Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information to accompany

Isolable Rubidium and Caesium Derivatives of Common Organic Carbonyl Compounds

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Contents

General Experimental

All reactions were performed under a protective argon or nitrogen atmosphere using either standard Schlenk or glove box techniques. Benzene and THF were dried by heating to reflux over sodium benzophenone ketyl and then distilled under nitrogen prior to use. C_6D_6 and THF-d_8 were stored over activated 4 Å molecular sieves.[1]

RbHMDS and CsHMDS were synthesised using commercially available reagents via literature preparations.[2,3] ^{n}BuLi (1.6 M in hexane) was purchased commercially from Sigma-Aldrich and used as received. Acetophenone and benzaldehyde reagents were purchased from Sigma-Aldrich and stored over activated 4 Å molecular sieves prior to use. All other reagents were purchased from commercial sources and were used as received.

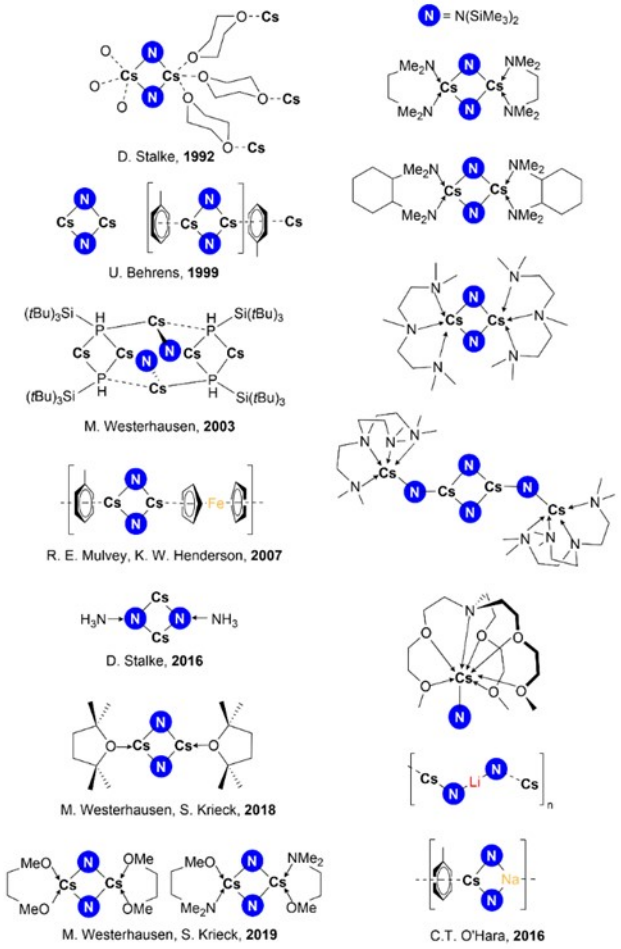
NMR spectra were recorded on a Bruker AV400 MHz spectrometer operating 400.13 MHz for ^{1}H, 100.62 MHz for ^{13}C and a Bruker AV500 MHz spectrometer operating at 65.6 MHz for ^{133}Cs. All ^{13}C NMR spectra were proton decoupled. ^{1}H, ^{13}C{^{1}H} and ^{133}Cs chemical shifts are expressed in parts per million (δ, ppm) and where appropriate referenced to residual solvent peaks or external references.

GC-MS was performed using an Agilent Technologies 7890A gas chromatography system with a 5975C inert XL EI/CI MSD with triple-axis detector. A Restek 30 m x 0.25 mm ID x 0.25 um column was used with helium as the mobile phase.

X-ray crystallography

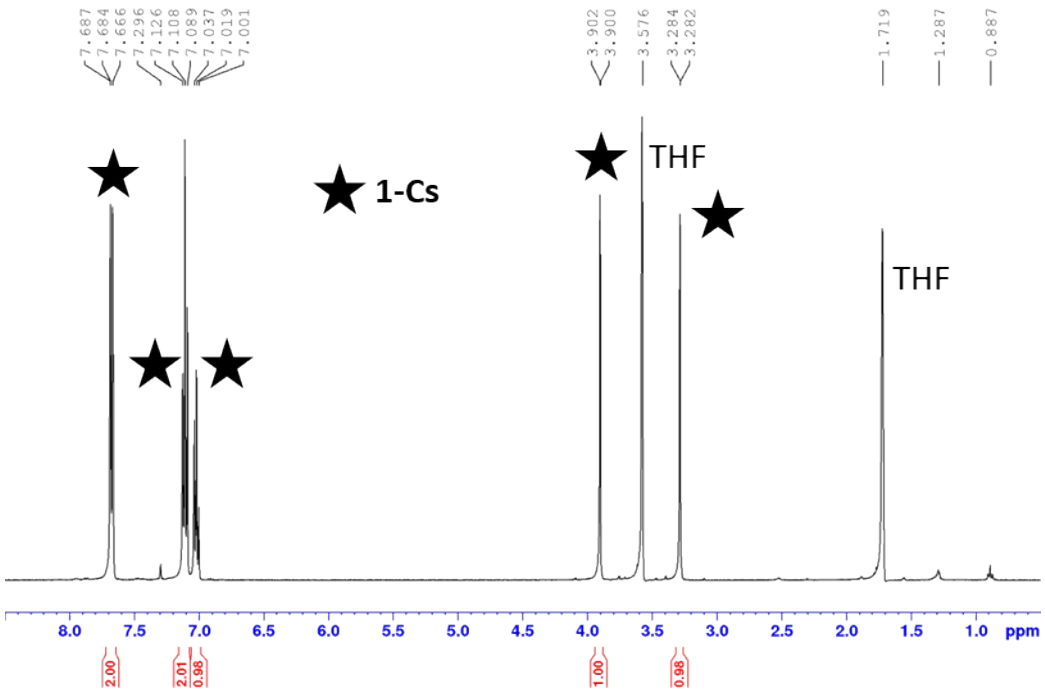
Data for were measured with a Rigaku Synergy-i instrument using monochromated (λ = 1.54184 Å) radiation. In all cases, data collection and processing used CrysalisPro software.[4] The structures were refined to convergence against F^2 using all independent reflections and SHELXL[5] as implemented within WinGX[6] or OLEX.[7] In all structures the non-hydrogen atoms were refined anisotropically and hydrogen atoms were placed in idealised positions and refined in riding modes. THF and phenyl groups of $C_{20.76}H_{22.51}CsO_{2.19}$ and THF groups of $C_{57}H_{57}Rb_3O_{5.25}$ were modelled as disordered. In each case appropriate constraints and restraints were applied to bond lengths and to displacement parameters so as to ensure that these approximate normal behaviour. In the case of $C_{57}H_{57}Rb_3O_{5.25}$ after many trial calculations, a partially present and disordered THF group has been placed in a somewhat unusual position between two Rb centres. This is the best solution found that reflects both the observed electron density distribution and our knowledge of the materials used in the synthesis of this compound. Selected crystallographic data and refinement parameters are presented in Table **S6**. Deposition numbers 2293054 to 2293058 contain the full supplementary crystallographic data for this paper in cif format. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service www.ccdc.cam.ac.uk/structures.

Figure S1: Reported X-ray crystallographically-characterised structures of $[CsN(SiMe_3)_2]$[10]

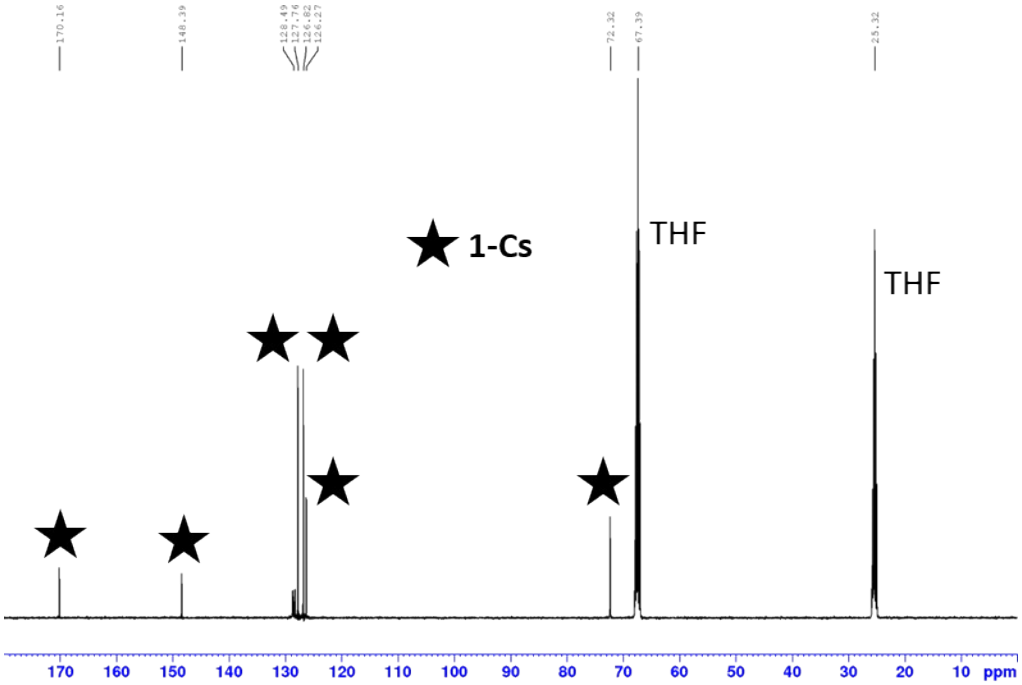


Synthesis of $[CsOC(CH_2)C_6H_5]_n$ (**1-Cs**)

