Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

Contents

1. Supporting Experimental Data

1.1. General experimental procedures

All experiments were conducted under an inert nitrogen atmosphere using standard Schlenk and glovebox techniques (MBraun, Labmaster SP). All solvents were degassed with nitrogen, dried over activated aluminium oxide (Solvent Purification System: Pure Solv400−4−MD, Innovative Technology) and stored over 3Å molecular sieves. THF was dried over sodium, distilled under N_2 atmosphere and stored over molecular sieves 3 Å. The aminoalkenes 2-dimethylpent-4-en-1-amine, 2,2-diphenylpent-4-en-1-amine and (1-allylcyclohexyl)-methanamine were synthesized according to literature procedures and stored under N_2 in a glovebox.[S1]

(*R*)-(−)-α-Methoxy-α-(trifluoromethyl)phenylacetyl chloride was synthesized from (*R*)-(−)-α-Methoxy-α-(trifluoromethyl)phenylacetic acid according to a literature known procedure.[S2] Anhydrous CaI_2 was synthesized by reacting the metals with I_2 in dry THF, removing excess of metal by filtration and evaporation of all solvents under high vacuum at 60 °C. The metal precursors $Ca(DMAT)_2{\cdot}(THF)_2$, $Ca[N(SiMe_3)_2]_2$ $Ca[N(SiMe_3)_2]_2{\cdot}(THF)_2$ and benzyl potassium were prepared according to literature procedures.[S3] Di-*n*-butyl magnesium was purchased from Sigma Aldrich, stripped of solvent and used without further purification. *Rac*-BINAM was prepared from naphthol and hydrazine hydrate using a modified workup procedure.[S4] The product was triturated with a mixture of petrol ether and ethyl acetate (1:1), washed thoroughly with petrol ether and subsequently recrystallized from ethyl acetate. Resolution of the racemic mixture was carried out according to a published procedure using (1*S*)-(+)-10-camphorsulfonic acid.[S5] Ligands, except ^{DPM}1-H_2, were prepared according to modified literature procedures.[S6]

2-naphtol, 5-chlorodibenzosuberane, (1*S*)-(+)-10-camphorsulfonic acid, potassium *tert.* butoxide, trimethyl acetyl chloride, $Pd_2(dba)_3$ and molecular sieves 3 Å were purchased from Sigma Aldrich and used without further purification. BINAP was purchased from Strem Chemicals and used without further purification. Hydrazine hydrate was purchased from Merck and used as received. Triethylamine (Sigma Aldrich, 99.5%) was dried over freshly ground calcium hydride, distilled under N_2 atmosphere and stored over molecular sieves 3 Å. Lithium aluminium hydride was purified by diethylether extraction and subsequent removal of all volatiles.

Benzophenone was recrystallized from *n*-hexane. Unspecified starting materials and research chemicals were obtained from commercial suppliers where appropriate and used without further purification.

Flash column chromatography was carried out using Grace Reveleris X2 with Grace Reveleris cartridges or hand packed cartridges filled with SiO_2 for chromatography (0.035-0.070 mm 60 A, deactivated) obtained from Sigma Aldrich. All solvents used for flash column chromatography or column chromatography were purified by distillation.

NMR spectra were measured on Bruker Avance III HD 400 MHz and Bruker Avance III HD 600 MHz spectrometers. Chemical shifts (δ) are given in ppm (parts per million) values, coupling constants (J) in Hz. For describing signal multiplicities common abbreviations were used: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), dm (doublet of multiplet) and br (broad). The spectra were referenced to the respective residual signals of the deuterated solvents.[S7] All deuterated solvents were purchased from Deutero GmbH (99.6% D) and dried over molecular sieves 3 Å under N_2.

Elemental analysis was performed with a Euro EA 3000 (Euro Vector) analyzer. All crystal structures have been measured on a SuperNova (Agilent) diffractometer with dual Cu and Mo microfocus sources and an Atlas S2 detector.

1.2. Ligand Synthesis

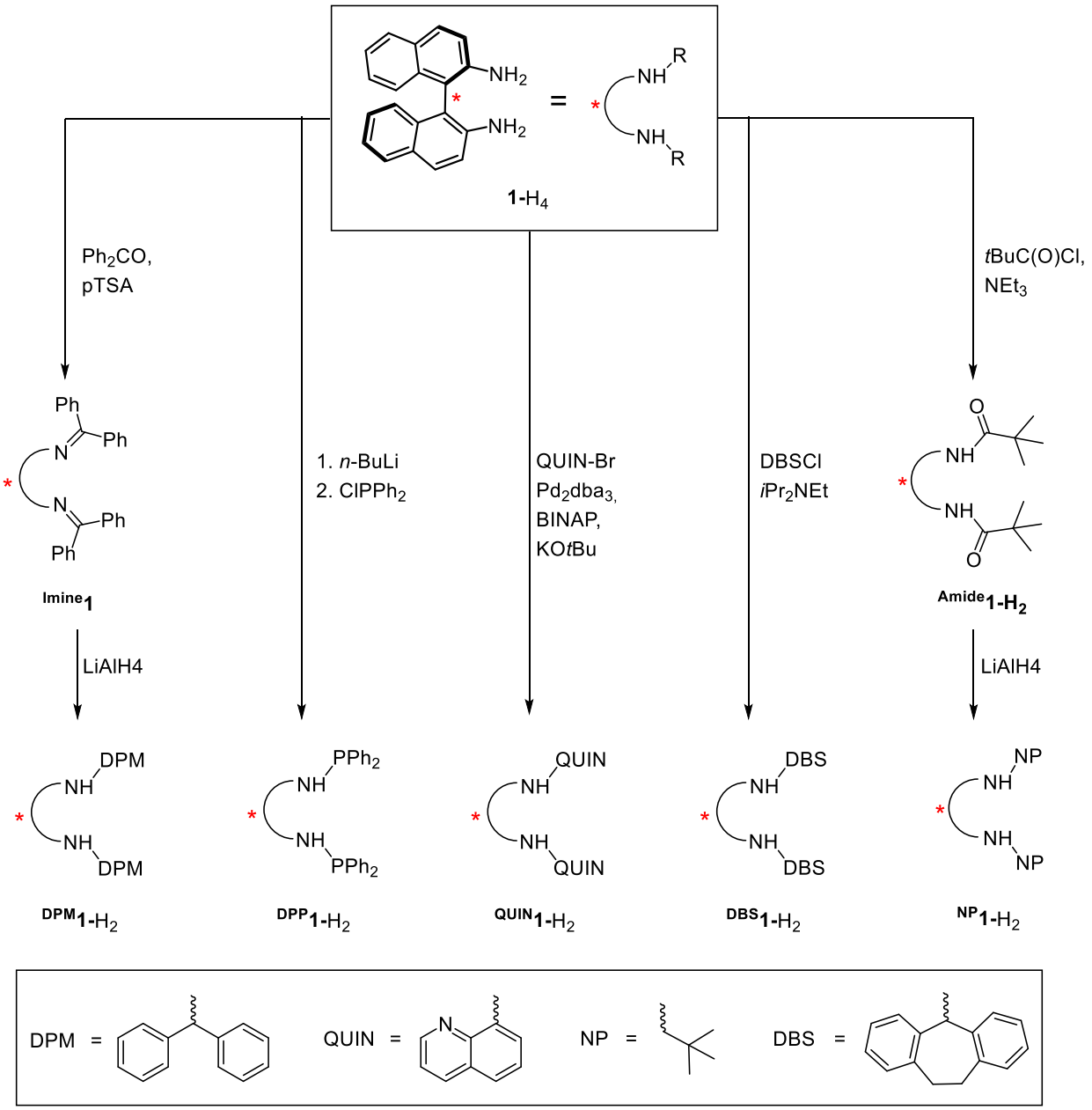
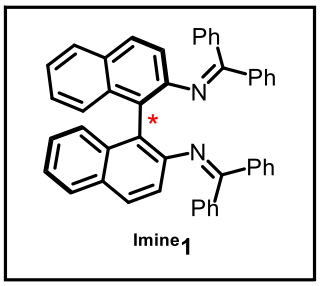


Figure S1: Synthesis of *R*-Binam derived ligands.

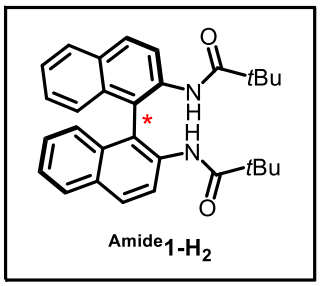
Synthesis of ^{Imine}1



Imine1

To a suspension of (*R*)-BINAM (4.00 g, 14.1 mmol) and benzophenone (5.14 g, 28.2 mmol) in toluene (20.0 mL), catalytic amounts of *p*-toluenesulfonic acid (0.24 g, 1.41 mmol) were added. The resulting mixture was refluxed in a Dean-Stark trap. The reaction was judged complete after 4 days by TLC analysis. While slowly cooling the reaction flask to room temperature, the product crystalized as bright yellow needles. A second crop was obtained by cooling the mother liquor to 5°C overnight. Subsequently the crystals were filtered off and the product batches were combined. Washing with hexane (3x50 mL) and drying under reduced pressure at 60°C yielded a bright yellow fluffy powder. Yield: 5.21 g, 8.51 mmol, 60%. ^{1}H NMR (600 MHz, chloroform-d_1, 25 °C): δ = 7.76 (d, ^{3}J = 6.9 Hz, 4H, CH_{Ar}), 7.67 (d, ^{3}J = 8.2 Hz, 4H, CH_{Ar}), 7.38 (d, ^{3}J = 7.1 Hz, 2H, CH_{Ar}), 7.30 (t, ^{3}J = 7.4 Hz, 6H, CH_{Ar}), 7.18 (t, ^{3}J = 7.1 Hz, 4H, CH_{Ar}), 7.00 (t, ^{3}J = 7.2 Hz, 2H, CH_{Ar}), 6.78 (t, ^{3}J = 7.6 Hz, 2H, CH_{Ar}), 6.72 (t, ^{3}J = 7.4 Hz, 3H, CH_{Ar}), 6.62 (d, ^{3}J = 7.5 Hz, 3H, CH_{Ar}), 6.42 (d, ^{3}J = 8.4 Hz, 2H, CH_{Ar}) ppm. ^{13}C{^{1}H} NMR (151 MHz, chloroform-d_1, 25 °C): δ = 166.7 (s, C=N), 147.1 (s, N-C), 140.7 (s, *ipso*-Ph), 136.4 (s, *ipso*-Ph), 133.7 (s, C_{Ar}), 130.3 (s, C_{Ar}), 130.2 (s, CH_{Ar}), 130.0 (s, CH_{Ar}), 129.8 (s, CH_{Ar}), 128.6 (s, CH_{Ar}), 128.0 (s, CH_{Ar}), 127.8 (s, CH_{Ar}), 127.5 (s, CH_{Ar}), 127.4 (s, CH_{Ar}), 126.6 (s, CH_{Ar}), 125.9 (s, CH_{Ar}), 123.5 (s, CH_{Ar}), 122.3 (s, CH_{Ar}), 121.8 (s, C_{Ar}) ppm.

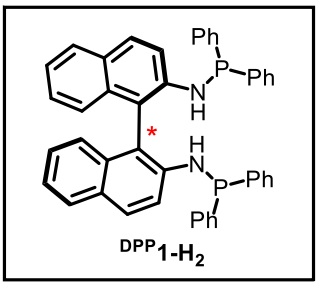
Synthesis of ^{Amide}1-H_2



^{Amide}1-H_2

^{Amide}**1**-H_2 was synthesized according to a slightly modified literature procedure.[S6d] (*R*)-BINAM (5.00 g, 17.6 mmol) was dissolved in a mixture of THF (125 mL) and triethylamine (7.12 g, 9.75 mL, 70.3 mmol). Pivaloyl chloride (4.73 g, 4.83 mL, 35.2 mmol) was added slowly via syringe and a white precipitate was formed upon addition. The suspension was stirred for 3 days at room temperature. The triethylammonium chloride precipitate was filtered off using celite and washed with THF (50 mL). All volatiles were removed under reduced pressure and a white foamy solid remained, which was recrystallized from a mixture of methanol and dichloromethane (6:1, 10 mL) to furnish the product as big, colorless crystals. Yield: 7.06 g, 15.7 mmol, 89%. ^{1}H NMR (600 MHz, chloroform-d_1, 25 °C): δ = 8.49 (d, ^{3}J = 9.0 Hz, 2H, CH_{Ar}), 8.05 (d, ^{3}J = 9.0 Hz, 2H, CH_{Ar}), 7.94 (d, ^{3}J = 8.2 Hz, 2H, CH_{Ar}), 7.45 (t, ^{3}J = 7.5 Hz, 2H, Ar), 7.31 (t, ^{3}J = 7.6 Hz, 2H, Ar), 7.18 (d, ^{3}J = 8.4 Hz, 2H, Ar), 7.13 (s, 2H, NH), 0.75 (s, 18H, $C(CH_3)_3$). $^{13}C\{^{1}H\}$ NMR (151 MHz, chloroform-d_1, 25 °C): δ = 177.2 (s, C=O), 135.3 (s, C_{Ar}), 132.3 (s, C_{Ar}), 131.3 (s, C_{Ar}), 129.9 (s, CH_{Ar}), 128.5 (s, CH_{Ar}), 127.5 (s, CH_{Ar}), 125.6 (s, CH_{Ar}), 125.0 (s, CH_{Ar}), 122.0 (s, CH_{Ar}), 121.2 (s, C_{Ar}), 39.5 (s, $C(CH_3)_3$), 27.0 (s, CH_3) ppm.

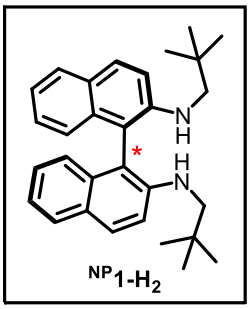
Synthesis of ^{DPP}1-H$_2$



^{DPP}1-H$_2$

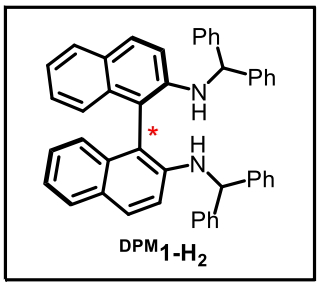
^{DPP}**1**-H$_2$ was synthesized according to a slightly modified literature procedure.[S6a] (*R*)-BINAM (2.54 g, 8.93 mmol) was dissolved in dry THF (50 mL) and cooled to -30°C. *n*-Butyllithium (7.0 mL, 17.5 mmol, 2.5M in hexanes) was added over a period of 30 min and an orange-yellow solid precipitated. The suspension was stirred for 30 min at -30°C and subsequently a solution of chlorodiphenylphosphine (3.2 mL, 3.93 g, 17.8 mmol) in THF (15 mL) was added within 50 min. After stirring for 1h the reaction mixture was slowly warmed to room temperature by thawing of the cooling bath and stirred for 24 h. All volatiles were removed under reduced pressure, the foamy residue was suspended in toluene (50 mL) and the LiCl precipitate was filtered off using celite. All volatiles were removed and the product was recrystallized twice from a mixture of hexane and toluene (9:1, 30 mL) to yield big, shiny, colorless crystals. The crystals were washed with cold hexane (2 mL) and dried under reduced pressure at 60°C. Yield: 4.95 g, 7.59 mmol, 85 %. ^{1}H NMR (400 MHz, benzene-d_6, 25 °C): δ = 8.15 (d, ^{3}J = 4.0 Hz, 1H, CH$_{Ar}$), 8.13 (d, ^{3}J = 4.0 Hz, 1H, CH$_{Ar}$), 7.65 (d, ^{3}J = 9.0 Hz, 2H, CH$_{Ar}$), 7.60 (d, ^{3}J = 8.1 Hz, 2H, CH$_{Ar}$), 7.25-7.24 (m, 6H, CH$_{Ar}$), 7.09 (t, ^{3}J = 7.1 Hz, 2H, CH$_{Ar}$), 7.05 (t, ^{3}J = 7.3 Hz, 4H, CH$_{Ar}$), 6.97-6.95 (m, 8H, CH$_{Ar}$), 6.90-6.87 (m, 2H, CH$_{Ar}$), 6.83 (m, 4H, ^{3}J = 6.6 Hz, CH$_{Ar}$), 4.90 (d, ^{3}J = 8.1 Hz, 2H, NH) ppm. ^{13}C{^{1}H} NMR (101 MHz, benzene-d_6, 25 °C): δ = 144.1 (d, $J_{C,P}$ = 18.2 Hz, 2C, C$_{Naph}$), 141.1 (d, $J_{C,P}$ = 31.5 Hz, 2C, C$_{Ph}$), 140.8 (d, $J_{C,P}$ = 27.2 Hz, 2C, C$_{Ph}$), 134.3 (s, 2C, C$_{Naph}$), 131.1 (d, $J_{C,P}$ = 31.5 Hz, 4C, C$_{Ph}$), 130.8 (d, $J_{C,P}$ = 20.5 Hz, 4C, C$_{Ph}$), 130.4 (d, $J_{C,P}$ = 1.8 Hz, 2C, C$_{Naph}$), 129.5 (d, $J_{C,P}$ = 1.8 Hz, 2C, C$_{Naph}$), 129.1 (s, 2C, C$_{Naph}$), 128.9 (d, $J_{C,P}$ = 3.2 Hz, 2C, C$_{Naph}$), 128.8 (d, $^{3}J_{C,P}$ = 6.4 Hz, 4C, C$_{Ph}$), 128.6 (d, $^{3}J_{C,P}$ = 6.4 Hz, 4C, C$_{Ph}$), 127.5 (s, 2C, C$_{Naph}$), 124.9 (s, 2C, C$_{Naph}$), 123.4 (s, 2C, C$_{Naph}$), 117.5 (d, $^{3}J_{C,P}$ = 23.8 Hz, 4C, C$_{Ph}$), 115.6 (d, $^{3}J_{C,P}$ = 3.6 Hz, 2C, C$_{Naph}$) ppm. ^{31}P NMR (243 MHz, benzene-d_6, 25 °C): δ = 27.2 (s, PPh$_2$) ppm. Elemental Analysis: C$_{44}$H$_{34}$N$_2$P$_2$ (M = 652.72): calc. C 80.97, H 5.25, N 4.29, found: C 80.55, H 5.29, N 4.19.

Synthesis of ^{NP}1-H_2



^{NP}**1**-H_2 was synthesized according to a slightly modified literature procedure.[S6d] Purified $LiAlH_4$ (2.65 g, 69.8 mmol), was dissolved in Et_2O (75 mL) and cooled to 0°C. A solution of ^{Amide}1-H_2 (7.03 g, 15.5 mmol) in THF (75 mL) was added dropwise. The resulting yellow solution was warmed to room temperature overnight. Subsequently the dark yellow solution was refluxed for 3 days. The green reaction mixture was cooled to room temperature and quenched with *iso*propanol and water. The white precipitate was filtered off and washed with dichloromethane (3 x 60 mL). The phases were separated and the aqueous phase was washed with Et_2O (20 mL). The combined organic phases were dried over $MgSO_4$, the solvent was removed and the remaining solid was dried under reduced pressure. The crude product was purified by flash column chromatography on SiO_2 (80 g) using heptane and ethylacetate (9:1) as eluent. Recrystallization from a mixture of methanol and DCM (5:1, 10 mL) furnished the product as white crystals. Subsequent drying under reduced pressure gave a white free flowing powder. Yield: 4.27 g, 10.1 mmol, 65 %. ^{1}H NMR (600 MHz, benzene-d_6, 25 °C): δ = 7.82 (d, ^3J = 9.0 Hz, 2H, CH_{Ar}), 7.76 (d, ^3J = 8.4 Hz, 2H, CH_{Ar}), 7.33 (dd, ^3J = 8.4 Hz, ^4J = 1.2 Hz, 2H, CH_{Ar}), 7.12 (ddd, ^3J = 8.1 Hz, 6.7 Hz, ^4J = 1.3 Hz, 2H, CH_{Ar}), 7.08 (ddd, ^3J = 8.2 Hz, 6.7 Hz, ^4J = 1.5 Hz, 2H, CH_{Ar}), 3.92 (t, ^3J = 6.3 Hz, 2H, NH), 2.79 (d, ^3J = 6.6 Hz, 1H, CH_2*t*Bu), 2.77 (d, ^3J = 6.6 Hz, 1H, CH_2*t*Bu), 2.68 (d, ^3J = 6.1 Hz, 1H, CH_2*t*Bu), 2.66 (d, ^3J = 6. 0Hz, 1H, CH_2*t*Bu), 0.57 (s, 18H, $C(CH_3)_3$) ppm. ^{13}C{^{1}H} NMR (151 MHz, benzene-d_6, 25 °C): δ = 145.6 (s, C_{Ar}), 134.7 (s, C_{Ar}), 129.9 (s, CH_{Ar}), 128.6 (s, CH_{Ar}), 128.1 (s, C_{Ar}), 127.3 (s, CH_{Ar}), 124.5 (s, CH_{Ar}), 122.2 (s, CH_{Ar}), 114.2 (s, CH_{Ar}), 112.0 (s, C_{Ar}), 55.4 (s, CH_2), 32.3 (s, $C(CH_3)_3$), 27.3 (s, CH_3) ppm. Elemental Analysis: $C_{30}H_{36}N_2$ (M = 616.81): calc. C 84.86, H 8.55, N 6.60, found: C 84.64, H 8.72, N 6.42.

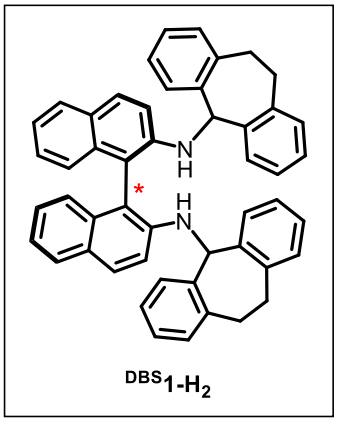
Synthesis of ^{DPM}1-H$_2$



^{DPM}1-H$_2$

Purified $LiAlH_4$ (1.21 g, 31.9 mmol) was dissolved in dry THF (100 mL) and a solution of ^{Imine}1 (3.91 g, 6.38 mmol) in dry THF (50 mL) was added drop wise. The yellow solution was stirred for 2 days at room temperature and subsequently refluxed for 1 days. The resulting greenish reaction mixture was quenched by addition of isopropanol and water. The organic layer was separated and the aqueous layer was extracted with chloroform (50 mL). The combined organic layers were washed with water (2x50 mL), brine (50 mL) and dried over magnesium sulfate. All volatiles were removed under reduced pressure and the yellowish crude product was purified by column chromatography on SiO_2 (80 g) using heptane and ethylacetate (85:15) as eluent. Drying under reduced pressure at 60°C resulted in a fine white powder. Yield: 2.97 g, 4.82 mmol, 76%. ^{1}H NMR (600 MHz, benzene-d_6, 25°C) δ = 7.58 – 7.56 (m, 2 H, CH_{Ar}), 7.49 (d, J = 9.0 Hz, 2H, CH_{Ar}), 7.34 – 7.32 (m, 2H, CH_{Ar}), 7.16 (m, 4H, CH_{Ar} obscured by benzene-d_6), 7.09 – 7.06 (m, 10H, CH_{Ar}), 7.02 – 6.97f (m, 6H, CH_{Ar}), 6.93 (t, J = 7.6 Hz, 4H, CH_{Ar}), 6.89 – 6.83 (m, 2H, CH_{Ar}), 5.60 (d, J = 5.6 Hz, 2H, CH_2), 4.74 (d, J = 5.7 Hz, 2H, NH) ppm. ^{13}C{^{1}H} NMR (151 MHz, chloroform-d_1, 25 °C): δ = 143.7 (s, *ipso*-Ph), 143.0 (s, *ipso*-Ph), 142.8 (s, C_{Ar}), 133.9 (s, C_{Ar}), 129.8 (s, CH_{Ar}), 128.8 (s, CH_{Ar}), 128.6 (s, CH_{Ar}), 128.2 (s, CH_{Ar}), 127.9 (s, C_{Ar}), 127.5 (s, CH_{Ar}), 127.4 (s, CH_{Ar}), 127.4 (s, CH_{Ar}), 127.3 (s, CH_{Ar}), 126.7 (s, CH_{Ar}), 124.3 (s, CH_{Ar}), 122.2 (s, CH_{Ar}), 114.8 (s, CH_{Ar}), 112.5 (s, C_{Ar}), 62.3 (s, CH_{NH}) ppm. Elemental Analysis: $C_{46}H_{36}N_2$ (M = 616.81): calc. C 89.58, H 5.88, N 4.54, found: C 89.58, H 6.05, N 4.40.

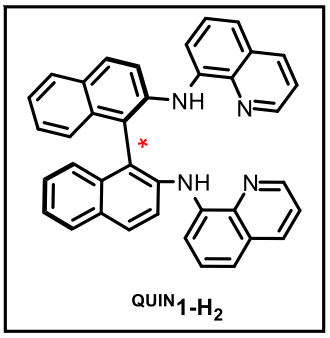
Synthesis of ^{DBS}1-H_2



^{DBS}1-H_2

^{DBS}**1**-H_2 was synthesized according to a slightly modified literature procedure.[S6b] (*R*)-BINAM (1.14 g, 4.01 mmol), and 5-chlorodibenzosuberane (2.28 g, 10.0 mmol) were suspended in dry acetonitrile (10 mL). Hünig´s base (1.48 g, 2.00 mL, 11.5 mmol) was added and the mixture was refluxed for 3 days until charged complete by TLC analysis. The orange/red reaction mixture was diluted with dichloromethane (50 mL) and filtered over Celite. The precipitate was washed with dichloromethane (20 mL) and the combined fractions were washed with water (2x 20 mL) and brine (20 mL). After drying over $MgSO_4$ all volatiles were removed under reduced pressure and the orange crude product was washed with a mixture of ethanol and dichloromethane (35 mL, 15:1). The yellowish crude product was purified by column chromatography on SiO_2 (80 g) using heptane and ethylacetate (85:15) as eluent. Subsequent drying under reduced pressure gave the product as white free flowing powder. Yield: 1.87 g, 2.81 mmol, 70 %. ^{1}H NMR (600 MHz, chloroform-d_1, 25 °C): δ = 7.82 (d, ^3J = 9.0 Hz, 2H, CH_{Ar}), 7.78 (d, ^3J = 8.0 Hz, 2H, CH_{Ar}), 7.23 – 7.19 (m, 4H, CH_{Ar}), 7.16 (dd, ^3J = 8.3, 6.8 Hz, 2H, CH_{Ar}), 7.08 (d, ^3J = 8.4 Hz, 2H, CH_{Ar}), 7.05 – 7.01 (m, 4H, CH_{Ar}), 6.97 (t, ^3J = 7.5 Hz, 6H, CH_{Ar}), 6.93 (d, ^3J = 7.6 Hz, 2H, CH_{Ar}), 6.90 – 6.86 (t, ^3J = 7.5 Hz, 2H, CH_{Ar}), 6.81 (t, ^3J = 8.6 Hz, 2H, CH_{Ar}), 5.95 (d, ^3J = 6.6 Hz, 2H, CH), 4.71 (d, ^3J = 6.7 Hz, 2H, NH), 3.11 – 3.08 (m, 4H, CH_2), 2.95 – 2.92 (m, 4H, CH_2) ppm. ^{13}C{^{1}H} NMR (151 MHz, chloroform-d_1, 25 °C): δ = 143.7 (s, C_{Ar}), 140.4 (s, C_{Ar}), 140.3 (s, C_{Ar}), 138.0 (s, C_{Ar}), 138.0 (s, C_{Ar}), 134.1 (s, C_{Ar}), 130.4 (s, CH_{Ar}), 130.3 (s, CH_{Ar}), 129.9 (s, CH_{Ar}), 128.2 (s, CH_{Ar}), 128.0 (s, C_{Ar}), 127.3 (s, CH_{Ar}), 127.2 (s, CH_{Ar}), 126.9 (s, CH_{Ar}), 126.3 (s, CH_{Ar}), 126.1 (s, CH_{Ar}), 125.7 (s, CH_{Ar}), 125.6 (s, CH_{Ar}), 124.4 (s, CH_{Ar}), 122.4 (s, CH_{Ar}), 115.2 (s, CH_{Ar}), 113.3 (s, C_{Ar}), 59.4 (s, CH), 32.3 (s, CH_2), 32.1 (s, CH_2) ppm. Elemental Analysis: $C_{46}H_{36}N_2$ (M = 668.88): calc. C 89.78, H 6.03, N 4.19, found: C 90.12, H 5.99, N 4.10.

Synthesis of ^{QUIN}1-H_2



^{QUIN}**1**-H_2 was synthesized according to a slightly modified literature procedure.[S6c] (*R*)-BINAM (2.10 g, 7.38 mmol), $Pd_2(dba)_3$ (350 mg, 0.39 mmol), (±)-BINAP (480 mg, 0.77 mmol) and sodium *tert*-butoxide (2.48 g, 23.2 mmol) were suspended in anhydrous toluene (200 mL). 8-Bromoquinoline (3.39 g, 16.3 mmol) was added and the black suspension was refluxed for 48 h. The reaction mixture was allowed to cool to room temperature and was dilute with pentane (1.00 L). The black suspension was filtered through celite resulting in a purple/black solution. All volatiles were removed under reduced pressure and the black crude product was triturated with isopropanol (10 mL) to furnish a dark purple solid. Purification by column chromatography on SiO_2 (180 g) using dichloromethane as eluent and drying under reduced pressure at 60°C furnished the product as a shiny yellow microcrystalline powder. Yield: 2.98 g, 5.54 mmol, 75%. ^{1}H NMR (400 MHz, benzene-d_6, 25°c) δ = 8.59 (s, 2H, NH), 8.07 (dd, ^3J = 4.3 Hz, ^4J = 1.8 Hz, 2H, CH_{Ar}), 8.04 (d, ^3J = 9.0 Hz, 2H, CH_{Ar}), 7.77 (d, ^3J = 8.8 Hz, 2H, CH_{Ar}), 7.70 (d, ^3J = 8.2 Hz, 2H, CH_{Ar}), 7.51 (d, ^3J = 8.4 Hz, 2H, CH_{Ar}), 7.44 (d, ^3J = 7.7 Hz, 2H, CH_{Ar}), 7.34 (dd, ^3J = 8.2 Hz, 1.8 Hz, 2H, CH_{Ar}), 7.14 (t, ^3J = 7.5 Hz, 2H, CH_{Ar}), 7.00 (t, ^3J = 7.6 Hz, 2H, CH_{Ar}), 6.92 (t, ^3J = 8.0 Hz, 2H, CH_{Ar}), 6.77 (d, ^3J = 8.1 Hz, 2H, CH_{Ar}), 6.55 (dd, ^3J = 8.3 Hz, 4.2 Hz, 2H, CH_{Ar}) ppm. ^{13}C{^{1}H} NMR (101 MHz, chloroform-d_1, 25°c) δ = 147.2 (s, CH_{Ar}), 140.3 (s, C_{Ar}), 138.8 (s, C_{Ar}), 138.7 (s, C_{Ar}), 135.8 (s, CH_{Ar}), 134.6 (s, C_{Ar}), 130.5 (s, C_{Ar}), 129.1 (s, CH_{Ar}), 128.6 (s, C_{Ar}), 128.2 (s, CH_{Ar}), 126.8 (s, CH_{Ar}), 126.6 (s, CH_{Ar}), 126.4 (s, CH_{Ar}), 125.8 (s, CH_{Ar}), 124.2 (s, CH_{Ar}), 122.1 (s, C_{Ar}), 121.3 (s, C_{Ar}), 121.1 (s, CH_{Ar}), 116.7 (s, CH_{Ar}), 107.9 (s, CH_{Ar}) ppm. Elemental Analysis: $C_{38}H_{26}N_4$ (M = 538.65): calc. C 84.73, H 4.87, N 10.40, found: C 84.55, H 4.80, N 10.29. Annotation: ^{13}C{^{1}H} NMR measurements were conducted in chloroform-d_1, due to higher solubility, while ^{1}H NMR was measured in benzene-d_6 due to a clear peak seperation.

1.3. NMR Spectra of Ligand Precursors and Ligands

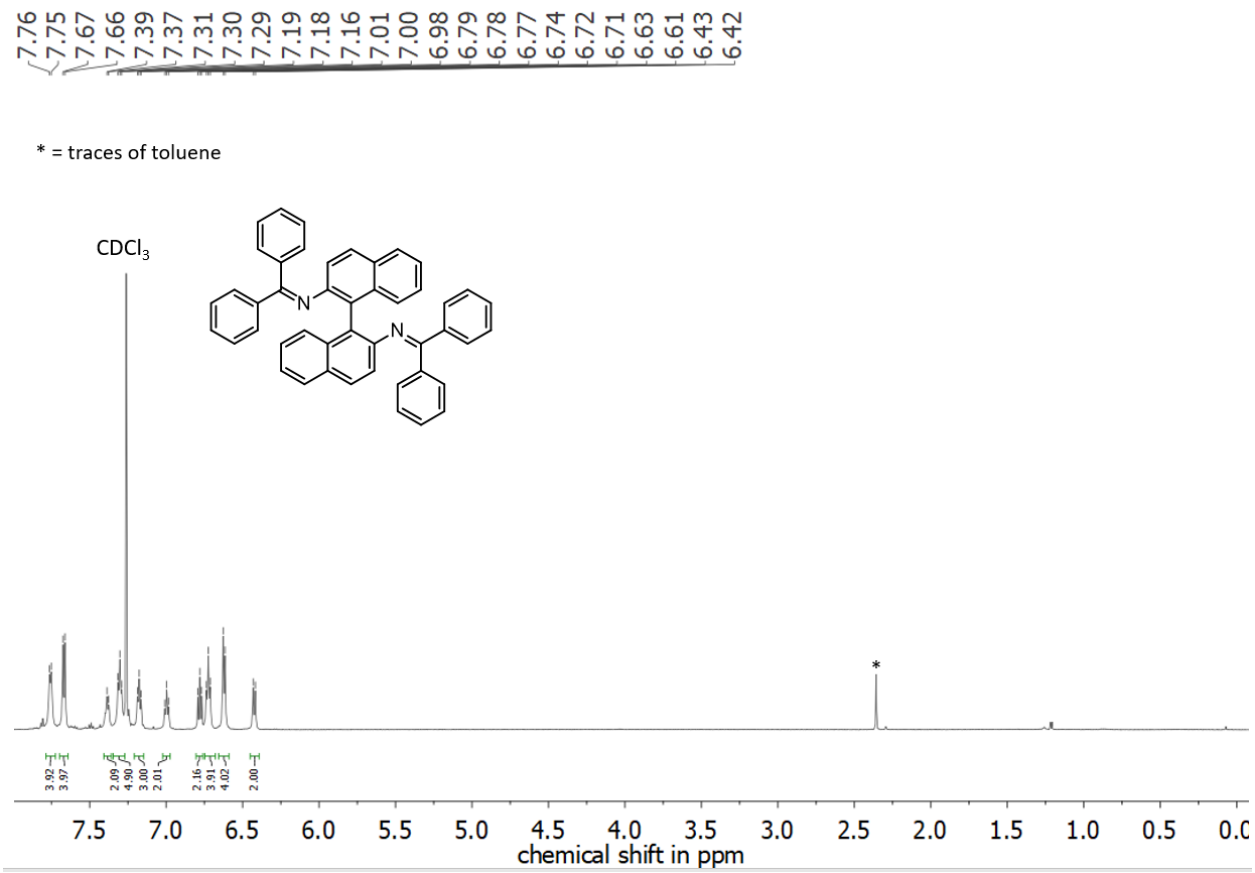


Figure S2: ^{1}H NMR (600 MHz, chloroform-d_1, 25°C) spectrum of ^{Imine}1.

