Supporting Information

C-H Functionalisation of [2.2]paracyclophane under Copper catalysis

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1. General Information

Chemicals: Unless otherwise noted, all reagents were obtained from commercial suppliers and used without further purification. Iodobenzenes and alkynes were procured from Bide Pharmatech; copper catalysts were obtained from J&K Scientific; TMSOTf, TfOH, $BF_3 \cdot Et_2O$ and *m*-CPBA were purchased from Energy Chemical; solvents were supplied by Sinopharm Chemical Reagent Co., Ltd.

NMR spectroscopy: ^1H and ^{13}C NMR spectra were acquired on Bruker AVANCE spectrometers (400 MHz) in $CDCl_3$ with tetramethylsilane (TMS) as the internal reference; ^{13}C NMR spectra were acquired on Bruker AVANCE spectrometers (101 MHz) in $CDCl_3$ with tetramethylsilane (TMS) as the internal reference; ^{19}F NMR spectra were acquired on Bruker AVANCE spectrometers (376 MHz) in $CDCl_3$ with tetramethylsilane (TMS) as the internal reference. Chemical shifts (δ) are reported in ppm relative to residual solvent signals: $CHCl_3$ (δ 7.26 ppm for ^1H) and $CDCl_3$ (δ 77.16 ppm for ^{13}C). Coupling constants (J) are expressed in Hz. Multiplicity descriptors: s (singlet), d (doublet), t (triplet), q (quartet), p (pentet), dd (doublet of doublets), td (triplet of doublets), ddd (doublet of doublet of doublets), m (multiplet), br (broad resonance).

Analytical Techniques:

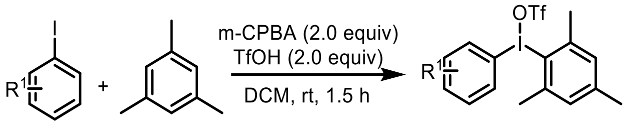
- **GC**: Agilent 7890B system equipped with an FID detector.
- **GC-MS**: Agilent 6890N GC coupled to a 5973N mass spectrometer, using dodecane as an internal standard.
- **HRMS**: High-resolution mass spectra were recorded in the EI (CI) mode on Agilent 8890 GC/7250Q-TOF MS; (ESI) mode on Agilent 6545 Q-TOF LC-MS
- **Chiral LC**: Agilent 1260 chromatography, using chiral HPLC columns Chiralpak® with hexane and i-PrOH as solvents.

General Procedures: Reagents were weighed under ambient laboratory conditions. Unless specified, reactions were performed in air without inert gas protection.

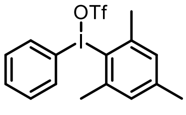
Abbreviations: Petroleum ether (PE), ethyl acetate (EA), 1,2-dichloroethane (DCE), dichloromethane (DCM), diethyl ether (Et_2O), *meta*-chloroperoxybenzoic acid (*m*-CPBA), trifluoromethanesulfonic acid (TfOH), sodium trifluoromethanesulfonate (NaOTf), trimethylsilyl trifluoromethanesulfonate (TMSOTf), 2,6-di-*tert*-butyl pyridine (DTBP).

2. Preparation and characterization of starting materials

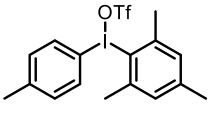
General method A [1-4]



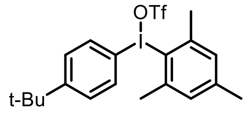
A mixture of iodobenzene (2 mmol) and 85% *m*-CPBA (0.8 g, 2.0 equiv) in dichloromethane (50 mL) was placed in a 100 mL round-bottom flask. The resulting suspension was cooled to 0 °C using an ice bath, followed by dropwise addition of trifluoromethanesulfonic acid (TfOH, 0.6 g, 2.0 equiv) while maintaining the temperature at 0 °C. After stirring at this temperature for 10 minutes, the reaction mixture was allowed to warm to room temperature and stirred for an additional 2 hours. Upon completion of the reaction as monitored by TLC, the solvent was removed under reduced pressure. The residual material was triturated with diethyl ether to afford the crude product as a white solid, which was subsequently collected by filtration. The filtered solid was washed with diethyl ether and dried under vacuum to yield mesityl iodonium trifluoromethanesulfonate. (**2a-2d, 2f, 2i, 2j, 2m, 2n** were prepared by this method).



2a



2b



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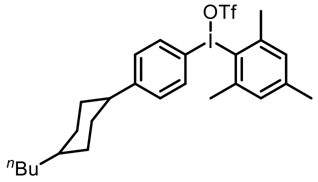
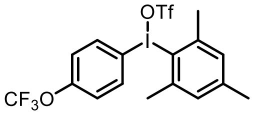


2d



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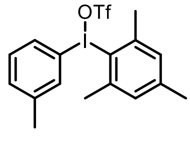

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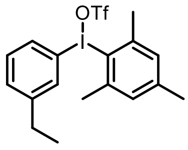

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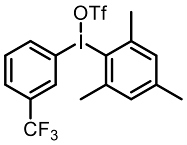
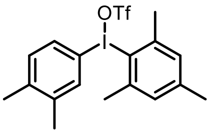


2m



2n

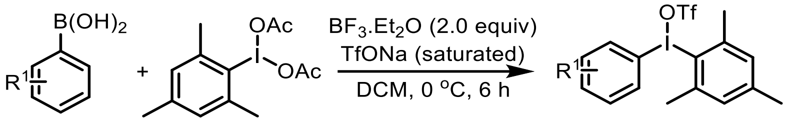
(4-(4-butylcyclohexyl) phenyl)(mesityl)-l3-iodanyl trifluoromethanesulfonate (2d)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.61 (d, *J* = 8.5 Hz, 2H), 7.26 (d, *J* = 8.6 Hz, 2H), 7.12 (s, 2H), 2.65 (s, 6H), 2.48 (tt, *J* = 12.1, 3.2 Hz, 1H), 2.38 (s, 3H), 2.10 (s, 1H), 1.87 (td, *J* = 11.5, 5.9 Hz, 4H), 1.52 - 1.11 (m, 8H), 1.11 - 0.94 (m, 2H), 0.96 - 0.83 (m, 3H).

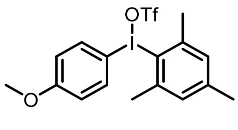
^{13}C NMR (101 MHz, Chloroform-*d*) δ 152.5, 144.3, 142.4 (2C), 133.2 (2C), 131.0 (2C), 130.3 (2C), 120.3, 120.3 (q, J = 285.3 Hz), 120.3, 107.8, 44.2, 37.0, 36.9, 33.9 (2C), 33.2 (2C), 29.1, 27.1 (2C), 22.9, 21.1, 14.1.

HRMS: calcd. [M-CF_3SO_3]$^+$ 462.1778; found: 462.1783.

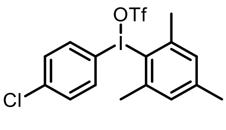
General method B



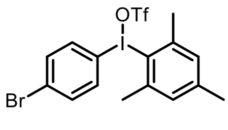
A mixture of boronic acid (2 mmol) in dichloromethane (50 mL) was placed in a 100 mL round-bottom flask under a nitrogen atmosphere. The resulting suspension was cooled to 0 °C using an ice bath, followed by dropwise addition of boron trifluoride diethyl etherate (0.5 mL, 2.0 equiv) via syringe while maintaining the temperature at 0 °C. The mixture was stirred at this temperature for 10 minutes, after which a solution of iodomesitylene diacetate (0.76 g, 1.05 equiv) in dichloromethane (15 mL) was introduced dropwise via syringe at 0 °C. Upon complete addition, the reaction mixture was allowed to warm to room temperature and stirred for 2 hours. The reaction was quenched with a saturated sodium triflate solution (20 mL), and the biphasic mixture was subjected to vigorous stirring for 30 minutes. The organic layer was separated, and the aqueous layer was extracted with dichloromethane (2 × 20 mL). The combined organic phases were washed sequentially with water and brine, dried over anhydrous sodium sulfate, and concentrated under reduced pressure. The residual material was triturated with diethyl ether to afford the crude product as a white solid. The solid was collected by filtration, washed with cold diethyl ether, and dried under vacuum to yield mesityl iodonium trifluoromethanesulfonate. (**2e, 2g, 2h, 2k, 2l, 2p, 2q** were prepared by this method).



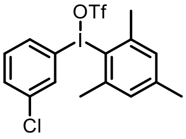
2e



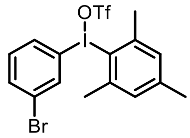
2g



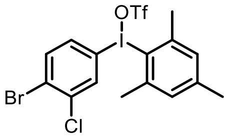
2h



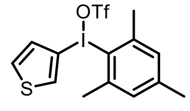
2k



2l

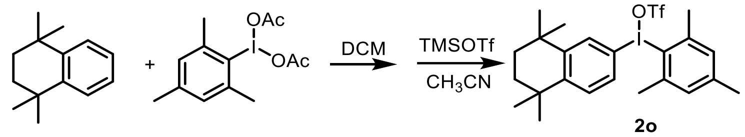


2p



2q

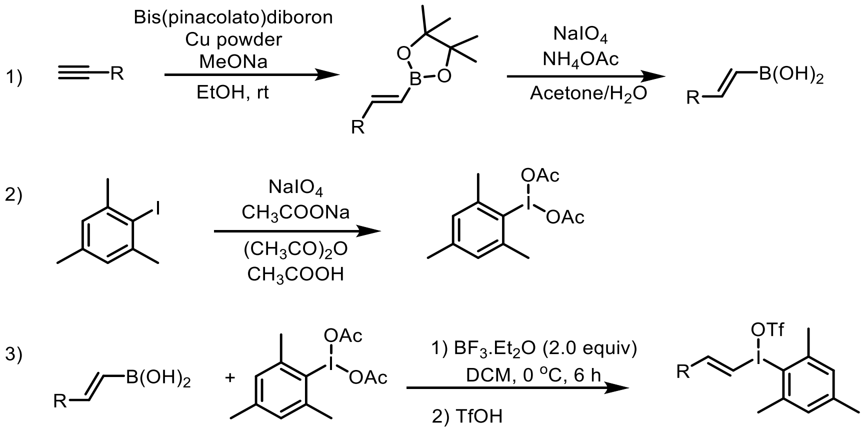
General method C



2o

A mixture of 1,1,4,4-tetramethyl-1,2,3,4-tetrahydronaphthalene (2 mmol) and iodomesitylene diacetate (0.76 g, 1.05 equiv) in dichloromethane (50 mL) was placed in a 100 mL round-bottom flask. After stirring at room temperature for 2 hours, the reaction mixture was concentrated under reduced pressure. The resulting residue was dissolved in acetonitrile, followed by dropwise addition of trimethylsilyl trifluoromethanesulfonate (TMSOTf, 0.88 g, 2.0 equiv.) at room temperature. The solution was stirred at this temperature for 6 hours, then concentrated under reduced pressure. The residual material was triturated with diethyl ether to afford a crude white solid, which was collected by filtration, washed with cold diethyl ether, and dried under vacuum to yield compound **2o**.

General method D[5]



Step 1

A mixture of phenylacetylene or alkyne (5.0 mmol) and bis(pinacolato)diboron (1.90 g, 7.5 mmol) in anhydrous ethanol (50 mL) was placed in a 100 mL round-bottom flask. Copper powder (0.032 g, 0.5 mmol) and sodium methoxide (0.027 g, 0.5 mmol) were added sequentially to the stirred solution at room temperature. After complete consumption of the starting material (monitored by TLC), the reaction mixture was quenched with brine (20 mL) and extracted with ethyl acetate (3 × 30 mL). The combined organic layers were dried over anhydrous magnesium sulfate, filtered, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 25:1) to afford the intermediate boronate ester.

The boronate ester was dissolved in a mixture of acetone (30 mL) and water (15 mL), followed by addition of ammonium acetate (NH_4OAc, 0.77 g, 10 mmol) and sodium periodate ($NaIO_4$, 2.13 g, 10 mmol). The resulting solution was stirred at room temperature for 12 h until complete consumption of the substrate (TLC). The mixture was diluted with ethyl acetate (50 mL), filtered through a Celite pad, and concentrated under reduced pressure to yield the aryl boronic acid as a white solid.

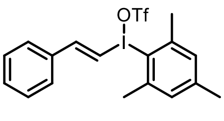
Step 2

A 500 mL round-bottom flask was charged with sodium periodate ($NaIO_4$, 4.40 g, 20.5 mmol) and sodium acetate (CH_3COONa, 3.60 g, 44.0 mmol) in glacial acetic acid (40 mL). Acetic anhydride (Ac_2O, 3.0 mL) was added dropwise, followed by introduction of iodoarene (20 mmol). The reaction mixture was heated under reflux for 2–8 h, cooled to room temperature, and poured into ice water (50 mL). The resulting precipitate was collected by filtration, washed with water (3 × 20 mL), and dried under vacuum. If residual impurities were observed, the crude product was triturated with hexane (10 mL), filtered, and washed with cold hexane to afford pure diacetoxyiodoarene.

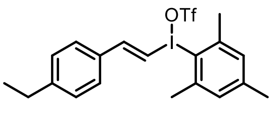
Step 3

A suspension of alkenyl boronic acid (5.0 mmol) in dry dichloromethane (DCM, 30 mL) was cooled to 0 °C under nitrogen. Boron trifluoride diethyl etherate ($BF_3 \cdot Et_2O$, 6.0 mmol, 1.2 equiv) was added dropwise via syringe, and the mixture was stirred at 0 °C for 15 min until a homogeneous solution formed. A solution of iodomesitylene diacetate (6.0 mmol, 1.2 equiv) in DCM (15 mL) was introduced dropwise via syringe, and the reaction was stirred for 3 h at 0 °C. Trifluoromethanesulfonic acid (TfOH, 6.0 mmol, 1.2 equiv) in DCM (5 mL) was then added, and stirring continued for an additional 1.5 h.

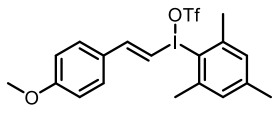
The reaction was quenched with water (50 mL), and the aqueous phase was extracted with DCM (3 × 10 mL). The combined organic layers were dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. The crude residue was recrystallized from diethyl ether or triturated with cold diethyl ether (20 mL) to yield the target iodonium salt. (**4a-4l** were prepared by this method).



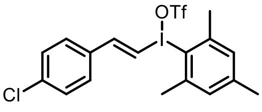
4a



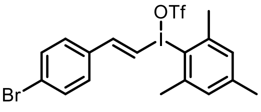
4b



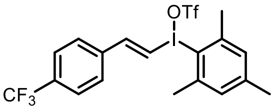
4c



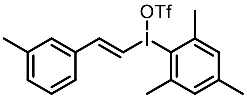
4d



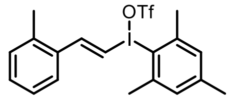
4e



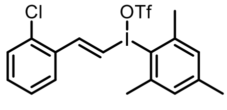
4f



4g



4h



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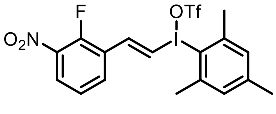

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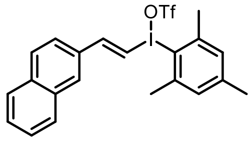

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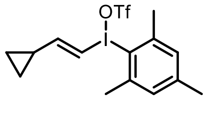
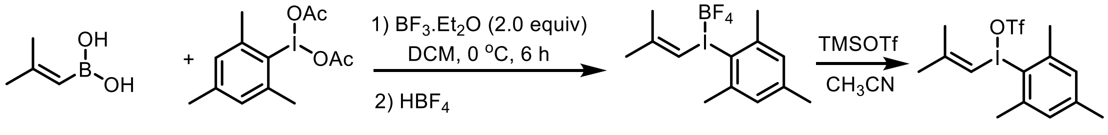


4l

General method E

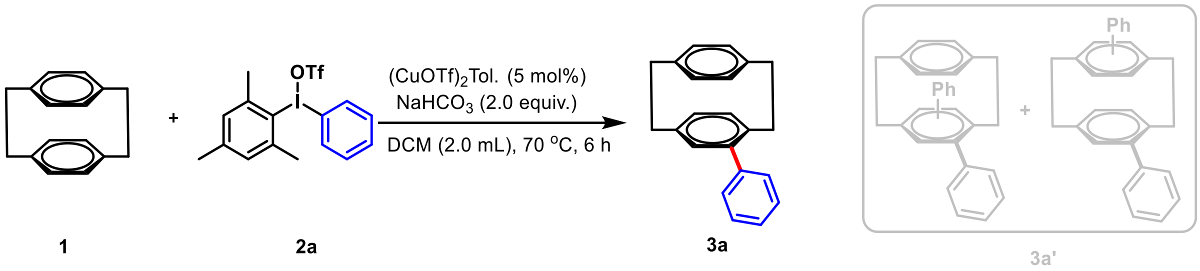


4m

Alkenyl boronic acid (5.0 mmol) in dry dichloromethane (DCM, 30 mL) was cooled to 0 °C under nitrogen. Boron trifluoride diethyl etherate ($BF_3 \cdot Et_2O$, 6.0 mmol, 1.2 equiv.) was added dropwise via syringe, and the mixture was stirred at 0 °C for 15 min until a homogeneous solution formed. A solution of iodomesitylene diacetate (6.0 mmol, 1.2 equiv.) in DCM (15 mL) was introduced dropwise via syringe, and the reaction was stirred for 3 h at 0 °C. Fluoroboric acid (HBF_4, 48% aqueous solution, 2.0 equiv.) then added, and stirring continued for an additional 1.5 h. then concentrated under reduced pressure. The residual material was triturated with diethyl ether to afford a crude white solid, which was collected by filtration, washed with cold diethyl ether, and dried under vacuum to yield. The resulting residue was dissolved in acetonitrile, followed by dropwise addition of trimethylsilyl trifluoromethanesulfonate (TMSOTf, 0.88 g, 2.0 equiv.) at room temperature. The solution was stirred at this temperature for 6 hours, then concentrated under reduced pressure. The residual material was triturated with diethyl ether to afford a crude white solid, which was collected by filtration, washed with cold diethyl ether, and dried under vacuum to yield compound **4m**.

3. Condition screening

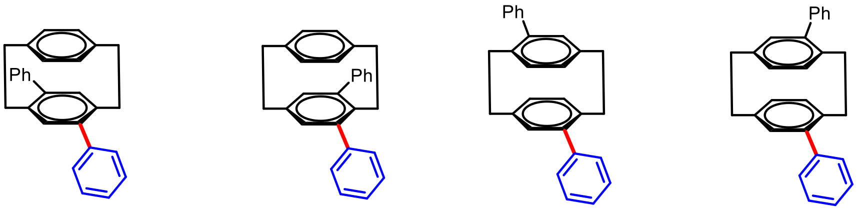
3.1 Table S1 : Conditions Screening for the C-H arylation of [2.2]paracyclophane



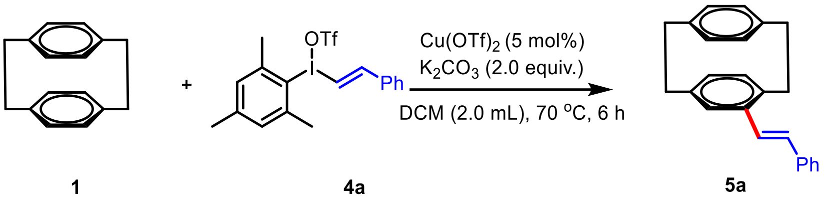
Entry	Variation from standard conditions	Yield of 3a (%)	Yield of 3a'
1	None	78	5
2	No $(CuOTf)_2$Tol.	n.r.	n.r.
3	No $NaHCO_3$	40	2
4	$[Mes\text{-}I\text{-}Ph]BF_4$ instead of [Mes-I-Ph]OTf	65	4
5	$[Mes\text{-}I\text{-}Ph]PF_6$ instead of [Mes-I-Ph]OTf	70	6
6	CuBr instead of $(CuOTf)_2$Tol.	76	5
7	$Cu(OAc)_2$ instead of $(CuOTf)_2$Tol.	63	3
8	$Cu(OTf)_2$ instead of $(CuOTf)_2$Tol.	71	6
9	2.5% $(CuOTf)_2$Tol. instead of 5% $(CuOTf)_2$Tol.	64	3
10	10% $(CuOTf)_2$Tol. instead of 5% $(CuOTf)_2$Tol.	77	9
11	Na_2CO_3 instead of $NaHCO_3$	56	8
12	K_2CO_3 instead of $NaHCO_3$	74	10
13	Et_3N instead of $NaHCO_3$	Trace	Trace
14	NaOH instead of $NaHCO_3$	67	6
15	DTBP instead of $NaHCO_3$	52	6
16	50 °C instead of 70 °C	64	4
17	90 °C instead of 70 °C	69	10
18	DCE instead of DCM	66	4
19	MeOH instead of DCM	n.r.	n.r.
20	THF instead of DCM	n.r.	n.r.
21	4 h instead of 6 h	61	4
22	8 h instead of 6 h	73	12
23	N_2 instead of air	77	5
24[b]	2.0 equiv. **2a** instead of 1.0 equiv. **2a**	64	23
25[b]	3.0 equiv. **2a** instead of 1.0 equiv. **2a**	58	36

Reaction conditions: [a]**1** (0.1 mmol, 2 equiv.), **2a** (0.05 mmol, 1.0 equiv.), [Cu] (5 mol%), and base (2.0 equiv.) were stirred in solvent (2.0 mL), 70 °C for 6 h. Yields were calculated based on **2a** determined by GC-MS. n.r. = no reaction. [b]Yields were calculated based on **1**.

According to the GC-MS spectra, we found several minor peaks at *m/z*: 360, which should be assigned to a mixture of diphenylation side products (**3a'**), the possible structures of which were depicted below:



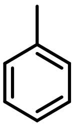
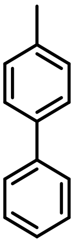
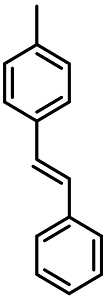
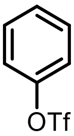
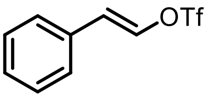
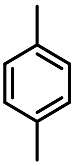
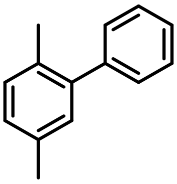
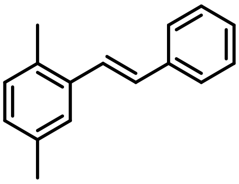
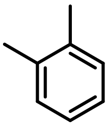
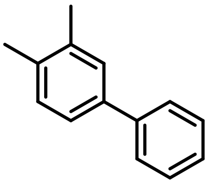
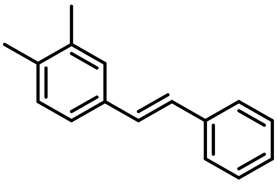
3.2 Table S2： Conditions Screening for the C-H alkenylation of [2.2]paracyclophane



Entry	Variation from standard conditions	Yield of 5a (%)
1	None	83
2	No Cu(OTf)$_2$	n.r.
3	No K$_2$CO$_3$	36
4	[Mes-I-(Styryl)]BF$_4$ instead of [Mes-I-(Styryl)]OTf	63
5	Cu(OAc)$_2$ instead of Cu(OTf)$_2$	25
6	(CuOTf)$_2$Tol instead of Cu(OTf)$_2$	40
7	CuOAc instead of Cu(OTf)$_2$	56
8	CuCl instead of Cu(OTf)$_2$	43
9	CuBr instead of Cu(OTf)$_2$	50
10	Na$_2$CO$_3$ instead of K$_2$CO$_3$	61
11	NaHCO$_3$ instead of K$_2$CO$_3$	70
12	DCE instead of DCM	46
13	MeCN instead of DCM	n.r.
14	HFIP instead of DCM	n.r.
15	CH$_3$NO$_2$ instead of DCM	n.r.
16	THF instead of DCM	n.r.
17	PhMe instead of DCM	12
18	CH$_3$OH instead of DCM	n.r.
19	4 h instead of 6 h	66
20	8 h instead of 6 h	83
21	90 °C instead of 70 °C	70

Reaction conditions: **1** (0.1 mmol, 1 equiv.), **4a** (0.15 mmol, 1.5 equiv.), Cu(OTf)$_2$ (5 mol%), K$_2$CO$_3$ (0.2 mmol, 2.0 equiv.), were stirred in solvent (2.0 mL), 70 °C for 6 h. Yields were calculated based on **1** and determined by GC-MS. n.r. = no reaction.

4. Control experiments

Reactants	**Arylation (Condition A)**	**Alkenylation (Condition B)**	**Yield of product Detected by GC-MS**
a 	 **Not detected**	 **Not detected**	 **or**  **95% yield** **93% yield**
b 	 **Not detected**	 **Not detected**	
c 	 **Not detected**	 **Not detected**	

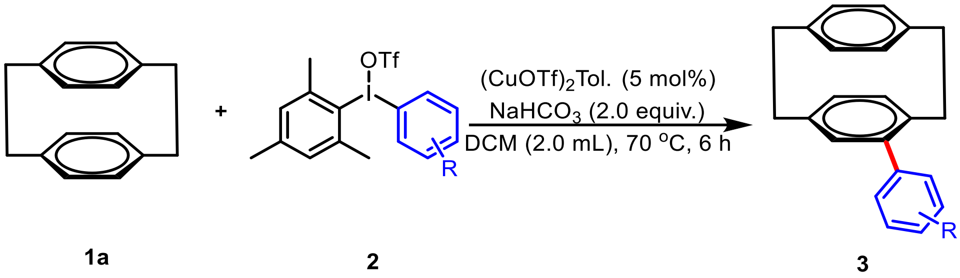
Arylation: Toluene (0.1 mmol, 2.0 equiv.), *p*-xylene (0.1 mmol, 2.0 equiv.), or *o*-xylene (0.1 mmol, 2.0 equiv.) was separately added to three 25ml Schlenk tubes. To each tube was added a mixture of the [Mes-I-Ph]OTf (**2,** 0.05 mmol), $(CuOTf)_2Tol$ (5 mol%), $NaHCO_3$ (2.0 equiv.) in DCM (2.0 mL) were heated to 70 °C and stirred for 6 h. After cooling, the clear upper layer was collected for GC-MS analysis to determine yields.

Alkenylation: Toluene (0.1 mmol, 2.0 equiv.), *p*-xylene(0.1 mmol, 2.0 equiv.), or *o*-xylene (0.1 mmol, 2.0 equiv.) were separately added to three 25ml Schlenk tubes, To each tube was added a mixture of the [2.2]paracyclophane **1** (0.1 mmol, 1.0 equiv.), [Mes-I-(styryl)]OTf (**4,** 0.15 mmol, 1.5 equiv.), K_2CO_3 (2.0 equiv.), $Cu(OTf)_2$ (5 mol%) in DCM (2.0 mL) was heated to 70 °C and stirred for 6 h. After cooling, the clear upper layer was collected for GC-MS analysis to determine yields.

In the abovementioned control experiments, no arylated products and alkenylated products were detected. Instead, the nucleophilic substitution (OTf) of iodium salts were observed.

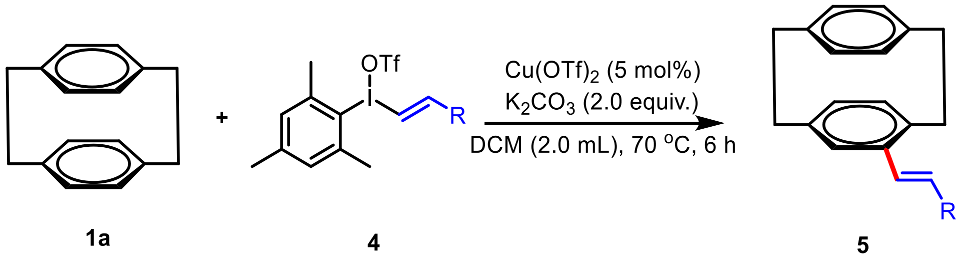
5. Typical experimental procedure

5.1 General procedure A



Condition A**:** A mixture of the [2.2]paracyclophane **1a** (0.1 mmol, 2.0 equiv.), [Mes-I-Ar]OTf **2** (0.05 mmol), $(CuOTf)_2Tol$ (5 mol%), $NaHCO_3$ (2.0 equiv.) in DCM (2.0 mL) was heated to 70 °C and stirred for 6 h in a 25 mL Schlenk tube. Then the reaction mixture was cooled to room temperature. Removal of solvent under reduced pressure afford a residue which is purified by chromatography on silica gel (PE/EA = 20:1, *v/v*) to afford the desired compound **3**.

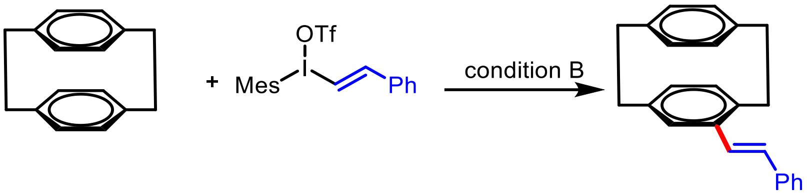
5.2 General procedure B



Condition B**:** A mixture of the [2.2]paracyclophane **1** (0.1 mmol, 1.0 equiv.), [Mes-I-(Alkenyl)]OTf **4** (0.15 mmol, 1.5 equiv.), K_2CO_3 (2.0 equiv.), $Cu(OTf)_2$ (5 mol%) in DCM (2.0 mL) was heated to 70 °C and stirred for 6 h in a 25 mL Schlenk tube. Then the reaction mixture was cooled to room temperature. Removal of solvent under reduced pressure afford a residue which is purified by chromatography on silica gel (PE/EA = 20:1, *v/v*) to afford the desired compound **5**.

6. Further transformation

6.1 Gram scale-up synthesis of alkenylated product 5a



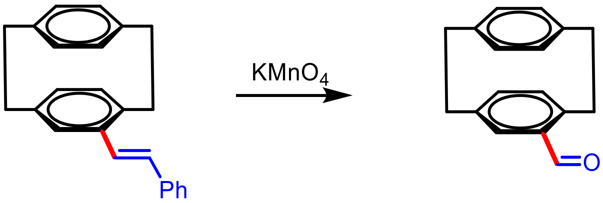
1a, 5 mmol, 1.04 g

5a, 81 %, 1.25 g

A mixture of the [2.2]paracyclophane **1** (5 mmol, 1.0 equiv.), [Mes-I-(Styryl)]OTf **4a** (7.5 mmol, 1.5 equiv.), K_2CO_3 (2.0 equiv.), $Cu(OTf)_2$ (5 mol%) in DCM (20.0 mL) was heated to 70 °C and stirred for 6 h in a 25 mL Schlenk tube. Then the reaction mixture was cooled to room temperature. Removal of solvent under reduced pressure afford a residue which is purified by chromatography on silica gel (PE/EA = 20:1, *v/v*) to afford the desired compound (**5a**, 81% yield).

6.2 Further transformation

Oxidative cleavage of 5a:



5a

6a

(E)-12-styryl-1,4(1,4)-dibenzenacyclohexaphane **(5a,** 2.0 mmol) was added to a flame-dried flask equipped with a magnetic stir bar in acetone (20 mL), 10% $KMnO_4$ (3.0 equiv., 6.0 mmol) was added dropwise at 0 °C. The reaction mixture was stirred at room temperature for 6 h. After the reaction was completed, the aqueous layer was extracted with dichloromethane (DCM, 10 mL × 3), and the combined organic layers were washed with brine, dried over anhydrous $MgSO_4$, filtered, the solvent was removed under reduced pressure, and the residue was purification *via* column chromatography on silica gel (200-300 mesh, PE/EA = 10:1, *v/v*) afforded the desired product as colorless liquid (**6a**, 95% yield).

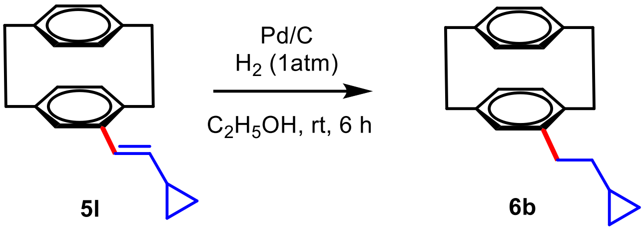
1,4(1,4)-dibenzenacyclohexaphane-12-carbaldehyde (6a)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.97 (s, 1H), 7.04 (d, *J* = 1.9 Hz, 1H), 6.75 (dd, *J* = 7.7, 2.0 Hz, 1H), 6.66 - 6.55 (m, 2H), 6.52 (dd, *J* = 7.8, 1.9 Hz, 1H), 6.49 - 6.35 (m, 2H), 4.13 (ddd, *J* = 12.3, 9.9, 1.8 Hz, 1H), 3.66 - 2.68 (m, 7H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 191.9, 143.2, 140.6, 139.5, 139.4, 138.1, 136.6, 136.3, 136.3 136.1, 133.2, 132.9, 132.3, 132.1, 35.3, 35.1, 35.0, 33.6.

HRMS (EI): [M]+ cacld for $C_{17}H_{16}O$ 236.1201, found: 236.1209.

Hydrogenation of 5l:



A flame-dried 50 mL flask equipped with a magnetic stir bar was charged with (E)-12-(2-cyclopropylvinyl)-1,4(1,4)-dibenzenacyclohexaphane (**5l**, 0.05 mmol) and 5% Pd/C (10.6 mg, 5 mol%). After evacuating and backfilling with H_2 (3 cycles), absolute ethanol (20 mL) was added *via* syringe. The mixture was stirred under 1 atm H_2 at rt for 6 h. The catalyst was washing with brine (15 mL) and extracted with dichloromethane (DCM, 10 mL × 3), dried over anhydrous $MgSO_4$. The filtrate was concentrated under reduced pressure, and the residue was purified by flash chromatography (silica gel, 200-300 mesh, gradient elution hexanes/EtOAc 20:1 to 10:1) to afford **6b** (0.121 g, 88%) as a colorless liquid.

