Supporting Information

Two C_2-Symmetric Chelating P_2-Bisphosphazene Superbases Connected *via* a Binaphthyl Backbone – Synthesis, Structural Features and Preparation of a Cationic Alkyl Aluminum Complex

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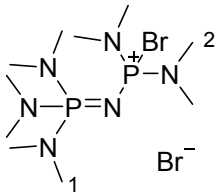
General Information

Reactions were carried out under inert atmosphere using standard Schlenk techniques. Moisture and air sensitive substances were stored in a conventional nitrogen-flushed glovebox. Solvents were purified according to literature procedures and kept under an inert atmosphere. $(Me_2N)_3P{=}N\text{-}P(NMe_2)_2$ was prepared over three steps according to literature-known procedures starting from commercially available $P(NMe_2)_3$.[1] $((CH_2)_4N)_3P{=}N\text{-}P(N(CH_2)_4)_2$ was prepared *via* a four-step procedure starting from PCl_3.[2]

Spectra were recorded on the following spectrometers: NMR: BRUKER DPX 250, BRUKER ARX300, BRUKER DRX400, BRUKER DRX500; IR: ATR-FT-IR; MS: LTQ-FT or QStarPulsar i (Finnigan); elemental analysis: CHN-Rapid (Heraeus).

Synthetic Procedures

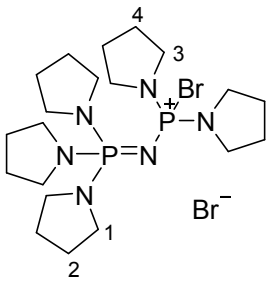
Preparation of [Tris(dimethylamino)phosphazenyl]bis(dimethylamino)bromophosphonium bromide (1)



Bromine (4.68 g, 29.3 mmol, 1.05 eq.) was added dropwise to a solution of [tris-(dimethylamino)phosphazenyl]bis(dimethylamino)phosphane (8.26 g, 27.9 mmol, 1.00 eq.) in benzene (35 mL) at 0 °C. The formation of an oily phase was observed and the reaction mixture was stirred for 30 min at 0 °C and for 2 h at room temperature. Supernatant benzene was decanted from the oily phase *via* a syringe and the remaining oil turned into a white solid after drying *in vacuo*. It was washed twice with hexane (25 mL). After drying *in vacuo* [tris(dimethylamino)phosphazenyl]bis(dimethylamino)bromophosphonium bromide (12.00 g, 26.3 mmol, 94%) was obtained as a white solid. Single crystals suitable for x-ray analysis were obtained from layering a concentrated solution of **1** in chlorobenzene with pentane at -30 °C.

^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ=2.81 (d, $^3J_{P\text{-}H}$ = 14.8 Hz, 12H, H(2)), 2.74 ppm (d, 18H, $^3J_{P\text{-}H}$ = 10.5 Hz, H(1)); ^{13}C NMR (76 MHz, $CDCl_3$, 25 °C, TMS): δ=37.8 (d, ^2J(P,C) = 3.6 Hz, C(2)), 37.2 ppm (d, ^2J(P,C) = 4.9 Hz, C(1)); ^{31}P NMR (101 MHz, [D$_3$]MeCN, 25 °C, 85% H_3PO_4): δ=23.5 (d, ^2J(P,P) = 54.8 Hz), -7.0 ppm (d, ^2J(P,P) = 54.8 Hz); ESI-MS (MeCN): *m*/*z* (%): 375 (100) [M^+]; HRMS (ESI): *m*/*z* calcd for $C_{10}H_{30}Br_1N_6P_2^+$: 375.1185 [M^+]; found: 375.1186; elemental analysis calcd (%) for $C_{10}H_{30}Br_2N_6P_2$: C 26.33, H 6.63, N 18.42; found: C 26.27, H 6.76, N 18.72.

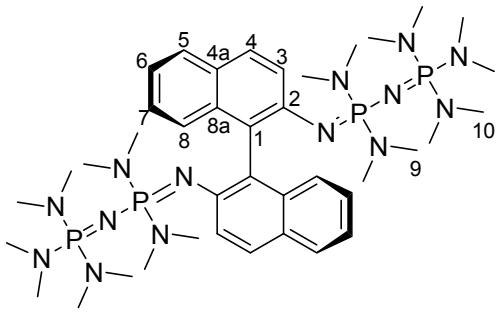
Preparation of [Tris(pyrrolidinyl)phosphazenyl]bis(pyrrolidinyl)bromophosphonium bromide (2)



Bromine (0.437 g, 2.738 mmol, 1.0 eq.) was added dropwise to a solution of [tris-(pyrrolidinyl)phosphazenyl]bis(pyrrolidinyl)phosphane (1.169 g, 2.738 mmol, 1.0 eq.) in benzene (25 mL) at 0 °C. A white solid precipitated and the suspension was stirred for 30 min at 0 °C and for 1 h at room temperature. All volatiles were removed *in vacuo* and the oily residue was triturated three times with diethyl ether (40 mL). After drying *in vacuo* [tris(pyrrolidinyl)phosphazenyl]bis(pyrrolidinyl)bromophosphonium bromide (1.338 g, 2.290 mmol, 84%) was obtained as a white solid.

^{1}H NMR (300 MHz, [D$_3$]MeCN, 25 °C, TMS): δ=3.24-3.14 (m, 20H, NCH_2), 1.93-1.84 ppm (m, 20H, NCH$_2$CH_2); ^{13}C NMR (76 MHz, [D$_3$]MeCN, 25 °C, TMS): δ=49.4 (d, ^{2}J(P,C) = 4.5 Hz, NCH$_2$), 47.7 (d, ^{2}J(P,C) = 5.1 Hz, NCH$_2$), 27.0-26.7 ppm (m, NCH$_2$$CH_2$); ^{31}P NMR (161 MHz, [D$_3$]MeCN, 25 °C, 85% H$_3$PO$_4$): δ=9.9 (d, ^{2}J(P,P) = 50.3 Hz), -5.8 ppm (d, ^{2}J(P,P) = 50.3 Hz); ESI-MS (MeCN): *m*/*z* (%): 505 (100) [M^+]; HRMS (ESI): *m*/*z* calcd for $C_{20}H_{40}Br_1N_6P_2^+$: 505.1968 [M^+]; found: 505.1961; elemental analysis calcd (%) for $C_{20}H_{40}Br_2N_6P_2$: C 40.97, H 6.88, N 14.33; found: C 40.93, H 6.91, N 14.66.

Preparation of 3

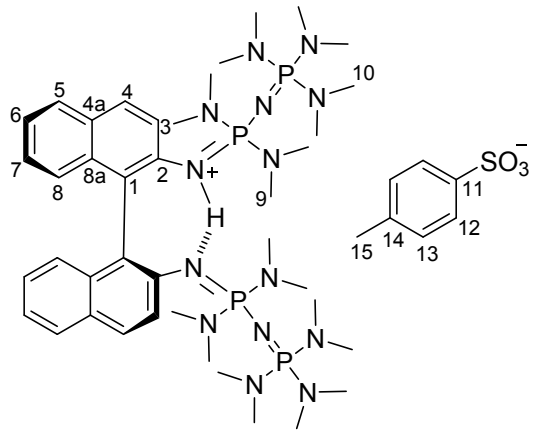


A solution of (*S*)-(–)-1,1'-binaphthyl-2,2'-diamine (200 mg, 0.703 mmol, 1.0 eq.) and triethylamine (285 mg, 2.812 mmol, 4.0 eq.) in toluene (20 mL) was added dropwise to a solution of [tris-(dimethylamino)phosphazenyl]bis(dimethylamino)-phosphane (642 mg, 1.407 mmol, 2.0 eq.) in toluene (30 mL) at 0 °C. The formation of a brown oily phase was observed and the reaction mixture was stirred for 1 h at 0 °C and for 2 h at 90 °C. A solution of KHMDS (561 mg, 2.812 mmol, 4.0 eq.) in toluene (20 mL) was added dropwise at 0 °C. The reaction mixture changed color to yellow and was stirred for 30 min at 0 °C and for 16 h at 90 °C. The suspension was filtered over celite and the filter cake was repeatedly extracted with boiling hexane. The filtrates were combined and evaporated to dryness *in vacuo*. The oily residue was extracted with acetonitrile (40 mL) and the acetonitrile phase was evaporated to dryness. **3** (173 mg, 0.198 mmol, 28%) was obtained as a highly viscous yellow oil that was stored at -30 °C and

is a yellow solid at this temperature. Single crystals suitable for x-ray analysis developed directly from the highly viscous oil.

^{1}H NMR (400 MHz, [D$_8$]THF, 25 °C, TMS): δ=7.44-7.41 (m, 2H, H(8)), 7.33 (d, ^{3}J(H,H) = 8.7 Hz, 2H, H(4)), 7.24 (d, ^{3}J(H,H) = 8.8 Hz, 2H, H(3)), 7.09-7.06 (m, 2H, H(5)), 6.76 (t, ^{3}J(H,H) = 6.4 Hz, 2H, H$_{Ar}$), 6.75 (t, ^{3}J(H,H) = 6.4 Hz, 2H, H$_{Ar}$), 2.53 (d, ^{3}J(P,H) = 9.7 Hz, 12H, N*CH$_3$*), 2.48 (d, ^{3}J(P,H) = 10.2 Hz, 36H, N*CH$_3$*), 2.21 ppm (d, ^{3}J(P,H) = 10.4 Hz, 12H, N*CH$_3$*); ^{13}C NMR (101 MHz, [D$_8$]THF, 25 °C, TMS): δ=149.9 (d, ^{2}J(P,C) = 3.3 Hz, C(2)), 136.8 (d, ^{3}J(P,C) = 3.4 Hz, C(1)), 127.5 (C$_{Ar}$), 127.5 (C$_{Ar}$), 127.3 (C(8)), 126.2 (C(5)), 126.4 (d, ^{3}J(P,C) = 10.8 Hz, C(3)), 125.2 (C(4)), 123.4 (C(7)), 118.6 (C(6)), 38.2 (d, ^{2}J(P,C) = 3.1 Hz, C(9)), 38.0 (d, ^{2}J(P,C) = 2.3 Hz, C(9)), 37.3 ppm (d, ^{2}J(P,C) = 4.3 Hz, C(10)); ^{31}P NMR (101 MHz, [D$_6$]benzene, 25 °C, 85% H$_3$PO$_4$): δ=13.4 (d, ^{2}J(P,P) = 49.9 Hz), 4.8 ppm (d, ^{2}J(P,P) = 49.4 Hz); ESI-MS (MeCN): *m*/*z* (%): 873 (80) [*M*$^+$], 579 (18) [C$_{30}$H$_{45}$N$_8$P$_2^+$], 437 (100) [*M*$^+$-C$_{20}$H$_{36}$N$_7$P$_2$], 415 (43) [*M*$^+$-C$_6$H$_{18}$N$_3$P-C$_{10}$H$_{30}$N$_6$P$_2$]; HRMS (ESI): *m*/*z* calcd for C$_{40}$H$_{73}$N$_{14}$P$_4^+$: 873.5088 [*M*$^+$]; found: 873.5068; elemental analysis calcd (%) for C$_{40}$H$_{72}$N$_{14}$P$_4$: C 55.03, H 8.31, N 22.46; found: C 54.17, H 8.54, N 22.22.

Preparation of 3·C$_7$H$_7$SO$_3$H

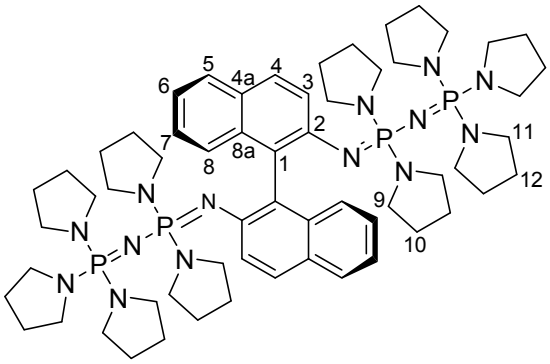


A solution of *para*-toluenesulfonic acid (20 mg, 0.115 mmol, 1.0 eq.) in THF (6 mL) was added dropwise to a solution of **3** (100 mg, 0.115 mmol, 1.0 eq.) in THF (6 mL). The reaction mixture was stirred for 1 h at room temperature and evaporated to dryness *in vacuo*. The highly viscous yellow residue was washed twice with pentane (15 mL). After drying *in vacuo* **3**·C$_7$H$_7$SO$_3$H (90 mg, 0.086 mmol, 75%) was obtained as a yellow solid.

