Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supplementary Information

Triflate-Functionalized Calix[6]arenes as Versatile Building Blocks: Application to the Synthesis of an Inherently Chiral Zn(II) Complex

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General Informations.

All reactions using dry solvents were conducted under argon atmosphere employing standard techniques. All solvents were reagent grade. Tetrahydrofuran and dichloromethane were respectively freshly distilled from sodium/benzophenone and calcium hydride under argon. Toluene (99.9%, Extra Dry over Molecular Sieve, Stabilized, AcroSeal) was purchased from ACROS Organics. Reactions were magnetically stirred and monitored by thin layer chromatography using Merck-Kiesegel 60F254 plates or Macherey-Nagel Pre Coated TLC-sheets Alugram® Xtra Sil/UV254. Flash chromatography was performed with silica gel 60 (particle size 35-70 μm) supplied by Merck. Yields refer to chromatographically and spectroscopically pure compounds unless otherwise stated. All organic layers were dried over Wa filters (hydrophobic phase separation papers, MN 616 WA (1/4)) supplied by Macherey-Nagel.

^{1}H NMR spectra were recorded at 300, 400 or 600 MHz. ^{13}C NMR spectra were recorded at 75, 100 or 150 MHz. Traces of residual solvents were used as internal standard for ^{1}H (7.26 ppm for $CHCl_3$) and for ^{13}C (77.16 ppm for $CDCl_3$). $CDCl_3$ was filtered through a short column of basic alumina to remove traces of DCl. Most of the ^{1}H NMR spectra signals were assigned on the basis of 2D NMR analyses (COSY, ROESY, HSQC, HMBC). Despite extensive signal averaging (thousands of scans), most ^{13}C NMR spectra showed poor signal-to-noise ratio because of the asymmetric functionalization pattern of the compounds and thus cannot be described (see Supplementary Information). Chemical shifts are quoted on the δ scale, coupling constants (*J*) are expressed in Hertz (Hz). Abbreviations: s for singlet; d for doublet; t for triplet; br for broad signal; m for massif. Melting points were recorded on a Stuart Scientific Analogue SMP11 or Büchi Melting Point B-545. IR analyses were performed with a FT-IR spectrometer using ATR (Attenuated Total Reflectance) method. ESI-MS and HRMS analyses were performed using methanol as solvent. Low resolution mass spectra were recorded with an ESI-MS spectrometer equipped with an ion-trap. High-resolution mass-spectra were obtained on Quadrupole Time of Flight (QTOF) 6520 series from Agilent Technologies, used in 4 GHz mode (High resolution mode), source was an electrospray ionization source (ESI), Multimode source (used in APCI mode) or a (MALDI-TOF MS LD+).

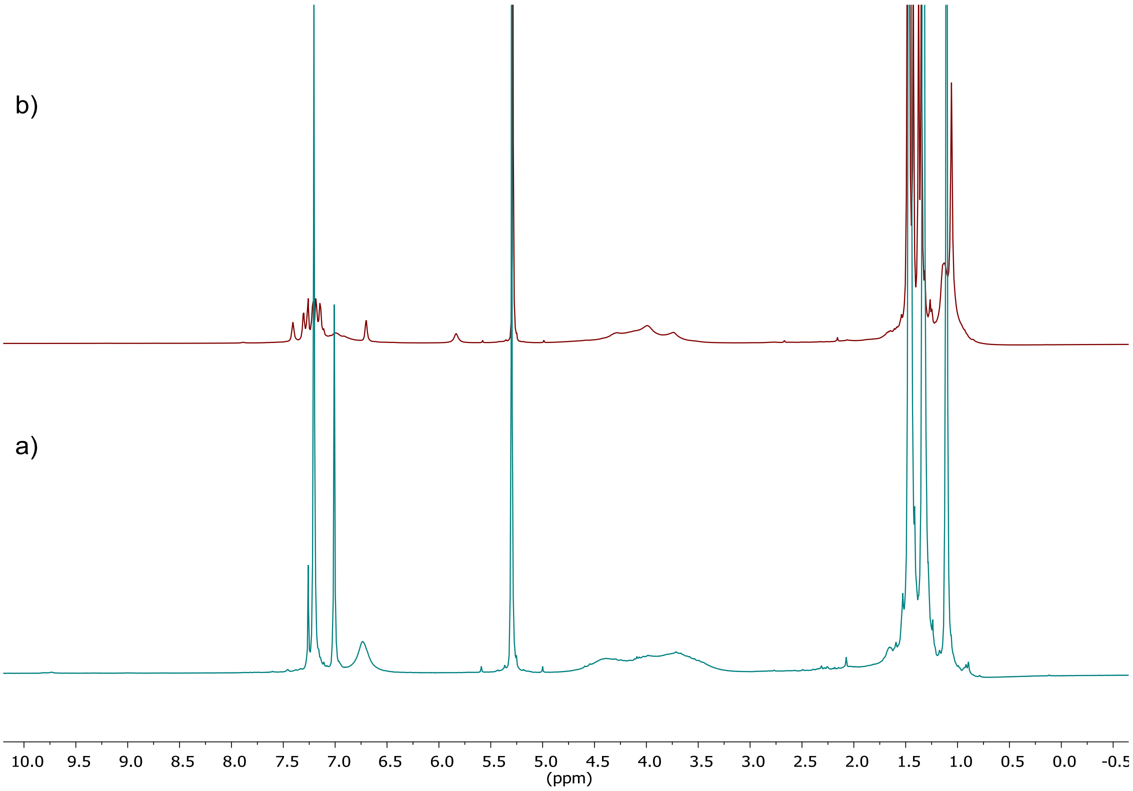


Figure S1. ^{1}H spectra of a) $X_6H_4Tf_2$ **2** and b) $X_6H_3Tf_3$ **3** (300 MHz, $CDCl_3$, 25 °C).

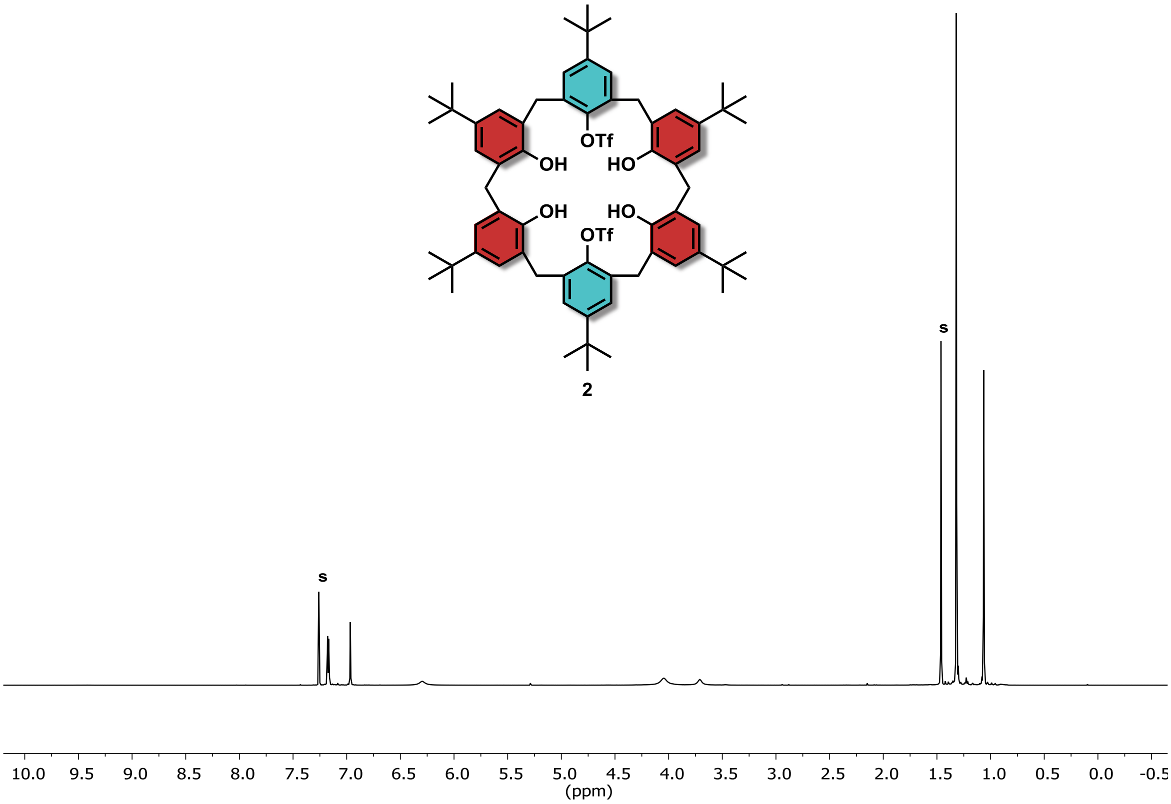


Figure S2. ^{1}H NMR spectrum of **2** (600 MHz, $CDCl_3$, 80 °C). S = residual solvents.

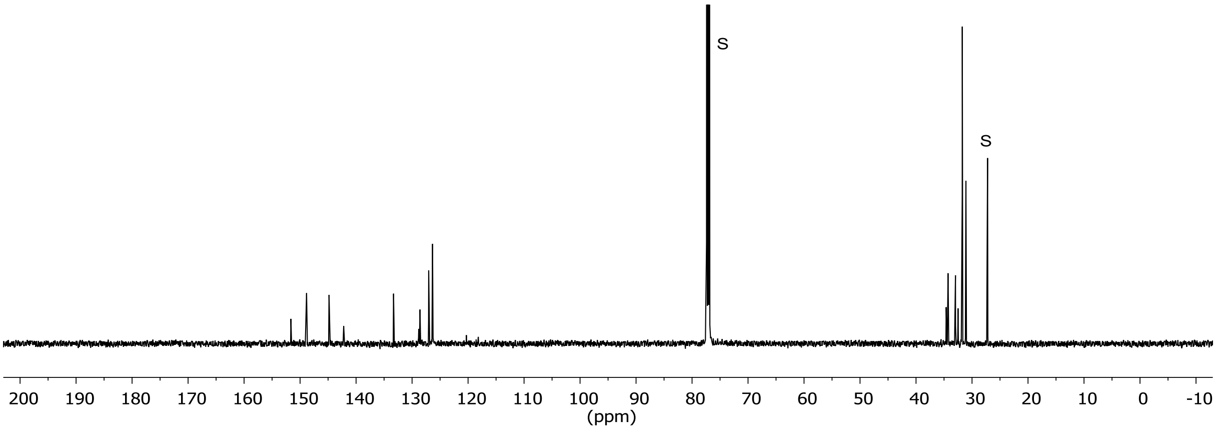


Figure S3. ^{13}C NMR spectrum of **2** (150 MHz, $CDCl_3$, 80 °C). S = residual solvents.

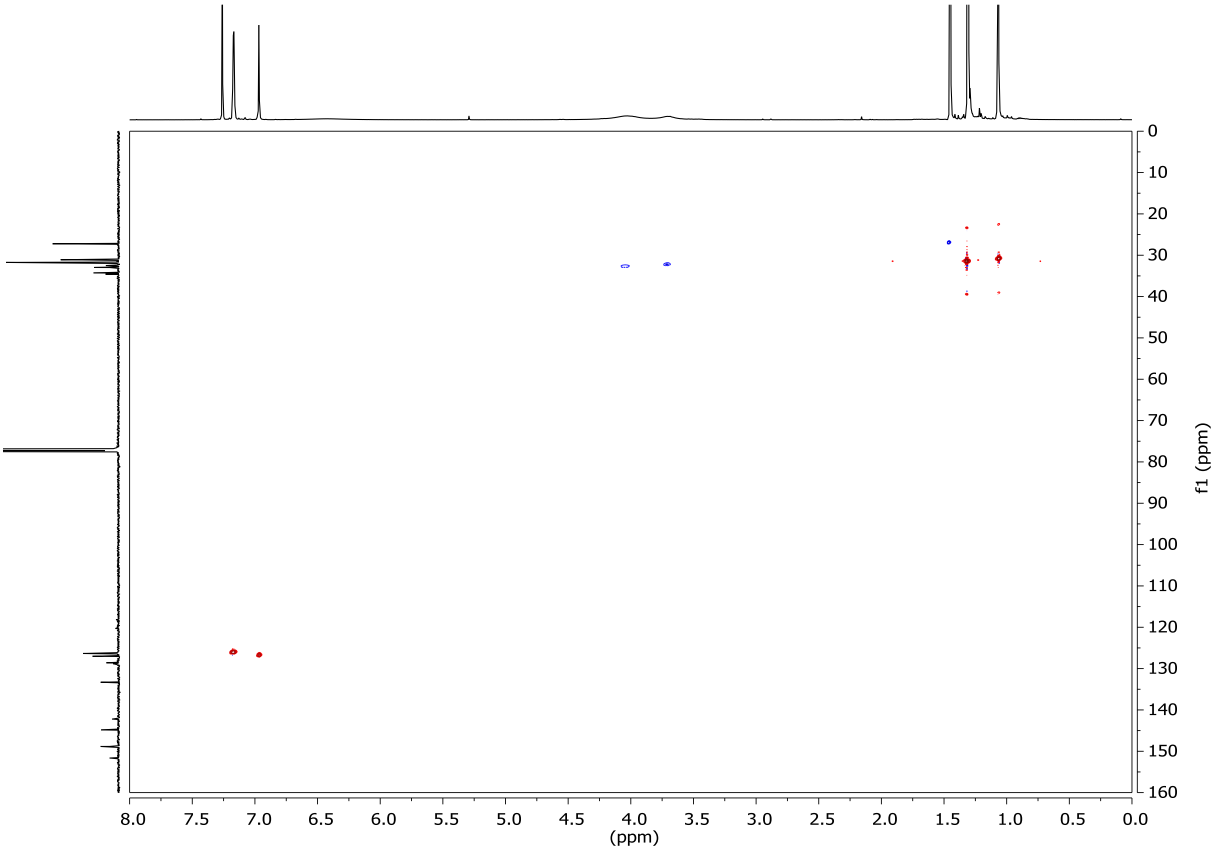


Figure S4. Edited ^{1}H-^{13}C HSQC spectrum of **2** (14.1 Tesla, CDCl$_3$, 80 °C).

