 5.3, 1.0 Hz, 1H), 7.96 (d, *J* = 7.6 Hz, 1H), 7.87 (ddd, *J* = 7.7, 3.4, 1.1 Hz, 1H), 7.58 – 7.40 (m, 9H), 7.35 (m, 6H).

$^{13}$C NMR (100 MHz, $CD_2Cl_2$) δ 167.93, 167.56 (d, *J* = 3.8 Hz), 151.50 (d, *J* = 10.7 Hz), 144.73, 144.65 (d, *J* = 1.3 Hz), 144.26, 143.23, 142.67, 141.51, 141.28 (d, *J* = 5.0 Hz), 140.78 (d, *J* = 5.5 Hz), 137.15, 136.42 (d, *J* = 18.3 Hz), 133.90, 133.63, 133.42, 132.46 (d, *J* = 2.1 Hz), 131.01 (d, *J* = 1.9 Hz), 130.71, 130.22 (d, *J* = 5.2 Hz), 129.20, 127.99 (d, *J* = 1.7 Hz), 127.77 (d, *J* = 15.6 Hz), 127.68 (d, *J* = 14.5 Hz), 126.91 (d, *J* = 11.6 Hz), 124.79, 122.30 (d, *J* = 1.7 Hz), 122.17.

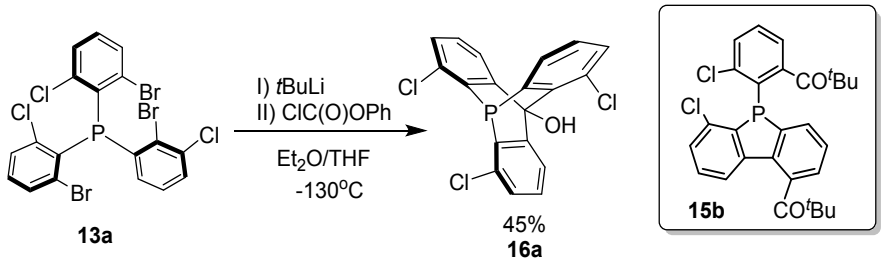
$^{31}$P NMR (161 MHz, $CD_2Cl_2$) δ -13.93.

HRMS (ESI$^+$): Calcd. for $C_{32}H_{20}O_4Cl_2P$ $[M + H]^+$: 569.04708 found: 569.04694.

m.p.: 199-200 °C

**TLC: $R_f$** = 0.59 (cyclohexane: AcOEt = 5:1)

### 1.5 General procedure and characterization data for 1,8,11-tris-chloro-9-phospha-10-hydroxytriptycene 16a and 9-phenyl-9-phosphorfluorene derivative 15b




A 1.9 M solution of *t*BuLi (8.2 mL, 15.62 mmol, 5.5 equiv.) in hexane was added dropwise to a solution of the selected phosphine **13a** (1.70 g, 2.84 mmol, 1.00 equiv.) in THF/ $Et_2O$ (25 mL/25 mL) at –130 °C and the reaction mixture was stirred for 4 h at this temperature. A solution of phenyl chloroformate (0.4 mL in 10 mL of THF, 3.1 mmol, 1.1 equiv.) was added dropwise to the reaction mixture over 10 min at –130 °C and the reaction mixture was stirred for 4 additional hours at this temperature and then allowed to warm up to room temperature overnight (**Note**: If the reaction temperature and the stiring speed are not well controlled, 9-phenyl-9-phosphorfluorene derivative **15b** is obtained as a side product in variable yields as a white powder. The reaction mixture was quenched with a saturated solution of $NH_4Cl$ (5 mL) and the solvents were removed under reduced pressure. The resulting crude product was purified by flash chromatography on silica gel (cyclohexane: AcOEt = 15:1) to provide **16a** as a white solid (0.50 g, 1.28 mmol, 45%).

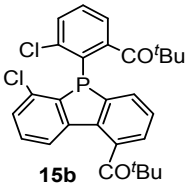
$^1$H NMR (400 MHz, $CD_2Cl_2$) δ 7.88 (dd, *J* = 7.6, 1.2 Hz, 2H), 7.79 (ddd, *J* = 11.5, 7.1, 1.3 Hz, 1H), 7.27 (t, *J* = 7.8 Hz, 2H), 7.24 – 7.18 (m, 3H), 7.10 (ddd, *J* = 8.1, 7.2, 2.0 Hz, 1H), 5.39 (s, 1H)

$^{13}$C NMR (100 MHz, $CD_2Cl_2$) δ 153.17 (d, *J* = 2.2 Hz), 133.42, 133.33, 133.31, 132.98, 130.41 (d, *J* = 1.4 Hz), 129.31, 128.18, 128.03, 127.27, 127.23, 122.13, 69.10.

$^{31}$P NMR (161 MHz, $CD_2Cl_2$) δ -88.92.

HRMS (ESI$^+$): Calcd. for $C_{19}H_{11}OCl_3P$ [M + H]$^+$: 390.96076 found: 390.96058.

**TLC: $R_f$** = 0.22 (cyclohexane: AcOEt = 5:1)




**15b**

$^1$H NMR (500 MHz, $CDCl_3$) δ 7.92 (ddd, *J* = 7.5, 5.3, 1.0 Hz, 1H), 7.52 (d, *J* = 7.9 Hz, 1H), 7.36 – 7.22 (m, 5H), 7.19 – 7.11 (m, 2H), 1.45 (s, 9H), 1.25 (s, 9H).

$^{13}$C NMR (126 MHz, $CDCl_3$) δ 216.09, 214.82 (d, *J* = 3.9 Hz), 153.63 (d, *J* = 44.3 Hz), 144.49 (d, *J* = 7.3 Hz), 140.79 (d, *J* = 4.5 Hz), 140.69 (s), 140.57 (d, *J* = 1.6 Hz), 137.95 (d, *J* = 4.9 Hz), 137.18 (s), 136.48 (d, *J* = 18.2 Hz), 130.95, 130.93, 130.55 (d, *J* = 20.7 Hz), 130.28 (d, *J* = 1.8 Hz), 127.60 (d, *J* = 33.9 Hz), 127.13, 127.06 (d, *J* = 2.7 Hz), 125.64, 123.18 (d, *J* = 11.8 Hz), 122.85, 46.10, 45.20, 28.17 (d, *J* = 3.3 Hz), 27.24.

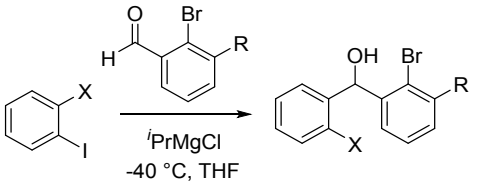
$^{31}$P NMR (202 MHz, $CDCl_3$) δ -11.51.

HRMS ($ESI^+$): Calcd. for $C_{28}H_{28}O_2Cl_2P$ $[M + H]^+$: 497.11985 found: 497.11976.

m.p.: 178-180 °C

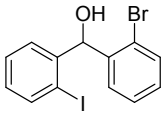
**TLC: $R_f$** = 0.46 (cyclohexane: AcOEt = 5:1)

### 1.6 General procedure and characterization for bis-(halogenated-phenyl)-methanol precursors



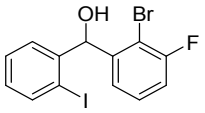

**17a**: X = I, R = Cl, 74%
**17b**: X = I, R = F, 76%
**17c**: X = I, R = $CF_3$, 70%
**21**: X = I, R = H, 72%
**27**: X = Br, R = Cl, 81%

Representative synthesis of **21**: In a pre-dried 500 mL Schlenk flask under argon atmosphere is added 1,2-diiodobenzene (13.0 mL, 100.00 mmol). Then, 150 mL of anhydrous THF are added and the mixture is cooled at -40°C (acetonitrile/$N_2$ cooling bath). A solution of *i*-PrMgCl (50.0 mL, 2.0 M, 100 mmol, 1.00 equiv) in THF is added dropwise to the resulting solution, which is stirred at the same temperature for 3h. 2-Bromobenzaldehyde is then added dropwise (9.8 mL, 84.00 mmol, 0.85 equiv) and the resulting solution is stirred for 1h at -40°C before being allowed to warm up to room temperature overnight. A milky white solution is obtained. The reaction is finally quenched with aqueous $NH_4Cl$ (150 mL). The two phases are separated. The aqueous phase is extracted with AcOEt (3 x 100 mL) and combined organic phases are dried over $MgSO_4$. Solvents are then removed under reduced pressure. The crude product was purified by silica gel column chromatography (eluant: cyclohexane:AcOEt = 4:1) affording the product as a white solid **21** (23.54 g, 60.69 mmol,72%). The same method can be used to obtain compounds **17a-c** and **27**.



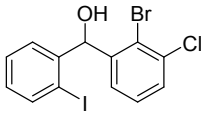

**21**

$^1$H NMR (400.0 MHz, $CDCl_3$): δ 7.87 (dd, *J* = 7.9, 1.1 Hz, 1H), 7.59 (d, *J* = 7.8 Hz, 1H), 7.38 – 7.27 (m, 4H), 7.24 – 7.16 (m, 1H), 7.02 (td, *J* = 7.6, 1.9 Hz, 1H), 6.24 (s, 1H, $C_{sp}^3$-H), 2.55 (s, 1H, OH). The $^1$H NMR is consistent with the reported data from the literature.[2]



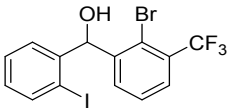

**17a**

$^1$H NMR (500 MHz, $CDCl_3$) δ 7.87 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.33 (td, *J* = 7.5, 1.1 Hz, 1H), 7.29 (td, *J* = 8.0, 5.4 Hz, 1H), 7.23 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.14 (d, *J* = 7.8 Hz, 1H), 7.10 (td, *J* = 8.2, 1.5 Hz, 1H), 7.01 (td, *J* = 1.7 Hz, 1H, $C_{sp}^3$-H), 6.23 (s, 1H, $C_{sp}^3$-H), 2.70 (s, 1H, OH).
$^{19}$F NMR (376 MHz, $CDCl_3$) δ -104.98 (t, *J* = 8.0 Hz).
NMR is consistent with the reported data from the literature.[2]



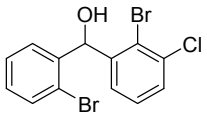

**17b**

$^1$H NMR (400 MHz, $CDCl_3$) δ 7.86 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.46 – 7.39 (m, 1H), 7.30 (td, *J* = 7.5, 1.2 Hz, 1H), 7.25 – 7.23 (m, 2H), 7.17 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.01 (td, *J* = 7.6, 1.7 Hz, 1H), 6.20 (d, *J* = 4.3 Hz, 1H, $C_{sp}^3$-H), 2.85 (d, *J* = 4.3 Hz, 1H, OH).




**17c**

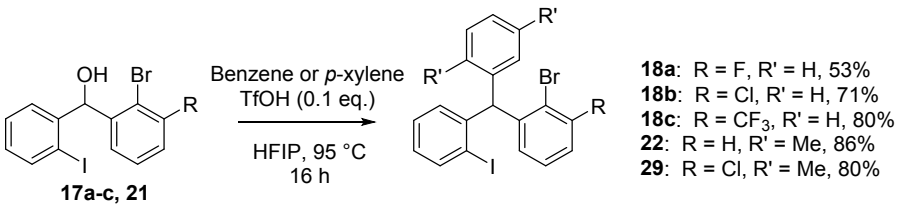
$^1$H NMR (400 MHz, $CDCl_3$) δ 7.88 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.68 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.60 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.44 (t, *J* = 7.8 Hz, 1H), 7.37 – 7.30 (m, 1H), 7.16 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.03 (td, *J* = 7.7, 1.7 Hz, 1H), 6.32 (s, 1H, $C_{sp}^3$-H), 2.82 (s, 1H, OH).
$^{19}$F NMR (376 MHz, $CDCl_3$) δ -61.92.



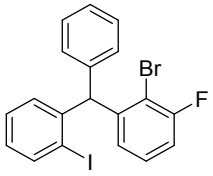

**27**

$^1$H NMR (500 MHz, $CDCl_3$) δ 7.57 (dd, *J* = 7.9, 1.1 Hz, 1H), 7.42 (dd, *J* = 7.3, 2.2 Hz, 1H), 7.28 (m, 2H), 7.25 – 7.20 (m, 2H), 7.17 (td, *J* = 1.8 Hz, 1.7 Hz, 1H), 6.40 (d, *J* = 4.2 Hz, 1H, $C_{sp}^3$-H), 2.67 (d, *J* = 4.2 Hz, 1H, OH).

## 1.7 General procedure and characterization data for trityl precursors



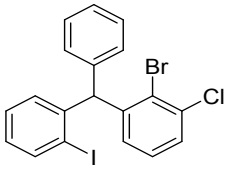

Representative synthesis with **18b**: In a 500 mL flask equipped with a magnetic stirrer is added (2-bromo-3-chloro-phenyl)(2-iodophenyl)methanol **17b** (35.0 g, 83.0 mmol, 1.0 equiv.), HFIP (150 mL), and benzene (37.0 mL, 414.8 mmol, 5.0 equiv.). Trifluoromethanesulfonic acid (0.73 mL, 8.3 mmol, 10 mol%) is then quickly added (in one shot) by means of a glass syringe (Warning: use a glass syringe, the triflic acid is very corrosive and will rapidly destroy a plastic syringe). The reaction flask is sealed with a glass stopper with a metallic clip and is stirred at 95 °C for 16 h. The reaction mixture is then allowed to cool down to room temperature before opening and evaporation under reduced pressure to dryness.[4] The crude solid residue was triturated in MeOH and a white solid precipitated and **18b** (28.5 g, 59.14 mmol, 71%) was obtained by filtration and by washing the solid with MeOH. The product **18b** was nearly pure and was used in the next step without further purification. Compound **18a**, **18c**, **22** and **29** were prepared with a similar procedure to that described for the synthesis of compound **18b.**




**18a**

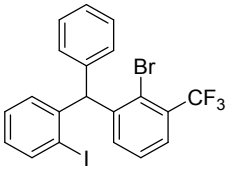
$^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.90 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.37 – 7.23 (m, 4H), 7.18 (td, *J* = 8.0, 5.6 Hz, 1H), 7.08 – 7.00 (m, 3H), 6.96 (td, *J* = 7.6, 1.7 Hz, 1H), 6.79 (dd, *J* = 7.8, 1.7 Hz, 1H), 6.59 (d, *J* = 7.8 Hz, 1H), 6.03 (s, 1H, $C_{sp}^3$-H).

$^{19}$F NMR (376 MHz, $CDCl_3$) δ -103.76.




**18b**

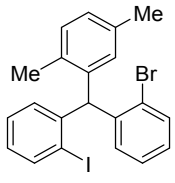
$^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.90 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.39 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.35 – 7.26 (m, 3H), 7.26 – 7.22 (m, 1H), 7.15 (t, *J* = 7.9 Hz, 1H), 7.04 – 7.00 (m, 2H), 6.96 (td, *J* = 7.6, 1.7 Hz, 1H), 6.77 (dd, *J* = 7.8, 1.7 Hz, 1H), 6.69 (ddd, *J* = 7.8, 1.6, 0.4 Hz, 1H), 6.06 (s, 1H, $C_{sp}^3$-H).




**18c**

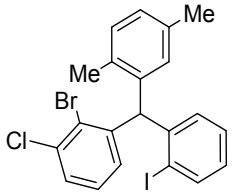
$^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 7.6 Hz, 1H), 7.61 (d, *J* = 7.2 Hz, 1H), 7.33 – 7.25 (m, 4H), 7.25 – 7.21 (m, 1H), 7.05 – 6.89 (m, 4H), 6.74 (d, *J* = 7.7 Hz, 1H), 6.13 (s, 1H, $C_{sp}^3$-H).

$^{19}$F NMR (376 MHz, $CDCl_3$) δ -61.99.




**22**

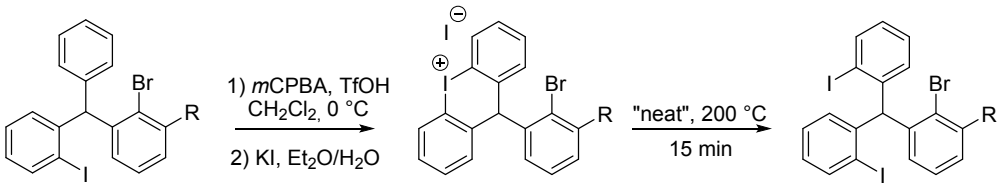
$^1$H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 7.8 Hz, 1H), 7.60 (d, *J* = 7.9 Hz, 1H), 7.30 – 7.17 (m, 2H), 7.17 – 7.07 (m, 2H), 7.04 – 6.91 (m, 2H), 6.77 (d, *J* = 7.7 Hz, 2H), 6.43 (s, 1H), 5.97 (s, 1H, $C_{sp}^3$-H), 2.21 (s, 3H), 2.15 (s, 3H).




**29**

$^1$H NMR (500 MHz, $CDCl_3$) δ 7.89 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.39 (dd, *J* = 8.1, 1.8 Hz, 1H), 7.24 (td, *J* = 7.6, 1.5 Hz, 1H), 7.14 (t, *J* = 7.9 Hz, 1H), 7.08 (t, *J* = 6.1 Hz, 1H), 7.00 (dd, *J* = 8.0, 2.0 Hz, 1H), 6.96 (td, *J* = 2.00, 1.85, 1.81 Hz, 1H), 6.75 (dd, *J* = 8.0, 1.9 Hz, 1H), 6.66 (dd, *J* = 8.0, 1.7 Hz, 1H), 6.40 (d, *J* = 2.0 Hz, 1H), 6.01 (s, 1H, $C_{sp}^3$-H), 2.21 (s, 3H), 2.14 (s, 3H).

## 1.8 General procedure and characterization data for trityl precursors 20a-c

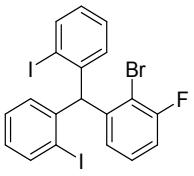



**18a**: R = F
**18b**: R = Cl
**18c**: R = $CF_3$

**19a**: R = F, 90%
**19b**: R = Cl, 83%
**19c**: R = $CF_3$, 92%

**20a**: R = F, 43%
**20b**: R = Cl, 61%
**20c**: R = $CF_3$, 51%

Representative synthesis for **20b**: The triphenylmethane compound **18b** was dissolved in dichloromethane (50 mL) and cooled to 0 °C. Meanwhile, 3-chloroperoxybenzoic acid (16.6 g, 70%-75%, 74 mmol, 1.25 equiv.) was added as a solid in portions over 10 mins. This mixture was stirred at 0 °C for 10 min and then trifluoromethanesulfonic acid (16 mL, 183.3 mmol, 3.1 eq.) was added via glass syringe over the course of 15 min. The reaction mixture turned dark brown. After an additional 30 min, the reaction mixture was allowed to warm to room temperature and stirred for 2 hours, and then the solvents ($CH_2Cl_2$ and TfOH) were removed under reduced pressure. The solid material was suspended in 200 mL of diethyl ether and 200 mL of water, and then solid potassium iodide (49 g, 295.7 mmol, 5.0 equiv.) was added and the mixture was shaken vigorously for 5 min, during which time a fine yellow precipitate developed. The precipitate was filtrated and washed with water and diethyl ether to afford the corresponding iodonium compound **19b** as a yellow solid (29.9 g, 49.19 mmol, 83%). Next, this iodonium compound **19b** (26 g, 42.77 mmol) was sealed in a Schlenk tube under $N_2$ and heated to 200 °C for 15 min, and then cooled to room temperature. The resulting dark violet residue was extracted with dichloromethane (150 mL) and washed successively with saturated aqueous sodium thiosulfate (100 mL), water (100 mL) and saturated aqueous sodium chloride (100 mL). The organic phase was dried over magnesium sulfate, filtered, and concentrated to dryness under reduced pressure.[5] The resulting crude product was recrystallized from methanol to give the desired product as an orange powder **20b** (15.9 g, 26.9 mmol, 61%). Similarly, compounds **20a** and **20c** were prepared by the same procedure from the trityl precursor **18a** and **18c**, respectively.




**20a**

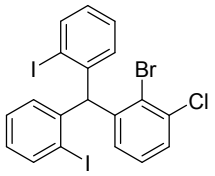
$^1$H NMR (400 MHz, $CDCl_3$) δ 7.91 (dd, *J* = 7.9, 1.2 Hz, 2H), 7.30 – 7.22 (m, 2H), 7.19 (td, *J* = 8.0, 5.5 Hz, 1H), 7.07 (td, *J* = 8.2, 1.5 Hz, 1H), 6.98 (td, *J* = 7.6, 1.6 Hz, 2H), 6.68 (dd, *J* = 7.7, 1.6 Hz, 2H), 6.49 (dd, *J* = 7.7, 0.6 Hz, 1H), 6.03 (s, 1H).

$^{13}$C NMR (100 MHz, $CDCl_3$) δ 147.17, 143.89, 140.34, 134.65, 130.62, 128.78, 128.25, 128.16 (d, *J* = 8.2 Hz), 126.47 (d, *J* = 3.3 Hz), 115.03 (d, *J* = 23.1 Hz), 113.67 (d, *J* = 20.3 Hz), 100.00, 65.31 (d, *J* = 2.9 Hz).

$^{19}$F NMR (376 MHz, $CDCl_3$) δ -103.64.

HRMS ($ESI^+$): Calcd. for $C_{19}H_{12}Br_1F_1I_2$ $[M + H]^+$: 591.81959, found: 591.81903.

m.p.: 148-150 °C



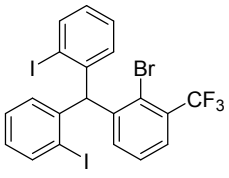

**20b**

$^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 7.8 Hz, 2H), 7.42 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.27 – 7.22 (m, 2H), 7.20 – 7.12 (m, 1H), 6.99 (td, *J* = 7.7, 1.4 Hz, 2H), 6.75 – 6.64 (m, 2H), 6.60 (dd, *J* = 7.8, 1.3 Hz, 1H), 6.05 (s, 1H).

$^{13}$C NMR (100 MHz, $CDCl_3$) δ 144.09, 143.90, 140.39, 136.13, 130.80, 129.29, 129.08, 128.83, 128.32, 127.82, 126.97, 100.04, 66.62.

HRMS (ESI$^+$): Calcd. for $C_{19}H_{12}Br_1Cl_1I_2$ [M + H]$^+$: 609.78725, found: 609.79279.

m.p.: 188-190 °C




**20c**

$^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.92 (d, *J* = 7.8 Hz, 2H), 7.65 (d, *J* = 7.7 Hz, 1H), 7.32 (t, *J* = 7.8 Hz, 1H), 7.26 (t, *J* = 7.4 Hz, 2H), 7.00 (t, *J* = 7.2 Hz, 2H), 6.90 (d, *J* = 7.6 Hz, 1H), 6.66 (s, 2H), 6.14 (s, 1H).

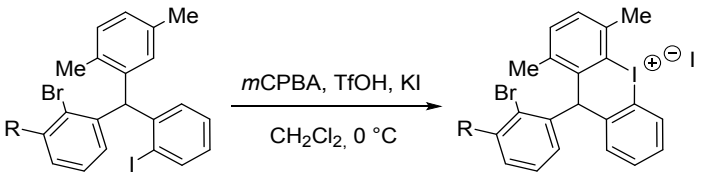
$^{13}$C NMR (126 MHz, $CDCl_3$) δ 144.17, 143.81, 140.52, 134.42, 131.64 (q, *J* = 30.5 Hz), 128.93, 128.40, 127.12, 126.67(q, *J* = 5.5 Hz), 124.75, 124.62, 121.90, 103.60, 65.90.

$^{19}$F NMR (476 MHz, $CDCl_3$) δ -62.02.

HRMS (ESI$^+$): Calcd. for $C_{20}H_{12}Br_1F_3I_2$ [M + H]$^+$: 641.81640, found: 641.82411.

m.p.: 140 °C

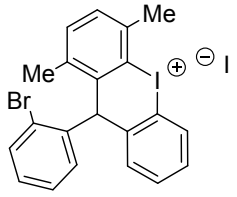
**1.9 General procedure and characterization data for the iodonium precursors 23 and 30**




**22** R = H
**29** R = Cl

**23** R = H, 88%
**30** R = Cl, 83%

Trityl Compounds **23** and **30** were prepared with a similar procedure to that described for the synthesis of compound **19a-c**, and the crude products were repeated washings with $Et_2O$ and water afforded the product **23** (88%) and **30** (83%) as a yellow fine powder, separately**.**

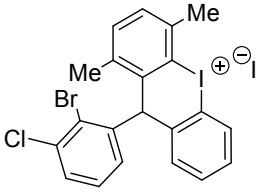



**23**

$^1$H NMR (400 MHz, $(CD_3)_2SO$) δ 8.23 (dd, *J* = 35.5, 7.6 Hz, 2H), 7.62 (t, *J* = 8.1 Hz, 2H), 7.41 (dd, *J* = 6.7, 4.6 Hz, 2H), 7.26 (m, 3H), 7.04 (d, *J* = 8.3 Hz, 1H), 6.30 (s, 1H), 2.58 (s, 3H), 2.52 (s, 3H).

$^{13}$C NMR (100MHz, $(CD_3)_2SO$) δ 139.07, 138.68, 138.38, 137.81, 135.25, 135.14, 134.73, 133.34, 133.33, 131.55, 130.98, 129.90, 129.60, 129.30, 127.51, 124.22, 123.70, 117.37, 55.41, 25.01, 20.30.

m.p.: The compound liquifies and decomposes (deep purple color) at 155°C



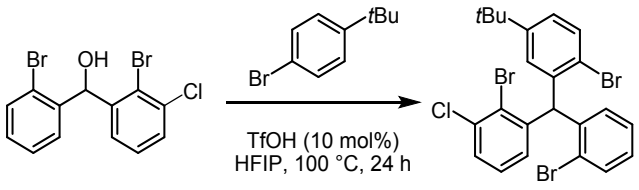

**30**

$^1$H NMR (500 MHz, $(CD_3)_2SO$) 8.30 (dd, *J* = 7.5, 0.9 Hz, 1H), 8.23 (d, *J* = 8.0 Hz, 1H), 7.63 (m, 2H), 7.43 (m, 2H), 7.33 (t, *J* = 8.0 Hz, 1H), 7.30 (d, *J* = 7.7 Hz, 1H), 7.06 (d, *J* = 8.0 Hz, 1H), 6.35 (s, 1H), 2.61 (s, 3H), 2.54 (s, 3H).

$^{13}$C NMR (126 MHz, $(CD_3)_2SO$) δ 138.73, 138.69, 138.22, 137.84, 137.77, 135.91, 135.40, 135.21, 133.33, 130.89, 130.18, 130.07, 129.62, 129.31, 128.23, 124.73, 123.87, 117.68, 56.13, 25.06, 20.23.

m.p.: The compound liquifies and decomposes (deep purple color) at 156°C

### 1.10 General procedure and characterization data for the trityl precursor 28




**27** **28** 67%

The same prepared procedure of **17b** was adapted for the preparation of compound **27**. In a 50 mL flask equipped with a magnetic stirrer was added (2-bromo-3-chloro-phenyl)(2-bromo phenyl)methanol (1.00 g, 2.67 mmol, 1.0 equiv.), HFIP (4 mL), and 1-bromo-4-tert-butylbenzene (2.3 mL, 13.4 mmol, 5.0 equiv.). Trifluoromethanesulfonic acid (24 µL, 0.27 mmol, 10 mol%) is then quickly added (in one shot) by means of a glass syringe. The reaction flask is sealed with a glass stopper and a metallic clip to prevent any popping and was stirred at 100°C for 24 h. The reaction mixture was then allowed to cool down to room temperature before opening and was evaporated under reduced pressure. Purification of the crude product by flash chromatography using cyclohexane as eluent afforded **28** (1.02 g, 1.79 mmol, 67%) as a colorless powder.

$^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.62 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.51 (d, *J* = 8.3 Hz, 1H), 7.41 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.23 (td, *J* = 7.5, 1.4 Hz, 1H), 7.19 – 7.11 (m, 3H), 6.72 (dd, *J* = 7.4, 1.9 Hz, 2H), 6.64 (ddd, *J* = 7.8, 1.5, 0.5 Hz, 1H), 6.41 (s, 1H), 1.15 (s, 9H).

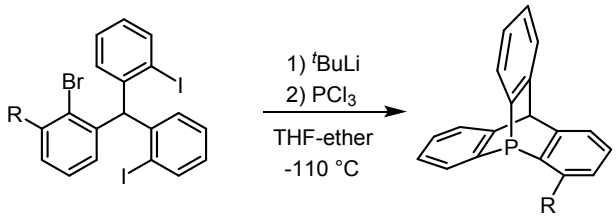
$^{13}$C NMR (100 MHz, $CDCl_3$) δ 150.65, 144.08, 140.85, 139.92, 136.05, 133.49, 132.84, 130.72, 129.00, 128.90, 128.69, 128.08, 127.70, 127.43, 126.41, 126.33, 125.76, 122.95, 57.57, 34.64, 31.22.

HRMS (ESI$^+$): Calcd. for $C_{23}H_{20}Br_3Cl$ $[M + H]^+$: 571.87556, found: 571.87552.

m.p.: 159 °C

**TLC: $R_f$** = 0.54 (cyclohexane: AcOEt = 5:1)

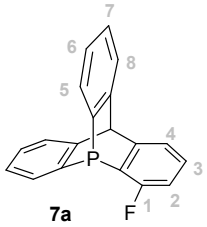
### 1.11 General procedure and characterization data for the substituted-9-phosphatriptycenes




**20a-c**

**7a**: R = F 48%
**7b**: R = Cl 60%
**7c**: R = $CF_3$ 42%

Representative procedure for **7b**: A solution of 1.9 M *t*BuLi in THF (52 mL, 98.7 mmol, 6.0 equiv.) at –110 °C was added to a solution of the precursor **20b** (10.0 g, 16.45 mmol, 1.0 eq) in THF/$Et_2O$ (1:1, 250 mL) over 5 min and the reaction mixture was stirred for 2 h at the same temperature. A solution of $PCl_3$ (1.7 mL in 10 mL of $Et_2O$ solution, 19.74 mmol, 1.1 equiv.) was added at -110 °C and the reaction mixture was stirred for 3 hours and allowed to warm up to room temperature overnight. The solvents were removed under reduced pressure and the resulting crude was purified by flash chromatography (cyclohexane: AcOEt = 15:1 to 5:1) giving a white solid **7b** (3.0 g, 9.8 mmol, 60%). Compound **7a** and **7c** were prepared by the same procedure and obtained with yields of 48% and 42%, respectively. Crystals suitable for X-ray diffraction analysis were obtained by slow evaporation of a saturated solution of **7a-b** in AcOEt.




**7a**

$^1$H NMR (400 MHz, $CDCl_3$) δ 7.83 (t, *J* = 8.5 Hz, 2H, H-5), 7.55 (d, *J* = 6.9 Hz, 2H, H-8), 7.34 (d, *J* = 7.3 Hz, 1H, H-4), 7.21 (t, *J* = 8.5 Hz, 2H, H-7), 7.18 – 7.07 (m, 3H, H-3, 6), 6.80 (tdd, *J* = 8.2, 4.1, 0.8 Hz, 1H, H-2), 5.64 (d, *J* = 1.8 Hz, 1H, $C_{sp}^3$-H).

$^{13}$C NMR (100 MHz, $CDCl_3$) δ 163.10, 152.64, 149.47, 139.83 (d, *J* = 8.9 Hz), 133.05, 132.67, 130.16 (d, *J* = 8.0 Hz), 128.82, 125.90, 125.66 (d, *J* = 12.7 Hz), 121.51 (d, *J* = 2.1 Hz), 112.81 (dd, *J* = 23.9, 2.9 Hz), 59.56.

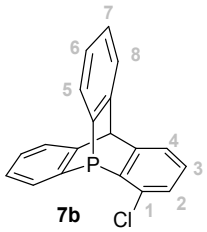
$^{31}$P NMR (202 MHz, $CDCl_3$) δ -83.38 (d, *J* = 36.0 Hz).

$^{19}$F NMR (376 MHz, $CDCl_3$) δ -107.87 (dd, *J* = 42.3, 6.0 Hz).

HRMS ($ESI^+$): Calcd. for $C_{19}H_{13}FP$ $[M + H]^+$: 291.07334 found: 291.07357.

m.p.: 258-259 °C

**TLC: $R_f$** = 0.54 (cyclohexane: AcOEt = 5:1)




**7b**

$^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.84 (t, *J* = 8.0 Hz, 2H, H-5), 7.54 (d, *J* = 7.3 Hz, 2H, H-8), 7.42 (dd, *J* = 6.3, 1.8 Hz, 1H, H-4), 7.21 (t, *J* = 7.4 Hz, 2H, H-7), 7.08 – 7.12 (m, 4H, H-2, 3, 6), 5.61 (s, 1H, $C_{sp^3}$-H).

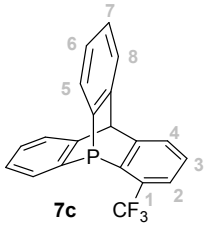
$^{13}$C NMR (100 MHz, $CDCl_3$) δ 151.96, 149.30 (d, *J* = 2.4 Hz), 140.25 (d, *J* = 9.5 Hz), 140.02 (d, *J* = 9.9 Hz), 138.33 (d, *J* = 26.6 Hz), 133.02 (d, *J* = 38.2 Hz), 129.47, 128.90, 126.24 (d, *J* = 3.2 Hz), 125.82, 125.67 (d, *J* = 12.7 Hz), 124.21, 60.33.

$^{31}$P NMR (161 MHz, $CDCl_3$) δ -72.46.

HRMS ($ESI^+$): Calcd. for $C_{19}H_{13}ClP$ $[M + H]^+$: 307.04379 found: 307.04402.

m.p.: 246-248 °C

**TLC: $R_f$** = 0.59 (cyclohexane: AcOEt = 5:1)




**7c**

$^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.84 (dd, *J* = 12.0, 4.2 Hz, 2H, H-5), 7.68 (d, *J* = 7.4 Hz, 1H, H-4), 7.54 (d, *J* = 7.2 Hz, 2H, H-8), 7.39 (dd, *J* = 7.7, 3.3 Hz, 1H, H-2), 7.30 – 7.17 (m, 3H, H-3, 7), 7.11 (tdd, *J* = 7.5, 2.2, 1.2 Hz, 2H, H-6), 5.67 (s, 1H, $C_{sp^3}$-H).

$^{13}$C NMR (125 MHz, $CDCl_3$) δ 151.58 (d, *J* = 3.1 Hz), 149.22 (d, *J* = 2.3 Hz), 140.91 (d, *J* = 23.3 Hz), 139.31 (d, *J* = 10.2 Hz), 133.29, 132.98, 129.16, 129.05, 128.17, 125.87, 125.77, 124.34 (q, *J* = 274.8 Hz), 122.46 (t, *J* = 5.3 Hz), 59.91.

$^{31}$P NMR (202 MHz, $CDCl_3$) δ -69.67 (q, *J* = 51.8 Hz).

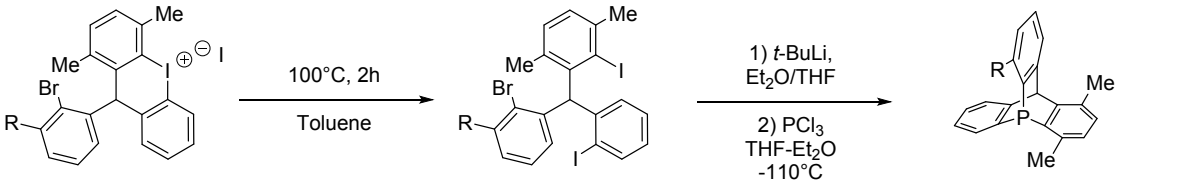
$^{19}$F NMR (376 MHz, $CDCl_3$) δ -57.81 (d, *J* = 51.6 Hz).

HRMS ($ESI^+$): Calcd. for $C_{20}H_{13}F_3P$ $[M + H]^+$: 341.07015 found: 341.06993.

m.p.: 227-228 °C

**TLC: $R_f$** = 0.45 (cyclohexane: AcOEt = 5:1)

### 1.12 General procedure and characterization data for the substituted-9-phosphatriptycenes 8a and 10a

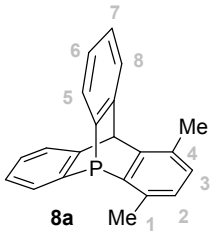



**23** R = H
**30** R = Cl

**24** R = H
**31** R = Cl

**8a** R = H, 12% over two steps
**10a** R = Cl, 4% over two steps

In a round-bottom flask equipped with a magnetic stirrer is added compound **23** (5.7 g, 9.4 mmol). It is then suspended in 25 mL of toluene. The flask is flushed with Ar and equipped with a condenser under Ar atmosphere. The yellow suspension is then stirred at 100°C for 2h. The reaction mixture turns deep purple after a few minutes at 100°C. The solvent is then evaporated under reduced pressure and the resulting purple solid is dissolved in dichloromethane, washed with sodium thiosulfate (100 mL), water (100 mL) and brine (100 mL). The organic phase is dried over $MgSO_4$ and the solvents are then removed under reduced pressure, yielding a dark brown oil. The crude product **24** is first purified by silica gel column chromatography using cyclohexane as eluent. A second purification by trituration in methanol, filtration and several washings with methanol afforded the product **24** as a white powder (2.9 g). Compound **24** was used as is for the next step. In a pre-dried 50 mL Schlenck flask under Ar and equipped with a magnetic stirrer is added compound **24** (0.6 g, 1.0 mmol). 20 mL of a 1:1 mixture of anhydrous THF and $Et_2O$ are added, the resulting clear solution is cooled down to -110°C. *t*-BuLi (2.1 mL, 4.0 mmol, 4.0 equiv.) is then added dropwise at -110°C. Further stirring at this temperature for 4h afforded an orange solution. 0.50 mL of a 1.59 M solution of $PCl_3$ (0.8 mmol, 0.8 equiv.) in anhydrous THF/$Et_2O$ is then added dropwise at -110°C. The resulting brown solution is stirred for one additional hour before being allowed to warm up to room temperature overnight. The reaction is quenched with aqueous $NH_4Cl$ (20 mL) and the organic phase is extracted with AcOEt (3 x 20 mL). The combined organic phases are dried over $MgSO_4$ before filtration and evaporation of the solvents under reduced pressure. The crude product is obtained as a brown oil and is purified by silica gel column chromatography (eluent= cyclohexane to cyclohexane/dichloromethane 7:3) to afford pure substituted-9-phosphatriptycenes **8a** as an off-white powder (72 mg, 12% over two steps). Crystals suitable for X-ray diffraction analysis were obtained by slow evaporation of a saturated solution of **8a** in AcOEt. Substituted-9-phosphatriptycene **10a** (12% over two steps) as a white solid was prepared similarly starting from compound **30**.




**8a**

$^1$H NMR (500 MHz, $CDCl_3$) δ 7.79 (t, *J* = 7.9 Hz, 2H, H-5), 7.53 (d, *J* = 7.3 Hz, 2H, H-8), 7.18 (t, *J* = 7.4 Hz, 2H, H-7), 7.08 (tdd, *J* = 7.3, 2.2, 1.1 Hz, 2H, H-6), 6.91 (d, *J* = 7.7 Hz, 1H, H-2), 6.82 (dd, *J* = 7.7, 4.6 Hz, 1H, H-3), 5.94 (s, 1H, $C_{sp^3}$-H), 2.66 (s, 3H), 2.58 (s, 3H).

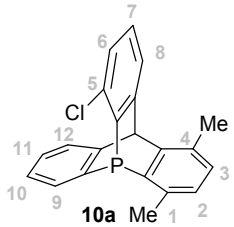
$^{13}$C NMR (126 MHz, $CDCl_3$) δ 149.70 (d, *J* = 3.0 Hz), 147.38 (d, *J* = 4.2 Hz), 141.15 (d, *J* = 8.5 Hz), 139.81 (d, *J* = 9.1 Hz), 139.18 (d, *J* = 26.0 Hz), 132.67 (d, *J* = 36.8 Hz), 130.88, 129.71, 128.49, 126.32 (d, *J* = 6.0 Hz), 125.83, 125.38 (d, *J* = 12.7 Hz), 55.57, 21.50 (d, *J* = 20.5 Hz), 19.48.

$^{31}$P NMR (202 MHz, $CDCl_3$): δ -74.9.

HRMS ($ESI^+$): Calcd. for $C_{21}H_{18}P$ $[M + H]^+$: 301.114613 found: 301.11482.

m.p.: 172°C

**TLC: $R_f$** = 0.38 in cyclohexane



**10a**

$^{1}$H NMR (500 MHz, $CDCl_3$): 7.83 (t, *J* = 8.0 Hz, 1H, H-9), 7.52 (d, *J* = 7.3 Hz, 1H, H-12), 7.39 (d, *J* = 6.7 Hz, 1H, H-8), 7.21 (t, *J* = 7.4 Hz, 1H, H-11), 7.13 – 7.04 (m, 3H, H-6, 7, 10), 6.92 (d, *J* = 7.6 Hz, 1H, H-2), 6.86 – 6.81 (m, 1H, H-3), 5.93 (s, 1H, $C_{sp}^{3}$-H), 2.68 (s, 3H), 2.56 (s, 3H).

$^{13}$C NMR (126 MHz, $CDCl_3$) δ 152.06 (d, *J* = 3.0 Hz), 149.49 (d, *J* = 2.7 Hz), 147.17 (d, *J* = 3.3 Hz), 140.37 (d, *J* = 9.8 Hz), 140.02 (d, *J* = 9.9 Hz), 139.50 (d, *J* = 27.5 Hz), 138.87 (d, *J* = 10.7 Hz), 138.17 (d, *J* = 27.3 Hz), 132.92 (d, *J* = 39.2 Hz), 130.86, 129.79, 129.18, 128.70, 126.40 (d, *J* = 6.6 Hz), 126.02 (d, *J* = 3.7 Hz), 125.69, 125.47 (d, *J* = 13.0 Hz), 124.09, 55.98 (d, *J* = 2.9 Hz), 21.39 (d, *J* = 21.5 Hz), 19.23.

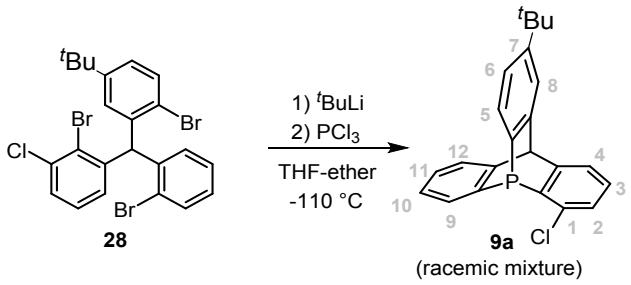
$^{31}$P NMR (202 MHz, $CDCl_3$): δ -82.70.

HRMS ($ESI^+$): Calcd. for $C_{21}H_{18}PCl$ $[M + H]^+$: 335.075641found: 335.07548.

m.p.: 233-234°C

**TLC: $R_f$** = 0.19 in cyclohexane

### 1.13 General procedure and characterization data for 9-phosphatriptycene derivative 9a




The unsymmetrically 9-phosphatriptycene derivative **9a** was prepared with a similar procedure to that described for the synthesis of 9-phosphatriptycenes **7a-c**. The crude product was purified by column chromatography (cyclohexane: AcOEt = 10:1) to provide compound **9a** (0.48 g, 1.24 mmol) with a yield of 69% as a colourless powder. Crystals suitable for X-ray diffraction analysis were obtained by slow evaporation of a saturated solution of **9a** in AcOEt

$^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.87 (t, *J* = 8.0 Hz, 1H, H-9), 7.82 (t, *J* = 8.1 Hz, 1H, H-5), 7.64 (s, 1H, H-8), 7.60 (d, *J* = 7.3 Hz, 1H, H-12), 7.46 (d, *J* = 7.0 Hz, 1H, H-4), 7.23 (t, *J* = 7.7 Hz, 1H, H-11), 7.18 – 7.17 (m, 1H, H-6), 7.13 – 7.06 (m, 3H, H-2, 3,10), 5.66 (s, 1H, $C_{sp^3}$-H), 1.33 (s, 9H, *t*Bu).

$^{13}$C NMR (126 MHz, $CDCl_3$) δ 152.35 (d, *J* = 1.7 Hz), 152.16 (d, *J* = 3.2 Hz), 149.53 (d, *J* = 3.0 Hz), 149.17 (d, *J* = 3.0 Hz), 140.56 (d, *J* = 9.7 Hz), 140.34 (d, *J* = 9.9 Hz), 138.18 (d, *J* = 26.6 Hz), 136.39 (d, *J* = 8.9 Hz), 132.86 (d, *J* = 38.3 Hz), 132.59 (d, *J* = 37.9 Hz), 129.32 (d, *J* = 1.0 Hz), 128.73 (d, *J* = 1.9 Hz), 126.11 (d, *J* = 3.6 Hz), 125.79 (d, *J* = 1.6 Hz), 125.56 (d, *J* = 12.7 Hz), 124.18, 123.09 (d, *J* = 1.8 Hz), 122.60 (d, *J* = 12.7 Hz), 60.73 (d, *J* = 2.5 Hz), 34.93, 31.44.

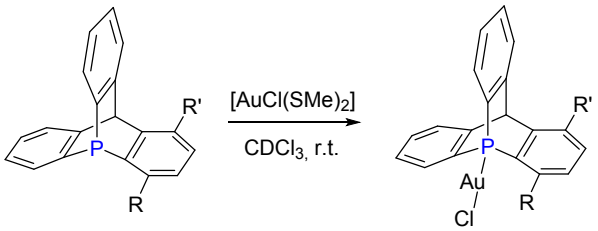
$^{31}$P NMR (202 MHz, $CDCl_3$) δ -73.50.

HRMS (ESI$^+$): Calcd. for $C_{23}H_{21}ClP$ $[M + H]^+$: 363.10639, found: 363.10617.

m.p.: 177-178 °C

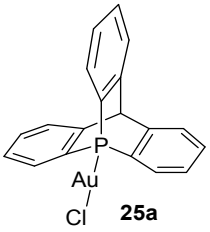
**TLC: $R_f$** = 0.63 (cyclohexane: AcOEt = 5:1)

### 1.14 General procedure and characterization data for the $Ar_3PAuCl$ complexes 25a-e




**[AuCl($R_3P$)]**
**25a-e**

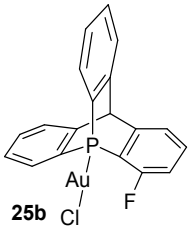
A NMR tube was charged with [AuCl($SMe_2$)] (10.0 mg, 3.4 × $10^{-2}$ mmol), 9-phospatriptycenes (3.4 × $10^{-2}$ mmol), and 1 mL of $CDCl_3$ in an argon glove box.[6] After measurements of the NMR spectra, the solvent was slowly evaporated under argon and the selected 9-phospatriptycene-Au complexes were obtained in quantitative yield as yellow crystals suitable for single-crystal X-ray diffraction analysis.




**25a**

$^1$H NMR (500 MHz, $CDCl_3$) δ 7.88 (dd, *J* = 14.3, 7.4 Hz, 3H), 7.68 – 7.42 (m, 3H), 7.31 – 7.21 (m, 3H), 7.19 (tdd, *J* = 7.7, 3.0, 1.1 Hz, 3H), 5.64 (s).

$^{31}$P NMR (202 MHz, $CDCl_3$) δ -1.89.

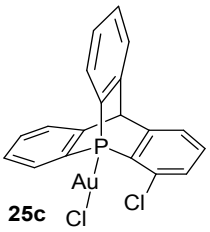



**25b**

$^1$H NMR (500 MHz, $CDCl_3$) δ 7.97 (dd, *J* = 14.7, 7.3 Hz, 2H), 7.62 (dd, *J* = 7.3, 3.0 Hz, 2H), 7.42 (d, *J* = 7.4 Hz, 1H), 7.37 – 7.23 (m, 5H), 6.89 (td, *J* = 8.3, 5.4 Hz, 1H), 5.69 (s, 1H).

$^{31}$P NMR (202 MHz, $CDCl_3$) δ -19.35 (d, *J* = 22.8 Hz).

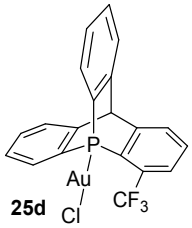
$^{19}$F NMR (376 MHz, $CDCl_3$) δ -105.10 (dd, *J* = 17.3, 11.7 Hz).




**25c**

$^1$H NMR (500 MHz, $CDCl_3$) δ 8.02 (dd, *J* = 14.6, 7.2 Hz, 2H), 7.64 – 7.59 (m, 2H), 7.55 – 7.46 (m, 1H), 7.35 (tt, *J* = 7.5, 1.3 Hz, 2H), 7.28 (ddd, *J* = 7.4, 3.1, 1.1 Hz, 2H), 7.24 – 7.22 (m, 1H), 7.20 – 7.19 (m, 1H), 5.66 (s, 1H).

$^{31}$P NMR (202 MHz, $CDCl_3$) δ -10.68.

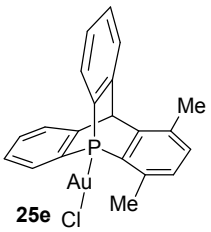



**25d**

$^{1}$H NMR (500 MHz, $CDCl_3$) δ 8.06 (ddd, *J* = 14.8, 7.3, 0.7 Hz, 2H), 7.81 (d, *J* = 7.5 Hz, 1H), 7.63 (dd, *J* = 7.3, 2.7 Hz, 2H), 7.55 (dd, *J* = 7.7, 4.6 Hz, 1H), 7.41 (t, *J* = 7.7 Hz, 1H), 7.35 (tt, *J* = 7.6, 1.3 Hz, 2H), 7.29 – 7.23 (m, 2H), 5.75 (s, 1H).

$^{31}$P NMR (202 MHz, $CDCl_3$) δ -5.60 (q, *J* = 17.2 Hz).

$^{19}$F NMR (376 MHz, $CDCl_3$) δ -53.58 (d, *J* = 19.4 Hz).