^{1}H NMR (300 MHz, [D$_3$]MeCN, 25 °C, TMS): δ=8.68 (br s, 1H, NH), 7.76 (d, ^{3}J(H,H) = 7.7 Hz, 2H, H$_{Ar}$), 7.75 (d, ^{3}J(H,H) = 8.7 Hz, 2H, H(4)), 7.60 (d, ^{3}J(H,H) = 8.1 Hz, 2H, H(12)), 7.44 (d, ^{3}J(H,H) = 8.8 Hz, 2H, H(3)), 7.16-7.12 (m, 4H, H(13, H$_{Ar}$)), 7.02 (dt, ^{3}J(H,H) = 7.6 Hz, ^{4}J(H,H) = 1.1 Hz, 2H, H$_{Ar}$), 6.86 (d, ^{3}J(H,H) = 8.5 Hz, 2H, H$_{Ar}$), 2.75 (d, ^{3}J(P,H) = 10.0 Hz, 12H, H(9)), 2.39 (d, ^{3}J(P,H) = 10.3 Hz, 36H, H(10)), 2.32 (s, 3H, H(15)), 2.21 ppm (d, $^{3}J_{P-H}$ = 11.1 Hz, 12H, H(9)); ^{13}C NMR (101 MHz, [D$_3$]MeCN, 25 °C, TMS): δ=147.3

(C_{Ar}), 144.2 (C_{Ar}), 139.1 (C(14)), 135.2 (d, J(P,C) = 1.2 Hz, C_{Ar}), 129.5 (C_{Ar}), 129.1 (C(13)), 128.6 (CH_{Ar}), 128.2 (CH_{Ar}), 127.5 (CH_{Ar}), 126.6 (C(12)), 126.0 (C(11)), 125.7 (CH_{Ar}), 125.4 (d, ^3J(P,C) = 6.6 Hz, C(3)), 122.9 (CH_{Ar}), 37.3 (d, ^2J(P,C) = 4.7 Hz, C(9)), 37.2 (d, ^2J(P,C) = 4.6 Hz, C(10)), 37.1 (d, ^2J(P,C) = 3.4 Hz, C(9)), 21.2 ppm (C(15)); ^{31}P NMR (101 MHz, [D_3]MeCN, 25 °C, 85% H_3PO_4): δ=18.7 (d, ^2J(P,P) = 60.8 Hz), 8.4 ppm (d, ^2J(P,P) = 60.8 Hz); ESI-MS (MeCN): *m*/*z* (%): 873 (8) [M^+], 579 (20) [$C_{30}H_{45}N_8P_2^+$], 437 (100) [M^+-$C_{20}H_{36}N_7P_2$], 415 (38) [M^+-$C_6H_{18}N_3P$-$C_{10}H_{30}N_6P_2$]; HRMS (ESI): *m*/*z* calcd for $C_{40}H_{73}N_{14}P_4^+$: 873.5088 [M^+]; found 873.5095; (–)-ESI-MS (MeCN): *m*/*z* (%): 171 (100) [M^-]; (–)-HRMS (ESI): *m*/*z* calcd for $C_7H_7O_3S^+$: 171.0121 [M^-]; found: 171.0122; elemental analysis calcd (%) for $C_{47}H_{80}N_{14}O_3P_4S$: C 54.01, H 7.71, N 18.76, S 3.07; found: C 53.48, H 7.96, N 19.44, S 2.58.

Preparation of 4

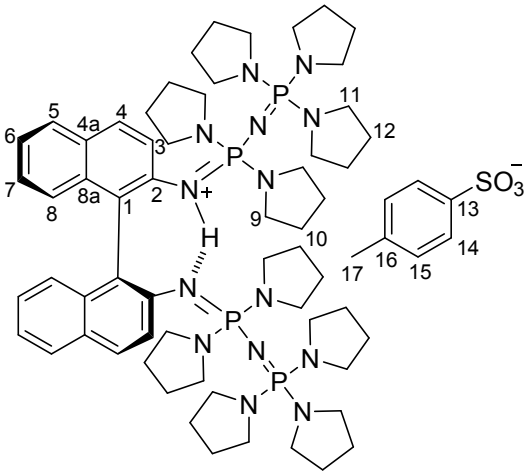


A solution of (*S*)-(–)-1,1'-binaphthyl-2,2'-diamine (100 mg, 0.352 mmol, 1.0 eq.) and triethylamine (142 mg, 1.408 mmol, 4.0 eq.) in toluene (15 mL) was added dropwise to a suspension of [tris(pyrrolidinyl)phosphazenyl]-bis(pyrrolidinyl)bromophosphonium bromide (413 mg, 0.704 mmol, 2.0 eq.) in toluene (15 mL). A white solid precipitated that subsequently turned into an yellow oily phase. The reaction mixture was stirred for 16 h at room temperature and for 24 h at 90 °C. A solution of NaHMDS (258 mg, 1.408 mmol, 4.0 eq.) in toluene (20 mL) was added dropwise at room temperature. The reaction mixture was stirred for another 5 h and filtered over celite. The filter cake was extracted with toluene (20 mL) and the filtrate was evaporated to dryness *in vavuo*. The yellow residue was repeatedly extracted with hexane and the combined hexane phases were concentrated to about 40 mL. The hexane solution was extracted twice with acetonitrile (15 mL) and evaporated to dryness *in vacuo*. **4** (219 mg, 0.193 mmol, 55%) was obtained as a yellow solid.

^{1}H NMR (500 MHz, [D_8]THF, 25 °C, TMS): δ=7.42-7.39 (m, 2H, H(8)), 7.29 (d, ^3J(H,H) = 8.7 Hz, 2H, H(4)), 7.26 (d, ^3J(H,H) = 8.7 Hz, 2H, H(3)), 7.03-7.00 (m, 2H, H(5)), 6.71 (t, ^3J(H,H) = 6.3 Hz, 2H, H_{Ar}), 6.70 (t, ^3J(H,H) = 6.5 Hz, 2H, H_{Ar}), 3.14-3.07 (m, 20H, NCH_2), 3.05-2.99 (m, 12H, NCH_2), 2.82-2.77 (m, 4H, NCH_2), 2.62-2.57 (m, 4H, NCH_2), 1.67-1.62

(m, 32H, NCH_2CH_2), 1.31-1.28 ppm (m, 8H, NCH_2CH_2); ^{13}C NMR (126 MHz, [D_8]THF, 25 °C, TMS): δ=150.5 (d, ^2J(P,C) = 2.5 Hz, C(2)), 137.0 (d, ^3J(P,C) = 3.2 Hz, C(1)), 127.4 (C_{Ar}), 127.2 (C_{Ar}), 127.2 (C_{Ar}), 127.0 (C_{Ar}), 127.0 (d, ^3J(P,C) = 11.5 Hz, C(3)), 124.8 (C(4)), 123.2 (C(7)), 118.1 (C(6)), 48.0 (d, ^2J(P,C) = 3.8 Hz, NCH_2), 47.5 (d, ^2J(P,C) = 2.9 Hz, NCH_2), 47.2 (d, ^2J(P,C) = 4.7 Hz, NCH_2), 27.4 (d, ^3J(P,C) = 8.0 Hz, NCH_2CH_2), 26.9 ppm (d, ^3J(P,C) = 8.3 Hz, NCH_2CH_2); ^{31}P NMR (122 MHz, [D_6]benzene, 25 °C, 85% H_3PO_4): δ=1.3 (d, ^2J(P,P) = 40.8 Hz), -8.3 ppm (d, ^2J(P,P) = 40.9 Hz); IR: $\tilde{\nu}$=3040 (w), 2960 (m), 2960 (m), 1610 (w), 1585 (m), 1545 (w), 1497 (m), 1459 (m), 1419 (w), 1359 (m), 1343 (m), 1293 (m), 1258 (s), 1197 (m), 1066 (s), 1006 (s), 911 (m), 887 (m), 868 (m), 795 (s), 739 (m), 697 (m), 568 (m), 532 (w), 482 (s), 435 cm^{-1} (w); ESI-MS (MeCN): *m*/*z* (%): 1134 (30) [M^+], 577 (100) [M^+-$C_{30}H_{46}N_7P_2$]; HRMS (ESI): *m*/*z* calcd for $C_{60}H_{93}N_{14}P_4^+$: 1133.6653 [M^+]; found: 1133.6657; elemental analysis calcd (%) for $C_{60}H_{92}N_{14}P_4$: C 63.58, H 8.18, N 17.30; found: C 63.31, H 8.04, N 17.50.

Preparation of 4·$C_7H_7SO_3H$

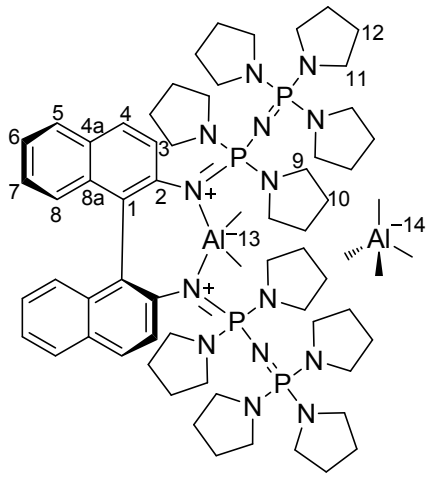


A solution of *para*-toluenesulfonic acid (15 mg, 0.088 mmol, 1.0 eq.) in THF (2.5 mL) was added dropwise to a solution of **4** (100 mg, 0.088 mmol, 1.0 eq.) in THF (10 mL). The reaction mixture was stirred for 1 h at room temperature and evaporated to dryness *in vacuo*. The yellow residue was washed twice with pentane (15 mL). After drying *in vacuo* **4**·$C_7H_7SO_3H$ (73 mg, 0.056 mmol, 64%) was obtained as a yellow solid.

^1H NMR (300 MHz, [D_8]THF, 25 °C, TMS): δ=8.34 (t, ^2J(P,H) = 7.4 Hz, 1H, NH), 7.74 (d, ^3J(H,H) = 8.0 Hz, 2H, H_{Ar}), 7.69 (d, ^3J(H,H) = 8.8 Hz, 2H, H(4)), 7.59 (d, ^3J(H,H) = 8.1 Hz, 2H, H(14)), 7.52 (d, ^3J(H,H) = 8.3 Hz, 2H, H(3)), 7.15-7.09 (m, 4H, H(15, H_{Ar})), 7.59 (dt, ^3J(H,H) = 7.6 Hz, ^4J(H,H) = 1.2 Hz, 2H, H_{Ar}), 6.80 (d, ^3J(H,H) = 8.5 Hz, 2H, H_{Ar}), 3.14-3.13 (m, 8H, NCH_2), 2.99-2.82 (m, 24H, H(11)), 2.81-2.73 (m, 4H, NCH_2), 2.69-2.61 (m, 4H, NCH_2), 2.32 (s, 3H, H(17)), 1.80-1.76 (m, 8H, NCH_2CH_2), 1.60-1.55 (m, 24H, H(12)), 1.41-1.36 ppm (m, 8H, NCH_2CH_2); ^{13}C NMR (101 MHz, [D_3]MeCN, 25 °C, TMS): δ=147.3 (C_{Ar}), 144.8 (C_{Ar}), 139.1 (C(16)), 135.4 (C_{Ar}), 129.6 (C_{Ar}), 129.1 (C(15)), 128.5 (CH_{Ar}), 127.8 (C(4)), 127.3 (CH_{Ar}), 126.6 (C(14)), 126.2 (C(13)), 126.0 (d, ^3J(P,C) = 6.6 Hz, C(3)), 125.6

(CH_{Ar}), 122.6 (CH_{Ar}), 47.8 (d, ^2J(P,C) = 5.0 Hz, N*C*H_2), 47.3 (d, ^2J(P,C) = 5.0 Hz, N*C*H_2), 47.1 (d, ^2J(P,C) = 4.0 Hz, N*C*H_2), 27.2 (d, ^3J(P,C) = 8.8 Hz, NCH$_2$*C*H$_2$), 26.8 (d, ^3J(P,C) = 8.6 Hz, NCH$_2$*C*H$_2$), 26.6 (d, ^3J(P,C) = 9.3 Hz, NCH$_2$*C*H$_2$), 21.2 ppm (C(17)); ^{31}P NMR (101 MHz, [D$_8$]THF, 25 °C, 85% H_3PO_4): δ=3.8 (d, ^2J(P,P) = 55.2 Hz), -0.6 ppm (d, ^2J(P,P) = 55.7 Hz); ESI-MS (MeCN): *m*/*z* (%): 1134 (66) [M^+], 709 (48) [$C_{40}H_{55}N_8P_2^+$], 567 (32) [M^+-$C_{30}H_{46}N_7P_2$], 427 (100) [$C_{20}H_{41}N_6P_2^+$]; HRMS (ESI): *m*/*z* calcd for $C_{60}H_{93}N_{14}P_4^+$: 1133.6653 [M^+]; found: 1133.6645; (–)-ESI-MS (MeCN): *m*/*z* (%): 171 (100) [M^-]; (–)-HRMS (ESI): *m*/*z* calcd for $C_7H_7O_3S^+$: 171.0121 [M^-]; found: 171.0123; elemental analysis calcd (%) for $C_{67}H_{100}N_{14}O_3P_4S$: C 61.64, H 7.72, N 15.02, S 2.46; found: C 61.41, H 7.45, N 15.52, S 1.97.