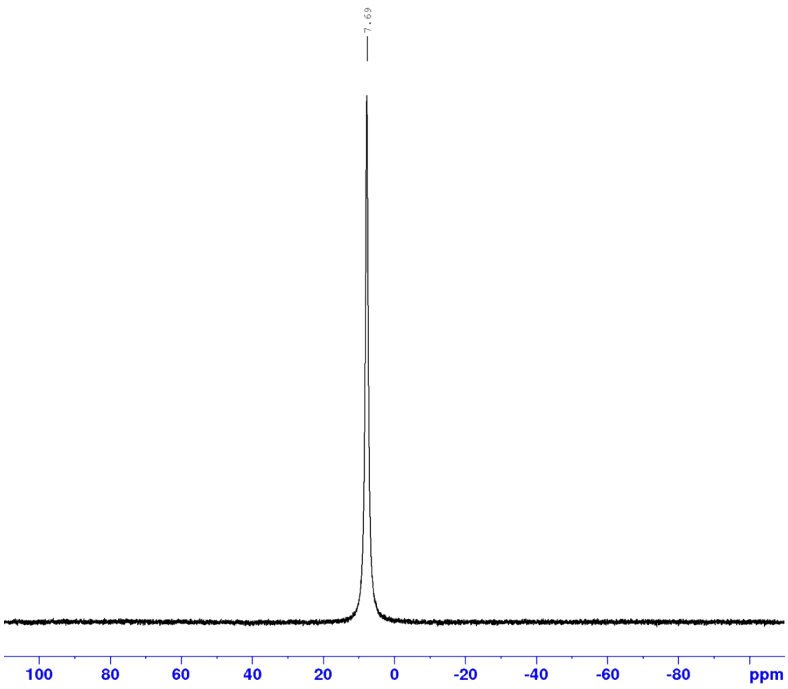
CsHMDS (0.0735 g, 0.25 mmol) was dissolved in benzene (10 ml) before acetophenone (29 µl, 0.25 mmol) was added to give an off-white suspension, and the reaction was stirred overnight. A small crop of colourless crystals of compound **1-Cs** was obtained from a yellow solution of THF layered with hexane in a -20 °C freezer (0.0212 g, 0.084 mmol, 33.6 %). Additional dark yellow solid was obtained by drying and removal of residual solvent in vacuo (0.0232 g, 0.092 mmol, 37 %).



^{1}H NMR (400.1 MHz, THF-d_8, 300 K): δ 7.68 (m, 2H, CH, Ph), 7.30 (residual C_6D_6), 7.11 (m, 2H, CH, Ph), 7.02 (tm, 1H, CH, Ph), 3.90 (m, 1H, CH_2, -CH_2), 3.58 (THF-d_8), 3.28 (m, 1H, CH_2, -CH_2), 1.72 (THF-d_8), 1.29 (residual hexane), 0.89 (residual hexane) ppm.



$^{13}C\{^{1}H\}$ NMR (100.6 MHz, THF-d_8, 300 K): δ 170.2 ($C_{quaternary}$, -C=O), 148.4 ($C_{quaternary}$, Ph), 128.5 (residual C_6D_6), 127.8 (CH_2, Ph), 126.8 (CH_2, Ph), 126.3 (CH, Ph), 72.3 (CH_2), 67.4 (THF-d_8), 25.3 (THF-d_8) ppm.



^{133}Cs NMR (65.6 MHz, THF-D_8, 300 K): δ 7.69 (**1-Cs**) ppm.

Note that if the reaction of acetophenone and CsHMDS in THF is monitored over the course of heating, conversion of **1-Cs** to **2-Cs** may be observed in the ^{1}H NMR spectrum, alongside consumption of acetophenone. This reaction was carried out in a J Youngs NMR tube at 0.05 mmol scale and as such a degree of error in addition of reagents is likely, despite care being taken to maintain a 1:1 stoichiometry.

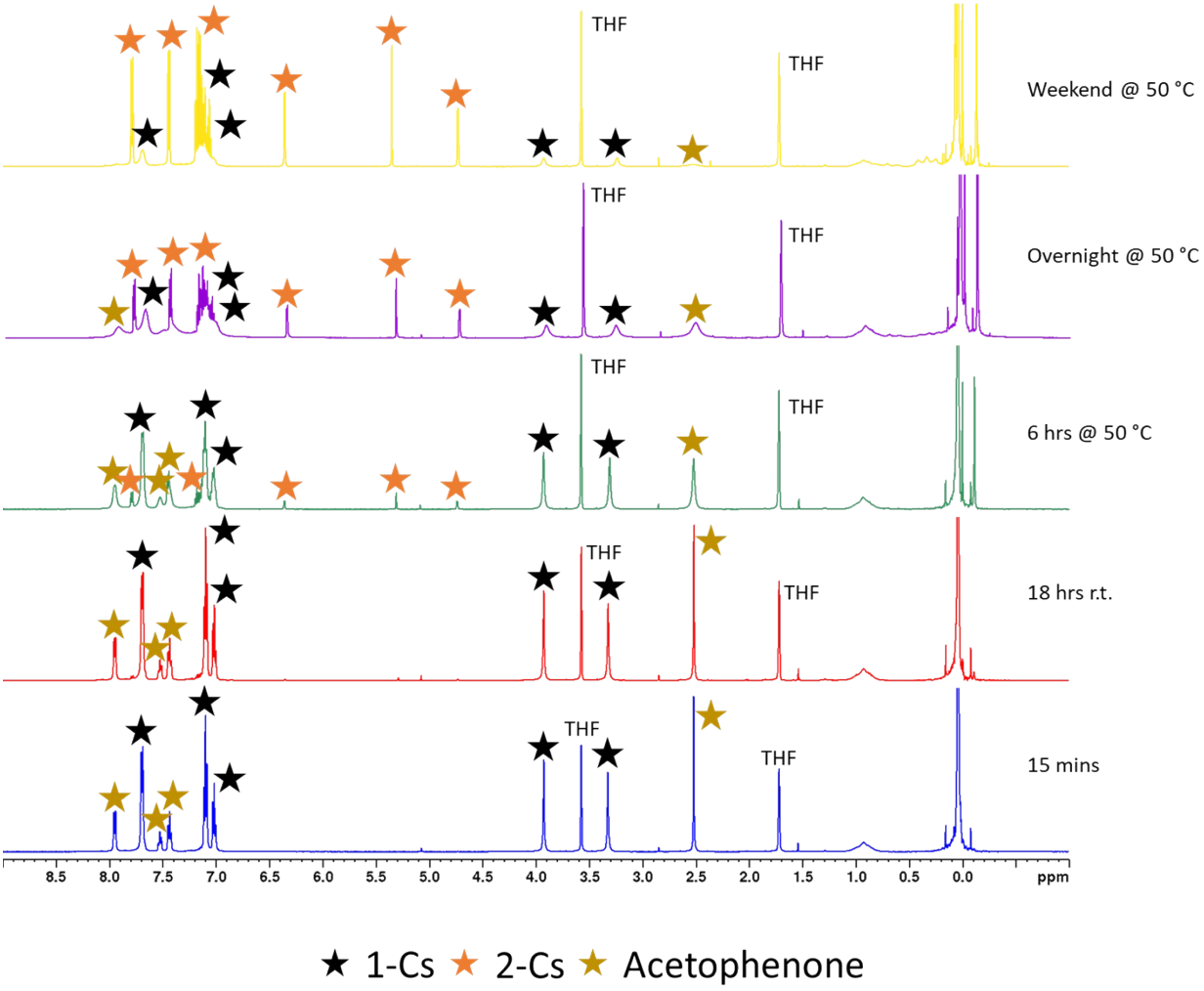


Figure S2: ORTEP diagram of $[CsOC(CH_2)C_6H_5]_n$ (**1-Cs**)

Structure of **1-Cs**, thermal ellipsoids are displayed at 20 % probability level.

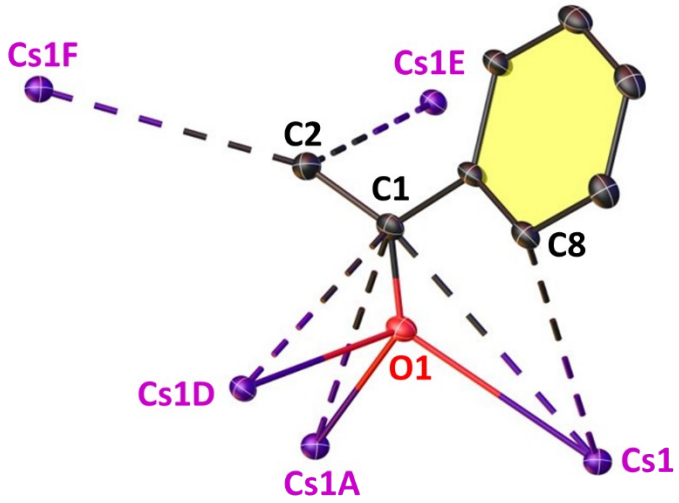


Table S1: Selected bond lengths (Å) and bond angles (°)

Bonds	**Bond Lengths (Å)**
Cs1 C2	3.458(8)
Cs1 O1	2.958(4)
Cs1 C1	3.288(6)
Cs1 C2	3.724(7)
Cs1 C8	3.599(7)
Cs1 O1	2.932(6)
Cs1 O1	2.963(4)
Cs1 C2	3.385(7)
C1 C2	1.38(1)
O1 C1	1.291(8)
C1 C3	1.503(9)
Cs1 O1	2.932(6)
Bonds	**Bond Angles (°)**
C3 C1 O1	117.1(6)
C3 C1 C2	119.7(6)
C2 C1 O1	123.2(6)
O1 Cs1 C2	74.7(2)
C2 Cs1 C8	79.2(2)
C8 Cs1 O1	49.9(1)
O1 Cs1 C2	161.2(2)
O1 Cs1 O1	114.7(1)
O1 Cs1 C1	97.3(1)
O1 Cs1 C2	76.8(2)
C8 Cs1 C2	120.2(2)

C8 Cs1 O1	98.5(1)
C8 Cs1 C1	75.5(2)
C8 Cs1 C2	66.7(2)
C8 Cs1 O1	138.6(1)
Cs1 C2 C1	146.7(5)
Cs1 C2 C1	95.7(5)
Cs1 C2 Cs1	117.0(2)
Cs1 C2 Cs1	86.8(2)
Cs1 O1 C1	93.0(4)
Cs1 C1 C2	97.4(5)
Cs1 O1 Cs1	101.4(1)
Cs1 O1 C1	125.6(4)
O1 Cs1 O1	88.9(1)
Cs1 O1 Cs1	91.1(1)

Hydrolysis of $[CsOC(CH_2)C_6H_5]_n$ (1-Cs)

After completion, the reaction mixture of 1-Cs was hydrolysed using a six-fold excess H_2O before being filtered, the resulting solution was dried in vacuo and used to perform NMR and Mass Spectroscopic studies. NMR of the final hydrolysed products was performed in $CDCl_3$ with adamantane as a standard, while GC-MS was carried out in MeOH. The NIST database was used to identify compounds of interest from the mass spectra.