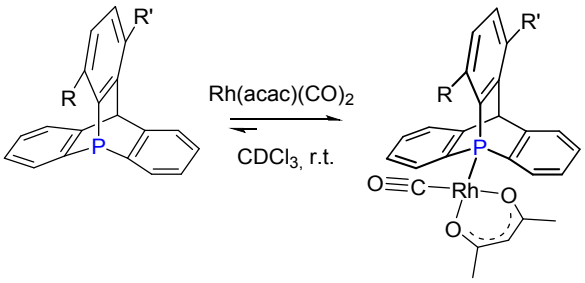



**25e**

$^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.98 (ddd, *J* = 8.5, 7.0, 0.9 Hz, 2H), 7.59 (dd, *J* = 7.2, 2.9 Hz, 2H), 7.31 (tt, *J* = 7.5, 1.3 Hz, 2H), 7.23 (tdd, *J* = 7.5, 3.1, 1.1 Hz, 2H), 7.04 (d, *J* = 7.7 Hz, 1H), 6.87 (dd, *J* = 7.6, 6.0 Hz, 1H), 5.98 (s, 1H), 3.01 (s, 3H), 2.59 (s, 3H)

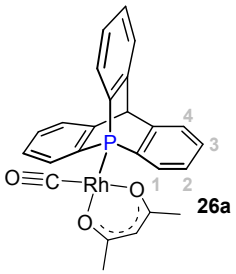
$^{31}$P NMR (202 MHz, $CDCl_3$) δ -13.44.

### 1.15 General procedure and characterization data for the Rh(acac)(CO)($PR_3$) complexes 26a-e




**[Rh(acac)(CO)($R_3P$)]**
**26a-e**

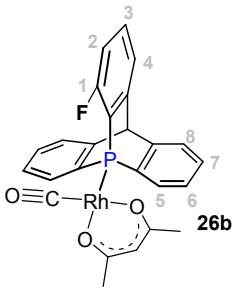
A NMR tube was charged with Rh(acac)$(CO)_2$ (10.0 mg, $3.8 \times 10^{-2}$ mmol), 9-phospatriptycenes ($3.67 \times 10^{-2}$ mmol), and 1 mL of $CDCl_3$ in an argon glove box. After measurements of the NMR spectra, the solvent was slowly evaporated under argon and the Rh(acac)(CO)($PR_3$) complexes were obtained in quantitative yield as yellow crystals suitable for single-crystal X-ray diffraction analysis. In all cases the yields in P-Rh complexes were nearly quantitative or higher than 97%.




**26a**

$^1$H NMR (500 MHz, $CDCl_3$) δ 8.44 (dd, *J* = 11.7, 7.4 Hz, 3H, H-1), 7.52 (d, *J* = 7.3 Hz, 3H, H-4), 7.19 (dddd, *J* = 10.1, 7.4, 5.1, 1.1 Hz, 6H, H-2 and H-3), 5.68 (s, 1H, $C_{sp}^3$-H), 5.57 (s, 1H), 2.25 (s, 3H, $CH_3$), 2.02 (s, 3H, $CH_3$).

$^{31}$P NMR (202 MHz, $CDCl_3$) δ 4.43 (d, *J* = 188.5 Hz).

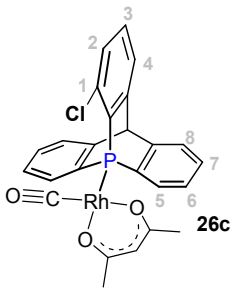



**26b**

$^1$H NMR (500 MHz, $CDCl_3$) δ 8.63 (dd, *J* = 11.6, 7.5 Hz, 2H, H-5), 7.58 – 7.50 (m, 2H, H-8), 7.33 (d, *J* = 7.4 Hz, 1H, H-4), 7.25 (t, *J* = 7.4 Hz, 2H, H-7), 7.22 – 7.15 (m, 3H, H-3, 6), 6.84 (td, *J* = 8.5, 4.8 Hz, 1H, H-2), 5.65 (s, 1H, $C_{sp}^3$-H), 5.57 (s, 1H), 2.22 (s, 3H), 1.99 (s, 3H).

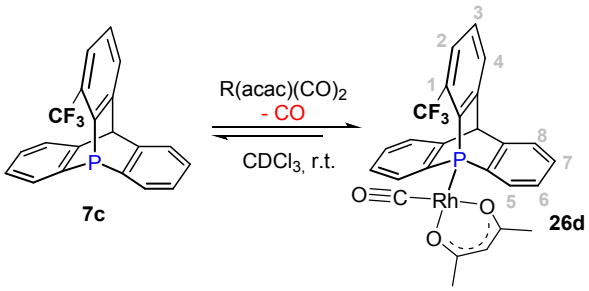
$^{31}$P NMR (202 MHz, $CDCl_3$) δ -11.58 (dd, $^1J_{P\text{-}Rh}$ = 191.8 Hz and $^3J_{P\text{-}F}$ = 11.4 Hz).

$^{19}$F NMR (376 MHz, $CDCl_3$) δ -102.99.




$^{1}$H NMR (500 MHz, $CDCl_3$) δ 8.56 – 8.43 (m, 2H, H-5), 7.52 (d, *J* = 7.3 Hz, 2H, H-8), 7.46 (dd, *J* = 5.2, 1.4 Hz, 1H, H-4), 7.24 – 7.23 (m, 2H, H-7), 7.19 – 7.15 (m, 4H, H-2, 3, 6), 5.63 (s, 1H, $C_{sp}^{3}$-H), 5.55 (s, 1H), 2.22 (s, 3H), 1.94 (s, 3H).

$^{31}$P NMR (202 MHz, $CDCl_3$) δ -0.51 (d, *J* = 195.5 Hz).

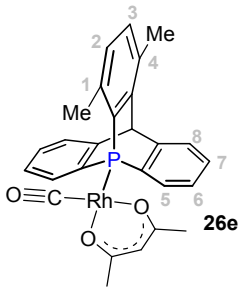



The association was not quantitative in this case and according to the $^{1}$H NMR integrals, the Rh-P complex was formed only in 15% yield under these conditions.

$^{1}$H NMR (500 MHz, $CDCl_3$) δ 8.59 (dd, *J* = 11.5, 7.5 Hz, 2H, H-5), 7.72 (d, *J* = 7.5 Hz, 1H, H-4), 7.57 – 7.54 (m, 2H, H-8), 7.34 (t, *J* = 7.7 Hz, 1H, H-2), 7.20 – 7.19 (m, 3H, H-3, 7), 7.16 (tdd, *J* = 7.5, 3.1, 1.2 Hz, 2H, H-6), 5.63 (s, 1H, $C_{sp}^{3}$-H), 5.60 (s, 1H), 2.22 (s, 3H), 1.96 (s, 3H).

$^{31}$P NMR (202 MHz, $CDCl_3$) δ 0.47 (dq, $^{1}J_{P\text{-}Rh}$ = 199.5 Hz and $^{4}J_{P\text{-}F}$ = 11.7 Hz)

$^{19}$F NMR (376 MHz, $CDCl_3$) δ -50.80 (d, *J* = 13.4 Hz).




$^{1}$H NMR (500 MHz, $CDCl_3$) δ 8.40 (dd, *J* = 10.6, 6.7 Hz, 2H, H-5), 7.51 (d, *J* = 7.7 Hz, 2H, H-8), 7.22 (t, *J* = 7.4 Hz, 2H, H-7), 7.14 (tdd, *J* = 7.4, 3.0, 1.4 Hz, 2H, H-6), 7.00 (d, *J* = 7.7 Hz, 1H, H-2), 6.87 (dd, *J* = 7.7, 5.0 Hz, 1H, H-3), 5.91 (s, 1H, $C_{sp}^{3}$-H), 5.64 (s, 1H), 3.36 (s, 3H), 2.61 (s, 3H), 2.23 (s, 3H), 1.93 (s, 3H).

$^{31}$P NMR (202 MHz, $CDCl_3$) δ -2.95 (d, *J* = 187.8 Hz).

## 2. Determination of Tolman electronic parameter.

### 2.1 IR measurements of the $\nu_{CO}$ stretching frequency in the Rh(acac)CO(9-phosphatriptycenes) complexes.

$Rh(acac)(CO)(PR_3)$ complexes were prepared by mixing a phosphine $PR_3$ and $Rh(CO)_2acac$ under stoichiometric amounts in 0.5 mL of $CH_2Cl_2$ in a glove-box and the solution was placed in a IR quartz cell. A linear correlation between the $\nu_{CO}$ stretching frequencies of $Rh(acac)(CO)(PR_3)$ and the $\nu_{CO}$ stretching frequencies of $Ni(CO)_3(PR_3)$ complexes used originally for determining the Tolman electronic parameter (**TEP**) has previously been reported by Carow,[7] which allowed us to determine the **TEP** value for 9-phosphatriptycenes. We also checked that our IR measurements of the $\nu_{CO}$ stretching frequency in several $Rh(acac)(CO)(PR_3)$ complexes were in agreement with literature data and found that our results are within a ±5 $cm^{-1}$ range from reported values (Table S1).

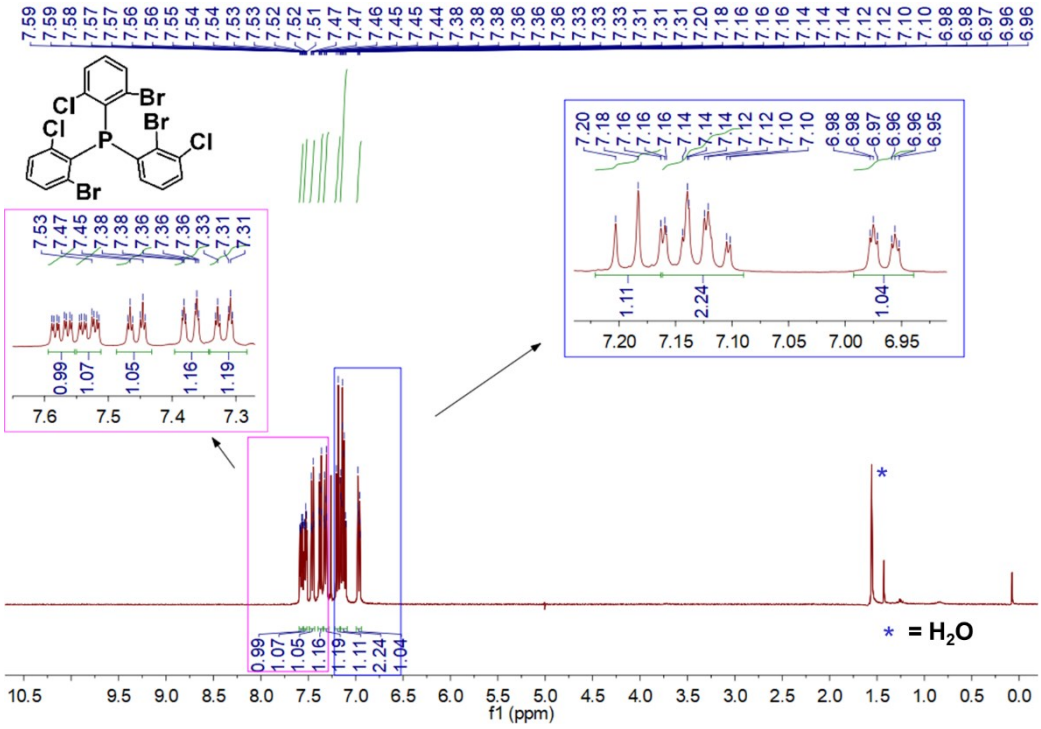
***Table S1***: Infrared stretching frequencies ($cm^{-1}$) and Tolman electronic parameter (**TEP**) for representative phosphines.

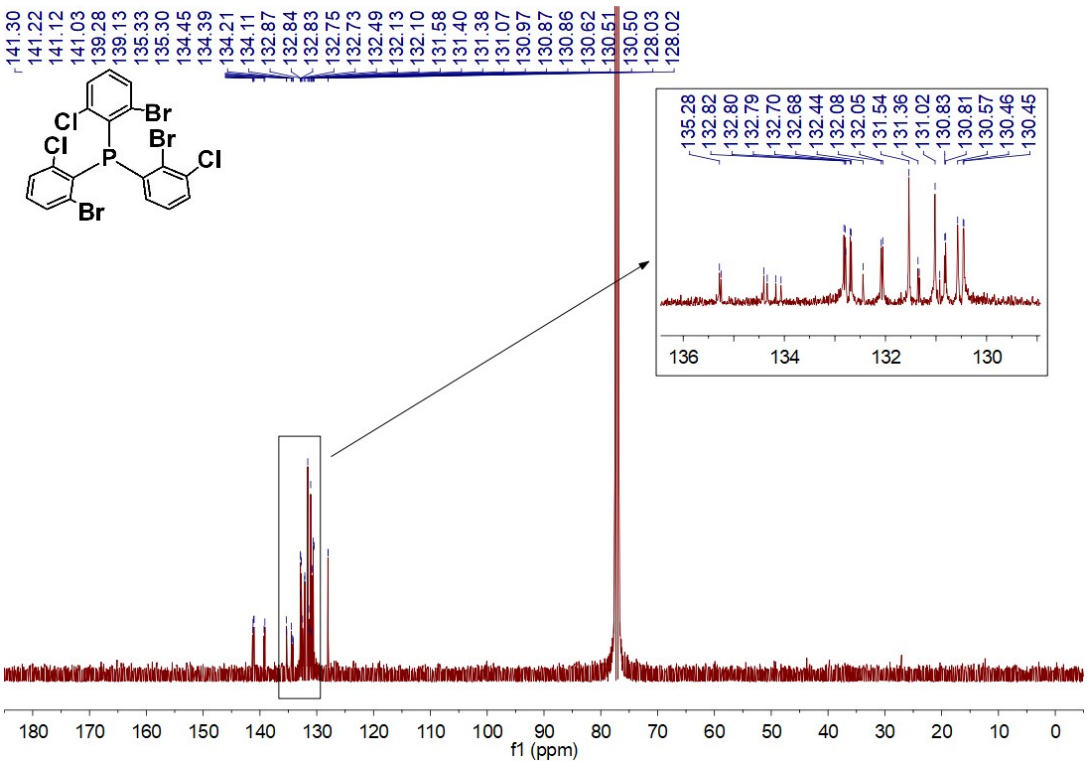
| **Phosphines in [Rh(acac)(CO)($R_3$P)] complexes** | **TEP[a] / $cm^{-1}$ (this work)** | ***V*(CO) Rh complex[b] / $cm^{-1}$** | ***V*(CO) Rh complex / $cm^{-1}$ (this work)** |
|---|---|---|---|
| F-P-triptycene (**7a**) | 2075 | not reported | 1983 |
| Cl-P-triptycene (**7b**) | 2075 | not reported | 1983 |
| $CF_3$-P-triptycene (**7c**) | 2073 | not reported | 1980 |
| 1,4-di-Me-P-triptycene (**8a**) | 2074 | not reported | 1982 |
| P-triptycene (**1**) | 2076[2] | not reported | 1985 |
| P(*p*-$CF_3C_6H_5)_3$ | 2074[a] | 1986 | -- |
| P(*p*-$ClC_6H_5)_3$ | 2073[a] | 1982 | 1980 |
| $PPh_3$ | 2069[a] | 1978 | 1976 |

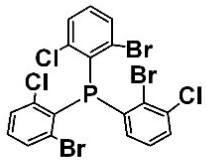
[a] The **TEP** values are ±5 $cm^{-1}$ range from reported values; [b] from reference 7.

## 3. Copies of all NMR spectra

### 3.1 Bis-(2-bromo-6-chlorophenyl)-(2-bromo-3-chlorophenyl)-phosphine 13a in $CDCl_3$: $^1$H-NMR (400 MHz), $^{13}$C-NMR (100 MHz), $^{31}$P-NMR (161 MHz)

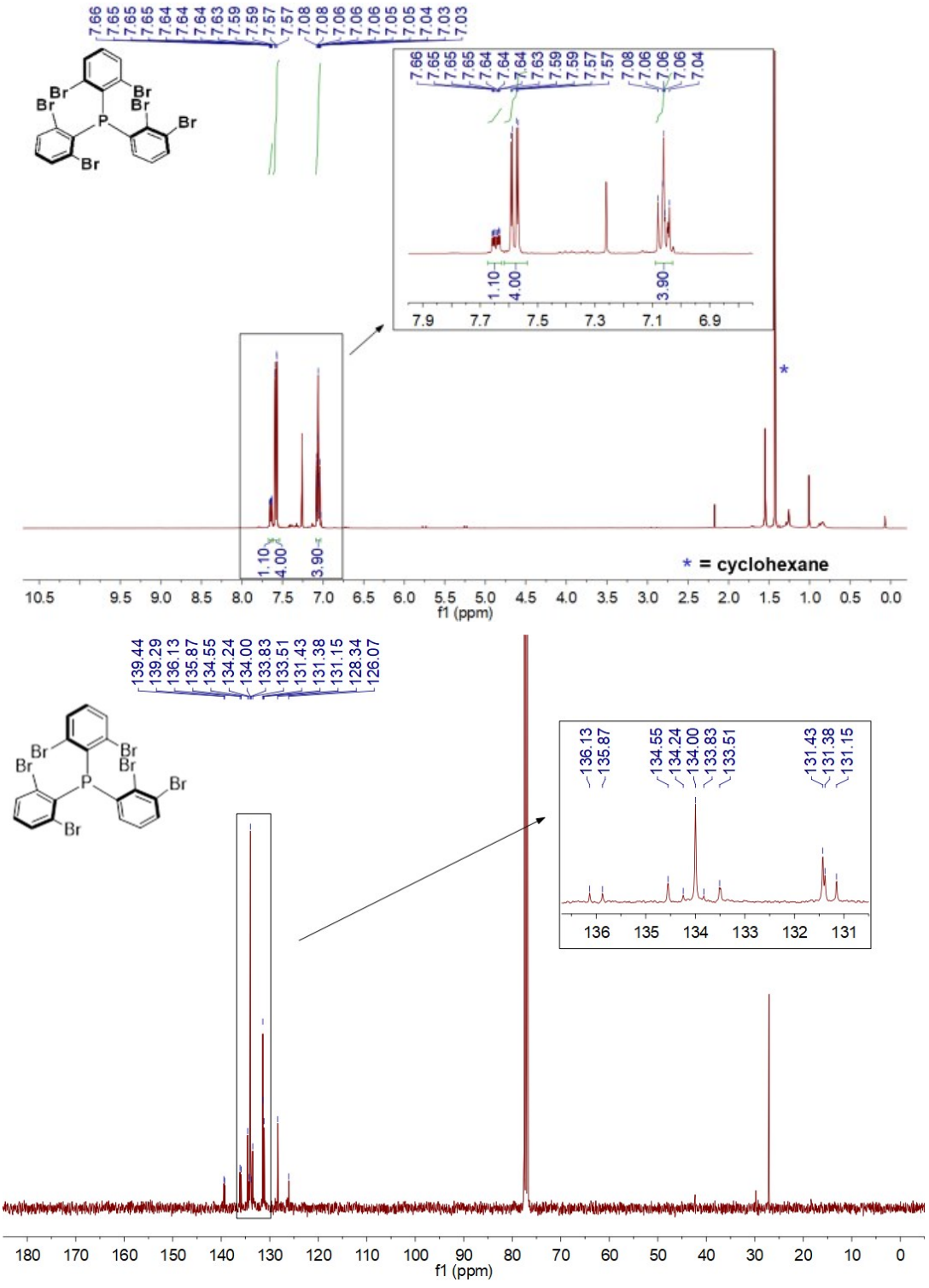


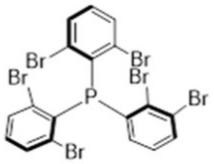




Cl
Br
Cl
Br
P
Cl
Br


13.85
100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90
f1 (ppm)

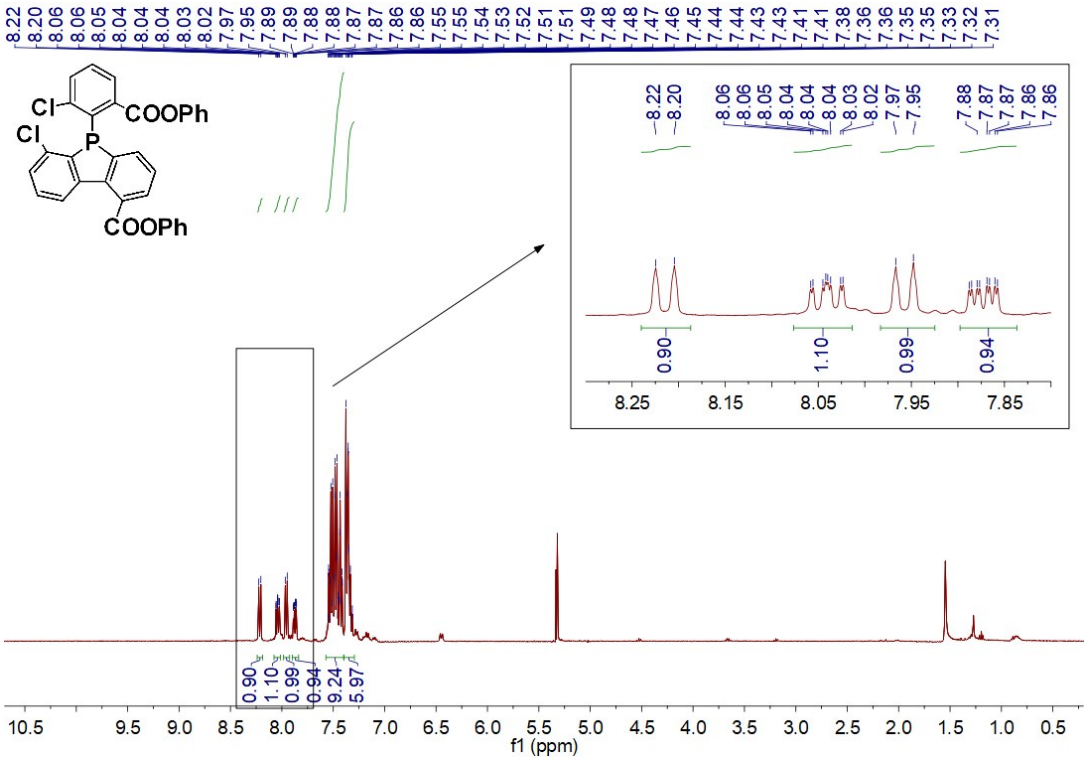
**3.2 Bis-(2,6-dibromo-phenyl)-(2,3-dibromophenyl) phosphine 13b in $CDCl_3$: $^{1}$H-NMR (400 MHz), $^{13}$C-NMR (100 MHz), $^{31}$P-NMR (161 MHz)**

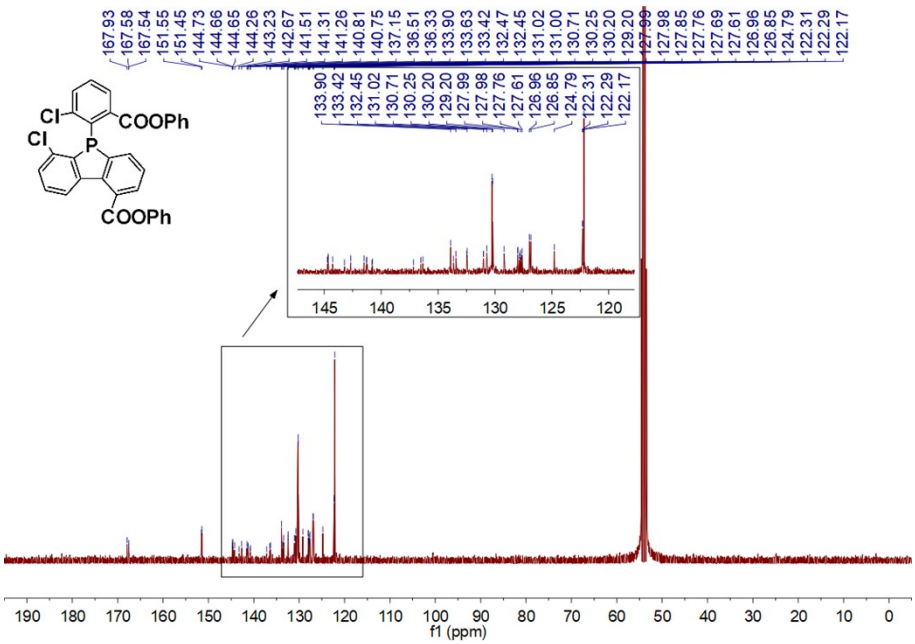


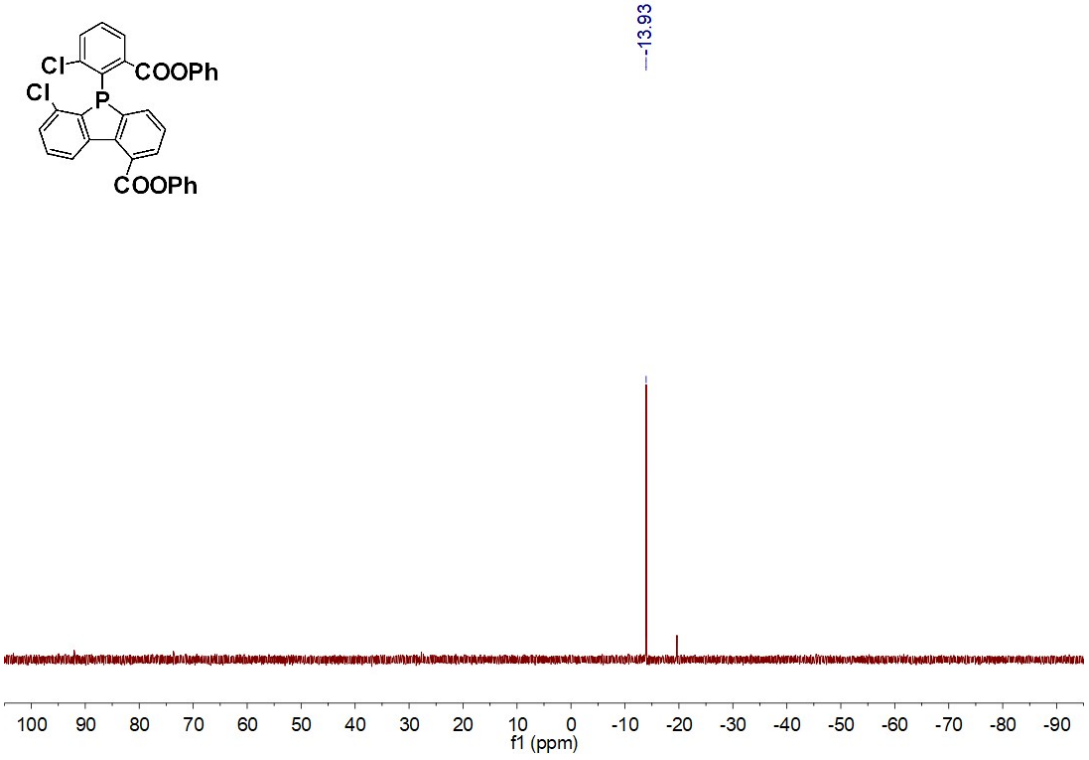

Br
Br
Br
Br
P
Br
Br


-27.30
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
f1 (ppm)

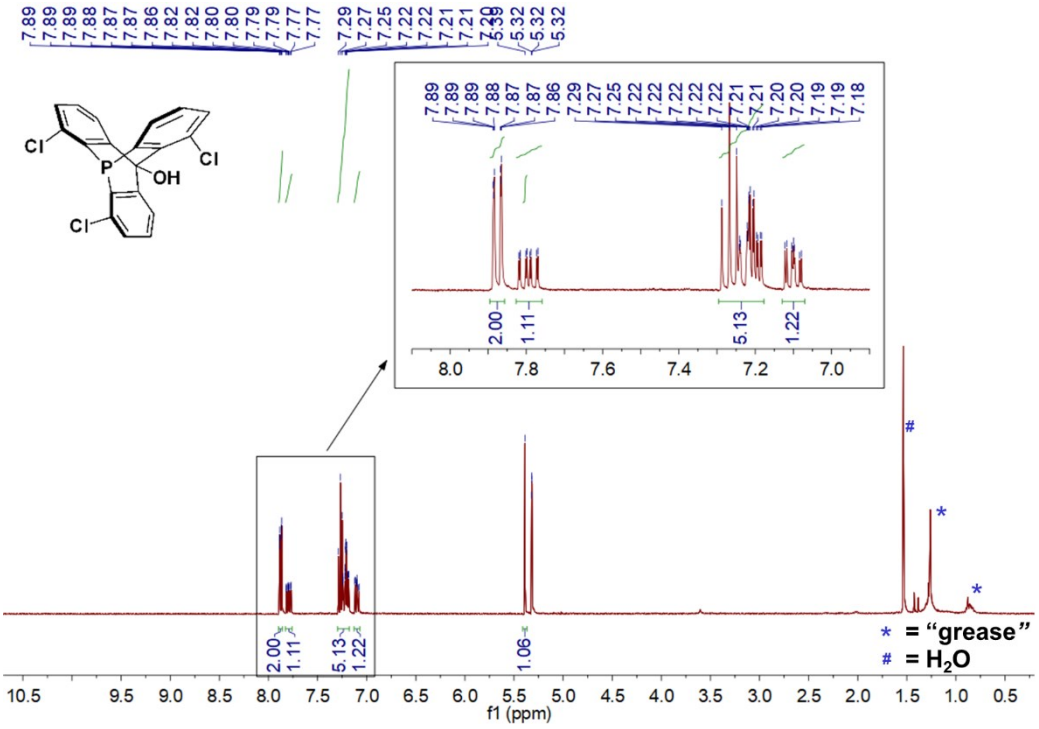
**3.3 9-phenyl-9-phosphafluorene derivative 15a in $CD_2Cl_2$: $^{1}$H-NMR (400 MHz), $^{13}$C-NMR (100 MHz), $^{31}$P-NMR (161 MHz)**

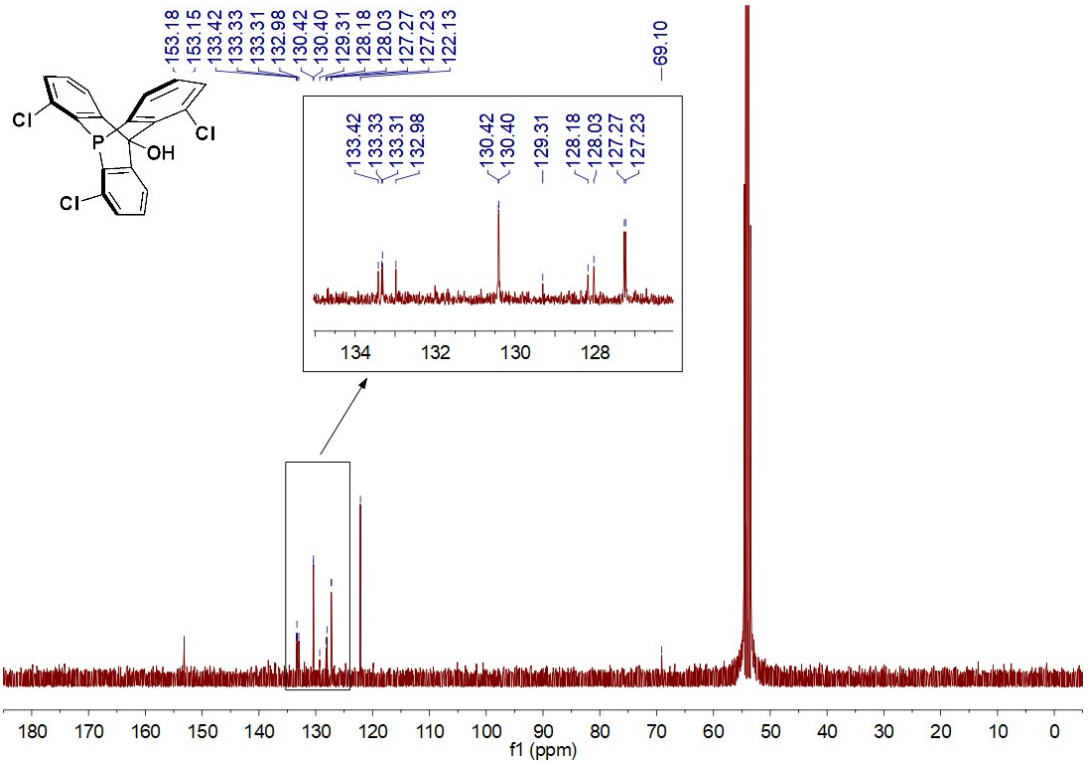


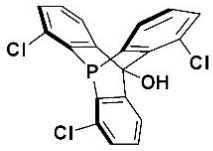




Cl
COOPh
Cl
P
COOPh
-13.93
100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90
f1 (ppm)

### 3.4 1,8,11-tris-chloro-9-phospha-10-hydroxytriptycene 16a in $CD_2Cl_2$: $^{1}H$-NMR (400 MHz), $^{13}C$-NMR (100 MHz), $^{31}P$-NMR (161 MHz)

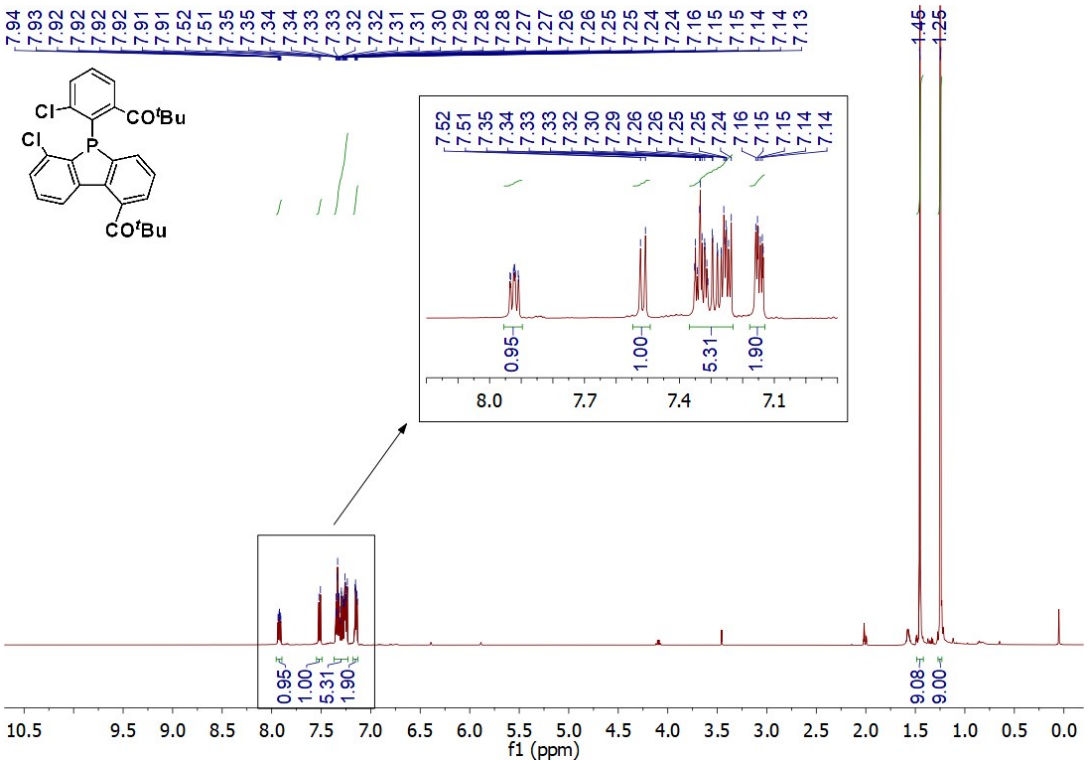


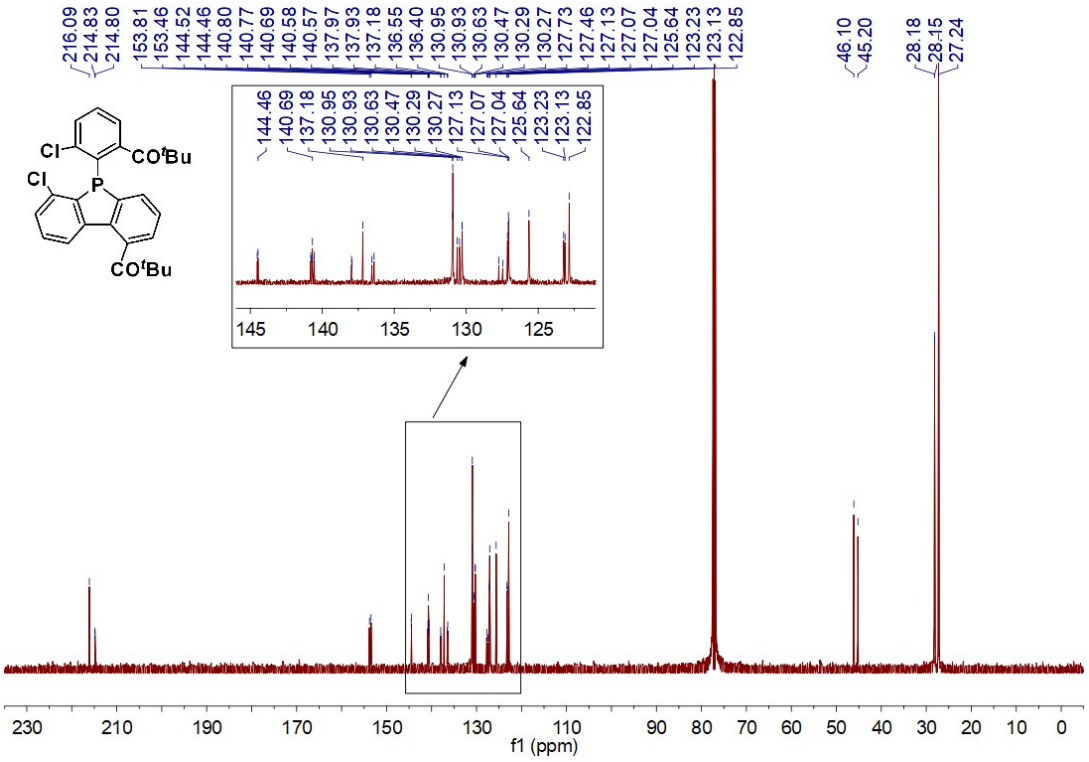



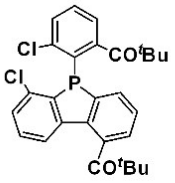

Cl
P
OH
Cl
Cl


88.92
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
f1 (ppm)

**3.5 9-phenyl-9-phosphorfluorene derivative 15b in $CDCl_3$: $^{1}H$-NMR (500 MHz), $^{13}C$-NMR (126 MHz), $^{31}P$-NMR (202 MHz)**

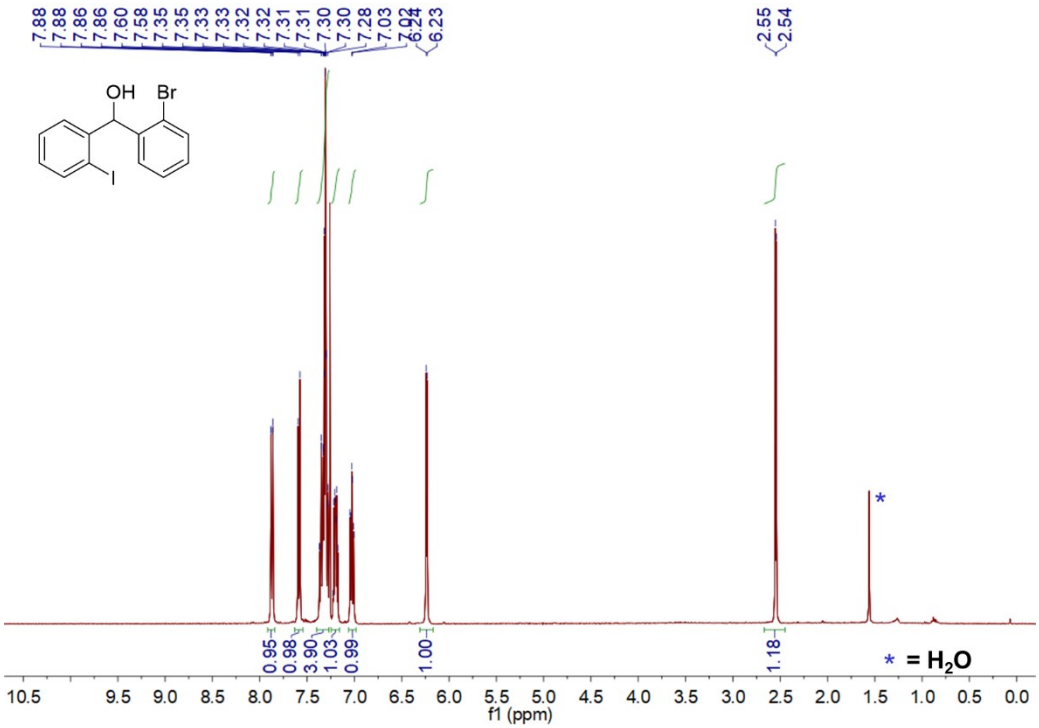


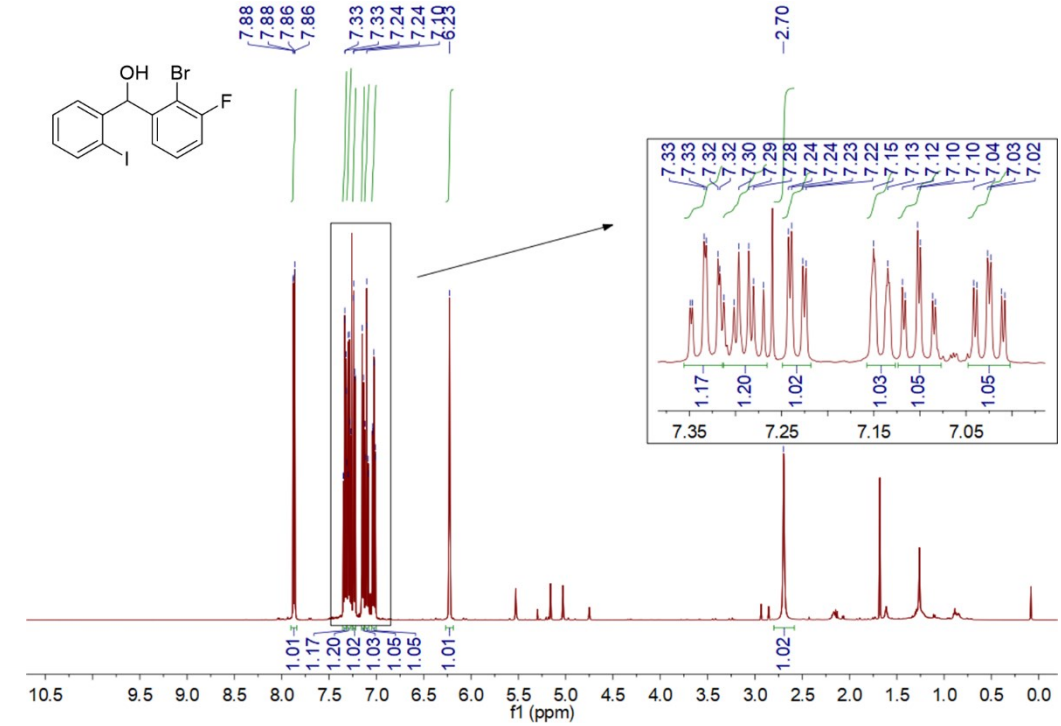

Cl
CO$^t$Bu
Cl
P
CO$^t$Bu

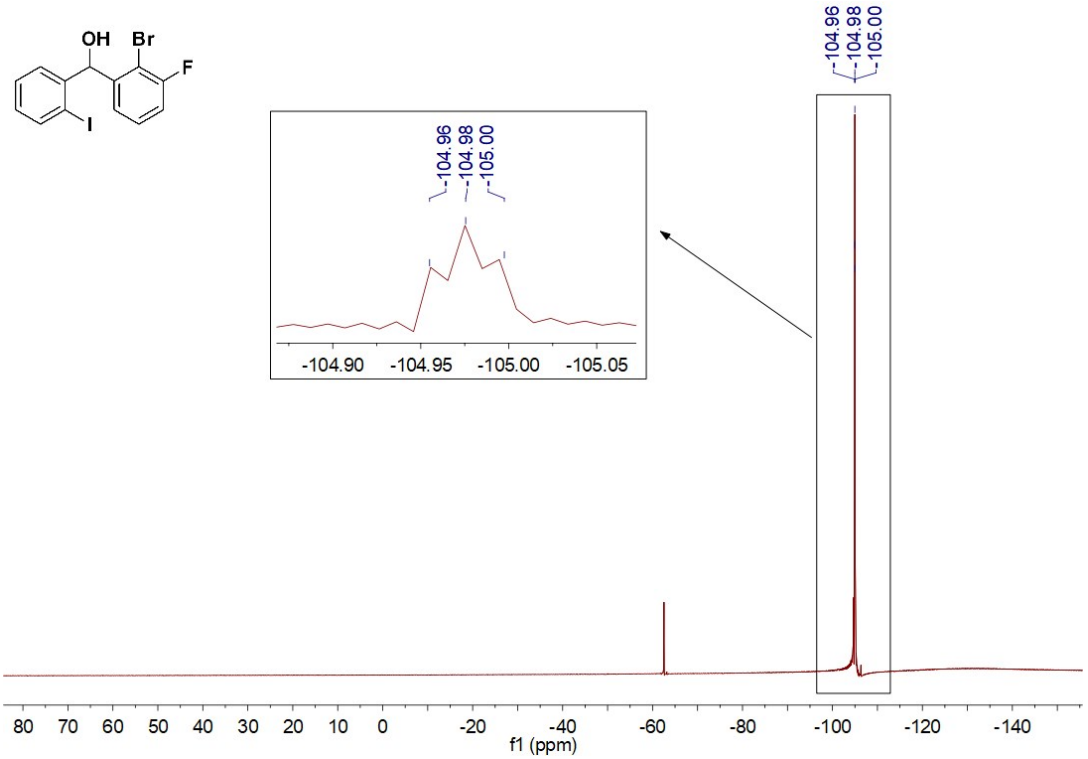

-11.51
100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90
f1 (ppm)

### 3.6 Bis-(halogenated-phenyl)-methanol precursor 21 in $CDCl_3$: $^1$H-NMR (400 MHz)

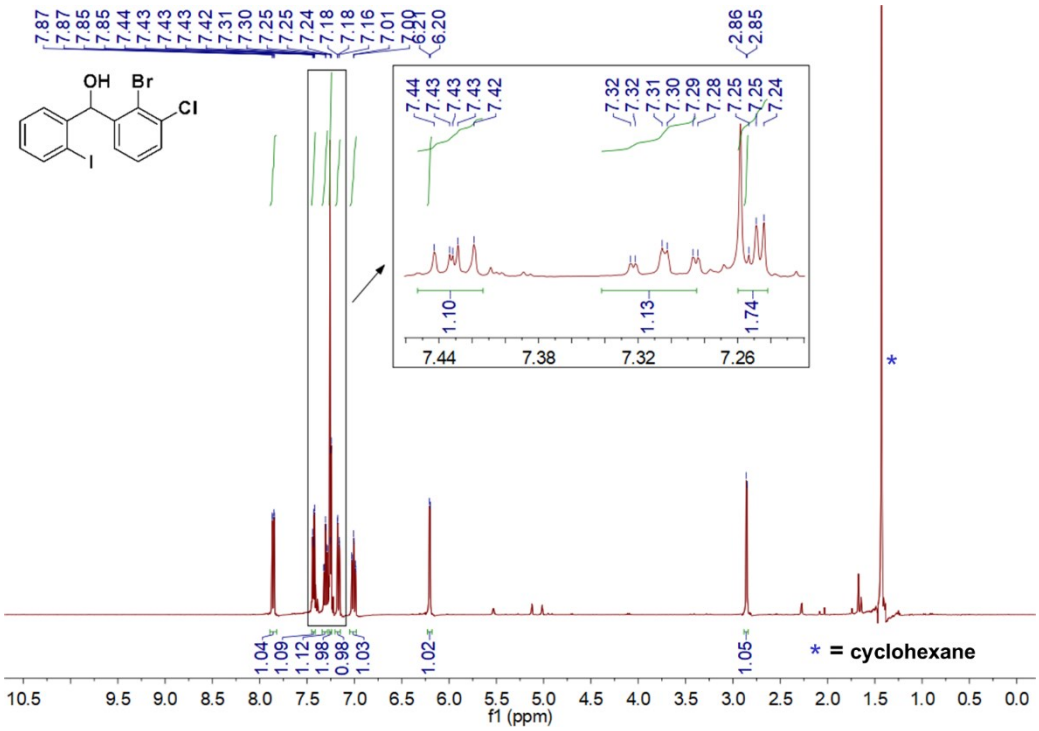


### 3.7 Bis-(halogenated-phenyl)-methanol precursor 17a in $CDCl_3$: $^1$H-NMR (400 MHz), $^{19}$F-NMR (376 MHz)

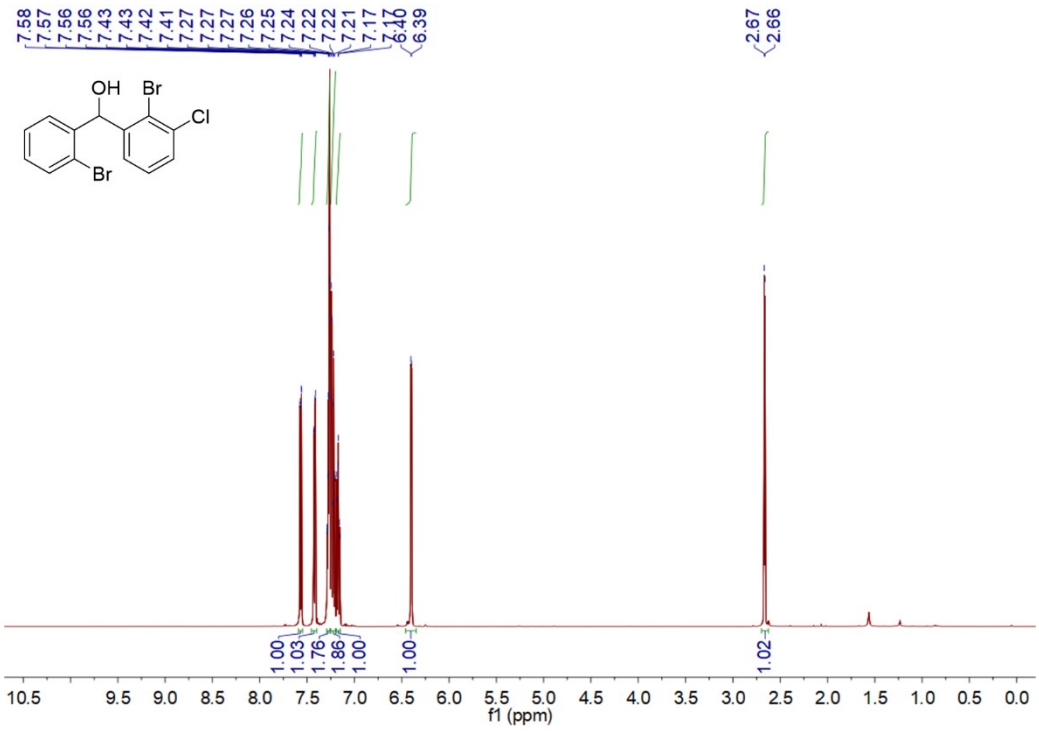


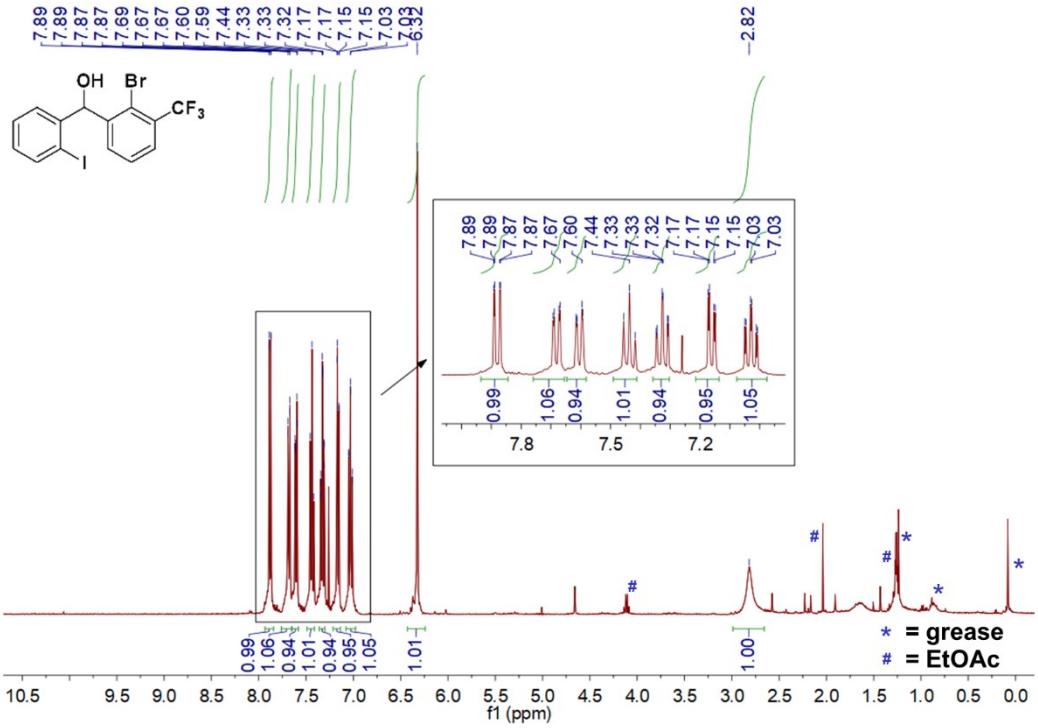
### 3.8 Bis-(halogenated-phenyl)-methanol precursor 17b in $CDCl_3$: $^1$H-NMR (400 MHz)

