Electronic Supplementary Information

An elusive thermal [2+2] cycloaddition driven by visible light photocatalysis: Tapping into strain to access C2-symmetric tricyclic rings

Kamaljeet Singh, Winston Trinh, and Jimmie D. Weaver III*

107 Physical Science, Department of Chemistry, Oklahoma State University, Stillwater, OK 74078.

*jimmie.weaver@okstate.edu

Table of contents

1. General Information S2

2. Synthesis of substrates S3

3. Investigation of the reactive intermediate (*trans*-cycloheptene) in the $[_{\pi}2_{s}+_{\pi}2_{a}]$ cycloaddition reaction S21

4. Radical trapping experiment S23

5. $[_{\pi}2_{s}+_{\pi}2_{a}]$ cycloaddition of other substrates S23

6. X-ray crystal structures S24

7. Computational Studies S25

8. References S39

9. ^{1}H, ^{19}F, and ^{13}C NMR data S40

1. General Information

All reagents were obtained from commercial suppliers (Aldrich, VWR, TCI chemicals, Oakwood chemicals, Alfa Aesar) and used without further purification unless otherwise noted. *N, N*-dimethylformamide (DMF) was used from solvent purification system. Reactions were monitored by thin layer chromatography (TLC) which was obtained from sorbent technology (Silica XHL TLC Plates w/UV254, glass backed 250 μm, 20 x 20 cm), and was visualized with ultraviolet light, or potassium permanganate stain. Additionally, reactions were occasionally monitored by ^{1}H, ^{19}F-NMR (400 MHz Bruker Avance III spectrometer).

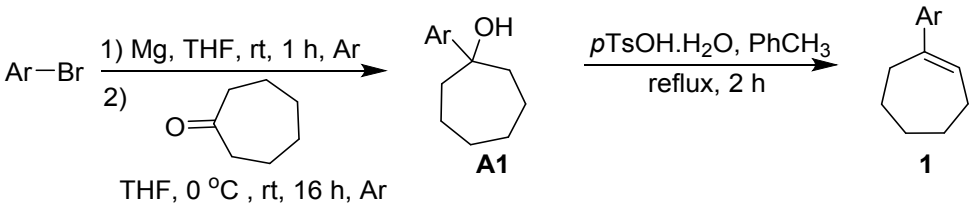
Photocatalytic reactions were set up in a light bath which is described below. Strips of blue LEDs, (18 LEDs/ft) were purchased from Solid Apollo and were wrapped around the outside walls of a glass crystallization dish and secured with masking tape, which was then wrapped with aluminum foil (pictured below). A lid, which rest on the top, was fashioned from cardboard, and holes were made such that reaction tubes were held firmly in the cardboard lid, which was placed on the top of the bath. Water was added to the bath such that the tubes were submerged in the water, which was maintained at 30 ^{o}C with the aid of a sand bath connected to a thermostat.

Flash chromatography was carried out with Acros Organics 60 Å, mesh 50-200 micron silica gel on an automated combiflash R_f version 2.1.19 equipped with UV and ELS detectors. NMR spectra were obtained on 400 MHz Bruker Avance III spectrometer or 400 MHz Unity Inova spectrometer or 600 MHz Unity Inova spectrometer unless otherwise noted. ^{1}H, ^{19}F and ^{13}C NMR chemical shifts are reported in ppm relative to the residual protio solvent peak (^{1}H, ^{13}C). Enantiomeric excess

was determined using Daicel Chiralpak AD-H column on HPLC instrument by Shimadzu, equipped with LC-20AD pump, SIL-20A autosampler and SPD-20AV UV detector. High resolution mass spectra (HRMS) analysis was performed on LTQ-OrbitrapXL by thermo scientific ltd.

2. Synthesis of substrates

2.1 Synthesis of phenylcycloheptenes[1]



General procedure for the synthesis of cycloheptanols **A1**

To an oven dried round bottom flask was added magnesium turnings (2.0 equiv) and dry THF (1.0 M) under Ar. To this mixture was added a pinch of iodine and stirred for 10 minutes. The aryl bromide (1.0 equiv) was added and the reaction mixture was stirred for 1 h. The reaction mixture was then cooled to 0 °C and then cycloheptanone (0.9 equiv) was added. The reaction mixture was then allowed to warm to rt and stirred overnight under Ar. After completion, the reaction mixture was quenched with sat. NH_4Cl and the reaction mixture was extracted with EtOAc. The organic layer was separated, dried over $MgSO_4$ and concentrated to obtain the crude product that was purified by column chromatography, over silica gel using EtOAc/hexanes as eluent, to obtain the desired alcohol **A1**.

General procedure for the synthesis of aryl cycloheptenes **1**[2]

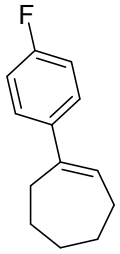
To the alcohol **A1** (1.0 equiv) was added toluene (0.5 M) and *p*-TsOH.H_2O (10 mol%). The reaction mixture was then refluxed until the disappearance of starting alcohol (TLC). The reaction mixture was then cooled to rt, and the reaction mixture was added EtOAc and sat. $NaHCO_3$ and the layers were separated. The organic layer was separated, dried over $MgSO_4$ and concentrated to obtain the desired aryl cycloheptenes **1** which was used further without any purification.

The percentage yield of various aryl cycloheptenes **1** are tabulated below.

S. No.	Ar	% yield (over three steps)
1.	4-F phenyl (**1g**)	81%
2.	3,4,5- trifluoro phenyl (**1h**)	60%
3.	3,5-bis CF_3 phenyl (**1i**)	61%

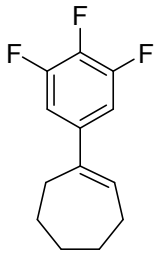
NMR characterization of compounds **1**

1g 1-(4-fluorophenyl)cyclohept-1-ene



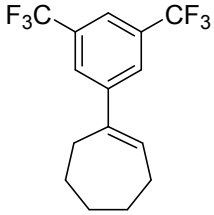
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.13 (m, 2H), 7.09 – 6.88 (m, 2H), 6.06 (t, *J* = 6.8 Hz, 1H), 2.65 – 2.56 (m, 2H), 2.33 – 2.23 (m, 2H), 1.92 – 1.80 (m, 2H), 1.68 – 1.63 (m, 2H), 1.63 – 1.51 (m, 2H).

1h 1-(3,4,5-trifluorophenyl)cyclohept-1-ene



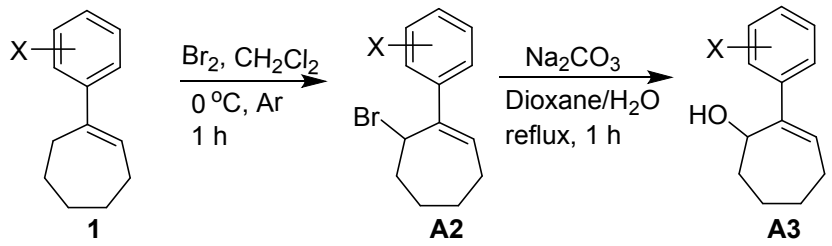
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.98 – 6.79 (m, 2H), 6.07 (t, *J* = 6.1 Hz, 1H), 2.62 – 2.41 (m, 2H), 2.39 – 2.14 (m, 2H), 1.93 – 1.72 (m, 2H), 1.69 – 1.58 (m, 2H), 1.58 – 1.44 (m, 2H).

1i 1-(3,5-bis(trifluoromethyl)phenyl)cyclohept-1-ene



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 – 7.69 (m, 2H), 7.69 (s, 1H), 6.21 (t, *J* = 6.7 Hz, 1H), 2.69 – 2.56 (m, 2H), 2.45 – 2.28 (m, 2H), 1.97 – 1.82 (m, 2H), 1.75 – 1.63 (m, 2H), 1.63 – 1.51 (m, 2H).

2.2 Synthesis of phenyl cycloheptenols **A3**



General procedure for the synthesis of allylic bromo cycloheptenes **A2**[1]

To an oven dried round bottom flask was added **1** (1.0 equiv) and CH_2Cl_2 (0.5 M) and the solution was cooled to 0 °C. A solution of Br_2 (1.0 equiv) in CH_2Cl_2 was added dropwise under Ar and the reaction mixture stirred at 0 °C for 1 hr. The reaction mixture was then allowed to warm to room temperature. After completion, the reaction mixture was washed with 5% $NaHCO_3$ solution. The organic layer was then dried over $MgSO_4$ and concentrated to obtain a light brown oil **A2**, which was used further without purification.

General procedure for the synthesis of phenyl cycloheptenols **A3**[3]

The allylic bromide **A2** (1.0 equiv) was dissolved in dioxane/water (1:1) (0.03 M) and then Na_2CO_3 (2.5 equiv) was added. The resulting mixture was refluxed for 1 h. After completion, the reaction mixture was cooled to rt and the solvent removed under reduced pressure. The residue was diluted with water and extracted with EtOAc (3 times). The combined organic layers were dried over $MgSO_4$ and concentrated to obtain the crude product that was purified by column chromatography, over silica gel using EtOAc/hexanes as eluent, to obtain the desired allylic alcohol **A3**.

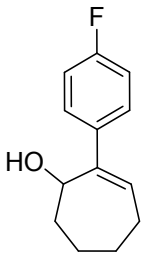
The percentage yield of various substituted phenylcycloheptenols **A3** are tabulated below.

S. No.	X	% yield (over two steps)
1.	F (**1a**)	21%
2.	Cl (**1b**)	51%
3.	H (**1c**)	39%
4.	CF_3 (**1d**)	52%

5.	3,5-bis CF_3(**1e**)	47%

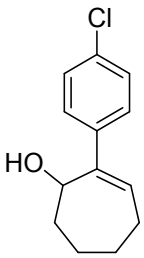
NMR characterization of compounds **A3**

1a 2-(4-fluorophenyl)cyclohept-2-en-1-ol



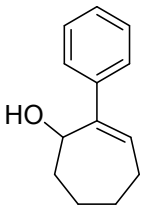
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.27 (m, 2H), 7.02 – 6.91 (m, 2H), 5.97 (d, *J* = 7.0 Hz, 1H), 4.75 (d, *J* = 7.7 Hz, 1H), 2.49 – 2.32 (m, 1H), 2.32 – 2.17 (m, 1H), 2.12 – 1.93 (m, 2H), 1.93 – 1.83 (m, 1H), 1.83 – 1.71 (m, 1H), 1.71 – 1.58 (m, 2H), 1.58 – 1.50 (m, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -112.09 – -119.88 (m). ^{19}F NMR (376 MHz, $CDCl_3$) δ -112.09 – -119.88 (m).

1b 2-(4-chlorophenyl)cyclohept-2-en-1-ol



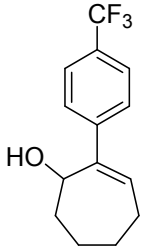
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (appr s, 4H), 6.01 (t, *J* = 7.1 Hz, 1H), 4.75 (d, *J* = 7.6 Hz, 1H), 2.55 – 2.33 (m, 1H), 2.33 – 2.16 (m, 1H), 2.10 – 1.97 (m, 2H), 1.92 – 1.83 (m, 1H), 1.82 – 1.75 (m, 1H), 1.69 – 1.59 (m, 2H), 1.59 – 1.50 (m, 1H).

1c 2-phenylcyclohept-2-en-1-ol



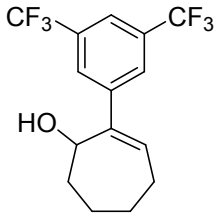
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.21 (m, 3H), 7.20 – 7.07 (m, 2H), 5.94 (t, *J* = 6.6 Hz, 1H), 4.73 (d, *J* = 7.8 Hz, 1H), 2.45 – 2.28 (m, 1H), 2.27 – 2.12 (m, 1H), 2.09 – 1.88 (m, 2H), 1.88 – 1.76 (m, 1H), 1.74 – 1.64 (m, 1H), 1.63 – 1.55 (m, 2H).

1d 2-(4-(trifluoromethyl)phenyl)cyclohept-2-en-1-ol



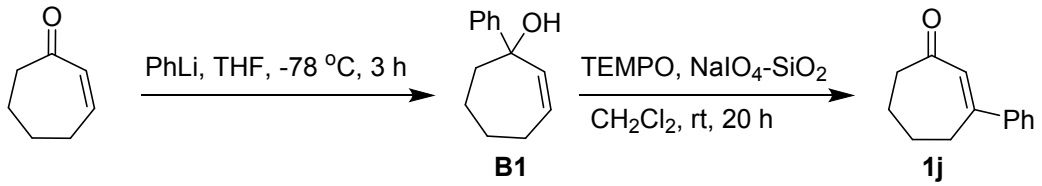
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 8.0 Hz, 2H), 7.45 (d, *J* = 8.0 Hz, 2H), 6.08 (t, *J* = 6.7 Hz, 1H), 4.79 (d, *J* = 7.5 Hz, 1H), 2.50 – 2.35 (m, 1H), 2.33 – 2.19 (m, 1H), 2.09 – 1.99 (m, 2H), 1.93 – 1.83 (m, 2H), 1.79 – 1.69 (m, 2H), 1.65 – 1.59 (m, 1H).

1e 2-(3,5-bis(trifluoromethyl)phenyl)cyclohept-2-en-1-ol



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (s, 2H), 7.73 (s, 1H), 6.14 (t, *J* = 6.6 Hz, 1H), 4.78 (d, *J* = 7.6, 2.1 Hz, 1H), 2.55 – 2.38 (m, 1H), 2.38 – 2.22 (m, 1H), 2.15 – 1.99 (m, 2H), 1.98 – 1.86 (m, 1H), 1.85 – 1.75 (m, 1H), 1.75 – 1.60 (m, 2H).

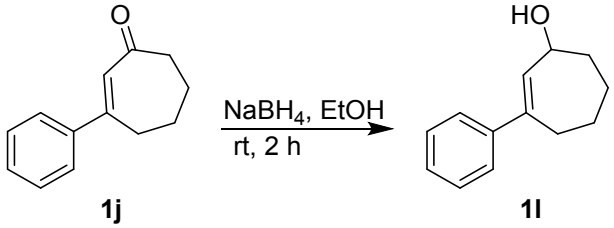
2.3 Synthesis of 3-phenylcyclohept-2-en-1-one (**1j**)[4].



To the solution of cycloheptenone (1.0 g, 9.08 mmol) in THF (0.3 M) was added PhLi (1.8 M in butyl ether, 13.62 mmol) dropwise at -78 °C and the reaction mixture was stirred for 3 h. The reaction mixture was then quenched with sat. NH_4Cl (30 mL) and extracted with EtOAc (30 mL). The organic layer was separated, dried over $MgSO_4$ and concentrated to obtain the crude product that was purified by column chromatography, over silica gel using EtOAc/hexanes = 5/95 as eluent, to obtain **B1** (1.0 g, 60%).

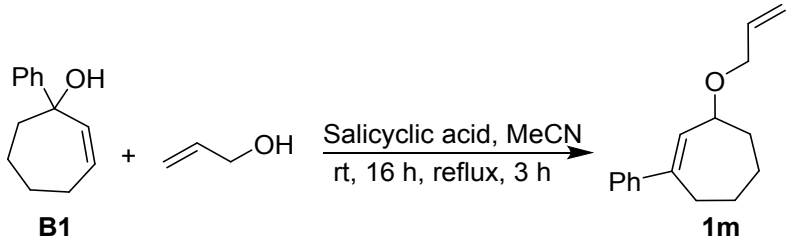
To the solution of **B1** (245.0 mg, 1.30 mmol) in CH_2Cl_2 (0.13 M) was added TEMPO (10 mol%) and $NaIO_4$-SiO_2 (4.0 g, 2.60 mmol) and the reaction mixture was stirred at rt for 20 h. The reaction mixture was filtered and the residue was washed with CH_2Cl_2 (20 mL). The filtrate was concentrated and then purified by column chromatography, over silica gel using EtOAc/hexanes = 4/96 as eluent, to obtain **1j** (100.0 mg, 41%).

2.4 Synthesis of 3-phenylcyclohept-2-en-1-ol (**1l**)



To a flame dried flask was added **1j** (145.0 mg, 0.78 mmol) and EtOH (0.3 M) under Ar. $NaBH_4$ (59.1 mg, 1.56 mmol) was added portionwise and the reaction mixture was stirred at rt for 2 h. After completion, the reaction mixture was quenched with sat. NH_4Cl and the solvent removed under reduced pressure. The residue obtained was diluted with EtOAc (20 mL) and washed with water (20 mL) and brine (20 mL). The organic layer was dried over $MgSO_4$ and concentrated to obtain the **1l** (144.7 mg, 99%). ^{1}H NMR (400 MHz, $CDCl_3$) 7.40 – 7.28 (4 H, m), 7.28 – 7.16 (1 H, m), 6.09 – 5.92 (1 H, m), 4.64 – 4.51 (1 H, m), 2.66 (1 H, dd, *J* 15.2, 7.1), 2.58 – 2.41 (1 H, m), 2.12 – 1.94 (1 H, m), 1.94 – 1.79 (2 H, m), 1.79 – 1.67 (2 H, m), 1.64 – 1.59 (1 H, m), 1.50 – 1.39 (1 H, m).

2.5 Synthesis of 3-(allyloxy)-1-phenylcyclohept-1-ene (**1m**)[5]

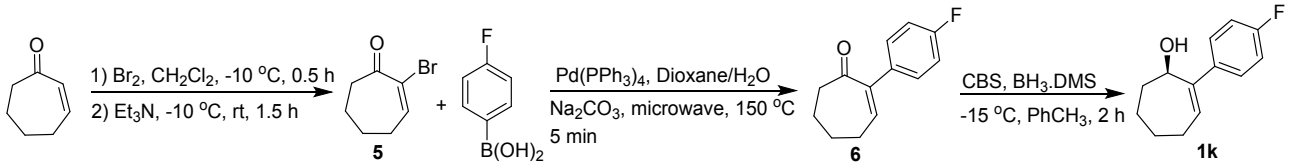


B1 **1m**

To an oven dried flask was added **B1** (188.1 mg, 1.0 mmol) and MeCN (0.2 M). To this solution was added allylic alcohol (1.0 mL, 14.7 mmol) and salicylic acid (10 mol%) and the reaction mixture was stirred at rt for 16 h and then refluxed for 3 h. After completion, the reaction mixture was quenched with sat. $NaHCO_3$ and extracted with EtOAc. The organic layer was separated, dried over $MgSO_4$ and concentrated to obtain the crude product that was purified by column chromatography, over silica gel using EtOAc/hexanes = 5/95 as eluent, to obtain **1m** (120.2 mg, 53%).

Similarly, 3-(cinnamyloxy)-1-phenylcyclohept-1-ene (**1n**) was synthesized in 60% yield using cinnamyl alcohol instead of allyl alcohol. ^{1}H NMR (400 MHz, CD_3CN) δ 7.47 (d, *J* = 8.0 Hz, 2H), 7.44 – 7.37 (m, 3H), 7.37 – 7.33 (m, 3H), 7.27 (dt, *J* = 8.2, 6.3 Hz, 2H), 6.68 (d, *J* = 16.1 Hz, 1H), 6.40 (dd, *J* = 16.0, 5.8 Hz, 1H), 6.09 (d, *J* = 4.0 Hz, 1H), 4.36 – 4.29 (m, 1H), 4.26 (dd, 1H), 4.20 (dd, *J* = 13.1, 5.8 Hz, 1H), 2.67 (dd, *J* = 15.0, 7.1 Hz, 1H), 2.60 – 2.44 (m, 1H), 2.09 – 1.99 (m, 1H), 1.99 – 1.93 (m, 1H), 1.90 – 1.70 (m, 2H), 1.67 – 1.55 (m, 1H), 1.52 – 1.37 (m, 1H).

2.6 Synthesis of (R)-2-(4-fluorophenyl)cyclohept-2-en-1-ol (**1k**)



2.6.1 Synthesis of 2-bromocyclohept-2-en-1-one (**5**)[6]

To an oven dried round bottom flask was added **1** (500.0 mg, 4.54 mmol) and CH_2Cl_2 (0.5 M) and the solution was cooled to -10 °C. A solution of Br_2 (0.26 mL, 4.99 mmol) in CH_2Cl_2 was added dropwise under Ar and the reaction mixture stirred for 30 min at -10 °C. Then Et_3N (0.89 mL, 6.35 mmol) was added and the reaction was allowed to warm to rt and stirred for 1.5 h. The reaction mixture was diluted with 1N HCl (10 ml) and extracted with CH_2Cl_2. The organic layer was separated, dried over $MgSO_4$ and concentrated to obtain the crude product that was purified by column chromatography, over silica gel using EtOAc/hexanes = 2/98 as eluent, to obtain **5** (500.2 mg, 60%).

2.6.2 Synthesis of 2-(4-fluorophenyl)cyclohept-2-en-1-one (**6**)[7]

To an oven dried microwave vial was added **5** (250 mg, 1.33 mmol), (4-fluorophenyl)boronic acid (229.9 mg, 1.60 mmol), tetrakis(triphenylphosphine)palladium(0) (4.0 mol%), Na_2CO_3 (338.4 mg, 3.19 mmol) and dioxane/water (4:1, 0.03 m). The reaction mixture was degassed with Ar for 15 min and the reaction vial was sealed with a cap. The reaction mixture was exposed to microwave irradiations at 150 °C for 5 min. After cooling, the reaction mixture was diluted with EtOAc and water and the layers were separated. The organic layer was dried over $MgSO_4$ and concentrated to obtain the crude product that was purified by column chromatography, over silica gel using EtOAc/hexanes = 5/95 as eluent, to obtain **6** (149.2 mg, 55%).

2.6.3 Synthesis of (R)-2-(4-fluorophenyl)cyclohept-2-en-1-ol (**1k**)[8]

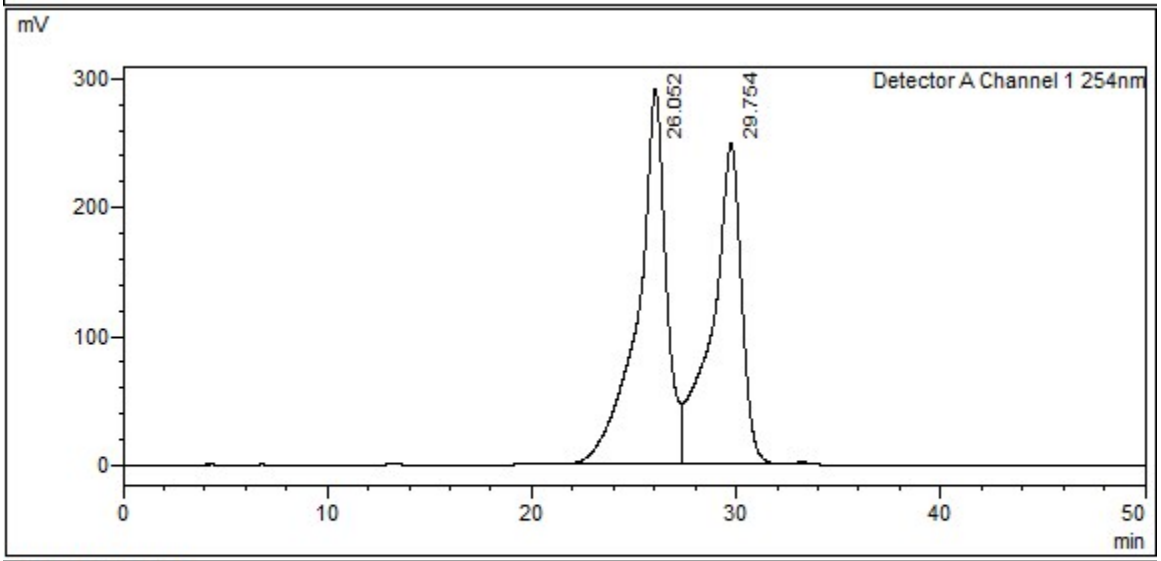
A solution of (S)-(−)-2-Methyl-CBS-oxazaborolidine (CBS) (149.6, 0.55 mmol) and borane dimethylsulfide complex (62.7 µL, 0.66 mmol) in toluene (0.03 M) was cooled to -15 °C. To this mixture was added a solution of **6** (110.2 mg, 0.55 mmol) in toluene (0.02 M) slowly over 15 min. The reaction mixture was stirred at -15 °C for 2 h and then quenched with 1 M HCl. The resulting mixture was extracted with Et_2O (20 mL). The organic layer was washed once with brine and

water, dried over $MgSO_4$, and concentrated to obtain the crude product that was purified by column chromatography, over silica gel using EtOAc/hexanes = 6/94 as eluent, to obtain **1k** (80 mg, 72%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.27 (m, 2H), 7.02 – 6.91 (m, 2H), 5.97 (d, *J* = 7.0 Hz, 1H), 4.75 (d, *J* = 7.7 Hz, 1H), 2.49 – 2.32 (m, 1H), 2.32 – 2.17 (m, 1H), 2.12 – 1.93 (m, 2H), 1.93 – 1.83 (m, 1H), 1.83 – 1.71 (m, 1H), 1.71 – 1.58 (m, 2H), 1.58 – 1.50 (m, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -112.09 – -119.88 (m).

The enantiomeric excess (ee) was determined by HPLC. Chiralpak IC column with 0.5% IPA in hexanes solvent system at a flow rate of 1.0 mL/min at rt was used. The *ee* of **1k** was found to be 96%.

HPLC trace for rac-**1k**

<Chromatogram>

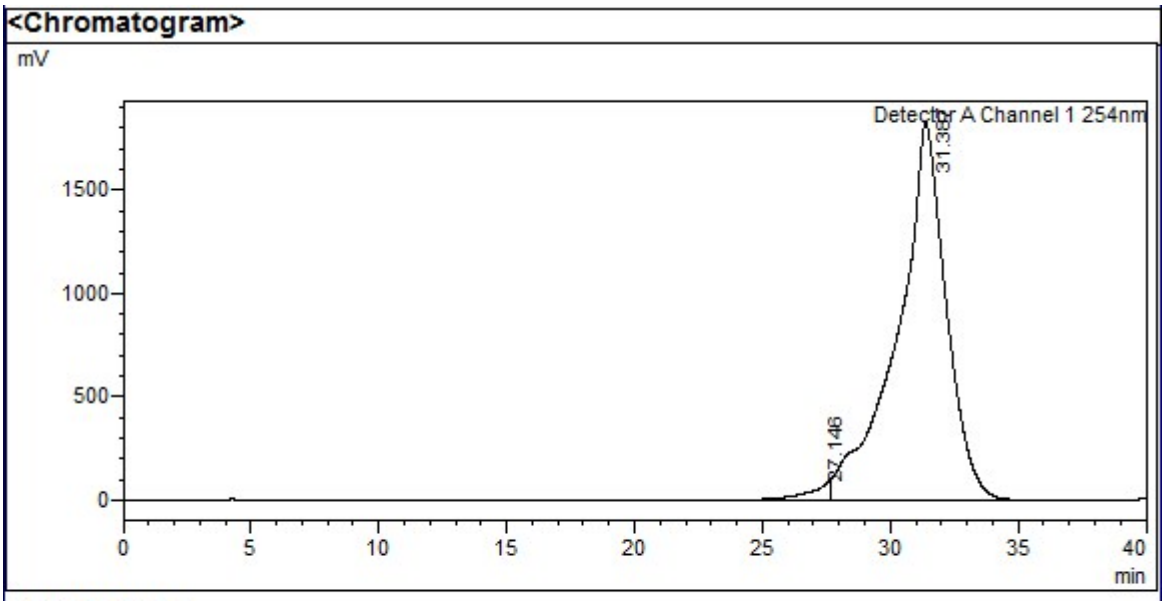


<Peak Table>

Detector A Channel 1 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	26.052	27968030	291287	52.759			
2	29.754	25043265	248963	47.241		V M	
Total		53011295	540250				

HPLC trace for **1k**

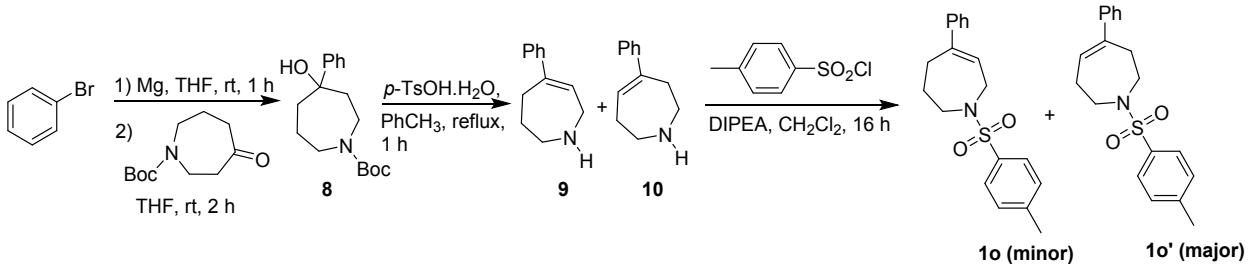


<Peak Table>

Detector A Channel 1 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	27.146	5037944	49160	2.049		M	
2	31.387	240816999	1819593	97.951		M	

2.7 Synthesis of 5-phenyl-1-tosyl-2,3,4,7-tetrahydro-1H-azepine (**1o**)

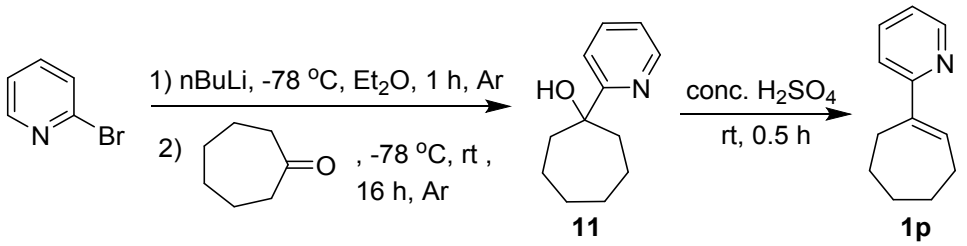


To an oven dried round bottom flask was added magnesium turnings (285.2 mg, 11.73 mmol) and dry THF (0.5 M) under Ar. To this mixture was added a pinch of iodine and stirred for 10 minutes. Then phenyl bromide (920.1 mg, 5.86 mmol) was added and the reaction mixture was stirred for 1 h. The reaction mixture was then cooled to 0 ^{o}C and then a solution of *tert*-butyl 4-oxoazepane-1-carboxylate (1.0 g, 4.69 mmol) in THF (2.3 M) was added dropwise. The reaction mixture was then allowed to warm to rt and stirred overnight under Ar. After completion, the reaction mixture was quenched with sat. NH_4Cl and the reaction mixture was extracted with EtOAc. The organic layer was separated, dried over $MgSO_4$ and concentrated to obtain the crude product (**8**) which was used further without purification.

The alcohol **8** (1.3 g, 4.65 mmol) was dissolved in toluene (0.5 M) and the *p*-TsOH.H_2O (934.2 mg, 4.91 mmol) was added and the reaction mixture was refluxed for 1 h. The reaction mixture was then cooled to rt. To the reaction mixture was added EtOAc and sat. $NaHCO_3$ and the layers were separated, and the organic layer was dried over $MgSO_4$, and concentrated to obtain an inseparable mixture of regioisomeric alkenes (**9** and **10**) in a quantitative yield (rr = 1.5:1).

To the regioisomeric mixture of alkenes (800 mg, 4.62 mmol) was added 4-methylbenzenesulfonyl chloride (1.1 g, 5.55 mmol), DIPEA (1.2 mL, 6.93 mmol) and CH_2Cl_2 (0.3 M). The reaction mixture was stirred at rt for 16 h. After completion, the reaction mixture was washed with water (10 mL) and brine (10 mL) dried over $MgSO_4$, concentrated and then purified by column chromatography, over silica gel using EtOAc/hexanes = 8/92 as eluent, to obtain **1o** (270 mg, 35%) and **1o´** (500 mg, 65%). NMR matched with literature reference.[9]

2.8 Synthesis of 2-(cyclohept-1-en-1-yl)pyridine (**1p**)[10]



To an oven dried round bottom flask was added 2-bromopyridine (865.2 mg, 5.48 mmol) and dry Et_2O (0.2 M) under Ar. The solution was cooled to -78 °C and n-BuLi (1.6 M in hexanes, 6.02 mmol) was added dropwise and the reaction mixture was stirred for 1 h. Cycloheptanone (556.8 mg, 4.94 mmol) was added dropwise and the reaction mixture was allowed to warm to rt and stirred for 16 h. The reaction mixture was then quenched with sat. NH_4Cl (30 mL) and extracted with EtOAc (30 mL). The organic layer was separated, dried over $MgSO_4$ and concentrated to obtain the crude product that was purified by column chromatography, over silica gel using EtOAc/hexanes = 5/95 as eluent, to obtain **11** (530 mg, 56% over two steps).

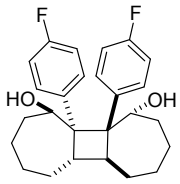
To the compound **11** (525.3 mg, 2.75 mmol) was added conc. H_2SO_4 (5 mL) and the reaction mixture was stirred at rt for 30 min. The reaction mixture was then neutralized with sat. $NaHCO_3$ and extracted with CH_2Cl_2 (2 x 20 ml). The organic layer was separated, dried over $MgSO_4$ and concentrated to obtain **1p** (310 mg, 65%) which was used further without purification.

2.9 General procedure **D** for the visible light mediated [$_{\pi}2_{s}$+ $_{\pi}2_{a}$] cycloaddition of phenyl cycloheptenes

To a 13 x 100 mm culture tube was added phenyl cycloheptene **1** (1.0 equiv), **Cat A** (0.125 mol%), and DMF or MeCN (0.5 M). The reaction mixture was sparged with Ar for 10 min. A septum was placed with a needle passing through it connected to the Ar source on other end. The reaction tube was exposed to blue LEDs at 30 ^{o}C. The progress of reaction was monitored by TLC. After complete disappearance of the starting phenyl cycloheptenes, **1**, the reaction mixture was diluted with EtOAc and washed with water. The organic layer was dried over $MgSO_4$ and concentrated to obtain the crude product that was purified by normal phase chromatography. Normal phase chromatography was performed with Teledyne ISCO automated chromatography system using silica as stationary phase and either EtOAc/hexanes or CH_2Cl_2/hexanes as mobile phase unless otherwise noted.

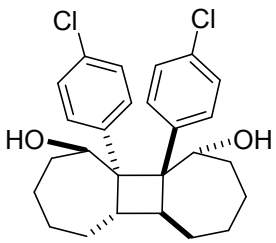
In case, where MeCN was used as solvent, the product crashes out of the solution. After completion of reaction, the white solid was filtered off and then washed with MeCN to remove the Ir catalyst. Drying under vacuum gave the desired product **2** which did not require any further purification.

2a (1R,5aS,5bS,10R,10aS,10bS)-10a,10b-bis(4-fluorophenyl)tetradecahydrocyclobuta-[1,2:3,4]di[7]annulene-1,10-diol



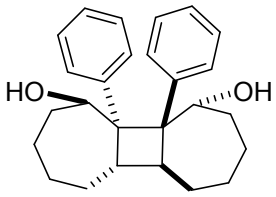
The general procedure **D** was followed using **1a** (100.0 mg, 0.48 mmol), **Cat A** (0.125 mol%) and DMF (1.0 mL) to afford **2a** in 55% yield as a white solid with dr >99:1 (crude dr = 16.2:12.1:4:1). The substrate was purified by column chromatography on silica gel (EtOAc/hexanes = 5:95). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 – 7.70 (m, 1H), 7.54 – 7.35 (m, 1H), 7.22 – 7.00 (m, 2H), 4.13 – 3.99 (m, 1H), 3.60 – 3.37 (m, 1H), 2.18 – 1.93 (m, 2H), 1.91 – 1.71 (m, 1H), 1.68 – 1.56 (m, 1H), 1.48 – 1.37 (m, 2H), 1.36 – 1.20 (m, 1H), 0.26 (t, J = 2.4 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.2 (d, J = 248.2 Hz), 140.4 (d, J = 3.8 Hz), 130.1 (d, J = 7.1 Hz), 128.5 (d, J = 7.2 Hz), 116.6 (d, J = 21.0 Hz), 115.8 (d, J = 20.5 Hz), 74.3, 61.5, 36.5, 34.5, 28.2, 26.9, 20.4. ^{19}F NMR (376 MHz, $CDCl_3$) δ -114.47 – -115.39 (m). HRMS (ESI) (m/z): $[M+Na]^+$ calcd. for $C_{26}H_{30}F_2NaO_2$: 435.2106, observed: 435.2096.

2b (1R,5aS,5bS,10R,10aS,10bS)-10a,10b-bis(4-chlorophenyl)tetradecahydrocyclobuta-[1,2:3,4]di[7]annulene-1,10-diol

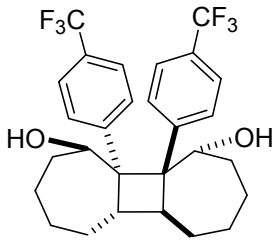


The general procedure **D** was followed using **1b** (100.0 mg, 0.45 mmol), **Cat A** (0.125 mol%) and DMF (0.90 mL) to afford **2b** in 74% yield as a white solid with dr >99:1 (crude dr = 7.8:3.8:1). The substrate was purified by column chromatography on silica gel (EtOAc/hexanes = 5:95). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 – 7.66 (m, 1H), 7.50 – 7.31 (m, 3H), 4.06 (s, 1H), 3.60 – 3.29 (m, 1H), 2.08 – 1.93 (m, 2H), 1.91 – 1.73 (m, 1H), 1.67 – 1.51 (m, 1H), 1.51 – 1.36 (m, 2H), 1.36 – 1.28 (m, 1H), 0.26 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.3, 132.6, 130.1, 129.6, 129.1, 128.3, 74.0, 62.0, 36.4, 34.6, 28.1, 26.8, 20.3. HRMS (ESI) (m/z): $[M+Na]^+$ calcd. for $C_{26}H_{30}Cl_2NaO_2$: 467.1515, observed: 467.1513.

2c (1R,5aS,5bS,10R,10aS,10bS)-10a,10b-diphenyltetradecahydrocyclobuta[1,2:3,4]di-[7]annulene-1,10-diol



The general procedure **D** was followed using **1c** (100.0 mg, 0.53 mmol), **Cat A** (0.125 mol%) and DMF (1.1 mL) to afford **2c** in 68% yield as a white solid with dr >99:1 (crude dr = 8.8:2.1:1). The substrate was purified by column chromatography on silica gel (EtOAc/hexanes = 5:95). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, J = 7.9 Hz, 1H), 7.58 – 7.37 (m, 3H), 7.37 – 7.27 (m, 1H), 4.13 (appr s, 1H), 3.73 – 3.40 (m, 1H), 2.20 – 1.92 (m, 2H), 1.92 – 1.73 (m, 1H), 1.73 – 1.46 (m, 3H), 1.43 – 1.34 (m, 1H), 1.34 – 1.28 (m, 1H), 0.28 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.9, 129.5, 129.0, 128.6, 127.1, 126.6, 74.4, 62.2, 36.4, 34.5, 28.3, 26.9, 20.5. HRMS (ESI) (m/z): $[M+Na]^+$ calcd. for $C_{26}H_{32}NaO_2$: 399.2295, observed: 399.2279.