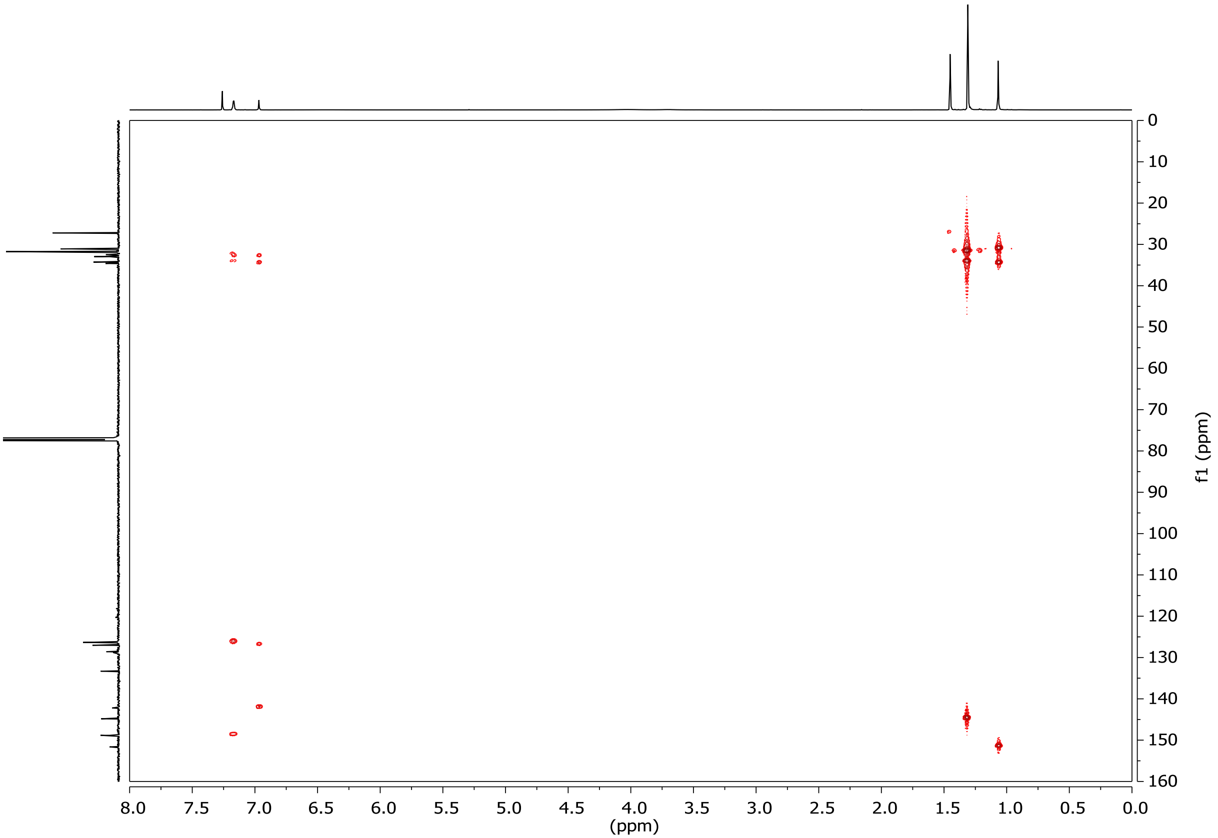


Figure S5. ^{1}H-^{13}C HMBC spectrum of **2** (8 Hz, 14.1 Tesla, CDCl$_3$, 80 °C).

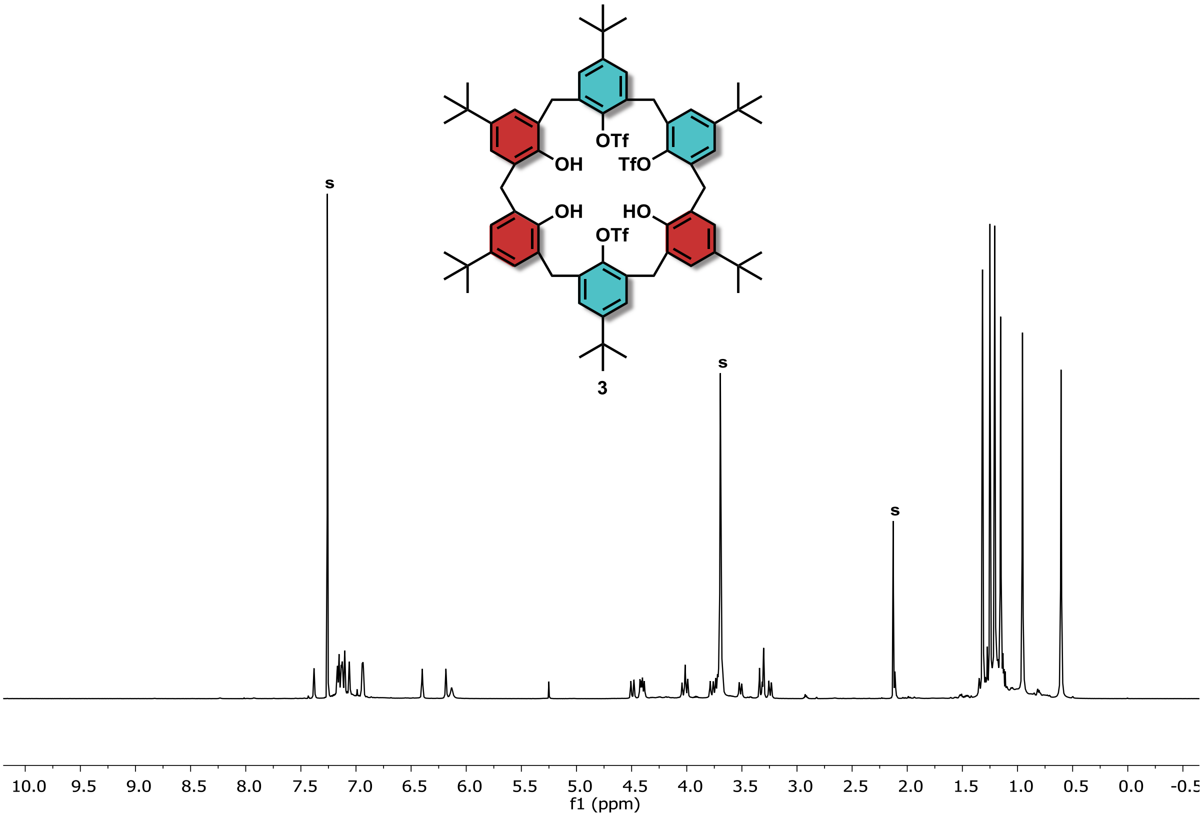


Figure S6. ^{1}H NMR spectrum of **3** (600 MHz, CDCl$_3$:CD$_3$OD, 9:1, 5 °C). S = residual solvents.

The ^{13}C NMR spectrum of **3** was obtained using a 5 mm J-Young valve NMR tube and about 45 mg of compound in 600 µL of solvent ($CDCl_3$:CD_3OD; 9:1). It was recorded at 9.4 T (~100 MHz) and 25°C using the same parameters as indicated here above but 60000 scans (60 h of measurement). 57 signals are expected, among which 30 signals of quaternary carbon atoms and 3 quadruplets for the CF_3 groups. The spectrum of **3** also shows superimposed signals. In addition, several signals exhibit FWHH (Full Width at Half Height) values ranging between 10 and 20 Hz; in contrast, the FWHH is about 2 Hz for the peaks of CD_3OD (including line broadening of 1 Hz due to exponential apodization of the free induction decay).

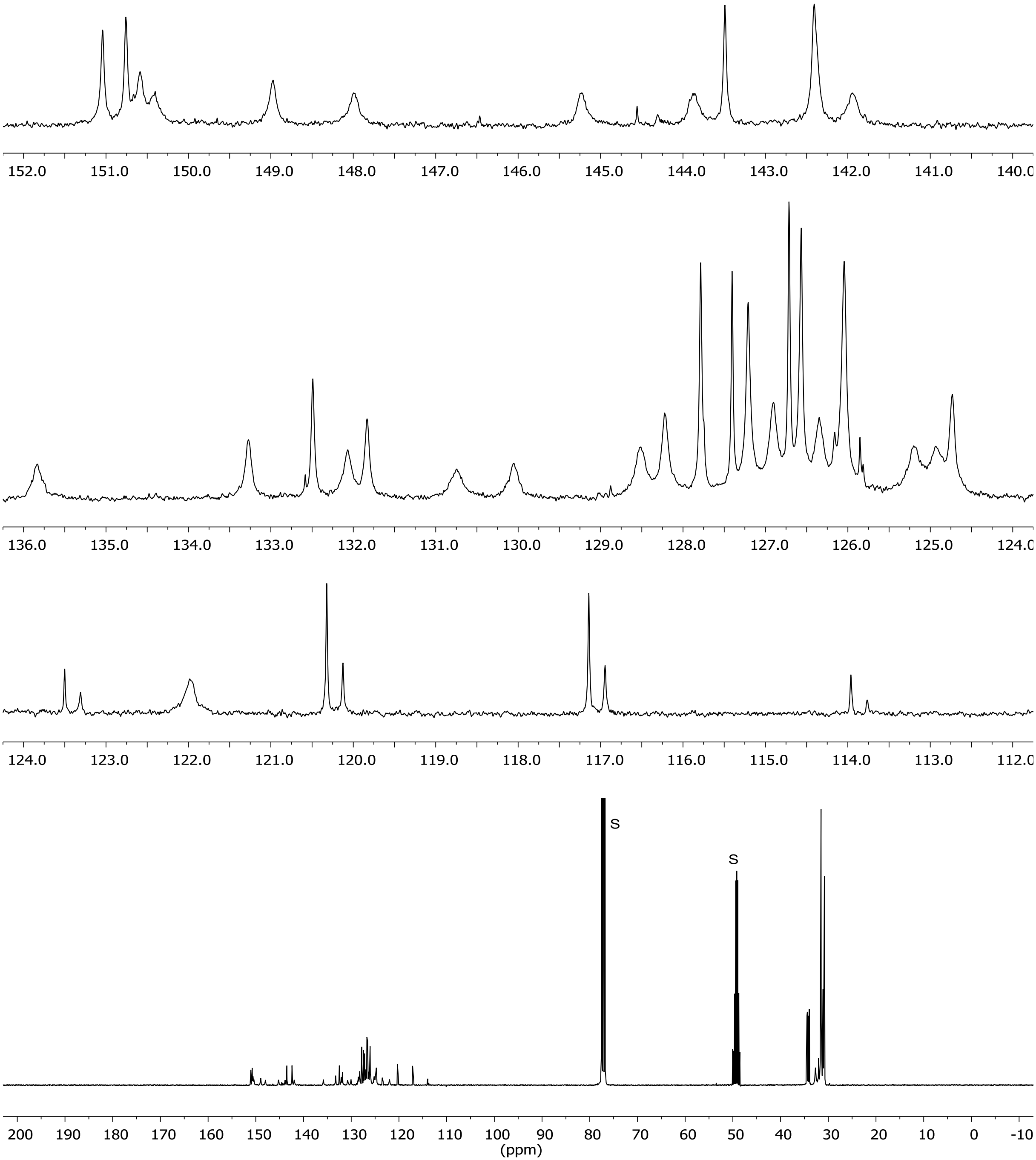


Figure S7. ^{13}C NMR spectrum of **3** (100 MHz, $CDCl_3$:CD_3OD, 9:1, 25 °C). S = residual solvents.

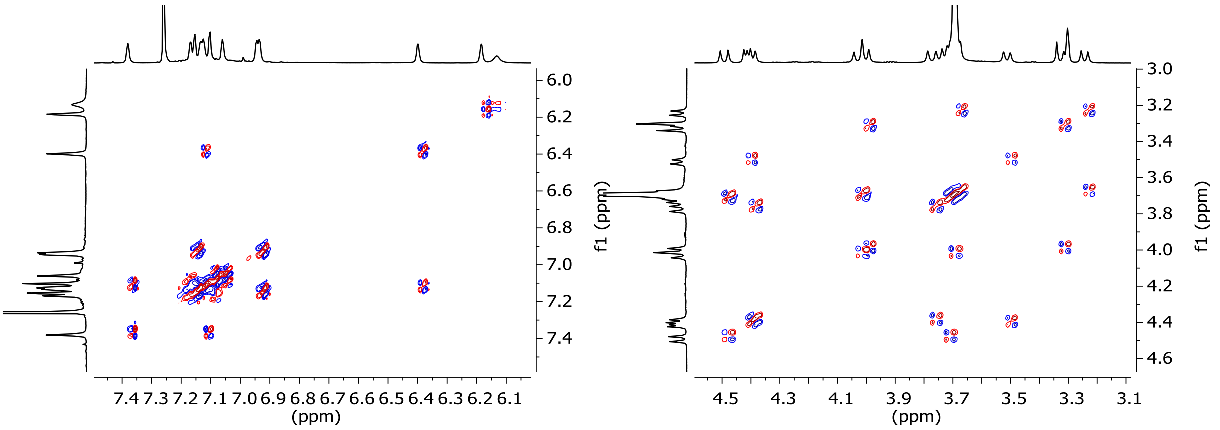


Figure S8. Regions of the dqfCOSY spectrum of **3** (600 MHz, $CDCl_3$:CD_3OD, 9:1, 5 °C). Left: low level cut-off showing ArH-ArH ^4J correlations. Right: high level cut-off showing $ArCH_2Ar$ ^2J correlations.

