Supplementary Information

Cylindrical Macrocyclic Compounds Synthesized by Connecting of Two Bowl-Shaped Calix[3]aramide Moieties: Structures and Chiroptical Properties

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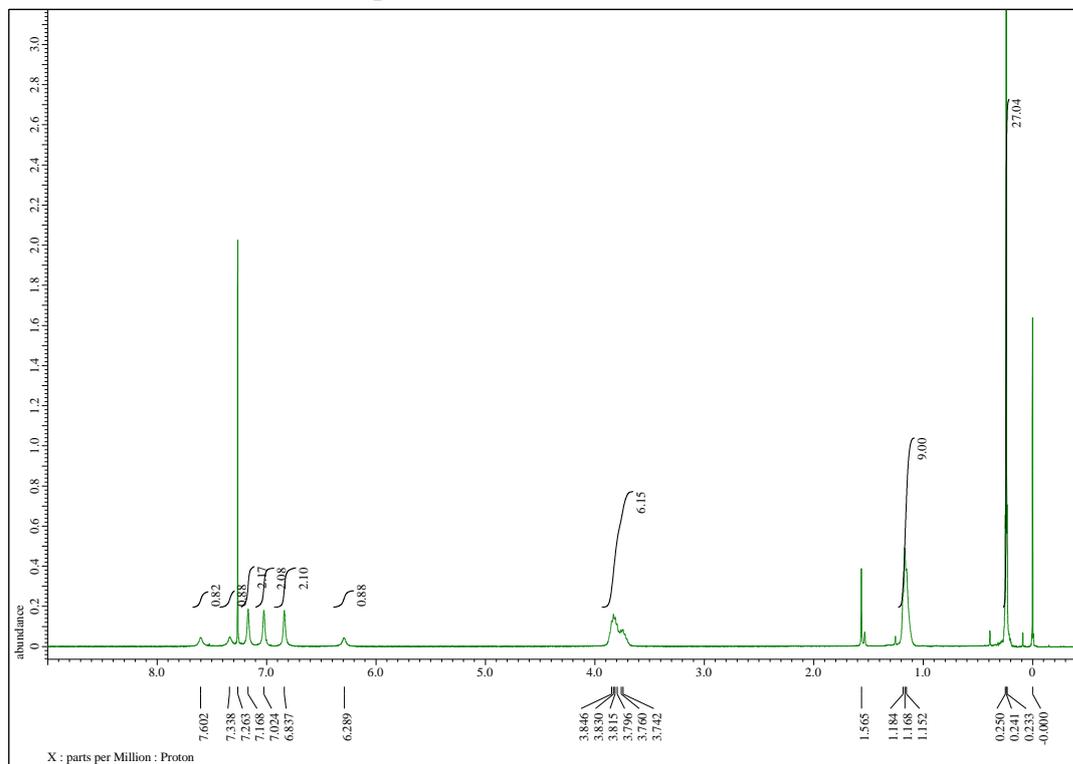

Fig. S1 ^{1}H NMR (400 MHz, CDCl$_3$) spectrum of calix[3]aramide **3**.
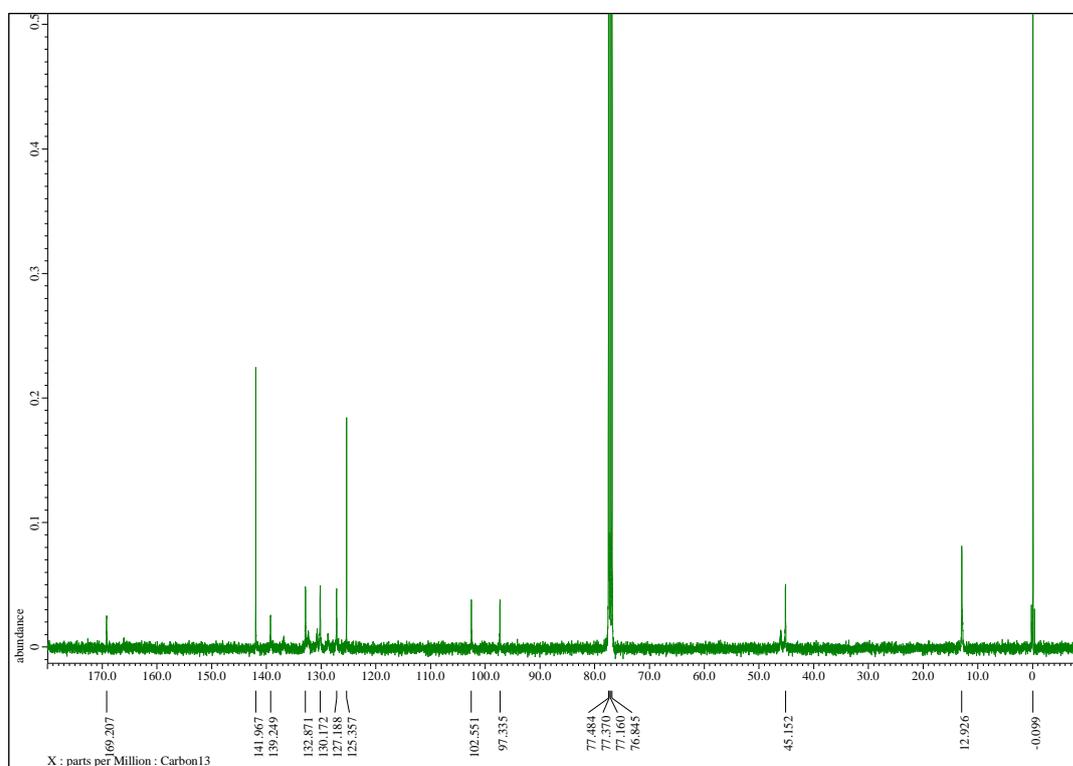

