ELECTRONIC SUPPLEMENTARY INFORMATION

A chiral member of the family of organic hexameric cages

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Experimental procedure and analysis of 2

To a solution of tetraformylresorcin[4]arene **1**[1] (0.243 mmol) in toluene (20 ml) a solution hydrazine monohydrate (2.916 mmol) in methanol (20 ml) was added. The reaction mixture was stirred for 48 hours. Methanol was evaporated, and the remaining off-white suspension was filtered through a G5 filter funnel, washed with methanol, and dried under vacuum. Product **2** was obtained in 69 % yield (0.157 mmol).

^{1}H NMR (DMSO-d_6, 400 MHz, 298 K): δ 11.16 (s, 2H), 8.22 (s, 1H), 7.40 (s, 1H), 6.80 (s, 2H), 4.40 (t, 1H), 2.13 (t, 2H), 1.47 – 1.30 (m, 1H), 0.93 (d, 6H).

^{13}C NMR (DMSO-d_6, 100 MHz, 298 K): δ 150.4, 140.2, 124.7, 123.8, 107.1, 41.5, 30.5, 26.0, 22.6.

HR-MS (ESI-TOF): *m/z* calculated for $(C_{48}H_{63}N_8O_8)^-$ $[M\text{-}H]^-$: 881.4925; experimental value: 881.4926.

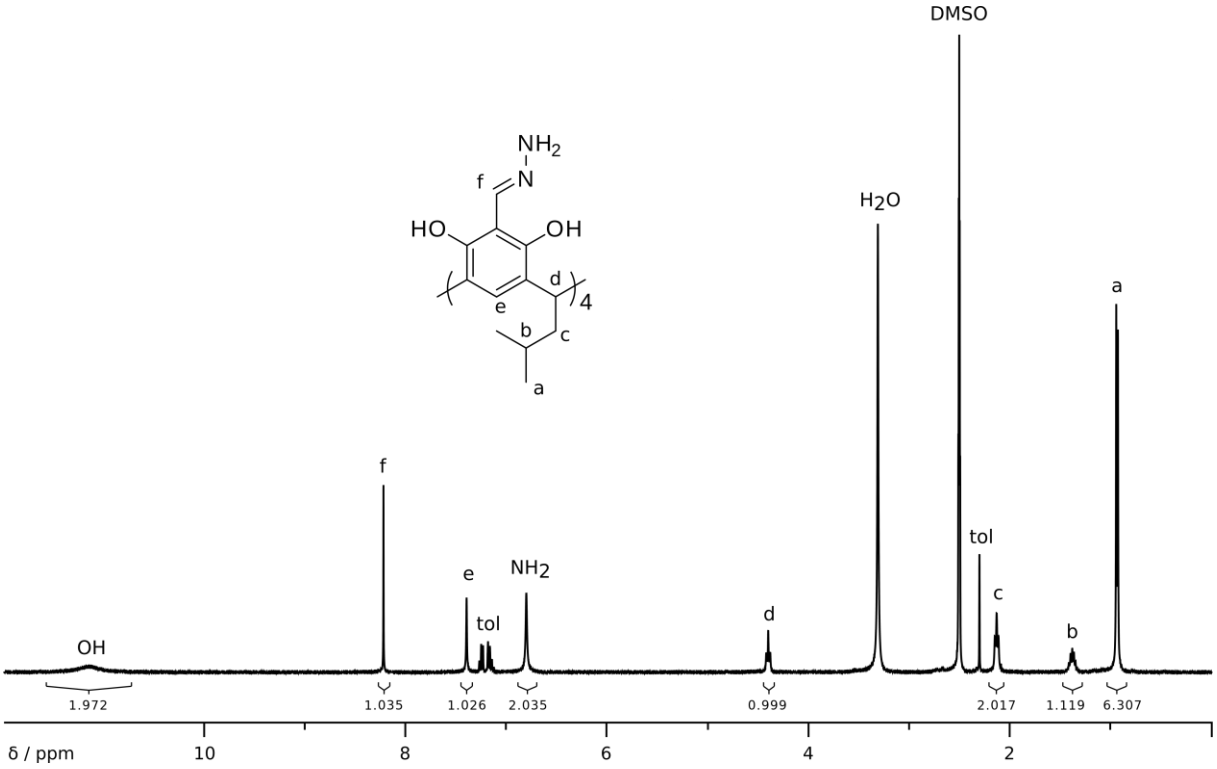

Figure S1. ^{1}H NMR spectrum of **2** (DMSO-d_6, 400 MHz, 298 K).