Preparation of [4-AlMe$_2$]$^+$[AlMe$_4$]$^-$



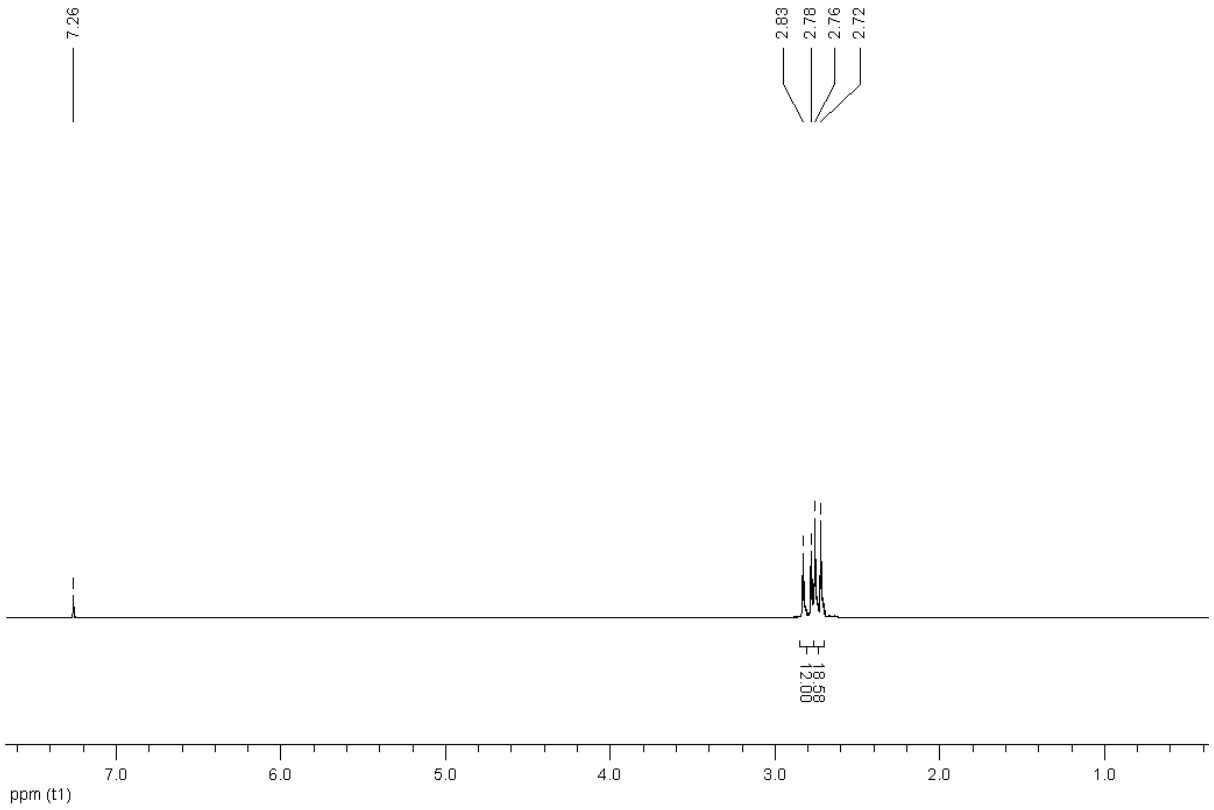
A solution of trimethylaluminum (6.4 mg, 0.088 mg, 2.0 eq.) in toluene (5 mL) was added dropwise to a solution of **4** (50.0 mg, 0.044 mmol, 1.0 eq.) in toluene (10 mL). The yellow solution of **4** decolorized and a white solid precipitated. The reaction mixture was stirred for 16 h at room temperature and was evaporated to dryness *in vacuo*. The residue was recrystallized from dichloromethane/pentane (1:2) and dried *in vacuo*. [**4**-AlMe$_2$]$^+$[AlMe$_4$]$^-$ (16 mg, 0.013 mmol, 28%) was obtained as a white solid. Single crystals suitable for x-ray analysis were obtained from layering a concentrated solution of [**4**-AlMe$_2$]$^+$[AlMe$_4$]$^-$ in dichloromethane with pentane at -30 °C.

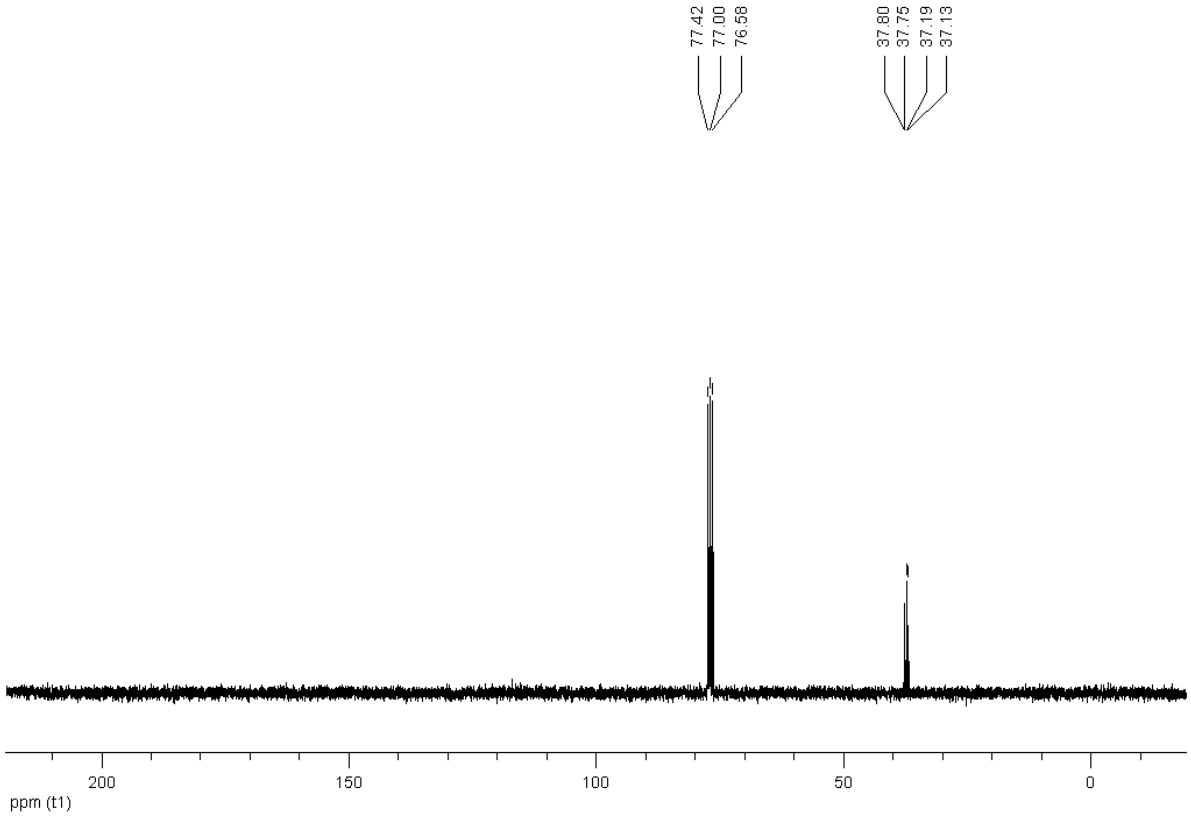
^{1}H NMR (400 MHz, [D$_2$]DCM, 25 °C, TMS): δ=7.85 (d, ^3J(H,H) = 8.1 Hz, 2H, H(5)), 7.76 (d, ^3J(H,H) = 8.6 Hz, 2H, H(4)), 7.52 (dd, ^3J(H,H) = 8.6 Hz, $^4J_{P\text{-}H}$ = 1.5 Hz, 2H, H(3)), 7.34-7.30 (m, 2H, H(6)), 7.13-7.07 (m, 4H, H(7,8)), 2.98-2.88 (m, 32H, N*CH*$_2$), 2.34-2.29 (m, 4H, N*CH*$_2$), 1.90-1.89 (m, 4H, N*CH*$_2$), 1.77-1.71 (m, 24H, H(12)), 1.66-1.63 (m, 8H, H(10)), 0.87-0.84 (m, 8H, H(10)), -0.85 (s, 6H, H(13)), -1.25 ppm (sext, 12H, ^2J(Al,H) = 6.3 Hz, H(14)); ^{13}C NMR (101 MHz, [D$_2$]DCM, 25 °C, TMS): δ=144.0 (d, ^2J(P,C) = 2.6 Hz, C(2)), 133.5 (C_{Ar}), 133.1 (d, ^3J(P,C) = 3.4 Hz, C(3)), 132.9 (d, ^3J(P,C) = 9.8 Hz, C(1)), 131.5 (C_{Ar}), 128.2 (C(5)), 127.6 (CH_{Ar}), 126.8 (C(4)), 125.2 (CH_{Ar}), 124.4 (C(6)), 47.1 (d, ^2J(P,C) = 4.2 Hz, N*C*H$_2$), 46.9 (d, ^2J(P,C) = 5.7 Hz, N*C*H$_2$), 46.7 (d, ^2J(P,C) = 5.5 Hz, NCH$_2$*C*H$_2$), 26.6 (d, ^3J(P,C) = 9.2 Hz, NCH$_2$*C*H$_2$), 26.4 (d, ^3J(P,C) = 8.4 Hz, NCH$_2$*C*H$_2$), 25.6 (d, ^3J(P,C) = 10.1 Hz, NCH$_2$*C*H$_2$), -5.40 (sext, ^1J(Al,C) = 70.6 Hz, C(14)) -6.36 ppm (C(13)); ^{31}P NMR

(101 MHz, [D_2]DCM, 25 °C, 85% H_3PO_4): δ=2.4 (d, ^2J(P,P) = 64.8 Hz), -5.4 ppm (d, ^2J(P,P) = 64.9 Hz); ESI-MS (CH_2Cl_2): *m*/*z* (%): 1190 (100) [M^+]; HRMS (ESI): *m*/*z* calcd for $C_{62}H_{98}AlN_{14}P_4^+$: 1189.6859 [$M^+$]; found: 1189.6855.

NMR Spectra

1:

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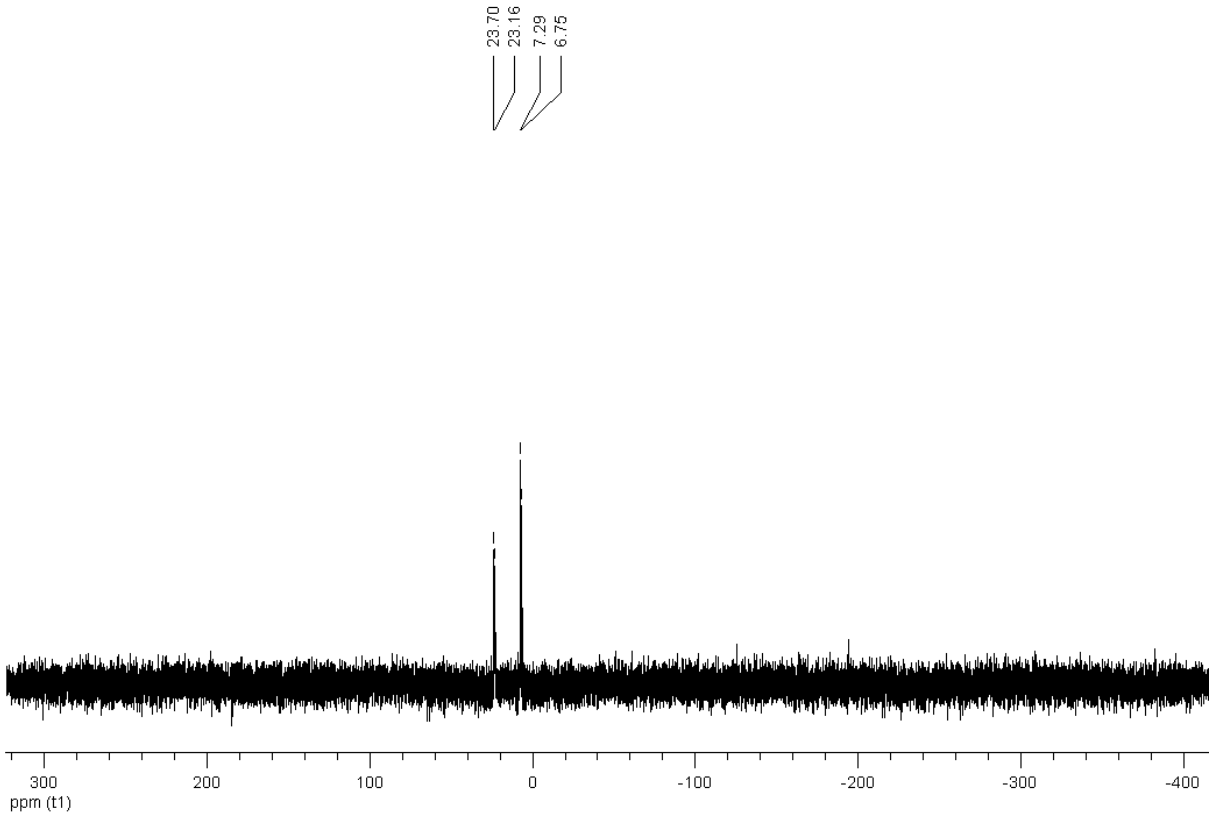
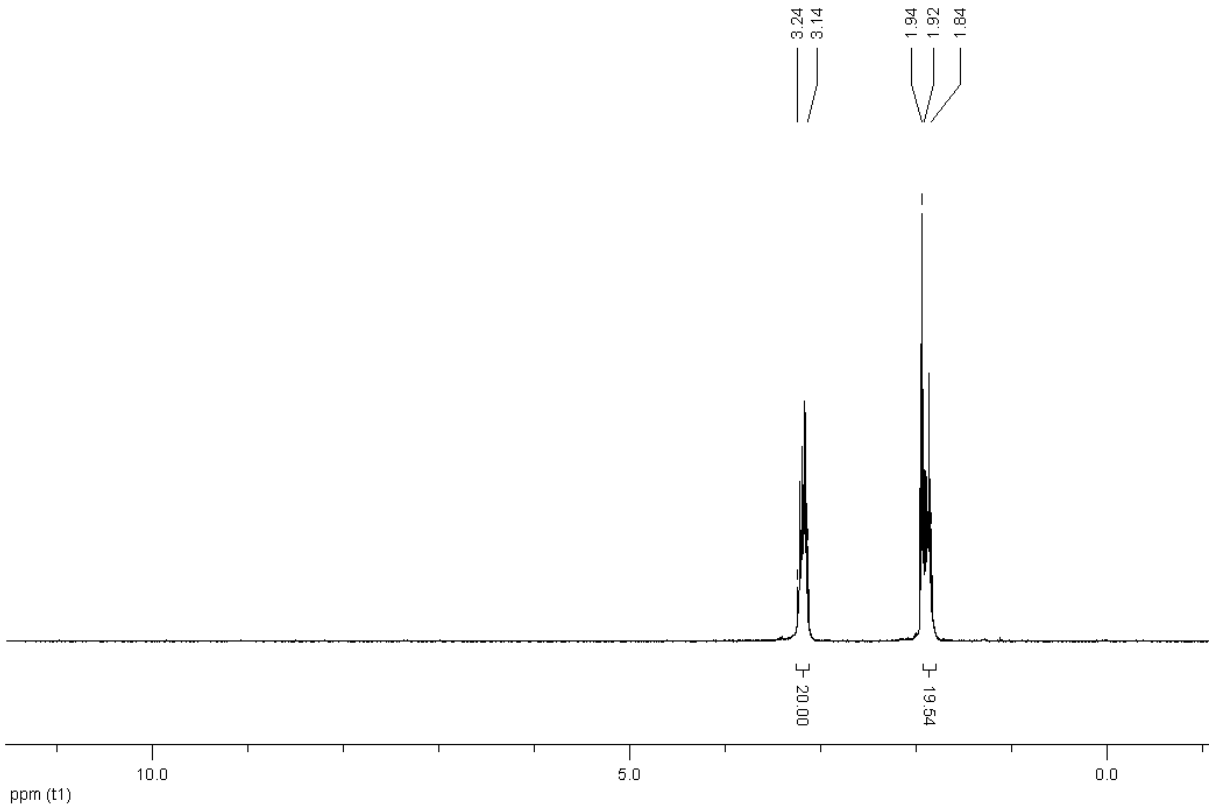
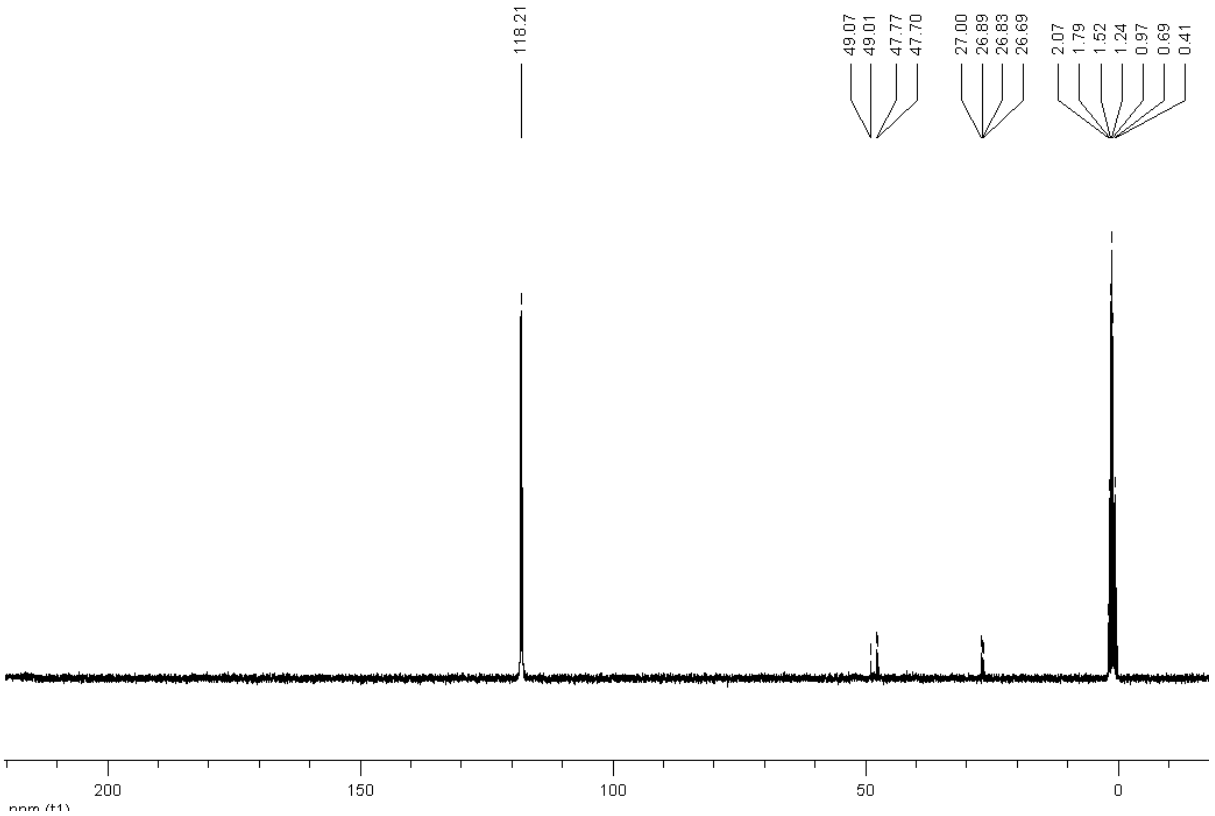
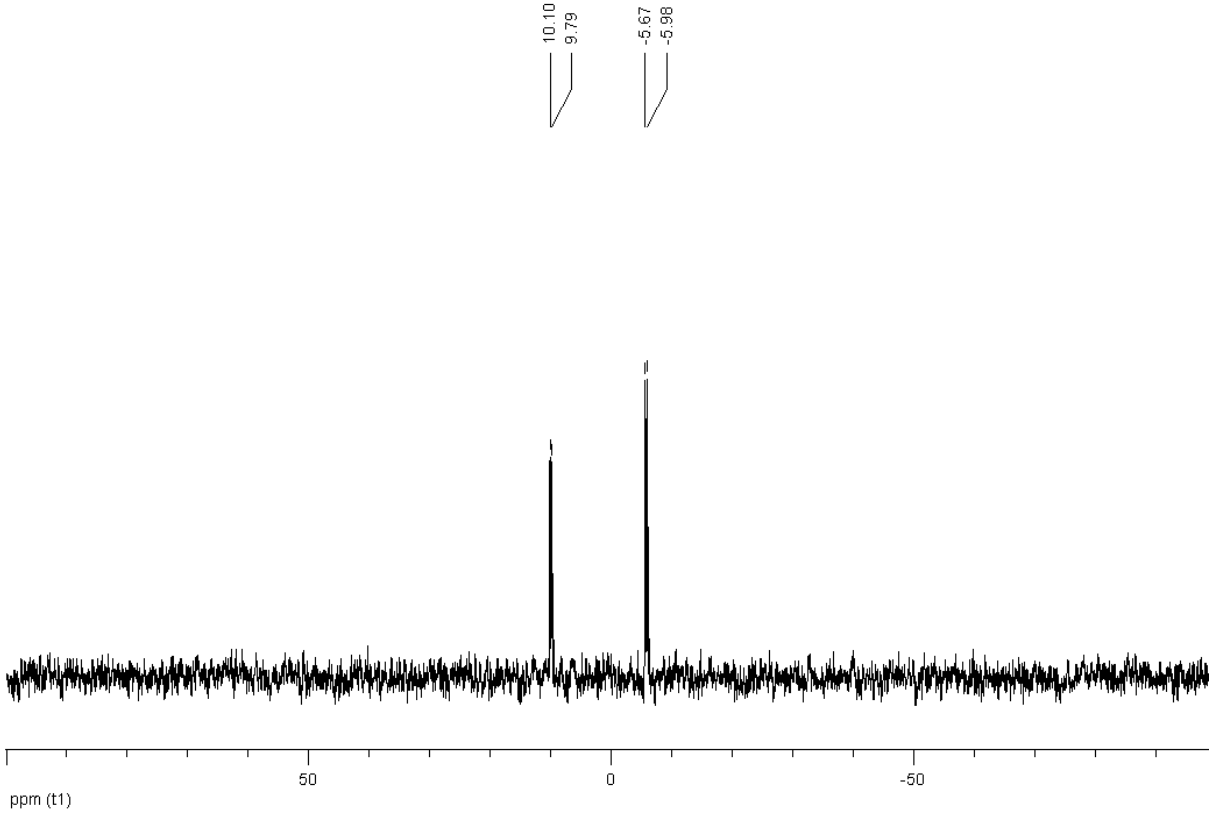
77.00
76.58
37.80
37.75
37.19
37.13
200
150
100
50
0
ppm (t1)


23.70
23.16
7.29
6.75
300
200
100
0
-100
-200
-300
-400
ppm (t1)

2:


3.24
3.14
1.94
1.92
1.84
20.00
19.54
10.0
5.0
0.0
ppm (t1)


118.21
49.07
49.01
47.77
47.70
27.00
26.89
26.83
26.69
2.07
1.79
1.52
1.24
0.97
0.69
0.41
200
150
100
50
0


10.10
9.79
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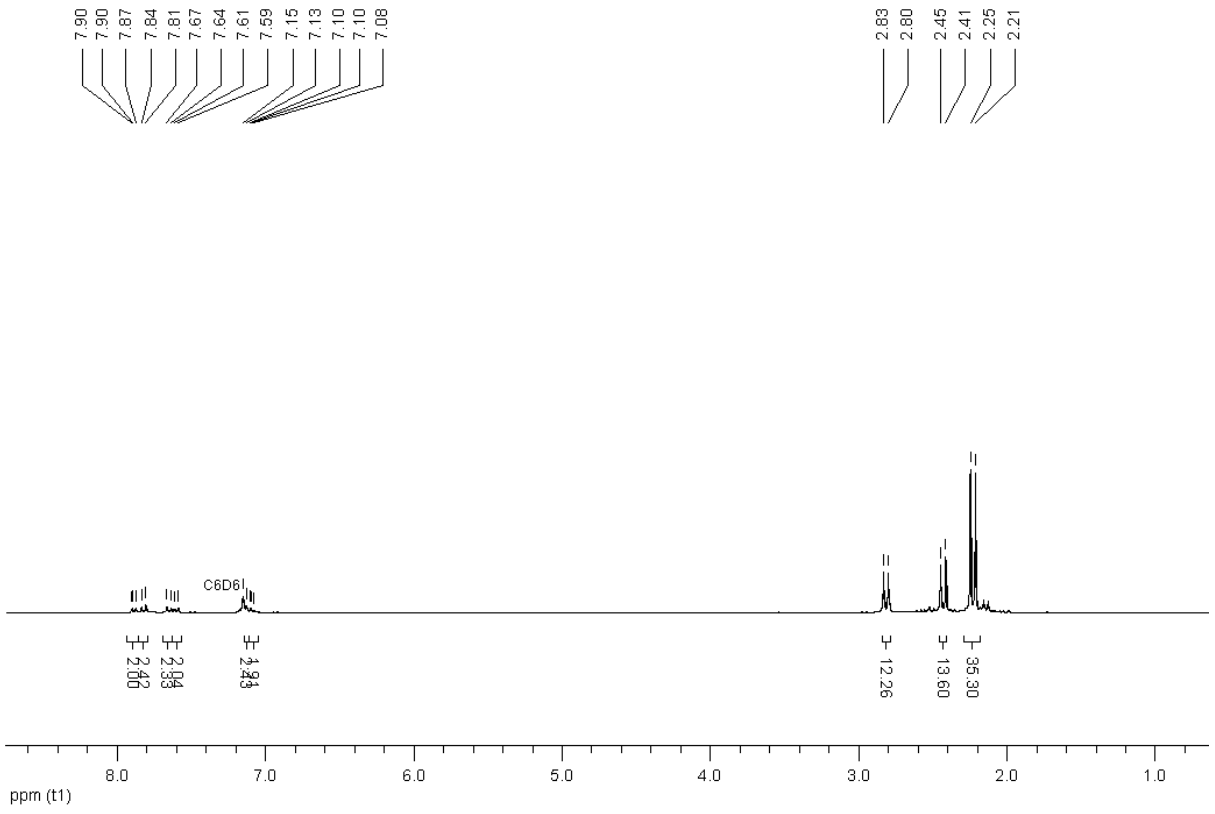
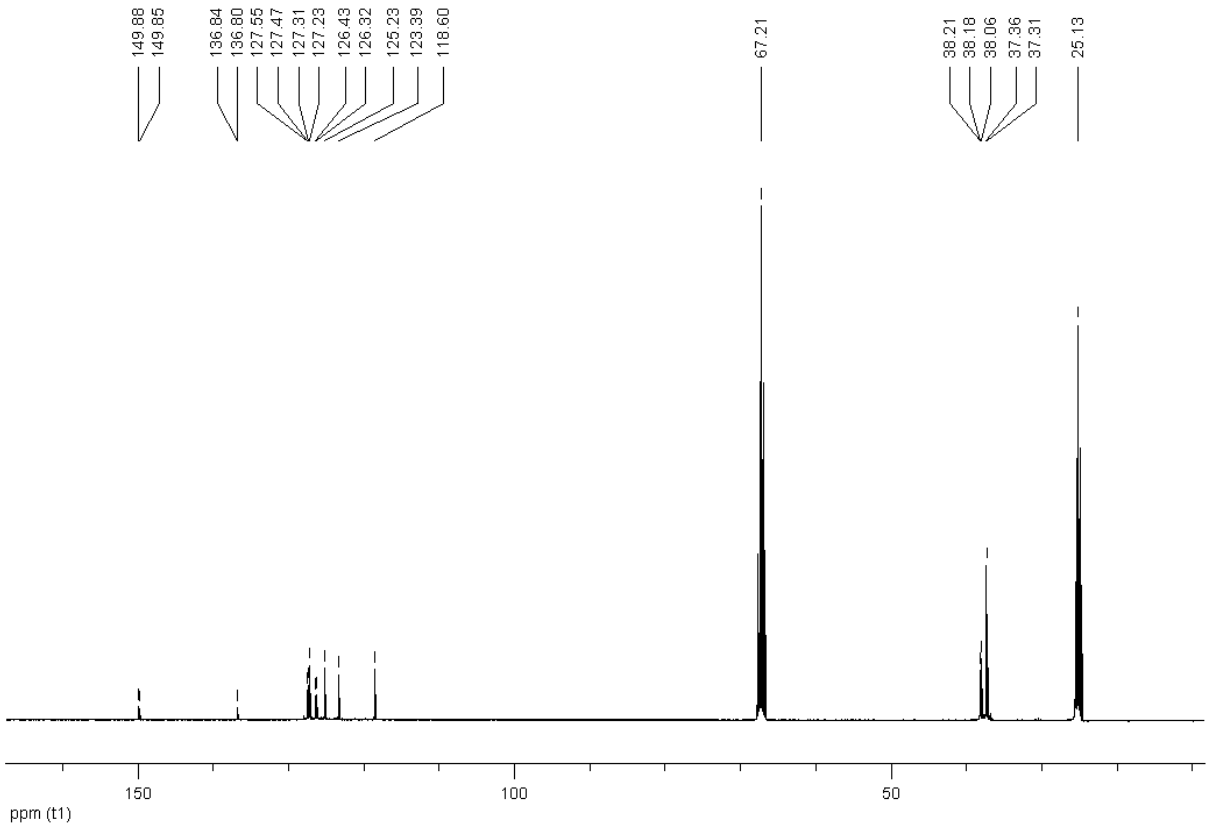
-5.98
50
0
-50
ppm (t1)