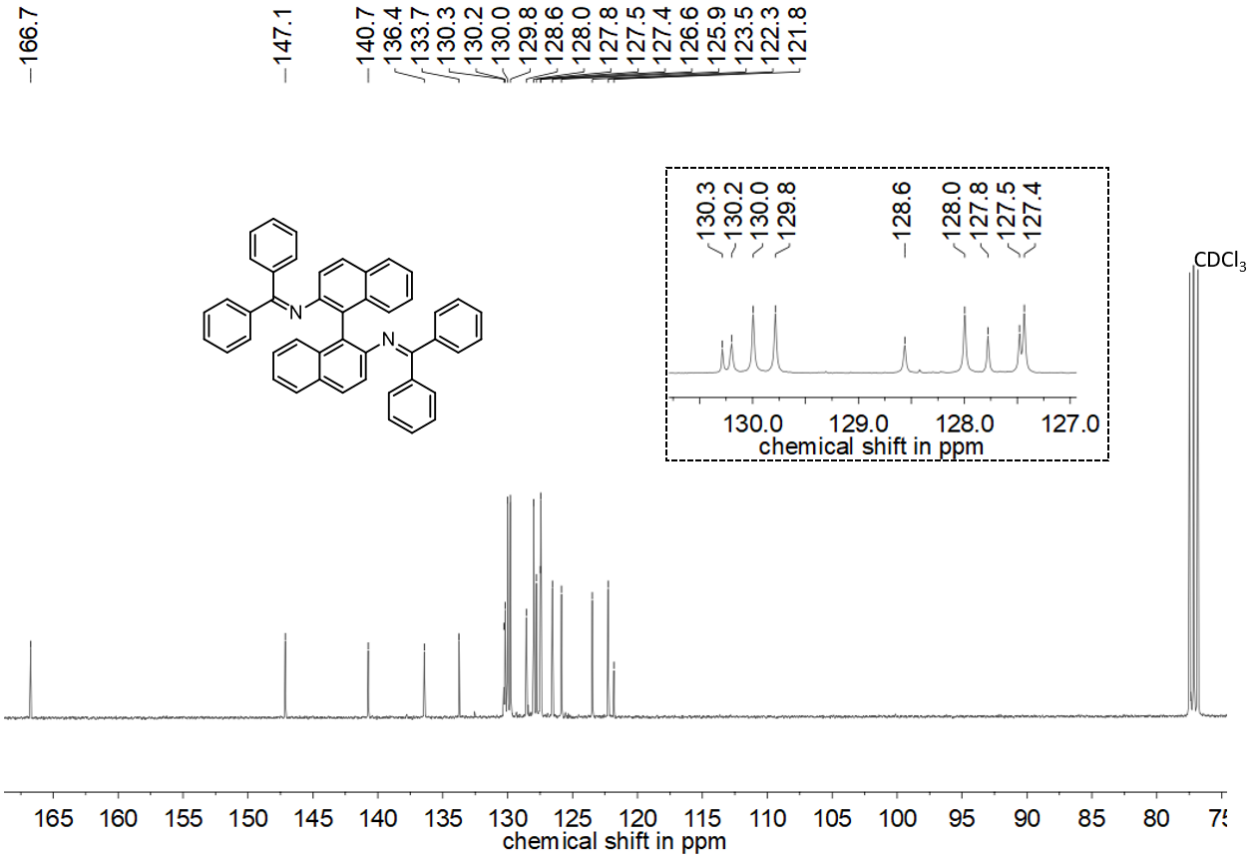


Figure S3: ^{13}C NMR (151 MHz, chloroform-d_1, 25°C) spectrum of $^{Imine}1$.

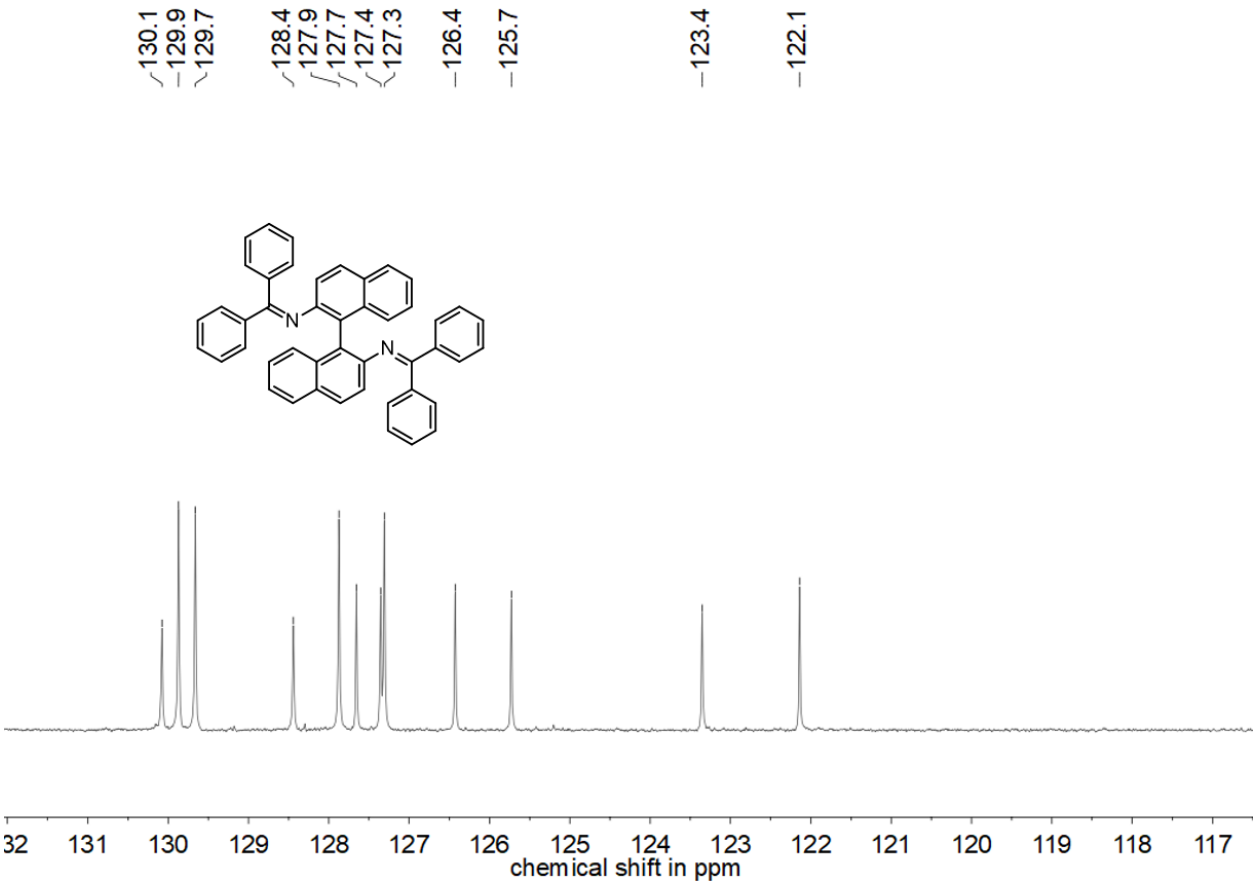


Figure S4: ^{13}C DEPT NMR (151 MHz, chloroform-d_1, 25°C) spectrum of ^{Imine}1.

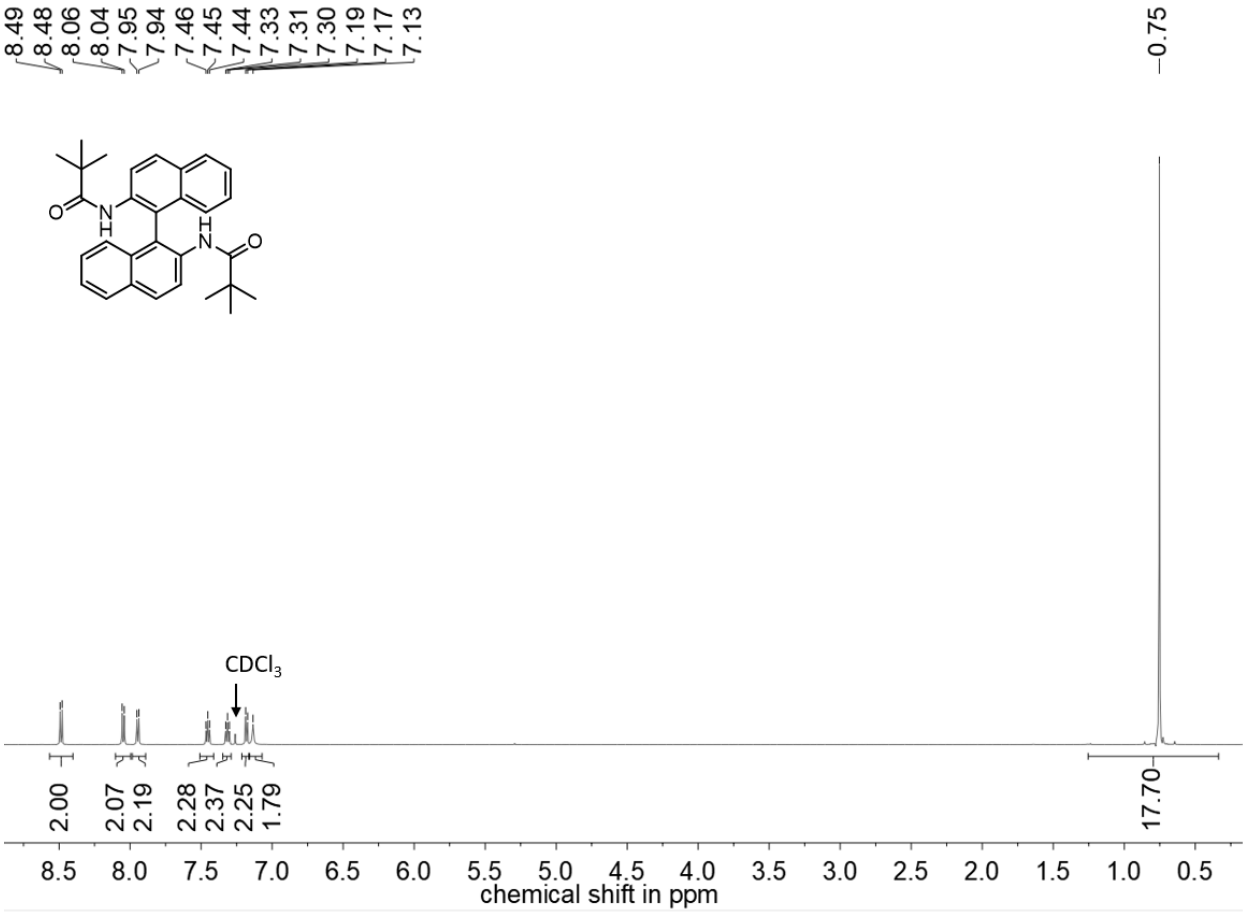


Figure S5: ^{1}H NMR (600 MHz, chloroform-d_1, 25°C) spectrum of ^{Amide}1-H_2.

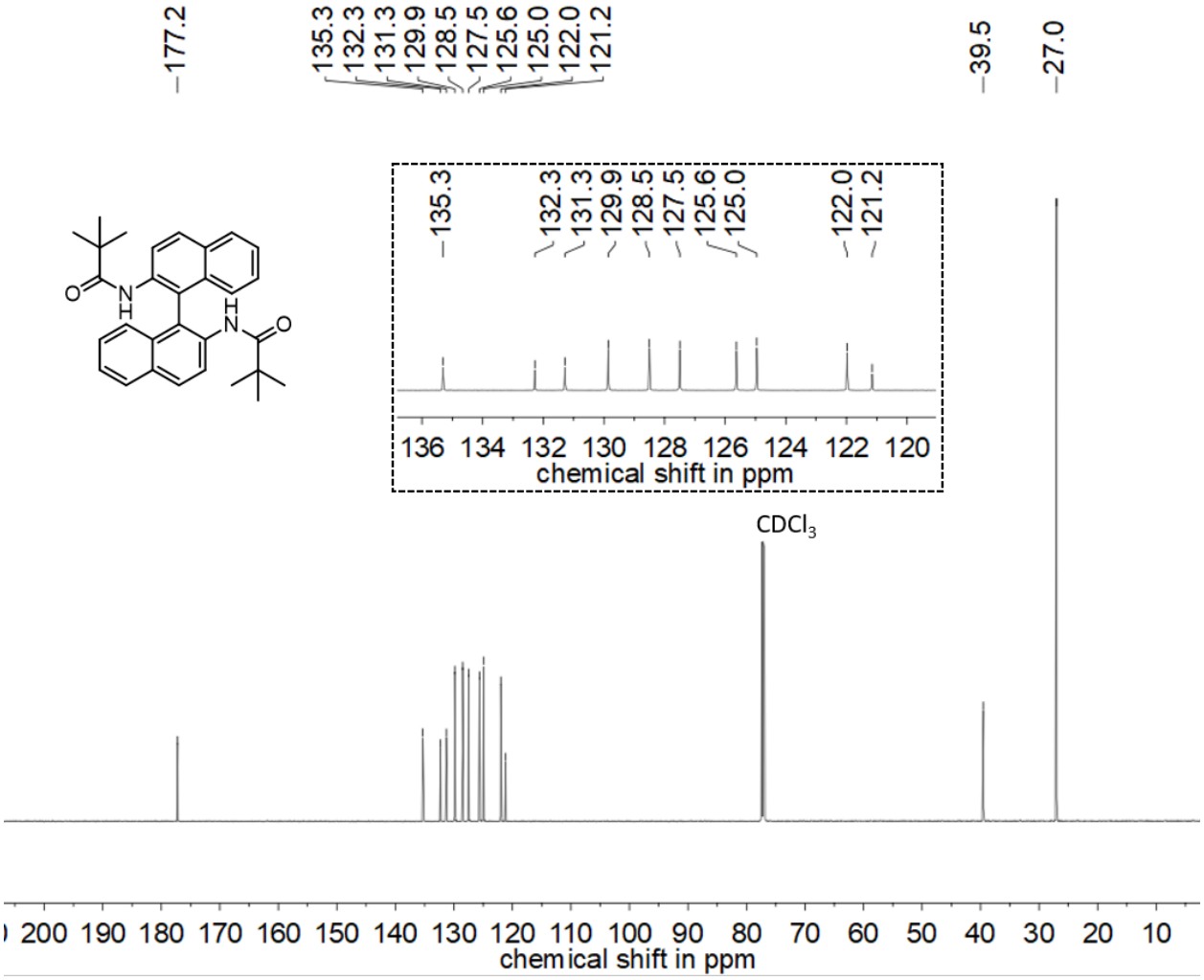


Figure S6: ^{13}C NMR (151 MHz, chloroform-d_1, 25°C) spectrum of ^{Amide}1-H_2.

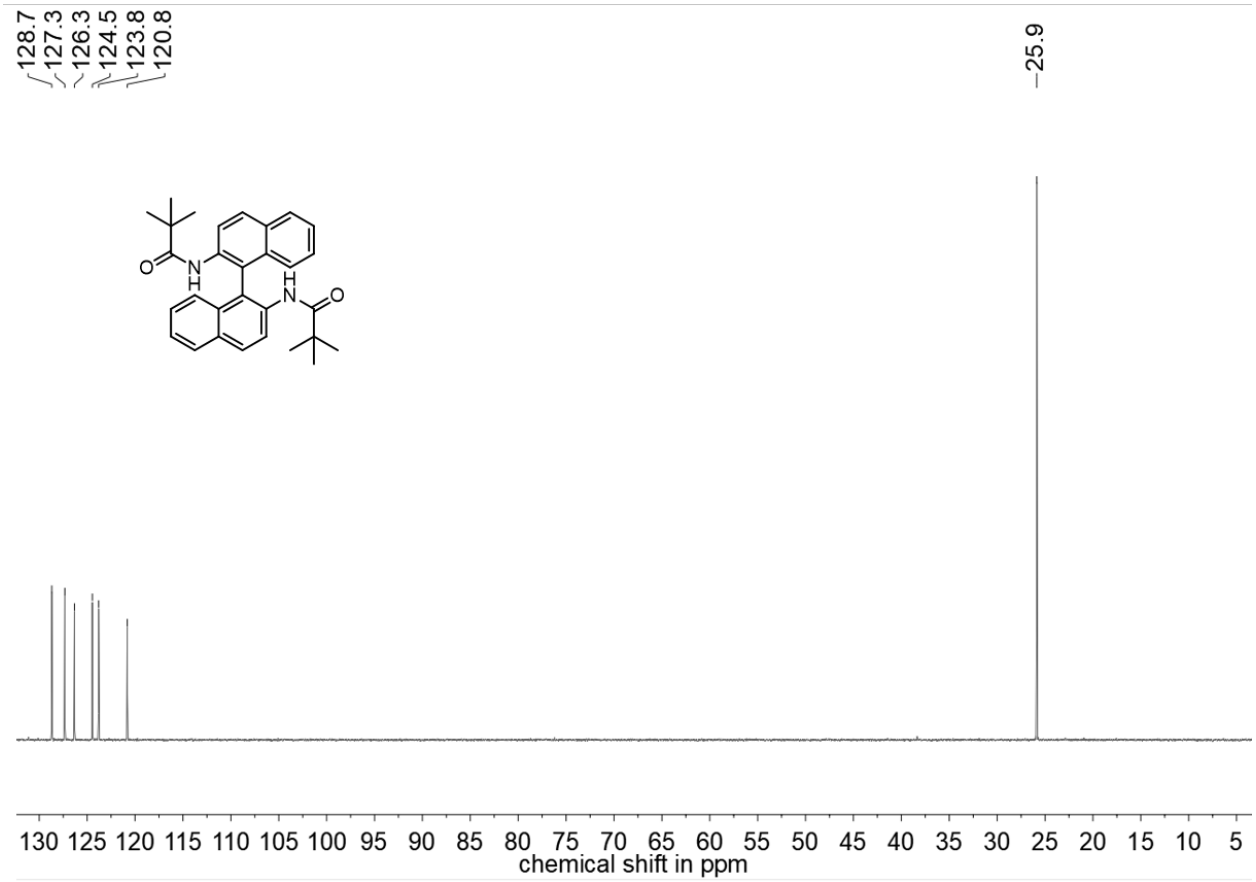


Figure S7: ^{13}C DEPT NMR (151 MHz, chloroform-d_1, 25°C) spectrum of ^{Amide}1-H_2.

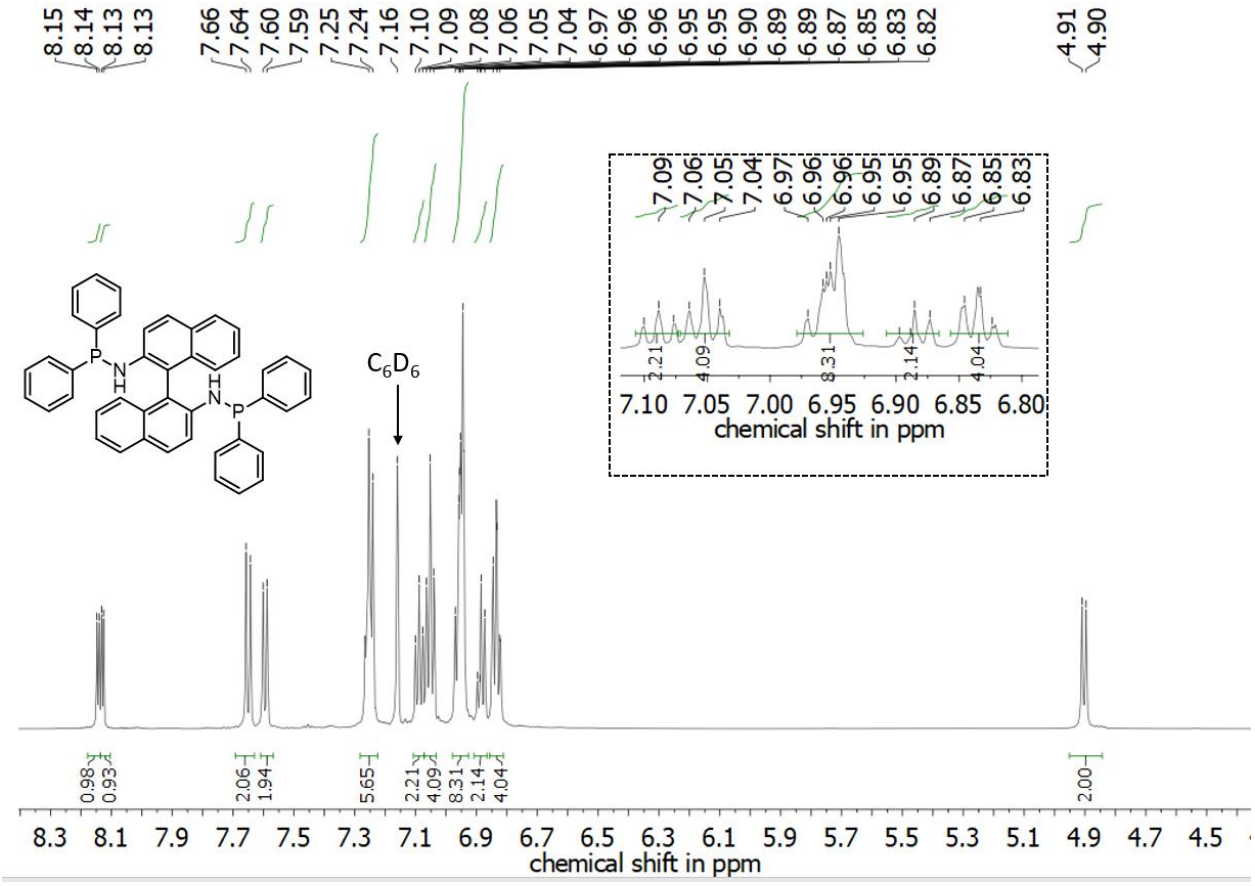


Figure S8: ^{1}H NMR (600 MHz, benzene-d_6, 25°C) spectrum of ^{DPP}1-H_2.

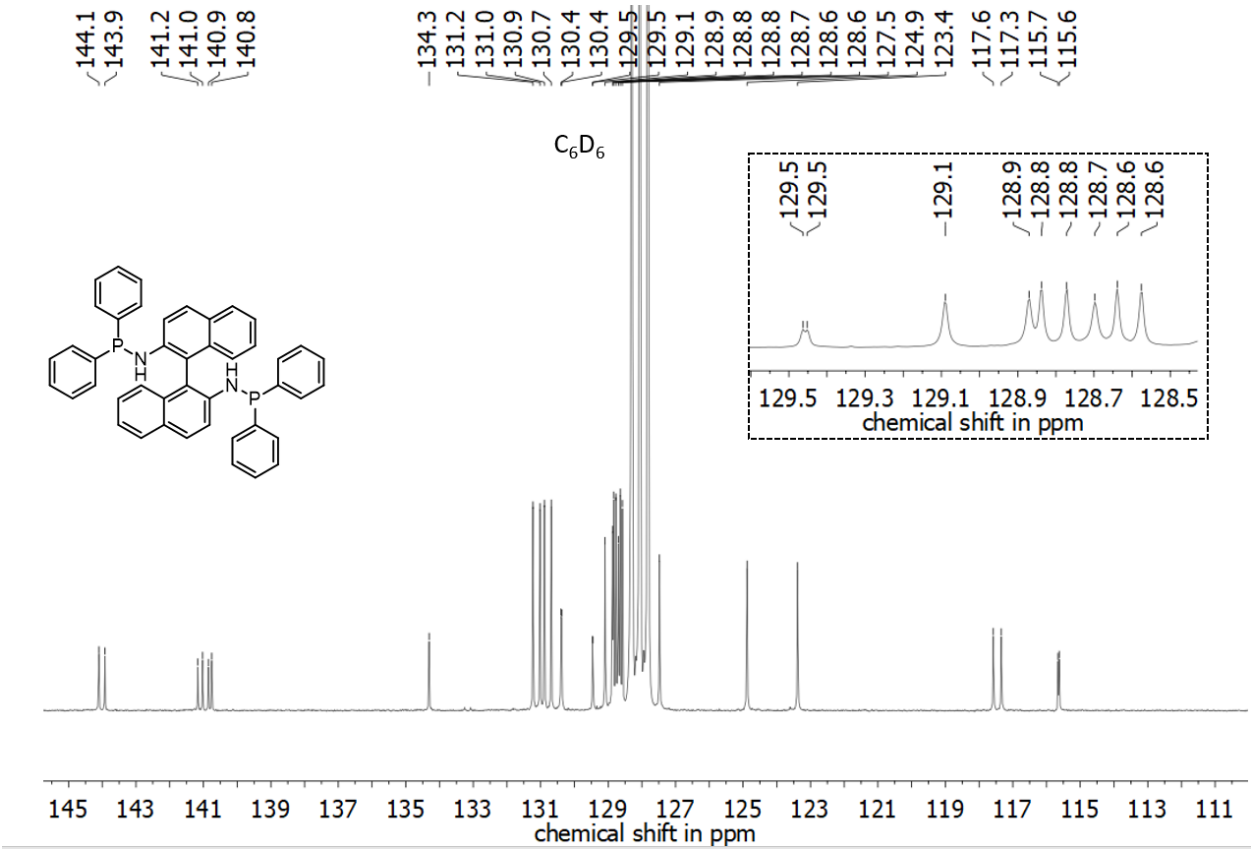


Figure S9: ^{13}C NMR (101 MHz, benzene-d_6, 25°C) spectrum of $^{DPP}1\text{-}H_2$.

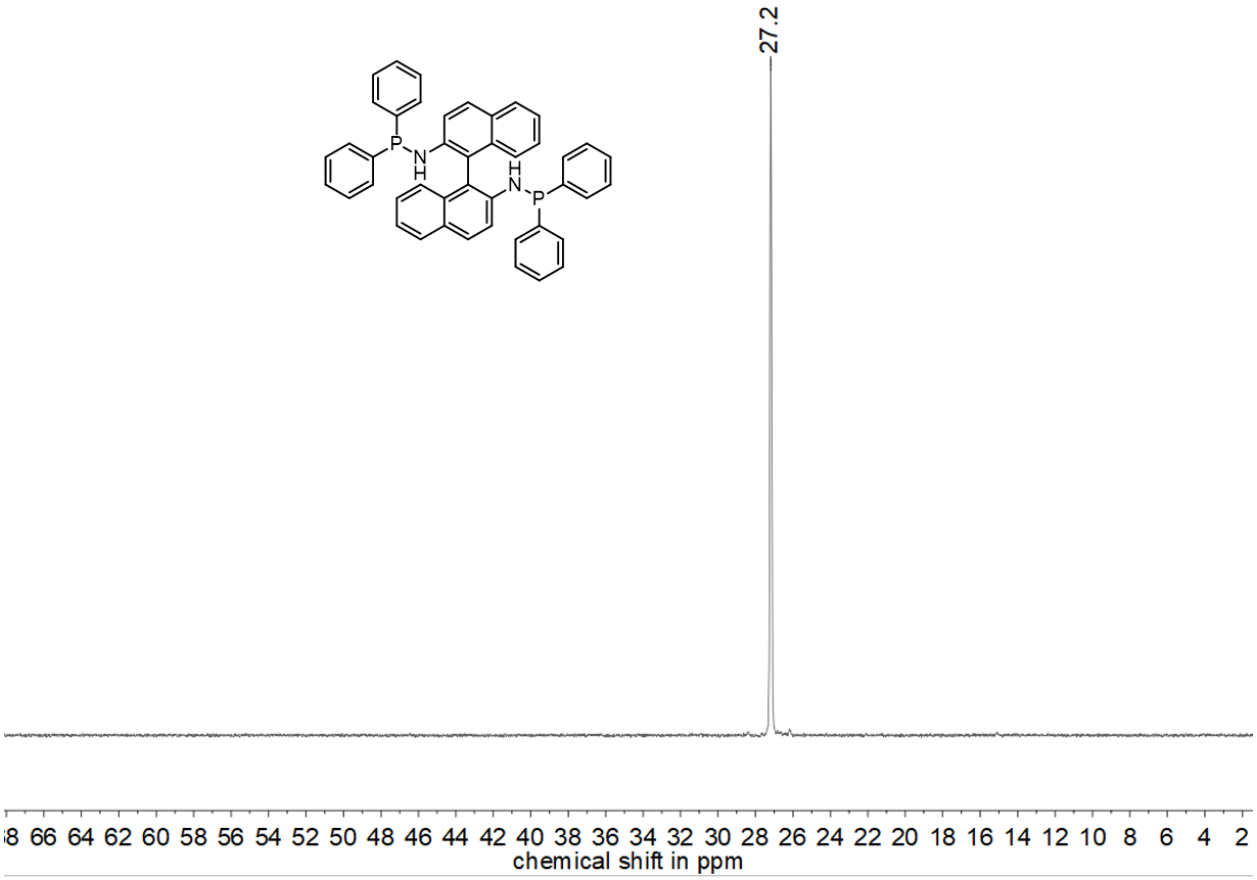


Figure S10: ^{31}P NMR (243 MHz, benzene-d_6, 25°C) spectrum of ^{DPP}1-H_2.

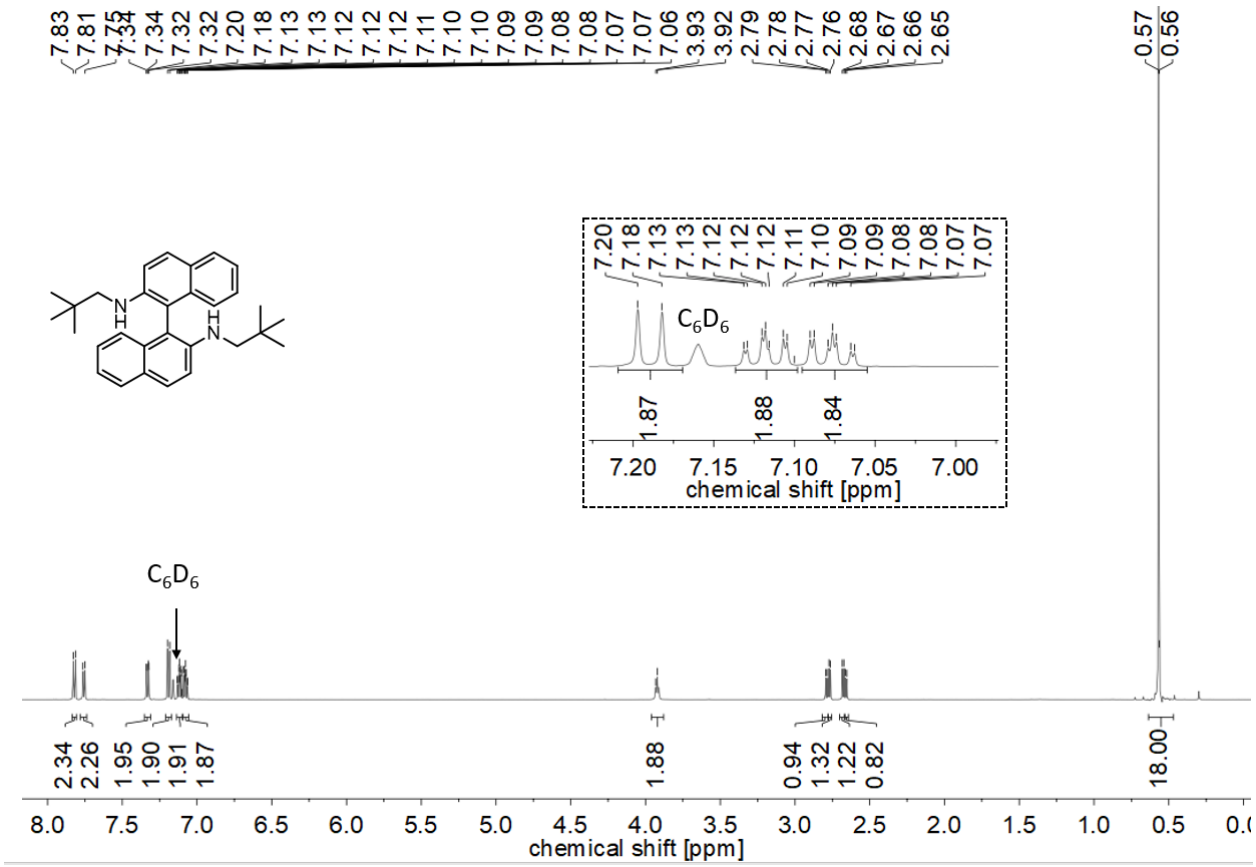


Figure S11: ^{1}H NMR (400 MHz, benzene-d_6, 25°C) spectrum of ^{NP}1-H$_2$.

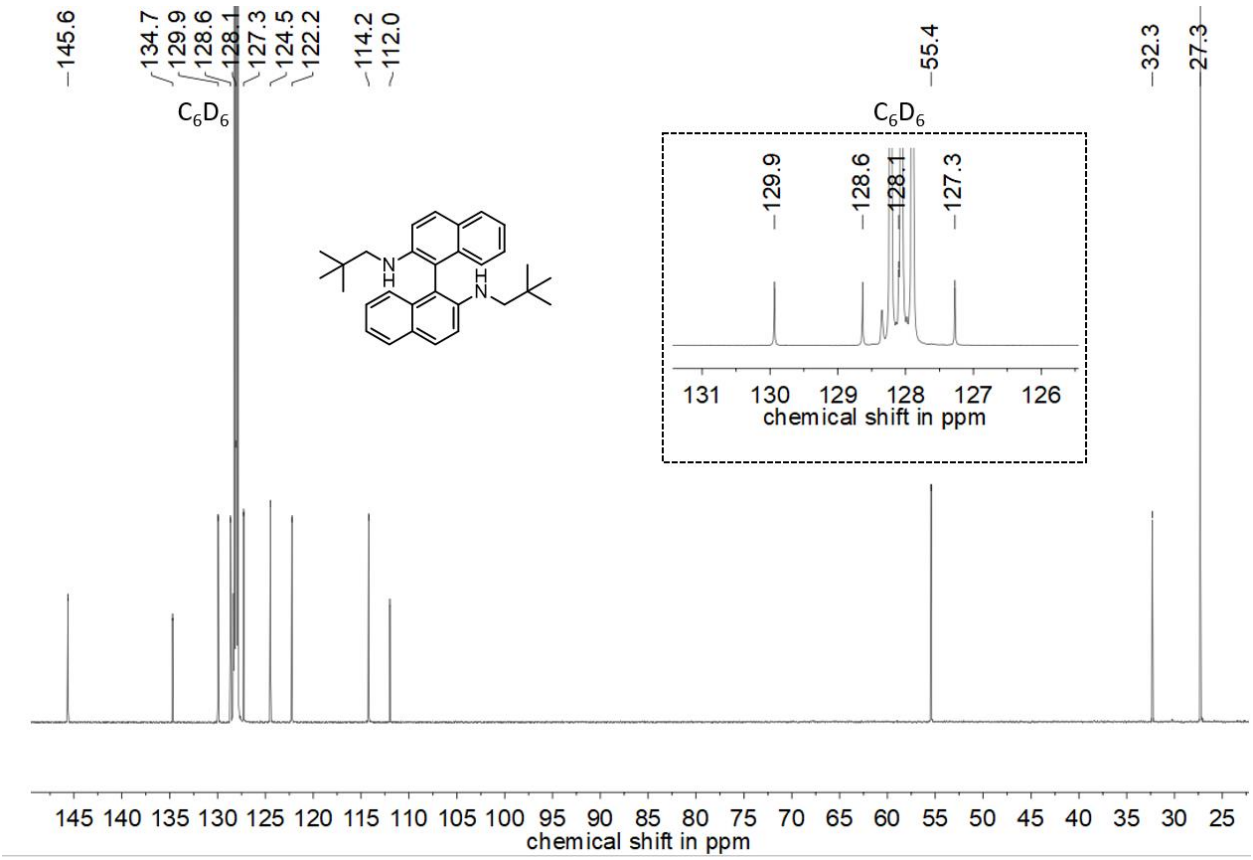


Figure S12: ^{13}C NMR (101 MHz, benzene-d_6, 25°C) spectrum of ^{NP}1-H_2.

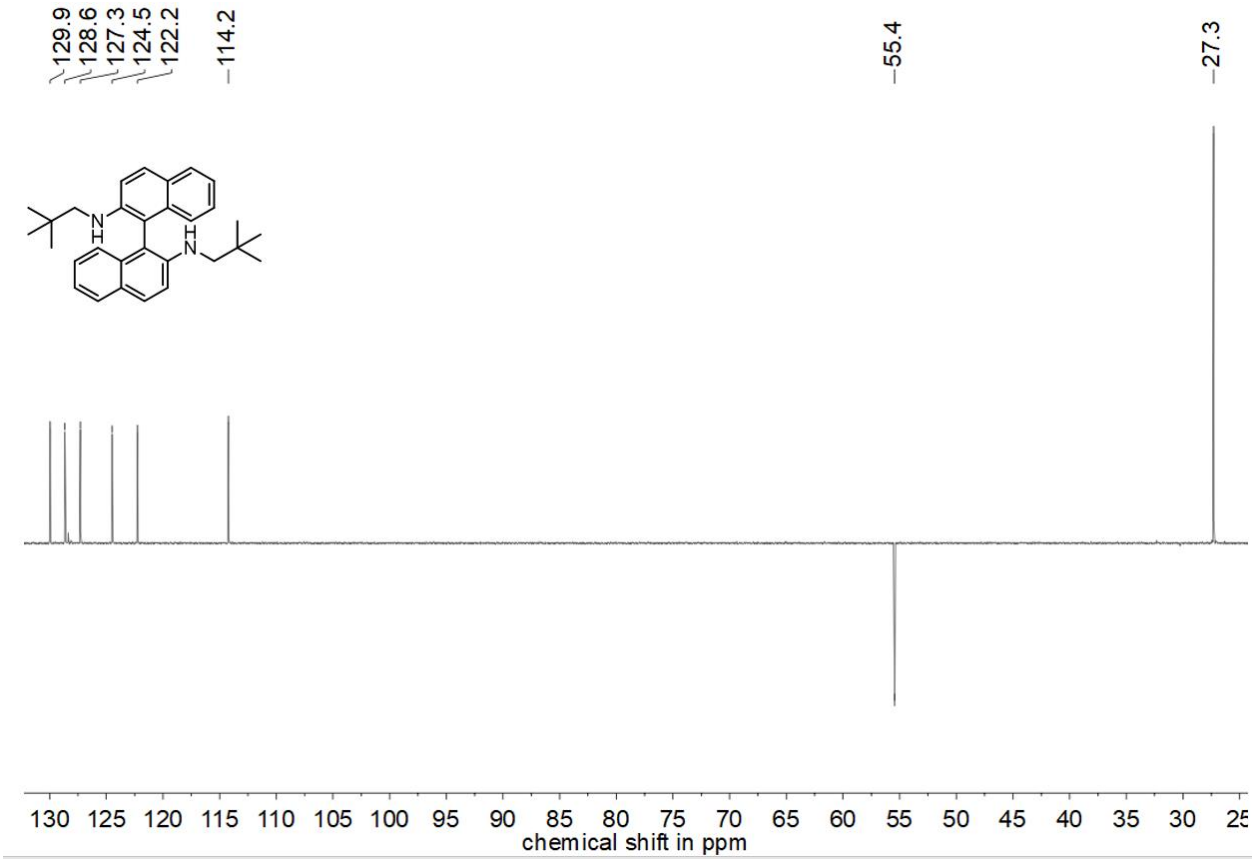


Figure S13: ^{13}C DEPT NMR (101 MHz, benzene-d_6, 25°C) spectrum of ^{NP}1-H_2.