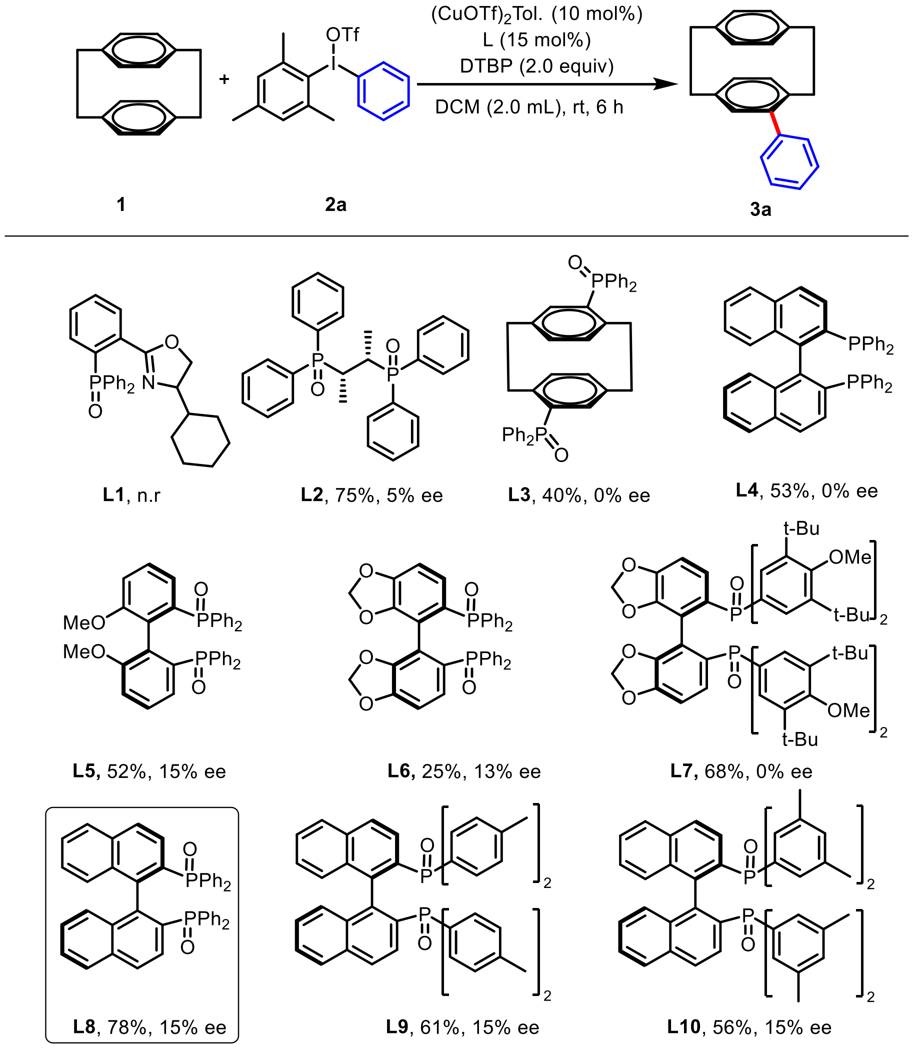
1^{2}-(2-cyclopropylethyl)-1,4(1,4)-dibenzenacyclohexaphane (6b)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.75 (dd, *J* = 7.8, 1.9 Hz, 1H), 6.61 - 6.49 (m, 2H), 6.48 - 6.38 (m, 3H), 6.18 (s, 1H), 3.42 (ddd, *J* = 13.4, 9.9, 2.1 Hz, 1H), 3.22 - 2.96 (m, 6H), 2.88- 2.69 (m, 2H), 2.52 - 2.32 (m, 1H), 1.46 - 1.34 (m, 2H), 0.86 - 0.63 (m, 1H), 0.60 - 0.40 (m, 2H), 0.21 - 0.06 (m, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 141.9, 139.6, 139.5, 139.4, 137.4, 134.6, 134.5, 133.3, 133.1, 132.1, 130.1, 128.9, 35.8, 35.4, 35.1, 34.5, 34.3, 33.5, 11.0, 4.7, 4.5.

HRMS (EI): $[M]^+$ cacld for $C_{21}H_{24}^+$ 276.1878, found: 276.1886.

6.3 Preliminary studies in Cu-catalysed asymmetric C-H arylation of PCP



1 **2a** **3a**

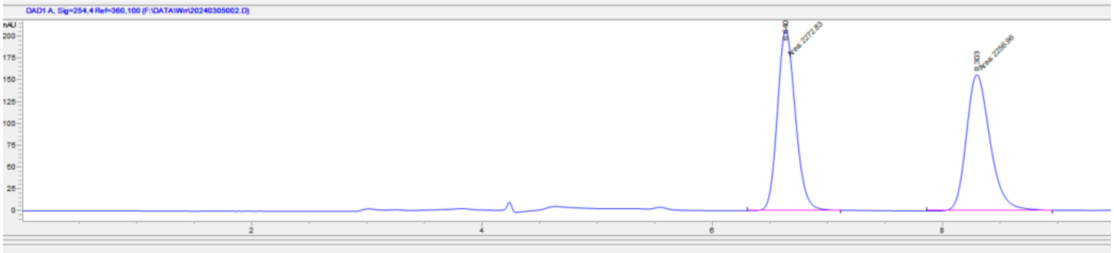
L1, n.r **L2**, 75%, 5% ee **L3**, 40%, 0% ee **L4**, 53%, 0% ee

L5, 52%, 15% ee **L6,** 25%, 13% ee **L7,** 68%, 0% ee

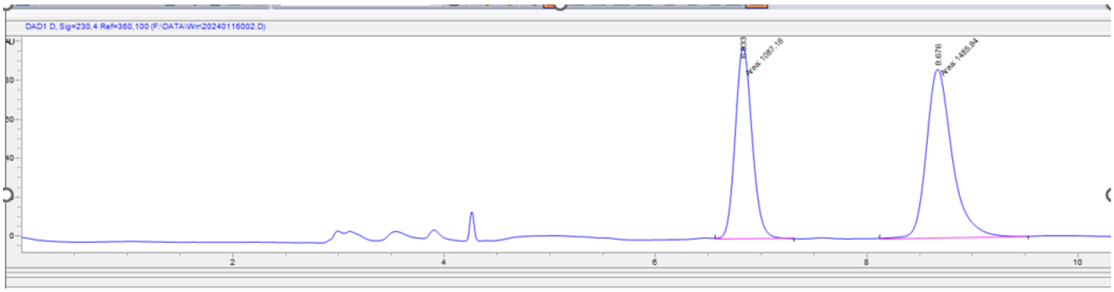
L8, 78%, 15% ee **L9**, 61%, 15% ee **L10**, 56%, 15% ee

Under anhydrous and oxygen-free conditions, to a dried tube equipped with a magnetic stir bar was added Cu(OTf)$_2$.Tol (10 mol%) and **L** (15 mol%), and CH_2Cl_2 (0.5 mL), stirring the reaction mixture for 30 mins at room temperature. Under oxygen-free conditions, to a suspension of **1** (0.1 mmol, 2.0 equiv.), **2a** (0.05 mmol, 1.0 equiv.) and CH_2Cl_2 (0.5 mL) in another dried 25 mL Schlenk tube was added DTBP (2.0 equiv.). After stirring the reaction mixture for 5 mins at room temperature, the above mixture containing Copper catalyst was transferred to the present Schlenk tube and stirred at 25˚C for overnight. After completion of the reaction (monitored by TLC), the solvent was removed under vacuum and the crude product. Purification via column chromatography on silica gel (PE/EA = 20/1, *v/v*) afforded **3a** as colorless oil.

L8: The enantiomeric excess was analysed by HPLC: *e.r.* = 58:42 (Chiralcel OD, i-propanol/hexane = 10/90, flow rate 1.0 mL/min, λ = 254 nm); t_{minor} = 6.64 min, t_{major} = 8.303 min.

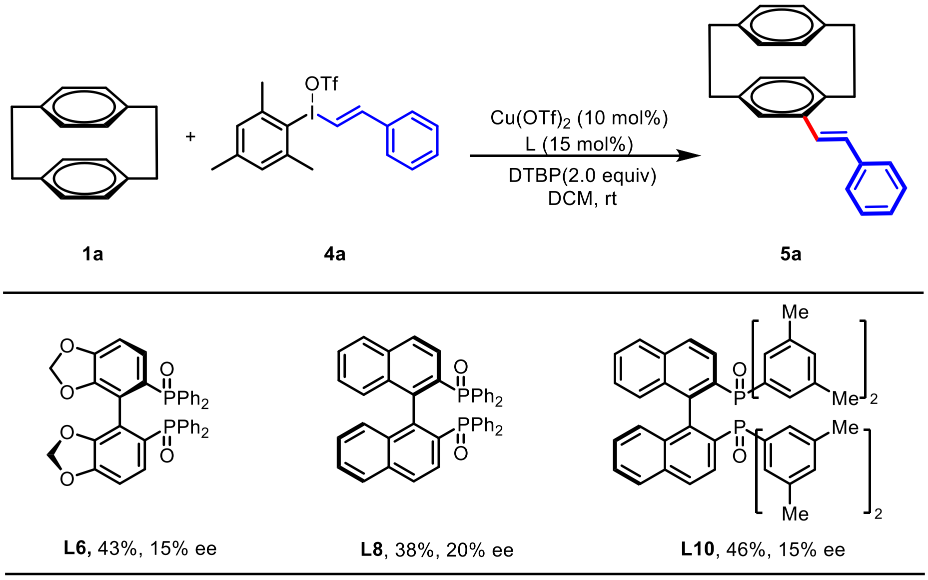


Peak#	Time	Area	Area %	Height	Width %	Symmetry factor
1	6.64	2272.8	50.175	207.5	0.1826	0.823
2	8.303	2257	49.825	156.2	0.2408	0.752



Peak#	Time	Area	Area %	Height	Width %	Symmetry factor
1	6.833	1087.2	42.2	42.251	0.1844	0.864
2	8.676	1485.9	57.8	57.749	0.2858	0.74

6.4 Preliminary studies in Cu-catalysed asymmetric C-H alkenylation of PCP



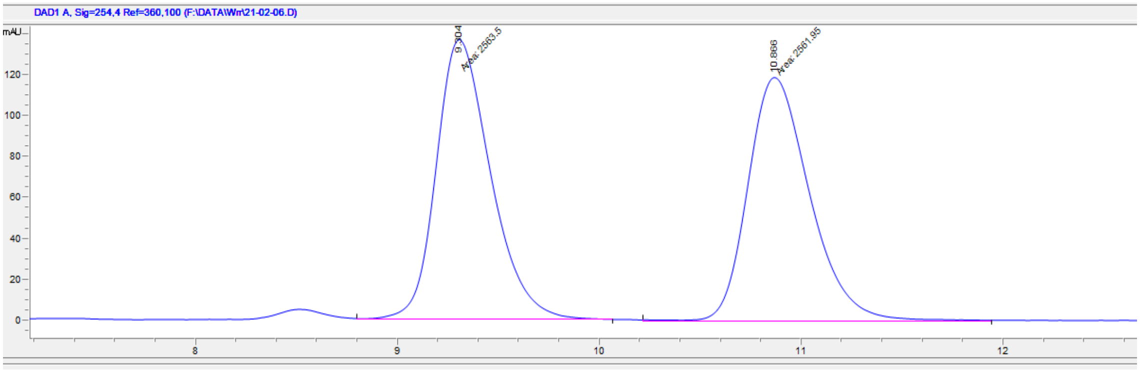
L6, 43%, 15% ee

L8, 38%, 20% ee

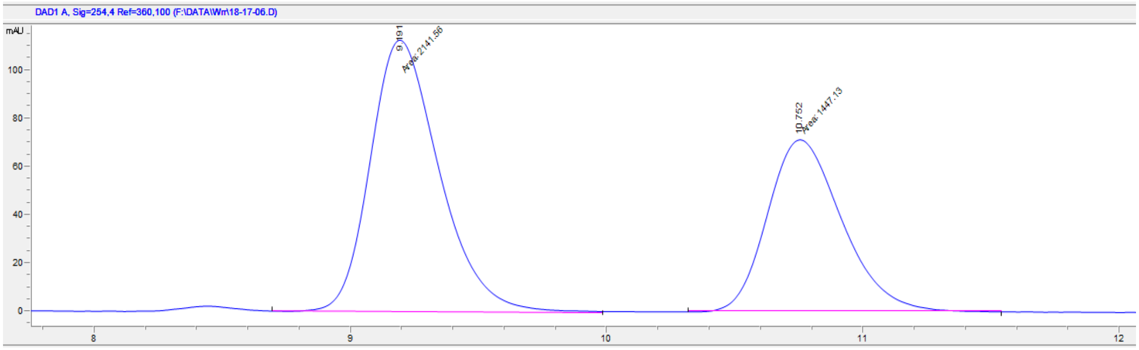
L10, 46%, 15% ee

Under anhydrous and oxygen-free conditions, to a dried tube equipped with a magnetic stir bar was added $Cu(OTf)_2$ (5.0 mg, 10 mol%) and **L** (15 mol%), and CH_2Cl_2 (0.5 mL), stirring the reaction mixture for 30 mins at room temperature. Under oxygen-free conditions, to a suspension of **1** (0.1 mmol, 2.0 equiv.), **4a** (0.05 mmol, 1.0 equiv.) and CH_2Cl_2 (0.5 mL) in another dried 25 mL Schlenk tube was added DTBP (2.0 equiv.). After stirring the reaction mixture for 5 mins at room temperature, the above mixture containing Copper catalyst was transferred to the present Schlenk tube and stirred at 25˚C for overnight. After completion of the reaction (monitored by TLC), the solvent was removed under vacuum and the crude product. Purification via column chromatography on silica gel (PE/EA = 20/1, *v/v*) afforded **5a** as colorless oil.

L8: The enantiomeric excess was analysed by HPLC: *e.r.* = 60:40 (Chiralcel OD, i-propanol/hexane = 5/95, flow rate 1.0 mL/min, λ = 254 nm); t_{minor} = 9.191 min, t_{major} = 10.752 min.

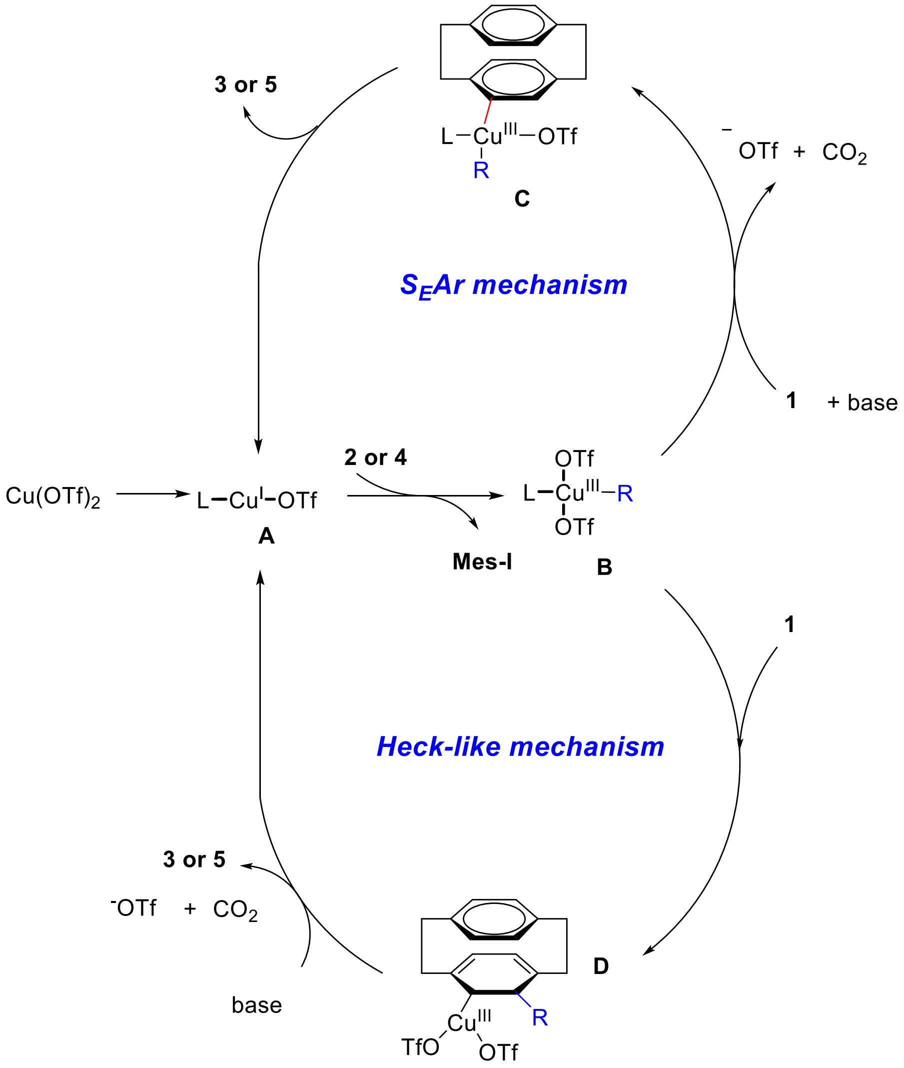


Peak#	Time	Area	Area %	Height	Width	Symmetry factor
1	9.304	2563.5	50.015	136.3	0.3135	0.721
2	10.866	2561.9	49.985	118.8	0.3594	0.732



Peak#	Time	Area	Area %	Height	Width	Symmetry factor
1	9.191	2141.6	59.675	113.2	0.3153	0.723
2	10.752	1447.1	40.325	71.5	0.3375	0.761

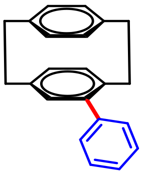
7. Proposed mechanism



On the basis of literature reports,[6, 7] a possible mechanism for the Cu-catalysed C-H bond alkenylation of PCP with hypervalent iodonium is depicted. Two distinct possible pathways were provided below: (1) S$_E$Ar process: [6] The actual catalytically reactive Cu(I)-OTf species **A** was in-situ generated from pre-catalyst (CuOTf)$_2$·Tol or Cu(OTf)$_2$, which undergoes oxidative addition towards diaryliodonium triflate to give a R-Cu(III)-OTf species **B** (R = aryl or alkenyl). Then, the electrophilic metalation of PCP by **B** in the presence of a base could furnish the R-Cu(III)-PCP species **C**. Finally, the reductive elimination of **C** gives the coupling product **3** or **5** and regenerates the reactive Cu(I)-OTf species; (2) Heck-like process:[2, 7] The R-Cu(III)-OTf species **B** undergoes electrophilic insertion to the phenyl ring in PCP to give the intermediate **D**. Next, the C-Cu bond breaks to transfer Cu(III) to Cu(I) and the free OTf anion abstracts the proton and restores the aromaticity.

8. Characterization of new compounds

8.1 Characterization of the arylated products

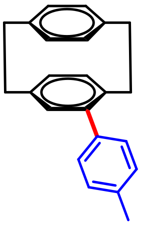


4-Phenyl[2.2]paracyclophane (3a): Purification *via* column chromatography on silica gel (PE/EA = 20/1, *v/v*) afforded **3a** (0.041 g, 0.146 mmol, 73 % yield). Colorless solid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.55 - 7.42 (m, 4H), 7.35 (ddd, *J* = 8.7, 5.5, 2.4 Hz, 1H), 6.68 - 6.46 (m, 7H), 3.43 (ddd, *J* = 12.5, 10.0, 3.1 Hz, 1H), 3.24 - 2.79 (m, 6H), 2.66 (ddd, *J* = 12.9, 9.9, 4.4 Hz, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 141.8, 141.3, 139.8, 139.7, 139.4, 137.0, 135.8, 133.1, 132.5, 132.2, 132.2, 132.1, 129.8, 129.7 (2C), 128.5 (2C), 126.7, 35.5, 35.2, 34.9, 34.1.

HRMS (EI): $[M]^+$ cacld for $C_{22}H_{20}^+$ 284.1560, found: 284.1565.

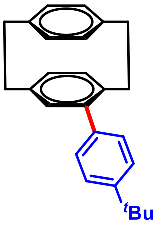


4-(4-Tolyl)[2.2]paracyclophane (3b): Purification *via* column chromatography on silica gel (PE/EA=20/1, *v/v*) afforded **3b** (0.041 g, 0.138 mmol, 69 % yield). Colorless solid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.35 (t, *J* = 7.5 Hz, 1H), 7.31 - 7.25 (m, 2H), 7.17 (d, *J* = 7.4 Hz, 1H), 6.62 (td, *J* = 7.6, 1.9 Hz, 2H), 6.56 (td, *J* = 4.6, 2.4 Hz, 4H), 6.48 (dd, *J* = 7.4, 1.7 Hz, 1H), 3.43 (ddd, *J* = 12.7, 10.0, 3.2 Hz, 1H), 3.22 - 2.79 (m, 6H), 2.68 (ddd, *J* = 12.9, 9.9, 4.5 Hz, 1H), 2.45 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 141.8, 139.8, 139.6, 139.4, 138.5, 137.0, 136.4, 135.8, 133.1, 132.5, 132.1 (2C), 132.1 (2C), 132.0, 129.8, 129.6, 129.2, 35.5, 35.3, 34.9, 34.2, 21.2.

HRMS (EI): $[M]^+$ Cacld for $C_{23}H_{22}^+$ 298.1721, found: 298.1721.

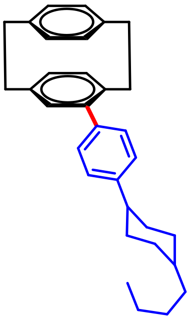


4-(4-(tert-butyl)phenyl)[2.2]paracyclophane (3c): Purification *via* column chromatography on silica gel (PE/EA=20/1, *v/v*) afforded **3c** (0.048 g, 0.142 mmol, 71 % yield). Colorless solid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.75 - 7.48 (m, 4H), 6.90 - 6.50 (m, 7H), 3.63 (ddt, *J* = 12.2, 9.0, 2.6 Hz, 1H), 3.38 - 2.94 (m, 6H), 2.86 (tdd, *J* = 10.7, 5.4, 2.0 Hz, 1H), 1.58 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 149.6, 141.9, 140.0, 139.7, 139.5, 138.5, 137.2, 135.9, 133.3, 132.6, 132.39 132.3, 132.1, 130.1, 129.5 (2C), 125.5 (2C), 35.7, 35.47, 35.1, 34.7, 34.3, 31.6 (3C).

HRMS (EI): $[M]^+$ cacld for $C_{26}H_{28}^+$ 340.5095, found: 340.5061.

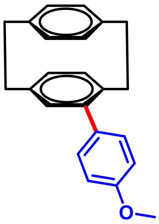


4-(4-(4-butylcyclohexyl)phenyl)[2.2]paracyclophane (3d): Purification *via* column chromatography on silica gel (PE/EA=10/1, *v/v*) afforded **3d** (0.034 g, 0.120 mmol, 60 % yield). Colorless solid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.46 - 7.30 (m, 4H), 6.66 (ddd, *J* = 7.8, 4.4, 1.9 Hz, 2H), 6.59 (ddd, *J* = 7.5, 5.4, 2.4 Hz, 4H), 6.51 (dd, *J* = 7.7, 1.9 Hz, 1H), 3.48 (ddd, *J* = 12.3, 9.9, 3.0 Hz, 1H), 3.33 - 2.80 (m, 6H), 2.72 (ddd, *J* = 12.9, 9.9, 4.3 Hz, 1H), 2.57 (ddd, *J* = 12.1, 8.7, 3.4 Hz, 1H), 2.06 - 1.89 (m, 4H), 1.67- 1.47 (m, 3H), 1.43 - 1.29 (m, 6H), 1.22 - 1.06 (m, 2H), 0.95 (td, *J* = 5.8, 4.7, 2.2 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 146.4, 141.9, 139.8, 139.5, 139.3, 138.8, 137.0, 135.7, 133.1, 132.5, 132.1, 132.1, 131.9, 129.9, 129.5 (2C), 126.9 (2C), 44.3, 37.4, 37.1, 35.5, 35.3, 34.9, 34.4, 34.4, 34.2, 33.7, 33.7, 29.2, 23.0, 14.1.

HRMS (EI): $[M]^+$ cacld for $C_{32}H_{38}^+$ 422.2974, found: 422.2983.

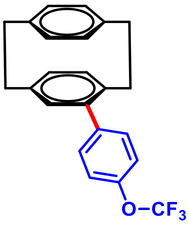


4-(4-methoxyphenyl)[2.2]paracyclophane (3e): Purification *via* column chromatography on silica gel (PE/EA=20/1, *v/v*) afforded **3e** (0.044 g, 0.142 mmol, 71 % yield). Colorless solid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.52 - 7.34 (m, 2H), 7.11 - 6.94 (m, 2H), 6.74 - 6.36 (m, 7H), 3.88 (s, 3H), 3.52 - 3.32 (m, 1H), 3.24 - 2.76 (m, 6H), 2.74 - 2.59 (m, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 158.7, 141.4, 139.8, 139.6, 139.3, 136.9, 135.7, 134.0, 133.1, 132.5, 132.0, 132.0, 131.8, 130.7 (2C), 129.7, 113.9 (2C), 55.3, 35.5, 35.2, 34.8, 34.2.

HRMS (EI): $[M]^+$ cacld for $C_{23}H_{22}O^+$ 314.1671, found: 314.1671.



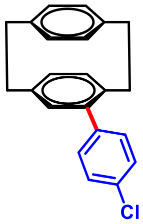
4-(4-(trifluoromethoxy)phenyl)[2.2]paracyclophane (3f): Purification *via* column chromatography on silica gel (PE/EA=10/1, *v/v*) afforded **3f** (0.025 g, 0.07 mmol, 35 % yield). Colorless solid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.55 -7.46 (m, 2H), 7.31 (d, *J* = 8.2 Hz, 2H), 6.73 - 6.41 (m, 7H), 3.36 (ddd, *J* = 11.7, 9.9, 2.5 Hz, 1H), 3.22 - 2.79 (m, 6H), 2.73 - 2.59 (m, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 148.2, 140.4, 139.9, 139.7, 139.6, 139.4, 137.0, 136.0, 133.2, 133.0, 132.6, 132.1, 132.0, 130.9 (2C), 129.6, 120.9 (2C), 120.6 (q, J = 257.1 Hz), 35.7, 35.5, 35.2, 34.9, 34.0.

^{19}F NMR (376 MHz, Chloroform-*d*) δ -57.68.

HRMS (EI): [M]+ cacld for $C_{23}H_{19}OF_3^+$ 368.1383, found: 368.1382.

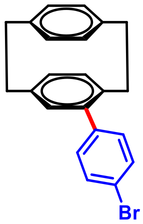


4-(4-chlorophenyl)[2.2]paracyclophane (3g): Purification *via* column chromatography on silica gel (PE/EA=10/1, *v/v*) afforded **3g** (0.034 g, 0.108 mmol, 54 % yield). Colorless solid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.40 (qd, *J* = 8.6, 1.4 Hz, 4H), 6.71 - 6.40 (m, 7H), 3.45 - 3.31 (m, 1H), 3.13 - 2.76 (m, 6H), 2.74 - 2.50 (m, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 140.6, 139.9, 139.7, 139.5, 137.0, 136.0, 133.3, 133.1, 132.9, 132.7, 132.6, 132.1, 132.0, 131.0 (2C), 129.7, 128.8 (2C), 35.5, 35.3, 34.9, 34.1.

HRMS (EI): [M]$^+$ cacld for $C_{22}H_{19}Cl^+$ 318.1170, found: 318.1167.

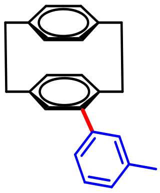


4-(4-bromopheny)[2.2]paracyclophane (3h): Purification *via* column chromatography on silica gel (PE/EA=10/1, *v/v*) afforded **3h** (0.047 g, 0.130 mmol, 65 % yield). Colorless solid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.79 - 7.48 (m, 2H), 7.43 - 7.29 (m, 2H), 6.73 - 6.29 (m, 7H), 3.50 - 3.28 (m, 1H), 3.23 - 2.79 (m, 6H), 2.72 - 2.50 (m, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 140.6, 140.2, 139.9, 139.7, 139.4, 137.0, 136.0, 133.2, 132.7, 132.6, 132.0, 131.9, 131.7 (2C), 131.3 (2C), 129.6, 121.1, 35.5, 35.2, 34.9, 34.1.

HRMS (EI): [M]$^+$ cacld for $C_{22}H_{19}Br^+$ 362.0665, found: 362.0661.

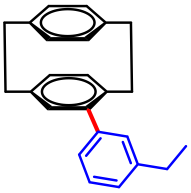


4-(3-tolyl)[2.2]paracyclophane (3i): Purification *via* column chromatography on silica gel (PE/EA = 20/1, *v/v*) afforded **3i** (0.041 g, 0.140 mmol, 70 % yield). Colorless solid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.53 -7.27 (m, 3H), 7.27 - 7.06 (m, 1H), 6.75 - 6.38 (m, 7H), 3.47 (ddd, *J* = 12.6, 10.0, 3.2 Hz, 1H), 3.27 - 2.83 (m, 6H), 2.73 (ddd, *J* = 13.0, 9.9, 4.5 Hz, 1H), 2.49 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 142.0, 141.3, 139.9, 139.7, 139.4, 137.9, 137.1, 135.8, 133.2, 132.6, 132.2, 132.2, 132.2, 130.5, 129.9, 128.4, 127.5, 126.8, 35.6, 35.3, 35.0, 34.2, 21.7.

HRMS (EI): $[M]^+$ cacld for $C_{23}H_{22}^+$ 298.1721, found: 298.1723.

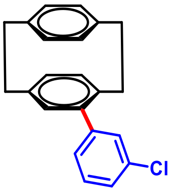


4-(3-ethylphenyl)[2.2]paracyclophane (3j): Purification *via* column chromatography on silica gel (PE/EA=20/1, *v/v*) afforded **3j** (0.041 g, 0.134 mmol, 67 % yield). Colorless solid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.54 - 7.32 (m, 3H), 7.30 - 7.23 (m, 1H), 6.76 - 6.61 (m, 5H), 6.56 (d, *J* = 11.0 Hz, 2H), 3.51 (ddd, *J* = 12.6, 10.0, 3.1 Hz, 1H), 3.30 - 2.68 (m, 9H), 1.40 (t, *J* = 7.6 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 144.3, 142.0, 141.3, 139.8, 139.6, 139.4, 137.1, 135.7, 133.15, 132.5, 132.1, 132.1 (2C), 129.9, 129.5, 128.4, 126.9, 126.3, 35.5, 35.2, 34.9, 34.2, 29.0, 15.7.

HRMS (EI): $[M]^+$ cacld for $C_{24}H_{24}^+$ 312.1873, found: 312.1872.

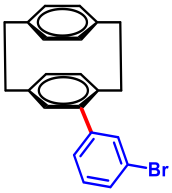


4-(3-chlorophenyl)[2.2]paracyclophane (3k): Purification *via* column chromatography on silica gel (PE/EA=20/1, *v/v*) afforded **3k** (0.041 g, 0.130 mmol, 65 % yield). Colorless solid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.56 (t, *J* = 1.8 Hz, 1H), 7.55 - 7.39 (m, 3H), 6.85 - 6.51 (m, 7H), 3.47 (ddd, *J* = 11.8, 9.9, 2.6 Hz, 1H), 3.32 - 2.88 (m, 6H), 2.76 (ddd, *J* = 12.8, 9.9, 4.0 Hz, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 143.1,140.4, 139.9, 139.6, 139.4, 137.0, 135.9, 133.2, 132.7, 132.6, 132.0, 132.0, 129.7, 129.7, 129.5, 127.9, 126.8, 35.5, 35.2, 34.9, 34.0.

HRMS (EI): $[M]^+$ cacld for $C_{22}H_{19}Cl^+$ 318.1170, found: 318.1167.

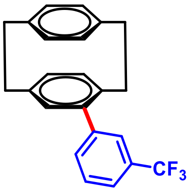


4-(3-bromophenyl)[2.2]paracyclophane (3l): Purification *via* column chromatography on silica gel (PE/EA=20/1, *v/v*) afforded **3l** (0.049 g, 0.136 mmol, 68 % yield). Colorless solid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.72 (t, *J* = 1.9 Hz, 1H), 7.58 (dt, *J* = 7.9, 1.6 Hz, 1H), 7.49 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.41 (dd, *J* = 8.8, 6.7 Hz, 1H), 6.85 - 6.49 (m, 7H), 3.47 (ddd, *J* = 11.8, 9.9, 2.6 Hz, 1H), 3.32 - 2.90 (m, 6H), 2.85 - 2.60 (m, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 143.3, 140.3, 139.9, 139.7, 139.5, 137.0, 136.0, 133.2, 132.8, 132.6, 132.5, 132.0, 132.0, 130.0, 129.7, 129.7, 128.4, 122.5, 35.5, 35.2, 34.9, 34.0.

HRMS (EI): $[M]^+$ cacld for $C_{22}H_{19}Br^+$ 362.0665, found: 362.0662.



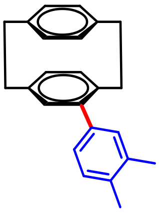
4-(3-(trifluoromethyl)phenyl)[2.2]paracyclophane (3m): Purification *via* column chromatography on silica gel (PE/EA=20/1, *v/v*) afforded **3m** (0.046 g, 0.130 mmol, 65 % yield). Colorless solid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.65 (t, *J* = 1.8 Hz, 1H), 7.56 – 7.32 (m, 3H), 6.81 - 6.33 (m, 7H), 3.42 (ddd, *J* = 11.9, 9.9, 2.6 Hz, 1H), 3.27 - 2.84 (m, 6H), 2.72 (ddd, *J* = 12.8, 9.9, 4.1 Hz, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 141.9, 140.3, 140.1, 139.6, 139.6, 139.5, 137.1, 136.1, 133.3, 133.0 (d, *J* = 3.7 Hz), 132.7, 132.1 (dd, *J* = 5.4, 3.4 Hz), 132.0, 130.9 (d, *J* = 32.0 Hz), 129.6, 129.0, 126.4 (q, *J* = 3.8 Hz), 124.3 (q, J = 273.1Hz),123.5 (q, *J* = 3.7 Hz), 35.5, 35.2, 34.9, 34.0.

^{19}F NMR (376 MHz, Chloroform-*d*) δ -57.68.

HRMS (EI): $[M]^+$ cacld for $C_{23}H_{19}F_3^+$ 352.1434, found: 354.1435.

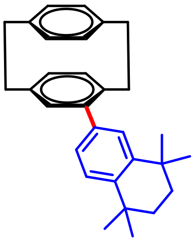


4-(3,4-dimethylphenyl)[2.2]paracyclophane (3n): Purification *via* column chromatography on silica gel (PE/EA=20/1, *v/v*) afforded **3n** (0.041 g, 0.132 mmol, 66 % yield). Colorless solid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.32 (d, *J* = 2.3 Hz, 2H), 6.71 (dd, *J* = 7.8, 1.9 Hz, 2H), 6.66-6.61 (m, 4H), 6.59 - 6.51 (m, 2H), 3.54 (ddd, *J* = 12.6, 10.0, 3.2 Hz, 1H), 3.25 - 2.90 (m, 6H), 2.84 - 2.72 (m, 1H), 2.45 (s, 3H), 2.42 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 141.9, 139.9, 139.6, 139.4, 139.0, 137.0, 136.5, 135.7, 135.1, 133.1, 132.5, 132.1, 132.1, 131.9, 131.0, 129.9, 129.8, 127.1, 35.5, 35.2, 34.9, 34.2, 20.0, 19.5.

HRMS (EI): $[M]^+$ cacld for $C_{24}H_{24}^+$ 312.1873, found: 312.1874.

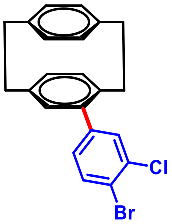


4-(5,5,8,8-tetramethyl-5,6,7,8-tetrahydronaphthalen-2-yl)[2.2]paracyclophane (3o): Purification *via* column chromatography on silica gel (PE/EA=20/1, *v/v*) afforded **3o** as white solid (0.052 g, 0.134 mmol, 67 % yield). Colorless solid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.51 - 7.37 (m, 2H), 7.34 - 7.23 (m, 1H), 6.78 - 6.49 (m, 7H), 3.49 (ddd, *J* = 12.4, 9.9, 3.1 Hz, 1H), 3.36 - 2.85 (m, 6H), 2.76 (ddd, *J* = 12.9, 9.8, 4.4 Hz, 1H), 1.80 (s, 4H), 1.60 - 1.24 (m, 12H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 144.6, 143.3, 142.2, 139.9, 139.6, 139.4, 138.2, 137.1, 135.7, 133.2, 132.5, 132.1, 132.1, 131.9, 129.9, 128.3, 126.6, 126.6, 35.6, 35.3, 35.2, 35.0, 34.4, 34.2, 34.1, 32.1, 32.0, 31.9.