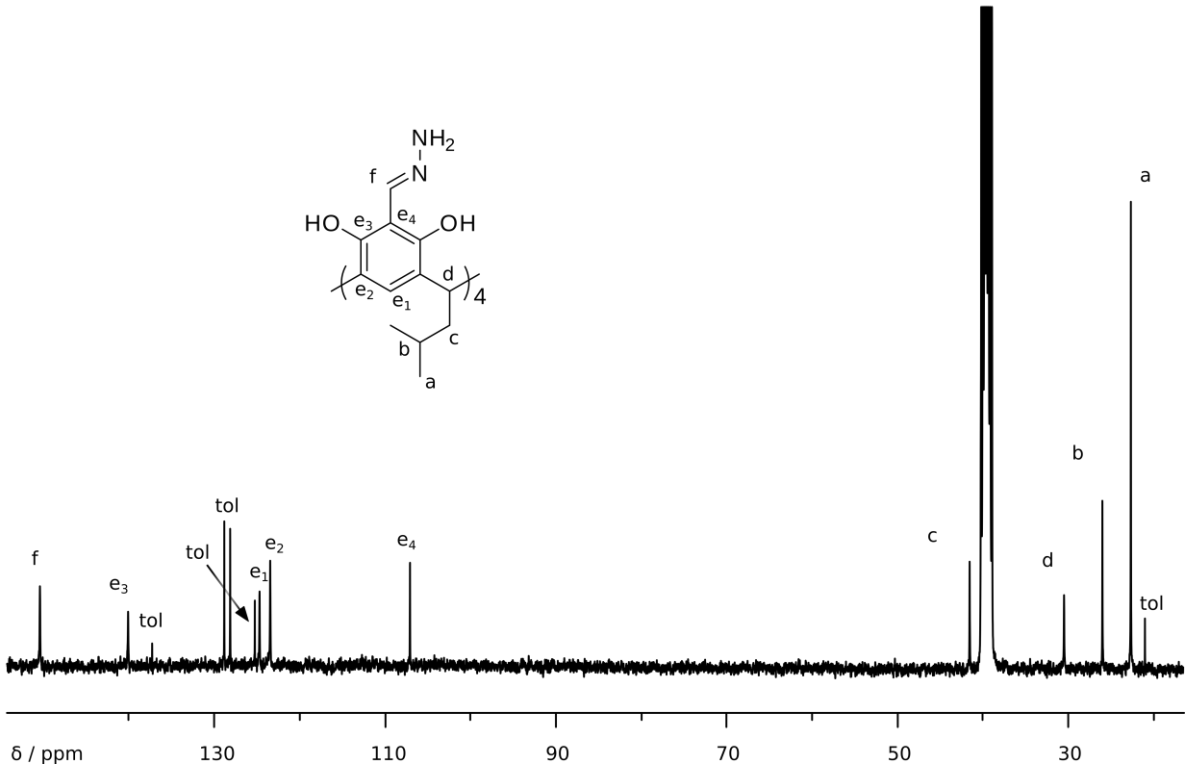

Figure S2. ^{13}C NMR spectrum of **2** (DMSO-d_6, 400 MHz, 298 K).

Experimental procedure and analysis of 3

Tetraformylresorcin[4]arene **1**[1] (0.267 g, 0.283 mmol) and **2** (0.275 g, 0.283 mmol) were dissolved in chloroform (40 ml) and stirred for 24 hours at 70°C. The solvent was partially evaporated and an excess of methanol was added to the residue, upon which a precipitate was formed. The solid product was filtered through a G5 funnel, washed with methanol and dried under vacuum to give **3** in quantitative yield (0.515 g, 0.105 mmol).

^{1}H NMR ($CDCl_3$, 600 MHz, 298 K): δ 13.34 (s, 1H), 9.15 (s, 1H), 8.59 (s, 1H), 7.40 (s, 1H), 4.56 (t, 1H), 2.22 – 2.02 (m, 2H), 1.58 – 1.43 (m, 1H), 1.01 (d, 6H).

^{13}C NMR ($CDCl_3$, 150 MHz, 298 K) δ: 161.0, 153.9, 153.6, 128.1, 123.6, 123.5, 107.1, 42.2, 30.2, 26.1, 22.8, 22.7.

DOSY Diffusion coefficient ($CDCl_3$, 600 MHz, 298 K): $2.7 \cdot 10^{-10}$ m^2 s^{-1}

HR-MS (ESI-TOF): *m/z* calculated for $(C_{288}H_{333}N_{24}O_{48})^{3-}$ $[M-3H]^{3-}$: 1631.811; experimental value: 1631.812

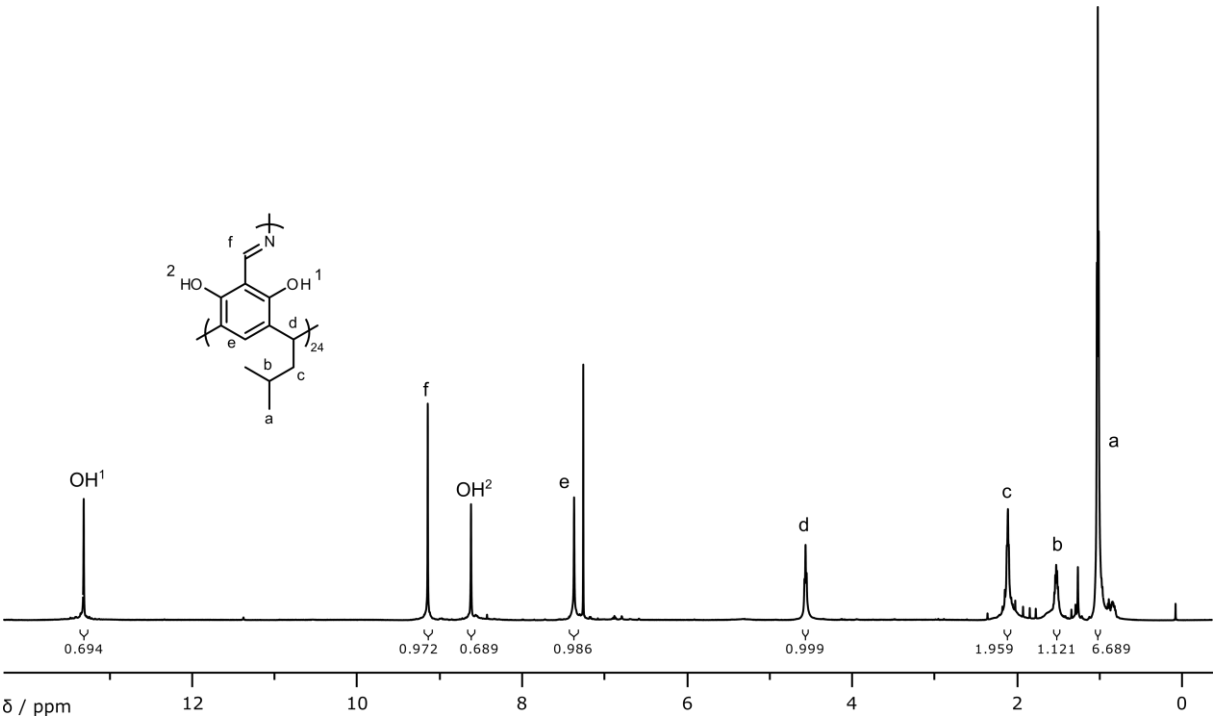

Figure S3. ^{1}H NMR of **3** ($CDCl_3$, 600 MHz, 298 K).

