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Supporting Information

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Strained Dehydro-[2,2]-paracyclophane Enabled Planar Chirality Construction and [2.2]Paracyclophane Functionalization

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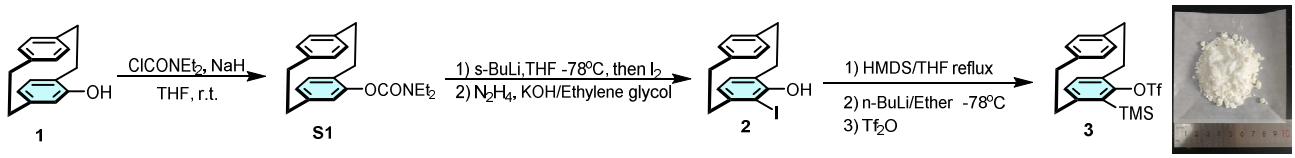
1. General Information

Unless otherwise noted, all reactions were carried out in a flame-dried glassware under a nitrogen atomsphere. All reagents were obtained commercially and used without further purification. Column chromatography was performed with silica gel (200–300 mesh) as the stationary phase. All catalytic reactions were performed in Schlenk tubes under an atmosphere of nitrogen. Thin-layer chromatography (TLC) was performed using silica gel pre-coated plastic sheets (Polygram SIL G/UV254, 0.2 mm, with fluorescent indicator).

Instrumentation: NMR spectra were recorded on a Bruker 400 MHz NMR spectrometer or a Bruker 500 MHz spectrometer and were calibrated using residual deuterated solvent as an internal reference ($CDCl_3$: 7.26 ppm for ^1H NMR and 77.16 ppm for ^{13}C NMR). The peak information was described as: br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet; coupling constants in Hz. The enantiomeric excess (e.e.) values of the products were determined by high-performance liquid chromatography (HPLC) analysis performed on Thermo Scientific Dionex UltiMate 3000 Series using a Diacel® chiral column (4.6 × 250 mm, particle size 5 μm). High-resolution mass spectra analysis data were obtained on a Thermoquest MAT 95 XL instrument. Optical rotations were measured using a 2.5 mL cell with a 10 cm path length on Hanon P850 Automatic Polarimeter and concentrations (c) is in g/100 mL.

Abbreviations used: e.e. = enantiomeric excess, r.t. = room temperature, TLC = thin layer chromatography, min = minute, h = hours, equiv. = equivalent, mL = Milliliter, L = liter, DCM = Dichloromethane, DCE = 1,2-Dichloroethane, MeOH = methanol, 2-PrOH = isopropanol, THF = Tetrahydrofuran, DME = 1,2-Dimethoxyehtane, MeCN = Acetonitrile, MTBE = Methyl tert-Butyl Ether, CPME = Cyclopentyl methyl ether, HMDS = 1,1,1,3,3,3-Hexamethyldisilazane, TEA = Triethylamine, Me = methyl, Et = ethyl, Bu = butyl, Tf = SO_2CF_3, TMS = Trimethylsilyl, TIPS = Triisopropylsilyl, Ph = Phenyl.

2. Synthesis of starting materials



2.1 Synthesis of 4-Diethylcarbamoyl[2.2]paracyclophane

To a solution of 4-Hydroxy[2.2]paracyclophane (70 g, 0.31 mol) in THF (500ml) was added NaH (15.9 g, 1.2 equiv.) in portions at 0 °C. Then Diethylcarbamoyl Chloride (44.1 g, 1.05 equiv.) was added dropwise via pressure equalizing funnel while keeping inner temperature between 0 °C. The reaction was stirred at room temperature about 8 h (determined by TLC). Then the reaction was cooled to 0 °C and quenched with water. The solvent was evaporated under reduced pressure, and the residue was dissolved in DCM (500 mL) and washed with water (200 mL × 2). The organic phases were dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel to afford title product (92.2 g, 91%). ^{1}H NMR (500 MHz, Chloroform-d) δ 6.85 (dd, *J* = 7.8, 2.0 Hz, 1H), 6.54 (dd, *J* = 7.8, 2.0 Hz, 1H), 6.48 (td, *J* = 5.7, 5.3, 2.9 Hz, 2H), 6.44 (dt, *J* = 7.8, 1.8 Hz, 2H), 6.03 (d, *J* = 1.8 Hz, 1H), 3.62 (d, *J* = 7.5 Hz, 2H), 3.39 (d, *J* = 7.4 Hz, 2H), 3.22 (ddd, *J* = 13.2, 10.2, 2.5 Hz, 1H), 3.15 – 2.93 (m, 6H), 2.71 (ddd, *J* = 13.4, 10.5, 5.8 Hz, 1H), 1.43 (t, *J* = 6.2 Hz, 3H), 1.21 (t, *J* = 7.1 Hz, 3H).