HRMS (EI): [M]+ cacld for $C_{30}H_{34}^+$ 394.2656, found: 394.2652.

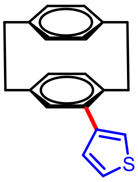


4-(4-bromo-3-chlorophenyl)[2.2]paracyclophane (3p): Purification *via* column chromatography on silica gel (PE/EA=10/1, *v/v*) afforded **3p** (0.036 g, 0.092 mmol, 46 % yield). Colorless solid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.73 (d, *J* = 8.2 Hz, 1H), 7.58 (s, 1H), 7.36 - 7.11 (m, 1H), 6.87 - 6.25 (m, 7H), 3.38 (t, *J* = 10.3 Hz, 1H), 3.27 - 2.84 (m, 6H), 2.79 - 2.56 (m, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 142.0, 140.1, 139.6, 139.5, 139.4, 136.9, 136.1, 134.5, 133.7, 133.3, 133.0, 132.7, 131.9, 131.8, 131.2, 129.5, 129.2, 120.8, 35.5, 35.1, 34.9, 34.0.

HRMS (EI): $[M]^+$ cacld for $C_{22}H_{18}BrCl^+$ 396.0275, found: 396.0272.



3-(1,4(1,4)-dibenzenacyclohexaphane-12-yl)thiophene (3q)

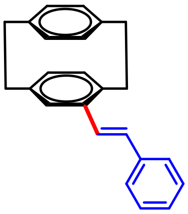
Purification *via* column chromatography on silica gel (PE/EA=20/1, *v/v*) afforded **3q** (0.4 mmol scale, 0.026 g, 0.092 mmol, 23 % yield). Colorless solid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.44 (dd, *J* = 4.9, 3.0 Hz, 1H), 7.35 (dd, *J* = 3.0, 1.3 Hz, 1H), 7.32 - 7.23 (m, 1H), 6.76 - 6.49 (m,7H), 3.64 - 3.52 (m, 1H), 3.25 - 2.88 (m, 6H), 2.78 - 2.66 (m, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 142.6, 139.8, 139.7, 139.4, 137.3, 136.8, 135.6, 133.2, 132.7, 132.7, 132.0, 131.9, 129.7, 128.9, 125.4, 122.2, 35.5, 35.2, 34.8, 34.4.

HRMS (EI): $[M]^+$ cacld for $C_{20}H_{18}S^+$ 290.1129, found: 290.1134.

8.2 characterization of the alkenylated products



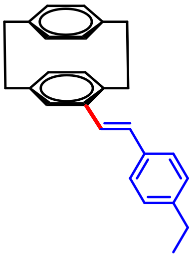
(E)-1^2-styryl-1,4(1,4)-dibenzenacyclohexaphane (5a):

Purification *via* column chromatography on silica gel (PE/EA=20/1, *v/v*) afforded **5a** (0.051 g, 0.166 mmol, 83 % yield). Colorless solid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.58 (d, *J* = 7.4 Hz, 2H), 7.41 (t, *J* = 7.6 Hz, 2H), 7.29 (t, *J* = 7.3 Hz, 1H), 7.19 (d, *J* = 16.2 Hz, 1H), 6.89 (d, *J* = 16.2 Hz, 1H), 6.73 - 6.65 (m, 2H), 6.58 - 6.42 (m, 5H), 3.59 (ddd, *J* = 13.4, 9.6, 1.4 Hz, 1H), 3.22 - 2.81 (m, 7H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 139.9, 139.4, 139.3, 138.4, 137.9, 137.4, 134.9, 133.1, 133.0, 131.8, 131.7, 130.2, 129.8, 129.1, 128.7 (2C), 127.5, 126.9, 126.5 (2C), 35.4, 35.2, 34.9, 34.0.

HRMS (EI): $[M]^+$ cacld for $C_{24}H_{22}^+$ 310.1722, found: 310.1735.



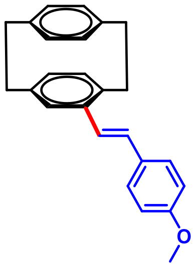
(E)-1^2-(4-ethylstyryl)-1,4(1,4)-dibenzenacyclohexaphane (5b):

Purification *via* column chromatography on silica gel (PE/EA=20/1, *v/v*) afforded **5b** (0.055 g, 0.162 mmol, 81 % yield). Colorless solid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.52 (d, *J* = 8.1 Hz, 2H), 7.25 (d, *J* = 7.8 Hz, 2H), 7.16 (d, *J* = 16.1 Hz, 1H), 6.89 (d, *J* = 16.1 Hz, 1H), 6.72 (dd, *J* = 7.8, 1.5 Hz, 1H), 6.66 (s, 1H), 6.58 - 6.41 (m, 5H), 3.65 - 3.55 (m, 1H), 3.22 - 2.81 (m, 7H), 2.70 (q, *J* = 7.6 Hz, 2H), 1.29 (t, *J* = 7.6 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 143.8, 139.9, 139.3, 139.2, 138.2, 137.6, 135.4, 134.9, 133.0, 132.9, 131.7, 131.6, 130.1, 129.8, 129.1, 128.3 (2C), 126.5 (2C), 126.0, 35.5, 35.2, 34.8, 34.0, 28.7, 15.6.

HRMS (EI): [M]+ cacld for $C_{26}H_{26}^+$ 338.2035, found: 338.2041.



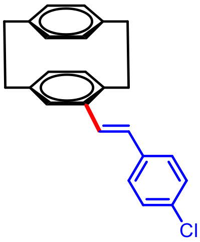
(E)-1^2-(4-methoxystyryl)-1,4(1,4)-dibenzenacyclohexaphane (5c):

Purification *via* column chromatography on silica gel (PE/EA=20/1, *v/v*) afforded **5c** (0.049 g, 0.144 mmol, 72 % yield). Colorless solid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.34 (t, *J* = 7.9 Hz, 1H), 7.23 - 7.16 (m, 2H), 7.15 - 7.08 (m, 1H), 6.92 - 6.83 (m, 2H), 6.74 - 6.65 (m, 2H), 6.58 - 6.42 (m, 5H), 3.90 (s, 3H), 3.64 - 3.52 (m, 1H), 3.23 - 2.81 (m, 7H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 139.9, 139.4, 139.3, 138.4, 138.3, 137.9, 137.5, 134.9, 133.0(2C), 131.8, 131.7, 130.2, 129.8, 129.3, 128.6, 128.3, 127.2, 126.7, 123.6, 35.5, 35.2, 34.9, 34.0, 21.5.

HRMS (EI): [M]+ cacld for $C_{25}H_{24}O^+$ 340.1827, found: 340.1833.



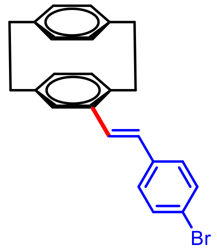
(E)-1^2-(4-chlorostyryl)-1,4(1,4)-dibenzenacyclohexaphane (5d):

Purification *via* column chromatography on silica gel (PE/EA=20/1, *v/v*) afforded **5d** (0.033 g, 0.096 mmol, 48 % yield). Colorless solid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.50 (d, *J* = 8.4 Hz, 2H), 7.37 (d, *J* = 8.4 Hz, 2H), 7.16 (d, *J* = 16.1 Hz, 1H), 6.83 (d, *J* = 16.1 Hz, 1H), 6.67 (d, *J* = 11.1 Hz, 2H), 6.50 (ddt, *J* = 29.4, 14.2, 7.7 Hz, 5H), 3.64 - 3.52 (m, 1H), 3.23 - 2.81 (m, 7H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 140.0, 139.3, 139.2, 138.4, 137.1, 136.4, 135.0, 133.0, 133.0, 133.0, 132.0, 131.7, 130.2, 129.8, 128.9(2C), 127.8, 127.6 (2C), 127.5, 35.4, 35.2, 34.9, 33.9.

HRMS (EI): [M]+ cacld for $C_{24}H_{21}Cl^+$ 344.1332, found: 344.1340.



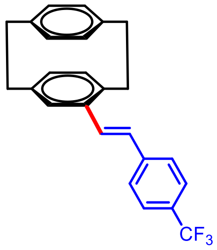
(E)-1^2-(4-bromostyryl)-1,4(1,4)-dibenzenacyclohexaphane (5e):

Purification *via* column chromatography on silica gel (PE/EA=20/1, *v/v*) afforded **5e** (0.050 g, 0.13 mmol, 65 % yield). Colorless solid.

^{1}H NMR (400 MHz, Chloroform-d) δ 7.59 - 7.52 (m, 2H), 7.46 (d, J = 8.5 Hz, 2H), 7.20 (d, J = 16.2 Hz, 1H), 6.84 (d, J = 16.1 Hz, 1H), 6.70 (d, J = 9.5 Hz, 2H), 6.61 - 6.44 (m, 5H), 3.65 - 3.55 (m, 1H), 3.26 - 2.84 (m, 7H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 140.0, 139.4, 139.2, 138.5, 137.0, 136.8, 135.0, 133.1, 133.0, 132.1, 131.8(2C), 131.7, 130.2, 129.8, 127.9(2C), 127.8, 127.5, 121.1, 35.4, 35.2, 34.9, 33.9.

HRMS (EI): [M]+ cacld for $C_{24}H_{21}Br^+$ 388.0827, found: 388.0834.



(E)-1^2-(4-(trifluoromethyl)styryl)-1,4(1,4)-dibenzenacyclohexaphane (5f):

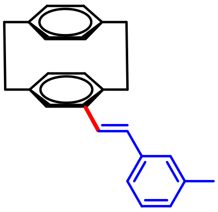
Purification *via* column chromatography on silica gel (PE/EA=20/1, *v/v*) afforded **5f** (0.048 g, 0.128 mmol, 64 % yield). Colorless solid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.68 (s, 4H), 7.30 (d, *J* = 15.9 Hz, 1H), 6.93 (d, *J* = 16.2 Hz, 1H), 6.74 - 6.66 (m, 2H), 6.62 - 6.44 (m, 5H), 3.67 - 3.57 (m, 1H), 3.26 - 2.87 (m, 7H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ141.3, 141.3, 140.1, 139.3, 139.1, 138.7, 136.7, 135.0, 133.0, 133.0, 132.4, 131.7, 130.2, 129.8, 129.2, 127.7 (q, J = 262.6 Hz), 127.5, 126.5 (2C), 125.6 (d, J = 3.8 Hz) (2C), 35.4, 35.2, 34.9, 33.9.

^{19}F NMR (376 MHz, Chloroform-*d*) δ -62.4.

HRMS (EI): [M]+ cacld for $C_{25}H_{21}F_3^+$ 378.1595, found: 378.1603.



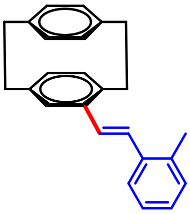
(E)-1^2-(3-methylstyryl)-1,4(1,4)-dibenzenacyclohexaphane (5g):

Purification *via* column chromatography on silica gel (PE/EA=20/1, *v/v*) afforded **5g** (0.45 g, 1.38 mmol, 69 % yield). Colorless solid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.40 (d, *J* = 5.7 Hz, 2H), 7.31 (t, *J* = 7.8 Hz, 1H), 7.19 (d, *J* = 16.2 Hz, 1H), 7.13 (d, *J* = 7.5 Hz, 1H), 6.88 (d, *J* = 16.1 Hz, 1H), 6.76 - 6.66 (m, 2H), 6.60 - 6.41 (m, 5H), 3.61 (ddd, *J* = 13.4, 9.7, 1.5 Hz, 1H), 3.22 - 2.82 (m, 7H), 2.44 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 159.9, 139.9, 139.6, 139.4, 139.3, 139.2, 138.4, 137.3, 134.9, 133.0, 131.8, 131.7, 130.2, 129.8, 129.7, 129.0, 127.2, 119.2, 112.8, 112.1, 55.3, 35.5, 35.2, 34.9, 34.0.

HRMS (EI): [M]+ cacld for $C_{25}H_{24}^+$ 324.1878, found: 324.1882.



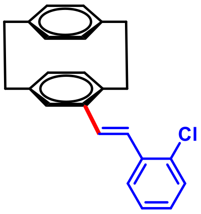
(E)-1^2-(2-methylstyryl)-1,4(1,4)-dibenzenacyclohexaphane (5h):

Purification *via* column chromatography on silica gel (PE/EA=20/1, *v/v*) afforded **5h** (0.045 g, 0.14 mmol, 70 % yield). Colorless solid.

^{1}H NMR (400 MHz, 1H NMR (400 MHz, Chloroform-d) δ 7.68 (d, J = 7.5 Hz, 1H), 7.30 (dd, J = 7.7, 3.7 Hz, 1H), 7.26 (d, J = 8.0 Hz, 2H), 7.17 - 7.05 (m, 2H), 6.80 (d, J = 7.8 Hz, 1H), 6.68 (s, 1H), 6.61 - 6.45 (m, 5H), 3.66 - 3.57 (m, 1H), 3.25 - 2.83 (m, 6H), 2.53 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 139.9, 139.3, 139.2, 138.4, 137.8, 137.1, 135.8, 134.9, 133.1, 133.0, 131.8, 131.6, 130.4(2C), 129.6, 128.5, 127.5, 127.3, 126.3, 125.5, 35.5, 35.2, 34.8, 34.0, 20.0.

HRMS (EI): [M]+ cacld for $C_{25}H_{24}^+$ 324.1878, found: 324.1881.



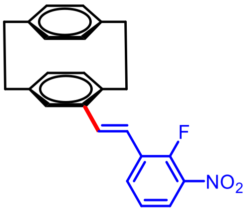
(E)-1^2-(2-chlorostyryl)-1,4(1,4)-dibenzenacyclohexaphane (5i):

Purification *via* column chromatography on silica gel (PE/EA=20/1, *v/v*) afforded **5i** (0.032 g, 0.094 mmol, 47 % yield). Colorless solid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.71 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.43 (dt, *J* = 7.9, 1.2 Hz, 1H), 7.37 - 7.28 (m, 2H), 7.24 (dd, *J* = 7.5, 1.6 Hz, 1H), 7.12 (d, *J* = 16.1 Hz, 1H), 6.77 (dd, *J* = 7.8, 1.9 Hz, 1H), 6.69 (d, *J* = 1.8 Hz, 1H), 6.60 - 6.39 (m, 5H), 3.75 - 3.40 (m, 1H), 3.30 - 2.61 (m, 7H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 140.0, 139.4, 139.1, 138.6, 137.2, 136.1, 134.9, 133.5, 133.1, 133.0, 132.2, 131.7, 130.4, 129.8, 129.7, 129.6, 128.4, 126.9, 126.6, 125.7, 35.4, 35.2, 34.8, 34.0.

HRMS (EI): [M]+ cacld for $C_{24}H_{21}Cl^+$ 344.1332, found: 344.1340.



(E)-1^2-(2-fluoro-3-nitrostyryl)-1,4(1,4)-dibenzenacyclohexaphane (5j):

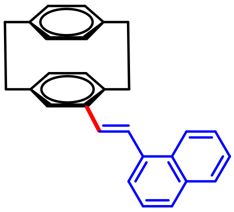
Purification *via* column chromatography on silica gel (PE/EA=10/1, *v/v*) afforded **5j** (0.046 g, 0.122 mmol, 61 % yield). Colorless solid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.92 (ddt, *J* = 10.0, 4.7, 2.2 Hz, 2H), 7.39 - 7.29 (m, 2H), 7.03 (d, *J* = 16.3 Hz, 1H), 6.74 - 6.62 (m, 2H), 6.59 - 6.41 (m, 5H), 3.62 - 3.52 (m, 1H), 3.25 - 2.85 (m, 7H).

^{13}C NMR (101 MHz, Chloroform-d) δ 152.7 (d, J = 266.4 Hz), 140.3, 139.4, 139.0 (d, J = 1.5 Hz), 136.4, 135.1, 133.1, 133.0, 132.9, 132.0, 131.9 (d, J = 5.2 Hz), 131.7, 130.3, 129.8, 129.0, 128.9, 124.1, 124.0, 124.0, 119.1, 119.0, 35.4, 35.1, 34.9, 33.9.

^{19}F NMR (376 MHz, Chloroform-*d*) δ -124.2.

HRMS (EI): [M]+ cacld for $C_{24}H_{20}NO_2F^+$ 373.1478, found: 373.1490.



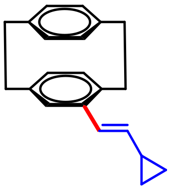
(E)-1^2-(2-(naphthalen-1-yl)vinyl)-1,4(1,4)-dibenzenacyclohexaphane (5k):

Purification *via* column chromatography on silica gel (PE/EA=20/1, *v/v*) afforded **5k** (0.037 g, 0.104 mmol, 52 % yield). Colorless solid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.34 (d, J = 8.3 Hz, 1H), 8.01 - 7.95 (m, 1H), 7.89 (dd, J = 14.0, 7.7 Hz, 2H), 7.73 (d, J = 15.8 Hz, 1H), 7.68 - 7.57 (m, 3H), 7.31 (d, J = 6.4 Hz, 1H), 6.92 - 6.82 (m, 2H), 6.68 - 6.51 (m, 5H), 3.69 (ddd, J = 13.4, 9.7, 1.4 Hz, 1H), 3.30 - 2.91 (m, 7H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 140.0, 139.4, 139.3, 138.5, 137.7, 135.7, 135.0, 133.8, 133.1, 133.1, 131.9, 131.7, 131.5, 130.5, 130.1, 129.7, 128.7, 128.0, 126.4, 126.2, 125.9, 125.8, 123.8, 123.6, 35.5, 35.3, 34.9, 34.0.

HRMS (EI): [M]+ cacld for $C_{28}H_{24}^+$ 360.1878, found: 360.1885.



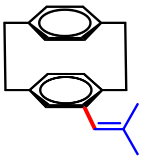
(E)-1^2-(2-cyclopropylvinyl)-1,4(1,4)-dibenzenacyclohexaphane (5l):

Purification *via* column chromatography on silica gel (PE/EA=20/1, *v/v*) afforded **5l** (0.037 g, 0.134 mmol, 67 % yield). Colorless solid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.77 - 6.71 (m, 1H), 6.56 - 6.46 (m, 3H), 6.39 (td, J = 9.3, 7.6, 4.5 Hz, 4H), 5.47 (dd, J = 15.6, 8.9 Hz, 1H), 3.53 - 3.43 (m, 1H), 3.18 - 2.71 (m, 7H), 1.64 (ddt, J = 12.4, 8.3, 4.3 Hz, 1H), 0.95 - 0.79 (m, 2H), 0.54 (ddt, J = 17.5, 9.7, 4.9 Hz, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 139.6, 139.4, 139.2, 137.9, 136.9, 135.6, 134.7, 133.0, 132.9, 131.7, 130.7, 130.0, 129.4, 125.7, 35.4, 35.2, 34.6, 33.8, 14.9, 7.4, 7.3.

HRMS (EI): [M]+ cacld for $C_{21}H_{22}^+$ 274.1722, found: 274.1731



(E)-1^2-(3-methylbut-1-en-1-yl)-1,4(1,4)-dibenzenacyclohexaphane (5m)

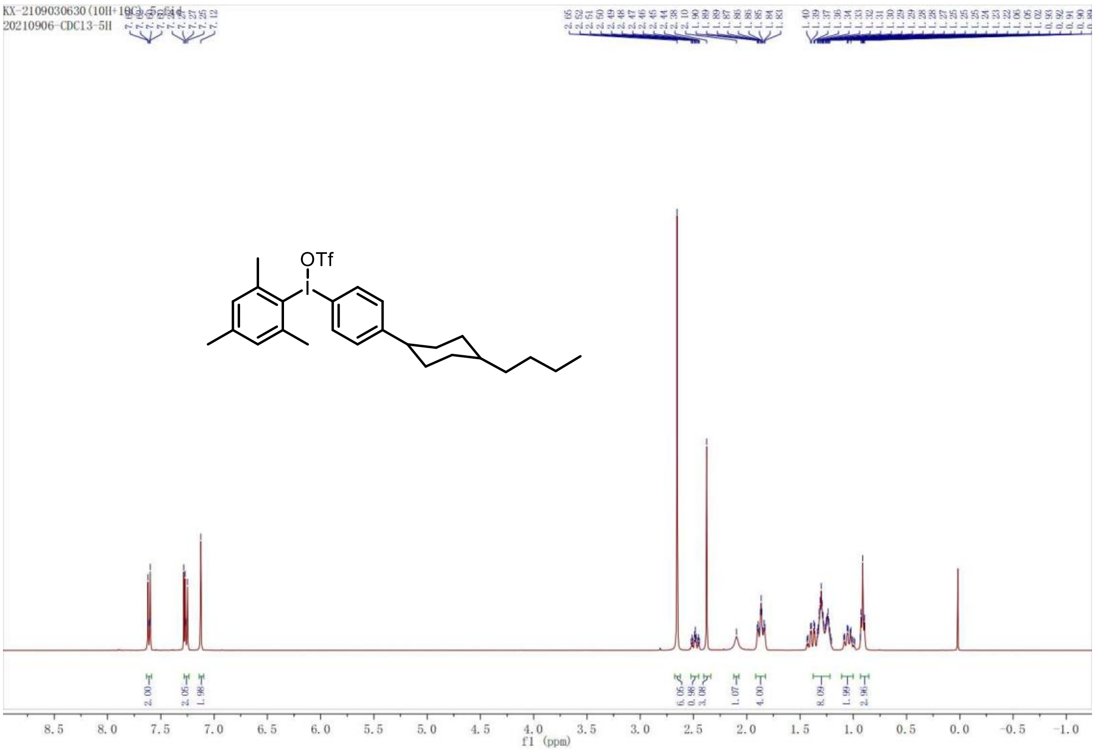
Purification *via* column chromatography on silica gel (PE/EA=30/1, *v/v*) afforded **5m** (0.027 g, 0.106 mmol, 53 % yield). Colorless solid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.79 (dd, *J* = 7.8, 1.9 Hz, 1H), 6.68 - 6.41 (m, 5H), 6.35 - 6.08 (m, 2H), 3.37 (ddd, *J* = 13.0, 9.0, 3.7 Hz, 1H), 3.24 - 2.93 (m, 6H), 2.85 (ddd, *J* = 13.2, 9.9, 6.3 Hz, 1H), 2.01 (d, *J* = 1.7 Hz, 3H), 1.72 (d, *J* = 1.5 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 139.7, 139.4, 139.0, 138.0, 135.0, 134.8, 134.4, 133.1 (2C), 132.9, 132.2, 130.8, 129.7, 124.7, 35.51, 35.25, 34.58, 33.98, 26.55, 19.51.

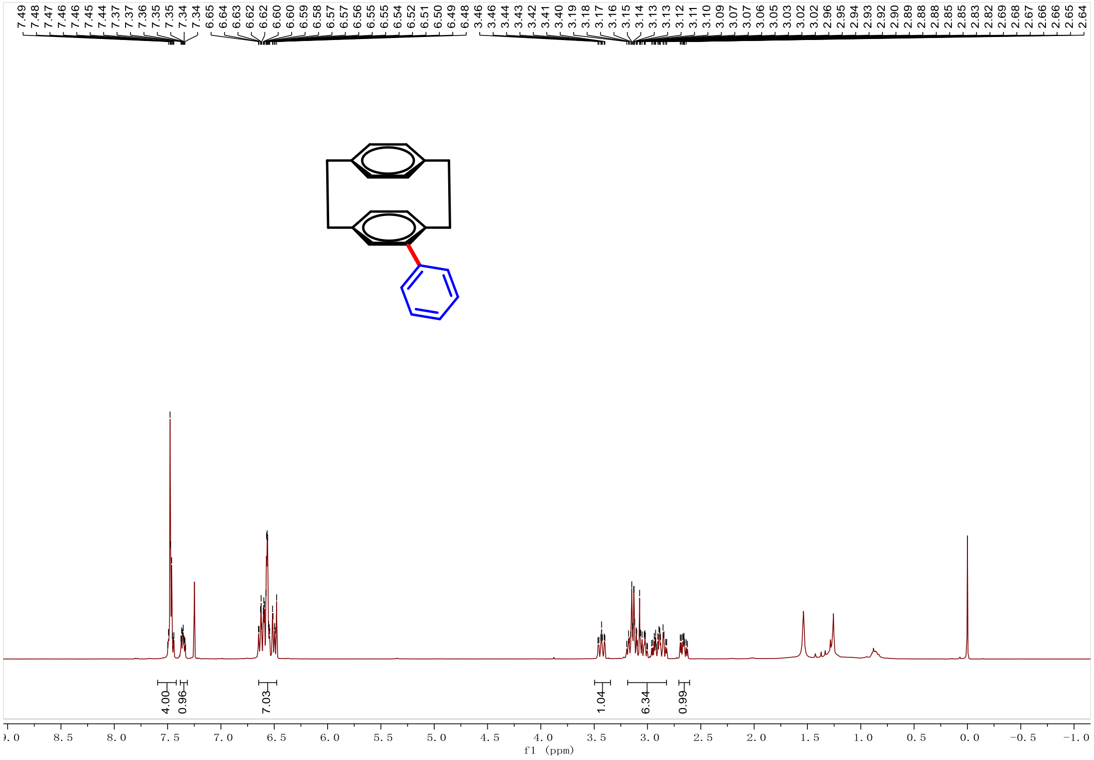
HRMS (EI): [M]+ cacld for $C_{20}H_{22}^+$ 262.1722, found: 262.1731.

9. NMR spectra

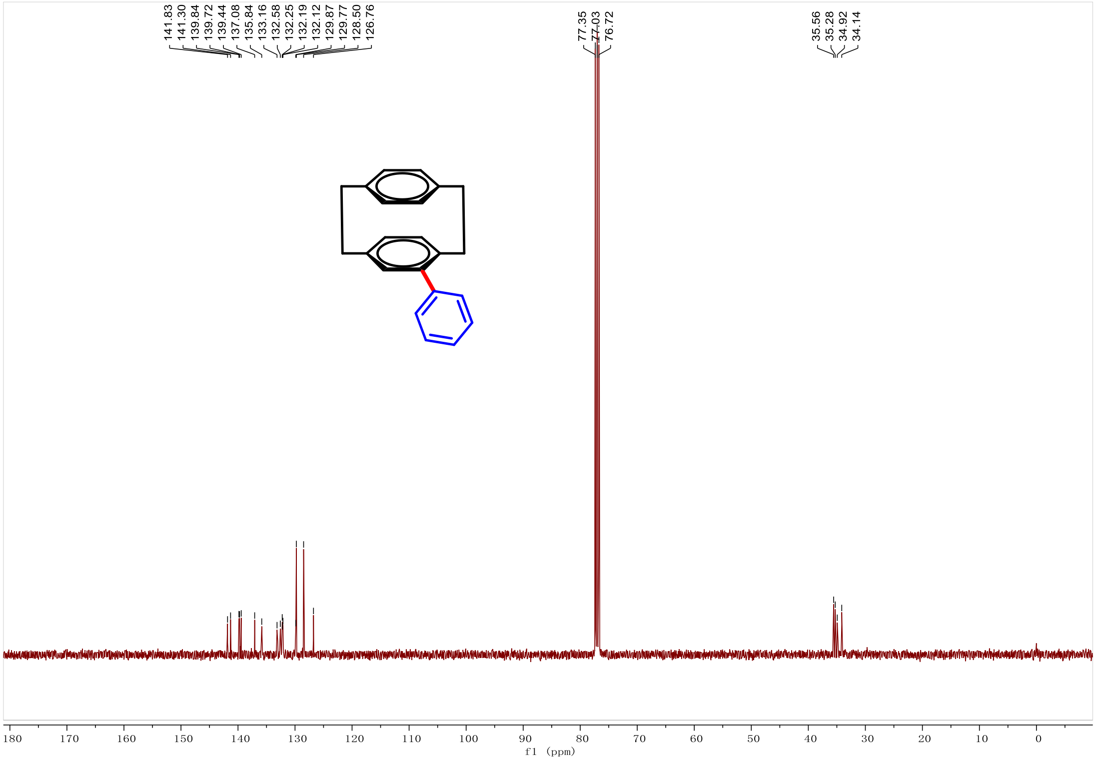


^{1}H NMR spectrum of 2d ($CDCl_3$, 400 MHz)

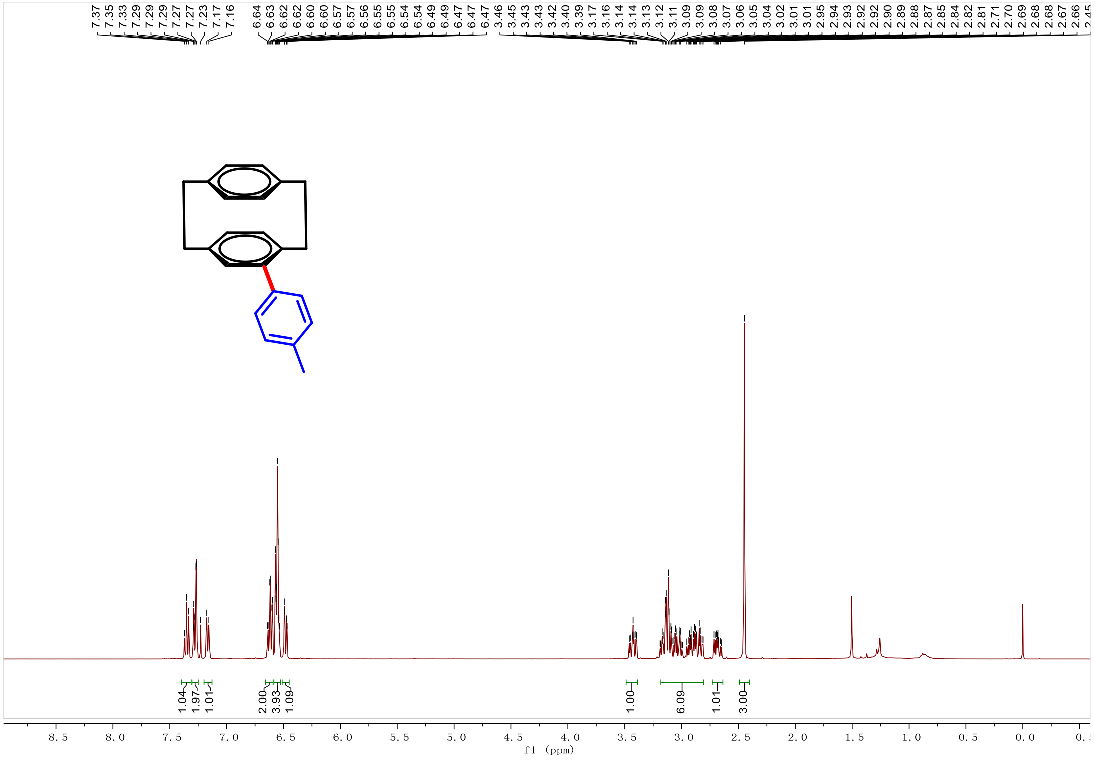
^{13}C NMR spectrum of 2d ($CDCl_3$, 101 MHz)



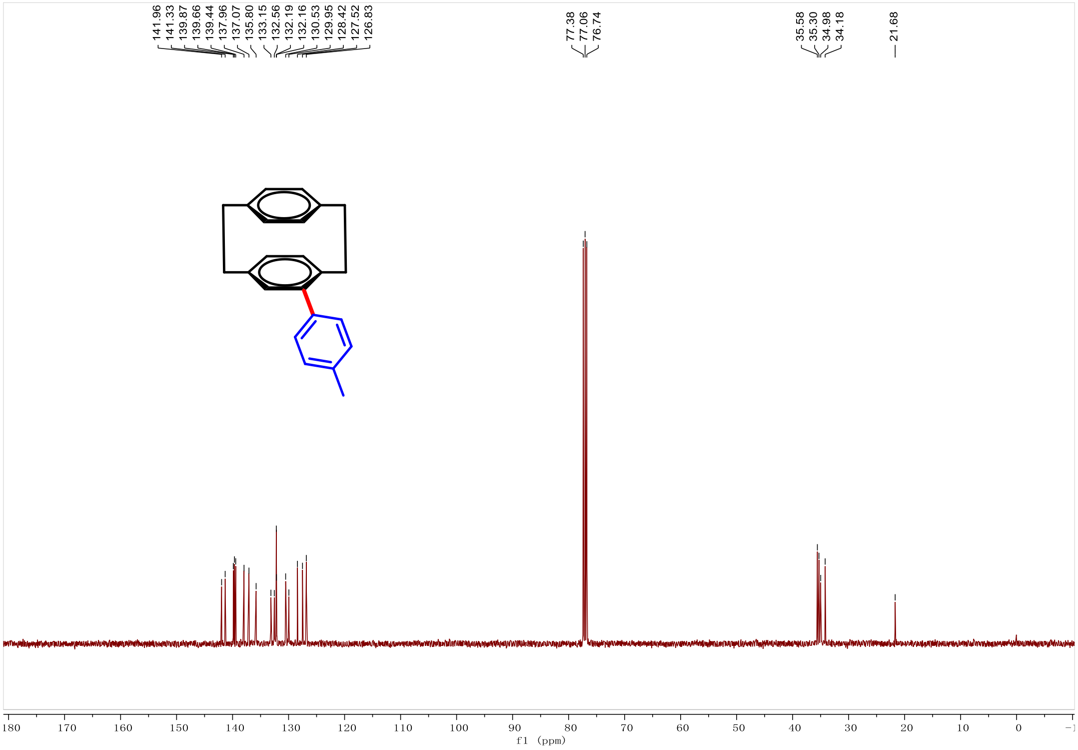
^{1}H NMR spectrum of 3a ($CDCl_3$, 400MHz)



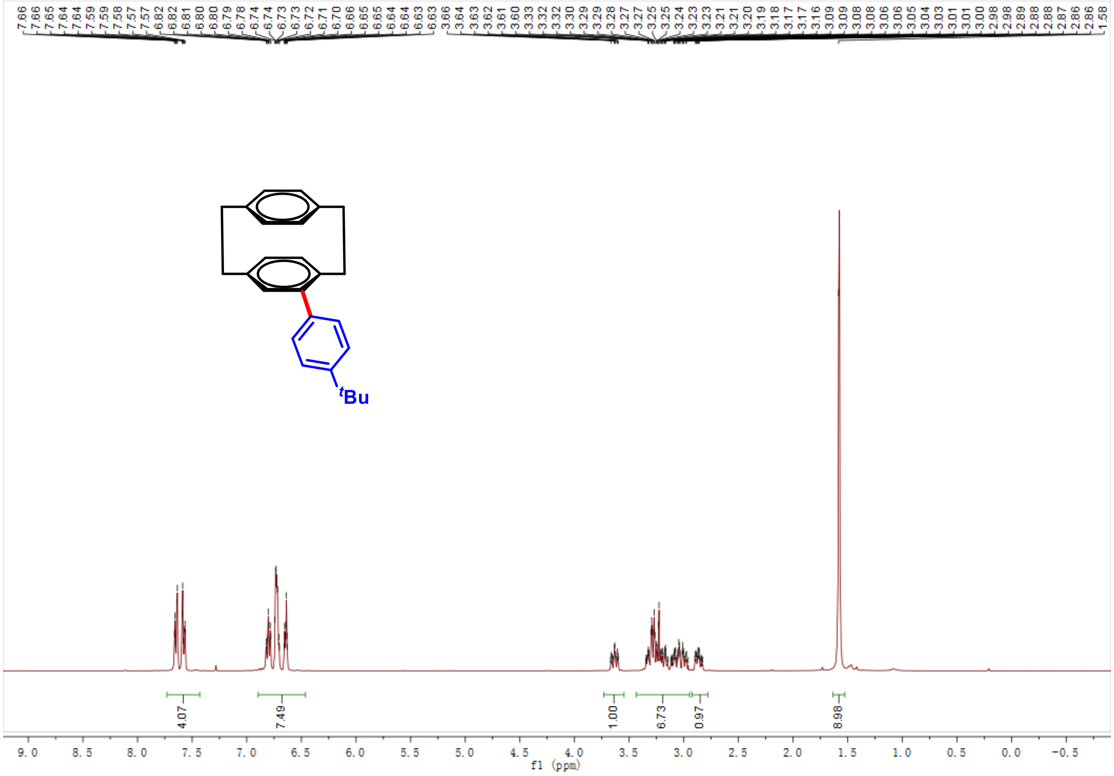
^{13}C NMR spectrum of 3a ($CDCl_3$, 101M)



