**Electronic Supplementary Information (ESI) for RSC Advances**

# A 4-*tert*-butylcalix[4]arene tetrahydroxamate podand based on the 1-oxypiperidine-2-one (1,2-PIPO$^-$) chelate. Self-assembly into a supramolecular ionophore driven by coordination of tetravalent zirconium or hafnium(IV)

Pawel Jewula,[a] Jean-Claude Chambron,*[a] Marie-José Penouilh,[a] Yoann Rousselin[a] and Michel Meyer*[a]

[a] *Institut de Chimie Moléculaire de l'Université de Bourgogne (ICMUB), UMR CNRS 6302, 9 avenue A. Savary, BP 47870, 21078 Dijon Cedex, France. E-mail: jean-claude.chambron@u-bourgogne.fr and michel.meyer@u-bourgogne.fr; Fax: +33 3 80 39 61 17; Tel: 33 3 80 39 61 16*

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**Table S1** Crystal data for **1**$Bn_4$

| | |
|---|---|
| Empirical formula | $C_{100.75}H_{123.5}N_8O_{17}$ |
| Molecular mass (g mol$^{-1}$) | 1718.06 |
| Colour | colourless |
| Crystal size (mm$^3$) | 0.30 × 0.25 × 0.10 |
| Crystal system | monoclinic |
| Space group | $P\ 2_1$ |
| $a$ (Å) | 15.6125(2) |
| $b$ (Å) | 18.2100(3) |
| $c$ (Å) | 18.3284(3) |
| $\beta$ (°) | 101.789(1) |
| $V$ (Å$^3$) | 5100.9(4) |
| $Z$ | 2 |
| $d_{cal}$ (g cm$^{-3}$) | 1.119 |
| $\mu$(Mo K$\alpha$) (mm$^{-1}$) | 0.076 |
| $F$(000) | 1839.0 |
| 2$\theta$ range (°) | 8.154 to 54.934 |
| $T$ (K) | 115(2) |
| $\lambda$ (Mo K$\alpha$) (Å) | 0.71073 |
| Numbers of collected reflections | 66668 |
| Numbers of independent reflections | 22535 [$R_{int}$ = 0.0437] |
| Data/restraints/parameters | 22535/25/1015 |
| Final R indexes ($I > 2\sigma(I)$)[a] | $R_1$ = 0.0703; $wR_2$ = 0.1827 |
| Final R indexes (all data)[a] | $R_1$ = 0.0863; $wR_2$ = 0.2007 |
| $\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å$^{-3}$) | 0.73, –0.580 |

[a] $R_1 = \Sigma||F_o| - |F_c|| / \Sigma|F_o|$, $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]\}^{1/2}$.

**Table S2** Atomic occupancy for **1**$Bn_4$

| Atom | Occupancy | Atom | Occupancy | Atom | Occupancy |
|---|---|---|---|---|---|
| C1A | 0.5 | H1AA | 0.25 | H1AB | 0.25 |
| H1AC | 0.25 | H1AD | 0.25 | H1AE | 0.25 |
| H1AF | 0.25 | O2A | 0.25 | H2A | 0.25 |
| O3B | 0.25 | H3B | 0.25 | C1B | 0.25 |
| H1BA | 0.25 | H1BB | 0.25 | H1BC | 0.25 |
| O2C | 0.25 | H2C | 0.25 | O2D | 0.25 |

**Table S3** Bond lengths for **1**$Bn_4$

| Atom | Atom | Length (Å) | Atom | Atom | Length (Å) |
|---|---|---|---|---|---|
| C1 | C2 | 1.528(6) | C56 | C55 | 1.3900 |
| C1 | C39 | 1.513(6) | C55 | C54 | 1.3900 |
| C2 | C3 | 1.395(6) | C59 | C60 | 1.531(5) |
| C2 | C7 | 1.406(5) | C59 | O2 | 1.426(5) |
| C3 | C4 | 1.396(6) | C60 | N3 | 1.331(5) |
| C4 | C5 | 1.387(6) | C60 | O8 | 1.230(5) |
| C4 | C8 | 1.529(6) | C61 | C62 | 1.510(6) |
| C5 | C6 | 1.398(6) | C61 | C65 | 1.531(6) |
| C6 | C7 | 1.391(6) | C61 | N3 | 1.455(5) |
| C6 | C12 | 1.522(5) | C62 | C63 | 1.522(7) |
| C7 | O1 | 1.392(5) | C63 | C64 | 1.500(8) |
| C8 | C9 | 1.531(7) | C64 | N4 | 1.453(6) |
| C8 | C10 | 1.536(7) | C65 | N4 | 1.344(6) |
| C8 | C11 | 1.531(7) | C65 | O9 | 1.219(6) |
| C12 | C13 | 1.519(5) | C66 | C67 | 1.504(6) |
| C13 | C14 | 1.401(5) | C66 | O10 | 1.452(7) |
| C13 | C18 | 1.391(5) | C67 | C68 | 1.3900 |
| C14 | C15 | 1.391(6) | C67 | C72 | 1.3900 |
| C15 | C16 | 1.402(6) | C68 | C69 | 1.3900 |
| C15 | C19 | 1.534(6) | C69 | C70 | 1.3900 |
| C16 | C17 | 1.392(5) | C70 | C71 | 1.3900 |
| C17 | C18 | 1.398(5) | C71 | C72 | 1.3900 |
| C17 | C23 | 1.518(5) | C73 | C74 | 1.514(6) |
| C18 | O2 | 1.389(4) | C73 | O3 | 1.443(5) |
| C19 | C20 | 1.534(7) | C74 | N5 | 1.330(6) |
| C19 | C21 | 1.533(8) | C74 | O11 | 1.234(6) |
| C19 | C22 | 1.533(8) | C75 | C76 | 1.518(6) |
| C23 | C24 | 1.536(5) | C75 | C79 | 1.547(6) |
| C24 | C25 | 1.393(5) | C75 | N5 | 1.448(5) |
| C24 | C29 | 1.401(5) | C76 | C77 | 1.511(6) |
| C25 | C26 | 1.391(6) | C77 | C78 | 1.497(7) |
| C26 | C27 | 1.394(6) | C78 | N6 | 1.462(6) |
| C26 | C30 | 1.542(6) | C79 | N6 | 1.341(6) |
| C27 | C28 | 1.397(6) | C79 | O12 | 1.219(6) |
| C28 | C29 | 1.407(5) | C80 | C81 | 1.508(6) |
| C28 | C34 | 1.518(5) | C80 | O13 | 1.448(6) |
| C29 | O3 | 1.391(4) | C81 | C86 | 1.3900 |
| C30 | C31 | 1.512(7) | C81 | C82 | 1.3900 |
| C30 | C32 | 1.521(7) | C86 | C85 | 1.3900 |
| C30 | C33 | 1.532(7) | C85 | C84 | 1.3900 |
| C34 | C35 | 1.503(5) | C84 | C83 | 1.3900 |
| C35 | C36 | 1.406(5) | C83 | C82 | 1.3900 |
| C35 | C40 | 1.400(5) | C87 | C88 | 1.516(6) |
| C36 | C37 | 1.390(6) | C87 | O4 | 1.432(5) |
| C37 | C38 | 1.397(6) | C88 | N7 | 1.340(6) |
| C37 | C41 | 1.532(5) | C88 | O14 | 1.233(5) |

| | | | | | |
|---|---|---|---|---|---|
| C38 | C39 | 1.399(6) | C89 | C90 | 1.528(8) |
| C39 | C40 | 1.400(6) | C89 | C93 | 1.524(8) |
| C40 | O4 | 1.383(4) | C89 | N7 | 1.457(6) |
| C41 | C42 | 1.528(6) | C90 | C91 | 1.528(7) |
| C41 | C43 | 1.533(7) | C91 | C92 | 1.508(7) |
| C41 | C44 | 1.536(7) | C92 | N8 | 1.452(7) |
| C45 | C46 | 1.526(6) | C93 | N8 | 1.331(7) |
| C45 | O1 | 1.431(5) | C93 | O15 | 1.228(6) |
| C46 | N1 | 1.332(6) | C94 | C95 | 1.493(8) |
| C46 | O5 | 1.224(5) | C94 | O16 | 1.473(9) |
| C47 | C48 | 1.512(6) | C95 | C96 | 1.3900 |
| C47 | C51 | 1.544(7) | C95 | C100 | 1.3900 |
| C47 | N1 | 1.448(5) | C96 | C97 | 1.3900 |
| C48 | C49 | 1.516(7) | C97 | C98 | 1.3900 |
| C49 | C50 | 1.518(10) | C98 | C99 | 1.3900 |
| C50 | N2 | 1.449(8) | C99 | C100 | 1.3900 |
| C51 | N2 | 1.365(6) | N2 | O7 | 1.419(6) |
| C51 | O6 | 1.209(6) | N4 | O10 | 1.415(5) |
| C52 | C53 | 1.549(9) | N6 | O13 | 1.411(5) |
| C52 | O7 | 1.464(9) | N8 | O16 | 1.406(5) |
| C53 | C58 | 1.3900 | C1A | O2A | 1.46(5) |
| C53 | C54 | 1.3900 | C1A | O3B | 1.47(4) |
| C58 | C57 | 1.3900 | C1B | O2C | 1.53(4) |
| C57 | C56 | 1.3900 | | | |

**Table S4** Bond angles for **1**$Bn_4$

| Atom | Atom | Atom | Angle (deg) | Atom | Atom | Atom | Angle (deg) |
|---|---|---|---|---|---|---|---|
| C39 | C1 | C2 | 110.0(3) | C58 | C53 | C52 | 118.3(5) |
| C3 | C2 | C1 | 118.7(4) | C58 | C53 | C54 | 120.0 |
| C3 | C2 | C7 | 118.2(4) | C54 | C53 | C52 | 121.6(5) |
| C7 | C2 | C1 | 123.0(4) | C53 | C58 | C57 | 120.0 |
| C2 | C3 | C4 | 122.9(4) | C56 | C57 | C58 | 120.0 |
| C3 | C4 | C8 | 120.9(4) | C55 | C56 | C57 | 120.0 |
| C5 | C4 | C3 | 116.7(4) | C54 | C55 | C56 | 120.0 |
| C5 | C4 | C8 | 122.4(4) | C55 | C54 | C53 | 120.0 |
| C4 | C5 | C6 | 122.8(4) | O2 | C59 | C60 | 111.3(3) |
| C5 | C6 | C12 | 117.4(4) | N3 | C60 | C59 | 113.3(4) |
| C7 | C6 | C5 | 118.7(4) | O8 | C60 | C59 | 123.0(3) |
| C7 | C6 | C12 | 123.8(4) | O8 | C60 | N3 | 123.7(4) |
| C6 | C7 | C2 | 120.5(4) | C62 | C61 | C65 | 113.7(4) |
| C6 | C7 | O1 | 119.3(3) | N3 | C61 | C62 | 112.9(4) |
| O1 | C7 | C2 | 120.0(4) | N3 | C61 | C65 | 107.2(4) |
| C4 | C8 | C9 | 108.5(4) | C61 | C62 | C63 | 109.6(4) |
| C4 | C8 | C10 | 110.2(4) | C64 | C63 | C62 | 109.9(4) |
| C4 | C8 | C11 | 112.6(4) | N4 | C64 | C63 | 110.6(4) |
| C9 | C8 | C10 | 108.7(4) | N4 | C65 | C61 | 115.8(4) |
| C11 | C8 | C9 | 107.9(5) | O9 | C65 | C61 | 122.3(4) |
| C11 | C8 | C10 | 108.8(4) | O9 | C65 | N4 | 121.8(4) |
| C13 | C12 | C6 | 108.6(3) | O10 | C66 | C67 | 113.3(4) |
| C14 | C13 | C12 | 121.3(3) | C68 | C67 | C66 | 119.3(4) |
| C18 | C13 | C12 | 119.8(3) | C68 | C67 | C72 | 120.0 |
| C18 | C13 | C14 | 118.6(3) | C72 | C67 | C66 | 120.7(4) |
| C15 | C14 | C13 | 122.1(4) | C67 | C68 | C69 | 120.0 |
| C14 | C15 | C16 | 117.1(3) | C68 | C69 | C70 | 120.0 |
| C14 | C15 | C19 | 122.8(4) | C71 | C70 | C69 | 120.0 |
| C16 | C15 | C19 | 120.1(4) | C72 | C71 | C70 | 120.0 |
| C17 | C16 | C15 | 122.6(4) | C71 | C72 | C67 | 120.0 |
| C16 | C17 | C18 | 118.1(3) | O3 | C73 | C74 | 113.8(3) |
| C16 | C17 | C23 | 119.8(3) | N5 | C74 | C73 | 115.8(4) |
| C18 | C17 | C23 | 121.8(3) | O11 | C74 | C73 | 119.4(4) |
| C13 | C18 | C17 | 121.3(3) | O11 | C74 | N5 | 124.8(4) |
| O2 | C18 | C13 | 116.7(3) | C76 | C75 | C79 | 113.2(4) |
| O2 | C18 | C17 | 121.6(3) | N5 | C75 | C76 | 110.4(4) |
| C20 | C19 | C15 | 109.9(4) | N5 | C75 | C79 | 109.8(3) |
| C21 | C19 | C15 | 109.0(4) | C77 | C76 | C75 | 111.3(4) |
| C21 | C19 | C20 | 109.6(5) | C78 | C77 | C76 | 110.2(4) |
| C22 | C19 | C15 | 111.8(4) | N6 | C78 | C77 | 110.2(4) |
| C22 | C19 | C20 | 107.1(5) | N6 | C79 | C75 | 114.5(4) |
| C22 | C19 | C21 | 109.3(4) | O12 | C79 | C75 | 121.3(4) |
| C17 | C23 | C24 | 108.8(3) | O12 | C79 | N6 | 123.8(4) |
| C25 | C24 | C23 | 118.7(3) | O13 | C80 | C81 | 112.2(4) |
| C25 | C24 | C29 | 118.5(3) | C86 | C81 | C80 | 119.8(3) |
| C29 | C24 | C23 | 122.8(3) | C86 | C81 | C82 | 120.0 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C26 | C25 | C24 | 122.6(4) | C82 | C81 | C80 | 120.1(3) |
| C25 | C26 | C27 | 116.9(4) | C81 | C86 | C85 | 120.0 |
| C25 | C26 | C30 | 119.5(4) | C84 | C85 | C86 | 120.0 |
| C27 | C26 | C30 | 123.5(4) | C83 | C84 | C85 | 120.0 |
| C26 | C27 | C28 | 122.9(4) | C84 | C83 | C82 | 120.0 |
| C27 | C28 | C29 | 117.9(4) | C83 | C82 | C81 | 120.0 |
| C27 | C28 | C34 | 118.8(3) | O4 | C87 | C88 | 112.1(3) |
| C29 | C28 | C34 | 123.3(3) | N7 | C88 | C87 | 113.0(4) |
| C24 | C29 | C28 | 120.4(3) | O14 | C88 | C87 | 123.3(4) |
| O3 | C29 | C24 | 120.1(3) | O14 | C88 | N7 | 123.6(4) |
| O3 | C29 | C28 | 119.4(3) | C93 | C89 | C90 | 113.3(4) |
| C31 | C30 | C26 | 112.2(4) | N7 | C89 | C90 | 113.1(4) |
| C31 | C30 | C32 | 110.1(5) | N7 | C89 | C93 | 107.0(4) |
| C31 | C30 | C33 | 108.2(4) | C89 | C90 | C91 | 108.0(4) |
| C32 | C30 | C26 | 108.5(4) | C92 | C91 | C90 | 109.6(4) |
| C32 | C30 | C33 | 107.6(4) | N8 | C92 | C91 | 110.8(4) |
| C33 | C30 | C26 | 110.2(4) | N8 | C93 | C89 | 116.9(4) |
| C35 | C34 | C28 | 113.6(3) | O15 | C93 | C89 | 121.2(5) |
| C36 | C35 | C34 | 122.2(3) | O15 | C93 | N8 | 121.9(6) |
| C40 | C35 | C34 | 120.2(3) | O16 | C94 | C95 | 113.8(5) |
| C40 | C35 | C36 | 117.6(3) | C96 | C95 | C94 | 117.9(5) |
| C37 | C36 | C35 | 122.7(4) | C96 | C95 | C100 | 120.0 |
| C36 | C37 | C38 | 117.1(4) | C100 | C95 | C94 | 122.1(5) |
| C36 | C37 | C41 | 123.5(4) | C97 | C96 | C95 | 120.0 |
| C38 | C37 | C41 | 119.4(4) | C96 | C97 | C98 | 120.0 |
| C37 | C38 | C39 | 122.6(4) | C99 | C98 | C97 | 120.0 |
| C38 | C39 | C1 | 120.7(4) | C98 | C99 | C100 | 120.0 |
| C38 | C39 | C40 | 117.8(4) | C99 | C100 | C95 | 120.0 |
| C40 | C39 | C1 | 121.4(3) | C46 | N1 | C47 | 122.7(3) |
| C39 | C40 | C35 | 121.4(3) | C51 | N2 | C50 | 125.9(5) |
| O4 | C40 | C35 | 118.0(3) | C51 | N2 | O7 | 114.6(5) |
| O4 | C40 | C39 | 120.3(3) | O7 | N2 | C50 | 111.9(5) |
| C37 | C41 | C43 | 108.7(3) | C60 | N3 | C61 | 123.0(4) |
| C37 | C41 | C44 | 112.1(4) | C65 | N4 | C64 | 128.4(4) |
| C42 | C41 | C37 | 110.4(4) | C65 | N4 | O10 | 116.9(4) |
| C42 | C41 | C43 | 109.8(4) | O10 | N4 | C64 | 112.1(4) |
| C42 | C41 | C44 | 107.9(4) | C74 | N5 | C75 | 124.0(4) |
| C43 | C41 | C44 | 107.8(4) | C79 | N6 | C78 | 127.4(4) |
| O1 | C45 | C46 | 114.3(4) | C79 | N6 | O13 | 116.4(4) |
| N1 | C46 | C45 | 117.4(4) | O13 | N6 | C78 | 112.2(4) |
| O5 | C46 | C45 | 117.5(4) | C88 | N7 | C89 | 123.9(4) |
| O5 | C46 | N1 | 125.1(4) | C93 | N8 | C92 | 127.6(4) |
| C48 | C47 | C51 | 113.8(4) | C93 | N8 | O16 | 117.6(5) |
| N1 | C47 | C48 | 110.9(4) | O16 | N8 | C92 | 110.8(5) |
| N1 | C47 | C51 | 110.2(4) | C7 | O1 | C45 | 115.1(3) |
| C47 | C48 | C49 | 109.6(4) | C18 | O2 | C59 | 117.9(3) |
| C48 | C49 | C50 | 108.5(5) | C29 | O3 | C73 | 113.8(3) |
| N2 | C50 | C49 | 108.8(5) | C40 | O4 | C87 | 115.3(3) |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| N2 | C51 | C47 | 114.0(5) | N2 | O7 | C52 | 109.2(5) |
| O6 | C51 | C47 | 122.4(4) | N4 | O10 | C66 | 110.4(4) |
| O6 | C51 | N2 | 123.4(5) | N6 | O13 | C80 | 110.1(4) |
| O7 | C52 | C53 | 108.8(7) | N8 | O16 | C94 | 110.7(5) |

