Electronic Supporting Information for

Barium complexes with crown-ether-functionalised amidinate and iminoanilide ligands for the hydrophosphination of vinylarenes

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Contents

Experimental section

General procedures

All manipulations were performed under inert atmosphere using standard Schlenk techniques or in a dry, solvent-free glove-box (Jacomex; O_2< 1 ppm, H_2O < 3 ppm). BaI_2 (Aldrich, 99.995% anhydrous beads) were used as received. $HN(SiMe_2H)_2$ (ABCR) was dried over CaH_2 and distilled prior to use. $[Ba\{N(SiMe_2H)_2\}_2.(thf)_2]$ and $[Ba\{N(SiMe_2H)_2\}_2.(thf)_2]_\infty$ were prepared following the literature procedure.[1]

Solvents (thf, Et_2O, petroleum ether bp 40-60 °C, and toluene) were purified and dried (water contents all below 10 ppm) over alumina columns (MBraun SPS); thf was further distilled under argon from sodium mirror/benzophenone ketyl prior to use. All deuterated solvents (Eurisotop, Saclay, France) were stored in sealed ampoules over activated 3 Å molecular sieves and were thoroughly degassed by several freeze-thaw-vacuum cycles prior to use.

NMR spectra were recorded on a Bruker spectrometer Avance III 400 MHz equipped with a BBOF pulsed field-gradient probe or a Bruker spectrometer Avance 500 MHz equipped with a dual pulse field gradient probehead. All ^1H and ^{13}C chemicals shifts were determined using residual signals of the deuterated solvents and were calibrated vs. $SiMe_4$ (δ = 0 ppm). Assignment of the signals was carried out using 1D (^1H, $^{13}C\{^1H\}$) and 2D (COSY, edited HSQC and HMBC) NMR experiments. Solid-state FTIR spectra were recorded between 400 and 4000 cm^{-1} as Nujol mulls in KBr plates on a Shimadzu IRAffinity-1 spectrometer. Elemental analyses were performed at the "*Centre de Mesures Physiques de l'Ouest*" (CRMPO, Rennes). However, the extreme air-sensitivity of the barium complexes precluded the acquisition of reliable and reproducible data sets. ESI mass spectra were recorded at the CRMPO Scanmat (Rennes, France) on an orbitrap type Thermo Fisher Scientific Q-Exactive instrument, with an ESI source in positive or negative mode by direct introduction at 5-10 $\mu g.mL^{-1}$. Samples were prepared as CH_2Cl_2 solutions with concentrations of 10 $\mu g.mL^{-1}$.

Protocol for hydrophosphination catalysis

In a typical experiment, the substrates, precatalyst and, if applicable, solvent (C_6D_6), were loaded in a Teflon-valved J-Young NMR tube under inert atmosphere, sealed and shaken vigorously, and introduced in the probe of the NMR spectrometer pre-set to the required temperature. Reaction times were measured from this point. The reactions were quenched by opening the tube to the air and adding non-dried C_6D_6 to the tube.

Synthesis of aziridine

(Scheme 1, step i)

An aqueous solution of NaOH (77.6 g, 1.94 mol) in deionized water (460 mL) was added to a 1L round-bottom flask containing 2-chloroethylamine hydrochloride (90.0 g, 0.77 mol). The resulting solution was stirred for 2 h at 50 °C. Aziridine was then recovered by distillation at 75 °C under partial static vacuum. It was then dried over NaOH pellets in a round-bottom flask stored at –30 °C overnight (a round-bottom flask must be used as the volume of the mixture will increase substantially during drying). Phase separation occurred, and aziridine was recovered as the upper layer of the biphasic mixture. The drying process was repeated once more, after what analytically pure aziridine was obtained as a colourless oil. Yield 24.9 g (75%). ^{1}H NMR ($CDCl_3$, 400.16 MHz, 298 K): δ = 4.61 (br s, 1H, N*H*), 1.55 (s, 4H, CH_2) ppm.

Caution! Aziridine is highly reactive and toxic. Extreme care must be applied when handling it.

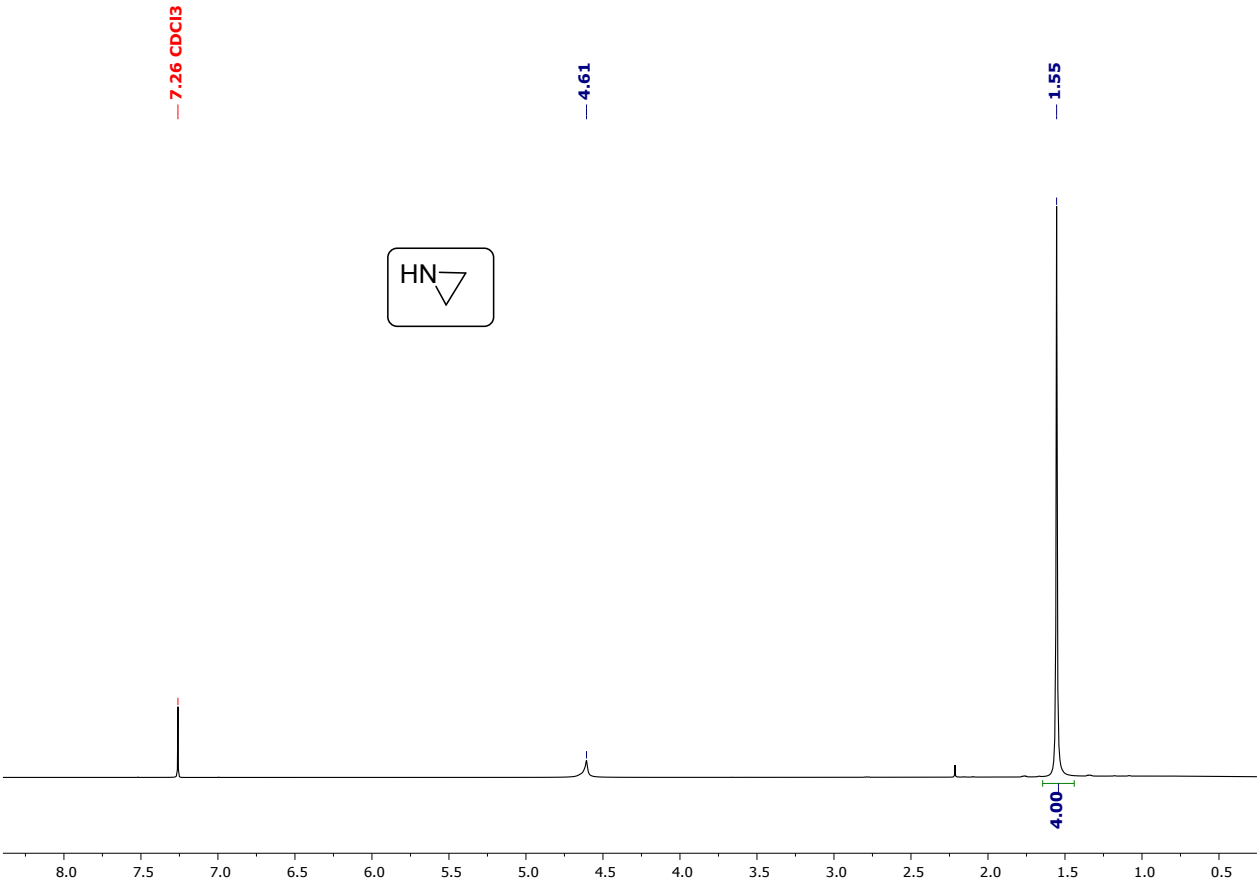

Figure S1. ^{1}H NMR spectrum ($CDCl_3$, 400.16 MHz, 298 K) of aziridine.

Synthesis of *N*-benzyloxycarbonyl-aziridine

(Scheme 1, step ii)

Dry Et_2O (400 mL), NEt_3 (38.8 mL, 280 mmol) and aziridine (3.6 mL, 70.0 mmol) were mixed in a 1L round-bottom flask under inert atmosphere. This mixture was cooled at 0 °C and benzyl chloroformate (11.9 mL, 80.0 mmol) was then added dropwise. The formation of a white solid was observed during the addition. After complete addition, the reaction mixture was stirred at 0 °C for 1 h and then at room temperature overnight. It was extracted with water (2×200 mL), and the combined aqueous layers were washed with CH_2Cl_2 (3×50 mL). The two organic layers were combined and eluted through a pad of silica gel. The volatiles were then removed under vacuum at a temperature below 40 °C. The resulting oil was purified by thin layer chromatography over silica gel, using first neat petroleum ether, and then 90:10 and 80:20 *v/v* mixtures of petroleum ether and Et_2O. After evaporation of the volatiles, the title compound was obtained as a colourless oil. Yield 6.3 g (51%). ^{1}H NMR ($CDCl_3$, 400.13 MHz, 298 K): δ = 7.37 (m, 5H, arom-*H*), 5.14 (s, 2H, C*H*$_2$Ph), 2.23 (s, 4H, NC*H*$_2$) ppm.

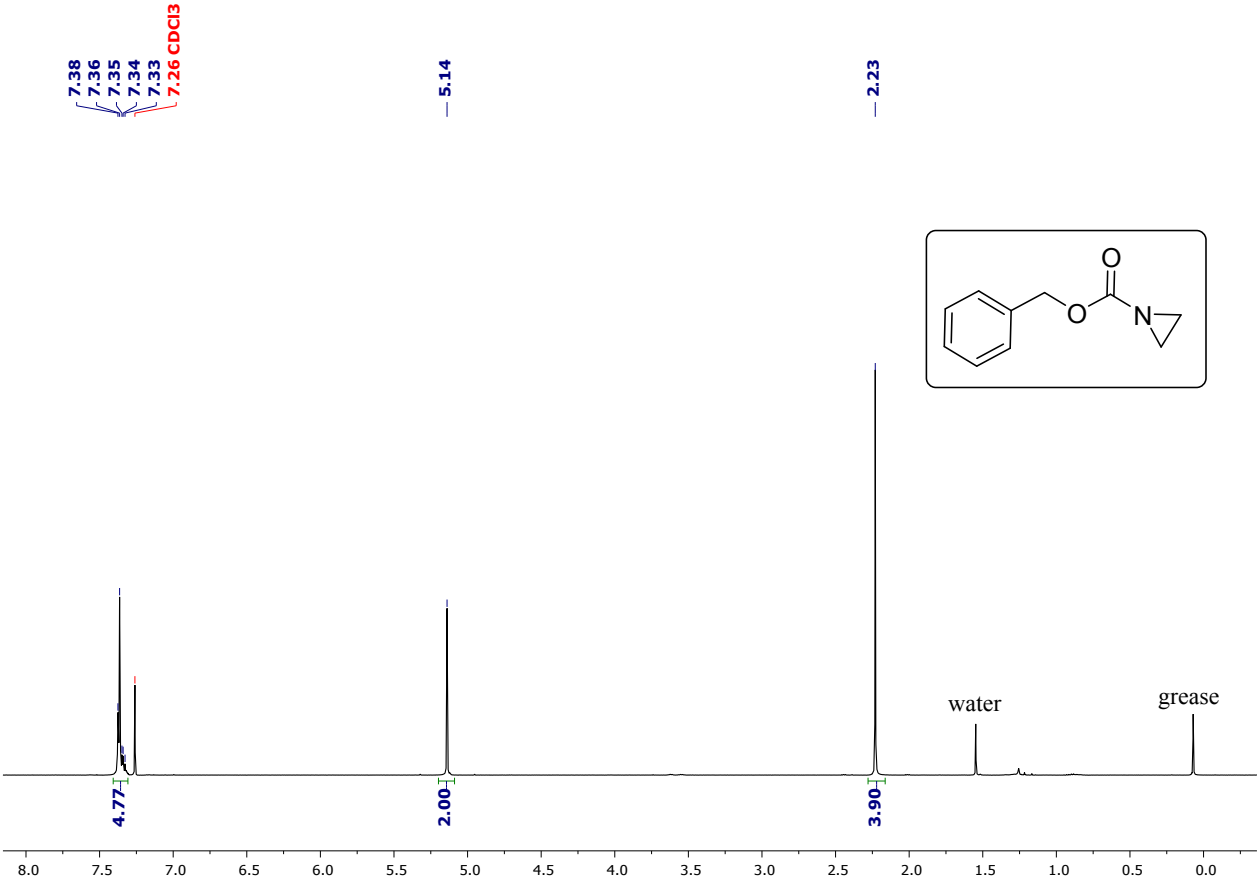

Figure S2. ^{1}H NMR spectrum ($CDCl_3$, 400.13 MHz, 298 K) of *N*-benzyloxycarbonyl-aziridine

Synthesis of triethylene glycol bis-*p*-toluenesulphonate

(Scheme 1, step iii)

N,*N*-Dimethylaminopyridine (0.78 g, 6.40 mmol), triethylene glycol (14.2 mL, 107 mmol) and dry CH_2Cl_2 (50 mL) were mixed in a 500 mL round-bottom flask under inert atmosphere. The mixture was cooled to 0 °C and a solution of tosyl chloride (46.7 g, 245 mmol) in dry CH_2Cl_2 (200 mL) was added. It was followed by the dropwise addition of neat NEt_3 (36.0 mL, 266 mmol). After complete addition, the reaction mixture was stirred at 0 °C for 1.5 h and then at room temperature overnight. The volatiles were removed under vacuum, and the residue was suspended in ethyl acetate and washed with water (2×100 mL). The aqueous phase was back-extracted with ethyl acetate (50 mL), and the combined organic layers were dried over $MgSO_4$ and then concentrated under vacuum. Crystallisation from ethyl acetate at –40 °C afforded the title compound as colourless crystals (41.7 g, 85%). ^{1}H NMR ($CDCl_3$, 400.13 MHz, 298 K): δ = 7.78 (d, $^3J_{HH}$ = 9.0 Hz, 4H, arom-*H*), 7.34 (d, $^3J_{HH}$ = 9.0 Hz, 4H, arom-*H*), 4.13 (t, $^3J_{HH}$ = 6.0 Hz, 4H, TsOCH_2), 3.65 (t, $^3J_{HH}$ = 6.0 Hz, 4H, TsOCH$_2$CH_2), 3.52 (s, 4H, CH_2OCH_2), 2.44 (s, 6H, CH_3) ppm.

