Electronic Supplementary Material (ESI) for Chemical Communications.

Supporting Information

Non-directed Pd-catalysed C–H Arylation of [2.2]Paracyclophane

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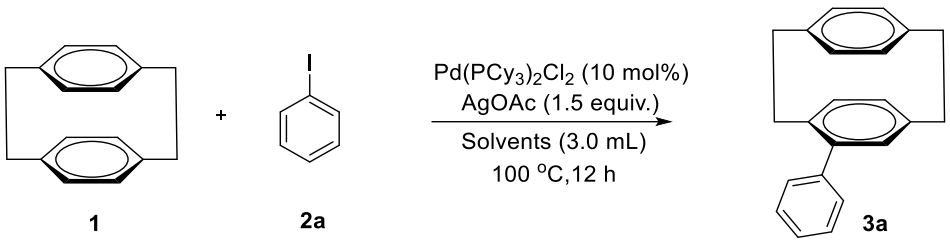
Table of Contents

I. General

Unless otherwise stated, all experiments were carried out under air atmosphere. The reagents and solvents were purchased from commercial suppliers and used without further purification unless noted. ^{1}H NMR and ^{13}C NMR spectra were obtained on a Bruker AVANCE III HD 400 in $CDCl_3$ using TMS as an internal standard, operating at 400 MHz and 101 MHz, respectively. Chemical shifts (δ) are expressed in ppm and coupling constants J are given in Hz. For $CDCl_3$ solutions the chemical shifts are reported as parts per million (ppm) to residual protium or carbon of the solvents; $CHCl_3$ δ (7.28 ppm) and $CDCl_3$ δ C (77.03 ppm). Multiplicities are reported using the following abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, td = triplet of doublets, ddd = doublet of doublet of doublets, m = multiplet. GC experiments were carried out using Agilent 7890B GC. GC-MS experiments that used dodecane as an internal standard were performed with a Thermo DSQ II, Trace GC Ultra. High resolution mass spectra (HRMS (EI-TOF)) were obtained on an Agilent 7250 Q-TOF GCMS spectrometer equipped with an EI source. And high resolution mass spectra (HRMS (ESI-TOF)) were obtained on an Agilent 6545 Q-TOF LCMS spectrometer equipped with an ESI source.

II. Optimization of reaction conditions

Table S1. Screening of solvents[a]

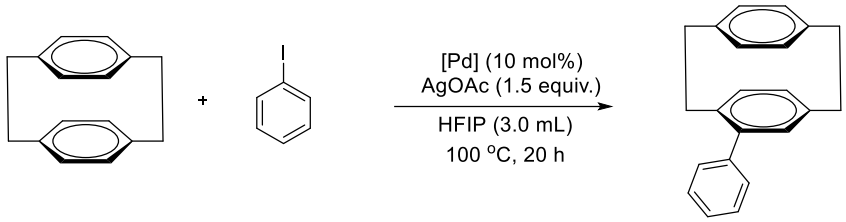


1 2a 3a

Entry	Solvent (3 mL)	Yield of 3a (%)
1	DCM	8
2	Toluene	9
3	Para-xylene	11
4	Mesitylene	5
5	THF	11
6	TFA	35
7	DCE	3
8	HFIP	45
9	Isopropyl alcohol	36

[a]Reaction conditions: **1** (1.5 equiv.), **2a** (0.05 mmol), $Pd(PCy_3)_2Cl_2$ (10 mol%), AgOAc (1.5 equiv.), Solvents (3.0 mL), 100 °C for 12 h. Yields were determined by GC-MS analysis using dodecane as an internal standard.

Table S2. Screening of catalysts[a]

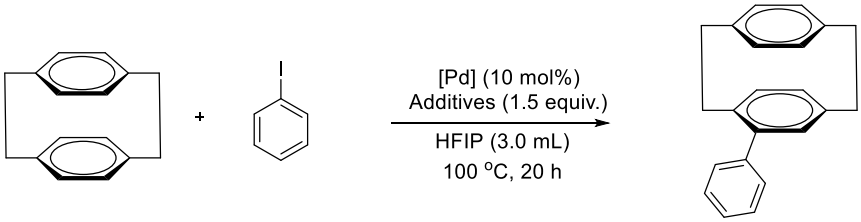


1 **2a** **3a**

Entry	[Pd] (10% mol)	Yield of 3a (%)
1	$Pd(OAc)_2$	45
2	$PdCl_2$	39
3	PdI_2	Nr
4	$Pd(TFA)_2$	57
5	$Pd(PCy_3)_2Cl_2$	65
6	$Pd(PPh_3)_2Cl_2$	58
7	$Pd(PPh_3)_4$	n.r.
8	$Pd_2(dba)_3$	37

[a]Reaction conditions: **1** (1.5 equiv.), **2a** (0.05 mmol), [Pd] (10% mol), AgOAc (1.5 equiv.), HFIP (3.0 mL), 100 °C for 20 h. Yields were determined by GC-MS analysis using dodecane as an internal standard.

Table S3. Screening of additives[a]

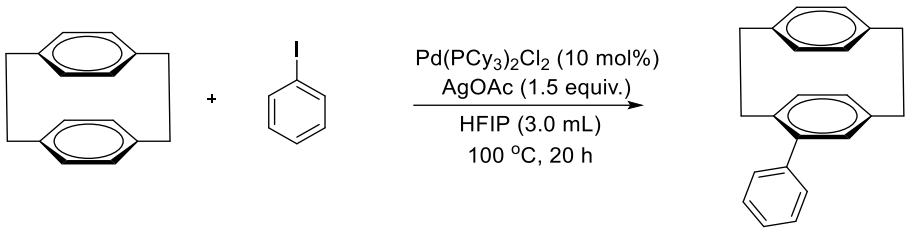


1 **2a** **3a**

Entry	Additives	Yield of 3a (%)
1	$AgBF_4$	17
2	$AgSbF_6$	12
3	AgI	3
4	$AgNTf_2$	20
5	$AgPF_6$	30
6	AgTFA	53
7	$AgPO_4$	33
8	$AgNO_2$	5
9	$AgNO_3$	21
10	PhCOOAg	56
11	AgOAc	65

[a]Reaction conditions: **1** (1.5 equiv.), **2a** (0.05 mmol), $Pd(PCy_3)_2Cl_2$ (10 mol%), additive (1.5 equiv.), HFIP (3.0 mL), 100 °C for 20 h. Yields were determined by GC-MS analysis using dodecane as an internal standard.

Table S4. Screening of the ratio of **1** and **2a**[a]

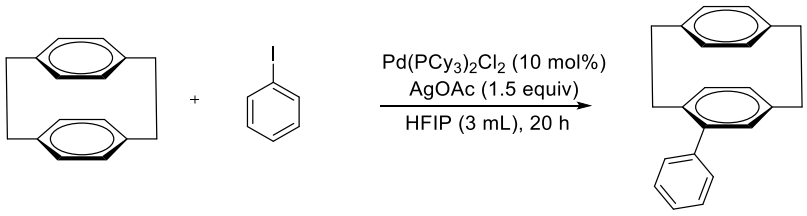


1 **2a** **3a**

Entry	1 (mmol)	2a (mmol)	Yield of 3a (%)
1	0.05	0.05	35 (19[b])
2	0.075	0.05	65 (11[b])
3	0.1	0.05	71 (5[b])

[a]Reaction conditions: **1**, **2a** were used as indicated, $Pd(PCy_3)_2Cl_2$ (10 mol%), AgOAc (1.5 equiv.), HFIP (3.0 mL), 100 °C for 20 h. Yields were determined by GC-MS analysis using dodecane as an internal standard. [b]The GC-MS yield of di-arylation product was provided in the parentheses.

Table S5. Screening of temperatures[a]

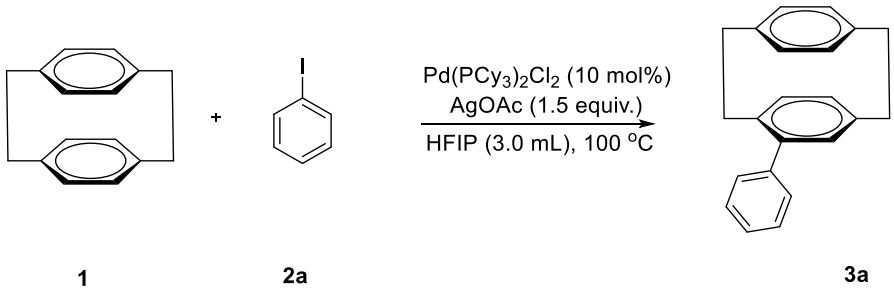


1 **2a** **3a**

Entry	[T (°C)]	Yield of 3a (%)
1	80	64(4[b])
2	100	71(5[b])
3	120	69(10[b])

[a]Reaction conditions: **1** (2.0 equiv), **2a** (0.05 mmol), $Pd(PCy_3)_2Cl_2$ (10 mol%), AgOAc (1.5 equiv.), HFIP (3.0 mL), stirred at indicated temperatures for 20 h. Yields were determined by GC-MS analysis using dodecane as an internal standard; [b]The GC-MS yield of di-arylation product was provided in the parentheses.

Table S6 Screening of reaction time[a]

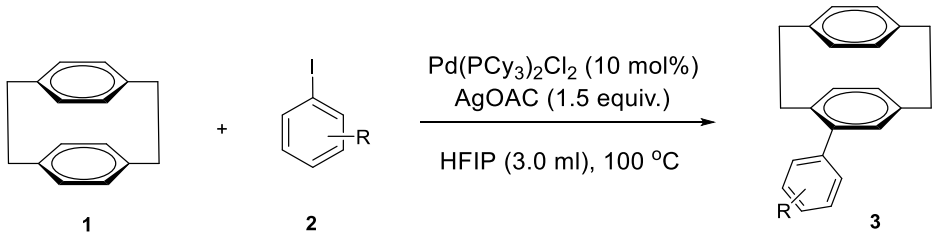


1 2a 3a

Entry	Time (h)	Yield of 3a (%)
1	16	59(2[b])
2	20	71(5[b])
3	24	78(8[b])
4	28	75(10[b])

[a]Reaction conditions: **1** (2.0 equiv.), **2a** (0.05 mmol), $Pd(PCy_3)_2Cl_2$ (10 mol%), AgOAc (1.5 equiv.), HFIP (3.0 mL), stirred at 100 °C for indicated time. Yields were determined by GC-MS analysis using dodecane as an internal standard; [b]The GC-MS yield of di-arylation product was provided in the parentheses.

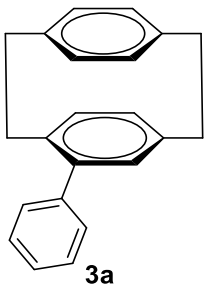
Ⅲ. General procedures for arylation of [2.2]paracyclophane



1 2 3

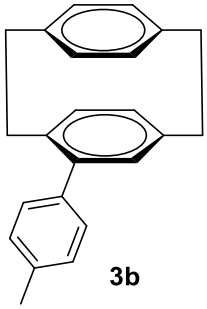
A mixture of the [2.2]paracyclophane (0.1 mmol, 2.0 equiv.), aryl iodides (0.05 mmol, 1.0 equiv.), $Pd(PCy_3)_2Cl_2$ (10 mol%), AgOAc (1.5 equiv.) in HFIP (3.0 mL) was heated to 100 ℃ and stirred for 24 h to 36 h. Then the reaction mixture was cooled to room temperature. Removal of solvent under reduced pressure afford a residue which is purified by chromatography on silica gel (petroleum ether/ethyl acetate = 100:0 to 30:1) to afford the desired compound **3a-3aa**.

Characterization of the arylation products.



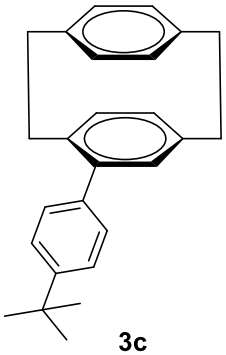
3a

4-Phenyl[2.2]paracyclophane (3a): Isolated as colorless solid (9.9 mg, 70% yield); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.55-7.47 (m, 4H), 7.43- 7.36 (m, 1H), 6.70- 6.45 (m, 7H), 3.52- 3.42 (m, 1H), 3.25- 3.03 (m, 4H), 3.01- 2.84 (m, 2H), 2.76- 2.65 (m, 1H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 141.8,141.3, 139.8, 139.7, 139.4, 137.1, 135.8, 133.1, 132.6, 132.2,132.2, 132.1, 129.9, 129.8, 128.5, 126.8, 35.6, 35.3, 34.9, 34.1 ppm. **HRMS (EI)**: $[M]^+$ cacld for $C_{22}H_{20}^+$ 284.1560, found: 284.1563.



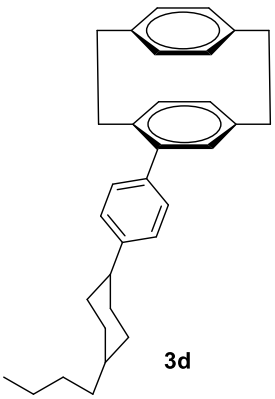
3b

4-(4-Tolyl)[2.2]paracyclophane (3b): Isolated as colorless solid (10.9 mg, 73% yield) **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.45-7.38 (m, 2H), 7.35-7.29 (m, 2H), 6.72-6.47 (m, 7H), 3.53-3.44 (m, 1H), 3.22-2.85 (m, 6H), 2.75-2.65 (m, 1H), 2.47 (s, 3H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 141.8, 139.9, 139.7, 139.4, 138.5, 137.1, 136.5, 135.8, 133.2, 132.6, 132.1, 132.1, 132.0, 129.9, 129.6, 129.3, 35.6, 35.3, 34.9, 34.2, 21.2 ppm. **HRMS (EI):** $[M]^+$ Cacld for $C_{23}H_{22}^+$ 298.1717, found: 298.1723.



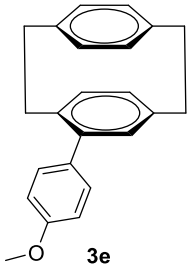
3c

4-(4-(tert-butyl)phenyl)[2.2]paracyclophane (3c): Isolated as colorless solid (11.7 mg, 69% yield); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.58 -7.33 (m, 4H), 6.83 -6.38 (m, 7H), 3.49 (ddd, *J* = 12.4, 10.0, 3.1 Hz, 1H), 3.22 -2.69 (m, 7H), 1.43 (s, 9H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 149.6, 141.8, 139.9, 139.6, 139.4, 138.4, 137.1, 135.7, 133.1, 132.5, 132.2, 132.2, 132.0, 130.0, 129.3, 125.4, 35.6, 35.3, 35.0, 34.5, 34.2, 31.5 ppm. **HRMS (EI):** $[M]^+$ cacld for $C_{26}H_{28}^+$ 340.2186, found: 340.2188.



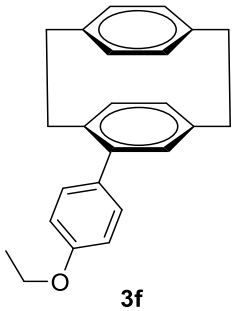
3d

4-(4-(4-butylcyclohexyl)phenyl)[2.2]paracyclophane (3d)： Isolated as colorless solid (13.9 mg, 66% yield); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.45-7.38 (m, 2H), 7.37-7.30 (m, 2H), 6.72-6.39 (m, 7H), 3.53-3.43 (m, 1H), 3.24-3.01 (m, 4H), 2.99-2.83 (m, 2H), 2.76-2.67 (m, 1H), 2.62-2.51 (m, 1H), 2.07-1.89 (m, 4H), 1.58-1.48 (m, 3H), 1.42-1.31 (m, 6H), 1.19-1.06 (m, 2H), 1.00-0.91 (m, 3H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 146.4, 141.9, 139.9, 139.6, 139.4, 138.8, 137.0, 135.7, 133.1, 132.5, 132.2, 132.2, 132.0, 129.9, 129.6, 126.9, 44.3, 37.4, 37.2, 35.6, 35.3, 35.0, 34.5, 34.4, 34.2, 33.7, 33.7, 29.3, 23.1, 14.2 ppm. **HRMS (EI)**: $[M]^+$ cacld for $C_{32}H_{38}^+$ 422.2969, found: 422.2970.



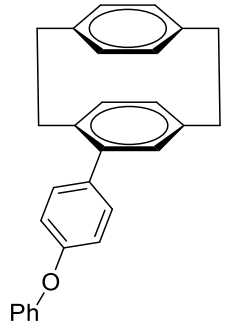
3e

4-(4-methoxyphenyl)[2.2]paracyclophane (3e): Isolated as colorless solid (11.2 mg, 71% yield); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.46-7.40 (m, 2H), 7.07-6.99 (m, 2H), 6.68-6.49 (m, 7H), 3.91 (s, 3H), 3.51-3.42 (m, 1H), 3.21-3.02 (m, 4H), 2.96-2.84 (m, 2H), 2.74-2.65 (m, 1H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.7, 141.4, 139.8, 139.7, 139.4, 136.9, 135. 8, 134.0, 133.1, 132.6, 132.0, 132.0, 131.8, 130.8, 129.7, 114.0, 55.3, 35.6, 35.3, 34.9, 34.3 ppm. **HRMS (EI):** $[M]^+$ cacld for $C_{23}H_{22}O^+$ 314.1665, found: 314.1670.



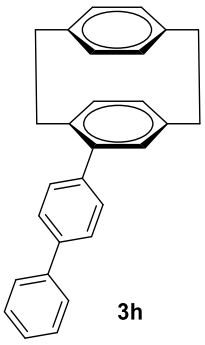
3f

4-(4-ethoxyphenyl)[2.2]paracyclophane (3f): Isolated as colorless solid (11.6 mg, 71% yield); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.45 -7.37 (m, 2H), 7.06 -6.99 (m, 2H), 6.68 -6.48 (m, 7H), 4.14 (q, *J* = 7.0 Hz, 2H), 3.51 -3.42 (m, 1H), 3.20 -3.01 (m, 4H), 2.95 -2.84 (m, 2H), 2.74 -2.64 (m, 1H), 1.50 (t, *J* = 7.0 Hz, 3H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.1, 141.5, 139.9, 139.6, 139.4, 136.9, 135.8, 133. 9, 133.1, 132.6, 132.0, 132.0, 131.8, 130.7, 129.7, 114.5, 63.5, 35.6, 35.3, 34.9, 34.3, 14.9 ppm. **HRMS (EI):** $[M]^+$ cacld for $C_{24}H_{24}O^+$ 328.1822, found: 328.1825.



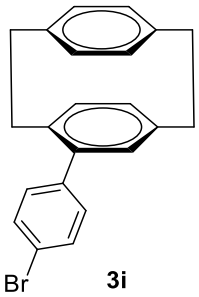
3g

4-(4-phenoxyphenyl)[2.2]paracyclophane (3g): Isolated as colorless solid (13.2 mg, 70% yield); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.50-7.38 (m, 4H), 7.23-7.03 (m, 5H), 6.69-6.49 (m, 7H), 3.52-3.42 (m, 1H), 3.21-2.88 (m, 6H), 2.79-2.67 (m, 1H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 157.1, 156.5, 141.2, 139.8, 139.7, 139.4, 137.0, 136.4, 135.9, 133.2, 132.6, 132.1, 132.1, 132.0, 131.0, 129.8, 129.7, 123.4, 119.2, 118.7, 35.6, 35.3, 34.9, 34.2 ppm. **HRMS (EI):** $[M]^+$ Cacld for $C_{28}H_{24}O^+$ 376.1822, found: 376.1826.



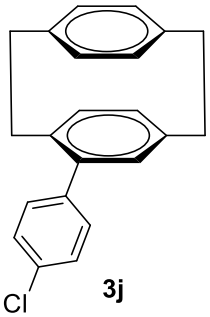
3h

4-([1,1'-biphenyl]-4-yl)[2.2]paracyclophane (3h): Isolated as colorless solid (12.2 mg, 68% yield); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.80 -7.68 (m, 4H), 7.63 -7.56 (m, 2H), 7.55 -7.48 (m, 2H), 7.45 -7.37 (m, 1H), 6.72 -6.48 (m, 7H), 3.59 -3.48 (m, 1H), 3.25 -3.05 (m, 4H), 3.03 -2.88 (m, 2H), 2.79 -2.71 (m, 1H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 141.4, 140.8, 140.3, 139.8, 139.8, 139.5, 139.4, 137.2, 135.9, 133.2, 132.6, 132.3, 132.1, 132.1, 130.1, 129.9, 128.8, 127.3, 127.2, 127.1, 35.6, 35.3, 35.0, 34.2 ppm. **HRMS (EI):** $[M]^+$ cacld for $C_{28}H_{24}^+$ 360.1873, found: 360.1875.



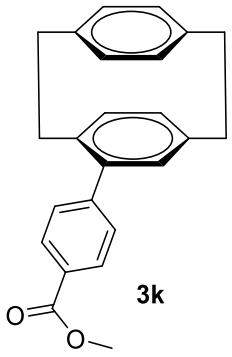
3i

4-(4-chlorophenyl)[2.2]paracyclophane (3i): Isolated as colorless solid (11.1 mg, 70% yield); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.60 -7.32 (m, 4H), 6.77 -6.46 (m, 7H), 3.47 -3.35 (m, 1H), 3.24 -3.12 (m, 3H), 3.10 -3.02 (m, 1H), 2.99 -2.86 (m, 2H), 2.76 -2.64 (m, 1H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 140.6, 139.9, 139.7, 139.7, 139.4, 137.0, 136.0, 133.2, 132.9, 132.7, 132.5, 132.0, 132.0, 130.9, 129.6, 128.7, 35.5, 35.2, 34.9, 34.1 ppm. **HRMS (EI):** $[M]^+$ cacld for $C_{22}H_{19}Cl^+$ 318.1170, found: 318.1169.



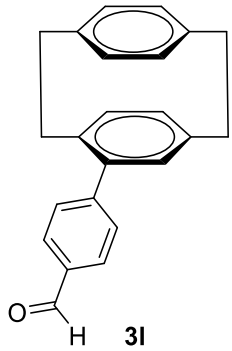
3j

4-(4-bromopheny)[2.2]paracyclophane (3j): Isolated as colorless solid (13.0 mg, 72% yield); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.70-7.53 (m, 2H), 7.42-7.34 (m, 2H), 6.74-6.36 (m, 7H), 3.45-3.35 (m, 1H), 3.21-2.86 (m, 6H), 2.75-2.65 (m, 1H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 140.6, 140.2, 139.9, 139.7, 139.4, 136.9, 136.0, 133.2, 132.7, 132.6, 132.0, 131.9, 131.7, 131.3, 129.6, 121.1, 35.5, 35.2, 34.9, 34.1 ppm. **HRMS (EI):** $[M]^+$ cacld for $C_{22}H_{19}Br^+$ 362.0665, found: 362.0667.



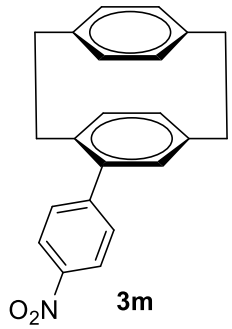
3k

4-(4-methylbenzoat)[2.2]paracyclophane (3k): Isolated as colorless solid (12.1 mg, 71% yield); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.24 -8.09 (m, 2H), 7.63 -7.52 (m, 2H), 6.71 -6.47 (m, 7H), 3.99 (s, 3H), 3.47 -3.38 (m, 1H), 3.23 -2.87 (m, 6H), 2.70 -2.60 (m, 1H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.2, 145.8, 140.8, 140.0, 139.7, 139.5, 137.3, 136.1, 133.2, 132.9, 132.7, 132.1, 132.0, 129.8, 129.8, 129.7, 128.5, 52.1, 35.5, 35.3, 34.9, 34.2 ppm. **HRMS (EI):** $[M]^+$ cacld for $C_{24}H_{22}O_2^+$ 342.1615, found: 342.1619.



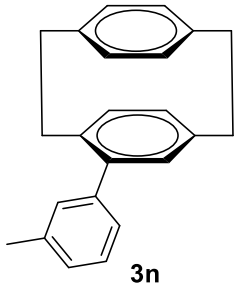
3l

4-(4-acetophenyl)[2.2]paracyclophane (3l): Isolated as colorless solid (11.4 mg, 73% yield); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.12 (s, 1H), 8.02 (d, *J* = 7.7 Hz, 2H), 7.68 (d, *J* = 7.8 Hz, 2H), 6.70-6.58 (m, 7H), 3.47-3.36 (m, 1H), 3.22-2.88 (m, 6H), 2.71-2.62 (m, 1H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 192.1, 147.4, 140.6, 140.1, 139.6, 139.6, 137.3, 136.2, 134.8, 133.3, 133.2, 132.7, 132.2, 132.0, 130.3, 130.1, 129.8, 35.5, 35.3, 35.0, 34.2 ppm. **HRMS (EI):** $[M]^+$ cacld for $C_{23}H_{20}O^+$ 312.1509, found: 312.1512.



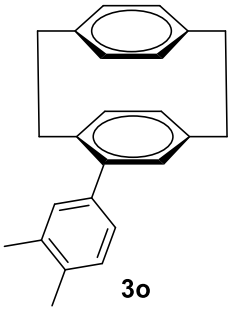
3m

4-(4-nitrophenyl)[2.2]paracyclophane (3m): Isolated as colorless solid (10.7 mg, 65% yield); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.37 (d, *J* = 8.2 Hz, 2H), 7.66 (d, *J* = 8.2 Hz, 2H), 6.70-6.51 (m, 7H), 3.41-3.32 (m, 1H), 3.24-2.91 (m, 6H), 2.72-2.62 (m, 1H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 147.8, 146.7, 140.3, 139.6, 139.6, 139.5, 137.3, 136.3, 133.6, 133.4, 132.8, 132.2, 131.9, 130.4, 129.6, 123.9, 35.5, 35.2, 35.0, 34.1 ppm. **HRMS (EI):** $[M]^+$ cacld for $C_{23}H_{20}O^+$ 329.1410, found: 329.1412.



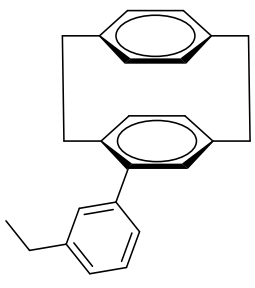
3n

4-(3-tolyl)[2.2]paracyclophane (3n): Isolated as colorless solid (10.7 mg, 72% yield); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.42 -7.29 (m, 3H), 7.21 (d, *J* = 7.3, 1.9 Hz, 1H), 6.79 -6.55 (m, 6H), 6.55 -6.49 (m, 1H), 3.51 -3.43 (m, 1H), 3.24 -3.03 (m, 4H), 3.00 -2.85 (m, 2H), 2.77 -2.69 (m, 1H), 2.49 (s, 3H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 141.9, 141.3, 139.9, 139.6, 139.4, 137.9, 137.1, 135.8, 133.1, 132.5, 132.2, 132.2, 132.2, 130.5, 129.9, 128.4, 127.5, 126.8, 35.6, 35.3, 35.0, 34.2, 21.6 ppm. **HRMS (EI):** $[M]^+$ cacld for $C_{23}H_{22}^+$ 298.1716, found: 298.1722.



3o

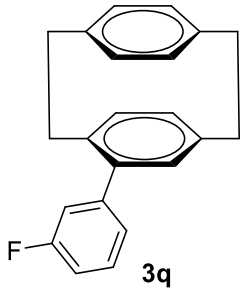
4-(3,4-dimethylphenyl)[2.2]paracyclophane (3o): Isolated as colorless solid (10.4 mg, 67% yield); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.28-7.23 (m, 3H), 6.70-6.63 (m, 2H), 6.63-6.55 (m, 4H), 6.54-6.48 (m, 1H), 3.55-3.43 (m, 1H), 3.21-2.85 (m, 6H), 2.78-2.67 (m, 1H), 2.40 (s, 3H), 2.37 (s, 3H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 141.9, 139.9, 139.6, 139.4, 139.0, 137.0, 136.5, 135.7, 135.1, 133.1, 132.5, 132.2, 132.1, 132.0, 131.0, 129.9, 129.8, 127.1, 35.6, 35.3, 34.9, 34.2, 20.1, 19.5 ppm. **HRMS (EI):** $[M]^+$ cacld for $C_{24}H_{24}^+$ 312.1873, found: 312.1875.



3p

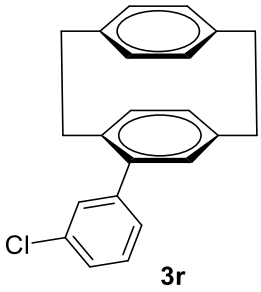
4-(3-ethylphenyl)[2.2]paracyclophane (3p): Isolated as colorless solid (10.6 mg, 68% yield); **^{1}H NMR**

(400 MHz, $CDCl_3$) δ 7.46-7.39 (m, 1H), 7.38-7.29 (m, 2H), 7.23 (d, 1H), 6.70-6.54 (m, 7H), 3.52-3.41 (m, 1H), 3.23-2.67 (m, 9H), 1.36 (t, *J* = 7.6 Hz, 3H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 144.3, 142.1, 141.3, 139.9, 139.7, 139.4, 137.1, 135.8, 133.2, 132.6, 132.2, 132.2, 132.2, 129.9, 129.5, 128.5, 127.0, 126.3, 35.6, 35.3, 34.9, 34.2, 29.0, 15.8 ppm. **HRMS (EI):** $[M]^+$ cacld for $C_{24}H_{24}^+$ 312.1873, found: 312.1871.