3:


7.90
7.90
7.87
7.84
7.81
7.67
7.64
7.61
7.59
7.15
7.13
7.10
7.10
7.08
2.83
2.80
2.45
2.41
2.25
2.21
C6D6
2.00
2.42
2.33
2.04
2.43
1.91
12.26
13.60
35.30
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)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149.85
136.84
136.80
127.55
127.47
127.31
127.23
126.43
126.32
125.23
123.39
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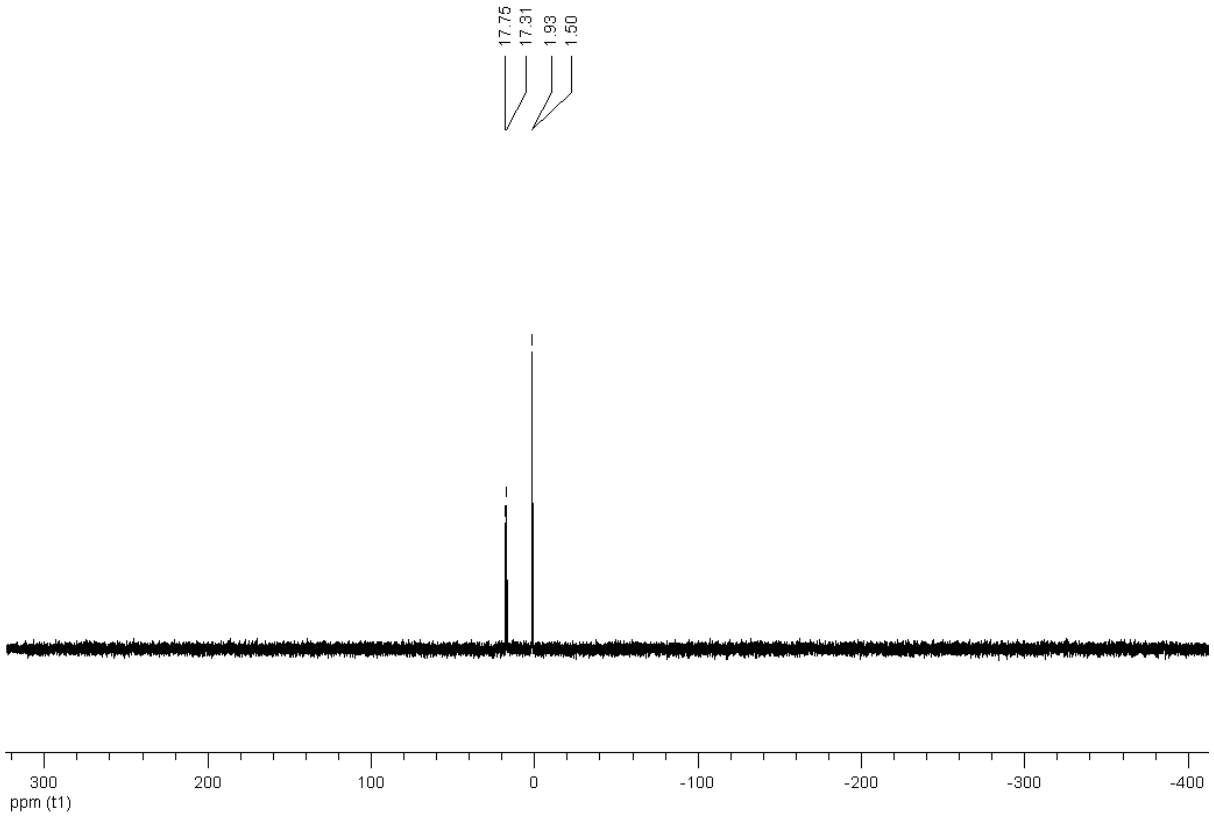
37.31
25.13
150
100
50
ppm (t1)


17.75
17.31
1.93
1.50
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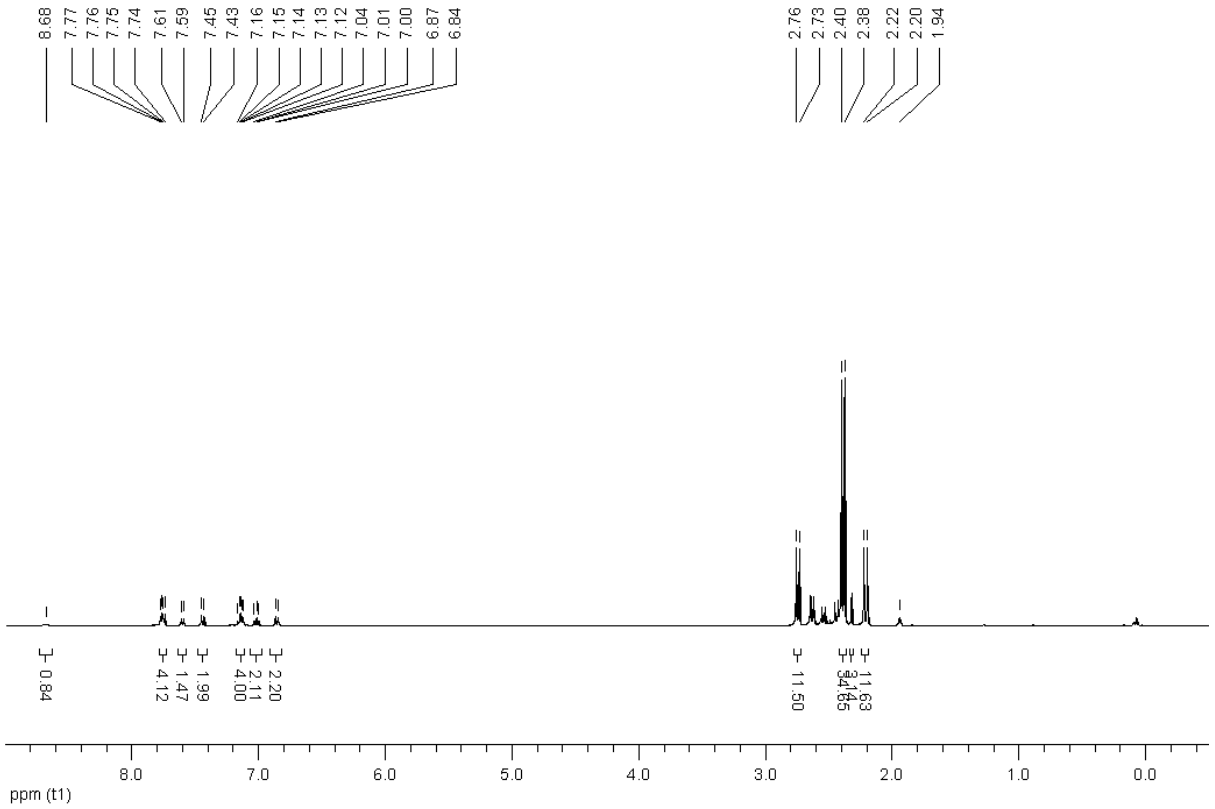
200
100
0
-100
-200
-300
-400
ppm (t1)

3·$C_7H_7SO_3H$:


8.68
7.77
7.76
7.75
7.74
7.61
7.59
7.45
7.43
7.16
7.15
7.14
7.13
7.12
7.04
7.01
7.00
6.87
6.84
2.76
2.73
2.40
2.38
2.22
2.20
1.94
0.84
4.12
1.47
1.99
4.00
2.11
2.20
1.50
3.45
3.45
1.63
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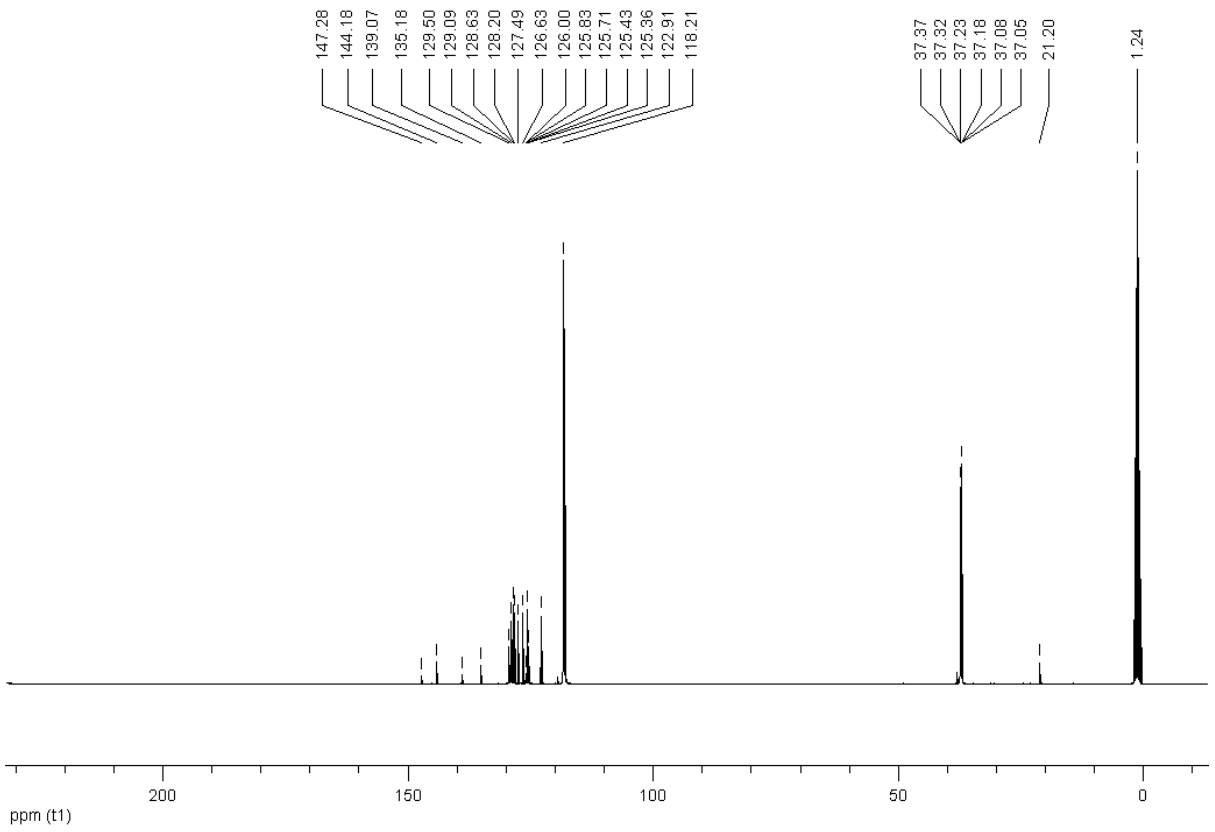
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)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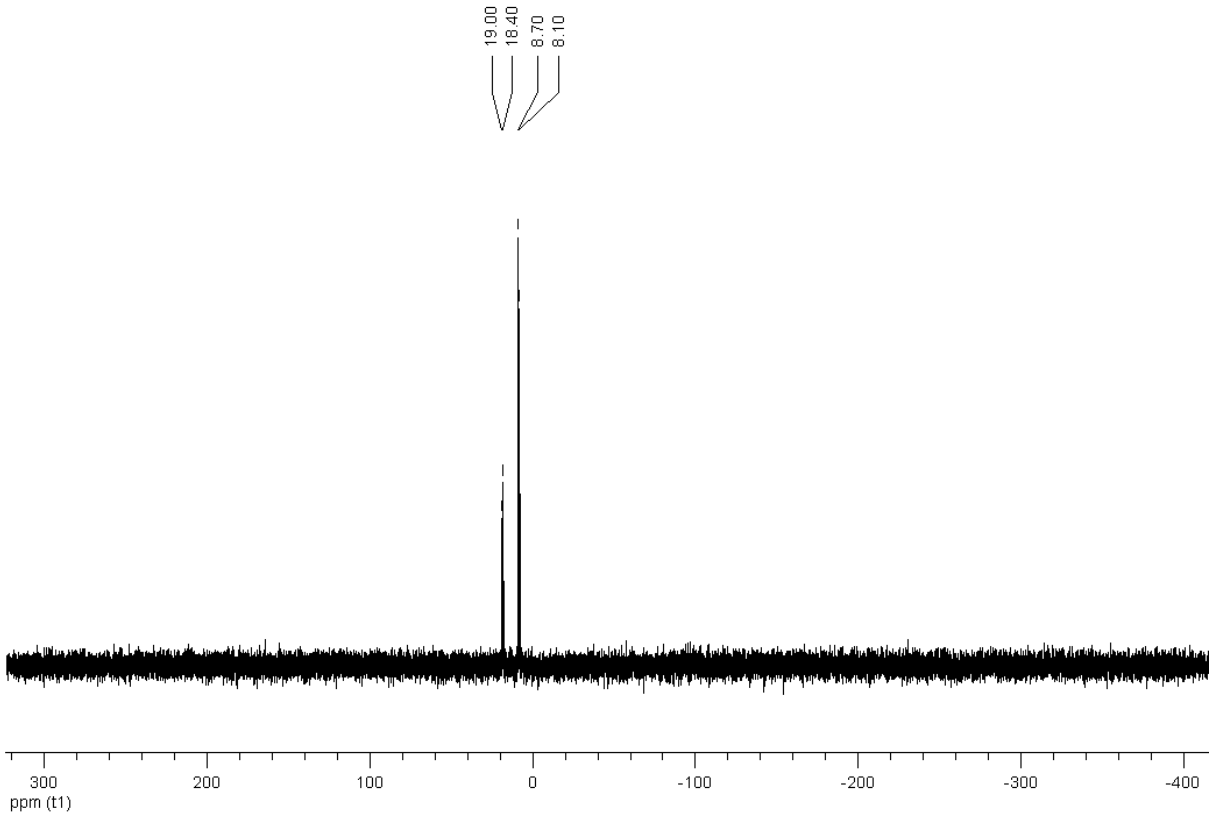
144.18
139.07
135.18
129.50
129.09
128.63
128.20
127.49
126.63
126.00
125.83
125.71
125.43
125.36
122.91
118.21
37.37
37.32
37.23
37.18
37.08
37.05
21.20
1.24
200
150
100
50
0
ppm (t1)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18.40
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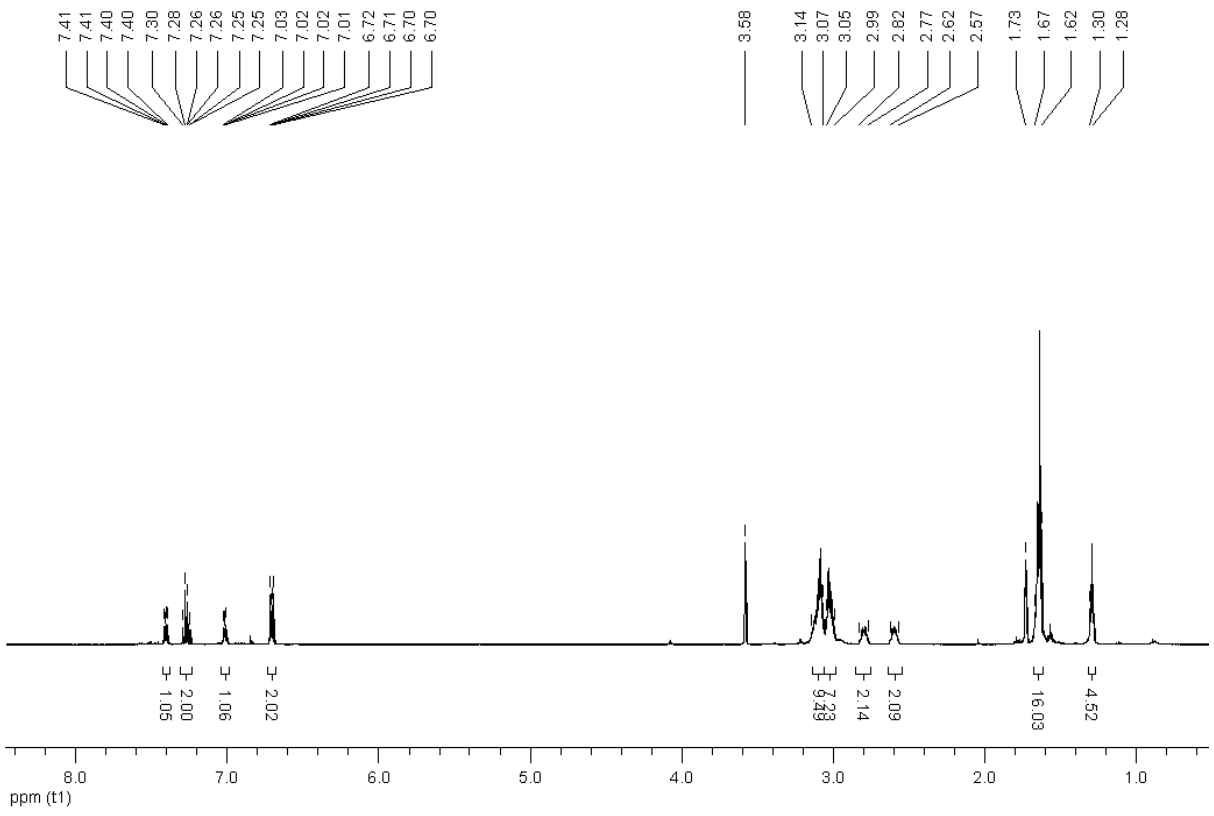
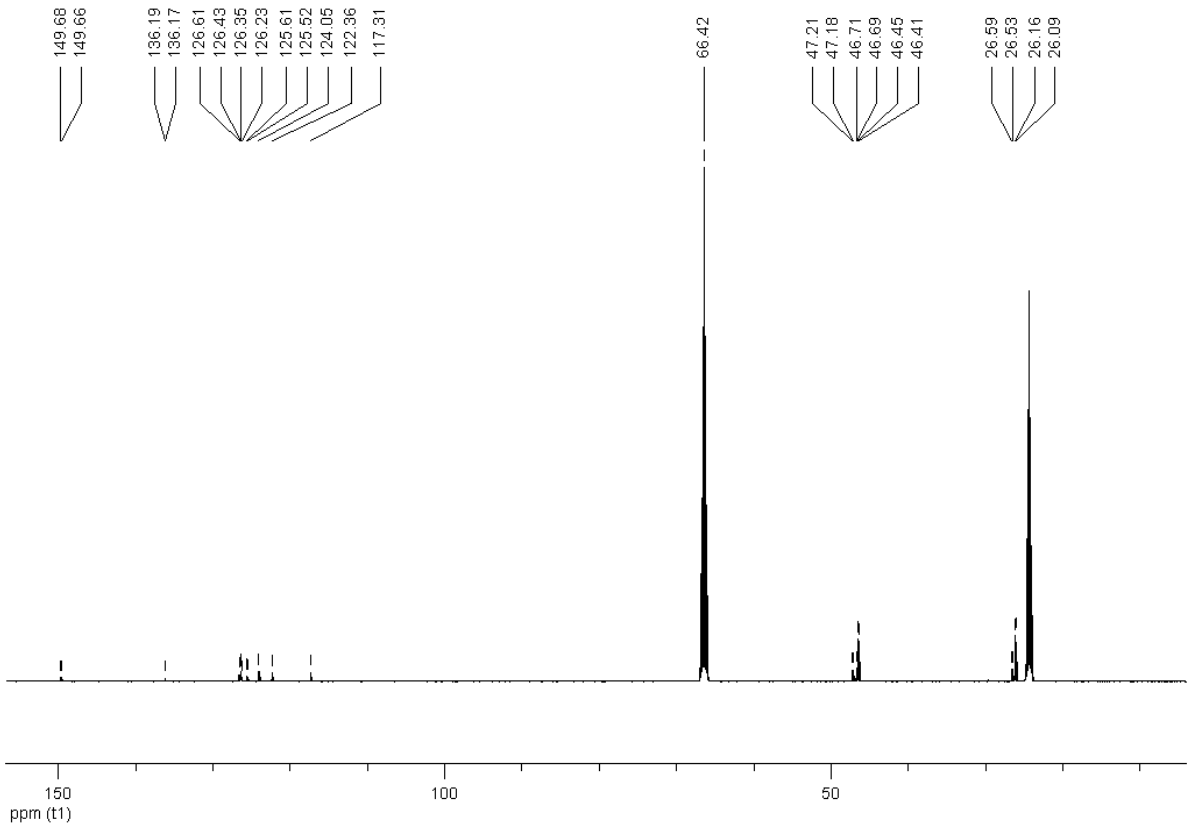
300
200
100
0
-100
-200
-300
-400
ppm (t1)

4:


