

Electronic Supporting Information

[18]Annulene put into new perspective

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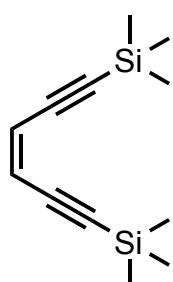
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1. General information

All chemicals were purchased from Sigma-Aldrich and used without any further purification. Solvents were distilled prior to usage. CH_2Cl_2 , CHCl_3 and EtOAc were distilled from K_2CO_3 prior to usage. THF and benzene were freshly distilled from Na/benzophenone prior to usage. Thin layer chromatography (TLC) was performed on Merck silica gel 60 F254, detected by UV-light (254 nm, 366 nm). Column chromatography and flash column chromatography were performed on Macherey–Nagel silica gel 60 M (230–400 mesh, 0.04–0.063 mm). NMR spectroscopy was performed on JEOL JNM EX 400 (^1H : 400 MHz, ^{13}C : 100 MHz) and JEOL JNM GX 400 (^1H : 400 MHz, ^{13}C : 100 MHz), and Bruker Avance 400 (^1H : 400 MHz, ^{13}C : 100 MHz). Deuterated solvents were purchased from Sigma Aldrich and used as received. Chemical shifts are referenced to residual protic impurities in the solvents (CHCl_3 : ^1H : 7.24 ppm; $\text{C}_2\text{H}_2\text{Cl}_4$: ^1H : 5.98 ppm; THF: ^1H : 3.57 ppm and 1.73 ppm) or the deuterated solvent itself (CDCl_3 : ^{13}C : 77.0 ppm; $\text{C}_2\text{D}_2\text{Cl}_4$: ^{13}C : 73.7 ppm; THF- D_8 : ^{13}C : 67.3 ppm and 25.2 ppm). The resonance multiplicities are indicated as “s” (singlet), “d” (doublet), and “m” (multiplet). Signals referred to as bs (broad singlet) are not clearly resolved or significantly broadened. IR spectra were recorded on a Bruker FT-IR Tensor 27 spectrometer with a Pike MIRacle ATR unit. LDI/MALDI-ToF mass spectrometry was performed on a Shimadzu AXIMA Confidence (nitrogen laser, 50 Hz, 337 nm). In case of MALDI, the following matrix was used: 2,5-dihydroxybenzoic acid (DHB). High resolution mass spectrometry was performed on a ESI-ToF mass spectrometer Bruker maXis 4G UHR MS/MS spectrometer. Uv/vis spectroscopy was carried out on a Varian Cary 5000 UV-Vis-NIR spectrometer. Solid state Uv/vis was performed on a quartz glass light path window. Unless otherwise noted, reactions were degassed by the following technique: The reaction mixture was sonicated at 25 °C for 1 min under vacuo, followed by a purge with N_2 -gas. This cycle was repeated three times.

2. Experimental procedures

(3Z)-1,6-Trimethylsilyl-hexa-3-ene-1,5-diyne (6)



$C_{12}H_{20}Si_2$
 $M = 220,46$

A 100 mL Schlenk round-bottom flask, protected from light, was charged with 337 mg (470 μ mol; 2 mol%) $Pd(PPh_3)_2Cl_2$, 183 mg (960 μ mol; 4 mol%) CuI and dissolved in a mixture of 12.0 mL *n*-butylamine and 35.0 mL benzene. The mixture was degassed and then 2.33 g (24.0 mmol) *cis*-1,2-dichloroethene was added. A solution of 5.19 g (52.8 mmol, 2.2 equiv.) trimethylsilylethyne in 10.0 mL benzene was added within 6 h by means of a PLASTIC syringe (20 mL) and a syringe pump. The reaction mixture was stirred at rt under N_2 -atmosphere over night for 15 h. The red solution was quenched with 40 mL of a saturated aqueous NH_4Cl solution, the layers were separated, the aqueous layer was extracted 3x 20 mL Et_2O , the combined organics were washed 1x 20 mL saturated solution of NH_4Cl , 1x 20 mL H_2O and 1x 20 mL brine. The crude solution was dried with $MgSO_4$, filtered, evaporated (100 mbar, 40 $^{\circ}C$) and purified by liquid chromatography (SiO_2 ; 4x25 cm; hexanes). The pale yellow oil was dried in vacuo, yielding the product in 90 % (4.76 g; 21.4 mmol).

Attention: In order to prevent cis/trans isomerization, the product should be stored in darkness at 4 $^{\circ}C$. Over a period of several months, no decomposition or isomerization was observed under these conditions.

R_f (solvent): 0.35 (hexanes);

1H NMR (400 MHz; $CDCl_3$; rt): δ [ppm] = 5.83 (s, 2H), 0.20 (s, 9H).

^{13}C NMR (100 MHz; $CDCl_3$; rt): δ [ppm] = 120.6, 103.4, 101.8, -0.1.

MS (MALDI, DHB): m/z (*rel. int.*) = 221 [M]⁺ (100).

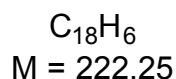
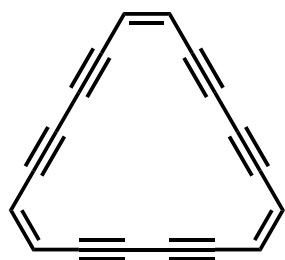
HRMS (APPI, toluene): m/z calc. for $C_{12}H_{20}Si_2$ [M]⁺: 220.109805, found: 220.110259.

IR (ATR, rt): $\tilde{\nu}$ [cm^{-1}] = 3044, 2960, 2900, 2156, 2122, 1680, 1568, 1408, 1387, 1249, 1069, 976, 836, 758, 699, 634.

Uv/vis (*n*-hexane; rt): λ_{max} [nm] (ϵ [$M^{-1}cm^{-1}$]) = 273 (20600), 289 (23300).

EA for $C_{12}H_{20}Si_2$: Calc.: C 65.38, H 9.14, Si 25.48; found: C 65.36, H 9.10;

1,3,7,9,13,15-Hexadehydro-[18]annulene (5)



A 100 mL Schlenk round-bottom flask, protected from light, was charged with 50.0 mL (50.0 mmol) of a 1 M TBAF/ THF solution at 0 °C under N₂-atmosphere. While stirring, 5.00 g (22.7 mmol) (3Z)-1,6-trimethylsilyl-hexa-3-ene-1,5-diyne were added neat via syringe over 2 min. The mixture turned black immediately and was stirred for 1 h. Then the mixture was cannulated to a 1 L round bottom flask equipped with a rubber septum and containing a vigorously stirred mixture of 30.0 g (150 mmol) Cu(OAc)₂·H₂O in 500 mL pyridine. The dark blue pyridine/Cu-mixture turned black immediately. The mixture was allowed to stir in darkness at rt for another 20 h, before it was quenched by pouring the mixture to a 600 mL mixture of 1:1 Et₂O/2 M HCl and stirred well for 15 min. The organic layer was separated. The aqueous layer was filtered through a Büchner funnel and the precipitate was washed with 150 mL Et₂O. The organic layer was separated again and all organics were combined. Additional Et₂O was added to give 500 mL of organics. The combined organics were washed with 4x 200 mL 1:1 saturated CuSO₄/H₂O solution, 1x 50 mL saturated NH₄Cl solution, 1x 50 mL brine and dried over Na₂SO₄ to yield a light brown solution. The solution was concentrated in vacuo and purified by liquid chromatography (SiO₂; 6x30 cm; 20:1 hexane/ EtOAc). The amber solid was dried in vacuo, yielding the product in 24 % (404 mg; 1.82 mmol).

Attention: While concentrating the solution on the rotary evaporator, do not exceed a temperature of over 35 °C. When precipitation in the flask occurs, further evaporation should be proceeded with an oil pump around 0 °C to prevent decomposition. The product is best stored in a frozen solution of benzene under argon atmosphere in the freezer. In the solid state, rapid decomposition can be observed.

R_f (solvent): 0.23 (20:1 hexanes/EtOAc);

¹H NMR (400 MHz; C₂D₂Cl₄; rt): δ [ppm] = 7.20 (s, 6H).

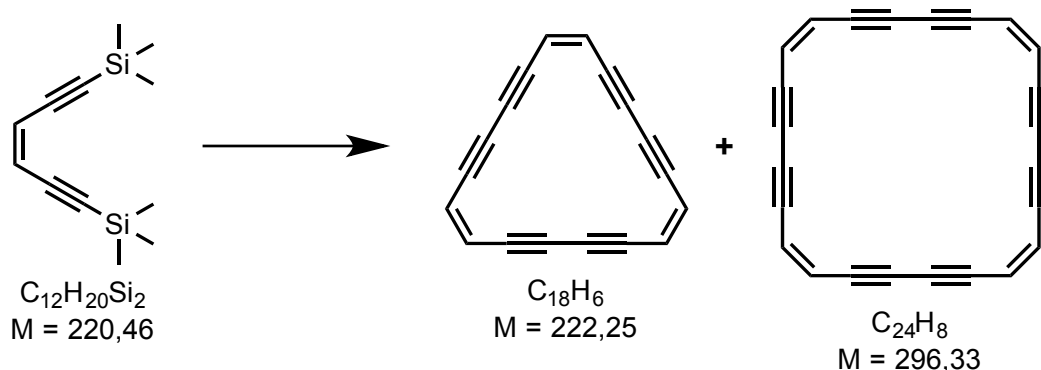
¹³C NMR (100 MHz; C₂D₂Cl₄; rt): δ [ppm] = 121.5, 83.5, 83.2.

HRMS (APPI, toluene): *m/z* calc. for C₁₈H₆ [M]⁺: 222.046402, found: 222.046492.

IR (ATR, rt): $\tilde{\nu}$ [cm⁻¹] = 3057, 2186, 2113, 1841, 1654, 1472, 1417, 1272, 1185, 951, 732.

Uv/vis (hexanes; rt): λ_{max} [nm] = 319sh, 334, 358, 368sh, 379, 389.

Uv/vis (cyclohexane; rt): λ_{max} [nm] (ϵ [M⁻¹cm⁻¹]) = 227 (25500), 236 (21500), 260 (5900), 315 sh (41000), 317 (41500), 333 (75800), 357 (13000), 366 (7400), 378 (15500), 388 (17600), 405 sh (790).¹



As **minor product**, cyclic tetramer ($C_{24}H_8$) was formed in 5 %.²

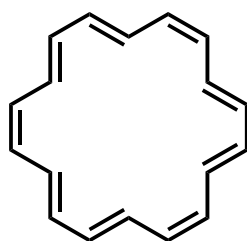
R_f (solvent): 0.12 (20:1 hexanes/EtOAc);

¹H NMR (400 MHz; C₂D₂Cl₄; rt): δ [ppm] = 6.07 (s, 8H).

¹³C NMR (100 MHz; C₂D₂Cl₄; rt): δ [ppm] = 121.4, 82.7, 82.6.

HRMS (APPI, MeOH): m/z calc. for $C_{24}H_8$ [M]⁺: 296.062052, found: 296.061979.

[18]Annulene (1)



C18H18
 $M = 234,34$

A 100 mL Schlenk round-bottom flask, was charged with 25 mg 5 % Pd/CO₃/Pb (Lindlar catalyst) and poisoned with 1 drop quinoline. The catalyst was suspended in 25 mL benzene and 60 mg (0.27 mmol) hexadehydro[18]annulene was added. The mixture was degassed under vacuo/ sonication for 1 min and the atmosphere was exchanged by H₂-gas. The mixture was stirred at rt under H₂-atmosphere for 1 h. The yellow greenish mixture was filtered, concentrated in vacuo, and purified by liquid chromatography (SiO₂ 2x20 cm; 23:1:1 pentane/cyclohexane/benzene). The brownish solid was dried in vacuo, yielding the product in 20 % (13 mg; 54 μ mol).

R_f (solvent): 0.42 (20:1 hexanes/EtOAc);

¹H NMR (400 MHz; THF-D₈; rt): δ [ppm] = 8.88 (bs, 12H), -1.92 (bs, 6H).

¹H NMR (400 MHz; THF-D₈; -40 °C): δ [ppm] = 9.24 (dd, 12H), -2.83 (m, 6H).

¹³C NMR (100 MHz; THF-D₈; -40 °C): δ [ppm] = 127.8, 121.5.

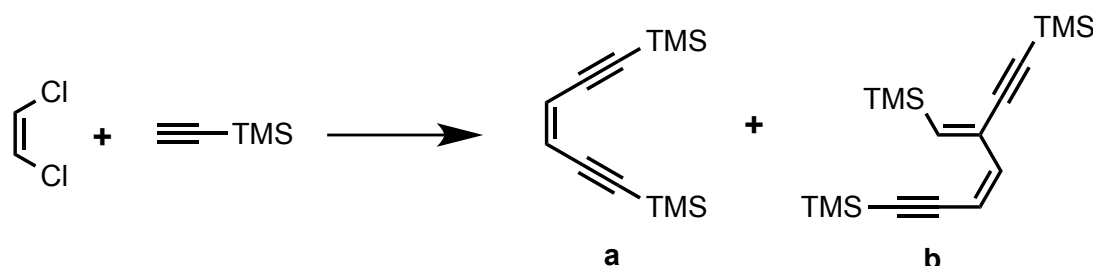
HRMS (APPI, toluene): m/z calc. for $C_{18}H_{18}$ [M]⁺: 234.140302, found: 234.140542.

IR (ATR, rt): $\tilde{\nu}$ [cm⁻¹] = 3057, 2186, 2113, 1841, 1654, 1472, 1417, 1272, 1185, 951, 732.

Uv/vis (CH₂Cl₂; rt): λ_{max} [nm] = 275 (300000), 454 (25000).

3. Additional experimental results

Coupling of TMS-acetylene and 1,2-dichloroethene to (3Z)-1,6-trimethylsilyl-hexa-3-ene-1,5-diyne



Scheme S1 Synthesis of 1,6-di-(trimethylsilyl)-hex-3-en-1,5-diyne **a**.