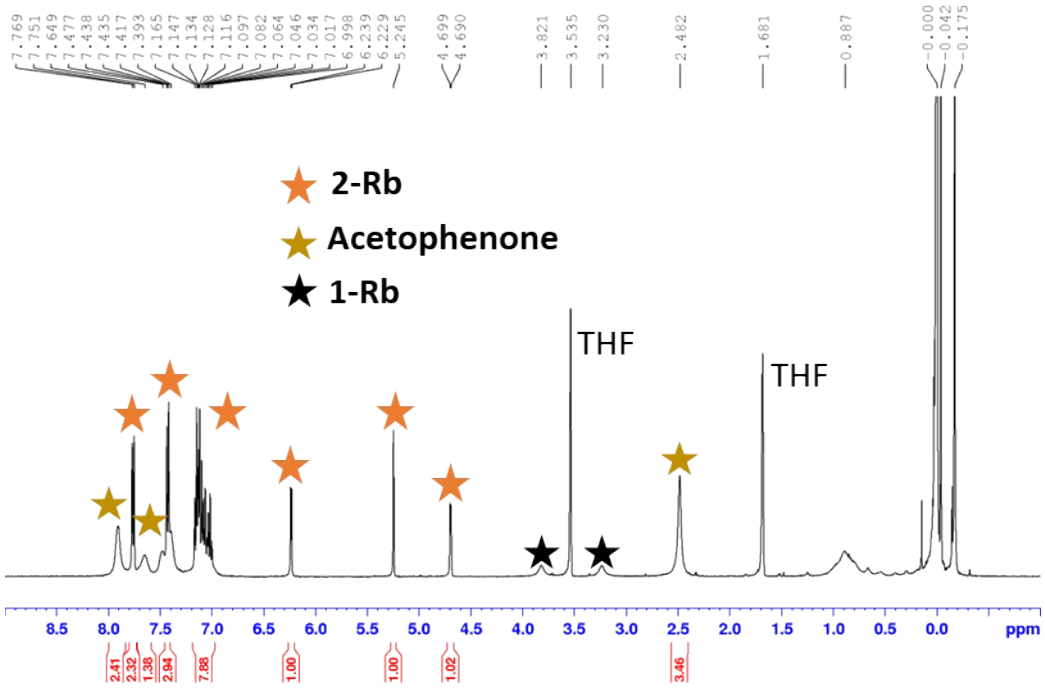
^{1}H NMR (400.1 MHz, $CDCl_3$, 300 K): δ 7.96 (m, 2H, CH, acetophenone), 7.57 (m, 1H, CH, acetophenone), 7.47 (m, 2H, CH, acetophenone), 7.26 ($CDCl_3$), 2.61 (s, 3H, CH_3, acetopheone), 1.88 (adamantane), 1.79 (adamantane), 1.26 (residual hexane), 0.86 (residual hexane), 0.06 (residual HMDS) ppm.

^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$, 300 K): δ 198.3 (C=O, acetophenone), 137.3 ($C_{quaternary}$, acetophenone), 133.2 (CH, acetophenone), 128.7 (CH, acetophenone), 128.5 (CH, acetophenone), 77.2 ($CDCl_3$), 37.9 (adamantane), 37.2 (unknown), 32.9 (unknown), 32.1 (residual hexane), 30.2 (unknown), 29.9 (unknown), 29.5 (unknown), 28.5 (adamantane), 27.2 (unknown), 26.7 (CH_3, acetophenone), 22.8 (residual hexane), 19.9 (unknown), 14.3 (residual hexane) ppm.

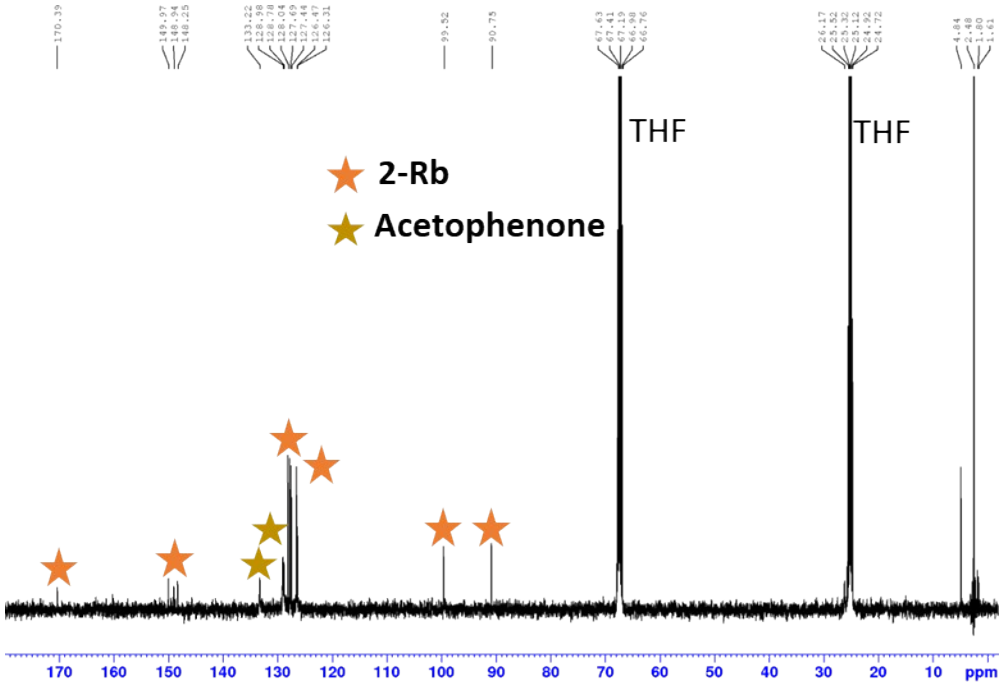
GC-MS (MeOH): Acetophenone (rt 7.5 mins, m/z 105).

Synthesis of $[RbOC(C_6H_5)CHC(CH_2)C_6H_5.THF]_n$ (2-Rb)

RbHMDS (0.0615 g, 0.25 mmol) dissolved in THF (1 ml) before acetophenone (58 µl, 0.5 mmol) was added to give a white suspension which gradually turned to a dark yellow solution when heated overnight at 70 ^{O}C. A small crop of colourless crystals of compound **2-Rb** was obtained from a solution of THF layered with hexane in a -20 °C freezer (0.0363 g, 0.101 mmol, 40 %). Additional dark yellow solid was obtained by drying and removal of residual solvent in vacuo (0.0148 g, 0.041 mmol, 17 %). Both isolated products gave essentially identical NMR spectra, though a trace amount of **1-Rb** was evident in the dark yellow solid sample.



^{1}H NMR (400.1 MHz, THF-d_8, 300 K): δ 7.91 (broad s, 2H, CH, acetophenone), 7.76 (m, 2H, CH, Ph), 7.65 (broad s, 2H, CH, acetophenone), 7.48-7.40 (broad s, CH, acetophenone), 7.43 (m, 3H, CH, Ph), 7.16-7.00 (broad m, 8H, CH, Ph), 6.23 (d, 1H, CH_2, -CH_2), 5.25 (s, 1H, CH, -CH), 4.69 (d, 1H, CH_2, -CH_2), 3.82 (residual 1-Rb intermediate), 3.53 (THF-d_8), 3.23 (residual 1-Rb intermediate), 2.48 (broad s, 4H, CH_3, acetophenone), 1.68 (THF-d_8), 0.89 (residual hexane), 0.04 (unknown), 0.00 (HMDS(H)), -0.18 (residual RbHMDS) ppm.



$^{13}C\{^{1}H\}$ NMR (100.6 MHz, THF-d_8, 300 K): δ 170.4 ($C_{quaternary}$, -C=O), 150.0 ($C_{quaternary}$, -*C*(CH_2)Ph), 148.9 ($C_{quaternary}$, Ph), 148.3 ($C_{quaternary}$, Ph), 133.2(CH, acetophenone) 129.0 (CH, acetophenone), 128.8 (CH, acetophenone), 128.0 (CH, Ph), 127.7 (CH, Ph), 127.4 (CH, Ph), 126.5 (CH, Ph), 126.3 (CH, Ph), 99.5 (CH_2, -CH_2), 90.8 (CH, -CH), 67.2 (THF-d_8), 25.1 (THF-d_8), 4.8 (RbHMDS), 2.5 [HMDS(H)] ppm.

Scheme S1: Proposed Mechanism for the formation of **2**

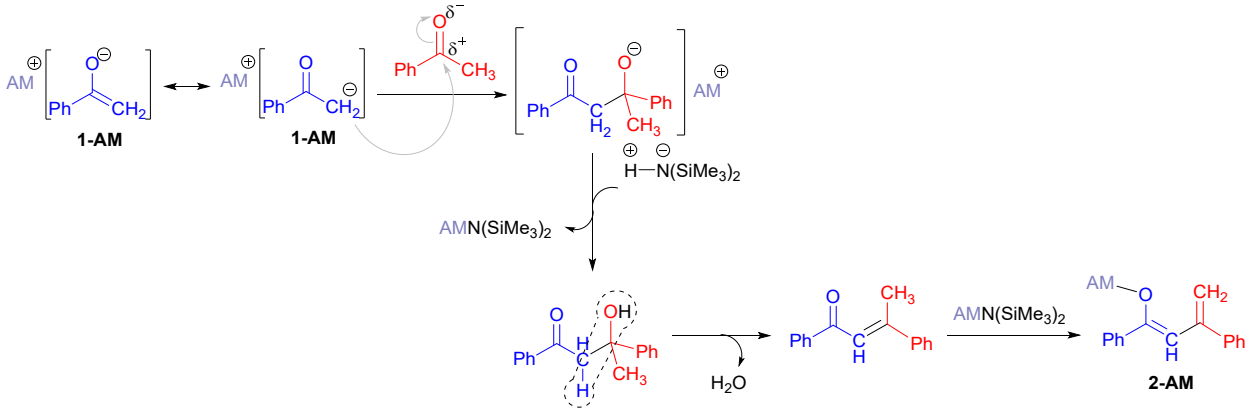


Figure S3: ORTEP diagram of $[RbOC(C_6H_5)CHC(CH_2)C_6H_5.THF]_n$ (**2-Rb**)

Structure of **2-Rb**, thermal ellipsoids are displayed at 20 % probability level.