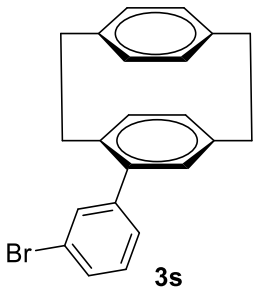
3q

4-(3-fluorophenyl)[2.2]paracyclophane (3q): Isolated as colorless solid (10.4 mg, 69% yield); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.50-7.40 (m, 1H), 7.30-7.27 (m, 1H), 7.24-7.15 (m, 1H), 7.12-6.99 (m, 1H), 6.90-6.32 (m, 7H), 3.50-3.41 (m, 1H), 3.23-2.88 (m, 6H), 2.77-2.66 (m, 1H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 163.0 (d, *J* = 245.3 Hz), 143.6 (d, *J* = 7.5 Hz), 140.6 (d, *J* = 2.1 Hz), 139.9, 139.7, 139.5, 137.1, 136.0, 133.2, 132.7, 132.6, 132.1, 132.0, 129.9 (d, *J* = 8.4 Hz), 129.8, 125.4 (d, *J* = 2.7 Hz), 116.4 (d, *J* = 21.4 Hz), 113.6 (d, *J* = 21.1 Hz), 35.5, 35.2, 34.9, 34.1 ppm. **HRMS (EI):** $[M]^+$ cacld for $C_{22}H_{19}F^+$ 302.1466, found: 302.1463.



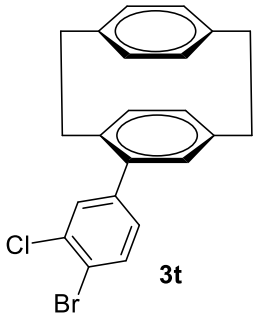
3r

4-(3-chlorophenyl)[2.2]paracyclophane (3r): Isolated as colorless solid (10.8 mg, 68% yield) **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.49 (t, *J* = 1.8 Hz, 1H), 7.45 -7.33 (m, 3H), 6.68 -6.54 (m, 7H), 3.46 -3.37 (m, 1H), 3.23 -3.05 (m, 4H), 3.02 -2.88 (m, 2H), 2.75 -2.67 (m, 1H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.1,140.4, 139.9, 139.7, 139.5, 137.1, 136.0, 133.2, 132.8, 132.6, 132.1, 132.0, 129.7, 129.7, 129.6, 127.9, 126.8, 35.5, 35.2, 34.9, 34.1 ppm. **HRMS (EI):** $[M]^+$ cacld for $C_{22}H_{19}Cl^+$ 318.1170, found: 318.1169.



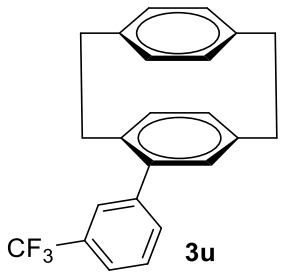
3s

4-(3-bromophenyl)[2.2]paracyclophane (3s): Isolated as colorless solid (12.3 mg, 68% yield); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.64 (s, 1H), 7.55-7.48 (m, 1H), 7.46-7.32 (m, 2H), 6.70-6.51 (m, 7H), 3.47-3.36 (m, 1H), 3.22-2.88 (m, 6H), 2.76-2.66 (m, 1H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.4, 140.3, 140.0, 139.7, 139.5, 137.1, 136.0, 133.2, 132.8, 132.7, 132.5, 132.1, 132.0, 130.1, 129.8, 129.7, 128.4, 122.5, 35.5, 35.2, 34.9, 34.0 ppm. **HRMS (EI):** $[M]^+$ cacld for $C_{22}H_{19}Br^+$ 362.0665, found: 362.0667.



3t

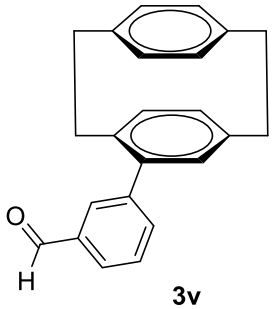
4-(4-bromo-3-chlorophenyl)[2.2]paracyclophane (3t): Isolated as colorless solid (12.8 mg, 65% yield); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.1 Hz, 1H), 7.58 (s, 1H), 7.25 (d, *J* = 8.3 Hz, 1H), 6.69-6.50 (m, 7H), 3.43-3.33 (m, 1H), 3.21-2.90 (m, 6H), 2.78-2.66 (m, 1H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 142.0, 140.2, 139.6, 139.5, 139.4, 137.0, 136.1, 134.5, 133.8, 133.3, 133.0, 132.7, 131.9, 131.9, 131.2, 129.6, 129.2, 120.9, 35.5, 35.2, 34.9, 34.0 ppm. **HRMS (EI):** $[M]^+$ cacld for $C_{22}H_{18}BrCl^+$ 396.0275, found: 396.0277.



3u

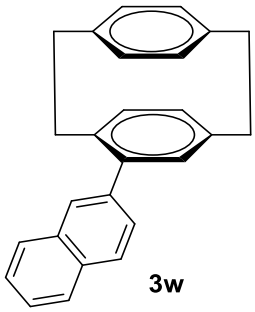
4-(3-(trifluoromethyl)phenyl)[2.2]paracyclophane (3u): Isolated as colorless solid (12.4 mg, 70% yield); 1H NMR (400 MHz, CDCl3) δ 7.65 (t, J = 1.8 Hz, 1H), 7.56 -7.49 (m, 1H), 7.46 -7.33 (m, 2H), 6.70 -6.53 (m, 7H), 3.46 -3.38 (m, 1H), 3.22 -2.88 (m, 6H), 2.76 -2.67 (m, 1H) ppm. **^{13}C NMR** (101

MHz, $CDCl_3$) δ 141.9, 140.4, 140.2, 139.7, 139.6, 137.1, 136.1, 133.3, 133.1, 133.0, 133.0, 132.8, 132.1, 132.0, 129.6, 129.1, 126.5 (q, *J* = 3.6 Hz), 124.3 (q, *J* = 270.1Hz), 123.5 (q, *J* = 3.6 Hz), 35.5, 35.2, 34.9, 34.0 ppm. **HRMS (EI):** $[M]^+$ cacld for $C_{23}H_{19}F_3^+$ 352.1434, found: 354.1436.



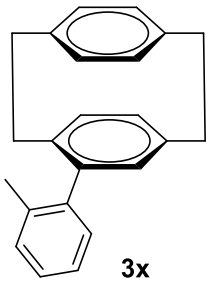
3v

4-(3-acetophenyl)[2.2]paracyclophane (3v): Isolated as colorless solid (10.1 mg, 65% yield); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.16 (s, 1H), 8.03 (s, 1H), 7.91 (d, 1H), 7.78 (d, 1H), 7.67 (t, *J* = 7.7 Hz, 1H), 6.80-6.43 (m, 7H), 3.46-3.34 (m, 1H), 3.27-2.88 (m, 6H), 2.71-2.61 (m, 1H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 192.5, 142.2, 140.4, 140.1, 139.6, 139.6, 137.1, 136.8, 136.1, 135.9, 133.3, 132.9, 132.7, 132.1, 132.1, 130.6, 129.7, 129.3, 128.4, 35.5, 35.2, 34.9, 34.1 ppm. **HRMS (EI):** $[M]^+$ cacld for $C_{23}H_{20}O^+$ 312.1509, found: 312.1512.



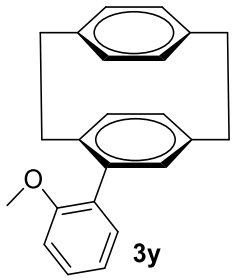
3w

4-(2-naphthyl)[2.2]paracyclophane (3w): Isolated as colorless solid (11.2 mg, 67% yield); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.11-7.78 (m, 4H), 7.70-7.46 (m, 3H), 6.94-6.44 (m, 7H), 3.56-3.48 (m, 1H), 3.28-2.83 (m, 6H), 2.69-2.60 (m, 1H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 141.7, 139.9, 139.9, 139.5, 138.9, 137.4, 136.0, 133.7, 133.2, 132.6, 132.4, 132.4, 132.4, 132.2, 129.9, 128.5, 128.2, 128.2, 128.0, 127.7, 126.1, 125.9, 35.6, 35.3, 34.9, 34.3 ppm. **HRMS (EI):** $[M]^+$ cacld for $C_{26}H_{22}^+$ 334.1717, found: 334.1719.



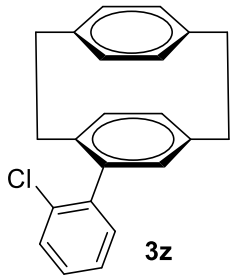
3x

4-(2-tolyl)[2.2]paracyclophane (3x): Isolated as colorless solid (7.8 mg, 52% yield); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.69-7.60 (m, 1H), 7.47-7.37 (m, 1H), 7.34-7.29 (m, 1H), 7.27-7.22 (m, 1H), 6.77-6.44 (m, 7H), 3.20-2.99 (m, 5H), 2.90-2.79 (m, 3H), 2.12 (s, 3H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 141.4, 139.9, 139.7, 139.5, 139.4, 138.5, 136.6, 134.4, 133.2, 132.8, 132.5, 132.4, 132.2, 130.1, 129.9, 129.8, 126.9, 126.0, 35.5, 35.3, 35.3, 33.5, 20.2 ppm. **HRMS (EI):** $[M]^+$ cacld for $C_{23}H_{22}^+$ 298.1716, found: 298.1721.



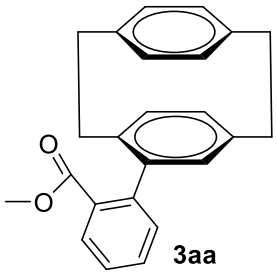
3y

4-(2-methoxyphenyl)[2.2]paracyclophane (3y)： Isolated as colorless solid (7.1 mg, 45% yield); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.63 -7.53 (m, 1H), 7.43 -7.34 (m, 1H), 7.22 -7.15 (m, 1H), 7.02 -6.94 (m, 1H), 6.72 -6.41 (m, 7H), 3.77 (s, 3H), 3.20 -2.97 (m, 6H), 2.90 -2.76 (m, 2H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 156.4, 140.1, 139.8, 139.4, 138.9, 136.4，134.2, 133.1, 132.7, 132.4, 132.4, 132.3, 131.3, 130.8, 129.9, 128.4, 120.9, 111.1, 55.5, 35.6, 35.4, 35.2, 34.1 ppm. **HRMS (EI):** $[M]^+$ cacld for $C_{23}H_{22}O^+$ 314.1665, found: 314.1669.



3z

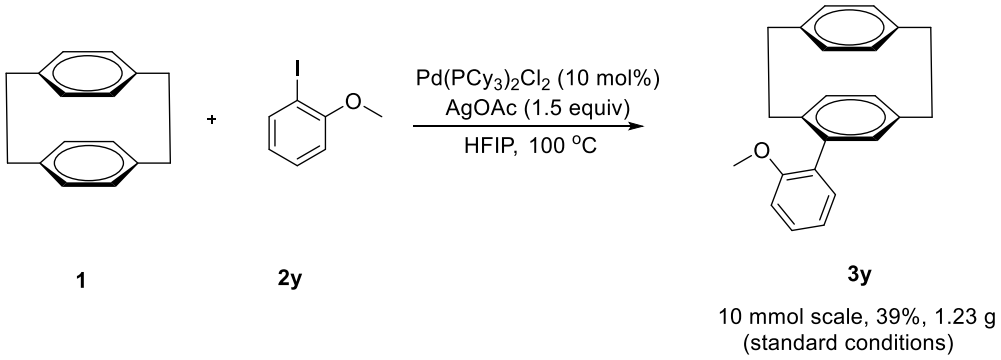
4-(2-chlorophenyl)[2.2]paracyclophane (3z): Isolated as colorless solid (6.8 mg, 43% yield); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.73 (d, 2H), 7.58 -7.39 (m, 2H), 7.34 (td, *J* = 7.7, 1.7 Hz, 1H), 6.82 -6.39 (m, 7H), 3.22 -2.83 (m, 8H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 140.1, 139.55, 139.6, 139.2, 137.3, 134.6, 134.0, 133.6, 133.4, 133.1, 132.4, 132.4, 132.3, 131.5, 129.8, 129.6, 128.3, 127.1, 35.5, 35.3, 35.3, 34.0 ppm. **HRMS (EI):** $[M]^+$ cacld for $C_{22}H_{19}Cl^+$ 318.1170, found: 318.1166.



3aa

4-(2-methylbenzoat)[2.2]paracyclophane (3aa): Isolated as colorless solid (8.6 mg, 50% yield); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.80- 7.68 (m, 3H), 7.47 (td, *J* = 7.4, 1.6 Hz, 1H), 6.77- 6.65 (m, 1H), 6.65- 6.41 (m, 6H), 3.49 (s, 3H), 3.29- 3.02 (m, 4H), 2.99- 2.65 (m, 4H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 169.9, 140.7, 139.8, 139.5, 139.5, 139.2, 137.9, 134.7, 133.5, 133.3, 133.2, 132.4, 132.1, 131.5, 131.3, 130.3, 129.8, 129.1, 126.9, 51.8, 35.5, 35.3, 35.2, 33.3 ppm. **HRMS (EI):** $[M]^+$ cacld for $C_{24}H_{22}O_2^+$ 342.1615, found: 342.1619.

Ⅳ. Gram-scale synthesis of 3y



1 2y 3y

10 mmol scale, 39%, 1.23 g
(standard conditions)

A mixture of the [2.2]paracyclophane (20.0 mmol, 4.16 g), **2y** (10 mmol, 2.34 g), $Pd(PCy_3)_2Cl_2$ (10 mol%), AgOAc (1.5 equiv) in HFIP (80.0 mL) was heated to 100 ℃ and stirred for 36 h. Then the reaction mixture was cooled to room temperature, then filter the reactants, washed filter residue with dichloromethane (3 × 25 mL). Removal of solvent under reduced pressure afford a residue which is purified by chromatography on silica gel (petroleum ether) to give the pure product **3y** in 39% yield (3.9 mmol, 1.23 g).

Ⅴ. Synthetic transformations

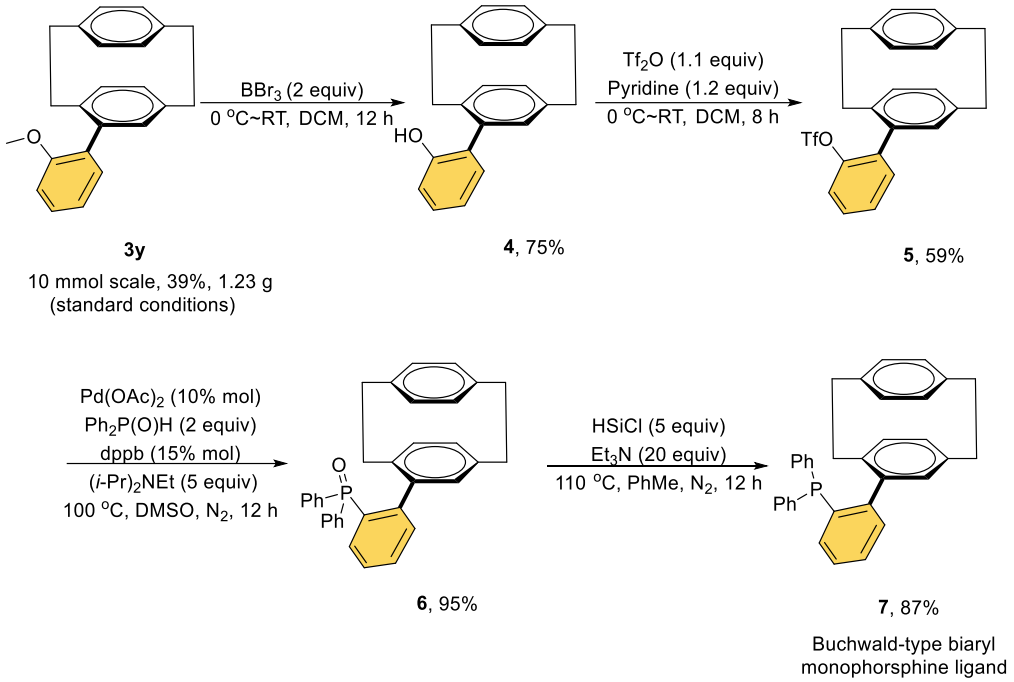
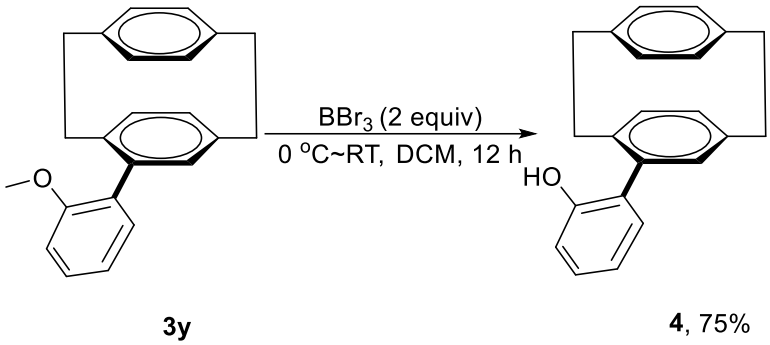
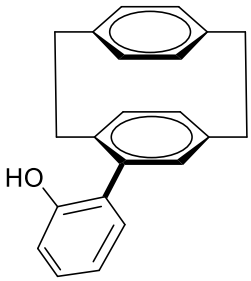


Figure S1 Synthesis of a phosphine ligand from **3y**

1) Synthesis of 4[1].



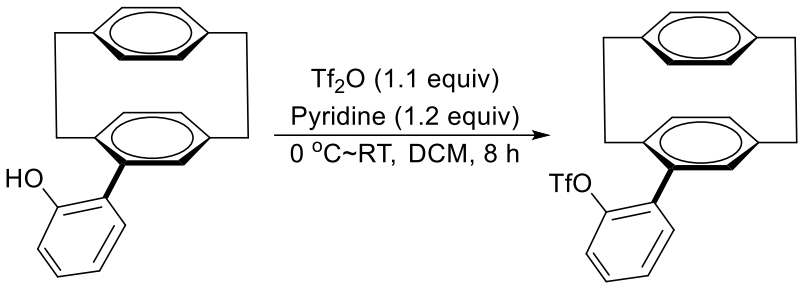
To a solution of compound **3y** (2.0 mmol, 628.0 mg) in anhydrous CH_2Cl_2 (30.0 mL) at 0 °C was added BBr_3 (4.0 mmol, 1000.0 mg) under N_2 atmosphere. After that the reaction mixture was raised to room temperature and stirred for 12 h. Then 1N HCl (20.0 mL) was added to quench the reaction. The resulting mixture was then extracted with CH_2Cl_2 (3 × 20.0 mL). The combined organic layers was dried over anhydrous $MgSO_4$, filtered and evaporated under reduced pressure. The residue was purified by flash silica gel chromatography with petroleum ether/ ethyl acetate (10: 1) to give the pure product **4** in 75% yield (1.5 mmol, 450.1 mg).



4

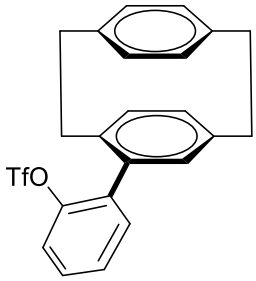
4-(2-phenol)[2.2]paracyclophane (4): Isolated as colorless solid (450.1 mg, 75% yield); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 7.6 Hz, 1H), 7.44-7.33 (m, 1H), 7.23-7.14 (m, 1H), 7.12-6.95 (m, 1H), 6.84-6.50 (m, 7H), 5.63 (s, 1H), 3.27-3.04 (m, 6H), 2.99-2.81 (m, 2H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 152.4, 141.8, 139.7, 139.7, 137.1, 136.0, 134.9, 133.7, 133.5, 133.3, 132.5, 132.3, 129.9, 129.2, 129.2, 127.6, 120.9, 115.3, 35.5, 35.4, 35.3, 33.7 ppm. **HRMS (EI):** $[M]^+$ cacld for $C_{22}H_{20}O^+$ 300.1509, found: 300.1508.

2) Synthesis of 5[2].



4 **5**, 59%

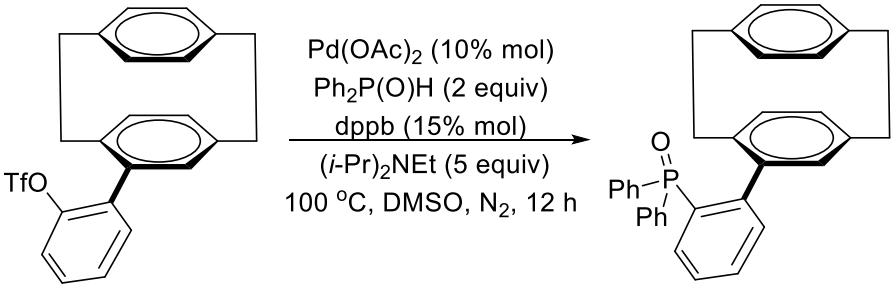
To a Schlenk tube was added **4** (1.3 mmol, 390.0 mg) and the tube was closed with a septum. The reaction tube was evacuated and backfilled with N_2 for 3 times and then anhydrous CH_2Cl_2 (10.0 mL) and pyridine (1.56 mmol, 123.3 mg) were added via syringe. The resulting solution was cooled to 0 ℃ and trifluoromethanesulfonic anhydride (0.81 mmol 733.2 mg) was slowly added. After that the reaction mixture was raised to room temperature and stirred for 8 h. Then the reaction mixture was directly subjected to column chromatography eluting with petroleum ether/ ethyl acetate (10: 1) to give the pure product **5** in 59% yield (0.77 mmol, 331.4 mg).



5

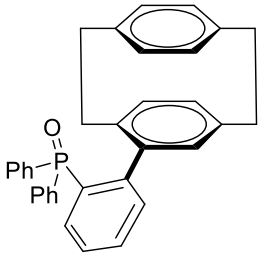
4-(2-trifluoromethanesulfonate phenyl)[2.2]paracyclophane (5): Isolated as colorless solid (331.4 mg, 59% yield); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 7.7 Hz, 1H), 7.64 (t, *J* = 7.6 Hz, 1H), 7.50 (t, *J* = 7.9 Hz, 1H), 7.39 (d, *J* = 8.3 Hz, 1H), 6.92-6.43 (m, 7H), 3.26-3.04 (m, 5H), 2.99-2.75 (m, 3H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 147.1, 139.8, 139.7, 139.7, 138.6, 135.1, 135.1, 134.1, 133.5, 133.5, 132.6, 132.5, 132.1, 131.8, 129.5, 128.9, 128.9, 121.9, 118.2 (q, *J* = 320.7 Hz), 35.5, 35.4, 35.2, 33.8 ppm. **HRMS (ESI - TOF):** $[M+Na]^+$ cacld for $C_{23}H_{19}F_3O_3SNa^+$ 455.0990, found: 455.0897.

3) Synthesis of 6[2].



5 **6**, 95%

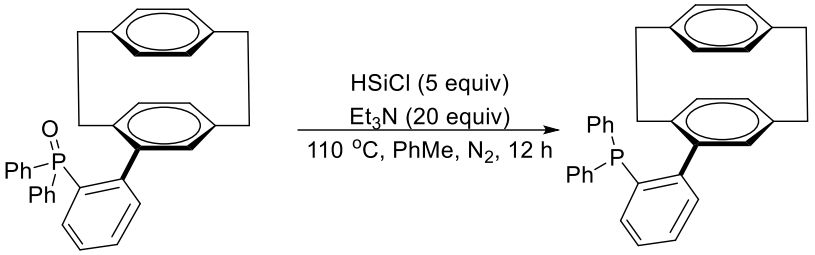
A mixture of the triflate **5** (0.4 mmol, 172.8 mg), $Ph_2P(O)H$ (0.8 mmol, 161.6 mg), $Pd(OAc)_2$ (0.04 mmol, 9.0 mg), dppb (0.04 mmol, 17.1 mg) and DIEA (2.0 mmol, 258.5 mg) in DMSO (4.0 mL) was heated to 100 ℃ and stirred for 12 h under N_2. Then the reaction mixture was cooled to room temperature. Finally, the reaction mixture was directly subjected to column chromatography eluting with petroleum ether/ ethyl acetate (3: 1) to give the pure product **6** in 95% yield (0.38 mmol, 183.9 mg).



6

4-(2-triphenylphosphine oxide)[2.2]paracyclophane (6): Isolated as colorless solid (183.9 mg, 95% yield); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.91-7.61 (m, 4H), 7.56-7.32 (m, 5H), 7.21-6.93 (m, 5H), 6.77-6.51 (m, 3H), 6.43 (d, *J* = 7.9 Hz, 1H), 6.27-6.02 (m, 3H), 3.10-2.70 (m, 8H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 147.1 (d, *J* = 8.5 Hz), 140.4, 140.0, 139.28, 137.7,137.7 (d, *J* = 3.5 Hz), 137.7 (d, *J* = 3.8 Hz), 134.7, 134.5 (d, *J* = 12.7 Hz), 133.6, 133.2, 132.6, 132.17, 132.1, 132.0, 132.0, 131.9, 131.0 (d, *J* = 11.9 Hz), 131.0 (d, *J* = 19.6 Hz), 130.7, 130.6, 130.3, 130.3, 129.9, 129.9, 128.2, 128.1, 127.5, 127.4, 126.4 (d, *J* = 12.9 Hz), 35.3, 35.3, 34.9, 34.9 ppm. **HRMS (ESI - TOF):** $[M+H]^+$ cacld for $C_{34}H_{30}OP^+$ 485.2029, found: 485.2031.

4) Synthesis of 7[2].



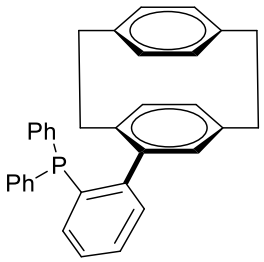
6

7, 87%

Buchwald-type biaryl monophorsphine ligand

To a Schlenk tube was added **6** (0.18 mmol, 87.3 mg) and the tube was closed with a septum. The reaction tube was evacuated and backfilled with N_2 for 3 times and then anhydrous toluene (2.0 mL) and Et_3N (3.6 mmol, 465.3 mg) were added via syringe and the mixture was treated with $HSiCl_3$ (0.9 mmol, 122.4 mg) at room temperature. Then the reaction was heated to reflux with stirring for 12 h. After cooling to room temperature, saturated $NaHCO_3$ aqueous solution was added to quench the reaction and the resulting precipitate was removed by filtration over celite and washed with CH_2Cl_2 (3 × 20.0 mL). The combined organic layer was separated and dried over anhydrous $MgSO_4$. filtered and evaporated

under reduced pressure Then the residue was subjected to column chromatography eluting with petroleum ether/ ethyl acetate (10: 1) to give the pure product **7** in 87% yield (0.15 mmol, 71.9 mg).



7

4-(2-triphenylphosphine)[2.2]paracyclophane (7): Isolated as colorless solid (71.9 mg, 87% yield); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.81-7.71 (m, 1H), 7.62-7.54 (m, 1H), 7.45-7.29 (m, 6H), 7.19-7.00 (m, 4H), 6.91-6.38 (m, 8H), 6.30 (s, 1H), 3.16-2.74 (m, 8H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 147.5 (d, *J* = 27.3 Hz), 140.2, 139.5, 139. 5 (d, *J* = 7.3 Hz), 138.8, 138.5 (d, *J* = 2.3 Hz), 138.0 (d, *J* = 13.7 Hz), 137.6 (d, *J* = 12.5 Hz), 137.4 (d, *J* = 13.8 Hz), 134.6, 134.5, 134.3, 133.8, 133.5, 133.3, 133.2, 133.2, 132.6, 132.4, 132.3, 130.0, 129.6 (d, *J* = 3.3 Hz), 128.9, 128.6, 128.5, 128.4, 127.9, 127.8, 127.7, 127.1, 35.5, 35.4, 35.3, 34.5 (d, *J* = 8.9 Hz) ppm. **^{31}P NMR** (162 MHz, $CDCl_3$) δ -11.41 ppm. **HRMS (ESI - TOF):** $[M+H]^+$ cacld for $C_{34}H_{30}P^+$ 469.2080, found: 469.2079.

Ⅵ. An alternative Pd(II)-Pd(IV)-Pd(II) catalytic pathway

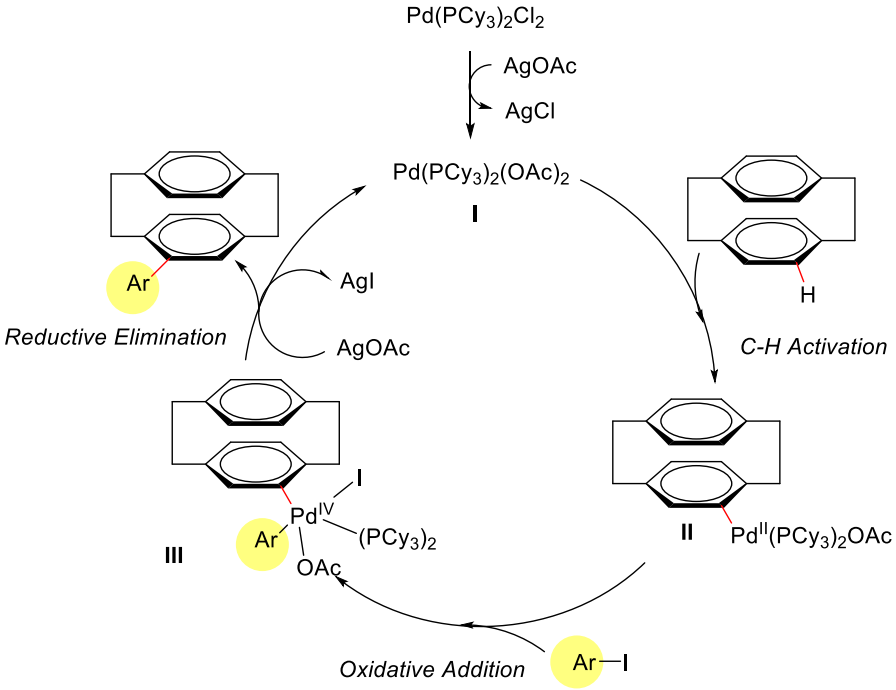


Figure S2 Possible mechanism involving a Pd(II)-Pd(IV)-Pd(II) catalytic cycle

On the basis of literature reports, [3] an alternative reaction mechanism involving a Pd(II)-Pd(IV)-Pd(II) catalytic pathway was depicted in Figure S2. The pre-catalyst $Pd(PCy_3)_2Cl_2$ undergoes anion exchange with AgOAc to generate $Pd(PCy_3)_2(OAc)_2$, which enable the C-H activation via a CMD process to give an PCP-Pd(II) species **II**. Then, the oxidative addition of aryl iodide with by **II** gives a Pd(IV) species **III**. In the presence of a halide abstraction reagent AgOAc, **III** undergoes reductive elimination to give the mono-arylated product **3** and regenerates the reactive Pd(II) species.