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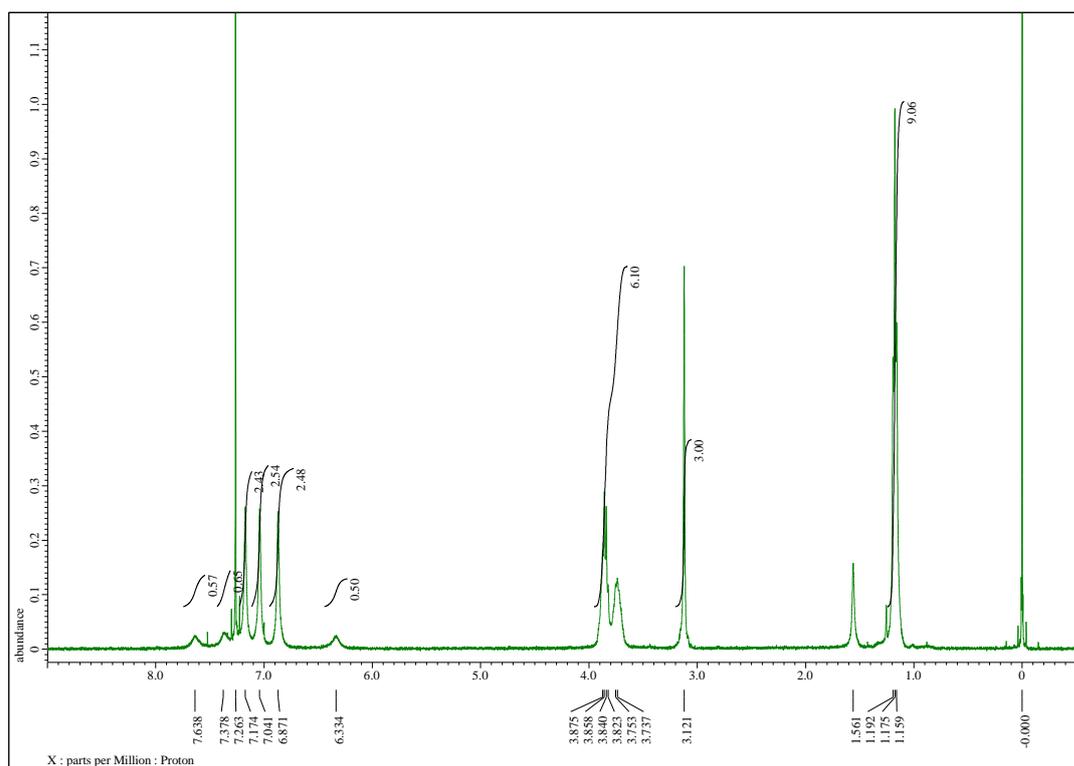
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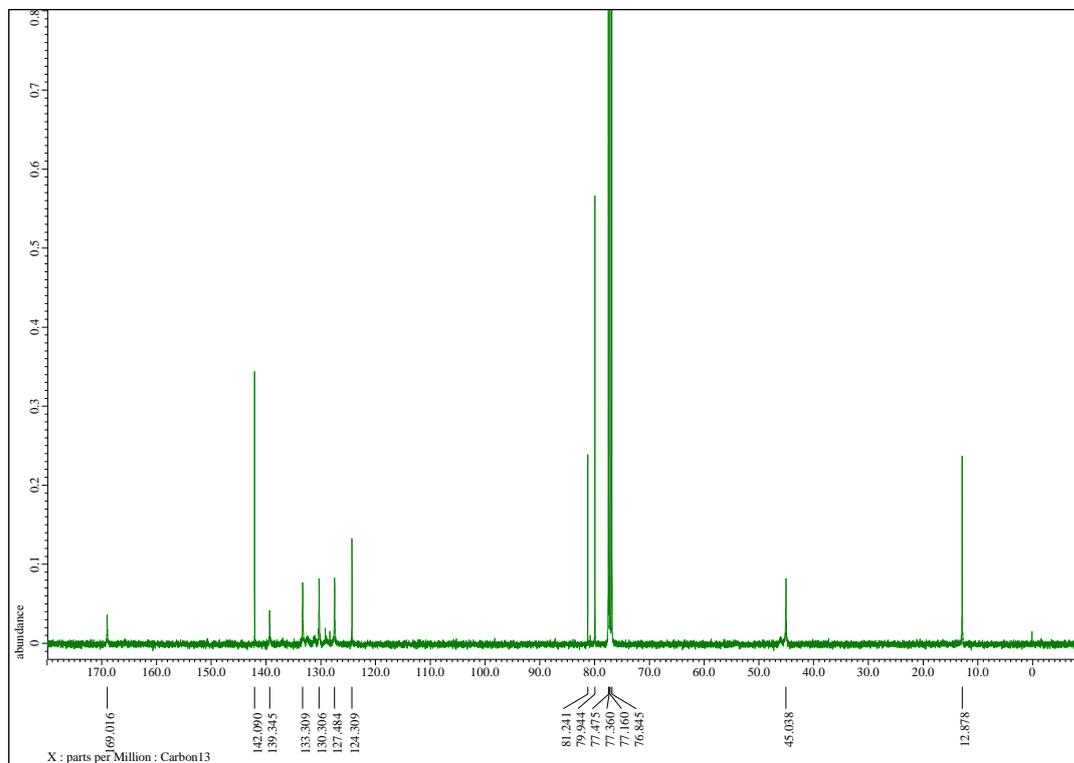
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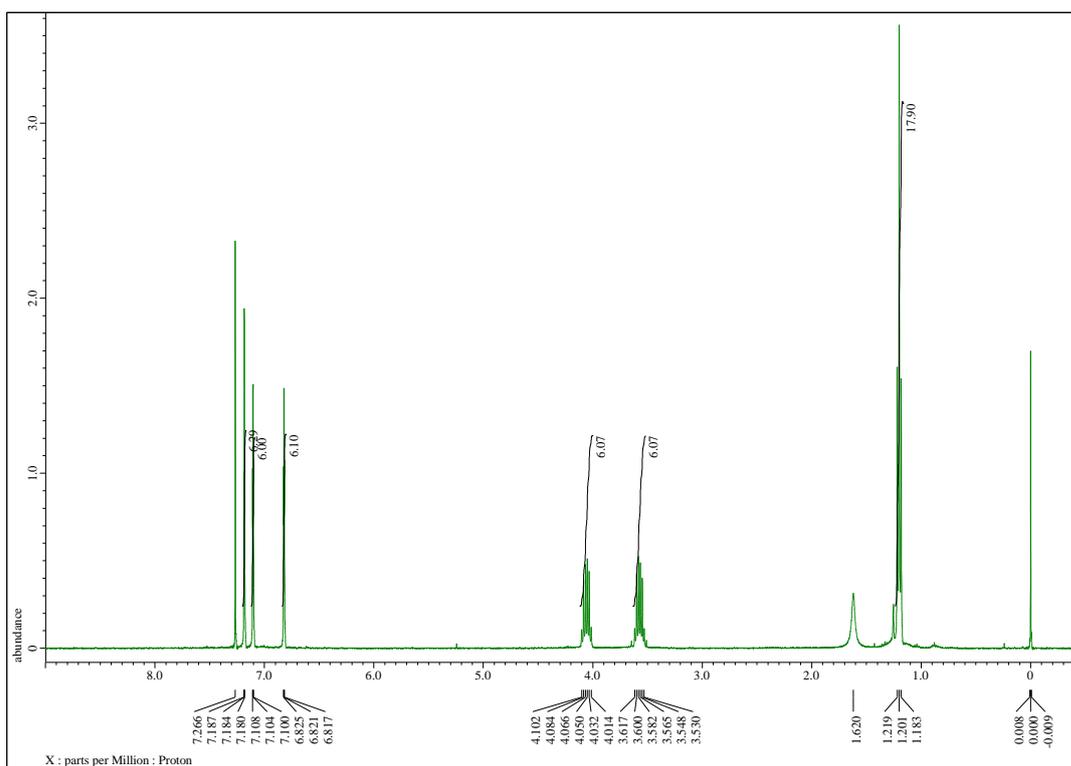
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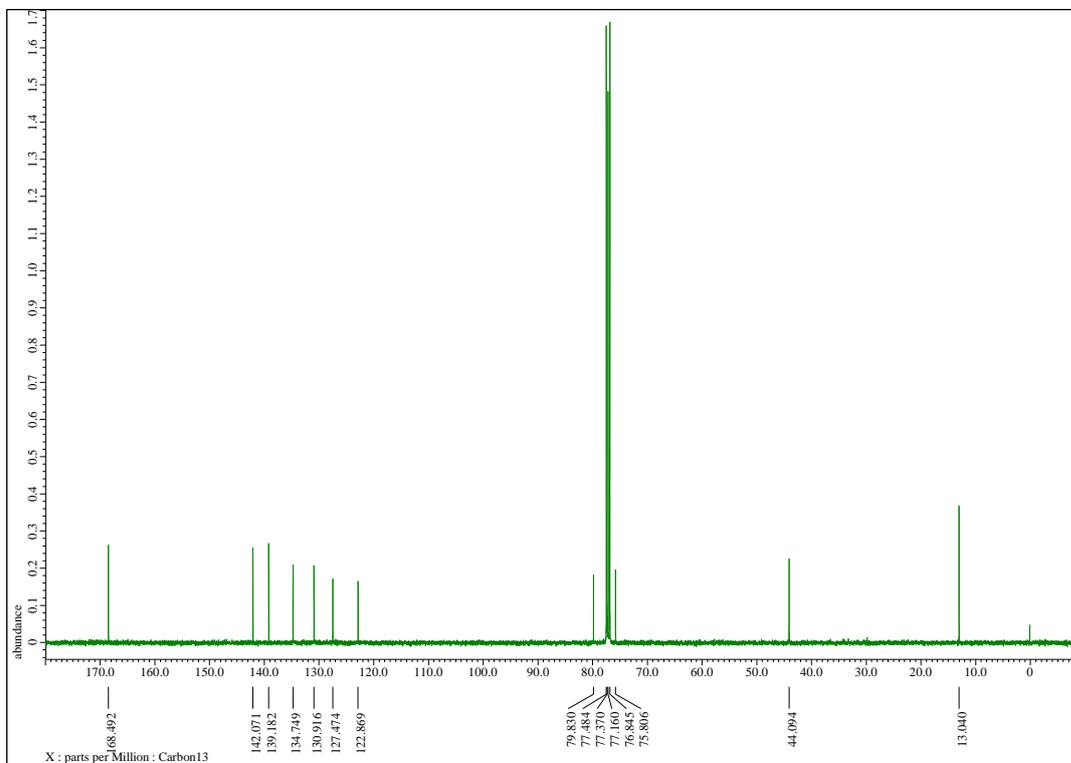
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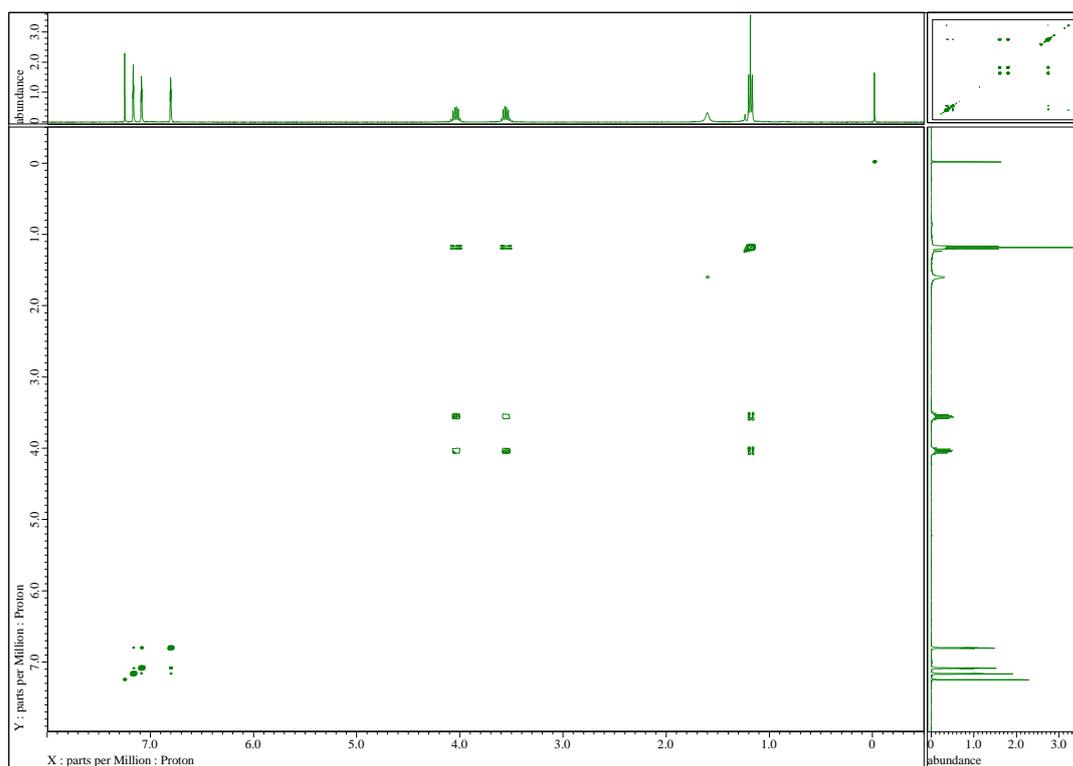
