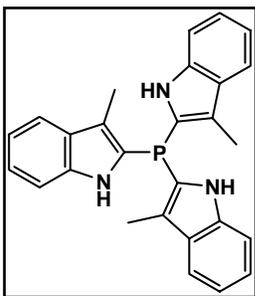# Tris-2-(3-methylindolyl)phosphine as an anion receptor

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General Considerations. All reactions and manipulations were carried out under an atmosphere of dinitrogen using standard Schlenk techniques unless otherwise stated. Trichlorophosphine (PCl₃), 1.6 M *n*-BuLi, NaBH₄, tetraethylammonium and tetrabutylammonium salts (fluoride, chloride, bromide, iodide, acetate, sulfate, nitrate, tetrafluoroborate) were purchased from Aldrich and used as received. 1-[(*N*,*N*-Dimethylamino)methyl]-3-methylindole,[1] and [Cu(MeCN)₄]BF₄,[2] were synthesized according to literature procedures. Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl still under a dinitrogen atmosphere. ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded on Varian 400 MHz or 300 MHz NMR systems, and referenced to SiMe₄ (TMS) and 85% H₃PO₄, respectively. Splitting patterns are indicated as s, singlet; d, doublet; t, triplet; q, quartet;, m, multiplet; br, broad peak.


Tris-2-(3-methylindolyl)phosphine, P(C₉H₈N)₃, 1. 1-[(*N*,*N*-Dimethylamino)methyl]-3-methylindole (4.25 g, 22.6 mmol) was dissolved in THF (60 mL) and cooled to -78°C. *n*-BuLi (17.0 mL, 27.2 mmol) was added dropwise over 10 minutes. The reaction was stirred at -78°C for 10 minutes, warmed to ambient temperature and stirred for 3 hours. The resulting orange mixture was cooled to -78°C, and PCl₃ (0.66 mL, 7.56 mmol) was added dropwise over 5 minutes. The mixture was allowed to warm to ambient temperature over 5 hours and then quenched with MeOH. Solvents