VII. X-Ray data for 3m

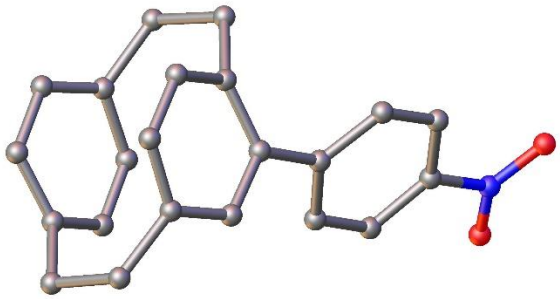


Figure S3. X-ray structure of **3m**

Table 1 Crystal data and structure refinement for CCDC2264045.

Identification code	CCDC2264045
Empirical formula	C22H19NO2
Formula weight	329.38
Temperature/K	193.00
Crystal system	orthorhombic
Space group	Pbca
a/Å	12.8035(3)
b/Å	7.4389(2)
c/Å	33.9834(7)
α/ °	90
β/ °	90
γ/ °	90
Volume/Å3	3236.71(13)
Z	8
ρcalcg/cm3	1.352
μ/mm 1	0.436
F(000)	1392.0
Crystal size/mm3	0.13 ×0.12 ×0.1

Radiation	GaKα (λ = 1.34139)
2Θ range for data collection/°	7.522 to 120.588
Index ranges	-16 ≤ h ≤ 10, -9 ≤ k ≤ 8, -43 ≤ l ≤ 43
Reflections collected	23768
Independent reflections	3573 [Rint = 0.0377, Rsigma = 0.0272]
Data/restraints/parameters	3573/0/226
Goodness-of-fit on F2	1.028
Final R indexes [I>=2σ (I)]	R1 = 0.0445, wR2 = 0.1209
Final R indexes [all data]	R1 = 0.0606, wR2 = 0.1326
Largest diff. peak/hole / e Å-3	0.17/-0.19

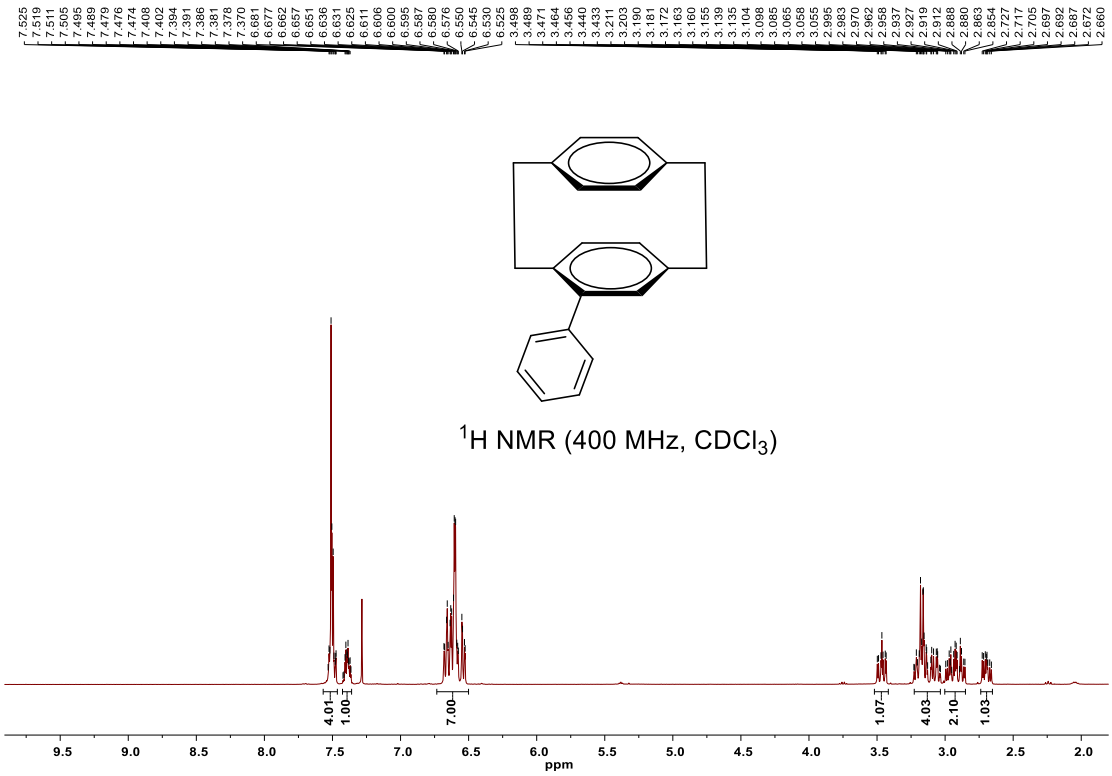
Ⅷ. References

[1] Q. J. Zhou, K. Worm and R. E. Dolle, *J. Org. Chem.*, 2004, **69**, 5147.

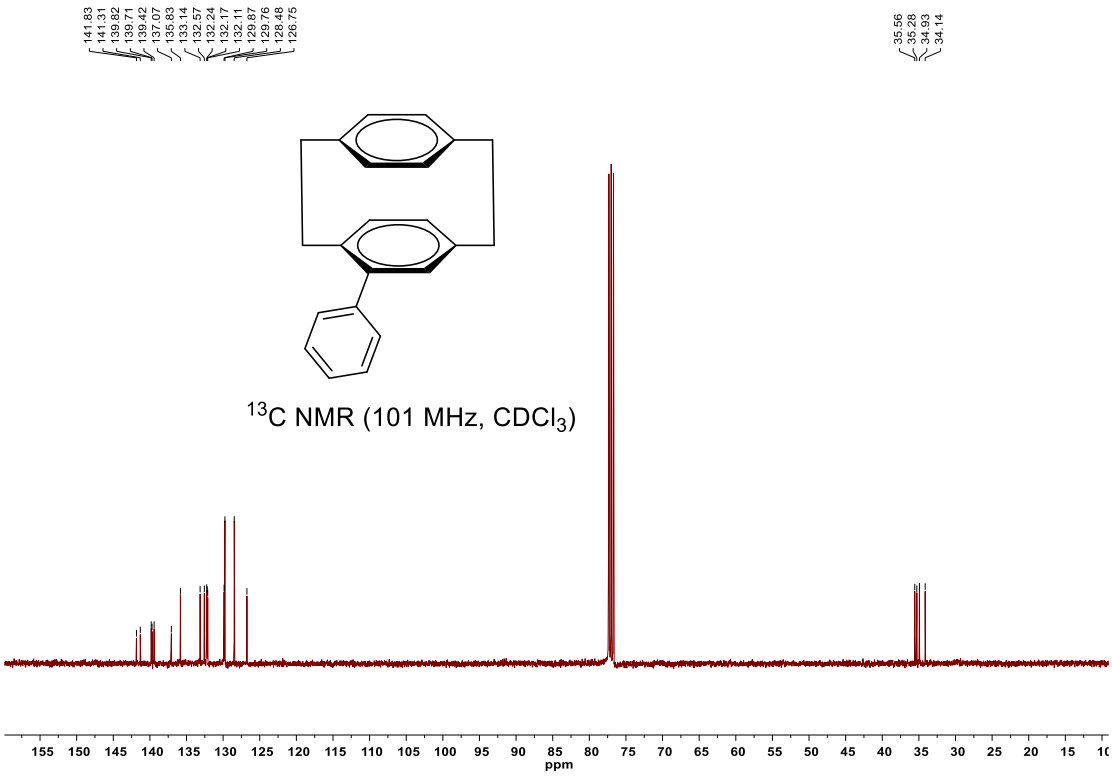
[2] Y. Lv, G. Luo, Q. Liu, Z. Jin, X. Zhang and Y. R. Chi, *Nat. Commun.* 2022, **13**, 36.

[3] (a) L. Y. Liu, J. X. Qiao, K. S. Yeung, W. R. Ewing and J. Q. Yu, *Angew. Chem. Int. Ed.*, 2020, **59**, 13831;. (b) L. Y. Liu, J. X. Qiao, K. S. Yeung, W. R. Ewing and J. Q. Yu, *J. Am. Chem. Soc.* 2019, **141**, 14870.

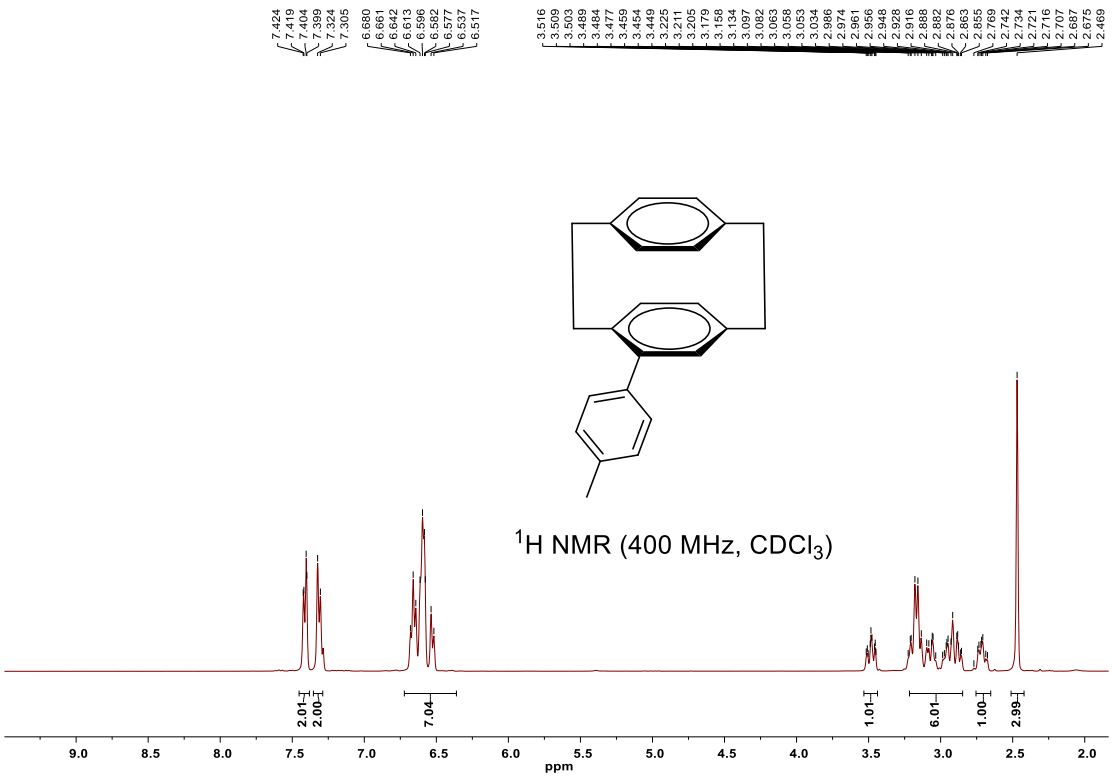
IX. NMR spectra



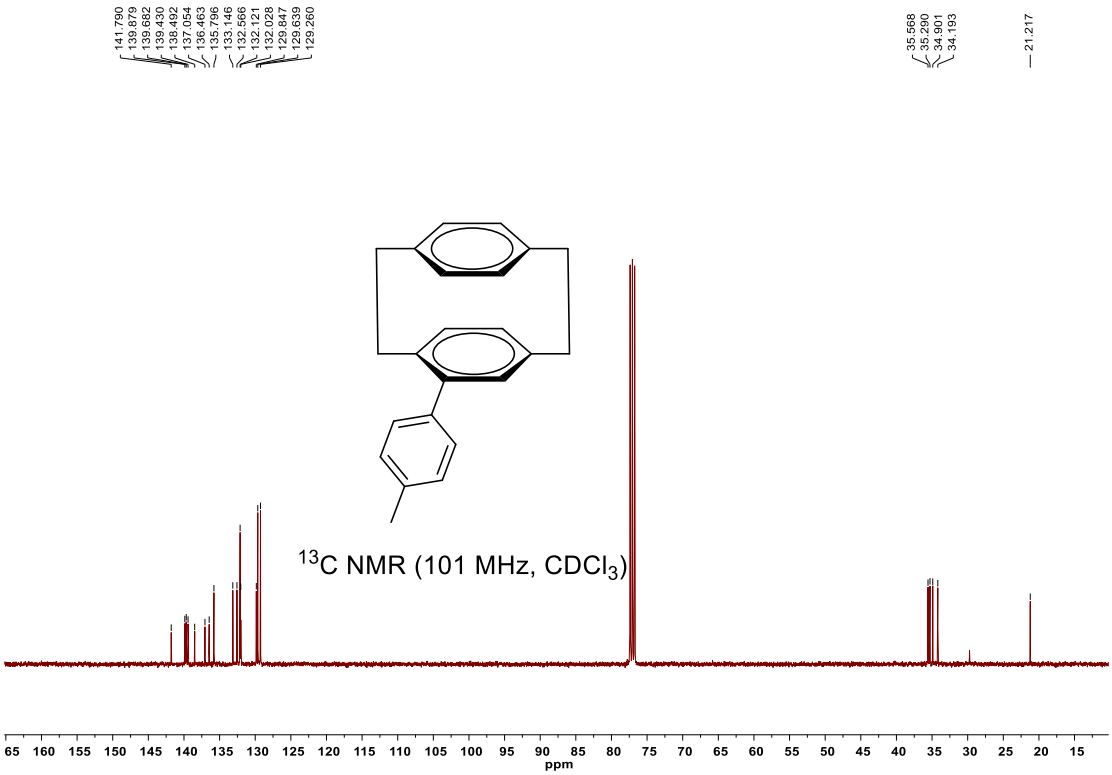
^{1}H NMR spectrum of 3a ($CDCl_3$, 400MHz)



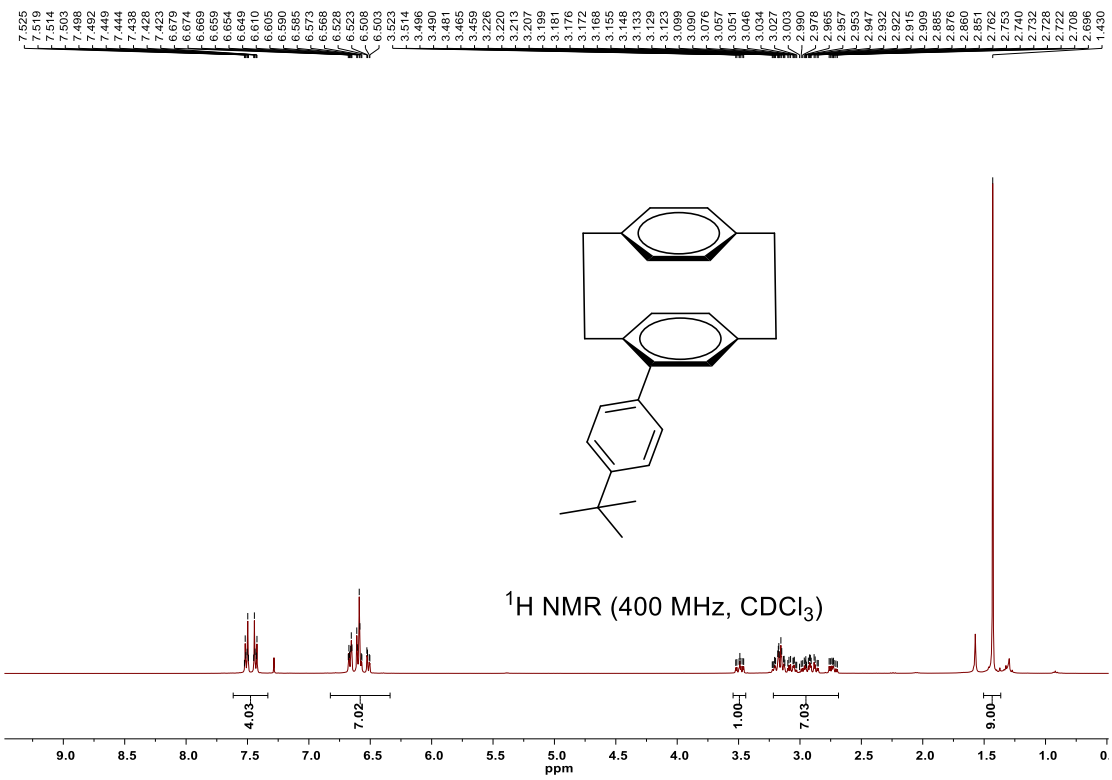
^{13}C NMR spectrum of 3a ($CDCl_3$, 101MHz)



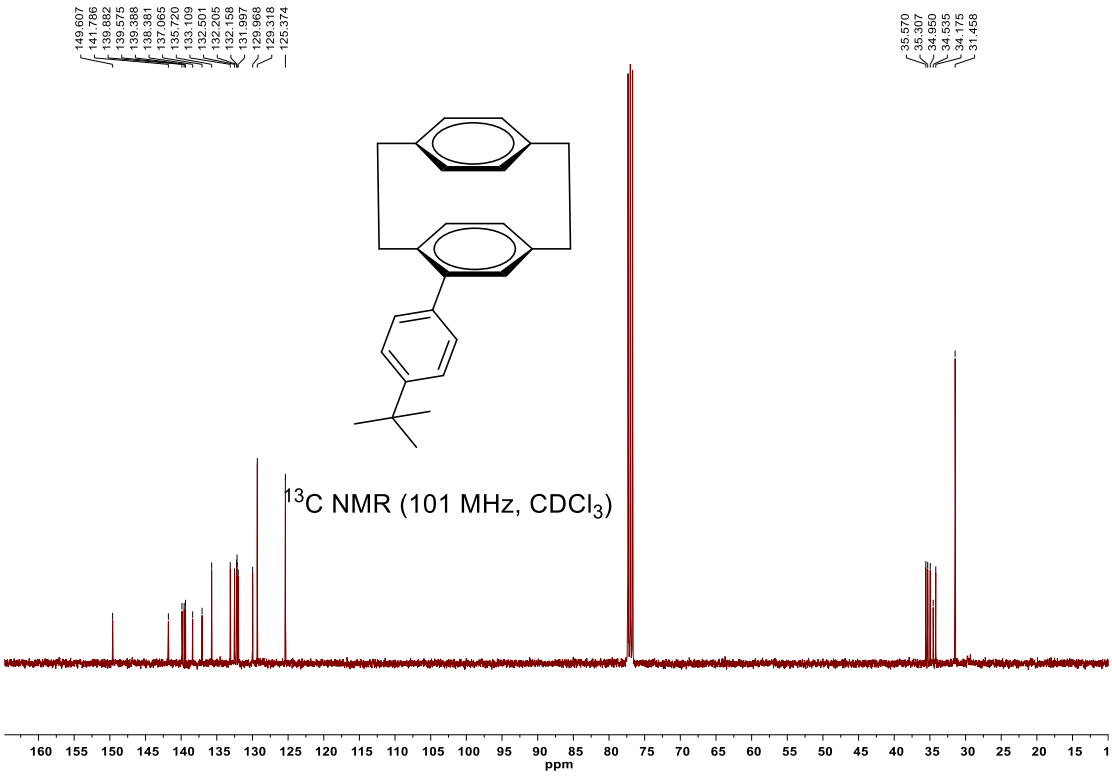
^{1}H NMR spectrum of 3b (CDCl$_3$, 400MHz)



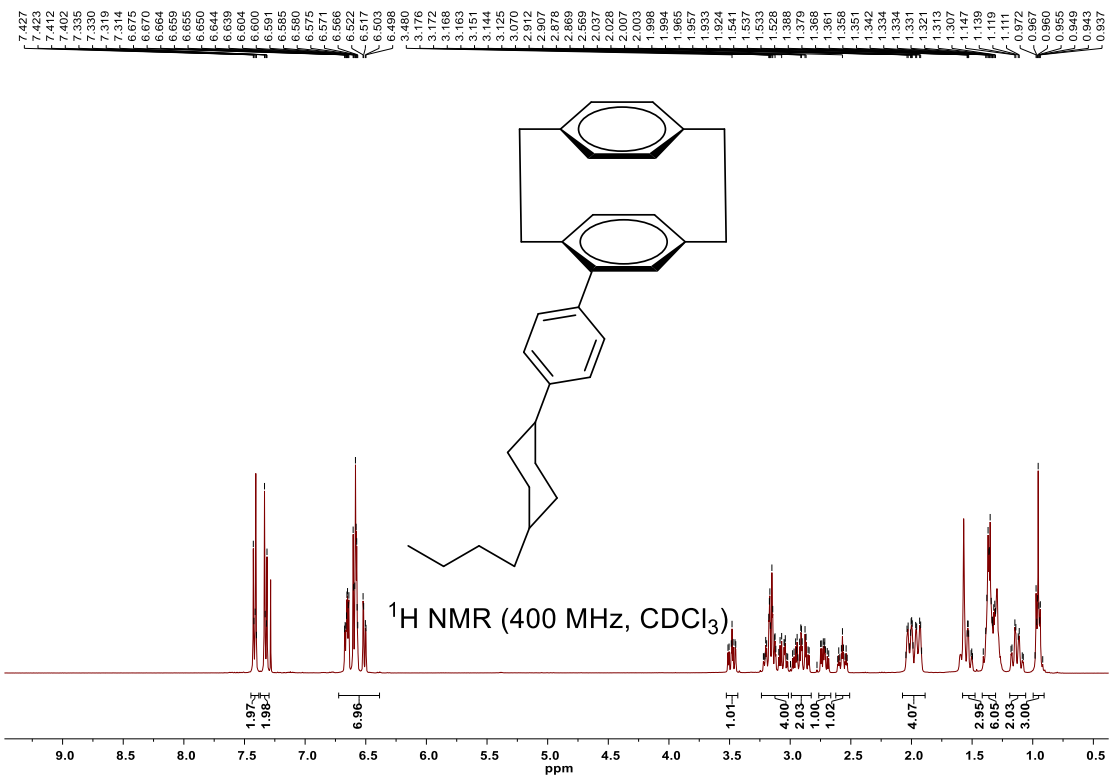
^{13}C NMR spectrum of 3b (CDCl$_3$, 101MHz)



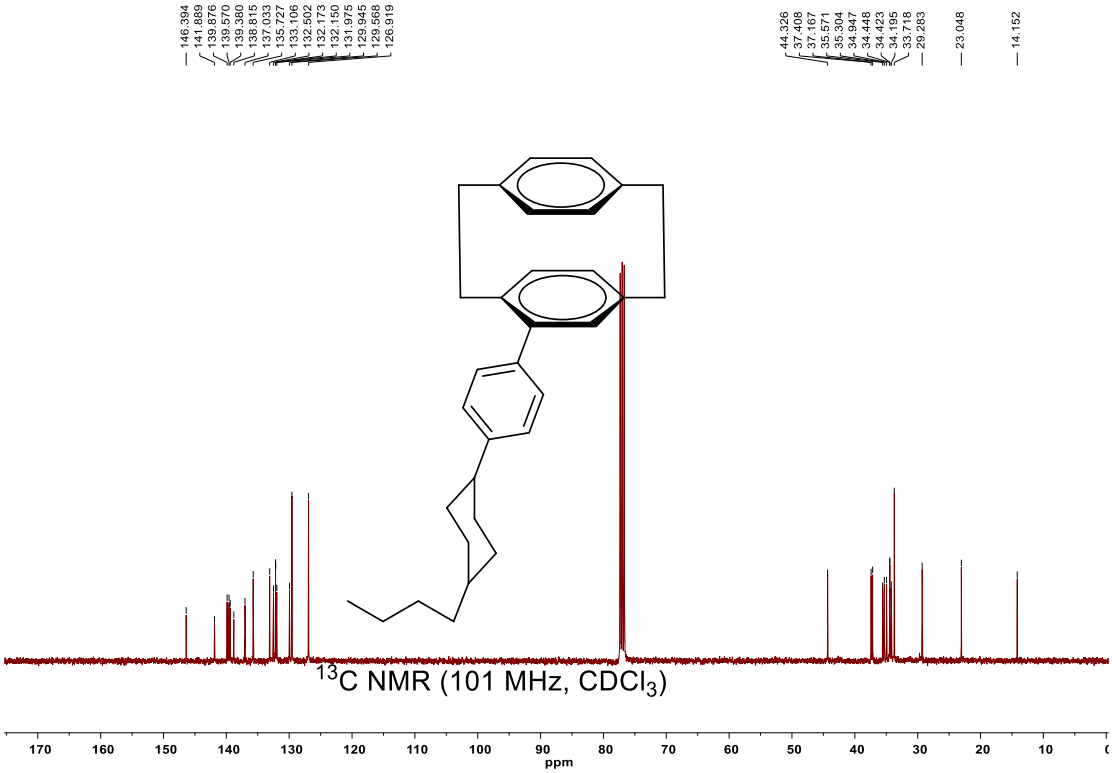
^{1}H NMR spectrum of 3c ($CDCl_3$, 400MHz)



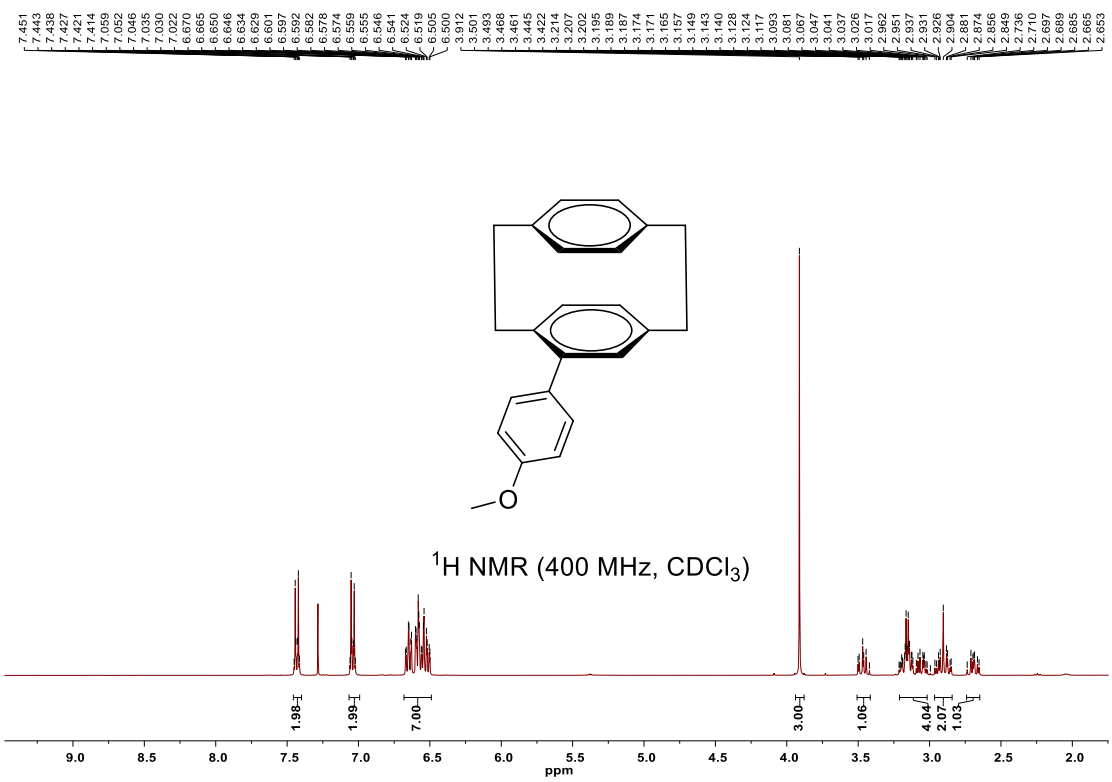
^{13}C NMR spectrum of 3c ($CDCl_3$, 101MHz)



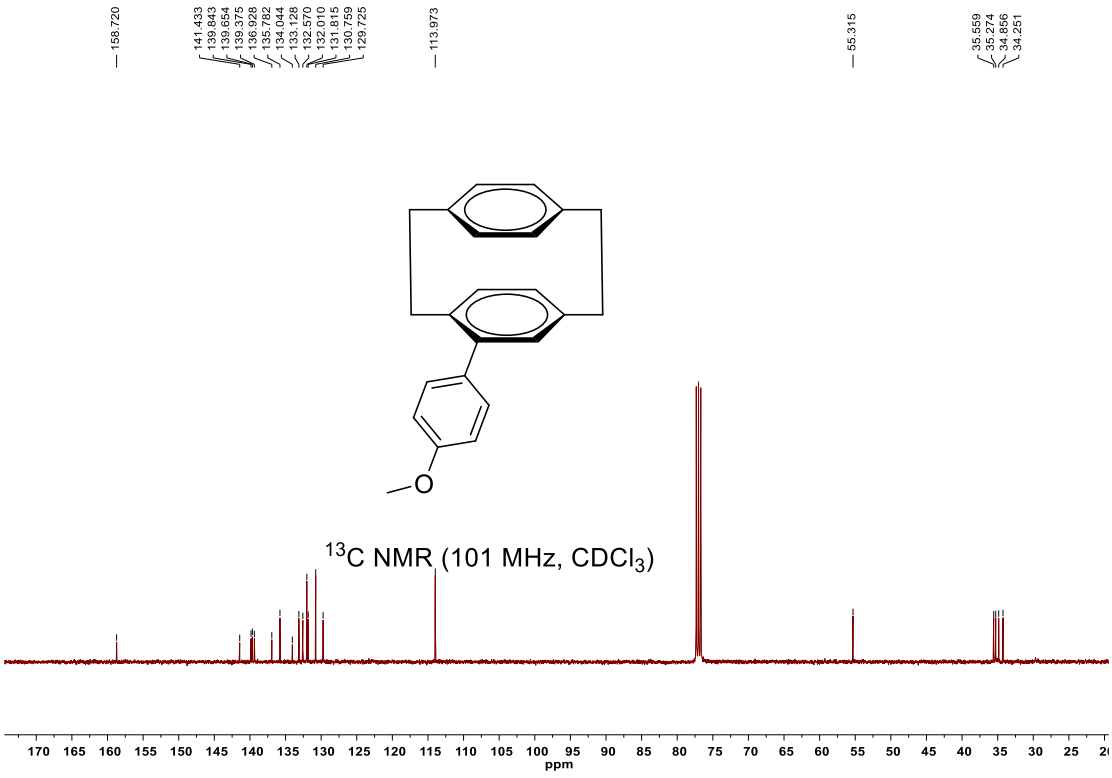
^{1}H NMR spectrum of 3d (CDCl$_3$, 400MHz)