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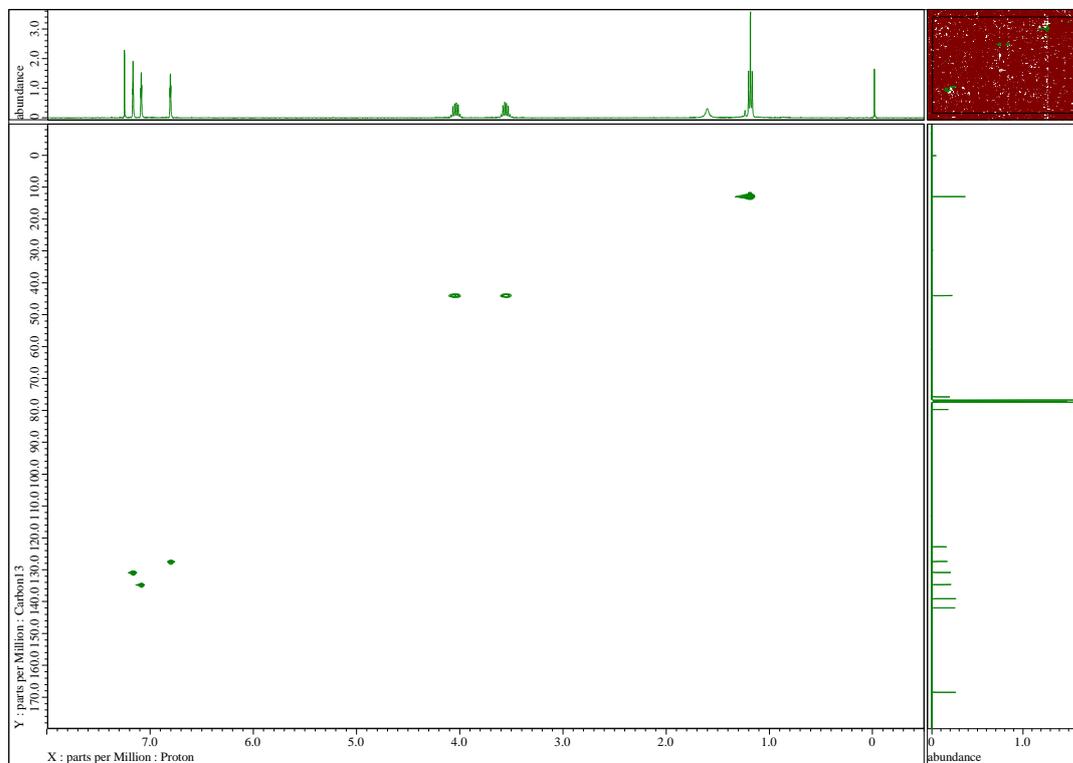
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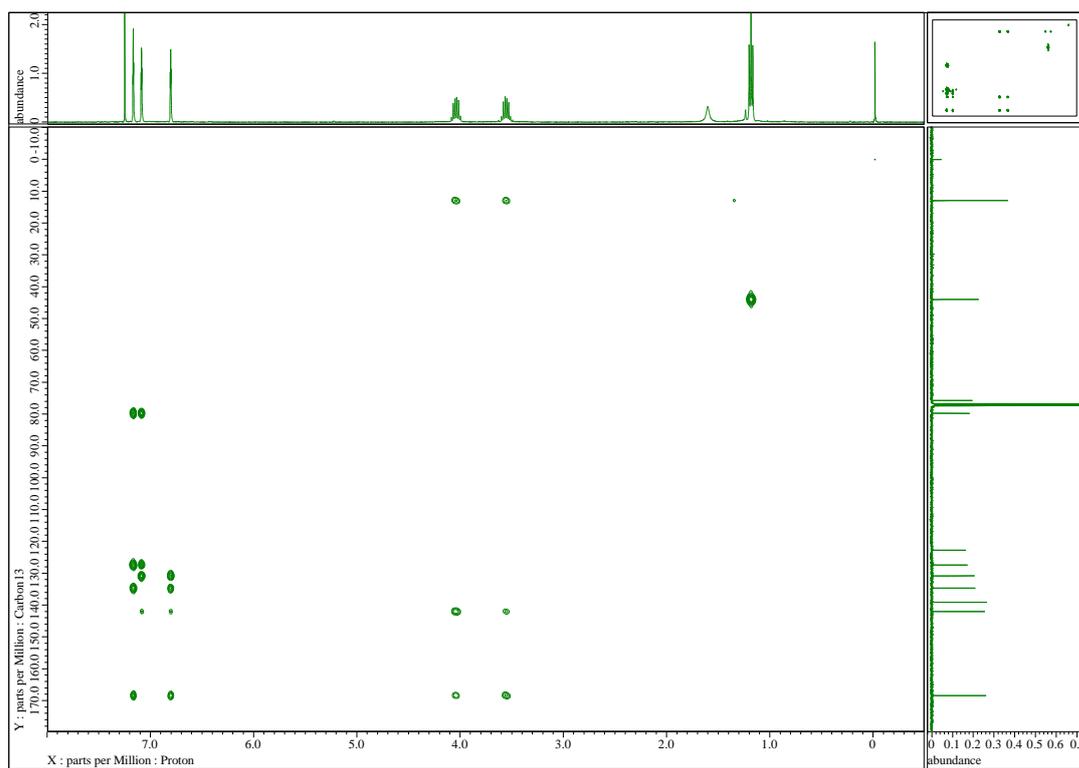
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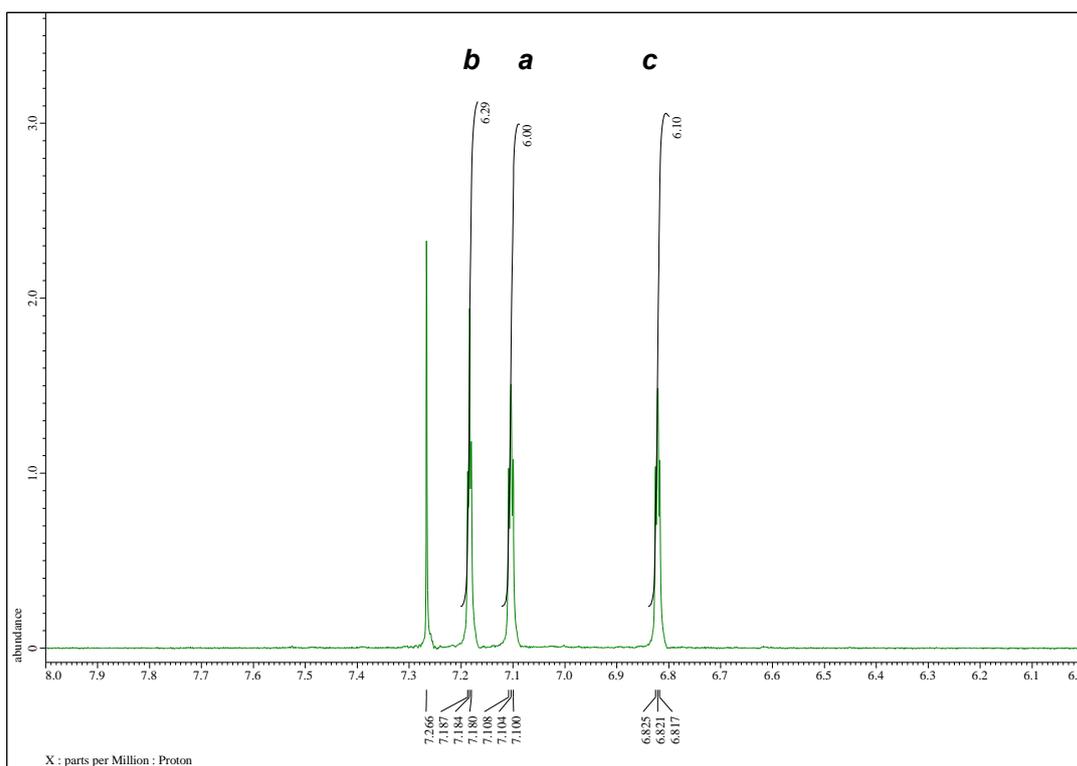
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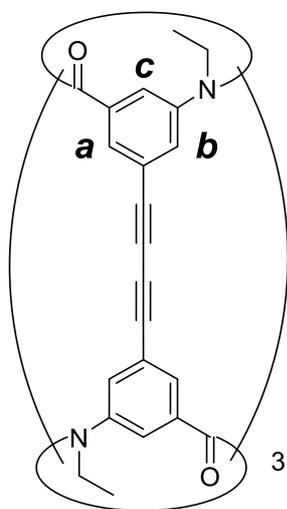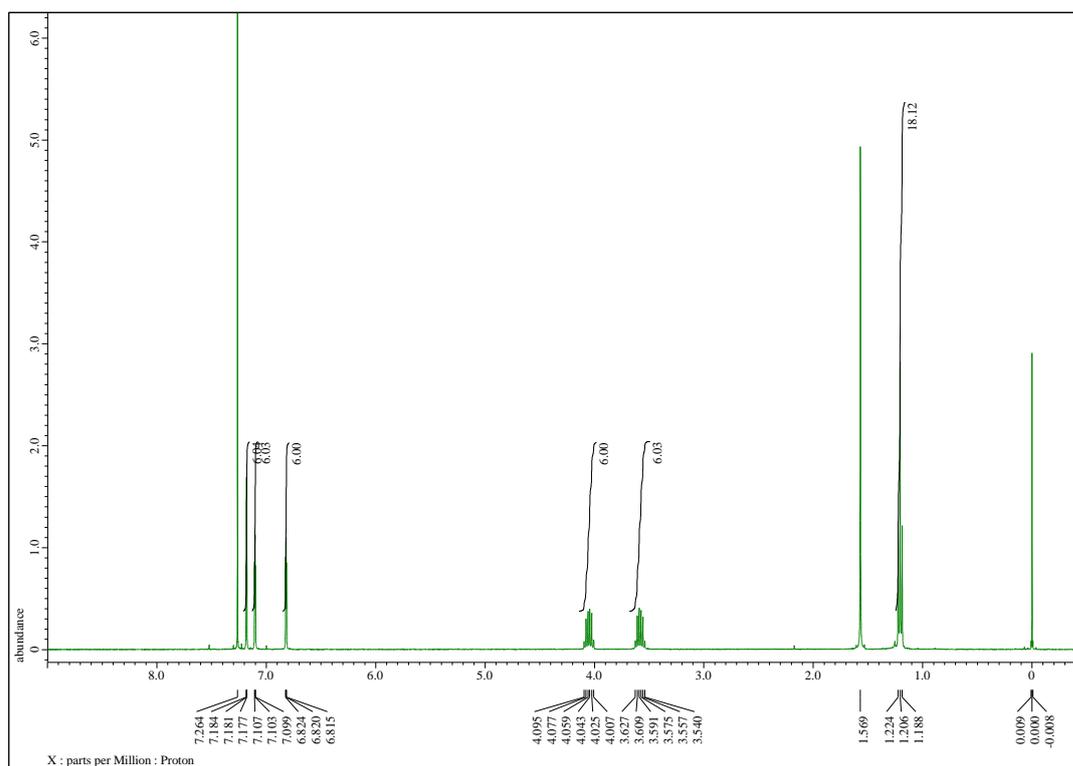