7.41
7.41
7.40
7.40
7.30
7.28
7.26
7.26
7.25
7.25
7.03
7.02
7.02
7.01
6.72
6.71
6.70
6.70
3.58
3.14
3.07
3.05
2.99
2.82
2.77
2.62
2.57
1.73
1.67
1.62
1.30
1.28
1.05
2.00
1.06
2.02
7.23
2.14
2.09
16.03
4.52
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)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136.19
136.17
126.61
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126.35
126.23
125.61
125.52
124.05
122.36
117.31
66.42
47.21
47.18
46.71
46.69
46.45
46.41
26.59
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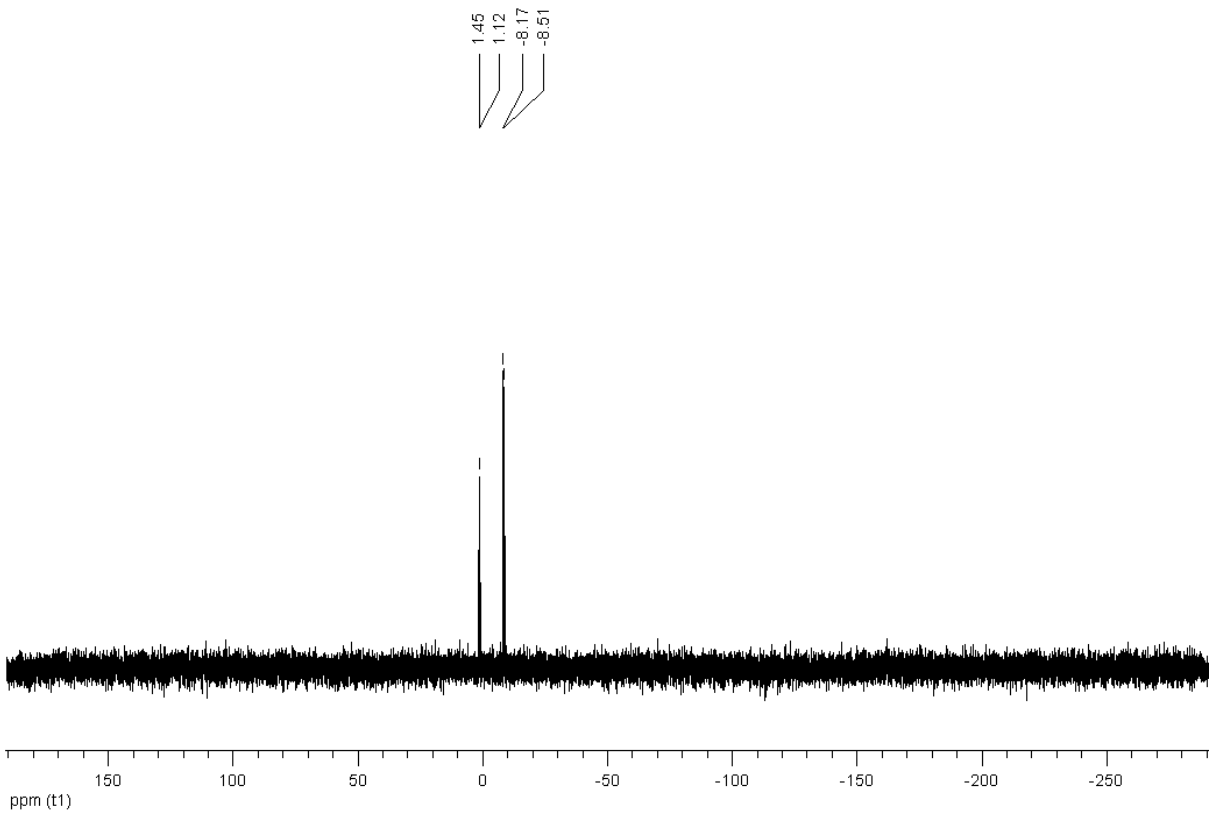
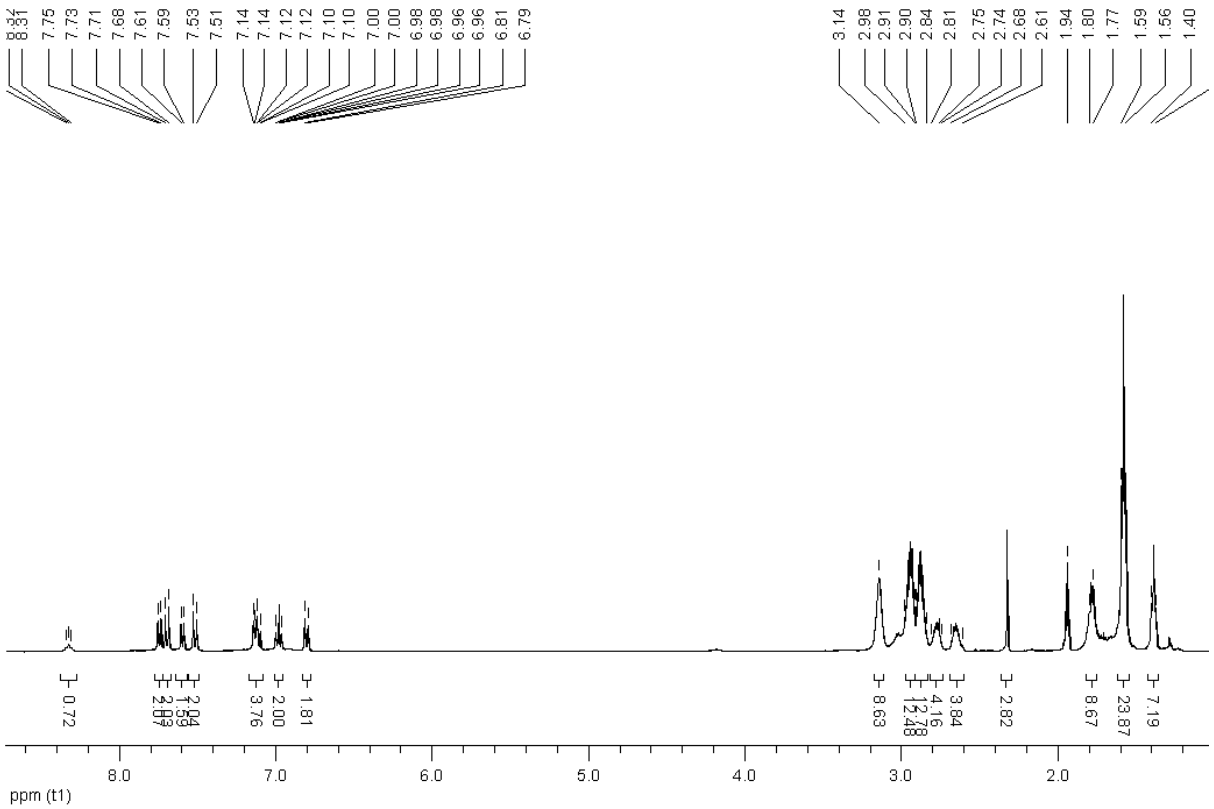
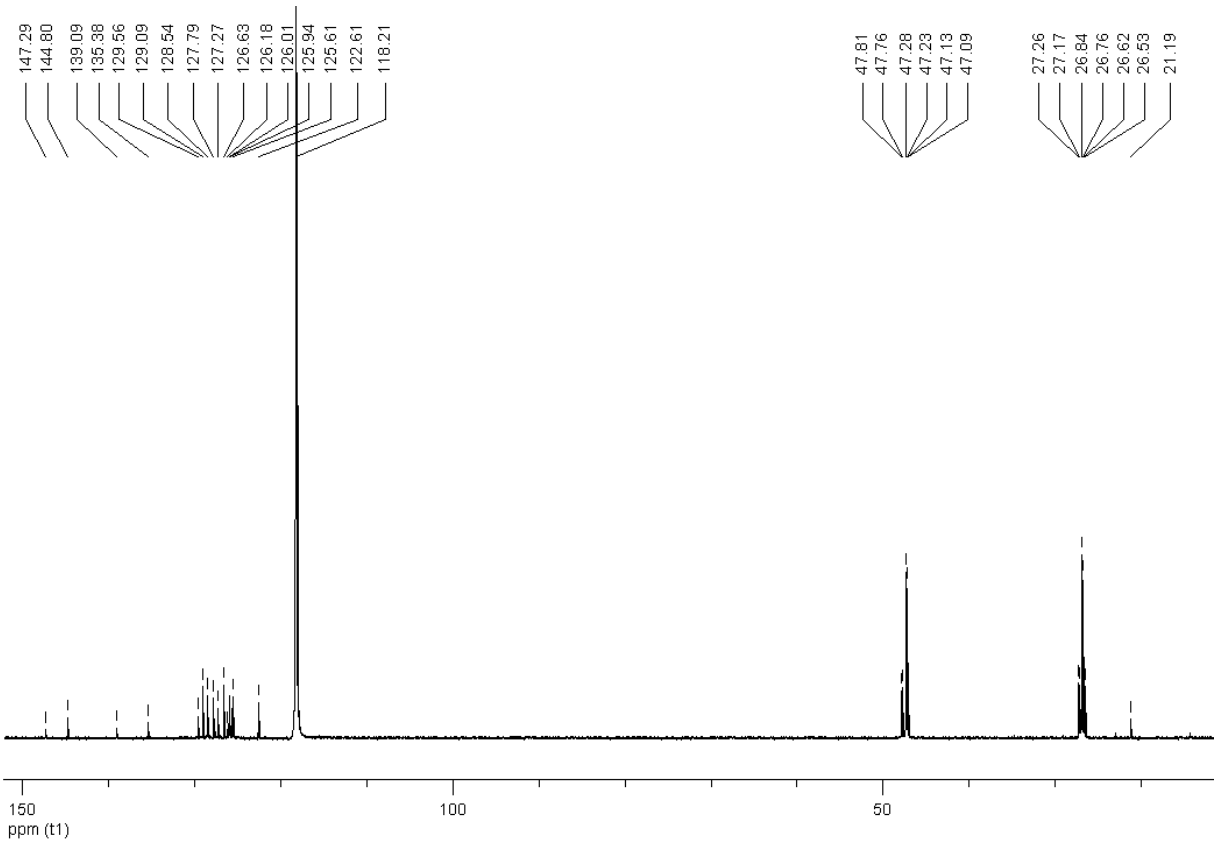
26.16
26.09
150
100
50
ppm (t1)


1.45
1.12
-8.17
-8.51
150
100
50
0
-50
-100
-150
-200
-250
ppm (t1)

4·$C_7H_7SO_3H$:


8.36
8.31
7.75
7.73
7.71
7.68
7.61
7.59
7.53
7.51
7.14
7.14
7.12
7.12
7.10
7.10
7.00
7.00
6.98
6.98
6.96
6.96
6.81
6.79
3.14
2.98
2.91
2.90
2.84
2.81
2.75
2.74
2.68
2.61
1.94
1.80
1.77
1.59
1.56
1.40
0.72
2.04
2.00
1.81
8.63
2.82
8.67
23.87
7.19
8.0
7.0
6.0
5.0
4.0
3.0
2.0
ppm (t1)


147.29
144.80
139.09
135.38
129.56
129.09
128.54
127.79
127.27
126.63
126.18
126.01
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125.61
122.61
118.21
47.81
47.76
47.28
47.23
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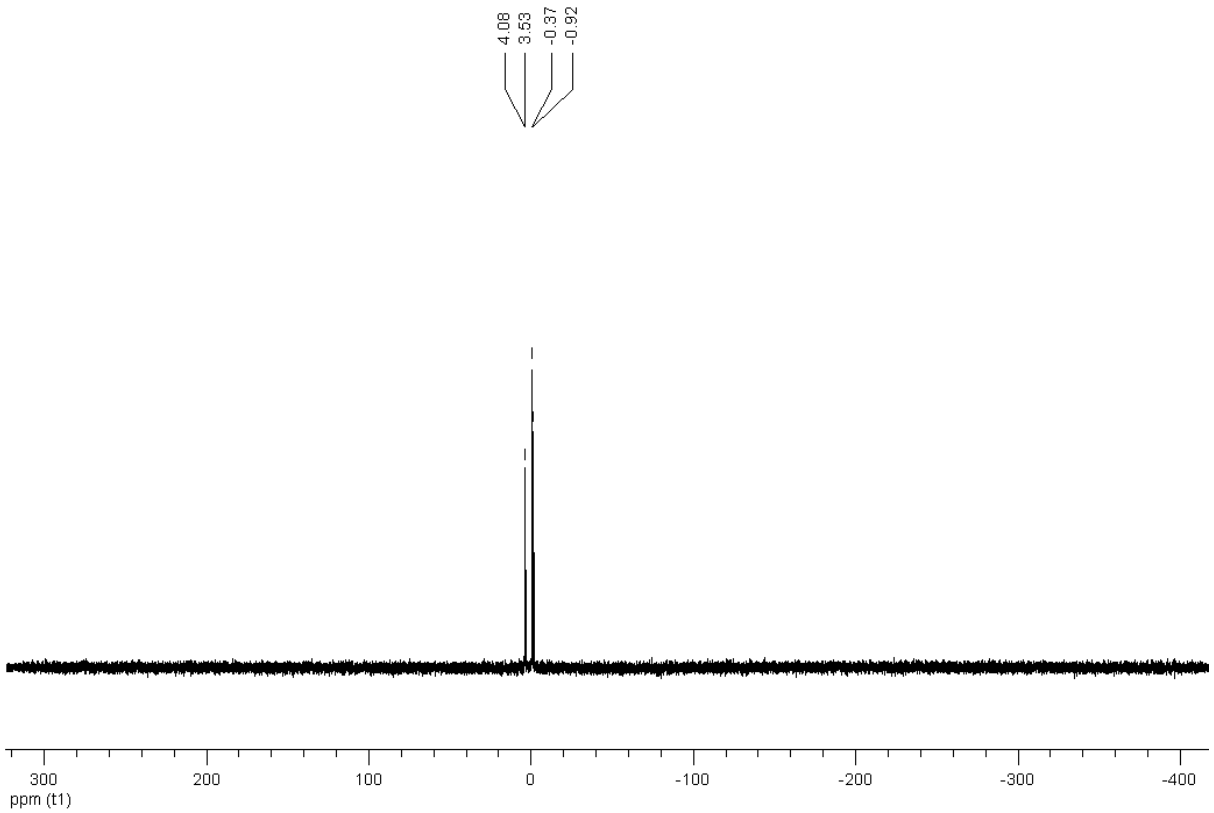
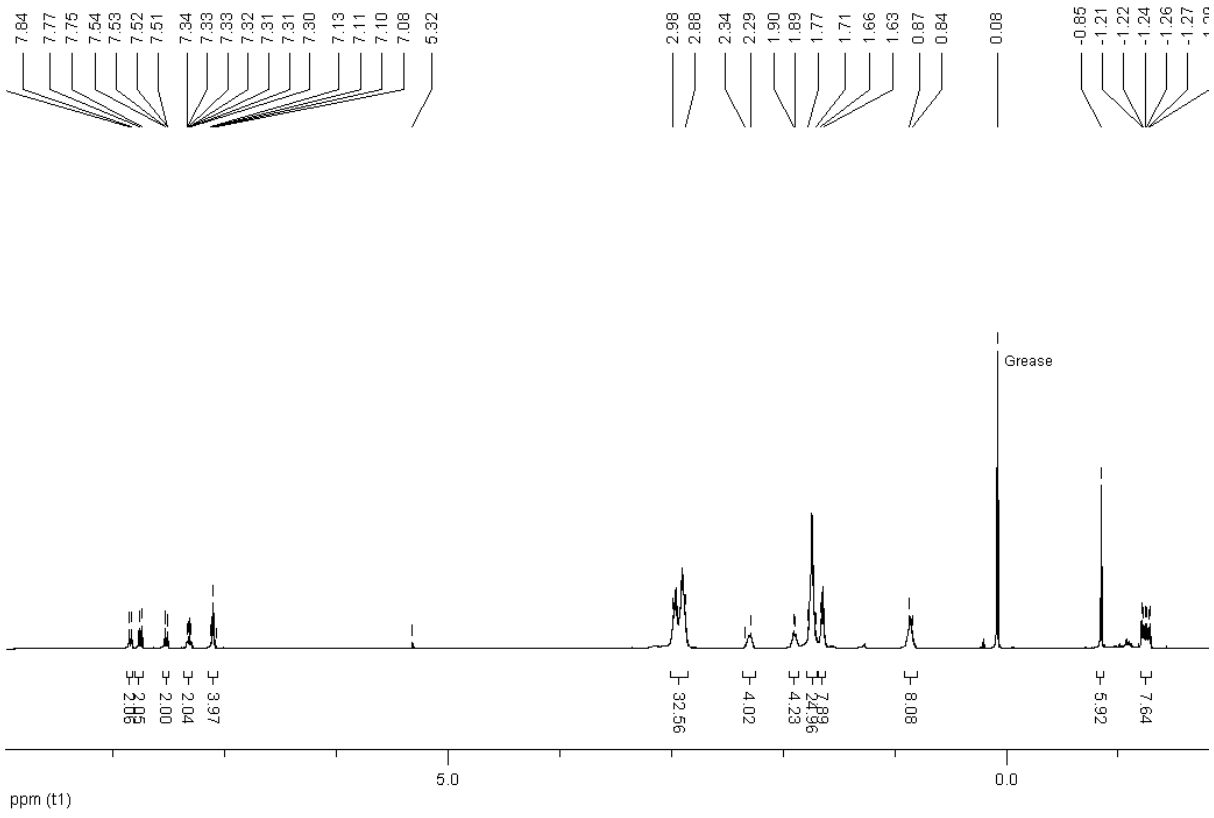
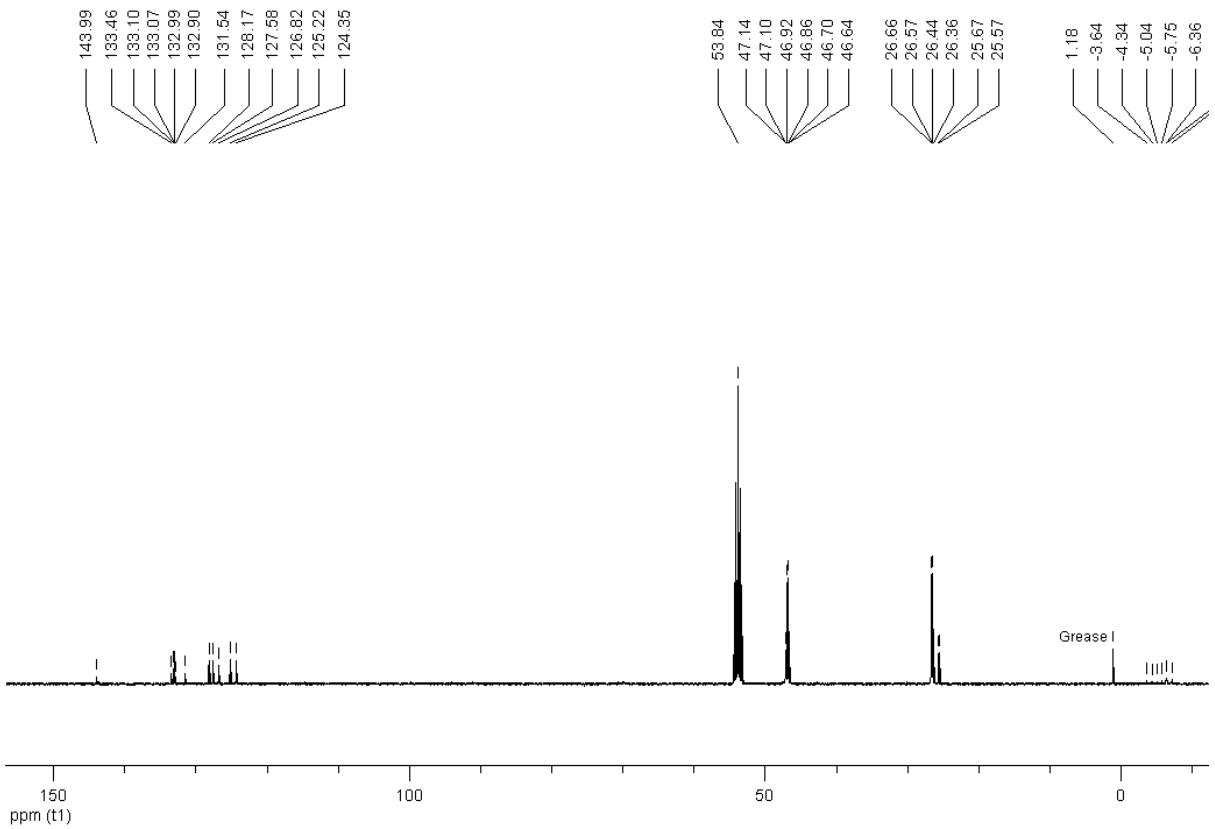
26.53
21.19
150
100
50
ppm (t1)