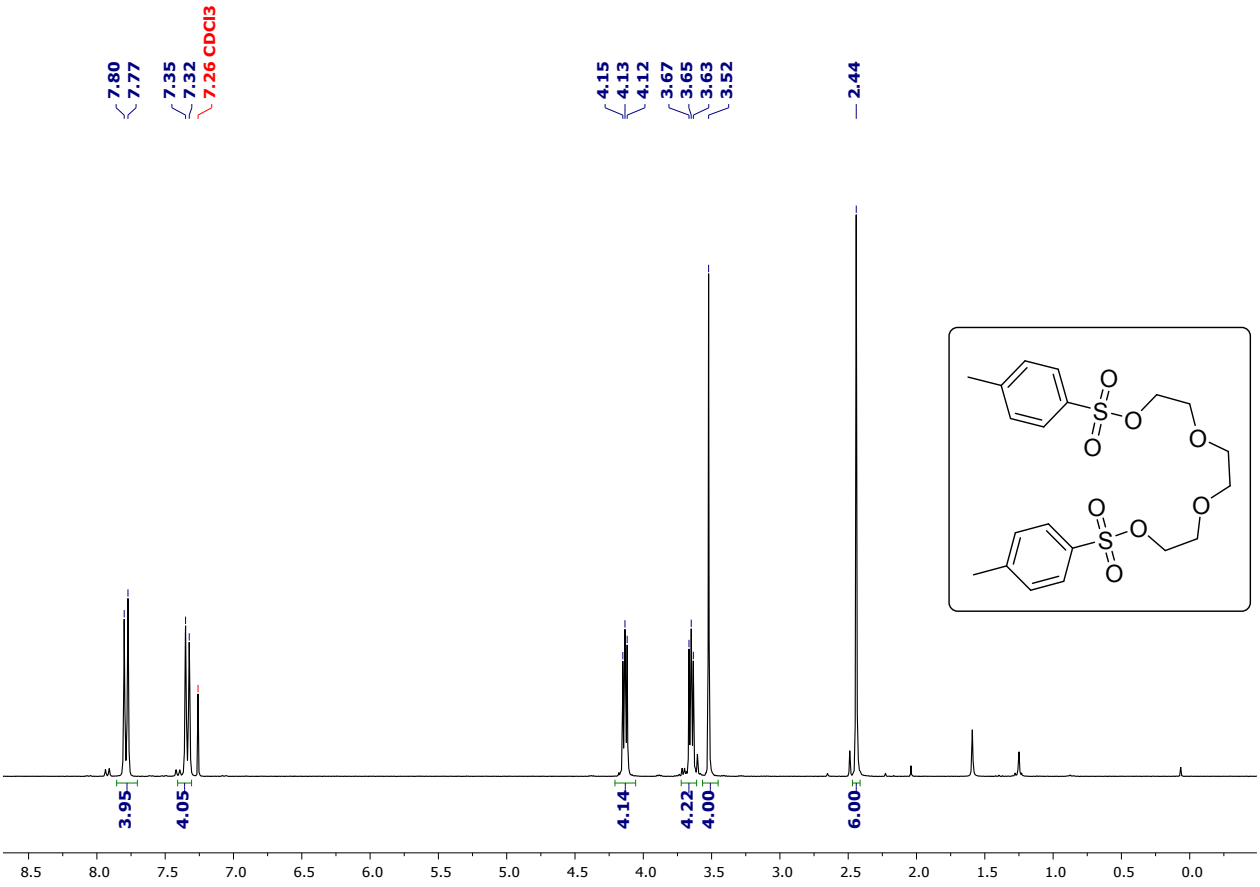

Figure S3. ^{1}H NMR spectrum ($CDCl_3$, 400.13 MHz, 298 K) of triethylene glycol bis-*p*-toluenesulphonate.

Synthesis of *N*-benzyl diethanolamine

(Scheme 1, step iv)

A solution of diethanolamine (6.09 g, 57.9 mmol) in acetone (15 mL) was added to a suspension of benzyl bromide (9.00 g, 52.6 mmol) and Na_2CO_3 (6.13 g, 57.9 mmol) in acetone (30 mL). The mixture was refluxed for 4 h. The volatiles were then removed under vacuum. Water (20 mL) was added to the resulting material, and the aqueous solution was extracted with CH_2Cl_2 (30 mL). The organic phase was dried over $MgSO_4$, and all volatiles were evaporated in vacuo to afford an oil which was washed with hexane (2×15 mL). The title compound was isolated as a colourless oil. Yield 8.22 g (80%). ^{1}H NMR ($CDCl_3$, 400.13 MHz, 298 K): δ = 7.32 (m, 5H, arom-*H*), 3.73 (s, 2H, C*H*$_2$Ph), 3.63 (t, $^3J_{HH}$ = 6.0 Hz, 4H, C*H*$_2$), 2.89 (s, br, 2H, O*H*), 2.74 (t, $^3J_{HH}$ = 6.0 Hz, 4H, C*H*$_2$) ppm.

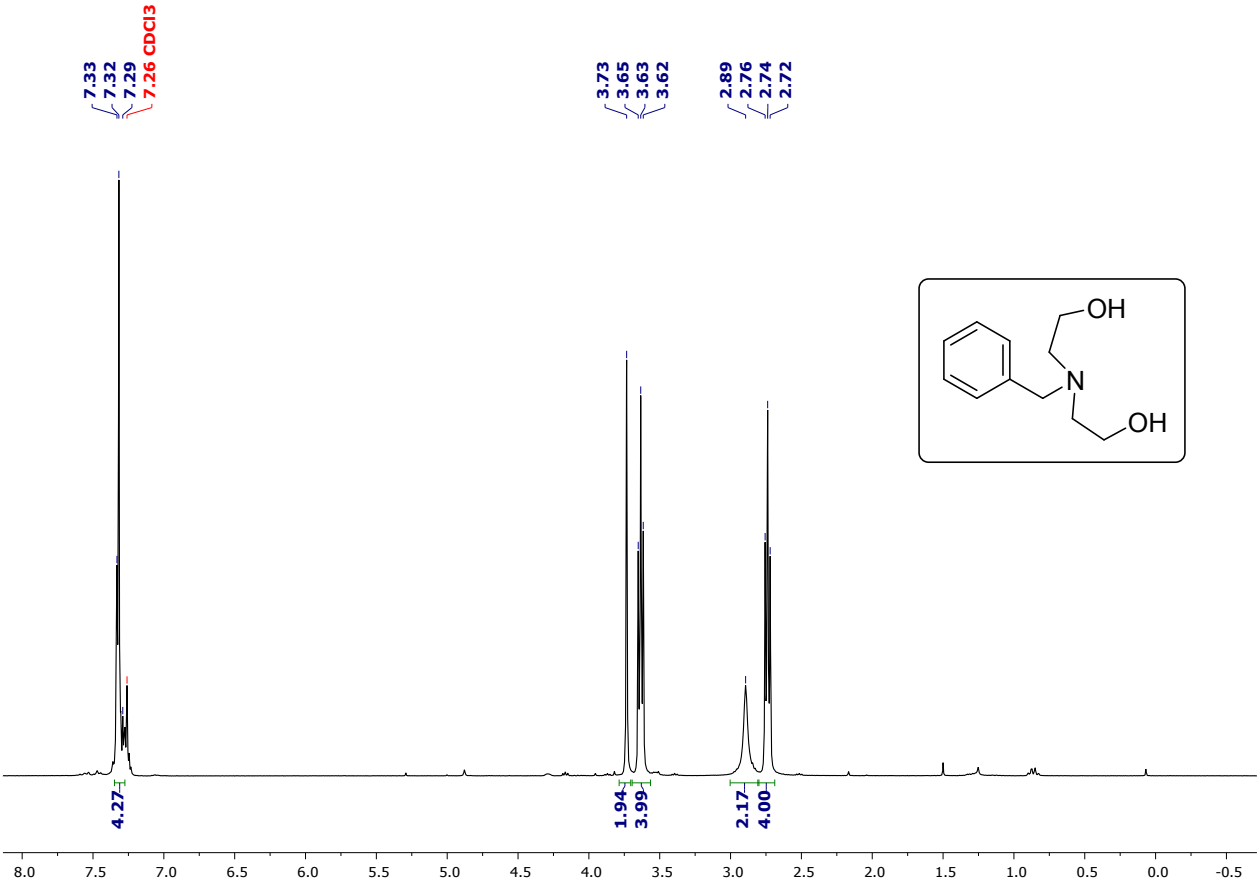

Figure S4. ^{1}H NMR spectrum ($CDCl_3$, 400.13 MHz, 298 K) of *N*-benzyl diethanolamine.

Synthesis of *N*-benzyl-protected 1-aza-15-c-5

(Scheme 1, step v)

In a 2 L round-bottom flask, a solution of *N*-benzyl-diethanolamine (9.80 g, 50.0 mmol) in toluene (100 ml) was added under very vigorous stirring to a mixture containing a 50% aqueous solution of NaOH (100 mL) and tetrabutylammonium bromide (4.04 g, 12.5 mmol). This addition was immediately followed by addition of a solution of triethylene glycol bis-*p*-toluenesulphonate (23.0 g, 50.0 mmol) in toluene (500 mL). The mixture was stirred at 70 °C for 10 h and then cooled down to room temperature. The organic layer was extracted and washed with water (3×100 mL). The volatiles were removed under vacuum, yielding an oil obtained which was then refluxed in hexane (150 mL) for 5 min. The solution was separated from insoluble material by filtration. This extraction process was repeated another three times. The organic layers were combined, and evaporation of the volatiles afforded a yellow oil (12.7 g, 82%) which was used without further purification. ^{1}H NMR ($CDCl_3$, 400.13 MHz, 298 K): δ = 7.32 (m, 5H, arom-*H*), 3.65 (m, 18H, C*H*$_2$), 2.83 (br m, 4H, C*H*$_2$) ppm.

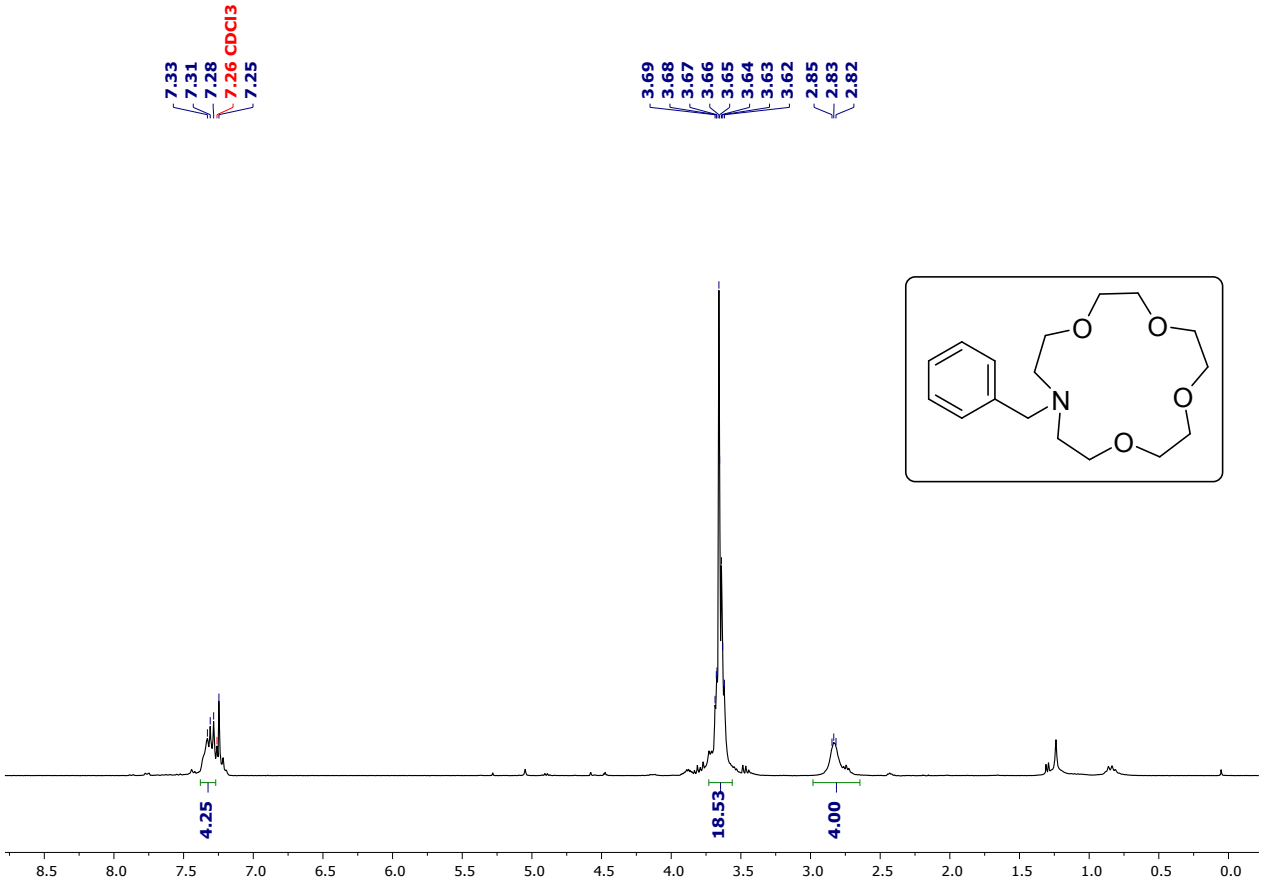

Figure S5. ^{1}H NMR spectrum ($CDCl_3$, 400.13 MHz, 298 K) of *N*-benzyl-protected 1-aza-15-c-5.

Synthesis of 1-aza-15-crown-5

(Scheme 1, step vi)

A solution of *N*-benzyl-protected 1-aza-15-c-5 (6.50 g, 21.0 mmol) and two drops of acetic acid in dry methanol (35 mL) were added under inert atmosphere to a 50 mL autoclave charged with Pd/C (400 mg). The reaction mixture was stirred for 12 h under a 10 bar pressure of H_2. The solution was then filtered over celite to dispose of solid materials, and volatiles were removed under vacuum. The resulting yellowish oil was trap-to-trap transferred at 100 °C to give the title compound as a colourless oil (3.68 g, 80%). The final compound contain residual acetic acid that could not be removed. ^{1}H NMR ($CDCl_3$, 400.13 MHz, 298 K): δ = 5.52 (br s, 1H, N*H*), 3.69 (m, 4H, CH_2), 3.66 (br s, 4H, CH_2), 3.63 (br s, 8H, CH_2), 2.87 (m, 4H, CH_2) ppm.

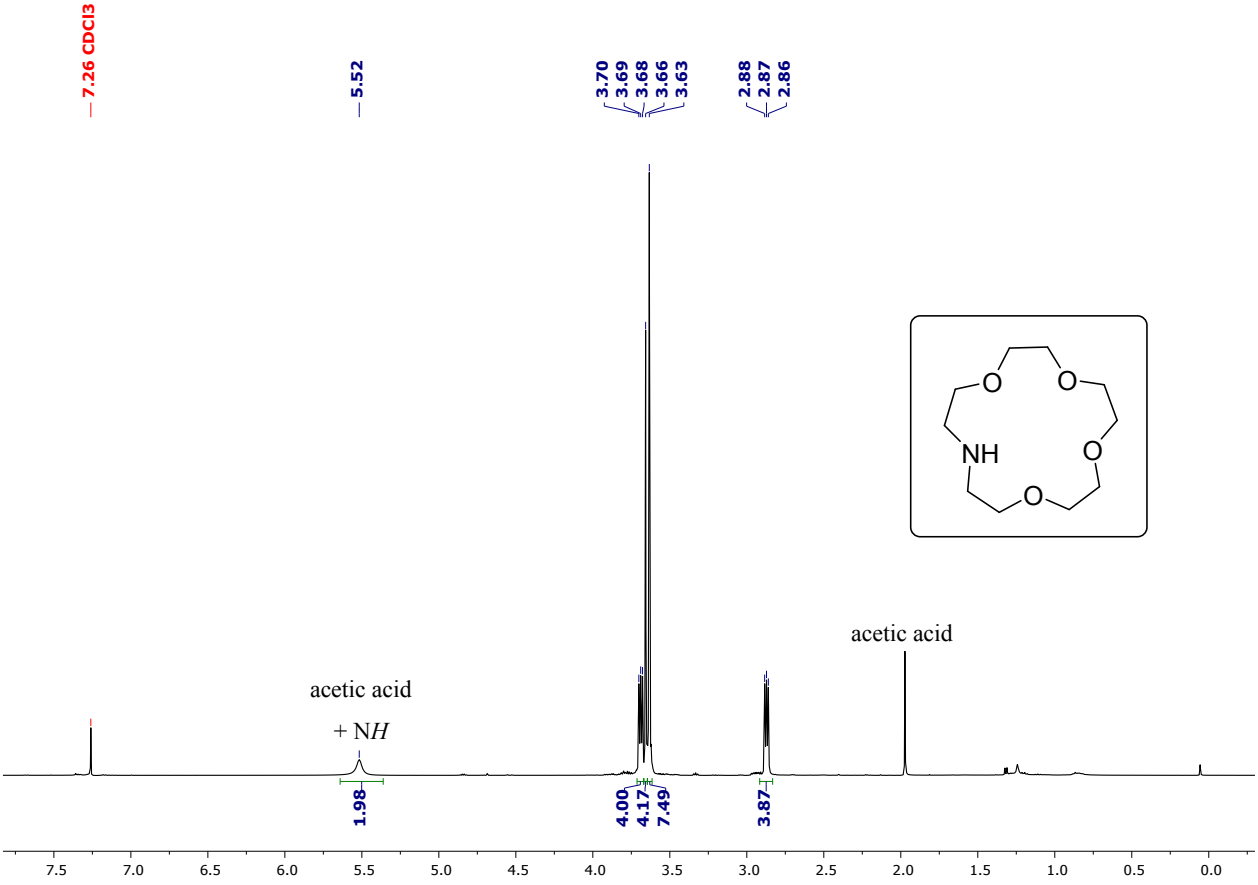

Figure S6. ^{1}H NMR spectrum ($CDCl_3$, 400.13 MHz, 298 K) of 1-aza-15-c-5.

