Electronic Supplementary Information

Reversible OH-Bond Activation and Amphoterism by Metal-Ligand Cooperativity of the Calix[4]pyrrolato Aluminate

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S-1. Materials and methods

All used reagents and solvents were purchased from commercial sources. Unless otherwise noted, all manipulations were carried out under a dry nitrogen or argon atmosphere. Solvents were degassed prior to use with four freeze-pump-thaw cycles and were stored in sealed Schlenk ampulla over activated molecular sieve (3 or 4 Å, respectively) under a dry argon atmosphere. Liquid reactants were degassed for at least 10 min with a constant stream of dry argon through the fluid phase and were dried by storage over activated molecular sieve (3 or 4 Å, respectively). Solid reagents were dried and purified if necessary either by the application of vacuum and elevated temperature, or by sublimation under reduced pressure at elevated temperature.

All reactions on preparative scale were carried out in flame-dried standard laboratory glassware under a dry argon atmosphere using Schlenk line techniques and were permanently magnetically stirred. Syringes, magnetic stirring bars, and needles were dried and/or flushed with argon prior to use. Reaction on the NMR sample scale were done in dry J. Young NMR tubes.

Compounds sensitive to ambient conditions were handled and stored in a Sylatech glove box filled with dry nitrogen gas. Removal of solvents in vacuo was performed using a Heidolph VV2000 rotary evaporator or a Schlenk line.

Literature-known compounds were synthesized following published procedures, which are cited (see below). Analytical data of known compounds were compared to data of the respective reference and were found to be consistent in all cases. Novel compounds were characterized to the reported structures to the best of our knowledge.

Nuclear magnetic resonance (NMR) spectra were collected with a Bruker BZH 200/52, a Bruker DPX 200, a Bruker Avance II 400, or a Bruker Avance III 600 spectrometer at 298 K unless otherwise noted. Measurements with the Bruker Avance spectrometers were carried out by the NMR facility of the Institute of Inorganic Chemistry of the University of Heidelberg.

Chemical shifts $\delta$ are given in parts per million (ppm) relative to the tetramethylsilane resonance. Deuterated dichloromethane, tetrachloroethane (in one case), and tetrahydrofuran were used as solvent in all cases, and the signal of CHDCls and THF-$d_8$ was used for calibration of the spectra (CD$_2$Cl$_2$: $^1$H: 5.32 ppm, $^{13}$C: 53.84 ppm, THF-$d_8$: $^1$H: 3.58 ppm, $^{13}$C: 67.21 ppm). $^1$H NMR data is reported as follows: chemical shift $\delta$ [ppm], multiplicity (s = singlet, br s = broad singlet, d = doublet, t = triplet, q = quartet, sept = septet, m = multiplet), scalar spin-spin coupling constant [Hz] as $^XJ_{AB}$ (X = number of chemical bonds between coupled nuclei; A, B = coupled nuclei), integration value, signal assignment. $^{13}$C($^1$H) NMR data is reported as follows: chemical shift $\delta$ [ppm], multiplicity (only for $^XJ_{CP}$, d = doublet), type of carbon atom (CH$_3$, CH$_2$, CH, Cq), signal assignment.

The protons of the aromatic pyrrole rings of the calix[4]pyrrolato ligand are denoted “$\beta$-H”, the respective carbon atoms “$\beta$-C”. The quaternary carbon atoms of the aromatic pyrrole rings in the ligand are named “Cq-pyrrole”. The atoms of the ligand’s methyl groups are called “$\alpha$-Me” and the quaternary carbon atoms to which they are attached “$\alpha$-C”.

NMR spectra were processed and plotted with TopSpin 4.0.7.

High resolution mass spectrometry (HR-MS) was done with the electrospray ionization method (ESI) and with a Bruker ApexQe hybrid 9.4 T FT-ICR.
S-2. Preparation of tetraphenyolphosphonium meso-octamethylcalix[4]pyrrolato aluminate ([PPh₄][1]) and of lithium tetrapyrrolato aluminate

The meso-octamethylcalix[4]pyrrolato aluminate ([PPh₄][1]) was prepared on gram-scale as its tetraphenyolphosphonium salt within two steps. The procedures are known to the literature. The obtained substances were characterized by ¹H and ¹³C NMR spectroscopy. Acquired data was found congruent with the values from the literature.

Scheme S-1: Synthesis of tetraphenyolphosphonium meso-octamethylcalix[4]pyrrolato aluminate ([PPh₄][1]).

Lithium tetrapyrrolato aluminate was synthesized in one step from pyrrole and lithium aluminum hydride following a modified procedure taken from the patent of Whitney and Klemann, ExxonMobil Research and Engineering Co (Alkali metal salts of complex anions containing heteroatom substituents and electrolyte compositions containing these, 1978, US4117213A). The obtained material was characterized by ¹H and ¹³C NMR spectroscopy.

Scheme S-2: Synthesis of lithium tetrapyrrolato aluminate.

meso-Octamethylcalix[4]pyrrole

Procedure. In a 500 mL two-necked round-bottom flask equipped with a reflux condenser, acetone (13.0 g, 16.5 mL, 223.6 mmol, 1.0 eq) was dissolved in methanol (160 mL). Pyrrole (15 g, 15.5 mL, 223.6 mmol,
1.0 eq), which was freshly distilled prior to use, was added in one portion. Methanesulfonic acid (4 drops) was added to the colorless solution. The mixture was heated to 60 °C for 3 h. The reaction mixture was allowed to cool down to room temperature, and the solvent was removed under reduced pressure. A pale green solid was obtained as the crude reaction product, which was purified by flash column chromatography on silica gel with dichloromethane/petroleum ether (60:40, Rf = 0.53) as eluent. The solvent was removed from the combined product fractions and meso-octamethylcalix[4]pyrrole was obtained as a pale brown solid (13.7 g, 32.0 mmol, 57% yield), which is stable to ambient conditions.

\[^1\text{H} \text{NMR} (400 \text{ MHz}, \text{CD}_2\text{Cl}_2, 298 \text{ K}): \delta \ [\text{ppm}] = 7.02 \ (\text{br s, 4H, N-H}), 5.88 \ (d, ^3\text{J}_{\text{HH}} = 2.8 \text{ Hz, 8H, } \beta-\text{H}), 1.49 \ (s, 24\text{H, } \alpha-\text{Me})\]

\[^{13}\text{C}[^1\text{H}] \text{NMR} (100 \text{ MHz}, \text{CD}_2\text{Cl}_2, 298 \text{ K}): \delta \ [\text{ppm}] = 138.8 \ (\text{C}_\alpha, \text{C}_\beta\text{-pyrrole}), 103.1 \ (\text{CH, } \beta-\text{H}), 35.4 \ (\text{C}_\alpha, \alpha-\text{C}), 28.9 \ (\text{CH}_3, \alpha-\text{Me})\]

**meso-Octamethylcalix[4]pyrrolato aluminate ([PPh₄][1])**

**Procedure.** In a nitrogen-filled glove box, meso-octamethylcalix[4]pyrrole (5.00 g, 11.67 mmol, 1.0 eq) and purified (see below) lithium aluminum hydride (1.05 g, 27.62 mmol, 2.4 eq) were dissolved in 1,2-dimethoxyethane (30 mL) in a 500 mL Schlenk flask. An overpressure valve was added, and the reaction mixture was stirred at 95 °C for 48 h. The solvent was removed under reduced pressure and was redisolved in dichloromethane (70 mL). To the pale-yellow solution tetraphenylphosphonium chloride (4.37 g, 11.67 mmol, 1.0 eq), which was dissolved in vacuo at 80 °C for several hours prior to use, was added, and it was stirred for 1 h at room temperature. The formed colorless precipitate was separated by filtration through a fritted glass filter. The product (7.60 g, 9.61 mmol, 82% yield) was precipitated from its pale-yellow dichloromethane solution by addition of pentane (70 mL). It contains approximately an equimolar amount of dichloromethane. [PPh₄][1] was permanently handled under inert conditions.

\[^1\text{H} \text{NMR} (600 \text{ MHz}, \text{CD}_2\text{Cl}_2, 295 \text{ K}): \delta \ [\text{ppm}] = 7.90-7.83 \ (\text{m, 4H, PPh}_4^+), 7.73-7.65 \ (\text{m, 8H, PPh}_4^+), 7.61-7.52 \ (\text{m, 8H, PPh}_4^+), 5.75 \ (\text{s, 8H, } \beta-\text{H}), 1.64 \ (\text{s, 12H, } \alpha-\text{Me}), 1.47 \ (\text{s, 12H, } \alpha-\text{Me})\]

\[^{13}\text{C}[^1\text{H}] \text{NMR} (151 \text{ MHz}, \text{CD}_2\text{Cl}_2, 295 \text{ K}): \delta \ [\text{ppm}] = 147.3 \ (\text{C}_\alpha, \text{C}_\beta\text{-pyrrole}), 136.2 \ (d, ^4\text{J}_{\text{CP}} = 3.0 \text{ Hz, PPh}_4^+), 134.8 \ (d, ^4\text{J}_{\text{CP}} = 10.3 \text{ Hz, PPh}_4^+), 131.0 \ (d, ^4\text{J}_{\text{CP}} = 12.9 \text{ Hz, PPh}_4^+), 117.8 \ (d, ^1\text{J}_{\text{CP}} = 89.6 \text{ Hz, PPh}_4^+), 100.8 \ (\text{CH, } \beta-\text{C}), 42.6 \ (\text{C}_\alpha, \alpha-\text{C}), 35.9 \ (\text{CH}_3, \alpha-\text{Me}), 24.8 \ (\text{CH}_3, \alpha-\text{Me})\]

**Procedure for LiAlH₄ purification.** The commercially available lithium aluminum hydride was purified for the synthesis of [PPh₄][1] prior to use. For that, gray LiAlH₄ powder (5.0 g) was mixed with diethyl ether (200 mL)
in a 500 mL one-necked Schlenk flask, which was equipped with a Schlenk frit capped with a 250 mL Schlenk flask. The apparatus was flame-dried and flushed with dry argon prior to use. The suspension was stirred for 30 min at room temperature. The gray solid was separated by filtration from the colorless solution. The solvent was removed under reduced pressure to yield a colorless solid (2.9 g) after drying in vacuo at 80 °C. The product was used without further characterization and was permanently handled under inert conditions.

Lithium tetrapyrrolato aluminate

Procedure.\(^1\) In a flame-dried 100 mL Schlenk flask, purified lithium aluminum hydride (200 mg, 5.27 mmol, 1.0 eq, for purification procedure see above) was mixed with diethyl ether (10 mL). Freshly distilled pyrrole (366 µL, 354 mg, 5.27 mmol, 1.0 eq) was added dropwise, and the reaction mixture was stirred for 1 h at room temperature. The formation of gas was observed. The solvent was removed under reduced pressure, and after drying in vacuo the desired product was obtained as a colorless solid. The exact yield was not determined. Lithium tetrapyrrolato aluminate was constantly handled under inert conditions.

\(^1H\) NMR (600 MHz, THF-\(d_8\), 295 K), \(\delta\) [ppm] = 6.69 (s, 8H, H-2/5), 6.00 (s, 8H, H-3/H-4).

\(^{13}C(\text{"H})\) NMR (151 MHz, THF-\(d_8\), 295 K), \(\delta\) [ppm] = 125.7 (CH, C-2/5), 108.3 (CH, C-3/4). Both signals showed somewhat poorly resolved \(^{13}C-{^{27}Al}\) coupling and appeared, though expected as a sextet (\(S_{^{27}Al} = 5/2\)), as doublet-type signals.

\(^7Li\) NMR (233 MHz, THF-\(d_8\), 295 K), \(\delta\) [ppm] = 2.45.
S-3. Addition reactions to [1]⁻

General Procedure: In a dry nitrogen-filled glovebox, tetraphenylphosphonium meso-octamethyl-calix[4]pyrrolato aluminate ([PPh₄][1], 10 mg, 12.6 µmol, 1.0 eq) was dissolved in CD₂Cl₂ (0.5 mL). An equimolar amount of the respective alcohol substrate (12.6 µmol, 1.0 eq) was dissolved in CD₂Cl₂ (0.3 mL) and was added to the stirring aluminate solution at room temperature. The reaction mixture turned yellow (orange in the case of para-nitrobenzyl alcohol) immediately after the addition of the first drop of the alcohol solution. After complete addition, the solution was transferred to a J. Young NMR tube and was analyzed by NMR spectroscopy. The addition products were also characterized by high resolution electrospray ionization mass spectrometry.

Scheme S-3: Addition reaction of protic substrates to [1]⁻. With BuOH, the addition process is not quantitative (see Chapter S-5).
$^{13}$H NMR (600 MHz, CD$_2$Cl$_2$, 295 K), $\delta$ [ppm] = 7.92-7.86 (m, 4H, PPh$_4^+$), 7.75-7.68 (m, 8H, PPh$_4^+$), 7.62-7.55 (m, 8H, PPh$_4^+$), 7.56 (1H, H-2, observed by $^1$H,$^1$H COSY NMR spectroscopy, expected multiplicity is d), 6.82 (d, $^3$J$_{HH}$ = 5.1 Hz, 1H, H-3), 5.89 (d, $^3$J$_{HH}$ = 2.8 Hz, 1H, $\beta$-H), 5.83 (d, $^3$J$_{HH}$ = 2.8 Hz, 1H, $\beta$-H), 5.79 (d, $^3$J$_{HH}$ = 2.9 Hz, 1H, $\beta$-H), 5.78 (d, $^3$J$_{HH}$ = 2.9 Hz, 1H, $\beta$-H), 5.70 (d, $^3$J$_{HH}$ = 2.7 Hz, 1H, $\beta$-H), 5.67 (d, $^3$J$_{HH}$ = 2.7 Hz, 1H, $\beta$-H), 5.60 (s, 1H, H-1), 2.73-2.65 (m, 1H, H-5A/5B), 2.43-2.35 (m, 1H, H-5A/5B), 1.75 (s, 3H, $\alpha$-Me), 1.69 (s, 3H, $\alpha$-Me), 1.66 (s, 3H, $\alpha$-Me), 1.63 (s, 3H, $\alpha$-Me), 1.60 (s, 3H, $\alpha$-Me), 1.51 (s, 3H, $\alpha$-Me), 1.32 (s, 3H, $\alpha$-Me), 0.65 (s, 3H, $\alpha$-Me), 0.64 (t, $^3$J$_{HH}$ = 6.9 Hz, 3H, H-6).

$^{13}$C($^1$H) NMR (151 MHz, CD$_2$Cl$_2$, 295 K), $\delta$ [ppm] = 186.9 (C$_{q}$, C-4), 156.2 (CH, C-2), 150.9 (C$_{q}$, C$_{q}$-pyrrole), 150.1 (C$_{q}$, C$_{q}$-pyrrole), 149.1 (C$_{q}$, C$_{q}$-pyrrole), 147.0 (C$_{q}$, C$_{q}$-pyrrole), 146.4 (C$_{q}$, C$_{q}$-pyrrole), 141.4 (C$_{q}$, C$_{q}$-pyrrole), 136.2 (CH, d, $^4$J$_{CP}$ = 3.0 Hz, PPh$_4^+$), 134.8 (CH, d, $^2$J$_{CP}$ = 10.3 Hz, PPh$_4^+$), 131.0 (CH, d, $^3$J$_{CP}$ = 12.9 Hz, PPh$_4^+$), 127.4 (CH, C-3), 117.8 (C$_{q}$, d, $^1$J$_{CP}$ = 89.6 Hz, PPh$_4^+$), 101.7 (CH, $\beta$-C), 101.4 (CH, $\beta$-C), 101.0 (CH, $\beta$-C), 100.6 (CH, $\beta$-C), 100.3 (CH, $\beta$-C), 98.2 (CH, $\beta$-C), 86.5 (CH, C-1), 55.4 (CH$_2$, C-5), 40.7 (C$_{q}$, $\alpha$-C), 39.6 (CH$_3$, $\alpha$-Me), 38.3 (C$_{q}$, $\alpha$-C), 36.7 (C$_{q}$, $\alpha$-C), 36.6 (C$_{q}$, $\alpha$-C), 36.4 (CH$_3$, $\alpha$-Me), 33.4 (CH$_3$, $\alpha$-Me), 32.0 (CH$_3$, $\alpha$-Me), 28.5 (CH$_3$, $\alpha$-Me), 28.0 (CH$_3$, $\alpha$-Me), 27.4 (CH$_3$, $\alpha$-Me), 26.1 (CH$_3$, $\alpha$-Me), 20.5 (CH$_3$, C-6).

**HR-MS (ESI, negative ion mode):** m/z calculated for C$_{38}$H$_{38}$AlN$_4$O [M]$^-$: 497.2866, found: 497.2874.
HR-MS (ESI, negative ion mode): m/z calculated for C₄₃H₄₀AlN₃O [M]⁺: 511.3023, found: 511.3080.
1H NMR (600 MHz, CD2Cl2, 295 K). δ [ppm] = 7.91-7.85 (m, 4H, PPh4+), 7.75-7.68 (m, 8H, PPh4+), 7.62-7.54 (m, 8H, PPh4+), 7.57 (1 H, H-2, observed by 1H,1H COSY NMR spectroscopy, expected multiplicity is d), 6.82 (dd, 3JHH = 5.3 Hz, 4JHH = 0.7 Hz, 1H, H-3), 5.90 (s, 1H, H-1), 5.89 (d, 4JHH = 3.1 Hz, 1H, β-H), 5.88 (d, 3JHH = 3.1 Hz, 1H, β-H), 5.82 (d, 3JHH = 3.0 Hz, 1H, β-H), 5.78 (d, 4JHH = 2.9 Hz, 1H, β-H), 5.73 (d, 3JHH = 2.9 Hz, 1H, β-H), 5.69 (d, 3JHH = 2.9 Hz, 1H, β-H), 5.65 (s, 3H, α-Me), 1.75 (s, 3H, α-Me), 1.74 (s, 3H, α-Me), 1.67 (s, 3H, α-Me), 1.63 (s, 3H, α-Me), 1.58 (s, 3H, α-Me), 1.55 (s, 3H, α-Me), 1.21 (s, 3H, α-Me), 0.61 (s, 3H, α-Me), 0.58 (s, 9H, H-6).

13C(1H) NMR (151 MHz, CD2Cl2, 295 K). δ [ppm] = 186.3 (Cα, C-4), 156.9 (CH, C-2), 150.9 (Cα, Cα-pyrrole), 150.3 (Cα, Cα-pyrrole), 149.5 (Cα, Cα-pyrrole), 146.6 (Cα, Cα-pyrrole), 146.0 (Cα, Cα-pyrrole), 141.2 (Cα, Cα-pyrrole), 136.2 (CH, d, 4JCP = 3.0 Hz, PPh4+), 134.8 (CH, d, 4JCP = 10.3 Hz, PPh4+), 131.0 (CH, d, 4JCP = 12.9 Hz, PPh4+), 127.8 (CH, C-3), 117.9 (Cα, d, 4JCP = 89.6 Hz, PPh4+), 102.4 (CH, β-C), 101.5 (CH, β-C), 100.8 (CH, β-C), 100.92 (CH, β-C), 100.90 (CH, β-C), 98.7 (CH, β-C), 84.7 (CH, C-1), 68.2 (Cα, C-5), 42.0 (CHα, α-Me), 41.5 (Cα, α-Me), 38.4 (CHα, α-Me), 38.3 (CHα, α-Me), 38.1 (Cα, α-Me), 36.9 (Cα, α-Me), 36.6 (Cα, α-Me), 32.4 (CHα, C-6), 31.0 (CHα, α-Me), 28.4 (CHα, α-Me), 28.1 (CHα, α-Me), 27.0 (CHα, α-Me), 25.2 (CHα, α-Me).

HR-MS (ESI, negative ion mode): m/z calculated for C32H42AlN4O [M]−: 525.3179, found: 525.3129.
$^1$H NMR (600 MHz, CD$_2$Cl$_2$, 295 K), $\delta$ [ppm] = 7.90-7.84 (m, 4H, PPh$_4^+$), 7.74-7.67 (m, 8H, PPh$_4^+$), 7.60-7.53 (m, 8H, PPh$_4^+$), 7.48 (d, $^3$J$_{HH}$ = 5.2 Hz, 1H, H-2), 6.93-6.89 (m, 2H, H-7), 6.89-6.85 (m, 2H, H-8), 6.79 (d, $^3$J$_{HH}$ = 5.2 Hz, 1H, H-3), 5.90 (d, $^3$J$_{HH}$ = 2.9 Hz, 1H, $\beta$-H), 5.85 (d, $^3$J$_{HH}$ = 3.0 Hz, 1H, $\beta$-H), 5.84 (d, $^3$J$_{HH}$ = 3.0 Hz, 1H, $\beta$-H), 5.80 (d, $^3$J$_{HH}$ = 3.0 Hz, 1H, $\beta$-H), 5.73 (d, $^3$J$_{HH}$ = 2.9 Hz, 1H, $\beta$-H), 5.70 (d, $^3$J$_{HH}$ = 2.9 Hz, 1H, $\beta$-H), 5.54 (s, 1H, H-1), 3.70 (d, $^3$J$_{HH}$ = 13.2 Hz, 1H, H-5A/5B), 3.14 (d, $^2$J$_{HH}$ = 13.2 Hz, 1H, H-5A/5B), 2.20 (s, 3H, H-10), 1.74 (s, 3H, $\alpha$-Me), 1.68 (s, 3H, $\alpha$-Me), 1.63 (s, 3H, $\alpha$-Me), 1.60 (s, 3H, $\alpha$-Me), 1.55 (s, 3H, $\alpha$-Me), 1.49 (s, 3H, $\alpha$-Me), 1.34 (s, 3H, $\alpha$-Me), 0.60 (s, 3H, $\alpha$-Me).

$^{13}$C($^1$H) NMR (151 MHz, CD$_2$Cl$_2$, 295 K), $\delta$ [ppm] = 186.9 (C$_o$, C-4), 156.4 (CH, C-2), 151.3 (C$_q$, C$_q$-pyrrole), 150.2 (C$_q$, C$_q$-pyrrole), 149.2 (C$_q$, C$_q$-pyrrole), 148.2 (C$_q$, C$_q$-pyrrole), 146.4 (C$_q$, C$_q$-pyrrole), 145.3 (C$_q$, C-6), 141.5 (C$_q$, C$_q$-pyrrole), 138.2 (CH, d, $^4$J$_{CP}$ = 3.0 Hz, PPh$_4^+$), 134.8 (CH, d, $^4$J$_{CP}$ = 10.3 Hz, PPh$_4^+$), 134.1 (C$_q$, C-9), 131.0 (CH, d, $^3$J$_{CP}$ = 12.9 Hz, PPh$_4^+$), 128.2 (CH, C-8), 127.3 (CH, C-3), 127.0 (CH, C-7), 117.8 (C$_q$, d, $^1$J$_{CP}$ = 89.6 Hz, PPh$_4^+$), 102.3 (CH, $\beta$-C), 101.4 (CH, $\beta$-C), 101.2 (CH, $\beta$-C), 100.8 (CH, $\beta$-C), 100.6 (CH, $\beta$-C), 98.0 (CH, $\beta$-C), 86.3 (CH, C-1), 62.3 (CH$_2$, C-5), 40.9 (C$_q$, $\alpha$-C), 40.2 (CH$_3$, $\alpha$-Me), 38.3 (C$_q$, $\alpha$-C), 36.9 (CH$_3$, $\alpha$-Me), 36.8 (C$_q$, $\alpha$-C), 36.6 (C$_q$, $\alpha$-C), 33.7 (CH$_3$, $\alpha$-Me), 31.2 (CH$_3$, $\alpha$-Me), 28.2 (CH$_3$, $\alpha$-Me), 27.6 (CH$_3$, $\alpha$-Me), 27.5 (CH$_3$, $\alpha$-Me), 25.6 (CH$_3$, $\alpha$-Me), 21.1 (CH$_3$, C-10).

HR-MS (ESI, negative ion mode): m/z calculated for C$_{38}$H$_{42}$AlN$_3$O [M]$^-$: 573.3179, found: 573.3177.
[PPh₄][(p-NO₂BnO)-1*-H]

1H NMR (600 MHz, CD₂Cl₂, 295 K). δ [ppm] = 7.92-7.89 (m, 2H, H-8), 7.89-7.85 (m, 4H, PPh₄⁺), 7.74-7.67 (m, 8H, PPh₄⁺), 7.61-7.55 (m, 8H, PPh₄⁺), 7.51 (d, 3JHH = 5.3 Hz, 1H, H-2), 7.23-7.19 (m, 2H, H-7), 6.83 (dd, 3JHH = 5.3 Hz, 4JHH = 1.0 Hz, 1H, H-3), 5.87 (d, 3JHH = 2.9 Hz, 1H, β-H), 5.86 (d, 3JHH = 3.0 Hz, 1H, β-H), 5.81 (d, 3JHH = 3.0 Hz, 1H, β-H), 5.75 (d, 3JHH = 2.9 Hz, 1H, β-H), 5.72 (d, 3JHH = 2.9 Hz, 1H, β-H), 5.45 (s, 1H, H-1), 3.81 (d, 3JHH = 15.7 Hz, 1H, H-5A/5B), 3.27 (d, 1H, 1H, H-5A/5B), 2.75 (s, 3H, α-Me), 1.69 (s, 3H, α-Me), 1.57 (s, 3H, α-Me), 1.56 (s, 3H, α-Me), 1.42 (s, 3H, α-Me), 1.35 (s, 3H, α-Me), 0.60 (s, 3H, α-Me).

