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Supporting Information

Bis- and Tris(pyrazolyl)borate/methane-Stabilized P^{III}-Centered Cations

Lianghu Gu, Gopinadhanpillai Gopakumar, Pauline Gualco, Walter Thiel, and Manuel Alcarazo*[a]

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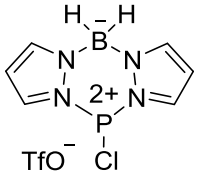
Table of Contents

Experimental procedures:

General: All reactions were carried out in flame-dried glassware under Ar. All solvents were purified by distillation over the appropiate drying agents and were transferred under Ar. IR: Nicolet FT-7199 spectrometer, wavenumbers in cm^{-1}. MS (EI): Finnigan MAT 8200 (70 eV), ESIMS: Finnigan MAT 95, accurate mass determinations: Bruker APEX III FT-MS (7 T magnet). NMR: Spectra were recorded on a Bruker AV 600, AV 400 or DPX 300; ^{1}H and ^{13}C chemical shifts (δ) are given in ppm relative to TMS, coupling constants (*J*) in Hz. The solvent signals were used as references and the chemical shifts converted to the TMS scale. Column chromatography was performed on Merck 60 silica gel (40-63 µm). Thin-layer chromatography (TLC) analysis was performed using Merck silica gel 60 F254 TLC plates, and visualized by UV.

All commercially available compounds (ABCR, Acros, Aldrich, Fischer) were used as received except TMSOTf that was distilled prior to use and then kept in Young type vessel. $K[H_2B(Pz)_2]$ **(1)**[1], $[H_2C(Pz)_2]$ **(8)**[2], bisoxazoline **(13)**[3], $K[HB(3,5\text{-}Me_2Pz)_3]$ **(15)**[4], $K[B(Pz)_4]$ **(16)**[5], $[HC(3,5\text{-}Me_2Pz)_3]$ **(17)**[6] were prepared according to literature procedures.

Compound **5**



PCl_3 (0.16 mL, 1.8 mmol) and TMSOTf (0.65 mL, 3.6 mmol) were added at – 78°C to a solution of $K[BH_2(Pz)_2]$ (**1**) (0.334 g, 1.8 mmol) in CH_2Cl_2 (5 mL). The mixture was allowed to warm up to room temperature overnight. Then the solvents were filtered off and the yellow solid was washed with CH_2Cl_2 (2 x 5 mL). The crude product thus obtained was extracted with CH_3CN (2 x 5 mL) at 0 °C and the combined solvents removed in vacuum to afford **5** a white solid (157 mg, 24 %).

mp: 95 °C (dec)

^{1}H NMR (CD_3CN, 300 MHz): δ = 8.60 (d, *J* = 2.1 Hz, 2H), 8.42 (s, 2H), 6.86 (m, 2H), 4.08 – 3.53 ppm (br s, 2H).

^{13}C NMR (CD_3CN, 100 MHz): δ = 146.9, 143.2 (d, J_{C-P} = 30.8 Hz), 122.2 (q, J_{C-F} = 320.2 Hz), 111.1 ppm (d, J_{C-P} = 6.0 Hz). ^{31}P NMR (CD_3CN, 121 MHz): δ = 85.7 ppm.

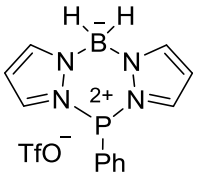
^{11}B NMR (CD_3CN, 128 MHz,): δ = 8.1 ppm.

^{19}F NMR (CD_3CN, 282 MHz): δ = – 79.3 ppm.

IR $\tilde{\nu}$ = 442, 516, 575, 633, 779, 913, 1024, 1060, 1084, 1162, 1225, 1419, 2456, 3112, 3139 cm^{-1}. Elemental analysis for $C_7H_8BClF_3N_4O_3PS$: calcd. C 23.20%, H 2.22%, N 15.46%; found: C 23.14%, H 2.56%, N 16.02%.

[1] Abernethy, R. J.; Hill, A. F.; Smith, M. K.; Willis, A. C. *Organometallics* **2009**, *28*, 6152.
[2] Machura, B.; Penczek, R.; Kruszynski, R.; Kłak, J; Mroziński, J.; Kusz, J. *Polyhedron* **2007**, *26*, 4833.
[3] Zhou J.; Tang Y. *Chem. Comm.* **2004**, 432.
[4] Malbosc, F.; Chauby, V.; Serra-Le Berre, C.; Etienne, M.; Daran, J. C.; Kalck, P. *Eur. J. Inorg. Chem.* **2001**, 2689.
[5] Lee, E.; Kamlet, A. S.; Powers, D. C.; Neumann, C. N.; Boursalian, G. B.; Furuya, T.; Choi, D. C.; Hooker, J. M.; Ritter, T. *Science* **2011**, *334*, 639.
[6] Neves, P.; Gago, S.; Balula, S. S.; Lopes, A. D.; Valente, A. A.; Cunha-Silva, L.; Almeida Paz, F. A.; Pillinger, M.; Rocha, J.; Silva, C. M.; Gonçalves, I. S. *Inorg. Chem.* **2011**, *50*, 3490.

Compound **6**



$PhPCl_2$ (1.5 mL, 10.7 mmol) and TMSOTf (1.9 mL, 10.7 mmol) were added at – 78°C to a suspension of $K[H_2B(Pz)_2]$ (**1**) (2.0 g, 10.7 mmol) in CH_2Cl_2 (10 mL) and the mixture was allowed to warm up to room temperature overnight. Then the solvents were filtered off, and the white solid thus obtained washed with CH_2Cl_2 (2 x 5 mL). The crude product was then extracted with CH_3CN (2 x 5 mL) at 0 °C and the combined solvents removed in vacuum to afford **6** as white solid (2.5 g, 57%). Colourless crystals suitable for X−ray crystallography were obtained from a CH_3CN/Et_2O solution at –30 °C.

mp: 101 °C (dec).

^{1}H NMR (CD_3CN, 400 MHz): δ = 8.62 (dd, J = 3.3 Hz, $J_{H–P}$ = 3.9 Hz, 2H), 8.29 (s, 2H), 7.57 (m, 1H), 7.48 (m, 2H), 7.09 (m, 2H), 6.88 (dd, J = 2.4 Hz, $J_{H–P}$ =5.1 Hz, 2H), 3.25 (br, $J_{H–B}$ = 138 Hz) ppm.

^{13}C NMR (CD_3CN, 101 MHz): δ = 145.8, 144.0 (d, $J_{C–P}$ = 26,7 Hz), 133.3, 131.6 (d, $J_{C–P}$ = 17.4 Hz), 130.7 (d, $J_{C–P}$ = 19.4 Hz), 130.3 (d, $J_{C–P}$ = 5.6 Hz), 122.2 (q, $J_{C–F}$ = 319.7 Hz), 110.7 ppm (d, $J_{C–P}$ = 5.2 Hz).

^{31}P NMR (CD_3CN, 162 MHz): δ = 87.1 ppm.

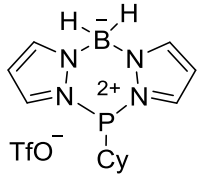
^{11}B NMR (CD_3CN, 128 MHz): δ = – 7.1 (t, $J_{B–H}$ = 105 Hz) ppm.

^{19}F NMR (CD_3CN, 282 MHz): δ = – 79.3 ppm.

IR $\tilde{\nu}$ = 416, 443, 465, 517, 633, 690, 746, 780, 950, 983,1027, 1061, 1092,1139, 1252, 1388, 1419, 2461, 3020, 3138 cm^{-1}.

Elemental analysis for $C_{13}H_{13}BF_3N_4O_3PS$: calcd. C 38.64%, H 3.24%, N 13.86%; found: C 38.80, H 3.92, N 13.67.

Compound **7**



$CyPCl_2$ (0.21 mL, 1.3 mmol) and TMSOTf (0.24 mL; 1.3 mmol,) were added at –78°C to a suspension of $K[H_2B(Pz)_2]$ (**1**) (250 mg, 1.3 mmol) in CH_2Cl_2 (5 mL) and the mixture was allowed to warm up to room temperature overnight. Then the solvents were filtered off and the white solid obtained washed with CH_2Cl_2 (2 x 5 mL). Then the crude product was extracted with CH_3CN (2 x 5 mL) at 0 °C and the organic solvents removed in vacuum to afford **7** as a white solid (302 mg, 55 %).

mp: 113 °C (dec).

^{1}H NMR (CD_3CN, 400 MHz): δ = 8.42 (dd, J = 3.3 Hz, $J_{H–P}$ = 3.3 Hz, 2H), 8.32 (s, 2H), 6.32 (dd, J = 2.7 Hz, $J_{H–P}$ = 4.6, Hz, 2H), 4.01 (br, $J_{H–B}$ = 128 Hz), 3.16 (m, 2H), 1.79 (m, 3H), 1.35 (m, 7H) ppm.

^{13}C NMR (CD_3CN, 101 MHz): δ = 145.5, 143.7 (d, $J_{C–P}$ = 25.3 Hz), 122.1 (q, $J_{C–F}$ = 320.9 Hz), 110.6 (d, $J_{C–P}$ = 5.4 Hz), 39.5 (d, $J_{C–P}$ = 20.5 Hz), 25.9, 25.8, 25.7, 25.6, 25.5 ppm. ^{31}P NMR (CD_3CN, 162 MHz): δ = 102.8 ppm.

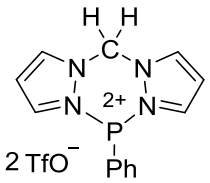
^{11}B NMR (CD_3CN, 128 MHz): δ = – 8.1 ppm.

^{19}F NMR (CD_3CN, 282 MHz): δ = –79.3 ppm.

IR $\tilde{\nu}$ = 697, 792, 875, 1027, 1073, 1137, 1222, 1263, 1414, 2425, 2490, 2859, 2928, 3105, 3137 cm^{-1}.

Elemental analysis for $C_{13}H_{19}BF_3N_4O_3PS$: calcd. C 38.07%, H 4.67%, N 13.66%; found: C 38.03%, H 4.23%, N 13.22%.

Compound **10**



$PhPCl_2$ (1.8 mL, 13.5 mmol) and TMSOTf (4.9 mL, 27.0 mmol) were added at – 78°C to a solution of $[H_2C(Pz)_2]$ (**8**) (2.0 g, 13.5 mmol) in CH_2Cl_2 (10 mL) and the mixture allowed to warm up to room temperature overnight. Then the solvents were filtered off and the white solid thus obtained washed with CH_2Cl_2 (2 x 5 mL). The crude product was dissolved in CH_3CN (5 mL), precipitated with Et_2O (15 mL) and dried in vacuum to afford **10** as a white solid (2.83 g, 38%). Colourless crystals suitable for X−ray crystallography were obtained from a CH_3CN/Et_2O solution at –30°C.

mp: 86 °C (dec).

^{1}H NMR (CD_3CN, 400 MHz): δ = 8.98 (dd, J = 2.5 Hz, $J_{H–P}$ = 2.5 Hz, 2H), 8.75 (s, 2H), 7.70 (m, 1H), 7.60 (m, 2H), 7.39 (m, 2H), 7.29 (d, J = 14.9 Hz, 1H), 7.10 (m, 2H), 5.87 (d, J = 14.9 Hz, 1H) ppm.

^{13}C NMR (CD_3CN, 101 MHz): δ = 147.9 (d, $J_{C–P}$ = 19.4 Hz), 145.1, 134.7, 131.9 (d, $J_{C–P}$ = 18.7 Hz), 131.0 (d, $J_{C–P}$ = 5.5 Hz), 128.3 (d, $J_{C–P}$ = 24.3 Hz), 121.9 (q, $J_{C–F}$ = 320.3 Hz), 111.7 (d, $J_{C–P}$ = 2.2 Hz), 63.3 ppm.

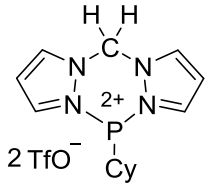
^{31}P NMR (CD_3CN, 162 MHz): δ = 85.8 ppm.

^{19}F NMR (CD_3CN, 282 MHz): δ = – 79.3 ppm.

IR $\tilde{\nu}$ = 675, 838, 894, 1029, 1162, 1220, 1241, 1377, 1563, 1580, 2827, 3136 cm^{-1}.

Elemental analysis for $C_{15}H_{13}F_6N_4O_6PS_2$: calcd. C 32.50%, H 2.36%, N 10.11%; found: C 32.11%, H 2.76%, N 10.60%.

Compound **11**



$CyPCl_2$ (0.26 mL, 1.7 mmol) and TMSOTf (0.61 mL, 3.4 mmol) were added at – 78°C to a suspension of $[H_2C(Pz)_2]$ (**8**) (250 mg, 1.7 mmol) in CH_2Cl_2 (5 mL) and the mixture allowed to warm up to room temperature overnight. The solvents were then evaporated in vacuum, the residue dissolved in CH_3CN (2 mL) and Et_2O (10 mL) was added to precipitate the product. White solid (433 mg, 46%).

mp: 93 °C (dec).

^{1}H NMR (CD_3CN, 400 MHz): δ = 8.80 (s, 2H), 8.76 (s, 2H), 7.56 (s, 1H), 7.05 (s, 2H), 6.84 (s, 1H), 2.97 (m, 1H), 1.94 (m, 2H), 1.85 (m, 1H), 1.54 (m, 4H), 1.34 (m, 3H), ppm.

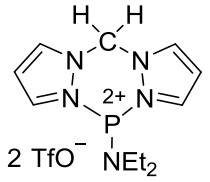
^{13}C NMR (CD_3CN, 101 MHz): δ = 147.3 (d, $J_{C–P}$ = 20.9 Hz), 144.9 (d, $J_{C–P}$ = 2.8 Hz), 121.9 (q, $J_{C–F}$ = 320.4 Hz), 112.1 (d, $J_{C–P}$ = 5.4 Hz), 63.4, 40.5 (d, $J_{C–P}$ = 26.9 Hz), 25.6, 25.5, 25.4, 25.3, 25.2 ppm.

^{31}P NMR (CD_3CN, 162 MHz): δ = 110.1 ppm.

^{19}F NMR (CD_3CN, 282 MHz): δ = – 79.3 ppm.

IR $\tilde{\nu}$ = 573, 609, 759, 1023, 1159, 1246, 1567, 2744, 2853, 3039, 3121 cm^{-1}.

Compound **12**



$(Et_2N)PCl_2$ (0.29 mL, 2.0 mmol) and TMSOTf (0.73 mL, 4.0 mmol) were added at – 78°C to a solution of $[H_2C(Pz)_2]$ (**8**) (296 mg, 2.0 mmol) in CH_2Cl_2 (4 mL) and the mixture was allowed to warm up to room temperature overnight. The solvents were then filtered off and the white solid thus obtained washed with CH_2Cl_2 (2 x 5 mL).

