Supporting Information for

Alkaline-earth complexes with macrocyclic-functionalised bis(phenolate)s and bis(fluoroalkoxide)s†

Joanna Hammoud,[a] Fatima Abou-Khalil,[a] Thierry Roisnel,[a] Vincent Dorcet,[a] Christophe Bour,[b] Vincent Gandon,[b,c] David Lebœuf,[d] Jean-François Carpentier[a] and Yann Sarazin[a]*

[a] Univ Rennes, CNRS, ISCR (Institut des Sciences Chimiques de Rennes) – UMR 6226, F-35000 Rennes, France.

[b] Institut de Chimie Moléculaire et des Matériaux d'Orsay (ICMMO), CNRS UMR 8182, Université Paris-Sud, Université Paris-Saclay, Bâtiment 420, 91405 Orsay cedex, France

[c] Laboratoire de Chimie Moléculaire (LCM), CNRS UMR 9168, Ecole Polytechnique, Institut Polytechnique de Paris, route de Saclay, 91128 Palaiseau cedex, France.

[d] Institut de Science et d'Ingénierie Supramoléculaires (ISIS), CNRS UMR 7006, Université de Strasbourg, 8 allée Gaspard Monge, 67000 Strasbourg, France

Corresponding author: yann.sarazin@univ-rennes1.fr

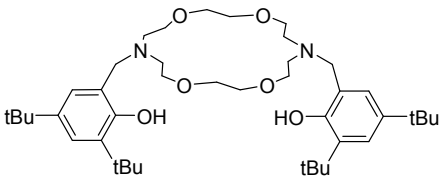
Contents

S1. Experimental procedures

General procedures.

All manipulations were performed under an inert atmosphere by using standard Schlenk techniques or in a dry, solvent-free glovebox (Jacomex; O_2 < 1 ppm, H_2O < 5 ppm). CaI_2, SrI_2 and BaI_2 beads (99.999%, Aldrich) were used as purchased. Solvents (thf, Et_2O, pentane and toluene) were purified and dried (water contents all in the range 1-5 ppm) over alumina columns (MBraun SPS). Thf was further distilled under argon from Na/benzophenone prior to use. Deuterated solvents (Eurisotop, Saclay, France) were stored in sealed ampoules over activated 3 Å molecular sieves and degassed by several freeze–thaw cycles. $[Ae\{N(SiMe_3)_2\}_2.(thf)_2]$[1] and $[Ae\{N(SiMe_3)_2\}_2]_2$[2] precursors were prepared following a published literature procedure. All NMR spectra were recorded with Bruker AM-400 or AM-500 spectrometers; assignment of the resonances was assisted by 1D (^1H, ^{13}C $\{^1H\}$) and 2D (COSY, HMBC, and HSQC) NMR experiments. Elemental analysis is provided for the proligands; attempts to obtain the reliable combustion analysis for the complexes were not successful (see Fig. S1).

$\{(N_2O_4)Ar_2O_2\}H_2$ (3-H_2): Formaldehyde (0.43 ml, 37 wt. % in H_2O, 0.57 mmol) was added to a mixture of 2,4-di-*tert*-butyl-phenol (0.95 g, 4.58 mmol) and 4,13-diaza-18-crown-6-ether (0.60 g, 2.29 mmol) in methanol (10 ml). The mixture was refluxed overnight. The volatiles were evaporated under vacuum to afford a sticky oil. Recrystallisation from hot methanol afforded the title compound as a colourless solid. Yield: 0.71 g, 45%. It is moderately soluble in aliphatic solvents, insoluble in diethyl ether, and dissolves well in thf and chlorinated solvents.



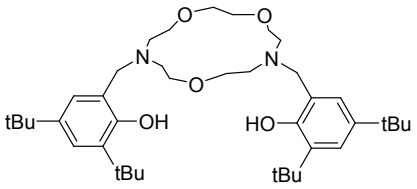
^1H NMR (400 MHz, C_6D_6, 298 K): δ = 11.05 (s, 2H, O*H*), 7.52 (d, $^4J_{HH}$ = 2.4 Hz, 2H, arom–*H*), 6.94 (d, $^4J_{HH}$ = 2.4 Hz, 2H, arom–*H*), 3.57 (s, 4H, ArCH_2N), 3.44 (t, $^3J_{HH}$ = 5.4 Hz, 8H, OCH_2CH_2O), 3.37 (s, 8H, OCH_2CH_2N), 2.70 (t, $^3J_{HH}$ = 5.4 Hz, 8H, NCH_2CH_2O), 1.74 (s, 18H, *o*-C(CH_3)$_3$), 1.38 (s, 18H, *p*-C(CH_3)$_3$) ppm.

$^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6, 298 K): δ = 155.29 (*i*-*C*OH), 140.61 (*p*-*C*$(CH_3)_3$), 136.15 (*o*-*C*$(CH_3)_3$), 123.86 (*m*-*C*H), 123.09 (*m*-*C*H), 122.47 (*o*-*C*CH_2N), 71.13 (O*C*H_2CH_2O), 69.64 (O*C*H_2CH_2N), 59.95 (Ar*C*H_2N), 54.02 (N*C*H_2CH_2O), 35.41 (*o*-*C*$(CH_3)_3$), 34.39 (*o*-*C*$(CH_3)_3$), 32.06 (*p*-C(*C*H_3)$_3$), 30.11 (*p*-C(*C*H_3)$_3$) ppm.

Anal. calc. for $C_{42}H_{70}N_2O_6$ (699.03 g.mol^{-1}): C 72.17, H 10.09, N 4.01, found C 71.8, H 10.2, N 4.1%.

HR-MS: m/z: 699.53066 $[M + H]^+$; calc. for$C_{42}H_{70}N_2O_6$: 699.5308; m/z: 721.51261 $[M + Na]^+$; calc. for $C_{42}H_{70}N_2O_6Na$: 721.5125.

{(N_2O_3)Ar_2O_2}H_2 (4-H_2): Formaldehyde (0.86 ml, 37 wt. % in H_2O, 11.45 mmol) was added to a mixture of 2,4-di-*tert*-butyl-phenol (1.89 g, 9.16 mmol) and 4,10-diaza-15-crown-5-ether (1.00 g, 4.58 mmol) in methanol (10 ml). The mixture was refluxed overnight. The resulting heavy oil was dried out of solvent, and then recrystallised from hot methanol (reflux). Yield: 1.40 g, 47%. It shows good solubility in aliphatic solvents, diethyl ether, and chlorinated solvents.



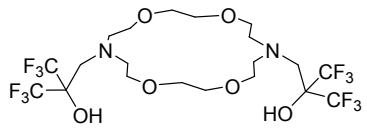
^{1}H NMR (400 MHz, C_6D_6, 298 K): δ = 10.93 (s, 2H, O*H*), 7.52 (d, $^4J_{HH}$ = 2.4 Hz, 2H, arom–*H*), 6.93 (d, $^4J_{HH}$ = 2.4 Hz, 2H, arom–*H*), 3.46 (s, 4H, ArCH_2N), 3.38 (t, $^3J_{HH}$ = 5.1 Hz, 4H, OCH_2CH_2O), 3.34 (s, 4H, OCH_2CH_2N), 3.32 (t, $^3J_{HH}$ = 5.4 Hz, 4H, OCH_2CH_2N), 2.64 (s, 4H, NCH_2CH_2O), 2.57 (t, $^3J_{HH}$ = 5.1 Hz, 4H, NCH_2CH_2O), 1.73 (s, 18H, *p*-C(CH_3)$_3$), 1.38 (s, 18H, *o*-C(CH_3)$_3$) ppm.

^{13}C{^{1}H} NMR (100 MHz, C_6D_6, 298 K): δ = 203.72 (*i*-*C*OH), 155.30 (*p*-*C*C(CH$_3$)$_3$), 140.58 (*o*-*C*C(CH$_3$)$_3$), 136.14 (*o*-*C*CH$_2$N), 123.85 (*m*-*C*H), 123.12 (*m*-*C*H), 122.55 (*m*-*C*H), 70.85 (O*C*H$_2$CH$_2$O), 69.39 (O*C*H$_2$CH$_2$N), 68.64 (O*C*H$_2$CH$_2$N), 60.40 (Ar*C*H$_2$N), 54.60 (N*C*H$_2$CH$_2$O), 54.33 (N*C*H$_2$CH$_2$O), 35.38 (*p*-*C*(CH$_3$)$_3$), 34.39 (*o*-*C*(CH$_3$)$_3$), 32.06 (*p*-C(*C*H$_3$)$_3$), 30.10 (*o*-C(*C*H$_3$)$_3$) ppm.

Anal. calc for $C_{40}H_{66}N_2O_5$ (654.98 g.mol^{-1}): C 73.35, H 10.16, N 4.28%; found C 73.1, H 10.1, N 4.2%.

HR-MS: m/z: 655.504 [M + H]$^+$; calc for $C_{40}H_{67}N_2O_5$: 655.50445; m/z: 677.4854 [M + Na]$^+$; calc for $C_{40}H_{66}N_2O_5Na$: 677.48639.

{(N_2O_4)$R^F_2O_2$}H_2 (5-H_2): A solution of 2,2-bis(trifluoromethyl)oxirane (0.62 ml, 5.70 mmol) in diethyl ether (10 ml) was added dropwise to a solution of 4,13-diaza-18-crown-6-ether (0.60 g, 2.29 mmol) in diethyl ether (10 ml) at 0 °C. The reaction mixture was warmed slowly to room temperature and stirred for 2 days. The volatile fraction was then removed under vacuum, and the title product was obtained as a white powder. Yield: 1.24 g, 87%. It displays excellent solubility in all common organic solvents, including aliphatic hydrocarbons.



^{1}H NMR (400 MHz, C_6D_6, 298 K): δ = 6.63 (s, 2H, O*H*), 3.24 (s, 8H, OCH_2CH_2O), 3.16 (t, $^3J_{HH}$ = 5.2 Hz, 8H, OCH_2CH_2N), 2.72 (s, 4H, C(CF$_3$)$_2$CH_2), 2.47 (t, $^3J_{HH}$ = 4.9 Hz, 8H, NCH_2CH_2O) ppm.

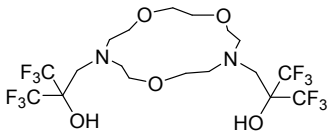
^{13}C{^{1}H} NMR (100 MHz, C_6D_6, 298 K): δ = 125.97 (q, $^1J_{CF}$ = 287.6 Hz, *C*F$_3$), 73.62 (hept, $^2J_{CF}$ = 28.5 Hz, *C*(CF$_3$)$_2$), 71.01 (O*C*H$_2$CH$_2$O), 69.58 (O*C*H$_2$CH$_2$N), 56.78 (N*C*H$_2$CH$_2$O), 54.58 (C(CF$_3$)$_2$*C*H$_2$) ppm.

^{19}F{^{1}H} NMR (376 MHz, C_6D_6, 298 K): δ = –77.13 (s, 12F, C*F*$_3$) ppm.

Anal. calc for $C_{20}H_{30}F_{12}N_2O_6$ (622.45 g.mol^{-1}): C 38.59, H 4.86, N 4.50%, found C 40.00, H 5.02, N 4.51%.

HR-MS: m/z: 623.1985 $[M + H]^+$; calc for $C_{20}H_{30}F_{12}N_2O_6$: 623.1990; m/z: 645.18045 $[M + Na]^+$; calc for $C_{20}H_{30}F_{12}N_2O_6Na$: 645.1811.

{(N_2O_3)$R^F_2O_2$}H_2 (6-H_2): A solution of 2,2–bis(trifluoromethyl)oxirane (1.25 ml, 11.45 mmol) in diethyl ether (10 ml) was added dropwise to a solution of 4,10-diaza-15-crown-5-ether (1.00 g, 4.58 mmol) in diethyl ether (10 ml) at 0 ˚C. The reaction mixture was warmed slowly to room temperature and stirred for 2 days. The volatile fraction was then removed under vacuum, and the title product was obtained as a white powder. Yield: 2.30 g, 87%. It displays excellent solubility in all common organic solvents, including aliphatic hydrocarbons.



^{1}H NMR (400 MHz, C_6D_6, 298 K): δ = 6.62 (s, 2H, O*H*), 3.20 (s, 4H, OCH_2CH_2O), 3.04 (m, 8H, OCH_2CH_2N), 2.62 (s, 4H, C(CF_3)$_2$CH_2), 2.40-2.31 (m, 8H, NCH_2CH_2O).

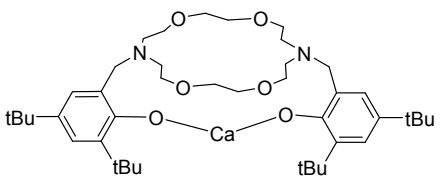
^{13}C{^{1}H} NMR (100 MHz, C_6D_6, 298 K): δ = 125.90 (q, $^1J_{CF}$ = 285.0 Hz, *C*F_3), 73.46 (hept, $^2J_{CF}$ = 28.5 Hz, *C*(CF_3)$_2$), 70.25 (O*C*H_2CH_2O), 68.92 (O*C*H_2CH_2N), 68.49 (O*C*H_2CH_2N), 57.34 (N*C*H_2CH_2O), 56.35 (N*C*H_2CH_2O), 54.49 (C(CF_3)$_2$*C*H_2N) ppm.

^{19}F{^{1}H} NMR (376 MHz, C_6D_6, 298 K): δ = –77.19 (s, 12F, C*F*$_3$) ppm.

Anal. calc. for $C_{18}H_{26}N_2O_5F_{12}$ (578.4 g.mol^{-1}): C 37.38, H 4.53, N 4.84%; found C 37.9, H 4.2, N 4.9%.

HR-MS: m/z: 601.4552 $[M + Na]^+$; calc for $C_{18}H_{26}N_2O_5F_{12}Na$: 601.15423.

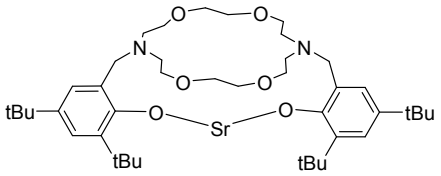
[{(N_2O_4)Ar_2O_2}Ca] (3-Ca): A solution of **3**-H_2 (0.30 g, 0.42 mmol) in difluorobenzene (10 ml) was added to a solution of [Ca{N(SiMe_3)$_2$}$_2$.(thf)$_2$] (0.22 g, 0.42 mmol) in difluorobenzene (15 ml). The reaction mixture was stirred for 2 h and the volatiles were removed under vacuum. The resulting white powder was washed with pentane (3 × 5.0 ml) and the product was dried under vacuum to constant weight. Yield: 0.21 g, 66%. The title compound shows good solubility in chlorinated solvents, thf and 1,2-difluorobenzene. However, it is insoluble in aliphatic solvents and diethyl ether.



^{1}H NMR (400 MHz, thf-d_8, 298 K): δ = 7.02 (d, $^{4}J_{HH}$ = 2.7 Hz, 2H, arom–*H*), 6.72 (d, $^{4}J_{HH}$ = 2.6 Hz, 2H, arom–*H*), 4.76 (d, $^{4}J_{HH}$ = 11.1 Hz, 2H, ArCH_2N), 4.01-3.90 (m, 4H, OCH_2CH_2O), 3.72 (m, 2H, OCH_2CH_2O), 3.64-3.60 (m, 4H, OCH_2CH_2N), 3.55-3.43 (m, 4H, OCH_2CH$_2$N), 3.41-3.31 (m, 2H, NCH_2CH$_2$O), 3.12-3.05 (m, 2H, NCH_2CH$_2$O), 2.94 (d, $^{4}J_{HH}$ = 11.2 Hz, 2H, ArCH_2N), 2.76-2.53 (m, 4H, NCH_2CH$_2$O), 2.32 (m, 2H, OCH_2CH_2O), 1.49 (s, 18H, *p*-C(CH_3)$_3$), 1.20 (s, 18H, *o*-C(CH_3)$_3$) ppm.

^{13}C{^{1}H} NMR (100 MHz, thf-d_8, 298 K): δ = 167.76 (*i*-*C*O), 134.99 (*p*-*C*(CH$_3$)$_3$), 130.20 (*o*-*C*C(CH$_3$)$_3$), 127.11 (*m*-*C*H), 124.77 (*o*-*C*CH$_2$N), 123.33 (*m*-*C*H), 71.90 (O*C*H$_2$CH$_2$N), 70.62 (O*C*H$_2$CH$_2$N), 69.41 (N*C*H$_2$CH$_2$O), 69.35 (O*C*H$_2$CH$_2$O), 64.99 (Ar*C*H$_2$N), 57.81 (O*C*H$_2$CH$_2$O), 50.79 (N*C*H$_2$CH$_2$O), 35.79 (*p*-*C*(CH$_3$)$_3$), 34.38 (*o*-*C*(CH$_3$)$_3$), 32.80 (*o*-C(*C*H$_3$)$_3$), 30.49 (*p*-C(*C*H$_3$)$_3$) ppm.

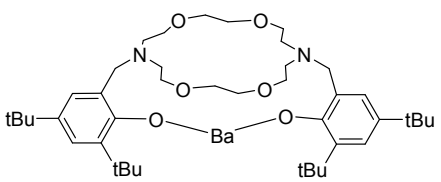
[{(N$_2$O$_4$)Ar$_2$O$_2$}Sr] (3-Sr): Following the same protocol described for **3-Ca,** the complex **3-Sr** was obtained by reacting (0.30 g, 0.42 mmol) of **3**-H$_2$ in difluorobenzene (10 ml) with a solution of [Sr{N(SiMe$_3$)$_2$}$_2$.(thf)$_2$] (0.24 g, 0.42 mmol) in difluorobenzene (10 ml). The title compound was obtained as a white powder. Yield: 0.25 g, 73%. It is insoluble in aliphatic solvents and diethyl ether; yet, it presents good solubility in chlorinated solvents, thf, and 1.2-difluorobenzene.



^{1}H NMR (400 MHz, CD_2Cl_2, 298 K): δ = 7.10 (m, 2H, arom–*H*), 6.82 (m, 2H, arom–*H*), 4.29 (d, $^{4}J_{HH}$ = 11.3 Hz, 2H, ArCH_2N), 3.93 – 3.76 (m, 2H, OCH_2CH_2O), 3.70 – 3.40 (m, 12H, overlapping OCH_2CH$_2$N & NCH_2CH$_2$O), 3.12 (m, 2H, OCH_2CH_2O), 3.04 (d, $^{4}J_{HH}$ = 10.8 Hz, 2H, ArCH_2N), 3.00 – 2.85 (m, 2H, OCH_2CH_2O), 2.77 – 2.53 (m, 2H, OCH_2CH_2O), 2.66 – 2.55 (m, 2H, NCH_2CH$_2$O), 2.48 – 2.35 (m, 2H, NCH_2CH$_2$O), 1.48 (s, 9H, *p*-C(CH_3)$_3$), 1.45 (s, 9H, *p*-C(CH_3)$_3$), 1.25 (s, 18H, *o*-C(CH_3)$_3$) ppm.

^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2, 298 K): δ = 166.90 (*i*-*C*O), 136.13 (*p*-*C*C(CH$_3$)$_3$), 135.83 (*p*-*C*C(CH$_3$)$_3$), 130.96 (*o*-*C*C(CH$_3$)$_3$), 130.62 (*o*-*C*C(CH$_3$)$_3$), 127.32 (*o*-*C*CH$_2$N), 124.39 (*o*-*C*C(CH$_3$)$_3$), 123.67 (*m*-*C*H), 123.60 (*m*-*C*H), 71.44 (O*C*H$_2$CH$_2$N), 70.38 (O*C*H$_2$CH$_2$N), 69.37 (N*C*H$_2$CH$_2$O), 69.08 (O*C*H$_2$CH$_2$O), 68.42 (O*C*H$_2$CH$_2$O), 64.58 (Ar*C*H$_2$N), 58.78 (N*C*H$_2$CH$_2$O), 57.52 (N*C*H$_2$CH$_2$O), 54.53 (O*C*H$_2$CH$_2$O), 50.22 (N*C*H$_2$CH$_2$O), 35.65 (*p*-*C*(CH$_3$)$_3$), 34.11 (*o*-*C*(CH$_3$)$_3$), 32.40 (*o*-C(*C*H$_3$)$_3$), 30.10 (*p*-C(*C*H$_3$)$_3$) ppm.

[{(N$_2$O$_4$)Ar$_2$O$_2$}Ba] (3-Ba): Following the same protocol described for **3-Ca,** the complex **3-Ba** was obtained by reacting (0.30 g, 0.42 mmol) of **3**-H$_2$ in difluorobenzene (10 ml) with a solution of [Ba{N(SiMe$_3$)$_2$}$_2$.(thf)$_2$] (0.26 g, 0.42 mmol) in

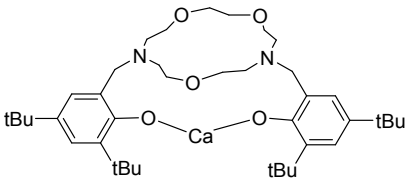


difluorobenzene (10 ml). The title compound was obtained as a white powder. Yield: 0.26 g, 73%. The title compound was only soluble in chlorinated solvents.

^{1}H NMR (400 MHz, CD_2Cl_2, 298 K): δ = 7.09 (m, 2H, arom–*H*), 6.82 (m, 2H, arom–*H*), 3.80 (m, 2H, ArCH_2N), 3.51-3.41 (m, 16H, overlapping OCH_2CH_2O & OCH_2CH_2N), 3.31 (d, $^{3}J_{HH}$ = 7.2 Hz, 2H, NCH_2CH_2O), 3.00 (d, $^{4}J_{HH}$ = 10.3 Hz, 2H, ArCH_2N), 2.95 (m, 2H, NCH_2CH_2O), 2.51 (m, 4H, NCH_2CH_2O), 1.44 (s, 6H, *p*-C(CH_3)$_3$), 1.41 (s, 12H, *p*-C(CH_3)$_3$), 1.25 (s, 12H, *o*-C(CH_3)$_3$), 1.23 (s, 6H, *o*-C(CH_3)$_3$) ppm.

^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2, 298 K): δ = 166.31 (*i*-*C*O), 136.82 (*p*-*C*C(CH$_3$)$_3$), 136.56 (*p*-*C*C(CH$_3$)$_3$), 130.79 (*o*-*C*C(CH$_3$)$_3$), 130.45 (*o*-*C*C(CH$_3$)$_3$), 127.28 (*o*-*C*CH$_2$N), 126.71 (*o*-*C*CH$_2$N), 124.65 (*m*-*C*H), 123.86 (*m*-*C*H), 123.74 (*m*-*C*H), 123.49 (*m*-*C*H), 70.34 (O*C*H$_2$CH$_2$O), 70.27 (O*C*H$_2$CH$_2$N), 70.02 (O*C*H$_2$CH$_2$N), 59.13 (Ar*C*H$_2$N), 58.59 (O*C*H$_2$CH$_2$N), 35.63 (*p*-*C*(CH$_3$)$_3$), 34.08 (*o*-*C*(CH$_3$)$_3$), 32.42 (*o*-C(*C*H$_3$)$_3$), 30.41 (*p*-C(*C*H$_3$)$_3$) ppm.

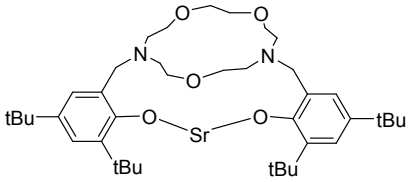
[{(N_2O_3)Ar_2O_2}Ca] (4-Ca): Following the same protocol described for **3-Ca,** the complex **4-Ca** was obtained by reacting (0.30 g, 0.46 mmol) of **4-**H_2 in diethyl ether (10 ml) with a solution of [Ca{N(SiMe$_3$)$_2$}$_2$.(thf)$_2$] (0.23 g, 0.46 mmol) in diethyl ether (10 ml). Yield: 0.24 g, 75%. The title compound shows poor solubility in aliphatic solvents and high solubility in thf and chlorinated solvents.



^{1}H NMR (400 MHz, thf-d_8, 298 K): δ = 7.03 (d, $^{4}J_{HH}$ = 2.8 Hz, 2H, arom–*H*), 6.73 (d, $^{4}J_{HH}$ = 2.7 Hz, 2H, arom–*H*), 4.04 (d, $^{4}J_{HH}$ = 11.2 Hz, 2H, ArCH_2N), 3.86-3.65 (m, 8H, OCH_2CH_2N), 3.55 (m, 2H, OCH_2CH_2O), 3.33 (m, 2H, OCH_2CH_2O), 3.24 (d, $^{4}J_{HH}$ = 11.3 Hz, 2H, ArCH_2N), 3.01 (m, 2H, NCH_2CH_2O), 2.77 (m, 2H, NCH_2CH_2O), 2.63 (m, 2H, NCH_2CH_2O), 2.51 (m, 2H, NCH_2CH_2O), 1.40 (s, 18H, *p*-C(CH_3)$_3$), 1.23 (s, 18H, *o*-C(CH_3)$_3$) ppm.

^{13}C{^{1}H} NMR (100 MHz, thf-d_8, 298 K): δ = 167.33 (*i*-*C*O), 136.25 (*p*-*C*C(CH$_3$)$_3$), 130.65 (*o*-*C*C(CH$_3$)$_3$), 126.22 (*o*-*C*CH$_2$N), 123.67 (*m*-*C*H), 123.64 (*m*-*C*H), 70.47 (O*C*H$_2$CH$_2$O), 70.17 (O*C*H$_2$CH$_2$O), 68.50 (O*C*H$_2$CH$_2$N), 66.49 (O*C*H$_2$CH$_2$N), 63.20 (Ar*C*H$_2$N), 55.15 (N*C*H$_2$CH$_2$O), 52.14 (N*C*H$_2$CH$_2$O), 36.04 (*p*-*C*(CH$_3$)$_3$), 34.42 (*o*-*C*(CH$_3$)$_3$), 32.81 (*o*-C(*C*H$_3$)$_3$), 30.92 (*p*-C(*C*H$_3$)$_3$) ppm.

[{(N_2O_3)Ar_2O_2}Sr] (4-Sr): Following the same protocol described for **3-Ca,** the complex **4-Sr** was obtained by reacting (0.30 g, 0.46 mmol) of **4-**H_2 in diethyl ether (10 ml) with a solution of

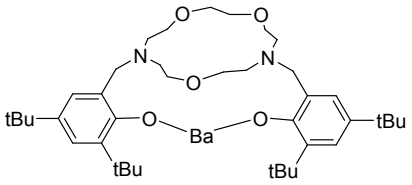


[Sr{N(SiMe$_3$)$_2$}$_2$.(thf)$_2$] (0.25 g, 0.46 mmol) in diethyl ether (10 ml). Yield: 0.23 g, 68%. The title compound is quite soluble in thf and chlorinated solvents, and insoluble in aliphatic solvents.

^{1}H NMR (400 MHz, thf-d_8, 298 K): δ = 7.02 (d, $^4J_{HH}$ = 2.7 Hz, 2H, arom–*H*), 6.70 (d, $^4J_{HH}$ = 2.7 Hz, 2H, arom–*H*), 3.94 (d, $^4J_{HH}$ = 10.8 Hz, 2H, ArC*H*$_2$N), 3.72 (m, 2H, OC*H*$_2$C*H*$_2$O), 3.54 (m, 8H, OC*H*$_2$CH$_2$N), 3.15 (d, $^4J_{HH}$ = 10.3 Hz, 2H, ArC*H*$_2$N), 3.11-3.06 (m, 2H, OC*H*$_2$C*H*$_2$O), 2.99 (m, 2H, NC*H*$_2$CH$_2$O), 2.65 (m, 2H, NC*H*$_2$CH$_2$O), 2.53 (m, 2H, NC*H*$_2$CH$_2$O), 2.37 (m, 2H, NC*H*$_2$CH$_2$O), 1.46 (s, 18H, *p*-C(C*H*$_3$)$_3$), 1.21 (s, 18H, *o*-C(C*H*$_3$)$_3$) ppm.

^{13}C{^{1}H} NMR (100 MHz, thf-d_8, 298 K): δ = 168.12 (*i*-*C*O), 136.04 (*p*-*C*C(CH$_3$)$_3$), 129.80 (*o*-*C*C(CH$_3$)$_3$), 126.75 (*o*-*C*CH$_2$N), 124.28 (*m*-*C*H), 123.42 (*m*-*C*H), 71.09 (O*C*H$_2$CH$_2$O), 70.36 (O*C*H$_2$CH$_2$O), 70.01 (O*C*H$_2$CH$_2$N), 65.52 (Ar*C*H$_2$N), 53.35 (N*C*H$_2$CH$_2$O), 36.18 (*p*-*C*(CH$_3$)$_3$), 34.37 (*o*-*C*(CH$_3$)$_3$), 32.83 (*o*-C(*C*H$_3$)$_3$), 30.77 (*p*-C(*C*H$_3$)$_3$) ppm.

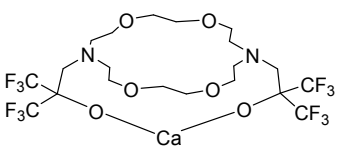
[{(N$_2$O$_3$)Ar$_2$O$_2$}Ba] (4-Ba): Following the same protocol described for **3-Ca,** the complex **4-Ba** was obtained by reacting (0.22 g, 0.33 mmol) of **4-**H$_2$ in diethyl ether (10 ml) with a solution of [Ba{N(SiMe$_3$)$_2$}$_2$.(thf)$_2$] (0.20 g, 0.33 mmol) in diethyl ether (10 ml). Yield 0.18 g, 68%. The title compound presents high solubility in difluorobenzene, thf and chlorinated solvents. It is mostly insoluble in diethyl ether and aliphatic solvents.



^{1}H NMR (400 MHz, thf-d_8, 298 K): δ = 7.03 (d, $^4J_{HH}$ = 2.6 Hz, 2H, arom–*H*), 6.71 (d, $^4J_{HH}$ = 2.7 Hz, 2H, arom–*H*), 3.86 (s, 2H, ArC*H*$_2$N), 3.71 (t, $^3J_{HH}$ = 10.1 Hz, 2H, OC*H*$_2$C*H*$_2$O), 3.60 (s, 2H, OC*H*$_2$C*H*$_2$O), 3.56 (s, 2H, OC*H*$_2$CH$_2$N), 3.54-3.41 (m, 4H, OC*H*$_2$CH$_2$N), 3.09 (m, 4H, overlapping ArC*H*$_2$N & OC*H*$_2$CH$_2$N), 2.95 (t, $^3J_{HH}$ = 12.2 Hz, 2H, NC*H*$_2$CH$_2$O), 2.67-2.49 (m, 4H, NC*H*$_2$CH$_2$O), 2.37 (d, $^3J_{HH}$ = 13.9 Hz, 2H, NC*H*$_2$CH$_2$O), 1.46 (s, 18H, *p*-C(C*H*$_3$)$_3$), 1.21 (s, 18H, *o*-C(C*H*$_3$)$_3$) ppm.

^{13}C{^{1}H} NMR (100 MHz, thf-d_8, 298 K): δ = 167.80 (*i*-*C*O), 135.82 (*p*-*C*C(CH$_3$)$_3$), 130.02 (*o*-*C*C(CH$_3$)$_3$), 127.04 (*o*-*C*CH$_2$N), 124.23 (*m*-*C*H), 123.45 (*m*-*C*H), 71.09 (O*C*H$_2$CH$_2$O), 70.77 (O*C*H$_2$CH$_2$O), 70.29 (O*C*H$_2$CH$_2$N), 68.14 (O*C*H$_2$CH$_2$N), 65.31 (Ar*C*H$_2$N), 57.99 (N*C*H$_2$CH$_2$O), 53.15 (N*C*H$_2$CH$_2$O), 36.09 (*p*-*C*(CH$_3$)$_3$), 34.39 (*o*-*C*(CH$_3$)$_3$), 32.83 (*o*-C(*C*H$_3$)$_3$), 30.71 (*p*-C(*C*H$_3$)$_3$) ppm.