were removed *in vacuo* to yield a yellow solid. Water (100 mL) was added to the solid, and the suspension extracted with DCM (3 x 100 mL). The organic layers were combined, dried over anhydrous $MgSO_4$, filtered, and concentrated *in vacuo* to afford dark orange oil. MeOH was added to triturate pure aminal-protected product as a white solid, which was isolated by filtration and dried *in vacuo* (2.09 g, 47%). Mp: 122°C; ^{31}P NMR (CD_2Cl_2, 121 MHz): δ -71.3 (s); ^{1}H NMR (CD_2Cl_2, 300 MHz): δ 7.48 (d, J = 8.1 Hz, 6H, Ar-H), 7.20 (t, J = 7.4 Hz, 3H, Ar-H), 7.07 (t, J = 7.4 Hz, 3H, Ar-H), 4.78 (d, J = 12 Hz, 3H, amine NCH_2), 4.62 (d, J = 12 Hz, 3H, anime NCH_2), 2.15 (s, 18H, amine $N(CH_3)_2$), 1.84 (s, 9H, indole CH_3); ^{13}C NMR (CD_2Cl_2, 75 MHz):.139.54, 130.14, 126.86, 123.08, 121.39, 119.64, 119.08, 111.06, 67.92, 42.86, 9.11; HRMS EI for $C_{36}H_{45}N_6P$: calcd *m/z* 592.344334, found *m/z* 592.344809; Microanalysis for $C_{36}H_{45}N_6P$: calcd (%) C = 72.94, H = 7.65, N = 14.18, found (%) C = 72.56, H = 7.57, N = 13.78.
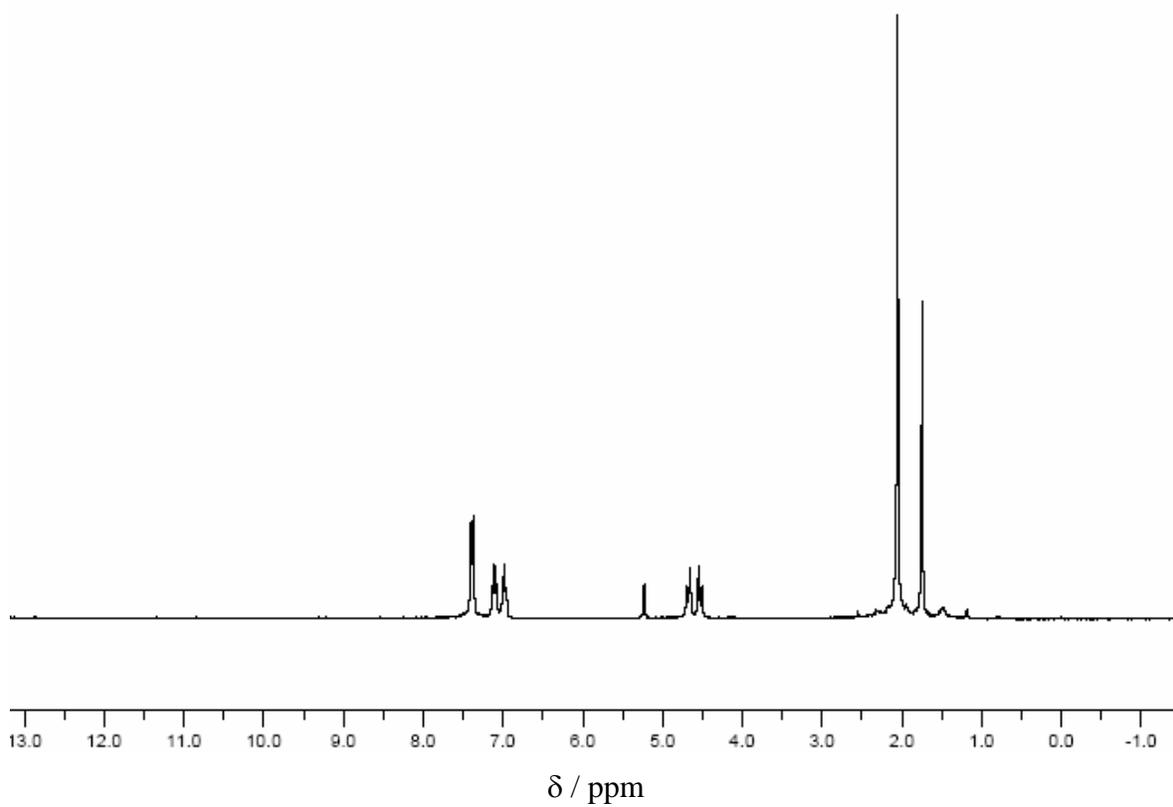
Figure S1. ^{1}H NMR spectrum of *N*, *N'*, *N''*-(Me$_2$NCH$_2$)$_3$-**1** recorded in CD$_2$Cl$_2$.
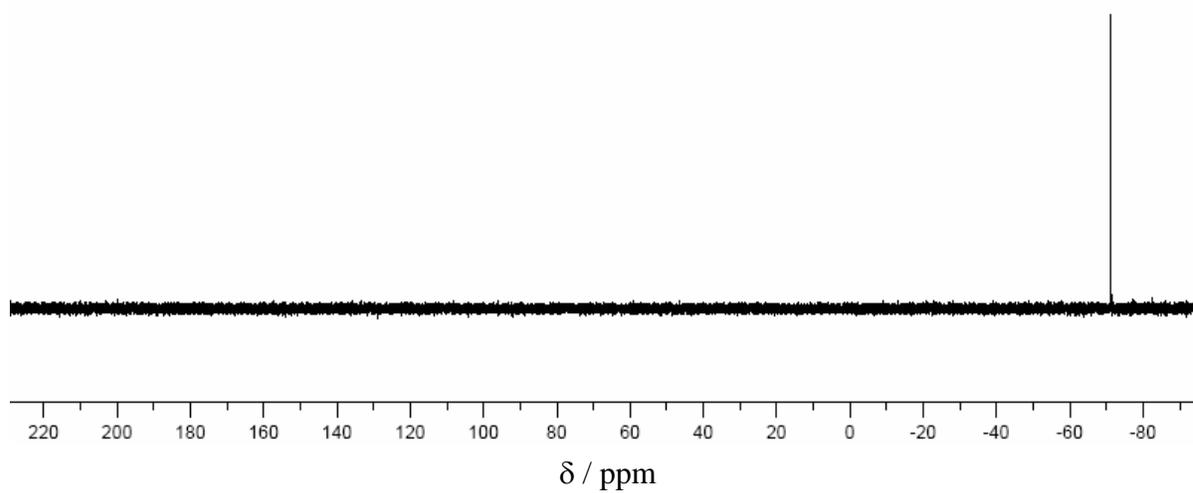
Figure S2. ^{31}P NMR spectrum of *N*, *N'*, *N''*-(Me$_2$NCH$_2$)$_3$-**1** recorded in CD$_2$Cl$_2$.
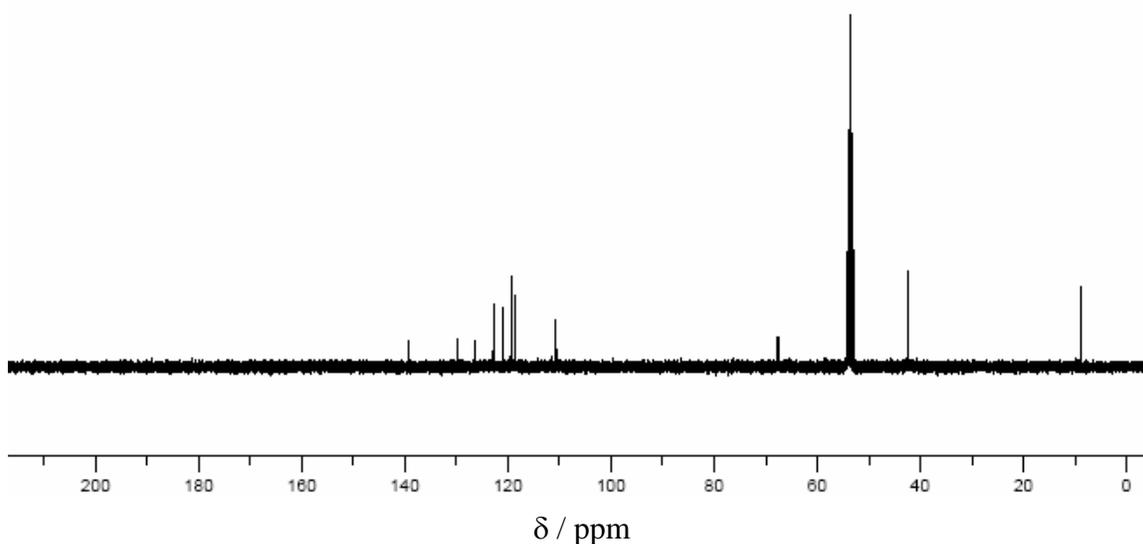
Figure S3. ^{13}C NMR spectrum of N, N', N''-(Me$_2$NCH$_2$)$_3$-**1** recorded in CD$_2$Cl$_2$.