.

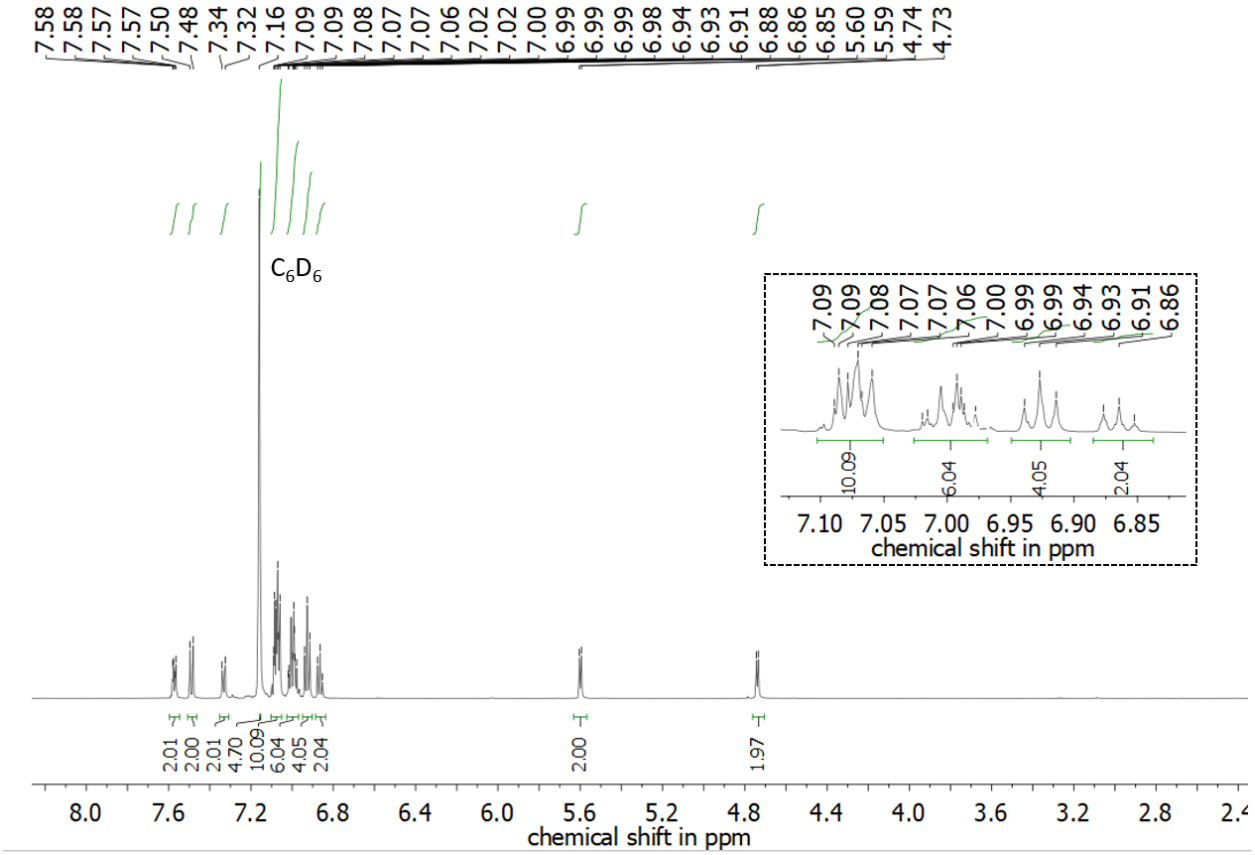


Figure S14: ^{1}H NMR (600 MHz, chloroform-d_1, 25°C) spectrum of ^{DPM}1-H_2.

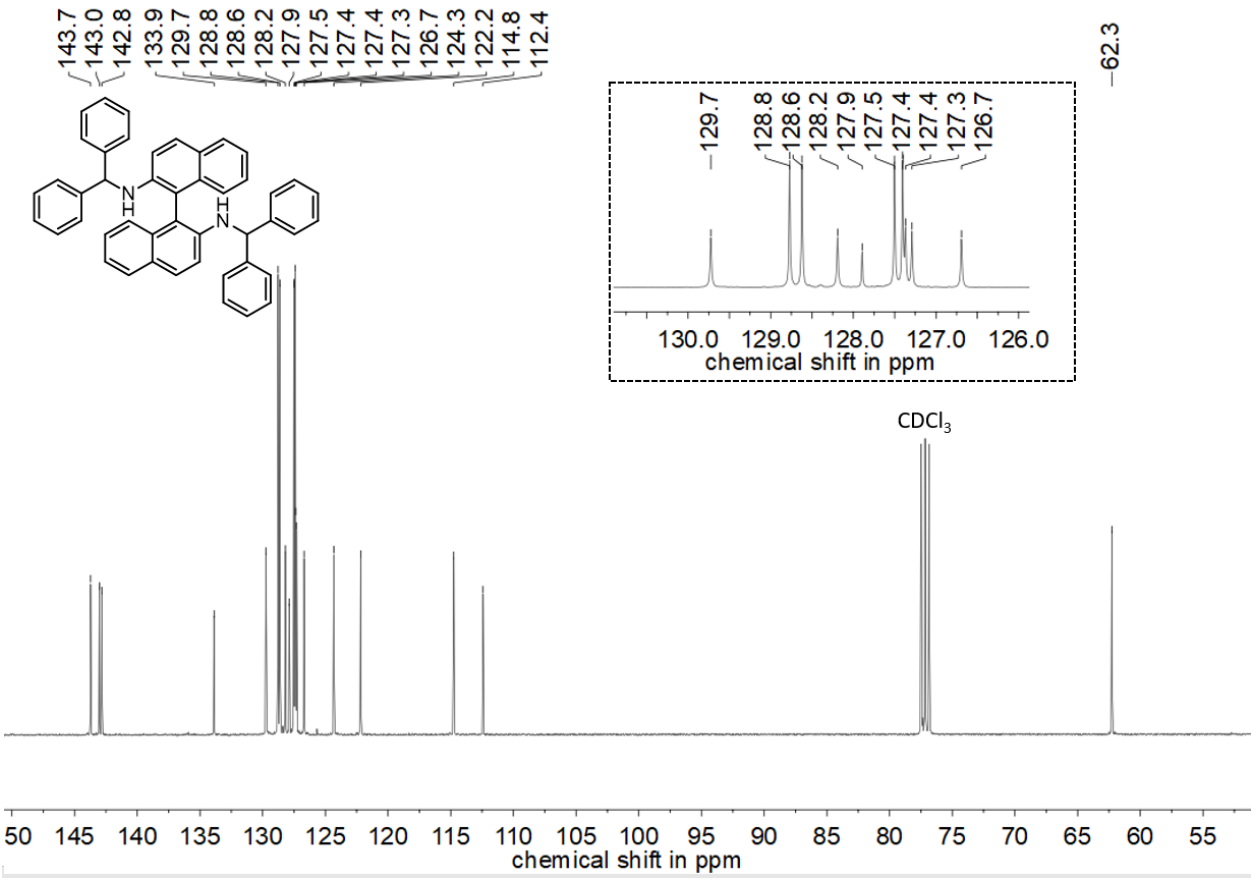


Figure S15: ^{13}C NMR (151 MHz, chloroform-d_1, 25°C) spectrum of ^{DPM}1-H$_2$.

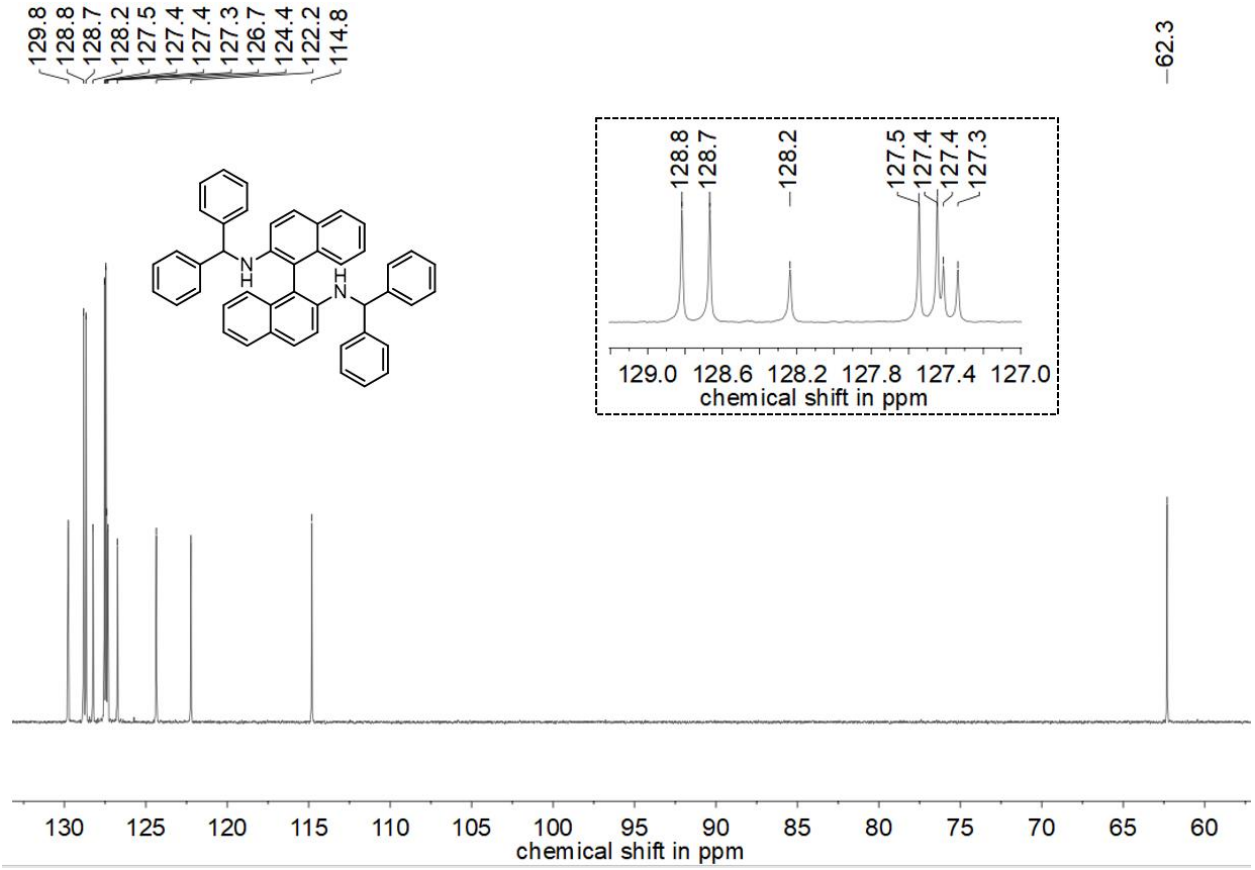


Figure S16: ^{13}C DEPT NMR (151 MHz, chloroform-d_1, 25°C) spectrum of ^{DPM}1-H_2.

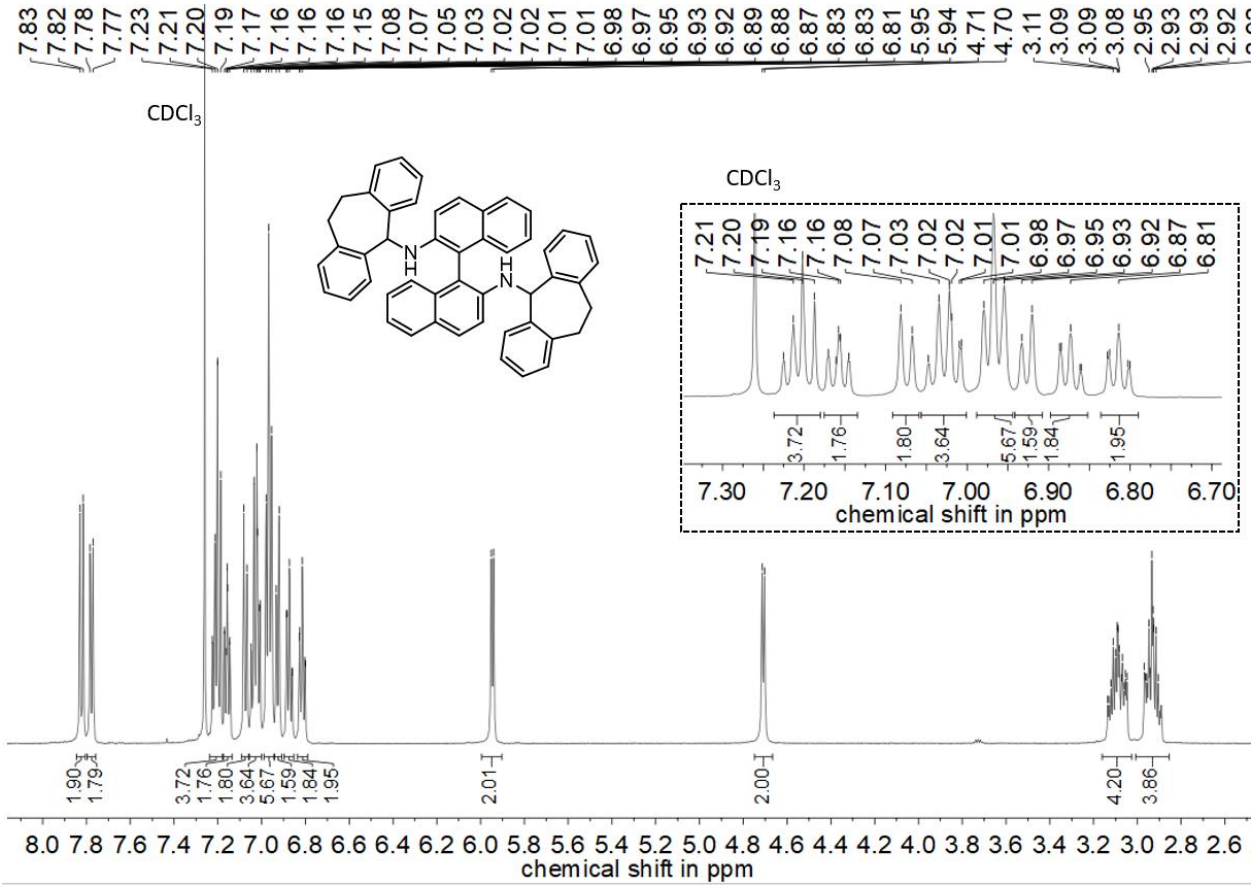


Figure S17: ^{1}H NMR (600 MHz, chloroform-d_1, 25°C) spectrum of ^{DBS}1-H_2.

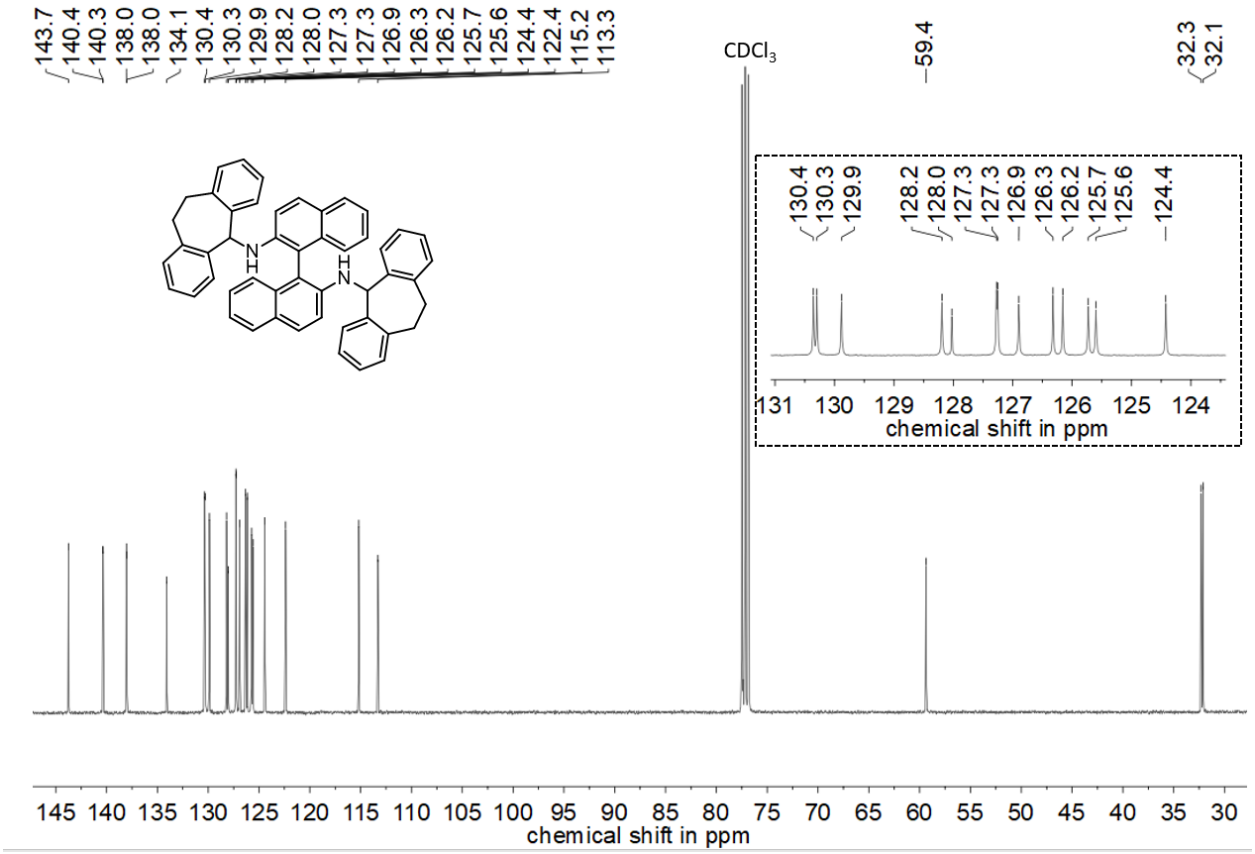


Figure S18: ^{13}C NMR (151 MHz, chloroform-d_1, 25°C) spectrum of ^{DBS}1-H$_2$.

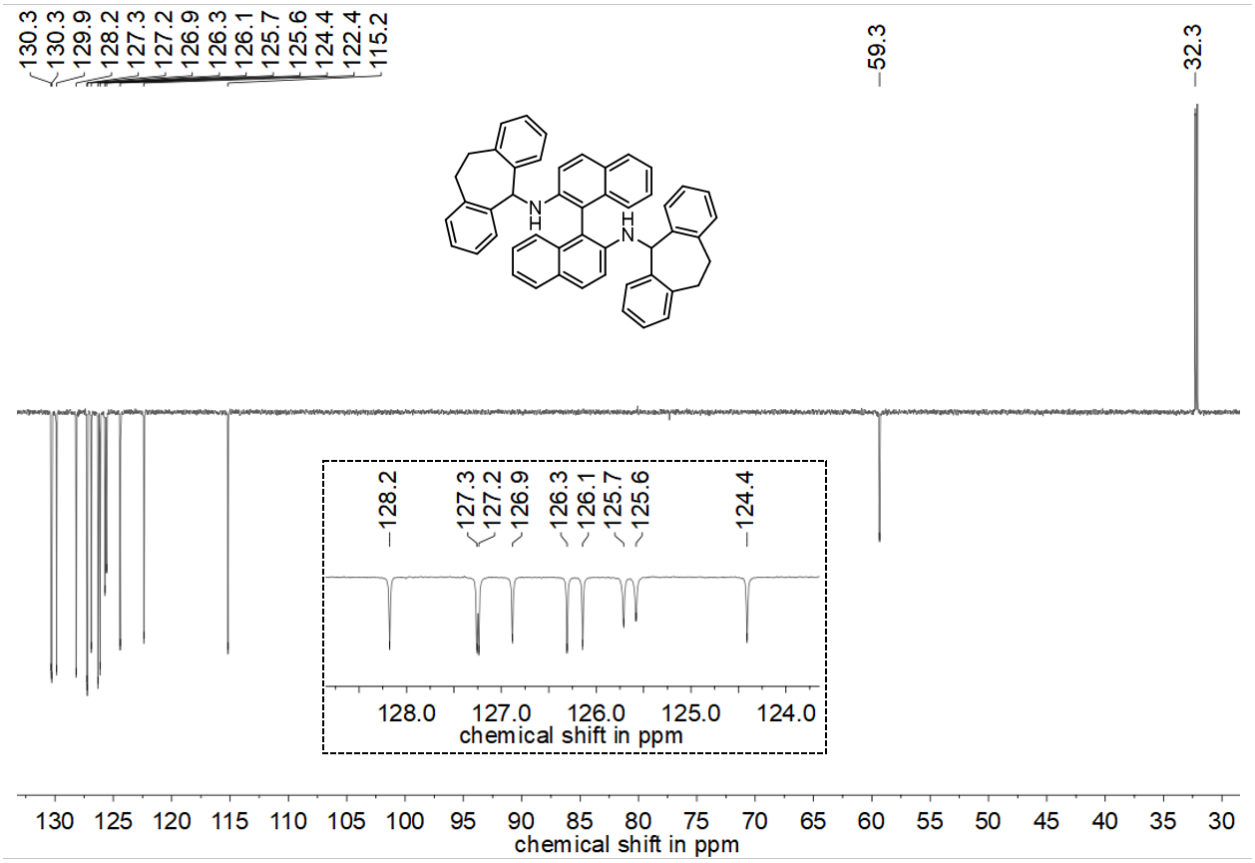


Figure S19: ^{13}C APT NMR (151 MHz, chloroform-d_1, 25°C) spectrum of ^{DBS}1-H_2.

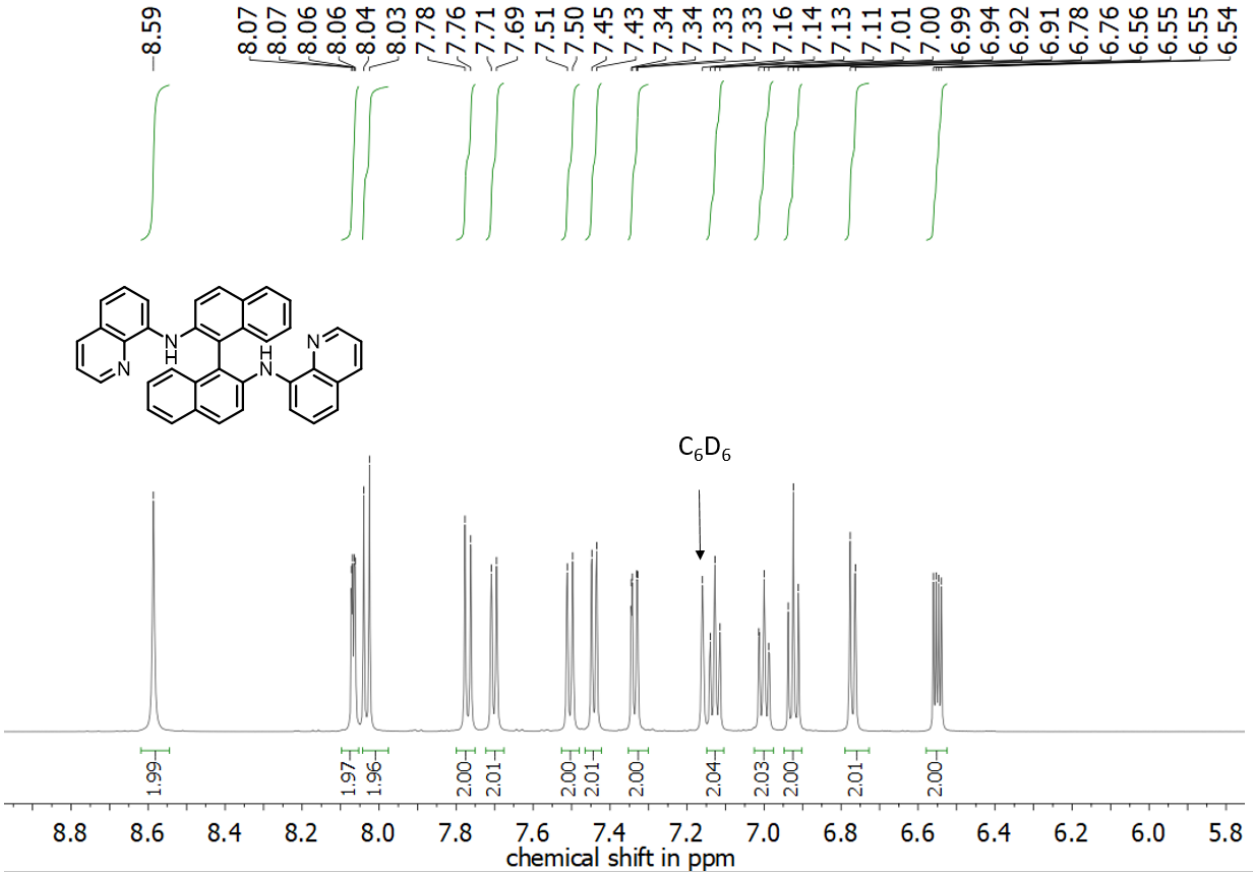


Figure S20: ^{1}H NMR (600 MHz, chloroform-d_1, 25°C) spectrum of ^{QUIN}1-H_2.

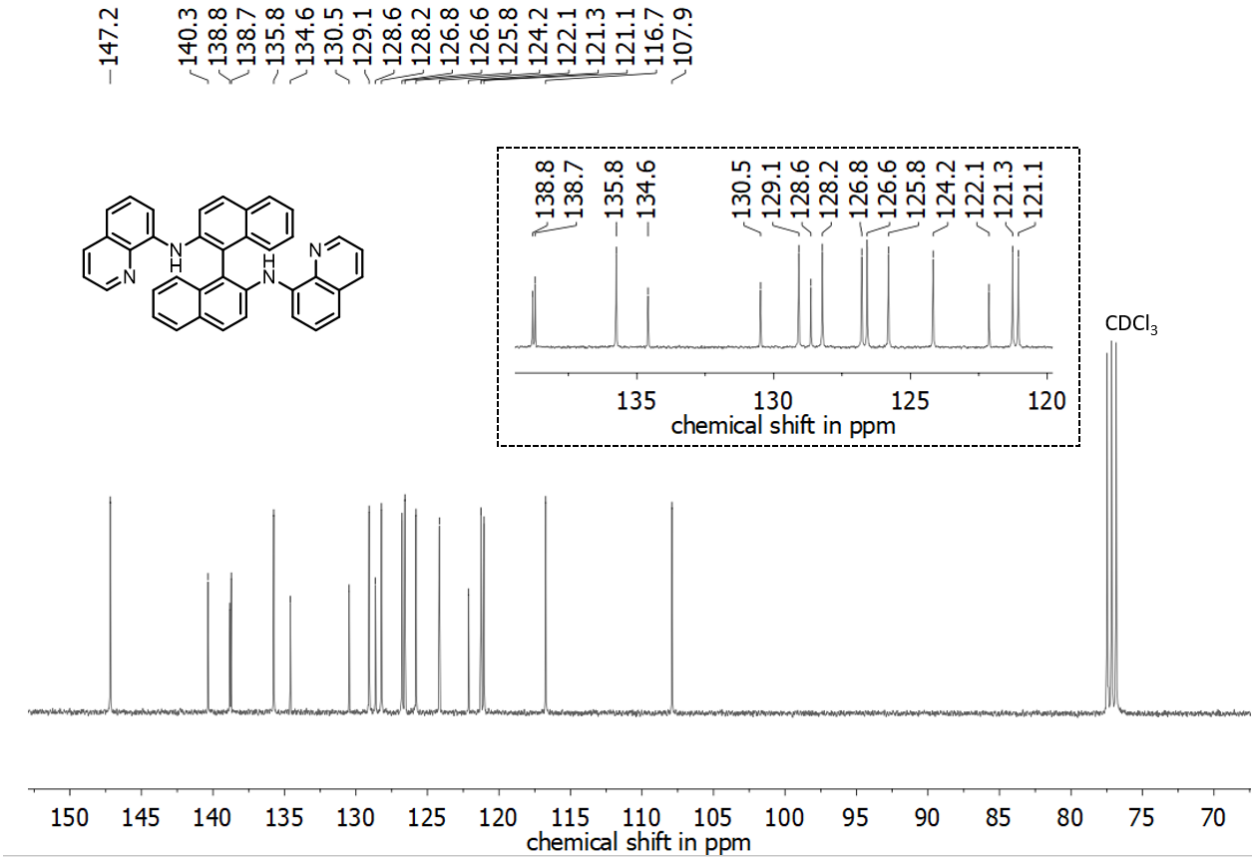


Figure S21: ^{13}C NMR (151 MHz, chloroform-d_1, 25°C) spectrum of ^{QUIN}1-H_2.

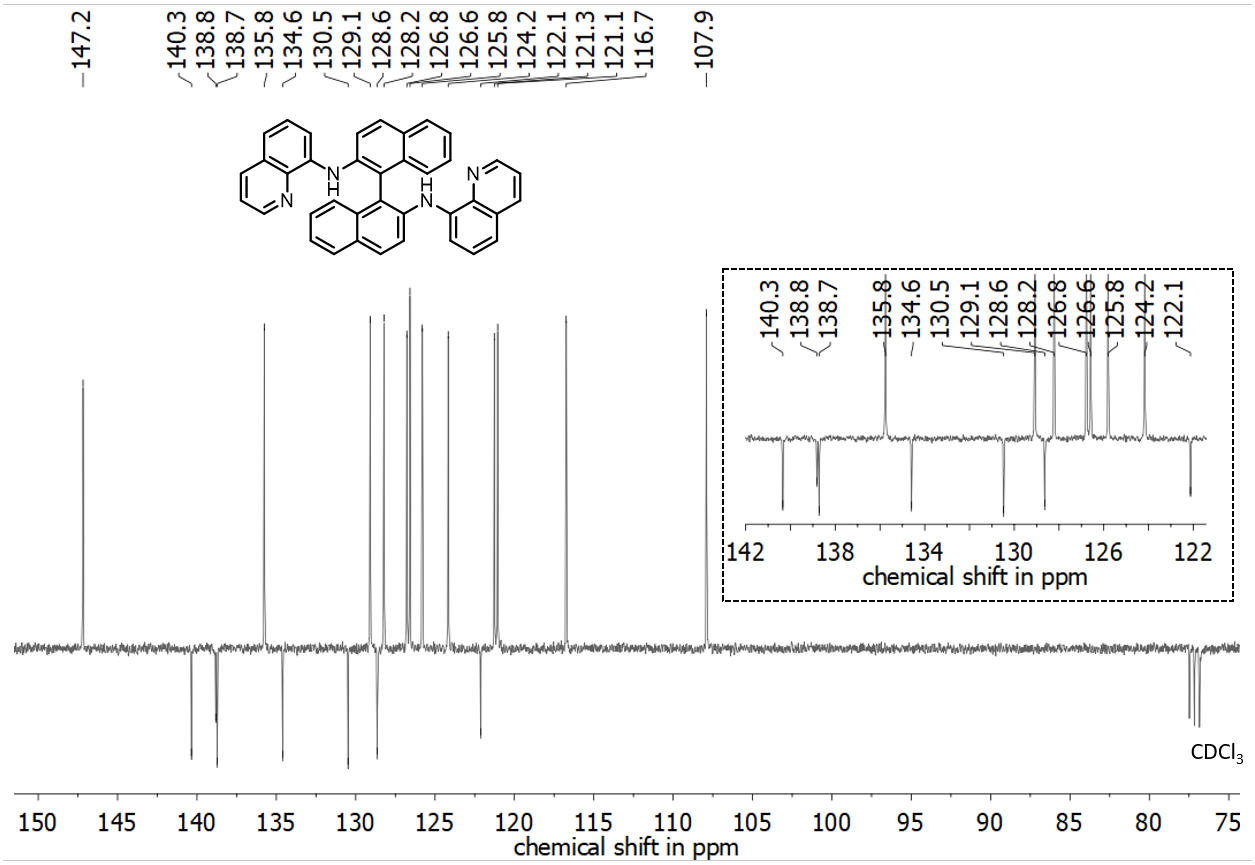
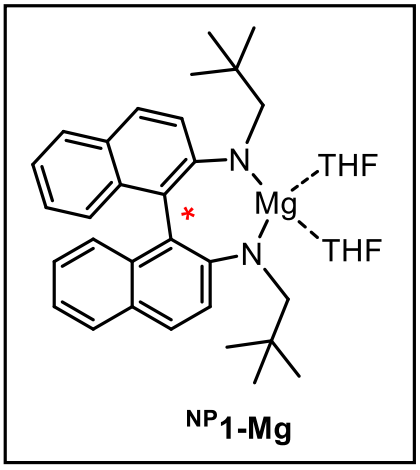


Figure S22: ^{13}C APT NMR (151 MHz, chloroform-d_1, 25°C) spectrum of ^{QUIN}1-H_2.

1.4. Synthesis of chiral Mg and Ca compounds

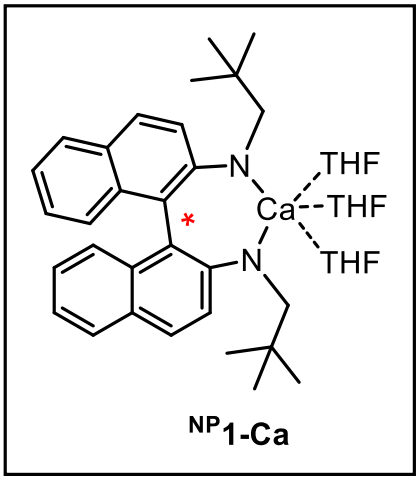
Synthesis of ^{NP}1-Mg



^{NP}1-Mg

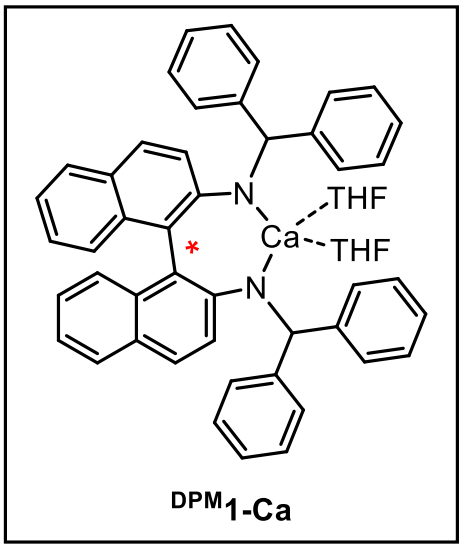
Solid di-*n*-butyl magnesium (65.0 mg, 0.47 mmol) and ^{NP}1-H_2 (200 mg, 0.47 mmol) were dissolved in a mixture of THF (2 mL) and benzene (2 mL). The yellow solution was stirred for 3 days. The solvent was evaporated and the resulting yellow powder was recrystallized from hot benzene. The crystals were washed with cold *n*-hexane (2x 1mL) and dried under vacuum. The product was obtained as dark yellow crystals. Crystals suitable for X-ray diffraction were obtained by slowly cooling of a saturated solution in THF and benzene (1:5). Yield: 187 mg, 0.36 mmol, 77 %. ^{1}H NMR (600 MHz, benzene-d_6, 25 °C): δ = 7.77 (d, *J* = 9.1 Hz, 2H, CH_{Ar}), 7.68 (d, *J* = 8.9 Hz, 2H, CH_{Ar}), 7.65 (d, *J* = 9.1 Hz, 2H, CH_{Ar}), 7.06 (d, *J* = 9.1 Hz, 2H, CH_{Ar}), 6.94 - 6.89 (m, 4H, CH_{Ar}), 3.86 (d, *J* = 12.7 Hz, 2H, CH_2), 3.55 (m, 8H, THF), 2.47 (d, *J* = 12.8 Hz, 2H, CH_2), 1.44 (m, 8H, THF), 0.89 (s, 18H, CH_3) ppm. ^{13}C APT NMR (151 MHz, benzene-d_6 + THF-d_8, 25 °C): δ = 159.0 (s, C_{Ar}), 137.5 (s, C_{Ar}), 127.8 (s, CH_{Ar}), 127.6 (s, CH_{Ar}), 126.9 (s, C_{Ar}), 126.1 (s, CH_{Ar}), 125.3 (s, CH_{Ar}), 119.2 (s, CH_{Ar}), 118.6 (s, C_{Ar}), 116.5 (s, CH_{Ar}), 67.9 (s, THF), 60.5 (s, CH_2), 35.9 (s, C), 28.8 (s, CH_3), 25.8 (s, THF) ppm. Elemental Analysis: $C_{38}H_{50}MgN_2O_2$ (591.14): calc. C 77.21, H 8.53, N 4.74; found: C 77.01, 8.43 H, 4.57 N.

