Supporting information for

Ene reaction between two alkynes? Doors open to thermally induced cycloisomerization of macrocyclic triynes and enediynes

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General considerations

Unless otherwise noted, materials were obtained from commercial suppliers and used without further purification. Solvents were removed under reduced pressure with a rotary evaporator. When necessary, reaction mixtures were chromatographed on silica gel (230-400 mesh) using a gradient solvent system as the eluent.

All 1D and 2D ^{1}H and ^{13}C NMR spectra were recorded on a 600, 400, 300 or 200 MHz NMR spectrometers at 298K using $CDCl_3$ as a deuterated solvent. Chemical shifts (δ) for ^{1}H and ^{13}C NMR were referenced to internal solvent resonances and reported relative to $SiMe_4$.The ^{2}H NMR spectrum of compound 3a-D (dissolved in $CHCl_3$) was recorded in a 500 MHz spectrometer using the lock deuterium coil.

Electrospray mass spectrometry analyses were recorded on an Esquire 6000 Ion Trap Mass Spectrometer (Bruker) equipped with an electrospray ion source. The instrument was operated in the positive ESI(+) ion mode.

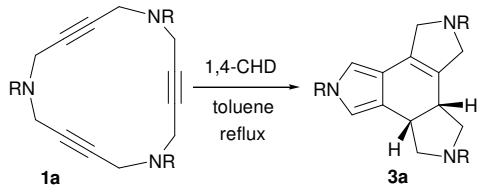
Synthesis of macrocycles **1a**,[1] **1b**,[1] anc **1c**,[2] has been previously reported.

The EPR spectra were obtained using a Bruker ELEXYS E500 X band spectrometer equipped with a field-frequency (F/F) lock accessory and built in NMR Gaussmeter. A rectangular TE102 cavity was used for the measurements. The signal to noise ratio of spectra was increased by accumulation of scans using the F/F lock accessory to guarantee large field reproducibility. Precautions to avoid undesirable spectral distortions and line broadenings, such as those arising from microwave power saturation and magnetic field over modulation, were also taken into account. To avoid dipolar line broadening from dissolved oxygen, solutions were always carefully degassed with pure Argon. To control the temperature a Bruker Variable Temperature Unit was used.

Calorimetric experiments were carried out in a heat conduction differential scanning calorimeter (DSC822 of Mettler Toledo) in an inert atmosphere of nitrogen.

Preparation and characterization data for cycloisomerized derivatives 3

Cycloisomerized derivative 3a

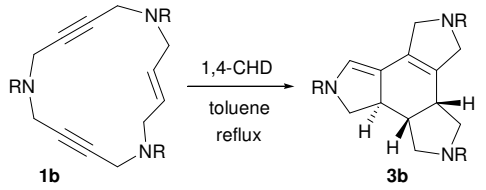


1a **3a**

R = SO_2(2,4,6-triisopropylphenyl)

In a 25 mL pressure flask, a mixture of 1,6,11-tris[(2,4,6-triisopropylphenyl)sulfonyl]-1,6,11-triazacyclopentadeca-3,8,13-triyne, **1a**, (0.049 g, 0.049 mmols) and 1,4-cyclohexadiene (0.095 mL, 1.00 mmol) were degassed and dissolved with toluene (10 mL), previously degassed. The mixture was stirred at reflux for 60h (TLC monitoring). The solvent was removed and the crude was purified by column chromatography using mixtures of hexanes:dichloromethane:ethyl acetate (60:40:2) as the eluent to give the cycloisomerized product **3a** (0.038g, 77% yield), as a colourless solid. m.p. 216-218ºC; IR(ATR): ν = 2955, 1311, 1150 cm^{-1}; ^{1}H NMR (600.13 MHz, $CDCl_3$, 298K, TMS): δ = 1.16-1.20 (m, 22H), 1.24-1.29 (m, 32H), 2.92 (m, 3H), 3.02 (m, 2H), 3.17 (m, 1H), 3.60 (q, *J* = 8.0 Hz, 1H), 3.68 (dd *J* = 9.2 Hz and 7.4 Hz, 1H), 3.74 (t, *J* = 9.2 Hz, 1H), 4.09 (m, 4H), 4.15 (q, *J* = 6.5 Hz, 2H), 4.21 (q, *J* = 6.5 Hz, 2H), 4.28 (m, 2H), 6.79 (s, 1H), 6.88 (s, 1H), 7.15 (s, 2H), 7.19 (s, 2H), 7.20 ppm (s, 2H); ^{13}C NMR (150.90 MHz, $CDCl_3$) δ = 23.4, 23.5, 23.6, 24.6, 24.65, 24.7, 24.8, 29.3, 29.4, 29.6, 29.7, 34.1, 34.2, 35.2, 38.2, 50.5, 52.4, 52.8, 54.5, 113.1, 117.0, 117.6, 121.8, 123.8, 123.9, 124.5, 124.7, 129.8, 130.5, 130.8, 131.2, 151.2, 151.3, 151.5, 153.2, 153.3, 154.8 ppm; HRMS (*m*/*z*) calcd. for $[C_{57}H_{81}N_3O_6S_3 + H]^+$: 1000.5360. Found: 1000.5322.

Cycloisomerized derivative 3b

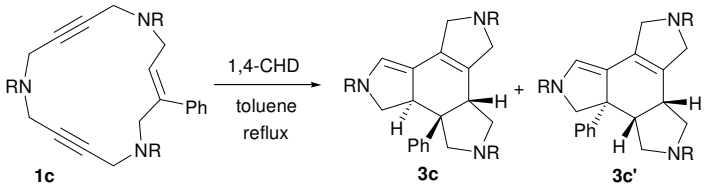


1b **3b**

R = SO_2(2,4,6-triisopropylphenyl)

In a 25 mL pressure flask, a mixture of (*E*)-1,6,11-tris[(2,4,6-triisopropylphenyl)sulfonyl]-1,6,11-triazacyclopentadeca-3-ene-8,13-diyne, **1b** (0.062 g, 0.062 mmols) and 1,4-cyclohexadiene (0.113 mL, 1.24 mmol) were degassed and dissolved with toluene (12 mL), previously degassed. The mixture was stirred at reflux for 6 days (TLC monitoring). The solvent was removed and the crude was purified by column chromatography using mixtures of hexanes:dichloromethane (1:9) as the eluent to give the cycloisomerized product **3b** (0.048g, 78% yield), as a colourless solid. m.p. 222-223ºC; IR(ATR): ν = 2958, 1602, 1308, 1151 cm^{-1}; ^{1}H-NMR (500.13 MHz, $CDCl_3$, 298K, TMS): δ = 1.21-1.32 (m, 54H), 2.40 (m, 1H), 2.93 (m, 5H), 3.12 (q, *J* = 10.4 Hz, 1H), 3.26 (m, 2H), 3.50 (m, 2H), 3.76 (t, *J* = 8.1 Hz, 1H), 4.05 (m, 2H), 4.12 (m, 4H), 4.19 (m, 4H), 6.33 (s, 1H), 7.17 (s, 2H), 7.20 (s, 2H), 7.22 ppm (s, 2H); ^{13}C-NMR (125.75 MHz, $CDCl_3$): δ = 23.5, 23.6, 24.7, 24.8, 29.3, 29.4, 29.5, 29.6, 29.7, 34.1, 34.2, 38.7, 41.9, 42.8, 49.7, 50.0, 51.9, 52.1, 54.9, 116.2, 123.4, 123.9, 124.1, 126.1, 129.9, 130.8, 131.0 131.2, 151.1, 151.2, 151.3, 153.3, 153.4, 153.8 ppm; HRMS (*m*/*z*) calcd. for $[C_{57}H_{83}N_3O_6S_3 + Na]^+$: 1024.5336. Found: 1024.5290.

Cycloisomerized derivatives 3c and 3c'



1c **3c** **3c'**

R = SO_2(4-methylphenyl)

In a 25 mL pressure flask, a mixture of (*Z*)-3-phenyl-1,6,11-tris[(4-methylphenyl)sulfonyl]-1,6,11-triazacyclopentadeca-3-ene-,8,13-diyne **1c** (0.020 g, 0.027 mmols) and 1,4-cyclohexadiene (0.051 mL, 0.54 mmol) were degassed and dissolved with toluene (4 mL), previously degassed. The mixture was stirred at reflux for 11 days (TLC monitoring). The solvent was removed and the crude was purified by column chromatography using mixtures of hexanes:dichloromethane (3:8) as the eluent to give a mixture of cycloisomerized products **3c** and **3c'** (0.016g, 81% yield), as a colourless solid. Pure samples of each of the two regiosiomeric products were obtained by column chromatography separation.

Spectroscopic data for **3c**: IR(ATR): ν = 2953, 1310, 1151 cm^{-1}; HRMS (*m/z*) calcd. for $[C_{39}H_{39}N_3O_6S_3 + H]^+$: 742.2074. Found: 742.2053; ^{1}H-NMR (500.13 MHz, $CDCl_3$, 298K, TMS): δ = 2.40 (s, 3H), 2.41 (s, 3H), 2.50 (s, 3H), 2.61 (dd, *J* = 9.4 and 10.8 Hz, 1H), 2.70 (t, *J* = 9.1, 1H), 3.05 (dd, *J* = 8.4 and 9.3 Hz, 1H), 3.16 (d, *J* = 9.5 Hz, 1H), 3.28 (dt, *J* = 10.0 and 8.1 Hz, 1H), 3.36 (t, *J* = 9.5 Hz, 1H), 3.61 (t, *J* = 10.0 Hz, 1H), 3.72 (d, *J* = 9.5 Hz, 1H), 4.02-4.07 (m, 2H), 4.18 (m, 1H), 4.35 (m, 1H), 6.19 (d, *J* = 2.1 Hz, 1H), 6.53 (d, *J* = 8.0 Hz, 2H), 7.02 (t, *J* = 8.0 Hz, 2H), 7.04 (d, *J* = 8.0 Hz, 1H), 7.08 (d, *J* = 8.3 Hz, 2H), 7.28 (d, *J* = 8.3 Hz, 2H), 7.31 (d, *J* = 8.3 Hz, 2H), 7.39 (d, *J* = 8.3 Hz, 2H), 7.66 (d, *J* = 8.3 Hz, 2H), 7.75 (d, *J* = 8.3 Hz, 2H) ppm; ^{13}C-NMR (125.75 MHz, $CDCl_3$): δ = 21.7, 21.7, 21.7, 43.5, 45.1, 48.4, 49.6, 51.3, 53.0, 57.0, 115.2, 125.0, 125.6, 126.2, 127.0, 127.4, 128.3, 128.8, 129.7, 129.9, 130.0, 130.9, 131.7, 132.4, 133.7, 135.2, 139.9, 143.6, 144.0, 144.2 ppm.

Spectroscopic data for **3c'**: IR(ATR): ν = 2957, 1308, 1149 cm^{-1}; HRMS (*m/z*) calcd. for $[C_{39}H_{39}N_3O_6S_3 + H]^+$: 742.2074. Found: 742.2065; ^{1}H-NMR (500.13 MHz, $CDCl_3$, 298K, TMS): δ = 1,89 (dd, *J* = 9.2 and 11.0 Hz, 1H), 2.34 (s, 3H), 2.42 (s, 3H), 2.50 (m, 4H), 2.55 (t, *J* = 6.8 Hz, 1H), 3.03 (t, *J* = 9.2, 1H), 3.30 (dd, *J* = 6.4 and 11.2 Hz, 1H), 3.37 (d, *J* = 10.5 Hz, 1H), 3.68 (d, *J* = 11.2 Hz, 1H), 3.92 (dt, *J* = 14.6 and 4.0 Hz, 1H), 4.02 (m, 1H), 4.25-4.40 (m, 3H), 6.39 (s, 1H), 6.80 (d, *J* = 8.0 Hz, 2H), 6.93 (t, *J* = 8.0 Hz, 2H), 7.06 (d, *J* = 8.3 Hz, 2H), 7.08 (t, *J* = 7.5 Hz, 1H), 7.23 (d, *J* = 8.3 Hz, 2H), 7.39-7.43 (m, 6H), 7.77 (d, *J* = 8.3 Hz, 2H) ppm; ^{13}C-NMR (125.75 MHz, $CDCl_3$): δ = 21.5, 21.5, 21.5, 39.0, 48.1, 48.6, 48.6, 53.1, 53.2, 56.2, 63.3, 122.0, 125.0, 125.1, 126.9, 127.1, 127.5, 127.7, 127.8, 128.1, 129.6, 129.7, 130.0, 130.9, 133.9, 134.6, 135.2, 140.1, 143.4, 143.9, 144.0 ppm.

NMR characterization for cycloisomerized derivatives 3

NMR spectra of compound 3a

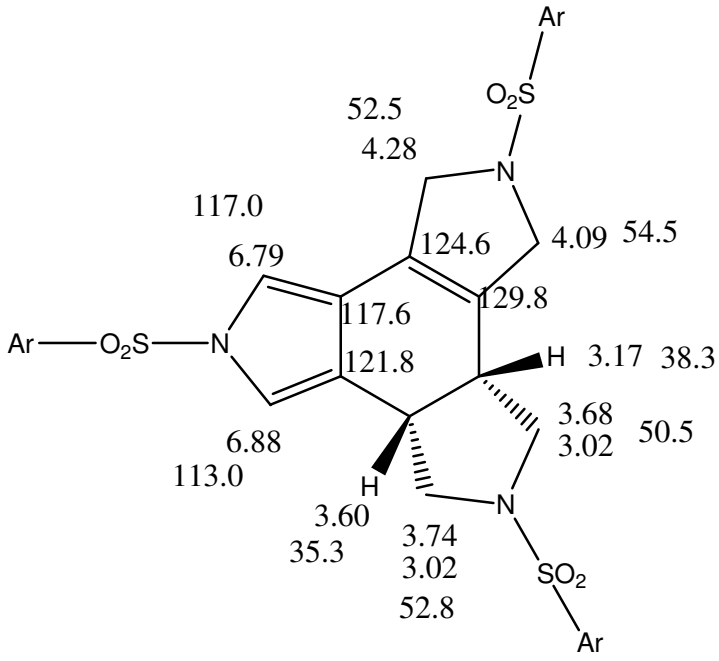


Figure S1: ^{1}H and ^{13}C NMR chemical shift assignment in compound **3a**

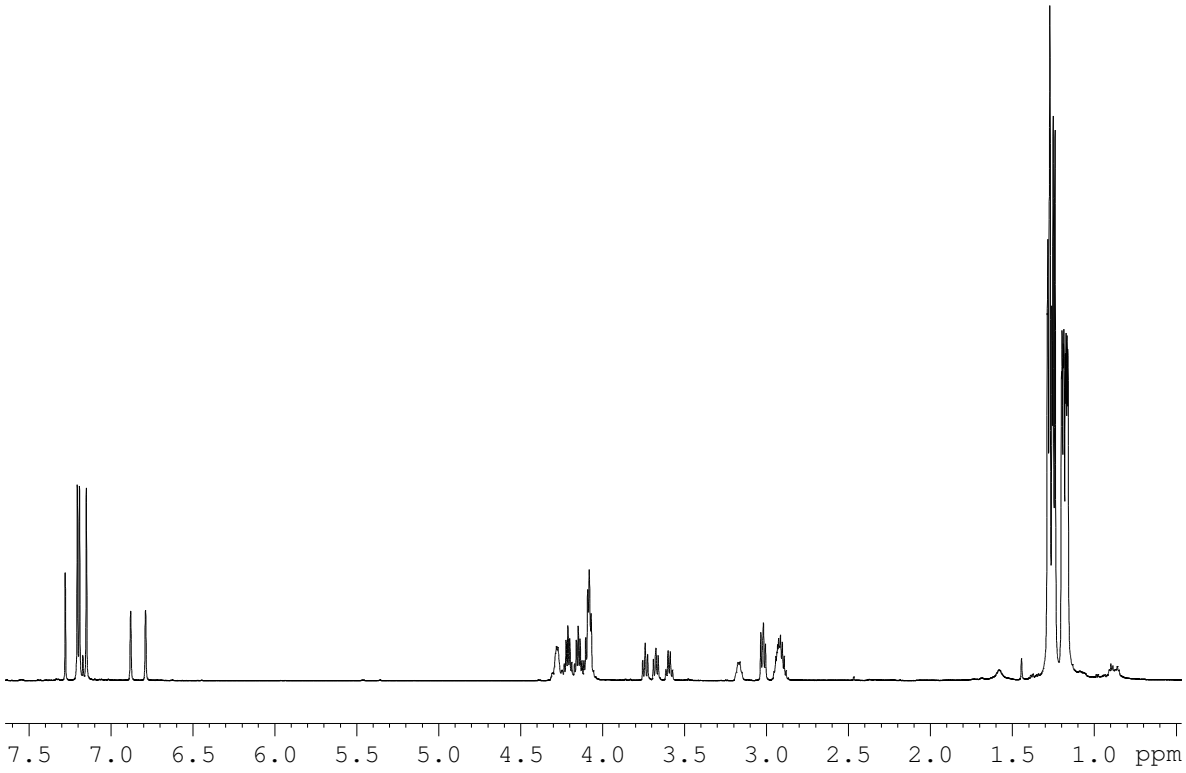


Figure S2: ^{1}H NMR spectrum (600.13MHz) of **3a** in $CDCl_3$.

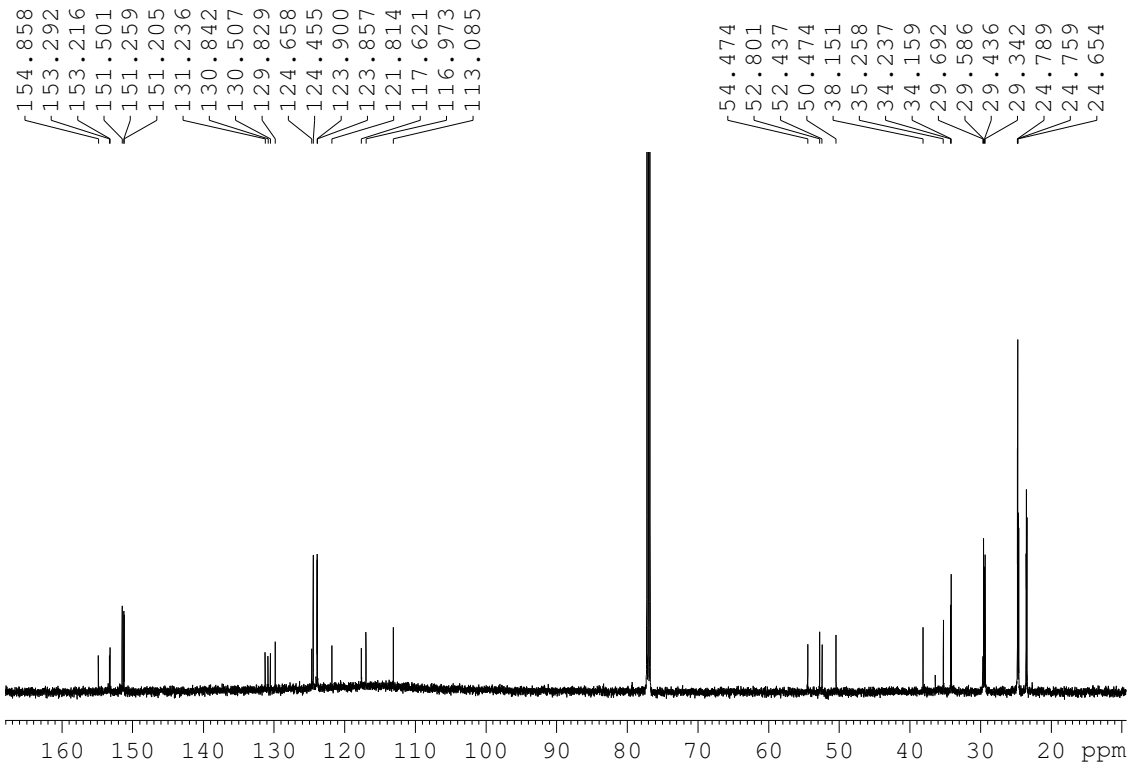


Figure S3: ^{1}H-decoupled ^{13}C NMR spectrum (150.90MHz) of **3a** in $CDCl_3$.

