CHEMISTRY
A EUROPEAN JOURNAL

Supporting Information

Synthesis and Structure of Carbene-Stabilized N-Centered Cations $[L_2N]^+$, $[L_2NR]^{2+}$, $[LNR_3]^{2+}$, and $[L_3N]^{3+}$

Ágnes Kozma, Gopinadhanpillai Gopakumar, Christophe Farès, Walter Thiel, and Manuel Alcarazo*[a]

chem_201204186_sm_miscellaneous_information.pdf

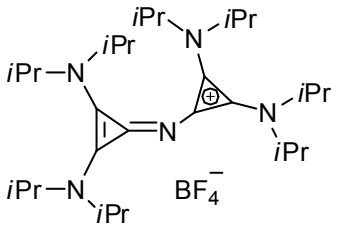
Table of Contents

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 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. For a selection of compounds, ^{15}N chemical shifts were also obtained in a $^{1}H,^{15}N$-HMBC at natural abundance on a Bruker AV 600 equipped with a TCI cryoprobe; this experiment was typically run for 5h with transfer delays optimized for 2 to 5 Hz heteronuclear couplings. For most samples, the 5-bond heteronuclear coupling $^{5}J_{HN}$ was large enough to obtain the signal from the central nitrogen. These chemical shifts are indirectly referenced to the signal from $CH_3{}^{15}NO_2$. 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. 2,3-bis(di*iso*propylamino)-1-chlorocyclopropenium tetrafluoroborate **1**, [1] 2,3-bis(di*iso*propylamino)-1-chlorocyclopropenium triflate **1(TfO)**, [2] *N,N*-Bis(trimethylsilyl)aniline [3], 2,3-bis(dimethylamino)-2-cyclopropen-1-one[4] and salts **8**[5] and **14**[6], were prepared according to literature procedures.

Compound 2:Chlorocyclopropenium salt **1** (500 mg, 1.39 mmol) was added to a suspension of KHMDS (139 mg, 0.70 mmol) in dry THF (17 mL) and the mixture was stirred for 1 day at 60 °C. Additional amount of KHMDS (80 mg, 0.40 mmol) were added after 24 and 48 hours maintaining the temperature at 60 °C. Finally, the organic solvents were evaporated in vacuum and the residue purified by column chromatography (CH_2Cl_2/MeOH: 97/3), affording the title compound as a pale yellow solid (207 mg, 52 %).



^{1}H NMR (400 MHz, CD_2Cl_2) δ = 1.27 (d, *J* = 6.8 Hz, 48H), 3.71 (sept, *J* = 6.8 Hz, 8H) ppm.

^{13}C NMR (101 MHz, CD_2Cl_2) δ = 22.3, 51.0, 121.5, 123.4 ppm.

^{15}N NMR (61 MHz, CD_2Cl_2) δ =-291.6 ($N_{central}$), -279.6 ppm (N(iPr)$_2$)

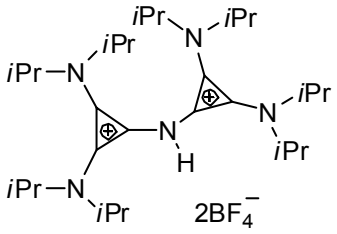
HRMS *calcd.* for $C_{30}H_{56}N_5B_1F_4$: 573.456491; *found* 573.456110.

IR (neat) $\tilde{\nu}$ = 752, 800, 879, 1022, 1045, 1089, 1129, 1161, 1194, 1217, 1260, 1335, 1361, 1387, 1455, 1478, 2876, 2936, 2978 cm^{-1}.

Melting point: 175-176 °C

[1] R. Weiss, K. G. Wagner, C. Priesner, J. Macheleid, *J. Am. Chem. Soc.* **1985**, *107*, 4491.
[2] Z. Yoshida, Y. Tawara, *J. Am. Chem. Soc.* **1971**, *93*, 2573.
[3] D. A. Pennington, P. N. Horton, M. B. Hursthouse, M. Bochmann, S. J. Lancaster, *Polyhedron* **2005**, *24*, 151.
[4] C. Wilkox, R. Breslow, *Tetrahedron Lett.* **1980**, *21*, 3241.
[5] H. Bruns, M. Patil, J. Carreras, A. Vázquez, W. Thiel, R. Goddard, M. Alcarazo, *Angew. Chem. Int. Ed.* **2010**, *49*, 3680.
[6] A. Landau, G. Seitz, *Chem. Ber*. **1991**, *124*, 665.

Compound 3: Tetrafluoroboric acid diethyl ether complex (24 µL, 0.18 mmol) was added to suspension of compound **2** (103 mg, 0.18 mmol) in dry DCM (3.5 mL) and the resulting solution stirred at rt for 2 hours. Subsequently, the solvent was evacuated and the residue dried, affording the title compound as a pale yellow solid (114 mg, 96 %).



^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.35 (d, *J* = 6.7 Hz, 48H), 3.95 (brs, 8H), 8.28 (brs, 1H) ppm.

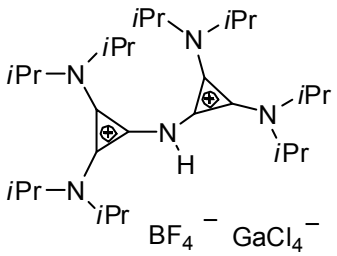
^{13}C NMR (101 MHz, $CDCl_3$) δ = 21.8, 52.5 (brs), 104.7, 125.6 ppm.

HRMS *calcd.* for $C_{30}H_{57}B_3F_{12}N_5^-$: 748.473724; *found* 748.473016.

IR (neat) $\tilde{\nu}$ = 762, 892, 1048, 1138, 1190, 1207, 1263, 1349, 1377, 1395, 1456, 1503, 1551, 1917, 2940, 2980, 3313 cm^{-1}.

Melting point: 223-224 °C

Compound 4: **2** (57.4 mg, 0.1 mmol) was added to a stirred suspension of $GaCl_3$ (35.2 mg, 0.2 mmol) in dry toluene (2.6 mL) and the resulting solution stirred at rt for 14 hours. Then, the solvent was evacuated and the residue extracted with CH_3CN (5 mL). Removal of the solvents under vacuum afforded the title compound as a pale yellow solid (56 mg, 71 %).



^{1}H NMR (400 MHz, CD_2Cl_2) δ = 1.37 (d, *J* = 6.7 Hz, 48H), 3.90 (brs, 8H), 8.32 (brs, 1H) ppm.

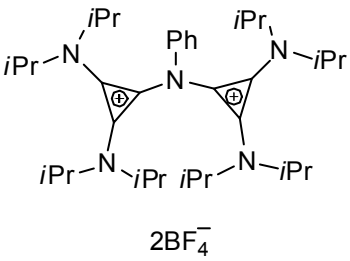
^{13}C NMR (101 MHz, CD_2Cl_2) δ = 21.9, 105.4, 126.0 ppm.

HRMS *calcd.* for: $[C_{30}H_{57}N_5GaCl_4]^+$ 696.262383; *found* 696.262350.

IR (neat) $\tilde{\nu}$ = 764, 894, 987, 1066, 1143, 1194, 1208, 1262, 1346, 1375, 1391, 1454, 1471, 1516, 1539, 1588, 1919, 2938, 2987, 3234 cm^{-1}.

Melting point: 222-223 °C

Compound 5: *N,N*-bis(trimethylsilyl)aniline (95 mg, 0.40 mmol) was added to a stirred suspension of chlorocyclopropenium salt **1** (287 mg, 0.80 mmol) in dry THF (4 mL) and the resulting mixture was heated at 60 °C for 3 days. After cooling to rt, the solvent was evacuated and the residue washed with THF (3 x 4 mL). Compound **5** was obtained as a white solid (233 mg, 79 %).



^{1}H NMR (400 MHz, CD_2Cl_2) δ = 1.10 (brs, 24H), 1.40 (brs, 24H), 3.69 (brs, 4H), 4.08 (brs, 4H), 7.37-7.44 (m, 1H), 7.55-7.62 (m, 2H), 7.64-7.69 (m, 2H) ppm.

^{13}C NMR (101 MHz, CD_2Cl_2) δ = 21.2, 22.7, 50.2, 56.6, 105.2, 125.6, 127.9, 129.7, 131.7, 139.1 ppm.

^{15}N NMR (61 MHz, CD_3CN) δ =-310.2 (*N*Ph), -260.3 ppm (-*N*(iPr)$_2$).

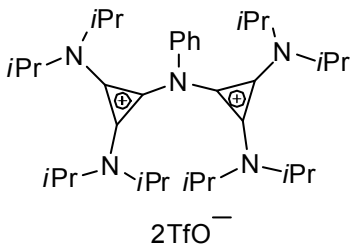
HRMS *calcd.* for $C_{36}H_{61}B_1F_4N_5^+$: 650.496812; *found* 650.497078.

IR (neat) $\tilde{\nu}$ = 697, 731, 766, 886, 1033, 1046, 1140, 1191, 1205, 1240, 1350, 1376, 1448, 1464, 1558, 1914, 2940, 2982 cm^{-1}.

Elemental analysis (%) *calcd.* for $C_{36}H_{61}B_2F_8N_5$: C: 58.63, H: 8.34, N: 9.50; *found*: C: 58.39; H: 8.39, N: 9.45

Melting point: 219 °C (decomposition)

Compound 5(TfO): **7** (132 mg, 0.40 mmol) was added to a stirred suspension of **1(TfO)** (170 mg, 0.40 mmol) in dry THF (4 mL) and the resulting mixture was heated at 60 °C for 3 days. After cooling to rt, the solvents were evacuated and the residue redisolved in CH_2Cl_2 (9 mL) and washed with a saturated aq. $Mg(OTf)_2$ solution (3 x 8 mL). The organic phase was then dried over Na_2SO_4, concentrated and the residue recrystallized from CH_2Cl_2/Et_2O to afford the desired compound as a white solid (281 mg, 81 %).



^{1}H NMR (400 MHz, CD_2Cl_2) δ = 1.10 (d, *J* = 4.6 Hz, 24H), 1.40 (d, *J* = 4.4 Hz, 24H), 3.70 (brs, 4H), 4.08 (brs, 4H), 7.38-7.44 (m, 1H), 7.55-7.61 (m, 2H) 7.65-7.69 (m, 2H) ppm.

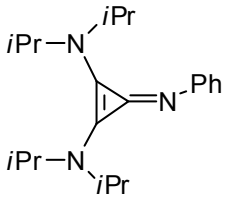
^{13}C NMR (101 MHz, CD_2Cl_2) δ = 21.0, 21.3, 22.6, 22.8, 50.0, 50.1, 56.5, 56.6, 105.1, 121.5 (q, *J* = 321.9 Hz), 125.6, 127.9, 129.7, 131.6, 139.1 ppm.

HRMS *calcd.* for $C_{37}H_{61}N_5O_3F_3S_1^+$: 712.444170; *found* 712.444513.

IR (neat) $\tilde{\nu}$ = 697, 753, 762, 885, 1020, 1031, 1140, 1207, 1222, 1264, 1344, 1375, 1446, 1461, 1563, 1592, 1911, 2941, 2990 cm^{-1}.

Melting point: 234 °C (decomposition)

Compound 7: Aniline (0.25 mL, 2.79 mmol) was added to a stirred suspension of **1** (500 mg, 1.39 mmol) in dry THF (11 mL) and the resulting mixture was heated at 60 °C for 1 day. After cooling to rt, the solvent was evacuated, the residue dissolved in CH_2Cl_2 (25 mL) and washed with a saturated aq. $NaBF_4$ solution (2 x 20 mL). Once dried over Na_2SO_4, the organic phase was concentrated in vacuum. Washing the solid obtained with Et_2O (2 x 4 mL) afforded **7H** as a pale brown solid (395 mg, 95 %).



^{1}H NMR (400 MHz, CD_2Cl_2) δ = 1.27 (d, *J* = 6.8 Hz, 24H), 3.76 (sept, *J* = 6.8 Hz, 4H), 7.22-7.27 (m, 3H), 7.38-7.44 (m, 2H), 7.90 (brs, 1H) ppm.

^{13}C NMR (101 MHz, CD_2Cl_2) δ = 22.2, 51.5, 112.9, 117.2, 123.2, 126.5, 129.9, 139.4 ppm.

HRMS *calcd.* for $C_{21}H_{34}N_3^+$: 328.274720; *found* 328.274461.

IR (neat) $\tilde{\nu}$ = 703, 767, 801, 895, 949, 991, 1032, 1045, 1062, 1080, 1109, 1146, 1193, 1205, 1234, 1354, 1377, 1450, 1468, 1504, 1527, 1595, 2937, 2977, 3300 cm^{-1}.

7 could be obtained by deprotonation of **7H** (374 mg, 0.90 mmol) with KH (72 mg, 1.80 mmol) in dry THF (7 mL) at 60 °C overnight as a white solid (283 mg, 96 %).

^{1}H NMR (400 MHz, CD_2Cl_2) δ = 1.23 (d, *J* = 6.8 Hz 24H), 3.68 (sept, *J* = 6.8 Hz, 4H), 6.68-6.74 (m, 1H), 6.80-6.85 (m, 2H), 7.10-7.15 (m, 2H) ppm.

^{13}C NMR (101 MHz, CD_2Cl_2) δ = 22.5, 49.9, 114.9, 118.8, 122.8, 125.3, 128.6, 156.4 ppm.

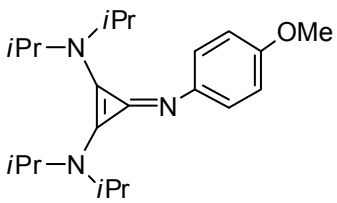
^{15}N NMR (61 MHz, CD_3CN) δ = -289.4 (-*N*(iPr)$_2$), -231.5 ppm (=*N*Ph).

HRMS *calcd.* for $C_{21}H_{34}N_3^+$: 328.274718; *found* 328.274436.

IR (neat) $\tilde{\nu}$ = 698, 752, 819, 888, 951, 994, 1039, 1049, 1129, 1165, 1202, 1218, 1270, 1323, 1365, 1438, 1471, 1482, 1511, 2871, 2933, 2968 cm^{-1}.

Melting point: 122-123 °C

Compound 9: 4-Methoxyaniline (246 mg, 2.00 mmol) was added to a stirred suspension of salt **1** (359 mg, 1.00 mmol) in dry THF (8 mL) and the resulting mixture was heated at 60 °C for 1 day. After cooling to rt, the



precipitate was filtered off and the filtrate concentrated. The thus obtained residue was suspended in CH_2Cl_2 (20 mL), washed with a saturated aq. $NaBF_4$ solution (2 x 20 mL) and dried over Na_2SO_4. After concentration of the organic phase and the residue was washed with Et_2O (2 x 4 mL) affording **9H** as a pale violet solid (375 mg, 84 %).

^{1}H NMR (400 MHz, CD_2Cl_2) δ = 1.25 (d, *J* = 6.8 Hz, 24H), 3.70 (sept, *J* = 6.8 Hz, 4H), 3.81 (s, 3H), 6.93 (d, *J* = 8.9 Hz, 2H), 7.22 (d, *J* = 8.8 Hz, 2H), 7.61 (brs, 1H) ppm.

^{13}C NMR (101 MHz, CD_2Cl_2) δ = 22.1, 51.3, 56.0, 114.1, 115.0, 115.9, 126.6, 131.7, 159.1 ppm.

HRMS *calcd.* for $C_{22}H_{36}N_3O_1^+$: 358.285286; *found* 358.285019.

IR (neat) $\tilde{\nu}$ = 670, 718, 782, 804, 829, 848, 948, 1038, 1141, 1192, 1212, 1236, 1296, 1353, 1372, 1450, 1505, 2972, 3294 cm^{-1}.

Deprotonation of **9H** (379 mg, 0.85 mmol) with KH (68 mg, 1.70 mmol) in dry THF (7 mL) at 60 °C overnight afforded the title compound as a light brown solid (298 mg, 98 %).

^{1}H NMR (400 MHz, CD_2Cl_2) δ = 1.21 (d, *J* = 6.8 Hz, 24H), 3.65 (sept, *J* = 6.8 Hz, 4H), 3.72 (s, 3H), 6.71 (d, *J* = 9.0 Hz, 2H), 6.76 (d, *J* = 9.0 Hz, 2H) ppm.

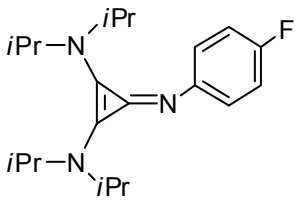
^{13}C NMR (101 MHz, CD_2Cl_2) δ = 22.5, 49.8, 55.9, 114.1, 114.4, 123.5, 125.7, 149.9, 153.6 ppm.

HRMS *calcd.* for $C_{22}H_{36}N_3O_1^+$: 358.285285; *found* 358.285110.

IR (neat) $\tilde{\nu}$ = 674, 709, 726, 776, 809, 837, 876, 958, 1027, 1041, 1098, 1119, 1133, 1158, 1223, 1258, 1313, 1364, 1433, 1463, 1495, 1522, 1881, 2936, 2971 cm^{-1}.

Melting point: 123-124 °C

Compound 10: 4-Fluoroaniline (0.1 mL, 1.11 mmol) was added to a stirred suspension of **1** (200 mg, 0.56 mmol) in dry THF (4 mL) and the resulting mixture heated at 60 °C for 1 day. After cooling to rt, the solvents were evaporated and the solid obtained extracted with CH_2Cl_2 (10 mL) and washed with saturated aq. $NaBF_4$ solution (3 x 15 mL). Once dried over Na_2SO_4, the organic phase was concentrated obtaining a residue that was washed with Et_2O (2 x 4 mL) affording the **10H** as a white solid (199 mg, 82 %).