[{(N$_2$O$_4$)R$^F_2$O$_2$}Ca] (5-Ca): A solution of **5-**H$_2$ (0.30 g, 0.48 mmol) in diethyl ether (15 ml) was added to a solution of [Ca{N(SiMe$_3$)$_2$}$_2$.(thf)$_2$] (0.24 g, 0.48 mmol) in diethyl ether (15 ml). The reaction mixture was stirred for 2 h and the volatiles were removed under vacuum. The



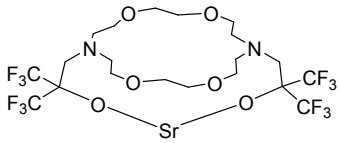
resulting white powder was washed with pentane (3 × 10 ml) and the product was completely dried under vacuum. Yield: 0.23 g, 72%. The title compound is insoluble in aliphatic solvents and diethyl ether, and dissolves well in chlorinated solvents and thf.

^{1}H NMR (400 MHz, CD_2Cl_2, 298 K): δ = 4.00 (h, $^{3}J_{HH}$ = 6.3 Hz, 4H, OCH_2CH_2O), 3.80-3.74 (m, 8H, OCH_2CH_2N), 3.67 (m, 2H, NCH_2CH_2O), 3.59-3.52 (m, 4H, OCH_2CH_2O), 3.06 (m, 2H, NCH_2CH_2O), 2.85 (s, 4H, C$(CF_3)_2$CH_2), 2.71 (m, 4H, NCH_2CH_2O) ppm.

^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2, 298 K): δ = 127.23 (q, $^{1}J_{CF}$ = 296.1 Hz, CF_3), 83.18 (hept, $^{2}J_{CF}$ = 24.9 Hz, C$(CF_3)_2$), 69.00 (OCH$_2$CH$_2$O), 68.00 (OCH$_2$CH$_2$N), 56.82 (NCH$_2$CH$_2$O), 56.57 (C$(CF_3)_2$CH$_2$) ppm.

^{19}F{^{1}H} NMR (376 MHz, CD_2Cl_2, 298 K): δ = –78.42 (s, 12F, CF_3) ppm.

[{$(N_2O_4)R^F{}_2O_2$}Sr] (5-Sr): Following the same protocol described for **5-Ca,** the complex **5-Sr** was obtained by reacting (0.30 g, 0.48 mmol) of **5-**H_2 in diethyl ether (10 ml) with a solution of [Sr{N$(SiMe_3)_2$}$_2$.$(thf)_2$] (0.27 g, 0.48 mmol) in diethyl ether (10 ml). Yield: 0.25 g, 73%. The title compound show good solubility in difluorobenzene, thf and chlorinated solvents. It is insoluble in aliphatic solvents and diethyl ether.

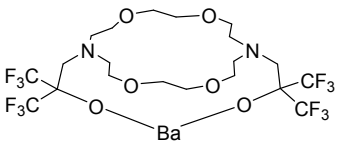


^{1}H NMR (400 MHz, CD_2Cl_2, 298 K): δ = 4.08-4.00 (m, 4H, OCH_2CH_2O), 3.87 (m, 4H, OCH_2CH_2O), 3.66-3.52 (m, 8H, OCH_2CH$_2$N), 2.83 (s, 4H, C$(CF_3)_2$CH_2), 2.81-2.69 (m, 8H, NCH_2CH$_2$O) ppm.

^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2, 298 K): δ = 126.60 (q, $^{1}J_{CF}$ = 296.0 Hz, CF_3), 81.62 (hept, $^{2}J_{CF}$ = 28.5 Hz, C$(CF_3)_2$), 69.83 (OCH$_2$CH$_2$O), 68.48 (OCH$_2$CH$_2$N), 59.83 (C$(CF_3)_2$CH$_2$), 55.79 (NCH$_2$CH$_2$O) ppm.

^{19}F{^{1}H} NMR (376 MHz, CD_2Cl_2, 298 K): δ = –78.36 (s, 12F, CF_3) ppm.

[{$(N_2O_4)R^F{}_2O_2$}Ba] (5-Ba): Following the same protocol described for **5-Ca,** the complex **5-Ba** was obtained by reacting (0.30 g, 0.48 mmol) of **5-**H_2 in diethyl ether (10 ml) with a solution of [Ba{N$(SiMe_3)_2$}$_2$.$(thf)_2$] (0.29 g, 0.48 mmol) in diethyl ether (10 ml). Yield: 0.29 g, 78%. The title compound is only very mildly soluble in chlorinated solvents.

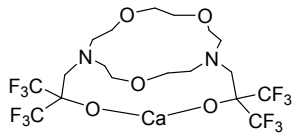


^{1}H NMR (400 MHz, CD_2Cl_2, 298 K): δ = 3.86-3.71 (m, 8H, OCH_2CH_2O), 3.64-3.59 (m, 8H, OCH_2CH$_2$N), 2.81 (s, 4H, C$(CF_3)_2$CH_2), 2.73 (m, 8H, NCH_2CH$_2$O) ppm.

$^{13}C\{^1H\}$ NMR (100 MHz, CD_2Cl_2, 298 K): δ = 127.35 (q, $^1J_{CF}$ = 295.6 Hz, CF_3), 82.42 (hept, $^2J_{CF}$ = 28.5 Hz, $C(CF_3)_2$), 70.89 (OCH_2CH_2O), 69.63 (OCH_2CH_2N), 59.16 ($C(CF_3)_2CH_2$), 55.85 (NCH_2CH_2O) ppm.

$^{19}F\{^1H\}$ NMR (376 MHz, CD_2Cl_2, 298 K): δ = –78.10 (s, 12F, CF_3) ppm.

[{(N_2O_3)$R^F_2O_2$}Ca] (6-Ca): Following the same protocol described for **5-Ca,** the complex **6-Ca** was obtained by reacting (0.30 g, 0.52 mmol) of **6**-H_2 in thf (10 ml) with a solution of [Ca{$N(SiMe_3)_2$}$_2$.$(thf)_2$] (0.26 g, 0.53 mmol) in thf (10 ml). Yield: 0.23 g, 72%. The title compound presented a poor solubility in aliphatic solvents and very high solubility in thf and chlorinated solvents.

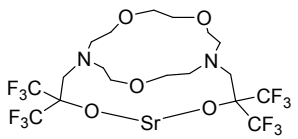


^1H NMR (400 MHz, CD_2Cl_2, 298 K): δ = 4.17 (t, $^3J_{HH}$ = 10.5 Hz, 2H, OCH_2CH_2N), 3.93-3.84 (m, 2H, OCH_2CH_2O), 3.78 (m, 2H, OCH_2CH_2O), 3.70-3.62 (m, 4H, OCH_2CH_2N), 3.46 (m, 2H, $C(CF_3)_2CH_2$), 3.10-2.93 (m, 6H, overlapping $C(CF_3)_2CH_2$ & NCH_2CH_2O), 2.83-2.70 (m, 4H, overlapping NCH_2CH_2O & OCH_2CH_2N), 2.48 (m, 2H, NCH_2CH_2O) ppm.

$^{13}C\{^1H\}$ NMR (100 MHz, CD_2Cl_2, 298 K): δ = 127.65 (q, $^1J_{CF}$ = 290.0 Hz, CF_3), 81.40 (hept, $^2J_{CF}$ = 28.5 Hz, $C(CF_3)_2)_2$), 68.97 (OCH_2CH_2O), 58.99 (OCH_2CH_2N), 56.12 (NCH_2CH_2O), 55.93 ($C(CF_3)_2CH_2$) ppm.

$^{19}F\{^1H\}$ NMR (376 MHz, CD_2Cl_2, 298 K): δ = –78.99 (br q, 6F, CF_3), –79.41 (br q, 6F, CF_3) ppm.

[{(N_2O_3)$R^F_2O_2$}Sr] (6-Sr): Following the same protocol described for **5-Ca,** the complex **6-Sr** was obtained by reacting (0.30 g, 0.52 mmol) of **6**-H_2 in diethyl ether (10 ml) with a solution of [Sr{$N(SiMe_3)_2$}$_2$.$(thf)_2$] (0.29 g, 0.52 mmol) in diethyl ether (10 ml). Yield: 0.14 g, 52%. The title compound presents a poor solubility in aliphatic solvents and high solubility in thf and chlorinated solvents.

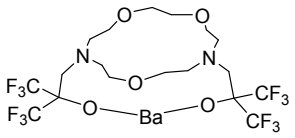


^1H NMR (400 MHz, thf-d_8, 328 K): δ = 3.83-3.71 (m, 6H, overlapping OCH_2CH_2N), 3.66-3.62 (m, 4H, OCH_2CH_2O), 3.50-3.44 (m, 2H, OCH_2CH_2N), 2.97-2.91 (m, 2H, NCH_2CH_2O), 2.93 (d, $^2J_{HH}$ = 14.8 Hz, 4H, $C(CF_3)_2CH_2$), 2.63-2.32 (m, 6H, NCH_2CH_2O) ppm.

$^{13}C\{^1H\}$ NMR (100 MHz, thf-d_8, 298 K): δ = 128.52 (q, $^1J_{CF}$ = 297.4 Hz, CF_3), 82.77 (hept, $^2J_{CF}$ = 28.5 Hz, $C(CF_3)_2$), 69.82 (OCH_2CH_2O), 68.88 (OCH_2CH_2N), 59.21 ($C(CF_3)_2CH_2$), 54.36 (NCH_2CH_2O) ppm.

$^{19}F\{^1H\}$ NMR (376 MHz, thf-d_8, 330 K): δ = –79.85 (s, 12F, CF_3).

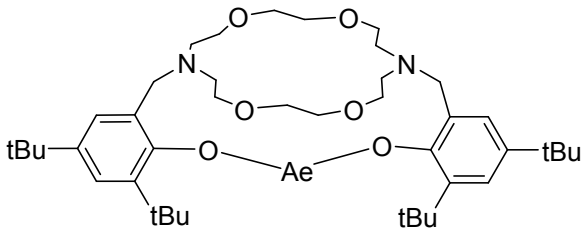
[{(N_2O_3)$R^F_2O_2$}Ba] (6-Ba): Following the same protocol described for **5-Ca,** the complex **6-Ba** was obtained by reacting (0.20 g, 0.35 mmol) of **6**-H_2 in diethyl ether (10 ml) with a solution of [Ba{N($SiMe_3$)$_2$}$_2$.(thf)$_2$] (0.21 g, 0.35 mmol) in diethyl ether (10 ml). Yield: 0.15 g, 60%. The title compound presents a poor solubility in aliphatic solvents and reasonable solubility in thf and chlorinated solvents.



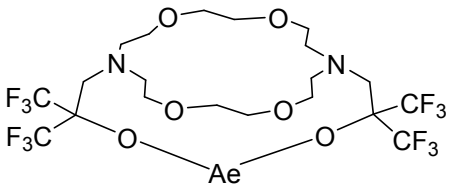
^{1}H NMR (400 MHz, thf-d_8, 298 K): δ = 4.18-3.90 (m, 4H, NCH_2CH$_2$O), 3.86-3.60 (m, 8H, OCH_2CH$_2$N), 3.50-3.01 (m, 6H, OCH_2CH_2O), 2.96 (d, $^2J_{HH}$ = 14.8 Hz, 2H, C(CF$_3$)$_2$CH_2), 2.60 (d, $^2J_{HH}$ = 14.8 Hz, 2H, C(CF$_3$)$_2$CH_2), 2.42-2.00 (m, 4H, NCH_2CH$_2$O) ppm.

^{13}C{^{1}H} NMR (100 MHz, thf-d_8, 298 K): δ = 127.89 (q, $^1J_{CF}$ = 288.0 Hz, CF$_3$), 86.21 (hept, $^2J_{CF}$ = 28.5 Hz, C(CF$_3$)$_2$), 70.12 (OCH$_2$CH$_2$O), 68.77 (OCH$_2$CH$_2$N), 57.96 (C(CF$_3$)$_2$$CH_2$), 54.60 (N$CH_2CH_2$O) ppm.

^{19}F{^{1}H} NMR (376 MHz, thf-d_8, 325 K): δ = –78.06 (s, 12F, CF_3). The spectrum (also recorded at VT) seems to suggest the presence of an impurity, but it proved impossible to remove it despite repeated attempts, while the moderate solubility and high fluxionality of the complex in solution proved very troublesome, incl. at low temperature.



3-Ae



5-Ae

Complex {(N_2O_4)Ar_2O_2}Ca (**3-Ca**): Anal. calc for $C_{42}H_{68}CaN_2O_6$ (737.09 g.mol^{-1}): C 68.44, H 9.30, N 3.80%; found C 65.3, H 9.0, N 3.4%.

Complex {(N_2O_4)Ar_2O_2}Sr (**3-Sr**): Anal. calc for $C_{42}H_{68}N_2O_6Sr$ (784.63 g.mol^{-1}): C 64.29, H 8.74, N 3.57%; found C 61.0, H 8.5, N 3.3%.

Complex {(N_2O_4)Ar_2O_2}Ba (**3-Ba**): Anal. calc for $C_{42}H_{68}N_2O_6Ba$ (834.34 g.mol^{-1}): C 60.46, H 8.22, N 3.36%; found C 57.8, H 7.8, N 3.2%.

Complex {(N_2O_4)$R^F_2O_2$}Ca (**5-Ca**): Anal. calc for $C_{20}H_{28}CaF_{12}N_2O_6$ (660.51 g.mol^{-1}): C 36.37, H 4.27, N 4.24%; found C 35.9, H 4.5, N 4.1%.

Complex {(N_2O_4)$R^F_2O_2$}Sr (**5-Sr**): Anal. calc for $C_{20}H_{28}F_{12}N_2O_6Sr$ (708.05 g.mol^{-1}): C 33.93, H 3.99, N 3.96%; found C 32.9, H 3.8, N 3.5%

Complex {(N_2O_4)$R^F_2O_2$}Ba (**5-Ba**): Anal. calc for $C_{20}H_{28}BaF_{12}N_2O_6$ (757.76 g.mol^{-1}): C 31.70, H 3.72, N 3.70%; found C 31.2, H 4.1, N 3.4%

Figure S1. Data sets for the elemental analysis performed on crystalline samples of **3-Ae** and **5-Ae** (Ae = Ca, Sr and Ba). Although the results are acceptable for H and N, they are repeatedly off the mark for C.

X–Ray diffraction crystallography for CCDC #1995095-1995102, 2009421, 2009385, 2009437, 2009320.

Crystals of the four proligands **3**-H_2 to **6**-H_2 and of the complexes **3-Ca**, **4-Ca**, **5-Ca**, **5-Sr**, **5-Ba**, **6-Sr.thf**, **6-Ba**, and **6-Sr.(H_2O)$_2$** suitable for X-ray diffraction analysis were obtained by recrystallisation of the purified products.

$\{(N_2O_4)Ar_2O_2\}H_2$ = **3**-H_2: ($C_{42}H_{70}N_2O_6$, 2(CH_4O)); M = 763.08. CCDC #2009421. D8 VENTURE Bruker AXS diffractometer, Mo-Kα radiation (λ = 0.71073 Å), T = 150(2) K; triclinic P -1 (I.T.#2), a = 9.669(4), b = 10.306(4), c = 11.284(4) Å, α = 77.298(14), β = 83.866(14), γ = 74.776(14) °, V = 1057.1(7) Å^3. Z = 1, d = 1.199 g.cm^{-3}, μ = 0.081 mm^{-1}. The structure was solved by dual-space algorithm using the *SHELXT* program,[3] and then refined with full-matrix least-squares methods based on F^2 (*SHELXL*).[4] All non-hydrogen atoms were refined with anisotropic atomic displacement parameters. H atoms were finally included in their calculated positions and treated as riding on their parent atom with constrained thermal parameters. A final refinement on F^2 with 4091 unique intensities and 254 parameters converged at ωR(F^2) = 0.4636 (R(F) = 0.1739) for 2149 observed reflections with I > 2σ(I).

$\{(N_2O_3)Ar_2O_2\}H_2$ = **4**-H_2: ($C_{40}H_{66}N_2O_5$); M = 654.94. CCDC #2009385, D8 VENTURE Bruker AXS diffractometer, Mo-Kα radiation (λ = 0.71073 Å), T = 150(2) K; triclinic P -1 (I.T.#2), a = 10.8782(13), b = 17.303(2), c = 22.116(3) Å, α = 74.944(4), β = 84.341(4), γ = 81.408(4) °, V = 3966.9(9) Å^3. Z = 4, d = 1.097 g.cm^{-3}, μ = 0.071 mm^{-1}. The structure was solved by dual-space algorithm using the *SHELXT* program,[3] and then refined with full-matrix least-square methods based on F^2 (*SHELXL-2014*).[4] All non-hydrogen atoms were refined with anisotropic atomic displacement parameters. H atoms were finally included in their calculated positions. A final refinement on F^2 with 18116 unique intensities and 889 parameters converged at ωR(F^2) = 0.1337 (R(F) = 0.0650) for 9692 observed reflections with I > 2σ(I).

$\{(N_2O_4)R^F{}_2O_2\}H_2$ = **5**-H_2: ($C_{20}H_{30}F_{12}N_2O_6$); M = 622.46. CCDC #2009437. D8 VENTURE Bruker AXS diffractometer equipped with a (CMOS) PHOTON 100 detector, Mo-Kα radiation (λ = 0.71073 Å, multilayer monochromator), T = 150(2) K; triclinic P -1 (I.T.#2), a = 5.5168(9), b = 10.777(2), c = 12.424(3) Å, α = 114.820(8), β = 95.801(7), γ = 99.354(8) °, V = 649.6(2) Å^3. Z = 1, d = 1.591 g.cm^{-3}, μ = 0.169 mm^{-1}. The structure was solved by dual-space algorithm using the *SHELXT* program,[3] and then refined with full-matrix least-squares methods based on F^2 (*SHELXL*).[4] All non-hydrogen atoms were refined with anisotropic atomic displacement parameters. Except **XXX** linked hydrogen atoms that were introduced in the structural model through Fourier difference maps analysis, H atoms were finally included in their calculated positions and treated as riding on their parent atom with constrained thermal

parameters. A final refinement on F^2 with 2845 unique intensities and 184 parameters converged at $\omega R(F^2) = 0.1474$ ($R(F) = 0.0688$) for 1684 observed reflections with $I > 2\sigma(I)$.

$\{(N_2O_3)R^F{}_2O_2\}H_2$ = **6**-H_2: ($C_{18}H_{26}F_{12}N_2O_5$); M = 578.41. CCDC #2009320. D8 VENTURE Bruker AXS diffractometer, Mo-Kα radiation (λ = 0.71073 Å), T = 150 K; triclinic P -1 (I.T.#2), a = 6.6356(8), b = 12.7690(14), c = 15.2327(15) Å, α = 68.157(3), β = 84.686(3), γ = 83.583(4) °, V = 1188.7(2) Å^3. Z = 2, d = 1.616 g.cm^{-3}, μ = 0.175 mm^{-1}. The structure was solved by dual-space algorithm using the *SHELXT* program,[3] and then refined with full-matrix least-square methods based on F^2 (*SHELXL-2014*).[4] All non-hydrogen atoms were refined with anisotropic atomic displacement parameters. Except oxygen linked hydrogen atoms that were introduced in the structural model through Fourier difference maps analysis, H atoms were finally included in their calculated positions. A final refinement on F^2 with 5448 unique intensities and 340 parameters converged at $\omega R(F^2) = 0.1306$ ($R(F) = 0.0509$) for 4470 observed reflections with $I > 2\sigma(I)$.

[$\{(N_2O_2)Ar_2O_2\}$Ca] = **3-Ca**: ($C_{42}H_{68}CaN_2O_6$); M = 737.06. CCDC #1995095. D8 VENTURE Bruker AXS diffractometer equipped with a (CMOS) PHOTON 100 detector, Mo-Kα radiation (λ = 0.71073 Å, multilayer monochromator), T = 150(2) K; orthorhombic *I b c a* (I.T.#73), a = 16.4124(8), b = 18.4546(10), c = 27.6735(12) Å, V = 8381.9(7) Å^3. Z = 8, d = 1.168 g.cm^{-3}, μ = 0.196 mm^{-1}. The structure was solved by dual-space algorithm using the *SHELXT* program,[3] and then refined with full-matrix least-squares methods based on F^2 (*SHELXL*).[4] All non-hydrogen atoms were refined with anisotropic atomic displacement parameters. H atoms were finally included in their calculated positions and treated as riding on their parent atom with constrained thermal parameters. A final refinement on F^2 with 4775 unique intensities and 238 parameters converged at $\omega R(F^2) = 0.1008$ ($R(F) = 0.0421$) for 4003 observed reflections with $I > 2\sigma(I)$.

[$\{(N_2O_3)Ar_2O_2\}$Ca] = **4-Ca**: ($C_{40}H_{64}CaN_2O_5$, C_4H_8O); M = 765.11. CCDC #1995096. D8 VENTURE Bruker AXS diffractometer, Mo-Kα radiation (λ = 0.71073 Å), T = 150 K; monoclinic *C* 2/*c* (I.T.#15), a = 32.4903(7), b = 14.7726(4), c = 18.2963(4) Å, β = 95.7960(10) °, V = 8736.7(4) Å^3. Z = 8, d = 1.163 g.cm^{-3}, μ = 0.190 mm^{-1}. The structure was solved by dual-space algorithm using the *SHELXT* program,[3] and then refined with full-matrix least-square methods based on F^2(*SHELXL*).[4] All non-hydrogen atoms were refined with anisotropic atomic displacement parameters. H atoms were finally included in their calculated positions. A final refinement on F^2 with 9970 unique intensities and 496 parameters converged at $\omega R(F^2) = 0.0958$ ($R(F) = 0.0380$) for 8436 observed reflections with $I > 2\sigma(I)$.

[$\{(N_2O_4)R^F{}_2O_2\}$Ca] = **5-Ca**: ($C_{20}H_{28}CaF_{12}N_2O_6$, $2(CH_2Cl_2)$); M = 830.37. CCDC #1995098. D8 VENTURE Bruker AXS diffractometer equipped with a (CMOS) PHOTON 100 detector, Mo-Kα radiation (λ = 0.71073 Å, multilayer monochromator), T = 150(2) K; monoclinic *C* 2/*c* (I.T.#15), a =

19.7814(19), b = 8.9550(8), c = 18.2461(18) Å, β = 95.159(3) °, V = 3219.1(5) Å^3. Z = 4, d = 1.713 g.cm^{-3}, μ = 0.637 mm^{-1}. The structure was solved by dual-space algorithm using the *SHELXT* program,[3] and then refined with full-matrix least-squares methods based on F^2 (*SHELXL*).[4] All non-hydrogen atoms were refined with anisotropic atomic displacement parameters. H atoms were finally included in their calculated positions and treated as riding on their parent atom with constrained thermal parameters. A final refinement on F^2 with 3638 unique intensities and 213 parameters converged at ωR(F^2) = 0.0802 (R(F) = 0.0356) for 3068 observed reflections with I > 2σ(I).

[{$(N_2O_4)R^F{}_2O_2$}Sr] = **5-Sr**: ($C_{20}H_{28}F_{12}N_2O_6Sr$); M = 708.06. CCDC #1995099. D8 VENTURE Bruker AXS diffractometer equipped with a (CMOS) PHOTON 100 detector, Mo-Kα radiation (λ = 0.71073 Å, multilayer monochromator), T = 150(2) K; monoclinic C 2/c (I.T.#15), a = 21.6408(16), b = 8.7328(8), c = 14.8071(13) Å, β = 112.570(3) °, V = 2584.0(4) Å^3. Z = 4, d = 1.820 g.cm^{-3}, μ = 2.214 mm^{-1}. The structure was solved by dual-space algorithm using the *SHELXT* program,[3] and then refined with full-matrix least-squares methods based on F^2 (*SHELXL*).[4] All non-hydrogen atoms were refined with anisotropic atomic displacement parameters. H atoms were finally included in their calculated positions and treated as riding on their parent atom with constrained thermal parameters. A final refinement on F^2 with 2964 unique intensities and 186 parameters converged at ωR(F^2) = 0.0461 (R(F) = 0.0187) for 2820 observed reflections with I > 2σ(I).

[{$(N_2O_4)R^F{}_2O_2$}Ba] = **5-Ba**: ($C_{20}H_{28}BaF_{12}N_2O_6$, 2($CH_2Cl_2$)); M = 927.63. CCDC #1995097. D8 VENTURE Bruker AXS diffractometer equipped with a (CMOS) PHOTON 100 detector, Mo-Kα radiation (λ = 0.71073 Å, multilayer monochromator), T = 150(2) K; monoclinic C 2/c (I.T.#15), a = 20.8202(16), b = 8.6412(8), c = 21.2767(18) Å, β = 119.027(3) °, V = 3347.1(5) Å^3. Z = 4, d = 1.841 g.cm^{-3}, μ = 1.612 mm^{-1}. The structure was solved by dual-space algorithm using the *SHELXT* program,[3] and then refined with full-matrix least-squares methods based on F^2 (*SHELXL*).[4] All non-hydrogen atoms were refined with anisotropic atomic displacement parameters. H atoms were finally included in their calculated positions and treated as riding on their parent atom with constrained thermal parameters. A final refinement on F^2 with 3831 unique intensities and 213 parameters converged at ωR(F^2) = 0.0567 (R(F) = 0.0232) for 3600 observed reflections with I > 2σ(I).

[{$(N_2O_3)R^F{}_2O_2$Sr.(thf)] = **6-Sr.thf**: ($C_{22}H_{32}F_{12}N_2O_6Sr$); M = 736.11. CCDC #1995102. D8 VENTURE Bruker AXS diffractometer, Mo-Kα radiation (λ = 0.71073 Å, multilayer monochromator), T = 150 K; orthorhombic P n a 2_1 (I.T.#33), a = 18.982(2), b = 10.4417(12), c = 14.3738(14) Å, V = 2849.0(6) Å^3. Z = 4, d = 1.716 g.cm^{-3}, μ = 2.011 mm^{-1}. The structure was solved by dual-space algorithm using the *SHELXT* program,[3] and then refined with full-matrix least-squares methods based on F^2 (*SHELXL*).[4] All non-hydrogen atoms were refined with anisotropic atomic displacement parameters. H atoms were finally included in their calculated positions and treated as riding on their parent atom with constrained

thermal parameters. A final refinement on F^2 with 6382 unique intensities and 389 parameters converged at $\omega R(F^2) = 0.0557$ ($R(F) = 0.0248$) for 5898 observed reflections with $I > 2\sigma(I)$.

[{$(N_2O_3)R^F_2O_2Ba$] = **6-Ba**: ($C_{36}H_{48}Ba_2F_{24}N_4O_{10}$, 2($C_4H_8O$)); M = 1571.67. CCDC #1995100. D8 VENTURE Bruker AXS diffractometer, Mo-Kα radiation (λ = 0.71073 Å), T = 150(2) K; monoclinic $P\,2_1/c$ (I.T.#14), a = 12.214(3), b = 10.364(2), c = 23.048(5) Å, β = 99.280(8) °, V = 2879.3(11) Å^3. Z = 2, d = 1.813 g.cm^{-3}, μ = 1.497 mm^{-1}. The structure was solved by dual-space algorithm using the *SHELXT* program,[3] and then refined with full-matrix least-square methods based on F^2 (*SHELXL-2014*).[4] All non-hydrogen atoms were refined with anisotropic atomic displacement parameters. H atoms were finally included in their calculated positions. A final refinement on F^2 with 6619 unique intensities and 388 parameters converged at $\omega R(F^2) = 0.1107$ ($R(F) = 0.0489$) for 5872 observed reflections with $I > 2\sigma(I)$.

[{$(N_2O_3)R^F_2O_2Sr.(H_2O)_2$] = **6-Sr.$H_2O$**: ($C_{18}H_{26}F_{12}N_2O_6Sr$, 3($CH_2Cl_2$), H_2O); M = 954.82. CCDC #1995101. D8 VENTURE Bruker AXS diffractometer equipped with a (CMOS) PHOTON 100 detector, Mo-Kα radiation (λ = 0.71073 Å, multilayer monochromator), T = 150(2) K; triclinic P -1 (I.T.#2), a = 11.5178(11), b = 12.8516(12), c = 13.4163(10) Å, α = 93.561(3), β = 112.062(3), γ = 99.661(3) °, V = 1797.3(3) Å^3. Z = 2, d = 1.764 g.cm^{-3}, μ = 2.049 mm^{-1}. The structure was solved by dual-space algorithm using the *SHELXT* program,[3] and then refined with full-matrix least-squares methods based on F^2 (*SHELXL*).[4] All non-hydrogen atoms were refined with anisotropic atomic displacement parameters. Except water molecules hydrogen atoms that were introduced in the structural model through Fourier difference maps analysis, H atoms were finally included in their calculated positions and treated as riding on their parent atom with constrained thermal parameters. A final refinement on F^2 with 8231 unique intensities and 454 parameters converged at $\omega R(F^2) = 0.1037$ ($R(F) = 0.0464$) for 6826 observed reflections with $I > 2\sigma(I)$.

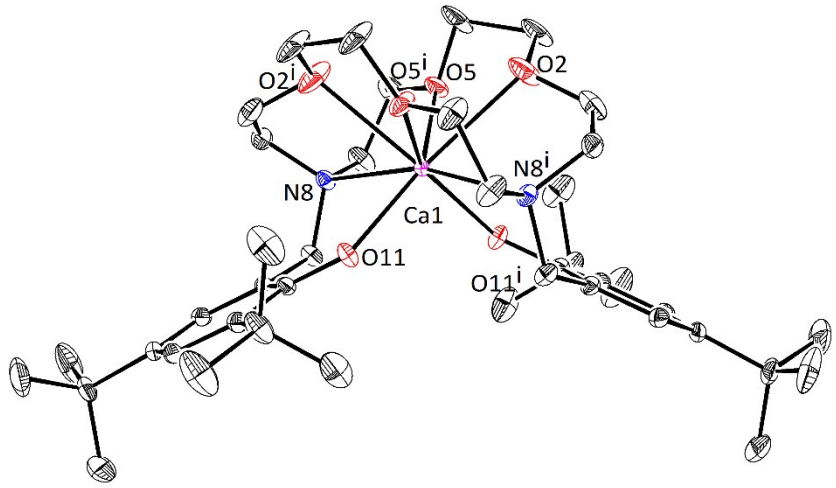


Figure S2: ORTEP representation of the molecular solid state structure of [{(N_2O_2)Ar_2O_2}Ca] (**3-Ca**). H atoms are omitted for clarity. Selected bond lengths (Å): Ca1–O2: 2.6167(13), Ca1–O5: 2.5054(11), Ca1–O11: 2.2449(11), Ca1–N8: 2.6430(13).

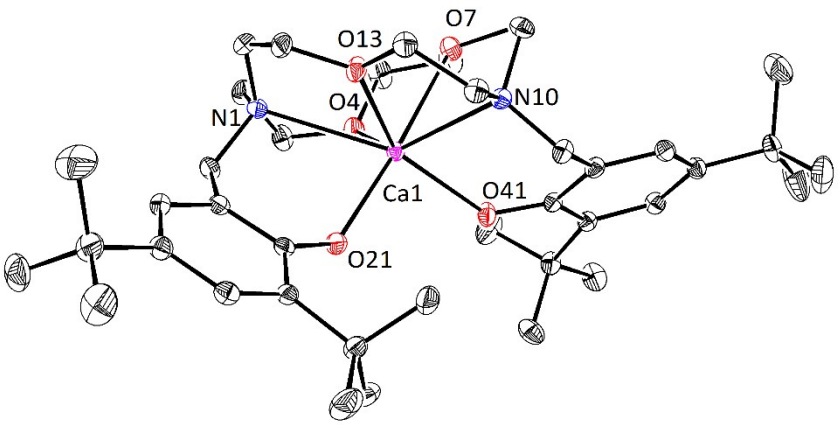


Figure S3: ORTEP representation of the molecular solid state structure of [{(N_2O_3)Ar_2O_2}Ca] (**4-Ca**). H atoms are omitted for clarity. Selected bond lengths (Å): Ca–O21: 2.2274(9), Ca–O41: 2.2540(9), Ca–O4: 2.4740(9), Ca–O13: 2.4747(9), Ca–O7: 2.513(1), Ca–N10: 2.5690(11), Ca–N1: 2.7380(11).