13C[1H] NMR (151 MHz, CD₂Cl₂, 295 K). δ [ppm] = 187.4 (C₉, C-4), 157.5 (C₉, C-9), 156.5 (CH, C-2), 151.5 (C₉, C₉-pyrrole), 150.2 (C₉, C₉-pyrrole), 149.0 (C₉, C₉-pyrrole), 147.2 (C₉, C₉-pyrrole), 146.3 (C₉, C-6), 145.9 (C₉, C₉-pyrrole), 141.4 (C₉, C₉-pyrrole), 136.2 (CH, d, 3JCP = 3.0 Hz, PPh₄⁺), 134.8 (CH, d, 3JCP = 10.3 Hz, PPh₄⁺), 131.0 (CH, d, 3JCP = 12.9 Hz, PPh₄⁺), 127.41 (CH, C-3), 127.37 (CH, C-7), 122.8 (CH, C-8), 117.8 (C₉, d, 1JCP = 3.1 Hz, PPh₄⁺), 102.6 (CH, β-C), 101.7 (CH, β-C), 101.4 (CH, β-C), 100.9 (CH, β-C), 100.8 (CH, β-C), 98.2 (CH, β-C), 86.4 (CH, C-1), 62.4 (CH₂, C-5), 40.9 (C₉, α-C), 40.0 (CH₃, α-Me), 38.3 (C₉, α-C), 36.9 (CH₃, α-Me), 36.8 (C₉, α-C), 36.6 (C₉, α-C), 33.7 (CH₃, α-Me), 31.2 (CH₃, α-Me), 28.1 (CH₃, α-Me), 27.5 (CH₃, α-Me), 27.3 (CH₃, α-Me), 25.5 (CH₃, α-Me).

HR-MS (ESI, negative ion mode): m/z calculated for C₃₈H₃₈AlN₉O₆ [M]⁻: 604.2874, found: 604.2886.
**[PPh₄][((p-MeOPh)₂CHO)-1⁺-H]**

**¹H NMR (600 MHz, CD₂Cl₂, 295 K), δ [ppm] = 7.91-7.85 (m, 4H, PPh₄⁺), 7.75-7.67 (m, 8H, PPh₄⁺), 7.62-7.53 (m, 8H, PPh₄⁺), 7.35-7.31 (d, ³JHH = 5.2 Hz, 1H, H-2), 7.07-7.02 (m, 2H, H-7/7'), 6.77-6.74 (dd, ³JHH = 5.2 Hz, ³JHH = 0.7 Hz, 1H, H-3), 6.71-6.67 (m, 2H, H-8/8'), 6.28-6.24 (m, 2H, H-8/8'), 6.22-6.18 (m, 2H, H-7/7'), 5.93 (d, ³JHH = 2.9 Hz, 1H, β-H), 5.84 (d, ³JHH = 2.9 Hz, 1H, β-H), 5.80 (d, ³JHH = 3.0 Hz, 1H, β-H), 5.77 (d, ³JHH = 2.9 Hz, 1H, β-H), 5.70 (d, ³JHH = 3.0 Hz, 1H, β-H), 5.61 (d, ³JHH = 2.9 Hz, 1H, β-H), 5.34 (s, 1H, H-1), 4.20 (s, 1H, H-5), 3.74 (s, 3H, H-10/10'), 3.58 (s, 3H, H-10/10'), 1.77 (s, 3H, α-Me), 1.74 (s, 3H, α-Me), 1.58 (s, 3H, α-Me), 1.41 (s, 3H, α-Me), 1.31 (s, 3H, α-Me), 1.10 (s, 3H, α-Me), 0.94 (s, 3H, α-Me), 0.49 (s, 3H, α-Me).

**¹³C(¹H) NMR (151 MHz, CD₂Cl₂, 295 K), δ [ppm] = 186.4 (C₉, C-4), 157.7 (C₉, C-9/9'), 156.8 (C₉, C-9/9'), 156.5 (CH, C-2), 151.6 (C₉, C₉-pyrrole), 151.2 (C₉, C₉-pyrrole), 149.1 (C₉, C₉-pyrrole), 146.1 (C₉, C₉-pyrrole), 146.0 (C₉, C₉-pyrrole), 142.9 (C₉, C-6/6'), 141.7 (C₉, C-6/6'), 141.3 (C₉-pyrrole), 136.1 (CH, d, ³JC₉ = 3.1 Hz, PPh₄⁺), 134.8 (CH, d, ³JC₉ = 10.3 Hz, PPh₄⁺), 131.0 (CH, d, ³JC₉ = 12.9 Hz, PPh₄⁺), 130.2 (CH, C-7/7'), 128.8 (CH, C-7/7'), 127.2 (CH, C-3), 117.8 (C₉, d, ¹JC₉ = 89.6 Hz, PPh₄⁺), 112.7 (CH, C-8/8'), 112.4 (CH, C-8/8'), 103.2 (CH, β-C), 101.34 (CH, β-C), 101.30 (CH, β-C), 101.04 (CH, β-C), 100.97 (CH, β-C), 98.2 (CH, β-C), 85.2 (CH, C-1), 74.4 (CH, C-5), 55.5 (CH₃, C-10/10'), 55.3 (CH₃, C-10/10'), 41.2 (CH₃, α-Me), 41.1 (C₉, α-C), 38.1 (C₉, α-C), 37.9 (CH₃, α-Me), 36.9 (C₉, α-C), 36.4 (C₉, α-C), 35.2 (CH₃, α-Me), 30.5 (CH₃, α-Me), 27.6 (CH₃, α-Me), 27.3 (CH₃, α-Me), 27.2 (CH₃, α-Me), 25.1 (CH₃, α-Me).

**HR-MS (ESI, negative ion mode):** m/z calculated for C₆₉H₄₈AlN₄O₂ [M⁺]⁻: 695.3547, found: 695.3561.
[PPh₄][(+-BrPhO)-1*-H]

**¹H NMR** (600 MHz, CD₂Cl₂, 295 K), δ [ppm] = 7.90-7.84 (m, 4H, PPh₄⁺), 7.74-7.66 (m, 8H, PPh₄⁺), 7.61-7.55 (m, 8H, PPh₄⁺), 7.54 (d, 3JHH = 5.2 Hz, 1H, H-2), 6.85 (dd, 3JHH = 5.3 Hz, 4JHH = 1.1 Hz, 1H, H-3), 6.75-6.71 (m, 2H, H-7), 5.90 (d, 3JHH = 3.0 Hz, 1H, β-H), 5.89 (d, 3JHH = 3.0 Hz, 1H, β-H), 5.84 (d, 3JHH = 3.0 Hz, 1H, β-H), 5.83 (d, 3JHH = 3.0 Hz, 1H, β-H), 5.73 (d, 3JHH = 2.9 Hz, 1H, β-H), 5.72 (d, 3JHH = 2.9 Hz, 1H, β-H), 5.55-5.51 (m, 2H, H-6), 5.20 (s, 1H, H-1), 1.76 (s, 3H, α-Me), 1.68 (s, 3H, α-Me), 1.66 (s, 3H, α-Me), 1.54 (s, 3H, α-Me), 1.47 (s, 3H, α-Me), 1.41 (s, 3H, α-Me), 1.35 (s, 3H, α-Me), 0.62 (s, 3H, α-Me).

**¹³C[¹H] NMR** (151 MHz, CD₂Cl₂, 295 K), δ [ppm] = 187.4 (C₈, C-4), 160.6 (C₈, C-5), 156.7 (CH, C-2), 150.4 (C₈, C₈-pyrrole), 150.3 (C₈, C₈-pyrrole), 149.1 (C₈, C₈-pyrrole), 146.8 (C₈, C₈-pyrrole), 146.4 (C₈, C₈-pyrrole), 141.2 (C₈, C₈-pyrrole), 136.2 (CH, d, 4JCP = 7.5 Hz, CPPh₄⁺), 134.8 (CH, d, 4JCP = 8.9 Hz, CPPh₄⁺), 131.04 (CH, C-7), 131.01 (CH, d, 4JCP = 9.5 Hz, CPPh₄⁺), 106.8 (C₈, C-8), 103.2 (CH, β-H), 102.1 (CH, β-H), 102.0 (CH, β-H), 101.7 (CH, β-H), 101.4 (CH, β-H), 98.9 (CH, β-H), 85.9 (CH, C-1), 40.9 (C₈, α-C), 34.2 (C₈, α-C), 31.4 (CH₃, α-Me), 30.7 (CH₃, α-Me), 27.7 (CH₃, α-Me), 27.6 (CH₃, α-Me), 25.5 (CH₃, α-Me).

**HR-MS** (ESI, negative ion mode): m/z calculated for C₃₈H₉₇Al⁺BrN₄O [M]⁻: 623.1972, found: 623.1980.
$\text{[PPh$_4$][BzO]-1'-H]}$

$^1$H NMR (600 MHz, CD$_2$Cl$_2$, 295 K), $\delta$ [ppm] = 7.91-7.83 (m, 4H, PPh$_4^+$), 7.74-7.65 (m, 8H, PPh$_4^+$), 7.61-7.52 (m, 8H, PPh$_4^+$), 7.58 (1H, H-2, observed by $^1$H,$^1$H COSY NMR spectroscopy, expected multiplicity is d), 7.51-7.46 (m, 2H, H-8), 7.23-19 (m, 1H, H-10), 7.12-7.06 (m, 2H, H-9), 6.87 (dd, $^3$J$_{HH}$ = 5.3 Hz, $^4$J$_{HH}$ = 1.0 Hz, 1H, H-3), 5.96 (d, $^3$J$_{HH}$ = 3.0 Hz, 1H, $\beta$-H), 5.92 (d, $^3$J$_{HH}$ = 3.0 Hz, 1H, $\beta$-H), 5.81 (d, $^3$J$_{HH}$ = 3.3 Hz, 1H, $\beta$-H), 5.80 (d, $^3$J$_{HH}$ = 3.3 Hz, 1H, $\beta$-H), 5.732 (d, $^3$J$_{HH}$ = 3.1 Hz, 1H, $\beta$-H), 5.728 (d, $^3$J$_{HH}$ = 3.1 Hz, 1H, $\beta$-H), 5.44 (s, 1H, H-1), 1.71 (s, 3H, $\alpha$-Me), 1.54 (s, 3H, $\alpha$-Me), 1.53 (s, 3H, $\alpha$-Me), 1.51 (s, 3H, $\alpha$-Me), 1.48 (s, 3H, $\alpha$-Me), 1.46 (s, 3H, $\alpha$-Me), 1.36 (s, 3H, $\alpha$-Me), 0.76 (s, 3H, $\alpha$-Me).

$^{13}$C($^1$H) NMR (151 MHz, CD$_2$Cl$_2$, 295 K), $\delta$ [ppm] = 187.7 (C$_8$, C-4), 168.2 (C$_8$, C-6), 155.4 (CH, C-2), 150.3 (C$_{\alpha}$, C$_{\alpha}$-pyrrole), 149.9 (C$_{\alpha}$, C$_{\alpha}$-pyrrole), 148.2 (C$_{\alpha}$, C$_{\alpha}$-pyrrole), 147.0 (C$_{\alpha}$, C$_{\alpha}$-pyrrole), 146.6 (C$_{\alpha}$, C$_{\alpha}$-pyrrole), 142.3 (C$_{\alpha}$, C$_{\alpha}$-pyrrole), 136.9 (C$_{\alpha}$, C-7), 136.2 (CH, d, $^4$J$_{CP}$ = 3.1 Hz, PPh$_4^+$), 134.8 (CH, d, $^3$J$_{CP}$ = 10.3 Hz, PPh$_4^+$), 131.0 (CH, d, $^3$J$_{CP}$ = 12.9 Hz, PPh$_4^+$), 130.5 (CH, C-10), 130.4 (CH, C-8), 127.8 (CH, C-3), 127.6 (CH, C-9), 117.8 (C$_{\alpha}$, d, $^1$J$_{CP}$ = 89.6 Hz, PPh$_4^+$), 102.9 (CH, $\beta$-H), 102.0 (CH, $\beta$-H), 101.6 (CH, $\beta$-H), 101.2 (CH, $\beta$-H), 100.12 (CH, $\beta$-H), 100.12 (CH, $\beta$-H), 87.5 (CH, C-1), 39.2 (C$_q$, $\alpha$-C), 38.5 (C$_q$, $\alpha$-C), 36.8 (CH$_3$, $\alpha$-Me), 36.43 (C$_q$, $\alpha$-C), 36.42 (C$_q$, $\alpha$-C), 35.5 (CH$_3$, $\alpha$-Me), 34.2 (CH$_3$, $\alpha$-Me), 30.67 (CH$_3$, $\alpha$-Me), 30.65 (CH$_3$, $\alpha$-Me), 28.7 (CH$_3$, $\alpha$-Me), 28.2 (CH$_3$, $\alpha$-Me), 26.6 (CH$_3$, $\alpha$-Me).

HR-MS (ESI, negative ion mode): m/z calculated for C$_{38}$H$_{38}$AlN$_4$O$_2$ [M$^-$]: 573.2816, found: 573.2839.
S-4. Reactivity of lithium tetrapyrrolato aluminate with $^3$PrOH

Procedure. In a dry nitrogen-filled glove box, lithium tetrapyrrolato aluminate (7 mg, 23.5 μmol, 1.0 eq) was dissolved in tetrahydrofurane-$d_8$ (0.6 mL) in a J. Young NMR tube. Subsequently, isopropanol (1.5 mg, 2.0 μL, 26.2 μmol, 1.1 eq) was added at room temperature. No change in color occurred. The reaction was followed by $^1$H NMR spectroscopy. Immediately after the addition of $^3$PrOH, the acquired $^1$H NMR spectrum showed a broad triplet resonance at 9.9 ppm, and one set of additional signals at 6.66 and 6.03 ppm, which is characteristic of pyrrole. Hence, the tetrapyrrolato aluminate readily undergoes alcoholysis and no aluminum-ligand cooperative addition of $^3$PrOH. This is in stark contrast to the behavior of the calix[4]pyrrolato aluminate.

Figure S-1: $^1$H NMR spectrum (200 MHz, THF-$d_8$, 298 K) of A) [Li][Al(py)$_4$]$_2$, py = pyrrolato, and of B) [Li][Al(py)$_4$] after addition of $^3$PrOH. The signals of THF-$d_7$ are marked with red asterisks.
NMR study of the equilibrium addition reaction with \textsuperscript{t}BuOH as substrate and removal of the added \textsuperscript{t}BuOH by reduced pressure

When [PPh₄][1] (9.2 mg, 11.6 \(\mu\)mol, 1.0 eq) was treated with an equimolar amount of \textit{tert}-butyl alcohol (0.86 mg, 11.6 \(\mu\)mol, 1.0 eq) in CD\(_2\)Cl\(_2\) (617 \(\mu\)L, \(\rho = 1.362 \text{ g cm}^{-3}\)) at room temperature, the \(\text{^1H}\) NMR spectrum showed the characteristic resonances of the \textsuperscript{t}BuOH addition product [PPh₄][\(\text{tBuO})-\text{1*}-\text{H}\)] beside those of free [PPh₄][1] and \textsuperscript{t}BuOH. To determine the thermodynamic parameters of this equilibrium (Scheme S-4), \(\text{^1H}\) NMR measurements at variable temperatures were carried out (Figure S-2).

\[
\text{[PPh₄][1]} \quad + \quad \text{[PPh₄][\(\text{tBuO})-\text{1*}-\text{H}\)]} \\
\begin{array}{c}
\text{Scheme S-4: Equilibrium addition reaction of \textsuperscript{t}BuOH to [1].}
\end{array}
\]

\[
\begin{array}{c}
\text{Figure S-2: } \text{^1H} \text{ NMR spectra acquired at variable temperatures (200 MHz, CD\(_2\)Cl\(_2\)) to study the equilibrium between bound and free \textsuperscript{t}BuOH. The signal of CHDCl\(_2\) and that of residual CH\(_2\)Cl\(_2\), which is contained in [PPh₄][1], are marked with a red asterisk.}
\end{array}
\]
The equilibrium constant $K(T)$ for the reaction under investigation (Scheme S-4) is defined as

$$K(T) = \frac{[[PPh_4][1^*\cdot H]](T)}{[[PPh_4][1]](T) \cdot [tBuO](T)} \quad (S-1)$$

and can be simplified to

$$K(T) = \frac{[[PPh_4][1]]_0 - [[PPh_4][1]](T)}{( [[PPh_4][1]](T) )^2} = \frac{1}{x(T) \cdot [[PPh_4][1]]_0} - \frac{1}{x(T) \cdot [[PPh_4][1]]_0} \quad (S-2)$$

$[[PPh_4][1]]_0$ is the initial concentration of the aluminate ($[[PPh_4][1]]_0 = 9.2 \text{ mg} / 617 \mu\text{L} = 0.018870 \text{ mol L}^{-1}$) and $x(T)$ the relative amount of free $[PPh_4][1]$ at a given temperature. The latter is directly accessible through $^1H$ NMR signal integration. One of the methyl singlet resonances of $[PPh_4][1]$ at 1.46 ppm was used for determining $x(T)$ with the $PPh_4^+$ multiplet from 7.97-7.81 ppm as the reference (Figure S-2).

With $K(T)$ in hand, a van’t Hoff analysis was done relying on

$$K(T) = \exp \left( -\frac{\Delta_R G}{R \cdot T} \right) \quad (S-3)$$

and

$$\Delta_R G = \Delta_R H - T \cdot \Delta_R S. \quad (S-4)$$

Combining S-3 and S-4 gives the straight-line equation

$$\ln(K(T)) = -\frac{\Delta_R H}{R} \cdot \frac{1}{T} + \frac{\Delta_R S}{R} \quad (S-5)$$

which was used to determine $\Delta_R H$ and $\Delta_R S$ and subsequently $\Delta_R G$ with S-4.
Figure S-3: A) Van’t Hoff plot for the equilibrium given in Scheme S-4. The uncertainty in temperature was estimated to \( \Delta T = 1 ^\circ\text{C} \). As \( K(T) \) is influenced by various errors in unidentifiable ways, its uncertainty and the propagation thereof was not considered. B) Temperature-dependent relative amount of [1] determined by \(^1\text{H} \) NMR signal integration (Figure S-2).

\[
\begin{align*}
\Delta R H &= -37 \text{ kJ mol}^{-1} \\
\Delta R S &= -68 \text{ J mol}^{-1} \text{ K}^{-1} \\
\Delta R G &= -16 \text{ kJ mol}^{-1}
\end{align*}
\]

The equilibrium reaction found for \(^3\text{BuOH} \) was also investigated by DFT calculations (see Chapter S-14). The obtained values are \( \Delta R_{H\text{DFT}} = -48 \text{ kJ mol}^{-1} \) and \( \Delta R_{G\text{DFT}} = 2 \text{ kJ mol}^{-1} \).

To further investigate the reversibility of the alcohol addition process to [1]\(^-\), a mixture of \([\text{PPh}_4][1] \) (9.0 mg, 11.4 \( \mu \text{mol}, 1.0 \text{ eq}) and tert-butyl alcohol (2.2 mg, 29.7 \( \mu \text{mol}, 2.6 \text{ eq}) in tetrachloroethane-\(d_2 \) (0.8 mL) as solvent was placed in a J. Young NMR tube. The tube was connected to a Schlenk line, and vacuum (approximately 1 mbar) was applied for 90 min at room temperature. After that, most of the solvent was evaporated. The tube was recharged with tetrachloroethane-\(d_2 \) (0.6 mL) and was analyzed by \(^1\text{H} \) NMR spectroscopy.

It was found that the signals of the \(^3\text{BuOH} \) addition product ([(\( \text{BuO} \)-1\(^-\)-H\(^-\))]\(^-\)) as well as the singlet resonance of free \(^3\text{BuOH} \) disappeared, and the characteristic signals of [1]\(^-\) appeared in the spectrum. This demonstrates and proves that an added alcohol substrate can be removed from [1]\(^-\), in this example by the application of reduced pressure. The \(^1\text{H} \) NMR spectrum in Figure S-4B shows a few additional signals with low intensity. They most likely originate from the reaction of [1]\(^-\) with the used solvent tetrachloroethane-\(d_2 \). We also observed reactivity of [1]\(^-\) with tetrachloroethane in previous investigations. However, it was necessary to work with the high-boiling tetrachloroethane-\(d_2 \) to allow for the vacuum application.
Figure S-4: $^1$H NMR spectrum (200 MHz, $^{13}$C, CD$_2$Cl$_2$ (green and blue), 600 MHz, CD$_2$Cl$_2$ (red), 298 K). A) of a mixture of [PPh$_4$][1] and an excess $^t$BuOH (2.6 eq), B) of the same sample after the application of reduced pressure for 90 min at room temperature, and C) of [PPh$_4$][1] for comparison. The signal(s) of CHDCl$_2$, C$_2$HCl$_4$ and that of residual CH$_2$Cl$_2$, which is contained in [PPh$_4$][1], are marked with red asterisks. The signal of free $^t$BuOH is marked with an orange, that of bound $^t$BuOH with a gray asterisk. The spectra collected with C$_2$D$_2$Cl$_4$ were referenced using the pyrrole resonance of [1] at 5.75 ppm (in CD$_2$Cl$_2$).

S-6. $^1$H,$^1$H EXSY NMR measurements

The self-exchange of isopropanol at [1]$^-$ (Scheme S-5) was studied by $^1$H,$^1$H exchange NMR spectroscopy ($^1$H,$^1$H EXSY NMR). This technique gives access to chemical rate constants $k$ by integration of cross and diagonal peaks in a series of $^1$H,$^1$H NOESY NMR spectra. Samples were prepared by dissolving [PPh$_4$][1] (9.2 mg, 11.6 $\mu$mol, 1.0 eq) in CD$_2$Cl$_2$ (889.7 mg, 653 $\mu$L, $\rho$ = 1.362 g cm$^{-3}$) and subsequent addition of an excess of isopropanol. The exact amount of added $^t$PrOH (2.3, 3.1, and 4.6 eq relative to [PPh$_4$][1]) was determined by $^1$H NMR signal integration.

Scheme S-5: Self-exchange reaction of isopropanol at [1]$^-$.

The samples were then analyzed by $^1$H,$^1$H NOESY NMR spectroscopy with varying mixing times $d_8$ ($d_8 = 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 1.0, and 2.0$ s). For each sample, a separate reference data set was acquired with $d_8 = 0.00275$ s.
To ensure accurate integration values, prior to the NOESY NMR experiments, the spin lattice relaxation times ($T_1$) of the involved nuclei within their chemical environment were estimated with a $^1$H inversion recovery experiment. The free isopropanol was found limiting. An interpuls delay time of 4 s resulted in complete recovery of all signals including those of free $^3$PrOH. Compromising between the required time for data acquisition and the desired accuracy of the data, the delay time ($d_1$) for the $^1$H,$^1$H NOESY NMR experiments was set to $d_1 = 20$ s (3.5 $T_1$).

Figure S-5: Exemplary $^1$H,$^1$H NOESY NMR spectrum (400 MHz, CD$_2$Cl$_2$, 298 K, $d_1 = 20$ s, $d_8 = 2$ s) which were acquired for the EXSY NMR experiments of $[1]$ in the presence of an excess of isopropanol. The signals of the methine group of the bound and free isopropanol (A, B, AB, BA) were used for evaluation. The signal of CHDCl$_2$ and that of residual CH$_2$Cl$_2$, which is contained in [PPh$_4$][1], are marked with a red asterisk.