A solution of THF/EtOH (120 mL, 1:1 v/v) was added to a solid mixture of the aminal-protected product (3.75 g, 6.33 mmol) and NaBH$_4$ (1.50 g, 39.7 mmol). The mixture was refluxed for 5 hours. The solution was reduced to dryness in vacuo and acidified water was added to the resultant white solid, which was extracted with DCM (3 x 100 mL). The organic phases were combined and dried over anhydrous MgSO$_4$, filtered and taken to dryness to afford a dark yellow coloured oil. MeOH was added to triturate pure product as a white solid, which was isolated by filtration and dried *in vacuo* (1.84 g, 69 %). Mp: 166°C; ^{31}P NMR (CD$_2$Cl$_2$, 121 MHz): δ -81.7 (s); ^1H NMR (CD$_2$Cl$_2$, 300 MHz): δ 7.90 (br s, 3H, indole NH), 7.60 (d, $J = 7.2$ Hz, 3H, Ar-H), 7.27 (d, $J = 7.5$ Hz, 3H, Ar-H), 7.21 – 7,12 (m, 6H, Ar-H), 2.41 (s, 9H, indole CH$_3$); ^{13}C NMR (CD$_2$Cl$_2$, 75 MHz): 138.94, 130.29, 125.53, 123.69, 121.34, 120.17, 119.54, 111.80, 9.90; HRMS EI for C$_{27}$H$_{24}$N$_3$P: calcd *m/z* 421.170357, found *m/z* 421.170786;