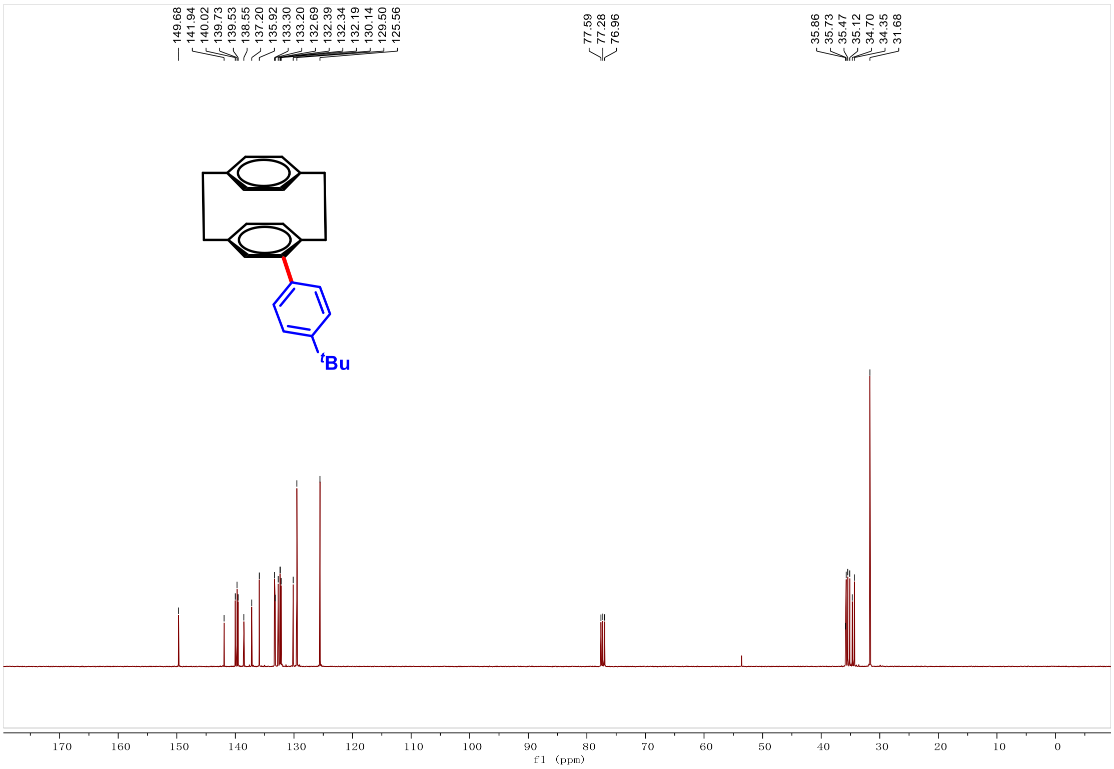
^{1}H NMR spectrum of 3b (CDCl$_3$, 400MHz)



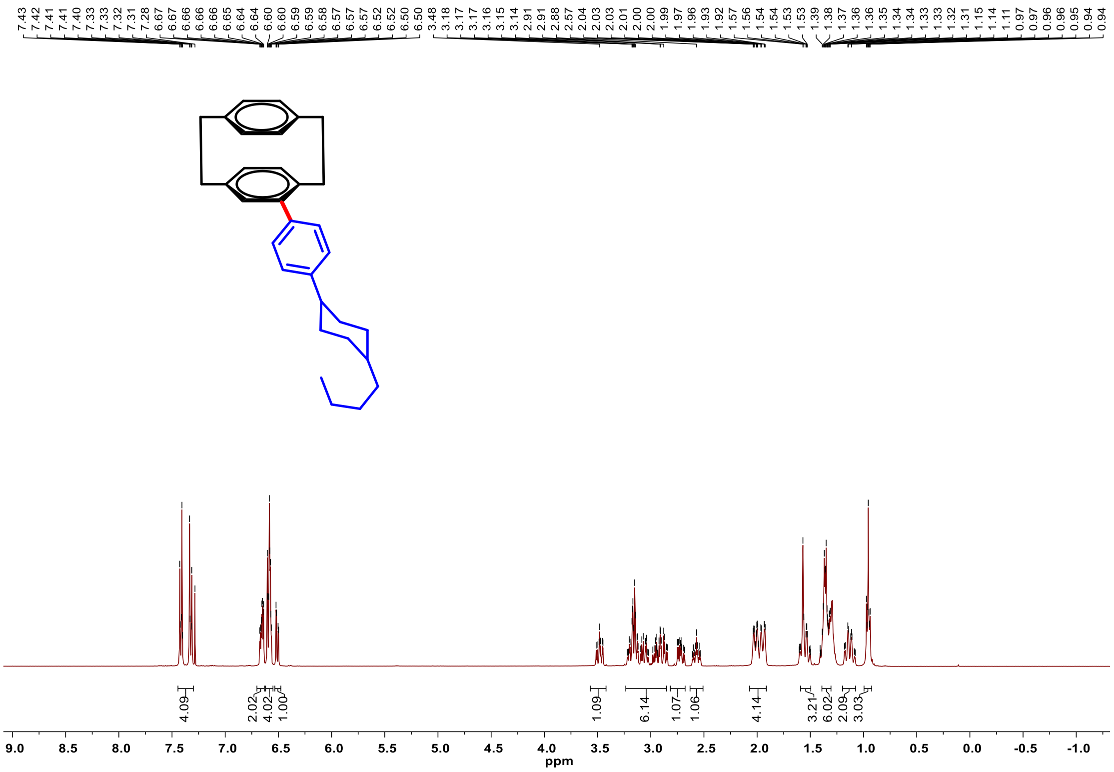
^{13}C NMR spectrum of 3b (CDCl$_3$, 101MHz)



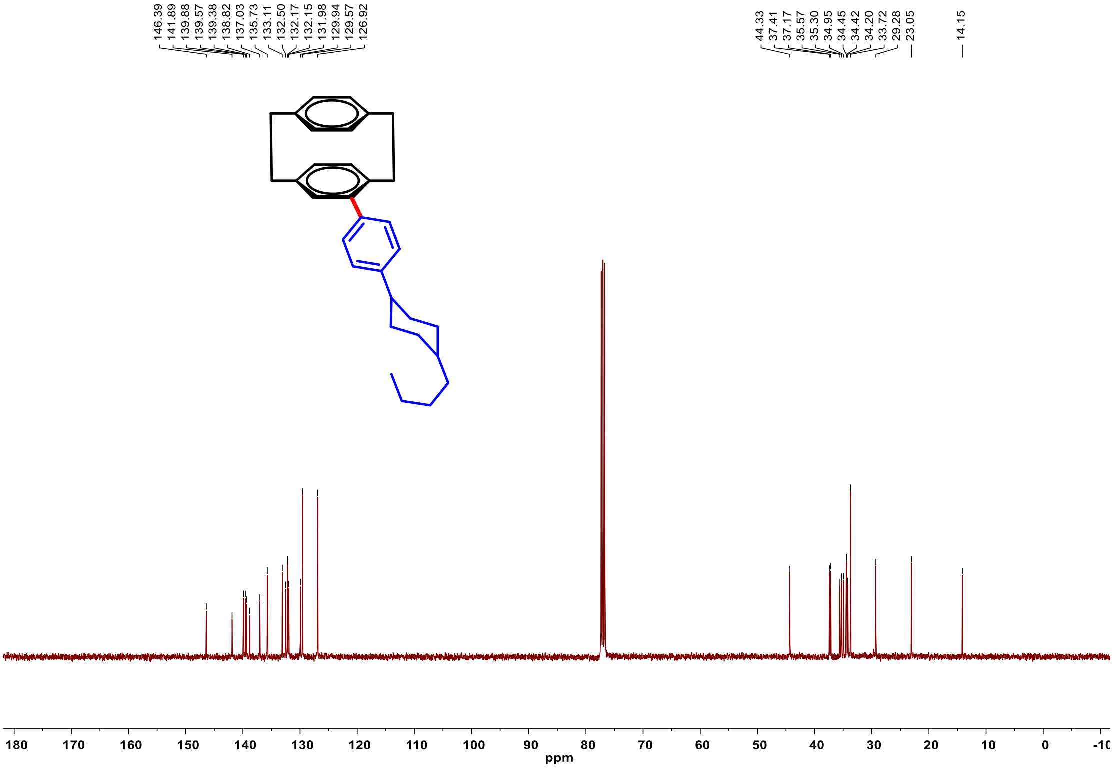
^{1}H NMR spectrum of 3c (CDCl$_3$, 400MHz)



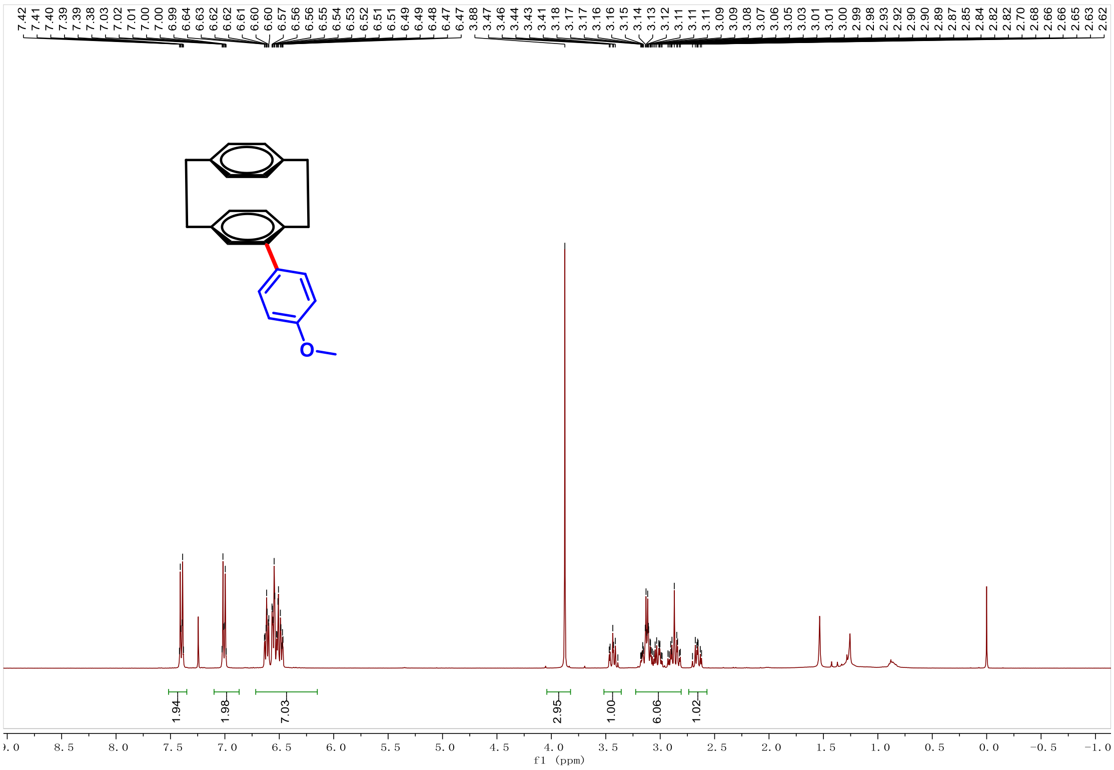
^{13}C NMR spectrum of 3c (CDCl$_3$, 101MHz)



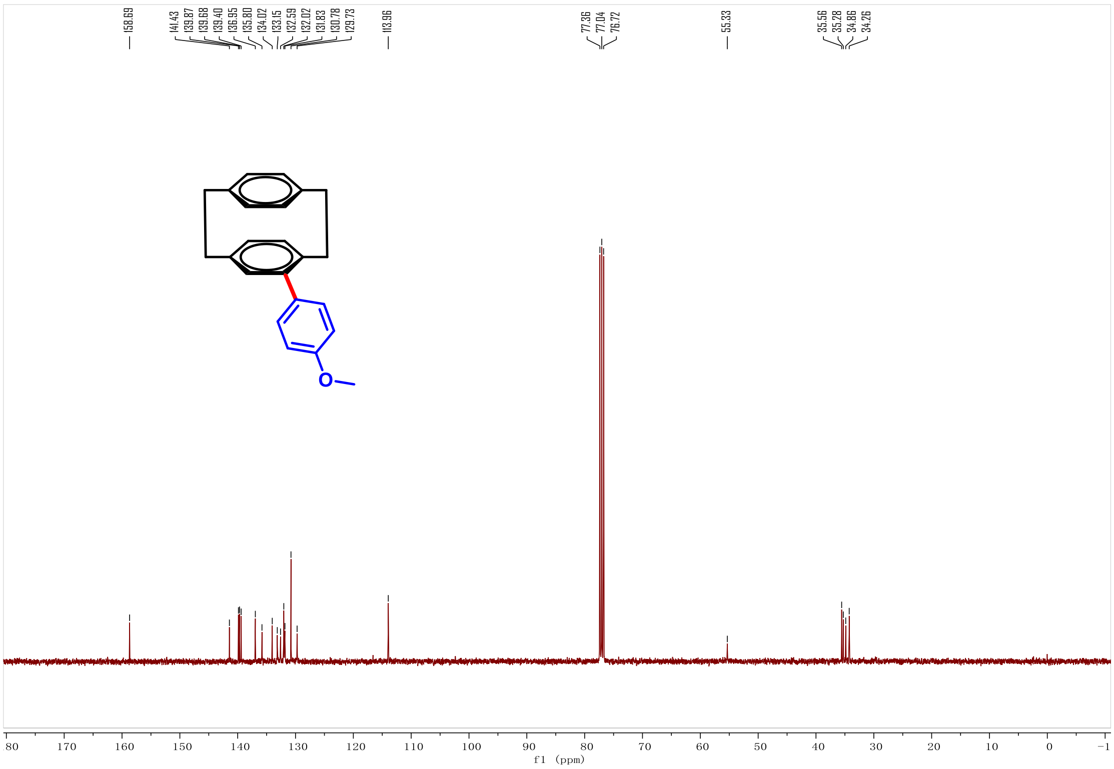
^{1}H NMR spectrum of 3d (CDCl$_3$, 400MHz)



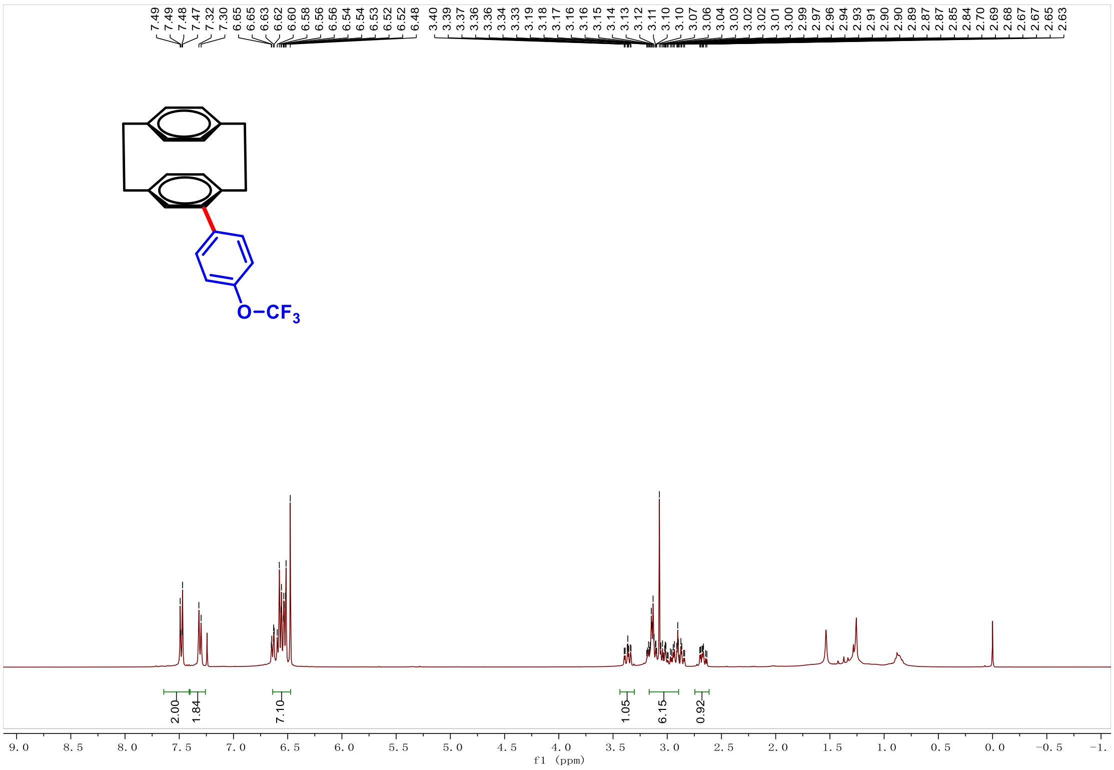
^{13}C NMR spectrum of 3d (CDCl$_3$, 101MHz)



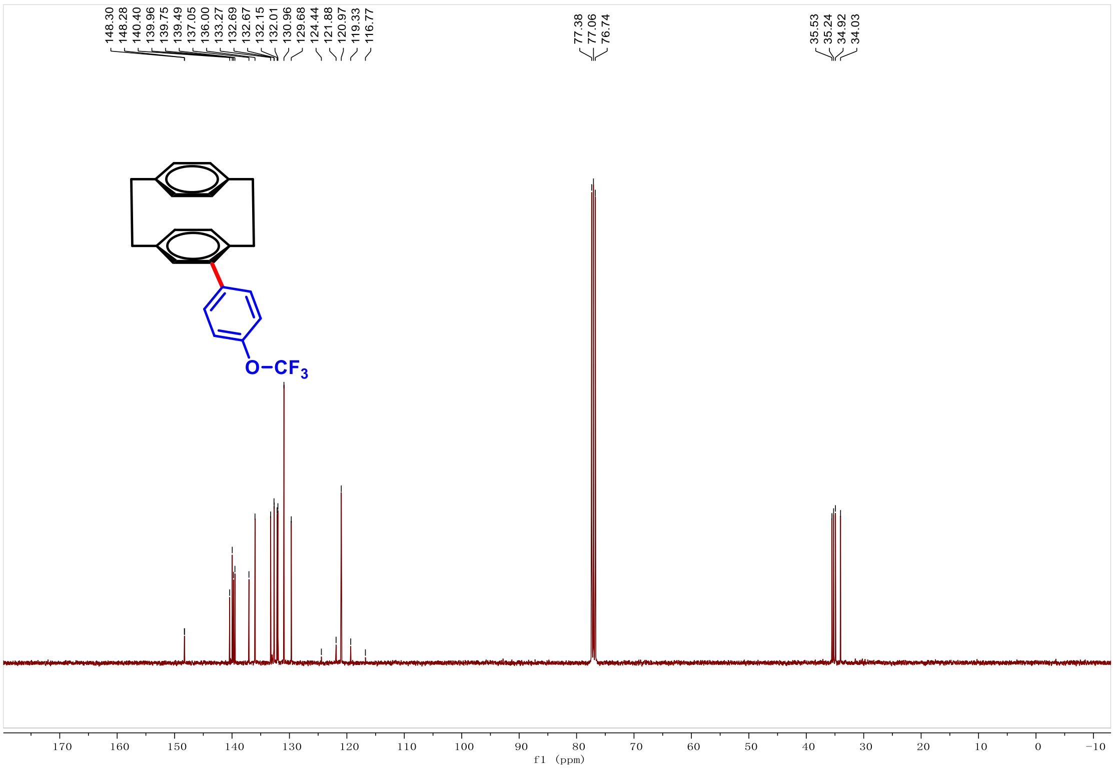
^{1}H NMR spectrum of 3e ($CDCl_3$, 400MHz)



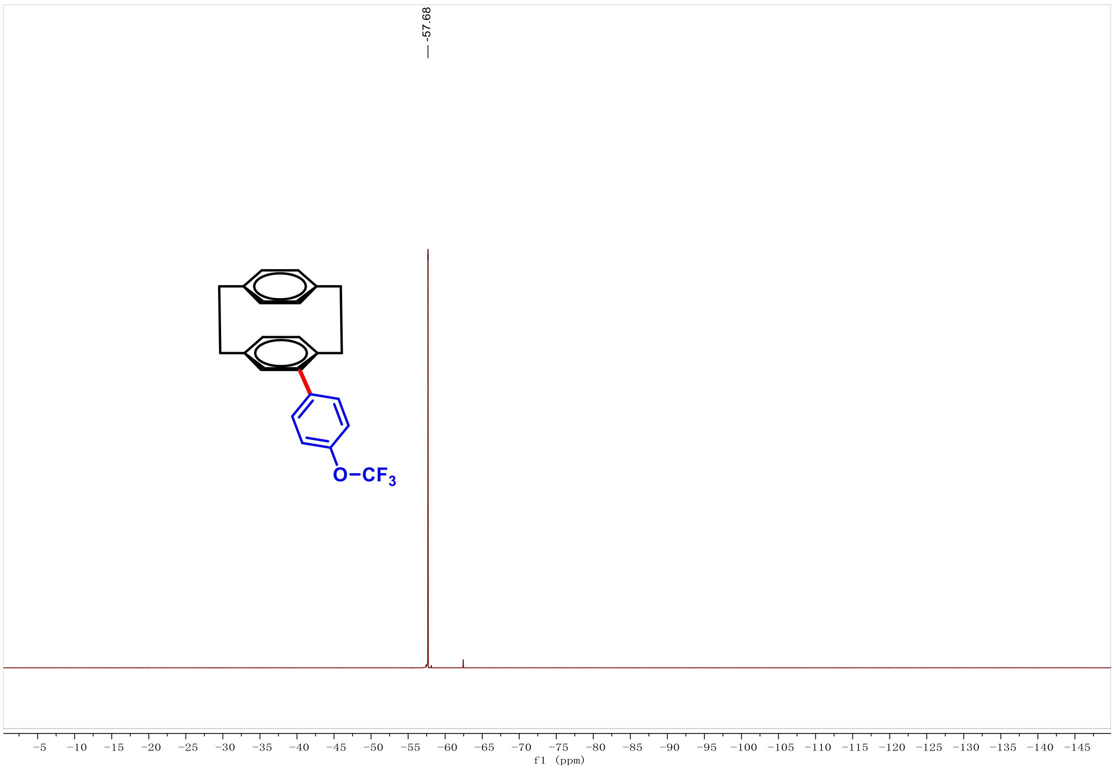
^{13}C NMR spectrum of 3e ($CDCl_3$, 101MHz)



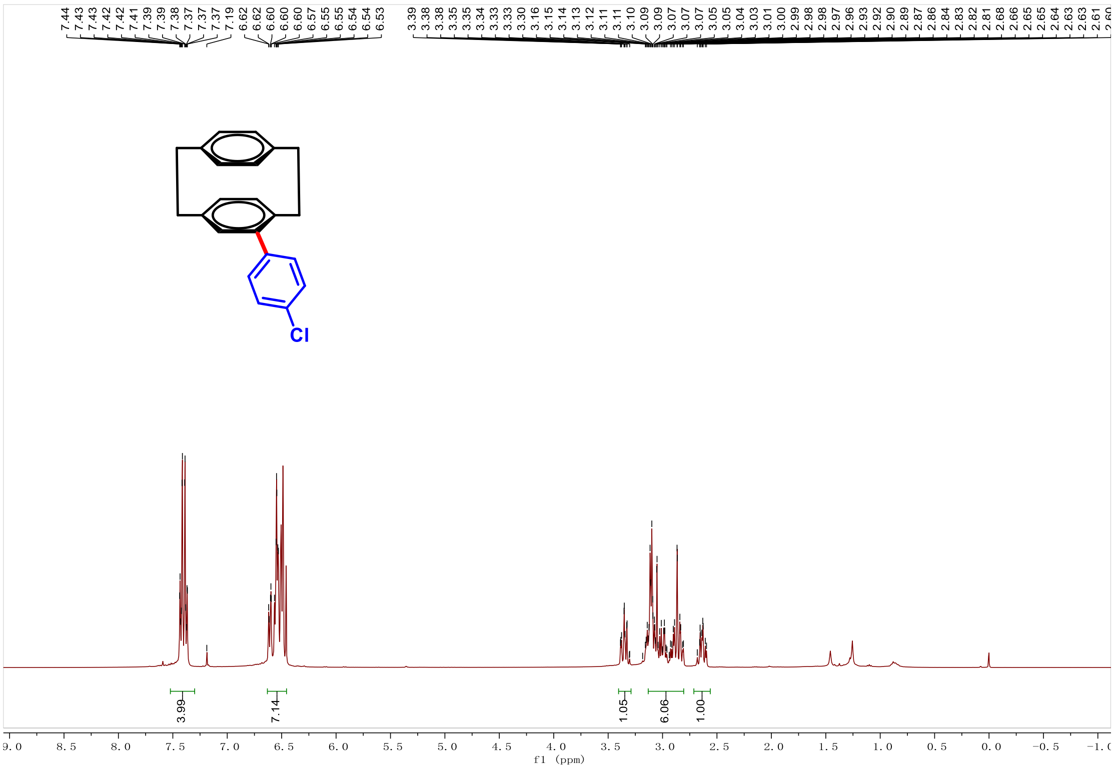
^{1}H NMR spectrum of 3f (CDCl$_3$, 400MHz)



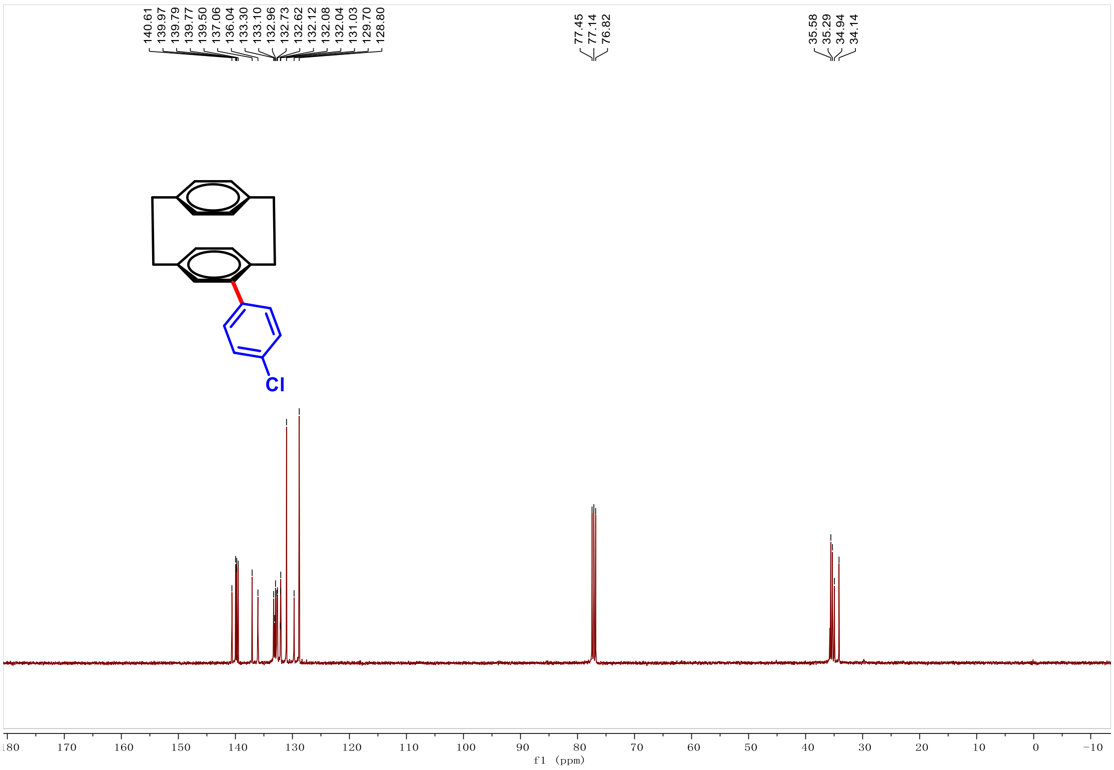
^{13}C NMR spectrum of 3f (CDCl$_3$, 101MHz)



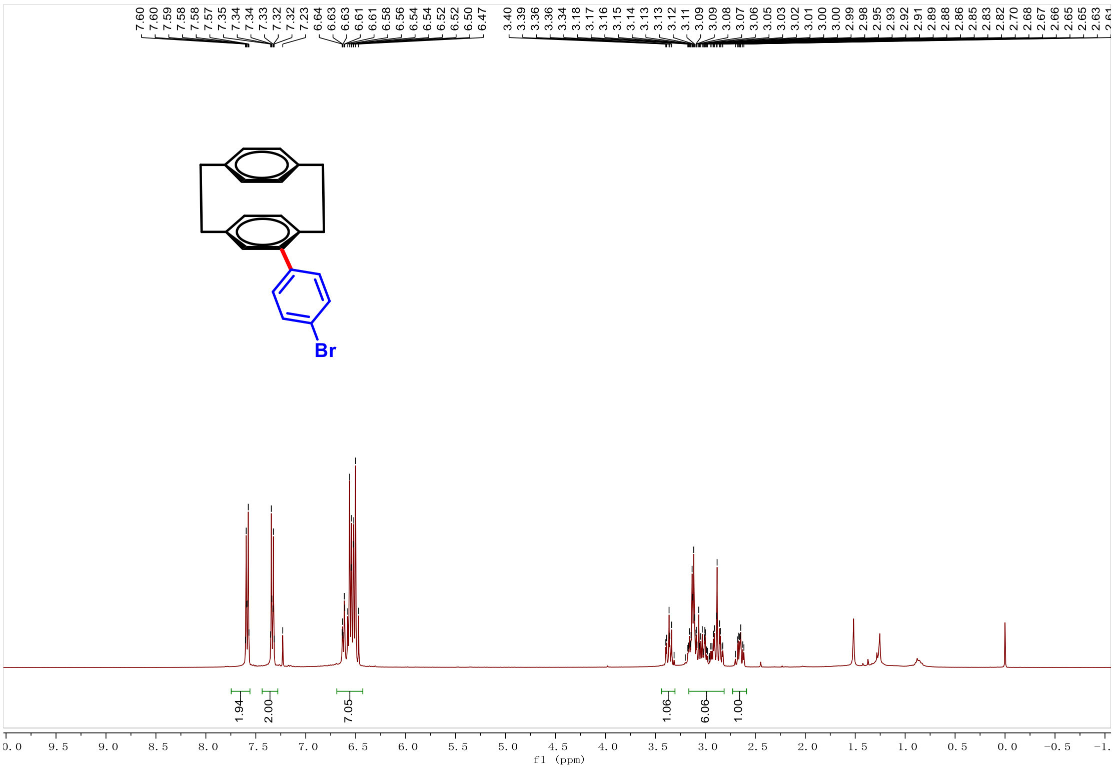
^{19}F NMR spectrum of 3f ($CDCl_3$, 376 MHz)



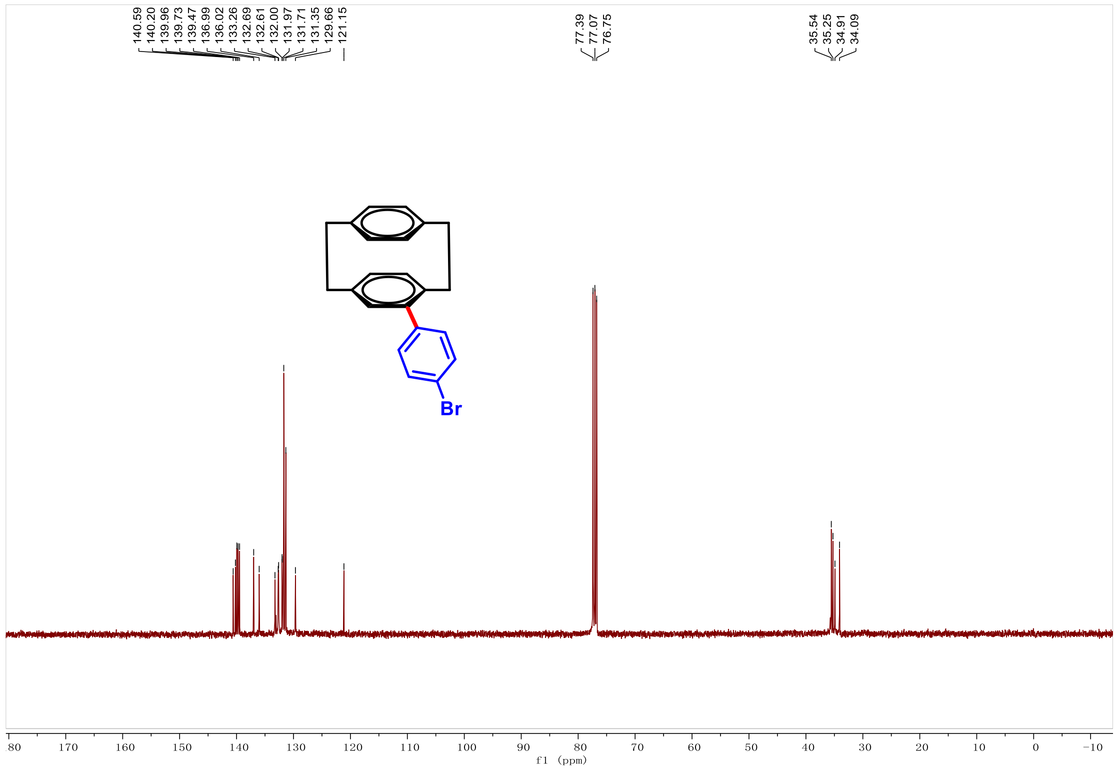
^{1}H NMR spectrum of 3g ($CDCl_3$, 400MHz)