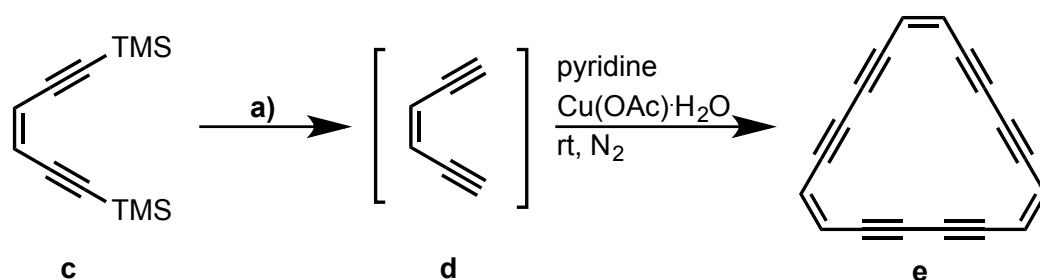
Overall procedure: catalyst and copper (I) iodide were placed in a Schlenk flask (50 ml). Solution of *cis*-1,2-dichloroethylene (776 mg, 8.0 mmol) and *n*-butylamine (4.0 mL) in benzene (4 mL) was added and the rest of material was washed from the vial with benzene (5 mL). The reaction vessel was closed with a fresh rubber septum and degassed. The reaction flask was isolated from day light by aluminum foil and a solution of TMS-ethyne in benzene (5 mL) was added during 6 h by means of a PLASTIC syringe (10 mL) and a syringe pump at rt. The reaction mixture was stirred for additional 17 h. The resulted dark red solution with large amount of precipitates was poured into a saturated solution of NH₄Cl (20 mL) and diethyl ether (20 mL). The organic layer was separated and the dark blue aqueous layer was extracted with diethyl ether (3x10 mL). The combined organics were washed with a saturated aqueous solution of NH₄Cl (10 mL), brine (2x10 mL), dried over MgSO₄, filtered and evaporated in vacuo (100 mbar, 40°C) to give a dark red oil. This oil was redissolved in hexanes (40 mL), filtered and evaporated in vacuo (100 mbar, 40 °C) to give the crude product as a dark red oil, which was analyzed by ¹H NMR. All mixtures contained only compounds **a** and, presumably, **b** by ¹H NMR data. Monochloro-compound was NOT detected in any reaction mixtures. Identification of **b** was assigned only by NMR data and literature search.³ Results of experiments are summarized in the Table 1.

Table S1 Synthesis of 1,6-di-(trimethylsilyl)-hex-3-en-1,5-diyne **a**.

N	TMS-ethyne, equiv.	Catalyst	Catalyst, [mol%]	Copper (I) iodide, [mol%]	Ratio a:b (by ¹ H NMR data)
1	2.5	Pd(PPh ₃) ₄	5	10	57 : 43
2	2.5	PdCl ₂ (PPh ₃) ₂	5	10	60 : 40
3 ^a	3.0	PdCl ₂ (PPh ₃) ₂	5	10	74 : 26
4	3.0	PdCl ₂ (PPh ₃) ₂	5	10	81 : 19
5	2.2	PdCl ₂ (PPh ₃) ₂	5	10	98 : 2
6^b	2.2	PdCl₂(PPh₃)₂	2	4	98 : 2

a – septum was not fresh; b – the reaction was done without protection from day light.

Deprotection of (3Z)-1,6-trimethylsilyl-hexa-3-ene-1,5-diyne and coupling to hexadehydro[18]annulene



Scheme S2 Improvement of deprotection of **c** to **d** by variation of fluoride sources.

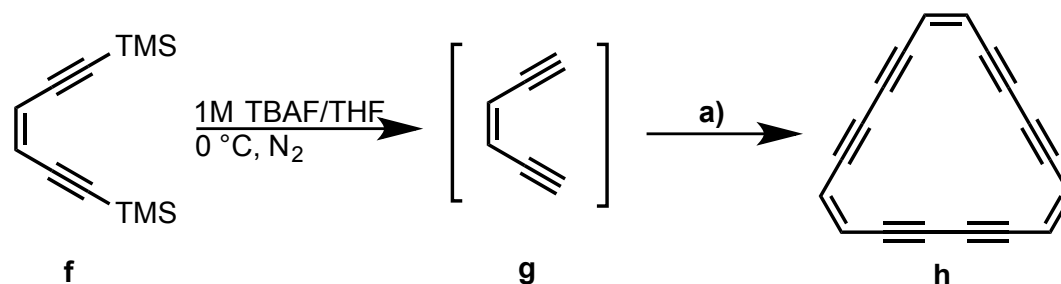
Overall procedure: Deprotecting agent was placed in a Schlenk flask (50 mL) and dissolved in 25 mL THF. Then 2.50 g (11.3 mmol) (3Z)-1,6-trimethylsilyl-hexa-3-ene-1,5-diyne **c** was added neat over 1 min. The reaction mixture was stirred for 3 h at rt and then cannulated to a mixture of $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ /pyridine. The quality of the deprotection was estimated by the isolated yield of hexadehydro[18]annulene **e**. A summary can be found in table S2.

Table S2 Improvement of deprotection of **c** to **d** by variation of fluoride sources.

N	F- source	Additional reagent/ solvent	Isolated yield of e [%]
1	CsF	H_2O	16
2	KF	H_2O	11
3	KF	10% 18-crown-6, H_2O	18
4	HF/pyridine	--	9
5 ^a	--	--	9
6 ^b	TBAF	--	19
7 ^c	TBAF	--	24

a – protected enediyne **c** was directly introduced to $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ /pyridine mixture. Deprotection occurred by Cu-mixture; b – stirred for 30 min; c – stirred for 1 h at 0 °C under N_2 -atmosphere.

Oxidative coupling to hexadehydro[18]annulene by variation of the Cu-system



Scheme S3 Improvement of the oxidative coupling to **h** by variation of the Cu-system.

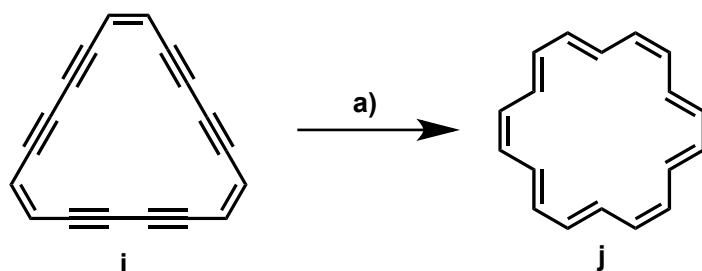
Overall procedure: 300 mg (1.36 mmol) (3Z)-1,6-trimethylsilyl-hexa-3-ene-1,5-diyne **f** was deprotected by TBAF/THF at 0 °C for 1 h. The reaction mixture containing **g**, was cannulated to a mixture of the Cu-system. A summary can be found in table S3.

Table S3 Improvement of synthesis of hexadecahydro[18]annulene **h** by variation of the Cu-system.

N	Cu-system	Virtual molarity of g in Cu-system [M]	Isolated yield of h [%]
1	Cu(OAc) ₂ ·H ₂ O/pyridine	0.010	4
2	Cu(OAc) ₂ ·H ₂ O/pyridine	0.030	13
3	Cu(OAc)₂·H₂O/pyridine	0.045	24
4	Cu(OAc) ₂ ·H ₂ O/pyridine	0.060	18
5	CuCl/TMEDA/O ₂ /acetone	0.045	0 ^a

a – by TLC, another mayor product was formed which was most likely the cyclic dimer (C₁₂H₄).

Synthesis of [18]annulene by variation of the reductive system



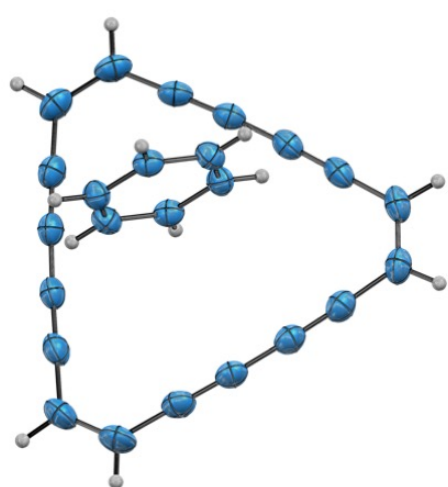
Scheme S4 Reduction of **i** to [18]annulene **j** by variation of reductive system.

Different reductive systems were applied to reduce **i** to **j**. The results are summarized in table S4.

Table S4 Summary of applied reductive systems for the synthesis of **j**.

N	Reductive system	Additive	Solvent	Temperature [°C]	Isolated yield of j [%]
1	5% Pd/BaSO ₄	quinoline	benzene	rt	15-20
2	5% Pd/BaSO ₄	pyridine	benzene	rt	12-16
3	5% Pd/CaCO₃/Pb	quinoline	benzene	rt	17-23
4	5% Pd/BaSO ₄	--	benzene	rt	5-10
5	5% Pd/CaCO ₃ /Pb	--	benzene	rt	5-10
6	10% Pd/CaCO ₃	--	benzene	rt	5-10
7	5% Pd/CaCO ₃ /Pb	quinoline	EtOAc	rt	5-10
8	5% Pd/CaCO ₃ /Pb	quinoline	EtOAc	0	0-5
9	5% Pd/CaCO ₃ /Pb	quinoline	EtOAc	-78	--
10	Na	--	NH ₃ (liquid)	-78	0
11	H ₂ SnBu ₃ / ZnCu*	--	MeOH	rt	0
12	CrCl ₂	--	MeOH	rt	0

4. X-ray data of hexadecylo[18]annulene



Crystal Data. $C_{24}H_{12}$, $M = 300.34$, tetragonal, $a = 21.6492(2)$ Å, $c = 14.6312(2)$ Å, $V = 6857.48(17)$ Å³, $T = 173.1(6)$, space group $I41/acd$ (no. 142), $Z = 16$, $\mu(\text{Cu K}\alpha) = 0.505$, 9384 reflections measured, 1342 unique ($R_{\text{int}} = 0.0315$) which were used in all calculations. The final wR_2 was 0.1203 (all data) and R_1 was 0.0388 ($I > 2\sigma(I)$).

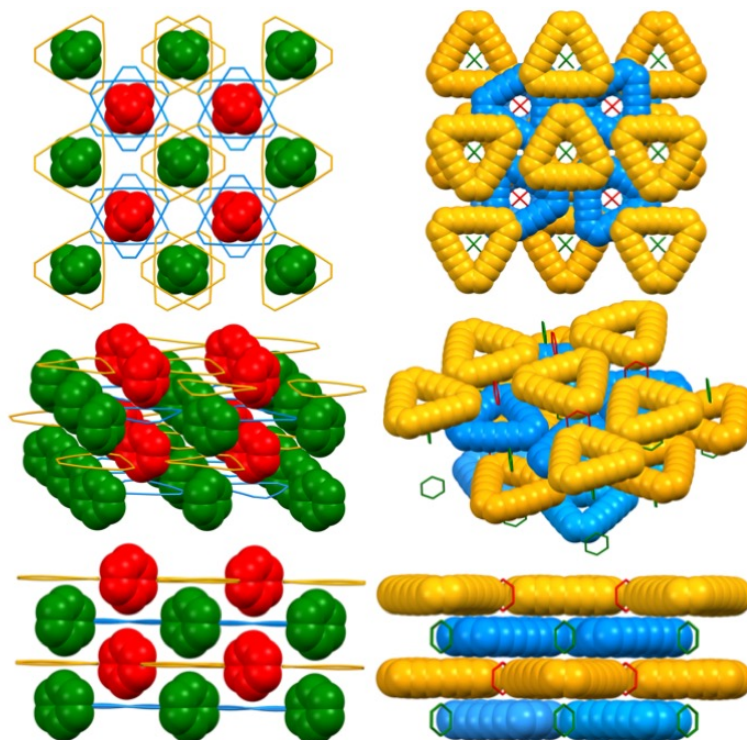


Fig. S1 left: Crystal data and depictions of hexadecylo[18]annulene **5**; right: crystal packing of **5** in benzene matrix; benzene depicted in green and red, **5** depicted in yellow and blue; hydrogens are omitted for clarity.

5. References

- 1 W. H. Okamura and F. Sondheimer, *J. Am. Chem. Soc.*, 1967, **89**, 5991–5992.
- 2 M. Suzuki, A. Comito, S. I. Khan and Y. Rubin, *Org. Lett.*, 2010, **12**, 2346–2349.
- 3 K. Peter, K. P. C. Vollhardt and L. S. Winn, *Tetrahedron Lett.*, 1985, **26**, 709–712.

6. Spectra of all compounds (Uv/vis, NMR, HRMS)

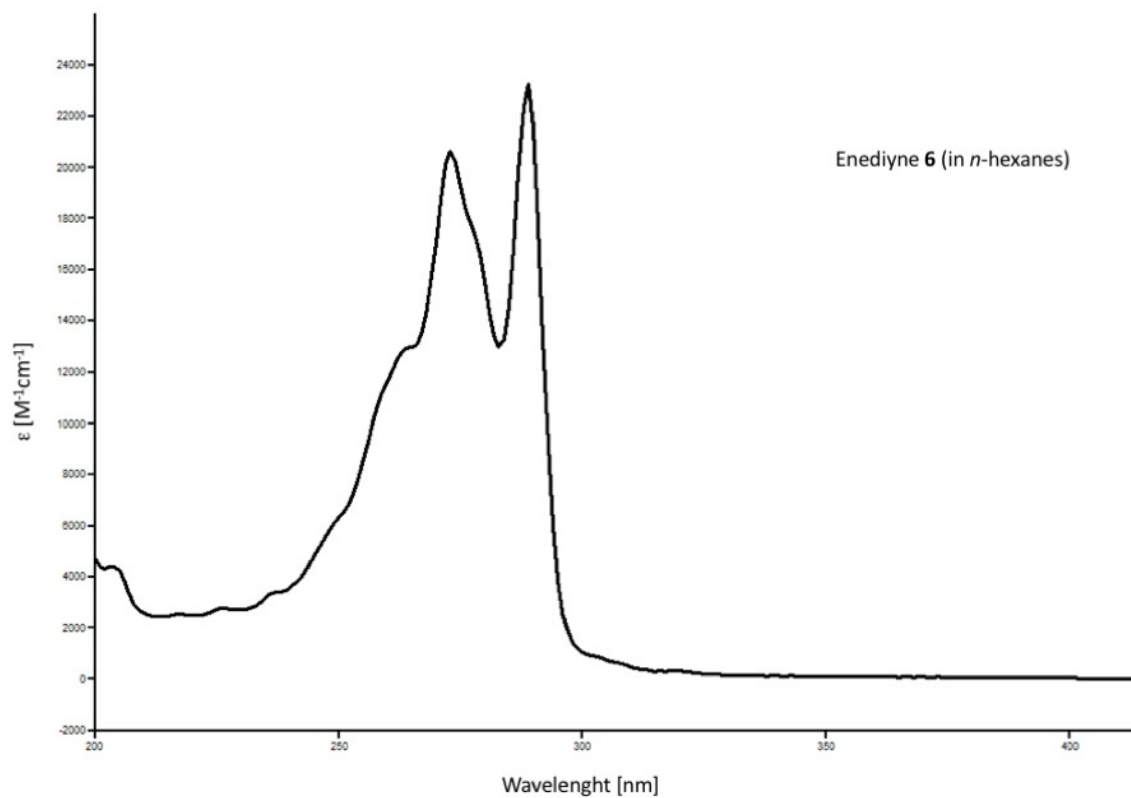


Fig. S2 UV/vis spectrum of 6 in *n*-hexane.