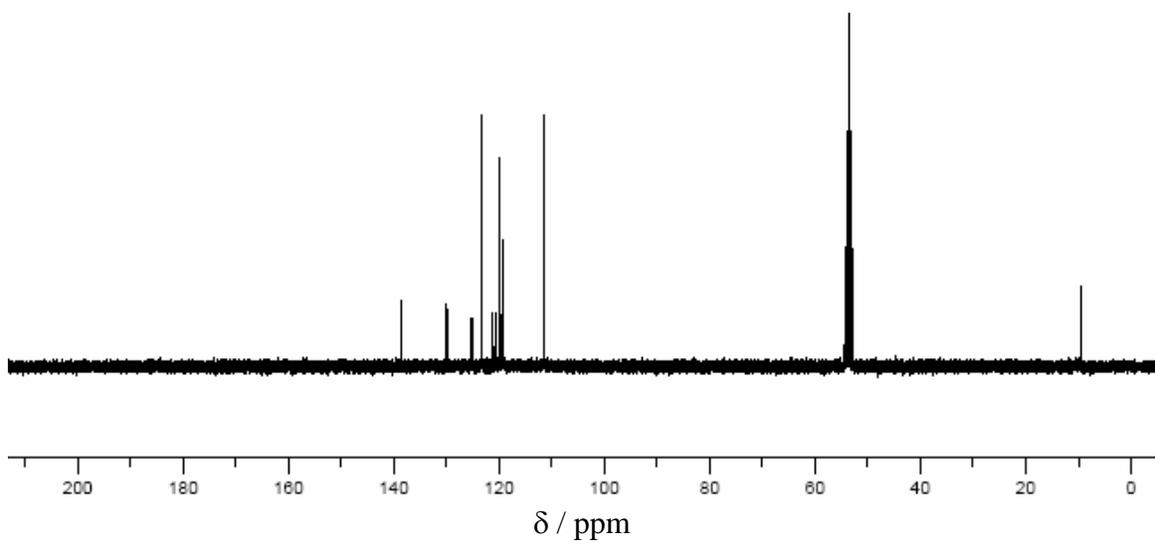Microanalysis for $C_{27}H_{24}N_3P$: calcd (%) C = 76.94, H = 5.74, N = 9.97, found (%)C = 76.70, H = 5.78, N = 9.79.
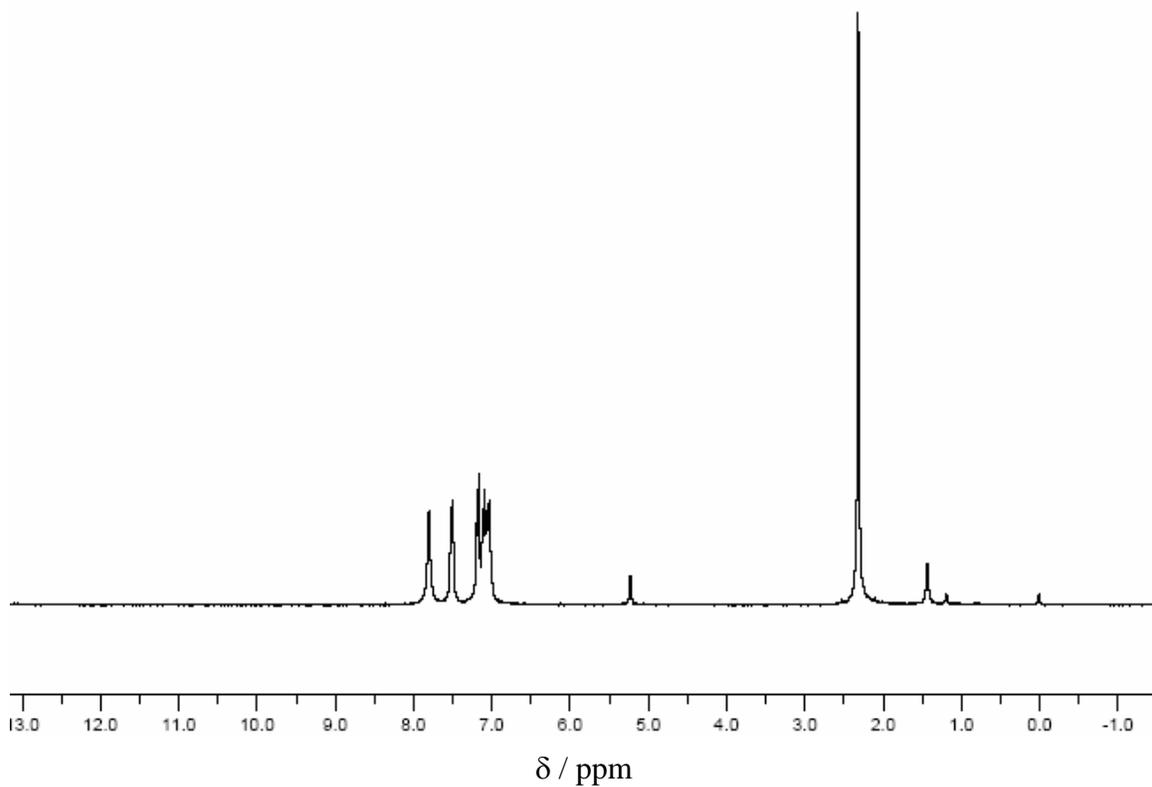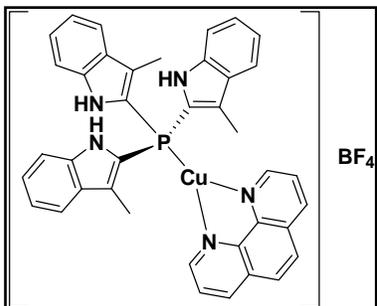