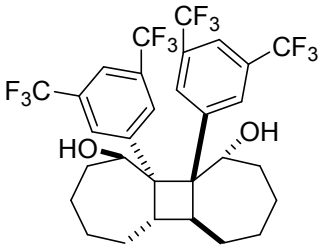


2d (1R,5aS,5bS,10R,10aS,10bS)-10a,10b-bis(4-(trifluoromethyl)phenyl)tetradecahydro-cyclobuta[1,2:3,4]di[7]annulene-1,10-diol

The general procedure **D** was followed using **1d** (150.0 mg, 0.59 mmol), **Cat A** (0.125 mol%) and DMF (1.2 mL) to afford **2d** in 57% yield as a white solid with dr >99:1 (crude dr = 1.6:1). The substrate was purified by column chromatography on silica gel (EtOAc/hexanes = 5:95). ^{1}H NMR

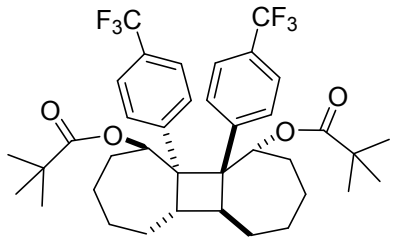
(400 MHz, $CDCl_3$) δ 7.99 (d, J = 8.0 Hz, 1H), 7.70 (t, J = 8.6 Hz, 2H), 7.59 (d, J = 8.1 Hz, 1H), 4.12 (appr s, 1H), 3.61 – 3.44 (m, 1H), 2.22 – 1.96 (m, 2H), 1.93 – 1.75 (m, 1H), 1.67 – 1.47 (m, 2H), 1.47 – 1.36 (m, 2H), 1.36 – 1.28 (m, 1H), 0.95 – 0.75 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.3, 129.2, 128.9 (q, J = 33.0 Hz), 127.2, 126.1 (q, J = 3.7 Hz), 125.9 (q, J = 3.7 Hz), 124.0 (q, J = 272.1 Hz), 73.9, 62.9, 36.6, 34.8, 28.2, 26.8, 20.3. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.57 (s, 3F). HRMS (ESI) (m/z): $[M+Na]^+$ calcd. for $C_{28}H_{30}F_6NaO_2$: 535.2042, observed: 535.2053.

2e (1R,5aS,5bS,10R,10aS,10bS)-10a,10b-bis(3,5-bis(trifluoromethyl)phenyl)tetradeca-hydrocyclobuta[1,2:3,4]di[7]annulene-1,10-diol



The general procedure **D** was followed using **1e** (100.0 mg, 0.31 mmol), **Cat A** (0.125 mol%) and DMF (0.6 mL) to afford **2e** in 69% yield as a white solid with dr >99:1 (crude dr = 5:3.3:1.2:1). The substrate was purified by column chromatography on silica gel (EtOAc/hexanes = 2:98). ^1H NMR (400 MHz, $CDCl_3$) δ 8.25 (s, 1H), 7.77 (s, 1H), 7.75 (s, 1H), 4.06 (s, 1H), 3.63 – 3.39 (m, 1H), 2.15 – 1.97 (m, 2H), 1.94 – 1.78 (m, 1H), 1.64 – 1.46 (m, 2H), 1.44 – 1.31 (m, 2H), 1.01 – 0.86 (m, 1H), 0.06 (appr. s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.8, 131.8 (q, J = 33.1 Hz), 131.3 (q, J = 33.0 Hz), 129.4, 126.4, 123.2 (q, J = 272.7 Hz), 123.3 (q, J = 272.7 Hz), 120.2 – 119.7 (m) 72.8, 61.9, 36.4, 35.7, 28.0, 26.6, 20.1. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.72 (s, 3F), -62.87 (s, 3F).

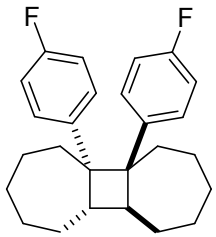
2f (1R,5aS,5bS,10R,10aS,10bS)-10a,10b-bis(4-(trifluoromethyl)phenyl)tetradecahydro-cyclobuta[1,2:3,4]di[7]annulene-1,10-diyl bis(2,2-dimethylpropanoate)



The general procedure **D** was followed using **1f** (60.0 mg, 0.18 mmol), **Cat A** (0.125 mol%) and DMF (0.4 mL) to afford **2f** in 84% yield as a white solid with dr = 7.1:1:1 (crude dr = 7.1:1:1). The substrate was purified by column chromatography on silica gel (EtOAc/hexanes = 2:98). ^1H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, J = 8.3 Hz, 1H), 7.62 – 7.56 (m, 3H), 5.38 – 5.22 (m, 1H), 3.55 – 3.32 (m, 1H), 2.24 – 2.08 (m, 2H), 1.95 – 1.73 (m, 1H), 1.67 – 1.47 (m, 2H), 1.34 – 1.23 (m, 2H), 0.85 (s, 9H), 0.67 – 0.55 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.0, 148.0, 129.1, 128.7, 128.1 (q, J = 33.0 Hz), 125.9 (q, J = 3.7 Hz), 125.1 (q, J = 3.8 Hz), 124.3 (q, J = 272.7 Hz), 76.3, 60.6, 40.0, 39.2, 32.0, 28.3, 27.1,

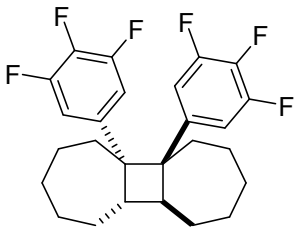
26.4, 21.2. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.16 (s, 3F). HRMS (ESI) (m/z): $[M+Na]^+$ calcd. for $C_{38}H_{46}F_6NaO_4$: 703.3193, observed: 703.3187.

2g (5aR,5bR,10aS,10bS)-5a,5b-bis(4-fluorophenyl)tetradecahydrocyclobuta[1,2:3,4]-di[7]annulene



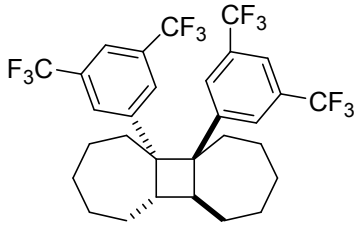
The general procedure **D** was followed using **1g** (114.2 mg, 0.60 mmol), **Cat A** (0.125 mol%) and MeCN (1.2 mL) to afford **2g** in 85% yield as a white solid with dr >99:1 (crude dr >11.5:1). The substrate was purified by column chromatography on silica gel (hexanes). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 – 7.58 (m, 1H), 7.22 – 7.10 (m, 1H), 7.09 – 6.92 (m, 2H), 2.98 – 2.69 (m, 1H), 2.05 – 1.93 (m, 1H), 1.93 – 1.80 (m, 1H), 1.79 – 1.63 (m, 2H), 1.62 – 1.49 (m, 1H), 1.49 – 1.37 (m, 1H), 1.33 – 1.09 (m, 2H), 0.95 – 0.71 (m, 1H), 0.41 (dt, J = 13.4, 3.7 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.8 (d, J = 244.2 Hz), 140.4 (d, J = 3.4 Hz), 129.9 (d, J = 7.4 Hz), 129.3 (d, J = 7.2 Hz), 115.2 (d, J = 20.7 Hz), 114.3 (d, J = 20.3 Hz), 55.8, 47.6, 42.0, 28.1, 27.9, 27.0, 26.7. ^{19}F NMR (376 MHz, $CDCl_3$) δ -115.34 – -121.61 (m, 1F).

2h (5aR,5bR,10aS,10bS)-5a,5b-bis(3,4,5-trifluorophenyl)tetradecahydrocyclobuta-[1,2:3,4]di[7]annulene



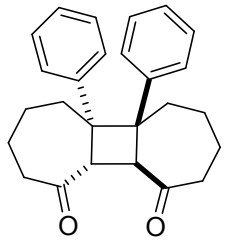
The general procedure **D** was followed using **1h** (150.0 mg, 0.66 mmol), **Cat A** (0.125 mol%) and MeCN (3.3 mL) to afford **2h** in 80% yield as a white solid with dr >99:1 (crude dr = 9:1). The substrate was purified by filtering the solid and then washing the solid with MeCN (1 mL). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 – 7.31 (m, 1H), 6.98 – 6.53 (m, 1H), 2.98 – 2.66 (m, 1H), 1.98 – 1.84 (m, 2H), 1.84 – 1.68 (m, 1H), 1.68 – 1.58 (m, 2H), 1.54 – 1.45 (m, 1H), 1.29 – 1.08 (m, 2H), 0.95 – 0.67 (m, 1H), 0.47 (td, J = 13.4, 3.4 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.4 (ddd, J = 65.6, 9.5, 4.5 Hz), 149.9 (ddd, J = 64.8, 9.6, 4.4 Hz), 140.7 (td, J = 6.5, 4.8 Hz), 137.7 (dt, J = 250.7, 15.5 Hz), 112.4 (dd, J = 17.3, 4.3 Hz), 112.2 – 111.8 (m), 56.3, 47.5, 41.4, 28.0, 27.4, 26.8, 26.4. ^{19}F NMR (376 MHz, $CDCl_3$) δ -131.93 – -137.50 (m), -163.74 (tt, J = 21.0, 6.6 Hz).

2i (5aR,5bR,10aS,10bS)-5a,5b-bis(3,5-bis(trifluoromethyl)phenyl)tetradecahydrocyclobuta[1,2:3,4]di[7]annulene



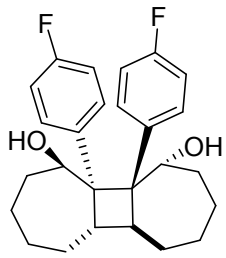
The general procedure **D** was followed using **1i** (200.0 mg, 0.65 mmol), **Cat A** (0.125 mol%) and MeCN (1.3 mL) to afford **2i** in 85% yield as a white solid with dr >99:1 (crude dr = 22.5:1.5:1). The substrate was purified by filtering the solid and then washing the solid with MeCN (1 mL). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (s, 1H), 7.80 (s, 1H), 7.60 (s, 1H), 3.08 – 2.74 (m, 1H), 2.11 – 1.95 (m, 2H), 1.92 – 1.77 (m, 1H), 1.79 – 1.70 (m, 1H), 1.69 – 1.44 (m, 2H), 1.34 – 1.03 (m, 2H), 0.79 – 0.63 (m, 1H), 0.39 (td, J = 13.4, 3.4 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.9, 131.9 (q, J= 33.0 Hz), 131.5 (q, J= 32.8 Hz), 128.3, 128.1, 123.6 (q, J= 272.8 Hz), 123.5 (q, J= 272.6 Hz), 120.3 – 119.7 (m), 56.8, 48.1, 42.1, 27.9, 27.6, 26.7, 26.4. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.81 (s, 3F), -62.86 (s, 3F).

2j (5aR,5bR,10aS,10bS)-5a,5b-diphenyldodecahydrocyclobuta[1,2:3,4]di[7]annulene-1,10-dione



The general procedure **D** was followed using **1j** (95.2 mg, 0.50 mmol), **Cat A** (0.125 mol%) and MeCN (1.0 mL) to afford **2j** in 70% yield as a white solid with dr >99:1 (crude dr = 9:1). The substrate was purified by filtering the solid and then washing the solid with MeCN (1 mL). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.39 (m, 1H), 7.39 – 7.27 (m, 4H), 3.86 (s, 3H), 2.57 (dd, J = 19.2, 4.5 Hz, 1H), 2.20 – 1.90 (m, 3H), 1.78 – 1.48 (m, 14H), 1.09 (t, J = 12.6 Hz, 1H), 0.72 (td, J = 13.4, 2.5 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 214.3, 141.1, 129.1, 128.8, 127.8, 126.8, 126.3, 57.1, 54.1, 43.8, 40.6, 26.7, 24.1. HRMS (ESI) (m/z): $[M+Na]^+$ calcd. for $C_{26}H_{28}NaO_2$: 395.1982, observed: 395.1991.

2k (1R,5aS,5bS,10R,10aS,10bS)-10a,10b-bis(4-fluorophenyl)tetradecahydrocyclobuta-[1,2:3,4]di[7]annulene-1,10-diol

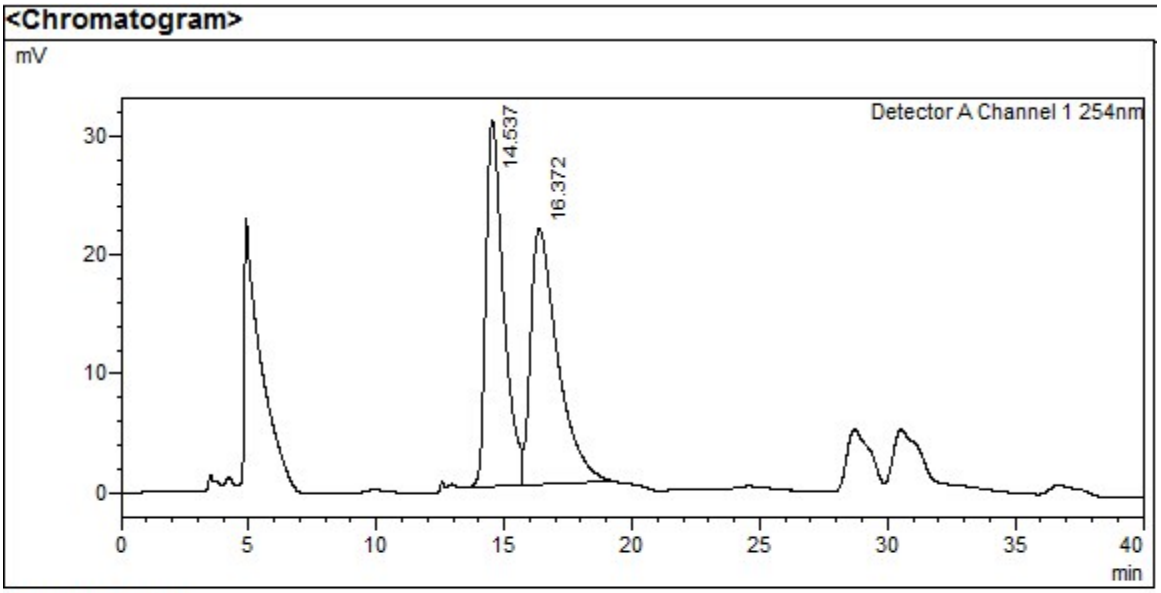


The general procedure **D** was followed using **1k** (38.1 mg, 0.18 mmol, 96% *ee*), **Cat A** (0.125 mol%) and DMF (0.36 mL) to afford **2k** in 58% yield (97% *ee*) as a white solid with dr = 11.5:1 (crude dr = 9.4:1:0.7). The substrate was purified by column chromatography on silica gel (EtOAc/hexanes = 5:95). ^{1}H

NMR (400 MHz, $CDCl_3$) δ 7.86 – 7.76 (m, 1H), 7.47 – 7.34 (m, 1H), 7.20 – 7.01 (m, 2H), 4.07 (s, 1H), 3.66 – 3.37 (m, 1H), 2.17 – 1.95 (m, 2H), 1.90 – 1.71 (m, 1H), 1.67 – 1.52 (m, 2H), 1.42 (dd, J = 22.0, 10.9 Hz, 1H), 1.30 (dt, J = 14.9, 7.2 Hz, 1H), 0.87 (t, J = 13.1 Hz, 1H), 0.27 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.2 (d, J = 248.3 Hz), 140.5 (d, J = 3.7 Hz), 130.1 (d, J = 7.2 Hz), 128.5 (d, J = 7.3 Hz), 116.6 (d, J = 21.0 Hz), 115.8 (d, J = 20.4 Hz), 74.3, 61.5, 36.5, 34.5, 28.2, 26.9, 20.4. ^{19}F NMR (376 MHz, $CDCl_3$) δ -113.79 – -115.53 (m, 1F).

The *ee* of the product was determined by HPLC using Chiralpak IC column and 0.5% IPA in hexanes as the mobile phase at a flow rate of 1.0 mL/min at rt. The *ee* of **2k** was found to be 97%.

HPLC trace of crude *rac*-**2a**

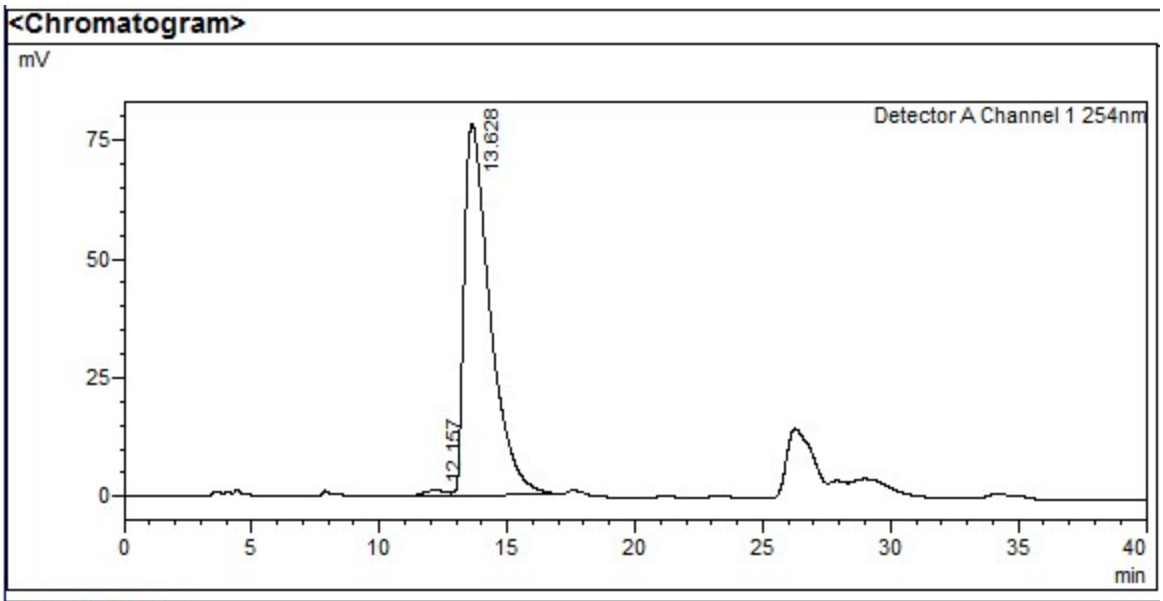


<Peak Table>

Detector A Channel 1 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	14.537	1480780	30750	48.551			
2	16.372	1569138	21447	51.449		V M	

HPLC trace of **2k**

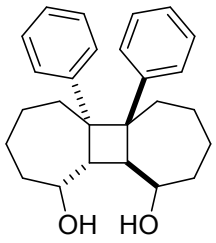


<Peak Table>

Detector A Channel 1 254nm

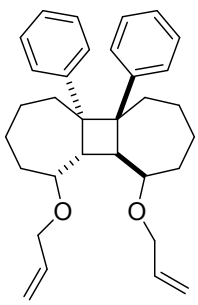
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	12.157	75563	1235	1.354		M	
2	13.628	5506896	78303	98.646		V	

2l (1R,5aR,5bR,10R,10aS,10bS)-5a,5b-diphenyltetradecahydrocyclobuta[1,2:3,4]di[7]-annulene-1,10-diol



The general procedure **D** was followed using **1l** (100.0 mg, 0.53 mmol), **Cat A** (0.125 mol%) and MeCN (1.1 mL) to afford **2l** in 60% yield as a white solid with dr >99:1 (crude dr = 8.3:1.5:1). The substrate was purified by column chromatography on silica gel (EtOAc/hexanes = 10:90). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, J = 7.8 Hz, 1H), 7.34 – 7.22 (m, 2H), 7.21 – 7.05 (m, 2H), 4.68 (d, J = 7.4 Hz, 1H), 2.94 (s, 1H), 2.84 – 2.60 (m, 1H), 1.83 – 1.65 (m, 2H), 1.65 – 1.53 (m, 1H), 1.51 – 1.26 (m, 3H), 0.77 (q, J = 11.8, 11.4 Hz, 1H), 0.64 – 0.41 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.0, 128.6, 128.2, 128.2, 128.0, 125.9, 71.7, 57.0, 53.9, 41.5, 36.6, 27.5, 22.4. HRMS (ESI) (m/z): $[M+Na]^+$ calcd. for $C_{26}H_{32}NaO_2$: 399.2295, observed: 399.2287.

2m (1R,5aR,5bR,10R,10aS,10bS)-1,10-bis(allyloxy)-5a,5b-diphenyltetradecahydrocyclo-buta [1,2:3,4]di[7]annulene

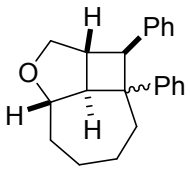


The general procedure **D** was followed using **1m** (110.0 mg, 0.48 mmol), **Cat A** (0.125 mol%) and MeCN (0.24 mL) to afford **2m** in 73% yield as a white solid with dr = 2.6:1 (crude dr = 2.6:1). The substrate was purified by column

chromatography on silica gel (EtOAc/hexanes = 5:95). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.89 (d, *J* = 7.8 Hz, 1H), 7.48 (d, *J* = 8.1 Hz, 1H), 7.39 – 7.27 (m, 6H), 7.25 – 7.14 (m, 6H), 6.16 – 5.88 (m, 2H), 5.45 – 5.24 (m, 2H), 5.24 – 5.10 (m, 2H), 4.33 – 3.95 (m, 6H), 3.93 – 3.72 (m, 1H), 3.22 – 3.06 (m, 2H), 2.10 (m, 1H), 1.95 – 1.68 (m, 4H), 1.52 (m, 3H), 1.46 – 1.22 (m, 7H), 1.13 – 0.75 (m, 5H), 0.54 (td, *J* = 13.6, 13.6, 3.7 Hz, 1H), 0.40 (td, *J* = 14.5, 14.0, 3.3 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.0, 142.9, 136.7, 136.3, 131.4, 128.6, 128.4, 128.3, 127.8, 127.7, 127.6, 127.5, 125.5, 125.3, 116.5, 115.4, 79.4, 78.2, 71.0, 69.8, 58.1, 57.1, 52.1, 49.4, 42.0, 41.3, 33.4, 31.2, 27.9, 27.3, 24.0, 22.3. HRMS (ESI) (m/z): $[M+Na]^+$ calcd. for $C_{32}H_{40}NaO_2$: 479.2921, observed: 479.2908.

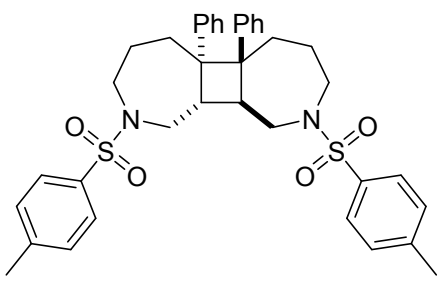
Given the low dr, it was relatively difficult to identify the distinguish product signals from the diastereomers, so all peaks were picked.

2n (1S,1aR,1a1S,3aS)-1,7a-diphenyldecahydro-3-oxacyclobuta[cd]azulene



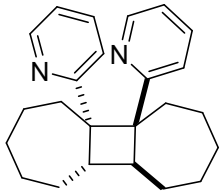
The general procedure **D** was followed using **1n** (120.0 mg, 0.40 mmol), **Cat A** (0.125 mol%) and MeCN (0.20 mL) to afford **2n** in 58% yield as a white solid with dr >99:1 (crude dr = 11.5:4.2:1). The substrate was purified by column chromatography on silica gel (CH_2Cl_2/hexanes = 50:50). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 – 7.03 (m, 6H), 6.98 (d, J = 6.9 Hz, 2H), 6.79 – 6.61 (m, 2H), 4.41 – 4.11 (m, 2H), 3.96 – 3.66 (m, 2H), 3.21 – 3.04 (m, 1H), 2.99 (t, J = 8.7 Hz, 1H), 2.55 – 2.30 (m, 2H), 2.09 (dd, J = 13.9, 10.7 Hz, 1H), 2.01 – 1.86 (m, 1H), 1.86 – 1.66 (m, 1H), 1.66 – 1.46 (m, 2H), 1.05 (q, J = 12.6, 11.6 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.1, 140.1, 128.4, 128.2, 127.7, 127.5, 126.3, 125.7, 83.3, 74.6, 61.4, 50.5, 48.3, 43.2, 40.3, 33.4, 27.6, 23.7. HRMS (ESI) (m/z): $[M+Na]^+$ calcd. for $C_{22}H_{24}NaO$: 327.1719, observed: 327.1708. The tentative diastereomeric relationship shown is based on magnitude of the coupling constants and NOE experiments. However, the entire structure has not been unambiguously assigned.

2o (5aR,5bR,10aS,10bS)-5a,5b-diphenyl-2,9-ditosyltetradecahydrocyclobuta[1,2-c:4,3-c']bis(azepine)



The general procedure **D** was followed using **1o** (60.0 mg, 0.18 mmol), **Cat A** (0.125 mol%) and DMF (0.90 mL) to

afford **2o** in 71% yield as a white solid with dr >99:1 (crude dr >99:1). The substrate was purified by column chromatography on silica gel (EtOAc/hexanes = 20:80). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, J = 7.6 Hz, 1H), 7.54 (d, J = 8.0 Hz, 2H), 7.42 – 7.30 (m, 2H), 7.27 – 7.15 (m, 4H), 4.29 – 3.99 (m, 1H), 3.67 – 3.40 (m, 1H), 3.08 – 2.87 (m, 2H), 2.54 – 2.44 (m, 1H), 2.42 (s, 3H), 1.99 – 1.76 (m, 1H), 1.46 – 1.34 (m, 1H), 1.34 – 1.15 (m, 1H), 0.50 (dt, J = 13.4, 3.5 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.3, 141.5, 135.2, 129.7, 128.4 (s, 2C), 128.3, 128.2, 127.4, 126.1, 57.0, 47.5, 47.2, 45.3, 41.5, 28.1, 21.6. HRMS (ESI) (m/z): $[M+H]^+$ calcd. for $C_{38}H_{42}N_2O_4S_2$: 655.2659, observed: 655.2651.



2p (5aS,5bS,10aS,10bS)-5a,5b-di(pyridin-2-yl)tetradecahydrocyclobuta[1,2:3,4]di[7]an-nulene

The general procedure **D** was followed using **1p** (100.0 mg, 0.58 mmol), **Cat A** (0.125 mol%) and DMF (1.2 mL) to afford **2p** in 65% yield as a white solid with dr >99:1. The substrate was purified by column chromatography on silica gel (EtOAc/hexanes = 4:96). ^{1}H NMR (400 MHz, C_6d_6) δ 8.59 (s, 1H), 7.32 – 7.06 (m, 2H), 6.80 – 6.49 (m, 1H), 3.66 (s, 1H), 3.04 (s, 1H), 2.15 – 1.64 (m, 2H), 1.60 – 1.42 (m, 2H), 1.41 – 1.06 (m, 3H), 1.06 – 0.82 (m, 1H), 0.63 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.7, 148.0, 135.2, 123.0, 120.3, 56.9, 47.8, 39.2, 28.5, 27.3, 26.6, 26.3. HRMS (ESI) (m/z): $[M+H]^+$ calcd. for $C_{24}H_{30}N_2$: 347.2482, observed: 347.2472.

3.0 Investigation of the reactive intermediate (*trans*-cycloheptene) in the $[_\pi2_s+_\pi2_a]$ cycloaddition reaction

The x-ray analysis of the major diastereomer **2a** revealed the formation of all *trans* substituted cyclobutane ring. We believe this stereochemical outcome results from the thermal reaction of highly strained ground state *trans*-cycloheptene with the *cis*-cycloheptene. However, we recognize that the same stereochemical outcome is also possible if the reaction were to take place between the triplet biradical and the singlet ground state *cis*-cycloheptene. Based on the below arguments, we believe that the cyclobutane formation is the result of $[_\pi2_s+_\pi2_a]$ of *trans*-cycloheptene with the *cis*-cycloheptene and not the photochemical $[_\pi2_s+_\pi2_s]$.

1) We have attempted the dimerization of phenyl cyclohexene under similar conditions, but it failed to produce any cyclobutane product. Furthermore, the triplet state energy of phenyl cyclohexene is expected to be similar to phenyl cycloheptene, suggesting that excitation likely occurs to both phenyl cyclohexene and cycloheptene. In contrast, the ground sate *trans*-cyclohexene, is expected to have a much shorter lifetime compared to the *trans*-cycloheptene analog. We believe if C–C bond formation were occurring through the triplet biradical, we should see similar results for these two substrates. Stated differently, the difference in their reactivity, is likely a result of the difference in populations of the *trans*-cycloalkenes.

2) Reactions that involve a triplet biradical which has been photosensitized, (such as Yoon's, Reiser's, and Lu's work) are generally not very fast. This is likely because the triplet biradical is a reactive intermediate that can relax back to the ground state by rotating and giving off energy. The consequence, is that the reactive intermediate has a shorter lifetime. While it is difficult to compare different reaction quantitatively, qualitatively it is evident from the relative rates of reaction. In our case, the reaction went to completion within 6 hours of irradiation using just 0.125 mol% of the Ir catalyst. In comparison, the photodimerization of the cinnamtes completed in 72 hours using 1 mol% of Ir catalyst (*Ref. 35* in manuscript). Reiser suggested that the reaction takes place from the triplet biradical intermediate. Due to short lifetime of this intermediate, the efficiency of these reactions are significantly lower.

3) We performed radical trapping experiment using TEMPO as the radical scavenger, which showed that the reaction was unaffected by the presence of TEMPO. This also supports the idea that the triplet biradical is not the key C–C bond forming intermediate, but rather gives rise to a longer lived *trans*-cycloheptene. If the reaction is taking place from the triplet biradical intermediate, then we should see some TEMPO adduct as byproduct and the decreased yields of the desired cyclobutane product. In fact, Lu (*Ref. 36* in manuscript) has shown that the [2+2] cycloaddition of styrenes and 1,4-dihydropyridines is affected in the presence of radical scavengers. They have observed decreased yields in the formation of desired cyclobutane products in presence of TEMPO (43%) as compared to in its absence (77%). Since the reaction is occurring from a triplet biradical, the radical scavenger can intercept the triplet biradical resulting in undesired byproducts.

4.0 Radical trapping experiment

In order to rule out the possibility of the triplet biradical being C–C bond forming intermediate, a reaction was set up using **1g** (23.8 mg, 0.13 mmol), **Cat A** (0.125 mol%) in MeCN (0.26 mL) containing 10 mol% TEMPO as the radical scavenger. The reaction mixture was exposed to reaction conditions. As expected, no other product was observed and **2g** was obtained as the major product (92% NMR yield). As no other radical scavenger adducts were observed, so the possibility that the reaction occurs from the triplet biradical can be ruled out. This outcome supports the argument that the reaction is most probably taking place between the *trans*-cycloheptene and its *cis*-isomer.

5.0 [$_{\pi}2_{s}+_{\pi}2_{a}$] cycloaddition of other substrates.

Apart from allylic alcohols, various other functional groups, such as, azide, nitro, sulfone, aniline, thioether, at the allylic position were also tested under the optimized reaction conditions (**3a-3g**, Table 3). Although desired product was formed in all of these cases, other undesired products were also observed, which made the isolation of the desired dimer product difficult. Also other substrates, containing a furan and benzothiazole ring in place of phenyl ring, were tested under the reaction conditions. In these cases messy reactions were observed.

Some other substrates that did not show any reactivity are outlined in **Table S1**. Compounds **4a**, **4b**, and **4c** did not undergo any reaction and were recovered unchanged after 18 h of irradiation.

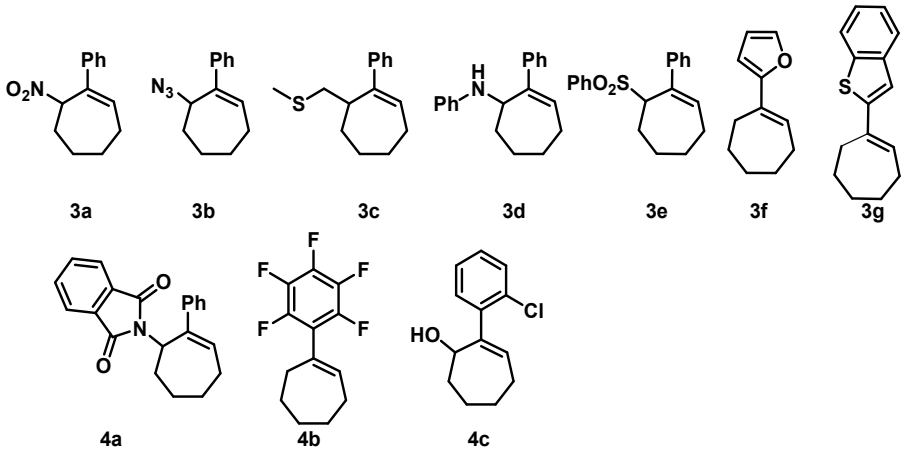
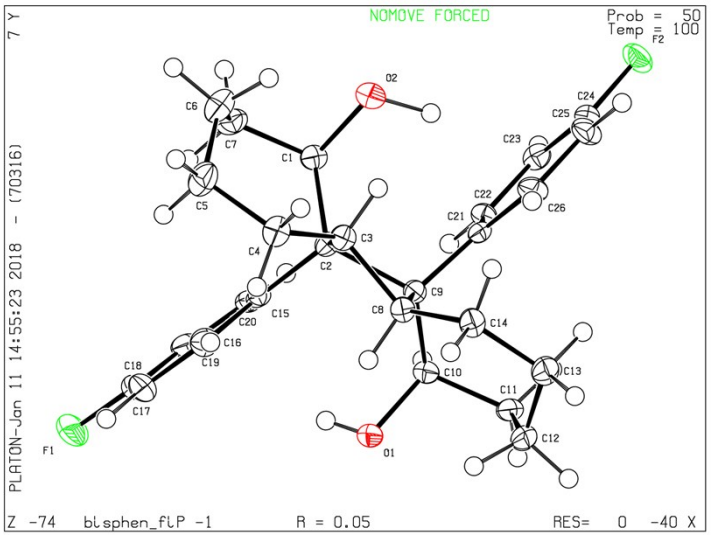
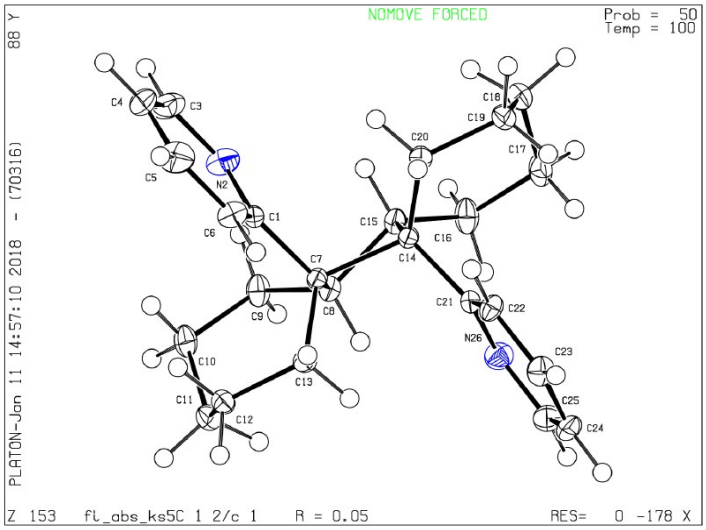


Table S1. Substrates producing undesired products/ no product

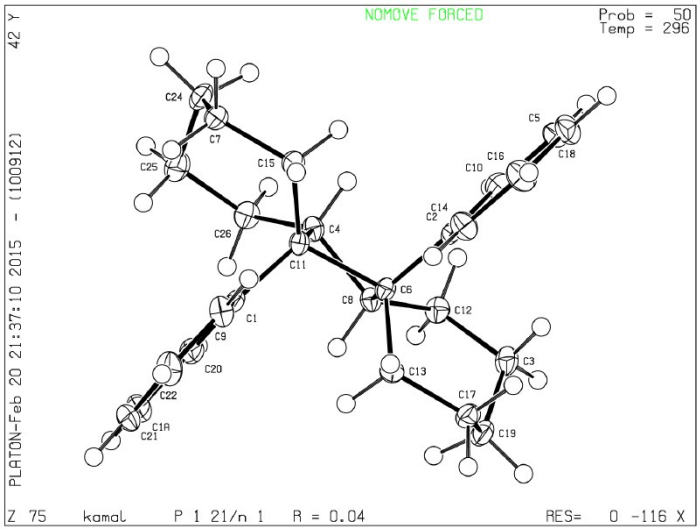


X-ray crystal structure of **2a**



X-ray crystal structure of **2p**

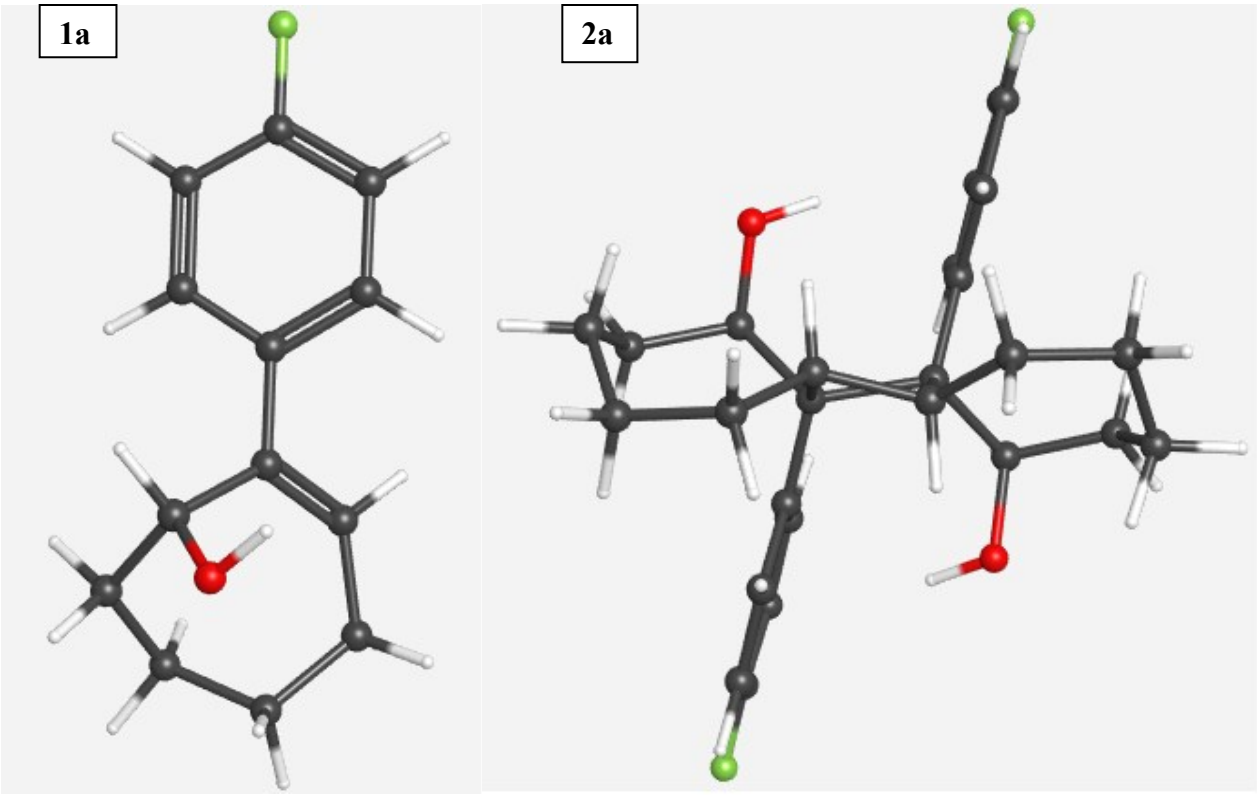
7.0 X-ray crystal structures

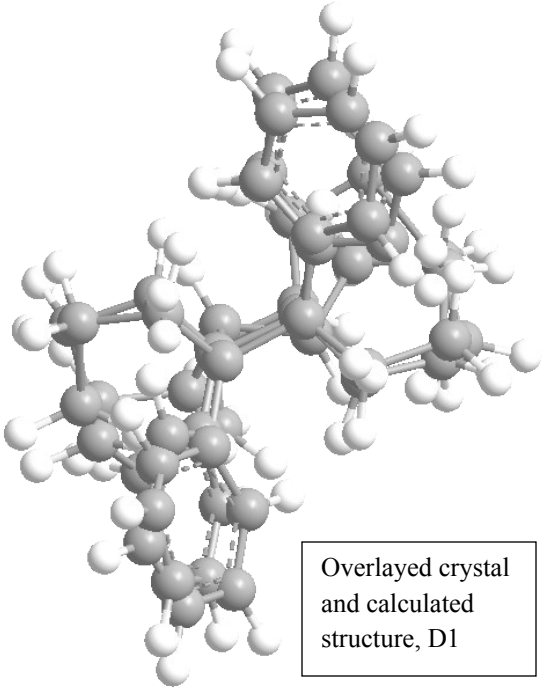


X-ray crystal structure of dimer of phenylcycloheptene

8.0 Computational Studies

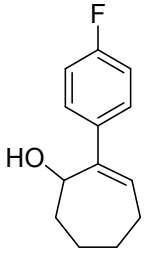
All density functional theory calculations were performed with the B3LYP functional. The basis set used for **1a** and **2a** are 6-31 G(d). WebMo software (version 17.0.008) was used to perform the calculations. The structures of **1a** was minimized to the lowest energy conformer. The X-ray crystal structure of **2a** was also minimized further to the lowest energy conformer. Then, the molecular energies for **1a** and **2a** were calculated. The energy calculations revealed that the $[_{\pi}2_s+_{\pi}2_a]$ cycloadduct **2a** is 5.0 kcal/mol higher in energy than the starting alkene **1a**. Therefore, the $[_{\pi}2_s+_{\pi}2_a]$ cycloaddition reaction is net endergonic in nature.