**Table S5** Torsion angles for **1**$Bn_4$

| Atom | Atom | Atom | Atom | Angle (deg) | Atom | Atom | Atom | Atom | Angle (deg) |
|---|---|---|---|---|---|---|---|---|---|
| C1 | C2 | C3 | C4 | 173.3(4) | C51 | C47 | C48 | C49 | 49.8(6) |
| C1 | C2 | C7 | C6 | –171.2(3) | C51 | C47 | N1 | C46 | –99.2(5) |
| C1 | C2 | C7 | O1 | 4.6(5) | C51 | N2 | O7 | C52 | 97.9(6) |
| C1 | C39 | C40 | C35 | 165.2(4) | C52 | C53 | C58 | C57 | –177.1(7) |
| C1 | C39 | C40 | O4 | –8.8(6) | C52 | C53 | C54 | C55 | 177.0(7) |
| C2 | C1 | C39 | C38 | 106.0(4) | C53 | C52 | O7 | N2 | 74.6(6) |
| C2 | C1 | C39 | C40 | –68.8(5) | C53 | C58 | C57 | C56 | 0.0 |
| C2 | C3 | C4 | C5 | –0.3(6) | C58 | C53 | C54 | C55 | 0.0 |
| C2 | C3 | C4 | C8 | –178.8(4) | C58 | C57 | C56 | C55 | 0.0 |
| C2 | C7 | O1 | C45 | 63.9(5) | C57 | C56 | C55 | C54 | 0.0 |
| C3 | C2 | C7 | C6 | 5.1(5) | C56 | C55 | C54 | C53 | 0.0 |
| C3 | C2 | C7 | O1 | –179.1(3) | C54 | C53 | C58 | C57 | 0.0 |
| C3 | C4 | C5 | C6 | 2.0(6) | C59 | C60 | N3 | C61 | –176.5(4) |
| C3 | C4 | C8 | C9 | –69.7(5) | C60 | C59 | O2 | C18 | –106.2(4) |
| C3 | C4 | C8 | C10 | 49.2(6) | C61 | C62 | C63 | C64 | –62.6(6) |
| C3 | C4 | C8 | C11 | 170.9(4) | C61 | C65 | N4 | C64 | 13.0(7) |
| C4 | C5 | C6 | C7 | –0.1(6) | C61 | C65 | N4 | O10 | 172.7(4) |
| C4 | C5 | C6 | C12 | –176.3(4) | C62 | C61 | C65 | N4 | –24.2(6) |
| C5 | C4 | C8 | C9 | 111.8(5) | C62 | C61 | C65 | O9 | 159.2(5) |
| C5 | C4 | C8 | C10 | –129.2(5) | C62 | C61 | N3 | C60 | 88.2(5) |
| C5 | C4 | C8 | C11 | –7.5(6) | C62 | C63 | C64 | N4 | 49.0(6) |
| C5 | C6 | C7 | C2 | –3.6(5) | C63 | C64 | N4 | C65 | –26.1(8) |
| C5 | C6 | C7 | O1 | –179.4(3) | C63 | C64 | N4 | O10 | 173.5(4) |
| C5 | C6 | C12 | C13 | 59.2(4) | C64 | N4 | O10 | C66 | –117.9(5) |
| C6 | C7 | O1 | C45 | –120.3(4) | C65 | C61 | C62 | C63 | 49.1(6) |
| C6 | C12 | C13 | C14 | –101.2(4) | C65 | C61 | N3 | C60 | –145.8(4) |
| C6 | C12 | C13 | C18 | 72.4(4) | C65 | N4 | O10 | C66 | 79.3(5) |
| C7 | C2 | C3 | C4 | –3.2(6) | C66 | C67 | C68 | C69 | –179.5(4) |
| C7 | C6 | C12 | C13 | –116.7(4) | C66 | C67 | C72 | C71 | 179.5(4) |
| C8 | C4 | C5 | C6 | –179.5(4) | C67 | C66 | O10 | N4 | 60.1(5) |
| C12 | C6 | C7 | C2 | 172.3(3) | C67 | C68 | C69 | C70 | 0.0 |
| C12 | C6 | C7 | O1 | –3.5(5) | C68 | C67 | C72 | C71 | 0.0 |
| C12 | C13 | C14 | C15 | 174.7(3) | C68 | C69 | C70 | C71 | 0.0 |
| C12 | C13 | C18 | C17 | –172.1(3) | C69 | C70 | C71 | C72 | 0.0 |
| C12 | C13 | C18 | O2 | 0.7(5) | C70 | C71 | C72 | C67 | 0.0 |
| C13 | C14 | C15 | C16 | –0.8(6) | C72 | C67 | C68 | C69 | 0.0 |
| C13 | C14 | C15 | C19 | –179.9(4) | C73 | C74 | N5 | C75 | –178.8(4) |
| C13 | C18 | O2 | C59 | 122.0(3) | C74 | C73 | O3 | C29 | 104.4(4) |
| C14 | C13 | C18 | C17 | 1.7(5) | C75 | C76 | C77 | C78 | –59.6(6) |
| C14 | C13 | C18 | O2 | 174.5(3) | C75 | C79 | N6 | C78 | 25.6(6) |
| C14 | C15 | C16 | C17 | –2.1(6) | C75 | C79 | N6 | O13 | –179.0(3) |
| C14 | C15 | C19 | C20 | 128.8(5) | C76 | C75 | C79 | N6 | –29.8(5) |
| C14 | C15 | C19 | C21 | –111.0(5) | C76 | C75 | C79 | O12 | 156.8(4) |
| C14 | C15 | C19 | C22 | 10.0(6) | C76 | C75 | N5 | C74 | 134.5(4) |
| C15 | C16 | C17 | C18 | 4.8(6) | C76 | C77 | C78 | N6 | 50.5(5) |
| C15 | C16 | C17 | C23 | –168.2(3) | C77 | C78 | N6 | C79 | –36.5(6) |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| C16 | C15 | C19 | C20 | –50.3(6) | C77 | C78 | N6 | O13 | 167.2(4) |
| C16 | C15 | C19 | C21 | 69.9(5) | C78 | N6 | O13 | C80 | –122.3(4) |
| C16 | C15 | C19 | C22 | –169.1(4) | C79 | C75 | C76 | C77 | 48.1(5) |
| C16 | C17 | C18 | C13 | –4.5(5) | C79 | C75 | N5 | C74 | –99.9(5) |
| C16 | C17 | C18 | O2 | –176.9(3) | C79 | N6 | O13 | C80 | 78.7(5) |
| C16 | C17 | C23 | C24 | 94.7(4) | C80 | C81 | C86 | C85 | –176.6(3) |
| C17 | C18 | O2 | C59 | –65.3(4) | C80 | C81 | C82 | C83 | 176.5(3) |
| C17 | C23 | C24 | C25 | –59.8(4) | C81 | C80 | O13 | N6 | 47.3(5) |
| C17 | C23 | C24 | C29 | 118.4(4) | C81 | C86 | C85 | C84 | 0.0 |
| C18 | C13 | C14 | C15 | 1.0(6) | C86 | C81 | C82 | C83 | 0.0 |
| C18 | C17 | C23 | C24 | –78.0(4) | C86 | C85 | C84 | C83 | 0.0 |
| C19 | C15 | C16 | C17 | 177.0(4) | C85 | C84 | C83 | C82 | 0.0 |
| C23 | C17 | C18 | C13 | 168.3(3) | C84 | C83 | C82 | C81 | 0.0 |
| C23 | C17 | C18 | O2 | –4.1(5) | C82 | C81 | C86 | C85 | 0.0 |
| C23 | C24 | C25 | C26 | 173.7(3) | C87 | C88 | N7 | C89 | 176.6(5) |
| C23 | C24 | C29 | C28 | –168.8(3) | C88 | C87 | O4 | C40 | –99.7(4) |
| C23 | C24 | C29 | O3 | 8.3(5) | C89 | C90 | C91 | C92 | –63.6(6) |
| C24 | C25 | C26 | C27 | –2.5(6) | C89 | C93 | N8 | C92 | 13.7(8) |
| C24 | C25 | C26 | C30 | 175.0(4) | C89 | C93 | N8 | O16 | 168.8(4) |
| C24 | C29 | O3 | C73 | 60.9(4) | C90 | C89 | C93 | N8 | –26.0(6) |
| C25 | C24 | C29 | C28 | 9.4(5) | C90 | C89 | C93 | O15 | 156.7(5) |
| C25 | C24 | C29 | O3 | –173.5(3) | C90 | C89 | N7 | C88 | 106.6(6) |
| C25 | C26 | C27 | C28 | 4.9(6) | C90 | C91 | C92 | N8 | 49.9(6) |
| C25 | C26 | C30 | C31 | 173.4(5) | C91 | C92 | N8 | C93 | –26.1(7) |
| C25 | C26 | C30 | C32 | –64.7(6) | C91 | C92 | N8 | O16 | 177.4(4) |
| C25 | C26 | C30 | C33 | 52.8(5) | C92 | N8 | O16 | C94 | –122.3(6) |
| C26 | C27 | C28 | C29 | –0.2(6) | C93 | C89 | C90 | C91 | 50.7(5) |
| C26 | C27 | C28 | C34 | 179.6(4) | C93 | C89 | N7 | C88 | –127.9(5) |
| C27 | C26 | C30 | C31 | –9.3(6) | C93 | N8 | O16 | C94 | 78.6(6) |
| C27 | C26 | C30 | C32 | 112.6(5) | C94 | C95 | C96 | C97 | 178.6(5) |
| C27 | C26 | C30 | C33 | –129.9(4) | C94 | C95 | C100 | C99 | –178.6(5) |
| C27 | C28 | C29 | C24 | –7.1(5) | C95 | C94 | O16 | N8 | 59.8(8) |
| C27 | C28 | C29 | O3 | 175.8(3) | C95 | C96 | C97 | C98 | 0.0 |
| C27 | C28 | C34 | C35 | 68.4(5) | C96 | C95 | C100 | C99 | 0.0 |
| C28 | C29 | O3 | C73 | –122.0(4) | C96 | C97 | C98 | C99 | 0.0 |
| C28 | C34 | C35 | C36 | –112.9(4) | C97 | C98 | C99 | C100 | 0.0 |
| C28 | C34 | C35 | C40 | 68.9(5) | C98 | C99 | C100 | C95 | 0.0 |
| C29 | C24 | C25 | C26 | –4.6(6) | C100 | C95 | C96 | C97 | 0.0 |
| C29 | C28 | C34 | C35 | –111.8(4) | N1 | C47 | C48 | C49 | 174.8(4) |
| C30 | C26 | C27 | C28 | –172.4(4) | N1 | C47 | C51 | N2 | –156.2(4) |
| C34 | C28 | C29 | C24 | 173.1(3) | N1 | C47 | C51 | O6 | 29.6(6) |
| C34 | C28 | C29 | O3 | –4.0(5) | N3 | C61 | C62 | C63 | 171.6(4) |
| C34 | C35 | C36 | C37 | –179.9(4) | N3 | C61 | C65 | N4 | –149.7(4) |
| C34 | C35 | C40 | C39 | –172.6(4) | N3 | C61 | C65 | O9 | 33.6(6) |
| C34 | C35 | C40 | O4 | 1.5(5) | N5 | C75 | C76 | C77 | 171.6(4) |
| C35 | C36 | C37 | C38 | –4.7(6) | N5 | C75 | C79 | N6 | –153.7(4) |
| C35 | C36 | C37 | C41 | 174.5(4) | N5 | C75 | C79 | O12 | 32.9(6) |
| C35 | C40 | O4 | C87 | 119.4(4) | N7 | C89 | C90 | C91 | 172.7(4) |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| C36 | C35 | C40 | C39 | 9.1(5) | N7 | C89 | C93 | N8 | –151.3(4) |
| C36 | C35 | C40 | O4 | –176.8(3) | N7 | C89 | C93 | O15 | 31.4(7) |
| C36 | C37 | C38 | C39 | 4.0(6) | O1 | C45 | C46 | N1 | 21.0(6) |
| C36 | C37 | C41 | C42 | 117.9(5) | O1 | C45 | C46 | O5 | –159.7(4) |
| C36 | C37 | C41 | C43 | –121.5(5) | O2 | C59 | C60 | N3 | –142.5(3) |
| C36 | C37 | C41 | C44 | –2.5(6) | O2 | C59 | C60 | O8 | 39.2(5) |
| C37 | C38 | C39 | C1 | –172.0(4) | O3 | C73 | C74 | N5 | 20.1(6) |
| C37 | C38 | C39 | C40 | 3.0(6) | O3 | C73 | C74 | O11 | –159.9(4) |
| C38 | C37 | C41 | C42 | –62.9(5) | O4 | C87 | C88 | N7 | –145.3(4) |
| C38 | C37 | C41 | C43 | 57.7(5) | O4 | C87 | C88 | O14 | 37.2(6) |
| C38 | C37 | C41 | C44 | 176.7(4) | O5 | C46 | N1 | C47 | 1.2(8) |
| C38 | C39 | C40 | C35 | –9.7(6) | O6 | C51 | N2 | C50 | –157.4(6) |
| C38 | C39 | C40 | O4 | 176.2(3) | O6 | C51 | N2 | O7 | –10.3(8) |
| C39 | C1 | C2 | C3 | –54.0(5) | O7 | C52 | C53 | C58 | 86.5(6) |
| C39 | C1 | C2 | C7 | 122.3(4) | O7 | C52 | C53 | C54 | –90.6(7) |
| C39 | C40 | O4 | C87 | –66.4(5) | O8 | C60 | N3 | C61 | 1.8(6) |
| C40 | C35 | C36 | C37 | –1.6(6) | O9 | C65 | N4 | C64 | –170.3(5) |
| C41 | C37 | C38 | C39 | –175.2(4) | O9 | C65 | N4 | O10 | –10.7(7) |
| C45 | C46 | N1 | C47 | –179.6(4) | O10 | C66 | C67 | C68 | –92.1(5) |
| C46 | C45 | O1 | C7 | 107.7(4) | O10 | C66 | C67 | C72 | 88.4(4) |
| C47 | C48 | C49 | C50 | –63.2(6) | O11 | C74 | N5 | C75 | 1.2(7) |
| C47 | C51 | N2 | C50 | 28.6(8) | O12 | C79 | N6 | C78 | –161.2(5) |
| C47 | C51 | N2 | O7 | 175.6(4) | O12 | C79 | N6 | O13 | –5.8(6) |
| C48 | C47 | C51 | N2 | –30.9(6) | O13 | C80 | C81 | C86 | 63.4(4) |
| C48 | C47 | C51 | O6 | 154.9(5) | O13 | C80 | C81 | C82 | –113.2(4) |
| C48 | C47 | N1 | C46 | 133.8(5) | O14 | C88 | N7 | C89 | –5.8(8) |
| C48 | C49 | C50 | N2 | 56.4(6) | O15 | C93 | N8 | C92 | –169.0(5) |
| C49 | C50 | N2 | C51 | –42.0(8) | O15 | C93 | N8 | O16 | –13.9(8) |
| C49 | C50 | N2 | O7 | 170.2(4) | O16 | C94 | C95 | C96 | –98.2(7) |
| C50 | N2 | O7 | C52 | –110.4(6) | O16 | C94 | C95 | C100 | 80.4(6) |

**Table S6** Spherical polar coordinates obtained by ring-puckering analysis of the four 1,2-PIPOBn pendants of **1**$Bn_4$

| Ring | $Q$ | $\phi$ (deg) | $\theta$ (deg) |
|---|---|---|---|
| A | 0.5067 | –91.47 | 139.79 |
| B | 0.4703 | –84.26 | 150.41 |
| C | 0.4898 | –89.21 | 139.78 |
| D | 0.5115 | –77.04 | 150.68 |

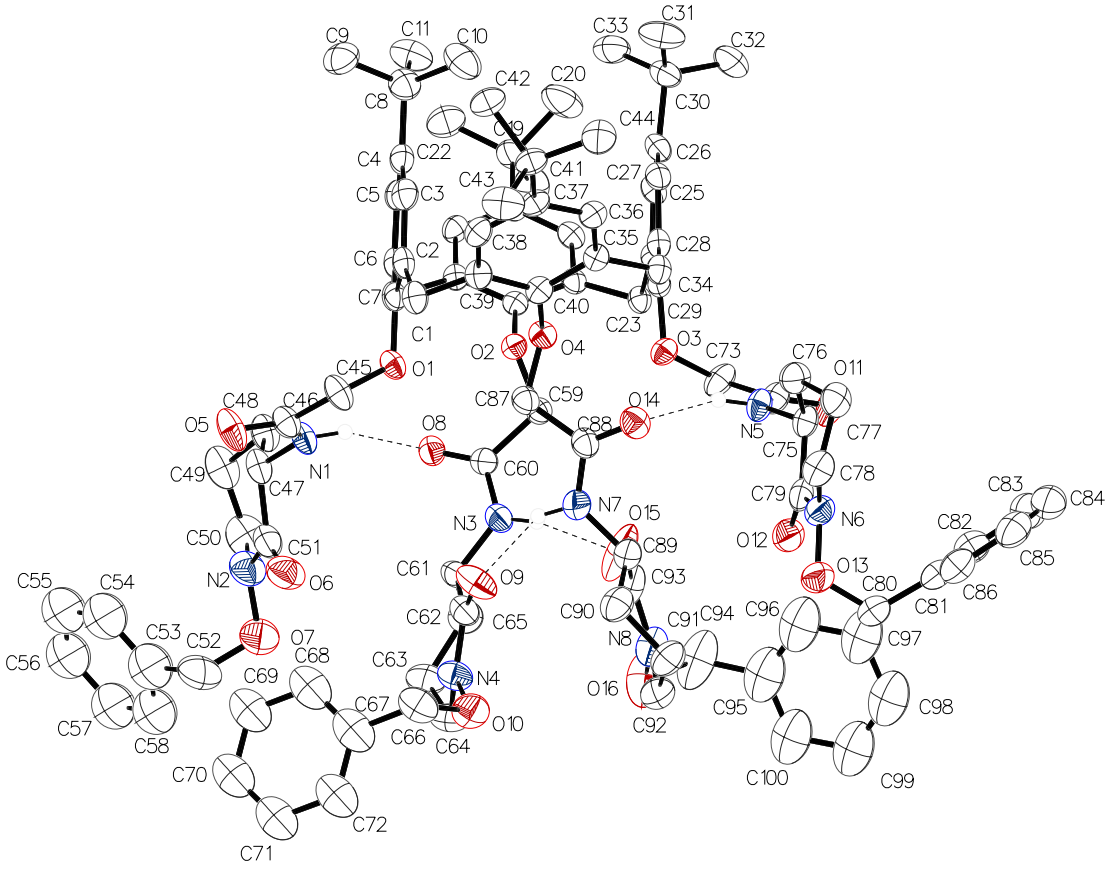


**Figure S1** ORTEP view of **1**$Bn_4$ viewed along the direction of rings A and C. All C–H hydrogen atoms have been omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen bonds are represented by dashed lines.