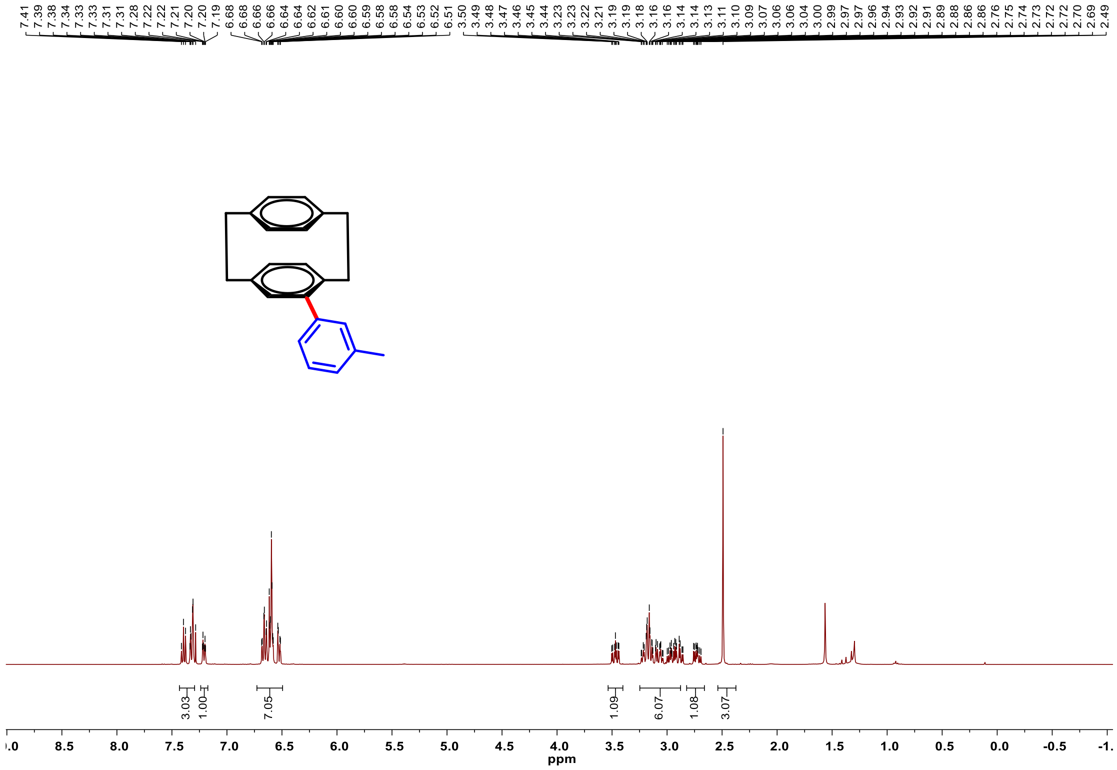
^{13}C NMR spectrum of 3g (CDCl$_3$, 101MHz)



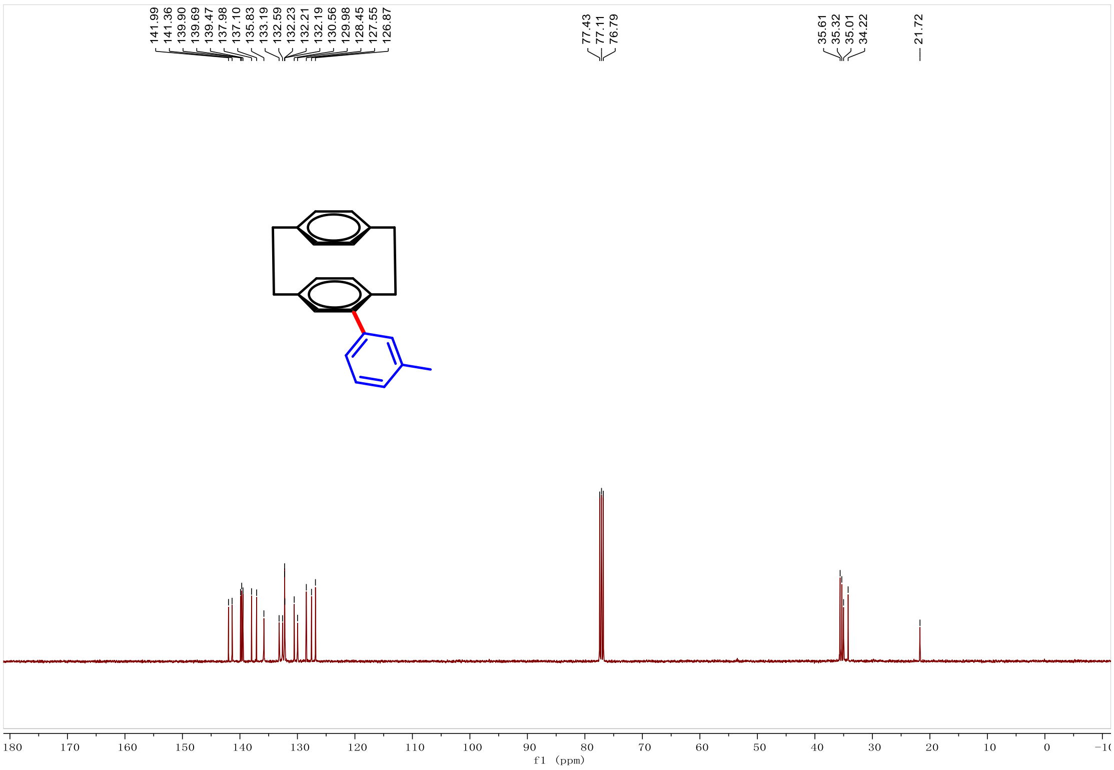
^{1}H NMR spectrum of 3h (CDCl$_3$, 400MHz)



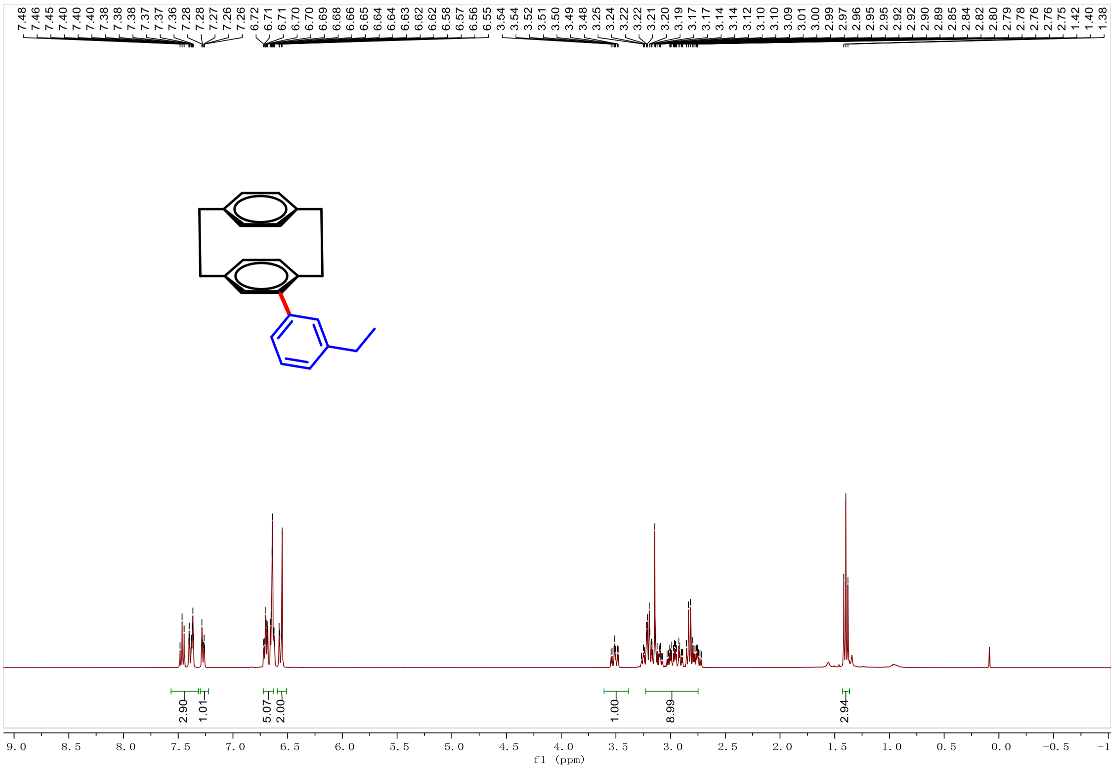
^{13}C NMR spectrum of 3h (CDCl$_3$, 101MHz)



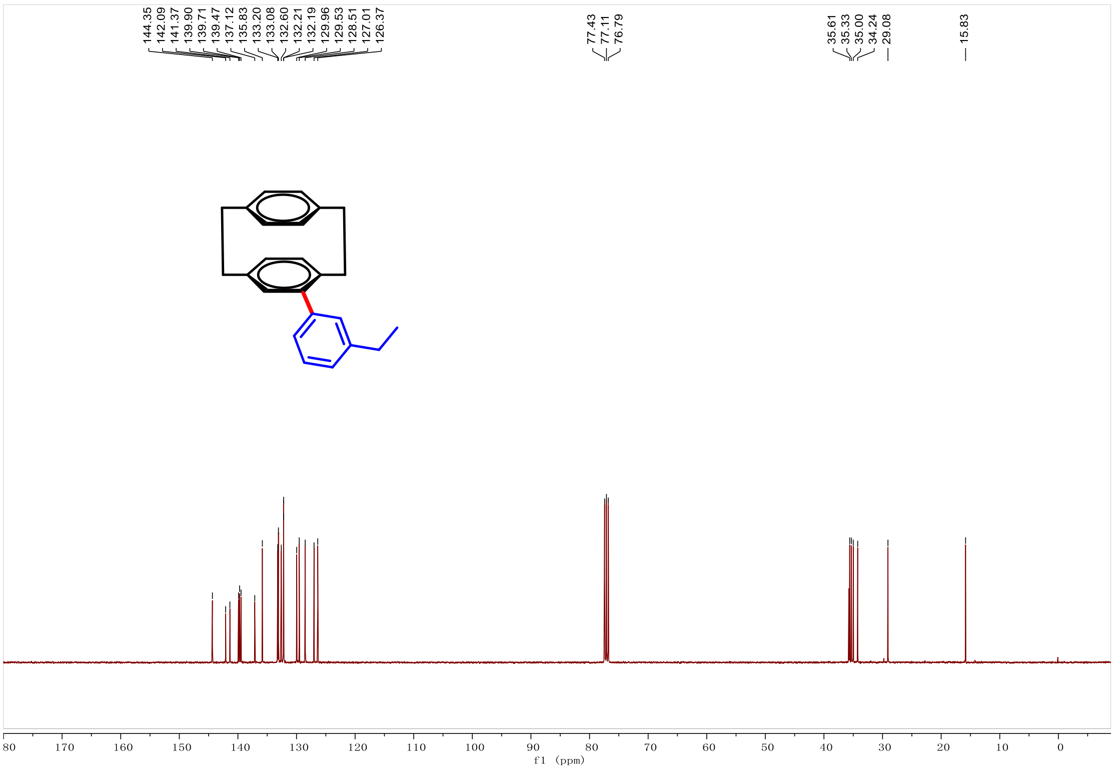
^{1}H NMR spectrum of 3i (CDCl$_3$, 400MHz)



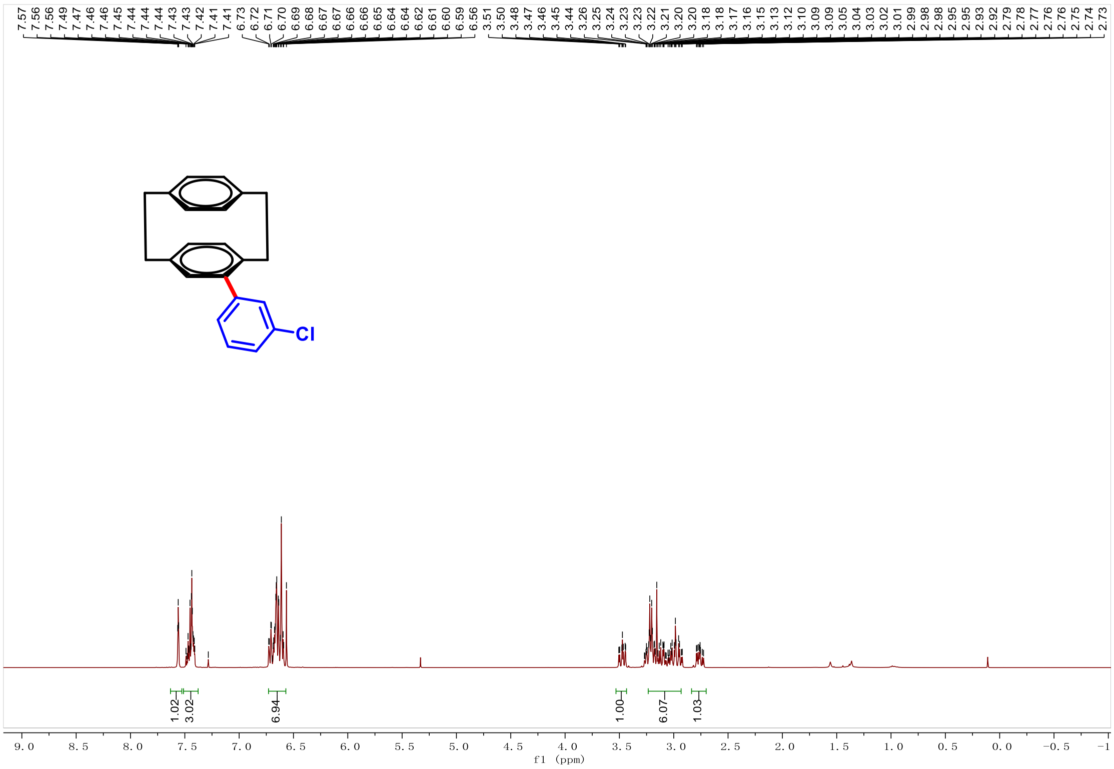
^{13}C NMR spectrum of 3i (CDCl$_3$, 101MHz)



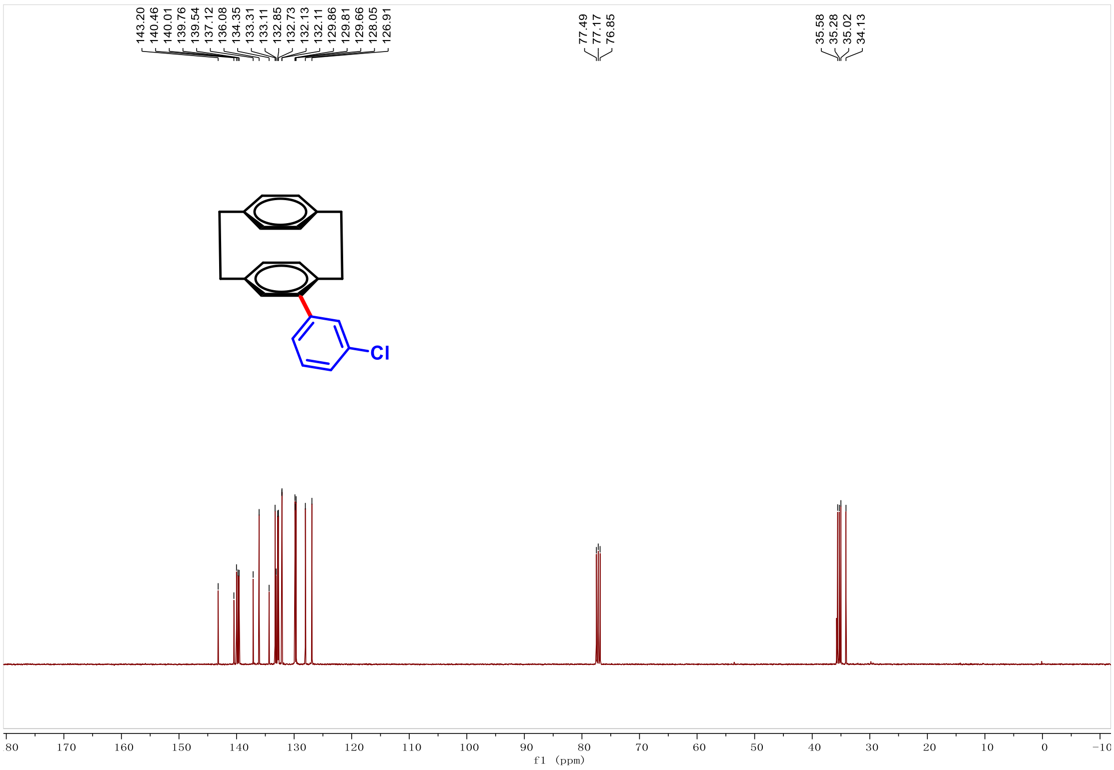
^{1}H NMR spectrum of 3j (CDCl$_3$, 400MHz)



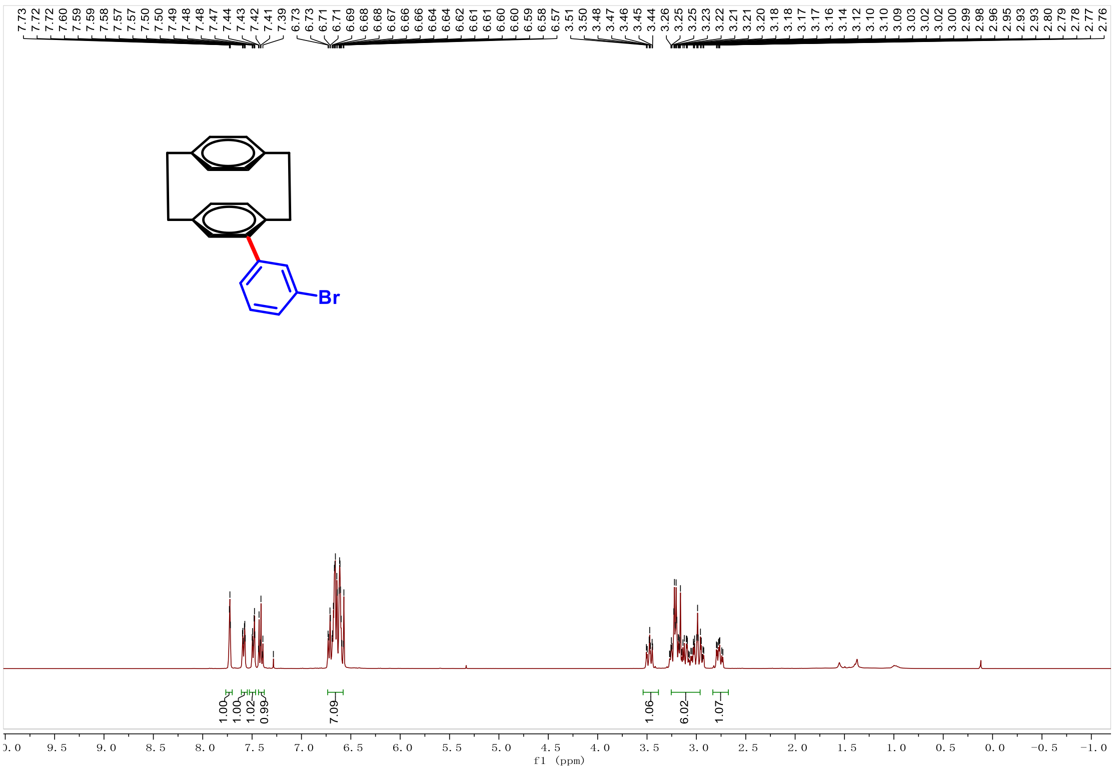
^{13}C NMR spectrum of 3j (CDCl$_3$, 101MHz)



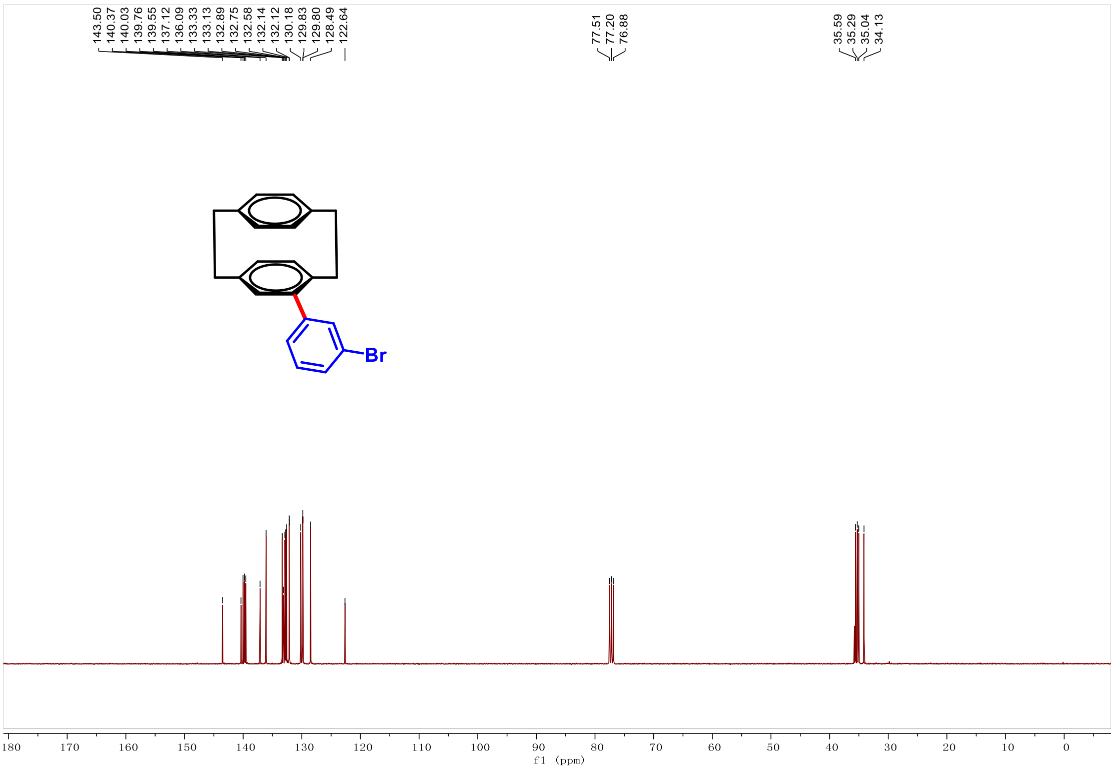
^{1}H NMR spectrum of 3k (CDCl$_3$, 400MHz)



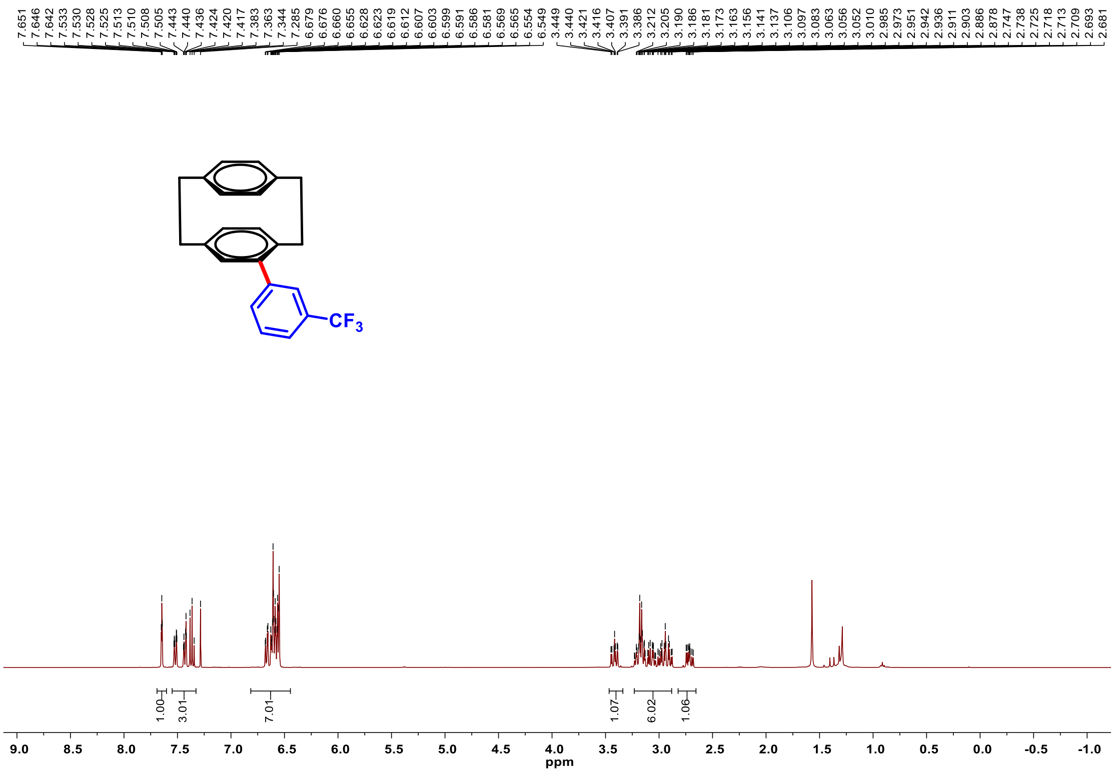
^{13}C NMR spectrum of 3k ($CDCl_3$, 101MHz)



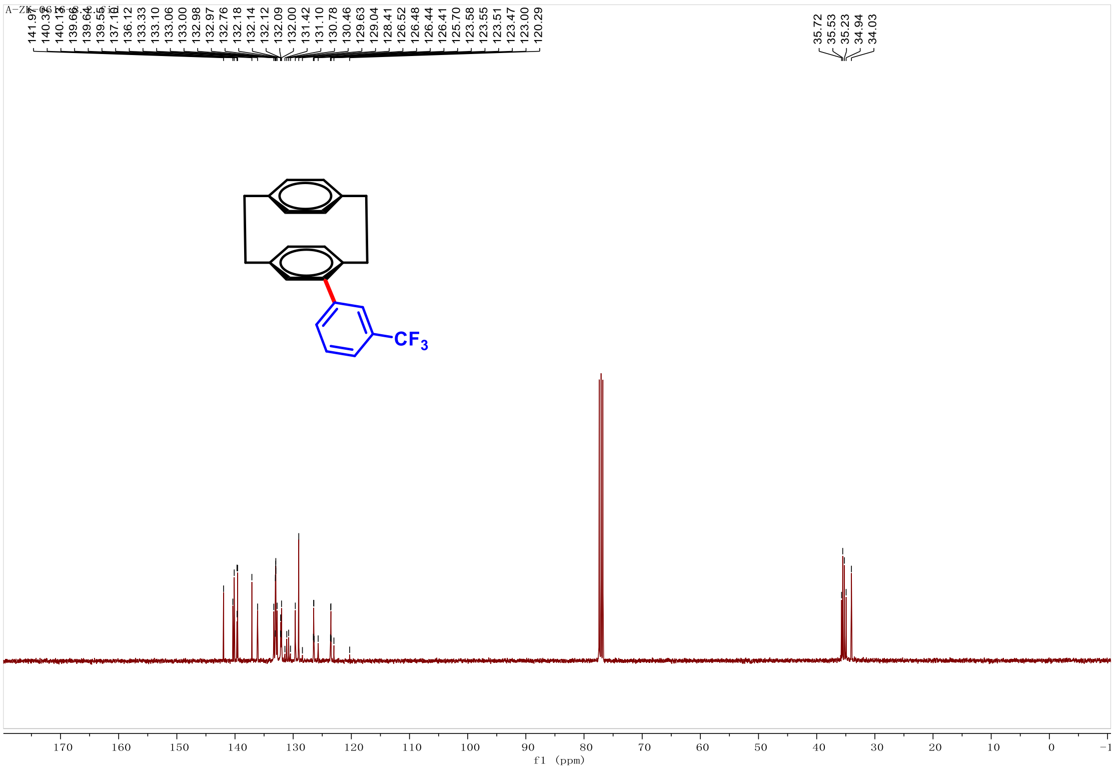
^{1}H NMR spectrum of 3l ($CDCl_3$, 400MHz)



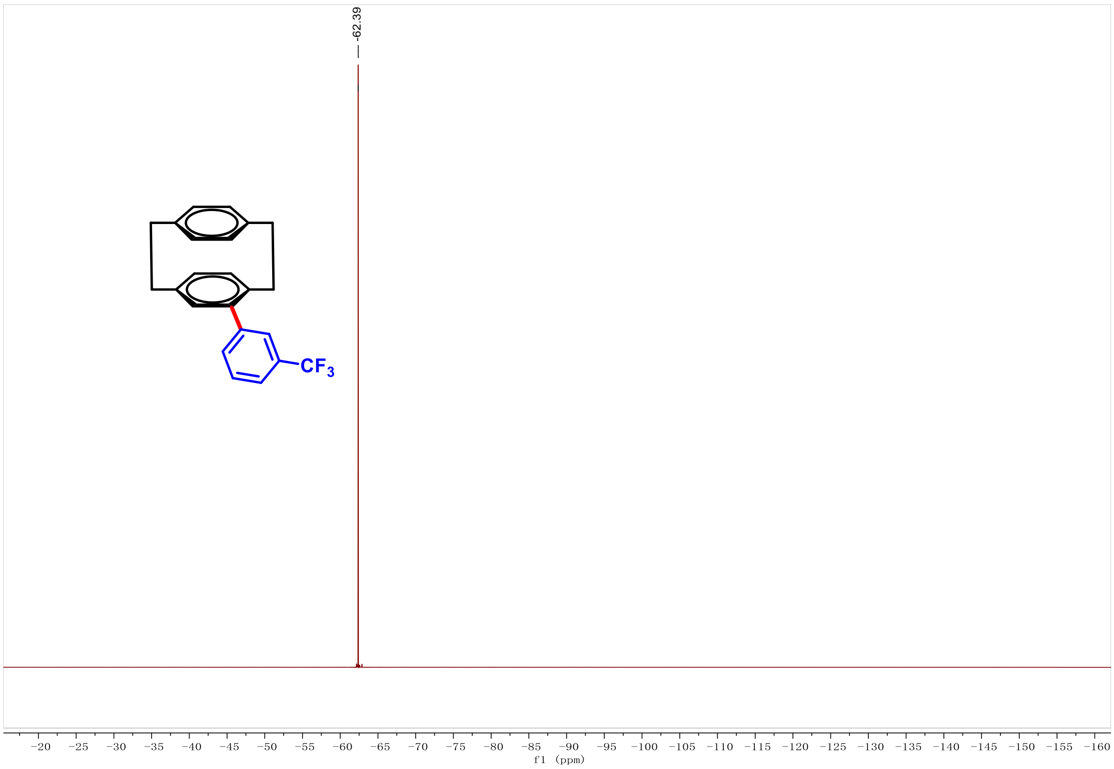
^{13}C NMR spectrum of 3l (CDCl$_3$, 101MHz)



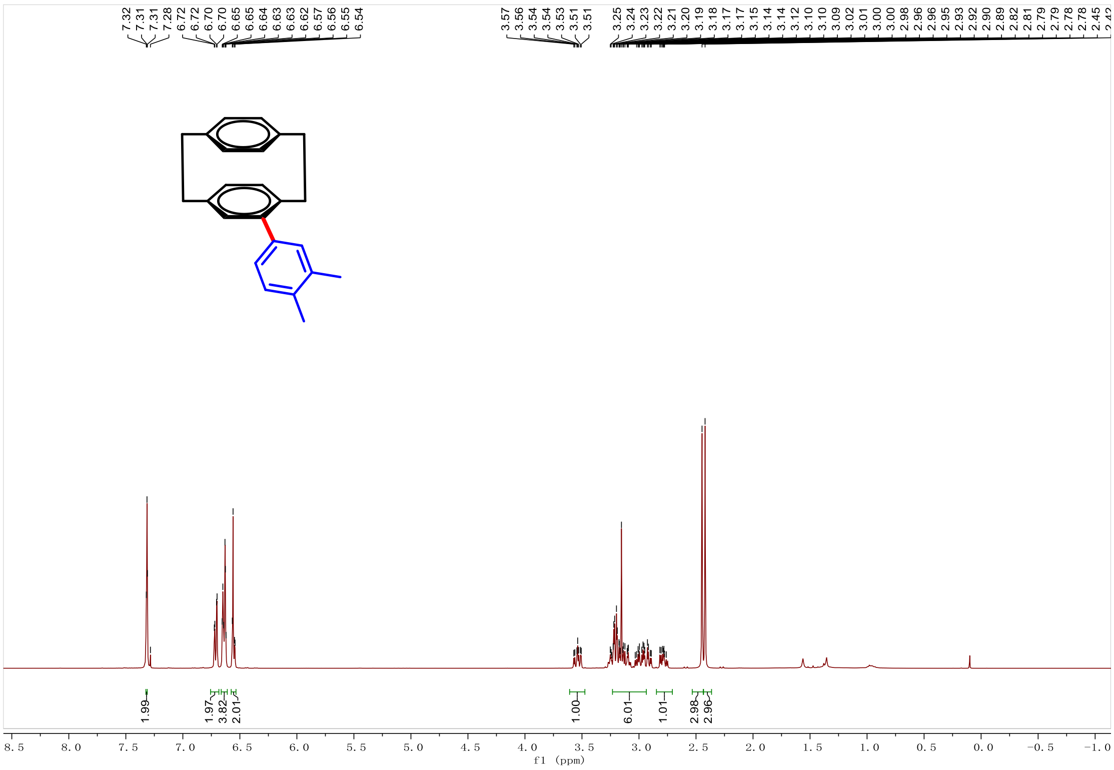
^{1}H NMR spectrum of 3m (CDCl$_3$, 400MHz)



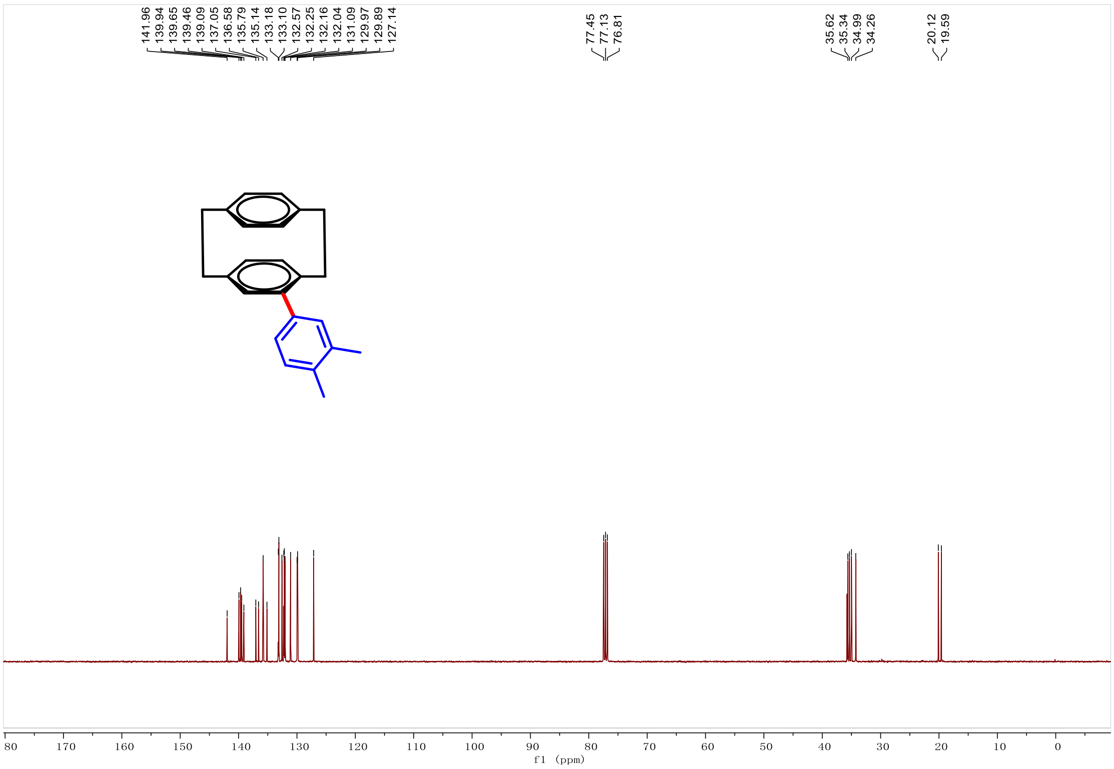
^{13}C NMR spectrum of 3m (CDCl$_3$, 101 MHz)