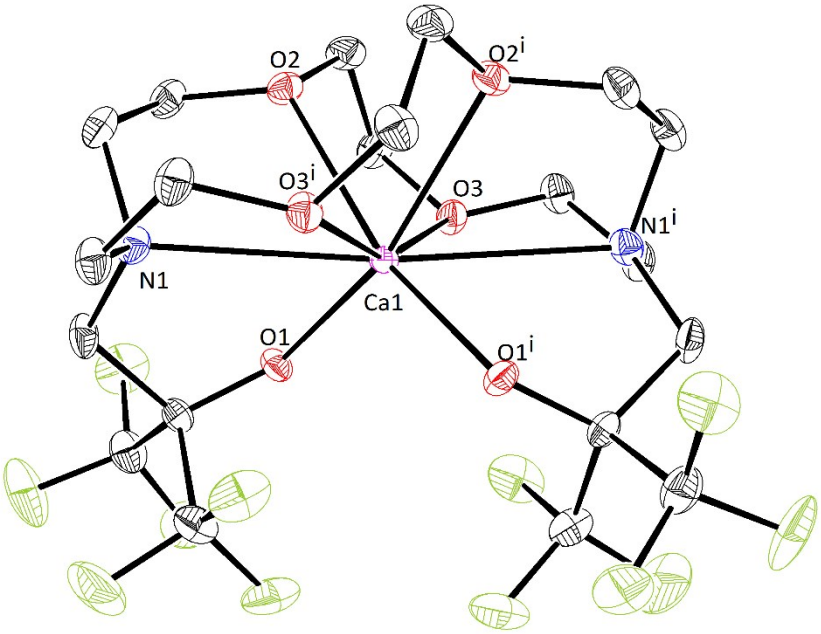


Figure S4: ORTEP representation of the molecular solid state structure of [{(N_2O_4)$R^F{}_2O_2$}Ca] (**5-Ca**). H atoms are omitted for clarity. Selected bond lengths (Å): Ca–O1: 2.2548(12), Ca–O2: 2.5302(13), Ca–O3: 2.5984(12), Ca–N1: 2.8724(15).

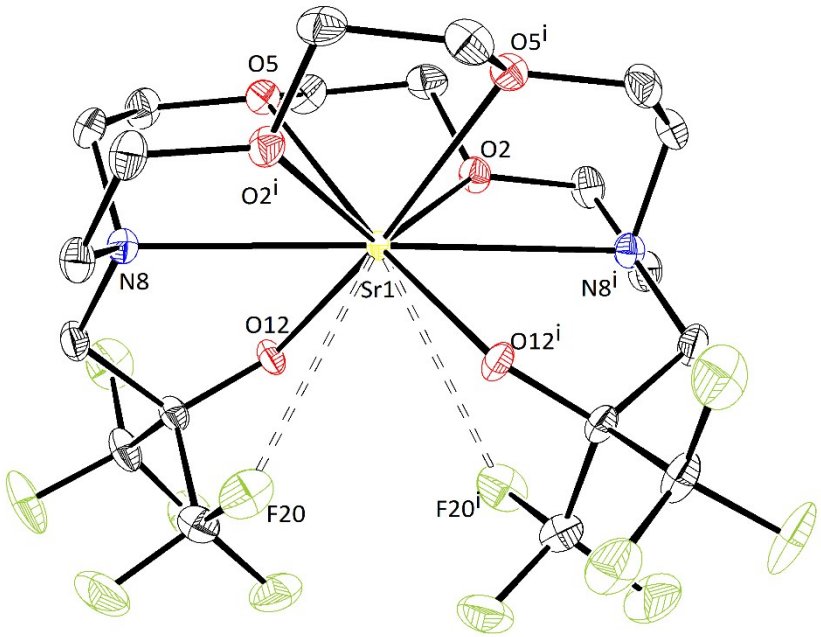


Figure S5: ORTEP representation of the molecular solid state structure of [{(N_2O_4)$R^F{}_2O_2$}Sr] (**5-Sr**). H atoms are omitted for clarity. Sr–O5: 2.7297(9), Sr–O2: 2.7172(9), Sr–O12: 2.4279(9), Sr–N8: 2.8542(11), Sr–F20: 3.1724(10). All Sr···F interactions are presented by dashed bonds.

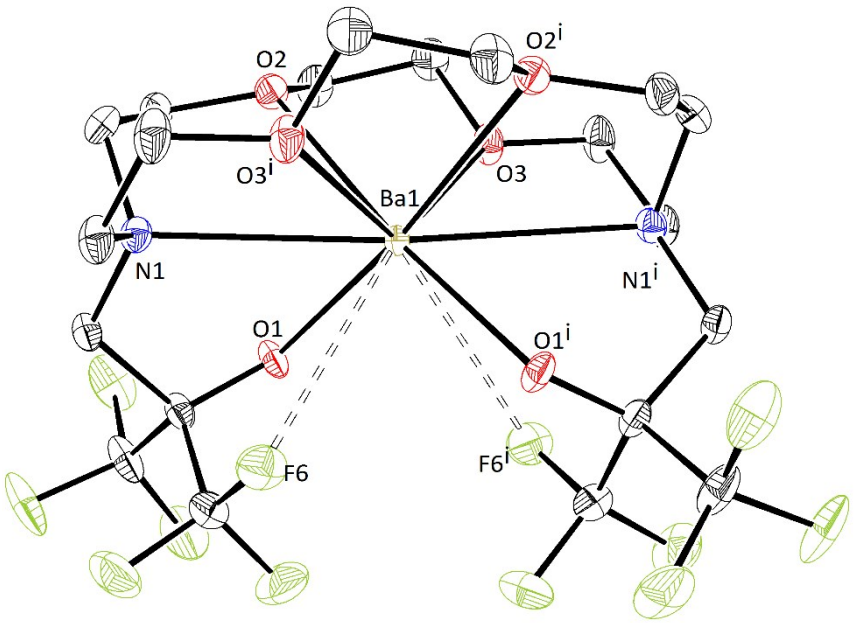


Figure S6: ORTEP representation of the molecular solid state structure of [{(N_2O_4)$R^F_2O_2$}Ba] (**5-Ba**). H atoms are omitted for clarity. Ba–O1: 2.5683(15), Ba–O2: 2.8527(15), Ba–O3: 2.82758(15), Ba–N1: 3.0046(17), Ba–F6: 3.1351(15). All Ba···F interactions are presented by dashed bonds.

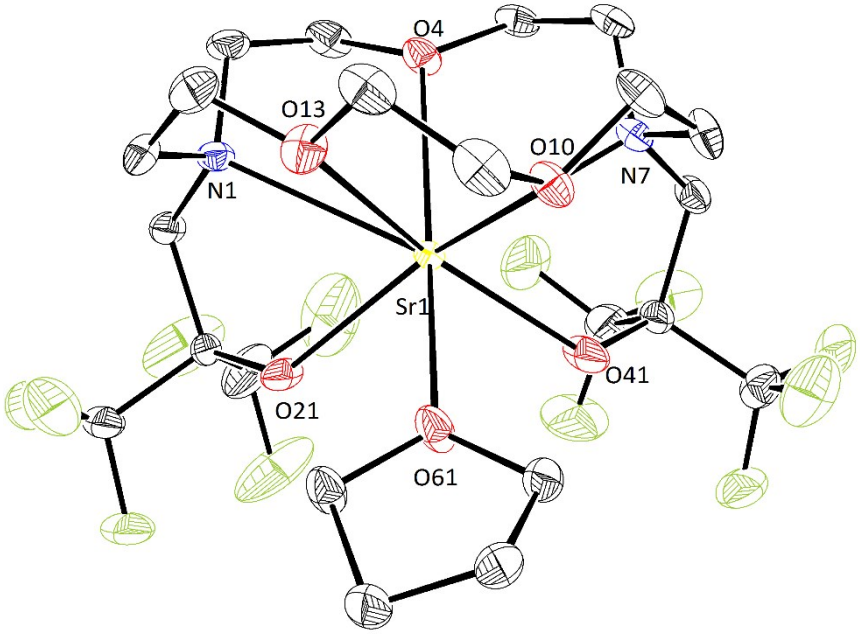


Figure S7: ORTEP representation of the molecular solid state structure of [{(N_2O_3)$R^F_2O_2$Sr.(thf)] (**6-Sr.thf**). Selected bond lengths (Å): Sr–O4: 2.762(2), Sr–O13: 2.709(2), Sr–O10: 2.660(2), Sr–O21: 2.404(2), Sr–O41: 2.393(2), Sr–O61: 2.5666(19), Sr–N1: 2.896(3), Sr–N7: 2.891(3).

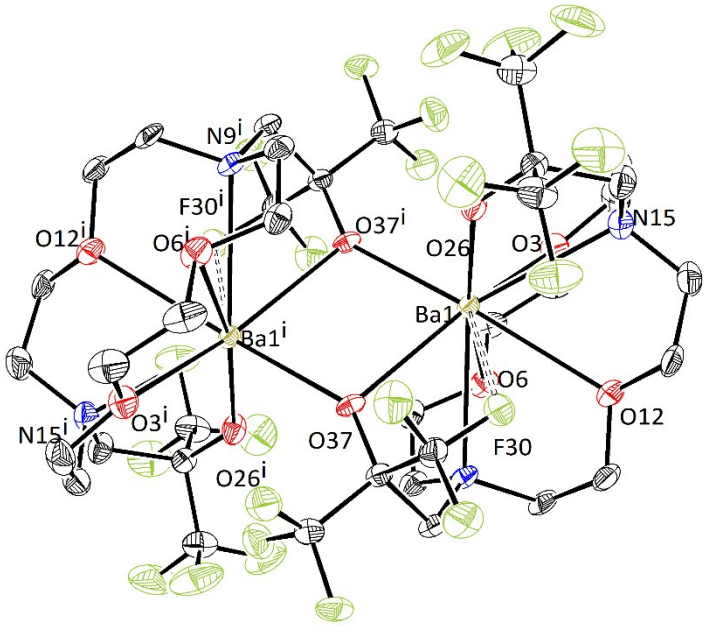


Figure S8: ORTEP representation of the molecular solid state structure of [{$(N_2O_3)R^F{}_2O_2Ba$] (**6-Ba**). H atoms are omitted for clarity. Selected bond lengths (Å):Ba1–O3: 2.792(4), Ba1–O12: 2.844(4), Ba1–O6: 2.969(4), Ba1–O26: 2.494(4), Ba1–O37: 2.632(3), Ba1–N15: 2.990(4), Ba1–N9: 2.971(4), Ba1–F30: 2.998(3). Both Ba···F30 interactions are shown by dashed bonds.

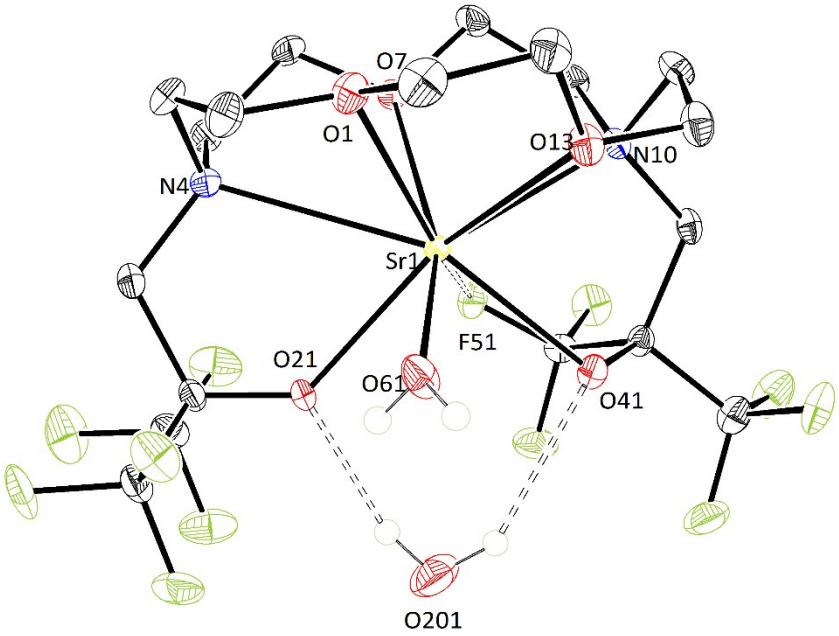


Figure S9: ORTEP representation of the molecular solid state structure of [{$(N_2O_3)R^F{}_2O_2Sr.(H_2O)_2$] (**6-Sr.($H_2O$)$_2$**). H atoms except those of H_2O molecules are omitted for clarity. Sr1–O21: 2.413(2), Sr1–O41: 2.5(2), Sr1–O61: 2.525(2), Sr1–N10: 2.856(3), Sr1–F51: 2.8632(19), Sr1–N4: 2.895(3). The single Sr···F51 interaction is shown by a dashed bond.

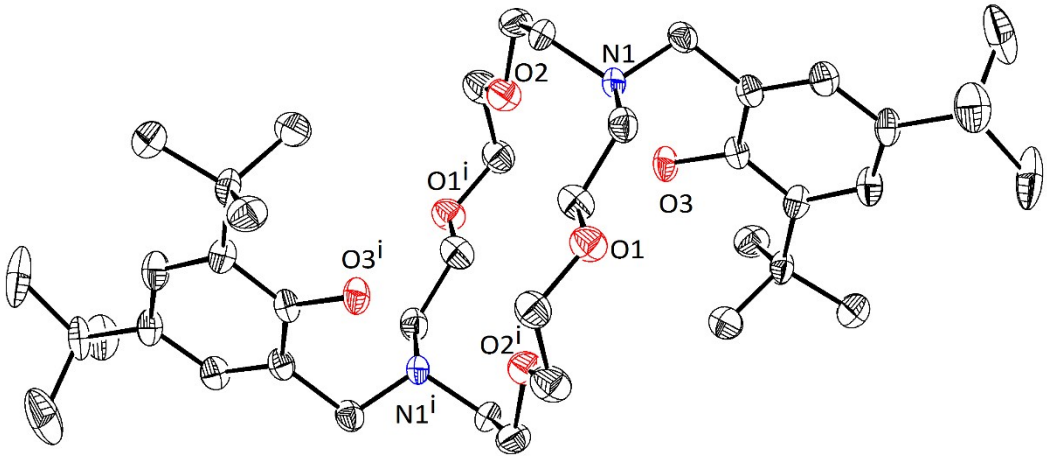


Figure S10: ORTEP representation of the molecular solid state structure of $\{(N_2O_4)Ar_2O_2\}H_2$ (**3-H₂**).

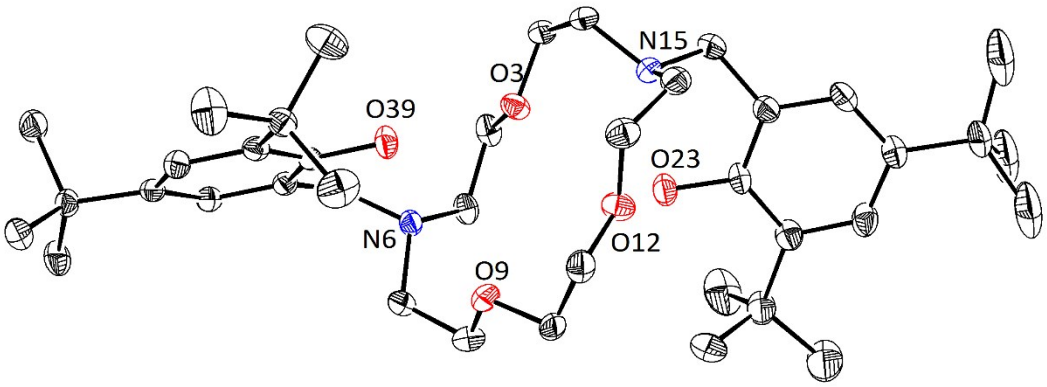


Figure S11: ORTEP representation of the molecular solid state structure of $\{(N_2O_3)Ar_2O_2\}H_2$ (**4-H₂**).

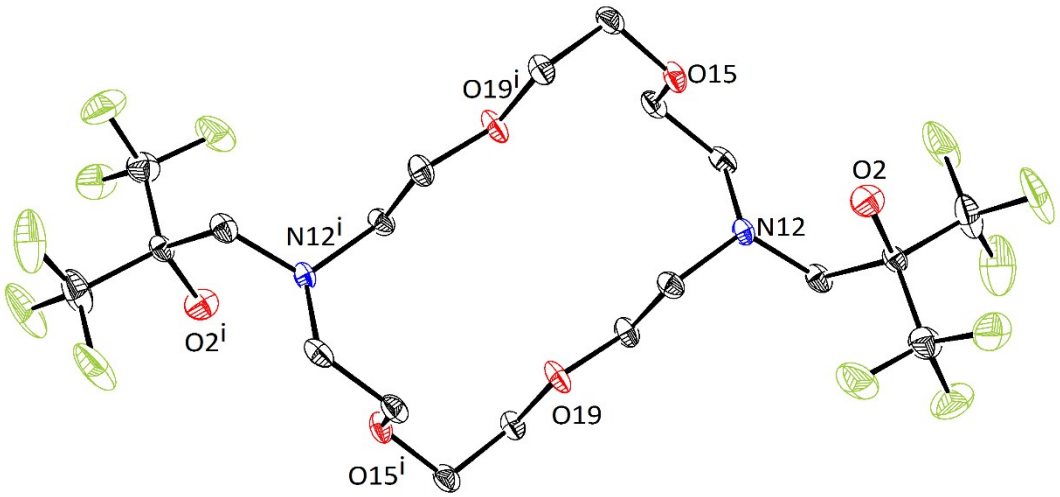


Figure S12: ORTEP representation of the molecular solid state structure of $\{(N_2O_4)R^F{}_2O_2\}H_2$ (**5-H$_2$**).

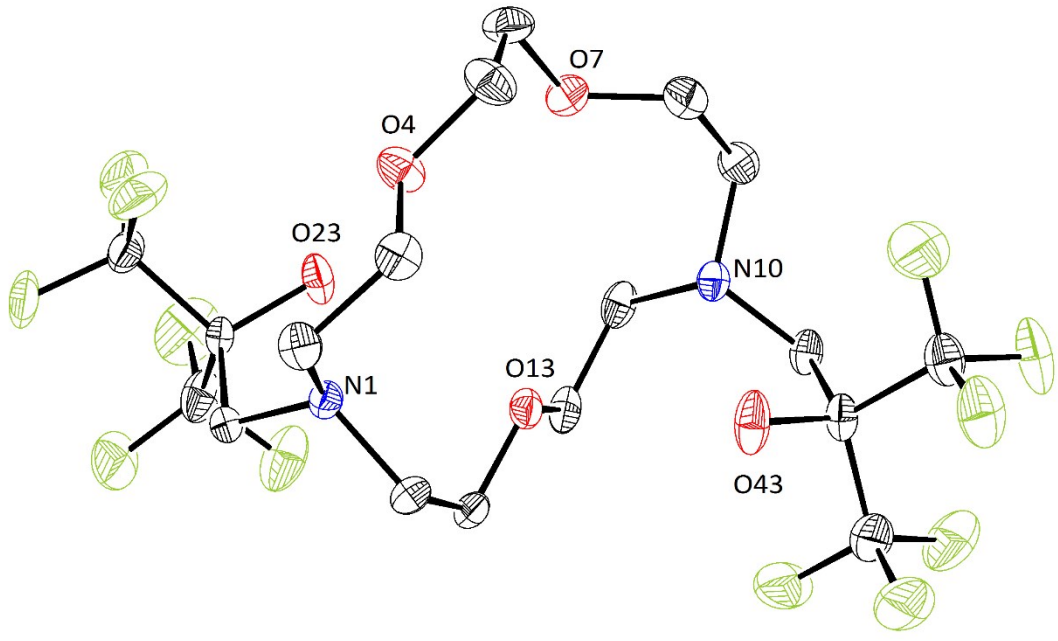


Figure S13: ORTEP representation of the molecular solid state structure of $\{(N_2O_3)R^F{}_2O_2\}H_2$ (**6-H$_2$**).

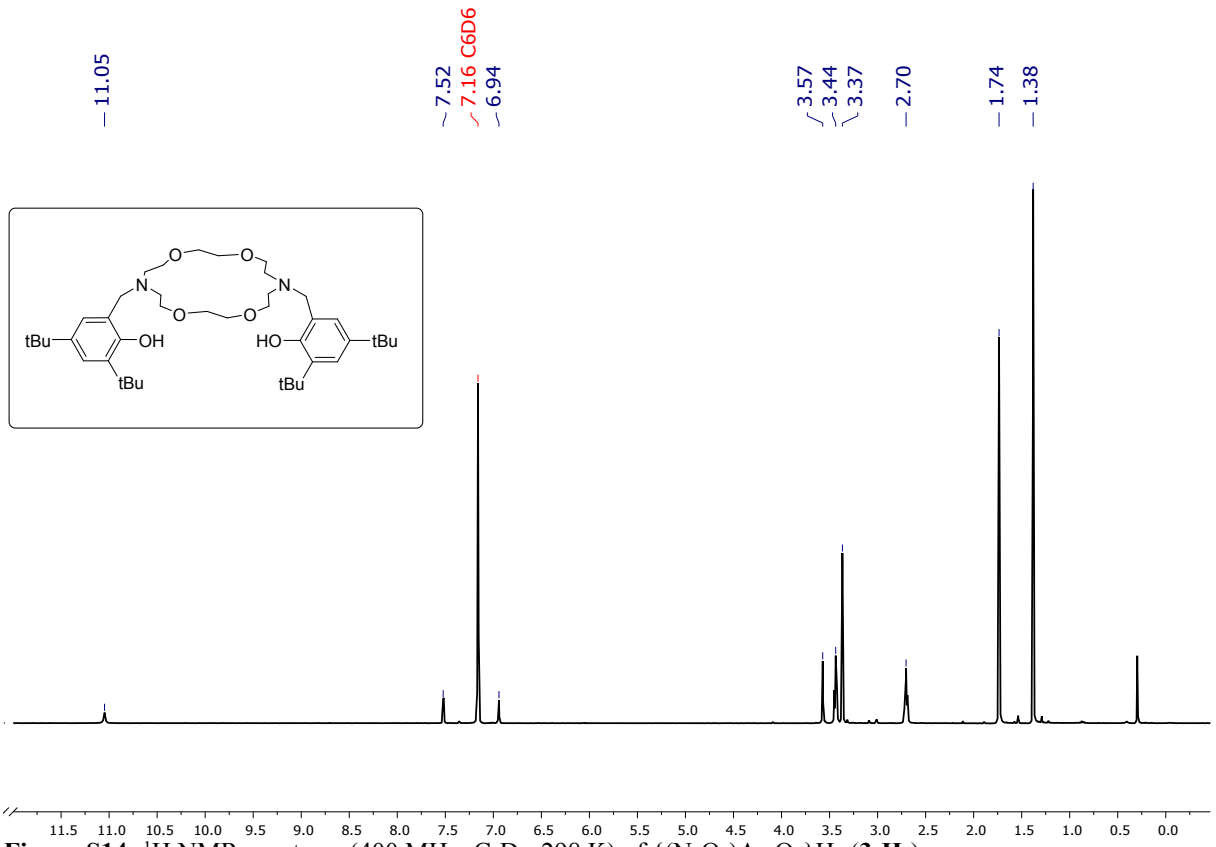


Figure S14: ^{1}H NMR spectrum (400 MHz, C_6D_6, 298 K) of $\{(N_2O_4)Ar_2O_2\}H_2$ (**3-H$_2$**).

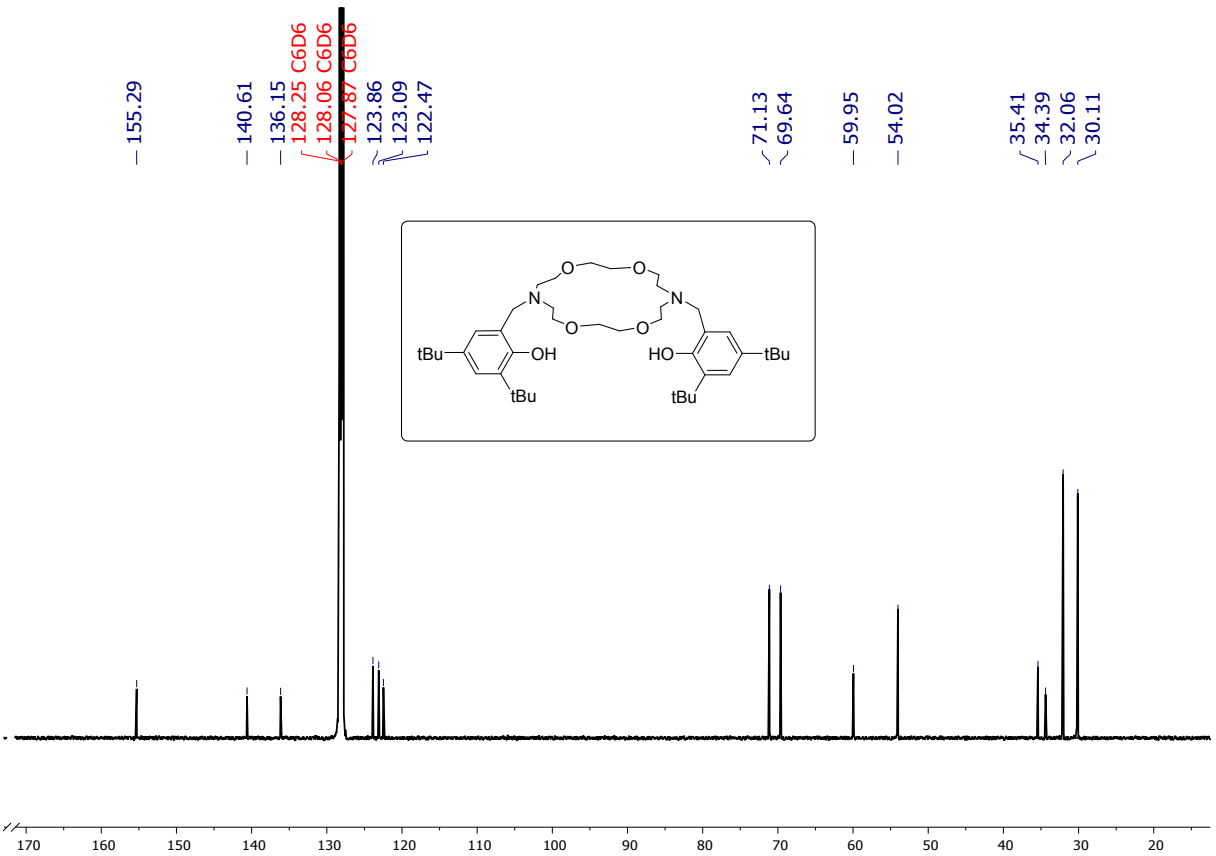


Figure S15: ^{13}C{^{1}H} NMR spectrum (100 MHz, C_6D_6, 298 K) of $\{(N_2O_4)Ar_2O_2\}H_2$ (**3-H$_2$**).

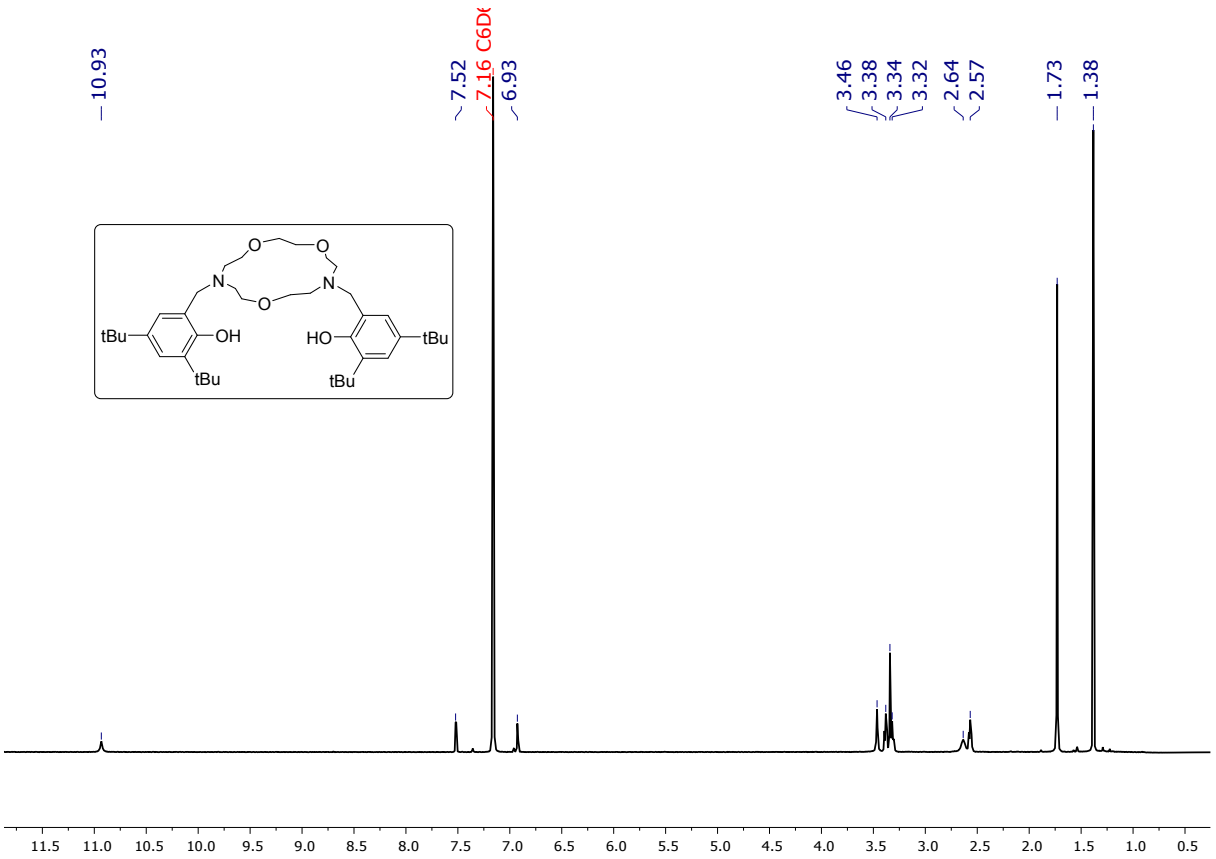


Figure S16: ^{1}H NMR spectrum (400 MHz, C_6D_6, 298 K) of $\{(N_2O_3)Ar_2O_2\}H_2$ (**4-H$_2$**).

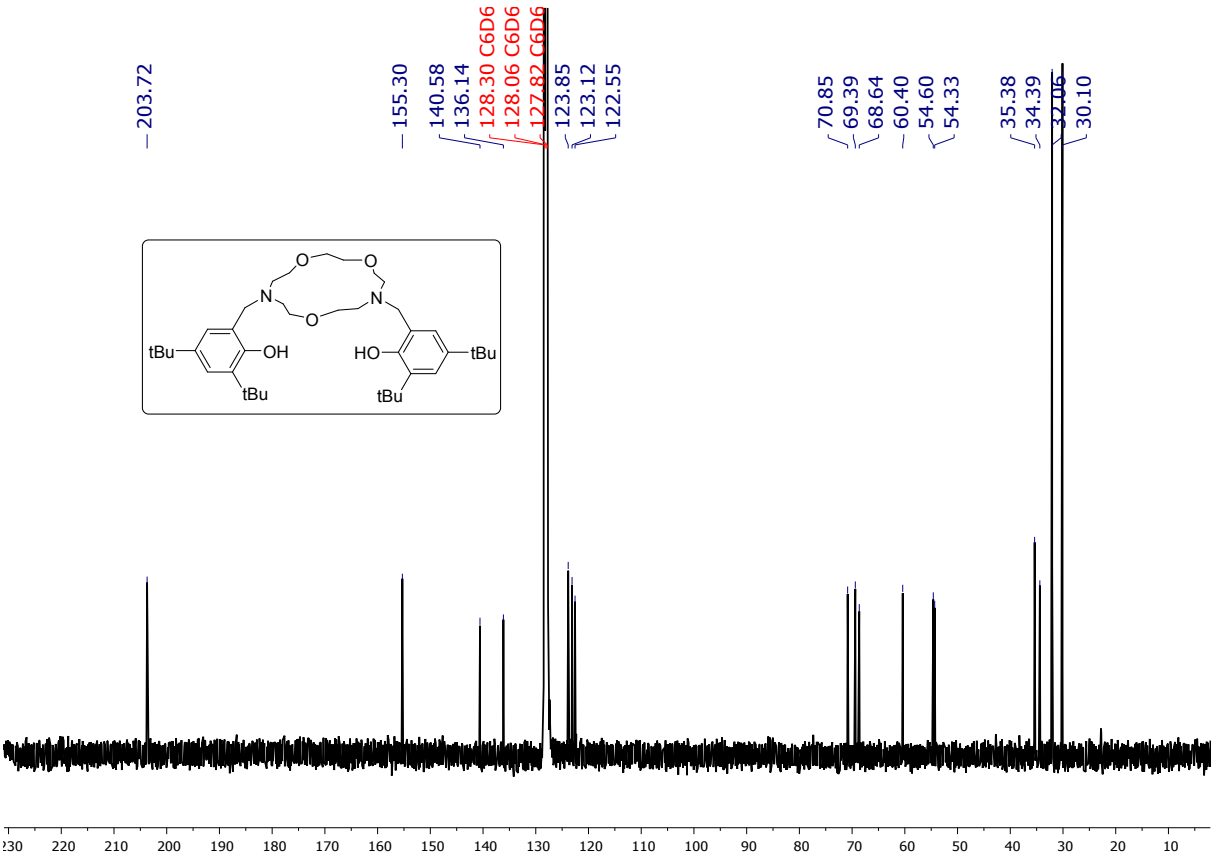


Figure S17: ^{13}C{^{1}H} NMR spectrum (100 MHz, C_6D_6, 298 K) of $\{(N_2O_3)Ar_2O_2\}H_2$ (**4-H$_2$**).