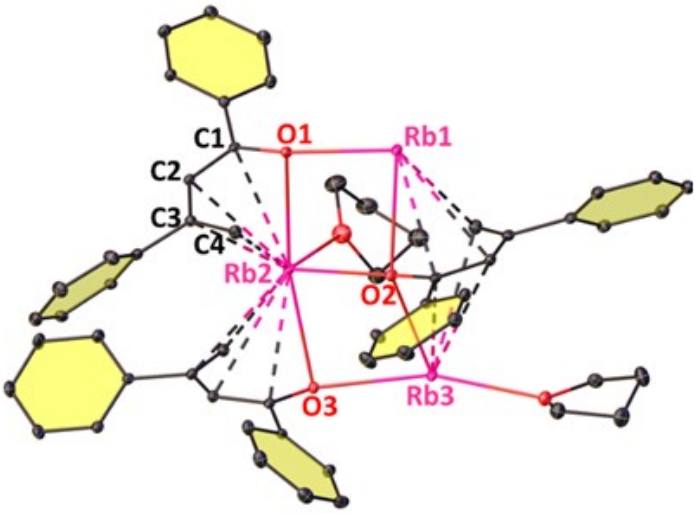


Table S2: Selected bond lengths (Å) and bond angles (°)

Bonds	Bond Lengths (Å)
Rb2 O1	2.770(4)
Rb2 O3	2.898(5)
Rb2 C36	3.303(7)
Rb2 C33	3.164(5)
Rb2 C34	3.285(5)
Rb2 C35	3.314(5)
Rb2 O4	2.983(7)
Rb2 C20	3.406(6)
Rb2 C18	3.456(6)
Rb2 C17	3.170(5)
Rb2 C19	3.620(5)
Rb2 O2	2.865(3)
Rb3 O2	2.797(3)
Rb3 O1	2.938(5)
Rb1 O1	2.943(5)
Rb1 O3	2.685(3)
Rb3 O5	2.890(4)
Rb3 C1	3.231(6)
Rb1 O1	2.943(5)
Rb1 C1	3.144(6)
Rb1 C2	3.361(6)
Rb1 C3	3.473(6)
Rb1 C4	3.430(8)

O3 C33	1.281(6)
C33 C34	1.375(7)
C34 C35	1.453(7)
C35 C36	1.348(7)
O2 C17	1.297(6)
C17 C18	1.372(7)
C18 C19	1.457(7)
C19 C20	1.327(7)
O1 C1	1.292(6)
C1 C2	1.384(7)
C2 C3	1.435(8)
C3 C4	1.352(8)
Bonds	**Bond Angles (°)**
Rb2 O4	92.5(2)
Rb2 C33	23.9(1)
Rb2 C34	44.1(1)
Rb2 C35	56.6(1)
Rb2 C36	56.3(1)
Rb2 O1	83.8(1)
Rb2 O2	165.9(1)
Rb2 C17	154.4(1)
Rb2 C18	144.2(1)
Rb2 C19	139.0(1)
Rb2 C20	138.6(1)
O3 Rb2 O1	83.8(1)
O1 Rb2 O2	82.5(1)
O1 Rb2 O4	96.0(2)
Rb2 O2 Rb3	93.9(1)
O2 Rb3 O1	80.7(1)
Rb3 O1 Rb2	92.9(1)
Rb2 O3 Rb1	95.6(1)
O3 Rb1 O1	84.5(1)
Rb1 O1 Rb2	92.8(1)

Hydrolysis of $[RbOC(C_6H_5)CHC(CH_2)C_6H_5.THF]_n$ (2-Rb)

After completion, the reaction mixture of 2-Rb was hydrolysed using a six-fold excess H_2O before being filtered, the resulting solution was dried in vacuo and used to perform NMR and Mass Spectroscopic studies. NMR of final hydrolysed products was performed in $CDCl_3$ with adamantane as a standard, while GC-MS was performed in MeOH. The NIST database was used to identify compounds of interest from the mass spectra.

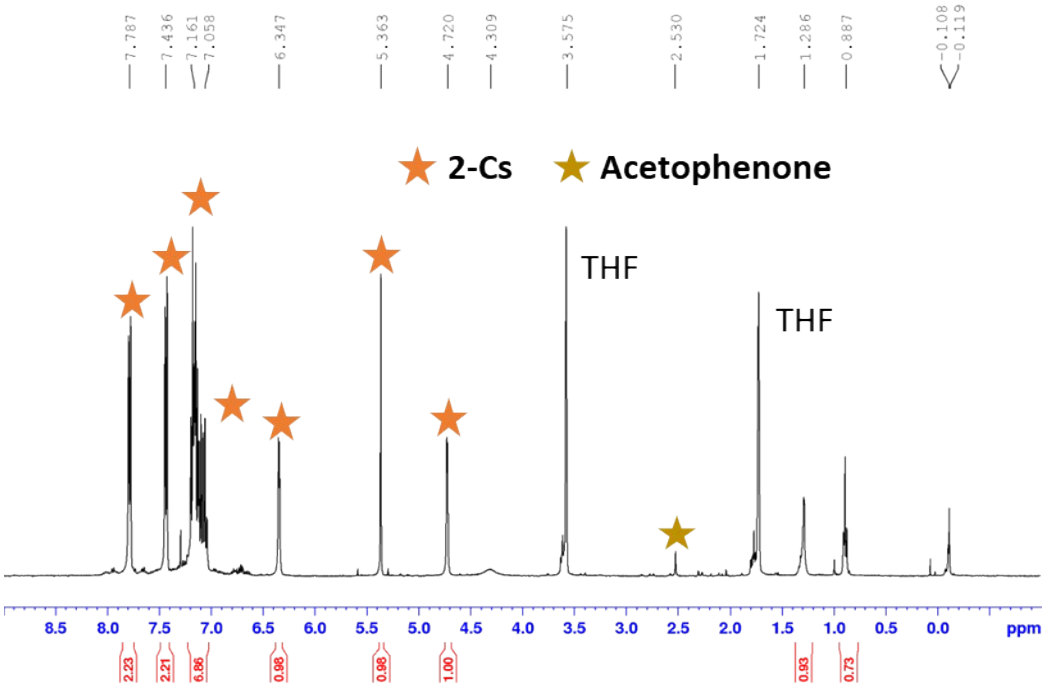
^{1}H NMR (400.1 MHz, $CDCl_3$, 300 K): δ 8.01 (m, 1H, CH, 1,3-diphenylbut-2-en-1-one), 7.98 (m, 2H, CH, acetophenone), 7.57 (m, 1H, CH, acetophenone), 7.47 (m, 2H, CH, acetophenone), 7.42 (m, 1H, CH, 1,3-diphenylbut-2-en-1-one), 7.26 ($CDCl_3$), 7.17 (m, 1H, CH, 1,3-diphenylbut-2-en-1-one), 2.61 (s, 3H, CH_3, acetopheone), 2.60 (s, 1H, CH_3, 1,3-diphenylbut-2-en-1-one), 1.87 (adamantane), 1.75 (adamantane), 1.26 (residual hexane), 0.86 (residual hexane), 0.16 (residual HMDS) ppm. Data comparable with literature report of 1,3-diphenylbut-2-en-1-one.[8]

^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$, 300 K): δ 198.2 (C=O, acetophenone), 137.3 ($C_{quaternary}$, acetophenone), 133.2 (CH, acetophenone), 132.7 (CH, 1,3-diphenylbut-2-en-1-one), 129.3 (CH, 1,3-diphenylbut-2-en-1-one), 128.7 (CH, acetophenone), 128.5 (CH, acetophenone), 126.6 (CH, 1,3-diphenylbut-2-en-1-one), 122.3 (CH, 1,3-diphenylbut-2-en-1-one), 77.2 ($CDCl_3$), 37.9 (adamantane), 37.2 (unknown), 30.2 (unknown), 29.8 (CH_3, 1,3-diphenylbut-2-en-1-one), 28.5 (adamantane), 27.2 (unknown), 26.7 (CH_3, acetophenone), 22.8 (residual hexane), 14.3 (residual hexane) ppm.

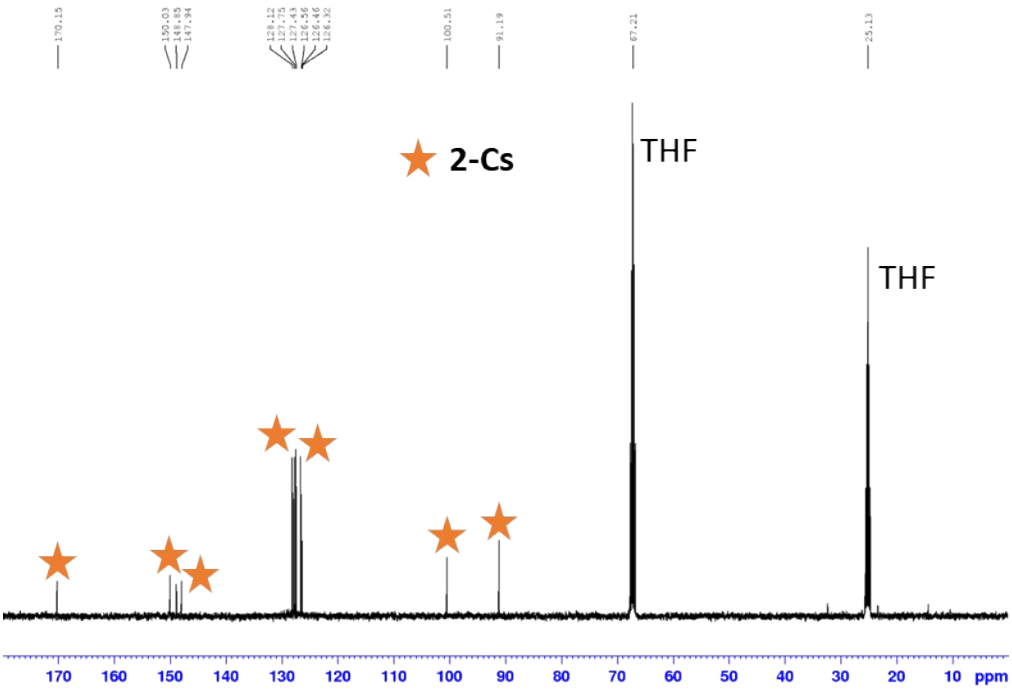
GC-MS (MeOH): Acetophenone (rt 7.5 mins, m/z 105), 1,3-diphenylbut-2-en-1-one (rt 12.8 and 13.6 mins, m/z 222).