2.2 Synthesis of 4-Hydroxy-5-iodo[2.2]paracyclophane[1]

In a 500 ml Schlenk flask, sec-Butyllithium (120 ml, 1.3 mol/L in hexane) was slowly added to a stirred mixed solution of **S2** (32.3 g, 0.1 mol) and tetramethylethyldiamine (17.5 g, 1.5 equiv.) in anhydrous THF (250 ml) under nitrogen atmosphere at -78 °C. The reaction mixture was allowed to stir at -78 °C for 2 h. Then Iodine (38.1 g, 1.5 equiv.) in THF (50 mL) was added dropwise via syringe over a period of 30 minutes, and the solution was allowed to warm slowly to room temperature overnight. Once quenched with saturated NH_4Cl aqueous, the reaction mixture was concentrated under reduced pressure to remove THF. The residue was dissolved in DCM (500 mL) and washed with water (200 mL × 2). The organic phases were

dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was used directly without further purification.

Above-mentioned intermediate and potassium hydroxide (138 g, 1.0 mol) were suspended in 500 mL of ethylene glycol. Hydrazine (31.3 g, 0.5 mol, 80% aqueous) was added and the mixture was heated at reflux for 8 h. During the reflux period, the mixture became homogenous. The solution was cooled to room temperature, transferred to a separatory funnel, acidified to pH = 1 with concd. HCl. The aqueous phase was extracted with DCM (100 mL × 3). The organic layers were combined, dried over Na_2SO_4, and solvent was removed under reduced pressure. The crude product was purified by column chromatography on silica gel to afford a white solid (28.2 g, 80%). ^{1}H NMR (500 MHz, Chloroform-d) δ 7.02 (dd, *J* = 7.8, 1.9 Hz, 1H), 6.77 (dd, *J* = 7.8, 1.9 Hz, 1H), 6.54 (dd, *J* = 7.8, 1.9 Hz, 1H), 6.49 (dd, *J* = 7.8, 1.8 Hz, 1H), 6.46 (d, *J* = 7.6 Hz, 1H), 6.26 (d, *J* = 7.6 Hz, 1H), 5.12 (s, 1H), 3.39 (ddd, *J* = 13.1, 9.0, 3.9 Hz, 1H), 3.29 – 3.22 (m, 1H), 3.13 – 3.04 (m, 3H), 3.04 – 2.94 (m, 2H), 2.70 (ddd, *J* = 13.3, 9.7, 6.3 Hz, 1H).

2.3 General procedure for the synthesis of 3

To a solution of 4-Hydroxy-5-iodo[2.2]paracyclophane (22.0 g, 62.8 mmol) in anhydrous THF (200 mL) was added 1,1,1,3,3,3-Hexamethyldisilazane (30.4 g, 3.0 equiv.). The reaction was heated at reflux for about 20 h (determined by TLC). After cooling to room temperature, the mixture was evaporated under reduced pressure at 70 ^{o}C to afford a colorless oil, which was used for the next step without further purification.

In a 250 ml Schlenk flask, n-Butyllithium (37.7 ml, 2.5 mol/L in hexane) was slowly added to a stirred solution of **2** in anhydrous Ethyl ether (250 ml) under nitrogen atmosphere at -78 ^{o}C. The reaction mixture was allowed to stir at -78 ^{o}C for 2 h. Then Triflic anhydride (26.6 g, 1.5 equiv.) in Ethyl ether (50 mL) was added dropwise via syringe. After stirring for an additional 3 h, the reaction was quenched with saturated NH_4Cl aqueous. The reaction mixture was concentrated under reduced pressure to remove THF. The residue was dissolved in DCM (200 mL) and washed with water (50 mL × 2). The organic phases were dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel to afford a white solid (22 g, 82%).