Figure S4. ^1H NMR spectrum of **1** recorded in CD_2Cl_2.
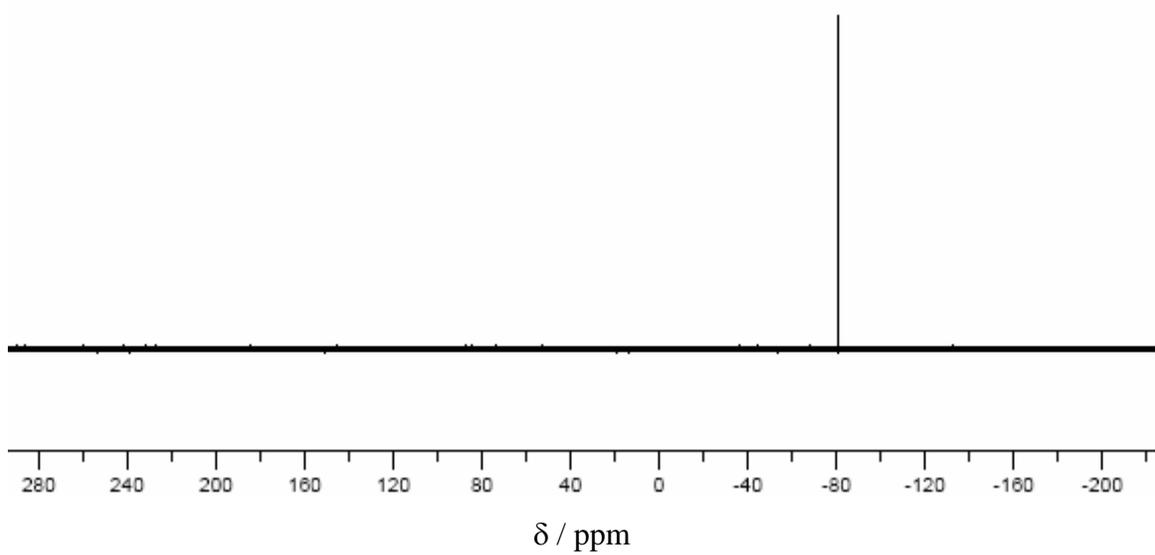
Figure S5. ^{31}P NMR spectrum of **1** recorded in CD_2Cl_2.

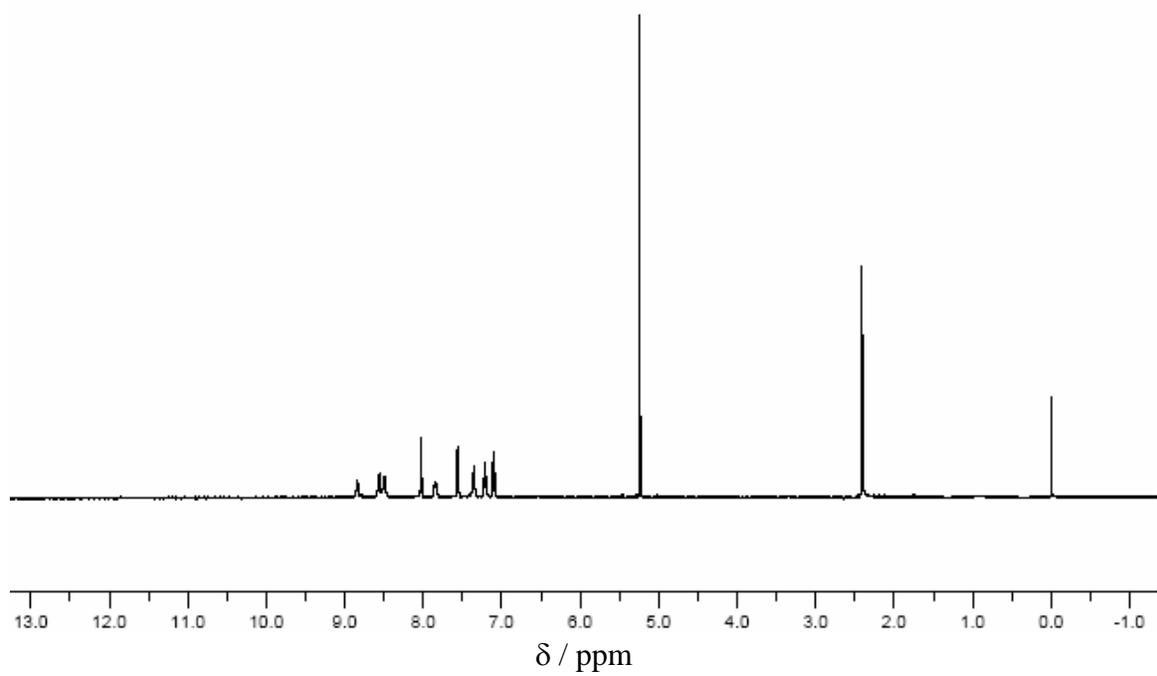**Figure S6.** ^{13}C NMR spectrum of **1** recorded in CD_2Cl_2.