^{1}H NMR (300 MHz, CD_2Cl_2) δ = 1.27 (d, *J* = 6.9 Hz, 24H), 3.73 (sept, *J* = 6.8 Hz, 4H), 7.06-7.15 (m, 2H), 7.23-7.31 (m, 2H), 7.90 (brs, 1H) ppm.

^{13}C NMR (101 MHz, CD_2Cl_2) δ = 22.1, 51.5, 113.1, 116.6 (d, *J* = 23.1 Hz), 116.7, 125.9 (d, *J* = 8.5 Hz), 135.5 (d, *J* = 2.9 Hz), 161.4 (d, *J* = 245.4 Hz) ppm.

^{19}F NMR (282 MHz, CD_2Cl_2) δ = -151.1, -151.0, -116.2 ppm.

HRMS *calcd.* for $C_{21}H_{33}F_1N_3^+$: 346.265297; *found* 346.265205.

IR (neat) $\tilde{\nu}$ = 670, 717, 794, 832, 1010, 1040, 1059, 1142, 1156, 1191, 1214, 1351, 1365, 1390, 1449, 1470, 1505, 1525, 2942, 2974, 3294 cm^{-1}.

10 could be obtained by deprotonation of **10H** (347 mg, 0.80 mmol) with KH (64 mg, 1.60 mmol) in THF (7 mL) at 60 °C overnight. (265 mg, 96 %).

^{1}H NMR (400 MHz, CD_2Cl_2) δ = 1.22 (d, *J* = 6.8 Hz, 24H), 3.65 (sept, *J* = 6.8 Hz, 4H), 6.72-6.89 (m, 4H) ppm.

^{13}C NMR (101 MHz, CD_2Cl_2) δ = 22.4, 49.9, 114.5, 114.8 (d, *J* = 21.8 Hz), 123.4 (d, *J* = 7.6 Hz), 125.5 (brs), 152.7, 157.3 (d, *J* = 234.4 Hz) ppm.

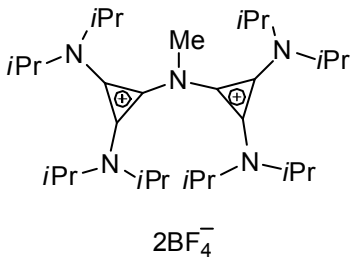
^{19}F NMR (282 MHz, CD_2Cl_2) δ = -127.9 ppm.

HRMS *calcd.* for $C_{21}H_{33}N_3F_1^+$: 346.265296; *found* 346.265212.

IR (neat) $\tilde{\nu}$ = 676, 719, 786, 819, 841, 950, 1040, 1049, 1085, 1130, 1166, 1202, 1217, 1274, 1320, 1363, 1436, 1485, 1515, 1893, 2874, 2934, 2975 cm^{-1}.

Melting point: 132-133 °C

Compound 11: Salt **8** (93 mg, 0.35 mmol) was added to a stirred suspension of **1** (126 mg, 0.35 mmol) in dry THF (3.5 mL) and the resulting mixture was heated at 60 °C for 3 days. After cooling to rt, the solvent was evacuated, the residue suspended in CH_2Cl_2 (9 mL) and filtered. After concentration of the filtrate, the residue was washed with Et_2O (3 x 3 mL) and crystallized from CH_2Cl_2/Et_2O to afford the desired compound as a white solid (106 mg, 49 %).



^{1}H NMR (400 MHz, CD_2Cl_2) δ = 1.37 (d, *J* = 6.8 Hz, 48H), 3.65 (s, 3H), 3.94 (sept, *J* = 6.8 Hz, 8H) ppm.

^{13}C NMR (101 MHz, CD_2Cl_2) δ = 21.9, 41.7, 53.1, 108.8, 126.9 ppm.

^{15}N NMR (61 MHz, CD_3CN) δ = -276.3(*N*Me), -263.2 ppm (*N*(iPr)$_2$)

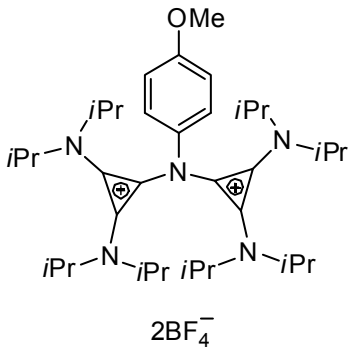
HRMS *calcd.* for $C_{31}H_{59}B_1F_4N_5^+$: 588.479409; *found* 588.479646.

IR (neat) $\tilde{\nu}$ = 708, 739, 875, 892, 1033, 1045, 1093, 1142, 1181, 1206, 1351, 1396, 1455, 1548, 1916, 2940, 2978 cm^{-1}.

Elemental analysis (%) *calcd.* for $C_{31}H_{59}B_2F_8N_5$: C: 55.12, H: 8.80, N: 10.37; *found*: C: 54.78; H: 8.84, N: 10.25.

Melting point: 259 °C (decomposition)

Compound 12: Compound **9** (125 mg, 0.35 mmol) was added to a stirred suspension of **1** (126 mg, 0.35 mmol) in dry THF (3.5 mL) and the resulting mixture was heated at 60 °C for 3 days. After cooling to rt, the solvent was evacuated and the residue suspended in CH_2Cl_2 (9 mL) and washed with a saturated aq. $NaBF_4$ solution (3 x 8 mL). Once dried over Na_2SO_4, the organic phase was concentrated, and the residue obtained washed with Et_2O (3 x 3 mL) and recrystallized from CH_2Cl_2/Et_2O. Violet solid (214 mg, 80 %).



^{1}H NMR (400 MHz, CD_2Cl_2) δ = 1.11 (brs, 24 H), 1.39 (brs, 24 H), 3.70 (brs, 4H), 3.82 (s, 3H), 4.05 (brs, 4H), 7.07 (d, *J* = 9.0 Hz, 2H), 7.52 (d, *J* = 9.0 Hz, 2H) ppm.

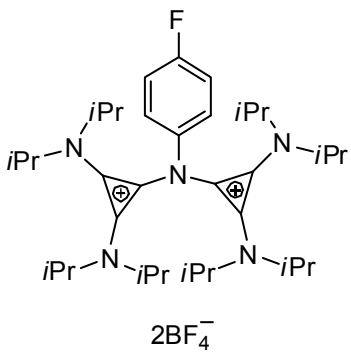
^{13}C NMR (101 MHz, CD_2Cl_2) δ = 21.1, 22.6, 50.1, 56.2, 56.6, 105.7, 116.6, 127.4, 127.4, 131.6, 160.7 ppm.

HRMS *calcd.* for $C_{37}H_{63}B_1F_4N_5O_1^+$: 680.507393; *found* 680.507756.

IR (neat) $\tilde{\nu}$ = 665, 729, 835, 886, 1047, 1141, 1159, 1207, 1261, 1305, 1350, 1376, 1452, 1508, 1561, 1915, 2940, 2983 cm^{-1}.

Melting point: 249 °C (decomposition)

Compound 13: Compound **10** (100 mg, 0.35 mmol) was added to a stirred suspension of **1** (126 mg, 0.35 mmol) in dry THF (3.5 mL) and the resulting mixture heated at 60 °C for 3 days. After cooling to rt, the solvent was evacuated, the residue suspended in CH_2Cl_2 (9 mL) and extracted with a saturated aq. $NaBF_4$ solution (3 x



8 mL). Once dried over Na_2SO_4, the organic phase was concentrated, washed with Et_2O (3 x 3 mL) and the residue crystallized from CH_2Cl_2/Et_2O. White solid (186 mg, 70 %).

^{1}H NMR (400 MHz, CD_2Cl_2) δ = 1.12 (brs,12H), 1.39 (brs, 12H), 3.70 (brs, 4H), 4.06 (brs, 4H), 7.25-7.32 (m, 2H), 7.66-7.73 (m, 2H) ppm.

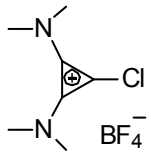
^{13}C NMR (101 MHz, CD_2Cl_2) δ = 21.1, 22.6, 50.2, 56.6, 105.0, 118.5 (d, *J* = 23.4 Hz), 127.8, 128.0 (d, *J* = 9.0 Hz), 135.1 (d, *J* = 2.2 Hz), 162.8 (d, *J* = 250.4 Hz) ppm.

^{19}F NMR (282 MHz, CD_2Cl_2) δ = -151.8, -151.7, -111.4 ppm.

HRMS *calcd.* for $C_{36}H_{60}B_1F_5N_5^+$: 668.485637; *found* 668.486347.

IR (neat) $\tilde{\nu}$ = 664, 816, 844, 884, 1032, 1046, 1157, 1191, 1206, 1220, 1351, 1376, 1453, 1505, 1563, 1912, 2983 cm^{-1}.

Compound 14: This compound was prepared similarly to the already known perchlorate analogue.[5] Oxalyl chloride (2318 mg, 18.28 mmol) was slowly added directly to a flask containing neat 2,3-bis(dimethylamino)-2-cyclopropen-1-one (800 mg, 5.71 mmol) at 0 °C and the mixture was stirred at rt for 15 minutes. After removing the excess of oxalyl chloride in vacuum, a pale brown solid was obtained. This solid (879 mg, 4.50 mmol) was disolved in dry CH_3CN (5 mL) and a suspension of $NaBF_4$ (494 mg, 4.50 mmol) in dry CH_3CN (5 mL) was added. The mixture was stirred for 2 hours at rt and then placed into the fridge for 30 minutes. The precipitated formed was discarded while evaporation of the solvent from the filtrate gave the desired product as a pale brown solid (842 mg, 76 %).



^{1}H NMR (400 MHz, CD_3CN) δ = 3.17 (s, 6H), 3.19 (s, 6H) ppm.

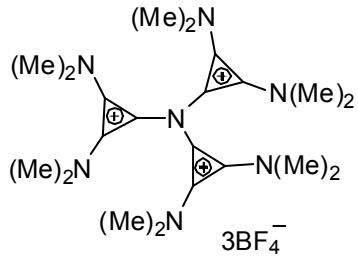
^{13}C NMR (101 MHz, CD_3CN) δ = 41.9, 42.5, 92.0, 135.4 ppm.

HRMS *calcd.* for $C_{14}H_{24}N_4B_1Cl_2F_4^+$: 405.141129; *found* 405.141423.

IR (neat) $\tilde{\nu}$ = 727, 797, 1030, 1096, 1213, 1238, 1278, 1391, 1418, 1409, 1451, 1635, 1729, 1954, 2950 cm^{-1}.

Melting point: 108-109 °C

Compound 15: Tris(trimethylsilyl)amine (150 mg, 0.60 mmol) was added to a stirred suspension of salt **14** (47 mg, 0.20 mmol) in dry THF (3 mL) and the resulting mixture heated at 120 °C for 13 hours in a microwave oven. After cooling to rt, the solvents were removed by filtration and the precipitate thus obtained washed with THF (4 x 4mL). Recrystallization of the residue from CH_3CN/Et_2O afforded the desired compound as a pale brown solid (53 mg, 41 %).



^{1}H NMR (400 MHz, CD_3CN) δ = 3.13 (s, 18H), 3.23 (s, 18H) ppm.

^{13}C NMR (101 MHz, CD_3CN) δ = 42.8, 43.5, 99.6, 128.1 ppm.

^{15}N NMR (61 MHz, CD_3CN) δ = -309.8 ppm ($N_{central}$)

HRMS *calcd.* for $C_{21}H_{36}B_2F_8N_7^+$: 560.310541; *found* 560.310449.

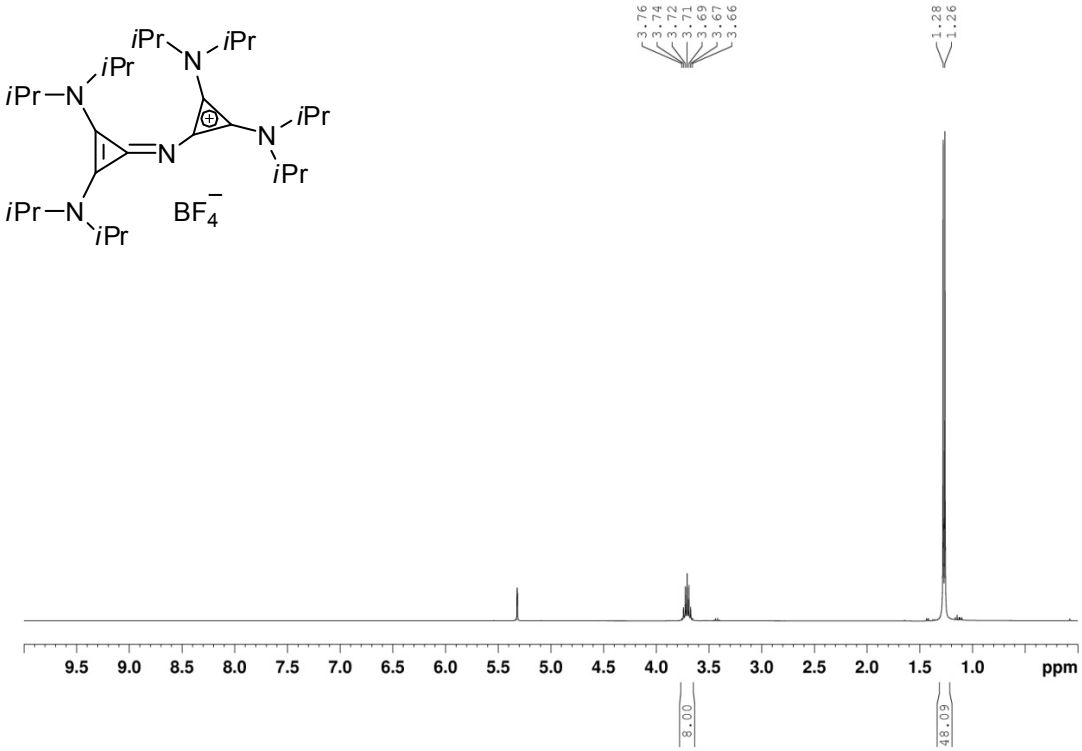
IR (neat) $\tilde{\nu}$ = 790, 1027, 1230, 1406, 1501, 1627, 1980, 2952 cm^{-1}.

Elemental analysis (%) *calcd.* for $C_{21}H_{36}B_3F_{12}N_7$: C: 38.99, H: 5.61, N: 15.15; *found*: C: 38.16; H: 5.73, N: 14.57.

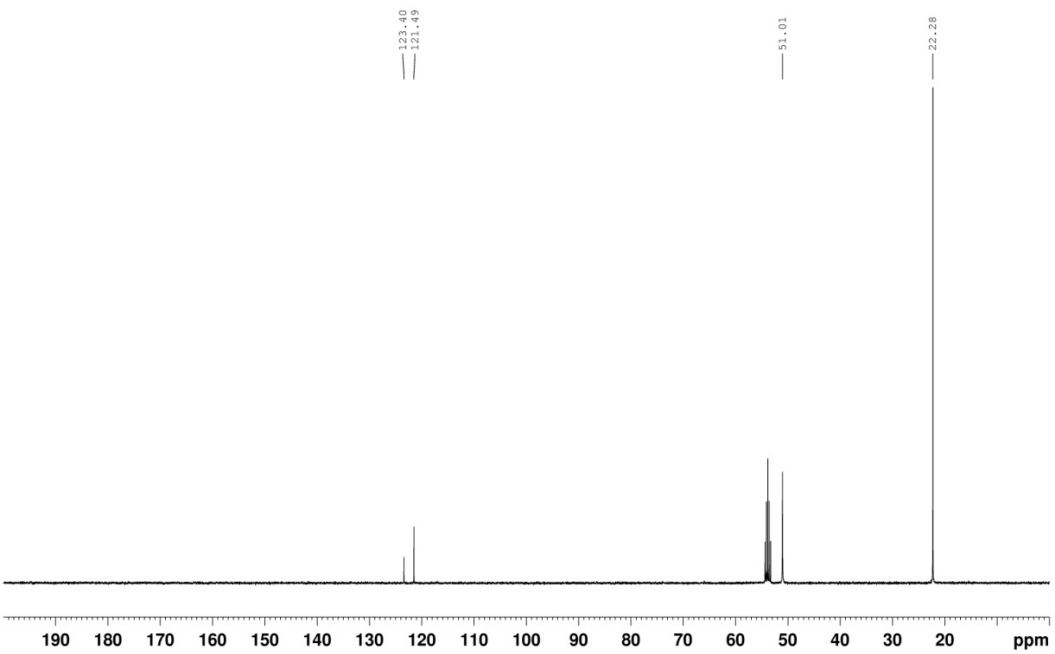
Melting point: 235 °C (decomposition)