Synthesis of ^{NP}1-Ca



$Ca(DMAT)_2{\cdot}(THF)_2$ (420 mg, 0.71 mmol) and ^{NP}1-H_2 (300 mg, 0.71 mmol) were dissolved in THF (4 mL). The solution turned orange-red while being heated to 60°C for 2 days. The solvent was removed, the residue was washed twice with a mixture of cold pentane (3 mL) and THF (0.1 mL) and subsequently dried under vacuum. The resulting fine orange powder was recrystallized from hot toluene yielding large orange crystals. After washing with *n*-hexane (2 mL) and drying in vacuum for 1 day at 60°C the product was obtained as an orange powder. Crystals suitable for X-ray diffraction were obtained by slowly cooling of a saturated solution in benzene. Yield: 450 mg, 0.66 mmol, 94 %. ^{1}H NMR (400 MHz, benzene-d_6 + THF-d_8, 25°C): δ = 7.58 (d, *J* = 9.2 Hz, 2H, CH_{Ar}), 7.54 (d, *J* = 7.8 Hz, 2H, CH_{Ar}), 7.34 (d, *J* = 9.2 Hz, 2H, CH_{Ar}), 7.23 (d, *J* = 8.5 Hz, 2H, CH_{Ar}), 6.98 (d, *J* = 7.1 Hz, 2H, CH_{Ar}), 3.53 (m, 12H, THF), 3.45 (d, *J* = 12.1 Hz, 2H, CH_2), 2.88 (d, *J* = 12.1 Hz, 2H, CH_2), 1.46 (m, 12H, THF), 0.99 (s, 18H, CH_3) ppm. ^{13}C APT NMR (151 MHz, THF-d_8, 25 °C): δ = 157.6 (s, C_{Ar}), 137.0 (s, C_{Ar}), 129.2 (s, CH_{Ar}), 127.1 (s, CH_{Ar}), 125.9 (s, CH_{Ar}), 125.8 (s, C_{Ar}), 125.3 (s, CH_{Ar}), 117.7 (s, CH_{Ar}), 116.3 (s, CH_{Ar}), 112.4 (s, C_{Ar}), 67.9 (s, THF), 62.6 (s, CH_2), 34.9 (s, C), 29.2 (s, CH_3), 25.8 (s, THF) ppm. Elemental Analysis: $C_{42}H_{58}CaN_2O_3$ (679.02): calc. C 74.29, H 8.61, N 4.13; found: C 73.83, H 8.60, 4.00 N.

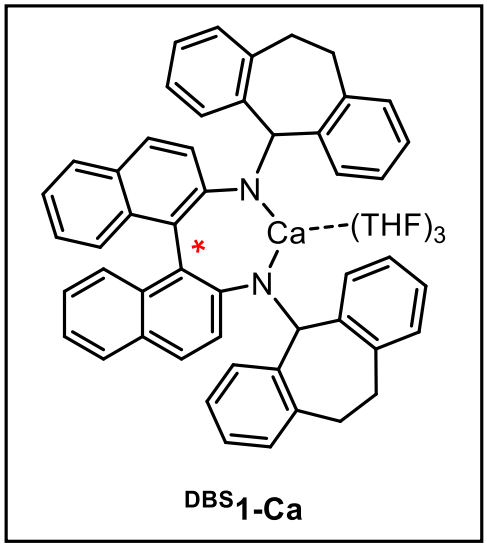
Synthesis of ^{DPM}1-Ca



^{DPM}1-Ca

$Ca(DMAT)_2{\cdot}(THF)_2$ (328 mg, 0.65 mmol) and ^{DPM}1-H_2 (400 mg, 0.65 mmol) were dissolved in THF (7 mL). The yellow suspension heated to 120°C for 4 h in a microwave, resulting in a clear orange solution and a black precipitate. The black precipitate was filtered over Celite and the black residue was washed with a mixture of toluene (1 mL) and hexane (2 mL). All volatiles were removed under reduced pressure, the orange crude product was trituated with pentane (3x 3 mL) and dried under reduced pressure. The resulting residue was crystallized from a hot, saturated mixture of toluene and THF (10:1) yielding yellow orange crystals. Washing with pentane (2x 1 mL) and drying under reduced pressure at 80°C for 1 day furnishes the product as yellow microcrystalline powder. Crystals suitable for X-ray diffraction were obtained by slowly cooling of a saturated solution in THF and toluene (1:10). Yield: 364 mg, 0.46 mmol, 70 %. ^{1}H NMR (600 MHz, benzene-d_6, 25°C) δ = 7.86 (d, J = 6.0 Hz, 4H, CH_{Ar}), 7.64 (d, J = 7.5 Hz, 2H, CH_{Ar}), 7.54 (dd, J = 9.1, 2.7 Hz, 2H, CH_{Ar}), 7.37 (d, J = 5.9 Hz, 3H, CH_{Ar}), 7.33 (dd, J = 9.1, 2.8 Hz, 2H, CH_{Ar}),7.24 – 7.19 (m, 6H, CH_{Ar}), 7.09 – 7.01 (m, 7H, CH_{Ar}), 6.82 – 6.78 (d, J = 26.7 Hz, 6H, CH_{Ar}), 5.75 (s, 2H, CH), 3.52 (s, 8H, THF), 1.44 (s, 8H, THF) ppm. ^{13}C APT NMR (151 MHz, benzene-d_6 + THF-d_8, 25 °C): δ = 156.9 (s, C_{Ar}), 150.6 (s, C_{Ar}), 150.3 (s, C_{Ar}), 137.6 (s, C_{Ar}), 129.5 (s, CH_{Ar}), 128.9 (s, CH_{Ar}), 128.4 (s, CH_{Ar}), 128.4 (s, CH_{Ar}), 128.3 (s, CH_{Ar}), 127.4 (s, CH_{Ar}), 126.8 (s, CH_{Ar}), 126.5 (s, C_{Ar}), 126.2 (s, CH_{Ar}), 126.0 (s, CH_{Ar}), 125.5 (s, CH_{Ar}), 119.1 (s, CH_{Ar}), 118.1 (s, CH_{Ar}), 115.1 (s, C_{Ar}), 69.1 (s, CH), 67.4 (s, THF), 25.4 (s, THF) ppm. Elemental Analysis: $C_{54}H_{50}CaN_2O_2$ (M = 798.35): calc. C 81.17, H 6.31, N 3.51; found: C 80.61, H 6.00, N 3.40.

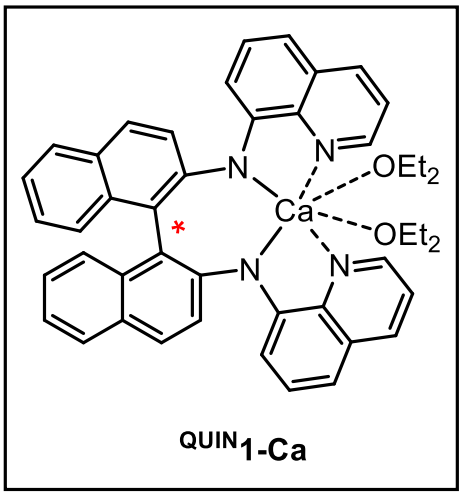
Synthesis of ^{DBS}1-Ca



^{DBS}1-Ca

$Ca[N(SiMe_3)_2]_2{\cdot}(THF)_2$ (567 mg, 1.13 mmol) and ^{DPM}1-H_2 (500 mg, 0.75 mmol) were dissolved in THF (5 mL) and microwaved at 160°C for 10 h. The resulting orange-black suspension was filtered through celite and the black residue was washed with THF (3 mL). All volatiles were removed under reduced pressure. The orange-yellow crude product was washed with a mixture of pentane (5 mL) and benzene (1 mL) and subsequently dried under reduced pressure. The resulting yellowish powder was recrystallized from a hot, saturated THF solution. The yellow crystals were washed with *n*-hexane (2 mL) and dried under reduced pressure. Drying under reduced pressure at 80°C for 1 day to furnish the product as a yellow microcystalline powder. Crystals suitable for X-ray diffraction were obtained by slowly cooling of a saturated solution THF solution to -30°C for prolonged time. Yield: 526 mg, 0.57 mmol, 76 %. ^{1}H NMR (600 MHz, benzene-d_6, 25°C) δ = 7.76 (d, *J* = 9.2 Hz, 2H, CH_{Ar}), 7.74 (d, *J* = 7.8 Hz, 2H, CH_{Ar}), 7.67 (t, *J* = 9.4 Hz, 4H, CH_{Ar}), 7.22-7.17 (m, 4H, CH_{Ar}), 7.11 (d, *J* = 8.4 Hz, 2H, CH_{Ar}), 7.03-7.00 (m, 2H, CH_{Ar}), 6.91 (d, *J* = 7.3 Hz, 2H, CH_{Ar}), 6.82-6.80 (m, 4H, CH_{Ar}), 6.70 (d, *J* = 7.6 Hz, 2H, CH_{Ar}), 6.61-6.58 (d, *J* = 20.2 Hz, 4H, CH_{Ar}), 5.74 (s, 2H, CH), 3.98 (t, *J* = 11.4 Hz, 2H, CH_2), 3.04 (q, *J* = 6.9 Hz, 7H, THF), 2.95 (q, *J* = 6.9 Hz, 7H, THF), 2.80 (t, *J* = 4.8 Hz, 1H, CH_2), 2.77 (t, *J* = 4.9 Hz, 1H, CH_2),2.68 (t, *J* = 12.7 Hz, 2H, CH_2), 2.10 (d, *J* = 11.4 Hz, 2H, CH_2), 1.19 (m, 2H, 14H, THF) ppm. ^{13}C APT NMR (151 MHz, benzene-d_6, 25°C) δ = 153.7 (s, C_{Ar}), 145.9 (s, C_{Ar}), 144.7 (s, C_{Ar}), 142.5 (s, C_{Ar}), 140.8 (s, C_{Ar}), 137.6 (s, C_{Ar}), 131.8 (s, CH_{Ar}), 130.3 (s, CH_{Ar}), 129.9 (s, CH_{Ar}), 129.6 (s, CH_{Ar}), 129.4 (s, CH_{Ar}), 128.5 (s, CH_{Ar}), 128.4 (s, CH_{Ar}), 127.5 (s, CH_{Ar}), 126.8 (s, CH_{Ar}), 126.2 (s, C_{Ar}), 126.2 (s, CH_{Ar}), 126.0 (s, CH_{Ar}), 125.2 (s, CH_{Ar}), 119.1 (s, CH_{Ar}), 116.1 (s, CH_{Ar}), 114.2 (s, C_{Ar}), 69.4 (s, CH), 68.1 (s, THF), 34.4 (s, CH_2), 31.8 (s, CH_2), 25.4 (s, THF) ppm. Elemental Analysis: $C_{62}H_{62}CaN_2O_3$ (M = 923.27): calc. C 80.66, H 6.77, N 3.03; found: C 80.10, H 6.43, 3.00 N.

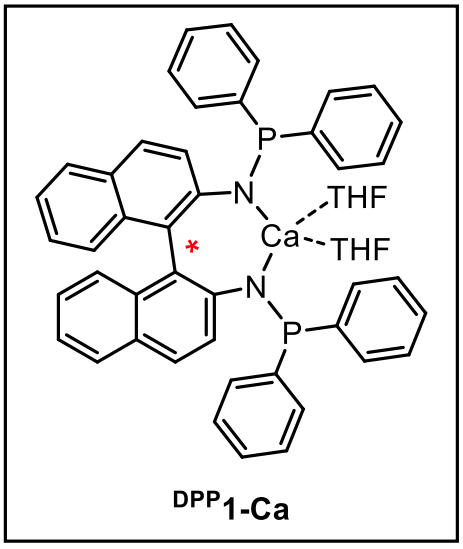
Synthesis of ^{QUIN}1-Ca



^{QUIN}1-Ca

^{QUIN}1-H_2 (360 mg, 0.69 mmol) and $Ca[N(SiMe_3)_2]_2$ (241 mg, 0.69 mmol) were suspended in a mixture of toluene (3 mL) and Et_2O (1 mL). After stirring at room temperature for 24 h, all volatiles were removed under reduced pressure. The deep purple residue was washed with pentane (3 x 2 mL) and dried under reduced pressure. Subsequently the crude product was recrystallized from hot benzene yielding purple crystals. After washing with *n*-hexane (2 mL) and removal of all volatiles under reduced pressure the product was obtained as microcrystalline purple powder. Crystals suitable for X-ray diffraction were obtained by slowly cooling a saturated Et_2O solution to -20°C. Yield: 380 mg, 0.52 mmol, 75 %. ^{1}H NMR (600 MHz, THF-d_8, 25°C) δ = 8.32 (d, *J* = 3.3 Hz, 2H, CH_{Ar}), 7.89 (d, *J* = 8.0 Hz, 2H, CH_{Ar}), 7.65 (d, *J* = 8.8 Hz, 2H, CH_{Ar}), 7.56 (d, *J* = 8.8 Hz, 2H, CH_{Ar}), 7.52 (d, *J* = 7.9 Hz, 2H, CH_{Ar}), 7.18 (d, *J* = 12.4 Hz, 2H, CH_{Ar}), 7.08 (d, *J* = 8.4 Hz, 2H, CH_{Ar}), 6.93 (q, *J* = 7.2 Hz, 4H, CH_{Ar}), 6.85 (t, *J* = 7.6 Hz, 2H, CH_{Ar}), 6.74 (d, *J* = 7.9 Hz, 2H, CH_{Ar}), 6.31 (d, *J* = 7.6 Hz, 2H, CH_{Ar}) ppm. ^{13}C APT NMR (151 MHz, THF, 25°C) δ = 156.2 (s, C_{Ar}), 151.9 (s, C_{Ar}), 143.6 (s, C_{Ar}), 142.6 (s, CH_{Ar}), 136.9 (s, C_{Ar}), 136.7 (s, CH_{Ar}), 131.6 (s, C_{Ar}), 129.7 (s, C_{Ar}), 129.4 (s, CH_{Ar}), 128.7 (s, C_{Ar}), 126.6 (s, CH_{Ar}), 126.2 (s, CH_{Ar}),125.8 (s, CH_{Ar}), 125.4 (s, CH_{Ar}), 123.8 (s, CH_{Ar}), 121.0 (s, CH_{Ar}), 119.7 (s, CH_{Ar}), 107.7 (s, CH_{Ar}), 104.8 (s, CH_{Ar}), 66.4 (QUIN, THF), 65.4 (s, Et_2O), 24.3 (QUIN, THF), 14.7 (s, Et_2O) ppm. Elemental Analysis: $C_{46}H_{44}CaN_4O_2$ (M = 724.96): calc. C 76.21, H 6.12, N 7.73; found: C 75.98, H 6.03, 7.80 N.

Synthesis of ^{DPP}1-Ca



^{DPP}1-Ca

$Ca[N(SiMe_3)_2]_2{\cdot}(THF)_2$ (232 mg, 0.46 mmol) and ^{DPP}1-H_2 (300 mg, 0.46 mmol) were dissolved in toluene (3 mL) and THF (1mL). The yellow solution was stirred for 1 day at room temperature. The solvent was removed and the residue was washed twice with a mixture of pentane (3 mL) and toluene (0.1 mL) and dried under reduced pressure. The resulting yellow powder was recrystallized from a saturated solution of hot benzene to furnish big yellow needles suitable for X-ray diffraction. Washing with a minimum amount of cold benzene and subsequent drying under reduced pressure for 1 day at 60°C gave the product as a bright yellow microcrystalline solid. Yield: 288 mg, 0.35 mmol, 75 %. ^{1}H NMR (400 MHz, benzene-d_6, 25 °C) δ 8.13 (dd, J = 9.6, 2.9 Hz, 2H, CH_{Ar}), 7.72 – 7.62 (m, 6H, CH_{Ar}), 7.59 (d, J = 8.9 Hz, 2H, CH_{Ar}), 7.51 – 7.43 (m, 4H, CH_{Ar}), 7.11 (d, J = 8.5 Hz, 2H, CH_{Ar}), 7.07 – 6.94 (m, 14H, CH_{Ar}), 6.89 (t, J = 7.6 Hz, 2H, CH_{Ar}), 3.54 (s, 8H, THF), 1.43 (s, 8H, THF) ppm. ^{13}C APT NMR (101 MHz, THF-d_8, 25 °C): δ = 155.5 (d, J_{CP} = 7.4 Hz, C_{Ar}), 147.9 (d, J_{CP} = 27.9 Hz, C_{Ar}), 147.4 (d, J_{CP} = 22.6 Hz, C_{Ar}), 136.6 (s, C_{Ar}), 133.0 (d, J_{CP} = 21.2 Hz, CH_{Ar}), 131.8 (d, J_{CP} = 18.6 Hz, CH_{Ar}), 128.7 (s, C_{Ar}), 128.2 (d, J_{CP} = 5.9 Hz, CH_{Ar}), 127.5 (d, J_{CP} = 4.6 Hz, CH_{Ar}), 127.2 (t, J_{CP} = 4.4 Hz, CH_{Ar}), 126.7 (d, J_{CP} = 43.6 Hz, CH_{Ar}), 126.3 (d, J_{CP} = 26.0 Hz, CH_{Ar}), 125.3 (s, CH_{Ar}), 120.8 (s, CH_{Ar}), 67.8 (s, THF), 25.9 (s, THF) ppm. ^{31}P NMR (243 MHz, THF-d_8): δ = -41.27 (s, $NPPh_2$) ppm. Elemental Analysis: $C_{52}H_{48}CaN_2O_2P_2$ (m = 834.99): calc. C 74.80, H 5.79, N 3.35; found: C 74.60, H 5.60, 3.30 N.

1.5. NMR Spectra of chiral Mg and Ca compounds

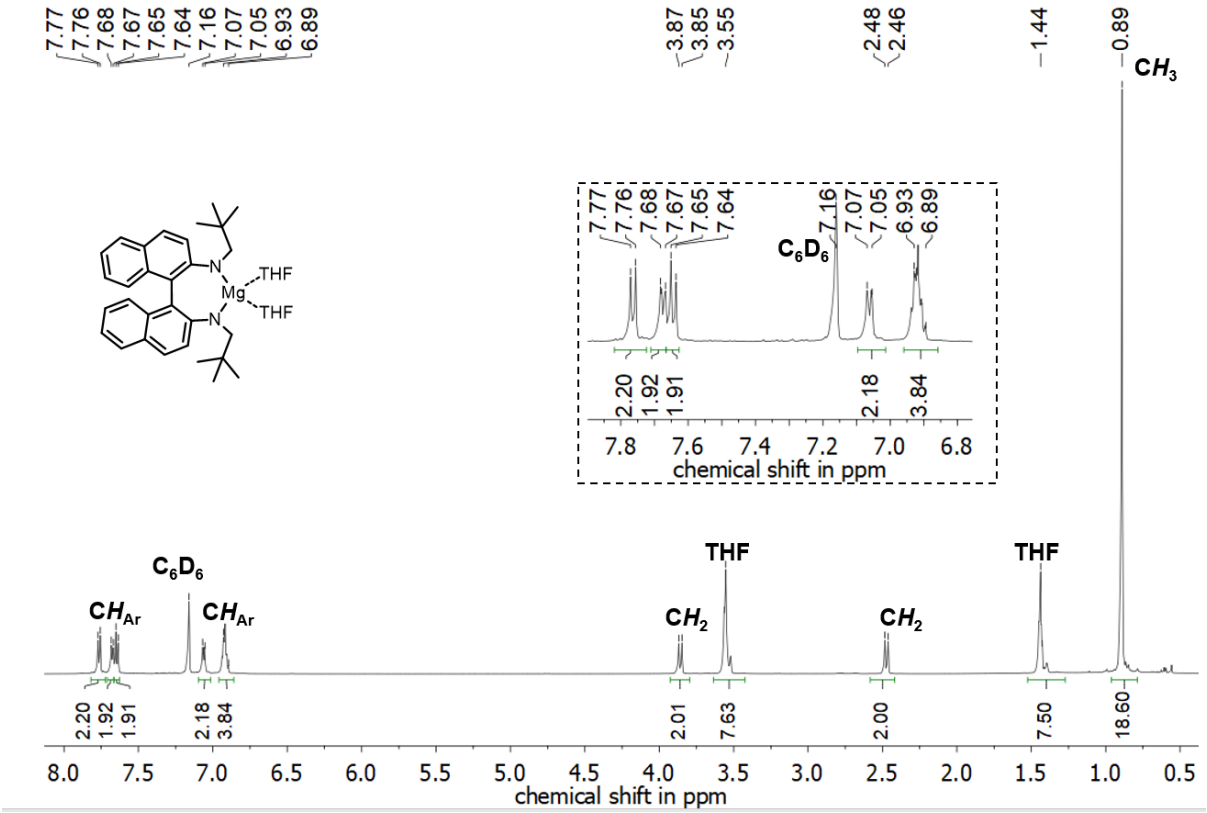


Figure S23: ^{1}H NMR (600 MHz, benzene-d_6, 25°C) spectrum of ^{NP}1-Mg.

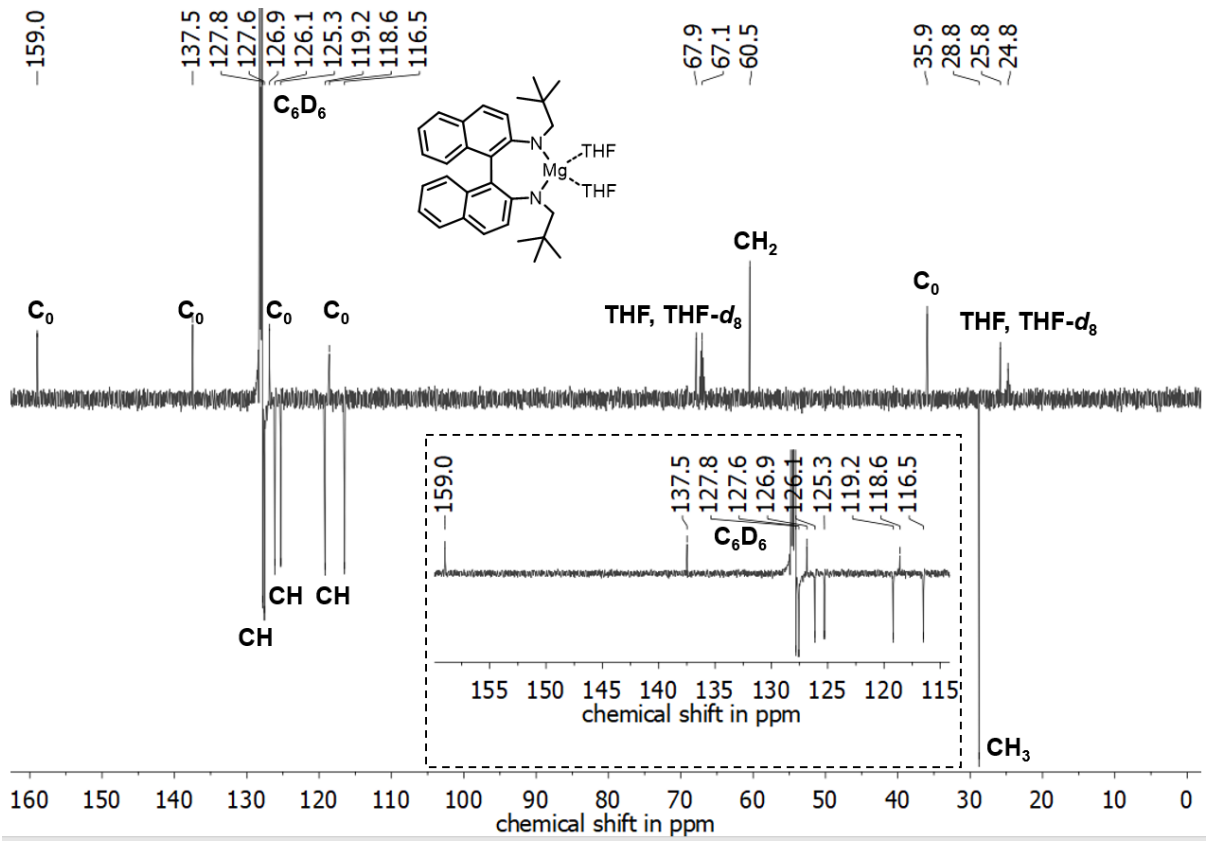


Figure S24: ^{13}C APT NMR (151 MHz, benzene-d_6 + THF-d_8, 25°C) spectrum of ^{NP}1-Mg.

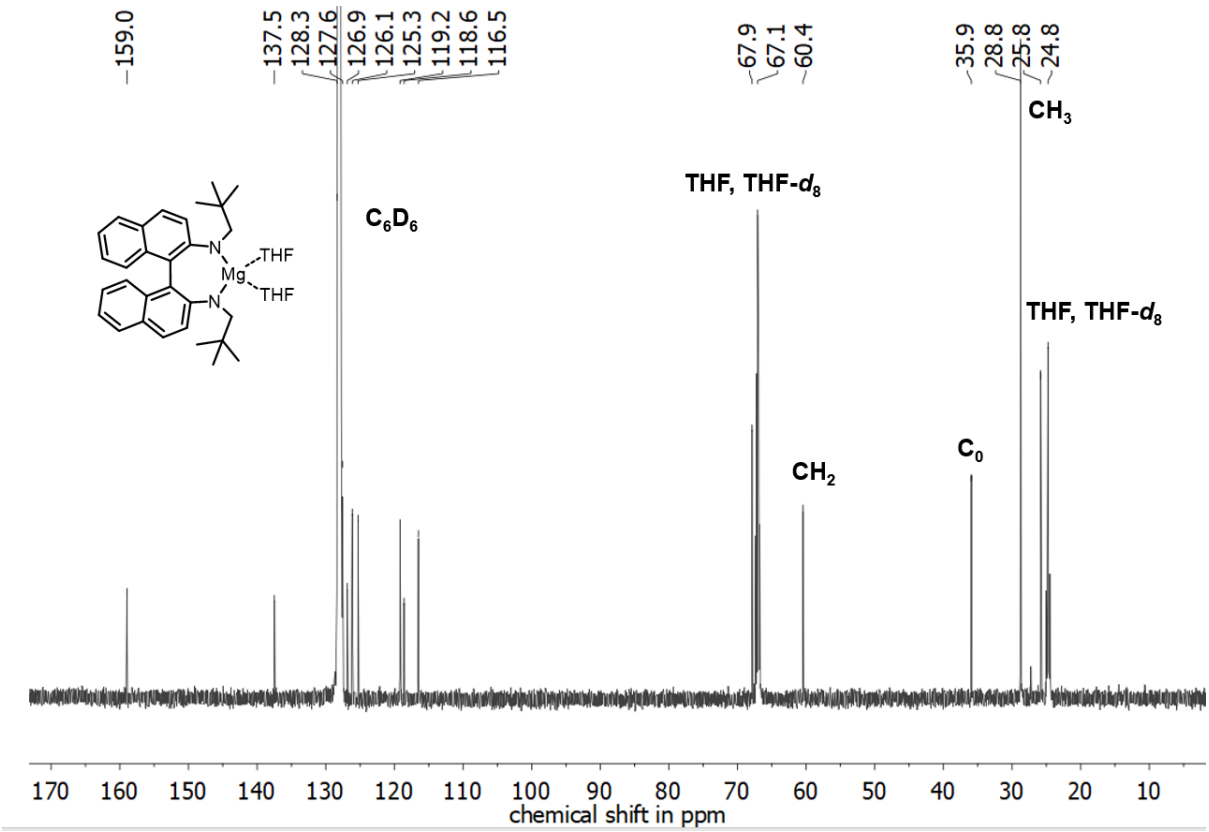


Figure S25: ^{13}C NMR (151 MHz, benzene-d_6, + THF-d_8, 25°C) spectrum of ^{NP}1-Mg.

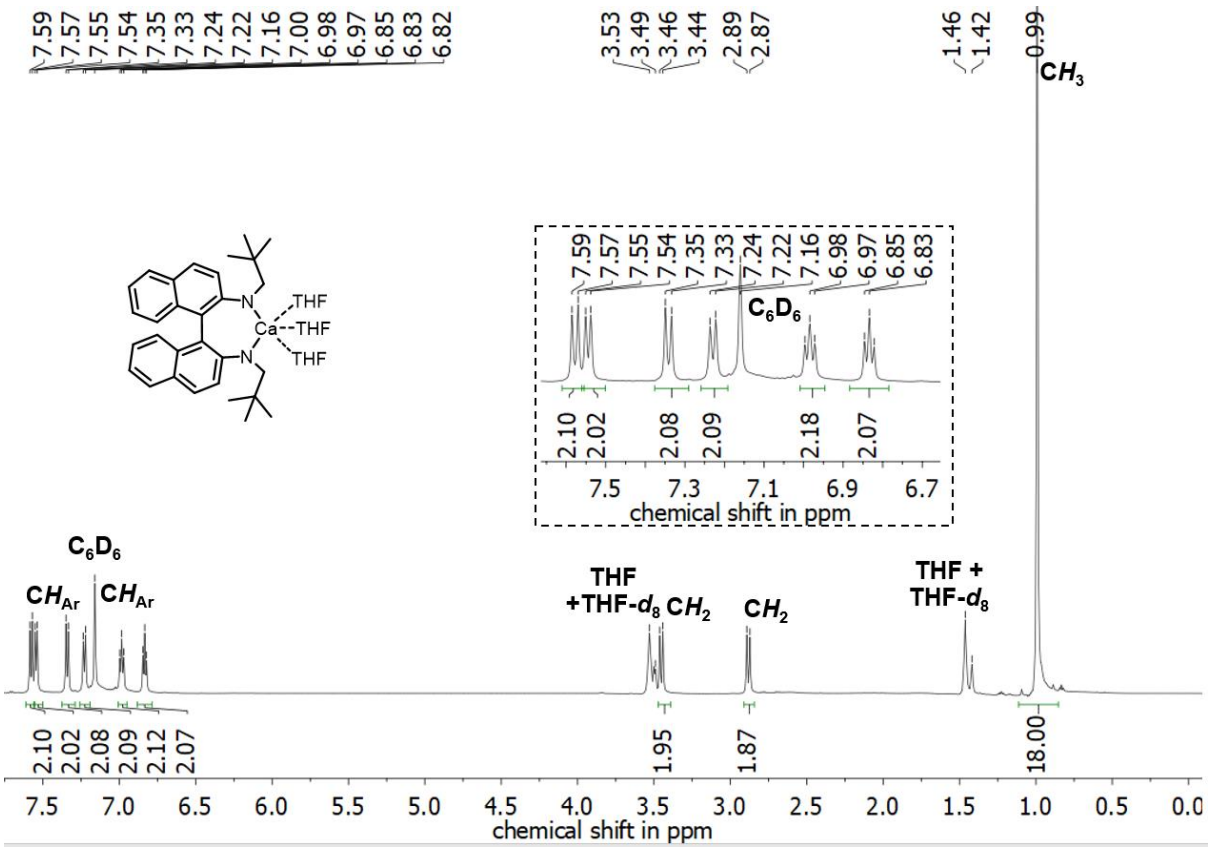


Figure S26: ^{1}H NMR (600 MHz, benzene-d_6, 25°C) spectrum of ^{NP}1-Ca.

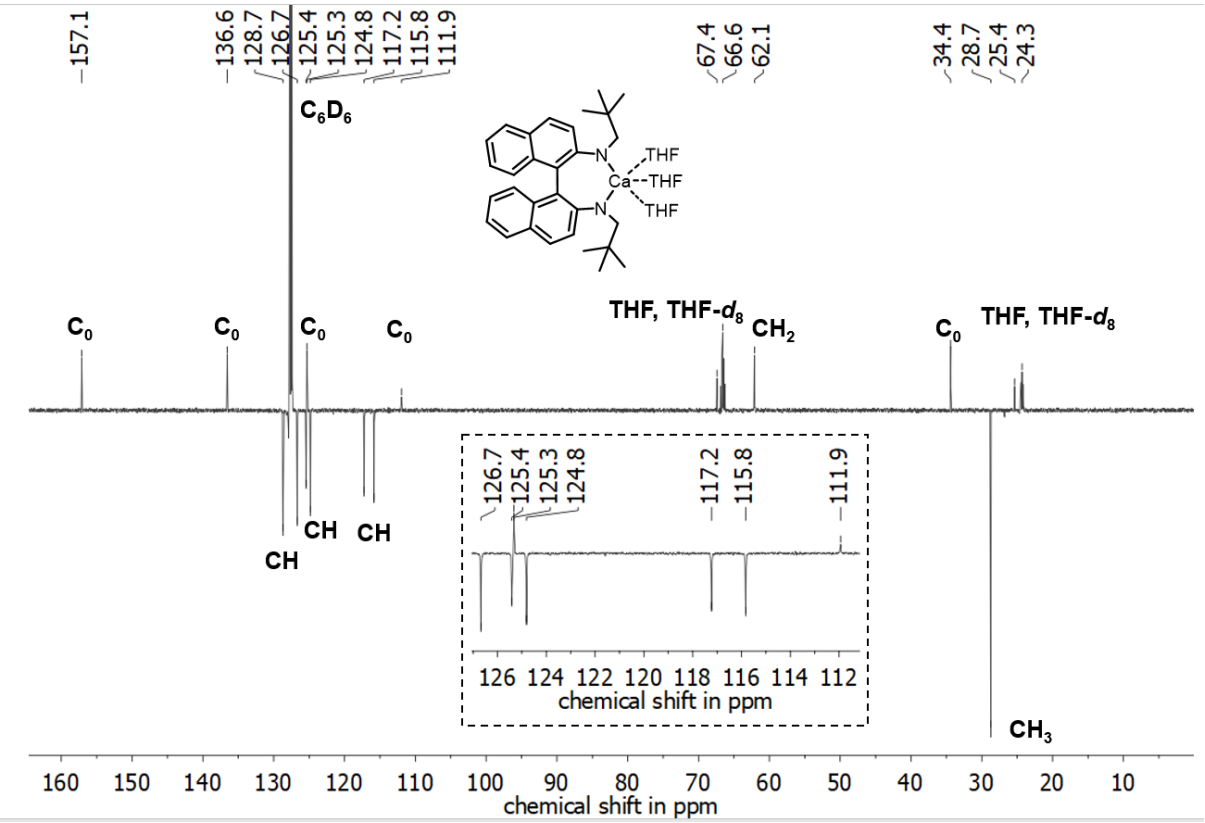


Figure S27: ^{13}C APT NMR (151 MHz, benzene-d_6 + THF-d_8, 25°C) spectrum of ^{NP}1-Ca.