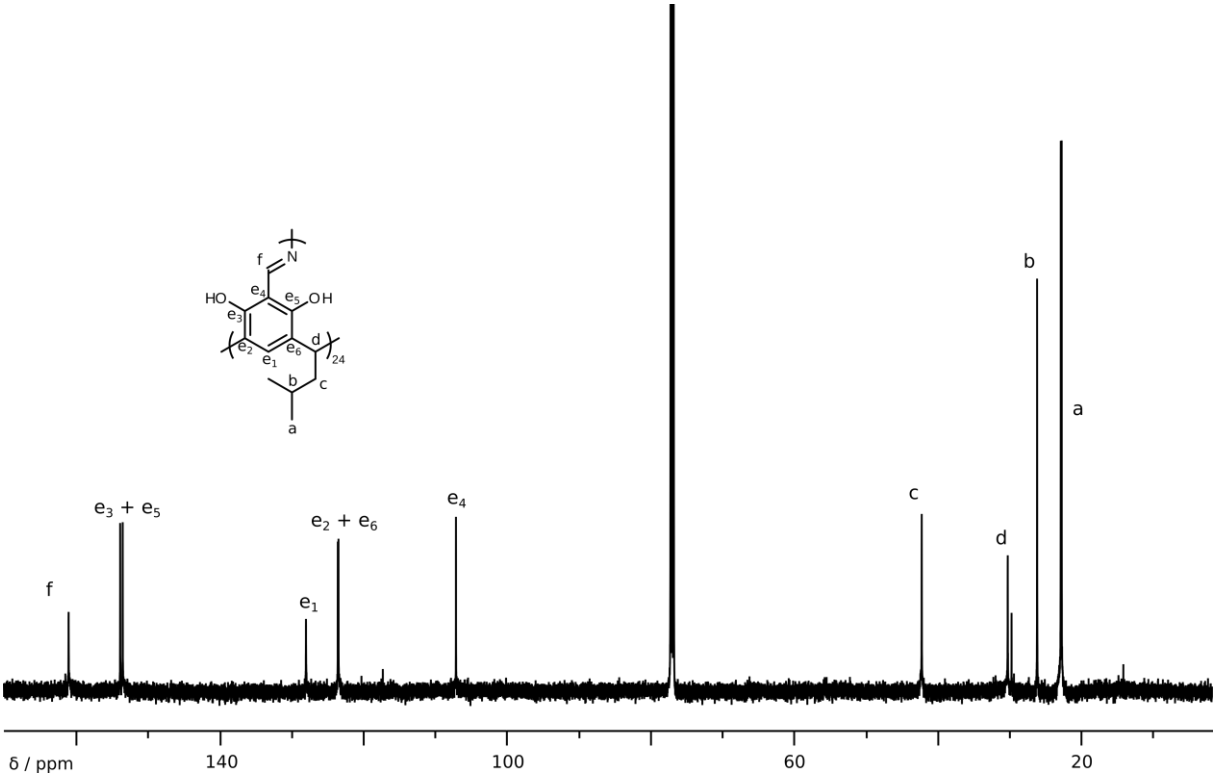

Figure S4. ^{13}C NMR spectrum of **3** ($CDCl_3$, 600 MHz, 298 K).

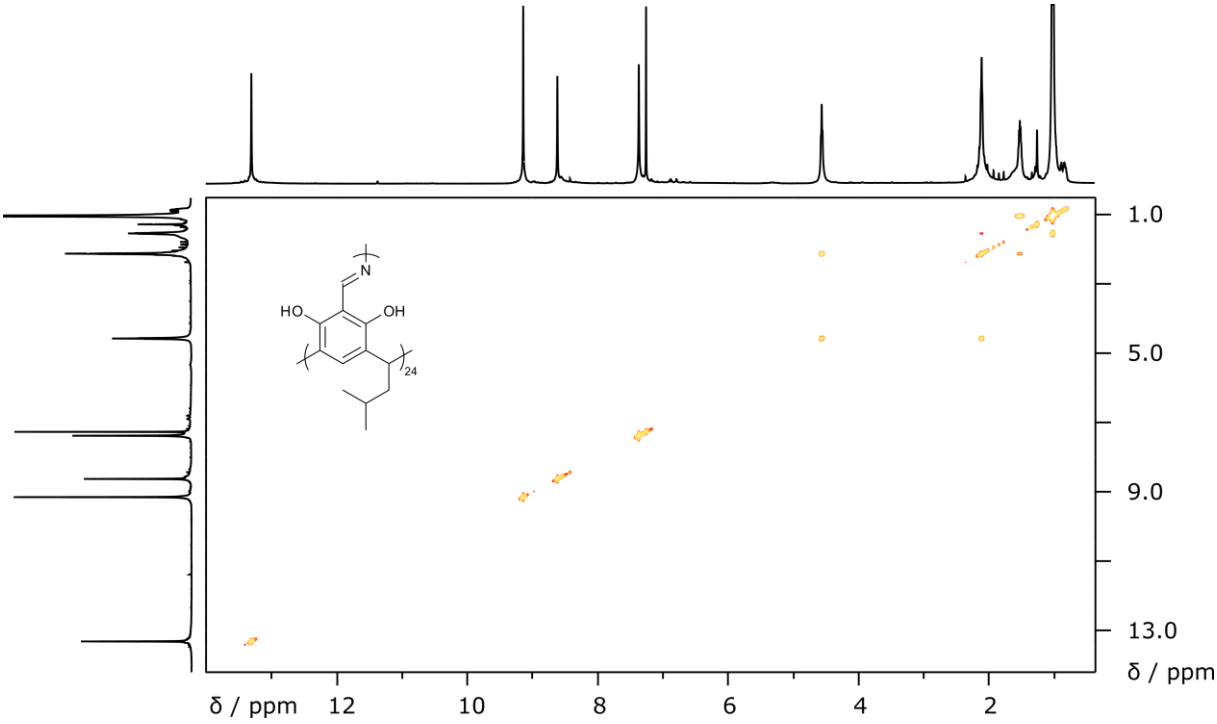

Figure S5. ^{1}H-^{1}H COSY spectrum of **3** ($CDCl_3$, 600 MHz, 298 K).