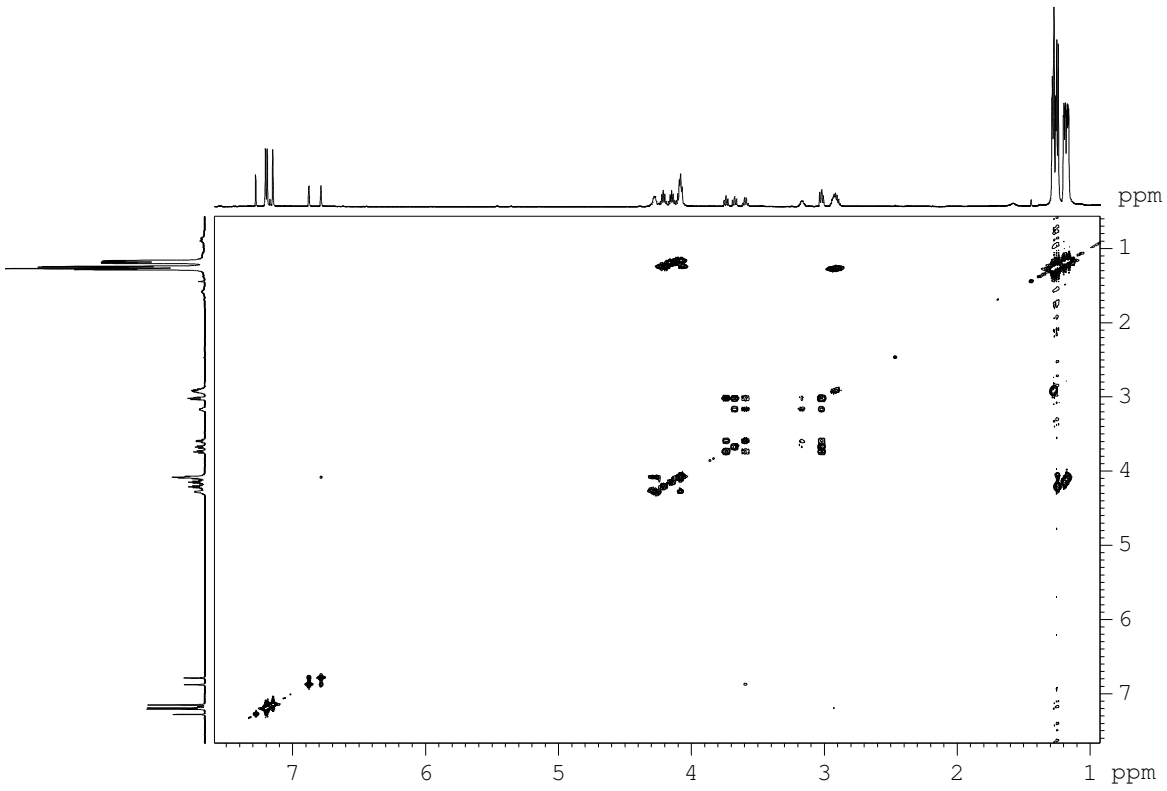


Figure S4: 2D ^{1}H-^{1}H COSY correlation spectrum of **3a** in $CDCl_3$.

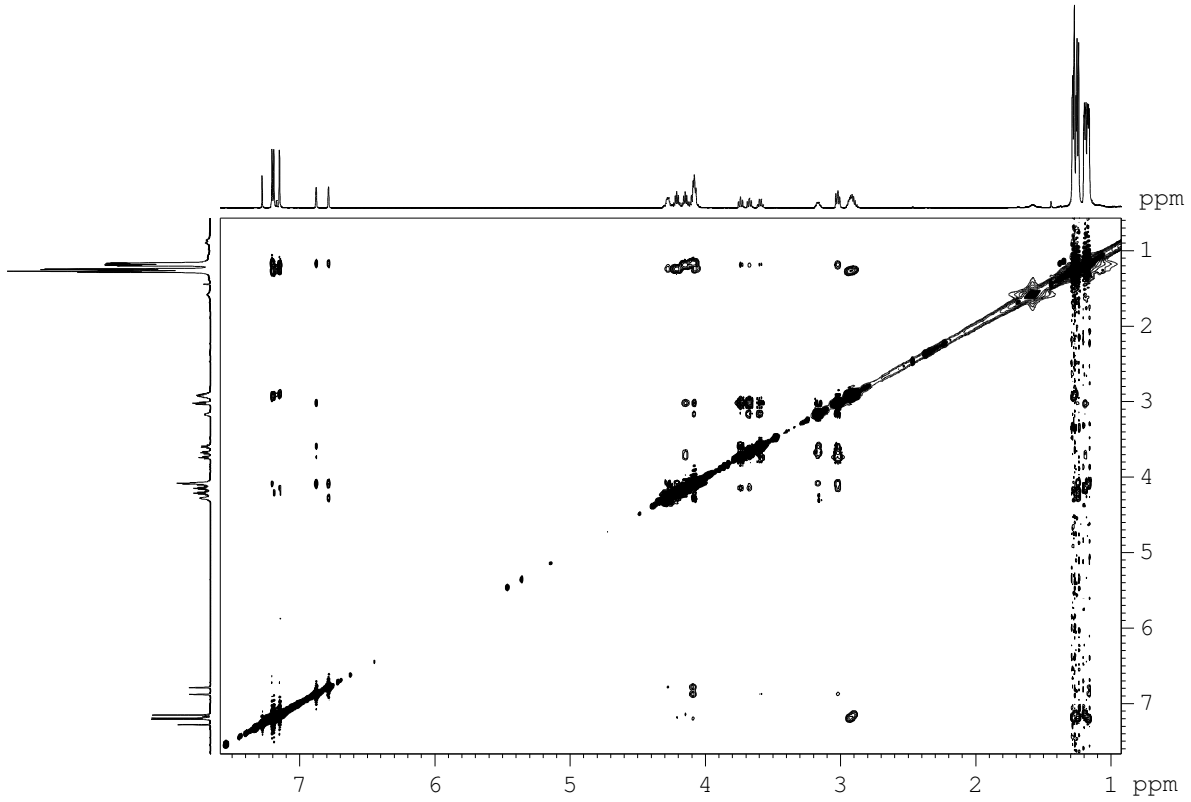


Figure S5: 2D 1H-1H NOESY correlation of **3a** in CDCl3.

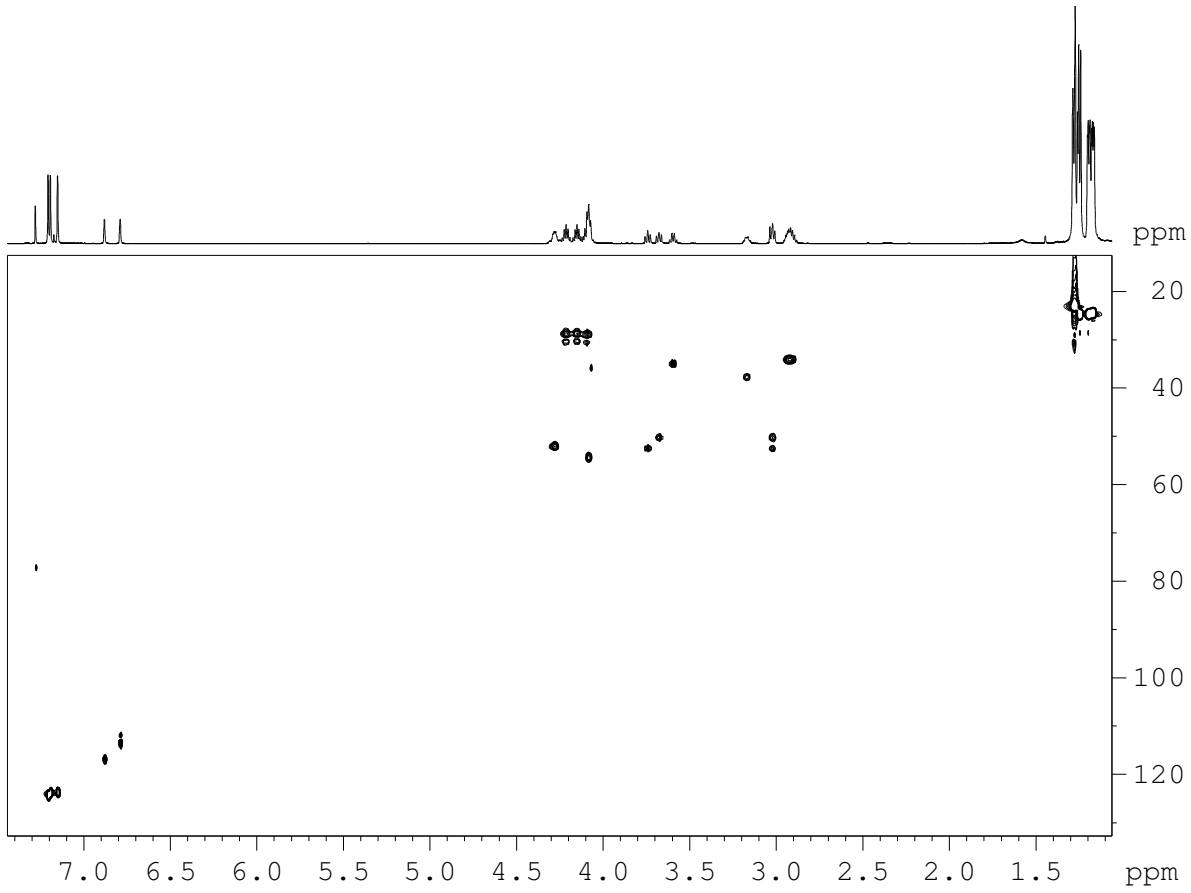


Figure S6: 2D ^{1}H-^{13}C HSQC correlation of **3a** in $CDCl_3$.

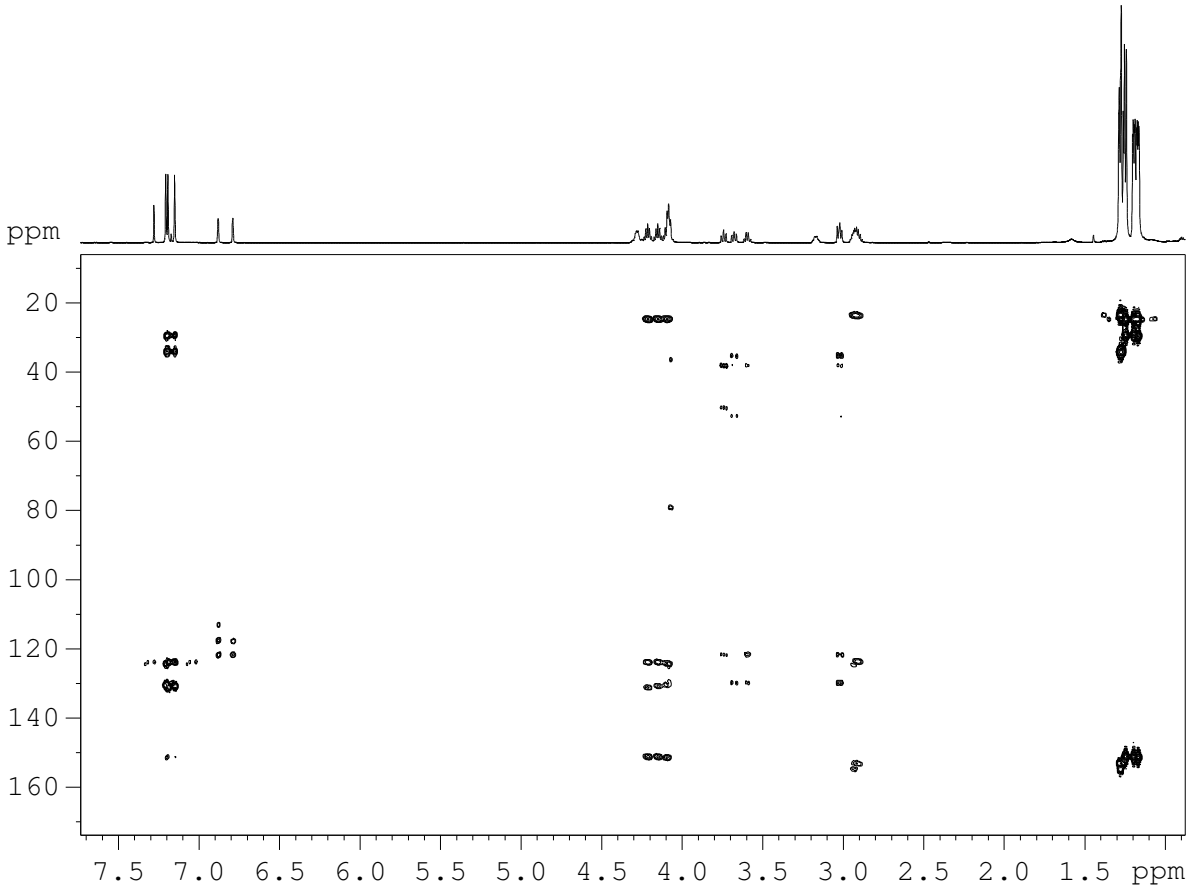


Figure S7: 2D ^{1}H-^{13}C HMBC correlation of **3a** in CDCl3.

NMR spectra of compound 3b

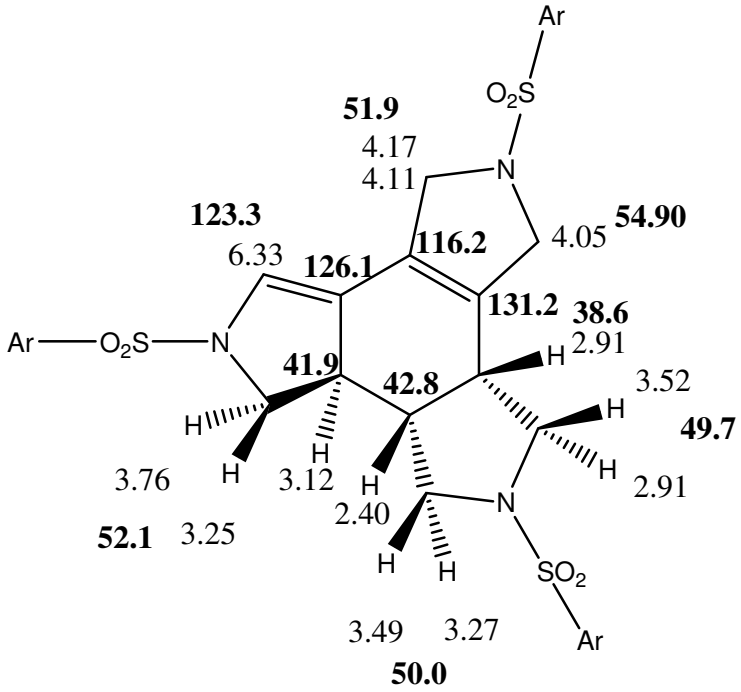


Figure S8: ^{1}H and ^{13}C NMR chemical shifts assignment in compound **3b**.

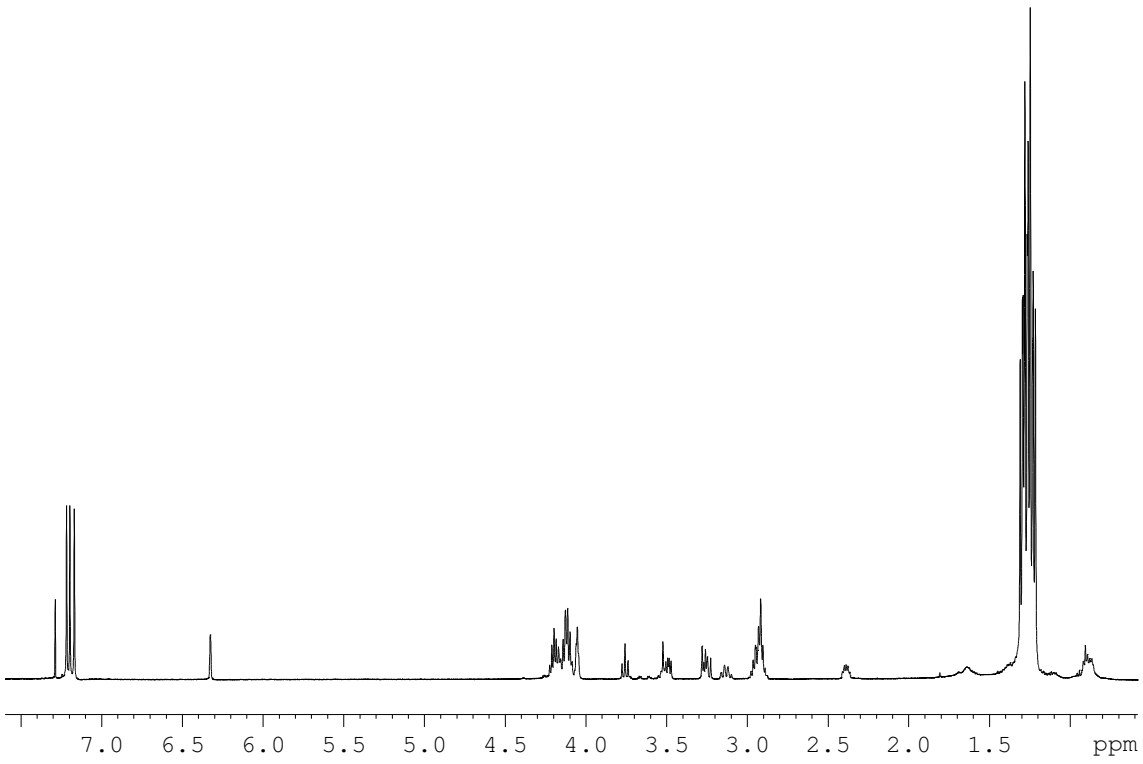


Figure S9: ^{1}H NMR (500.13MHz) spectrum of **3b** in $CDCl_3$.

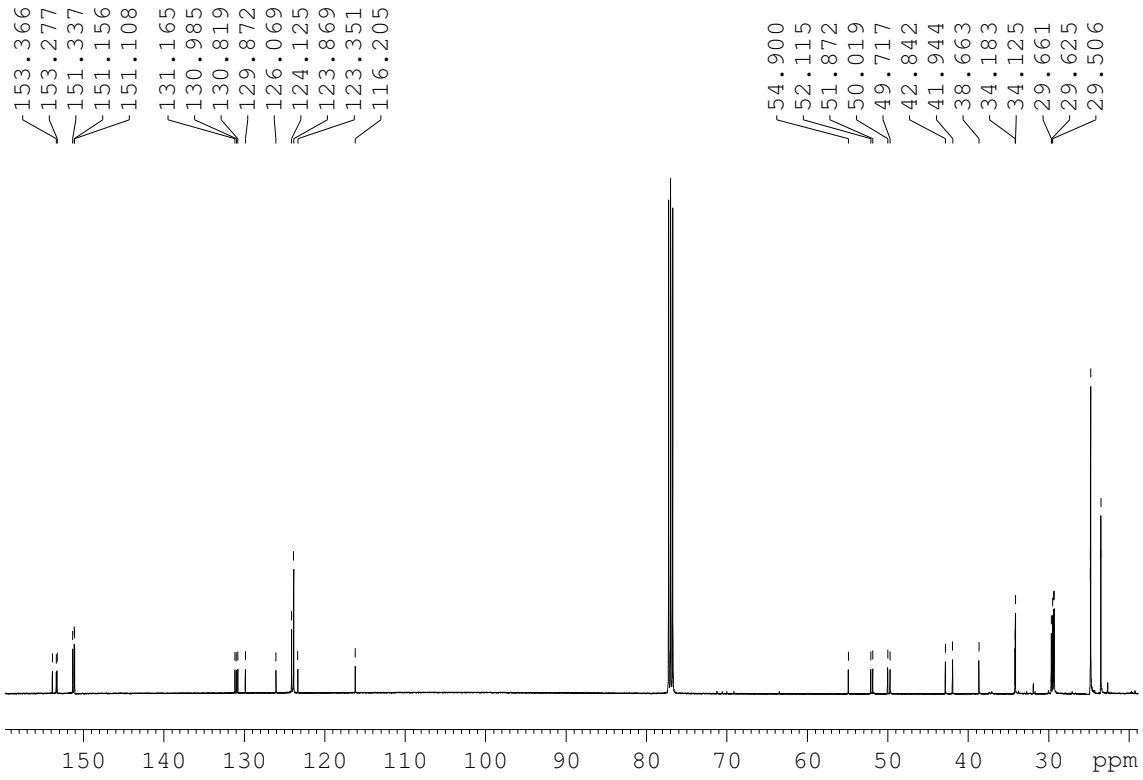


Figure S10: ^{1}H-decoupled ^{13}C NMR (125.75MHz) spectrum of **3b** in $CDCl_3$.