NMR spectra

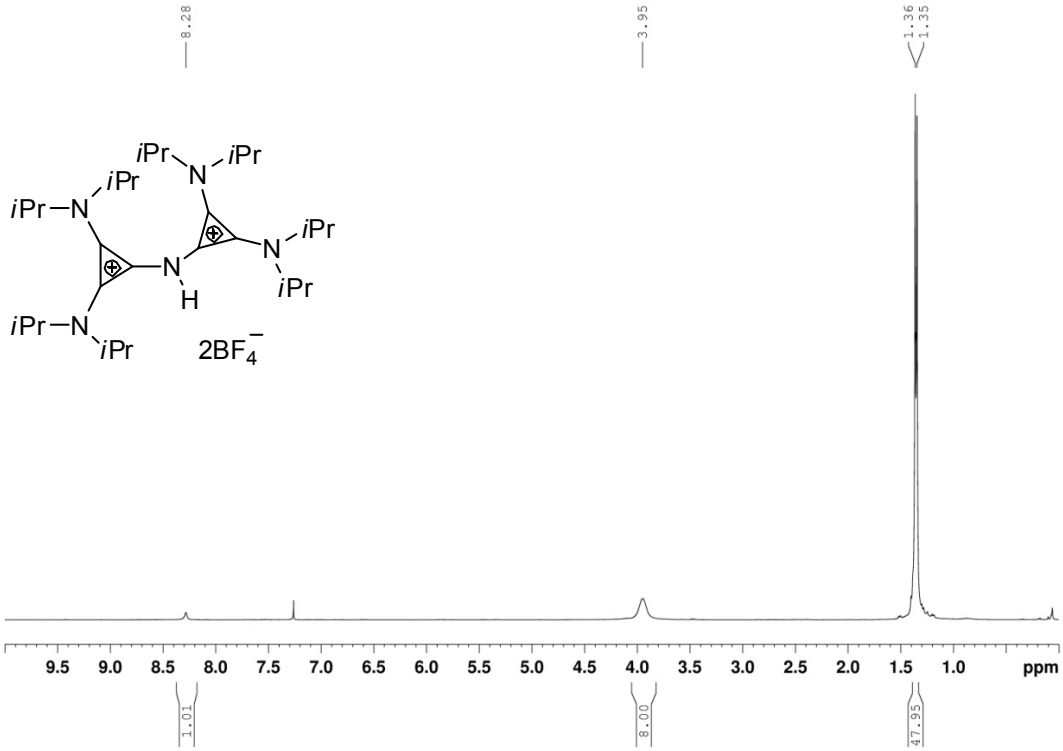
^{1}H NMR (400 MHz, CD_2Cl_2) **2**



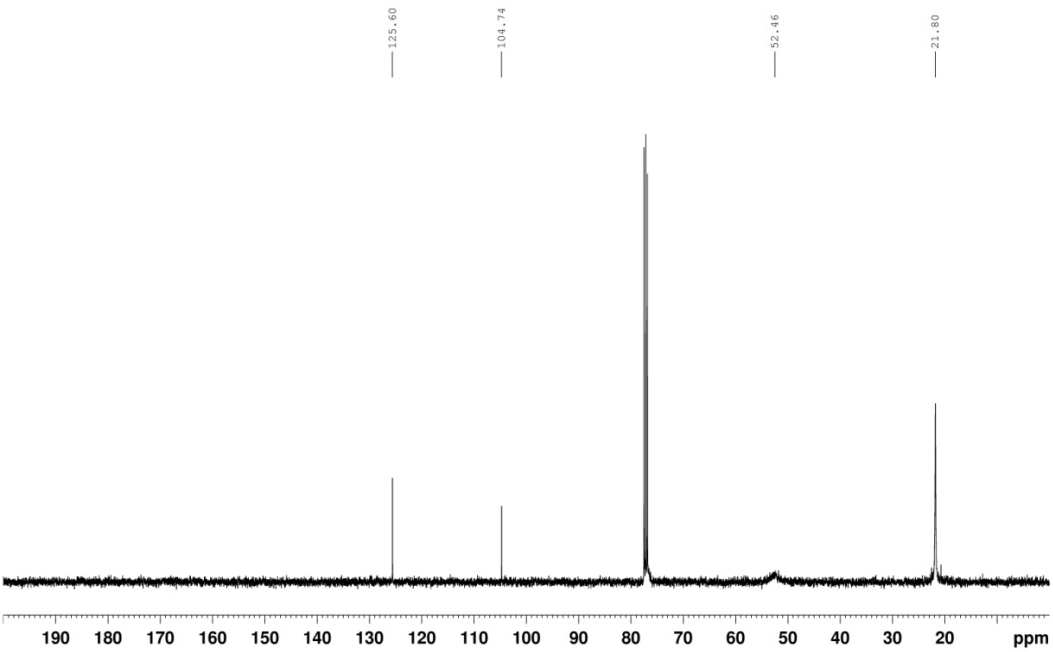
^{13}C NMR (101 MHz, CD_2Cl_2) **2**



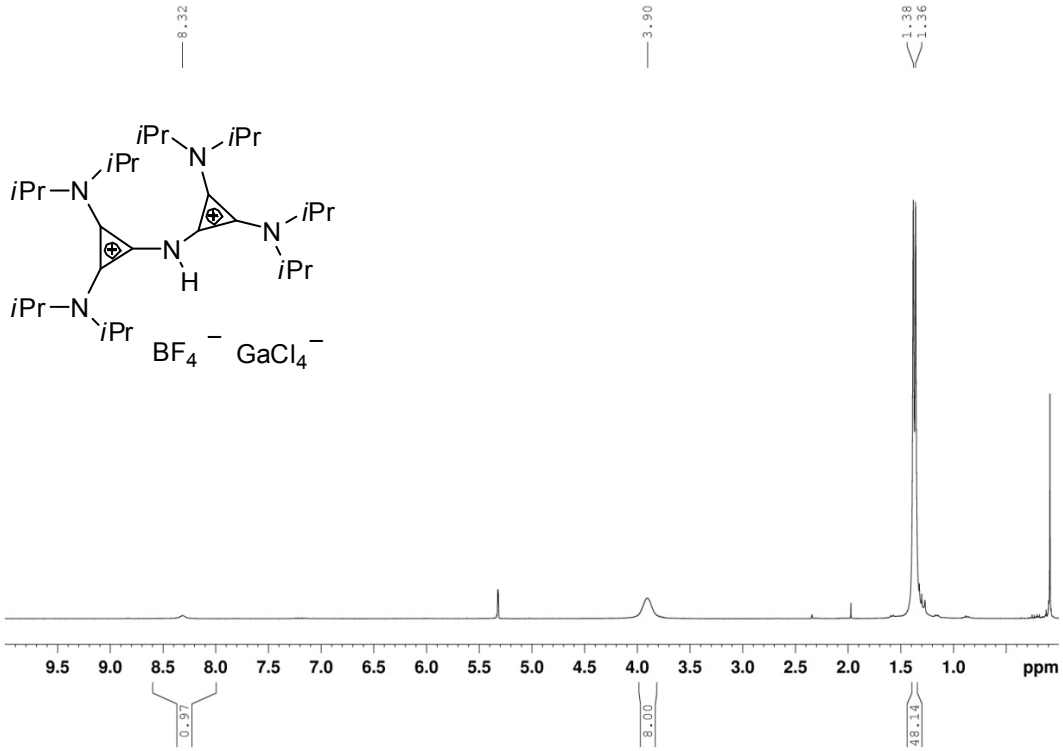
^{1}H NMR (400 MHz, $CDCl_3$) **3**



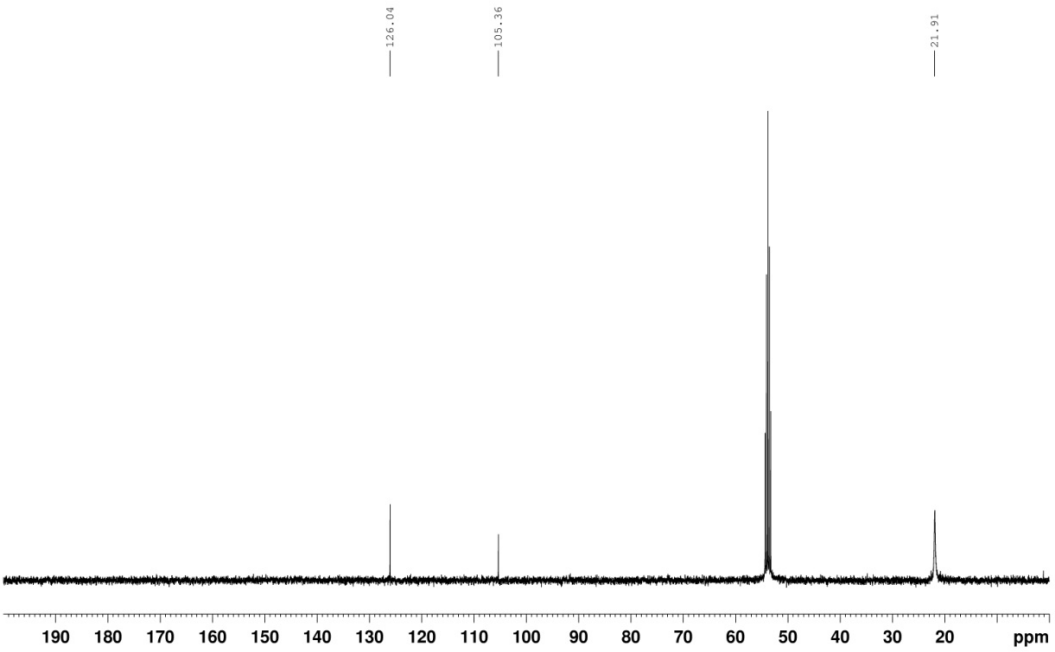
^{13}C NMR (101 MHz, $CDCl_3$) **3**



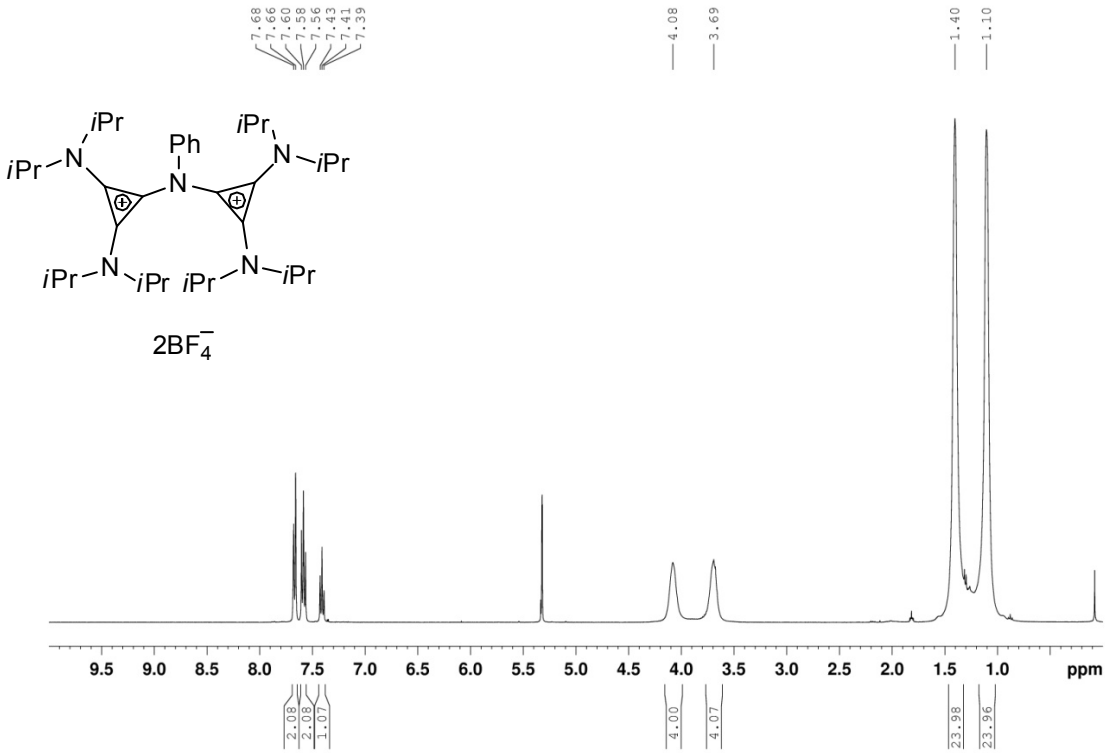
^{1}H NMR (400 MHz, CD_2Cl_2) **4**



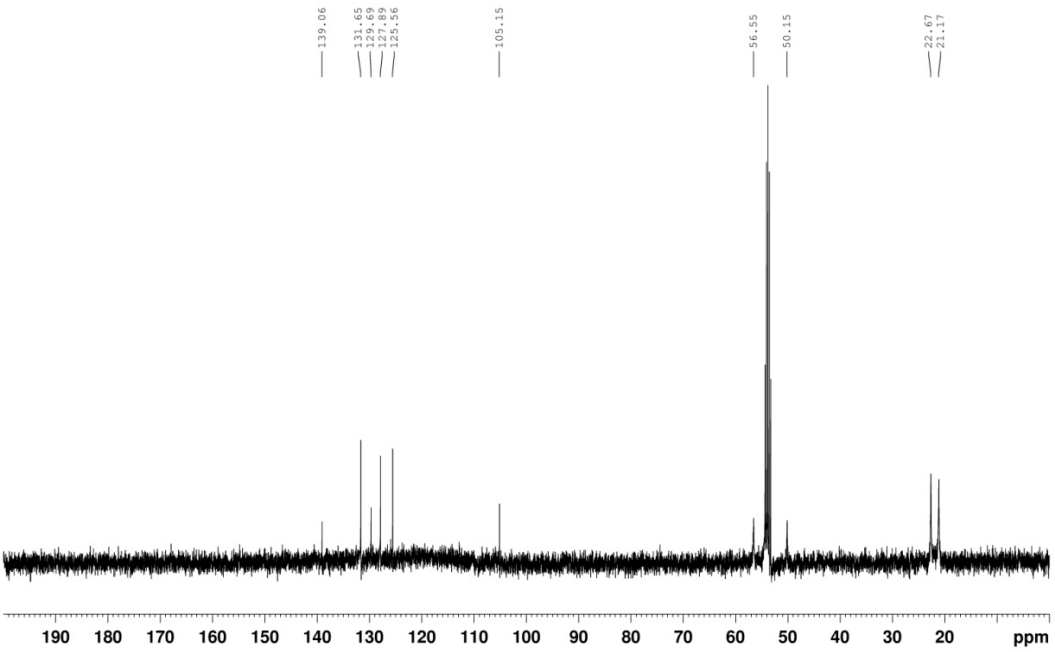
^{13}C NMR (101 MHz, CD_2Cl_2) **4**



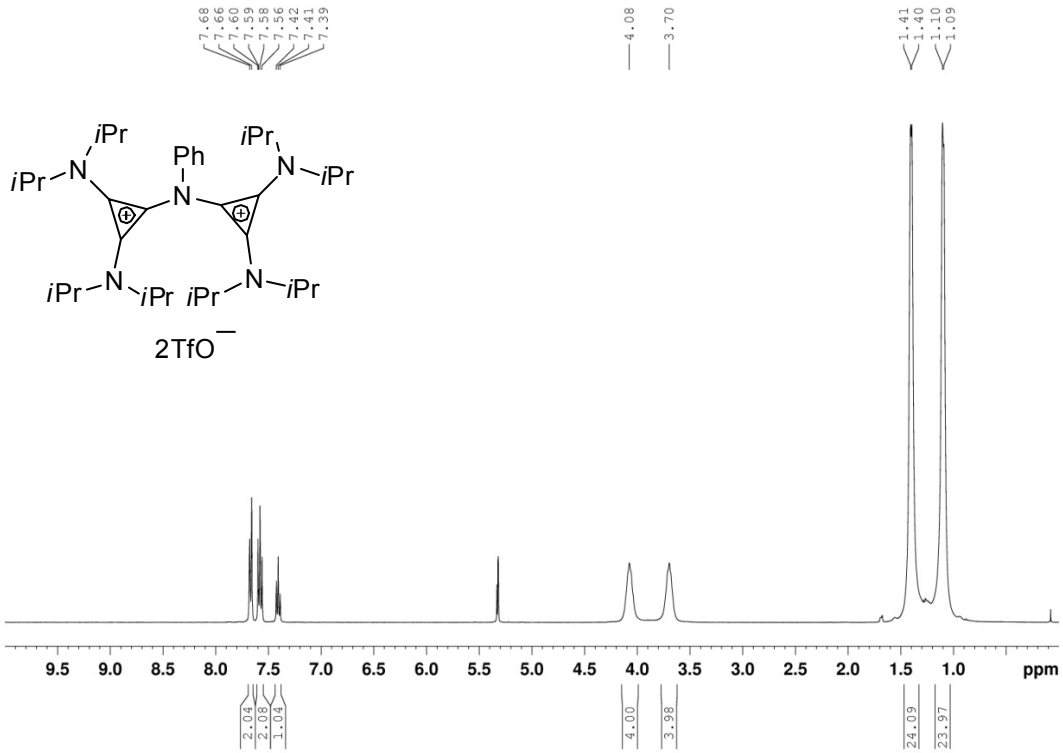
^{1}H NMR (400 MHz, CD_2Cl_2) **5**



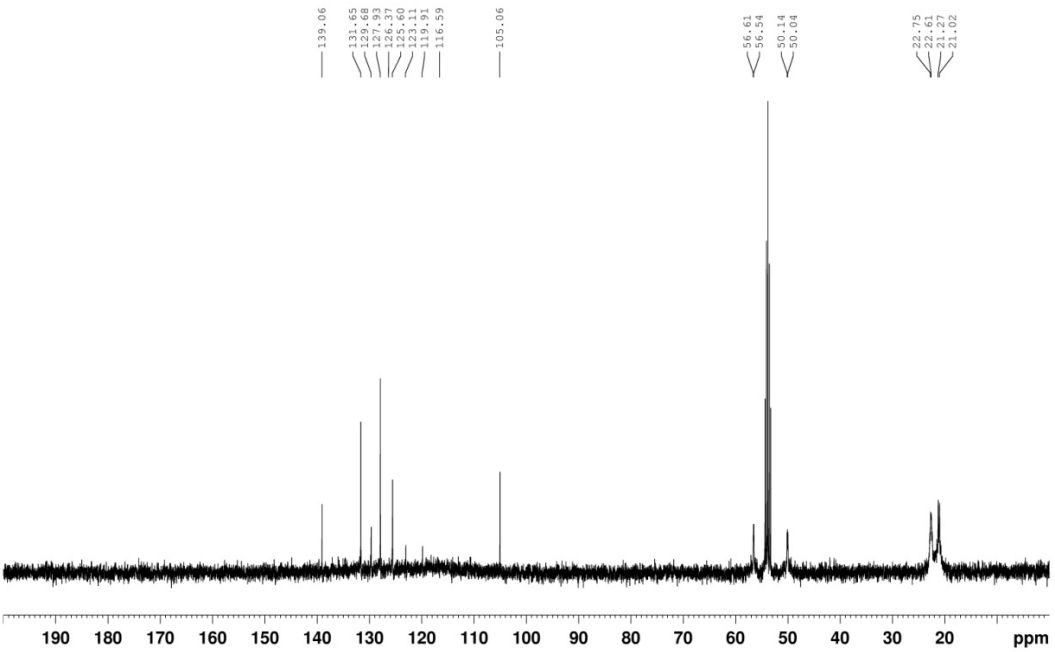
^{13}C NMR (101 MHz, CD_2Cl_2) **5**



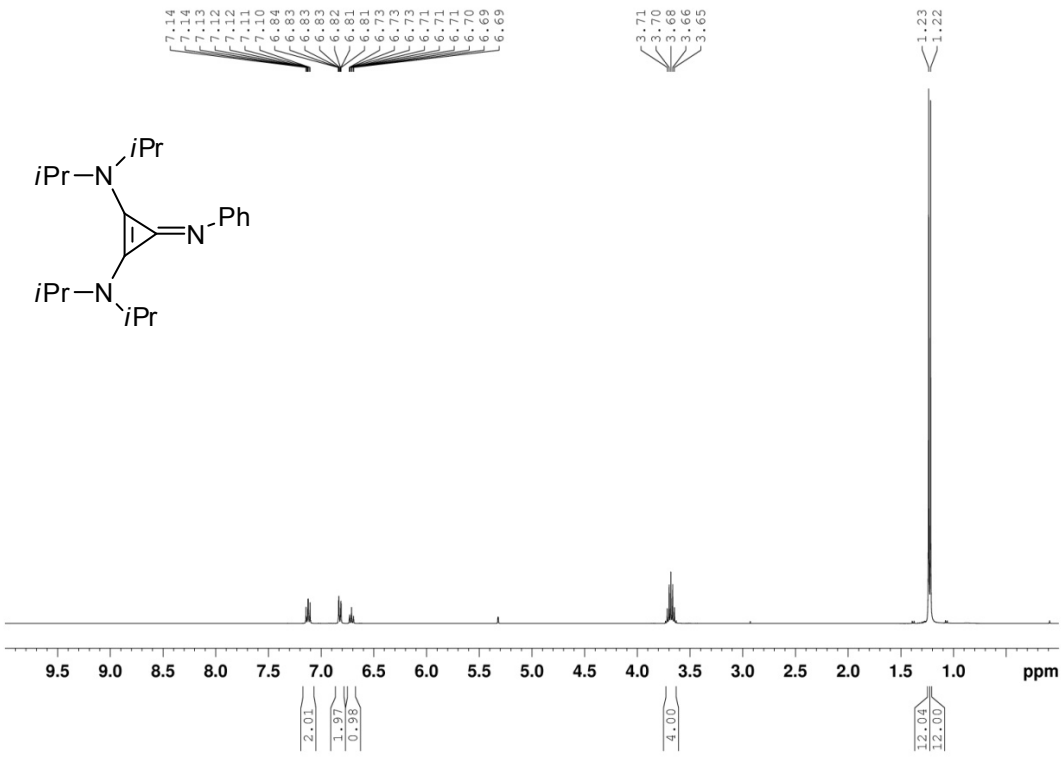
^{1}H NMR (400 MHz, CD_2Cl_2) **5(TfO)**