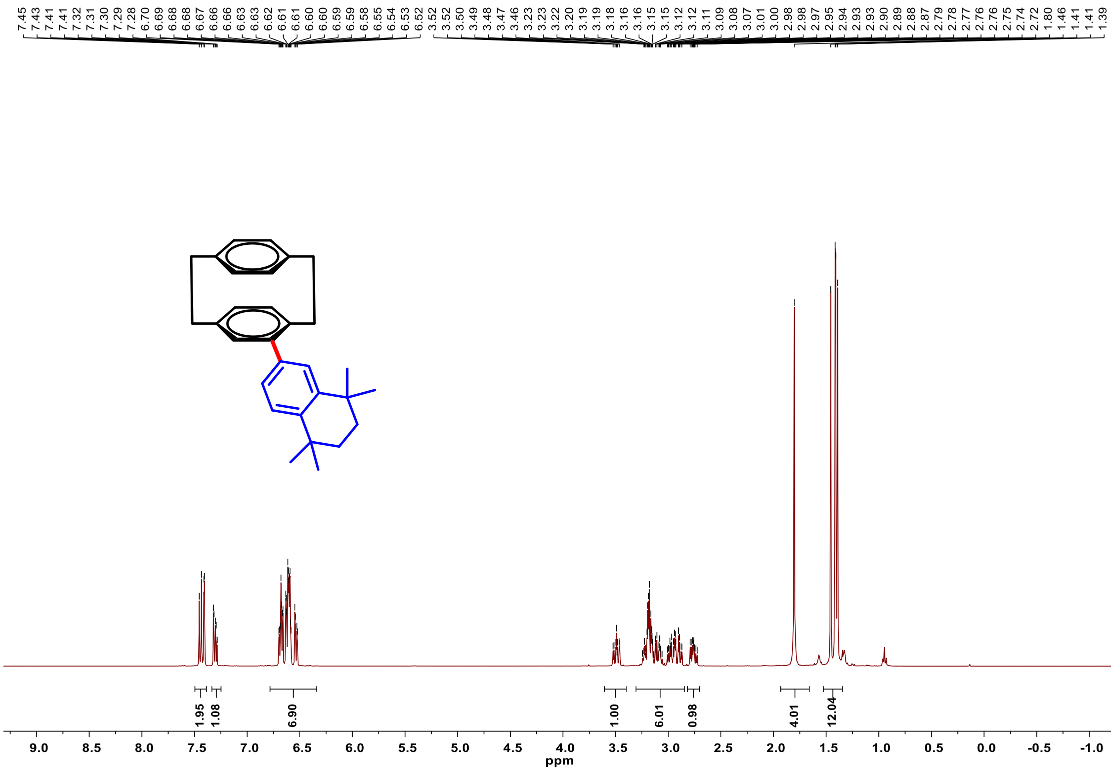
^{19}F NMR spectrum of 3m (CDCl$_3$, 376 MHz)



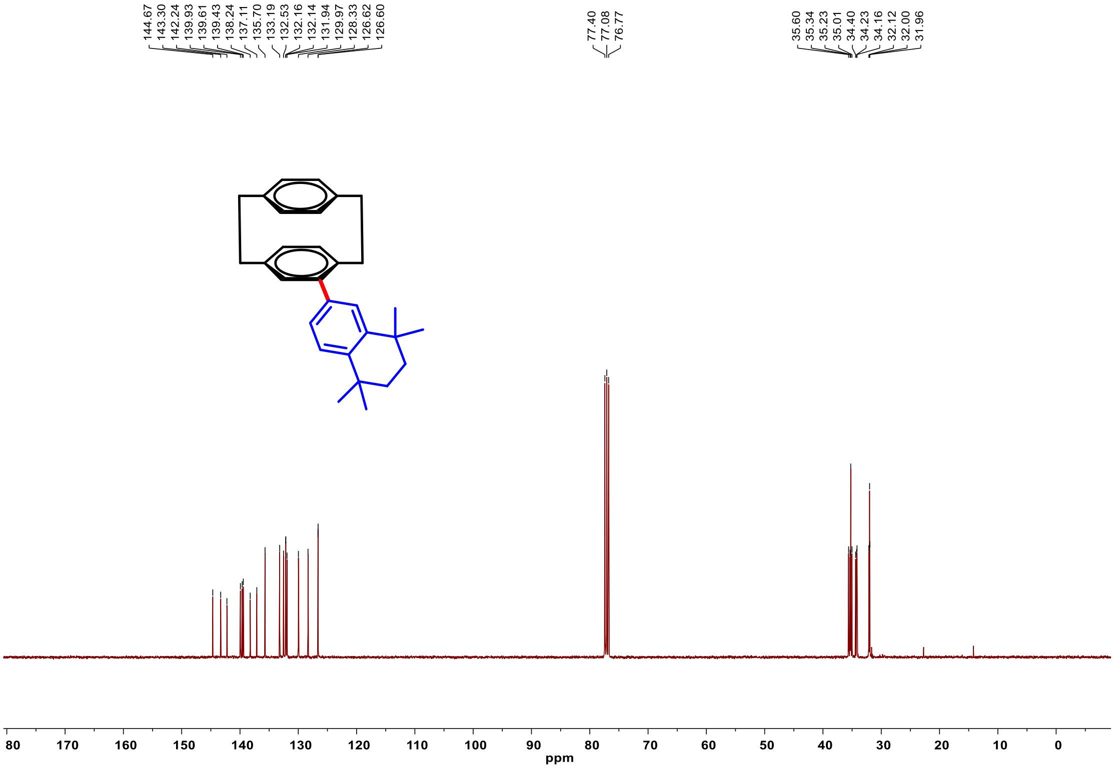
^{1}H NMR spectrum of 3n (CDCl$_3$, 400MHz)



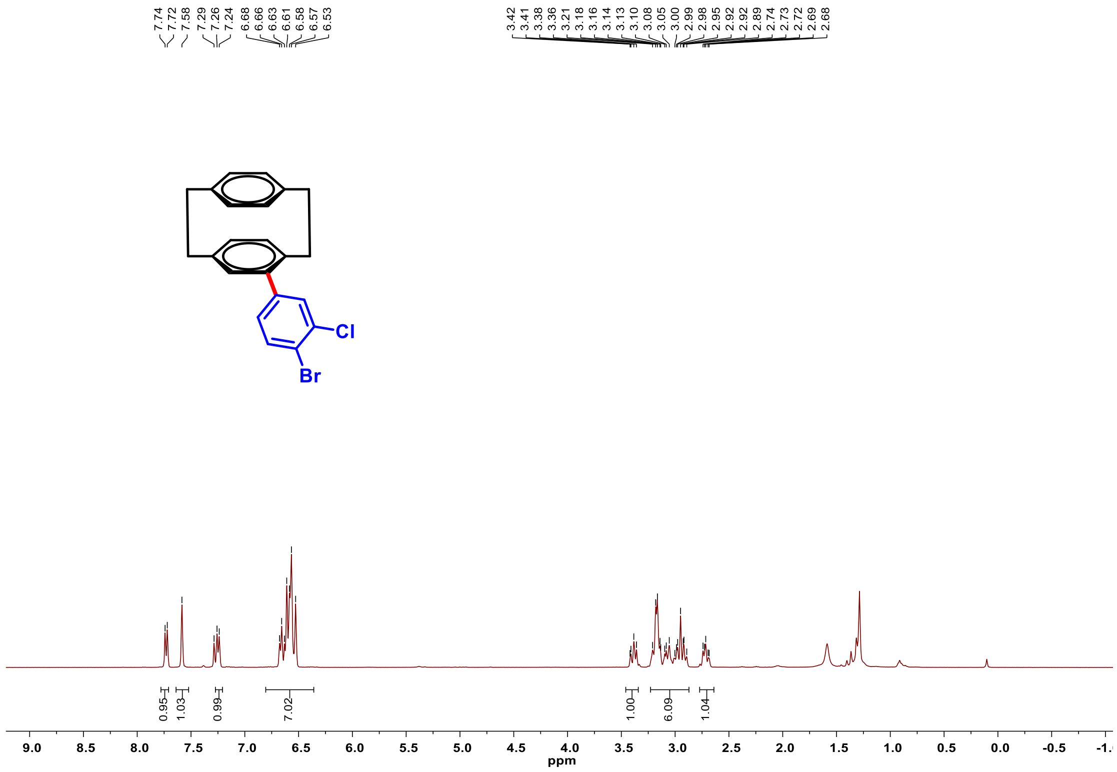
^{13}C NMR spectrum of 3n (CDCl$_3$, 101MHz)



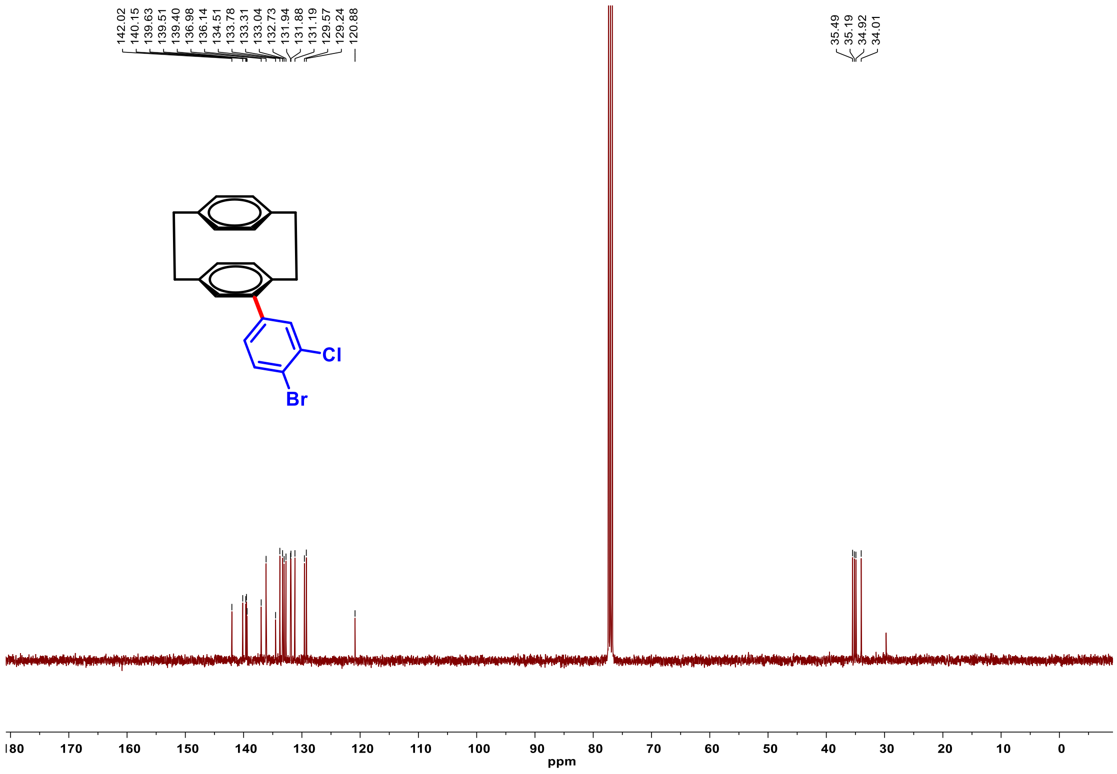
^{1}H NMR spectrum of 3o (CDCl$_3$, 400MHz)



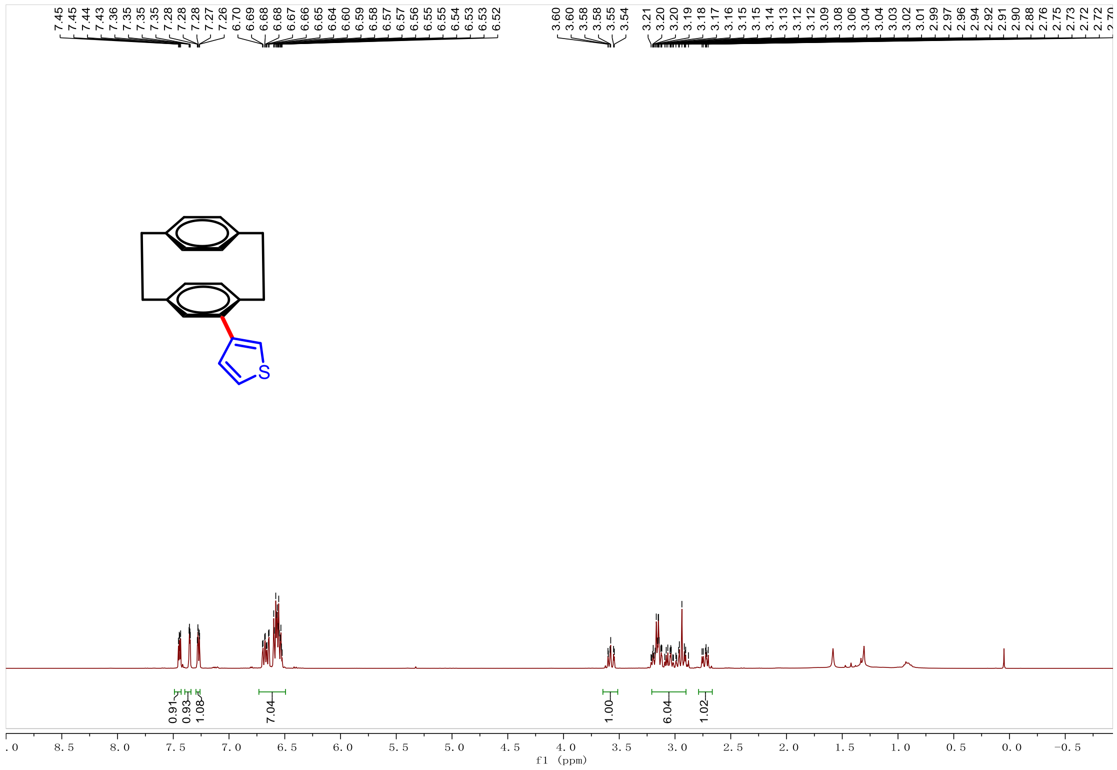
^{13}C NMR spectrum of 3o (CDCl$_3$, 101MHz)



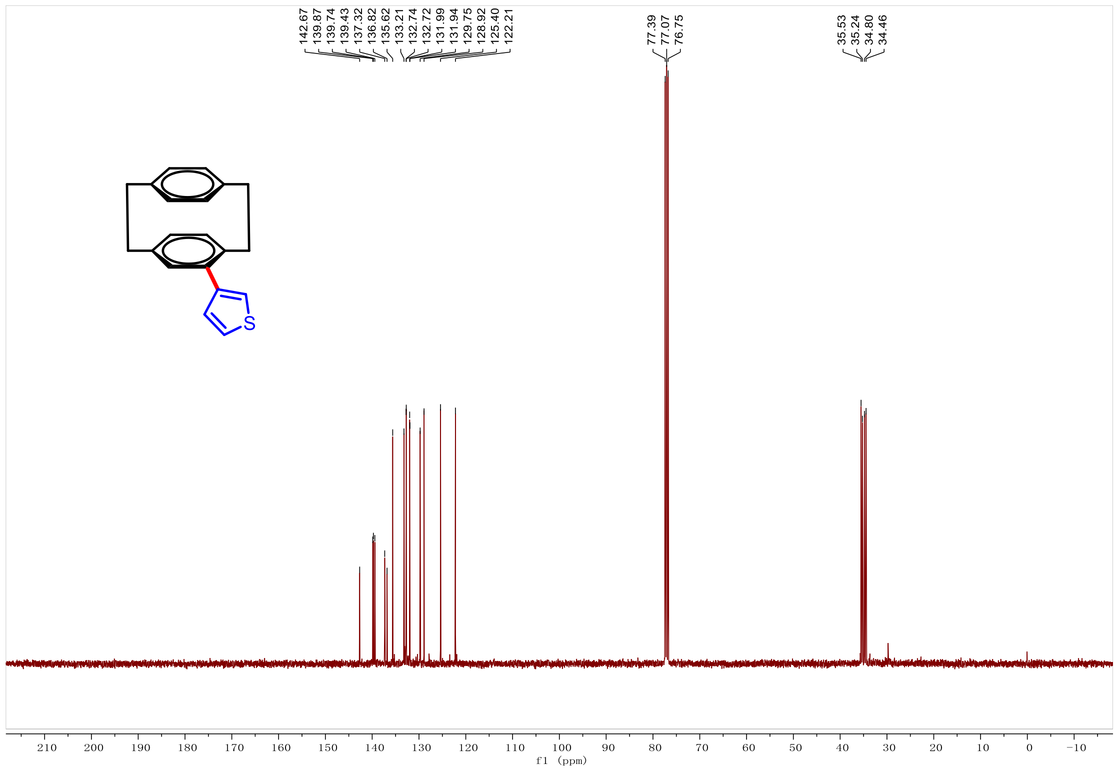
^{1}**H NMR spectrum of 3p (CDCl$_3$, 400MHz)**



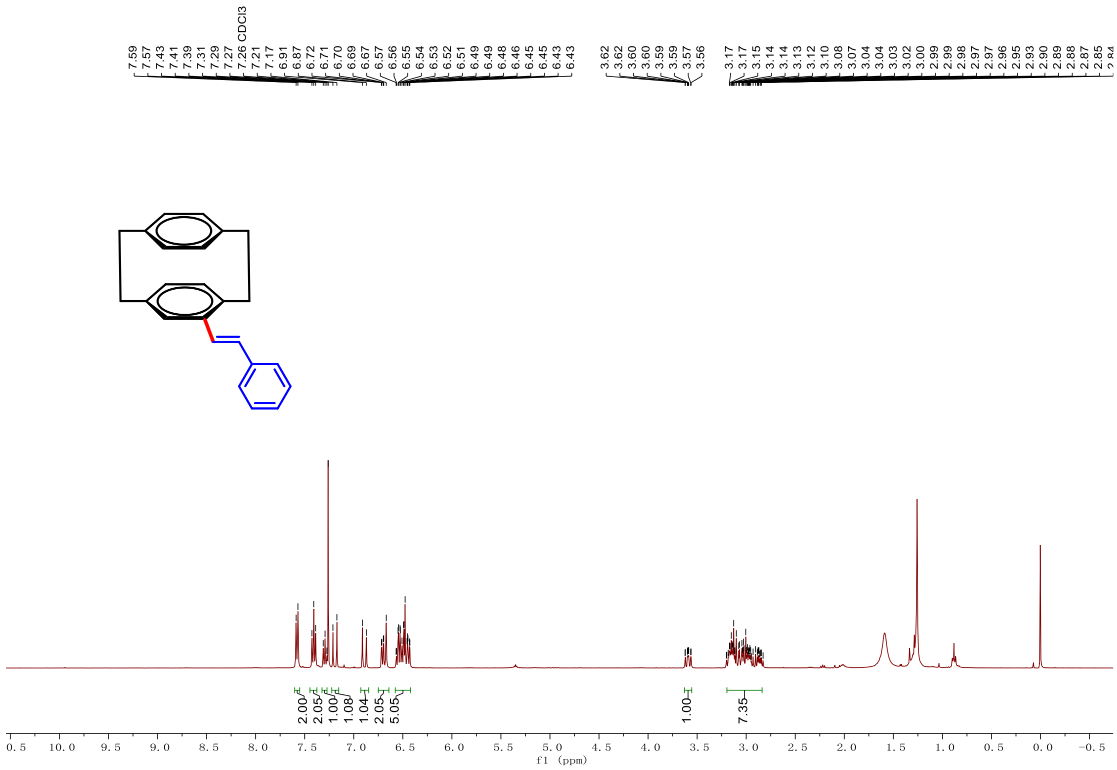
^{13}**C NMR spectrum of 3p (CDCl$_3$, 101MHz)**



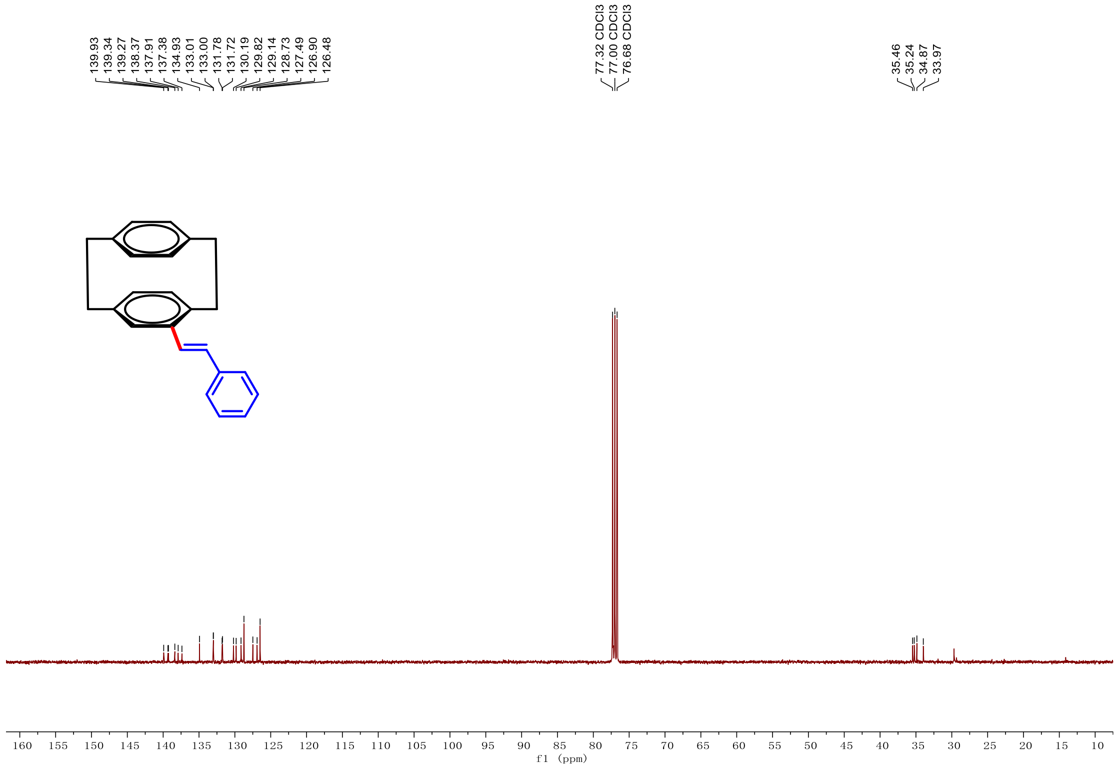
^{1}H NMR spectrum of 3q (CDCl$_3$, 400MHz)



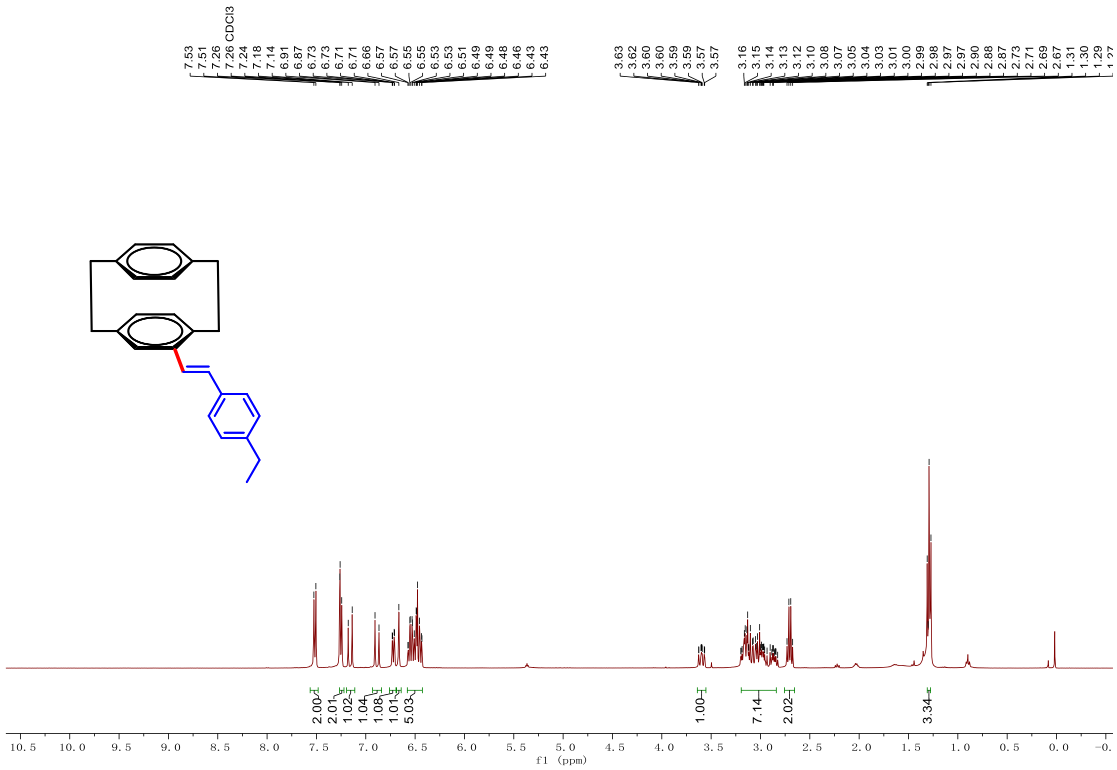
^{13}C NMR spectrum of 3q (CDCl$_3$, 101MHz)



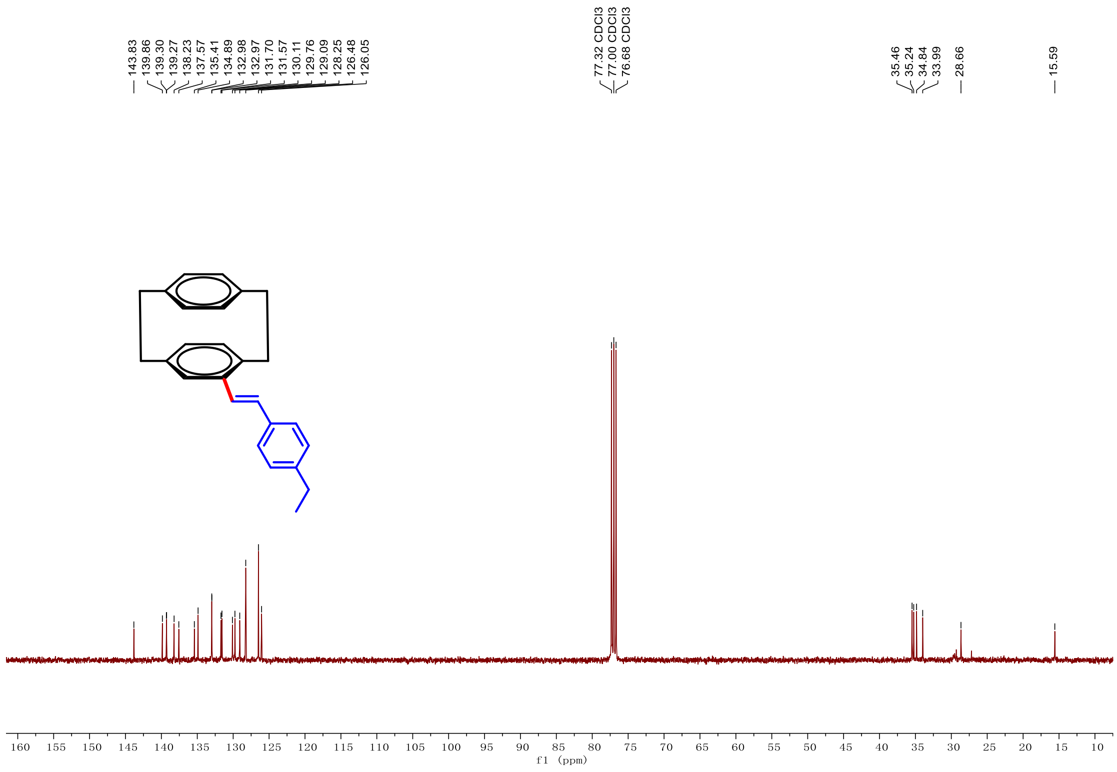
^{1}H NMR spectrum of 5a ($CDCl_3$, 400MHz)



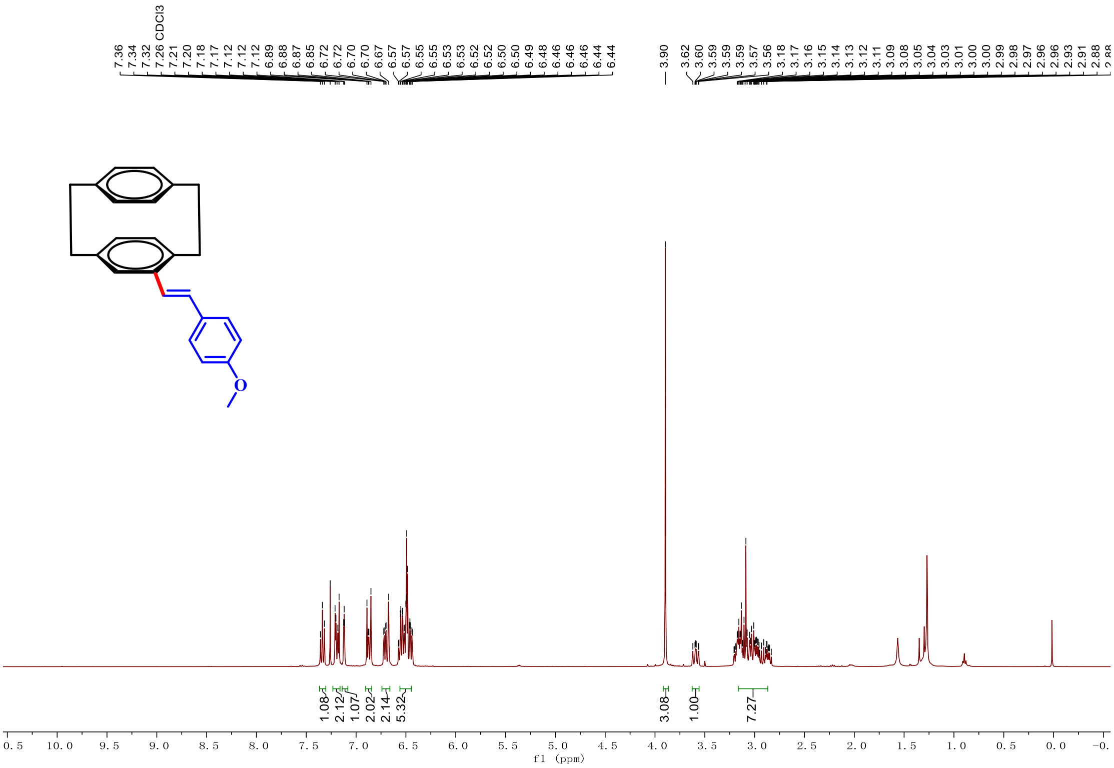
^{13}C NMR spectrum of 5a ($CDCl_3$, 101MHz)



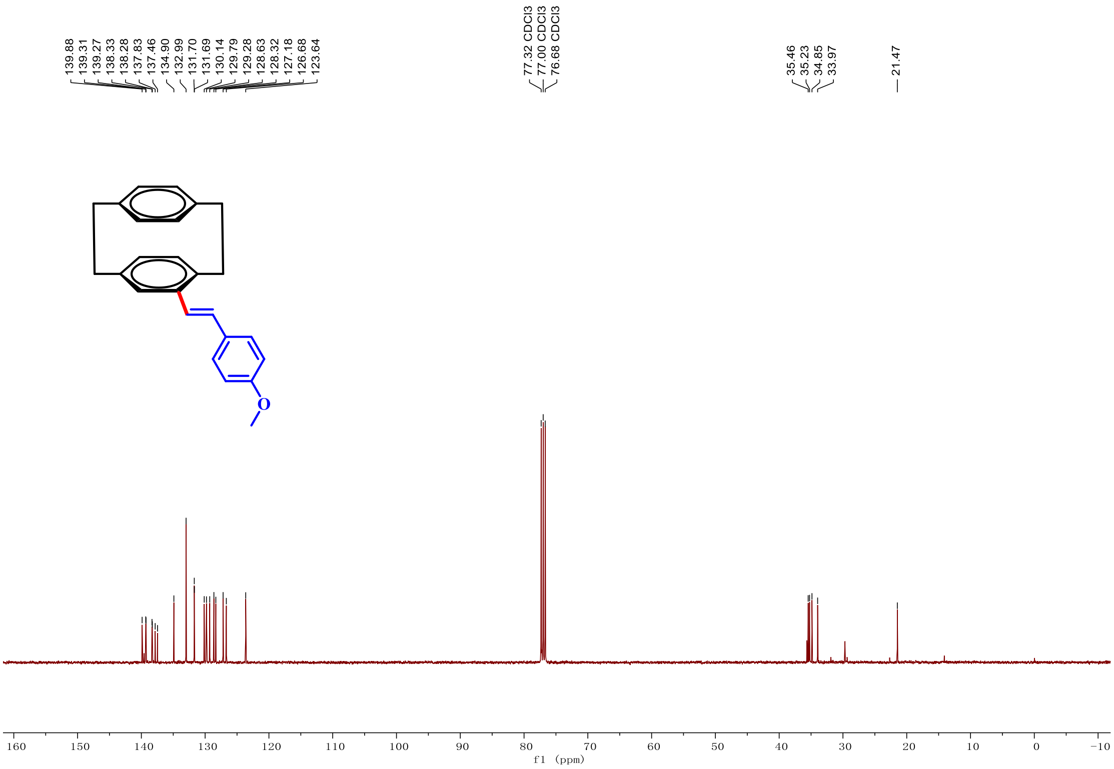
^{1}H NMR spectrum of 5b (CDCl$_3$, 400MHz)



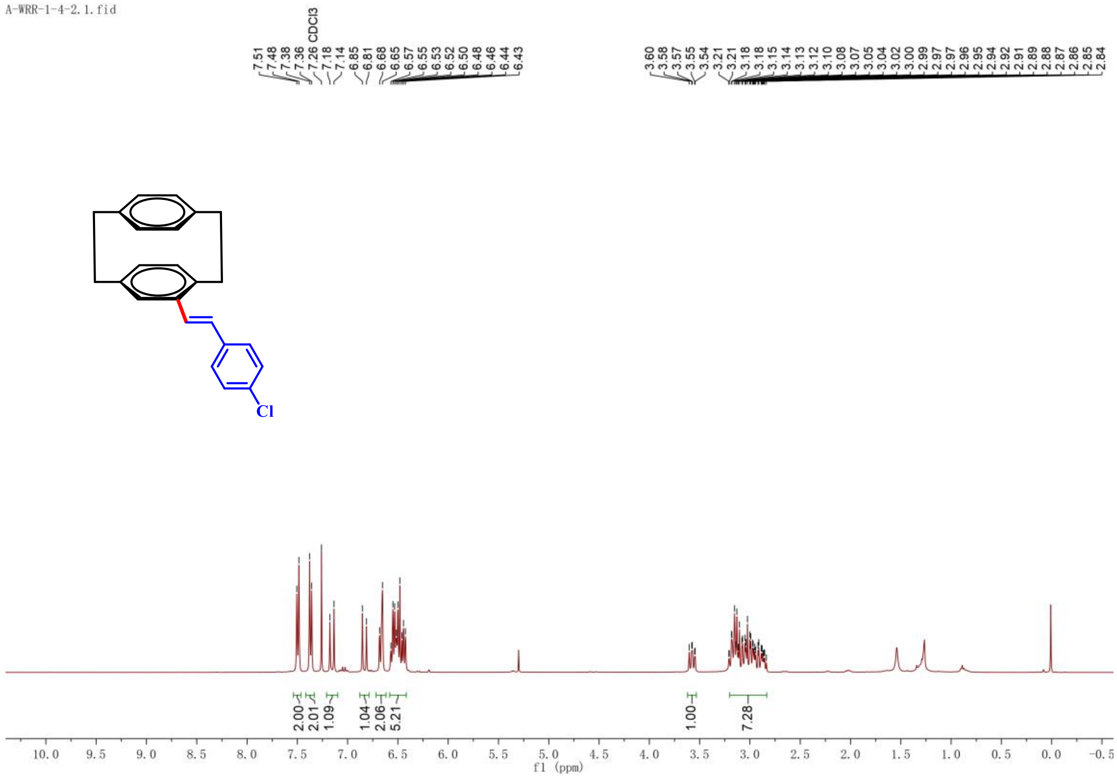
^{13}C NMR spectrum of 5b (CDCl$_3$, 101MHz)