Crude **12** was then dissolved in CH_3CN and precipitated with Et_2O (362 mg, 33%). Colourless crystals suitable for X−ray crystallography were obtained from CH_3CN/Et_2O solution at – 30°C. mp: 103 °C (dec).

^{1}H NMR (CD_3CN, 400 MHz): δ = 8.69 (s, 2H), 8.61 (s, 2H), 7.27 (d, *J* = 11.36 Hz, 1H), 7.08 (t, *J* = 2.88 Hz, 1H), 7.08 (d, 11.36 Hz, 1H), 3.38 (m, 4H), 1.23 (t, *J* = 7.1 Hz, 6H) ppm.

^{13}C NMR (CD_3CN, 75 MHz): δ = 143.7 (d, $J_{C–P}$ = 9.0 Hz), 142.1, 111.7, 63.2, 43.9, 43.7, 13.8, 13.7 ppm.

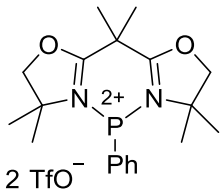
^{31}P NMR (CD_3CN, 162 MHz): δ = 107.8 ppm.

^{19}F NMR (CD_3CN, 282 MHz): δ = – 79.3 ppm.

IR $\tilde{\nu}$ = 515, 574, 632, 759, 1023, 1100, 1158, 1347, 1391, 1445, 1522, 1567, 2854, 2997, 3120 cm^{-1}.

Elemental analysis for $C_{13}H_{18}F_6N_5O_6PS_2$: calcd. C 28.42%, H 3.40%, N 12.75%; found: C 28.23%, H 3.28%, N 12.75%.

Compound **14**



$PhPCl_2$ (0.75 mL, 5.4 mmol) and TMSOTf (2.0 mL, 10.8 mmol) were added at – 78°C to a suspension of bisoxazoline **13** (1.28 g, 5.4 mmol) in CH_2Cl_2 (20 mL) and the mixture allowed to warm up to room temperature overnight. Filtration of the solvent afforded a white solid that was subsequently washed with CH_2Cl_2 (2 x 10 mL). Crude **14** was then dissolved in CH_3CN at 0°C and precipitated with Et_2O. White solid (1.55 g, 45%).

mp: 65-68 °C.

^{1}H NMR (CD_3CN, 300 MHz): δ = 8.11 – 8.05 (m, 2H), 7.94 – 7.90 (m, 1H), 7.80 – 7.74 (m, 2H), 5.08 – 5.04 (m, 4H), 2.19 (s, 3H), 2.04 (s, 3H), 1.85 (s, 6H), 1.08 (s, 6H) ppm.

^{13}C NMR (CD_3CN, 75 MHz): δ = 175.7 (d, $J_{C–P}$ = 6.9 Hz), 138.1 , 135.9 (d, $J_{C–P}$ = 33.9 Hz), 131.7 (d, $J_{C–P}$ = 11.1 Hz), 129.3 (d, $J_{C–P}$ = 29.2 Hz), 86.3 , 75.6 (d, 12.9), 41.9 (d, *J* = 1.1 Hz), 29.6, 26.5 (d, *J* = 2.1 Hz), 25.6 (d, *J* = 10.0 Hz), 22.7 (d, *J* = 1.9 Hz) ppm.

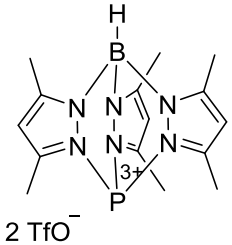
^{31}P NMR (CD_3CN, 162 MHz): δ = 88.8 ppm.

^{19}F NMR (CD_3CN, 282 MHz): δ = – 79.17 ppm.

IR $\tilde{\nu}$ = 435, 493, 516, 573, 634, 693, 739, 934, 1026, 1149, 1245, 1329, 1382, 1495, 1599, 1656, 2941 cm^{-1}.

Elemental analysis for $C_{21}H_{27}F_6N_2O_8PS_2$: calcd. C 39.13%, H 4.22%, N 4.35%; found: C 38.83%, H 4.22%, N 4.35%.

Compound **18**



PCl_3 (0.56 mL, 6.4 mmol) and TMSOTf (2.3 mL, 12.8 mmol) were added at – 78°C to a suspension of K[HB(3,5-Me_2Pz)$_3$] (**15**) (2.05 g, 6.1 mmol) in CH_2Cl_2 (10 mL) and the mixture was allowed to warm up to room temperature overnight. Filtration of the solid afforded a white solid that was subsequently washed with CH_2Cl_2 (2 x 5 mL). The crude product was extracted with CH_3CN (2 x 10 mL) the solvent evaporated in vacuum to afford **18** as a white solid (1.134 g, 24%). Colourless crystals suitable for X−ray crystallography were obtained from CH_3CN/Et_2O solution at –30°C.

mp: 118 °C (dec).

^{1}H NMR (CD_3CN, 300 MHz): δ = 6.44 (d, $J_{H–P}$ =4.4, Hz, 3H), 4.79 (br, $J_{H–B}$ = 162 Hz), 2.70 (s, 9H), 2.57 (s, 9H) ppm.

^{13}C NMR (CD_3CN, 101 MHz): δ = 158.3, 156.2 (d, $J_{C–P}$ = 19.3 Hz), 122.0 (d, $J_{C–F}$ = 320.7 Hz), 111.2 (q, $J_{C–P}$ = 2.2 Hz), 13.1 (d, $J_{C–P}$ = 8.8 Hz), 12.8 ppm.

^{31}P NMR (CD_3CN, 121 MHz): δ = 7.3 ppm.

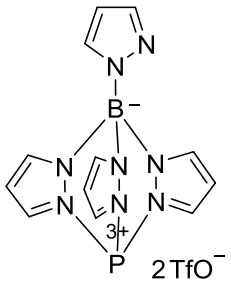
^{11}B NMR (CD_3CN, 128 MHz): δ = – 9.9 (d, $J_{B–H}$ = 129 Hz) ppm.

^{19}F NMR (CD_3CN, 282 MHz): δ = – 79.3 ppm.

IR $\tilde{\nu}$ = 516, 573, 605, 633, 691, 756, 789, 906, 1023, 1099, 1160, 1223, 1435, 1522, 2700, 3040, 3142 cm^{-1}.

Elemental analysis for $C_{17}H_{22}BF_6N_6O_6PS_2$: calcd. C 32.60%, H 3.54%, N 13.42%; found: C 32.14%, H 3.78%, N 13.34%.

Compound **19**



PCl_3 (0.16 mL, 1.8 mmol) and TMSOTf (0.65 mL, 3.6 mmol) were added at – 78°C to a solution of K[B(Pz)$_4$] (**16**) (572 mg, 1.8 mmol) in CH_2Cl_2 (5 mL) and the mixture was allowed to warm up to room temperature overnight. After filtration of the supernatant the white solid obtained was washed with CH_2Cl_2 (2 x 5 mL) and extracted with CH_3CN (2 x 10 mL). Evaporation of the solvent in vacuum afforded **19** as a white solid (588 mg, 43%). Colourless crystals suitable for X−ray crystallography were obtained from a CH_3CN/Et_2O solution at 5 °C.

mp: 122 °C (dec).

^{1}H NMR (CD_3CN, 300 MHz): δ = 8.86 (s, 3H), 8.61 (s, 3H), 8.28 (s, 1H), 8.08 (s, 1H), 6.85 (d, J_{H-P} = 2.6, 3H), 6.82 (s, 1H).

^{13}C NMR (CD_3CN, 75 MHz): δ = 146.5 (d, $J_{C–P}$ = 19.3 Hz), 145.5, 136.3, 121.8 (q, $J_{C–F}$ = 320.2 Hz), 110.8, 110.7 (d, $J_{C–P}$ = 3.2 Hz) ppm.

^{31}P NMR (CD_3CN, 121 MHz): δ = – 0.4 ppm.

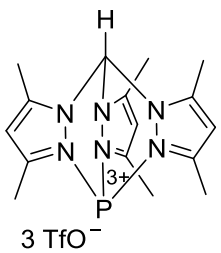
^{11}B NMR (CD_3CN, 128 MHz): δ = – 1.3 ppm.

^{19}F NMR (CD_3CN, 282 MHz): δ = – 79.3 ppm.

IR $\tilde{\nu}$ = 567, 594, 766, 864, 1065, 1109, 1157, 1243, 1392, 1157, 2659, 3133 cm^{-1}.

Elemental analysis for $C_{14}H_{12}BF_6N_8O_6PS_2$: calcd. C 27.65%, H 1.99%, N 18.42%; found: C 27.96%, H 1.67%, N 18.14%.

Compound **20**



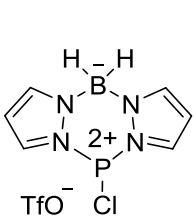
PCl_3 (0.23 mL, 2.6 mmol) and TMSOTf (1.4 mL, 7.9 mmol) were added at – 78°C to a solution of [HC(3,5-Me_2Pz)$_3$] (**17**) (790 mg, 2.6 mmol) in CH_2Cl_2 (5 mL) and the mixture was allowed to warm up to room temperature overnight. Filtration of the solvents afforded a white solid that was washed with CH_2Cl_2 (2 x 5 mL). Crude **20** was then dissolved in CH_3CN (5 mL) and precipitated with Et_2O (15 mL) to afford a white solid (608 mg, 29%).

mp: 102 °C (dec).

^{1}H NMR (CD_3CN, 400 MHz): δ = 9.60 (s, 1H), 6.75 (d, $J_{H–P}$ =4.8 Hz, 3H), 2.89 (s, 9H), 2.88 (s, 9H) ppm.
^{13}C NMR (CD_3CN, 101 MHz): δ = 161.6 (d, $J_{C–P}$ = 15.2 Hz), 158.5, 121.8 (q, $J_{C–F}$ = 320.2 Hz), 112.6, 70.8 (d, $J_{C–P}$ = 3.6 Hz), 15.1 (d, $J_{C–P}$ = 5.4 Hz), 13.6 ppm.
^{31}P NMR (CD_3CN, 121 MHz): δ = – 9.9 ppm.
^{19}F NMR (CD_3CN, 282 MHz): δ = – 79.2 ppm.
IR $\tilde{\nu}$ = 447, 515, 573, 631, 707, 760, 844, 944, 1022, 1078, 1160, 1207, 1417, 1584, 2709, 2940, 3135 cm^{-1}.
Elemental analysis for $C_{19}H_{22}F_9N_6O_9PS_3$: calcd. C 29.39 %, H 2.86%, N 10.82 %; found: C 29.52%, H 3.02%, N 10.50%.

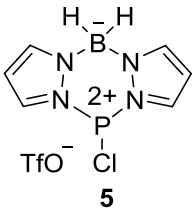
NMR spectra

^{1}H NMR (CD_3CN, 300 MHz)



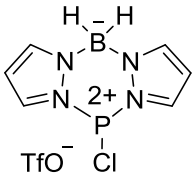
5

^{13}C NMR (CD_3CN, 75 MHz)



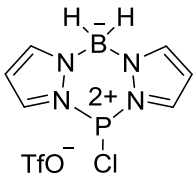
5

^{31}P NMR (CD_3CN, 162 MHz)



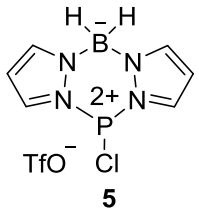
5

^{11}B NMR (CD_3CN, 128 MHz)



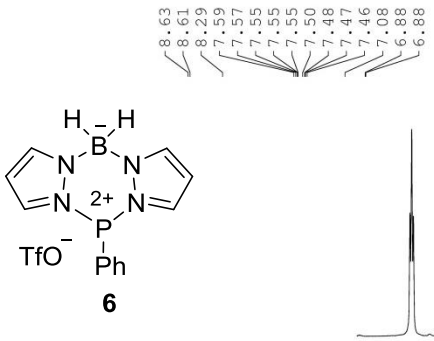
5

^{19}F NMR (CD_3CN, 282 MHz



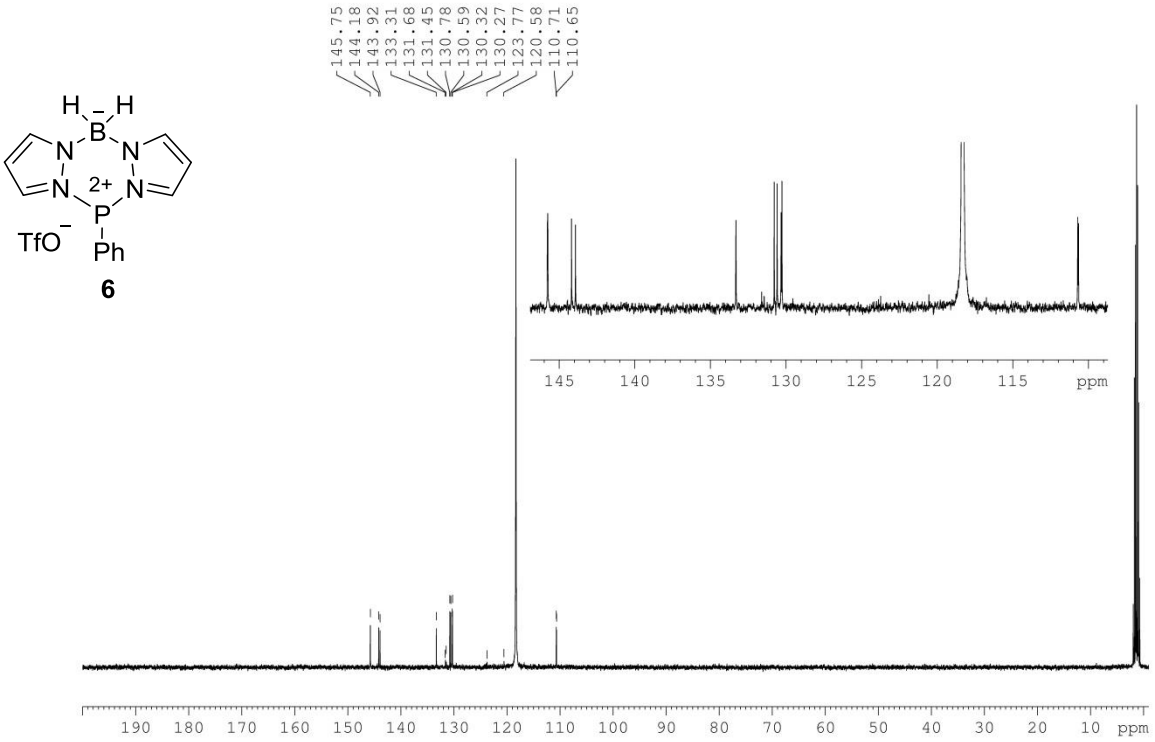
5

^{1}H NMR (CD_3CN, 400 MHz)