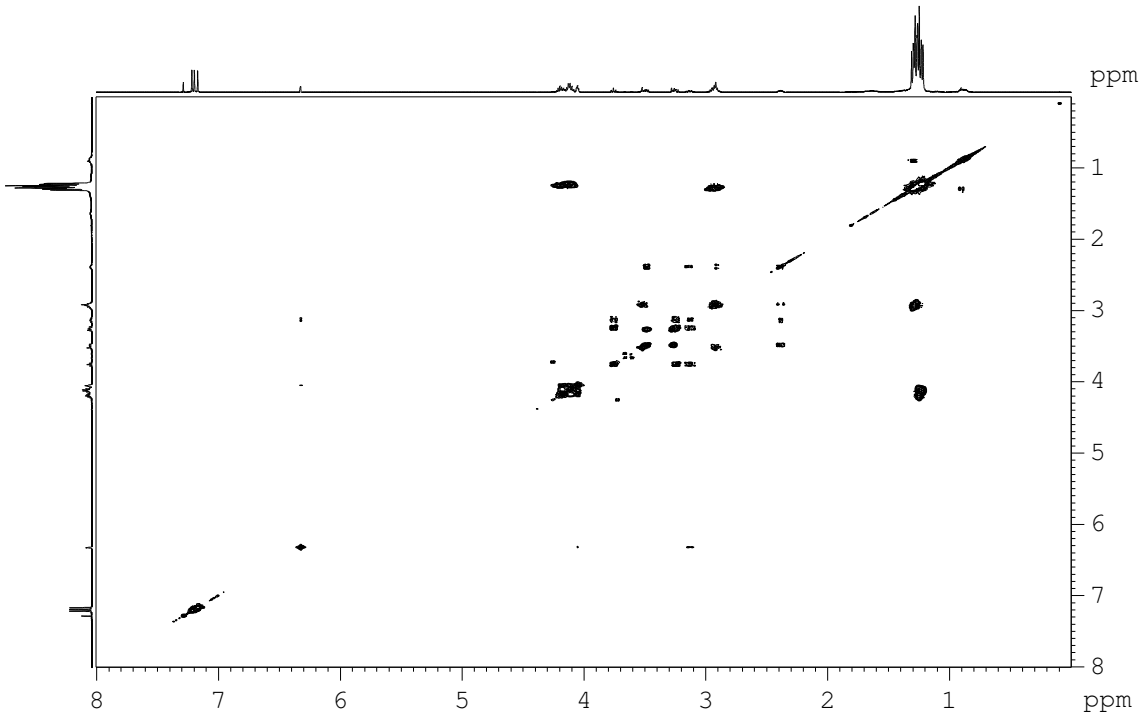


Figure S11: 2D ^{1}H-^{1}H COSY correlation spectrum of **3b** in $CDCl_3$.

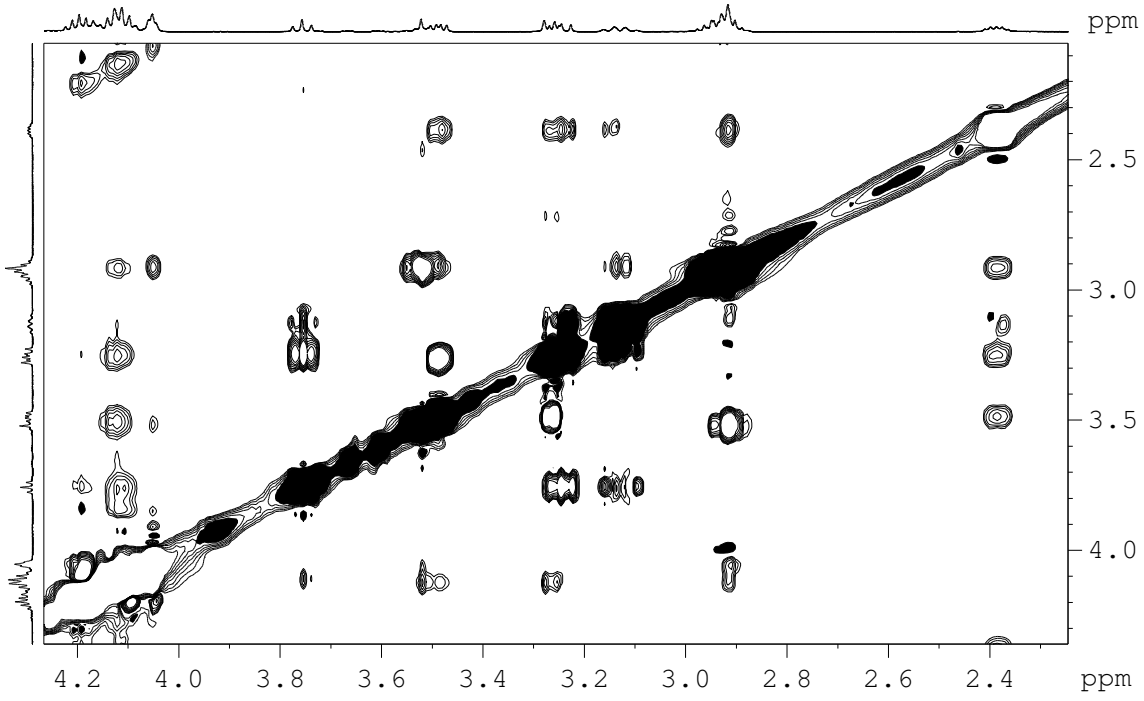


Figure S12: Expansion of the 2D ^{1}H-^{1}H NOESY correlation spectrum of **3b** in $CDCl_3$.

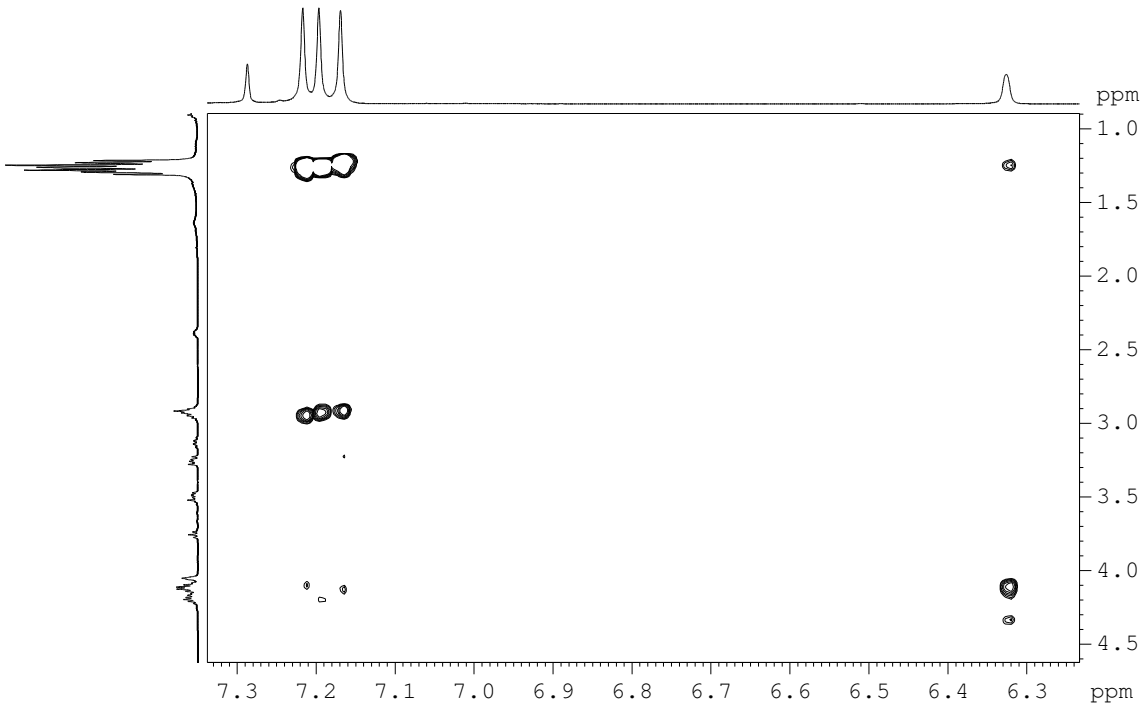


Figure S13: Expansion of the 2D ^{1}H-^{1}H NOESY correlation spectrum of **3b** in $CDCl_3$.

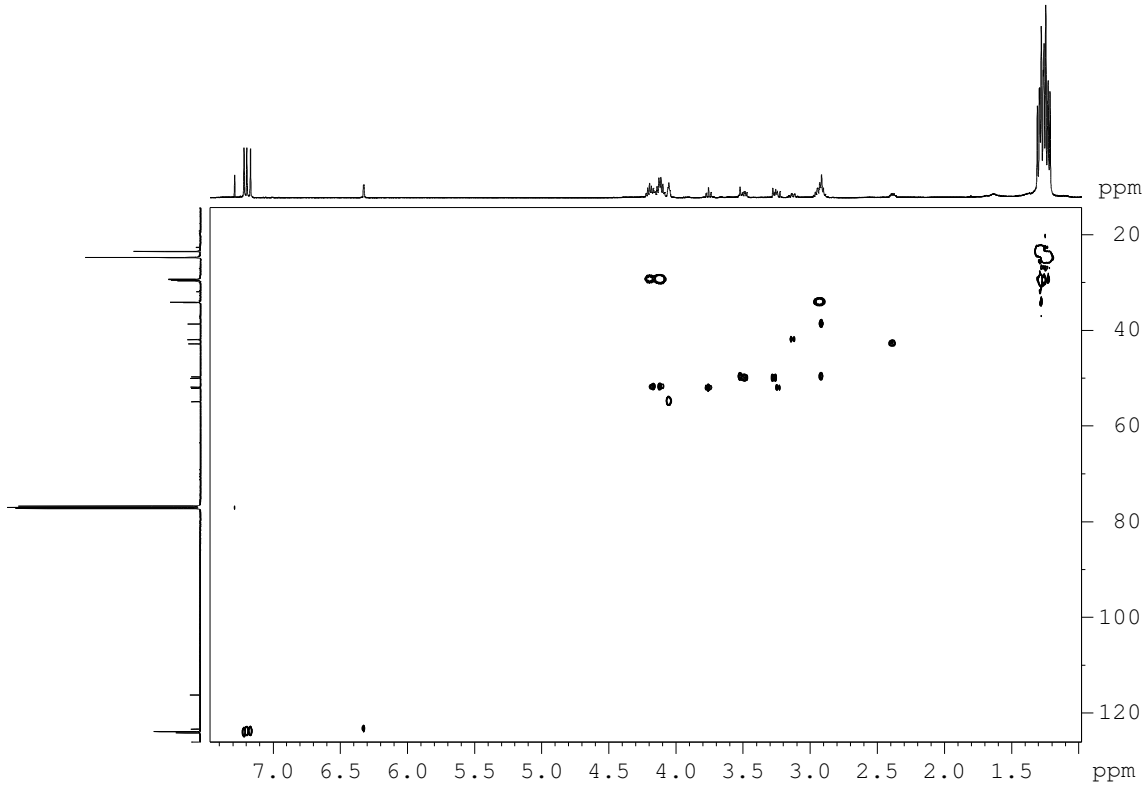


Figure S14: 2D ^{1}H-^{13}C HSQC correlation spectrum of **3b** in $CDCl_3$.

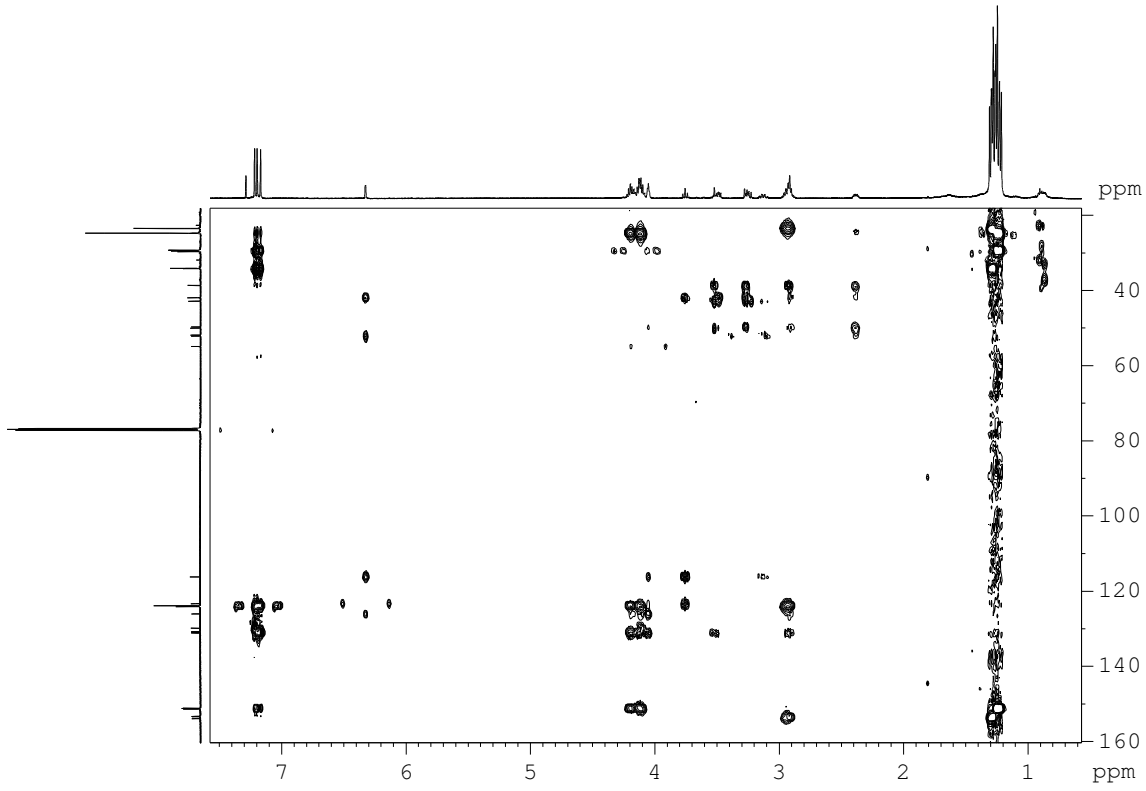


Figure S15: 2D ^{1}H-^{13}C HMBC correlation spectrum of **3b** in $CDCl_3$.

NMR spectra of compound 3a-D

NMR (500 MHz) spectra for deuterated **3a** (referred as **3a-D**) derivative, recorded in $CDCl_3$ solution except for ^{2}H-NMR which was recorded in $CHCl_3$ solution.

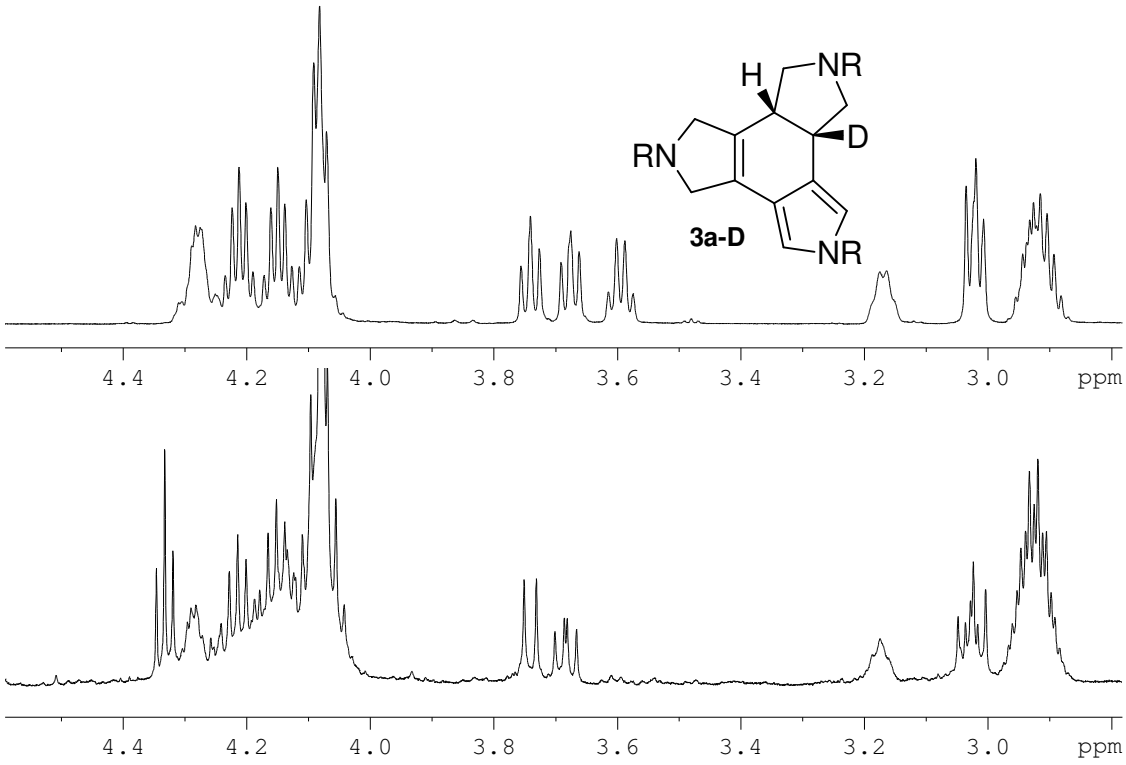


Figure S16: ^{1}H NMR (500.13MHz) spectra for deuterated **3a(D)** (below) and ^{1}H NMR (600.13MHz) spectra for non-deuterated **3a** (above). Apart from the disappearance of the 3.6 ppm signal, the multiplicity of the neighbouring protons at 3.02, 3.18 and 3.74 ppm is simplified.