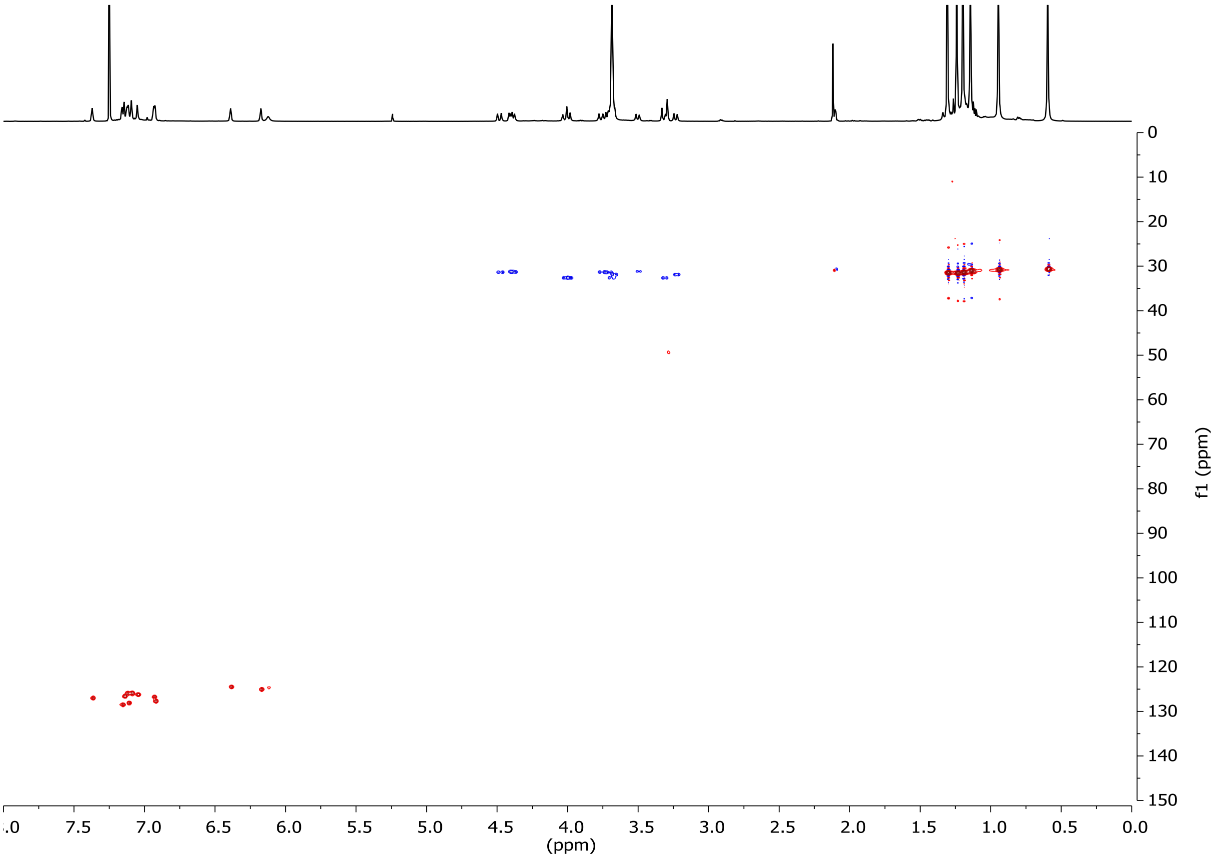


Figure S9. Edited ^1H-^{13}C HSQC spectrum of **3** (14.1 Tesla, $CDCl_3$:CD_3OD, 9:1, 5 °C).

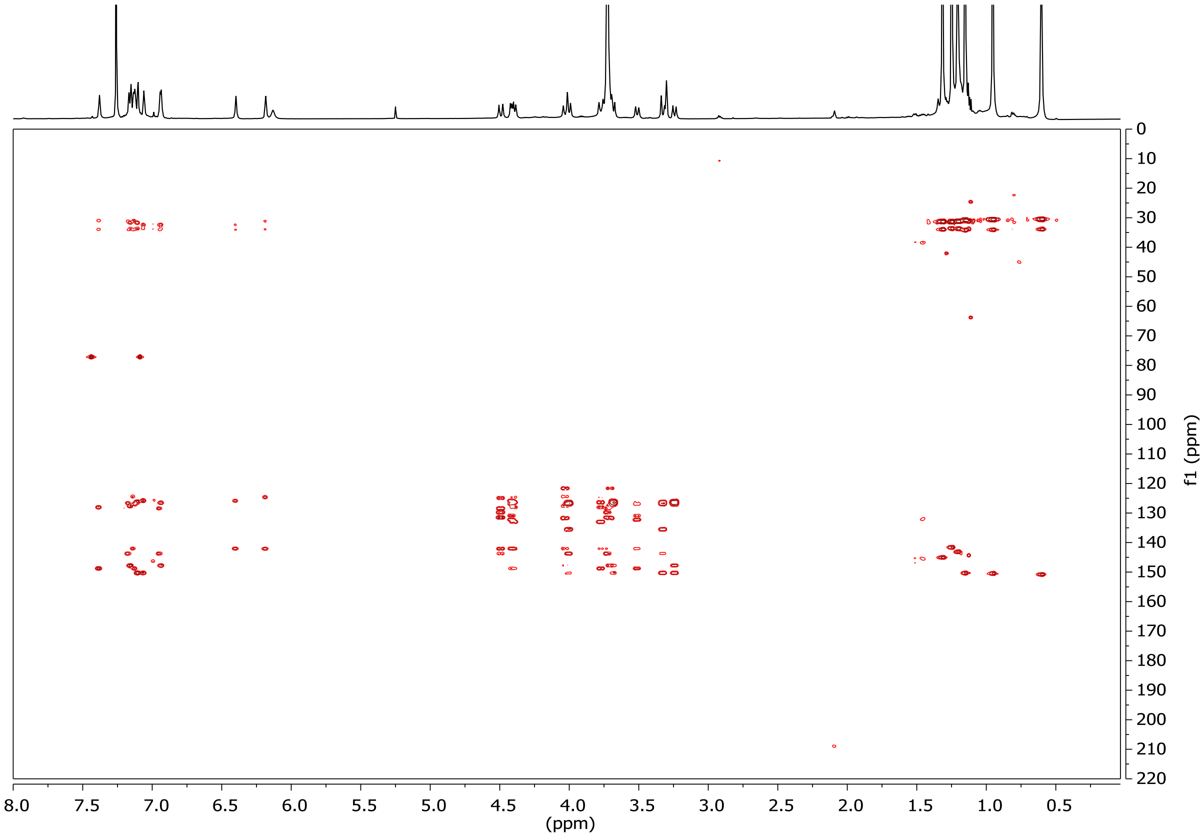


Figure S10. ^{1}H-^{13}C HMBC spectrum of **3** (8 Hz, 14.1 Tesla, $CDCl_3$:CD_3OD, 9:1, 5 °C).

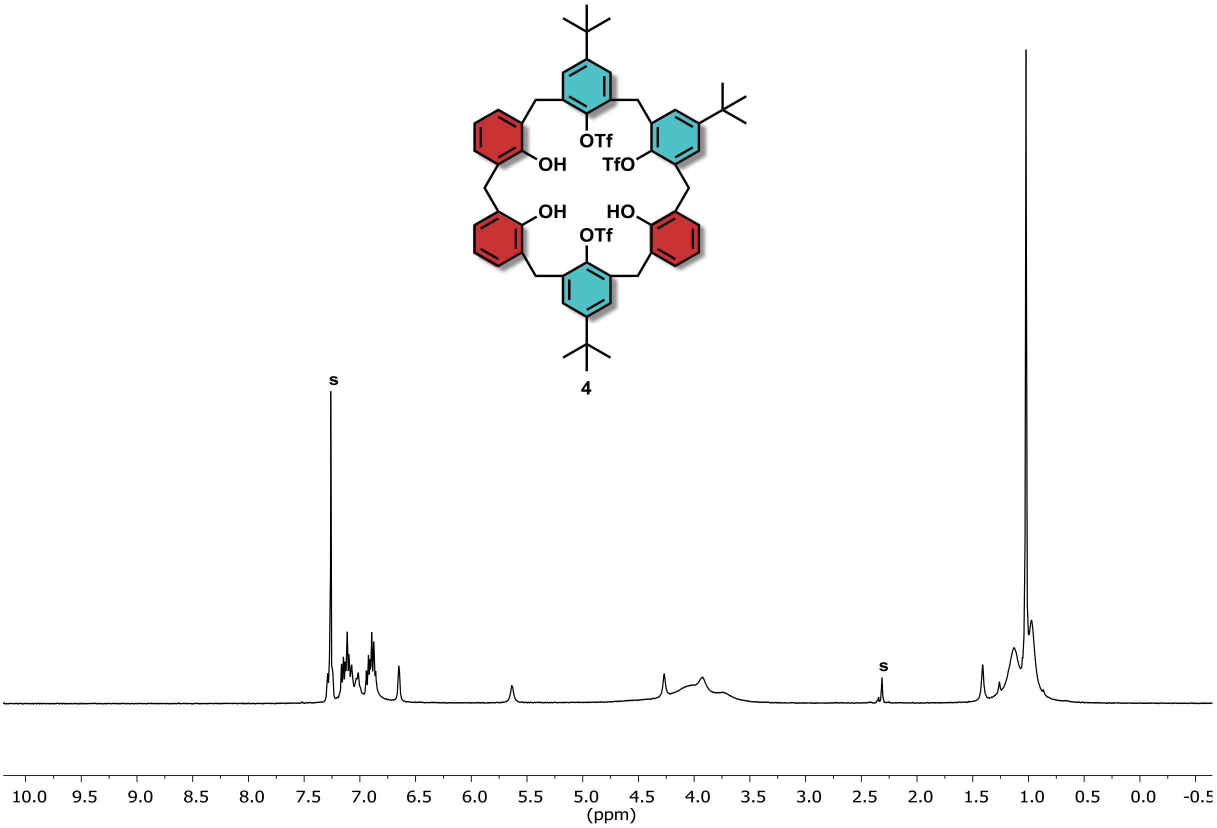


Figure S11. ^{1}H NMR spectrum of **4** (400 MHz, $CDCl_3$, 25 °C). S = residual solvents.

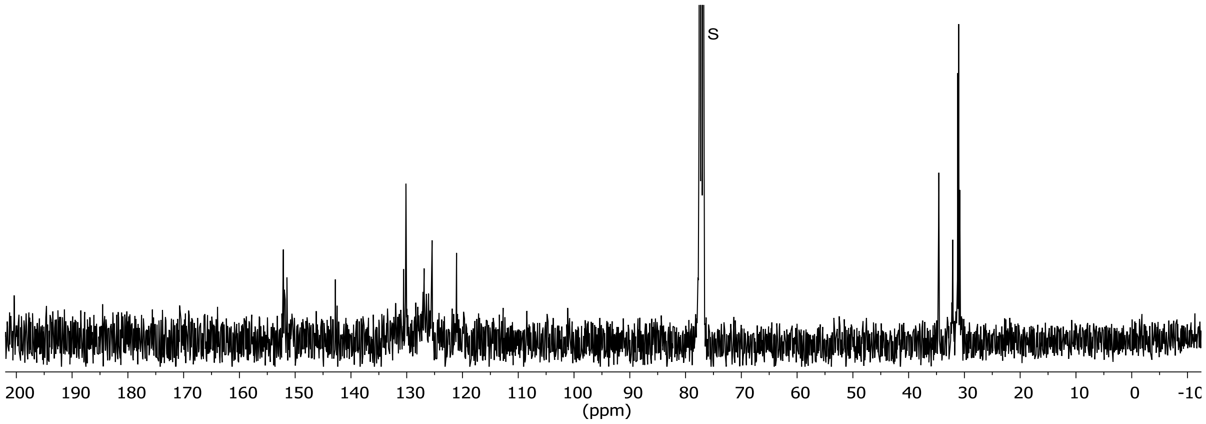


Figure S12. ^{13}C NMR spectrum of **4** (100 MHz, $CDCl_3$, 25 °C). S = residual solvent.

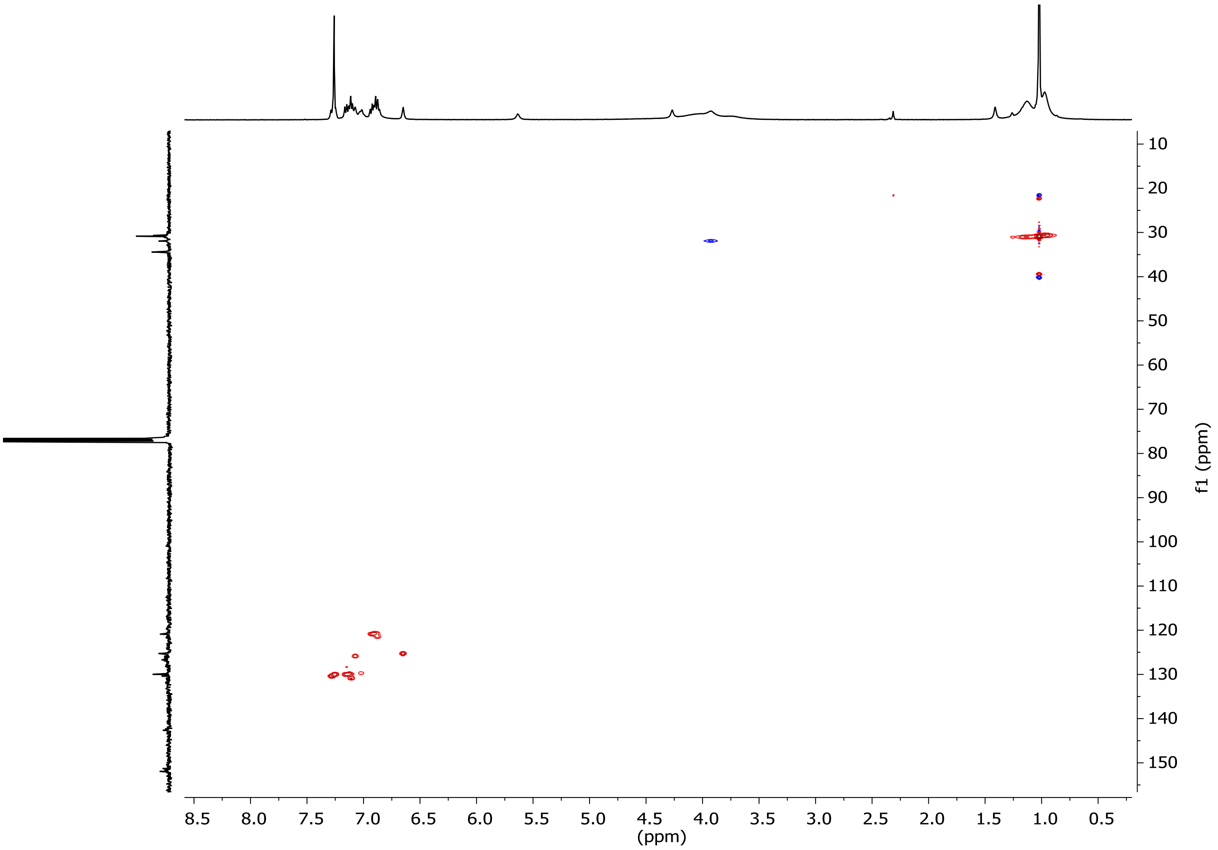
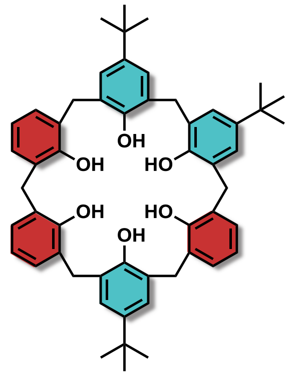


Figure S13. Edited ^{1}H-^{13}C HSQC spectrum of **4** (9.4 Tesla, $CDCl_3$, 25 °C).