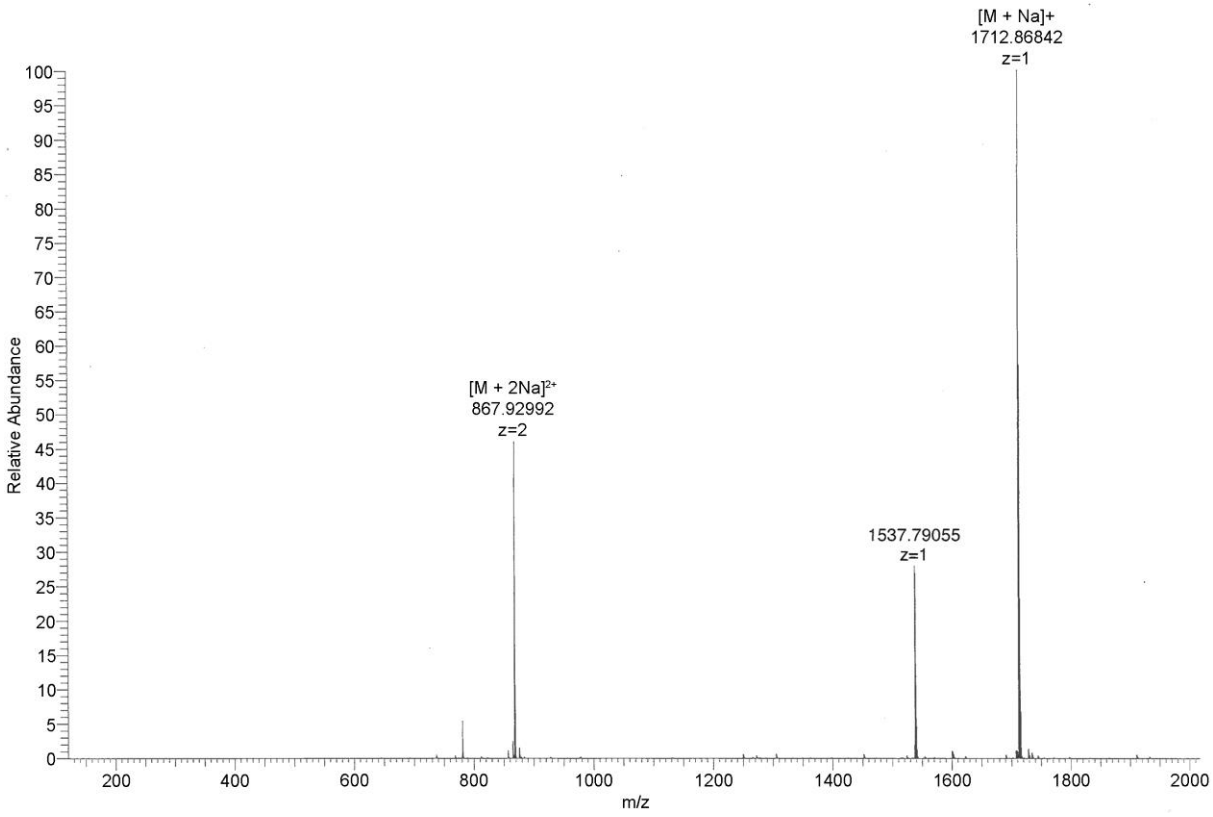


**Figure S2** ESI mass spectrum of **1**$Bn_4$.

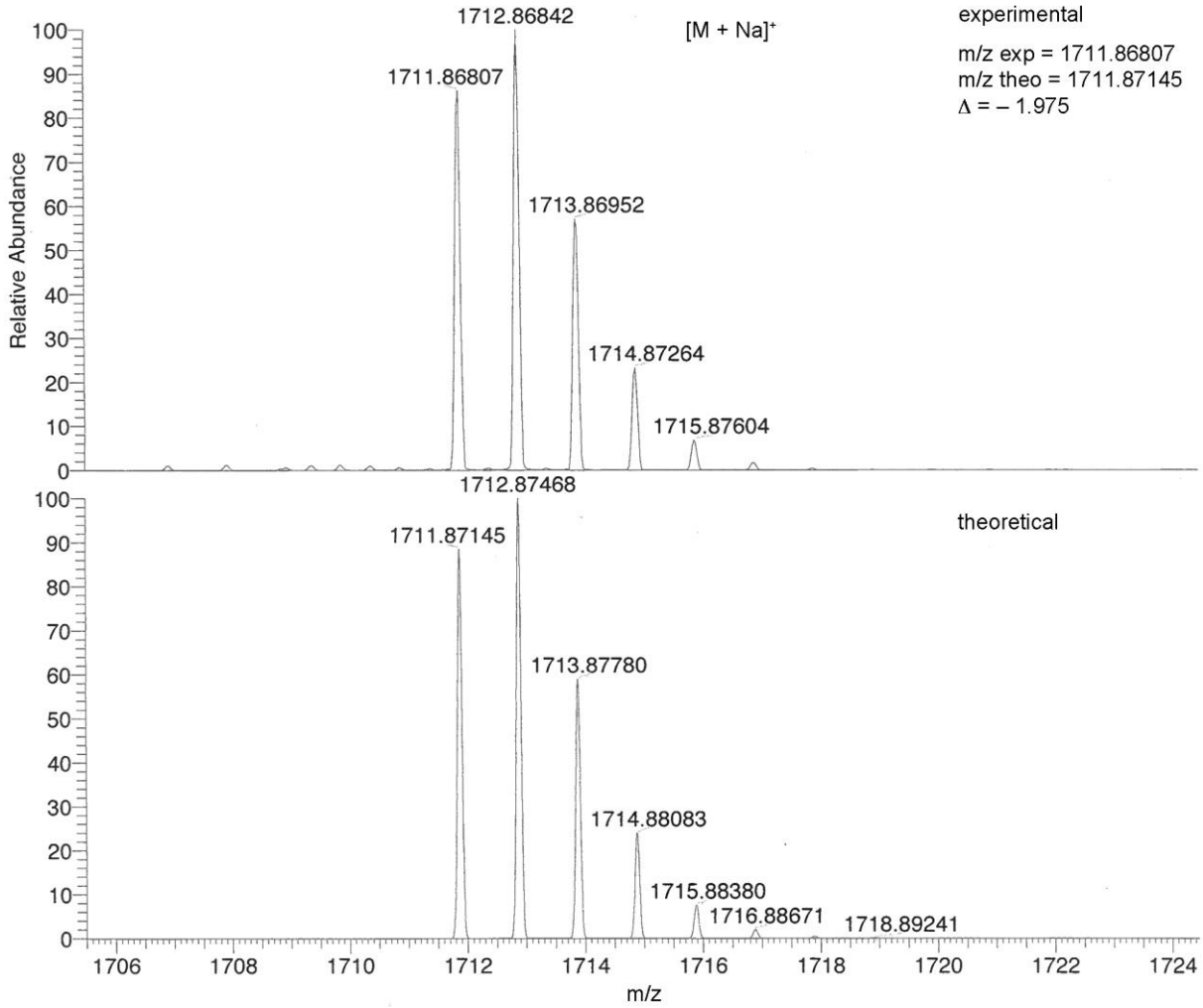


**Figure S3** ESI mass spectrum of **1**$Bn_4$ (detail).

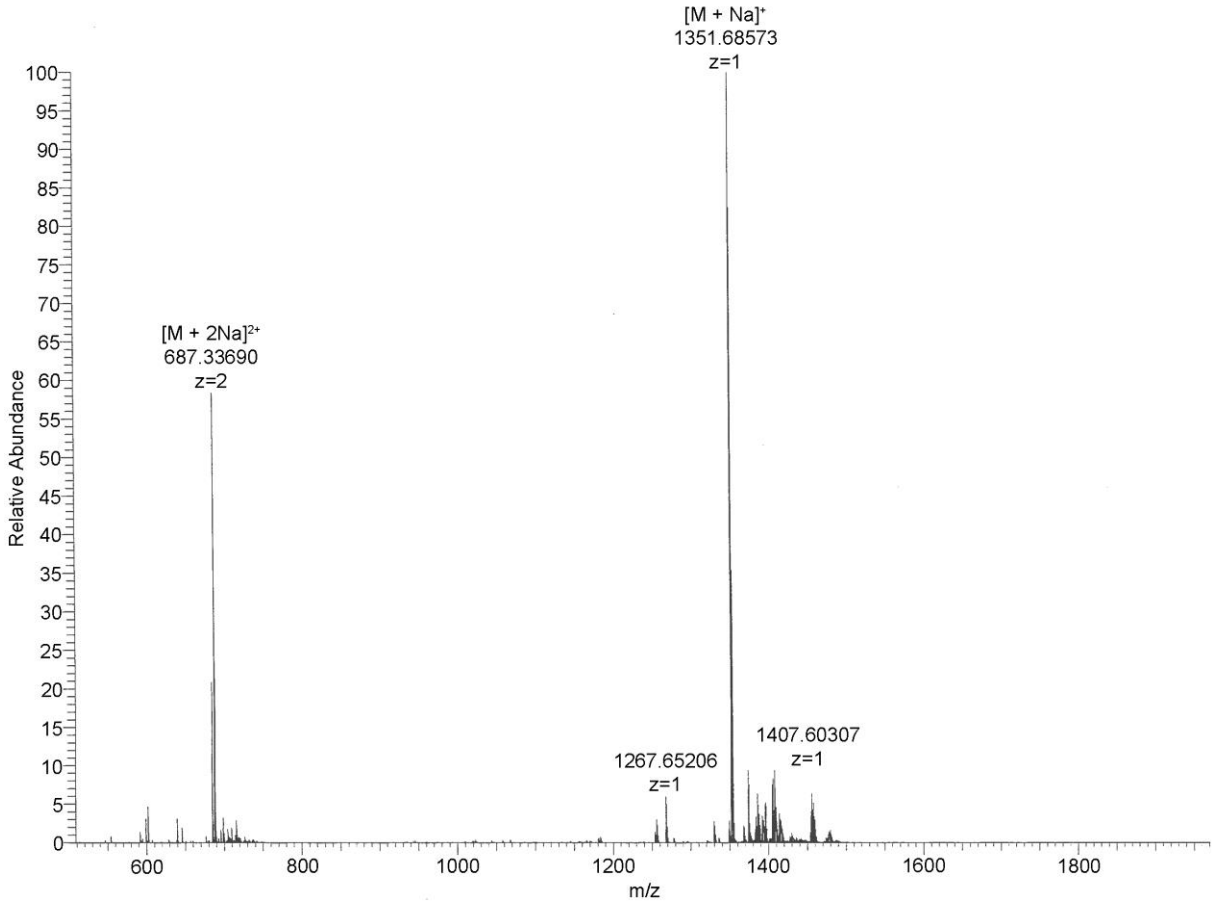


**Figure S4** ESI mass spectrum of **1**$H_4$.

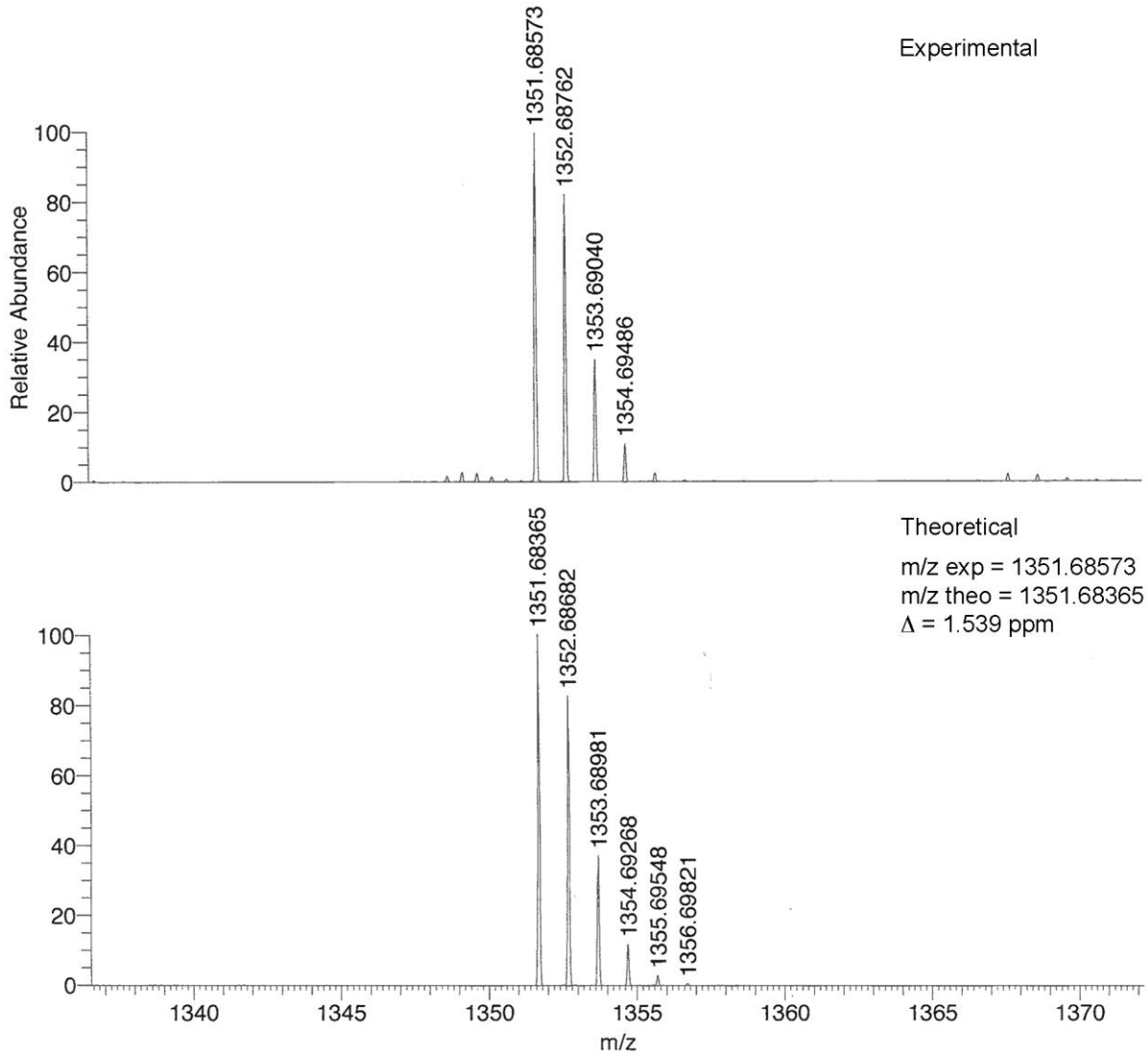


**Figure S5** ESI mass spectrum of **1**$H_4$ (detail).

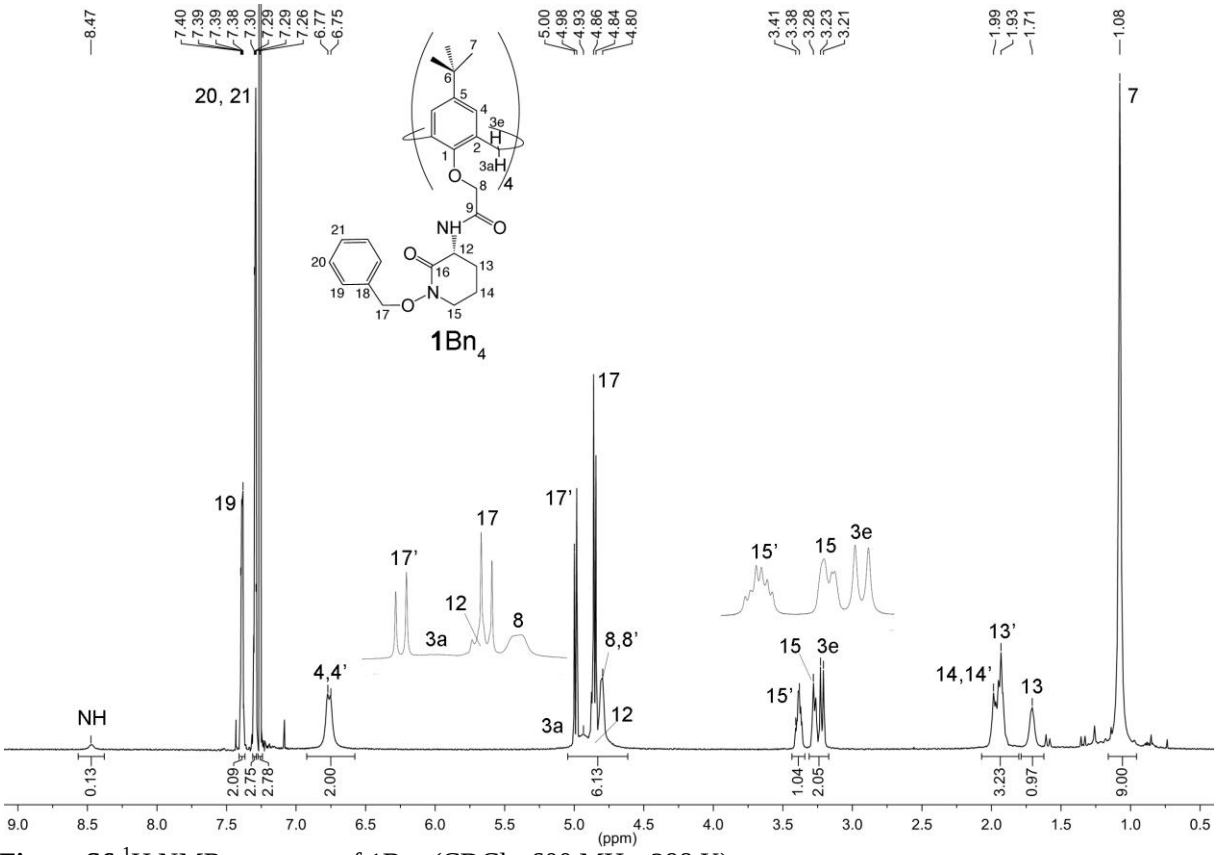


**Figure S6** $^{1}$H NMR spectrum of 1Bn$_4$ ($CDCl_3$, 600 MHz, 298 K).

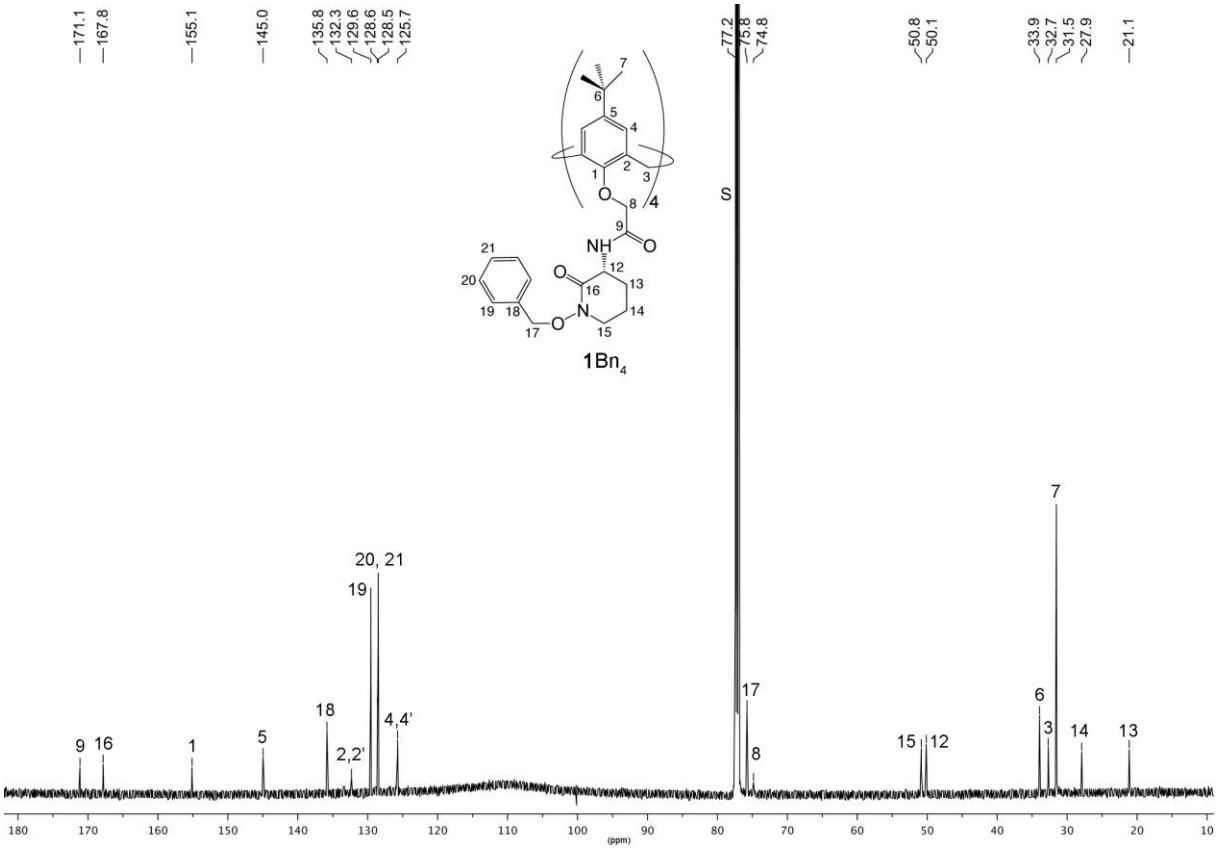


**Figure S7** $^{13}$C NMR spectrum of **1**Bn$_4$ ($CDCl_3$, 150 MHz, 298 K).

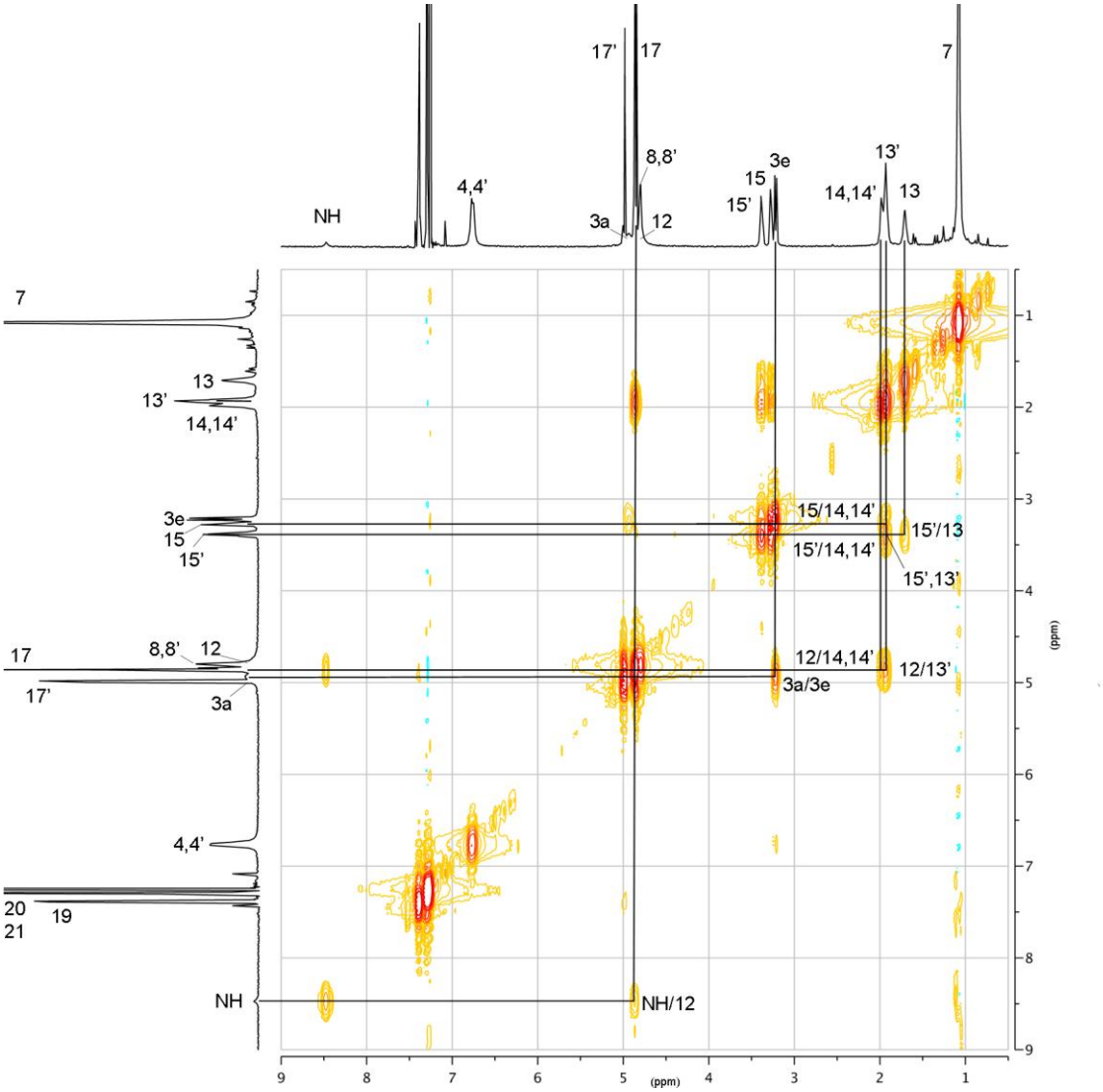