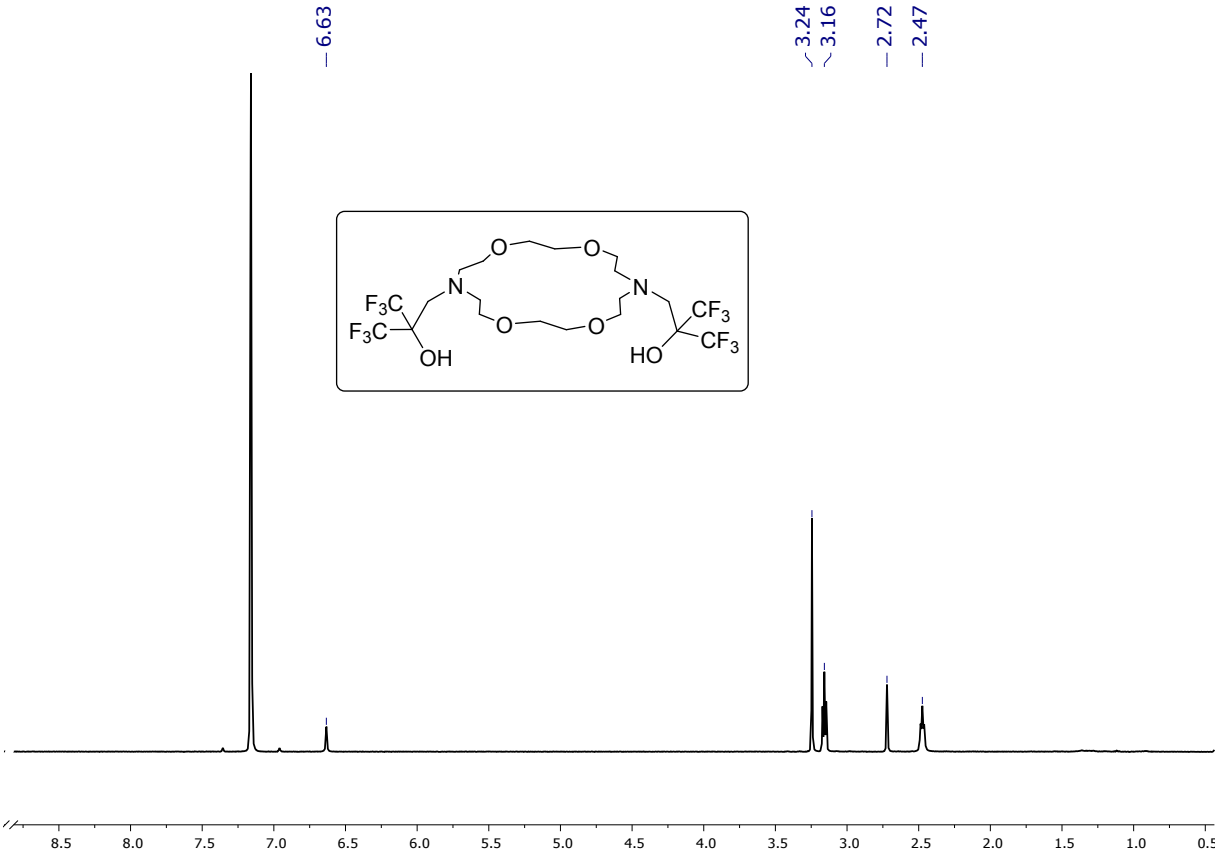


Figure S18: ^{1}H NMR spectrum (400 MHz, C_6D_6, 298 K) of $\{(N_2O_4)R^F{}_2O_2\}H_2$ (**5-H$_2$**).

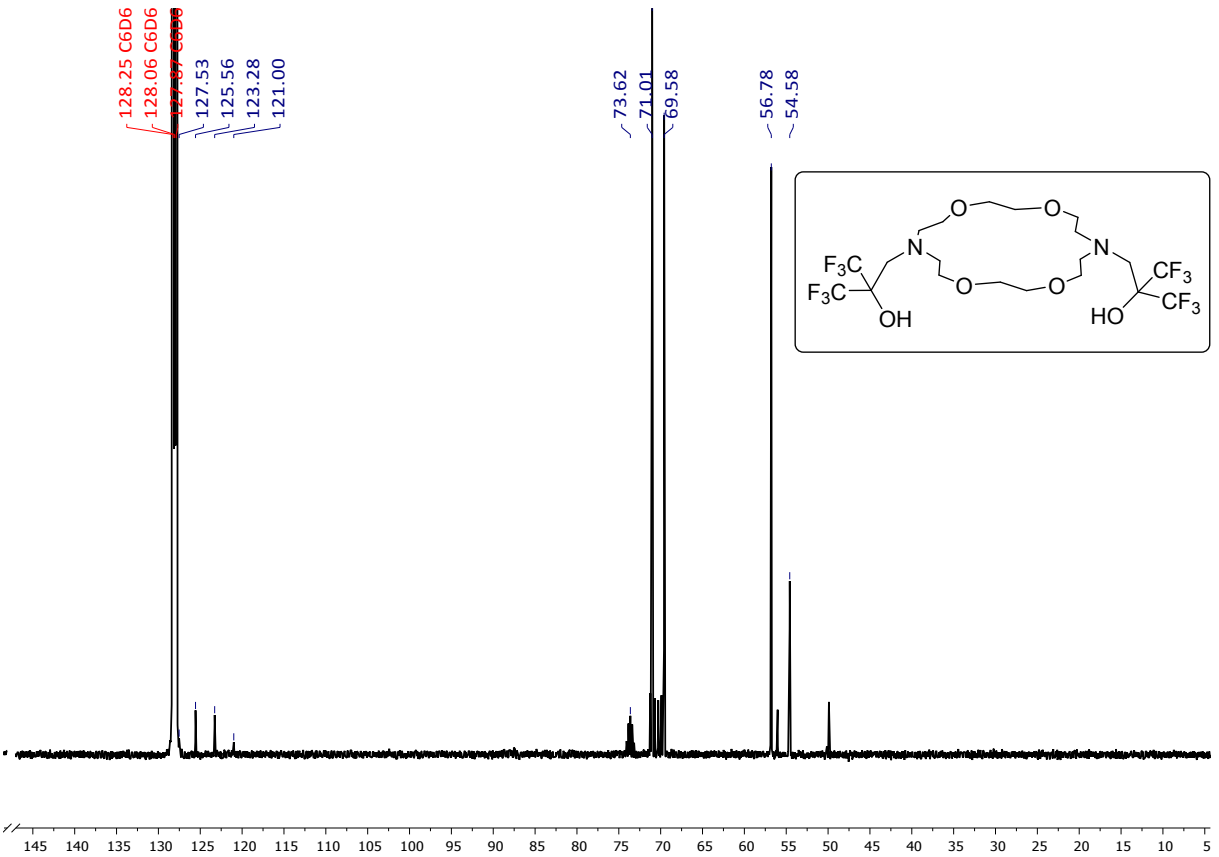


Figure S19: $^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, C_6D_6, 298 K) of $\{(N_2O_4)R^F{}_2O_2\}H_2$ (**5-H$_2$**).

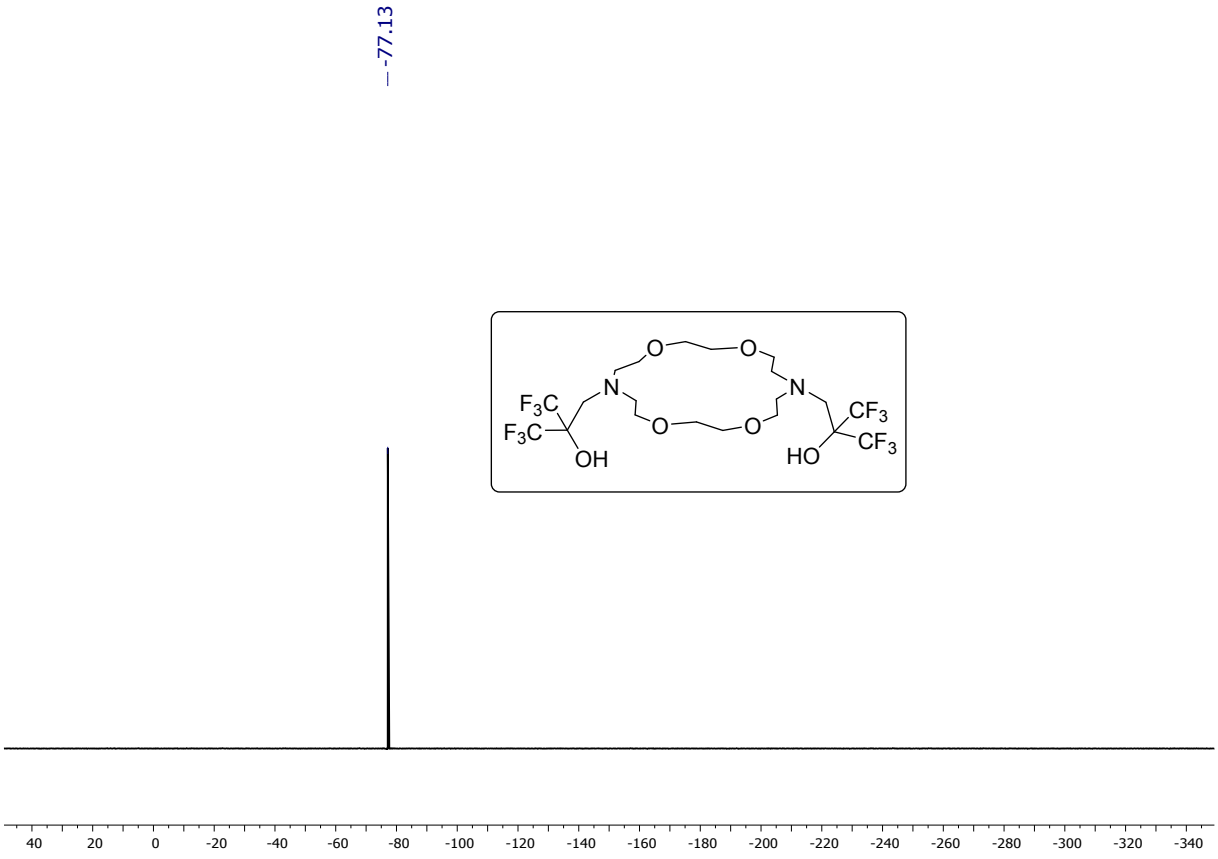


Figure S20: $^{19}F\{^{1}H\}$ NMR (376 MHz, C_6D_6, 298 K) of $\{(N_2O_4)R^F{}_2O_2\}H_2$ (**5-H$_2$**).

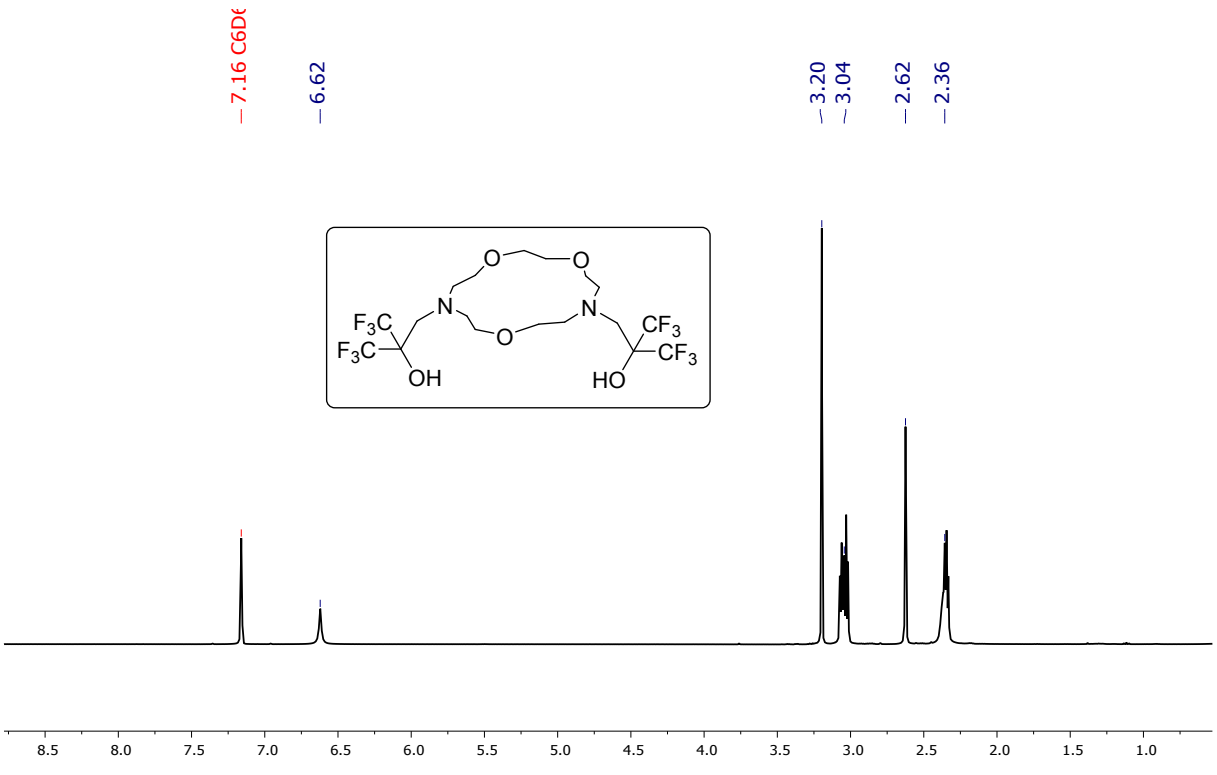


Figure S21: ^{1}H NMR spectrum (400 MHz, C_6D_6, 298 K) of $\{(N_2O_3)R^F{}_2O_2\}H_2$ (**6-H$_2$**).

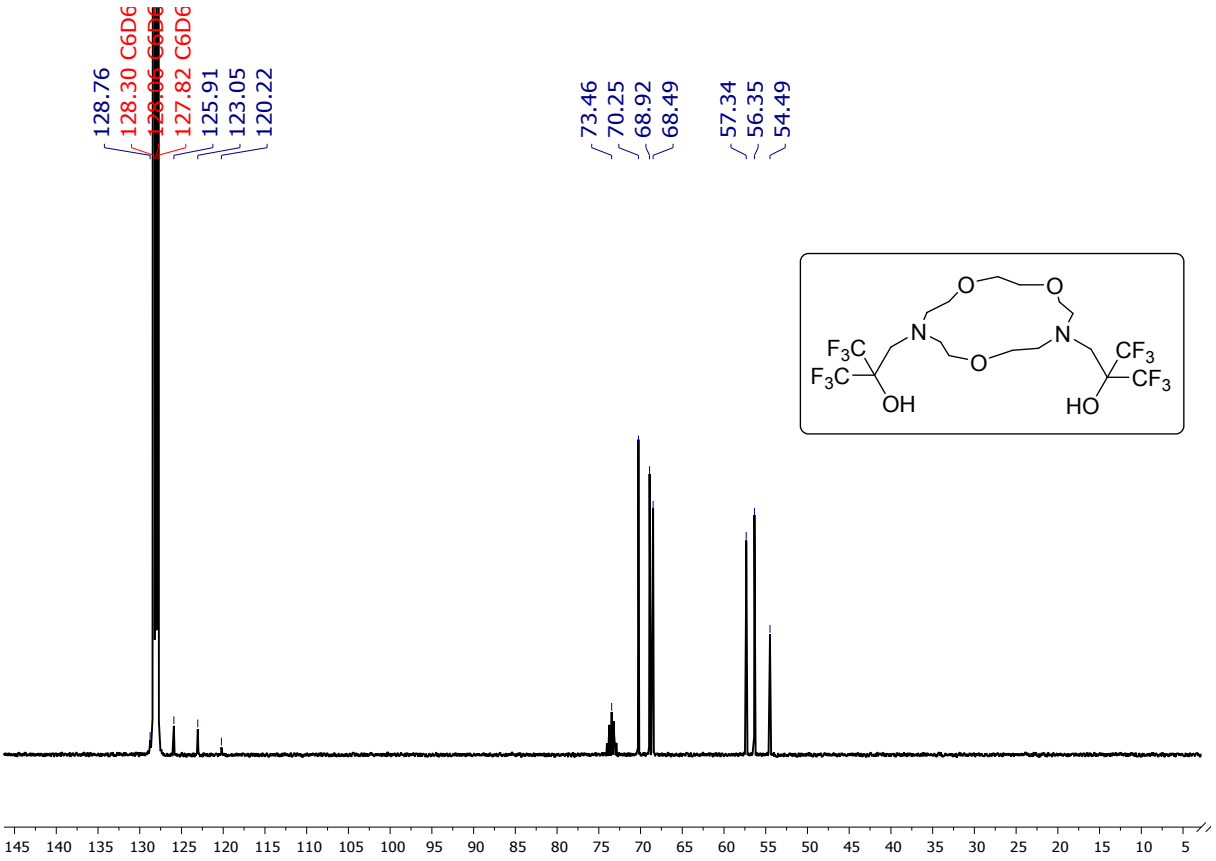


Figure S22: $^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, C_6D_6, 298 K) of $\{(N_2O_3)R^F{}_2O_2\}H_2$ (**6-H$_2$**).

Figure S23: $^{19}F\{^{1}H\}$ NMR (376 MHz, C_6D_6, 298 K) of $\{(N_2O_3)R^F{}_2O_2\}H_2$ (**6-H$_2$**).

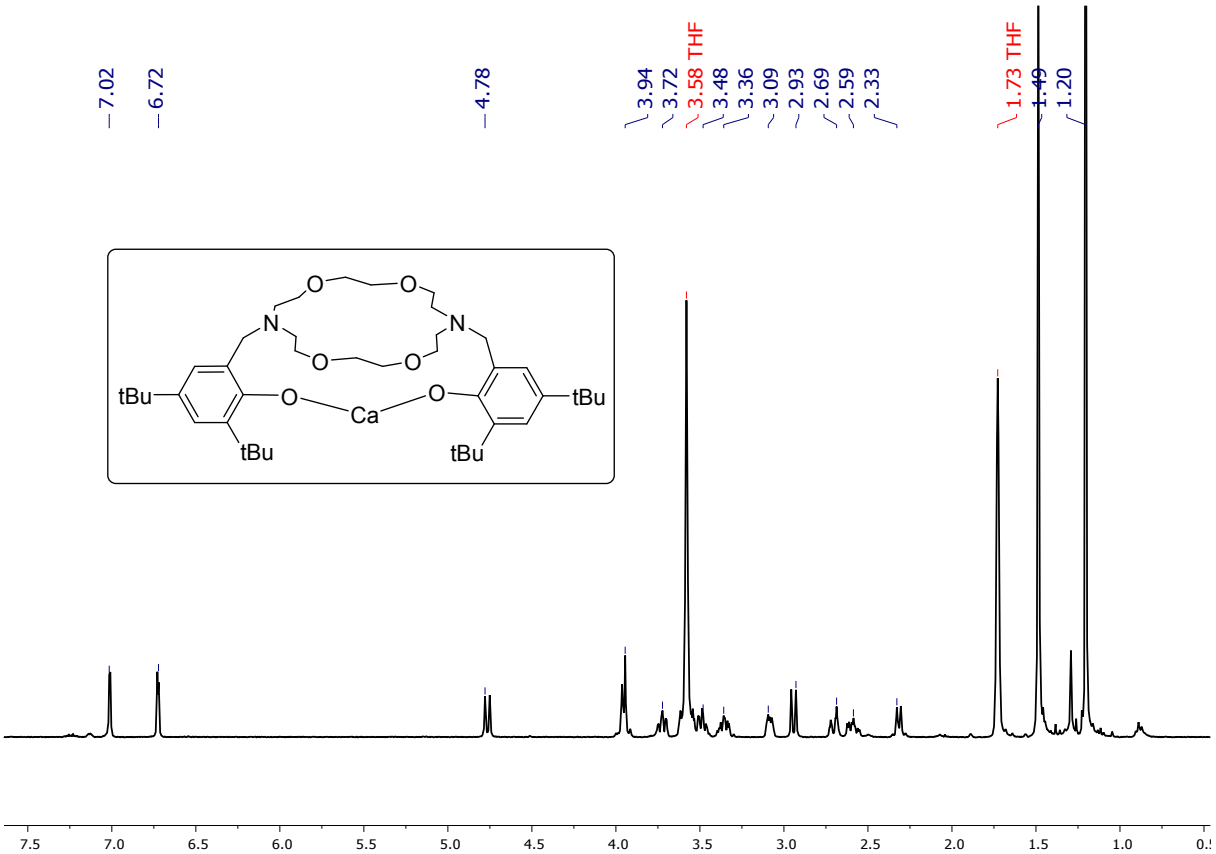


Figure S24: ^{1}H NMR spectrum (400 MHz, thf-d_8, 298 K) of [$\{(N_2O_4)Ar_2O_2\}Ca$] (**3-Ca**).

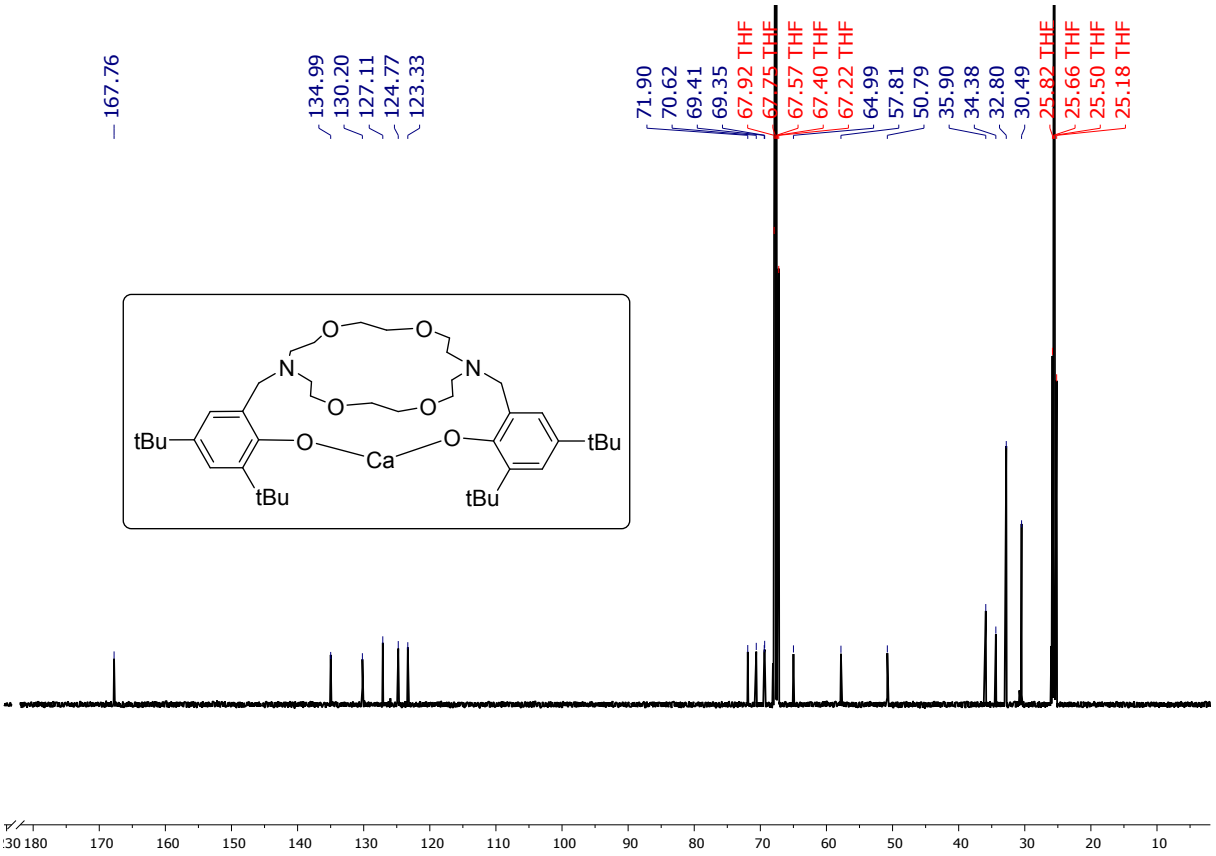


Figure S25: $^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, thf-d_8, 298 K) of [{(N_2O_4)Ar_2O_2}Ca] (**3-Ca**).

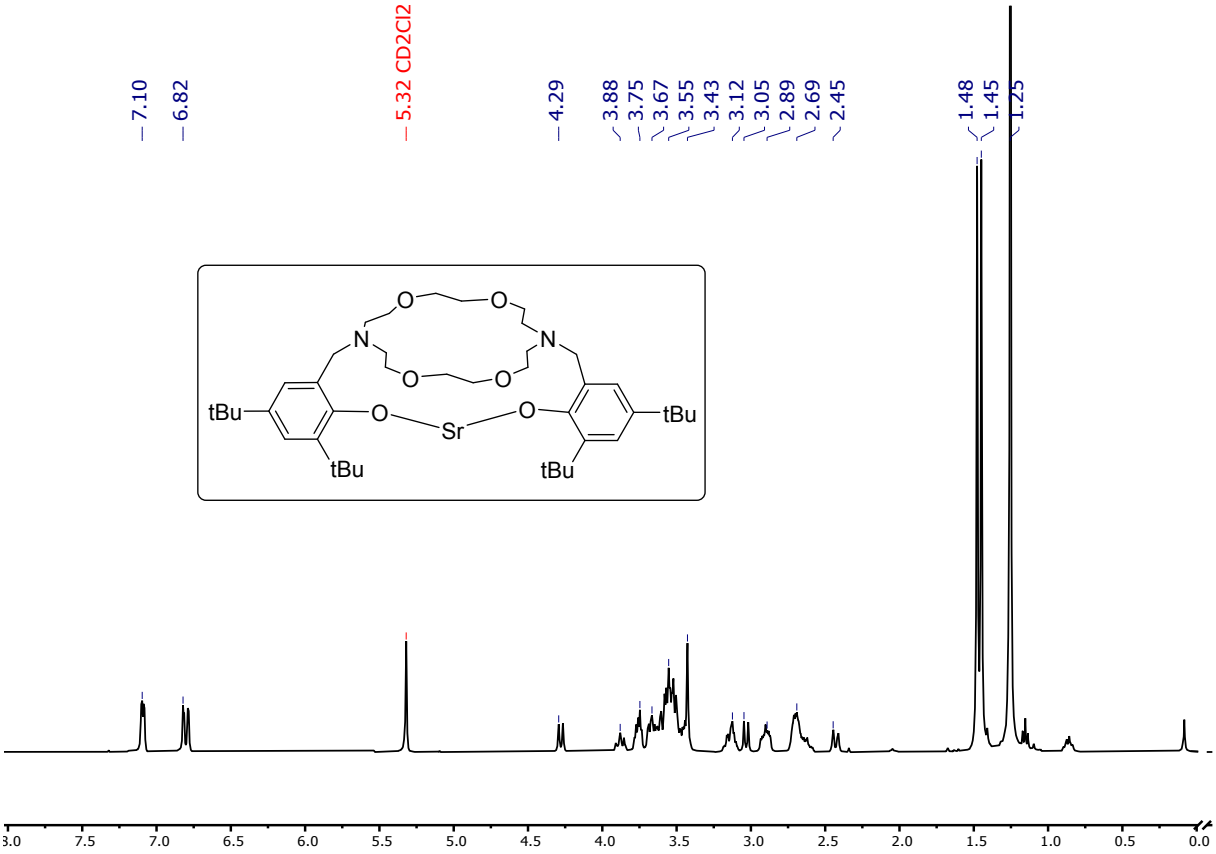


Figure S26: ^{1}H NMR spectrum (400 MHz, CD_2Cl_2, 298 K) of [{(N_2O_4)Ar_2O_2}Sr] (**3-Sr**).

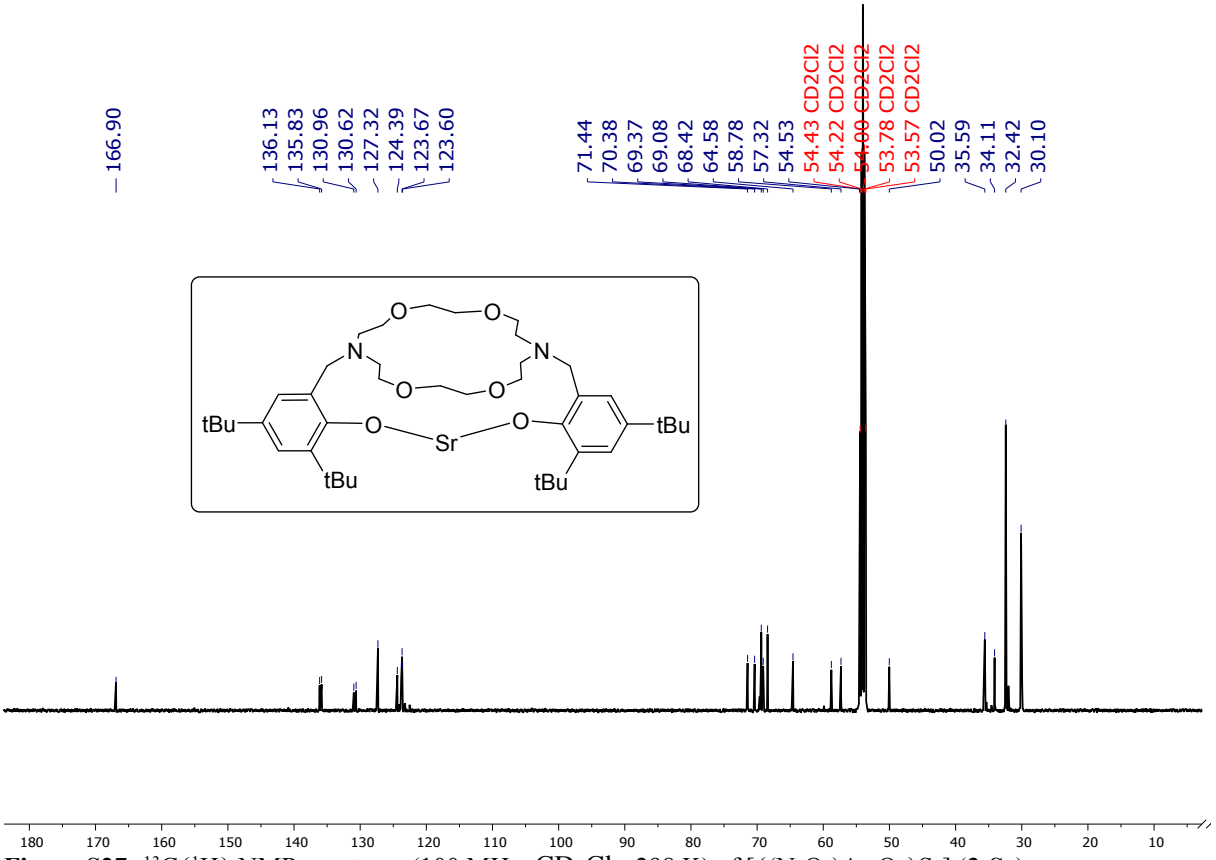


Figure S27: $^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, CD_2Cl_2, 298 K) of [{(N_2O_4)Ar_2O_2}Sr] (**3-Sr**).

