Supporting Information

Double [3+2]-dimerisation cascade synthesis of bis(triazolyl)diphosphanes, a new scaffold for bidentate diphosphanes

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I. General information

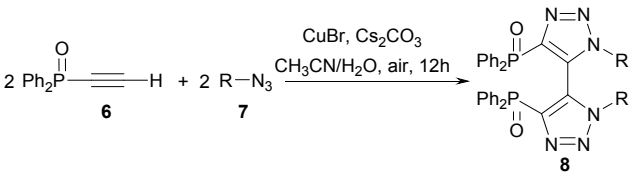
All reactions were carried out under an argon or nitrogen atmosphere using standard Schlenk techniques otherwise stated. Solvents were carefully dried by conventional or were purified with an MBRAUN Solvent Purification System. ^{1}H, ^{13}C and ^{31}P NMR spectra were recorded with a Bruker Avance 500 FT-NMR or a bruker Avance 400 spectrometer. The resonances were calibrated relative to the residual solvent peaks and are reported with positive values downfield from TMS. NMR multiplicities are abbreviated as follows: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad signal. Chemical shifts (δ) and coupling constants (J) were expressed in ppm and Hz, respectively. For all characterized compounds, the peak assignments in the ^{1}H and ^{13}C NMR spectra were based on COSY, HSQC and HMBC 2D experiments. HRMS were obtained from dichloromethane solutions with a Xevo G2 Q TOF spectrometer by the electrospray method or with a LC-TOF spectrometer (Micromass).

II. Synthesis of bistriazolyl phosphane oxides 8.1-8.7

II.1. General procedure

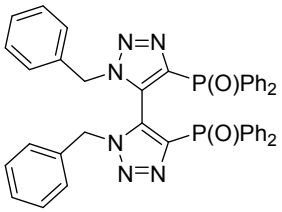
In a round bottom flask, ethynyldiphenylphosphane oxide (250 mg, 1.1 mmol) was dissolved in acetonitrile (3 mL). Then the corresponding azide (3.3 mmol) and aqueous cesium carbonate solution at 2 $mol.L^{-1}$ (1.65 mL) were added followed by copper bromide (158 mg, 1 mmol). The resulting mixture was stirred at room temperature in an open vessel for 12 hours. After complete reaction as monitored by TLC, the solvent was removed under reduced pressure and the residue was dissolved in dichloromethane, washed with aqueous ammonia solution (10%, 3 x 10mL), brine, then dried over magnesium sulfate and the solvent was evaporated under reduced pressure. The product was isolated as specified below.

Synthesis of bistriazolylphosphane dioxides 8.1-8.7



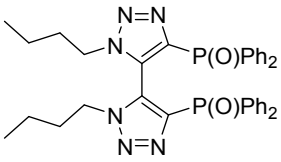
	R	Yield		R	Yield
8.1	Bn	49	**8.6**	CH_2CO_2Me	20
8.2	*n*-Bu	42	**8.7**	CH_2OBn	12
8.3	*i*-Bu	23	**8.8**	$CH_2C(O)Me$	-
8.4	*c*-Hex	6	**8.9**	$CH_2C(O)Ph$	-
8.5	CH_2CO_2Bn	29			

II.2. 4,4’-bis(diphenylphosphinoxy)-1,1’-dibenzyl-5,5’-bis-1,2,3-triazole dioxide, 8.1



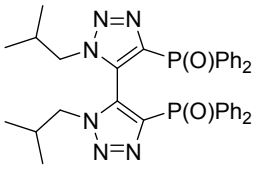
The compound was isolated as a white solid after recrystallization from ethanol; **Yield** : 49%; **^{1}H NMR** (400,13 MHz, $CDCl_3$) δ 8.13 - 7.97 (m, 4H), 7.65 - 7.41 (m, 10H), 7.39 - 7.08 (m, 12H), 6.91 - 6.77 (m, 4H), 5.51 (d, *J* = -14.7 Hz, 2H), 4.70 (d, *J* = -14.7 Hz, 2H); **^{13}C NMR** (100,61 MHz, $CDCl_3$) δ 141.18 (d, *J* = 130.4 Hz), 132.88 (s), 132.36 (d, *J* = 2.8 Hz), 132.04 (d, *J* = 2.8 Hz), 131.65 (d, *J* = 10.0 Hz), 131.39 (dd, J = 55.3 Hz, *J* = 109.07 Hz), 131.23 (d, *J* = 10.9 Hz), 130.85 (d, *J* = 241.7 Hz), 128.92(s), 128.83 (s), 128.62 (d, *J* = 12.6 Hz), 128.54 (d, *J* = 12.8 Hz), 128.15 (s), 53.13 (s); **^{31}P NMR** (161.97 MHz, $CDCl_3$) δ 16.80 (s); **HRMS (EI):** *m/z* Calcd. for $C_{42}H_{34}N_6O_2P_2$ $[M+H]^+$:717.22; Found: 717.2306; **mp** : 224.5-227.4°C.

II.3. 4,4’-bis(diphenylphosphinoxy)-1,1-dibutyl-5,5’-bis-1,2,3-triazole dioxide, 8.2



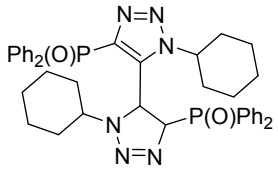
The compound was isolated as a white solid after purification by a chromatography column on silica gel with as eluent a mixture of dichloromethane-isopropanol (98/2); **Yield** : 42%; **^{1}H NMR** (400,13 MHz, $CDCl_3$) δ7. 96 (dd, *J* = 7.6 Hz, *J* = 12.1 Hz, 4H), 7.61 - 7.35(m, 10H), 7.33 - 7.21 (m, 2H), 7.20 - 7.08 (m, 4H), 4.23 - 4.40 (m, 2H), 4.13 - 4.01 (m, 2H), 1.92-1.78(m, 2H), 1.77 - 1.64 (m, 2H), 1.22 - 1.08 (m, 4H), 0.78 (t, J = 7.4 Hz, 6H); **^{13}C NMR** (100,61 MHz, $CDCl_3$) δ140.82 (d, *J* = 130,0 Hz), 133.27 (d, *J* = 2.7 Hz), 131.98 (d, *J* = 2.7 Hz), 131.66 (d, *J* = 10,0 Hz), 131.57 (dd, *J* = 29 Hz, *J* = 110.3 Hz), 131.27 (d, *J* = 10.9 Hz), 130.42 (d, *J* = 21.9 Hz), 129,57 (d, *J* = 12.7 Hz), 129.47 (d, *J* = 13,0 Hz), 49.40 (s), 31.07 (s), 19.84 (s), 13.31 (s); **^{31}P NMR** (161.97 MHz, $CDCl_3$) δ16,52 (s); **HRMS (EI):** *m/z* Calcd. for $C_{36}H_{38}N_6O_2P_2$ $[M+H]^+$:649.25; Found: 649.2607; **mp** : 172.2-172.7 °C.

II.4. 4,4’-bis(diphenylphosphinoxy)-1,1’-diisobutyl-5,5’-bis-1,2,3-triazole dioxide, 8.3



The compound was isolated as a white solid after purification by a chromatography column on silica gel with as eluent a mixture of dichloromethane-isopropanol (98/2); **Yield** : 23%; **^{1}H NMR** (400,13 MHz, $CDCl_3$) δ 8.05 - 7.92 (m, 4H), 7.61 - 7.44 (m, 10H), 7.38 - 7.27 (m, 2H), 7.23 - 7.14 (m, 4H), 4.20 (dd, *J* = 7.5 Hz, *J* = -13.9 Hz, 2H), 3.88 (dd, *J* = 7.4 Hz, *J* = -13.9 Hz, 2H), 2.10 (ht, *J* = 6.87 Hz, *J* = 6.87 Hz, 2H), 0.81 (d, *J* = 6.7 Hz, 6H), 0.73 (d, *J* = 6.6 Hz, 6H); **^{13}C NMR** (100,61 MHz, $CDCl_3$) δ 140.87 (d, *J* = 131.2 Hz), 133.26 (d, *J* = 41.9 Hz), 132.27 (d, *J* = 2.7 Hz), 132.00 (d, *J* = 2.8 Hz), 131.71 (d, *J* = 10.0 Hz), 131.22 (d, *J* = 10.8 Hz), 130.67 (d, *J* = 22 Hz), 128.58 (d, *J* = 12.6 Hz), 128.08 (d, *J* = 13.0 Hz), 56.97 (s), 28.02 (s), 20.16 (s), 20.03 (s); **^{31}P NMR** (161.97 MHz, $CDCl_3$) δ 16.5 (s); **HRMS (EI):** *m/z* Calcd. for $C_{36}H_{38}N_6O_2P_2$ $[M+H]^+$:649.25; Found: 649.2618; **mp** : 237.1-238.0 °C.

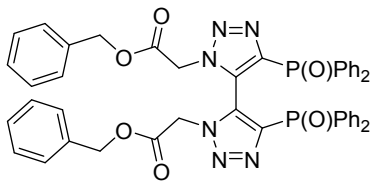
II.5. 4,4’-bis(diphenylphosphinoxy)-1,1’-dicyclohexyl-5,5’-bis-1,2,3-triazole dioxide, 8.4



The compound was isolated as a white solid after sublimation; **Yield** : 6%; **^{1}H NMR** (400,13 MHz, $CDCl_3$) δ7.95 - 7.89 (qt, 3H), 7.51 - 7.38 (m, 11H), 7.27 - 7.21 (m, 6H), 3.70 (tt, *J* = 11.74 Hz,3.70 Hz, 2H), 2.53 - 2.56 (m, 2H), 2.11 - 2.02 (m, 2H), 1.91 - 1.83 (m, 2H), 1.75 - 1.66 (m, 4H), 1.56 - 1.48 (m, 4H), 1.18 - 1.11 (m, 2H), 0.99 - 0.89 (m, 2H), 0,84 - 0.74 (m, 2H); **^{13}C NMR** (100,61 MHz, $CDCl_3$) δ 140.47 (d, *J* = 132.1 Hz), 133.13 (d, *J* = 40.3 Hz), 132.23 (d, *J* = 2.9 Hz), 131.94 (d, *J* = 2.8 Hz), 131.79 (d, *J* =

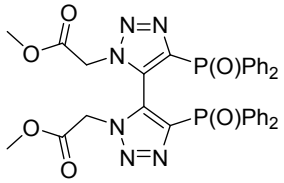
10 Hz), 131.56 (d, *J* = 11 Hz), 130.20 (d, *J* = 21.9 Hz), 128.62 (d, *J* = 12.6 Hz), 128.40 (d, *J* = 13,0 Hz), 34.27 (s), 59.71 (s), 32.35 (s), 25.39 (s), 25.22 (s), 24.89 (s); **^{31}P NMR** (161.97 MHz, $CDCl_3$) δ 17,07 (s); **HRMS (EI):** *m/z* Calcd. for $C_{40}H_{42}N_6O_2P_2$ $[M+H]^+$:701.28; Found: 701.2908; **mp** : 282.4-283.0 °C.

II.6. 4,4'-bis(diphenylphosphinoxy)-1,1'-bis(benzyloxyacetyl)-5,5'-bis-1,2,3-triazole dioxide, 8.5



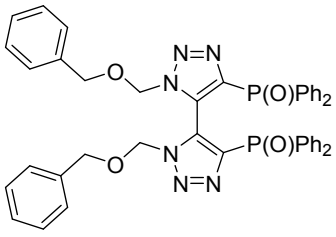
The compound was isolated as a white solid after purification by a chromatography column on silica gel with as eluent a mixture of dichloromethane-isopropanol (98/2); **Yield** : 28%; **^{1}H NMR** (400,13 MHz, $CDCl_3$) δ 7.97 - 7.89 (m, 4H), 7,59 - 7,52 (m, 2H), 7.51 - 7.39 (m, 8H), 7.34 - 7.28 (m, 8H), 7.25 - 7.19 (m, 4H), 7.17 - 7.09 (m, 4H), 5.40 (d, *J* = -17.8 Hz, 2H), 5.18 (d, *J* = -17.8 Hz, 2H), 5.05 (d, *J* = -12.1 Hz, 2H), 4.99 (d, *J* = -12.1 Hz, 2H); **^{13}C NMR** (100,61 MHz, $CDCl_3$) δ 165.89 (s), 141.10 (d, *J* = 129.7 Hz), 134.58 (s), 132.54 (d, *J* = 2.7 Hz), 132.3 (dd, *J* = 20.8 Hz, *J* = 110.9 Hz), 132.19 (d, *J* = 2.7 Hz), 131.83 (d, *J* = 10.2 Hz), 131.82 (d, *J* = 21.7 Hz), 131.21 (d, *J* = 10.9 Hz), 128,77 (d, *J* = 12.6 Hz), 128.75 (s), 128,72 (s), 128.55 (s), 128.5 (d, *J* = 13.0 Hz), 68.04 (s), 50.11 (s); **^{31}P NMR** (161.97 MHz, $CDCl_3$) δ 17,36 (s); **HRMS (EI):** *m/z* Calcd. for $C_{46}H_{38}N_6O_6P_2$ $[M+H]^+$:833.23; Found: 833.2400; **mp** : 157.4-157.9 °C.

II.7. 4,4'-bis(diphenylphosphinoxy)-1,1'-bis(methoxyacetyl) -5,5'-bis-1,2,3-triazole dioxide, 8.6



The compound was isolated as a white solid after purification by a chromatography column on silica gel with as eluent a mixture of dichloromethane-isopropanol (98/2); **Yield** : 20%; **^{1}H NMR** (400,13 MHz, $CDCl_3$) δ 7.92 - 7.84 (m, 4H), 7.50 - 7.32 (m, 10H), 7.24 - 7.18 (m, 2H), 7.09 - 7.03 (m, 4H), 5.29 (d, *J* = -17.8 Hz, 2H), 5.06 (d, *J* = -17.8 Hz, 2H), 3.58 (s, 6H); **^{13}C NMR** (100,61 MHz, $CDCl_3$) δ 166.45 (s), 147.07 (d, *J* = 129.0 Hz), 132.57 (d, *J* = 2.78 Hz), 132.19 (d, *J* = 2.8 Hz), 131.82 (d, *J* = 10.9 Hz), 131.6 (dd, *J* = 23.4 Hz, *J* = 110.81 Hz), 131.17 (d, *J* = 10.9 Hz), 130.93 5 (s), 128,78 (d, *J* = 12.8 Hz), 128.5 (d, *J* = 13,0 Hz), 52.99 (s), 49.89 (s); **^{31}P NMR** (161.97 MHz, $CDCl_3$) δ 17.22 (s); **HRMS (EI):** *m/z* Calcd. for $C_{34}H_{30}N_6O_6P_2$ $[M+H]^+$:681.17; Found: 681.1790; **mp** : 211.7-212.1°C.

II.8. 4,4'-bis(diphenylphosphinoxy)-1,1'-bis(benzyloxymethyl)-5,5'-bis-1,2,3-triazole dioxide, 8.7

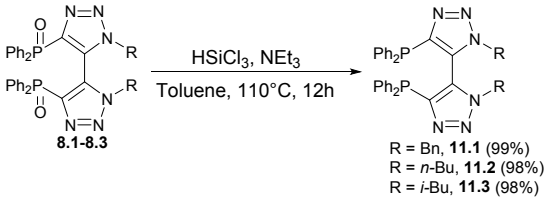


The compound was isolated as a white solid after purification by a chromatography column on silica gel with as eluent a mixture of dichloromethane-isopropanol (98/2); **Yield** : 12%; **^{1}H NMR** (400,13 MHz, $CDCl_3$) δ 8.04-7.89 (m, 4H), 7.64 - 7.40 (m, 10H), 7.37 - 7.11 (m, 16H), 5.87 (d, *J* = -11.2 Hz, 2H), 5.75 (d, *J* = -11.2 Hz, 2H), 4.42 (s, 4H); **^{13}C NMR** (100,61 MHz, $CDCl_3$) δ 141.51 (d, *J* = 129.5 Hz), 135.72 (s), 132.43 (d, *J* = 2.6 Hz), 132.07 (d, *J* = 2.7 Hz), 131.84 (dd, *J* = 31.1 Hz, *J* = 111 Hz), 131.78 (d, *J* = 10.2 Hz), 131.22 (d, *J* = 10.9 Hz), 130.84 (dd, *J* = 21.3 Hz), 128.64 (d, *J* = 12.8 Hz), 128.50 (s), 128.42 (d, *J* = 12.9 Hz), 128.36 (s), 128.26 (s), 76.79 (s), 71.29 (s); **^{31}P NMR** (161.97 MHz, $CDCl_3$) δ 17,34 (s); **HRMS (EI):** *m/z* Calcd. for $C_{36}H_{38}N_6O_2P_2$ $[M+H]^+$:777.24; Found: 777.25183; **mp** : 154.0-154.8 °C.

III. Reduction of bistriazolylphosphane oxides 8 into bisphosphanes 11

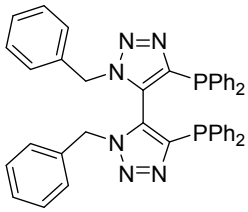
III.1. General procedure

To a mixture of bistriazole (1eq) and triethylamine (12 eq) in anhydrous toluene (0.15 mol.ml^{-1}) was added dropwise trichlorosilane (10 eq) at room temperature under a nitrogen atmosphere. The mixture was stirred at reflux for 12 h. After complete reduction, observed by ^{31}P RMN, the reaction mixture was quenched with 2M NaOH aq and diluted with dichloromethane and water. The organic layer was separated, washed with water and dried over Na_2SO_4. After concentration under vacuum, the diphosphane was obtained.



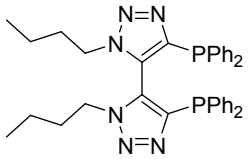
Scheme 1. Reduction of the bis(triazolylphosphane) oxides **8.1**-**8.3** to diphosphanes **11.1-11.3**.

III.2. 4,4'-bis(diphenylphosphino)-1,1'-dibenzyl-5,5'-bis-1,2,3-triazole, 11-Bn



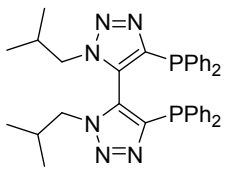
The compound was isolated as a white solid after precipitation with diethylether and pentane; **Yield** : 99%; **^{1}H NMR** (400,13 MHz, $CDCl_3$) δ 7.68 - 7.65 (m, 4H), 7.40 - 7.16 (m, 22H), 6.84 - 6.82 (m, 4H), 4.98 (d, *J* = -14.9 Hz, 2H), 4.55 (d, *J* = -14.9 Hz, 2H); **^{13}C NMR** (100,61 MHz, $CDCl_3$) δ 145.74 - 145.72 (m (ABX)), 145.57 - 145.56 (m (ABX)), 13.49 - 135.44 (m (ABX)), 134.92 - 134.87 (m (ABX)), 134.48 (d, *J* = 21.7 Hz), 133.38 (s), 133.30 (d, *J* = 20.7 Hz), 130.56 (d, *J* = 44.4 Hz), 129.14 (d, *J* = 65 Hz), 128.93 (s), 128.67 (s), 128.67 - 128.59(m (ABX)), 128.41-128.32 (m (ABX)), 128.22 (s), 52.49 - 52.45 (m (ABX)); **^{31}P NMR** (161.97 MHz, $CDCl_3$) δ - 37.97 (s); **HRMS (EI):** *m/z* Calcd. for $C_{42}H_{34}N_6P_2$ $[M+H]^+$:685.23; Found: 685.2398; **mp** : 205.4-206.5 °C.

III.3. 4,4'bis(diphenylphosphino)-1,1'-dibutyl-5,5'-bis-1,2,3-triazole, 11-Bu



The compound was isolated as a white solid after precipitation with diethylether and pentane; **Yield** : 98%; **^{1}H NMR** (400,13 MHz, $CDCl_3$) δ 7.48 - 7.58 (m, 4H), 7.30 - 7.22 (m, 6H), 7.21 - 7.06 (m, 10H), 3.96 - 3.78 (m, 4H), 1.63 - 1.50 (m, 4H), 1.08 - 0.89 (m, 4H), 0.63 (t, *J* = 7.4 Hz, 6H); **^{13}C NMR** (100,61 MHz, $CDCl_3$) δ 144.02 - 145.96 (m (ABX)), 144.88 - 144.82 m (ABX)), 135.51 - 135.46 (m (ABX)), 135.08 - 135.04 (m (ABX)), 134,37 - 134.14 (m (ABX)), 133.48 - 133.24 (m (ABX)), 130.64 (d, *J* = 44.9 Hz), 129.11 (d, *J* = 53.3 Hz), 128.71 - 128.59 (m (ABX)), 128.44 - 128.32 (m (ABX)), 49.07 (m (ABX)), 31.72 (m (ABX)), 19.81 (s), 13.30 (s); **^{31}P NMR** (161.97 MHz, $CDCl_3$) δ - 37.75 (s); **HRMS (EI):** *m/z* Calcd. for $C_{36}H_{38}N_6P_2$ $[M+H]^+$: 617.26; Found: 617.2715; mp : 154.1-155.0 °C.

III.4. 4,4'bis(diphenylphosphino)-1,1'-diisobutyl-5,5'-bis-1,2,3-triazole, 11-iBu



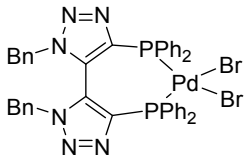
The compound was isolated as a white solid after precipitation with diethylether and pentane; **Yield** : 98%; **^{1}H NMR** (400,13 MHz, $CDCl_3$) δ 7.99 - 7.49 (m, 4H), 7.28 - 7.23 (m, 6H), 7.22 - 7.16 (m, 4H), 7.16 - 7.07 (m, 6H), 3.79 (dd, *J* = 7.6 Hz, *J* = 13.6 Hz, 2H), 3.67 (dd, *J* = 7.6 Hz, *J* = 13.6 Hz, 2H), 1.99 - 1.75 (m, 2H), 0.61 (d, *J* = 6.7 Hz, 6H), 0.58 (d, *J* = 6.7 Hz, 6H); **^{13}C NMR** (100,61 MHz, $CDCl_3$) δ 145.15 - 145.06 (m (ABX)), 144.96 - 144.91 (m (ABX)), 135.71 - 135.67 (m (ABX)), 135.05 - 135.00 (m (ABX)), 133.56 - 133.29 (m

(ABX)), 133.13 - 133.14 (m (ABX)), 131.20 (d, *J* = 1.20 Hz), 130.74 (d, *J* = 1.37 Hz), 129.06 (d, *J* = 66.8 Hz), 128.68 - 128.50 (m (ABX)), 128.42 - 128.24 (m (ABX)), 56.45 - 56.6 (m (ABX)), 45.85 (s), 28.68 (s), 19.88 (s); **^{31}P NMR** (161.97 MHz, $CDCl_3$) δ - 38.08 (s) ; **HRMS (EI):** *m/z* Calcd. for $C_{36}H_{38}N_6P_2$ $[M+H]^+$: 617.26 ; Found: 617.2714; **mp** : 154.2-154.8 °C.

IV. Synthesis of complexes 12-17

IV.1. Synthesis of the palladium complex 13

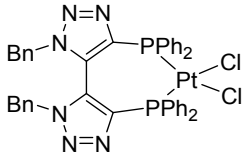
In a Schlenk tube under argon, a mixture of compound **11.1** (20 mg, 0.029 mmol) and bis(acetonitrile)dibromopalladium (10.1mg, 0.029 mmol) was dissolved in dry chloroform (2 ml). The reaction was carried out at room temperature for 2 hours. The solvent was evaporated and the resulting orange solid was washed by dry pentane. After evaporation of the solvent, 22.1 mg of **12.1** were obtained (yield = 80%).



^{1}H{^{31}P} NMR (500 MHz, $CDCl_3$) δ (ppm) : 7.98 (4H, m, PPh_2), 7.63 (4H, m, PPh_2), 7.52 (2H, m, PPh_2), 7.49 (2H, m, PPh_2), 7.46 (4H, m, PPh_2), 7.36 (4H, m, PPh_2), 7.32 (2H, m, Ph/Bn), 7.25 (4H, m, Ph/Bn), 6.77 (4H, m, Ph/Bn), 4.69 (2H, d, J = 15.7 Hz, NCH_2), 4.49 (2H, d, J = 15.7 Hz, NCH_2). **^{13}C{^{1}H} NMR (500 MHz, $CDCl_3$) δ (ppm) :** 141.7 (J_{CP} = 61.1 Hz, quat, PCN), 135.8 (J_{CP} = 6.5 Hz, PPh_2), 133.9 (J_{CP} =5.0 Hz, PPh_2), 132.9 (PPh_2), 132.1 (quat, Ph/Bn), 131.2 (PPh_2), 129.2 (J_{CP} = 6.3 Hz, PPh_2), 129.2 (Ph/Bn), 129.0 (Ph/Bn), 128.2 (quat, J_{CP} = 19.9 Hz, PPh_2), 127.7 (J_{CP} = 6.0 Hz, PPh_2), 127.6 (quat, PCCN)127.1 (Ph/Bn), 125.8 (quat, J_{CP} = 40.8 Hz, PPh_2), 52.5 (NCPh). **^{31}P{^{1}H} NMR (500 MHz, $CDCl_3$) δ (ppm):** 8.4. **HR/MS (ES+) m/e:** 871.0541 (M-Br, 100%) (calc. M: 871.0311).

IV.2. Synthesis of the platinum complex 14

In a Schlenk tube, under argon, a mixture of ligand **11.1** (20 mg, 0.029 mmol) and bis(benzonitrile)dichloroplatinum (13.7 mg, 0.029 mmol) was dissolved in dry chloroform (2 ml). The reaction was carried out at reflux for 2 hours. The solvent was evaporated and the resulting white solid was washed by dry pentane. After evaporation of the solvent, 19.3 mg of **14.1** were obtained (yield = 70%).