**Figure S8** $^{1}$H-$^{1}$H COSY NMR spectrum of **1**Bn$_4$ ($CDCl_3$, 600 MHz, 298 K).

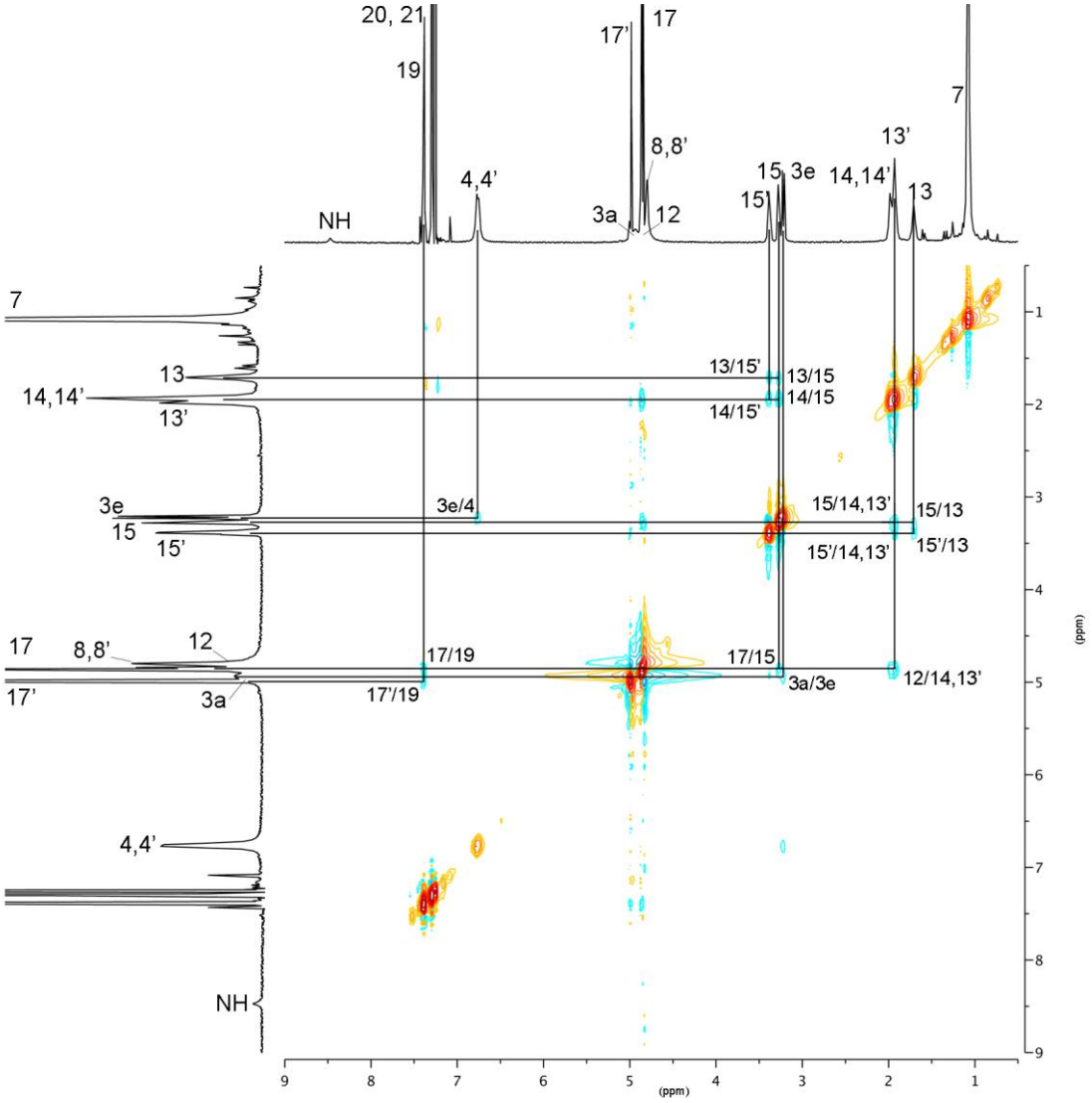


**Figure S9** $^{1}$H-$^{1}$H ROESY NMR spectrum of **1**Bn$_4$ ($CDCl_3$, 600 MHz, 298 K).

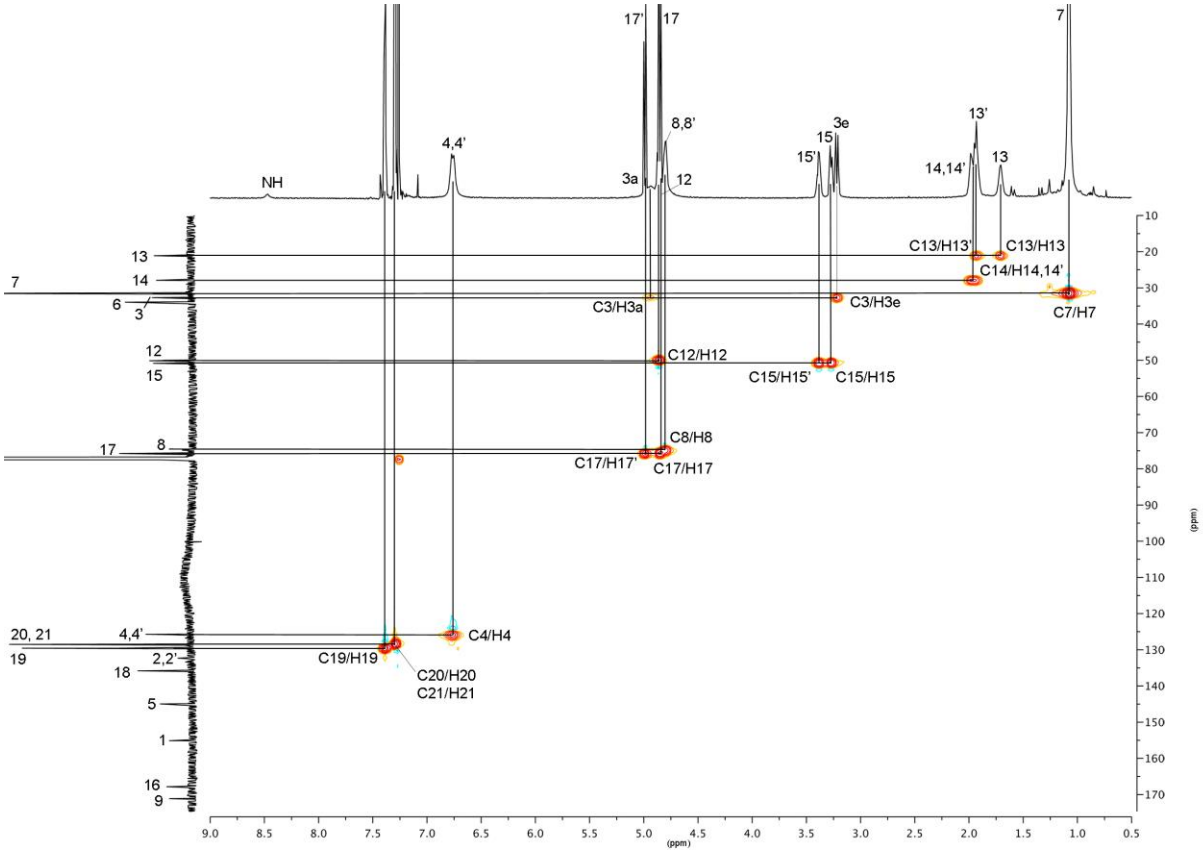


**Figure S10** $^{13}C$-$^{1}H$ HSQC NMR spectrum of **1**$Bn_4$ ($CDCl_3$, 600 MHz, 298 K).

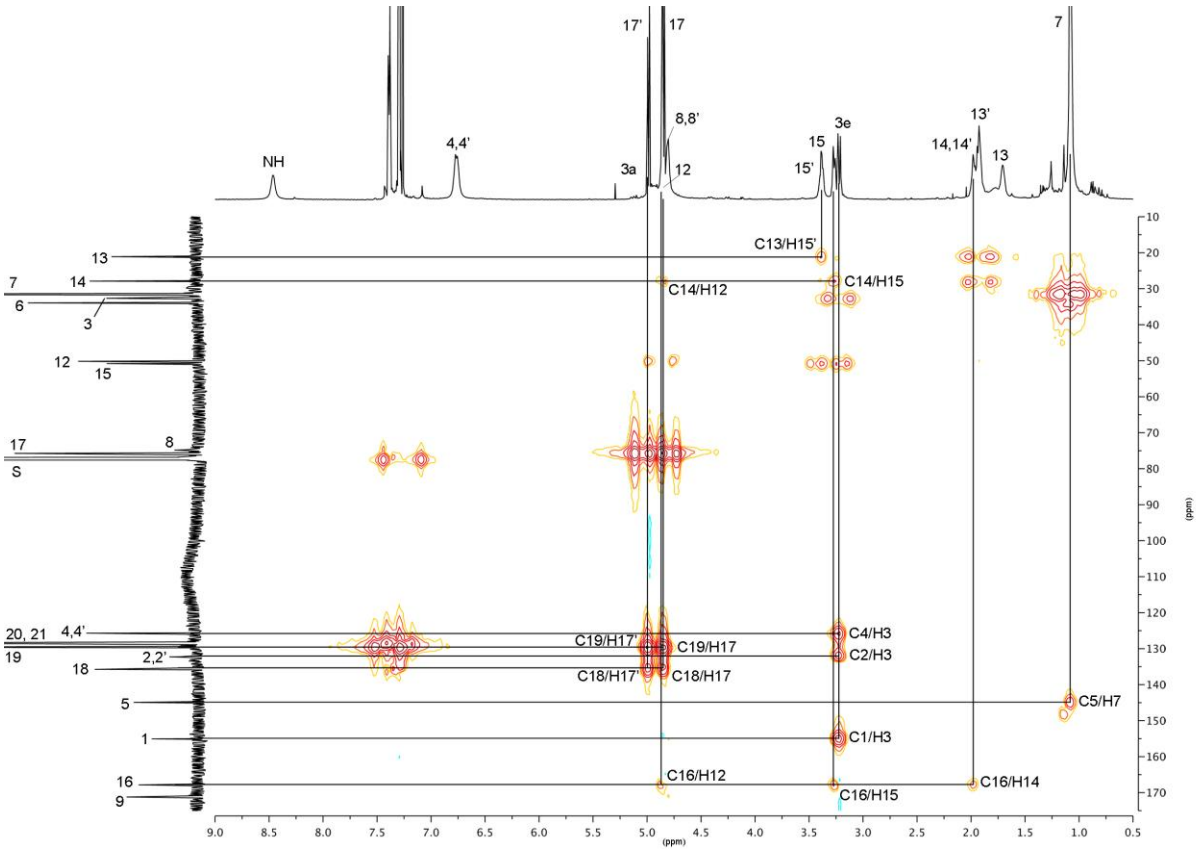


**Figure S11** $^{13}C$-$^{1}H$ HMBC NMR spectrum of **1**$Bn_4$ ($CDCl_3$, 600 MHz, 298 K).

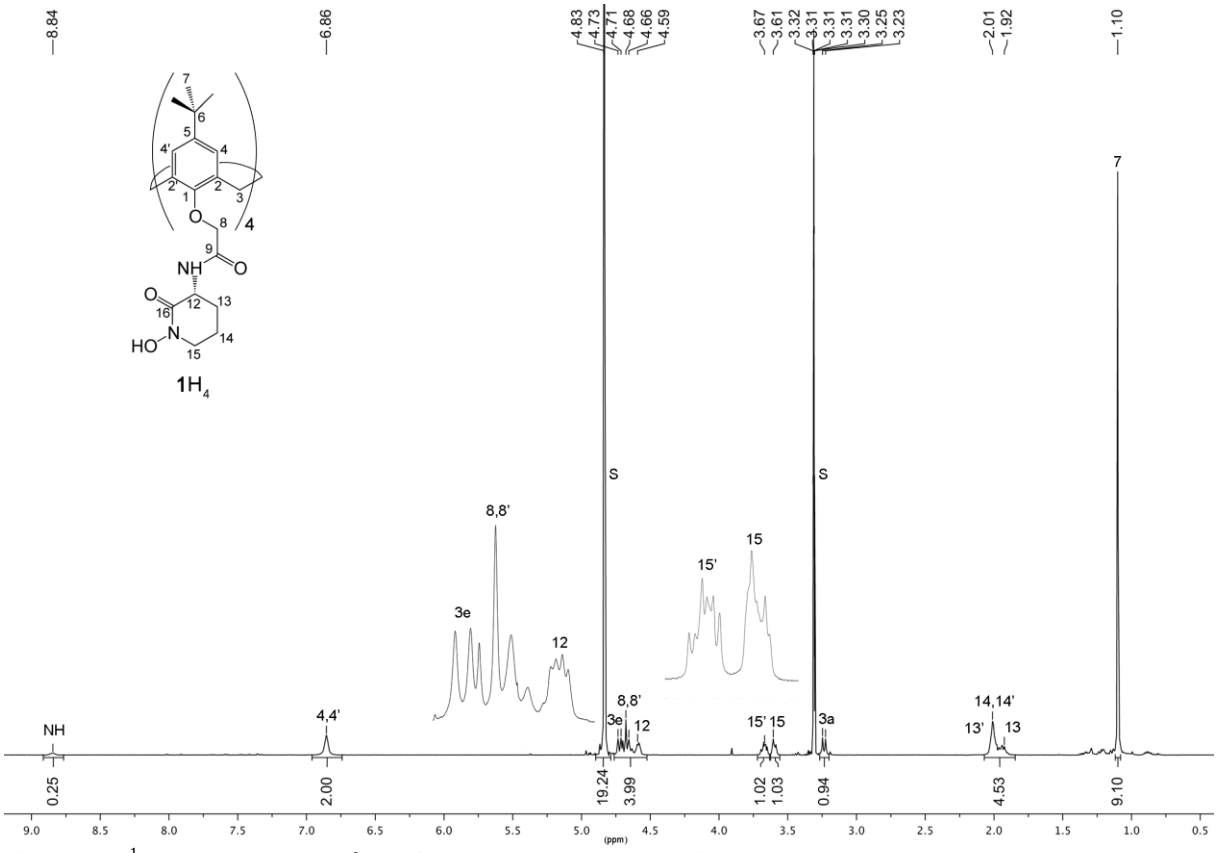


**Figure S12** $^{1}$H NMR spectrum of **1**H$_4$ (CD$_3$OD, 600 MHz, 300 K).

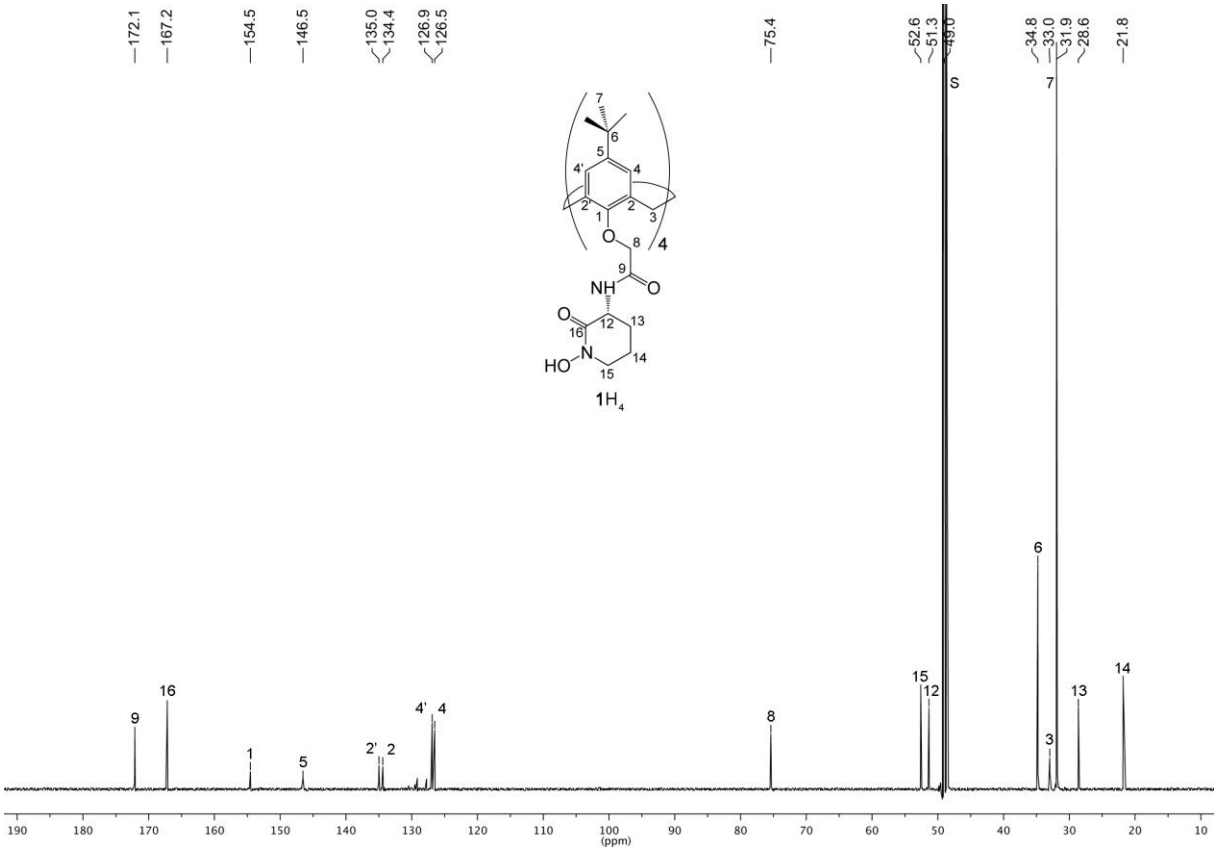