Overlayed crystal and calculated structure, D1

Cartesian Coordinates

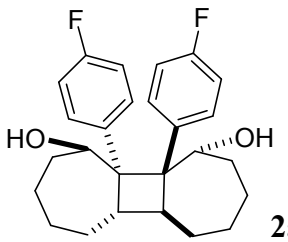


1a

```
Gaussian 03:  AM64L-G03RevD.01 13-Oct-2005
B3LYP/6-31G(d) SP Geom=Connectivity
Symbolic Z-matrix:
Charge =  0 Multiplicity = 1

Stoichiometry    C13H15FO
 Framework group C1[X(C13H15FO)]
 Deg. of freedom    84
 Full point group                 C1
 Largest Abelian subgroup         C1      NOp   1
 Largest concise Abelian subgroup C1      NOp   1
```

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.354334	-0.955974	0.678746
2	6	0	0.605008	0.228344	0.063233
3	6	0	-0.883087	0.133795	0.008984
4	6	0	-1.699915	1.217976	0.377265
5	6	0	-3.090089	1.141256	0.311846
6	6	0	-3.674474	-0.042609	-0.121149
7	6	0	-2.908558	-1.142857	-0.486702
8	6	0	-1.519881	-1.046848	-0.415716
9	1	0	-0.922512	-1.901680	-0.720421
10	1	0	-3.398887	-2.050230	-0.824159
11	9	0	-5.020840	-0.128835	-0.181056
12	1	0	-3.719814	1.975375	0.604227
13	1	0	-1.237650	2.131326	0.740271
14	6	0	1.217233	1.352015	-0.359283
15	6	0	2.680788	1.711397	-0.435669
16	6	0	3.731514	0.598662	-0.267917
17	6	0	3.345357	-0.691032	-1.010428
18	6	0	2.413502	-1.623763	-0.211659
19	1	0	1.902725	-2.303543	-0.906560
20	1	0	3.006579	-2.256137	0.460996
21	1	0	4.247294	-1.258509	-1.271828
22	1	0	2.871335	-0.423733	-1.964853
23	1	0	3.886521	0.380309	0.791669
24	1	0	4.681795	0.982336	-0.660805
25	1	0	2.880126	2.525656	0.279565
26	1	0	2.824806	2.173050	-1.425045
27	1	0	0.568271	2.139595	-0.744811
28	8	0	2.019856	-0.561184	1.893329
29	1	0	1.393427	-0.020040	2.399826
30	1	0	0.614313	-1.726972	0.935500



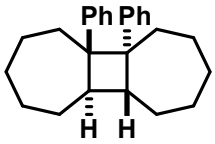
2a

Gaussian 03: AM64L-G03RevD.01 13-Oct-2005
B3LYP/6-31G(d) SP Geom=Connectivity
Symbolic Z-matrix:
Charge = 0 Multiplicity = 1

Stoichiometry C26H30F2O2
Framework group C1[X(C26H30F2O2)]
Deg. of freedom 174
Full point group C1
Largest Abelian subgroup C1 NOp 1
Largest concise Abelian subgroup C1 NOp 1

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.562596	0.611605	0.128035
2	6	0	-1.918419	0.122003	-0.386890
3	6	0	-2.116861	0.008899	-1.779672
4	6	0	-3.324440	-0.423887	-2.328690
5	6	0	-4.365607	-0.760003	-1.472878
6	9	0	-5.538944	-1.176354	-1.990716
7	6	0	-4.214571	-0.687785	-0.094708
8	6	0	-2.998089	-0.251338	0.433252
9	1	0	-2.891493	-0.228016	1.508345
10	1	0	-5.037113	-0.975435	0.552006
11	1	0	-3.461652	-0.504445	-3.402157
12	1	0	-1.309906	0.255828	-2.462223
13	6	0	0.562582	-0.611519	0.128079
14	6	0	1.918431	-0.122025	-0.386881
15	6	0	2.998178	0.251141	0.433239
16	1	0	2.891621	0.227772	1.508335
17	6	0	4.214692	0.687470	-0.094745
18	1	0	5.037292	0.974991	0.551953
19	6	0	4.365686	0.759731	-1.472917
20	9	0	5.539054	1.175965	-1.990779
21	6	0	3.324451	0.423769	-2.328707
22	6	0	2.116841	-0.008902	-1.779666
23	1	0	1.309837	-0.255716	-2.462199
24	1	0	3.461637	0.504350	-3.402175
25	6	0	0.281065	-2.005309	-0.553261
26	8	0	-0.950055	-2.611991	-0.177187
27	1	0	-1.672788	-2.093037	-0.557613
28	1	0	0.301425	-1.889643	-1.646442
29	6	0	1.350927	-3.050586	-0.175389
30	1	0	2.336193	-2.713459	-0.516347
31	1	0	1.103645	-3.946019	-0.758536

32	6	0	1.427419	-3.458896	1.312260
33	1	0	0.422983	-3.710979	1.672635
34	1	0	2.005433	-4.391459	1.352543
35	6	0	2.111715	-2.450090	2.257829
36	1	0	3.023692	-2.089852	1.765338
37	1	0	2.450879	-2.983757	3.155421
38	6	0	1.254392	-1.246415	2.714991
39	1	0	0.657380	-1.550328	3.586011
40	1	0	1.914054	-0.450718	3.087275
41	6	0	0.269346	-0.718290	1.663356
42	1	0	-0.594543	-1.391282	1.693346
43	6	0	-0.269350	0.718503	1.663302
44	1	0	0.594539	1.391498	1.693230
45	6	0	-1.254381	1.246710	2.714913
46	1	0	-0.657354	1.550692	3.585899
47	1	0	-1.914031	0.451039	3.087273
48	6	0	-2.111723	2.450348	2.257686
49	1	0	-3.023725	2.090069	1.765273
50	1	0	-2.450843	2.984094	3.155248
51	6	0	-1.427481	3.459072	1.311992
52	1	0	-0.423036	3.711209	1.672303
53	1	0	-2.005509	4.391629	1.352204
54	6	0	-1.351038	3.050613	-0.175618
55	1	0	-2.336301	2.713404	-0.516503
56	1	0	-1.103820	3.945998	-0.758865
57	6	0	-0.281137	2.005355	-0.553420
58	8	0	0.949945	2.612142	-0.177399
59	1	0	1.672708	2.093217	-0.557803
60	1	0	-0.301506	1.889603	-1.646593



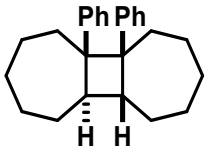
D1

Gaussian 03: AM64L-G03RevD.01 13-Oct-2005
B3LYP/6-31G(d) SP Geom=Connectivity
Symbolic Z-matrix:
Charge = 0 Multiplicity = 1

Stoichiometry C26H32
Framework group C1[X(C26H32)]
Deg. of freedom 168
Full point group C1
Largest Abelian subgroup C1 NOp 1
Largest concise Abelian subgroup C1 NOp 1
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.772630	2.761736	-0.602479
2	6	0	1.978949	3.216125	0.860158
3	6	0	2.545387	2.149028	1.822696
4	6	0	1.517146	1.162279	2.418595

5	6	0	0.430242	0.736559	1.424270
6	6	0	0.680231	0.473229	-0.107906
7	6	0	0.598542	1.802732	-0.887826
8	1	0	0.543371	1.634513	-1.969860
9	1	0	-0.336478	2.307266	-0.623475
10	6	0	-0.658729	-0.490138	-0.033951
11	6	0	-0.343632	-0.591499	1.502267
12	6	0	-1.382745	-0.993807	2.544944
13	6	0	-1.921032	-2.412374	2.266443
14	6	0	-2.668923	-2.555099	0.924183
15	6	0	-1.844686	-2.790007	-0.365722
16	6	0	-0.606472	-1.895757	-0.664723
17	1	0	-0.463899	-1.855368	-1.750937
18	1	0	0.291580	-2.390891	-0.284986
19	1	0	-1.500028	-3.833060	-0.376174
20	1	0	-2.552842	-2.706202	-1.199717
21	1	0	-3.361369	-3.404224	1.002499
22	1	0	-3.303891	-1.671130	0.789512
23	1	0	-2.609089	-2.684668	3.077797
24	1	0	-1.093391	-3.135828	2.316525
25	1	0	-0.908746	-0.977289	3.537158
26	1	0	-2.227097	-0.297844	2.599037
27	1	0	0.419717	-1.379101	1.561931
28	6	0	-1.894807	0.282835	-0.506822
29	6	0	-2.266646	0.208257	-1.862968
30	6	0	-3.350673	0.921942	-2.373086
31	6	0	-4.108255	1.745162	-1.540290
32	6	0	-3.755711	1.845354	-0.195797
33	6	0	-2.667322	1.129756	0.308326
34	1	0	-2.424584	1.247251	1.356448
35	1	0	-4.327400	2.484218	0.472825
36	1	0	-4.955734	2.300393	-1.933085
37	1	0	-3.601049	0.832164	-3.427286
38	1	0	-1.696133	-0.416218	-2.542708
39	6	0	1.897058	-0.342960	-0.554791
40	6	0	2.792800	-0.980763	0.319212
41	6	0	3.865255	-1.742173	-0.152709
42	6	0	4.075863	-1.896969	-1.520979
43	6	0	3.192984	-1.283402	-2.410537
44	6	0	2.125837	-0.524482	-1.933051
45	1	0	1.452842	-0.070974	-2.653988
46	1	0	3.332060	-1.395457	-3.482991
47	1	0	4.910757	-2.487121	-1.889076
48	1	0	4.536789	-2.213972	0.560390
49	1	0	2.662179	-0.892756	1.389666
50	1	0	-0.301029	1.551594	1.425799
51	1	0	1.014581	1.641160	3.270972
52	1	0	2.047046	0.301020	2.844869
53	1	0	3.321307	1.586378	1.288808
54	1	0	3.055858	2.653267	2.653880
55	1	0	2.689298	4.053262	0.836822
56	1	0	1.043336	3.633508	1.261440
57	1	0	1.613129	3.659271	-1.215783
58	1	0	2.709159	2.313452	-0.961054



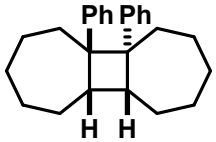
D2

```
Gaussian 03:  AM64L-G03RevD.01 13-Oct-2005
B3LYP/6-31G(d) SP Geom=Connectivity
Symbolic Z-matrix:
Charge = 0 Multiplicity = 1

Stoichiometry    C26H32
 Framework group  C1[X(C26H32)]
 Deg. of freedom   168
 Full point group                 C1
 Largest Abelian subgroup         C1      NOp   1
 Largest concise Abelian subgroup C1      NOp   1
                         Standard orientation:
```

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	3.020023	-1.002834	1.828230
2	6	0	3.768436	-1.246565	0.493645
3	6	0	3.306739	-2.400267	-0.422222
4	6	0	2.094943	-2.064628	-1.315210
5	6	0	0.875119	-1.738200	-0.460096
6	6	0	0.826312	-0.497395	0.485372
7	6	0	1.466085	-0.842190	1.842915
8	1	0	1.196184	-0.111825	2.616092
9	1	0	1.027441	-1.785120	2.180870
10	6	0	-0.804563	-0.594713	0.341906
11	6	0	-0.570373	-1.473753	-0.955932
12	6	0	-1.401376	-2.747425	-1.179401
13	6	0	-2.932033	-2.605468	-1.250602
14	6	0	-3.566586	-1.692084	-0.183195
15	6	0	-2.992999	-1.739963	1.247675
16	6	0	-1.471252	-1.465043	1.436185
17	1	0	-1.326099	-1.006070	2.420647
18	1	0	-0.945446	-2.422650	1.490541
19	1	0	-3.217427	-2.713135	1.706086
20	1	0	-3.555383	-0.999990	1.830365
21	1	0	-3.514650	-0.658032	-0.532404
22	1	0	-4.638350	-1.924755	-0.120694
23	1	0	-3.228257	-2.226114	-2.238516
24	1	0	-3.358948	-3.615616	-1.180830
25	1	0	-1.045434	-3.228144	-2.101787
26	1	0	-1.161489	-3.456652	-0.376835
27	1	0	-0.589239	-0.857031	-1.859730
28	6	0	-1.504599	0.759509	0.239169
29	6	0	-1.686346	1.530628	1.400460
30	6	0	-2.298244	2.782770	1.358303
31	6	0	-2.751648	3.303675	0.145843

32	6	0	-2.577951	2.557073	-1.018268
33	6	0	-1.959940	1.305789	-0.969209
34	1	0	-1.843452	0.748903	-1.893354
35	1	0	-2.922391	2.946339	-1.973137
36	1	0	-3.231214	4.278204	0.109585
37	1	0	-2.420453	3.351698	2.276734
38	1	0	-1.337285	1.152653	2.357433
39	6	0	1.353533	0.831373	-0.073877
40	6	0	1.391595	1.126514	-1.448787
41	6	0	1.856277	2.351636	-1.928238
42	6	0	2.294184	3.336860	-1.044788
43	6	0	2.249431	3.077348	0.323681
44	6	0	1.785399	1.848877	0.795256
45	1	0	1.760090	1.691528	1.867489
46	1	0	2.575180	3.832767	1.034495
47	1	0	2.658865	4.290871	-1.416013
48	1	0	1.872141	2.532420	-3.000222
49	1	0	1.050330	0.396247	-2.171672
50	1	0	0.781383	-2.601329	0.213509
51	1	0	2.365559	-1.246386	-1.990549
52	1	0	1.864451	-2.931727	-1.950995
53	1	0	4.147029	-2.680624	-1.071296
54	1	0	3.080573	-3.291497	0.182747
55	1	0	4.816038	-1.429517	0.769431
56	1	0	3.776240	-0.320975	-0.093584
57	1	0	3.471442	-0.103567	2.264877
58	1	0	3.271574	-1.820013	2.517827



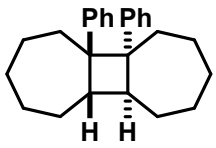
D3

Gaussian 03: AM64L-G03RevD.01 13-Oct-2005
B3LYP/6-31G(d) SP Geom=Connectivity
Symbolic Z-matrix:
Charge = 0 Multiplicity = 1

Stoichiometry C26H32
Framework group C1[X(C26H32)]
Deg. of freedom 168
Full point group C1
Largest Abelian subgroup C1 NOp 1
Largest concise Abelian subgroup C1 NOp 1
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.764020	2.749263	0.632773
2	6	0	-2.130129	2.997740	-0.840435
3	6	0	-0.959630	3.218496	-1.815698
4	6	0	0.082225	2.067121	-1.883044
5	6	0	-0.505940	0.694440	-1.533029
6	6	0	-0.773899	0.424925	0.005304

7	6	0	-0.662637	1.696248	0.875934
8	1	0	-0.659994	1.430879	1.938998
9	1	0	0.312295	2.156712	0.705228
10	6	0	0.546455	-0.562695	0.004414
11	6	0	0.424330	-0.541953	-1.558186
12	6	0	1.584993	-0.759998	-2.532403
13	6	0	2.531346	-1.899052	-2.088946
14	6	0	1.860723	-3.111849	-1.405473
15	6	0	1.539897	-2.949315	0.098415
16	6	0	0.371390	-2.020973	0.491335
17	1	0	-0.556325	-2.421472	0.068151
18	1	0	0.242455	-2.075119	1.578450
19	1	0	1.309020	-3.944882	0.501947
20	1	0	2.454173	-2.621210	0.611403
21	1	0	2.552278	-3.960716	-1.490758
22	1	0	0.957291	-3.411625	-1.956906
23	1	0	3.082923	-2.248882	-2.971532
24	1	0	3.286343	-1.499653	-1.400490
25	1	0	2.168477	0.150740	-2.710954
26	1	0	1.146307	-1.016318	-3.507796
27	1	0	-0.252431	-1.381957	-1.755012
28	6	0	1.743722	0.078354	0.714815
29	6	0	2.773426	0.780905	0.068916
30	6	0	3.830781	1.357287	0.778523
31	6	0	3.891487	1.254142	2.166197
32	6	0	2.875650	0.568629	2.833793
33	6	0	1.826362	-0.006116	2.118953
34	1	0	1.050585	-0.525572	2.672947
35	1	0	2.897106	0.479548	3.917170
36	1	0	4.713279	1.700863	2.719295
37	1	0	4.608744	1.888027	0.235249
38	1	0	2.761385	0.890505	-1.006631
39	6	0	-2.064042	-0.332437	0.338758
40	6	0	-2.981586	-0.778018	-0.625315
41	6	0	-4.138943	-1.476579	-0.270009
42	6	0	-4.414199	-1.755287	1.066564
43	6	0	-3.512494	-1.329625	2.043673
44	6	0	-2.361099	-0.633059	1.682440
45	1	0	-1.676595	-0.321381	2.465889
46	1	0	-3.704487	-1.540226	3.092893
47	1	0	-5.314543	-2.296660	1.344333
48	1	0	-4.825664	-1.800629	-1.048120
49	1	0	-2.806251	-0.585236	-1.677979
50	1	0	-1.382902	0.563278	-2.175246
51	1	0	0.488788	2.018154	-2.902392
52	1	0	0.934962	2.298265	-1.239172
53	1	0	-0.442297	4.156324	-1.571856
54	1	0	-1.392237	3.367058	-2.814355
55	1	0	-2.794909	3.870727	-0.892175
56	1	0	-2.730716	2.152269	-1.197739
57	1	0	-1.432681	3.689477	1.095514
58	1	0	-2.679388	2.455157	1.162033



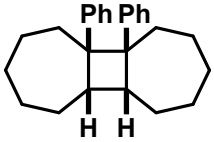
D4

Gaussian 03: AM64L-G03RevD.01 13-Oct-2005
B3LYP/6-31G(d) SP Geom=Connectivity
Symbolic Z-matrix:
Charge = 0 Multiplicity = 1

 Stoichiometry   C26H32
 Framework group C1[X(C26H32)]
 Deg. of freedom   168
 Full point group   C1
 Largest Abelian subgroup   C1   NOp   1
 Largest concise Abelian subgroup C1   NOp   1
                         Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.712535	-0.035598	2.748325
2	6	0	1.474005	-1.354649	3.510709
3	6	0	0.762628	-2.460322	2.707663
4	6	0	1.233689	-2.611900	1.252365
5	6	0	0.657369	-1.629297	0.216876
6	6	0	0.688853	-0.073031	0.365404
7	6	0	0.544142	0.397367	1.838264
8	1	0	-0.402207	0.036871	2.256469
9	1	0	0.455017	1.488090	1.845816
10	6	0	-0.747432	-0.052121	-0.417851
11	6	0	-0.864838	-1.573910	-0.021259
12	6	0	-1.523651	-2.665519	-0.901361
13	6	0	-2.360136	-2.156437	-2.086229
14	6	0	-1.515028	-1.723798	-3.295199
15	6	0	-0.301275	-0.846588	-2.939633
16	6	0	-0.628059	0.281771	-1.946593
17	1	0	-1.576514	0.727997	-2.268784
18	1	0	0.118192	1.075313	-2.059371
19	1	0	0.080472	-0.389798	-3.862210
20	1	0	0.517132	-1.471869	-2.568392
21	1	0	-1.161453	-2.616203	-3.830416
22	1	0	-2.160236	-1.181012	-3.999846
23	1	0	-3.055647	-2.943307	-2.406610
24	1	0	-2.987135	-1.320201	-1.750326
25	1	0	-2.164628	-3.287532	-0.263486
26	1	0	-0.745564	-3.343688	-1.282333
27	1	0	-1.350922	-1.600612	0.957556
28	6	0	-1.822916	0.873980	0.161375
29	6	0	-2.975960	0.391378	0.798133
30	6	0	-3.958933	1.256645	1.287799
31	6	0	-3.814657	2.635801	1.156000
32	6	0	-2.681712	3.138427	0.512651
33	6	0	-1.710520	2.269911	0.017983
34	1	0	-0.854418	2.685992	-0.503152
35	1	0	-2.555315	4.211214	0.388807
36	1	0	-4.575307	3.309900	1.540562
37	1	0	-4.840374	0.843686	1.772148
38	1	0	-3.128671	-0.676852	0.911781

39	6	0	1.875492	0.648853	-0.277075
40	6	0	1.943920	2.054790	-0.294765
41	6	0	3.020784	2.730385	-0.866871
42	6	0	4.081962	2.017844	-1.428097
43	6	0	4.046264	0.625400	-1.404889
44	6	0	2.957664	-0.045015	-0.840328
45	1	0	2.969385	-1.129755	-0.833231
46	1	0	4.868093	0.050946	-1.825119
47	1	0	4.925383	2.541467	-1.870079
48	1	0	3.032858	3.817532	-0.866362
49	1	0	1.145280	2.637332	0.152424
50	1	0	1.122365	-1.889722	-0.739020
51	1	0	2.332439	-2.570840	1.222063
52	1	0	0.969237	-3.620592	0.901882
53	1	0	0.909720	-3.414722	3.230034
54	1	0	-0.321585	-2.289122	2.721477
55	1	0	0.882819	-1.152655	4.414340
56	1	0	2.444088	-1.730506	3.863940
57	1	0	1.917002	0.753521	3.482726
58	1	0	2.625361	-0.117067	2.146338



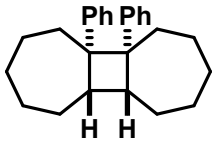
D5

Gaussian 03: AM64L-G03RevD.01 13-Oct-2005
B3LYP/6-31G(d) SP Geom=Connectivity
Symbolic Z-matrix:
Charge = 0 Multiplicity = 1

Stoichiometry C26H32
Framework group C1[X(C26H32)]
Deg. of freedom 168
Full point group C1
Largest Abelian subgroup C1 NOp 1
Largest concise Abelian subgroup C1 NOp 1
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.236353	3.056049	-1.008231
2	6	0	-2.513235	3.447911	-0.233648
3	6	0	-2.983235	2.445034	0.836867
4	6	0	-1.875937	1.872999	1.740064
5	6	0	-0.953458	0.761215	1.201539
6	6	0	-0.249275	0.802777	-0.194449
7	6	0	-1.083681	1.543122	-1.278576
8	1	0	-2.080080	1.100413	-1.369410
9	1	0	-0.600096	1.391717	-2.250076
10	6	0	-0.404518	-0.822739	-0.241336
11	6	0	-1.452306	-0.694669	0.930328
12	6	0	-2.933172	-0.957496	0.620928
13	6	0	-3.258794	-2.450304	0.410199

14	6	0	-2.929947	-2.996904	-0.987025
15	6	0	-1.462315	-2.878854	-1.428636
16	6	0	-0.959475	-1.422326	-1.550358
17	1	0	-0.198792	-1.358756	-2.335873
18	1	0	-1.787573	-0.811837	-1.918609
19	1	0	-1.365507	-3.367124	-2.407530
20	1	0	-0.818492	-3.445181	-0.744086
21	1	0	-3.226685	-4.054030	-1.027041
22	1	0	-3.560293	-2.477742	-1.725143
23	1	0	-4.330661	-2.606714	0.592171
24	1	0	-2.731678	-3.043944	1.171758
25	1	0	-3.514941	-0.592141	1.478193
26	1	0	-3.289765	-0.389846	-0.246709
27	1	0	-1.221255	-1.362257	1.767822
28	6	0	0.886383	-1.552560	0.192540
29	6	0	1.760086	-2.122130	-0.752104
30	6	0	2.937848	-2.769873	-0.378951
31	6	0	3.294185	-2.870536	0.964433
32	6	0	2.451859	-2.309677	1.921836
33	6	0	1.273740	-1.666304	1.539992
34	1	0	0.657225	-1.247393	2.326795
35	1	0	2.705790	-2.371049	2.977184
36	1	0	4.210238	-3.375376	1.259159
37	1	0	3.576348	-3.197534	-1.148027
38	1	0	1.528265	-2.072144	-1.809541
39	6	0	1.174909	1.352707	-0.241285
40	6	0	1.738604	2.081630	0.814355
41	6	0	3.030619	2.608256	0.728416
42	6	0	3.794501	2.413394	-0.420156
43	6	0	3.249871	1.691274	-1.484403
44	6	0	1.958949	1.175590	-1.394305
45	1	0	1.555492	0.619017	-2.236025
46	1	0	3.832366	1.528856	-2.387941
47	1	0	4.800466	2.818919	-0.488362
48	1	0	3.435770	3.172689	1.564655
49	1	0	1.165315	2.254551	1.720113
50	1	0	-0.164285	0.663346	1.955227
51	1	0	-1.247115	2.708838	2.081476
52	1	0	-2.342846	1.474120	2.652608
53	1	0	-3.717886	2.953907	1.475471
54	1	0	-3.533239	1.628107	0.360585
55	1	0	-2.345034	4.426778	0.235888
56	1	0	-3.340472	3.595248	-0.941503
57	1	0	-1.232655	3.596897	-1.962735
58	1	0	-0.353056	3.414155	-0.468686



D6

Gaussian 03: AM64L-G03RevD.01 13-Oct-2005
B3LYP/6-31G(d) SP Geom=Connectivity

Symbolic Z-matrix:
Charge = 0 Multiplicity = 1

Stoichiometry C26H32
Framework group C1[X(C26H32)]
Deg. of freedom 168
Full point group C1
Largest Abelian subgroup C1 NOp 1
Largest concise Abelian subgroup C1 NOp 1
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.236353	3.056049	-1.008231
2	6	0	-2.513235	3.447911	-0.233648
3	6	0	-2.983235	2.445034	0.836867
4	6	0	-1.875937	1.872999	1.740064
5	6	0	-0.953458	0.761215	1.201539
6	6	0	-0.249275	0.802777	-0.194449
7	6	0	-1.083681	1.543122	-1.278576
8	1	0	-2.080080	1.100413	-1.369410
9	1	0	-0.600096	1.391717	-2.250076
10	6	0	-0.404518	-0.822739	-0.241336
11	6	0	-1.452306	-0.694669	0.930328
12	6	0	-2.933172	-0.957496	0.620928
13	6	0	-3.258794	-2.450304	0.410199
14	6	0	-2.929947	-2.996904	-0.987025
15	6	0	-1.462315	-2.878854	-1.428636
16	6	0	-0.959475	-1.422326	-1.550358
17	1	0	-0.198792	-1.358756	-2.335873
18	1	0	-1.787573	-0.811837	-1.918609
19	1	0	-1.365507	-3.367124	-2.407530
20	1	0	-0.818492	-3.445181	-0.744086
21	1	0	-3.226685	-4.054030	-1.027041
22	1	0	-3.560293	-2.477742	-1.725143
23	1	0	-4.330661	-2.606714	0.592171
24	1	0	-2.731678	-3.043944	1.171758
25	1	0	-3.514941	-0.592141	1.478193
26	1	0	-3.289765	-0.389846	-0.246709
27	1	0	-1.221255	-1.362257	1.767822
28	6	0	0.886383	-1.552560	0.192540
29	6	0	1.760086	-2.122130	-0.752104
30	6	0	2.937848	-2.769873	-0.378951
31	6	0	3.294185	-2.870536	0.964433
32	6	0	2.451859	-2.309677	1.921836
33	6	0	1.273740	-1.666304	1.539992
34	1	0	0.657225	-1.247393	2.326795
35	1	0	2.705790	-2.371049	2.977184
36	1	0	4.210238	-3.375376	1.259159
37	1	0	3.576348	-3.197534	-1.148027
38	1	0	1.528265	-2.072144	-1.809541
39	6	0	1.174909	1.352707	-0.241285
40	6	0	1.738604	2.081630	0.814355
41	6	0	3.030619	2.608256	0.728416
42	6	0	3.794501	2.413394	-0.420156
43	6	0	3.249871	1.691274	-1.484403

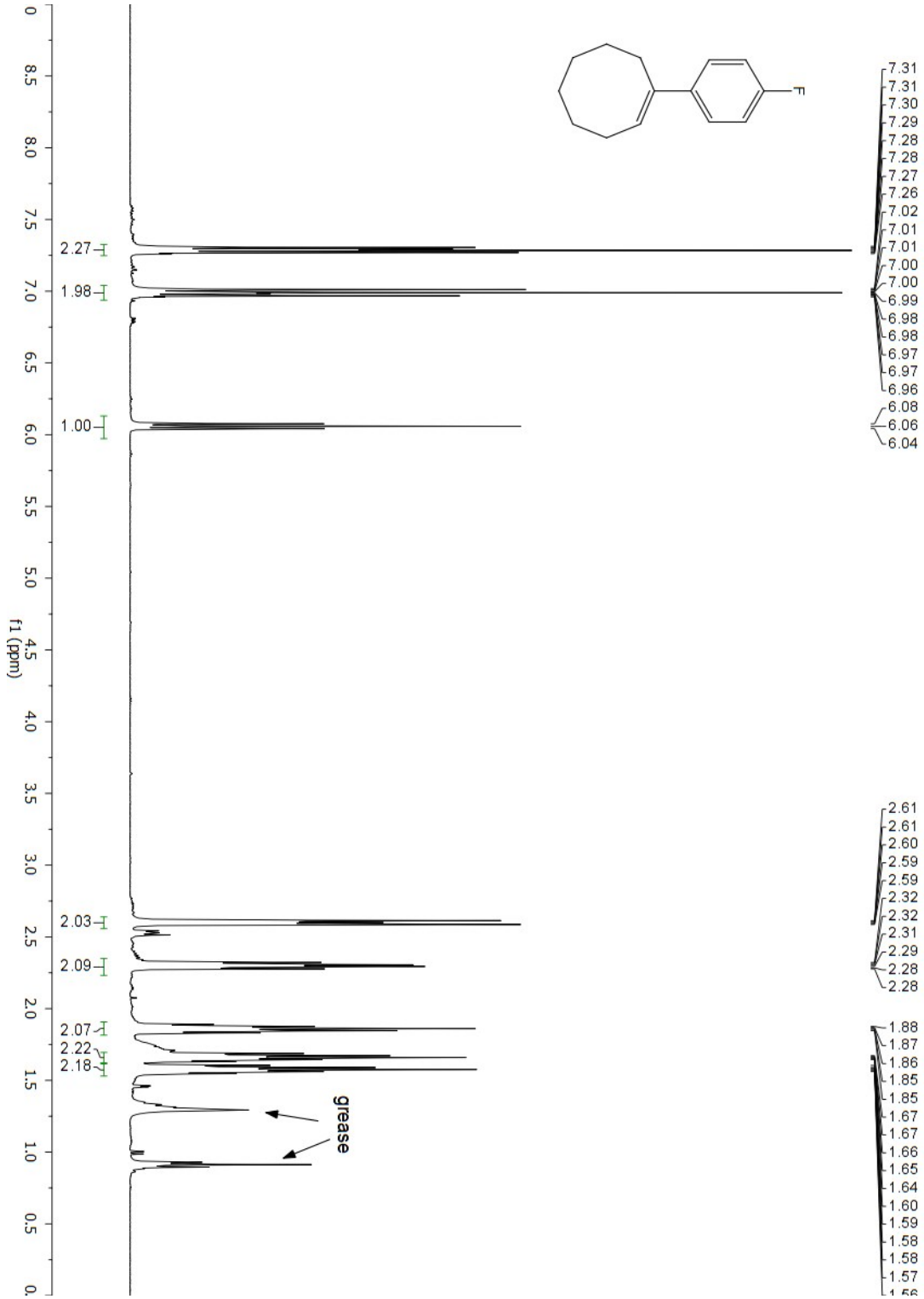
44	6	0	1.958949	1.175590	-1.394305
45	1	0	1.555492	0.619017	-2.236025
46	1	0	3.832366	1.528856	-2.387941
47	1	0	4.800466	2.818919	-0.488362
48	1	0	3.435770	3.172689	1.564655
49	1	0	1.165315	2.254551	1.720113
50	1	0	-0.164285	0.663346	1.955227
51	1	0	-1.247115	2.708838	2.081476
52	1	0	-2.342846	1.474120	2.652608
53	1	0	-3.717886	2.953907	1.475471
54	1	0	-3.533239	1.628107	0.360585
55	1	0	-2.345034	4.426778	0.235888
56	1	0	-3.340472	3.595248	-0.941503
57	1	0	-1.232655	3.596897	-1.962735
58	1	0	-0.353056	3.414155	-0.468686

9.0 References

1. G.-A. Lee, H.-Y. Lee, W.-C. Wang and C.-H. Cherng, *Tetrahedron*, 2014, **70**, 2956.
2. C.-Y. Huang and A. G. Doyle, *J. Am. Chem. Soc.*, 2015, **137**, 5638.
3. P. P. Fu, C. Cortez, K. B. Sukumaran and R. G. Harvey, *J. Org. Chem.*, 1979, **44**, 4265.
4. M. Shibuya, M. Tomizawa and Y. Iwabuchi, *Org. Lett.*, 2008, **10**, 4715.
5. J. A. McCubbin, S. Voth and O. V. Krokhin, *J. Org. Chem.*, 2011, **76**, 8537.
6. Y. Kobayashi, C. Feng, A. Ikoma, N. Ogawa and T. Hirotsu, *Org. Lett.*, 2014, **16**, 760.
7. Y. S. Song, B. T. Kim and J.-N. Heo, *Tetrahedron Lett.*, 2005, **46**, 5987.
8. H. Sundén, J.-N. Ma, L. K. Hansen, A.-L. Gustavsson, E. S. Burstein and R. Olsson, *ChemMedChem*, 2013, **8**, 1283.
9. S. F. Neelamkavil, C. D. Boyle, S. Chackalamannil, W. J. Greenlee, L. Zhang and G. Terracina, *Bioorg. Med. Chem. Lett.*, 2009, **19**, 4563.
10. Z. Bingwei, H. Yuanyuan and W. Congyang, *Angew. Chem. Int. Ed.*, 2015, **54**, 13659.