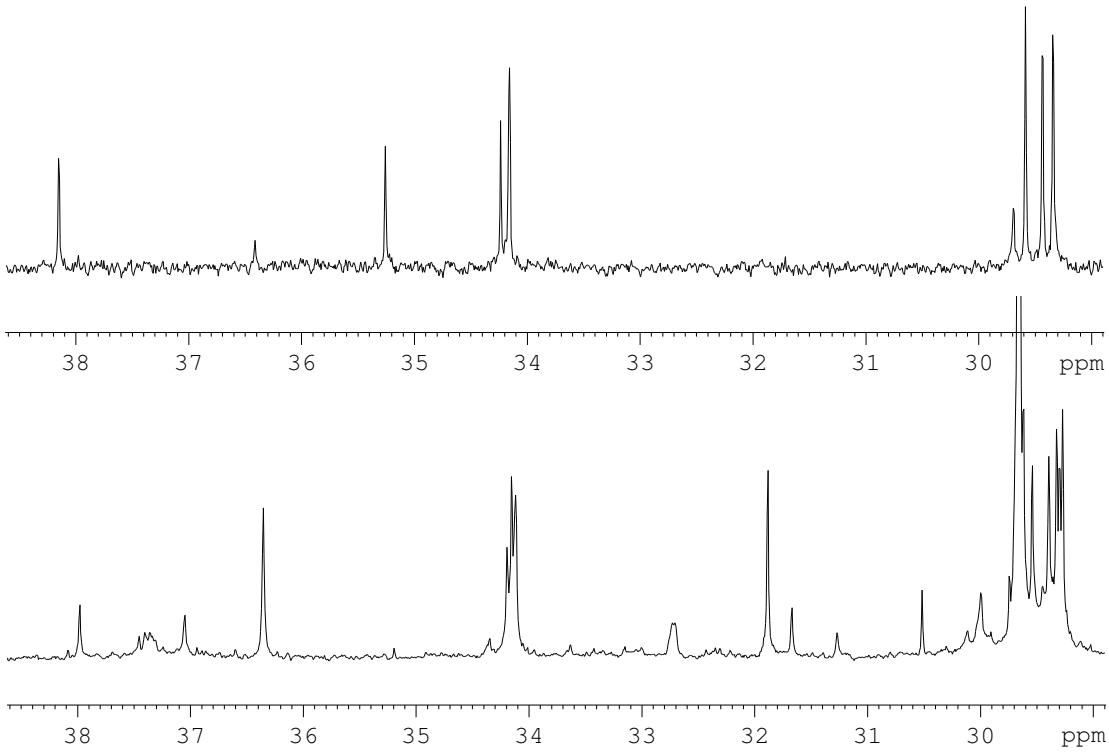


Figure S17: ^{13}C NMR spectra for deuterated **3a-D** (below) and non-deuterated **3a** (above). The signal at 35.5 ppm disappears. It should be observed as a 1:1:1 triplet but it seems to behave as a low-relaxed quaternary carbon.

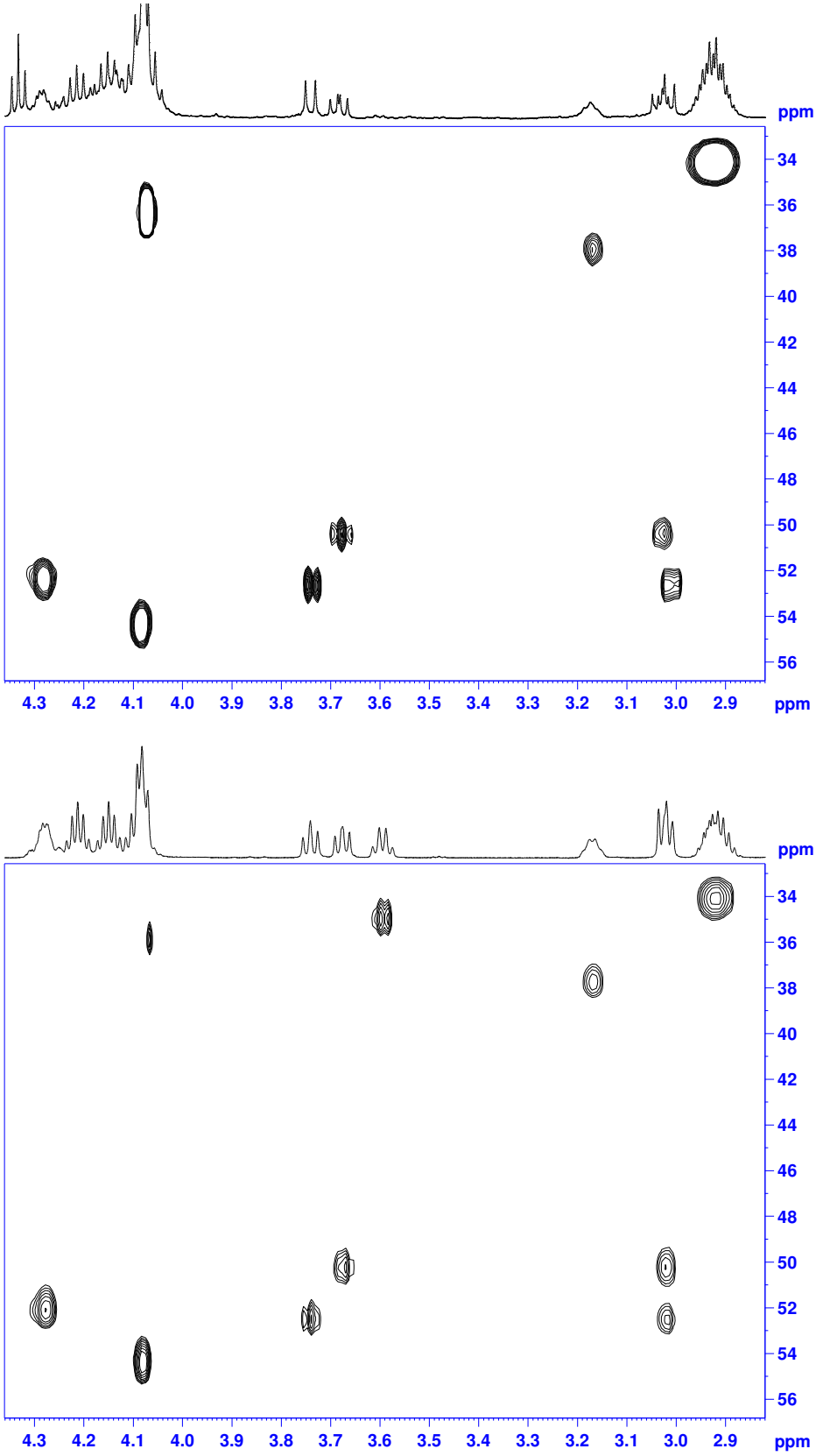


Figure S18: Expansion plot of 2D ^{1}H-^{13}C HSQC correlation spectra for deuterated **3a-D** (top) and non-deuterated **3a** (bottom).

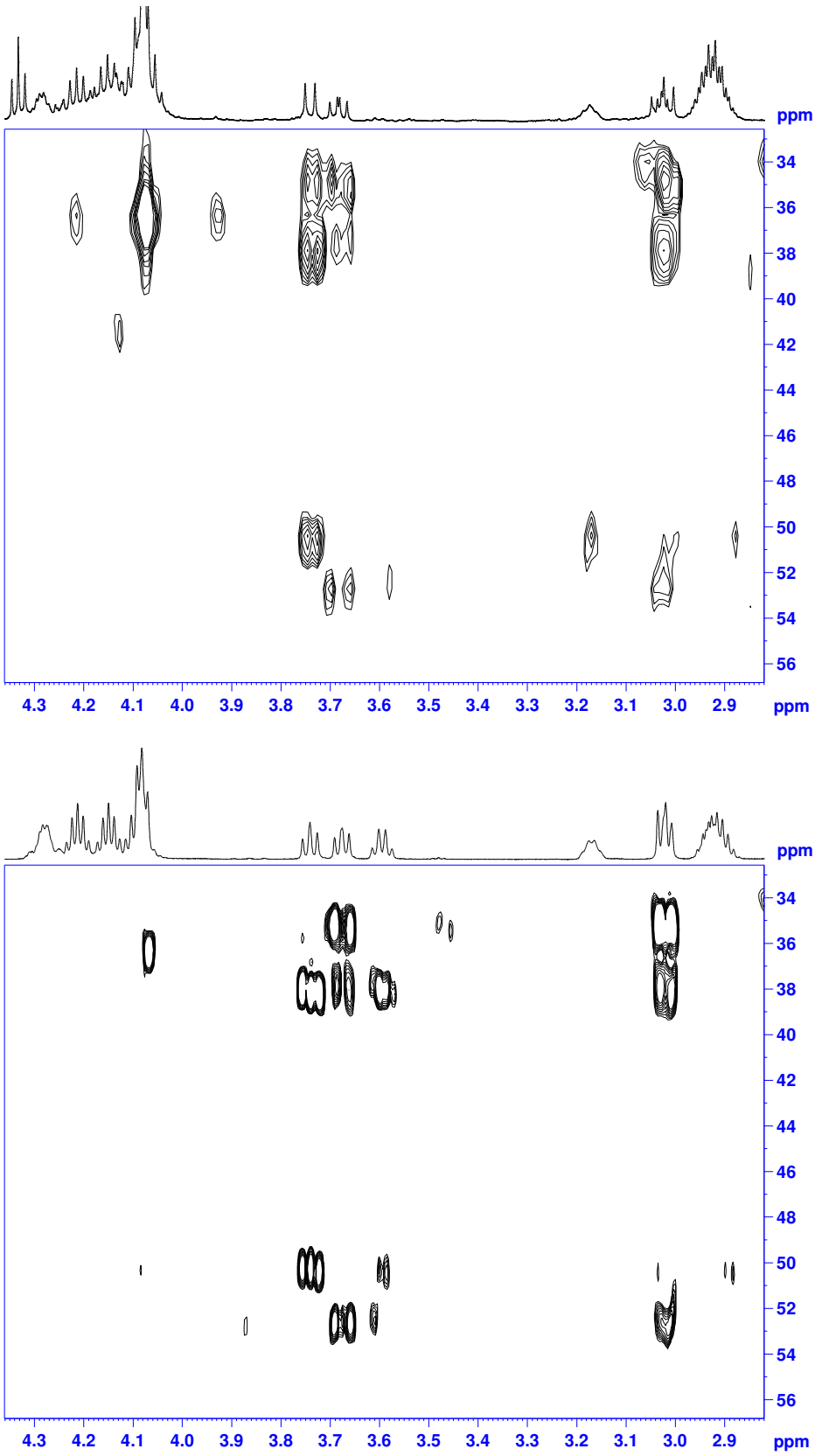


Figure S19: Expansion plots of the 2D HMBC spectra for deuterated **3a-D** (top) and nondeuterated **3a** (bottom) derivatives. Correlation between the carbon at 35.3 ppm (which could not be observed in the normal ^{13}C NMR spectra) and the neighbouring protons is observed.

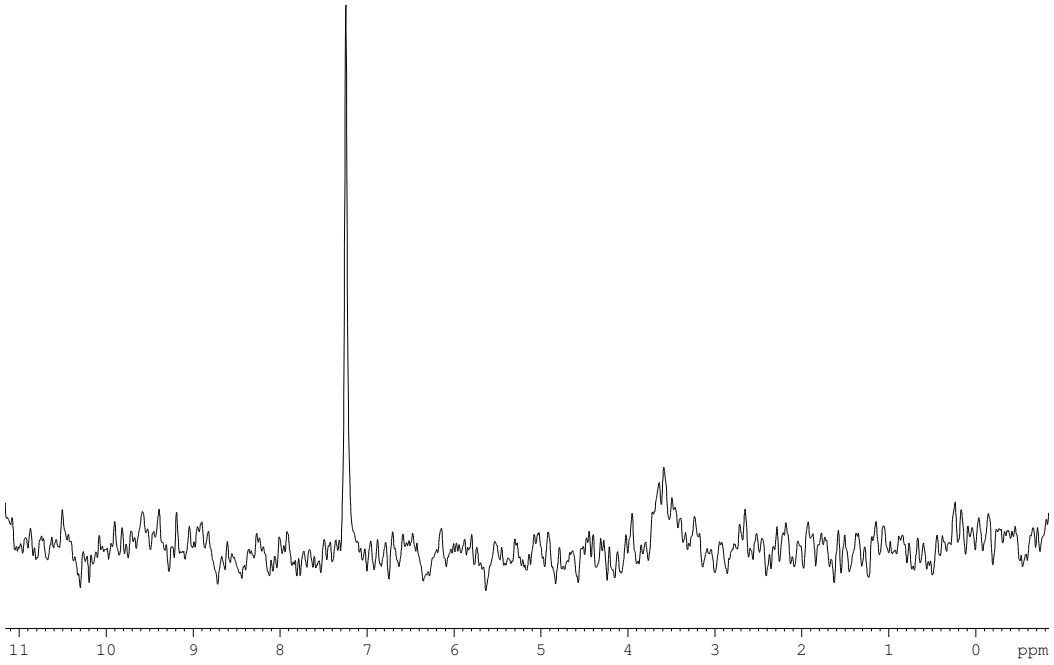


Figure S20: ^{2}H NMR spectrum (76.77MHz) for deuterated **3a-D** in $CHCl_3$ solution. A broad signal is observed at 3.6 ppm. The signal at 7.24 corresponds to the $CDCl_3$ present at natural abundances.

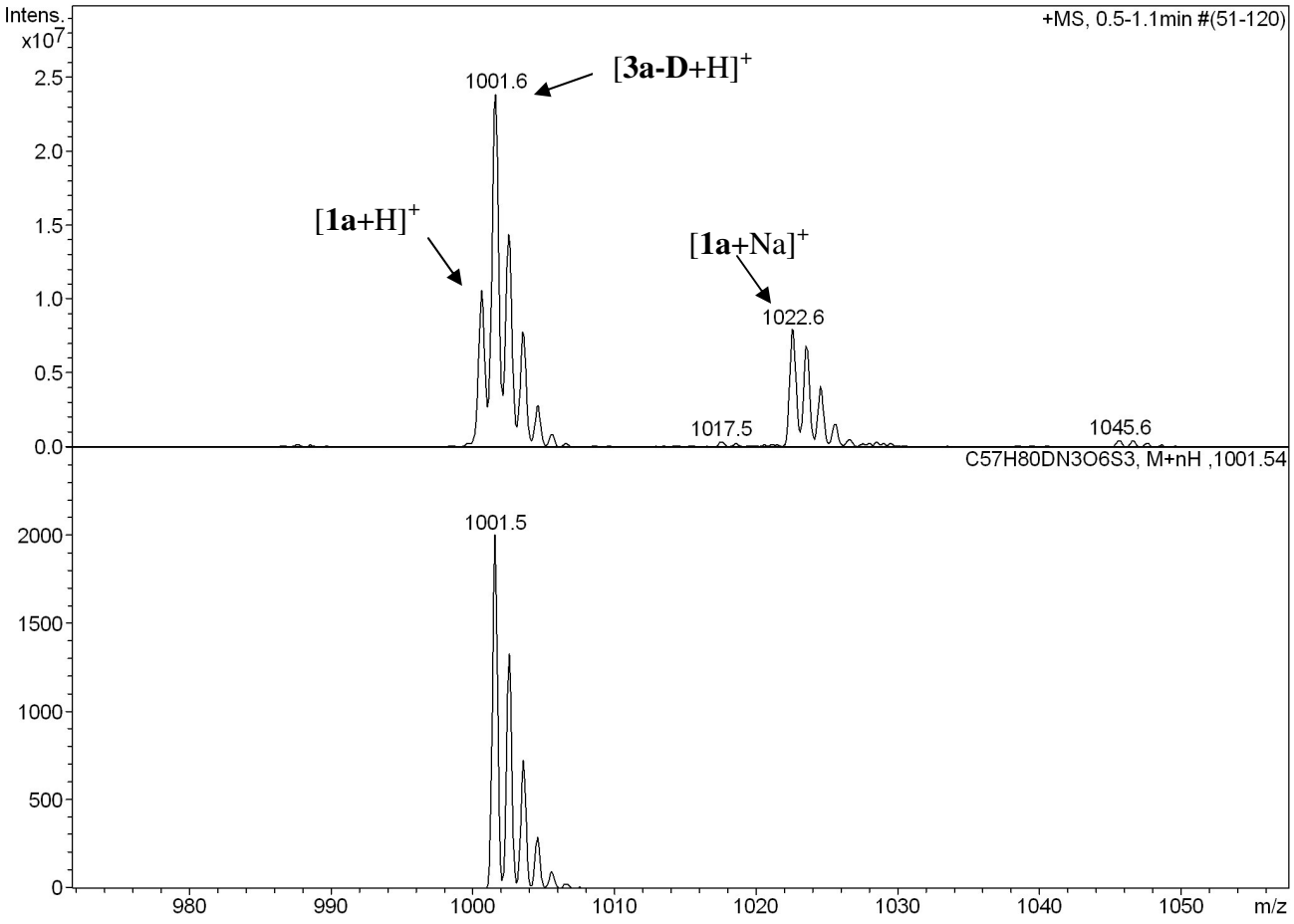


Figure S21: ESI-MS spectra for **3a-D** impurified with traces of unreacted starting macrocycle **1a**.

NMR spectra of compound 3c

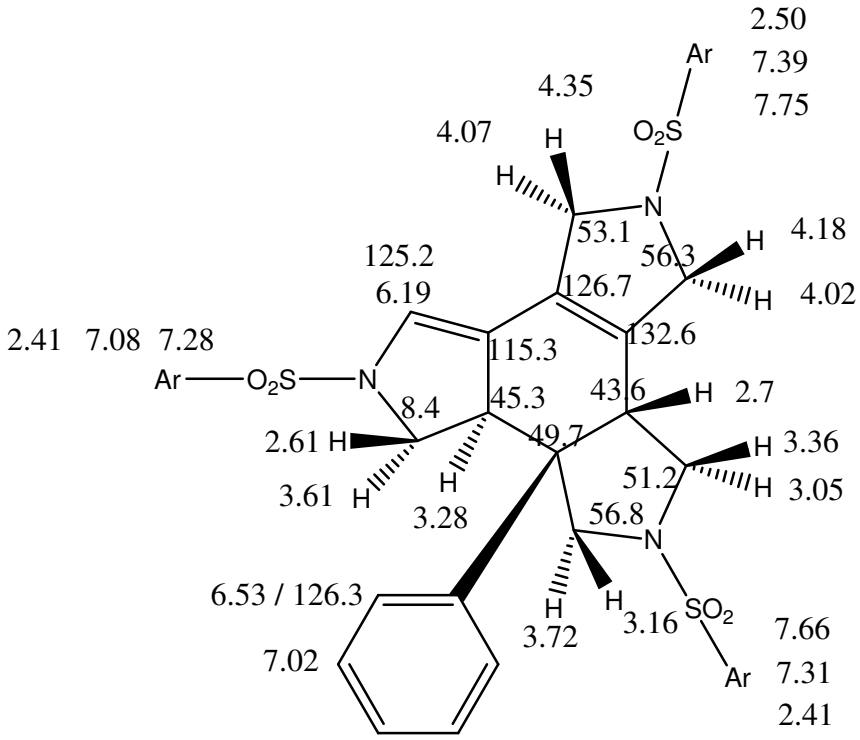


Figure S22: ^{1}H and ^{13}C NMR chemical shifts of compound **3c**.