Synthesis of *N*-benzyloxycarbonyl-protected (1-aza-15-c-5)ethan-1-amine

(Scheme 1, step vii)

In a 500 mL round-bottom flask, a solution of *N*-benzyloxycarbonyl-aziridine (3.72 g, 21.0 mmol) in a mixture 1:1 *v/v* of dry toluene and dry acetonitrile (250 ml) was added under argon to 1-aza-15-crown-5 (4.58 g, 21.0 mmol). The reaction mixture was then refluxed for 24 h, after what volatiles were removed in vacuo. The resulting yellow oil was purified by column chromatography (silica), using a 99:1 *v/v* mixture of CH_2Cl_2 and MeOH as the eluent. The title compound was isolated as a yellowish oil (5.85 g, 70%).^{1}H NMR ($CDCl_3$, 400.13 MHz, 298 K): δ = 7.34 (m, 5H, arom-*H*), 6.06 (br s, 1H, N*H*), 5.09 (s, 2H, CH_2Ph), 3.60-3.54 (m, 16H, CH_2), 3.28 (br s, 2H, CH_2), 2.72-2.65 (br m, 6H, CH_2) ppm.

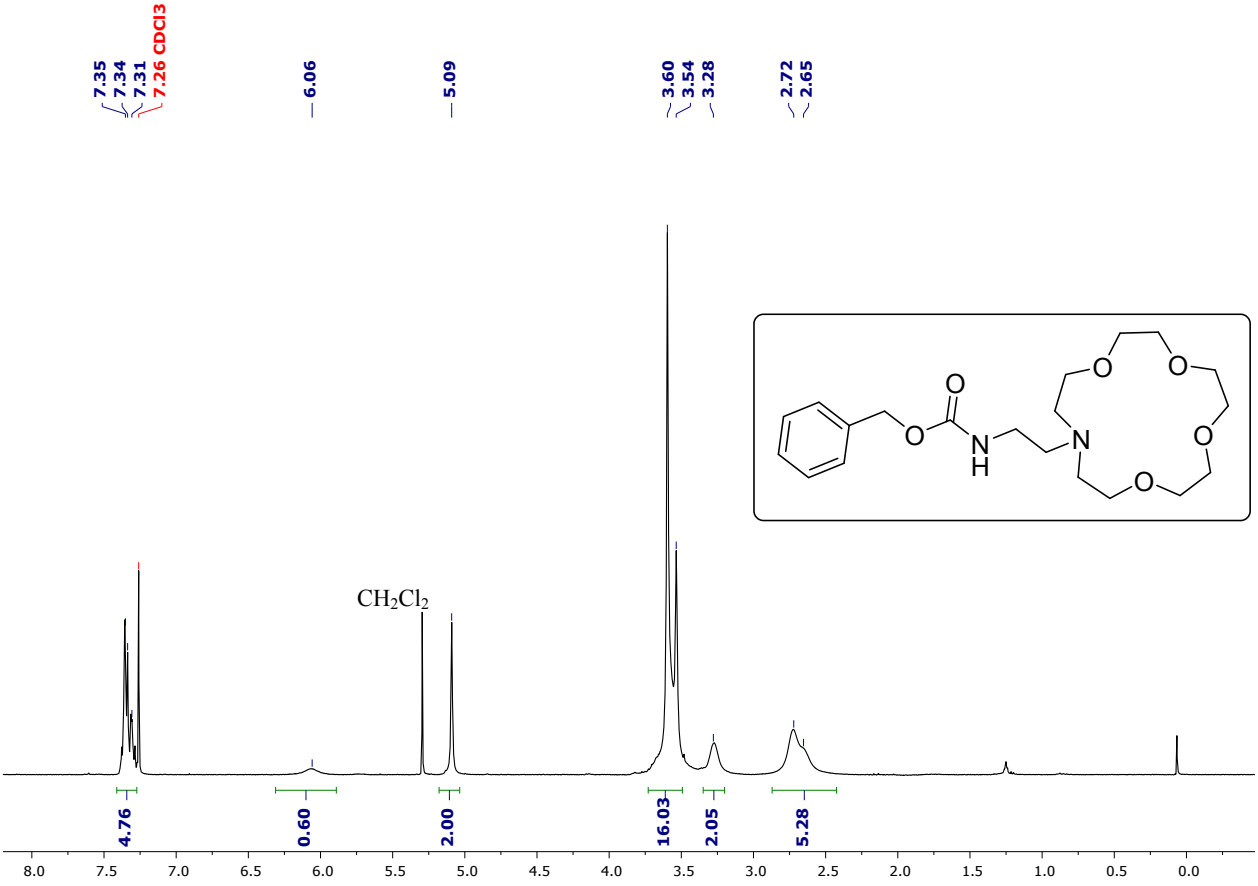

Figure S7. ^{1}H NMR spectrum ($CDCl_3$, 400.13 MHz, 298 K) of *N*-benzyloxycarbonyl-protected (1-aza-15-c-5)ethan-1-amine.

Synthesis of (1-aza-15-c-5)ethan-1-amine (A)

(Scheme 1, step viii)

A solution of *N*-benzyloxycarbonyl-(1-aza-15-c-5)ethan-1-amine (5.70 g, 14.4 mmol) in dry methanol (110 mL) was added under argon to a 250 mL round-bottom flask a charged with Pd/C (0.40 g). H_2 was bubbled in the reaction mixture for 3 h. The bubbling of H_2 was then stopped, the reaction vessel was closed, and the mixture was stirred overnight. Solid materials were then removed by filtration over filter paper, and the volatiles were removed under vacuum. The title compound was obtained as a yellowish oil (3.66 g, 97%). ^{1}H NMR ($CDCl_3$, 400.13 MHz, 298 K): δ = 3.65 (m, 12H, OCH_2), 3.60 (t, $^3J_{HH}$ = 6.0 Hz, 4H, NCH$_2$CH_2O), 2.74 (m, 6H, H$_2$NCH$_2$CH_2N and NCH_2CH$_2$O), 2.60 (t, $^3J_{HH}$ = 5.9 Hz, 2H, CH_2NH$_2$), 2.32 (br s, 2H, NH_2) ppm.

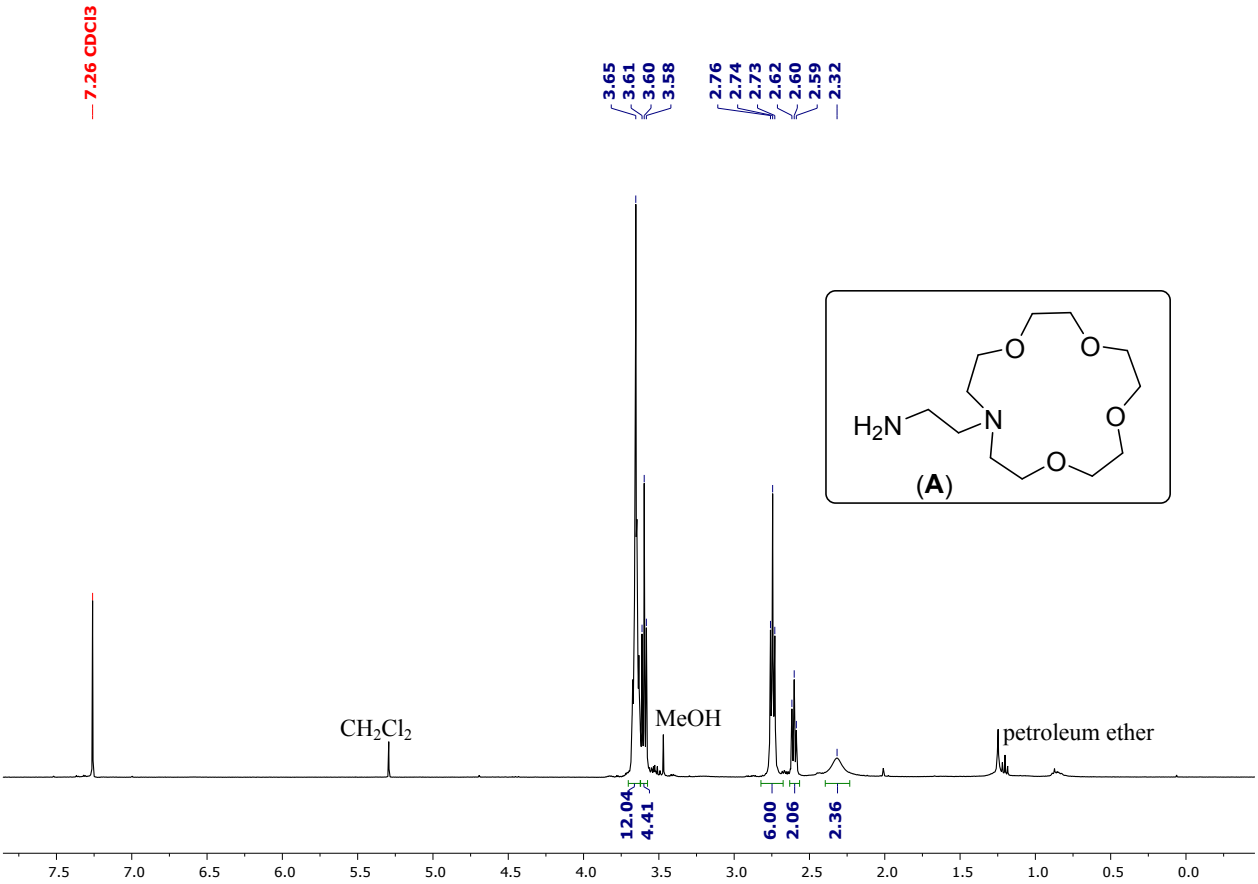

Figure S8. ^{1}H NMR spectrum ($CDCl_3$, 400.13 MHz, 298 K) of (1-aza-15-c-5)ethan-1-amine.

Synthesis of 2-(2-bromophenyl)-1,3-dioxolane

(Scheme 1, step ix)

In a Dean-Stark apparatus, a mixture of 2-bromobenzaldehyde (3.0 mL, 25.7 mmol), ethylene glycol (1.9 mL, 33.4 mmol) and *p*-toluenesulphonic acid (45.0 mg, 0.25 mmol) in toluene (40 mL) was refluxed until no more water was collected (ca. 2 d). The mixture then was cooled and washed with 10% aqueous sodium hydroxide (2×30 mL), then deionized water (2×30 mL) and finally with brine (30 mL). The organic layer was dried over $MgSO_4$, and removal of the volatiles under reduced pressure afforded the title compound as a yellow viscous oil. Yield 3.60 g (61%).

^{1}H NMR ($CDCl_3$, 400.13 MHz, 298 K): δ 7.61-7.56 (m, 2H, arom-*H*), 7.33 (m, 1H, arom-*H*), 7.24-7.22 (m, 1H, arom-*H*), 6.11 (s, 1H, *o*-Br-C_6H_4-C*H*), 4.19-4.05 (m, 4H, OCH_2) ppm.

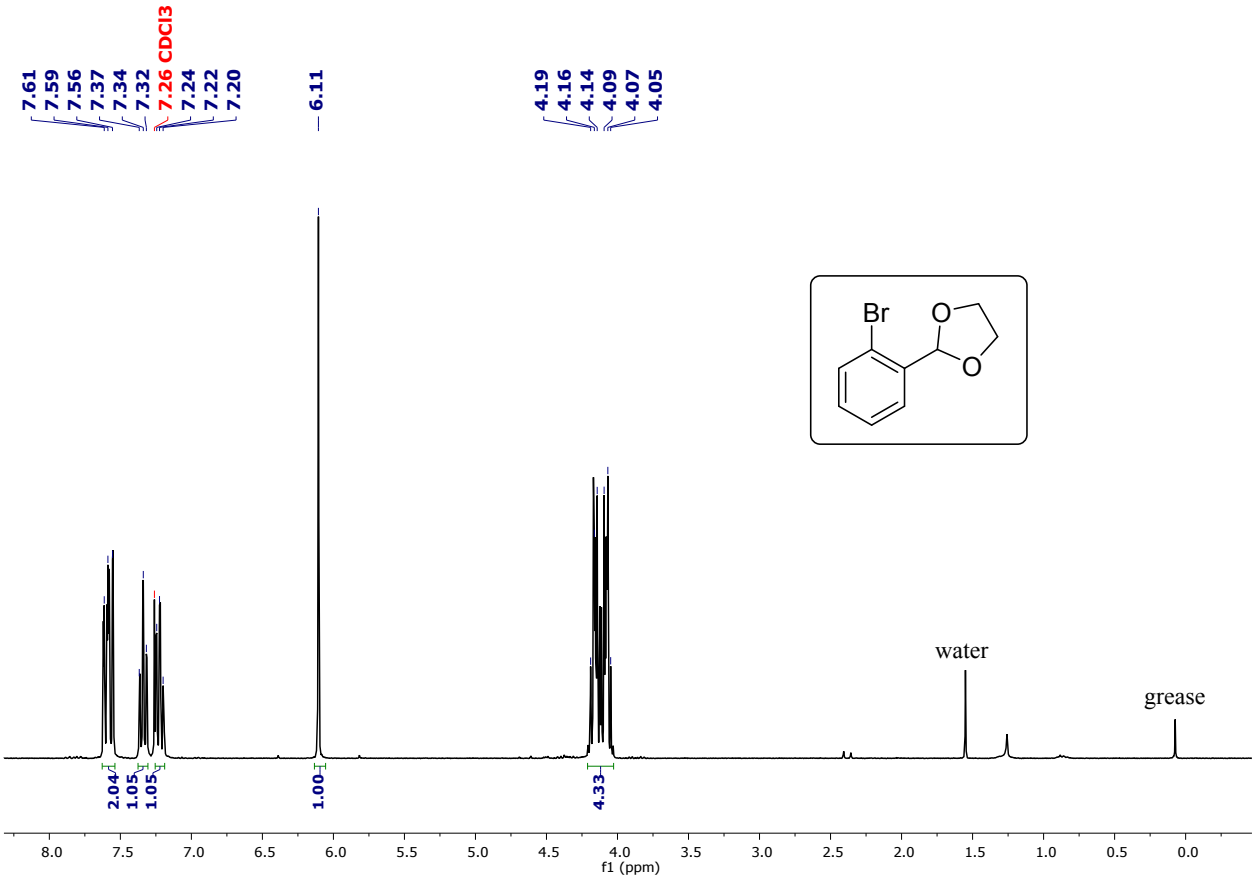

Figure S9. ^{1}H NMR spectrum ($CDCl_3$, 298 K, 400.13 MHz) of 2-(2-bromophenyl)-1,3-dioxolane.