**Figure S13** $^{13}$C NMR spectrum of **1**H$_4$ (CD$_3$OD, 150 MHz, 300 K).

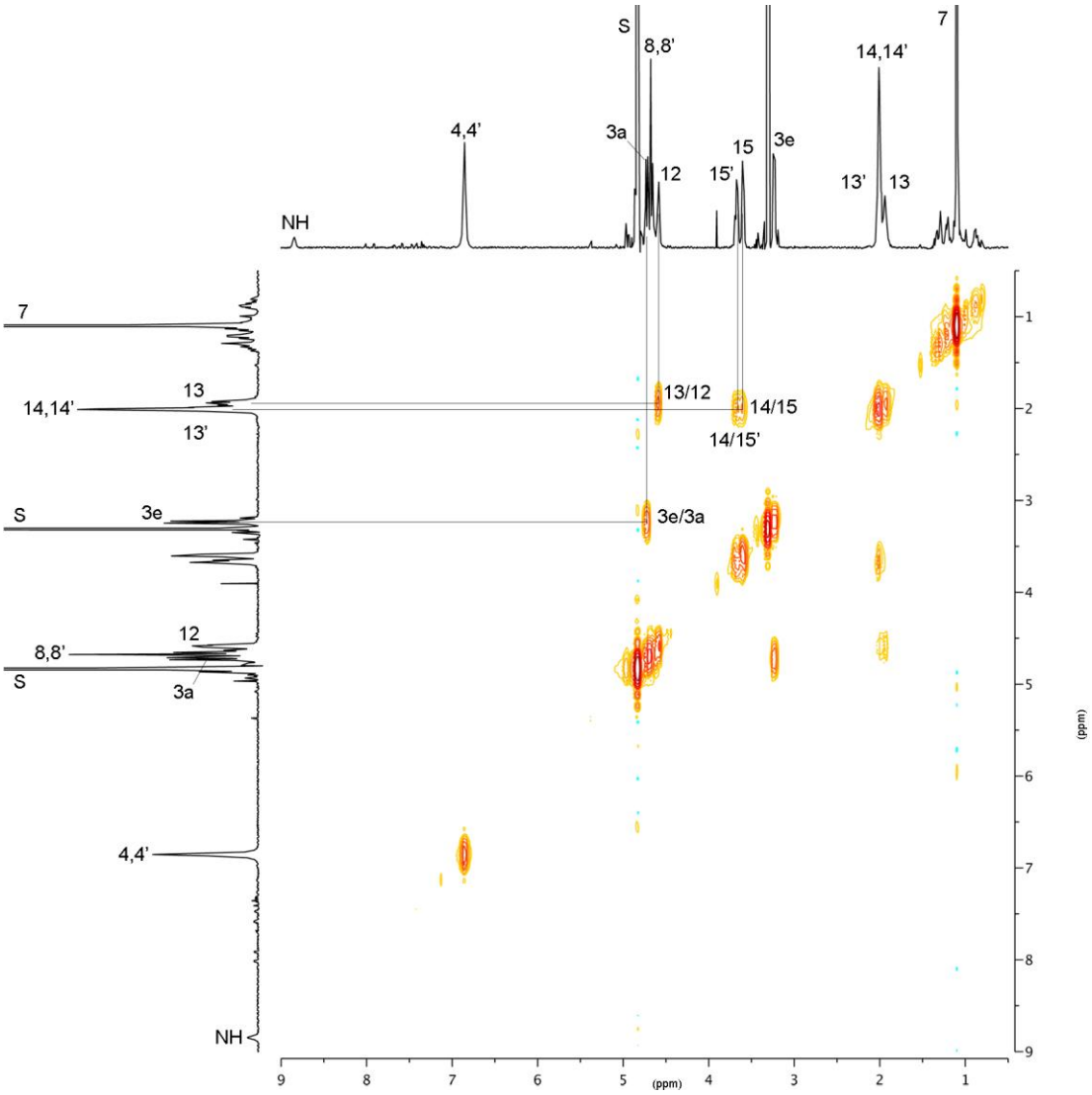


**Figure S14** $^{1}$H-$^{1}$H COSY NMR spectrum of **1**$H_4$ ($CD_3OD$, 600 MHz, 300 K).

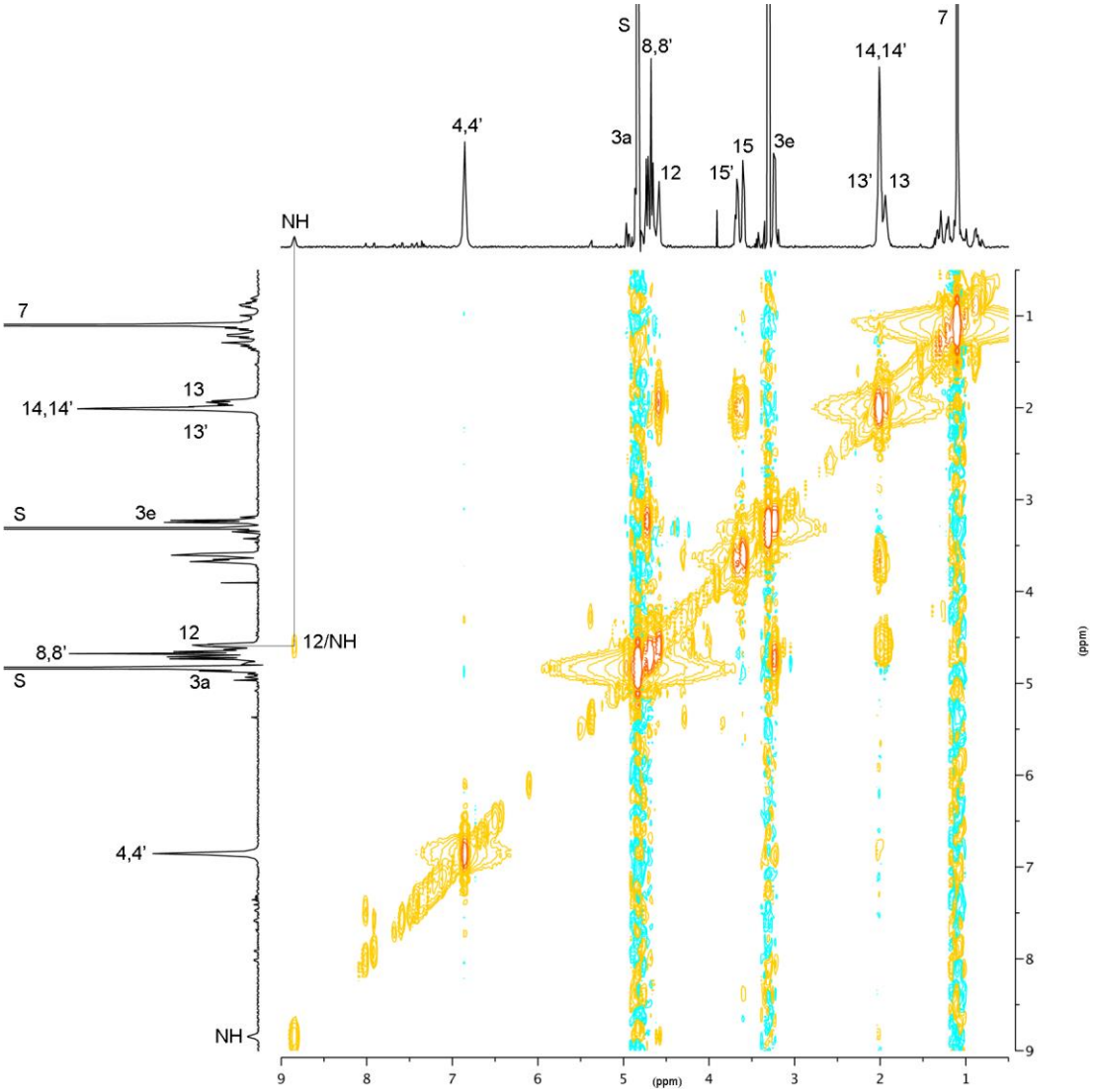


**Figure S15** $^{1}$H-$^{1}$H COSY NMR spectrum of **1**$H_4$ ($CD_3OD$, 600 MHz, 300 K).

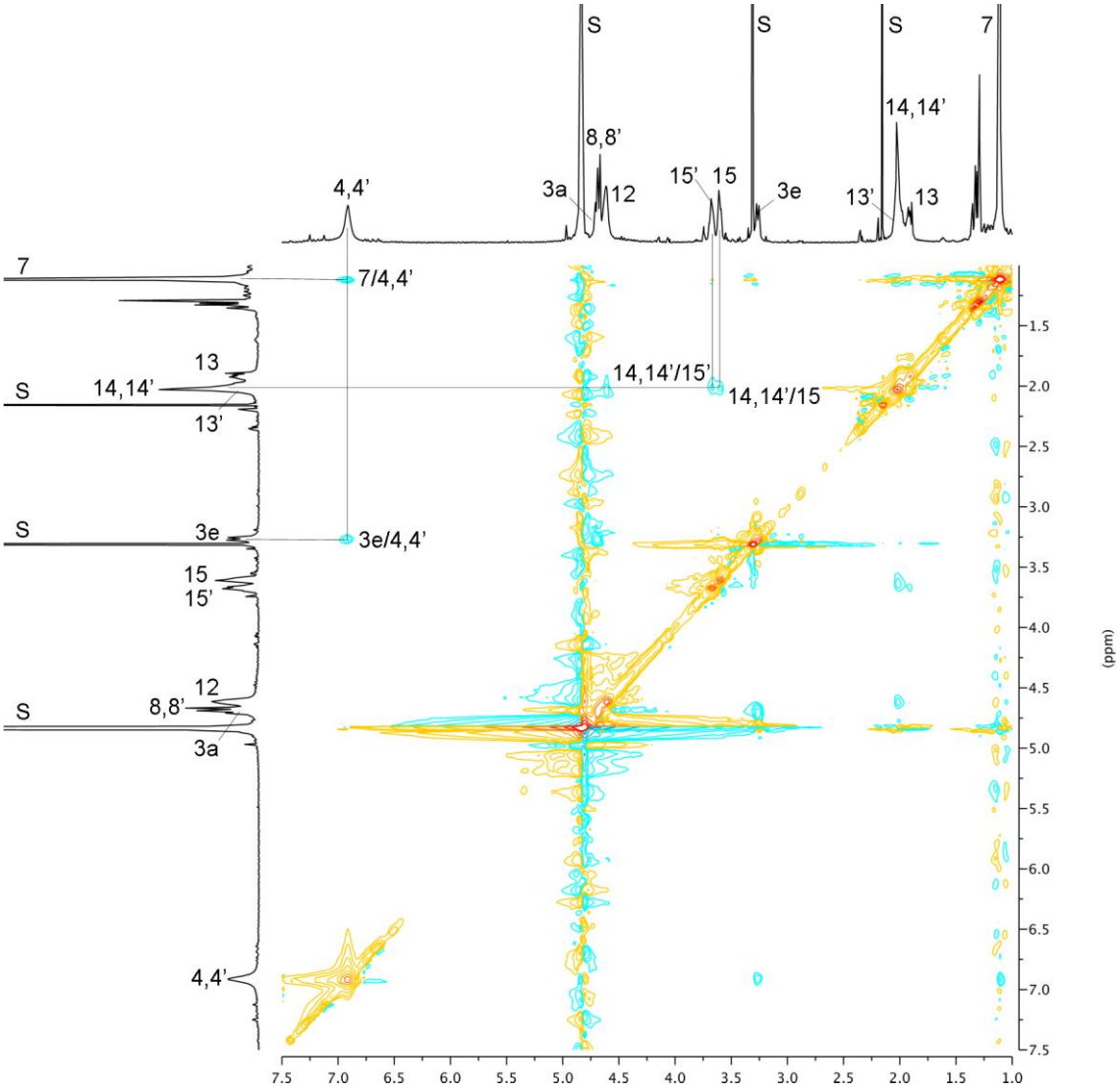


**Figure S16** $^{1}$H-$^{1}$H ROESY NMR spectrum of **1**$H_4$ ($CD_3OD$, 600 MHz, 300 K).

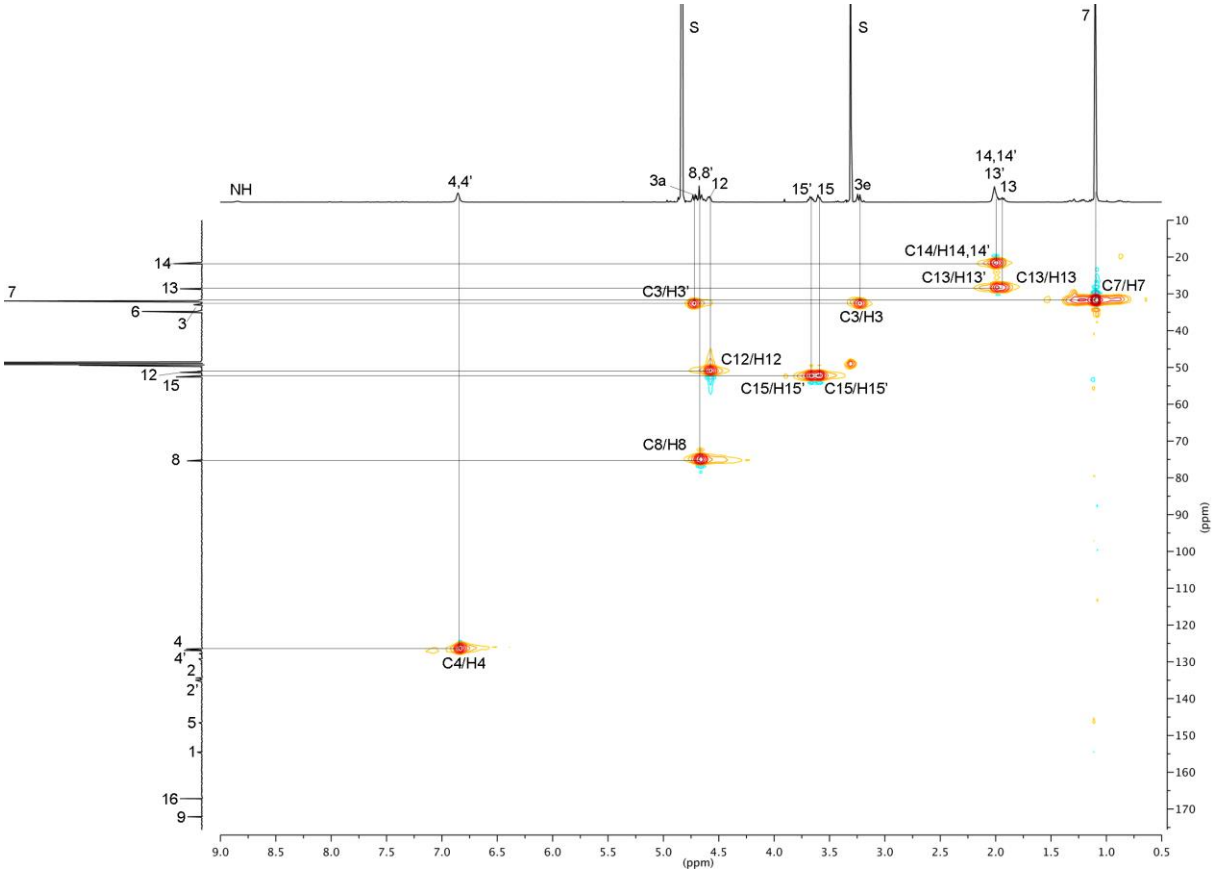