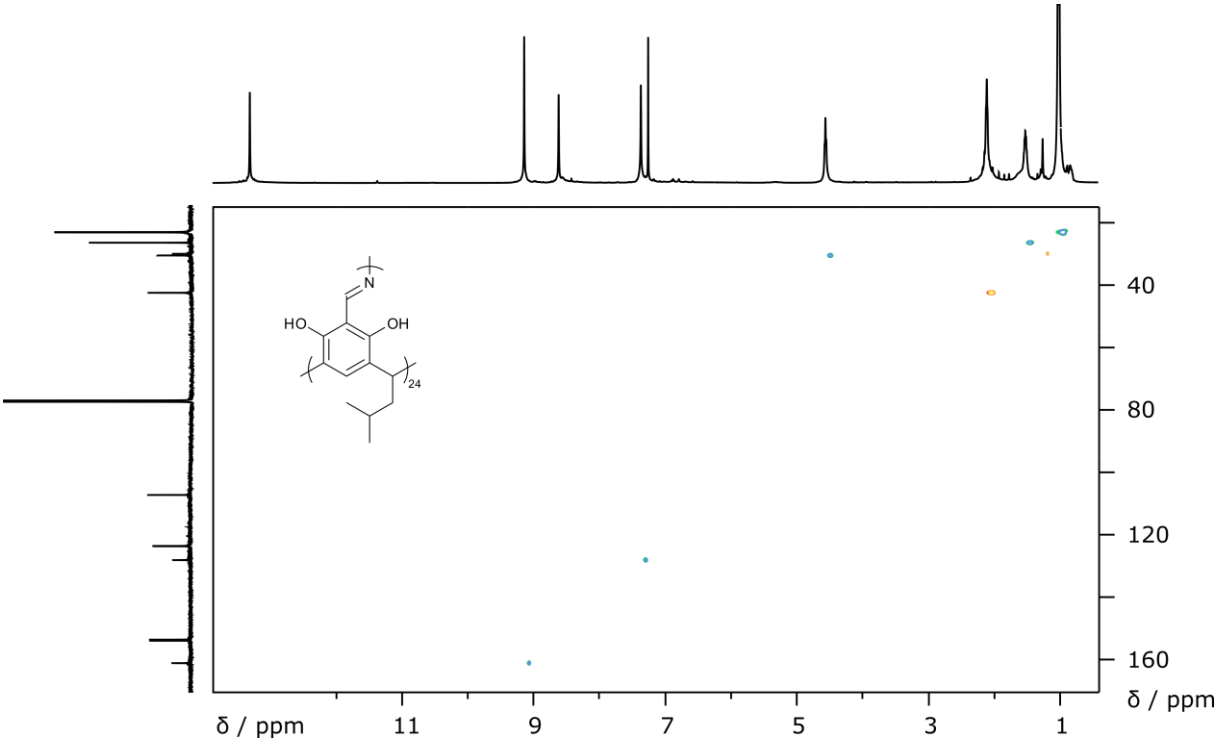

Figure S6. ^{1}H-^{13}C HSQC spectrum of **3** ($CDCl_3$, 600 MHz, 298 K).

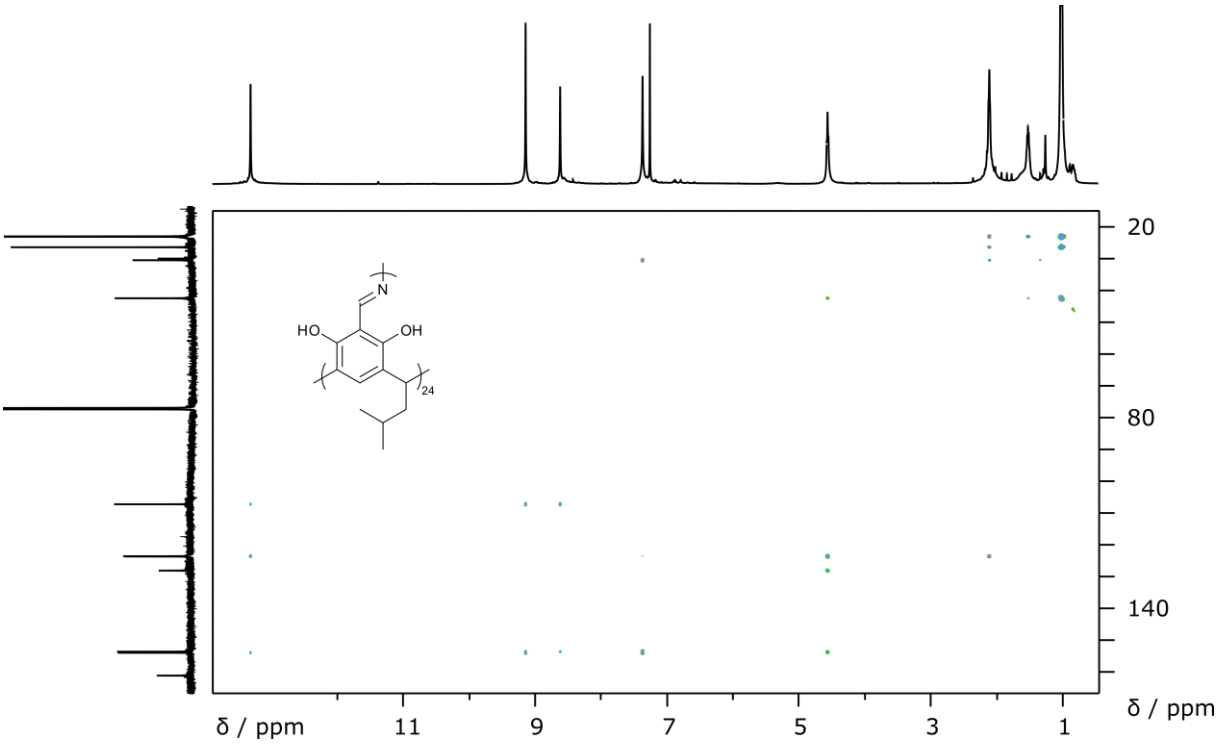

Figure S7. ^{1}H-^{13}C HMBC spectrum of **3** ($CDCl_3$, 600 MHz, 298 K).