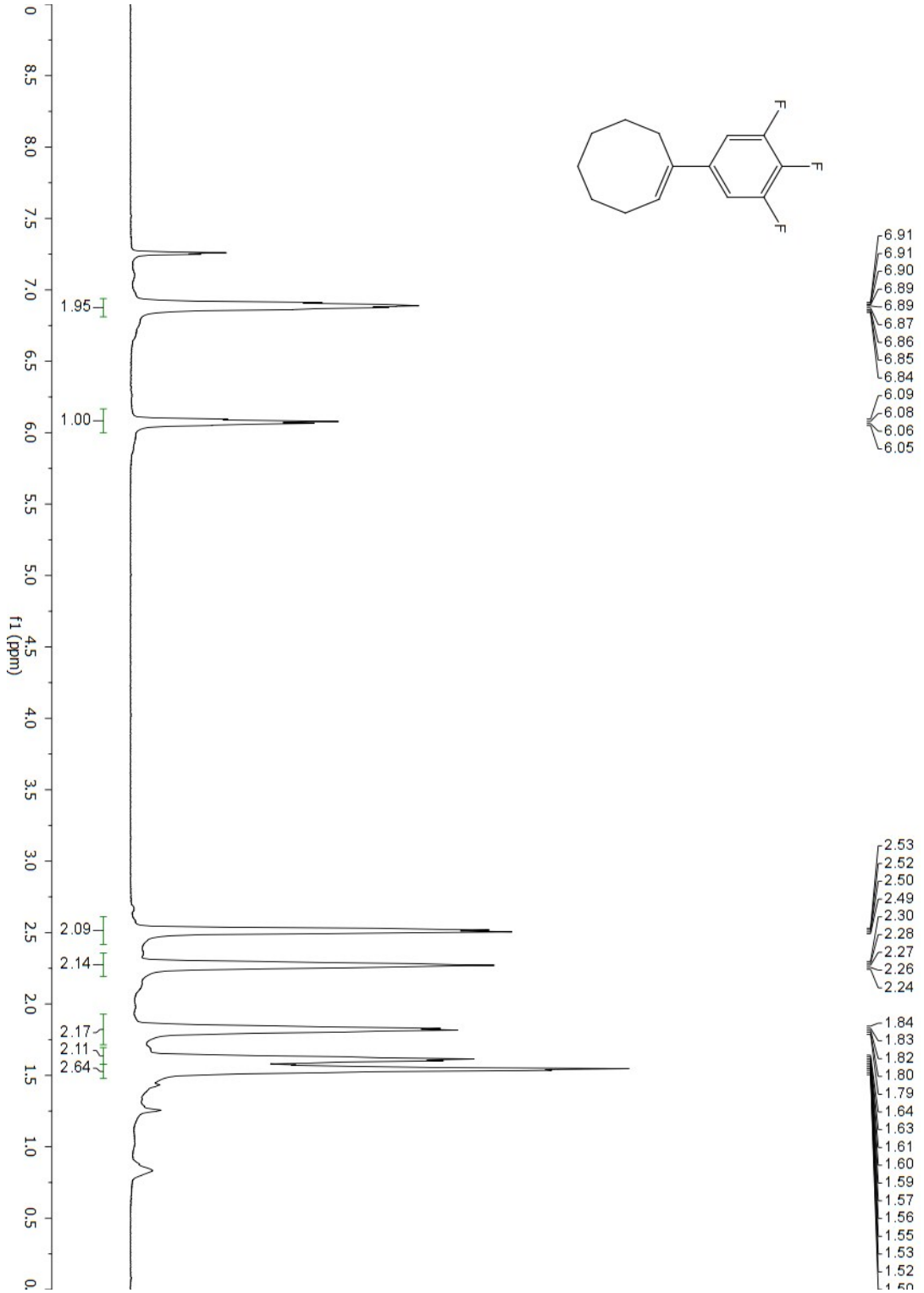
^{1}H NMR (400 MHz, $CDCl_3$)

1g 1-(4-fluorophenyl)cyclohept-1-ene



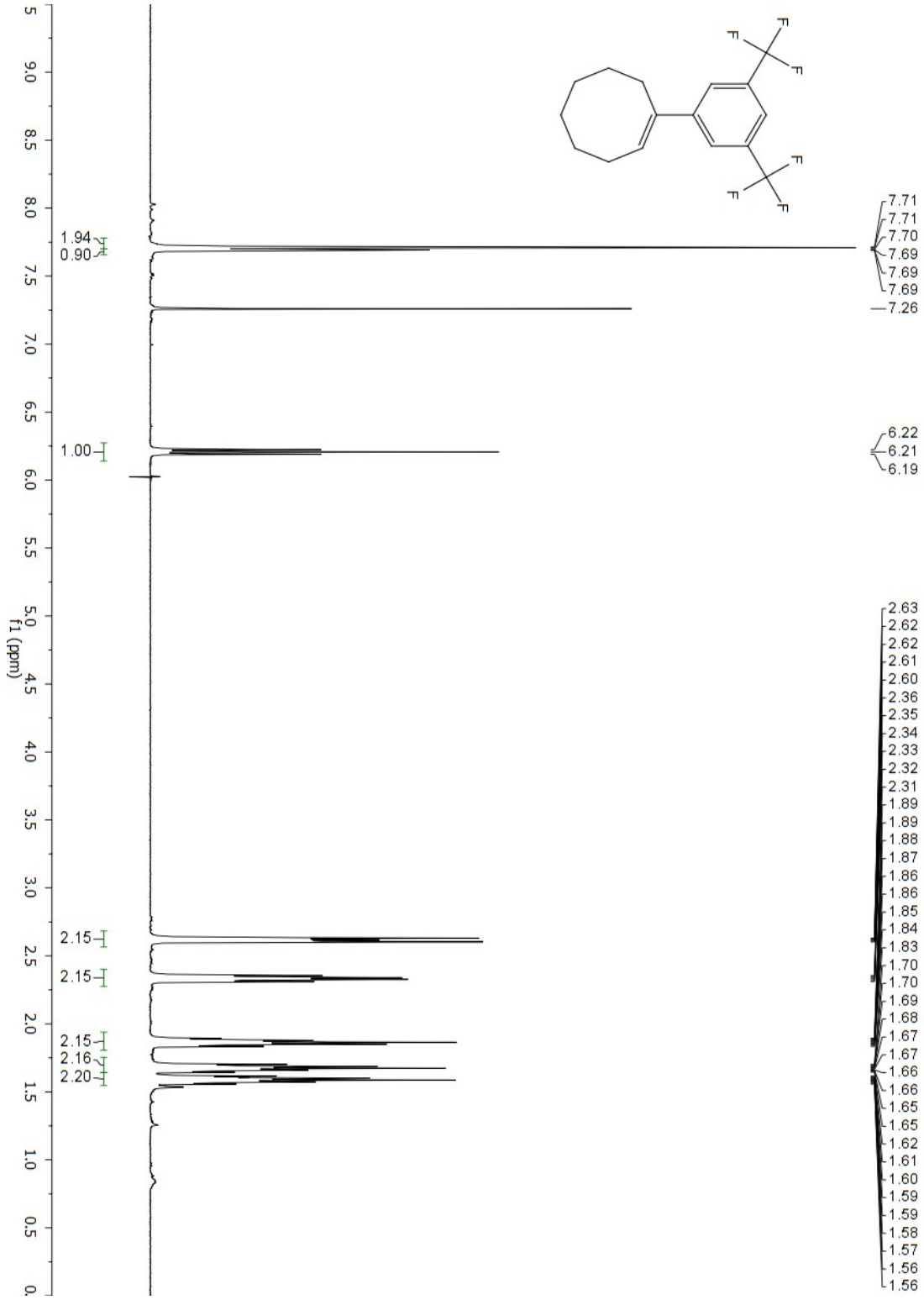
^{1}H NMR (400 MHz, $CDCl_3$)

1h 1-(3,4,5-trifluorophenyl)cyclohept-1-ene



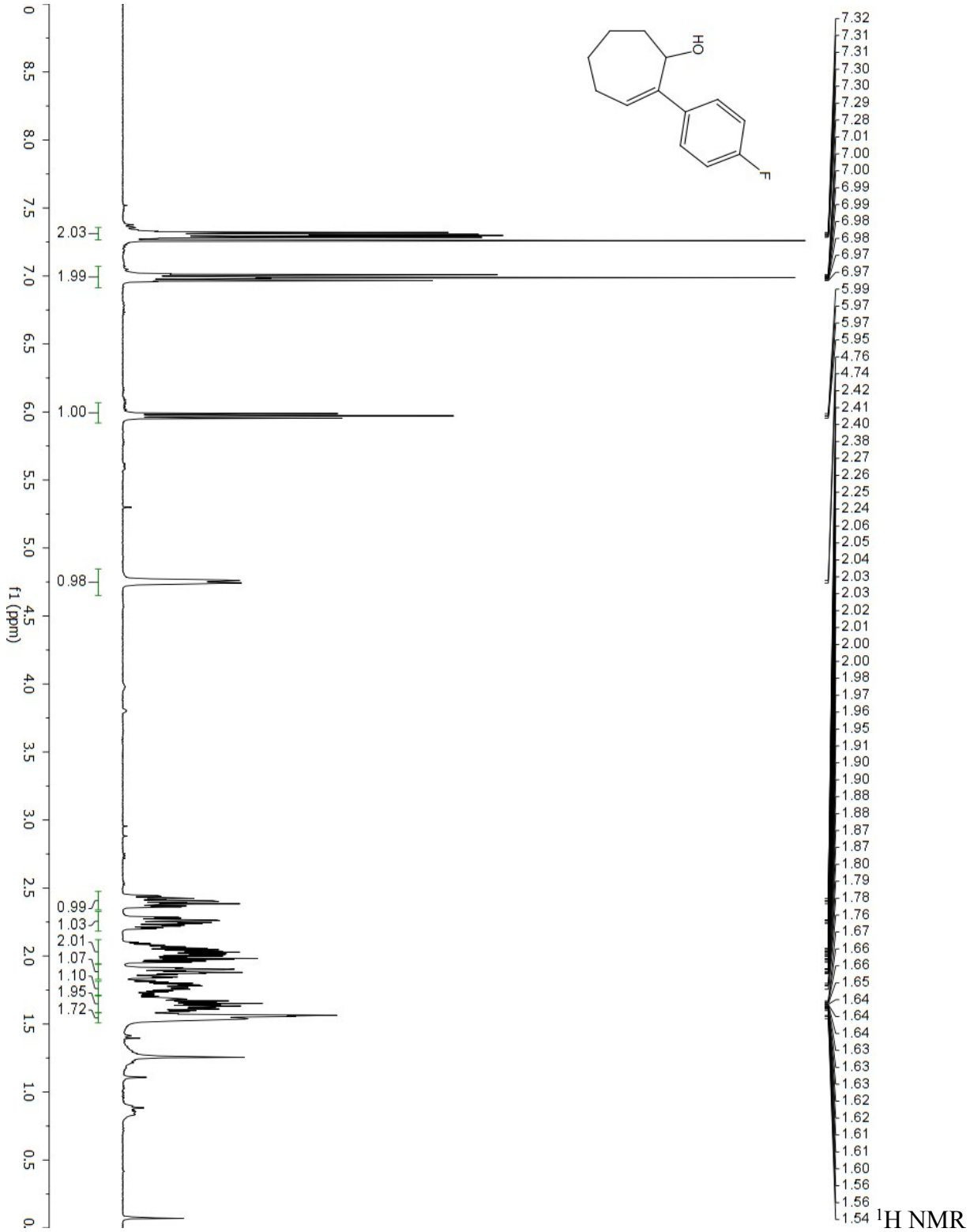
^{1}H NMR (400 MHz, $CDCl_3$)

1i 1-(3,5-bis(trifluoromethyl)phenyl)cyclohept-1-ene



^{1}H NMR (400 MHz, $CDCl_3$)

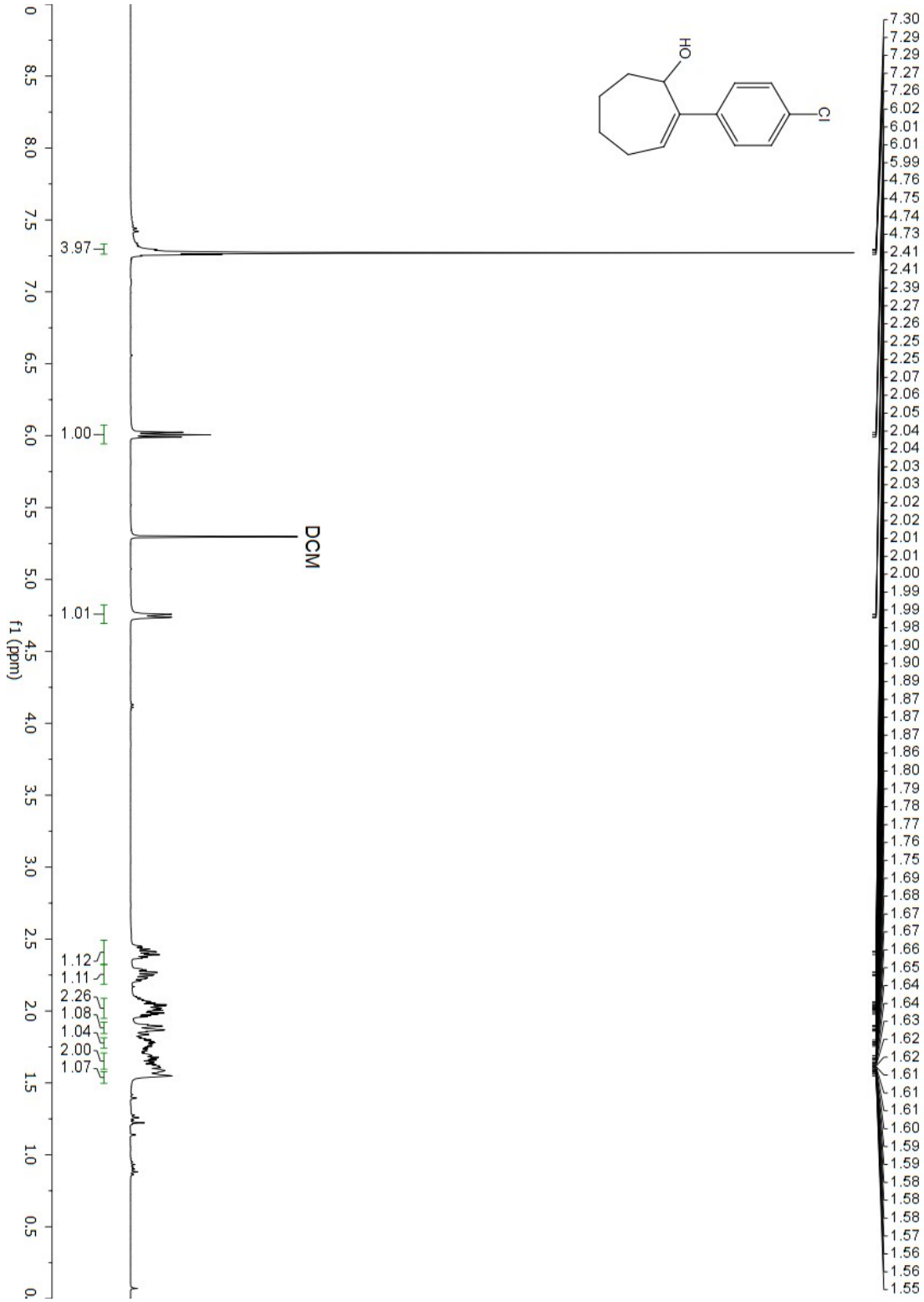
1a 2-(4-fluorophenyl)cyclohept-2-en-1-ol



^{1}H NMR

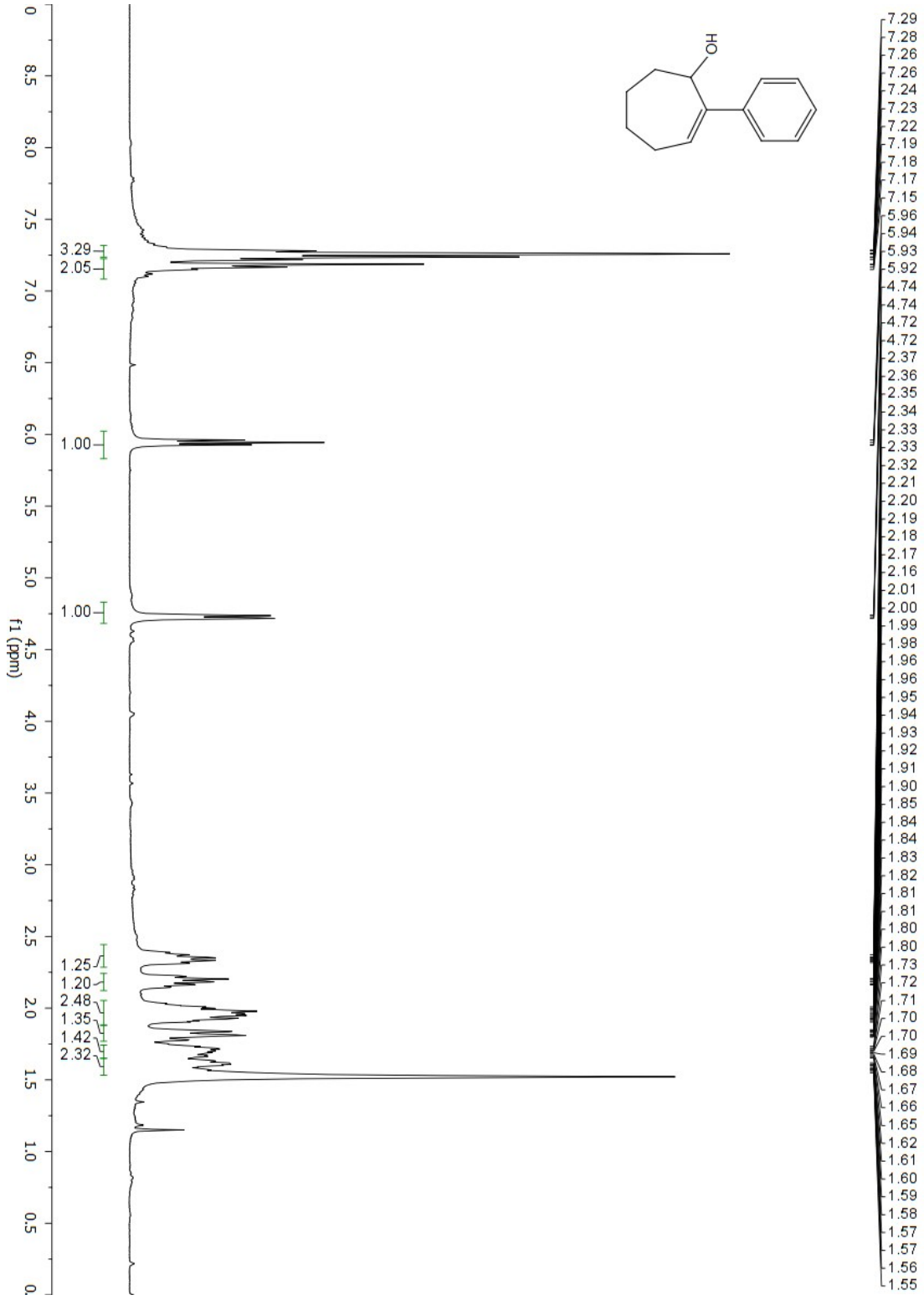
(400 MHz, $CDCl_3$)

1b 2-(4-chlorophenyl)cyclohept-2-en-1-ol



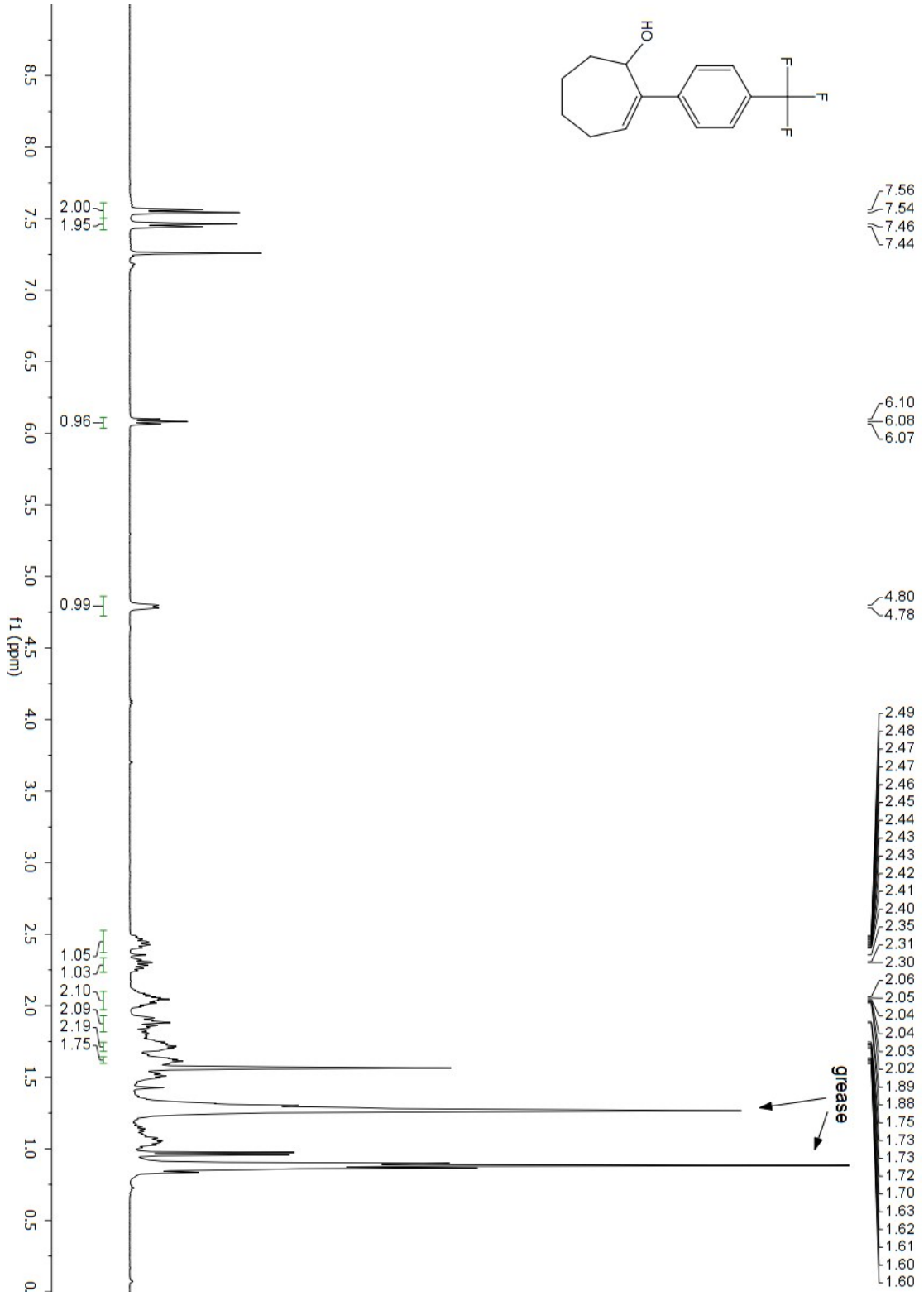
^{1}H NMR (400 MHz, $CDCl_3$)

1c 2-phenylcyclohept-2-en-1-ol



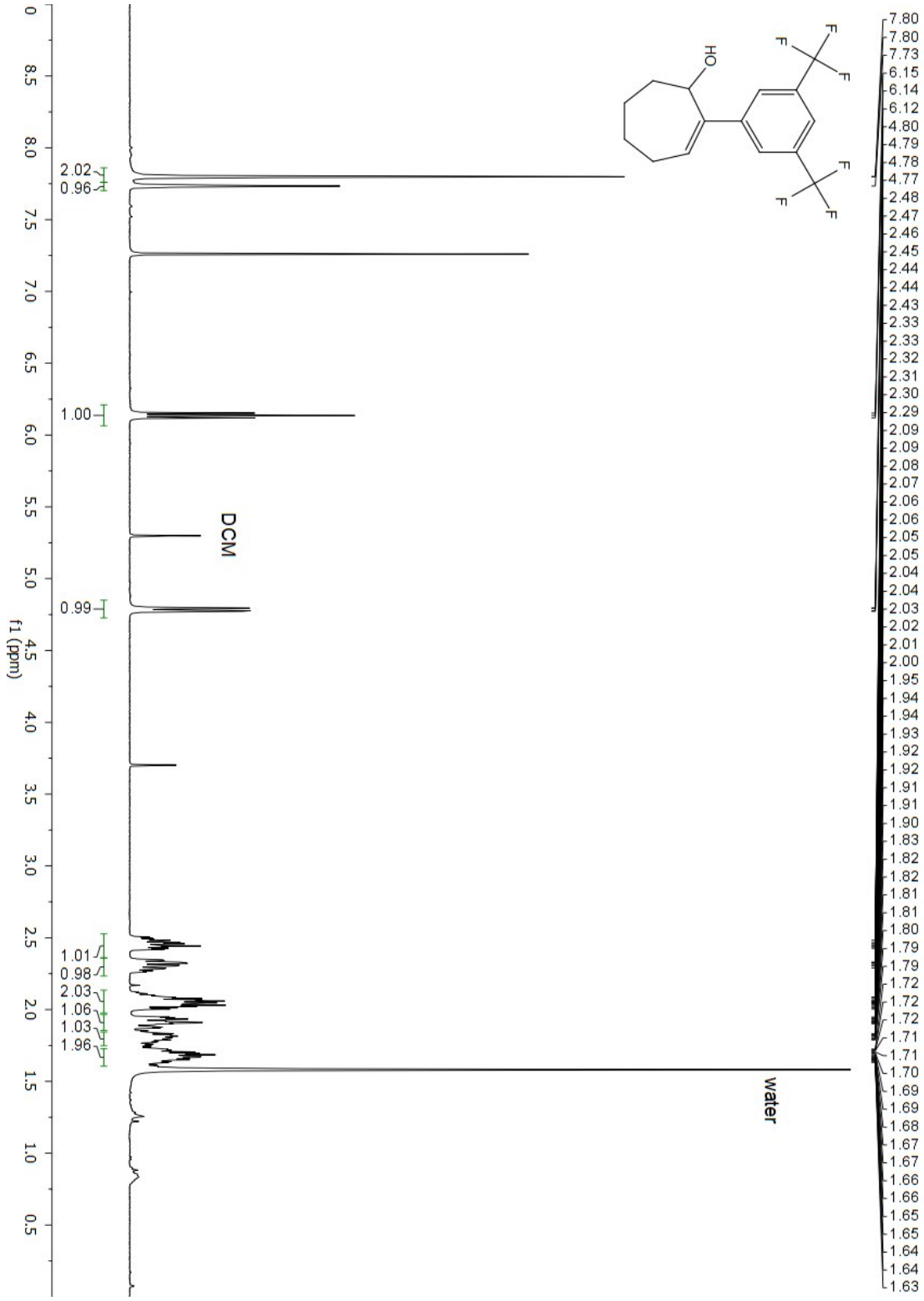
^{1}H NMR (400 MHz, $CDCl_3$)

1d 2-(4-(trifluoromethyl)phenyl)cyclohept-2-en-1-ol



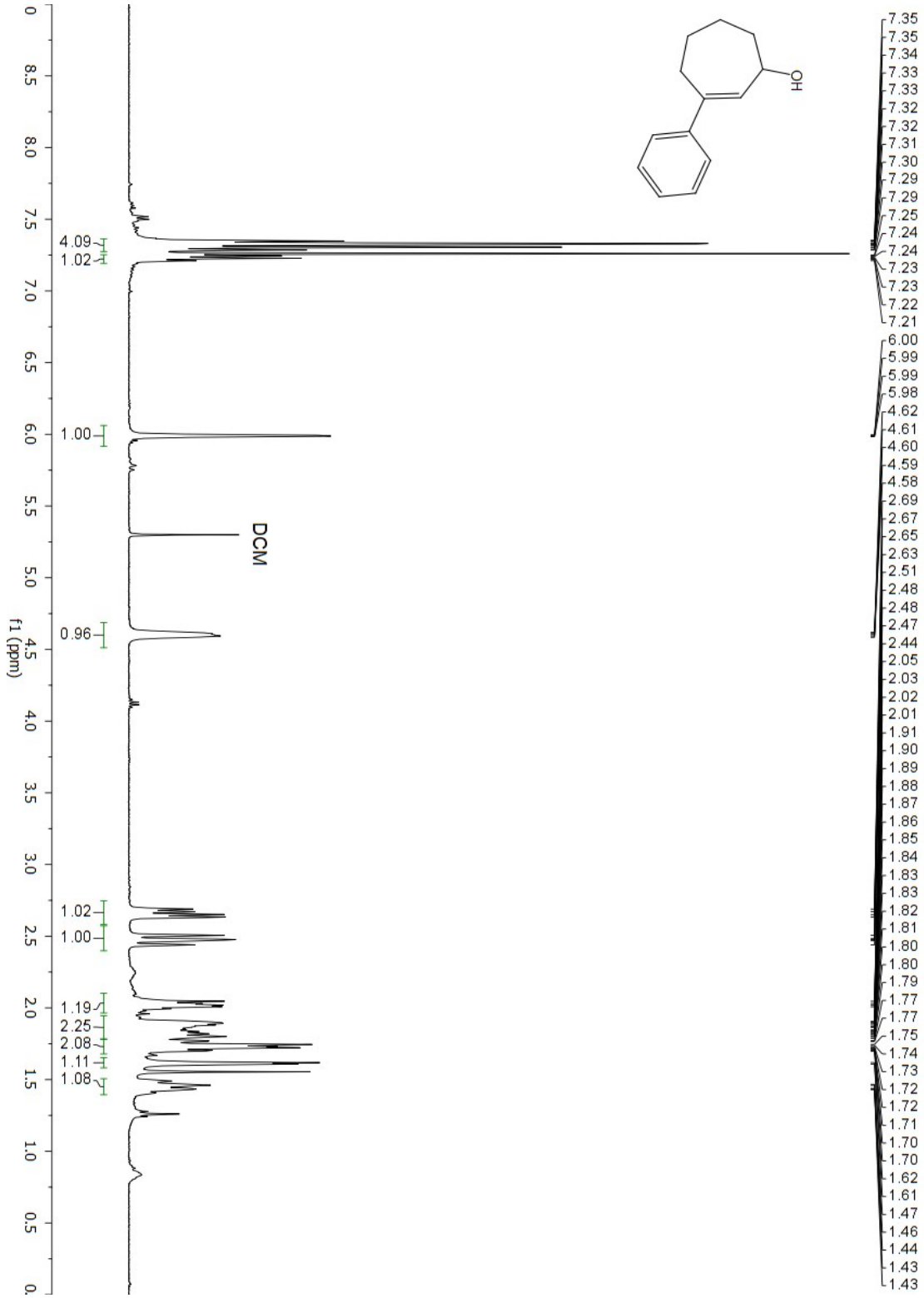
^{1}H NMR (400 MHz, $CDCl_3$)

1e 2-(3,5-bis(trifluoromethyl)phenyl)cyclohept-2-en-1-ol



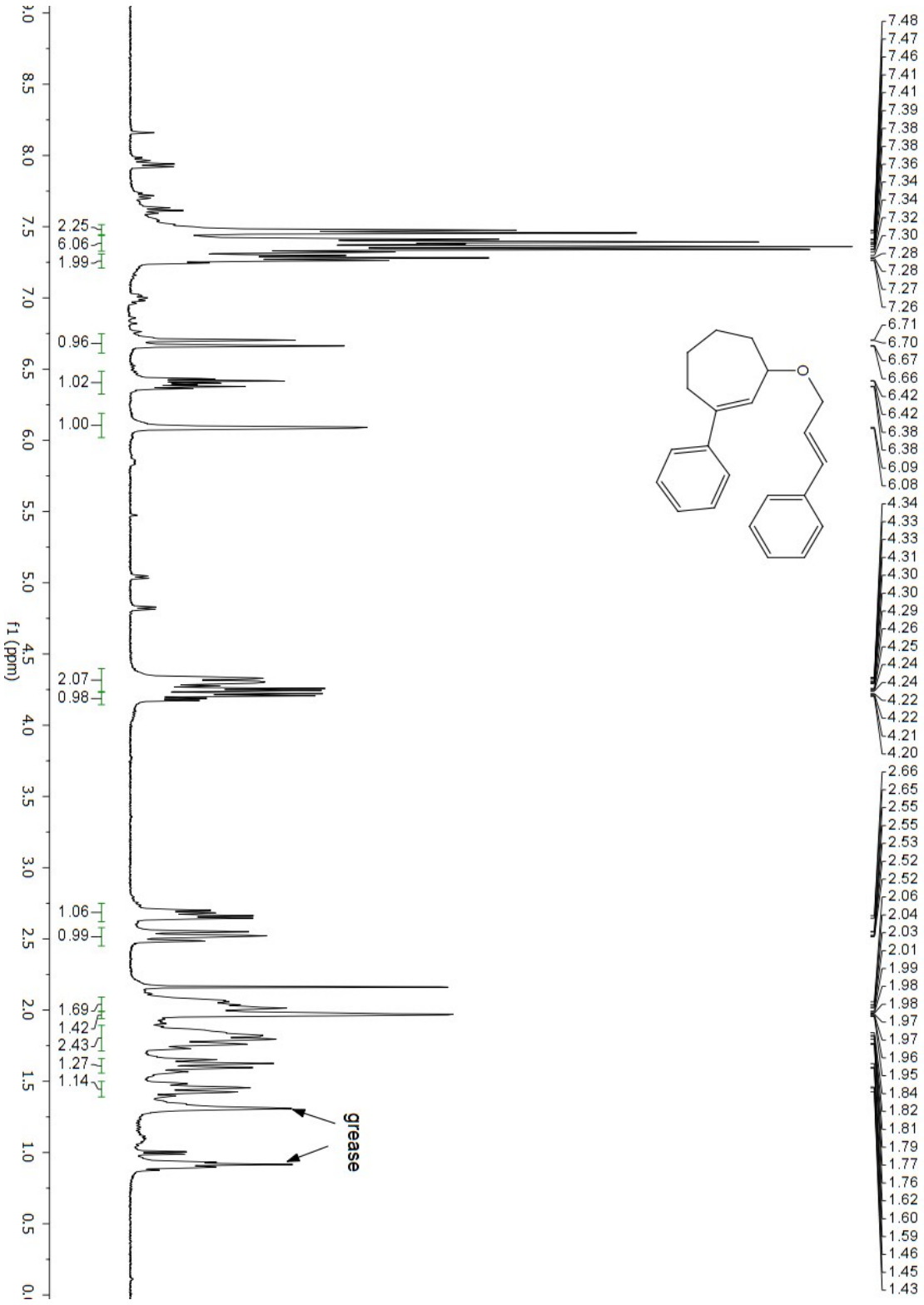
^{1}H NMR (400 MHz, $CDCl_3$)

1l (3-phenylcyclohept-2-en-1-ol)



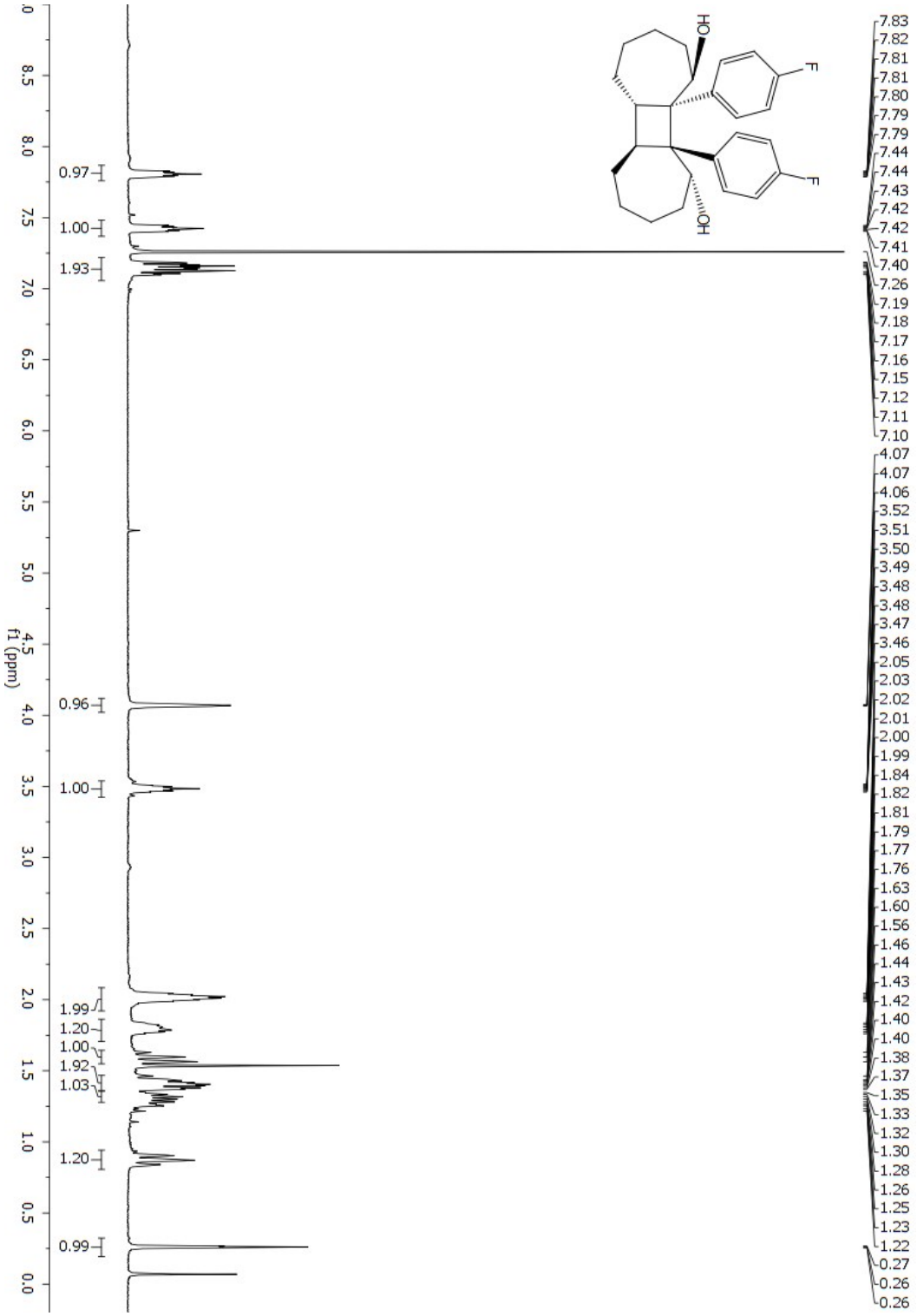
^{1}H NMR (400 MHz, CD_3CN)

1n (3-(cinnamyloxy)-1-phenylcyclohept-1-ene)