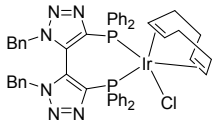


^{1}H{^{31}P} NMR (500 MHz, $CDCl_3$) δ (ppm) : 7.93 (4H, m, PPh_2), 7.63 (4H, m, , PPh_2), 7.50 (2H, m, , PPh_2), 7.48 (2H, m, , PPh_2), 7.45 (4H, m, , PPh_2), 7.34 (4H, m,), 7.33 (2H, m, Ph/Bn), 7.25 (4H, m, Ph/Bn), 6.77 (4H, m, Ph/Bn), 4.74 (2H, d, J = 15.3 Hz, NCH_2), 4.60 (2H, d, J = 15.3 Hz, NCH_2). **^{13}C{^{1}H} NMR (500 MHz, CDCl3) δ (ppm) :** 140.4 (J_{CP} = 82 Hz, quat, PCN), 135.4 (J_{CP} = 6.5 Hz, PPh_2), 134.2 (J_{CP} = 4.9 Hz,PPh_2), 132.8 (PPh_2), 132.2 (quat, Ph/Bn), 131.4 (PPh_2), 129.2 (Ph/Bn), 129.0 (PPh_2), 129.0 (Ph/Bn), 127.7 (J_{CP} = 6.0 Hz, PPh_2), 127.6 (J_{CP} = 6.4 Hz, quat, PCCN), 127.0 (Ph/Bn), 125.5 (quat, J_{CP} = 29.8 Hz, PPh_2), 125.1 (quat, J_{CP} = 41.2 Hz PPh_2), 52.6 (NCPh). **^{31}P{^{1}H} NMR (500 MHz, CDCl3) δ (ppm):** -5.1. **HR/MS (ES+) m/e:** 915.1645 (M-Cl, 100%) (calc. M: 915.2381).

A single crystal of **14** suitable for X-ray diffraction analysis was obtained by slow diffusion of pentane in a dichloromethane solution.

IV.3. Synthesis of the iridium complex 16

In a Schlenk tube under argon, a mixture of compound **11.1** (20 mg, 0.029 mmol) and $[Ir(cod)Cl]_2$ (9.8 mg, 0.015 mmol) was dissolved in dry dichloromethane (2 ml). The reaction was carried out at room temperature for 45 minutes. The solvent was evaporated and the resulting yellow solid was washed by dry pentane. After evaporation of the solvent, 29.3 mg of **16** were obtained (yield = 99%).

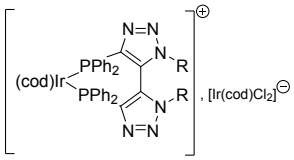


$^{1}H\{^{31}P\}$ NMR (500 MHz, $CDCl_3$) δ (ppm) : 7.75 (4H, m, PPh_2), 7.57 (4H, m, PPh_2), 7.44 (6H, m, PPh_2), 7.33 (2H, m, PPh_2), 7.25 (4H, m, PPh_2), 7.17 (2H, m, Ph/Bn), 7.07 (4H, m, Ph/Bn), 6.77 (4H, m, Ph/Bn), 4.65 (2H, d, J = 15.3 Hz, NCH_2), 4.58 (2H, d, J = 15.3 Hz, NCH_2), 3.67 (2H, m, COD), 3.13 (2H, m, COD), 2.00 (2H, m, COD), 1.74 (2H, m, COD), 1.69 (2H, m, COD), 1.53 (2H, m, COD). **$^{13}C\{^{1}H\}$ NMR (500 MHz, $CDCl_3$) δ (ppm) :** 144.9 (quat, J_{CP} = 49.1 Hz, PCN), 135.3 (J_{CP} = 11.7 Hz, PPh_2), 133.1 (J_{CP} = 9.4 Hz, PPh_2), 132.8 (quat, Ph/Bn), 132.6 (quat, PPh_2), 132.0 (quat, PPh_2), 130.3 (PPh_2), 129.4 (PPh_2), 128.8 (Ph/Bn), 128.4 (Ph/Bn), 128.3 (quat, J_{CP} = 26 Hz, PC<u>C</u>N)128.0 (PPh_2), 127.6 (PPh_2), 127.4 (Ph/Bn), 68.7 (J_{CP} = 7.9 Hz, COD), 67.0 (J_{CP} = 6.8 Hz, COD), 52.5 (NCPh), 32.9 (COD), 32.1 (COD). **$^{31}P\{^{1}H\}$ NMR (500 MHz, $CDCl_3$) δ (ppm):** -17.8. **HR/MS (ES+) m/e:** 985.2919 (M-Cl, 80%) (calc. M: 985.2888).

A single crystal of **16** suitable for X-ray diffraction analysis has been obtained by slow diffusion of pentane in a dichloromethane solution.

IV.4. Synthesis of the iridium complex 17

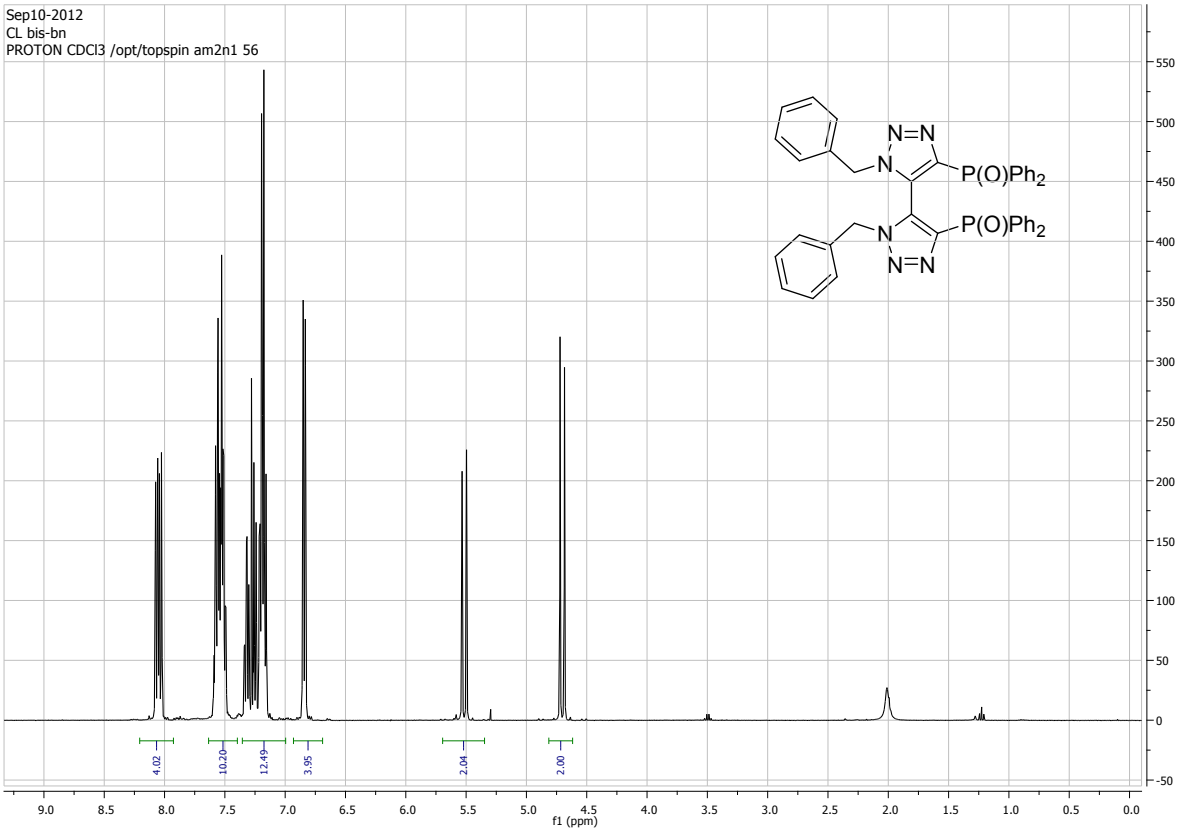
In a Schlenk tube under argon, a mixture of compound **11.1** (20 mg, 0.029 mmol) and $Ir(COD)Cl]_2$ (19.6 mg, 0.029 mmol) was dissolved in dry dichloromethane (4 ml). The mixture was strirred at room temperature for 45 minutes. The solvent was then evaporated and the resulting yellow solid was washed by dry pentane. After evaporation of the solvent, 35.4 mg of **17.1** were obtained (yield = 90%).

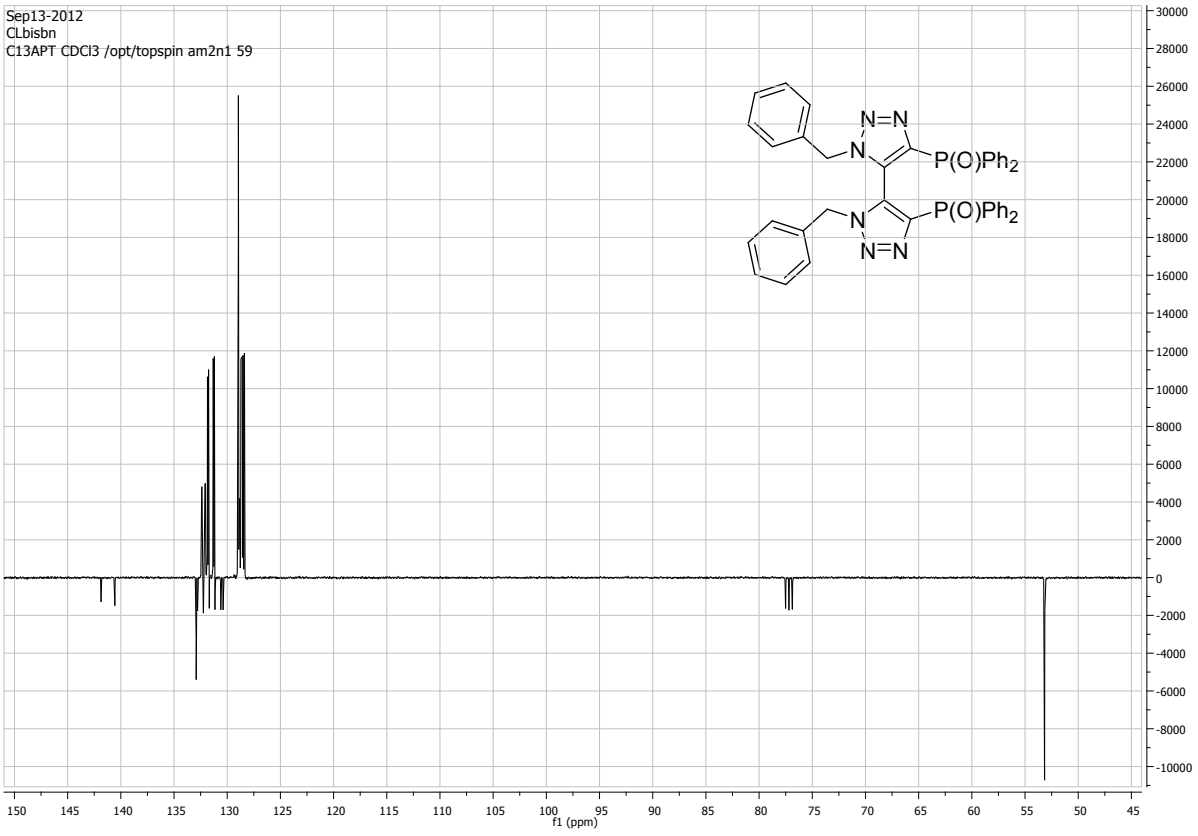


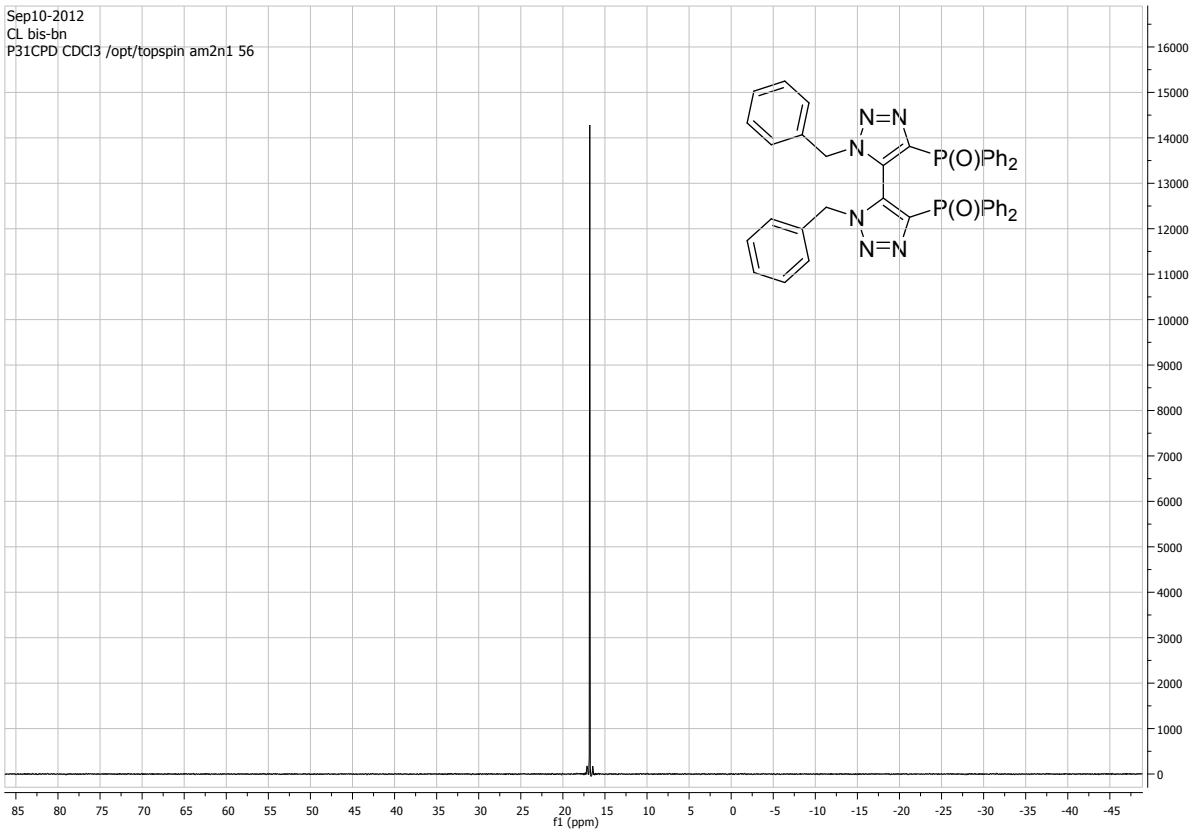
$^{1}H\{^{31}P\}$ NMR (500 MHz, $CDCl_3$) δ (ppm) : 7.67 (4H, m, PPh_2), 7.50 (4H, m, PPh_2), 7.50 (2H, m, PPh_2), 7.31 (2H, m, PPh_2), 7.30 (4H, m, PPh_2), 7.24 (4H, m, PPh_2), 6.97 (2H, m, Ph/Bn), 6.91 (4H, m, Ph/Bn), 6.63 (4H, m, Ph/Bn), 5.26 (2H,m, COD), 5.17 (2H, m, COD), 4.92 (2H, d, J = 15.6 Hz, NCH_2), 4.26 (2H, d, J = 15.6 Hz,NCH_2), 2.68 (2H, m, COD), 2.48 (2H, m, COD), 2.37 (2H, m, COD), 2.15 (4H, m, COD), 2.14 (2H, m, COD), 1.98 (2H, m, COD), 1.76 (2H, m, COD), 1.67 (2H, m, COD), 1.45 (2H, m, COD). **$^{13}C\{^{1}H\}$ NMR (500 MHz, $CDCl_3$) δ (ppm) :** 140.5 (quat, J_{CP} = 70.2 Hz, PCN), 137.4 (J_{CP} = 13.6 Hz, PPh_2), 133.5 (quat, Ph/Bn), 132.6 (J_{CP} = 9.0 Hz, PPh_2), 132.0 (PPh_2), 130.1 (PPh_2), 128.3 (Ph/Bn), 128.2 (J_{CP} = 11.2 Hz, PPh_2), 127.7 (J_{CP} = 10.8 Hz, PPh_2), 127.6 (Ph/Bn), 127.3 (Ph/Bn), 127.1 (quat, J_{CP} = 11.0 Hz, PC<u>C</u>N), 125.3 (quat, J_{CP} = 53.9 Hz, PPh_2), 94.8 (J_{CP} = 13.4 Hz, COD), 94.3 (J_{CP} = 16.1 Hz, COD), 55.4 (COD), 53.2 (COD), 51.7 (NCPh), 34.3 (COD), 32.1 (COD), 29.9 (COD), 29.1 (COD). **$^{31}P\{^{1}H\}$ NMR (500 MHz, $CDCl_3$) δ (ppm):** 8.7. **HR/MS (ES+) m/e:** 985.2916 (M of cation, 100%) (calc. M: 985.2888).

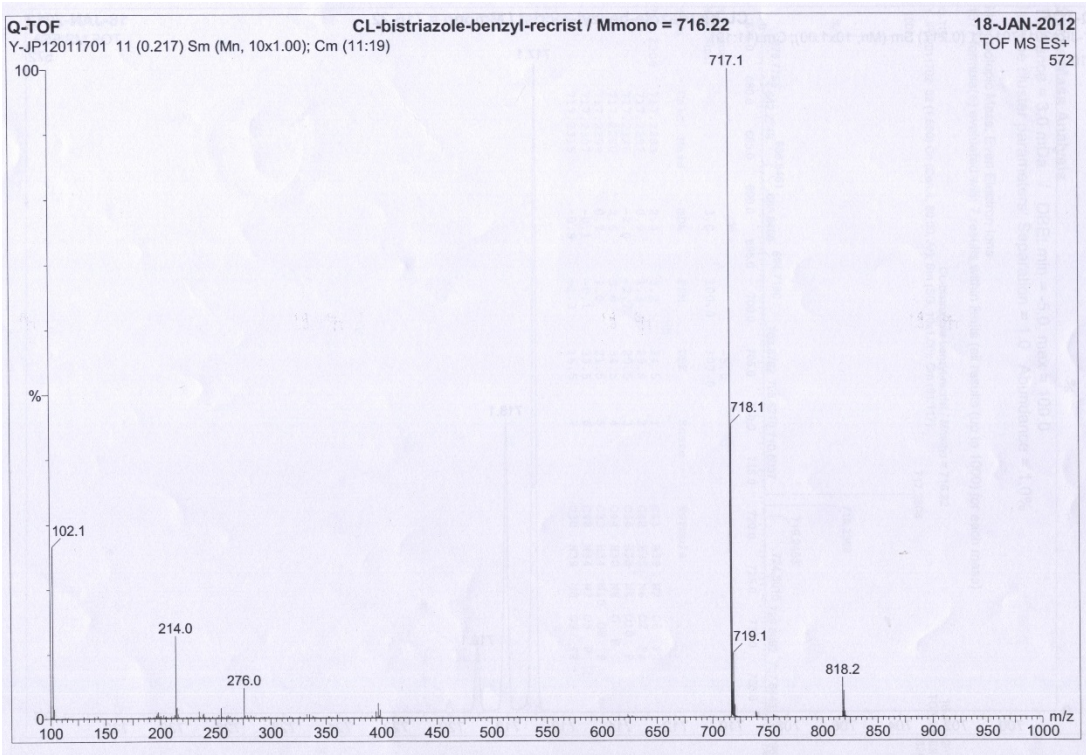
V. Copies of spectra for phosphane oxides 8.1-8.7

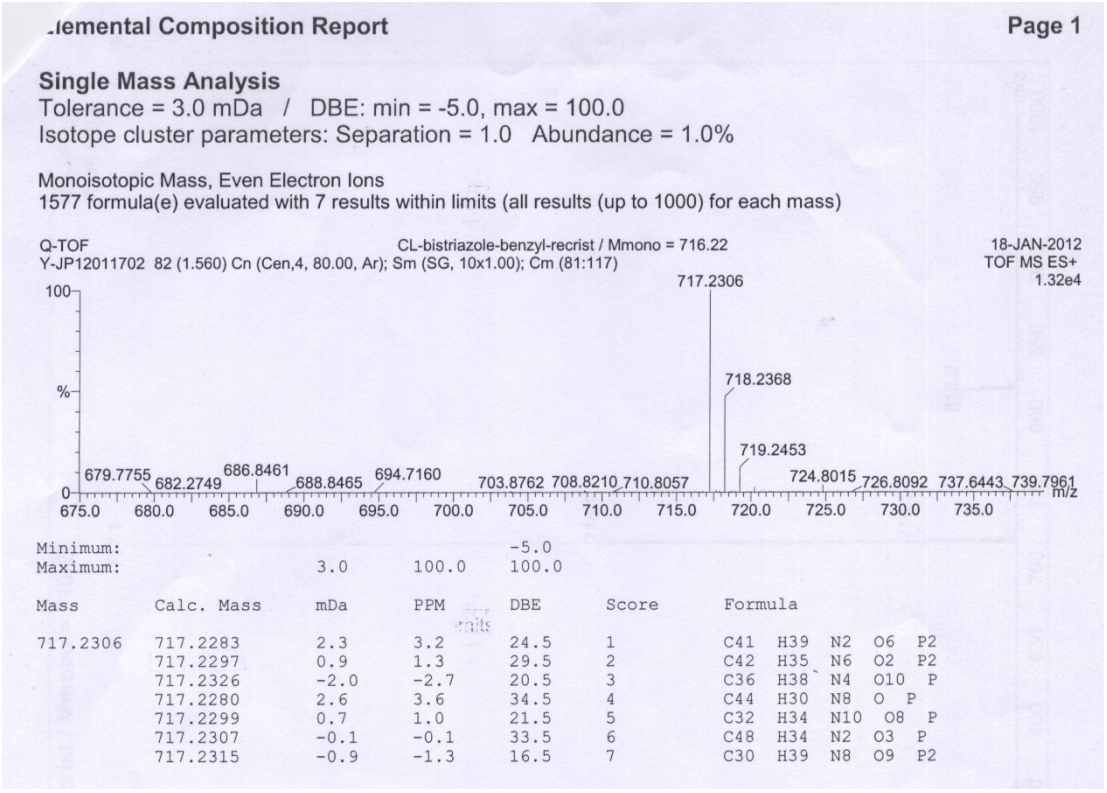
V.1. 4,4'-bis(diphenylphosphinoxy)-1,1'-dibenzyl-5,5'-bis-1,2,3-triazole 8.1



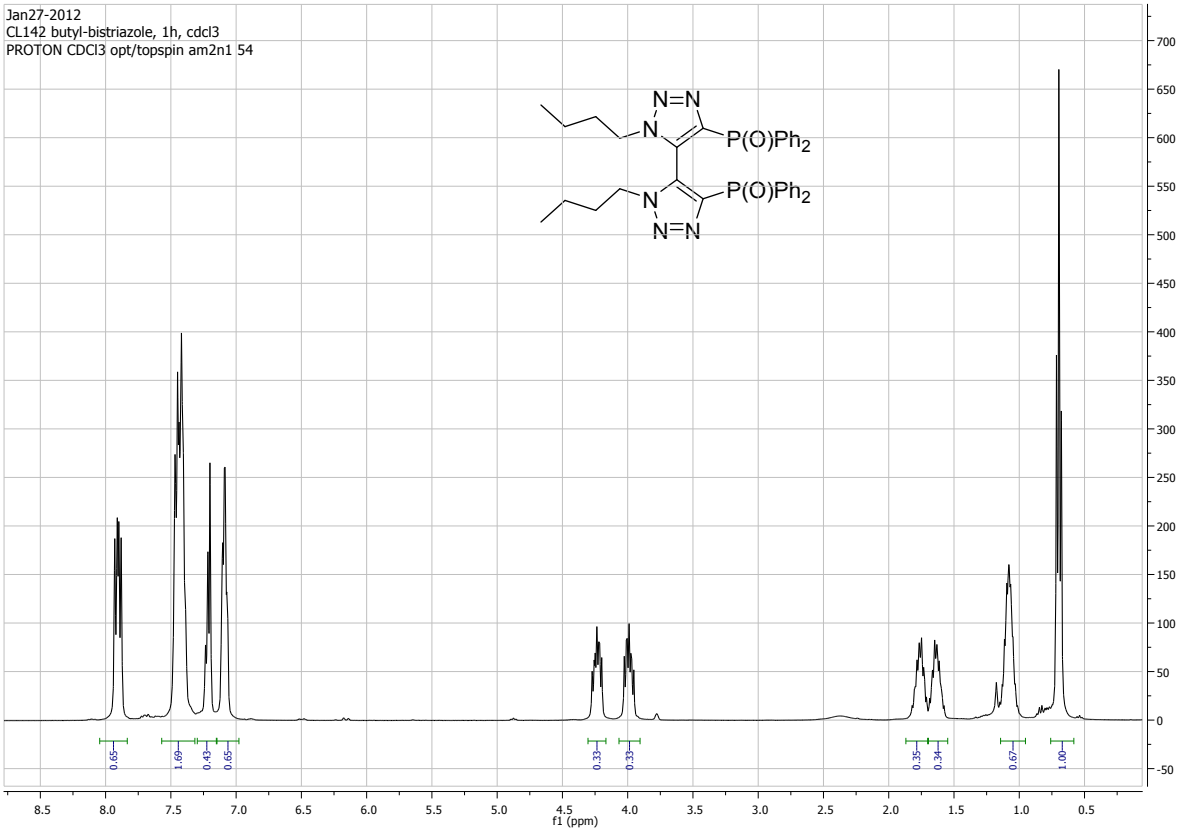


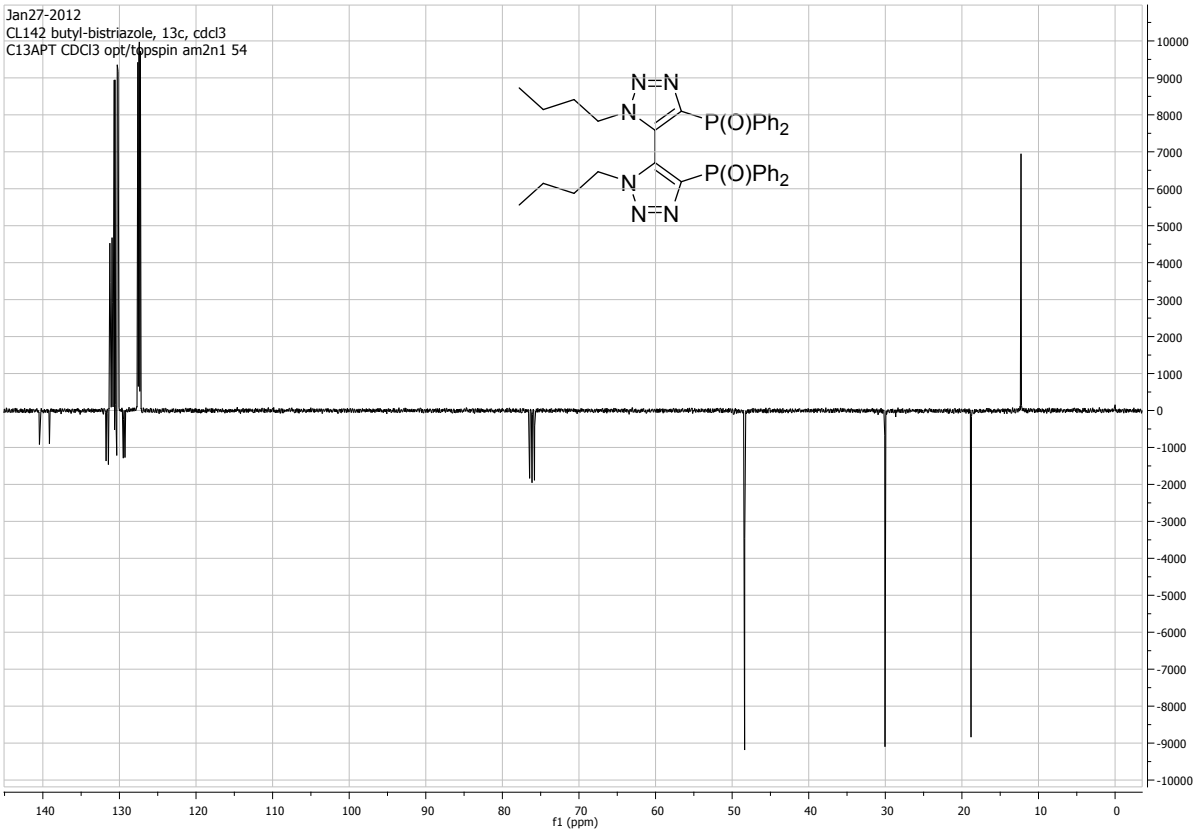

Sep10-2012
CL bis-bn
P31CPD CDCl3 /opt/topspin am2n1 56
N=N
N
P(O)Ph2
P(O)Ph2
N
N=N
f1 (ppm)