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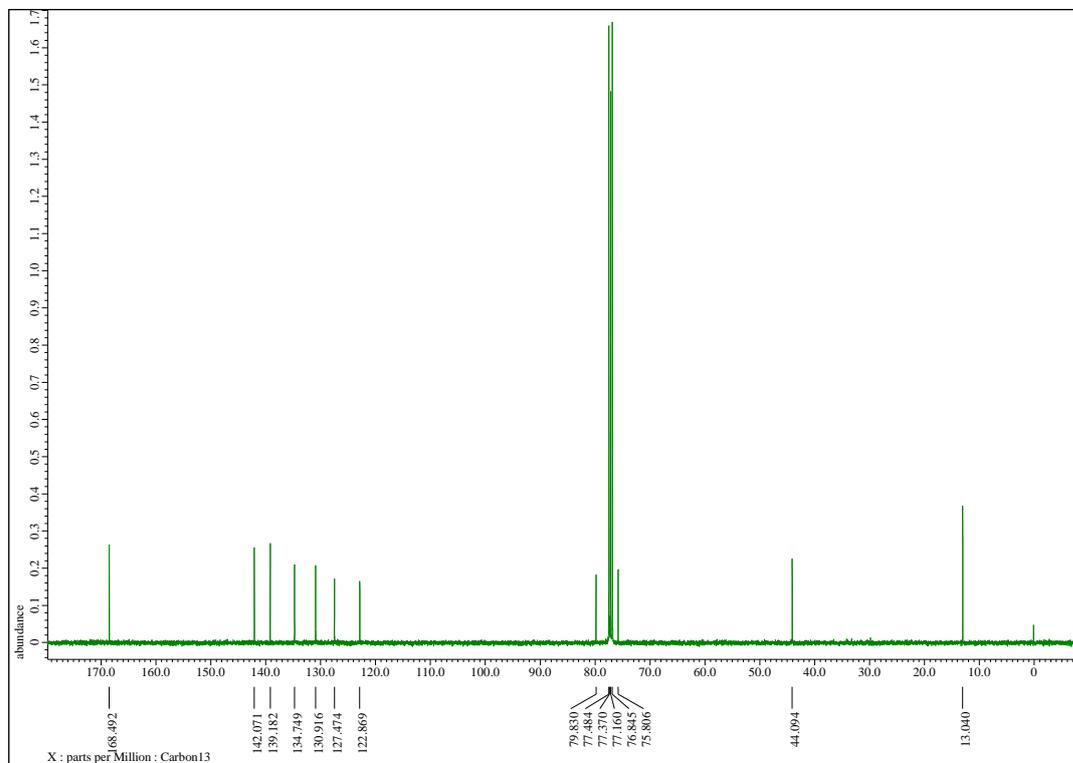
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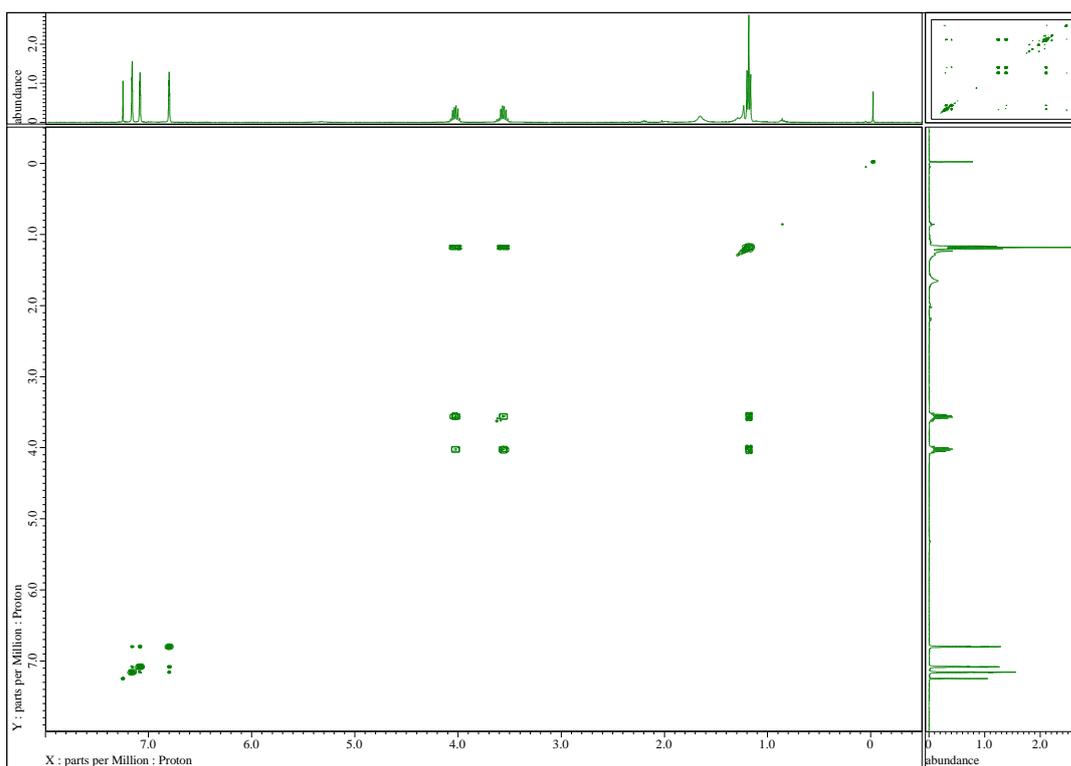
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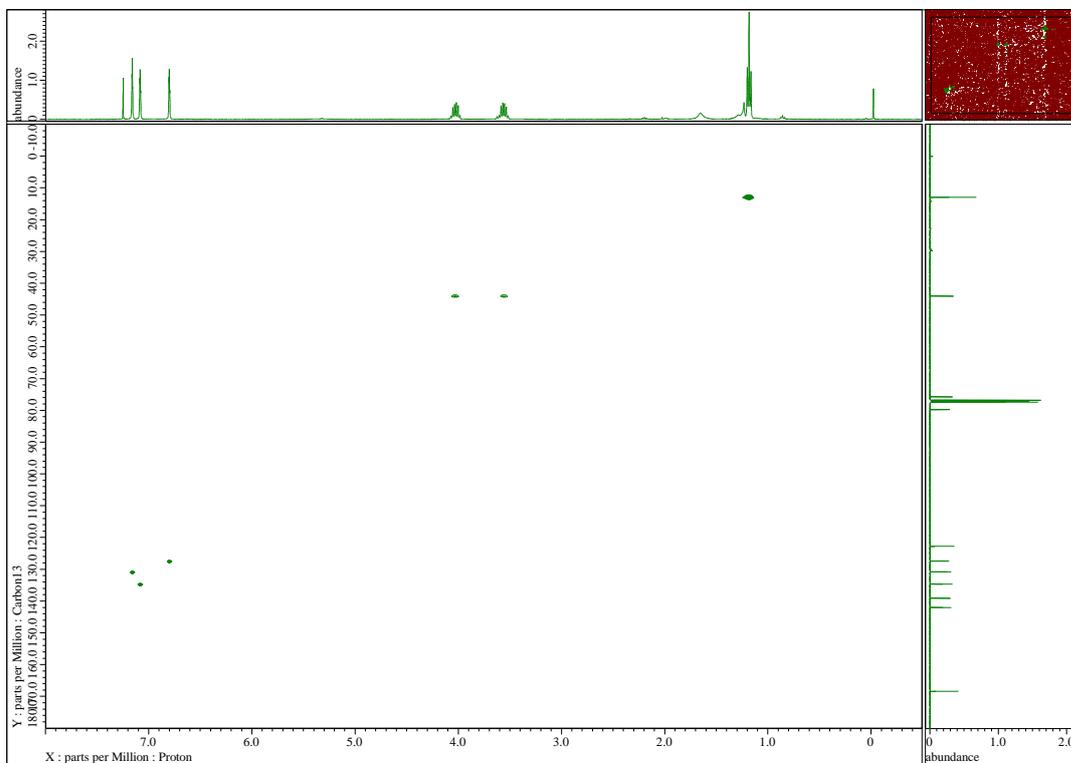
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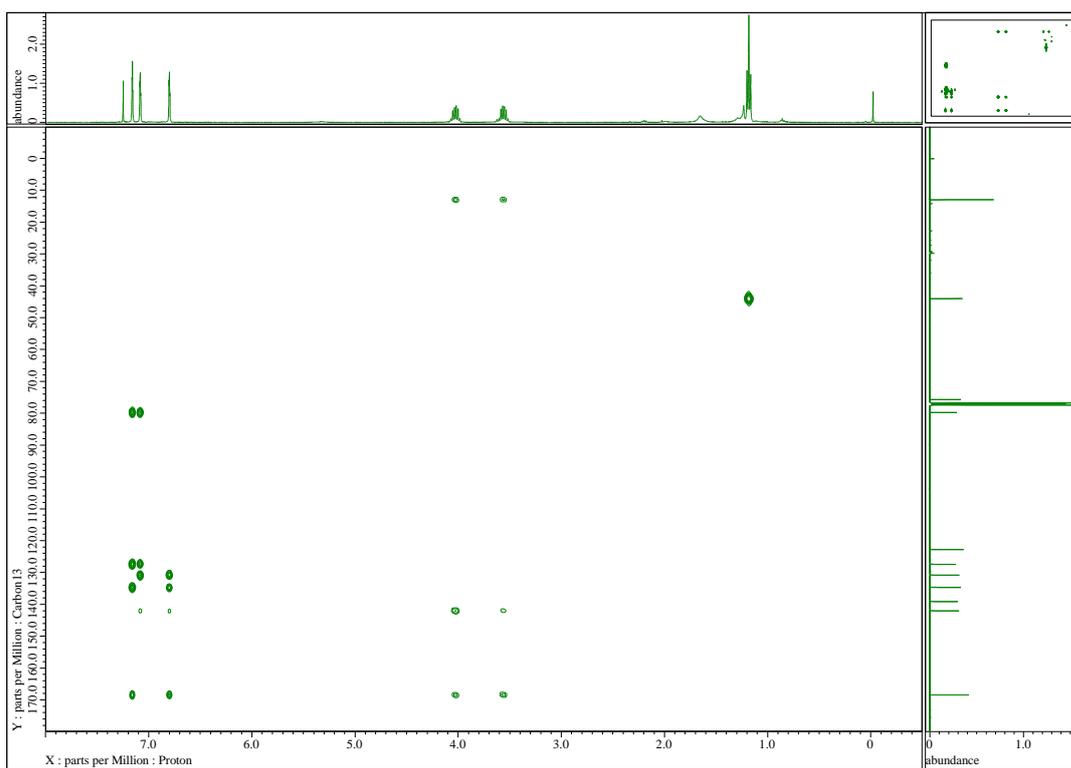
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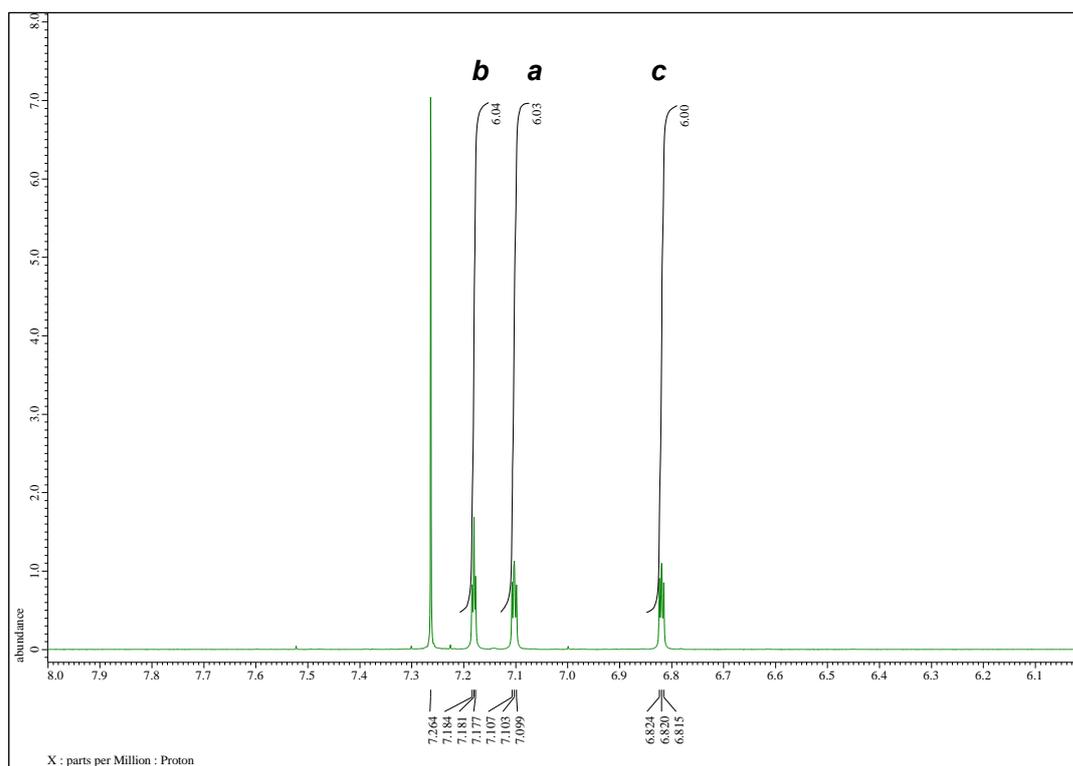