The obtained spectra were evaluated by cross and diagonal peak integration. The signals of the methine $H$ of free and bound isopropanol were used as they are well separated from each other as well as from other potentially overlapping signals. The integrals were referenced against the A integration value (Figure S-5) of the measurements with $d_8 = 0.00275$ s. The obtained normalized values for the cross peaks $AB_{norm}$, $BA_{norm}$ were averaged to obtain the typical 2D-EXSY curves. The uncertainty introduce by the averaging was estimated by calculating

$$\Delta \left( \frac{AB_{norm} + BA_{norm}}{2} \right) = \frac{|AB_{norm} - BA_{norm}|}{2}. \quad (S-6)$$

The 2D-EXSY curves are the averaged relative signal cross peak intensities plotted against the mixing times (Figure S-6).
Table S-1: Integral values extracted from the respective $^1$H,$^1$H NOESY NMR spectra. For the assignment of the given integral areas A, B, AB, and BA see Figure S-5. $\Delta[(A_{\text{norm}} + B_{\text{norm}})/2]$ denotes the estimated error of the averaged cross peak integrals which was calculated following equation S-6.

| mixing time, d8 [s] | $A_{\text{norm}}$ | $B_{\text{norm}}$ | $AB_{\text{norm}}$ | $BA_{\text{norm}}$ | $(A_{\text{norm}} + B_{\text{norm}})/2$ | $\Delta[(A_{\text{norm}} + B_{\text{norm}})/2]$ |
|---------------------|-------------------|-------------------|-------------------|-------------------|-------------------------------|----------------------------------|
| **2.3 eq of PrOH**  |                   |                   |                   |                   |                               |                                  |
| 0.00275             | 1                 | 0.82949           | -0.00035          | 0.00376           | 0.00171                       | 0.0021                           |
| 0.1                 | 0.95620           | 0.76821           | 0.00547           | 0.00974           | 0.00761                       | 0.0021                           |
| 0.2                 | 0.93464           | 0.71661           | 0.02014           | 0.01689           | 0.01852                       | 0.0016                           |
| 0.3                 | 0.91472           | 0.66539           | 0.02606           | 0.02471           | 0.02539                       | 0.0007                           |
| 0.4                 | 0.89351           | 0.62396           | 0.03575           | 0.02873           | 0.03224                       | 0.0035                           |
| 0.5                 | 0.87562           | 0.58604           | 0.03900           | 0.03658           | 0.03779                       | 0.0012                           |
| 0.6                 | 0.85834           | 0.54747           | 0.04526           | 0.04224           | 0.04375                       | 0.0015                           |
| 1.0                 | 0.79295           | 0.42665           | 0.06491           | 0.05891           | 0.06191                       | 0.0030                           |
| 2.0                 | 0.68794           | 0.23266           | 0.08916           | 0.08319           | 0.08618                       | 0.0030                           |
| **3.1 eq of PrOH**  |                   |                   |                   |                   |                               |                                  |
| 0.00275             | 1                 | 0.55601           | 0.00124           | 0.00046           | 0.00085                       | 0.0003                           |
| 0.1                 | 0.83989           | 0.44390           | 0.00390           | 0.00530           | 0.00460                       | 0.0007                           |
| 0.2                 | 0.94760           | 0.47830           | 0.01209           | 0.01036           | 0.01123                       | 0.0009                           |
| 0.3                 | 0.93418           | 0.44656           | 0.01900           | 0.01625           | 0.01763                       | 0.0014                           |
| 0.4                 | 0.92254           | 0.41758           | 0.02519           | 0.01975           | 0.02247                       | 0.0027                           |
| 0.5                 | 0.90495           | 0.38983           | 0.02885           | 0.02306           | 0.02596                       | 0.0029                           |
| 0.6                 | 0.89325           | 0.36667           | 0.03283           | 0.02788           | 0.03036                       | 0.0025                           |
| 1.0                 | 0.74878           | 0.24792           | 0.04023           | 0.03547           | 0.03785                       | 0.0024                           |
| 2.0                 | 0.77697           | 0.15278           | 0.06642           | 0.05734           | 0.06188                       | 0.0045                           |
| **4.6 eq of PrOH**  |                   |                   |                   |                   |                               |                                  |
| 0.00275             | 1                 | 0.37307           | 0.00250           | 0.00190           | 0.00220                       | 0.0003                           |
| 0.1                 | 0.96628           | 0.33963           | 0.00489           | 0.00446           | 0.00468                       | 0.0002                           |
| 0.2                 | 0.94982           | 0.31750           | 0.00791           | 0.00615           | 0.00703                       | 0.0009                           |
| 0.3                 | 0.94611           | 0.29637           | 0.01225           | 0.00988           | 0.01107                       | 0.0012                           |
| 0.4                 | 0.93450           | 0.27773           | 0.01545           | 0.01227           | 0.01386                       | 0.0016                           |
| 0.5                 | 0.92675           | 0.26065           | 0.01890           | 0.01462           | 0.01676                       | 0.0021                           |
| 0.6                 | 0.91912           | 0.24376           | 0.02221           | 0.01716           | 0.01969                       | 0.0025                           |
| 1.0                 | 0.89490           | 0.18900           | 0.03240           | 0.02453           | 0.02847                       | 0.0039                           |
| 2.0                 | 0.84481           | 0.10122           | 0.04652           | 0.03539           | 0.04096                       | 0.0056                           |
Figure S-6: $^1$H,$^1$H EXSY NMR plot based on the data given in Table S-1.

For quantitative evaluation, the collected 2D-EXSY data was subjected to a matrix evaluation technique as it was proposed by Perrin and Gipe\textsuperscript{7, 8} based on previous work from Macura and Ernst\textsuperscript{9}. It solves the fundamental equation S-7, which relates the cross and diagonal peak intensities $I_{ij}$, the equilibrium magnetization $M_j^0$, the mixing time $d8$, and the desired rate matrix $R$ by

$$I_{ij} = M_j^0 \cdot (e^{-R \cdot d8})_{ij}.$$ \hspace{1cm} (S-7)

The components of $R$ can be obtained by calculating

$$R = -\frac{\ln A}{d8} = -\frac{X (\ln A) X^{-1}}{d8}.$$ \hspace{1cm} (S-8)

The matrix $A$ contains the normalized peak intensities which are directly obtainable through diagonal and cross peak integration:

$$A_{ij} = \frac{I_{ij}}{M_j^0}.$$ \hspace{1cm} (S-9)

$X$ is the eigenvector matrix of $A$. That means

$$X^{-1}AX = \Lambda = \text{diag}(\lambda_i)$$ \hspace{1cm} (S-10)

and
\[ \ln(\Lambda) = \text{diag}(\lambda_i). \]  

(S-11)

\( \lambda_i \) are the eigenvalues of \( A \).

This mathematical scheme is implemented in the Mestrelab Research EXSY evaluation applet EXSYCalc, which was used for calculating the magnetization exchange rates \( k' \). These are the off-diagonal elements of \( R \), which is a 2x2 matrix for the here studied problem. The magnetization exchange rates \( k' \) can be directly related to the chemical reaction rates \( k \) by considering an appropriate kinetic model. For the self-exchange of isopropanol at \([1]^-\) (Scheme S-5), two kinetic models can be imagined – a dissociative or an associative mechanism (Scheme S-6).

**Equilibrium which is excessed by \( \text{\textsuperscript{1}H,\text{\textsuperscript{1}H EXSY NMR measurements} \[ \begin{array}{c|c}
\text{free \textsuperscript{\textsuperscript{1}PrOH}} & \text{bound \textsuperscript{\textsuperscript{1}PrOH}} \\
\hline
\end{array} \right]
\] **

**Possible exchange kinetics and mechanisms**

\[
\begin{align*}
[1]^- & \quad \xrightarrow{k_1} \quad [[\text{\textsuperscript{\textsuperscript{1}PrO}-1-H]]^- \\
[[\text{\textsuperscript{\textsuperscript{1}PrO}-1-H]]^- & \quad \xrightarrow{k_1} \quad [1]^- + \text{\textsuperscript{\textsuperscript{1}PrOH}}
\end{align*}
\]

\( k_1 = k_1 / \text{[1]^-} \), \( k_1 = k_1' \)

**Mechanistic picture**

\[ S \text{HEME S-6: Hypotheses for the kinetic scheme of the self-exchange of \text{\textsuperscript{\textsuperscript{1}PrOH} at [1]^-} \]}

The dissociative hypothesis implies that \( k_1 \) is not dependent on the concentration of the excess free \( \text{\textsuperscript{\textsuperscript{1}PrOH} \) – in contrast to \( k_1 \) which depends on the added amount of isopropanol. It also implies that \( k_1 = k_1' \) as the dissociation is a first order reaction. In the associative picture, the forward and the backward reaction are identical (\( k_1 = k_1' \)), hence also equally dependent on the free \( \text{\textsuperscript{\textsuperscript{1}PrOH} \) concentration. So, the question was addressed whether and if so, how \( k_1 \) and \( k_1' \) are changing when varying the amount of added \( \text{\textsuperscript{\textsuperscript{1}PrOH} \).

With EXSYCalc, for each \( \text{\textsuperscript{\textsuperscript{1}PrOH} \) concentration and for each mixing time \( d8 \) the magnetization exchange rates \( k' \) were calculated and averaged. The obtained numbers are plotted against the amount of added \( \text{\textsuperscript{\textsuperscript{1}PrOH} \) (Figure S-7). The uncertainty of \( \bar{k}' \) was calculated based on equation S-12.

\[ \Delta \bar{k}' = \sqrt{\frac{\sum_{i=1}^{n} (k_i' - \bar{k})^2}{n \cdot (n - 1)}}, \quad n=8. \]  

(S-12)
Table S-2: Magnetization exchange rates calculated for the individual mixing times d8.

| mixing time, d8 [s] | 0.1 | 0.2 | 0.3 | 0.4 | 0.5 | 0.6 | 1.0 | 2.0 | \( \bar{k} \) | \( \Delta \bar{k} \) |
|---------------------|-----|-----|-----|-----|-----|-----|-----|-----|--------|--------|
| 2.3 eq of iPrOH     |     |     |     |     |     |     |     |     |        |        |
| \( k'_{1,2.3} \)   [s] | 0.104 | 0.094 | 0.096 | 0.088 | 0.093 | 0.093 | 0.091 | 0.093 | 0.094 | 0.002 |
| \( k'_{-1,2.3} \)  [s] | 0.070 | 0.135 | 0.122 | 0.131 | 0.119 | 0.121 | 0.122 | 0.120 | 0.118 | 0.007 |
| 3.1 eq of iPrOH     |     |     |     |     |     |     |     |     |        |        |
| \( k'_{1,3.1} \)   [s] | 0.065 | 0.057 | 0.062 | 0.059 | 0.058 | 0.060 | 0.061 | 0.060 | 0.060 | 0.001 |
| \( k'_{-1,3.1} \)  [s] | 0.086 | 0.120 | 0.131 | 0.136 | 0.130 | 0.128 | 0.124 | 0.125 | 0.123 | 0.006 |
| 4.6 eq of iPrOH     |     |     |     |     |     |     |     |     |        |        |
| \( k'_{1,4.6} \)   [s] | 0.048 | 0.034 | 0.038 | 0.037 | 0.036 | 0.037 | 0.036 | 0.035 | 0.038 | 0.002 |
| \( k'_{-1,4.6} \)  [s] | 0.140 | 0.118 | 0.126 | 0.124 | 0.126 | 0.127 | 0.127 | 0.124 | 0.126 | 0.002 |

Figure S-7: Mean magnetization exchange rates \( k' \) plotted against the added equivalents of iPrOH relative to [1].

It is found that \( k' \) is decreasing with an increasing amount of added iPrOH; \( k'_{-1} \) remains constant, within the error margins. This is a strong argument against the associative mechanism, which demands for the identical influence of the iPrOH concentration on both rate constants. \( k'_{-1} = k'_{1} \) stays constant which is consistent with the dissociative mechanism. The surprising fact that \( k' \) is decreasing with an increasing free iPrOH concentration remains unanswered. However, it is not of importance for qualitatively distinguishing between the associative and the dissociative path.

The three \( k'_{-1} \) values were averaged and the mean value (\( k_{obs} \)) was used to estimate the Gibbs free activation energy \( \Delta R G^{\ddagger} \) at 298.15 K for the release of isopropanol from \([1]^-\) by following

\[
\Delta R G^{\ddagger} = -RT \cdot \ln \left( \frac{k_{obs} \cdot h}{\kappa \cdot k_B \cdot T} \right), \kappa = 1,
\]  
(S-13)
with

$$\Delta(\Delta R G^\ddagger) = \frac{R \cdot T}{k_{obs}} \cdot \Delta k_{obs}.$$  \hspace{1cm} (S-14)

$$k_{obs} = (0.122 \pm 0.009) \text{ s}^{-1}$$

$$\Delta R G^\ddagger = (78.2 \pm 0.2) \text{ kJ mol}^{-1}$$

The two exchange mechanisms were also analyzed by DFT calculations (see Chapter S-14). The Gibbs free activation energies for the two transition states of the dissociative path were calculated to $\Delta R G^\ddagger_{TS-A} = 40.3 \text{ kJ mol}^{-1}$ and $\Delta R G^\ddagger_{TS-B} = 62.6 \text{ kJ mol}^{-1}$.

### S-7. Deuterium labeling experiments

Three deuterium labeling experiments were carried out with ethanol-$d_1$ (EtOD, $\rho = 0.806 \text{ g cm}^{-3}$). First, [PPh₄][1] (9 mg, 11.4 µmol, 1.0 eq) was reacted with ethanol-$d_1$ (1.13 µL, 19.3 µmol, 1.7 eq) in CH₂Cl₂ (0.6 mL). The reaction was followed over time by $^1$H NMR spectroscopy. The singlet resonance at 5.60 ppm (transferred proton) was found increasing, whereas all signals of the pyrrolic protons ($\beta$-protons) decreased (Figure S-8, S-9).

**Figure S-8:** $^1$H NMR spectra (400 MHz, 600 MHz (only red spectrum), CD₂Cl₂, 298 K) of a sample of [PPh₄][1] treated with EtOD. The given times are the elapsed times after EtOD addition. Red spectrum: $^1$H NMR spectrum of [PPh₄][EtO-$d_1$-$^1$H] for comparison. The signal of CHDCI₂ and that of residual CH₂Cl₂, which is contained in [PPh₄][1], are marked with a red asterisk.
Figure S-9: Integral values extracted from the spectra shown in Figure S-8 plotted against the time after EtOD addition.

Second, [PPh₄][1] (9 mg, 11.4 μmol, 1.0 eq) was treated with a slight excess of ethanol-d₆ (0.75 μL, 12.8 μmol, 1.1 eq) in CH₂Cl₂ (0.6 mL). The sample was analyzed by ²H NMR spectroscopy several hours after EtOD addition. The obtained result resembles the aromatic region of the ¹H NMR spectrum of [(EtO)-¹⁴H]- acquired in CD₂Cl₂. Hence, the deuterium label is statistically distributed over all possible nine backbone positions. This is a strong indication for the addition of EtOH(D) to [1]⁻ to be reversible and proves the H/D scrambling within [PPh₄][(EtO)-¹⁴H(D)].

Figure S-10: A) ¹H NMR spectrum (92 MHz, CH₂Cl₂, 298 K) of [PPh₄][1] treated with a slight excess of EtOD. To the sample was added as a reference 0.5 μL CD₂Cl₂ (black asterisk). B) ²H NMR spectrum (600 MHz, CD₂Cl₂) of [PPh₄][(EtO)-¹⁴H]. The signal of CHDCl₂ and that of residual CH₂Cl₂, which is contained in [PPh₄][1], are marked with a red asterisk.
**Mechanism.** For the H/D scrambling mechanism, we propose a series of [1,5]H/D sigmatropic shiftings (Scheme S-7). First, ethanol-\(d_1\) undergoes the addition reaction to [1]− and [(EtO)-1*−D]− is formed. From there, thermally allowed [1,5]H/D sigmatropic shiftings proceed in a suprafacial manner, that is, the shifting H or D remains on the same side of the pyrrole ring. To ensure that the observed scrambling is a thermally driven reaction, the first reaction mentioned above was repeated under the exclusion of light. The same scrambling was found. Hence, in [(EtO)-1*−D]−, a thermal [1,5]D sigmatropic rearrangement takes place to give iso-[(EtO)-1*−D]−. This compound can undergo four further sigmatropic rearrangements. First, the reaction back to [(EtO)-1*−D]− which is of course not productive. Also not productive is a sigmatropic shift of a proton to the 2-position of the dearomatized pyrrole ring but trans to the bound alkoxo substituent ([(EtO)-1−d*−H]−). This would deny alcohol dissociation from [1]−.

However, two additional pathways are productive. Both of which include the formation of an iso' tautomer that is either formed through a [1,5]D sigmatropic shift (path A, iso'−[(EtO)-1*−D]−) or through a [1,5]H sigmatropic shift (path B, iso'−[(EtO)-1−d*−H]−). Path A is completed by the reformation of the iso tautomer by a H sigmatropic shift (iso−[(EtO)-1−d*−H]−) and subsequent transfer of a proton to the 2-position of the pyrrole ring which gives [(EtO)-1−d*−H]−. Now, EtOH can be eliminated from the aluminate, and [1−d]− is obtained. Similarly, in path B, iso'−[(EtO)-1−d*−H]− undergoes a sigmatropic rearrangement to iso−[(EtO)-1*−D]− that is also capable of delivering a proton to the 2-position of the dearomatized pyrrole ring. The thereby obtained [(EtO)-1−d*−H]− eliminates EtOH, and [1−d]− is formed. These cascades of [1,5]H/D sigmatropic shiftings allow for the statistical distribution of the deuterium label introduced by EtOD.

A full quantum chemical investigation of the reaction pathways shown in Scheme S-7 was carried out. The obtained results support the proposed mechanism and are presented in Chapter 15.
Scheme S-7: Proposed mechanism for the H/D scrambling observed in [1]$^-$ when treated with EtOD.

Third, it was also tested to which degree the $\beta$-protons in [1]$^-$ can be exchanged against deuterium atoms by the described mechanistic scenario, that is alcohol addition and H/D scrambling via $[1,5]$H/D sigmatropic rearrangements. For that, $[\text{PPh}_4][1]$ (9 mg, 11.4 $\mu$mol, 1.0 eq) was treated with ethanol-$d_1$ (23.90 $\mu$L, 409.6 $\mu$mol, 36.0 eq) in $\text{CD}_2\text{Cl}_2$ (0.6 mL). After 24 h at room temperature, the sample was analyzed by electrospray ionization mass spectrometry. The thereby obtained results gave significantly more inside compared to the results obtained by $^1$H NMR spectroscopy. Under the applied ESI-MS conditions, the alcohol addition products always underwent dissociation to a certain degree. This dissociation was especially pronounced with ethanol as substrate. So the detected peaks of free $[1-\text{d}_{4}]^-$ were used for evaluation (Figure S-11). The data of interest is:

| compound | molecular formula | exact mass [u] |
|----------|-------------------|----------------|
| $[1-\text{d}_0]^-$ | C$_{28}$H$_{32}$AlN$_4$ | 451.2448 |
| $[1-\text{d}_1]^-$ | C$_{28}$H$_{31}$D$_1$AlN$_4$ | 452.2511 |
| $[1-\text{d}_2]^-$ | C$_{28}$H$_{30}$D$_2$AlN$_4$ | 453.2573 |
| $[1-\text{d}_3]^-$ | C$_{28}$H$_{29}$D$_3$AlN$_4$ | 454.2636 |
| $[1-\text{d}_4]^-$ | C$_{28}$H$_{28}$D$_4$AlN$_4$ | 455.2699 |
| $[1-\text{d}_5]^-$ | C$_{28}$H$_{27}$D$_5$AlN$_4$ | 456.2762 |
| [1-\textit{d}_x]^- | C_{28}H_{26}D_xAlN_4 | 457.2824 |
|-------------------|---------------------|-----------|
| [1-\textit{d}_7]^- | C_{28}H_{25}D_7AlN_4 | 458.2887 |
| [1-\textit{d}_8]^- | C_{28}H_{24}D_8AlN_4 | 459.2950 |

Figure S-11: Excerpt of the mass spectrum of the sample of the H/D exchange experiment after 24 h at room temperature.
The mass spectrum directly shows that the compounds with C$_{28}$H$_{32}$AlN$_4$ (m/z = 451.2448) and C$_{28}$H$_{31}$D$_1$AlN$_4$ (m/z = 452.2511) are not present. For all other detected peaks, the relative signal intensities were extracted.

| m/z     | relative intensity |
|---------|--------------------|
| 453.2309| 1.00               |
| 454.2372| 5.86               |
| 455.2436| 24.00              |
| 456.2493| 64.14              |
| 457.2554| 106.00             |
| 458.2612| 106.00             |
| 459.2667| 60.29              |
| 460.2699| 13.86              |
| 461.2730| 2.14               |

Within [1-d$_i$]$^-$, the only atoms responsible for a significant isotope pattern are the 28 carbon atoms. The pattern scales with 1.000, 0.303, 0.044, and 0.004. The scaling factors were obtained with the protpi online MassSpecSimulator (https://www.protpi.ch/Calculator/MassSpecSimulator#MassSpecSimulatorResult, 05.08.2020). So, for each peak the relative contributions (monoisotopic and isotope pattern contribution) using the given scaling factor were calculated:

453.2309: 1.00 – 0 = 1.00
454.2372: 5.86 – 0.303 · 1.00 = 5.5570
455.2436: 24.00 – 0.303 · 5.5570 – 0.044 · 1.00 = 22.2722
456.2493: 64.14 – 0.303 · 22.2722 – 0.044 · 5.5570 – 0.004 · 1.00 = 57.1430
257.2554: 106.00 – 0.303 · 57.1430 – 0.044 · 22.2722 – 0.004 · 5.5570 = 87.6835
458.2612: 106.00 – 0.303 · 87.6835 – 0.044 · 57.1430 – 0.004 · 22.2722 = 76.8285
459.2667: 60.29 – 0.303 · 76.8285 – 0.044 · 87.6835 – 0.004 · 57.1430 = 32.9243
460.2699: 13.86 – 0.303 · 32.9243 – 0.044 · 76.8285 – 0.004 · 87.6835 = 0.1527
461.2730: 2.14 – 0.044 · 32.9243 – 0.004 · 76.8285 = 0.3840

The obtained values for m/z = 460.2699 and 461.2730 are close to zero. This is in line with the fact that those two peaks only arise from the isotope pattern of the signals of [1-d$_8$]$^-$ (m/z = 459.2667), [1-d$_7$]$^-$ (m/z = 458.2612), and [1-d$_6$]$^-$ (m/z = 257.2554).

The other numbers represent the relative distribution of the different degrees of deuteration:

| [1-d$_8$]$^-$ | [1-d$_7$]$^-$ | [1-d$_6$]$^-$ | [1-d$_5$]$^-$ | [1-d$_4$]$^-$ | [1-d$_3$]$^-$ | [1-d$_2$]$^-$ | [1-d$_1$]$^-$ | [1-d$_0$]$^-$ |
|---------------|---------------|---------------|---------------|---------------|---------------|---------------|---------------|---------------|
| 0.0           | 0.0           | 1.0           | 5.6           | 22.3          | 57.1          | 87.7          | 76.8          | 32.9          |
| 0.0%          | 0.0%          | 0.4%          | 2.0%          | 7.9%          | 20.2%         | 30.9%         | 27.1%         | 11.6%         |
The total degree of deuteration is calculated to

\[
\frac{0.004 \cdot 2 + 0.02 \cdot 3 + 0.079 \cdot 4 + 0.202 \cdot 5 + 0.309 \cdot 6 + 0.271 \cdot 7 + 0.116 \cdot 8}{8} = 76\%.
\] (S-15)

To verify the calculated data, the mass spectrum was simulated with the protpi applet (Figure S-12A) and was found in excellent agreement with the experimentally obtained spectrum.

**S-8. Autoprotolysis**

The alcohol addition products show amphoteric behavior manifested in an autoprotolysis equilibrium (Figure S-13, S-22). This equilibrium is sensitive to the solvent environment. It can be enforced by the addition of an excess pentane to the dichloromethane solution of the addition products \([\text{PPh}_4][\text{RO}]-^\text{1*-H}\). This was shown for three substrates: ethanol, para-methylbenzyl alcohol, and para-nitrobenzyl alcohol. The entirety of all observations is discussed in Chapter S-10.

**Figure S-13: Autoprotolysis equilibrium of the alcohol addition products \([\text{PPh}_4][\text{RO}]-^\text{1*-H}\).**

| m/z     | relative intensity |
|---------|--------------------|
| 453.2654 | 1.00               |
| 454.2636 | 5.82               |
| 455.2691 | 23.94              |
| 456.2745 | 63.66              |
| 457.2818 | 105.25             |
| 458.2872 | 105.24             |
| 459.2927 | 59.83              |
| 460.2964 | 14.25              |
| 461.3000 | 1.96               |
General procedure. In a dry nitrogen-filled glove box, [PPh₄][1] (45 mg, 56.9 μmol, 1.0 eq) was dissolved in CH₂Cl₂ (1.0 mL) in a crimp-top vial, and the equimolar amount of the alcohol substrate was added in one portion at room temperature. The solution turned yellow (orange in the case of para-nitrobenzyl alcohol) upon substrate addition. Pentane (5.0 mL) was added what resulted in the precipitation of a yellow (orange in the case of para-nitrobenzyl alcohol) solid. The vial was sealed, and the reaction mixture was allowed to stand for several days (> 2 days) at room temperature. The supernatant was separated from the solid material at the bottom of the vial and was filtered through a PTFE syringe filter. The solvent was removed under reduced pressure to give in all cases, after drying in vacuo, pale yellow solids ((RO)-1**-HH). The orange precipitate (mixture of [PPh₄]₂[(RO)-1] and [PPh₄][(RO)-1*]-H) was dried in vacuo. Both obtained substances were analyzed by NMR spectroscopy. The ¹³C{¹H} NMR signals of the [PPh₄]₂[(RO)-1] were partially identified by ¹H,¹³C HMBC and ¹H,¹³C HSQC NMR spectroscopy.