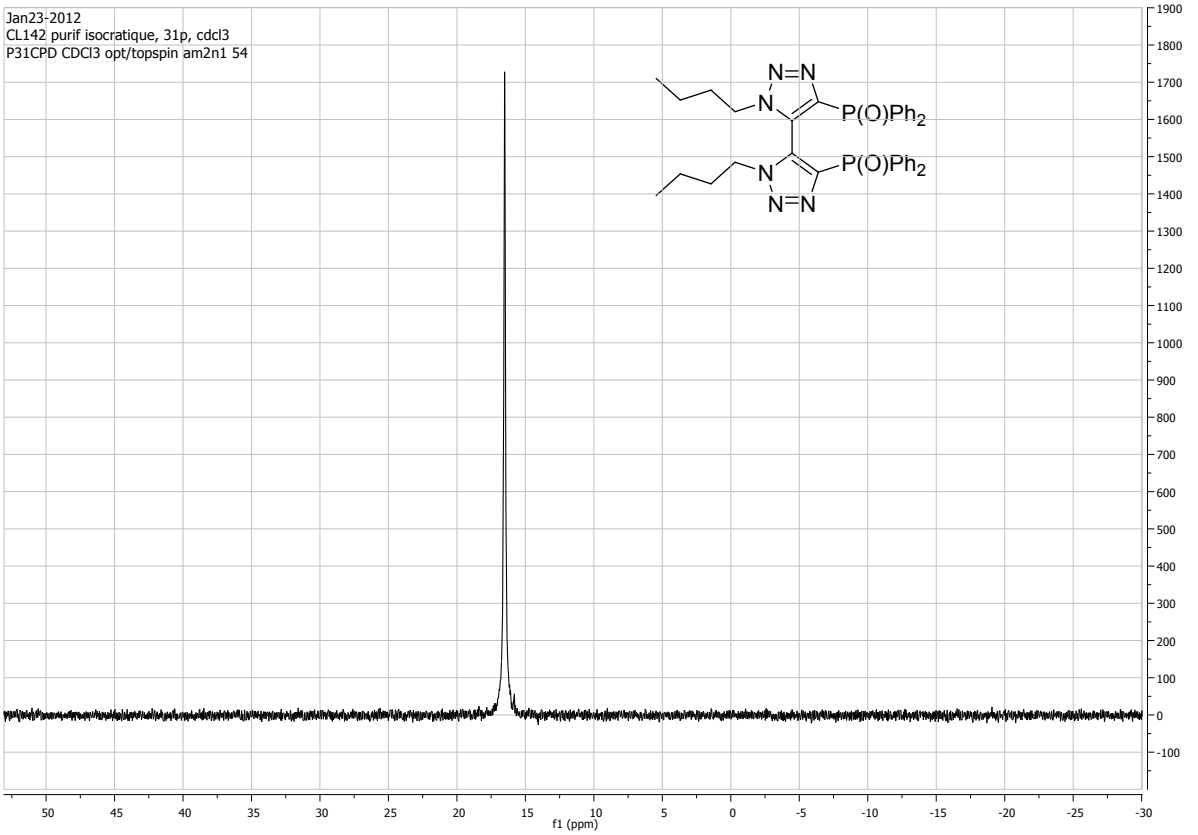

Q-TOF
CL-bistriazole-benzyl-recrist / Mmono = 716.22
18-JAN-2012
Y-JP12011701 11 (0.217) Sm (Mn, 10x1.00); Cm (11:19)
TOF MS ES+
572
717.1
718.1
719.1
818.2
102.1
214.0
276.0
%
m/z



V.2. 4,4’-bis(diphenylphosphinoxy)-1,1-dibutyl-5,5’-bis-1,2,3-triazole 8.2




Jan27-2012
CL142 butyl-bistriazole, 13c, cdcl3
C13APT CDCl3 opt/topspin am2n1 54
N=N
N
P(O)Ph2
P(O)Ph2
N
N=N
f1 (ppm)


Jan23-2012
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P31CPD CDCl3 opt/topspin am2n1 54
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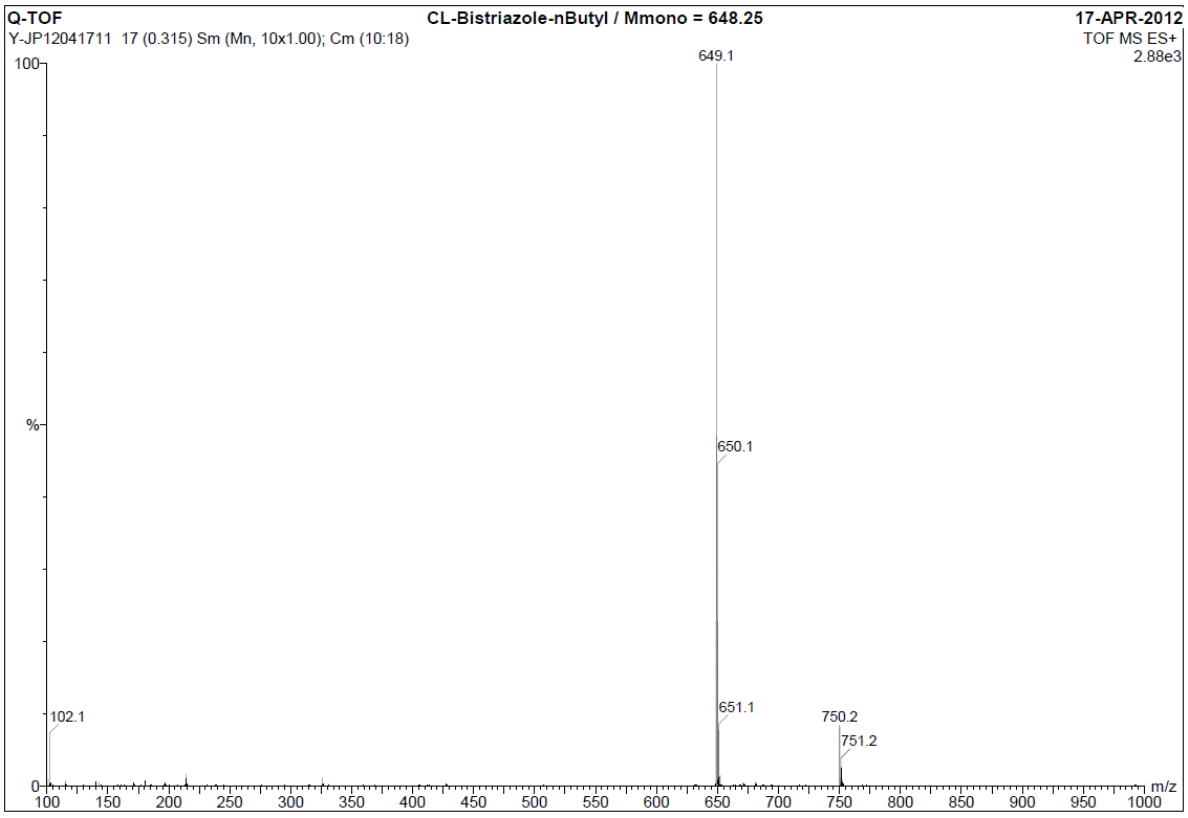
N
P(O)Ph2
P(O)Ph2
N
N=N
f1 (ppm)



mental Composition Report

Page 1

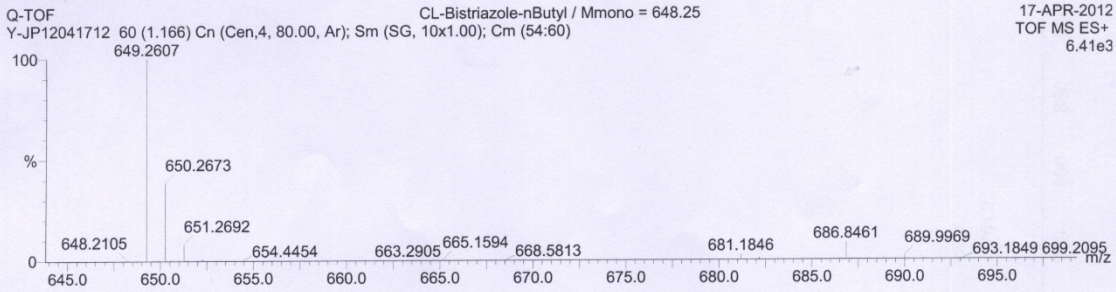
Single Mass Analysis

Tolerance = 3.0 mDa / DBE: min = -10.0, max = 100.0

Isotope cluster parameters: Separation = 1.0 Abundance = 1.0%

Monoisotopic Mass, Even Electron Ions

767 formula(e) evaluated with 3 results within limits (all results (up to 1000) for each mass)



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Maximum:		3.0	10.0	100.0		
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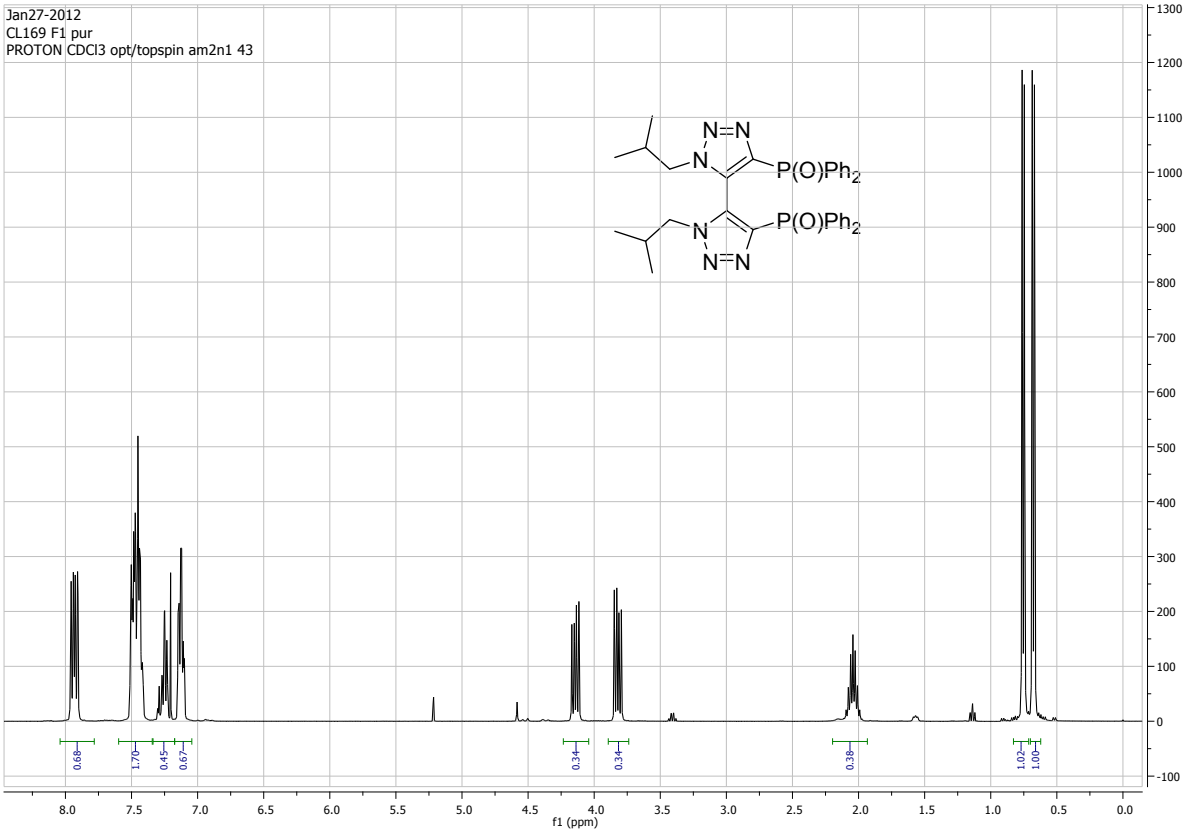
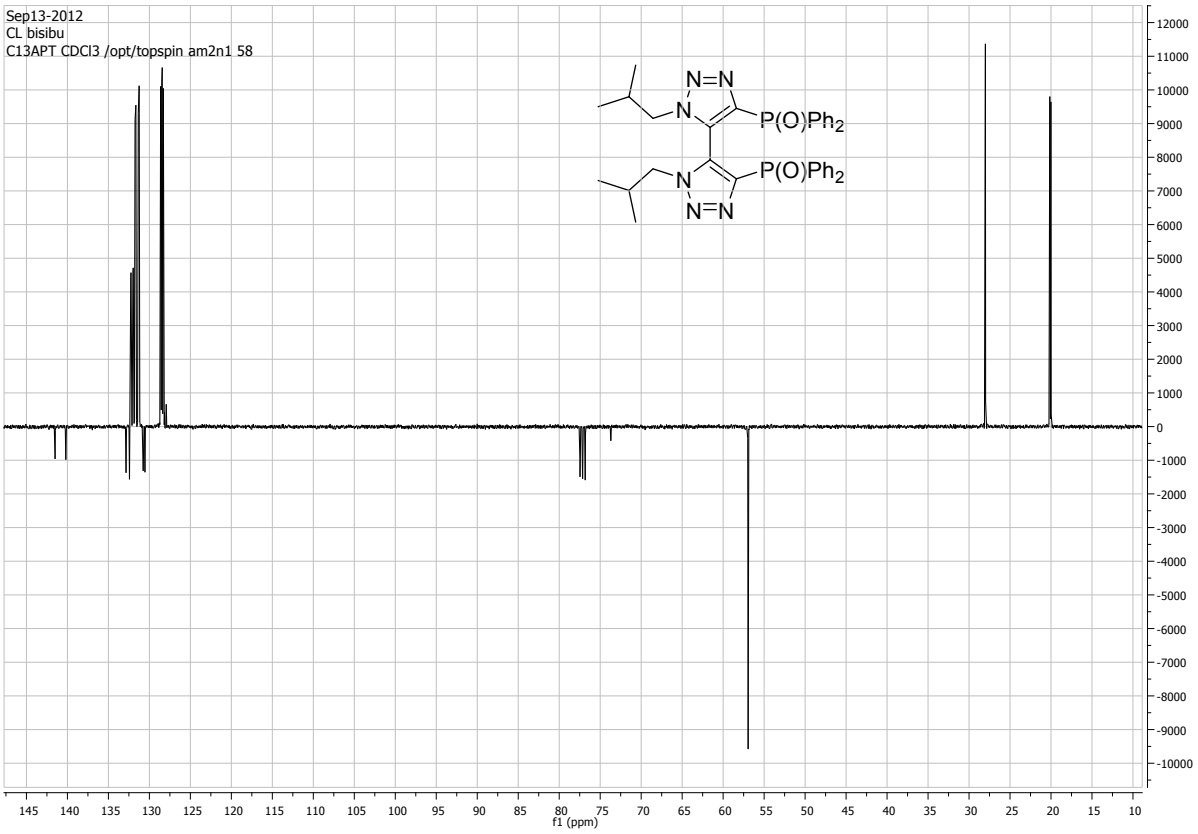
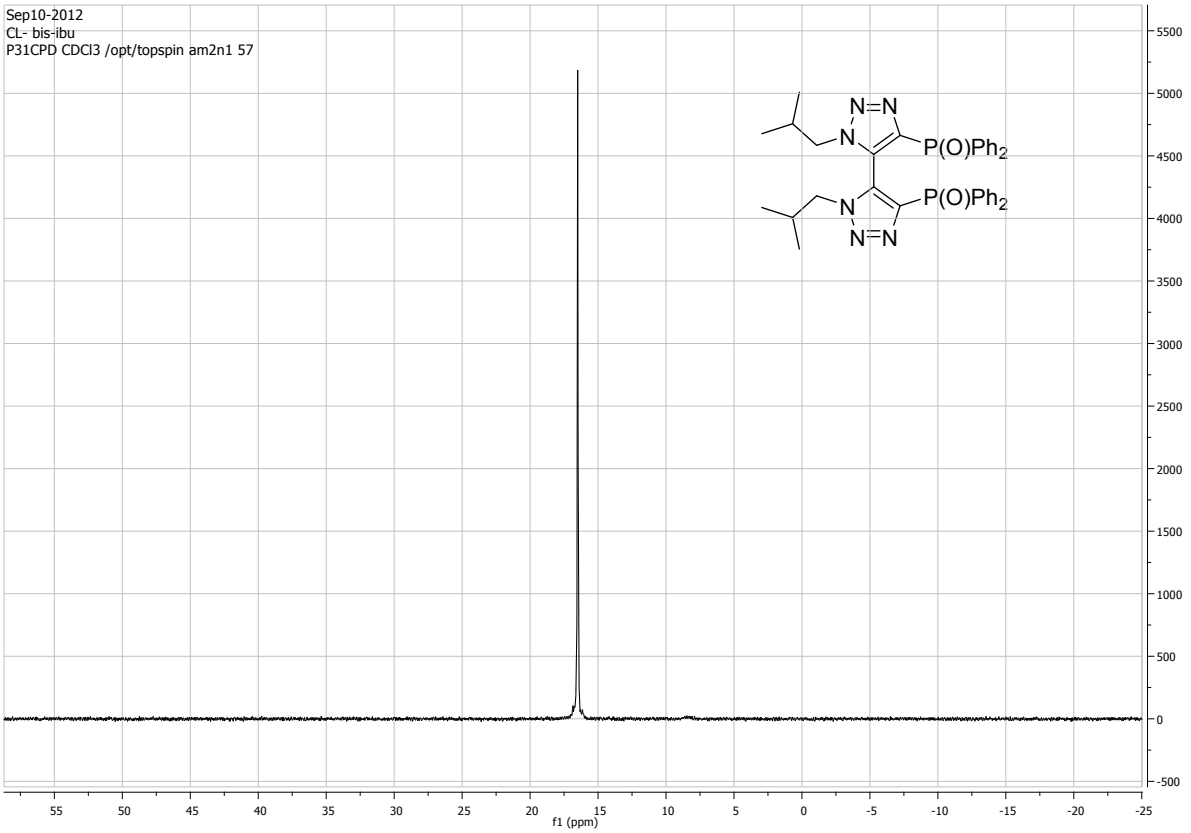
	649.2610	-0.3	-0.4	21.5	2	C36 H39 N6 O2 P2
	649.2628	-2.1	-3.3	8.5	3	C24 H43 N8 O9 P2

V.3. 4,4’-bis(diphenylphosphinoxy)-1,1’-diisobutyl-5,5’-bis-1,2,3-triazole 8.3






Sep10-2012
CL- bis-ibu
P31CPD CDCl3 /opt/topspin am2n1 57
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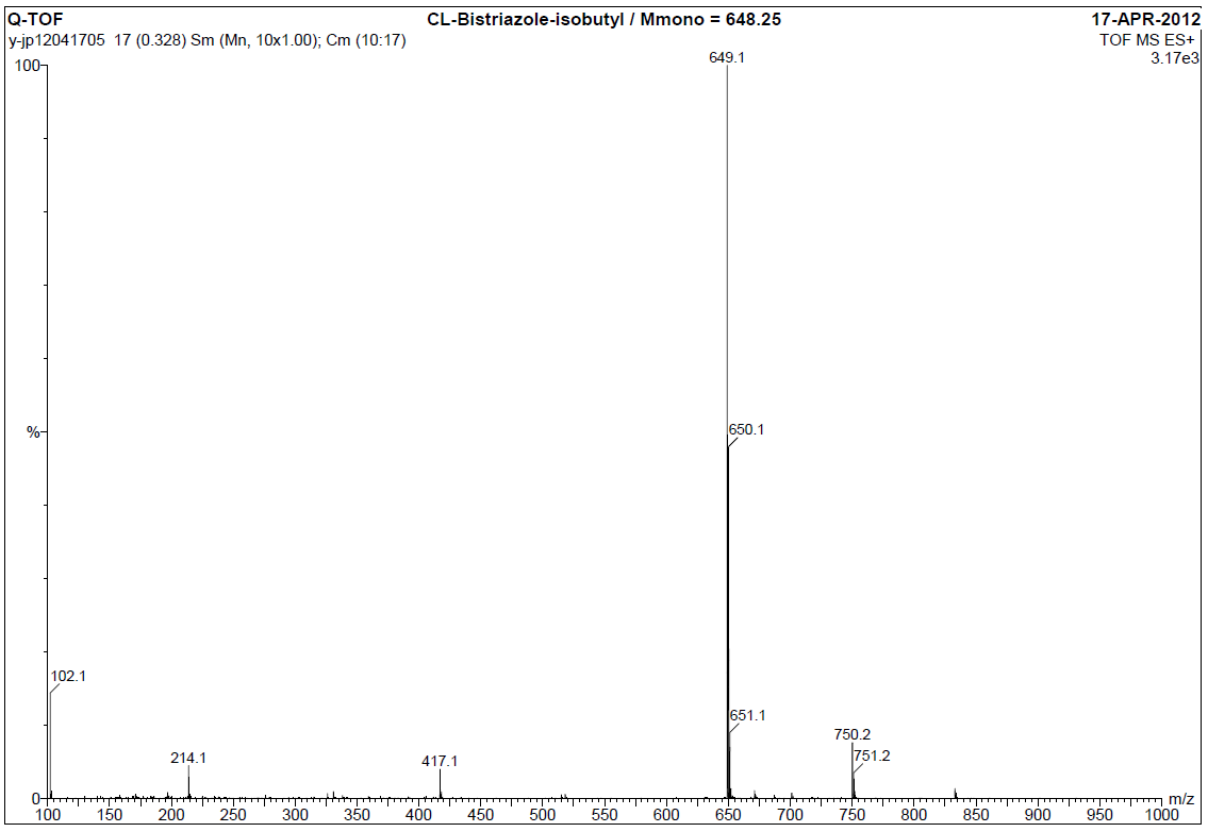
N
P(O)Ph2
N
P(O)Ph2
N=N
f1 (ppm)

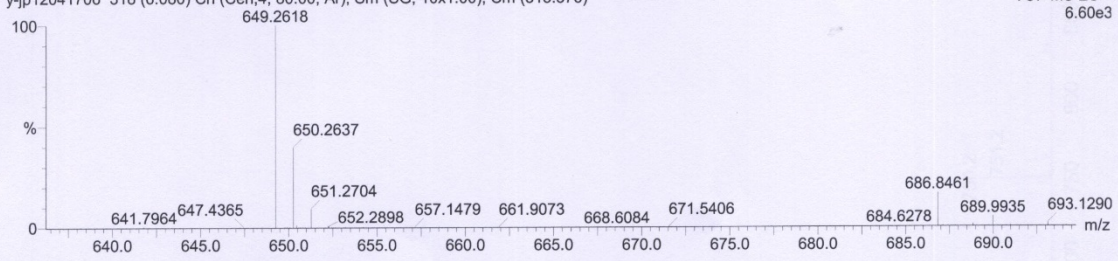

Q-TOF
CL-Bistriazole-isobutyl / Mmono = 648.25
17-APR-2012
y-jp12041705 17 (0.328) Sm (Mn, 10x1.00); Cm (10:17)
TOF MS ES+
3.17e3
649.1
650.1
102.1
651.1
750.2
751.2
214.1
417.1
%
m/z

Elemental Composition Report Page 1

Single Mass Analysis
Tolerance = 3.0 mDa / DBE: min = -10.0, max = 100.0
Isotope cluster parameters: Separation = 1.0 Abundance = 1.0%