Synthesis of 2-(2,6-diisopropyl-phenylamino)benzaldehyde (B)

(Scheme 1, steps x and xi)

2-(2-Bromophenyl)-1,3-dioxolane (3.60 g, 15.7 mmol) and then P*t*Bu$_3$ (0.31 mL, 0.31 mmol) and 2,6-diisopropylaniline (3.2 mL, 17.1 mmol) were added to a suspension of Pd(OAc)$_2$ (0.03 g, 0.15 mmol) and NaO*t*Bu (3.01 g, 31.4 mmol) in thf (50 mL). The mixture was refluxed for 16 h, cooled down to room temperature and filtered. The organic layer was extracted with ethyl acetate and washed with deionized water. It was then dried over $MgSO_4$ and the volatiles were removed under vacuum. The resulting solid was mixed with trifluoroacetic acid (1.10 g, 9.6 mmol) in methanol (30 mL) and stirred for 1 h at room temperature. The solvent was then removed under reduced pressure. The residue was extracted with ethyl acetate and washed twice with deionized water. The organic layer was then dried over $MgSO_4$, and after filtration the solvent was evaporated. The product was purified by column chromatography (diethyl ether - petroleum ether 5:95 *v/v*) to afford the title compound as a yellow solid. Yield 1.60 g (38%). ^{1}H NMR ($CDCl_3$, 400.13 MHz, 298 K): δ = 9.97 (s, 1H, C_6H_3NH), 9.56 (s, 1H, C_6H_4CHO), 7.55 (d, 1H, $^3J_{HH}$ = 7.7 Hz, arom-*H*), 7.39–7.27 (m, 4H, arom-*H)*, 6.73 (t, 1H, $^3J_{HH}$ = 7.4 Hz, arom-*H)*, 6.22 (d, 1H, $^3J_{HH}$ = 8.6 Hz, arom-*H)*, 3.05 (hept, 2H, $^3J_{HH}$ = 6.9 Hz, $CH(CH_3)_2$), 1.15 (d, 6H, $^3J_{HH}$ = 6.9 Hz, $CH(CH_3)_2$), 1.11 (d, 6H, $^3J_{HH}$ = 6.9 Hz, $CH(CH_3)_2$) ppm.

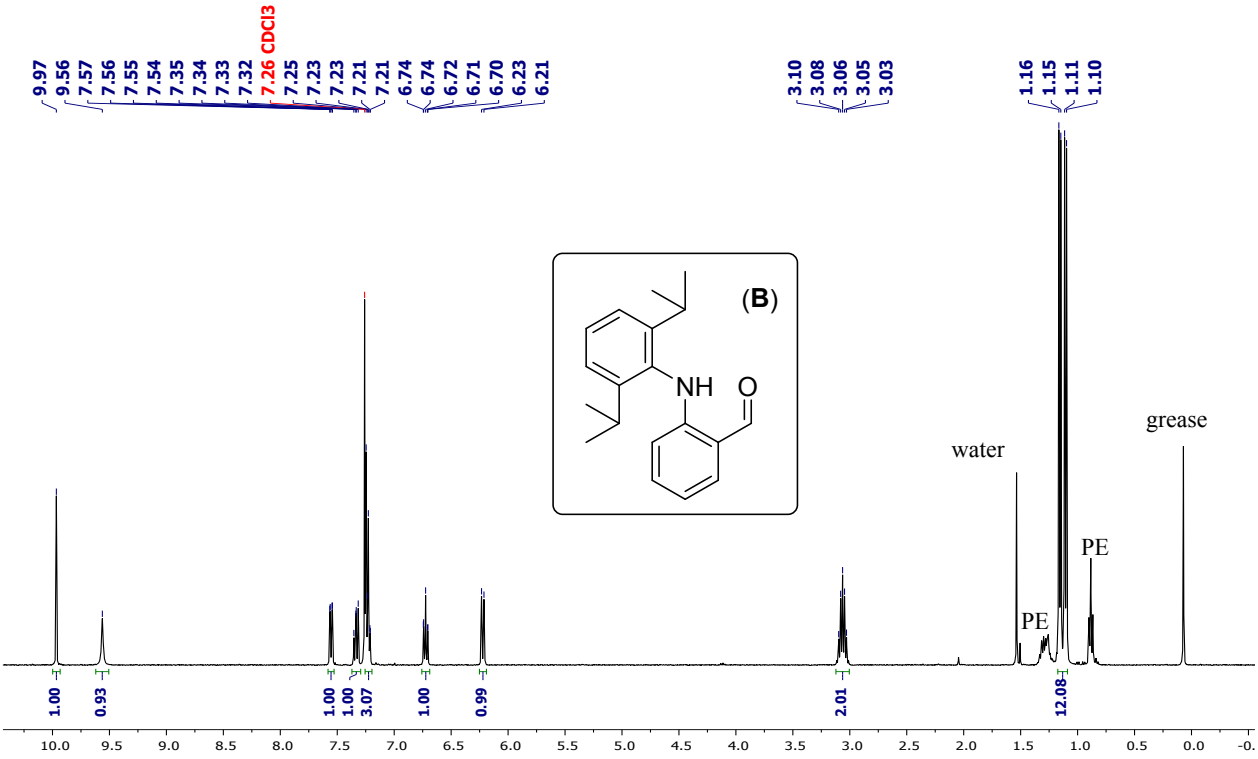

Figure S10. ^{1}H NMR spectrum ($CDCl_3$, 298 K, 400.13 MHz) of 2-(2,6-diisopropyl-phenylamino) benzaldehyde (**B**).

Synthesis of AdC(=O)NHDipp

(Scheme 1, step xii)

2,6-Diisoprylaniline (7.14 g, 40.0 mmol) was added dropwise at room temperature to a solution of 1-adamantanecarbonyl chloride (8.00 g, 40.0 mmol) and NEt_3 (4.48 g, 44.0 mmol) in toluene (250 mL). The mixture was stirred at 70 °C for 3 h. The resulting white suspension obtained was carefully extracted with water (2×250 mL). The organic layers were recovered and the volatiles were pumped off under vacuum to afford the title product as a white solid. (12.85 g, 94%). ^{1}H NMR ($CDCl_3$, 400.16 MHz, 298 K): δ = 7.26 (m overlapping with solvent, 1H, para-*H*), 7.17-7.15 (d, $^3J_{HH}$ = 7.6 Hz, 2H, meta-*H*), 6.78 (br, 1H, N*H*), 3.00 (hept, $^3J_{HH}$ = 6.8 Hz, 2H, C*H*$(CH_3)_2$), 2.12 (br s, 3H, adamantyl-*H*), 2.04 (br s, 6H, adamantyl-*H*), 1.79 (br s, 6H, adamantyl-*H*), 1.19 (d, $^3J_{HH}$ = 6.8 Hz, 12H, C*H*$_3$) ppm.

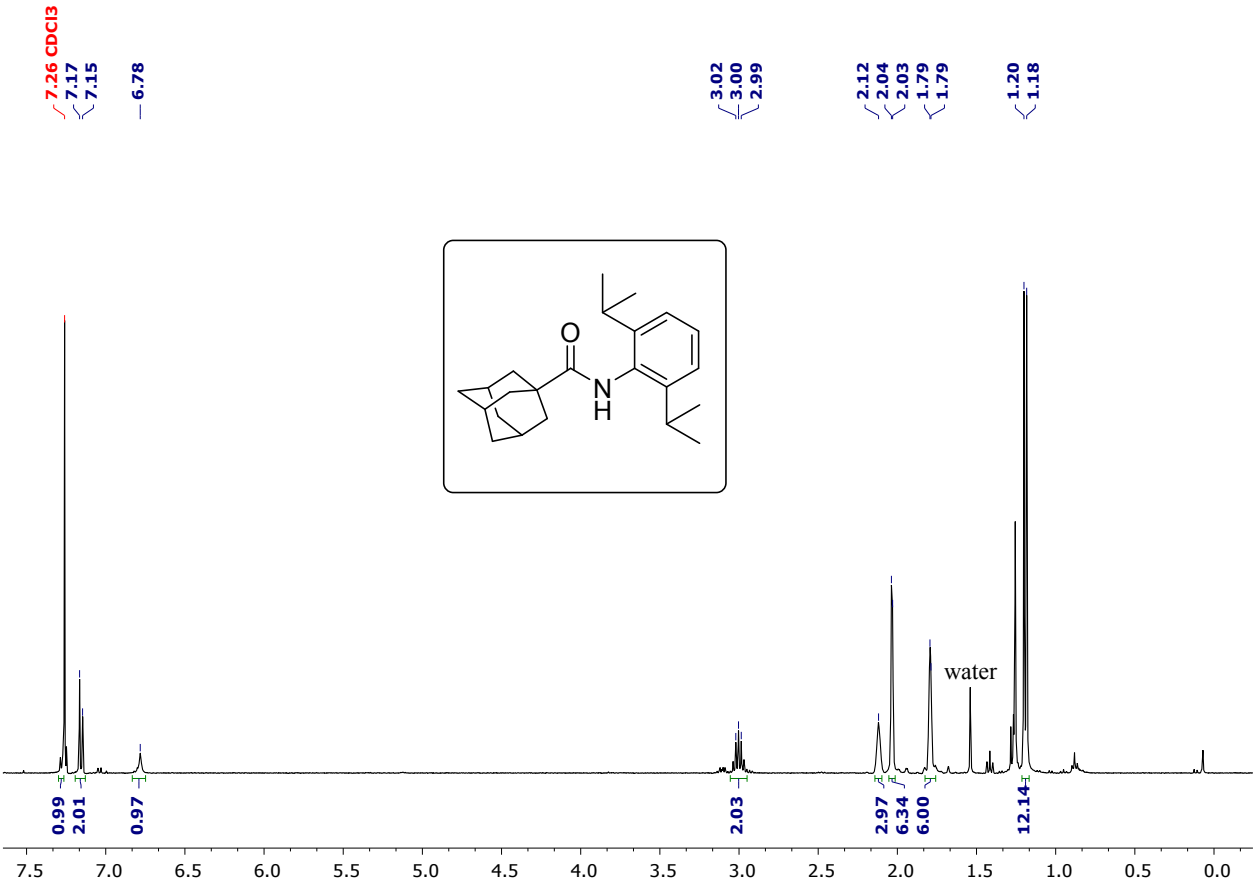

Figure S11. ^{1}H NMR spectrum ($CDCl_3$, 298 K, 400.13 MHz) of AdC(=O)NHDipp.

Synthesis of AdC(Cl)NDipp (C)

(Scheme 1, step xiii)

Thionyl chloride (93.7 g, 778 mmol) was added under vigorous stirring to a flask containing AdC(=O)NHDipp (10.7 g, 32.0 mmol). The resulting mixture was refluxed for 3 h, then cooled down at room temperature. The volatiles were removed under vacuum to afford the title compound as an oil which crystallised slowly on standing at room temperature (10.2 g, 90%). ^{1}H NMR ($CDCl_3$, 400.16 MHz, 298 K): δ = 7.12 (m, 3H, para- and meta-*H*), 2.75 (hept, $^{3}J_{HH}$ = 7.0 Hz, 2H, C*H*$(CH_3)_2$), 2.13-2.11 (br m, 9H, Ad), 1.79 (br m, 6H, Ad), 1.18 (br m, 12H, CH_3) ppm.

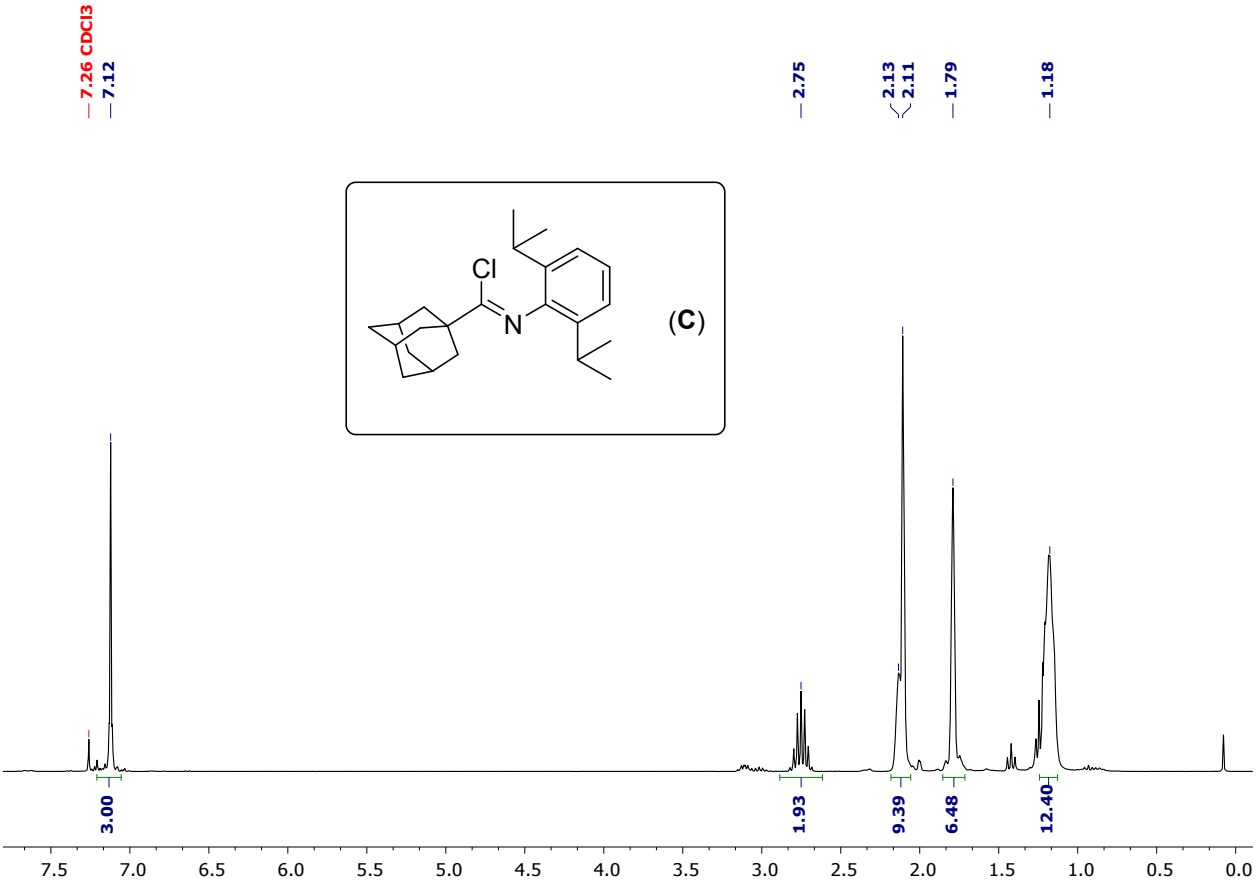

Figure S12. ^{1}H NMR spectrum ($CDCl_3$, 298 K, 400.13 MHz) of AdC(Cl)NDipp (**C**).

Synthesis of {I^A^{crown}}H

(Scheme 1, step xiv)

A mixture of **B** (1.00 g, 3.50 mmol) and a first fraction of **A** (0.46 g, 1.75 mmol) in petroleum ether (20 mL) was refluxed in a Dean-Stark apparatus overnight. The solvent was then evaporated to monitor conversion (aliquot for ^{1}H NMR spectroscopy). The remaining of **A** (0.54 g, 2.06 mmol) was introduced over the course of 8 days as four identical fractions dissolved in petroleum ether (135 mg each in 20 mL of solvent), and reflux of the reaction mixture was maintained for a total of 8 days. Complete conversion of **B** was observed. The mixture was then filtered to eliminate insoluble materials and the volatiles were removed under vacuum. The title compound was obtained as an analytically pure colourless oil (1.60 g, 90%) which afforded X-ray quality crystals upon extended drying under dynamic vacuum at room temperature.

^{1}H NMR ($CDCl_3$, 400.13 MHz, 298 K): δ = 10.50 (s, 1H, N*H*), 8.46 (s, 1H, C*H*=N), 7.35-7.24 (m, 4H, arom-*H*), 7.08 (m, 1H, arom-*H*), 6.67 (m, 1H, arom-*H*), 6.21 (d, 1H, $^3J_{HH}$ = 8.3 Hz, arom-*H*), 3.74 (t, 2H, $^3J_{HH}$ = 7.0 Hz, CH_2), 3.67-3.63 (m, 16H, OCH_2), 3.11 (hept, $^3J_{HH}$ = 6.9 Hz, 2H, C*H*), 2.86 (m, 6H, NCH_2), 1.16 (d, 6H, $^3J_{HH}$ = 6.9 Hz, CH(CH_3)$_2$), 1.14 (d, 6H, $^3J_{HH}$ = 6.9 Hz, CH(CH_3)$_2$) ppm.