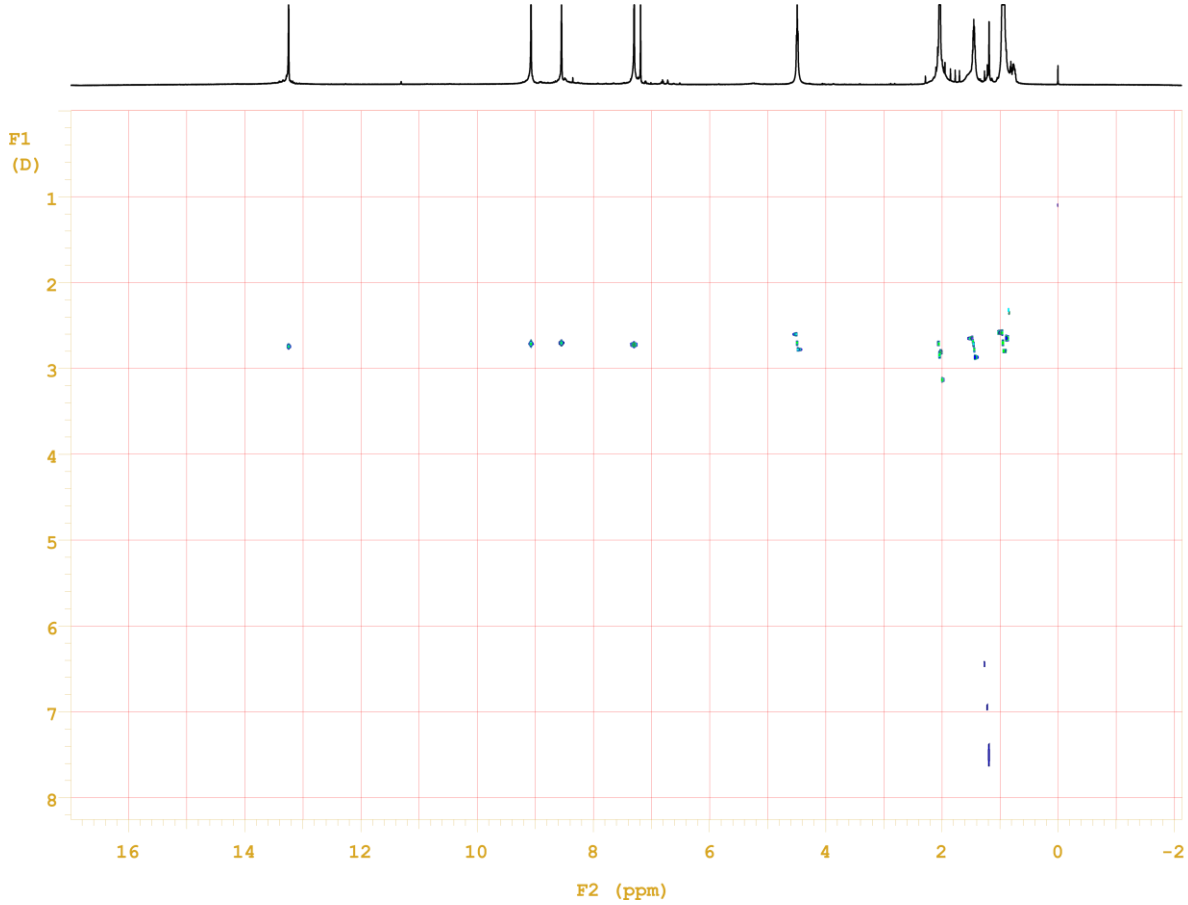

Figure S8. DOSY spectrum of **3** ($CDCl_3$, 600 MHz, 298 K).

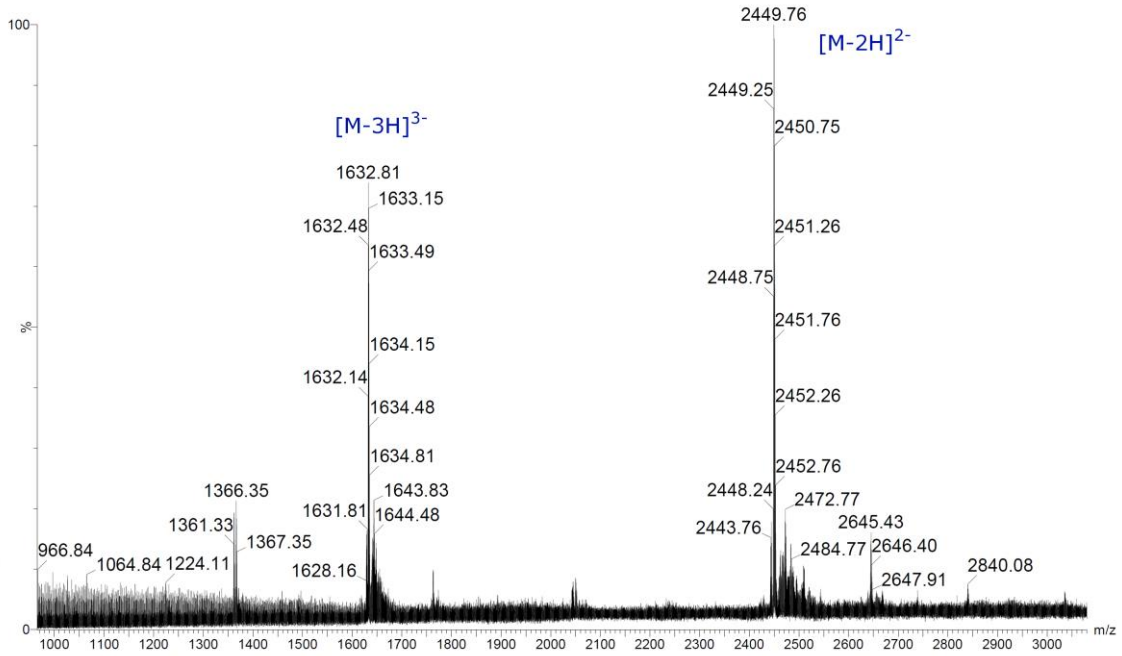

Figure S9. ESI-TOF MS spectrum of **3**.