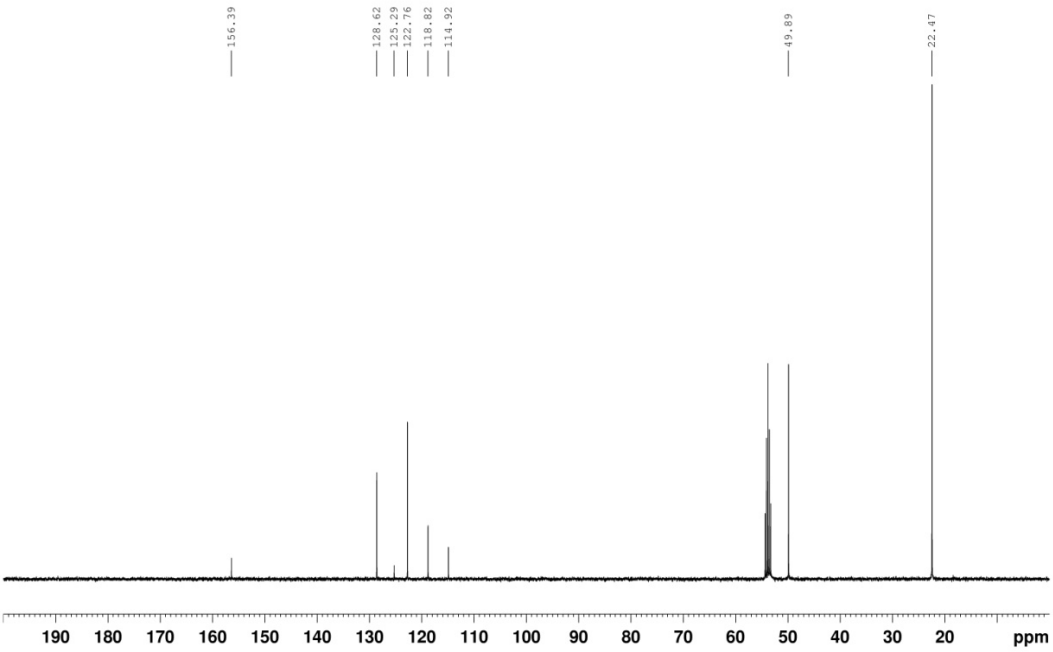
^{13}C NMR (101 MHz, CD_2Cl_2) **5TfO**



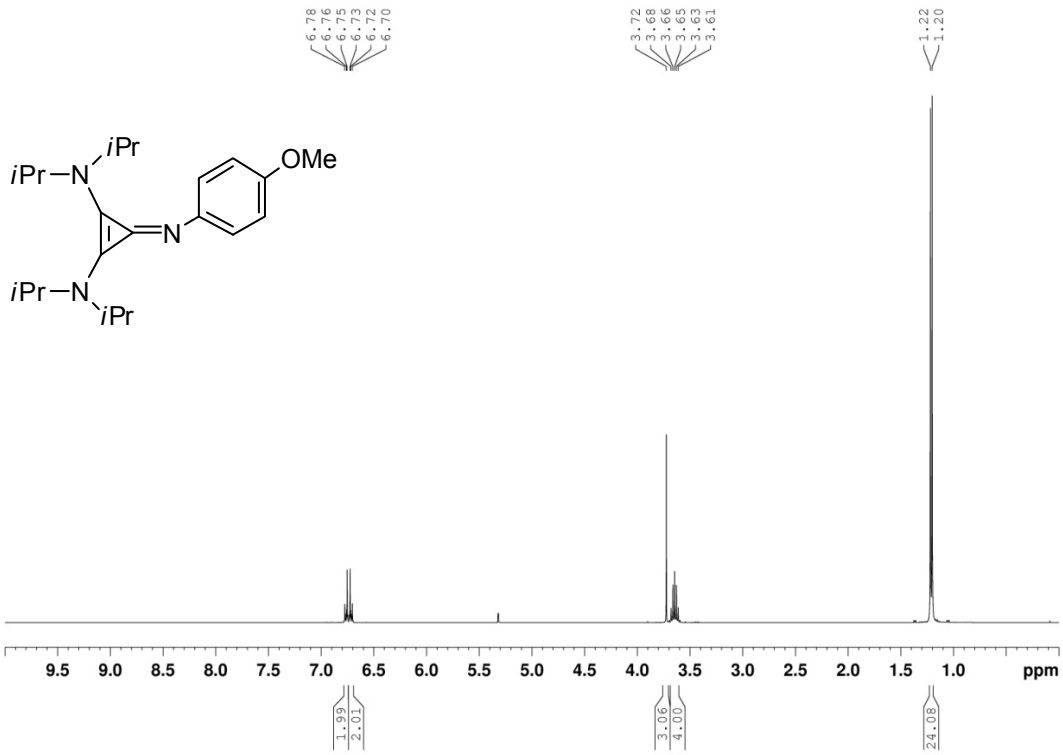
^{1}H NMR (400 MHz, CD_2Cl_2) **7**



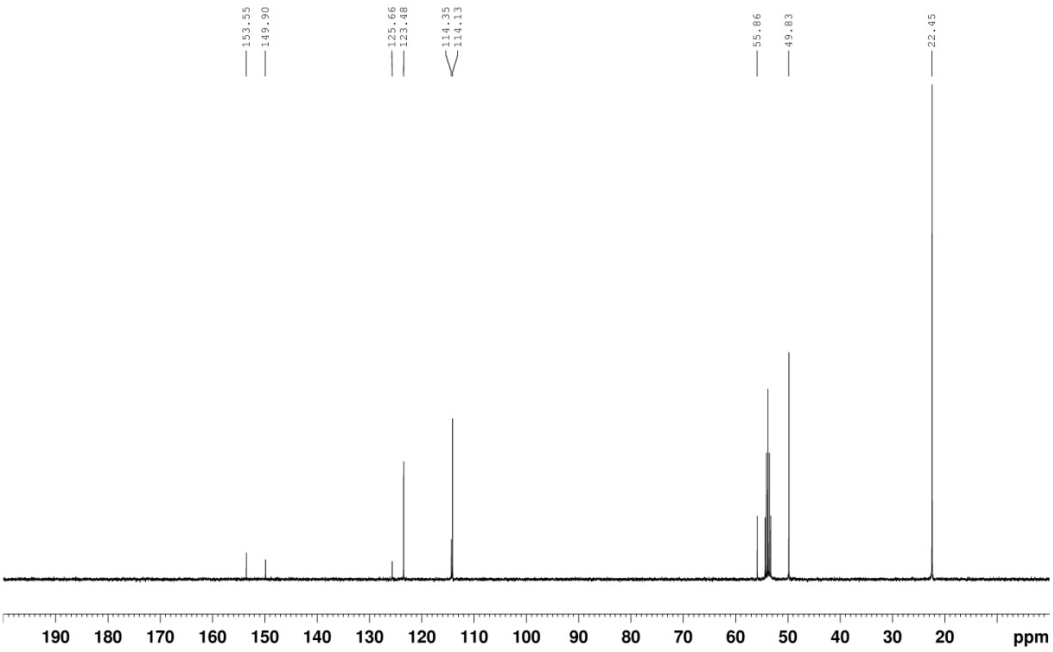
^{13}C NMR (101 MHz, CD_2Cl_2) **7**



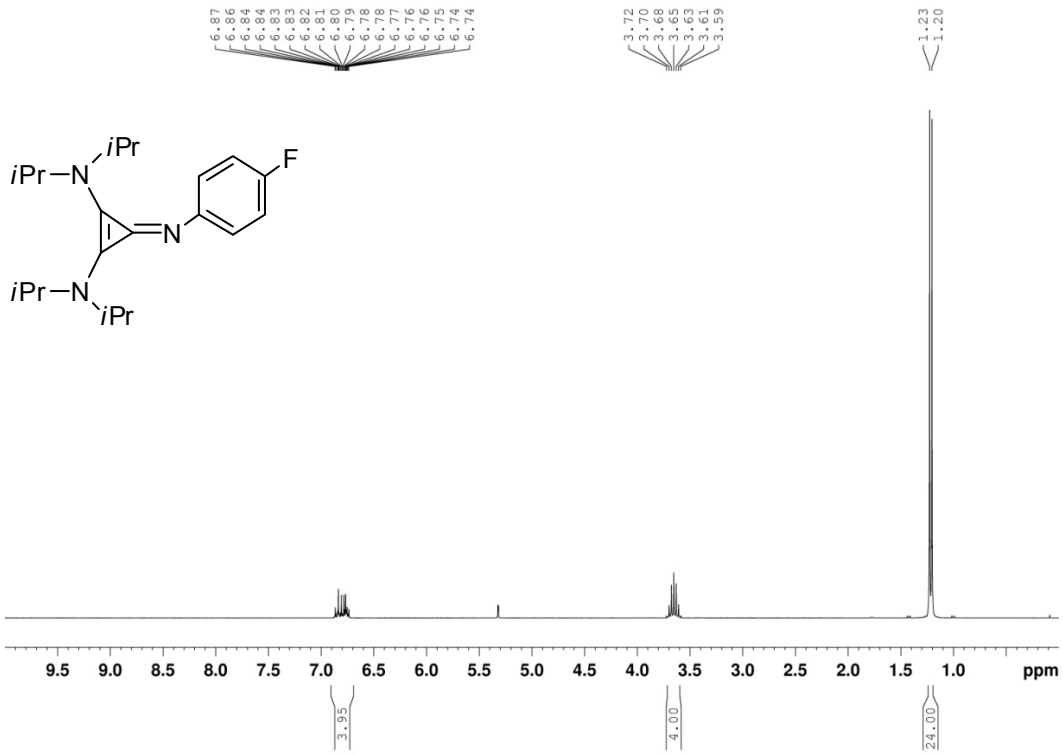
^{1}H NMR (400 MHz, CD_2Cl_2) **9**



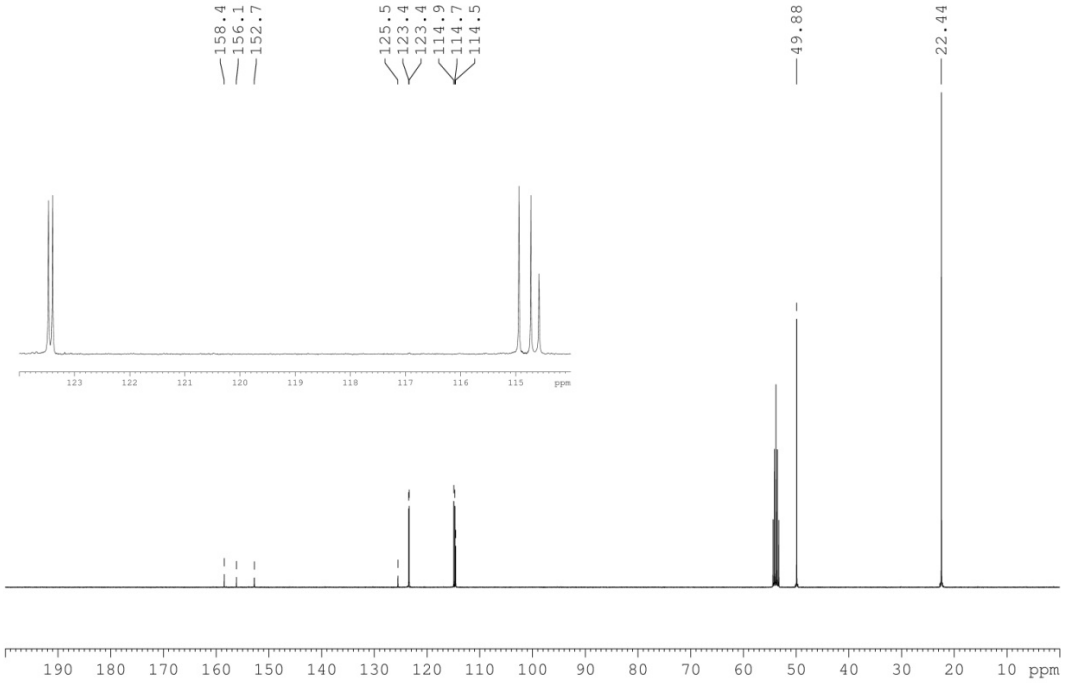
^{13}C NMR (101 MHz, CD_2Cl_2) **9**



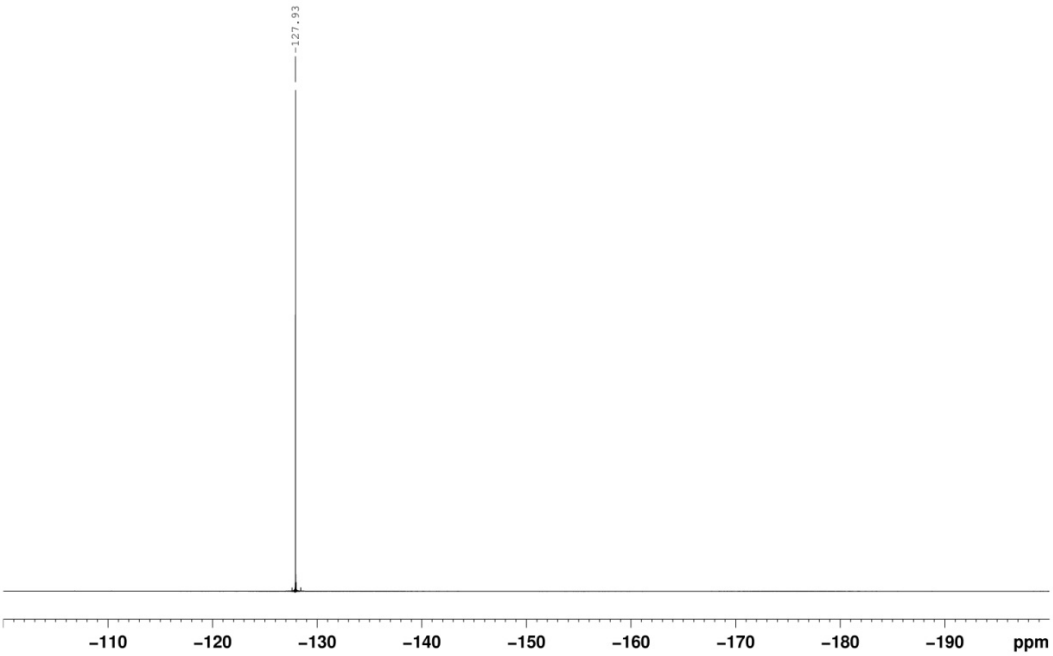
^{1}H NMR (400 MHz, CD_2Cl_2) **10**



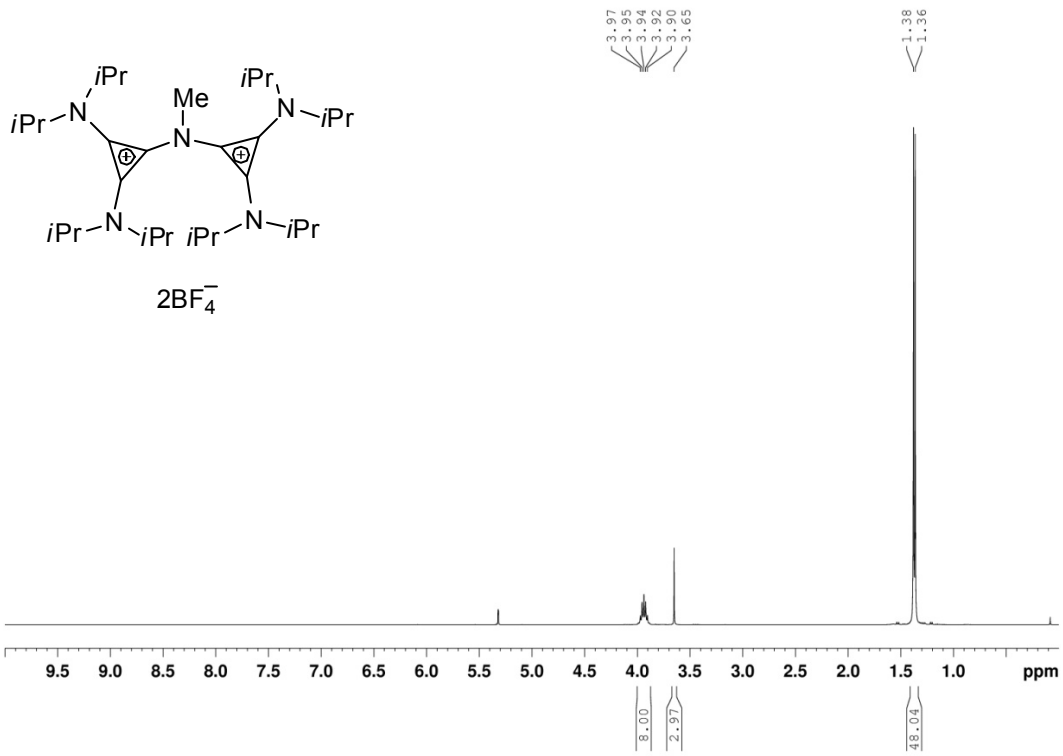
^{13}C NMR (101 MHz, CD_2Cl_2) **10**



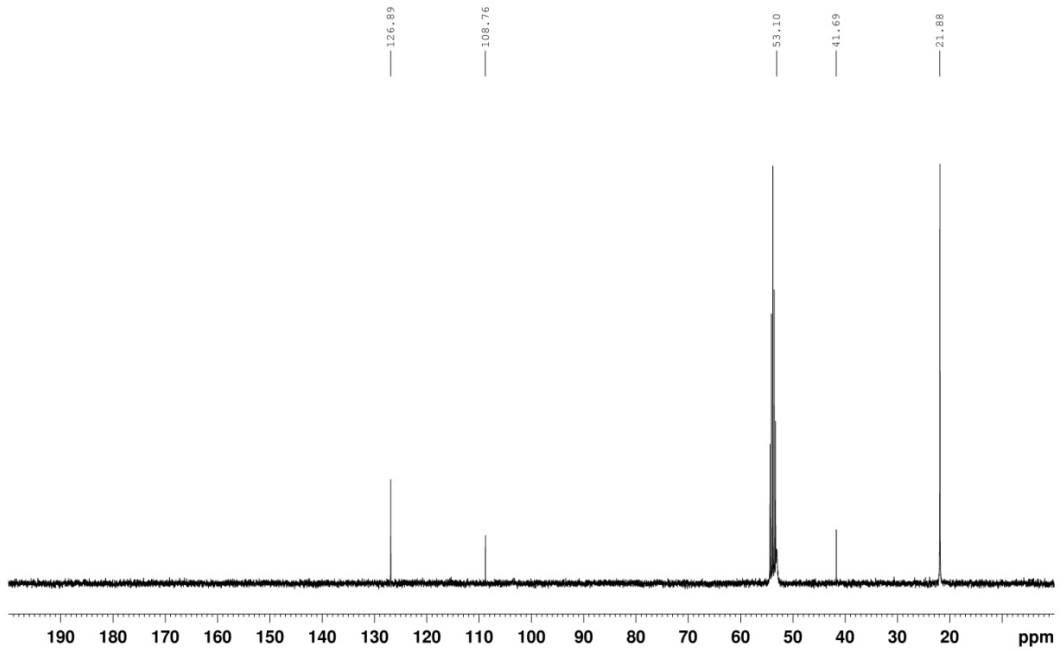
^{19}F NMR (282 MHz, CD_2Cl_2) **10**



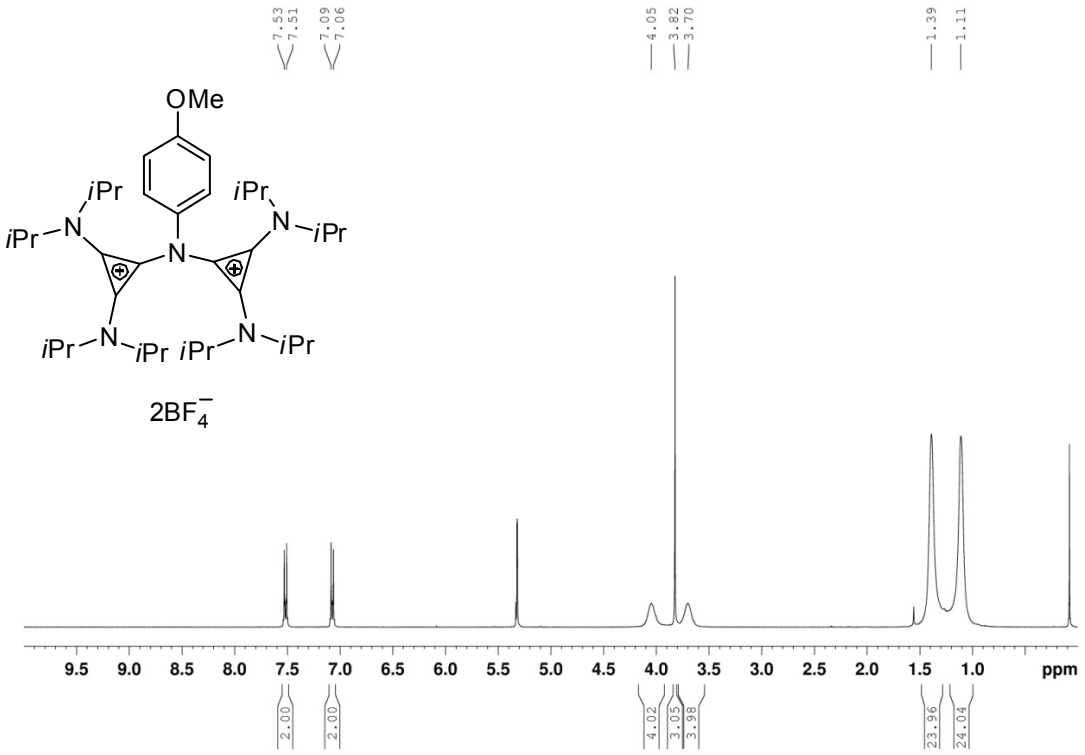
^{1}H NMR (400 MHz, CD_2Cl_2) **11**



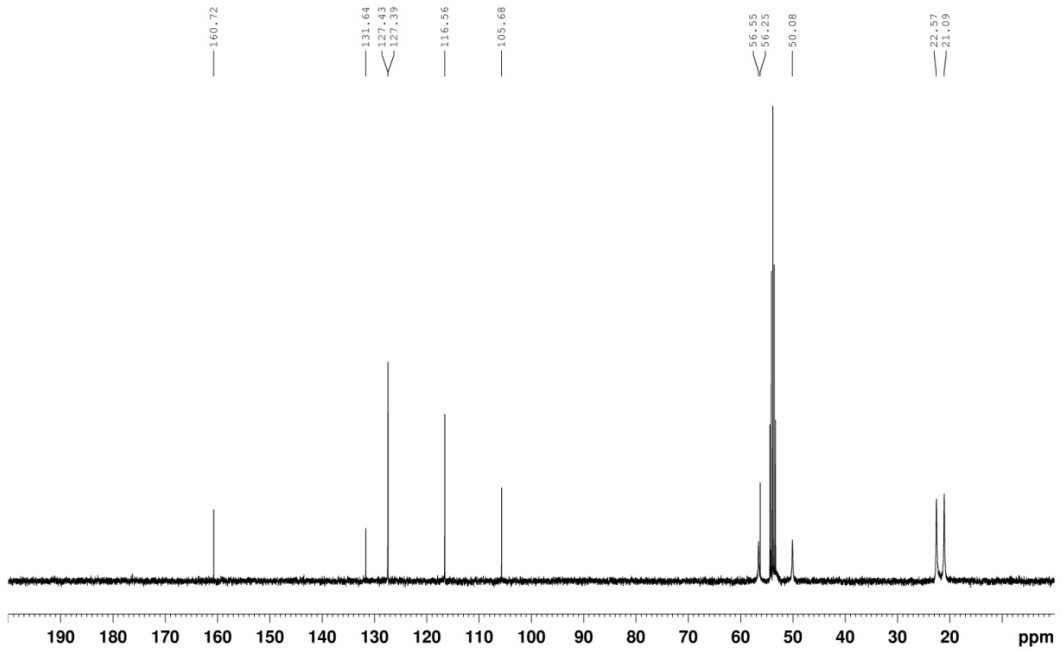
^{13}C NMR (101 MHz, CD_2Cl_2) **11**



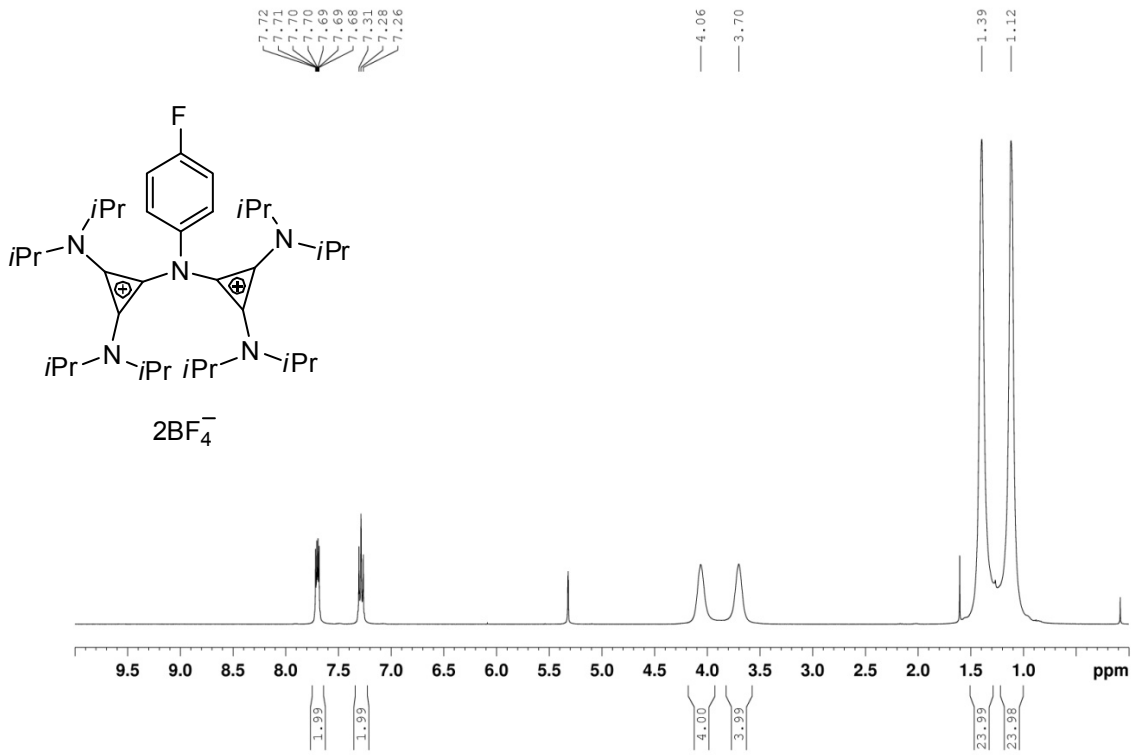
^{1}H NMR (400 MHz, CD_2Cl_2) **12**



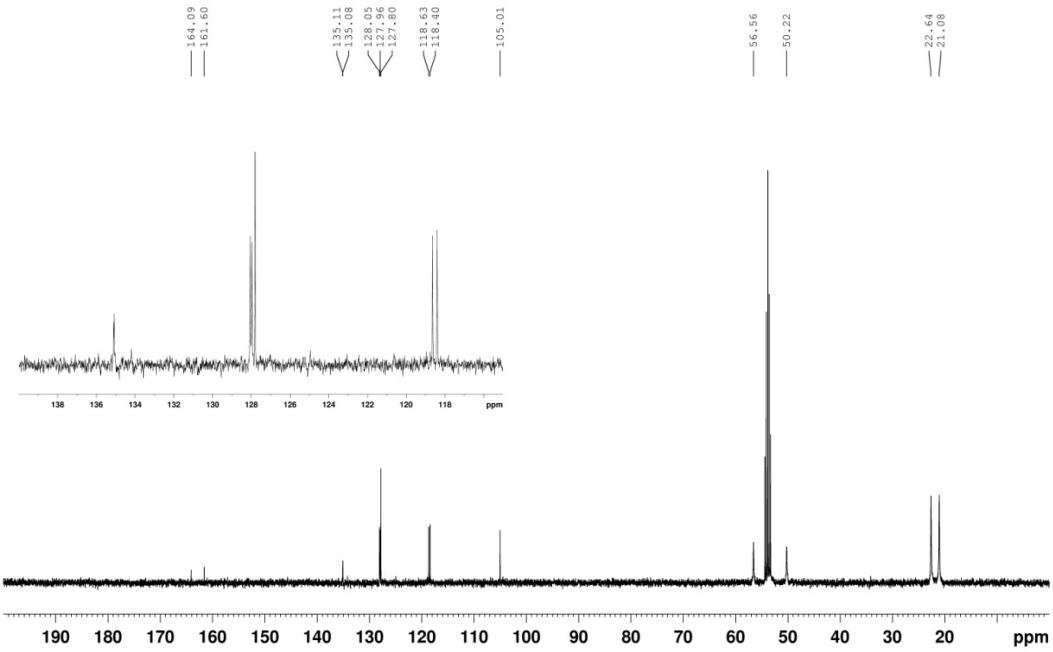
^{13}C NMR (101 MHz, CD_2Cl_2) **12**



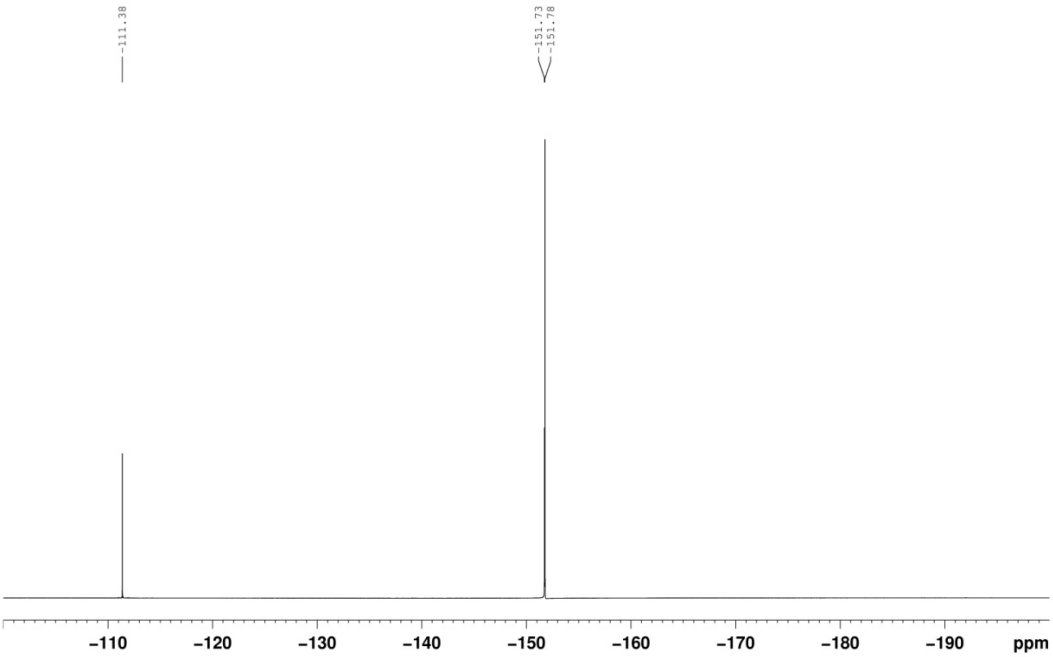
^{1}H NMR (400 MHz, CD_2Cl_2) **13**



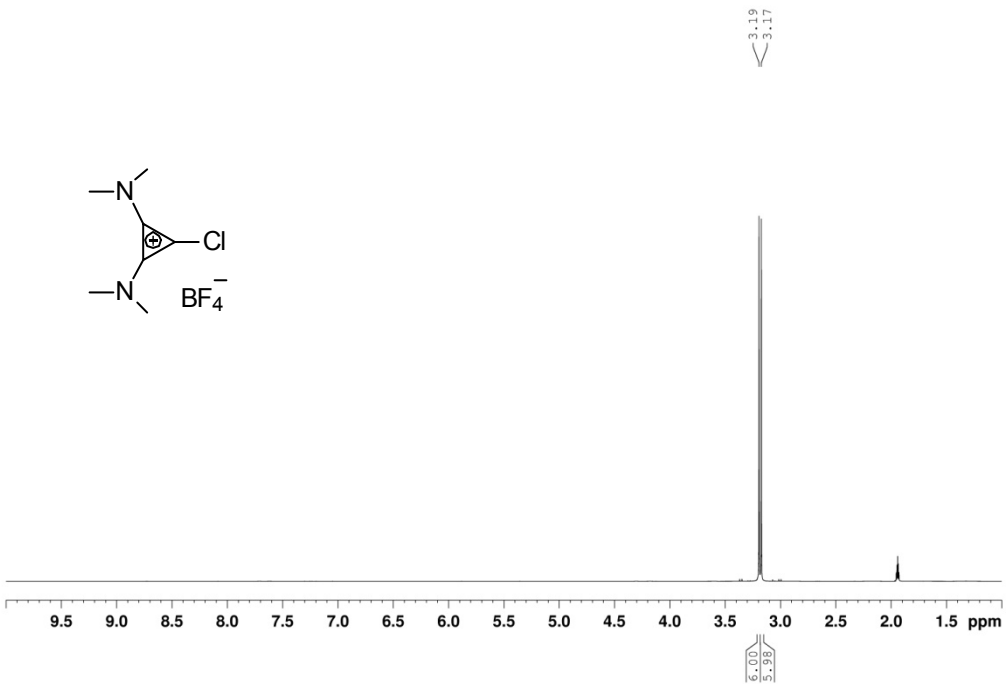
^{13}C NMR (101 MHz, CD_2Cl_2) **13**



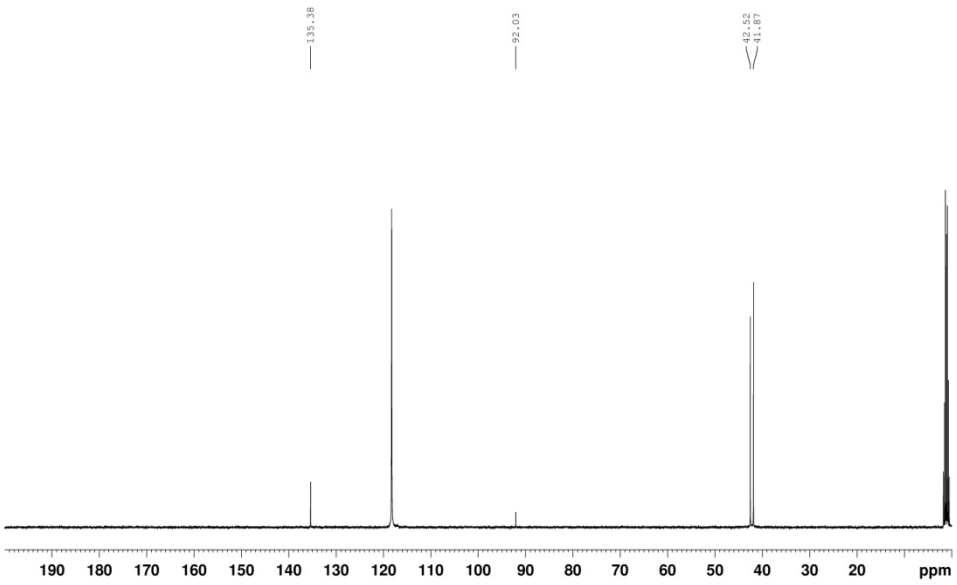
^{19}F NMR (282 MHz, CD_2Cl_2) **13**



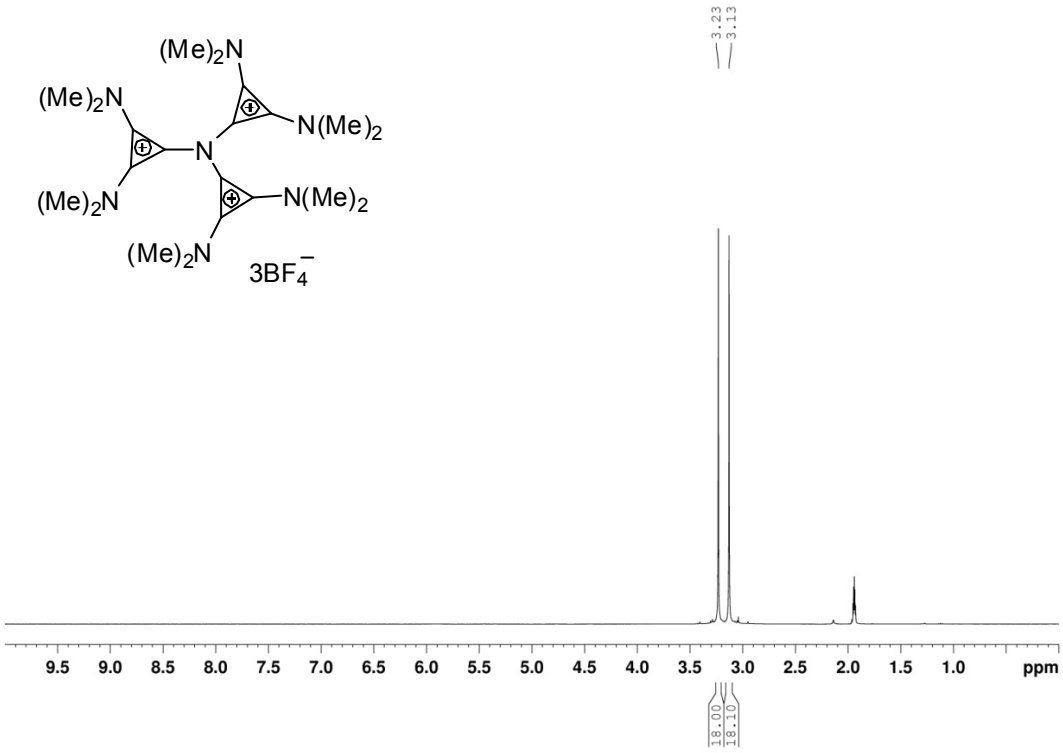
^{1}H NMR (400 MHz, CD_3CN) **14**



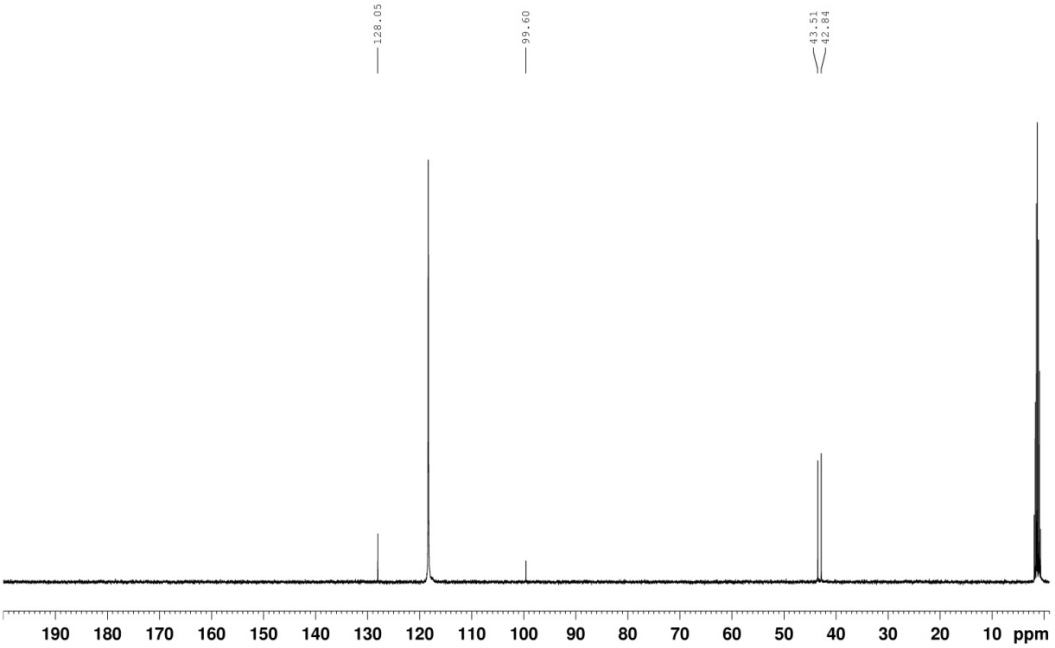
^{13}C NMR (101 MHz, CD_3CN) **14**



^{1}H NMR (400 MHz, CD_3CN) **15**



^{13}C NMR (101 MHz, CD_3CN) **15**



Computational Methods

Geometry optimizations were carried out using the BP86[7,8] functional in combination with def2-TZVP basis sets.