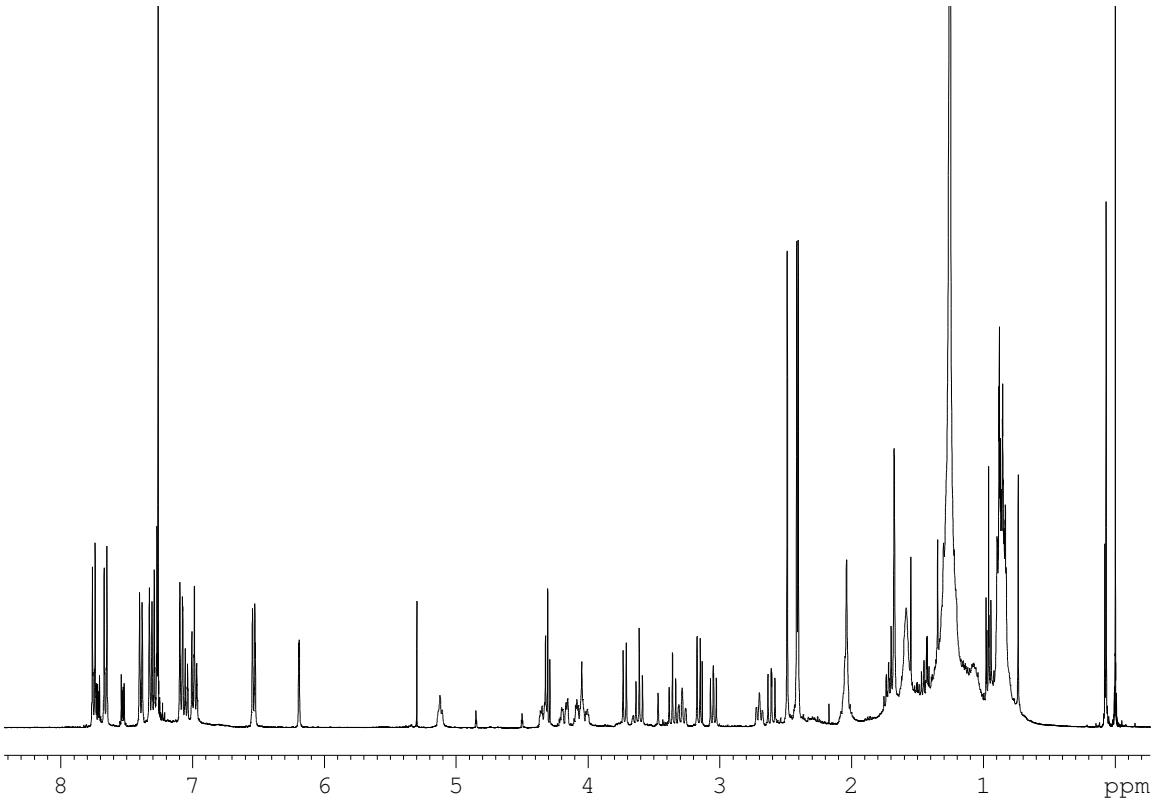


Figure S23: ^{1}H NMR spectrum (400.13MHz) of **3c** in $CDCl_3$.

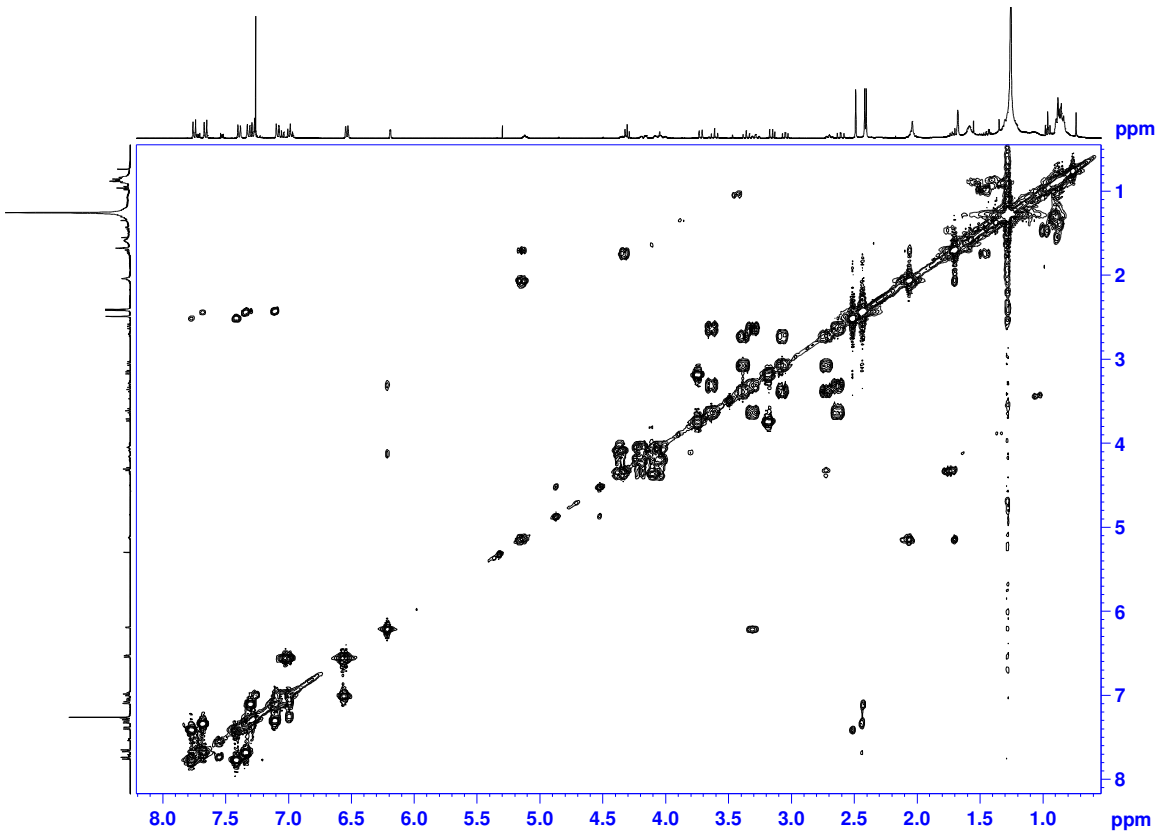


Figure S24: 2D ^{1}H-^{1}H COSY correlation spectrum of **3c** in $CDCl_3$.

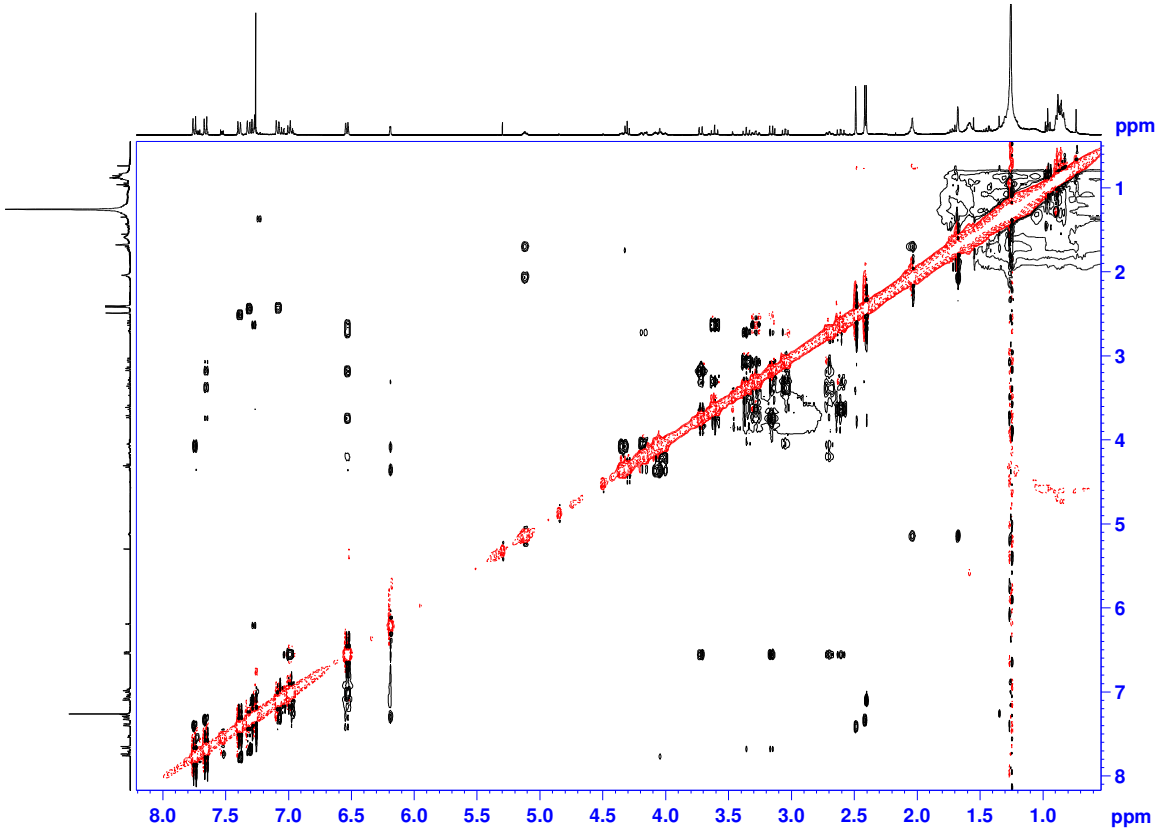


Figure S25: 2D ^{1}H-^{1}H NOESY correlation spectrum of **3c** in $CDCl_3$.

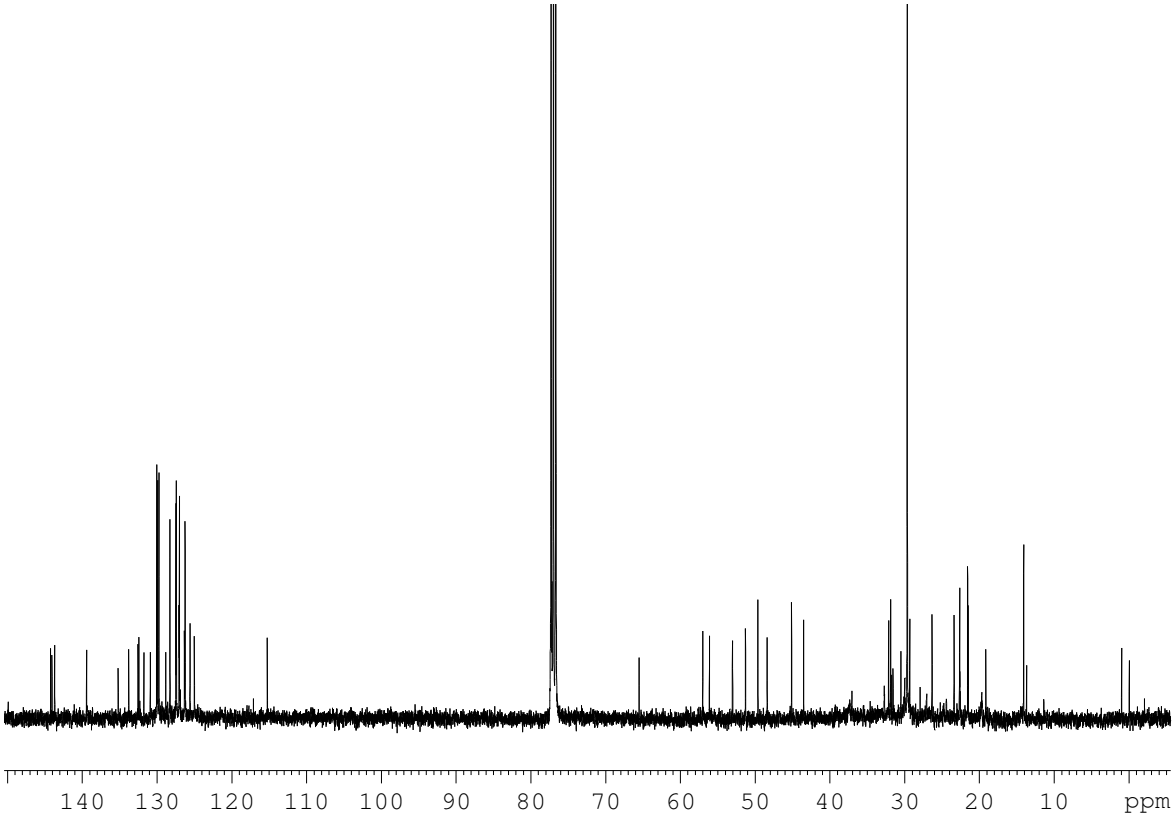


Figure S26: ^{1}H-decoupled ^{13}C NMR spectrum (100.61MHz) of **3c** in $CDCl_3$.

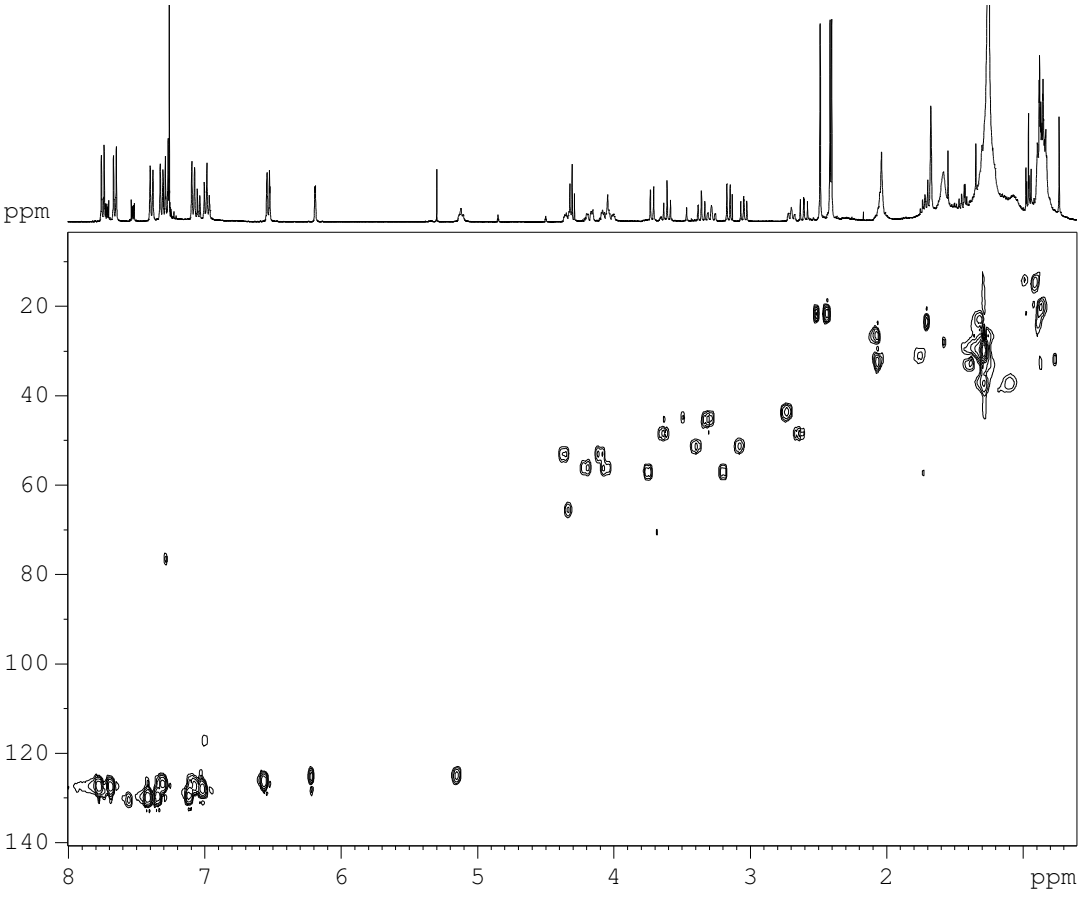


Figure S27: 2D ^{1}H-^{13}C HSQC correlation of **3c** in $CDCl_3$.

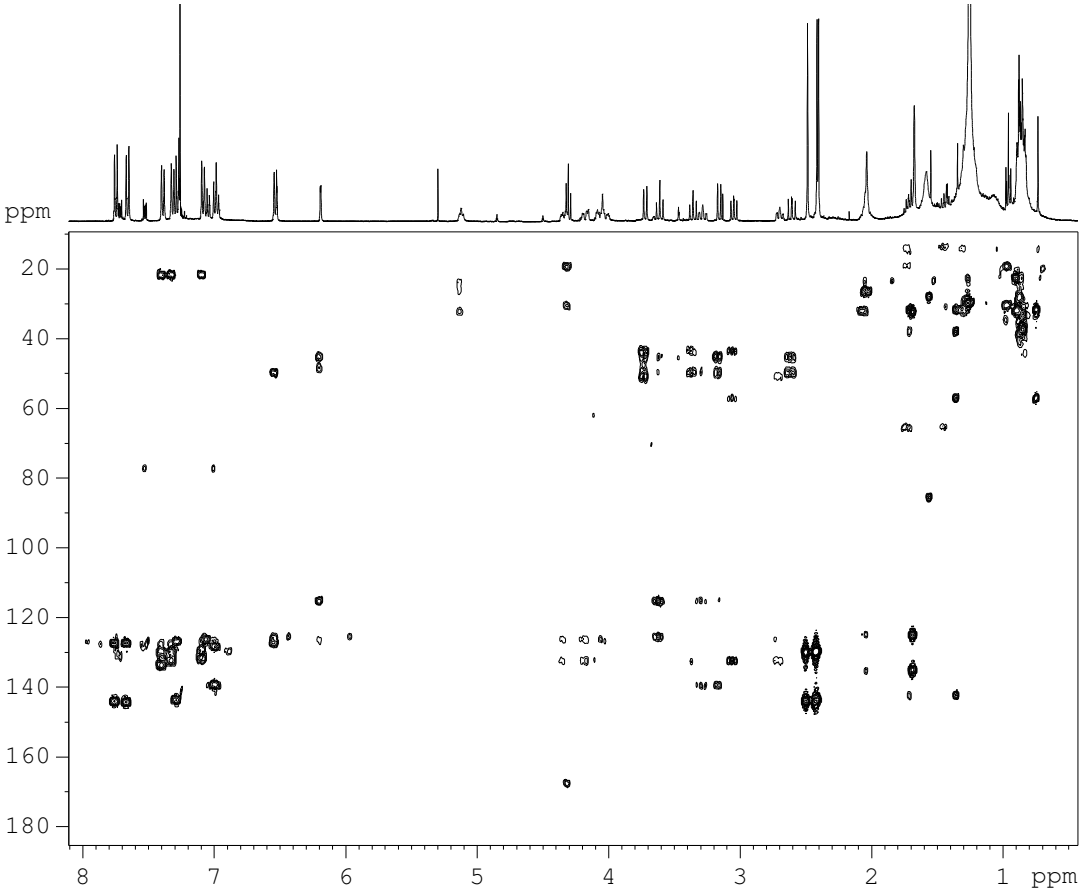


Figure S28: 2D ^{1}H-^{13}C HMBC correlation of **3c** in $CDCl_3$.

NMR spectra of compound 3c'

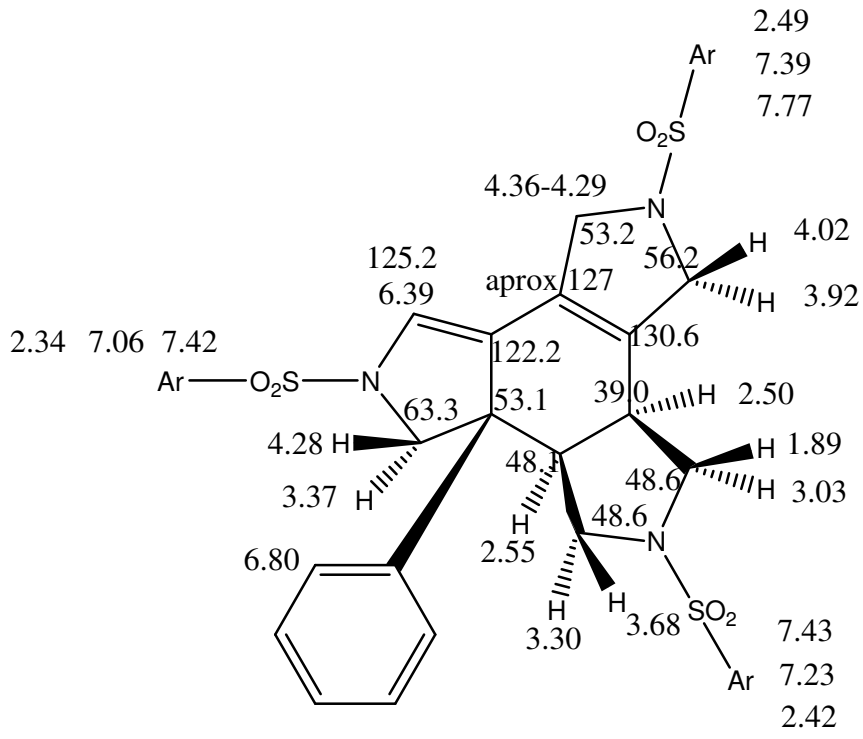


Figure S29: ^{1}H and ^{13}C NMR chemical shifts of compound **3c'**.