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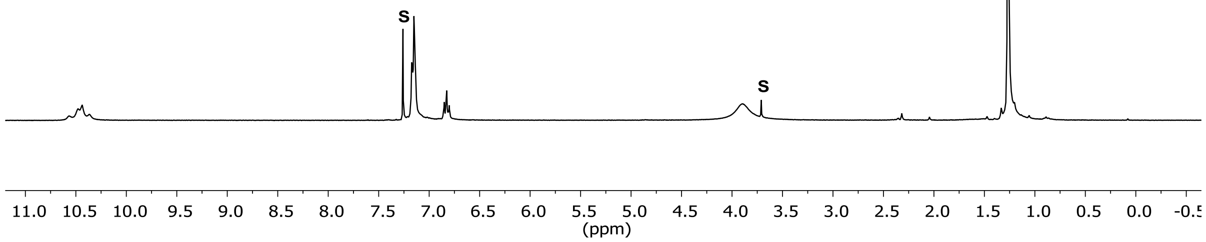

Figure S14. ^{1}H NMR spectrum of **5** (300 MHz, $CDCl_3$, 25 °C). S = residual solvents.

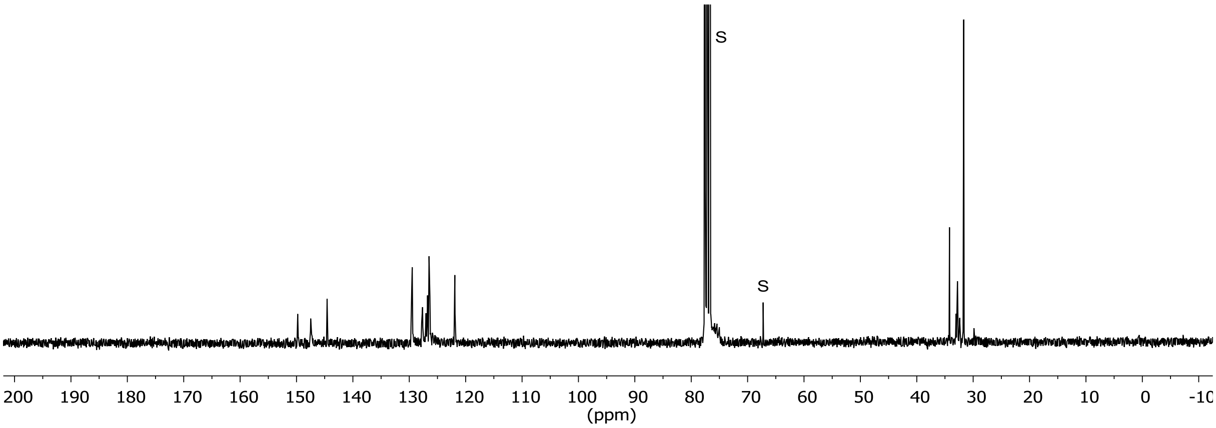

Figure S15. ^{13}C NMR spectrum of **5** (75 MHz, $CDCl_3$, 25 °C). S = residual solvents.

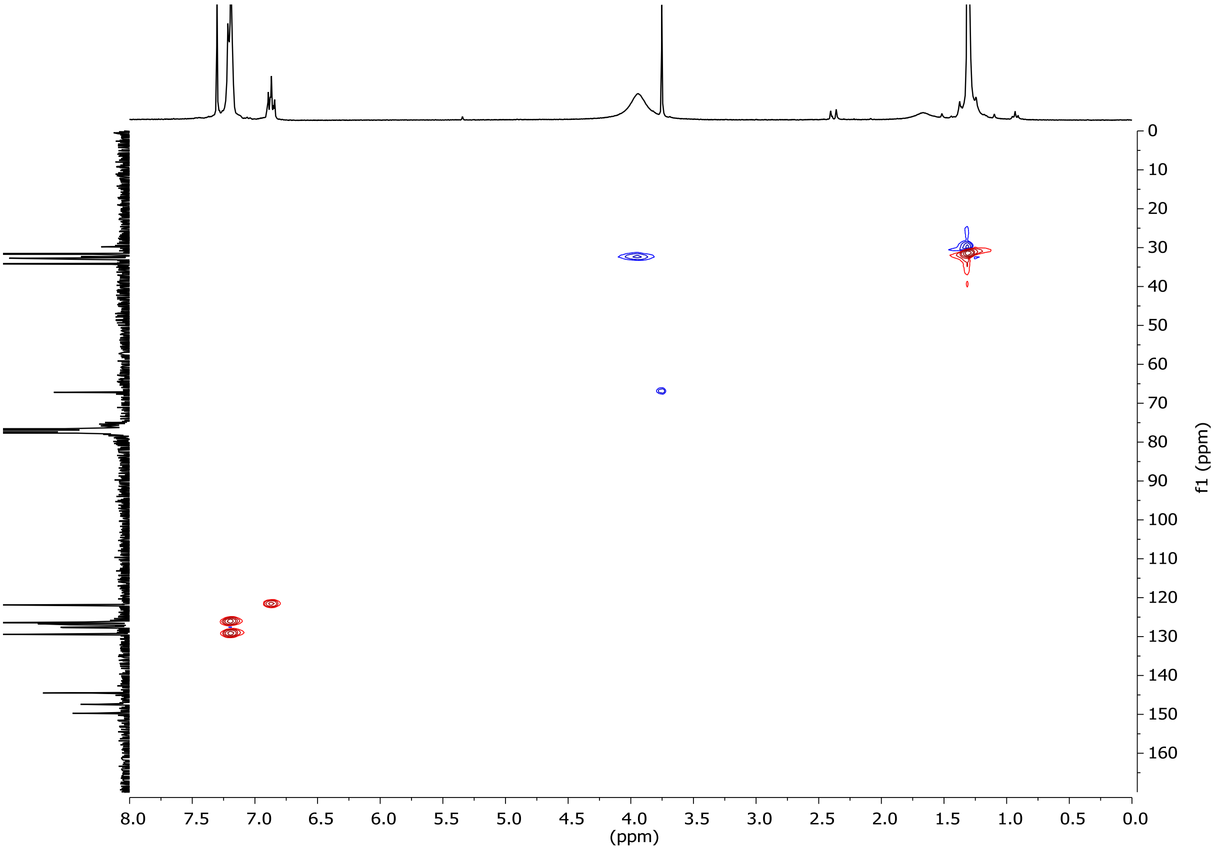

Figure S16. Edited ^{1}H-^{13}C HSQC spectrum of **5** (7.0 Tesla, $CDCl_3$, 25 °C).

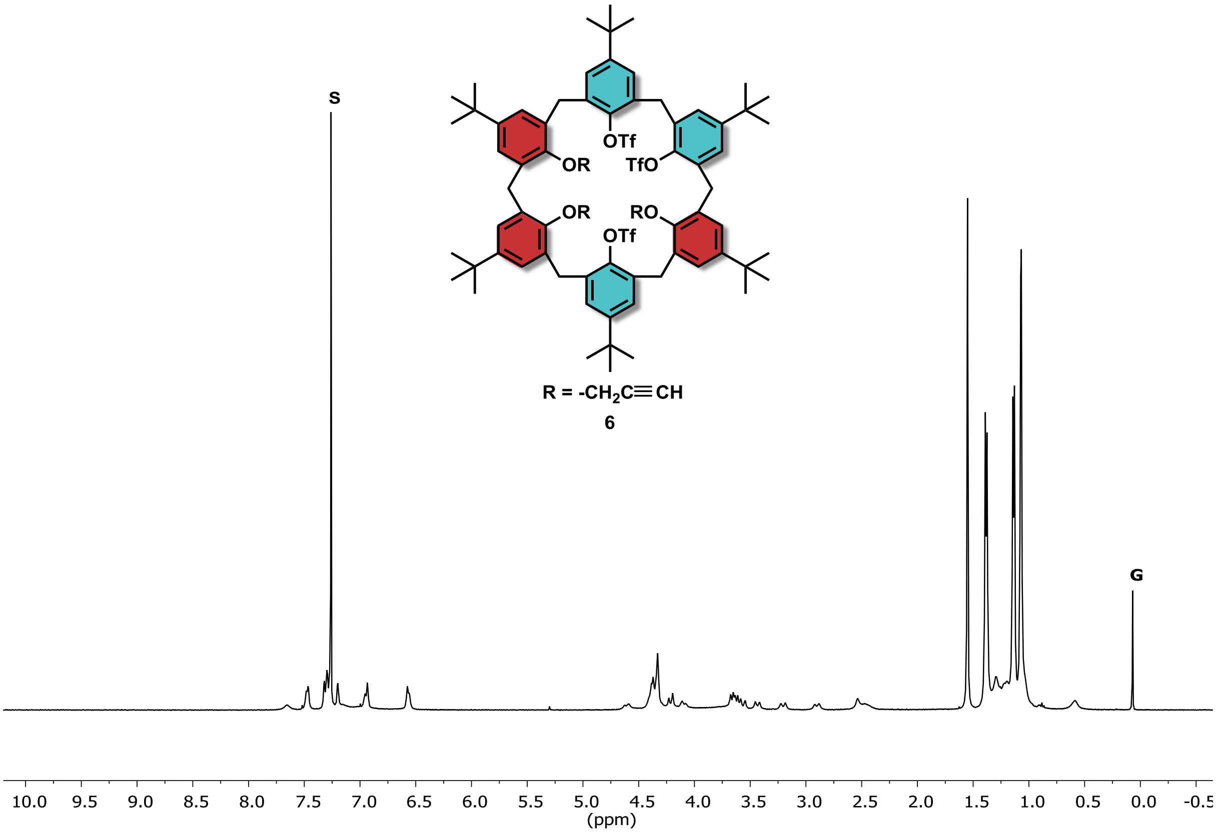

Figure S17. ^{1}H NMR spectrum of **6** (400 MHz, $CDCl_3$, 25 °C). S = residual solvent; G = grease.

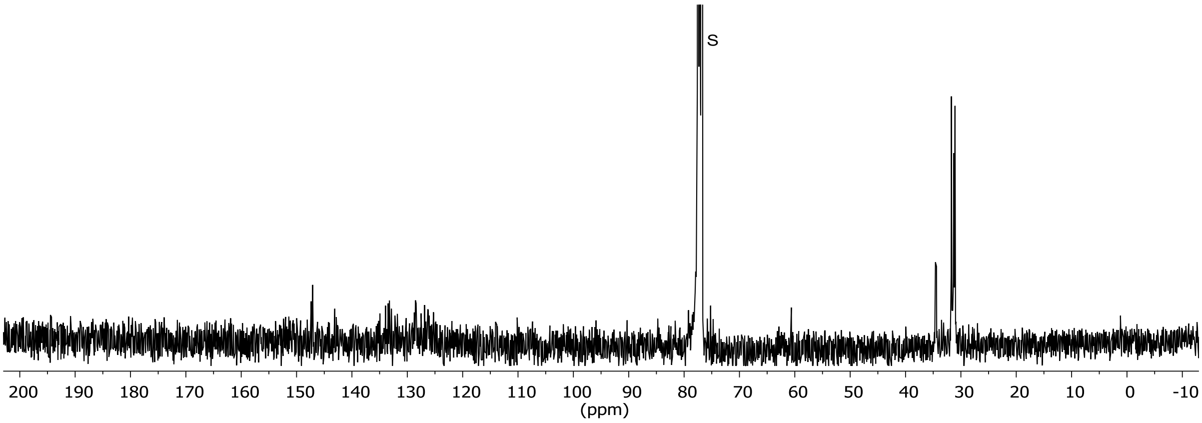

Figure S18. ^{13}C NMR spectrum of **6** (100 MHz, $CDCl_3$, 25 °C). S = residual solvent.

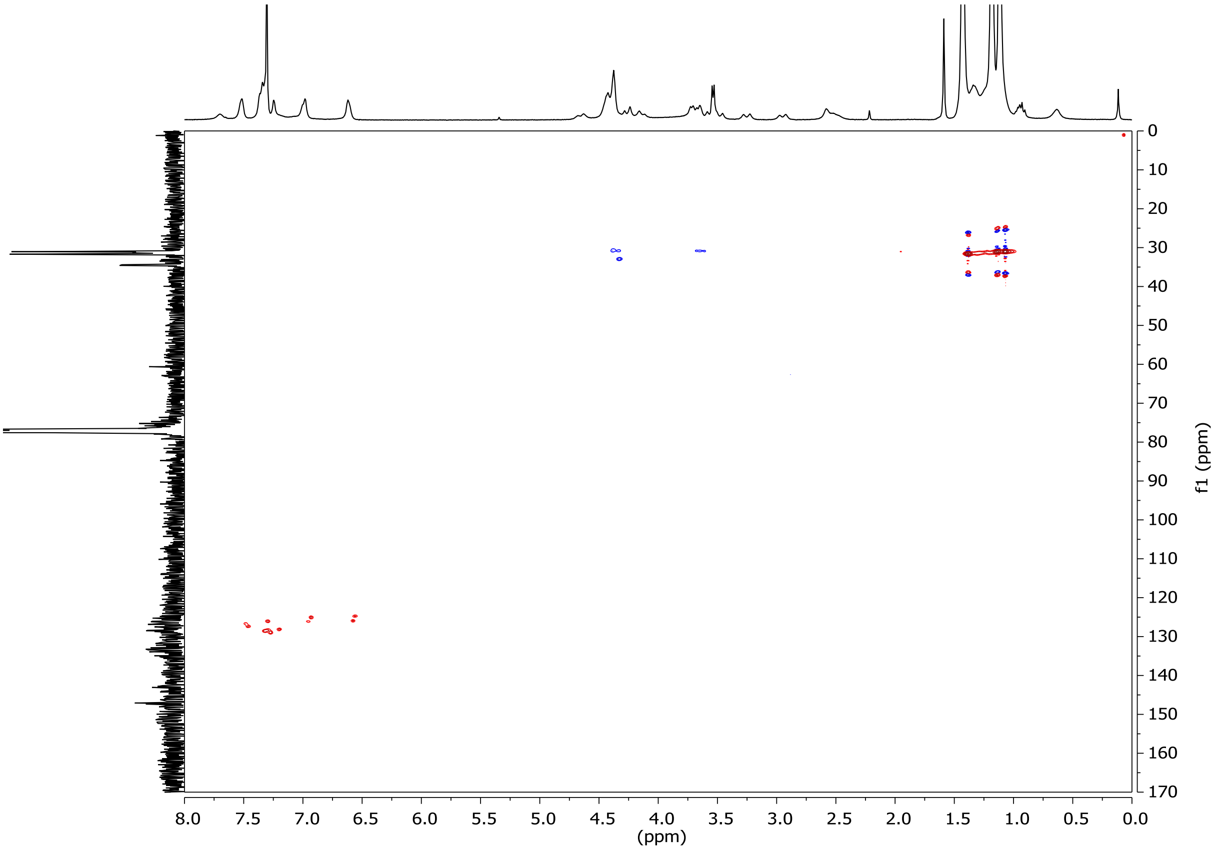

Figure S19. Edited ^{1}H-^{13}C HSQC spectrum of **6** (9.4 Tesla, CDCl$_3$, 25 °C).