[9] The resolution-of-identity (RI) approximation[10] was applied in conjunction with the appropriate auxiliary basis sets to speed up the calculations. Relevant stationary points were characterized as minima by evaluating the harmonic vibrational frequencies at the same level (RI-BP86/def2-TZVP). All geometry optimizations were done using the TURBOMOLE (version 6.4) program.[11] In order to gain insight into the electronic structure of the complexes, a Natural Bond Orbital (NBO) analysis was performed using NBO version 3.1[12] as implemented in the Gaussian 09 program package.[13]

TABLES

Table S1. Computed bond distances and Wiberg bond indices.

Compounds	Bond distances[a] in Å		Wiberg bond indices[b] in a.u.	
	N-C (cyclopropyl)	N-C (phenyl/methyl)	N-C (cyclopropyl)	N-C (phenyl/methyl)
$[L_2N]^+$	1.33	--	1.31	--
$[L_2NMe]^{2+}$	1.38	1.48	1.06	0.91
$[L_2NPh]^{2+}$	1.38	1.45	1.05	0.92
$[L_3N]^{3+}$	1.40	--	1.00	--

[a] BP86/def2-TZVP level
[b] BP86/6-311+G** level

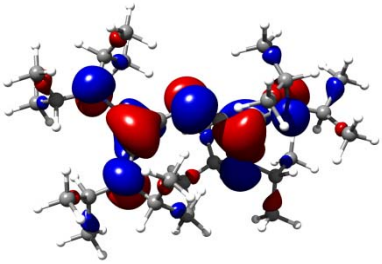
[7] A. D. Becke, *Phys. Rev. A.* **1988**, *38*, 3098.
[8] J. P. Perdew, *Phys. Rev. B.* **1986**, *33*, 8822.
[9] F. Weigend, R. Ahlrichs, *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297.
[10] (a) K. Eichkorn, O. Treutler, H. Öhm, M. Häser, R. Ahlrichs, *Chem. Phys. Lett.* **1995**, *242*, 652.
(b) K. Eichkorn, F. Weigend, O. Treutler, R. Ahlrichs, *Theor. Chem. Acc.* **1997**, *97*, 119.
(c) F. Weigend, *Phys. Chem. Chem. Phys.* **2002**, *4*, 4285.
[11] (a) R. Ahlrichs, M. Bär, M. Häser, H. Horn, C. Kölmel, *Chem. Phys. Lett.* **1989**, *162*, 165.
(b) TURBOMOLE V6.4 **2012**, a development of University of Karlsruhe and Forschungszentrum Karlsruhe GmbH, **1989-2007**, TURBOMOLE GmbH, since 2007; available from http://www.turbomole.com
[12] (a) NBO Version 3.1, E. D. Glendening, A. E. Reed, J. E. Carpenter, F. Weinhold.