**Figure S17** $^{13}C$-$^{1}H$ HSQC NMR spectrum of **1**$H_4$ ($CD_3OD$, 600 MHz, 300 K).

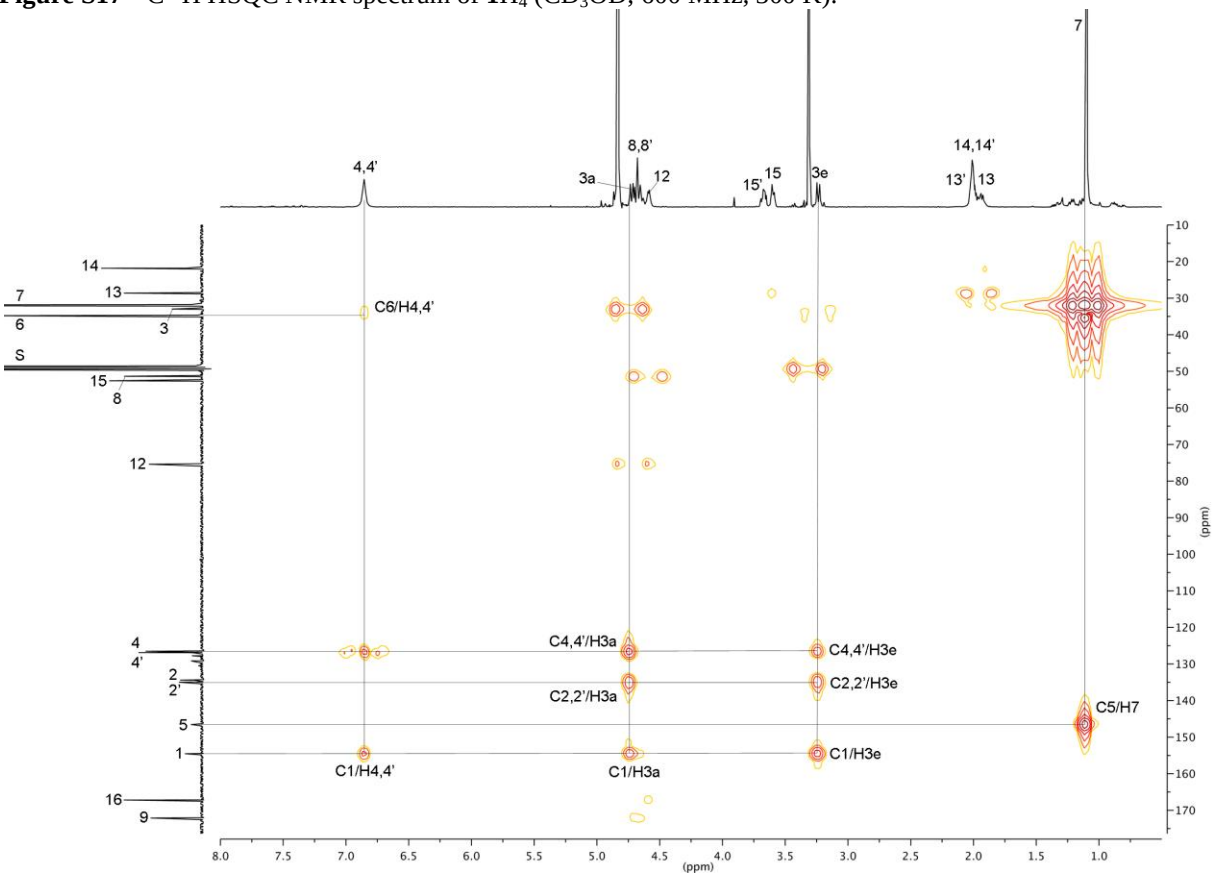


**Figure S18** $^{13}C$-$^{1}H$ HMBC NMR spectrum of 1$H_4$ ($CD_3OD$, 600 MHz, 300 K).

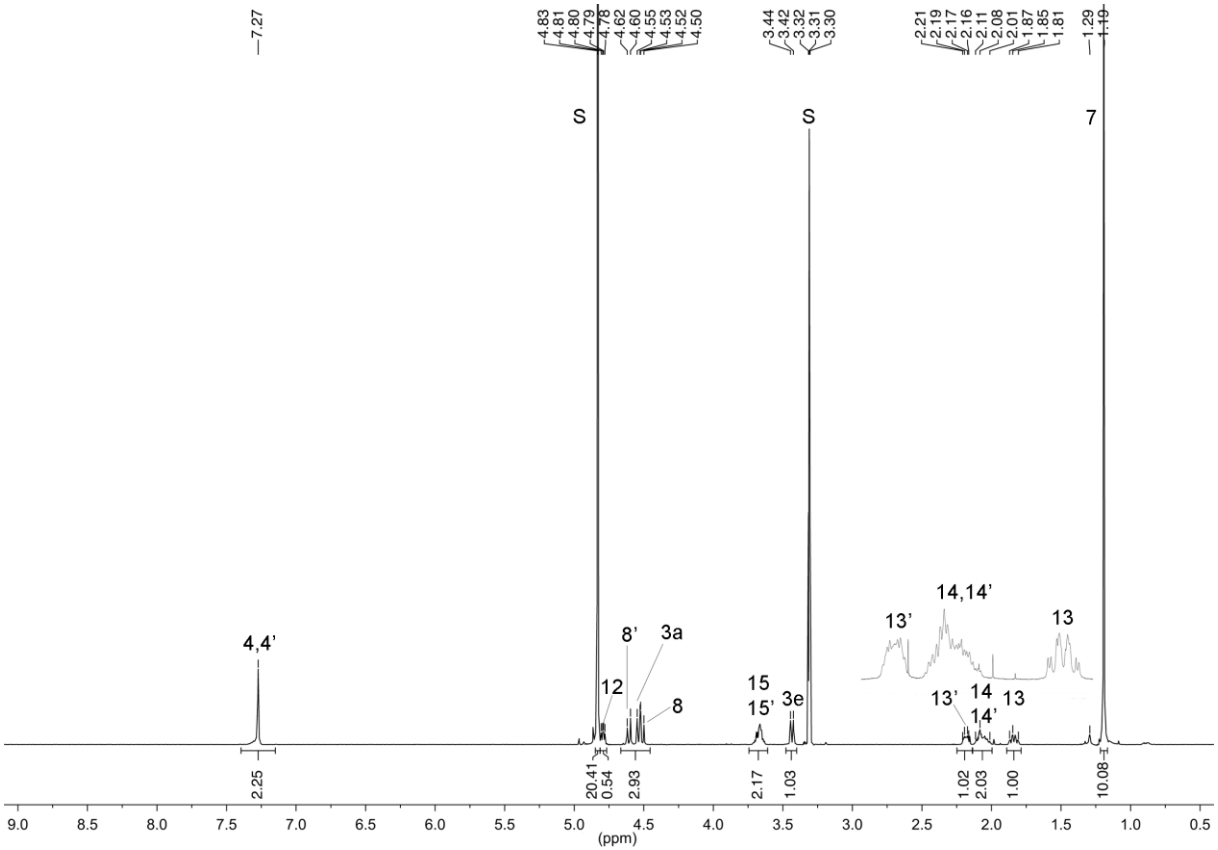


**Figure S19** $^{1}$H NMR spectrum of **1**$H_4$ + 1 equiv. NaCl ($CD_3OD$, 600 MHz, 300 K).

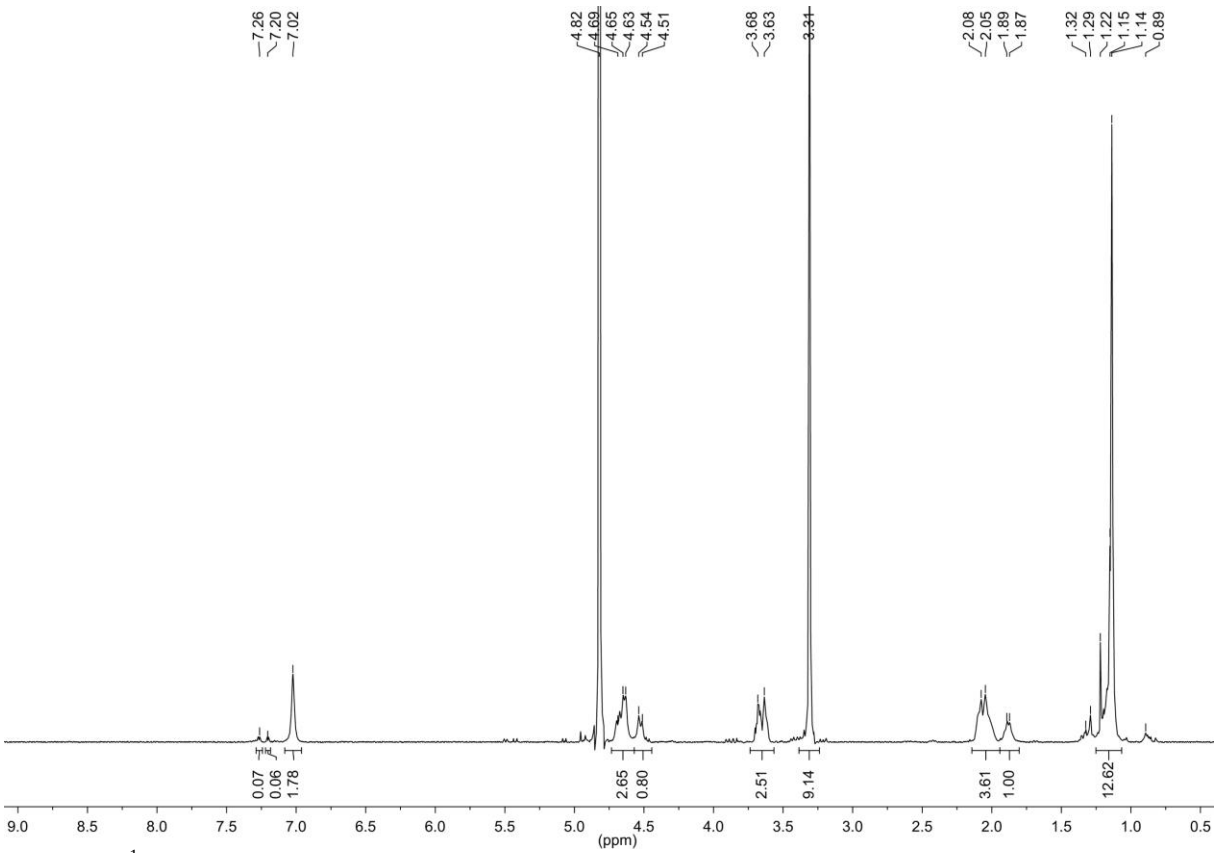


**Figure S20** $^{1}$H NMR spectrum of **1**$H_4$ + 1 equiv. KCl ($CD_3OD$, 600 MHz, 300 K).

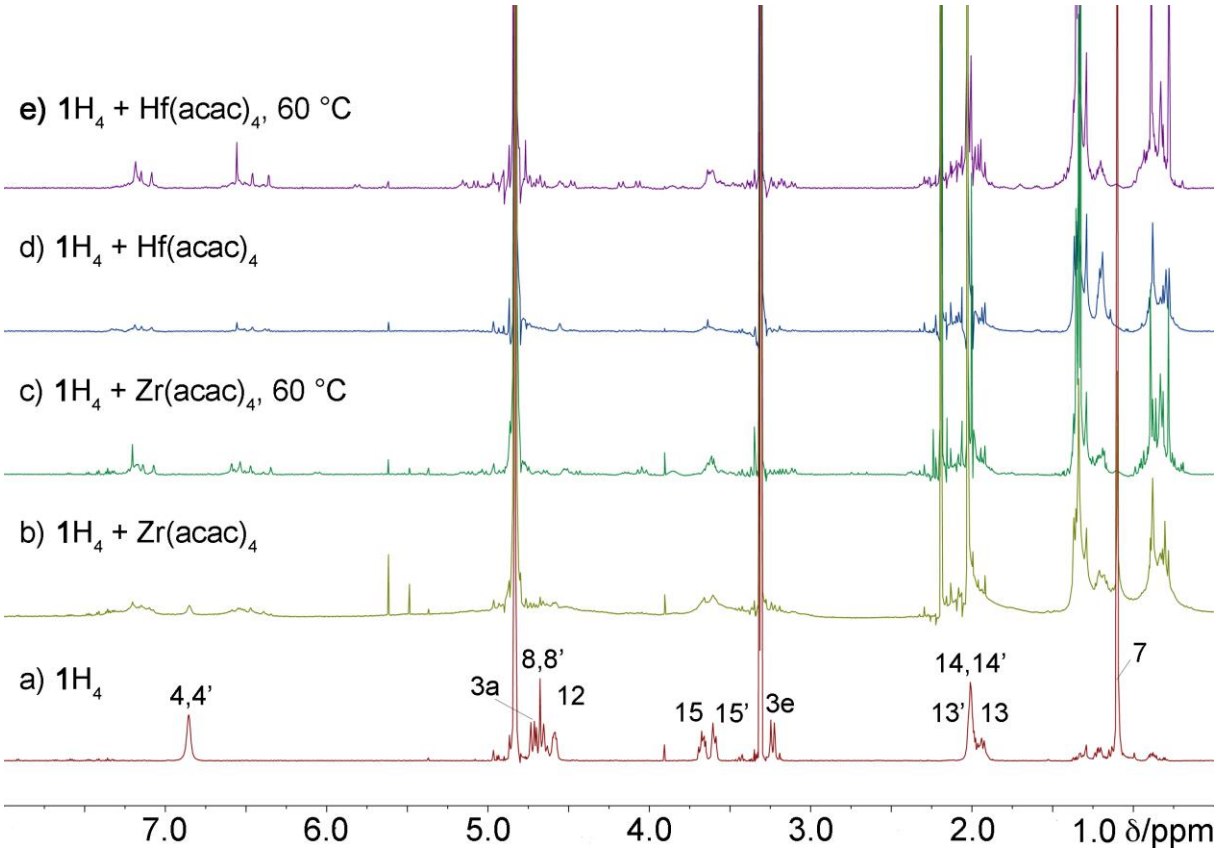


**Figure S21** Stacked plot of the $^{1}$H NMR spectra of **1**$H_4$ and **1**$H_4$ + 1 equiv. M(acac)$_4$, M = Zr or Hf ($CD_3OD$, 600 MHz).