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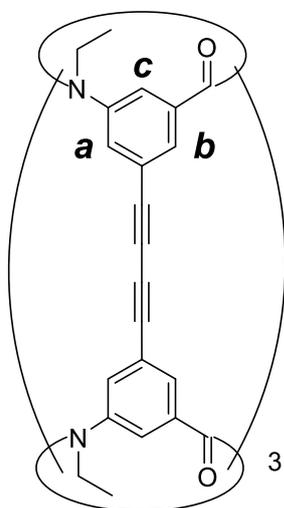
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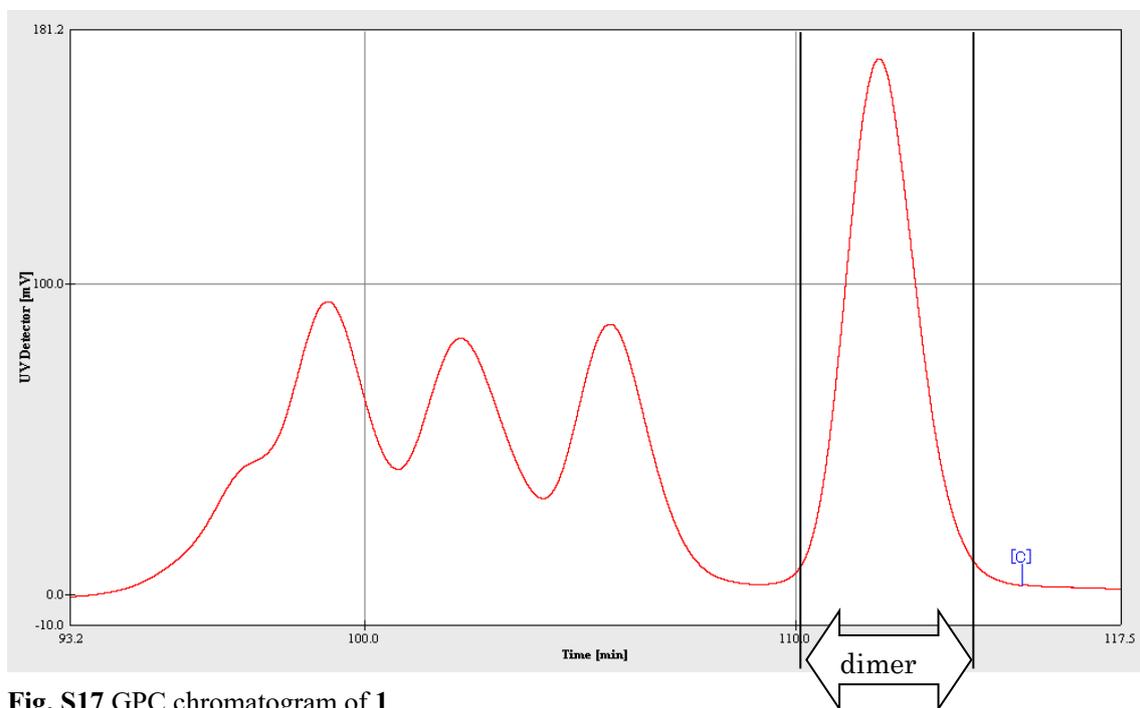
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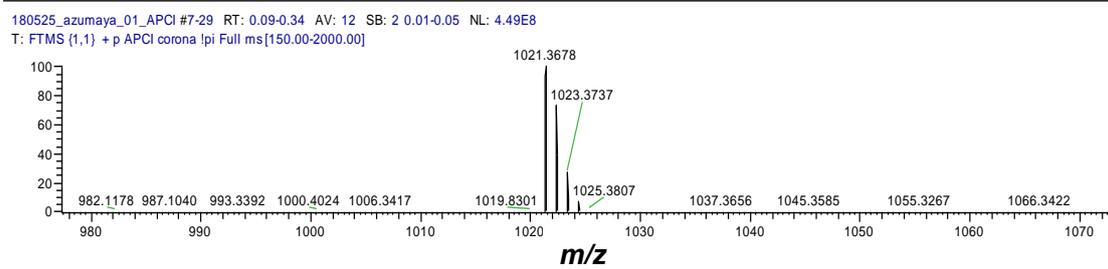
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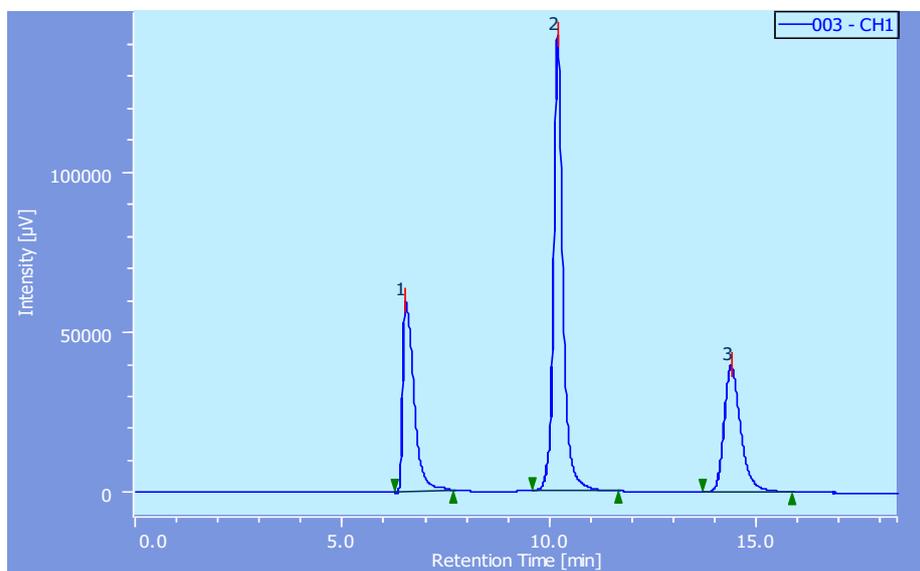
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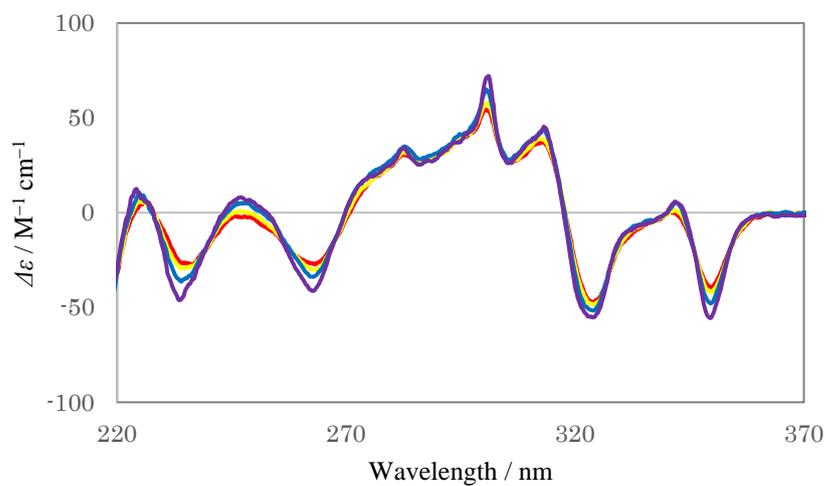