(b) J. P. Foster, F. Weinhold, *J. Am. Chem. Soc.*, **1980**, *102,* 7211.
(c) A. E. Reed, F. Weinhold, *J. Chem. Phys.*, **1983**, *78,* 4066.
(d) A. E. Reed, R. B. Weinstock, F. Weinhold, *J. Chem. Phys.*, **1985**, *83*, 735.
(e) A. E. Reed, F. Weinhold, *J. Chem. Phys.*, **1985**, *83*, 1736.
(f) J. E. Carpenter, F. Weinhold, *J. Mol. Struct. (Theochem)*, **1988**, *46*, 41.
(g) A. E. Reed, L. A. Curtiss, F. Weinhold, *Chem. Rev.*, **1988**, *88*, 899.
[13] Gaussian 09, Revision B.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, **2009**.

Table S2. Computed natural charges and occupancies at BP86/6-311+G** level.

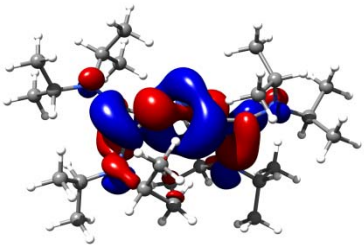
Compounds	Natural charges (*e*)			Occupancy
	q(N)	q(C) [phenyl/methyl]	q(C) [cyclopropyl]	LP(N)
$[L_2N]^+$	-0.60	--	0.21	1.76
$[L_2NMe]^{2+}$	-0.47	-0.39	0.16	1.70
$[L_2NPh]^{2+}$	-0.47	0.12	0.16	1.69
$[L_3N]^{3+}$	-0.45	--	0.13	1.69

Table S3. Molecular orbital energies at BP86/def2-TZVP level.

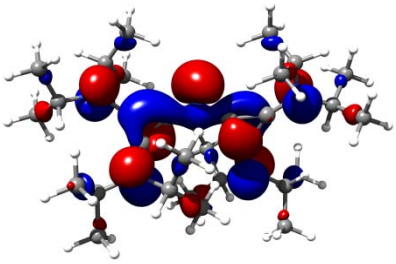
Compounds	Orbital energies (eV)	
	HOMO	LUMO
$[L_2N]^+$	-7.074	-3.364
$[L_2NMe]^{2+}$	-10.657	-7.213
$[L_2NPh]^{2+}$	-10.516	-7.111
$[L_3N]^{3+}$	-13.783	-10.415



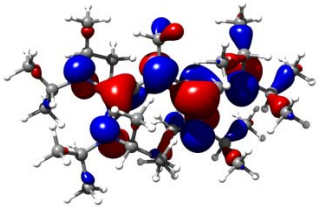
[L$_2$N]$^+$ HOMO



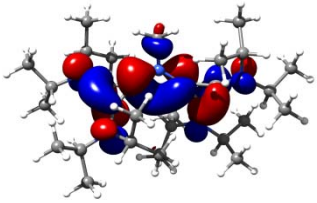
[L$_2$N]$^+$ LUMO



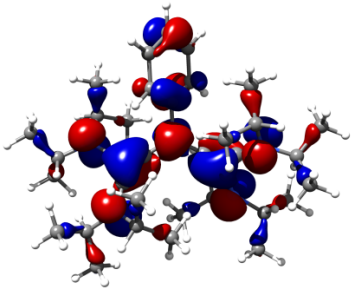
[L$_2$N]$^+$ HOMO-1



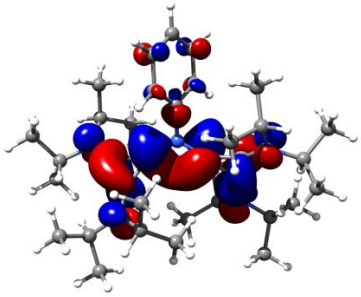
[L$_2$NMe]$^{2+}$ HOMO



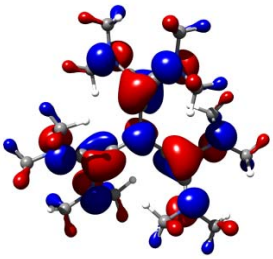
[L$_2$NMe]$^{2+}$ LUMO



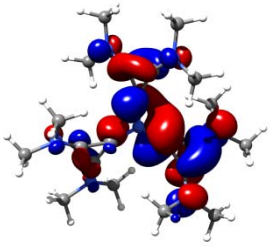
[L$_2$NPh]$^{2+}$ HOMO



[L$_2$NPh]$^{2+}$ LUMO



[L$_3$N]$^{3+}$ HOMO



[L$_3$N]$^{3+}$ LUMO

Figure S1. Highest occupied and lowest unoccupied molecular orbitals of **[L$_2$N]$^+$, [L$_2$NMe]$^{2+}$, [L$_2$NPh]$^{2+}$, [L$_3$N]$^{3+}$**.