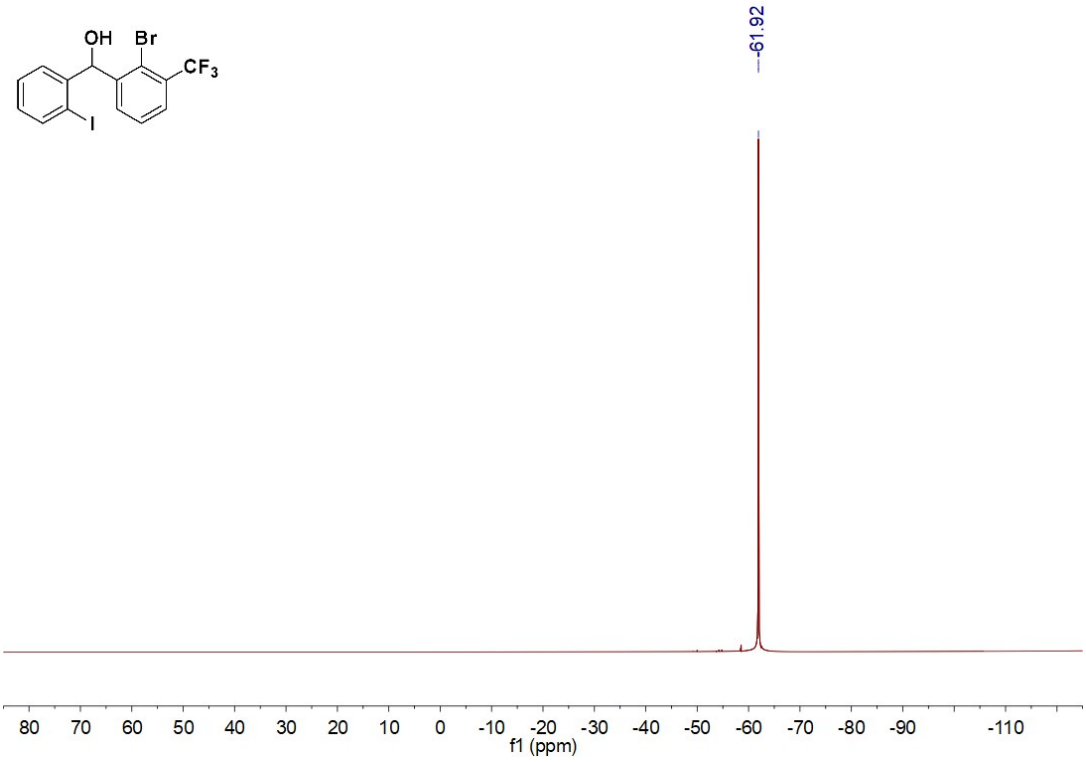



### 3.9 Bis-(halogenated-phenyl)-methanol precursor 27 in $CDCl_3$: $^1$H-NMR (500 MHz)

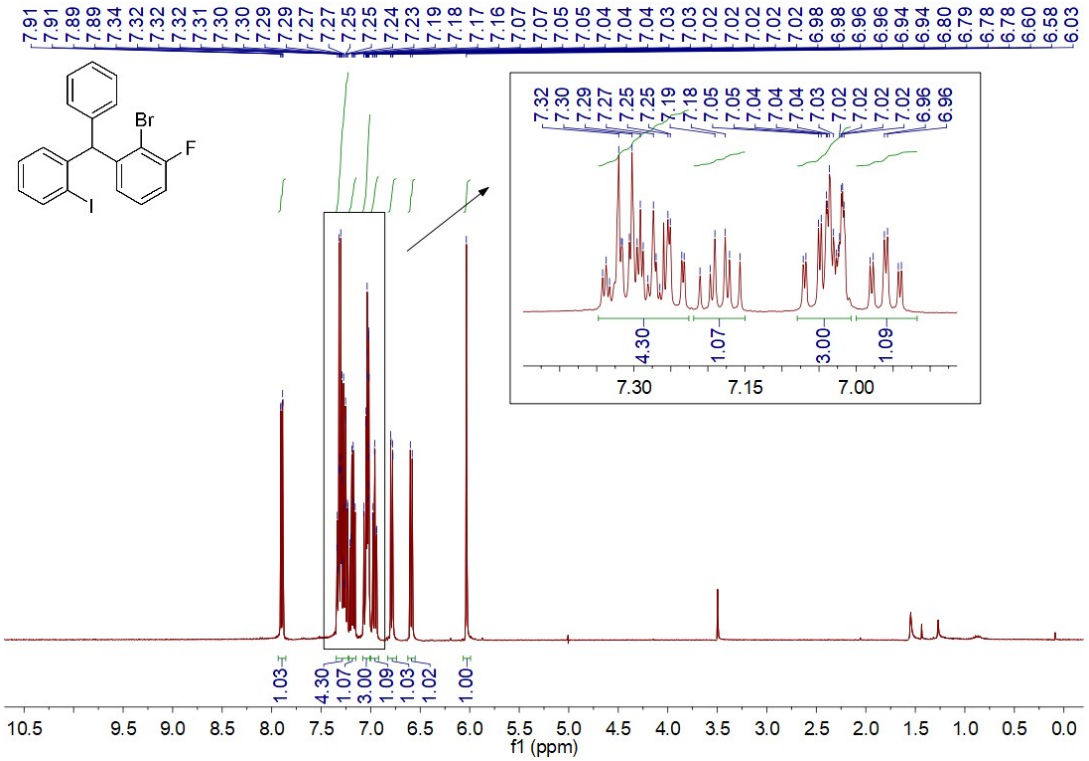


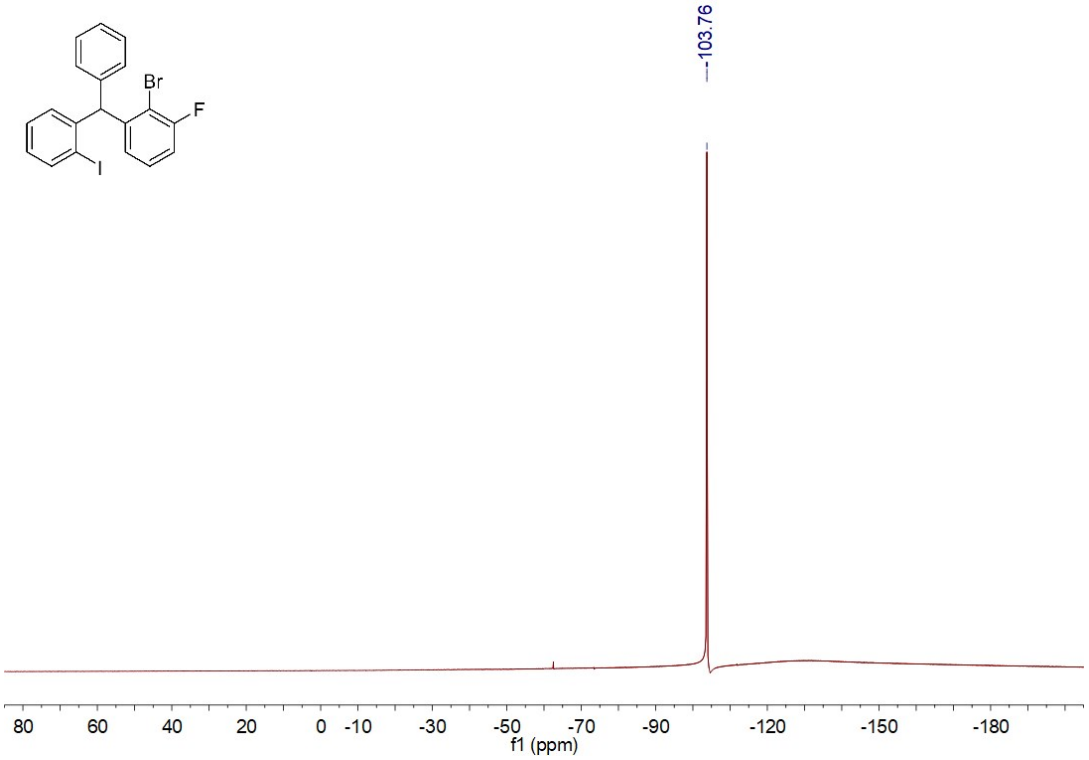
### 3.10 Bis-(halogenated-phenyl)-methanol precursor 17c in $CDCl_3$: $^1$H-NMR (400 MHz), $^{19}$F-NMR (376 MHz)



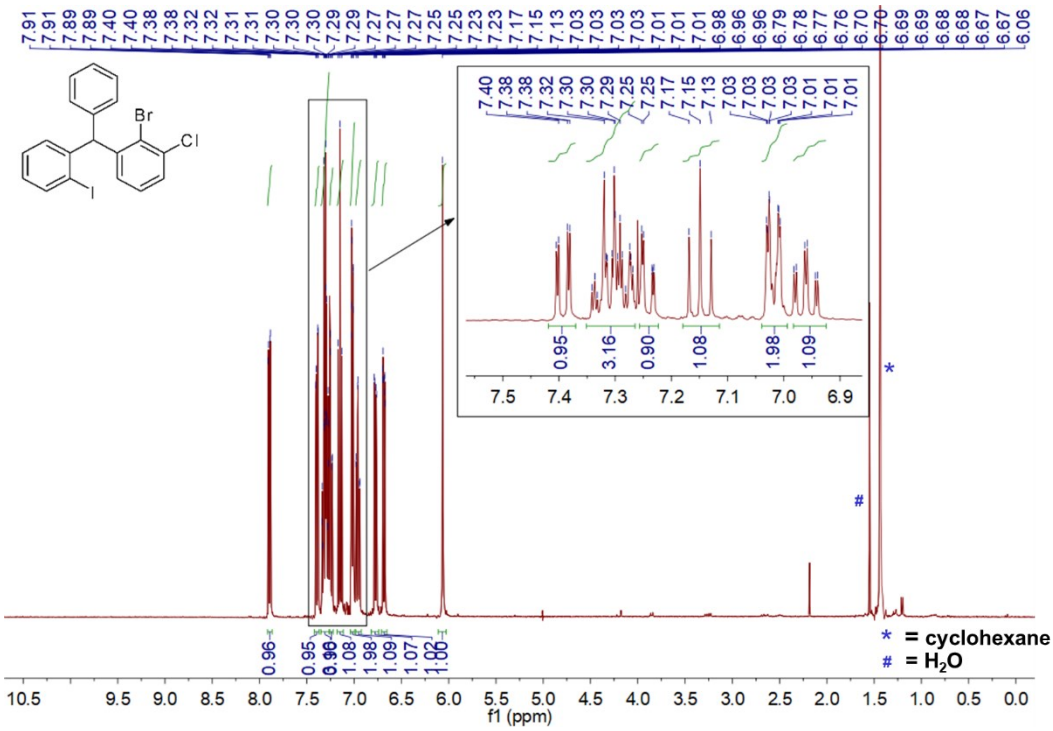



### 3.11 Trityl precursor 18a in $CDCl_3$: $^{1}H$-NMR (400 MHz), $^{19}F$-NMR (376 MHz)

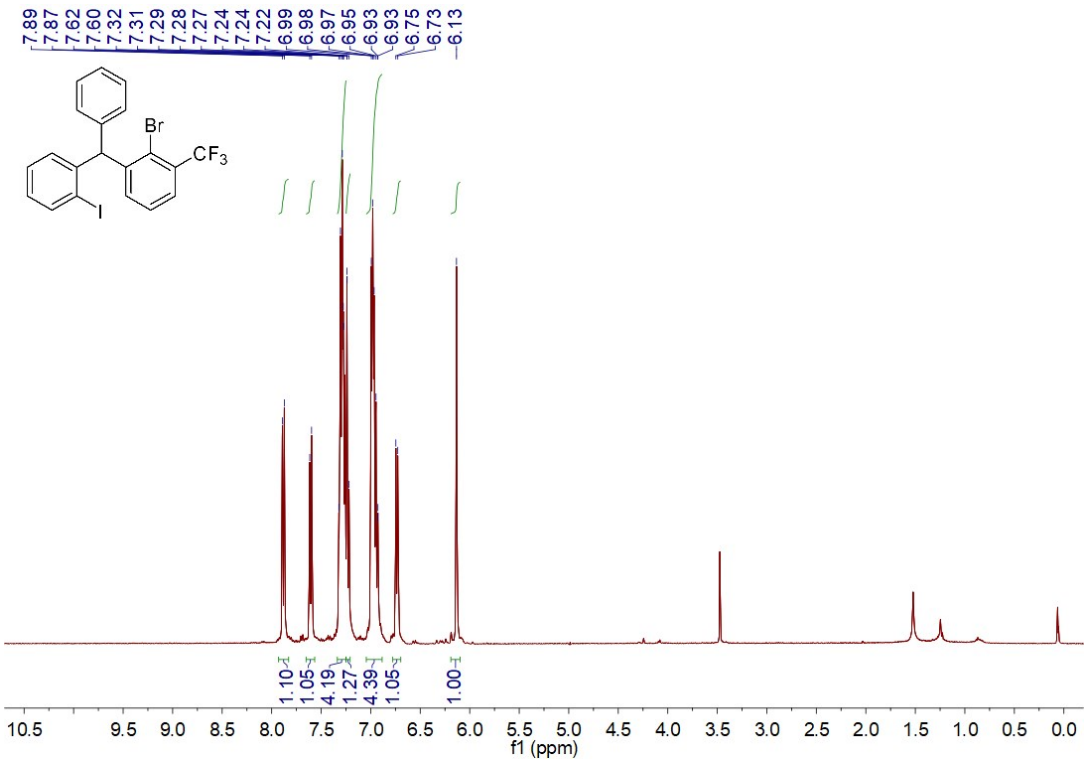


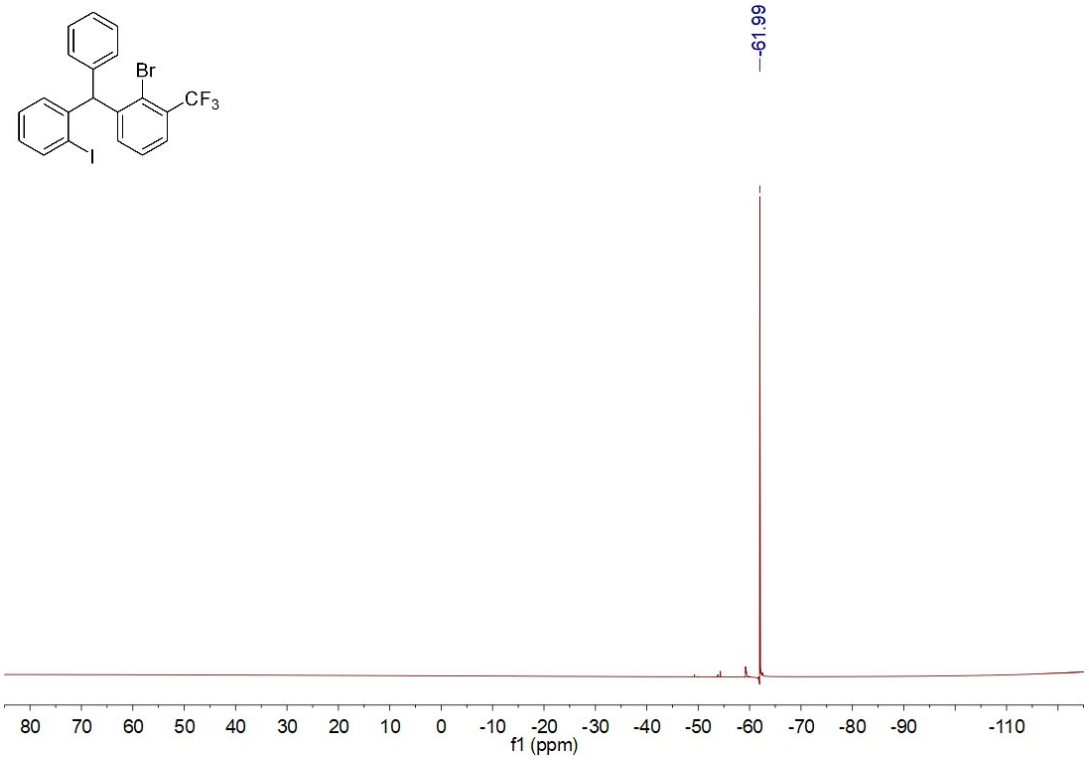



### 3.12 Trityl precursor 18b in $CDCl_3$: $^1$H-NMR (400 MHz)

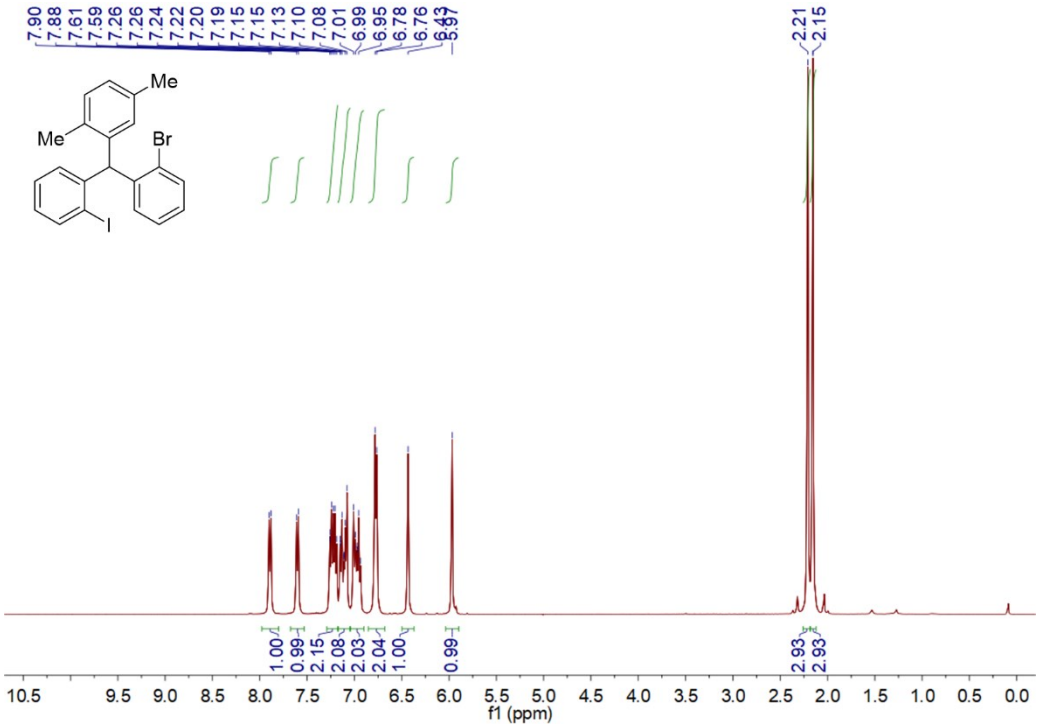


### 3.13 Trityl precursor 18c in $CDCl_3$: $^1$H-NMR (400 MHz), $^{19}$F-NMR (376 MHz)

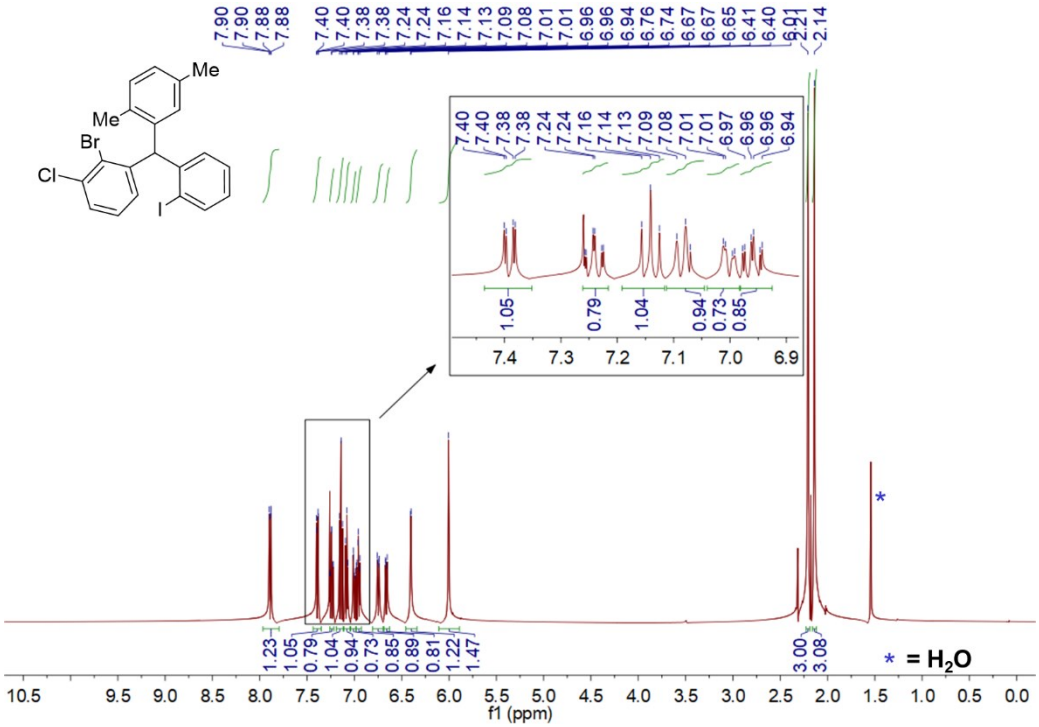


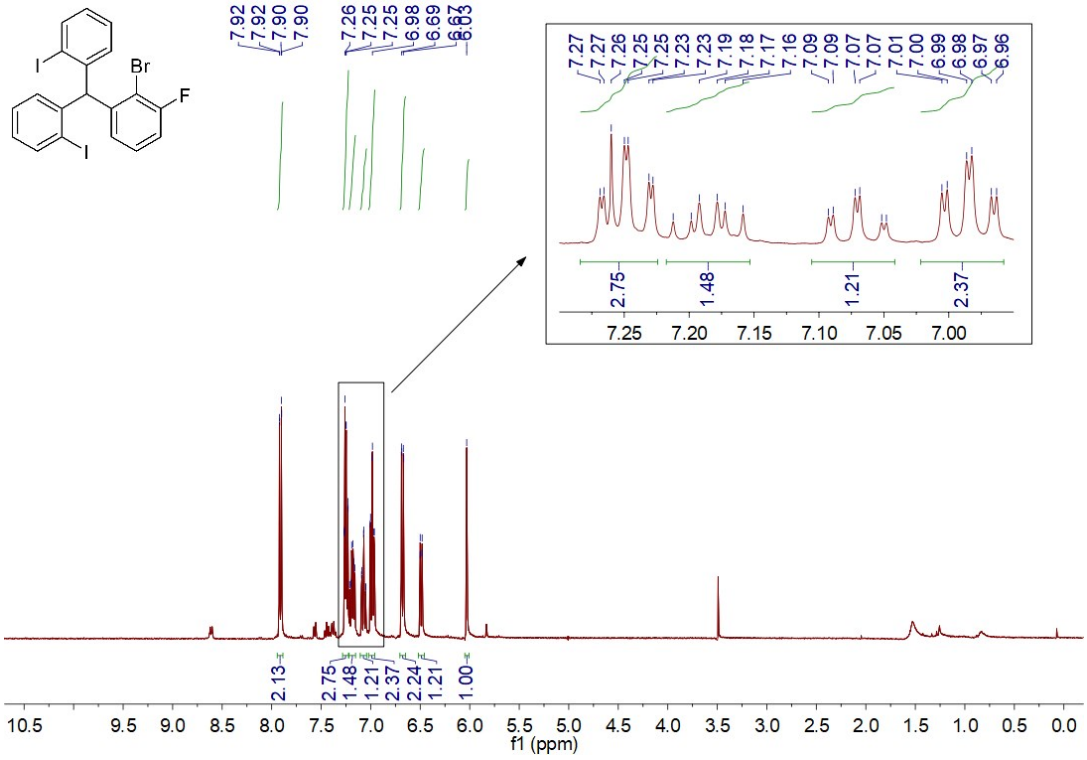
### 3.14 Trityl precursor 22 in $CDCl_3$: $^1$H-NMR (400 MHz)

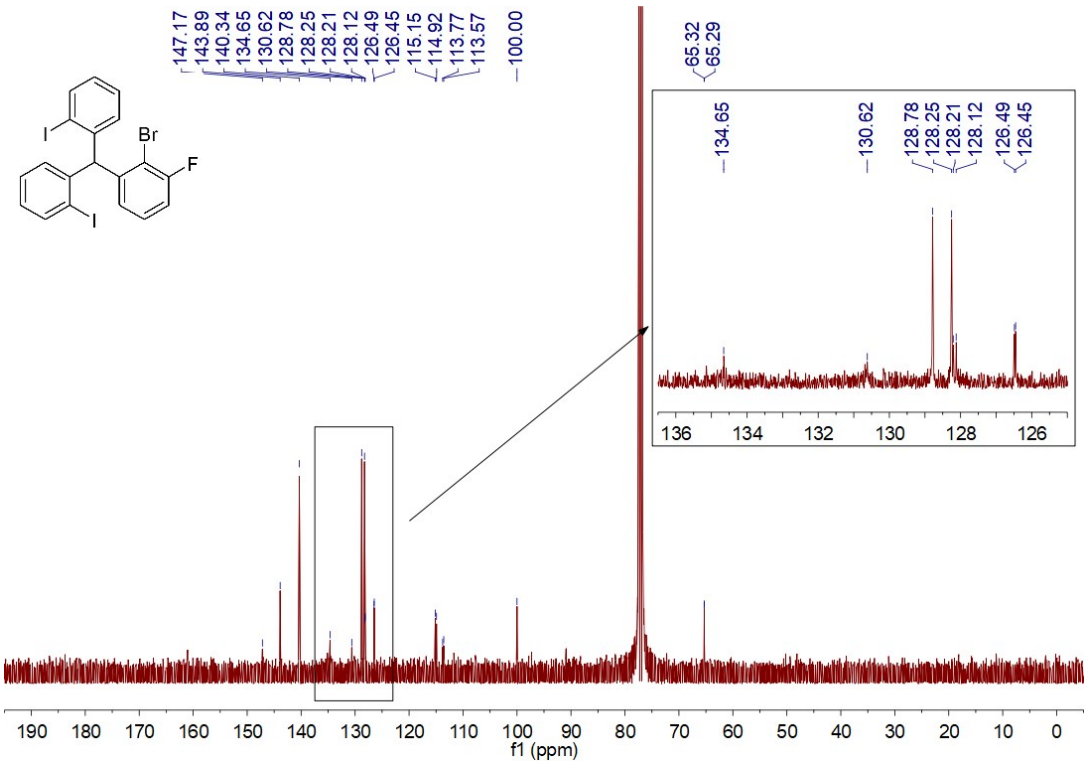


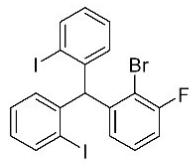

### 3.15 Trityl precursor 29 in $CDCl_3$: $^1$H-NMR (500 MHz)



**3.16 Trityl precursor 20a in $CDCl_3$: $^{1}H$-NMR (400 MHz), $^{13}C$-NMR (100 MHz), $^{19}F$-NMR (376 MHz)**

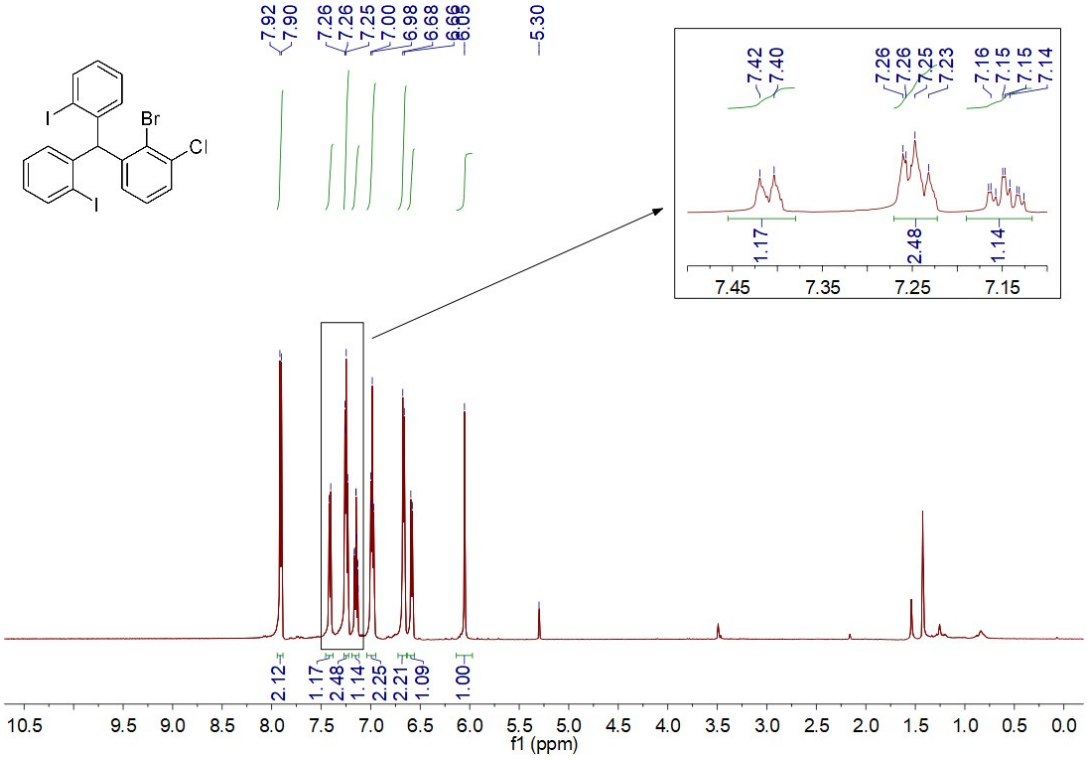


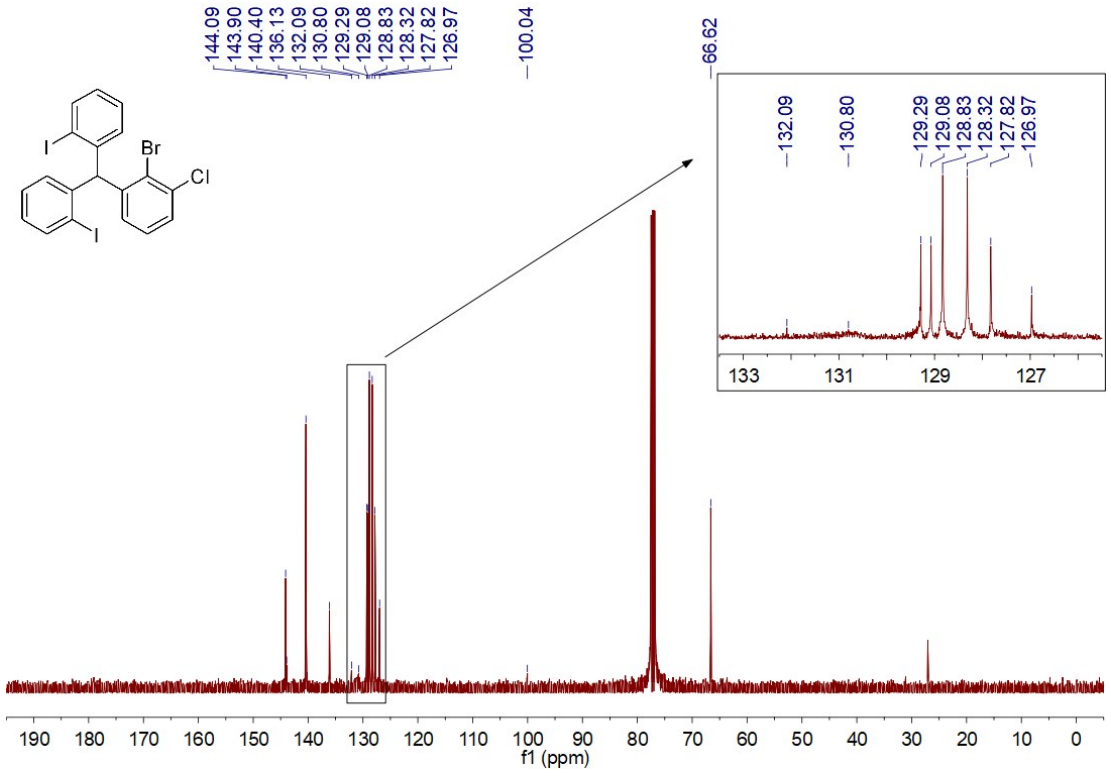




I
Br
F
I

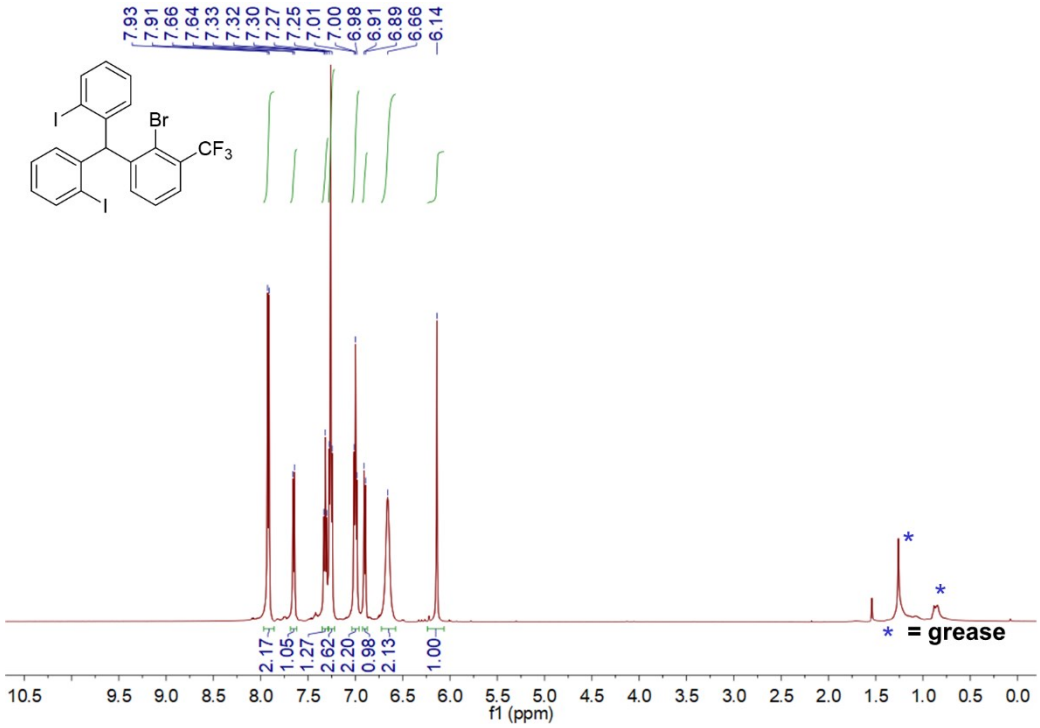

-103.64
80
60
40
20
0
-10
-30
-50
-70
-90
-120
-150
-180
f1 (ppm)

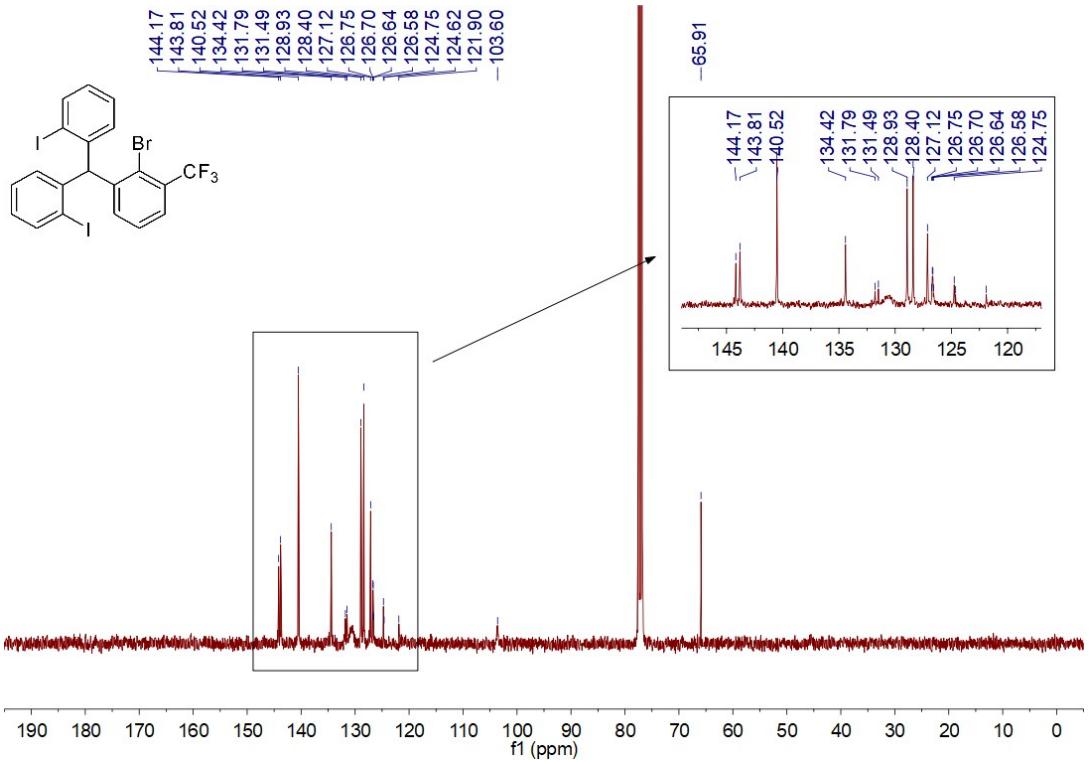
### 3.17 Trityl precursor 20b in $CDCl_3$: $^{1}H$-NMR (400 MHz), $^{13}C$-NMR (100 MHz)

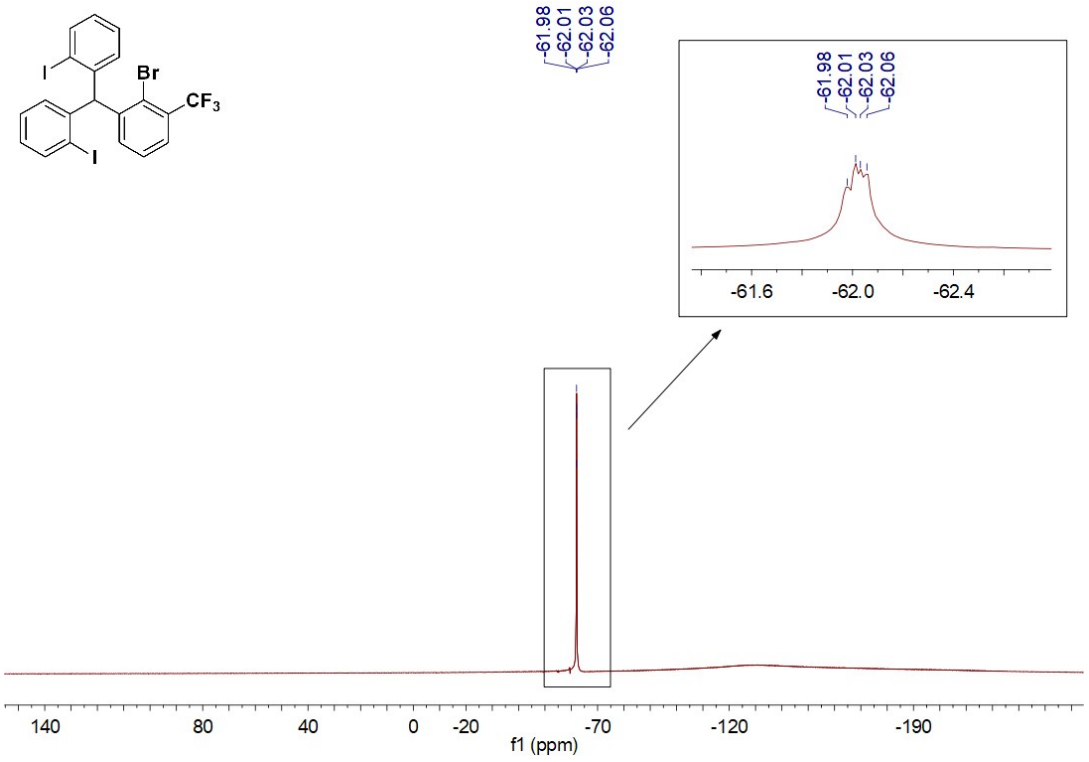


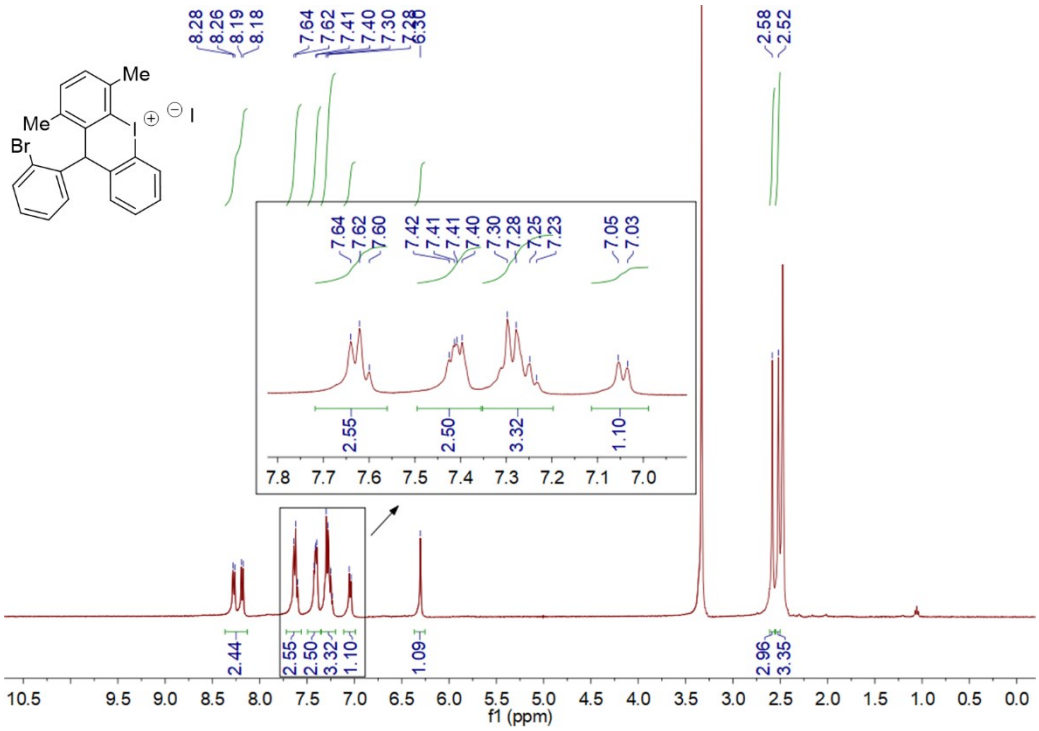
**3.18 Trityl precursor 20c in $CDCl_3$: $^{1}H$-NMR (500 MHz), $^{13}C$-NMR (126 MHz), $^{19}F$-NMR (476 MHz)**

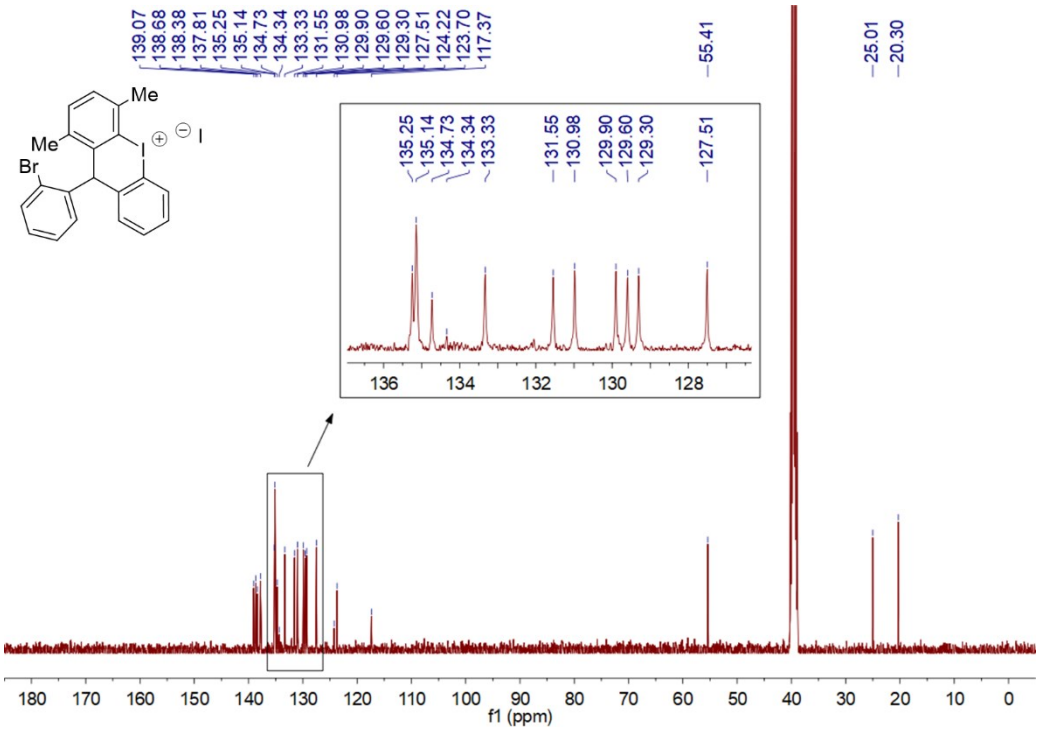


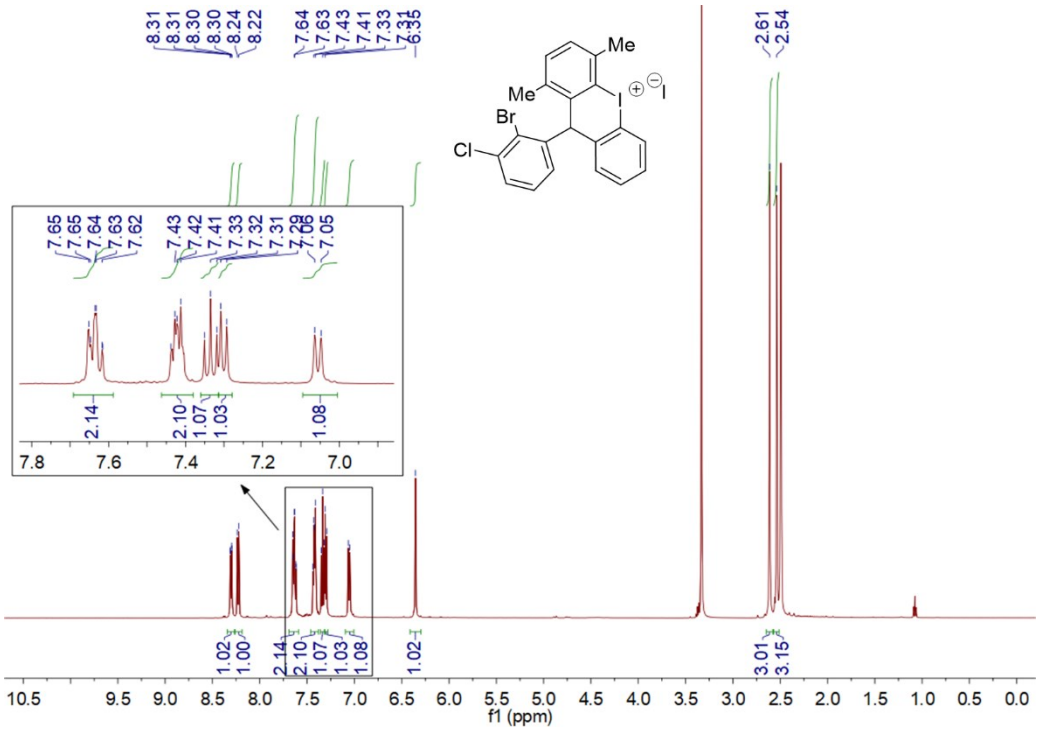

I
Br
CF3
I
-61.98
-62.01
-62.03
-62.06
-61.98
-62.01
-62.03
-62.06
-61.6
-62.0
-62.4
140
80
40
0
-20
-70
-120
-190
f1 (ppm)