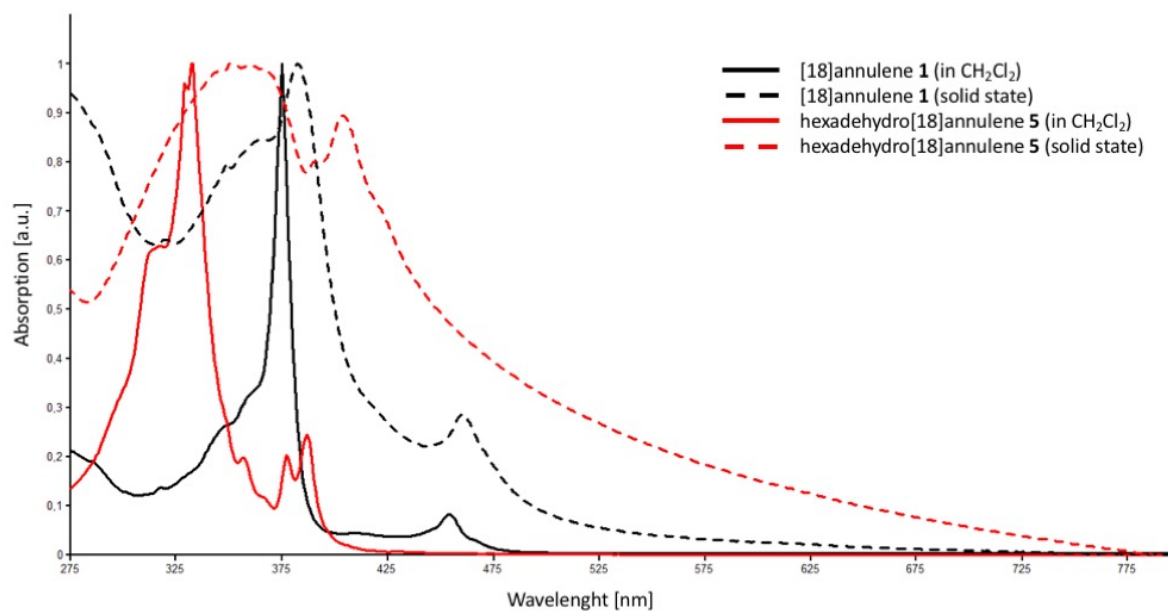


Fig. S3 normalized UV/vis spectra of 1 and 5 in solution and in the solid state.

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DATIM Wed Sep 30 15:45:25 2015

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IRFIN	10600.0 Hz
FREQ	8000.0 Hz
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PW3	10.0 us
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PI2	1.000 ms
PI3	1.00 ms
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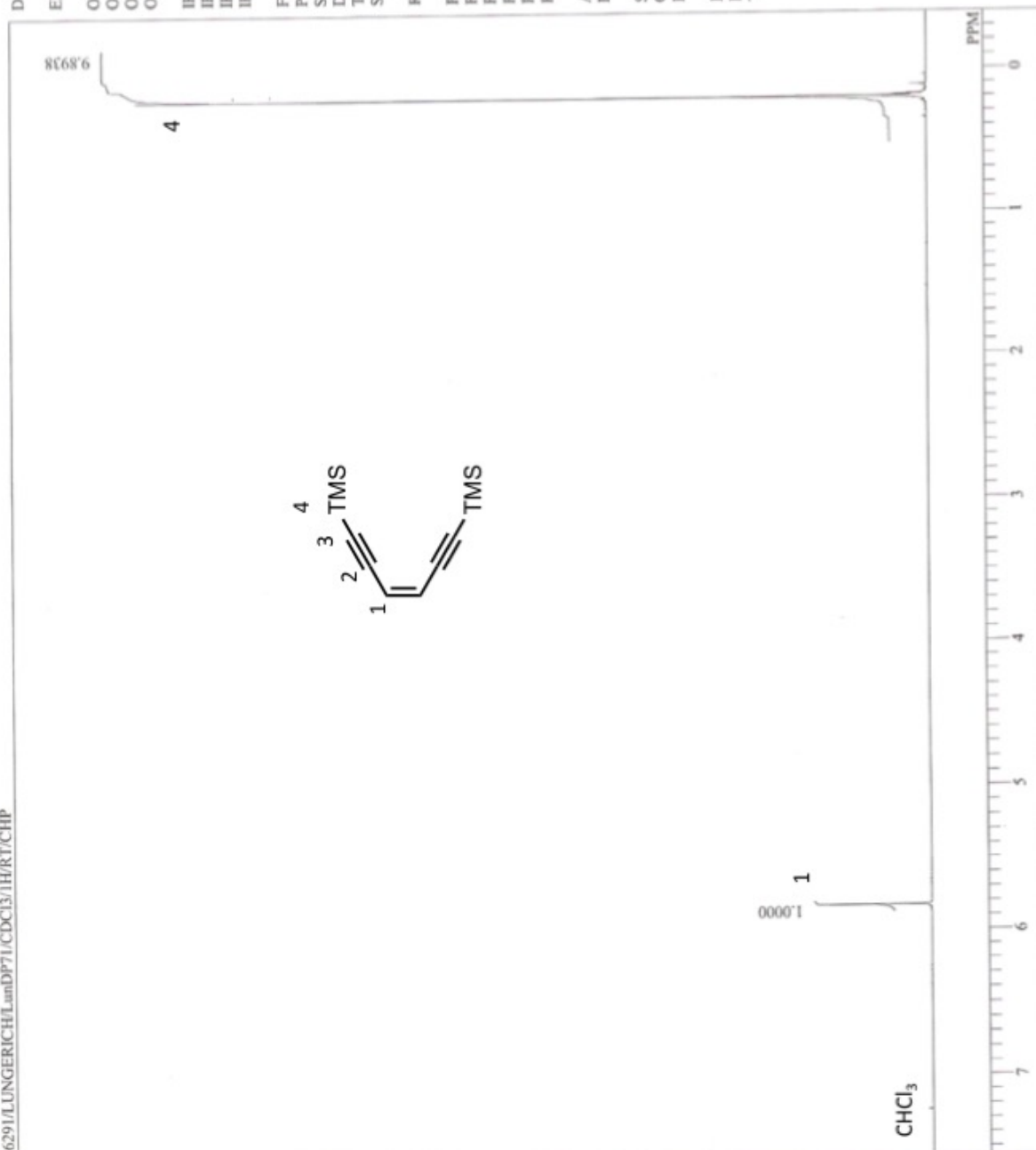


Fig. S4 ¹H NMR of **6** in CDCl₃ at rt (400 MHz).

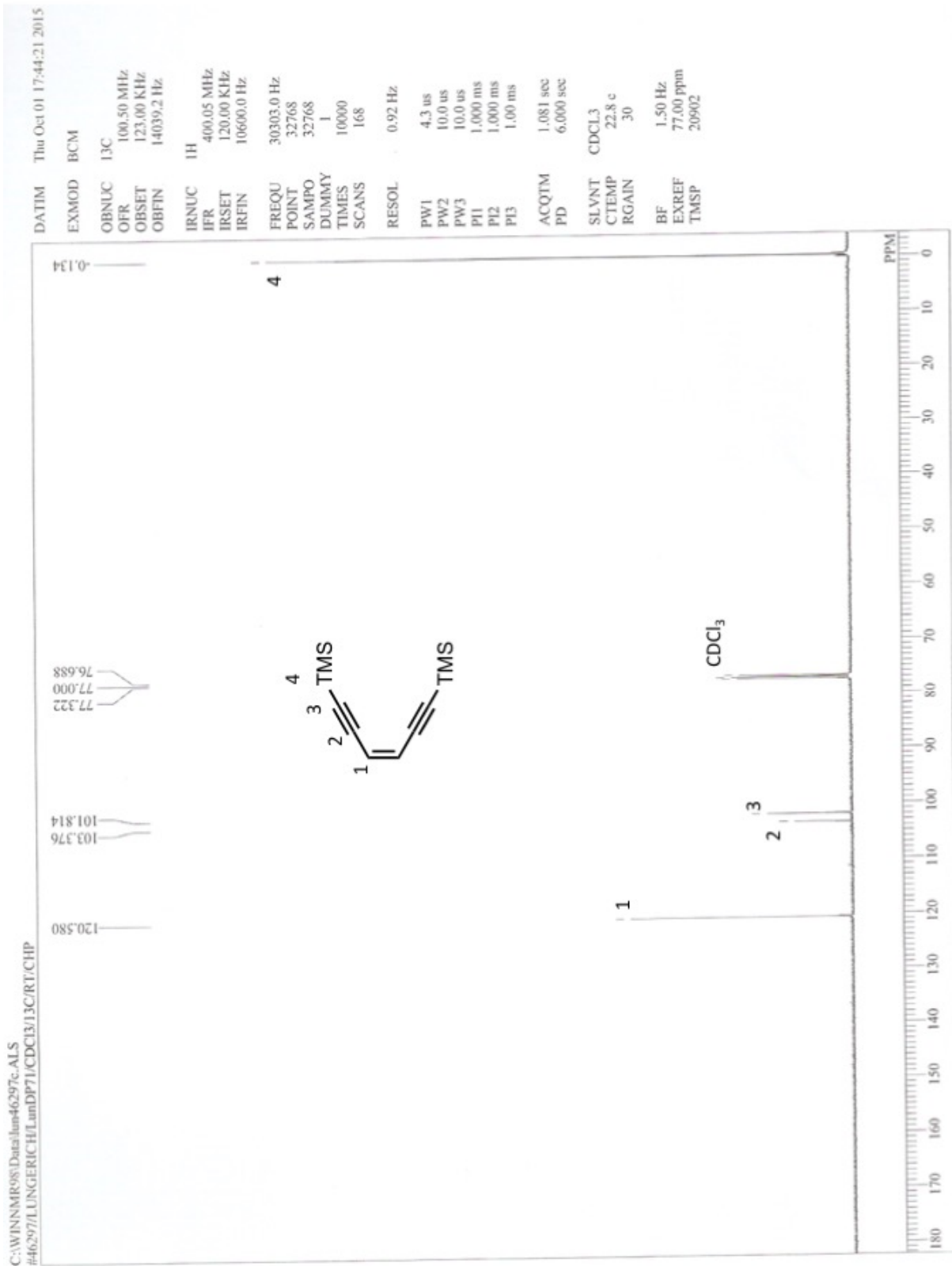


Fig. S5 ¹³C NMR of 6 in CDCl₃ at rt (100 MHz).

Display Report

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 Operator: MD
 Sample Name: maXis 4G
 Instrument: MD
 Comment: Toluol
 Sample Name: 20183

Acquisition Parameter
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 Scan End: 1400 m/z
 Ion Polarity: Positive
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 Set End Plate Offset: -500 V
 Set Collision Cell RF: 2500.0 Vpp
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 Set Dry Heater: 200 °C
 Set Dry Gas: 2.0 l/min
 Set Divert Valve: Waste



Fig. S6 HRMS of 6 (APPI, toluene).

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#46448/LUNGERICH/LunDM2/CP1H/Nospin/RT/CHP

DATIM Fri Nov 06 11:01:59 2015

EXMOD NON

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OBFIN 3738.5 Hz

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FREQU 8000.0 Hz
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TIMES 48
SCANS 48

RESOL 0.12 Hz

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PW2 10.0 us
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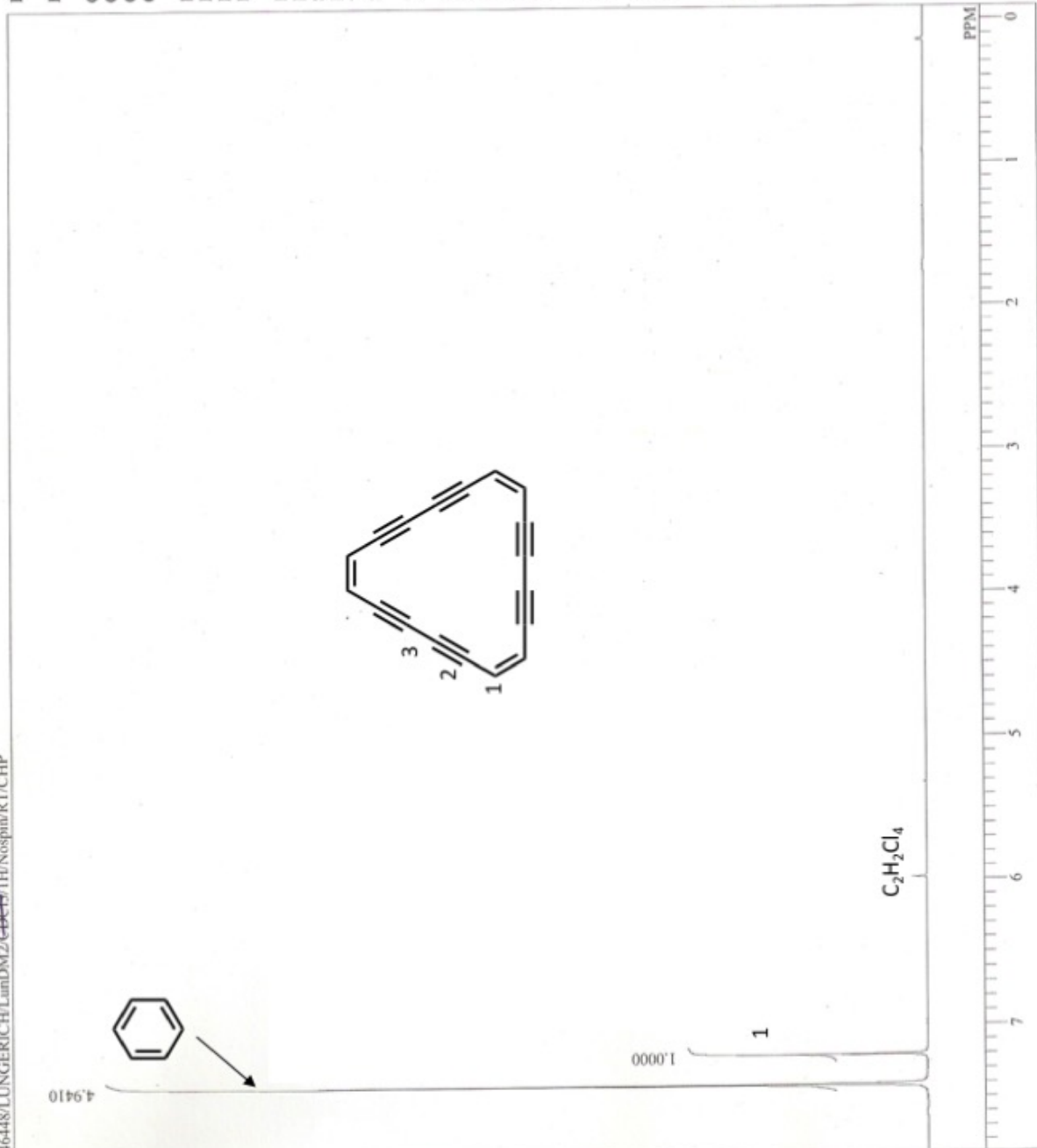


Fig. S7 ¹H NMR of 5 in C₂D₂Cl₄ at rt (400 MHz).