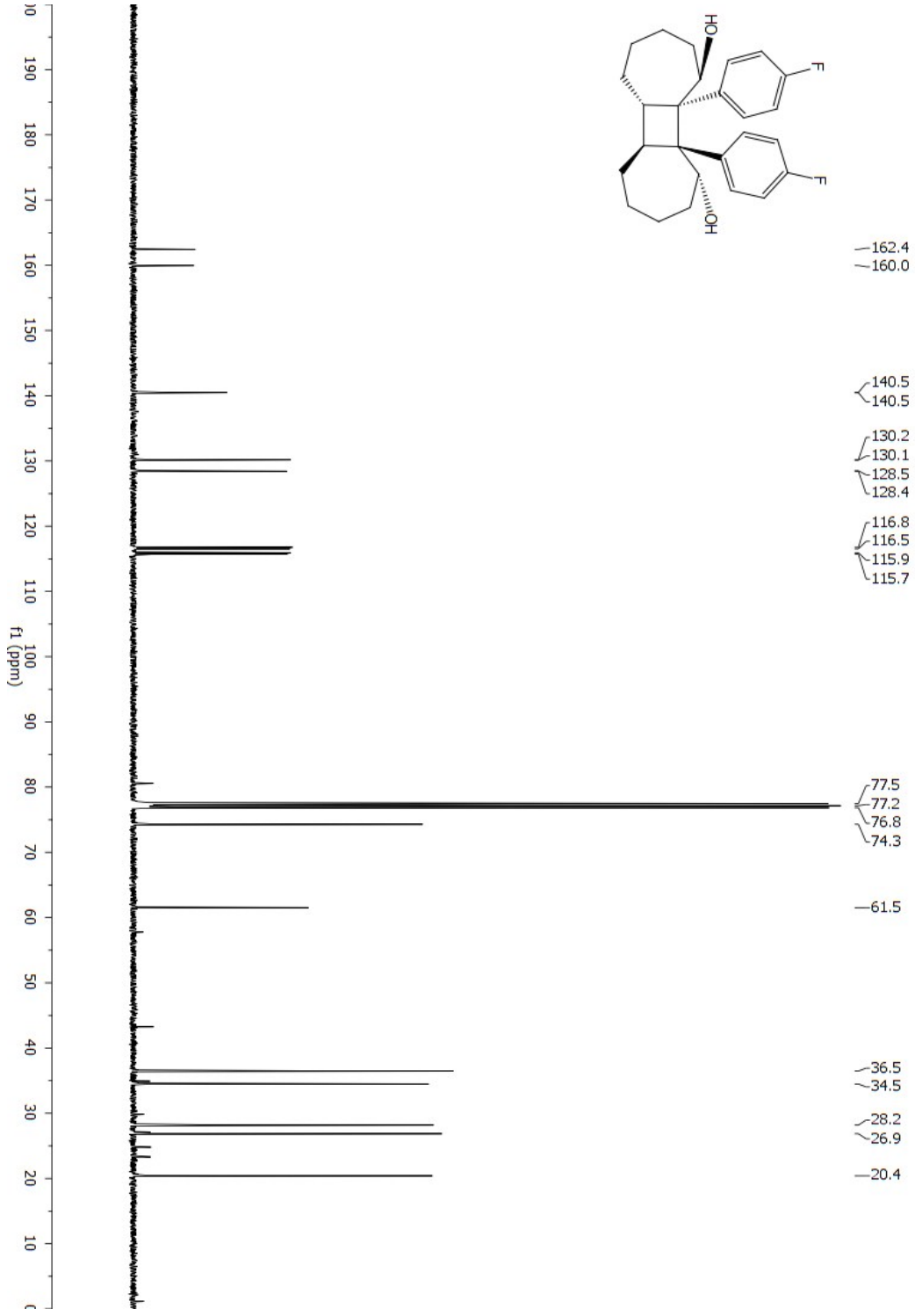
^{1}H NMR (400 MHz, $CDCl_3$)

2a (1R,5aS,5bS,10R,10aS,10bS)-10a,10b-bis(4-fluorophenyl)tetradecahydrocyclobuta-[1,2:3,4]di[7]annulene-1,10-diol



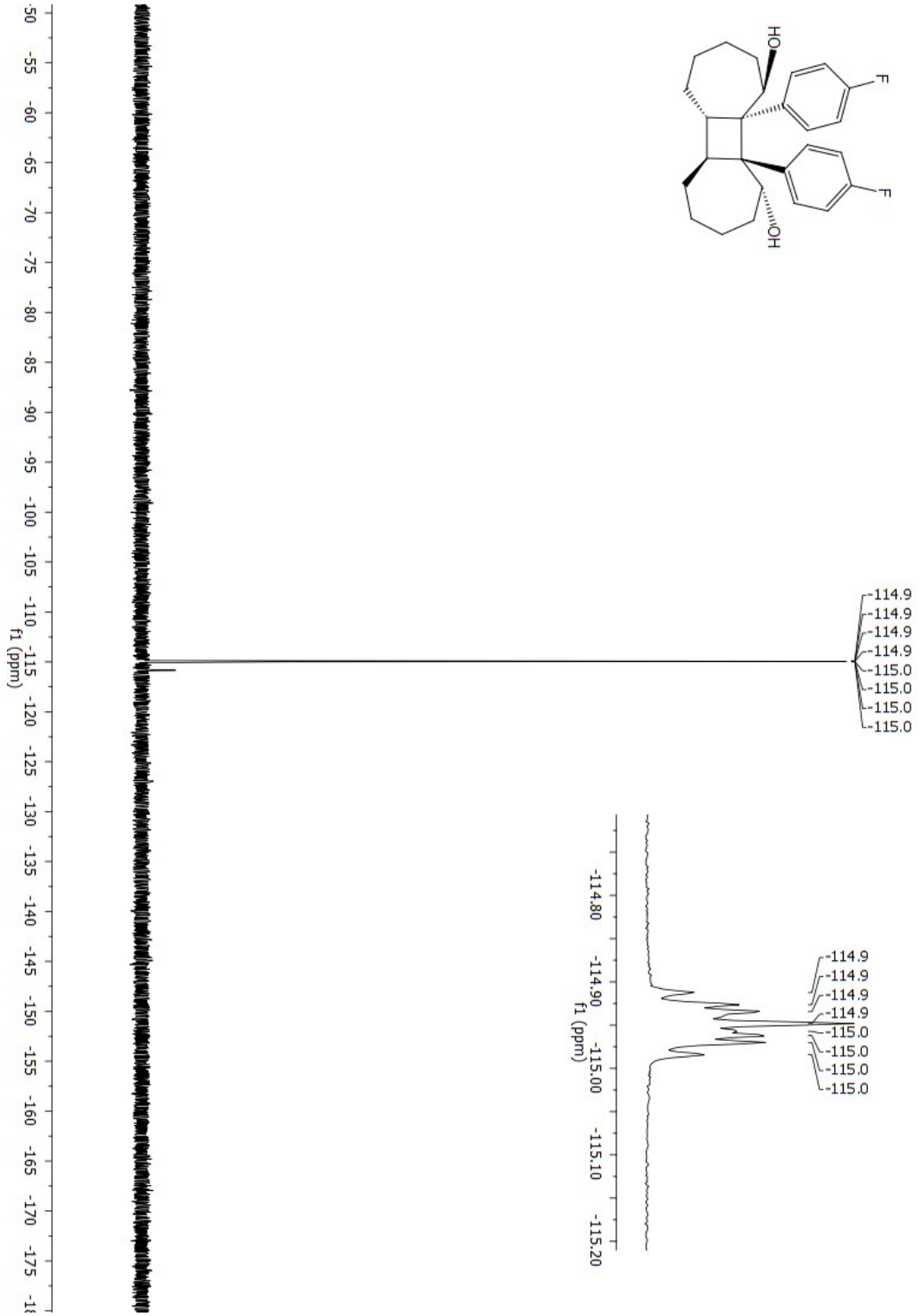
^{13}C NMR (101 MHz, $CDCl_3$)

2a (1R,5aS,5bS,10R,10aS,10bS)-10a,10b-bis(4-fluorophenyl)tetradecahydrocyclobuta-[1,2:3,4]di[7]annulene-1,10-diol



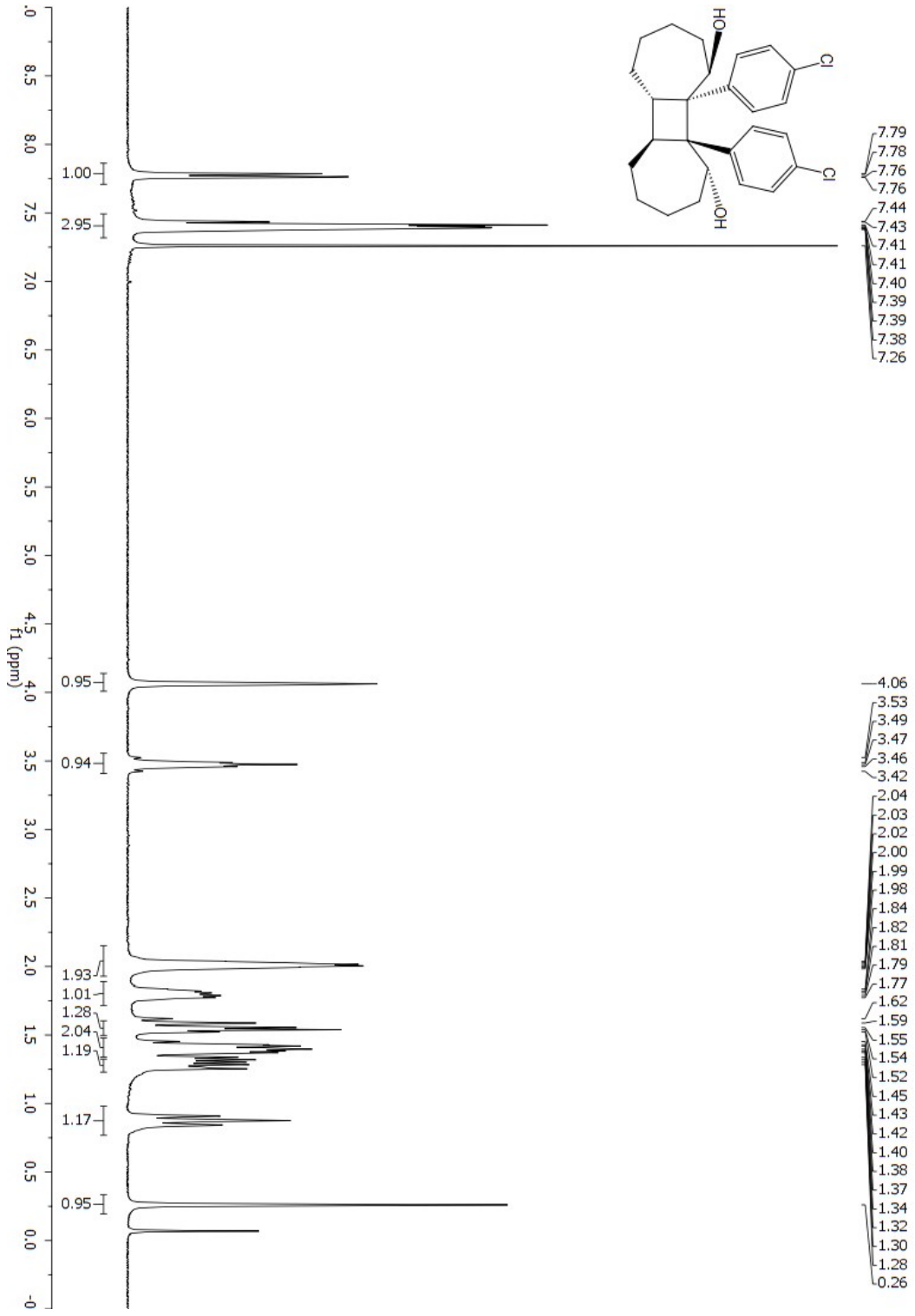
^{19}F NMR (376 MHz, $CDCl_3$)

2a (1R,5aS,5bS,10R,10aS,10bS)-10a,10b-bis(4-fluorophenyl)tetradecahydrocyclobuta-[1,2:3,4]di[7]annulene-1,10-diol



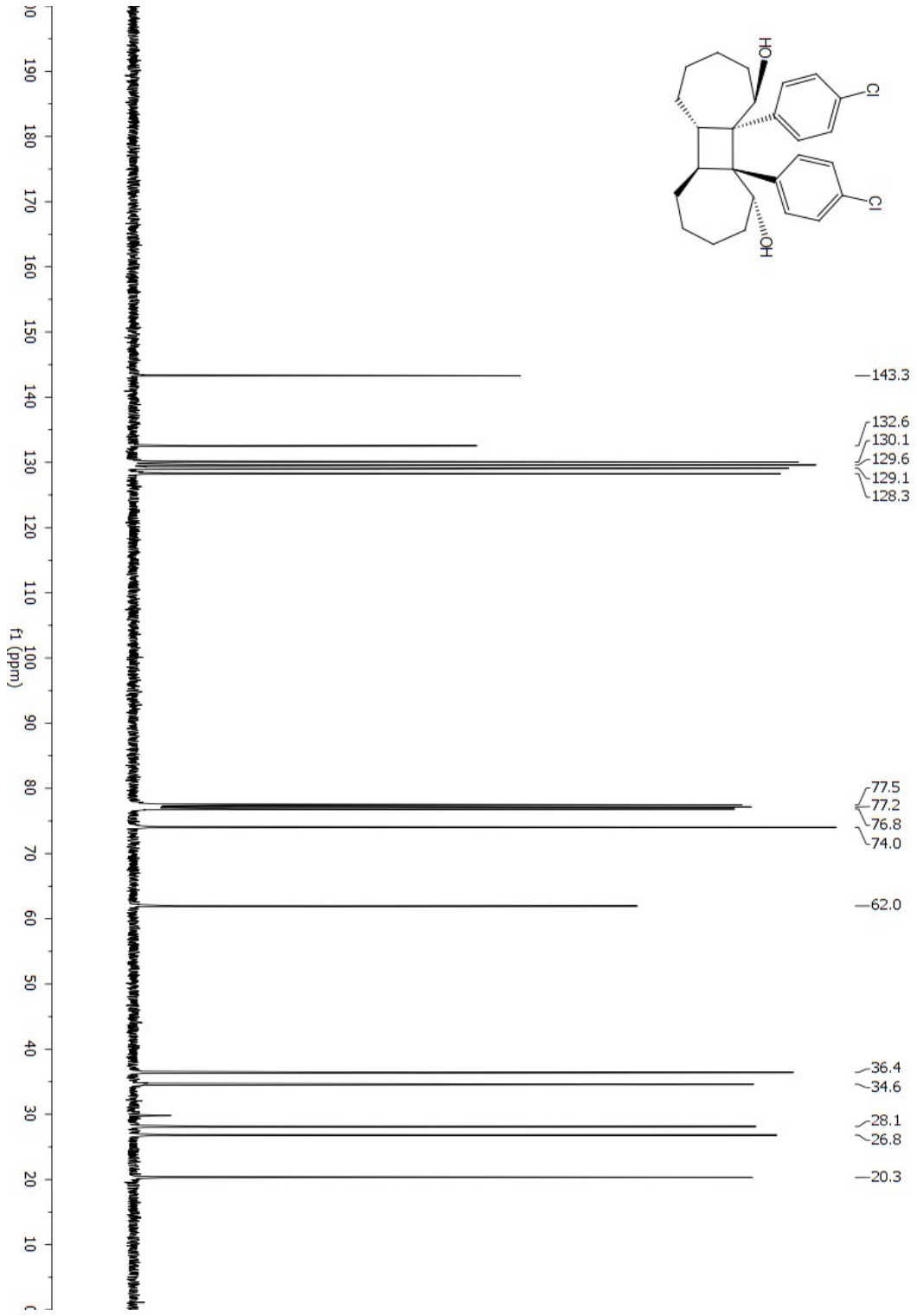
^{1}H NMR (400 MHz, $CDCl_3$)

2b (1R,5aS,5bS,10R,10aS,10bS)-10a,10b-bis(4-chlorophenyl)tetradecahydrocyclobuta-[1,2:3,4]di[7]annulene-1,10-diol



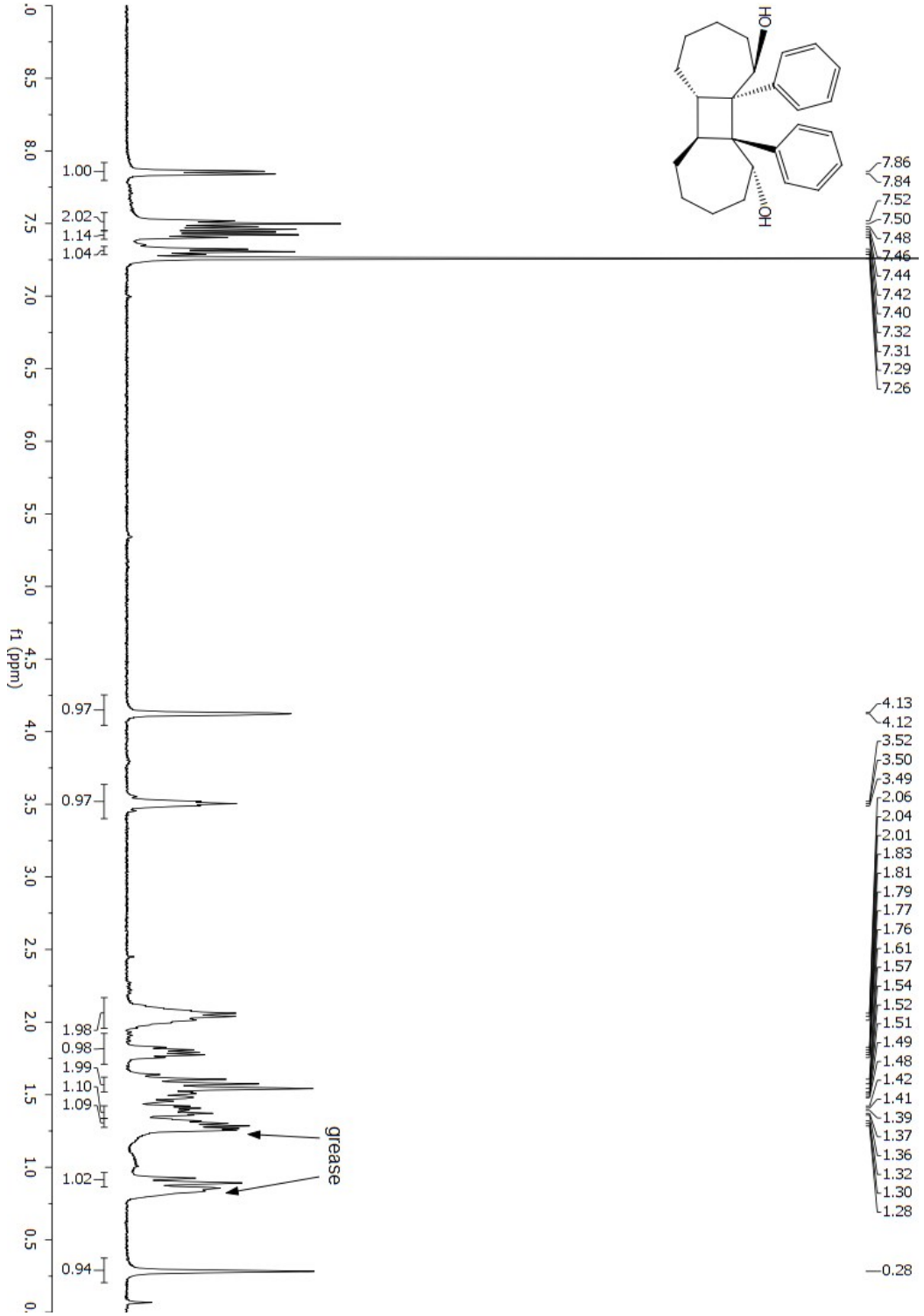
^{13}C NMR (101 MHz, $CDCl_3$)

2b (1R,5aS,5bS,10R,10aS,10bS)-10a,10b-bis(4-chlorophenyl)tetradecahydrocyclobuta-[1,2:3,4]di[7]annulene-1,10-diol



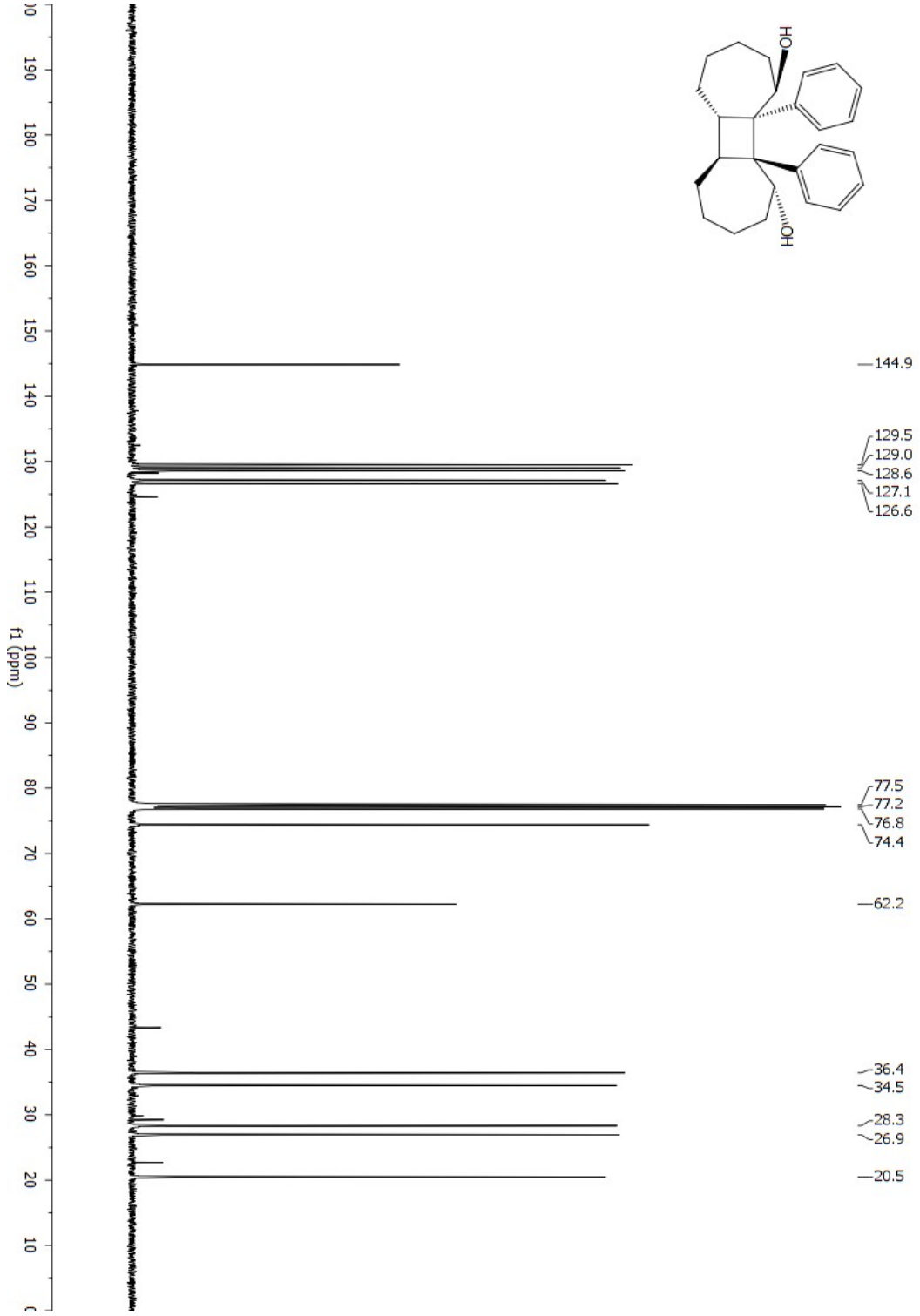
^{1}H NMR (400 MHz, $CDCl_3$)

2c (1R,5aS,5bS,10R,10aS,10bS)-10a,10b-diphenyltetradecahydrocyclobuta[1,2:3,4]di-[7]annulene-1,10-diol



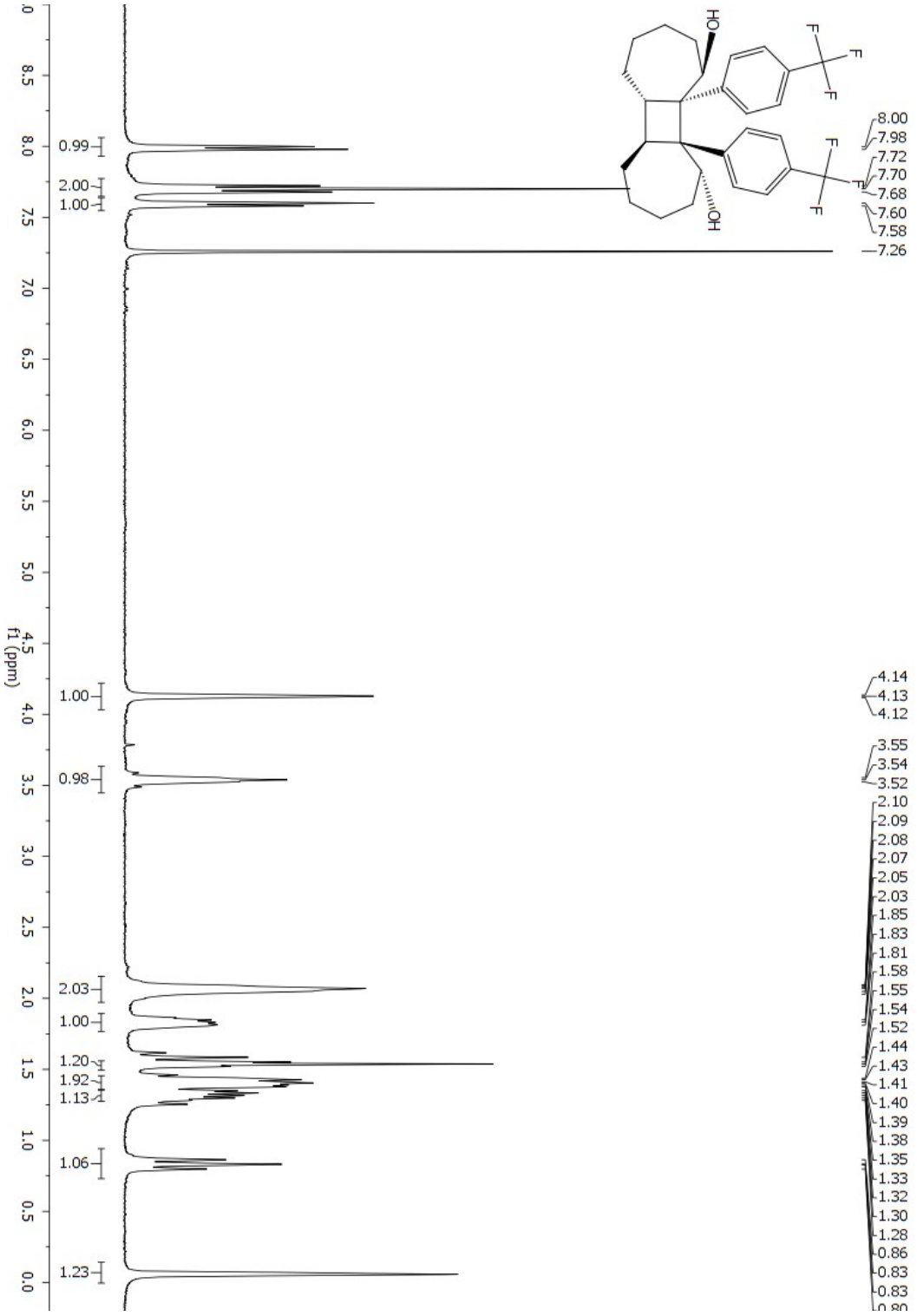
^{13}C NMR (101 MHz, $CDCl_3$)

2c (1R,5aS,5bS,10R,10aS,10bS)-10a,10b-diphenyltetradecahydrocyclobuta[1,2:3,4]di-[7]annulene-1,10-diol



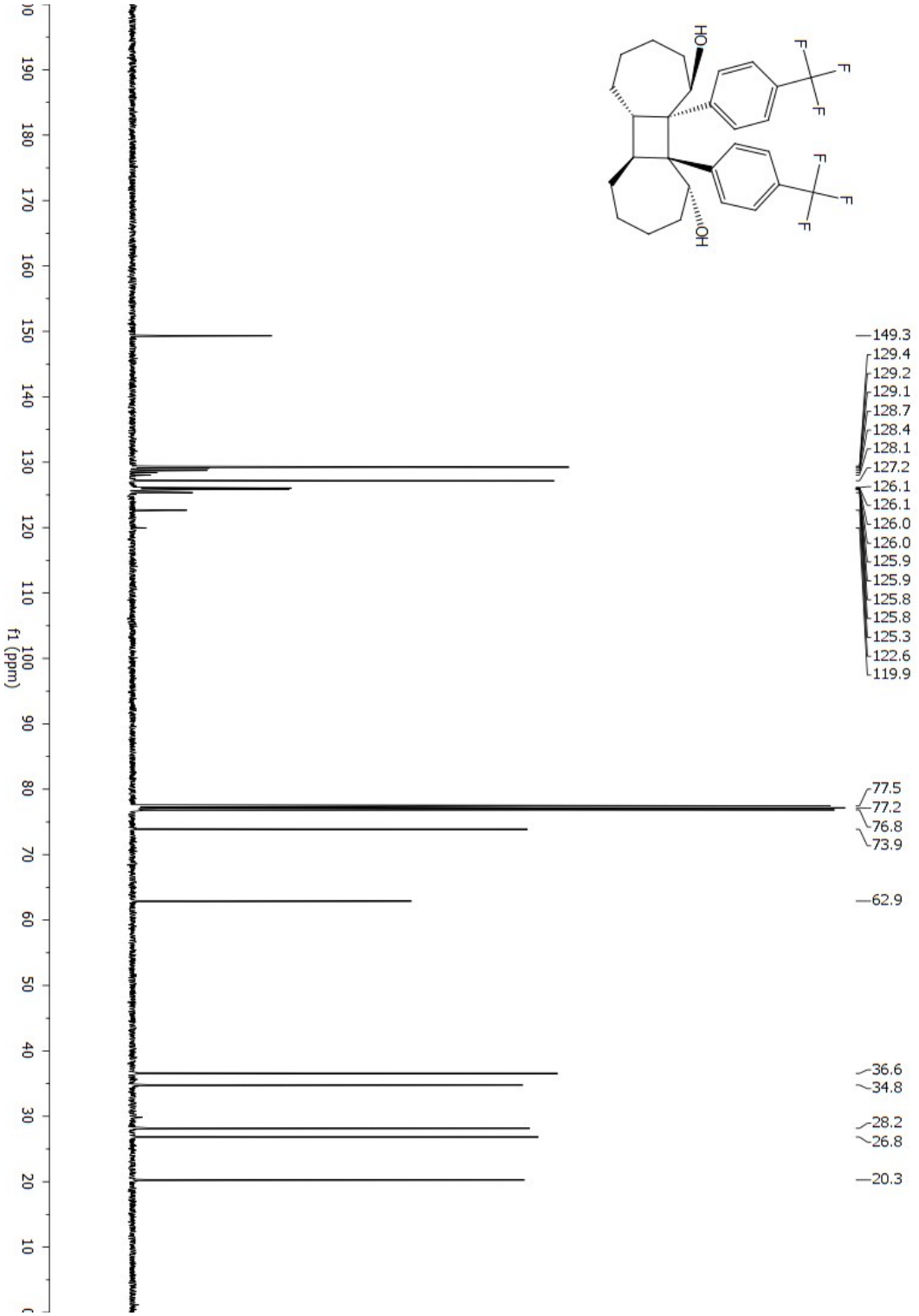
^{1}H NMR (400 MHz, $CDCl_3$)

2d (1R,5aS,5bS,10R,10aS,10bS)-10a,10b-bis(4-(trifluoromethyl)phenyl)tetradecahydro-cyclobuta[1,2:3,4]di[7]annulene-1,10-diol



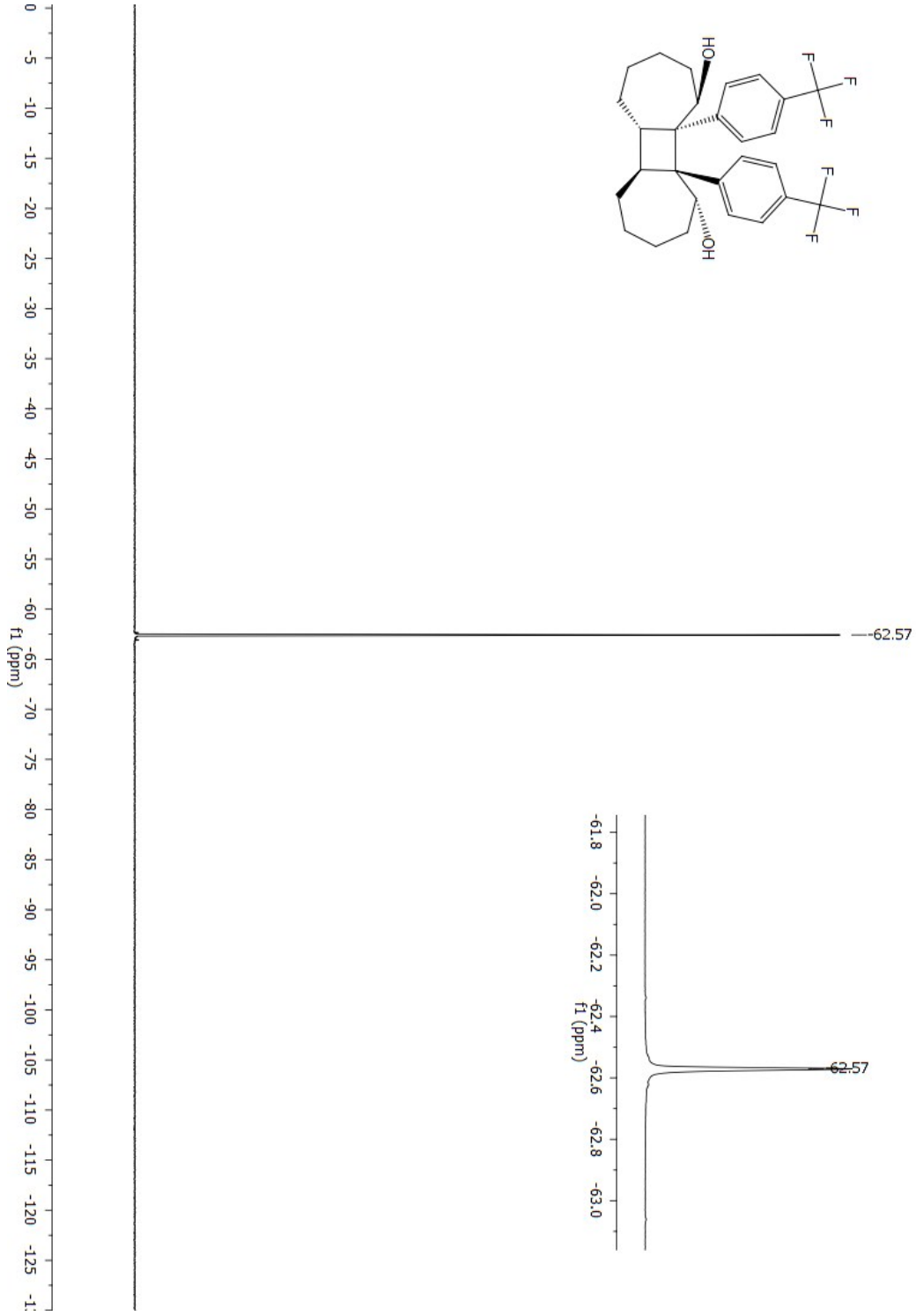
^{13}C NMR (101 MHz, $CDCl_3$)

2d (1R,5aS,5bS,10R,10aS,10bS)-10a,10b-bis(4-(trifluoromethyl)phenyl)tetradecahydro-cyclobuta[1,2:3,4]di[7]annulene-1,10-diol



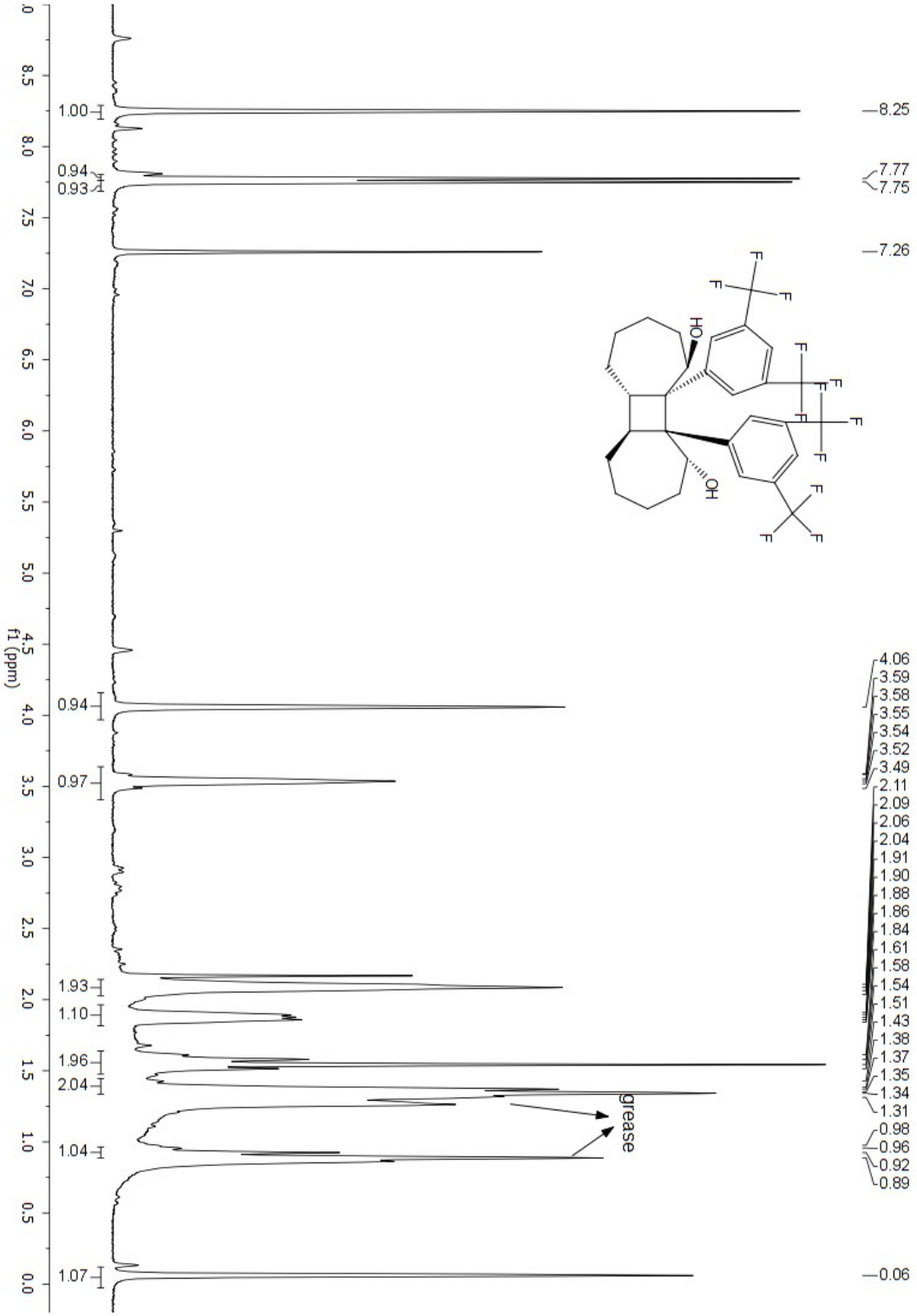
^{19}F NMR (376 MHz, $CDCl_3$)

2d (1R,5aS,5bS,10R,10aS,10bS)-10a,10b-bis(4-(trifluoromethyl)phenyl)tetradecahydro-cyclobuta[1,2:3,4]di[7]annulene-1,10-diol