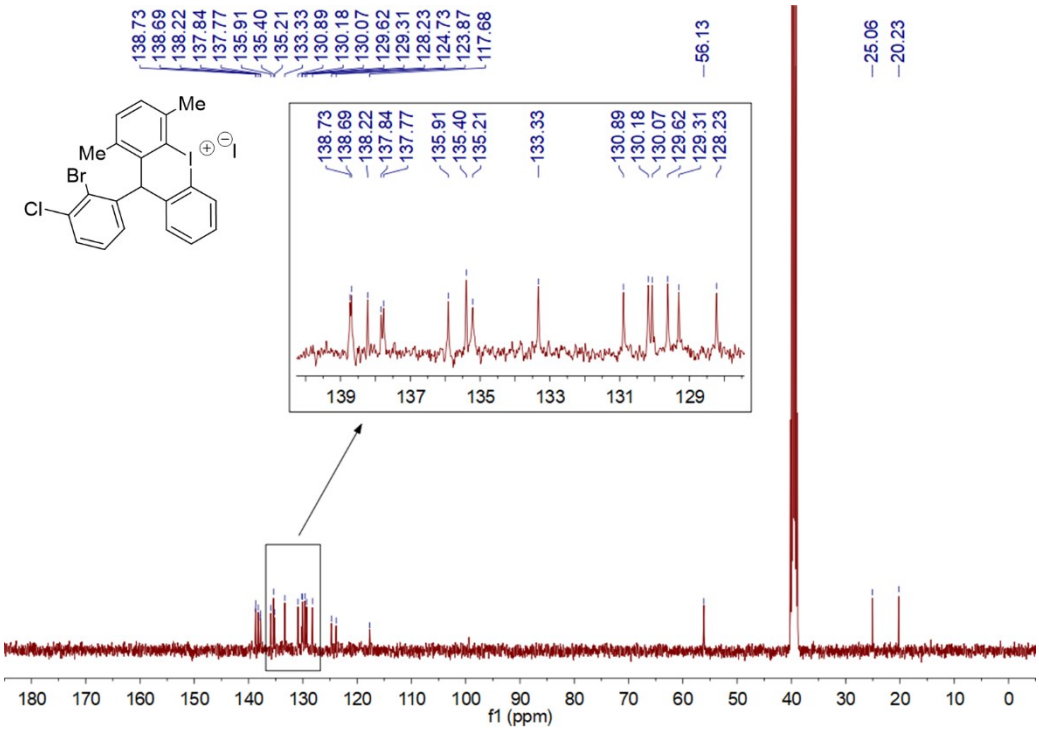
**3.19 Triphenylmethane iodonium salt 23 in $(CD_3)_2SO$: $^1$H-NMR (400 MHz), $^{13}$C-NMR (100 MHz)**



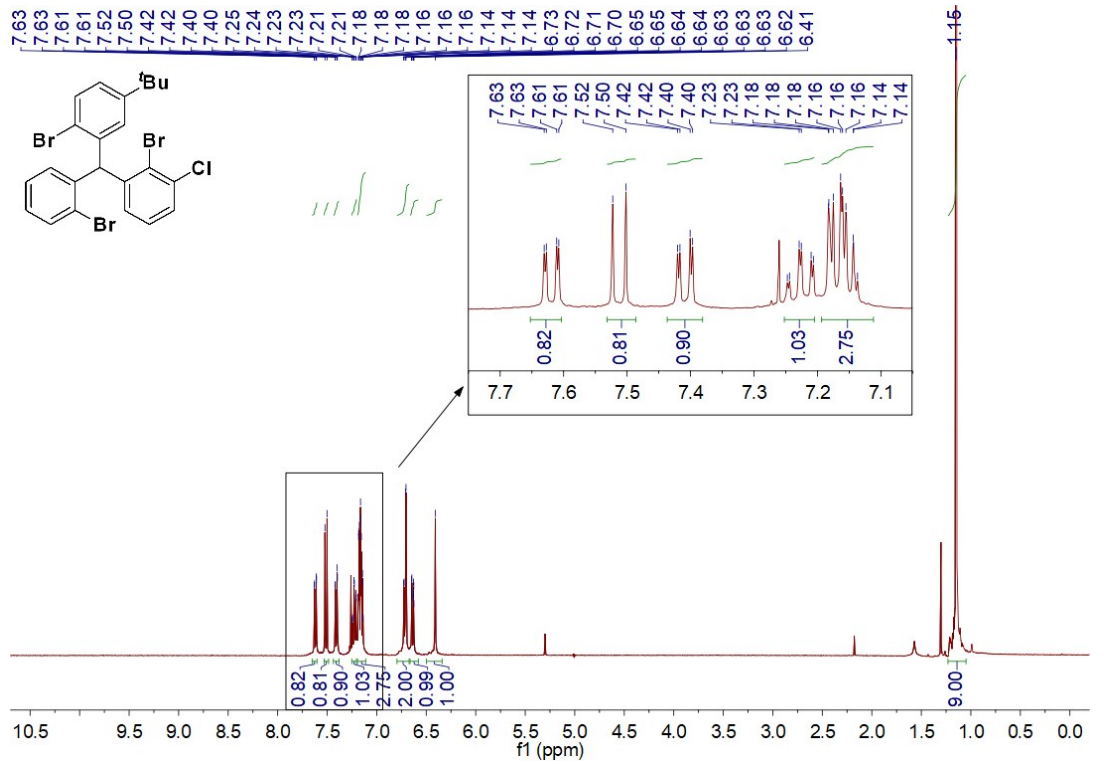



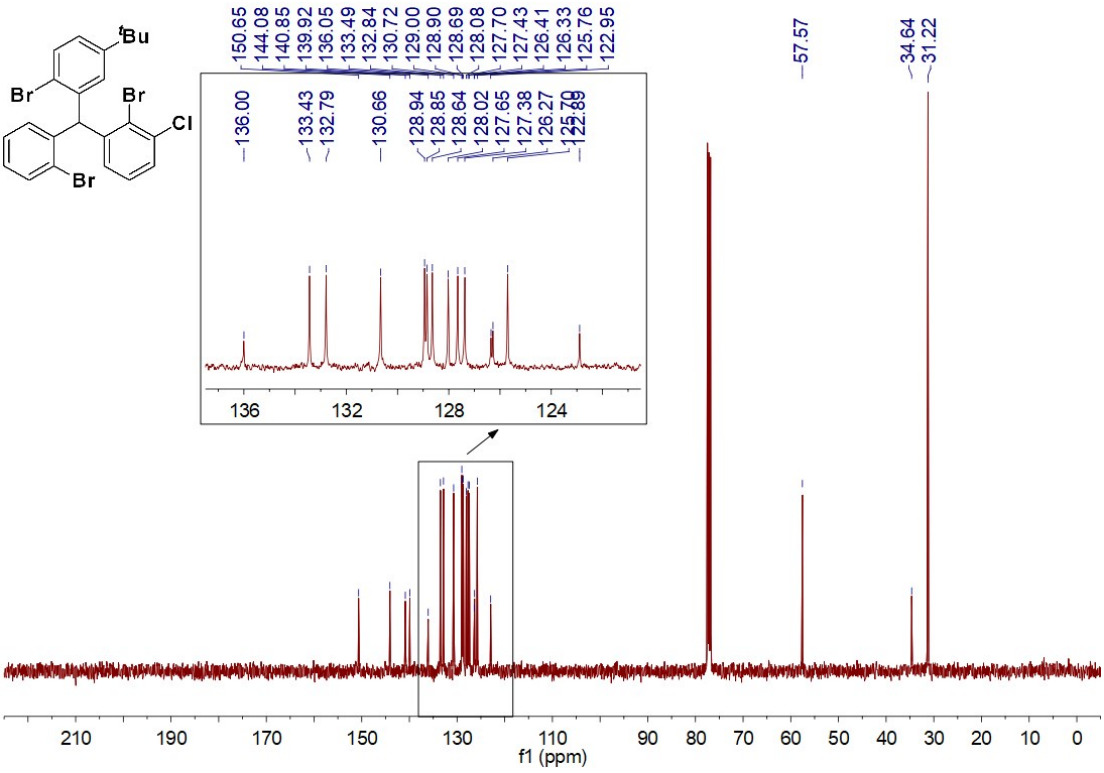
**3.20 Triphenylmethane iodonium salt 30 in $(CD_3)_2SO$: $^1$H-NMR (400 MHz), $^{13}$C-NMR (100 MHz)**



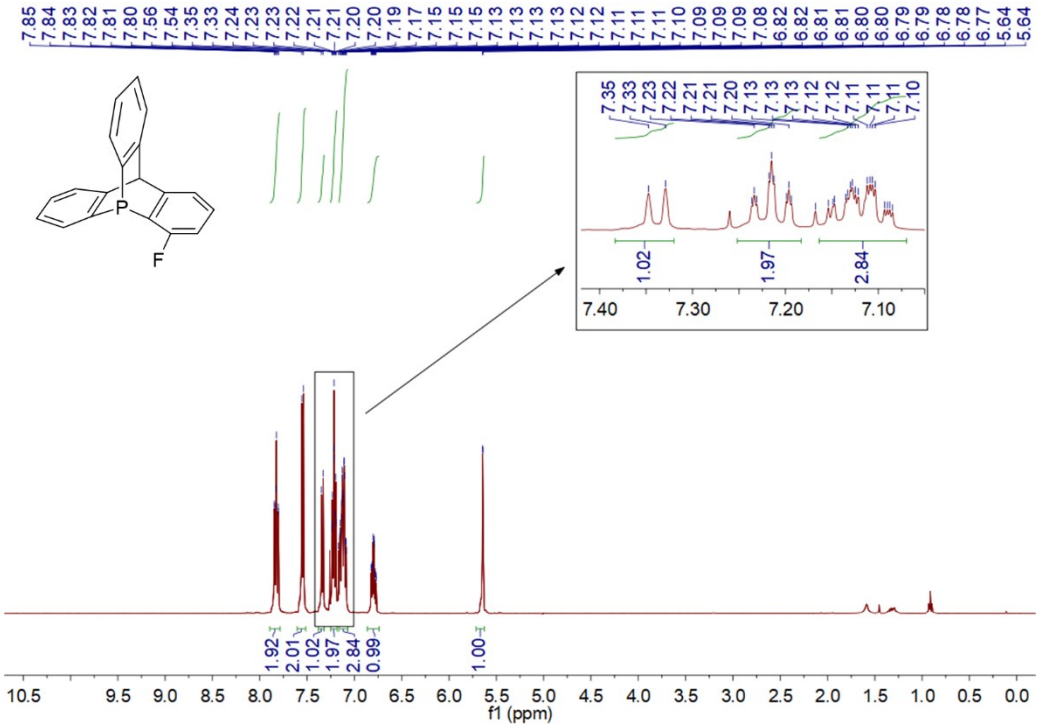



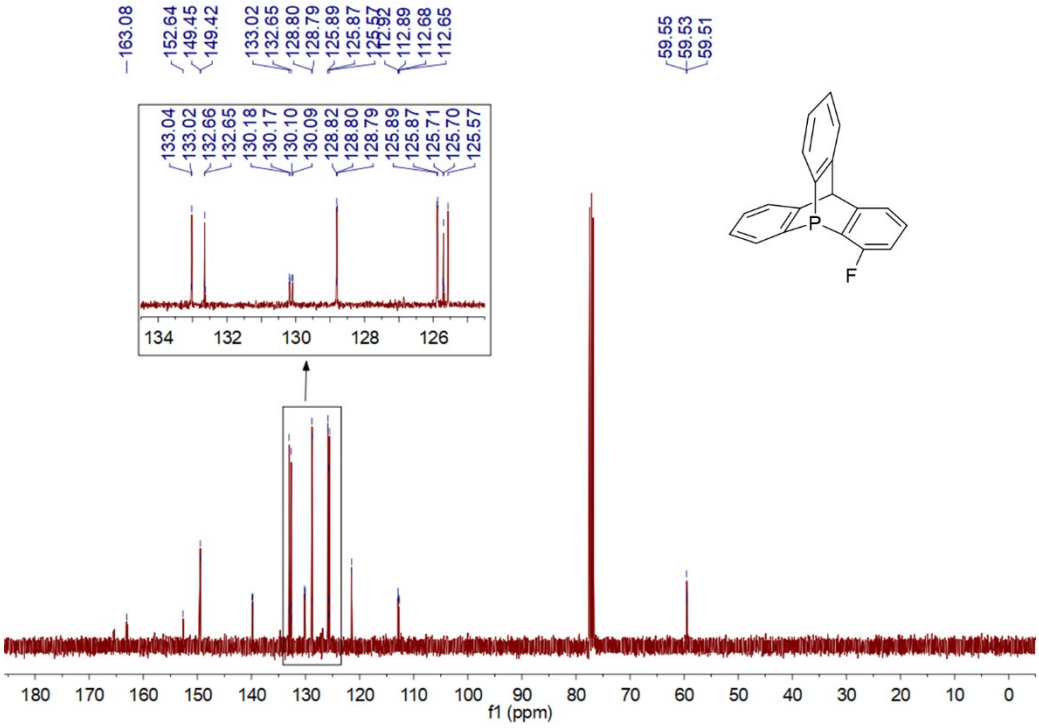
### 3.21 Trityl precursor 28 in $CDCl_3$: $^{1}H$-NMR (400 MHz), $^{13}C$-NMR (100 MHz)

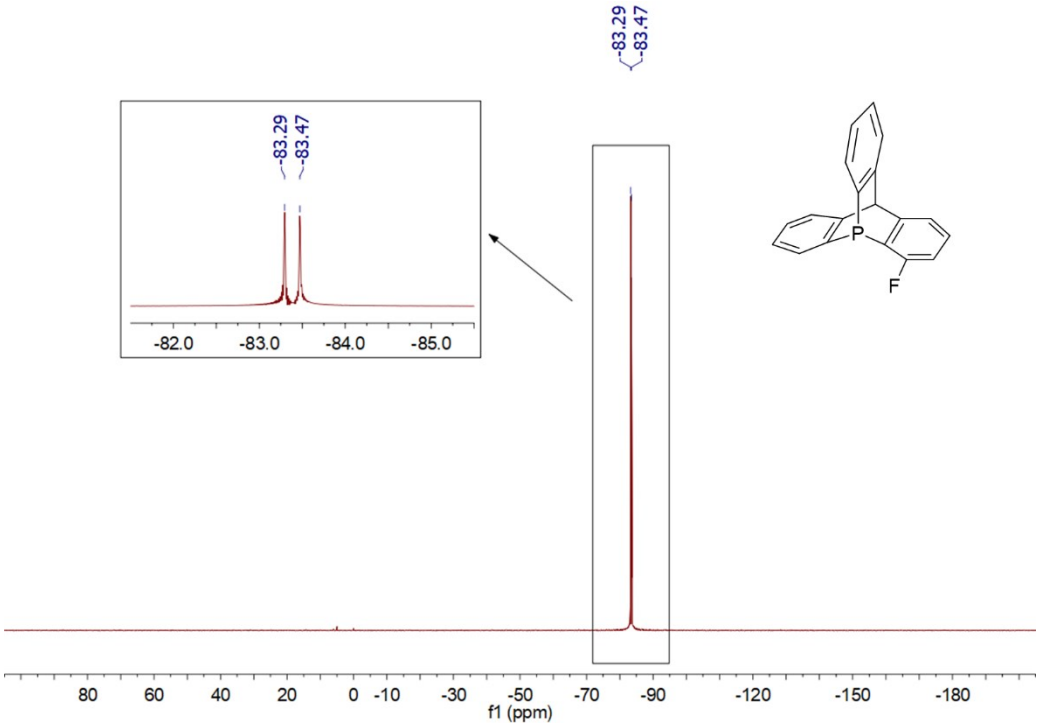


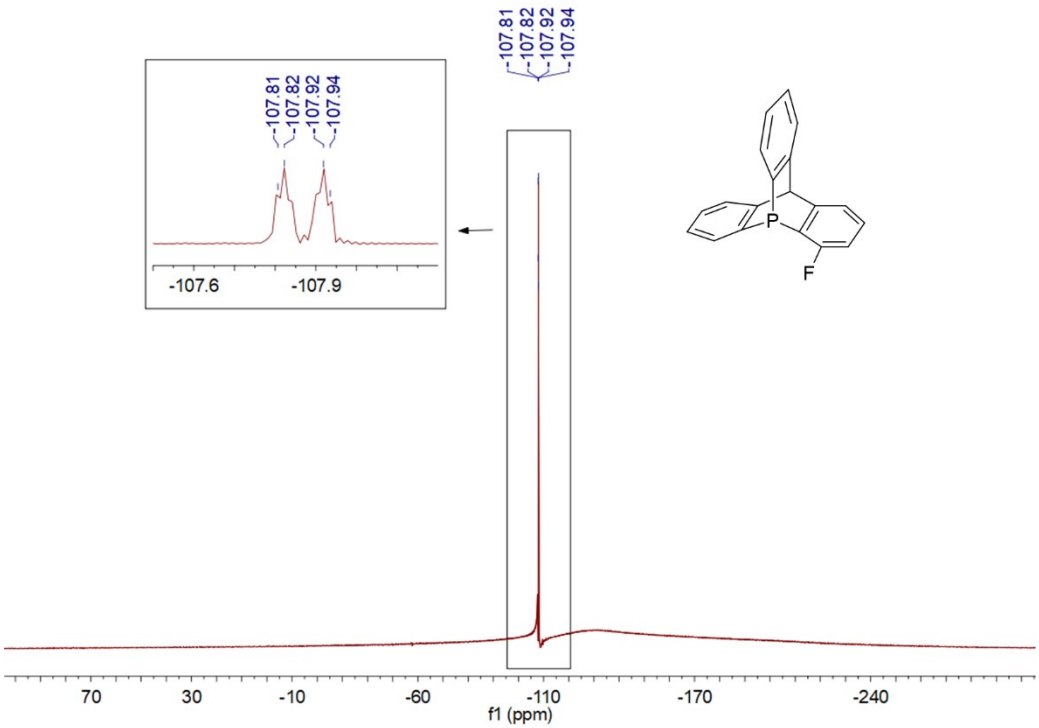



**3.22 F-substituted-9-phosphatriptycene 7a in $CDCl_3$: $^{1}H$-NMR (400 MHz), $^{13}C$-NMR (100 MHz), $^{31}P$-NMR (202 MHz), $^{19}F$-NMR (376 MHz)**

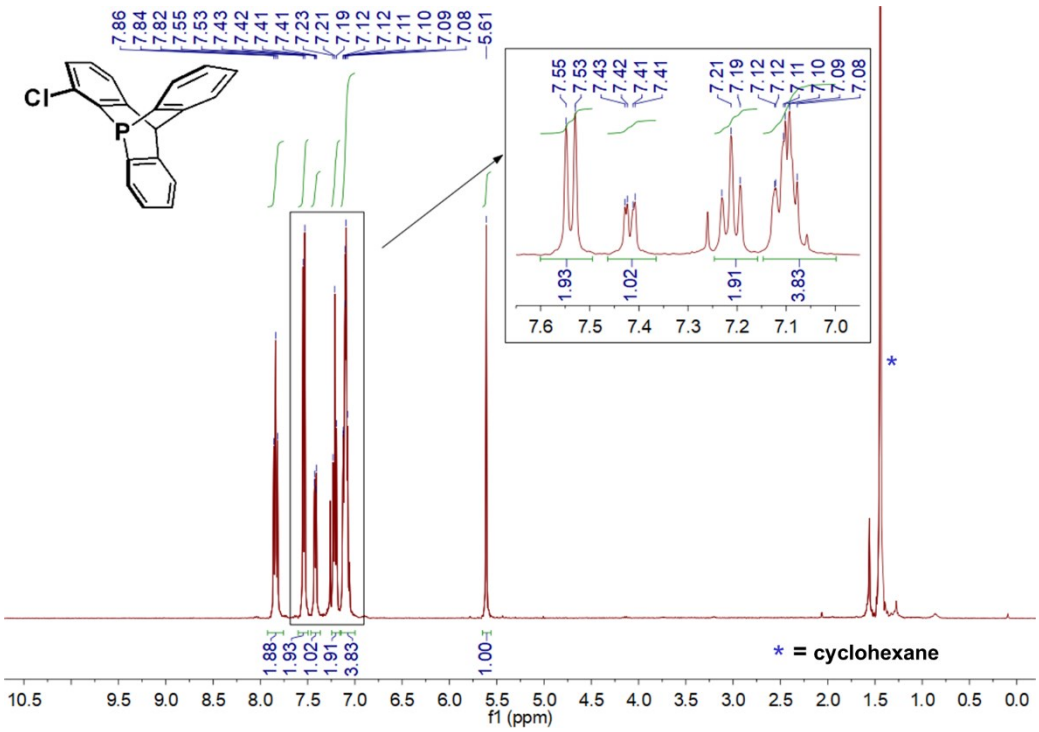


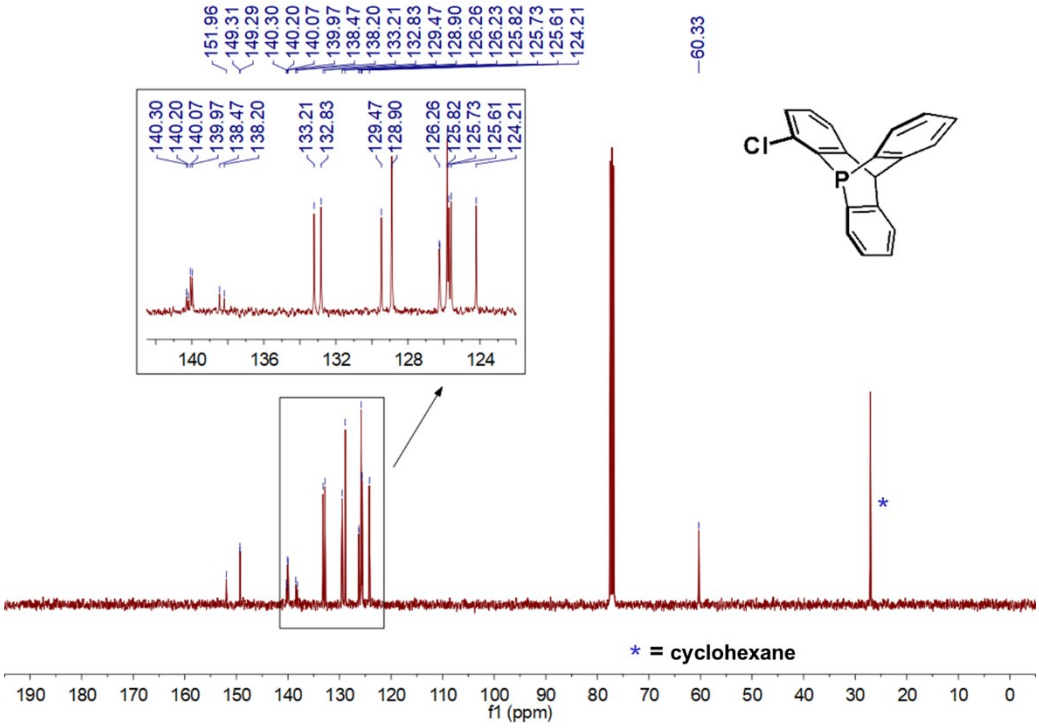



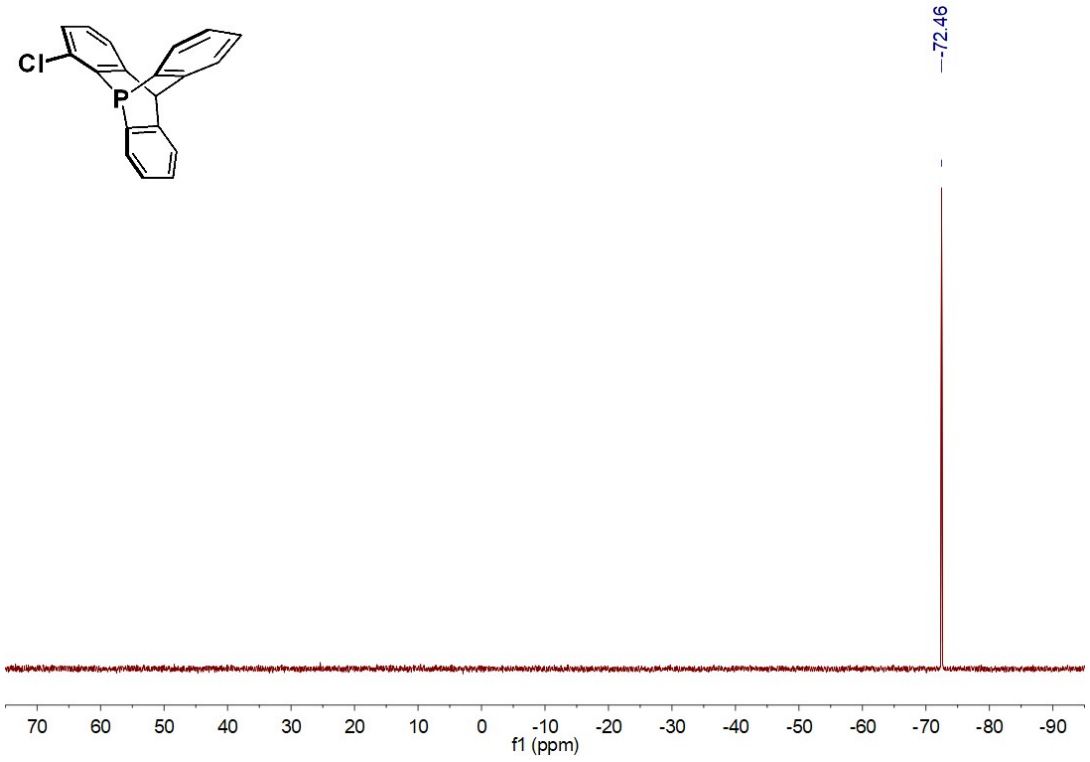

-83.29
-83.47
-82.0
-83.0
-84.0
-85.0
P
F
80
60
40
20
0
-10
-30
-50
-70
-90
-120
-150
-180
f1 (ppm)


-107.81
-107.82
-107.92
-107.94
-107.6
-107.9
P
F
70
30
-10
-60
-110
-170
-240
f1 (ppm)

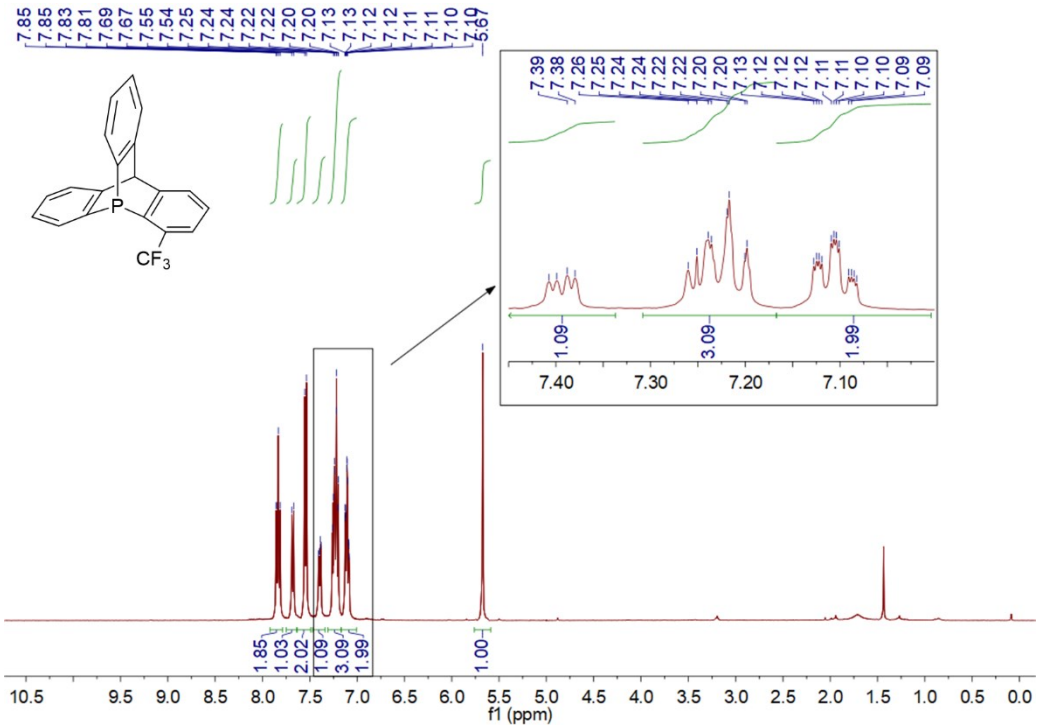
### 3.23 Cl-substituted-9-phosphatriptycene 7b in $CDCl_3$: $^{1}H$-NMR (400 MHz), $^{13}C$-NMR (100 MHz), $^{31}P$-NMR (161 MHz)

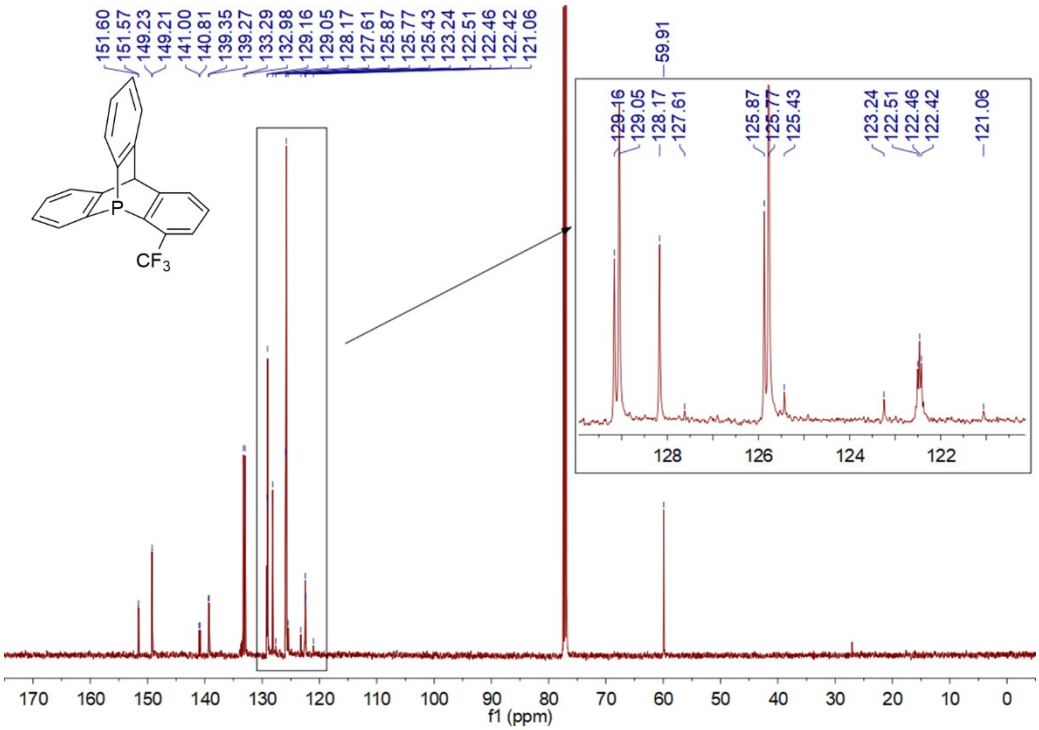


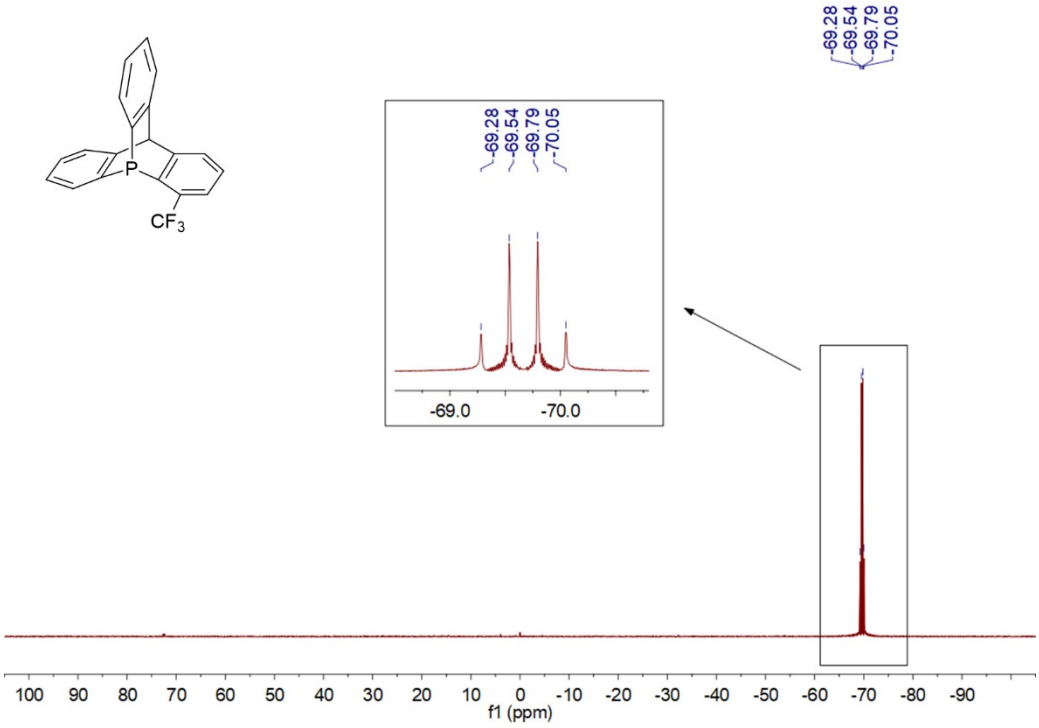



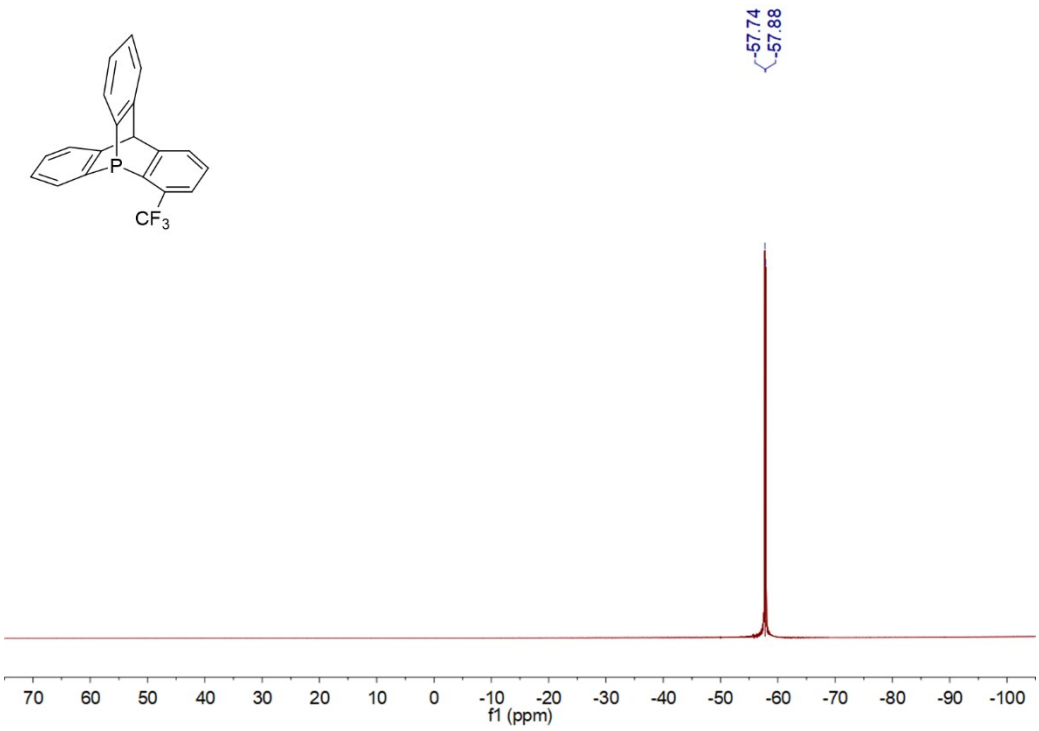

Cl
P
-72.46
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
f1 (ppm)

**3.24 $CF_3$-substituted-9-phosphatriptycene 7c in $CDCl_3$: $^{1}$H-NMR (400 MHz), $^{13}$C-NMR (100 MHz), $^{31}$P-NMR (202 MHz), $^{19}$F-NMR (376 MHz)**

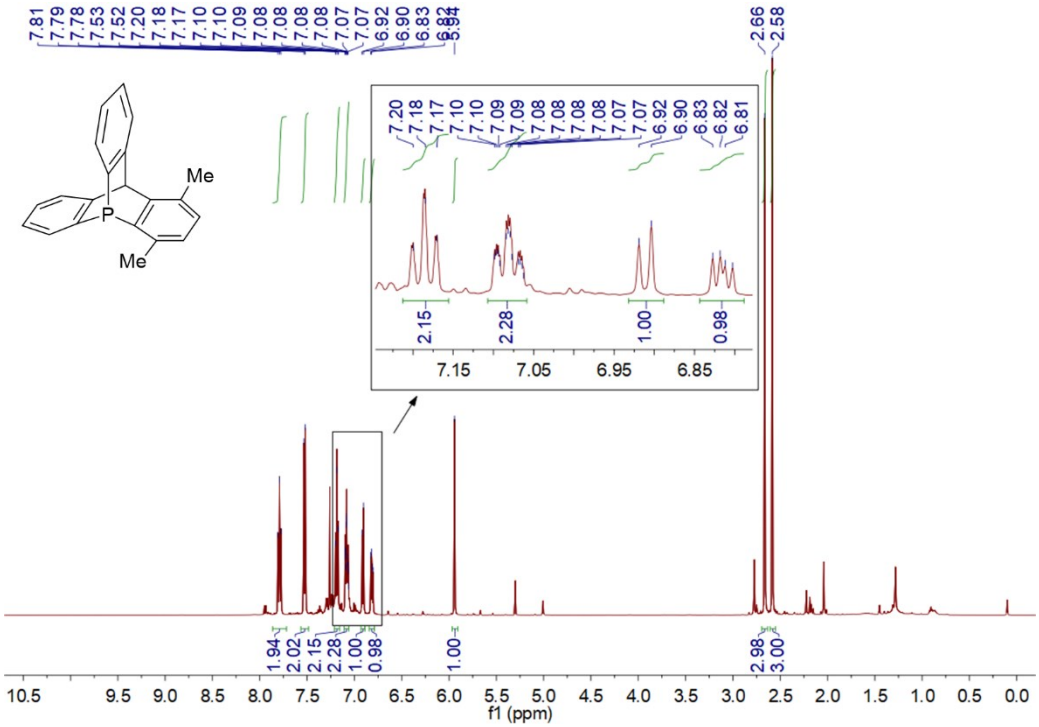


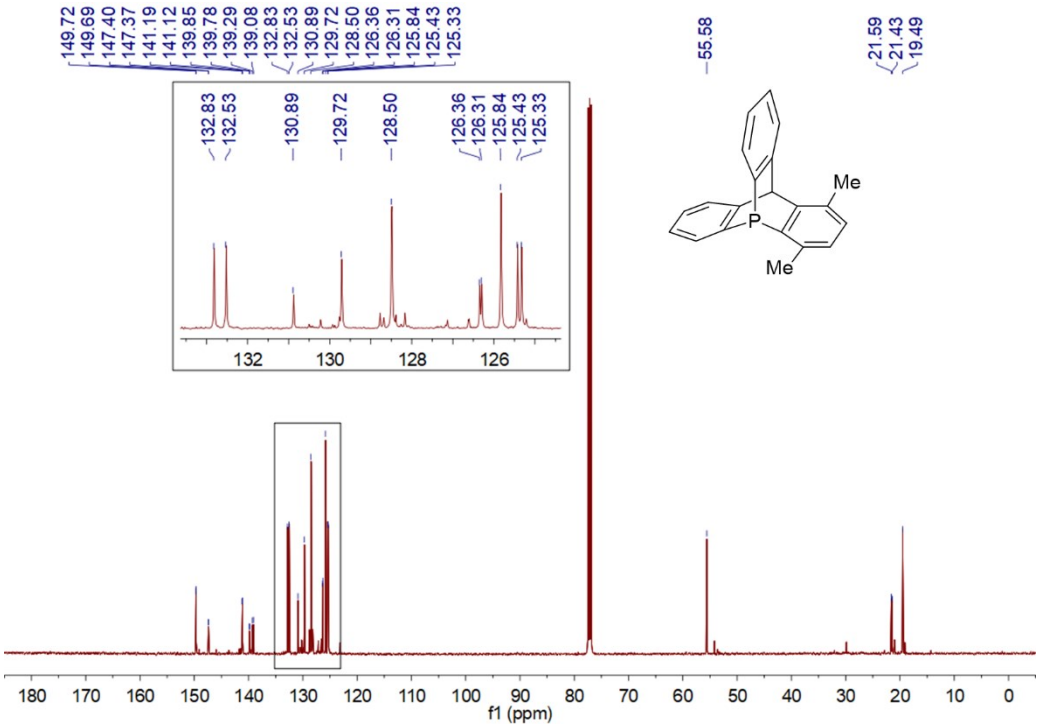



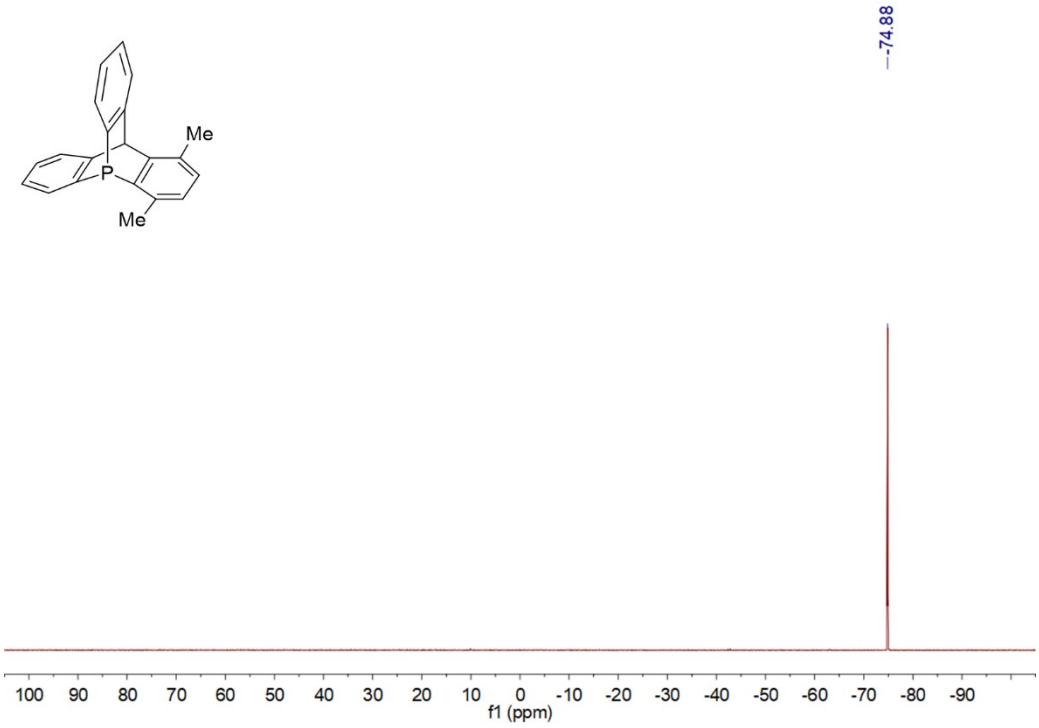

-69.28
-69.54
-69.79
-70.05
P
CF3
-69.0
-70.0
100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90
f1 (ppm)


-57.74
-57.88
P
CF3
70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100
f1 (ppm)

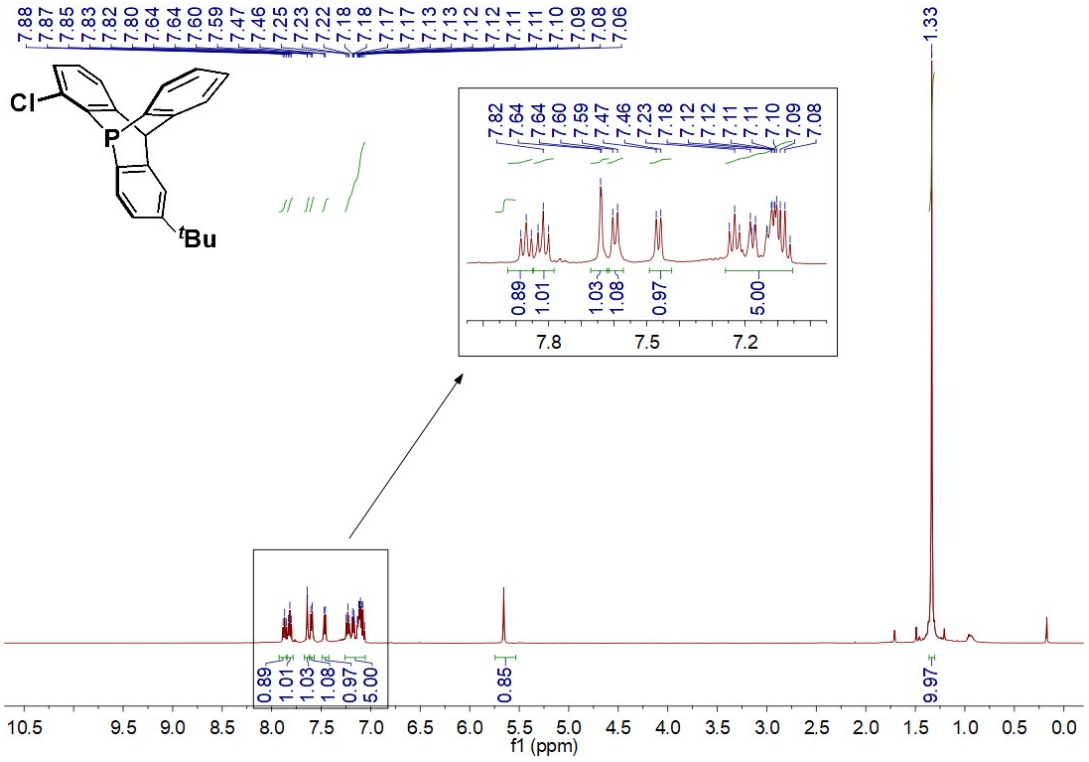
**3.25 1,4-dimethyl-9-phosphatriptycene 8a in $CDCl_3$: $^{1}H$-NMR (500 MHz), $^{13}C$-NMR (126 MHz), $^{31}P$-NMR (202 MHz)**

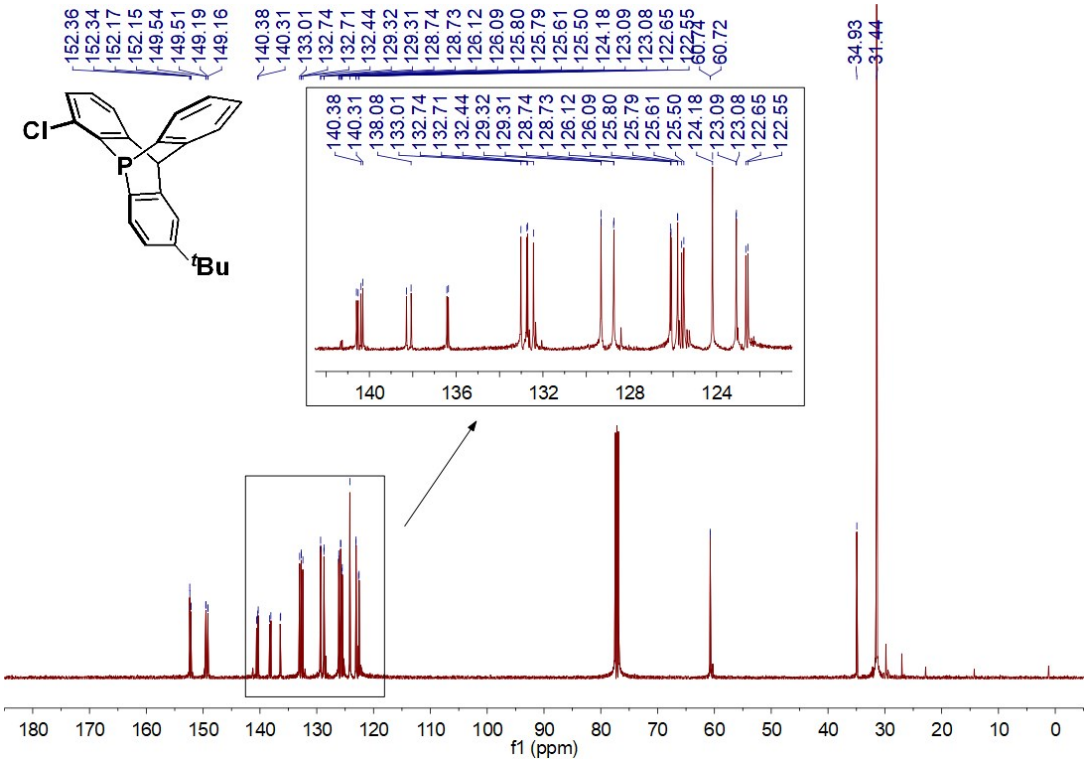


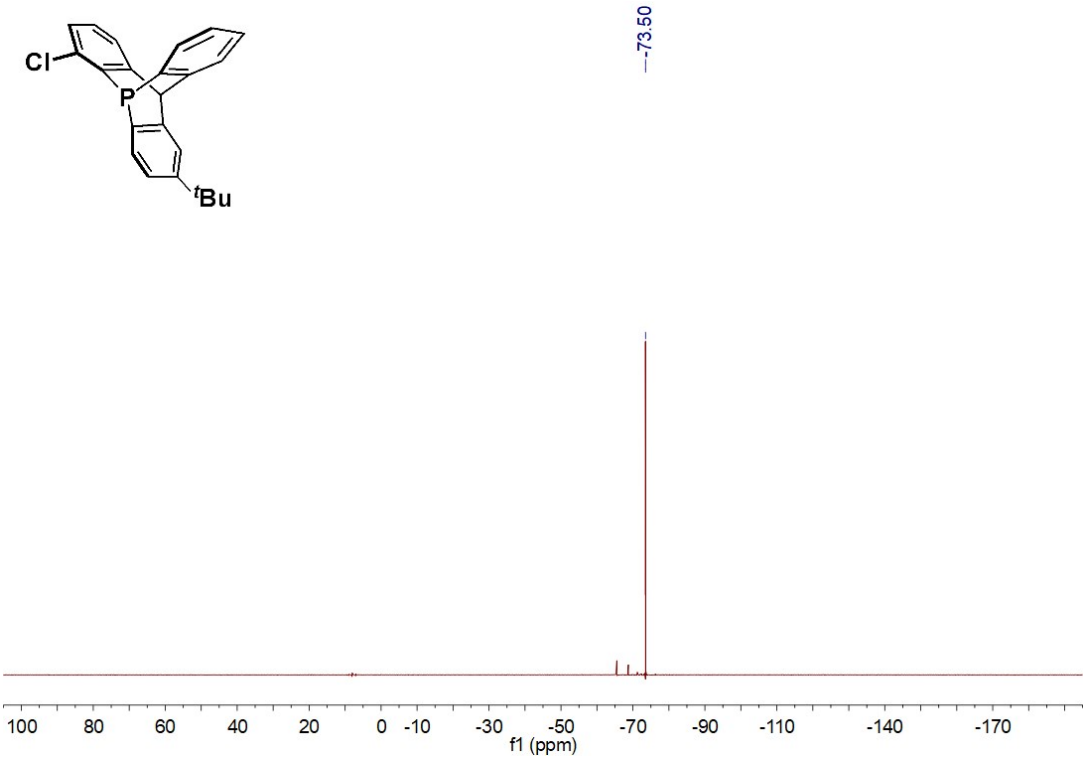




Me
P
Me
-74.88
100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90
f1 (ppm)