[Cu(1)(1,10-phenanthroline)]BF$_4$. Dissolved [Cu(MeCN)$_4$]BF$_4$ (0.168 g, 0.242 mmol), **1** (0.229 g, 0.543 mmol) and 1,10-phenanthroline (0.049 g, 0.272 mmol) in DCM (20 mL) to give a clear yellow solution. The resultant yellow solution was placed into a vial containing Et$_2$O. X-ray quality single crystals were formed within one week (0.061 g, 34 %). ^{31}P NMR (CD$_2$Cl$_2$, 161 MHz): δ -63.2 (br s); ^{1}H NMR (CD$_2$Cl$_2$, 400 MHz): δ 8.92 (br s, J_{NHF} = 3.6 Hz, 3H, indole NH), 8.65 (d, J = 8.4 Hz, 2H, Ar-H), 8.57 (s, 2H, Ar-H), 8.10 (s, 2H, Ar-H), 7.93 (dd, J = 4.4, 8.0 Hz, 2H, Ar-H), 7.64 (d, J = 8.0 Hz, 3H, Ar-H), 7.44 (d, J = 8.0 Hz, 3H, Ar-H), 7.29 (t, J = 7.6 Hz, 3H, Ar-H), 7.18 (t, J = 7.6 Hz, 3H, Ar-H), 2.49 (s, 9H, indole CH$_3$); ^{13}C NMR (CD$_2$Cl$_2$, 100 MHz): 150.88, 143.85, 139.55, 138.77, 129, 630, 127.46, 126.00, 125.60, 124.54, 121.56, 120.34, 119.41, 112.25, 10.36; HRMS ESI$^+$ for [M$^+$] ion C$_{39}$N$_{32}$N$_5$PCu$^+$: calcd m/z 664.1657, found m/z 664.1685.

Figure S7. ^1H NMR spectrum of **3** recorded in CD_2Cl_2.
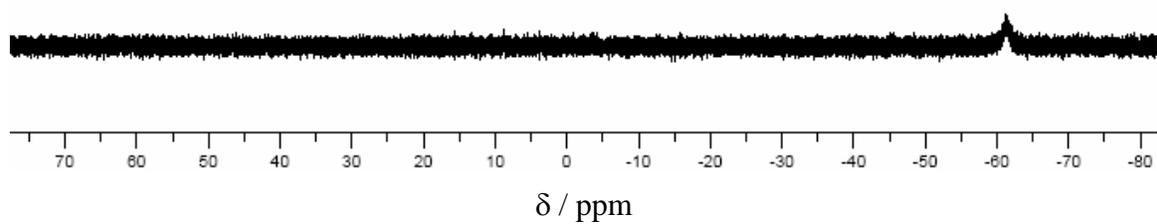

**Figure S8.** ^{31}P NMR spectrum of **3** recorded in CD_2Cl_2.
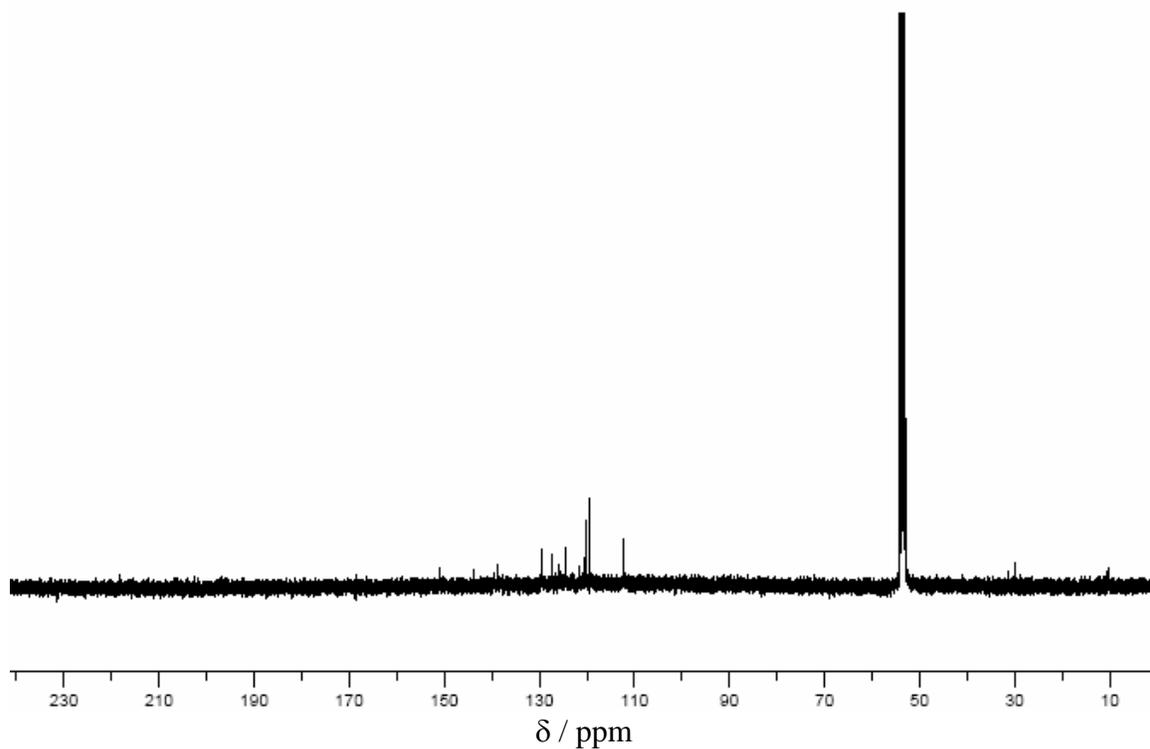
Figure S9. ^{13}C NMR spectrum of **3** recorded in CD_2Cl_2.