C:\WINNMR98\Data\lms46448-ALS

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DATIM Fri Nov 06 11:15:51 2015

EXMOD	BCM
OBNUC	13C
OFR	100.50 MHz
OBSF	123.00 KHz
OBFIN	14039.2 Hz
IRNUC	1H
IFR	400.05 MHz
IRSET	120.00 KHz
IRFIN	10600.0 Hz
FREQ	30303.0 Hz
POINT	32768
SAMPO	32768
DUMMY	1
TIMES	10000
SCANS	104
RESOL	0.92 Hz
PW1	4.3 us
PW2	10.0 us
PW3	10.0 us
PI1	1.000 ms
PI2	1.000 ms
PI3	1.00 ms
ACQTM	1.081 sec
PD	6.000 sec
SLVNT	TCLF
CTEMP	22.9 c
RGAIN	30
BF	1.50 Hz
EXREF	73.70 ppm
TMSP	21241

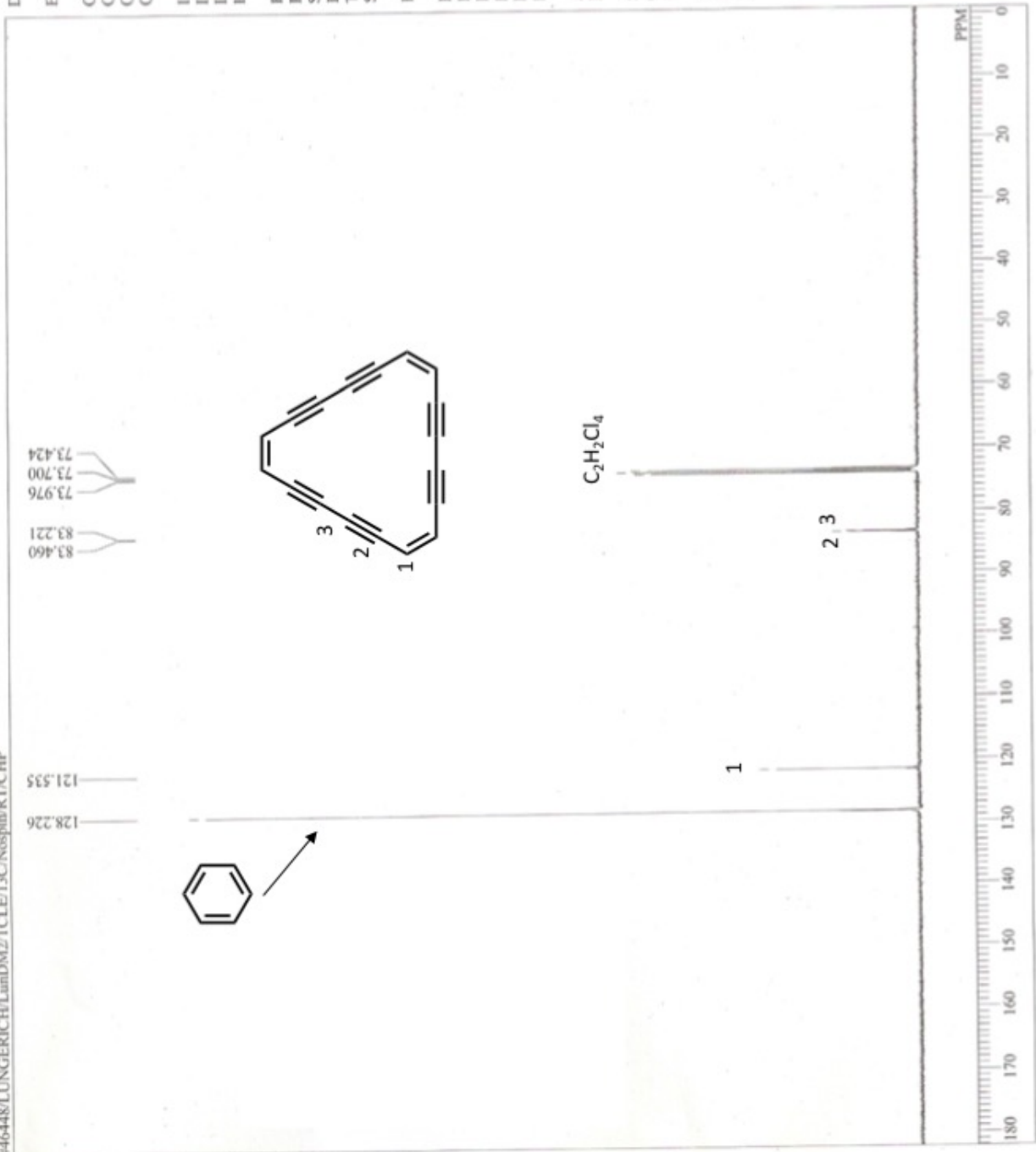


Fig. S8 ¹³C NMR of 5 in C₂D₂Cl₄ at rt (100 MHz).

DATIM Fri Nov 06 11:15:51 2015

EXMOD BCM
OBNUC 13C
OPR 100.50 MHz
OBSET 123.00 KHz
OBFIN 14039.2 Hz
IRNUC 1H
IFR 400.05 MHz
IRSET 120.00 KHz
IRFIN 106000.0 Hz
FREQU 30303.0 Hz
POINT 32768
SAMPO 32768
DUMMY 1
TIMES 10000
SCANS 104
RESOL 0.92 Hz
PW1 4.3 us
PW2 10.0 us
PW3 10.0 us
PI1 1.000 ms
PI2 1.000 ms
PI3 1.00 ms
ACQTM 1.081 sec
PD 6.000 sec
SLVNT TCLE
CTEMP 22.9 c
RGAIN 30
BF 1.50 Hz
EXREF 73.70 ppm
TMSP 21241

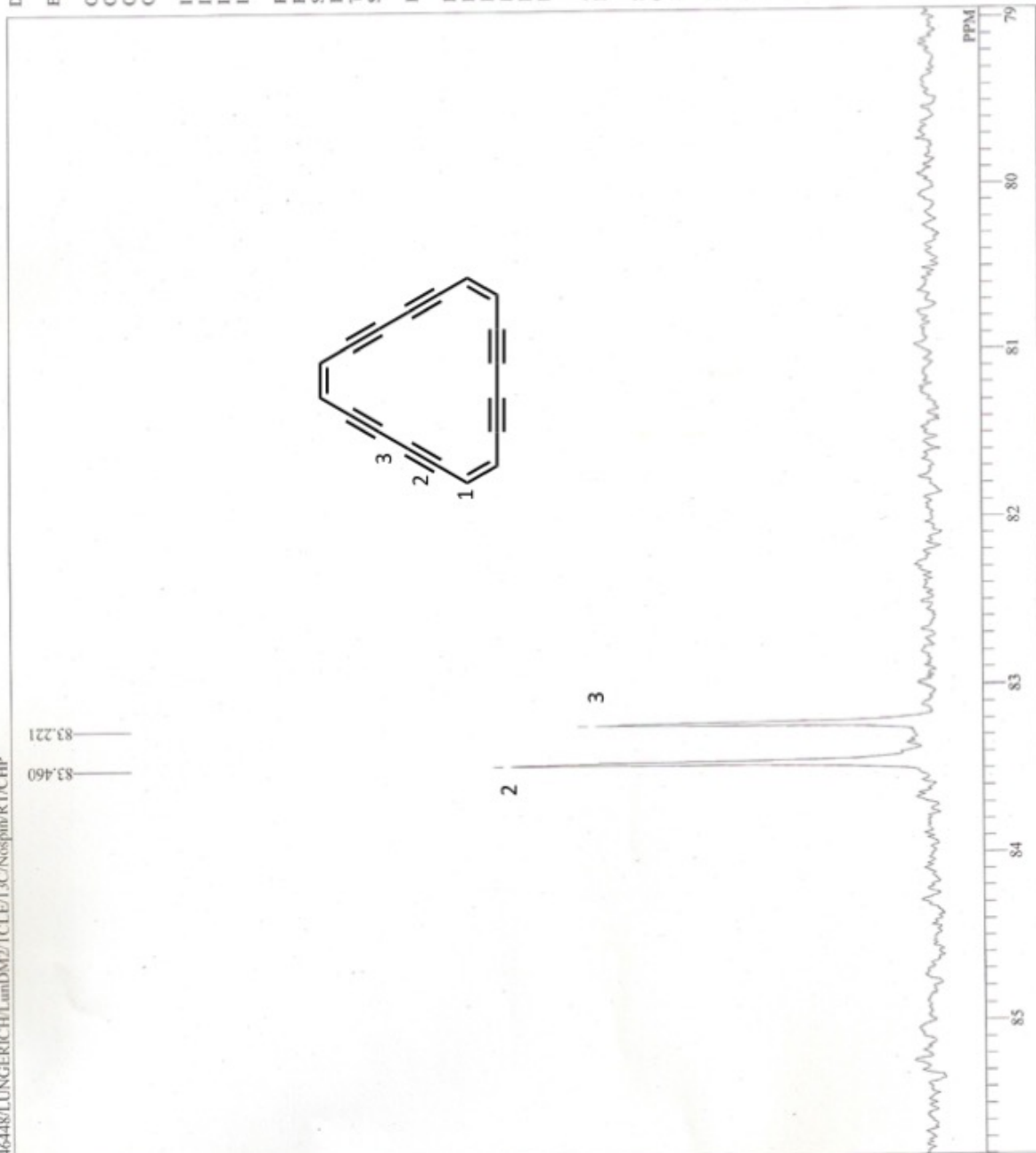


Fig. S9 Zoom-in of ^{13}C NMR of **5** in $\text{C}_2\text{D}_2\text{Cl}_4$ at rt (100 MHz).

Display Report

Analysis Info
Analysis Name: D:\Data\Jux-2015-Lungerich-DL-18-A6-.d
Method: APPI-Klei-Meinhardt-.m
Sample Name: Tol
Comment: Tol
Acquisition Date: 4/17/2015 12:06:28 PM
Operator: MD
Instrument: maXis 4G
20183

Acquisition Parameter
Source Type: APPI
Focus: Not active
Scan Begin: 100 m/z
Scan End: 1000 m/z
Ion Polarity: Positive
Set Capillary: 600 V
Set End Plate Offset: -500 V
Set Collision Cell RF: 1000.0 Vpp
Nebulizer: 3.0 Bar
Set Dry Heater: 200 °C
Set Dry Gas: 3.0 l/min
Set Divert Valve: Waste

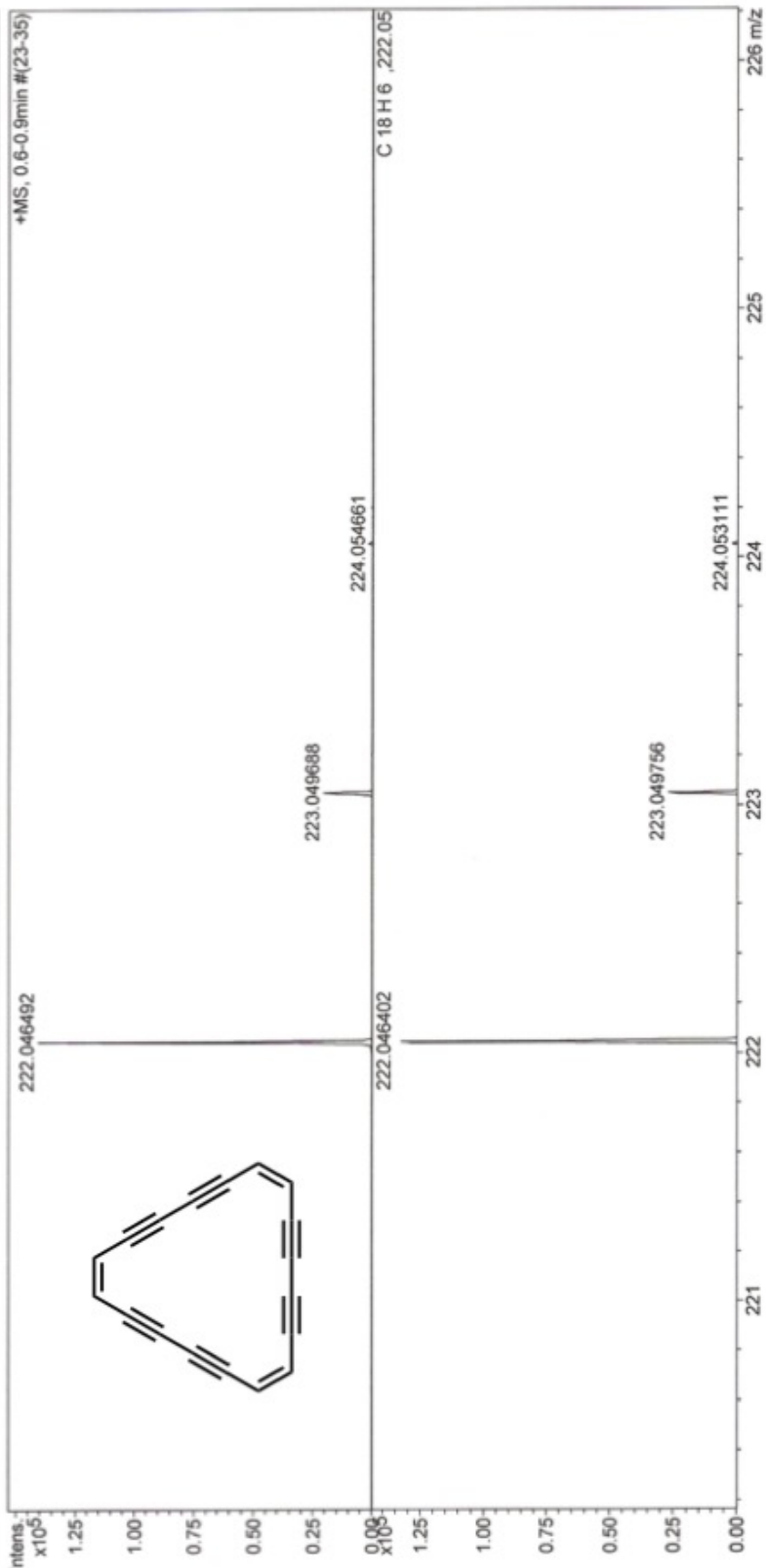


Fig. S10 HRMS of 5 (APPI, toluene).