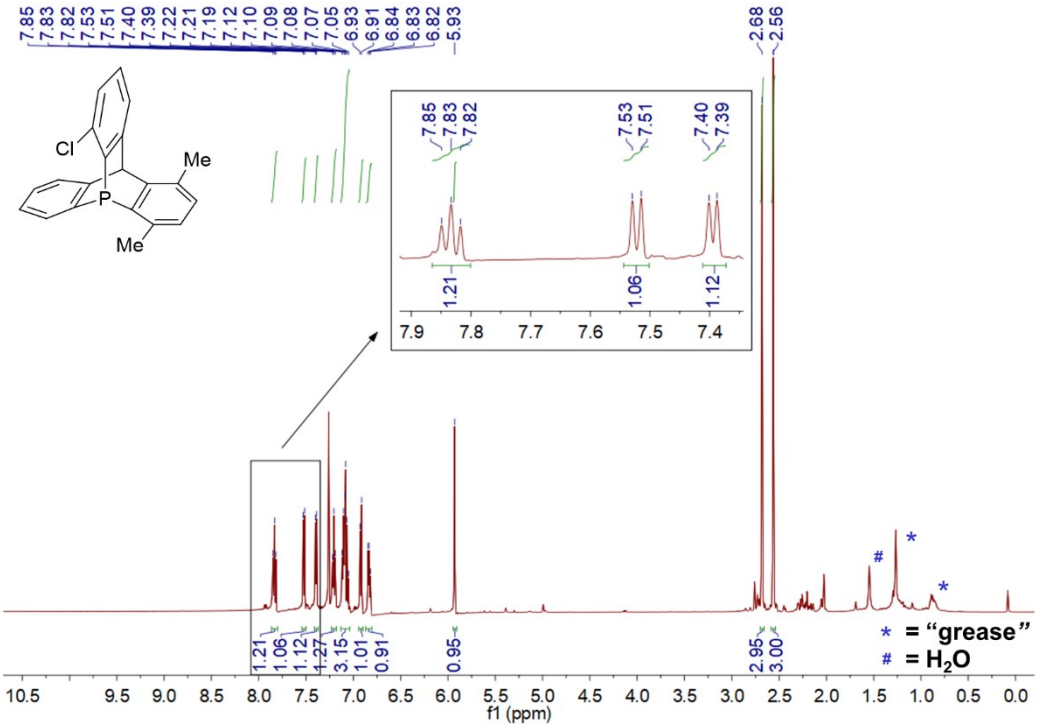
**3.26 Unsymmetrically 9-phosphatriptycene derivative 9a in $CDCl_3$: $^{1}$H-NMR (500 MHz), $^{13}$C-NMR (126 MHz), $^{31}$P-NMR (202 MHz)**

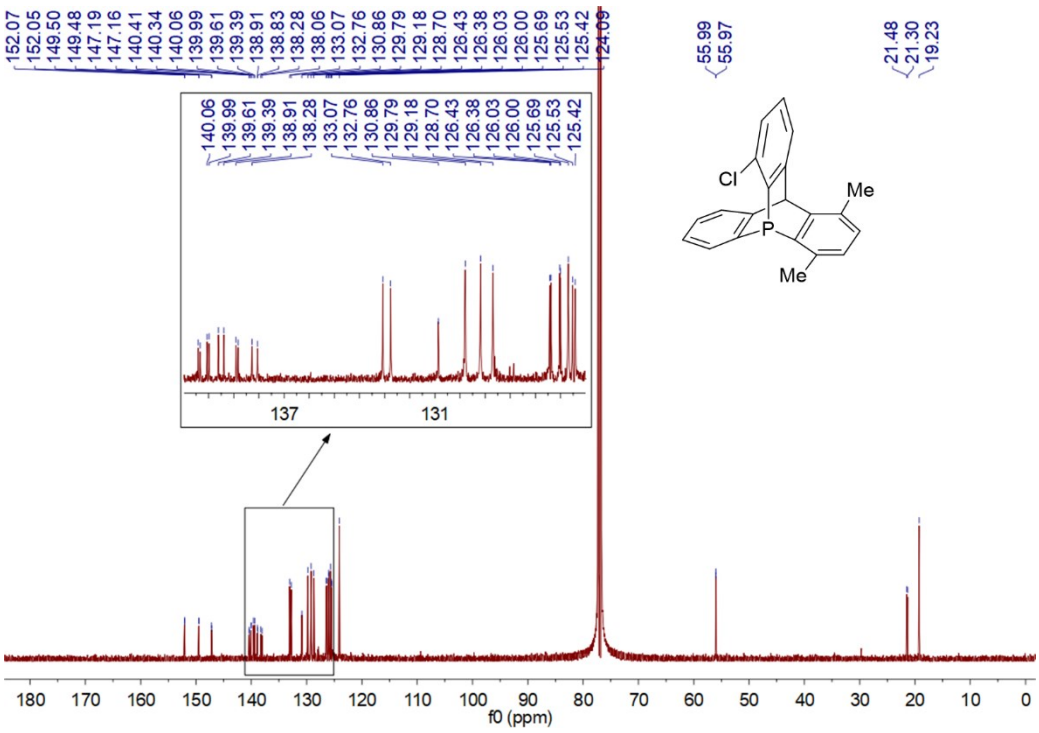


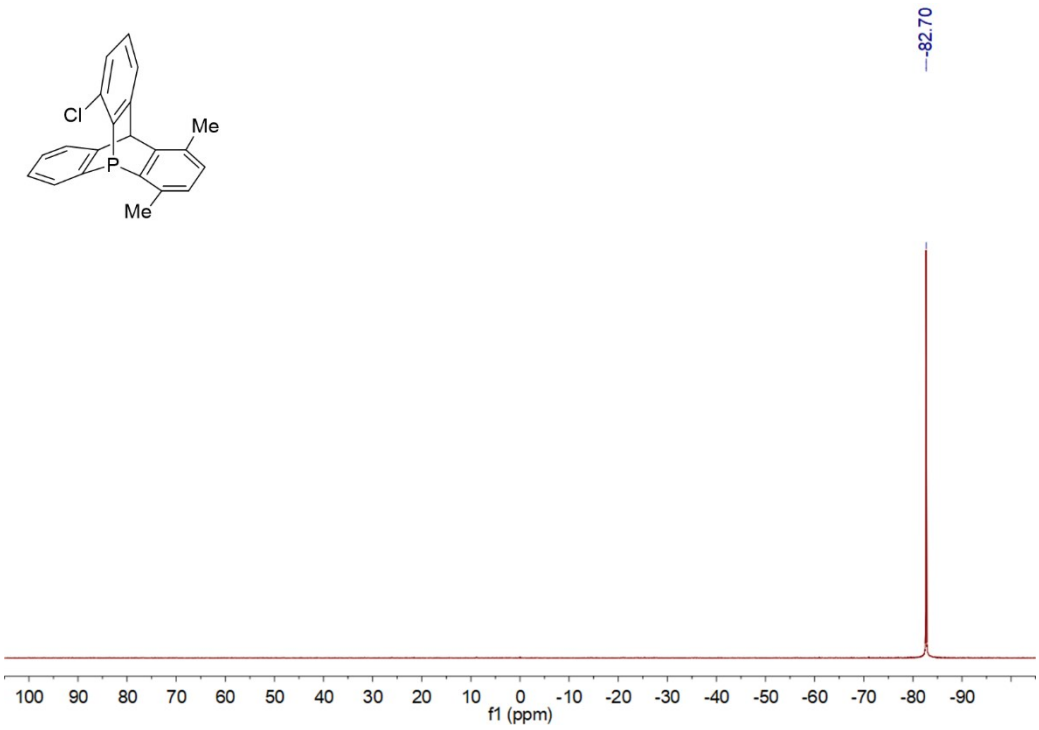




Cl
P
tBu
-73.50
100
80
60
40
20
0
-10
-30
-50
-70
-90
-110
-140
-170
f1 (ppm)

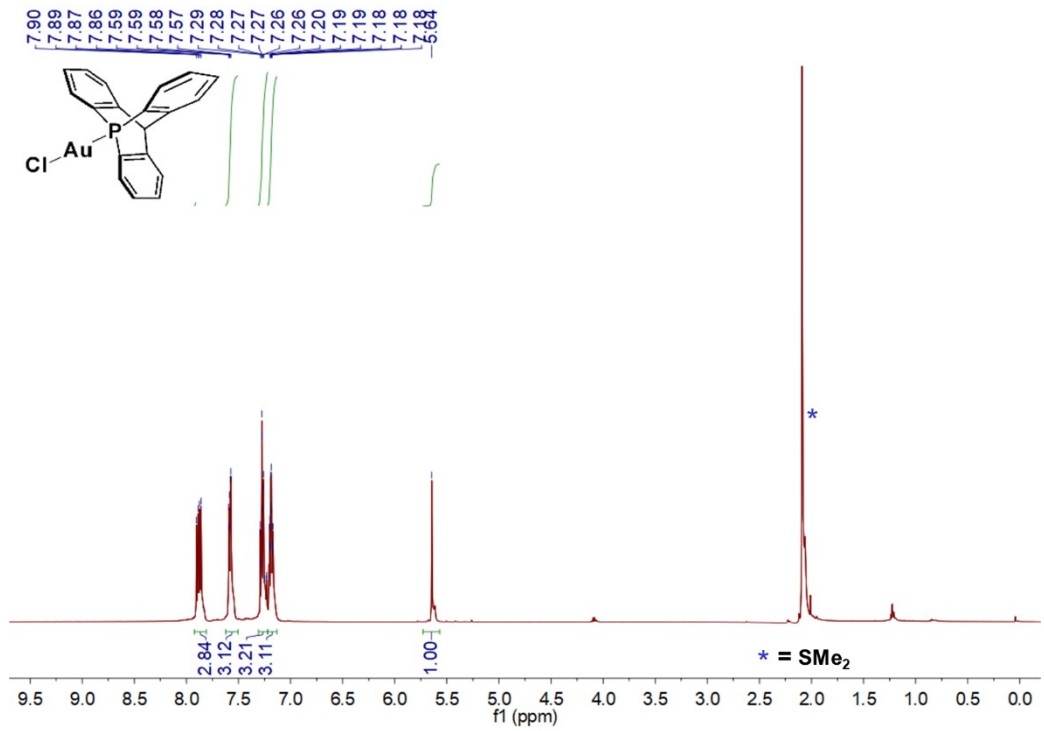
**3.27 1-chloro-5,8-dimethyl-9-phosphatriptycene 10a in $CDCl_3$: $^{1}$H-NMR (500 MHz), $^{13}$C-NMR (126 MHz), $^{31}$P-NMR (202 MHz)**

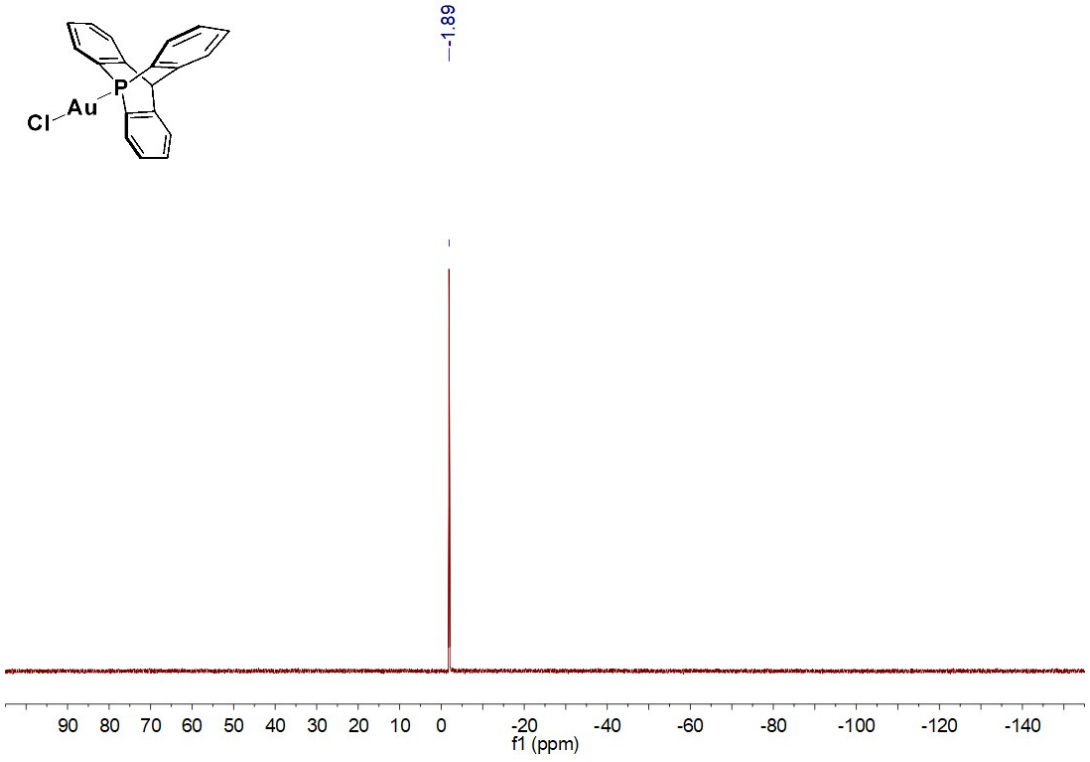


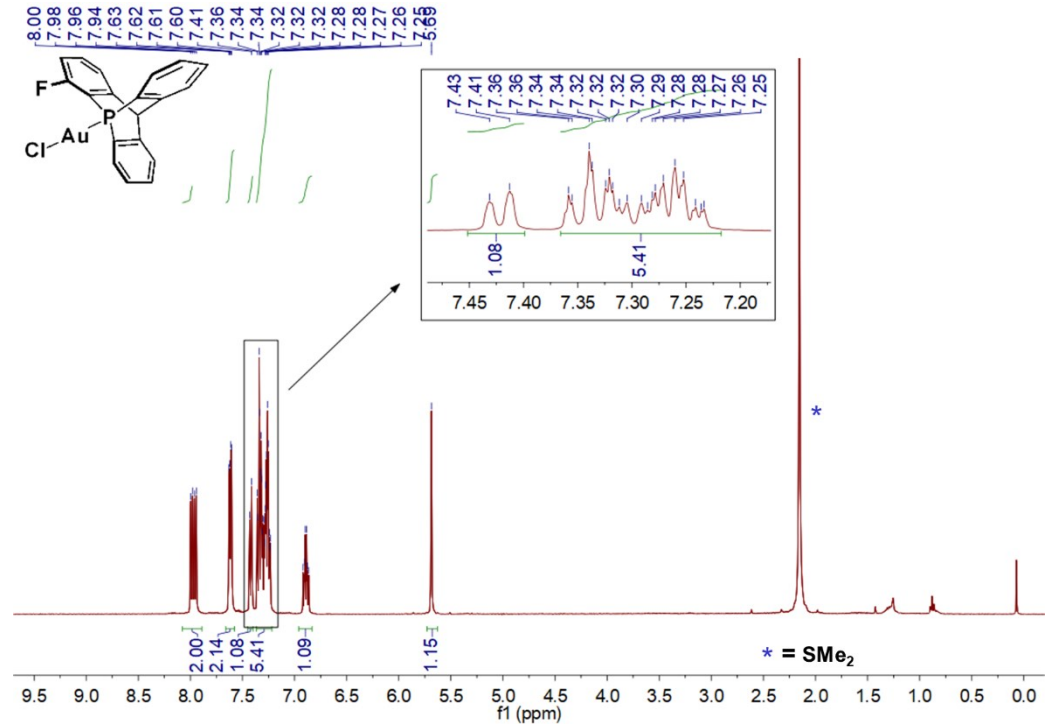

Cl
Me
P
Me
-82.70
100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90
f1 (ppm)

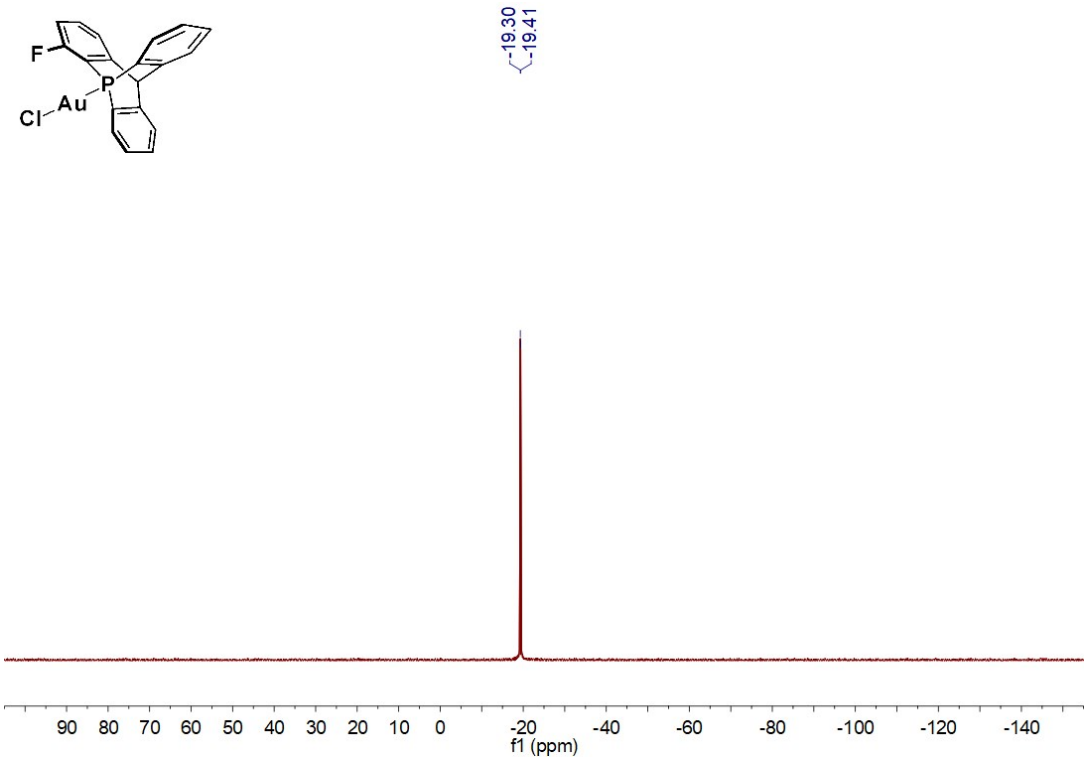
**3.28 Au-9-phosphatriptycene complex 25a in $CDCl_3$: $^{1}H$-NMR (500 MHz), $^{31}P$-NMR (202 MHz)**

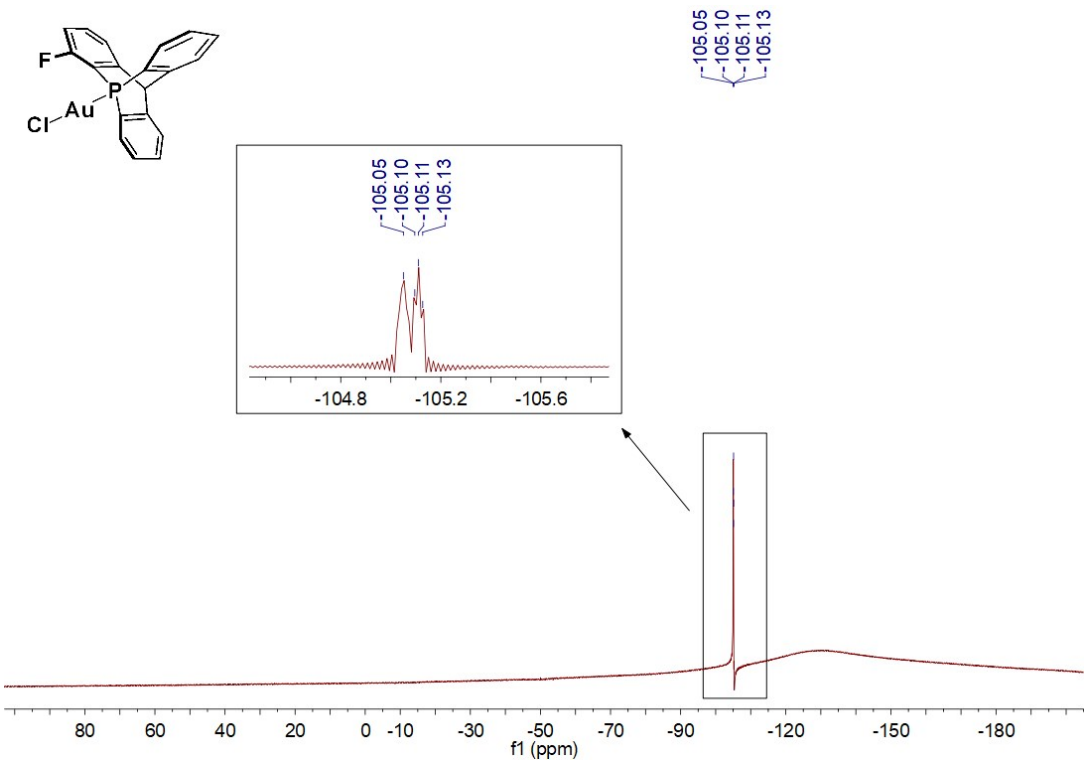


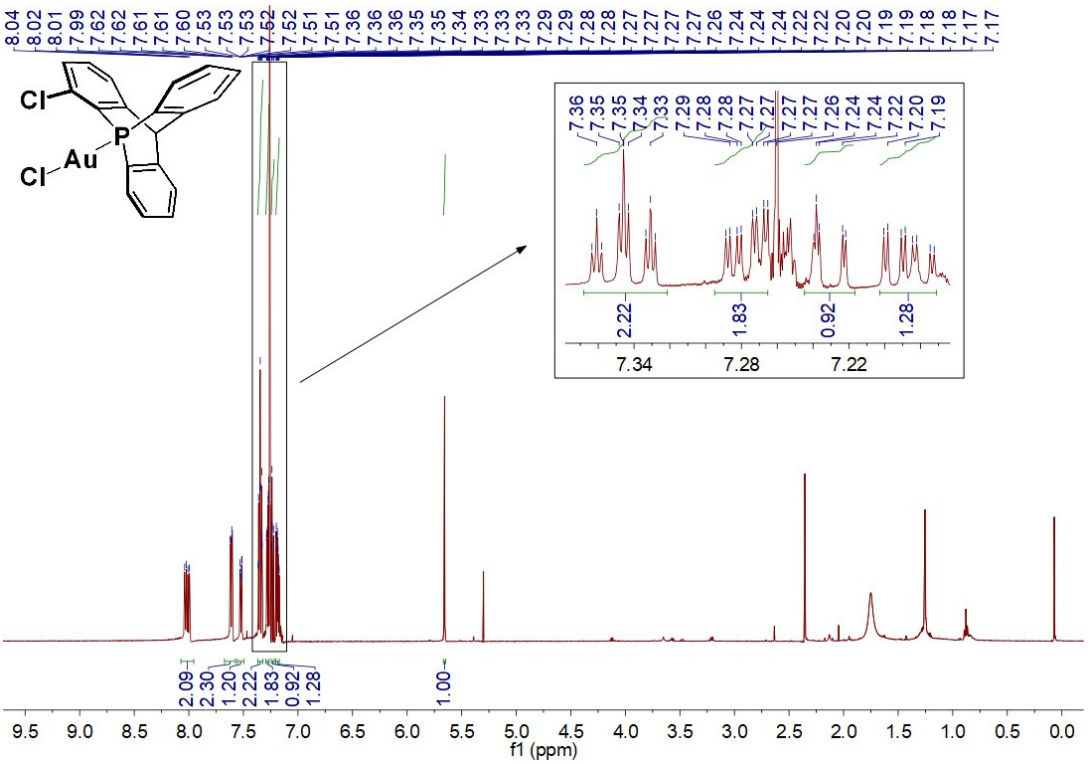
**3.29 Au-F-9-phosphatriptycene complex 25b in $CDCl_3$: $^{1}H$-NMR (500 MHz), $^{31}P$-NMR (202 MHz), $^{19}F$-NMR (376 MHz)**

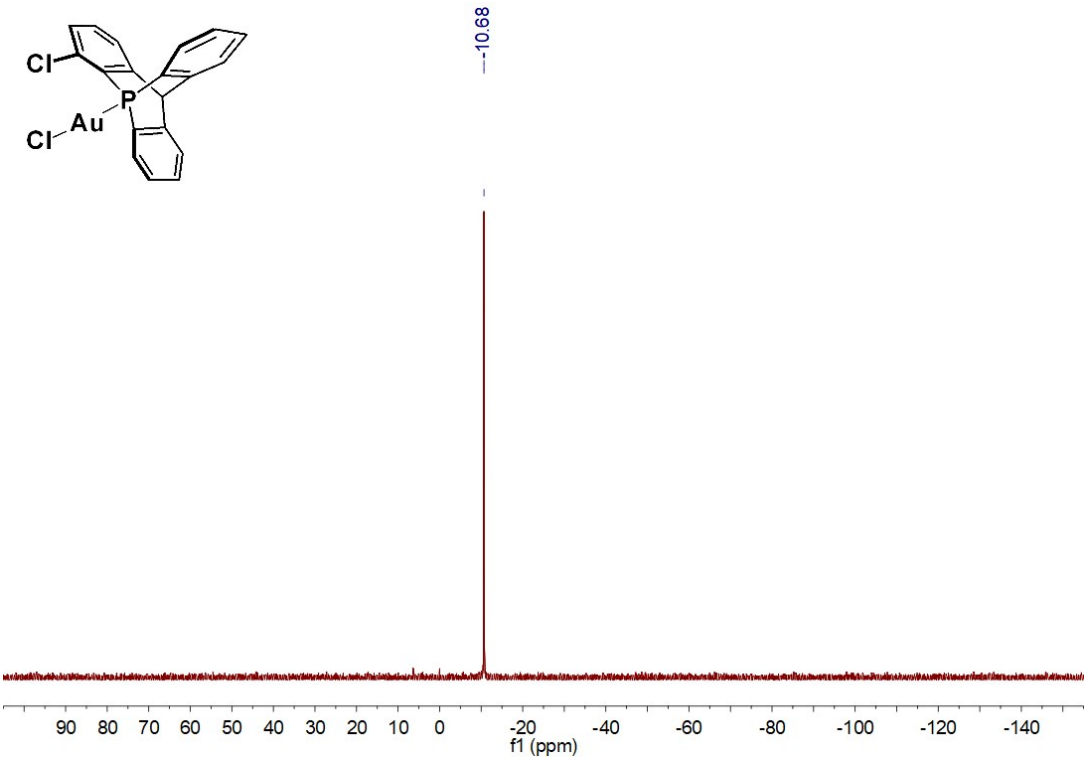


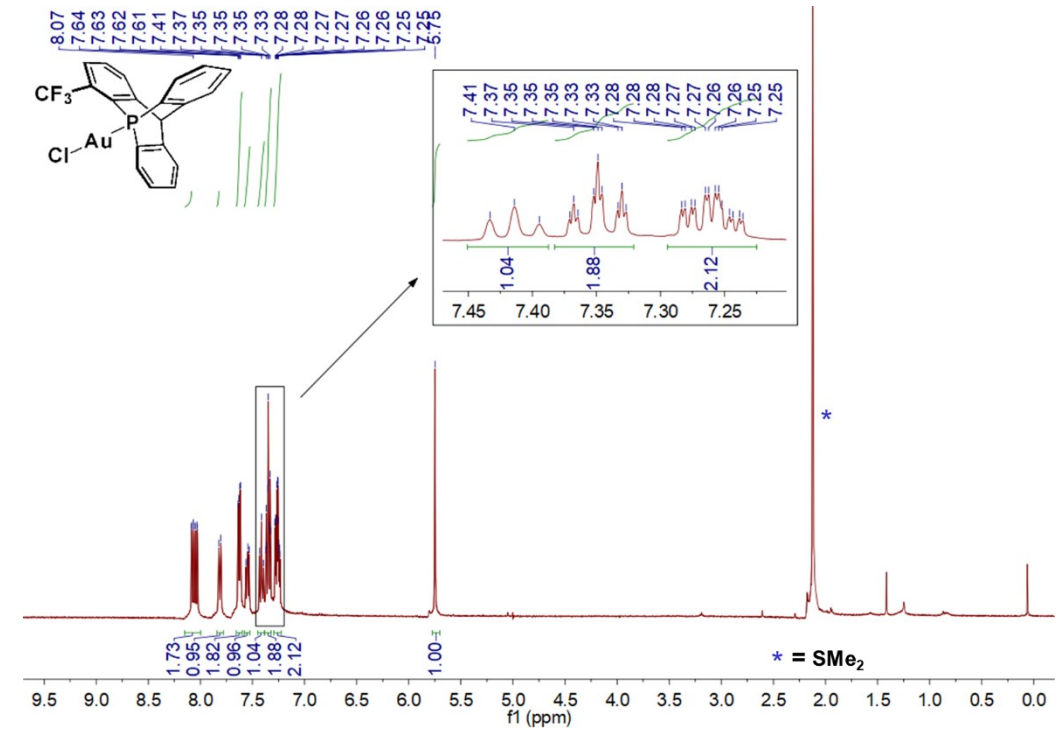

F
P
Cl
Au
-105.05
-105.10
-105.11
-105.13
-104.8
-105.2
-105.6
80
60
40
20
0
-10
-30
-50
-70
-90
-120
-150
-180
f1 (ppm)

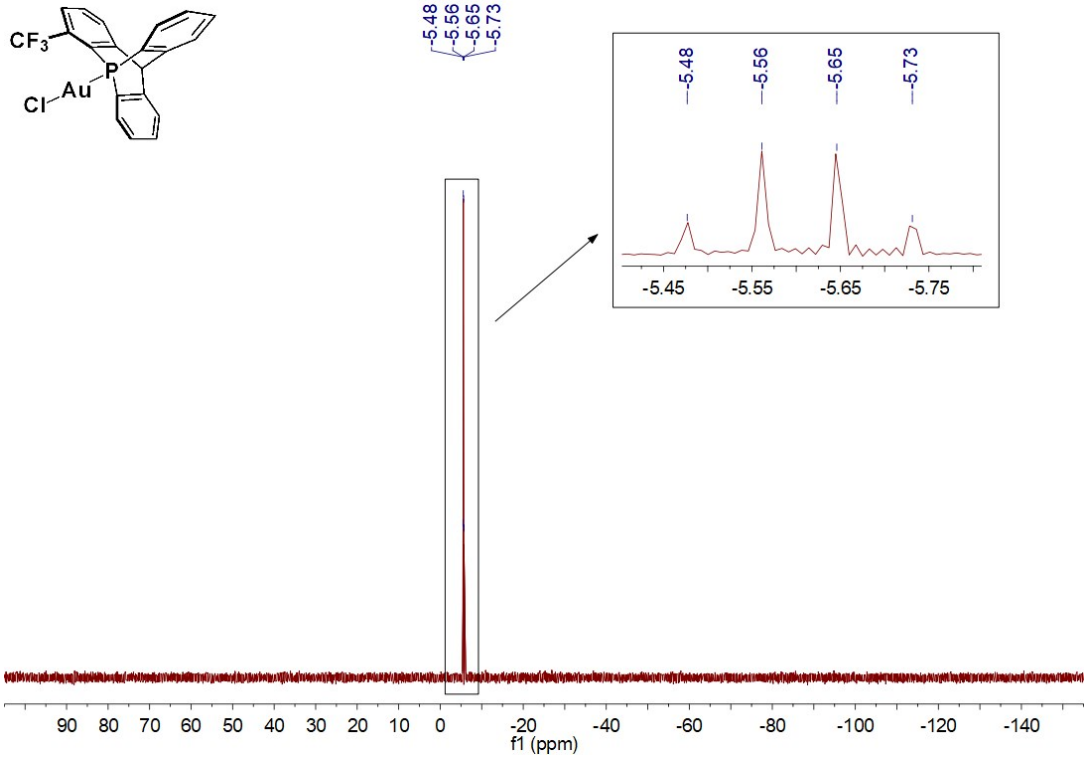
**3.30 Au-Cl-9-phosphatriptycene complex 25c in $CDCl_3$: $^{1}$H-NMR (500 MHz), $^{31}$P-NMR (202 MHz)**

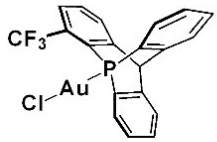


### 3.31 Au-$CF_3$-9-phosphatriptycene complex 25d in $CDCl_3$: $^1$H-NMR (500 MHz), $^{31}$P-NMR (202 MHz), $^{19}$F-NMR (376 MHz)

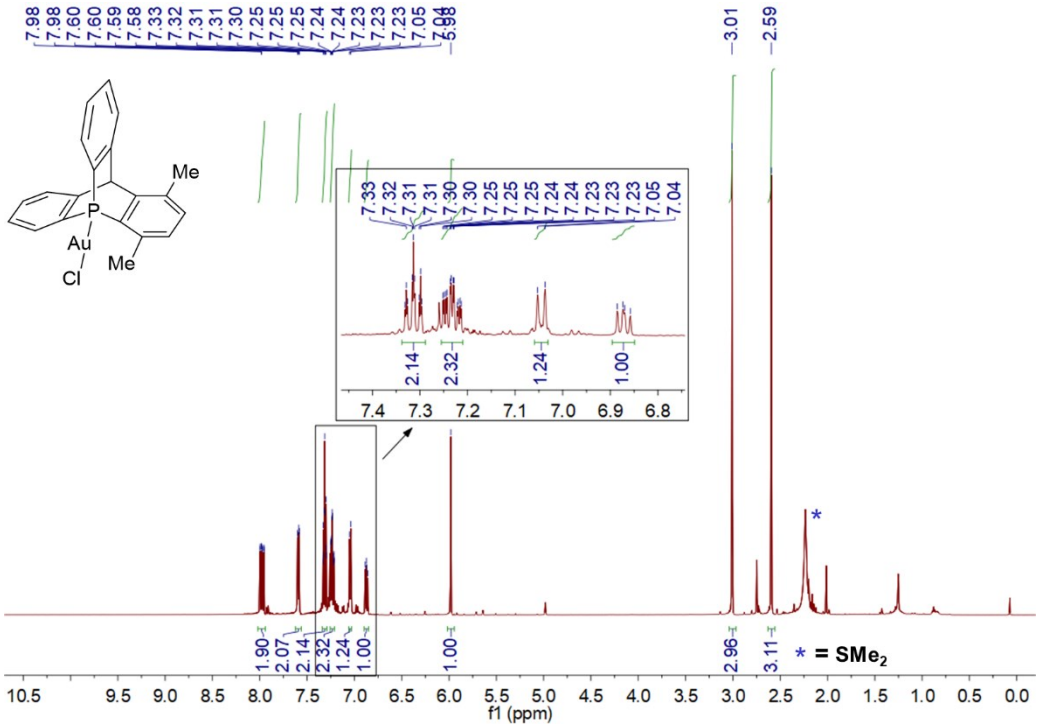


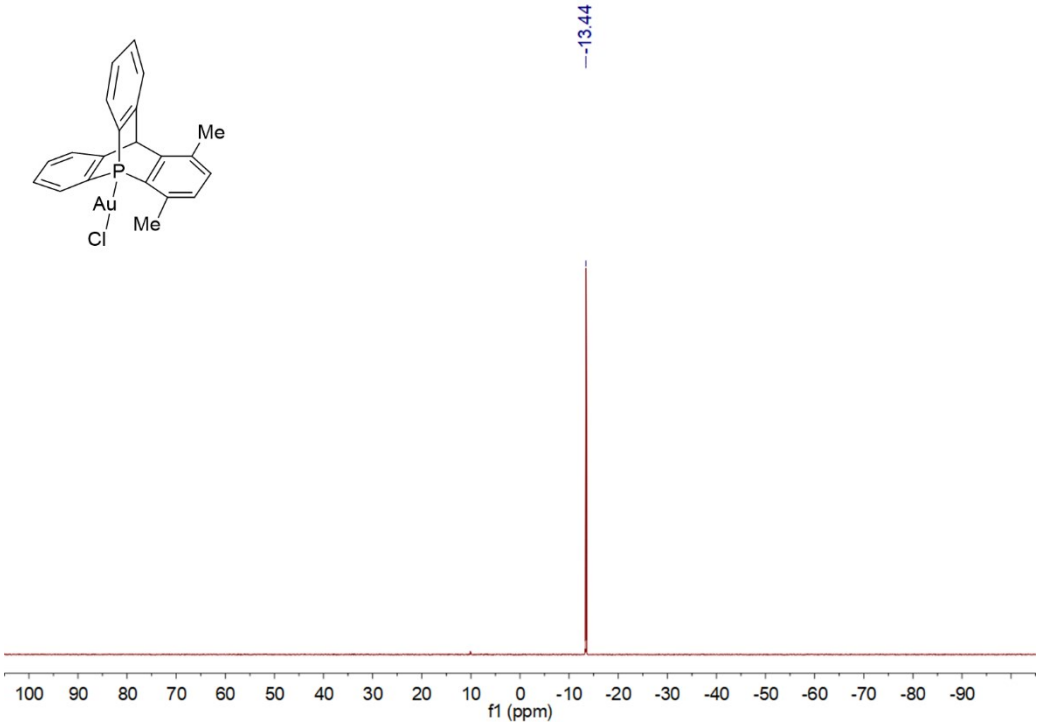




CF3
P
Cl
Au

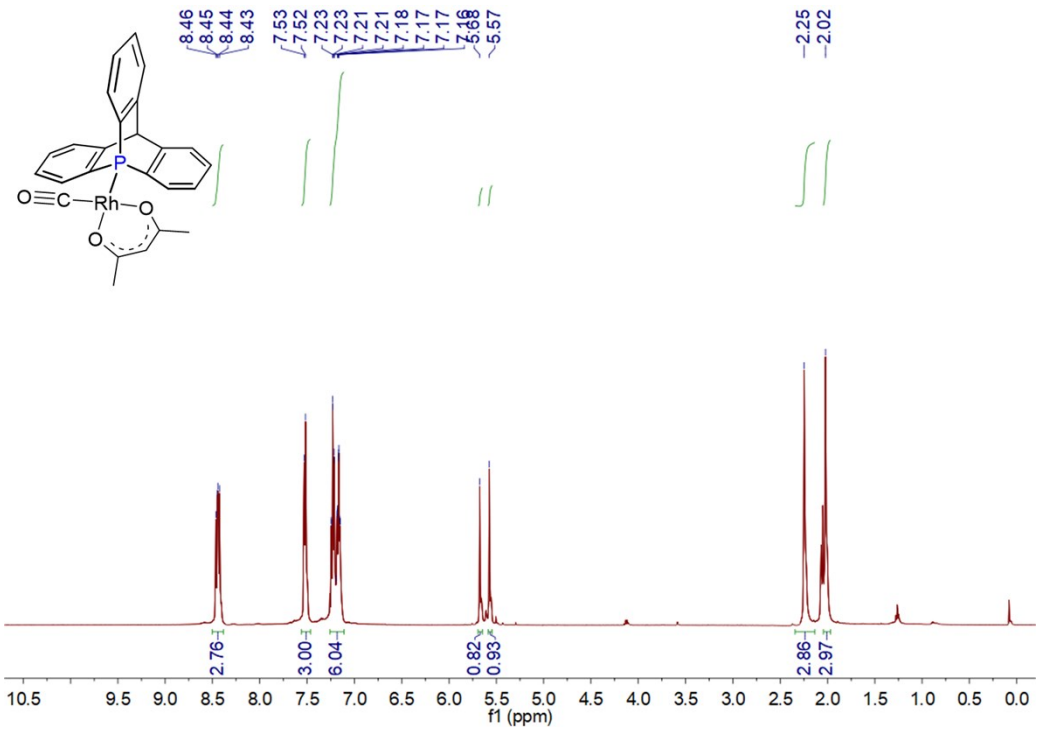

-53.56
-53.61
90 80 70 60 50 40 30 20 10 0 -20 -40 -60 -80 -100 -120 -140
f1 (ppm)

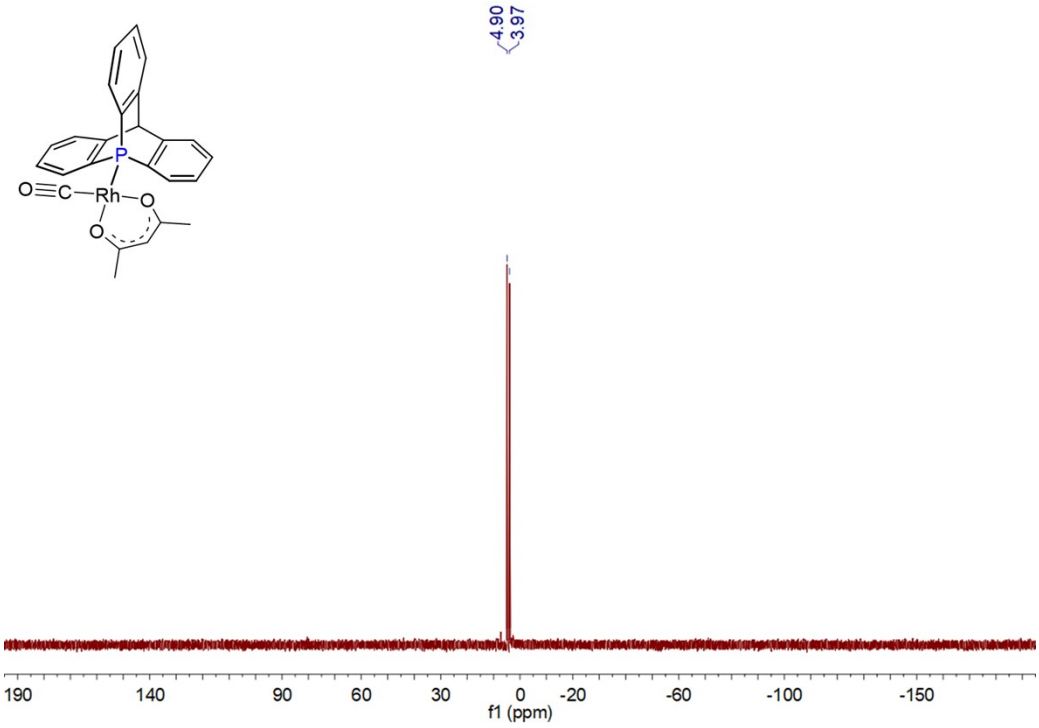
**3.32 Au-1,4-dimethyl-9-phosphatriptycene complex 25e in $CDCl_3$: $^{1}$H-NMR (500 MHz), $^{31}$P-NMR (202 MHz)**



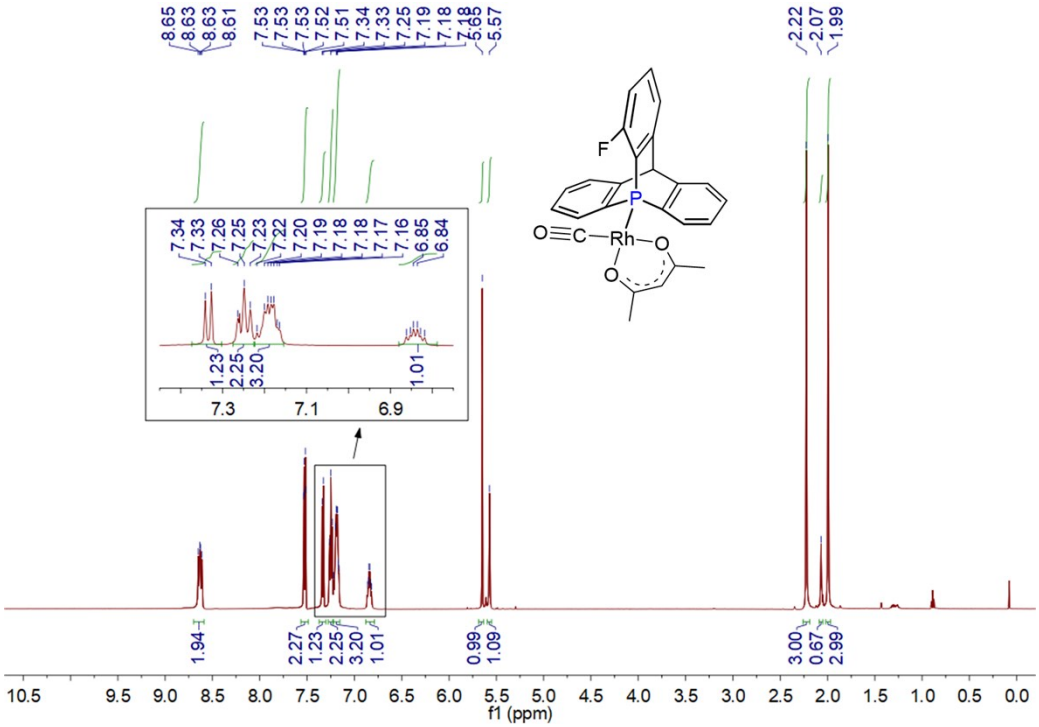



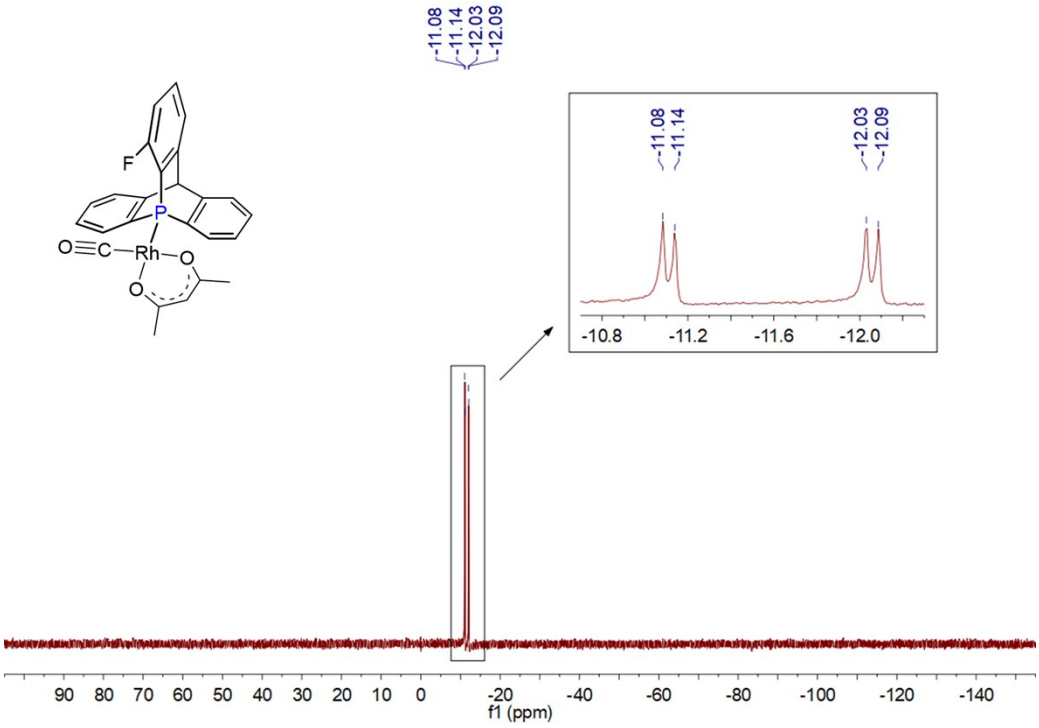
**3.33 Rh-9-phosphatriptycene complex 26a in $CDCl_3$: $^{1}H$-NMR (500 MHz), $^{31}P$-NMR (202 MHz)**

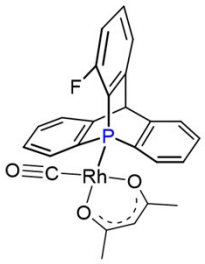


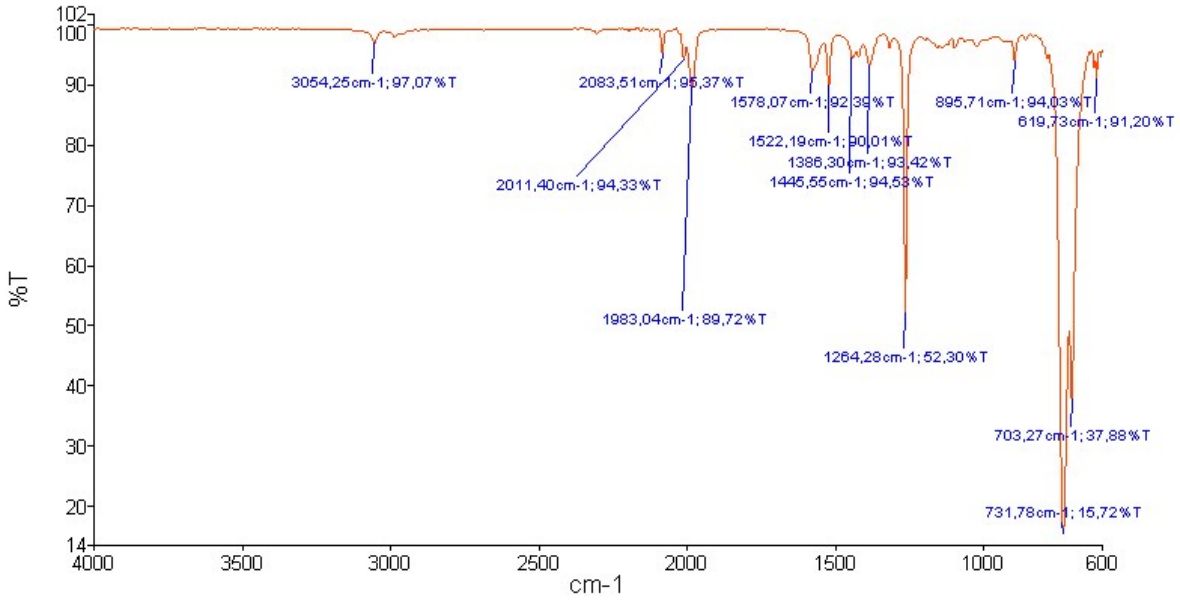
**3.34 Rh-F-9-phosphatriptycene complex 26b in $CDCl_3$: $^{1}H$-NMR (500 MHz), $^{31}P$-NMR (202 MHz), $^{19}F$-NMR (376 MHz). The IR measured in $CH_2Cl_2$**