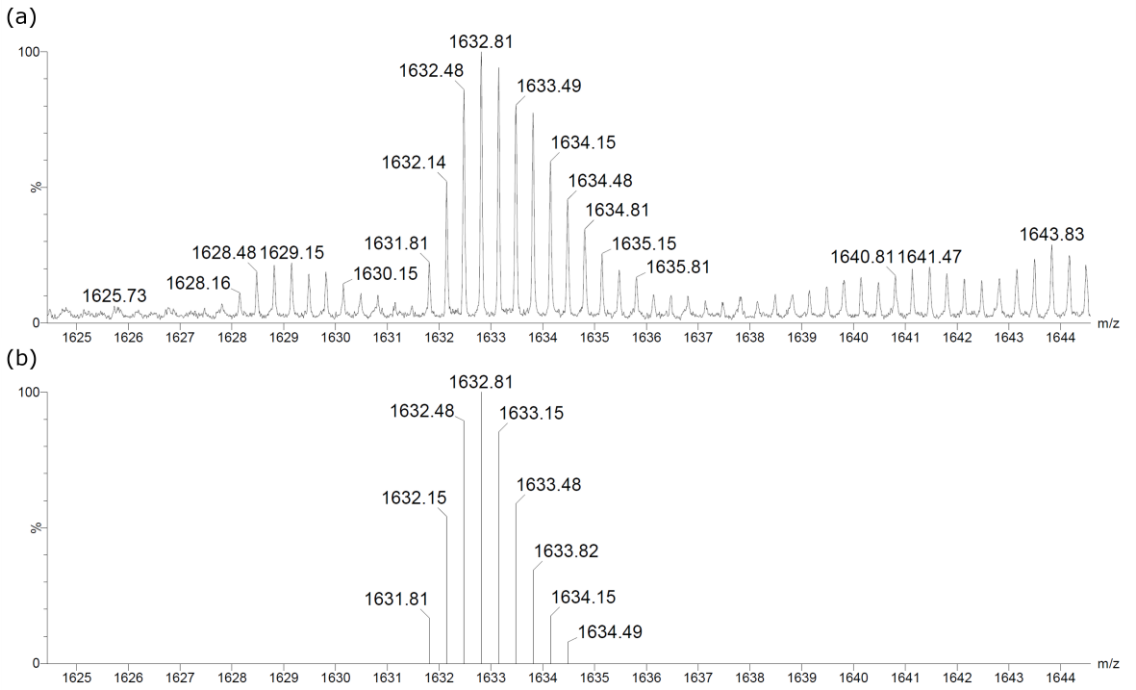

Figure S10. (a) MS peak corresponding to the $[M-3H]^{3-}$ ion in the spectrum of **3** and (b) theoretically calculated isotope profile for $[M-3H]^{3-}$.

Crystallographic data for 3

CCDC 1539623 contains the supplementary crystallographic data for this paper. This data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

Crystal data for **3**	
Moiety formula	$C_{288}H_{336}N_{24}O_{48} \times 13.5(C_7H_8)$
Empirical formula	$C_{382.5}H_{444}N_{24}O_{48}$
Formula weight	6145.59
Temperature (K)	100
Wavelength (Å)	1.54184
Crystal system	Trigonal
Space group	R-3c
Unit cell dimensions a/b/c (Å) α/β/γ (°)	36.9553(7) 36.9553(7) 119.924(3) 90 90 120
Unit cell volume (Å^3)	141838(6)
Z	12
Calculated density (g/cm^3)	0.863
Absorption coefficient (mm^{-1})	0.452
F(000)	39492
θ range for data collection (°)	71.214 – 3.673
Index ranges	-73 < h < 74 -45 < k < 43 -88 < l < 99
Reflections collected	41648
Independent reflections	30276 (R_{int} = 0.1141)
Completeness to θ_{max}	0.99
Refinement statistics	
Final R indices [>2σ(I)]	0.0829
R indices [all data]	0.1497
Goodness-of-fit	0.864
Largest diff. peak and hole (e/Å^3)	0.411 / - 0.288

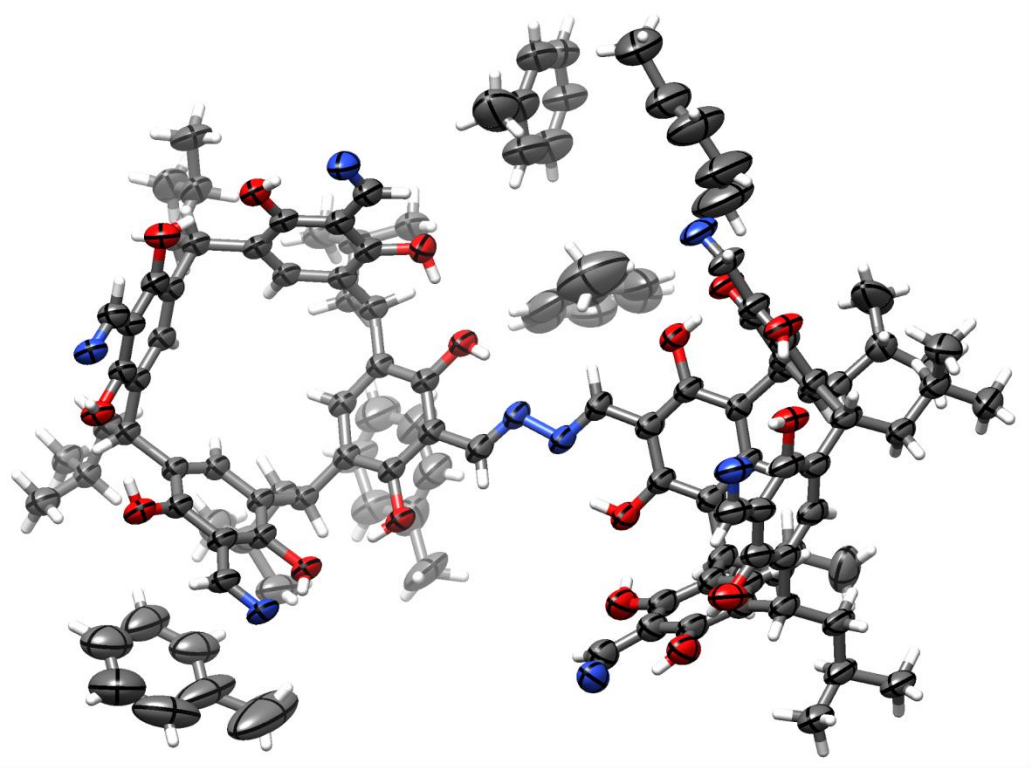

Figure S11. ORTEP representation of the asymmetric unit of the crystal structure of **3** with thermal ellipsoids scaled at 50% probability.

Ab initio calculations

All theoretical calculations were performed within the density functional theory (DFT) using Gaussian 09 program suite.[2] The geometry of the initial structure (MODEL-1) was retrieved from the crystal structure of **3** and then it was optimized by ground state method at the B3LYP/6-31G(d) level.
Excited electronic states were determined at the B3LYP/6-31G(d) level by means of the time-dependent DFT (TD DFT) approach (100 excited states). The ECD and UV spectra were simulated by overlapping Gaussian functions for each transition. Presentation of molecular orbitals was performed by using the GaussView program.