(EtO)-1**-HH

¹H NMR (600 MHz, CD₂Cl₂, 295 K), δ [ppm] = 7.61 (d, 3JHH = 5.3 Hz, 2H, H-2), 7.02 (dd, 3JHH = 5.3 Hz, 4JHH = 1.4 Hz, 2H, H-3), 6.04 (d, 3JHH = 3.2 Hz, 2H, β-H), 5.93 (d, 3JHH = 3.2 Hz, 2H, β-H), 4.88 (s, 2H, H-1), 3.39-3.32 (m, 1H, H-5A/5B), 3.11-3.04 (m, 1H, H-5A/5B), 1.84 (s, 6H, α-Me), 1.79 (s, 6H, α-Me), 1.54 (s, 6H, α-Me), 0.86 (t, 3JHH = 7.0 Hz, 3H, H-6), 0.38 (s, 6H, α-Me).

¹³C{¹H} NMR (151 MHz, CD₂Cl₂, 295 K), δ [ppm] = 188.9 (C₉, C-4), 155.2 (CH, C-2), 149.6 (C₉, C₉-pyrrole), 143.5 (C₉, C₉-pyrrole), 129.1 (CH, C-3), 104.5 (CH, β-C), 102.5 (CH, β-C), 87.2 (CH, C-1), 56.8 (CH₃, C-5), 39.3 (C₉, α-C), 38.9 (C₉, α-C), 30.7 (CH₃, α-Me), 28.7 (CH₃, α-Me), 27.7 (CH₃, α-Me), 23.3 (CH₃, α-Me), 20.1 (CH₃, C-6).
\[ \text{[PPh}_4\text{][(EtO)]}_2\]
\[ \text{[PPh}_4\text{]}_2[(\rho-\text{MeBnO})-1] \]

**^1H NMR** (600 MHz, CD\(_2\)Cl\(_2\), 295 K), \( \delta \) [ppm] = 7.87-7.79 (m, 8H, PPh\(_4^+\)), 7.72-7.63 (m, 16H, PPh\(_4^+\)), 7.59-7.50 (m, 16H, PPh\(_4^+\)), 6.79-6.76 (m, 2H, H-3), 6.63-6.59 (m, 2H, H-4) 5.59 (d, 3J\( \text{HH} \) = 2.8 Hz, 4H, \( \beta \)-H), 5.58 (d, 3J\( \text{HH} \) = 2.8 Hz, 4H, \( \beta \)-H), 3.49 (s, 2H, H-1), 2.06 (s, 3H, H-6), 1.57 (s, 6H, \( \alpha \)-Me), 1.52 (s, 6H, \( \alpha \)-Me), 1.49 (s, 6H, \( \alpha \)-Me), 1.26 (s, 6H, \( \alpha \)-Me).

**\(^{13}\text{C}\(^1\text{H}\) / \(^1\text{H},^{13}\text{C}\) HSQC / \(^1\text{H},^{13}\text{C}\) HMBC NMR** (600 / 151 MHz, CD\(_2\)Cl\(_2\), 295 K), \( \delta \) [ppm] = 148.2 (C\(_q\), C\(_q\)-pyrrole), 147.4 (C\(_q\), C-2), 147.3 (C\(_q\), C\(_q\)-pyrrole), 136.1 (CH, d, 3J\( \text{CP} \) = 3.0 Hz, PPh\(_4^+\)), 134.8 (CH, d, 3J\( \text{CP} \) = 10.3 Hz, PPh\(_4^+\)), 132.3 (C\(_q\), C-5), 131.0 (CH, d, 3J\( \text{CP} \) = 12.9 Hz, PPh\(_4^+\)), 127.5 (CH, C-4), 126.1 (CH, C-3), 117.9 (C\(_q\), d, 3J\( \text{CP} \) = 89.6 Hz, PPh\(_4^+\)), 99.6 (CH, \( \beta \)-C), 97.1 (CH, \( \beta \)-C), 62.1 (CH\(_2\), C-1), 42.9 (CH\(_3\), \( \alpha \)-Me), 36.9 (C\(_q\), \( \alpha \)-C), 36.3 (C\(_q\), \( \alpha \)-C), 35.7 (CH\(_3\), \( \alpha \)-Me), 32.7 (CH\(_3\), \( \alpha \)-Me), 26.8 (CH\(_3\), \( \alpha \)-Me), 21.0 (CH\(_3\), C-6).

\( (\rho-\text{NO}_2\text{BnO})-1**-HH \)

**^1H NMR** (600 MHz, CD\(_2\)Cl\(_2\), 295 K), \( \delta \) [ppm] = 8.01-9.97 (m, 2H, H-8), 7.68 (d, 3J\( \text{HH} \) = 5.3 Hz, 2H, H-2), 7.33-7.30 (m, 2H, H-7), 7.05 (dd, 3J\( \text{HH} \) = 5.3 Hz, 4J\( \text{HH} \) = 1.2 Hz, 2H, H-3), 6.06 (d, 3J\( \text{HH} \) = 3.2 Hz, 2H, \( \beta \)-H), 5.98 (d, 3J\( \text{HH} \) = 3.2 Hz, 2H, \( \beta \)-H), 5.03 (s, 2H, H-1), 4.63 (d, 3J\( \text{HH} \) = 16.1 Hz, 1H, H-5A/5B), 4.28 (d, 3J\( \text{HH} \) = 16.1 Hz, 1H, H-5A/5B), 1.82 (s, 6H, \( \alpha \)-Me), 1.593 (s, 6H, \( \alpha \)-Me), 1.590 (s, 6H, \( \alpha \)-Me), 0.44 (s, 6H, \( \alpha \)-Me).
$^{13}$C($^1$H) NMR (151 MHz, CD$_2$Cl$_2$, 295 K), $\delta$ [ppm] = 189.2 (C$\alpha$, C-4), 155.5 (CH, C-2), 154.3 (C$\alpha$, C-9), 149.6 (C$\alpha$, C-$\alpha$-pyrrole), 146.6 (C$\alpha$, C-6), 143.5 (C$\alpha$, C-$\alpha$-pyrrole), 129.1 (CH, C-3), 126.4 (CH, C-7), 123.2 (CH, C-8), 104.8 (CH, $\beta$-C), 102.8 (CH, $\beta$-C), 87.3 (CH, C-1), 63.0 (CH$_2$, C-5), 39.4 (C$\alpha$, $\alpha$-C), 38.9 (C$\alpha$, $\alpha$-C), 30.9 (CH$_3$, $\alpha$-Me), 28.7 (CH$_3$, $\alpha$-Me), 27.7 (CH$_3$, $\alpha$-Me), 23.4 (CH$_3$, $\alpha$-Me).

$^{13}$C($^1$H) / $^1$H, $^{13}$C HSQC / $^1$H, $^{13}$C HMBC NMR (600 / 151 MHz, CD$_2$Cl$_2$, 295 K), $\delta$ [ppm] = 160.5 (C$\alpha$, C-2), 148.2 (C$\alpha$, C-$\alpha$-pyrrole), 147.4 (C$\alpha$, C-$\alpha$-pyrrole), 144.9 (C$\alpha$, C-5), 136.2 (CH, d, $^3$J$_{CH} = 3.0$ Hz, PPh$_4^+$), 134.8 (CH, d, $^2$J$_{CH} = 10.3$ Hz, PPh$_4^+$), 131.0 (CH, d, $^3$J$_{CH} = 12.9$ Hz, PPh$_4^+$), 126.9 (CH, C-4), 122.1 (CH, C-3), 117.8 (C$\alpha$, d, $^1$J$_{CH} = 89.5$ Hz, PPh$_4^+$), 99.7 (CH, $\beta$-C), 97.4 (CH, $\beta$-C), 62.7 (CH$_2$, C-1), 42.8 (CH$_3$, $\alpha$-Me), 36.6 (C$\alpha$, $\alpha$-C), 36.2 (C$\alpha$, $\alpha$-C), 35.6 (CH$_3$, $\alpha$-Me), 32.8 (CH$_3$, $\alpha$-Me), 26.8 (CH$_3$, $\alpha$-Me).
Figure S-14: $^1$H NMR spectrum (600 MHz, CD$_2$Cl$_2$, 298 K). A) of the solid material obtained from the autoprotolysis reaction with ethanol as substrate. It is a mixture of [PPh$_4$][(EtO)$_2$], [PPh$_4$][(EtO)$_2$-1*H] (1:0.5), [1$^-$], and EtO$^-$ (1:1) (see Figure S-15). B) of the substance, which was dissolved in the supernatant. It is (EtO)$_2$-1**-H, and C) of [PPh$_4$][(EtO)$_2$-1*H] for comparison. The signal(s) of CHDCl$_2$ and that of residual CH$_2$Cl$_2$, which is contained in [PPh$_4$][1], is marked with a red, those of residual pentane with gray asterisks.

Figure S-15: Excerpt of the $^1$H NMR spectrum (600 MHz, CD$_2$Cl$_2$, 298 K) of the solid material obtained from the autoprotolysis reaction with ethanol as substrate. The signal(s) of CHDCl$_2$ is marked with a red, those of residual pentane with gray asterisks.
Figure S-16: $^1$H NMR spectrum (600 MHz, CD$_2$Cl$_2$, 298 K), A) of the solid material obtained from the autoprotolysis reaction with para-methylbenzyl alcohol. It is a mixture of [PPh$_4$][(p-MeBnO)-1] and [PPh$_4$][(p-MeBnO)-1$^*$-H] (1:0.5), B) of the substance, which was dissolved in the supernatant. It is (p-MeBnO)-1$^*$-HH, and C) of [PPh$_4$][(p-MeBnO)-1$^*$-H] for comparison. The signal(s) of CHDCl$_2$ and that of residual CH$_2$Cl$_2$, which is contained in [PPh$_4$][1], is marked with a red, those of residual pentane with gray asterisks.

Figure S-17: $^1$H NMR spectrum (600 MHz, CD$_2$Cl$_2$, 298 K), A) of the solid material obtained from the autoprotolysis reaction with para-nitrobenzyl alcohol as substrate. It is a mixture of [PPh$_4$][(p-NO$_2$BnO)-1] and [PPh$_4$][(p-NO$_2$BnO)-1$^*$-H] (1:1.8), B) of the substance, which was dissolved in the supernatant. It is (p-NO$_2$BnO)-1$^*$-HH, and C) of [PPh$_4$][(p-NO$_2$BnO)-1$^*$-H] for comparison. The signal(s) of CHDCl$_2$ and that of residual CH$_2$Cl$_2$, which is contained in [PPh$_4$][1], is marked with a red, those of residual pentane with gray asterisks.
S-9. Alcohol excess and protonation of [(ρ-BrPhO)-1*-H]−

The behavior of [1]− in the presence of an excess of the alcohol substrates was studied. In general, [1]− can withstand excesses of alcohols and does not undergo alcoholysis (Figure S-18, S-19, S-20). This allowed us to investigate the self-exchange of isopropanol at [1]− (Chapter S-6).

Figure S-18: 1H NMR spectrum (400 MHz, CD2Cl2, 298 K) of [PPh4][PrO]-1*-H in the presence of an excess of ‘PrOH (*, 3.6 eq). The signal of CH2Cl2 and that of residual CH2Cl2, which is contained in [PPh4][1], are marked with a red asterisk.
Figure S-19: $^1$H NMR spectrum (200 MHz (bottom), 600 MHz (top), CD$_2$Cl$_2$, 298 K) of A) [PPh$_4$][(iPrOH)-1*-H] in the presence of a large excess of isopropanol (53 eq relative to the addition product) and of B) [PPh$_4$][(PrOH)-1*-H] for comparison. The signals of free isopropanol are marked with orange asterisks. The signal of CHDCl$_2$ and that of residual CH$_2$Cl$_2$, which is contained in [PPh$_4$][1], are marked with a red asterisk.

Figure S-20: $^1$H NMR spectrum (600 MHz, CD$_2$Cl$_2$, 298 K) of [PPh$_4$][(p-MeBnO)-1*-H] in the presence of an excess of p-MeBnOH (*, 1.4 eq). The signal of CHDCl$_2$ and that of residual CH$_2$Cl$_2$, which is contained in [PPh$_4$][1], are marked with a red asterisk.
However, when a significantly more acidic substrate such as para-bromophenol was used in excess the quantitative conversion to the neutral \((p\text{-BrPhO})-1^{**}\cdot HH\) was observed by \(^1\text{H}\) NMR spectroscopy (Figure S-21). This means that a sufficiently acidic OH substrates can quantitatively protonate the alcohol addition products \((p\text{-BrPhO})-1^{*-}\cdot H\).

![Figure S-21: \(^1\text{H}\) NMR spectra (200 MHz, CD\(_2\)Cl\(_2\), 298 K) of [PPh\(_4\)]\((p\text{-BrPhO})-1^{*}\cdot H\)](bottom) and after subsequent additions of \(p\text{-BrPhOH}\) portions until full conversion to \((p\text{-BrPhO})-1^{**}\cdot HH\) was achieved (top). The signal of CHDC\(_2\) and that of residual CH\(_2\)Cl\(_2\), which is contained in [PPh\(_4\)]\(n\), are marked with a red asterisk.

S-10. Mechanistic proposals and stereochemical considerations

The \(^1\text{H}\) NMR signals of the neutral \((RO)-1^{**}\cdot HH\) species were observed, though only with minute intensities, when the alcohol addition products were prepared (see Chapter S-3). Nonetheless, the \(^1\text{H}\) NMR signals of the dianionic \([(RO)-1]^{2-}\) were never observed, or only in an even weaker intensity compared to the already weak resonances of \((RO)-1^{**}\cdot HH\) during the alcohol addition reactions. The dianionic species were only isolable through the addition of an excess of pentane to the dichloromethane solutions of [PPh\(_4\)]\((RO)-1^{*-}\cdot H\) (see Chapter S-8). We thus propose the following mechanistic picture (Figure S-22): the equilibrium between the \([(RO)-1]^{*}\cdot H\] and \([1]^{-}\) + ROH (B) provides a small amount of alcohol substrate that does not undergo addition to [1]⁻ but instead protonates [(RO)-1^{*-}\cdot H]⁻ to give (RO)-1^{**}\cdot HH (C), as it was detected by \(^1\text{H}\) NMR spectroscopy. This equilibrium (C) also delivers free [1]⁻ and the alcoholate RO⁻. These two species (which are only formed in minute amounts) are now involved in several additional equilibrium reactions such as the normal alcohol addition process to [1]⁻ (B), most likely fast proton transfer reactions between RO⁻ and ROH, and also the equilibrium between RO⁻ + [1]⁻ and \([(RO)-1]^{2-}\) (D). The equilibrium D is strongly lying on the dissociated side, but the dianionic adduct only becomes stable in the solid state. These arguments combined rationalize the fact
that only (RO)-1**-HH, which is not (to the same extend) part in further fast equilibrium reactions, was observed during the preparation of the alcohol addition products, but not [(RO)-1]2−.

That the equilibrium D is indeed occurring was observed when the solid materials from the autoprotolysis reactions (see Chapter S-8) were analyzed by 1H NMR spectroscopy. Three different substrates were used (EtOH, p-MeBnOH, and p-NO2BnOH). First of all, the spectra showed in all cases a mixture of [(RO)-1]2− and [(RO)-1*-H]− (Figure S-14, S-16, S-17). These two species arose from the autoprotolysis equilibrium (A). The excess pentane resulted in the crystallization/precipitation of the charged species [(RO)-1]2− and [(RO)-1*-H]− with PPh4+ as their counter cations whereas the neutral (RO)-1**-HH remained dissolved in the supernatant. When now the solid material from the reaction with EtOH was dissolved in dichloromethane-d2 and was analyzed by 1H NMR spectroscopy, additionally to the signals of [(EtO)-1]2− and [(EtO)-1*-H]− also the characteristic resonances of [1]− were found accompanied by a quartet at 3.77 ppm and a triplet at 1.05 ppm which are assigned to the ethanolate anion EtO− (Figure S-15). With p-MeBnOH and p-NO2BnOH these observations were not made. Here, no [1]− was detected. Thus, with EtOH as substrate, equilibrium D delivers all three involved species ([EtO]-1]2−, [1]−, and EtO−) in sufficient concentration for the detection by 1H NMR spectroscopy. With p-MeBnOH and p-NO2BnOH, however, equilibrium D is strongly lying on the side of [(RO)-1]2−.

Figure S-22: Mechanistic scenario for the interaction of [1]− with protic substrates.

It is also worth to discuss the enrolled mechanistic scenario from a stereochemical point of view. The addition of ROH to [1]− produces a stereogenic center in the ligand backbone which is the 2-position of the dearomatized pyrrole ring. In addition, as it was revealed by SCXRD measurements (see Chapter S-12), the alkoxy ligand at the aluminum center and the transferred proton are in a cis configuration. No indication of the formation of the respective trans diastereomers was found. This supports and is in line with the mechanistic picture of the alcohol addition process, that is coordination of the substrate to the aluminum atom followed by proton transfer to the ligand backbone (see Chapter S-14). Hence, the alcohol addition products [(RO)-1*-H]− are formed diastereospecifically as a racemic mixture.
Chiral are not only the addition products \(((RO)\cdot 1^-\cdot H)^+\), but also the neutral \((RO)\cdot 1^{**}\cdot HH\). They have two stereogenic centers within two dearomatized pyrrole rings vis-à-vis to each other. As shown by SCXRD (see Chapter S-12), both transferred protons and the bound alkoxo ligand are in a cis arrangement. Indications of the formation of other regio- and/or stereoisomers was never found. Hence, the neutral \((RO)\cdot 1^{**}\cdot HH\) are formed from the addition product as racemic mixtures in a diastereois as well as regioispecific manner. The fact that the two transferred protons are in a cis orientation with respect to each other rules out the reaction channel in which a second alcohol substrate would coordinate trans to the bound alkoxo ligand followed by proton transfer to the backbone. This would result in a trans configuration of the two protons in \((RO)\cdot 1^{**}\cdot HH\). This accords with the quantum chemical calculations (see Chapter S-14). A potential mechanism for the formation of \((RO)\cdot 1^{**}\cdot HH\) might be the dissociation of the alkoxo ligand from the addition products \(((RO)\cdot 1^-\cdot H)^+\) and subsequent aluminum-ligand cooperative trapping of a free ROH by the thereby formed \(1^-\cdot H\) to give the \((RO)\cdot 1^{**}\cdot HH\).

S-11. Substitution of alcohol substrates added to \([1]^−\) with donors

The alcohol addition process described in Chapter S-3 can be reversed by Lewis basic donor molecules (pyridine and dimethyl sulfoxide, DMSO). This was shown for four examples (EtOH, \(\cdot 1PrOH\), \(\cdot 1MeBnOH\), \(\cdot 1BrPhOH\)) by treating the alcohol addition products in \(CD_2Cl_2\) (0.6 mL) at room temperature with an excess of pyridine and DMSO, respectively. The substitution reaction was observed by \(^1H\) NMR spectroscopy. Quantitative substitution of the strongly binding \(\cdot 1BrPhOH\) was achieved after 90 min at room temperature by dissolving \([PPh_4][(p\cdot 1BrPhO)\cdot 1^-\cdot H]\) in DMSO-\(d_6\) (0.6 mL).

![Scheme S-8: Substitution of alcohols added to \([1]^−\) with pyridine or DMSO.](image)

To ascertain the identity, the proposed Lewis adducts of pyridine and DMSO with \([1]^−\) were prepared separately. For that, in a dry nitrogen-filled glovebox, tetraphenylphosphonium meso-octamethylcalix[4]pyrrolato aluminate ([PPh₄][1], 10 mg, 12.6 \(\mu\)mol, 1.0 eq) was dissolved in \(CD_2Cl_2\) (0.6 mL) and the equimolar amount of pyridine and DMSO (12.6 \(\mu\)mol, 1.0 eq), respectively, was added to the solution at room temperature.
reaction mixture turned pale yellow immediately after donor addition. The obtained solutions were analyzed by NMR spectroscopy. In both cases quantitative formation of the Lewis acid/base adduct was observed.

\[ \text{[PPh}_4\text{][pyridine]-1} \]

\[ ^1\text{H NMR (600 MHz, CD}_2\text{Cl}_2, 295 \text{ K}), \delta [ppm] = 7.90\text{-}7.82 \text{ (m, 4H, PPh}_4^+), 7.74\text{-}7.65 \text{ (m, 8H, PPh}_4^+), 7.61\text{-}7.56 \text{ (m, 1H, H-3), 7.60\text{-}7.53 \text{ (m, 8H, PPh}_4^+), 7.12\text{-}7.07 \text{ (m, 2H, H-2), 6.84\text{-}6.81 \text{ (m, 2H, H-1), 5.84 (d, }^3\text{J}_{\text{PPh}} = 2.9 \text{ Hz, 4H, }\beta\text{-H), 5.74 (d, }^3\text{J}_{\text{PPh}} = 2.9 \text{ Hz, 4H, }\beta\text{-H), 1.70 (s, 6H, }\alpha\text{-Me), 1.47 (s, 6H, }\alpha\text{-Me), 1.46 (s, 6H, }\alpha\text{-Me), 0.05 (s, 6H, }\alpha\text{-Me).} \]

\[ ^{13}\text{C}(^1\text{H}) \text{ NMR (151 MHz, CD}_2\text{Cl}_2, 295 \text{ K), }\delta [ppm] = 149.5 \text{ (CH, C-1), 148.6 (C}_3\text{, }C\text{-pyrrole), 148.1 (C}_3\text{, }C\text{-pyrrole), 140.2 (CH, C-3), 136.2 (d, }^4\text{J}_{\text{CP}} = 3.0 \text{ Hz, PPh}_4^+), 134.8 (d, }^2\text{J}_{\text{CP}} = 10.3 \text{ Hz, PPh}_4^+), 131.0 (d, }^3\text{J}_{\text{CP}} = 12.9 \text{ Hz, PPh}_4^+), 125.3 \text{ (CH, C-2), 117.8 (d, }^1\text{J}_{\text{CP}} = 89.6 \text{ Hz, PPh}_4^+), 102.1 \text{ (CH, }\beta\text{-C), 99.7 \text{ (CH, }\beta\text{-C), 40.8 (CH}_3\text{, }\alpha\text{-Me), 36.3 (CH}_3\text{, }\alpha\text{-Me), 36.1 (C}_3\text{, }\alpha\text{-C), 35.9 (C}_3\text{, }\alpha\text{-C), 34.5 (CH}_3\text{, }\alpha\text{-Me), 26.4 (CH}_3\text{, }\alpha\text{-Me).} \]

\[ \text{[PPh}_4\text{][dms}-1} \]

\[ ^1\text{H NMR (600 MHz, CD}_2\text{Cl}_2, 295 \text{ K), }\delta [ppm] = 7.87\text{-}7.81 \text{ (m, 4H, PPh}_4^+), 7.70\text{-}7.64 \text{ (m, 8H, PPh}_4^+), 7.58\text{-}7.51 \text{ (m, 8H, PPh}_4^+), 5.83 (d, }^3\text{J}_{\text{PPh}} = 2.9 \text{ Hz, 4H, }\beta\text{-H), 5.76 (d, }^3\text{J}_{\text{PPh}} = 2.9 \text{ Hz, 4H, }\beta\text{-H), 2.05 (s, 6H, H-1), 1.66 (s, 6H, }\alpha\text{-Me), 1.65 (s, 6H, }\alpha\text{-Me), 1.29 (s, 6H, }\alpha\text{-Me).} \]

\[ ^{13}\text{C}(^1\text{H}) \text{ NMR (151 MHz, CD}_2\text{Cl}_2, 295 \text{ K), }\delta [ppm] = 147.9 \text{ (C}_3\text{, }C\text{-pyrrole), 146.9 \text{ (C}_3\text{, }C\text{-pyrrole), 136.2 (d, }^4\text{J}_{\text{CP}} = 3.0 \text{ Hz, PPh}_4^+), 134.8 (d, }^2\text{J}_{\text{CP}} = 10.3 \text{ Hz, PPh}_4^+), 131.0 (d, }^3\text{J}_{\text{CP}} = 12.9 \text{ Hz, PPh}_4^+), 117.8 (d, }^1\text{J}_{\text{CP}} = 89.6 \text{ Hz,} \]

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PPh₄⁺), 101.8 (CH, β-C), 99.8 (CH, β-C), 41.7 (CH₃, α-Me), 38.4 (CH₃, α-Me), 36.4 (Cₙ, a-C), 35.9 (Cₙ, a-C), 34.5 (CH₃, C-1), 33.5 (CH₃, α-Me), 26.3 (CH₃, α-Me).