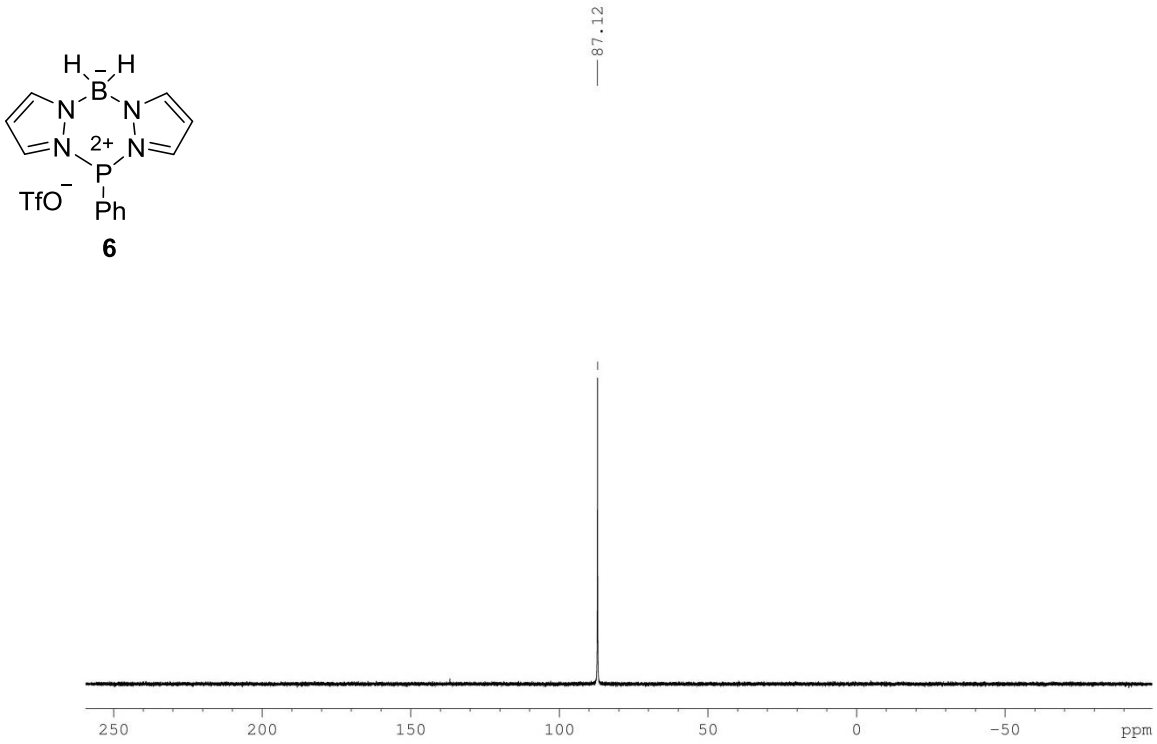
6

^{13}C NMR (CD_3CN, 101 MHz)



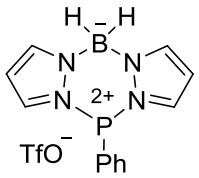
6

^{31}P NMR (CD_3CN, 162 MHz)



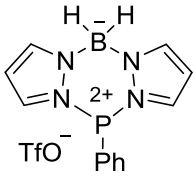
6

^{11}B NMR (CD_3CN, 128 MHz)



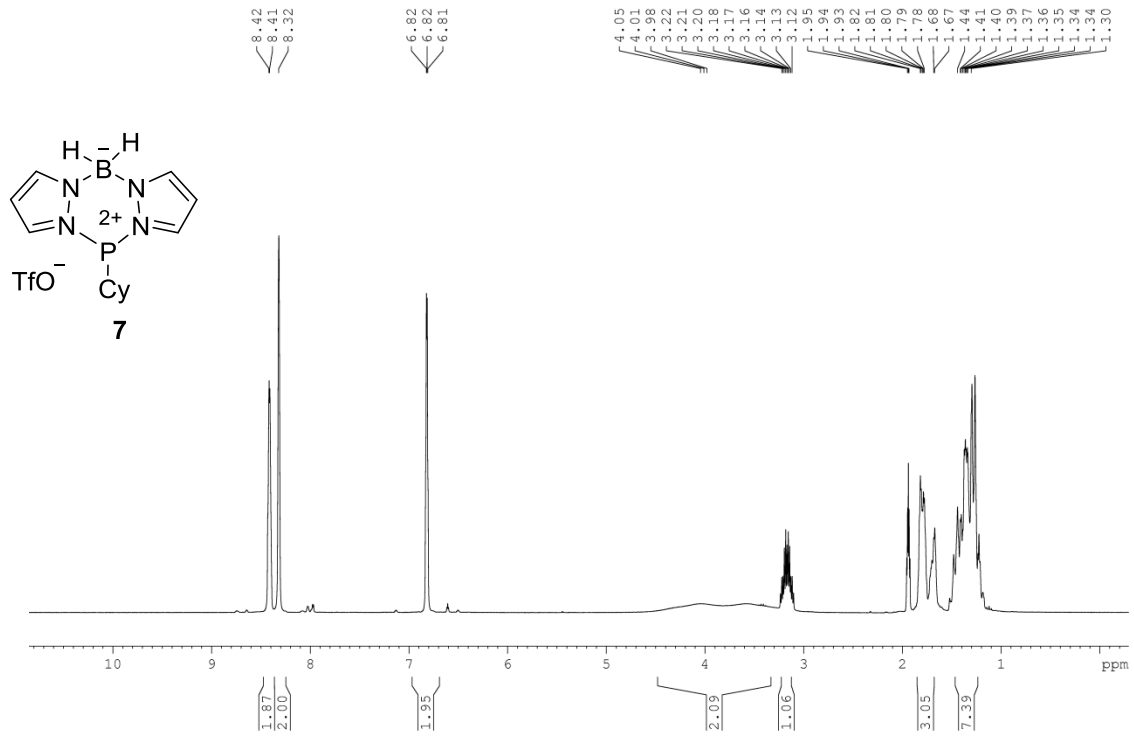
6

^{19}F NMR (CD_3CN, 282 MHz)

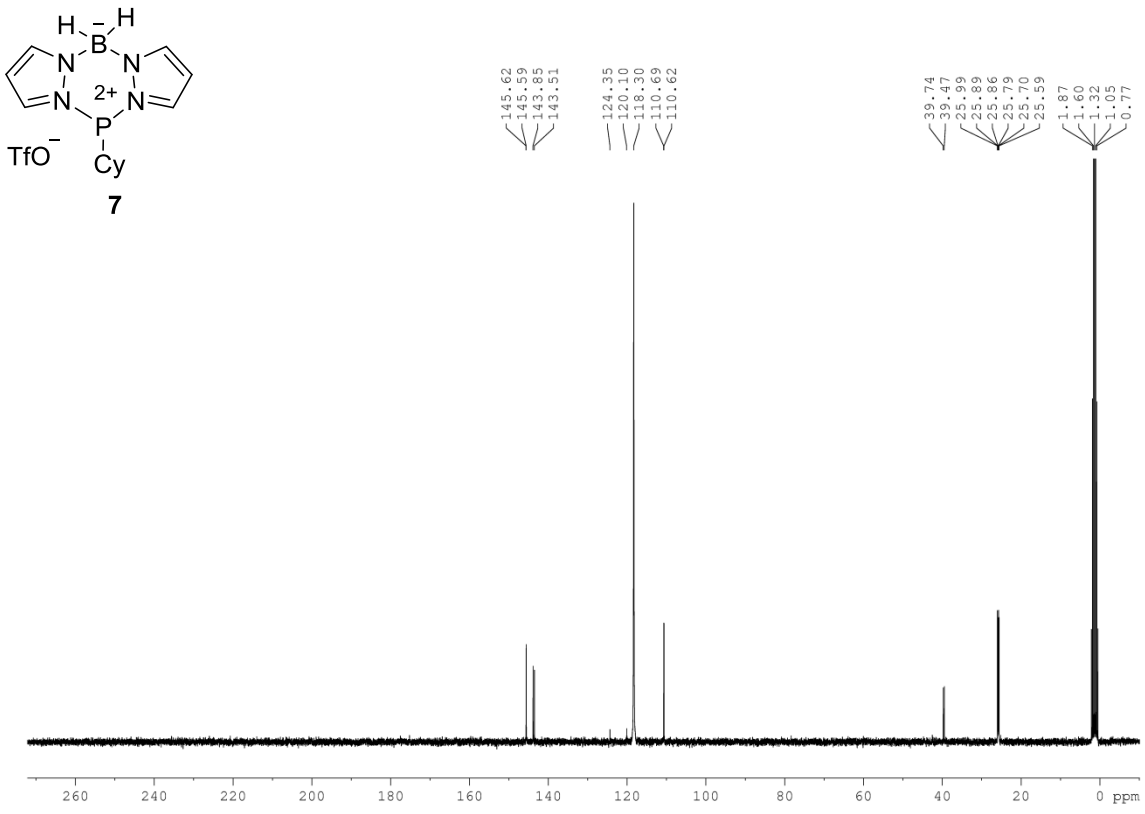


6

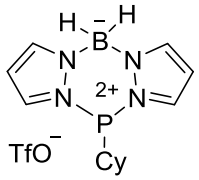
^{1}H NMR (CD_3CN, 400 MHz)



^{13}C NMR (CD_3CN, 101 MHz)

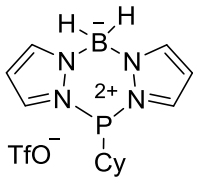


^{31}P NMR (CD_3CN, 162 MHz)



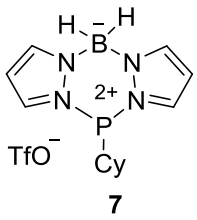
7

^{11}B NMR (CD_3CN, 128 MHz)



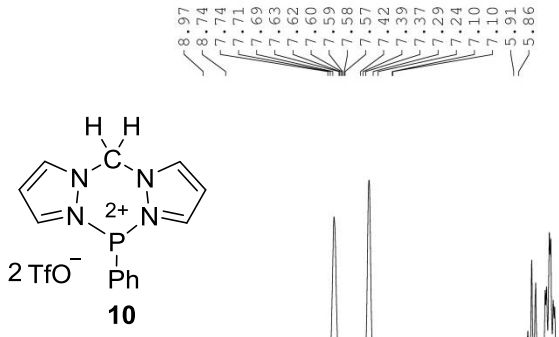
7

^{19}F NMR (CD_3CN, 282 MHz)



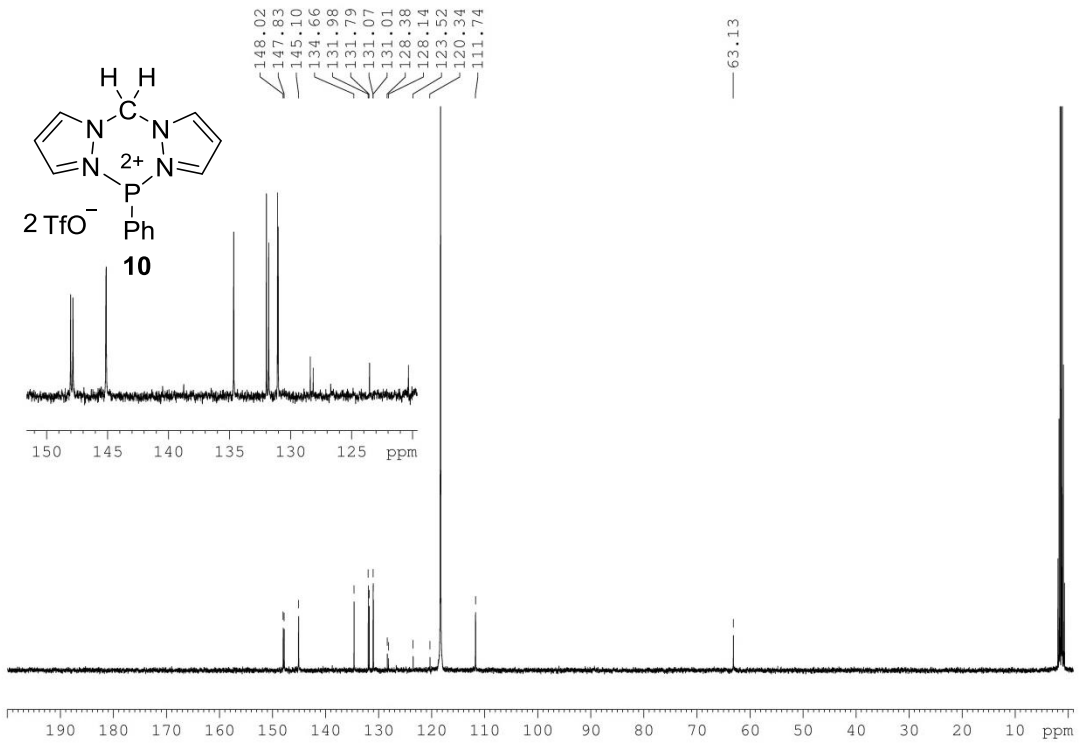
7

^{1}H NMR (CD_3CN, 400 MHz)

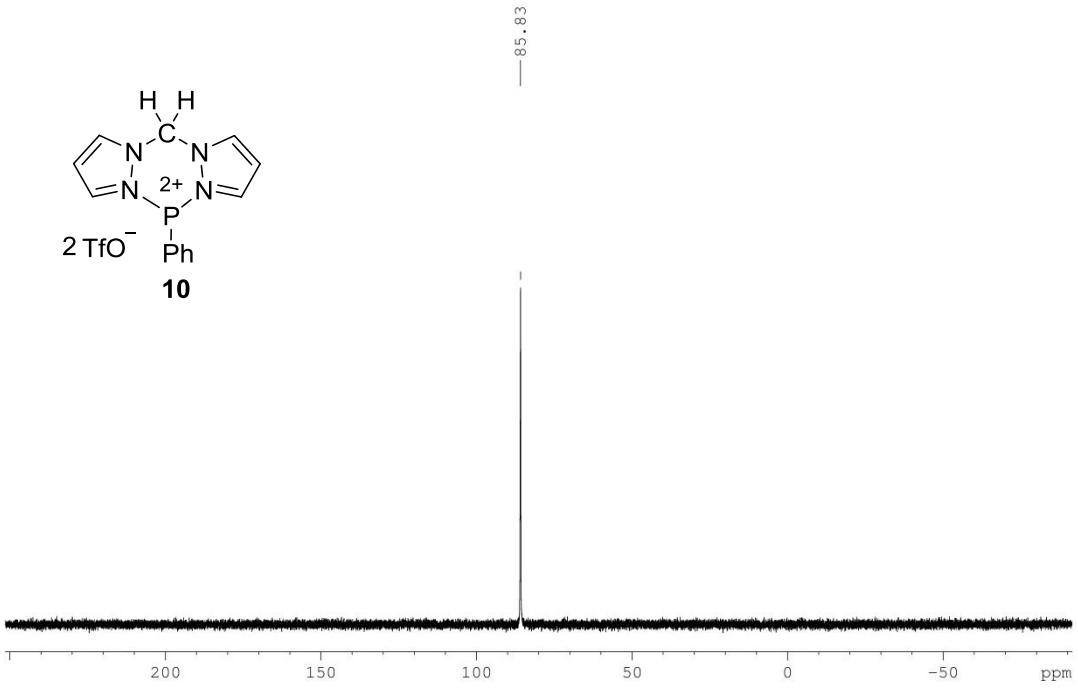


10

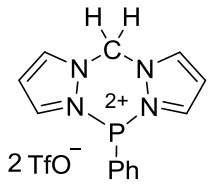
^{13}C NMR (CD_3CN, 101 MHz)