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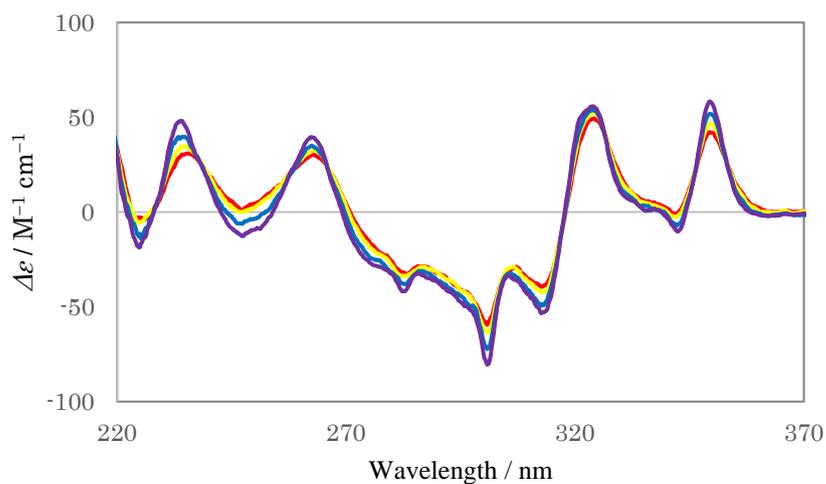
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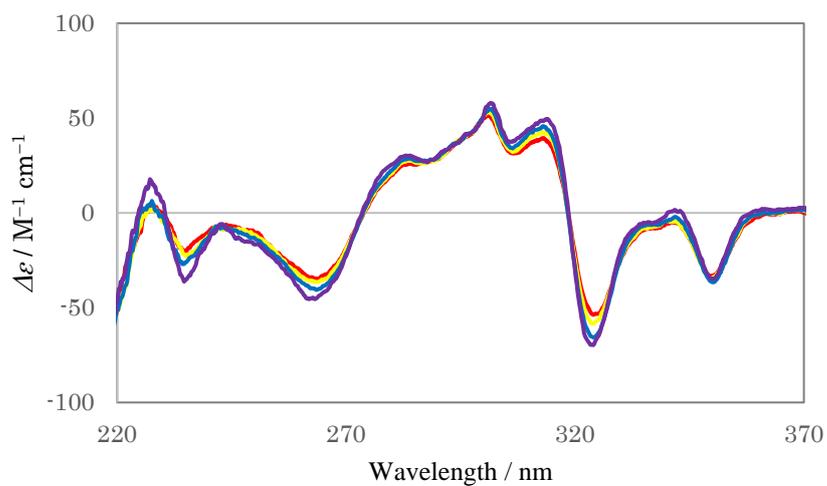
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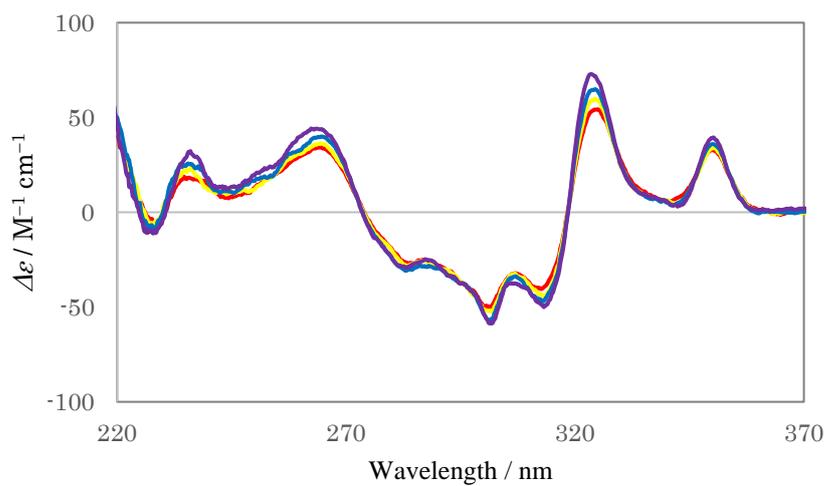
Fig. S23 Temperature dependent ECD spectra of **1**–(*MM*) in THF (red line: 20 °C, yellow line: −10 °C, blue line: −50 °C, purple line: −90 °C).