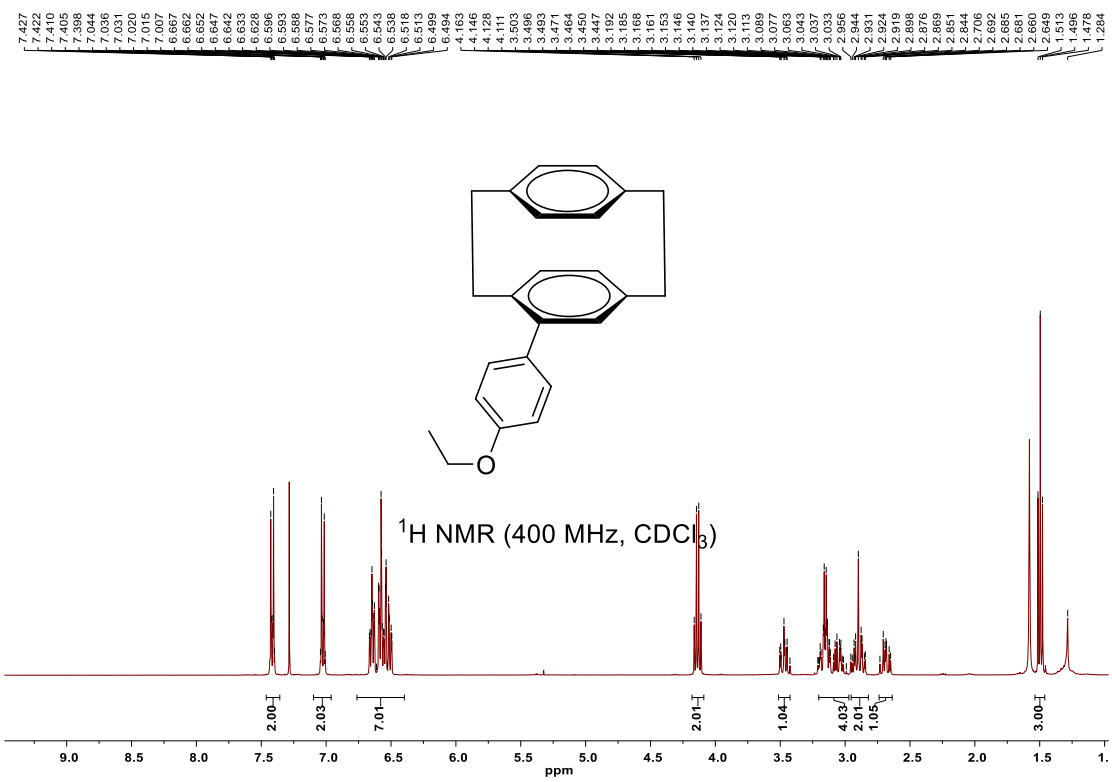
^{13}C NMR spectrum of 3d (CDCl$_3$, 101MHz)



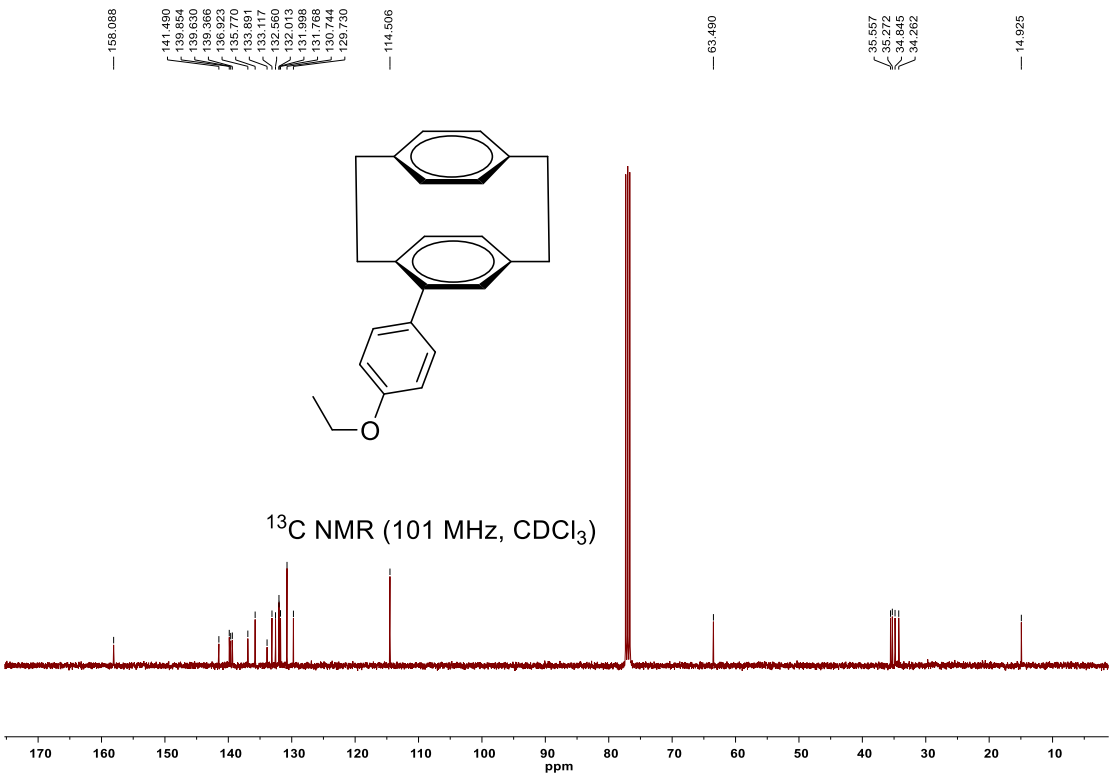
^{1}H NMR spectrum of 3e (CDCl$_3$, 400MHz)



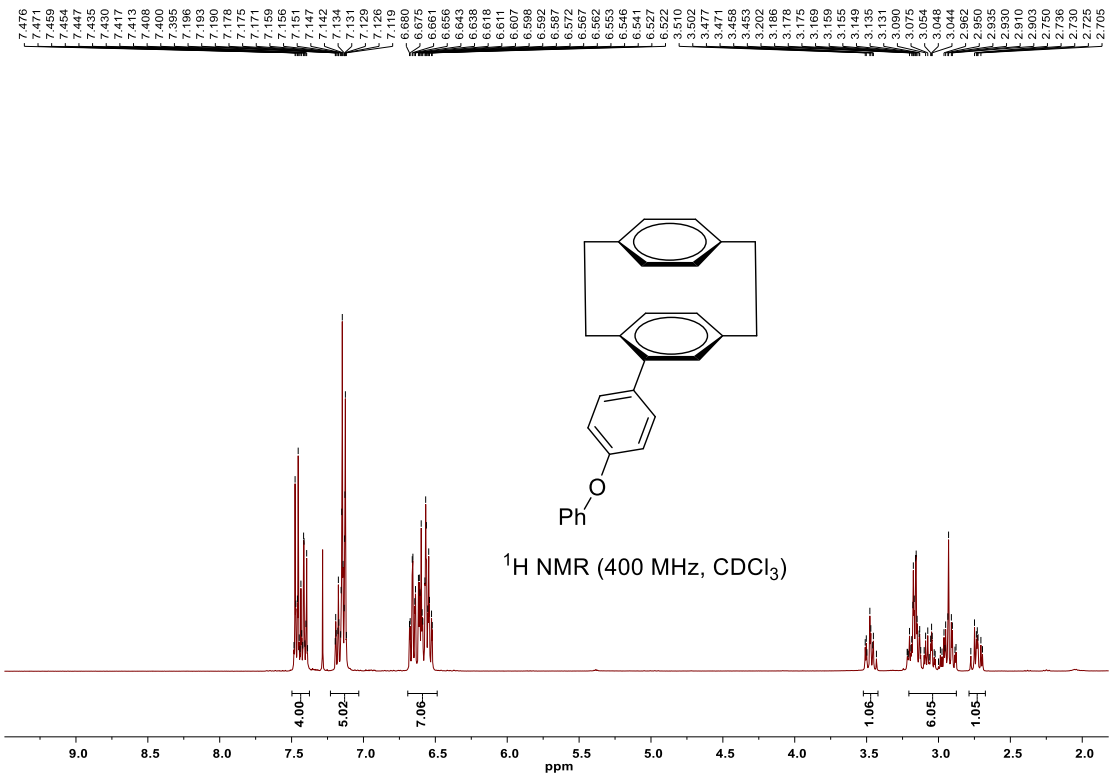
^{13}C NMR spectrum of 3e (CDCl$_3$, 101MHz)



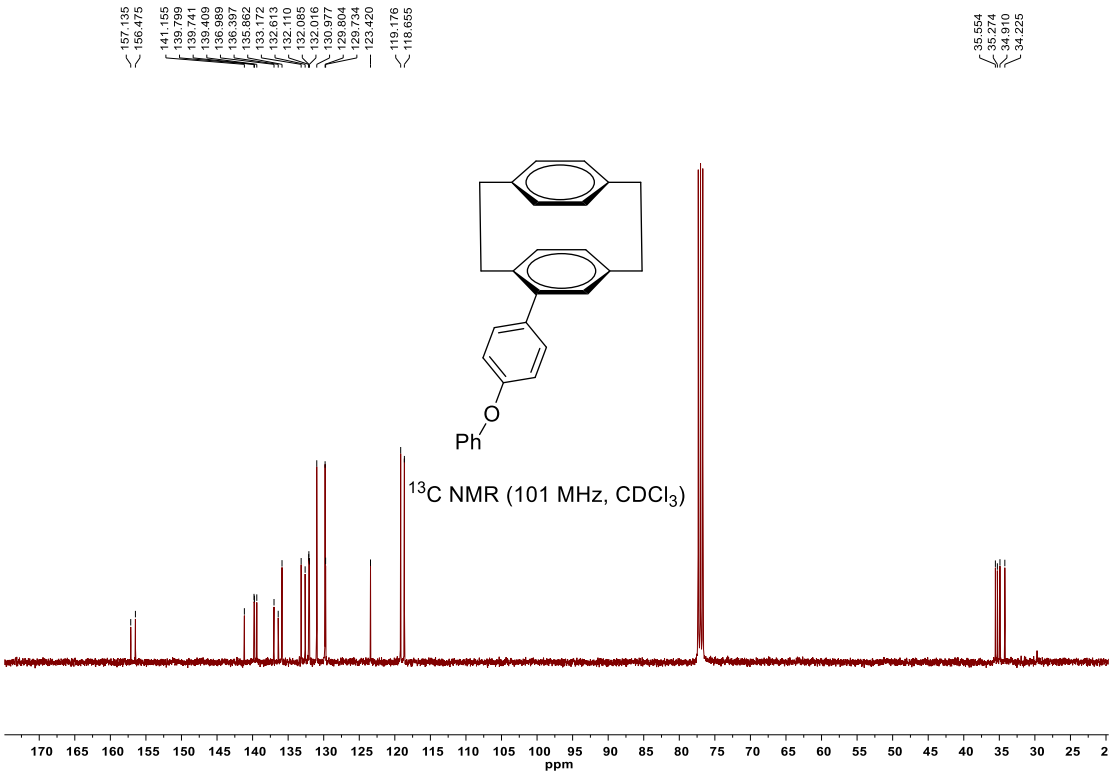
^{1}H NMR spectrum of 3f (CDCl$_3$, 400MHz)



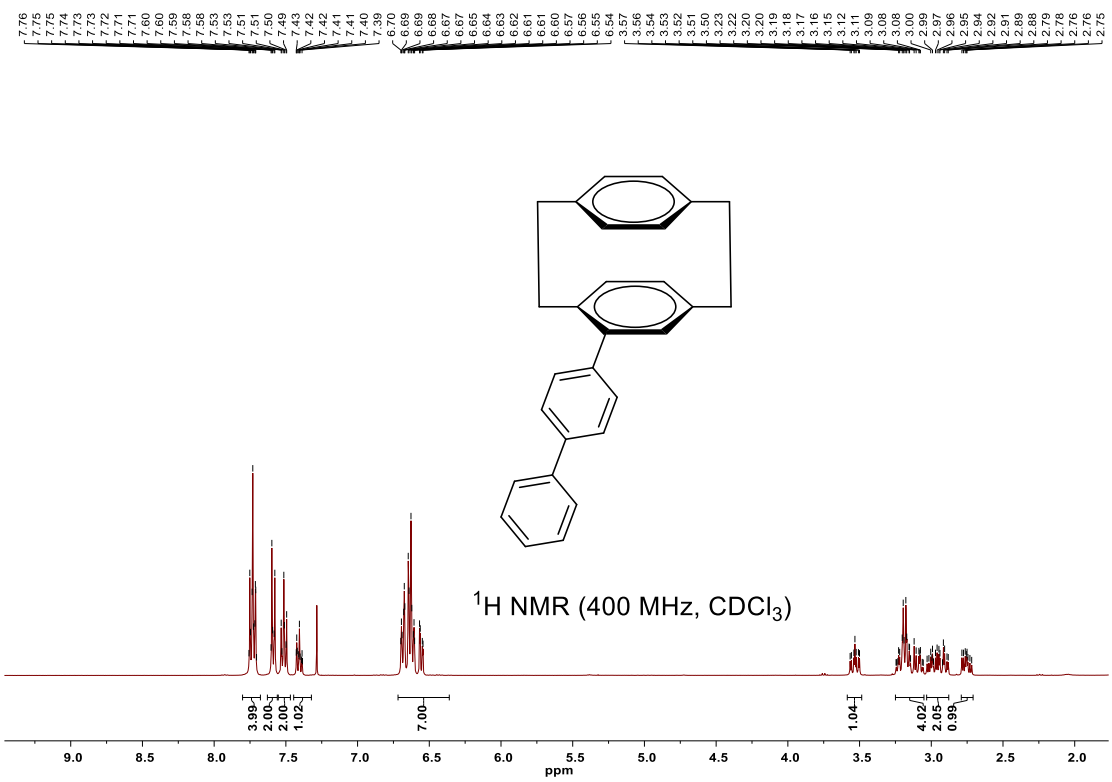
^{1}H NMR spectrum of 3f (CDCl$_3$, 101MHz)



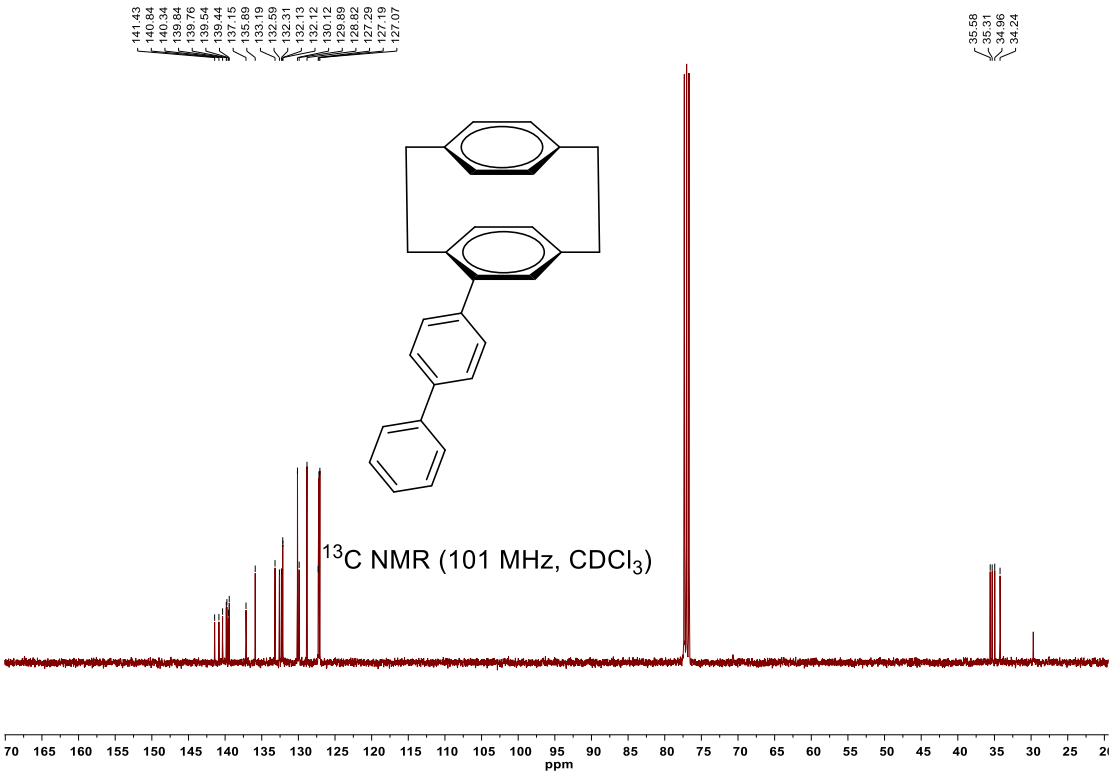
^{1}H NMR spectrum of 3g ($CDCl_3$, 400MHz)



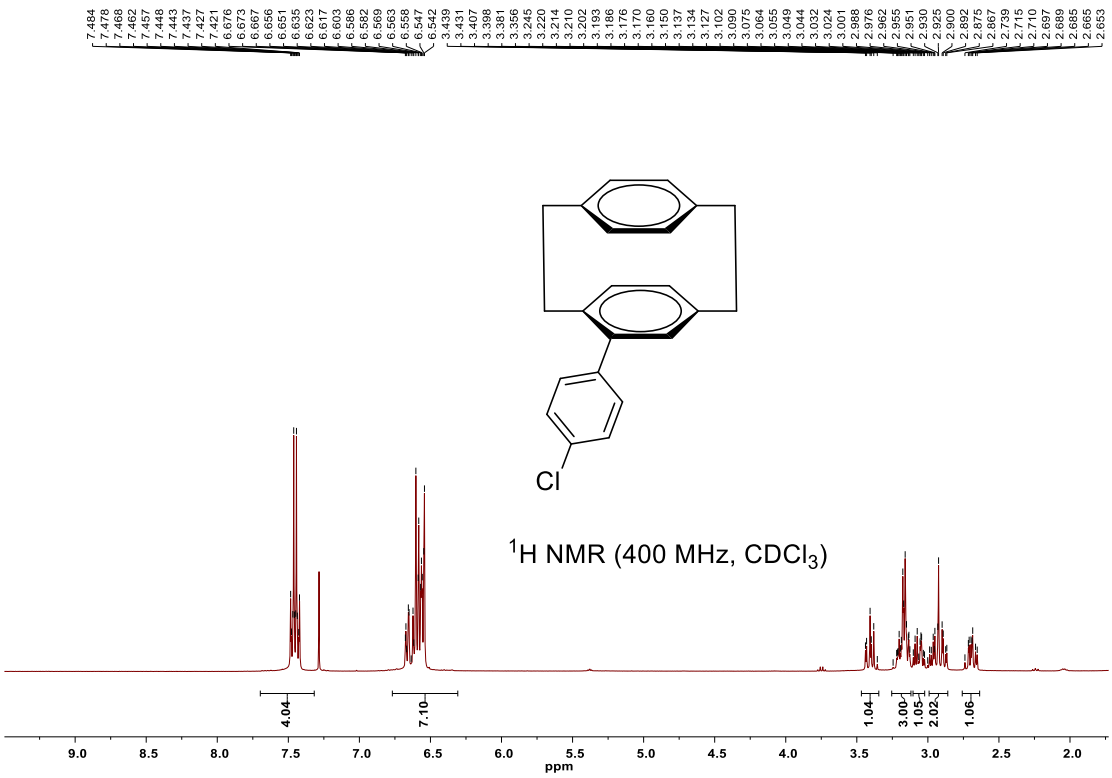
^{13}C NMR spectrum of 3g ($CDCl_3$, 101MHz)



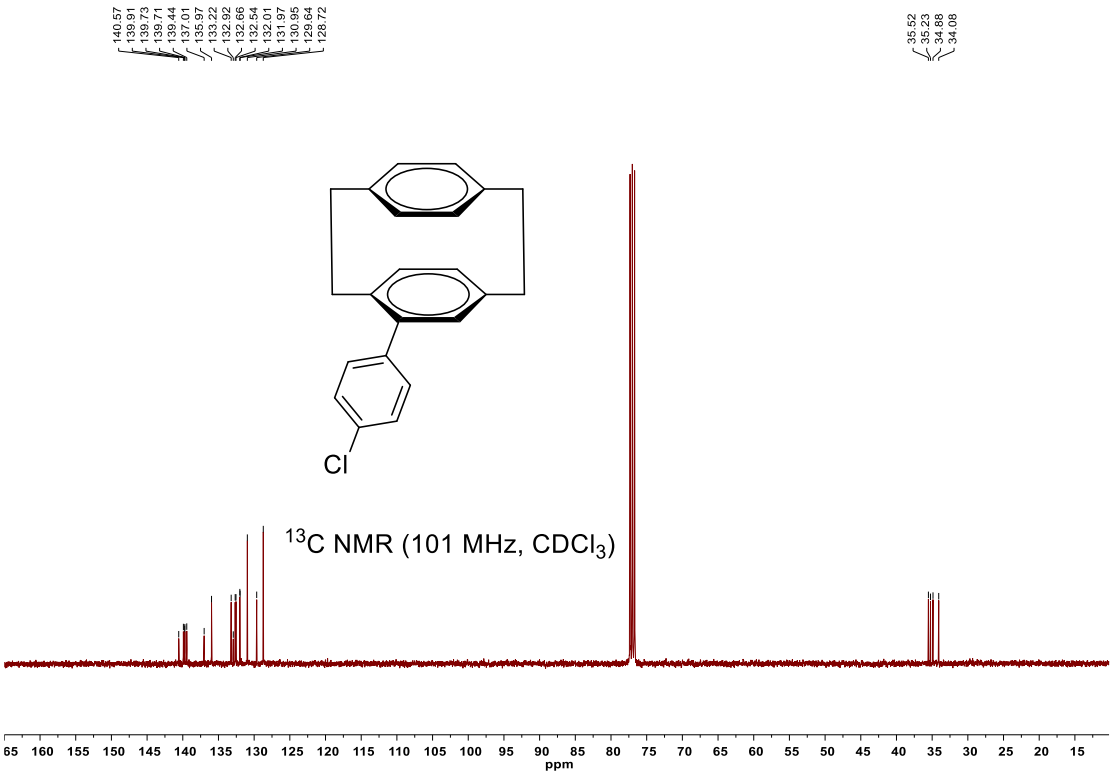
^{1}H NMR spectrum of 3h ($CDCl_3$, 400MHz)



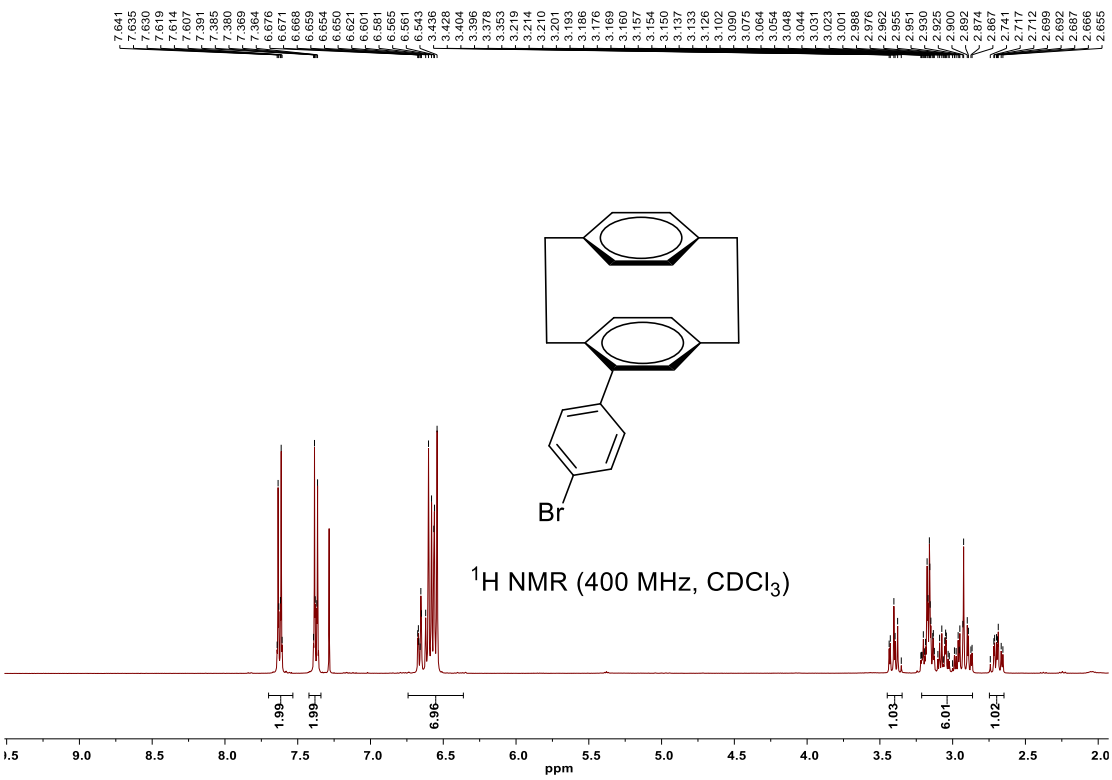
^{13}C NMR spectrum of 3h ($CDCl_3$, 101MHz)



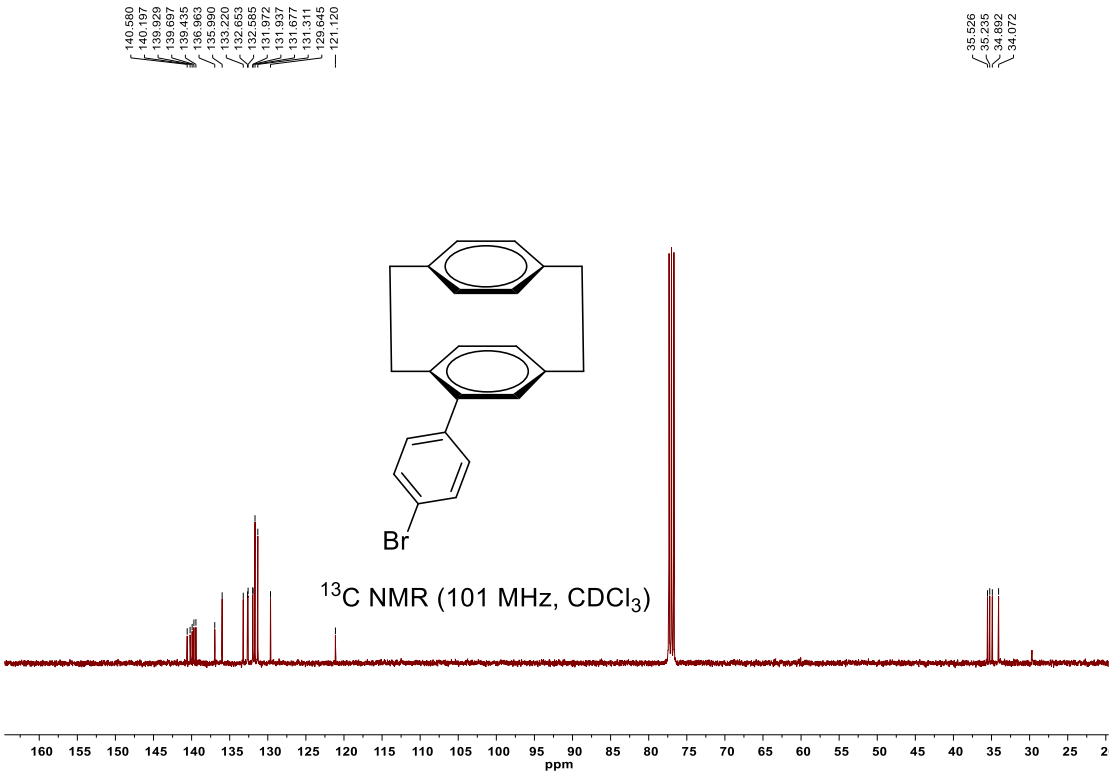
^{1}H NMR spectrum of 3i (CDCl$_3$, 400MHz)



^{1}H NMR spectrum of 3i (CDCl$_3$, 101MHz)