^{31}P NMR (CD_3CN, 162 MHz)

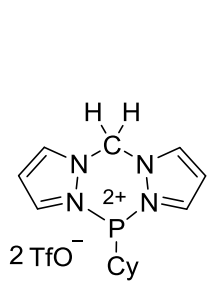


^{19}F NMR (CD_3CN, 282 MHz)



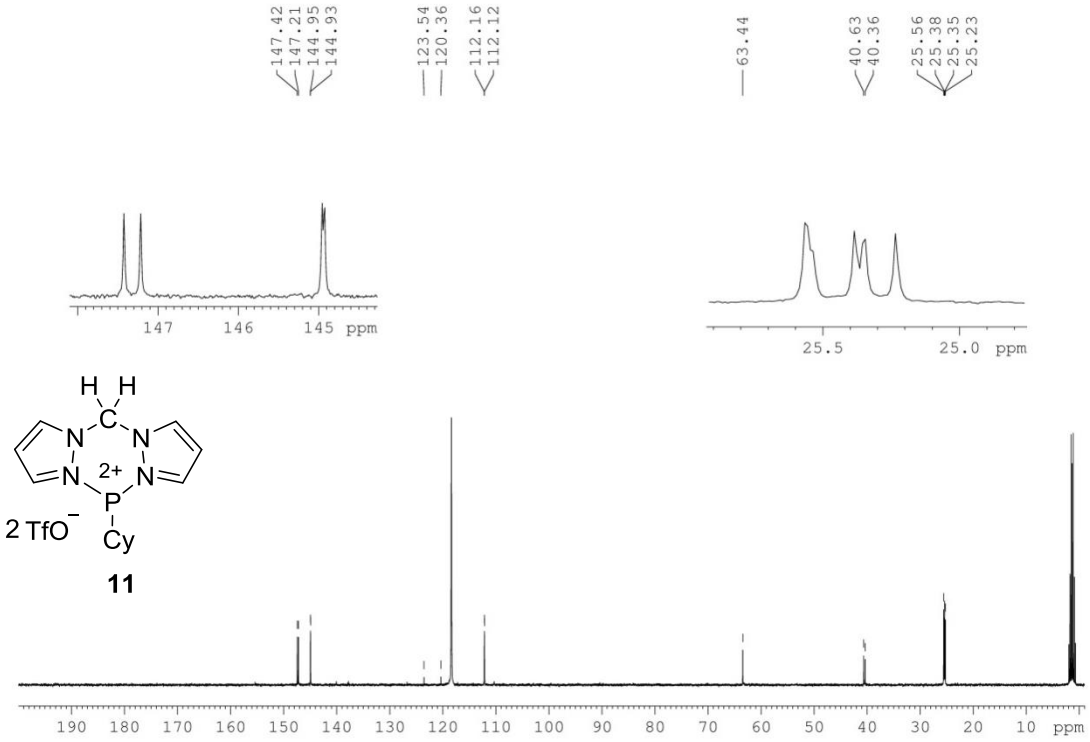
10

^{1}H NMR (CD_3CN, 400 MHz)

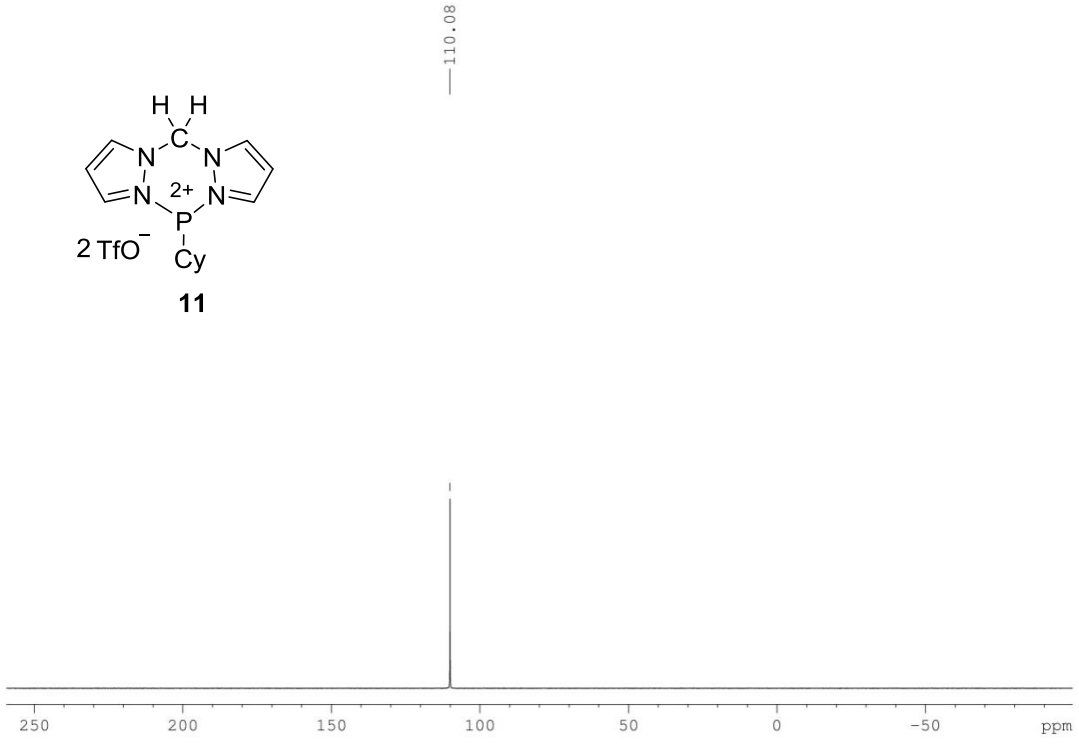


11

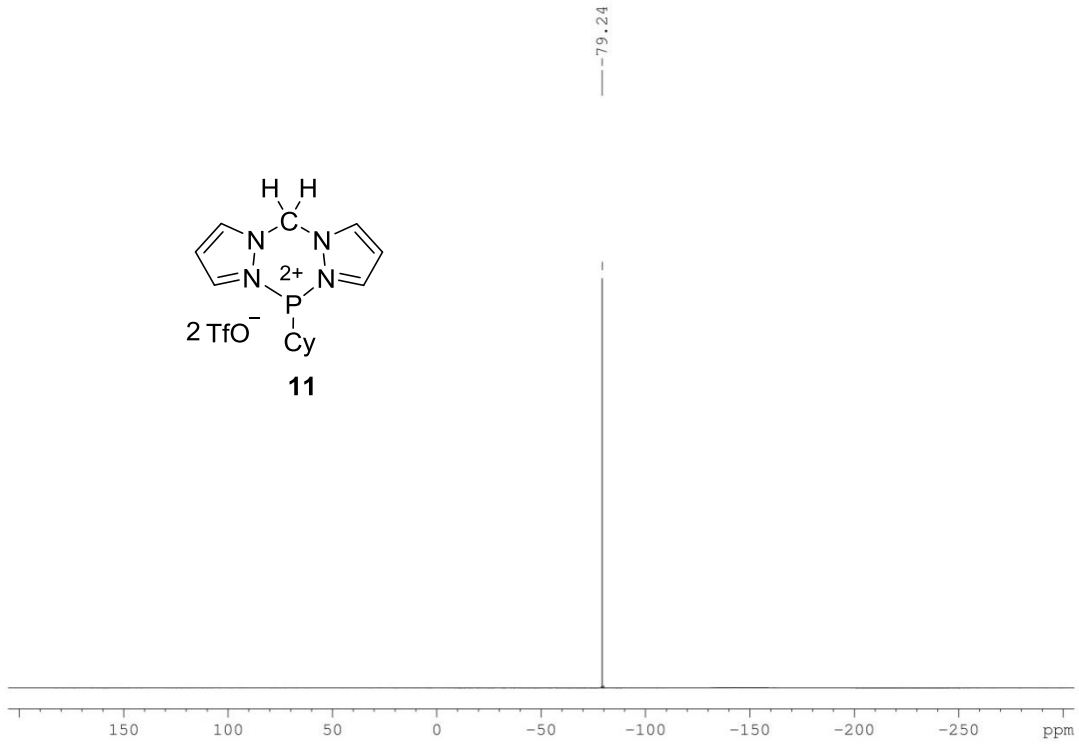
^{13}C NMR (CD_3CN, 101 MHz)



^{31}P NMR (CD_3CN, 162 MHz)

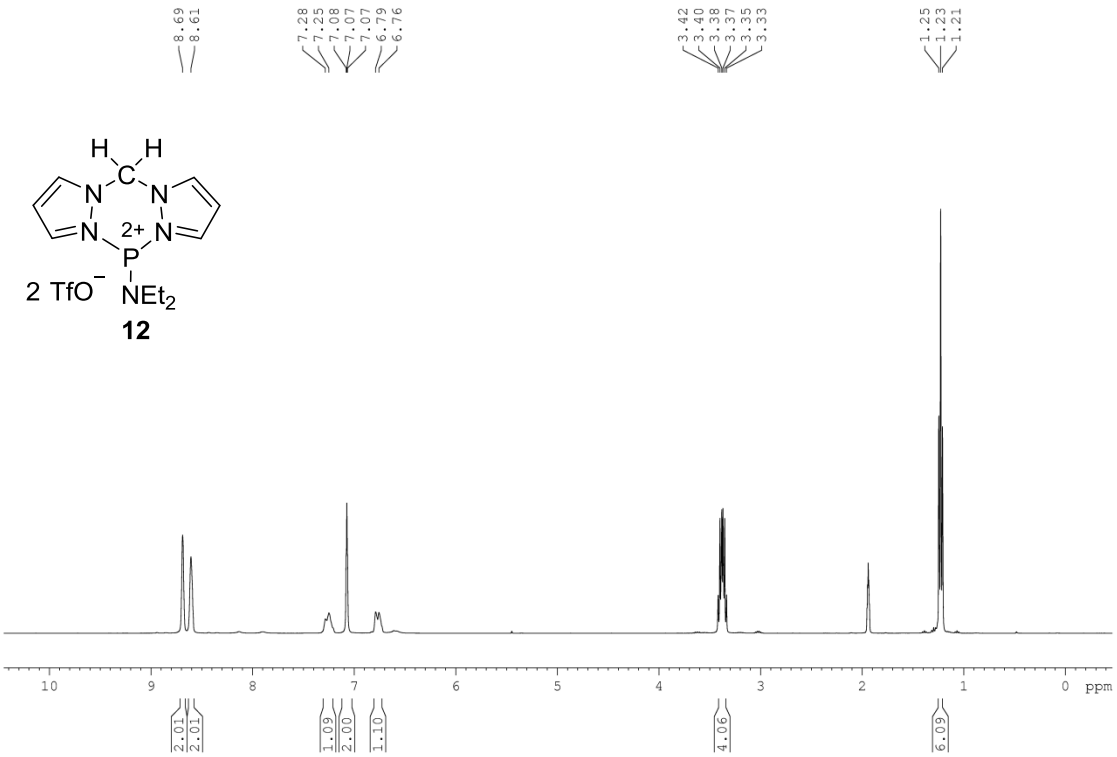


^{19}F NMR (CD_3CN, 282 MHz)



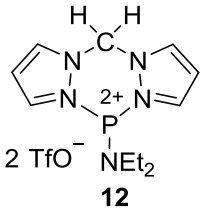
11

^{1}H NMR (CD_3CN, 300 MHz)



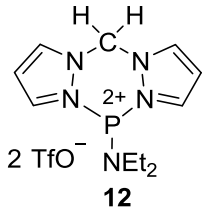
12

^{13}C NMR (CD_3CN, 75 MHz)



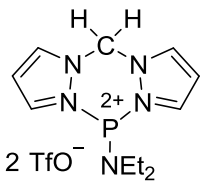
12

^{31}P NMR (CD_3CN, 121 MHz)



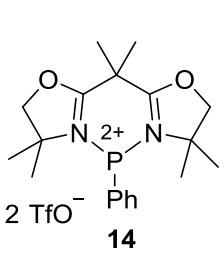
12

^{11}F NMR (CD_3CN, 282 MHz)



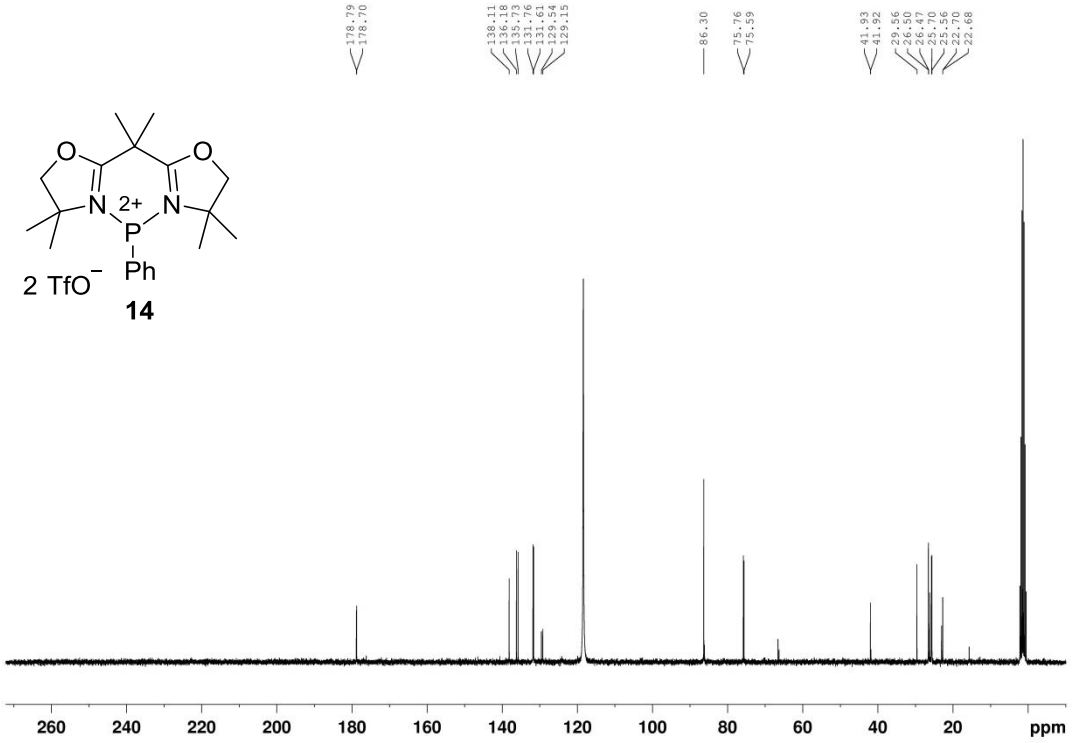
12

^{1}H NMR (CD_3CN, 300 MHz)