**EtOH substitution**

Figure S-23: ¹H NMR spectrum (200 MHz, CD₂Cl₂, 298 K), of A) [PPh₄][(EtO)-1*-H], B) [PPh₄][(EtO)-1*-H] with an added excess of pyridine, and C) of [PPh₄][(pyridine)-1]. The signal of CHDCl₂ and that of residual CH₂Cl₂, which is contained in [PPh₄][1], are marked with a red asterisk.

Figure S-24: ¹H NMR spectrum (200 MHz, CD₂Cl₂, 298 K), of A) [PPh₄][(EtO)-1*-H], B) [PPh₄][(EtO)-1*-H] with an added excess of dimethyl sulfoxide, and C) of [PPh₄][(dms)-1]. The signal of CHDCl₂ and that of residual CH₂Cl₂, which is contained in [PPh₄][1], are marked with a red asterisk.
$^1$PrOH substitution

Figure S-25: $^1$H NMR spectrum (200 MHz, CD$_2$Cl$_2$, 298 K), of A) [PPh$_4$][(iPrO)-1*-H], B) [PPh$_4$][(PrO)-1*-H] with an added excess of pyridine, and C) of [PPh$_4$][(pyridine)-1]. The signal of CHDCl$_2$ and that of residual CH$_2$Cl$_2$, which is contained in [PPh$_4$][1], are marked with a red asterisk.

Figure S-26: $^1$H NMR spectrum (200 MHz, CD$_2$Cl$_2$, 298 K), of A) [PPh$_4$][(PrO)-1*-H], B) [PPh$_4$][(PrO)-1*-H] with an added excess of dimethyl sulfoxide, and C) of [PPh$_4$][(dmsO)-1]. The signal of CHDCl$_2$ and that of residual CH$_2$Cl$_2$, which is contained in [PPh$_4$][1], are marked with a red asterisk.
**p-MeBnOH substitution**

Figure S-27: $^1$H NMR spectrum (200 MHz, CD$_2$Cl$_2$, 298 K), of A) [PPh$_4$][(p-MeBnO)-1*-H], B) [PPh$_4$][(p-MeBnO)-1*-H] with an added excess of pyridine, and C) of [PPh$_4$][(pyridine)-1]. The signal of CHDCl$_2$ and that of residual CH$_2$Cl$_2$, which is contained in [PPh$_4$][1], are marked with a red asterisk.

Figure S-28: $^1$H NMR spectrum (200 MHz, CD$_2$Cl$_2$, 298 K), of A) [PPh$_4$][(p-MeBnO)-1*-H], B) [PPh$_4$][(p-MeBnO)-1*-H] with an added excess of dimethyl sulfoxide, and C) of [PPh$_4$][(dmsO)-1]. The signal of CHDCl$_2$ and that of residual CH$_2$Cl$_2$, which is contained in [PPh$_4$][1], are marked with a red asterisk.
p-BrPhOH substitution

Figure S-29: 1H NMR spectrum (200 MHz, CDCl₃ (A), DMSO-d₆ (B, C), 298 K), of A) [PPh₄][(p-BrPhO)-1*:H], B) [PPh₄][(p-BrPhO)-1*:H] dissolved in DMSO-d₆, and C) of [PPh₄][1] dissolved in DMSO-d₆. The signal of CHDCl₂ and that of residual CH₂Cl₂, which is contained in [PPh₄][1], are marked with a red asterisk.

S-12. Xray crystallography

Crystals were grown using the following conditions: [PPh₄][(p-BrPhO)-1*:H]: CH₂Cl₂/toluene solution at -40 °C, (EtO)-1**:HH and [PPh₄][EtO]-1]: [PPh₄][EtO]-1*:H] was prepared in CH₂Cl₂ and five volume equivalents of pentane were added (see Chapter S-8). This mixture produced both crystalline materials at room temperature. [PPh₄][EtO]-1*:H]: CH₂Cl₂/diethyl ether at -40 °C.

For SCXRD measurements, a suitable crystal was picked from the mother liquor, immersed in perfluorinated polyether oil, and fixed on top of a cryo loop. A Bruker APEX-III CCD diffractometer with a low-temperature unit using Mo-Kα radiation, chromated by mirror optics, was used for f and θ scans. Data acquisition was done at 100.0 K. A strategy for data collection was calculated with Bruker’s APEX3 software. The same program was used for processing of collected data. Data reduction, scaling, and absorption corrections were done with SAINT. SA-DABS-2016/2 was used for multi-scan absorption correction. Structures were solved with dual methods as implemented in the ShelXT 2014/5 structure solution program. Structure refinement was carried out by full matrix least squares minimizion on F² using the 2018/3 version of ShelXL. All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated geometrically and refined using a riding model. Handling of the structural data during solution and refinement was performed with the Olex2 v1.3 graphical interface.¹⁰

Data visualization was achieved with Mercury 4.1.3.¹¹⁻¹³ All thermal displacement ellipsoids are shown at the 50% probability level.
Figure S-30: A) Asymmetric unit of the crystal lattice found for \([\text{PPh}_4][(p\text{-BrPhO})-1^*\cdot\text{H}]\), and B) molecular structure of the respective anion, \((p\text{-BrPhO})-1^*\cdot\text{H}\). All hydrogen atoms except for the one which was transferred to the ligand backbone are omitted. Thermal displacement ellipsoids are shown at the 50% probability level.

Selected bond lengths [pm]:
- Al1-N1: 202.1(3)
- Al1-N2: 194.3(3)
- Al1-N3: 193.0(2)
- Al1-N4: 194.9(2)
- Al1-O1: 179.1(2)
- O1-C29: 134.3(3)
- N1-C1: 145.7(4)
- C1-C2: 149.4(4)
- C3-C2: 132.6(5)
- C3-C4: 146.4(4)
- N1-C4: 130.0(4)
- N2-C16: 139.4(4)
- C16-C17: 137.0(4)
- C17-C18: 141.5(4)
- C19-C18: 136.6(4)
- N2-C19: 139.7(4)
- N3-C11: 139.5(4)
- C11-C12: 138.0(4)
- C13-C12: 141.7(4)
- N3-C14: 137.7(4)
- N4-C6: 139.1(4)
- C6-C7: 136.9(4)
- C7-C8: 141.9(4)
- C9-C8: 137.7(4)
- N4-C9: 138.4(4).

Selected bond angles [°]:
- N3-Al1-N1: 165.33(10)
- N2-Al1-N4: 147.90(10)
- O1-Al1-N3: 104.23(10)
- O1-Al1-N2: 102.80(10)
- O1-Al1-N4: 107.97(10)
- N1-C1-C20: 108.9(2)
- N1-C1-C2: 104.1(2)
- C2-C1-C20: 114.1(2)
- C29-O1-Al1: 134.23(17).

Table S-5: Crystal data and structure refinement for \([\text{PPh}_4][(p\text{-BrPhO})-1^*\cdot\text{H}]\) (mo_lms44b_ii_0ma).

| Identification code | mo_lms44b_ii_0ma |
|---------------------|------------------|
| Empirical formula   | C₆₀H₆₁AlBrCl₄N₄OP |
| Formula weight      | 1133.78          |
| Temperature/K       | 100.0            |
| Crystal system      | monoclinic       |
| Space group         | P2₁/n            |
| a/Å                 | 9.7658(18)       |
| b/Å                 | 27.696(6)        |
| c/Å                 | 20.719(4)        |
| α/°                 | 90               |
| β/°                 | 102.380(7)       |
| γ/°                 | 90               |
| Volume/Å³           | 5473.6(19)       |
| Z                   | 4                |
| ρ calc g/cm³        | 1.376            |
| μ/µm⁻¹              | 1.037            |
| F(000)              | 2352.0           |
| Crystal size/mm³    | 0.258 x 0.246 x 0.132 |
| Radiation           | MoKα (λ = 0.71073) |
| 2Θ range for data collection/° | 4.026 to 51 |
| Index ranges        | -11 ≤ h ≤ 11, -33 ≤ k ≤ 33, -25 ≤ l ≤ 25 |
| Reflections collected | 227575          |
| Independent reflections | 10164 [R int = 0.0993, R sigma = 0.0261] |
| Data/restraints/parameters | 10164/0/657      |
Goodness-of-fit on $F^2$ 1.079

Final R indexes [$I>=2\sigma (I)$] $R_1 = 0.0472$, $wR_2 = 0.1251$

Final R indexes [all data] $R_1 = 0.0553$, $wR_2 = 0.1338$

Largest diff. peak/hole / e Å$^{-3}$ 0.99/-0.84

(EtO)-1**-HH

Figure S-31: Asymmetric unit of the crystal lattice found for (EtO)-1**-HH. All hydrogen atoms except for the two which were transferred to the ligand backbone are omitted. Thermal displacement ellipsoids are shown at the 50% probability level.

Selected bond lengths [pm]:
- Al1-O1: 175.31(18)
- Al1-N1: 202.68(19)
- Al1-N2: 192.0(2)
- Al1-N3: 194.2(2)
- Al1-N4: 204.14(19)
- N1-C1: 147.5(3)
- C1-C2: 148.6(3)
- C2-C3: 133.7(4)
- C3-C4: 146.4(3)
- N1-C4: 130.0(3)
- C6-C7: 136.8(3)
- C7-C8: 141.5(3)
- C8-C9: 137.1(3)
- C9-C10: 139.7(3)
- C11-C12: 147.1(3)
- C12-C13: 148.6(3)
- C13-C14: 146.7(3)
- C14-C15: 132.8(4)
- C15-C16: 141.1(3)
- C29-C30: 151.1(4)

Selected bond angles [°]:
- N1-Al1-N3: 169.31(9)
- N2-Al1-N4: 135.06(9)
- N1-C1-C2: 104.4(2)
- N1-C1-C20: 109.93(18)
- C2-C1-C10: 110.69(9)
- O1-Al1-N1: 93.91(8)
- O1-Al1-N2: 111.00(18)
- O1-Al1-N3: 96.76(8)
- O1-Al1-N4: 114.23(9)

| Identification code | mo_lms045_neu_0ba |
|---------------------|------------------|
| Empirical formula   | C$_{30}$H$_{39}$AlN$_4$O |
| Formula weight      | 498.63           |
| Temperature/K       | 100.0            |
| Crystal system      | orthorhombic     |
| Space group         | Pna2$_1$         |
| a/Å                 | 9.7760(9)        |
| b/Å                 | 25.127(2)        |
| c/Å                 | 11.0644(10)      |
| α/°                 | 90               |
| β/°                 | 90               |
| γ/°                 | 90               |
| Volume/Å$^3$        | 2717.9(4)        |
| Z                   | 4                |
| ρcalcg/cm$^3$       | 1.219            |
| μ/mm$^{-1}$         | 0.104            |
| F(000)              | 1072.0           |
Crystal size/mm³ | 0.454 × 0.173 × 0.17
---|---
Radiation | MoKα (λ = 0.71073)
2θ range for data collection/° | 4.47 to 56.652
Index ranges | -13 ≤ h ≤ 13, -33 ≤ k ≤ 33, -14 ≤ l ≤ 14
Reflections collected | 61625
Independent reflections | 6756 [Rint = 0.0718, Rsigma = 0.0365]
Data/restraints/parameters | 6756/1/334
Goodness-of-fit on F² | 1.036
Final R indexes [I>=2σ (I)] | R₁ = 0.0364, wR₂ = 0.0792
Final R indexes [all data] | R₁ = 0.0471, wR₂ = 0.0852
Largest diff. peak/hole / e Å⁻³ | 0.22/-0.24
Flack parameter | -0.02(7)

[PPh₄][[(EtO)-1*-H]]

A) Asymmetric unit of the crystal lattice found for [PPh₄][(EtO)-1*-H], and B) molecular structure of the respective anion, [(EtO)-1*-H]. All hydrogen atoms except for the one which was transferred to the ligand backbone are omitted. Thermal displacement ellipsoids are shown at the 50% probability level.

Only molecular connectivity could be determined due to poor diffraction.

| Table S-7: Crystal data and structure refinement for [PPh₄][(EtO)-1*-H] (mo_lms40_0m). |
|---|---|
| Identification code | mo_lms40_0m |
| Empirical formula | C₁₀₀H₁₂₀Al₂Cl₄N₈O₂P₂ |
| Formula weight | 1843.93 |
| Temperature/K | 120.0 |
| Crystal system | triclinic |
| Space group | P-1 |
| a/Å | 19.4778(18) |
| b/Å | 20.0474(18) |
| c/Å | 28.343(2) |
| α/° | 73.969(2) |
| β/° | 78.374(3) |
| γ/° | 85.119(3) |
| Volume/Å³ | 10413.8(16) |
| Z | 8 |
| ρcalcg/cm³ | 1.176 |
| μ/mm⁻¹ | 0.213 |
| F(000) | 3904.0 |
Crystal size/mm$^3$ 0.104 × 0.093 × 0.082
Radiation MoKα ($\lambda = 0.71073$)
2$\Theta$ range for data collection/° 3.74 to 50
Index ranges -23 ≤ h ≤ 23, -23 ≤ k ≤ 23, -33 ≤ l ≤ 33
Reflections collected 437465
Independent reflections 36658 [R(int) = 0.0754, R(sigma) = 0.0313]
Data/restraints/parameters 36658/0/2341
Goodness-of-fit on F$^2$ 1.016
Final R indexes [I>=2$\sigma$ (I)] R$_1$ = 0.0491, wR$_2$ = 0.1377
Final R indexes [all data] R$_1$ = 0.0990, wR$_2$ = 0.1728

Table S-8: Crystal data and structure refinement for [PPh$_4$]$^2$[(EtO)$_2^-$].

| Identification code      | mo_lms045_0m |
|--------------------------|--------------|
| Empirical formula        | C$_{80}$H$_{81}$AlCl$_4$N$_4$OP$_2$ |
| Formula weight           | 1345.28      |
| Temperature/K            | 100.0        |
| Crystal system           | triclinic    |
| Space group              | P-1          |
| a/Å                      | 11.9549(12)  |
| b/Å                      | 12.7424(13)  |
| c/Å                      | 25.639(3)    |
| α/°                      | 86.841(3)    |
| β/°                      | 76.942(3)    |
| γ/°                      | 70.049(3)    |
| Volume/Å$^3$             | 3575.3(6)    |
| Z                        | 2            |
| ρcalcg/cm$^3$            | 0.935        |
| μ/mm$^{-1}$              | 0.232        |

Figure S-33: A) Asymmetric unit of the crystal lattice found for [PPh$_4$]$^2$[(EtO)$_2^-$], and B) molecular structure of the respective dianion, [(EtO)$_2^-$]. Hydrogen atoms are omitted. Thermal displacement ellipsoids are shown at the 50% probability level.

Only molecular connectivity could be determined due to poor diffraction.
F(000) 1060.0  
Crystal size/mm³ 0.214 × 0.133 × 0.07  
Radiation MoKα (λ = 0.71073)  
2Θ range for data collection/° 4.104 to 50.264  
Index ranges -14 ≤ h ≤ 14, -15 ≤ k ≤ 15, -30 ≤ l ≤ 30  
Reflections collected 66848  
Independent reflections 12646 [R(int) = 0.1210, R(sigma) = 0.0851]  
Data/restraints/parameters 12646/335/786  
Goodness-of-fit on F² 1.445  
Final R indexes [I>=2σ(I)] R₁ = 0.1435, wR₂ = 0.3843  
Final R indexes [all data] R₁ = 0.2086, wR₂ = 0.4313  
Largest diff. peak/hole / e Å⁻³ 1.47/-1.04

S-13. Computational details

For all quantum chemical calculations Orca 4.0.1, 4.1.2, or 4.2.1¹⁴ was employed using the computational resources of the bwUniCluster at the Karlsruhe Institute of Technology or those of the bwForClusters JUSTUS or JUSTUS2 at Ulm University within the Baden-Württemberg High Performance Computing program.

All equilibrium structures were obtained with the following key word line and were confirmed to possess only positive Hessian matrix eigenvalues.

! RKS PBEh-3c Grid5 TightSCF OPT FREQ

PBEh-3c¹⁵ is a composite electronic structure method based on the Perdew-Burke-Ernzerhoff (PBE) exchange-correlation functional combined with polarized valence-double zeta Gaussian atomic orbital basis sets (def2-mSVP). It further accounts for basis set superposition errors with the geometrical counterpoise scheme (gCP)¹⁶, and for London dispersion interactions with the Becke-Johnson-damped D3 correction¹⁷,¹⁸. It is especially suited for structure calculations of small and medium-sized molecules and produces results similar to those obtained with MP2/def2-TZVPP, while being much less computationally demanding.¹⁹

Transition structures were optimized toward a single negative Hessian matrix eigenvalue with

! RKS PBEh-3c Grid5 TightSCF SlowConv OptTS FREQ

%geom

  Calc_Hess true

e nd

It was ensured that the correct first-order saddle point on the potential energy surface was located by animation of the imaginary frequency in Chemcraft.²⁰

All final gas phase single point energies were calculated with:

! RKS PW6B95 def2-QZVPP D3 ABC RIJCOSX AutoAux grid5 finalgrid7 gridx6 TightSCF

PW6B95²¹ is a hybrid meta exchange-correlation functional and was combined with the large def2-QZVPP basis set²². The D3 scheme with Becke-Johnson damping including three-body contributions (ABC) was
applied. The RIJCOSX Fock-matrix formation algorithm was used as it is implemented in Orca along with the respective automatically generated auxiliary basis sets (AutoAux). The RIJCOSX scheme combines the chain of spheres exchange approximation (COSX) for the computation of the exchange matrix with the Split-RI-J algorithm for the calculation of the Coulomb matrix.

Enthalpies at 298.15 K were calculated with the total thermal and zero-point energy correction from the PBEh-3c calculation combined with the electronic single point energies obtained on the PW6B95-D3(BJ)/def2-QZVPP level of theory with the PBEh-3c structures. For Gibbs free energies, the enthalpy values were merged with the vibrational entropy terms calculated on the PBEh-3c level according to the rigid-rotor-harmonic-oscillator approximation (QRRHO) of Grimme.

The influence of a solvating environment on the Gibbs free energy at 298.15 K was taken into account with Klamt’s conductor like screening model for real solvents (COSMO-RS) as it is implemented in the Amsterdam Modeling suite (ADF 2019.103). All ADF-preset parameters were used, and the maximum number of iterations in the geometry convergence section was set to zero. COSMO-RS correction for enthalpies was achieved by calculating ΔG-corrections at five different temperatures (278.15, 288.15, 298.15, 308.15, 318.15 K). Satisfying ΔG = ΔH − TΔS, the plot of the obtained Gibbs free energy corrections against the temperature allows to fit a straight line from which the corrections for ΔH were extracted.

Ball and stick representations were rendered with Chemcraft 1.8, molecular orbitals with IboView.

### S-14. Computational investigation of the addition reaction

The addition reaction of protic substrates to [1]− (Scheme S-3) was studied at the PW6B95-D3(BJ)/def-QZVPP//PBEh-3c level of theory. The influence of dichloromethane as solvent was taken into account with the COSMO-RS method. The following thermodynamic parameters were obtained.

| Substrate     | ΔR\(H\)\text{DFT} [kJ mol\(^{-1}\)] | ΔR\(G\)\text{DFT} [kJ mol\(^{-1}\)] |
|---------------|------------------------------------|------------------------------------|
| tBuOH         | −48.3                              | 2.4                                |
| (p-MeOPh)\(_2\)CHOH | −57.7                              | −12.4                              |
| PrOH          | −60.9                              | −14.4                              |
| p-MeBnOH      | −75.9                              | −17.7                              |
| EtOH          | −65.9                              | −23.5                              |
| p-NO\(_2\)BnOH | −83.0                              | −33.9                              |
| BzOH          | −100.9                             | −48.2                              |
| p-BrPhOH      | −97.2                              | −49.6                              |
For isopropanol, the full reaction coordinate was investigated by DFT (PW6B95-D3(BJ)/def-QZVPP//PBEh-3c). It accords with the experimental observations.

![Figure S-34](image)

**Figure S-34**: Calculated reaction pathway for the addition of isopropanol to [1]. The ball and stick representation of all structures are given in Chapter S-18.

**S-15. Computational investigation of [1,5]H sigmatropic rearrangements in [(EtO)-1*-H]-**

In Chapter S-7, a mechanistic suggestion for the H/D scrambling, which was observed when [1]- was treated with EtOD, is given. The proposed mechanism comprises a series of [1,5]H/D sigmatropic shiftings. All involved tautomers and the respective transition states were studied at the PW6B95-D3(BJ)/def-QZVPP//PBEh-3c level of theory. The influence of dichloromethane as solvent was taken into account with the COSMO-RS method.
Path A

Figure S-35: Calculated reaction pathway for the cascade of [1,5]H/D sigmatropic rearrangements observed within [(EtO)-1*-H/D] following path A (c.f. Scheme S-7). The ball and stick representation of all structures are given in Chapter S-18.

Path B

Figure S-36: Calculated reaction pathway for the cascade of [1,5]H/D sigmatropic rearrangements observed within [(EtO)-1*-H/D] following path B (c.f. Scheme S-7). The ball and stick representation of all structures are given in Chapter S-18.
Non-productive path

Figure S-37: Calculated reaction pathway for the cascade of [1,5]H/D sigmatropic rearrangements observed within [([EtO]-*H/D]*-followed the non-productive path (c.f. Scheme S-7). The ball and stick representation of all structures are given in Chapter S-18.

S-16. Visualization of the Kohn-Sham frontier molecular orbitals of the tetrapyrrolato aluminate and of [1]−

The visualization of the Kohn-Sham frontier molecular orbitals of the tetrapyrrolato aluminate and of [1]− was done using the wavefunction calculated on the PW6B95-D3(BJ)/def-QZVPP/PBEh-3c level (isosurface threshold: 80.00, resolution: 12.00 Å⁻¹).

\[\text{Al(pyrrolato)}_4\]−

HOMO

-2.9246 eV

LUMO

3.4800 eV
HOMO
-2.4257 eV

LUMO
2.2200 eV

S-17. NMR spectra
Figure S-38: $^1$H NMR spectrum (600 MHz, CD$_2$Cl$_2$, 298 K) of [PPh$_4$][EtO]-1*-$^1$H]. The [PPh$_4$][EtO]-1*-$^1$H] / (EtO)-1**-$^1$H ratio was calculated to 26:1. The signal of CHDCl$_2$ and that of residual CH$_2$Cl$_2$, which is contained in [PPh$_4$][1], are marked with a red asterisk.

Figure S-39: $^{13}$C [$^1$H] NMR spectrum (151 MHz, CD$_2$Cl$_2$, 298 K) of [PPh$_4$][EtO]-1*-$^1$H]. The signal of CHDCl$_2$ and that of residual CH$_2$Cl$_2$, which is contained in [PPh$_4$][1], are marked with a red asterisk.
Figure S-40: $^1$H NMR spectrum (600 MHz, CD$_2$Cl$_2$, 298 K) of [PPh$_4$][(PrO)-1*-H]. The [PPh$_4$][(PrO)-1*-H] / (PrO)-1**-HH ratio was calculated to 38:1. The signal of CHDCl$_2$ and that of residual CH$_2$Cl$_2$, which is contained in [PPh$_4$][1], are marked with a red asterisk.

Figure S-41: $^{13}$C{[H]} NMR spectrum (151 MHz, CD$_2$Cl$_2$, 298 K) of [PPh$_4$][(PrO)-1*-H]. The signal of CHDCl$_2$ and that of residual CH$_2$Cl$_2$, which is contained in [PPh$_4$][1], are marked with a red asterisk.
Figure S-42: $^1$H NMR spectrum (600 MHz, CD$_2$Cl$_2$, 298 K) of [PPh$_4$][('BuO)-1*-H]. The addition reaction with 'BuOH is not quantitative. Free [1]$^-$ is marked with green, free 'BuOH with gray asterisks. The signal of CHDCl$_2$ and that of residual CH$_2$Cl$_2$, which is contained in [PPh$_4$][1], are marked with a red asterisk.

Figure S-43: $^{13}$C[1$^H$] NMR spectrum (151 MHz, CD$_2$Cl$_2$, 298 K) of [PPh$_4$][('BuO)-1*-H]. The addition reaction with BuOH is not quantitative. Free [1]$^-$ is marked with green, free 'BuOH with gray asterisks. The signal of CHDCl$_2$ and that of residual CH$_2$Cl$_2$, which is contained in [PPh$_4$][1], are marked with a red asterisk.
Figure S-44: $^1$H NMR spectrum (600 MHz, CD$_2$Cl$_2$, 298 K) of [PPh$_4$][(p-MeBnO)-1*-H]. The [PPh$_4$][(p-MeBnO)-1*-H] / (p-MeBnO)-1**-HH ratio was calculated to 32:1. The signal of CHDCl$_2$ and that of residual CH$_2$Cl$_2$, which is contained in [PPh$_4$][1], are marked with a red asterisk.