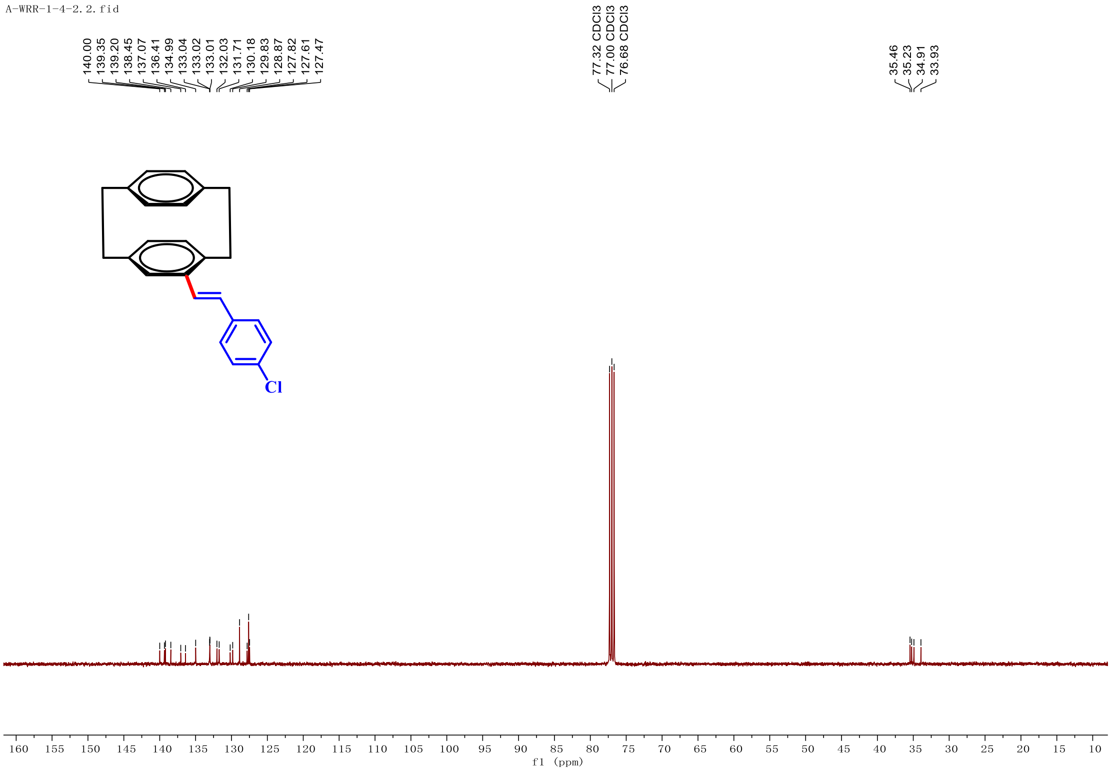
^{1}H NMR spectrum of 5c ($CDCl_3$, 400MHz)



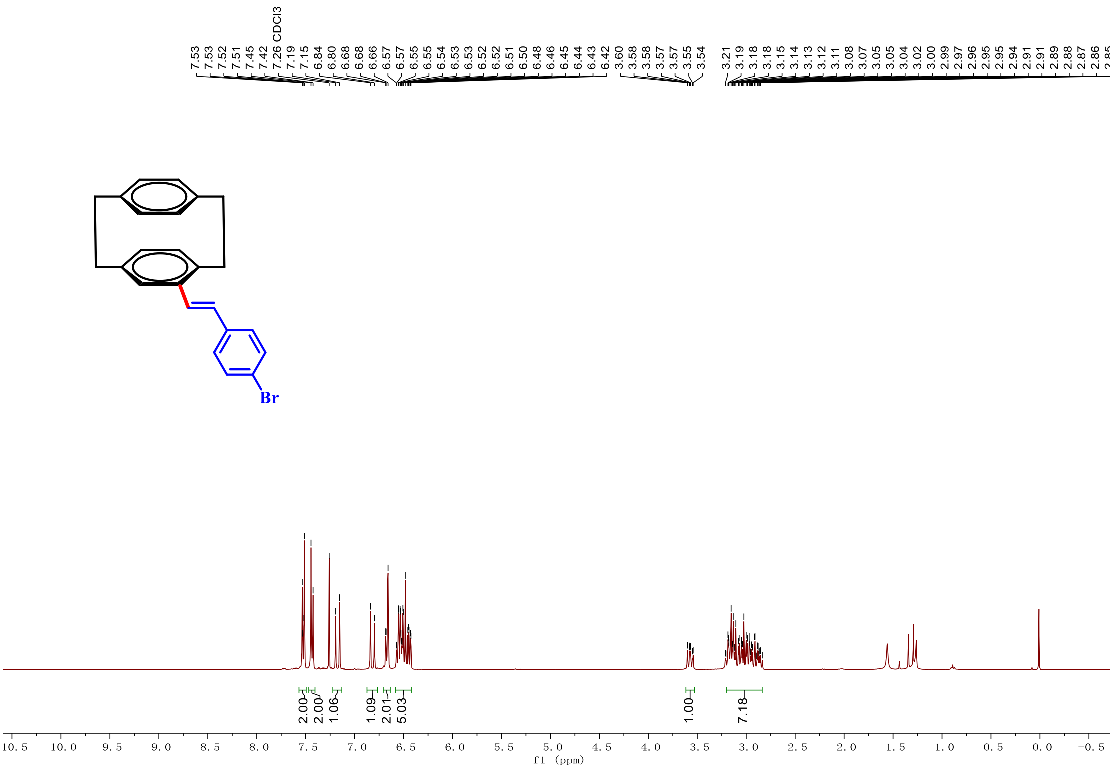
^{13}C NMR spectrum of 5c ($CDCl_3$, 101MHz)



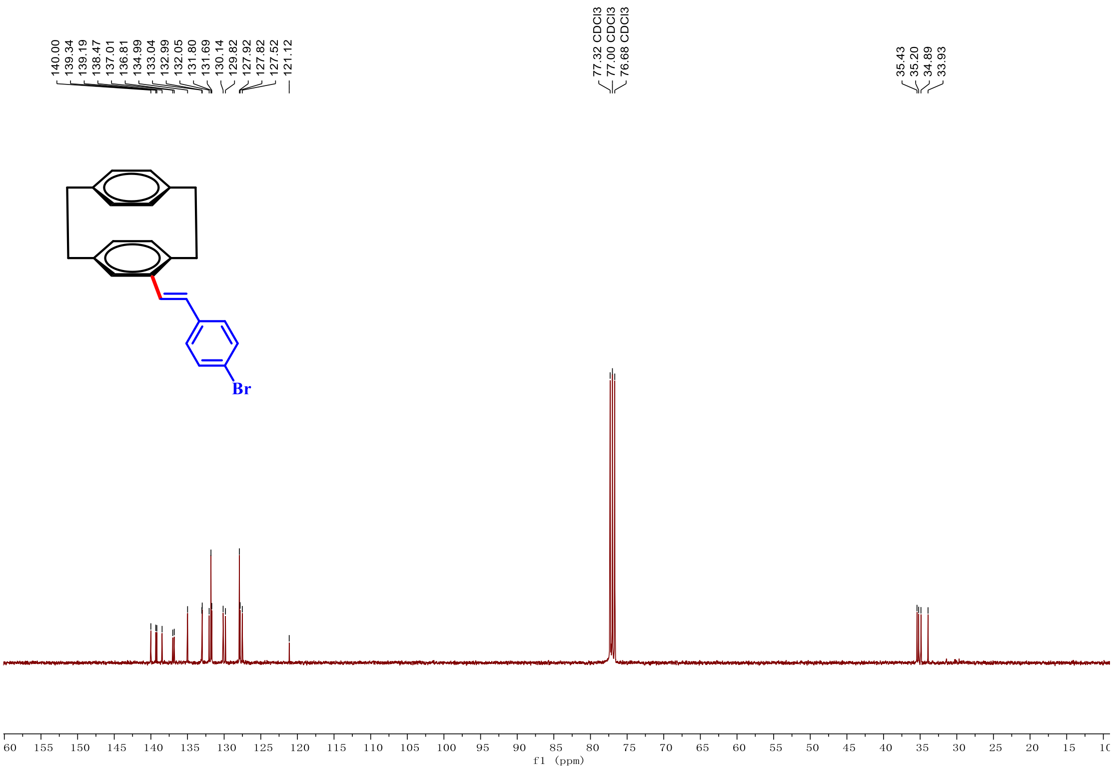
^{1}H NMR spectrum of 5d (CDCl$_3$, 400MHz)



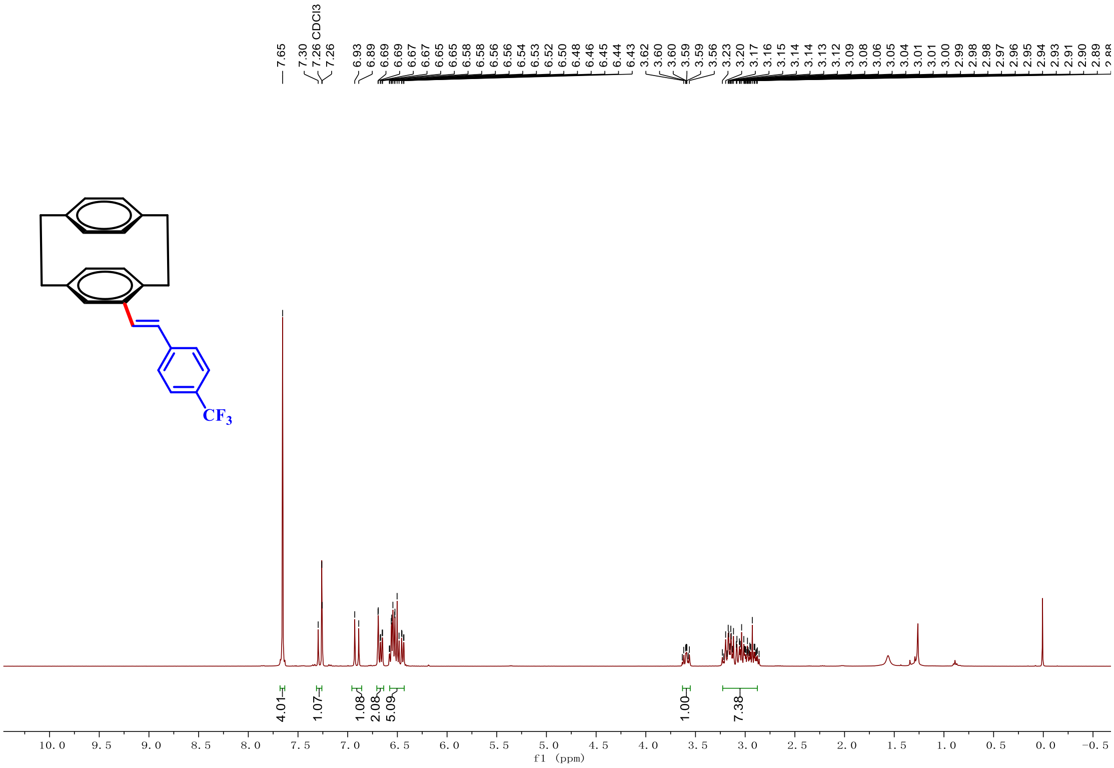
^{13}C NMR spectrum of 5d (CDCl$_3$, 101MHz)



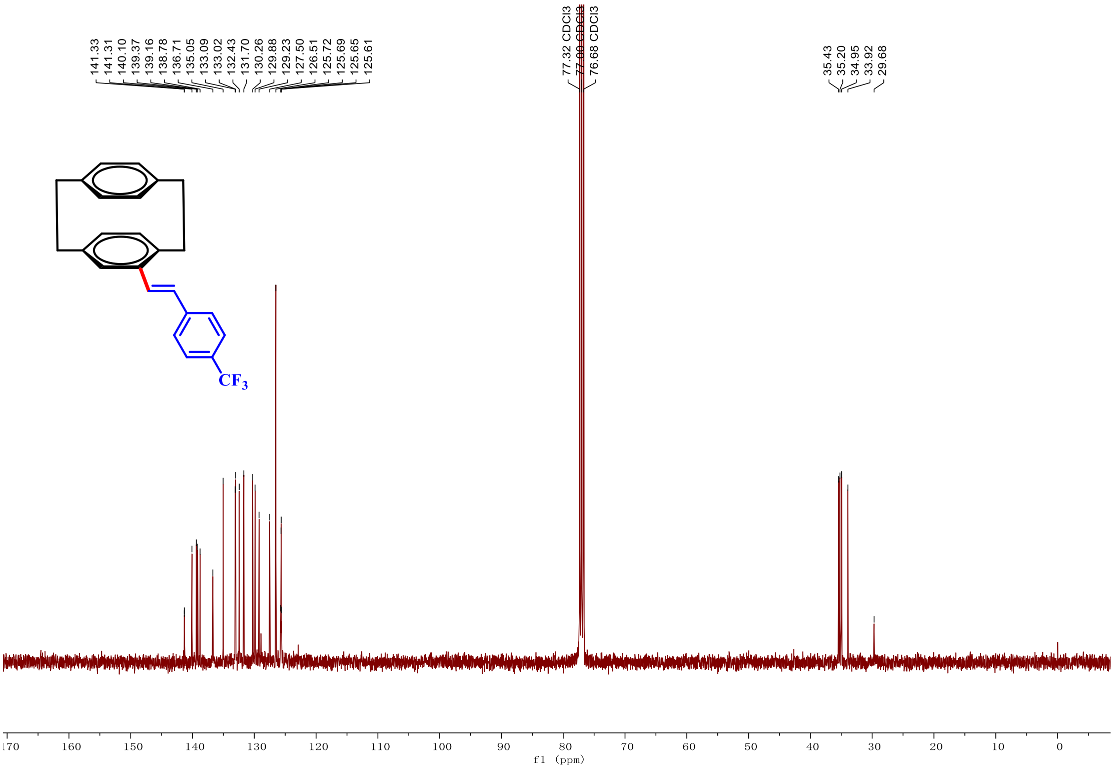
^{1}H NMR spectrum of 5e (CDCl$_3$, 400MHz)



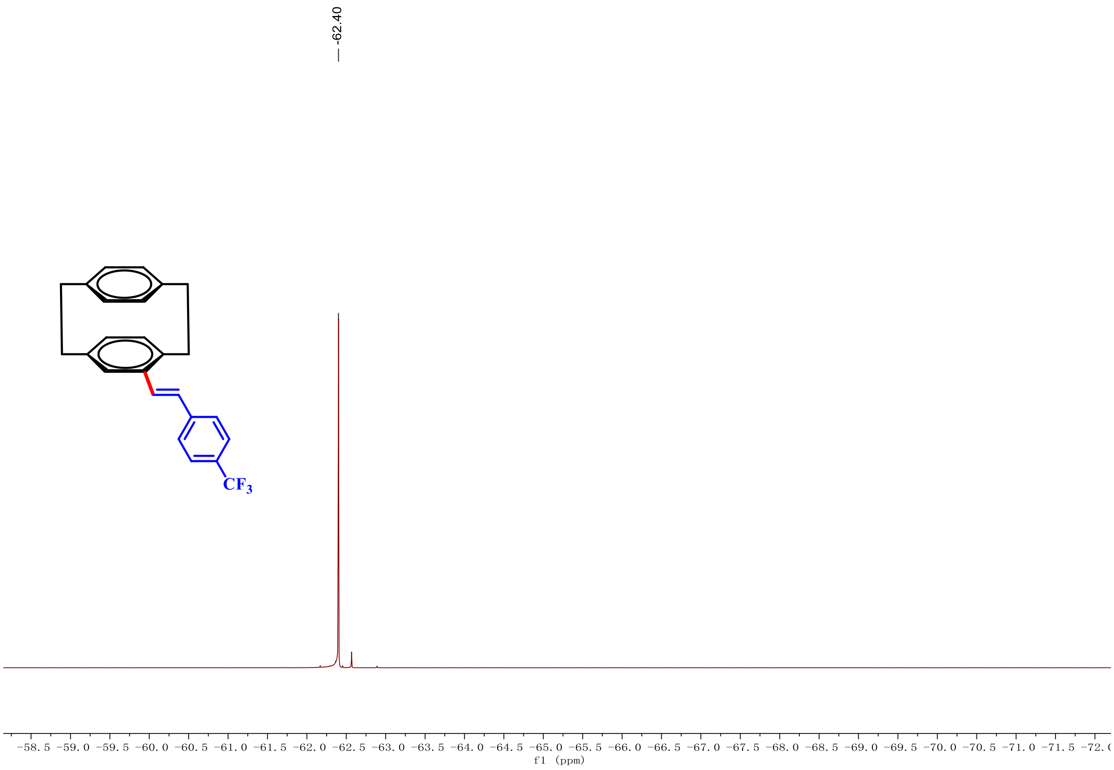
^{13}C NMR spectrum of 5e (CDCl$_3$, 101MHz)



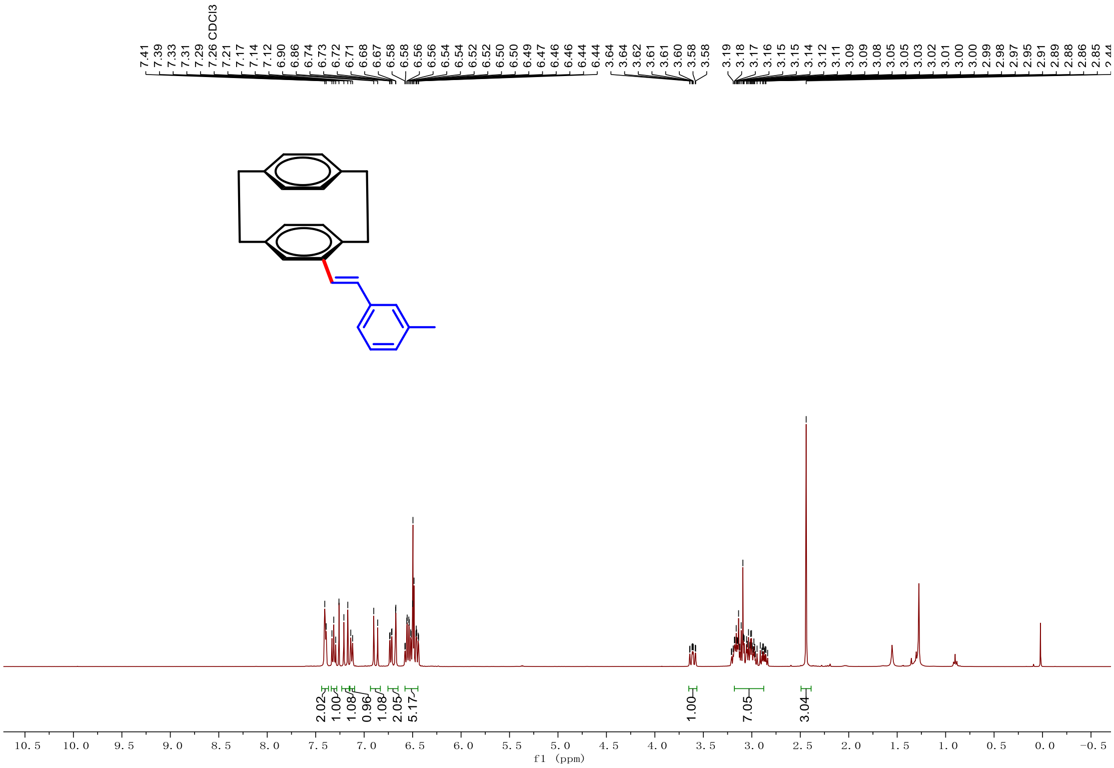
^{1}H NMR spectrum of 5f (CDCl$_3$, 400MHz)



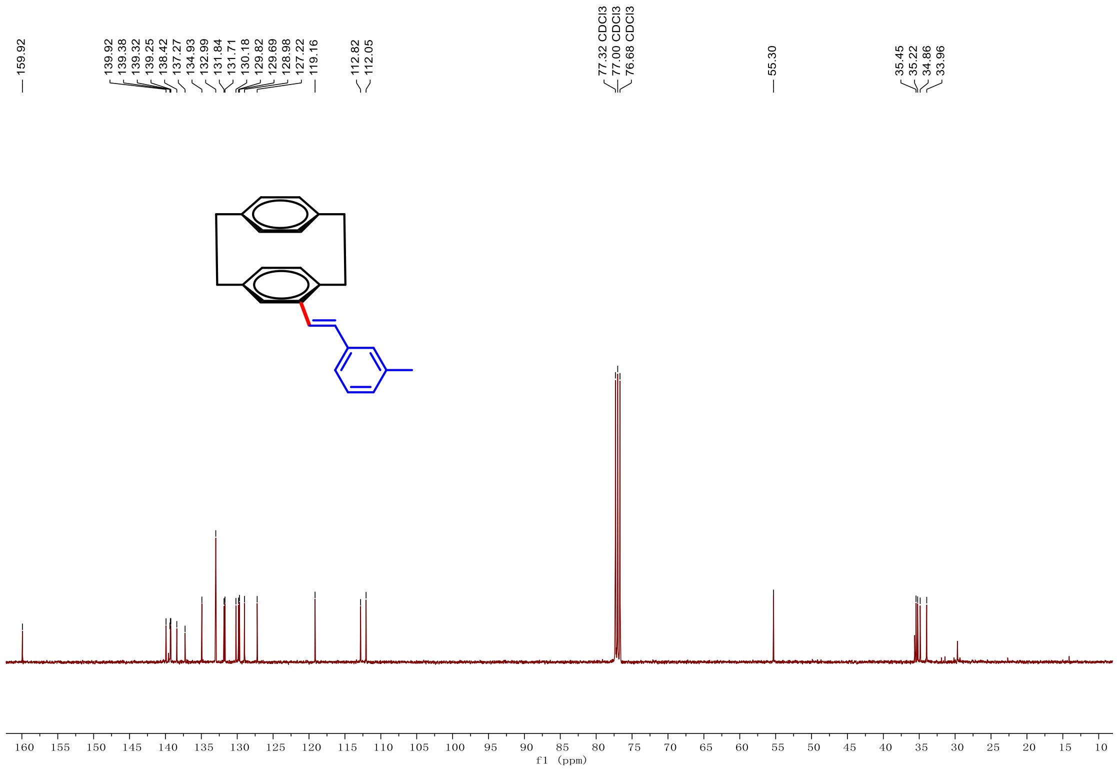
^{13}C NMR spectrum of 5f (CDCl$_3$, 101MHz)



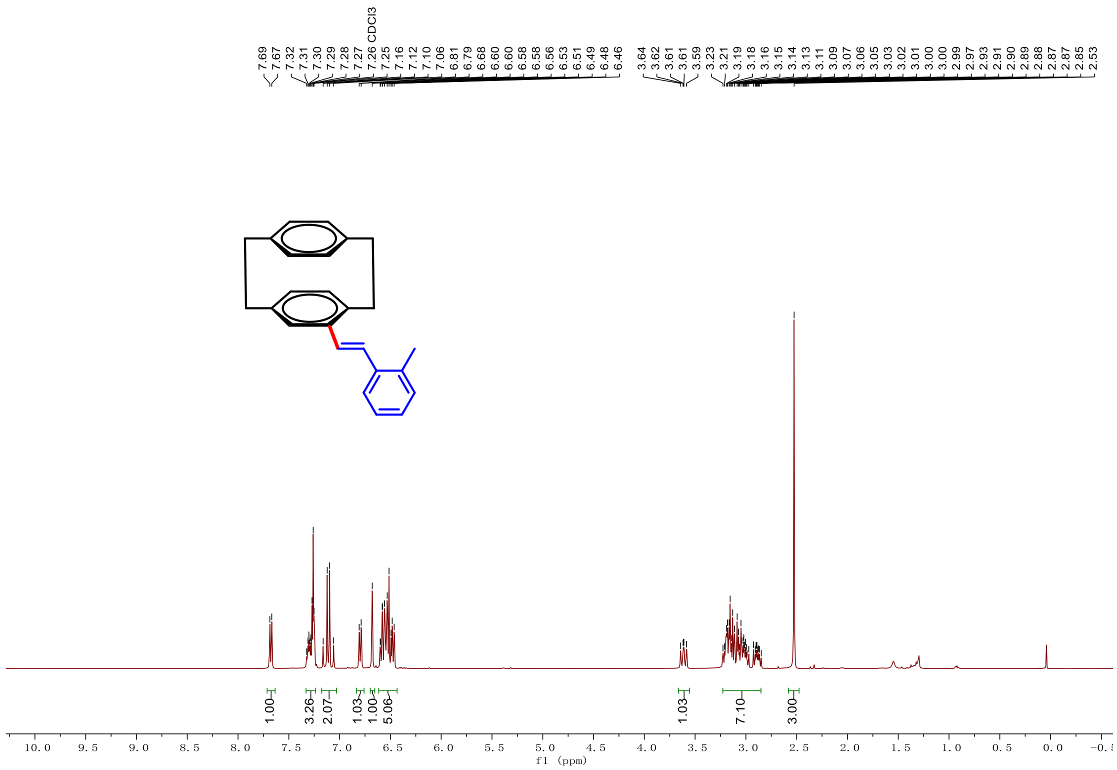
^{19}**F NMR spectrum of 5f (CDCl$_3$, 376MHz)**



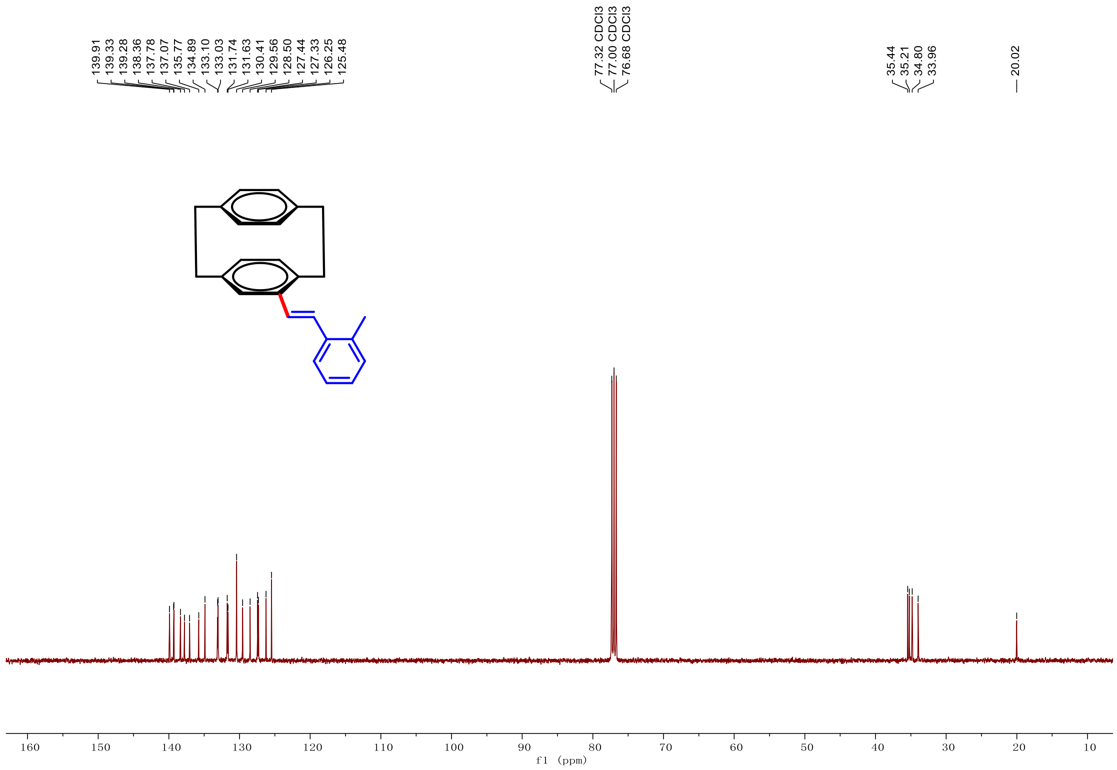
^{1}**H NMR spectrum of 5g (CDCl$_3$, 400MHz)**



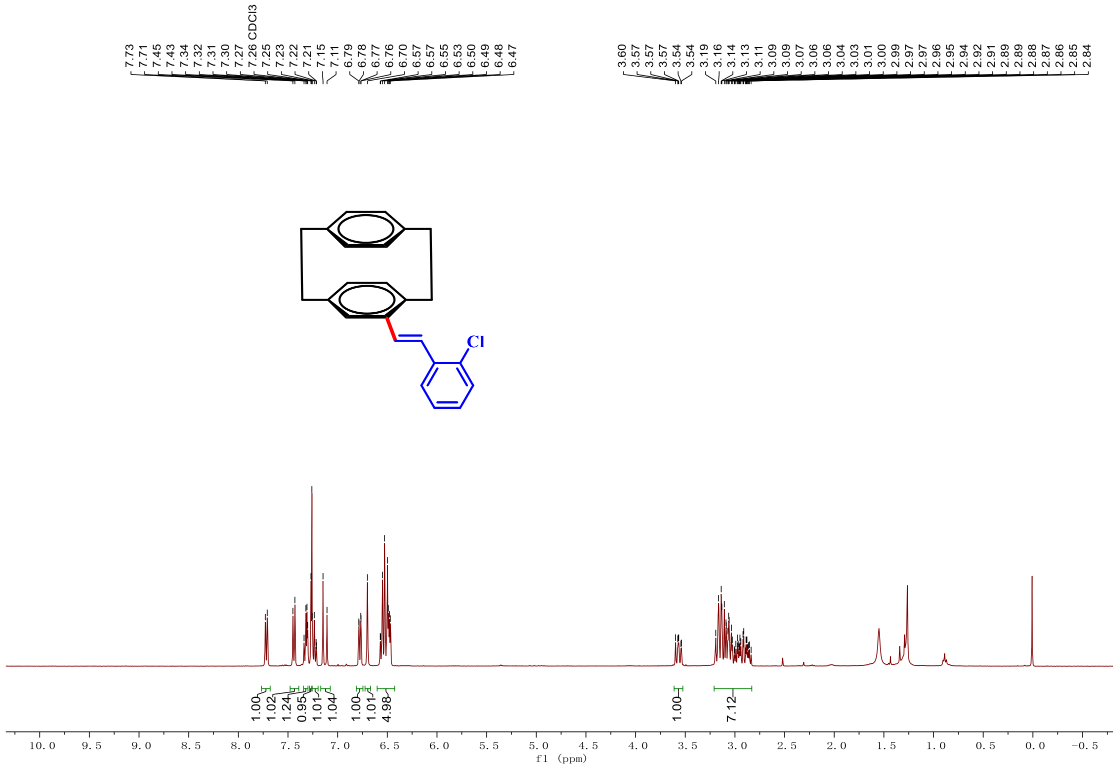
^{13}C NMR spectrum of 5g ($CDCl_3$, 101MHz)



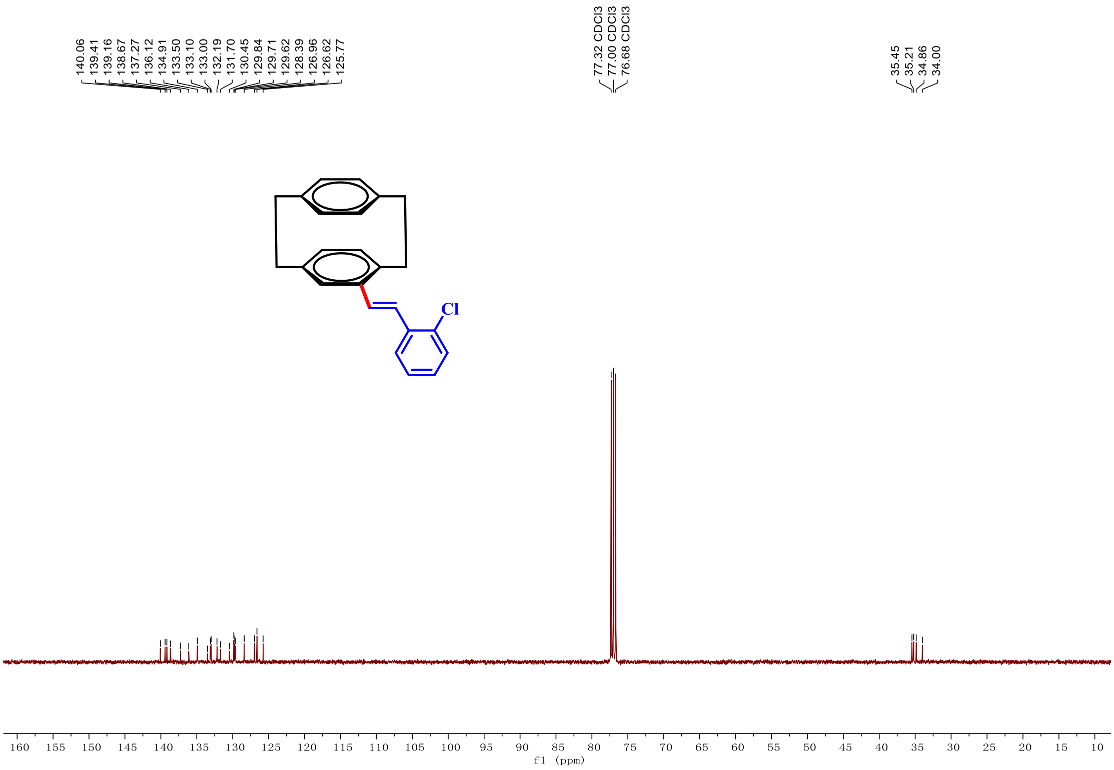
^{1}H NMR spectrum of 5h ($CDCl_3$, 400MHz)