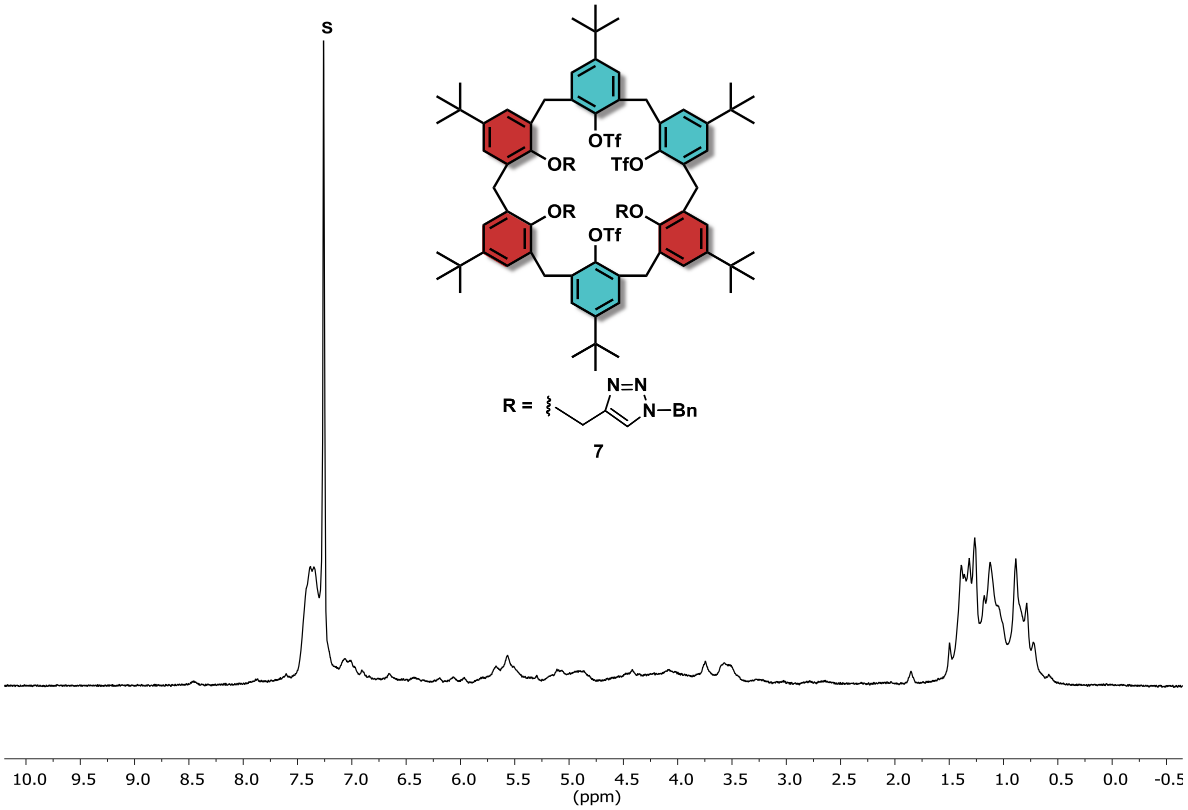

Figure S20. ^{1}H NMR spectrum of **7** (300 MHz, $CDCl_3$, 25 °C). S = residual solvent.

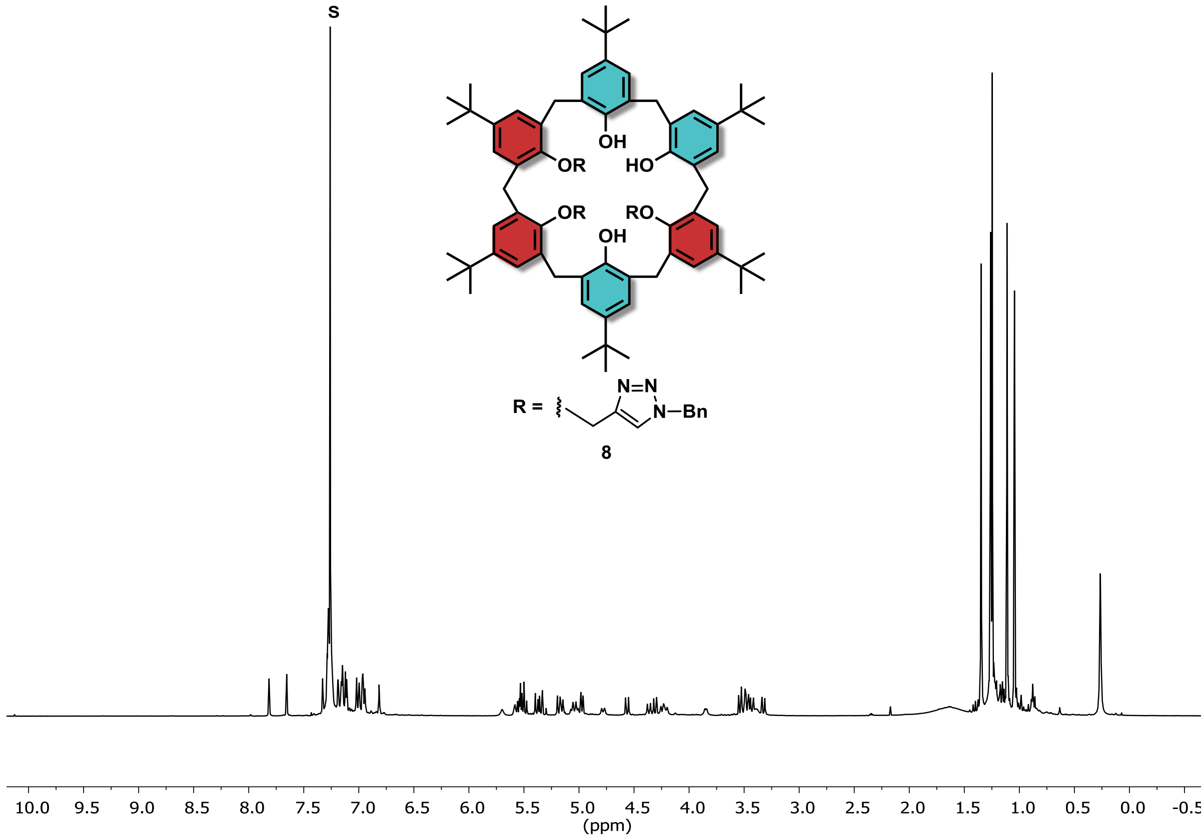

Figure S21. ^{1}H NMR spectrum of **8** (600 MHz, $CDCl_3$, 25 °C). S = residual solvent.

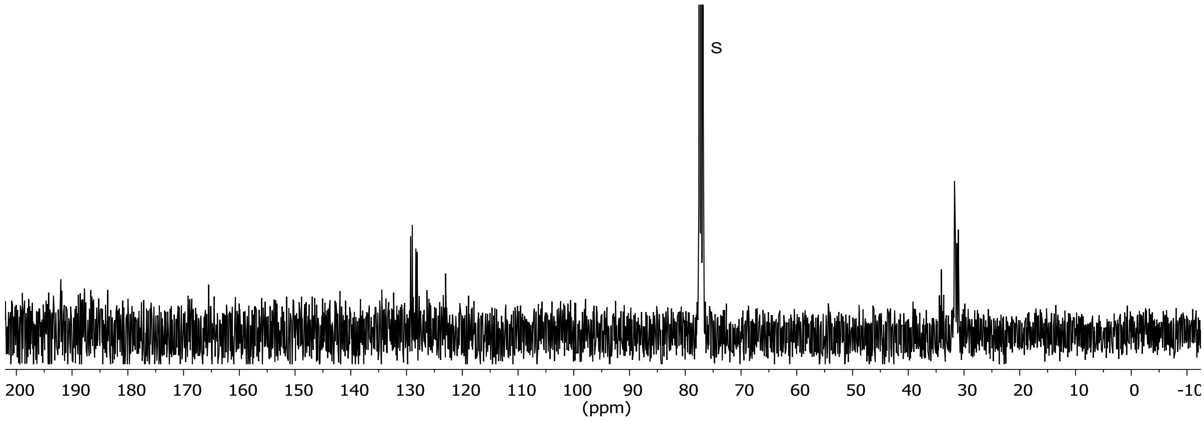

Figure S22. ^{13}C NMR spectrum of **8** (100 MHz, $CDCl_3$, 25 °C). S = residual solvent.

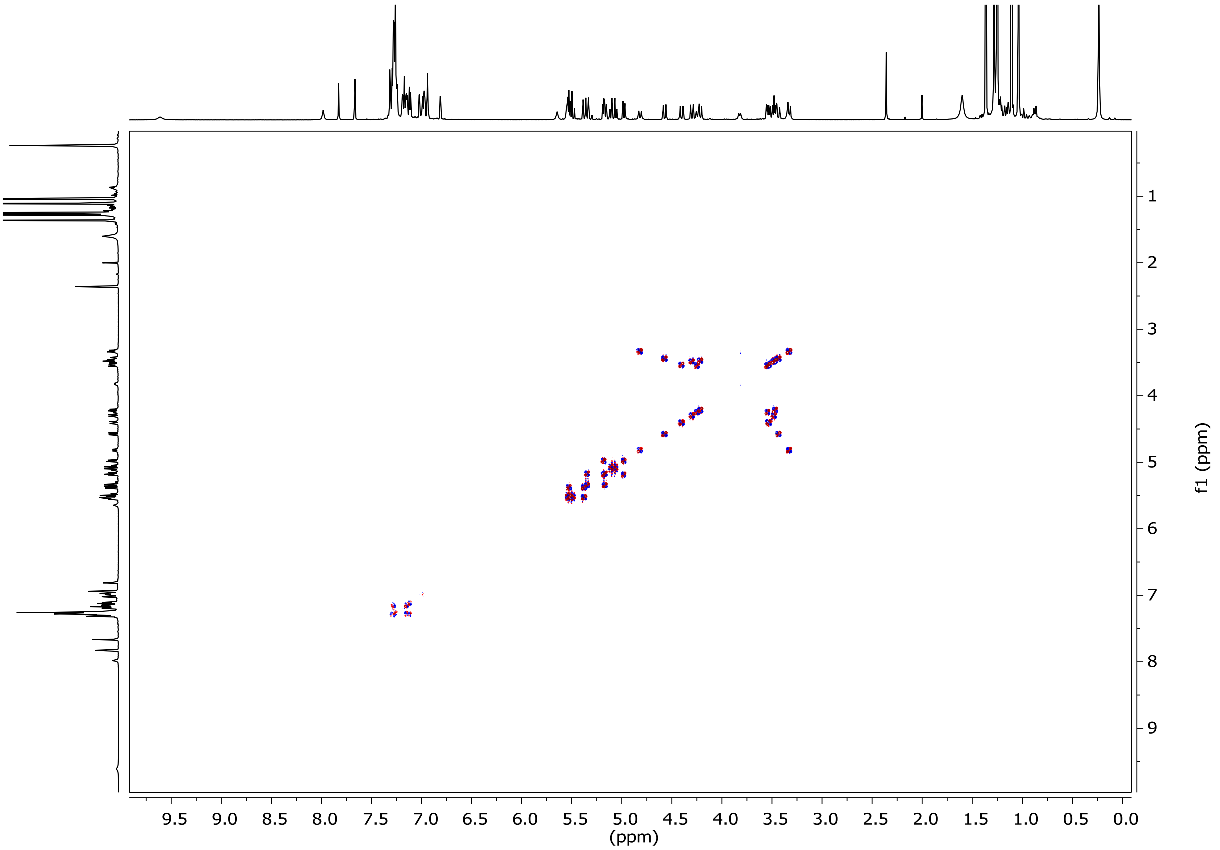

Figure S23. dqfCOSY spectrum of **8** (600 MHz, $CDCl_3$, 25 °C).