C:\WINNMR98\Data\umd46449h.ALS
 #46449/LUNGERICH.LumDDL-M2-2\TCLE\1H\Nospin\RT/CHP

DATIM Fri Nov 06 11:42:25 2015

EXMOD	NON
OBNUC	1H
OFR	400.05 MHz
OBSET	129.10 KHz
OBFIN	3738.5 Hz
IRNUC	1H
IFR	400.05 MHz
IRSET	120.00 KHz
IRFIN	106000.0 Hz
FREQU	8000.0 Hz
POINT	65536
SAMPO	32768
DUMMY	8
TIMES	56
SCANS	48
RESOL	0.12 Hz
PW1	10.0 us
PW2	10.0 us
PW3	10.0 us
PI1	1.000 ms
PI2	1.000 ms
PI3	1.00 ms
ACQTM	4.096 sec
PD	4.000 sec
TCLE	21.9 c
RGAIN	16
BF	0.12 Hz
EXREF	5.98 ppm
TMSP	44330

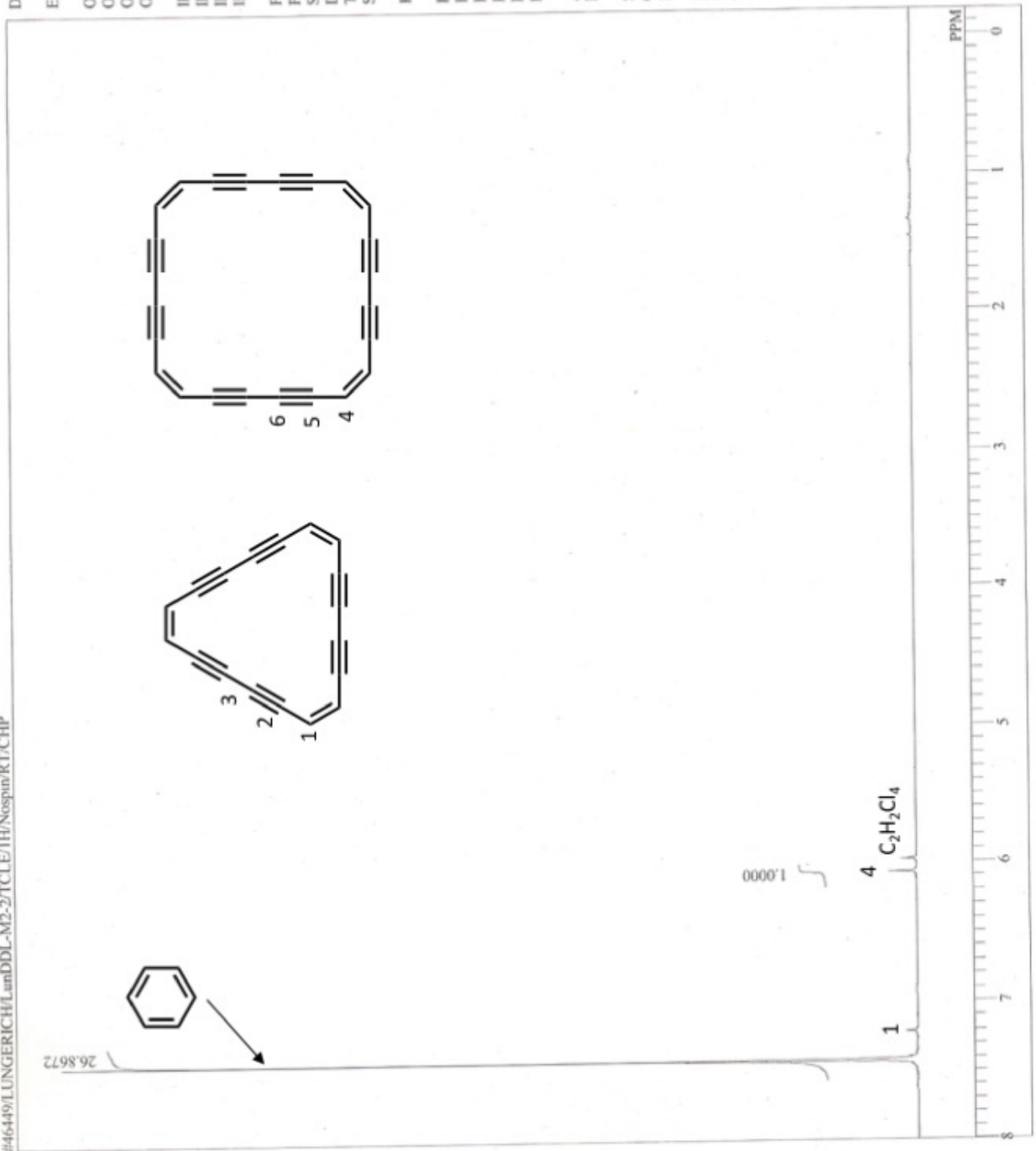


Fig. S11 Comparison of ¹H NMR of 5 and cyclic tetramer in C₂D₂Cl₄ at rt (400 MHz).

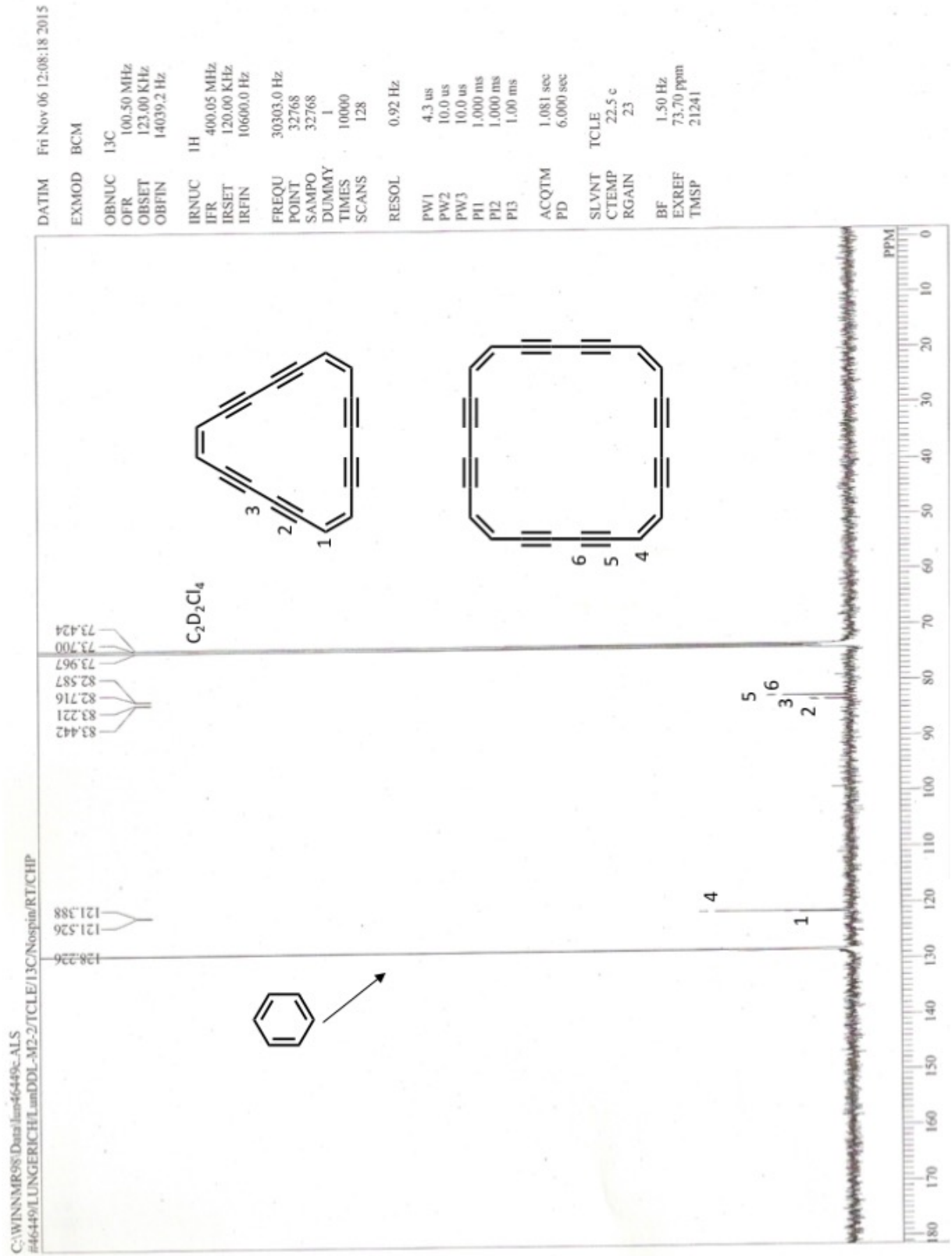


Fig. S12 Comparison of ^{13}C NMR of 5 and cyclic tetramer in $C_2D_2Cl_4$ at rt (100 MHz).

MIR98:Data\lum6448c-ALS
91LUNGERICH\lumDDL-M2-2\TCLC/13C\Nospin/RT/CHP

DATIM Fri Nov 06 12:08:18 2015

EXMOD BCM

OBNUC 13C
OFR 100.50 MHz
OBSET 123.00 KHz
OBFIN 14039.2 Hz

IRNUC 1H
IRF 400.05 MHz
IRSET 120.00 KHz
IRFIN 106000.0 Hz

FREQU 30303.0 Hz
POINT -32768
SAMPO 32768
DUMMY 1
TIMES 10000
SCANS 128

RESOL 0.92 Hz

PW1 4.3 us
PW2 10.0 us
PW3 10.0 us
PI1 1.000 ms
PI2 1.000 ms
PI3 1.00 ms

ACQTM 1.081 sec
PD 6.000 sec

SLVNT
CTEMP 22.5 c
RGAIN 23

BF 1.50 Hz
EXREF 73.70 ppm
TMSP 21241

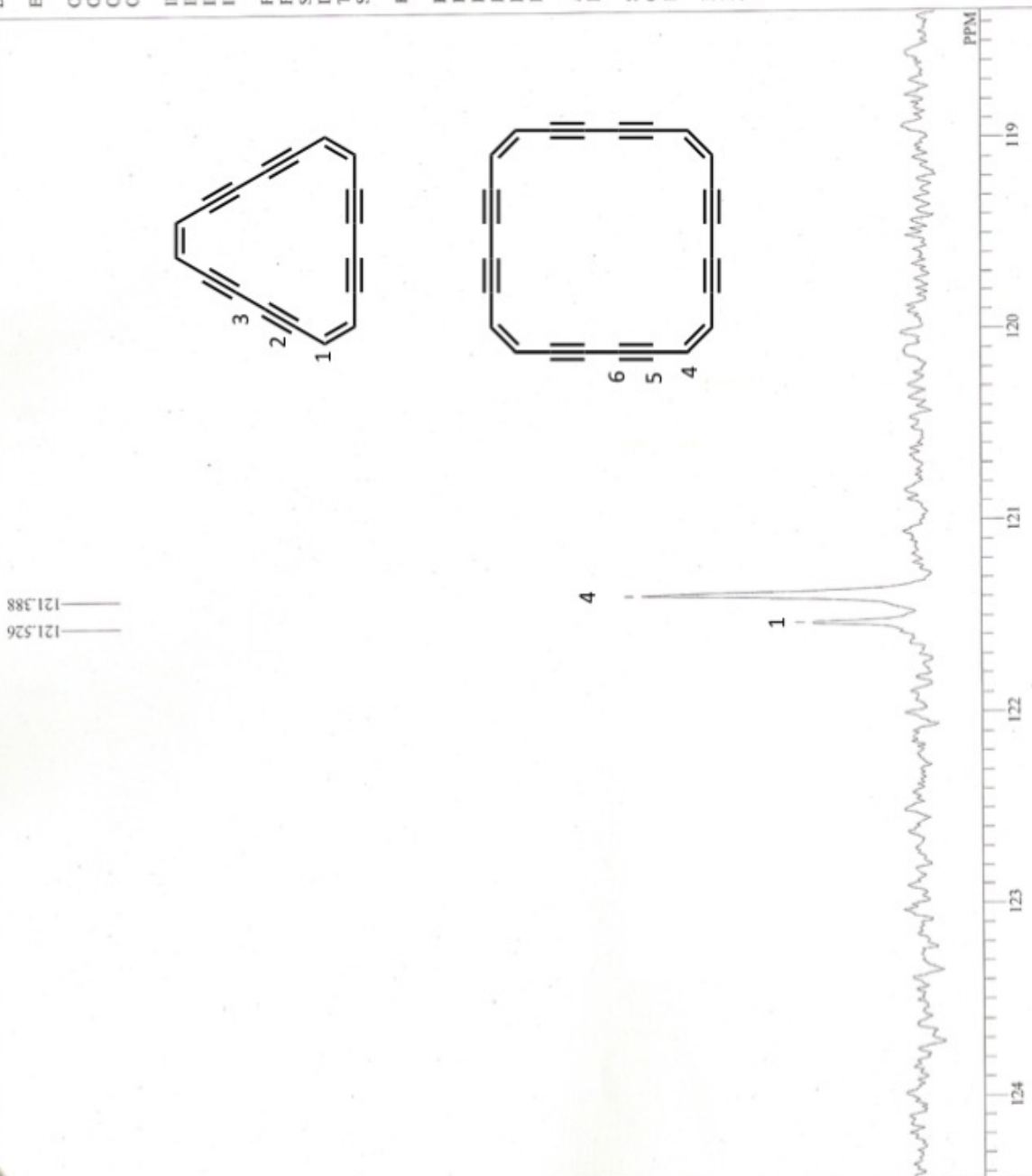


Fig. S13 Zoom-in of comparison of ¹³C NMR of **5** and cyclic tetramer in C₂D₂Cl₄ at rt (100 MHz).