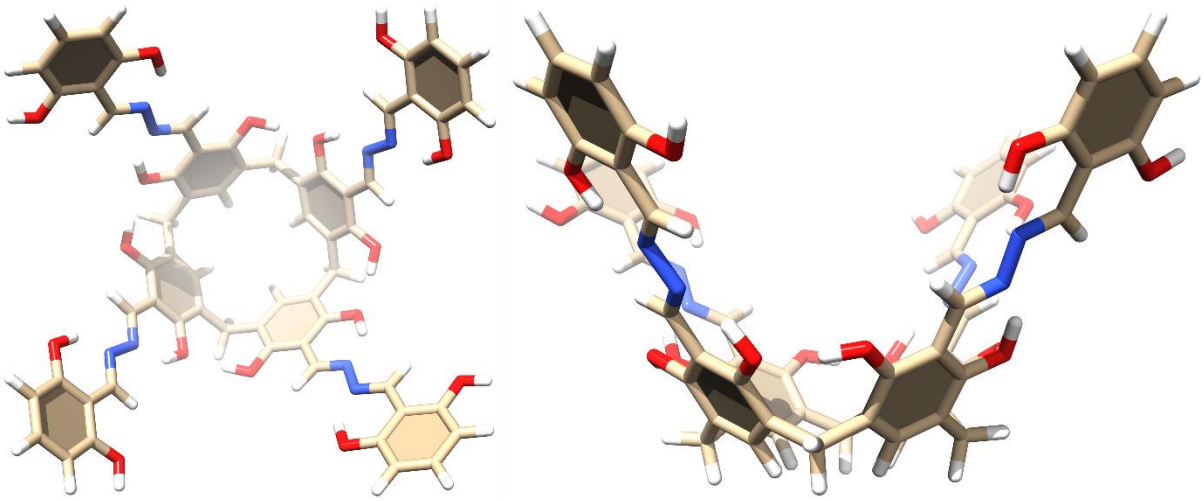

Figure S12. Molecular model (MODEL-1) used for theoretical calculations (initial geometry was retrieved from the crystal structure of **3**).

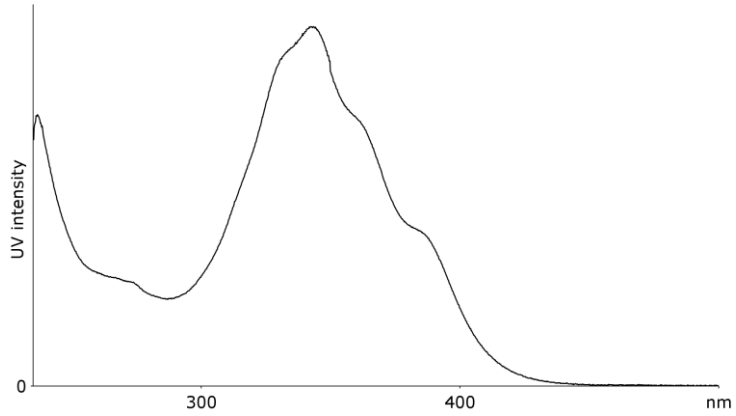

Figure S13. Experimental UV spectrum of **3** in $CHCl_3$.

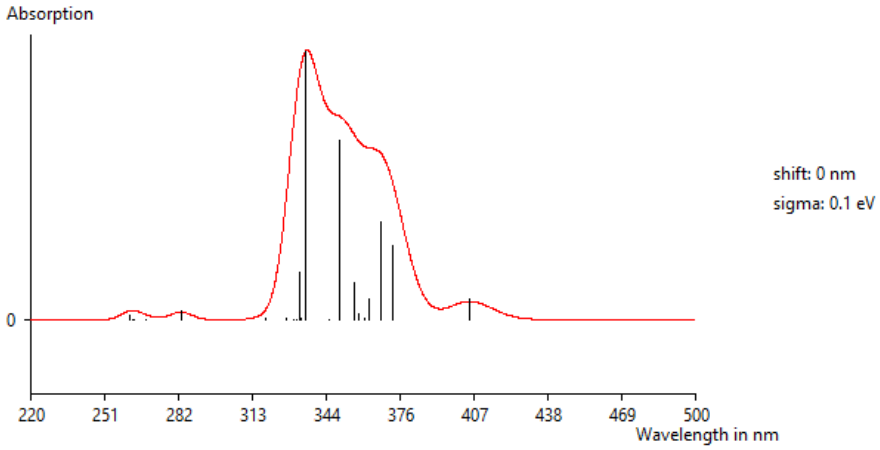

Figure S14. Theoretically calculated UV spectrum for MODEL-1 (B3LYP/6-31G(d)).

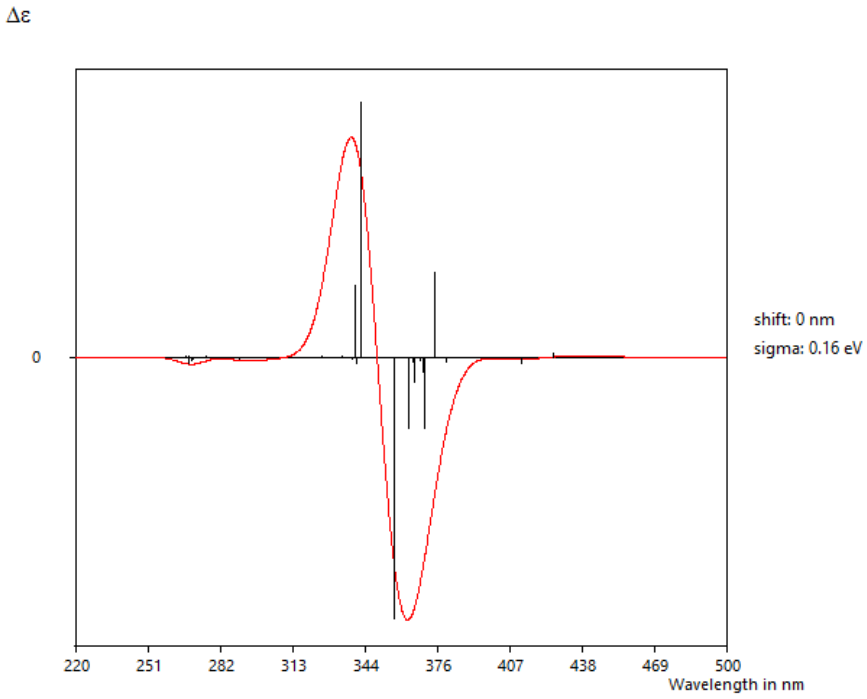

Figure S15. Theoretically calculated CD spectrum for MODEL-1 (B3LYP/6-31G(d)).