^{1}H NMR (500 MHz, Chloroform-d) δ 6.70 (dd, *J* = 8.1, 1.8 Hz, 1H), 6.67 – 6.62 (m, 2H), 6.52 (d, *J* = 7.8 Hz, 1H), 6.46 (d, *J* = 7.7 Hz, 1H), 6.35 (dd, *J* = 8.3, 1.9 Hz, 1H), 3.53 – 3.46 (m, 1H), 3.43 – 3.37 (m, 1H), 3.26 – 3.19 (m, 1H), 3.19 – 3.13 (m, 1H), 3.04 – 2.95 (m, 4H), 0.51 (s, 9H).

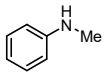
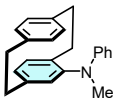
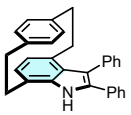
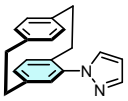
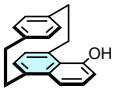
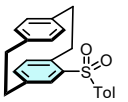
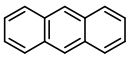
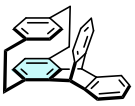
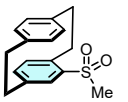
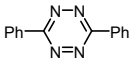
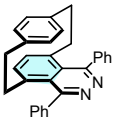
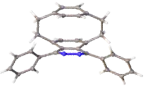
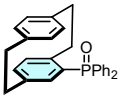
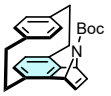
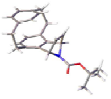
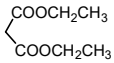
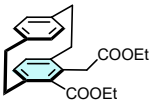
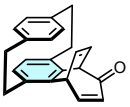
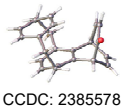
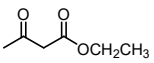
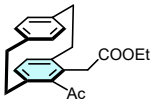
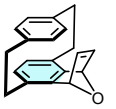
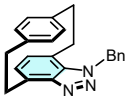
^{19}F NMR (471 MHz, Chloroform-d) δ -73.13.

^{13}C NMR (126 MHz, Chloroform-d) δ 151.14, 148.62, 139.77, 138.87, 137.92, 135.21, 133.23, 133.10, 132.97, 131.94, 131.64, 130.18, 36.00, 35.76, 34.88, 32.05, 2.88.

HRMS (APCI) Calculated for $C_{20}H_{24}F_3O_3SSi$ $[M+H]^+$: 429.1163; Found: 429.1151.

3. Scope of trapping reactions[2]

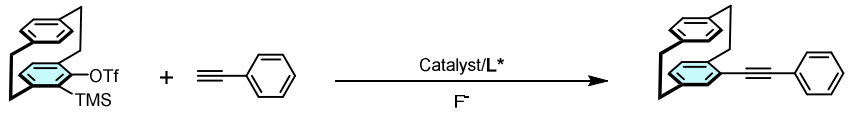
Figure S1. List of capture product[a,b,c]

Entry	Trapping agent	Product	Yield	Entry	Trapping agent	Product	X-ray crystal structure	Yield
1			96%	9			-	54%
2			87%	10			-	84%
3			94%	11			 CCDC: 2380667	94%
4			82%	12			 CCDC: 2380679	53%
5			95%	13			 CCDC: 2385577	87% (1:4)
6			76%	14			 CCDC: 2385578	93% (1:1.7)
7			76%	15				77% (1:2)
8	BnN_3		90%					

[a]Reaction conditions: 3 (0.2 mmol, 1.0 equiv), trapping agent (0.6 mmol, 3.0 equiv.), CsF (3.0 equiv), CH_3CN (3.0 mL), 25°C, 12 h. [b]Isolated yields after silica gel column chromatography, [c]Entry 3, 4, 10 were conducted at 60 °C, Entry 5, 12 were conducted at 80 °C.