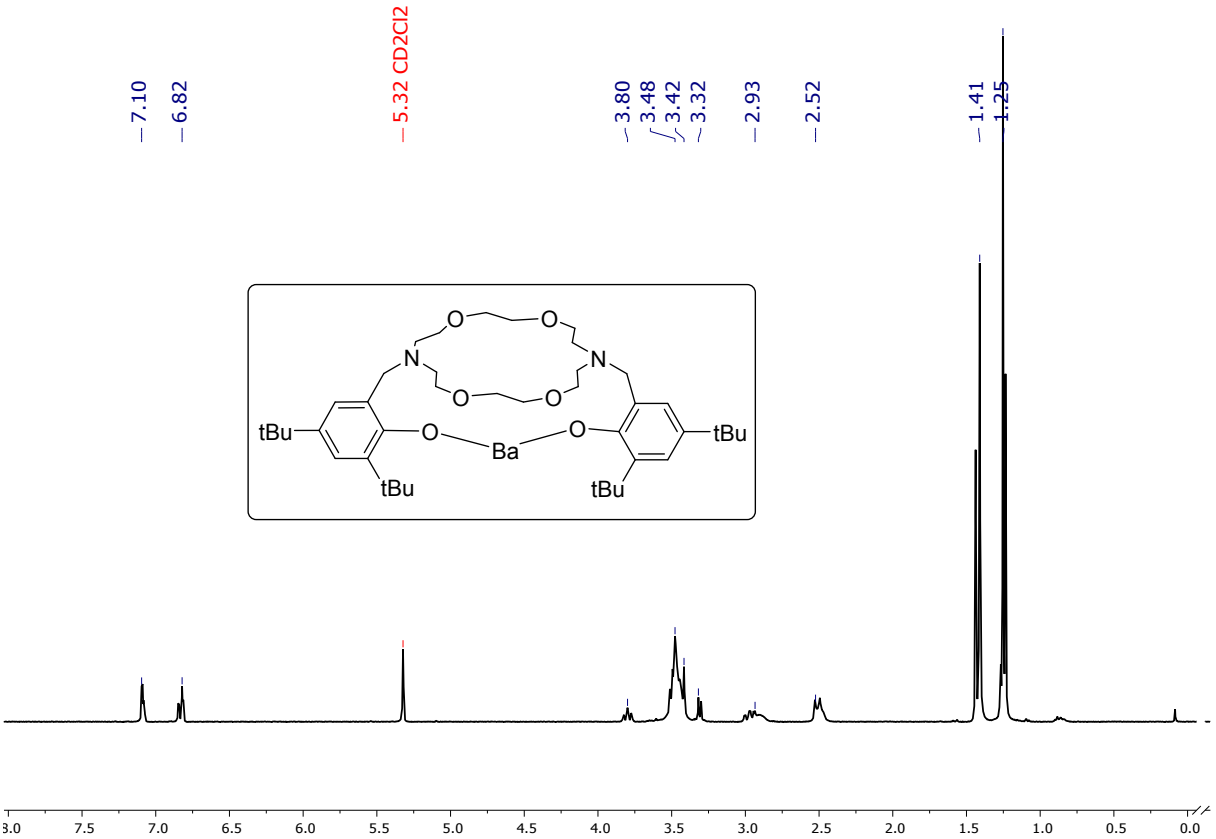


Figure S28: ^{1}H NMR spectrum (400 MHz, CD_2Cl_2, 298 K) of [{(N_2O_4)Ar_2O_2}Ba] (**3-Ba**).

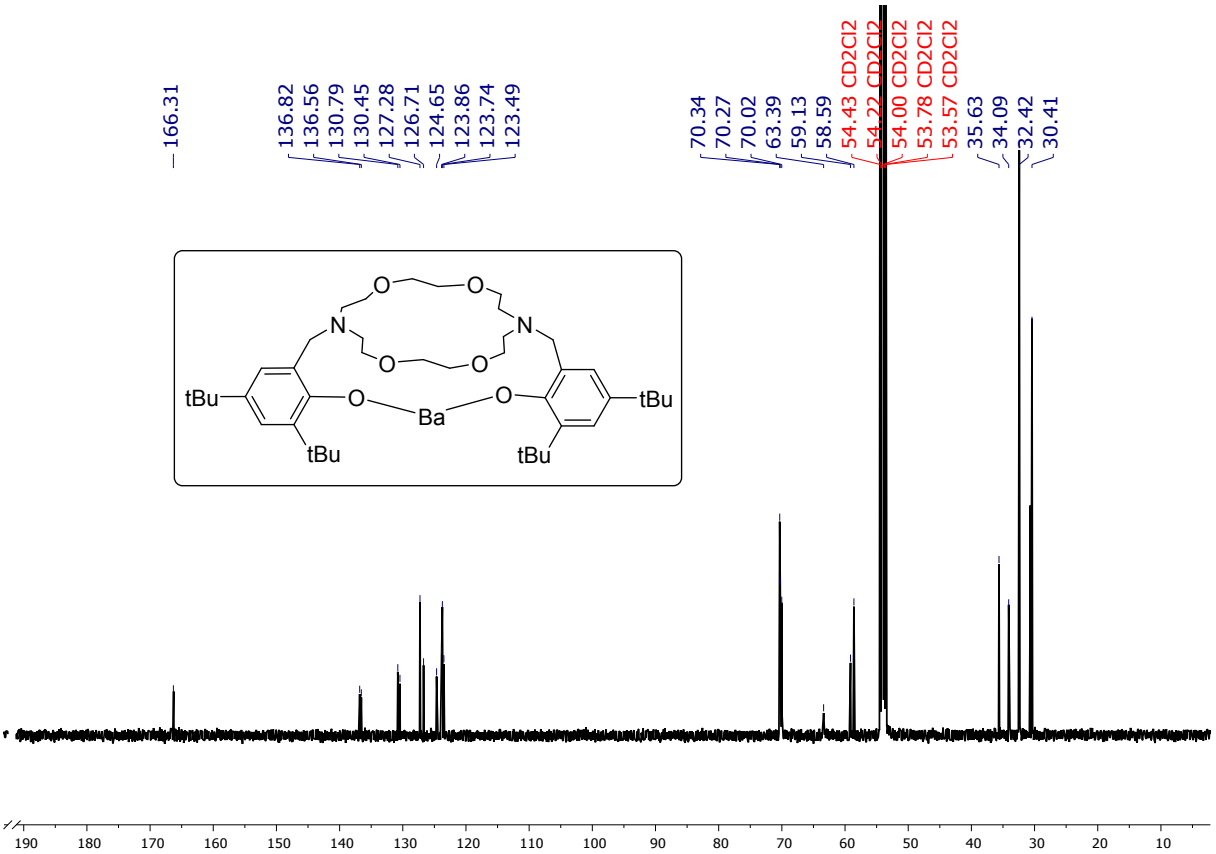


Figure S29: $^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, CD_2Cl_2, 298 K) of [{(N_2O_4)Ar_2O_2}Ba] (**3-Ba**).

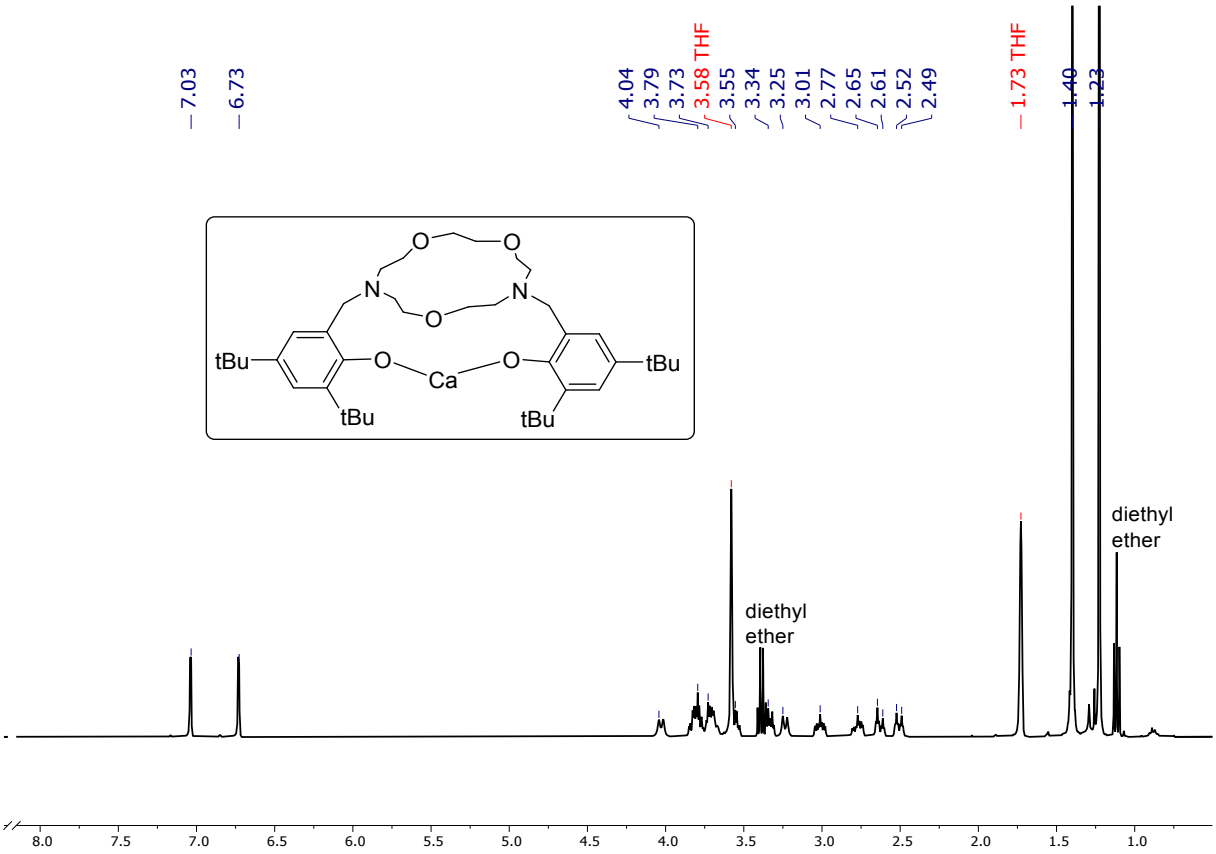


Figure S30: ^{1}H NMR spectrum (400 MHz, thf-d_8, 298 K) of [{(N_2O_3)Ar_2O_2}Ca] (**4-Ca**).

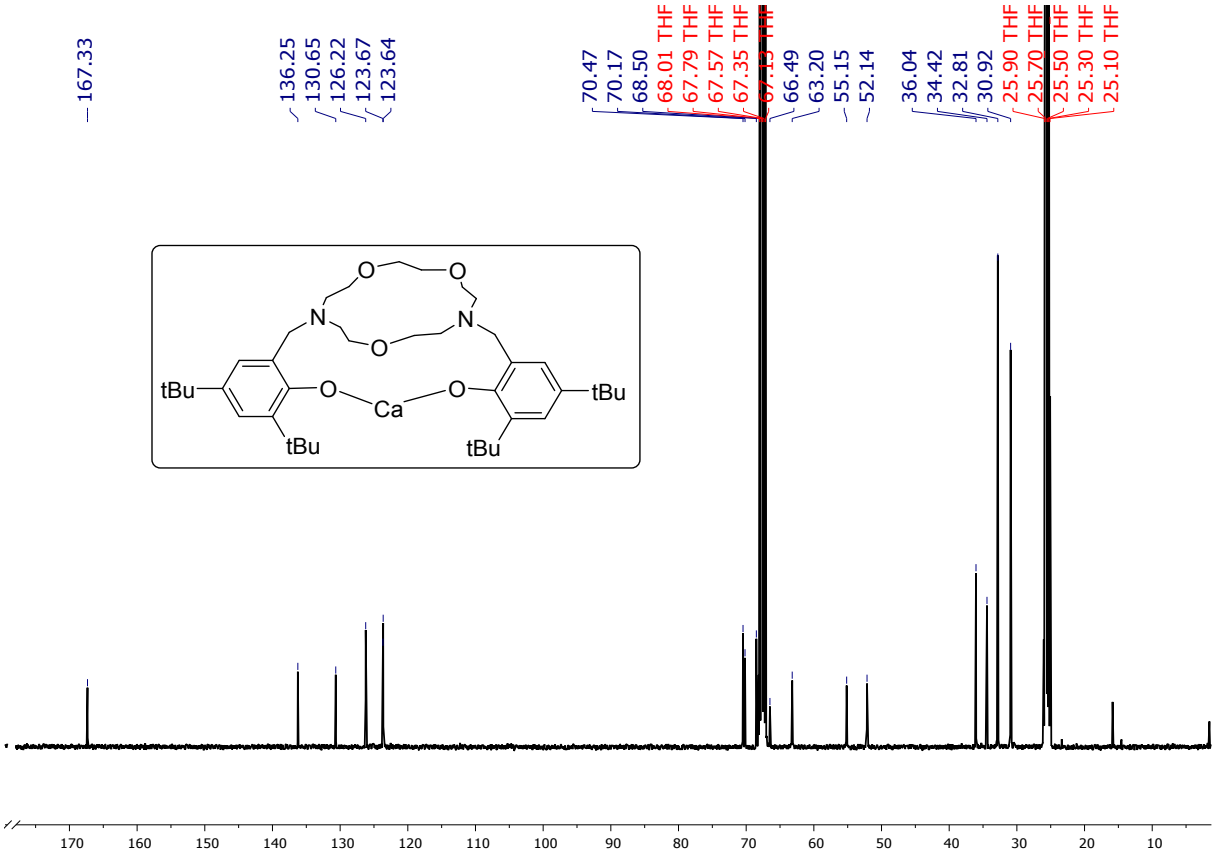


Figure S31: $^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, thf-d_8, 298 K) of [{(N_2O_3)Ar_2O_2}Ca] (**4-Ca**).

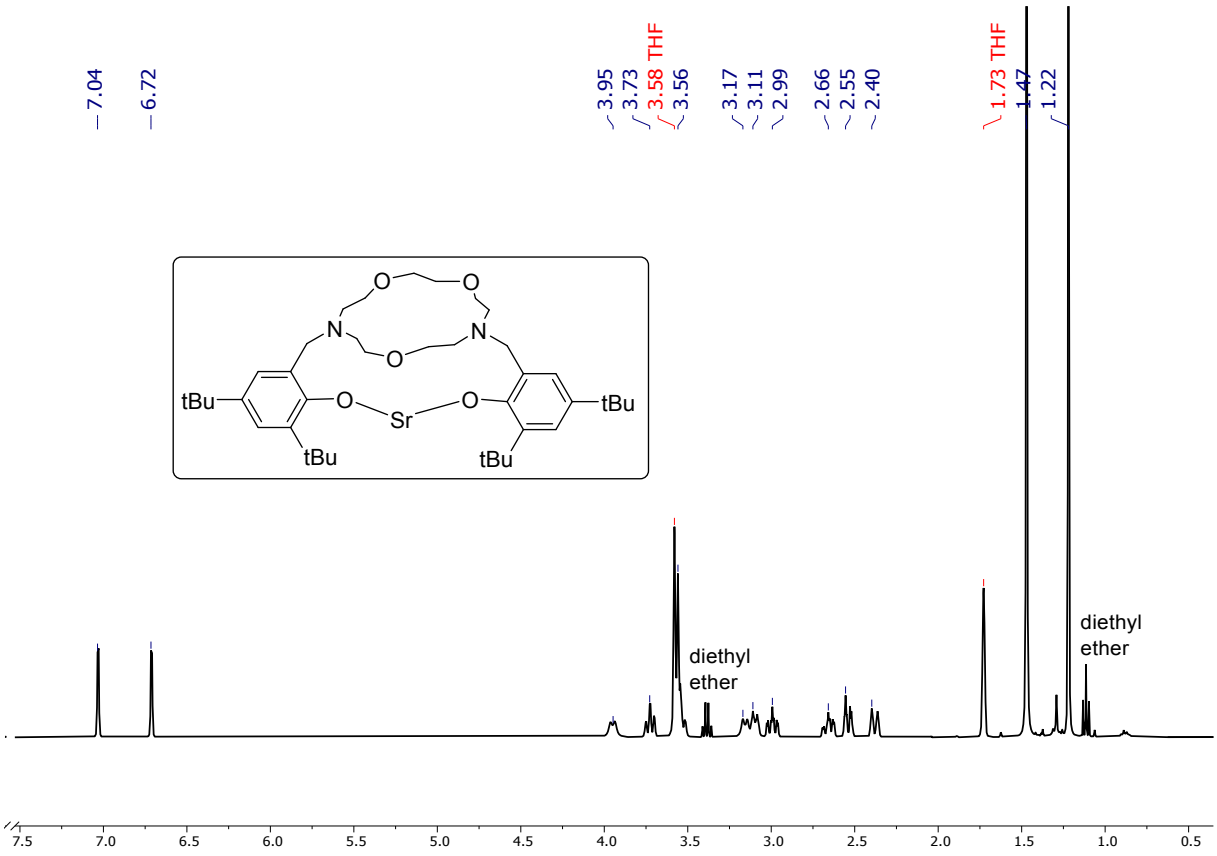


Figure S32: ^{1}H NMR spectrum (400 MHz, thf-d_8, 298 K) of [{(N_2O_3)Ar_2O_2}Sr] (**4-Sr**).

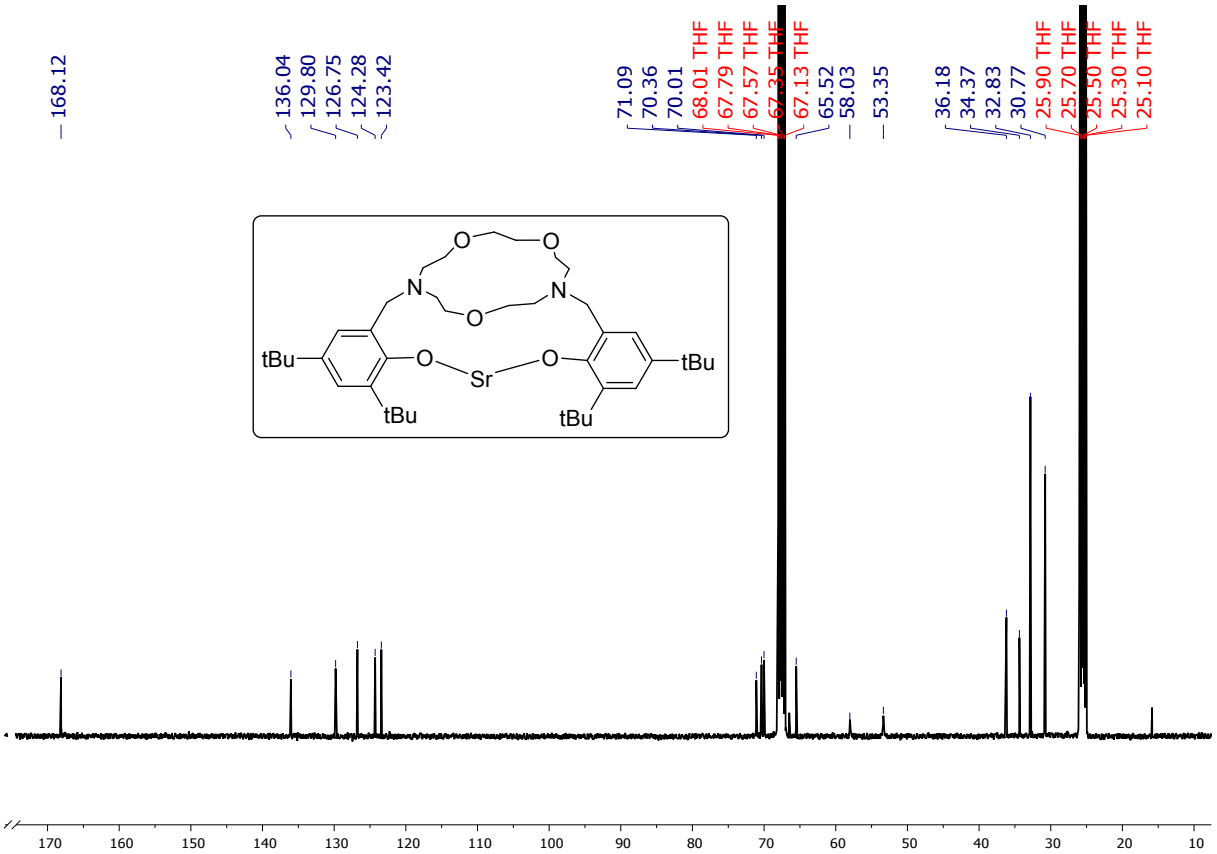


Figure S33: $^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, thf-d_8, 298 K) of [{(N_2O_3)Ar_2O_2}Sr] (**4-Sr**).

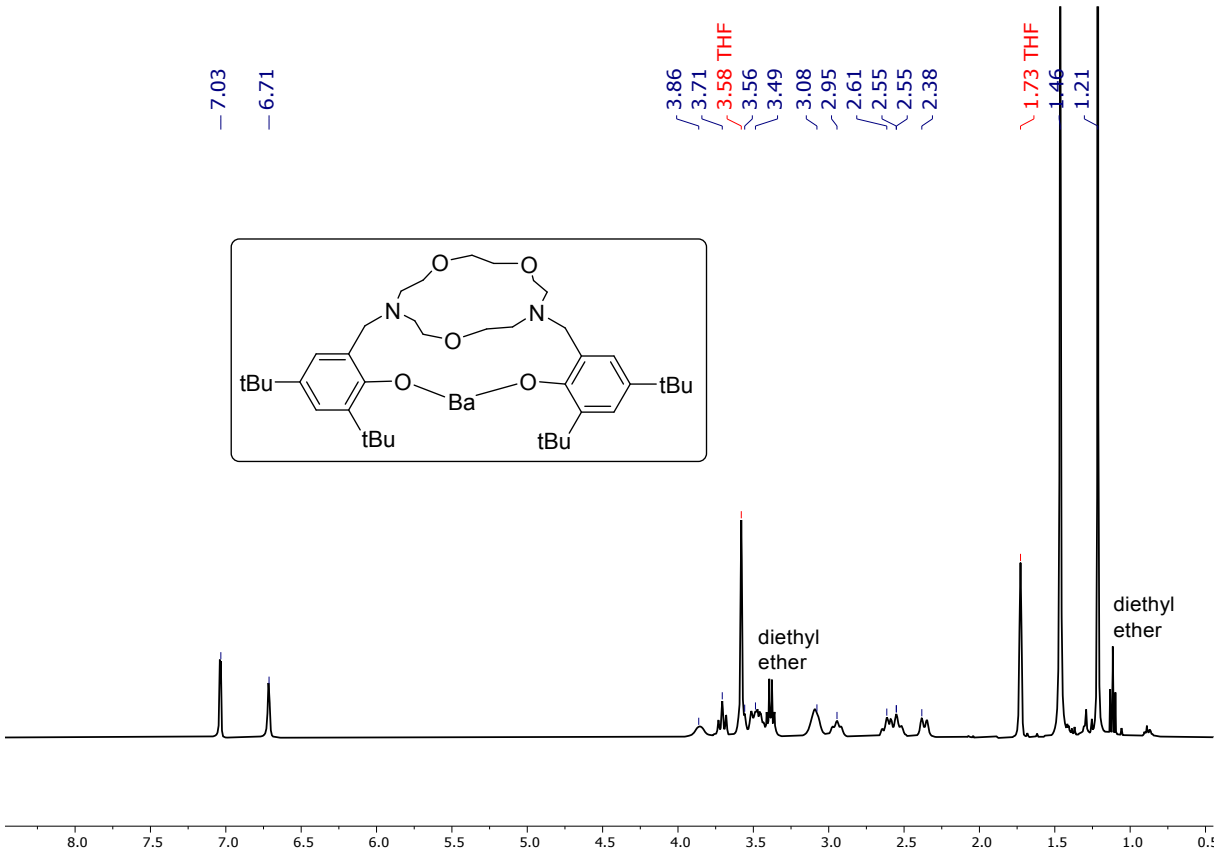


Figure S34: ^{1}H NMR spectrum (400 MHz, thf-d_8, 298 K) of [{(N_2O_3)Ar_2O_2}Ba] (**4-Ba**).

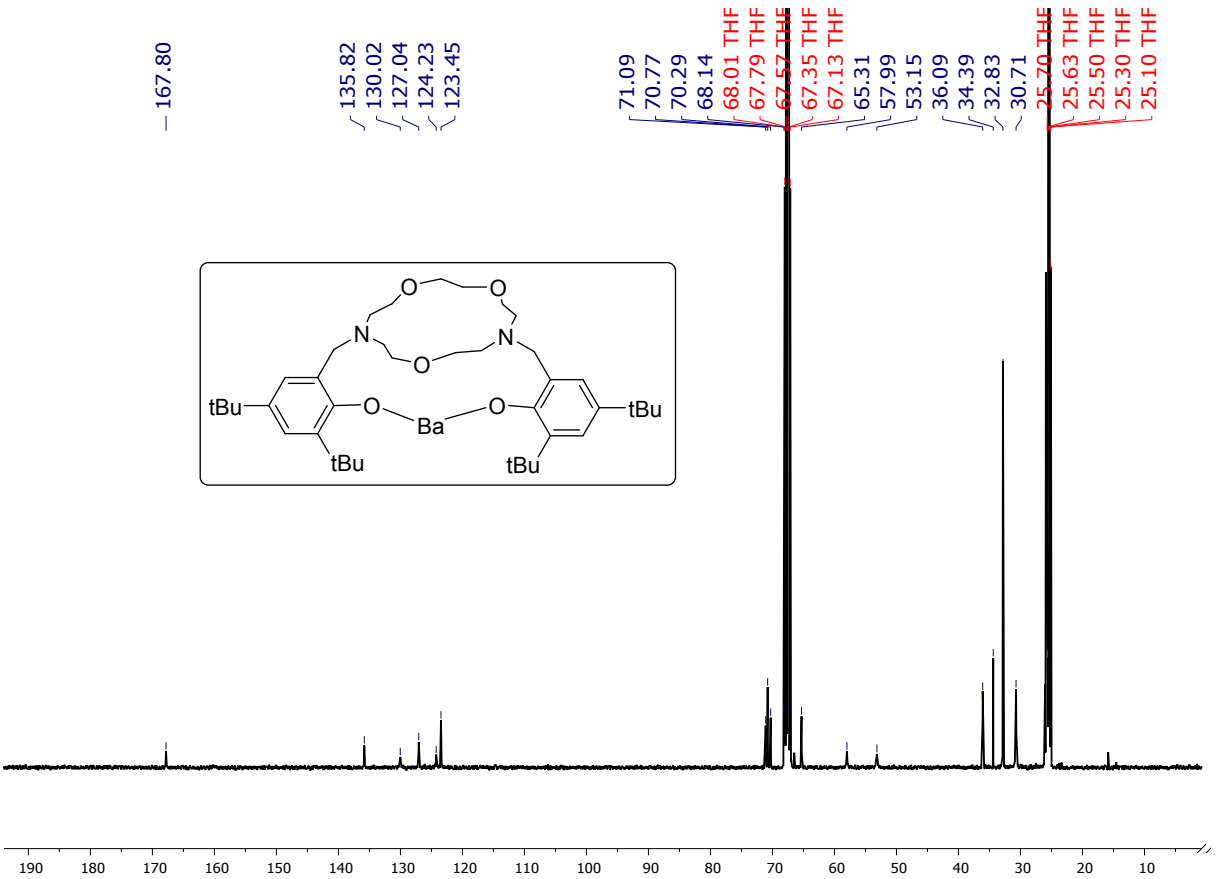


Figure S35: $^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, thf-d_8, 298 K) of [{$(N_2O_3)Ar_2O_2$}Ba] (**4-Ba**).

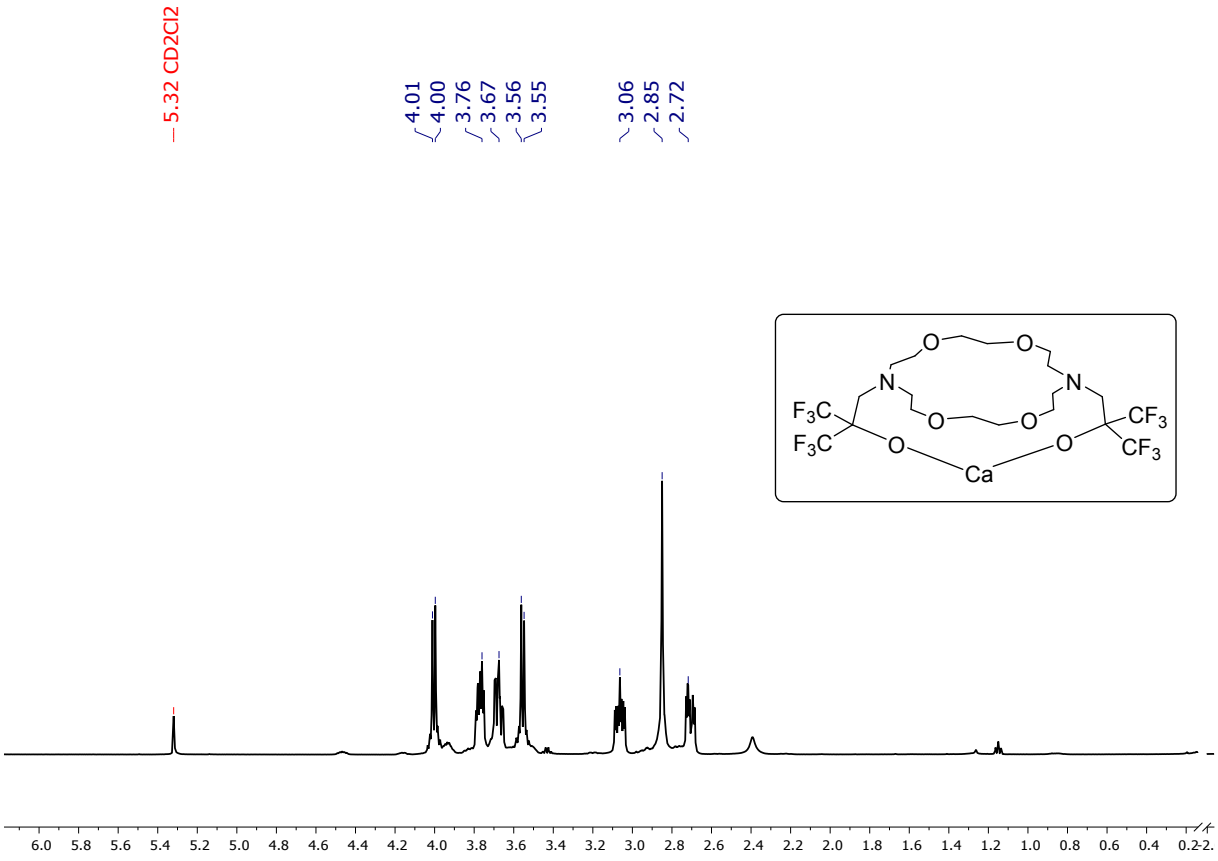


Figure S36: ^{1}H NMR spectrum (400 MHz, CD_2Cl_2, 298 K) of [{$(N_2O_4)R^F{}_2O_2$}Ca] (**5-Ca**).