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



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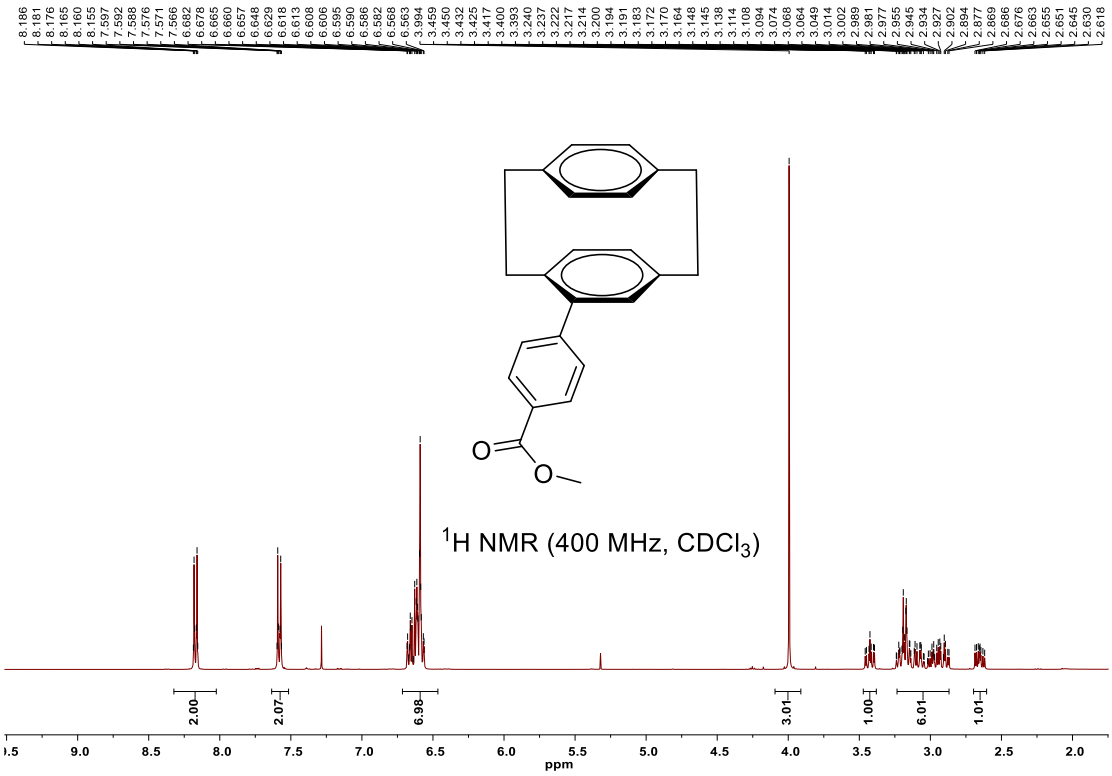
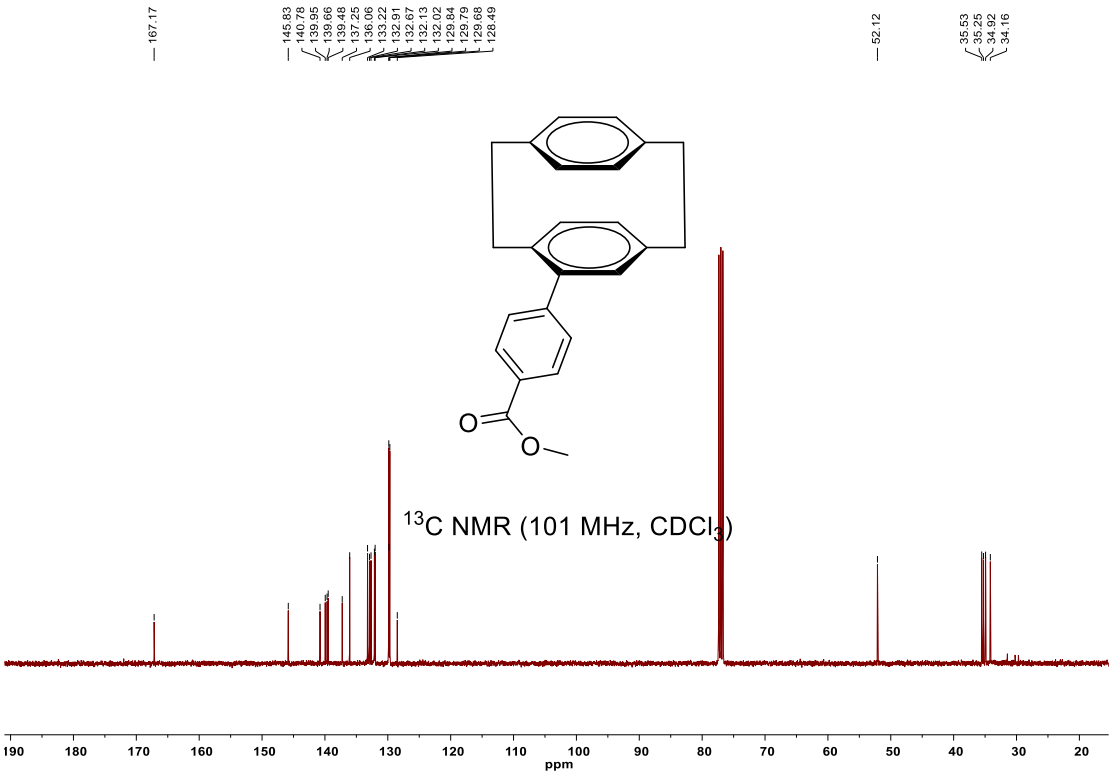
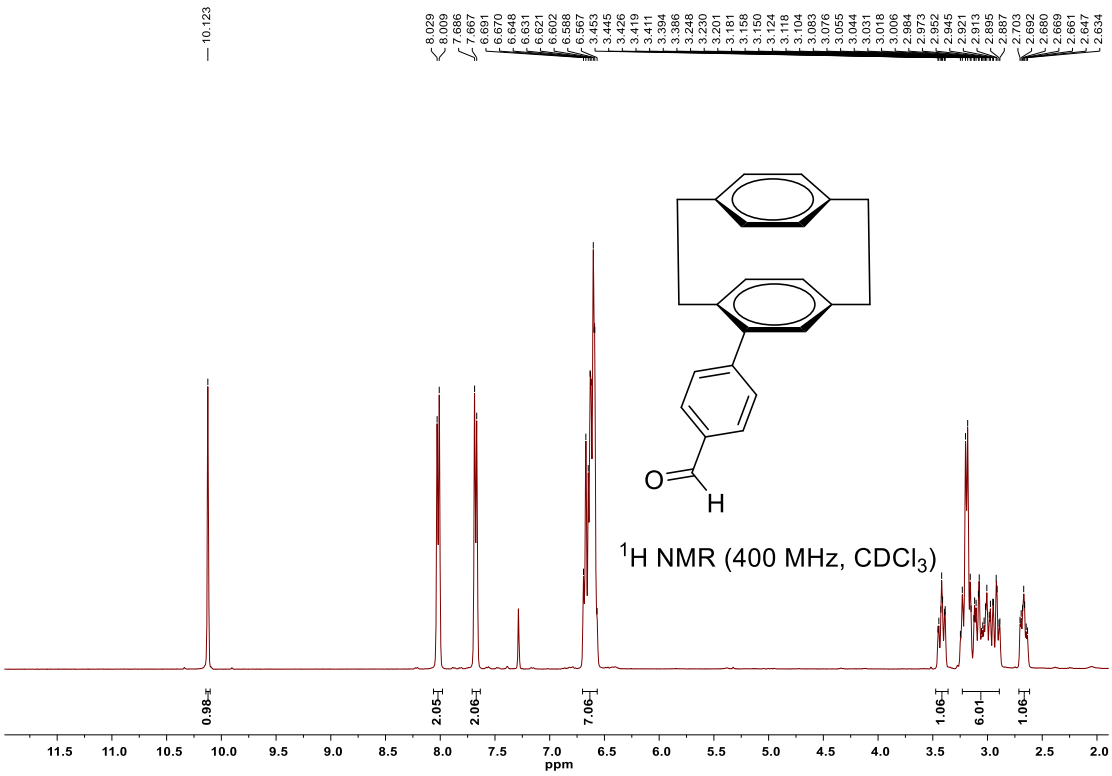


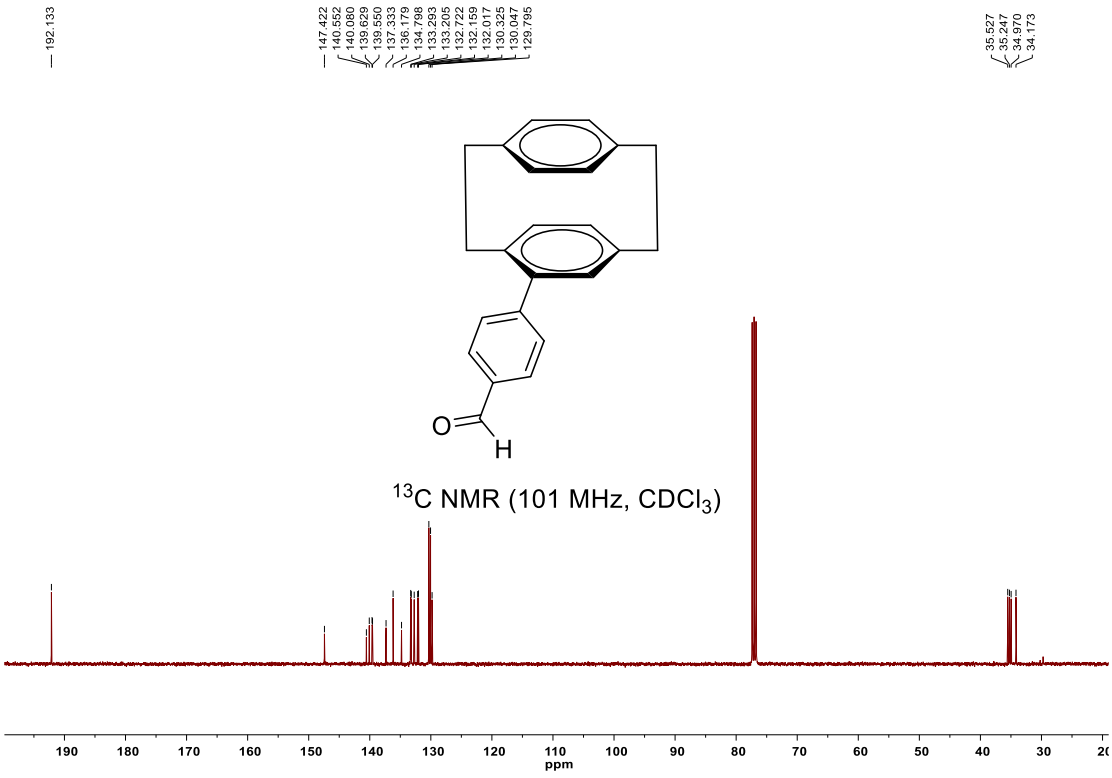
^{1}H NMR spectrum of 3k ($CDCl_3$, 400MHz)



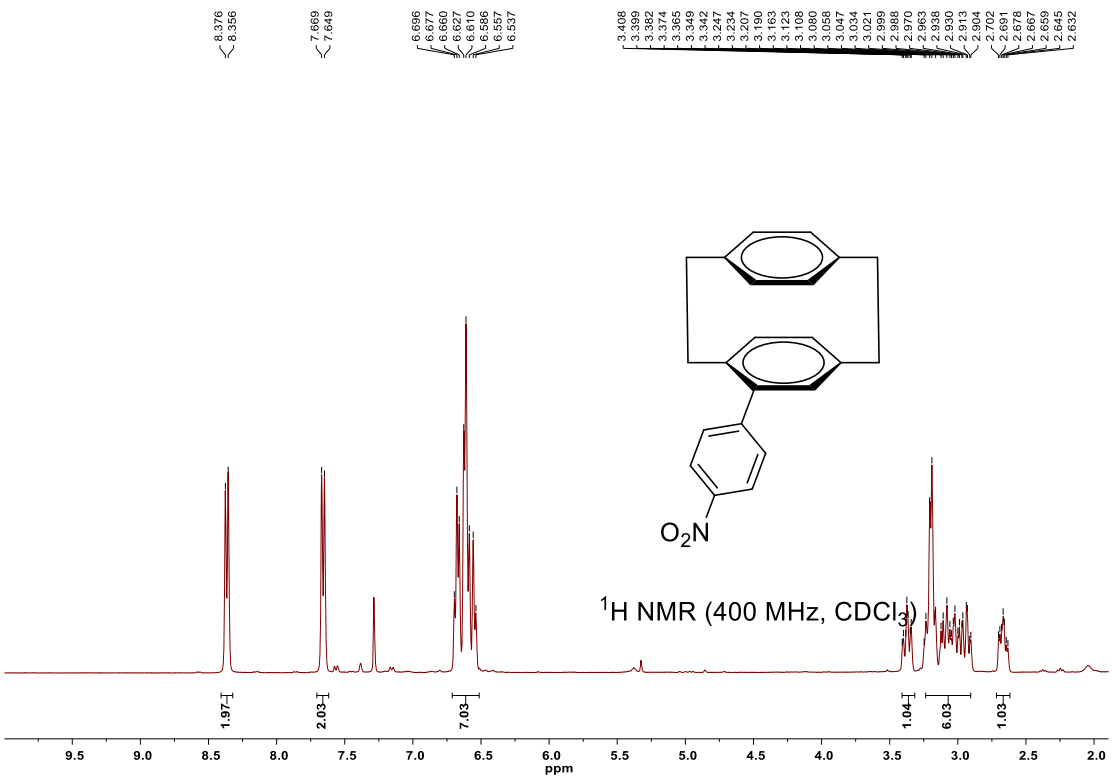
^{13}C NMR spectrum of 3k ($CDCl_3$, 101MHz)



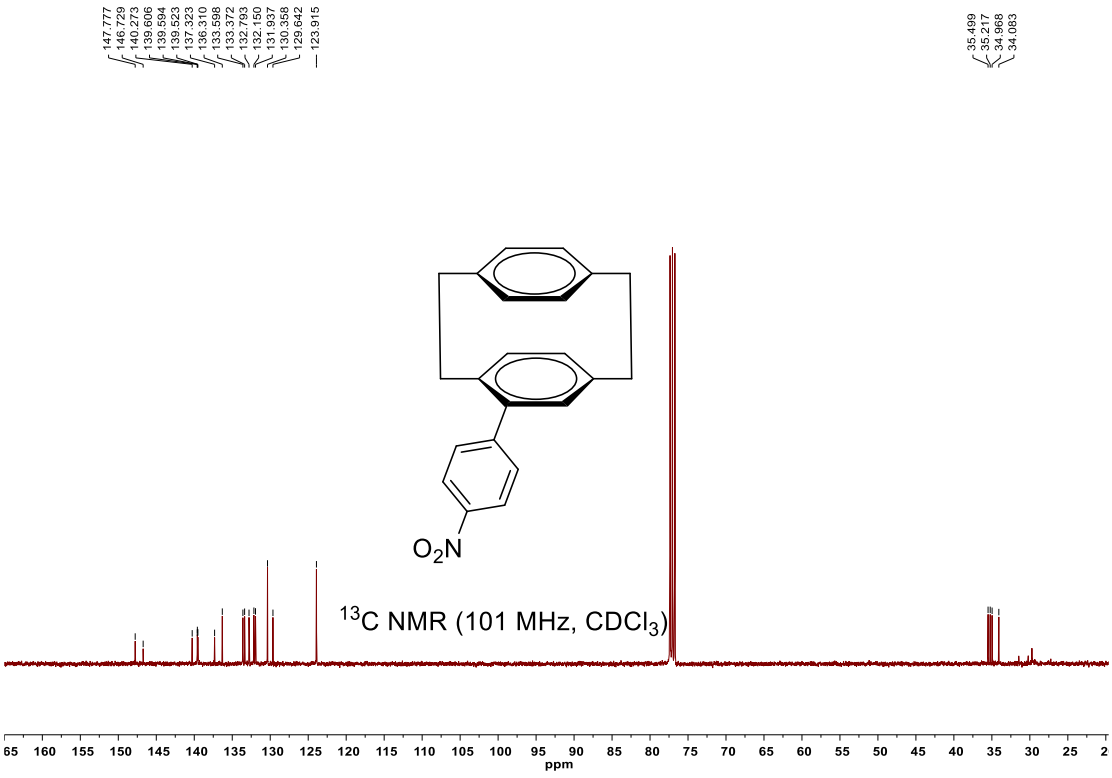
^{1}H NMR spectrum of 3l (CDCl$_3$, 400MHz)



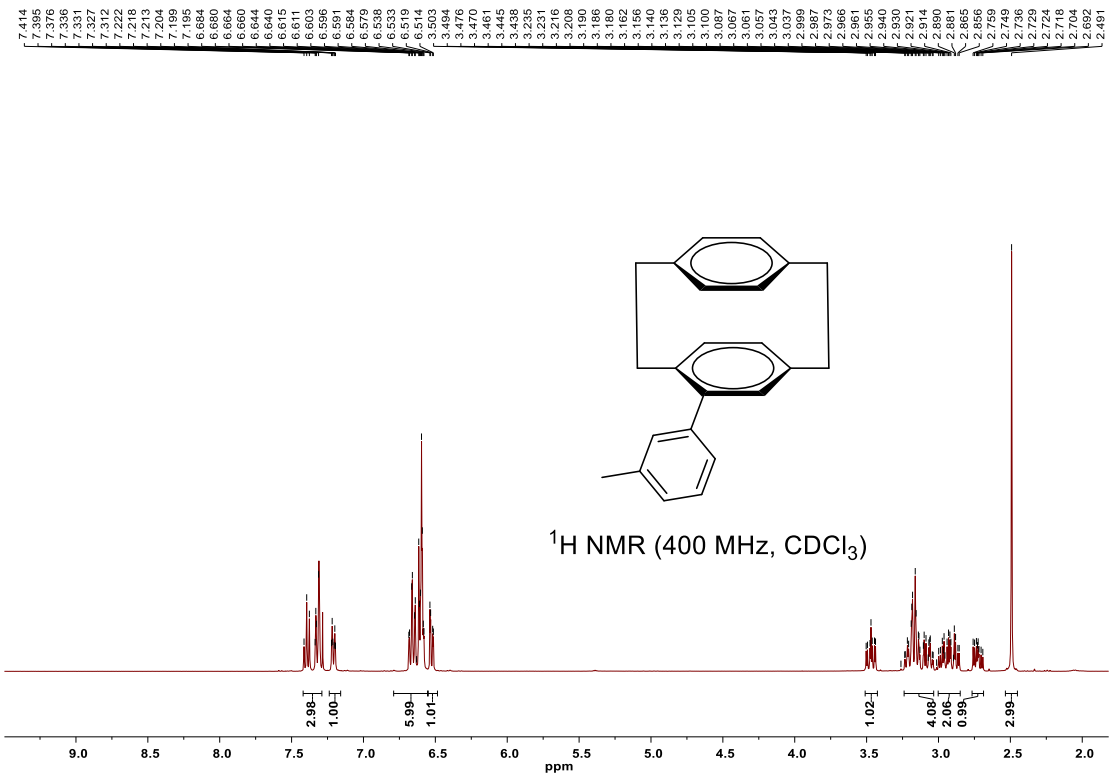
^{13}C NMR spectrum of 3l (CDCl$_3$, 101MHz)



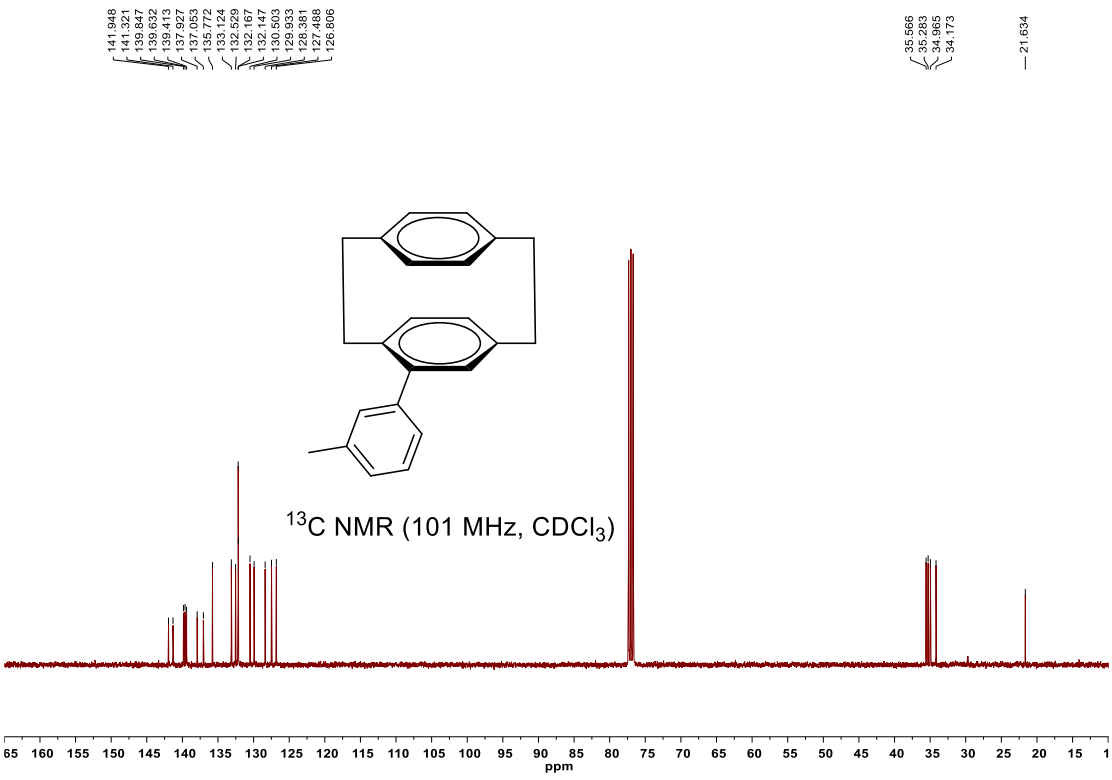
^{1}H NMR spectrum of 3m ($CDCl_3$, 400MHz)



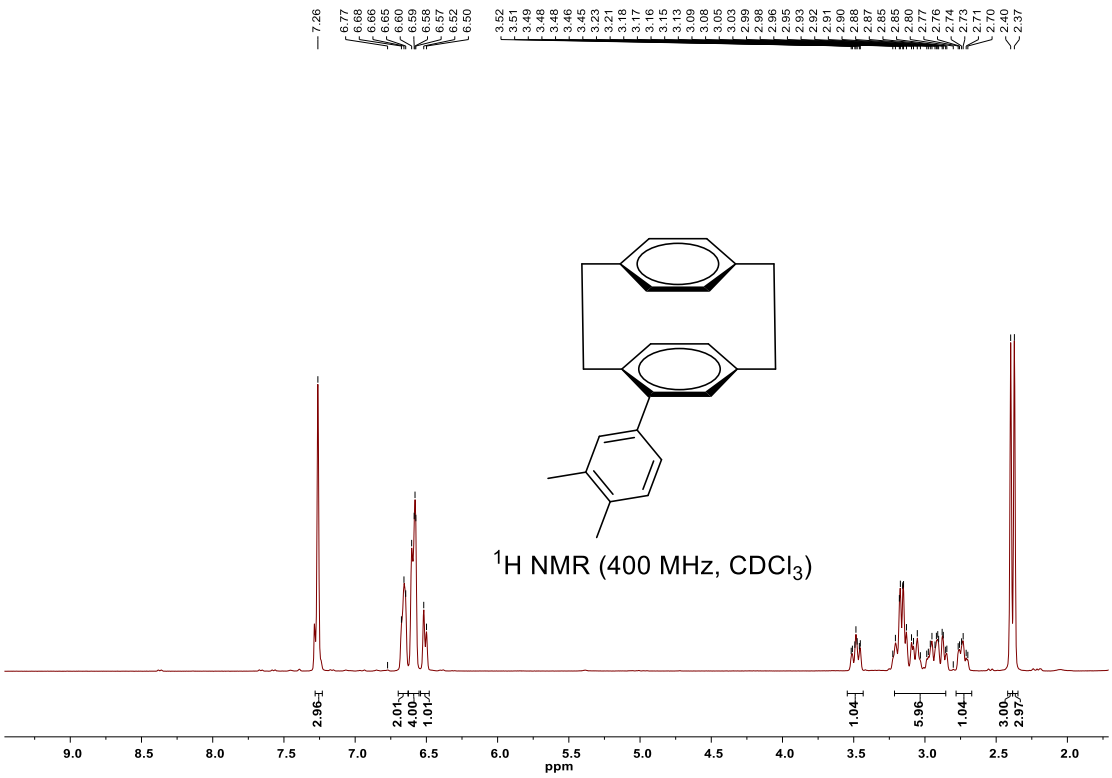
^{13}C NMR spectrum of 3m ($CDCl_3$, 101MHz)



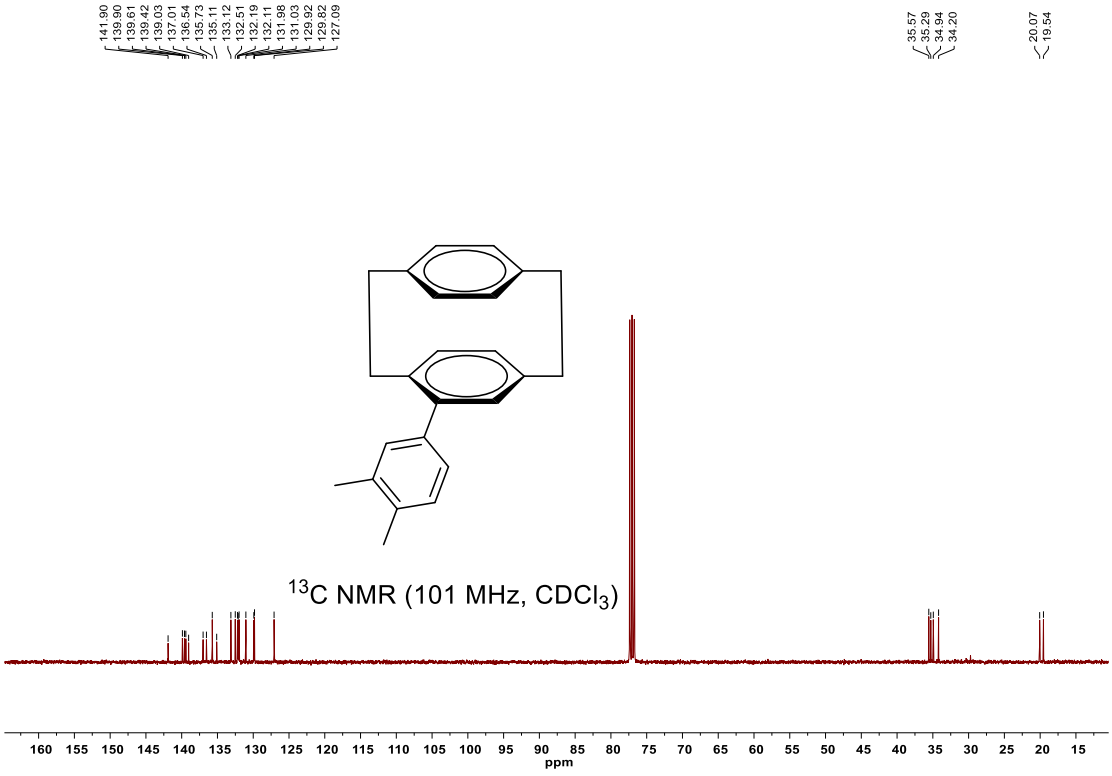
^{1}H NMR spectrum of 3n (CDCl$_3$, 400MHz)



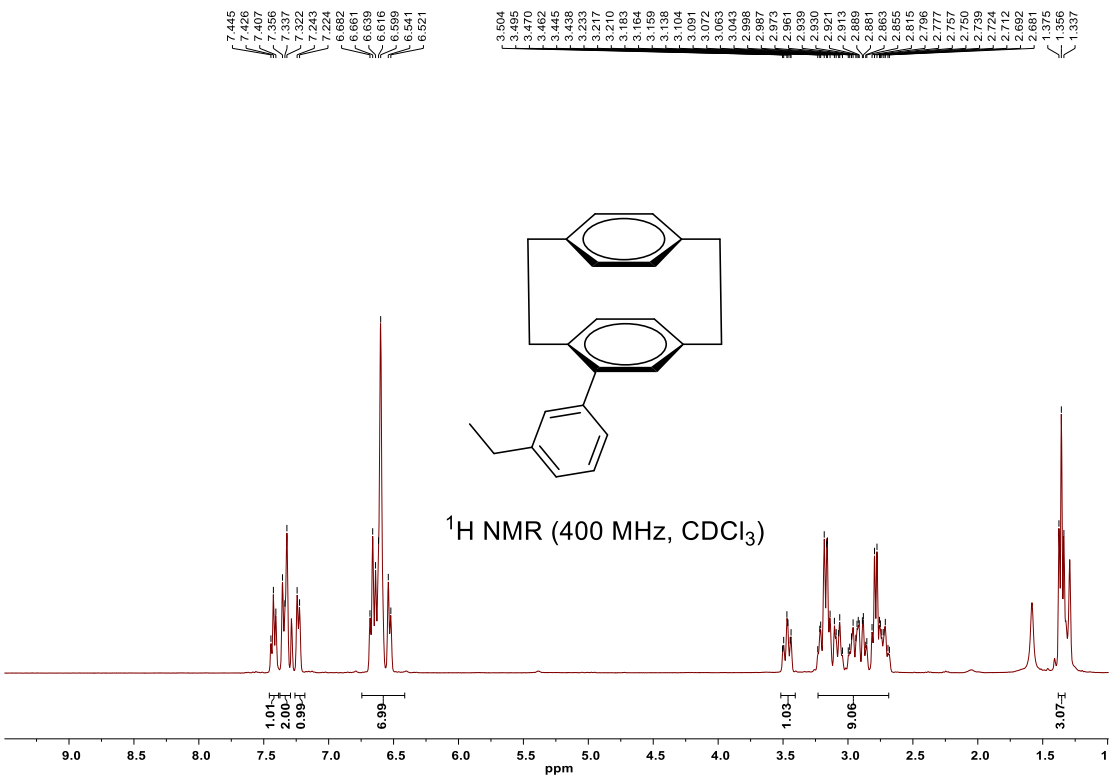
^{13}C NMR spectrum of 3n (CDCl$_3$, 101MHz)