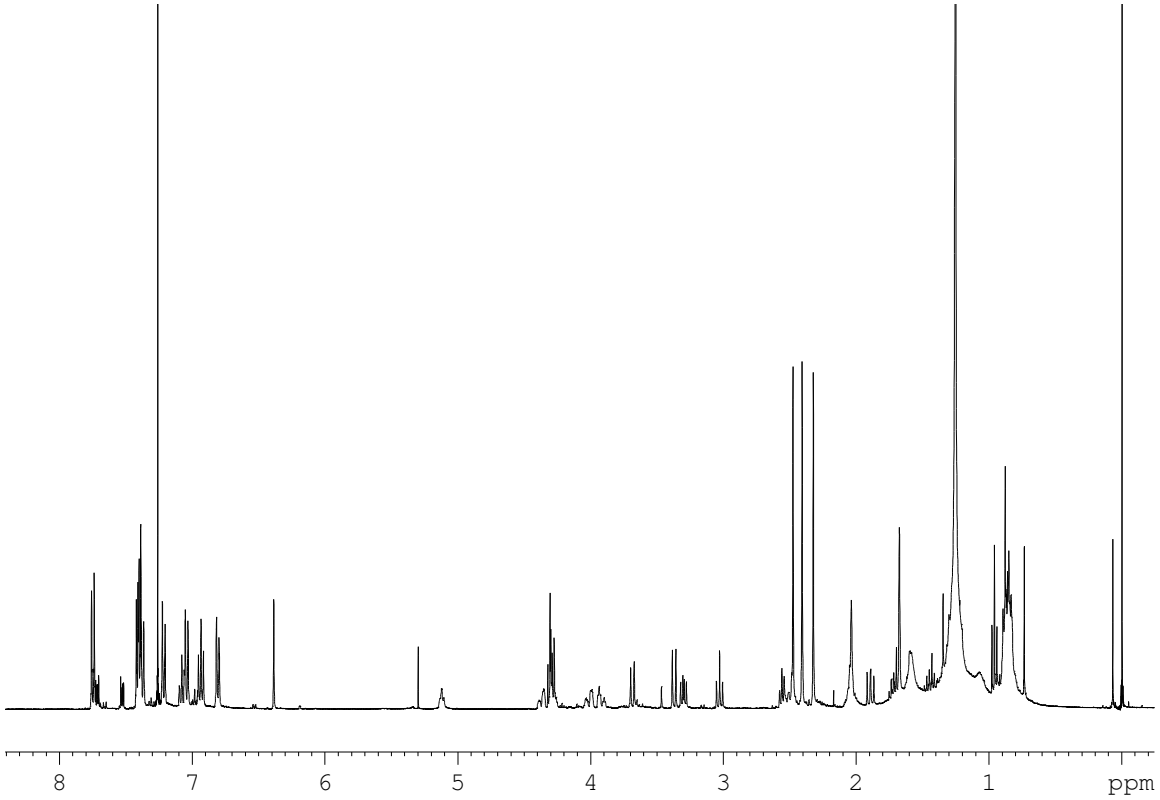


Figure S30: ^{1}H NMR spectrum (400.13MHz) of **3c'** in $CDCl_3$.

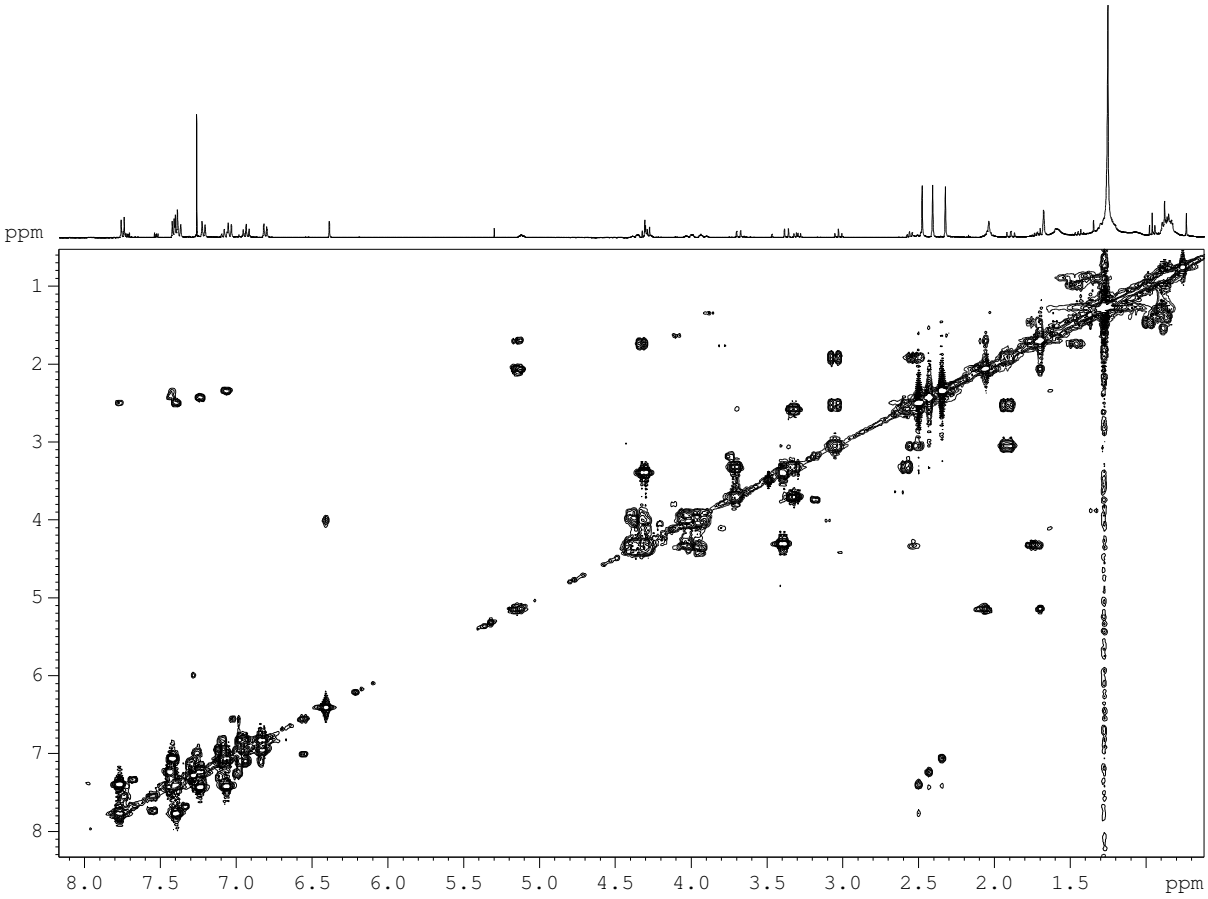


Figure S31: 2D ^{1}H-^{1}H COSY correlation spectrum of **3c'** in $CDCl_3$.

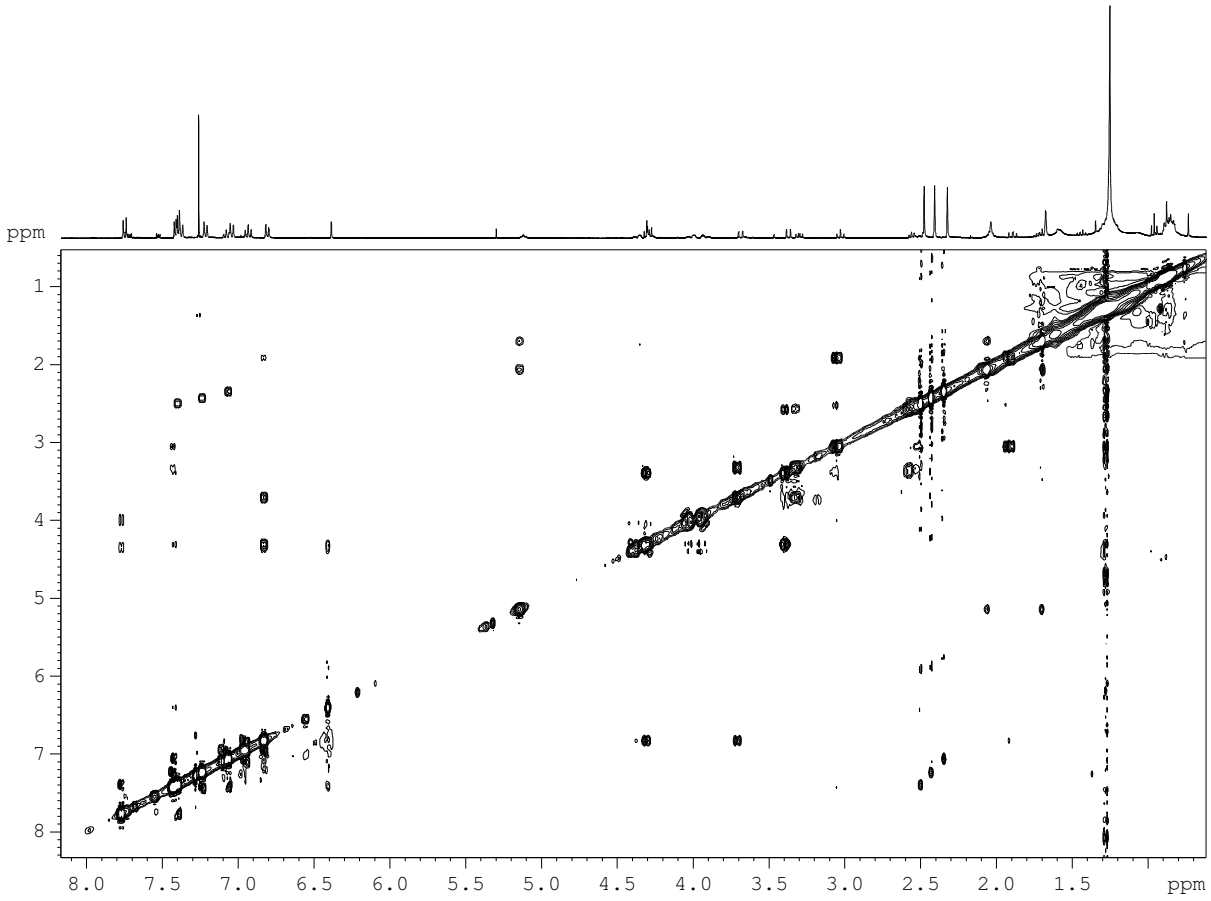


Figure S32: 2D ^{1}H-^{1}H NOESY correlation spectrum of **3c'** in $CDCl_3$.

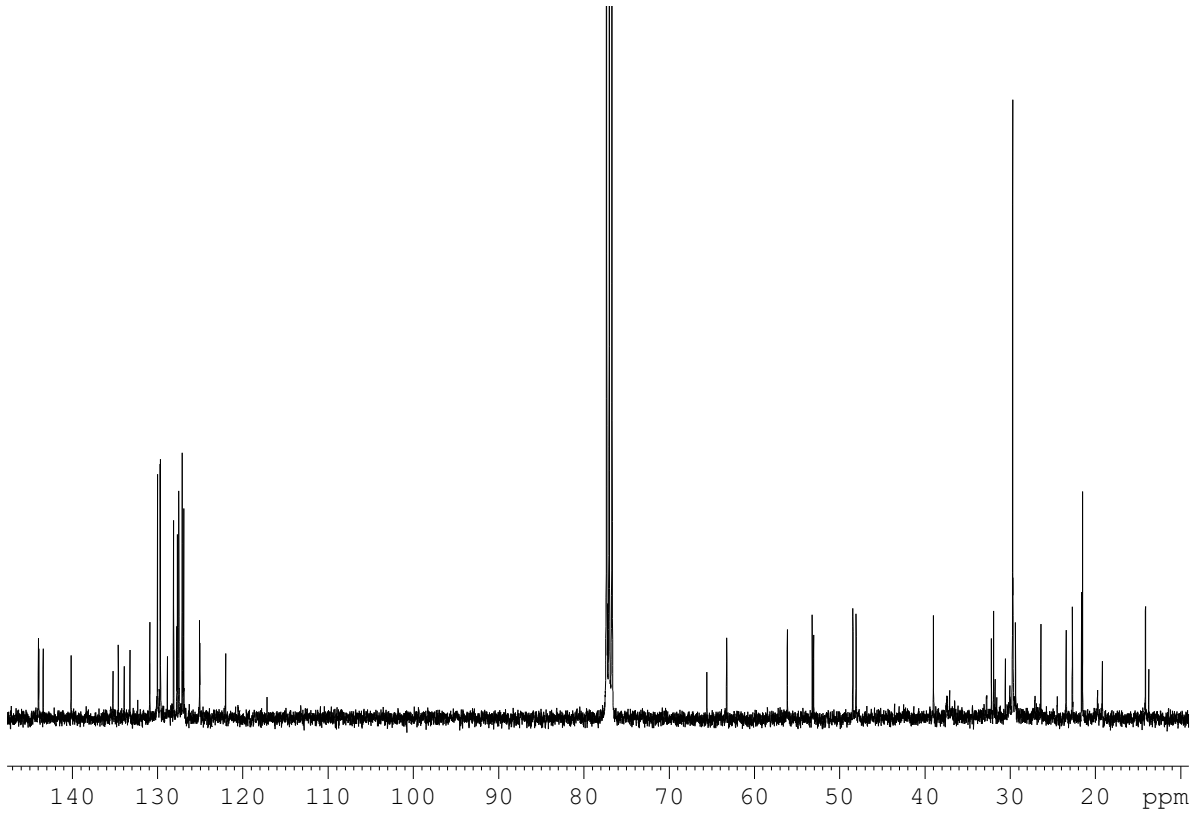


Figure S33: ^{1}H-decoupled ^{13}C NMR spectrum (100.61MHz) of **3c'** in $CDCl_3$.

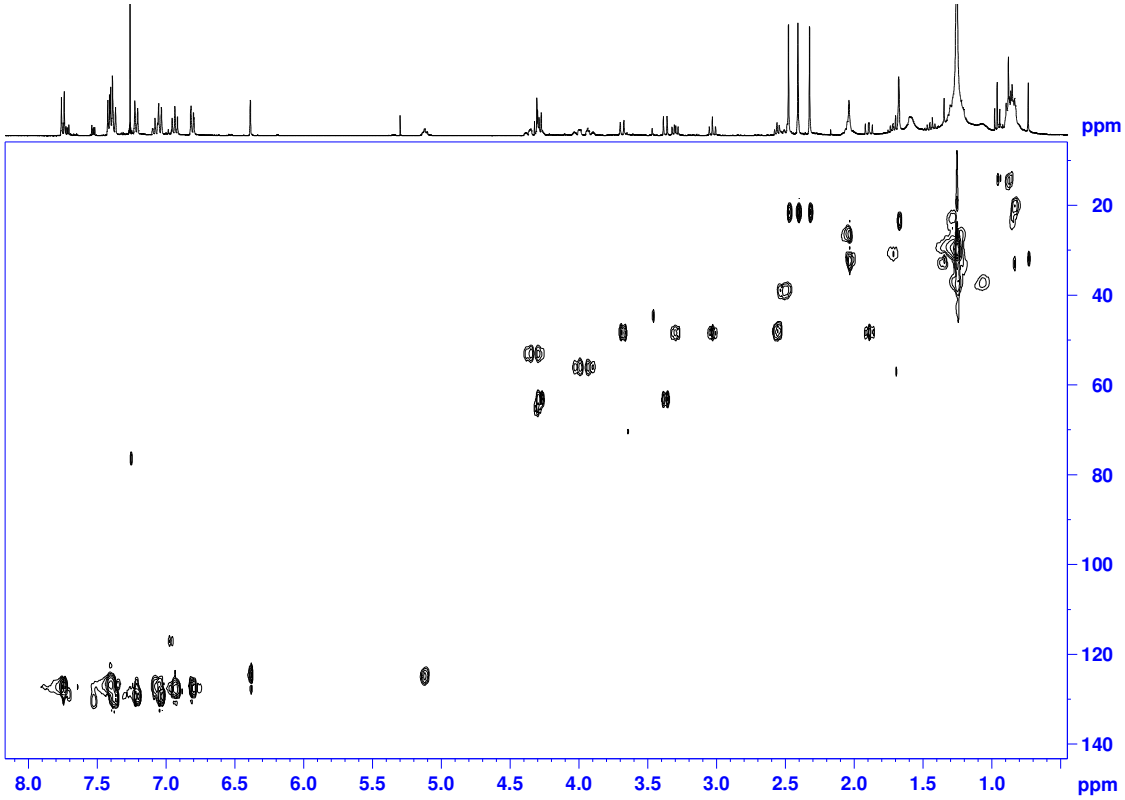


Figure S34: 2D ^{1}H-^{13}C HSQC correlation of **3c'** in $CDCl_3$.

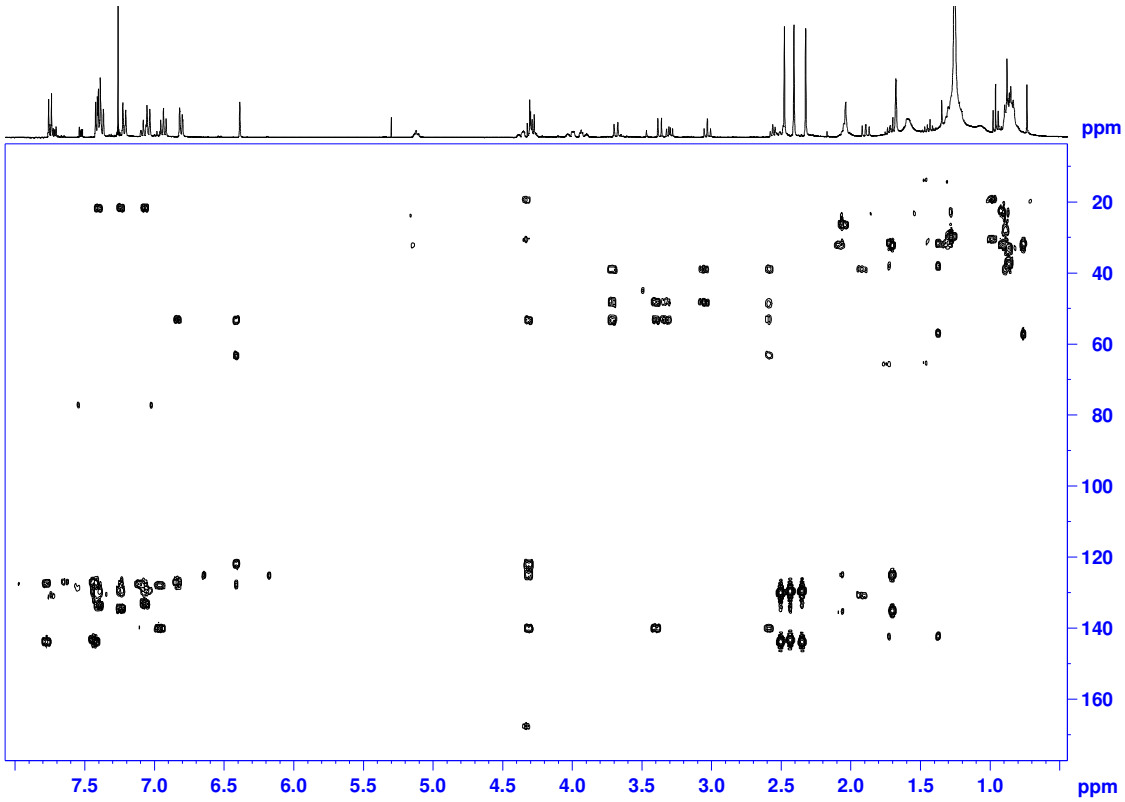


Figure S35: 2D ^{1}H-^{13}C HMBC correlation of **3c'** in $CDCl_3$.