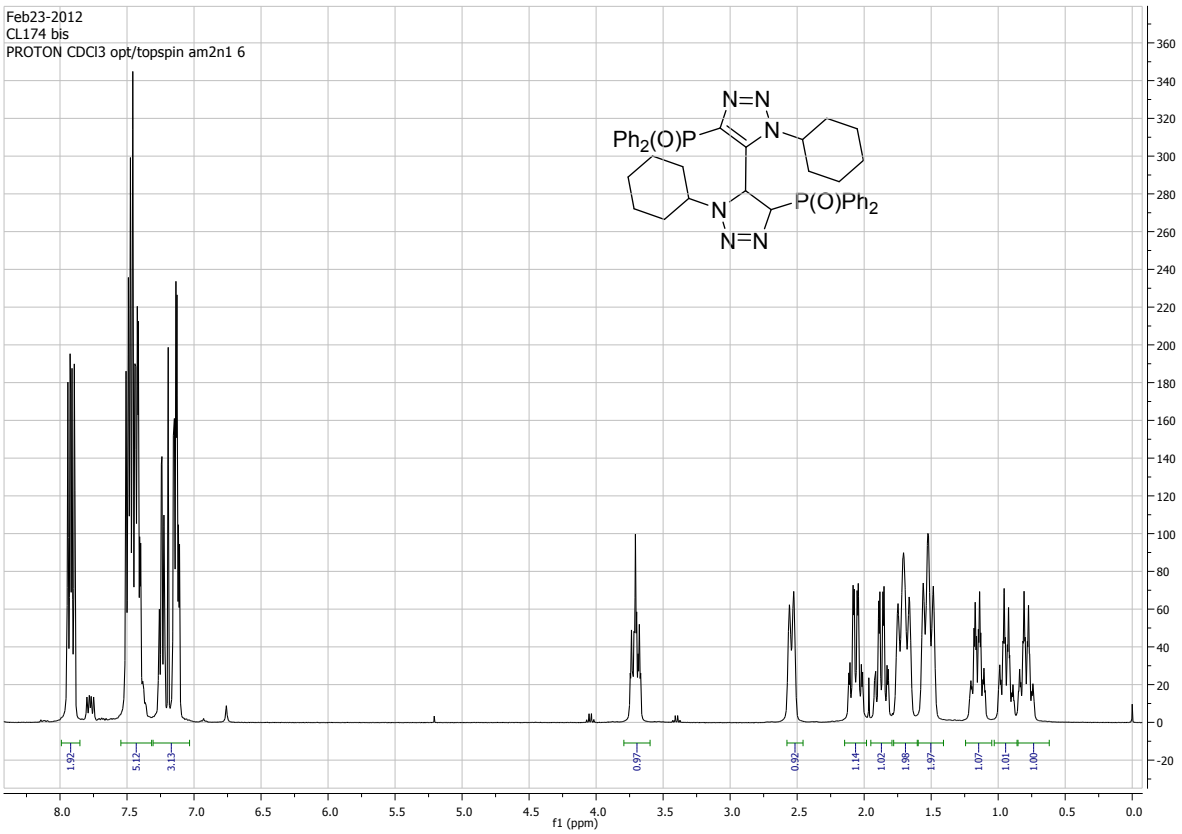
Monoisotopic Mass, Even Electron Ions
767 formula(e) evaluated with 3 results within limits (all results (up to 1000) for each mass)

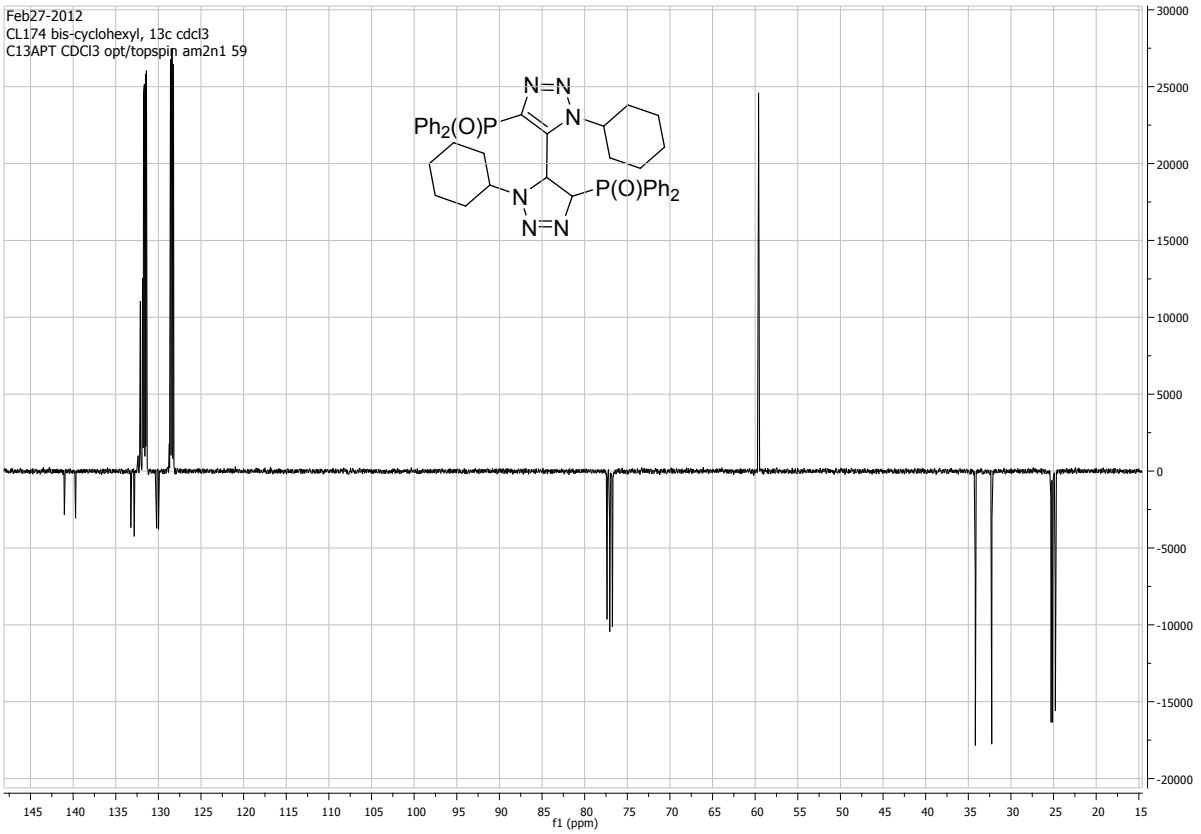
Q-TOF CL-Bistriazole-isobutyl / Mmono = 648.25 17-APR-2012
y-jp12041706 318 (6.080) Cn (Cen,4, 80.00, Ar); Sm (SG, 10x1.00); Cm (315:376) TOF MS ES+
6.60e3



Minimum:				-10.0		
Maximum:		3.0	10.0	100.0		
Mass	Calc. Mass	mDa	PPM	DBE	Score	Formula
649.2618	649.2596	2.2	3.3	16.5	1	C35 H43 N2 O6 P2
	649.2610	0.8	1.3	21.5	2	C36 H39 N6 O2 P2
	649.2628	-1.0	-1.6	8.5	3	C24 H43 N8 O9 P2

V.4. 4,4’-bis(diphenylphosphinoxy)-1,1’-dicyclohexyl-5,5’-bis-1,2,3-triazole 8.4




Feb27-2012
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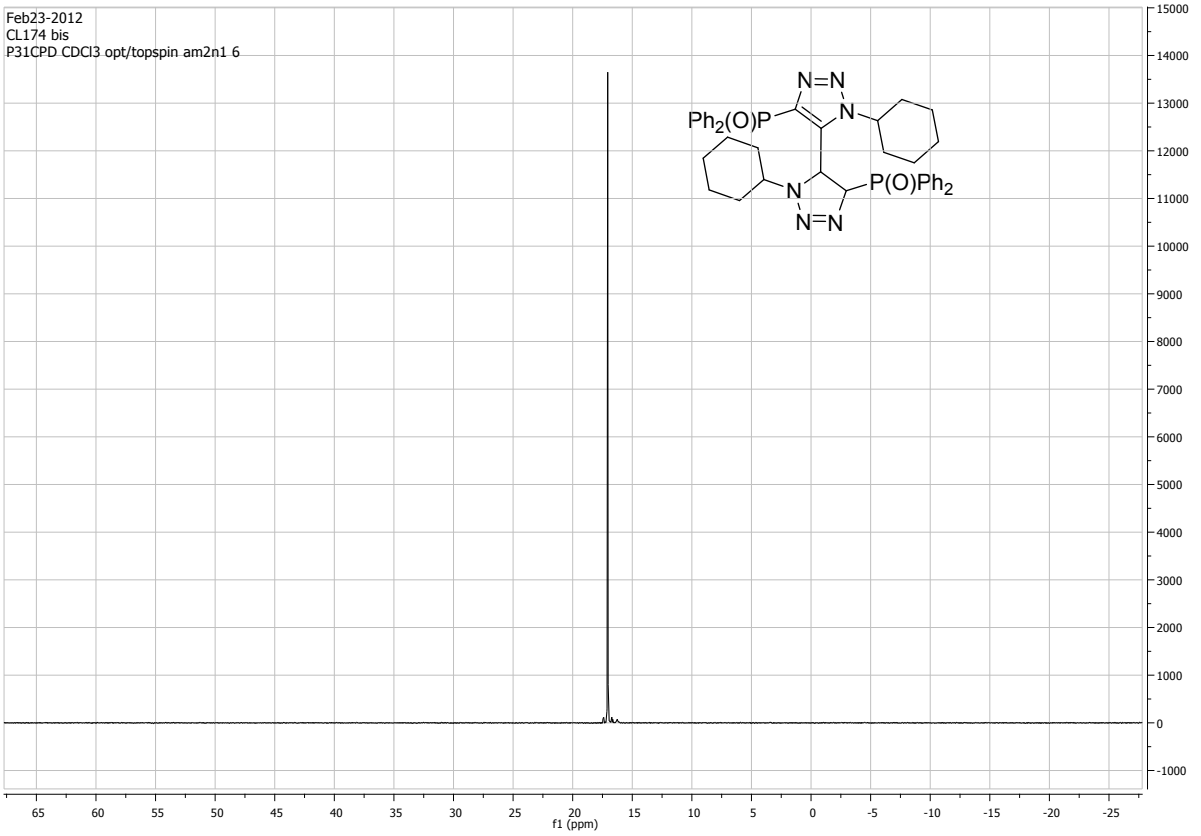
C13APT CDCl3 opt/topspin am2n1 59
Ph2(O)P
P(O)Ph2
f1 (ppm)


Feb23-2012
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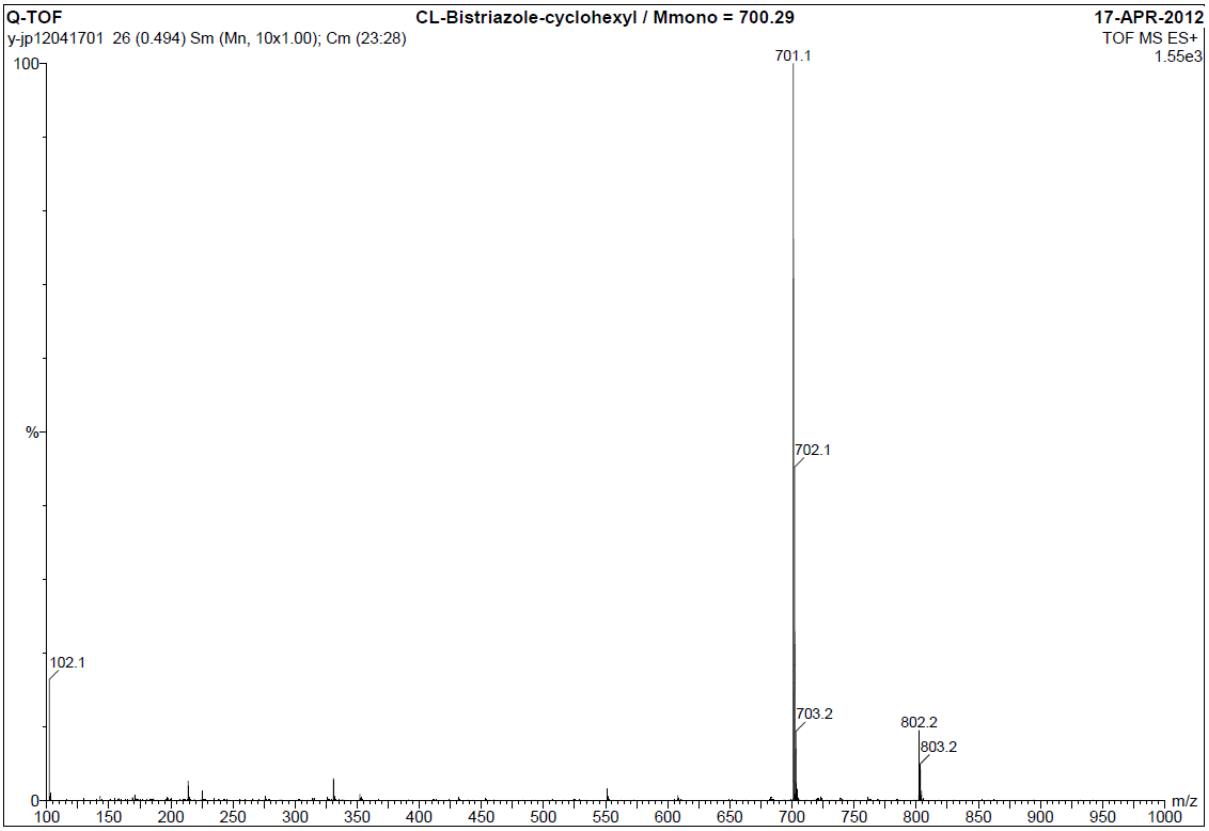
P31CPD CDCl3 opt/topspin am2n1 6
Ph2(O)P
P(O)Ph2
f1 (ppm)



Elemental Composition Report

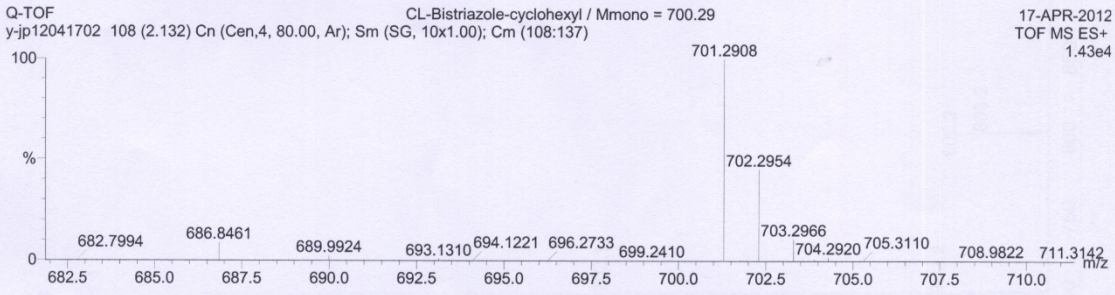
Single Mass Analysis

Tolerance = 3.0 mDa / DBE: min = -10.0, max = 100.0

Isotope cluster parameters: Separation = 1.0 Abundance = 1.0%

Monoisotopic Mass, Even Electron Ions

831 formula(e) evaluated with 3 results within limits (all results (up to 1000) for each mass)



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Maximum:		3.0	10.0	100.0		
Mass	Calc. Mass	mDa	PPM	DBE	Score	Formula
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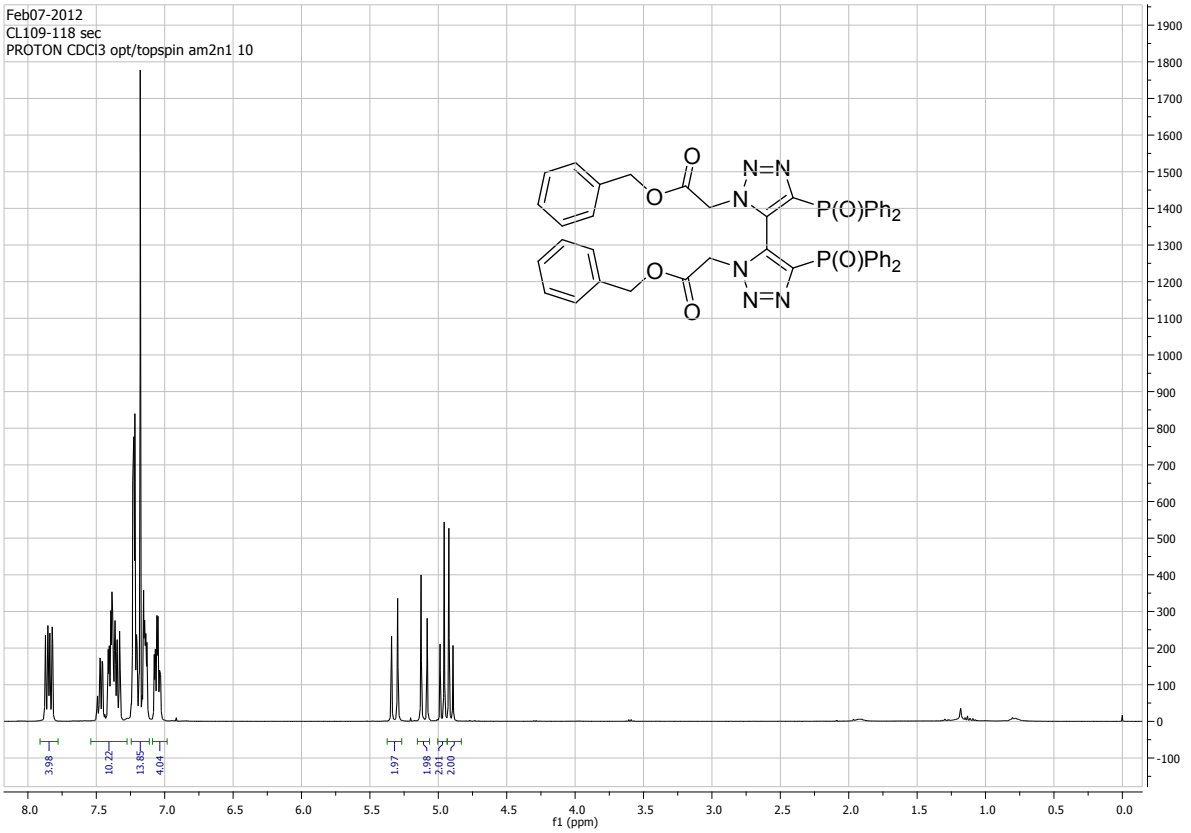
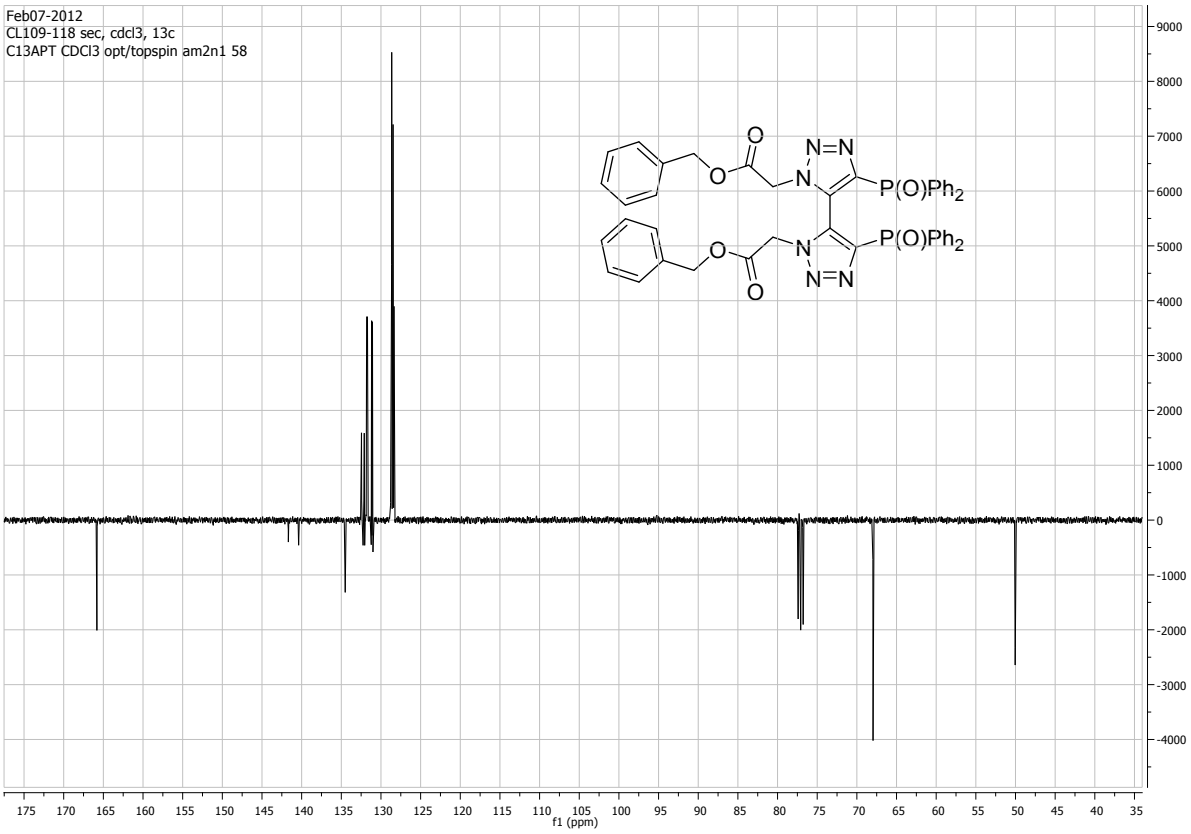
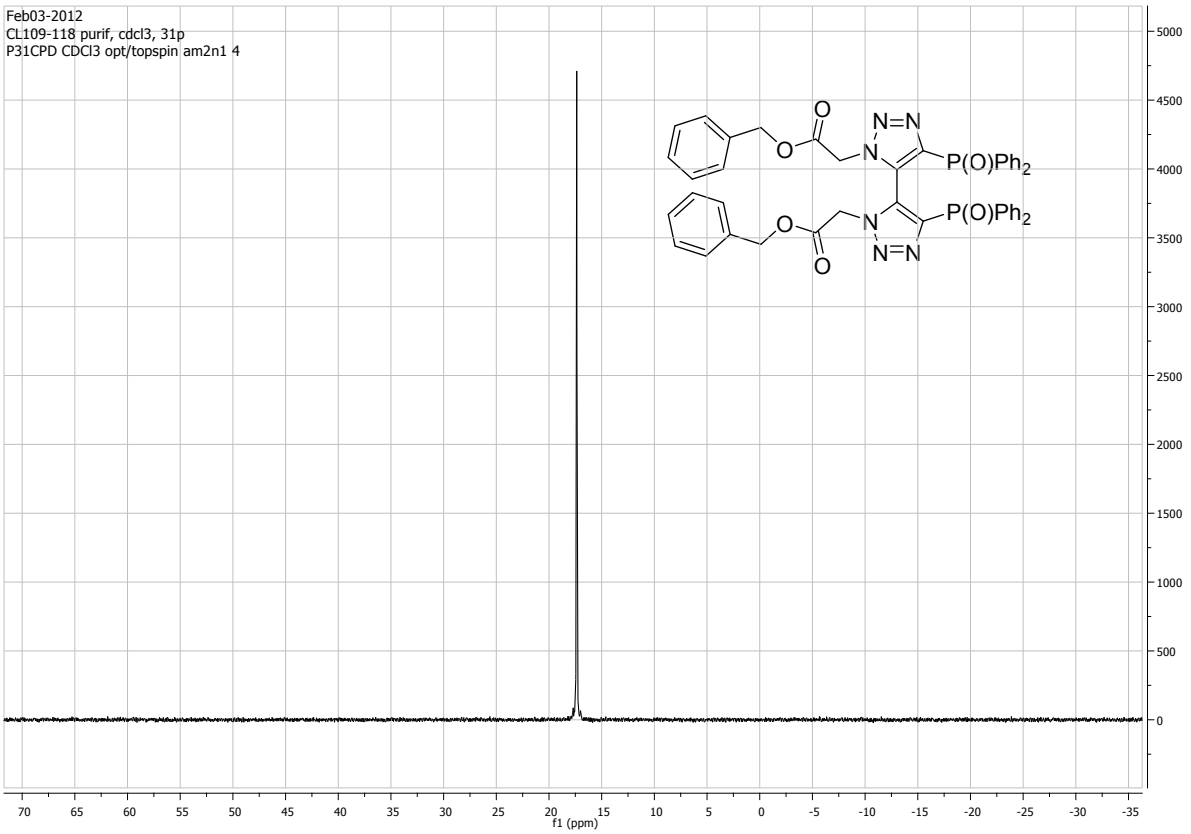
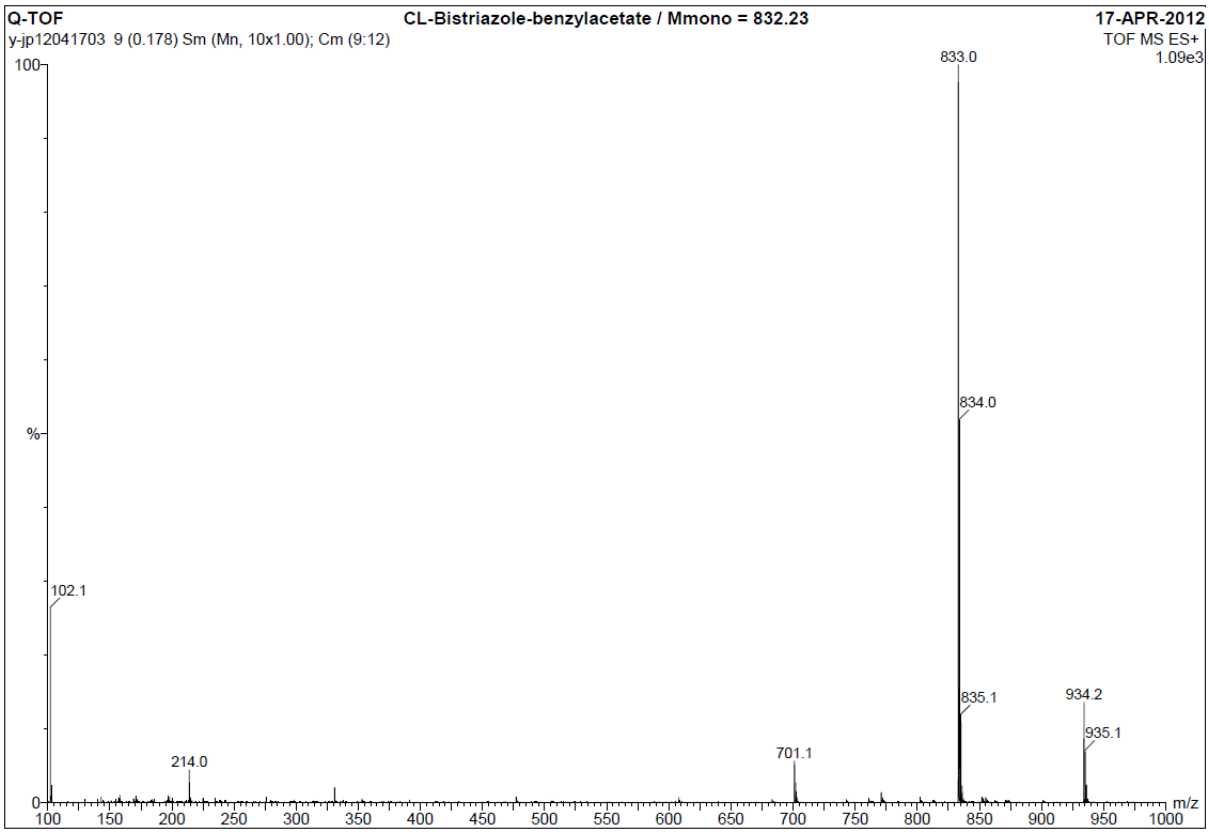
	701.2923	-1.5	-2.1	23.5	2	C40 H43 N6 O2 P2
	701.2883	2.5	3.6	19.5	3	C35 H43 N8 O4 P2