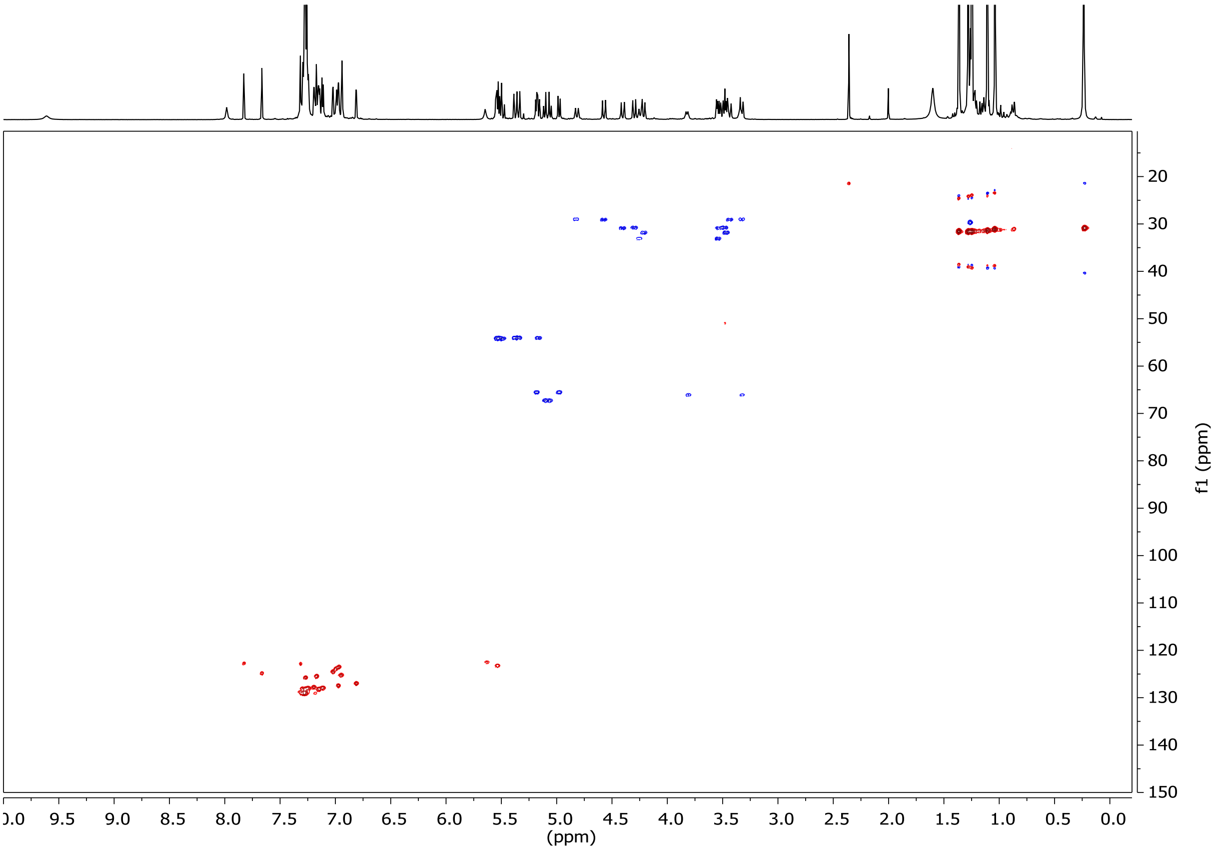

Figure S24. Edited ^1H-^{13}C HSQC spectrum of **8** (14.1 Tesla, $CDCl_3$, 25 °C).

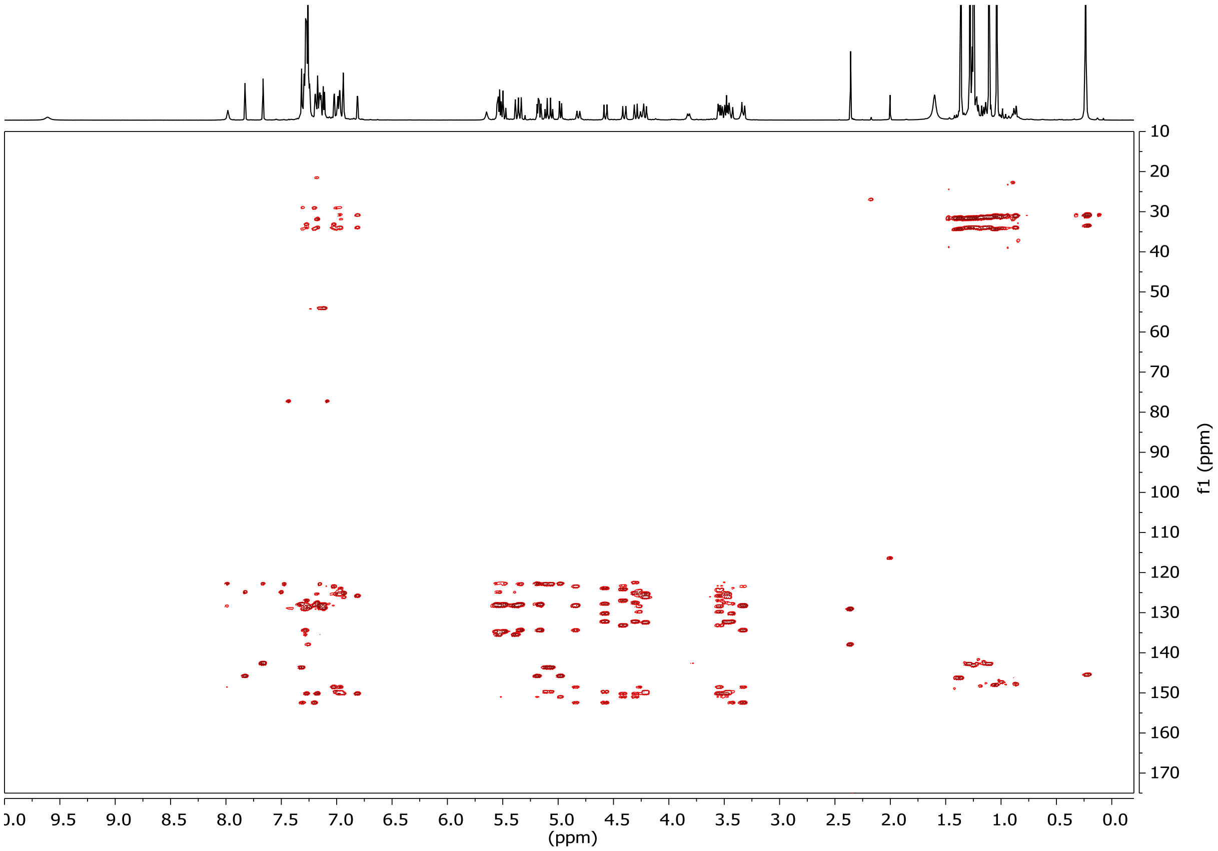

Figure S25. ^{1}H-^{13}C HMBC spectrum of **8** (8 Hz, 14.1 Tesla, CDCl$_3$, 25 °C).

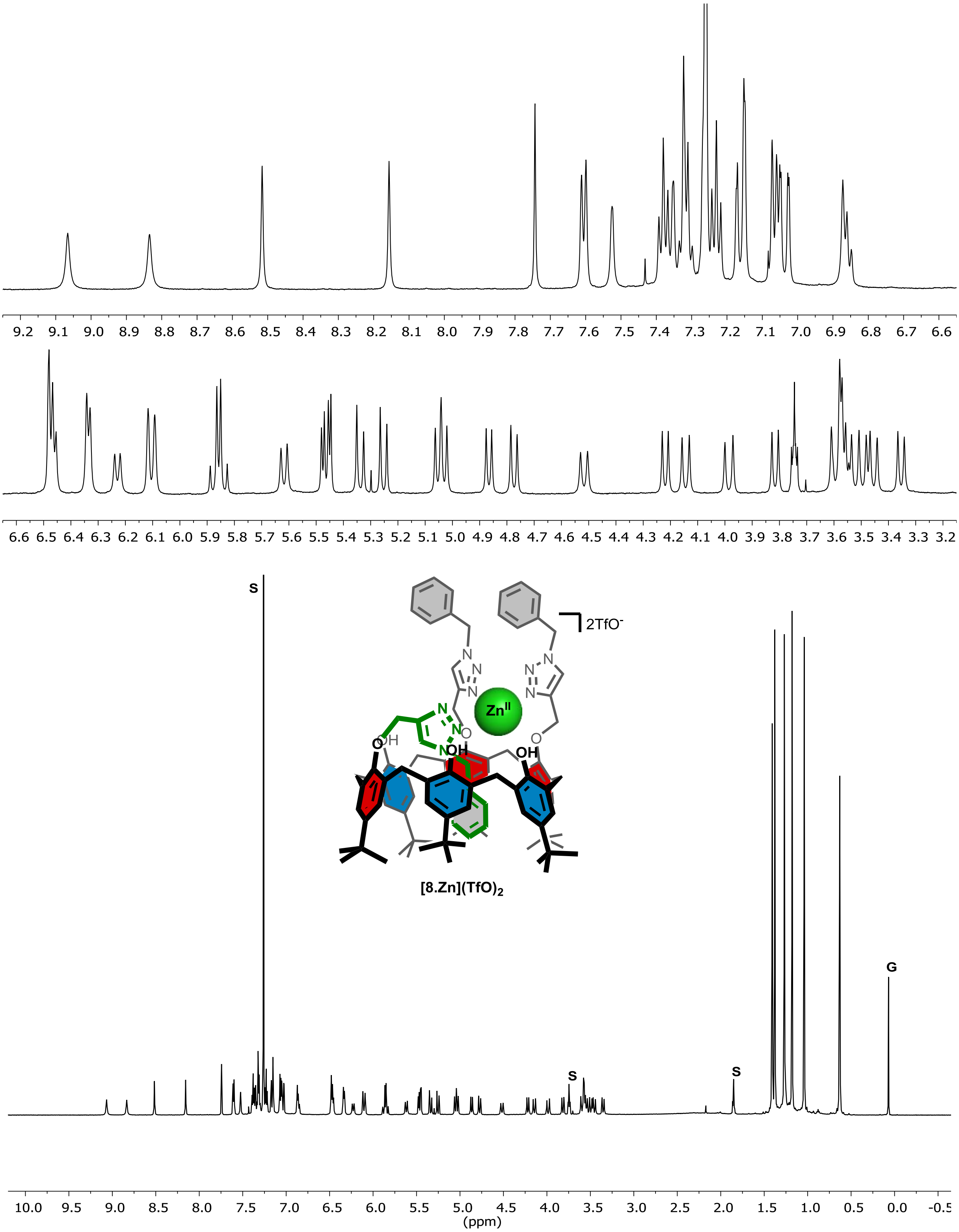

Figure S26. ^{1}H NMR spectrum of **[8.Zn](TfO)$_2$** (600 MHz, CDCl$_3$, 25 °C). S = residual solvents; G = grease.

The ^{13}C NMR spectrum of **[8.Zn](TfO)$_2$** was obtained using a 5 mm Shigemi NMR microtube and about 11 mg of compound dissolved in 300 µL of solvent ($CDCl_3$). It was recorded at 14.1 T (~150 MHz) and 25°C using the following acquisition parameters: relaxation delay of 3 s, pulse flip angle of 30°, acquisition time of 0.6 s, spectral window of 270 ppm centered at about 110 ppm and 65000 scans (65 h of measurement). 79 signals are expected for **[8.Zn](TfO)$_2$**, among which 36 signals of quaternary carbon atoms and 1 quadruplet for the CF_3 group (TfO^-). Only 70 signals were observed due to some overlapping signals.

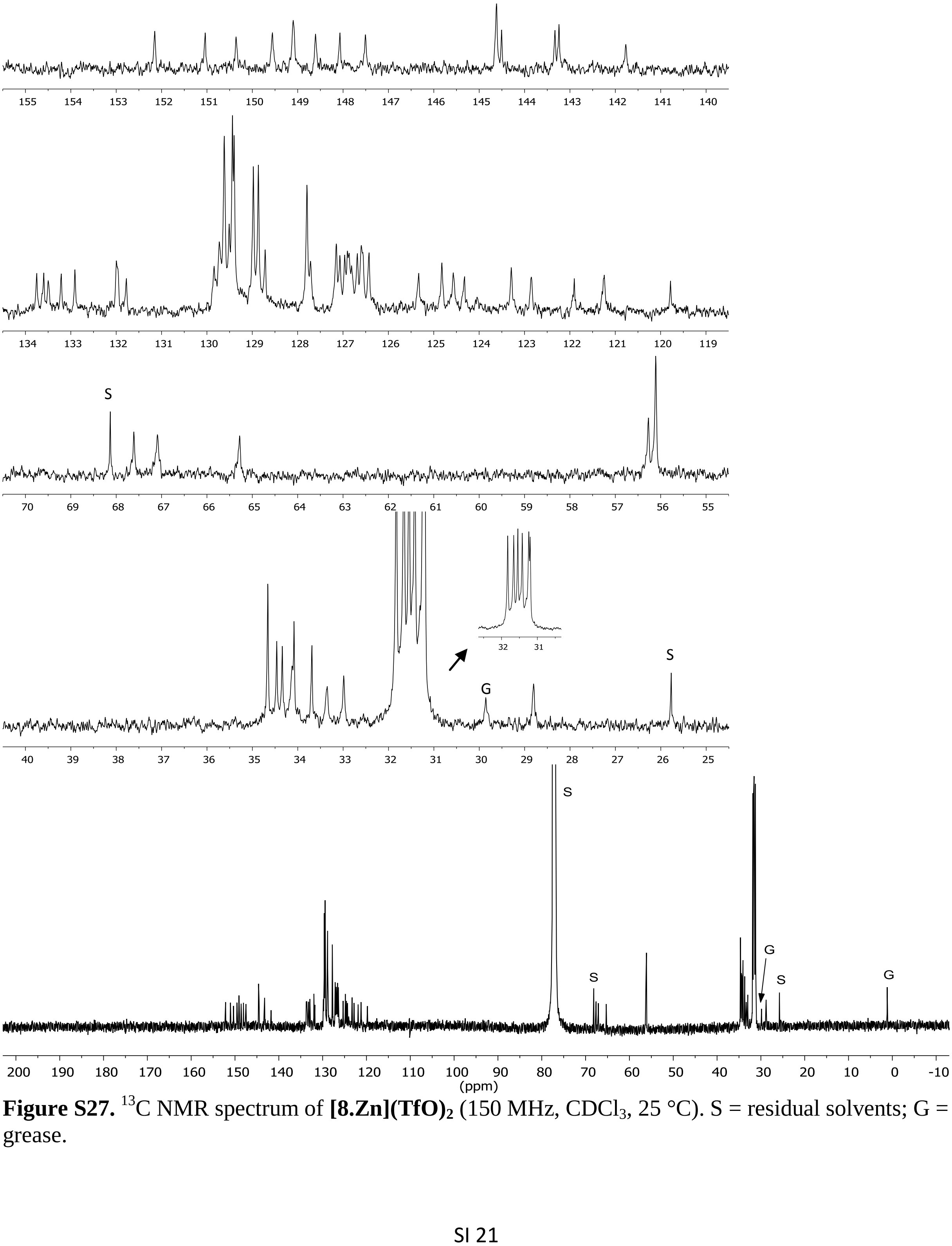

Figure S27. ^{13}C NMR spectrum of **[8.Zn](TfO)$_2$** (150 MHz, $CDCl_3$, 25 °C). S = residual solvents; G = grease.