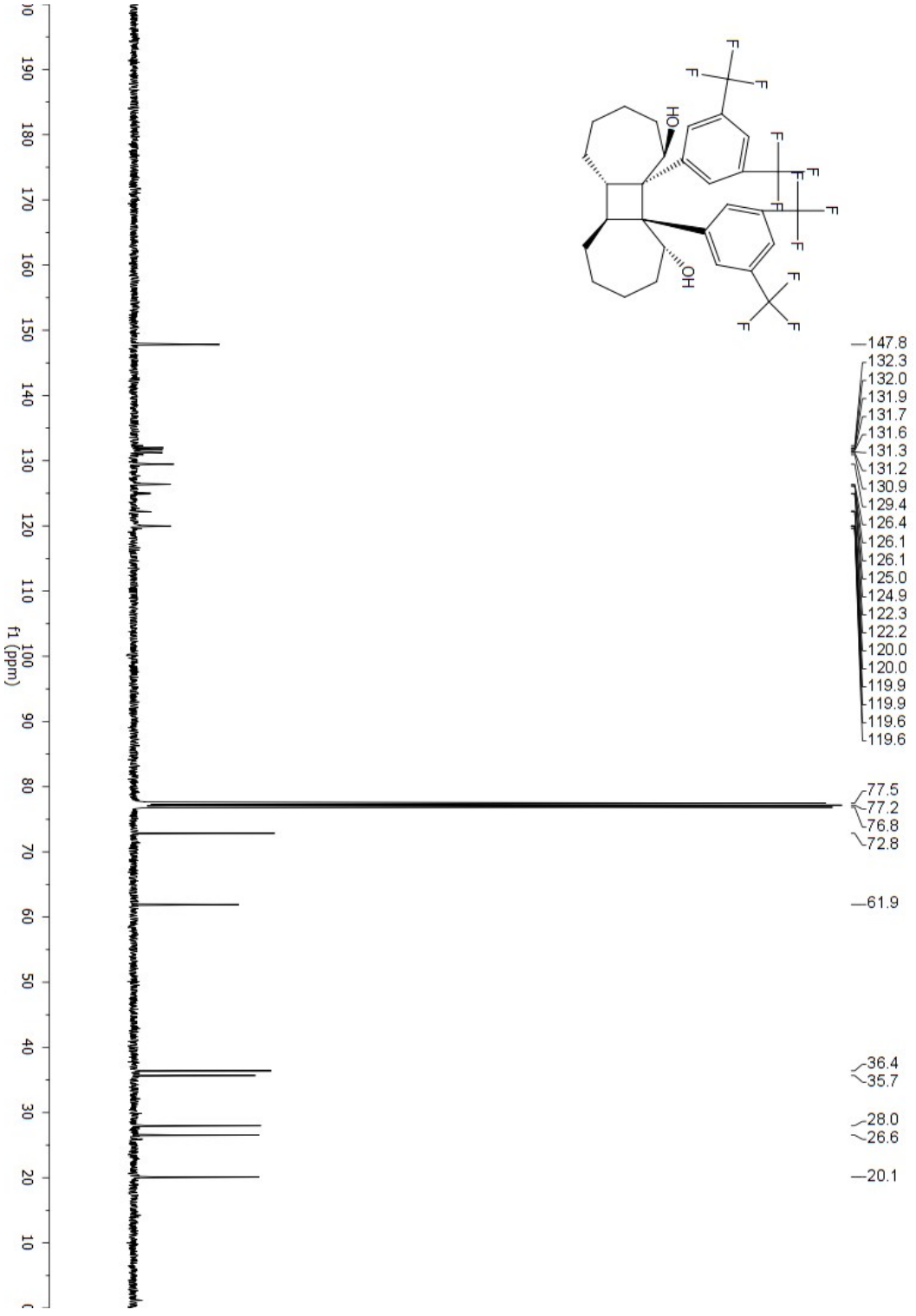
^{1}H NMR (400 MHz, $CDCl_3$)

2e (1R,5aS,5bS,10R,10aS,10bS)-10a,10b-bis(3,5-bis(trifluoromethyl)phenyl)tetradeca-hydrocyclobuta[1,2:3,4]di[7]annulene-1,10-diol



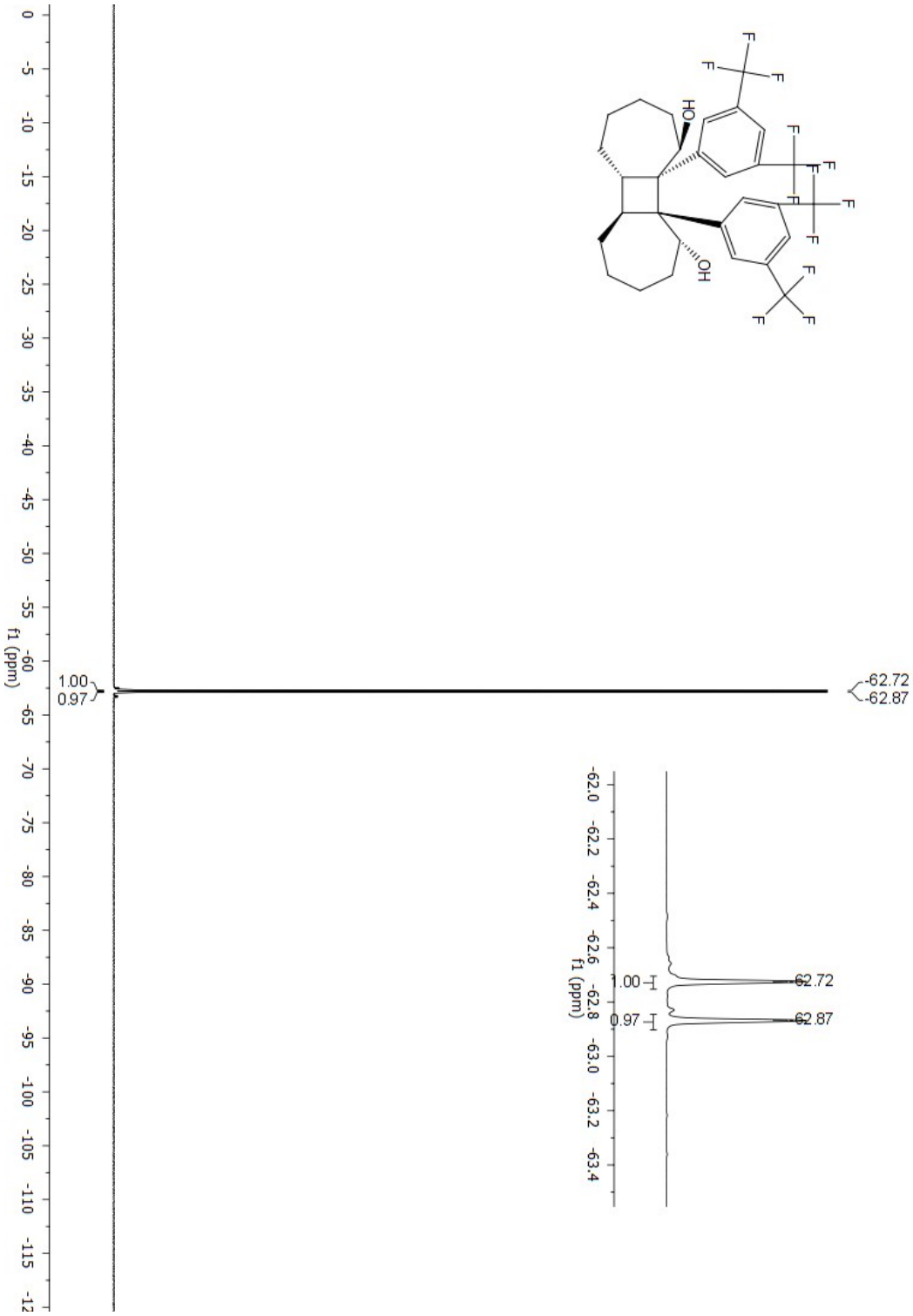
^{13}C NMR (101 MHz, $CDCl_3$)

2e (1R,5aS,5bS,10R,10aS,10bS)-10a,10b-bis(3,5-bis(trifluoromethyl)phenyl)tetradeca-hydrocyclobuta[1,2:3,4]di[7]annulene-1,10-diol



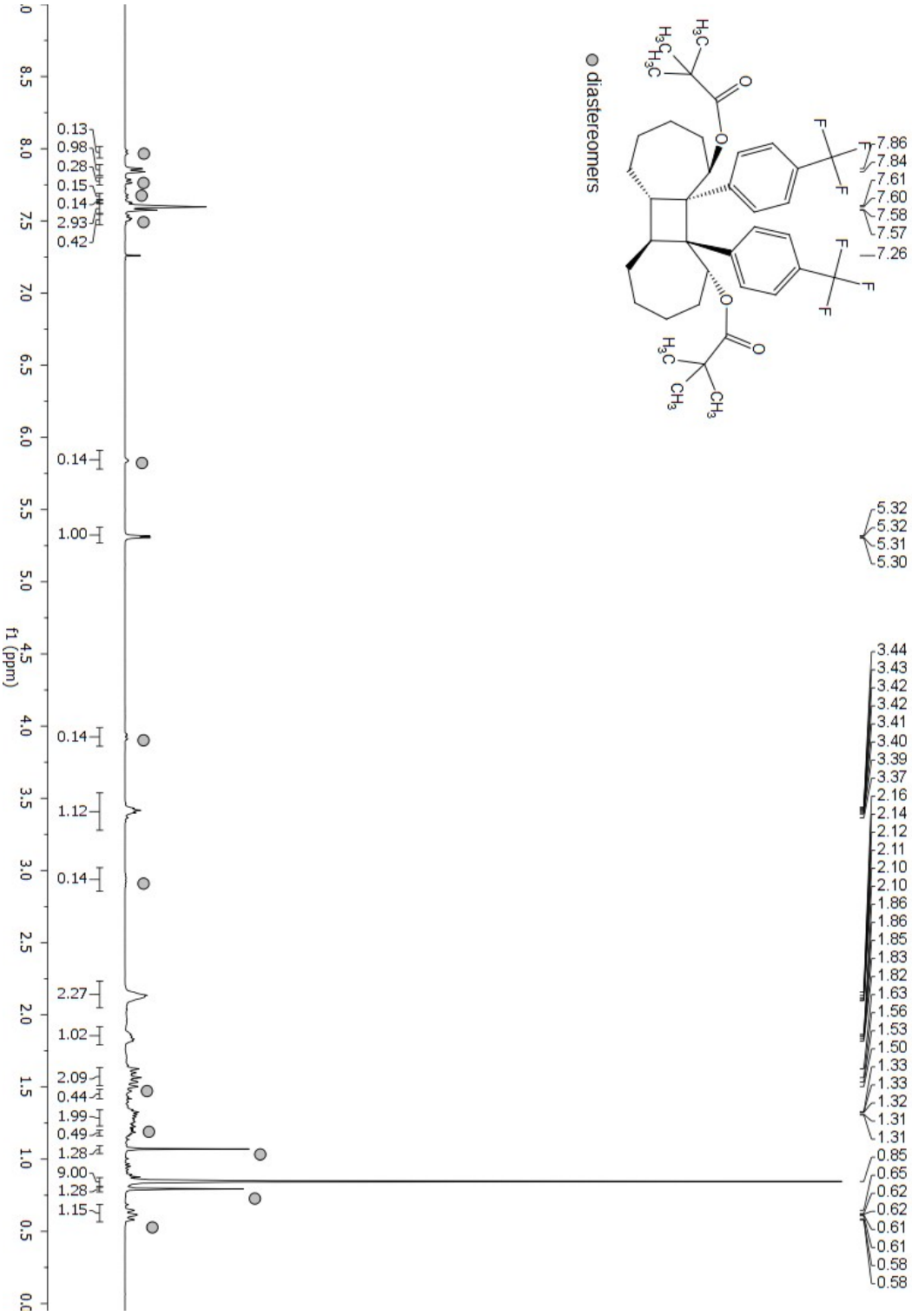
^{19}F NMR (376 MHz, $CDCl_3$)

2e (1R,5aS,5bS,10R,10aS,10bS)-10a,10b-bis(3,5-bis(trifluoromethyl)phenyl)tetradeca-hydrocyclobuta[1,2:3,4]di[7]annulene-1,10-diol



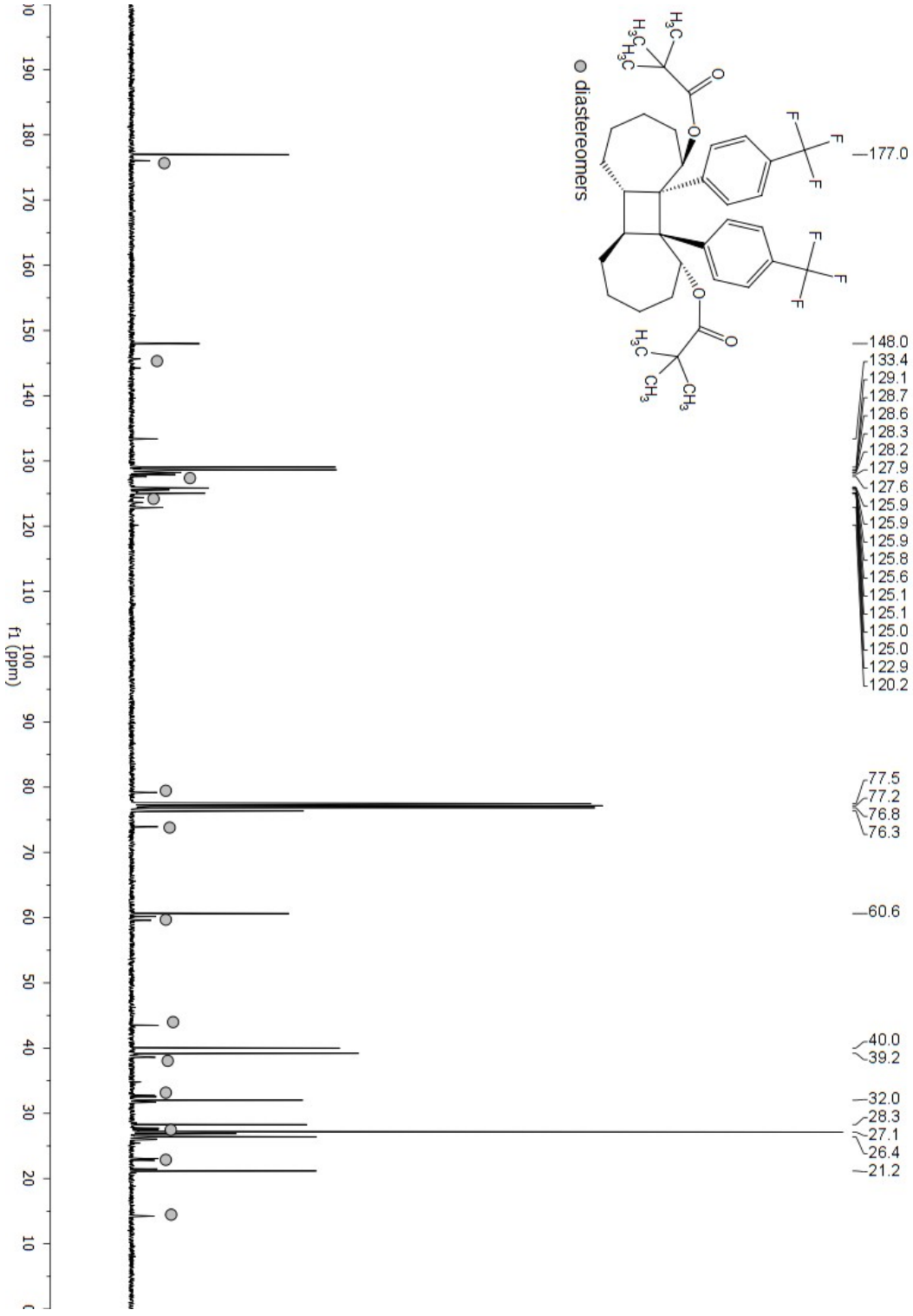
^{1}H NMR (400 MHz, $CDCl_3$)

2f (1R,5aS,5bS,10R,10aS,10bS)-10a,10b-bis(4-(trifluoromethyl)phenyl)tetradecahydro-cyclobuta[1,2:3,4]di[7]annulene-1,10-diyl bis(2,2-dimethylpropanoate)



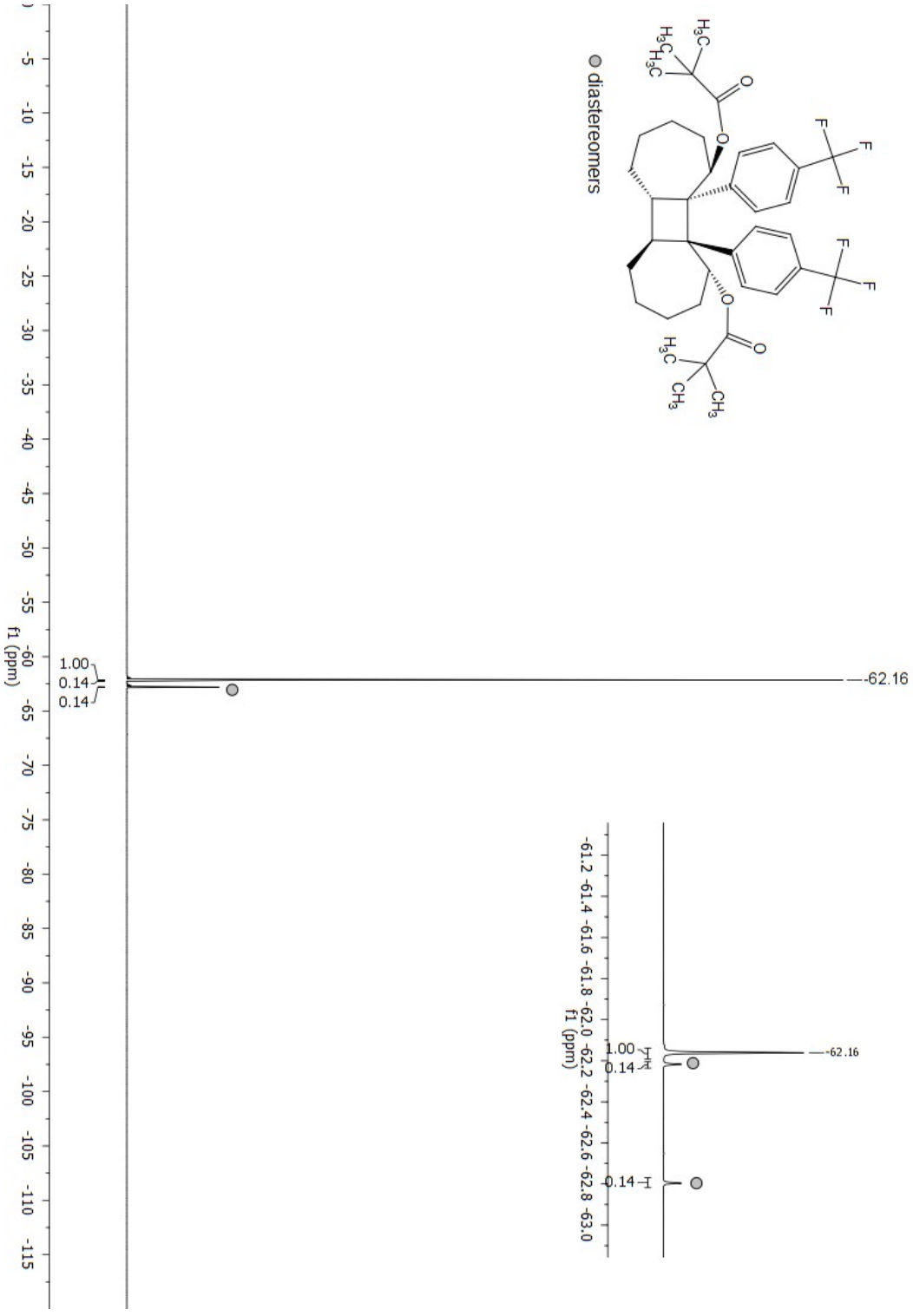
^{13}C NMR (101 MHz, $CDCl_3$)

2f (1R,5aS,5bS,10R,10aS,10bS)-10a,10b-bis(4-(trifluoromethyl)phenyl)tetradecahydro-cyclobuta[1,2:3,4]di[7]annulene-1,10-diyl bis(2,2-dimethylpropanoate)



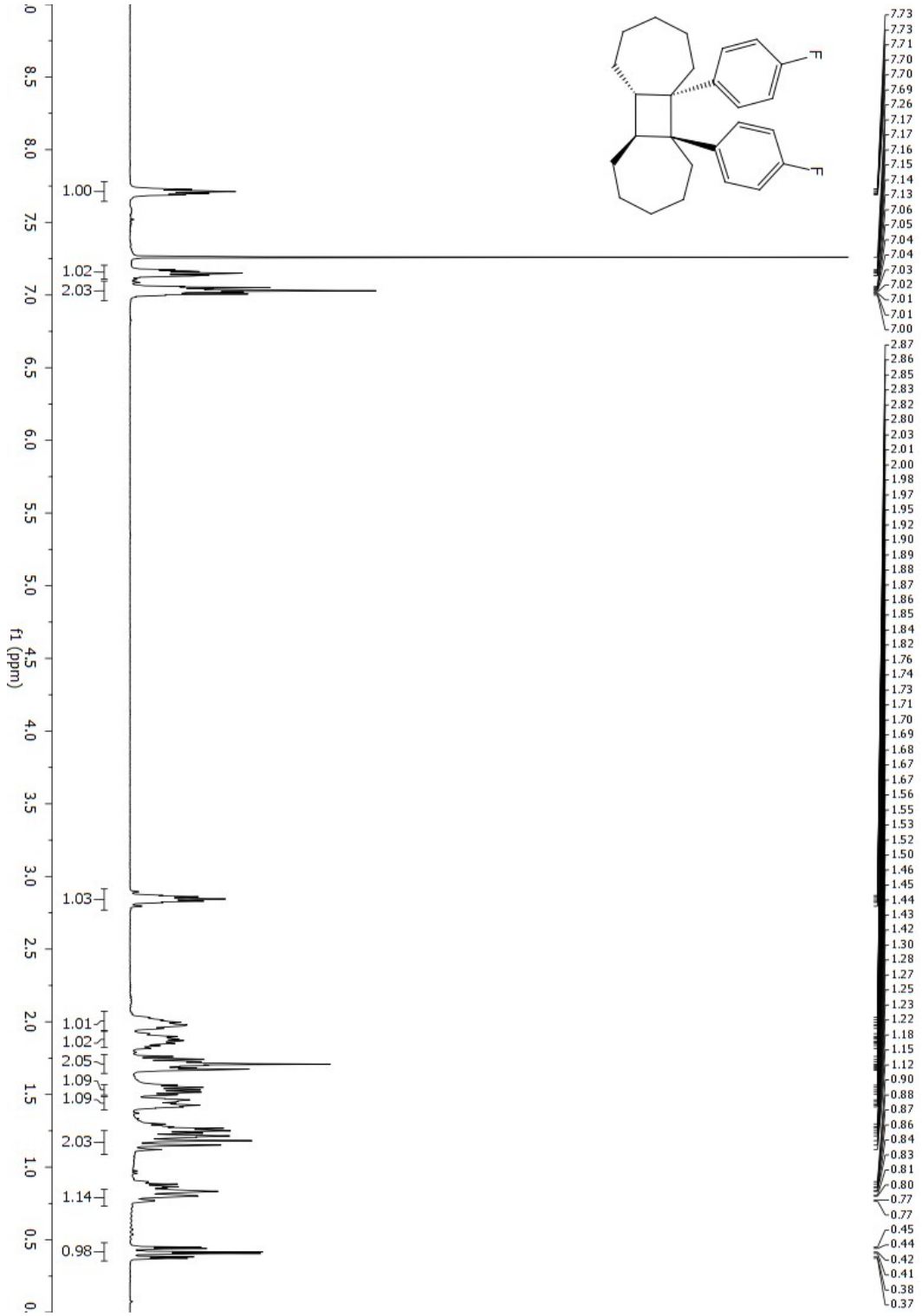
^{19}F NMR (376 MHz, $CDCl_3$)

2f (1R,5aS,5bS,10R,10aS,10bS)-10a,10b-bis(4-(trifluoromethyl)phenyl)tetradecahydro-cyclobuta[1,2:3,4]di[7]annulene-1,10-diyl bis(2,2-dimethylpropanoate)



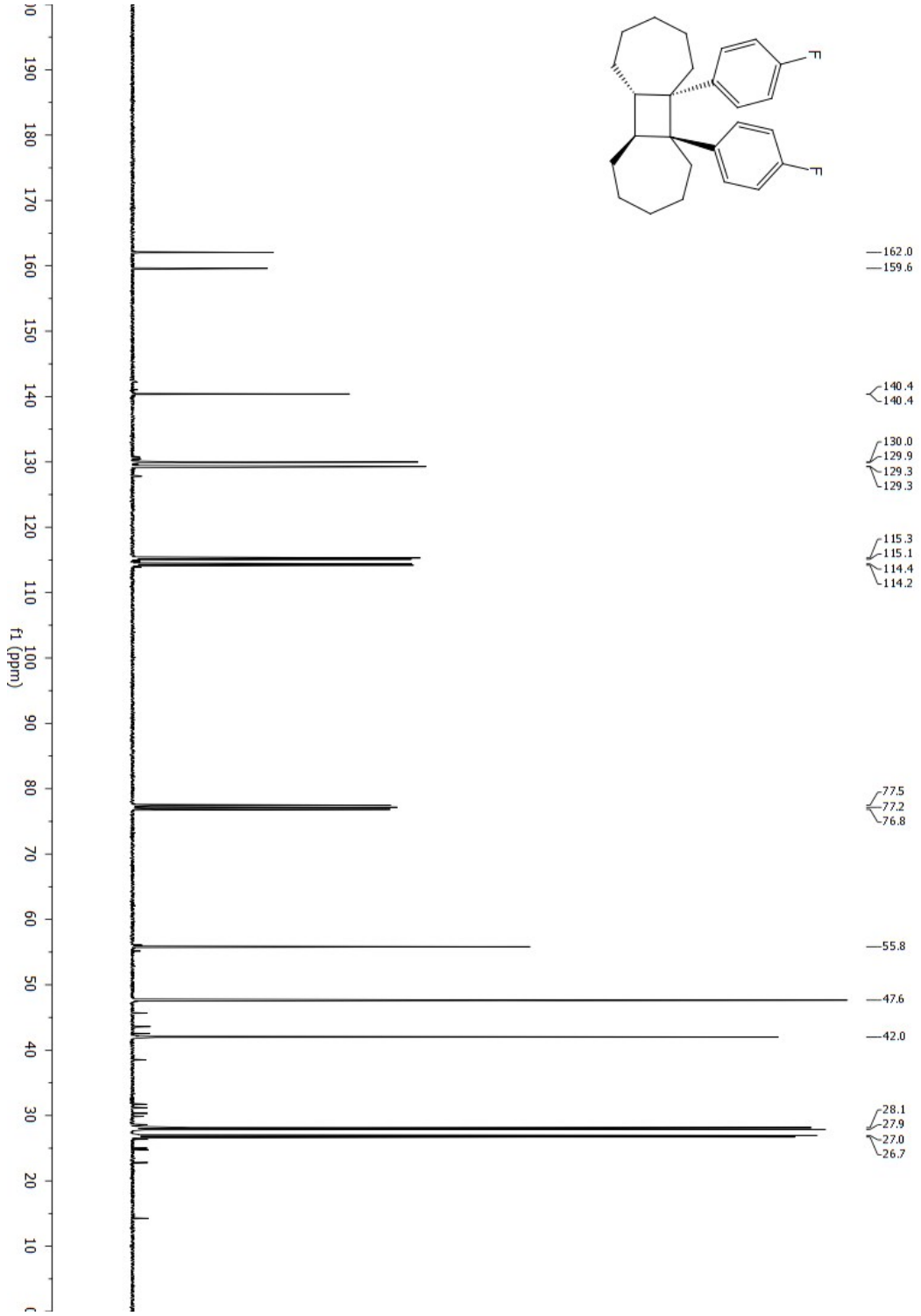
^{1}H NMR (400 MHz, $CDCl_3$)

2g (5aR,5bR,10aS,10bS)-5a,5b-bis(4-fluorophenyl)tetradecahydrocyclobuta[1,2:3,4]-di[7]annulene



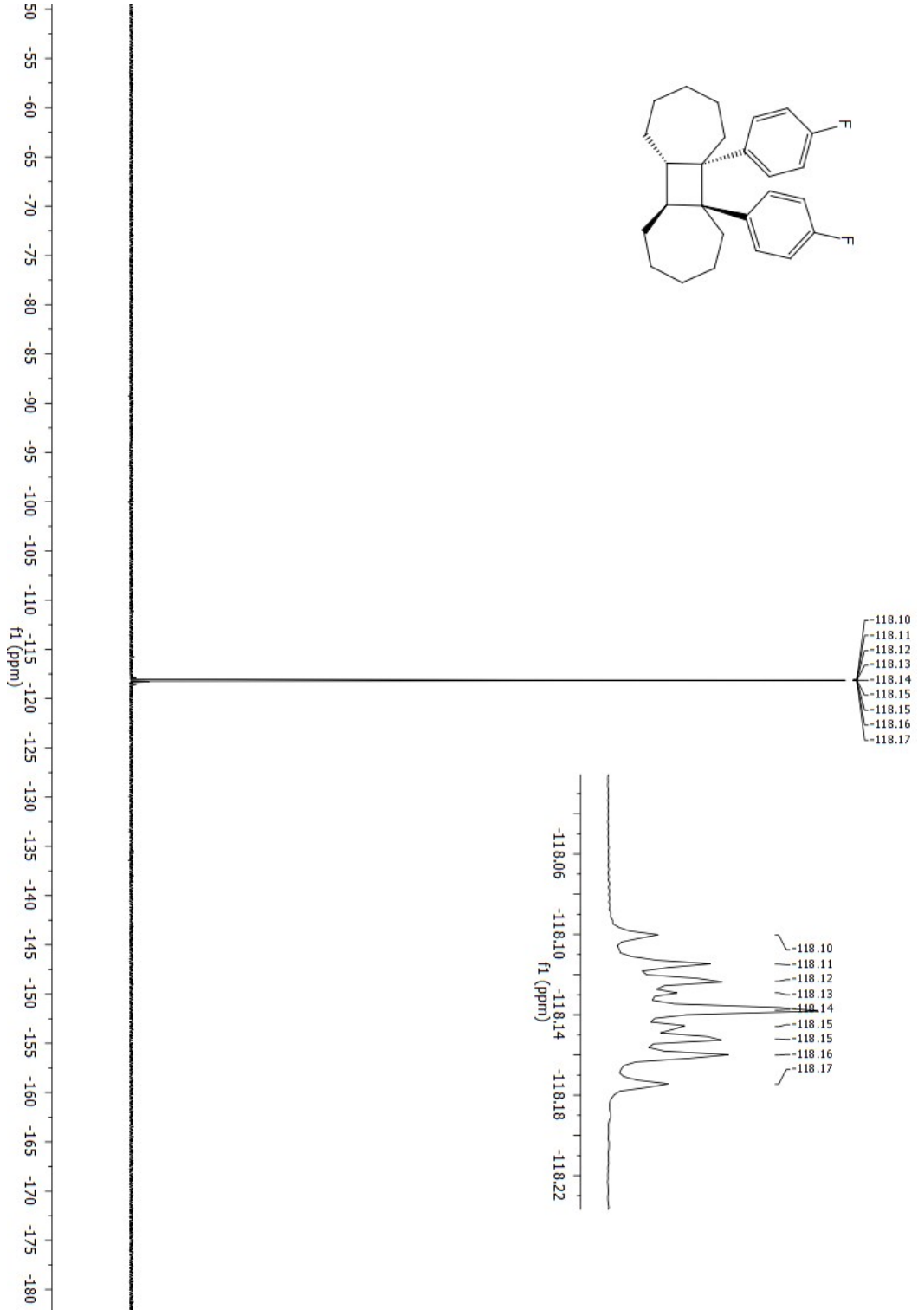
^{13}C NMR (101 MHz, $CDCl_3$)

2g (5aR,5bR,10aS,10bS)-5a,5b-bis(4-fluorophenyl)tetradecahydrocyclobuta[1,2:3,4]-di[7]annulene



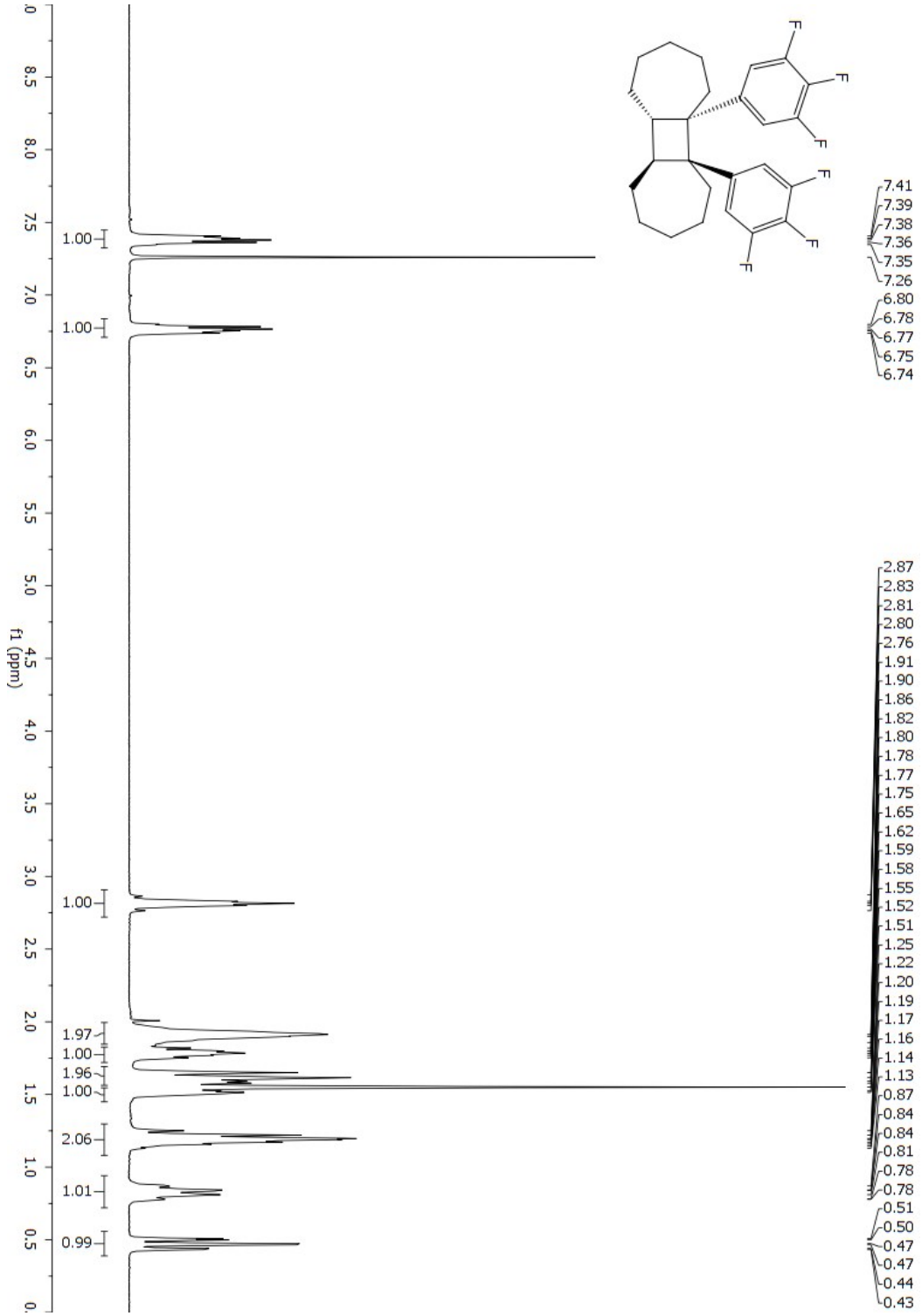
^{19}F NMR (376 MHz, $CDCl_3$)

2g (5aR,5bR,10aS,10bS)-5a,5b-bis(4-fluorophenyl)tetradecahydrocyclobuta[1,2:3,4]-di[7]annulene



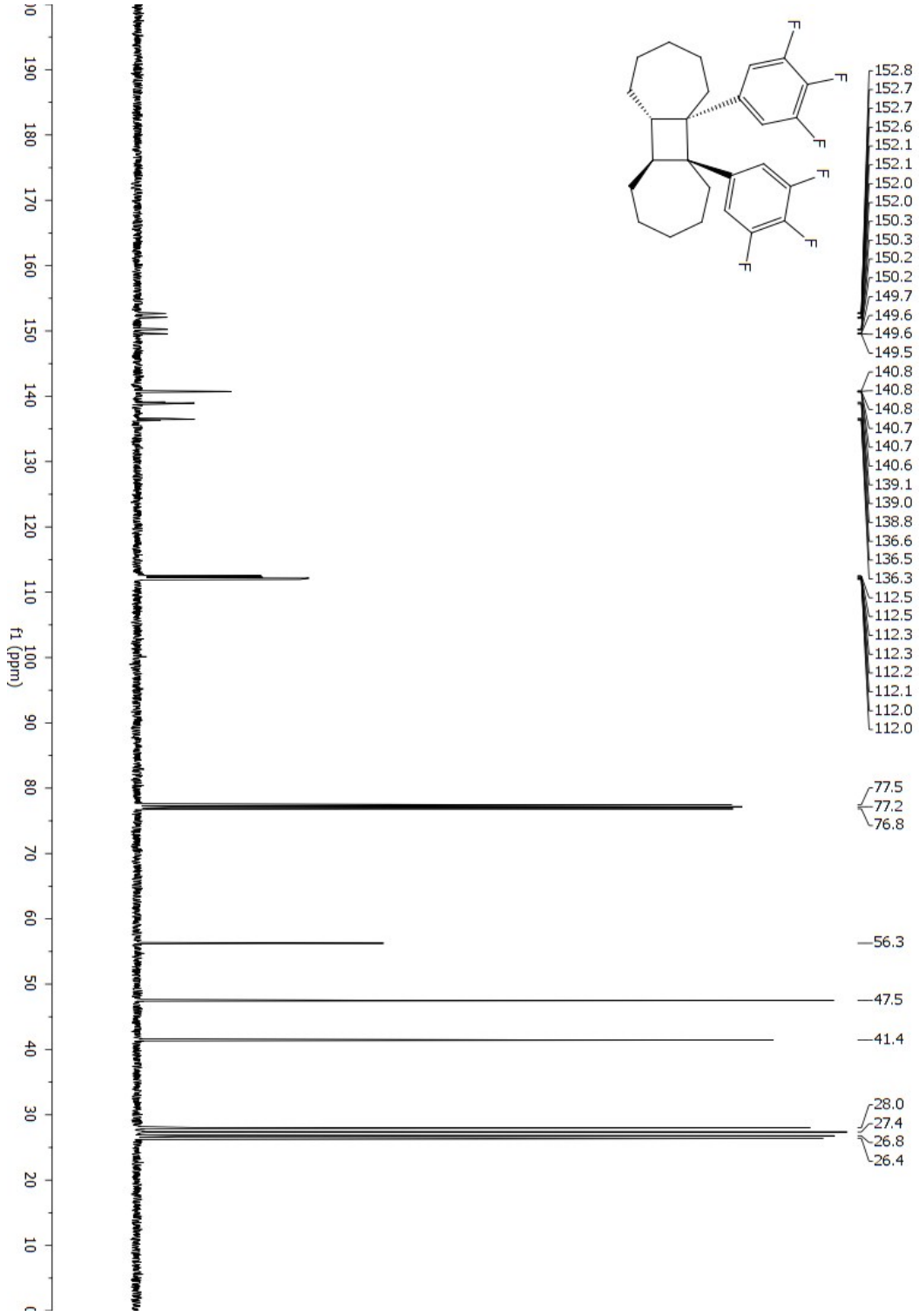
^{1}H NMR (400 MHz, $CDCl_3$)