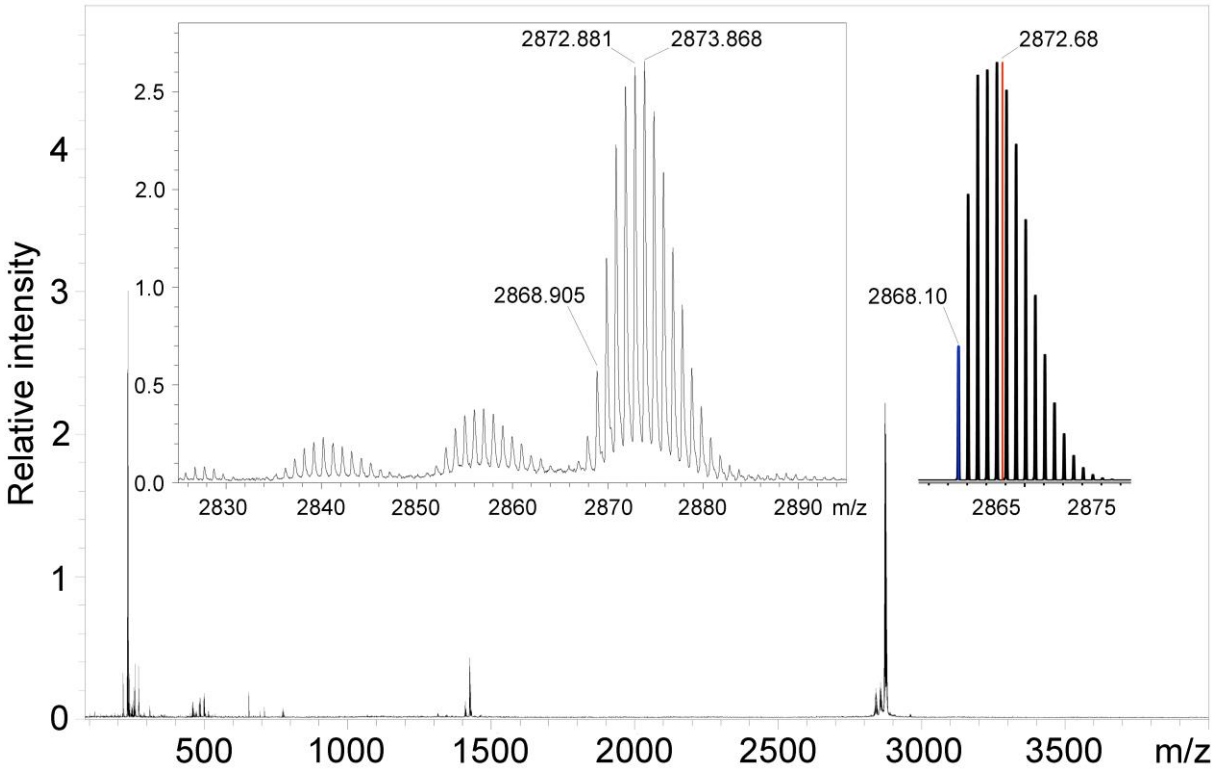


**Figure S22** MALDI-TOF mass spectrum of **1**$H_4$ + 1 equiv. $Zr(acac)_4$ + 0.5 equiv. KCl.

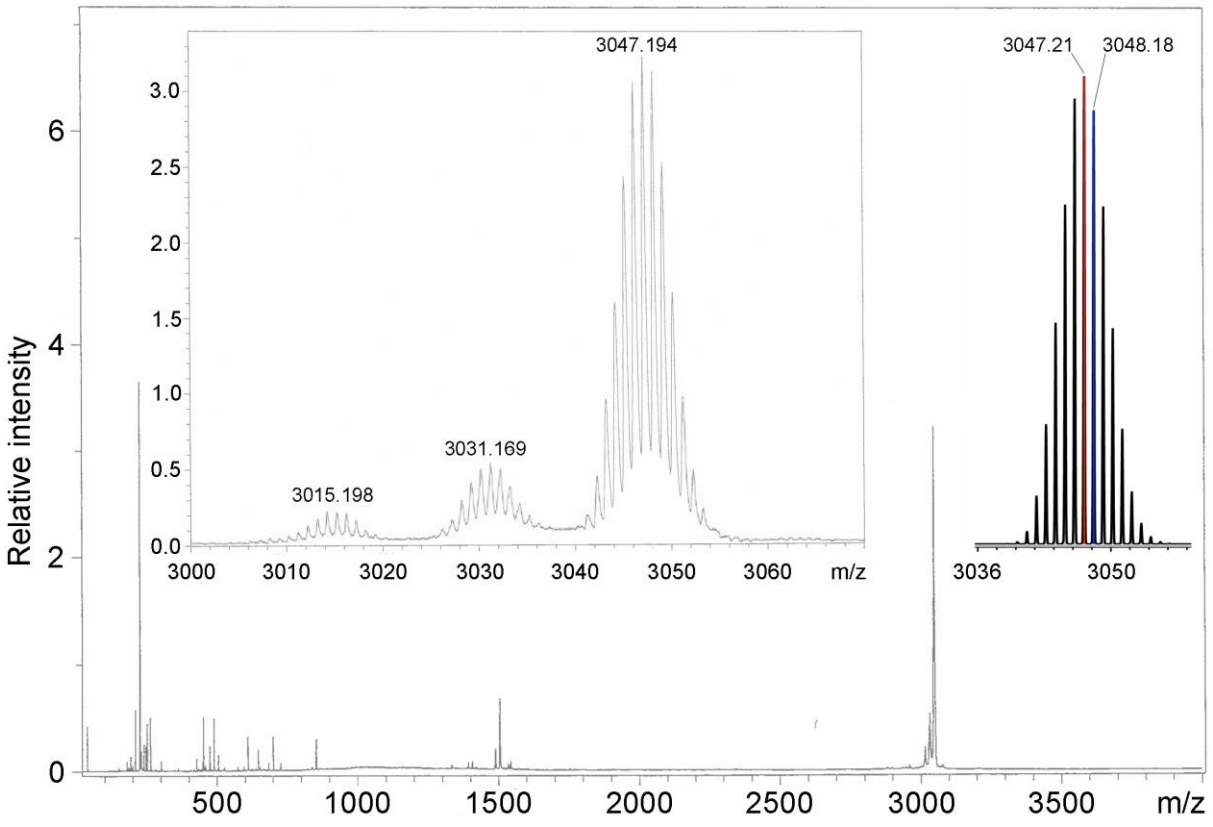


**Figure S23** MALDI-TOF mass spectrum of **1**$H_4$ + 1 equiv. $Hf(acac)_4$ + 0.5 equiv. KCl.

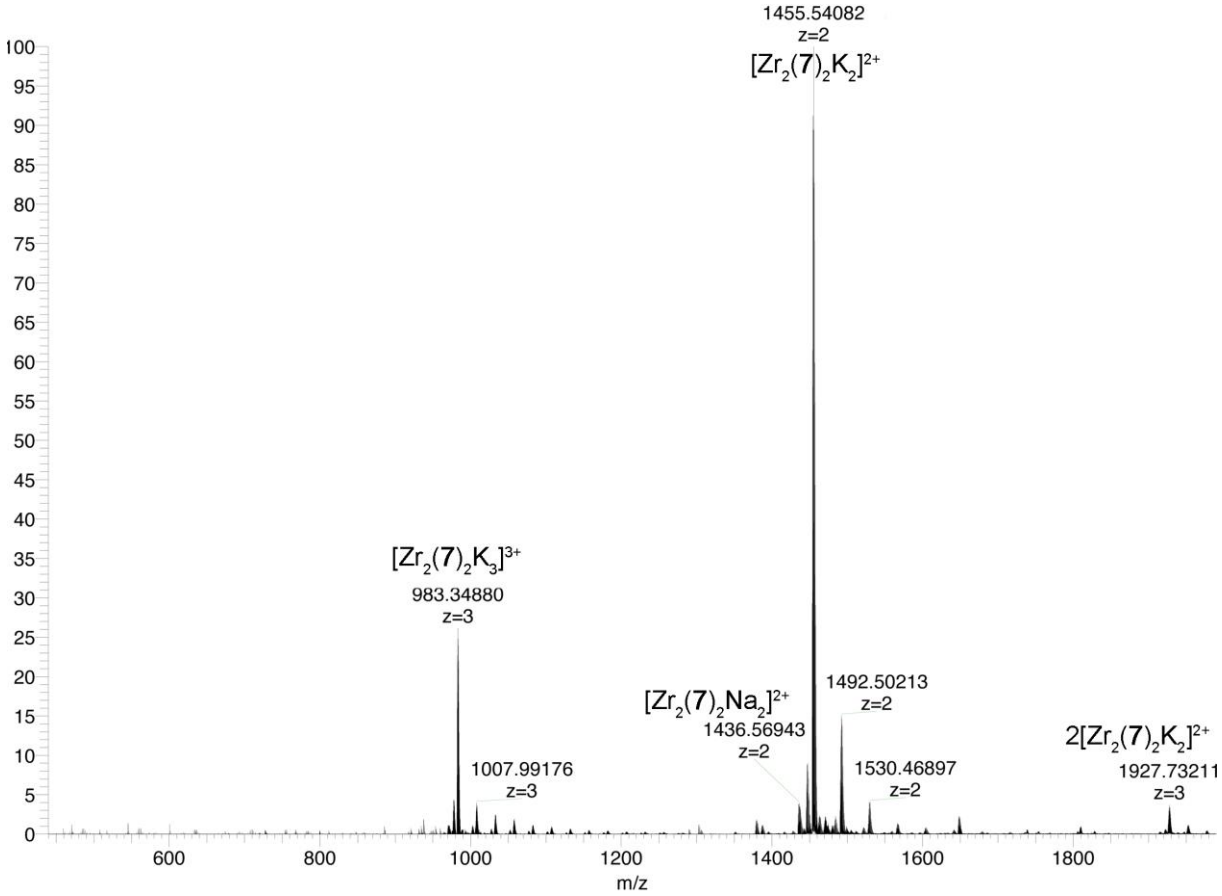


**Figure S24** ESI mass spectrum of **1**$H_4$ + 1 equiv. $Zr(acac)_4$ + 0.5 equiv. KCl.

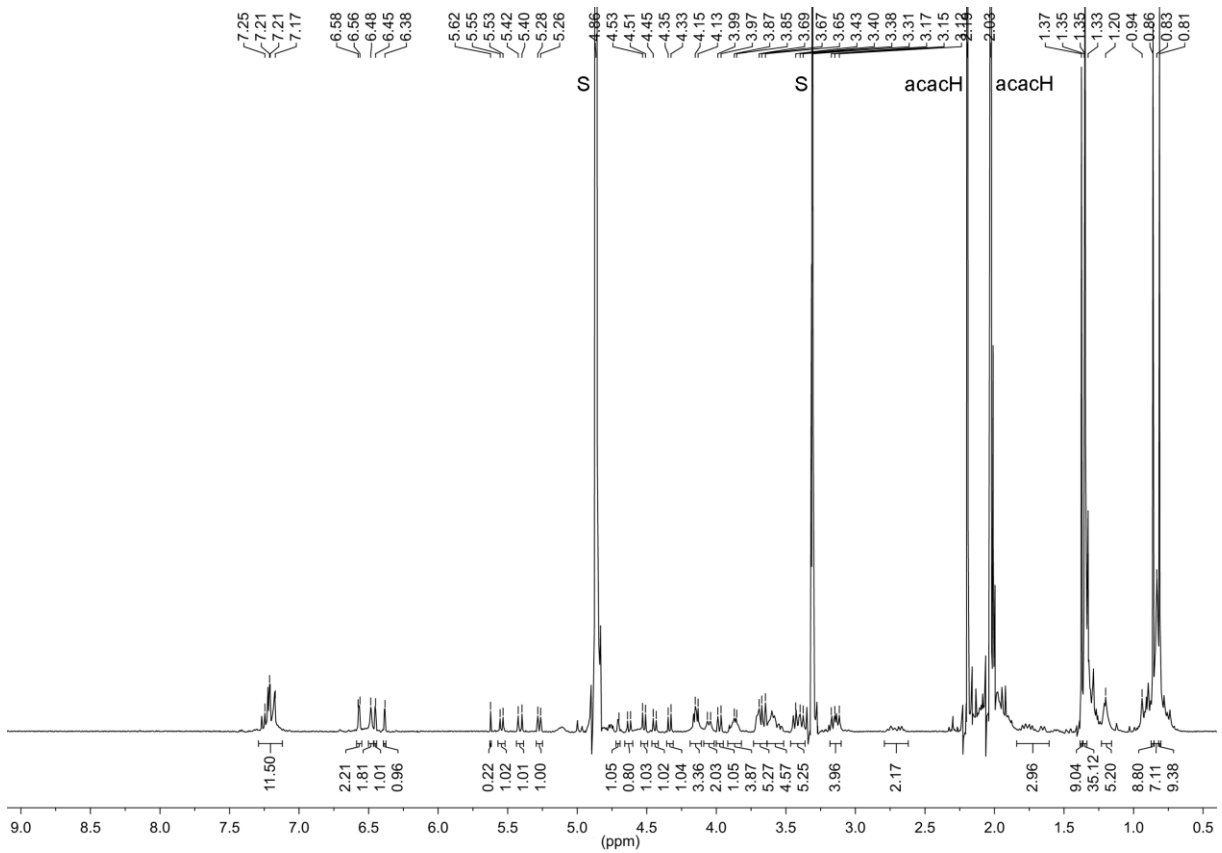


**Figure S25** $^1$H NMR spectrum of **1**$H_4$ + 1 equiv. $Zr(acac)_4$ + 0.5 equiv. KCl ($CD_3OD$, 600 MHz, 300 K).

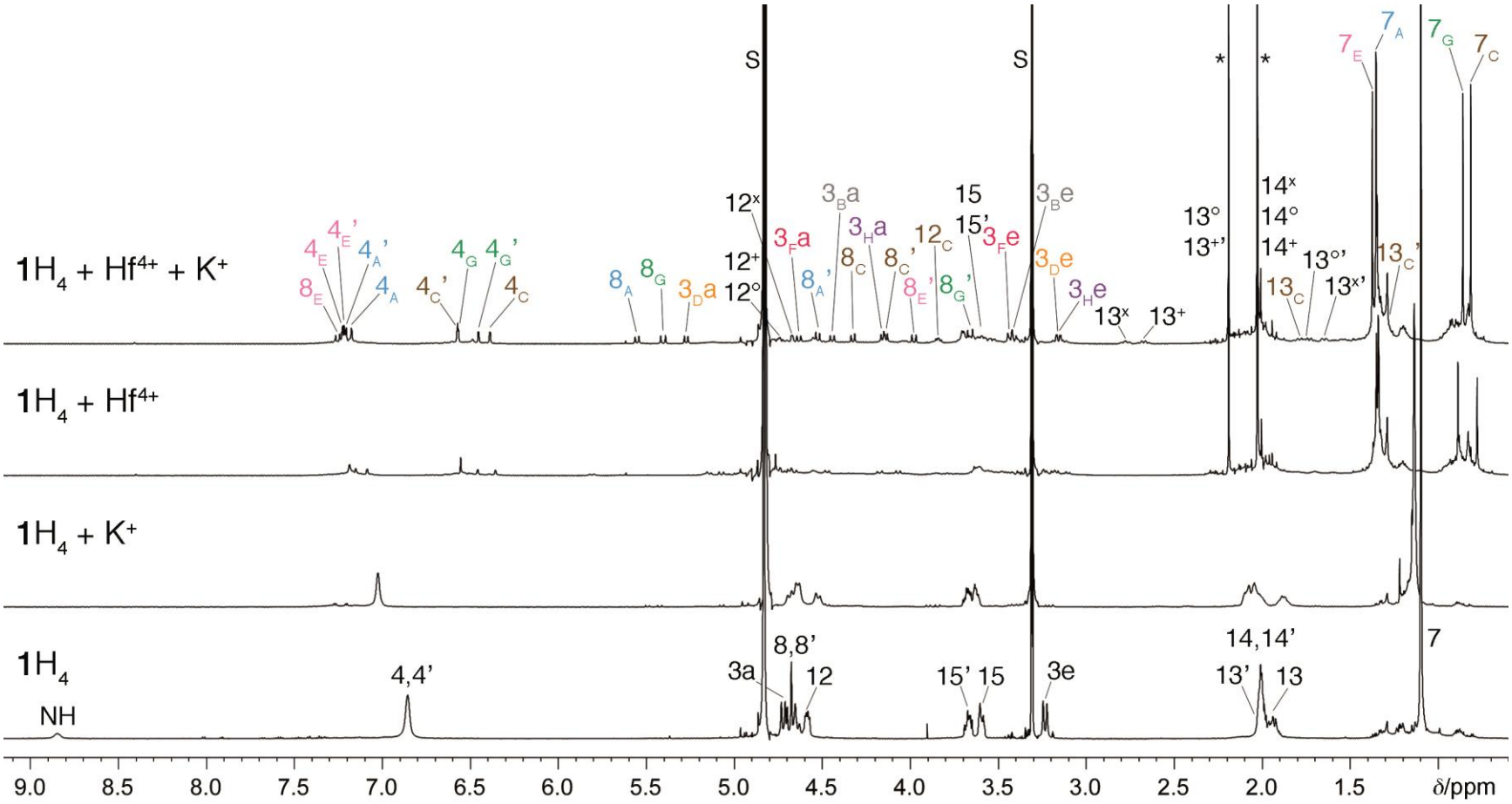


**Figure S26.** Stacked plot of the $^{1}$H NMR spectra ($CD_3OD$, 600 MHz, 300 K) of (bottom to top) **1**$H_4$, **1**$H_4$ + KCl (1:1), **1**$H_4$ + Hf(acac)$_4$ (1:1), and **1**$H_4$ + Hf(acac)$_4$ + KCl (2:2:1) obtained after heating the solutions at 60 °C. The labels s and ∗ mark solvent and acetylacetone, respectively.

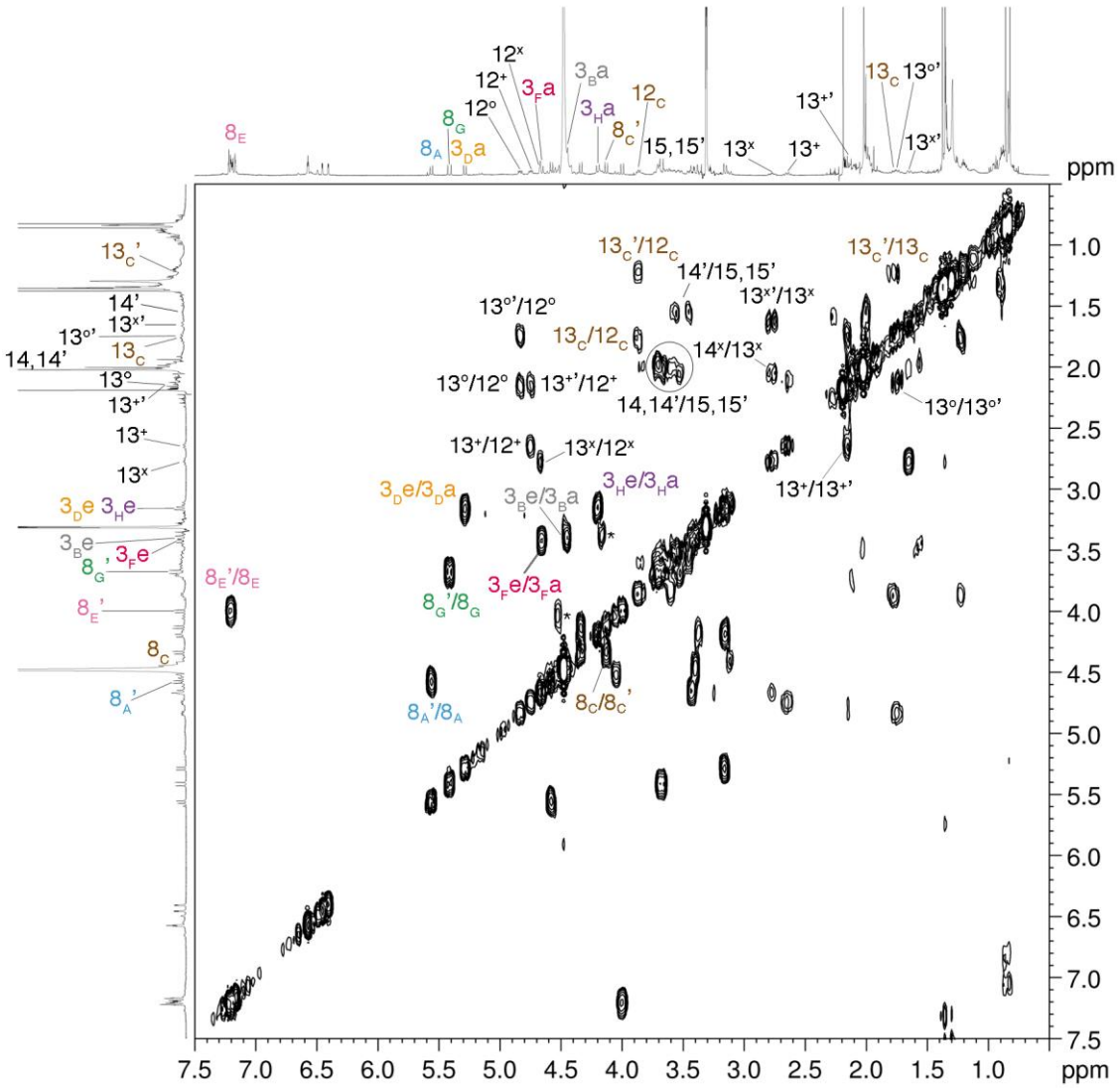


**Figure S27** $^{1}$H-$^{1}$H COSY NMR spectrum of **1**$H_4$ + 1 equiv. Hf(acac)$_4$ + 0.5 equiv. KCl ($CD_3OD$, 600 MHz, 335 K).

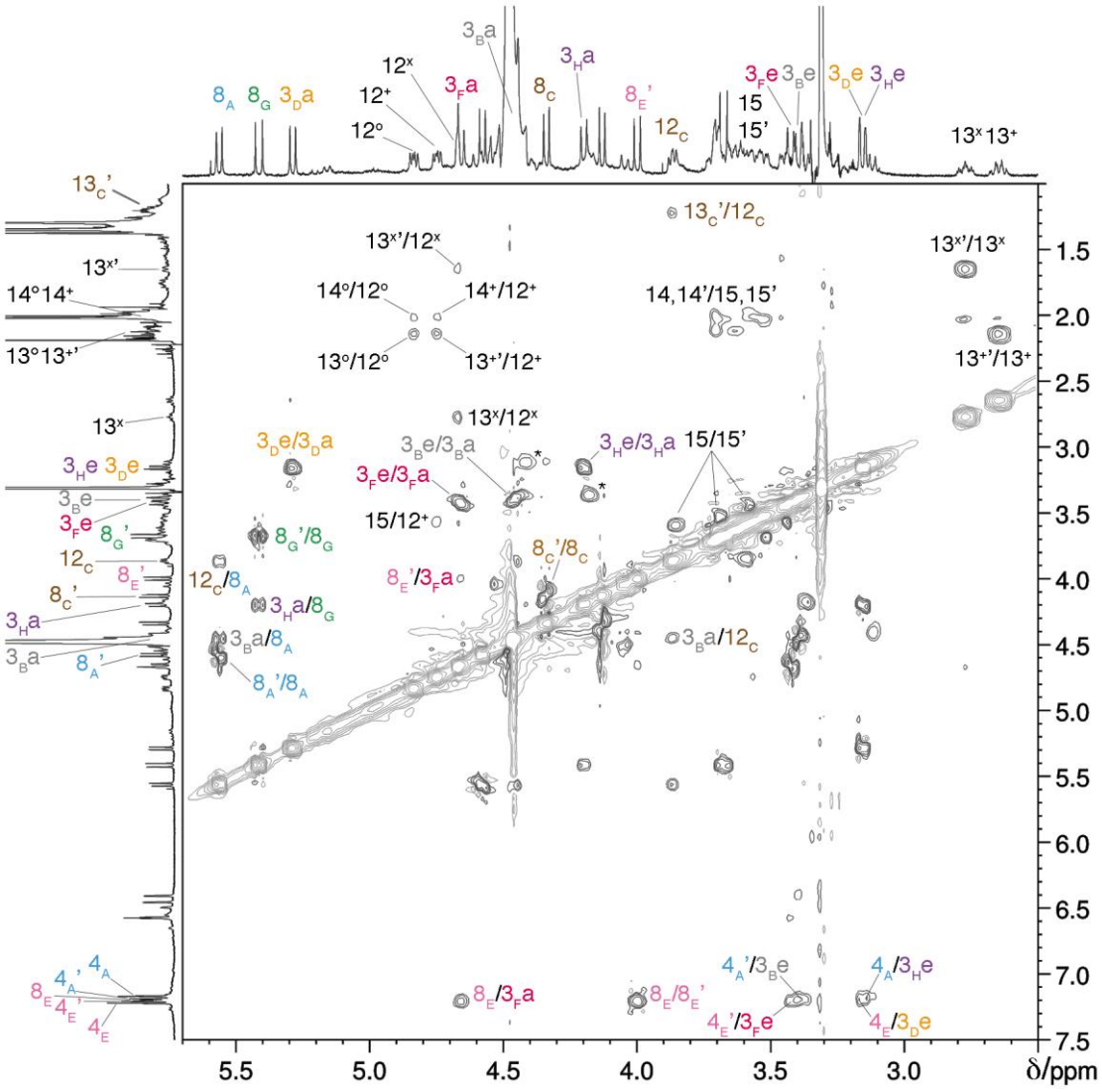


**Figure S28** $^{1}$H-$^{1}$H ROESY NMR spectrum of **1**H$_4$ + 1 equiv. Hf(acac)$_4$ + 0.5 equiv. KCl (CD$_3$OD, 600 MHz, 335 K).

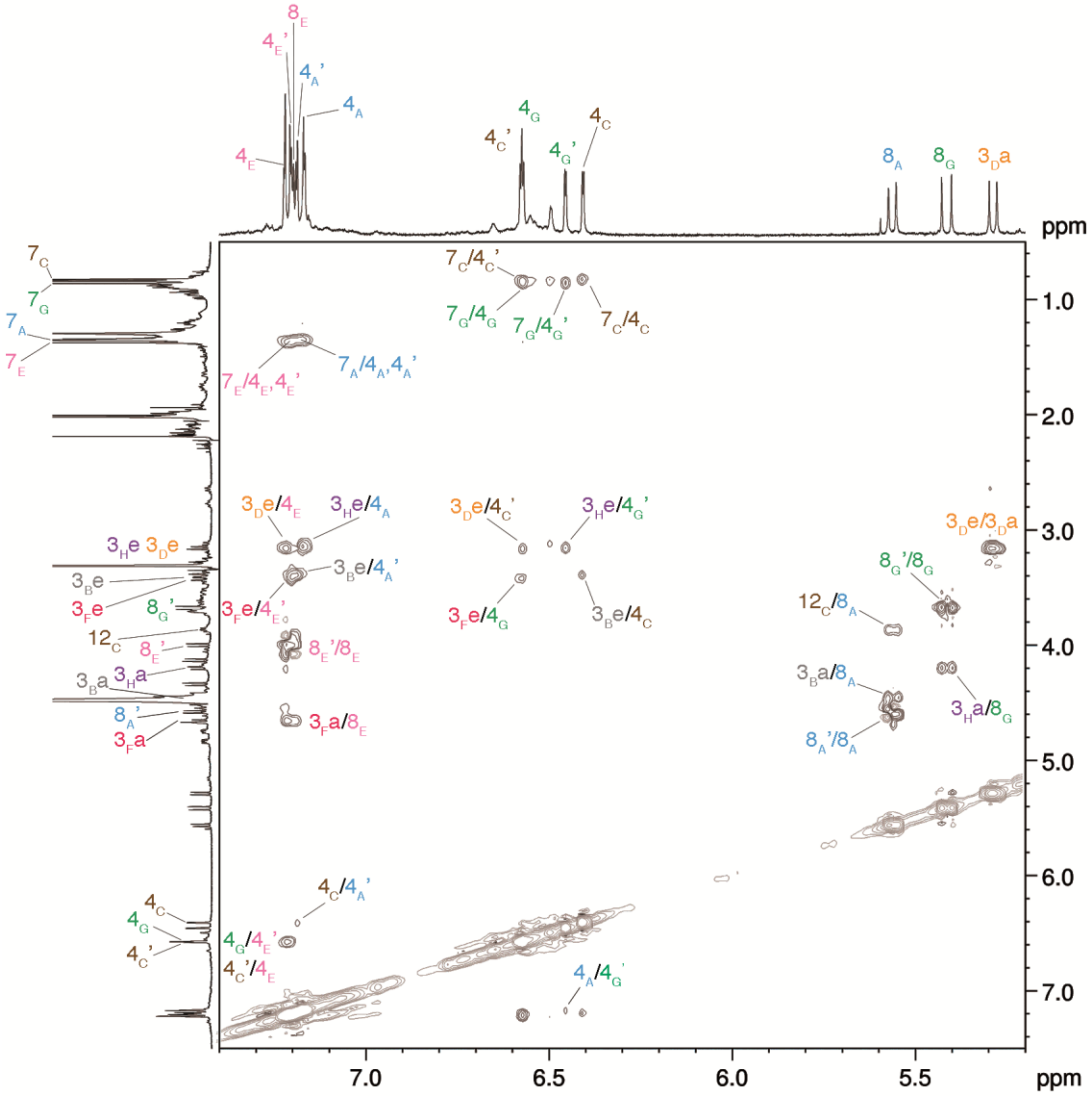


**Figure S29** $^{1}$H-$^{1}$H ROESY NMR spectrum of **1**$H_4$ + 1 equiv. Hf(acac)$_4$ + 0.5 equiv. KCl ($CD_3OD$, 600 MHz, 335 K).