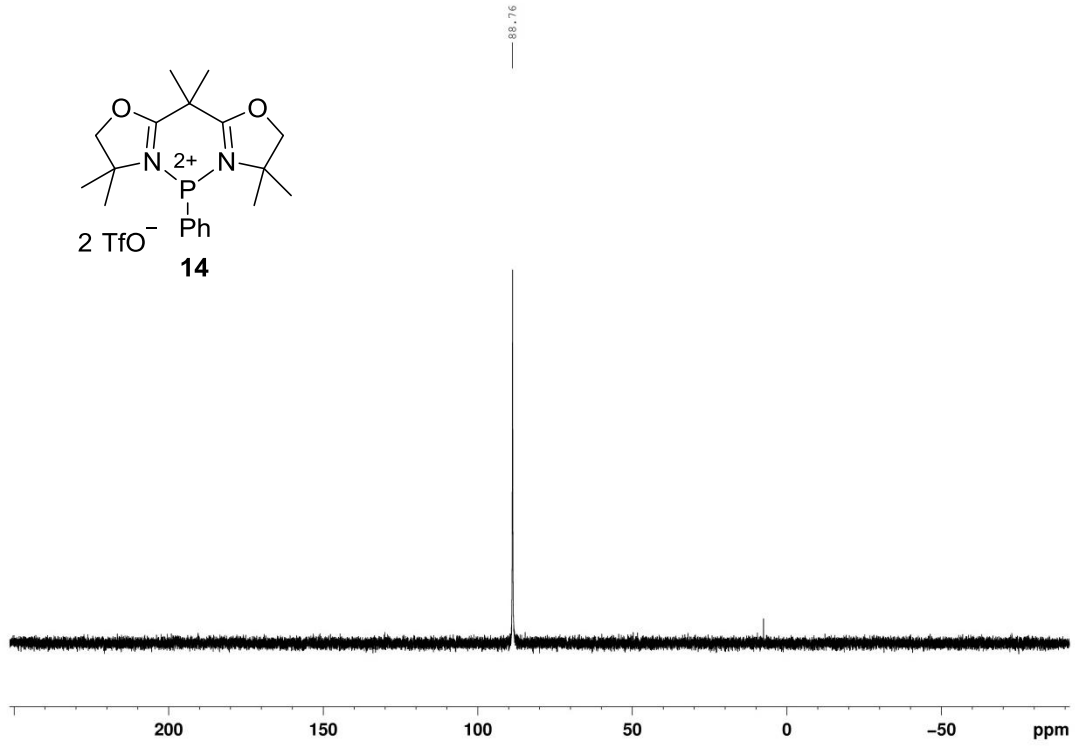


14

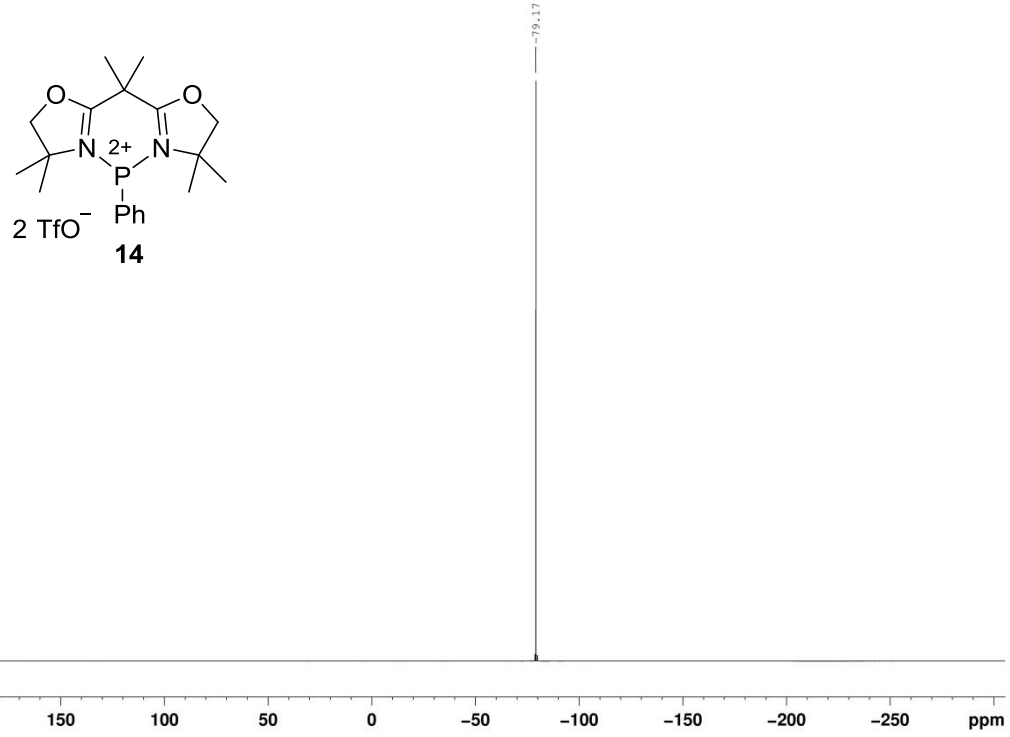
^{13}C NMR (CD_3CN, 101 MHz)



^{31}P NMR (CD_3CN, 162 MHz)



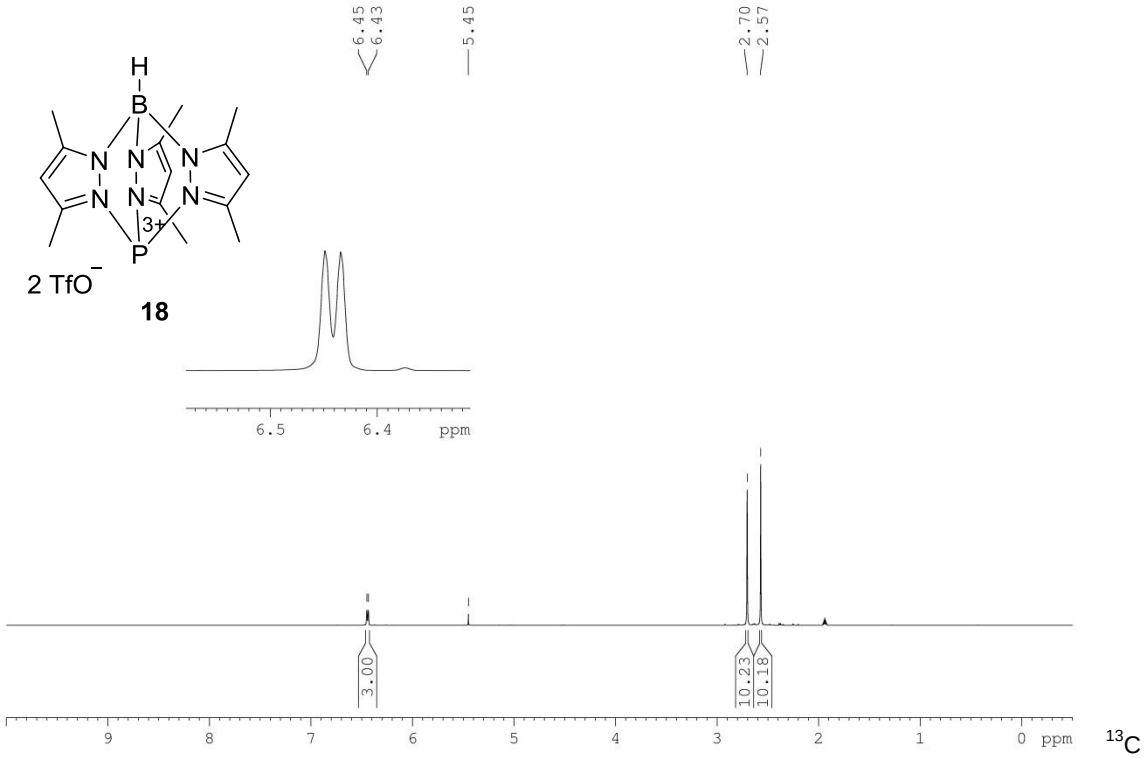
^{19}F NMR (CD_3CN, 282 MHz)



2 TfO^-

14

^{1}H NMR (CD_3CN, 400 MHz)

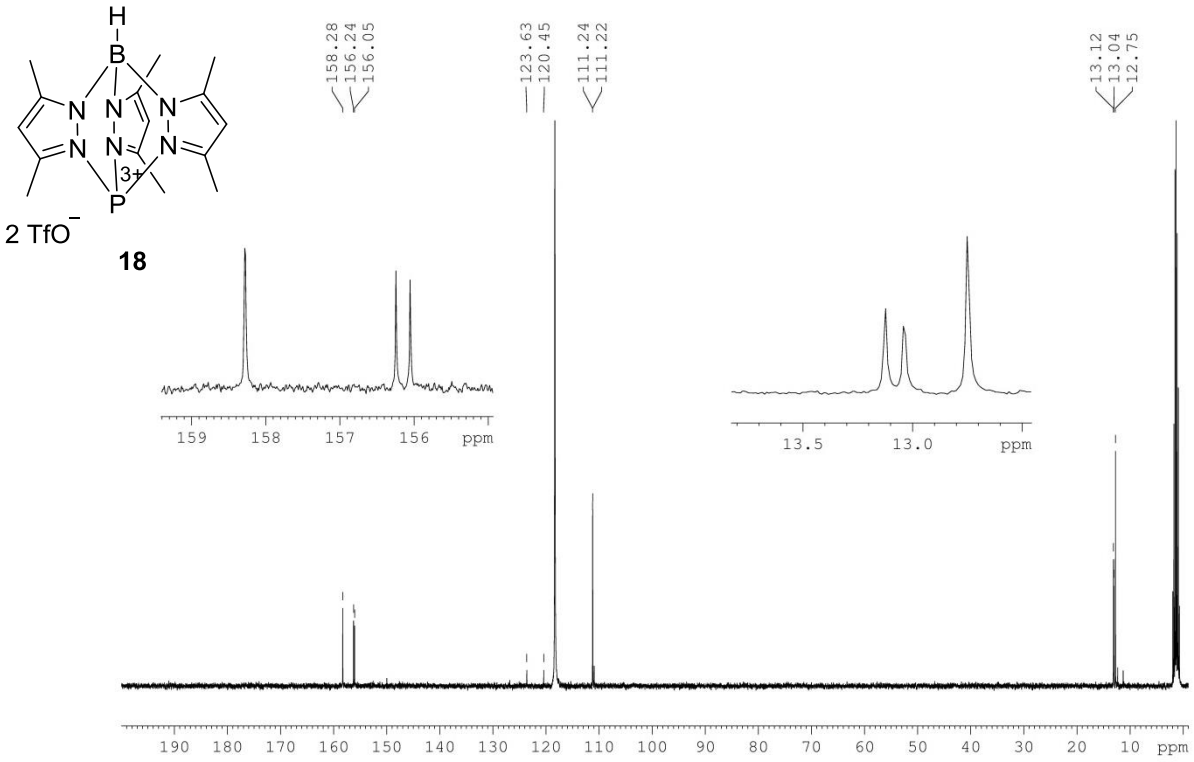


2 TfO^-

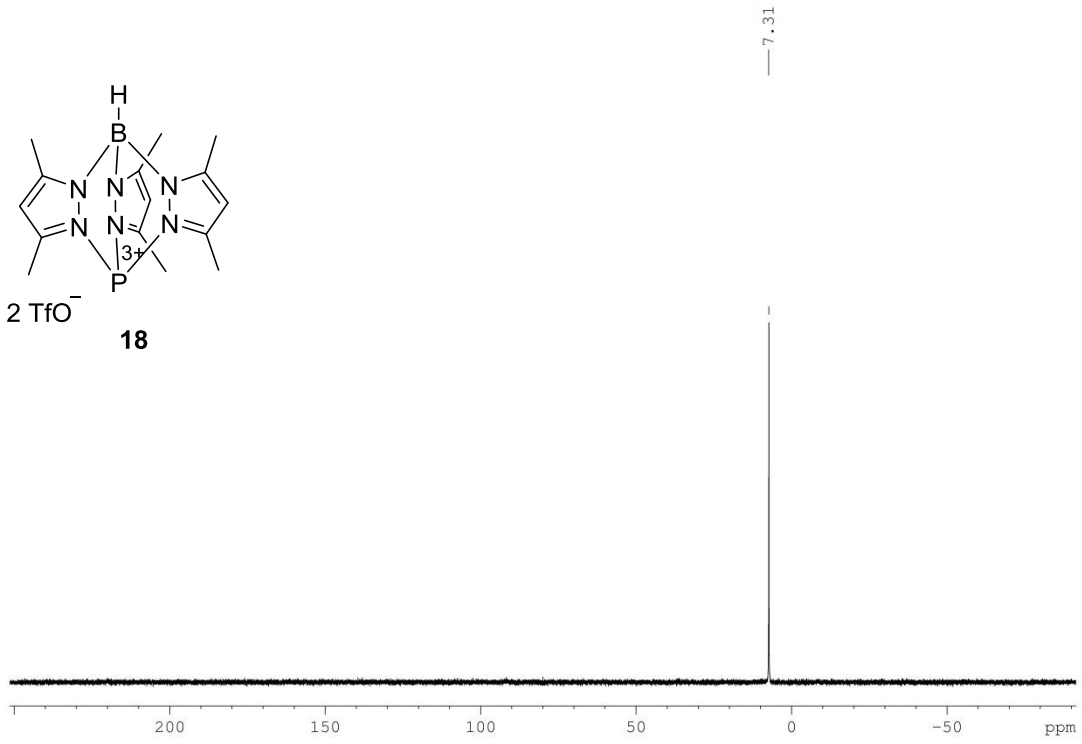
18

^{13}C

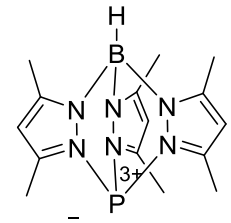
NMR (CD_3CN, 101 MHz)