2h (5aR,5bR,10aS,10bS)-5a,5b-bis(3,4,5-trifluorophenyl)tetradecahydrocyclobuta-[1,2:3,4]di[7]annulene



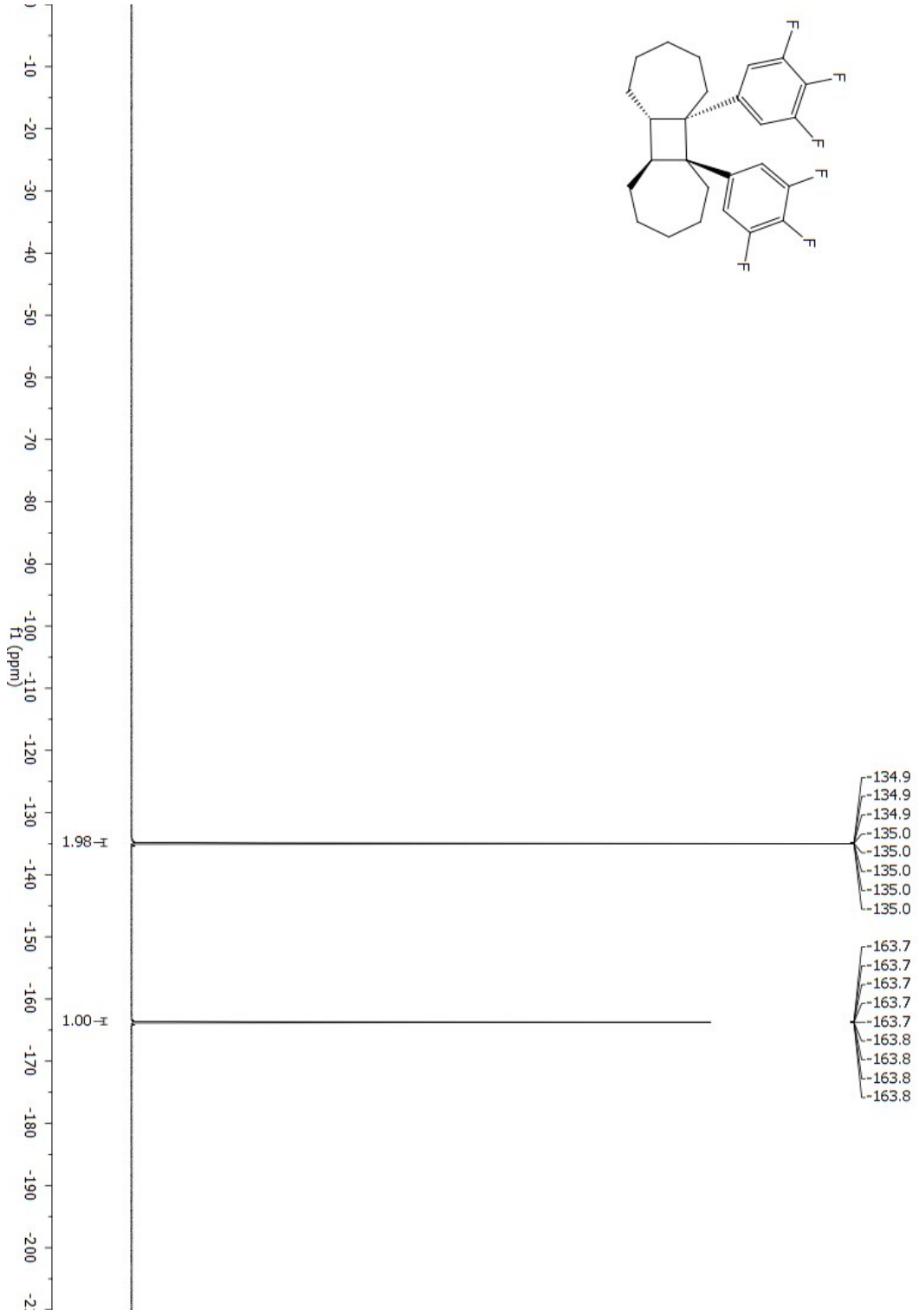
^{13}C NMR (101 MHz, $CDCl_3$)

2h (5aR,5bR,10aS,10bS)-5a,5b-bis(3,4,5-trifluorophenyl)tetradecahydrocyclobuta-[1,2:3,4]di[7]annulene



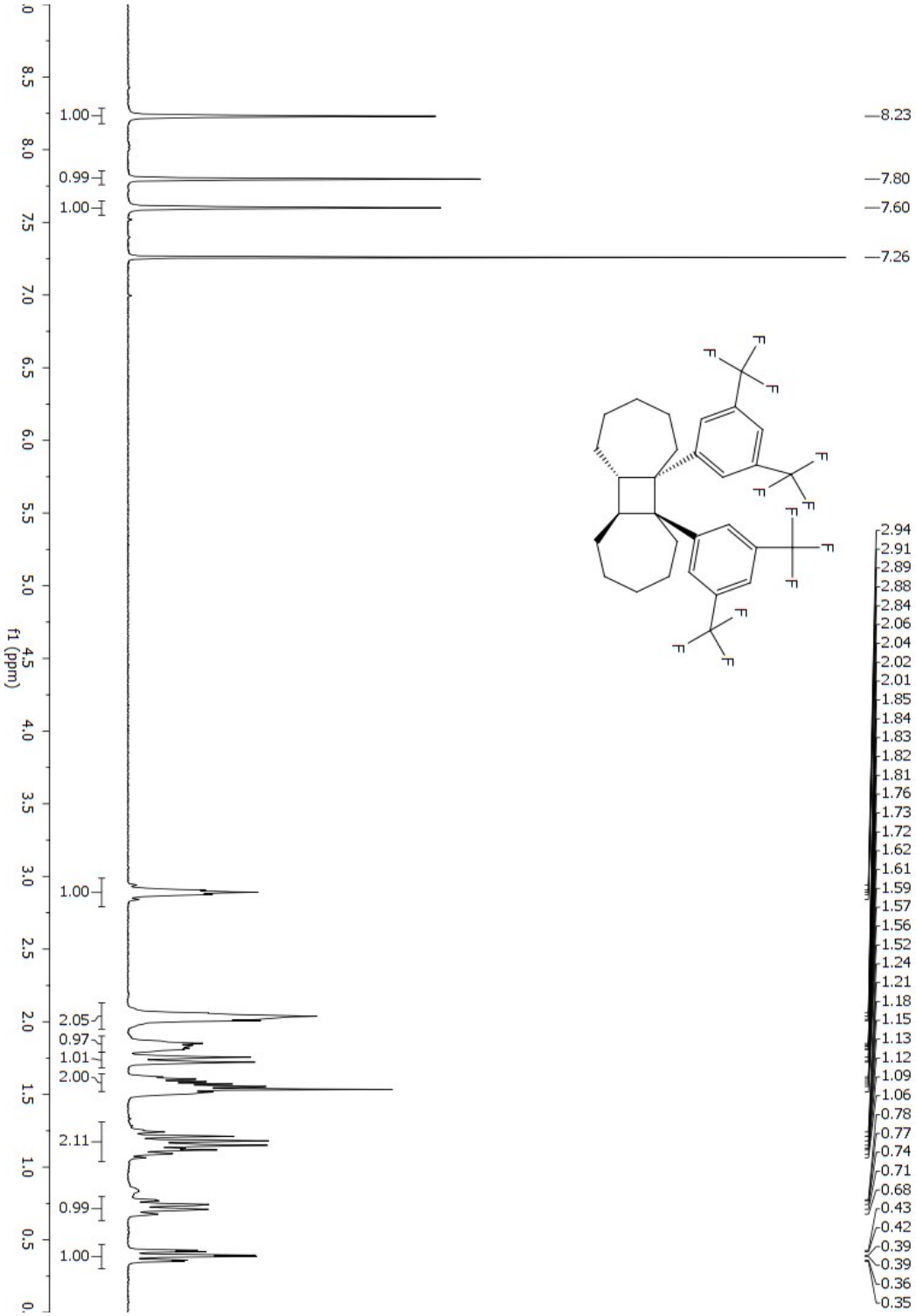
^{19}F NMR (376 MHz, $CDCl_3$)

2h (5aR,5bR,10aS,10bS)-5a,5b-bis(3,4,5-trifluorophenyl)tetradecahydrocyclobuta-[1,2:3,4]di[7]annulene



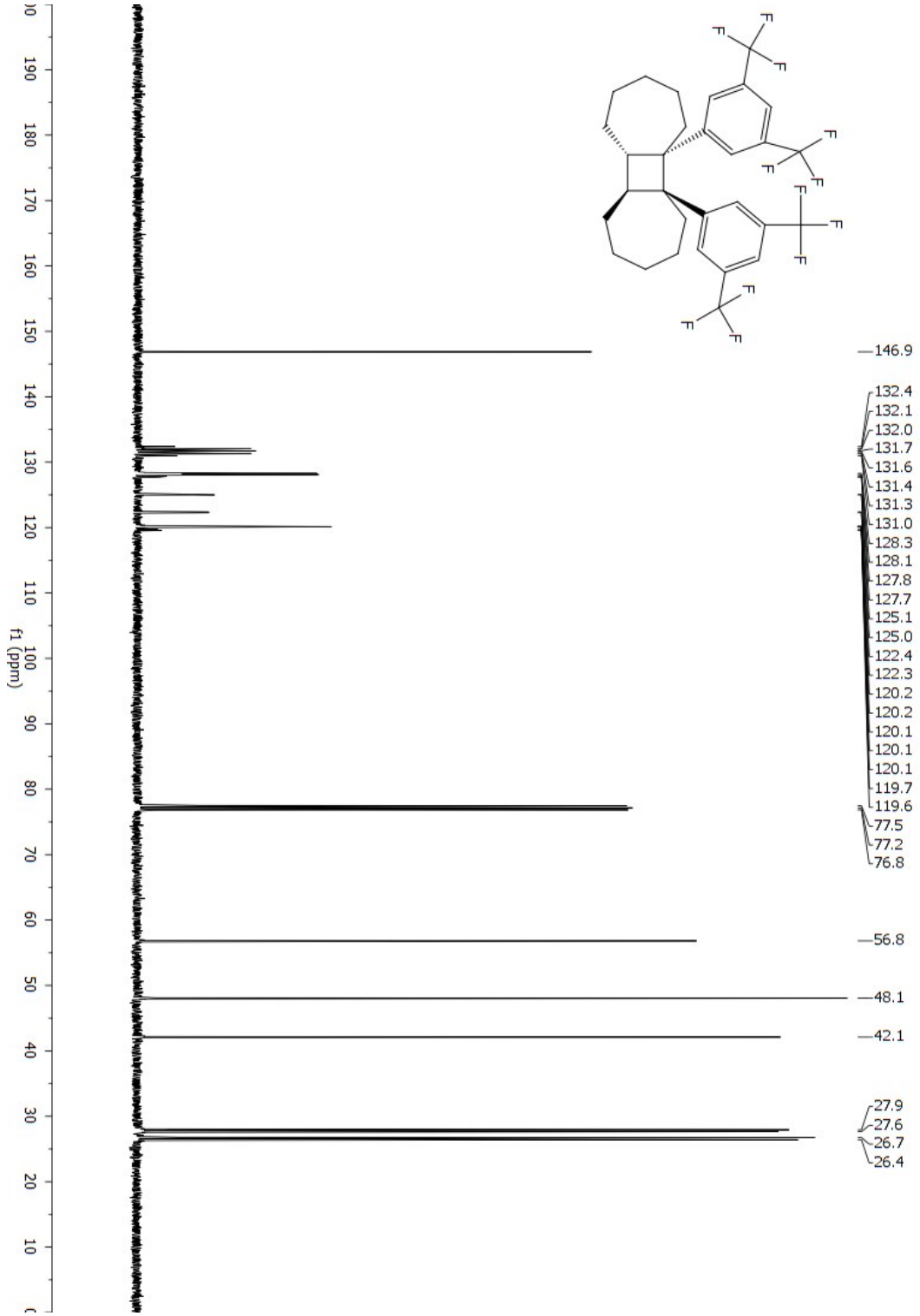
^{1}H NMR (400 MHz, $CDCl_3$)

2i (5aR,5bR,10aS,10bS)-5a,5b-bis(3,5-bis(trifluoromethyl)phenyl)tetradecahydrocyclobuta[1,2:3,4]di[7]annulene



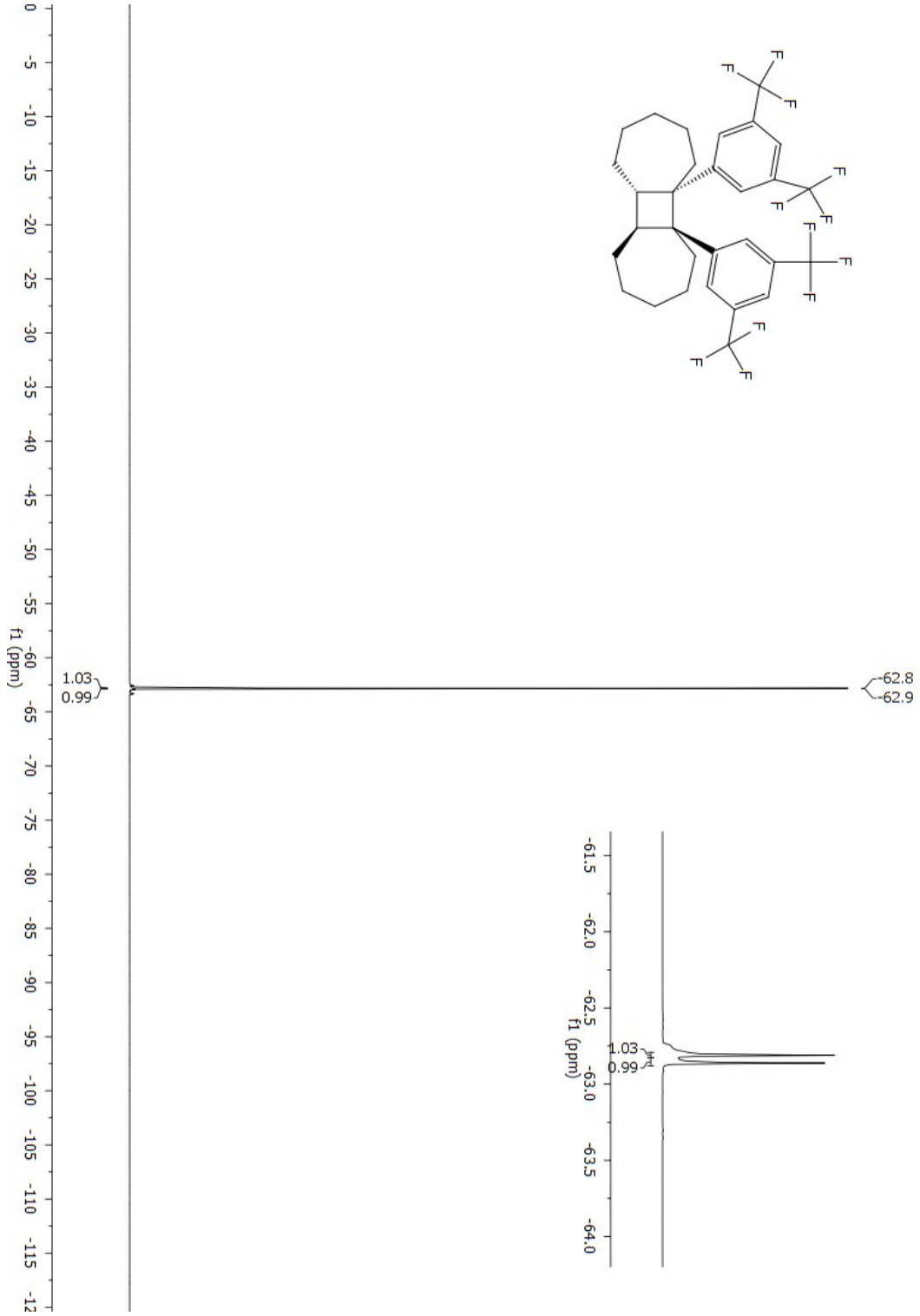
^{13}C NMR (101 MHz, $CDCl_3$)

2i (5aR,5bR,10aS,10bS)-5a,5b-bis(3,5-bis(trifluoromethyl)phenyl)tetradecahydrocyclobuta[1,2:3,4]di[7]annulene



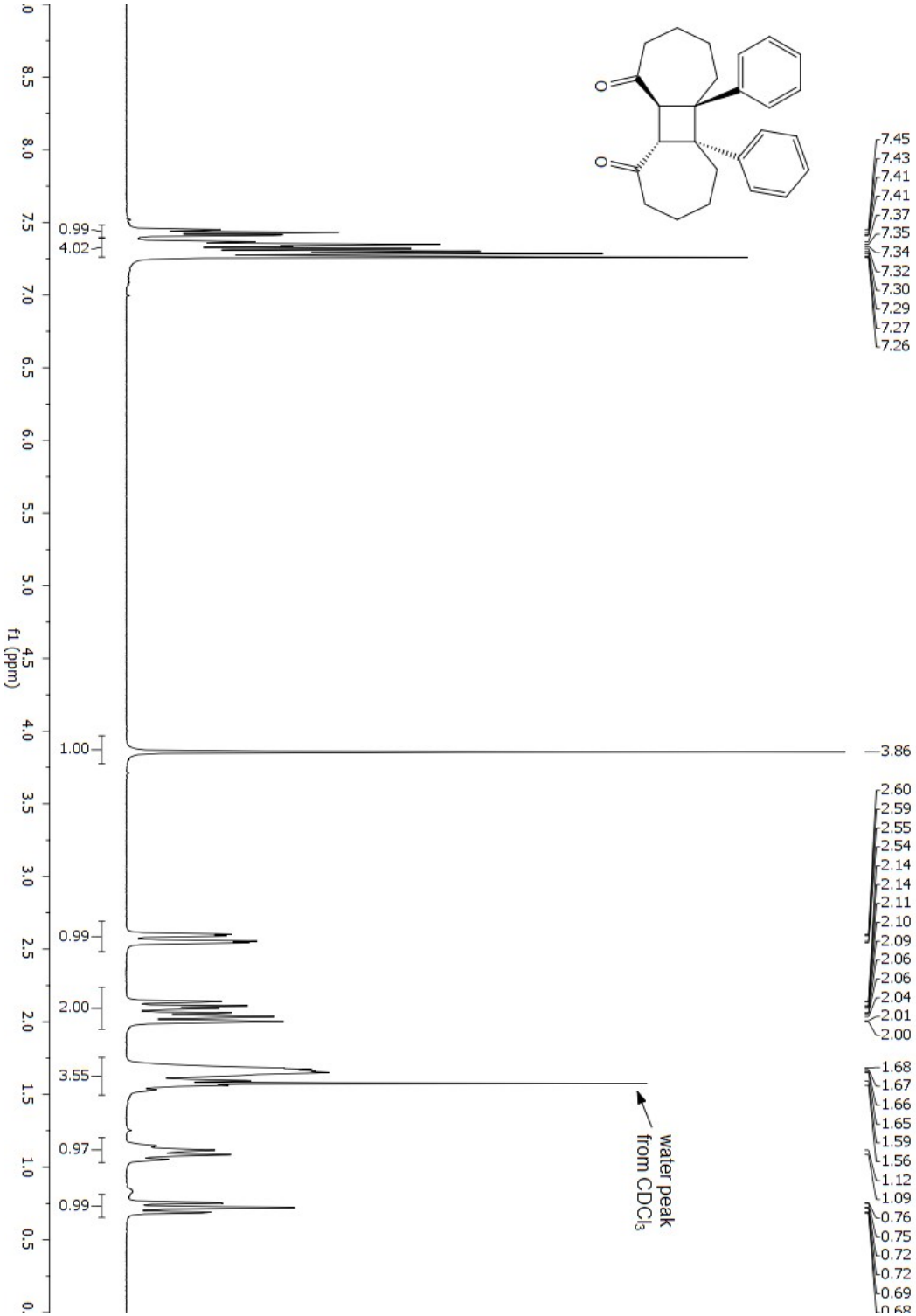
^{19}F NMR (376 MHz, $CDCl_3$)

2i (5aR,5bR,10aS,10bS)-5a,5b-bis(3,5-bis(trifluoromethyl)phenyl)tetradecahydrocyclobuta[1,2:3,4]di[7]annulene



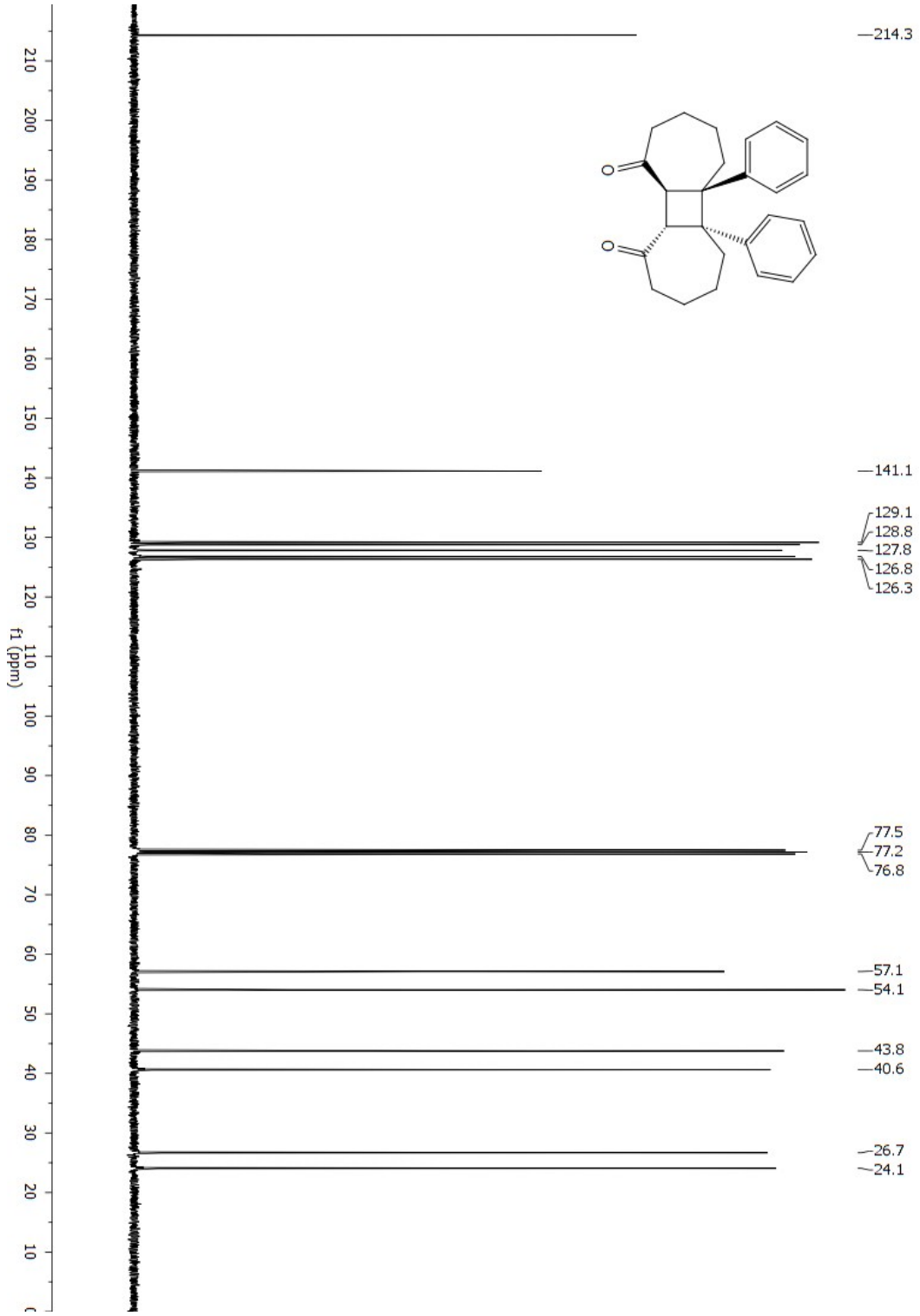
^{1}H NMR (400 MHz, $CDCl_3$)

2j (5aR,5bR,10aS,10bS)-5a,5b-diphenyldodecahydrocyclobuta[1,2:3,4]di[7]annulene-1,10-dione



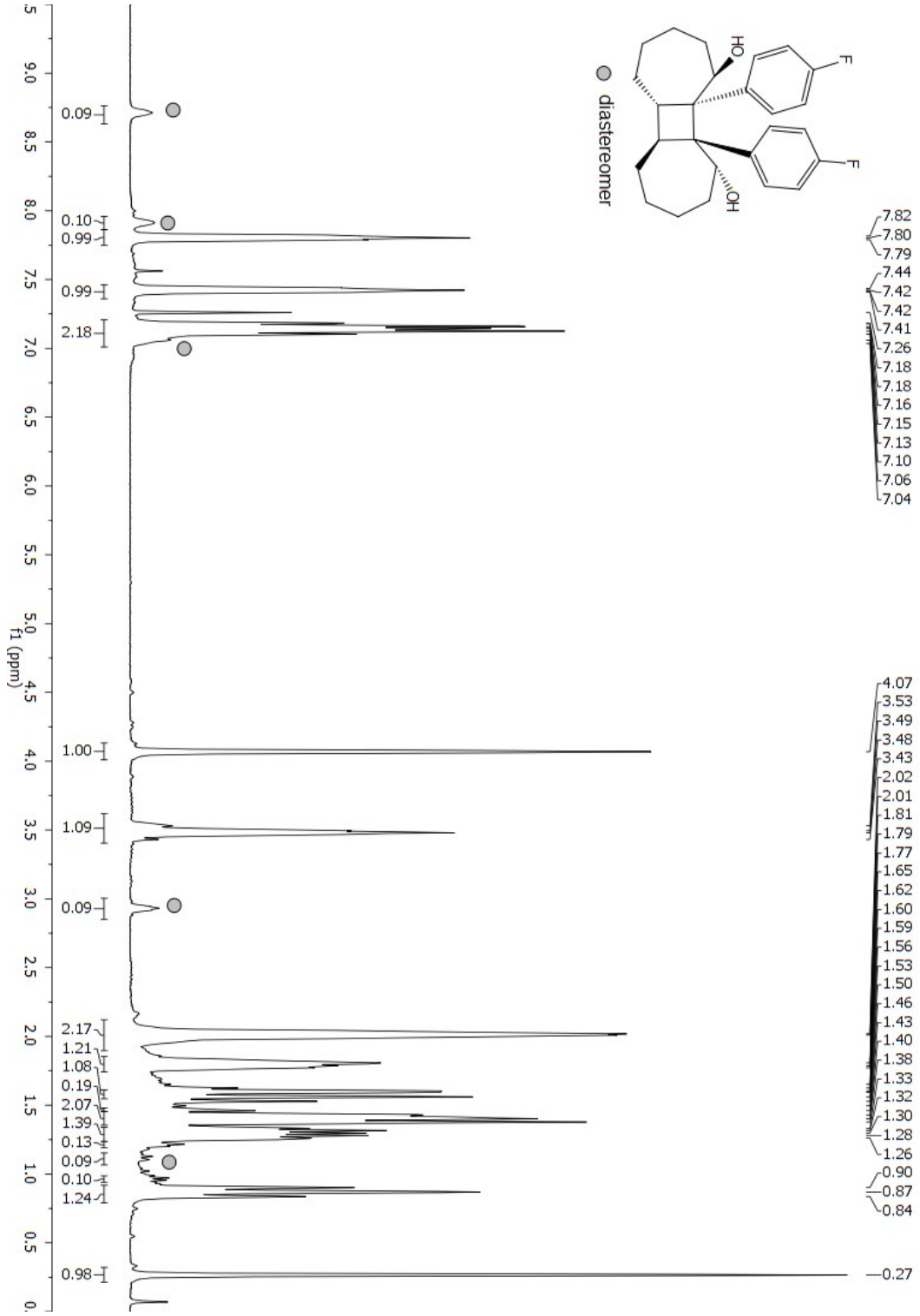
^{13}C NMR (101 MHz, $CDCl_3$)

2j (5aR,5bR,10aS,10bS)-5a,5b-diphenyldodecahydrocyclobuta[1,2:3,4]di[7]annulene-1,10-dione



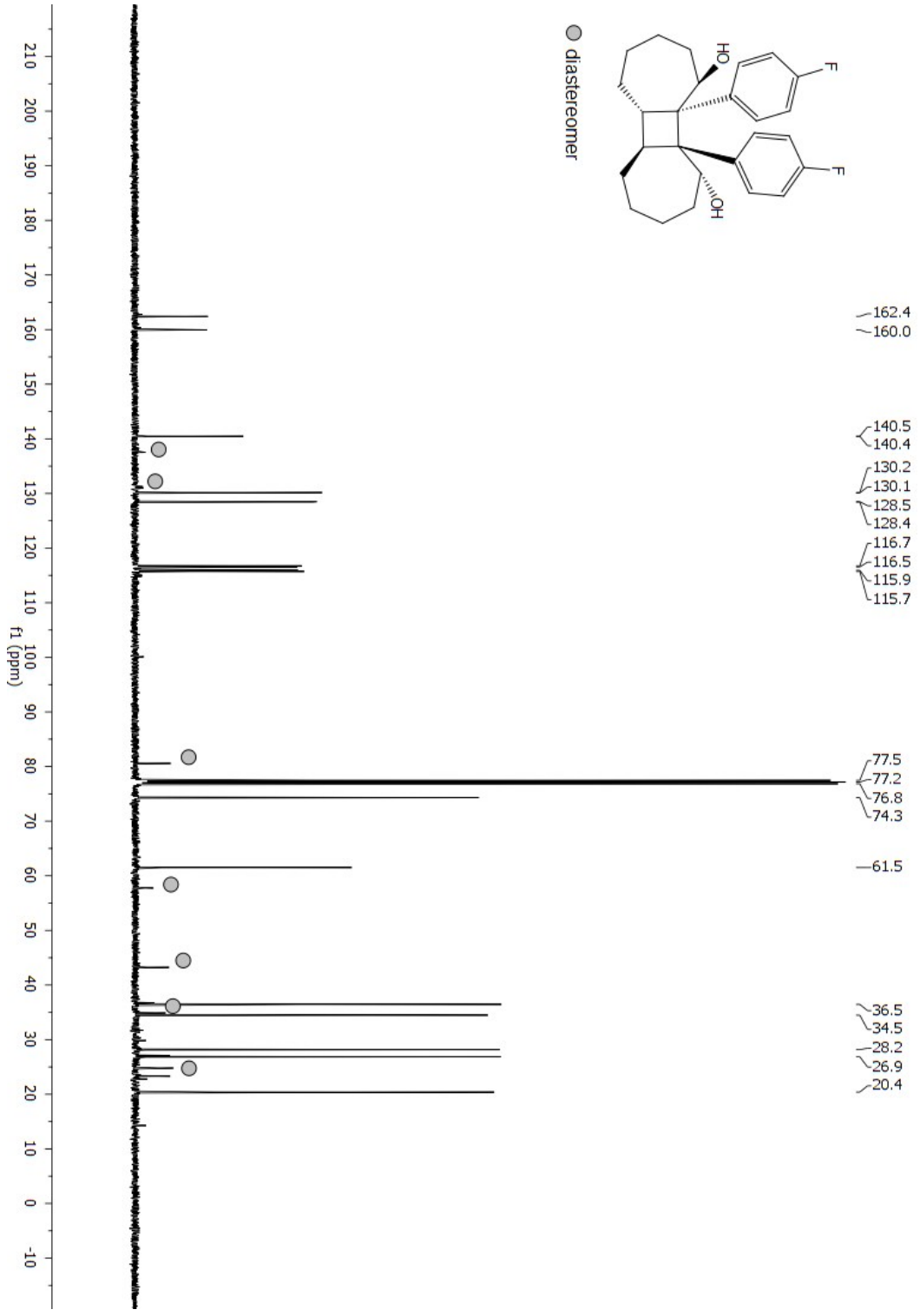
^{1}H NMR (400 MHz, $CDCl_3$)

2k (1R,5aS,5bS,10R,10aS,10bS)-10a,10b-bis(4-fluorophenyl)tetradecahydrocyclobuta-[1,2:3,4]di[7]annulene-1,10-diol



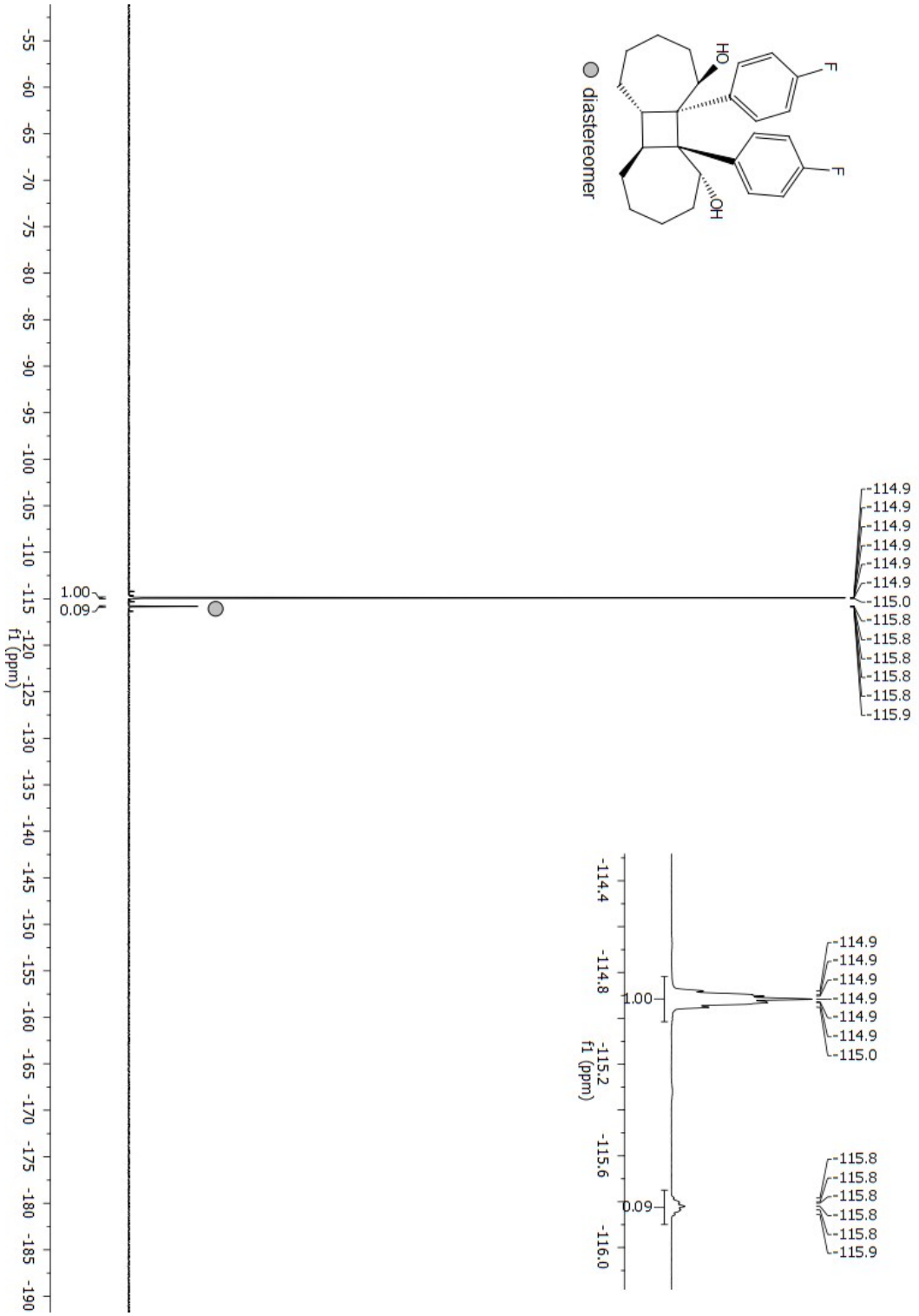
^{13}C NMR (101 MHz, $CDCl_3$)

2k (1R,5aS,5bS,10R,10aS,10bS)-10a,10b-bis(4-fluorophenyl)tetradecahydrocyclobuta-[1,2:3,4]di[7]annulene-1,10-diol