Synthesis of $[CsOC(C_6H_5)CHC(CH_2)C_6H_5.THF]_n$ (2-Cs)

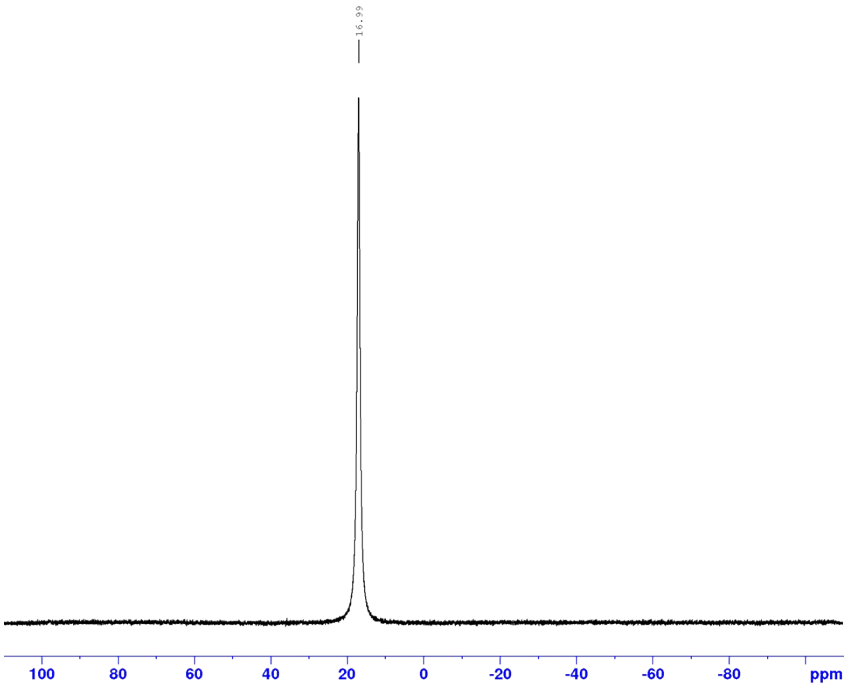
CsHMDS (0.0735 g, 0.25 mmol) dissolved in THF (1 ml) before acetophenone (58 µl, 0.5 mmol) was added to give a pale-orange suspension which darkened upon heating overnight at 70 °C. Only a very small number of colourless crystals of **2-Cs**, suitable for X-ray crystallography authentication, was obtained from a solution of THF layered with hexane in a -20 °C freezer. An orange solid was obtained by drying and removal of residual solvent in vacuo (0.0707 g, 0.166 mmol, 66 %).



^{1}H NMR (400.1 MHz, THF-d_8, 300 K): δ 7.79 (m, 2H, CH, Ph), 7.44 (m, 2H, CH, Ph), 7.16 (broad m, 5H, CH, Ph), 7.06 (broad m, 2H, CH, Ph), 6.35 (d, 1H, CH_2, -CH_2), 5.36 (s, 1H, CH, -CH), 4.72 (d, 1H, CH_2, -CH_2), 4.31 (unknown), 3.58 (THF-d_8), 2.53 (residual acetophenone), 1.72 (THF-d_8), 1.29 (residual hexane), 0.89 (residual hexane), -0.12 (residual CsHMDS) ppm.



$^{13}C\{^{1}H\}$ NMR (100.6 MHz, THF-d_8, 300 K): δ 170.2 ($C_{quaternary}$, -C=O), 150.0 ($C_{quaternary}$, -*C*(CH_2)Ph), 148.8 ($C_{quaternary}$, Ph), 147.9 ($C_{quaternary}$, Ph), 128.1 (CH, Ph), 127.8 (CH, Ph), 127.4 (CH, Ph), 126.6 (CH, Ph), 126.5 (CH, Ph), 126.3 (CH, Ph), 100.5 (CH_2, -CH_2), 91.2 (CH, -CH), 67.2 (THF-d8), 25.1 (THF-d_8) ppm.



^{133}Cs NMR (65.6 MHz, THF-D_8, 300 K): δ 16.99 (**2-Cs**) ppm.

Figure S4: ORTEP diagram of $[CsOC(C_6H_5)CHC(CH_2)C_6H_5.THF]_n$ (**2-Cs**)

Structure of **2-Cs**, thermal ellipsoids are displayed at 20 % probability level.

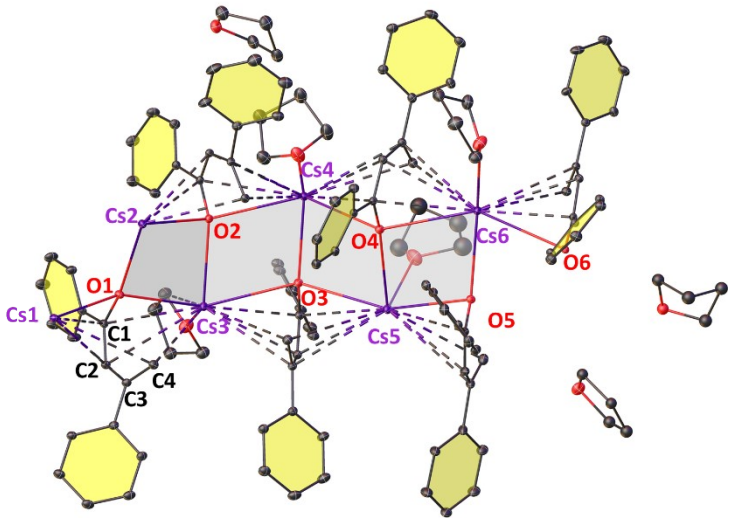


Table S3: Selected bond lengths (Å) and bond angles (°)

Bonds	Bond Lengths (Å)
Cs1 O13	3.153(6)
Cs1 O5	3.248(5)
Cs1 O1	3.176(4)
Cs1 O6	2.854(4)
Cs2 O6	3.164(3)
Cs2 O1	2.869(4)
Cs1 O1	3.176(4)
Cs3 O1	3.074(5)
Cs3 O2	2.940(4)
Cs2 O2	3.111(3)
Cs3 O3	3.189(5)
Cs4 O3	2.885(4)
Cs4 O2	3.187(4)
Cs4 O4	3.146(5)
Cs5 O3	3.185(5)
Cs5 O4	2.894(4)
Cs5 O5	3.061(5)
Cs6 O5	2.947(4)
Cs6 O4	3.314(5)
Cs3 O7	3.066(7)
Cs4 O9	3.050(7)
Cs4 O2	3.187(4)
Cs4 O4	3.146(5)
Cs1 O5	3.248(5)

Cs1 O6	2.854(4)
Cs6 O6	3.122(4)
Cs6 O11	3.181(5)
Cs5 O10	3.089(9)
Cs5 O4	2.894(4)
Cs5 O3	3.185(5)
Bonds	**Bond Angles (°)**
O5 Cs1 O6	71.2(1)
O6 Cs1 O1	85.7(1)
O6 Cs1 O13	110.5(1)
O5 Cs1 O13	112.1(1)
O1 Cs1 O13	127.5(1)
O5 Cs1 O1	120.3(1)
O1 Cs3 O2	80.1(1)
O12 Cs2 O6	74.0(5)
O6 Cs2 O2	159.5(1)
O2 Cs2 O12	118.8(5)
O12 Cs2 O1	82.9(5)
O2 Cs3 O7	115.9(2)
O7 Cs3 O1	106.5(2)
Cs3 O3 Cs4	106.8(1)
Cs4 O2 Cs3	105.4(1)
O3 Cs3 O2	73.5(1)
O2 Cs4 O3	74.3(1)
O3 Cs4 O9	103.8(2)
O9 Cs4 O2	95.2(2)
O3 Cs3 O1	148.2(1)
O3 Cs5 O4	79.3(1)
Cs4 O3 Cs5	97.9(1)
Cs5 O4 Cs4	98.5(1)
Cs5 O4 Cs6	99.7(1)
Cs6 O5 Cs5	104.6(1)
O5 Cs5 O4	77.8(1)
O4 Cs6 O5	73.2(1)
O5 Cs1 O6	71.2(1)
O6 Cs6 O5	72.0(1)
Cs6 O5 Cs1	105.5(1)
Cs1 O6 Cs6	111.2(1)
O11 Cs6 O6	100.8(2)
O6 Cs6 O4	145.1(1)
O4 Cs6 O11	107.6(2)
O11 Cs6 O5	144.6(2)
Cs1 O5 Cs5	144.5(2)

Cs5 O3 Cs3	143.6(1)
O2 Cs4 O4	130.4(1)
O9 Cs4 O4	132.2(2)
O10 Cs5 O4	83.2(2)
O10 Cs5 O3	82.1(2)
O10 Cs5 O5	93.1(2)

Hydrolysis of $[CsOC(C_6H_5)CHC(CH_2)C_6H_5.THF]_n$ (2-Cs)

After completion, the reaction mixture of 2-Cs was hydrolysed using a six-fold excess H_2O before being filtered, the resulting solution was dried in vacuo and used to perform NMR and Mass Spectroscopic studies. NMR of final hydrolysed products was performed in $CDCl_3$ with adamantane as a standard, while GC-MS was carried out in MeOH. The NIST database was used to identify compounds of interest from the mass spectra.