^{31}P NMR (CD_3CN, 162 MHz)



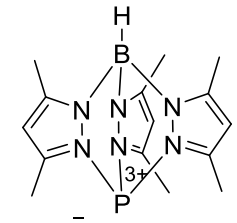
^{11}B NMR (CD_3CN, 128 MHz)



2 TfO^-

18

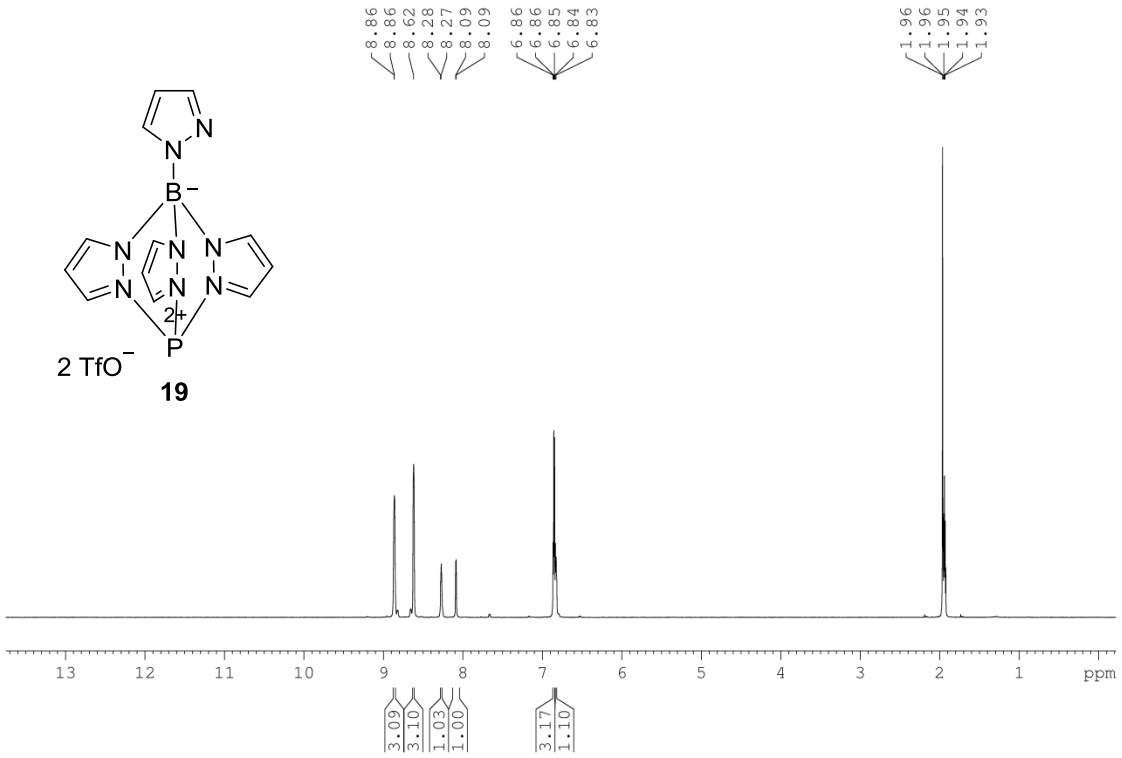
^{19}F NMR (CD_3CN, 282 MHz)



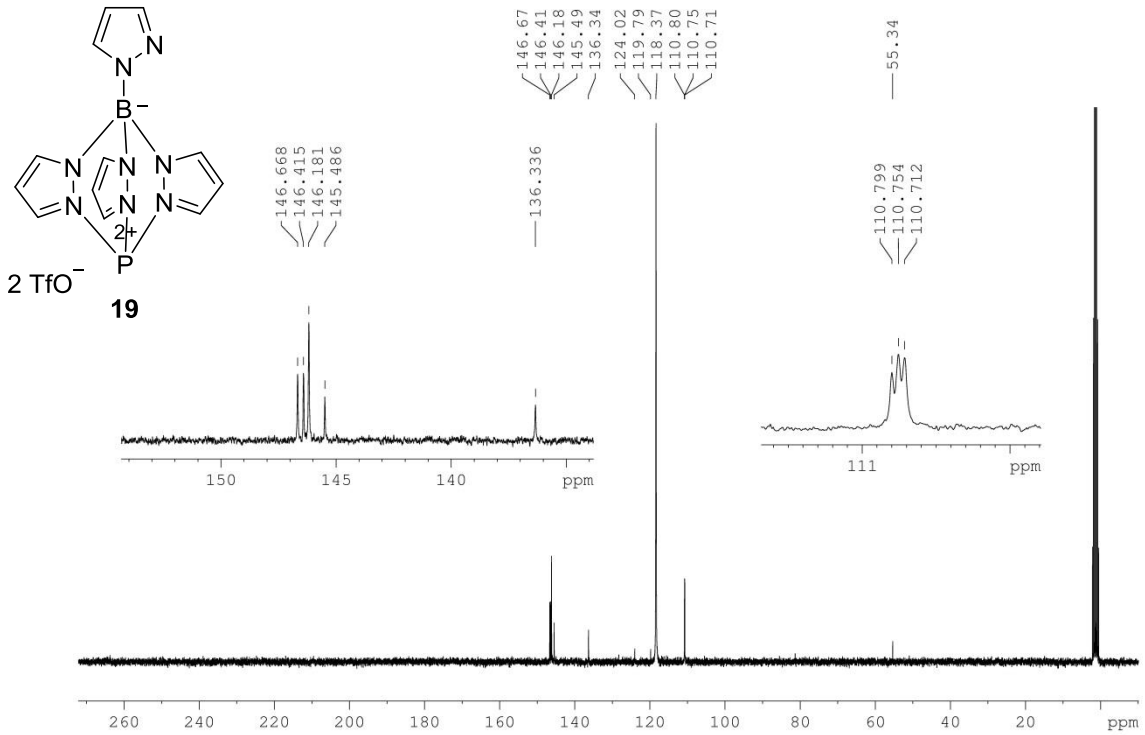
2 TfO^-

18

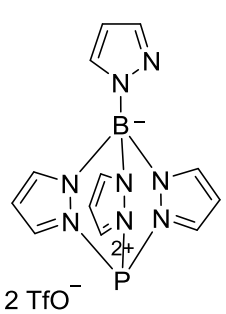
^{1}H NMR (CD_3CN, 300 MHz)



^{13}C NMR (CD_3CN, 75 MHz)

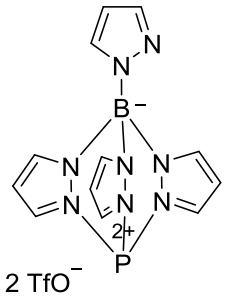


^{31}P NMR (CD_3CN, 121 MHz)



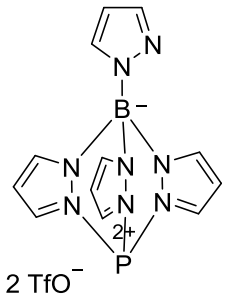
19

^{11}B NMR (CD_3CN, 96 MHz)



19

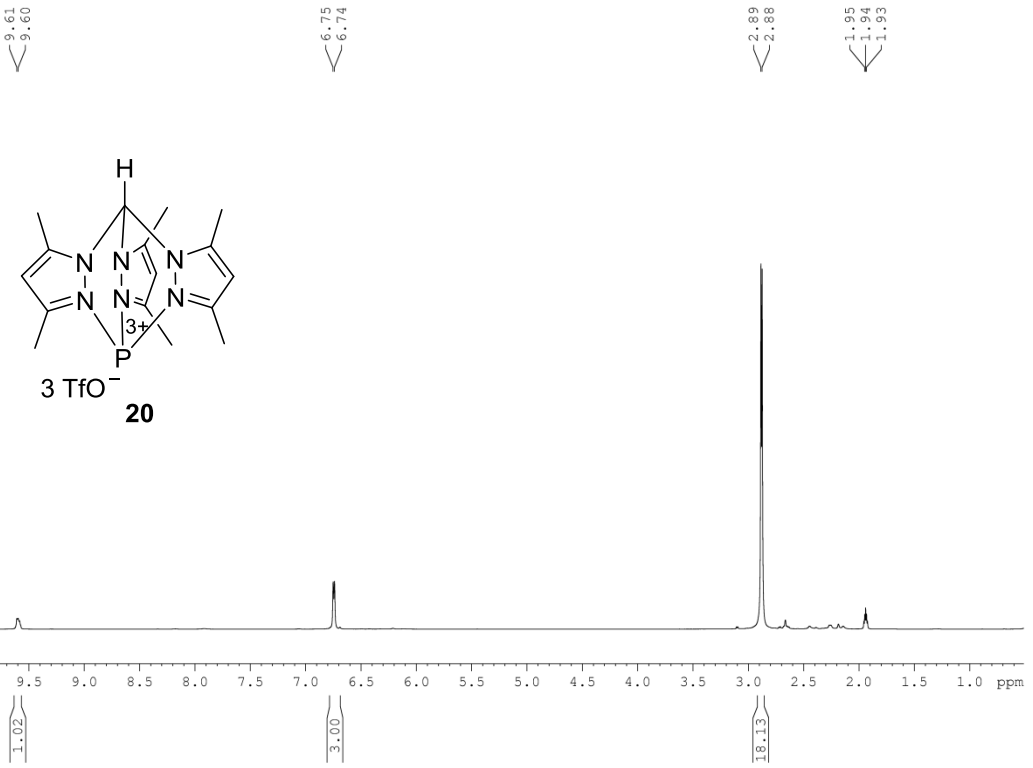
^{11}F NMR (CD_3CN, 282 MHz)



2 TfO^-

19

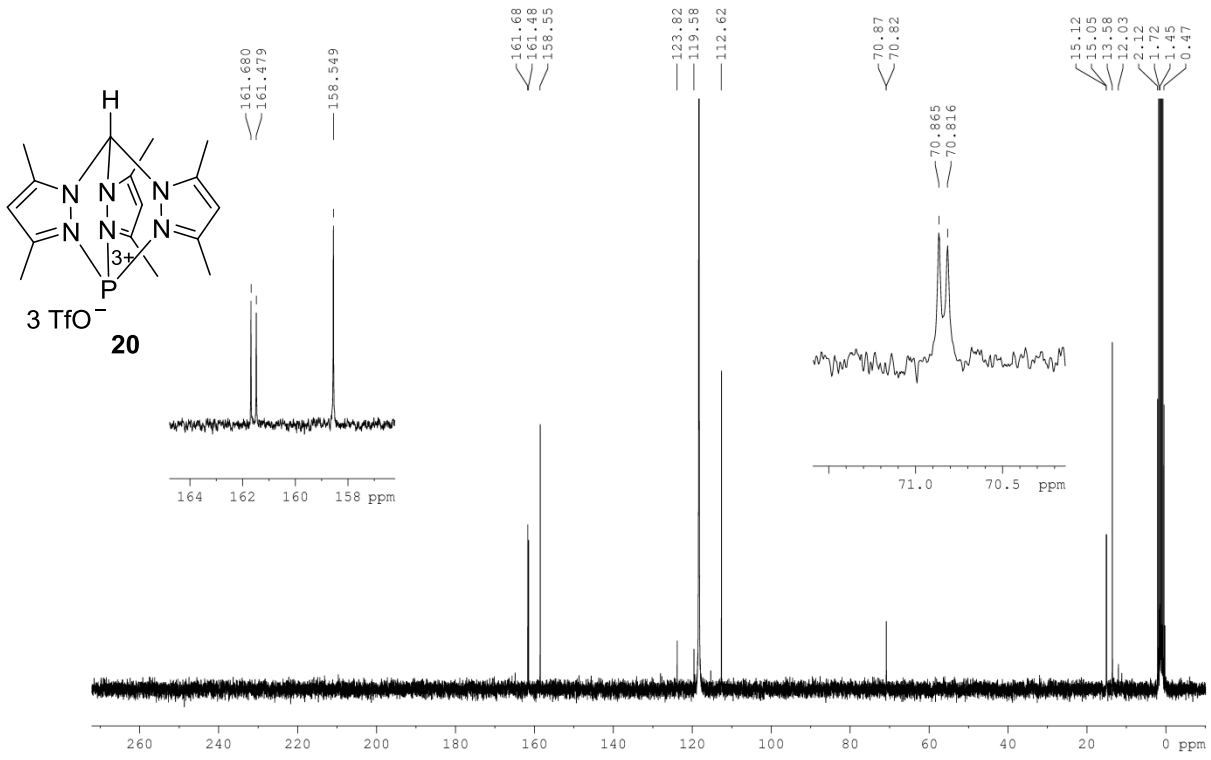
^{1}H NMR (CD_3CN, 300 MHz)