NMR981>Data\lum46449c-ALS
449/LUNGERICH/LumDDL-M2-2/TCLE/13C/Nospin/RT/CHP

DA:TIM Fri Nov 06 12:08:18 2015

EXMOD BCM

OBNUC 13C
OFR 100.50 MHz
OBSET 123.00 KHz
OBFIN 14039.2 Hz

IRNUC 1H
IFR 400.05 MHz
IRSET 120.00 KHz
IRFIN 10600.0 Hz

FREQU 30303.0 Hz
POINT 32768
SAMPO 32768
DUMMY 1
TIMES 10000
SCANS 128

RESOL 0.92 Hz

PW1 4.3 us
PW2 10.0 us
PW3 10.0 us
PI1 1.000 ms
PI2 1.000 ms
PI3 1.00 ms

ACQTM 1.081 sec
PD 6.000 sec

SLVNT TCLE
CTEMP 22.5 c
RGAIN 23

BF 1.50 Hz
EXREF 73.70 ppm
TMSP 21241

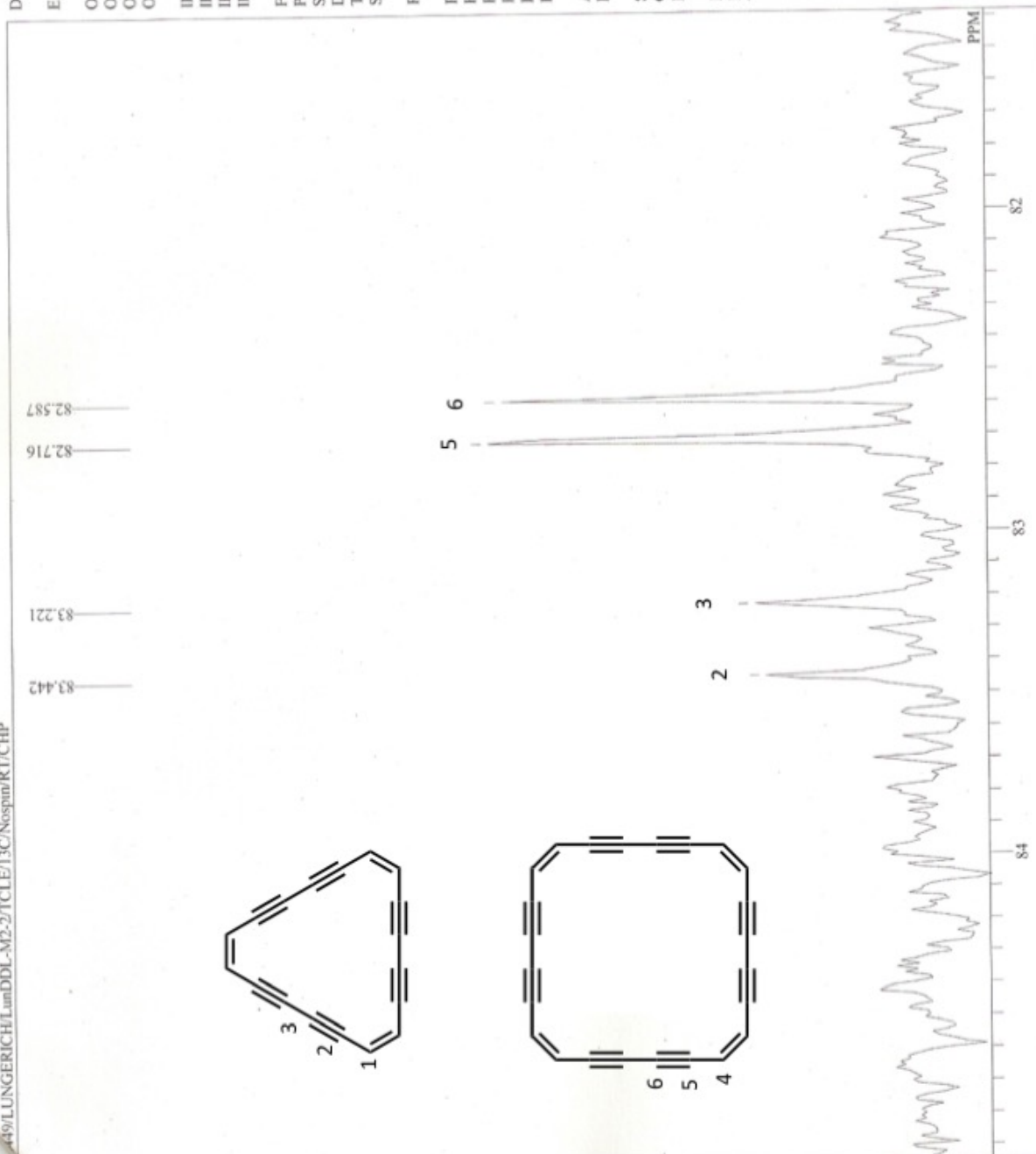


Fig. 14 Zoom-in of comparison of ¹³C NMR of 5 and cyclic tetramer in C₂D₂Cl₄ at rt (100 MHz).

Display Report

Analysis Info		Acquisition Date	11/5/2015 3:09:39 PM
Analysis Name	D:\Data\Jux-2015-Lungerich-DL-M-2-2-appi-.d	Operator	MD
Method	APPI-kleine-Massen-ab-100-.m	Instrument	maxis 4G
Sample Name			20183
Comment	MeOH		

Acquisition Parameter		Set Nebulizer	3.0 Bar
Source Type	APPI	Set Dry Heater	200 °C
Focus	Not active	Set Dry Gas	2.0 l/min
Scan Begin	100 m/z	Set Divert Valve	Waste
Scan End	1400 m/z		
		Ion Polarity	Positive
		Set Capillary	800 V
		Set End Plate Offset	-500 V
		Set Collision Cell RF	2500.0 Vpp

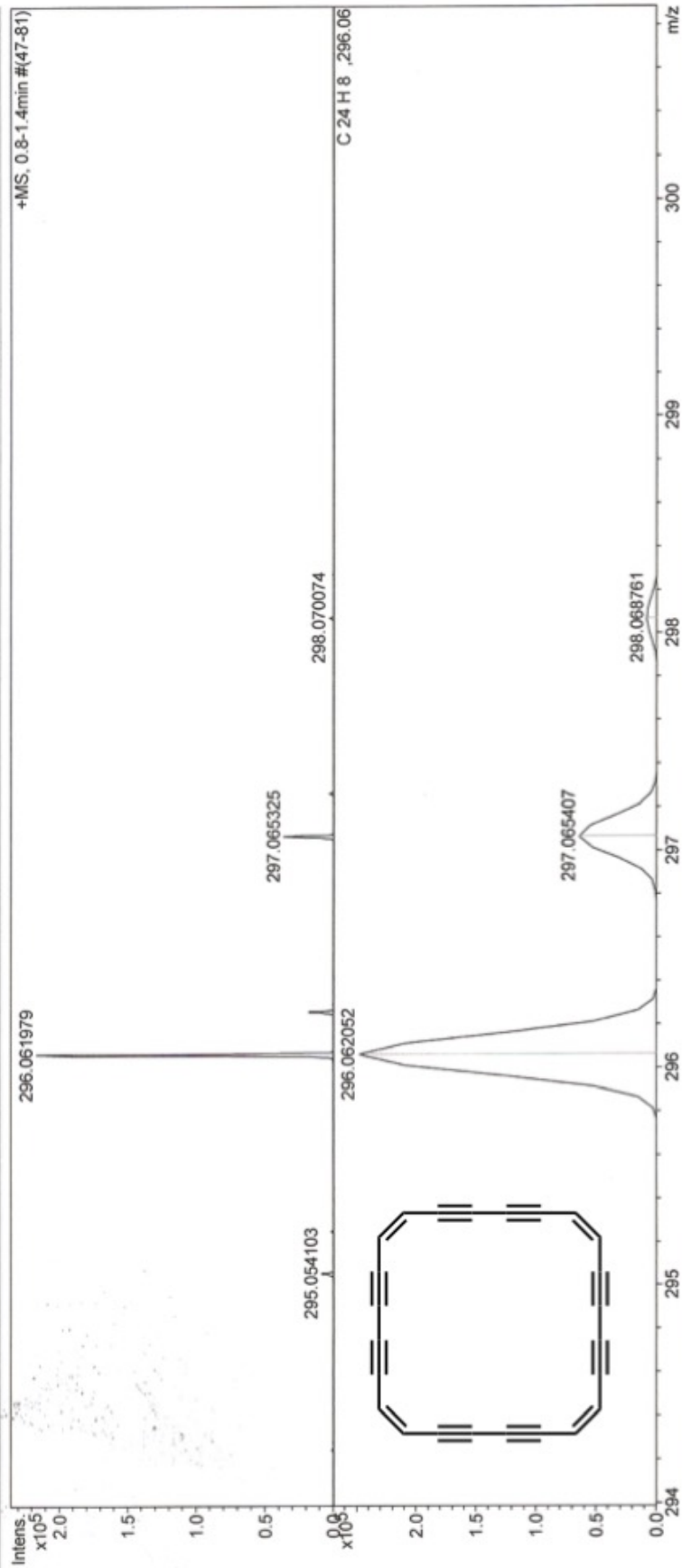


Fig. S15 HRMS of cyclic tetramer (APPI, MeOH).

104265/Lungerich/Lund M-3 sublimierte Kristalle/3mg/1H/THF-d8/25DEG/Maid



Current Data Parameters
NAME 41u104265
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20151218
Time 13.06
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT THF
NS 32
DS 2
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9583745 sec
RG 228.1
DW 60.400 usec
DE 9.00 usec
TE 298.4 K
D1 2.00000000 sec
TDO 1

==== CHANNEL f1 =====
NUC1 1H
P1 12.13 usec
PL1 0 dB
SFO1 400.1324710 MHz

F2 - Processing parameters
SI 32768
SF 400.1300143 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

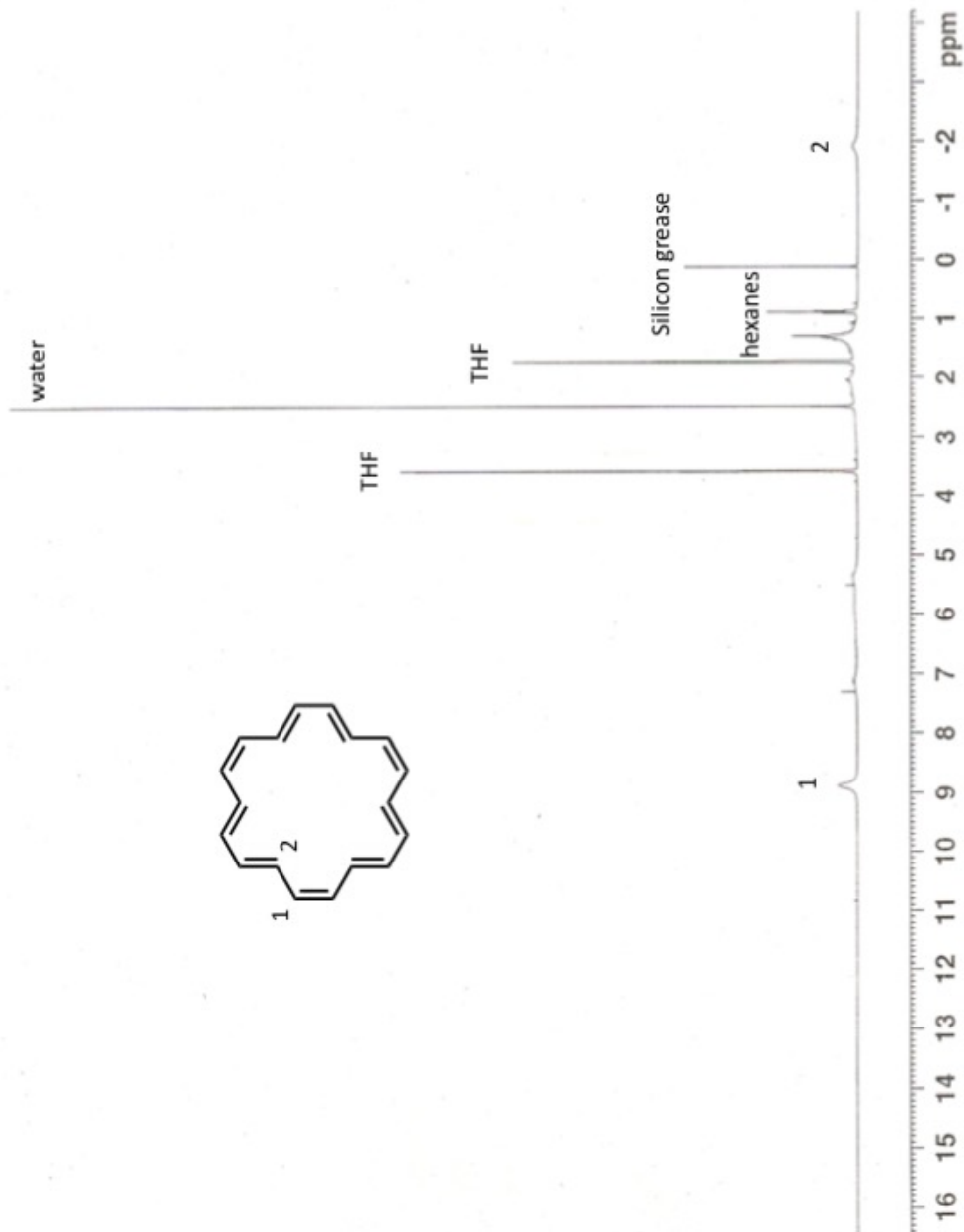


Fig. S16 ^1H NMR of sublimed **1** in THF- D_8 at rt (400 MHz); crystals were carefully washed with hexanes, CH_2Cl_2 , benzene and dried under N_2 -flow.

104265/Lungerich/Lund M-3 sublimierte Kristalle/3mg/1H/THF-d8/25DEG/Maid

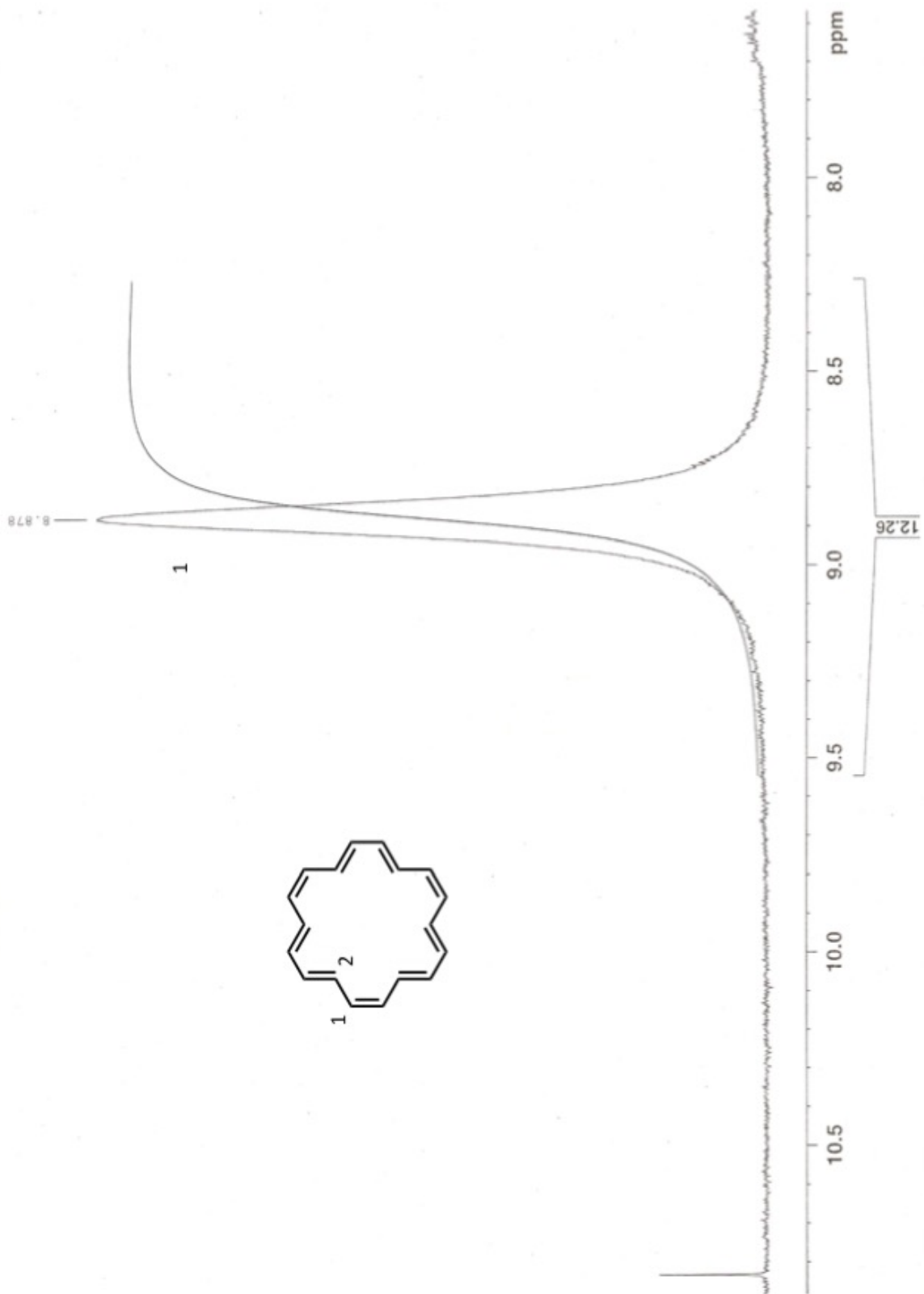


Fig. S17 Zoom-in of ^1H NMR of **1** in THF- D_8 at rt (400 MHz).