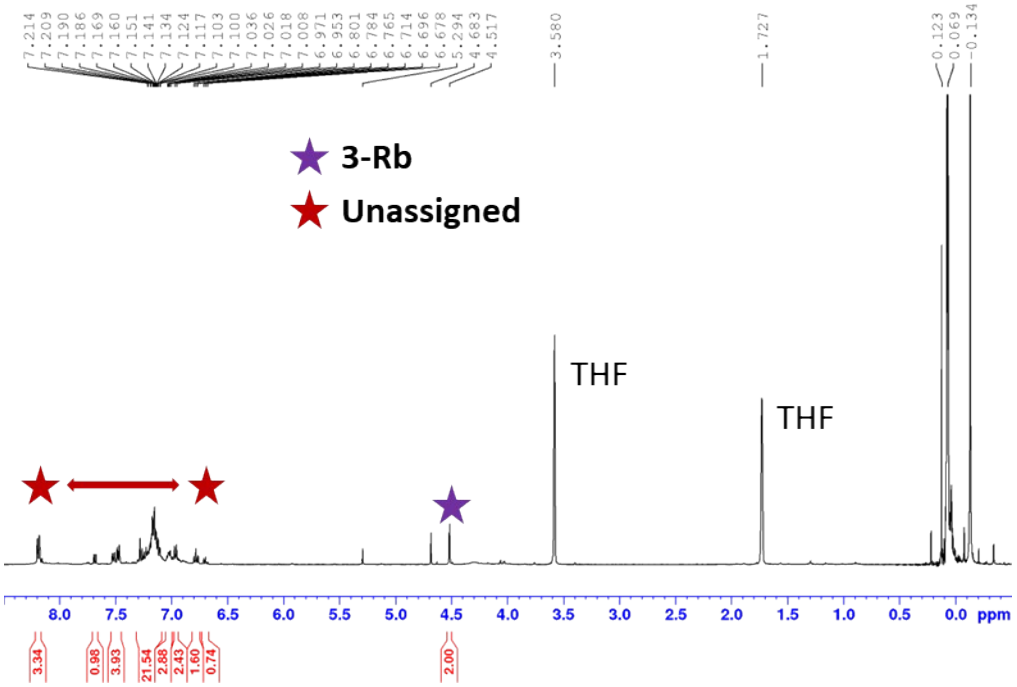
^{1}H NMR (400.1 MHz, $CDCl_3$, 300 K): δ 8.01 (m, 1H, CH, 1,3-diphenylbut-2-en-1-one), 7.98 (m, 3H, CH, acetophenone), 7.56 (m, 3H, CH, acetophenone), 7.47 (m, 3H, CH, acetophenone), 7.41 (m, 2H, CH, 1,3-diphenylbut-2-en-1-one), 7.26 ($CDCl_3$), 7.17 (m, 1H, CH, 1,3-diphenylbut-2-en-1-one), 2.61 (s, 3H, CH_3, acetopheone), 2.60 (d, 1H, CH_3, 1,3-diphenylbut-2-en-1-one), 1.88 (adamantane), 1.75 (adamantane), 1.26 (residual hexane), 0.86 (residual hexane), 0.06 (residual HMDS) ppm. Data comparable with literature report of 1,3-diphenylbut-2-en-1-one.[8]

^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$, 300 K): δ 198.2 (C=O, acetophenone), 192.0 (C=O, 1,3-diphenylbut-2-en-1-one), 155.2 ($C_{quaternary}$, 1,3-diphenylbut-2-en-1-one), 143.0 ($C_{quaternary}$, 1,3-diphenylbut-2-en-1-one), 139.5 $C_{quaternary}$, 1,3-diphenylbut-2-en-1-one), 137.3 ($C_{quaternary}$, acetophenone), 133.2 (CH, acetophenone), 132.7 (CH, 1,3-diphenylbut-2-en-1-one), 129.3 (CH, 1,3-diphenylbut-2-en-1-one), 128.8 (CH, acetophenone), 128.7 (CH, acetophenone), 128.5 (CH, acetophenone), 128.4 (CH, acetophenone), 126.6 (CH, 1,3-diphenylbut-2-en-1-one), 122.3 (CH, 1,3-diphenylbut-2-en-1-one), 77.2 ($CDCl_3$), 37.9 (adamantane), 32.1 (unknown), 29.8 (CH_3, 1,3-diphenylbut-2-en-1-one), 28.5 (adamantane), 26.7 (CH_3, acetophenone), 22.8 (residual hexane), 19.0 (unknown), 14.3 (residual hexane) ppm.

GC-MS (MeOH): Acetophenone (rt 7.5 mins, m/z 105), 1,3-diphenylbut-2-en-1-one (rt 12.8 and 13.6 mins, m/z 222).

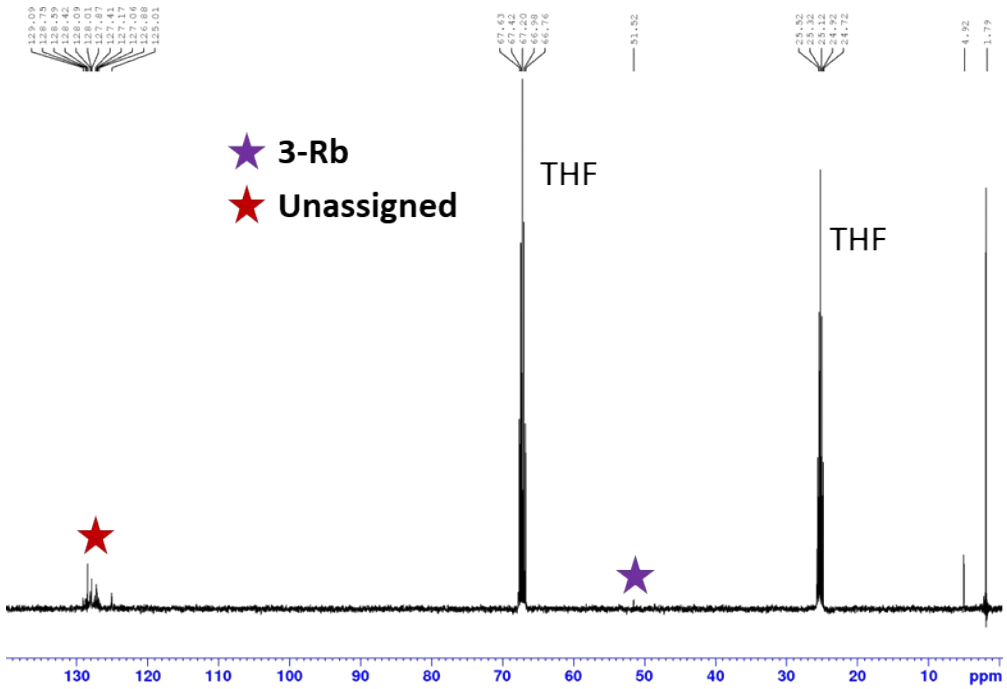
Synthesis of $[RbOC(C_6H_5)NCH_2C_6H_5]_n$ (**3-Rb**)

RbHMDS (0.147 g, 0.5 mmol) was dissolved in dried THF (2 ml) before benzaldehyde (51 µl, 0.5 mmol) was added to afford a pale-yellow solution which quickly turned to dark blue and then dark pink upon mixing at room temperature. The reaction was then heated overnight at 70°C. This THF solution layered with hexane gave a heterogeneous mixture of dark pink solid and colourless crystals of **3-Rb** (crude yield, 0.0561 g, 0.190 mmol, 38 %). This mixture was poorly soluble in THF-D_8.



^{1}H NMR (400.1 MHz, THF-D_8, 300 K): δ 8.19-6.87 (aromatic signals could not be assigned), 5.29 (unknown impurity), 4.68 (unknown impurity), 4.52 (s, 2H, CH_2, **3-Rb**), 3.58 (THF-d_8), 1.73 (THF-d_8) 0.12 (unknown impurity), 0.07 [HMDS(H)], -0.13 (RbHMDS) ppm.

Limited solubility of **3-Rb** resulted in a poor quality ^{13}C NMR spectrum.



$^{13}C\{^{1}H\}$ NMR (100.6 MHz, THF-d_8, 300 K): δ 129.1-125.0 (aromatic signals could not be assigned), 67.2 (THF-d_8), 51.5 (CH_2, **3-Rb**), 25.1 (THF-d_8), 4.92 (RbHMDS), 1.8 [HMDS(H)] ppm.

Figure S5: ORTEP diagram of $[RbOC(C_6H_5)NCH_2C_6H_5]_n$ (**3-Rb**)

(Top) Structure of **3-Rb**, with thermal ellipsoids displayed at 20 % probability level; (bottom) section of the infinite network structure of $[RbOC(Ph)=NCH_2Ph]_{\infty}$ (**3**-Rb). Thermal ellipsoids of all non-C/H atoms are displayed at 25% probability, and C atoms reduced to 5% for clarity. H atoms are omitted, and aromatic rings are shaded in yellow, grey, and teal for clear depiction of M---π interactions. C_t depicts the centroid of Ph rings.