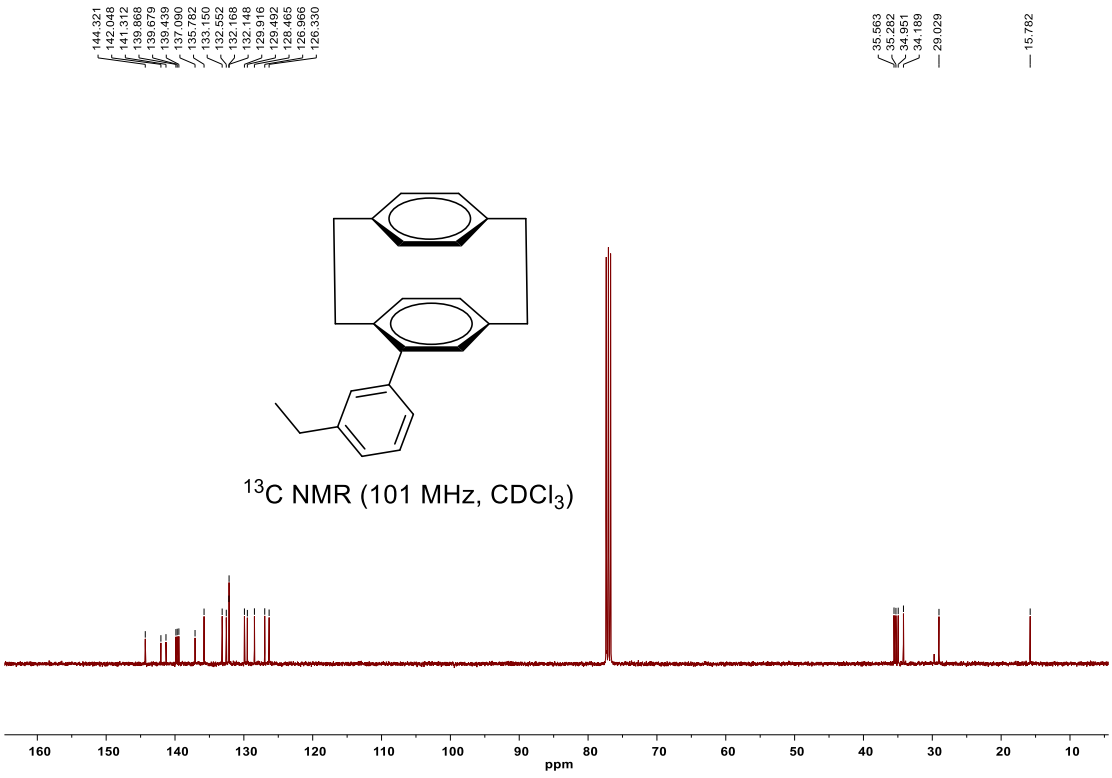
^{1}H NMR spectrum of 3o (CDCl$_3$, 400MHz)



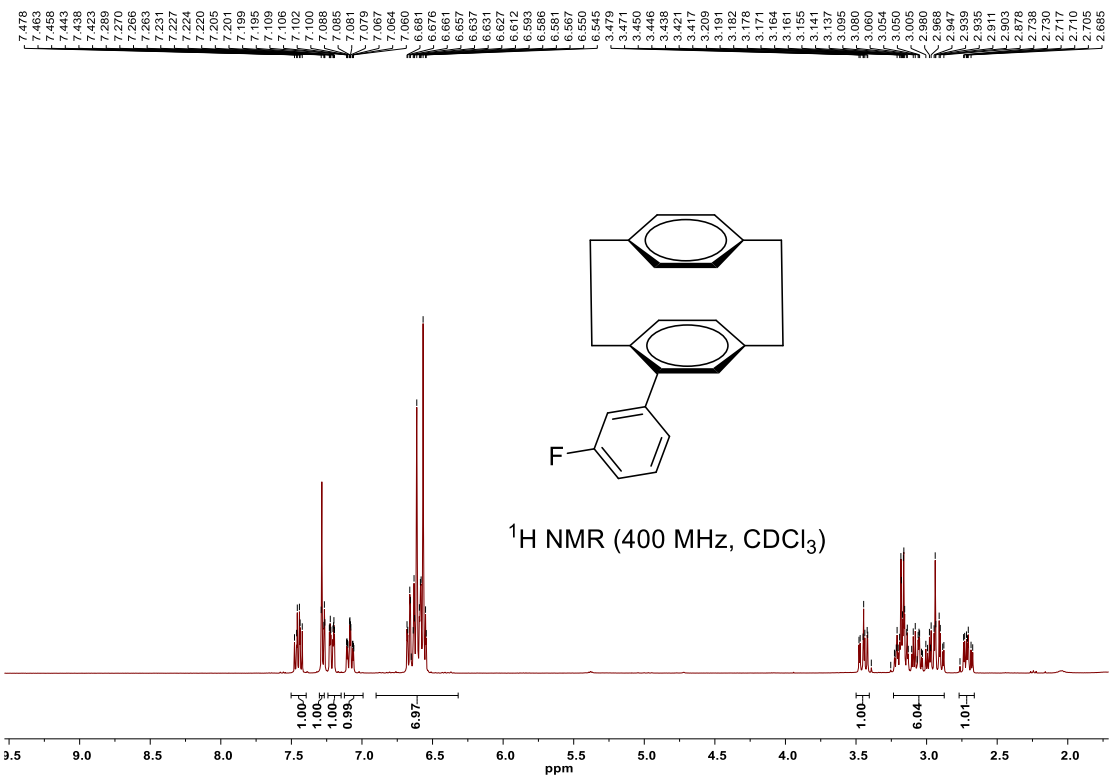
^{13}C NMR spectrum of 3o (CDCl$_3$, 101MHz)



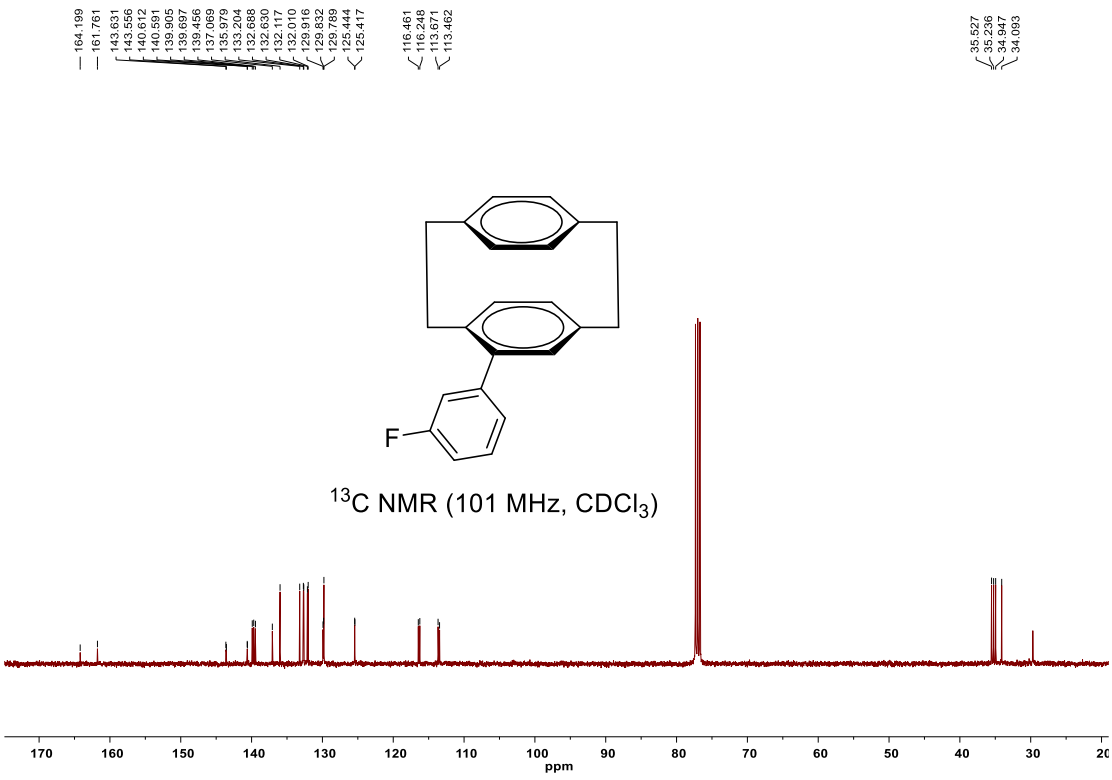
^{1}H NMR spectrum of 3p (CDCl$_3$, 400MHz)



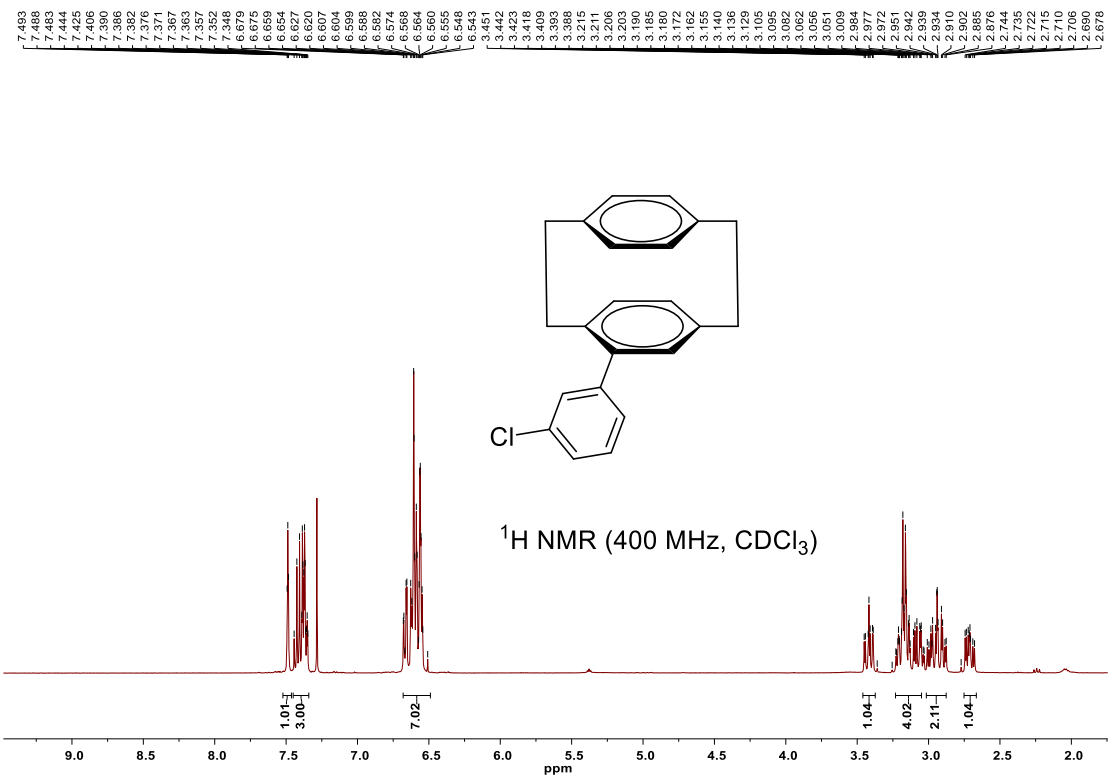
^{13}C NMR spectrum of 3p (CDCl$_3$, 101MHz)



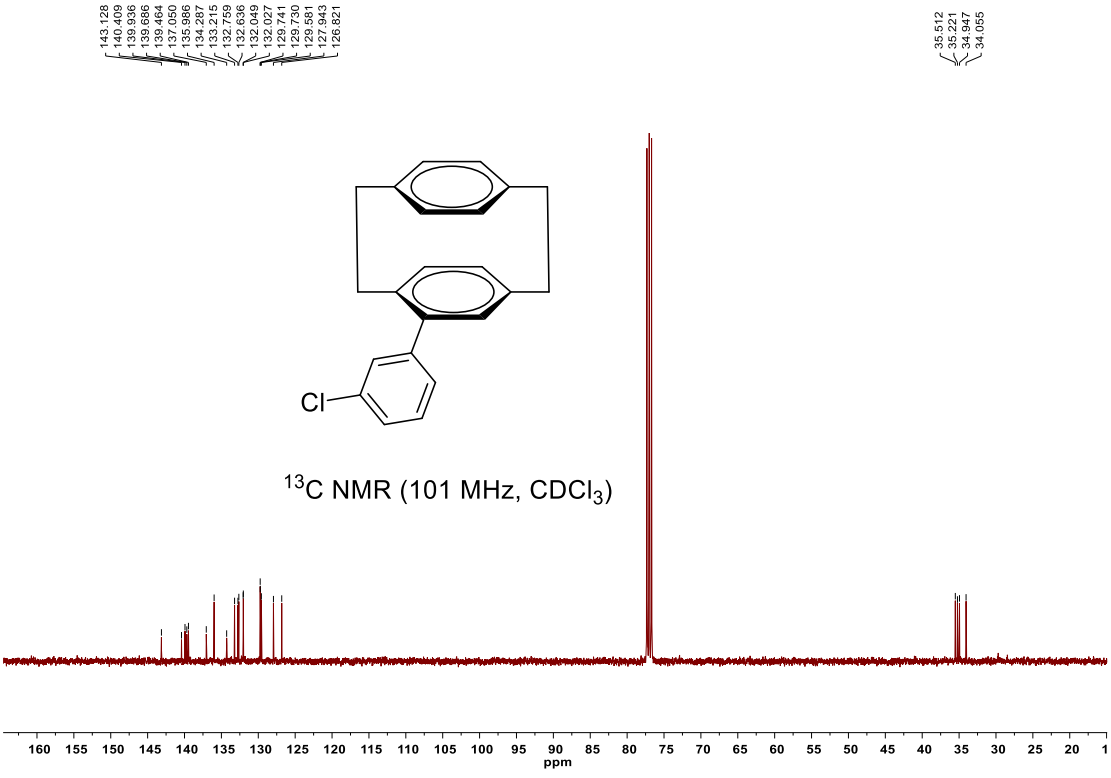
^{1}H NMR spectrum of 3q ($CDCl_3$, 400MHz)



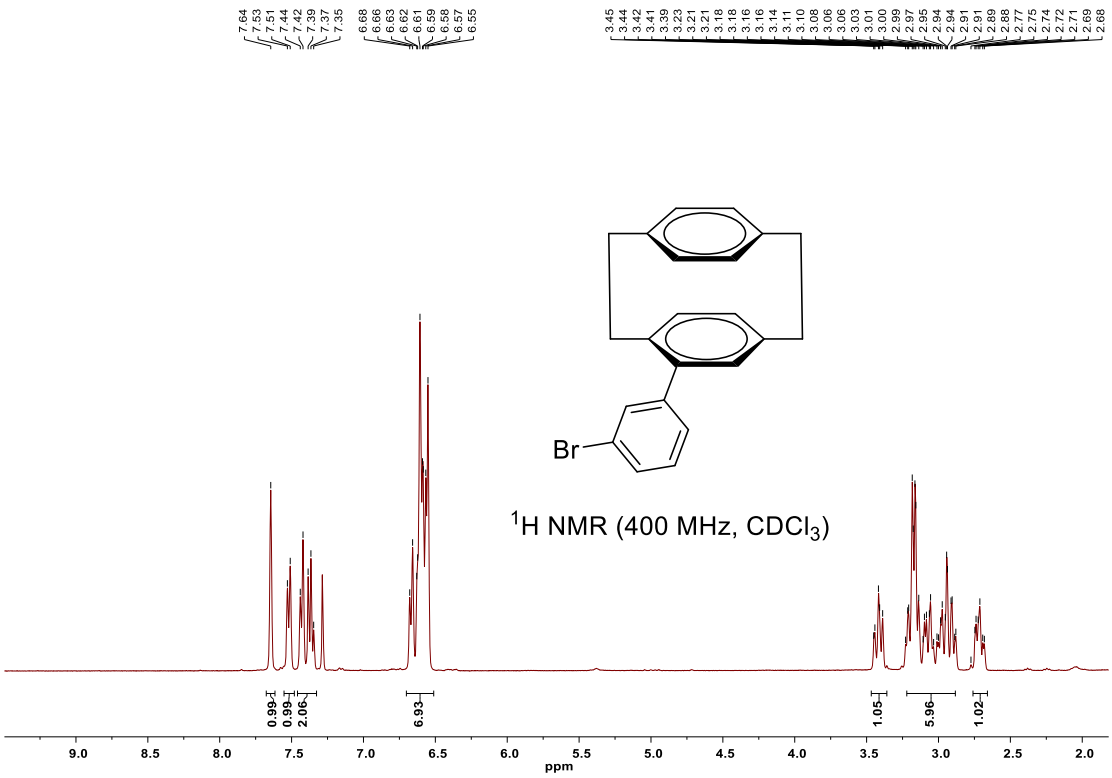
^{13}C NMR spectrum of 3q ($CDCl_3$, 101MHz)



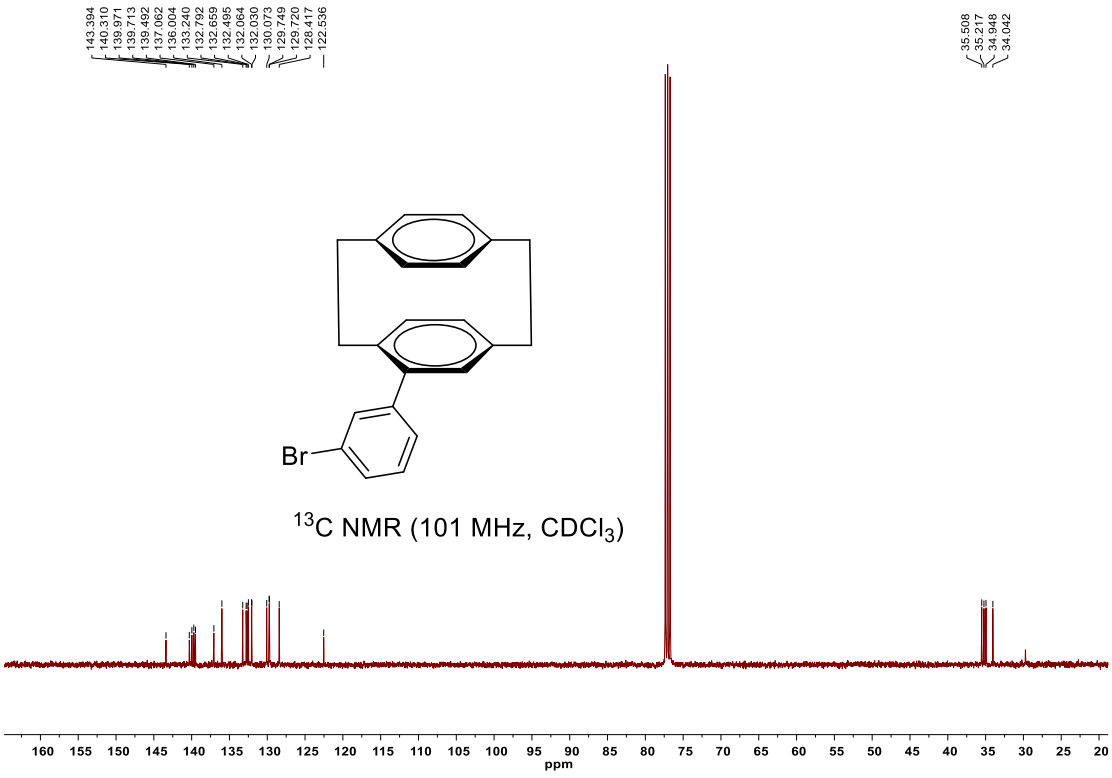
^{1}H NMR spectrum of 3r ($CDCl_3$, 400MHz)



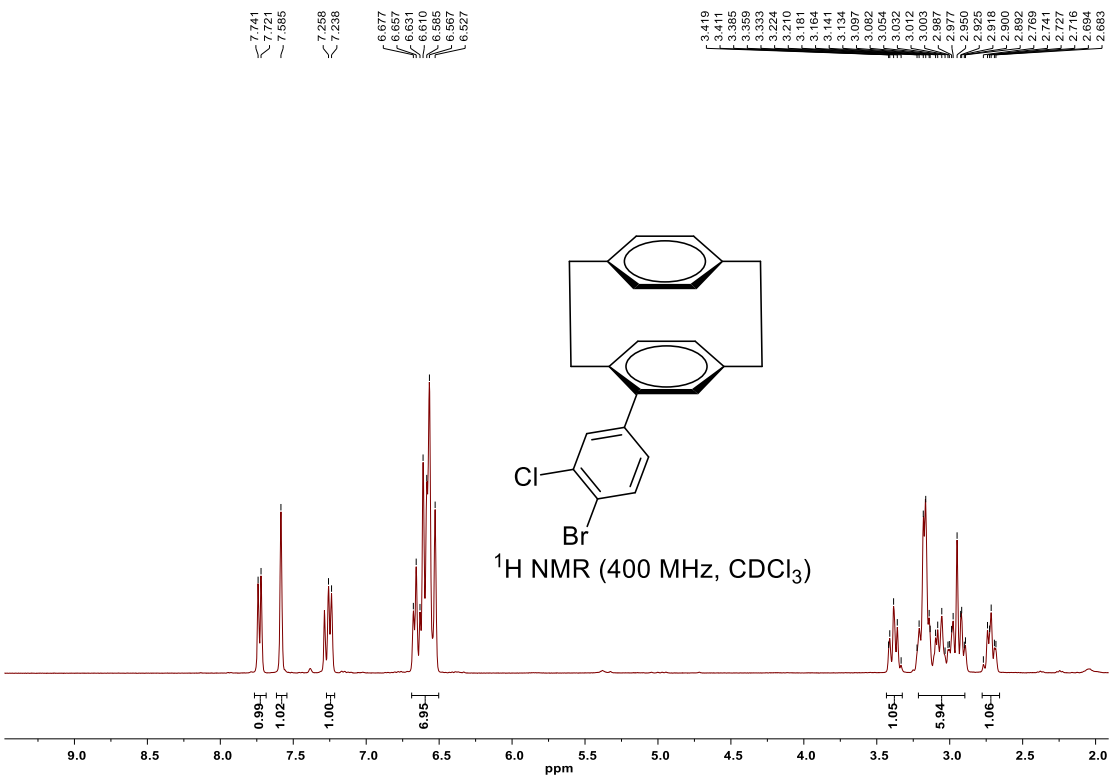
^{13}C NMR spectrum of 3r ($CDCl_3$, 101MHz)



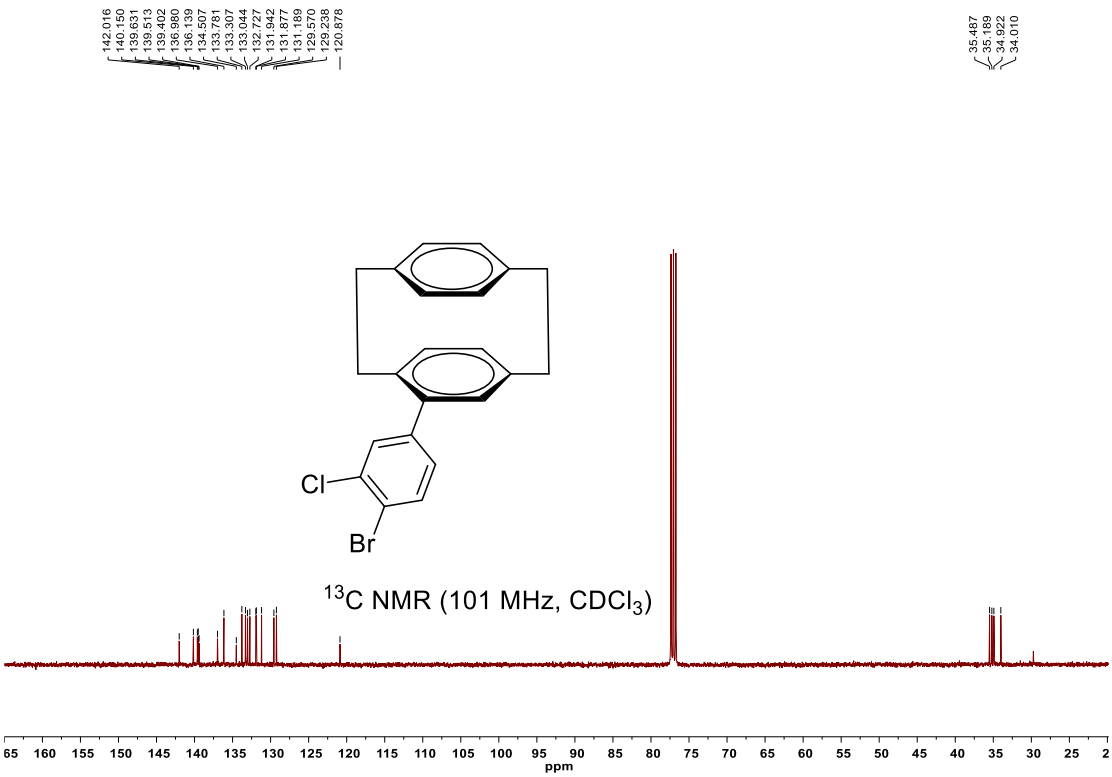
^{1}H NMR spectrum of 3s ($CDCl_3$, 400MHz)



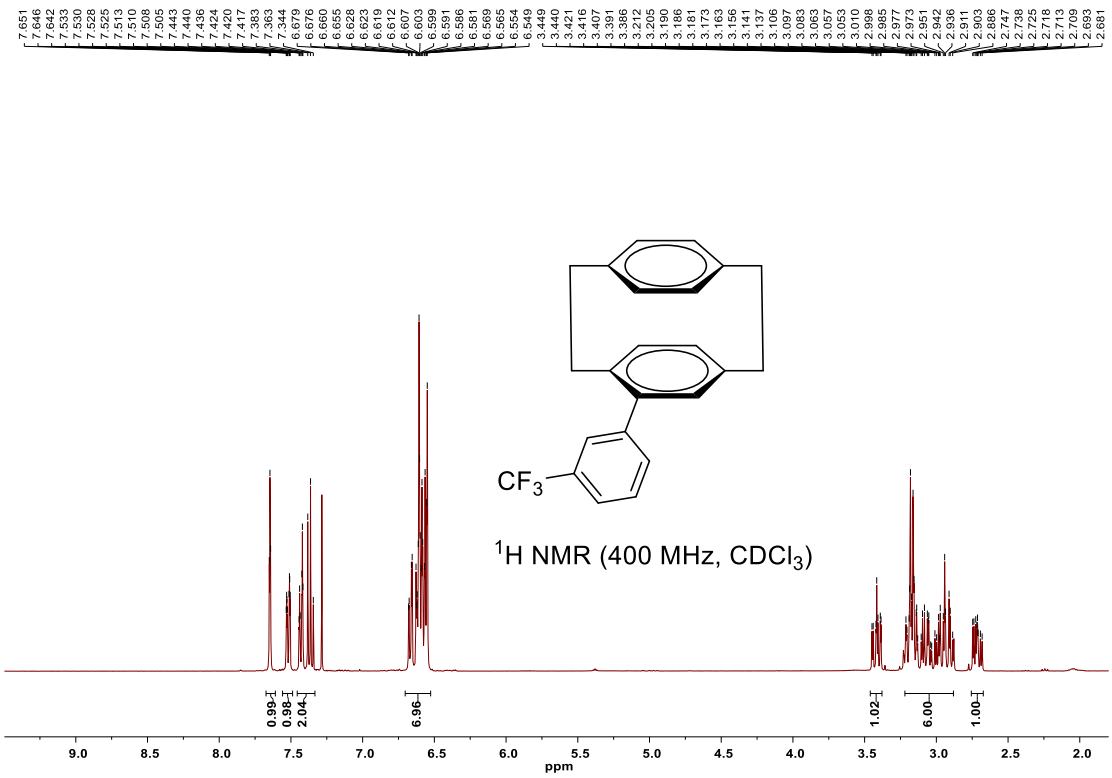
^{13}C NMR spectrum of 3s ($CDCl_3$, 101MHz)



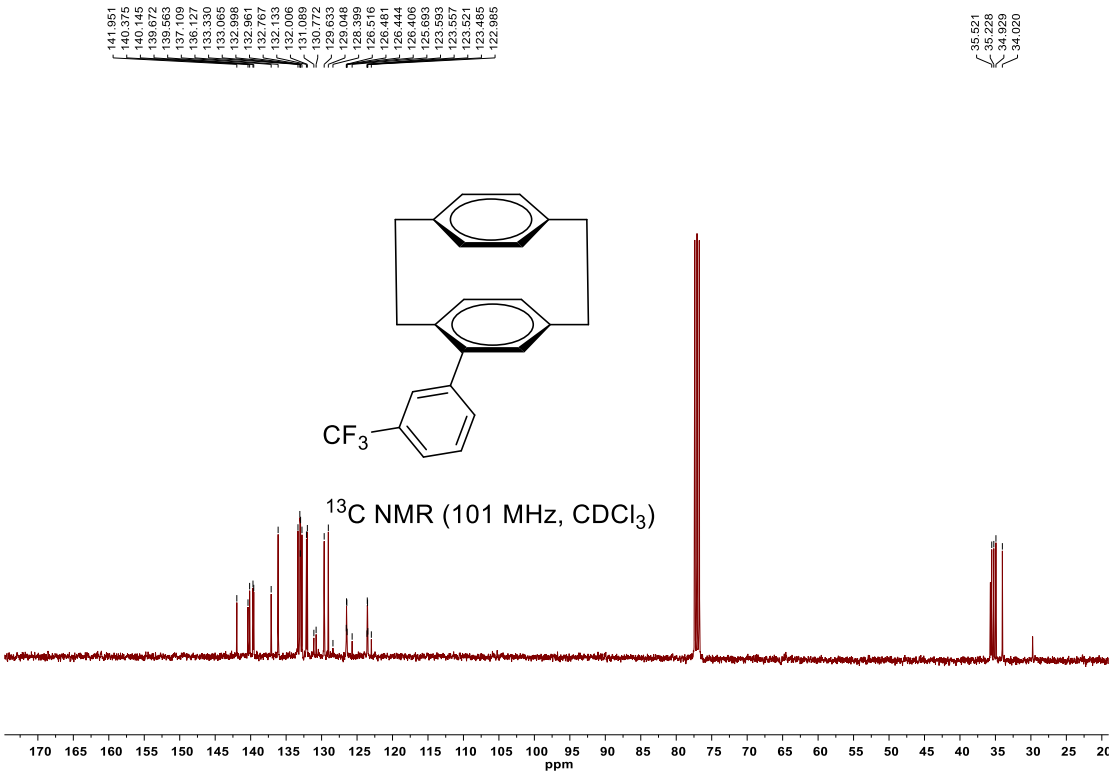
^{1}H NMR spectrum of 3t ($CDCl_3$, 400MHz)