104265/Lungerich/Lund M-3 sublimierte Kristalle/3mg/1H/THF-d8/25DEG/Maid

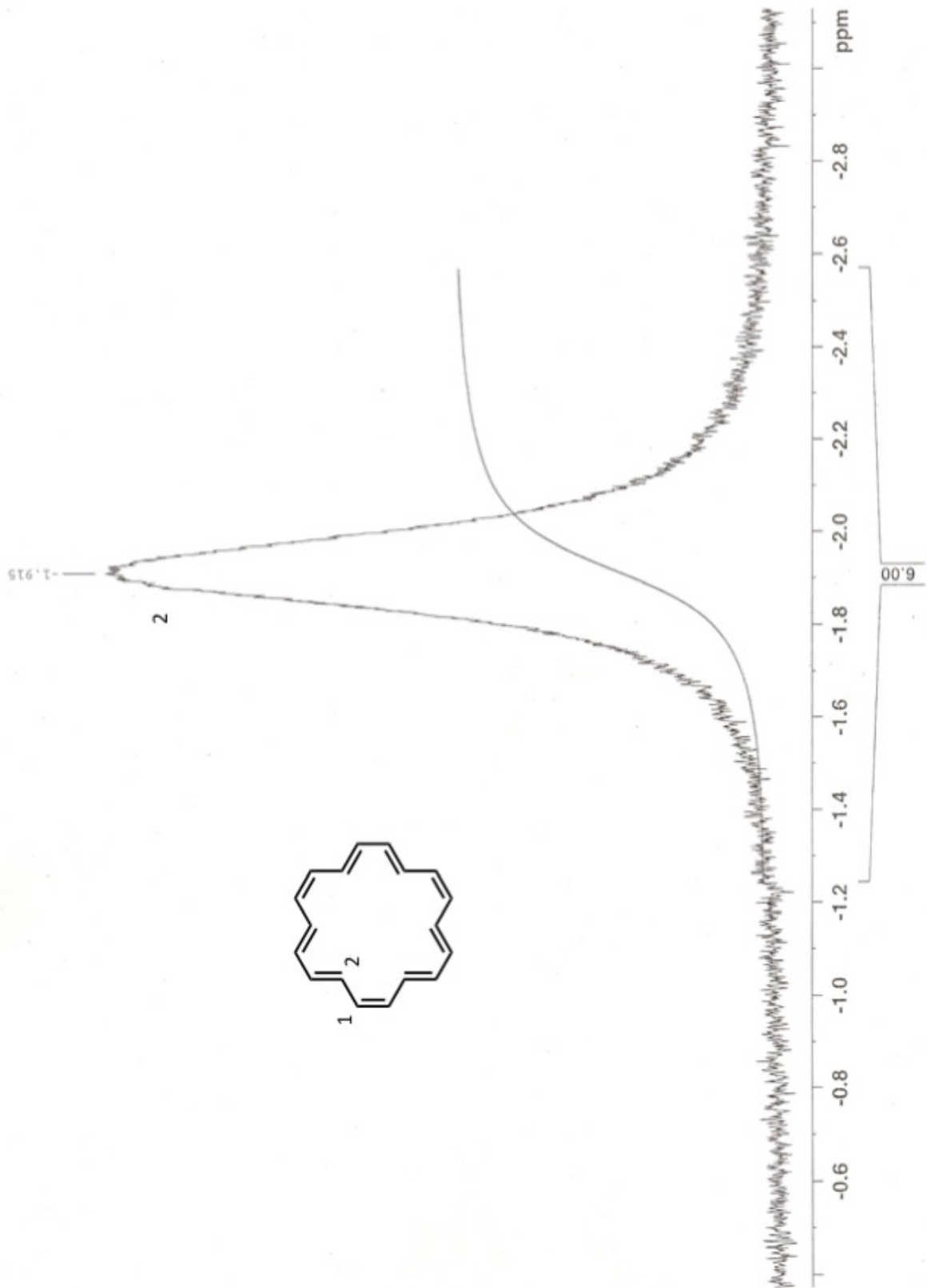


Fig. S18 Zoom-in of ^1H NMR of **1** in THF- D_8 at rt (400 MHz).

104130TLungerich/LunD-M3/11mg/1H/THF-d8/-40DEG/Maid

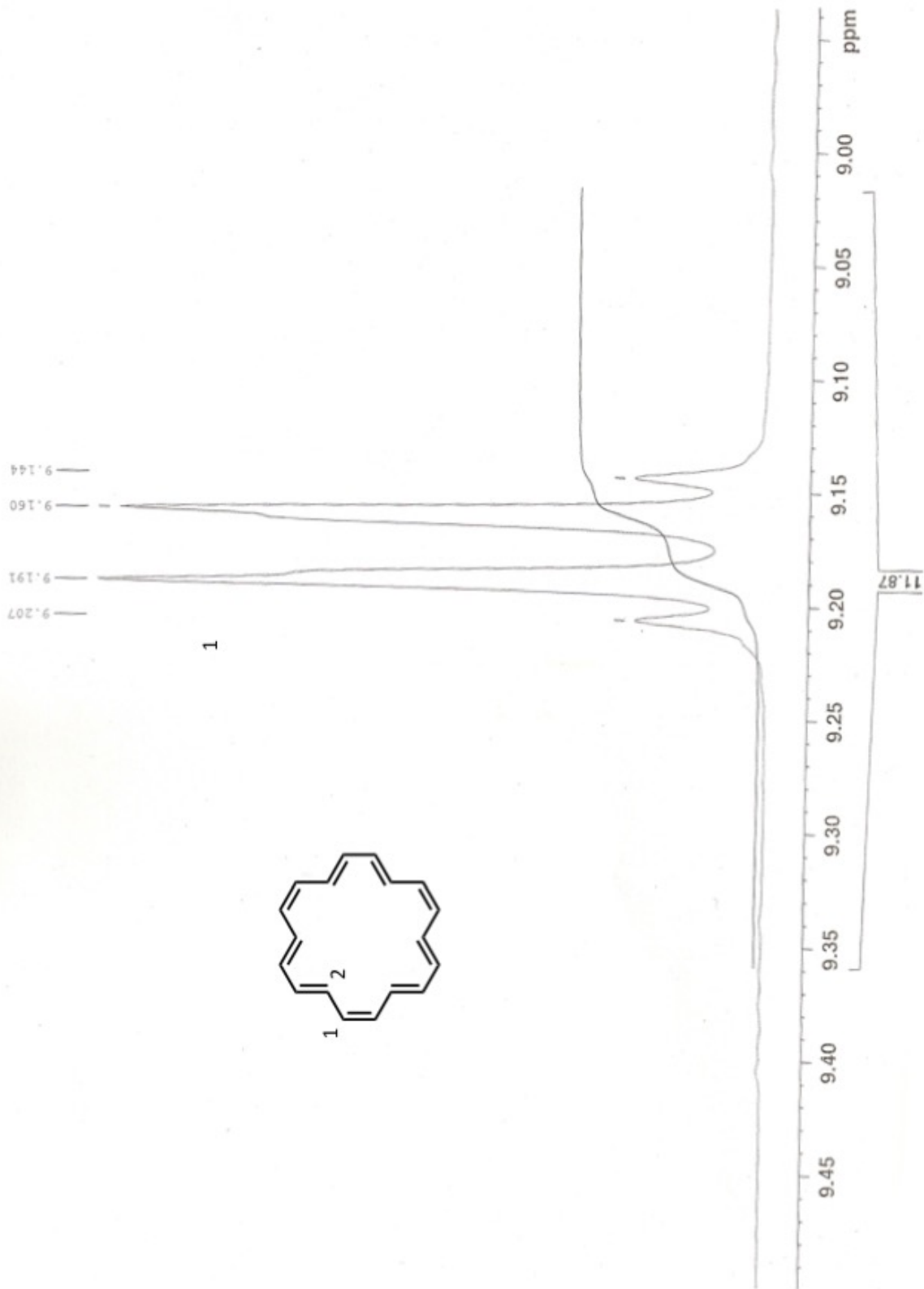


Fig. S19 Zoom-in of ^1H NMR of **1** in THF- D_8 at -40°C (400 MHz).

104130TLungerich/LunD-M3/11mg/1H/THF-d8/-40DEG/Maid

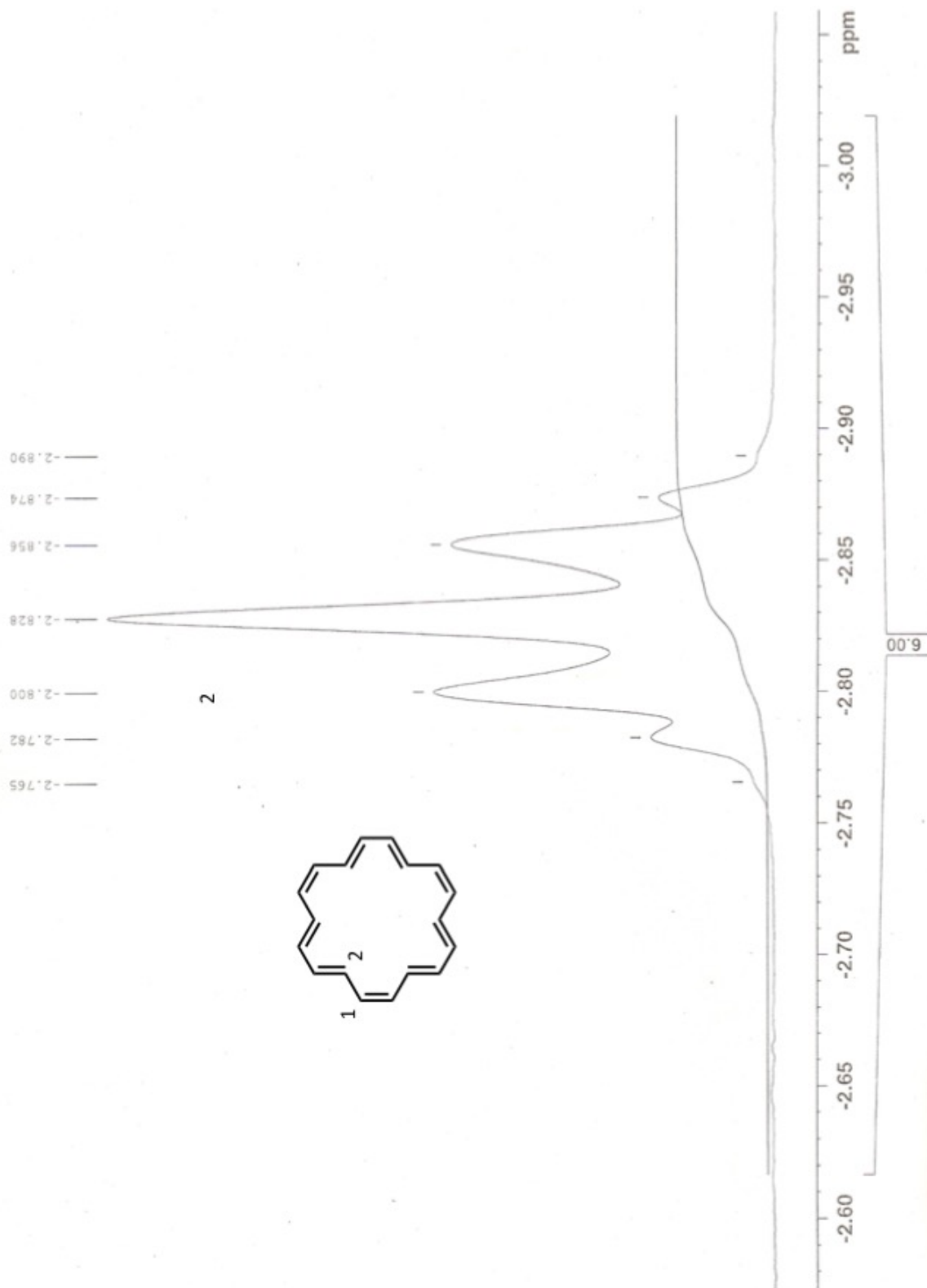


Fig. S20 Zoom-in of ¹H NMR of **1** in THF-D₈ at -40 °C (400 MHz).