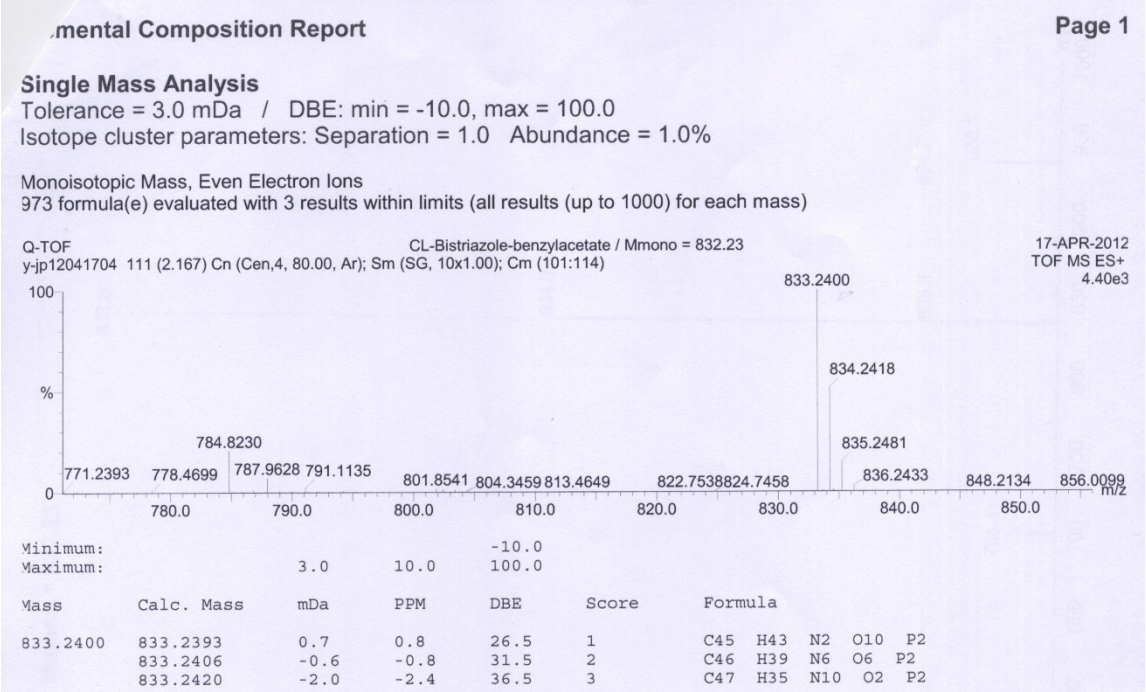
V.5. 4,4’-bis(diphenylphosphinoxy)-1,1’-bis(benzyloxyacetyl)-5,5’-bis-1,2,3-triazole 8.5



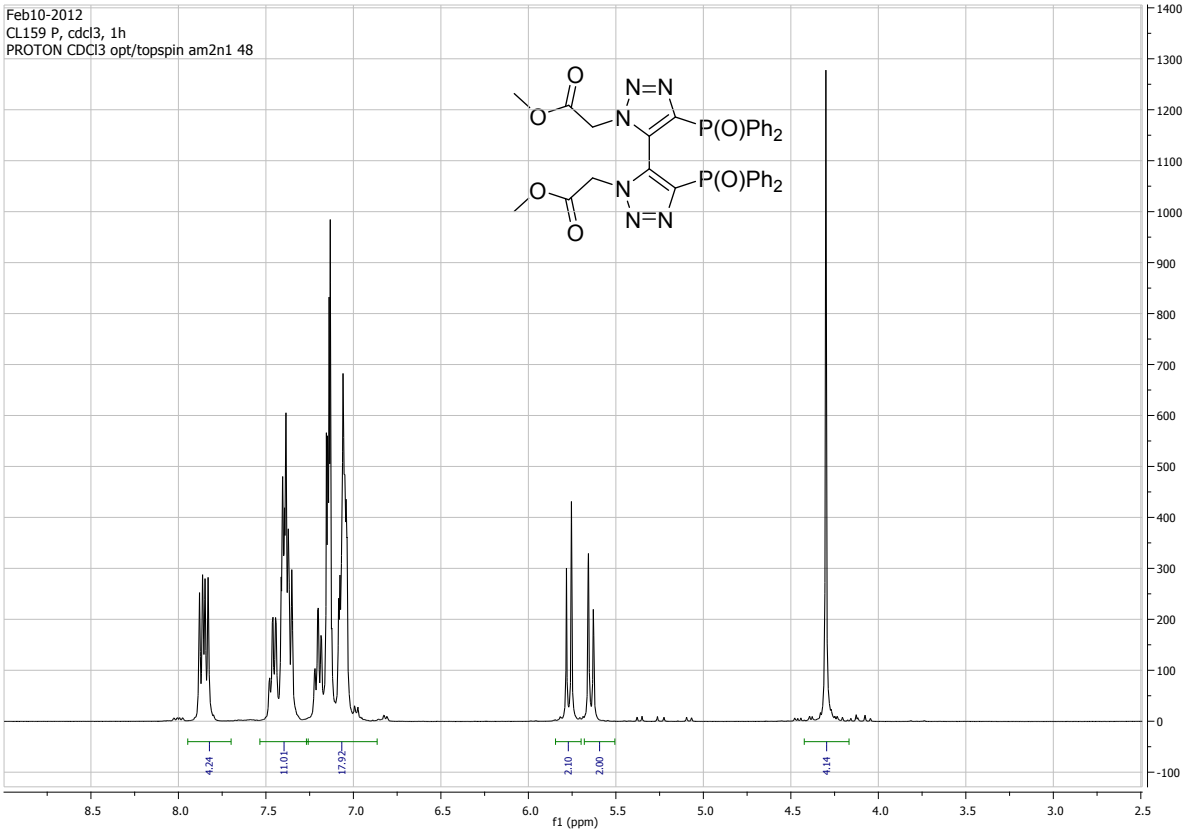


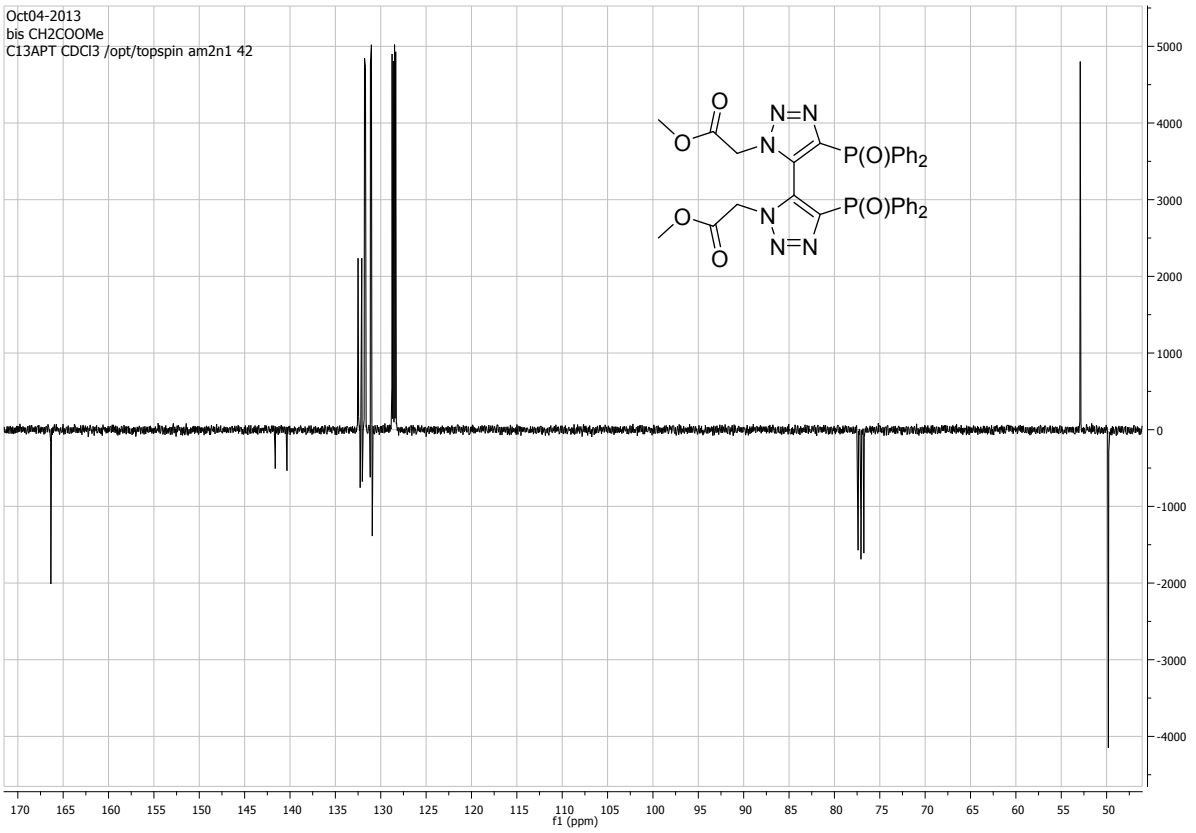

Feb03-2012
CL109-118 purif, cdcl3, 31p
P31CPD CDCl3 opt/topspin am2n1 4
P(O)Ph2
P(O)Ph2
f1 (ppm)

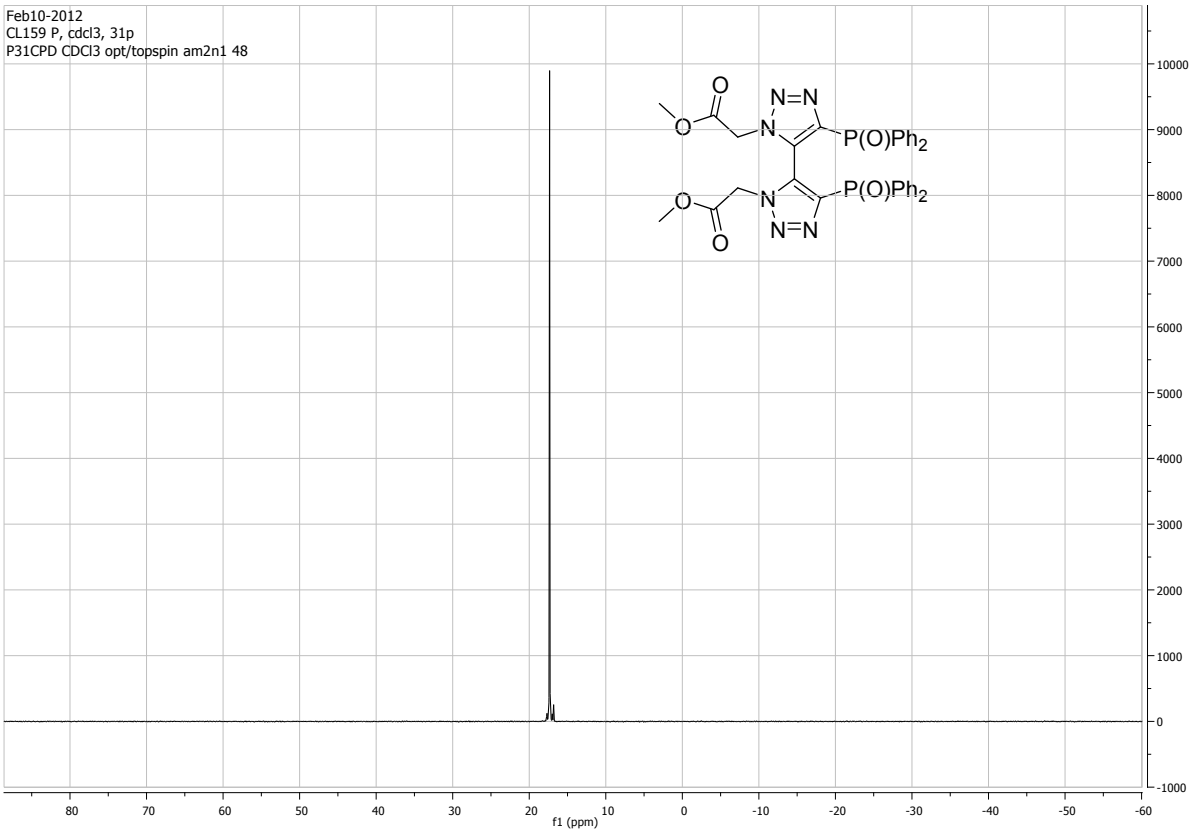

Q-TOF
CL-Bistriazole-benzylacetate / Mmono = 832.23
17-APR-2012
y-jp12041703 9 (0.178) Sm (Mn, 10x1.00); Cm (9:12)
TOF MS ES+
1.09e3
833.0
834.0
102.1
835.1
934.2
935.1
214.0
701.1
%
m/z

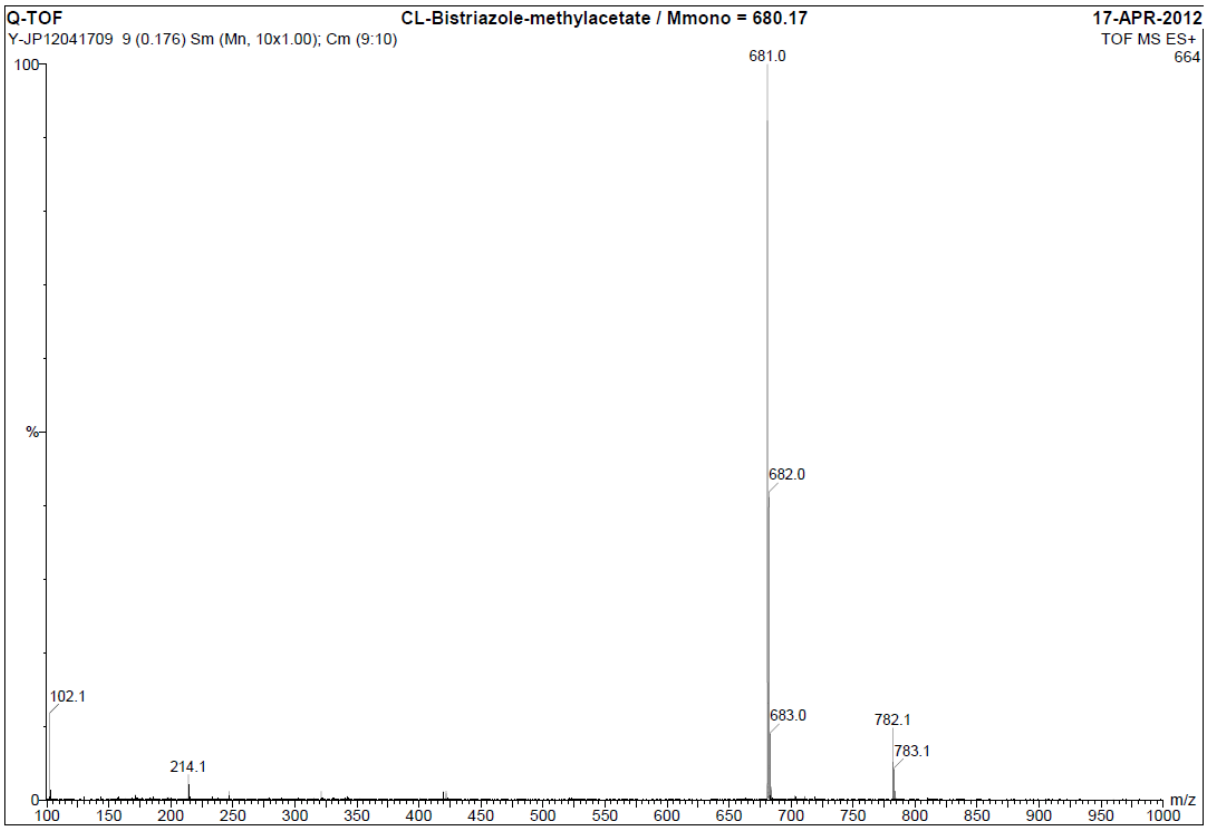


V.6. 4,4’-bis(diphenylphosphinoxy)-1,1’-bis(methoxyacetyl) -5,5’-bis-1,2,3-triazole dioxide 8.6




Oct04-2013
bis CH2COOMe
C13APT CDCl3 /opt/topspin am2n1 42
P(O)Ph2
P(O)Ph2
f1 (ppm)


Feb10-2012
CL159 P, cdcl3, 31p
P31CPD CDCl3 opt/topspin am2n1 48
P(O)Ph2
P(O)Ph2
f1 (ppm)



Elemental Composition Report

Page 1

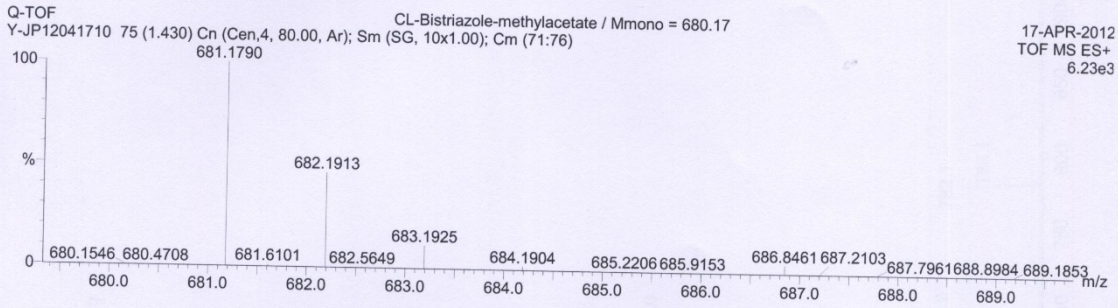
Single Mass Analysis

Tolerance = 3.0 mDa / DBE: min = -10.0, max = 100.0

Isotope cluster parameters: Separation = 1.0 Abundance = 1.0%

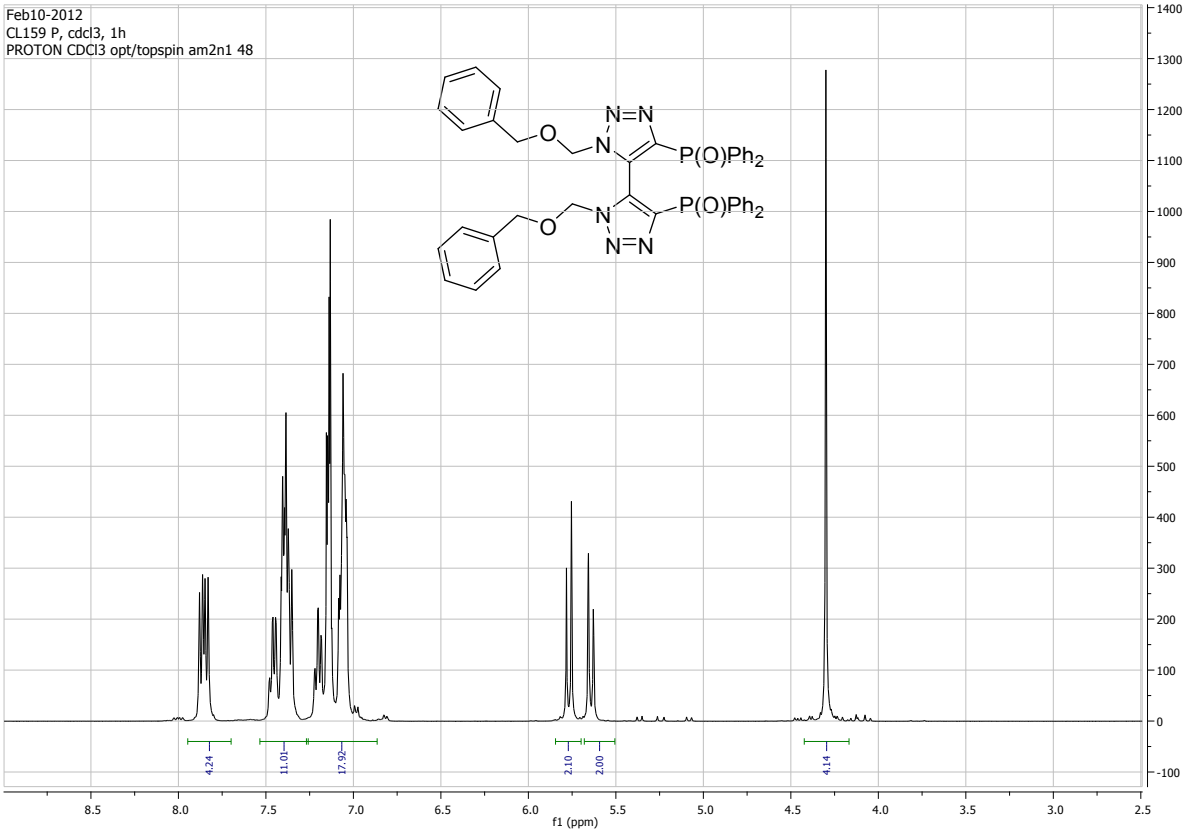
Monoisotopic Mass, Even Electron Ions

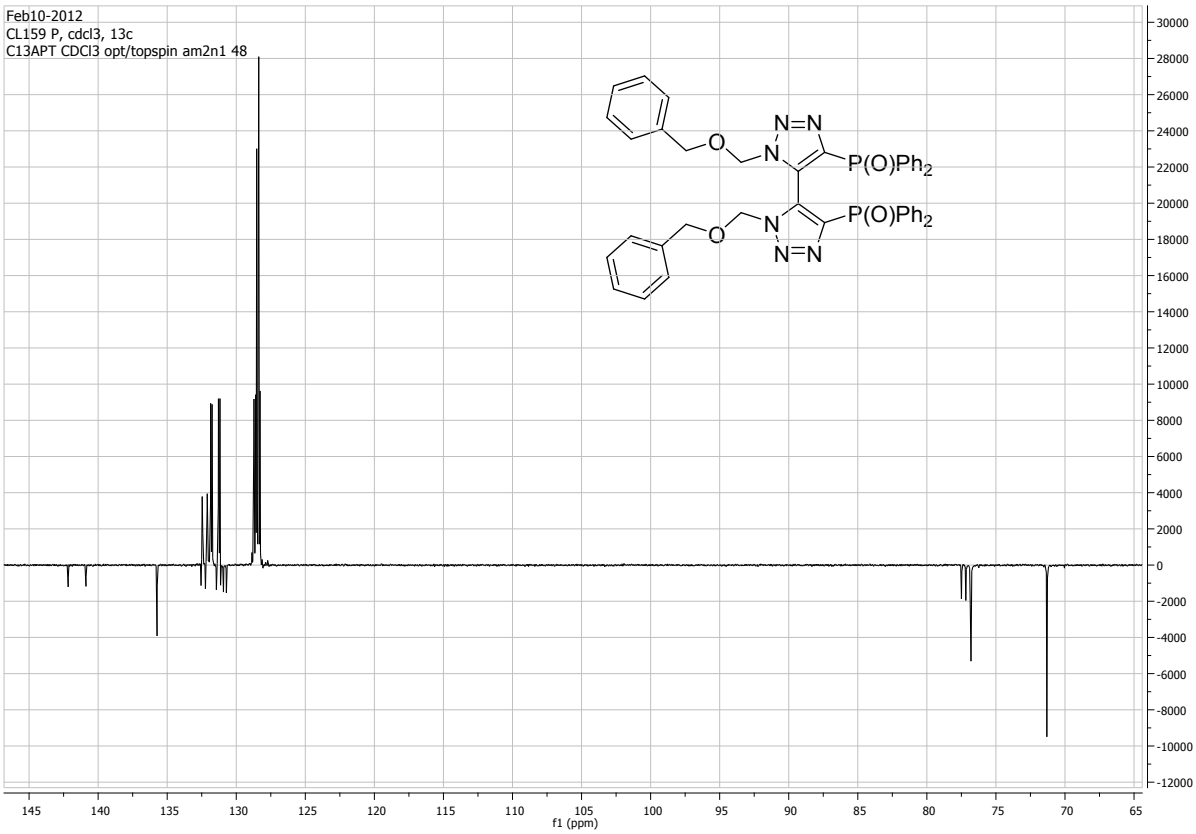
302 formula(e) evaluated with 3 results within limits (all results (up to 1000) for each mass)