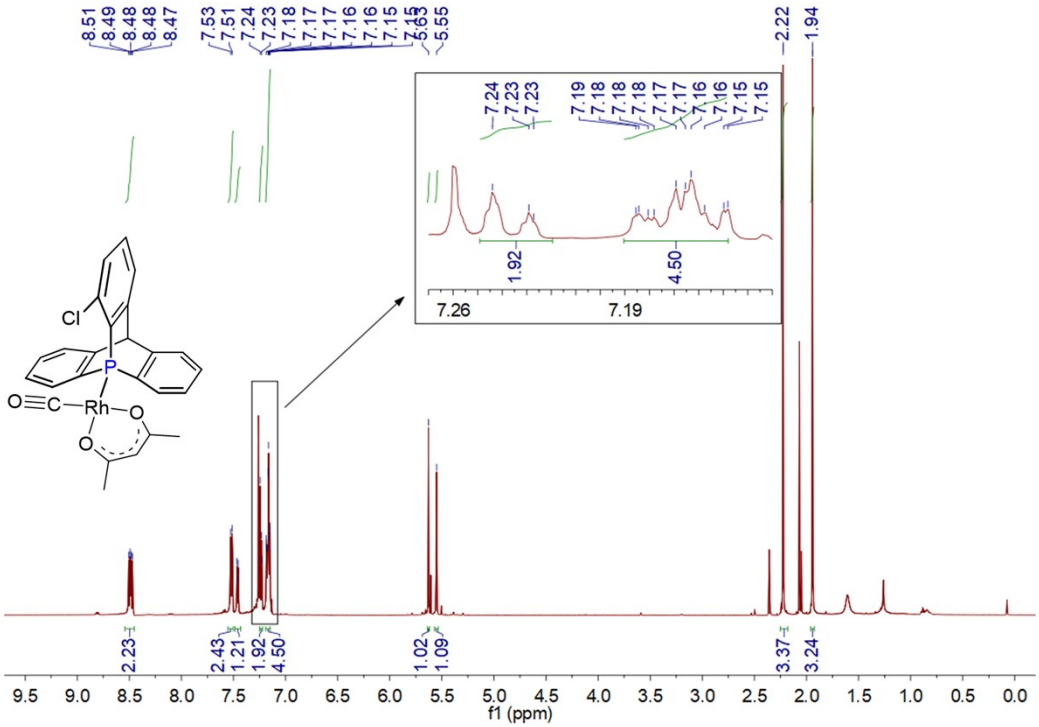



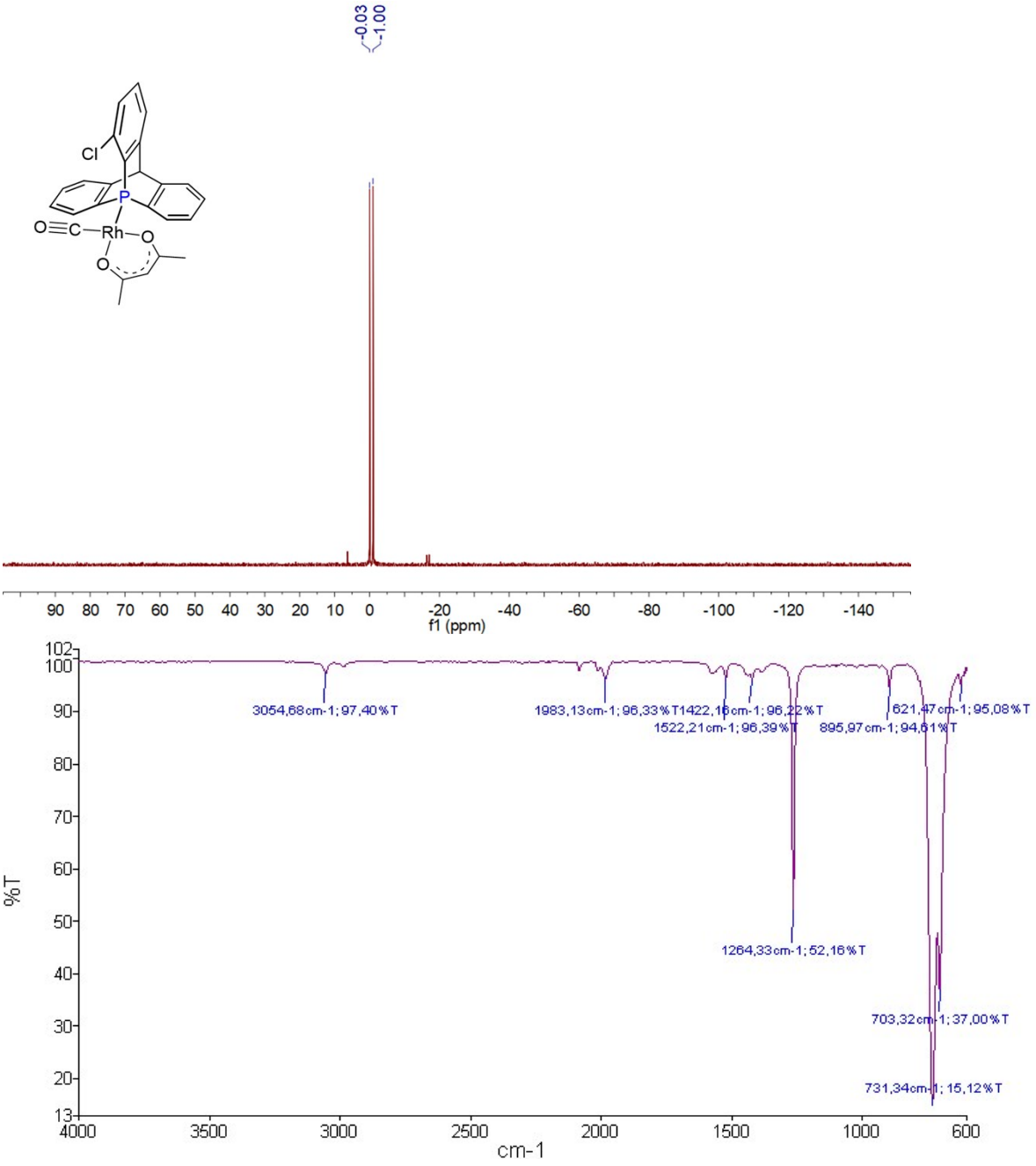

F
P
O≡C—Rh—O
O


102.96
102.99
80
60
40
20
0
-10
-30
-50
-70
-90
-120
-150
-180
f1 (ppm)

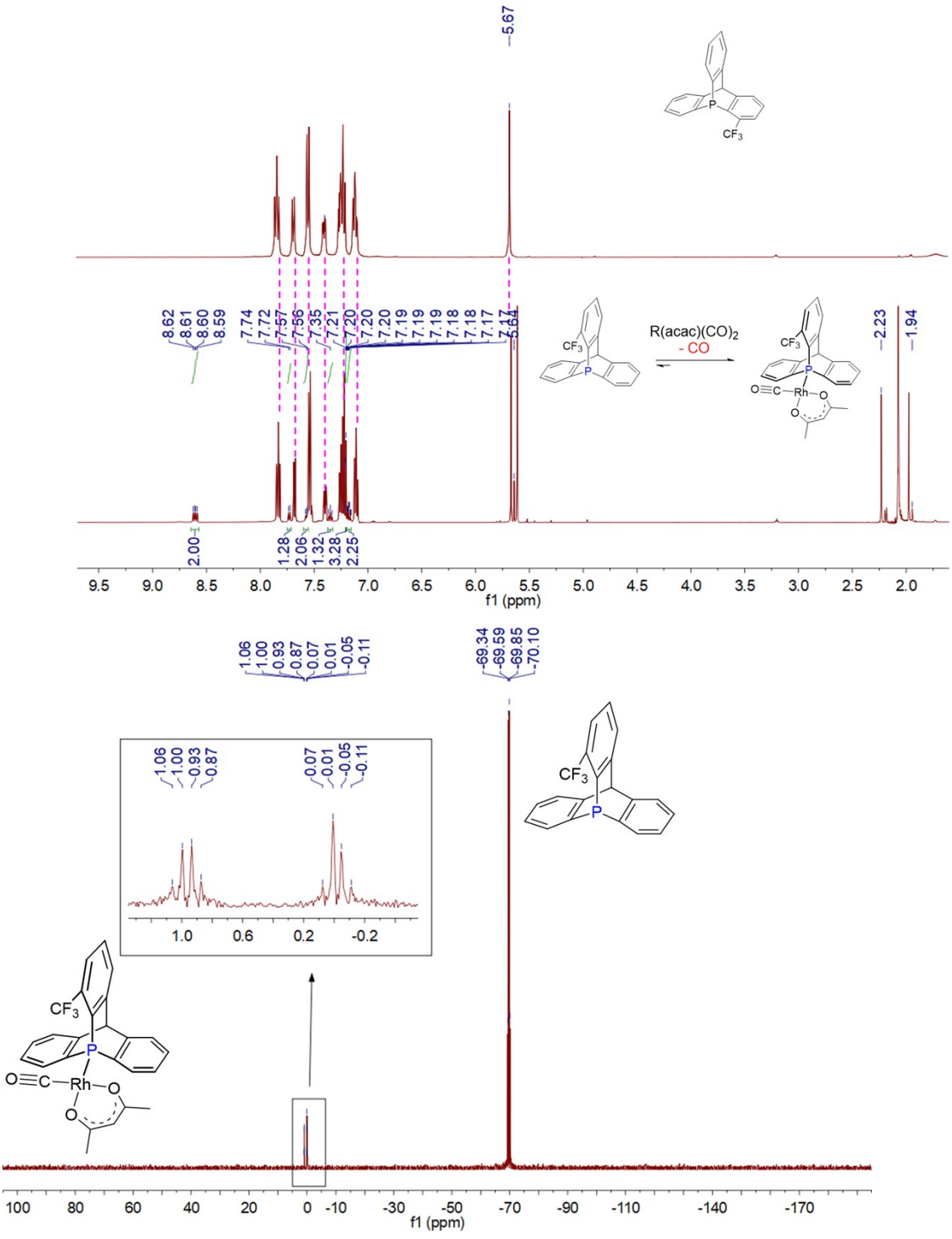

3054,25cm-1;97,07%T
2083,51cm-1;95,37%T
1578,07cm-1;92,39%T
895,71cm-1;94,03%T
619,73cm-1;91,20%T
1522,19cm-1;90,01%T
1386,30cm-1;93,42%T
1445,55cm-1;94,53%T
2011,40cm-1;94,33%T
1983,04cm-1;89,72%T
1264,28cm-1;52,30%T
703,27cm-1;37,88%T
731,78cm-1;15,72%T
%T
cm-1

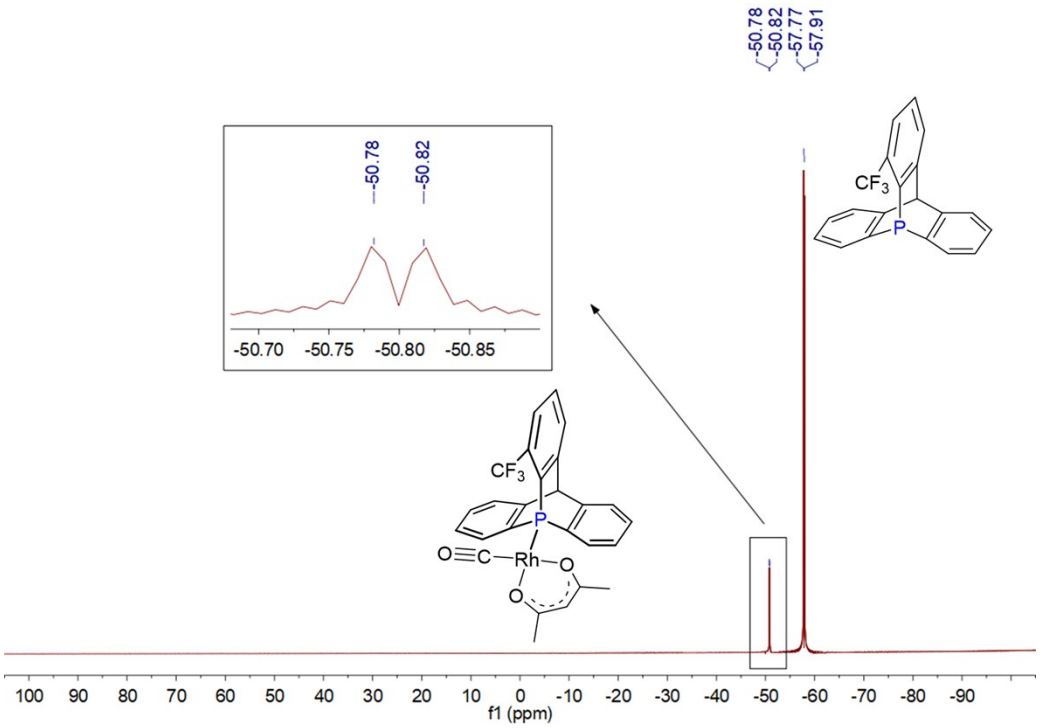
**3.35 Rh-Cl-9-phosphatriptycene complex 26c in $CDCl_3$: $^1$H-NMR (500 MHz), $^{31}$P-NMR (202 MHz). The IR measured in $CH_2Cl_2$**

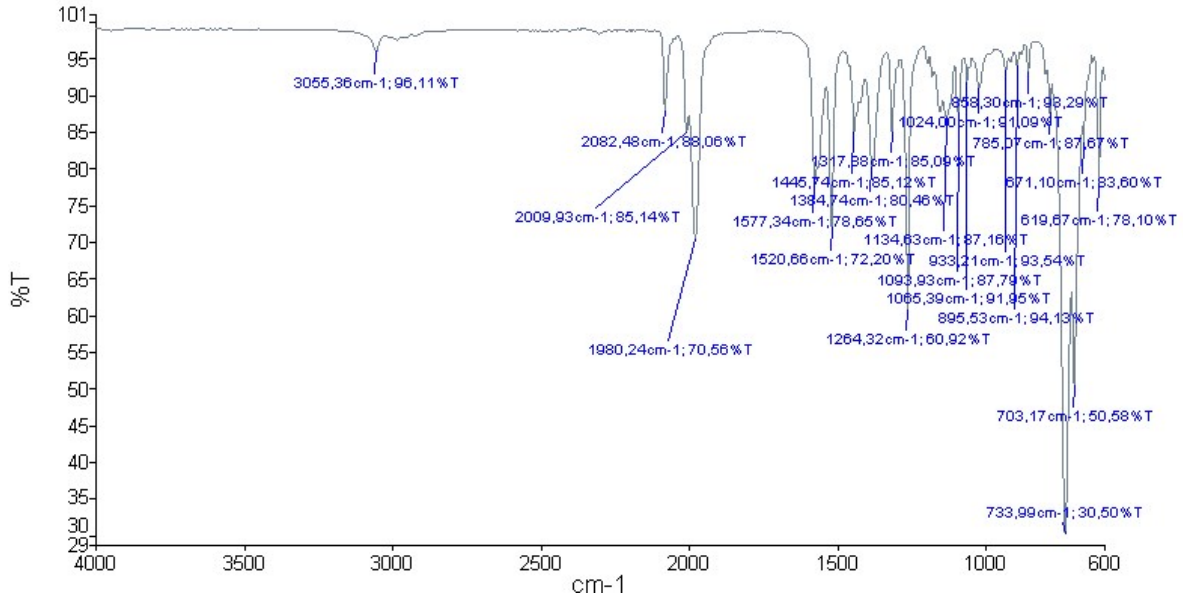



-0.03
-1.00
Cl
P
O≡C—Rh—O
O
90 80 70 60 50 40 30 20 10 0 -20 -40 -60 -80 -100 -120 -140
f1 (ppm)
%T
3054,68cm-1;97,40%T
1983,13cm-1;96,33%T
1422,16cm-1;96,22%T
1522,21cm-1;96,39%T
895,97cm-1;94,61%T
621,47cm-1;95,08%T
1264,33cm-1;52,16%T
703,32cm-1;37,00%T
731,34cm-1;15,12%T
4000 3500 3000 2500 2000 1500 1000 600
cm-1

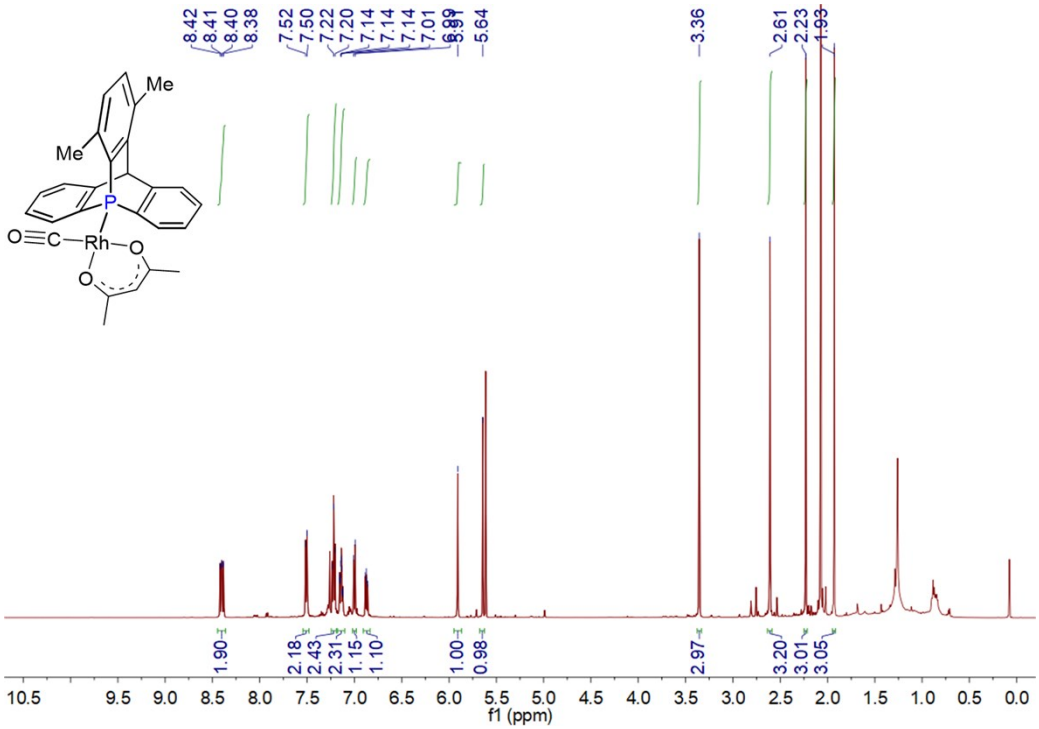
**3.36 Rh-$CF_3$-9-phosphatriptycene complex 26d in $CDCl_3$: $^1$H-NMR (500 MHz), $^{31}$P-NMR (202 MHz), $^{19}$F-NMR (376 MHz). The IR measured in $CH_2Cl_2$**

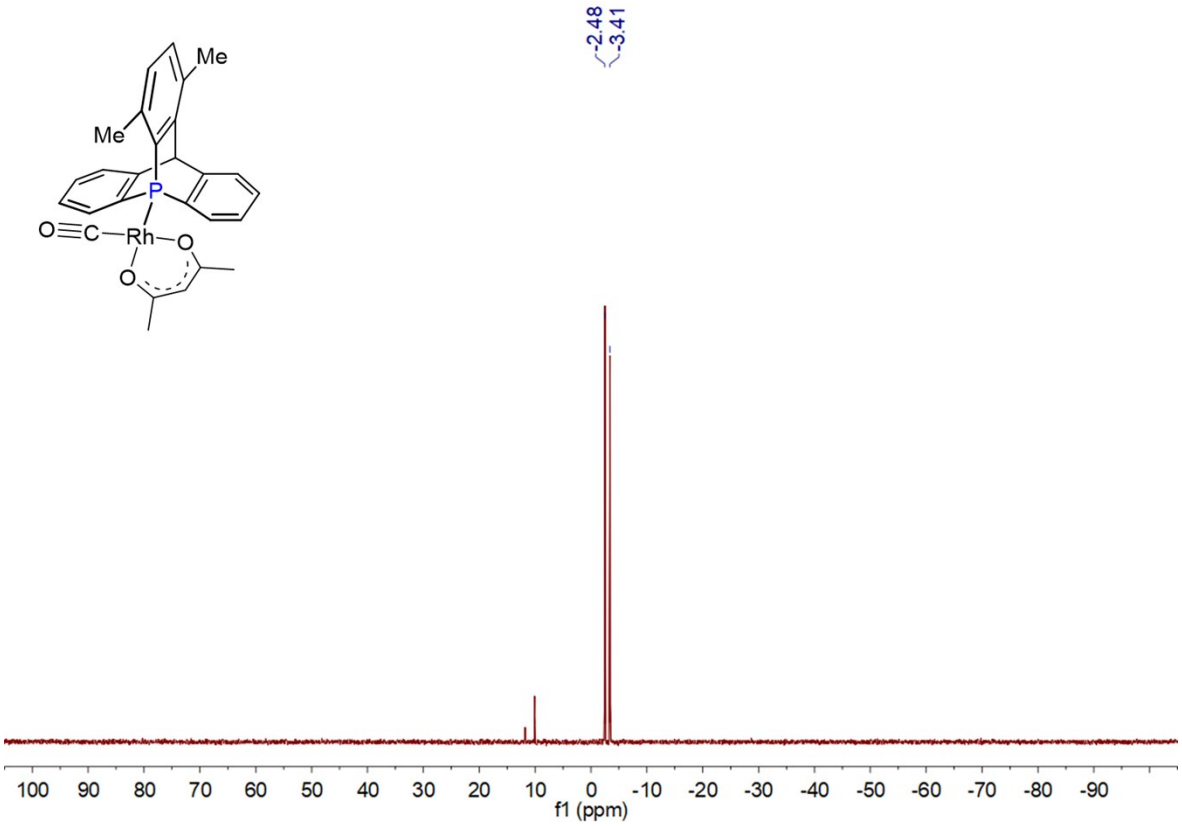


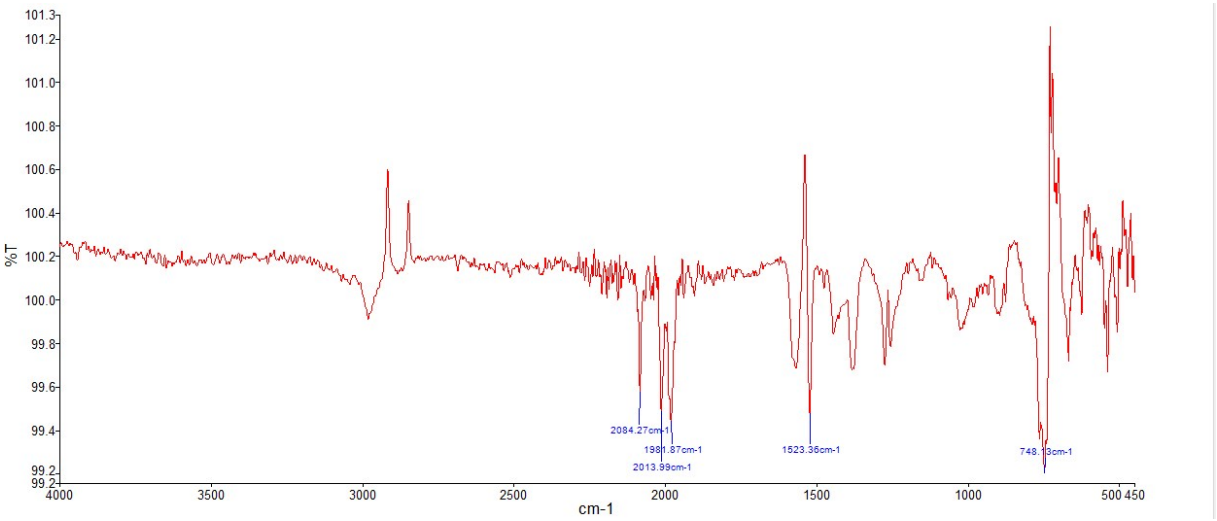

-50.78
-50.82
-57.77
-57.91
-50.78
-50.82
-50.70
-50.75
-50.80
-50.85
CF3
P
O≡C—Rh—O
O
100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90
f1 (ppm)


%T
cm-1
3055,36cm-1;96,11%T
2082,48cm-1;88,06%T
2009,93cm-1;85,14%T
1980,24cm-1;70,56%T
1577,34cm-1;78,65%T
1520,66cm-1;72,20%T
1445,74cm-1;85,12%T
1384,74cm-1;80,46%T
1317,38cm-1;85,09%T
1264,32cm-1;60,92%T
1134,63cm-1;87,16%T
1093,93cm-1;87,79%T
1065,39cm-1;91,95%T
1024,00cm-1;91,09%T
968,30cm-1;98,29%T
933,21cm-1;93,54%T
895,53cm-1;94,13%T
785,07cm-1;87,67%T
703,17cm-1;50,58%T
671,10cm-1;83,60%T
619,67cm-1;78,10%T
733,99cm-1;30,50%T

**3.37 Rh-1,4-dimethyl-9-phosphatriptycene complex 26e in $CDCl_3$: $^1$H-NMR (500 MHz), $^{31}$P-NMR (202 MHz). The IR measured in $CH_2Cl_2$**






## 4. Computational studies

### 4.1 Methods

Computations have been carried out using the Jaguar 8.5 pseudospectral program package.[8] All species have been fully geometry optimized, and the Cartesian coordinates are supplied in section 4.3. Density Functional Theory (DFT) was applied by the means of the M06-2X functional. The standard split valence polarized 6-31+G(d) basis set was used for all atoms. Electronic energies were obtained after corresponding fully analytical single point calculations, at the M06-2X/6-311+G(d,p) level of theory. Solvation energies were obtained by single point calculations using the Poisson-Boltzmann polarisable continuum method as implemented in Jaguar, at the M06-2X/6-31+G(d) level, using the parameters appropriate for benzene. Zero point energy and thermal contributions to enthalpy were computed by performing frequency calculations at the M06-2X/6-31+G(d) level of theory.

PA and MCA values are calculated (at the M06-2X/6-31+G(d)(benzene) level) as the difference in enthalpy at 298 K between the neutral and the protonated and methylated phosphine, respectively.

The $He_8$_steric parameters were computed by optimizing the 9-phosphatriptycene geometries at the BP86/6-31+G(d) level, its tertiary phosphorus atom constrained to lie at 2.28 Å above the centroid, and perpendicular to the plane, of a helium ring which is constituted by eight helium atoms with a 2.5 Å radius (Figure S1).[9]

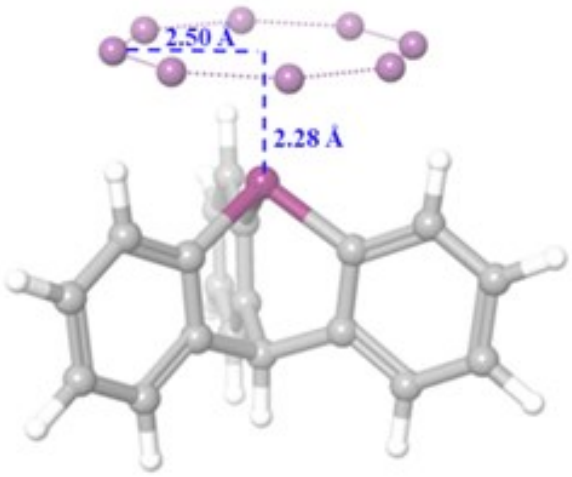



**Figure S1.** Geometric model used for computation of the $He_8$_steric parameter (helium atoms in violet and phosphorus atom in dark purple).

### 4.2 Calculations of proton affinities (PA) of triarylphosphines and correlation with p$K_a$

The computed proton affinity (**PA**) of weak phosphines is reported in Table S2. The correlation between computed **PA** and experimental p$K_a$[10] (Figure S2) was used to estimate the p$K_a$ of 9-phosphatriptycene (**1**). Linear correlation of **PA** versus p$K_a$($H_2O$) indicate that p$K_a$($H_2O$) value ranges from -1.58 to 0.03 for 9-phosphatriptycenes (Table S2). For comparison, the p$K_a$($H_2O$) value of $PPh_3$, *p*-$CF_3$-$PPh_3$ and *p*-Cl-$PPh_3$ is 3.28, -1.39 and 0.87, respectively.

***Table S2***: Computed (M06-2X/6-31+G*(benzene)) proton affinities (**PA**) with their corresponding estimated p$K_a$ values of selected triarylphosphines.

| Lewis Base | PA[c] (kcal/mol) | p$K_a$($H_2O$) |
|---|---|---|
| Cl-P-triptycene (**7a**) | 233.5 | -1.17[a] |
| F-P-triptycene (**7b**) | 233.3 | -1.24[a] |
| $CF_3$-P-triptycene (**7c**) | 232.2 | -1.58[a] |
| di-Me-P-triptycene (**8a**) | 237.3 | 0.03[a] |
| P-triptycene (**1**) | 235.9 | -0.42[a] |
| $PPh_3$ | 247.5 | 3.28[b] |
| P(*p*-Cl-$C_6H_4$)$_3$ | 240.2 | 0.87[b] |
| P(*p*-$CF_3$-$C_6H_4$)$_3$ | 232.7 | -1.39[b] |

[a] Estimated using the correlation between computed **PA** and experimental pKa (see Figure S2); [b] See reference 10; [c] **PA** stands for proton affinity.

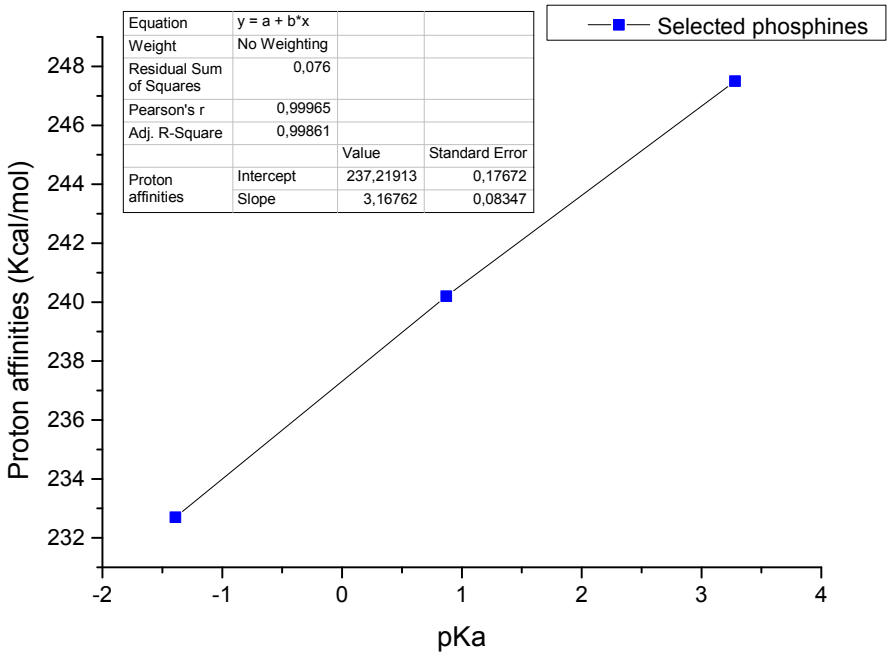



**Figure S2**. Proton affinities of selected triarylphosphines and correlation with their pKa.

### 4.3 Structures and relative energies

**$CH_3^+$**
E(M06-2X/6-31+G*)(benzene) = -39.5328
E(M06-2X/6-311+G**) = -39.4627
H(M06-2X/6-31+G*)(benzene) = -39.4269

| | | | |
|---|---|---|---|
| C1 | 3.0866238012 | 1.9106818130 | 7.6383553560 |
| H2 | 3.5785105737 | 1.0806431251 | 8.1480060734 |
| H3 | 3.0900339464 | 1.9611140453 | 6.5484598852 |
| H4 | 2.5915698264 | 2.6901651085 | 8.2195519526 |

**He-ring**
E(BP86 /6-31G*) = -23.1552

| | | | |
|---|---|---|---|
| He1 | 2.4999755124# | 0.0000000000# | 0.0000000000# |
| He2 | -2.4999755124# | 0.0000000000# | 0.0000000000# |
| He3 | 0.0000000000# | 2.4999755124# | 0.0000000000# |
| He4 | 0.0000000000# | -2.4999755124# | 0.0000000000# |
| He5 | 1.7677496376# | 1.7677496376# | 0.0000000000# |
| He6 | -1.7677496376# | -1.7677496376# | 0.0000000000# |
| He7 | -1.7677496376# | 1.7677496376# | 0.0000000000# |
| He8 | 1.7677496376# | -1.7677496376# | 0.0000000000# |
| X9 | -0.0000500000# | 0.0000125000# | 0.0000000000# |

**$PPh_3$**
E(M06-2X/6-31+G*)(benzene) = -1035.9854
E(M06-2X/6-311+G**) = -1036.1637
H(M06-2X/6-31+G*)(benzene) = -1036.8757
E(BP86/6-31G*) = -1036.2968

| | | | |
|---|---|---|---|
| C1 | -0.9467945442 | -0.2931628374 | 1.7960146778 |
| C2 | -1.8585686879 | -1.2664111717 | 2.2174402567 |
| C3 | -0.4056808164 | 0.5837643163 | 2.7453823510 |
| C4 | -2.2258486277 | -1.3535558021 | 3.5604083750 |
| C5 | -0.7828669324 | 0.5055292630 | 4.0834600654 |
| C6 | -1.6940815267 | -0.4669172665 | 4.4941757719 |
| C7 | -1.1232271239 | -1.5685767006 | -0.7459289707 |
| C8 | -2.3649073037 | -1.5988688866 | -1.3892621555 |
| C9 | -0.3622105577 | -2.7435210255 | -0.6892875868 |
| C10 | -2.8364587918 | -2.7828016139 | -1.9568853882 |
| C11 | -0.8392768024 | -3.9283293118 | -1.2438389897 |
| C12 | -2.0789336623 | -3.9495815983 | -1.8821169041 |
| C13 | -1.5776075313 | 1.2323502063 | -0.5219718696 |
| C14 | -2.6984633317 | 1.6523039086 | 0.2018444034 |
| C15 | -1.3177476335 | 1.8188015008 | -1.7674075324 |
| C16 | -3.5453358931 | 2.6324440264 | -0.3157531556 |
| C17 | -2.1706909351 | 2.7875699336 | -2.2897801951 |
| C18 | -3.2872155917 | 3.1980923947 | -1.5624404687 |
| P19 | -0.3997858208 | -0.0682507918 | 0.0483409969 |
| H20 | -0.4407035831 | 1.5108342766 | -2.3331137138 |
| H21 | -1.9590519185 | 3.2281048277 | -3.2597811613 |
| H22 | -3.9494428431 | 3.9598234571 | -1.9634688260 |
| H23 | -4.4116653276 | 2.9510074596 | 0.2571467755 |
| H24 | -2.9152588759 | 1.2134332811 | 1.1722771838 |
| H25 | 0.3152604334 | 1.3359624571 | 2.4314291634 |
| H26 | -0.3593670872 | 1.1968807881 | 4.8062274291 |
| H27 | -1.9836155109 | -0.5366587804 | 5.5386285896 |

| | | | |
|---|---|---|---|
| H28 | -2.9334115758 | -2.1153660055 | 3.8754267683 |
| H29 | -2.2868556515 | -1.9587675412 | 1.4972808276 |
| H30 | 0.6119859750 | -2.7288852678 | -0.2046789585 |
| H31 | -0.2394665088 | -4.8320415448 | -1.1862979937 |
| H32 | -2.4492678751 | -4.8698817121 | -2.3242328070 |
| H33 | -3.8012942876 | -2.7918433117 | -2.4561255267 |
| H34 | -2.9690629416 | -0.6973299140 | -1.4488132304 |

**$PPh_3$-$H^+$**
E(M06-2X/6-31+G*)(benzene) = -1036.3901
E(M06-2X/6-311+G**) = -1036.5358
H(M06-2X/6-31+G*)(benzene) = -1036.2702

| | | | |
|---|---|---|---|
| C1 | -1.0714665870 | -0.3132687414 | 1.8955367989 |
| C2 | -1.8898987132 | -1.3360985316 | 2.3856880420 |
| C3 | -0.4760847845 | 0.6132175729 | 2.7625831450 |
| C4 | -2.1110950617 | -1.4285538803 | 3.7579387108 |
| C5 | -0.7027816829 | 0.5075013860 | 4.1299481076 |
| C6 | -1.5193240021 | -0.5116784518 | 4.6243089761 |
| C7 | -1.2384868539 | -1.6336685830 | -0.7519069081 |
| C8 | -2.3652946973 | -1.6740830609 | -1.5792627654 |
| C9 | -0.4387903027 | -2.7698498180 | -0.5654755540 |
| C10 | -2.6899829707 | -2.8650756177 | -2.2253623883 |
| C11 | -0.7726077898 | -3.9503467685 | -1.2184294132 |
| C12 | -1.8965647878 | -3.9959255456 | -2.0459900102 |
| C13 | -1.7167077390 | 1.2814577619 | -0.5149389575 |
| C14 | -2.7890311648 | 1.8177867113 | 0.2054793084 |
| C15 | -1.3559396443 | 1.7995239699 | -1.7660850992 |
| C16 | -3.5053508585 | 2.8821052439 | -0.3370762914 |
| C17 | -2.0774925141 | 2.8637109954 | -2.2942016305 |
| C18 | -3.1500102094 | 3.4016326443 | -1.5801878945 |
| P19 | -0.8201757051 | -0.1296099555 | 0.1304333589 |
| H20 | -0.5224199358 | 1.3788459872 | -2.3243795427 |
| H21 | -1.8022281234 | 3.2753901718 | -3.2595398971 |
| H22 | -3.7087822847 | 4.2342058420 | -1.9957003199 |
| H23 | -4.3375891416 | 3.3067547490 | 0.2144591038 |
| H24 | -3.0597006891 | 1.4162004815 | 1.1785811915 |
| H25 | 0.1566799741 | 1.4099127523 | 2.3775522162 |
| H26 | -0.2416484105 | 1.2164457640 | 4.8095268220 |
| H27 | -1.6915153974 | -0.5920149825 | 5.6929345924 |
| H28 | -2.7427847618 | -2.2196156444 | 4.1482743648 |
| H29 | -2.3455383701 | -2.0543809030 | 1.7090393354 |
| H30 | 0.4345112157 | -2.7362929452 | 0.0823560566 |
| H31 | -0.1564689478 | -4.8333306469 | -1.0847236049 |
| H32 | -2.1518020716 | -4.9196284763 | -2.5556286974 |
| H33 | -3.5610667092 | -2.9061386960 | -2.8708635357 |
| H34 | -2.9801713260 | -0.7896454831 | -1.7231803419 |
| H35 | 0.5442175455 | 0.1171034905 | -0.0738990582 |

**$PPh_3$-$CH_3^+$**
E(M06-2X/6-31+G*)(benzene) = -1075.7053
E(M06-2X/6-311+G**) = -1075.8610
H(M06-2X/6-31+G*)(benzene) = -1075.5643

| | | | |
|---|---|---|---|
| C1 | -1.2952918313 | -0.5021454871 | 1.7785585537 |
| C2 | -2.0364834281 | -1.6570252009 | 2.0494636711 |
| C3 | -0.9743455087 | 0.3968838316 | 2.8058294428 |
| C4 | -2.4492918456 | -1.9138741302 | 3.3553906736 |
| C5 | -1.3911790511 | 0.1298971152 | 4.1048898055 |
| C6 | -2.1261399000 | -1.0252740981 | 4.3780978747 |

| | | | |
|---|---|---|---|
| C7 | -1.0004092682 | -1.5714085665 | -0.9497884217 |
| C8 | -2.0044807265 | -1.5909541226 | -1.9230124526 |
| C9 | -0.1737712572 | -2.6872740489 | -0.7545223447 |
| C10 | -2.1739563501 | -2.7302549773 | -2.7074812472 |
| C11 | -0.3519746737 | -3.8181331805 | -1.5429857647 |
| C12 | -1.3502198609 | -3.8374822435 | -2.5190996082 |
| C13 | -1.7202368649 | 1.2604962289 | -0.5443141935 |
| C14 | -2.8783116424 | 1.6910994626 | 0.1116186192 |
| C15 | -1.2972807242 | 1.8837324666 | -1.7270938568 |
| C16 | -3.6086493872 | 2.7538206387 | -0.4168604889 |
| C17 | -2.0336623775 | 2.9433159863 | -2.2446553048 |
| C18 | -3.1869158858 | 3.3780116380 | -1.5886487085 |
| P19 | -0.7754270961 | -0.1280406441 | 0.0983717341 |
| H20 | -0.4058129285 | 1.5442422554 | -2.2491438787 |
| H21 | -1.7084480574 | 3.4302671341 | -3.1581461831 |
| H22 | -3.7573904543 | 4.2074587194 | -1.9944504579 |
| H23 | -4.5058650733 | 3.0934326009 | 0.0900569869 |
| H24 | -3.2075664086 | 1.2071398952 | 1.0270375626 |
| H25 | -0.4117762652 | 1.3041644568 | 2.5983207888 |
| H26 | -1.1432368168 | 0.8212347688 | 4.9036049201 |
| H27 | -2.4474645042 | -1.2313929396 | 5.3941659331 |
| H28 | -3.0221252048 | -2.8097248218 | 3.5712415029 |
| H29 | -2.2883871083 | -2.3520254115 | 1.2532284363 |
| H30 | 0.5978472144 | -2.6832256996 | 0.0118590528 |
| H31 | 0.2862698831 | -4.6834768301 | -1.3971335481 |
| H32 | -1.4845710686 | -4.7215457649 | -3.1343897243 |
| H33 | -2.9496392124 | -2.7497992769 | -3.4659119073 |
| H34 | -2.6474557615 | -0.7277668311 | -2.0714106180 |
| C35 | 0.9828024529 | 0.3156984175 | 0.1124769523 |
| H36 | 1.3386805339 | 0.4415125770 | -0.9130048956 |
| H37 | 1.1221032793 | 1.2505201889 | 0.6607481251 |
| H38 | 1.5571442118 | -0.4767545650 | 0.5983390029 |

**P(*p*-Cl-$C_6H_4$)$_3$**
E(M06-2X/6-31+G*)(benzene) = -2414.6952
E(M06-2X/6-311+G**) = -2414.9659
H(M06-2X/6-31+G*)(benzene) = -2.414.7030

| | | | |
|---|---|---|---|
| C1 | -0.9220962634 | -0.2845226874 | 1.7885311423 |
| C2 | -1.8389250683 | -1.2533460535 | 2.2087174372 |
| C3 | -0.3734059719 | 0.5803476286 | 2.7443146599 |
| C4 | -2.2078895697 | -1.3535831385 | 3.5493120540 |
| C5 | -0.7427510206 | 0.5009025161 | 4.0833879486 |
| C6 | -1.6595200277 | -0.4712835657 | 4.4738364027 |
| C7 | -1.0886925660 | -1.5609689693 | -0.7493264144 |
| C8 | -2.3411455520 | -1.6046854517 | -1.3701638235 |
| C9 | -0.3146435102 | -2.7279666773 | -0.7154771782 |
| C10 | -2.8164177823 | -2.7863270781 | -1.9367263204 |
| C11 | -0.7816621828 | -3.9177873896 | -1.2652794282 |
| C12 | -2.0332650338 | -3.9339952344 | -1.8742662564 |
| C13 | -1.5467314912 | 1.2399524930 | -0.5327441930 |
| C14 | -2.6672730623 | 1.6668641268 | 0.1870113825 |
| C15 | -1.2846465401 | 1.8263258088 | -1.7776696873 |
| C16 | -3.5129958460 | 2.6496071144 | -0.3250087996 |
| C17 | -2.1273992165 | 2.7985944488 | -2.3072236815 |
| C18 | -3.2373488269 | 3.2029620578 | -1.5707843077 |
| P19 | -0.3698451219 | -0.0585307237 | 0.0431644213 |
| H20 | -0.4091806455 | 1.5189522516 | -2.3456035615 |
| H21 | -1.9243507552 | 3.2470363055 | -3.2741738345 |

| | | | |
|---|---|---|---|
| Cl22 | -4.2925373981 | 4.4283686818 | -2.2173720505 |
| H23 | -4.3809164968 | 2.9821530161 | 0.2352074764 |
| H24 | -2.8913520835 | 1.2334299129 | 1.1581215722 |
| H25 | 0.3536284333 | 1.3301307429 | 2.4397290754 |
| H26 | -0.3199529736 | 1.1758424880 | 4.8203004728 |
| Cl27 | -2.1196881520 | -0.5889822914 | 6.1494275434 |
| H28 | -2.9173098360 | -2.1074657698 | 3.8750400876 |
| H29 | -2.2757182185 | -1.9415411972 | 1.4899859253 |
| H30 | 0.6690788076 | -2.7100811689 | -0.2513906619 |
| H31 | -0.1816363580 | -4.8212449584 | -1.2328655947 |
| Cl32 | -2.6233161302 | -5.4141948296 | -2.5770992707 |
| H33 | -3.7873099143 | -2.8190453857 | -2.4204916235 |
| H34 | -2.9600397814 | -0.7125380968 | -1.4168047771 |

**P(*p*-Cl-$C_6H_4$)$_3$-$H^+$**

E(M06-2X/6-31+G*)(benzene) = -2415.0875

E(M06-2X/6-311+G**) = -2415.3244

H(M06-2X/6-31+G*)(benzene) = -2.415.0858

| | | | |
|---|---|---|---|
| C1 | -0.9781849727 | -0.2934311812 | 1.8694268055 |
| C2 | -1.7550856979 | -1.3385450308 | 2.3804224275 |
| C3 | -0.4108063859 | 0.6590858375 | 2.7283435547 |
| C4 | -1.9678693121 | -1.4314199815 | 3.7516391465 |
| C5 | -0.6203420330 | 0.5645896420 | 4.0965676398 |
| C6 | -1.3999567562 | -0.4809670489 | 4.5991016854 |
| C7 | -1.1567440441 | -1.6340279380 | -0.7666355413 |
| C8 | -2.3296072450 | -1.7049819645 | -1.5259968340 |
| C9 | -0.3168639331 | -2.7504059869 | -0.6457559425 |
| C10 | -2.6666115336 | -2.8944363187 | -2.1626130671 |
| C11 | -0.6513765223 | -3.9363180090 | -1.2837395229 |
| C12 | -1.8265674567 | -4.0003921022 | -2.0374161343 |
| C13 | -1.6266796491 | 1.2817449234 | -0.5516783134 |
| C14 | -2.6787566524 | 1.8500902875 | 0.1744461852 |
| C15 | -1.2825344630 | 1.7797818222 | -1.8165184479 |
| C16 | -3.3908108010 | 2.9157591134 | -0.3650836478 |
| C17 | -1.9908309960 | 2.8452092192 | -2.3535749972 |
| C18 | -3.0426163389 | 3.4054680350 | -1.6234579227 |
| H19 | -0.4663838031 | 1.3423530846 | -2.3872169056 |
| H20 | -1.7348833754 | 3.2466716144 | -3.3282709053 |
| Cl21 | -3.9216381593 | 4.7289909313 | -2.2917157879 |
| H22 | -4.2087607925 | 3.3693005247 | 0.1842962192 |
| H23 | -2.9451773618 | 1.4708654851 | 1.1575229722 |
| H24 | 0.1928314268 | 1.4754333487 | 2.3380106535 |
| H25 | -0.1849020188 | 1.2894653885 | 4.7760600102 |
| Cl26 | -1.6595201055 | -0.5967264793 | 6.2991776011 |
| H27 | -2.5667200141 | -2.2356071708 | 4.1653932958 |
| H28 | -2.1929498910 | -2.0814260293 | 1.7190234100 |
| H29 | 0.5966055271 | -2.7026611097 | -0.0571326580 |
| H30 | -0.0107510082 | -4.8082276936 | -1.2055487828 |
| Cl31 | -2.2404704326 | -5.4742622544 | -2.8294513121 |
| H32 | -3.5714227372 | -2.9672330531 | -2.7563627947 |
| H33 | -2.9799175566 | -0.8401424135 | -1.6278343700 |
| P34 | -0.7340159753 | -0.1263378544 | 0.1026122511 |
| H35 | 0.6309473706 | 0.1093261805 | -0.1126438940 |