CARTESIAN COORDINATES OF OPTIMIZED GEOMETRIES
(BP86/def2-TZVP, Å)

1. $[L_2N]^+$

c	7.0914791633	14.9542753901	2.8034079423
c	6.5007785938	16.1397372709	3.5712673096
c	5.8273637150	17.1515133161	2.6385187174
n	7.5249750924	16.7910974486	4.4382751725
c	7.3059618430	16.8610500252	5.9058530502
c	7.3344629472	15.4693413529	6.5476937039
c	8.5981641123	17.3390941933	3.8687710218
c	9.8291985255	18.0110522387	3.9428644680
c	9.2760834335	17.6787637428	2.6896167505
n	9.1504359422	17.8002863255	1.3734445535
c	10.1374516018	17.7361913148	0.4884784747
c	11.2607634604	17.1333477302	-0.1135792684
c	10.5318374137	18.1158703666	-0.8023651512
n	10.3052408740	18.8688713965	-1.8785961480
c	11.0938978952	18.6939628524	-3.1255375368
c	11.9090273238	19.9483343225	-3.4585964906
n	10.7760328240	18.6056987493	4.6827576877
c	11.6447589968	19.6535770982	4.0793187421
c	10.8126583581	20.7790328914	3.4566019501
c	10.8316718971	18.3791462738	6.1509600508
c	12.2251027697	17.9185497926	6.5935812795
c	6.0313603073	17.6367562914	6.2575315225
c	10.3446379746	19.5952540534	6.9476358364
c	12.6613051677	19.0735894543	3.0937391822
c	9.1928162047	19.8619269036	-1.8455138516
c	7.8298329262	19.1769005006	-1.6980032814
n	12.2523765643	16.2305993943	-0.0986813960
c	12.1699053362	15.0489468403	0.8045937448
c	10.8740077029	14.2625929644	0.5793321676
c	13.3221973746	16.2775036968	-1.1299554929
c	14.7154971084	16.2811363326	-0.4905864807
c	9.4227801248	20.9224436132	-0.7655880573
c	10.2162447035	18.2426582074	-4.2986330881
c	13.1707304222	15.1713359857	-2.1805178569
c	12.3705472914	15.4214365719	2.2749903469
h	5.7474523981	15.7547336036	4.2729379129
h	7.5626165721	14.2309027010	3.4820478459
h	7.8403333909	15.2960151691	2.0749525063
h	6.2979517432	14.4366146845	2.2471070633
h	6.5503814503	17.5575198663	1.9163778757
h	5.3865943084	17.9843083051	3.2022526434
h	5.0233082663	16.6599137705	2.0734236685
h	8.1607552043	17.4354572380	6.2893668222
h	5.1267420875	17.1155637805	5.9142727729
h	6.0410972595	18.6419468515	5.8161955930
h	5.9518683959	17.7418734082	7.3482348403
h	8.2726546296	14.9441223894	6.3225370523
h	6.4984443546	14.8453773172	6.2002672673
h	7.2432559628	15.5579326118	7.6387873994
h	10.1400600076	17.5433984431	6.3290808650
h	9.3309484990	19.8932406266	6.6465861472
h	11.0101165537	20.4602287874	6.8134198413
h	10.3286656549	19.3611732803	8.0211072609
h	12.9802828806	18.7057747863	6.4581965409
h	12.5456149073	17.0288981582	6.0354061111
h	12.2084204231	17.6647297867	7.6622184513
h	12.2013355102	20.0726972771	4.9294552723
h	12.1617113535	18.6339679841	2.2191042924

h	13.2780666674	18.2998249721	3.5686457400
h	13.3272880613	19.8700584170	2.7333860504
h	10.1181288662	21.2145685764	4.1873003043
h	10.2266062188	20.4113930345	2.6021560445
h	11.4722859767	21.5791514414	3.0936816643
h	9.2323628195	20.3552990306	-2.8267280408
h	10.3992013801	21.4110977994	-0.8840574079
h	9.3691246539	20.4747836688	0.2367540350
h	8.6436674411	21.6947985128	-0.8278988475
h	7.7501102539	18.6742930554	-0.7233022559
h	7.6660269554	18.4358380231	-2.4914579611
h	7.0270395246	19.9249853260	-1.7608563465
h	11.7939546594	17.8776473441	-2.9014179095
h	9.4921601428	19.0164459861	-4.5885039544
h	9.6643338771	17.3248247155	-4.0553096394
h	10.8465263696	18.0406051971	-5.1755911488
h	12.5609776876	20.2339244156	-2.6220751747
h	11.2595619504	20.8025203480	-3.6972085170
h	12.5401861471	19.7628744640	-4.3384705708
h	13.1883844008	17.2507544668	-1.6238972085
h	12.1806072820	15.2006062253	-2.6557301866
h	13.3107257096	14.1734878480	-1.7405297447
h	13.9308108345	15.2903474316	-2.9651935849
h	14.9353001060	15.3333873809	0.0214413136
h	14.8184965621	17.1002080520	0.2332159022
h	15.4794332386	16.4139115720	-1.2689012398
h	13.0120154099	14.4115659388	0.5011125527
h	11.5552742429	16.0627415258	2.6374442890
h	13.3217021890	15.9481137838	2.4253982969
h	12.3800098116	14.5117216751	2.8911882346
h	10.7647958266	13.9648730591	-0.4718078361
h	9.9952578441	14.8607423105	0.8606102750
h	10.8729014582	13.3525024188	1.1944519838

2. $[L_2NMe]^{2+}$

c	13.3802843442	5.9317135092	15.9514334475
c	14.2967551425	5.9641307378	17.1759526629
c	15.0904196422	4.6710331548	17.3586315630
n	15.1925190815	7.1707315138	17.1937584527
c	14.8081513507	8.3199187466	18.0857092280
c	15.0033559617	7.9605111681	19.5604106758
c	16.3270462151	7.2023698802	16.5250541943
c	17.5508653787	7.8957924514	16.2236462437
c	17.2126280334	6.7165499365	15.5620272070
n	17.4434076960	5.8428472150	14.5169050174
c	16.3273293413	5.5266825796	13.6003371326
c	18.6327153176	5.1523739869	14.4089821901
c	19.5970911746	4.5332841451	13.6123622334
c	19.6707905983	4.4856405416	15.0481414783
n	20.2167450327	4.1299066653	16.1985439788
c	21.5113009478	3.3836892436	16.3281701760
c	21.4025784050	1.9422334851	15.8216561157
c	19.4476925225	4.4113814058	17.4570138100
c	18.9918719060	3.1156224810	18.1336633544
n	18.3527781746	8.9216698189	16.4238490370
c	19.4196651761	9.2579941415	15.4228447370
c	18.8342940383	9.4069581027	14.0182686402
c	18.1522605421	9.8465221505	17.5903273777
c	19.4303778149	9.9799549284	18.4216843980
c	13.3962733768	8.8273401250	17.7865315144
c	17.6003384056	11.2007492690	17.1399139677

c	20.5892585717	8.2757816921	15.4818972753
n	20.0826515959	4.1894045758	12.4333547042
c	19.4395463698	4.6395089349	11.1537118829
c	19.2081550300	6.1508537776	11.1320991084
c	21.3400751881	3.3787074732	12.3229276488
c	21.1060822441	2.0619581939	11.5805841946
c	20.2346916650	5.3177431085	18.4065401178
c	22.6830527041	4.1793805178	15.7511090771
c	22.4793362432	4.2019752343	11.7149401096
c	18.1990928313	3.8074651658	10.8175836974
h	13.6686294726	6.0962275053	18.0674107245
h	12.8129585011	6.8628793038	15.8385826033
h	12.6588015975	5.1104037302	16.0579161758
h	13.9448705288	5.7553643879	15.0272602882
h	15.7363475881	4.4580399860	16.4945205450
h	14.3939780902	3.8285085296	17.4597605154
h	15.7102698747	4.7057698954	18.2643593137
h	15.5084534658	9.1213213609	17.8168422766
h	13.2779228570	9.1108433324	16.7326990463
h	13.2068945488	9.7201422198	18.3972056471
h	12.6233572983	8.0917951341	18.0461541914
h	14.3140989581	7.1684689057	19.8847482201
h	14.7968837304	8.8407563642	20.1837299948
h	16.0309149159	7.6303582267	19.7674390640
h	17.4034131294	9.3423852273	18.2161377745
h	18.3224519312	11.7521739676	16.5218425785
h	17.3899221104	11.8230211228	18.0201482138
h	16.6684852981	11.0932765983	16.5679395170
h	19.8009561698	9.0029329290	18.7582310526
h	19.2139340557	10.5829559204	19.3135967704
h	20.2327089692	10.4944075421	17.8753159740
h	19.7844562974	10.2423522014	15.7445209461
h	21.0222365069	8.2263308356	16.4889869822
h	21.3790278297	8.6014907173	14.7916840944
h	20.2782091221	7.2651501205	15.1800129094
h	18.4671635675	8.4461691565	13.6293788907
h	19.6109348948	9.7684325084	13.3313739748
h	18.0076505039	10.1293362325	14.0009782741
h	18.5543355847	4.9576845107	17.1191328623
h	21.1274194074	4.8217742742	18.8107383587
h	19.6017490646	5.5797862439	19.2652360899
h	20.5485558987	6.2460664435	17.9117612266
h	18.4003051399	2.4880469966	17.4543199276
h	18.3689452513	3.3583070520	19.0050407484
h	19.8416712185	2.5254680019	18.5032739684
h	21.6662973096	3.3292647969	17.4140325666
h	22.5879602665	4.3482525123	14.6708550299
h	23.6188653083	3.6297424568	15.9172614671
h	22.7744120620	5.1570314648	16.2419057118
h	20.6190834132	1.3915539918	16.3570398711
h	22.3544373677	1.4210660040	15.9892596480
h	21.1776275578	1.8849477822	14.7491334560
h	21.6060726384	3.1435964286	13.3594884891
h	22.6443928755	5.1387616715	12.2645184129
h	22.3013910728	4.4460190821	10.6586152177
h	23.4078754615	3.6167541558	11.7545888104
h	20.3021654879	1.4711154780	12.0394360754
h	22.0268160803	1.4646835823	11.6126773830
h	20.8644070457	2.2206134070	10.5205280403
h	20.1986856557	4.4202683552	10.3915561455
h	17.4207084703	3.8898650963	11.5867415108
h	18.4470760696	2.7445501837	10.7100745823

h	17.7704969036	4.1501018379	9.8662611143
h	18.4748235899	6.4777070164	11.8820050253
h	18.8247862764	6.4478658917	10.1472137147
h	20.1445269248	6.6963390918	11.3076746415
h	15.8717797404	4.5549176148	13.8363833894
h	16.6948703137	5.5140882453	12.5692436634
h	15.5770872789	6.3193037789	13.6786398307

3. $[L_2NPh]^{2+}$

c	6.1285716784	6.6041271957	18.5209279832
c	5.9680184517	6.9507195481	17.1760509668
c	4.7011070359	7.2814227816	16.6858348073
c	3.5927092919	7.2701318722	17.5362109401
c	3.7630355187	6.9197111914	18.8794386040
c	5.0257184382	6.5841055622	19.3782547753
n	2.6127305051	6.9030744813	19.7677565646
c	2.6650221361	7.6335914413	20.9403549707
c	2.5068348841	7.7145270640	22.3235034148
n	2.1186031075	7.2221310666	23.4852971111
c	1.8554885717	5.7565297750	23.6543376972
c	0.5523165425	5.3238683958	22.9826926323
c	1.5083972815	6.1512618310	19.4112603251
c	0.1325290114	6.0392897310	19.2135381831
n	-1.1010804974	6.5006716679	19.3015155582
c	-1.3661660864	7.9580946674	19.5307268879
c	-1.0631471765	8.3808083543	20.9682460120
c	1.0237604083	4.9892972143	18.8085621521
n	1.1783951538	3.8220280695	18.2185936841
c	0.0030359428	3.1494868043	17.5658277375
c	-0.5117069308	1.9878832154	18.4199762064
c	-0.6521420048	8.8191327841	18.4886615747
c	0.3143353988	2.7273446419	16.1283690593
c	-2.2759626219	5.5968262572	19.0624220151
c	-3.2532102186	5.6310052048	20.2401173585
c	-2.9558990435	5.9032972045	17.7260370951
c	2.4785144371	3.0677434424	18.2615894295
c	3.4729228953	3.5536796339	17.2066184350
c	3.0707196444	3.0507412534	19.6691766253
c	3.1038953865	8.7913762442	21.5860684544
n	3.6928314880	9.9693241344	21.6103608889
c	4.0242361228	10.6170506403	22.9262256945
c	3.0640807286	11.7685662836	23.2330119000
c	3.0610768741	4.9252385741	23.2163167787
c	5.4922510194	11.0430095923	22.9958345410
c	2.0326293085	8.1003558819	24.7004570763
c	0.6428786865	8.0304766860	25.3394702794
c	3.1527861223	7.7910996521	25.6960248227
c	3.9695312947	10.7529205610	20.3579321372
c	5.2428764234	10.2922019158	19.6479345268
c	2.7543250904	10.7788539629	19.4340821024
h	-1.8445181023	4.5877354444	19.0245068815
h	-3.7610972504	5.1782294812	17.5477933054
h	-2.2512625767	5.8430160639	16.8849035531
h	-3.4147186886	6.9019561048	17.7195387364
h	-3.7512486650	6.6048836935	20.3427845587
h	-2.7552431968	5.3860583470	21.1875619477
h	-4.0409574017	4.8850421609	20.0712256112
h	-2.4474260270	8.0594668328	19.3687607408
h	-0.9487569745	9.8694014699	18.6084591586
h	-0.9115574206	8.5099000811	17.4679055338
h	0.4401380187	8.7689750403	18.6043031879

h	0.0105159345	8.3007467622	21.1889501179
h	-1.6176364091	7.7688095609	21.6902049531
h	-1.3578215766	9.4287892545	21.1140135253
h	2.1852757340	2.0390471950	18.0108864109
h	3.9366945954	2.3762114357	19.6902399603
h	2.3431045205	2.6914614979	20.4090421435
h	3.4270749730	4.0459855560	19.9691746358
h	3.8196928710	4.5720684310	17.4218877055
h	3.0387673249	3.5385723224	16.2000926343
h	4.3498807213	2.8923270085	17.2042791079
h	-0.7689561821	3.9291232677	17.5158473888
h	1.0672768551	1.9289579000	16.0798298227
h	0.6561265825	3.5741549428	15.5192364918
h	-0.6022889164	2.3313920242	15.6715924429
h	-1.4185973620	1.5692187868	17.9638655317
h	-0.7599627066	2.3105571755	19.4406857595
h	0.2214414702	1.1717450025	18.4866099641
h	2.6042703243	7.5360453340	17.1587215332
h	4.5742047702	7.5573508065	15.6388056338
h	6.8304720661	6.9630944381	16.5097912926
h	2.1644143291	9.1200305547	24.3146368689
h	3.1078325003	8.5004455896	26.5332999056
h	4.1454770209	7.8727310738	25.2323757887
h	3.0544004468	6.7833931707	26.1232935420
h	0.4310319257	7.0435458412	25.7731864232
h	-0.1472949967	8.2782424730	24.6193735134
h	0.5918258714	8.7578077168	26.1607472838
h	1.7355532275	5.6322487864	24.7386165164
h	2.8849156088	3.8659904401	23.4459808150
h	3.9741739252	5.2360301858	23.7402292357
h	3.2336470792	5.0055111353	22.1334895792
h	0.6139809692	5.4272460092	21.8901640779
h	-0.2993067883	5.9138568674	23.3440694185
h	0.3541201373	4.2677416303	23.2094194353
h	4.1306004301	11.7752024732	20.7264121944
h	2.9446674782	11.4707186693	18.6033162680
h	1.8539141481	11.1217066645	19.9610136309
h	2.5591985659	9.7902192611	18.9958937336
h	5.1297695670	9.2803171081	19.2385669856
h	6.1103428996	10.3013210042	20.3185351031
h	5.4579196987	10.9721275385	18.8124400577
h	3.8791836050	9.8221316431	23.6690745738
h	5.7253196225	11.8554099604	22.2949713508
h	6.1707497283	10.2023758631	22.8019625763
h	5.7022920781	11.4191949015	24.0060043989
h	3.2750124044	12.1663312412	24.2347999934
h	2.0150010765	11.4426894068	23.2084801487
h	3.1822499171	12.6013875814	22.5257591094
h	5.1457840725	6.3052137644	20.4263278936
h	7.1142922757	6.3403865334	18.9045312513