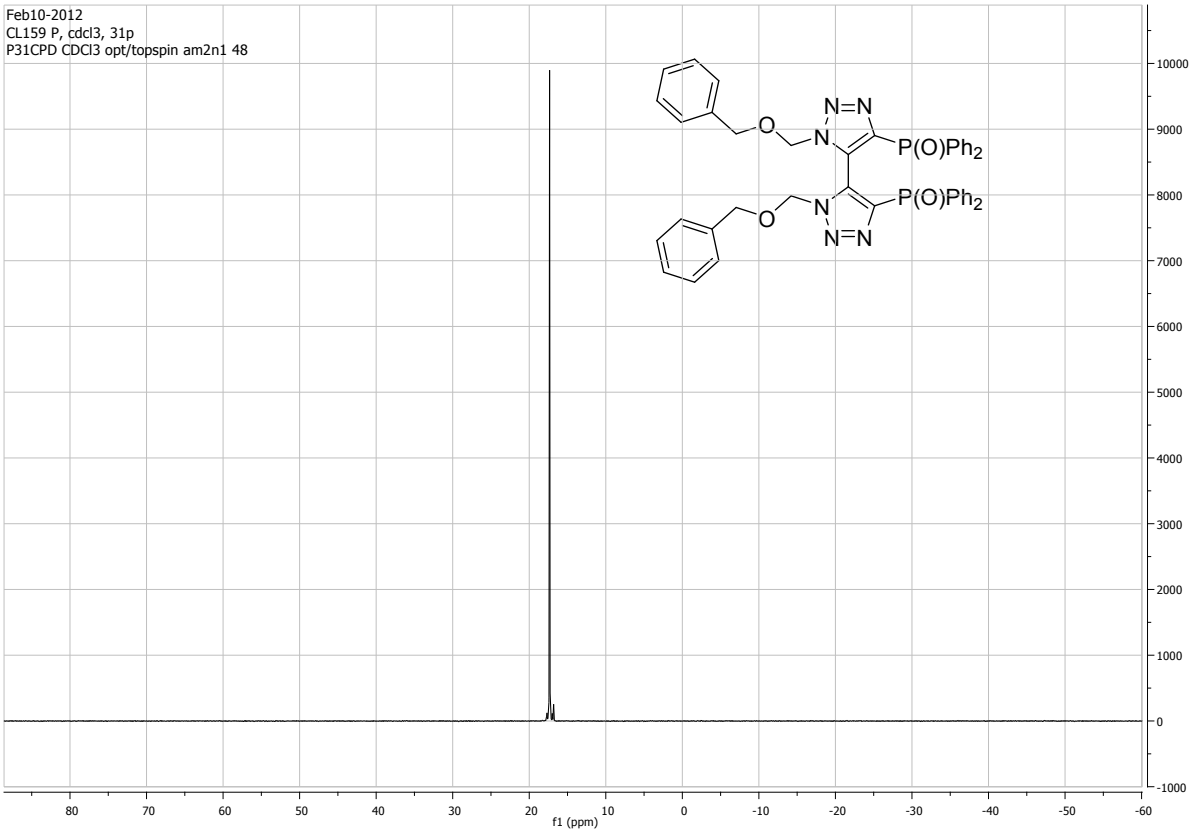


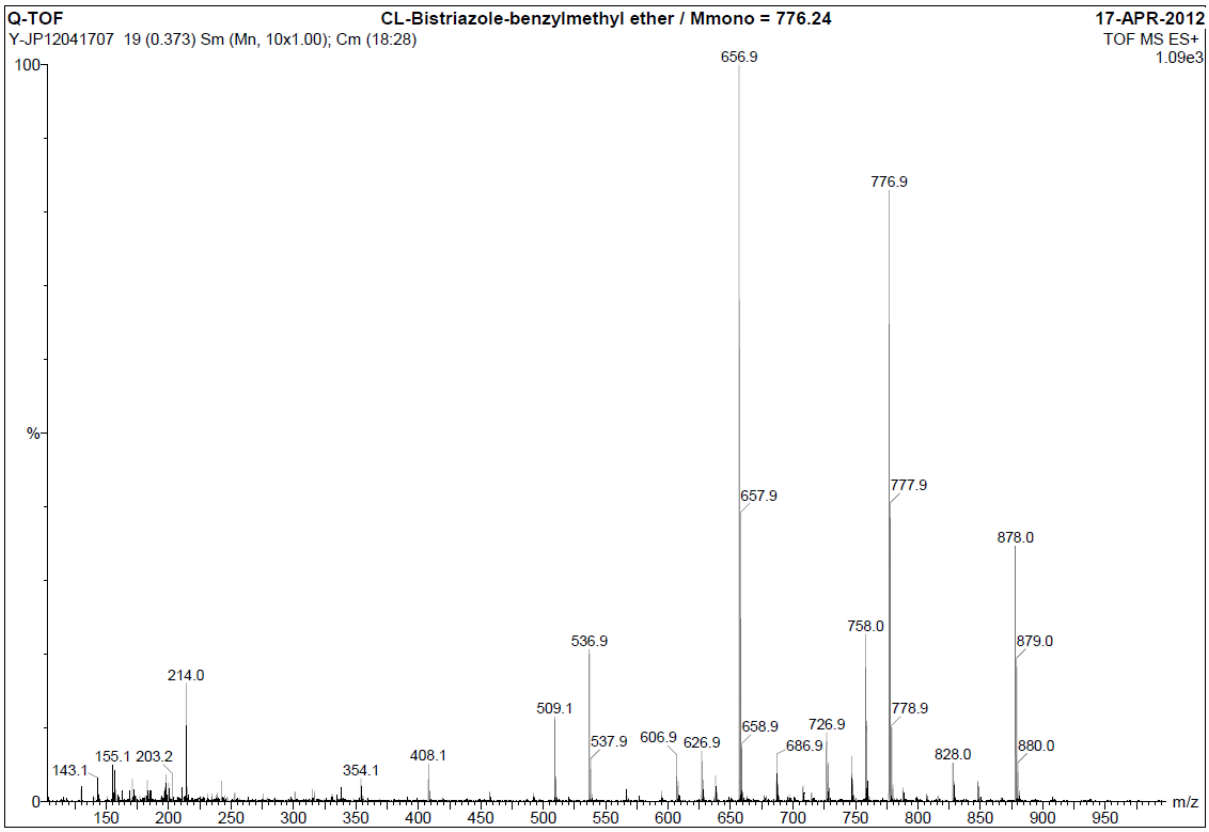
Minimum:				-10.0		
Maximum:		3.0	10.0	100.0		
Mass	Calc. Mass	mDa	PPM	DBE	Score	Formula
681.1790	681.1794	-0.4	-0.5	28.5	1	C35 H27 N10 O2 P2
	681.1780	1.0	1.4	23.5	2	C34 H31 N6 O6 P2
	681.1767	2.3	3.4	18.5	3	C33 H35 N2 O10 P2

V.7. 4,4'bis(diphenylphosphino)-1,1'-(dibenzyloxy)dimethyl-5,5'-bis-1,2,3-triazole dioxide 8.7






Feb10-2012
CL159 P, cdcl3, 31p
P31CPD CDCl3 opt/topspin am2n1 48
N=N
N
O
P(O)Ph2
P(O)Ph2
N
O
N
N=N
f1 (ppm)


Q-TOF
CL-Bistriazole-benzylmethyl ether / Mmono = 776.24
17-APR-2012
Y-JP12041707 19 (0.373) Sm (Mn, 10x1.00); Cm (18:28)
TOF MS ES+
1.09e3
656.9
776.9
657.9
777.9
878.0
758.0
879.0
536.9
214.0
509.1
778.9
658.9
726.9
537.9
606.9
626.9
686.9
828.0
880.0
155.1 203.2
143.1
354.1
408.1
%
m/z

mental Composition Report

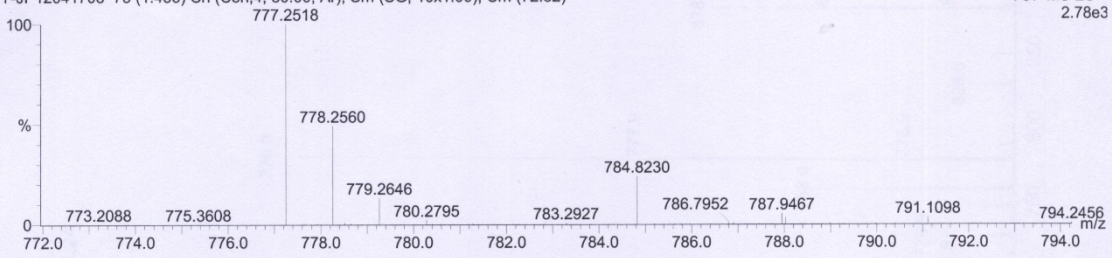
Single Mass Analysis
Tolerance = 3.0 mDa / DBE: min = -10.0, max = 100.0
Isotope cluster parameters: Separation = 1.0 Abundance = 1.0%

Monoisotopic Mass, Even Electron Ions
917 formula(e) evaluated with 2 results within limits (all results (up to 1000) for each mass)

Q-TOF
Y-JP12041708 75 (1.456) Cn (Cen,4, 80.00, Ar); Sm (SG, 10x1.00); Cm (72:82)

CL-Bistriazole-benzylmethyl ether / Mmono = 776.24

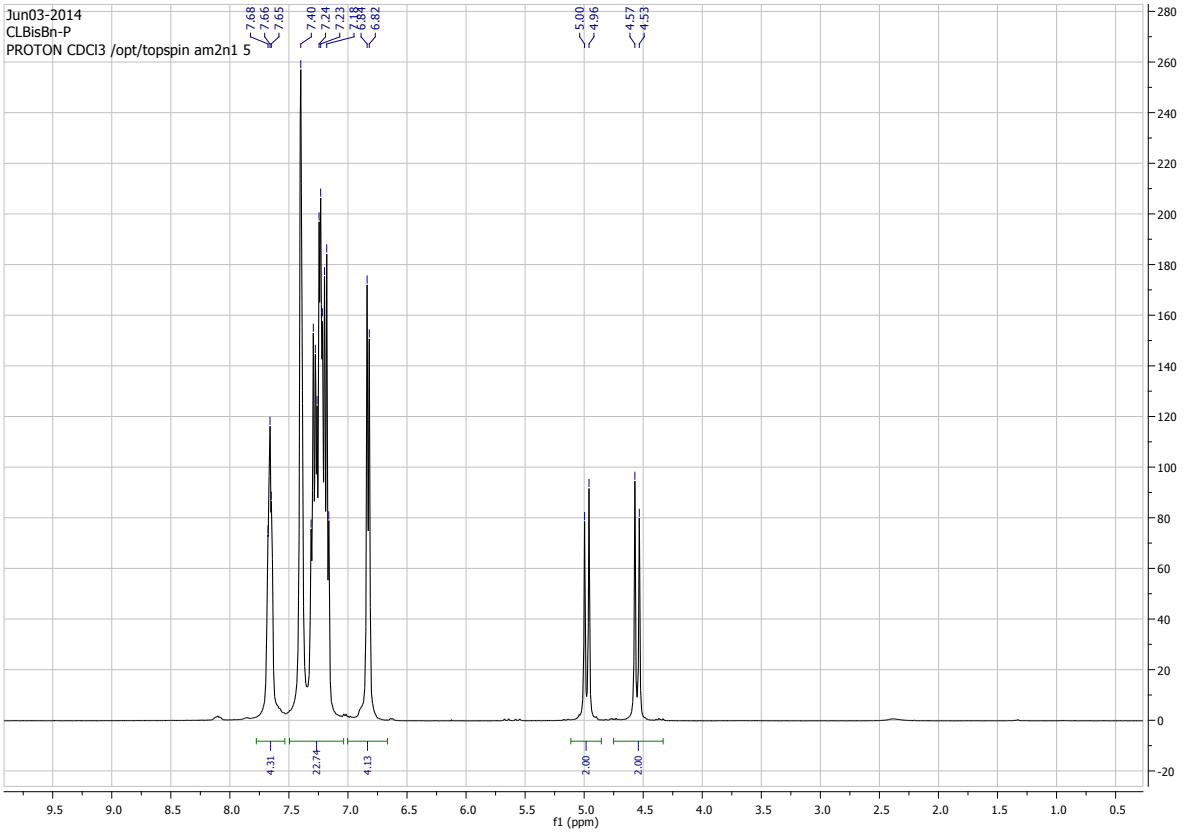
17-APR-2012
TOF MS ES+
2.78e3

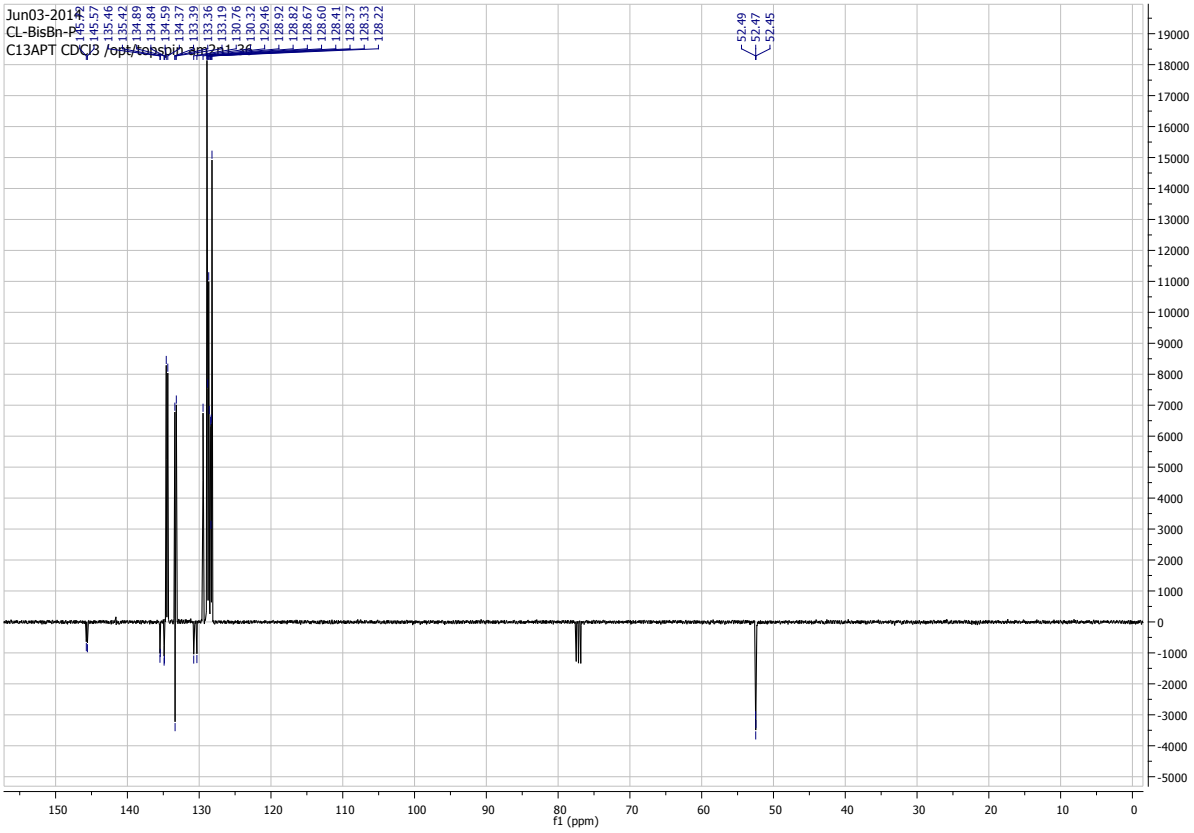


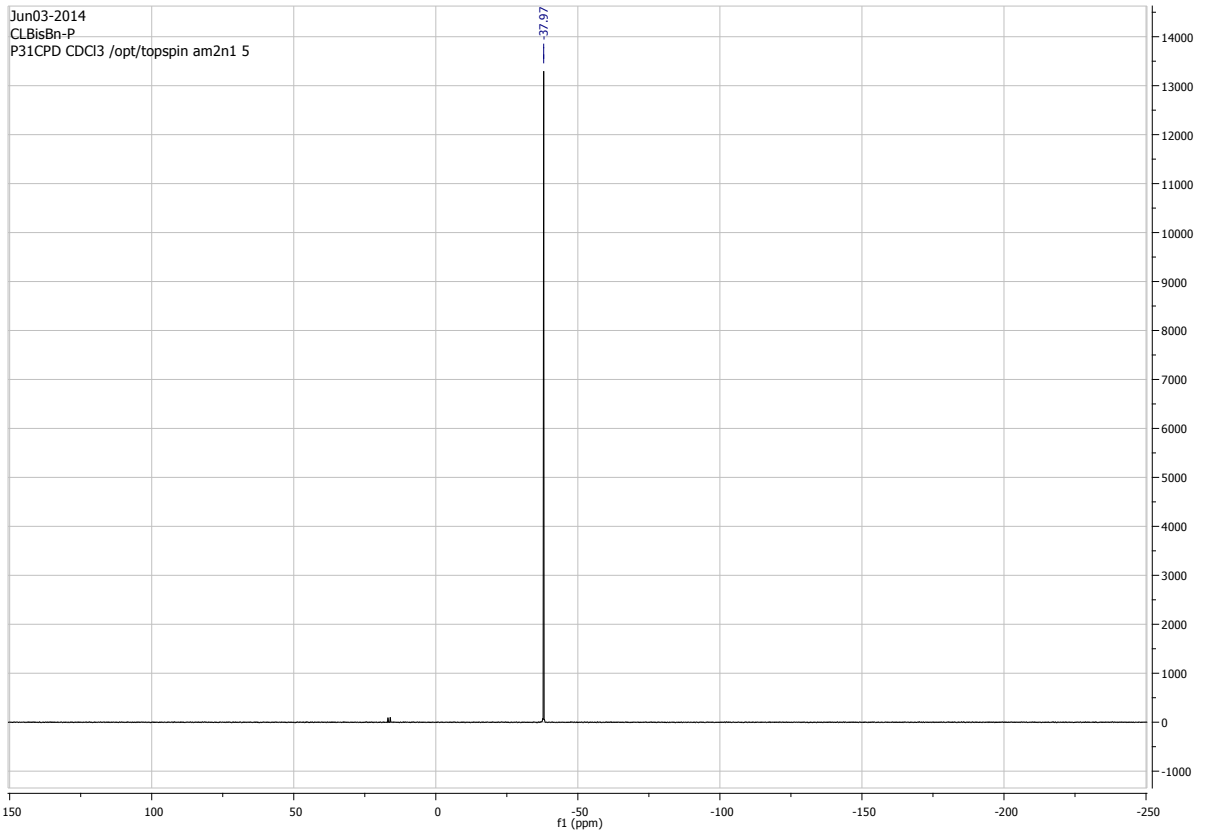
Minimum:				-10.0		
Maximum:		3.0	10.0	100.0		
Mass	Calc. Mass	mDa	PPM	DBE	Score	Formula
777.2518	777.2495	2.3	3.0	24.5	1	C43 H43 N2 O8 P2
	777.2508	1.0	1.3	29.5	2	C44 H39 N6 O4 P2

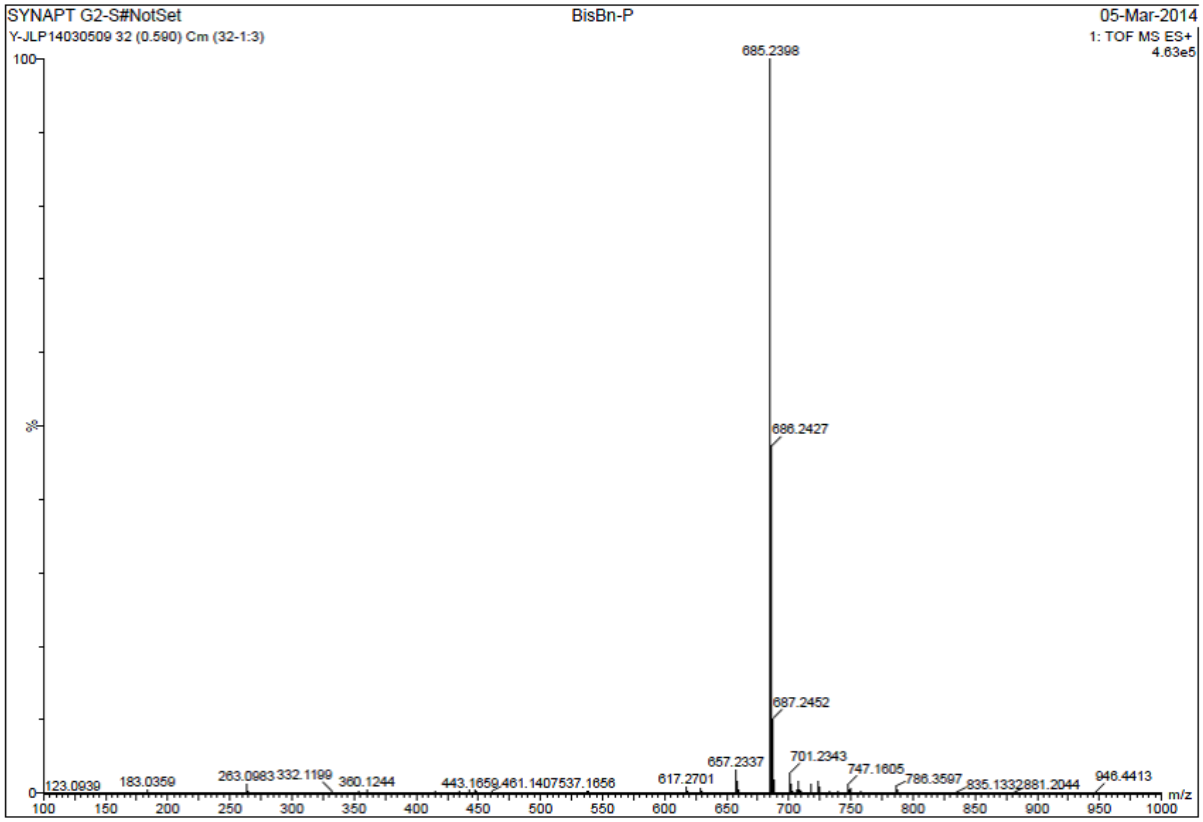
VI. Copies of spectra for phosphanes 11.1 – 11.3

VI.1. 4,4’-bis(diphenylphosphino)-1,1’-dibenzyl-5,5’-bis-1,2,3-triazole 11.1






Jun03-2014
CLBisBn-P
P31CPD CDCl3 /opt/topspin am2n1 5
37.97
f1 (ppm)

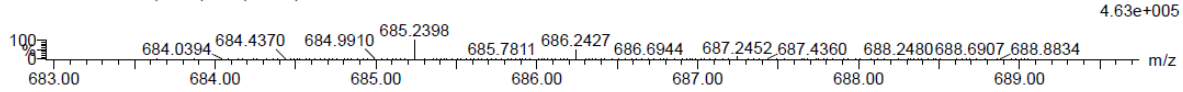

SYNAPT G2-S#NotSet
BisBn-P
05-Mar-2014
Y-JLP14030509 32 (0.590) Cm (32-1:3)
1: TOF MS ES+
4.63e5
685.2398
686.2427
687.2452
657.2337
701.2343
747.1605
786.3597
835.1332
881.2044
946.4413
617.2701
443.1659
461.1407
537.1656
263.0983
332.1199
360.1244
183.0359
123.0939
%
m/z

Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 1.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

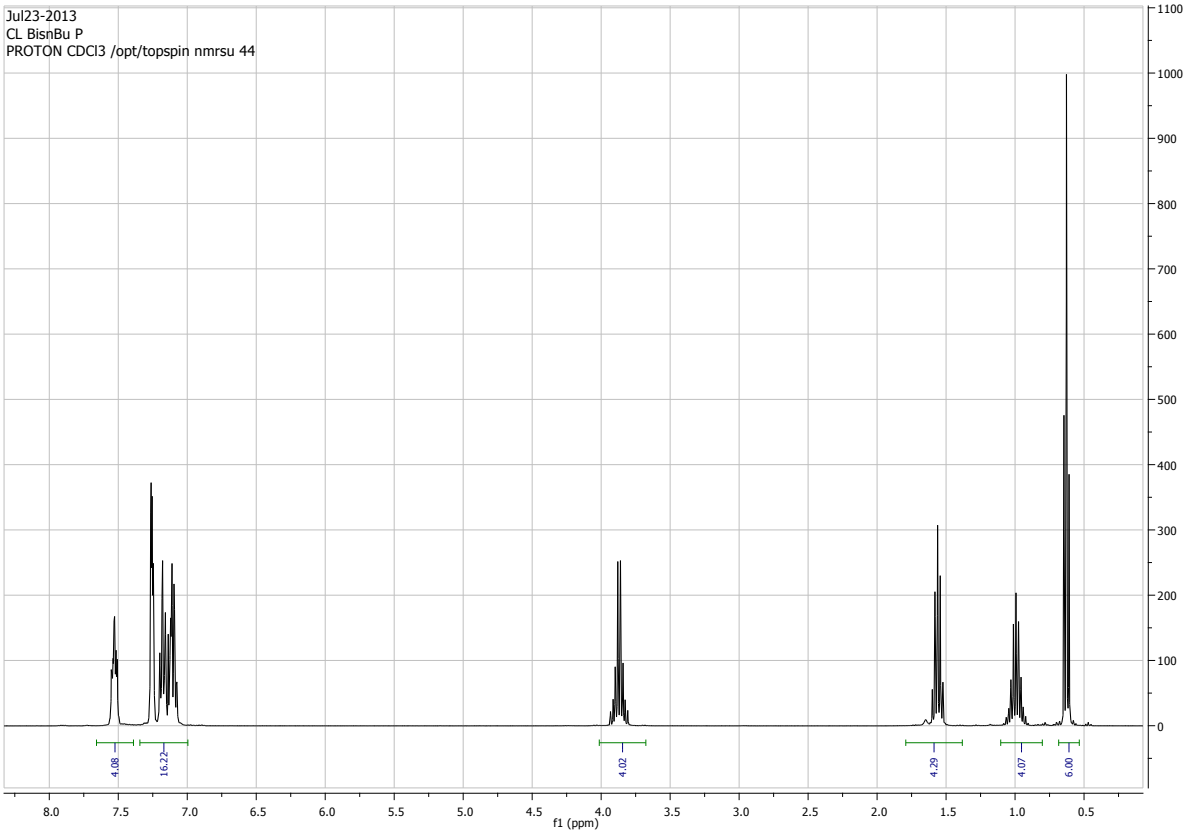
Monoisotopic Mass, Even Electron Ions
905 formula(e) evaluated with 3 results within limits (up to 20 best isotopic matches for each mass)
Elements Used:
C: 0-100 H: 0-150 N: 0-30 P: 0-3