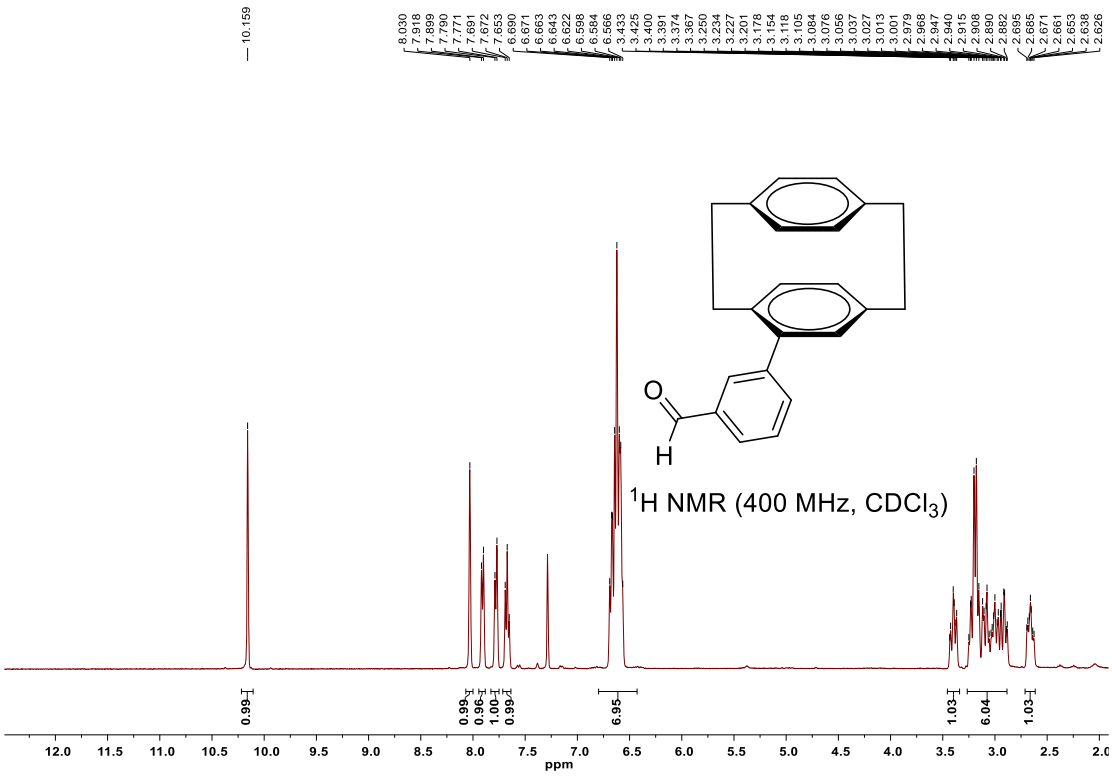
^{13}C NMR spectrum of 3t ($CDCl_3$, 101MHz)



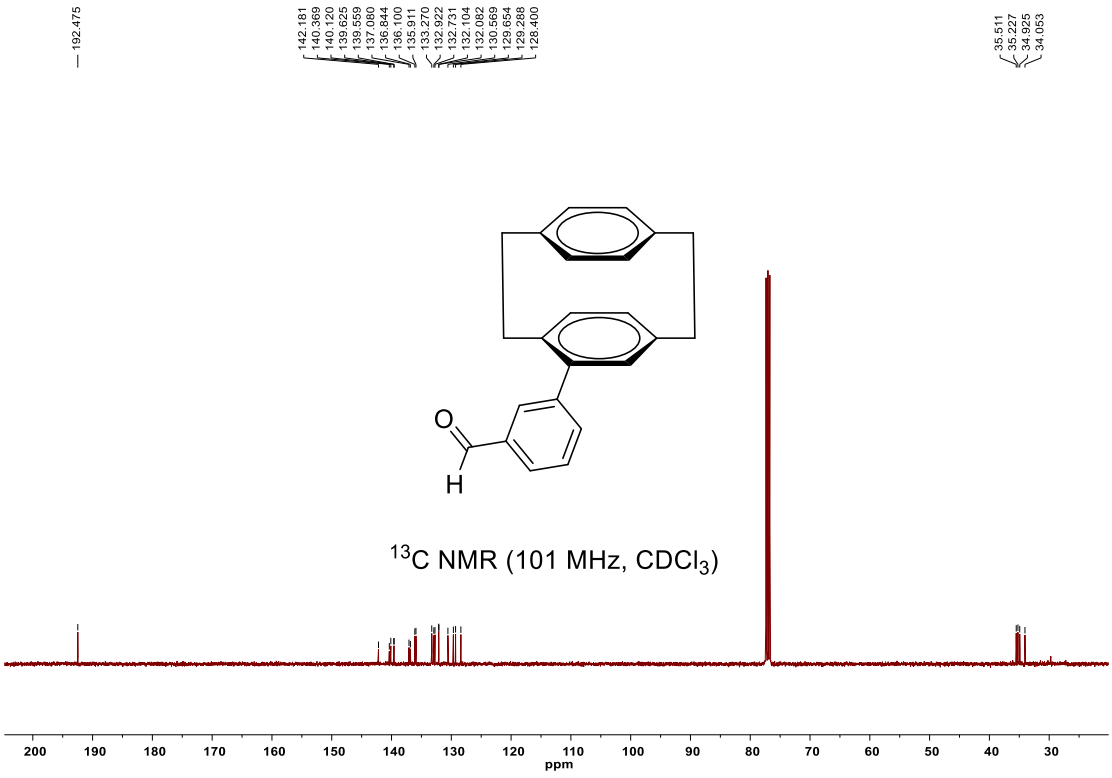
^{1}H NMR spectrum of 3u ($CDCl_3$, 400MHz)



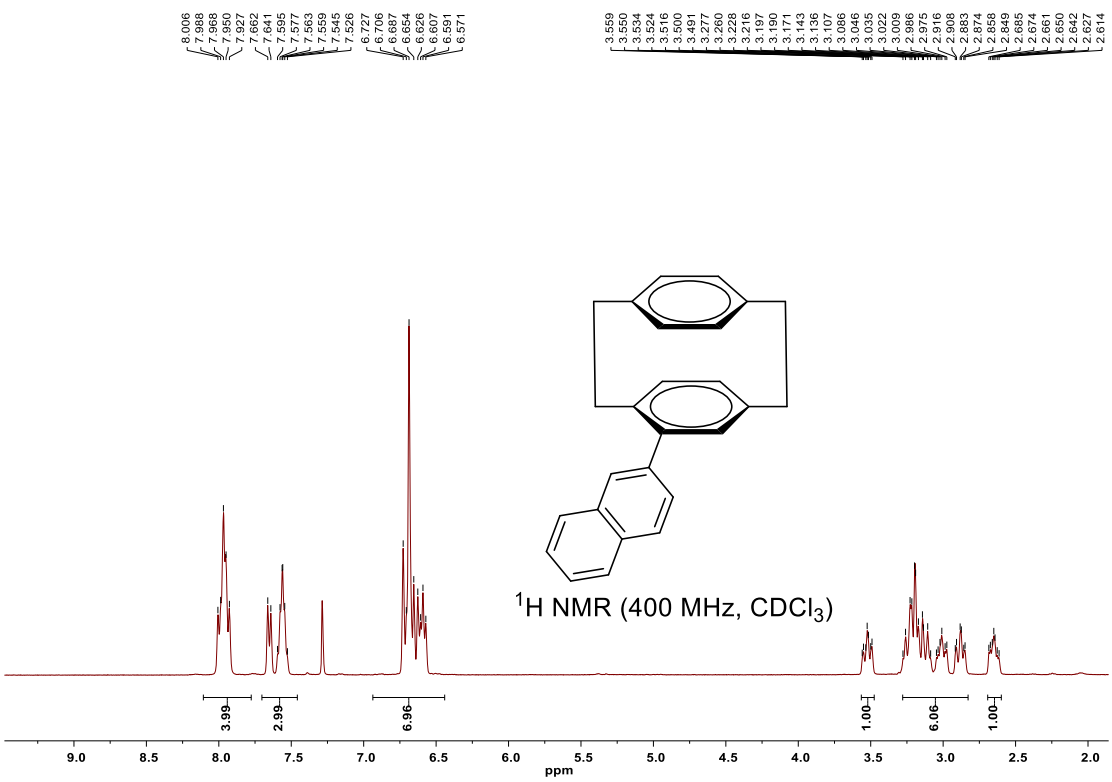
^{13}C NMR spectrum of 3u ($CDCl_3$, 101MHz)



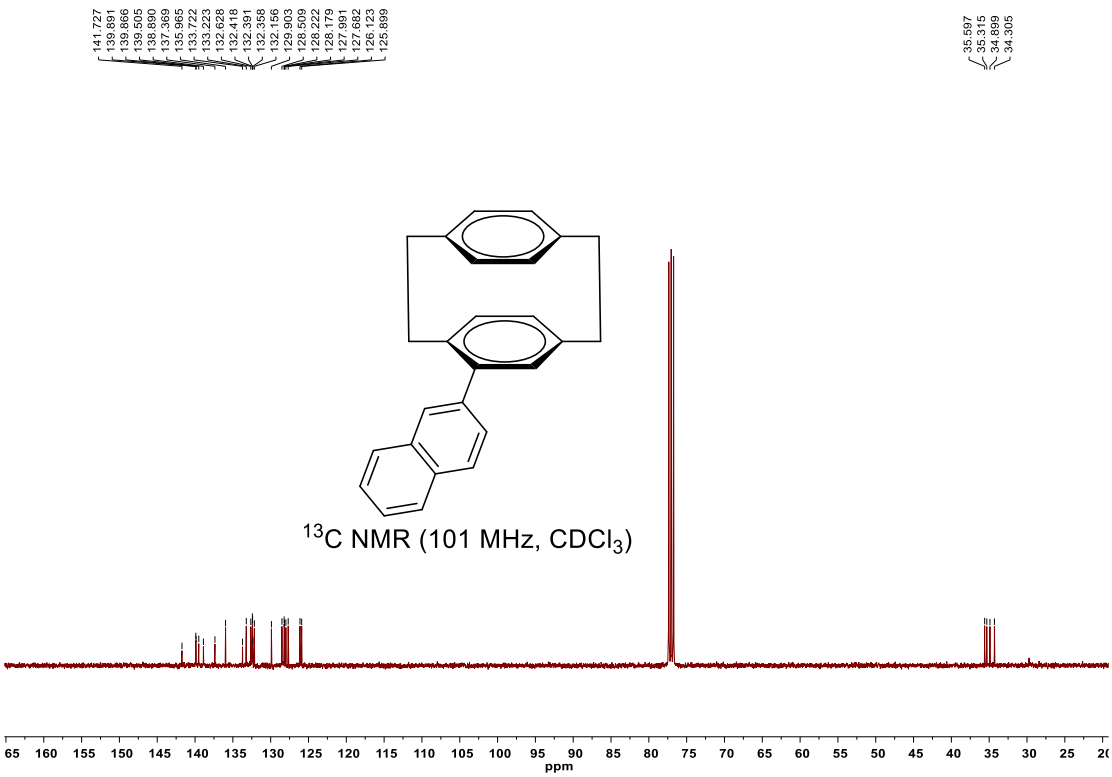
^{1}H NMR spectrum of 3v (CDCl$_3$, 400MHz)



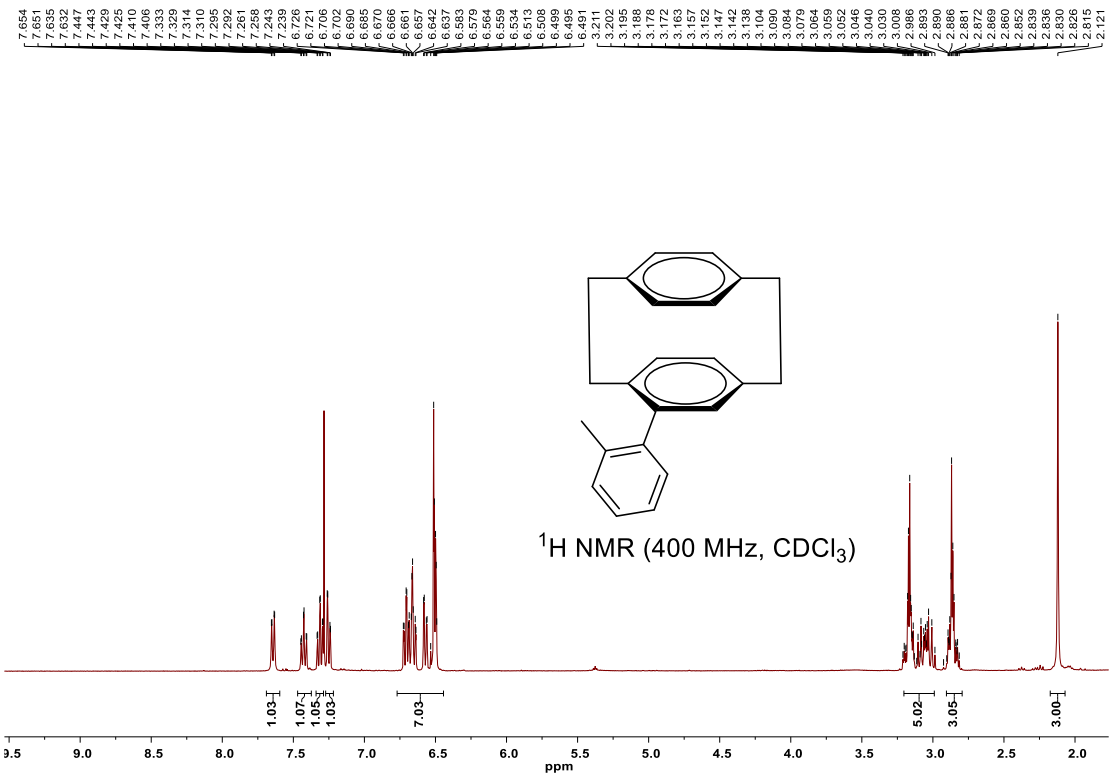
^{13}C NMR spectrum of 3v (CDCl$_3$, 101MHz)



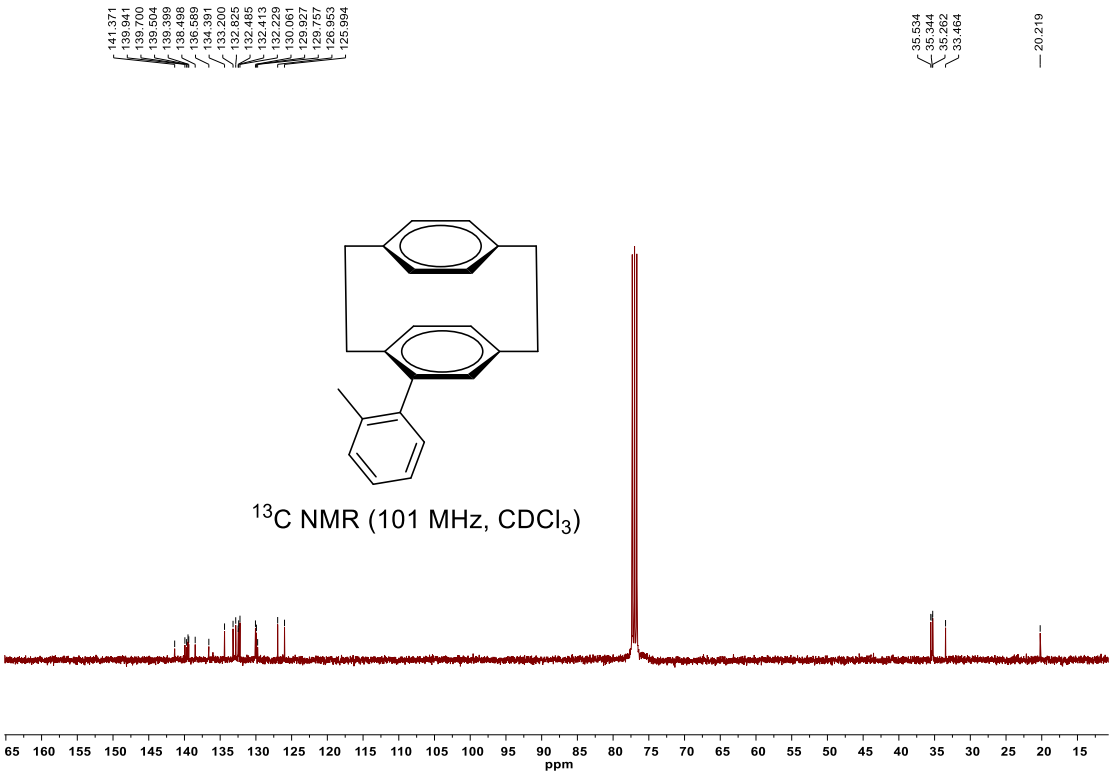
^{1}H NMR spectrum of 3w ($CDCl_3$, 400MHz)



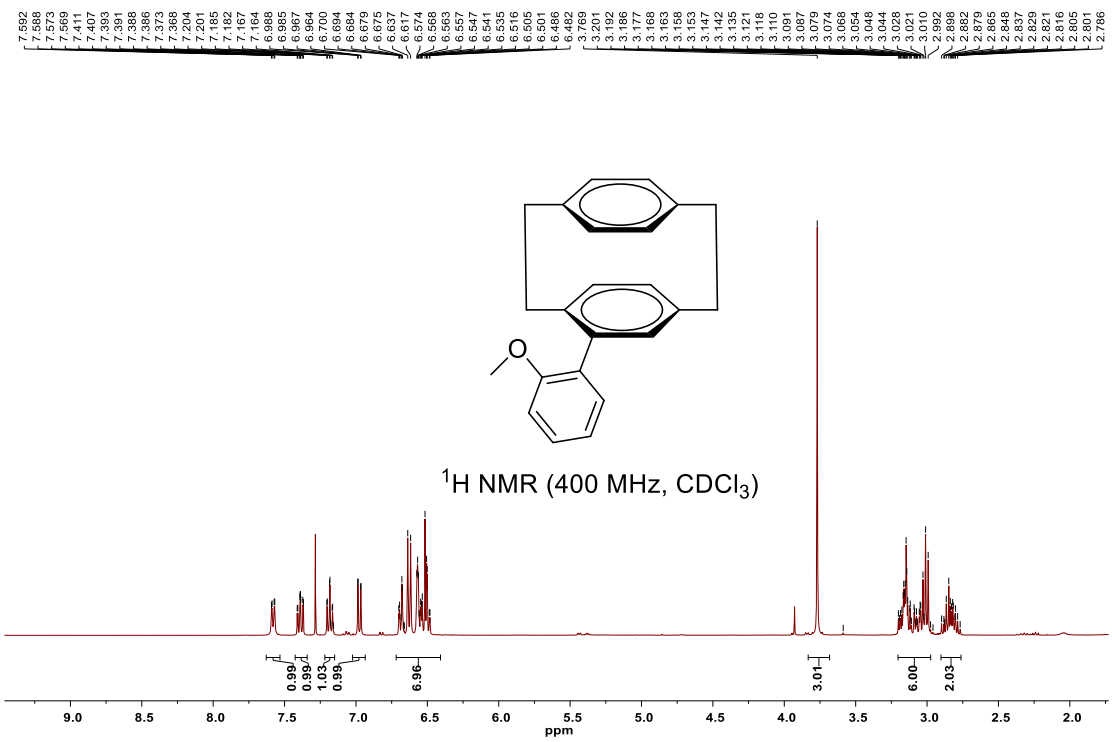
^{13}C NMR spectrum of 3w ($CDCl_3$, 101MHz)



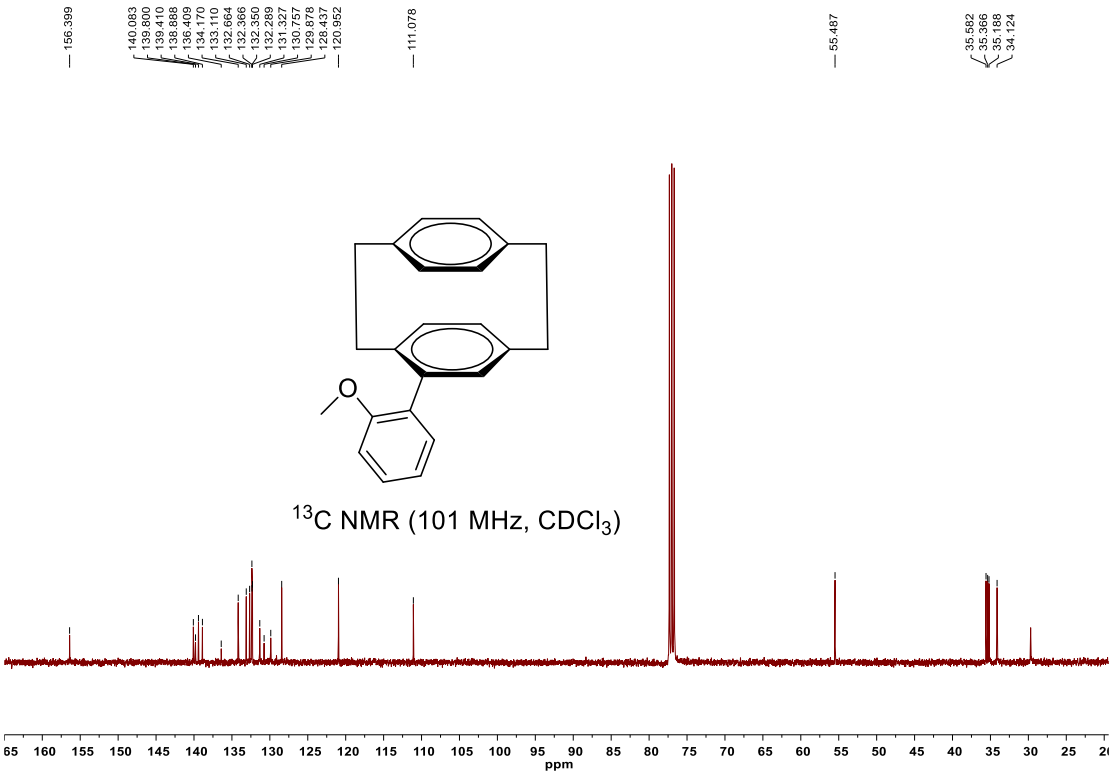
^{1}H NMR spectrum of 3x ($CDCl_3$, 400MHz)



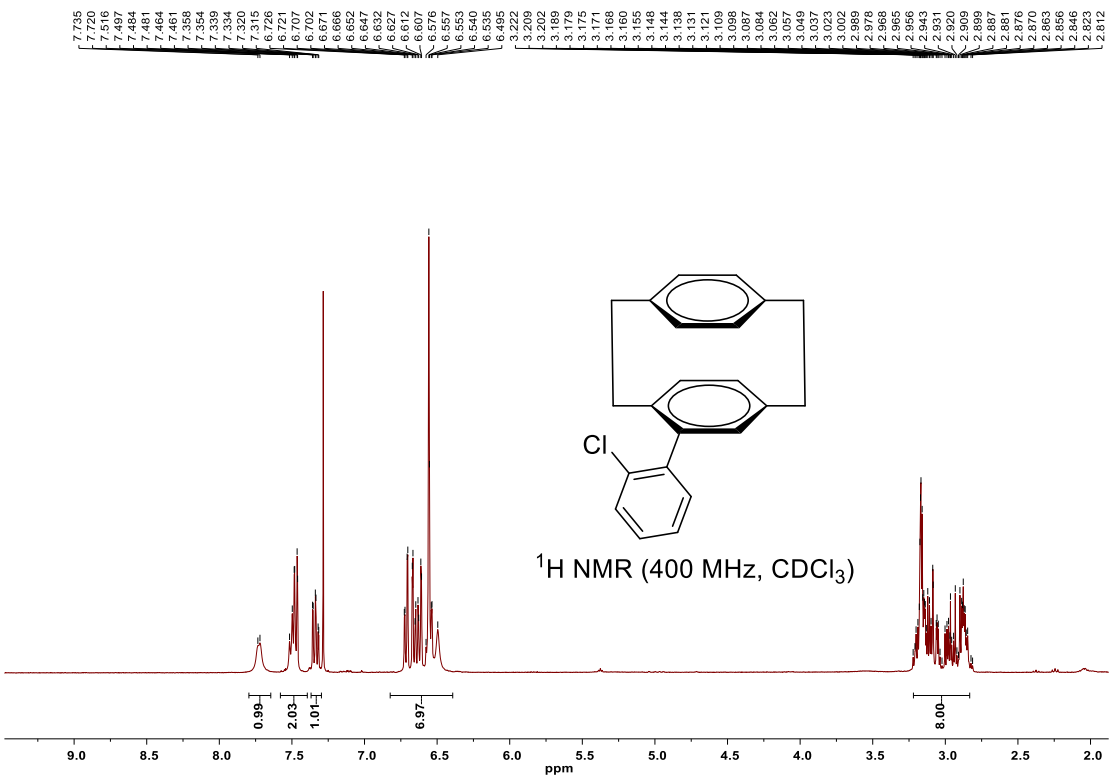
^{13}C NMR spectrum of 3x ($CDCl_3$, 101MHz)



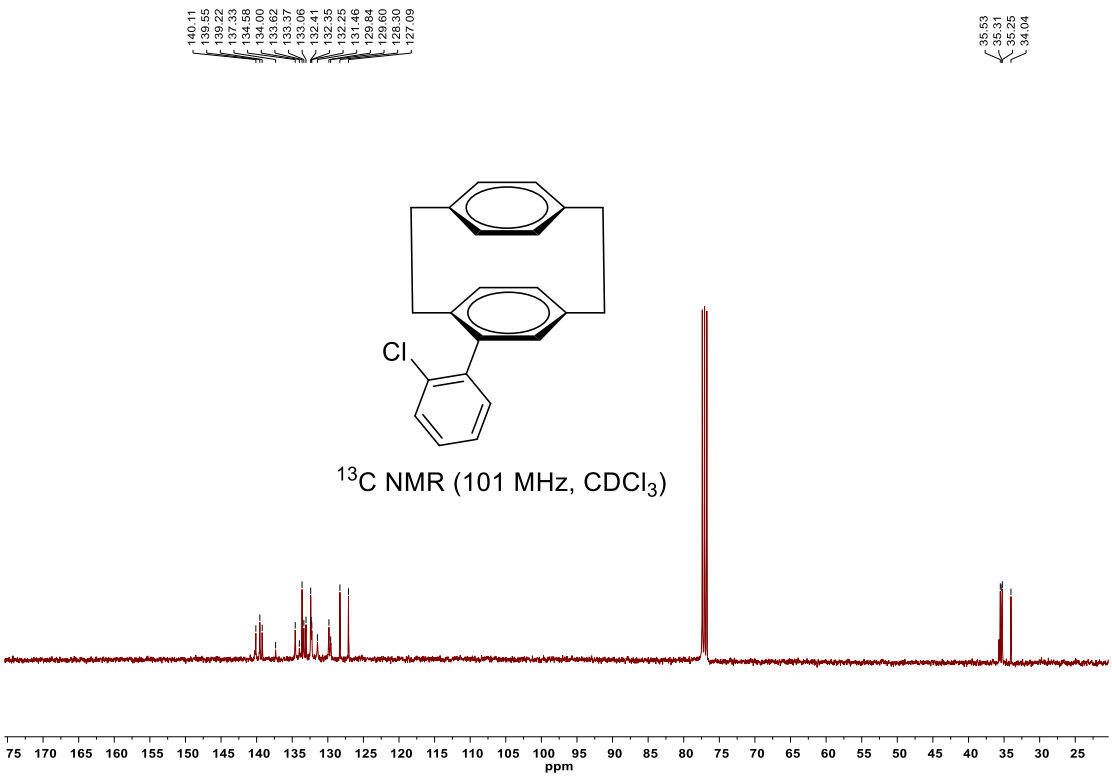
^{1}H NMR spectrum of 3y ($CDCl_3$, 400MHz)