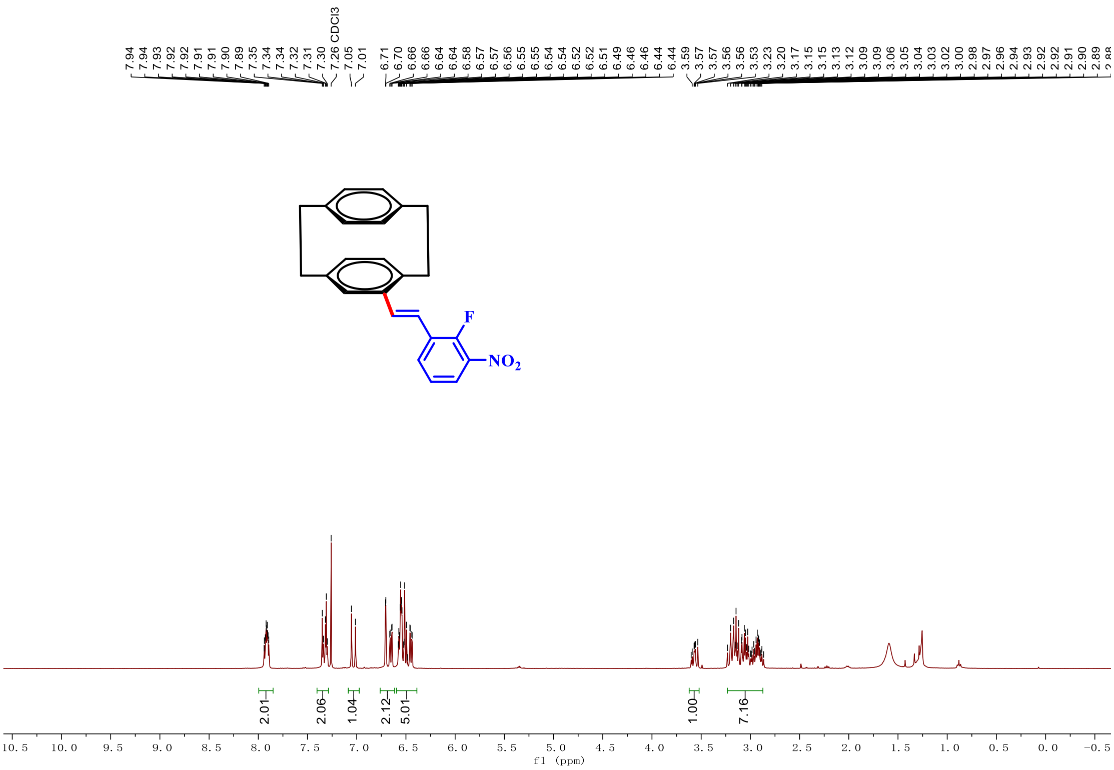
^{13}C NMR spectrum of 5h ($CDCl_3$, 101MHz)



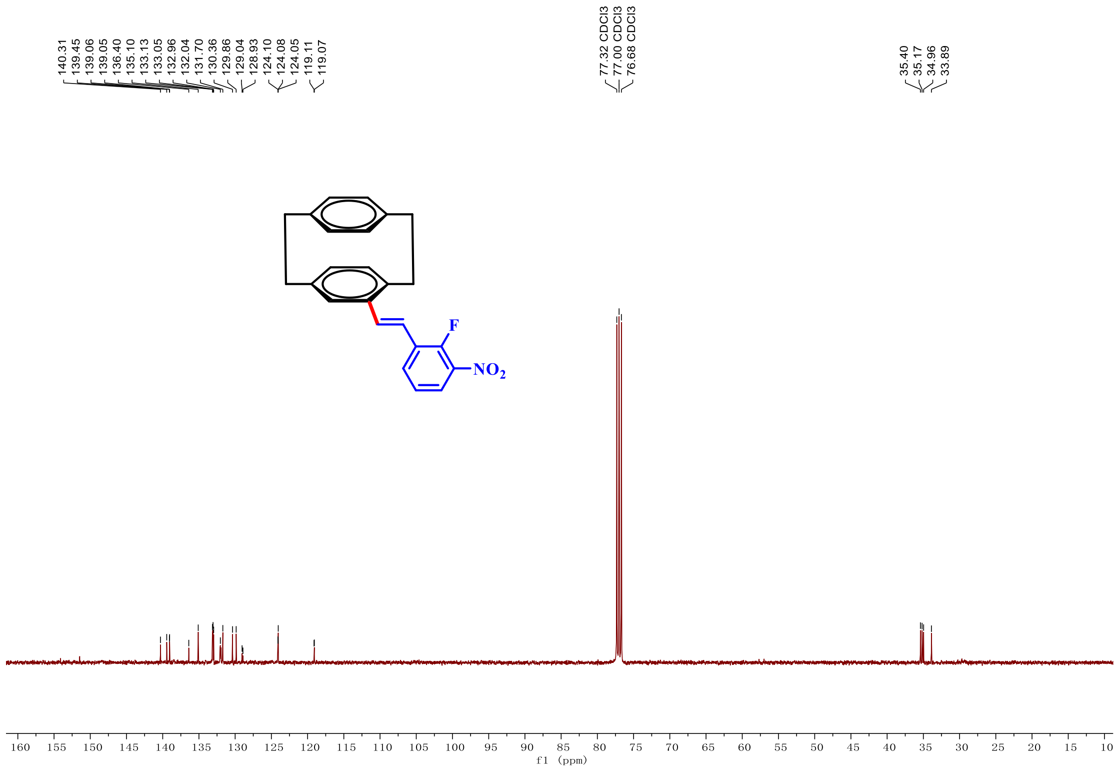
^{1}H NMR spectrum of 5i ($CDCl_3$, 400MHz)



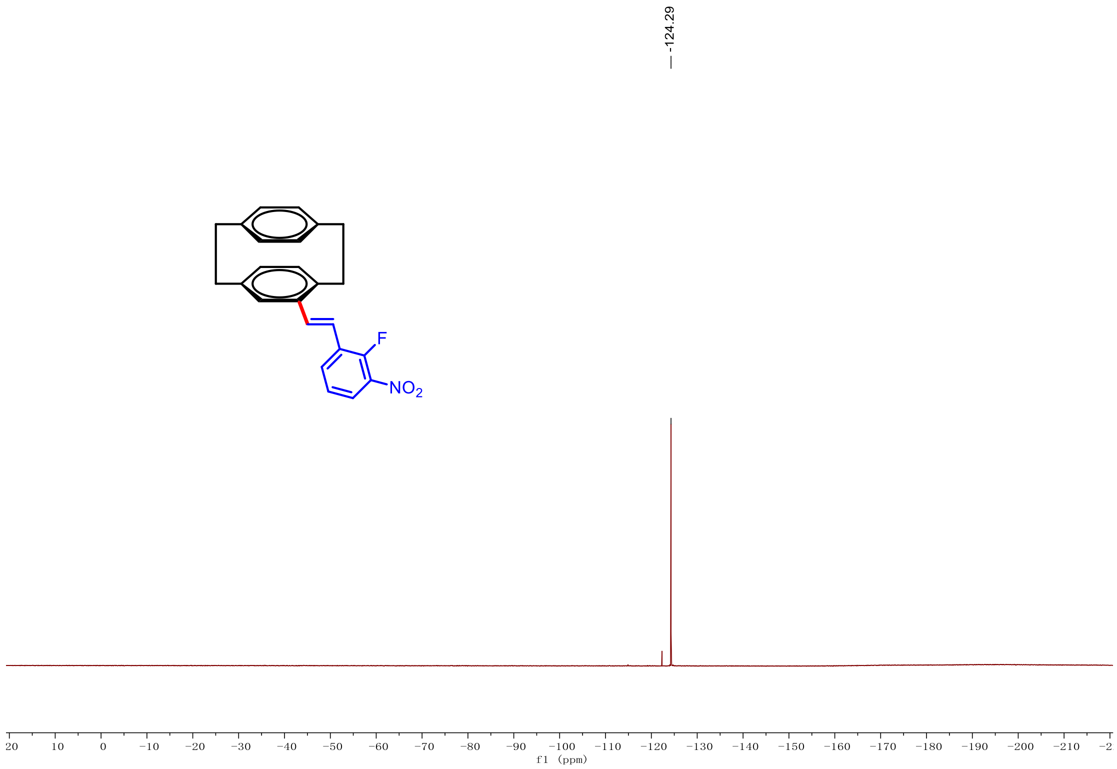
^{13}C NMR spectrum of 5i ($CDCl_3$, 101MHz)



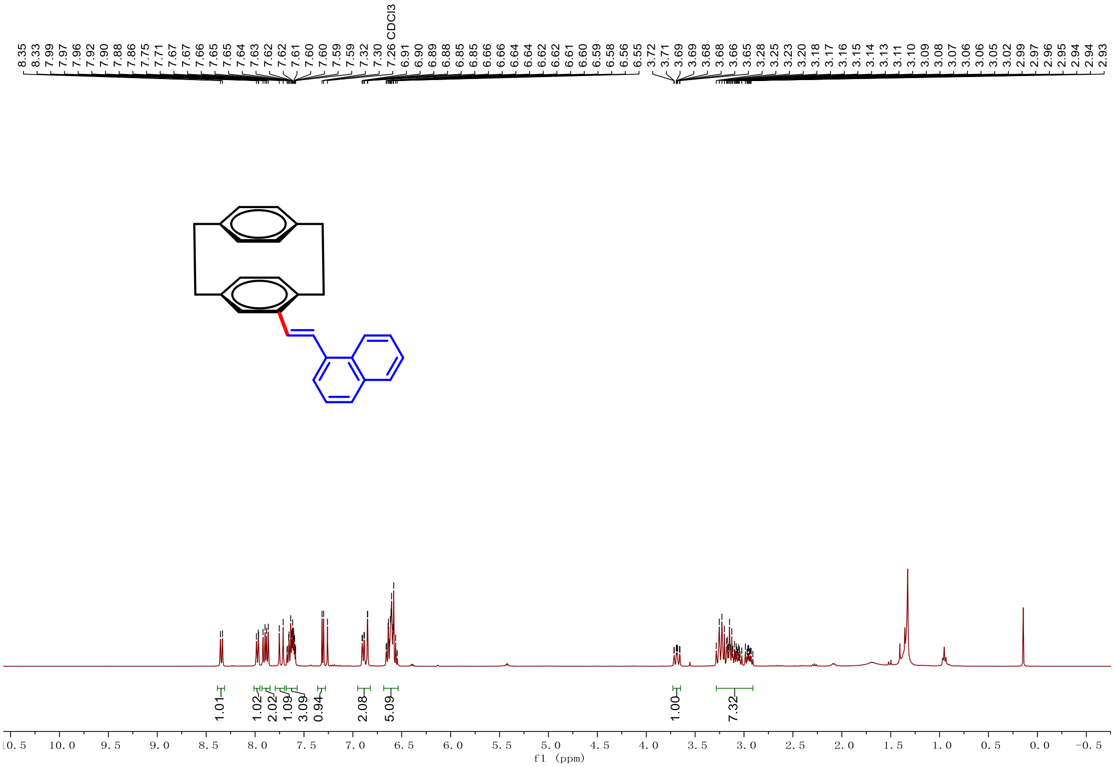
^{1}H NMR spectrum of 5j ($CDCl_3$, 400MHz)



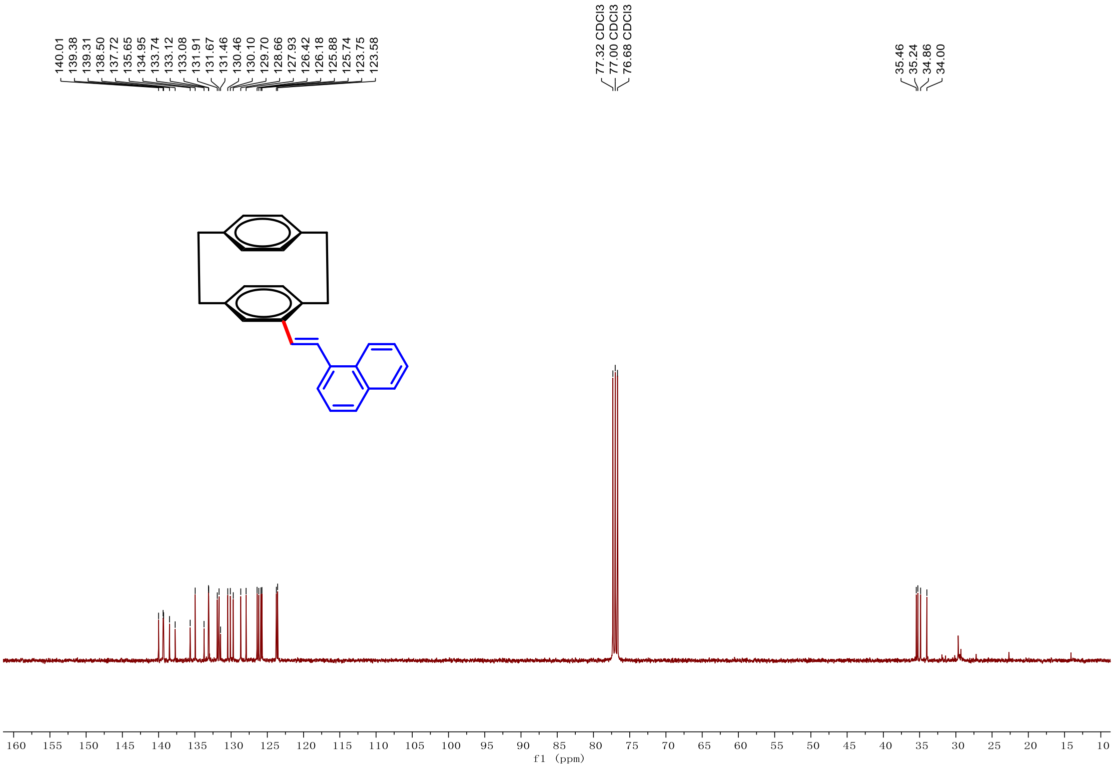
^{13}C NMR spectrum of 5j (CDCl$_3$, 101MHz)



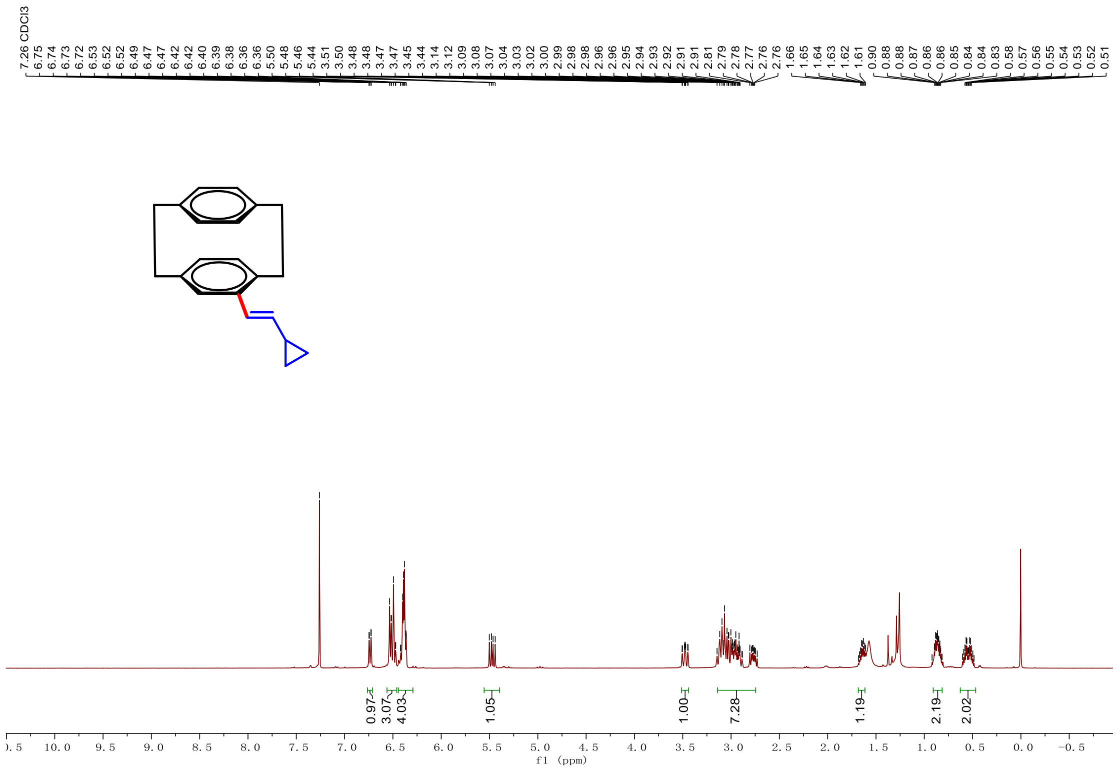
^{19}F NMR spectrum of 5j (CDCl$_3$, 376MHz)



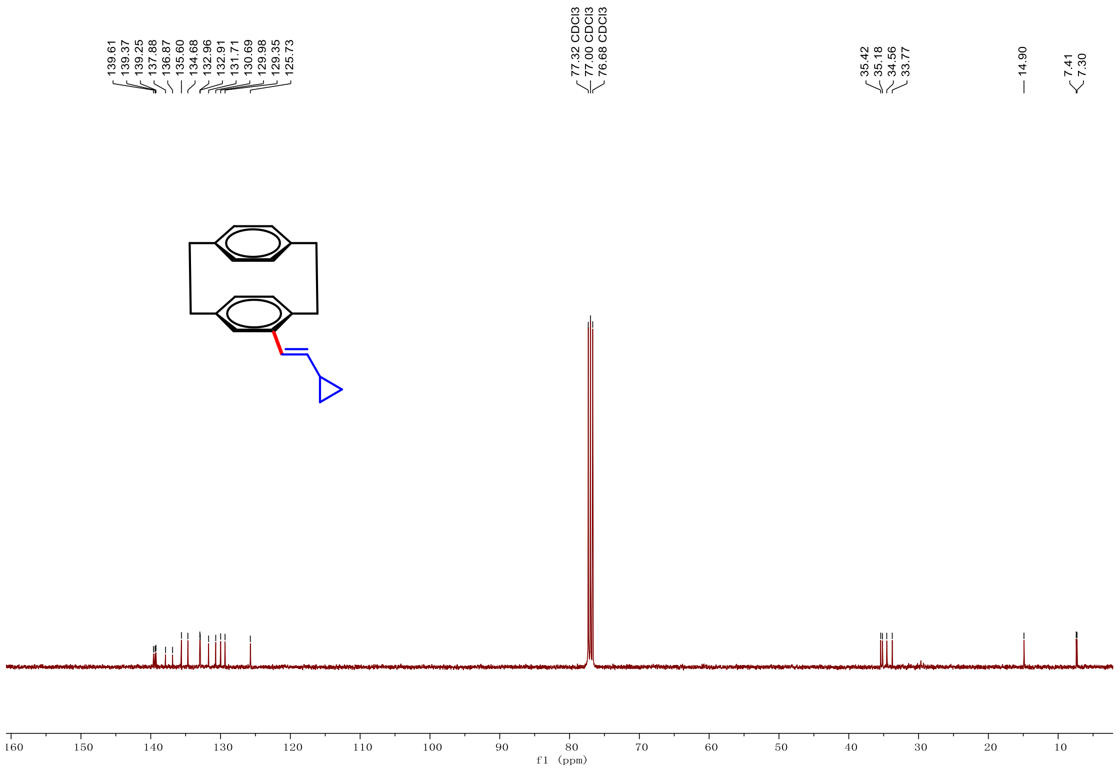
^{1}H NMR spectrum of 5k (CDCl$_3$, 400MHz)



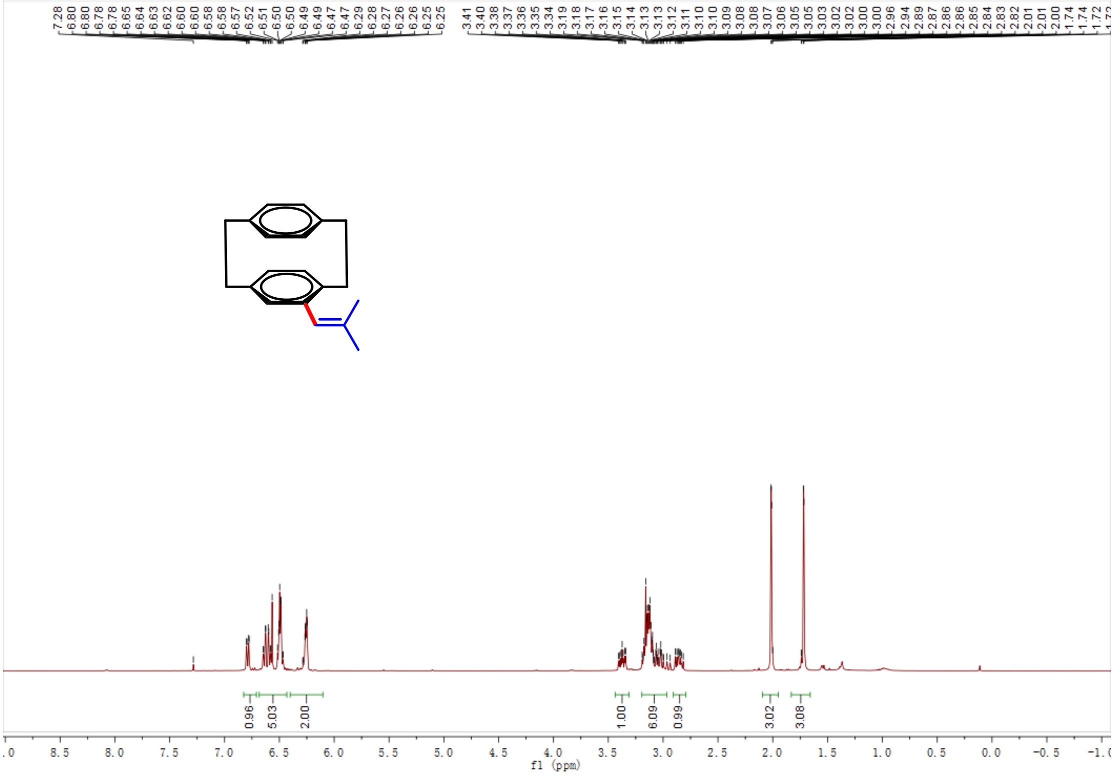
^{13}C NMR spectrum of 5k (CDCl$_3$, 101MHz)



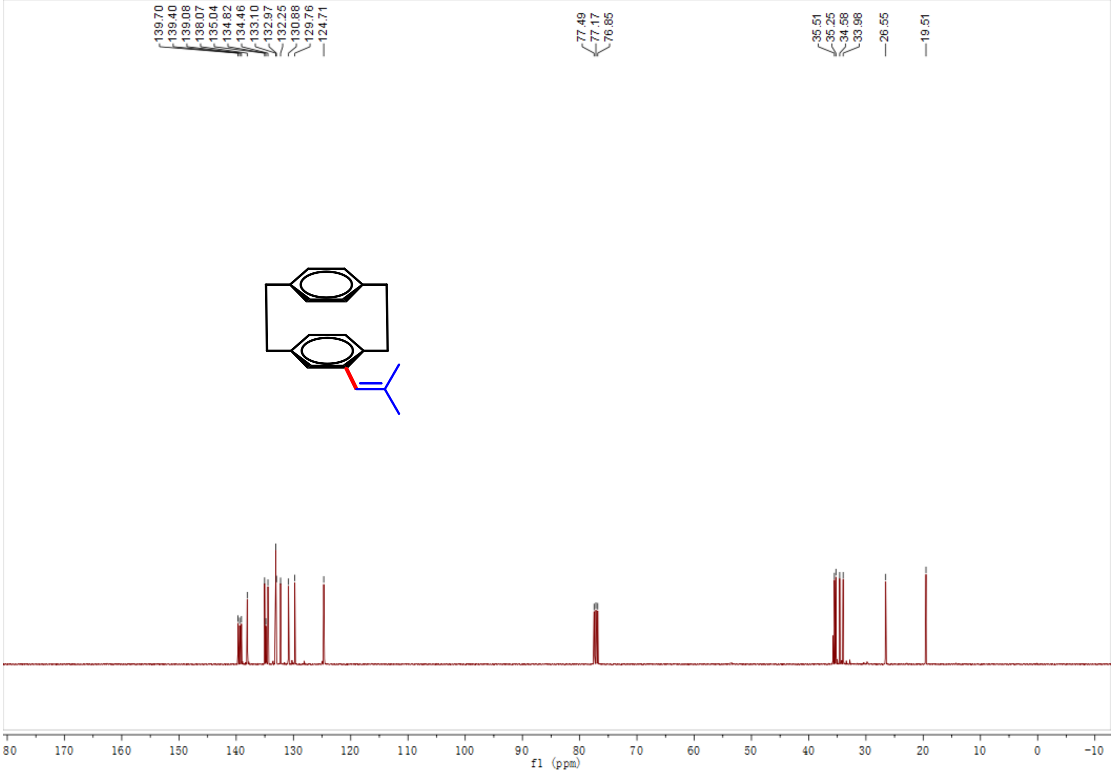
^{1}H NMR spectrum of 5l ($CDCl_3$, 400MHz)



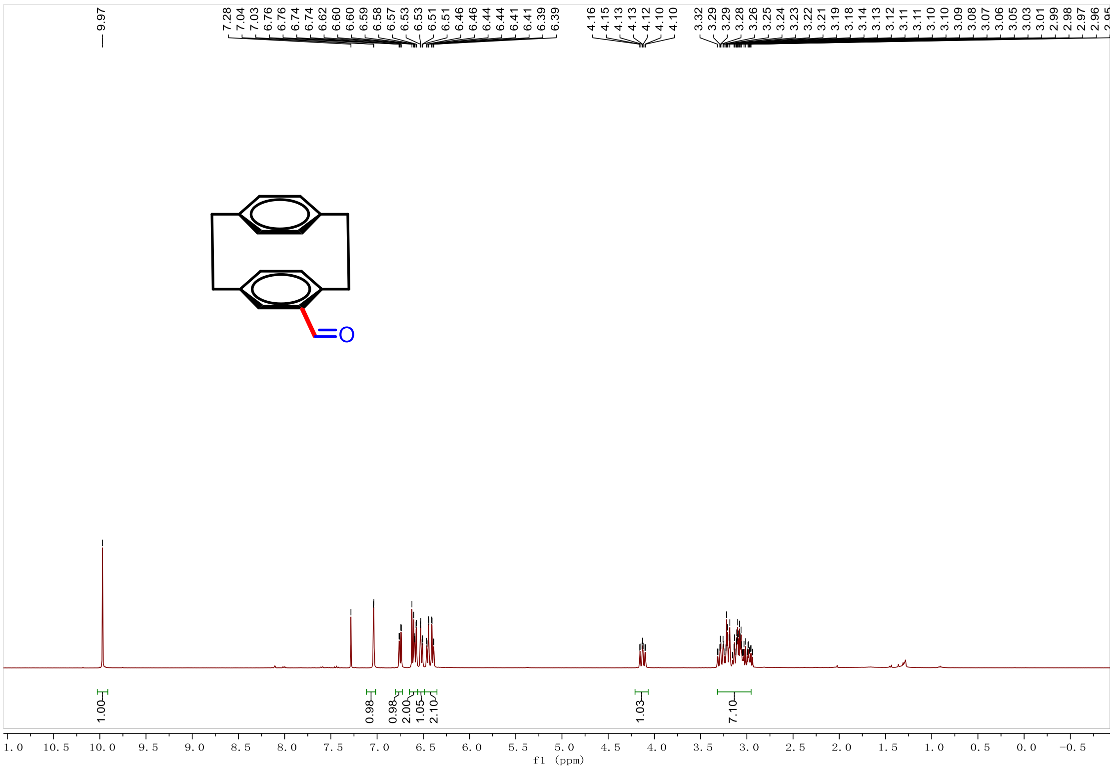
^{13}C NMR spectrum of 5l ($CDCl_3$, 101MHz)



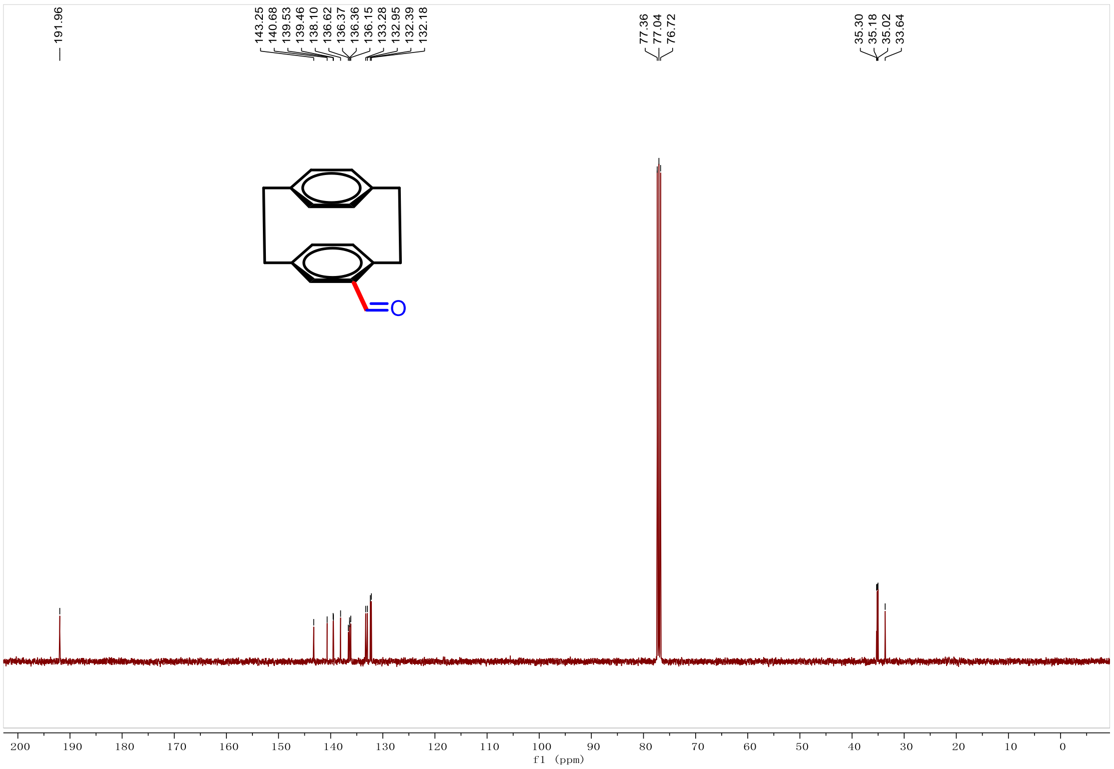
^{1}**H NMR spectrum of 5m (CDCl$_3$, 400MHz)**



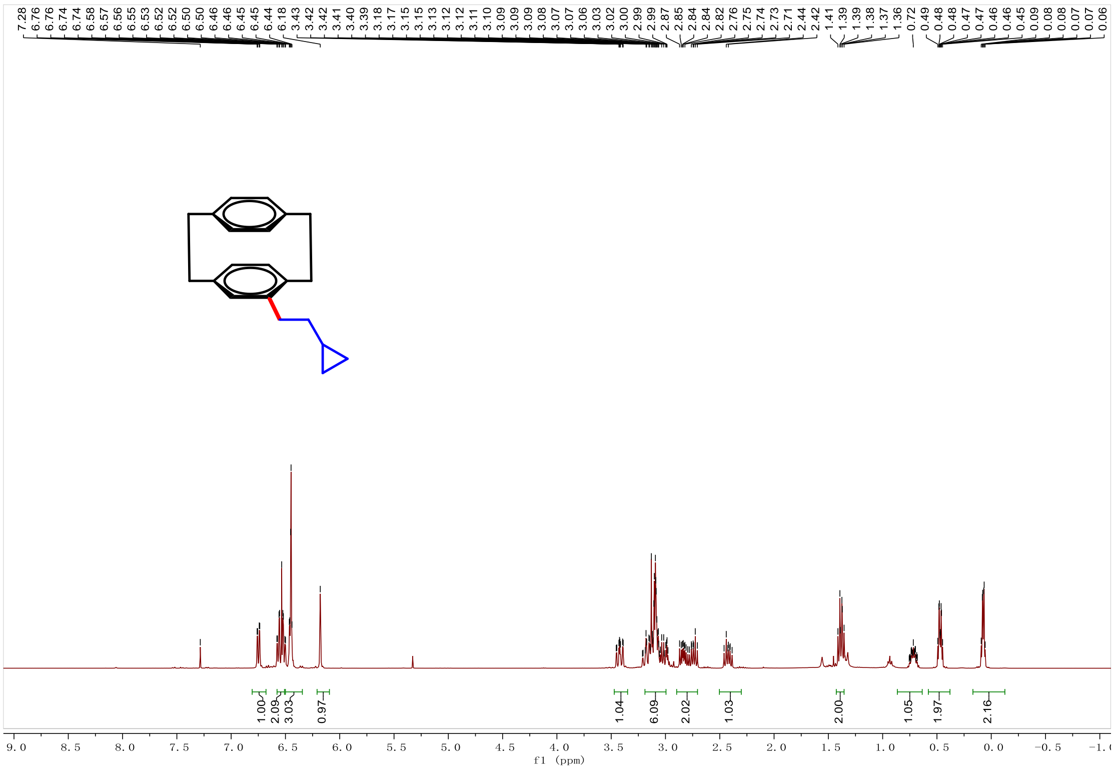
^{13}**C NMR spectrum of 5m (CDCl$_3$, 101MHz)**



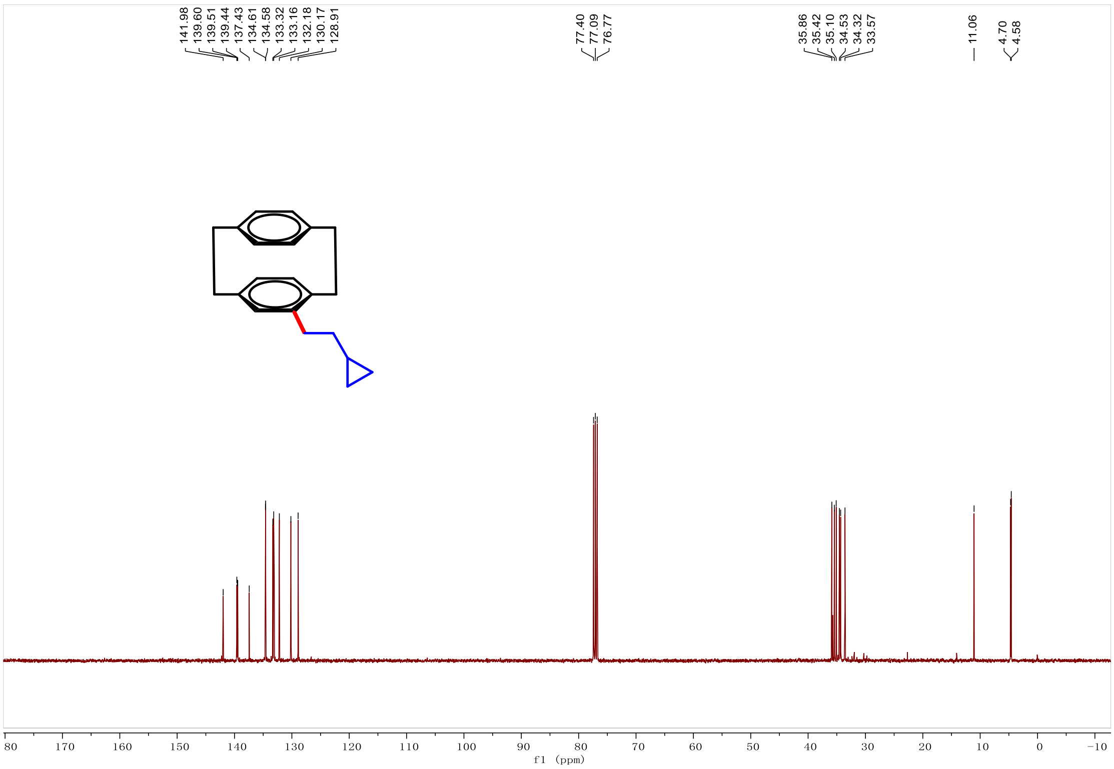
^{1}H NMR spectrum of 6a ($CDCl_3$, 400MHz)



^{13}C NMR spectrum of 6a ($CDCl_3$, 101MHz)



^{1}H NMR spectrum of 6b (CDCl$_3$, 400MHz)



^{13}C NMR spectrum of 6b (CDCl$_3$, 101MHz)

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