4. Condition Optimization

Table S1. Investigation of the Cu catalysts, Ligands and F⁻ resource[a, b,c]



Entry	Catalyst	Ligand	F⁻	Solvent	T/℃	Yield/%	Ee/%
1	$Cu(MeCN)_4PF_6$	L1	CsF	MeCN	60	94	78
2	$Cu(MeCN)_4PF_6$	L1	CsF	MeCN	40	85	84
3	$Cu(MeCN)_4PF_6$	L2	CsF	MeCN	60	78	20
4	$Cu(MeCN)_4PF_6$	L3	CsF	MeCN	60	42	0
5	$Cu(MeCN)_4PF_6$	L4	CsF	MeCN	60	75	25
6	$Cu(MeCN)_4PF_6$	L5	CsF	MeCN	60	52	28
7	$Cu(MeCN)_4PF_6$	L6	KF+18-Crown-6	MeCN	40	87	89
8	$Cu(MeCN)_4PF_6$	L7	KF+18-Crown-6	MeCN	40	85	60
9	$Cu(MeCN)_4PF_6$	L8	KF+18-Crown-6	MeCN	40	74	67
10	$Cu(MeCN)_4PF_6$	L9	KF+18-Crown-6	MeCN	40	79	72
11	CuI	L6	KF+18-Crown-6	MeCN	40	94	79
12	CuOTf	L6	KF+18-Crown-6	MeCN	40	94	86
13	CuTc	L6	KF+18-Crown-6	MeCN	40	87	86
14	$Cu(MeCN)_4PF_6$	L6	KF+18-Crown-6	MeCN	25	82	86

[a]Reaction conditions: 3 (0.24 mmol, 1.2 equiv), terminal alkyne (0.20 mmol, 1.0 equiv), [Cu] (10 mol %), ligand (11 mol %), F⁻ (4.0 equiv), MeCN (2.0 mL), 12 h. [b]Isolated yields after silica gel column chromatography, [c]ee was determined by HPLC analysis.

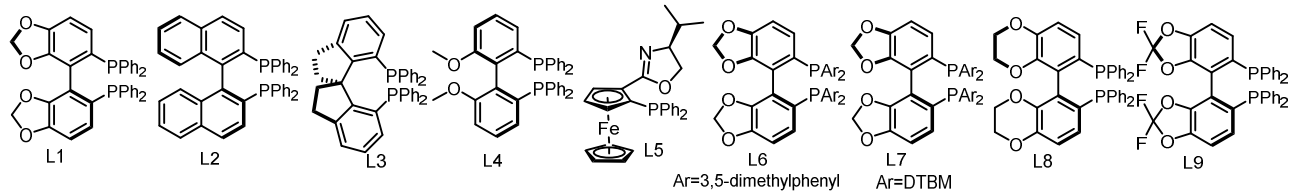
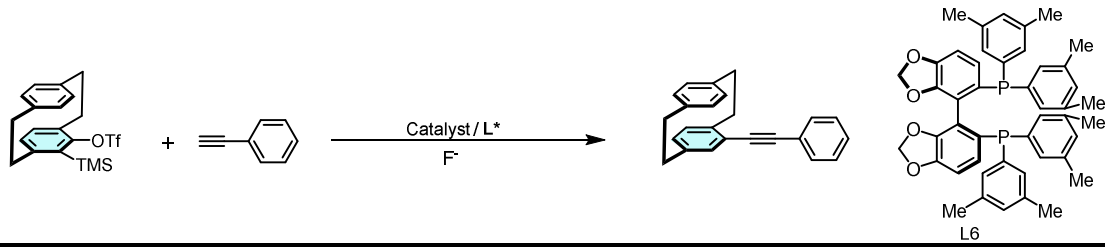


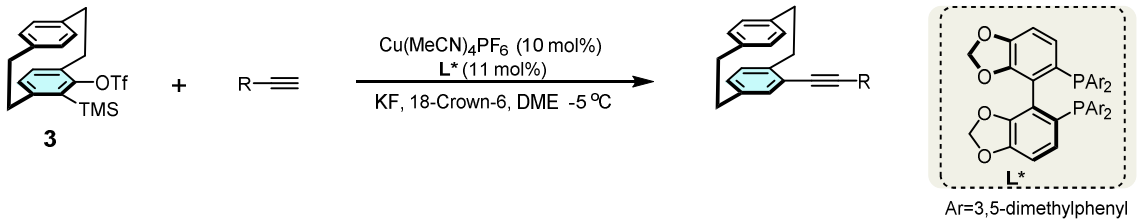
Table S2. Investigation of the Solvents and Temperature[a, b,c]