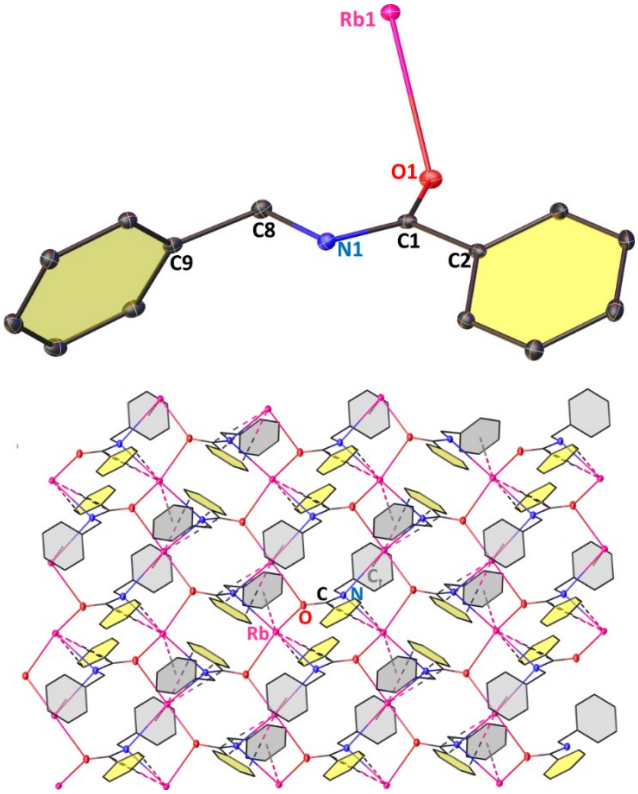


Table S4: Selected bond lengths (Å) and bond angles (°)

Bonds	**Bond Lengths (Å)**
O1 C1	1.301(3)
C1 C2	1.509(3)
C1 N1	1.315(4)
N1 C8	1.464(2)
C8 C9	1.498(4)
N1 Rb1	3.363(2)
N1 Rb1	3.029(2)
Rb1 O1	2.877(2)
Rb1 O1	3.006(2)
Rb1 C9	3.296(2)
Rb1 C7	3.528(3)
Bonds	**Bond Angles (°)**
O1 Rb1 O1	152.78(5)

O1 Rb1 N1	80.22(5)
O1 Rb1 N1	101.69(5)
O1 Rb1 N1	84.61(5)
O1 Rb1 C9	99.52(5)
N1 Rb1 N1	156.61(5)
N1 Rb1 C9	42.94(5)
C9 Rb1 N1	159.10(5)
Rb1 O1 Rb1	100.91(6)
O1 Rb1 N1	83.98(5)
Rb1 N1 Rb1	90.29(5)
Rb1 O1 C1	136.2(1)
Rb1 N1 C1	105.6(1)
N1 C1 O1	126.1(2)
N1 C1 C2	115.7(2)
C2 C1 O1	118.2(2)
Rb1 N1 C8	116.2(1)
Rb1 O1 C1	116.5(1)
Rb1 N1 C1	132.8(1)
O1 C1 N1	126.1(2)
C1 N1 C8	112.8(2)

Hydrolysis of $[RbOC(C_6H_5)NCH_2C_6H_5]_n$ (3-Rb)

After completion, the reaction mixture of 3-Rb was hydrolysed using a six-fold excess H_2O before being filtered, the resulting solution was dried in vacuo and used to perform NMR and Mass Spectroscopic studies. NMR of final hydrolysed products was performed in $CDCl_3$ with adamantane as a standard, while GC-MS was carried out in MeOH. The NIST database was used to identify compounds of interest from the mass spectra.

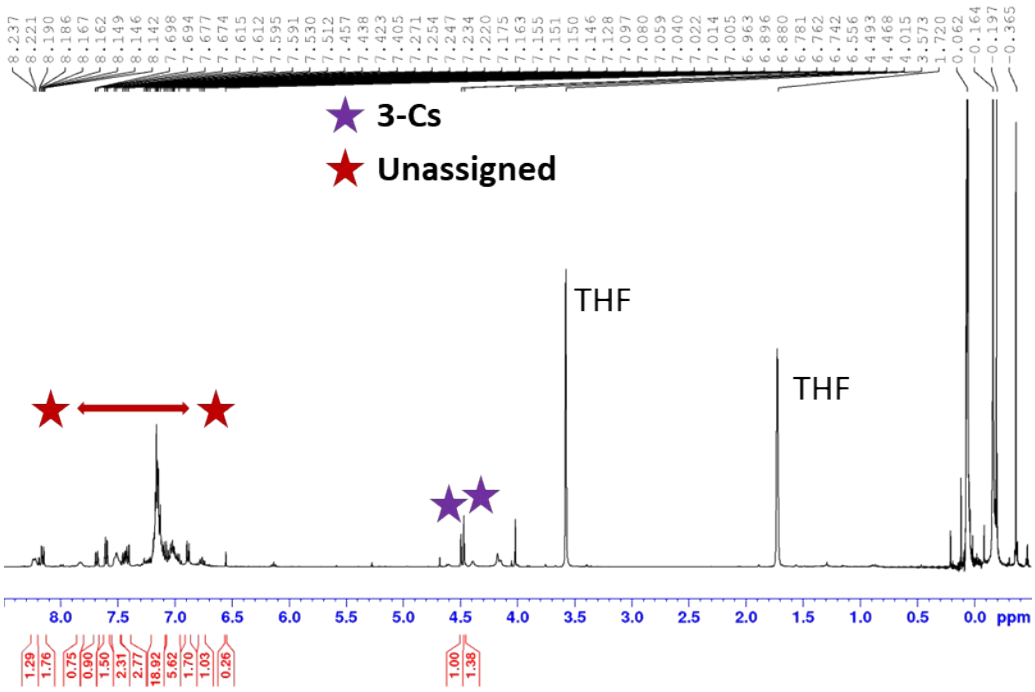
^{1}H NMR (400.1 MHz, $CDCl_3$, 300 K): δ 8.23-7.02 (aromatic signals could not be assigned), 7.26 ($CDCl_3$), 4.66 (s, 1H, CH_2, N-benzylbenzamide), 4.63 (s, 1H, CH_2, N-benzylbenzamide), 1.88 (adamantane), 1.76 (adamantane), 1.26 (residual hexane), 0.86 (residual hexane), 0.15 (residual HMDS) ppm. Comparable with literature report.[9]

^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$, 300 K): δ 131.7-125.9 (aromatic signals could not be assigned), 77.2 ($CDCl_3$), 44.2 (CH_2, N-benzylbenzamide), 37.9 (adamantane), 29.8 (unknown), 28.5 (adamantane), 22.9 (residual hexane), 14.2 (residual hexane), 1.5 (residual HMDS) ppm.

GC-MS (MeOH): Benzaldehyde (rt 6.3 mins, m/z 106), N-Benzylbenzamide (rt 13.7 mins, m/z 211).

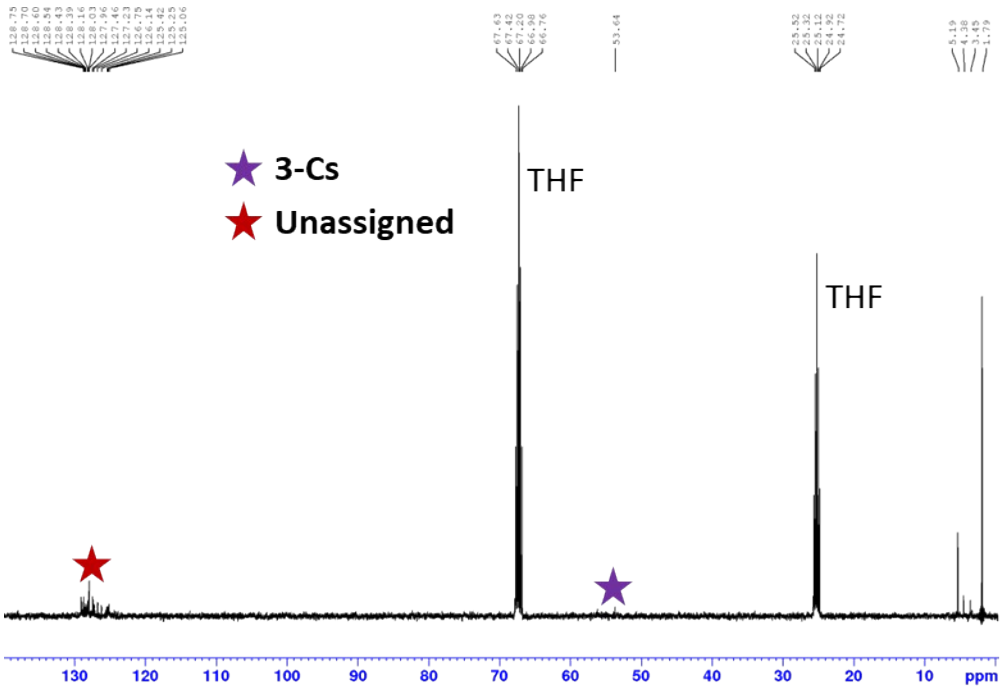
Synthesis of $[CsOC(C_6H_5)NCH_2C_6H_5]_n$ (**3-Cs**)

CsHMDS (0.147 g, 0.5 mmol) was dissolved in THF (2 ml) before benzaldehyde (51 µl, 0.5 mmol) was added to give a pale-yellow solution which quickly turned to dark blue and then to a deep purple upon mixing at room temperature. The reaction was then heated overnight at 70 °C. The THF solution layered with hexane gave a heterogeneous mixture of purple solid and colourless crystals of **3-Cs** (Crude yield, 0.126 g, 0.367 mmol, 73 %). Similarly to **3-Rb**, this mixture showed poor solubility in the NMR solvent.