$[4\text{-}AlMe_2]^+[AlMe_4]^-$:




143.99
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133.07
132.99
132.90
131.54
128.17
127.58
126.82
125.22
124.35
53.84
47.14
47.10
46.92
46.86
46.70
46.64
26.66
26.57
26.44
26.36
25.67
25.57
1.18
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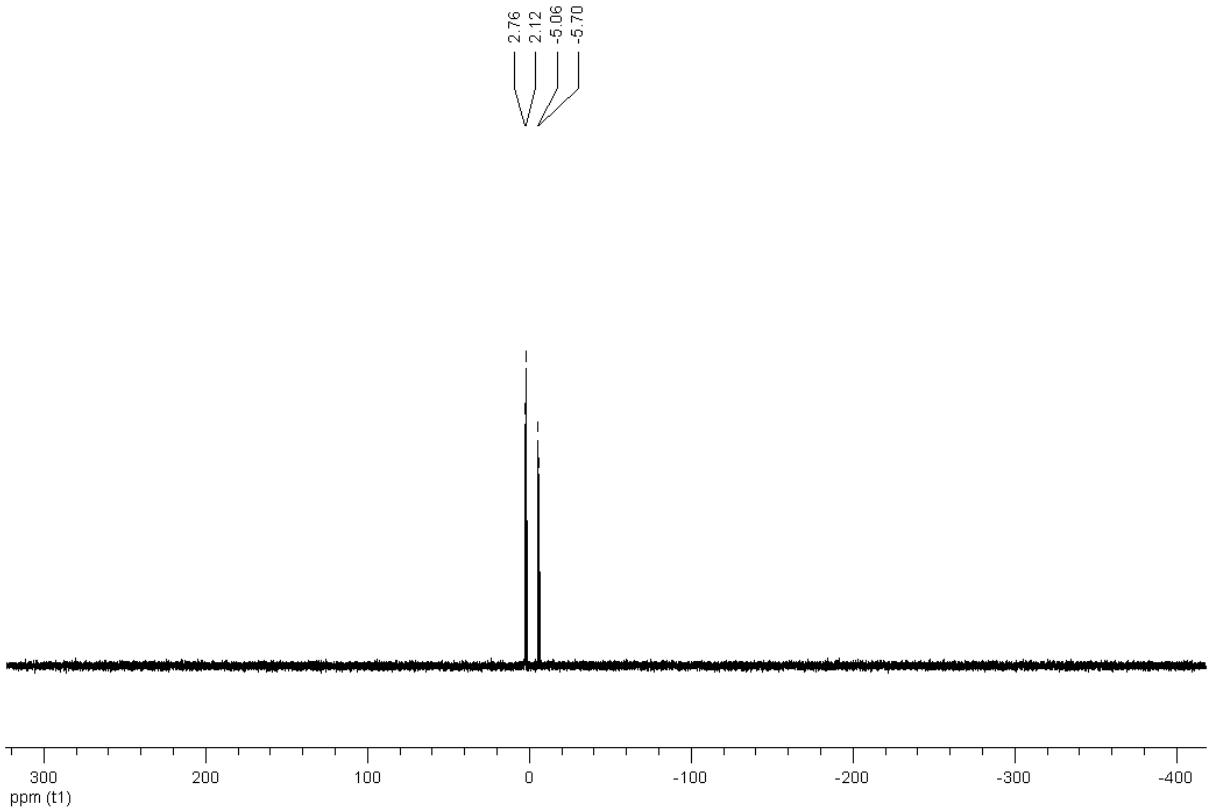
-5.04
-5.75
-6.36
Grease I
150
100
50
0
ppm (t1)


2.76
2.12
-5.06
-5.70
300
200
100
0
-100
-200
-300
-400
ppm (t1)

Crystallographic Information

IPDS 2T (Stoe) and D8 QUEST (Bruker) diffractometers were used for data collection by the x-ray department at the Philipps-Universität Marburg (Dr. K. Harms, M. Marsch, and R. Riedel). Data collection, reduction and cell refinement were performed with Stoe IPDS Software or Apex2 (Bruker). Structures were solved with SIR92[3] or SIR97[4] and refined against F^2 with SHELXL-97[5] within the interface of WinGX.[6] Furthermore, the programs Mercury 3.1[7] und Platon[8] were used during structure refinement. Absorption correction was performed with semi-empirical methods within WinGX (multi-scan[9]) or APEX2 (multi-scan[10])

.

Hydrogen atoms were calculated in their idealized positions and refined with fixed isotropic thermal parameters. All molecular structures were illustrated with Diamond 3[11] using thermal ellipsoids at the 30% probability level. Hydrogen atoms are omitted for clarity.

Crystal data and experimental conditions are listed in table S1. Selected bonding distances and angles with standard deviations in parentheses are collected in table S4 and S5. The corresponding CIF files providing full information concerning the molecular structures and experimental conditions are deposited at the Cambridge Crystallographic Data Center (**3**: 977138, [**4**-$AlMe_2$]$^+$[$AlMe_4$]$^-$: 977139, **1**: 977140).

Molecular Structure of 1

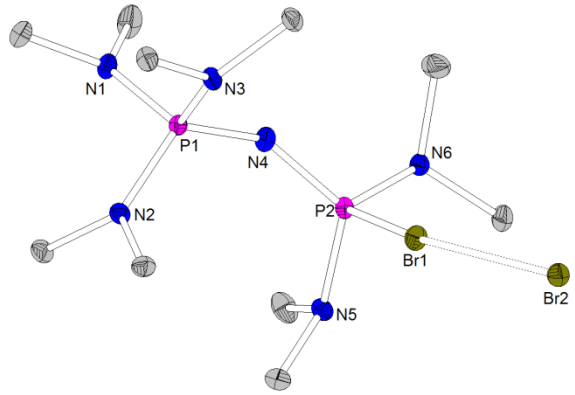


Figure S1. Molecular structure of **1** (ellipsoids with 30% probability). Hydrogen atoms are omitted for clarity. Selected bond lengths /Å and angles /°: P1-N1 1.630(2), P1-N2 1.632(2), P1-N3 1.638(2), P1-N4 1.592(2), N4-P2 1.551(2), P2-N5 1.650(2), P2-N6 1.636(2), P2-Br1 2.208(1), Br1···Br2 3.4774(3), P1-N4-P2 139.1(1).

Table S1. Crystal data and experimental conditions.

	3	**$[4\text{-}AlMe_2]^+[AlMe_4]^-$**	**1**
empirical formula	$C_{40}H_{72}N_{14}P_4$	$C_{66}H_{110}Al_2N_{14}P_4$	$C_{10}H_{30}Br_2N_6P_2$
mol. weight [g mol^{-1}]	873.00	1277.53	456.16
crystal habit	colorless prism	colorless plate	colorless block
crystal size [mm^3]	0.32 · 0.22 · 0.16	0.34 · 0.10 · 0.04	0.25 · 0.22 · 0.19
crystal system	triclinic	monoclinic	triclinic
space group	*P*1	*P*1211	*P*-1
a [Å]	10.510(5)	10.751(3)	8.1153(5)
b [Å]	13.359(5)	33.100(7)	9.5111(6)
c [Å]	16.907(5)	10.900(3)	13.1754(9)
α [°]	87.900(5)	90	108.141(5)
β [°]	89.867(5)	116.309(13)	92.459(5)
γ [°]	82.977(5)	90	94.663(5)
volume [Å^3]	2354.4(16)	3477.1(16)	960.71(11)
Z	2	2	2
density [g cm^{-3}]	1.231	1.220	1.577
T [K]	100(2)	100(2)	100(2)
absorption coeff. [mm^{-1}]	0.206	0.184	4.387
Θ range [°]	2.3 to 25.0	2.2 to 25.1	1.6 to 26.7
index ranges	-12 <= h <= 12, -15 <= k <= 15, -20 <= l <= 19	-12 <= h <= 12, -39 <= k <= 39, -13 <= l <= 12	-9 <= h <= 10, -12 <= k <= 11, -16 <= l <= 16
reflns collected	15745	25958	
independent reflns	11795 [R(int) = 0.0492]	12333 [R(int) = 0.1140]	4040 [R(int) = 0.0440]
absorption correction	multi-scan	multi-scan	multi-scan
max. and min. transmission	0.7455 and 0.5234	0.7455 and 0.4904	0.5252 and 0.2588
transmissiondata/restraints/parameters	11795 / 46 / 1074	12333 / 190 / 787	4040 / 0 / 191
goodness-of-fit on F^2	1.080	1.048	1.011
final R indices [I>2s(I)]	R1 = 0.0667	R1 = 0.0702	R1 = 0.0258
R indices (all data)	wR2 = 0.1754	wR2 = 0.1675	wR2 = 0.0599
larg. diff. peak/hole [e Å^{-3}]	1.121 / -0.541	0.568 / -0.559	0.749 / -0.594
treatment of H atoms	constr	constr	constr

[1] A. P. Marchenko, G. N. Koidan, A. M. Pinchuk and A. V. Kursanov, *Zh. Obshch. Khim.* 1983, **54**, 1774-1782.
[2] a) D. J. Dellinger, D. M. Sheehan, N. K. Christensen, J. G. Lindberg and M. H. Caruthers, *J. Am. Chem. Soc.* 2003, **125**, 940-950; b) J. F. Kögel, B. Oelkers, B. Kovačević and J. Sundermeyer, *J. Am. Chem. Soc.* 2013, **135**, 17768-17774.

[3] A. Altomare, G. L. Cascarano, C. Giacovazzo and A. Guagliardi, *J. Appl. Cryst.* 1993, **26**, 343-350.
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