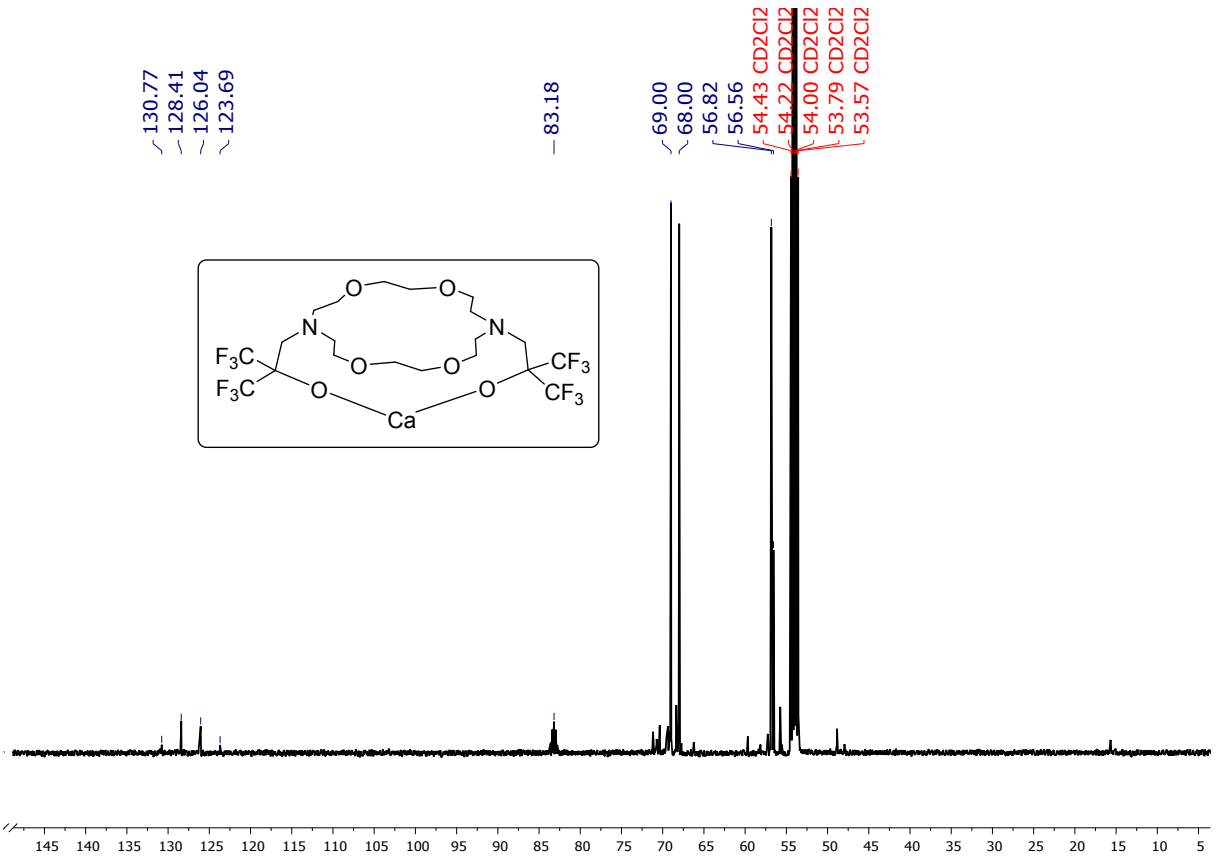


Figure S37: $^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, CD_2Cl_2, 298 K) of [{$(N_2O_4)R^F{}_2O_2$}Ca] (**5-Ca**).

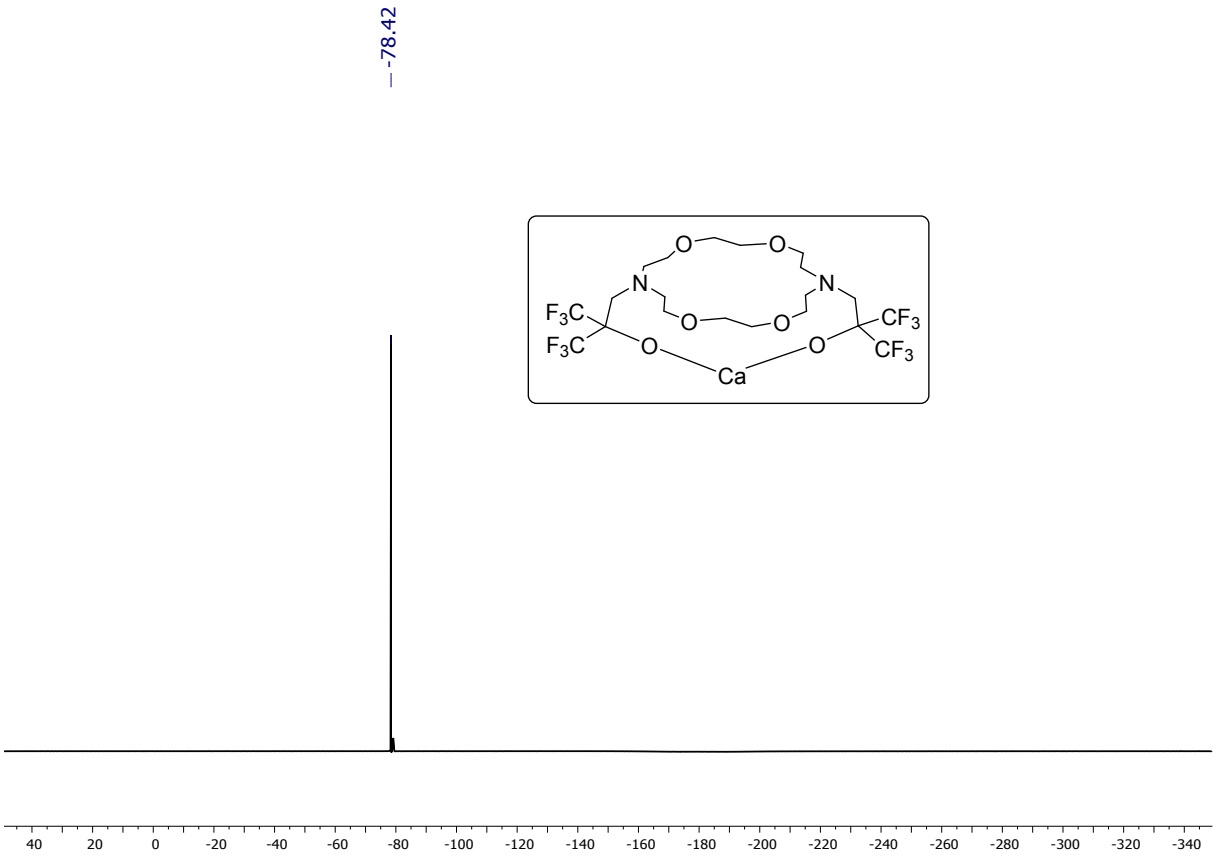


Figure S38: $^{19}F\{^{1}H\}$ NMR (376 MHz, CD_2Cl_2, 298 K) of [{$(N_2O_4)R^F{}_2O_2$}Ca] (**5-Ca**).

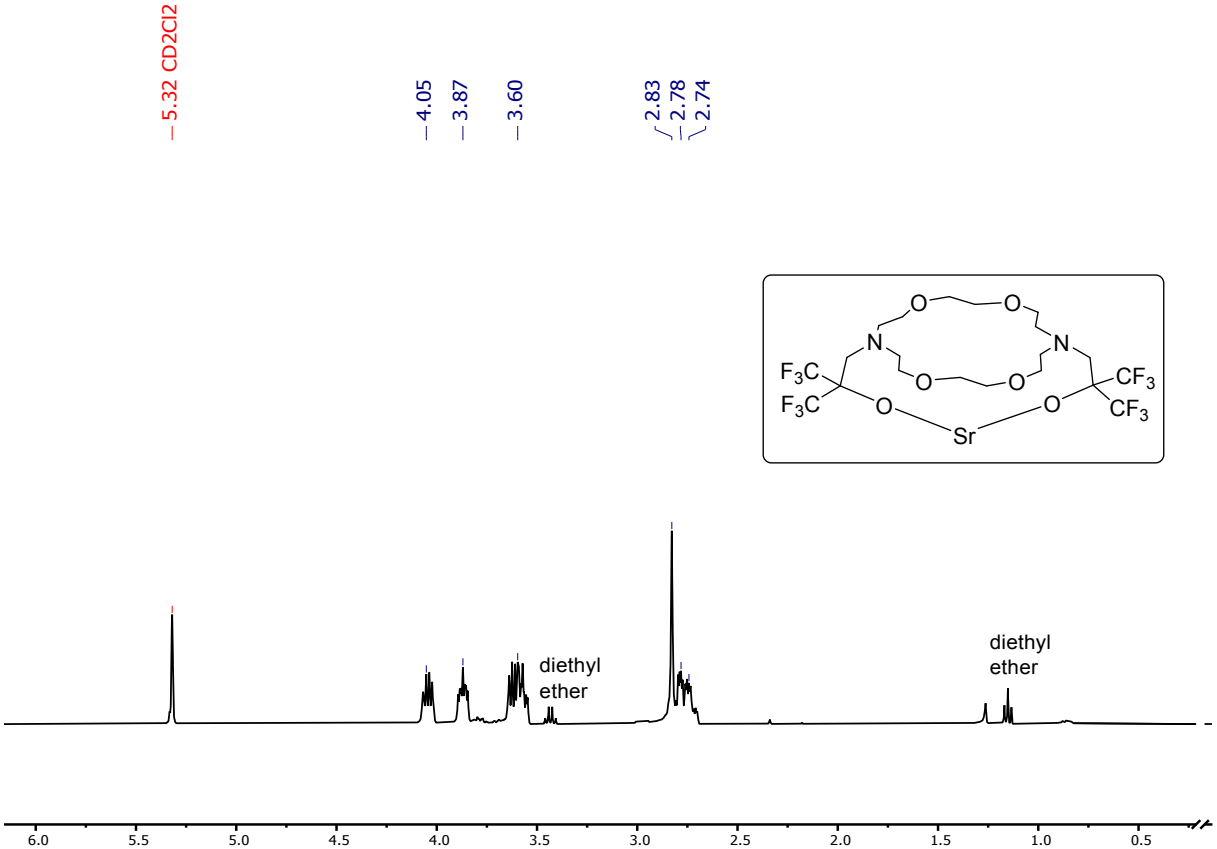


Figure S39: ^{1}H NMR spectrum (400 MHz, CD_2Cl_2, 298 K) of [{$(N_2O_4)R^F{}_2O_2$}Sr] (**5-Sr**).

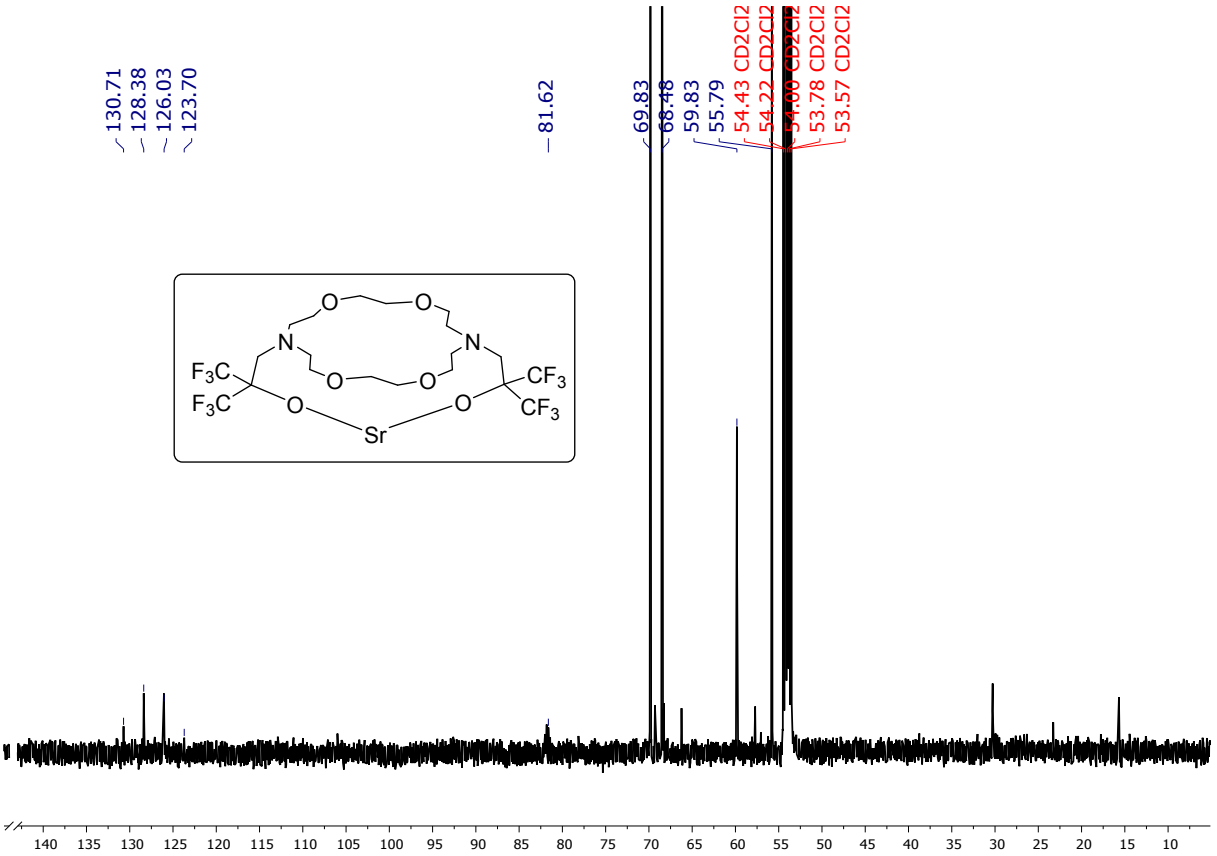


Figure S40: ^{13}C{^{1}H} NMR spectrum (100 MHz, CD_2Cl_2, 298 K) of [{$(N_2O_4)R^F{}_2O_2$}Sr] (**5-Sr**).

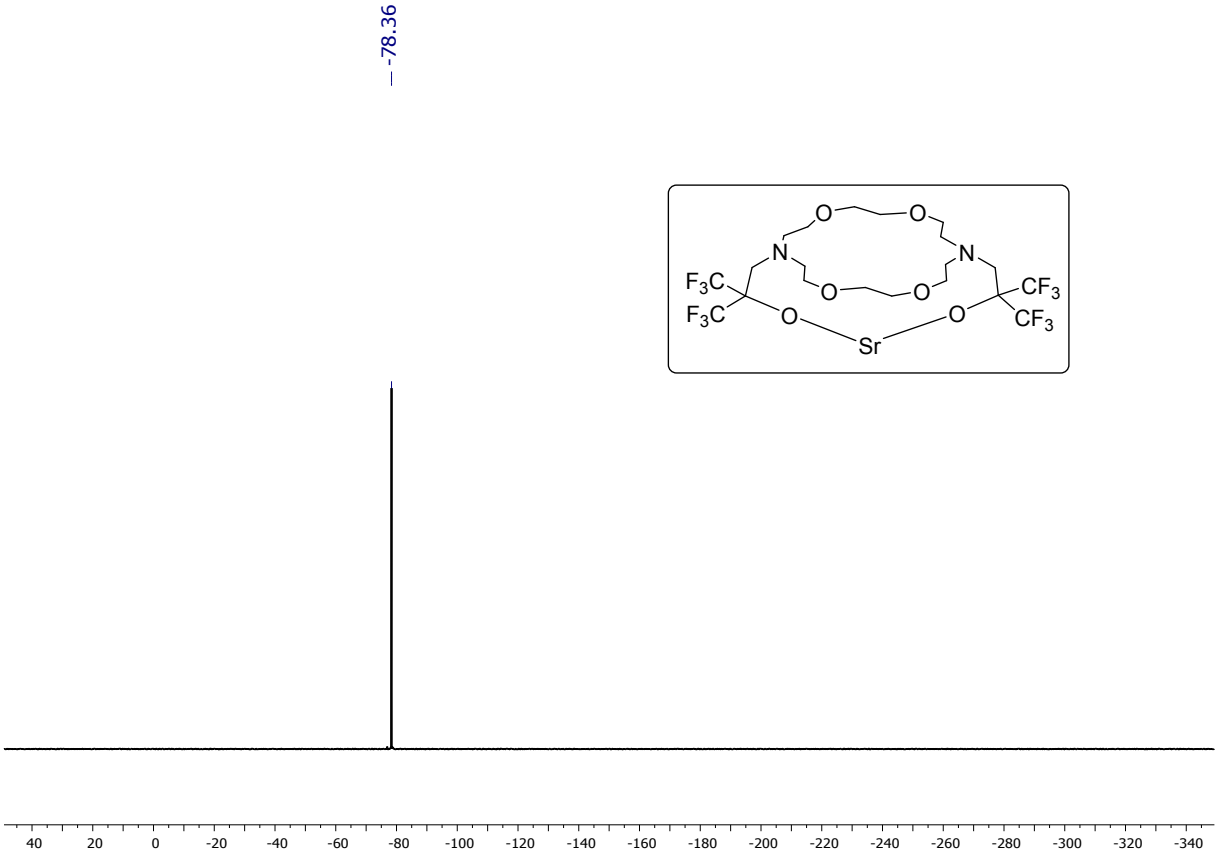


Figure S41: $^{19}F\{^{1}H\}$ NMR (376 MHz, CD_2Cl_2, 298 K) of [{$(N_2O_4)R^F{}_2O_2$}Sr] (**5-Sr**).

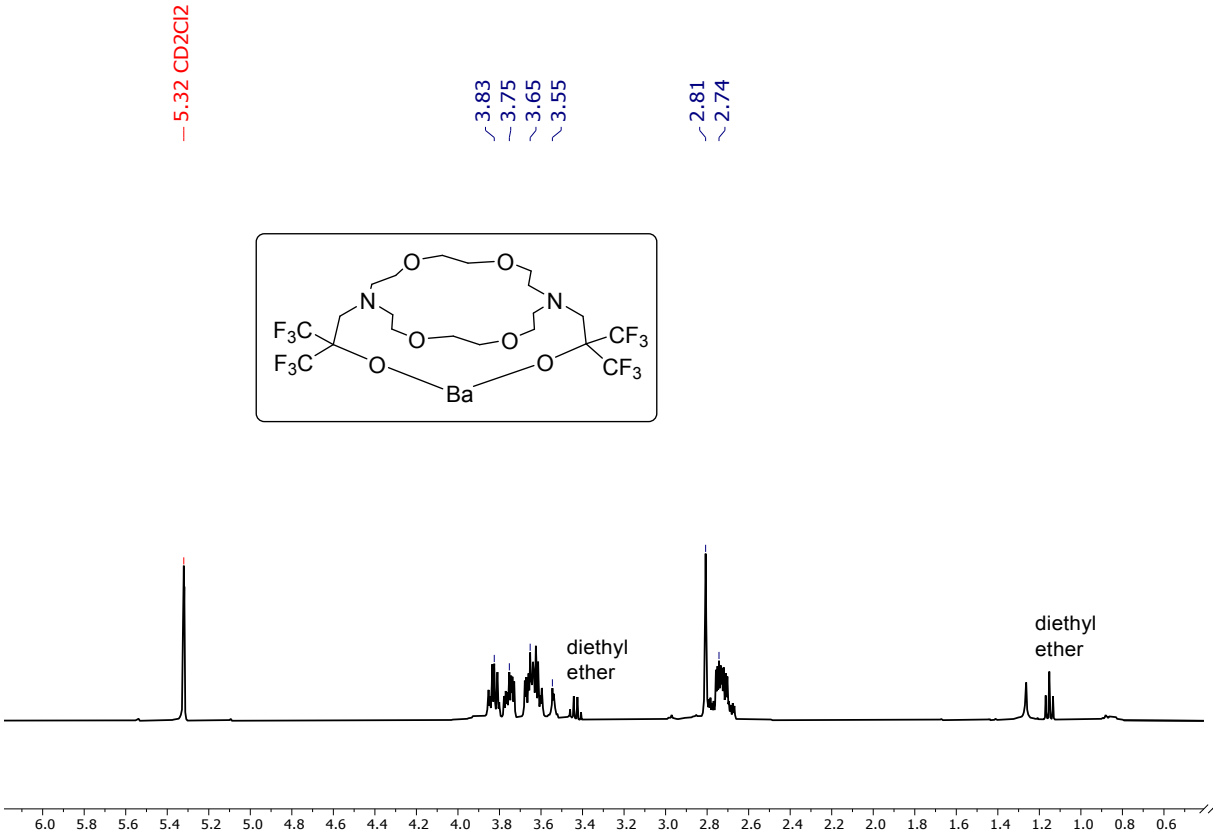


Figure S42: ^{1}H NMR spectrum (400 MHz, CD_2Cl_2, 298 K) of [{$(N_2O_4)R^F{}_2O_2$}Ba] (**5-Ba**).

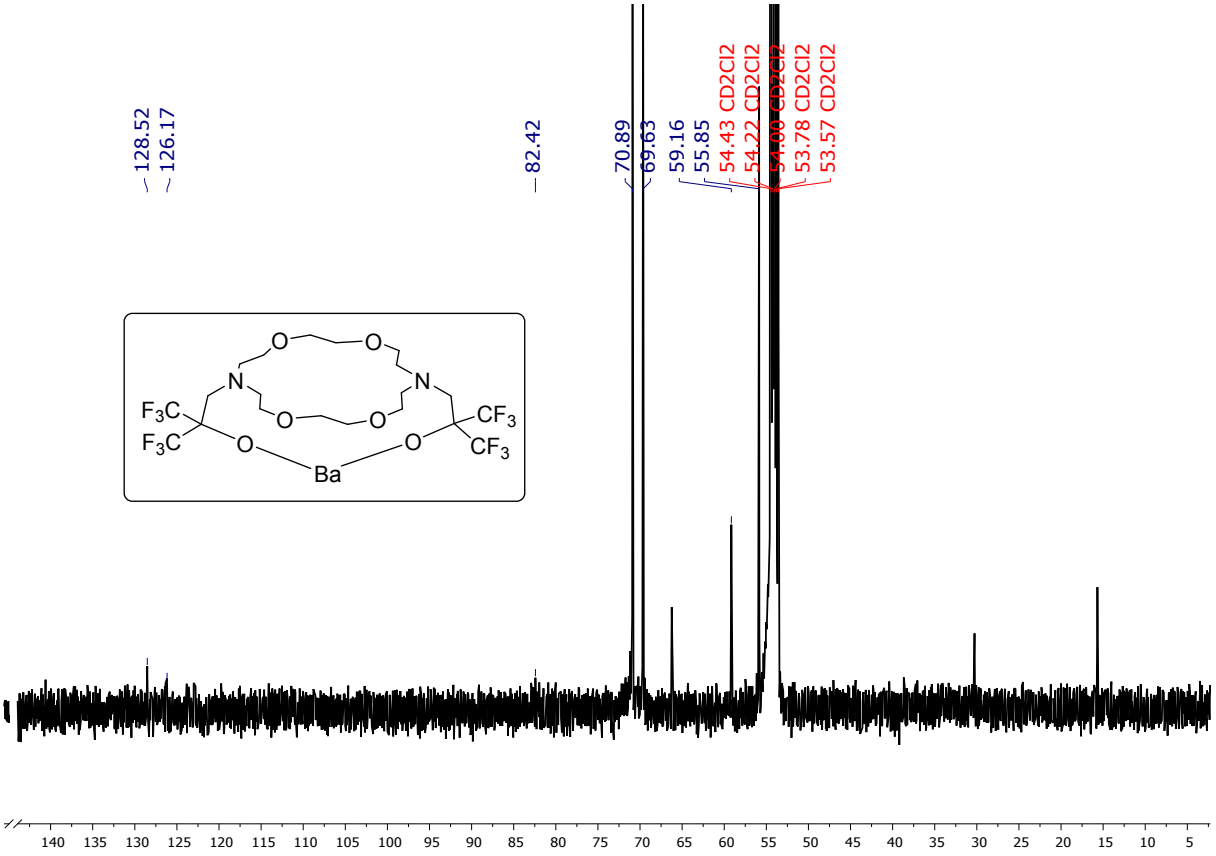


Figure S43: $^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, CD_2Cl_2, 298 K) of [{$(N_2O_4)R^F{}_2O_2$}Ba] (**5-Ba**). The very poor solubility of this complex precludes this acquisition of high-resolution data.

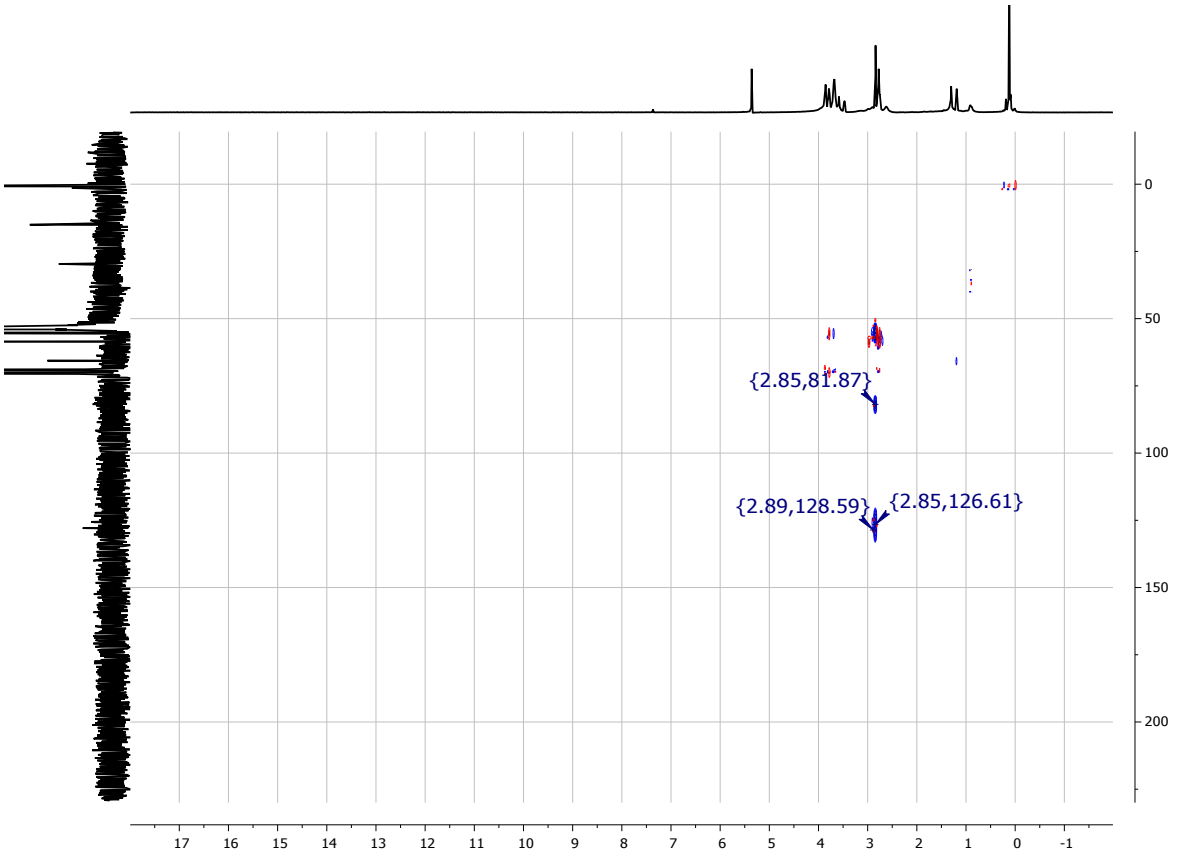


Figure S44: HMBC spectrum (500 MHz, CD_2Cl_2, 298 K) of [{$(N_2O_4)R^F{}_2O_2$}Ba] (**5-Ba**).

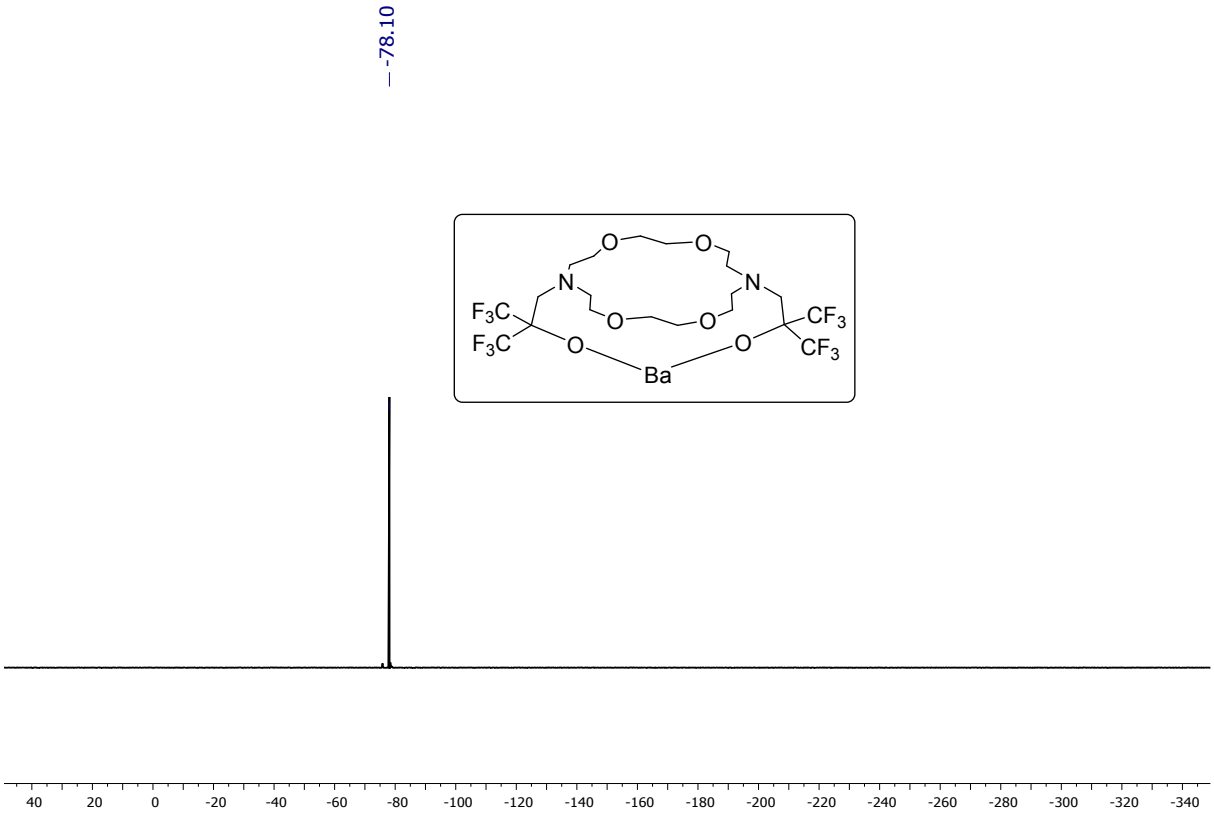


Figure S45: $^{19}F\{^1H\}$ NMR (376 MHz, CD_2Cl_2, 298 K) of [{$(N_2O_4)R^F{}_2O_2$}Ba] (**5-Ba**).