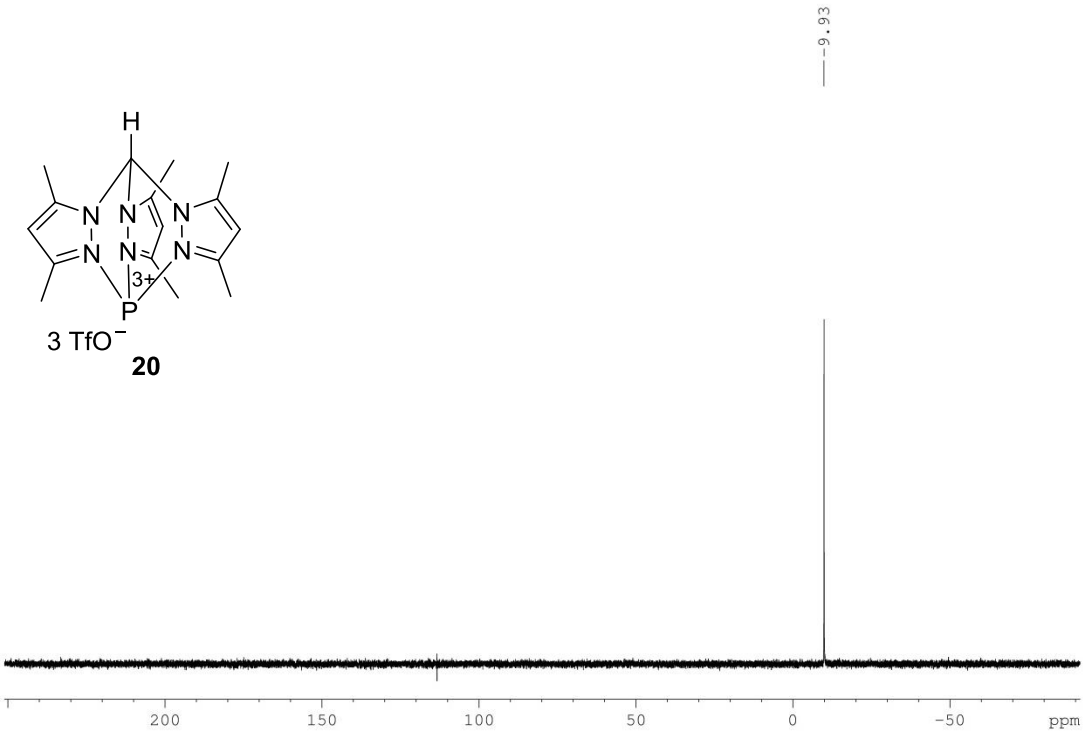
3 TfO^-

20

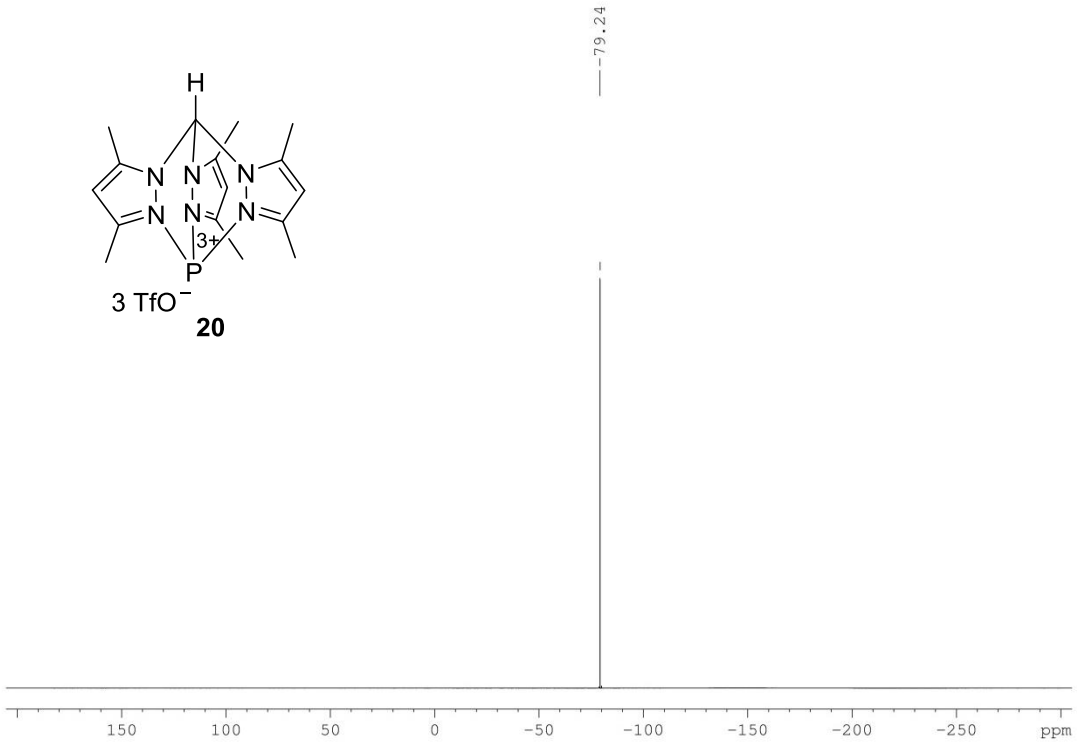
^{13}C NMR (CD_3CN, 100 MHz)



^{31}P NMR (CD_3CN, 121 MHz)

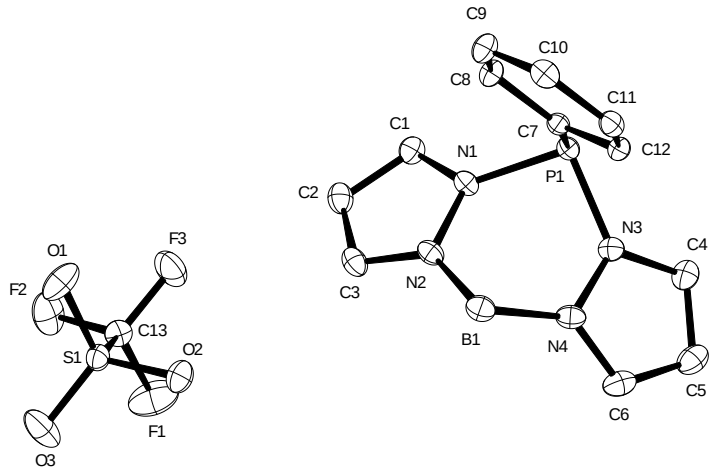


^{19}F NMR (CD_3CN, 282 MHz)



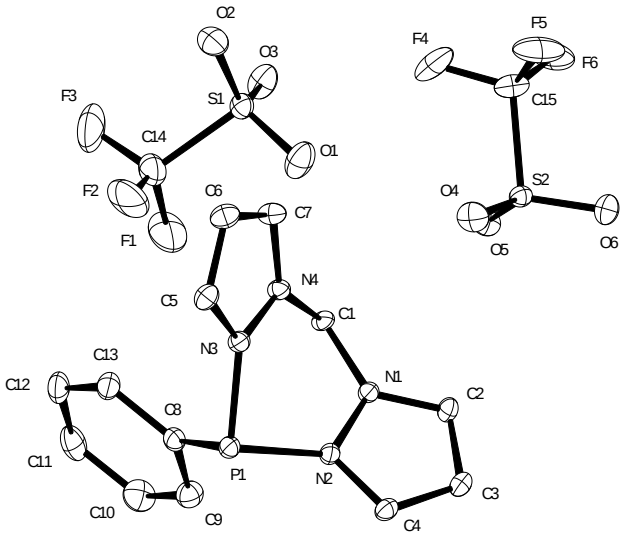
X-ray Structures

Compound **6**



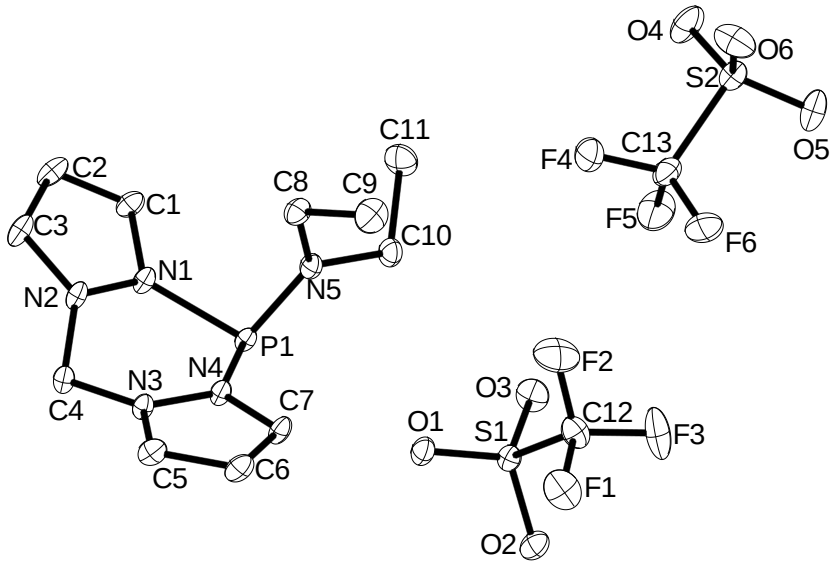
Empirical formula	$C_{13}H_{13}BF_3N_4O_3PS$	
Color	colourless	
Formula weight	404.11 g · mol^{-1}	
Temperature	100 K	
Wavelength	0.71073 Å	
Crystal system	ORTHORHOMBIC	
Space group	**$Pna2_1$, (no. 33)**	
Unit cell dimensions	a = 20.258(2) Å	α= 90°.
	b = 10.0335(10) Å	β= 90°.
	c = 8.2844(8) Å	γ = 90°.
Volume	1683.9(3) Å^3	
Z	4	
Density (calculated)	1.594 Mg · m^{-3}	
Absorption coefficient	0.341 mm^{-1}	
F(000)	824 e	
Crystal size	0.48 x 0.07 x 0.05 mm^3	
q range for data collection	2.01 to 28.39°.	
Index ranges	-27 ≤ h ≤ 27, -13≤ k ≤ 13, -11 ≤ l ≤ 11	
Reflections collected	39971	
Independent reflections	4204 [R_{int} = 0.0253]	
Reflections with I>2s(I)	4118	
Completeness to q = 27.50°	100.0 %	
Absorption correction	Gaussian	
Max. and min. transmission	0.98 and 0.91	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4204 / 1 / 243	
Goodness-of-fit on F^2	1.063	
Final R indices [I>2s(I)]	R_1 = 0.0222	wR^2 = 0.0599
R indices (all data)	R_1 = 0.0229	wR^2 = 0.0604
Absolute structure parameter	-0.03(5)	
Largest diff. peak and hole	0.3 and -0.2 e·Å^{-3}	

Compound **10**



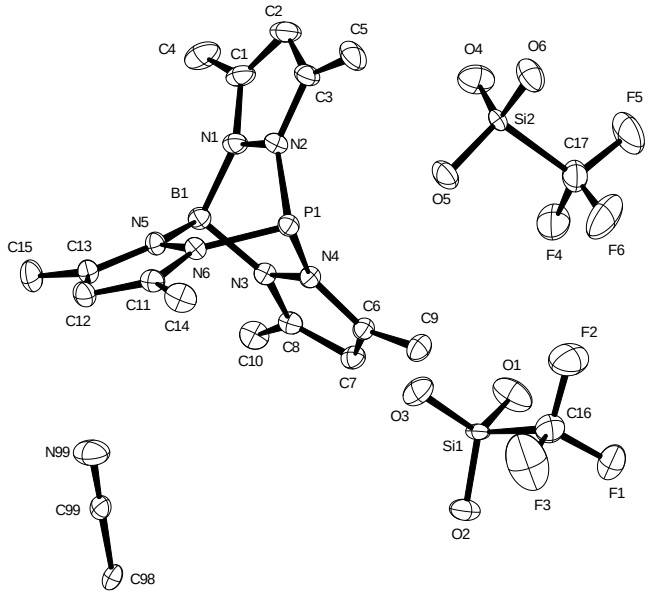
Empirical formula	$C_{15}H_{13}F_6N_4O_6PS_2$	
Color	colourless	
Formula weight	554.38 g · mol^{-1}	
Temperature	100 K	
Wavelength	0.71073 Å	
Crystal system	TRICLINIC	
Space group	**P$\bar{1}$, (no. 2)**	
Unit cell dimensions	a = 9.1777(11) Å	α= 102.624(3)°.
	b = 9.9125(12) Å	β= 98.632(3)°.
	c = 13.419(2) Å	γ = 112.612(2)°.
Volume	1061.9(3) Å^3	
Z	2	
Density (calculated)	1.734 Mg · m^{-3}	
Absorption coefficient	0.421 mm^{-1}	
F(000)	560 e	
Crystal size	0.11 x 0.07 x 0.03 mm^3	
q range for data collection	2.34 to 31.16°.	
Index ranges	-13 ≤ h ≤ 13, -14 ≤ k ≤ 14, -19 ≤ l ≤ 19	
Reflections collected	31528	
Independent reflections	6834 [R_{int} = 0.0306]	
Reflections with I>2s(I)	5721	
Completeness to q = 31.16°	99.5 %	
Absorption correction	Gaussian	
Max. and min. transmission	0.99and 0.95	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6834 / 0 / 307	
Goodness-of-fit on F^2	1.035	
Final R indices [I>2s(I)]	R_1 = 0.0385	wR^2 = 0.0975
R indices (all data)	R_1 = 0.0491	wR^2 = 0.1039
Largest diff. peak and hole	1.2 and -0.6 e · Å^{-3}	

Compound **12**



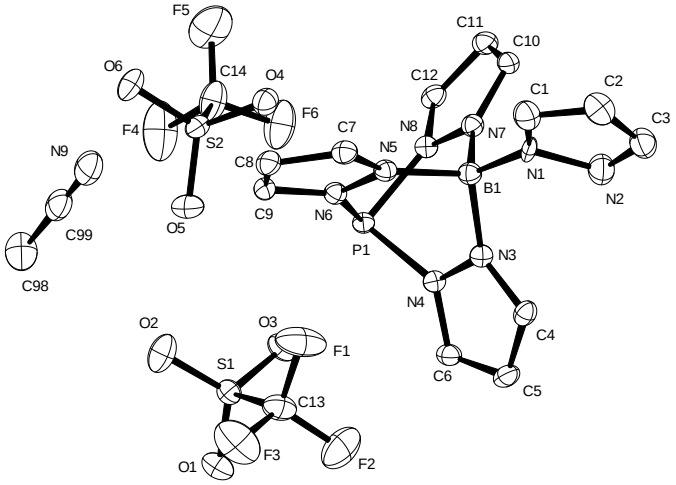
Empirical formula	C_{13} H_{18} F_6 N_5 O_6 P S_2
Color	colourless
Formula weight	549.41 g·mol^{-1}
Temperature	100 K
Wavelength	0.71073 Å
Crystal system	MONOCLINIC
Space group	p 2_1/n, (no. 14)
Unit cell dimensions	a = 12.814(3) Å α= 90°.
	b = 12.704(3) Å β= 113.697(4)°.
	c = 14.321(3) Å γ = 90°.
Volume	2134.8(9) Å^3
Z	4
Density (calculated)	1.709 Mg·m^{-3}
Absorption coefficient	0.419 mm-1
F(000)	1120 e
Crystal size	0.31 x 0.27 x 0.20 mm^3
q range for data collection	1.80 to 31.38°.
Index ranges	-18 ≤ h ≤ 18, -18 ≤ k ≤ 18, -20 ≤ l ≤ 20
Reflections collected	58788
Independent reflections	6998 [Rint = 0.0543]
Reflections with I>2s(I)	5519
Completeness to q = 31.38°	99.6 %
Absorption correction	Gaussian
Max. and min. transmission	0.92807 and 0.86261
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6998 / 0 / 300
Goodness-of-fit on F^2	1.075
Final R indices [I>2s(I)]	R1 = 0.0342 wR2 = 0.0847
R indices (all data)	R1 = 0.0524 wR2 = 0.09
Largest diff. peak and hole	0.733 and -0.555 e·Å^{-3}