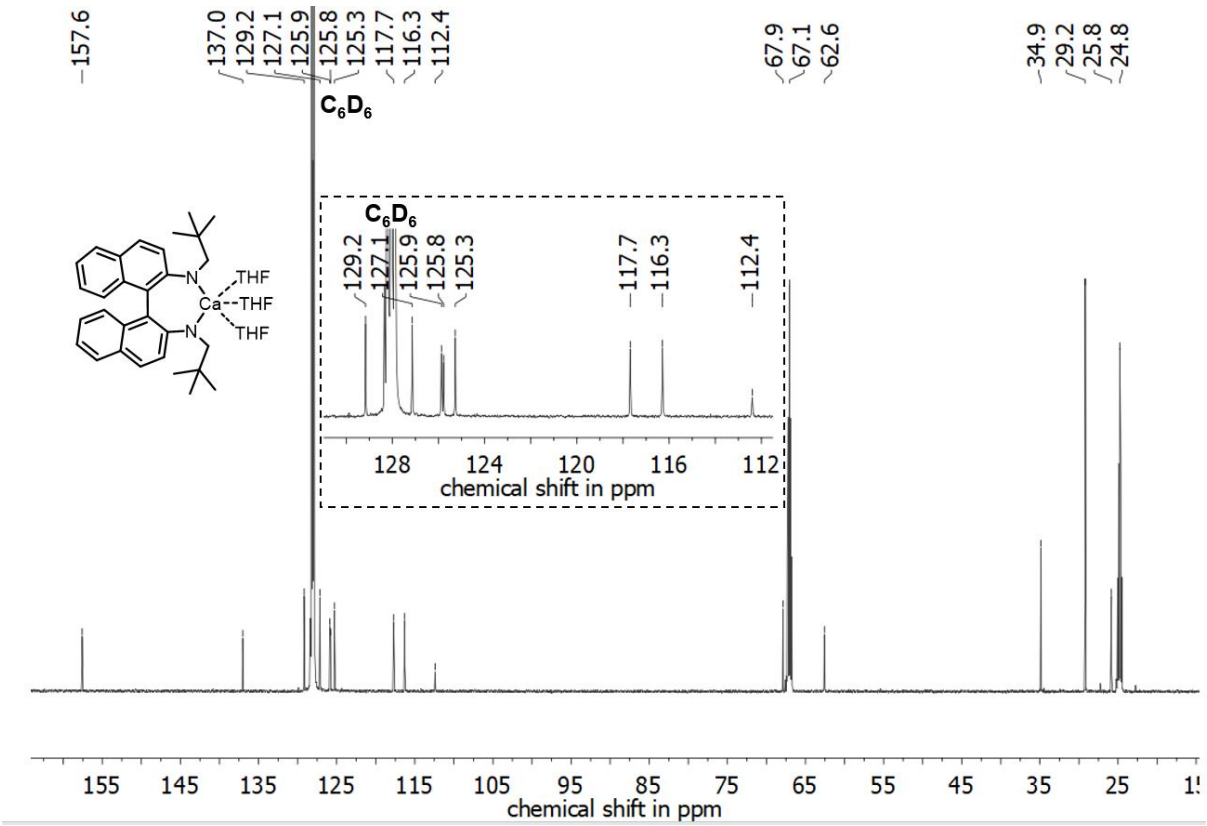


Figure S28: ^{13}C NMR (151 MHz, benzene-d_6 + THF-d_8, 25°C) spectrum of ^{NP}1-Ca.

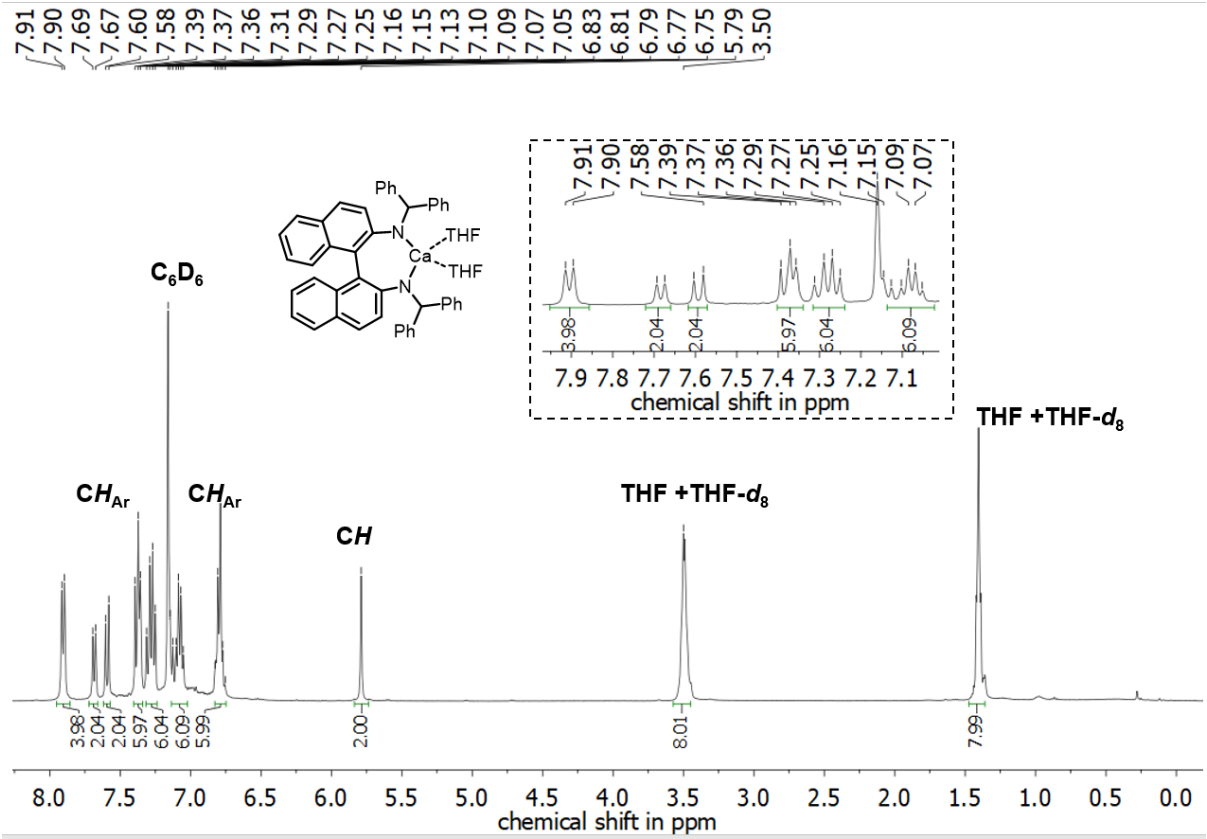


Figure S29: ^{1}H NMR (600 MHz, benzene-d_6, 25°C) spectrum of ^{DPM}1-Ca.

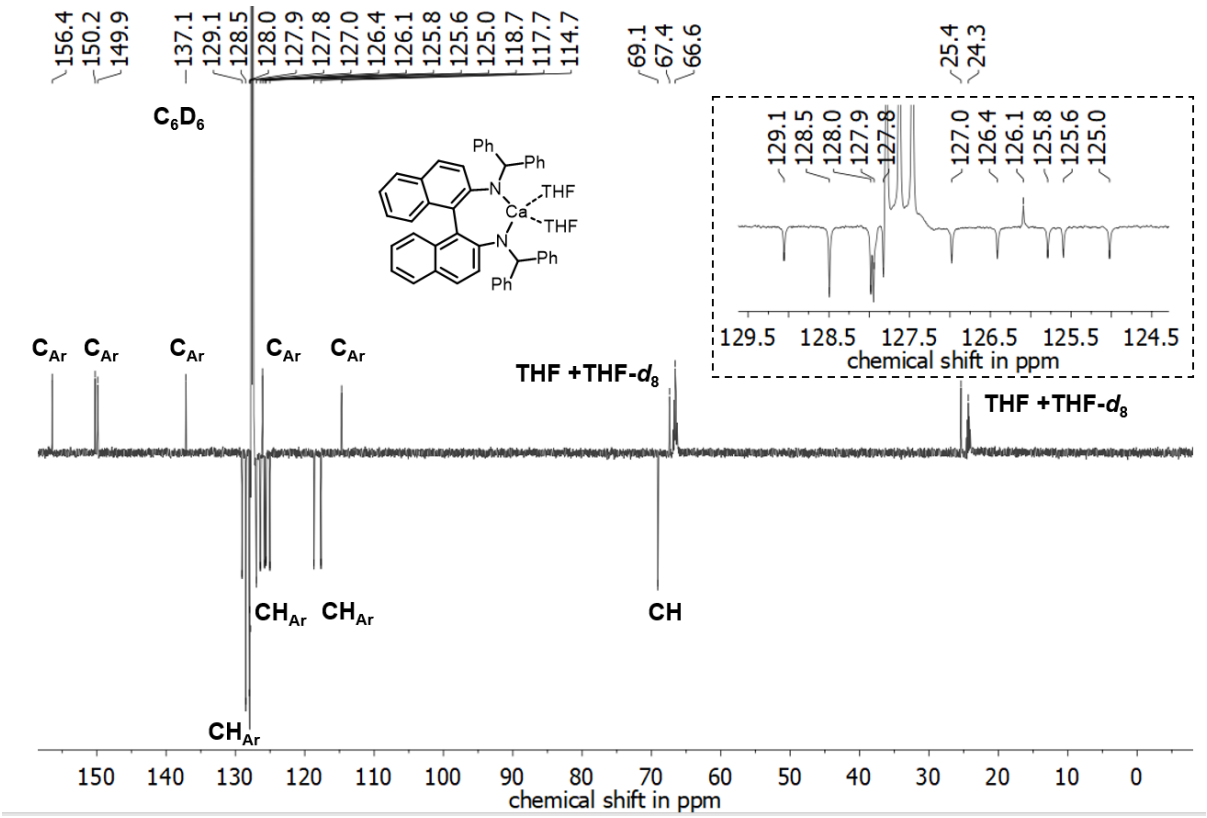


Figure S30: ^{13}C APT NMR (151 MHz, benzene-d_6 + THF-d_8, 25°C) spectrum of ^{DPM}1-Ca.

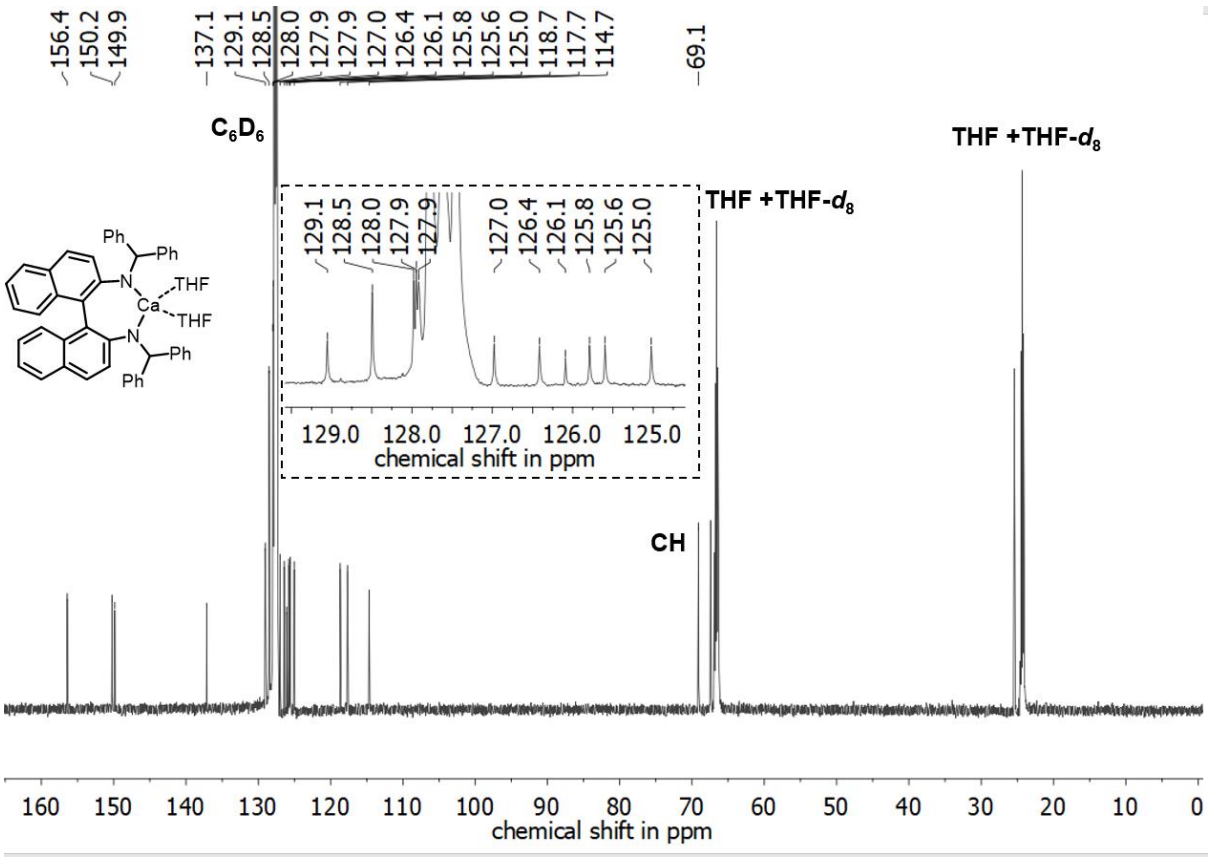


Figure S31: ^{13}C NMR (151 MHz, benzene-d_6 + THF-d_8, 25°C) spectrum ^{DPM}1-Ca.

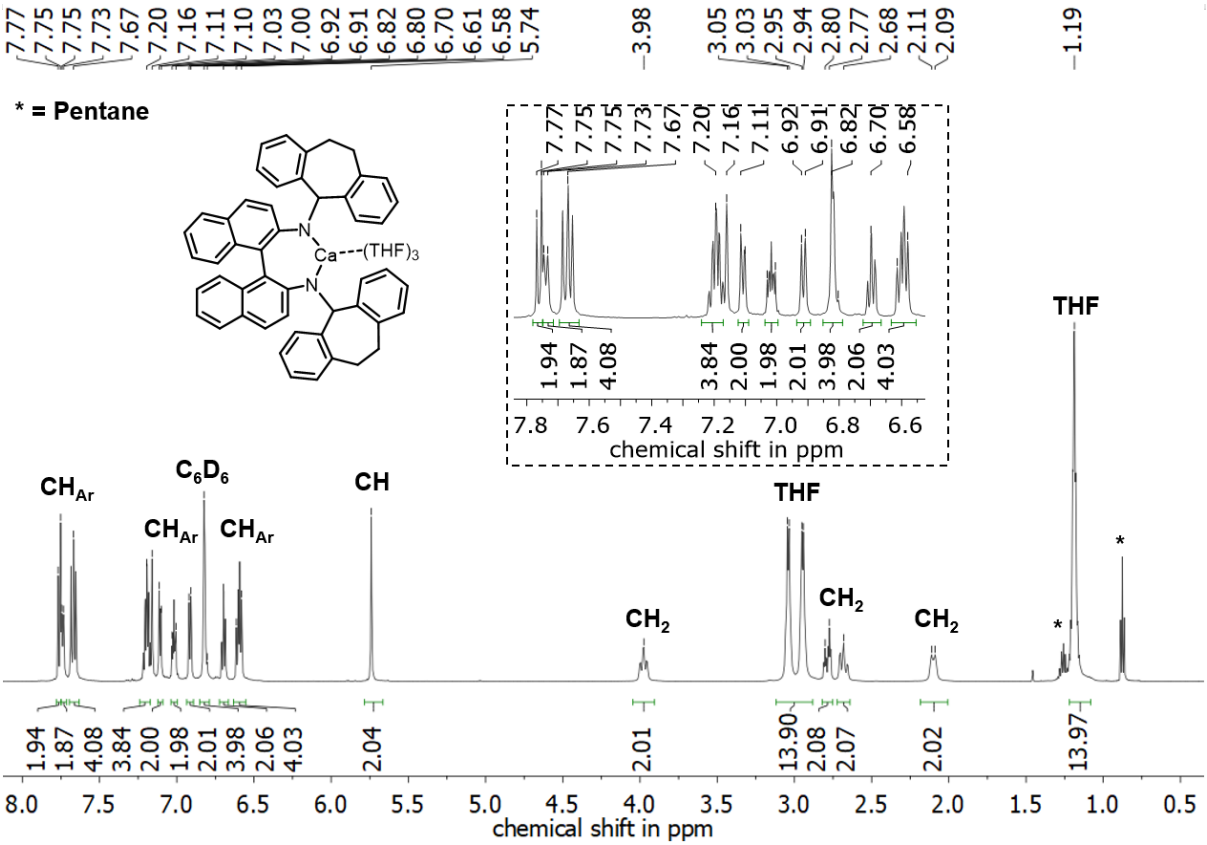


Figure S32: ^{1}H NMR (600 MHz, benzene-d_6, 25°C) spectrum of ^{DBS}1-Ca. Residual pentane results from contamination of benzene-d_6.

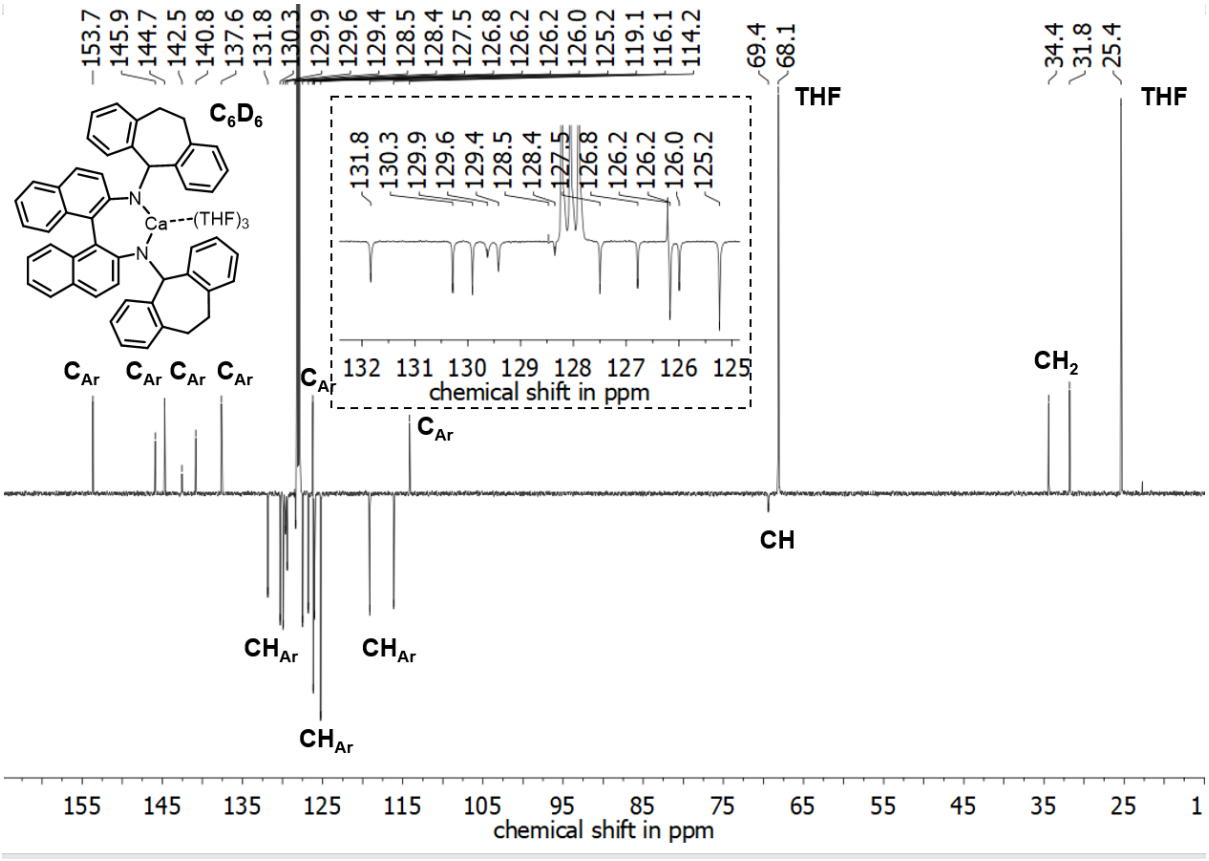


Figure S33: ^{13}C APT NMR (151 MHz, benzene-d_6, 25°C) spectrum of ^{DBS}1-Ca.

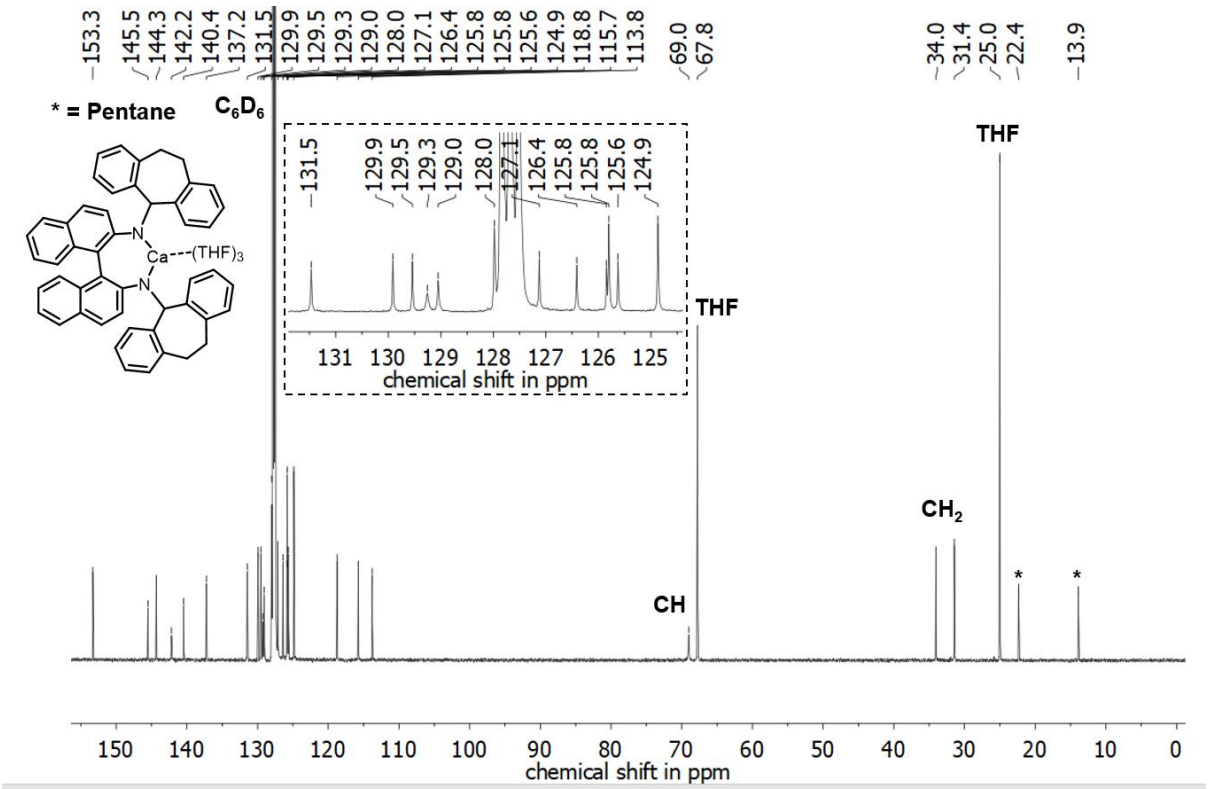


Figure S34: ^{13}C NMR (151 MHz, benzene-d_6, 25°C) spectrum of ^{DBS}1-Ca. Residual pentane results from contamination of benzene-d_6.

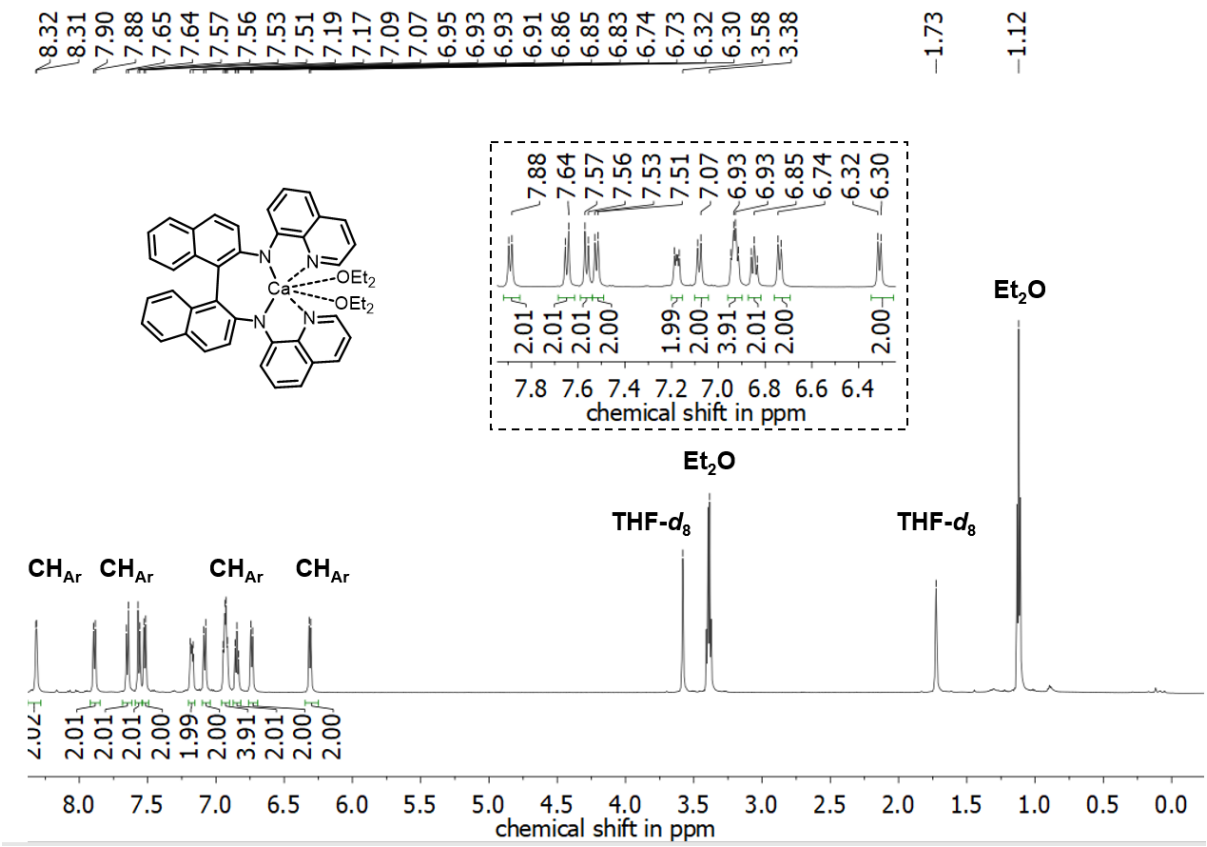


Figure S35: ^{1}H NMR (600 MHz, THF-d_8, 25°C) spectrum of ^{QUIN}1-Ca.

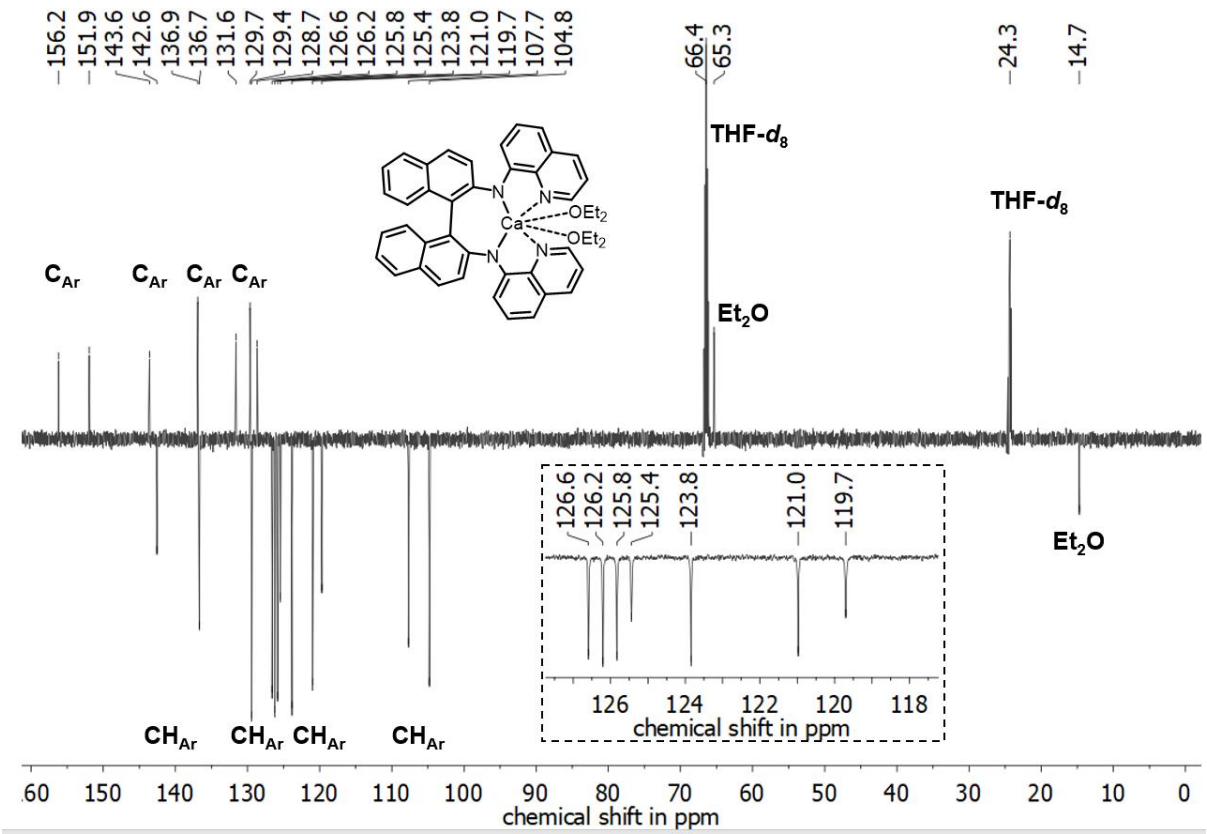


Figure S36: ^{13}C APT NMR (151 MHz, THF-d_8, 25°C) spectrum of ^{QUIN}1-Ca.

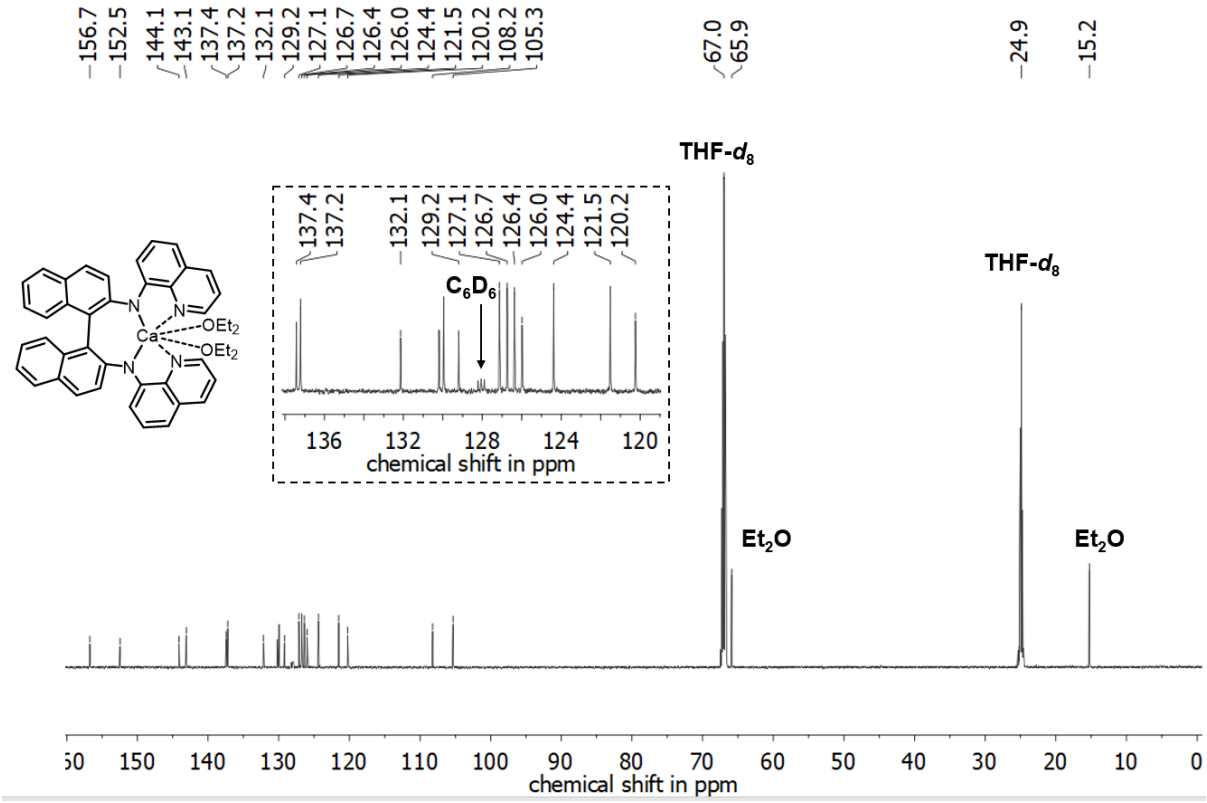


Figure S37: ^{13}C NMR (151 MHz, THF-d_8, 25°C) spectrum of ^{QUIN}1-Ca.

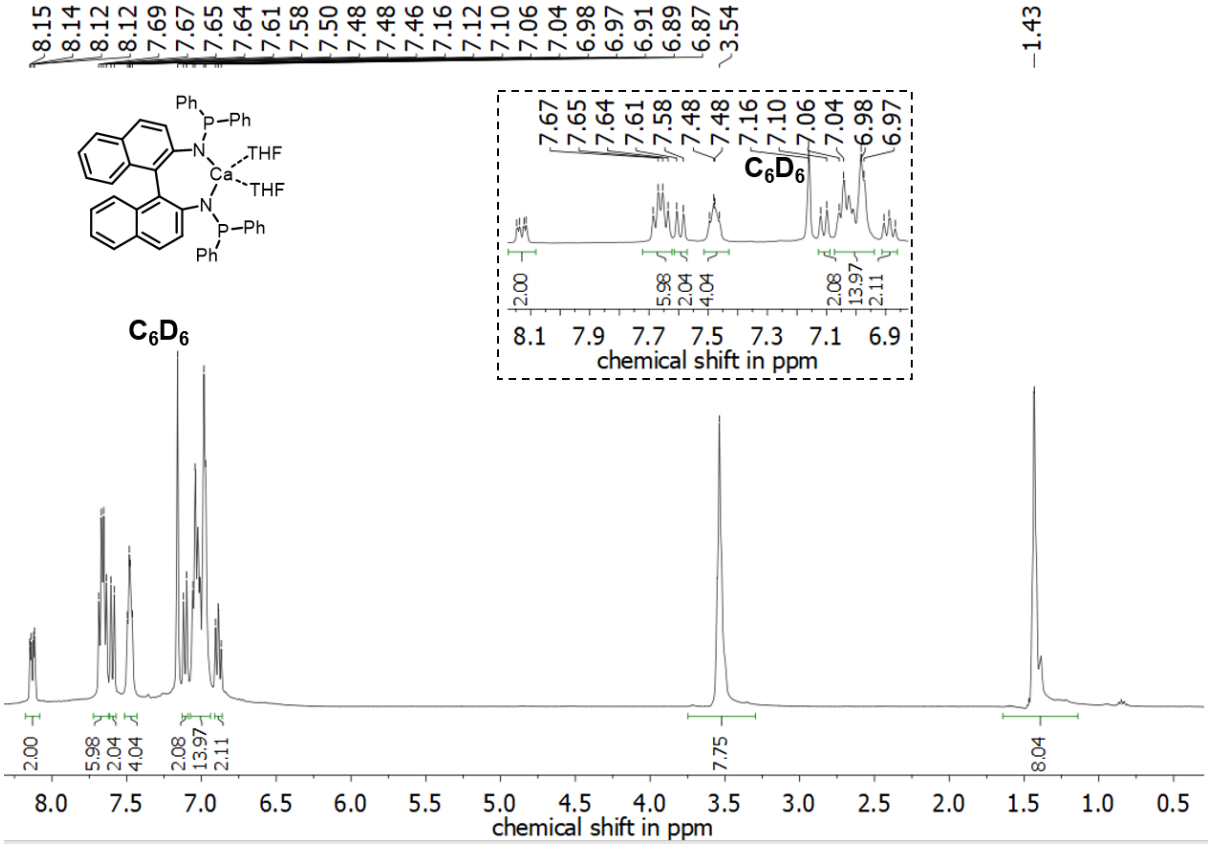


Figure S38: ^{1}H NMR (151 MHz, benzene-d_6 + THF-d_8, 25°C) spectrum of ^{DPP}1-Ca.