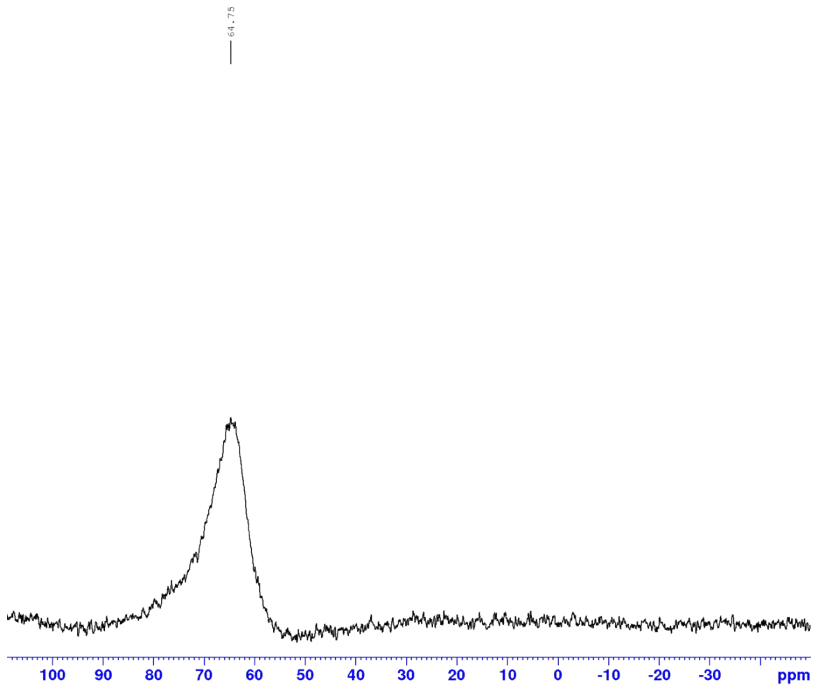


^{1}H NMR (400.1 MHz, THF-d_8, 300 K): δ 8.23-6.56 (aromatic signals could not be assigned), 4.49 (s, 1H, CH_2, **3-Cs**), 4.47 (s, 1H, CH_2, **3-Cs**), 4.18 (unknown impurity) 4.52 (s, unknown impurity), 3.57 (THF-d_8), 1.72 (THF-d_8), 0.07 [HMDS(H)], -0.16 (CsHMDS), -0.20 (unknown impurity), -0.37 (unknown impurity) ppm.

Limited solubility of **3-Cs** results in poor quality ^{13}C and ^{133}Cs NMR spectra.



$^{13}C\{^{1}H\}$ NMR (100.6 MHz, THF-d_8, 300 K): δ 129.1-125.1 (aromatic signals could not be assigned), 67.2 (THF-d_8), 53.6 (CH_2, **3-Cs**), 25.1 (THF-d_8), 5.19 (CsHMDS), 4.38 (unknown impurities), 3.4 (unknown impurities), 1.8 [HMDS(H)] ppm.



^{133}Cs NMR (65.6 MHz, THF-d_8, 300 K): δ 64.75 (**3-Cs**) ppm.

Figure S6: ORTEP diagram of $[CsOC(C_6H_5)NCH_2C_6H_5]_n$ (**3-Cs**)

Structure of **3-Cs**, thermal ellipsoids are displayed at 20 % probability level.

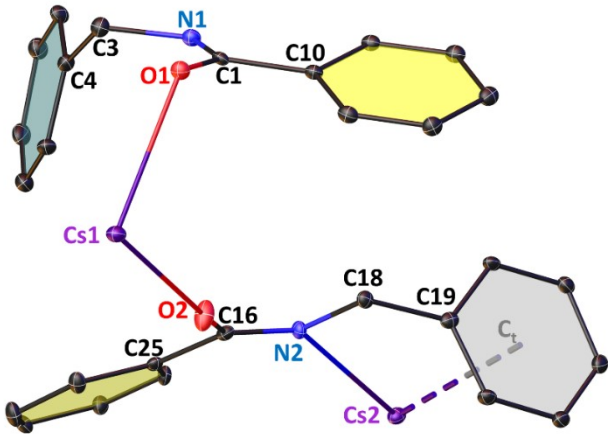


Table S5: Selected bond lengths (Å) and bond angles (°)

Bonds	Bond Lengths (Å)
Cs2 O1	2.770(4)
Cs2 O3	2.898(5)
Cs2 C36	3.303(7)
Cs2 C33	3.164(5)
Cs2 C34	3.285(5)
Cs2 C35	3.314(5)
Cs2 O4	2.983(7)
Cs2 C20	3.406(6)
Cs2 C18	3.456(6)
Cs2 C17	3.170(5)
Cs2 C19	3.620(5)
Cs2 O2	2.865(3)
Cs3 O2	2.797(3)
Cs3 O1	2.938(5)
Cs1 O1	2.943(5)
Cs1 O3	2.685(3)
Cs3 O5	2.890(4)
Cs3 C1	3.231(6)
Cs1 O1	2.943(5)
Cs1 C1	3.144(6)
Cs1 C2	3.361(6)
Cs1 C3	3.473(6)
Cs1 C4	3.430(8)
O3 C33	1.281(6)
C33 C34	1.375(7)

C34 C35	1.453(7)
C35 C36	1.348(7)
O2 C17	1.297(6)
C17 C18	1.372(7)
C18 C19	1.457(7)
C19 C20	1.327(7)
O1 C1	1.292(6)
C1 C2	1.384(7)
C2 C3	1.435(8)
C3 C4	1.352(8)
Cs2---C_t	3.359
Bonds	**Bond Angles (°)**
O3 Cs2 O4	92.5(2)
O3 Cs2 C33	23.9(1)
O3 Cs2 C34	44.1(1)
O3 Cs2 C35	56.6(1)
O3 Cs2 C36	56.3(1)
O3 Cs2 O1	83.8(1)
O3 Cs2 O2	165.9(1)
O3 Cs2 C17	154.4(1)
O3 Cs2 C18	144.2(1)
O3 Cs2 C19	139.0(1)
O3 Cs2 C20	138.6(1)
O3 Cs2 O1	83.8(1)
O1 Cs2 O2	82.5(1)
O1 Cs2 O4	96.0(2)
Cs2 O2 Cs3	93.9(1)
O2 Cs 3 O1	80.7(1)
Cs 3 O1 Cs2	92.9(1)
Cs 2 O3 Cs1	95.6(1)
O3 Cs 1 O1	84.5(1)
Cs 1 O1 Cs2	92.8(1)

Hydrolysis of $[CsOC(C_6H_5)NCH_2C_6H_5]_n$ (3-Cs)

After completion, the reaction mixture of 3-Cs was hydrolysed with a six-fold excess H_2O before being filtered, the resulting solution was dried in vacuo and used to perform NMR and Mass Spectroscopic studies. NMR of final hydrolysed products was performed in $CDCl_3$ with adamantane as a standard, while GC-MS was carried out in MeOH. The NIST database was used to identify compounds of interest from the mass spectra.

^{1}H NMR (400.1 MHz, $CDCl_3$, 300 K): δ 8.00-7.02 (aromatic signals could not be assigned), 7.26 ($CDCl_3$), 6.39 (s, 1H, -NH, N-benzylbenzamide), 4.66 (s, 1H, CH_2, N-benzylbenzamide), 4.62 (s, 1H, CH_2, N-benzylbenzamide), 4.57 (unknown), 1.88 (adamantane), 1.76 (adamantane), 1.26 (residual hexane), 0.86 (residual hexane), 0.15 (residual HMDS) ppm. Data for N-benzylbenzamide is comparable with a literature report.[9]

^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$, 300 K): δ 138.3-126.2 (aromatic signals could not be assigned), 77.2 ($CDCl_3$), 44.3 (CH_2, N-benzylbenzamide), 37.9 (adamantane), 29.8 (unknown), 28.5 (adamantane), 22.8 (residual hexane), 14.2 (residual hexane), 1.5 (residual HMDS) ppm.

GC-MS (MeOH): Benzaldehyde (rt 6.3 mins, m/z 106), N-Benzylbenzamide (rt 13.7 mins, m/z 211).

Table S6: Selected X-ray crystal structural data and refinement details for compounds 1-3

Compound	1-Cs	2-Rb	2-Cs	3-Rb	3-Cs
	$[CsOC(CH_2)C_6H_5]_n$	$[RbOC(C_6H_5)CHC(CH_2)C_6H_5.THF]_n$	$[CsOC(C_6H_5)CHC(CH_2)C_6H_5.THF]_n$	$[RbOC(C_6H_5)NCH_2C_6H_5]_n$	$[CsOC(C_6H_5)NCH_2C_6H_5]_n$
CCDC	2293054	2293057	2293058	2293055	2293056
Instrument	Rigaku	Rigaku	Rigaku	Rigaku	Rigaku
Empirical Formula	C_8H_7CsO	$C_{57}H_{57}Rb_3O_{5.25}$	$C_{20.76}H_{22.51}CsO_{2.19}$	$C_{14}H_{12}RbNO$	$C_{14}H_{12}CsNO$
Molecular Mass	252.05	1082.43	439.89	295.72	343.16
X-ray wavelength Å	Cu Kα (λ 1.54184)	Cu Kα (λ 1.54184)	Cu Kα (λ 1.54184)	Cu Kα (λ 1.54184)	Cu Kα (λ 1.54184)
Space Group	P b c a	C 1 2/c 1	P -1	P 1 21/c 1	P c a 21
Crystal system	orthorhombic	monoclinic	triclinic	monoclinic	orthorhombic
Temperature (K)	100(2)	200(2)	159.99(10)	220.00(10)	220(2)
a/Å	6.77660(10)	25.4358(3)	13.3301(2)	12.69990(10)	18.6607(4)
b/Å	8.3061(2)	15.8158(2)	16.6470(2)	8.71240(10)	6.0929(2)
c/Å	29.6225(6)	26.6220(3)	28.3794(2)	12.20280(10)	22.6838(7)
α/°	90	90	73.5210(10)	90	90
β/°	90	92.4240(10)	83.5790(10)	113.8780(10)	90
γ/°	90	90	80.0460(10)	90	90
Volume/Å^3	1667.37(6)	10700.1(2)	5934.82(13)	1234.63(2)	2579.10(13)
Z	8	8	12	4	8
2θmax °	146.4	146.4	147.8	146.1	148.9
Measured Reflections	6552	35064	111321	25780	37960
Unique Reflections	1667	10480	23704	2459	5087
R_{int}	0.0833	0.0388	0.0498	0.0224	0.0494
Observed Reflections [I>2σI]	1354	6670	19131	2378	4496
No. parameters	99	653	1391	162	308
Goodness of Fit	1.057	1.076	1.083	1.075	1.194
R [on F, obs refs only]	0.0495	0.0482	0.0507	0.0243	0.0389
ωR [on F^2, all data]	0.1378	0.1802	0.1511	0.0640	0.1147
Largest diff. peak /hole/Å^{-3}	1.58/-1.21	0.89/-0.79	1.02/-1.57	0.44/-0.38	0.93/-0.89

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