Compound **18**



Empirical formula	$C_{18}H_{23.50}BF_6N_{6.50}O_6PS_2$	
Color	colourless	
Formula weight	646.83 g · mol^{-1}	
Temperature	100 K	
Wavelength	0.71073 Å	
Crystal system	MONOCLINIC	
Space group	**$P2_1/n$, (no. 14)**	
Unit cell dimensions	a = 12.9893(16) Å	α= 90°.
	b = 10.6028(13) Å	β= 94.762(2)°.
	c = 21.575(3) Å	γ = 90°.
Volume	2961.1(6) Å^3	
Z	4	
Density (calculated)	1.451 Mg · m^{-3}	
Absorption coefficient	0.315 mm^{-1}	
F(000)	1324 e	
Crystal size	0.33 x 0.26 x 0.16 mm^3	
q range for data collection	1.89 to 36.32°.	
Index ranges	-21 ≤ h ≤ 21, -17 ≤ k ≤ 17, -35 ≤ l ≤ 35	
Reflections collected	111154	
Independent reflections	14234 [R_{int} = 0.0235]	
Reflections with I>2s(I)	12489	
Completeness to q = 27.50°	99.6 %	
Absorption correction	Gaussian	
Max. and min. transmission	0.95 and 0.78	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	14234 / 0 / 390	
Goodness-of-fit on F^2	1.081	
Final R indices [I>2s(I)]	R_1 = 0.0511	wR^2 = 0.1672
R indices (all data)	R_1 = 0.0573	wR^2 = 0.1752
Largest diff. peak and hole	2.0 and -0.6 e · Å^{-3}	

Compound **19**



Empirical formula	$C_{16}H_{15}BF_6N_9O_6PS_2$	
Color	colourless	
Formula weight	649.27 $g \cdot mol^{-1}$	
Temperature	100 K	
Wavelength	1.54178 Å	
Crystal system	TRICLINIC	
Space group	**P$\bar{1}$, (no. 2)**	
Unit cell dimensions	a = 11.615(15) Å	α= 115.626(15)°.
	b = 11.639(9) Å	β= 102.37(2)°.
	c = 11.913(9) Å	γ = 105.87(2)°.
Volume	1290(2) $Å^3$	
Z	2	
Density (calculated)	1.672 $Mg \cdot m^{-3}$	
Absorption coefficient	3.361 mm^{-1}	
F(000)	656 e	
Crystal size	0.58 x 0.34 x 0.12 mm^3	
q range for data collection	4.28 to 63.68°.	
Index ranges	$-13 \le h \le 13$, $-13 \le k \le 13$, $-13 \le l \le 13$	
Reflections collected	34084	
Independent reflections	4161 [R_{int} = 0.0469]	
Reflections with I>2s(I)	4028	
Completeness to q = 63.68°	97.7 %	
Absorption correction	Gaussian	
Max. and min. transmission	0.68 and 0.17	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4161 / 0 / 371	
Goodness-of-fit on F^2	1.054	
Final R indices [I>2s(I)]	R_1 = 0.0357	wR^2 = 0.0916
R indices (all data)	R_1 = 0.0366	wR^2 = 0.0922
Largest diff. peak and hole	0.484 and -0.433 e $\cdot Å^{-3}$	

Computational Methods

Geometry optimizations were carried out using BP86[7,8] functional in combination with def2-QZVPP basis sets.[9,10] The resolution-of-identity (RI) approximation[11,12,13] was applied in conjunction with the appropriate auxiliary basis sets to speed up the calculations. Empirical Grimme-type dispersion corrections were also incorporated during this step using the latest parametrization (DFT-D3).[14] All relevant stationary points were characterized as minima by evaluating the harmonic vibrational frequencies at the same level (RI-BP86/def2-QZVPP+D3) that had been applied for geometry optimization. All geometry optimizations were carried out using the TURBOMOLE (version 6.4) suite of programs.[15,16] To gain insight into the electronic structure of the complexes, a Natural Bond Orbital (NBO) analysis was performed using NBO version 3.1[17] as implemented in Gaussian 09 program package.[18]

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TABLES

Table S1. NBO charges and Wiberg bond indices for different molecules calculated at the BP86/6-311++G** level.

Compound	NBO charge on P atom	Selected *Wiberg bond indices* in a.u. (*Wi*)			
		P1-N3/N6	P1-N4/N7	P1-N5	P1-C1/C2
18	1.40	0.755	0.754	0.753	--
20	1.46	0.735	0.733	0.735	--
10	1.29	0.686	0.684	--	0.953
12	1.39	0.576	0.572	1.13	--
6	1.23	0.727	0.728	--	0.937

CARTESIAN COORDINATES OF OPTIMIZED GEOMETRIES (RI-BP86/def2-QZVPP + D3, Å)

18

p	3.1155004355	9.1574618258	7.9190489206
n	1.1622279390	7.4401824098	7.1581369381
n	2.0132775200	8.4633189443	6.7556969981
n	2.7756414498	6.6354301009	8.8593491669
n	3.6936755740	7.6252984644	8.5235815853
n	1.0626979397	8.3154308222	9.4735925410
n	1.9114152280	9.3719797394	9.1657500693
c	0.4178994978	7.0771953030	6.0935740843
c	0.8006905271	7.8771704424	4.9981196768
h	0.3892216769	7.8241092903	3.9973646193
c	1.7976330853	8.7403696104	5.4211035059
c	-0.6255284639	6.0218060095	6.1564231592
h	-0.4018109454	5.2647279200	6.9139774349
h	-0.7236164938	5.5342694511	5.1808640179
h	-1.6000221148	6.4704567954	6.3983160200
c	2.5544018382	9.7854300652	4.6816658663
h	2.4072676019	10.7803400601	5.1234950809
h	2.2096448026	9.8234295141	3.6442792306
h	3.6321546459	9.5736065676	4.6722617268
c	4.9734942436	7.1582746557	8.7484587741
c	4.8411092590	5.8672784148	9.2279192384
h	5.6530728604	5.2072139920	9.5085943358
c	3.4656739402	5.5598285431	9.2890920758
c	6.1871335280	7.9774660082	8.4884593544
h	6.2575559293	8.2725006236	7.4326214010
h	7.0811400577	7.3977889215	8.7361247330
h	6.1961321776	8.8908736849	9.0983425154
c	2.8210889319	4.2996004844	9.7378361182
h	3.0886362346	4.0974058920	10.7835508944
h	3.1987077652	3.4573544200	9.1432467683
h	1.7318760622	4.3319403356	9.6532747035
c	1.6133134045	10.4495389299	9.9736906538
c	0.5669538009	10.0503306728	10.7889854489
h	0.0820472519	10.6580285646	11.5434255736
c	0.2397904472	8.7188656509	10.4632393331
c	2.3419041042	11.7435121516	9.8933117727
h	3.4080139051	11.6211747203	10.1280938432
h	1.9178286989	12.4493058701	10.6134561043
h	2.2626752278	12.1919834486	8.8935549878
c	-0.7909653511	7.8360251834	11.0674836541
h	-1.2038131650	7.1273127974	10.3422807142
h	-1.6056341787	8.4396065979	11.4801874489
h	-0.3552560307	7.2587644795	11.8959224921

b	1.2742000453	7.0084798230	8.6521042904
h	0.5198092099	6.1393291782	8.9502040216

20

p	3.2089083957	9.2502875125	7.8846869181
n	1.2377394137	7.5099840476	7.2175962464
n	2.0683264692	8.5260769912	6.7530708579
n	2.7978432453	6.7357399109	8.8166105924
n	3.7574757610	7.6896011155	8.4876779592
n	1.1748484015	8.3378861677	9.4323724837
n	1.9997355161	9.4243465923	9.1519944255
c	0.4141553331	7.0928993619	6.2057360520
c	0.7431543955	7.8641356432	5.0888203397
h	0.2764769296	7.7842205663	4.1122961955
c	1.7673719866	8.7530374665	5.4263098946
c	-0.5977059237	6.0221423754	6.3763241645
h	-0.1376815137	5.0772656668	6.6991768568
h	-1.1044449777	5.8375949710	5.4236693093
h	-1.3636296444	6.3079142692	7.1119042826
c	2.4590868073	9.7654200293	4.5952180552
h	1.7208283109	10.4524811690	4.1572165398
h	2.9654063562	9.2698818764	3.7537108037
h	3.1990292165	10.3542913801	5.1483858833
c	5.0027705621	7.1380213839	8.7056001452
c	4.7908408283	5.8377625326	9.1699757195
h	5.5696119028	5.1308622274	9.4375814963
c	3.4175186209	5.5887880042	9.2360468801
c	6.2700856704	7.8665115296	8.4656726278
h	6.1264114570	8.8788728269	8.0709631123
h	6.8941923453	7.3011983714	7.7586806115
h	6.8402065002	7.9359796322	9.4037144325
c	2.6796190900	4.3809795446	9.6779363635
h	2.2833731837	4.5176932459	10.6959512195
h	3.3597147327	3.5231217007	9.7053918565
h	1.8455829619	4.1298945083	9.0092272476
c	1.6304060258	10.4670137937	9.9768033238
c	0.5707238754	10.0046333945	10.7595446573
h	0.0472634617	10.5828054064	11.5141173718
c	0.2872333807	8.6793454352	10.4174311007
c	2.3012741863	11.7879720795	9.9700997853
h	2.8333259065	11.9376740434	10.9218177077
h	1.5488049295	12.5855165834	9.8996460215
h	3.0181393399	11.9115928751	9.1502606507
c	-0.7212998363	7.7429624519	10.9683219455
h	-1.1584103647	7.0880823719	10.2039744365
h	-1.5343417634	8.3097074820	11.4353236238
h	-0.2724657553	7.1132131054	11.7522723703
c	1.4138939593	7.1503068330	8.6199049003
h	0.7274604239	6.3460789040	8.9010244257

10

p	1.0967050787	0.8230176957	9.7943706255
n	-0.7122183982	1.1977838619	7.6892289976
n	0.2806678115	0.4189364299	8.2377806272
n	1.0894764868	2.5776480300	9.3850134432
n	0.0353417492	3.1934226490	8.7495376107
c	-1.1411304356	2.4069126747	8.3875804515
h	-1.6935716832	2.1315766926	9.2959104724
h	-1.7710339726	2.9987607156	7.7176816369
c	-1.0901148831	0.6640165077	6.5062609118
h	-1.8574937336	1.1359420584	5.8999345853
c	-0.3412428425	-0.4906879830	6.2902827194
h	-0.4045560649	-1.1542949782	5.4361758651
c	0.5168918721	-0.6072301082	7.3790453178
h	1.2825542333	-1.3445223528	7.6011554294
c	2.0581614136	3.5124224093	9.5701471850
h	2.9981200894	3.2430820487	10.0424933958
c	1.6116348193	4.7299888423	9.0668890022
h	2.1477599197	5.6715894170	9.0667978733
c	0.3430021028	4.4931546050	8.5421938139
h	-0.3519563275	5.1583340392	8.0385250220
c	-0.3223894994	0.7623849489	10.9142997166
c	-1.1549559813	-0.3729754622	10.8964002448
h	-1.0527365956	-1.1380339117	10.1259411537
c	-2.1266176890	-0.5220587513	11.8859409701
h	-2.7782069344	-1.3940358663	11.8727019298
c	-2.2594770855	0.4409384238	12.8915471494
h	-3.0159182820	0.3148245804	13.6643352265
c	-1.4231825548	1.5615891618	12.9140201824
h	-1.5285063250	2.3077053975	13.6997564198
c	-0.4463823489	1.7277611849	11.9319539620
h	0.2074281528	2.5996516581	11.9702407837

12

n	2.3472044977	7.5137771703	4.8869581951
c	2.8148183344	7.6639835660	6.1489802928
c	2.3732373975	8.8835148584	6.6597275162
c	1.6064844324	9.4667559515	5.6574525738
n	1.6042897634	8.6279892803	4.5931362768
c	0.8387724915	8.6750478448	3.3552338651
n	1.7073140752	8.3137967166	2.2454213472
c	1.8382774767	8.8574385143	1.0110829239
c	2.6918742790	8.0431489147	0.2750268657
c	3.0539660067	6.9963724532	1.1218311563
n	2.4522294173	7.1667289194	2.3224979158
p	2.4680335341	5.9882451419	3.7917362544

n	4.0459485163	5.6225455758	3.9083423082
c	4.3420690037	4.1521858804	4.0544082238
c	5.0896138189	3.5801847396	2.8602683045
c	5.1997979683	6.5606552031	3.7836541406
c	6.2151776035	6.4191232762	4.9110924333
h	3.7116112285	6.1502919318	0.9531599724
h	3.0157337353	8.1979817866	-0.7471122848
h	1.3197863045	9.7733514705	0.7454198741
h	-0.0117338799	7.9788406154	3.4109150150
h	0.4682887320	9.6930213569	3.2032551305
h	1.0670029001	10.4082931895	5.6284334189
h	2.5882229097	9.2982695112	7.6371122321
h	3.4414270281	6.8997223043	6.5948408728
h	4.7928663847	7.5793393165	3.7540148684
h	5.6796702061	6.3760423500	2.8125082952
h	6.9897922712	7.1851141119	4.7867274002
h	6.7167134921	5.4455820328	4.8969242441
h	5.7566213543	6.5590153772	5.8974187450
h	3.3777356105	3.6409549008	4.1933932058
h	4.9049882275	4.0260548144	4.9869897434
h	6.0767249710	4.0386924010	2.7282553571
h	4.5141146618	3.6945490101	1.9321857949
h	5.2495275018	2.5070951239	3.0196923676

6

p	11.1419453600	8.0387198424	3.9235770828
n	11.9869652485	6.5059348145	4.1834270999
n	11.5494975518	5.3052043634	3.6802415000
n	9.5285184936	7.3342146796	4.0950312119
n	9.1832861364	6.1028667260	3.5936731877
c	13.1560415351	6.3071390870	4.8612313564
h	13.6549992258	7.1348715919	5.3521962292
c	13.4776304053	4.9647134665	4.7774557333
h	14.3388954061	4.4706977480	5.2072372858
c	12.4381593701	4.3730651602	4.0429798597
h	12.2712575374	3.3376102584	3.7686777199
c	8.4349588716	7.8971724549	4.6891472400
h	8.5060441710	8.8687079977	5.1649282199
c	7.3737218910	7.0207698102	4.5528598860
h	6.3628088967	7.1574266441	4.9132901150
c	7.8903103100	5.9056421588	3.8750470173
h	7.4152685718	4.9742725671	3.5883549344
c	11.2535482912	8.1799003503	2.1152225656
c	12.4816862710	7.9420099972	1.4807360129
h	13.3328453481	7.5506386460	2.0384429949
c	12.6079202953	8.1851628801	0.1135286206
h	13.5559655690	7.9871678601	-0.3837638061
c	11.5207733873	8.6740459674	-0.6153940469
h	11.6230049564	8.8602779294	-1.6831196698

c	10.3024566766	8.9229420753	0.0214743396
h	9.4541961519	9.2994193456	-0.5476091438
c	10.1646734332	8.6832494568	1.3882287971
h	9.2065464452	8.8706860304	1.8735113437
b	10.2207404583	5.1860716502	2.8483735073
h	10.4027082489	5.6051816779	1.7335812706
h	9.8354262258	4.0493191980	2.8996292692