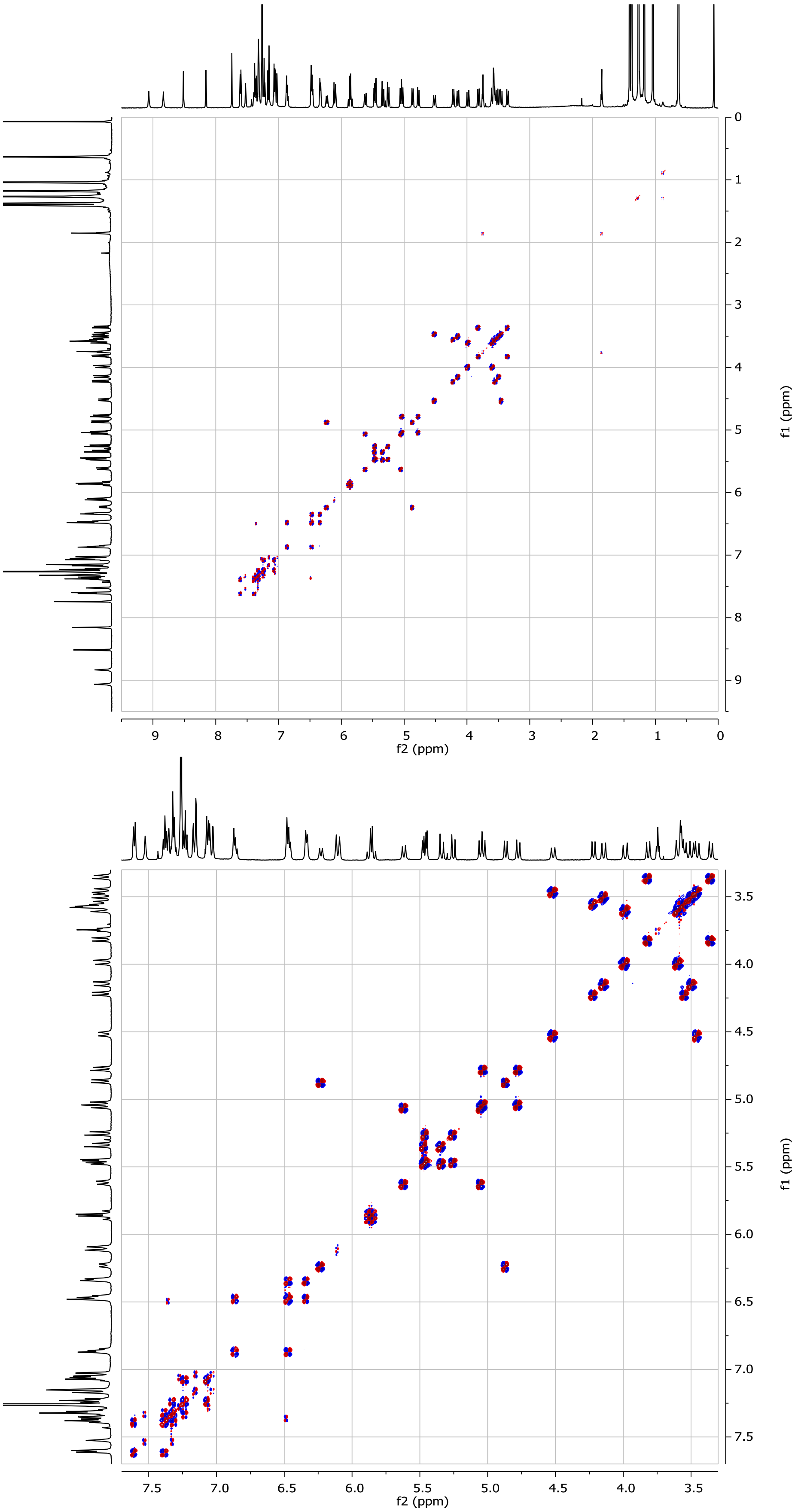

Figure S28. dqfCOSY spectrum of [**8.Zn](TfO)$_2$** (600 MHz, CDCl$_3$, 25 °C).

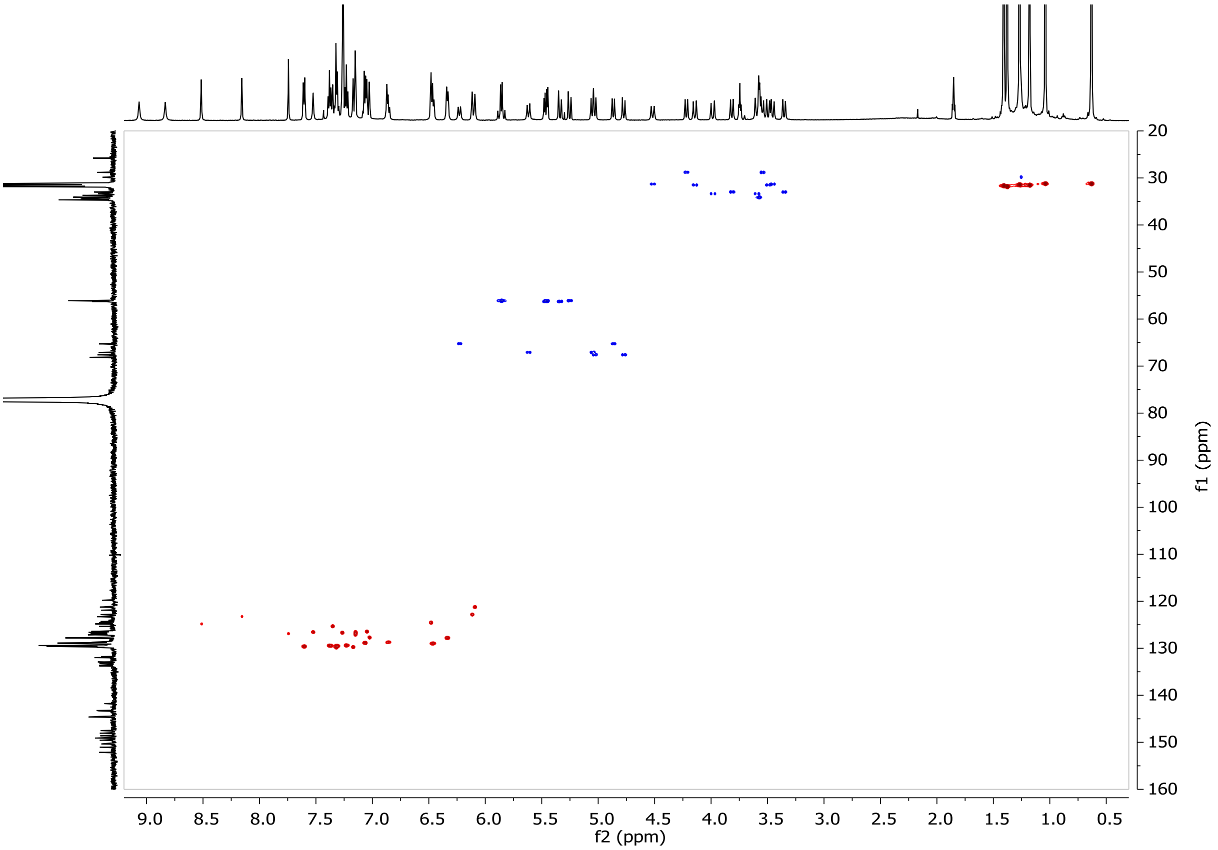

Figure S29. Edited ^{1}H-^{13}C HSQC spectrum of [**8.Zn](TfO)$_2$** (14.1 Tesla, CDCl$_3$, 25 °C).

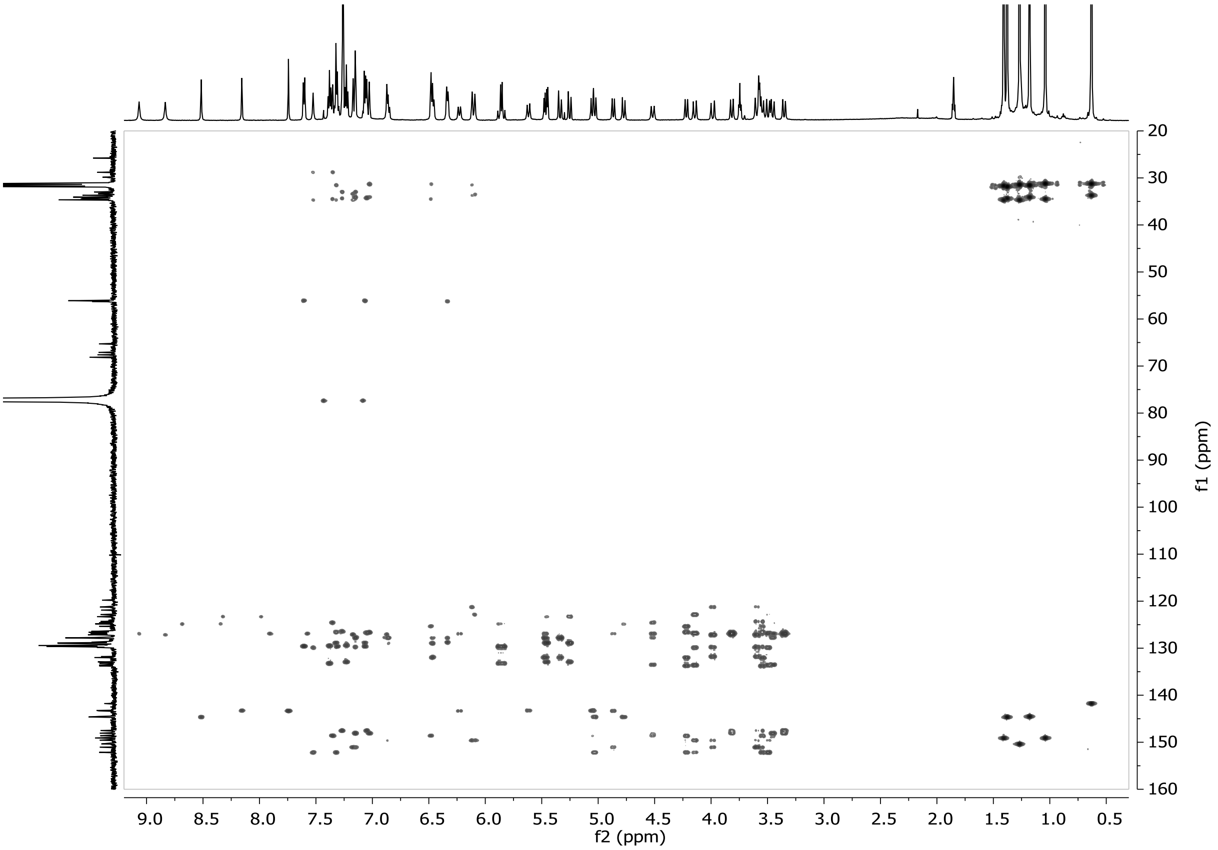

Figure S30. ^{1}H-^{13}C HMBC spectrum of [**8.Zn](TfO)$_2$** (8 Hz, 14.1 Tesla, CDCl$_3$, 25 °C).

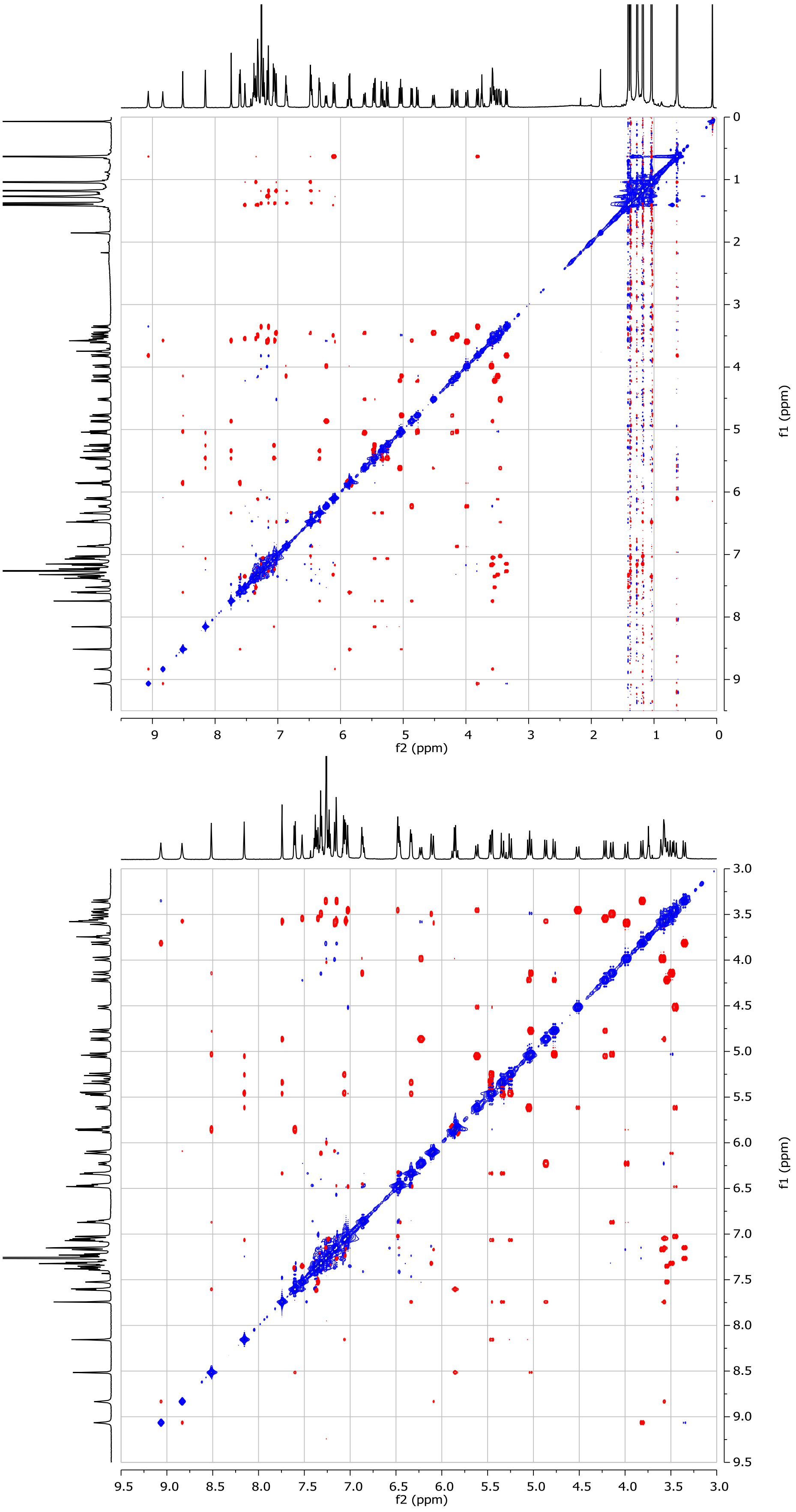

Figure S31. ROESY spectrum of [**8.Zn](TfO)$_2$** (τ_m: 500 ms, 600 MHz, $CDCl_3$, 25 °C).