^{13}C{^{1}H} NMR ($CDCl_3$, 100.62 MHz, 298 K): δ = 165.21 (*C*H=N), 149.41 (arom-*C*), 147.45 (arom-*C*), 135.17 (arom-*C*), 133.50 (arom-*C*), 130.95 (arom-*C*), 127.16 (arom-*C*), 123.67 (arom-*C*), 116.68 (arom-*C*), 114.94 (arom-*C*), 111.63 (arom-*C*), 71.04 (*C*H_2O), 70.47 (*C*H_2O), 70.27 (*C*H_2O), 70.21 (*C*H_2O), 59.77 (N*C*H_2CH$_2$N=CH), 57.93 (N*C*H_2CH$_2$O), 55.17 ((NCH$_2$*C*H_2N=CH), 28.43 (*C*H(CH$_3$)$_2$), 24.92 (CH(*C*H$_3$)$_2$), 22.93 (CH(*C*H$_3$)$_2$) ppm.

Anal. Calcd for $C_{31}H_{47}N_3O_4$ (525.72 g·mol^{-1}): theoretical, C 70.82%, H 9.01%, N 7.99%; found C 69.65%, H 8.90 %, N 7.83 %.

Mass spectrometry ESI [M + Na$^+$] ($C_{31}H_{47}N_3O_4Na$) *m/z* theoretical: 548.3459; found 548.3457.

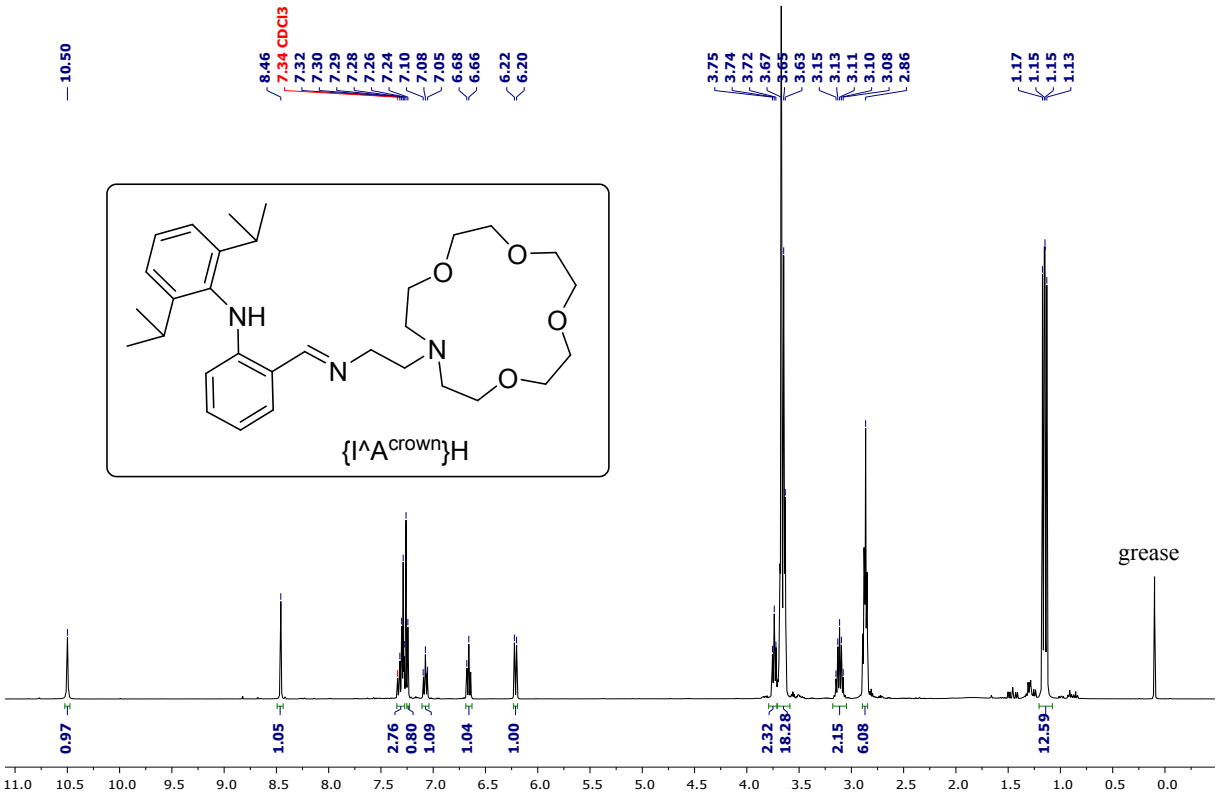

Figure S13. ^{1}H NMR spectrum ($CDCl_3$, 298 K, 400.16 MHz) of {I^A^{crown}}H.

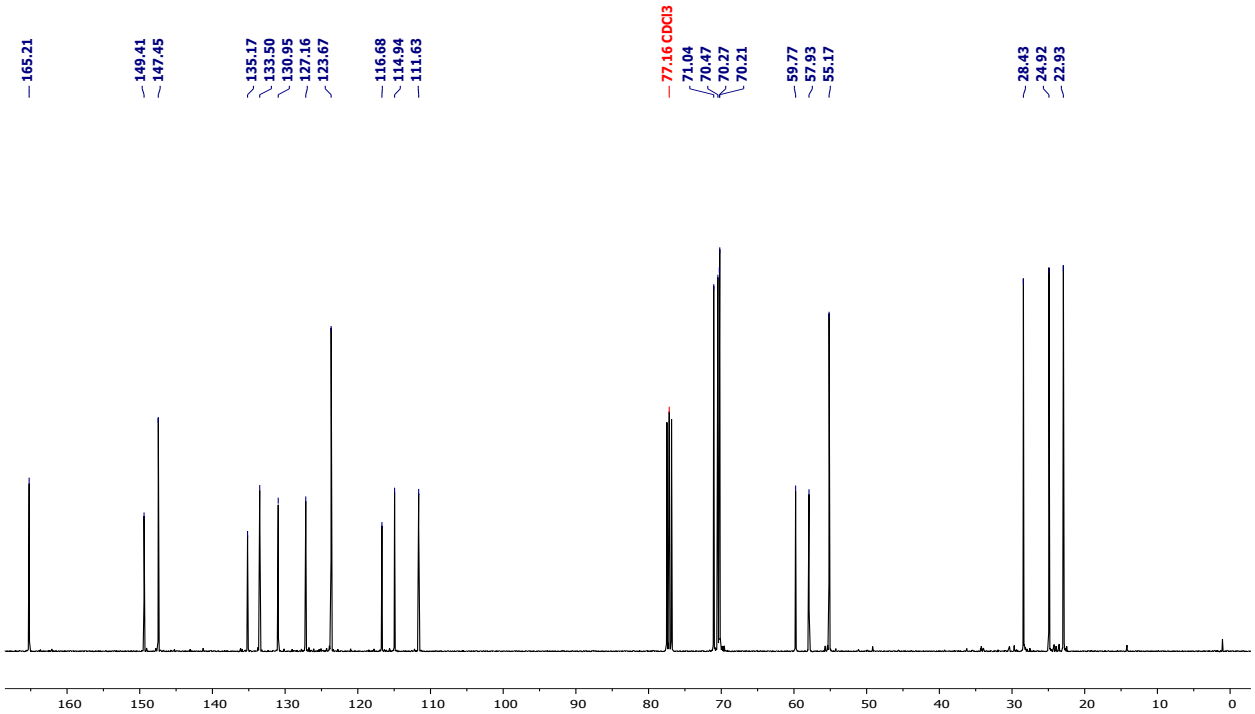

Figure S14. ^{13}C{^{1}H} NMR spectrum ($CDCl_3$, 298 K, 100.16 MHz) of {I^A^{crown}}H.

Synthesis of {Am^{crown}}H

(Scheme 1, step xv)

A solution of **A** (1.80 g, 6.9 mmol) in CH_2Cl_2 (25 mL) was added dropwise to a solution of **C** (3.68 g, 10.3 mmol) and dry NEt_3 (28.7 ml, 205.8 mmol) in CH_2Cl_2 (25 mL). The mixture was stirred at room temperature for 36 h, during which the precipitation of ammonium chloride was observed. After addition of water (25 mL), the organic layer was recovered and washed with distilled water (25 mL), and the volatiles were removed in vacuo. The resulting oily residue was suspended in petroleum ether (20 ml), and the suspension was filtered over sintered glass to remove insoluble impurities. The filtrate was then concentrated to the third of the initial volume and stored in the freezer at –43 °C. Colorless crystals of {Am^{crown}}H were obtained after 4 days (1.54 mg, 39%).

^{1}H NMR ($CDCl_3$, 500.13 MHz, 298 K): δ = 6.94 (d, $^3J_{HH}$ = 8.0 Hz, 2H, meta-*H*), 6.84 (t, $^3J_{HH}$ = 8.0 Hz, para-*H*), 5.46 (br s, 1H, N*H*), 3.66-3.62 (m, 12H, OCH_2CH_2), 3.57 (t, $^3J_{HH}$ = 6.0 Hz, 4H, OCH_2CH_2N), 3.01 (hept, $^3J_{HH}$ = 7.0 Hz, 2H, C*H*(CH_3)$_2$), 2.62 (t, $^3J_{HH}$ = 6.0 Hz, 4H, OCH$_2$CH_2N), 2.43 (m, 2H, NCH$_2$CH_2NH), 2.34 (m, 2H, NCH_2CH$_2$NH), 2.08 (br s, 3H, adamantyl-*H*), 2.00 (br s, 6H, adamantyl-*H*), 1.76 (br s, 6H, adamantly-*H*), 1.16 (d, $^3J_{HH}$ = 7.0 Hz, 12H, CH_3) ppm.

^{13}C{^{1}H} NMR ($CDCl_3$, 125.77 MHz, 298 K): δ = 157.18 (*C*H=N), 147.43 (arom-*C*), 137.83 (arom-*C*), 121.73 (arom-*C*), 120.63 (arom-*C*), 71.26 (O*C*H$_2$), 70.60 (O*C*H$_2$), 70.35 (O*C*H$_2$), 70.26 (O*C*H$_2$CH$_2$N), 55.72 (N*C*H$_2$CH$_2$NH), 54.65 (OCH$_2$*C*H$_2$N), 40.95 (adamantyl-*C*), 40.56 (adamantyl-*C*), 39.71 (adamantyl-*C*), 37.01 (adamantyl-*C*), 28.98 (adamantyl-*C*), 28.37 (*C*H(CH_3)$_2$), 23.33 (CH(*C*H$_3$)$_2$), 22.62 (CH(*C*H$_3$)$_2$) ppm.

Anal. Calcd for $C_{35}H_{57}N_3O_4$ (583.86 g·mol^{-1}): C, 72.00; H, 9.84; N, 7.20; O, 10.96. Found: C, 72.12; H, 9.82; N, 7.00.

Mass spectrometry: [M-H]$^+$, m/z theoretical 584.4422, found 584.4420 (0 ppm).

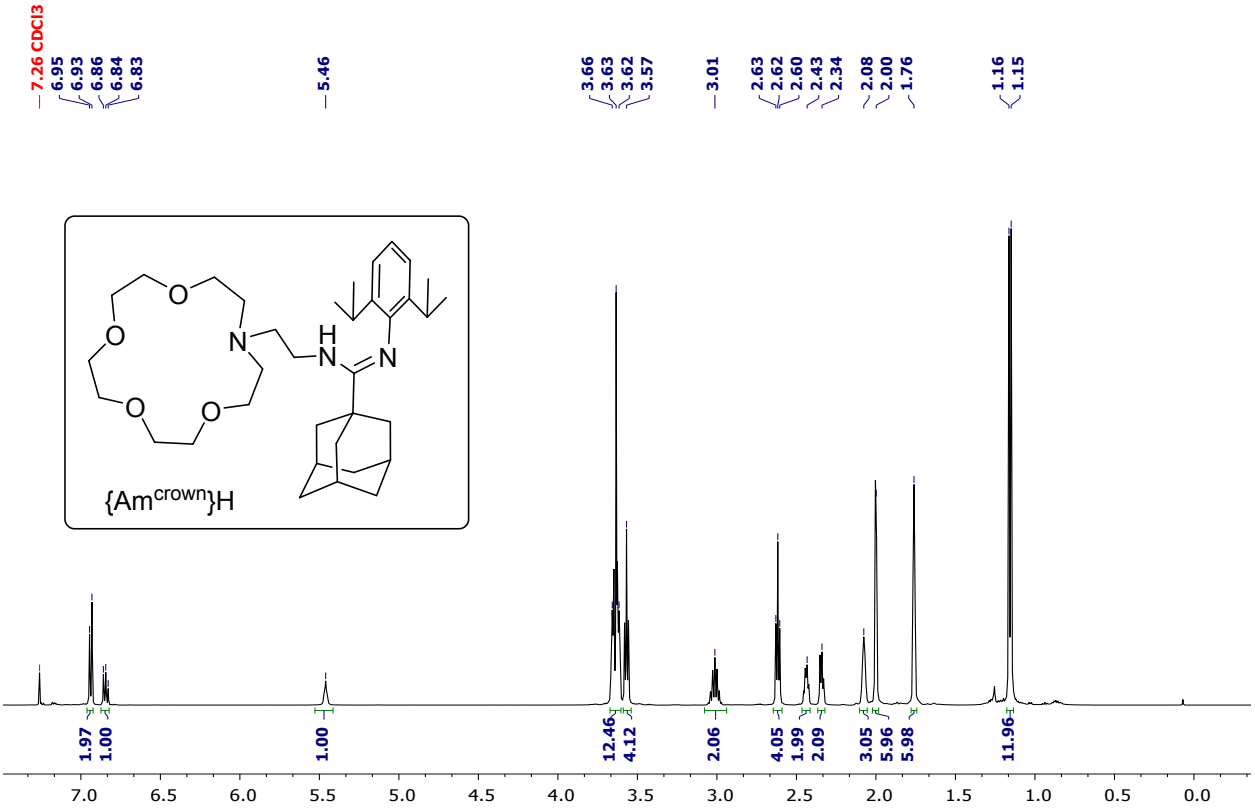

Figure S15. ^{1}H NMR spectrum ($CDCl_3$, 298 K, 500.13 MHz) of {Am^{crown}}H.

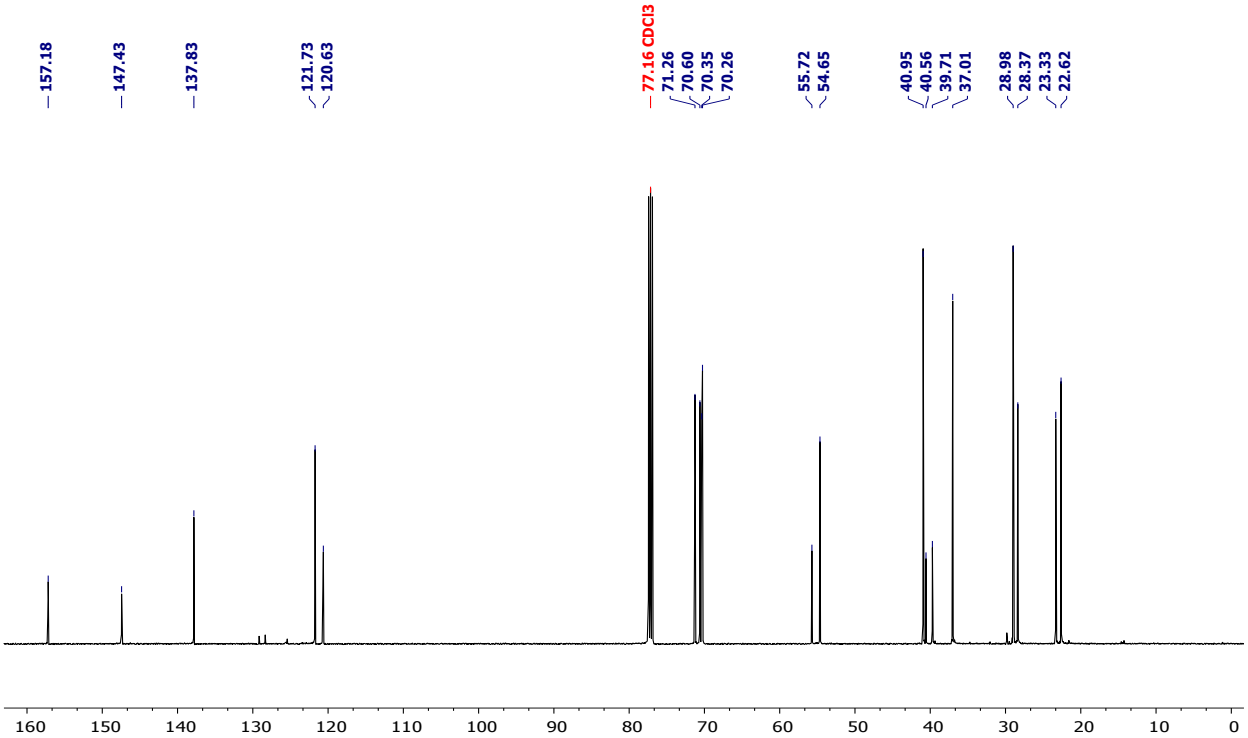

Figure S16. $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$, 298 K, 125.77 MHz) of {Am^{crown}}H.