**P(*p*-$CF_3$-$C_6H_4$)$_3$**
E(M06-2X/6-31+G*)(benzene) = -2046.8548
E(M06-2X/6-311+G**) = -2047.31898373111
H(M06-2X/6-31+G*)(benzene) = -2.047.0094

| | | | |
|---|---|---|---|
| C1 | -0.8642212494 | -0.3100956066 | 1.7976706989 |
| C2 | -1.7694204928 | -1.2908831429 | 2.2189124189 |
| C3 | -0.3422607738 | 0.5841889403 | 2.7398705587 |
| C4 | -2.1563678600 | -1.3626835562 | 3.5538469106 |
| C5 | -0.7369523112 | 0.5268825832 | 4.0736384461 |
| C6 | -1.6452767618 | -0.4490661880 | 4.4739592541 |
| C7 | -1.0342324759 | -1.5808423997 | -0.7512723017 |
| C8 | -2.2793069109 | -1.6037521605 | -1.3894740511 |
| C9 | -0.2630381179 | -2.7500398440 | -0.7243435999 |
| C10 | -2.7451198021 | -2.7725995358 | -1.9863479904 |
| C11 | -0.7286548832 | -3.9245176893 | -1.3070083956 |
| C12 | -1.9686863044 | -3.9278002825 | -1.9421067836 |
| C13 | -1.4928271482 | 1.2115628633 | -0.5117218301 |
| C14 | -2.6132179403 | 1.6258134466 | 0.2163517846 |
| C15 | -1.2398015991 | 1.7929823002 | -1.7607176471 |
| C16 | -3.4699063301 | 2.5955830198 | -0.2985097807 |
| C17 | -2.0986924453 | 2.7527204376 | -2.2862110303 |
| C18 | -3.2130742164 | 3.1496477426 | -1.5499072399 |
| P19 | -0.3075679803 | -0.0860007438 | 0.0529973098 |
| H20 | -0.3653593462 | 1.4881710028 | -2.3310963936 |
| H21 | -1.9043820988 | 3.1907468973 | -3.2601223595 |
| H22 | -4.3418668771 | 2.9106064362 | 0.2665194865 |
| H23 | -2.8284473347 | 1.1894732266 | 1.1875113153 |
| H24 | 0.3776273705 | 1.3374598002 | 2.4281267211 |
| H25 | -0.3342227216 | 1.2278770387 | 4.7971866860 |
| H26 | -2.8584383817 | -2.1249076668 | 3.8797749031 |
| H27 | -2.1804501244 | -1.9999964808 | 1.5059280027 |
| H28 | 0.7147575285 | -2.7411017404 | -0.2483568742 |
| H29 | -0.1250564612 | -4.8262758183 | -1.2850741572 |
| H30 | -3.7074834900 | -2.7838918423 | -2.4890148397 |
| H31 | -2.8919604334 | -0.7077060229 | -1.4290640196 |
| C32 | -2.1244105967 | -0.5175505595 | 5.8972389138 |
| F33 | -1.3769380597 | 0.2285583426 | 6.7252603798 |
| F34 | -3.3944016469 | -0.0808404739 | 6.0091693063 |
| F35 | -2.1107034381 | -1.7776374227 | 6.3666883281 |
| C36 | -4.1168467595 | 4.2264849498 | -2.0818803427 |
| F37 | -4.1181494864 | 4.2641667235 | -3.4248884012 |
| F38 | -5.3885792805 | 4.0570306203 | -1.6817547029 |
| F39 | -3.7361588587 | 5.4469438767 | -1.6574835350 |
| C40 | -2.4984658370 | -5.1968272791 | -2.5495715331 |
| F41 | -1.5118095822 | -6.0303610591 | -2.9181285223 |
| F42 | -3.2773171055 | -5.8727504581 | -1.6820248618 |
| F43 | -3.2505092931 | -4.9562534983 | -3.6368046200 |

**P(*p*-$CF_3$-$C_6H_4$)$_3$-$H^+$**
E(M06-2X/6-31+G*)(benzene) = -2047.2361
E(M06-2X/6-311+G**) = -2047.6621
H(M06-2X/6-31+G*)(benzene) = -2.047.3803

| | | | |
|---|---|---|---|
| C1 | -0.9822709304 | -0.2790968747 | 1.8761830937 |
| C2 | -1.7806461139 | -1.3149879347 | 2.3711189259 |
| C3 | -0.3921507457 | 0.6555262066 | 2.7372592230 |
| C4 | -1.9910256628 | -1.4135398426 | 3.7433644942 |
| C5 | -0.6054767646 | 0.5489754295 | 4.1061515764 |
| C6 | -1.4030179472 | -0.4843955749 | 4.5974580899 |
| C7 | -1.1494826901 | -1.6220555757 | -0.7624113392 |
| C8 | -2.3408311818 | -1.7051813390 | -1.4895830213 |
| C9 | -0.2835138398 | -2.7192822032 | -0.6626446645 |
| C10 | -2.6685269635 | -2.9013039407 | -2.1226406104 |
| C11 | -0.6165343790 | -3.9081220897 | -1.2989312089 |
| C12 | -1.8059403749 | -3.9892497416 | -2.0235626701 |
| C13 | -1.6291589046 | 1.2959208109 | -0.5570945987 |
| C14 | -2.6180923119 | 1.9253451308 | 0.2041089853 |
| C15 | -1.3361913288 | 1.7226346748 | -1.8599914718 |
| C16 | -3.3217253488 | 2.9943522243 | -0.3459359897 |
| C17 | -2.0408772277 | 2.7899450555 | -2.4001438281 |
| C18 | -3.0280311162 | 3.4170651473 | -1.6385846541 |
| H19 | -0.5666346144 | 1.2316745885 | -2.4511688379 |
| H20 | -1.8212344902 | 3.1407445801 | -3.4034132190 |
| H21 | -4.0881518214 | 3.4997594815 | 0.2324246441 |
| H22 | -2.8396883792 | 1.5958442130 | 1.2153905438 |
| H23 | 0.2311752330 | 1.4586578545 | 2.3511210159 |
| H24 | -0.1475915708 | 1.2568528382 | 4.7893162213 |
| H25 | -2.6011520773 | -2.2151613635 | 4.1470162980 |
| H26 | -2.2295550544 | -2.0432185487 | 1.7012581541 |
| H27 | 0.6436599091 | -2.6527207160 | -0.0984097781 |
| H28 | 0.0469729372 | -4.7650699819 | -1.2422623760 |
| H29 | -3.5848499642 | -2.9823875810 | -2.6981304762 |
| H30 | -3.0059161707 | -0.8498177645 | -1.5721159975 |
| P31 | -0.7297270157 | -0.1090035097 | 0.1071080205 |
| H32 | 0.6363166552 | 0.1236401586 | -0.1001223527 |
| C33 | -2.1818538360 | -5.3016386241 | -2.6752047143 |
| F34 | -1.0961702934 | -5.9706281060 | -3.0785697212 |
| F35 | -2.8409809162 | -6.0819073983 | -1.8064659851 |
| F36 | -2.9743876483 | -5.1100870312 | -3.7348651506 |
| C37 | -1.6741975400 | -0.5767024952 | 6.0827966642 |
| F38 | -0.6814405957 | -0.0342468204 | 6.7950593874 |
| F39 | -2.8040499933 | 0.0757779234 | 6.3922732825 |
| F40 | -1.8210952902 | -1.8485820654 | 6.4692894116 |
| C41 | -3.8225618828 | 4.5470122379 | -2.2551842308 |
| F42 | -3.0723173867 | 5.2605724182 | -3.1020459194 |
| F43 | -4.8643996513 | 4.0615482966 | -2.9458076087 |
| F44 | -4.3017024924 | 5.3738388124 | -1.3202695628 |

**9-phosphatriptycene**

E(M06-2X/6-31+G*)(benzene) = -1072.9051
E(M06-2X/6-311+G**) = -1073.0850
E(BP86/6-31G*) = -1073.2223
H(M06-2X/6-31+G*)(benzene) = -1072.8127

| | | | |
|---|---|---|---|
| C1 | -2.0918068395 | 1.3671487355 | 6.3299126470 |
| C2 | -2.1816119929 | 2.6396491834 | 5.7589799018 |
| C3 | -1.0710603973 | 3.4779419327 | 5.7335285899 |
| C4 | 0.1408993348 | 3.0477279407 | 6.2805426780 |
| C5 | 0.2331842723 | 1.7812377868 | 6.8495015044 |
| C6 | 1.6645511090 | -0.5156764413 | 6.7272075718 |
| C7 | 2.7314818186 | -1.1086646444 | 6.0593342812 |
| C8 | 2.5559556048 | -2.3411686816 | 5.4243140210 |
| C9 | 1.3160080033 | -2.9719914825 | 5.4613470157 |
| C10 | 0.2424290277 | -2.3787476356 | 6.1313591490 |
| C11 | 0.4150772986 | -1.1528476488 | 6.7632968362 |
| C12 | -0.8873226971 | 0.9372022932 | 6.8742622184 |
| H13 | -2.9607317049 | 0.7137271458 | 6.3481386773 |
| H14 | -3.1235689171 | 2.9735977109 | 5.3337037876 |
| H15 | -1.1446085896 | 4.4658971435 | 5.2887041967 |
| H16 | 1.0109703611 | 3.6993959214 | 6.2624727861 |
| H17 | 3.6984838784 | -0.6124617157 | 6.0326206222 |
| H18 | 3.3877038026 | -2.8050235840 | 4.9024590880 |
| H19 | 1.1793927992 | -3.9298193248 | 4.9678774046 |
| H20 | -0.7257290089 | -2.8734862417 | 6.1586123959 |
| C21 | -0.4362084382 | -0.4728746180 | 11.3420481055 |
| C22 | 0.7387559657 | 0.2506725949 | 11.5229888143 |
| C23 | 1.4332791197 | 0.7427240731 | 10.4146178393 |
| C24 | 0.9468634687 | 0.5076546630 | 9.1323212401 |
| C25 | -0.2378998524 | -0.2219311504 | 8.9516506102 |
| C26 | -0.9272300632 | -0.7107441115 | 10.0552848910 |
| H27 | -0.9759622869 | -0.8556576982 | 12.2033069370 |
| H28 | 1.1172963115 | 0.4332923545 | 12.5243210158 |
| H29 | 2.3516132182 | 1.3083405065 | 10.5514943907 |
| H30 | -1.8453859018 | -1.2769424272 | 9.9166733973 |
| P31 | 1.7922909276 | 1.1153063416 | 7.5987010941 |
| C32 | -0.6957869699 | -0.4314117745 | 7.5145532652 |
| H33 | -1.6248705185 | -1.0087097995 | 7.4825867855 |

**9-phosphatriptycene-H$^+$**

E(M06-2X/6-31+G*)(benzene) = -1073.2899
E(M06-2X/6-311+G**) = -1073.4355
H(M06-2X/6-31+G*)(benzene) = -1073.1886

| | | | |
|---|---|---|---|
| C1 | -2.1113595670 | 1.3652622233 | 6.3191360344 |
| C2 | -2.1995512408 | 2.6387974883 | 5.7494203512 |
| C3 | -1.0981027107 | 3.4910959649 | 5.7212560199 |
| C4 | 0.1192342681 | 3.0813432190 | 6.2658002143 |
| C5 | 0.1928923407 | 1.8125473557 | 6.8290016771 |
| C6 | 1.6775150136 | -0.5527260532 | 6.7020237594 |
| C7 | 2.7591575517 | -1.1243163046 | 6.0416776444 |
| C8 | 2.5716283474 | -2.3549326397 | 5.4118467151 |
| C9 | 1.3273768253 | -2.9798208593 | 5.4533978820 |
| C10 | 0.2479644036 | -2.3935564048 | 6.1209501142 |
| C11 | 0.4140682402 | -1.1690366287 | 6.7541650483 |

| | | | |
|---|---|---|---|
| C12 | -0.9087920267 | 0.9387491319 | 6.8664855158 |
| H13 | -2.9787909441 | 0.7115084838 | 6.3332321600 |
| H14 | -3.1418393735 | 2.9667854869 | 5.3223629490 |
| H15 | -1.1831146526 | 4.4761657121 | 5.2750824365 |
| H16 | 0.9811718835 | 3.7418146003 | 6.2464960620 |
| H17 | 3.7270639604 | -0.6326143121 | 6.0120793574 |
| H18 | 3.3989565988 | -2.8231744025 | 4.8893626479 |
| H19 | 1.1917979100 | -3.9370179607 | 4.9601417618 |
| H20 | -0.7165567712 | -2.8927613109 | 6.1445016917 |
| C21 | -0.4458420580 | -0.4830902219 | 11.3538158688 |
| C22 | 0.7269597301 | 0.2423212115 | 11.5505246134 |
| C23 | 1.4326119511 | 0.7439500463 | 10.4566588816 |
| C24 | 0.9321346673 | 0.4979429385 | 9.1831045725 |
| C25 | -0.2503449622 | -0.2324154148 | 8.9654077994 |
| C26 | -0.9381180435 | -0.7228639718 | 10.0674927921 |
| H27 | -0.9874732117 | -0.8690468395 | 12.2114695766 |
| H28 | 1.0955819053 | 0.4196639275 | 12.5551938921 |
| H29 | 2.3472635800 | 1.3105367650 | 10.6045762270 |
| H30 | -1.8542762519 | -1.2900087368 | 9.9297597683 |
| C31 | -0.6985758744 | -0.4357754256 | 7.5129020548 |
| H32 | -1.6236938156 | -1.0147930495 | 7.4798111565 |
| P33 | 1.5980035299 | 1.0015253079 | 7.5952091518 |
| H34 | 2.7821429408 | 1.7437861593 | 7.6370248384 |

**9-phosphatriptycene-$CH_3^+$**

E(M06-2X/6-31+G*)(benzene) = -1112.6077
E(M06-2X/6-311+G**) = -1112.7643
H(M06-2X/6-31+G*)(benzene) = -1112.4852

| | | | |
|---|---|---|---|
| C1 | -2.2765227378 | 1.5618503405 | 7.0554238041 |
| C2 | -2.4344733082 | 2.9356546264 | 6.8499161514 |
| C3 | -1.3376152677 | 3.7937001214 | 6.8629773272 |
| C4 | -0.0561249841 | 3.2875879572 | 7.0838365879 |
| C5 | 0.0890649237 | 1.9200419869 | 7.2868387507 |
| C6 | 1.4938543278 | -0.2866795041 | 6.3394320874 |
| C7 | 2.4486644842 | -0.6478784410 | 5.3956528995 |
| C8 | 2.1502238926 | -1.6869714774 | 4.5132523792 |
| C9 | 0.9206240294 | -2.3363190151 | 4.5895851100 |
| C10 | -0.0320290689 | -1.9645923953 | 5.5428711738 |
| C11 | 0.2481999768 | -0.9328383104 | 6.4285393624 |
| C12 | -1.0084594650 | 1.0412925025 | 7.2760344762 |
| H13 | -3.1413312671 | 0.9044024387 | 7.0427039322 |
| H14 | -3.4277420591 | 3.3376186760 | 6.6775686942 |
| H15 | -1.4766180620 | 4.8573606105 | 6.7016004592 |
| H16 | 0.8020299968 | 3.9540131469 | 7.0948453343 |
| H17 | 3.4073555557 | -0.1395106948 | 5.3389678974 |
| H18 | 2.8790724479 | -1.9871510176 | 3.7679717859 |
| H19 | 0.6967084481 | -3.1435874124 | 3.8996292950 |
| H20 | -0.9869652098 | -2.4804014231 | 5.5909400421 |
| C21 | 0.1461952668 | -1.4488197948 | 11.1239025232 |
| C22 | 1.3449200098 | -0.7640981085 | 11.3069737626 |
| C23 | 1.8702246705 | 0.0148661933 | 10.2752397161 |
| C24 | 1.1694846737 | 0.0847857242 | 9.0765324378 |
| C25 | -0.0419256772 | -0.6006479738 | 8.8769003252 |
| C26 | -0.5500823731 | -1.3709907778 | 9.9141456800 |
| H27 | -0.2551122639 | -2.0524725021 | 11.9316016559 |
| H28 | 1.8733245953 | -0.8345988128 | 12.2517306446 |
| H29 | 2.8052527280 | 0.5505309914 | 10.4147439183 |
| H30 | -1.4841818478 | -1.9106017987 | 9.7856270111 |

| | | | |
|---|---|---|---|
| C31 | -0.7190718284 | -0.4445330087 | 7.5114972597 |
| H32 | -1.6461352450 | -1.0210167377 | 7.4799279472 |
| P33 | 1.6019407964 | 0.9989490366 | 7.5907653720 |
| C34 | 3.1273347211 | 1.9484058963 | 7.6432763701 |
| H35 | 3.9680107835 | 1.2767292728 | 7.8362788912 |
| H36 | 3.2764987889 | 2.4524367126 | 6.6846133291 |
| H37 | 3.0658038455 | 2.6936100021 | 8.4409694719 |

**P-trip-He$_8$-ring complex**

E(BP86/6-31G*) = -1096.3628

| | | | |
|---|---|---|---|
| He1 | 3.7736000000# | 3.4440000000# | 5.4276000000# |
| He2 | 3.7668000000# | 1.0683000000# | 9.8272000000# |
| He3 | 5.2223000000# | 0.4646000000# | 6.6623000000# |
| He4 | 2.3180000000# | 4.0477000000# | 8.5926000000# |
| He5 | 4.7994000000# | 1.8292000000# | 5.3895000000# |
| He6 | 2.7423000000# | 2.6840000000# | 9.8658000000# |
| He7 | 4.7946000000# | 0.1494000000# | 8.5004000000# |
| He8 | 2.7457000000# | 4.3629000000# | 6.7544000000# |
| X9 | 3.7702000000# | 2.2561000000# | 7.6274000000# |
| C10 | -1.7389000000 | 1.4132000000 | 5.0296000000 |
| C11 | -1.7874000000 | 2.7417000000 | 4.5763000000 |
| C12 | -0.7148000000 | 3.6034000000 | 4.8370000000 |
| C13 | 0.4029000000 | 3.1449000000 | 5.5572000000 |
| C14 | 0.4577000000 | 1.8224000000 | 6.0246000000 |
| C15 | 1.9737000000 | -0.4353000000 | 5.8746000000 |
| C16 | 3.1414000000 | -0.9295000000 | 5.2710000000 |
| C17 | 3.0942000000 | -2.0650000000 | 4.4427000000 |
| C18 | 1.8774000000 | -2.7168000000 | 4.2071000000 |
| C19 | 0.7000000000 | -2.2225000000 | 4.7915000000 |
| C20 | 0.7457000000 | -1.0886000000 | 5.6132000000 |
| C21 | -0.6249000000 | 0.9548000000 | 5.7452000000 |
| H22 | -2.5704000000 | 0.7277000000 | 4.8219000000 |
| H23 | -2.6602000000 | 3.0973000000 | 4.0165000000 |
| H24 | -0.7403000000 | 4.6395000000 | 4.4798000000 |
| H25 | 1.2291000000 | 3.8303000000 | 5.7407000000 |
| H26 | 4.0970000000 | -0.4335000000 | 5.4311000000 |
| H27 | 4.0168000000 | -2.4358000000 | 3.9812000000 |
| H28 | 1.8391000000 | -3.6037000000 | 3.5641000000 |
| H29 | -0.2613000000 | -2.7169000000 | 4.6023000000 |
| C30 | -1.0293000000 | -1.0480000000 | 10.0037000000 |
| C31 | 0.0602000000 | -0.3345000000 | 10.5184000000 |
| C32 | 0.9559000000 | 0.3145000000 | 9.6503000000 |
| C33 | 0.7733000000 | 0.2565000000 | 8.2589000000 |
| C34 | -0.3343000000 | -0.4614000000 | 7.7493000000 |
| C35 | -1.2262000000 | -1.1090000000 | 8.6149000000 |
| H36 | -1.7281000000 | -1.5554000000 | 10.6788000000 |
| H37 | 0.2204000000 | -0.2775000000 | 11.6013000000 |
| H38 | 1.7926000000 | 0.8657000000 | 10.0751000000 |
| H39 | -2.0790000000 | -1.6617000000 | 8.2005000000 |
| P40 | 1.9136000000# | 1.0923000000# | 6.9973000000# |
| C41 | -0.5076000000 | -0.4848000000 | 6.2368000000 |
| H42 | -1.4023000000 | -1.0669000000 | 5.9551000000 |

**Cl-phosphatriptycene**

E(M06-2X/6-31+G*)(benzene)= -1532.4742
E(M06-2X/6-311+G**) = -1532.6847
E(BP86/6-31G*) = -1532.8495
H(M06-2X/6-31+G*)(benzene) = -1532.4210

| | | | |
|---|---|---|---|
| P1 | 3.1890524228 | 3.4351625269 | 4.3337671086 |
| C2 | 1.9908776313 | 4.7787549172 | 4.7732859683 |
| C3 | 2.3393388853 | 5.8737875313 | 5.5583980276 |
| C4 | 1.3862323771 | 6.8553738653 | 5.8430846609 |
| H5 | 1.6554776676 | 7.7110291841 | 6.4554803595 |
| C6 | 0.0931571888 | 6.7348920221 | 5.3422574472 |
| H7 | -0.6476959998 | 7.4978673083 | 5.5637213813 |
| C8 | -0.2597743447 | 5.6352455994 | 4.5549911394 |
| H9 | -1.2712245113 | 5.5435405864 | 4.1653728586 |
| C10 | 0.6875587670 | 4.6588128688 | 4.2704770433 |
| C11 | 0.3985245817 | 3.4263495329 | 3.4253261503 |
| H12 | -0.6420286847 | 3.4211071726 | 3.0878191178 |
| C13 | 1.3523792675 | 3.4242684791 | 2.2393942495 |
| C14 | 0.9319965616 | 3.4224651604 | 0.9146062890 |
| H15 | -0.1300609339 | 3.4242369466 | 0.6795066822 |
| C16 | 1.8790864223 | 3.4187906084 | -0.1130964660 |
| H17 | 1.5499550135 | 3.4177986389 | -1.1483470023 |
| C18 | 3.2388805291 | 3.4159767802 | 0.1838783498 |
| H19 | 3.9713739943 | 3.4123334543 | -0.6181048457 |
| C20 | 3.6628802262 | 3.4172650980 | 1.5153699777 |
| C21 | 2.7217240985 | 3.4216219947 | 2.5404517915 |
| Cl22 | 3.9175620293 | 0.7528219861 | 6.2014889075 |
| C23 | 1.9987313743 | 2.0721699516 | 4.7710012091 |
| C24 | 2.3108095069 | 0.9615047571 | 5.5481129150 |
| C25 | 1.3580706216 | -0.0187878114 | 5.8305876028 |
| H26 | 1.6330629505 | -0.8737482151 | 6.4394901362 |
| C27 | 0.0712498642 | 0.1189233745 | 5.3253734110 |
| H28 | -0.6729597993 | -0.6413902003 | 5.5432010628 |
| C29 | -0.2674109234 | 1.2251578184 | 4.5436023407 |
| H30 | -1.2751732665 | 1.3302949727 | 4.1497687861 |
| C31 | 0.6911546615 | 2.1928341596 | 4.2699849195 |
| H32 | 3.3504874266 | 5.9628156469 | 5.9476854911 |
| H33 | 4.7238136065 | 3.4145172547 | 1.7526339084 |

**Cl-phosphatriptycene+$H^+$**

E(M06-2X /6-31+G*)(benzene) = -1532.8550
E(M06-2X/6-311+G**) = -1533.0332
H(M06-2X/6-31+G*)(benzene) = -1532.7931

| | | | |
|---|---|---|---|
| P1 | 2.9815187663 | 3.4441690820 | 4.3252351195 |
| C2 | 1.9678957733 | 4.8327235669 | 4.8357917770 |
| C3 | 2.3217930778 | 5.9181020206 | 5.6292957554 |
| C4 | 1.3517854502 | 6.8857867160 | 5.8919485242 |
| H5 | 1.6009158397 | 7.7430633820 | 6.5081523027 |
| C6 | 0.0688872110 | 6.7514979045 | 5.3662382304 |
| H7 | -0.6784179421 | 7.5098354745 | 5.5767167529 |
| C8 | -0.2739376805 | 5.6537076855 | 4.5711428107 |
| H9 | -1.2790239574 | 5.5627839325 | 4.1692456151 |
| C10 | 0.6772809607 | 4.6801209536 | 4.2978715186 |
| C11 | 0.4111546827 | 3.4359271961 | 3.4421540717 |
| H12 | -0.6213266244 | 3.4349396850 | 3.0860319620 |
| C13 | 1.3830548033 | 3.4347274135 | 2.2560193243 |
| C14 | 0.9864132775 | 3.4331464244 | 0.9254282894 |

| | | | |
|---|---|---|---|
| H15 | -0.0696468892 | 3.4326324212 | 0.6710159155 |
| C16 | 1.9532698009 | 3.4325663450 | -0.0845420611 |
| H17 | 1.6377888065 | 3.4317791731 | -1.1229838264 |
| C18 | 3.3122405590 | 3.4328058370 | 0.2211487148 |
| H19 | 4.0495672559 | 3.4317639376 | -0.5745243099 |
| C20 | 3.7314223527 | 3.4341155118 | 1.5517646999 |
| C21 | 2.7594131760 | 3.4351916175 | 2.5458700697 |
| Cl22 | 3.9193952463 | 0.8099383353 | 6.2561487362 |
| C23 | 1.9709892182 | 2.0474710080 | 4.8280437038 |
| C24 | 2.3151822889 | 0.9549956780 | 5.6139903030 |
| C25 | 1.3606863099 | -0.0234897013 | 5.8822121334 |
| H26 | 1.6258936211 | -0.8777990385 | 6.4956493134 |
| C27 | 0.0793505623 | 0.1137861549 | 5.3564273587 |
| H28 | -0.6613059609 | -0.6506959136 | 5.5679042687 |
| C29 | -0.2705199543 | 1.2118618422 | 4.5649094035 |
| H30 | -1.2760671142 | 1.2991144904 | 4.1647372350 |
| C31 | 0.6772283266 | 2.1891892712 | 4.2950989061 |
| H32 | 3.3233174916 | 6.0166509278 | 6.0374512602 |
| H33 | 4.7895214557 | 3.4331728934 | 1.7961966594 |
| H34 | 4.3010707503 | 3.4452573490 | 4.7807506319 |

**Cl-phosphatriptycene+Me$^+$**

E(M06-2X /6-31+G*)(benzene) = -1572.1729
E(M06-2X/6-311+G**) = -1572.3617
H(M06-2X/6-311+G**)(benzene) = -1572.0898

| | | | |
|---|---|---|---|
| P1 | -0.0533248927 | -0.0063800442 | -0.0001871044 |
| C2 | -0.8631937654 | -0.8060995844 | 1.3906936564 |
| C3 | -0.2605906267 | -1.4254991344 | 2.4800224387 |
| C4 | -1.0792948138 | -2.0004374518 | 3.4528823852 |
| C5 | -2.4648202627 | -1.9460671036 | 3.3209390263 |
| C6 | -3.0595600147 | -1.3199962161 | 2.2214104809 |
| C7 | -2.2587996534 | -0.7441172114 | 1.2444930747 |
| C8 | -2.7957304117 | -0.0336451924 | -0.0001667796 |
| C9 | -2.2587841833 | -0.7434903743 | -1.2456007076 |
| C10 | -3.0590484267 | -1.3189457993 | -2.2232143004 |
| C11 | -2.4643257344 | -1.9449526805 | -3.3230093778 |
| C12 | -1.0787074755 | -1.9992634103 | -3.4544428758 |
| C13 | -0.2603026950 | -1.4247348085 | -2.4809981640 |
| C14 | -0.8630986053 | -0.8059440564 | -1.3912558596 |
| Cl15 | 1.3687057447 | 3.1444761685 | 0.0023760137 |
| C16 | -0.8829818541 | 1.6008483319 | 0.0002501577 |
| C17 | -0.3489971376 | 2.8850753792 | 0.0006433707 |
| C18 | -1.1960701604 | 3.9916235051 | 0.0001292620 |
| C19 | -2.5728324130 | 3.7984132179 | -0.0004581019 |
| C20 | -3.1193116857 | 2.5130919504 | -0.0008540777 |
| C21 | -2.2791971560 | 1.4087962373 | -0.0001789442 |
| C22 | 1.7418297990 | -0.1193999539 | -0.0022104891 |
| H23 | 2.0055587242 | -1.1815323559 | -0.0066745308 |
| H24 | 2.1457988378 | 0.3698021124 | -0.8910754687 |
| H25 | 2.1483730037 | 0.3629236221 | 0.8892099711 |
| H26 | 0.8206388609 | -1.4658436840 | 2.5802110275 |
| H27 | -0.6331360461 | -2.4895543059 | 4.3122348972 |
| H28 | -3.0937376452 | -2.3962484168 | 4.0823018553 |
| H29 | -4.1416528507 | -1.2854071233 | 2.1315228777 |
| H30 | -3.8877469296 | -0.0385029874 | 0.0000677614 |
| H31 | -4.1412014725 | -1.2843770627 | -2.1337017590 |
| H32 | -3.0931477947 | -2.3948844072 | -4.0845956934 |
| H33 | -0.6321560781 | -2.4876822414 | -4.3140353347 |

| | | | |
|---|---|---|---|
| H34 | 0.8209547517 | -1.4648256675 | -2.5812290903 |
| H35 | -0.7705625404 | 4.9893110451 | 0.0006231003 |
| H36 | -3.2293464941 | 4.6624751984 | -0.0010437811 |
| H37 | -4.1965971715 | 2.3766275997 | -0.0006676651 |

**Cl-phosphatriptycene-$He_8$-ring complex**

E(BP86/6-31G*) = -1555.9751

| | | | |
|---|---|---|---|
| He1 | 3.7736000000# | 3.4440000000# | 5.4276000000# |
| He2 | 3.7667995223# | 1.0683005516# | 9.8271999260# |
| He3 | 5.2223000000# | 0.4646000000# | 6.6623000000# |
| He4 | 2.3180000000# | 4.0477000000# | 8.5926000000# |
| He5 | 4.7994000000# | 1.8292000000# | 5.3895000000# |
| He6 | 2.7423004334# | 2.6839994715# | 9.8658000610# |
| He7 | 4.7946000426# | 0.1494000267# | 8.5004000146# |
| He8 | 2.7457000000# | 4.3629000000# | 6.7544000000# |
| X9 | 3.7702000000# | 2.2561000000# | 7.6274000000# |
| C10 | -1.6531784432 | 2.2692364667 | 5.1258873934 |
| C11 | -1.8126806295 | 3.6245720131 | 5.4484061631 |
| C12 | -0.8748579980 | 4.2378535814 | 6.2868066519 |
| C13 | 0.2352347698 | 3.5179534031 | 6.7625792433 |
| C14 | 0.4417157948 | 2.1732124343 | 6.4067519934 |
| C15 | 2.0788772308 | 0.1345839594 | 5.3442425269 |
| C16 | 3.2940136108 | -0.2841075816 | 4.7734185312 |
| C17 | 3.3257984096 | -0.9931943253 | 3.5601163403 |
| C18 | 2.1378997358 | -1.3083406796 | 2.8913543016 |
| C19 | 0.9137678171 | -0.9404462630 | 3.4668045496 |
| C20 | 0.8869914993 | -0.2427170947 | 4.6825288725 |
| C21 | -0.5507002441 | 1.5524977930 | 5.6126060948 |
| H22 | -2.3981827580 | 1.7545785855 | 4.5060929748 |
| H23 | -2.6736130619 | 4.1854112665 | 5.0676312034 |
| H24 | -0.9997554265 | 5.2857682886 | 6.5829776384 |
| H25 | 0.9215281563 | 4.0261520124 | 7.4290963894 |
| H26 | 4.2375408650 | -0.0822396192 | 5.2650756069 |
| H27 | 4.2925404395 | -1.3003309765 | 3.1448335193 |
| H28 | 2.1593470862 | -1.8539934944 | 1.9411515607 |
| H29 | -0.0320123328 | -1.2104289606 | 2.9803633985 |
| C30 | -1.3217503417 | -2.1939219567 | 8.3389585431 |
| C31 | -0.3196486149 | -1.8528760658 | 9.2479883372 |
| C32 | 0.6499730864 | -0.8918543101 | 8.8991031281 |
| C33 | 0.6610233285 | -0.2442050994 | 7.6489009568 |
| C34 | -0.3785681489 | -0.6162310249 | 6.7526654076 |
| C35 | -1.3494515033 | -1.5689717311 | 7.0847142076 |
| H36 | -2.0767183846 | -2.9404954715 | 8.6081907483 |
| H37 | -0.2708822325 | -2.3186517056 | 10.2364681860 |
| H38 | -2.1295059096 | -1.8194403347 | 6.3561895951 |
| P39 | 1.9136000017# | 1.0922999502# | 6.9972999984# |
| C40 | -0.4178656188 | 0.0620097859 | 5.3851726004 |
| H41 | -1.2720311364 | -0.3191609746 | 4.8001055998 |
| Cl42 | 1.8439453270 | -0.5582609125 | 10.1477385977 |

**F-Phosphatriptycene**

E(M06-2X/6-31+G*)(benzene) = -1172.1182
E(M06-2X/6-311+G**) = -1172.3264
E(BP86/6-31G*) = -1172.4582
H(M06-2X/6-311+G**)(benzene) = -1172.0618

| | | | |
|---|---|---|---|
| P1 | -0.9127034394 | -0.6972960501 | -1.2156021615 |
| C2 | -0.2237372100 | 1.0099486784 | -1.4354040621 |
| C3 | -0.3448294189 | 1.7274861429 | -2.6216125552 |
| C4 | 0.1938469632 | 3.0138137693 | -2.7138475285 |
| C5 | 0.8499988669 | 3.5731358912 | -1.6211956763 |
| C6 | 0.9736099708 | 2.8543899551 | -0.4289065319 |
| C7 | 0.4373462046 | 1.5754799433 | -0.3352936753 |
| C8 | 0.5217607786 | 0.7211488697 | 0.9218277393 |
| C9 | -0.8951216362 | 0.3736653456 | 1.3569353287 |
| C10 | -1.4149794115 | 0.7006672701 | 2.6037729673 |
| C11 | -2.7286970187 | 0.3457701189 | 2.9224273816 |
| C12 | -3.5168221761 | -0.3333559634 | 1.9979739366 |
| C13 | -2.9951674723 | -0.6635397171 | 0.7440976242 |
| C14 | -1.6877058391 | -0.3107447216 | 0.4239530947 |
| F15 | 0.7175732758 | -3.2930210945 | -1.7713159262 |
| C16 | 0.6480802949 | -1.3443572303 | -0.4460589720 |
| C17 | 1.2634664509 | -2.5325466178 | -0.8015117426 |
| C18 | 2.4318770493 | -2.9819272588 | -0.1965357982 |
| C19 | 2.9999280020 | -2.2022784499 | 0.8049690057 |
| C20 | 2.4071376511 | -0.9968278634 | 1.1911145934 |
| C21 | 1.2392116520 | -0.5738726896 | 0.5673325835 |
| H22 | -0.8575149743 | 1.2868536556 | -3.4730531590 |
| H23 | 0.0999594407 | 3.5753521154 | -3.6386393676 |
| H24 | 1.2689028503 | 4.5726835556 | -1.6928807350 |
| H25 | 1.4867739062 | 3.2938789854 | 0.4233167576 |
| H26 | 1.0534572479 | 1.2516173155 | 1.7174824385 |
| H27 | -0.8010118607 | 1.2316133360 | 3.3276158267 |
| H28 | -3.1341355118 | 0.6025801077 | 3.8967861880 |
| H29 | -4.5370408214 | -0.6077021187 | 2.2493382074 |
| H30 | -3.6075904283 | -1.1943587484 | 0.0194805146 |
| H31 | 2.8701253590 | -3.9215403466 | -0.5157776691 |
| H32 | 3.9120932488 | -2.5365166796 | 1.2897061634 |
| H33 | 2.8568603262 | -0.3930789060 | 1.9746619313 |

**F-phosphatriptycene-H**

E(M06-2X/6-31+G*)(benzene) = -1172.4988
E(M06-2X/6-311+G**) = -1172.6736
H(M06-2X/6-31+G*)(benzene) = -1172.4336

| | | | |
|---|---|---|---|
| P1 | -1.2127087780 | 1.2220823515 | 0.3946846314 |
| C2 | 0.4270966075 | 1.9384553186 | 0.5240781012 |
| C3 | 0.7803610064 | 3.2560560903 | 0.7924656795 |
| C4 | 2.1371285851 | 3.5772824172 | 0.8434689509 |
| C5 | 3.0978678548 | 2.5925249654 | 0.6279759868 |
| C6 | 2.7285140503 | 1.2718691317 | 0.3564072935 |
| C7 | 1.3839305180 | 0.9312107179 | 0.3012122656 |
| C8 | 0.8711913245 | -0.4841739595 | 0.0095899708 |
| C9 | 0.0089106620 | -0.9484844124 | 1.1898623139 |
| C10 | 0.2751030243 | -2.0824236308 | 1.9455189456 |
| C11 | -0.5707282904 | -2.4224880368 | 3.0054682417 |
| C12 | -1.6807517371 | -1.6415441075 | 3.3181576040 |
| C13 | -1.9660850337 | -0.4979853401 | 2.5716524515 |
| C14 | -1.1164007125 | -0.1710347487 | 1.5207493046 |
| F15 | -3.0364716361 | 1.3378123928 | -2.1817676580 |
| C16 | -1.1270970961 | 0.4066980048 | -1.1954594766 |
| C17 | -1.9792702338 | 0.5194284125 | -2.2789207724 |
| C18 | -1.7492866112 | -0.1974073739 | -3.4441316636 |

| | | | |
|---|---|---|---|
| C19 | -0.6374624010 | -1.0336694325 | -3.4942599331 |
| C20 | 0.2367205503 | -1.1607079062 | -2.4075555330 |
| C21 | -0.0041578409 | -0.4385571176 | -1.2480880046 |
| H22 | -2.2895873262 | 2.0931564261 | 0.5714214051 |
| H23 | 0.0265489631 | 4.0199383759 | 0.9583990800 |
| H24 | 2.4402478770 | 4.5977731643 | 1.0512804679 |
| H25 | 4.1507553724 | 2.8520540173 | 0.6701682508 |
| H26 | 3.4899185160 | 0.5152780996 | 0.1893601038 |
| H27 | 1.7101790678 | -1.1673194524 | -0.1375573316 |
| H28 | 1.1369690758 | -2.7017095516 | 1.7140843019 |
| H29 | -0.3571945839 | -3.3097096672 | 3.5927725614 |
| H30 | -2.3274442607 | -1.9197562460 | 4.1433178889 |
| H31 | -2.8309267704 | 0.1139519229 | 2.8099626760 |
| H32 | -2.4306040050 | -0.0936200940 | -4.2812949908 |
| H33 | -0.4457927620 | -1.6000205406 | -4.3997455454 |
| H34 | 1.0965176099 | -1.8201443436 | -2.4735208317 |

**F-phosphatriptycene-Me**

E(M06-2X/6-31+G*)(benzene) = -1211.8181
E(M06-2X/6-311+G**) = -1212.0038
H(M06-2X/6-31+G*)(benzene) = -1211.7317

| | | | |
|---|---|---|---|
| P1 | 1.3198292569 | 0.1761140805 | 0.1685527734 |
| C2 | 0.5493412807 | 1.8002672952 | 0.1752197941 |
| C3 | 1.1767813515 | 3.0408417068 | 0.1864899185 |
| C4 | 0.3813957743 | 4.1875979173 | 0.1907291452 |
| C5 | -1.0066368782 | 4.0738667784 | 0.1843847946 |
| C6 | -1.6263420734 | 2.8208098055 | 0.1752743625 |
| C7 | -0.8508417949 | 1.6695685503 | 0.1707453800 |
| C8 | -1.4246545214 | 0.2493245260 | 0.1633917374 |
| C9 | -0.9052983902 | -0.4840813481 | -1.0776151609 |
| C10 | -1.7251511873 | -1.0246593099 | -2.0592473375 |
| C11 | -1.1545542922 | -1.6745990983 | -3.1579349884 |
| C12 | 0.2277103307 | -1.7899082709 | -3.2841083807 |
| C13 | 1.0669272499 | -1.2522620417 | -2.3070355923 |
| C14 | 0.4884033891 | -0.6081512234 | -1.2191391245 |
| F15 | 2.3527275057 | -1.3342159693 | 2.7406308459 |
| C16 | 0.4723615885 | -0.6005194067 | 1.5472042851 |
| C17 | 1.0146911504 | -1.2451358506 | 2.6440968113 |
| C18 | 0.2077802831 | -1.7924394931 | 3.6306304440 |
| C19 | -1.1722722563 | -1.6765659084 | 3.4893505070 |
| C20 | -1.7437717406 | -1.0278748724 | 2.3882796125 |
| C21 | -0.9228783027 | -0.4850684666 | 1.4104573521 |
| C22 | 3.1159499526 | 0.1334984056 | 0.1767640875 |
| H23 | 2.2601010614 | 3.1248578810 | 0.1926852966 |
| H24 | 0.8474511520 | 5.1669969261 | 0.1995576729 |
| H25 | -1.6187037520 | 4.9700101424 | 0.1873564039 |
| H26 | -2.7104690245 | 2.7484945257 | 0.1714976922 |
| H27 | -2.5161522241 | 0.2808690263 | 0.1564309192 |
| H28 | -2.8050509494 | -0.9422341841 | -1.9740896003 |
| H29 | -1.7998669993 | -2.0948807741 | -3.9226026729 |
| H30 | 0.6558313994 | -2.2975985628 | -4.1418100619 |
| H31 | 2.1457021389 | -1.3406457940 | -2.4018100174 |
| H32 | 0.6605357595 | -2.2923622349 | 4.4796685964 |
| H33 | -1.8175774089 | -2.0997040785 | 4.2522942843 |
| H34 | -2.8232314021 | -0.9508380363 | 2.3011850127 |
| H35 | 3.4548561723 | -0.9054240585 | 0.1804769159 |
| H36 | 3.4916818711 | 0.6472660767 | -0.7121692075 |
| H37 | 3.4833812749 | 0.6283610336 | 1.0792232740 |

**F-P-trip-$He_8$-ring complex**

E(BP86/6-31G*) = -1195.5935

| | | | |
|---|---|---|---|
| He1 | 3.7736000000# | 3.4440000000# | 5.4276000000# |
| He2 | 3.7667996230# | 1.0682997565# | 9.8271997047# |
| He3 | 5.2223000001# | 0.4646000000# | 6.6623000000# |
| He4 | 2.3180000001# | 4.0477000001# | 8.5926000000# |
| He5 | 4.7994000000# | 1.8292000000# | 5.3895000000# |
| He6 | 2.7423001956# | 2.6840002518# | 9.8658001791# |
| He7 | 4.7946002050# | 0.1494001283# | 8.5004000699# |
| He8 | 2.7457000000# | 4.3629000000# | 6.7544000000# |
| X9 | 3.7702000000# | 2.2561000000# | 7.6274000000# |
| C10 | -1.8469431626 | 1.9354186242 | 5.3793540015 |
| C11 | -2.0126837246 | 3.3197329132 | 5.5411674480 |
| C12 | -1.0090648018 | 4.0607424122 | 6.1769171874 |
| C13 | 0.1669688668 | 3.4305378487 | 6.6217547131 |
| C14 | 0.3645710287 | 2.0521016111 | 6.4323003050 |
| C15 | 1.9796657555 | 0.0094471948 | 5.4324157131 |
| C16 | 3.1621656422 | -0.3404869797 | 4.7584239840 |
| C17 | 3.1266666750 | -1.1518227231 | 3.6106988270 |
| C18 | 1.9059436044 | -1.6310008267 | 3.1209587308 |
| C19 | 0.7190544827 | -1.3137106525 | 3.7987448863 |
| C20 | 0.7567809479 | -0.5101763851 | 4.9464939220 |
| C21 | -0.6770964590 | 1.3077937257 | 5.8295481793 |
| H22 | -2.6365897358 | 1.3341156735 | 4.9112906064 |
| H23 | -2.9273230302 | 3.8092243139 | 5.1878776341 |
| H24 | -1.1346480516 | 5.1379843986 | 6.3360738409 |
| H25 | 0.9132586331 | 4.0316227642 | 7.1326722873 |
| H26 | 4.1276586278 | -0.0000724724 | 5.1211869806 |
| H27 | 4.0639862805 | -1.4083556442 | 3.1036321963 |
| H28 | 1.8748788236 | -2.2593152571 | 2.2234216418 |
| H29 | -0.2435678248 | -1.7005785356 | 3.4412390517 |
| C30 | -0.9408922344 | -2.1223399502 | 9.0428888514 |
| C31 | 0.1321221173 | -1.6187867402 | 9.7837742253 |
| C32 | 0.9821322839 | -0.6697578699 | 9.1955485400 |
| C33 | 0.8150123047 | -0.1958135569 | 7.8879391352 |
| C34 | -0.2875503812 | -0.7217165475 | 7.1675750272 |
| C35 | -1.1524964300 | -1.6699763041 | 7.7300736326 |
| H36 | -1.6139443590 | -2.8629367123 | 9.4883736665 |
| H37 | 0.3322731705 | -1.9386265232 | 10.8108537837 |
| F38 | 1.9997862515 | -0.2116501945 | 9.9633009464 |
| H39 | -1.9937813837 | -2.0528838359 | 7.1406741723 |
| P40 | 1.9135999763# | 1.0922998632# | 6.9973000462# |
| C41 | -0.4952248798 | -0.1989548148 | 5.7478466570 |
| H42 | -1.3796297954 | -0.6739765863 | 5.2893579349 |

**$CF_3$-phosphatriptycene**

E(M06-2X /6-31+G*)(benzene) = -1409.8603
E(M06-2X/6-311+G**) = -1410.1355
E(BP86/6-31G*) = -1410.2604
H(M06-2X/6-31+G*)(benzene) = -1409.8552

| | | | |
|---|---|---|---|
| P1 | 1.3899965702 | -2.8784751405 | -0.0009978385 |
| C2 | 2.4627345964 | -3.5362987092 | -1.3592318920 |

| | | | |
|---|---|---|---|
| C3 | 1.9495846332 | -4.2123838974 | -2.4621334946 |
| C4 | 2.8172045000 | -4.6913494691 | -3.4469356896 |
| C5 | 4.1888865807 | -4.4910593623 | -3.3230061162 |
| C6 | 4.7063289152 | -3.8107770397 | -2.2173584495 |
| C7 | 3.8442504842 | -3.3342064021 | -1.2369416893 |
| C8 | 4.3098248063 | -2.5760549677 | -0.0025568050 |
| C9 | 3.8451387167 | -3.3329700937 | 1.2333830197 |
| C10 | 4.7077350529 | -3.8103106788 | 2.2131326209 |
| C11 | 4.1907066249 | -4.4901541993 | 3.3193902321 |
| C12 | 2.8190432085 | -4.6896267815 | 3.4446225092 |
| C13 | 1.9508574664 | -4.2103133419 | 2.4604678305 |
| C14 | 2.4635487952 | -3.5346743945 | 1.3569826156 |
| C15 | 0.0510773959 | 0.0531260048 | 0.0011937638 |
| C16 | 2.2265142435 | -1.2056178945 | -0.0016214375 |
| C17 | 1.5580309436 | 0.0204751956 | 0.0005844853 |
| C18 | 2.2691554236 | 1.2211956806 | 0.0029713153 |
| C19 | 3.6595646997 | 1.1980323945 | 0.0026867278 |
| C20 | 4.3399599732 | -0.0185912921 | 0.0003162461 |
| C21 | 3.6286196933 | -1.2144220206 | -0.0020487847 |
| F22 | -0.4291051394 | 1.3086770259 | -0.0011749018 |
| F23 | -0.4644115557 | -0.5641561483 | -1.0780281445 |
| F24 | -0.4632475305 | -0.5596484085 | 1.0835790020 |
| H25 | 0.8772808897 | -4.3650474055 | -2.5543652954 |
| H26 | 2.4197182977 | -5.2189323546 | -4.3086991650 |
| H27 | 4.8625072620 | -4.8637490871 | -4.0889723968 |
| H28 | 5.7783966040 | -3.6544355119 | -2.1235640832 |
| H29 | 5.3979526074 | -2.4621604433 | -0.0029459783 |
| H30 | 5.7798921941 | -3.6551064273 | 2.1183461985 |
| H31 | 4.8648139148 | -4.8635483026 | 4.0846174336 |
| H32 | 2.4220082054 | -5.2167973997 | 4.3068635493 |
| H33 | 0.8785663420 | -4.3626695972 | 2.5535268031 |
| H34 | 1.7351932638 | 2.1647350224 | 0.0048688498 |
| H35 | 4.2139611943 | 2.1311426458 | 0.0049916648 |
| H36 | 5.4270512258 | -0.0361757386 | -0.0003004548 |

**$CF_3$-phosphatriptycene-$H^+$**

E(M06-2X/6-31+G*)(benzene) = -1410.2397
E(M06-2X/6-311+G**) = -1410.4825
H(M06-2X/6-31+G*)(benzene) = -1410.2252

| | | | |
|---|---|---|---|
| P1 | 1.6653965127 | -2.8047015958 | -0.0018608563 |
| C2 | 2.5253578467 | -3.5250020049 | -1.4004328250 |
| C3 | 1.9852624784 | -4.1911230311 | -2.4948999425 |
| C4 | 2.8600312645 | -4.6729905853 | -3.4689104730 |
| C5 | 4.2330599274 | -4.4815151806 | -3.3331617479 |
| C6 | 4.7621274303 | -3.8071149533 | -2.2286540536 |
| C7 | 3.9082298055 | -3.3207231638 | -1.2480998345 |
| C8 | 4.3760736678 | -2.5614136898 | -0.0014205746 |
| C9 | 3.9070641774 | -3.3177560193 | 1.2473027057 |
| C10 | 4.7598604861 | -3.8061581655 | 2.2278734074 |
| C11 | 4.2293993592 | -4.4812539504 | 3.3314510919 |
| C12 | 2.8562316177 | -4.6724619545 | 3.4659136555 |
| C13 | 1.9825730173 | -4.1893361333 | 2.4915793961 |
| C14 | 2.5239641041 | -3.5212100169 | 1.3989187043 |
| C15 | 0.1327777004 | 0.0571294220 | 0.0017288563 |
| C16 | 2.3228029099 | -1.1242219403 | -0.0029523594 |
| C17 | 1.6365232439 | 0.0869545820 | -0.0013333215 |
| C18 | 2.3519308156 | 1.2784701456 | -0.0007753795 |
| C19 | 3.7465479104 | 1.2385260507 | -0.0017627166 |

| | | | |
|---|---|---|---|
| C20 | 4.4315086264 | 0.0237516618 | -0.0025881588 |
| C21 | 3.7227196402 | -1.1749975891 | -0.0030211150 |
| F22 | -0.4139507545 | 1.2640438890 | 0.0001692142 |
| F23 | -0.3235847373 | -0.6162821728 | 1.0811058414 |
| F24 | -0.3280110850 | -0.6211822194 | -1.0728367819 |
| H25 | 0.2752064496 | -2.9307970215 | -0.0012069791 |
| H26 | 0.9135845376 | -4.3345488444 | -2.5957838648 |
| H27 | 2.4662312433 | -5.1966957319 | -4.3333572672 |
| H28 | 4.9046706925 | -4.8600488713 | -4.0969823357 |
| H29 | 5.8351540331 | -3.6641166771 | -2.1380948631 |
| H30 | 5.4640890332 | -2.4669501111 | -0.0010584495 |
| H31 | 5.8331236672 | -3.6647944193 | 2.1377283464 |
| H32 | 4.9002343747 | -4.8615453894 | 4.0951084171 |
| H33 | 2.4615085143 | -5.1972175283 | 4.3293173833 |
| H34 | 0.9107645378 | -4.3328315766 | 2.5911832484 |
| H35 | 1.8241264276 | 2.2261529041 | 0.0005181212 |
| H36 | 4.3053812871 | 2.1683833106 | -0.0012594436 |
| H37 | 5.5175900597 | 0.0112423943 | -0.0032351737 |