EPR data

Experimental conditions

All experiments were run in toluene (the same bottle was used for all experiments) at 373K and EPR spectra were recorded for over 4h. ([**1a**] = $5x10^{-3}$ M). Spin adducts **B** and **C** present analogous evolution with time: their EPR signal began to be observed after 13 minutes of reaction and its intensity increased for 3.5h, after which the intensity was maintained.

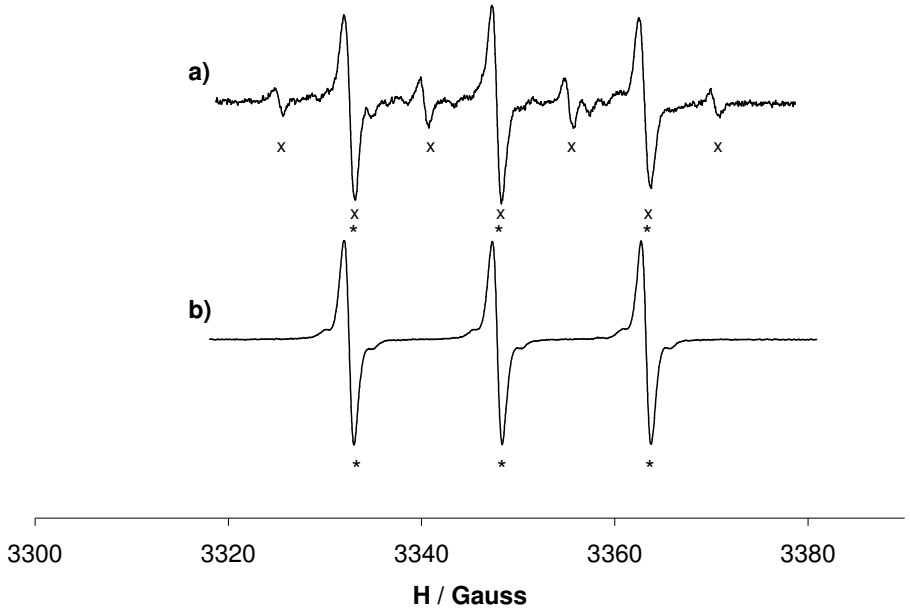


Figure S36. a) EPR spectrum of compound **1a** with an excess of MNP in toluene at 373 K, at 100 min. of reaction. Spin adduct A (*) and spin adduct B (x) are detected, Entry 2, Table 2. **b)** Blank: EPR spectrum of MNP in toluene at 373 K, at 100 min. of reaction. Spin adduct A (*) is detected, Entry 3, Table 2.

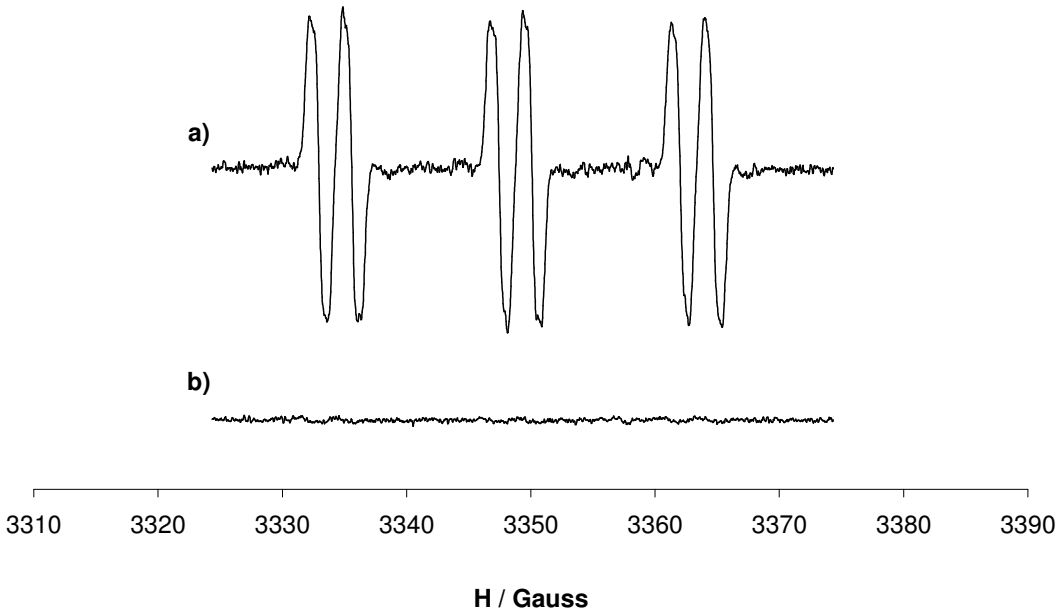


Figure S37. a) EPR spectrum of compound **1a** with an excess of PBN in toluene at 373 K, at 100 min. of reaction. Spin adduct C is detected, Entry 4, Table 2. **b)** Blank: EPR spectrum of PBN in toluene at 373 K, at 100 min. of reaction. No radical species are detected, Entry 5, Table 2.

Theoretical data

Computational methods

All geometry optimizations have been performed using the hybrid DFT B3LYP[3-5] method with the Gaussian03[6] program package. The geometry optimizations were performed without symmetry constraints. Analytical Hessians were computed to determine the nature of stationary points (one or zero imaginary frequencies for transition states (TSs) and minima, respectively) and to calculate unscaled zero-point energies (ZPEs) as well as thermal corrections and entropy effects using the standard statistical-mechanics relationships for an ideal gas.[7] These two latter terms were computed at 298.15 K and 1 atm to provide the reported relative Gibbs free energies (ΔG_{298}). Furthermore, the connectivity between stationary points was established by intrinsic reaction path[8] calculations. The all-electron cc-pVDZ basis set was used for O, N, C, and H atoms.[9] Relative energies were computed taking into account the total number of molecules present. The SO_2-Ar moieties present in the experimental **1a** triacetylenic azamacrocycle were substituted by H atoms to reduce the computational cost of the calculations involving these substituents. For a similar system we found that this substitution reduces the exothermicity of the cyclization process by approximately 10%.[10] Although this is not a minor reduction, we consider that the use of the reduced model does not alter significantly the conclusions that would be reached with the real system. A previous study on related species found that solvent effects due to toluene and acetonitrile in [2+2+2] cyclotrimerizations are minor, likely due to the absence of charged or polarized intermediates and transition states in the reaction mechanism.[11] Because the reactions studied are carried out in toluene solution, solvent effects have not been included in the present calculations. Finally, since there is no experimental data suggesting the presence of paramagnetic intermediates, our studies were limited to the singlet-spin potential energy surfaces. All reported distances and angles are in Å and degrees, respectively.

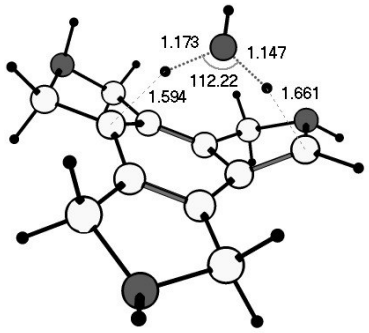


Figure S38. Optimized structure (B3LYP/cc-pVDZ) for **TS_{H2O}(5a,2a).**

Table S1. Cartesian coordinates (in Å) for all species and imaginary frequencies (in brackets, cm^{-1}) for the transition states occurring in the thermal cycloaddition of the macrocycle **1a**.

1a (nimag=0)

N	-0.063826000	-0.077996000	-0.000924000
C	0.036582000	-0.061159000	1.466890000
N	4.561531000	-0.089749000	3.519195000
C	1.345686000	-0.514722000	1.946073000
N	2.186688000	5.097471000	1.470558000
C	2.449670000	-0.809113000	2.358771000
C	3.795001000	-1.148300000	2.856982000
C	4.921047000	1.067716000	2.687911000
C	3.955365000	2.180895000	2.635605000
C	3.210881000	3.142461000	2.666429000
C	2.407691000	4.377033000	2.732752000
C	0.998229000	4.712848000	0.705528000
C	0.939818000	3.336715000	0.178207000
C	0.920277000	2.201399000	-0.257831000
C	0.903315000	0.789984000	-0.684829000
H	-1.006861000	0.230935000	-0.243935000
H	-0.144790000	0.945000000	1.902086000
H	-0.751934000	-0.728176000	1.854291000
H	4.054946000	0.234880000	4.343633000
H	3.016304000	5.005714000	0.883201000
H	4.401655000	-1.527858000	2.015823000
H	3.715131000	-1.987783000	3.568789000
H	5.876928000	1.472769000	3.067271000
H	5.131915000	0.703976000	1.667778000
H	2.913633000	5.067143000	3.432447000
H	1.422797000	4.162114000	3.181266000
H	0.115131000	4.890573000	1.344479000
H	0.906116000	5.423667000	-0.133647000
H	1.909533000	0.367051000	-0.526770000
H	0.701486000	0.723481000	-1.766494000

$1a_{H2O}$ (nimag=0)

N	2.343195000	-2.241566000	0.913204000
C	2.126412000	-0.920485000	1.516097000
H	1.108084000	-0.880627000	1.934773000
H	2.822650000	-0.825666000	2.365241000
N	1.311771000	2.865280000	-1.679749000
C	2.284372000	0.238147000	0.613334000
N	-3.144273000	-1.061143000	-0.690484000
C	2.397333000	1.149193000	-0.186528000
C	2.534232000	2.253340000	-1.155972000
H	3.132174000	3.060436000	-0.699326000
H	3.126864000	1.895389000	-2.016672000
C	0.419407000	1.980055000	-2.442768000
H	1.033434000	1.202620000	-2.929404000
H	-0.029765000	2.567579000	-3.264213000
C	-0.686126000	1.345213000	-1.703592000
C	-1.681982000	0.872887000	-1.188368000
C	-2.920357000	0.386305000	-0.556763000
H	-3.766922000	0.890857000	-1.051972000
H	-2.914152000	0.718331000	0.501420000
C	-2.493746000	-1.885292000	0.341299000
H	-2.563651000	-1.434207000	1.353903000
H	-3.034126000	-2.846410000	0.375803000
C	-1.075078000	-2.147831000	0.077846000
C	0.109872000	-2.361406000	-0.071885000
C	1.549948000	-2.503533000	-0.299476000
H	1.815937000	-1.832853000	-1.144944000
H	1.780470000	-3.533327000	-0.622084000
H	-4.148556000	-1.217709000	-0.612219000
H	0.788738000	3.302118000	-0.921248000
H	3.327853000	-2.326889000	0.654422000
O	-0.827796000	0.594005000	1.967571000
H	-0.476313000	0.727201000	1.069573000
H	-0.540189000	1.390034000	2.438714000

TS(1a,4a) (nimag=1) (-598*i*)

N	1.061874000	2.664477000	0.530194000
C	0.024317000	1.834446000	1.103501000
N	-3.565540000	-0.962164000	-0.294220000
C	-1.252253000	1.766711000	0.461432000
N	1.994687000	-2.359792000	0.049934000
C	-2.026535000	0.901454000	-0.010413000
C	-3.320868000	0.452207000	-0.596269000
C	-2.295466000	-1.672212000	-0.452668000
C	-1.129224000	-0.962627000	0.175414000
C	0.004268000	-0.989214000	0.717086000
C	1.186417000	-1.805358000	1.146815000
C	3.052421000	-1.480598000	-0.464338000
C	2.630359000	-0.105576000	-0.785869000
C	2.153804000	1.006142000	-0.911455000
C	1.489482000	2.318017000	-0.830504000
H	1.871119000	2.657190000	1.150314000
H	0.252595000	0.620728000	1.043521000
H	-0.047195000	2.058196000	2.180602000
H	-3.828655000	-1.022873000	0.692837000
H	1.368476000	-2.610740000	-0.716216000
H	-3.284053000	0.576653000	-1.693730000
H	-4.158672000	1.061940000	-0.226880000
H	-2.394119000	-2.686673000	-0.034671000
H	-2.094656000	-1.783197000	-1.534289000
H	0.805193000	-2.652450000	1.745967000
H	1.860832000	-1.237532000	1.807317000
H	3.859892000	-1.435313000	0.288942000
H	3.492414000	-1.971102000	-1.348022000
H	0.599516000	2.332362000	-1.481377000
H	2.159835000	3.114809000	-1.192067000

TS_{H2O}(1a,4a) (nimag=1) (-375*i*)

C	1.090388000	-0.672577000	0.233016000
C	1.504919000	0.708789000	0.053922000
C	2.273053000	-1.560888000	-0.140383000
C	2.868311000	0.661147000	-0.623970000
N	3.403885000	-0.628241000	-0.177269000
H	4.146009000	-0.962707000	-0.790134000
H	3.526340000	1.489176000	-0.316094000
H	2.734205000	0.731729000	-1.729210000
H	2.443394000	-2.361138000	0.600735000
H	2.066893000	-2.059345000	-1.115384000
C	0.888465000	1.873687000	0.381560000
C	-0.161994000	-1.165412000	0.436403000
C	-0.770681000	-2.260671000	0.957650000
C	-0.367809000	2.085906000	1.177666000
N	-1.480749000	2.762498000	0.485614000
N	-1.923274000	-2.718807000	0.340947000
C	-1.842857000	2.184149000	-0.824204000
C	-2.268213000	-1.850359000	-0.774591000
C	-1.644593000	-0.477995000	-0.545745000
C	-1.871180000	0.726399000	-0.794435000
H	-1.260438000	3.750944000	0.345626000
H	-2.686984000	-2.956028000	0.970493000
H	-0.468238000	-2.735062000	1.894641000
H	1.405273000	2.796987000	0.081739000
H	-0.132560000	2.726921000	2.047069000
H	-0.735361000	1.129087000	1.572565000
H	-3.357961000	-1.783527000	-0.895403000
H	-1.842307000	-2.260887000	-1.706807000
H	-1.175797000	2.493698000	-1.656003000
H	-2.848359000	2.578946000	-1.070207000

4a (nimag=0)

C	0.065891000	-0.203534000	-0.195370000
C	-0.165620000	-0.073200000	1.264523000
C	1.573955000	-0.163050000	-0.417303000
C	1.194905000	0.159121000	1.895183000
N	2.108402000	-0.449072000	0.919269000
H	3.060802000	-0.104169000	1.027254000
H	1.303893000	-0.325017000	2.878313000
H	1.358673000	1.253065000	2.041772000
H	1.912681000	-0.915316000	-1.147180000
H	1.858879000	0.838406000	-0.811727000
C	-1.378869000	-0.024664000	1.836178000
C	-0.875950000	-0.160644000	-1.119903000
C	-1.973964000	-0.077202000	-1.850962000
C	-1.714254000	0.453290000	3.216613000
N	-2.765634000	1.480945000	3.123267000
N	-2.698925000	1.091541000	-2.136884000
C	-2.350117000	2.725571000	2.459542000
C	-2.175842000	2.378394000	-1.681064000
C	-2.247598000	2.531416000	-0.220156000
C	-2.293621000	2.618533000	0.990898000
H	-3.080575000	1.717796000	4.064102000
H	-3.053389000	1.124886000	-3.089534000
H	-2.432290000	-0.982731000	-2.268874000
H	-2.248327000	-0.229412000	1.204720000
H	-2.136101000	-0.366308000	3.827070000
H	-0.800790000	0.814151000	3.738179000
H	-2.784120000	3.160975000	-2.163506000
H	-1.124715000	2.536509000	-2.003675000
H	-1.363405000	3.097085000	2.819726000
H	-3.089982000	3.498856000	2.727069000

$4a_{H2O}$ (nimag=0)

C	1.066032000	-0.826803000	0.461269000
C	1.492118000	0.599304000	0.508383000
C	2.233613000	-1.604376000	-0.148564000
C	2.937450000	0.636763000	0.025853000
N	3.390534000	-0.757269000	0.172229000
H	4.185897000	-0.958346000	-0.433715000
H	3.569123000	1.293359000	0.641028000
H	2.970555000	0.989019000	-1.027132000
H	2.340982000	-2.609771000	0.283160000
H	2.071293000	-1.714518000	-1.243021000
C	0.816395000	1.715410000	0.847589000
C	-0.065015000	-1.399268000	0.830629000
C	-1.159818000	-2.018268000	1.233858000
C	-0.625126000	1.856092000	1.266557000
N	-1.463229000	2.687415000	0.382865000
N	-2.369034000	-2.154547000	0.534421000
C	-1.545678000	2.239014000	-1.017081000
C	-2.415157000	-1.789862000	-0.880916000
C	-2.227674000	-0.344809000	-1.052738000
C	-1.987126000	0.843121000	-1.095329000
H	-1.115911000	3.648448000	0.382631000
H	-2.848297000	-3.027367000	0.736781000
H	-1.204540000	-2.423351000	2.253051000
H	1.375294000	2.660473000	0.785582000
H	-0.670176000	2.330399000	2.262893000
H	-1.100547000	0.872015000	1.359340000
H	-3.398221000	-2.099671000	-1.269873000
H	-1.643043000	-2.323923000	-1.475081000
H	-0.585559000	2.316720000	-1.571968000
H	-2.265922000	2.898117000	-1.531242000
H	3.602358000	0.272638000	3.180247000
O	4.436807000	0.046955000	2.742934000
H	4.128317000	-0.469058000	1.966690000

TS(4a,5a) (nimag=1) (-375*i*)

C	1.090388000	-0.672577000	0.233016000
C	1.504919000	0.708789000	0.053922000
C	2.273053000	-1.560888000	-0.140383000
C	2.868311000	0.661147000	-0.623970000
N	3.403885000	-0.628241000	-0.177269000
H	4.146009000	-0.962707000	-0.790134000
H	3.526340000	1.489176000	-0.316094000
H	2.734205000	0.731729000	-1.729210000
H	2.443394000	-2.361138000	0.600735000
H	2.066893000	-2.059345000	-1.115384000
C	0.888465000	1.873687000	0.381560000
C	-0.161994000	-1.165412000	0.436403000
C	-0.770681000	-2.260671000	0.957650000
C	-0.367809000	2.085906000	1.177666000
N	-1.480749000	2.762498000	0.485614000
N	-1.923274000	-2.718807000	0.340947000
C	-1.842857000	2.184149000	-0.824204000
C	-2.268213000	-1.850359000	-0.774591000
C	-1.644593000	-0.477995000	-0.545745000
C	-1.871180000	0.726399000	-0.794435000
H	-1.260438000	3.750944000	0.345626000
H	-2.686984000	-2.956028000	0.970493000
H	-0.468238000	-2.735062000	1.894641000
H	1.405273000	2.796987000	0.081739000
H	-0.132560000	2.726921000	2.047069000
H	-0.735361000	1.129087000	1.572565000
H	-3.357961000	-1.783527000	-0.895403000
H	-1.842307000	-2.260887000	-1.706807000
H	-1.175797000	2.493698000	-1.656003000
H	-2.848359000	2.578946000	-1.070207000

TS_{H2O}(4a,5a) (nimag=1) (-375*i*)