Synthesis of [{I^A^{crown}}BaN(SiMe$_2$H)$_2$] (5)

A solution of {I^A^{crown}}H (0.11 g, 0.21 mmol) and [Ba{N(SiMe$_2$H)$_2$}$_2$.(thf)$_2$] (0.11 g, 0.20 mmol) in benzene (4.0 mL) was stirred for 2 h. The volatiles were then removed under vacuum to yield **5** as an orange solid which was washed with petroleum ether (5 mL). Yield 0.13 g (86%). X-ray quality crystals were grown from a saturated benzene solution. NMR characterisation was performed in thf-d_8 due to the insufficient solubility of **5** in aromatic solvents.

^{1}H NMR (thf-d_8, 500.13 MHz, 298 K): δ = 8.04 (s, 1H, C*H*=N), 7.04 (d, $^3J_{HH}$ = 7.5 Hz, 2H, arom-*H*), 6.92 (d, $^3J_{HH}$ = 8.0 Hz, 1H, arom-*H*), 6.87 (t, $^3J_{HH}$ = 7.5 Hz, 1H, arom-*H*), 6.52 (m, 1H, arom-*H*), 5.84 (t, $^3J_{HH}$ = 7.0 Hz, 1H, arom-*H*), 5.74 (d, $^3j_{HH}$ = 9.0 Hz, arom-*H*), 4.57 (m, 2H, Si*H*), 3.80-3.23 (overlapping br m, 22H, OC*H*$_2$ and C*H*(CH$_3$)$_2$), 2.94 (m, 2H, NC*H*$_2$), 2.65 (m, 2H, NC*H*$_2$), 1.15 (m, 6H, CH(C*H*$_3$)$_2$), 0.96 (br s, 6H, CH(C*H*$_3$)$_2$), –0.14 ppm (br s, 12H, Si(C*H*$_3$)$_2$) ppm.

^{13}C{^{1}H} (thf-d_8, 125.77 MHz, 298 K): δ = 168.19 (*C*H=N), 158.66 (arom-*C*), 145.19 (arom-*C*), 139.42 (arom-*C*), 130.71 (arom-*C*), 124.15 (arom-*C*), 122.12 (arom-*C*), 118.87 (arom-*C*), 118.56 (arom-*C*), 108.17 (arom-*C*), 70.16 (O*C*H$_2$), 69.47 (O*C*H$_2$), 69.26 (O*C*H$_2$), 68.74 (O*C*H$_2$), 68.10 (O*C*H$_2$), 60.24 (N*C*H$_2$), 59.20 (N*C*H$_2$), 55.24 (N*C*H$_2$), 28.54 (*C*H(CH$_3$)$_2$), 26.40 (CH(*C*H$_3$)$_2$), 25.99 (CH(*C*H$_3$)$_2$), 5.64 (Si*C*H$_3$) ppm. Traces of free {I^A^{crown}}H due to minimal hydrolysis during sample analysis are also visible.

^{29}Si{^{1}H} NMR (thf-d_8, 79.49 MHz, 298 K): δ = –30.09 (*Si*H) ppm.

FTIR (Nujol mull in KBr): $\tilde{\upsilon}_{Si-H}$ = 2052.3 (s), 1990.5 (s), 1728.2 (w), 1604.8 (s), 1512.2 (s) 1458.2 (s), 1357.9 (s), 1303.9 (m), 1234.4 (s), 1103.28 (s), 1072.4 (s), 941.3 (s), 895.0 (s), 825.5 (s), 771.5 (m), 740.7 (s), 663.5 (m) 624.9 (m), 532.3 (w), 424.3 (s). Bands above 2300 cm^{-1} are only for Nujol.

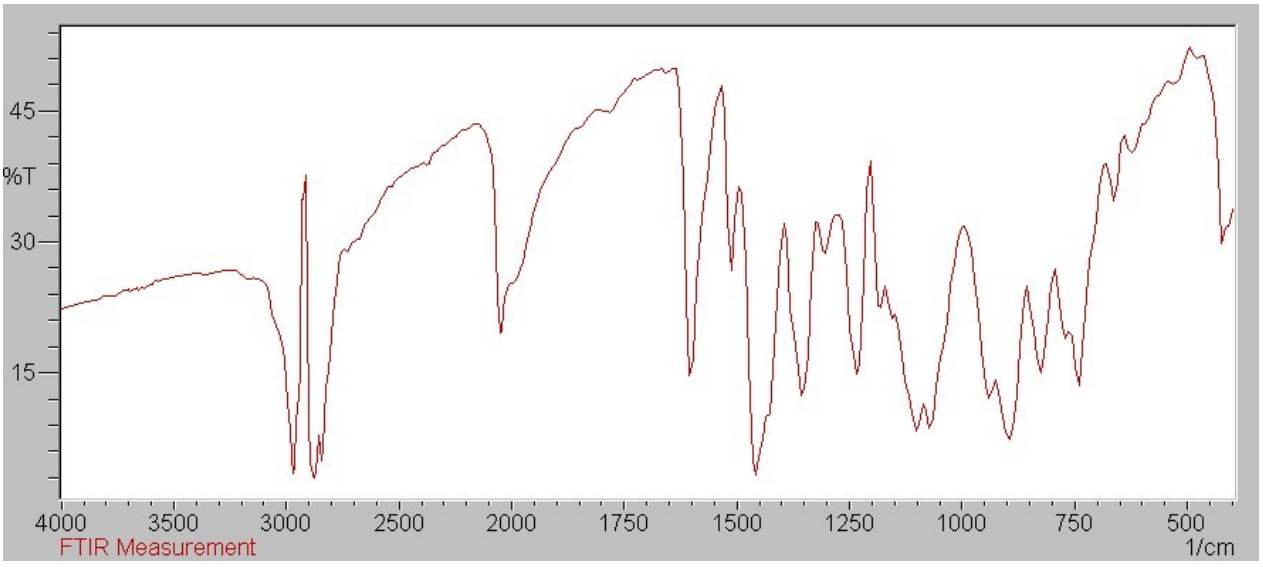

Figure S17. FTIR spectrum (Nujol mull in KBr) of [{I^A^{crown}}BaN(SiMe$_2$H)$_2$] (**5**).

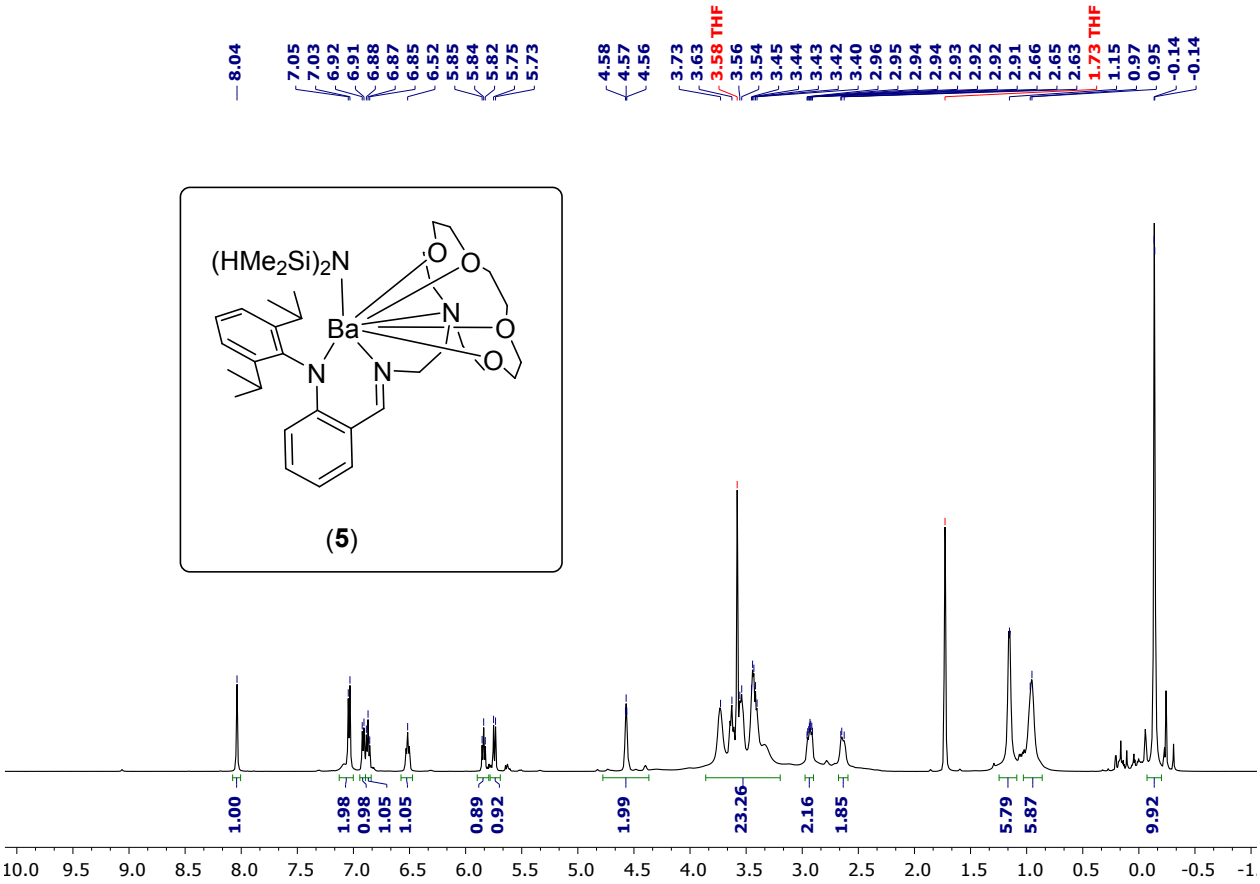

Figure S18. ^{1}H NMR spectrum (thf-d_8, 298 K, 500.13 MHz) of [{I^A^{crown}}BaN(SiMe$_2$H)$_2$] (**5**).

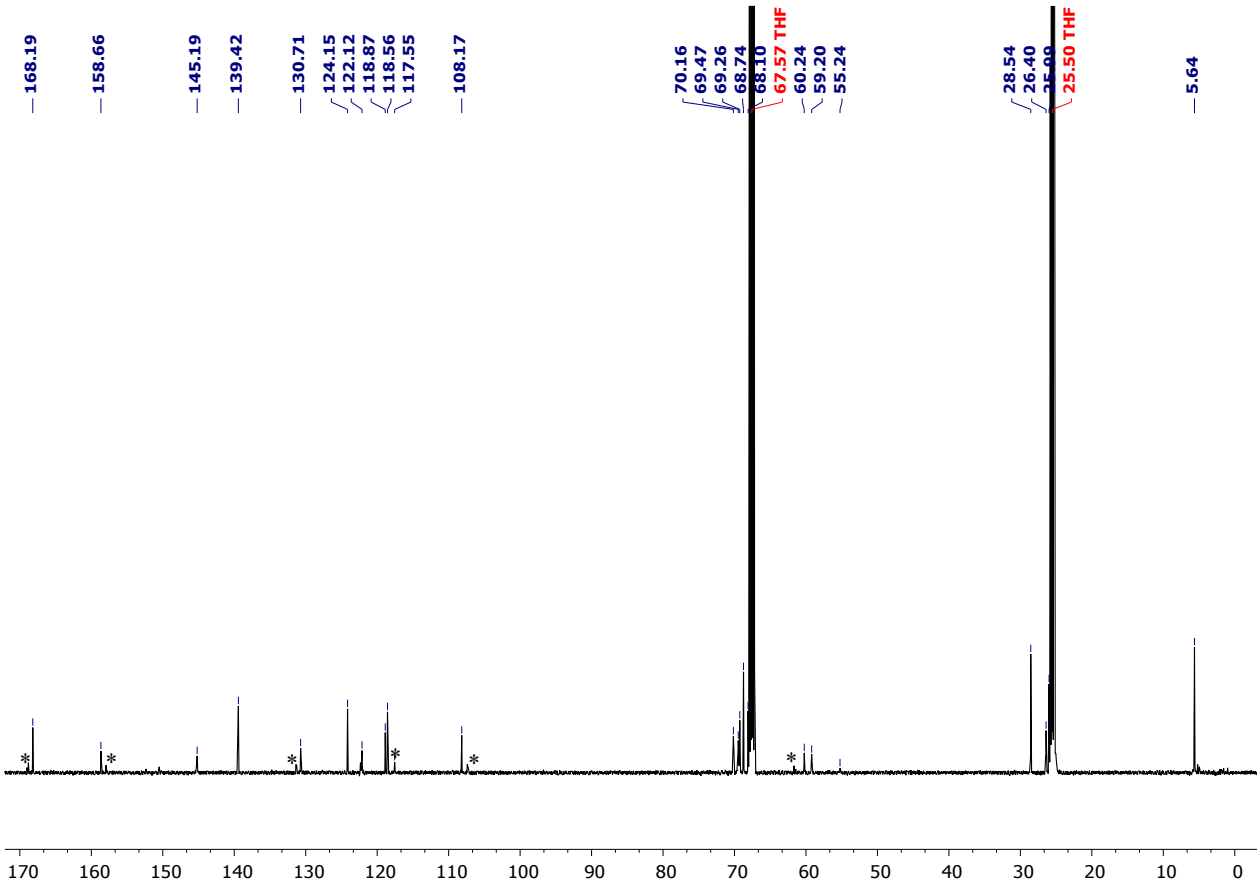

Figure S19. $^{13}C\{^{1}H\}$ NMR spectrum (thf-d_8, 298 K, 125.77 MHz) of [{I^A^{crown}}BaN(SiMe$_2$H)$_2$] (**5**). Traces of free {I^A^{crown}}H resulting from minimal hydrolysis during sample analysis are also visible, denoted *.