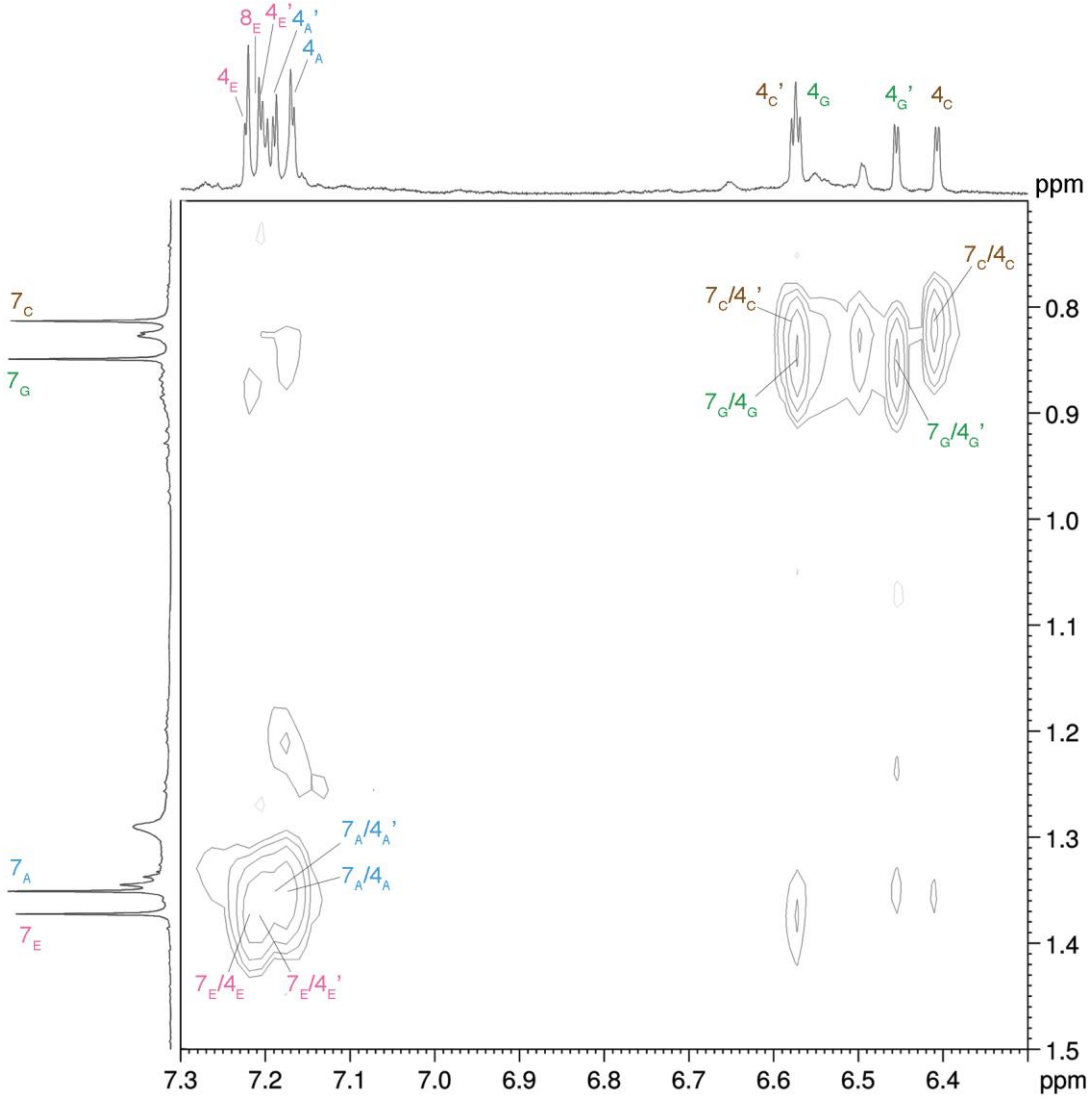


**Figure S30** $^{1}$H-$^{1}$H ROESY NMR spectrum of **1**$H_4$ + 1 equiv. Hf(acac)$_4$ + 0.5 equiv. KCl ($CD_3OD$, 600 MHz, 335 K).

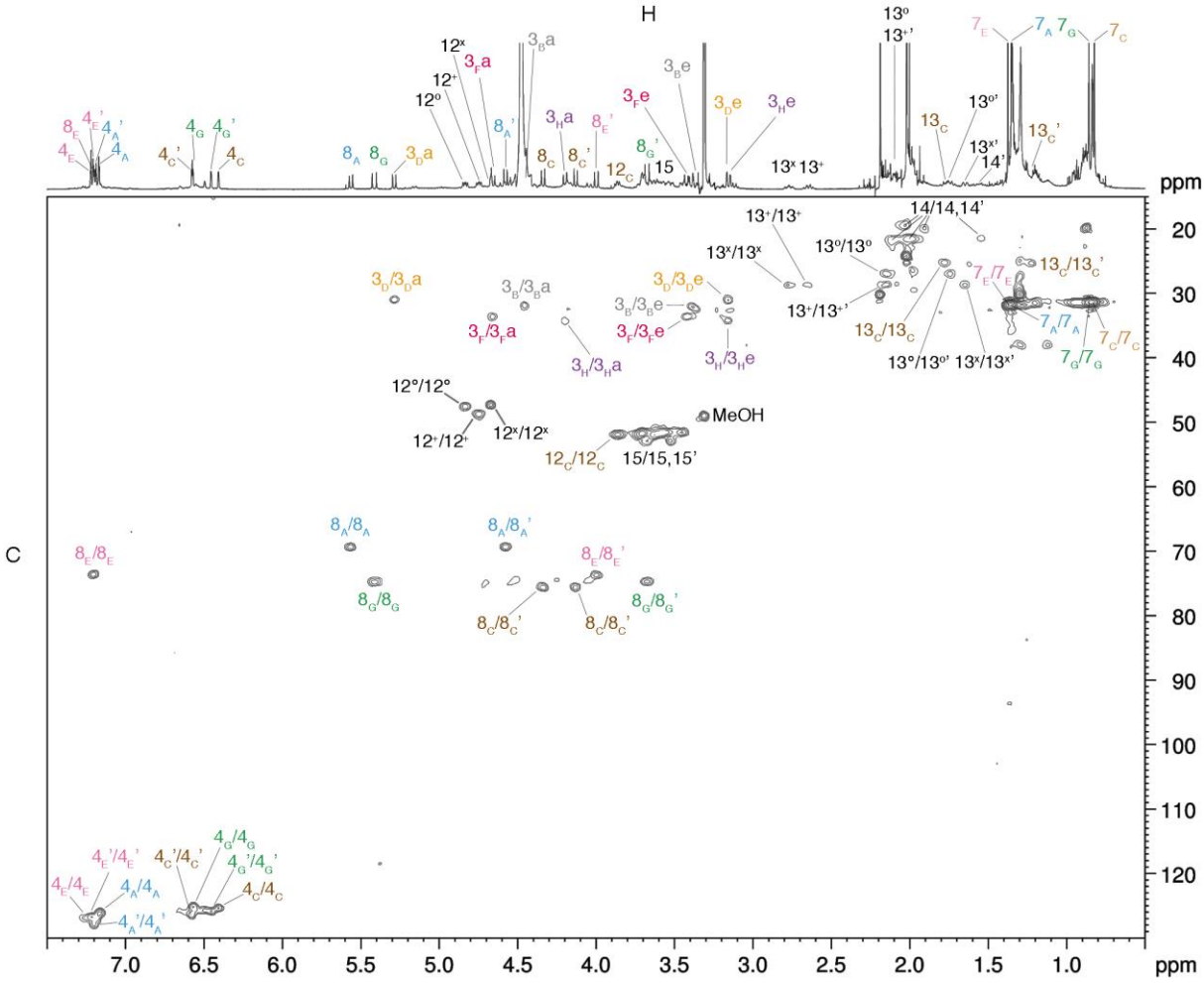


**Figure S31** $^{13}C$-$^{1}H$ HSQC NMR spectrum of **1**$H_4$ + 1 equiv. $Hf(acac)_4$ + 0.5 equiv. KCl ($CD_3OD$, 600 MHz, 335 K).

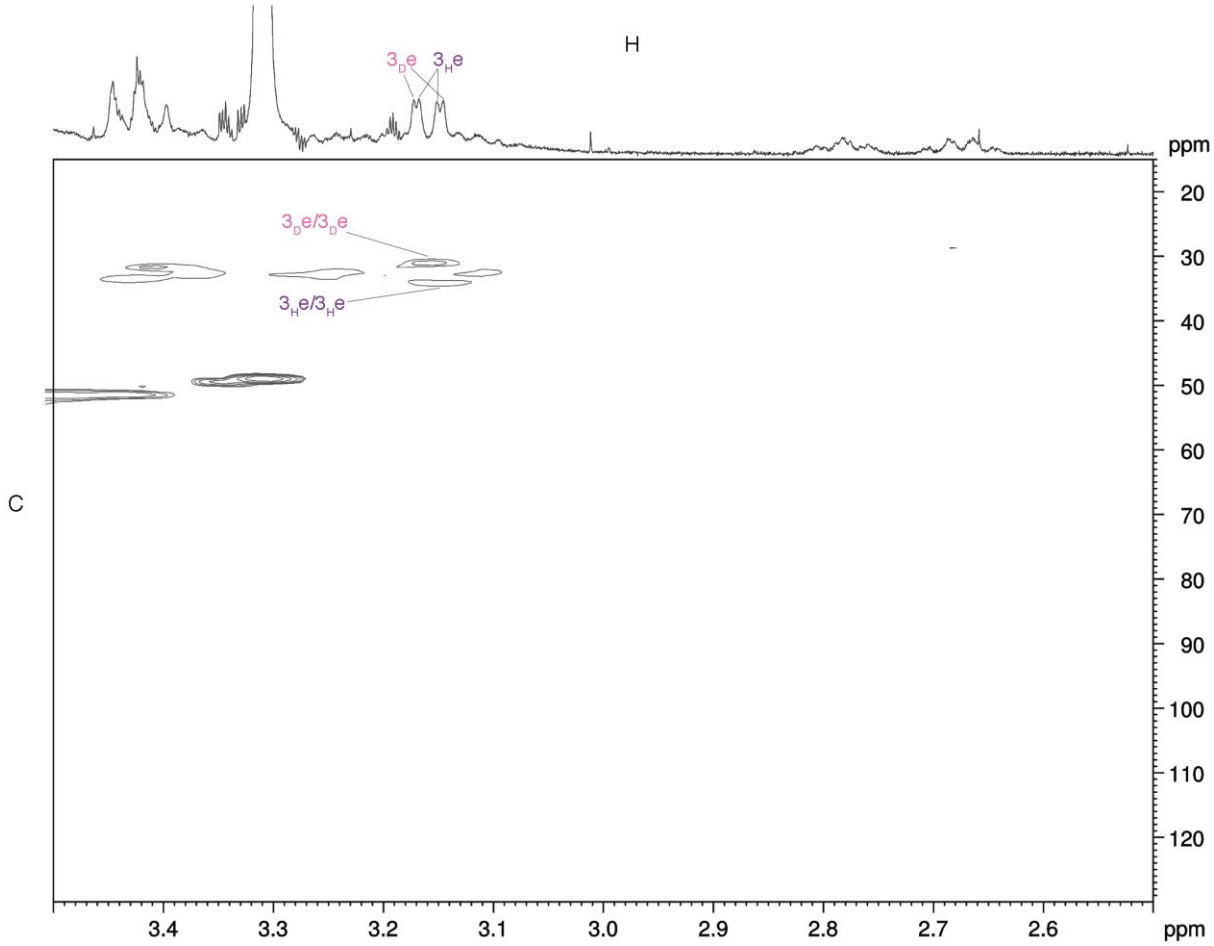


**Figure S32** $^{13}C$-$^{1}H$ HSQC NMR spectrum of **1**$H_4$ + 1 equiv. Hf(acac)$_4$ + 0.5 equiv. KCl ($CD_3OD$, 600 MHz, 300 K).

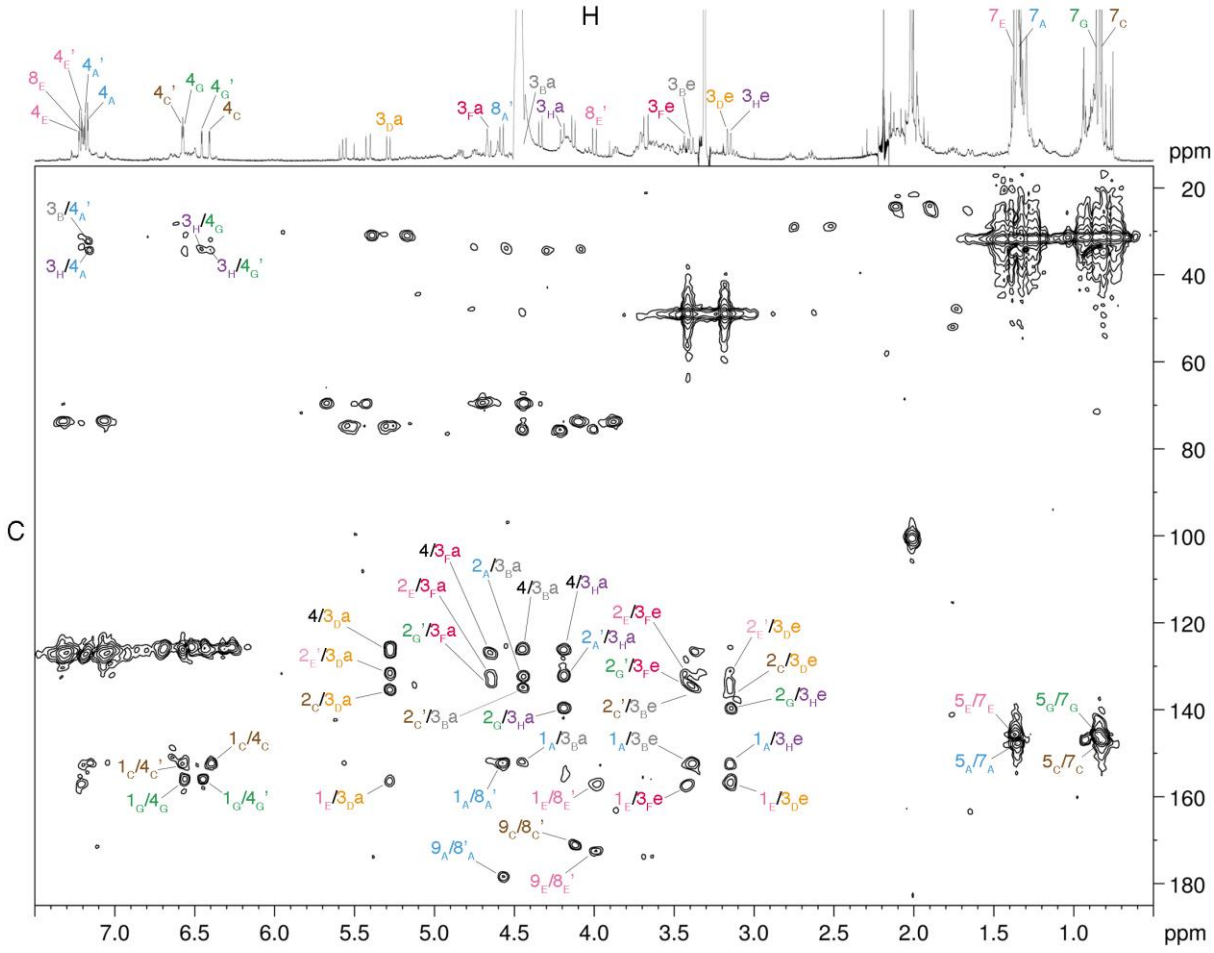


**Figure S33** $^{13}C$-$^{1}H$ HMBC NMR spectrum of **1**$H_4$ + 1 equiv. $Hf(acac)_4$ + 0.5 equiv. KCl ($CD_3OD$, 600 MHz, 335 K).

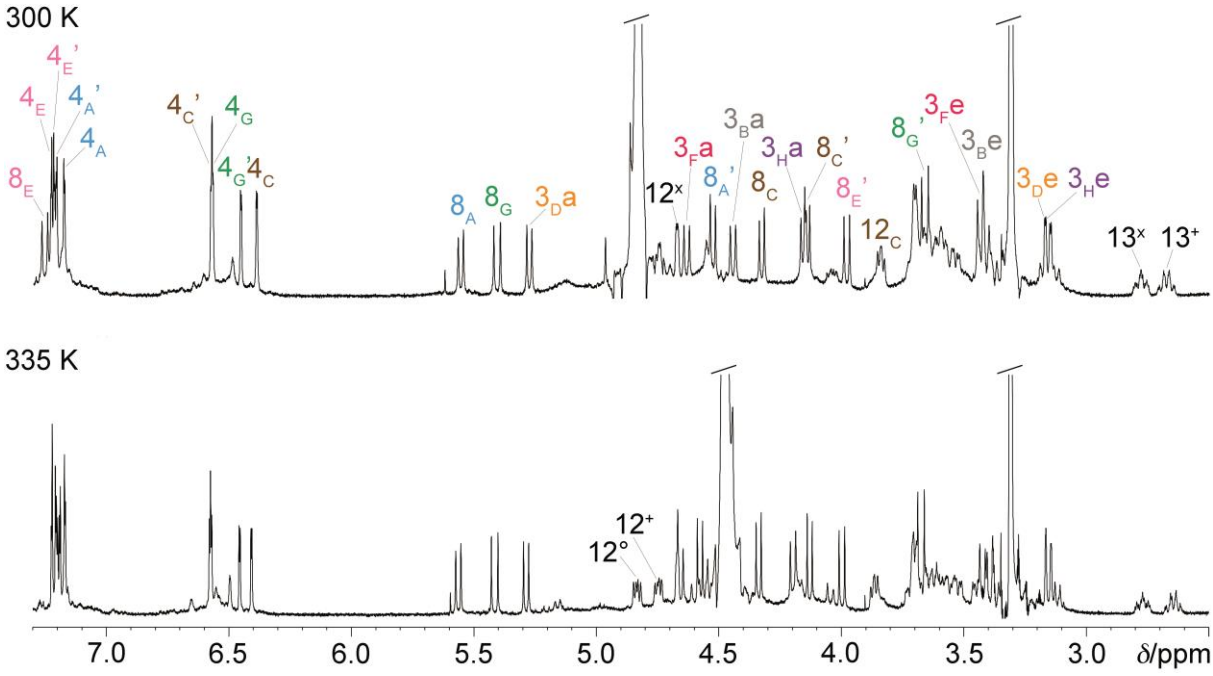


**Figure S34** Comparison of the $^{1}$H NMR spectra of **1**$H_4$ + 1 equiv. Hf(acac)$_4$ + 0.5 equiv. KCl at $T$ = 300 and 335 K ($CD_3OD$, 600 MHz).