Defined by the sign of the dihedral angle θ of the two C=O groups
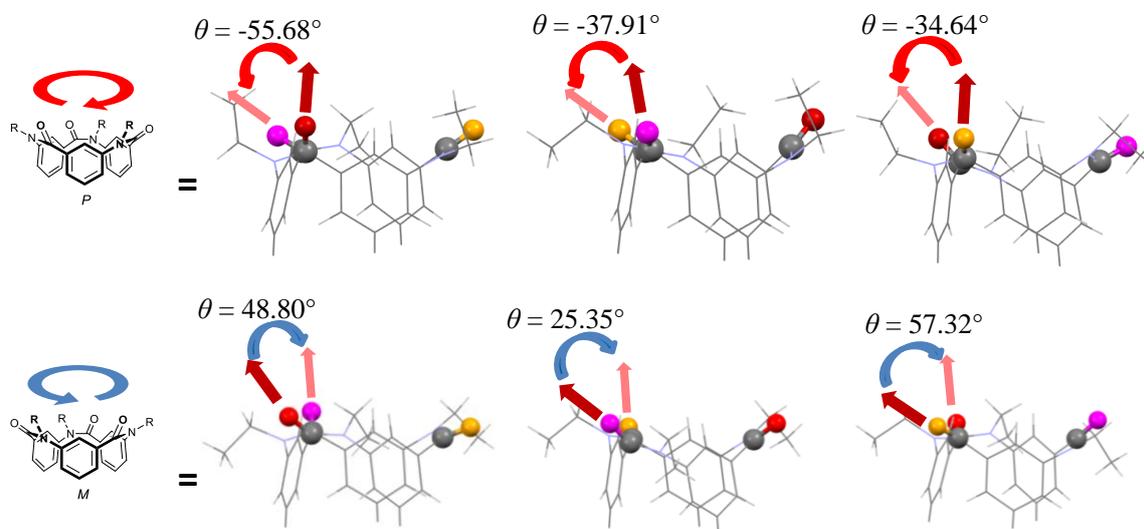
Fig. S24 The illustrative representation of the definition θ (the dihedral angle of two C=O groups) of all angles. Colors: C, gray spheres; O, red, magenta and orange spheres.