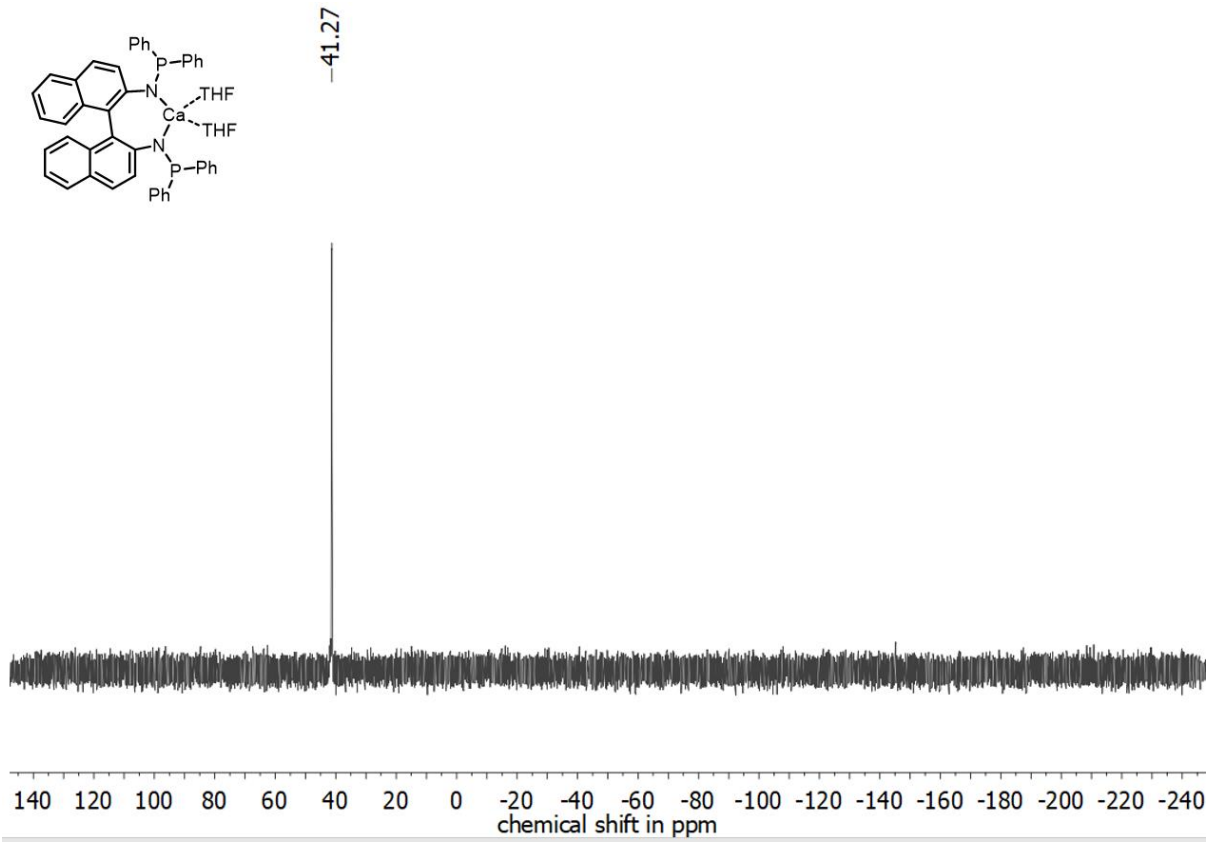


Figure S39: ^{31}P NMR (162 MHz, benzene-d_6 + THF-d_8, 25°C) spectrum of ^{DPP}1-Ca.

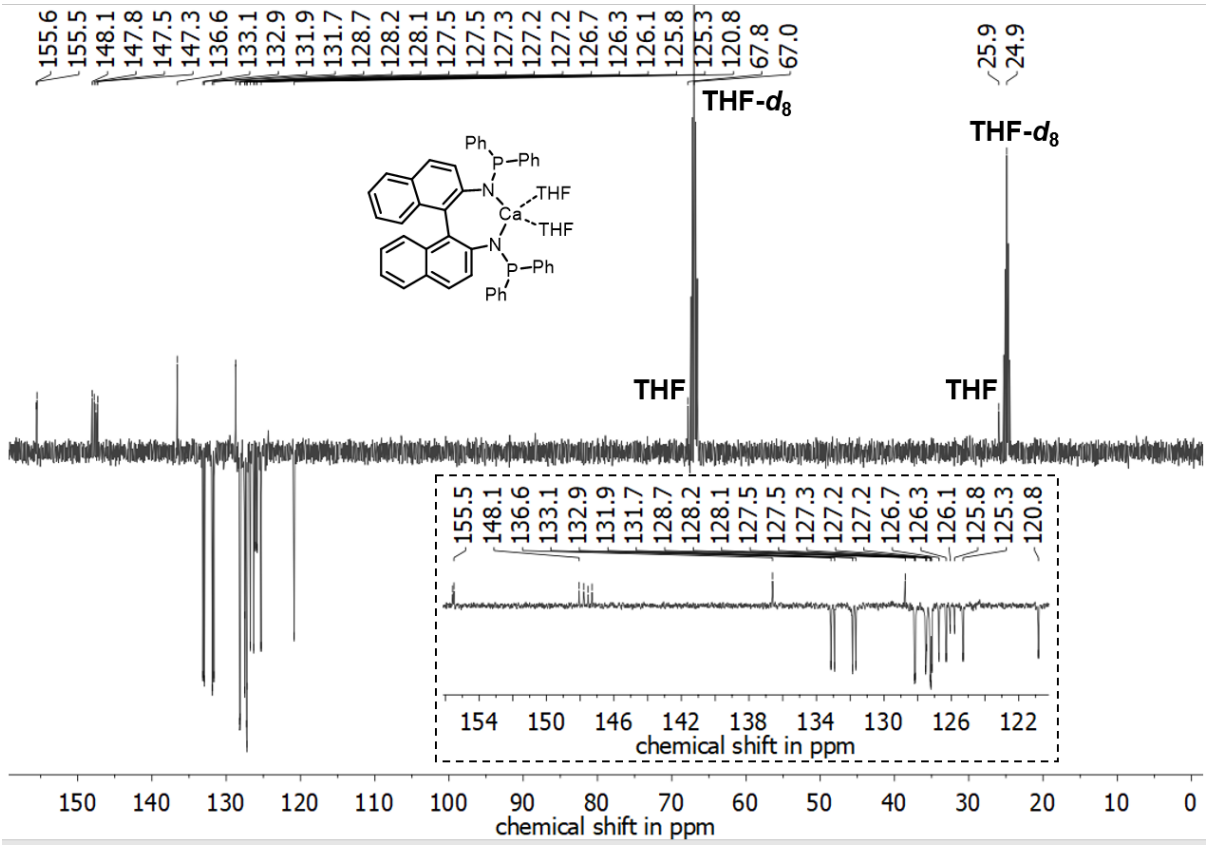


Figure S40: ^{13}C APT NMR (101 MHz, THF-d_8, 25°C) spectrum of ^{DPP}1-Ca.

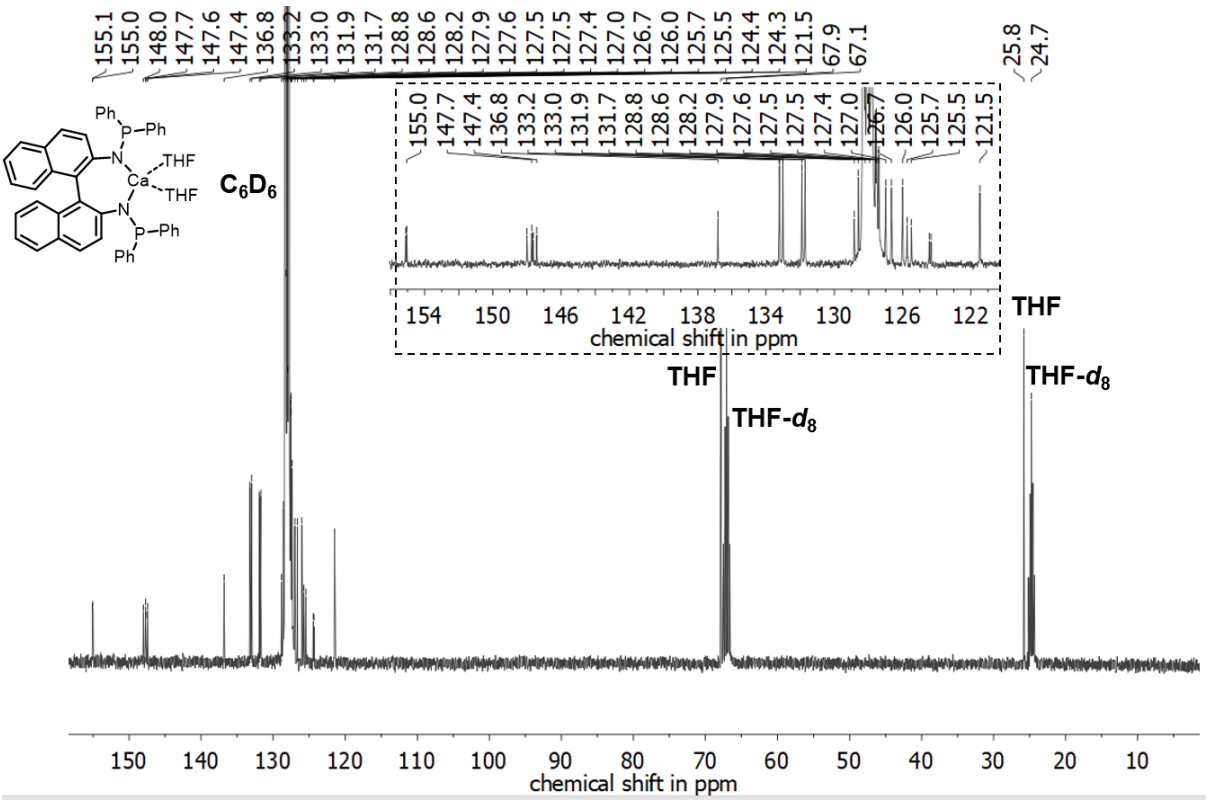


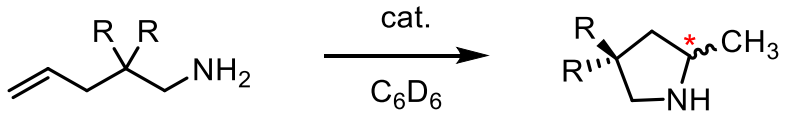
Figure S41: ^{13}C NMR (151 MHz, benzene-d_6 + THF-d_8, 25°C) spectrum of ^{DPP}1-Ca.

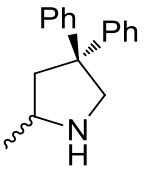
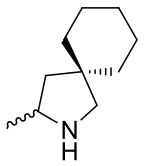
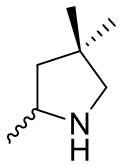
1.6. Catalysis

General

Catalytic intramolecular alkene hydroamination experiments were performed in J-Young NMR tubes. The tube was loaded inside an N_2 filled glovebox with the aminoalkene substrate (0.169 mmol) and the catalyst (8.50-17.0 µmol, 5-10 mol%), dissolved in 550 µL of benzene-d_6. Catalytic conversions were monitored by ^{1}H NMR and run to completion or until no further catalytic progress was observed. The enantiomeric excess was determined by derivatization with (*R*)-O-acetyl-mandelic acid (0.254 mmol, 1.5 eq.) and subsequent integration of the characteristic proton signals related to the formed diastereomers. In case of insufficient peak separation, (*R*)-(−)-α-methoxy-α-(trifluoromethyl)phenylacetyl chloride (0.254 mmol, 1.5 eq.) was used in combination with triethylamine (0.254 mmol, 1.5 eq.) for derivatization. The resulting fluorinated diastereomers were analyzed by integration of the corresponding ^{19}F NMR signals. ^{19}F NMR spectra were measured at various temperatures (room temperature to 70°C) and the spectrum with the best peak separation was chosen for integration in order to determine the diastereomer ratio. The assignment of signals is based on data in the literature.[S8] All experimental data are summarized in Table S1.

Table S1: Catalytic intramolecular alkene hydroamination.



Entry	Product	Catalyst	Loading [mol%]	T [°C]	t	Conv. [%]	ee [%]
1		^{DBS}**1-Ca**	10	RT	3 d	99	57
2		^{DPM}**1-Ca**	10	RT	1 d	99	32
3		^{NP}**1-Ca**	5	RT	5 min	99	18
4		^{NP}**1-Mg**	5	RT	45 min	99	13
5		^{DPP}**1-Ca**	10	100°C	1 d	94	4
6		^{QUIN}**1-Ca**	10	100°C	1 d	-	-
7		^{DBS}**1-Ca**	10	60°C	20 h	99	27
8		^{DPM}**1-Ca**	10	60°C	3 h	99	16
9		^{NP}**1-Ca**	5	RT	10 min	99	13
10		^{NP}**1-Mg**	5	100°C	1 d	99	7
11		^{DPP}**1-Ca**	10	100°C	3 d	-	-
12		^{QUIN}**1-Ca**	10	100°C	2 d	-	-
13		^{DBS}**1-Ca**	10	100°C	20 h	99	27
14		^{DPM}**1-Ca**	10	100°C	1 d	99	14
15		^{NP}**1-Ca**	10	60°C	1 h	99	10
16		^{NP}**1-Mg**	10	100°C	2 d	-	-
17		^{DPP}**1-Ca**	10	100°C	2 d	-	-
18		^{QUIN}**1-Ca**	10	100°C	2 d	-	-

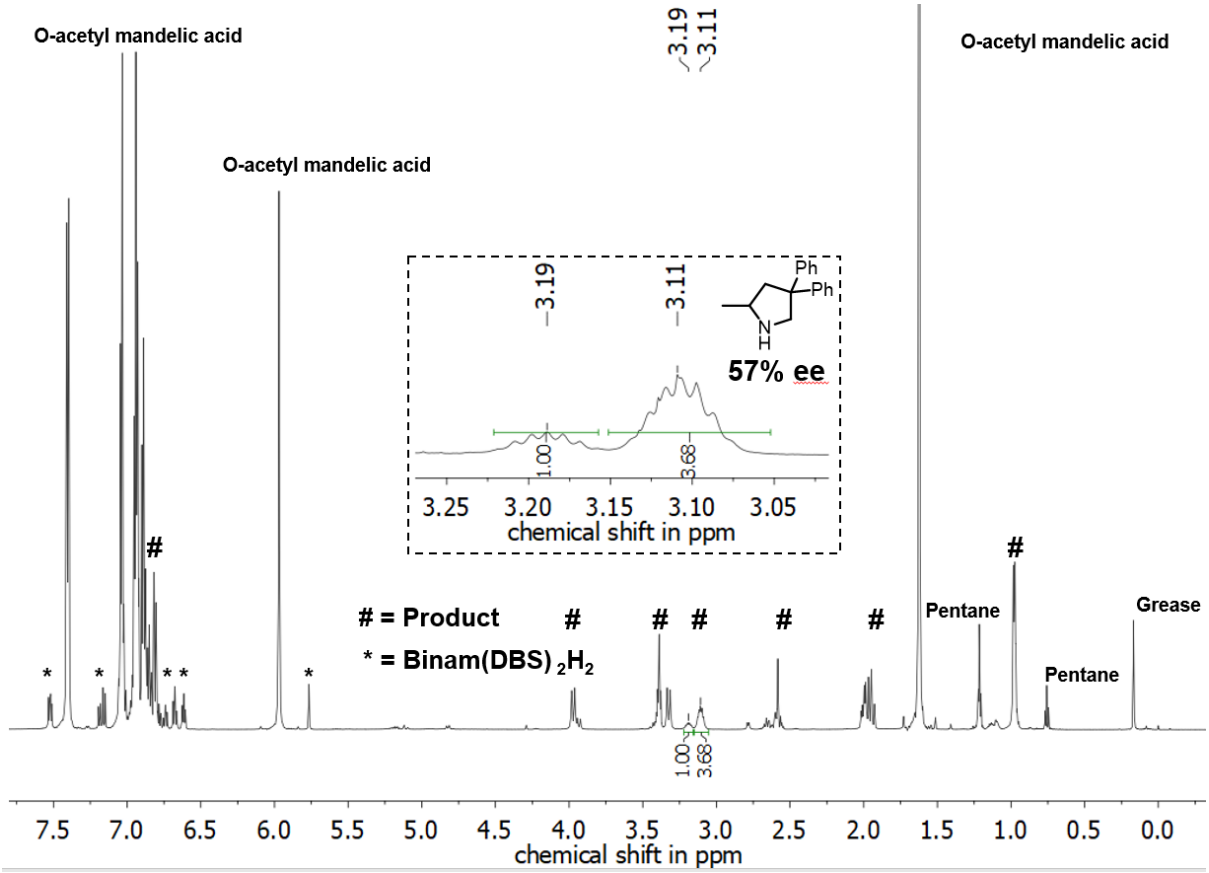


Figure S42: Determination of the enantiomeric excess for the cyclization product of $H_2C{=}CHCH_2CPh_2CH_2NH_2$ catalyzed by ^{DBS}1-Ca at room temperature, using (*R*)-O-acetyl-mandelic acid.

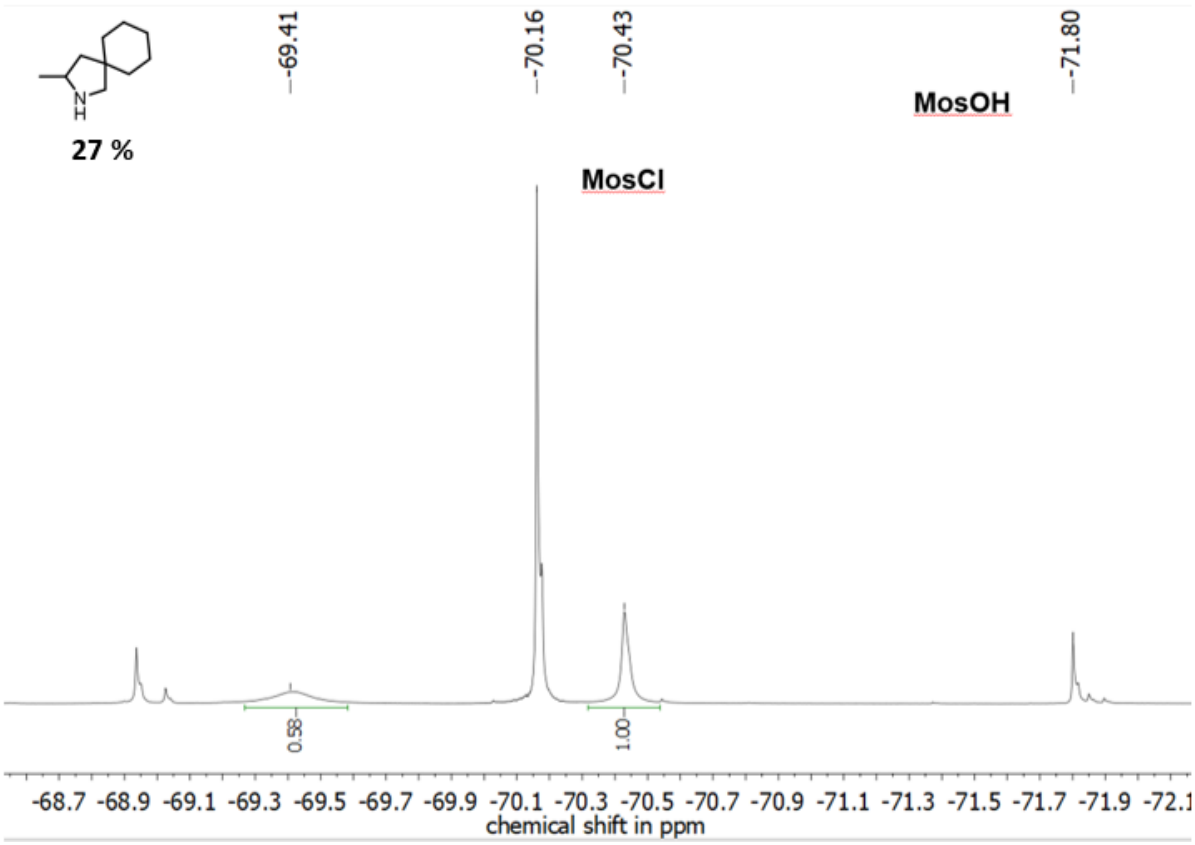


Figure S43: Determination of the enantiomeric excess for the cyclization product of $H_2C{=}CHCH_2C(CH_2)_5CH_2NH_2$ catalyzed by ^{DBS}1-Ca at 60°C, using (*R*)-(−)-α-Methoxy-α-(trifluoromethyl)phenylacetyl chloride.

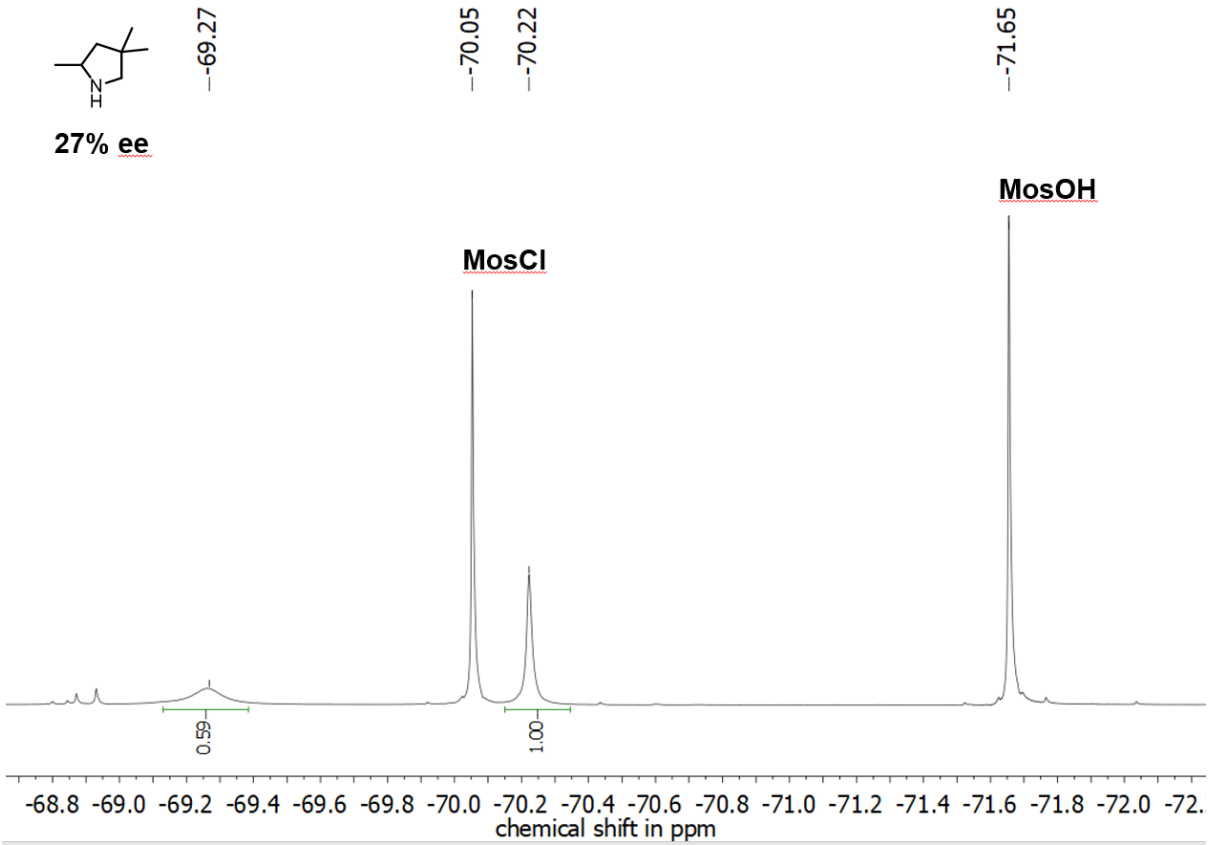


Figure S44: Determination of the enantiomeric excess for the cyclization product of $H_2C{=}CHCH_2CMe_2CH_2NH_2$ catalyzed by ^{DBS}1-Ca at 100°C, using (*R*)-(−)-α-Methoxy-α-(trifluoromethyl)phenylacetyl chloride.

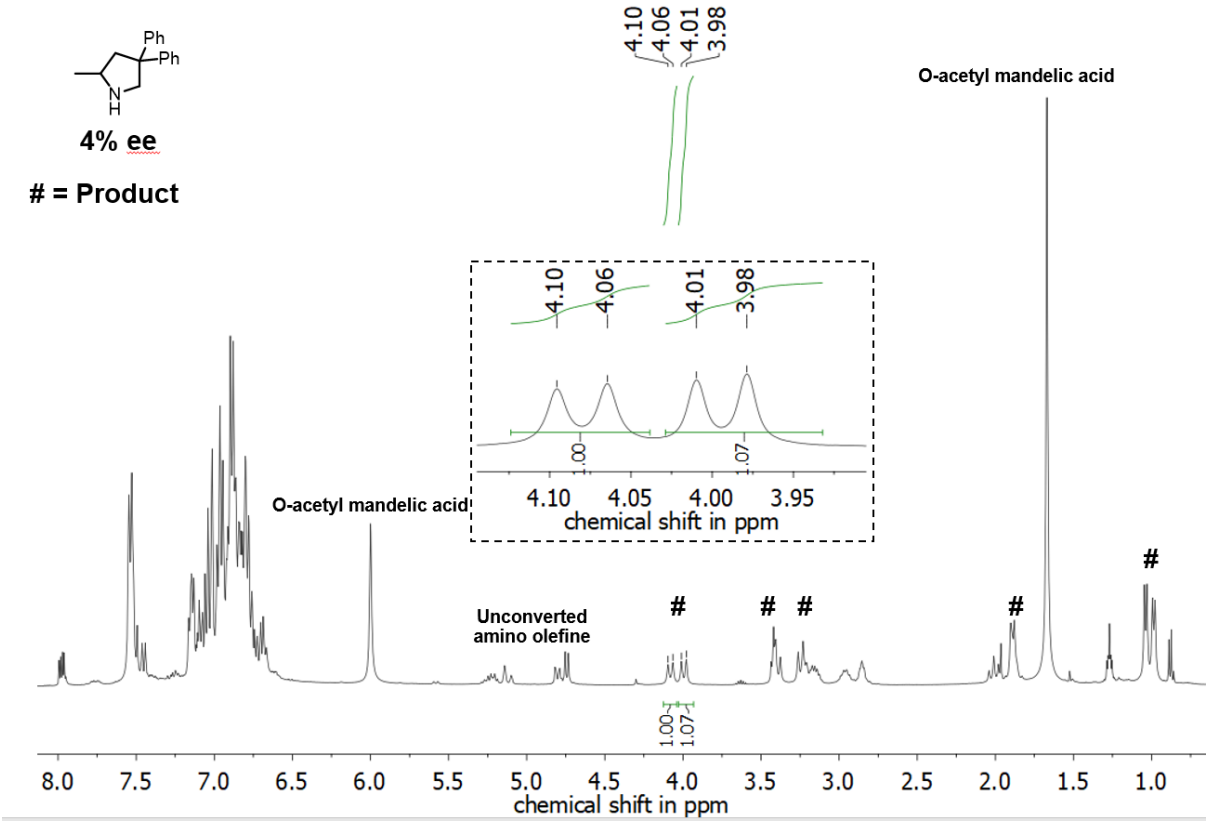


Figure S45: Determination of the enantiomeric excess for the cyclization product of $H_2C{=}CHCH_2CPh_2CH_2NH_2$ catalyzed by ^{DPP}1-Ca at 100°C, using (*R*)-O-acetyl-mandelic acid.

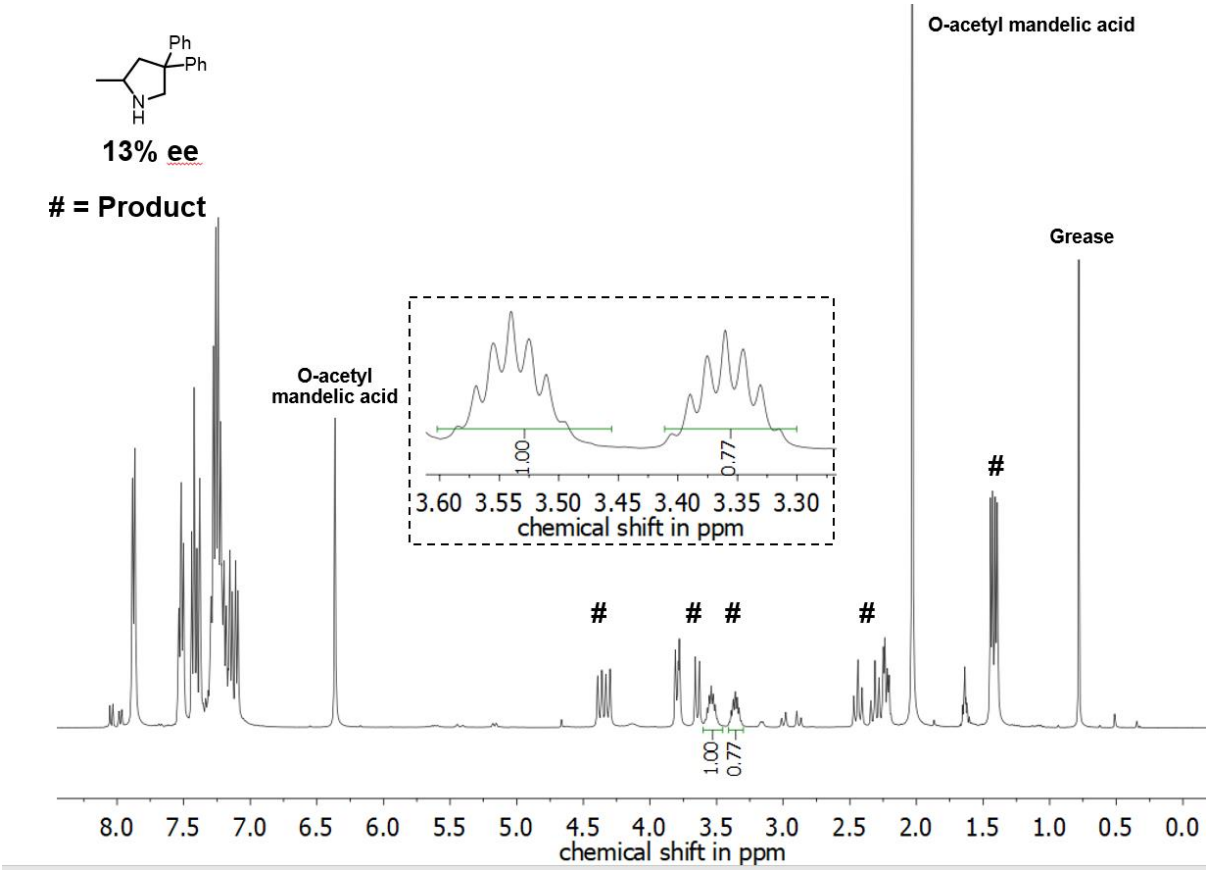


Figure S46: Determination of the enantiomeric excess for the cyclization product of $H_2C{=}CHCH_2CPh_2CH_2NH_2$ catalyzed by ^{NP}1-Mg at room temperature, using (*R*)-O-acetyl-mandelic acid.

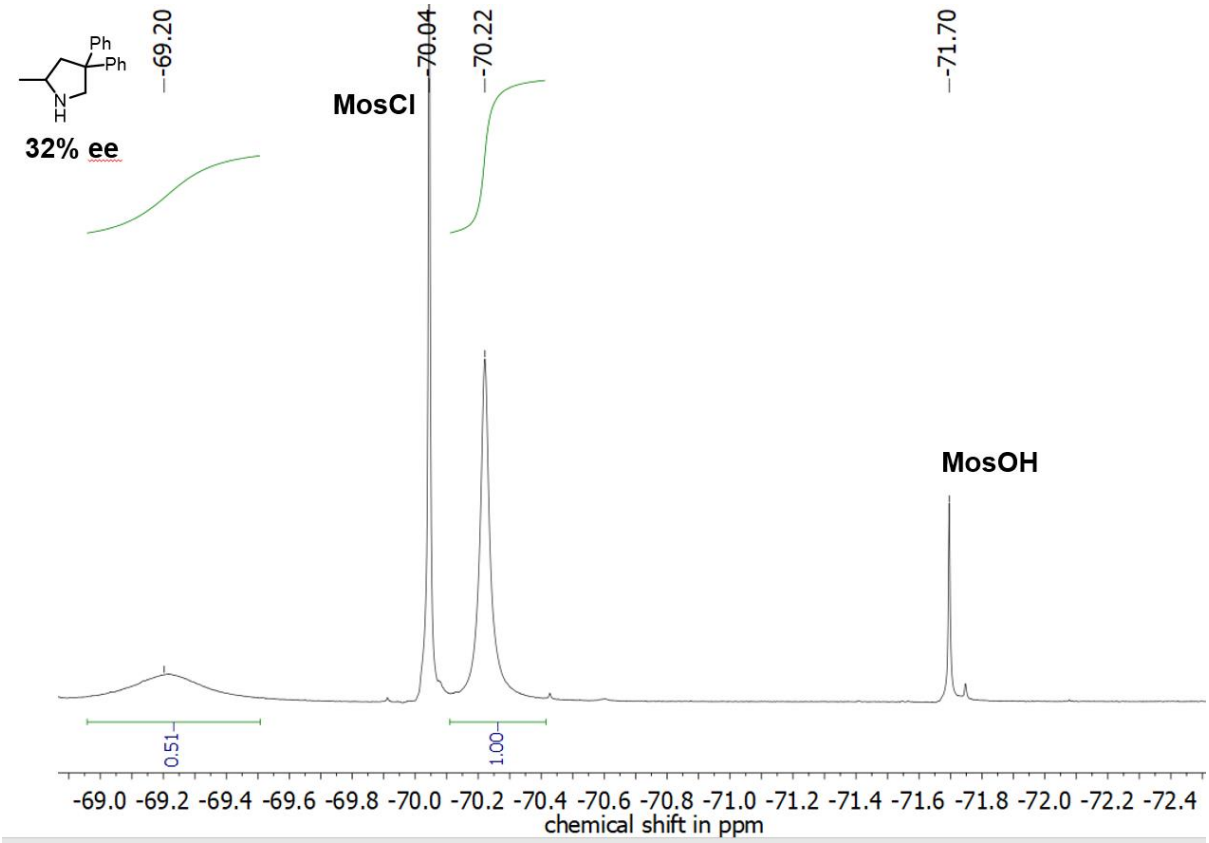


Figure S47: Determination of the enantiomeric excess for the cyclization product of $H_2C{=}CHCH_2CPh_2CH_2NH_2$ catalyzed by ^{DPM}1-Ca at room temperature, using (*R*)-(−)-α-Methoxy-α-(trifluoromethyl)phenylacetyl chloride.

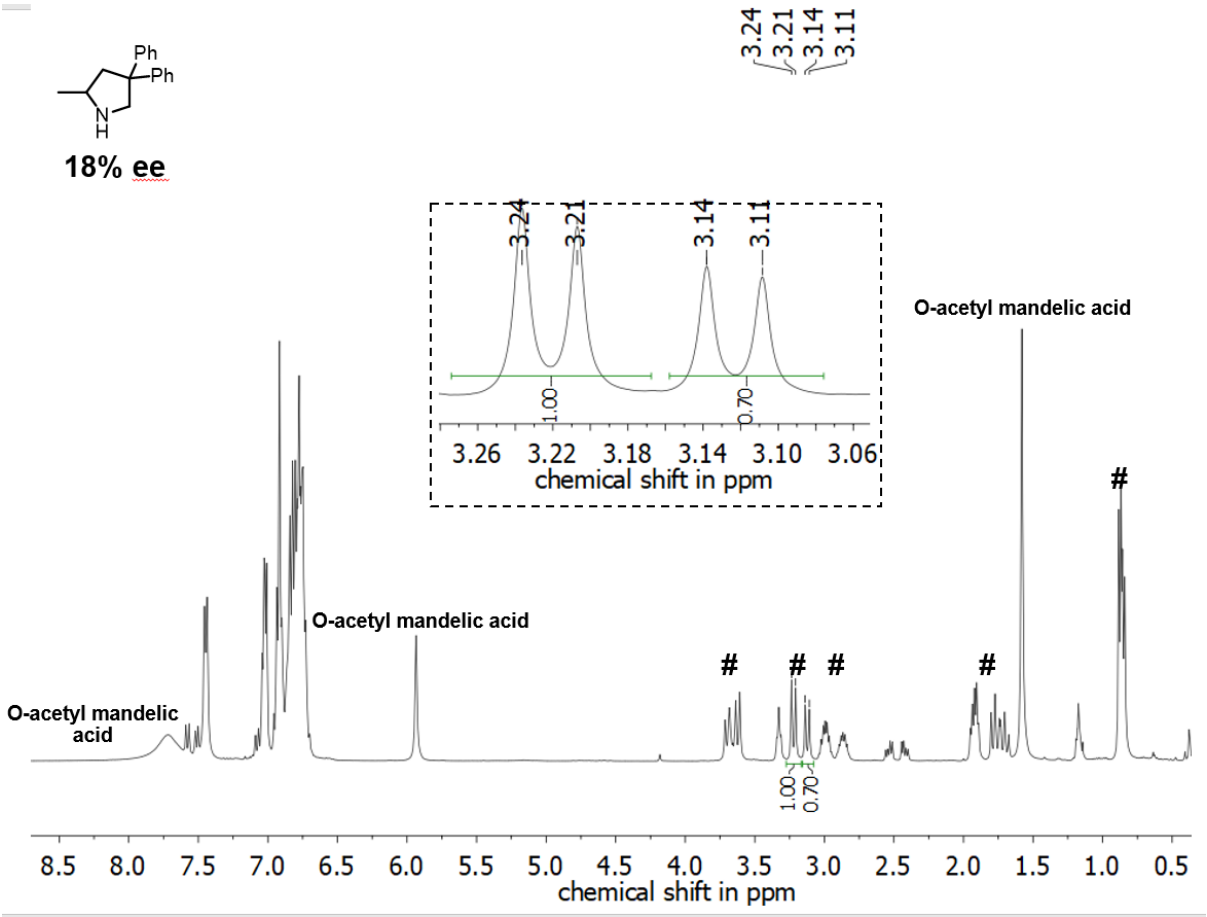


Figure S48: Determination of the enantiomeric excess for the cyclization product of $H_2C{=}CHCH_2CPh_2CH_2NH_2$ catalyzed by ^{NP}1-Ca at room temperature, using (*R*)-O-acetyl-mandelic acid.