Entry	Catalyst	Ligand	F⁻	Solvent	Additive	T/℃	Yield/%	Ee/%
1	$Cu(MeCN)_4PF_6$	L6	KF+18-Crown-6	THF	-	40	94	85.6
2	$Cu(MeCN)_4PF_6$	L6	KF+18-Crown-6	THF	-	25	92	89.6
3	$Cu(MeCN)_4PF_6$	L6	KF+18-Crown-6	THF	NaBARF	25	96	89.4
4[d]	$Cu(MeCN)_4PF_6$	L6	KF+18-Crown-6	THF	-	0	91	92.8
5[d]	$Cu(MeCN)_4PF_6$	L6	KF+18-Crown-6	THF	-	-10	81	95
6[d]	$Cu(MeCN)_4PF_6$	L6	TBAF	THF	-	-20	N.P.	N/A
7[d]	$Cu(MeCN)_4PF_6$	L6	KF+18-Crown-6	DME	-	-10	88	95
8[d]	**$Cu(MeCN)_4PF_6$**	**L6**	**KF+18-Crown-6**	**DME**	**-**	**-5**	**92**	**95**
9[d]	$Cu(MeCN)_4PF_6$ 5%	L6 5.5%	KF+18-Crown-6	DME	-	-5	93	94
10[d]	$Cu(MeCN)_4PF_6$	L6	KF+18-Crown-6	CPME	-	-10	<5	ND
11[d]	$Cu(MeCN)_4PF_6$	L6	KF+18-Crown-6	MTBE	-	-10	NR	N/A

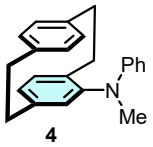
[a]Reaction conditions: 3 (0.24 mmol, 1.2 equiv), terminal alkyne (0.20 mmol, 1.0 equiv), [Cu] (10 mol %), ligand (11 mol %), F⁻ (4.0 equiv), MeCN (2.0 mL), 12 h. [b]Isolated yields after silica gel column chromatography, [c]ee was determined by HPLC analysis, [d]The reaction time is 24 h.

5. General Procedure



To a flame-dried and Nitrogen-purged Schlenk tube were added $Cu(CH_3CN)_4PF_6$ (0.02 mmol, 7.4 mg), (S)-(-)-DM-SEGPHOS (0.022 mmol, 15.9 mg), KF (0.8 mmol, 46.7 mg), 18-Crown-6 (0.8 mmol, 211 mg) and a stirring bar. The Schlenk tube was then evacuated and filled with N_2. This cycle was repeated three times and followed by addition of 1,2-Dimethoxyehtane (1 mL). The mixture was stirred at room temperature for 15 min before cooled to -5 °C. Then a solution of **3** (0.24 mmol, 102.8 mg), Alkyne (0.2 mmol) in 1,2-Dimethoxyethane (1 mL) was added via syringe. The resulting mixture was stirred vigorously at -5 °C for 24 h. Afterward, the solvent was removed under vacuum. The pure product was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 50:1 to 20:1) to afford the target molecule.

6. Characterization data of the products



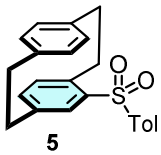
4

Pale yellow solid, 60.2 mg, 96% yield.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.25 – 7.18 (m, 2H), 7.01 (d, *J* = 7.7 Hz, 2H), 6.92 (t, *J* = 7.3 Hz, 1H), 6.79 (dd, *J* = 7.8, 1.7 Hz, 1H), 6.61 (dd, *J* = 7.8, 1.7 Hz, 1H), 6.54 – 6.50 (m, 2H), 6.39 (d, *J* = 7.6 Hz, 1H), 6.35 (dd, *J* = 7.6, 1.5 Hz, 1H), 6.07 – 5.95 (m, 1H), 3.43 (s, 3H), 3.14 – 3.04 (m, 3H), 3.04 – 2.90 (m, 3H), 2.66 (ddd, *J* = 13.5, 9.0, 2.8 Hz, 1H), 2.51 (ddd, *J* = 13.8, 9.8, 6.9 Hz, 1H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 150.82, 145.70, 141.01, 140.22, 138.95, 136.35, 133.79, 133.14, 133.05, 133.00, 131.22, 129.60, 129.15, 127.69, 123.97, 121.12, 119.58, 40.76, 35.52, 35.45, 35.08, 34.61.