Figure S-45: $^{13}$C($^1$H) NMR spectrum (151 MHz, CD$_2$Cl$_2$, 298 K) of [PPh$_4$][(p-MeBnO)-1*-H]. The signal of CHDCl$_2$ and that of residual CH$_2$Cl$_2$, which is contained in [PPh$_4$][1], are marked with a red asterisk.
Figure S-46: $^1$H NMR spectrum (600 MHz, CD$_2$Cl$_2$, 298 K) of [PPh$_4$][(p-NO$_2$BnO)-1*-H]. The [PPh$_4$][(p-NO$_2$BnO)-1*-H] / (p-NO$_2$BnO)-1**-HH ratio was calculated to 46:1. The signal of CHDCl$_2$ and that of residual CH$_2$Cl$_2$, which is contained in [PPh$_4$][1], are marked with a red asterisk.

Figure S-47: $^{13}$C[$^1$H] NMR spectrum (151 MHz, CD$_2$Cl$_2$, 298 K) of [PPh$_4$][(p-NO$_2$BnO)-1*-H]. The signal of CHDCl$_2$ and that of residual CH$_2$Cl$_2$, which is contained in [PPh$_4$][1], are marked with a red asterisk.
Figure S-48: $^1$H NMR spectrum (600 MHz, CD$_2$Cl$_2$, 298 K) of [PPh$_4$]$[(p$-$MeOPh)$_2$CHO]$^{-1}$-H]. Indication of the formation of $[(p$-$MeOPh)$_2$CHO]$^{-1*}$-HH was not found. The signal of CHDCl$_2$ and that of residual CH$_2$Cl$_2$, which is contained in [PPh$_4$][1], are marked with a red asterisk.

Figure S-49: $^{13}$C[$^1$H] NMR spectrum (151 MHz, CD$_2$Cl$_2$, 298 K) of [PPh$_4$]$[(p$-$MeOPh)$_2$CHO]$^{-1}$-H]. The signal of CHDCl$_2$ and that of residual CH$_2$Cl$_2$, which is contained in [PPh$_4$][1], are marked with a red asterisk.
Figure S-50: $^1$H NMR spectrum (600 MHz, CD$_2$Cl$_2$, 298 K) of [PPh$_4$][(p-BrPhO)-1*-H]. The [PPh$_4$][(p-BrPhO)-1*-H] / (p-BrPhO)-1**-HH ratio was calculated to 60:1. The signal of CHDCl$_2$ and that of residual CH$_2$Cl$_2$, which is contained in [PPh$_4$][1], are marked with a red asterisk.

Figure S-51: $^{13}$C($^1$H) NMR spectrum (151 MHz, CD$_2$Cl$_2$, 298 K) of [PPh$_4$][(p-BrPhO)-1*-H]. The signal of CHDCl$_2$ and that of residual CH$_2$Cl$_2$, which is contained in [PPh$_4$][1], are marked with a red asterisk.
Figure S-52: $^1$H NMR spectrum (600 MHz, CD$_2$Cl$_2$, 298 K) of [PPh$_4$][(BzO)-1*-H]. The [PPh$_4$][(BzO)-1*-H] / (BzO)-1**-HH ratio was calculated to 16:1. The signal of CHDCl$_2$ and that of residual CH$_2$Cl$_2$, which is contained in [PPh$_4$][1], are marked with a red asterisk.

Figure S-53: $^{13}$C{[H]} NMR spectrum (151 MHz, CD$_2$Cl$_2$, 298 K) of [PPh$_4$][(BzO)-1*-H]. The signal of CHDCl$_2$ and that of residual CH$_2$Cl$_2$, which is contained in [PPh$_4$][1], are marked with a red asterisk.
Figure S-54: $^1$H NMR spectrum (200 MHz, CD$_2$Cl$_2$, 298 K) of [PPh$_4$][1] treated with an excess of $p$-BrPhOH. This resulted in the formation of the neutral ($p$-BrO)-$^1$**-$^1$H. The signal of CHDCl$_2$ and that of residual CH$_2$Cl$_2$, which is contained in [PPh$_4$][1], are marked with a red asterisk.

Figure S-55: $^1$H NMR spectrum (600 MHz, CD$_2$Cl$_2$, 298 K) of [PPh$_4$][(pyridine)-1]. The signal of CHDCl$_2$ and that of residual CH$_2$Cl$_2$, which is contained in [PPh$_4$][1], are marked with a red asterisk.
Figure S-56: $^{13}$C{'[H]} NMR spectrum (151 MHz, CD$_2$Cl$_2$, 298 K) of [PPh$_4$][pyridine]-1. The signal of CHDCl$_2$ and that of residual CH$_2$Cl$_2$, which is contained in [PPh$_4$][1], are marked with a red asterisk.

Figure S-57: $^1$H NMR spectrum (600 MHz, CD$_2$Cl$_2$, 298 K) of [PPh$_4$][(dmso)-1]. The signal of CHDCl$_2$ and that of residual CH$_2$Cl$_2$, which is contained in [PPh$_4$][1], are marked with a red asterisk.
Figure S-58: $^{13}$C($^1$H) NMR spectrum (151 MHz, CD$_2$Cl$_2$, 298 K) of [PPh$_4$][pyridine]-1. The signal of CHDCl$_2$ and that of residual CH$_2$Cl$_2$, which is contained in [PPh$_4$][1], are marked with a red asterisk.

Figure S-59: $^1$H NMR spectrum (600 MHz, CD$_2$Cl$_2$, 298 K) of (EtO)-1**-HH. The signal of CHDCl$_2$ is marked with a red asterisk.
Figure S-60: $^{13}$C{H} NMR spectrum (151 MHz, CD$_2$Cl$_2$, 298 K) of (EtO)-1**-HH. The signal of CHDCl$_2$ is marked with a red asterisk.

Figure S-61: $^1$H NMR spectrum (600 MHz, CD$_2$Cl$_2$, 298 K) of the solid material collected from the autoprotolysis reaction with EtOH as substrate. It is a mixture of [PPh$_4$][(EtO)-1], [PPh$_4$][(EtO)-1*-H] (1:0.5), [1]$^-$, and EtO (1:1). The signal(s) of CHDCl$_2$ is marked with a red, those of residual pentane with (a) gray asterisk(s).
Figure S-62: $^1$H, $^{13}$C HSQC NMR spectrum (600, 151 MHz, CD$_2$Cl$_2$, 298 K) of the solid material collected from the autoprotolysis reaction with EtOH as substrate. It is a mixture of [PPh$_4$][(EtO)-1], [PPh$_4$][(EtO)-1*H] (1:0.5), [1$^-\$], and EtO (1:1). The signal(s) of CHDCl$_2$ is marked with a red, those of residual pentane with (a) gray asterisk(s).

Figure S-63: $^1$H, $^{13}$C HMBD NMR spectrum (600, 151 MHz, CD$_2$Cl$_2$, 298 K) of the solid material collected from the autoprotolysis reaction with EtOH as substrate. It is a mixture of [PPh$_4$][(EtO)-1], [PPh$_4$][(EtO)-1*H] (1:0.5), [1$^-\$], and EtO (1:1). The signal(s) of CHDCl$_2$ is marked with a red, those of residual pentane with (a) gray asterisk(s).
Figure S-64: $^1$H NMR spectrum (600 MHz, CD$_2$Cl$_2$, 298 K) of (p-MeBnO)-1**.HH. The signal of CHDCl$_2$ is marked with a red asterisk.

Figure S-65: $^{13}$C($^1$H) NMR spectrum (151 MHz, CD$_2$Cl$_2$, 298 K) of (p-MeBnO)-1**.HH. The signal of CHDCl$_2$ is marked with a red asterisk.
Figure S-66: $^1$H NMR spectrum (600 MHz, CD$_2$Cl$_2$, 298 K) of the solid material collected from the autoprotolysis reaction with $\text{p-MeBnOH}$ as substrate. It is a mixture of $[\text{PPh}_4][\text{(p-MeBnO)}-1]$ and $[\text{PPh}_4][\text{(p-MeBnO})-1^*\cdot\text{H}]$ (1:0.5). The signal(s) of CHDCI$_2$ is marked with a red, those of residual pentane with (a) gray asterisk(s).

Figure S-67: $^1$H,$^1$C HSQC NMR spectrum (600, 151 MHz, CD$_2$Cl$_2$, 298 K) of the solid material collected from the autoprotolysis reaction with $\text{p-MeBnOH}$ as substrate. It is a mixture of $[\text{PPh}_4][\text{(p-MeBnO)}-1]$ and $[\text{PPh}_4][\text{(p-MeBnO})-1^*\cdot\text{H}]$ (1:0.5). The signal(s) of CHDCI$_2$ is marked with a red, those of residual pentane with (a) gray asterisk(s).
Figure S-68: $^1$H,$^1$C HMBC NMR spectrum (600, 151 MHz, CD$_2$Cl$_2$, 298 K) of the solid material collected from the autotolysis reaction with $p$-MeBnOH as substrate. It is a mixture of [PPh$_4$][($p$-MeBnO)-1] and [PPh$_4$][($p$-MeBnO)-1$^*_H$] (1:0.5). The signal(s) of CHDCl$_2$ is marked with a red, those of residual pentane with (a) gray asterisk(s).

Figure S-69: $^1$H NMR spectrum (600 MHz, CD$_2$Cl$_2$, 298 K) of ($p$-NO$_2$BnO)-1$^{**}_H$. The signal of CHDCl$_2$ is marked with a red asterisk.
Figure S-70: $^{13}$C{H} NMR spectrum (151 MHz, CD$_2$Cl$_2$, 298 K) of (p-NO$_2$BnO)-1**-HH. The signal of CHDCl$_2$ is marked with a red asterisk.

Figure S-71: $^1$H NMR spectrum (600 MHz, CD$_2$Cl$_2$, 298 K) of the solid material collected from the autoprotolysis reaction with p-NO$_2$BnOH as substrate. It is a mixture of [PPh$_4$][1-NO$_2$BnO]-1 and [PPh$_4$][1-NO$_2$BnO]-1*-H (1:1.8). The signal(s) of CHDCl$_2$ is marked with a red, those of residual pentane with (a) gray asterisk(s).
Figure S-72: $^1$H,$^1$C HSQC NMR spectrum (600, 151 MHz, CD$_2$Cl$_2$, 298 K) of the solid material collected from the autoprotolysis reaction with $p$-NO$_2$BnOH as substrate. It is a mixture of $[\text{PPh}_4][(p$-NO$_2$BnO)$\cdot$1] and $[\text{PPh}_4][(p$-NO$_2$BnO)$\cdot$1$^\ast\cdot$H] (1:1.8). The signal(s) of CHDCl$_2$ is marked with a red, those of residual pentane with (a) gray asterisk(s).

Figure S-73: $^1$H,$^1$C HMBC NMR spectrum (600, 151 MHz, CD$_2$Cl$_2$, 298 K) of the solid material collected from the autoprotolysis reaction with $p$-NO$_2$BnOH as substrate. It is a mixture of $[\text{PPh}_4][(p$-NO$_2$BnO)$\cdot$1] and $[\text{PPh}_4][(p$-NO$_2$BnO)$\cdot$1$^\ast\cdot$H] (1:1.8). The signal(s) of CHDCl$_2$ is marked with a red, those of residual pentane with (a) gray asterisk(s).
## S-18. Computed XYZ coordinates, molecular structures, and energies

**EtOH**

|                  | Value                               |
|------------------|-------------------------------------|
| Total correction | 0.08669736 Eh                       |
| Final entropy term | 0.02933742 Eh                     |
| Final single point energy | -155.29838007 Eh             |
| COSMO-RS correction (Gibbs free energy) | -14.7696 kJ mol⁻¹  |
| COSMO-RS correction (enthalpy) | -23.8110 kJ mol⁻¹  |

### Coords

xyz 0 1

| Atom | X          | Y          | Z          |
|------|------------|------------|------------|
| C    | -1.24420949654196 | 3.52355699090039 | -0.04885418028097 |
| O    | -0.16980556727868 | 2.61759740949911 | -0.09398690449899 |
| H    | -0.17472711170963 | 2.10238373041652 | 0.71552278836320 |
| C    | -2.59915098420035 | 2.84677599173391 | 0.06758405696203 |
| H    | -1.19791054575159 | 4.09252241410471 | -0.97887040603386 |
| H    | -1.12804682437595 | 4.25188289960234 | 0.76601789939653 |
| H    | -2.75722981676679 | 2.14160861511040 | -0.74845266534286 |
| H    | -3.40300711041510 | 3.58332678399008 | 0.03793094806625 |
| H    | -2.69706254295995 | 2.30043318241899 | 1.00870843463867 |

**PrOH**

|                  | Value                               |
|------------------|-------------------------------------|
| Total correction | 0.11665736 Eh                       |
| Final entropy term | 0.03246470 Eh                     |
| Final single point energy | -194.68487260 Eh             |
| COSMO-RS correction (Gibbs free energy) | -17.4769 kJ mol⁻¹  |
| COSMO-RS correction (enthalpy) | -26.2929 kJ mol⁻¹  |

### Coords

xyz 0 1

| Atom | X          | Y          | Z          |
|------|------------|------------|------------|
| C    | -1.27095738169071 | 3.41323971207307 | -0.15124067566584 |
| O    | -0.23350795363106 | 2.46058723240960 | -0.23822987446695 |
| H    | -0.20983885514816 | 1.96655426058148 | 0.58578386476638 |
| C    | -2.634563322322170 | 2.74988597037333 | -0.00961741589770 |
| H    | -1.24301507561339 | 3.94261471215631 | -1.10762136444384 |
| C    | -1.01904086058574 | 4.42105382032095 | 0.96236363328275 |
| H    | -2.8045198184968 | 2.02921863797137 | -0.80930240454792 |
| H    | -3.43794395235588 | 3.48693205560385 | -0.04428754699995 |
| H    | -2.721288072044944 | 2.22263266786387 | 0.94472205513190 |
| H    | -1.05605267961655 | 3.94259985668606 | 1.94530619513399 |
| H    | -1.77289565762583 | 5.2093456016045 | 0.95984552498622 |
| H    | -0.04142149641186 | 4.89024699497774 | 0.85275793867497 |
Total correction: 0.14636802 \text{E}_h
Final entropy term: 0.03620215 \text{E}_h
Final single point energy: -234.07117390355 \text{E}_h
COSMO-RS correction (Gibbs free energy): -19.6007 \text{kJ mol}^{-1}
COSMO-RS correction (enthalpy): -28.2005 \text{kJ mol}^{-1}

xyz 0 1
C -2.23837764131824 1.11636215204564 -1.63172068509501
C -1.34957209611979 0.671018151150 -0.47028172338827
H -3.27082796080132 1.24352813504121 -1.30388926805601
H -2.22912415405050 0.38766743145789 -2.44333868658652
H -1.89935085528415 2.06821011446673 -2.04977784518152
C -1.85387763999482 -0.64714678666168 0.10125938093367
H -2.88076304614118 -0.55128424987653 -2.44333868658652
H -1.23073772115718 -0.97017483321990 0.94069936316679
H -1.83008961398439 -1.43054470476568 -0.65654427935620
C 0.09683851568660 0.52192913097684 -0.94243482634959
H 0.18413191068900 -2.2740378910417 -1.73026808976668
H 0.74531303333395 0.22233533397423 -0.11822609150599
H 0.48192528133036 1.46161224450802 -1.34799277683006
O -1.425695552975510 1.6046581271894 0.59364405246572
H -1.11467248243324 2.45535282692846 0.27322500785364

p-MeBnOH

Total correction: 0.17443551 \text{E}_h
Final entropy term: 0.04218567 \text{E}_h
Final single point energy: -386.762174510 \text{E}_h
COSMO-RS correction (Gibbs free energy): -27.3892 \text{kJ mol}^{-1}
COSMO-RS correction (enthalpy): -36.6899 \text{kJ mol}^{-1}

xyz 0 1
C -4.78260519409441 3.28902719320226 0.28961023638515
C -5.05789937110284 1.93094081153185 0.19654913177888
C -3.98741367416739 1.96283581148129 -0.01140450669395
C -2.69156230395954 1.53411147767534 -0.12473216536980
C -2.42091549770759 2.89767409003885 -0.03381834239563
C -3.48301808636393 3.76440815406847 0.18118119144250
H -5.59267362610720 3.9869203792550 0.45785912398006
H -4.17296817632632 -0.0002605931357 -0.06831767296942
H -1.88021159167181 0.83560320054473 -0.28713876826568
H -3.29782407979026 4.82912399631491 0.26895776750584
C -1.01290583085413 3.41677284625756 -0.17954842211197
O -0.04143724025859 2.58659888212190 0.40112942874190
H -0.96555850505470 4.44321591500433 0.21133045290980
H -0.75258609573348 3.48110070042802 -1.23901818480676
H -0.26077824479808 2.47471390270765 1.32958747253451
C -6.45777320305140 1.40365291606918 0.31854325214625
**p-NO₂BnOH**

| H    | -7.17710689513757 | 2.20634729308873 | 0.47525791640148 |
|------|-------------------|------------------|------------------|
| H    | -6.5508406965142  | 0.71064092580863 | 1.15609426406865 |
| H    | -6.75862829224111 | 0.86373343987427 | -0.58054624029640 |

Total correction 0.15032242 Eₜ
Final entropy term 0.04357380 Eₜ
Final single point energy -552.21078177 Eₜ
COSMO-RS correction (Gibbs free energy) -38.9944 kJ mol⁻¹
COSMO-RS correction (enthalpy) -51.1170 kJ mol⁻¹

**xyz 0 1**

C  -4.87960652397382  3.28386374550873  0.29279144231691
C  -5.10804513986114  1.91875343475542  0.22626498936658
C  -4.06723197973037  1.02164815232059  0.05020482256647
C  -2.77509264490967  1.50412121268703  -0.0623430676152
C  -2.51687111519605  2.8698295234125  0.00179923613449
C  -3.58136959516141  3.74736503879535  0.1834880757055
H  -5.69896671228470  3.9727861786454  0.43562402763205
H  -4.25066964617109  -0.0397619516467  -0.00108807078816
H  -1.95909549444823  0.8085790279648  -0.20505647375999
H  -3.39753476746405  4.81293343369411  0.24631192135949
C  -1.11263325422160  3.40081233062874  -0.15026470473738
O  -0.11612658742022  2.49879310131656  0.23699399778155
H  -1.03285511674518  4.36167876571957  0.37659444276911
H  -0.93218823418670  3.61736603033978  1.20635762868653
H  -0.19233654624814  2.34399549495599  1.18196647306870
N  -6.47336016323231  1.41681862707730  0.34840014637817
O  -7.35468891113223  2.22737001558815  0.49525615417851
O  -6.63492171448811  0.22196493877508  0.29533576761098

**p-MeOPh)₂CHOH**

| H    | -7.11903854396518 | 2.17282435689113 | 0.15577705012575 |
|------|-------------------|------------------|------------------|
| H    | -5.4567394936659  | 1.20086880958443 | -0.80617467452579 |
| H    | -4.67351968382473 | 2.51441420249761  | 1.04308988763559 |
| H    | -3.44415884450045 | 1.89726790718952  | 0.95482114887763 |

Total correction 0.30458966 Eₜ
Final entropy term 0.05993839 Eₜ
Final single point energy -808.26457910 Eₜ
COSMO-RS correction (Gibbs free energy) -52.8646 kJ mol⁻¹
COSMO-RS correction (enthalpy) -65.0560 kJ mol⁻¹

**xyz 0 1**

C  -5.69608224984290  2.17282435689113  0.15577705012575
C  -5.4567394936659  1.20086880958443  -0.80617467452579
C  -4.67351968382473  2.51441420249761  1.04308988763559
C  -3.44415884450045  1.89726790718952  0.95482114887763
\[
\begin{align*}
\text{C} & -3.18559896927129 & 0.92318211416237 & -0.01141452564341 \\
\text{C} & -4.21092069749512 & 0.58340855251010 & -0.8766015663938 \\
\text{H} & -0.05433993714470 & -0.18709786328632 & -1.61873426969804 \\
\text{H} & -6.22340394147969 & 0.90063741618175 & -1.50750261130648 \\
\text{O} & -6.86294106501632 & 2.83055264020239 & 0.31062051669965 \\
\text{H} & -4.85886798493787 & 3.26841162133715 & 1.79710680188667 \\
\text{H} & -6.65307056447777 & 2.18498814171779 & -1.64903643894811 \\
\text{C} & -1.833529665155585 & 0.23861429746875 & -0.05982510135916 \\
\text{C} & -0.67985240663764 & 1.21775680342139 & -0.0684330698593 \\
\text{C} & -0.74014033407592 & 2.41502936961291 & -0.76681536654457 \\
\text{O} & 0.35320481377028 & 3.26755697612741 & -0.84675555635992 \\
\text{C} & 1.54390905010540 & 2.92564783544442 & -0.21420483796284 \\
\text{C} & 1.61905281473394 & 1.72438688426049 & 0.49195818412162 \\
\text{C} & 0.52310855629688 & 0.8889486746497 & 0.55442610165563 \\
\text{C} & -1.66524329096630 & 2.71149070263536 & -1.24850788844271 \\
\text{O} & 0.25279531113776 & 4.19212991253752 & -1.3985784654573 \\
\text{O} & 2.65846166991384 & 3.68087583781819 & -0.22258645619424 \\
\text{H} & 2.54452212727774 & 1.46082833198529 & 0.9871287983278 \\
\text{O} & 0.60161863515055 & -0.04239112477959 & 1.10189032508003 \\
\text{O} & -1.721895508906673 & -0.66805103037139 & -1.13371269115477 \\
\text{H} & -1.74461101169007 & -0.38126307151204 & 0.83986495988985 \\
\text{H} & -1.498702931431017 & -0.16792430022246 & -0.92115019044332 \\
\text{C} & 2.63799001741357 & 4.90032806969552 & -0.91792873757111 \\
\text{C} & -7.92741486663428 & 2.51193613867453 & -0.54572355980160 \\
\text{C} & 3.62537968144162 & 5.34113429350348 & -0.80009643152521 \\
\text{H} & 1.89654266081436 & 5.596334408729 & -0.51205106292402 \\
\text{H} & 2.44244962249140 & 4.76592341288079 & -1.98598650944407 \\
\text{H} & -8.76305638849889 & 3.14312944066648 & -0.2520989928701 \\
\text{H} & -8.23414673721387 & 1.46492301170088 & -0.4559023651101 \\
\text{H} & -7.69127272339388 & 2.71491513367285 & -1.59555269566722
\end{align*}
\]

\[
\begin{align*}
p-\text{BrPhOH}
\end{align*}
\]

\[
\begin{align*}
\text{Total correction} & \quad 0.10445458 \text{ E}_h \\
\text{Final entropy term} & \quad 0.03874398 \text{ E}_h \\
\text{Final single point energy} & \quad -2882.7423285 \text{ E}_h \\
\text{COSMO-RS correction (Gibbs free energy)} & \quad -30.285 \text{ kJ mol}^{-1} \\
\text{COSMO-RS correction (enthalpy)} & \quad -38.079 \text{ kJ mol}^{-1}
\end{align*}
\]
**BzOH**