Titration Methods

^{1}H NMR titration experiments were carried out by dissolving **1** (15.4 µmol) in CD_2Cl_2 (0.65 mL) and adding sequential 10 µL aliquots of a solution of the selected anions as their tetrabutylammonium (NBu$_4$) salts (154 µmol) in CD_2Cl_2 (1 mL) (which corresponds to 0.1eq of anion) to **1** until saturation. Association constants, K_a, were determined by non-linear least-squares fit of the data using the program EQNMR.[3]
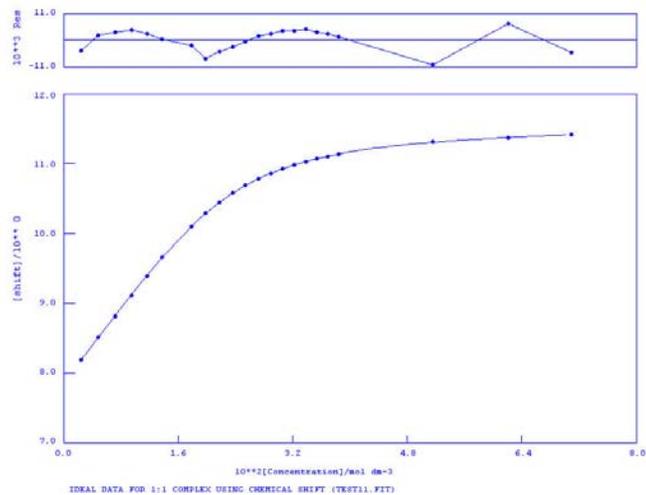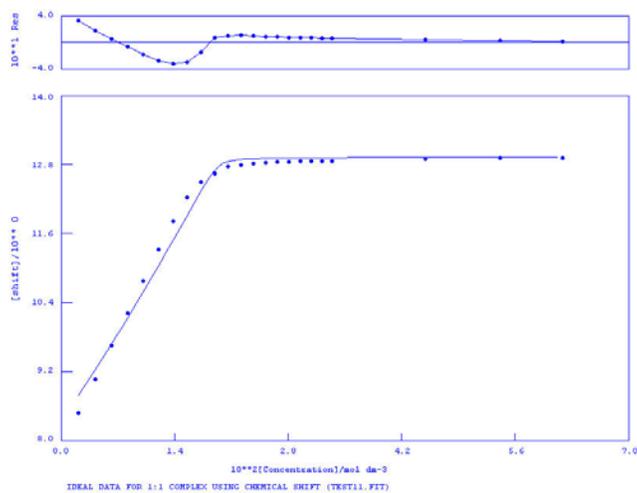
Figure S10. Fit plot for titration experiment of **1** with tetrabutylammonium chloride in CD$_2$Cl$_2$.
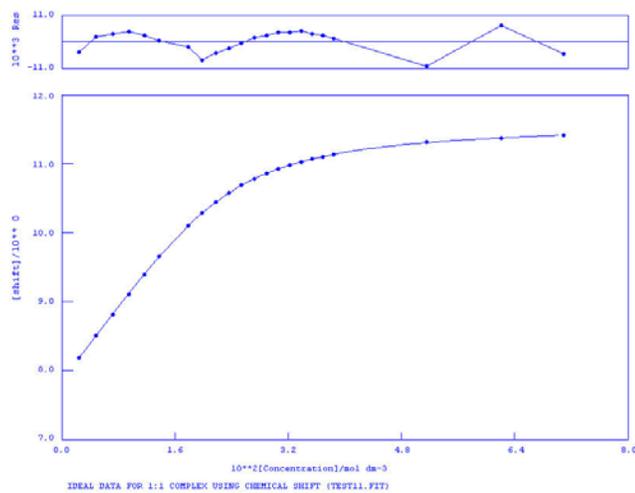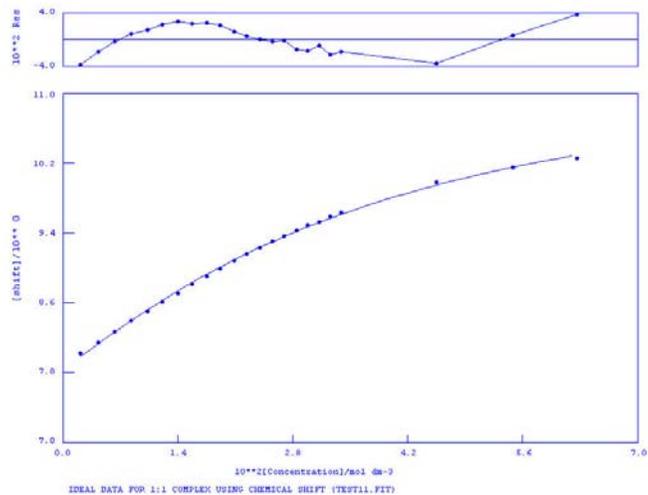