HRMS (ESI) Calculated for $C_{23}H_{24}N$ $[M+H]^+$: 314.1904; Found: 314.1902.



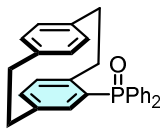
5

Pale yellow solid, 60.2 mg, 94% yield.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.64 (d, *J* = 8.3 Hz, 2H), 7.38 (d, *J* = 1.9 Hz, 1H), 7.21 (d, *J* = 8.1 Hz, 2H), 6.85 (dd, *J* = 7.8, 1.9 Hz, 1H), 6.65 (dd, *J* = 7.8, 1.9 Hz, 1H), 6.56 (qd, *J* = 7.8, 1.9 Hz, 2H), 6.51 (dd, *J* = 7.9, 1.9 Hz, 1H), 6.47 (d, *J* = 7.6 Hz, 1H), 3.88 (ddd, *J* = 12.7, 10.5, 2.0 Hz, 1H), 3.43 (ddd, *J* = 12.6, 10.4, 5.6 Hz, 1H), 3.28 – 3.17 (m, 2H), 3.14 (ddd, *J* = 12.6, 10.6, 2.0 Hz, 1H), 3.10 – 2.98 (m, 2H), 2.86 (ddd, *J* = 13.0, 10.6, 5.6 Hz, 1H), 2.35 (s, 3H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 143.66, 141.42, 140.03, 139.73, 139.54, 139.38, 138.19, 137.96, 137.78, 133.67, 132.86, 132.50, 132.46, 132.13, 129.69, 127.22, 35.76, 35.25, 35.10, 35.06, 21.60.

HRMS (ESI) Calculated for $C_{23}H_{23}O_2S$ $[M+H]^+$: 363.1414; Found: 363.1414.



6

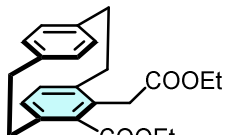
Colourless solid, 77.6 mg, 95% yield.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.70 (ddd, *J* = 11.5, 8.3, 1.5 Hz, 2H), 7.55 (ddt, *J* = 11.7, 6.7, 1.4 Hz, 3H), 7.50 – 7.43 (m, 3H), 7.37 (ddd, *J* = 8.4, 6.7, 2.9 Hz, 2H), 7.18 (dd, *J* = 7.9, 1.9 Hz, 1H), 6.63 (dt, *J* = 7.8, 1.4 Hz, 3H), 6.61 – 6.48 (m, 1H), 6.35 – 6.19 (m, 1H), 3.63 – 3.43 (m, 2H), 3.10 (dddd, *J* = 13.0, 10.5, 8.1, 2.9 Hz, 2H), 3.04 – 2.92 (m, 2H), 2.92 – 2.82 (m, 1H), 2.75 (ddd, *J* = 13.2, 10.4, 5.2 Hz, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 146.26, 146.18, 140.16, 139.67, 139.54, 139.09, 137.07, 137.04, 137.00, 136.88, 136.30, 136.18, 135.85, 134.94, 134.82, 133.38, 132.86, 132.47, 132.35, 132.24, 132.15, 131.97, 131.60, 131.57, 131.51, 131.49, 130.76, 129.71, 128.52, 128.42, 128.40, 128.30, 35.79, 35.74, 35.26, 35.18.

^{31}P NMR (162 MHz, Chloroform-*d*) δ 26.98.

HRMS (ESI) Calculated for $C_{28}H_{26}OP$ $[M+H]^+$: 409.1716; Found: 409.1720.