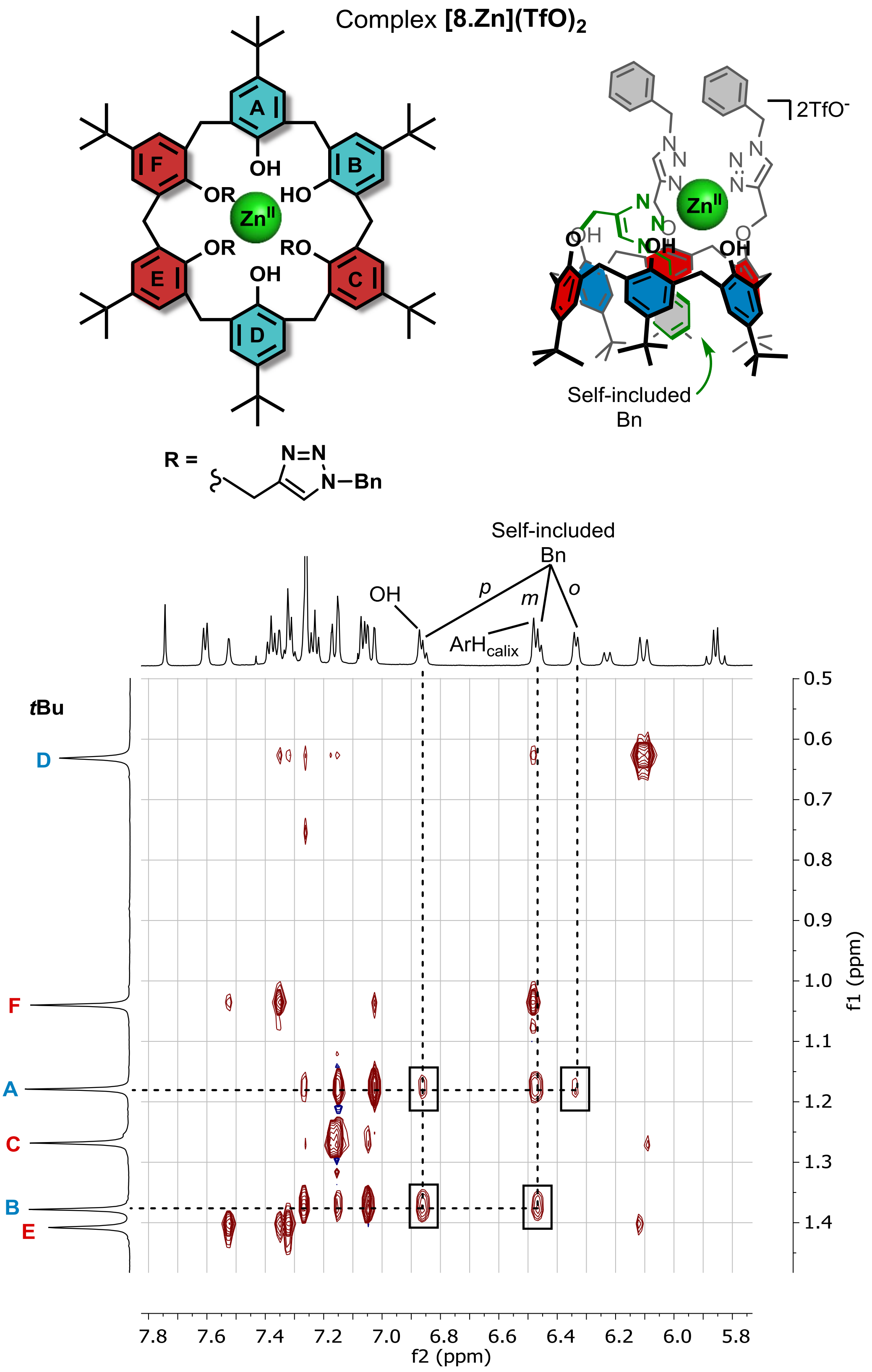

Figure S32. Region of the ROESY spectrum of **[8.Zn](TfO)$_2$** (τ_m: 500 ms, 600 MHz, CDCl$_3$, 25°C). Boxed correlations show Overhauser effects between the aromatic ^{1}H of the self-included benzyl group and the ^{1}H of two Ar-*t*Bu groups.

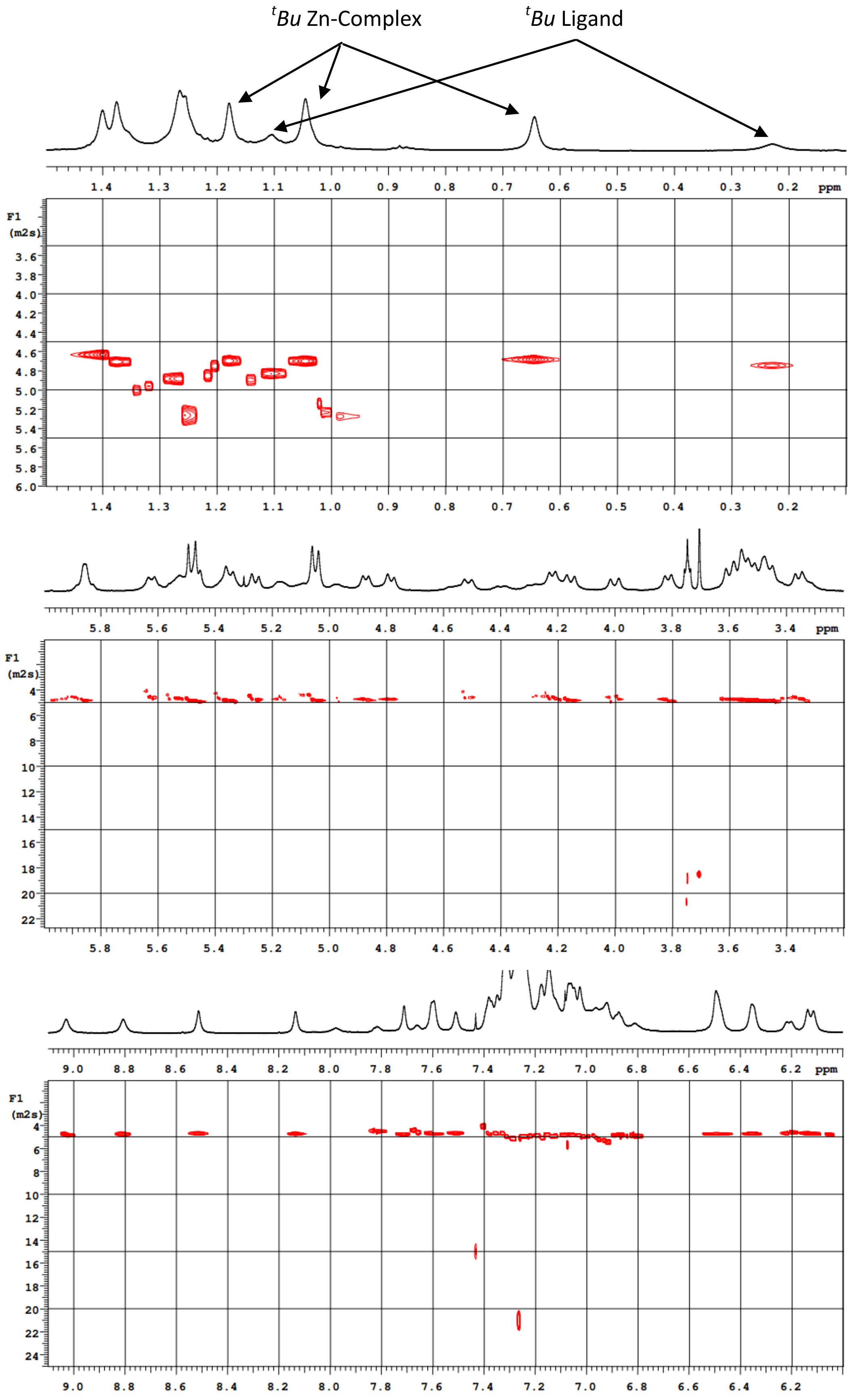

Figure S33. DOSY (Dbppste_cc) spectra of a mixture of **8** and **[8.Zn](TfO)$_2$** (600 MHz, CDCl$_3$, 25 °C).

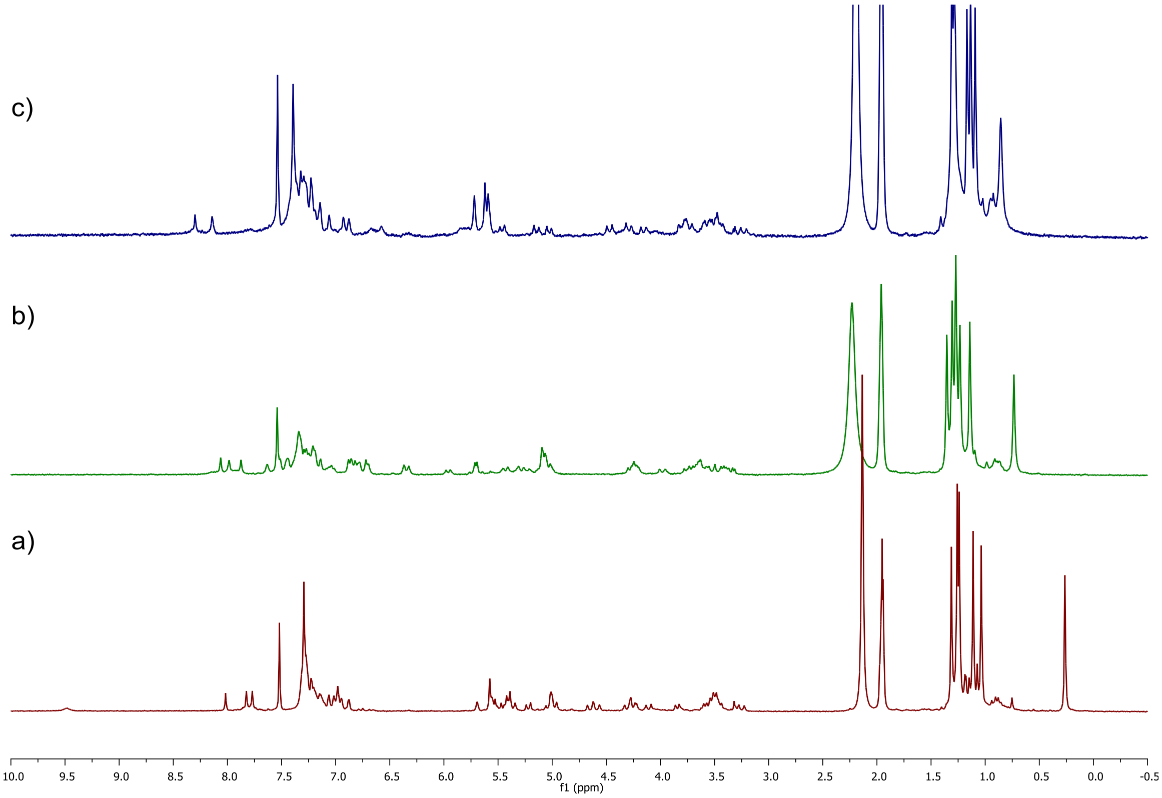

Figure S34. ^{1}H spectra of a) **8**, b) **[8.Pb](ClO$_4$)$_2$** and c) **[8.Hg](ClO$_4$)$_2$** (300 MHz, CD_3CN:$CDCl_3$ 2:1, 25 °C). The complexes **[8.Pb](ClO$_4$)$_2$** and **[8.Hg](ClO$_4$)$_2$** were respectively obtained by the addition of 1 equivalent of $Pb(ClO_4)_2$ and $Hg(ClO_4)_2$ to the ligand **8** in a mixture of $CD_3CN/CDCl_3$ (2:1).

Table S35: Reaction conditions for the selective formation of $X_6H_4Tf_2$ **2** and $X_6H_3Tf_3$ **3** from calix[6]arene **1**.

Tf_2O (equiv.)	Base	Solvent	*T* (°C)	*t* (h)	$1:1^{+1OTf}:1^{+2OTf}$ (**2**)$:1^{+3OTf}$ (**3**)$:1^{+4OTf}:1^{+5OTf}$ ratio[a]	Yields (%)[b] of **2** and **3**
3	Pyridine (6 equiv.)	DCM	25	24	20:2:30:35:11:2	_
4	Pyridine (8 equiv.)	DCM	25	24	15:1:25:35:15:9	30[c] and 24[d]
5	Pyridine (8 equiv.)	DCM	25	48	3:2:40:38:17:0	_
5	Pyridine (10 equiv.)	DCM	25	24	0:0:0:0:95:5	_
3	K_2CO_3 (4 equiv.)	DCM	25	2	65:20:15:0:0:0	_
3	K_2CO_3 (3 equiv.)	DCM	25	24	55:40:5:0:0:0	_
3	K_2CO_3 (3 equiv.)	MeCN	25	24	30:55:15:0:0:0	_
3	K_2CO_3 (3 equiv.)	DCM	25	48	30:50:20:0:0:0	_
6	K_2CO_3 (6 equiv.)	DCM	25	48	10:10:75:5:0:0	_
3	DMAP (5 equiv.)	Acetone	25	24	70:30:0:0:0:0	_
2.5	DMAP (2.5 equiv.)	DCM	40	5	0:0:90:10:0:0	71[c]
5	Cs_2CO_3 (3 equiv.)	DCM	25	24	0:5:45:40:10:0	_
2.5	Cs_2CO_3 (4 equiv.)	DCM	25	3.5	5:5:50:40:0:0	31[c] and 37[d]

[a] Determined by ESI-MS analysis of the reaction mixture.

[b] Calculated after flash chromatography purification.

[c] Yield for $X_6H_4Tf_2$ **2**.

[d] Yield for $X_6H_3Tf_3$ **3**.