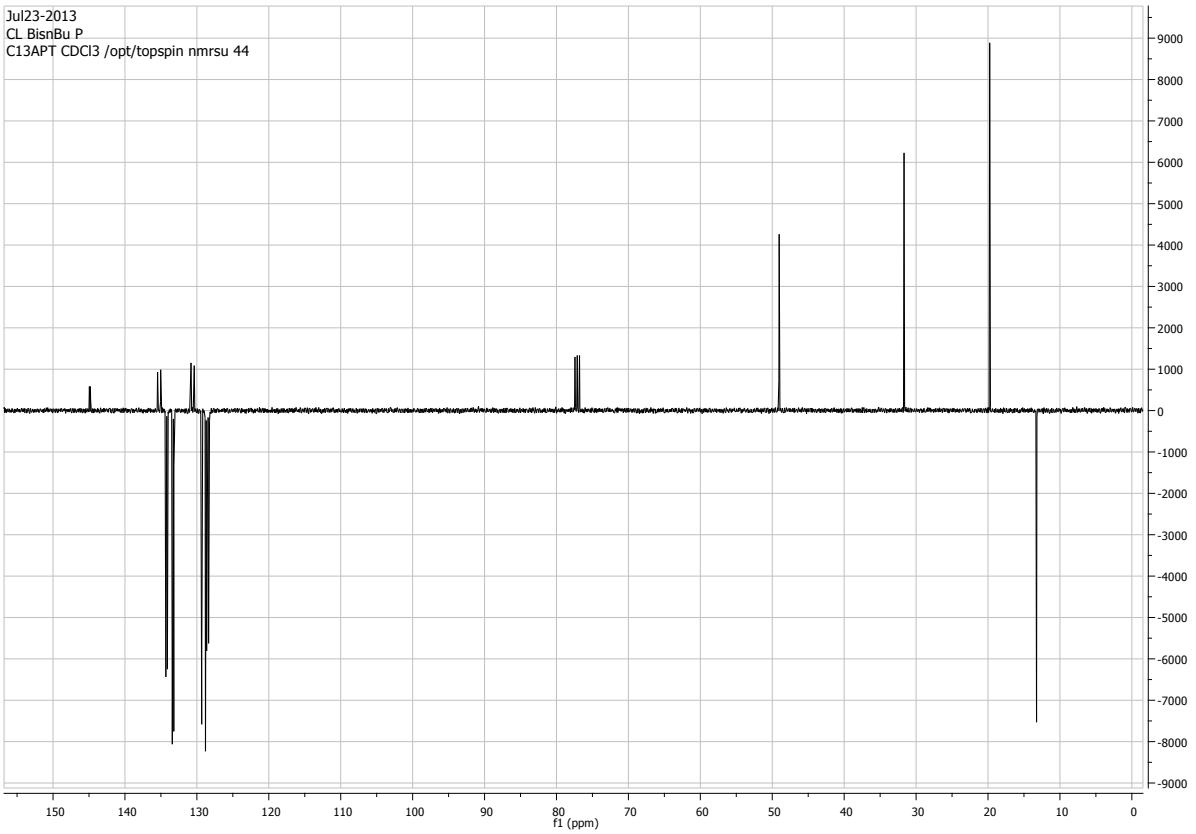
SYNAPT G2-S#NotSet BisBn-P 05-Mar-2014
Y-JLP14030509 32 (0.590) Cm (32-1:3) 1: TOF MS ES+
4.63e+005

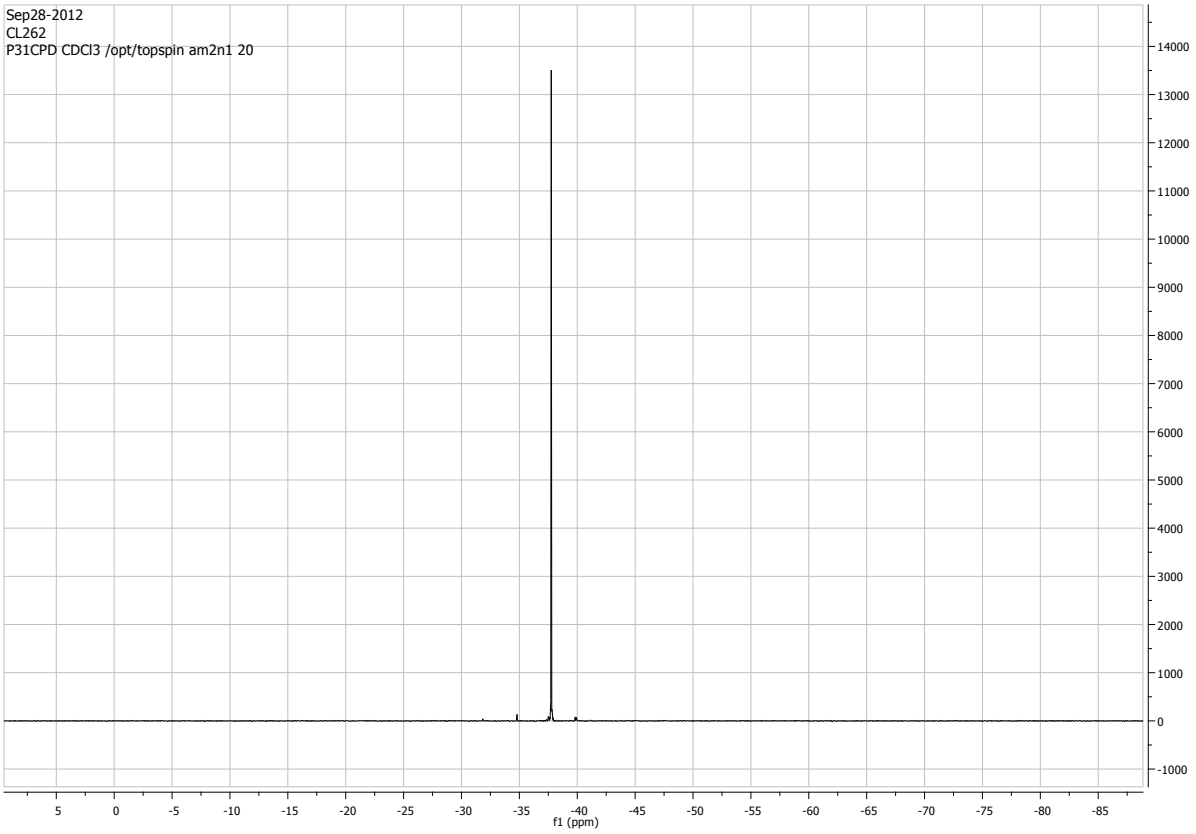


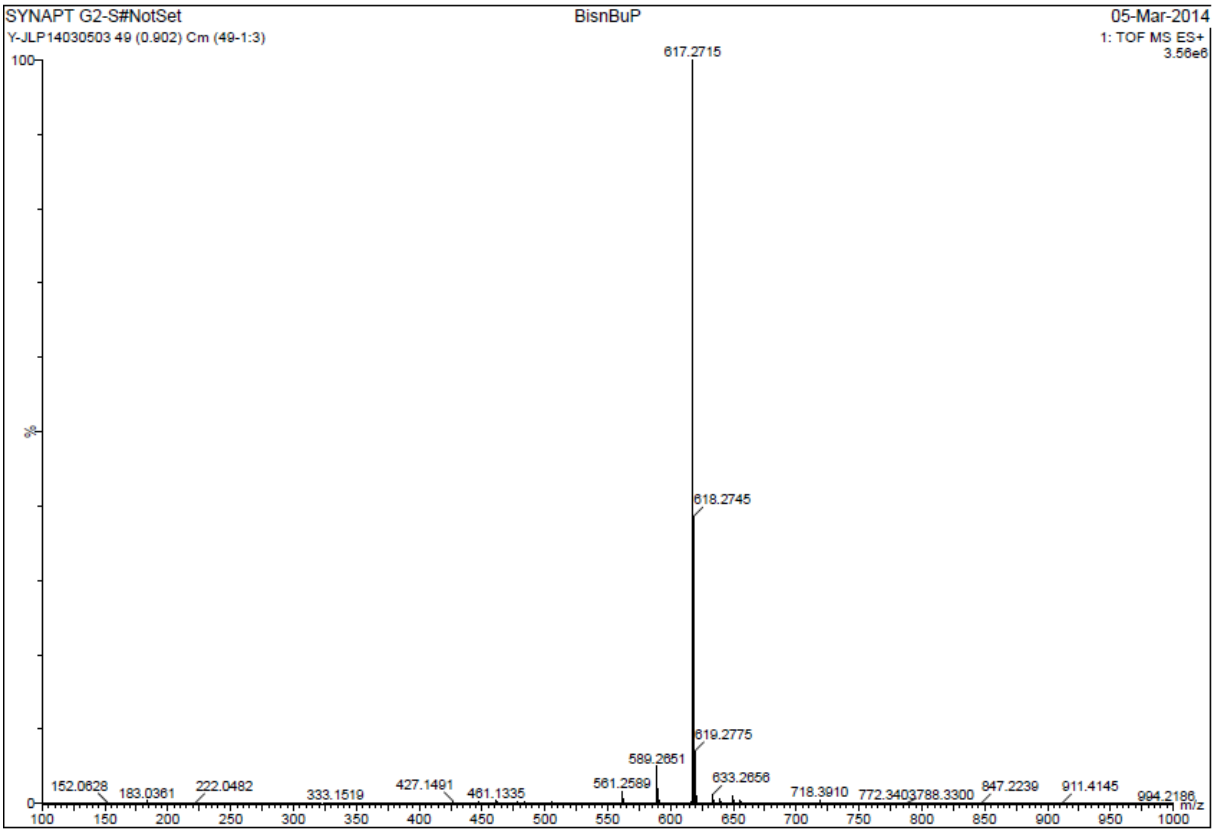
Minimum:				-1.5				
Maximum:		1000.0	1.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
685.2398	685.2398	0.0	0.0	29.5	834.5	0.002	99.82	C42 H35 N6 P2
	685.2392	0.6	0.9	38.5	840.8	6.329	0.18	C50 H29 N4
	685.2393	0.5	0.7	18.5	845.6	11.137	0.00	C21 H32 N22 P3

VI.2. 4,4’bis(diphenylphosphino)-1,1’-dibutyl-5,5’-bis-1,2,3-triazole 11.2




Jul23-2013
CL BisnBu P
C13APT CDCl3 /opt/topspin nmrsu 44
f1 (ppm)

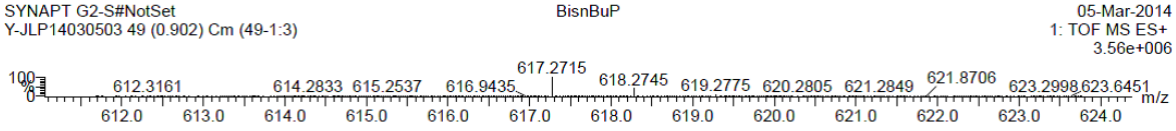

Sep28-2012
CL262
P31CPD CDCl3 /opt/topspin am2n1 20
f1 (ppm)



Elemental Composition Report **Page 1**

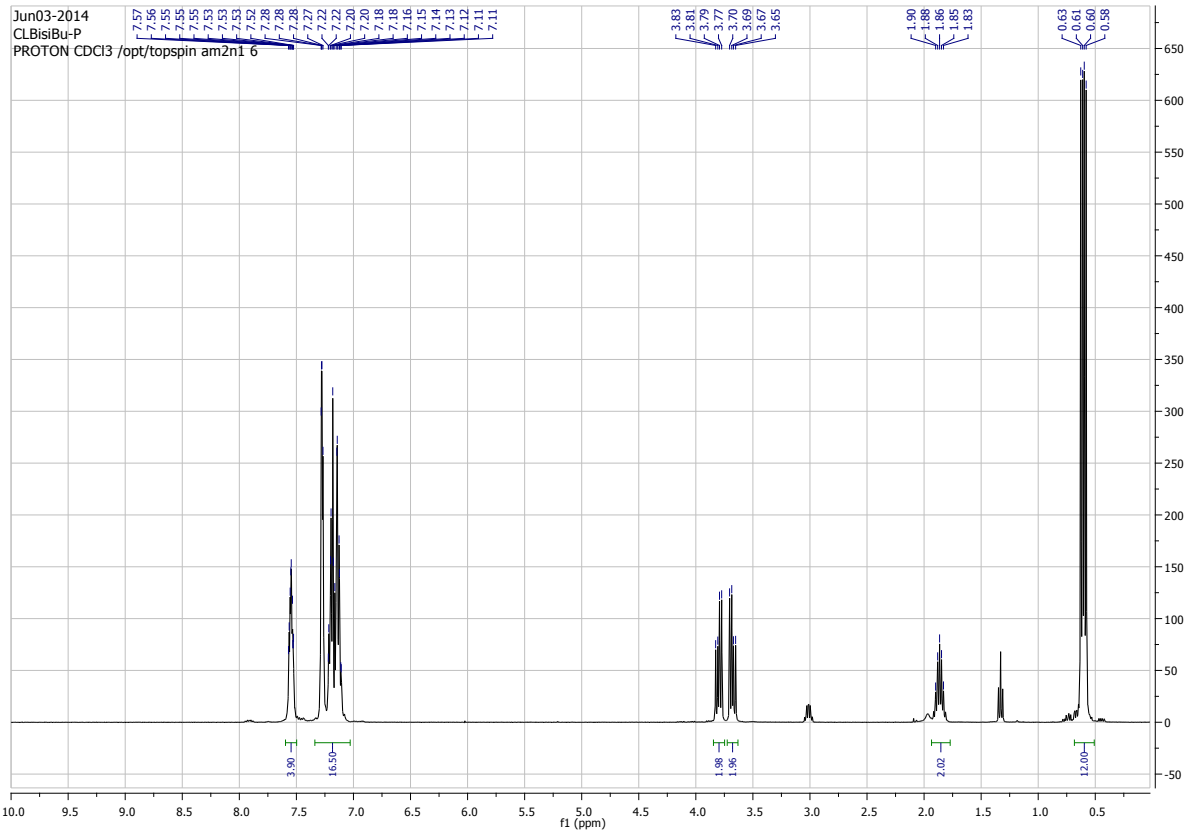
Single Mass Analysis
Tolerance = 1.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

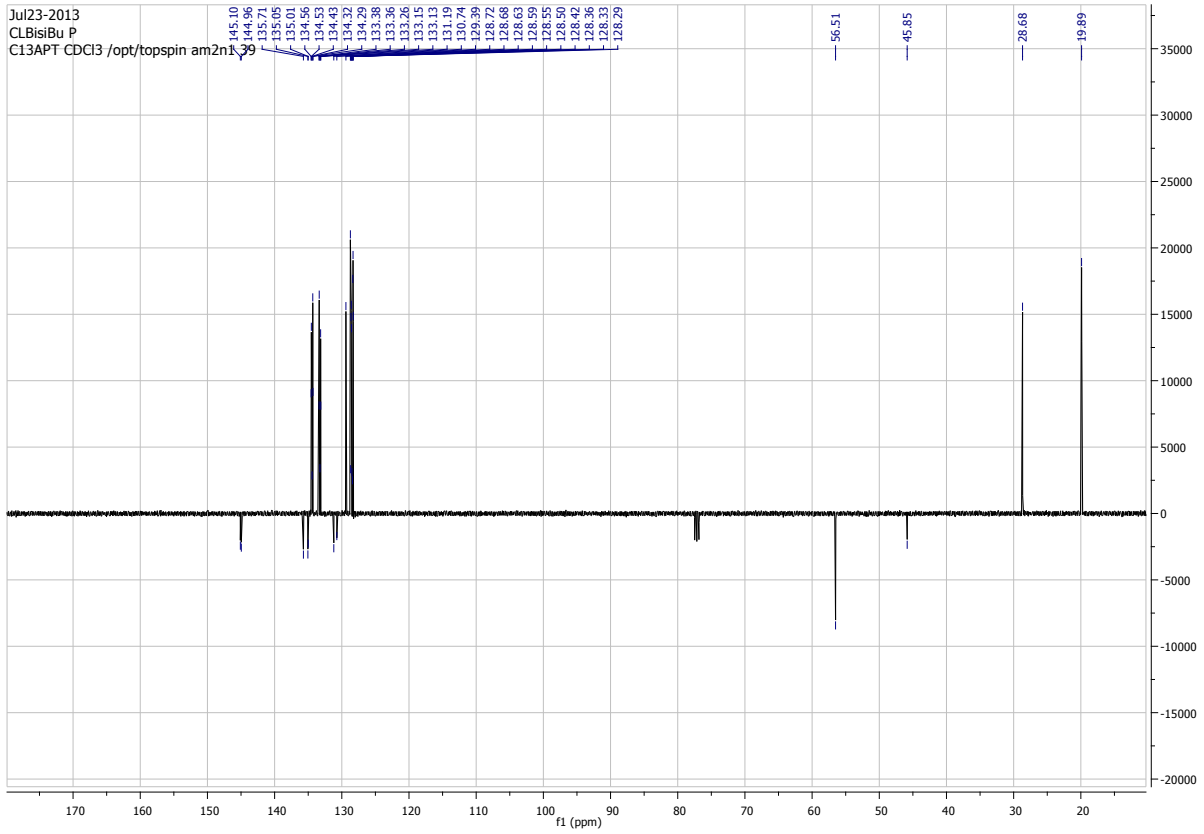
Monoisotopic Mass, Even Electron Ions
803 formula(e) evaluated with 1 results within limits (up to 20 best isotopic matches for each mass)
Elements Used:
C: 0-100 H: 0-150 N: 0-30 P: 0-3

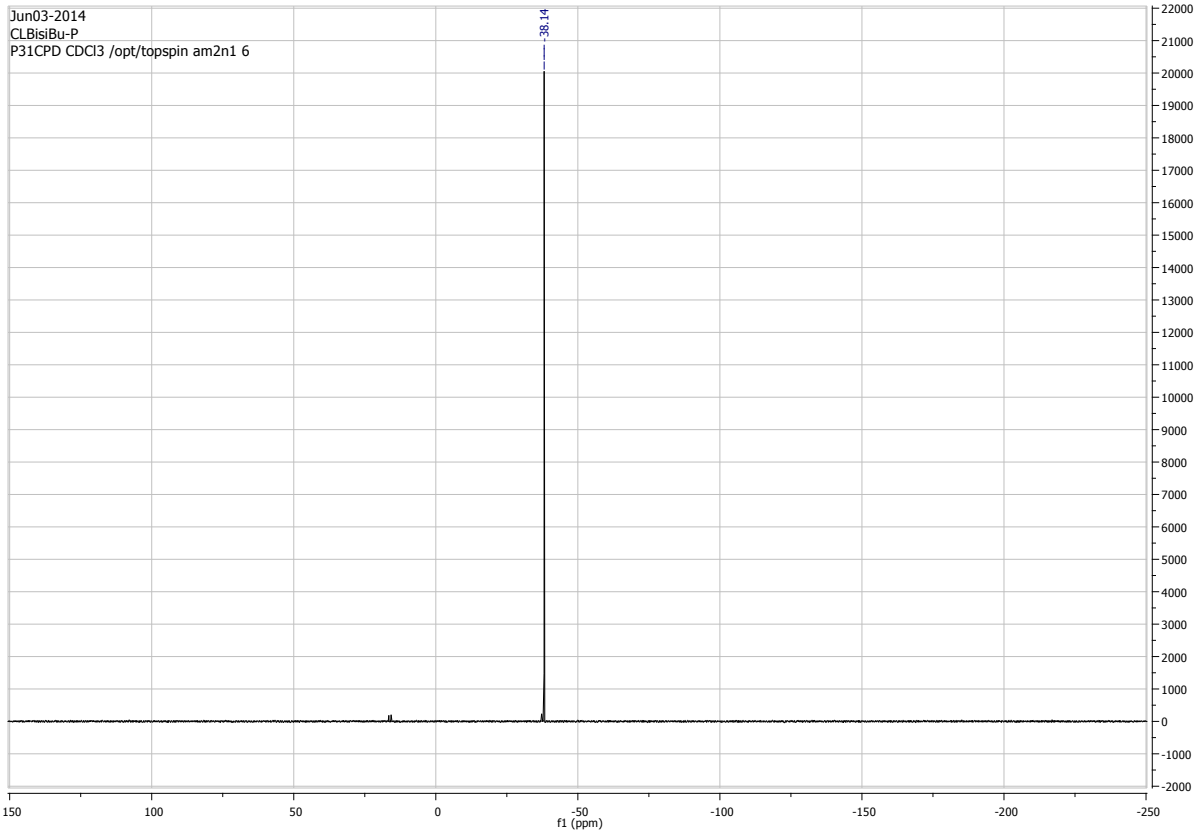


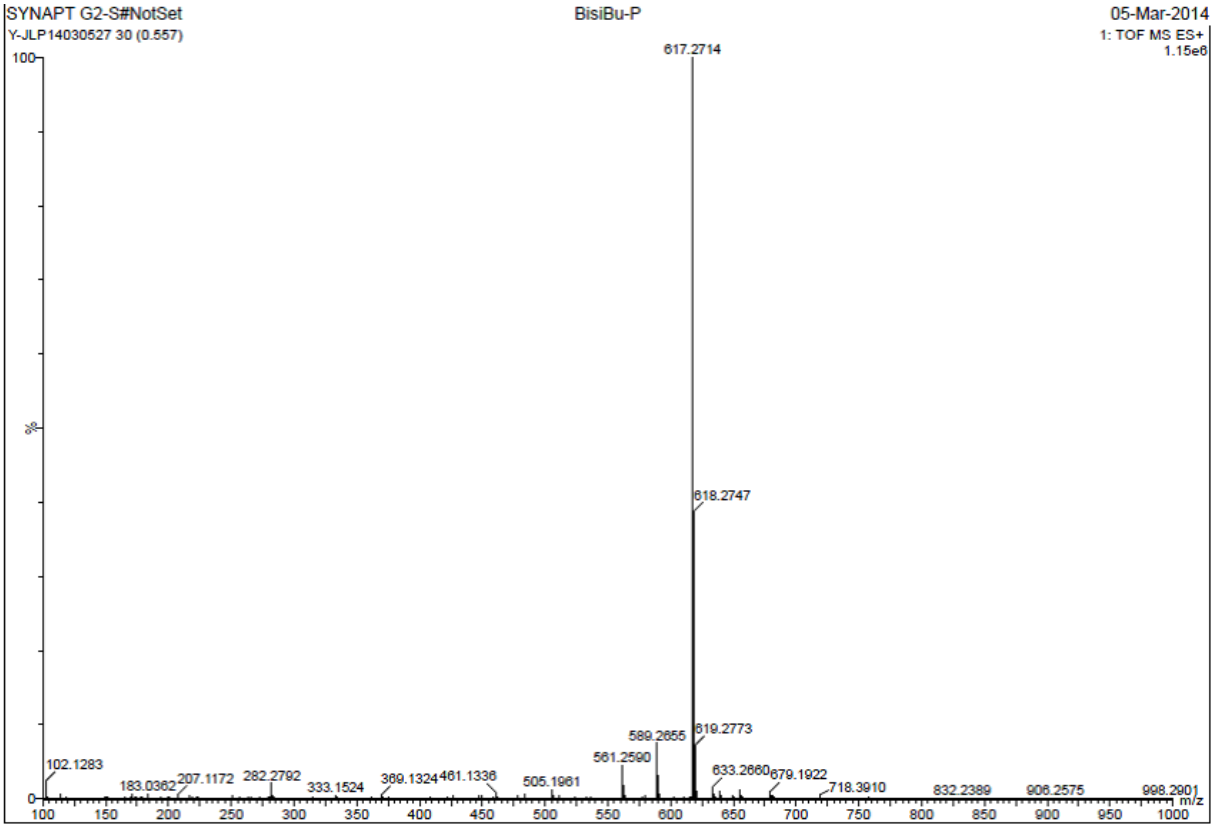
Minimum:				-1.5				
Maximum:		1000.0	1.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
617.2715	617.2711	0.4	0.6	21.5	1329.7	n/a	n/a	C36 H39 N6 P2

VI.3. 4,4’bis(diphenylphosphino)-1,1’-diisobutyl-5,5’-bis-1,2,3-triazole 11.3






Jun03-2014
CLBisiBu-P
P31CPD CDCl3 /opt/topspin am2n1 6
38.14
f1 (ppm)

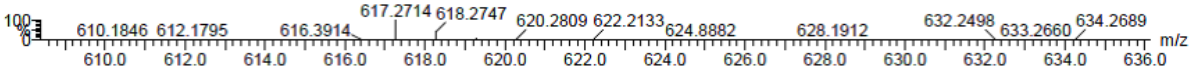

SYNAPT G2-S#NotSet
Y-JLP14030527 30 (0.557)
BisiBu-P
05-Mar-2014
1: TOF MS ES+
1.15e6
617.2714
618.2747
589.2655
619.2773
561.2590
102.1283
183.0362
207.1172
282.2792
333.1524
389.1324
461.1336
505.1961
633.2660
679.1922
718.3910
832.2389
906.2575
998.2901
%
m/z

Single Mass Analysis

Tolerance = 2.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
565 formula(e) evaluated with 2 results within limits (up to 20 best isotopic matches for each mass)
Elements Used:
C: 0-100 H: 0-150 N: 1-30 P: 1-3

SYNAPT G2-S#NotSet BisiBu-P 05-Mar-2014
Y-JLP14030527 30 (0.557) 1: TOF MS ES+
1.15e+006



Minimum:				-1.5				
Maximum:		1000.0	2.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
617.2714	617.2711	0.3	0.5	21.5	1186.1	0.000	100.00	C36 H39 N6 P2
	617.2706	0.8	1.3	10.5	1198.1	11.955	0.00	C15 H36 N22 P3

VII. X-ray crystallography.

A single crystal of each compound was mounted under inert perfluoropolyether at the tip of a cryoloop and cooled in the cryostream of either an Oxford-Diffraction XCALIBUR SAPPHIRE-I CCD diffractometer or an Agilent Technologies GEMINI EOS CCD diffractometer. Data were collected using the monochromatic MoKα radiation (λ= 0.71073).