**$CF_3$-phosphatriptycene-$Me^+$**

E(M06-2X/6-31+G*)(benzene) = -1449.5568
E(M06-2X/6-311+G**) = -1449.8108
H(M06-2X/6-311+G**)(benzene) = -1449.5216

| | | | |
|---|---|---|---|
| P1 | 4.0495517239 | -2.3075907376 | -0.2255118296 |
| C2 | 3.2216983368 | -3.1237306529 | -1.5962940605 |
| C3 | 3.8178415049 | -3.7577207156 | -2.6811455128 |
| C4 | 2.9930337811 | -4.3208359092 | -3.6557306614 |
| C5 | 1.6082840631 | -4.2408859667 | -3.5301686707 |
| C6 | 1.0202294756 | -3.6003498697 | -2.4352291821 |
| C7 | 1.8276185043 | -3.0347094369 | -1.4581235028 |
| C8 | 1.3021404777 | -2.3124653709 | -0.2163145312 |
| C9 | 1.8279696315 | -0.8759433970 | -0.2130618280 |
| C10 | 1.0208972609 | 0.2532545264 | -0.2143293509 |
| C11 | 1.6092856779 | 1.5216592198 | -0.2082535228 |
| C12 | 2.9941340086 | 1.6702236346 | -0.1996413910 |
| C13 | 3.8184978326 | 0.5442328639 | -0.1976075462 |
| C14 | 3.2219884015 | -0.7120874410 | -0.2044714271 |
| C15 | 5.2603758919 | -3.8689146992 | 2.4791094077 |
| C16 | 3.2357219972 | -3.1236157814 | 1.1876924269 |
| C17 | 3.7697690734 | -3.7697307241 | 2.3048630799 |
| C18 | 2.9219073374 | -4.3223710217 | 3.2596122650 |
| C19 | 1.5419204498 | -4.2288127028 | 3.0969903651 |
| C20 | 1.0037474439 | -3.5853205513 | 1.9858614742 |
| C21 | 1.8425271629 | -3.0287583723 | 1.0237890309 |
| F22 | 5.6113997269 | -4.5147145572 | 3.5841290165 |
| F23 | 5.8220371906 | -2.6410045374 | 2.5211501593 |
| F24 | 5.8255640961 | -4.5057814960 | 1.4302726966 |
| C25 | 5.8347332365 | -2.1961865025 | -0.4183448748 |
| H26 | 4.8985054492 | -3.8192995882 | -2.7756060736 |
| H27 | 3.4341592656 | -4.8216724001 | -4.5109441542 |
| H28 | 0.9743281442 | -4.6818231332 | -4.2928247300 |
| H29 | -0.0614729195 | -3.5454136875 | -2.3506439711 |
| H30 | 0.2101684501 | -2.3193203263 | -0.2045713856 |
| H31 | -0.0608141748 | 0.1524064925 | -0.2209285166 |
| H32 | 0.9753170484 | 2.4026291870 | -0.2101844756 |
| H33 | 3.4355526094 | 2.6611221809 | -0.1937027273 |
| H34 | 4.8991511402 | 0.6566305935 | -0.1898720131 |
| H35 | 3.3427857654 | -4.8232248959 | 4.1244883746 |

| | | | |
|---|---|---|---|
| H36 | 0.8835468384 | -4.6610630653 | 3.8430521871 |
| H37 | -0.0735055671 | -3.5160350905 | 1.8649959184 |
| H38 | 6.2764978122 | -3.1915737078 | -0.4852121322 |
| H39 | 6.0103876721 | -1.6470544691 | -1.3491234272 |
| H40 | 6.2790486219 | -1.6580313509 | 0.4203317938 |

**$CF_3$-phosphatriptycene-$He_8$-ring complex**

E(BP86/6-31G*) = -1433.3820

| | | | |
|---|---|---|---|
| He1 | 3.7735999708# | 3.4439999911# | 5.4275999836# |
| He2 | 3.7667984401# | 1.0683020985# | 9.8271999902# |
| He3 | 5.2222999705# | 0.4646000247# | 6.6623000132# |
| He4 | 2.3179999739# | 4.0477000001# | 8.5925999582# |
| He5 | 4.7994000144# | 1.8292000090# | 5.3895000049# |
| He6 | 2.7423014964# | 2.6839978257# | 9.8657998878# |
| He7 | 4.7946001271# | 0.1494000515# | 8.5004000387# |
| He8 | 2.7457000420# | 4.3628999919# | 6.7544000471# |
| X9 | 3.7702000000# | 2.2561000000# | 7.6274000000# |
| C10 | -1.5590698026 | 2.4029158225 | 5.0259236842 |
| C11 | -1.7209319397 | 3.7427252436 | 5.4054747592 |
| C12 | -0.8208365201 | 4.2997596741 | 6.3209828555 |
| C13 | 0.2582128325 | 3.5437457271 | 6.8116799148 |
| C14 | 0.4750796607 | 2.2173809237 | 6.3962542503 |
| C15 | 2.1195513136 | 0.1693809411 | 5.3256187092 |
| C16 | 3.3415313336 | -0.2923477151 | 4.8042945482 |
| C17 | 3.4064713528 | -0.9650902517 | 3.5719195546 |
| C18 | 2.2437304593 | -1.2019034973 | 2.8307700528 |
| C19 | 1.0086454636 | -0.8014396946 | 3.3586898745 |
| C20 | 0.9497196689 | -0.1434920305 | 4.5952506534 |
| C21 | -0.4886859733 | 1.6503368290 | 5.5302708511 |
| H22 | -2.2793025916 | 1.9261113689 | 4.3492748101 |
| H23 | -2.5563947318 | 4.3323974201 | 5.0117937456 |
| H24 | -0.9512057619 | 5.3315140376 | 6.6671597520 |
| H25 | 0.9093962005 | 4.0101309128 | 7.5395896980 |
| H26 | 4.2642468188 | -0.1596856929 | 5.3533061397 |
| H27 | 4.3792903557 | -1.3060413625 | 3.1994244629 |
| H28 | 2.2910958430 | -1.7167386394 | 1.8644489952 |
| H29 | 0.0775337771 | -1.0184620000 | 2.8202338032 |
| C30 | -1.4568307834 | -2.1717940672 | 8.0766778122 |
| C31 | -0.4842570657 | -1.8921505323 | 9.0379410163 |
| C32 | 0.5302925374 | -0.9464078941 | 8.7855076561 |
| C33 | 0.5985500574 | -0.2512367620 | 7.5532877666 |
| C34 | -0.4034462595 | -0.5559699277 | 6.5969022769 |
| C35 | -1.4111771334 | -1.4969885232 | 6.8520161076 |
| H36 | -2.2419156115 | -2.9075745413 | 8.2808962592 |
| H37 | -0.4992350810 | -2.4057806591 | 10.0021225050 |
| H38 | -2.1638448425 | -1.6981037352 | 6.0797624525 |
| P39 | 1.9135999648# | 1.0923000074# | 6.9973000763# |
| C40 | -0.3748650318 | 0.1684409602 | 5.2532349073 |
| H41 | -1.2121469195 | -0.1738096232 | 4.6214006705 |
| F42 | 1.5237301820 | 0.5806777242 | 10.3054551549 |
| C43 | 1.5316118225 | -0.7186430659 | 9.8902376572 |
| F44 | 1.2817425214 | -1.4812284487 | 10.9962066307 |
| F45 | 2.7958924656 | -1.0287995960 | 9.4833310876 |

**1,4-di-Me-phosphatriptycene**

E(M06-2X/6-31+G*)(benzene)= -1151.4954
E(M06-2X/6-311+G**) = -1151.6948
E(BP86/6-31G*) = -1151.8484
H(M06-2X/6-31+G*)(benzene) = -1151.3639

| | | | |
|---|---|---|---|
| P1 | 1.4026056661 | -2.8301039745 | -0.0005240499 |
| C2 | 2.4497393734 | -3.5256219253 | -1.3582977378 |
| C3 | 1.9304292505 | -4.2023625997 | -2.4577561008 |
| C4 | 2.7930668237 | -4.6919071422 | -3.4422071420 |
| C5 | 4.1666100307 | -4.5018464069 | -3.3202349085 |
| C6 | 4.6897887607 | -3.8235952159 | -2.2159828571 |
| C7 | 3.8327933632 | -3.3359637143 | -1.2358187236 |
| C8 | 4.3114035249 | -2.5861019594 | -0.0014560975 |
| C9 | 3.8335702523 | -3.3350931486 | 1.2339039424 |
| C10 | 4.6910054773 | -3.8239833101 | 2.2130124864 |
| C11 | 4.1682459543 | -4.5026740178 | 3.3172567776 |
| C12 | 2.7947692306 | -4.6924126313 | 3.4400644606 |
| C13 | 1.9316404932 | -4.2021007947 | 2.4563965641 |
| C14 | 2.4505148000 | -3.5248304479 | 1.3570272702 |
| C15 | 0.0349526700 | 0.0551158879 | 0.0017152191 |
| C16 | 2.2623380757 | -1.1799640463 | -0.0010966945 |
| C17 | 1.5448895577 | 0.0191079409 | 0.0006464580 |
| C18 | 2.2787452438 | 1.2116875394 | 0.0017570947 |
| C19 | 3.6653224660 | 1.1964325413 | 0.0015699740 |
| C20 | 4.3950492930 | -0.0008231840 | 0.0002025769 |
| C21 | 3.6708579308 | -1.1971724911 | -0.0013365694 |
| C22 | 5.9040527240 | 0.0983385675 | -0.0002119808 |
| H23 | 0.8568539769 | -4.3489730695 | -2.5478862935 |
| H24 | 2.3909899765 | -5.2205025988 | -4.3014452883 |
| H25 | 4.8367311531 | -4.8821890955 | -4.0857284056 |
| H26 | 5.7635651291 | -3.6771540510 | -2.1227035066 |
| H27 | 5.3999415619 | -2.5305933131 | -0.0019523397 |
| H28 | 5.7648406250 | -3.6784884289 | 2.1189121159 |
| H29 | 4.8388733611 | -4.8841360277 | 4.0817605677 |
| H30 | 2.3931086436 | -5.2213411477 | 4.2992898640 |
| H31 | 0.8581014618 | -4.3488388819 | 2.5468608677 |
| H32 | -0.3242850321 | 1.0878071312 | 0.0006913465 |
| H33 | -0.3791544944 | -0.4486877811 | -0.8777778437 |
| H34 | -0.3776900094 | -0.4463265248 | 0.8832842174 |
| H35 | 1.7511575812 | 2.1624953754 | 0.0033599703 |
| H36 | 4.2086727677 | 2.1394604578 | 0.0028038646 |
| H37 | 6.4065227709 | -0.8690171855 | 0.0050851636 |
| H38 | 6.2498012342 | 0.6429199334 | -0.8854163458 |
| H39 | 6.2495872184 | 0.6523391840 | 0.8791738422 |

**1,4-di-Me-phosphatriptycene-$H^+$**

E(M06-2X/6-31+G*)(benzene) = -1151.8823
E(M06-2X/6-311+G**) = -1152.0502
H(M06-2X/6-31+G*)(benzene) = -1151.7422

| | | | |
|---|---|---|---|
| P1 | 1.6826757788 | -2.7721094745 | 0.0001412194 |
| C2 | 2.5200122833 | -3.5200952779 | -1.3981122824 |
| C3 | 1.9780554425 | -4.1912646887 | -2.4883811406 |
| C4 | 2.8506666014 | -4.6797217167 | -3.4611009243 |
| C5 | 4.2244593033 | -4.4907275774 | -3.3271189744 |
| C6 | 4.7549984884 | -3.8145333060 | -2.2249091444 |

| | | | |
|---|---|---|---|
| C7 | 3.9028086679 | -3.3205669518 | -1.2458237770 |
| C8 | 4.3758112757 | -2.5652071676 | 0.0007384009 |
| C9 | 3.9023015078 | -3.3191157856 | 1.2480083720 |
| C10 | 4.7539426531 | -3.8167618883 | 2.2256871362 |
| C11 | 4.2224923580 | -4.4951638292 | 3.3261660800 |
| C12 | 2.8485501955 | -4.6835945808 | 3.4593903329 |
| C13 | 1.9765309284 | -4.1922374767 | 2.4876022786 |
| C14 | 2.5192890960 | -3.5177206321 | 1.3997673880 |
| C15 | 0.0967676571 | 0.1016668909 | -0.0013430425 |
| C16 | 2.3412082903 | -1.1012477902 | -0.0013249990 |
| C17 | 1.6046875356 | 0.0815112686 | -0.0018098174 |
| C18 | 2.3531256624 | 1.2637295040 | -0.0020507217 |
| C19 | 3.7400166485 | 1.2323695324 | -0.0015303350 |
| C20 | 4.4760459344 | 0.0352557500 | -0.0008352292 |
| C21 | 3.7522221963 | -1.1580944562 | -0.0005856206 |
| C22 | 5.9822868611 | 0.1306527667 | -0.0012059207 |
| H23 | 0.2906608061 | -2.8908650085 | 0.0006150130 |
| H24 | 0.9061803424 | -4.3355274505 | -2.5872206983 |
| H25 | 2.4554287261 | -5.2075166556 | -4.3224597876 |
| H26 | 4.8946887262 | -4.8743155637 | -4.0897071619 |
| H27 | 5.8286809322 | -3.6757887765 | -2.1338526793 |
| H28 | 5.4629934108 | -2.5123823658 | 0.0008438539 |
| H29 | 5.8278502681 | -3.6798814997 | 2.1345060566 |
| H30 | 4.8923404265 | -4.8819961096 | 4.0874594728 |
| H31 | 2.4527712536 | -5.2135454783 | 4.3191797117 |
| H32 | 0.9045690186 | -4.3365028326 | 2.5855778280 |
| H33 | -0.2737680599 | 1.1286684798 | -0.0056523051 |
| H34 | -0.3151606448 | -0.3947618545 | -0.8873609311 |
| H35 | -0.3140241752 | -0.3870145535 | 0.8895324569 |
| H36 | 1.8367455694 | 2.2192694986 | -0.0020934306 |
| H37 | 4.2861258719 | 2.1726604720 | -0.0017329644 |
| H38 | 6.4828848176 | -0.8371433694 | 0.0066589442 |
| H39 | 6.3260456904 | 0.6728603139 | -0.8875178546 |
| H40 | 6.3257153183 | 0.6867483552 | 0.8765238685 |

**1,4-di-Me-phosphatriptycene-Me$^+$**

E(M06-2X/6-31+G*)(benzene) = -1191.1987
E(M06-2X/6-311+G**) = -1191.3768
H(M06-2X/6-31+G*)(benzene) = -1191.0373

| | | | |
|---|---|---|---|
| P1 | 4.5746604445 | -2.0534954286 | -0.3189915476 |
| C2 | 3.7767601393 | -2.8541117033 | -1.7148395982 |
| C3 | 4.3758419770 | -3.4841435227 | -2.8000494611 |
| C4 | 3.5538784088 | -4.0441603935 | -3.7789098500 |
| C5 | 2.1686503782 | -3.9641615512 | -3.6565966092 |
| C6 | 1.5784271651 | -3.3256015880 | -2.5621044911 |
| C7 | 2.3825367370 | -2.7632514898 | -1.5796571020 |
| C8 | 1.8494245065 | -2.0386335171 | -0.3420765531 |
| C9 | 2.3840483124 | -0.6049806738 | -0.3348951822 |
| C10 | 1.5811985095 | 0.5279380681 | -0.3400551678 |
| C11 | 2.1727328305 | 1.7945472049 | -0.3354054162 |
| C12 | 3.5581587271 | 1.9394404961 | -0.3269302864 |
| C13 | 4.3788833027 | 0.8107219364 | -0.3216520380 |
| C14 | 3.7784446655 | -0.4435642468 | -0.3246109146 |
| C15 | 5.8549327888 | -3.5930263356 | 2.3548678286 |
| C16 | 3.7574928232 | -2.8592295897 | 1.0789112544 |
| C17 | 4.3611875430 | -3.4879127036 | 2.1689461258 |
| C18 | 3.4959803582 | -4.0384014956 | 3.1217323168 |
| C19 | 2.1207530051 | -3.9565963098 | 2.9769719760 |

| | | | |
|---|---|---|---|
| C20 | 1.5125692253 | -3.3241479399 | 1.8806067008 |
| C21 | 2.3535792188 | -2.7655587813 | 0.9162295975 |
| C22 | 0.0030428489 | -3.3026224280 | 1.8355883331 |
| C23 | 6.3707140170 | -1.9835725671 | -0.4416814795 |
| H24 | 5.4568873514 | -3.5448947483 | -2.8926391196 |
| H25 | 3.9967992867 | -4.5416256727 | -4.6351971570 |
| H26 | 1.5366318110 | -4.4023181708 | -4.4224464277 |
| H27 | 0.4963902289 | -3.2689627076 | -2.4813607010 |
| H28 | 0.7618303926 | -2.0201323353 | -0.3728615059 |
| H29 | 0.4990710799 | 0.4305284165 | -0.3486447911 |
| H30 | 1.5412895004 | 2.6772971219 | -0.3397808752 |
| H31 | 4.0020854357 | 2.9292602032 | -0.3244658421 |
| H32 | 5.4600223370 | 0.9202689051 | -0.3151947291 |
| H33 | 6.0833183674 | -4.1325805767 | 3.2762481492 |
| H34 | 6.3312987950 | -4.1413166294 | 1.5356123414 |
| H35 | 6.3263549857 | -2.6079095700 | 2.4346377838 |
| H36 | 3.9157168400 | -4.5386549085 | 3.9896891936 |
| H37 | 1.4830313257 | -4.3978475009 | 3.7392247835 |
| H38 | -0.4091456882 | -2.7905559300 | 0.9667251027 |
| H39 | -0.3869671279 | -4.3252475236 | 1.8301500742 |
| H40 | -0.3926014708 | -2.8070968362 | 2.7275799315 |
| H41 | 6.7911304129 | -2.9901219587 | -0.4867332378 |
| H42 | 6.6151123161 | -1.4464912004 | -1.3635480591 |
| H43 | 6.7922888466 | -1.4489792101 | 0.4118135568 |

**1,4-di-Me-phosphatriptycene-$He_8$-ring complex**

E(BP86/6-31G*) = -1174.9755

| | | | |
|---|---|---|---|
| He1 | 3.7735998619# | 3.4439999372# | 5.4275999081# |
| He2 | 3.7667986375# | 1.0683011068# | 9.8271998407# |
| He3 | 5.2222998776# | 0.4646000821# | 6.6622999567# |
| He4 | 2.3179998505# | 4.0476999175# | 8.5925998806# |
| He5 | 4.7994000186# | 1.8291998666# | 5.3895001043# |
| He6 | 2.7423011687# | 2.6839986136# | 9.8657999992# |
| He7 | 4.7946003826# | 0.1494001887# | 8.5004001218# |
| He8 | 2.7457000978# | 4.3628999926# | 6.7544000526# |
| X9 | 3.7702000000# | 2.2561000000# | 7.6274000000# |
| C10 | -1.6691386216 | 2.2598188320 | 5.1622793773 |
| C11 | -1.8377516329 | 3.6129535249 | 5.4887503931 |
| C12 | -0.8955243861 | 4.2323718425 | 6.3176328961 |
| C13 | 0.2244537324 | 3.5200086895 | 6.7819403959 |
| C14 | 0.4374316334 | 2.1762232652 | 6.4250772050 |
| C15 | 2.0764598691 | 0.1536093830 | 5.3297580579 |
| C16 | 3.3007802873 | -0.2449946378 | 4.7651106551 |
| C17 | 3.3378925931 | -0.9213033919 | 3.5367780431 |
| C18 | 2.1538634389 | -1.2100263961 | 2.8529965208 |
| C19 | 0.9054173134 | -0.8768719428 | 3.4097397649 |
| C20 | 0.8858782733 | -0.2165453520 | 4.6601968488 |
| C21 | -0.5560029075 | 1.5503483539 | 5.6364421631 |
| H22 | -2.4169578207 | 1.7395788561 | 4.5501820469 |
| H23 | -2.7073670604 | 4.1674638011 | 5.1181932171 |
| H24 | -1.0241428313 | 5.2796983066 | 6.6149907197 |
| H25 | 0.9137244535 | 4.0372385423 | 7.4385736245 |
| H26 | 4.2373423814 | -0.0614691188 | 5.2748904363 |
| H27 | 4.3041234788 | -1.2211007775 | 3.1143222787 |
| H28 | 2.1887440421 | -1.7233935615 | 1.8839219323 |
| C29 | -1.2382412439 | -2.2339776648 | 8.3384333128 |
| C30 | -0.2201928827 | -1.8838573231 | 9.2290619708 |
| C31 | 0.7505232559 | -0.9062942154 | 8.9123563521 |

| | | | |
|---|---|---|---|
| C32 | 0.6910671369 | -0.2639913428 | 7.6510141584 |
| C33 | -0.3445515416 | -0.6297710531 | 6.7556664523 |
| C34 | -1.2993302785 | -1.5992776967 | 7.0919142583 |
| H35 | -1.9783511029 | -2.9941559624 | 8.6131030073 |
| H36 | -0.1638026512 | -2.3748296810 | 10.2085381830 |
| H37 | -2.0897305416 | -1.8527551679 | 6.3744140209 |
| P38 | 1.9136001048# | 1.0923002949# | 6.9973001361# |
| C39 | -0.4117251633 | 0.0629843665 | 5.3967991644 |
| H40 | -1.2784651643 | -0.3130273137 | 4.8319574368 |
| H41 | 1.7751947157 | 0.4495710993 | 10.2647783248 |
| C42 | 1.8031277626 | -0.6066521301 | 9.9523061216 |
| H43 | 1.6467573626 | -1.2259374576 | 10.8520187266 |
| H44 | 2.8176090961 | -0.8153956847 | 9.5751178799 |
| C45 | -0.3680225227 | -1.2446983858 | 2.6711148186 |
| H46 | -0.9752131294 | -1.9818206324 | 3.2294402224 |
| H47 | -1.0112726140 | -0.3643832768 | 2.4862764513 |
| H48 | -0.1305411032 | -1.6917303069 | 1.6907328384 |

**1,4-di-Me-5-Cl-phosphatriptycene**

E(BP86/6-31G*) = -1611.4758

| | | | |
|---|---|---|---|
| P1 | -4.6618828485 | -0.0923851042 | 0.0252958689 |
| C2 | -2.7878227511 | -0.1147951235 | 0.0023235461 |
| C3 | -2.0706308341 | -1.3291120563 | -0.0057143598 |
| C4 | -0.6630386122 | -1.2464822080 | -0.0070286695 |
| C5 | -0.0096902113 | -0.0123617426 | -0.0001043422 |
| C6 | -0.7169605947 | 1.2096093699 | 0.0029942156 |
| C7 | -2.1271048234 | 1.1398660721 | 0.0008044512 |
| C8 | -3.0509104100 | 2.3699163274 | -0.0065884098 |
| C9 | -3.9389698713 | 2.3232345883 | 1.2376128847 |
| C10 | -3.9601713186 | 3.3245144210 | 2.2174023623 |
| C11 | -4.8110858741 | 3.1954507129 | 3.3297084067 |
| C12 | -5.6401076121 | 2.0720923191 | 3.4617355388 |
| C13 | -5.6225006784 | 1.0660530019 | 2.4795044510 |
| C14 | -4.7724973264 | 1.1921890676 | 1.3710640691 |
| Cl15 | -6.6774261466 | -0.3500656027 | -2.6784670518 |
| C16 | -4.7797548500 | 1.1599721441 | -1.3587281197 |
| C17 | -5.6152028766 | 1.0491019019 | -2.4794245976 |
| C18 | -5.6360367155 | 2.0383326992 | -3.4775416190 |
| C19 | -4.8045668111 | 3.1573750786 | -3.3472404035 |
| C20 | -3.9585418533 | 3.2920739199 | -2.2337865823 |
| C21 | -3.9463760510 | 2.2979711220 | -1.2471425164 |
| C22 | -2.7555495298 | -2.6820141714 | -0.0150523534 |
| H23 | -0.0730805882 | -2.1715357013 | -0.0130190475 |
| C24 | 0.0889766659 | 2.4970092420 | 0.0097089209 |
| H25 | -2.4754157970 | 3.3079788547 | -0.0223547335 |
| H26 | -3.3140564518 | 4.2058915283 | 2.1176843333 |
| H27 | -4.8249387421 | 3.9792948814 | 4.0957467137 |
| H28 | -6.3028116409 | 1.9770091295 | 4.3294820868 |
| H29 | -6.2693212224 | 0.1857981063 | 2.5755437154 |
| H30 | -6.2979972993 | 1.9242976397 | -4.3411055829 |
| H31 | -4.8176508234 | 3.9311239403 | -4.1230213072 |
| H32 | -3.3090992430 | 4.1702849449 | -2.1365688839 |
| H33 | 1.0876839479 | 0.0138853509 | 0.0018301657 |
| H34 | -2.0109186410 | -3.4962376675 | -0.0403741618 |
| H35 | -3.3870159166 | -2.8288915466 | 0.8799825730 |
| H36 | -3.4173357391 | -2.8002858337 | -0.8919711752 |
| H37 | -0.5306300849 | 3.4065470556 | 0.0283356366 |

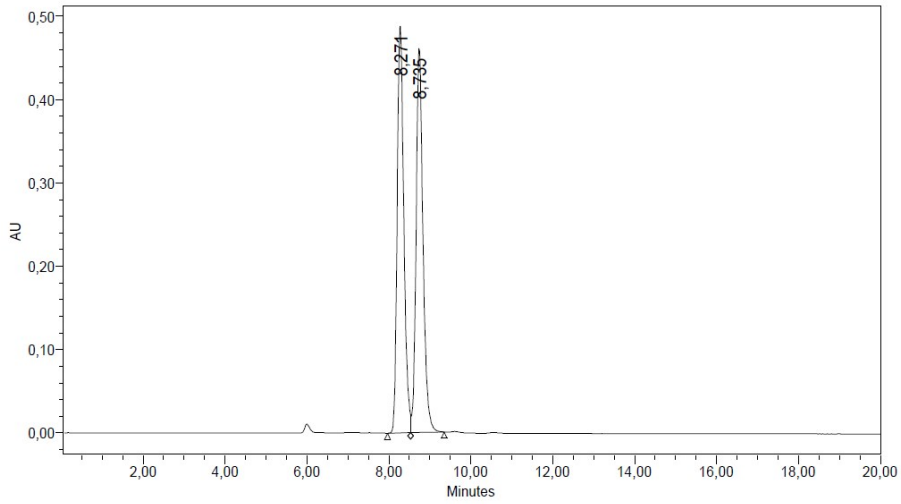
| | | | |
|---|---|---|---|
| H38 | 0.7541520868 | 2.5366675956 | 0.8921673862 |
| H39 | 0.7367800425 | 2.5596320307 | -0.8843582003 |

**1,4-di-Me-5-Cl-phosphatriptycene-$He_8$-ring complex**

E(BP86/6-31G*) = -1634.5750

| | | | |
|---|---|---|---|
| He1 | 3.7735997905# | 3.4440000715# | 5.4275996700# |
| He2 | 3.7667996661# | 1.0683014324# | 9.8272002842# |
| He3 | 5.2222996589# | 0.4646001217# | 6.6623000341# |
| He4 | 2.3179996810# | 4.0477001642# | 8.5926000324# |
| He5 | 4.7993999322# | 1.8291998299# | 5.3895003020# |
| He6 | 2.7423005364# | 2.6839982710# | 9.8657996832# |
| He7 | 4.7946001169# | 0.1493998445# | 8.5004000005# |
| He8 | 2.7457003078# | 4.3628995220# | 6.7544001069# |
| X9 | 3.7702000000# | 2.2561000000# | 7.6274000000# |
| C10 | -1.8384966092 | 0.5324157720 | 5.1758550783 |
| C11 | -2.4065903990 | 1.8017334737 | 5.0099982159 |
| C12 | -1.7280615291 | 2.9150984224 | 5.5065302351 |
| C13 | -0.4717480630 | 2.7591381410 | 6.1252519693 |
| C14 | 0.1735706526 | 1.5092488595 | 6.2361601343 |
| C15 | 2.2936523120 | -0.2171261809 | 5.5928856381 |
| C16 | 3.4917382695 | -0.3523941043 | 4.8634110216 |
| C17 | 3.6556457545 | -1.3169351925 | 3.8532059299 |
| C18 | 2.6174402810 | -2.1925375742 | 3.5235731996 |
| C19 | 1.4117819022 | -2.0819527248 | 4.2254746977 |
| C20 | 1.2642573624 | -1.1173109475 | 5.2338292637 |
| C21 | -0.5864995013 | 0.3932079725 | 5.7897019551 |
| H22 | -2.3727060616 | -0.3633060476 | 4.8378616004 |
| H23 | -3.3822806741 | 1.9216217888 | 4.5268938224 |
| H24 | -2.1615617898 | 3.9170452780 | 5.4394451139 |
| Cl25 | 0.1811422209 | 4.2419857762 | 6.8162259280 |
| H26 | 4.3375401604 | 0.2840009478 | 5.0452965898 |
| H27 | 4.6145518915 | -1.3682558894 | 3.3248898016 |
| H28 | 2.7391777208 | -2.9436614909 | 2.7351821643 |
| H29 | 0.5675947264 | -2.7434239510 | 3.9943089254 |
| C30 | -0.0037960244 | -2.4996349772 | 9.5033200390 |
| C31 | 0.4693707769 | -1.3971636680 | 10.2127862401 |
| C32 | 0.9227485954 | -0.2203570074 | 9.5767630876 |
| C33 | 0.9938064908 | -0.2136273888 | 8.1552733663 |
| C34 | 0.2901534868 | -1.2391436972 | 7.4718370375 |
| C35 | -0.1780115033 | -2.4091672159 | 8.1123936760 |
| H36 | -0.3261226676 | -3.4025023564 | 10.0364787399 |
| H37 | 0.4517755983 | -1.4146903405 | 11.3102289535 |
| C38 | -0.8647819527 | -3.5335865187 | 7.3605376142 |
| P39 | 1.9136003100# | 1.0923007428# | 6.9972998868# |
| C40 | -0.0200106968 | -1.0023435490 | 5.9999018619 |
| H41 | -0.7475388623 | -1.7443611764 | 5.6379142002 |
| H42 | 0.9351793403 | 1.9227627566 | 9.9306045655 |
| C43 | 1.0797401840 | 0.9843676700 | 10.4809372990 |
| H44 | 0.2918894656 | 0.9390189700 | 11.2539141738 |
| H45 | 2.0433033233 | 1.0267468089 | 11.0123382052 |
| H46 | -0.2663972264 | -3.8880024353 | 6.5013832393 |
| H47 | -1.0275120050 | -4.3965084543 | 8.0287326222 |
| H48 | -1.8564701058 | -3.2342035219 | 6.9693382498 |

## 5. Chiral HPLC analysis




| | RT | Area | % Area | Height |
|---|---|---|---|---|
| 1 | 8,271 | 5433455 | 49,97 | 489923 |
| 2 | 8,735 | 5440408 | 50,03 | 462904 |

HPLC_column Daicel Chiralpak IA 250x4.6mm

**Figure S3.** Chiral HPLC analysis of the racemic phosphatriptycene **9a**.

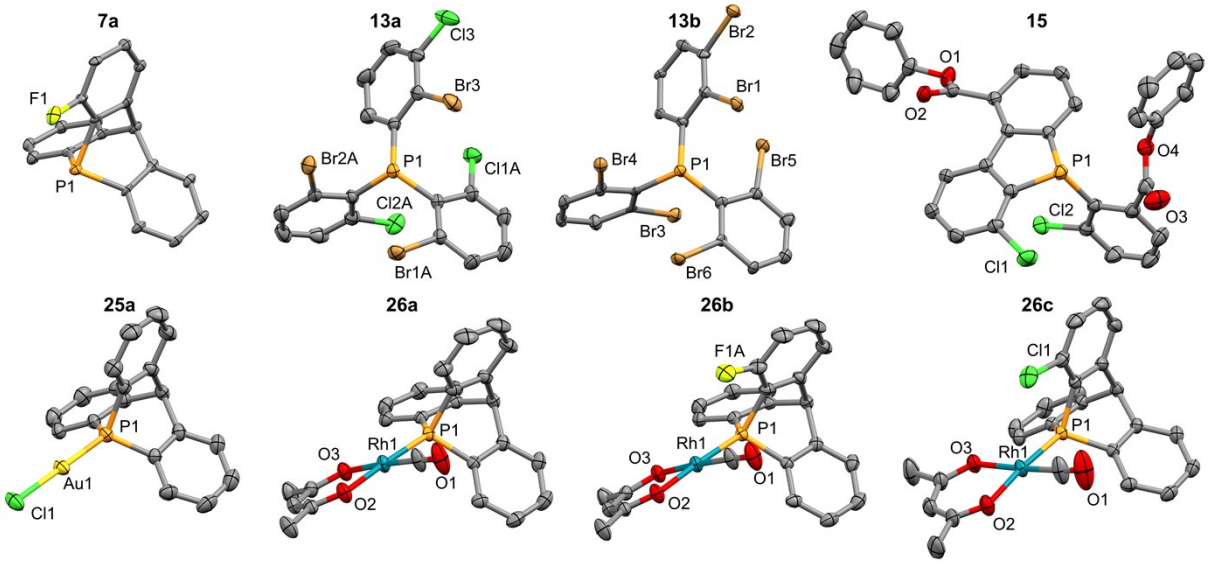
| HPLC conditions | |
|---|---|
| HPLC system: | Waters Alliance 2690 + Waters PDA 996 |
| Stationnary Phase: | Daicel Chiralpak IA 250x4.6 mm 5 µm |
| Mobile phase: | isocratic condition – isohexane/isopropanol 98/02 |
| Flow Rate: | 0.5 mL/min |
| Exctracted wavelength: | 220 nm |
| Oven Temperature: | 20 °C |

**Table S3.** Chiral HPLC analysis of the racemic phosphatriptycene **9a**.

## 6. Crystallographic data

Single-crystals X-ray diffraction data collected using an Oxford Diffraction Gemini Ultra R diffractometer (fine-focus sealed tube with multilayer mirror for Cu Kα radiation or graphite monochromator for Mo Kα radiation) (all datasets, except **10a**) or MAR345 image plate (Incoatec IμS microfocus source with Montel multilayer optics ELM33). The data were integrated using the CrysAlisPro software.[11] The structures were solved by the dual-space algorithm implemented in SHELXT,[12] and refined by full-matrix least squares on $|F|^2$ using SHELXL-2018/3,[13] the shelXLe,[14] and Olex2 software.[15] Non-hydrogen atoms were refined anisotropically; and hydrogen atoms in most of the cases were located from the difference Fourier map but placed on calculated positions in riding mode with equivalent isotropic temperature factors fixed at 1.2 times $U_{eq}$ of the parent atoms (1.5 times $U_{eq}$ for methyl groups). Absolute configuration, in cases where applicable, where established by anomalous-dispersion effects in diffraction measurements on the crystal.

For the structures not shown in the main text, see Figure below.



Details of single-crystal X-ray diffraction data collection and determination are given the below tables.

| | **7a** | **7b** | **8a** |
|---|---|---|---|
| Chemical formula | $C_{19}H_{12}FP$ | $C_{19}H_{12}ClP$ | $C_{21}H_{17}P$ |
| $M_r$ | 290.26 | 306.71 | 300.32 |
| Crystal system, space group | Monoclinic, *I*2/*a* | Monoclinic, $P2_1/m$ | Monoclinic, $P2_1/n$ |
| Temperature (K) | 100 | 295 | 295 |
| *a*, *b*, *c* (Å) | 13.8967 (8), 8.1179 (3), 13.4003 (7) | 7.2135 (3), 13.7539 (4), 8.1944 (3) | 8.6630 (4), 8.8328 (4), 20.9003 (8) |
| α, β, γ (°) | 90, 113.349 (7), 90 | 90, 113.053 (4), 90 | 90, 98.024 (4), 90 |
| *V* (Å$^3$) | 1387.93 (14) | 748.07 (5) | 1583.62 (12) |
| *Z* | 4 | 2 | 4 |
| Radiation type | Cu *K*α | | Mo *K*α |
| μ (mm$^{-1}$) | 1.76 | 3.16 | 0.17 |
| Crystal size (mm) | 0.60 × 0.54 × 0.41 | 0.19 × 0.15 × 0.02 | 0.66 × 0.42 × 0.37 |
| Diffractometer | Oxford Diffraction Xcalibur, Ruby, Gemini Ultra | | |
| Absorption correction | Analytical | | Gaussian |
| $T_{min}$, $T_{max}$ | 0.495, 0.613 | 0.662, 0.941 | 0.595, 1.000 |
| No. of measured, independent and observed [$I > 2\sigma(I)$] reflections | 3246, 1216, 1191 | 2755, 2755, 1966 | 10088, 4830, 3752 |
| $R_{int}$ | 0.038 | 0.036 | 0.018 |
| $\theta_{max}$ (°) | 67.3 | 67.2 | 30.5 |
| $(\sin\theta/\lambda)_{max}$ (Å$^{-1}$) | 0.598 | 0.598 | 0.714 |
| $R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S* | 0.069, 0.154, 1.36 | 0.066, 0.208, 1.08 | 0.046, 0.127, 1.03 |
| No. of reflections | 1216 | 2755 | 4830 |
| No. of parameters | 214 | 120 | 220 |
| No. of restraints | 209 | 1 | 18 |
| H-atom treatment | constrained | | |
| $\Delta\rho_{max}$, $\Delta\rho_{min}$ (e·Å$^{-3}$) | 0.17, -0.37 | 0.31, -0.26 | 0.29, -0.20 |
| CCDC deposition number | 2061849 | 2061850 | 2061851 |

| | **9a** | **10a** | **13a** |
|---|---|---|---|
| Chemical formula | $C_{23}H_{20}ClP$ | $C_{21}H_{16}ClP$ | $C_{18}H_9Br_3Cl_3P$ |
| $M_r$ | 362.81 | 334.76 | 602.27 |
| Crystal system, space group | Monoclinic, $P2_1/m$ | Triclinic, $P\bar{1}$ | Monoclinic, $P2_1/c$ |
| Temperature (K) | 295 | 295 | 295 |
| *a*, *b*, *c* (Å) | 8.1914 (2), 13.7899 (4), 8.6284 (2) | 13.9870 (17), 16.009 (4), 16.436 (4) | 31.4777 (8), 8.5972 (2), 14.8825 (4) |
| α, β, γ (°) | 90, 99.365 (3), 90 | 74.36 (2), 89.257 (14), 79.319 (16) | 90, 94.161 (3), 90 |
| *V* (Å$^3$) | 961.67 (5) | 3480.1 (13) | 4016.89 (19) |
| *Z* | 2 | 8 | 8 |
| Radiation type | Cu *K*α | Mo *K*α | Cu *K*α |
| μ (mm$^{-1}$) | 2.54 | 0.31 | 11.88 |
| Crystal size (mm) | 0.29 × 0.07 × 0.03 | 0.20 × 0.14 × 0.07 | 0.11 × 0.09 × 0.01 |
| Diffractometer | Oxford Diffraction Xcalibur, Ruby, Gemini Ultra | MAR345 image plate | Oxford Diffraction Xcalibur, Ruby, Gemini Ultra |
| Absorption correction | Gaussian | Multi-scan | Analytical |
| $T_{min}$, $T_{max}$ | 0.673, 0.931 | 0.689, 1.000 | 0.373, 0.863 |
| No. of measured, independent and observed [$I > 2\sigma(I)$] reflections | 2998, 2998, 2585 | 17918, 4206, 2334 | 12995, 6263, 4873 |
| $R_{int}$ | 0.043 | 0.147 | 0.034 |
| $\theta_{max}$ (°) | 67.2 | 17.2 | 62.6 |
| $(\sin\theta/\lambda)_{max}$ (Å$^{-1}$) | 0.598 | 0.417 | 0.576 |
| $R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S* | 0.052, 0.155, 1.15 | 0.088, 0.235, 1.04 | 0.043, 0.103, 1.06 |
| No. of reflections | 2998 | 4206 | 6263 |
| No. of parameters | 140 | 887 | 527 |
| No. of restraints | 4 | 760 | 84 |
| H-atom treatment | mixed | constrained | |
| $\Delta\rho_{max}$, $\Delta\rho_{min}$ (e·Å$^{-3}$) | 0.38, -0.27 | 0.27, -0.25 | 0.97, -0.79 |
| CCDC deposition number | 2061852 | 2061853 | 2061854 |

| | **13b** | **15a** | **25a** |
|---|---|---|---|
| Chemical formula | $C_{18}H_9Br_6P$ | $C_{32}H_{19}Cl_2O_4P$ | $C_{19}H_{13}AuClP$ |
| $M_r$ | 735.68 | 569.34 | 504.68 |
| Crystal system, space group | Triclinic, $P\bar{1}$ | Triclinic, $P\bar{1}$ | Monoclinic, $P2_1/n$ |
| Temperature (K) | 100 | 295 | 295 |
| *a*, *b*, *c* (Å) | 7.4004 (9), 8.9219 (12), 15.889 (3) | 8.7704 (4), 9.6774 (3), 16.3912 (4) | 8.26532 (9), 14.28693 (14), 14.00053 (14) |
| α, β, γ (°) | 78.126 (13), 82.433 (12), 81.201 (11) | 106.886 (3), 96.369 (3), 92.054 (3) | 90, 91.8231 (9), 90 |
| *V* (Å$^3$) | 1009.1 (3) | 1319.60 (9) | 1652.43 (3) |
| *Z* | 2 | 2 | 4 |
| Radiation type | Cu *K*α | Mo *K*α | Cu *K*α |
| μ (mm$^{-1}$) | 15.12 | 0.35 | 19.06 |
| Crystal size (mm) | 0.43 × 0.06 × 0.02 | 0.52 × 0.13 × 0.05 | 0.36 × 0.27 × 0.06 |
| Diffractometer | Oxford Diffraction Xcalibur, Ruby, Gemini ultra | | |
| Absorption correction | Gaussian | Analytical | |
| $T_{min}$, $T_{max}$ | 0.153, 0.736 | 0.855, 0.985 | 0.062, 0.495 |
| No. of measured, independent and observed [$I > 2\sigma(I)$] reflections | 2316, 2316, 1816 | 12095, 5383, 4209 | 7819, 2934, 2690 |
| $R_{int}$ | 0.071 | 0.022 | 0.032 |
| $\theta_{max}$ (°) | 40.8 | 26.4 | 67.2 |
| $(\sin\theta/\lambda)_{max}$ (Å$^{-1}$) | 0.424 | 0.625 | 0.598 |
| $R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S* | 0.074, 0.227, 1.10 | 0.038, 0.102, 1.03 | 0.030, 0.076, 1.07 |
| No. of reflections | 2316 | 5383 | 2934 |
| No. of parameters | 227 | 352 | 199 |
| No. of restraints | 171 | 0 | 0 |
| H-atom treatment | constrained | | |
| $\Delta\rho_{max}$, $\Delta\rho_{min}$ (e·Å$^{-3}$) | 1.02, -1.22 | 0.33, -0.19 | 1.64, -1.18 |
| CCDC deposition number | 2061855 | 2061856 | 2061857 |

| | **25d** | **26a** | **26b** |
|---|---|---|---|
| Chemical formula | $2(C_{20}H_{12}AuClF_3P)\cdot C_7H_8$ | $C_{25}H_{20}O_3PRh$ | $C_{25}H_{19}FO_3PRh$ |
| $M_r$ | 1237.50 | 502.29 | 520.28 |
| Crystal system, space group | Monoclinic, $P2_1/n$ | Triclinic, $P\bar{1}$ | Triclinic, $P\bar{1}$ |
| Temperature (K) | 100 | 295 | 295 |
| $a$, $b$, $c$ (Å) | 14.81554 (13), 17.38646 (13), 16.11733 (12) | 9.3940 (2), 15.7924 (3), 16.7012 (4) | 9.5012 (2), 15.7667 (5), 16.6900 (5) |
| α, β, γ (°) | 90, 90.9329 (7), 90 | 65.676 (2), 80.915 (2), 76.193 (2) | 65.119 (3), 80.211 (2), 75.563 (2) |
| $V$ (Å$^3$) | 4151.11 (6) | 2187.53 (10) | 2190.45 (12) |
| $Z$ | 4 | 4 | 4 |
| Radiation type | Cu $K\alpha$ | | |
| μ (mm$^{-1}$) | 15.54 | 7.20 | 7.28 |
| Crystal size (mm) | 0.30 × 0.22 × 0.18 | 0.33 × 0.12 × 0.06 | 0.11 × 0.07 × 0.06 |
| Diffractometer | Oxford Diffraction Xcalibur, Ruby, Gemini Ultra | | |
| Absorption correction | Analytical | | |
| $T_{min}$, $T_{max}$ | 0.064, 0.234 | 0.258, 0.671 | 0.596, 0.727 |
| No. of measured, independent and observed [$I > 2\sigma(I)$] reflections | 28416, 7376, 7267 | 21822, 7739, 7213 | 21134, 7736, 6495 |
| $R_{int}$ | 0.026 | 0.026 | 0.041 |
| $\theta_{max}$ (°) | 67.2 | 67.2 | 67.1 |
| $(\sin\theta/\lambda)_{max}$ (Å$^{-1}$) | 0.598 | 0.598 | 0.597 |
| $R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, $S$ | 0.029, 0.071, 1.19 | 0.024, 0.063, 1.04 | 0.035, 0.102, 1.04 |
| No. of reflections | 7376 | 7739 | 7736 |
| No. of parameters | 598 | 545 | 583 |
| No. of restraints | 105 | 0 | 8 |
| H-atom treatment | constrained | | |
| $\Delta\rho_{max}$, $\Delta\rho_{min}$ (e·Å$^{-3}$) | 1.12, -1.91 | 0.40, -0.43 | 0.92, -0.67 |
| CCDC deposition number | 2061858 | 2061859 | 2061860 |

| | **26c** | **26d** |
|---|---|---|
| Chemical formula | $C_{25}H_{19}ClO_3PRh$ | $C_{26}H_{19}F_3O_3PRh$ |
| $M_r$ | 536.73 | 570.29 |
| Crystal system, space group | Monoclinic, $P2_1/c$ | Orthorhombic, $P2_12_12_1$ |
| Temperature (K) | 295 | 295 |
| *a*, *b*, *c* (Å) | 8.62702 (10), 21.4229 (2), 12.62171 (15) | 8.26668 (8), 15.72226(15), 17.67340 (19) |
| α, β, γ (°) | 90, 107.1655 (13), 90 | 90, 90, 90 |
| *V* (Å$^3$) | 2228.78 (5) | 2297.03 (4) |
| *Z* | 4 | 4 |
| Radiation type | Cu *K*σ | |
| μ (mm$^{-1}$) | 8.18 | 7.13 |
| Crystal size (mm) | 0.36 × 0.23 × 0.16 | 0.41 × 0.22 × 0.05 |
| Diffractometer | Oxford Diffraction Xcalibur, Ruby, Gemini Ultra | |
| Absorption correction | Analytical | |
| $T_{min}$, $T_{max}$ | 0.230, 0.416 | 0.110, 0.688 |
| No. of measured, independent and observed [$I > 2\sigma(I)$] reflections | 11623, 3948, 3716 | 13181, 4062, 3941 |
| $R_{int}$ | 0.025 | 0.039 |
| $\theta_{max}$ (°) | 67.0 | 67.1 |
| $(\sin\theta/\lambda)_{max}$ (Å$^{-1}$) | 0.597 | 0.597 |
| $R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, $S$ | 0.029, 0.074, 1.09 | 0.027, 0.068, 1.01 |
| No. of reflections | 3948 | 4062 |
| No. of parameters | 292 | 309 |
| No. of restraints | 0 | 0 |
| H-atom treatment | constrained | |
| $\Delta\rho_{max}$, $\Delta\rho_{min}$ (e·Å$^{-3}$) | 0.52, -0.59 | 0.47, -0.46 |
| Absolute structure | – | Flack x determined using 1611 quotients |
| Absolute structure parameter | – | -0.024 (7) |
| CCDC deposition number | 2061861 | 2061862 |

## 7. References


1. S. Ito, K. Koshino, K. Mikami, *Chem*. *Asian J*. 2018, **13**, 830.
2. A. Ben Saida, A. Chardon, A. Osi, N. Tumanov, J. Wouters, A. I. Adjieufack, B. Champagne, G. Berionni, *Angew. Chem. Int. Ed.* 2019, **58**, 16889.
3. L. Hu, D. Mahaut, N. Tumanov, J. Wouters, R. Robiette, G. Berionni, 2019, **84**, 11268.
4. V. D. Vuković, E. Richmond, E. Wolf, J. Moran, *Angew. Chem. Int. Ed.* 2017, **56**, 3085.
5. S. E. Creutz, J. C. Peters, *J. Am. Chem. Soc.* 2014, **136**, 1105.
6. L. Y. Chen, P. Ren, B. P. Carrow, *J*. *Am*. *Chem*. *Soc*. 2016, **138**, 6392.
7. J. A. Werra, M. A. Wünsche, P. Rathmann, P. Mehlmann, P. Löwe, F. Dielmann, *Z*. *Anorg. Allg*. *Chem*. 2020, **646**, 1.
8. Calculations were carried out at the M06-2X/6-31+G(d)(benzene) level of theory using the Jaguar 8.5 pseudospectral program package (Jaguar 8.5, Schrodinger, Inc., New York, NY, 2014).
9. J. Jover, N. Fey, M. Purdie, G. C. Lloyd-Jones, J. N. Harvey, *J. Mol. Catal. A: Chem*. 2010, **324**, 39.
10. A. J. Poë, D. H. Farrar, Y. Zheng, *J. Am. Chem. Soc*. 1992, **114**, 5146.
11. Rigaku Oxford Diffraction. CrysAlis PRO. Rigaku Oxford Diffraction: Oxford, UK 2018.
12. G. M. Sheldrick, *Acta Crystallogr. Sect. A Found. Adv.* 2015, **71**, 3.
13. G. M. Sheldrick, *Acta Crystallogr. Sect. C Struct. Chem.* 2015, **71**, 3.
14. C. B. Hübschle, G. M. Sheldrick, B. Dittrich, *J. Appl. Crystallogr.* 2011, **44**, 1281.
15. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, Puschmann, H. *J. Appl.Crystallogr.* 2009, **42**, 339.