2. X-ray crystallographic structures

X-ray data were collected on a Rigaku XtaLAB P200 diffractometer with multi-layer mirror monochromated Cu$K\alpha$ ($\lambda = 1.54187$Å) and a hybrid photon counting detector (PILATUS 200K). The crystal structure was solved by direct methods (SHELXT Version 2014/5)[S1] and refined by full-matrix least-squares SHELXL-2014/7.[S2] The frame data were integrated, and the absorption correction was calculated using the Rigaku CrystalClear, CrysAlisPro program package. All non-hydrogen atoms were refined anisotropically. CCDC 1992363 (**1-(PM)**), 1992335 (**1-(MM)**), 1992336 (**1-(racemic mixture)**)) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

1-(PM): $C_{66}H_{48}N_6O_6$, $M_r = 1021.17$, $0.380 \times 0.050 \times 0.030$ mm, orthorhombic, $P2_12_12_1$ (no. 19), $a = 13.94016(11)$, $b = 20.05398(18)$, $c = 23.6535(2)$ Å, $\alpha = \beta = \gamma = 90°$ $V = 6612.47(10)$ Å^3, $Z = 4$, $D_{calcd.} = 1.029$ gcm^{-3}, $2\theta_{max} = 68.243$, $T = 93$ K, 43644 reflections measured, 12030 unique ($R_{int} = 0.0469$), $\mu = 0.535$ mm^{-1}, $T_{max} = 0.984$, $T_{min} = 0.531$, Flack parameter = 0.25(8).[S3] The final R_1 ([$I > 2\sigma(I)$] on $|F|$) and wR_2 were 0.0443 and 0.1209 (all data on F^2) for 712 parameters and 0 restraint. The residual electron densities (peak and hole) were 0.53 and -0.24 eÅ^{-3}. All non-H-atoms were refined anisotropically, and H-atoms were fixed in geometrically estimated positions and refined using the riding model. C47 and C90 (and each connecting hydrogen atoms) are terminal methyl groups of a disordered **1**-(PM), and the occupancy factors were 0.5 respectively. The crystal may include some disordered solvent molecules. Removal of the solvent molecules and subsequent refinement were executed using SQUEEZE, part of the PLATON program.[S4] PLATON/SQUEEZE shows the total potential solvent accessible void volume is 1679 Å^3 and residual electrons count 427 in the unit cell.

1-(MM): $C_{66}H_{48}N_6O_6 \cdot 4(C_7H_8)$, $M_r = 1389.70$, $0.110 \times 0.100 \times 0.040$ mm, monoclinic, $P2_1$ (no. 4), $a = 13.24395(6)$, $b = 15.40880(9)$, $c = 18.44394(11)$ Å, $\beta = 90.3886(5)$ °, $V = 3763.83(4)$ Å^3, $Z = 2$, $D_{calcd.} = 1.226$ gcm^{-3}, $2\theta_{max} = 68.247$, $T = 93$ K, 49930 reflections measured, 13384 unique ($R_{int} = 0.0375$), $\mu = 0.605$ mm^{-1}, $T_{max} = 0.976$, $T_{min} = 0.890$, Flack parameter = 0.04(5).[S3] The final R_1 ([$I > 2\sigma(I)$] on $|F|$) and wR_2 were 0.0367 and 0.1012 (all data on F^2) for 965 parameters and 1 restraint. The residual electron densities (peak and hole) were 0.52 and -0.25 eÅ^{-3}. All non-H-atoms were refined anisotropically, and H-atoms were fixed in geometrically estimated positions and refined using the riding model.

1-(racemic mixture): $C_{66}H_{48}N_6O_6 \cdot 3(C_7H_8)$, $M_r = 1297.56$, $0.177 \times 0.064 \times 0.020$ mm, monoclinic, $P2_1/c$ (no. 14), $a = 15.62470(10)$, $b = 16.17640(10)$, $c = 27.9001(2)$ Å, $\beta = 97.4931(7)$ °, $V = 6991.57(8)$ Å^3, $Z = 4$, $D_{calcd.} = 1.233$ gcm^{-3}, $2\theta_{max} = 68.248$, $T = 93$ K, 91416 reflections measured, 12754 unique

($R_{int} = 0.0435$), $\mu = 0.615$ mm^{-1}, $T_{max} = 0.988$, $T_{min} = 0.855$. The final R_1 ([$I > 2\sigma(I)$] on $|F|$) and wR_2 were 0.0443 and 0.1250 (all data on F^2) for 916 parameters and 0 restraints. The residual electron densities (peak and hole) were 0.38 and -0.32 eÅ^{-3}. All non-H-atoms were refined anisotropically, and H-atoms were fixed in geometrically estimated positions and refined using the riding model. C52A and C52B (and each connecting hydrogen atoms) are terminal methyl groups of a disordered **1**-(*racemic mixture*). C52A and C52B have about 0.702 and 0.298 of occupancies respectively (total occupancy is 1.0).

3. References

S1. G. M. Sheldrick, *Acta Crystallogr.,* 2014, **A70**, C1437.

S2. G. M. Sheldrick, *Acta Crystallogr.,* 2015, **C71**, 3–8.

S3. (a) H. D. Flack and G. Bernardinelli, *Acta Crystallogr.,* 1999, **A55**, 908–915; (b) H. D. Flack and G. Bernardinelli, *J. Appl. Crystallogr.,* 2000, **33**, 1143–1148.

S4. A. L. Spek, *Acta Crystallogr.,* 2015, **C71**, 9–18.