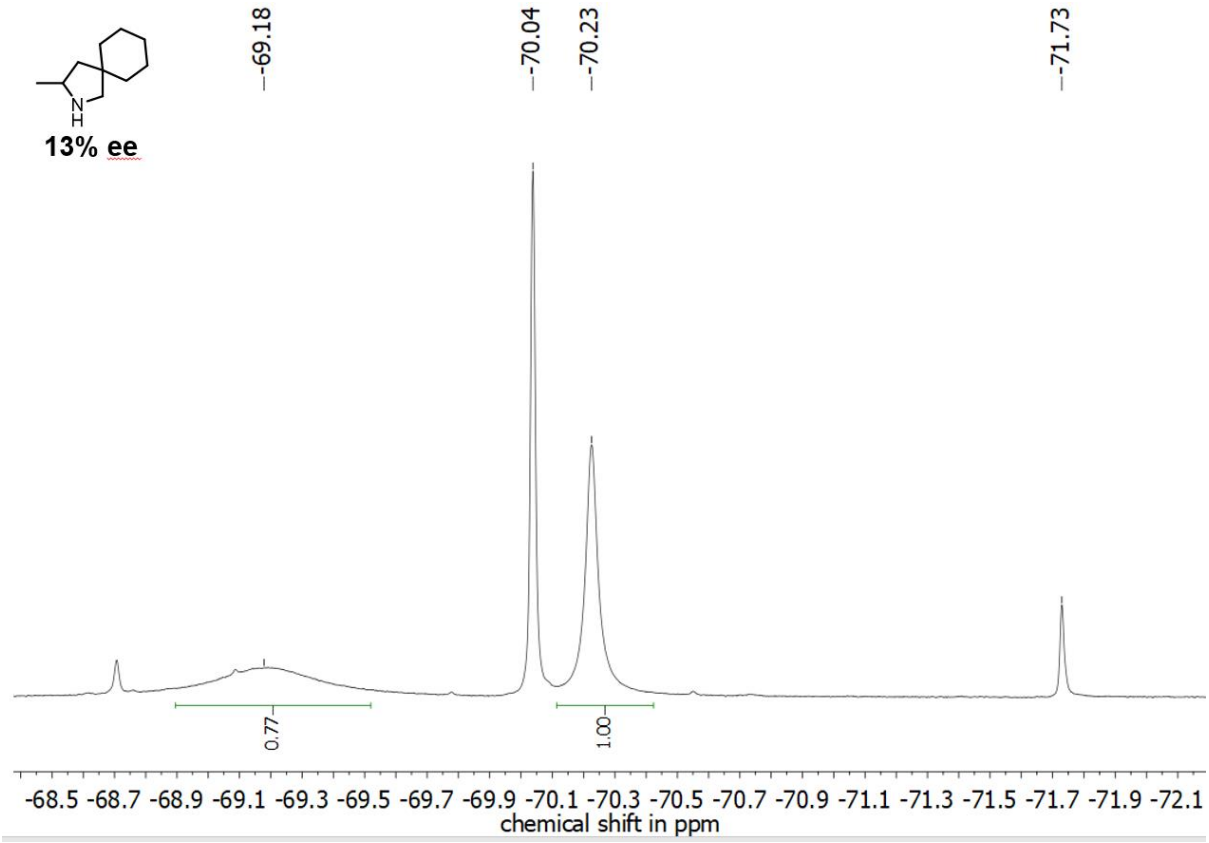


Figure S49: Determination of the enantiomeric excess for the cyclization product of $H_2C{=}CHCH_2C(CH_2)_5CH_2NH_2$ catalyzed by ^{NP}1-Ca at room temperature, using (*R*)-(−)-α-Methoxy-α-(trifluoromethyl)phenylacetyl chloride.

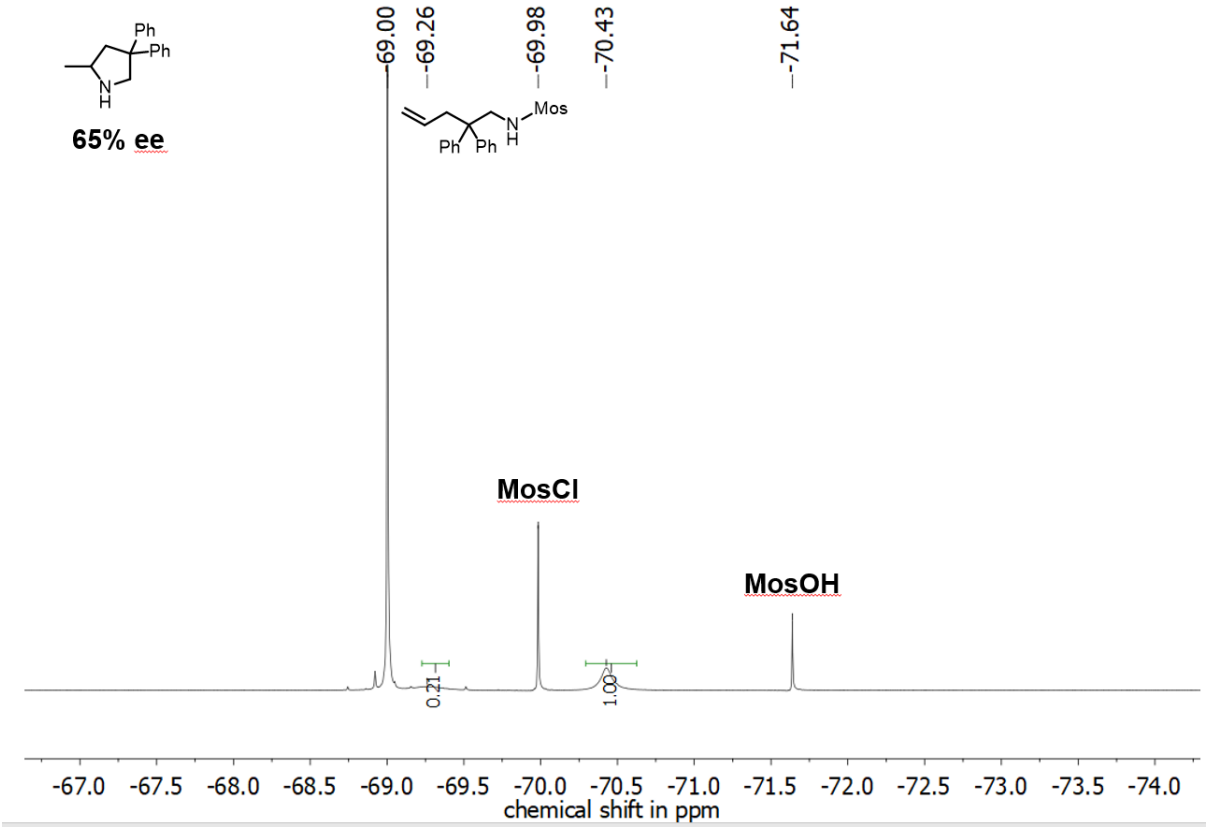


Figure S50: Determination of the enantiomeric excess for the cyclization product of $H_2C{=}CHCH_2CPh_2CH_2NH_2$ catalyzed by ^{DBS}1-Ca at room temperature (40% conversion), using (*R*)-(−)-α-Methoxy-α-(trifluoromethyl)phenylacetyl chloride.

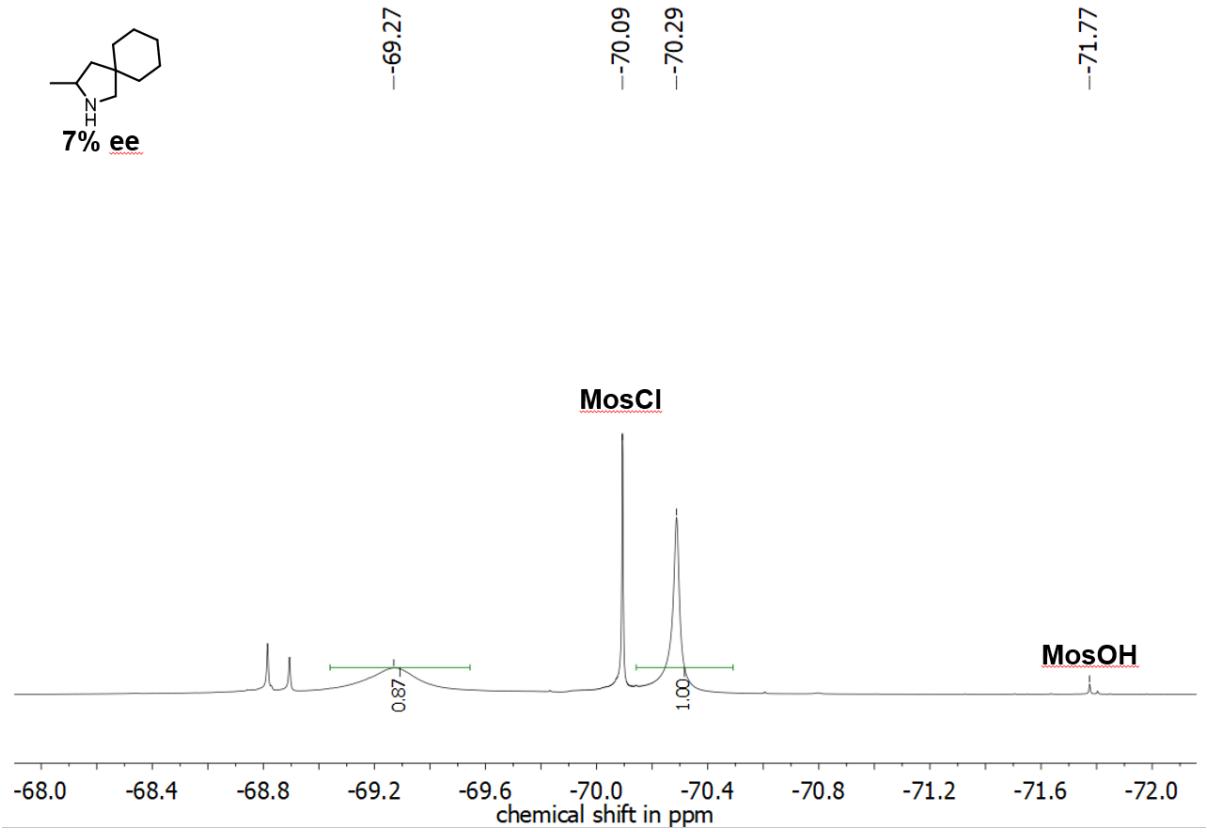


Figure S51: Determination of the enantiomeric excess for the cyclization product of $H_2C{=}CHCH_2C(CH_3)_2CH_2NH_2$ catalyzed by ^{NP}1-Mg at room temperature, using (*R*)-(−)-α-Methoxy-α-(trifluoromethyl)phenylacetyl chloride.

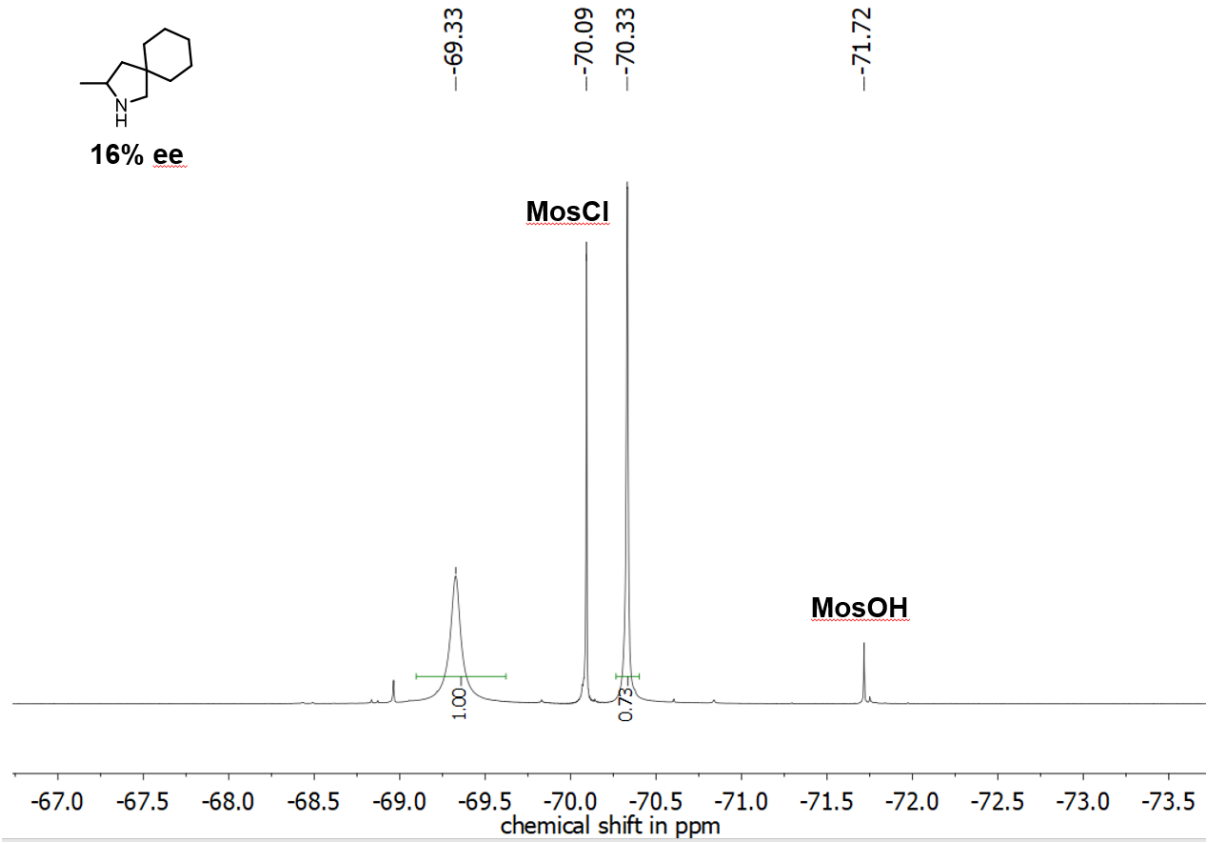


Figure S52: Determination of the enantiomeric excess for the cyclization product of $H_2C{=}CHCH_2C(CH_2)_5CH_2NH_2$ catalyzed by ^{DPM}1-Ca at room temperature, using (*R*)-(−)-α-Methoxy-α-(trifluoromethyl)phenylacetyl chloride.

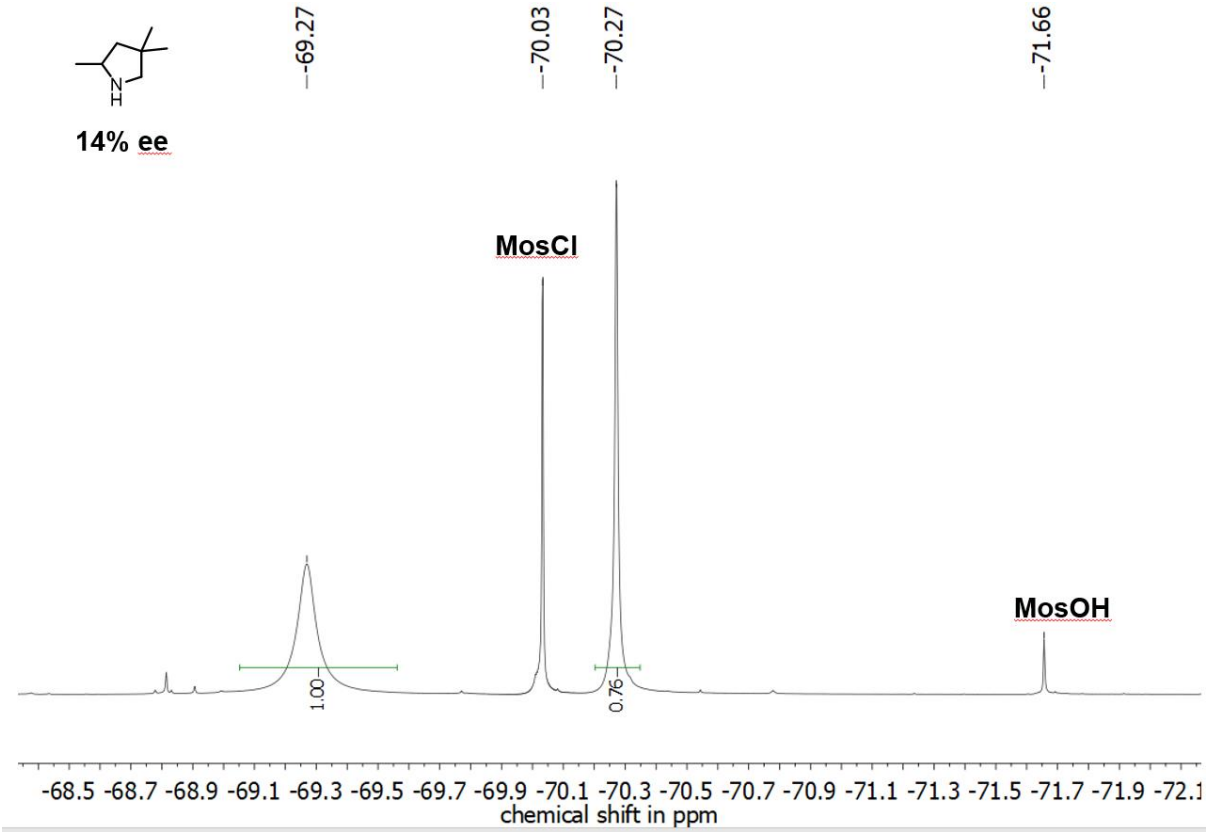


Figure S53: Determination of the enantiomeric excess for the cyclization product of $H_2C{=}CHCH_2C(CH_3)_2CH_2NH_2$ catalyzed by ^{DPM}1-Ca at room temperature, using (*R*)-(−)-α-Methoxy-α-(trifluoromethyl)phenylacetyl chloride.

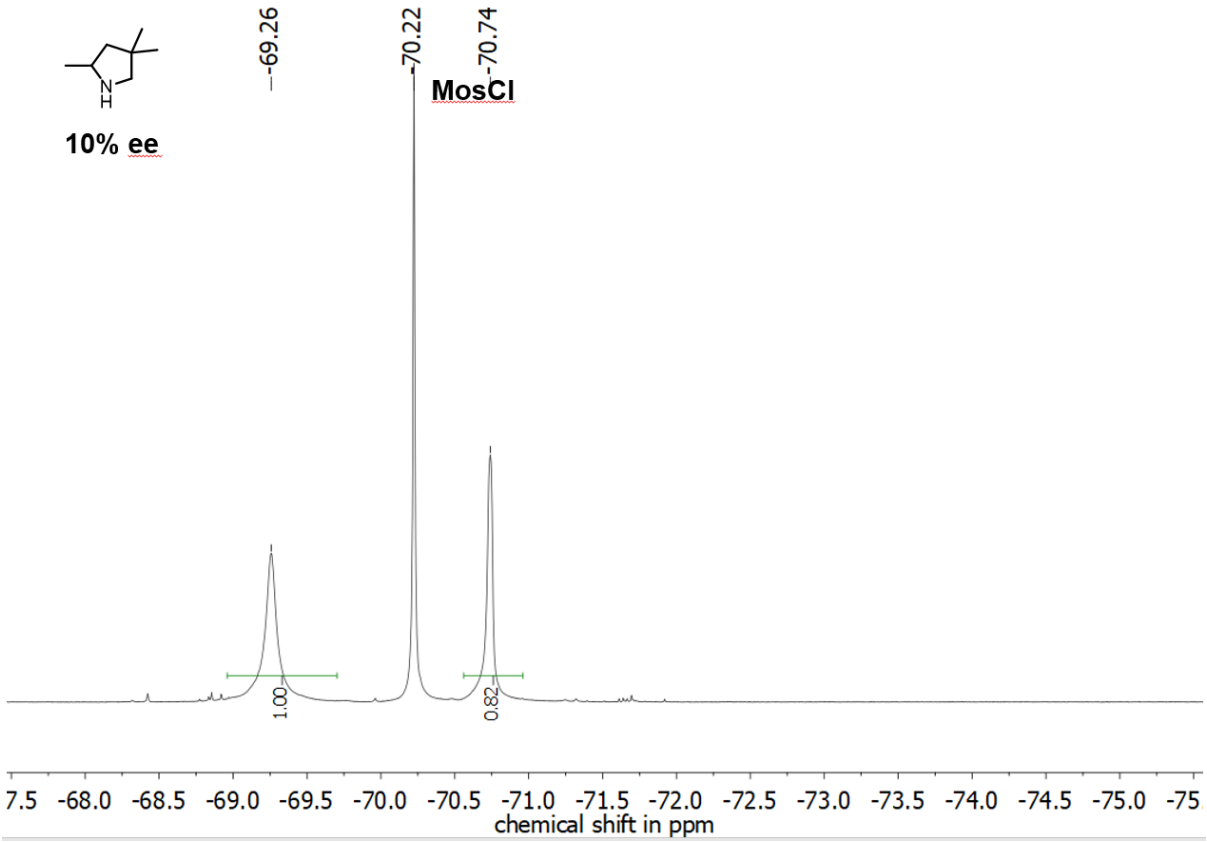


Figure S54: Determination of the enantiomeric excess for the cyclization product of $H_2C{=}CHCH_2C(CH_3)_2CH_2NH_2$ catalyzed by ^{NP}1-Ca at room temperature, using (*R*)-(−)-α-Methoxy-α-(trifluoromethyl)phenylacetyl chloride.

1.7. Crystal structure determination

The crystal structure data of the compounds mentioned below has been deposited with the Cambridge Crystallographic Data Centre. CCDC 2056448 (^{NP}1-Mg), 2056449 (^{NP}1-Ca), 2056450 (^{DBS}1-Ca), 2056451 (^{DPM}1-Ca), 2056452 (^{DPP}1-Ca), and 2056453 (^{QUIN}1-Ca), contain the supplementary crystallographic data for the compounds. This data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

1.7.1 Crystal structure of ^{NP}1-Mg

A yellow crystal of compound ^{NP}1-Mg was embedded in inert perfluoropolyalkylether (viscosity 1800 cSt; ABCR GmbH) and mounted using a Hampton Research CryoLoop. The crystal was then flash cooled to 100.0(6) K in a nitrogen gas stream and kept at this temperature during the experiment. The crystal structure was measured on an Agilent SuperNova diffractometer with Atlas S2 detector using a CuKα microfocus source. The measured data was processed with the CrysAlisPro (v40.67a) software package.[S9] Using Olex2,[S10] the structure was solved with the ShelXT[S11] structure solution program using Intrinsic Phasing and refined with the ShelXL[S12] refinement package using Least Squares Minimization. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. The asymmetric unit contains symmetry-independent molecules. Disorder of the following moieties was observed: One naphthyl subunit, three of the four THF ligands and one neopentyl group. The disorder was modeled with the help of similarity restraints (SIMU, SADI) and rigid bond restraints (RIGU).[S13] The relative occupancies of the two alternative orientations of each group were refined to 0.568(18)/0.432(18) (THF 1), 0.727(8)/0.273(8) (THF 2), 0.52(3)/0.48(3) (THF 3), 0.64(2)/0.36(2) (naphthyl) and 0.65(3)/0.35(2) (Np), respectively.

Table S2: Crystal data and structure refinement for ^{NP}1-Mg.

Identification code	hasj160602a
Empirical formula	$C_{38}H_{50}MgN_2O_2$
Formula weight	591.11
Temperature/K	100.0(6)
Crystal system	monoclinic
Space group	$P2_1$
a/Å	10.05338(11)
b/Å	18.29549(18)
c/Å	19.0563(2)
α/°	90
β/°	100.7365(10)
γ/°	90
Volume/Å^3	3443.69(6)
Z	4
ρ_{calc}/g·cm^{-3}	1.140
μ/mm^{-1}	0.698
F(000)	1280.0
Crystal size/mm^3	0.315 × 0.159 × 0.045
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	6.756 to 147.35
Index ranges	-12 ≤ h ≤ 8, -22 ≤ k ≤ 22, -22 ≤ l ≤ 23
Reflections collected	38522
Independent reflections	13501 [R_{int} = 0.0331, R_{sigma} = 0.0311]
Data/restraints/parameters	13501/1712/1038
Goodness-of-fit on F^2	0.983
Final R indexes [I>=2σ (I)]	R_1 = 0.0312, wR_2 = 0.0799
Final R indexes [all data]	R_1 = 0.0330, wR_2 = 0.0816
Largest diff. peak/hole / e Å^{-3}	0.23/-0.24

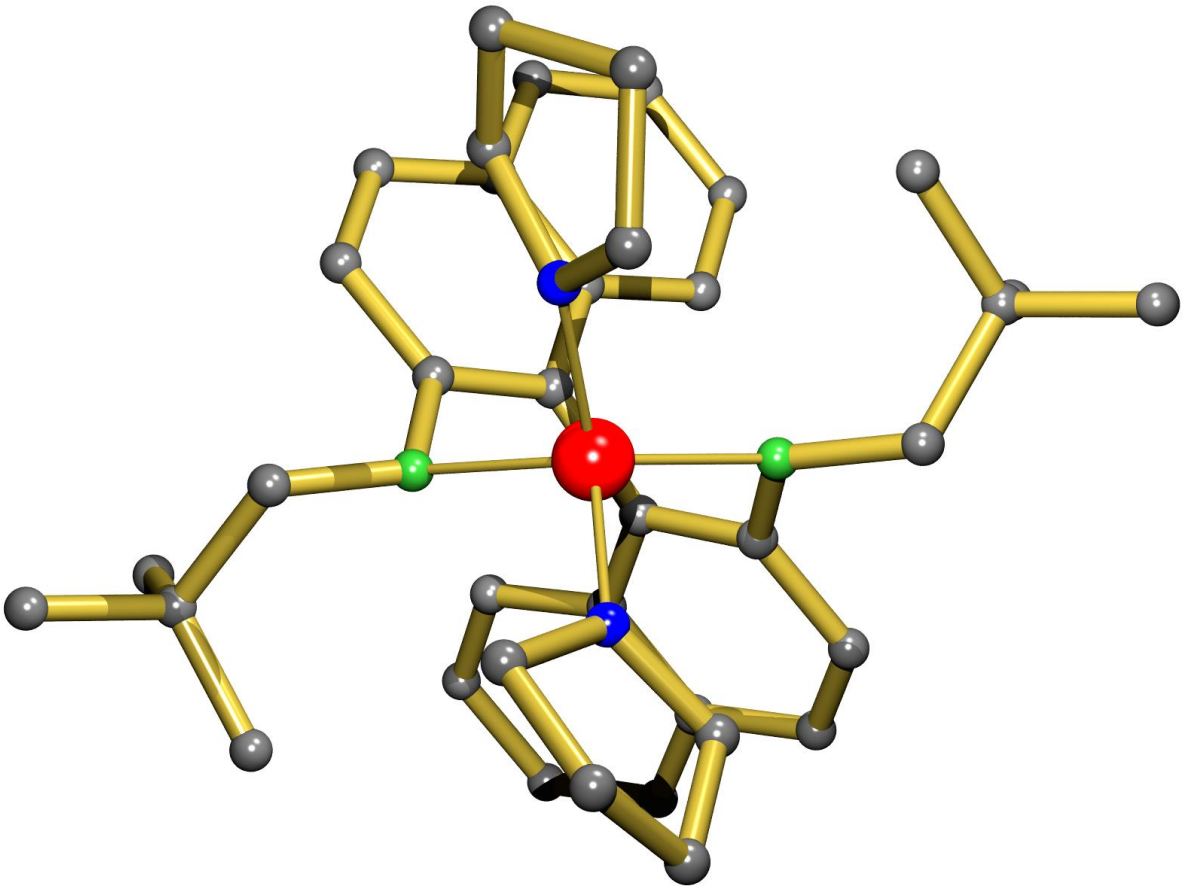


Figure S55: Crystal structure of ^{NP}1-Mg.

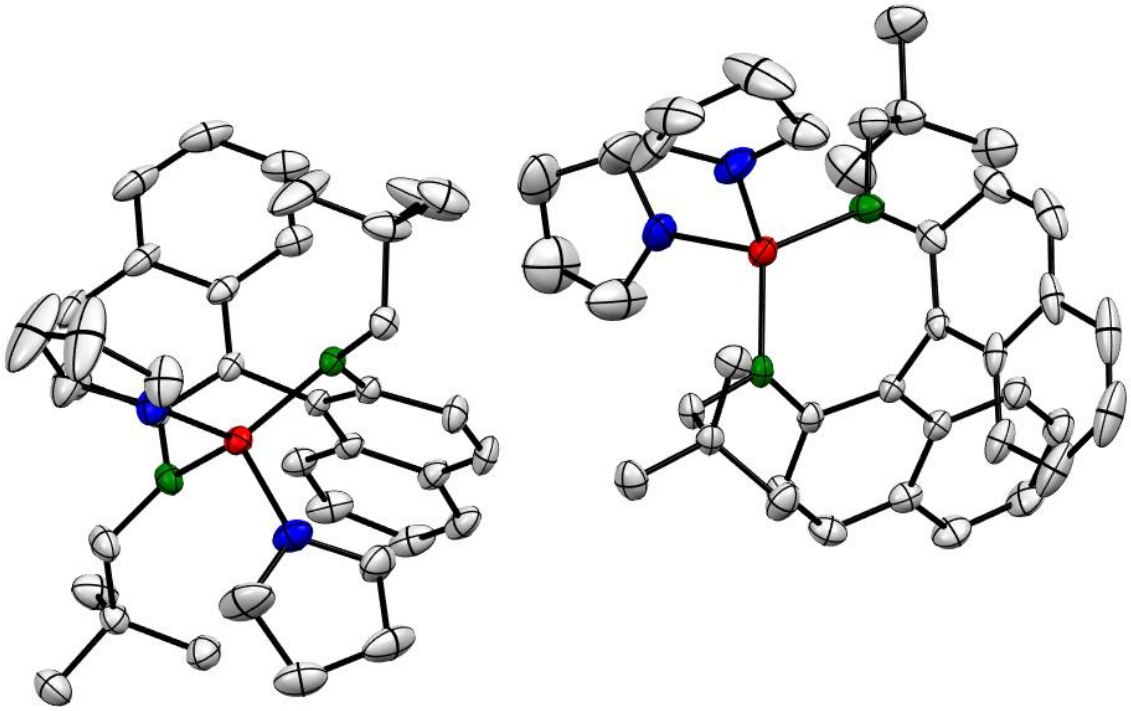


Figure S56: ORTEP plot of ^{NP}1-Mg. Ellipsoids are at 50% probability.

1.7.2 Crystal structure of ^{DBS}1-Ca

A yellow crystal of compound ^{DBS}1-Ca was embedded in inert perfluoropolyalkylether (viscosity 1800 cSt; ABCR GmbH) and mounted using a Hampton Research CryoLoop. The crystal was then flash cooled to 100.0(2) K in a nitrogen gas stream and kept at this temperature during the experiment. The crystal structure was measured on an Agilent SuperNova diffractometer with Atlas S2 detector using a CuKα microfocus source. The measured data was processed with the CrysAlisPro (v40.67a) software package.[S9] The crystal under investigation suffered from non-merohedral twinning. Using Olex2,[S10] the structure was solved with the ShelXT[S11] structure solution program using Intrinsic Phasing and refined with the ShelXL[S12] refinement package using Least Squares Minimization. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. Disorder of one THF ligand and of all four co-crystallized THF molecules was observed. The disorder was modeled with the help of similarity restraints (SIMU, SADI). The relative occupancies of the two alternative orientations of each THF were refined to 0.656(18)/0.344(18) (THF 1, ligand), 0.739(7)/0.261(7) (THF 2), 0.746(8)/0.254(8) (THF 3), 0.573(9)/0.427(9) (THF 4) and 0.539(14)/0.461(14) (THF 5), respectively.

Table S3: Crystal data and structure refinement for ^{DBS}1-Ca.

Identification code	hasj160712b
Empirical formula	$C_{78}H_{94}CaN_2O_7$
Formula weight	1211.63
Temperature/K	100.0(2)
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	11.46322(13)
b/Å	18.50990(18)
c/Å	31.3065(3)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	6642.71(12)
Z	4
ρ_{calc}/g·cm^{-3}	1.212
μ/mm^{-1}	1.255
F(000)	2608.0
Crystal size/mm^3	0.325 × 0.134 × 0.115
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	8.214 to 146.978
Index ranges	-10 ≤ h ≤ 14, -22 ≤ k ≤ 22, -38 ≤ l ≤ 27
Reflections collected	44568
Independent reflections	13199 [R_{int} = 0.0329, R_{sigma} = 0.0291]
Data/restraints/parameters	13199/1640/996
Goodness-of-fit on F^2	1.035
Final R indexes [I>=2σ (I)]	R_1 = 0.0474, wR_2 = 0.1276
Final R indexes [all data]	R_1 = 0.0493, wR_2 = 0.1295
Largest diff. peak/hole / e Å^{-3}	0.42/-0.29

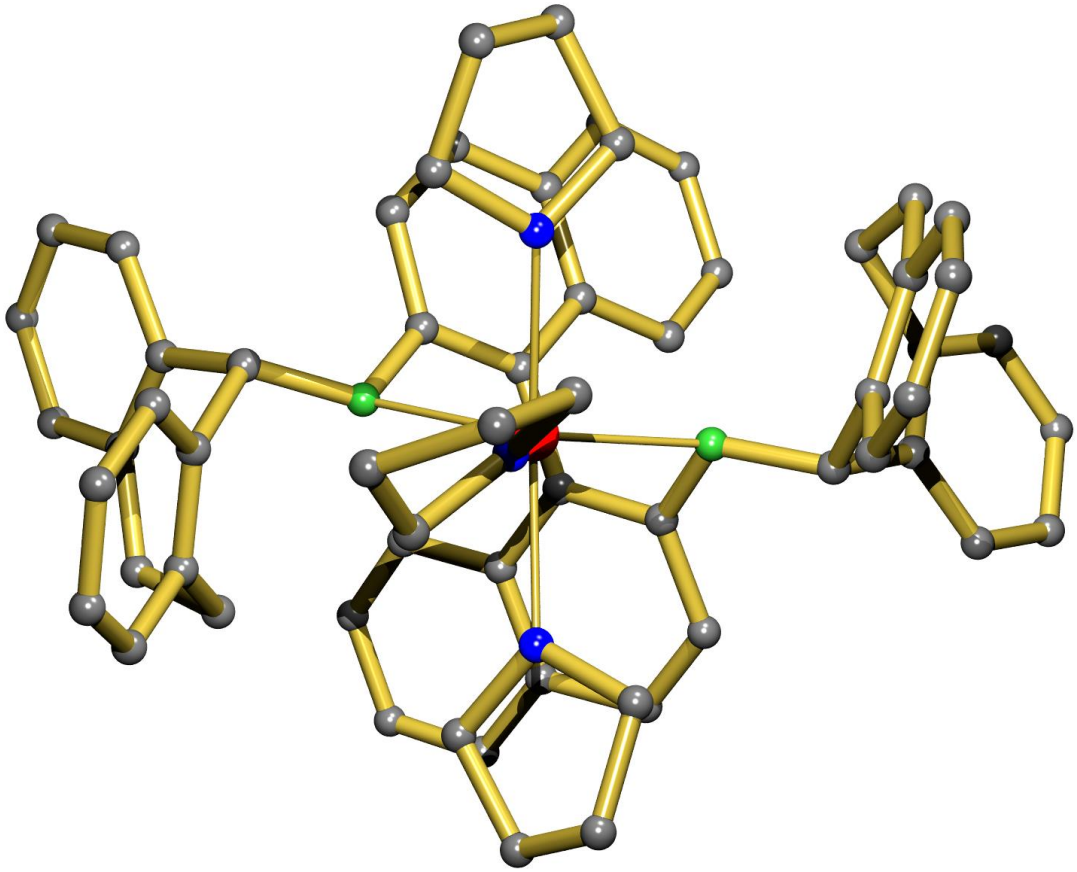


Figure S57: Crystal structure of ^{DBS}1-Ca.