C	0.606112000	-0.828328000	-0.023490000
C	1.168523000	0.481664000	-0.308003000
C	1.581390000	-1.878005000	-0.545701000
C	2.387678000	0.251145000	-1.191049000
N	2.807917000	-1.109082000	-0.810046000
H	3.377264000	-1.545434000	-1.534459000
H	3.202533000	0.958417000	-0.983118000
H	2.101786000	0.332422000	-2.262085000
H	1.771401000	-2.677740000	0.189577000
H	1.165407000	-2.360383000	-1.456323000
C	0.778678000	1.724222000	0.080553000
C	-0.650970000	-1.141816000	0.393205000
C	-1.310673000	-2.138932000	1.035558000
C	-0.300208000	2.119464000	1.049374000
N	-1.403321000	2.933752000	0.506377000
N	-2.596764000	-2.438603000	0.623227000
C	-2.039171000	2.392237000	-0.710638000
C	-3.003039000	-1.540151000	-0.446798000
C	-2.169118000	-0.266990000	-0.368849000
C	-2.259935000	0.953562000	-0.622194000
H	-1.077156000	3.880514000	0.301317000
H	-3.273646000	-2.579116000	1.369770000
H	-0.928513000	-2.641979000	1.927391000
H	1.363148000	2.562453000	-0.325217000
H	0.149733000	2.735105000	1.849420000
H	-0.729116000	1.229198000	1.529092000
H	-4.077972000	-1.322160000	-0.386757000
H	-2.801402000	-2.013016000	-1.423834000
H	-1.474768000	2.592635000	-1.645326000
H	-3.008528000	2.918040000	-0.815473000
O	4.505984000	0.167489000	1.141710000
H	3.799048000	0.598208000	1.644889000
H	4.002489000	-0.477987000	0.598746000

5a (nimag=0)

C	-0.085823000	1.458889000	-0.056973000
C	-1.284055000	0.652321000	-0.051337000
C	-1.216357000	-0.693682000	-0.168227000
C	0.058104000	-1.442073000	-0.419832000
C	1.294802000	-0.569835000	-0.267373000
C	1.205748000	0.762888000	-0.117800000
C	0.160503000	2.791326000	0.066021000
C	2.280322000	1.819943000	0.066654000
C	0.463870000	-2.633857000	0.486441000
C	2.480029000	-1.491246000	-0.065365000
C	-2.717218000	1.100979000	0.072751000
C	-2.598777000	-1.288877000	-0.144095000
N	1.524809000	3.091143000	-0.014791000
N	1.907456000	-2.829237000	0.241687000
N	-3.445855000	-0.162417000	0.286620000
H	2.005183000	-3.412465000	-0.589655000
H	1.852831000	3.844948000	0.582646000
H	-4.345578000	-0.163415000	-0.187395000
H	3.141305000	-1.557223000	-0.948700000
H	3.111555000	-1.137607000	0.772028000
H	3.056177000	1.780116000	-0.714946000
H	2.791077000	1.717250000	1.044926000
H	-0.556446000	3.604521000	0.179806000
H	0.297981000	-2.368395000	1.546006000
H	-0.083203000	-3.566312000	0.279992000
H	-2.864253000	-1.695904000	-1.148251000
H	-2.684864000	-2.137676000	0.562094000
H	-3.028927000	1.652204000	-0.842625000
H	-2.870260000	1.793920000	0.922184000
H	0.025652000	-1.851042000	-1.457900000

$5a_{H2O}$ (nimag=0)

C	0.279058000	1.458049000	-0.134193000
C	1.514867000	0.743289000	0.088846000
C	1.525760000	-0.603715000	0.218294000
C	0.285205000	-1.445752000	0.256710000
C	-0.965806000	-0.671828000	-0.135907000
C	-0.946475000	0.665784000	-0.296153000
C	-0.044846000	2.768135000	-0.314042000
C	-2.046155000	1.632552000	-0.695732000
C	0.132512000	-2.679960000	-0.672043000
C	-2.021581000	-1.682118000	-0.547754000
C	2.910682000	1.297610000	0.212277000
C	2.930348000	-1.092609000	0.451542000
N	-1.420292000	2.958967000	-0.481377000
N	-1.312106000	-2.981741000	-0.674049000
N	3.755432000	0.091409000	0.154004000
H	-1.515232000	-3.531838000	0.161435000
H	-1.694190000	3.692535000	-1.129136000
H	4.556720000	0.161099000	0.776317000
H	-2.851369000	-1.757713000	0.174224000
H	-2.470537000	-1.391930000	-1.516836000
H	-2.946021000	1.507521000	-0.075058000
H	-2.342813000	1.494805000	-1.754671000
H	0.616042000	3.635153000	-0.306759000
H	0.458619000	-2.417930000	-1.694713000
H	0.704738000	-3.562383000	-0.347878000
H	3.041416000	-1.470869000	1.495184000
H	3.202125000	-1.937817000	-0.210265000
H	3.013256000	1.875223000	1.158416000
H	3.161643000	1.995984000	-0.608877000
H	0.160911000	-1.838613000	1.293892000
H	-2.473792000	0.099965000	1.715455000
O	-3.431002000	-0.005646000	1.848640000
H	-3.656148000	0.674915000	2.499046000

TS(5a,3a) (nimag=1) (-596*i*)

C	0.061690000	1.501678000	0.109140000
C	1.243663000	0.687895000	0.093079000
C	1.184132000	-0.659099000	0.253063000
C	-0.056968000	-1.462222000	0.537689000
C	-1.310573000	-0.638945000	0.342299000
C	-1.256740000	0.790672000	0.318505000
C	-0.205512000	2.810648000	-0.178167000
C	-2.260316000	1.832888000	0.009845000
C	-0.365373000	-2.635657000	-0.442876000
C	-2.436395000	-1.507045000	-0.119027000
C	2.667476000	1.137808000	-0.123581000
C	2.566366000	-1.243498000	0.150311000
N	-1.580991000	2.999822000	-0.262187000
N	-1.825970000	-2.835568000	-0.395309000
N	3.389653000	-0.126898000	-0.343137000
H	-2.027635000	-3.437080000	0.405177000
H	-2.009716000	3.914629000	-0.175883000
H	4.311070000	-0.114950000	0.086732000
H	-3.276457000	-1.654290000	0.594663000
H	-2.908092000	-1.077449000	-1.036584000
H	-1.494941000	1.027407000	1.420615000
H	-3.338608000	1.805497000	0.125340000
H	0.469913000	3.641444000	-0.368881000
H	-0.069640000	-2.338810000	-1.465262000
H	0.147325000	-3.579855000	-0.196488000
H	2.885426000	-1.640029000	1.142877000
H	2.604263000	-2.103005000	-0.546602000
H	3.029855000	1.714885000	0.756486000
H	2.766750000	1.808114000	-0.999277000
H	0.042943000	-1.918736000	1.559838000

TS_{H2O}(5a,3a) (nimag=1) (-1673*i*)

C	-0.119189000	-1.430092000	-0.279123000
C	-1.412205000	-0.816842000	-0.036956000
C	-1.494497000	0.495991000	0.267251000
C	-0.323639000	1.432036000	0.388015000
C	1.053636000	0.764892000	0.124712000
C	1.026454000	-0.592199000	-0.317426000
C	0.325034000	-2.744711000	-0.422356000
C	2.214873000	-1.448146000	-0.372611000
C	-0.302861000	2.621490000	-0.618269000
C	1.903199000	1.831907000	-0.637923000
C	-2.772192000	-1.462893000	-0.014538000
C	-2.931359000	0.875106000	0.515367000
N	1.675169000	-2.775942000	-0.503311000
N	1.094647000	3.060408000	-0.693683000
N	-3.684600000	-0.309837000	0.067521000
H	1.294986000	3.605930000	0.147368000
H	2.220158000	-3.604211000	-0.695205000
H	-4.483242000	-0.501038000	0.667082000
H	2.864769000	2.031759000	-0.141690000
H	2.123085000	1.488225000	-1.665240000
H	2.664989000	-1.094218000	0.727255000
H	3.031422000	-1.220208000	-1.073017000
H	-0.255797000	-3.666093000	-0.452248000
H	-0.624820000	2.264515000	-1.613527000
H	-0.955436000	3.461193000	-0.333482000
H	-3.082324000	1.126856000	1.590649000
H	-3.236902000	1.773841000	-0.054768000
H	-2.854363000	-2.165628000	0.845892000
H	-2.971121000	-2.061526000	-0.924780000
H	-0.336924000	1.875455000	1.405623000
O	2.950035000	-0.045760000	1.773778000
H	2.557705000	-0.414822000	2.582754000
H	1.843494000	0.484413000	1.126570000

TS_{H2O}(5a,6) (nimag=1) (-2093*i*)

C	-0.300375000	1.435600000	-0.421766000
C	-1.477553000	0.618371000	-0.187352000
C	-1.390575000	-0.730597000	-0.130799000
C	-0.130870000	-1.457900000	-0.498493000
C	1.112746000	-0.593583000	-0.278331000
C	0.985156000	0.797391000	-0.528964000
C	-0.071474000	2.803733000	-0.297208000
C	1.990984000	1.816417000	-0.274393000
C	0.330906000	-2.750093000	0.194262000
C	2.276129000	-1.532886000	-0.578706000
C	-2.892856000	1.070137000	0.066840000
C	-2.744951000	-1.326016000	0.141066000
N	1.258152000	3.052503000	-0.265591000
N	1.765227000	-2.873639000	-0.164298000
N	-3.552742000	-0.158963000	0.540811000
H	1.851269000	-3.513935000	-0.950807000
H	1.675106000	3.971813000	-0.250103000
H	-4.509590000	-0.227412000	0.202982000
H	2.549444000	-1.529848000	-1.653334000
H	3.179922000	-1.268634000	-0.003657000
H	2.954847000	1.838955000	-0.794209000
H	2.207606000	1.305764000	0.940590000
H	-0.793620000	3.611366000	-0.183751000
H	0.221888000	-2.652709000	1.289917000
H	-0.217377000	-3.652426000	-0.119114000
H	-3.127151000	-1.849888000	-0.766505000
H	-2.721914000	-2.084499000	0.946683000
H	-3.337578000	1.491020000	-0.863343000
H	-2.953868000	1.870215000	0.830515000
H	-0.203542000	-1.707675000	-1.586137000
O	2.219324000	0.366085000	1.919534000
H	1.561195000	0.678161000	2.561418000
H	1.490716000	-0.251703000	1.029196000

3a (nimag=0)

C	0.271135000	-1.356465000	-0.015817000
C	-1.079742000	-0.835377000	0.009598000
C	-1.316717000	0.455634000	0.308956000
C	-0.263060000	1.485179000	0.608406000
C	1.191775000	0.913220000	0.838618000
C	1.366629000	-0.508843000	0.357480000
C	0.791514000	-2.597526000	-0.347857000
C	2.515586000	-1.265450000	0.245404000
C	-0.087144000	2.539829000	-0.536542000
C	2.072023000	1.930455000	0.079613000
C	-2.370954000	-1.574587000	-0.222606000
C	-2.798854000	0.726187000	0.316111000
N	2.154916000	-2.527130000	-0.183850000
N	1.243403000	2.259117000	-1.074696000
N	-3.370541000	-0.492420000	-0.283742000
H	1.613496000	3.048948000	-1.603455000
H	2.799806000	-3.281830000	-0.368335000
H	-4.242416000	-0.760500000	0.165935000
H	2.283004000	2.803717000	0.740390000
H	3.036687000	1.504962000	-0.237415000
H	3.557163000	-1.020707000	0.436526000
H	0.309559000	-3.507770000	-0.692879000
H	-0.851032000	2.433969000	-1.322757000
H	-0.178755000	3.563876000	-0.111409000
H	-3.153224000	0.926120000	1.354653000
H	-3.072493000	1.621762000	-0.276366000
H	-2.550802000	-2.308794000	0.594598000
H	-2.358788000	-2.154797000	-1.165502000
H	1.428546000	0.952282000	1.914909000
H	-0.568346000	2.028264000	1.518943000

$3a_{H2O}$ (nimag=0)

C	0.300428000	-1.182302000	-0.497713000
C	-1.094112000	-0.954339000	-0.175934000
C	-1.501404000	0.226425000	0.327163000
C	-0.616068000	1.415902000	0.573938000
C	0.933174000	1.127141000	0.503145000
C	1.271686000	-0.167334000	-0.202327000
C	0.967249000	-2.247437000	-1.083318000
C	2.499582000	-0.657539000	-0.609771000
C	-0.841781000	2.580610000	-0.450445000
C	1.468626000	2.377782000	-0.222349000
C	-2.249419000	-1.914073000	-0.289797000
C	-2.979817000	0.188099000	0.614271000
N	2.299252000	-1.915318000	-1.145247000
N	0.415559000	2.646793000	-1.196147000
N	-3.421846000	-1.056774000	-0.037849000
H	0.535841000	3.549420000	-1.655665000
H	3.023650000	-2.498191000	-1.539638000
H	-4.131566000	-1.539073000	0.507774000
H	1.616352000	3.198548000	0.517071000
H	2.431914000	2.200875000	-0.725590000
H	3.492008000	-0.214706000	-0.586347000
H	0.603551000	-3.198289000	-1.462247000
H	-1.683490000	2.379827000	-1.131961000
H	-1.071568000	3.517419000	0.102871000
H	-3.163053000	0.211514000	1.714026000
H	-3.516634000	1.063373000	0.197998000
H	-2.136321000	-2.749080000	0.437859000
H	-2.309398000	-2.381253000	-1.291773000
H	1.344364000	1.070471000	1.522777000
H	-0.844575000	1.807466000	1.579560000
H	1.330606000	-1.107032000	2.940535000
O	2.260952000	-0.854468000	2.840476000
H	2.391079000	-0.956052000	1.882475000

6 (nimag=0)

C	0.893694000	1.289175000	0.042044000
C	1.570963000	0.002802000	-0.051159000
C	0.888007000	-1.152378000	0.126609000
C	-0.568297000	-1.125392000	0.494329000
C	-1.286333000	0.049906000	-0.209529000
C	-0.550723000	1.332082000	0.042086000
C	1.342830000	2.593597000	0.177926000
C	-0.920485000	2.654426000	0.175171000
C	-1.515367000	-2.282418000	0.172658000
C	-2.735954000	-0.190376000	0.219506000
C	3.037699000	-0.276248000	-0.256902000
C	1.827936000	-2.326453000	0.080997000
N	0.235981000	3.407213000	0.256706000
N	-2.855519000	-1.667276000	0.324852000
N	3.070125000	-1.736977000	-0.451364000
H	-3.500280000	-2.029759000	-0.372638000
H	0.265046000	4.406813000	0.399463000
H	3.897066000	-2.156389000	-0.033629000
H	-2.930817000	0.279164000	1.202377000
H	-3.469428000	0.222460000	-0.491924000
H	-1.898476000	3.127333000	0.196392000
H	2.346877000	3.003163000	0.243286000
H	-1.325699000	-2.658571000	-0.852947000
H	-1.398140000	-3.131304000	0.866880000
H	1.938064000	-2.774117000	1.096243000
H	1.465604000	-3.140427000	-0.575573000
H	3.628234000	0.075252000	0.620586000
H	3.448622000	0.250278000	-1.139046000
H	-1.218035000	-0.156626000	-1.298133000
H	-0.630385000	-0.931978000	1.584883000
H	0.843433000	0.529150000	2.775402000
O	0.038596000	0.777780000	3.253935000
H	-0.428216000	1.293538000	2.577313000

TS_{H2O}(5a,2a)

C	-0.040234000	-1.404072000	-0.387518000
C	-1.284827000	-0.697642000	-0.409960000
C	-1.266075000	0.663731000	-0.202837000
C	-0.025554000	1.337748000	0.045422000
C	1.175457000	0.685318000	-0.458292000
C	1.178781000	-0.661369000	-0.679896000
C	0.355025000	-2.563084000	0.298186000
C	2.312304000	-1.670204000	-0.693936000
C	0.273029000	2.832810000	0.079466000
C	2.270173000	1.733457000	-0.527859000
C	-2.694542000	-1.216581000	-0.306290000
C	-2.676699000	1.159899000	-0.007053000
N	1.795362000	-2.748296000	0.193430000
N	1.748716000	2.925354000	0.178712000
N	-3.491415000	0.015814000	-0.448587000
H	1.986343000	2.816206000	1.167175000
H	2.027795000	-3.669669000	-0.172689000
H	-4.371925000	-0.039767000	0.058428000
H	3.236967000	1.414946000	-0.103498000
H	2.461344000	1.991520000	-1.587015000
H	3.257317000	-1.251853000	-0.305535000
H	2.521540000	-2.048330000	-1.717001000
H	-0.255352000	-3.437318000	0.534777000
H	-0.052839000	3.326705000	-0.857292000
H	-0.196760000	3.380069000	0.911104000
H	-2.826367000	1.444589000	1.060214000
H	-2.903262000	2.059640000	-0.607961000
H	-2.845279000	-1.740467000	0.668787000
H	-2.952978000	-1.941938000	-1.098224000
H	0.125141000	0.499470000	1.392784000
H	1.093273000	-0.401308000	2.489793000
O	0.208038000	-0.441335000	2.088743000
H	0.201066000	-1.421978000	1.494726000

DSC analysis

Experimental conditions

Crystalline samples of macrocycles **1a** were placed inside an aluminium crucible and were subjected to several constant heating rates (from 0.25 to 10ºC/min). During the experiments, a continuous flow of 40 ml/min of high purity N_2 was kept. The content of the crucible was analyzed by means of ^{1}H NMR at different stages of the DSC analysis to ensure that the DSC bands corresponded to the transformations detected by NMR.

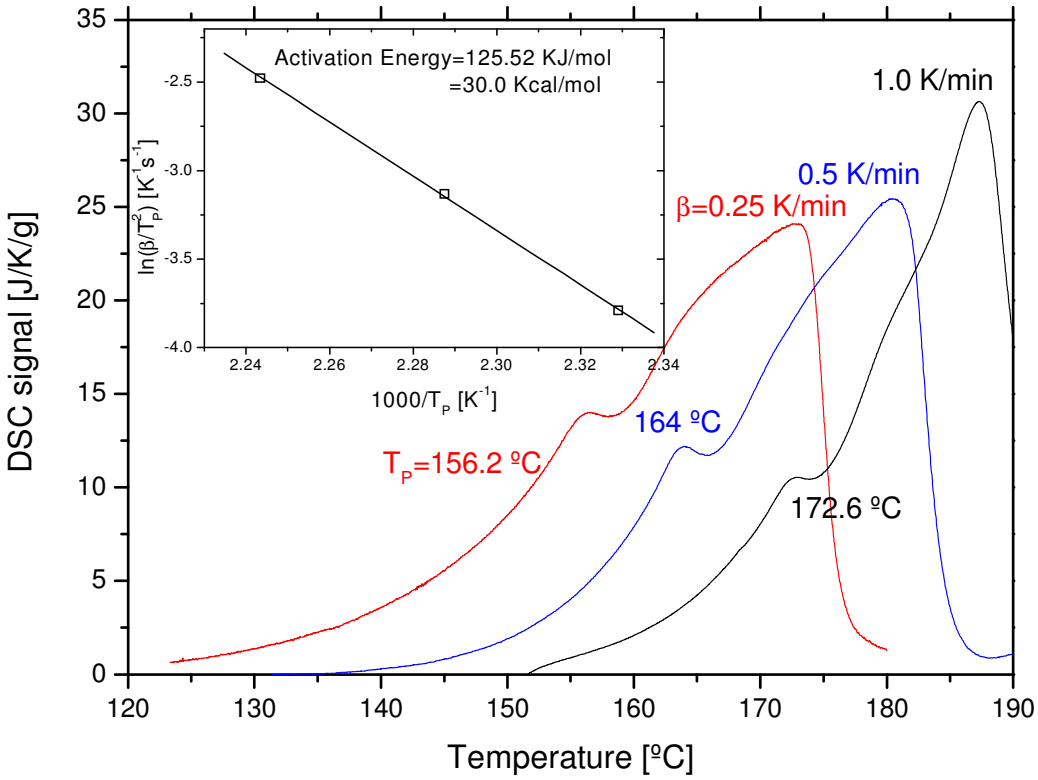


Figure S39. DSC thermograms of the sample **1a** obtained at three different heating rates, β. The peak temperatures, T_p, for the first process are indicated. Inset, Kissinger plot related to the first process. The activation energy of this process is obtained from the slope of the Kissinger plot.[12,13]

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