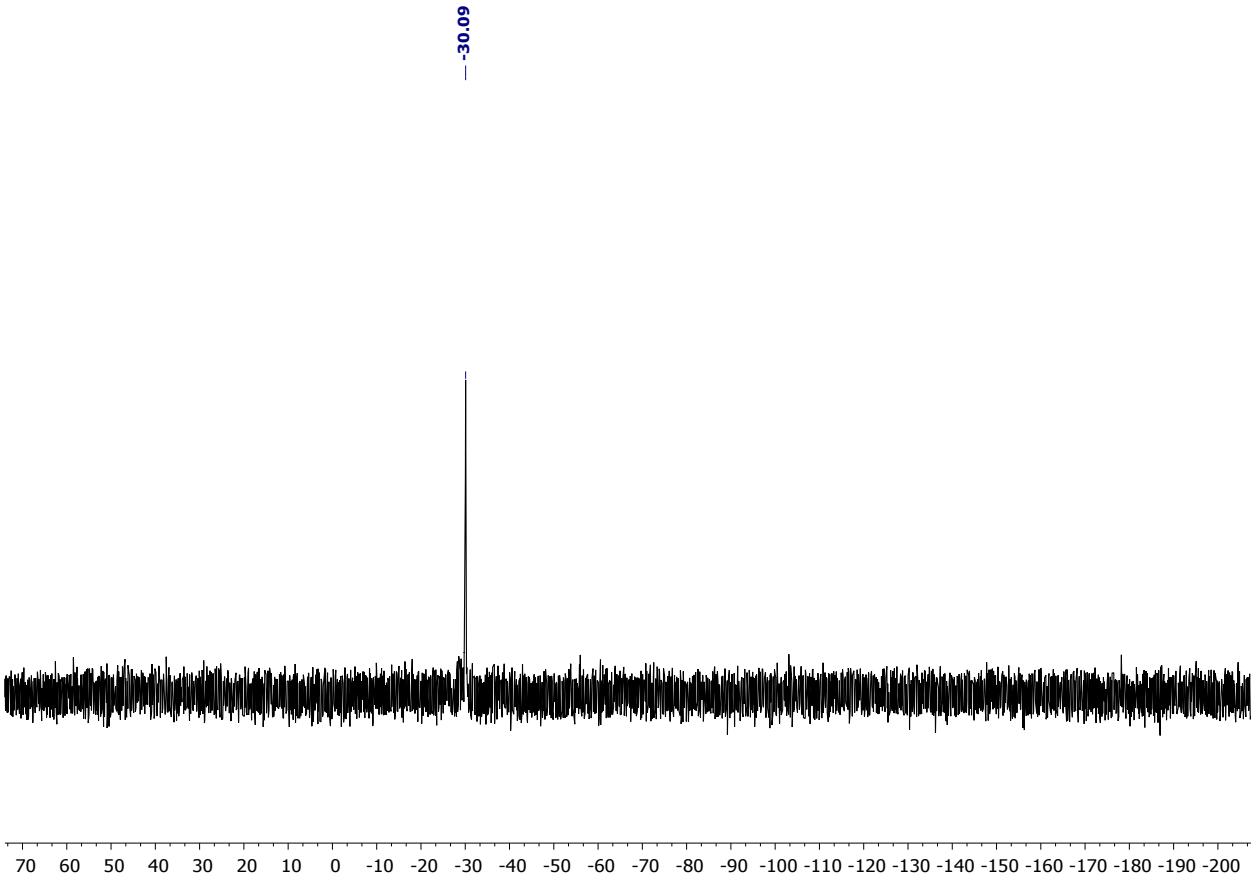

Figure S20. ^{29}Si NMR spectrum (thf-d_8, 298 K, 79.49 MHz) of [{I^A^{crown}}BaN(SiMe$_2$H)$_2$] (**5**).

Synthesis of [{Am^{crown}}BaN(SiMe$_2$H)$_2$] (6)

{Am^{crown}}H (90.0 mg, 0.15 mmol) and Ba[N(SiMe$_2$H)$_2$]$_2$ (60.0 mg, 0.15 mmol) were mixed and stirred in benzene (2.0 ml) at room temperature for 5 min, and the solution was kept at room temperature without stirring for 24 h. After 15-20 min, the formation of colourless crystals was observed. After 24 h the solution was removed with a cannula and the crystals were dried under vacuum (114 mg, 85%). Single crystals suitable crystals for XRD analysis were obtained from C_6D_6.

^{1}H NMR (thf-d_8, 500.13 MHz, 298 K): δ = 6.67 (d, $^3J_{HH}$ = 7.0 Hz, 2H, meta-*H*), 6.36 (t, $^3J_{HH}$ = 7.0 Hz, 1H, para-*H*), 5.64 (s, 2H, $^1J_{29Si\text{-}1H}$ = 160.2 Hz, Si*H*), 3.92 (m, 6H, OC*H*$_2$), 3.77 (m, 6H, OC*H*$_2$), 3.65-3.55 (m, 4H, OC*H*$_2$CH$_2$N), 3.21 (hept, $^3J_{HH}$ = 7.0 Hz, 2H, C*H*(CH$_3$)$_2$), 3.02 (m, 2H, NC*H*$_2$CH$_2$NH), 2.55 (m, 4H, OCH$_2$C*H*$_2$N), 2.10 (br s, 8H, adamantyl-*H*), 2.02 (br s, 3H, adamantyl-*H*), 1.77 (m, 2H, NCH$_2$C*H*$_2$NH), 1.73 (br s, 4H, adamantyl-*H*), 1.14 (d, $^3J_{HH}$ = 7.0 Hz, 6H, CH(C*H*$_3$)$_2$), 1.07 (d, $^3J_{HH}$ = 7.0 Hz, 6H, CH(C*H*$_3$)$_2$), –0.01 (s, 12H, SiC*H*$_3$) ppm.

^{13}C{^{1}H} NMR (thf-d_8, 125.77 MHz, 298 K): δ = 164.61 (N*C*N), 153.93 (arom-*C*), 137.31 (arom-*C*), 121.36 (arom-*C*), 116.18 (arom-*C*), 70.50 (O*C*H$_2$), 69.71 (O*C*H$_2$), 69.60 (O*C*H$_2$), 68.98 (O*C*H$_2$CH$_2$N), 62.37 (N*C*H$_2$CH$_2$NH), 55.69 (OCH$_2$*C*H$_2$N), 44.68 (adamantyl-C), 44.33 (adamantyl-C), 44.15 (adamantyl-C), 38.75 (adamantyl-C), 30.87 (adamantyl-C), 29.18 (*C*H(CH$_3$)$_2$), 24.64 (CH(*C*H$_3$)$_2$), 23.03 (CH(*C*H$_3$)$_2$), 5.24 (Si*C*H$_3$) ppm.

^{29}Si{^{1}H} NMR (thf-d_8, 79.49 MHz, 298 K): δ = –30.92 (*Si*H) ppm.

FTIR (Nujol mull in KBr): $\tilde{\upsilon}_{Si\text{-}H}$ = 2276.0 (m), 2013.7 (s), 1975.1 (s), 1782.2 (w), 1658.8 (w), 1535.3 (s), 1458.2 ((s), 1373.3 (s), 1303.9 (m), 1234.4 (s), 1111.0 (s), 1080.1 (s), 895.0 (m), 817.8 (m), 748.4 (s), 378.9 (w), 632.6 (w), 493.8 (s). Bands above 2300 cm^{-1} are only for Nujol.

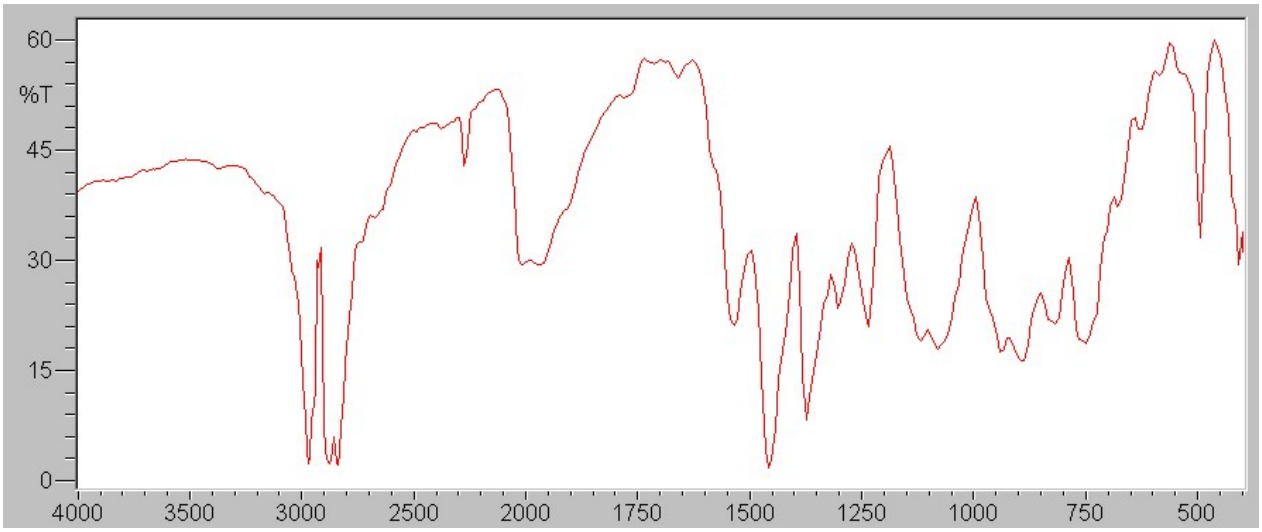

Figure S21. FTIR spectrum (Nujol mull in KBr) of [{Am^{crown}}BaN(SiMe$_2$H)$_2$] (**6**).

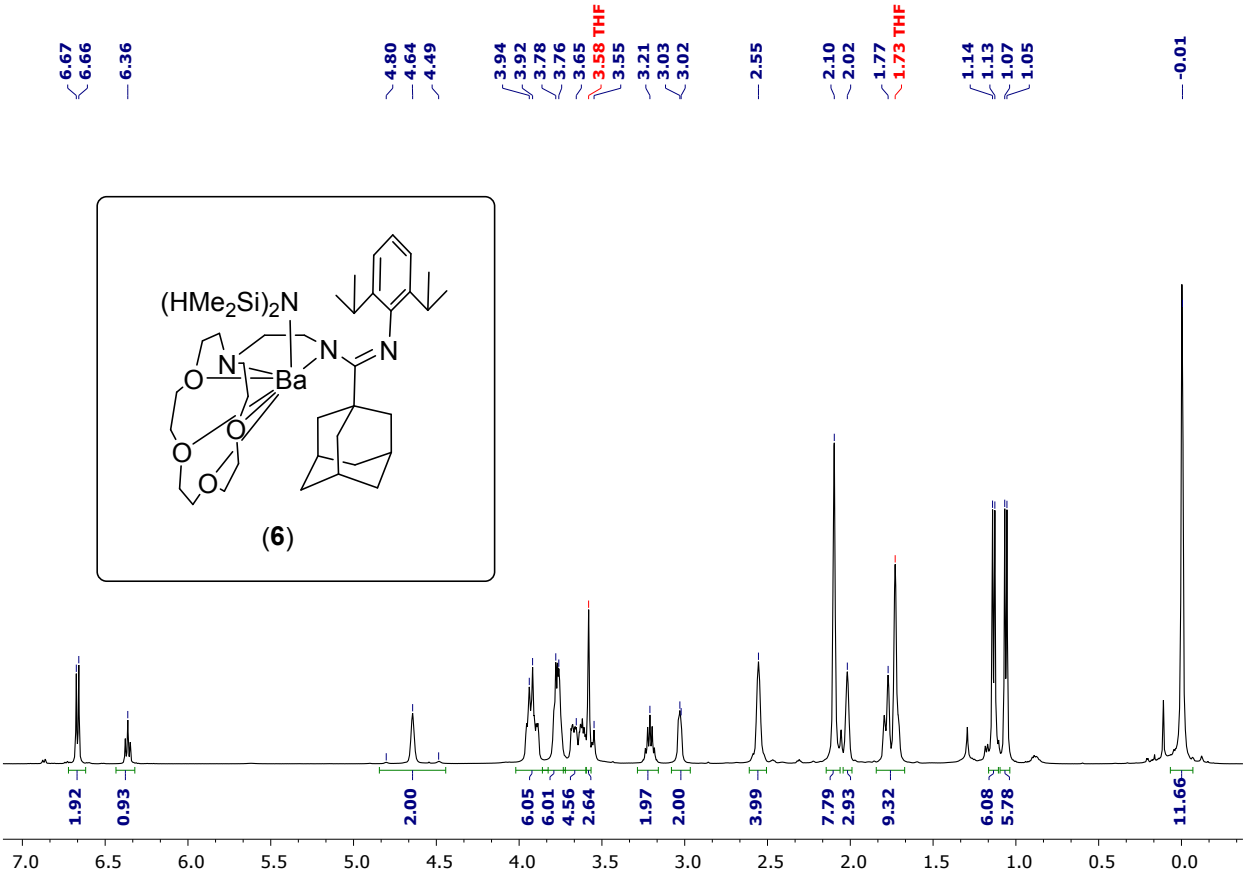

Figure S22. ^{1}H NMR spectrum (thf-d_8, 298 K, 500.13 MHz) of [{Am^{crown}}BaN(SiMe$_2$H)$_2$] (**6**).

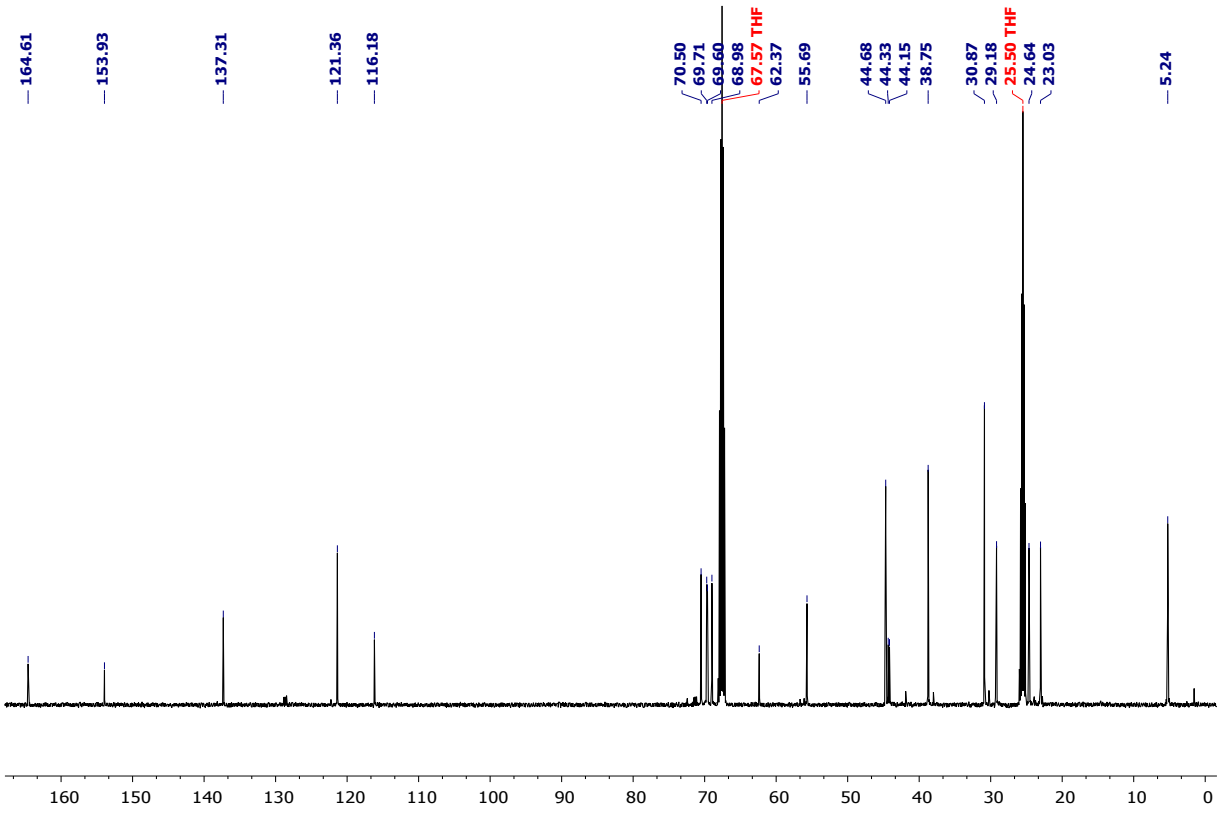

Figure S23. $^{13}C\{^{1}H\}$ NMR spectrum (thf-d_8, 298 K, 125.77 MHz) of [{Am^{crown}}BaN(SiMe$_2$H)$_2$] (**6**).