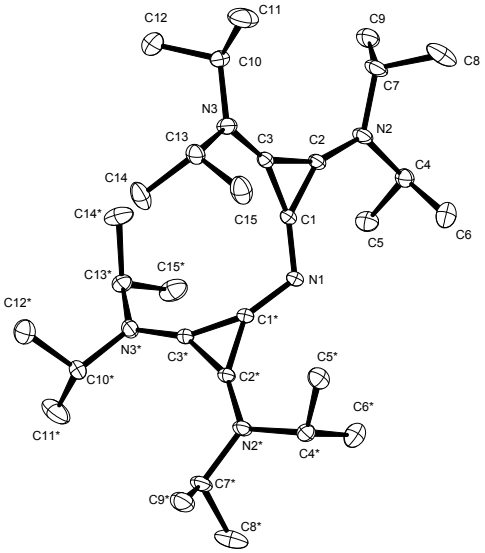
4. $[L_3N]^{3+}$

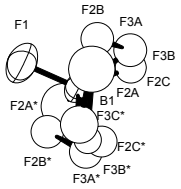
c	2.6443463428	10.6467958703	10.2432357238
n	2.6312186641	11.6910622747	9.2049940136
c	1.5243325245	12.6637102946	9.2832155988
c	3.5190510549	11.7003517661	8.2414727678
c	4.0094621034	12.2669325989	7.0142568157
c	4.6991700233	11.2452200162	7.6600655324
n	5.7948911820	10.3801169737	7.6955544280
c	6.4564797952	10.1390290483	8.9014893761
c	6.9738759508	10.6308818810	10.0962663637

c	7.0669757818	9.2346132513	9.7654848267
n	7.4842143594	8.0286223831	10.0630416491
c	8.2904829212	7.7319885614	11.2625263648
c	6.2299698809	9.7566322336	6.5237118446
c	7.2840211335	9.3563304752	5.7073405633
c	5.9183573641	9.0913281013	5.3412419137
n	5.0512334790	8.6172285916	4.4811903160
c	5.4418152160	8.0593164877	3.1721508923
c	3.6166652549	8.5476893720	4.8069179357
c	7.1028641437	6.8666878345	9.2424067390
n	3.8571187223	13.0997411015	6.0143230304
c	4.9211234874	13.2907027152	5.0142363504
c	2.6618330288	13.9496479009	5.8524230525
n	8.5641302221	9.2374207217	5.4552355863
c	9.5698646124	9.9220877634	6.2852942406
c	9.0876827069	8.4813877361	4.3012955926
n	7.1837885793	11.6068388871	10.9448775473
c	6.9137598918	13.0069605245	10.5766752086
c	7.7653133681	11.3939362415	12.2839405300
h	1.6976090309	10.0899599149	10.2140565315
h	2.7489681313	11.1099139081	11.2334945347
h	3.4728158907	9.9536306375	10.0662741322
h	1.7289296937	13.5229256267	8.6391393631
h	1.4388477266	13.0166222636	10.3186503198
h	0.5783050308	12.1872602677	8.9914366294
h	2.3367970865	13.9040445586	4.8051758321
h	2.9002320085	14.9920835116	6.1048865975
h	1.8487894627	13.5846019308	6.4851426625
h	5.2469940427	14.3399571022	5.0230490764
h	4.5369261615	13.0502615006	4.0140237875
h	5.7757109892	12.6482068800	5.2495603923
h	3.2842916958	7.5009724475	4.7729923214
h	3.0411541241	9.1234435440	4.0698688184
h	3.4409084023	8.9465892911	5.8111728213
h	6.4618852459	8.3605547824	2.9212792963
h	4.7626193033	8.4528760067	2.4052520989
h	5.3625430483	6.9635365392	3.1876756562
h	8.3120287197	7.8283035268	3.8930244286
h	9.9258039722	7.8585762006	4.6392191290
h	9.4483321884	9.1721486209	3.5268724735
h	10.1485527780	10.6161144730	5.6604432011
h	10.2567396153	9.1833876341	6.7191727762
h	9.0756271106	10.4849729706	7.0834806865
h	6.5368442571	6.1538437289	9.8577639363
h	8.0053907158	6.3672423975	8.8656263391
h	6.4785491853	7.1899318135	8.4031221236
h	8.7126563363	8.6530072140	11.6726550883
h	9.1151310246	7.0667556083	10.9768908193
h	7.6737640917	7.2277378619	12.0192724338
h	7.7092016123	10.3372603829	12.5576306940
h	7.1882123863	11.9748653989	13.0145035496
h	8.8091281130	11.7359266642	12.3035941722
h	6.5267887509	13.0570772322	9.5539470731
h	7.8445389759	13.5873273179	10.6377420866
h	6.1836913465	13.4390808219	11.2739640573

X-Ray strucutres

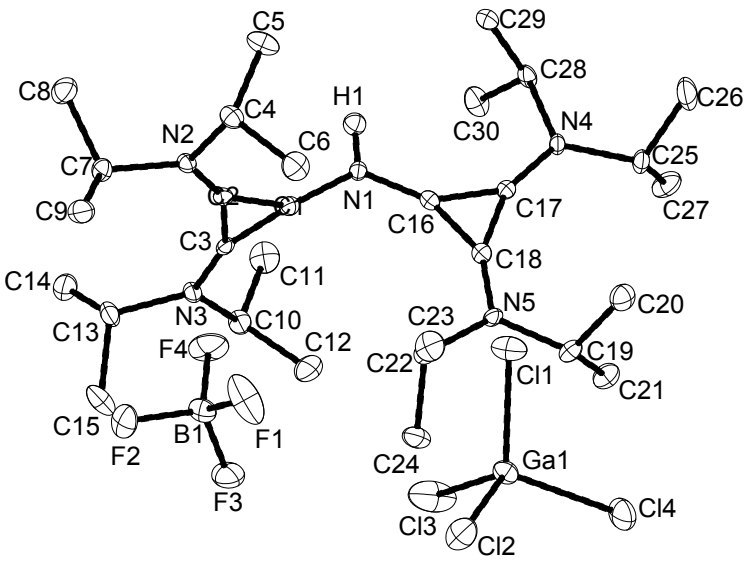
Compound **2**





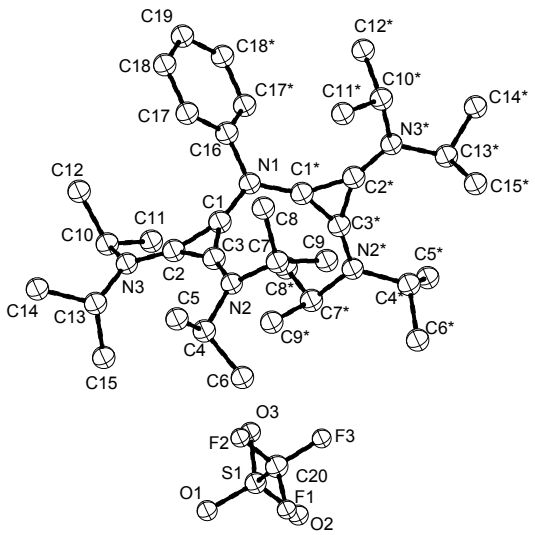
Empirical formula	$C_{30}H_{56}N_5^+ \cdot BF_4^-$	
Color	colourless	
Formula weight	573.61 $g \cdot mol^{-1}$	
Temperature	100 K	
Wavelength	0.71073 Å	
Crystal system	MONOCLINIC	
Space group	C2/c, (no. 15)	
Unit cell dimensions	a = 16.8763(17) Å	α = 90°.
	b = 19.577(2) Å	β = 120.553(2)°.
	c = 11.6565(12) Å	γ = 90°.
Volume	3316.5(6) $Å^3$	
Z	4	
Density (calculated)	1.149 $Mg \cdot m^{-3}$	
Absorption coefficient	0.083 mm^{-1}	
F(000)	1248 e	
Crystal size	0.330 x 0.261 x 0.082 mm^3	
θ range for data collection	1.75 to 37.17°.	
Index ranges	$-28 \le h \le 28$, $-32 \le k \le 33$, $-19 \le l \le 19$	
Reflections collected	63706	
Independent reflections	8173 [R_{int} = 0.0285]	
Reflections with I>2σ(I)	6656	
Completeness to θ = 27.50°	100.0 %	
Absorption correction	Gaussian	
Max. and min. transmission	0.99 and 0.98	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	8173 / 0 / 201	
Goodness-of-fit on F^2	1.044	
Final R indices [I>2σ(I)]	R_1 = 0.0625	wR^2 = 0.1709
R indices (all data)	R_1 = 0.0764	wR^2 = 0.1835
Largest diff. peak and hole	1.110 and -1.004 e $\cdot Å^{-3}$	

Compound **4**



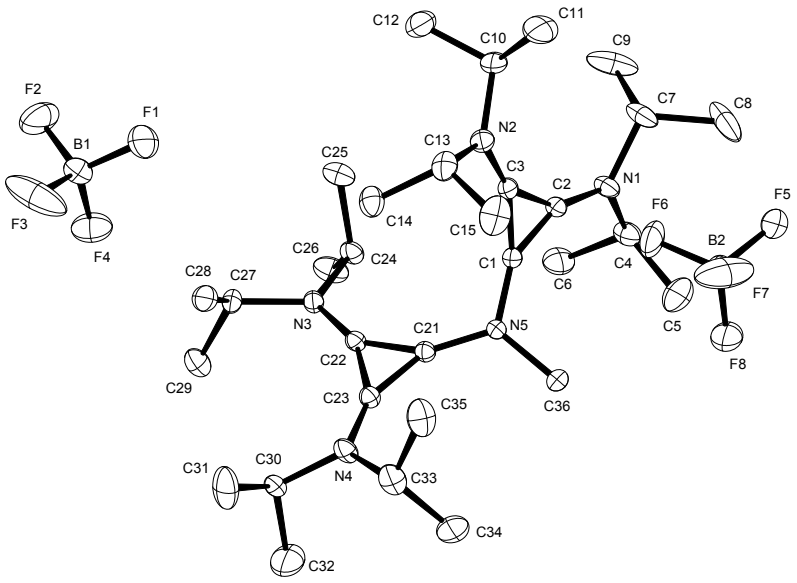
Empirical formula	$C_{30}H_{57}BCl_4F_4GaN_5$	
Color	colourless	
Formula weight	786.14 g·mol^{-1}	
Temperature	100 K	
Wavelength	0.71073 Å	
Crystal system	MONOCLINIC	
Space group	p 2_1/n, (no. 14)	
Unit cell dimensions	a = 13.8508(9) Å	α = 90°.
	b = 15.2339(12) Å	β= 109.855(5)°.
	c = 20.1399(10) Å	γ = 90°.
Volume	3996.9(5) Å^3	
Z	4	
Density (calculated)	1.306 Mg·m^{-3}	
Absorption coefficient	1.001 mm^{-1}	
F(000)	1648 e	
Crystal size	0.16 x 0.06 x 0.02 mm^3	
θ range for data collection	3.07 to 29.00°.	
Index ranges	$-18 \leq h \leq 18$, $-20 \leq k \leq 20$, $-27 \leq l \leq 27$	
Reflections collected	57956	
Independent reflections	10595 [R_{int} = 0.0921]	
Reflections with I>2σ (I)	7048	
Completeness to θ = 27.50°	99.8 %	
Absorption correction	Gaussian	
Max. and min. transmission	0.98258 and 0.89743	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	10595 / 0 / 422	
Goodness-of-fit on F^2	1.106	
Final R indices [I>2σ (I)]	R_1 = 0.0559	wR^2 = 0.0937
R indices (all data)	R_1 = 0.1068	wR^2 = 0.1086
Largest diff. peak and hole	0.450 and -0.504 e·Å^{-3}	

Compound **5(TfO)**



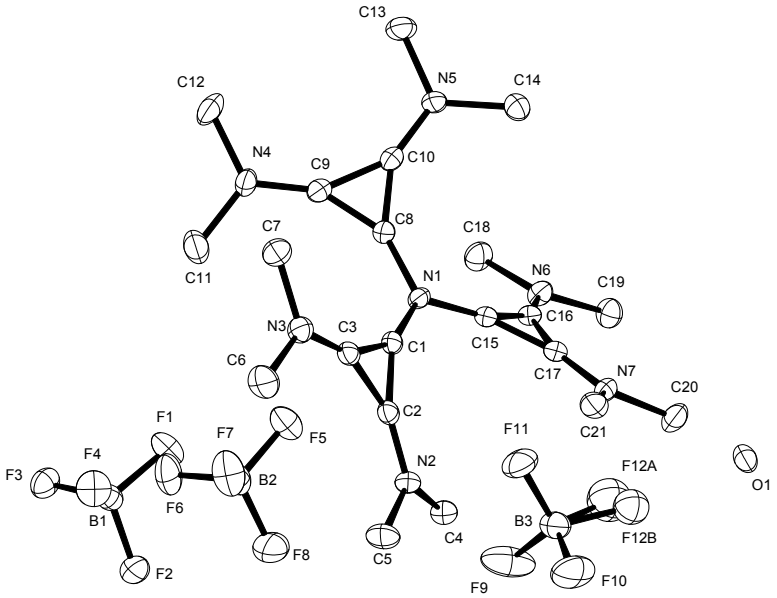
Empirical formula	$C_{38}H_{61}F_6N_5O_6S_2$	
Color	colourless	
Formula weight	862.04 g · mol^{-1}	
Temperature	100 K	
Wavelength	0.71073 Å	
Crystal system	TETRAGONAL	
Space group	p 43 21 2, (no. 96)	
Unit cell dimensions	a = 10.7973 (6) Å	α = 90°.
	b = 10.7973 (6) Å	β = 90°.
	c = 39.0810(13) Å	γ = 90°.
Volume	4556.1(4) Å^3	
Z	4	
Density (calculated)	1.257 Mg · m^{-3}	
Absorption coefficient	0.188 mm^{-1}	
F(000)	1832 e	
Crystal size	0.18 x 0.17 x 0.16 mm^3	
θ range for data collection	2.86 to 31.82°.	
Index ranges	$-16 \leq h \leq 16$, $-16 \leq k \leq 15$, $-57 \leq 1 \leq 57$	
Reflections collected	66441	
Independent reflections	7772 [R_{int} = 0.0414]	
Reflections with I>2σ(I)	6764	
Completeness to θ = 27.50°	99.8 %	
Absorption correction	Gaussian	
Max. and min. transmission	0.97598 and 0.96843	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7772 / 0 / 267	
Goodness-of-fit on F^2	1.116	
Final R indices [I>2σ(I)]	R_1 = 0.0434	w R^2 = 0.0967
R indices (all data)	R_1 = 0.0556	w R^2 = 0.1039
Absolute structure parameter	-0.04(7)	
Largest diff. peak and hole	0.390 and -0.568 e · Å^{-3}	

Compound **11**



Empirical formula	$C_{31}H_{59}B_2F_8N_5$	
Color	colourless	
Formula weight	675.45 g · mol^{-1}	
Temperature	100 K	
Wavelength	0.71073 Å	
Crystal system	ORTHORHOMBIC	
Space group	Pbca, (no. 61)	
Unit cell dimensions	a = 17.1328(15) Å	α = 90°.
	b = 13.996(2) Å	β= 90°.
	c = 31.391(7) Å	γ = 90°.
Volume	7527(2) Å^3	
Z	8	
Density (calculated)	1.192 Mg · m^{-3}	
Absorption coefficient	0.097 mm^{-1}	
F(000)	2896 e	
Crystal size	0.40 x 0.38 x 0.33 mm^3	
θ range for data collection	2.71 to 32.03°.	
Index ranges	$-25 \leq h \leq 25$, $-20 \leq k \leq 20$, $-46 \leq 1 \leq 46$	
Reflections collected	92524	
Independent reflections	13048 [R_{int} = 0.0464]	
Reflections with I>2σ(I)	9310	
Completeness to θ = 32.03°	99.6 %	
Absorption correction	Gaussian	
Max. and min. transmission	0.97 and 0.96	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	13048 / 0 / 432	
Goodness-of-fit on F^2	1.080	
Final R indices [I>2σ (I)]	R_1 = 0.0668	wR^2 = 0.1583
R indices (all data)	R_1 = 0.0995	wR^2 = 0.1838
Largest diff. peak and hole	0.984 and -0.994 e · Å^{-3}	

Compound **15**



Empirical formula	$C_{21}H_{36}B_3F_{12}N_7O_{0.25}$	
Color	colourless	
Formula weight	651.00 g · mol^{-1}	
Temperature	100 K	
Wavelength	0.71073 Å	
Crystal system	MONOCLINIC	
Space group	P 21/n, (no. 14)	
Unit cell dimensions	a = 12.149(2) Å	α = 90°.
	b = 12.495(2) Å	β= 92.304(3)°.
	c = 19.670(4) Å	γ = 90°.
Volume	2983.7(10) Å^3	
Z	4	
Density (calculated)	1.449 Mg · m^{-3}	
Absorption coefficient	0.140 mm^{-1}	
F(000)	1344 e	
Crystal size	0.08 x 0.07 x 0.05 mm^3	
θ range for data collection	1.93 to 23.51°.	
Index ranges	$-13 \le h \le 13$, $-13 \le k \le 13$, $-22 \le 1 \le 22$	
Reflections collected	45846	
Independent reflections	4405 [R_{int} = 0.0516]	
Reflections with I>2σ(I)	3619	
Completeness to θ = 23.51°	99.7 %	
Absorption correction	Gaussian	
Max. and min. transmission	0.75 and 0.67	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4405 / 0 / 408	
Goodness-of-fit on F^2	1.094	
Final R indices [I>2σ(I)]	R_1 = 0.0441	wR^2 = 0.1041
R indices (all data)	R_1 = 0.0571	wR^2 = 0.1122
Largest diff. peak and hole	0.492 and -0.554 e · Å^{-3}	