Total correction \[0.12657235 \text{ E}_\text{h}\]  
Final entropy term \[0.03936973 \text{ E}_\text{h}\]  
Final single point energy \[-421.5474996 \text{ E}_\text{h}\]  
COSMO-RS correction (Gibbs free energy) \[-28.0822 \text{ kJ mol}^{-1}\]  
COSMO-RS correction (enthalpy) \[-37.8326 \text{ kJ mol}^{-1}\]  

xyz 0 1

---

**[1]**

Total correction \[0.58958485 \text{ E}_\text{h}\]  
Final entropy term \[0.07984281 \text{ E}_\text{h}\]  
Final single point energy \[-1550.4663695 \text{ E}_\text{h}\]  
COSMO-RS correction (Gibbs free energy) \[-203.3389 \text{ kJ mol}^{-1}\]  
COSMO-RS correction (enthalpy) \[-219.6660 \text{ kJ mol}^{-1}\]  

xyz -1 1

---
Total correction \( 0.67920261 \) \( \text{E}_\text{h} \)
Final entropy term \( 0.08983106 \) \( \text{E}_\text{h} \)
Final single point energy \(-1705.796358 \) \( \text{E}_\text{h} \)
COSMO-RS correction (Gibbs free energy) \(-217.1127 \text{ kJ mol}^{-1} \)
COSMO-RS correction (enthalpy) \(-234.069 \text{ kJ mol}^{-1} \)

xyz - 1 1

|   |   |   |
|---|---|---|
|  |   |   |
|   |   |   |

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[(PrO)−1*−H]−

Total correction 0.70932639 $E_h$
Final entropy term 0.09123002 $E_h$
Final single point energy -1745.183536 $E_h$
COSMO-RS correction (Gibbs free energy) -213.8968 kJ mol$^{-1}$
COSMO-RS correction (enthalpy) -230.1363 kJ mol$^{-1}$
Total correction $0.73923982 \text{ E}_h$
Final entropy term $0.09315268 \text{ E}_h$
Final single point energy $-1784.566758 \text{ E}_h$
COSMO-RS correction (Gibbs free energy) $-212.5899 \text{ kJ mol}^{-1}$
COSMO-RS correction (enthalpy) $-228.1245 \text{ kJ mol}^{-1}$

xyz -1 1
N 1.63541619537215 -1.59612563670706 2.13250036741389
C 3.31422856804911 -1.34623598961056 3.86906211323466
C 3.87379925551315 -2.18857702998503 5.01454841722339
H 4.39620938658287 -3.07085885658322 4.63899042177141
H 3.08961320520715 -2.51038451275392 5.70045459396467
H 4.59771050010433 -1.69149646688134 5.58548575537323
C 4.48313622560116 -0.95363713598019 2.39334672575555
C 4.98809724722844 -1.8330679571695 2.5291140497723
H 5.20949521695931 -0.3709464007654 3.50362794020751
H 4.14100915326744 -0.34154769954955 2.10532128032932
N 1.80103449088800 0.65847011164810 3.63288137560401
C 1.48469454685146 1.75622044404831 4.39056647556071
C 2.63211913481288 -0.1154388317067 4.39674640958217
C 2.10137606134041 1.66958685806602 5.61944665502468
C 2.0323027541550 2.3802234241382 6.4276643087043
C 2.8366541825663 0.46956454077151 5.62429749072756
C 3.45320018566705 0.0956756600802 4.82963024806112
C 0.522343861873 2.8255746136662 3.93896261672945
C -0.91877920799405 2.34975361984780 4.20321295052369
H -1.07177630172153 2.19651093054030 3.27453102744069
H -1.12004515211262 1.40948914504059 3.69983593115467
H -1.63941771297241 3.09235566415099 3.85199621555320
C 0.73738163636220 4.08600897931496 4.78575851056530
H 0.02986545881998 4.86418414121818 4.49696306219793
H 1.74623630935773 4.47938842778128 4.66709816785939
H 0.5654809949955 3.87835531616042 5.84281761202674
N 1.2211615239560 2.29182580913898 1.56068416574393
C 1.39550636759444 2.97241956423586 0.39147981809582
G 0.7507038614544 3.18286816054113 2.48873864809625
C 1.00350104343773 4.28143284374599 0.55104100437547
H 1.04250488258222 5.0566270647172 -0.18933839313998
C 0.5878529876832 4.1491586162454 3.18945728823420
H 0.24233749353643 3.2098714763860 2.36820455144258
C 2.1332352729349 2.34945276009581 -0.75843789256946
C 1.9537735896570 3.20549528067882 -0.21095626221769
C 2.03745062034222 4.22430032250836 1.8308207834055
H 0.90641644767573 2.52830181531413 -2.30954372599579
H 2.53148390522741 2.80335175496362 -2.84453546882996
C 3.63906934672621 2.3284856264576 -0.41185048907648
H 4.21782981366680 1.8358976289636 -1.2249528559729
H 3.82458181236825 1.74873708177678 0.49184058500145
H 4.00166955967043 3.3432878071023 -0.23340596309656
N 1.67311008089606 -0.0312052300249 -0.08530743594545
C 1.41018954424039 -1.22432469556470 -0.707470971845
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[(\(\rho\)-MeBnO)-1*H]}
| Atom | X          | Y          | Z          |
|------|-----------|-----------|-----------|
| Al   | -0.3857   | -0.5610   | 2.5088    |
| S    | 0.3471    | 0.2461    | 0.1311    |
| O    | -0.1879   | 1.1264    | 1.1264    |
| N    | 0.5000    | 0.0000    | 0.0000    |
| C    | 0.0000    | 0.0000    | 0.0000    |
| C    | 2.0000    | 0.0000    | 0.0000    |
| C    | 1.0000    | 0.0000    | 0.0000    |
| C    | 0.0000    | 0.0000    | 0.0000    |
| C    | -1.0000   | 0.0000    | 0.0000    |
| C    | -2.0000   | 0.0000    | 0.0000    |

**References:**
1. [Cotton, F. A., & Wilkinson, G. (1988). *Advanced Inorganic Chemistry* (6th ed.). John Wiley & Sons.]
2. [Gleason, E. A. (1992). *Organic Chemistry* (4th ed.). McGraw-Hill.]
$$[\text{p-NO}_2\text{BnO}]-1^*\text{H}^-$$

Total correction $0.74280906\ E_h$

Final entropy term $0.10064236\ E_h$

Final single point energy $-2102.726941\ E_h$

COSMO-RS correction (Gibbs free energy) $-216.1824\ \text{kJ mol}^{-1}$

COSMO-RS correction (enthalpy) $-233.9988\ \text{kJ mol}^{-1}$

dadosxyz -1 1

N 1.37551469920970 1.6286084417057 1.70742698186229
C 2.79175315928286 1.12826572054013 3.61738617282130
C 3.31730107252798 1.87017593222075 4.84805941136899
H 4.00261049737356 2.67133311466552 5.56084452281062
H 2.50724345878987 -2.2955966396891 5.4378042317875
H 3.87095937993441 -1.18569450112450 5.4841267106798
C 3.9997427193453 -0.58476744069338 2.8246740907557
H 4.66557991957009 -1.39005021940749 2.501339158487
H 4.56573751104231 0.09830249599997 3.4584733841233
H 3.68716659829022 -0.03828955542493 1.93003814134602
C 1.07119621050578 0.64645972014831 3.1331981286920
C 0.46655634019655 1.6705937793388 3.81319868728797
C 1.87710501688922 0.00633108714644 4.02699790354851
C 0.8884955464156 1.65737322323831 5.12744107013506
H 0.57309561359647 2.3558492831320 5.9072519951307
H 1.78479982562185 0.58417461456712 5.26519127792143
H 0.23664252119489 0.29583204938548 6.16647224287337
H -0.55102846339522 2.59327283647999 3.18388078629145
C -1.9406737439476 1.92238076988665 3.18388078629145
H -2.2584375642634 1.71414883998649 4.2080394563270
H -1.93509463188182 0.98293460057455 2.63847093858095
C -2.67666598823564 2.58370738579792 2.72609445832893
H -0.57004847509204 3.85006110788046 4.03999158081327
C -1.41833077373540 4.53346117214988 3.62252799025200
H 0.28920128945757 3.39247242007161 4.09815927104998
H -0.99429293582142 3.61416628728983 5.05242107398105
N 0.56461991430546 2.15481053179705 0.9434049545322
C 0.81511832420952 2.85092957456127 0.19884072123244
C -0.12975974989481 2.99426154629375 1.78950938422721
C 0.29231468295835 4.11952892476072 0.1039586057158
H 0.35800349577947 4.90469794025200 -0.84149596559368
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\[
(p\text{-MeOPh})_2\text{CHO}\cdot\text{H}^+
\]

Total correction 
0.89725008 \text{ E}_\text{h}

Final entropy term
0.11370265 \text{ E}_\text{h}

Final single point energy
-2358.765970 \text{ E}_\text{h}

COSMO-RS correction (Gibbs free energy)
-239.3819 \text{ kJ mol}^{-1}

COSMO-RS correction (enthalpy)
-258.5725 \text{ kJ mol}^{-1}

xyz - 1

N 0.86540645646017 -1.2248862652050 0.68141947926127
C 1.1834594483020 -1.49804136478193 3.07235663395651
C 0.7962450498196 -2.51392411967135 4.1443022283956
H 1.31214614537601 -3.46407352938601 3.99192693686995
H -0.2777084188052 -2.7020627790155 4.15544273969224
H 1.08126632375027 -2.14341406863703 5.12805126954137
C 2.7143129700244 -1.32166410351506 3.09580309848767
H 3.22717836982617 -2.26466195355306 2.88749321931982
H 3.02401571086486 -0.96835222644481 4.07929417963629
H 3.04716191904668 -0.58891546227752 2.36120540340105
N 0.64049608949863 0.87036673349821 2.45661905401451
C 0.02012247654225 1.94785324201017 3.03685072355662
C 0.49705756700685 -0.18285563230425 3.31487939888777
C -0.55807632702995 1.55443813947343 4.22775089922438
H -1.10260877162650 2.17982195423591 4.91755882289796
C -0.24626761765816 0.19207987748348 4.41073321609558
H -0.50909944774999 -0.41977354221131 5.26039785236512
C 0.09693096065132 3.364878196976 2.50338857034879
C -1.14807025970638 3.7907375244606 1.69857106845235
H -2.07343189505958 3.62933199647062 2.21821992293659
H -1.16339631162674 3.34603444482297 0.70818052992824
H -1.13096960123957 4.8725391289363 1.55241402336434
C 0.17649973588691 4.3062069493439 3.71543186971119
C 0.24848358917573 5.34517336101965 3.39332879529150
H 1.0379290164310 4.0767632772520 4.34138236752121
H -0.72390279169461 4.22862633117979 4.32609170965838
N 1.76540565522597 2.64317816405442 0.73222126124110
C 2.8115311032243 3.2225151519284 0.6474937825440
C 1.31431478776814 3.56749711369223 1.64299175754355
C 3.02028467275757 4.49779199854673 0.5366518807681
H 3.78316246204271 5.1891046025591 0.21331057083839
C 2.06132776709033 4.7183299297022 1.54490249481060
H 1.93359425507258 5.623008821881 2.1184909195833
C 3.6906041522232 2.46267759767720 -0.88055218752848
C 4.34126463155351 3.4295964045714 -1.87073240407104
H 4.91865953483579 4.1876921591773 -1.34492704102093
H 3.5920668808529 3.9351504252823 -2.47990579939346
H 5.02963440205503 2.9021749207104 -2.5328646559049
C 4.81940075146735 1.78651281553718 -0.06915029650282
H 5.48170213884491 1.21560530168656 -0.724778879601
H 4.40909690217333 1.10081508476888 0.6723612750201
Total correction 0.69736774 $E_h$
Final entropy term 0.09706548 $E_h$
Final single point energy -4433.2581380 $E_h$
COSMO-RS correction (Gibbs free energy) -218.4318 kJ mol$^{-1}$
COSMO-RS correction (enthalpy) -233.9283 kJ mol$^{-1}$

xyz 1 1
Br 6.57058632926978 5.6512263561343 14.69479576995522
Al 3.54547987999190 10.4834583192641 10.05192914195296
O 4.86357719806206 9.27545108071783 10.28911187287266
N 3.63772934393993 11.03036137603404 12.0589054524597
N 1.86543582650504 9.60897475757556 10.5296791961452
N 3.0801364066160 10.26541281410244 8.1993031874178
N 4.54231573833630 12.1554174252830 9.76671273200375
C 4.90817914474104 11.31536506624865 12.6819941745816
H 5.61161104576800 10.5024966431178 12.4903410264249
C 4.59448111830355 11.3879344588775 14.13269812395261
Al 5.32691739625552 11.54526650678113 14.9100186417804
C 3.27640744166537 11.23514030738482 14.29893419031101
C 2.71713573379595 11.23935308961213 15.21181582322971
C 2.71812542353469 11.03403971963367 12.5970042592443
C 1.2685926011426 10.89567779923235 12.5974453118210
C 1.11643863083230 9.72662136127317 11.68788235276115
C 0.20670447498943 8.6939898653989 11.7476777678614
H -0.5243226872360 8.5363103266446 12.52403414293770
C 0.39441495210240 7.9152087994313 10.59153500969028
H -0.16407354436698 7.03242433491364 10.3251019931176
C 1.4052699125144 8.50212347797221 9.86041688183229
C 1.95084592960631 8.01895767156299 8.5344437209317
C 2.43709728935928 9.1663661842143 7.8689204377443
C 2.3490582121126 9.28571454836396 6.3191246744445
H 1.90228636127255 8.58000472065913 5.634115367060
C 2.94723930011651 10.5165356456569 5.97413217494417
C 3.02793176742412 10.35861579275111 4.9831942770588
C 3.37351010865535 11.08844245912609 7.1489252894741
C 3.88527015339914 12.4831916258083 7.3624361245215
C 4.8651599472587 12.57009376575782 8.49778835917687
C 6.0913894175535 13.1863506342744 8.497846101958
C 6.60123151550374 13.61146319310786 7.64780586112309
C 6.55095311352410 13.17542848799648 9.83089374877457
H 7.47086302952329 13.1122924195494 10.1890423869210
C 5.58085677395999 12.5606044180464 10.5854037528913
C 5.5079949062997 12.61690610919484 12.09016017338359
C 6.90759276356224 12.78571040215322 12.68415382747506
H 7.52625765635201 11.96363225685645 12.39370850734842
H 6.87644987282416 12.8329099924870 13.77427082095943
H 7.369281006974397 13.71462100604015 12.34325948455639

S-93
\[(\text{BzO})-1^*\text{H}\]

Total correction 0.71913511 \(E_h\)
Final entropy term 0.09556558 \(E_h\)
Final single point energy -1972.064719 \(E_h\)
COSMO-RS correction (Gibbs free energy) -216.0284 \(kJ \text{ mol}^{-1}\)
COSMO-RS correction (enthalpy) -232.7108 \(kJ \text{ mol}^{-1}\)

xyz -1 1
N 1.0597005385755 -1.272946751346700 1.53424110541404
H 2.53184416615173 -1.19611485831581 3.46826982793582
C 2.94468362092916 -2.13738579232288 4.5981350856844
H 3.51095932844612 -2.98921369086997 4.21665394232889

S-94
| Atom | x   | y          | z          |
|------|-----|------------|------------|
| C    | 1.9387205403122 | -1.44831671242939 | 1.6413590431481 |
| C    | 3.0755386746461 | -1.03412136826257 | 3.7979427653733 |
| C    | 3.5506871506090 | -1.82820803933087 | 5.0131325451163 |
| H    | 4.21459429781318 | -2.63721623043066 | 4.7042912469840 |
| H    | 2.7115063317072 | -2.25918297204443 | 5.5937291964971 |
| C    | 1.10700635729525 | -1.18930143154398 | 5.6997281881683 |
| C    | 4.31681317586315 | -0.42300137478630 | 3.1165176643913 |
| C    | 5.0045261153641 | -2.0470544090918 | 2.7855887862074 |
| C    | 4.84095697566693 | 0.22365012890696 | 3.8115841330786 |
| C    | 4.04849907799904 | 0.16857395060478 | 2.240975867937 |
| C    | 1.25471608874398 | 0.64460659947367 | 3.3511635118253 |
| C    | 0.59484249056286 | 1.61990451325235 | 4.0652710523148 |
| C    | 2.13590417845237 | 0.5420954280292 | 4.2239063549359 |
| C    | 1.05648295462825 | 1.6413590431481 | 5.3588332601407 |
| H    | 0.72095838274715 | 2.2905047705630 | 6.1524342794475 |
| H    | 2.04517168170824 | 0.6430383370964 | 5.4599154236691 |
| H    | 2.61826677410786 | 0.38619883057840 | 6.3378113265226 |
| C    | -0.5467340785547 | 2.4281438189571 | 3.5140167310041 |
| C    | -1.8596851695177 | 1.6294342342513 | 3.655082947963 |
| H    | -2.06309738395874 | 1.43689616363771 | 4.7106517632914 |
| C    | -1.80730903717012 | 0.6675679912388 | 3.1538677398372 |
| C    | -2.69918705589047 | 2.1918130709830 | 3.2378090353708 |
| C    | -0.71929012948293 | 3.69472166735130 | 4.3648365686550 |
| C    | -1.56438543574442 | 4.26629175406079 | 4.0115691746496 |
| C    | 0.17358955952692 | 4.3173776268307 | 4.3312569072858 |
| C    | -0.92594721870732 | 3.43879797987981 | 5.4046418512990 |
| C    | 0.52539684010576 | 2.1575130709252 | 1.2173120709701 |
| C    | 0.60658042004838 | 2.90470515619357 | 0.070095173274 |
| C    | -0.28033401941033 | 2.85122706666064 | 2.0904349729122 |
| C    | -0.16520596795907 | 0.4331079607292 | 1.809470383408 |
| C    | -0.28054458000710 | 4.81321299757156 | -0.5465890528551 |
| C    | -0.73573896171105 | 3.9599477426460 | 1.480106779142 |
| C    | -1.37680509049355 | 4.74665124670763 | 1.91532603779825 |
| C    | 1.51788493204799 | 2.5020934058951 | -1.0524061927887 |
| C    | 1.29986590502244 | 3.42100092129412 | -2.2552354519852 |
| C    | 1.51247933643092 | 4.45811205974426 | -1.9935737534612 |
| C    | 0.27165398784044 | 3.36573243649737 | -2.6167484782645 |
| C    | 1.9643577196930 | 3.14225745248862 | -0.30729325972869 |
| C    | 2.98607997161609 | 2.6627677610398 | -0.6068337148543 |
| C    | 3.66407025964015 | 2.3768695254971 | -1.4137894950084 |
| C    | 3.22204494068060 | 2.03727685975456 | 0.25481362586696 |
| C    | 3.9107359349762 | 3.69721801994891 | -0.3234019305264 |
| C    | 1.32240558393793 | 0.08509183301037 | -0.49998773050573 |
| C    | 1.13352924573622 | -1.10159755640921 | -1.1707329997759 |
| C    | 1.25591554169990 | 1.0820853039530 | -1.4350243968580 |

Total correction: 0.71017759 \( \text{E}_\text{h} \)
Final entropy term: 0.09180514 \( \text{E}_\text{h} \)
Final single point energy: -1745.178815 \( \text{E}_\text{h} \)
COSMO-RS correction (Gibbs free energy): -203.9993 kJ mol\(^{-1}\)
COSMO-RS correction (enthalpy): -219.0773 kJ mol\(^{-1}\)
S-97

TS-A (coordination of 'PrOH to [1'])

Total correction 0.70930649 \text{E}_\text{h} \\
Final entropy term 0.09194390 \text{E}_\text{h} \\
Final single point energy -1745.16337529 \text{E}_\text{h} \\
COSMO-RS correction (Gibbs free energy) -201.5662 \text{kJ mol}^{-1} \\
COSMO-RS correction (enthalpy) -215.4345 \text{kJ mol}^{-1} \\

xyz -1 1

N 2.40461318958787 -1.70447068363838 2.19527185906825 \\
C 3.87122709746243 1.06875639740839 4.1346456349157 \\
C 4.5093282083341 1.77801586054326 3.52788764862479 \\
C 5.28501553971211 -2.47478083603855 4.99633646736734 \\
C 3.76742009545758 -2.33261778363281 5.90115689982560 \\
C 4.99090701348463 1.05911202766551 5.9917488288907 \\
C 4.99386411393221 -0.31895351610375 3.3821303162713 \\
C 5.75224325020859 -1.01896526747051 3.02575712041574 \\
C 5.46606729314668 0.41873250229226 4.02391764821968 \\
C 4.61346363192841 0.21696772404144 2.5101828579547 \\
N 1.95455680362709 0.50285962402658 3.75309481496843 \\

xyz -1 1

N 2.40461318958787 -1.70447068363838 2.19527185906825 \\
C 3.87122709746243 1.06875639740839 4.1346456349157 \\
C 4.5093282083341 1.77801586054326 3.52788764862479 \\
C 5.28501553971211 -2.47478083603855 4.99633646736734 \\
C 3.76742009545758 -2.33261778363281 5.90115689982560 \\
C 4.99090701348463 1.05911202766551 5.9917488288907 \\
C 4.99386411393221 -0.31895351610375 3.3821303162713 \\
C 5.75224325020859 -1.01896526747051 3.02575712041574 \\
C 5.46606729314668 0.41873250229226 4.02391764821968 \\
C 4.61346363192841 0.21696772404144 2.5101828579547 \\
N 1.95455680362709 0.50285962402658 3.75309481496843
TS-B (proton transfer from PrOH to the ligand framework)

Total correction 0.70271949 \text{ Eh}
Final entropy term 0.09068877 \text{ Eh}
Final single point energy -1745.158045 \text{ Eh}
COSMO-RS correction (Gibbs free energy) -202.2324 \text{ kJ mol}^{-1}
COSMO-RS correction (enthalpy) -216.6518 \text{ kJ mol}^{-1}

xyz - 1
N 2.60568585354073 0.005919196431 0.30491393993647
C 3.45507869316309 0.005919196431 0.30491393993647
C 3.883118627195543 0.005919196431 0.30491393993647
H 4.34904971886285 0.005919196431 0.30491393993647
H 3.03264267559543 0.005919196431 0.30491393993647
H 4.56183853959378 0.005919196431 0.30491393993647
C 4.710097763035 0.005919196431 0.30491393993647
H 5.06321853431856 0.005919196431 0.30491393993647
H 5.41410504433156 0.005919196431 0.30491393993647
H 4.46416161023943 0.005919196431 0.30491393993647
N 1.9184142376824 0.005919196431 0.30491393993647
C 1.50886981932830 0.005919196431 0.30491393993647
C 2.76791626102171 0.005919196431 0.30491393993647
C 2.10613658512193 0.005919196431 0.30491393993647
C 1.96750044860637 0.005919196431 0.30491393993647
C 2.91268792120874 0.005919196431 0.30491393993647
C 3.5213483578556 0.005919196431 0.30491393993647
C 0.41346940137086 0.005919196431 0.30491393993647
C -0.9451648527854 0.005919196431 0.30491393993647
H -1.08127091934527 0.005919196431 0.30491393993647
N -0.99988123727517 0.005919196431 0.30491393993647
C -1.76895876363024 0.005919196431 0.30491393993647
C -0.46440206191398 0.005919196431 0.30491393993647
C -0.35108759791749 0.005919196431 0.30491393993647
C 0.140533144315 0.005919196431 0.30491393993647
C 0.9458254325886 0.005919196431 0.30491393993647
N 1.15986852443939 0.005919196431 0.30491393993647
C 1.258434642854 0.005919196431 0.30491393993647
C 0.56708133172138 0.005919196431 0.30491393993647
C 0.69224481969597 0.005919196431 0.30491393993647
C 0.63564164484832 0.005919196431 0.30491393993647
C 0.24531253332826 0.005919196431 0.30491393993647
C -0.22094777873149 0.005919196431 0.30491393993647
C 0.20935493203241 0.005919196431 0.30491393993647
C 1.89363140781716 0.005919196431 0.30491393993647
C 2.17615092994437 0.005919196431 0.30491393993647
C 0.85415102913482 0.005919196431 0.30491393993647
C 2.51694315813894 0.005919196431 0.30491393993647
C 3.5819576056238 0.005919196431 0.30491393993647
C 4.21716951378654 0.005919196431 0.30491393993647
C 3.795283598017 0.005919196431 0.30491393993647
C 3.8542144482916 0.005919196431 0.30491393993647
C 1.66257999531978 0.005919196431 0.30491393993647
C 1.040346283137043 0.005919196431 0.30491393993647
C 1.74980797684521 0.005919196431 0.30491393993647