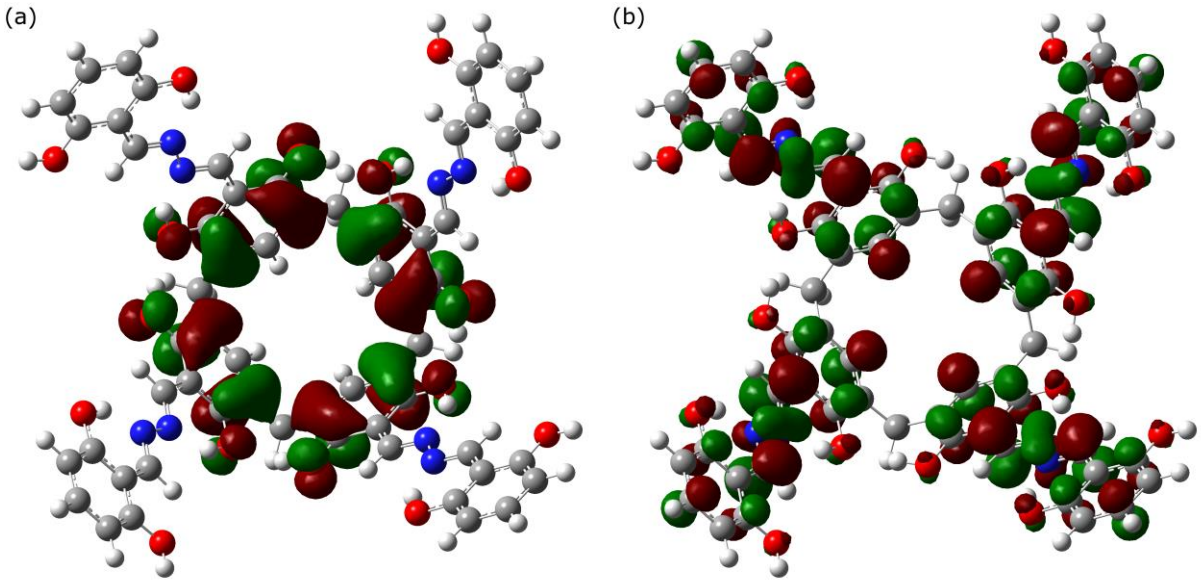

Figure S16. Graphical representation of (a) HOMO and (b) LUMO orbitals for MODEL-1.

Atomic Cartesian coordinates for MODEL-1 optimized geometry:

C	8.69546800	-4.11060300	-4.69931500
H	9.31001600	-4.28082700	-5.57918200
C	7.77656800	-2.59977900	-3.05872200
C	7.10308600	-3.68415800	-2.42454300
C	7.26059300	-4.98150000	-2.97512100
C	6.27429600	-3.49772100	-1.25653000
H	5.78696900	-4.37206300	-0.82379600
C	3.23167800	0.53434500	3.72649800
C	2.58057300	-0.57977200	4.26533500
H	1.94726600	-0.42711300	5.13781000
C	2.69841300	-1.87587000	3.76127200
C	3.54552500	-2.06270900	2.66456000
C	4.23444200	-0.97415300	2.07016300
C	4.05126500	0.33009600	2.60435600
C	5.08238400	-1.15128300	0.91268900
H	5.55471500	-0.26978900	0.48084500
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C	-0.57961500	-2.58045900	4.26557300
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C	-1.87572000	-2.69828100	3.76150800
C	-2.06259000	-3.54548000	2.66487600
C	-0.97407300	-4.23450700	2.07053700
C	0.33016700	-4.05137100	2.60474500
C	-1.15123800	-5.08246900	0.91307800
H	-0.26976200	-5.55487300	0.48127800
C	-3.23148300	-0.53431100	3.72676800
C	-2.58037300	0.57982900	4.26551600
H	-1.94701300	0.42724700	5.13796300
C	-2.69825300	1.87591000	3.76138500
C	-3.54543200	2.06268300	2.66473100
C	-4.23436700	0.97408200	2.07040800
C	-4.05113000	-0.33012700	2.60465000

C	-5.08237100	1.15111000	0.91295600
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C	0.57982200	2.58052900	4.26539500
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C	0.97411500	4.23444400	2.07024000
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N	2.32277800	5.27784300	0.38613900
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H	6.77497300	-6.82643100	-2.81834800
O	7.67749100	-1.34340300	-2.59960800
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O	4.73220900	1.32974200	1.99447800
H	4.29618400	2.20059900	2.13942400
O	3.68890400	-3.32521500	2.17317300
H	4.31507200	-3.28262200	1.38490200
O	1.32980300	-4.73243100	1.99497600
H	2.20065100	-4.29640300	2.13993100
O	-3.32511400	-3.68886300	2.17351000
H	-3.28251300	-4.31501200	1.38522700
O	-4.73204900	-1.32982300	1.99483700
H	-4.29610300	-2.20069100	2.13997500
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C	4.98155600	7.26037300	-2.97504600
O	1.34350400	7.67789600	-2.59961500
C	4.11091600	8.69538200	-4.69925600
H	4.28125400	9.30989900	-5.57912300
O	5.99851900	6.60196800	-2.34383600
H	6.82641400	6.77451200	-2.81819600
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H	-9.31042500	4.28003200	-5.57901000
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H	-6.77541200	6.82588800	-2.81837500
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H	-6.82616800	-6.77288500	-2.81918200
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H	-1.77111700	2.84819400	5.42346200
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H	3.95738800	2.49366100	4.27447000
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H	2.49385400	-3.95729200	4.27463500
C	-3.03345200	-1.90980600	4.35247500
H	-3.95713300	-2.49364400	4.27482100
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H	-6.20051600	-8.15360400	-4.50828300
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H	-1.97760400	-9.06757700	-4.65137800
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C	-8.04827400	5.19706900	-4.10097000
H	-8.15590100	6.19988900	-4.50752900

[1] M. Grajda, M. Wierzbicki, P. Cmoch, A. Szumna, *J. Org. Chem.*, 2013, **78**, 11597-11601.

[2] *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, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, **2009**.