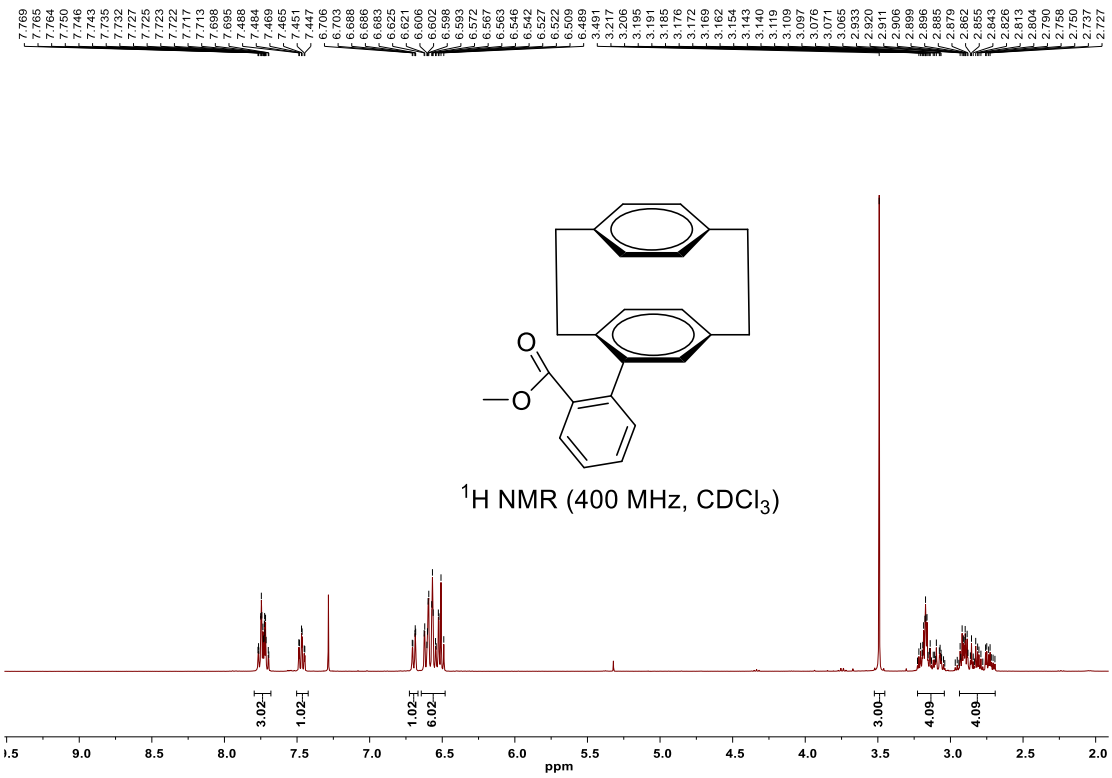
^{13}C NMR spectrum of 3y ($CDCl_3$, 101MHz)



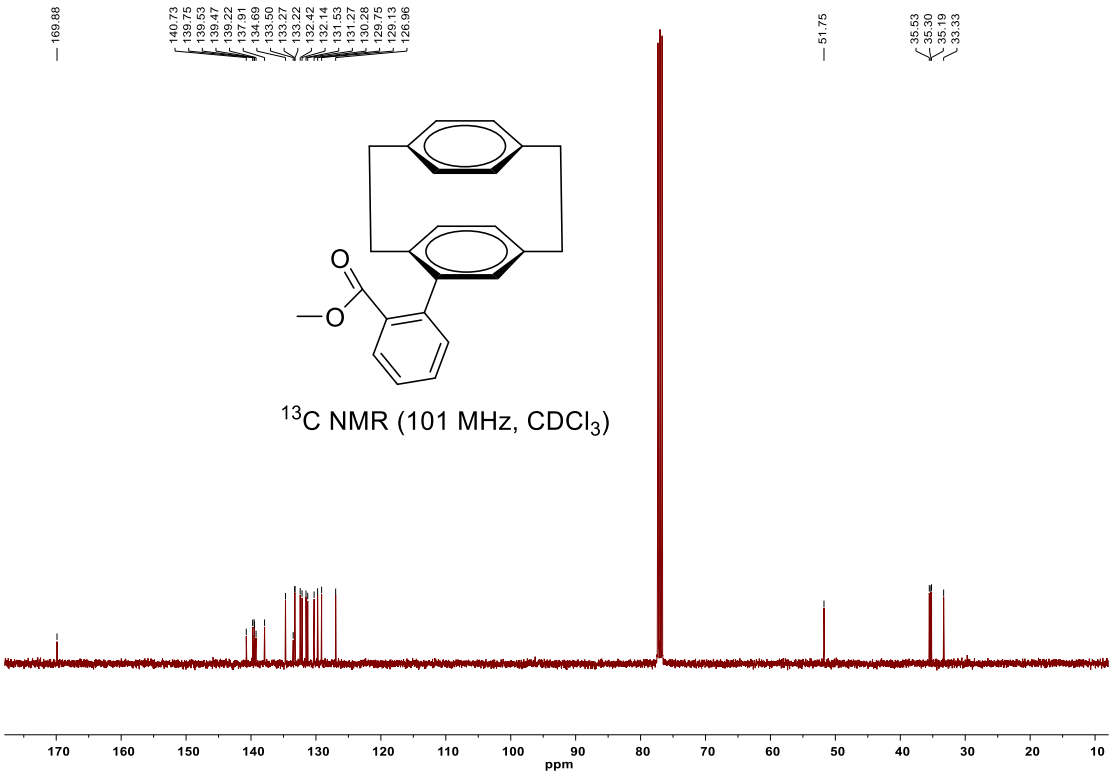
^{1}H NMR spectrum of 3z (CDCl$_3$, 400MHz)



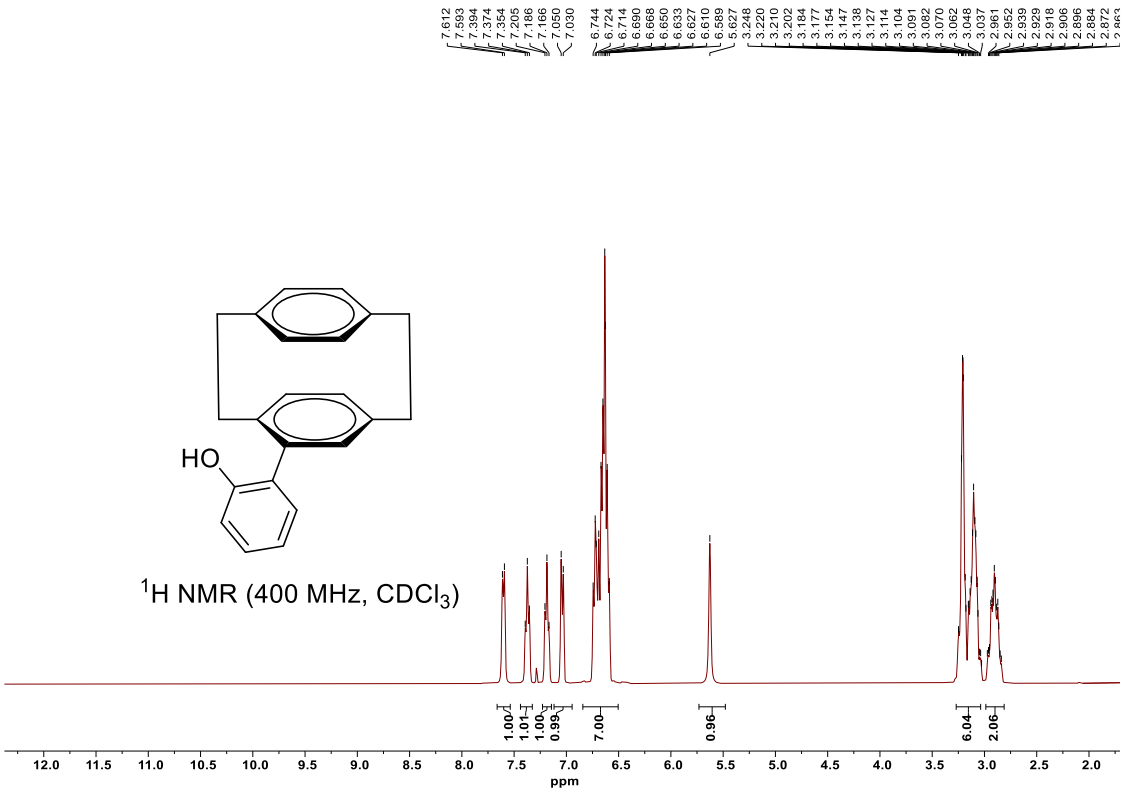
^{13}C NMR spectrum of 3z (CDCl$_3$, 101MHz)



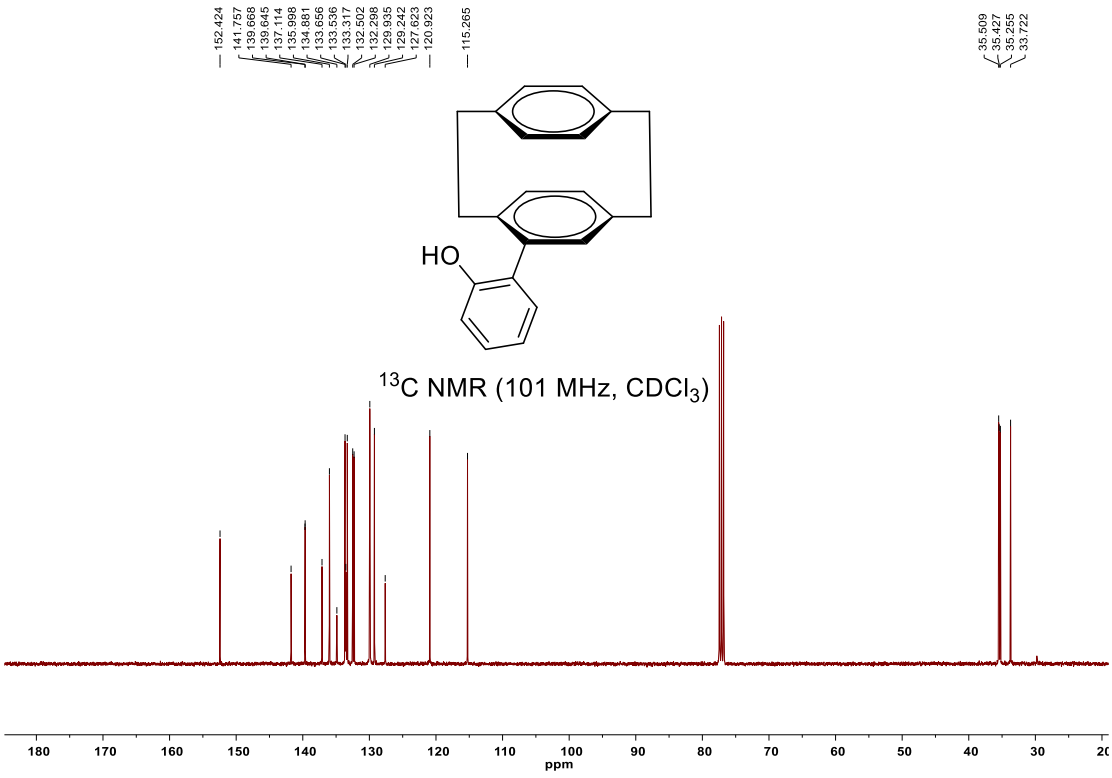
^{1}H NMR spectrum of 3aa ($CDCl_3$, 400MHz)



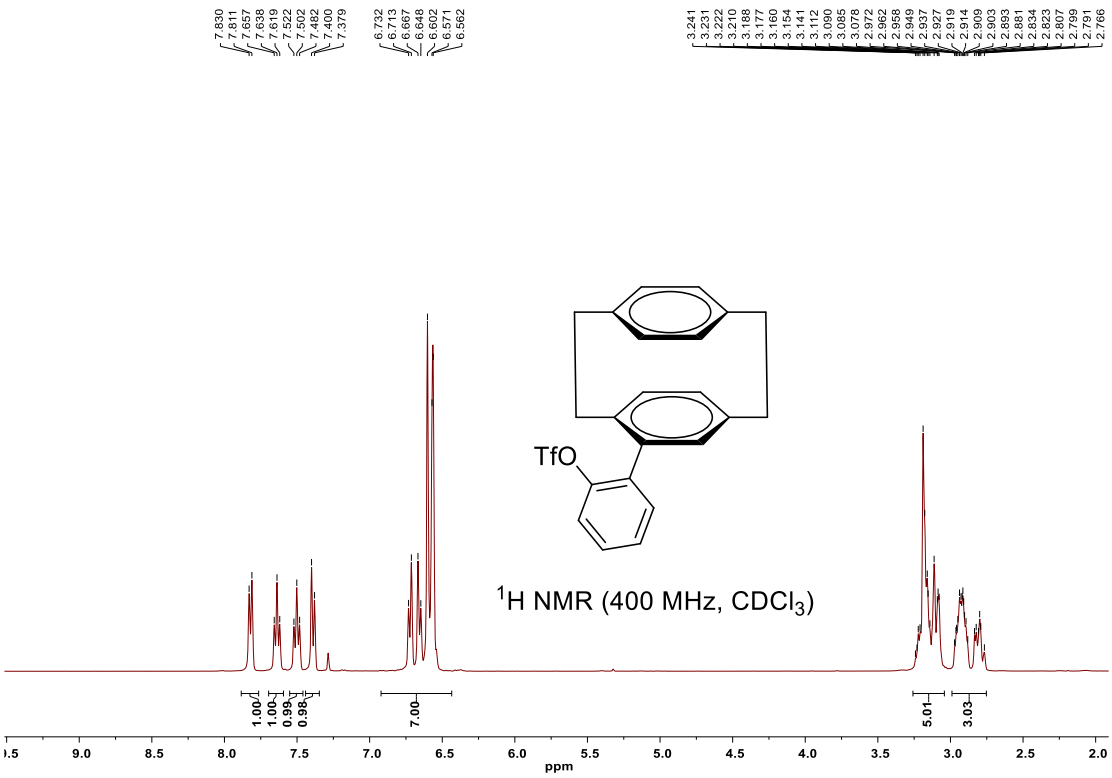
^{13}C NMR spectrum of 3aa ($CDCl_3$, 101MHz)



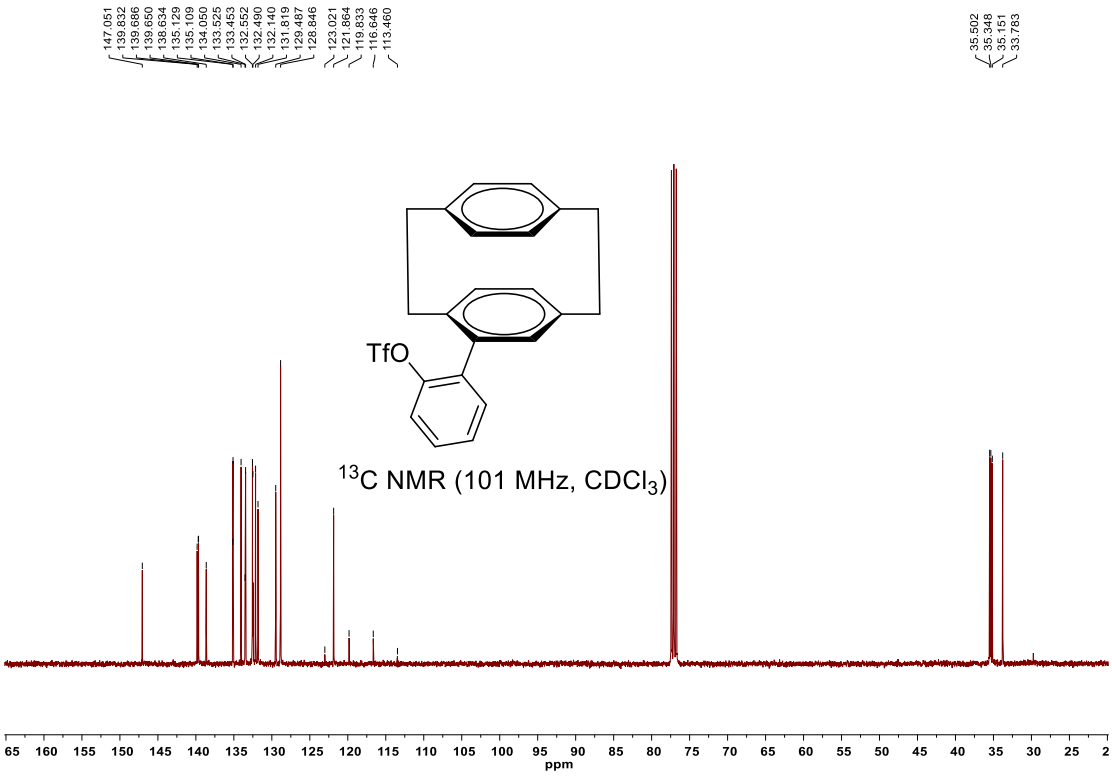
^{1}H NMR spectrum of 4 (CDCl$_3$, 400MHz)



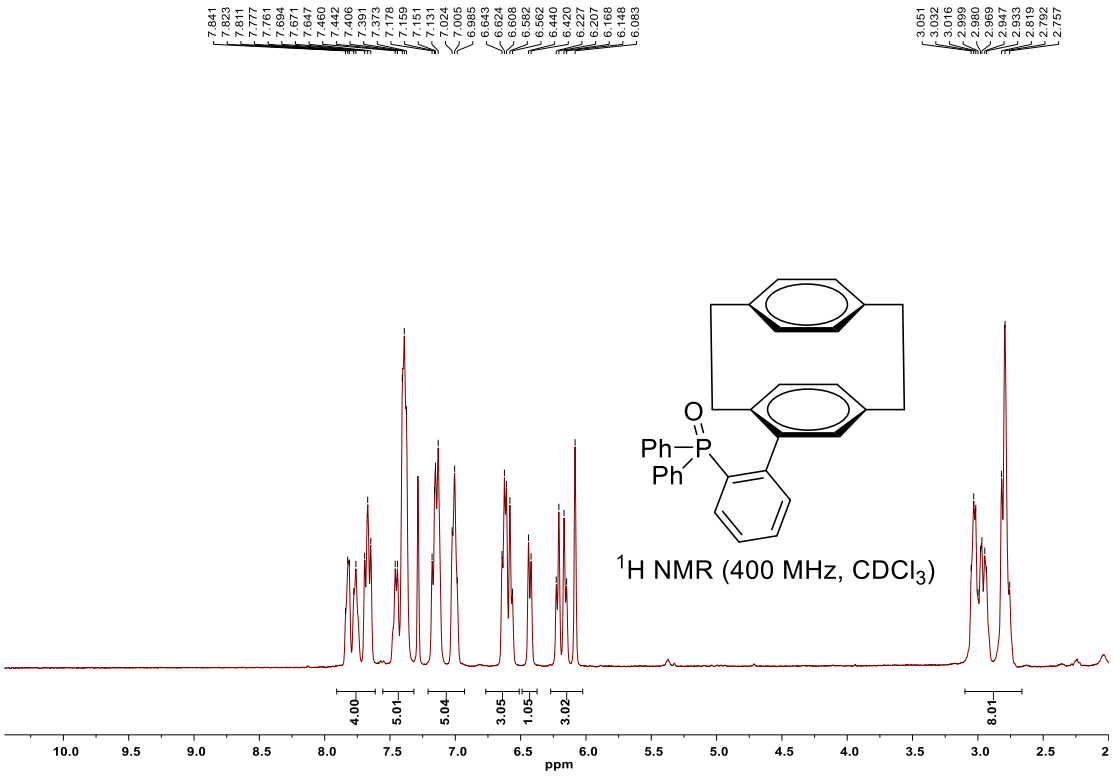
^{13}C NMR spectrum of 4 (CDCl$_3$, 101MHz)



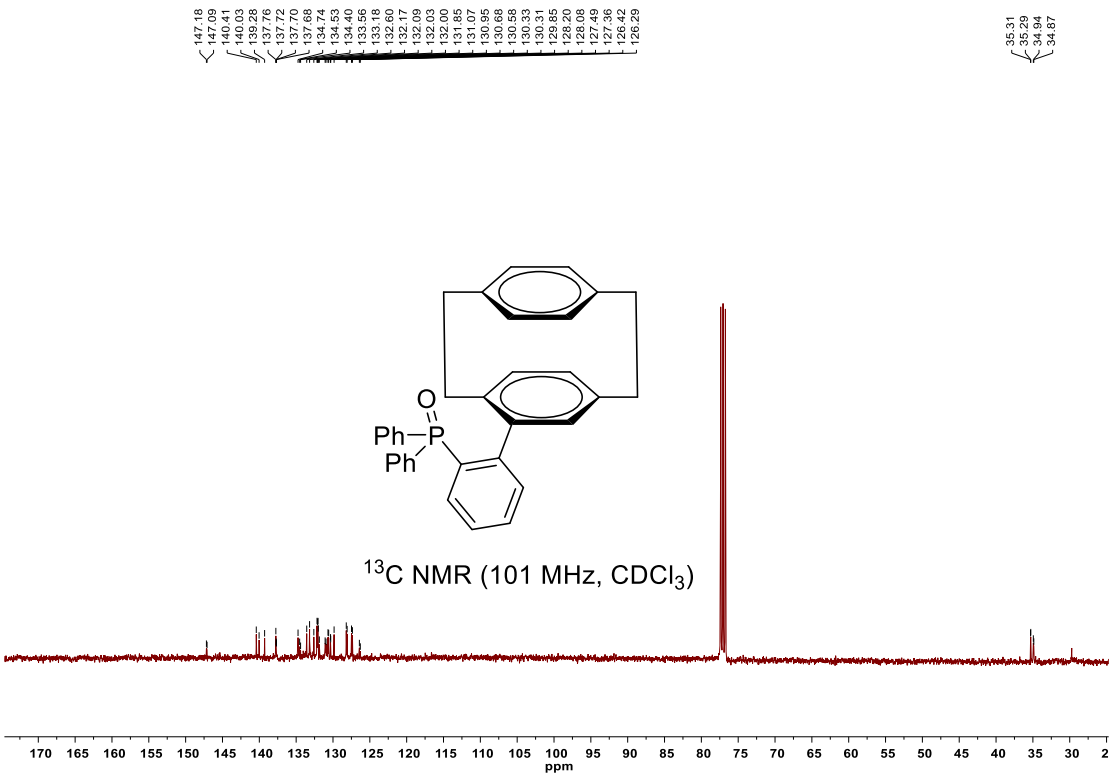
^{1}H NMR spectrum of 5 ($CDCl_3$, 400MHz)



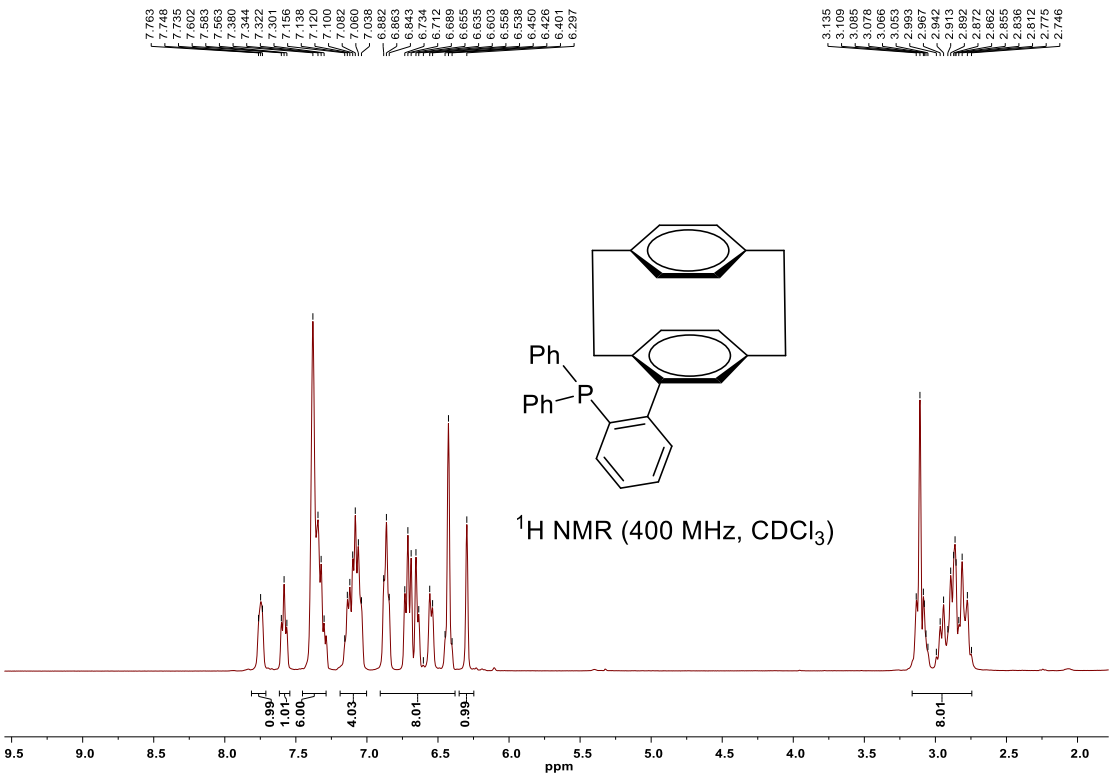
^{13}C NMR spectrum of 5 ($CDCl_3$, 101MHz)



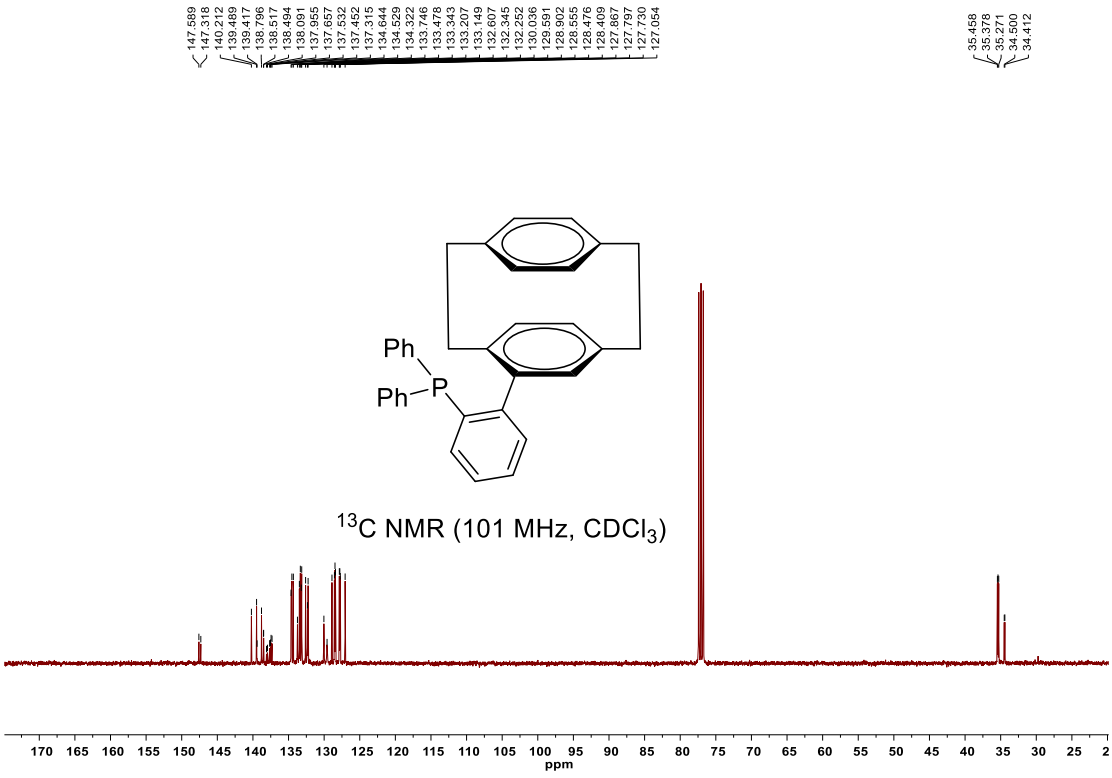
^{1}H NMR spectrum of 6 ($CDCl_3$, 400MHz)



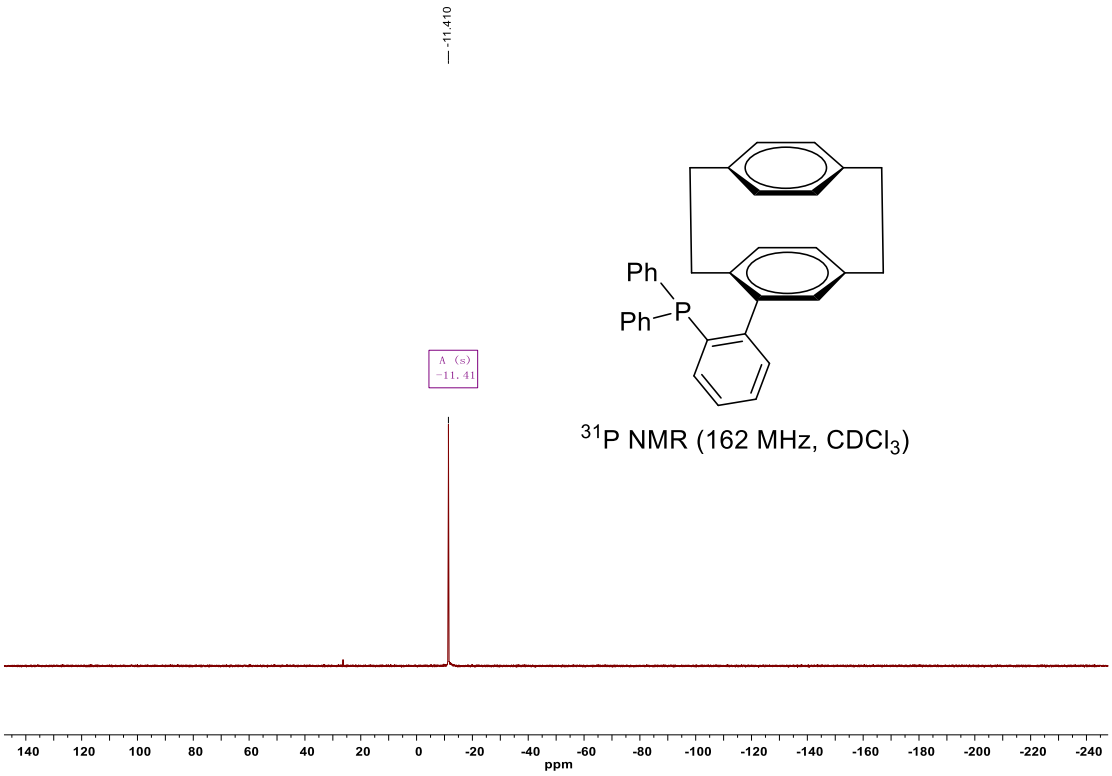
^{13}C NMR spectrum of 6 ($CDCl_3$, 101MHz)



^{1}H NMR spectrum of 7 ($CDCl_3$, 400MHz)



^{13}C NMR spectrum of 7 ($CDCl_3$, 101MHz)



^{32}P NMR spectrum of 7 ($CDCl_3$, 162MHz)