The structures were solved by direct methods (SIR97) [1] and refined by least-squares procedures on F2 using SHELXL-97 [2]. All H atoms attached to carbon were introduced in idealised positions and treated as riding on their parent atoms in the calculations. The drawing of the molecules was realised with the help of ORTEP3. [3]

Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 1031965-1031970. Copies of the data can be obtained free of charge on application to the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

VII.1. 4,4'-bis(diphenylphosphinoxy)-1,1'-dibenzyl-5,5'-bis-1,2,3-triazole 8.1

Crystal data

$2(C_{42}H_{34}N_6O_2P_2)\cdot C_2H_3N$	V = 3756.64 (11) Å^3
M_r = 1474.44	Z = 2
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation
a = 12.8008 (2) Å	μ = 0.16 mm^{-1}
b = 16.6628 (3) Å	T = 175 K
c = 17.8668 (3) Å	0.43 × 0.35 × 0.25 mm
β = 99.6830 (17)°	

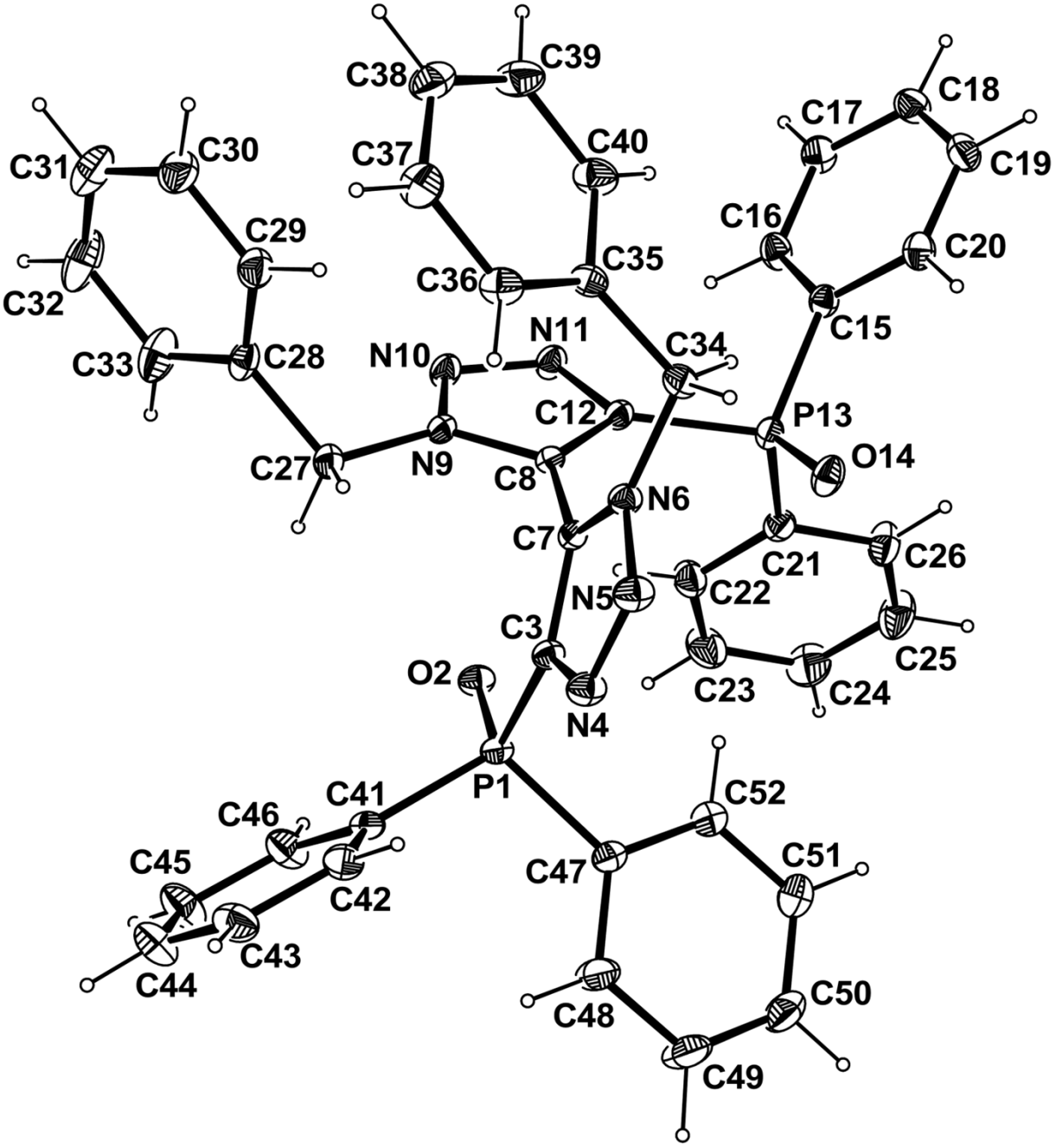
Data collection

Xcalibur, Sapphire2, large Be window diffractometer	9225 independent reflections
Absorption correction: multi-scan *CrysAlis PRO*, Oxford Diffraction Ltd., Version 1.171.34.40 (release 27-08-2010 CrysAlis171 .NET) (compiled Aug 27 2010,11:50:40) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.	7926 reflections with $I > 2.0\sigma(I)$
T_{min} = 0.955, T_{max} = 1.000	R_{int} = 0.023
64742 measured reflections	θ_{max} = 29.1°

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.045	2 restraints
$wR(F^2)$ = 0.143	H-atom parameters constrained
S = 0.85	$\Delta\rho_{max}$ = 0.49 e Å^{-3}

9225 reflections	$\Delta\rho_{min}$ = −0.67 e Å^{-3}
476 parameters	



VII.2. 4,4'-bis(diphenylphosphinoxy)-1,1'-diisobutyl-5,5'-bis-1,2,3-triazole 8.3

Crystal data

	V = *6752.5 (2)* Å^3
M_r = 848.66	*Z* = *8*
Monoclinic, *C2/c*	*Mo Kα radiation*
a = *23.4908 (5)* Å	*μ* = *0.17* mm^{-1}
b = *11.0856 (2)* Å	*T* = *175* K

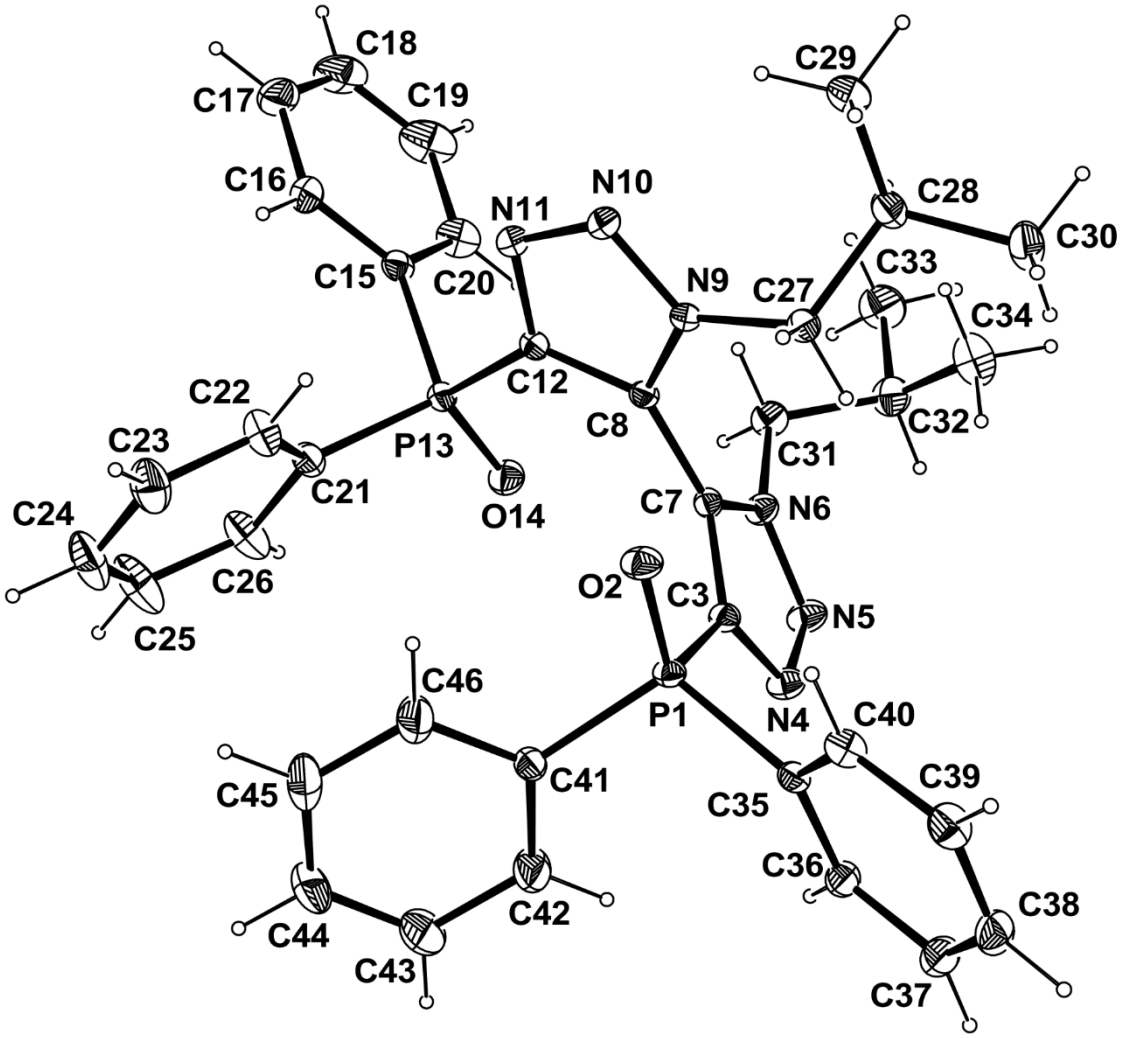
c = 25.9333 (5) Å	*0.30 × 0.25 × 0.15 mm*
β = 90.8818 (18)°	

Data collection

Xcalibur, Sapphire3, Gemini diffractometer	*8090 independent reflections*
Absorption correction: multi-scan CrysAlis PRO, Agilent Technologies, Version 1.171.36.24 (release 03-12-2012 CrysAlis171 .NET) (compiled Dec 3 2012,18:21:49) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.	*6655 reflections with I > 2.0σ(I)*
T_{min} *= 0.877,* T_{max} *= 1.000*	R_{int} *= 0.047*
27328 measured reflections	ϑ_{max} *= 29.3°*

Refinement

$R[F^2 > 2\sigma(F^2)]$ *= 0.049*	*415 parameters*
$wR(F^2)$ *= 0.055*	*0 restraints*
S = 1.09	$\Delta\rho_{max}$ *= 0.40 e Å*$^{-3}$
6655 reflections	$\Delta\rho_{min}$ *= −0.27 e Å*$^{-3}$



VII.3. dichloro(4,4'-bis(diphenylphosphinoxy)-1,1'-dibenzyl-5,5'-bis-1,2,3-triazole)palladium 12.1

Crystal data

$C_{42}H_{34}Cl_2N_6P_2Pd \cdot CHCl_3$	V = 8524.8 (3) Å^3
M_r = 981.36	Z = 8
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
a = 20.0222 (3) Å	μ = 0.86 mm^{-1}
b = 18.8861 (4) Å	T = 175 K
c = 22.6056 (4) Å	0.25 × 0.20 × 0.15 mm
β = 94.2374 (16)°	

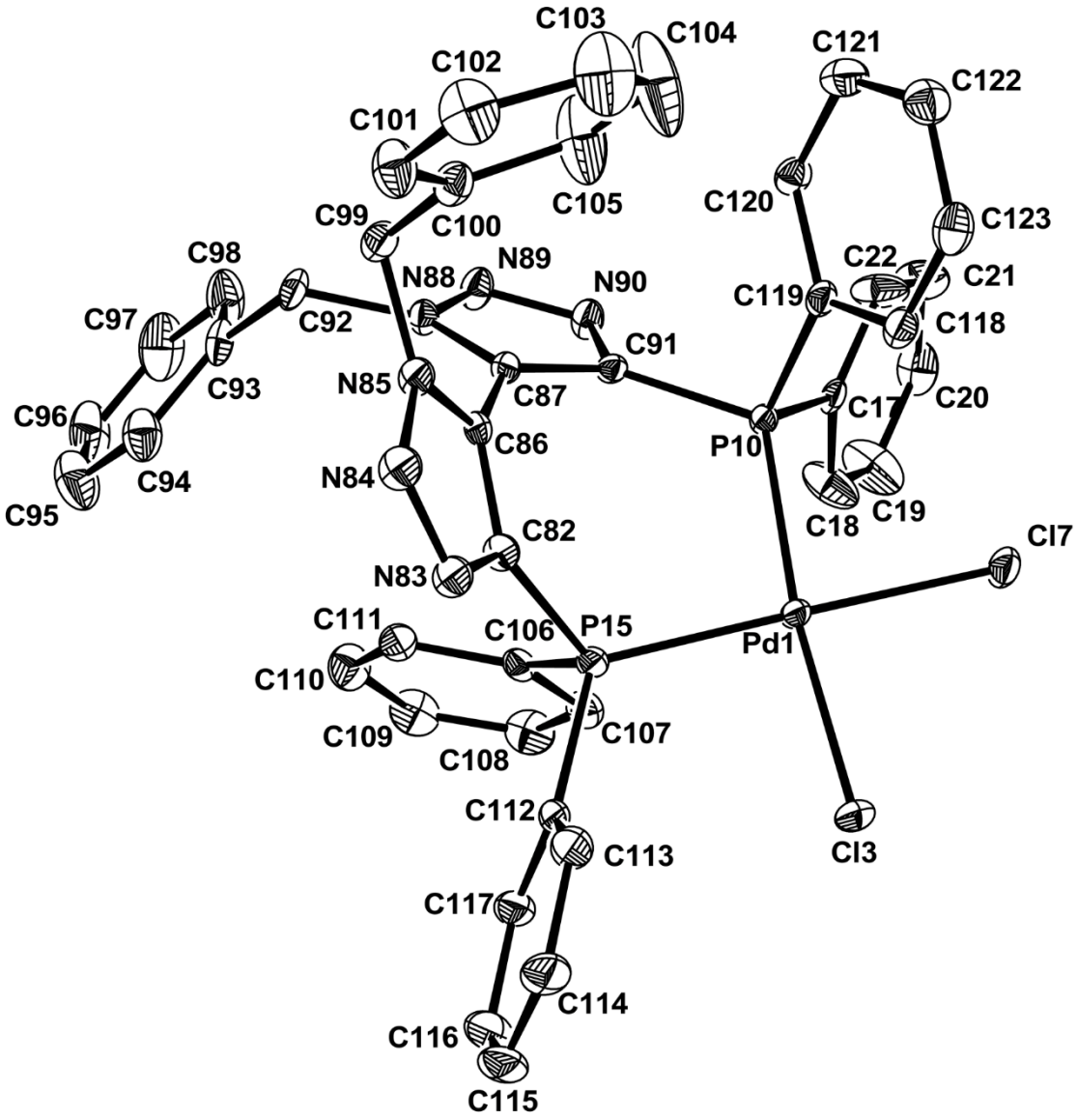
Data collection

Xcalibur, Sapphire3, Gemini diffractometer	14409 independent reflections

Absorption correction: multi-scan *CrysAlis PRO*, Agilent Technologies, Version 1.171.36.24 (release 03-12-2012 CrysAlis171 .NET) (compiled Dec 3 2012,18:21:49) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.	10170 reflections with $I > 2.0\sigma(I)$
T_{min} = 0.990, T_{max} = 1.000	R_{int} = 0.032
32286 measured reflections	θ_{max} = 26.5°

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.044	0 restraints
$wR(F^2)$ = 0.025	H-atom parameters constrained
S = 1.12	$\Delta\rho_{max}$ = 1.64 e Å^{-3}
10170 reflections	$\Delta\rho_{min}$ = −1.63 e Å^{-3}
1027 parameters	



VII.4. dichloro(4,4'-bis(diphenylphosphinoxy)-1,1'-dibenzyl-5,5'-bis-1,2,3-triazole)platinum 14

Crystal data

$C_{84}H_{68}Cl_4N_{12}P_4Pt_2$	V = 8678 (4) Å^3
M_r = 1901.36	Z = 4
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
a = 25.778 (5) Å	μ = 3.47 mm^{-1}
b = 17.954 (5) Å	T = 180 K
c = 19.364 (5) Å	0.18 × 0.12 × 0.05 mm
β = 104.467 (5)°	

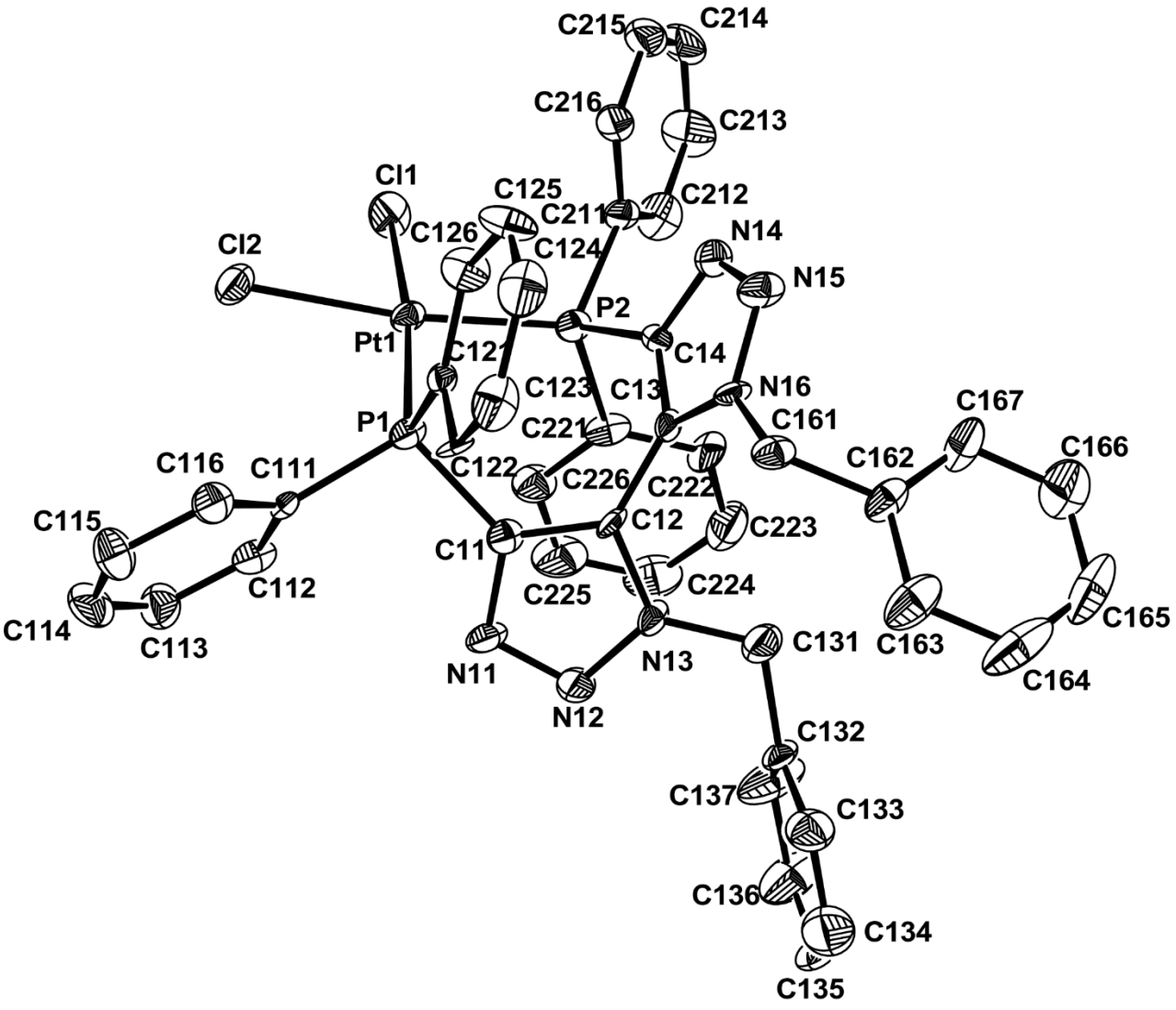
Data collection

Bruker	APEX-II	CCD	7804 independent reflections

diffractometer	
Absorption correction: multi-scan *SADABS* (Sheldrick, 2008)	6507 reflections with $I > 2\sigma(I)$
T_{min} = 0.540, T_{max} = 0.744	R_{int} = 0.073
70384 measured reflections	θ_{max} = 19.8°

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.032	0 restraints
$wR(F^2)$ = 0.075	H-atom parameters constrained
S = 1.04	$w = 1/[\sigma^2(F_o^2) + (0.0405P)^2 + 11.5437P]$ where $P = (F_o^2 + 2F_c^2)/3$
7804 reflections	$\Delta\rho_{max}$ = 0.72 e Å^{-3}
955 parameters	$\Delta\rho_{min}$ = −0.46 e Å^{-3}



VII.5. (4,4'-bis(diphenylphosphinoxy)-1,1'-dibenzyl-5,5'-bis-1,2,3-triazole)iridium(cycloctadiene)chloride 16

Crystal data

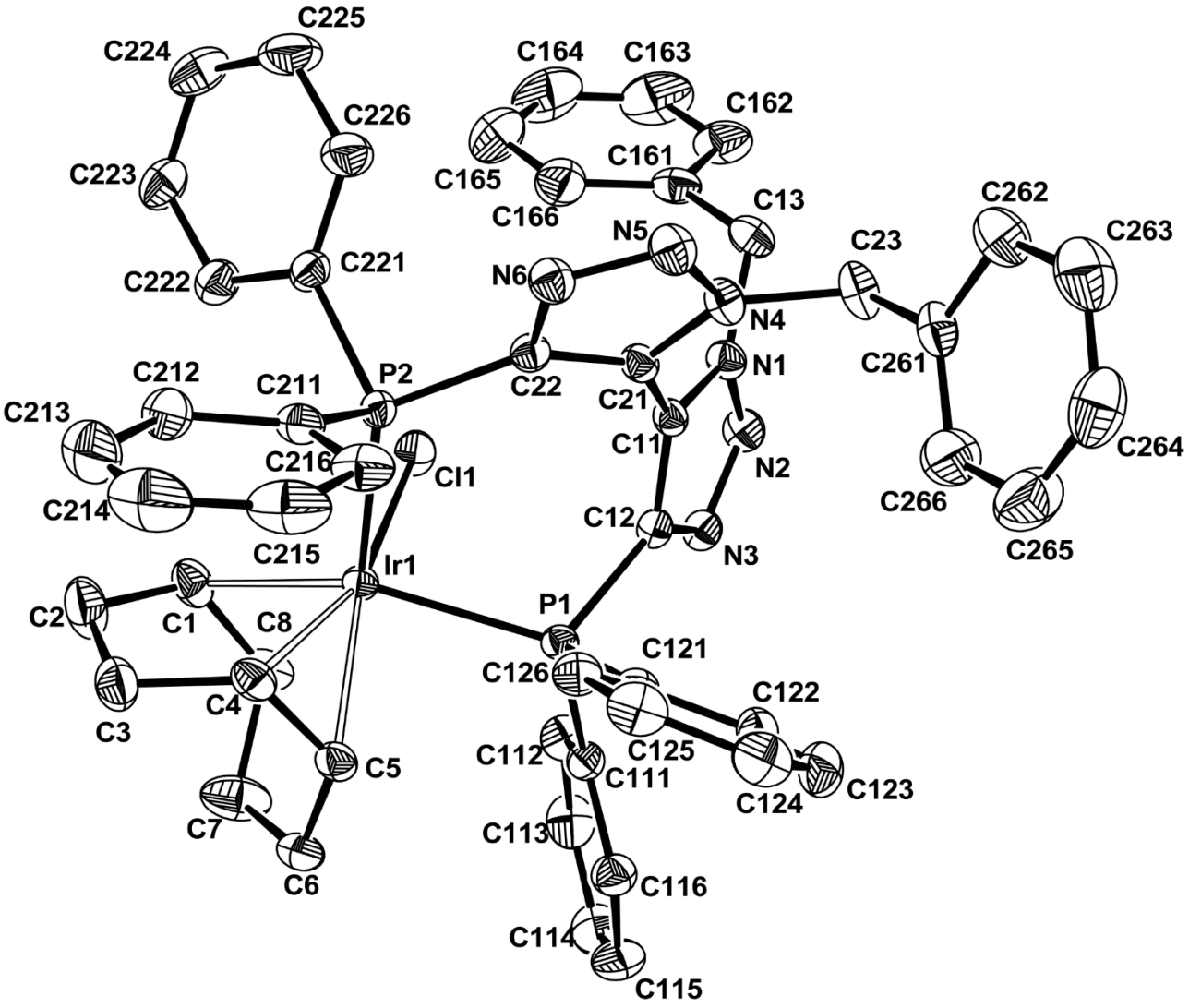
$C_{50}H_{46}ClIrN_6P_2{\cdot}(CHCl_3)_3$	γ = 111.798 (2)°
M_r = 1378.62	V = 2767.68 (10) Å^3
Triclinic, *P*	Z = 2
a = 14.3765 (3) Å	Mo $K\alpha$ radiation
b = 14.3894 (3) Å	μ = 3.00 mm^{-1}
c = 16.3672 (3) Å	T = 180 K
α = 113.044 (2)°	0.37 × 0.27 × 0.06 mm
β = 95.930 (2)°	

Data collection

Xcalibur, Eos, Gemini ultra diffractometer	15709 independent reflections
Absorption correction: multi-scan Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm. *CrysAlis PRO* (Agilent Technologies,2012)	14139 reflections with $I > 2\sigma(I)$
T_{min} = 0.825, T_{max} = 1.000	R_{int} = 0.033
73416 measured reflections	θ_{max} = 30.0°

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.026	0 restraints
$wR(F^2)$ = 0.063	H-atom parameters constrained
S = 1.04	$\Delta\rho_{max}$ = 1.27 e Å^{-3}
15709 reflections	$\Delta\rho_{min}$ = −1.21 e Å^{-3}
649 parameters	



VIII. References

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