Figure S11. Fit plot for titration experiment of **1** with tetrabutylammonium bromide in CD$_2$Cl$_2$.
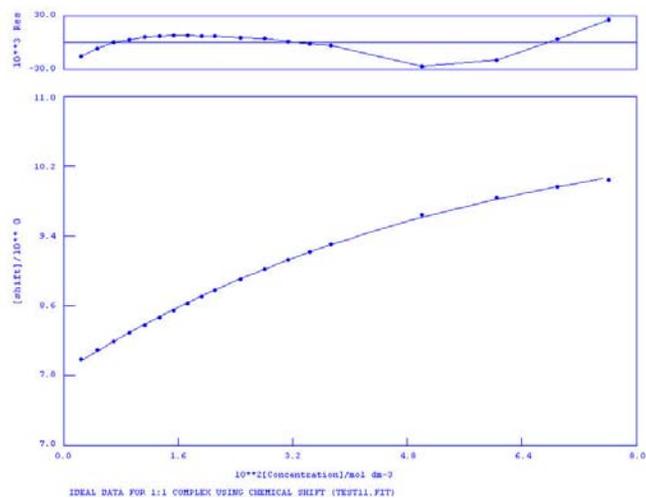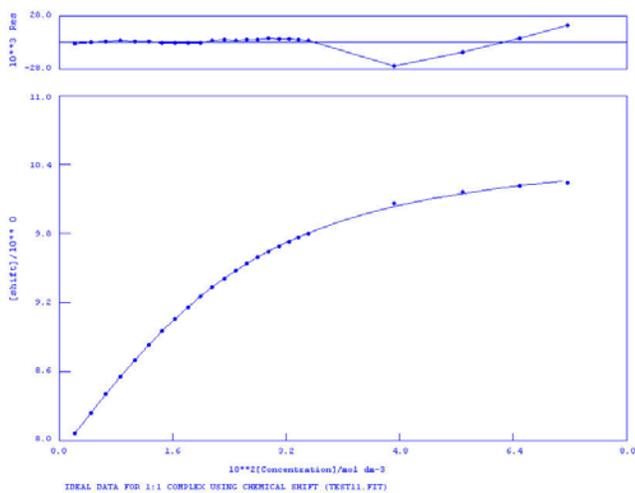
Figure S12. Fit plot for titration experiment of **1** with tetrabutylammonium iodide in CD$_2$Cl$_2$.

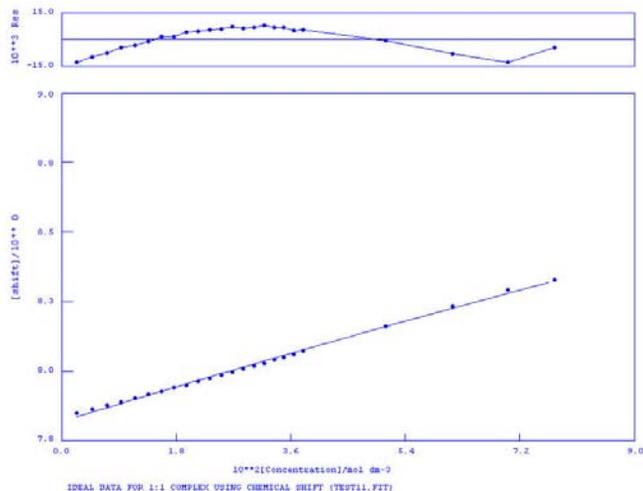

Figure S13. Fit plot for titration experiment of **1** with tetrabutylammonium acetate in CD$_2$Cl$_2$.

Figure S14. Fit plot for titration experiment of **1** with tetrabutylammonium hydrogensulfate in CD$_2$Cl$_2$.

Figure S15. Fit plot for titration experiment of **1** with tetrabutylammonium nitrate in CD$_2$Cl$_2$.

Figure S16. Fit plot for titration experiment of **1** with tetrabutylammonium tetrafluoroborate in CD_2Cl_2.

X-ray Crystallography. X-ray data were collected on a Nonius Kappa CCD diffractometer using graphite monochromated Mo Kα radiation (λ = 0.71073 Å). A combination of 1° ϕ and ω (with κ offsets) scans were used to collect sufficient data. The data frames were integrated and scaled using the Denzo-SMN package.[4] The structures were solved and refined with the SHELXTL-PC v6.12 software package.[5] Refinement was by full-matrix least squares on F^2 using data (including negative intensities) with hydrogen atoms bonded to carbon atoms included in calculated positions and treated as riding atoms. Absorption corrections were made for every structure. All the heavy atoms were refined anisotropically.

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