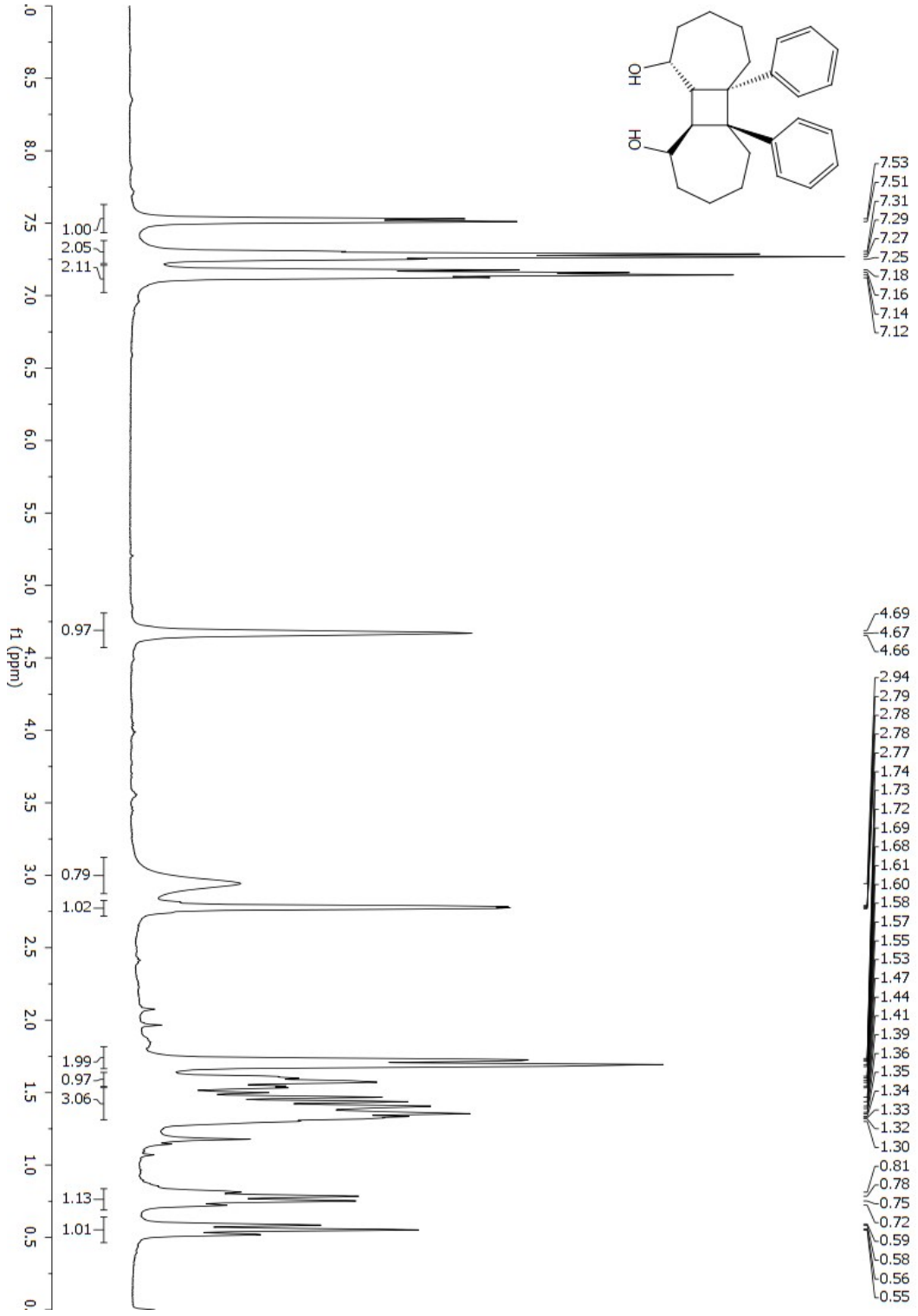
^{19}F NMR (376 MHz, $CDCl_3$)

2k (1R,5aS,5bS,10R,10aS,10bS)-10a,10b-bis(4-fluorophenyl)tetradecahydrocyclobuta-[1,2:3,4]di[7]annulene-1,10-diol



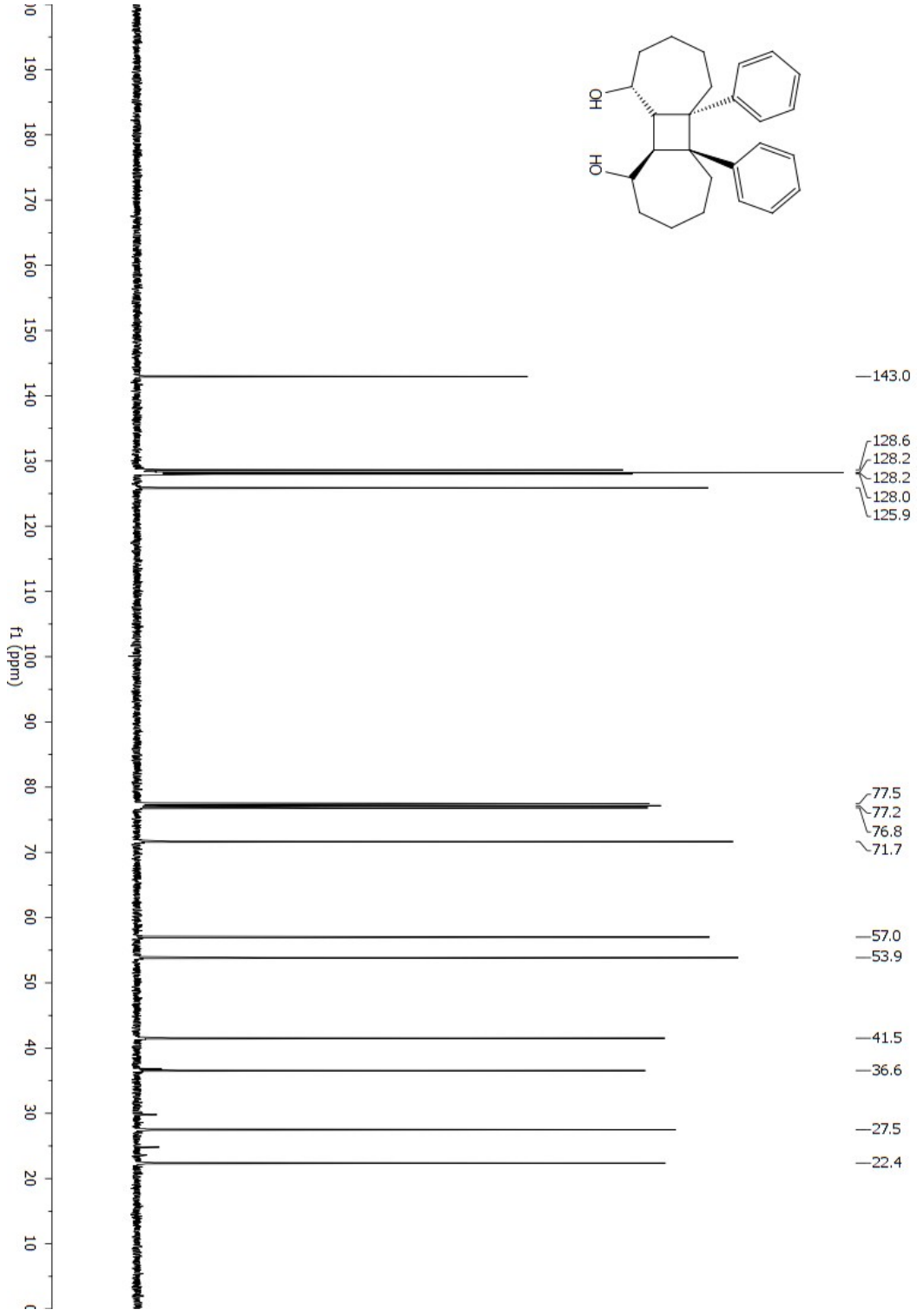
^{1}H NMR (400 MHz, $CDCl_3$)

2l (1R,5aR,5bR,10R,10aS,10bS)-5a,5b-diphenyltetradecahydrocyclobuta[1,2:3,4]di[7]-annulene-1,10-diol



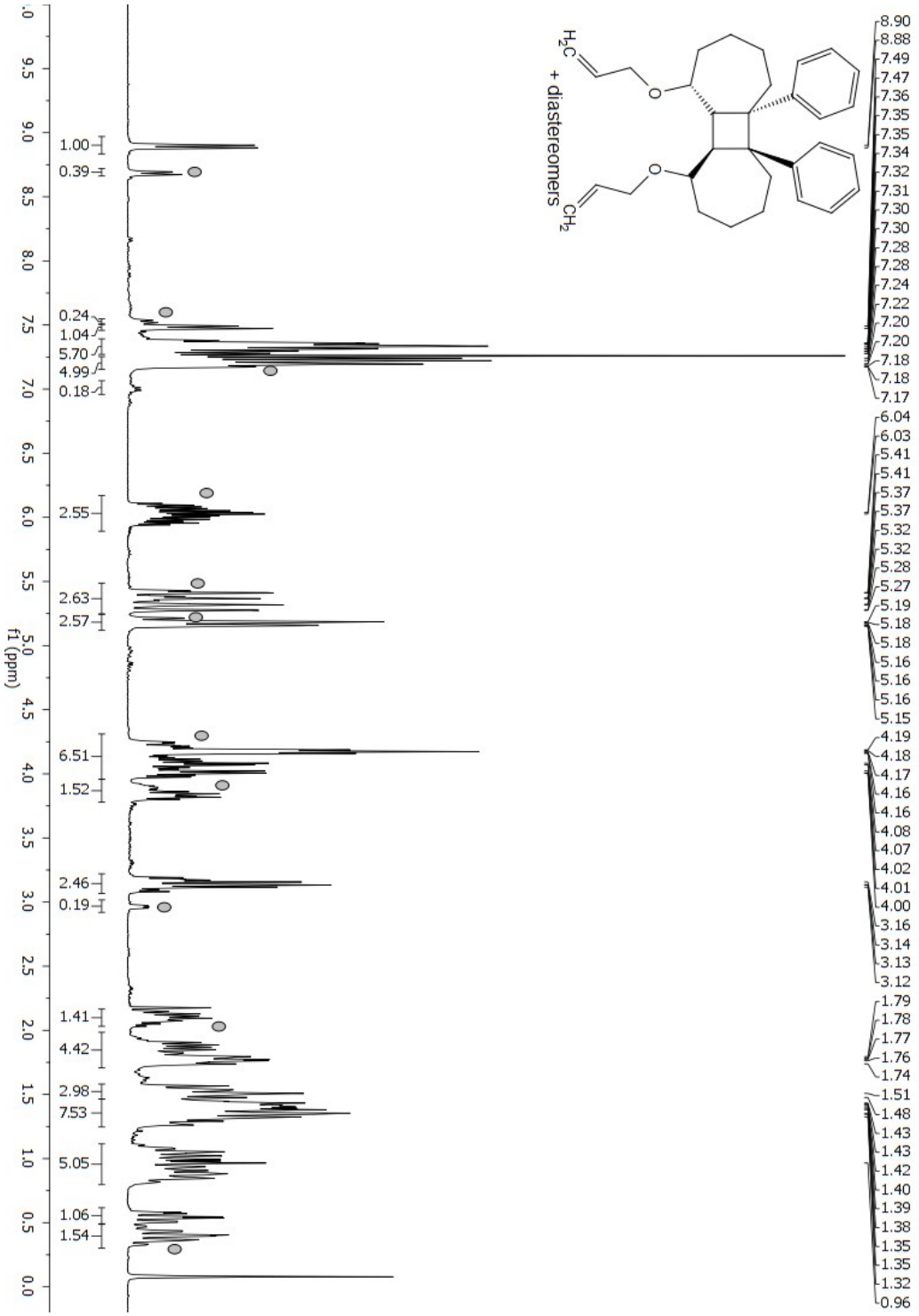
^{13}C NMR (101 MHz, $CDCl_3$)

2l (1R,5aR,5bR,10R,10aS,10bS)-5a,5b-diphenyltetradecahydrocyclobuta[1,2:3,4]di[7]-annulene-1,10-diol



^{1}H NMR (400 MHz, $CDCl_3$

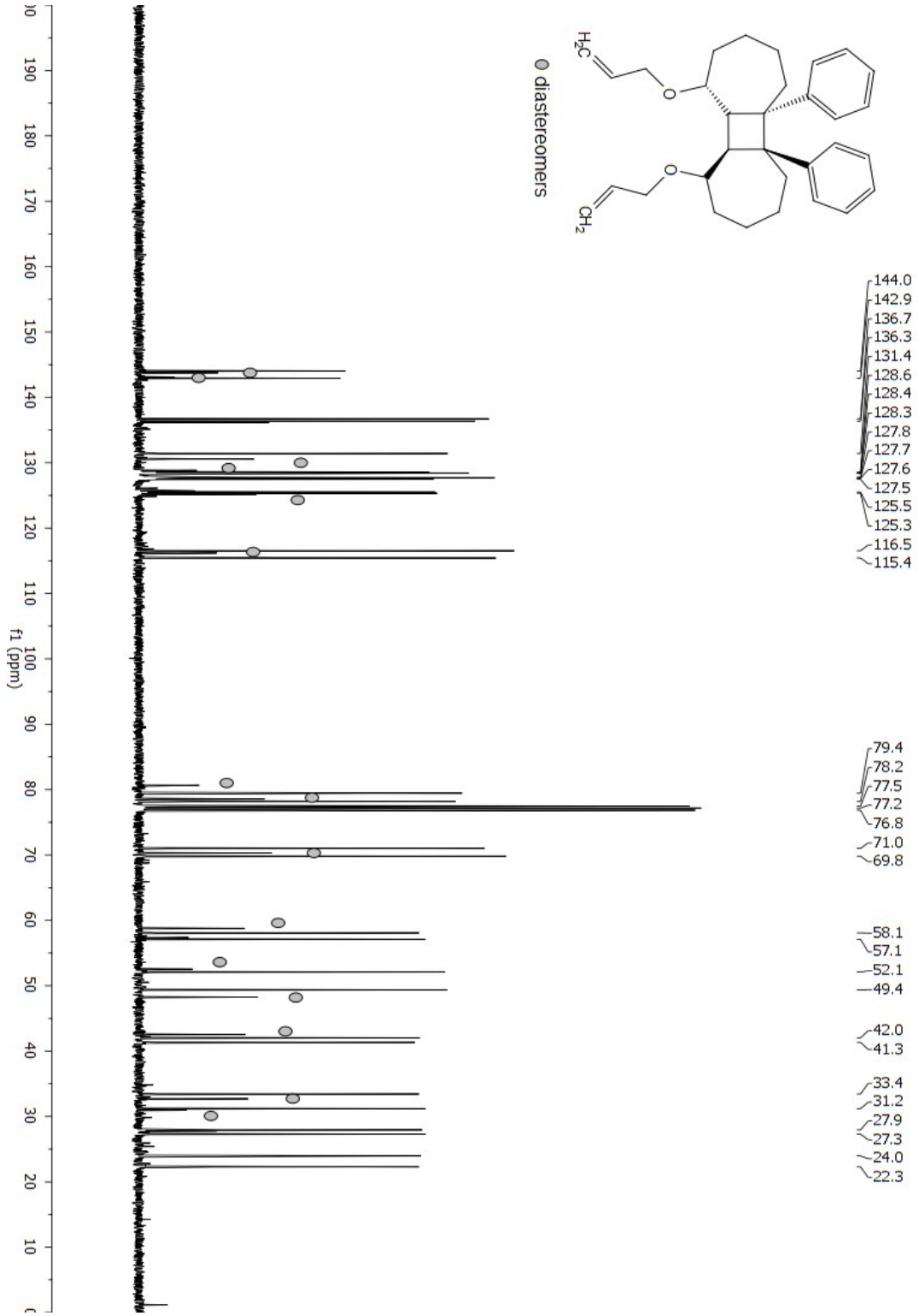
2m (1R,5aR,5bR,10R,10aS,10bS)-1,10-bis(allyloxy)-5a,5b-diphenyltetradecahydrocyclo-



buta [1,2:3,4]di[7]annulene

^{13}C NMR (101 MHz, $CDCl_3$)

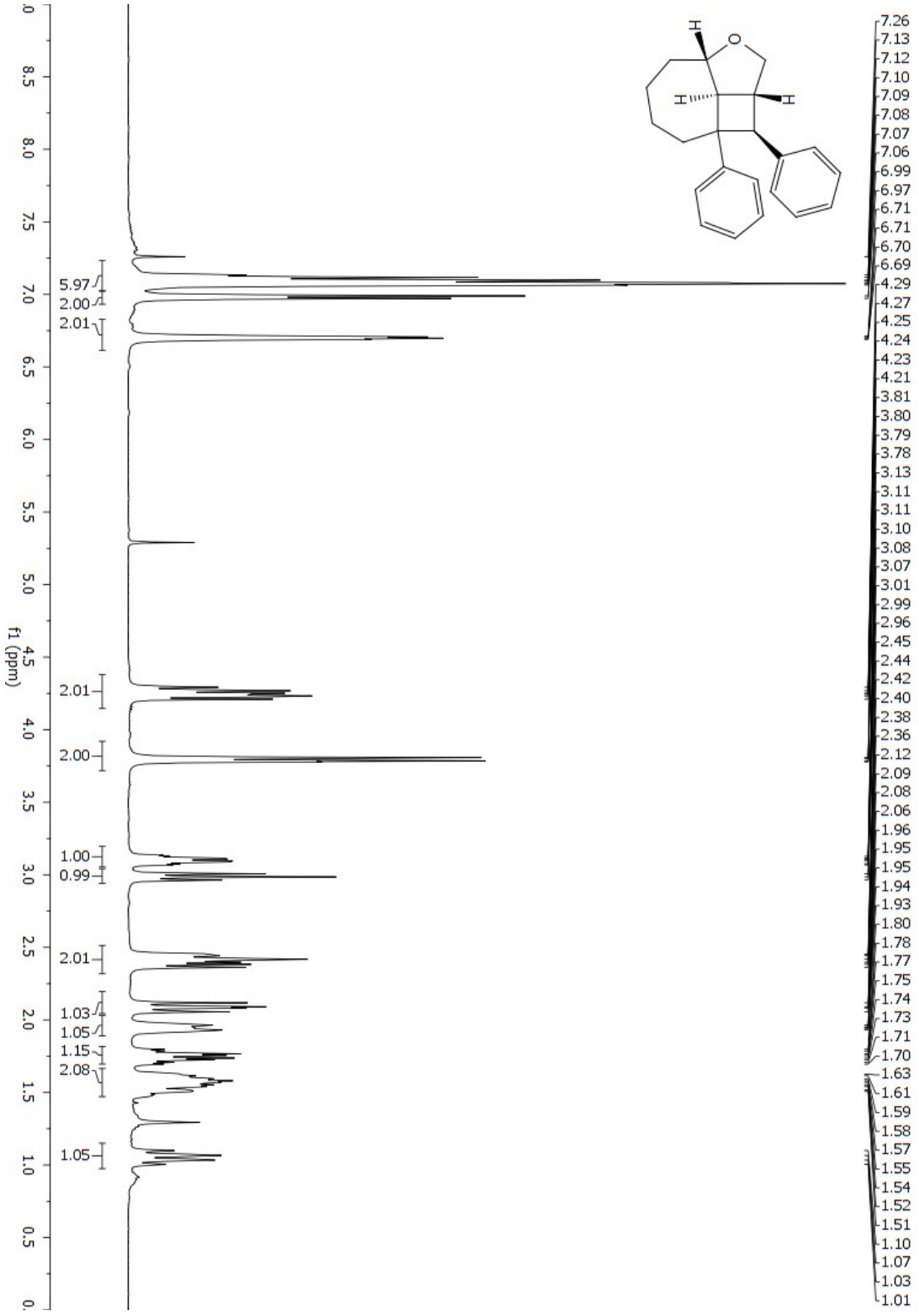
2m (1R,5aR,5bR,10R,10aS,10bS)-1,10-bis(allyloxy)-5a,5b-diphenyltetradecahydrocyclo-



buta [1,2:3,4]di[7]annulene

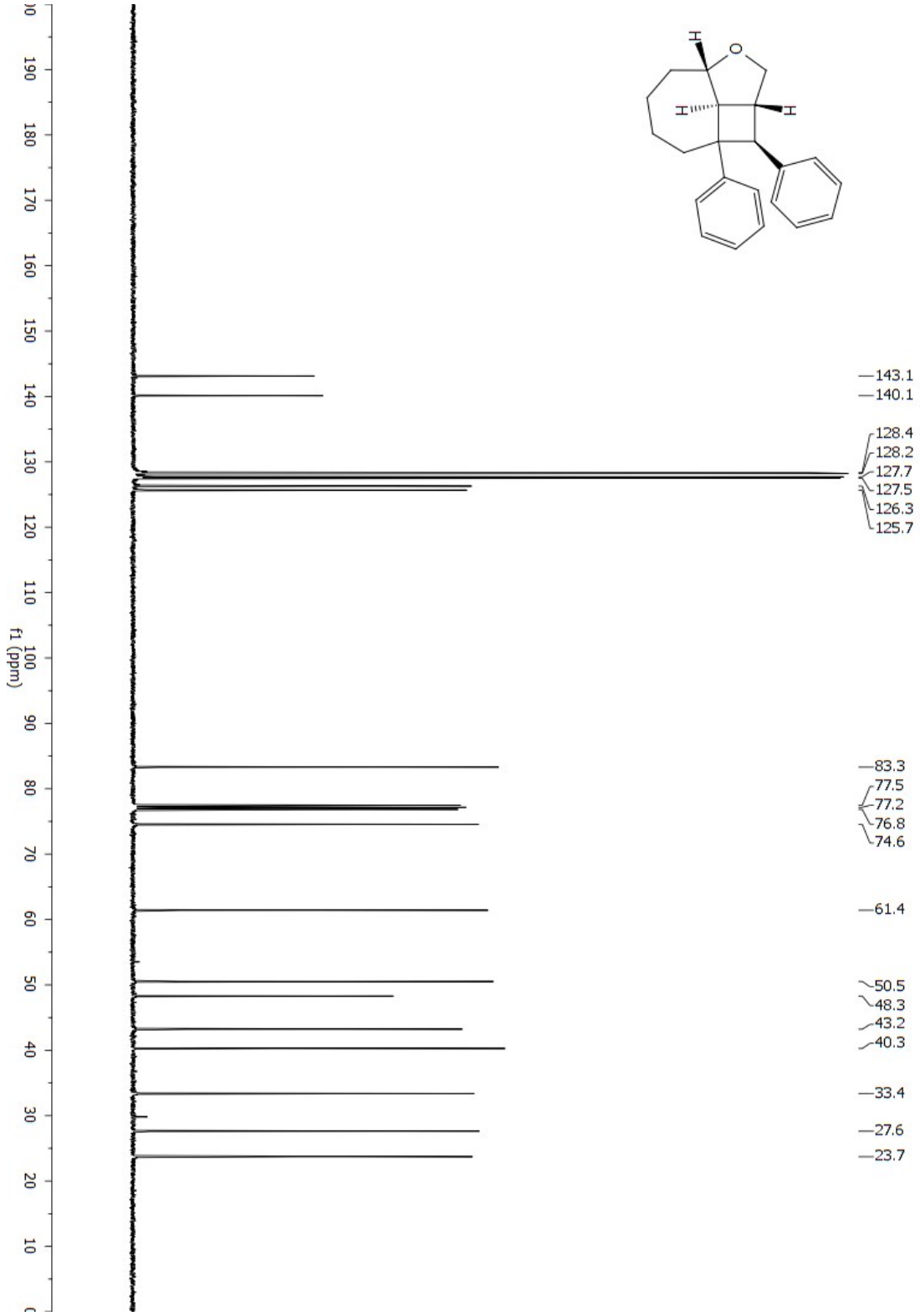
^{1}H NMR (400 MHz, $CDCl_3$)

2n (1S,1aR,1a1S,3aS)-1,7a-diphenyldecahydro-3-oxacyclobuta[cd]azulene



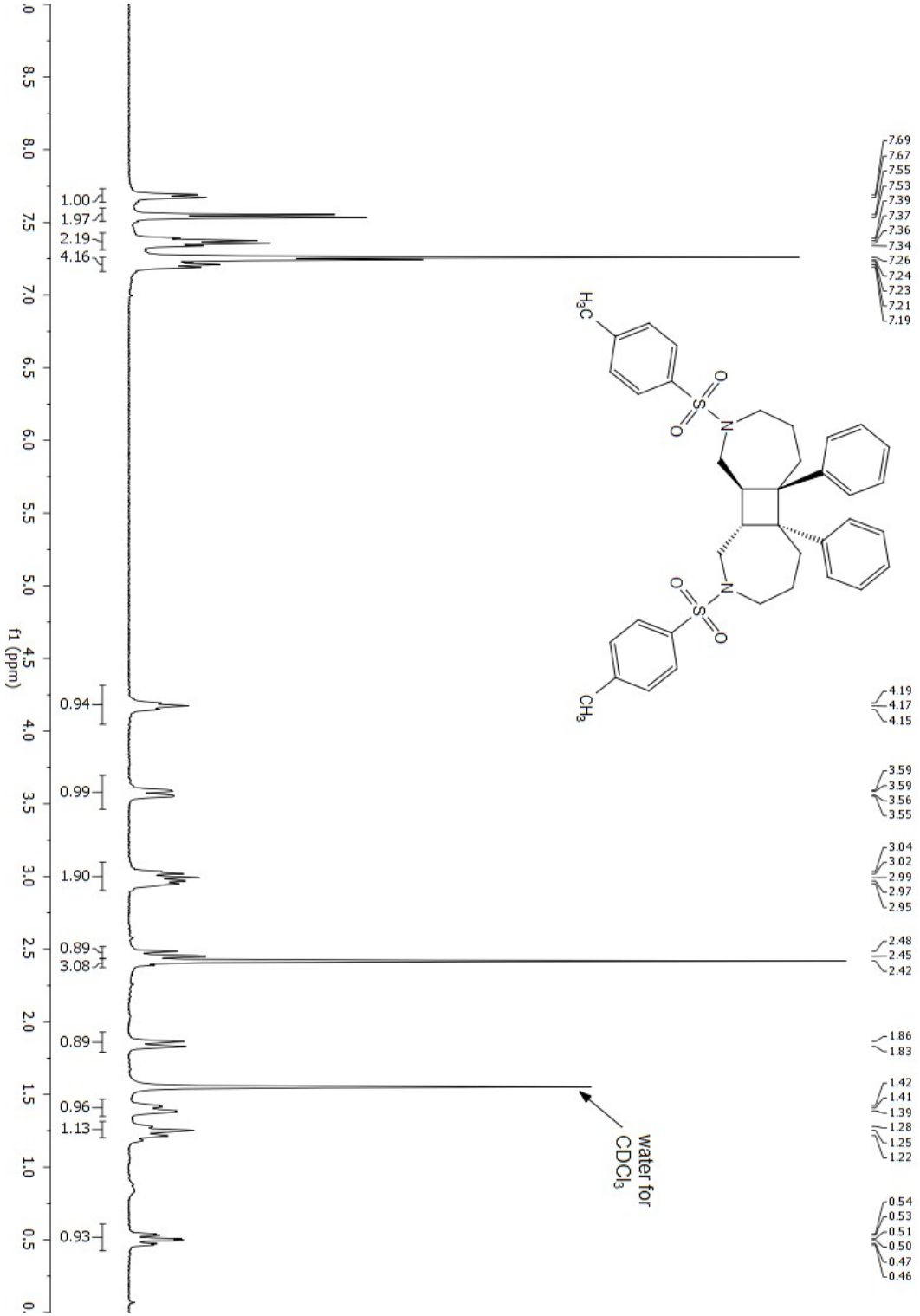
^{13}C NMR (101 MHz, $CDCl_3$)

2n (1S,1aR,1a1S,3aS)-1,7a-diphenyldecahydro-3-oxacyclobuta[cd]azulene



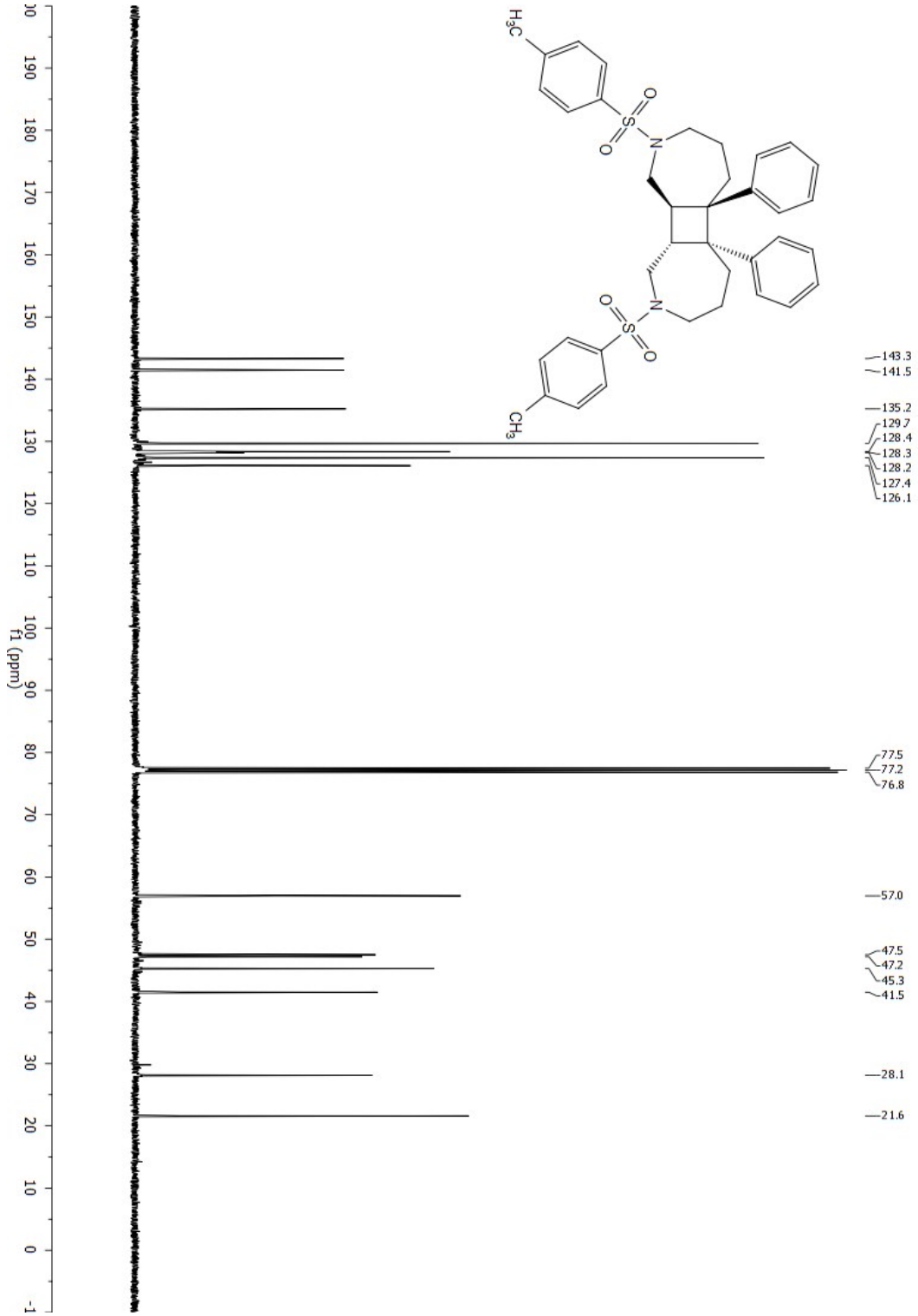
^{1}H NMR (400 MHz, $CDCl_3$)

2o (5aR,5bR,10aS,10bS)-5a,5b-diphenyl-2,9-ditosyltetradecahydrocyclobuta[1,2-c:4,3-c']bis(azepine)



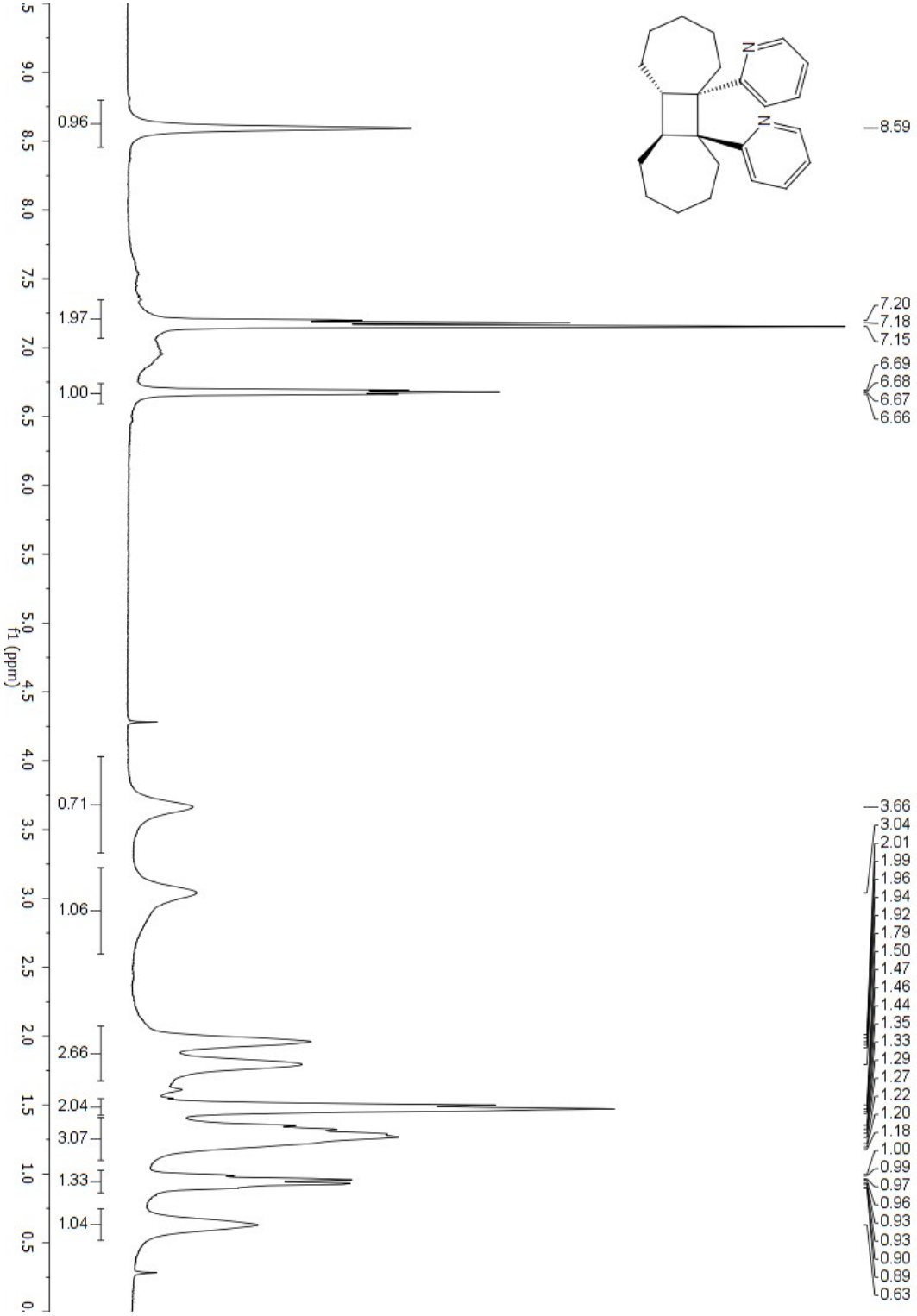
^{13}C NMR (101 MHz, $CDCl_3$)

2o (5aR,5bR,10aS,10bS)-5a,5b-diphenyl-2,9-ditosyltetradecahydrocyclobuta[1,2-c:4,3-c']bis(azepine)



^{1}H NMR (400 MHz, $CDCl_3$)

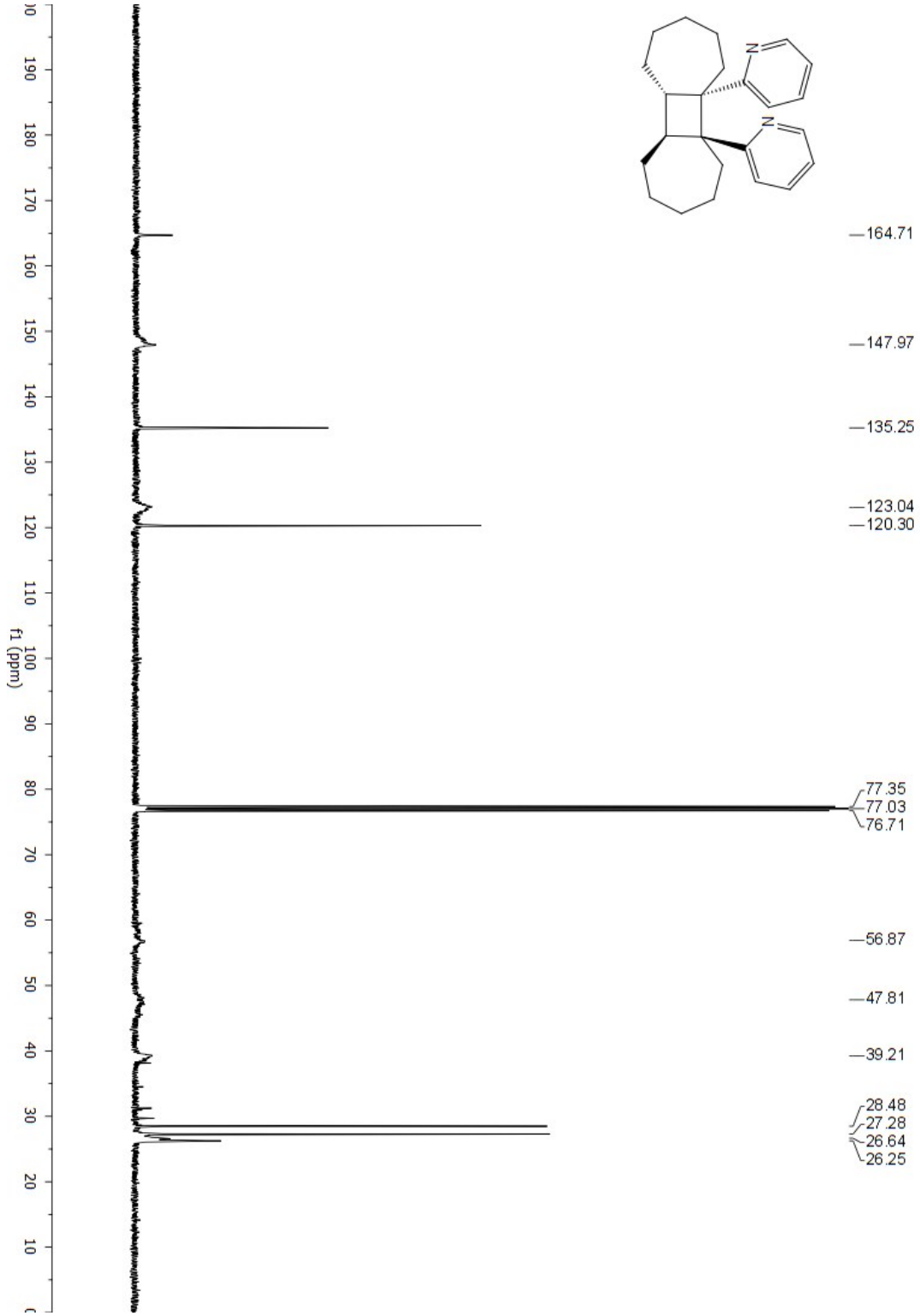
2p (5aS,5bS,10aS,10bS)-5a,5b-di(pyridin-2-yl)tetradecahydrocyclobuta[1,2:3,4]di[7]an-



nulene

^{13}C NMR (101 MHz, $CDCl_3$)

2p (5aS,5bS,10aS,10bS)-5a,5b-di(pyridin-2-yl)tetradecahydrocyclobuta[1,2:3,4]di[7]an-



nulene