104130TLungerich/LunD-M3/11mg/13C/THF-d8/-40DEG/Maid



Current Data Parameters
NAME 4lu104131
EXPNO 433
PROCNO 1

F2 - Acquisition Parameters

Date_ 20151215
Time 14.26
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT THF
NS 208
DS 4
SWH 20080.320 Hz
FIDRES 0.306401 Hz
AQ 1.6318464 sec
RG 46341
DM 24.900 usec
DE 9.00 usec
TE 233.1 K
D1 4.0000000 sec
d11 0.0300000 sec
DELTA 3.9000010 sec
TD0 1
SF01 100.6177596 MHz
NUC1 13C
P1 7.00 usec
PLM1 -1.00000000 W
SF02 400.1316005 MHz
NUC2 1H
CFPRG[2] waltz16
PCPD2 116.00 usec
PLM2 -1.00000000 W
PLM12 -1.00000000 W
PLM13 -1.00000000 W

F2 - Processing parameters
SI 32768
SF 100.6126909 MHz
WDW 0
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

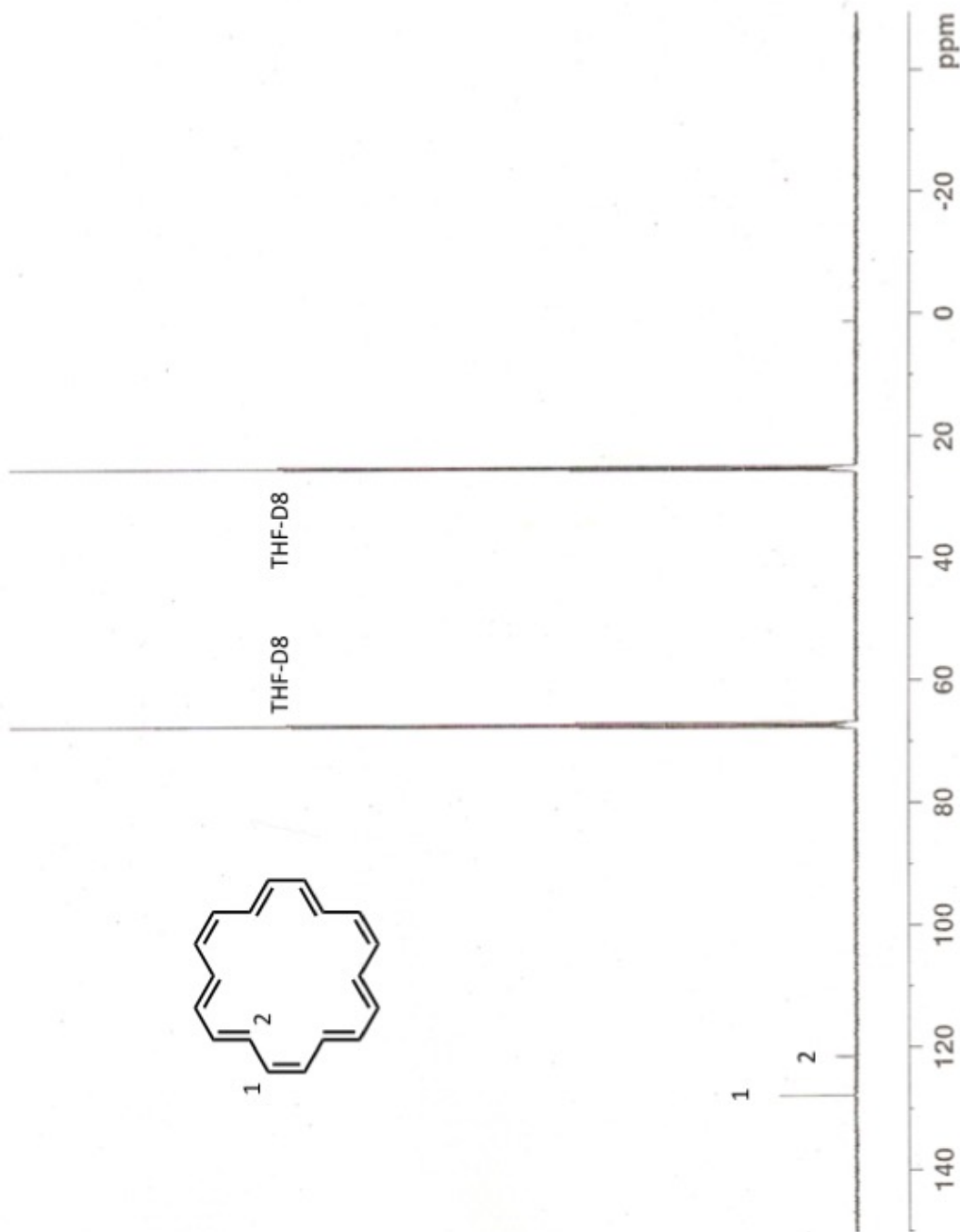


Fig. S21 ¹³C NMR of 1 in THF-D₈ at -40 °C (100 MHz).

104130TLungerich/LunD-M3/11mg/¹³C/THF-d8/-40DEG/Maid

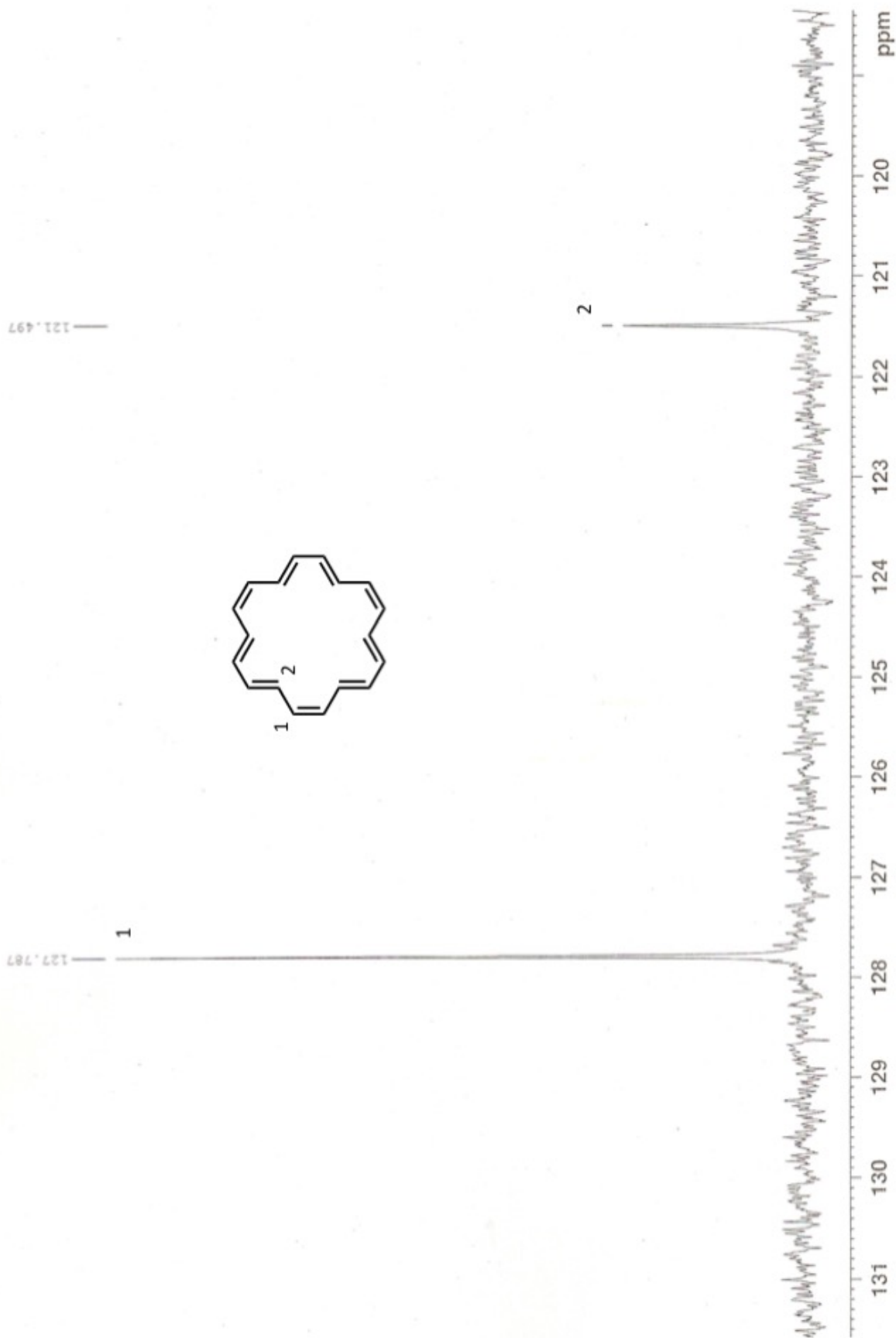


Fig. S22 Zoom-in of ¹³C NMR of **1** in THF-D₈ at -40 °C (100 MHz).

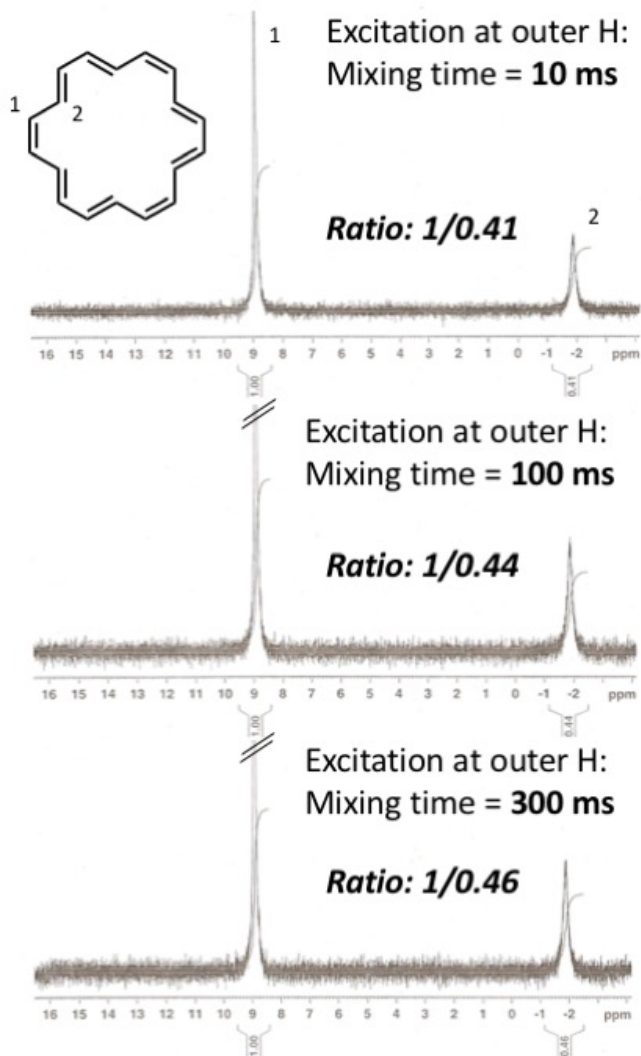


Fig. S23 ^1H EXCY-NMR of **1** in THF-D_8 at rt (400 MHz); different mixing times indicate rapid exchange of inner and outer protons at rt.

Display Report

Analysis Info
Analysis Name: D:\Data\lux-2016-lungerich-18-a-appi-.d
Method: APPI-kleine-ab-140-.m
Sample Name: Tol
Comment: Tol
Acquisition Date: 1/22/2016 11:39:43 AM
Operator: MD
Instrument: maXis 4G
20183

Acquisition Parameter

Source Type	APPI	Ion Polarity	Positive	Set Nebulizer	3.0 Bar
Focus	Not active	Set Capillary	600 V	Set Dry Heater	200 °C
Scan Begin	100 m/z	Set End Plate Offset	-500 V	Set Dry Gas	3.0 l/min
Scan End	1000 m/z	Set Collision Cell RF	1000.0 Vpp	Set Divert Valve	Waste

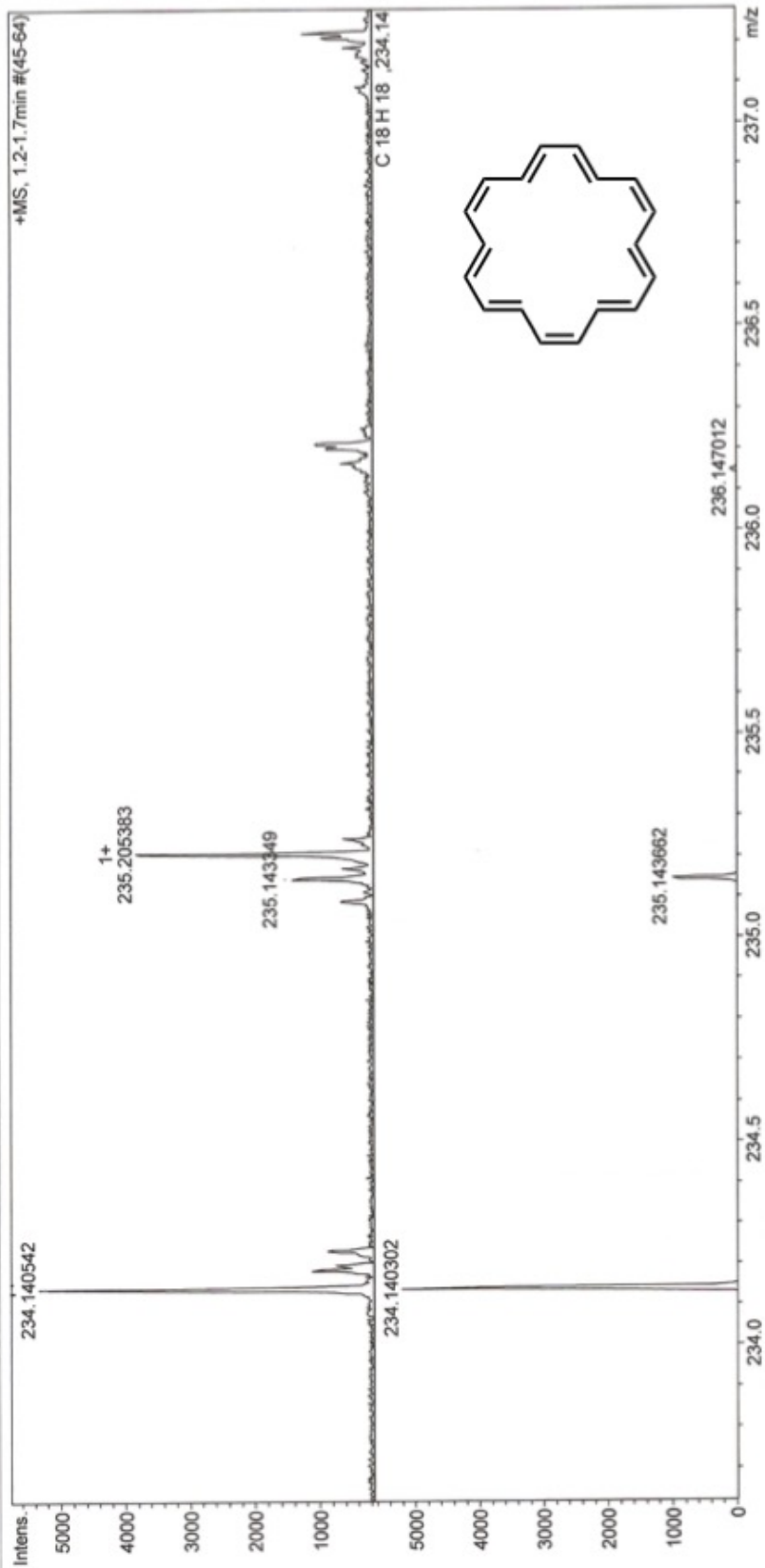


Fig. S24 HRMS of 1 (APPI, toluene).