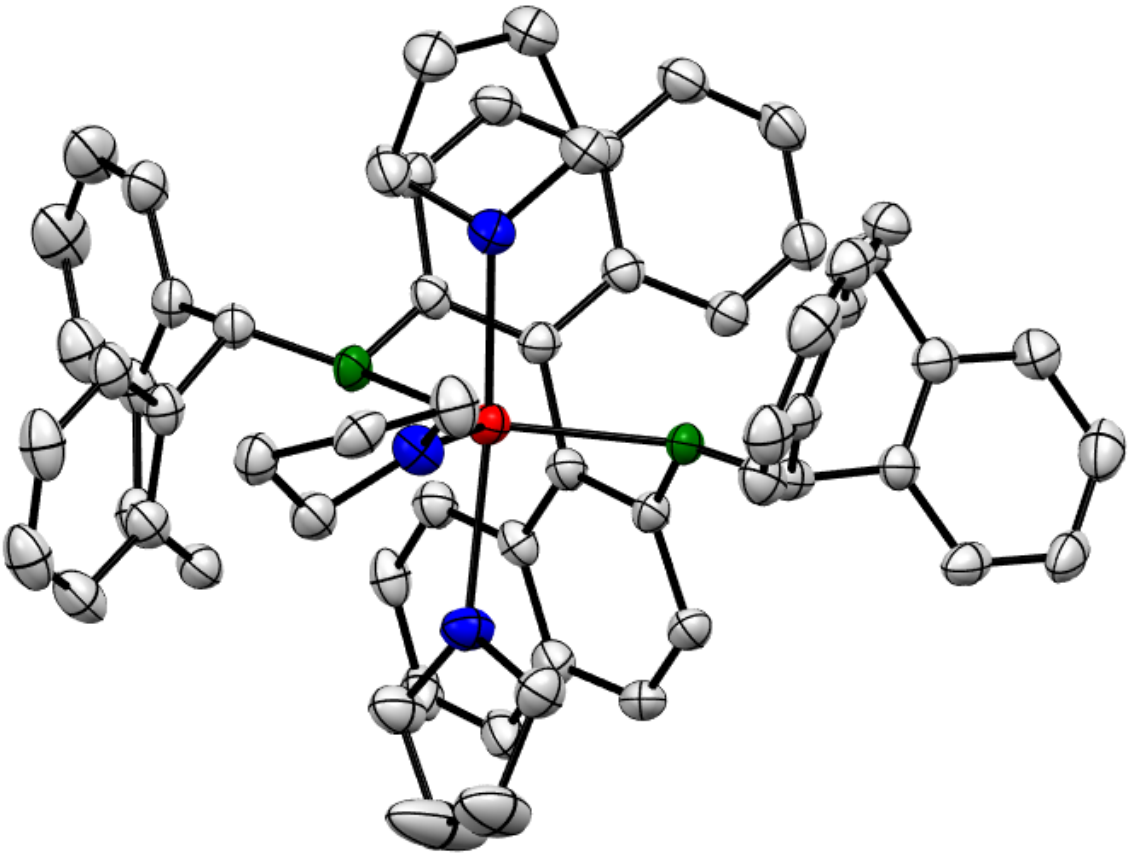


Figure S58: ORTEP plot of ^{DBS}1-Ca. Ellipsoids are at 50% probability. Co crystalized solvents were omitted for clarity.

1.7.3 Crystal structure of ^{DPM}1-Ca

A yellow crystal of the ^{DBS}1-Ca was embedded in inert perfluoropolyalkylether (viscosity 1800 cSt; ABCR GmbH) and mounted using a Hampton Research CryoLoop. The crystal was then flash cooled to 100.0(2) K in a nitrogen gas stream and kept at this temperature during the experiment. The crystal structure was measured on an Agilent SuperNova diffractometer with Atlas S2 detector using a CuKα microfocus source. The measured data was processed with the CrysAlisPro (v40.67a) software package.[S10] Using Olex2,[S11] the structure was solved with the ShelXT[S12] structure solution program using Intrinsic Phasing and refined with the ShelXL[S13] refinement package using Least Squares Minimization. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. Disorder of a THF ligand was observed and modeled with the help of similarity restraints (SIMU, SADI). The relative occupancies of the two alternative orientations of the ligand were refined to 0.858(11) and 0.142(11).

Table S4: Crystal data and structure refinement for ^{DPM}1-Ca

Identification code	hasj160726b
Empirical formula	$C_{61}H_{58}CaN_2O_2$
Formula weight	891.17
Temperature/K	100.0(2)
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	15.21280(10)
b/Å	15.60600(10)
c/Å	20.6921(2)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	4912.53(7)
Z	4
ρ_{calc}/g·cm^{-3}	1.205
μ/mm^{-1}	1.447
F(000)	1896.0
Crystal size/mm^3	0.171 × 0.098 × 0.074
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	8.116 to 147.752
Index ranges	-18 ≤ h ≤ 18, -19 ≤ k ≤ 18, -25 ≤ l ≤ 23
Reflections collected	54293
Independent reflections	9770 [R_{int} = 0.0566, R_{sigma} = 0.0291]
Data/restraints/parameters	9770/229/633
Goodness-of-fit on F^2	1.101
Final R indexes [I>=2σ (I)]	R_1 = 0.0380, wR_2 = 0.0987
Final R indexes [all data]	R_1 = 0.0394, wR_2 = 0.1004
Largest diff. peak/hole / e Å^{-3}	0.58/-0.26

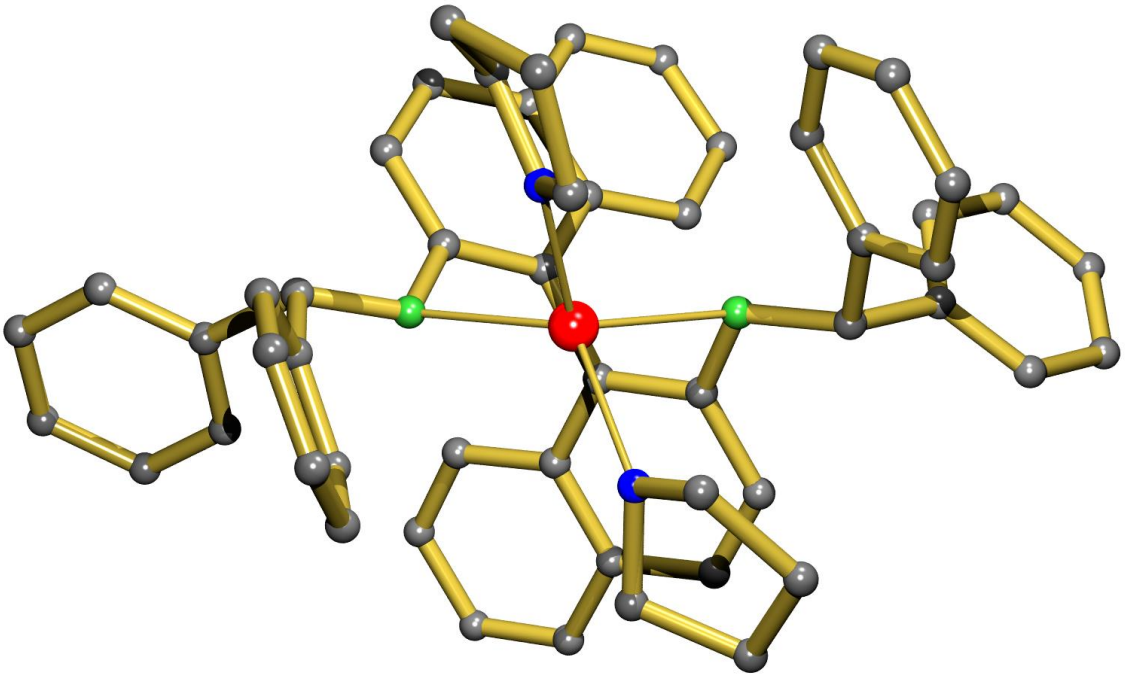


Figure S59: Crystal structure of ^{DPM}1-Ca.

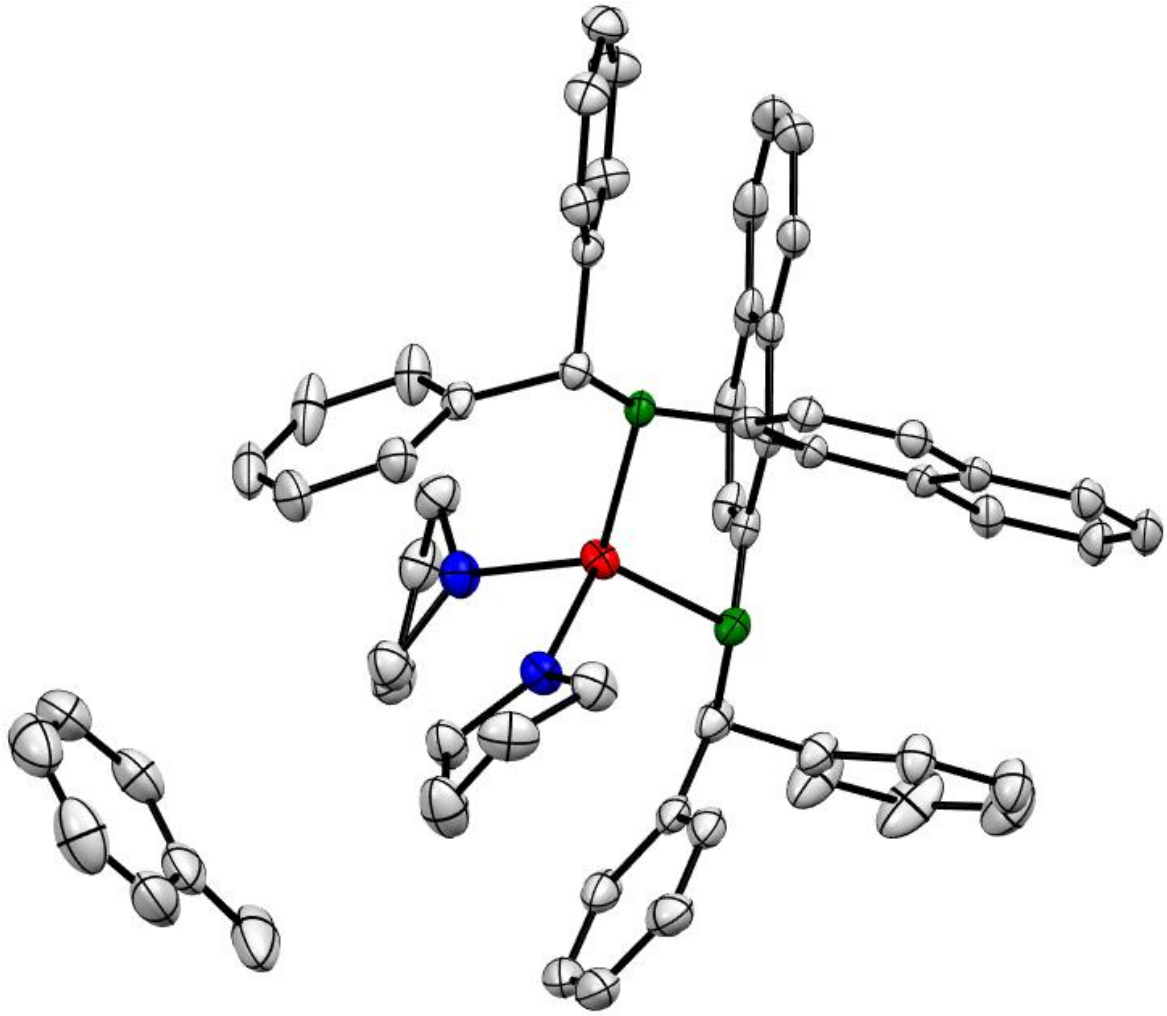


Figure S60: ORTEP plot of ^{DPM}1-Ca. Ellipsoids are at 50% probability

1.7.4 Crystal structure of ^{Np}1-Ca

An orange crystal of compound ^{Np}1-Ca·solvent was embedded in inert perfluoropolyalkylether (viscosity 1800 cSt; ABCR GmbH) and mounted using a Hampton Research CryoLoop. The crystal was then flash cooled to 100.0(2) K in a nitrogen gas stream and kept at this temperature during the experiment. The crystal structure was measured on an Agilent SuperNova diffractometer with Atlas S2 detector using a CuKα microfocus source. The measured data was processed with the CrysAlisPro (v40.67a) software package.[S9] Using Olex2,[S10] the structure was solved with the ShelXT[S11] structure solution program using Intrinsic Phasing and refined with the ShelXL[S12] refinement package using least squares minimization. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. Disorder of one half of the ^{Np}1-ligand as well as of two THF ligands and of one co-crystallized THF was observed. Modeling was done with the help of similarity restraints (SIMU, SADI) and rigid bond restraints (RIGU).[S13]. The relative occupancies of the two alternative orientations of these moieties were refined to 0.508(7)/0.492(7) (half of ^{Np}1-ligand), 0.867(7)/0.133(7) (THF ligand 1), 0.63(2)/0.37(2) (THF ligand 2) and 0.60(3)/0.40(3) (co-crystallized THF), respectively.

The disorder of additional solvent molecules (mixture of THF/Toluene) was more severe and a suitable disorder model could not be built. Therefore, the contribution of these solvent molecules to the structure factors was secured by back-Fourier transformation using the solvent mask routine[S14,S15] of the program Olex2.[S10] The solvent accessible voids treated this way had a size of 623.3 Å^3/unit cell (13.1% of the unit cell) and contained 204.6 electrons/unit cell.

Table S5: Crystal data and structure refinement for ^{NP}1-Ca

Identification code	hasj160901a
Empirical formula	$C_{46}H_{66}CaN_2O_4$[a)]
Formula weight	751.08[a)]
Temperature/K	100.0(2)
Crystal system	orthorhombic
Space group	$P2_12_12$
a/Å	21.5853(5)
b/Å	19.8516(5)
c/Å	11.0900(3)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	4752.1(2)
Z	4
ρ_{calc}/g·cm^{-3}	1.050[a)]
μ/mm^{-1}	1.434[a)]
F(000)	1632.0[a)]
Crystal size/mm^3	0.405 × 0.201 × 0.132
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	6.048 to 148.308
Index ranges	-24 ≤ h ≤ 26, -24 ≤ k ≤ 23, -13 ≤ l ≤ 11
Reflections collected	31954
Independent reflections	9461 [R_{int} = 0.0354, R_{sigma} = 0.0292]
Data/restraints/parameters	9461/2173/725
Goodness-of-fit on F^2	1.027
Final R indexes [I>=2σ (I)]	R_1 = 0.0751, wR_2 = 0.2181
Final R indexes [all data]	R_1 = 0.0813, wR_2 = 0.2273
Largest diff. peak/hole / e Å^{-3}	1.13/-0.36

a) Contribution of the masked disordered solvent neglected.

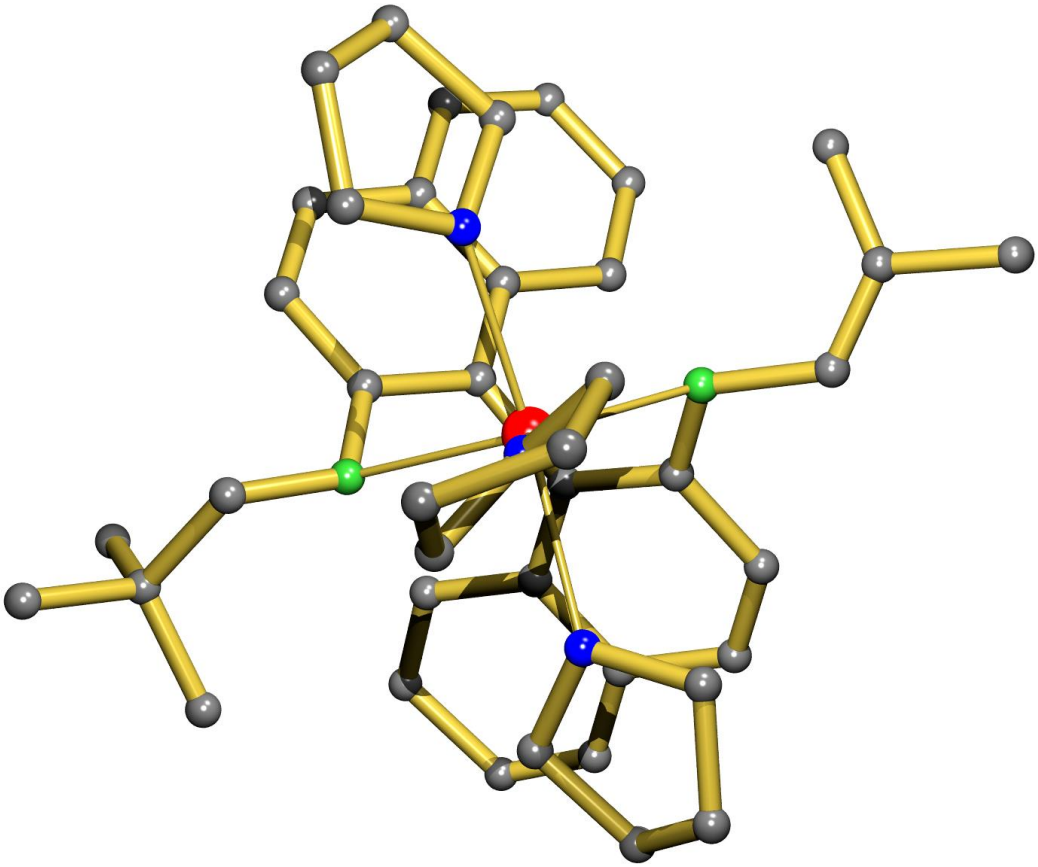


Figure S61: Crystal structure of ^{NP}1-Ca.

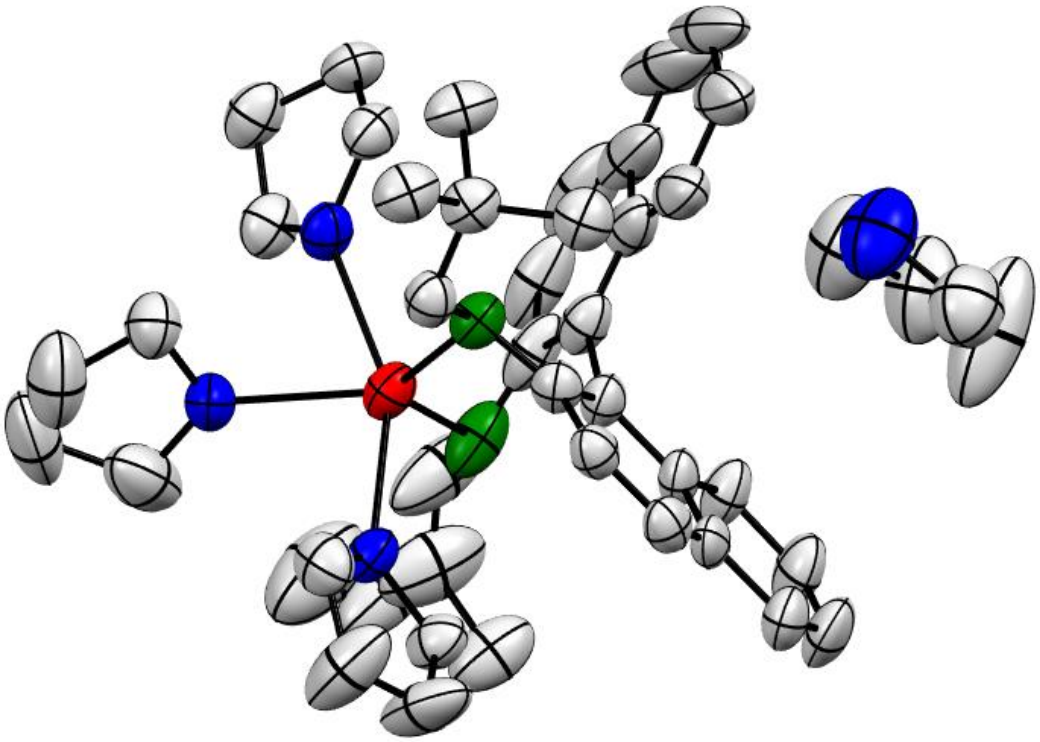


Figure S62: ORTEP plot of ^{NP}1-Ca. Ellipsoids are at 50% probability.

1.7.5 Crystal structure of ^{DPP}1-Ca

A yellow crystal of compound ^{DPP}1-Ca was embedded in inert perfluoropolyalkylether (viscosity 1800 cSt; ABCR GmbH) and mounted using a Hampton Research CryoLoop. The crystal was then flash cooled to 100.0(2) K in a nitrogen gas stream and kept at this temperature during the experiment. The crystal structure was measured on an Agilent SuperNova diffractometer with Atlas S2 detector using a CuKα microfocus source. The measured data was processed with the CrysAlisPro (v40.67a) software package.[S9] Using Olex2,[S10] the structure was solved with the ShelXT[S11] structure solution program using Intrinsic phasing and refined with the ShelXL[S12] refinement package using least squares minimization. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. The asymmetric unit contains symmetry-independent molecules.

Table S6: Crystal data and structure refinement for ^{DPP}1-Ca

Identification code	hasj170516a
Empirical formula	$C_{58}H_{54}CaN_2O_2P_2$
Formula weight	913.05
Temperature/K	100.0(2)
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	20.5914(3)
b/Å	20.9696(3)
c/Å	22.3214(3)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	9638.2(2)
Z	8
ρ_{calc}/g·cm^{-3}	1.258
μ/mm^{-1}	2.097
F(000)	3856.0
Crystal size/mm^3	0.202 × 0.199 × 0.042
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	5.782 to 147.368
Index ranges	-24 ≤ h ≤ 25, -26 ≤ k ≤ 26, -27 ≤ l ≤ 27
Reflections collected	63403
Independent reflections	19026 [R_{int} = 0.0250, R_{sigma} = 0.0230]
Data/restraints/parameters	19026/0/1171
Goodness-of-fit on F^2	1.023
Final R indexes [I>=2σ (I)]	R_1 = 0.0275, wR_2 = 0.0692
Final R indexes [all data]	R_1 = 0.0290, wR_2 = 0.0703
Largest diff. peak/hole / e Å^{-3}	0.34/-0.36

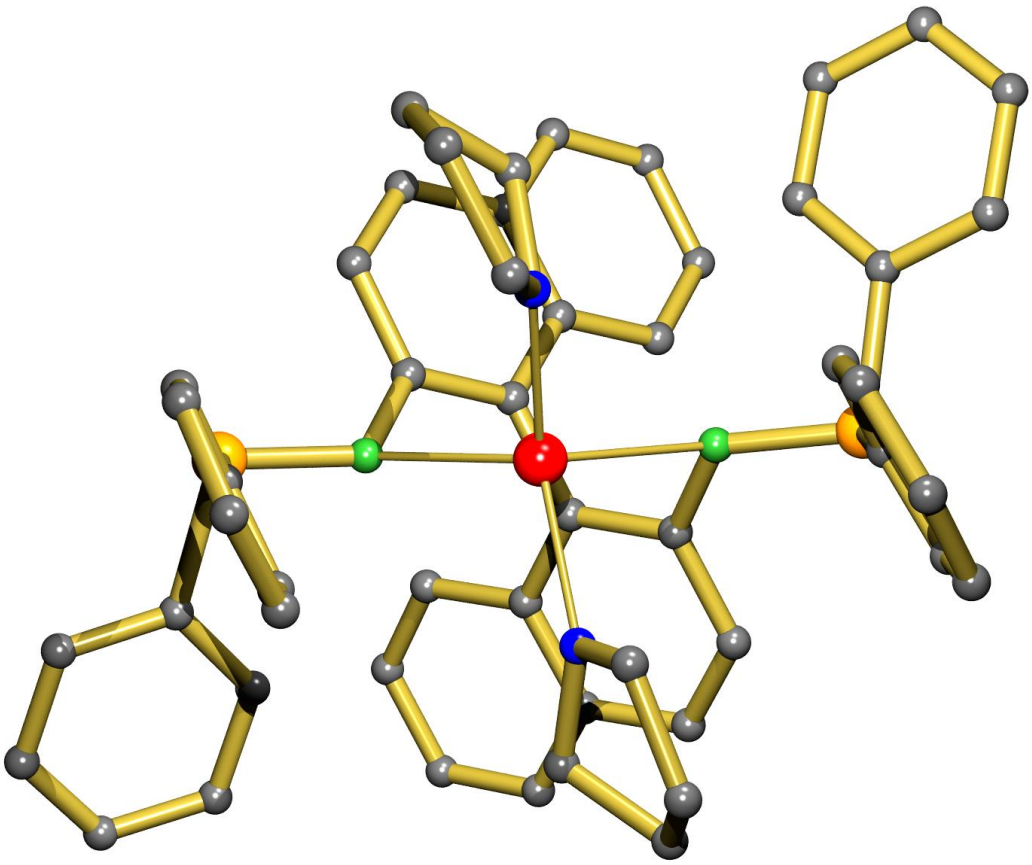


Figure S63: Crystal structure of ^{DPP}1-Ca.

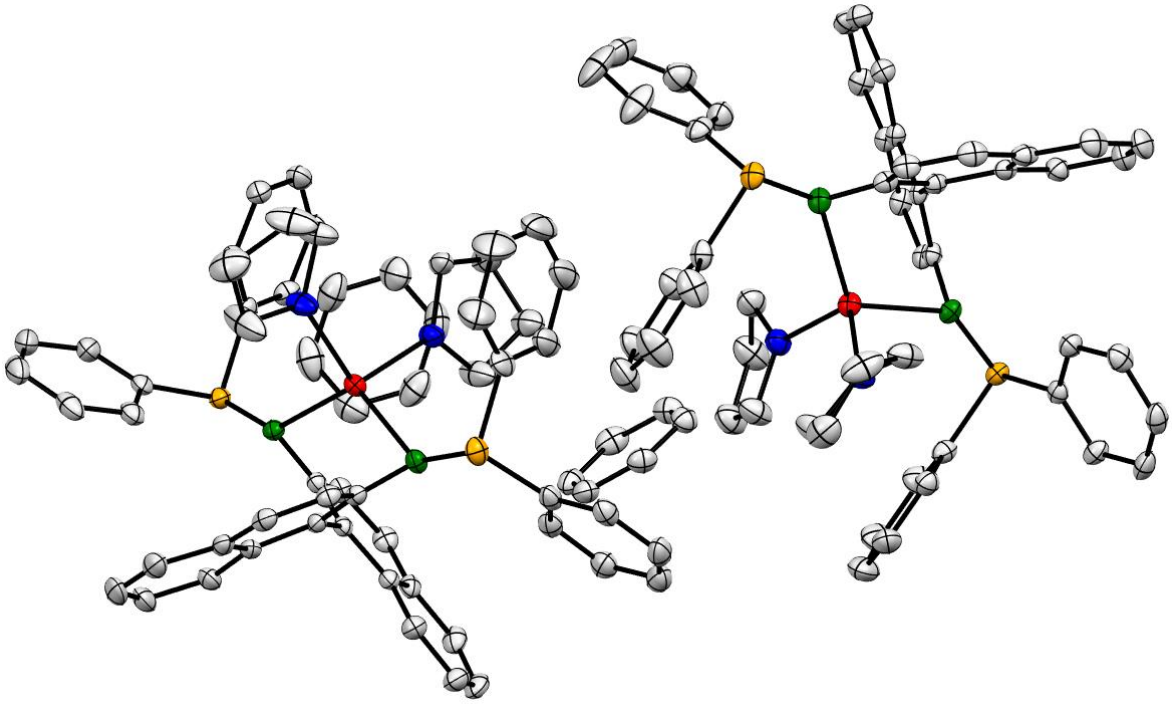


Figure S64: ORTEP plot of ^{DPP}1-Ca. Ellipsoids are at 50% probability.

1.7.6 Crystal structure of [^{QUIN}1-Ca(OEt$_2$)$_{1.76}$(thf)$_{0.24}$]·Et$_2$O

A red crystal of the composition [^{QUIN}1-Ca(OEt$_2$)$_{1.76}$(thf)$_{0.24}$]·Et$_2$O was embedded in inert perfluoropolyalkylether (viscosity 1800 cSt; ABCR GmbH) and mounted using a Hampton Research CryoLoop. The crystal was then flash cooled to 100.0(1) K in a nitrogen gas stream and kept at this temperature during the experiment. The crystal structure was measured on an Agilent SuperNova diffractometer with Atlas S2 detector using a CuKα microfocus source. The measured data was processed with the CrysAlisPro (v40.67a) software package.[S9] Using Olex2,[S10] the structure was solved with the ShelXT[S11] structure solution program using intrinsic phasing and refined with the ShelXL[S12] refinement package using least squares minimization. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. The compound exhibits substitutional disorder. One of its diethyl ether ligands is replaced partially by THF. This disorder was modeled with the help of similarity restraints (SIMU). As a result, site occupancy factors of 0.758(6) and 0.242(6) for diethylether and THF, respectively, were obtained.

Table S7: Crystal data and structure refinement for ^{QUIN}1-Ca

Identification code	hasj171016a
Empirical formula	$C_{50}H_{53.52}CaN_4O_3$
Formula weight	798.57
Temperature/K	100.0(1)
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	11.26267(11)
b/Å	11.38212(12)
c/Å	32.9097(3)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	4218.79(7)
Z	4
ρ_{calc}/g·cm^{-3}	1.257
μ/mm^{-1}	1.653
F(000)	1702.0
Crystal size/mm^3	0.341 × 0.084 × 0.07
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	8.22 to 147.234
Index ranges	-13 ≤ h ≤ 12, -13 ≤ k ≤ 13, -40 ≤ l ≤ 39
Reflections collected	40928
Independent reflections	8387 [R_{int} = 0.0341, R_{sigma} = 0.0264]
Data/restraints/parameters	8387/270/575
Goodness-of-fit on F^2	1.059
Final R indexes [I>=2σ (I)]	R_1 = 0.0349, wR_2 = 0.0783
Final R indexes [all data]	R_1 = 0.0367, wR_2 = 0.0792
Largest diff. peak/hole / e Å^{-3}	0.24/-0.36

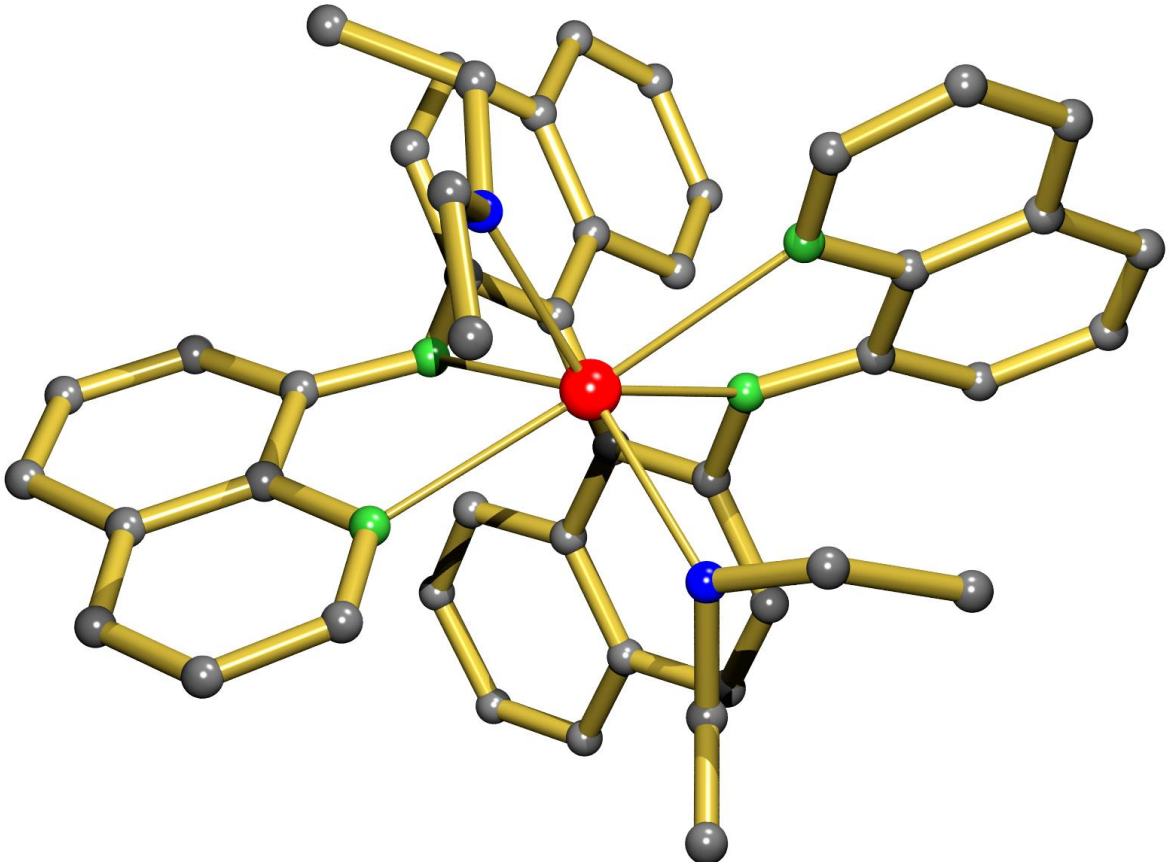


Figure S65: Crystal structure of ^{QUIN}1-Ca.

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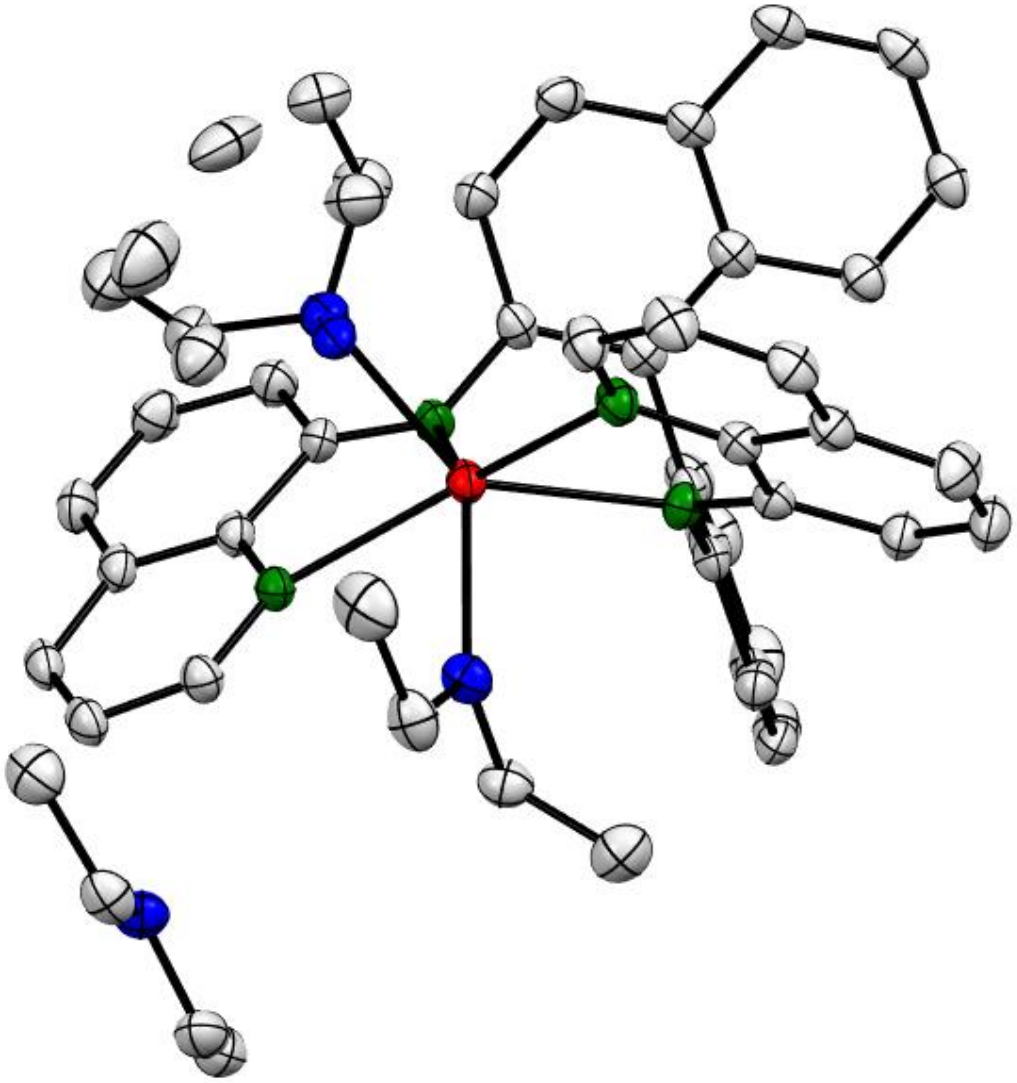

Figure S66: ORTEP plot of ^{QUIN}1-Ca. Ellipsoids are at 50% probability.

2. References:

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