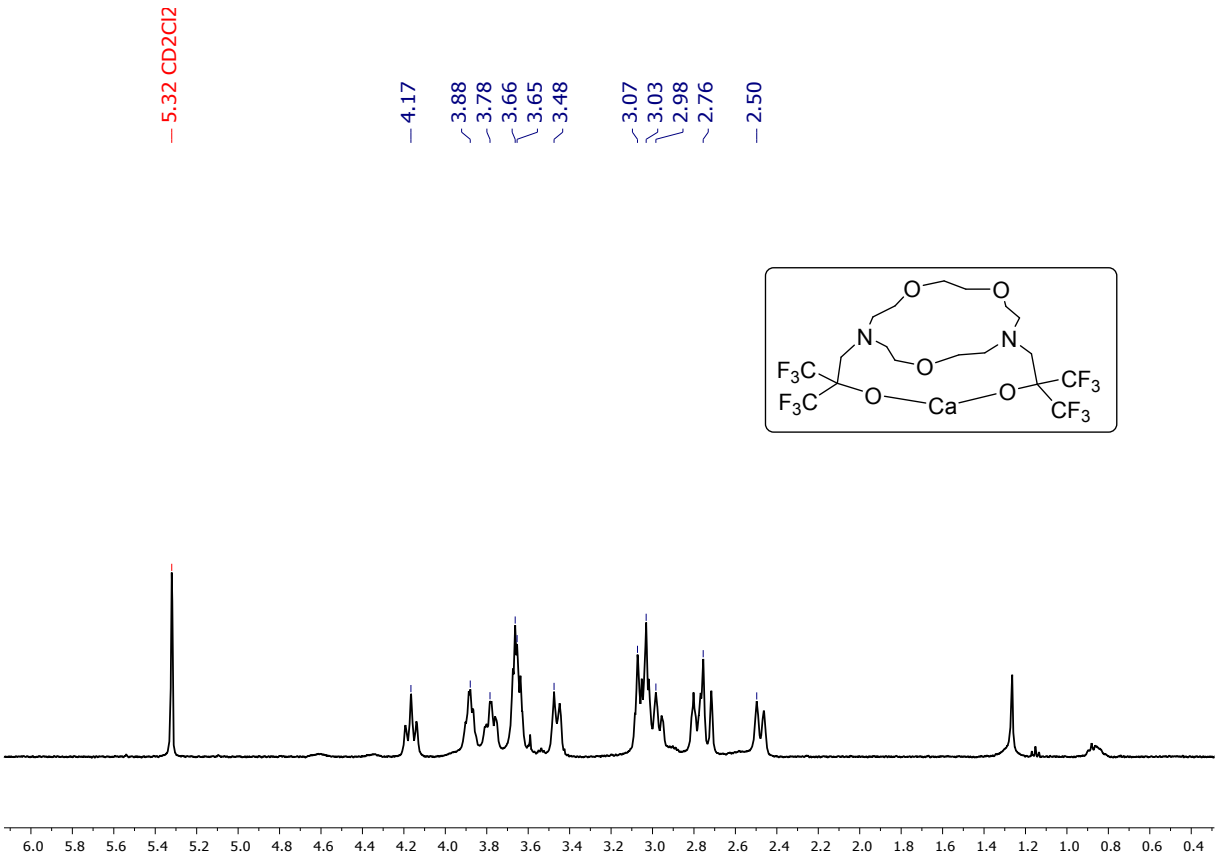


Figure S46: ^{1}H NMR spectrum (400 MHz, CD_2Cl_2, 298 K) of [{$(N_2O_3)R^F{}_2O_2$}Ca] (**6-Ca**).

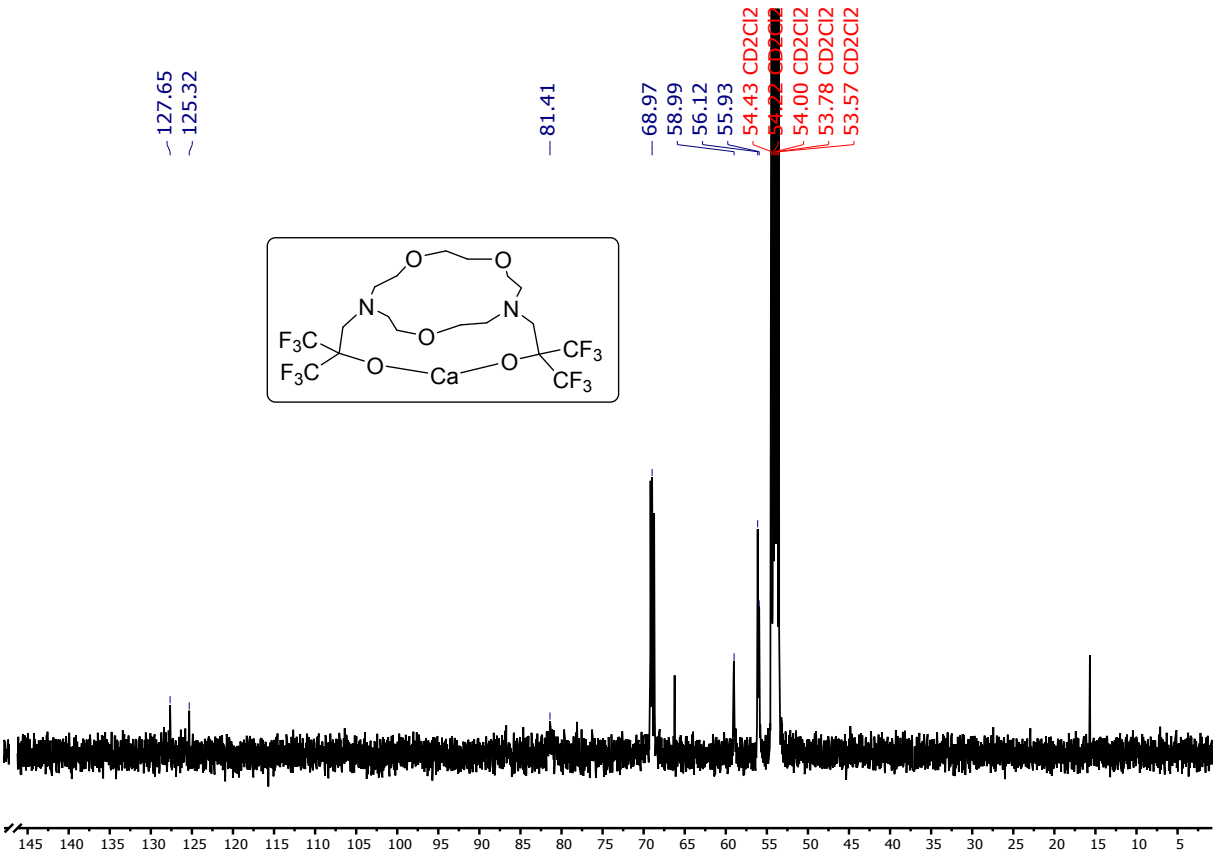


Figure S47: ^{13}C{^{1}H} NMR spectrum (100 MHz, CD_2Cl_2, 298 K) of [{$(N_2O_3)R^F{}_2O_2$}Ca] (**6-Ca**).

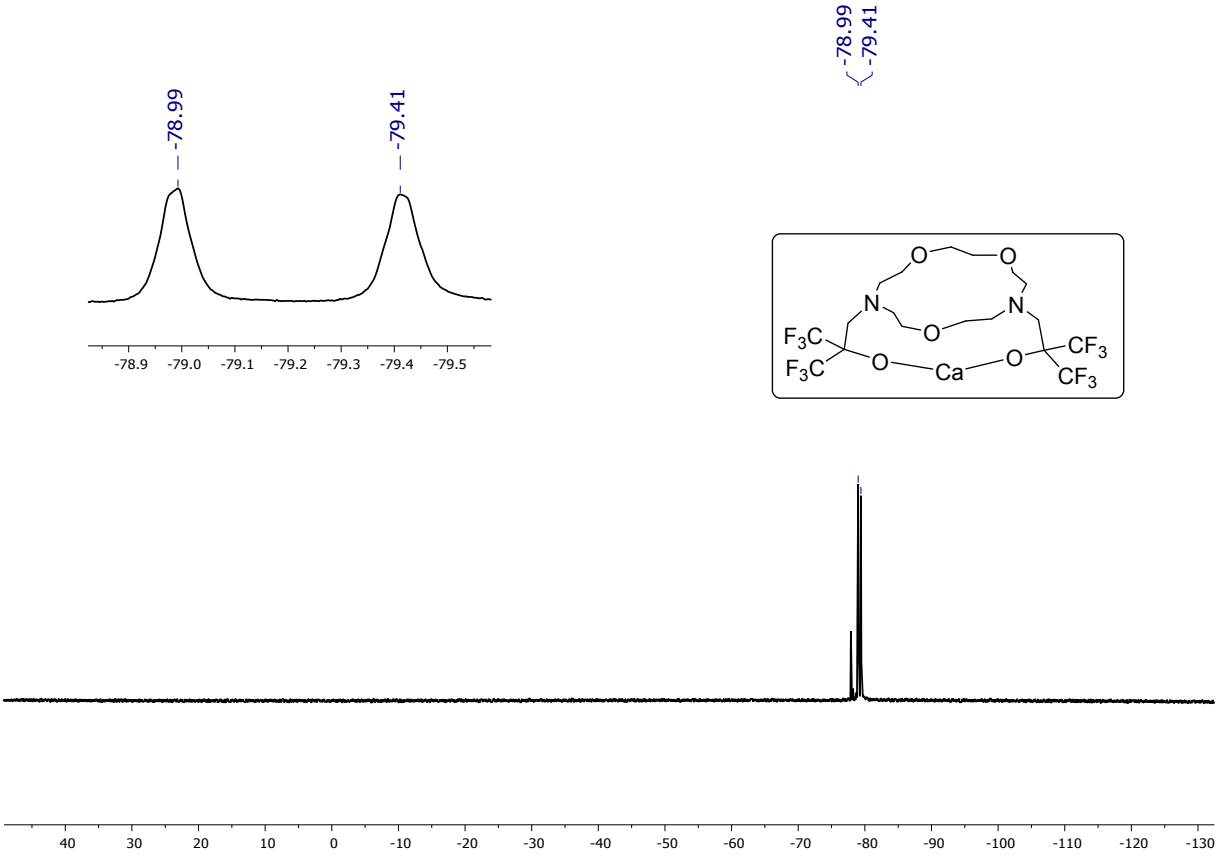


Figure S48: $^{19}F\{^{1}H\}$ NMR (376 MHz, CD_2Cl_2, 298 K) of [{$(N_2O_3)R^F{}_2O_2$}Ca] (**6-Ca**).

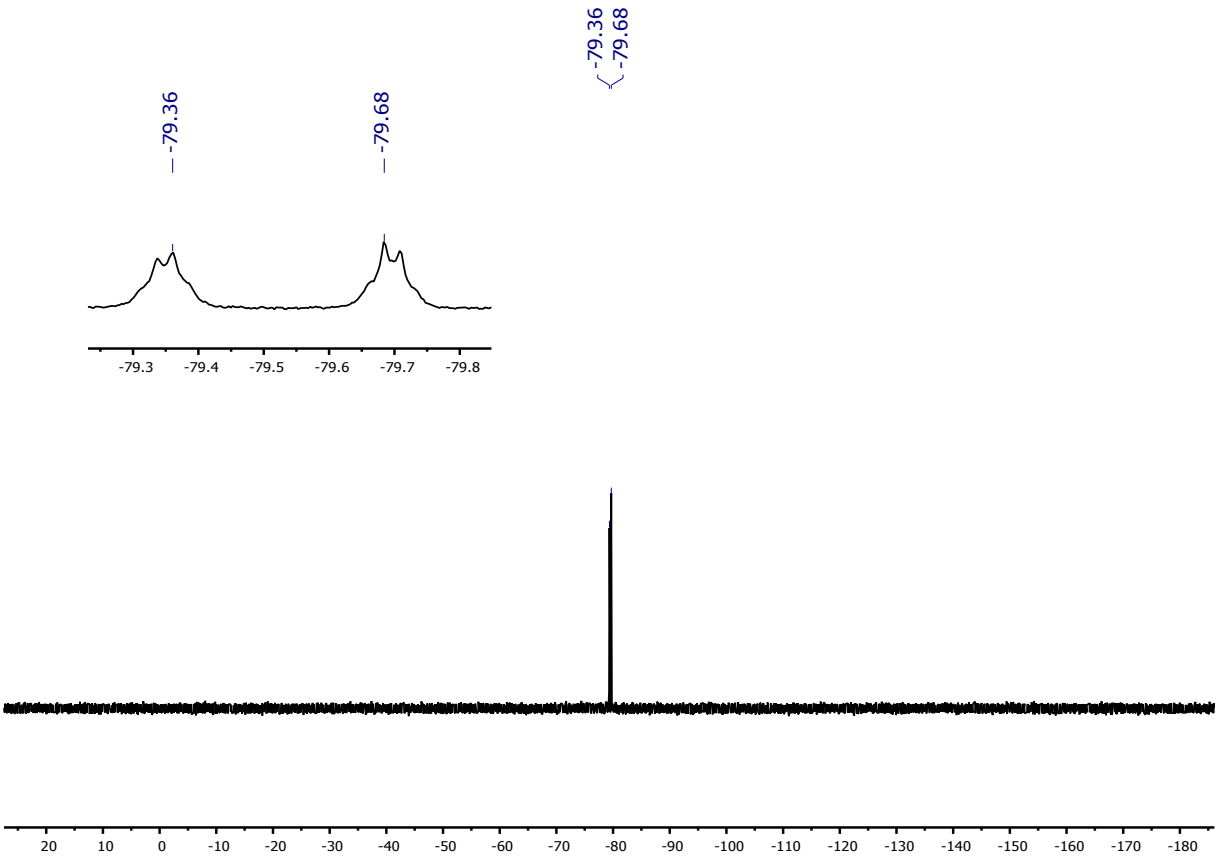


Figure S49: $^{19}F\{^{1}H\}$ NMR (376 MHz, thf-d_8, 298 K) of [{(N_2O_3)$R^F{}_2O_2$}Ca] (**6-Ca**).

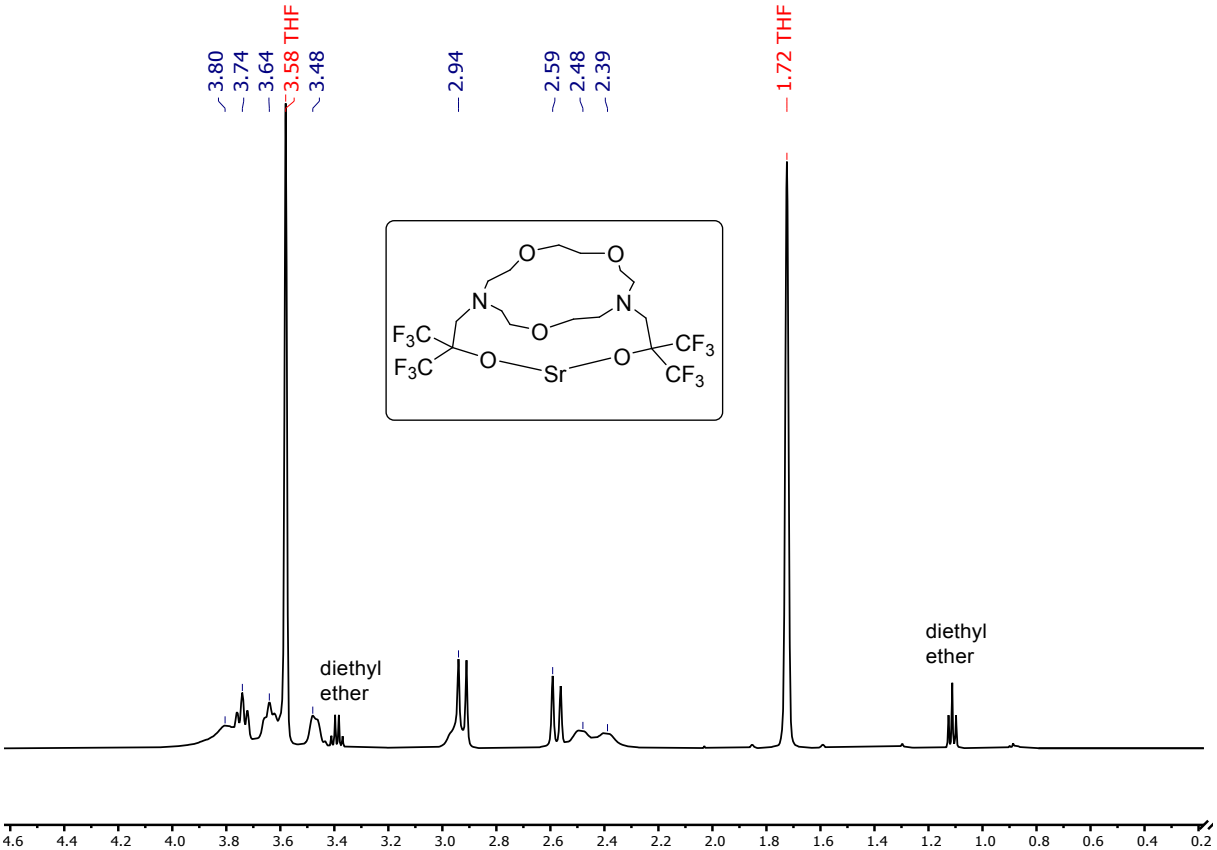


Figure S50: ^{1}H NMR spectrum (400 MHz, thf-d_8, 328 K) of [{(N_2O_3)$R^F{}_2O_2$Sr] (**6-Sr**).

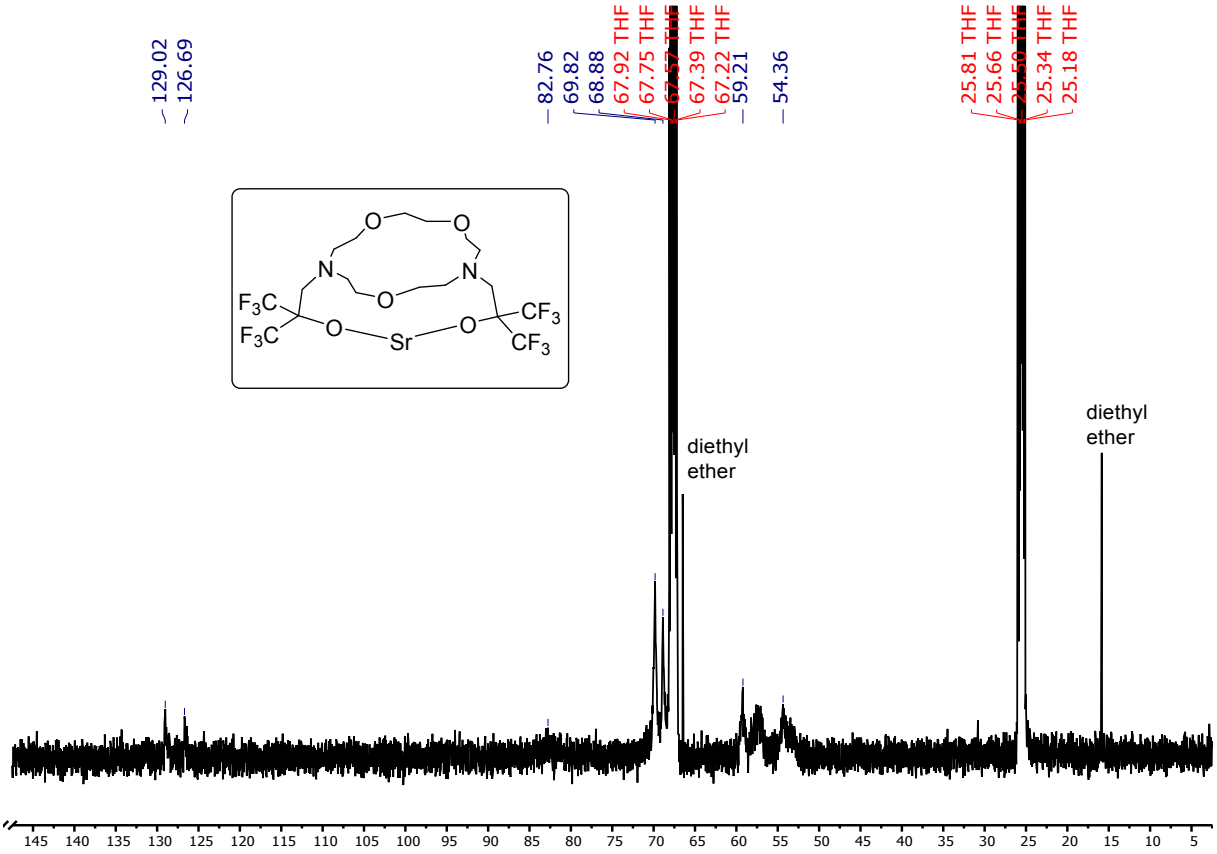


Figure S51: $^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, thf-d_8, 298 K) of [{(N_2O_3) $R^F{}_2O_2Sr$] (**6-Sr**).

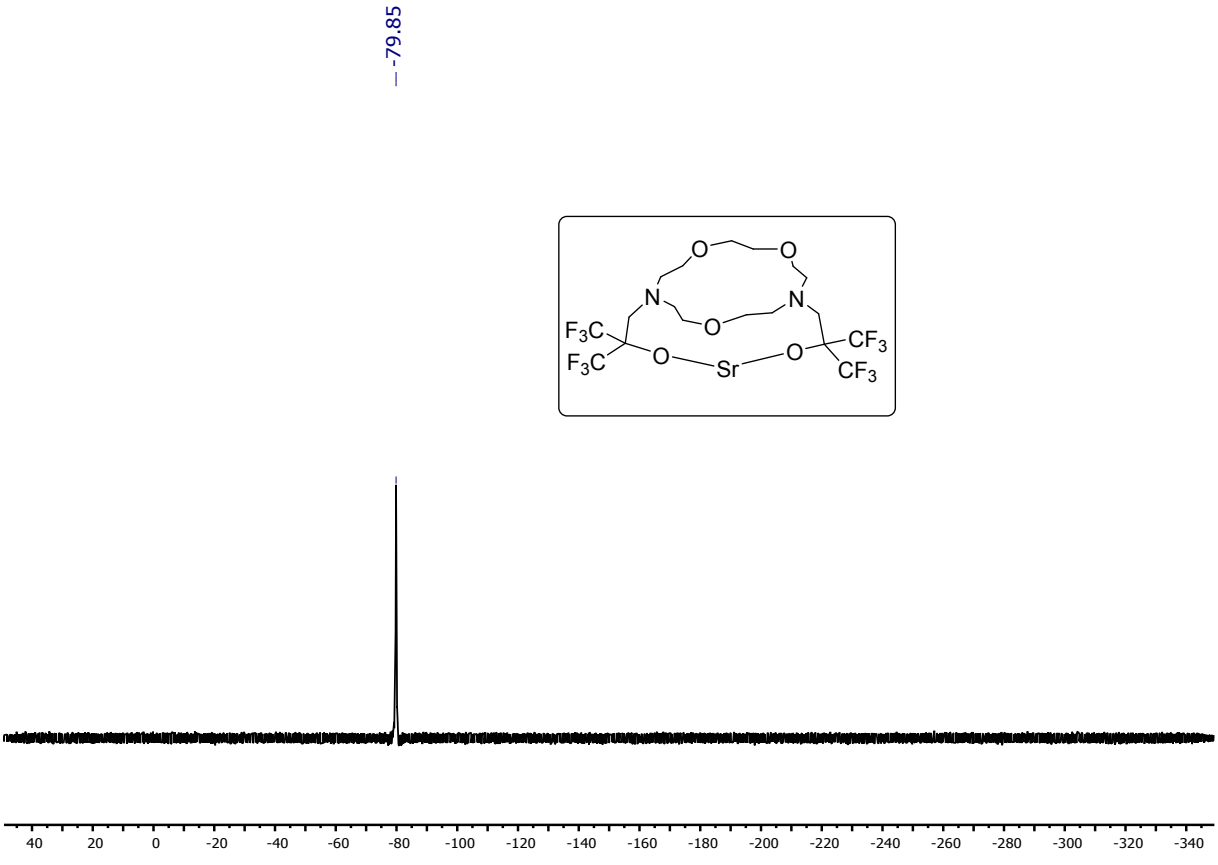


Figure S52: $^{19}F\{^{1}H\}$ NMR (376 MHz, thf-d_8, 330 K) of [{(N_2O_3) $R^F{}_2O_2Sr$] (**6-Sr**).

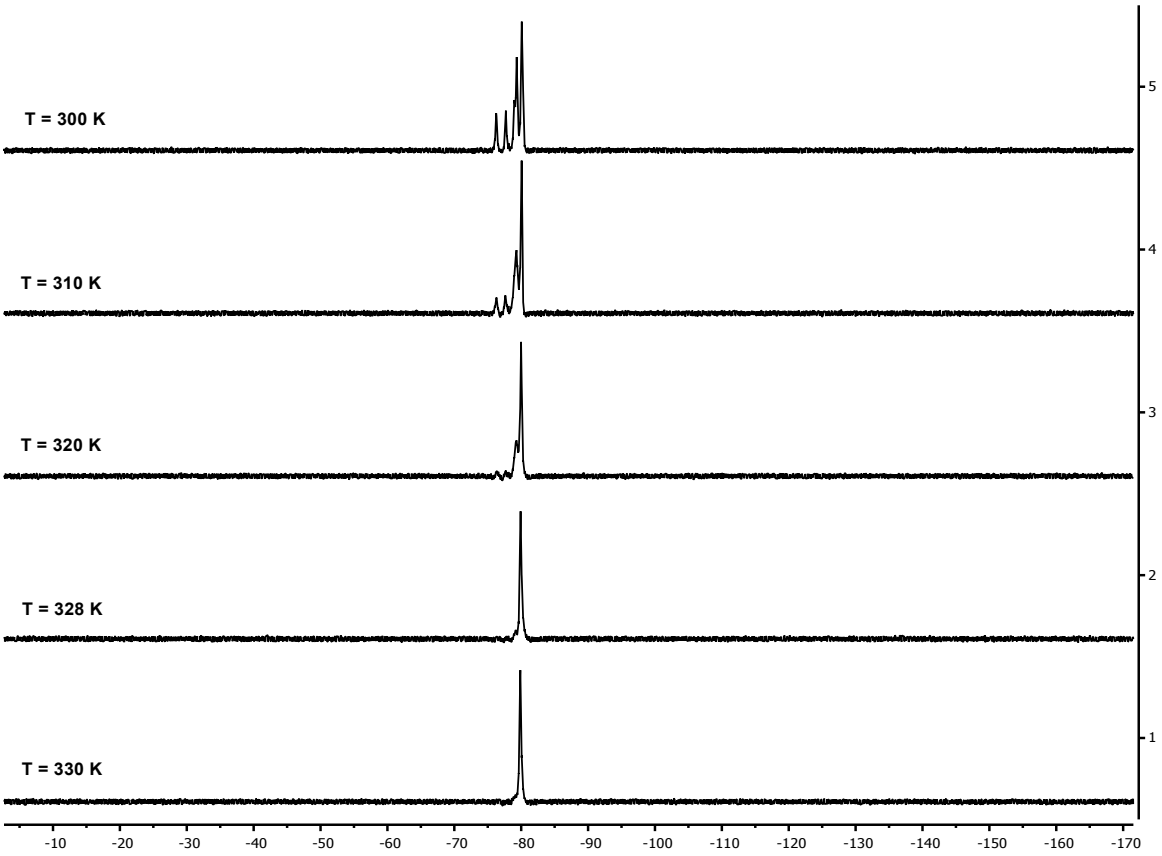


Figure S53: Variable temperature $^{19}F\{^{1}H\}$ NMR (376 MHz, thf-d_8) of [{(N_2O_3) $R^F{}_2O_2Sr$] (**6-Sr**).

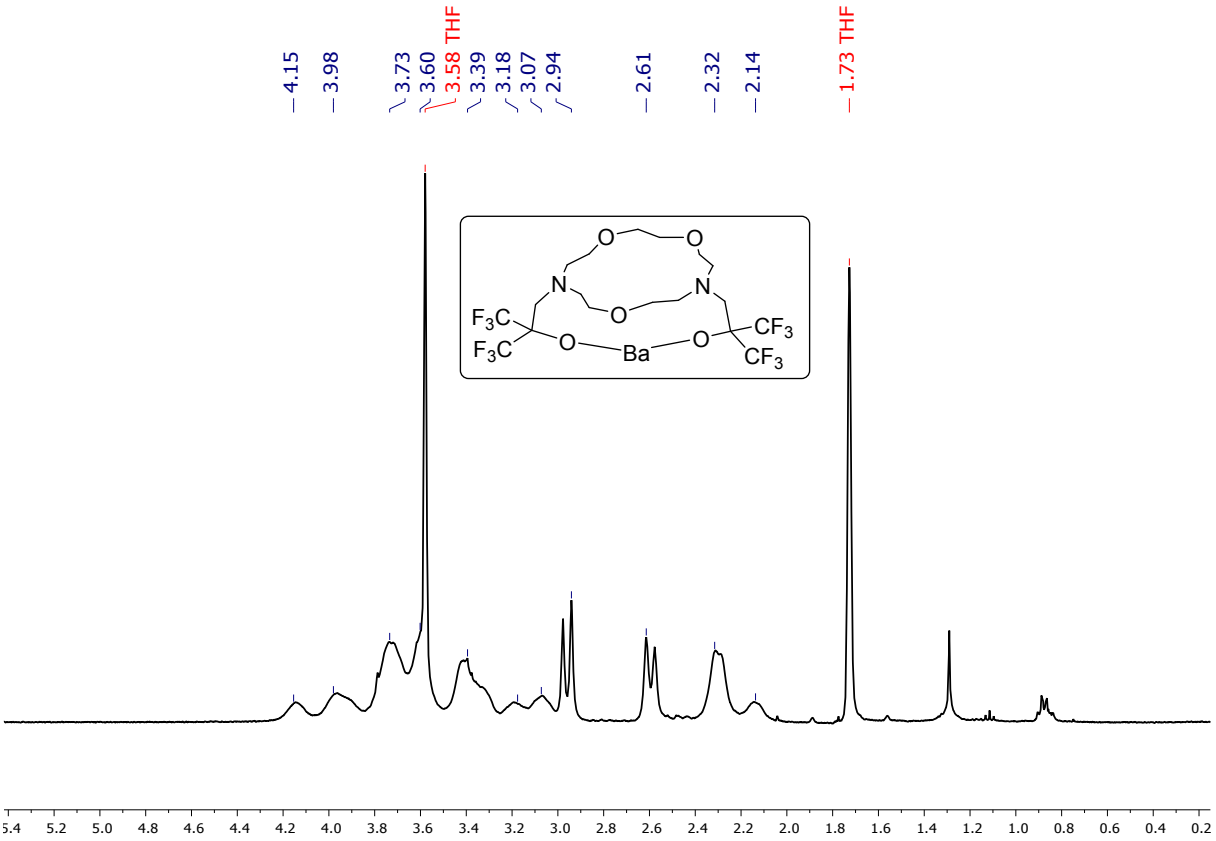


Figure S54: ^{1}H NMR spectrum (400 MHz, thf-d_8, 298 K) of [{(N_2O_3)$R^F{}_2O_2$}Ba] (**6-Ba**).

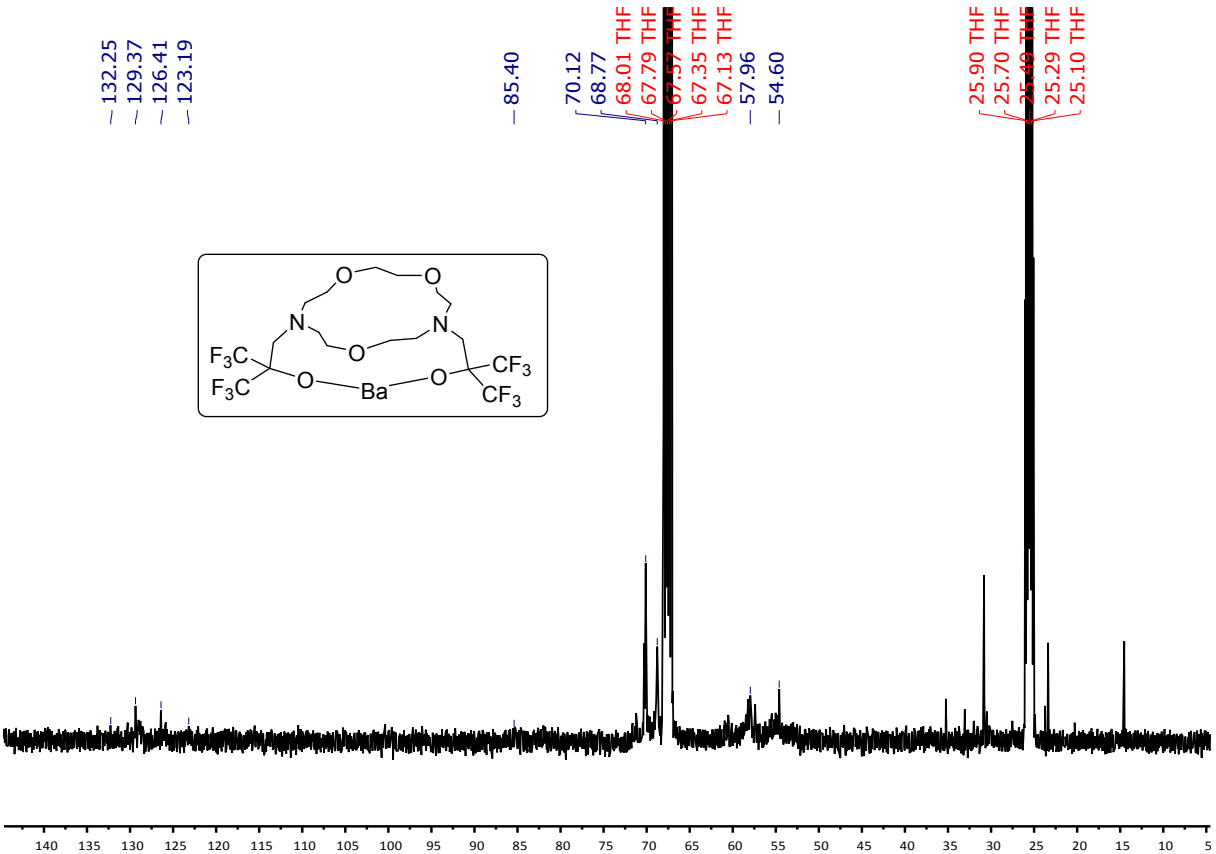


Figure S55: ^{13}C{^{1}H} NMR spectrum (100 MHz, thf-d_8, 298 K) of [{(N_2O_3)$R^F{}_2O_2$}Ba] (**6-Ba**).