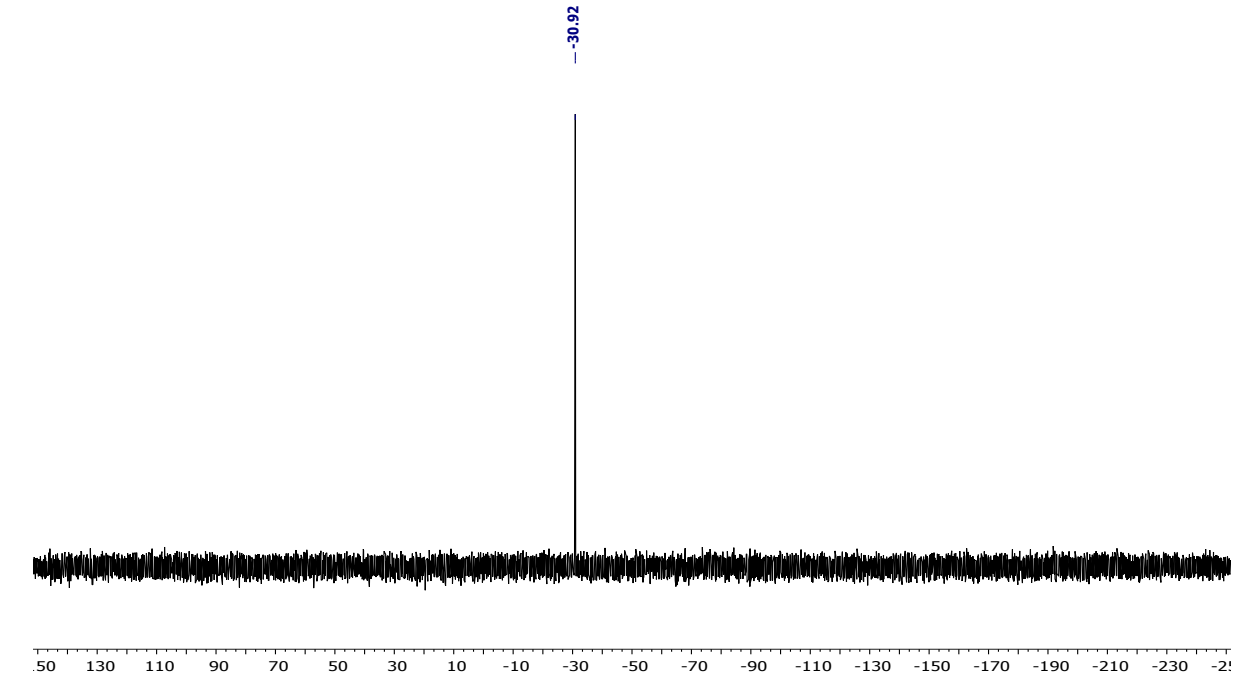

Figure S24. ^{29}Si NMR spectrum (thf-d_8, 298 K, 79.49 MHz) of [{Am^{crown}}BaN(SiMe$_2$H)$_2$] (**6**).

Attempted synthesis of [{I^A^{crown}}BaPPh$_2$] (7)

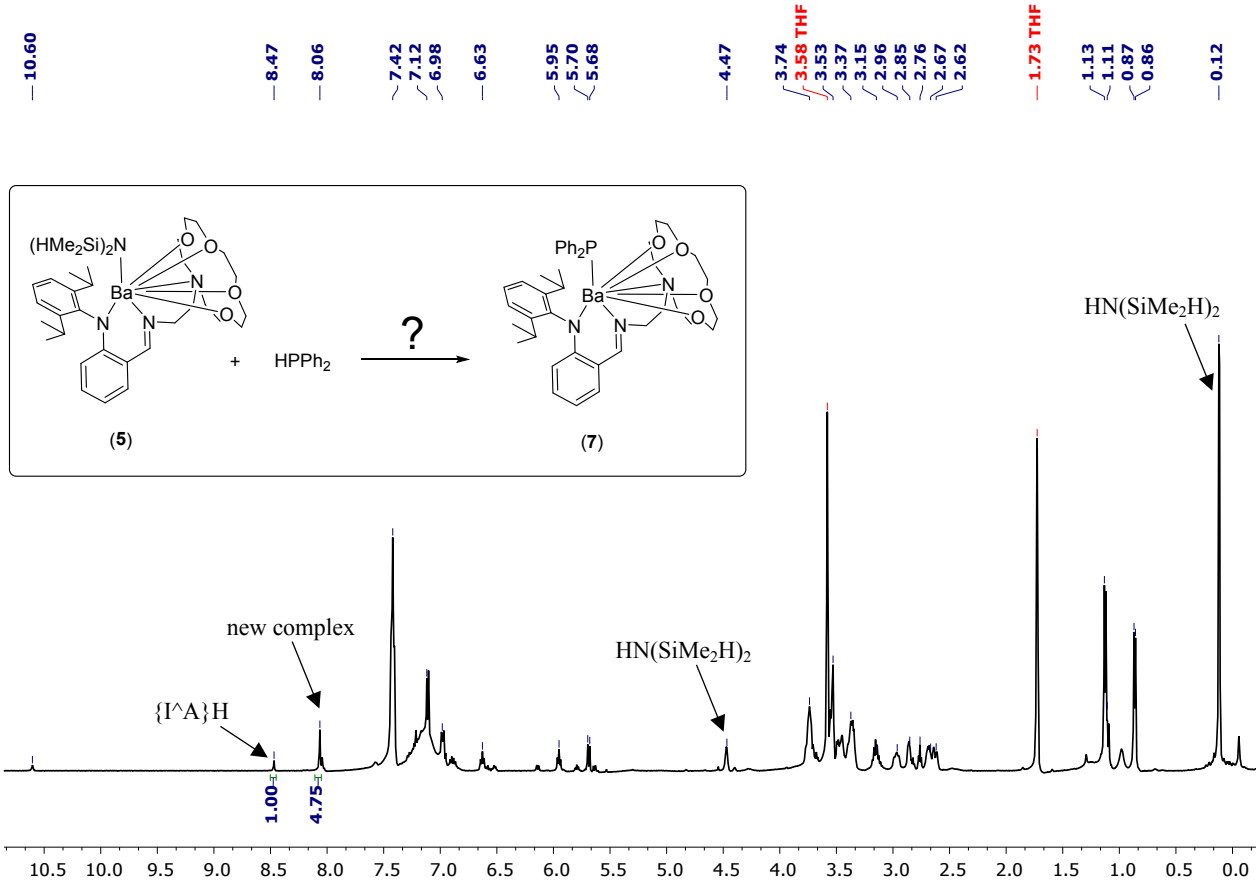

Figure S25. ^{1}H NMR spectrum (thf-d_8, 500.13 MHz, 298 K) of the reaction between **5** and HPPh$_2$. Reaction carried out in the J-Young NMR tube at 298 K in thf-d_8. Reaction time 30 min.

Attempted synthesis of [{I^A^{crown}}BaPPh$_2$] (7)

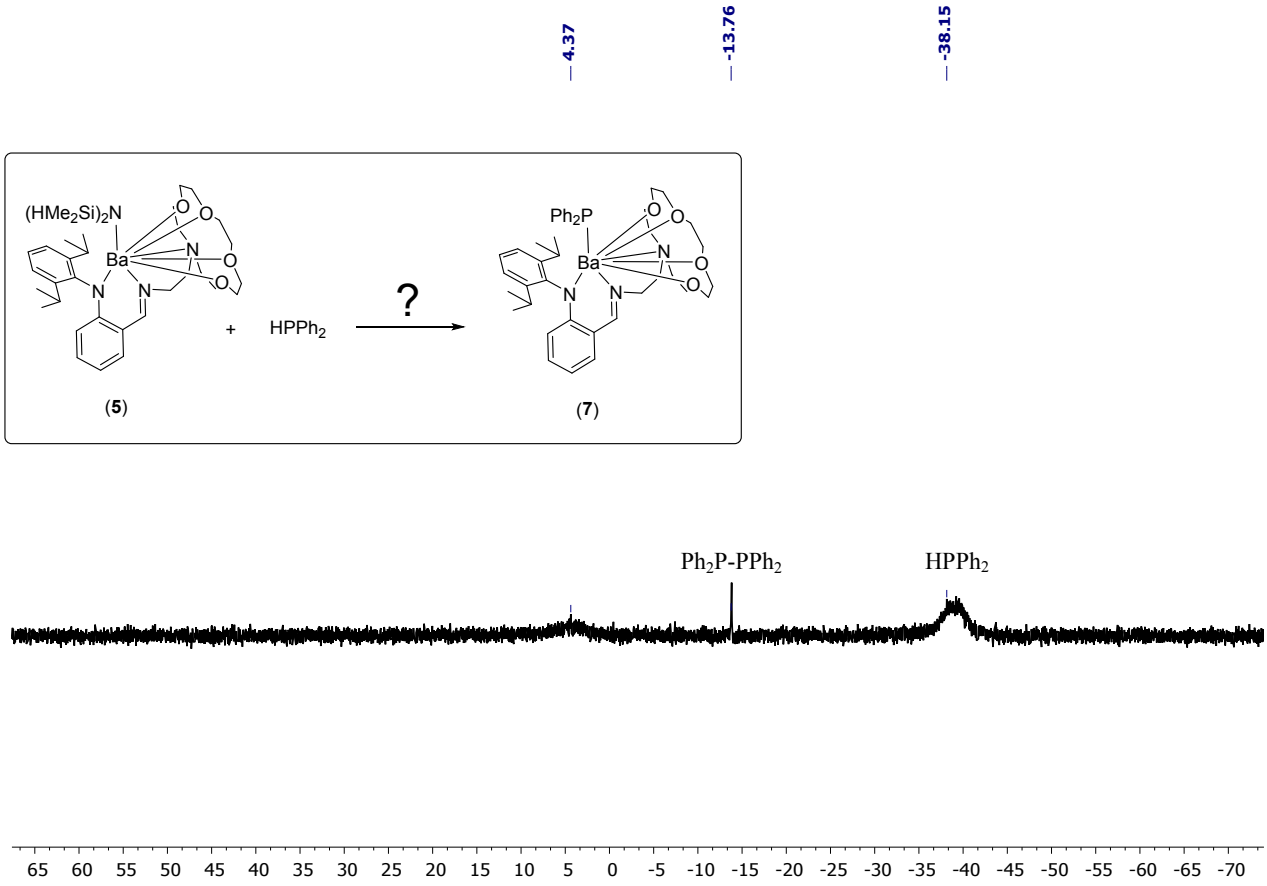

Figure S26. ^{31}P NMR spectrum (thf-d_8, 161.98 MHz, 298 K) of the reaction between **5** and $HPPh_2$. Reaction carried out in a J-Young NMR tube at 298 K in thf-d_8. Reaction time 30 min. The resulting compound, assumed to be **7**, gives rise to a very weak, broad resonance centred on 4.37 ppm. Residual $HPPh_2$ and by-product Ph_2P-PPh_2 appear respectively at –38.1 and –13.8 ppm.

X-ray diffraction crystallography

X-ray diffraction data for all compounds (CCDC 1896037-1896039 and 1897231) were collected at 150 K using a Bruker APEX CCD diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). A combination ω and Φ scans was carried out to obtain at least a unique data set. The structures were solved by dual-space algorithm using the SHELXT program, and then refined with full-matrix least-squares methods based on F^2 (SHELXL).[2] The Si*H* hydrogen atoms could be found from the Fourier difference analysis. Other hydrogen atom contributions were calculated, but not refined. Carbon-, oxygen-, and nitrogen- bound hydrogen atoms were placed at calculated positions and forced to ride on the attached atom. All non-hydrogen atoms were refined with anisotropic displacement parameters. The locations of the largest peaks in the final difference Fourier map calculation as well as the magnitude of the residual electron densities were of no chemical significance.

Table S27. Crystal data and structure refinement for {I^A}H and [{I^A^{crown}}BaN(SiMe$_2$H)$_2$] (**5**)

	{I^A}H	[{I^A^{crown}}BaN(SiMe$_2$H)$_2$] (**5**)
CCDC number	1896039	1896037
Formula	C31 H47 N3 O4	C35 H60 Ba N4 O4 Si2
Mol. wt	525.71	794.39
Crystal system	Triclinic	Orthorhombic
Space group	P –1	Pbca
a [Å]	8.4534(7)	20.2803(14)
b [Å]	15.7051(16)	19.1095(14)
c [Å]	23.035(2)	20.6121(13)
α [°]	82.635(3)	90
β [°]	89.876(3)	90
γ [°]	78.763(3)	90
V [Å^3]	2973.9(5)	7988.1(9)
Z	4	8
Density (g cm^{-3})	1.174	1.321
Abs. coeff., (mm^{-1})	0.077	1.093
F(000)	1144	3312
Crystal size, mm	0.480 × 0.220 × 0.110	0.260 × 0.210 × 0.040
θ range [°]	3.003 to 27.481	2.131 to 27.538
Limiting indices	10 < h < 10	26 < h < 25
	20 < k < 20	24 < k < 24
	29 < l < 29	26 < l < 25
R(int)	0.1256	0.1228
Reflections collected	62869 / 1355	49018 / 9031
Refl. Unique [I > 2σ (I)]	8877	5979
Completeness to θ	0.997	0.980
Data/ restraints/ param.	13555 / 0 / 699	9031 / 0 / 429
Goodness-of-fit	1.149	1.006
R_1 [I > 2σ (I)] (all data)	0.1037 (0.1465)	0.0445 (0.0913)
wR_2 [I > 2σ (I)] (all data)	0.2880 (0.3265)	0.0739 (0.0876)
Largest diff. [e A^{-3}]	1.396 and -0.570	0.587 and -0.610

Table S28. Crystal data and structure refinement for [{Am^{crown}}BaN(SiMe$_2$H)$_2$] (**6**) and {I^A^{crown}}BaPPh$_2$] (**7**)

	[{Am^{crown}}BaN(SiMe$_2$H)$_2$] (**6**)	{I^A^{crown}}BaPPh$_2$] (**7**)
CCDC number	1897231	1896038
Formula	C45 H76 Ba N4 O4 Si2	C43 H56 Ba N3 O4 P, C6H6
Mol. wt	930.61	925.32
Crystal system	Orthorhombic	Monoclinic
Space group	Pbca	P 2$_1$/c
a [Å]	21.046(3)	14.4189(15)
b [Å]	18.864(2)	17.878(2)
c [Å]	24.456(3)	18.9056(19)
α [°]	90	90
β [°]	90	108.664(3)
γ [°]	90	90
V [Å^3]	9710(2)	4617.2(9)
Z	8	4
Density (g cm^{-3})	1.273	1.331
Abs. coeff., (mm^{-1})	0.910	0.940
F(000)	3920	1920
Crystal size, mm	0.390 × 0.350 × 0.290	0.400 × 0.340 × 0.320
θ range [°]	2.159 to 27.605	2.982 to 27.483
Limiting indices	27 < h < 27	18 < h < 18
	24 < k < 24	23 < k < 20
	28 < l < 31	24 < l < 24
R(int)	0.0965	0.0334
Reflections collected	80328 / 11173	47566 / 10557
Refl. Unique [I > 2σ (I)]	9075	8959
Completeness to θ	0.992	0.997
Data/ restraints/ param.	11173 / 0 / 385	10557 / 0 / 439
Goodness-of-fit	1.253	1.118
R$_1$ [I > 2σ (I)] (all data)	0.1495 (0.1696)	0.0385 (0.0497)
wR$_2$ [I > 2σ (I)] (all data)	0.3152 (0.3255)	0.0862 (0.0959)
Largest diff. [e A^{-3}]	2.259 and -2.736	1.984 and -1.814

References

1 (*a*) Y. Sarazin, D. Roşca, V. Poirier, T. Roisnel, A. Silvestru, L. Maron and J.-F. Carpentier, *Organometallics*, 2010, **29**, 6569; (*b*) N. Romero, S.-C. Roşca, Y. Sarazin, J.-F. Carpentier, L. Vendier, S. Mallet-Ladeira, C. Dinoi and M. Etienne, *Chem. Eur. J.*, 2015, **21**, 4115.

2 (*a*) G. M. Sheldrick, *Acta Cryst. Sect. A*, 2015, **71**, 3; (*b*) G.M. Sheldrick, *Acta Cryst. Sect. C*, 2015, **71**, 3.