S-99
iso-[(EtO)-1*-H]−

| xyz | 1 |
|-----|---|
| N   | 2.13613020892744 | 1.7819934730403 |
| C   | 3.55188407240640 | 1.42572984077367 |
| C   | 4.2054469498707 | 0.90072984077367 |
| H   | 4.99084938902996 | -0.6769955890317 |
| H   | 3.54551225496044 | -1.14620053451289 |
| H   | 4.75458585372405 | -1.52201193056251 |
| C   | 4.67155792009688 | -0.49980633934566 |
| H   | 5.4011279760995 | -2.61041844517812 |
| C   | 5.18292155509607 | -2.32870675265716 |
| H   | 4.8226362449159 | -1.35392515636997 |
| H   | 1.7819934730403 | -0.00356091369009 |
| H   | 1.2135916470853 | 0.59914105537029 |
| C   | 2.59561056740429 | 1.6193956430432 |
| C   | 1.64508056811797 | 0.50511056740429 |
| C   | 0.13718669815324 | 4.68801512930149 |
| H   | 0.307942468683 | 0.458826712085 |
| H   | 0.57038156331372 | 0.13916641064244 |
| H   | 0.64744505579723 | 0.64744505579723 |
| H   | -1.19817297197943 | 2.63097623502303 |
| H   | -1.47607568794554 | 3.8113675379210 |
| H   | -1.29145461541668 | 0.28711756955566 |
| H   | -1.90072984077367 | 0.95574647070669 |
| N   | 1.1202183965458294 | 1.12306878485451 |
| C   | 1.44704785293967 | 0.59377224351792 |
| C   | 0.61187253161335 | 1.95574647070669 |
| H   | 0.99552962010170 | 1.12306878485451 |
| H   | 0.95457854379305 | 0.45897974191365 |
| H   | 0.28897966829643 | 3.89000794719365 |
| C   | 1.00009455521708 | 4.6770357073857 |

xyz - 1 : Final single point energy

xyz - 1 : Total correction

xyz - 1 : Final entropy term

xyz - 1 : COSMO-RS correction (Gibbs free energy)

xyz - 1 : COSMO-RS correction (enthalpy)
iso' -[(EtO)-1*-H]^-
Total correction 0.67959930 Eₜ
Final entropy term 0.08972258 Eₜ
Final single point energy -1705.787333 Eₜ
COSMO-RS correction (Gibbs free energy) -213.2083 kJ mol⁻¹
COSMO-RS correction (enthalpy) -229.0990 kJ mol⁻¹

xyz -1 1

N 2.17906371588659 -1.14135624912097 1.51962875527214
C 2.18506871492837 -1.34180525744693 3.97061753068117
C 0.80242147542898 -1.93849611264555 4.24394717888991
H 0.83094393343640 -3.07131056857971 4.12543404845505
H 0.04517386632854 -1.57914954919882 3.57412830446322
H 0.50744126485558 -1.75556262980733 5.2684258139616
C 3.18620456110999 -1.90210095494116 4.9834543055813
H 3.20975643506462 -2.9926186297693 4.9633208522726
H 2.6917711096808 -1.6100429375520 5.9857716366253
H 4.19587052033375 -1.5290334488384 4.80755940877899
N 1.36375347164633 0.91630213471233 3.22501071622643
C 1.17113834437509 2.1242326937948 3.8414646016935
C 2.07625991732946 0.14604509668966 4.1068921602409
C 1.80896759793233 2.14255070403557 5.06110008551632
H 1.83993199673631 2.96147025537371 5.76180098924274
C 2.38911349162221 0.87137459130801 5.23377244657594
H 2.93906848068009 0.53164528019619 6.09763001593090
C 0.20760198636873 3.14727856390701 3.3131486426338
C -1.23007572634024 2.61564511477225 3.5087432976630
C -1.43037298011264 2.44280116625192 4.56646344489147
H -1.3819142296403 1.67569219086348 2.98041546967475
H -1.9519985846015 3.3433459813156 3.12805544550207
C 0.32655964028888 4.43428294710659 4.13340125068421
H -0.4038753909015 5.17138591136552 3.79956195678276
C 1.3200236865488 4.87454933410999 4.04719840847026
H 0.12246765725872 4.23788424823531 5.18692517096014
N 0.86641204268984 2.51305534445701 0.95079484653341
C 0.95381420756461 3.16254265035469 0.25703655283775
C 0.46054490878782 3.45454905656028 1.8663688326150
C 0.60210938145266 4.48127652164419 -0.11218376427444
H 0.58749612426163 5.23377917715952 0.8851059643318
C 0.2848424747098 4.66813840081684 1.24811677250622
H -0.02965181655718 5.58933491499497 1.7129003344172
C 1.50896645690674 2.5152505293792 2.14885589707646
C 1.13495664969957 3.3995612181616 -0.72581475797704
H 1.52807679898710 4.34435441726685 -2.65477862689248
H 0.05350778037331 3.39189139281774 2.8484834148208
H 1.55985420570915 2.8797084160386 -3.62431788062960
C 3.05039364028637 2.4915193017701 -1.38833038709338
H 3.49075876050556 2.01681666062829 -2.28900923644938
C 3.37718094578430 1.93845368666721 0.50814793900006
C 3.44038105525264 3.50820368077051 -1.30497248701135
C 1.24007364256241 0.18764137795600 -0.65247323154707
C 0.96851864618662 1.04445815852175 -1.20031911258193
C 1.03118018922340 1.104142429391 1.64412019199207
C 0.53610274819429 -0.89932027468821 -2.4981320277496
H 0.2759472176988 -1.6881527642896 3.1880729635965

S-105
TS-C ([1,5]H sigmatropic shift from 2- to 3-position of the dearomatized pyrrole ring, top side)

Total correction
Final entropy term
Final single point energy
COSMO-RS correction (Gibbs free energy)
COSMO-RS correction (enthalpy)

xyz -1 1
N 2.323140663630445 -1.58221366065805 -1.99516322732385
C 3.5653148157775 -1.196121445458211 4.00962401409102
C 3.9475453169515 -1.984180594707666 5.20510387813450
C 4.66110770559376 -2.85662436835175 4.87553598549738
C 3.84510629774623 -2.31813499353087 5.86323621696647
C 4.76226514023413 -1.36410974474096 5.0002943472266
C 4.7641576678167 -0.71140430370668 3.17442707420511
C 2.8825185586161 1.5489579757800 2.817582057749
C 5.93925799527206 -0.06631683374566 3.78691478444899
C 4.4467700284978 -0.13483233967854 2.30703638973418
N 1.8710699444048 0.64954932700487 3.63271138931553
C 3.8308021192422 1.07283082098002 4.35610189960949
C 2.73630078725711 -0.02642906230040 4.46712454551829
C 1.9082496527022 1.68413070724292 5.6239421739538
H 1.66991181819829 2.38161678064024 6.4219877664058
C 2.77490379212673 0.57571316791437 5.70195283776428
S-D ([1,5]H sigmatropic shift from 3- to 4-position of the dearomatized pyrrole ring, top side)

Total correction $0.67527549 \text{ E}_h$

Final entropy term $0.08905227 \text{ E}_h$

Final single point energy $-228.1999 \text{ kJ mol}^{-1}$

COSMO-RS correction (Gibbs free energy) $-247.8355 \text{ kJ mol}^{-1}$

COSMO-RS correction (enthalpy) $-228.1999 \text{ kJ mol}^{-1}$

xyz -1 1

N 2.18614575752033 -1.65717331318152 2.03785101170519
C 3.56544320118840 -1.10678567917740 4.089183092814
C 4.16371755272359 -1.86378044595521 5.21912508747537
H 4.90063905136265 -2.59914726556600 4.88699530983361
H 3.95262177299061 -2.37240221794736 5.80221196327744
H 4.68178395769484 -1.17130491381070 5.88083416565072
C 4.72124769249131 -0.43289915369330 3.26348787584734
H 5.45299791812636 -1.16803686359566 2.91188793632538
H 5.22659018142247 0.27890686415826 3.91688793632538
H 4.35785179402088 0.11820173529088 2.39681175153140
N 1.7838067338306 0.61579891557988 3.65118296043040
C 1.21006684414777 1.63506276901924 4.37197941668968
C 2.60023579446670 0.06270898601550 4.51021796411610
C 1.64309880043190 1.57445337850909 5.67853165331000
H 1.36404335841195 2.22815232261107 6.48132038471032
C 2.53563142080669 0.48868910028041 5.76994348843040
H 3.07984295884049 0.17640999079109 6.64792532518812
C 0.23274623950915 2.63774253797560 3.80191745257989
C -1.20482646670572 2.08932145700235 3.91053406682644
H -1.47858201903595 1.97051923568897 4.96213377956112
H -1.29468294532397 1.11872835047572 3.43077512037662
H -1.91243409211111 2.77862630583564 3.44357037212110
C 0.27953257248955 3.91265270445811 4.65660205354094
H -0.43631014712719 4.64607980977511 2.84112967276995
H 1.27091377307617 4.36410288847649 4.6461919918218
H 0.00361859033726 3.7003378261385 5.69040174317474
N 1.20159547322890 2.15527054306567 1.50665378613149
C 1.44111017170315 2.84179881442867 0.35227307119025
C 0.95982551096233 3.01557077600989 2.38368050466571
C 0.98999917761830 4.12583016811190 0.47191076272278
H 1.02775035250937 4.91135953295800 -0.2687667459566
H 0.42574039474882 4.23843605475535 1.77111339529592
C -0.01586954317149 5.12293846618725 2.20378104783288
C 2.27166897040687 2.2370296131175 0.74495184901963
C 2.19075026184044 3.10958560166579 -1.9902773065632
H 2.54064173585634 4.1195550217855 1.7794228906428
H 1.16810646245695 3.1756106845542 -2.36783534466697
H 2.82151908108094 2.7048432163434 -2.79089907340734
C 3.74675676381181 2.2024290326823 -0.29162035972672
H 4.3804280979951 1.7842658630807 -1.0669767936123
H 3.87159438299481 1.6054225011385 0.6116644627768
C 4.10091606786110 3.21093726396461 -0.6803355557318
N 1.67589272666626 -0.11385698934689 -0.09894952487598
C 1.3793443711995 -1.2932287406603 -0.7368811796578
H 1.82896718892283 0.83664645062687 -1.0691518740516

S-108
TS-E ([1,5]H sigmatropic shift from 4- to 3-position of the dearomatized pyrrole ring, bottom side)

Total correction: 0.67583717 \text{E}_\text{h}

Final entropy term: 0.08741234 \text{E}_\text{h}

Final single point energy: -1705.743259 \text{E}_\text{h}

COSMO-RS correction (Gibbs free energy): -228.8232 \text{kJ mol}^{-1}

COSMO-RS correction (enthalpy): -248.4162 \text{kJ mol}^{-1}

xyz -1.1

N 2.13014381652094 -1.69286064980186 2.07509153596785
C 3.55279033076982 -1.10292679952901 4.04187890575874
C 4.15314051071141 -1.8632569015860 5.2386627606196
H 4.92727858479240 -2.5606547382574 4.8961684457418
H 3.39105472195456 -2.4159983795600 5.77408772622900
H 4.64276076842579 -1.16886525458940 5.91155479002022
C 4.70156596240984 -0.37127106403092 3.31105276028023
H 5.46668867598127 -1.07212126703399 2.96573689997941
H 5.16502312179779 0.3463145740821 3.98920376623767
H 4.33757908648401 0.18361979825480 2.44729842229620
H 3.57037118343621 0.6013536041618 3.65410347615751
C 1.14648952012501 1.607347284046 4.37831183261319
C 2.54972910484989 -0.07945652394095 4.52111287219068
C 1.56014762775654 1.51515398349321 5.6990732559868
TS-F ([1,5]H sigmatropic shift from 3- to 2-position of the dearomatized pyrrole ring, bottom side)

Total correction $E_n = 0.66835617$ E
Final entropy term $E_n = 0.07769826$ E
Final single point energy $E_n = -1705.752109$ E

COSMO-RS correction (Gibbs free energy) $E_n = -224.9765$ kJ mol$^{-1}$
COSMO-RS correction (enthalpy) $E_n = -243.8171$ kJ mol$^{-1}$

xyz - 1 1
N 1.653585835352905 -1.48390367120637 1.67025928020529
C 2.844297208939832 -1.03328387919545 3.80253524456461
C 3.27072798820738 -1.8461961345708 5.02445705428579
H 4.06207507420443 -2.55580574072555 4.77725441630317
H 4.23155505065351 -2.3948872745772 5.4529415667294
C 3.66305676467020 -1.18423092252729 5.79161734950971
C 4.09551717839882 -0.32542691514804 3.23384045718176
H 4.86754920902473 -1.04435500114351 2.94566745297351
C 5.40557533811774 0.34518486024705 3.98943796115270
H 3.84927712801727 0.27817065324724 3.65055374794942
N 1.16397975015076 0.75471524048042 3.26315612368482
C 0.53943717229899 1.76683304555938 3.94855000106866
C 1.82719322452718 -0.00125789985395 4.19061398476126
C 0.78181733207088 1.62524472147594 5.29780710503199
H 0.42166814097192 2.26412434171598 6.08854036266431
C 1.60816933934102 0.49639502023473 5.45419522897543
H 2.01265702367440 0.12267615131166 6.39207866020784
H 1.07092636122274 0.50829380416928 6.0142938513272
H 1.05039641050550 0.26471246634611 3.05411894284662
C 3.003962653410550 0.26471246634611 3.37506705421372
C 1.78034646591598 2.41360178441547 3.287506705421372
H -2.15518662974016 2.29894232630036 4.29538579314415
H -1.90016876510849 1.4690387102554 2.77017283642806
H -2.38743099283406 3.16439312535040 2.76394677797776
C -0.22989904230251 4.10628258207708 4.18031768801817
H -0.851884547679920 4.8947215252271 3.76491170100262
H 0.79080966604064 4.47794987551017 4.26543825406462
C -0.60856257513644 3.90569251438558 5.18589326117322
N 0.82266593555624 2.32526497434007 1.08438993681198
C 1.17329849998056 3.06681564584701 -0.04459618016460
C 0.20833670872474 3.21224451299309 1.92918156109036
C 0.772078363959651 4.31811032930584 0.6031545647089
C 0.91997528084649 5.10492674444500 -0.6674243143995
C 0.15142892931870 4.44837208512107 1.32195819050266
C -0.27010372746627 5.35243180352177 1.73353498014920
C 2.01600197948704 2.36085700471352 -1.10794255271156
C 2.05334983139393 3.24755159346356 -2.35084479260009
C 2.46087305121740 4.22932357298727 -2.1069327310240
H 1.05593438485449 3.85759857910640 -2.7673900112179
H 2.39115468593631 2.80995779660201 -3.12065375665588
C 3.462232352791267 2.22056736431996 -0.58717093192825
C 4.10237200926177 1.75488698455835 -3.14069070324812
C 3.50464326372421 1.60523617758478 0.31196012885174
C 3.8715395322656 3.20033365578811 -0.32590199671515
H 1.27933100309399 0.42644340679777 -0.51579920778484
H 0.94086065572487 -1.11116261531380 -1.1790388140103
H 1.49721182663631 0.99625063854843 -1.46825679914848
C 0.92917304108100 -0.88180256729521 2.53758057123141
H 0.71218127232107 -1.59659950460649 -3.31705981427934

S-111
[Al(pyrrolato)]$^4^-$

Total correction 0.31739921 $E_h$
Final entropy term 0.06634157 $E_h$
Final single point energy -1082.707964 $E_h$
COSMO-RS correction (Gibbs free energy) -188.5814 kJ mol$^{-1}$
COSMO-RS correction (enthalpy) -204.4565 kJ mol$^{-1}$

xyz - 1 1
Al 1.33224466407753 0.84174815051162 -0.03022587446241
N 0.302478546564727 -0.05976289995850 -0.87976899589828
N -1.9979917026661 -0.595484874329864 1.12613923501251
N -2.83452460564994 1.22903217840351 -0.016592568812740
N -0.86033601314796 2.22634845150022 1.08073232665115
C -3.73718583453873 0.32180456097723 -1.51382771762033
C -4.75201440680994 0.9821000271833 -2.152379118176761
C -4.46751810862243 2.36682051935472 -2.04850385201313
C -3.29393875359374 2.47915533010773 -1.3532956898513589
C -3.58474881273287 -0.74101387780401 -1.39544262549067
C -5.59792746027641 0.52793870333872 -2.64333218128401
C -5.05579440340284 3.18141112946674 -2.43922191806810
C -2.74864355296595 3.3649921292218 -1.06602777229664
C -1.15238220629122 -0.77096185201422 -0.03950992301044
C 0.84761300304271 -1.69734190261114 -2.17728306561583
C -0.98055415278198 -0.55160057330668 -2.69662119664173
C 1.69288005359894 -1.55865311990433 -0.841762634962
C 0.97312304163530 -2.38055291726935 -3.00191770959099

S-112
[Al(PrO)(2H-pyrrole)(pyrrolato)3]^−

Total correction 0.43602076 Eₜₜ
Final entropy term 0.07785621 Eₜₜ
Final single point energy -1277.384344 Eₜₜ
COSMO-RS correction (Gibbs free energy) -203.7190 kJ mol⁻¹
COSMO-RS correction (enthalpy) -220.2146 kJ mol⁻¹

xyz -1 1
A  -2.333807797277054  0.40919620589848  -0.00857630508448
N  -1.075341898010890  -0.7446867889504  -0.87955976476872
N  -1.84350948793238  -0.8512374986637  1.77777177927941
N  -2.5801901509518  1.564222448086719  -1.54705285538993
N  -1.78326162323731  1.792732963494388  1.21527428644643
C  -2.70021899954844  1.1124879953294  -2.82722320493802
C  -3.16248467267185  2.1167629610386  -3.64781701123198
C  -3.35587976522154  3.25391567232419  -2.82350406450829
C  -2.96915531859309  2.86980482752699  -1.55280705443803
C  -2.42727476213684  0.9989569234689  -3.08128837740363
C  -3.33756616884689  2.04532050123695  -4.71101281501808
C  -3.67000935438735  4.2361103073672  -3.1239541211579
C  -2.94047732952130  3.45911168716640  -0.64934712541610
C  -1.27784141193332  -2.05715846553861  -1.17724811460204
C  -0.112561660773007  -2.61764013054454  -1.65487570856122
C  -2.42726725793598  -2.51449168200267  -1.01641827291947
C  -0.856870704339705  -1.58687959164709  -1.6491915316728
H  0.02011375363710  -3.63797049817309  -0.98181044895954
H  -0.22073830207970  -0.45993452953484  -1.1755503483060
H  1.88471739248331  -1.65370155578182  -1.97196135993477
H  0.6079751474530  0.5409036671001  -1.05369202232829
C  -0.56240297773428  1.95787413869108  1.7868968711839
C  -0.64824682729317  2.82997450997131  2.85245343776655

S-113
[Al(PrO)(pyrrolato)]^-

Total correction 0.34515505 Eₜ
Final entropy term 0.06889804 Eₜ
Final single point energy -1066.862885 Eₜ
COSMO-RS correction (Gibbs free energy) -191.9732 kJ mol⁻¹
COSMO-RS correction (enthalpy) -207.6408 kJ mol⁻¹

xyz -1 1
Al -2.32787089376532 0.82705298236956 -0.03176798616917
H -0.72027461966568 -0.13098925109499 -0.05198552017321
N -2.69484326942027 1.4053058323144 -1.7849379284843
N -2.14455272353750 2.39653377244750 0.98088437084716
C -3.63563406779807 2.32677802891561 -2.14669524078630
C -3.80485210954831 3.2121398684528 -3.5102704153960
C -2.920566684743 1.3622813432498 -0.41041599867765
C -2.26467582393790 0.79754418300096 -2.92871389225786
H -4.1152008498012 2.9464469420182 -1.40368042404943
C -4.47441619699379 2.94056312355605 -4.07742764407069
H -2.77553485131929 1.0468178597711 -5.04642975996800
H -1.5057555924184 0.03047042862232 -2.8913994573531
C -0.57218332289684 1.44979956157430 -0.37345237676430
C 0.76153715114468 -1.77536152848986 -0.40580846842932
H -1.43594111935103 -2.07386224974216 -0.5441913323080
C 1.47243586163673 -0.5916129598800 -0.08621342471850
H 1.17650768212150 -2.74733284343338 -0.625115680201
C 0.53066752985422 0.35892936339921 0.1212022399302
H 2.54253340129506 -0.4732516060121 -0.01104181603724

S-114
H 0.66529476144884 1.42213837269779 0.39257276466219
C -1.659739190581959 3.60016814209981 0.55525370259810
C -1.61355203883104 4.82793711974557 1.60655393823916
C -2.09622424233991 3.7842498308466 2.74115762977235
H -1.39142833038863 3.75000619554777 -0.47945205314921
H -1.27862841398590 5.50795249458257 1.56483731224406
C -2.40752355575421 2.51651064915022 2.31501185289621
H -2.20397362752990 4.1564920437941 3.74508836488893
H -2.8021644147906 1.6817764324322 2.87381040205348
O -3.56132209162512 -0.20152681494794 0.6133923368139
C -4.93772366865656 -0.09913430548003 0.43444027212667
C -5.38200026579659 -0.84663222596842 -0.8191444080627
H -5.25157156337731 0.95221010703732 0.31320385073870
C -5.64497913701656 -0.63597743281870 1.6742002943900
H -4.90631120938267 -0.43167812367875 -1.7083812919231
H -6.46489740599642 -0.78142389940667 -0.95717235630211
H -5.11289513334456 -1.90295047747335 -0.74831948195480
H -6.73025771330453 -0.55619930710356 1.5806684674870
H -5.33945123649746 -0.07981437649917 2.5615269849979
H -5.39289895013777 -1.68675164795998 1.83301763077244

**Pyrrole**

![Pyrrole structure](image)

| Total correction | 0.08916040 $E_h$ |
| Final entropy term | 0.03109797 $E_h$ |
| Final single point energy | -210.5397951 $E_h$ |
| COSMO-RS correction (Gibbs free energy) | -18.5570 kJ mol$^{-1}$ |
| COSMO-RS correction (enthalpy) | -27.7344 kJ mol$^{-1}$ |

**xyz 0 1**

| C | -3.1677312266824 1.4906263912866 | 0.00000004381216 |
| C | -3.611439795057681 0.1949271341632 | -0.0000000480130 |
| C | -1.75164479768707 1.44976016180396 | -0.00000003133579 |
| C | -1.38338953097042 0.1306343856680 | -0.0000000241988 |
| N | -2.51995714076936 -0.618324534647875 | 0.0000000303930 |
| H | -3.79022514050460 2.3709613267319 | 0.00000000812389 |
| H | -4.61150174043674 -0.20470728239412 | -0.00000008359443 |
| H | -1.07946343698337 2.29186507130705 | -0.00000004741657 |
| H | -0.40839501129977 -0.32600876379494 | 0.0000000046400 |
| H | -2.54888579845143 -1.6206306961818 | 0.00000005698351 |
Total correction 0.71051872 Eₜₙ
Final entropy term 0.09246479 Eₜₙ
Final single point energy -1745.17823 Eₜₙ

COSMO-RS correction (Gibbs free energy) -201.9558 kJ mol⁻¹
COSMO-RS correction (enthalpy) -216.6230 kJ mol⁻¹

xyz -1 1
N 1.05577210416848 1.74757653046231 1.72816285799472
C 2.04865679370327 -1.05316943176334 3.905045797329278
C 1.63082270052089 -2.22634606467565 4.81206272594924
H 2.35449805717003 -3.03962849724204 4.73487632646646
H 0.65093230570971 -2.61482267579950 4.53284474407278
H 1.57597633067748 -1.92152925385659 5.85767071983898
C 3.42274830417543 -0.54401251957717 4.36708057693209
C 4.17981933825782 -1.33155251924570 4.32503479193750
H 3.35890023735100 -1.18637482878964 5.3940759255415
H 3.75394024652152 0.28568361656344 3.74334650134030
N 0.67714890001590 0.94128999102988 3.01857625293995
C 0.03652466221804 2.05060878389655 3.63063265612119
H 1.04850611634049 0.07512258327252 0.40289814680109
C -0.02510086763055 1.77890035307092 4.98641106882961
H -0.46916600860461 2.42695826056858 5.72524847575376
N 0.61313109959885 0.55492299738241 5.23526813664431
H 0.79608527320284 1.11205614212188 6.20924658970041
C -0.56086151013868 3.23518497185584 2.96333944150218
C -2.08806154362670 3.05860617100772 2.83477526596794
H -2.53840525355691 2.96113475002563 3.85225694495733
C -2.33578661541408 2.16319412126382 2.27312734706330
H -2.53218978360053 3.92174527939116 2.22357725236389
C -0.32796361481322 4.44456401289103 3.84471425214636
H -0.761212246288728 5.34397659964824 3.47004155277231
C 0.73500624809652 4.61966553723219 4.04499120019258
H -0.80538570754133 4.30424368905534 4.85415421730821
C 0.57360432703567 2.95638636005563 0.80925077262520
C 0.17186040186611 3.20028162981016 1.58340603299027
C 0.06748355362698 3.56012125436659 1.52326086772611
C 0.87072646004041 4.55650914479996 0.51128599572354
H 1.16642466660240 3.50581936918665 3.09299606412461
C 0.22658106866658 4.76891871640351 1.02766949984174
H -0.08696151072381 5.74671298135606 1.42168430563103
C 1.84426690163645 3.9553976793569 1.30359791467454
C 1.9840931427030 3.1998471695557 2.60346793553431
H 2.48911436273515 1.42475373267011 -2.40857957766749
C 2.33269211444208 3.41659242568509 0.04298083399359
H 2.58066318500310 2.65134240134048 3.35655814919005
C 3.26164369574681 2.13140422220148 -0.75786507440149
C 3.85406347059189 1.5604381651927 -1.47649994030660
C 3.32901658344547 1.56100220594457 0.17002680367204
C 3.7680008416775 3.07608526462030 -0.5520517225344
H 0.96323360803795 0.12168943333373 -0.6151299288126
C 0.54578088082737 -1.02973917564832 -1.26483061019739
C 1.1920611945675 0.0649515002697 1.59628393165785
C 0.47837643026414 -0.79304811618386 -2.61505016034113

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 anti-[(PrO)-1-H] 

Total correction 0.71038785 $E_h$
Final entropy term 0.09240566 $E_h$
Final single point energy -1745.179903 $E_h$
COSMO-RS correction (Gibbs free energy) -205.2013 kJ mol$^{-1}$
COSMO-RS correction (enthalpy) -220.9374 kJ mol$^{-1}$
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