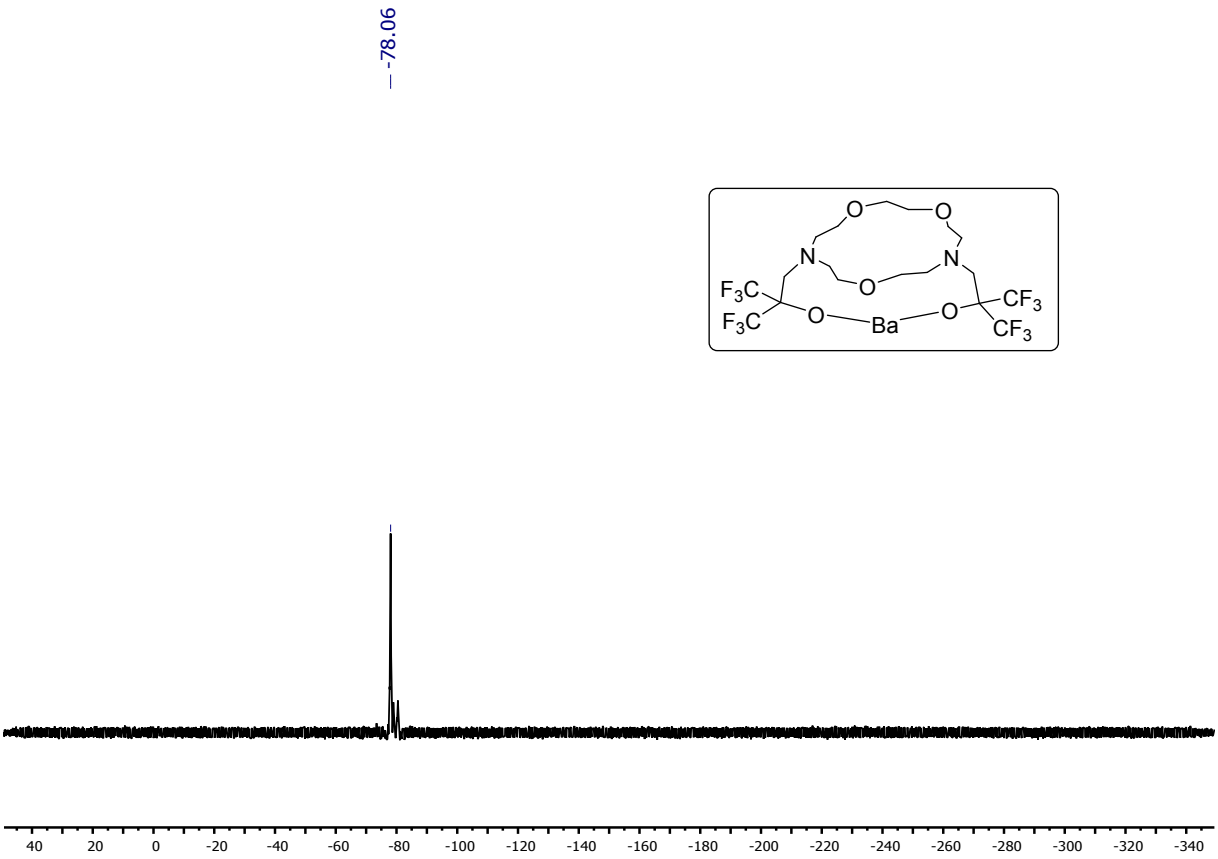


Figure S56: $^{19}F\{^{1}H\}$ NMR (376 MHz, thf-d_8, 325 K) of [{$(N_2O_3)R^F{}_2O_2$}Ba] (**6-Ba**).

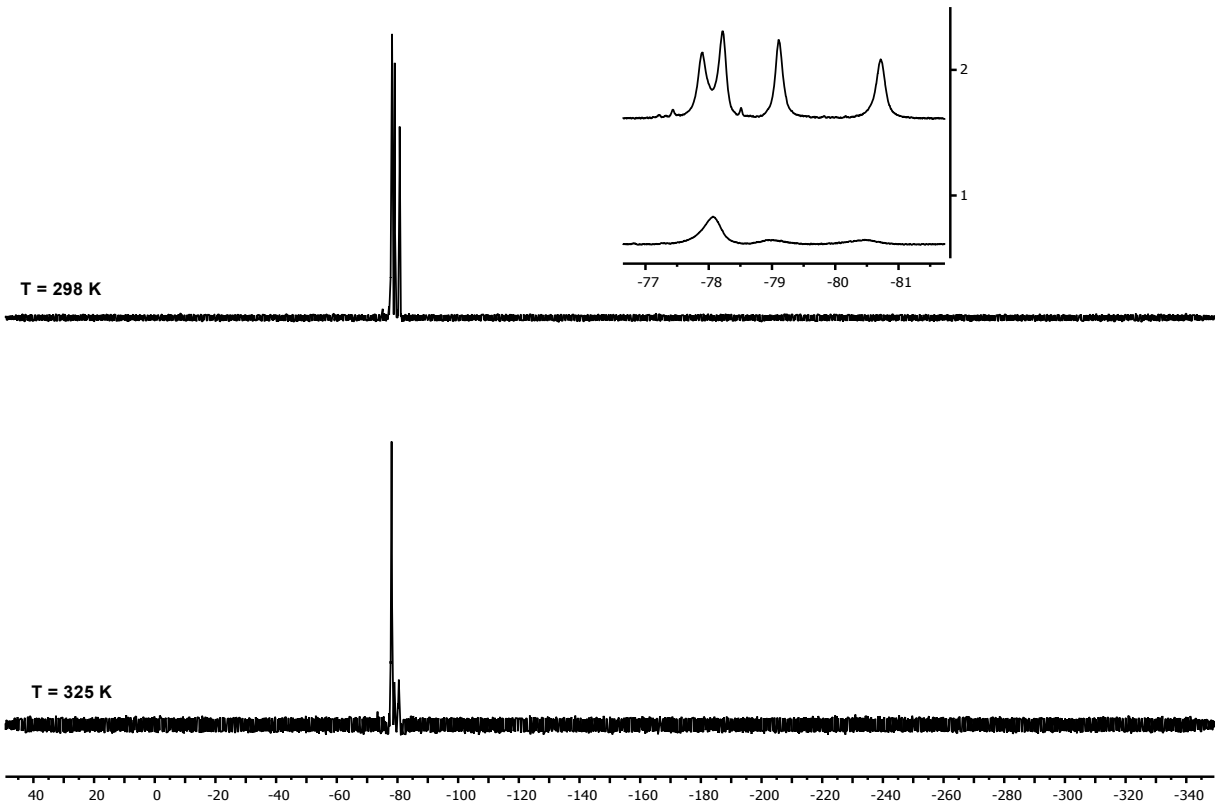


Figure S57: Variable temperature $^{19}F\{^{1}H\}$ NMR (376 MHz, thf-d_8) of [{$(N_2O_3)R^F{}_2O_2$}Ba] (**6-Ba**).

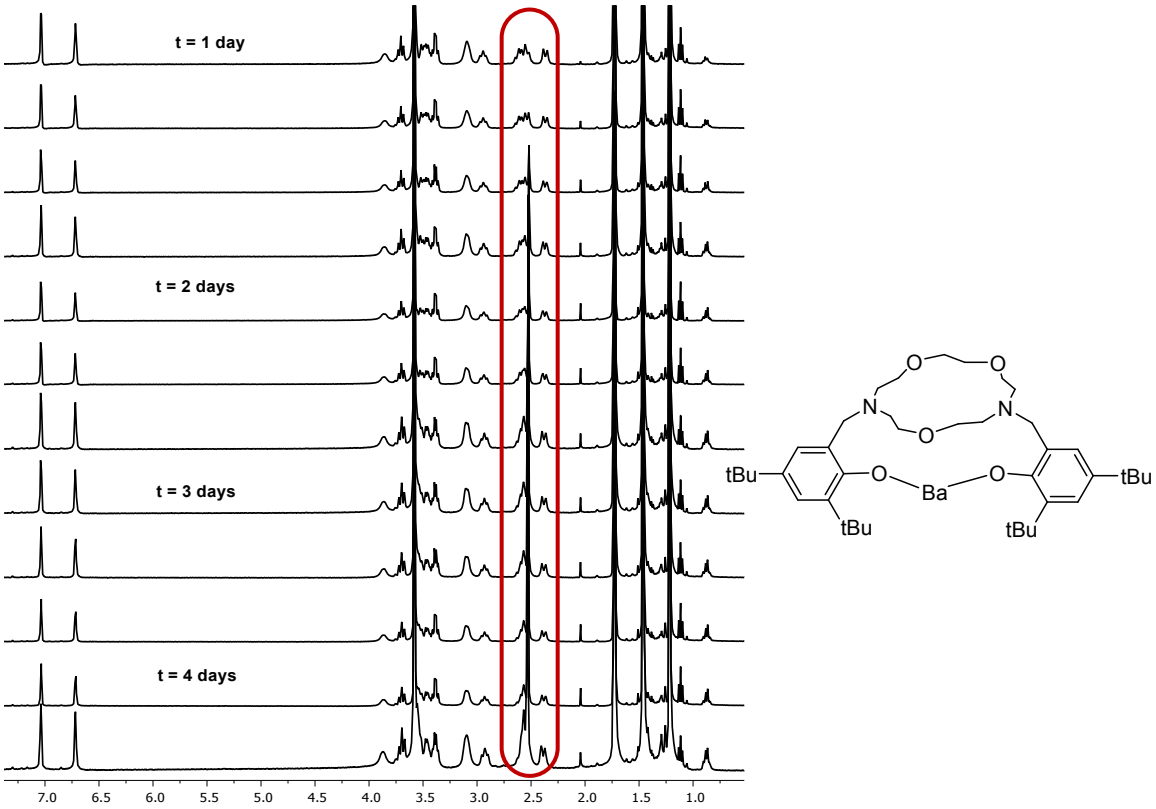


Figure S58: Monitoring of the ^{1}H NMR spectrum (400 MHz, thf-d_8, 298 K) of [{$(N_2O_3)Ar_2O_2$}Ba] (**4-Ba**) after exposition to air for 4 consecutive days. The singlet at 2.51 ppm corresponds to water in increasing concentration.

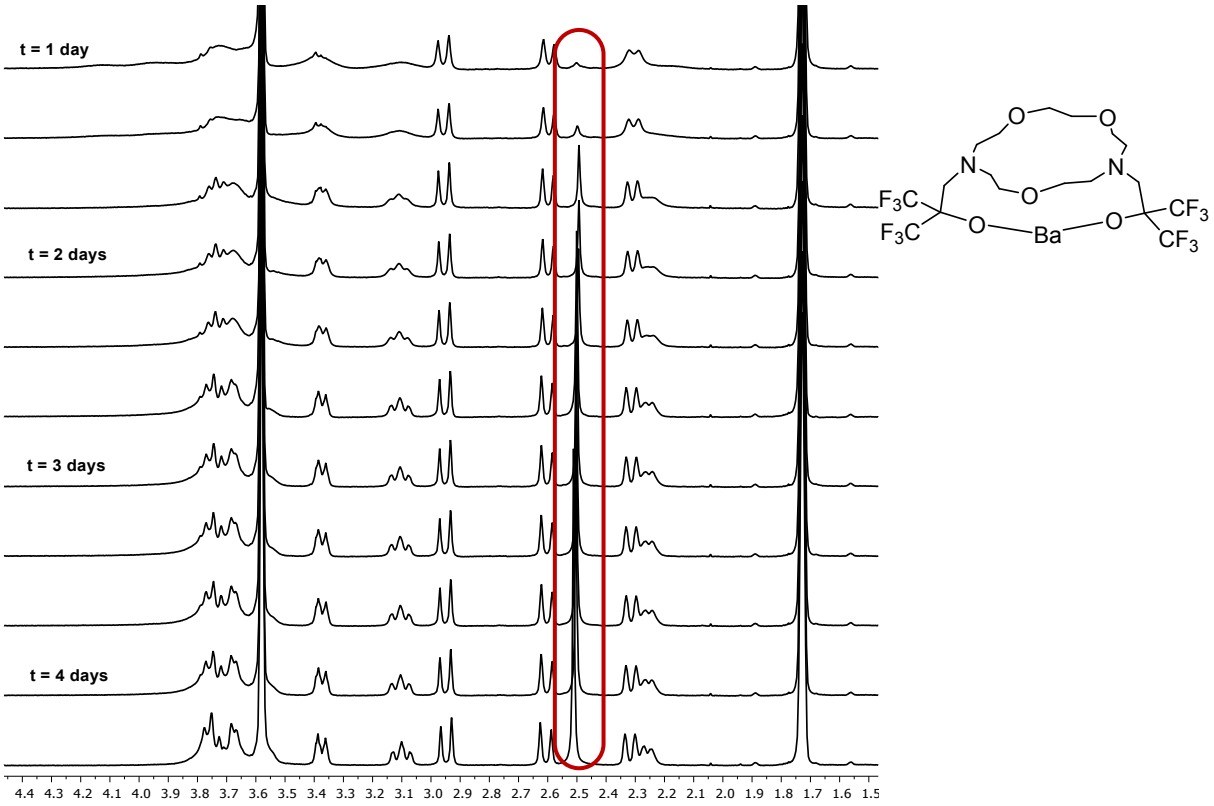


Figure S59: Monitoring of the ^{1}H NMR spectrum (400 MHz, thf-d_8, 298 K) of [{$(N_2O_3)R^F{}_2O_2$}Ba] (**6-Ba**) after exposition to air for 4 consecutive days. The singlet at 2.51 ppm corresponds to water in increasing concentration.

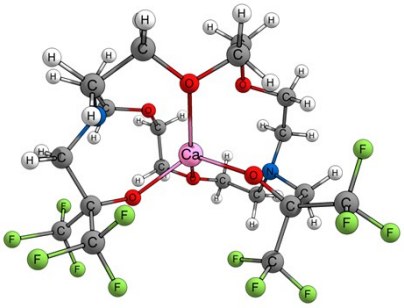
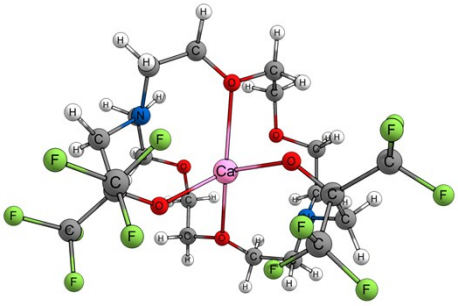
S60. DFT Computations

To obtain the GEI of complexes **5**-Ca and **5**-Sr (see the manuscript), two different methods were used, as described by Stephan and co-workers.[5] In the first one (A), geometry optimisation was carried out on Gaussian 09[6] using the BP86[7] functional and the def2-TZVP[8] basis set; the energy was recalculated at the MP2[9]/def2-TZVPP[7] level.[6a] For the second protocol (B), geometry optimisation was performed on Gaussian 09[7] using the B3LYP6 functional and the def2-TZVP[8] basis set.[6b]

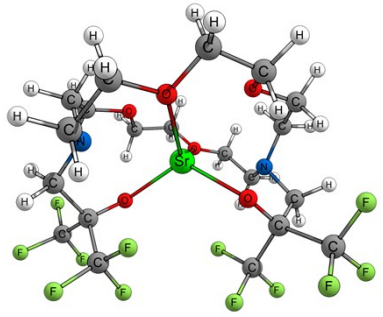
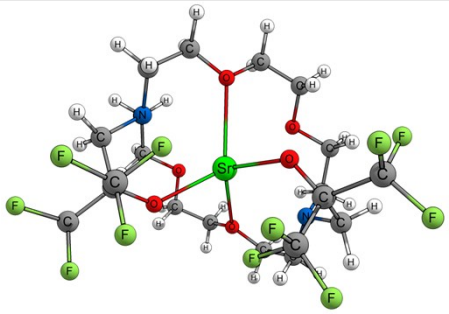
Table S1. Components of the GEI Calculation

	DFT method	E HOMO (eV)	E-LUMO (eV)	μ	η	GEI
5-Ca	A	-10.2497934	2.30727156	-3.9712609	12.5570649	0.628
5-Sr	A	-10.1100546	1.7487323	-4.18066115	11.8587869	0.738
5-Ca	B	-6.18418865	-0.11614083	-3.15016474	6.06804783	0.818
5-Sr	B	-6.02110997	-0.345586689	-3.183348329	5.675523281	0.892

Table S2. Coordinates (x,y,z) and single point energy (Hartree) of the computed species

Method A				Method B			
							
EUMP2 = -0.32110702819610D+04				EUMP2 = -0.32110702819610D+04			
Ca	-0.000011	0.665994	0.000008	Ca	-0.000011	0.665994	0.000008
O	-1.801263	-0.438112	-0.64815	O	-1.801263	-0.438112	-0.64815
O	-1.62562	2.863864	-0.565494	O	-1.62562	2.863864	-0.565494
O	-0.192612	1.223731	-2.512155	O	-0.192612	1.223731	-2.512155
N	-2.49272	0.960953	1.624424	N	-2.49272	0.960953	1.624424
C	-2.794152	-1.025824	0.040745	C	-2.794152	-1.025824	0.040745
C	-2.271303	-2.336669	0.736309	C	-2.271303	-2.336669	0.736309
C	-3.969999	-1.401224	-0.934918	C	-3.969999	-1.401224	-0.934918
C	-3.425666	-0.088497	1.168575	C	-3.425666	-0.088497	1.168575
H	-4.321223	0.387763	0.744376	H	-4.321223	0.387763	0.744376
H	-3.777217	-0.690776	2.020286	H	-3.777217	-0.690776	2.020286
C	-2.107064	0.795564	3.033955	C	-2.107064	0.795564	3.033955
H	-1.892567	-0.269111	3.194137	H	-1.892567	-0.269111	3.194137
H	-2.922458	1.082653	3.735439	H	-2.922458	1.082653	3.735439
C	-3.002007	2.310569	1.343586	C	-3.002007	2.310569	1.343586
H	-2.382364	3.04735	1.876775	H	-2.382364	3.04735	1.876775
H	-4.043143	2.438801	1.715906	H	-4.043143	2.438801	1.715906
C	-2.985359	2.66932	-0.1306	C	-2.985359	2.66932	-0.1306
H	-3.467371	1.88032	-0.731656	H	-3.467371	1.88032	-0.731656
H	-3.543595	3.613621	-0.278973	H	-3.543595	3.613621	-0.278973

C	-1.556801	3.155585	-1.973773	C	-1.556801	3.155585	-1.973773
H	-0.665505	3.787997	-2.113094	H	-0.665505	3.787997	-2.113094
H	-2.441179	3.742407	-2.284077	H	-2.441179	3.742407	-2.284077
C	-1.44422	1.877435	-2.793171	C	-1.44422	1.877435	-2.793171
H	-2.220029	1.153391	-2.503782	H	-2.220029	1.153391	-2.503782
H	-1.529609	2.092681	-3.873298	H	-1.529609	2.092681	-3.873298
C	0.863514	1.588027	-3.405154	C	0.863514	1.588027	-3.405154
H	1.042086	2.680301	-3.369199	H	1.042086	2.680301	-3.369199
H	0.575756	1.336647	-4.443223	H	0.575756	1.336647	-4.443223
F	-1.284592	-1.997277	1.62647	F	-1.284592	-1.997277	1.62647
F	-3.225382	-3.000963	1.459407	F	-3.225382	-3.000963	1.459407
F	-1.735738	-3.21945	-0.126306	F	-1.735738	-3.21945	-0.126306
F	-5.070554	-1.902006	-0.296715	F	-5.070554	-1.902006	-0.296715
F	-4.397473	-0.273454	-1.593725	F	-4.397473	-0.273454	-1.593725
F	-3.614856	-2.288518	-1.885552	F	-3.614856	-2.288518	-1.885552
O	1.801252	-0.438097	0.648149	O	1.801252	-0.438097	0.648149
O	1.625568	2.863903	0.565483	O	1.625568	2.863903	0.565483
O	0.192594	1.22376	2.512161	O	0.192594	1.22376	2.512161
N	2.492716	0.96099	-1.624414	N	2.492716	0.96099	-1.624414
C	2.794167	-1.025779	-0.040734	C	2.794167	-1.025779	-0.040734
C	2.271357	-2.336613	-0.736331	C	2.271357	-2.336613	-0.736331
C	3.969995	-1.401213	0.934938	C	3.969995	-1.401213	0.934938
C	3.425686	-0.088429	-1.168545	C	3.425686	-0.088429	-1.168545
H	4.321223	0.387855	-0.744331	H	4.321223	0.387855	-0.744331
H	3.777267	-0.690698	-2.02025	H	3.777267	-0.690698	-2.02025
C	2.107054	0.795565	-3.033939	C	2.107054	0.795565	-3.033939
H	1.892572	-0.269117	-3.194098	H	1.892572	-0.269117	-3.194098
H	2.922441	1.082653	-3.735433	H	2.922441	1.082653	-3.735433
C	3.001963	2.310624	-1.343599	C	3.001963	2.310624	-1.343599
H	2.382295	3.047379	-1.876795	H	2.382295	3.047379	-1.876795
H	4.043094	2.438883	-1.715925	H	4.043094	2.438883	-1.715925
C	2.985311	2.669392	0.130583	C	2.985311	2.669392	0.130583
H	3.46735	1.880415	0.731647	H	3.46735	1.880415	0.731647
H	3.543521	3.613711	0.278944	H	3.543521	3.613711	0.278944
C	1.556747	3.155633	1.97376	C	1.556747	3.155633	1.97376
H	0.66544	3.78803	2.113078	H	0.66544	3.78803	2.113078
H	2.441115	3.742475	2.284057	H	2.441115	3.742475	2.284057
C	1.444191	1.877488	2.793168	C	1.444191	1.877488	2.793168
H	2.220013	1.153456	2.503783	H	2.220013	1.153456	2.503783
H	1.52958	2.092745	3.873293	H	1.52958	2.092745	3.873293
C	-0.863536	1.58805	3.405159	C	-0.863536	1.58805	3.405159
H	-1.042123	2.68032	3.369193	H	-1.042123	2.68032	3.369193
H	-0.575772	1.336684	4.44323	H	-0.575772	1.336684	4.44323
F	1.28476	-1.997201	-1.626612	F	1.28476	-1.997201	-1.626612
F	3.225519	-3.000936	-1.459295	F	3.225519	-3.000936	-1.459295
F	1.73569	-3.219365	0.126252	F	1.73569	-3.219365	0.126252
F	5.070519	-1.902061	0.296734	F	5.070519	-1.902061	0.296734
F	4.397521	-0.273462	1.593747	F	4.397521	-0.273462	1.593747

F	3.61481	-2.288499	1.885564	F	3.61481	-2.288499	1.885564
							
EUMP2 = -0.25656627583173D+04				EUMP2 = -0.25656627583173D+04			
C	-1.192375	1.79158	3.484388	C	-1.192375	1.79158	3.484388
H	-1.612665	2.814773	3.528224	H	-1.612665	2.814773	3.528224
H	-0.873603	1.526458	4.510473	H	-0.873603	1.526458	4.510473
O	-0.060677	1.775908	2.608512	O	-0.060677	1.775908	2.608512
C	0.930381	2.730696	3.009444	C	0.930381	2.730696	3.009444
H	1.117886	2.641979	4.096356	H	1.117886	2.641979	4.096356
H	0.566692	3.756003	2.802645	H	0.566692	3.756003	2.802645
C	2.219109	2.448676	2.282837	C	2.219109	2.448676	2.282837
H	2.995422	3.140295	2.664803	H	2.995422	3.140295	2.664803
H	2.538037	1.405488	2.460268	H	2.538037	1.405488	2.460268
O	2.041269	2.641895	0.871186	O	2.041269	2.641895	0.871186
C	3.30811	2.478271	0.208776	C	3.30811	2.478271	0.208776
H	3.857797	1.649745	0.683563	H	3.857797	1.649745	0.683563
H	3.902999	3.403559	0.337256	H	3.902999	3.403559	0.337256
C	3.117541	2.219706	-1.272647	C	3.117541	2.219706	-1.272647
H	2.442552	2.993978	-1.667269	H	2.442552	2.993978	-1.667269
H	4.104473	2.369689	-1.767456	H	4.104473	2.369689	-1.767456
N	2.55832	0.893331	-1.586432	N	2.55832	0.893331	-1.586432
C	2.218313	0.773534	-3.014559	C	2.218313	0.773534	-3.014559
H	1.817052	-0.236997	-3.174706	H	1.817052	-0.236997	-3.174706
H	3.112526	0.881801	-3.669511	H	3.112526	0.881801	-3.669511
C	3.45294	-0.207746	-1.161027	C	3.45294	-0.207746	-1.161027
H	4.400156	0.211656	-0.792395	H	4.400156	0.211656	-0.792395
H	3.71653	-0.833794	-2.0262	H	3.71653	-0.833794	-2.0262
C	2.822314	-1.102982	0.001684	C	2.822314	-1.102982	0.001684
O	1.934035	-0.451706	0.769686	O	1.934035	-0.451706	0.769686
C	4.027522	-1.613562	0.874843	C	4.027522	-1.613562	0.874843
F	4.63653	-0.54911	1.490437	F	4.63653	-0.54911	1.490437
F	3.652922	-2.461185	1.854008	F	3.652922	-2.461185	1.854008
F	5.004361	-2.236601	0.145766	F	5.004361	-2.236601	0.145766
C	2.131685	-2.339769	-0.685993	C	2.131685	-2.339769	-0.685993
F	1.610252	-3.219231	0.186461	F	1.610252	-3.219231	0.186461
F	2.934117	-3.042654	-1.5411	F	2.934117	-3.042654	-1.5411
F	1.08543	-1.867857	-1.451856	F	1.08543	-1.867857	-1.451856
Sr	0.000003	0.716444	0	Sr	0.000003	0.716444	0
C	1.192388	1.791555	-3.484388	C	1.192388	1.791555	-3.484388
H	1.612684	2.814745	-3.528235	H	1.612684	2.814745	-3.528235

H	0.873616	1.526424	-4.510472	H	0.873616	1.526424	-4.510472
O	0.06069	1.775897	-2.608513	O	0.06069	1.775897	-2.608513
C	-0.930365	2.730684	-3.009452	C	-0.930365	2.730684	-3.009452
H	-1.117867	2.641964	-4.096363	H	-1.117867	2.641964	-4.096363
H	-0.566677	3.755992	-2.802653	H	-0.566677	3.755992	-2.802653
C	-2.219095	2.448668	-2.282846	C	-2.219095	2.448668	-2.282846
H	-2.995406	3.140288	-2.664812	H	-2.995406	3.140288	-2.664812
H	-2.538026	1.40548	-2.460276	H	-2.538026	1.40548	-2.460276
O	-2.041254	2.641886	-0.871194	O	-2.041254	2.641886	-0.871194
C	-3.308096	2.478261	-0.208785	C	-3.308096	2.478261	-0.208785
H	-3.857776	1.649726	-0.683565	H	-3.857776	1.649726	-0.683565
H	-3.90299	3.403543	-0.337275	H	-3.90299	3.403543	-0.337275
C	-3.117528	2.219711	1.272641	C	-3.117528	2.219711	1.272641
H	-2.442537	2.993986	1.667254	H	-2.442537	2.993986	1.667254
H	-4.104459	2.369701	1.767448	H	-4.104459	2.369701	1.767448
N	-2.558308	0.893339	1.586441	N	-2.558308	0.893339	1.586441
C	-2.218302	0.773558	3.01457	C	-2.218302	0.773558	3.01457
H	-1.817042	-0.236971	3.174729	H	-1.817042	-0.236971	3.174729
H	-3.112515	0.881833	3.66952	H	-3.112515	0.881833	3.66952
C	-3.452928	-0.207742	1.161047	C	-3.452928	-0.207742	1.161047
H	-4.400148	0.211659	0.792421	H	-4.400148	0.211659	0.792421
H	-3.71651	-0.833791	2.02622	H	-3.71651	-0.833791	2.02622
C	-2.822315	-1.102976	-0.001674	C	-2.822315	-1.102976	-0.001674
O	-1.934032	-0.451705	-0.769674	O	-1.934032	-0.451705	-0.769674
C	-4.027535	-1.613528	-0.874831	C	-4.027535	-1.613528	-0.874831
F	-4.636522	-0.549057	-1.490414	F	-4.636522	-0.549057	-1.490414
F	-3.65295	-2.461154	-1.853999	F	-3.65295	-2.461154	-1.853999
F	-5.004381	-2.236552	-0.145754	F	-5.004381	-2.236552	-0.145754
C	-2.131705	-2.339785	0.685985	C	-2.131705	-2.339785	0.685985
F	-1.610388	-3.219296	-0.186488	F	-1.610388	-3.219296	-0.186488
F	-2.934116	-3.042608	1.541162	F	-2.934116	-3.042608	1.541162
F	-1.085364	-1.86792	1.451761	F	-1.085364	-1.86792	1.451761

S61. References

1 D. C. Bradley, M. B. Hursthouse, A. A. Ibrahim, K. M. Abdul Malik, M. Motevalli, R. Möseler, H. Powell, J. D. Runnacles and A. C. Sullivan, *Polyhedron*, 1990, **9**, 2959.

2 M. Westerhausen, *Inorg.Chem*., 1991, **30**, 96.

3 G. M. Sheldrick, *Acta Cryst*., A71, **2015**, 3.

4 Sheldrick G.M., *Acta Cryst*., C71, **2015**, 3.

5 (*a*) A. R. Jupp, T. C. Johnstone and D. W. Stephan, *Dalton. Trans*, **2018**, 47, 7029; (*b*) A. R. Jupp, T. C. Johnstone and D. W. Stephan, *Inorg. Chem.*, **2018**, 57, 14764.

6 Gaussian 09, Revision D.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman and D. J. Fox, Gaussian, Inc., Wallingford CT, 2016.

7 A. D. Becke, *Phys. Rev. A*, 1988, **38**, 3098.

8 F. Weigend and R. Ahlrichs, *Phys. Chem. Chem. Phys*., 2005, **7**, 3297.

9 M. Head-Gordon, J. A. Pople and M. J. Frisch, *Chem. Phys. Lett*. 1988, **153**, 503.

10 (*a*) A. D. Becke, *J. Chem. Phys*. 1993, **98**, 5648; (*b*) C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B*, 1988, **37**, 785; (*c*) S. H. Vosko, L. Wilk and M. Nusair, *Can. J. Phys*., 1980, **58**, 1200; (*d*) P. J. Stephens, F. J. Devlin, C. F. Chabalowski and M. J. Frisch, *J. Phys. Chem*. 1994, **98**, 11623.