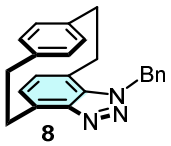
7

White solid, 55.7 mg, 76% yield.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 6.78 (dd, *J* = 7.9, 1.8 Hz, 1H), 6.57 (dt, *J* = 9.8, 7.9 Hz, 3H), 6.50 (dd, *J* = 9.7, 7.2 Hz, 2H), 4.33 (q, *J* = 7.1 Hz, 2H), 4.09 (q, *J* = 7.1 Hz, 2H), 3.65 (d, *J* = 16.5 Hz, 1H), 3.53 (d, *J* = 16.4 Hz, 1H), 3.39 – 3.30 (m, 1H), 3.26 (ddd, *J* = 13.1, 10.4, 2.9 Hz, 1H), 3.20 – 3.09 (m, 2H), 3.08 – 2.99 (m, 2H), 2.92 (tdd, *J* = 14.1, 12.3, 7.5 Hz, 2H), 1.37 (t, *J* = 7.2 Hz, 3H), 1.21 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 170.91, 168.99, 139.72, 139.47, 139.36, 139.20, 136.50, 133.72, 133.34, 132.85, 132.46, 131.63, 131.35, 129.10, 60.85, 60.80, 36.70, 34.97, 34.28, 34.11, 33.29, 14.23.

HRMS (ESI) Calculated for $C_{23}H_{27}O_4$ $[M+H]^+$: 367.1904; Found: 367.1905.



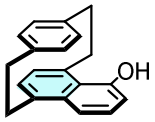
8

White solid, 61.1 mg, 90% yield.

^{1}H NMR (500 MHz, Chloroform-d) δ 7.30 – 7.22 (m, 3H), 7.17 – 7.03 (m, 2H), 6.66 – 6.54 (m, 2H), 6.42 (ddd, J = 45.4, 7.8, 1.5 Hz, 2H), 6.20 (d, J = 15.9 Hz, 1H), 5.96 (dd, J = 7.8, 1.6 Hz, 1H), 5.79 (dd, J = 7.8, 1.7 Hz, 1H), 5.59 (d, J = 15.9 Hz, 1H), 4.06 – 3.90 (m, 1H), 3.39 (dd, J = 13.7, 10.2 Hz, 1H), 3.23 – 3.09 (m, 2H), 3.09 – 2.99 (m, 2H), 2.93 (ddd, J = 14.2, 10.7, 6.8 Hz, 1H), 2.69 (ddd, J = 13.4, 10.1, 6.8 Hz, 1H), 1.42(s, 2H).

^{13}C NMR (126 MHz, Chloroform-d) δ 149.26, 139.00, 137.13, 135.95, 134.37, 134.17, 133.08, 132.56, 131.42, 129.32, 128.95, 128.30, 128.07, 126.88, 126.02, 123.27, 52.79, 35.17, 34.70, 32.37, 31.01, 27.02.

HRMS (ESI) Calculated for $C_{23}H_{22}N_3$ $[M+H]^+$: 340.1809; Found: 340.1809.



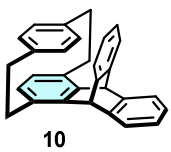
9

White solid, 46.1 mg, 84% yield.

^{1}H NMR (500 MHz, Chloroform-d) δ 7.30 (d, J = 8.3 Hz, 1H), 7.28 – 7.20 (m, 1H), 6.73 (d, J = 1.4 Hz, 2H), 6.70 – 6.64 (m, 1H), 6.54 – 6.43 (m, 2H), 5.81 – 5.70 (m, 2H), 5.10 (s, 1H), 4.29 (dd, J = 12.9, 9.5 Hz, 1H), 3.89 – 3.66 (m, 1H), 3.15 (dd, J = 24.3, 12.9 Hz, 2H), 3.10 – 3.03 (m, 1H), 3.02 – 2.91 (m, 2H), 2.87 (dt, J = 12.7, 8.8 Hz, 1H).

^{13}C NMR (126 MHz, Chloroform-d) δ 153.25, 139.02, 137.81, 137.77, 136.91, 135.77, 132.68, 132.29, 131.46, 131.11, 128.07, 127.89, 125.49, 125.25, 118.49, 110.24, 37.82, 35.01, 34.27, 33.52.

HRMS (ESI) Calculated for $C_{20}H_{18}O$ $[M+H]^+$: 275.1431; Found: 275.1430.



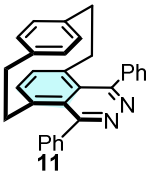
10

White solid, 72.7 mg, 94% yield.

^{1}H NMR (500 MHz, Chloroform-d) δ 7.59 (dd, J = 5.3, 3.2 Hz, 2H), 7.29 (dd, J = 5.3, 3.2 Hz, 2H), 7.21 (dd, J = 5.4, 3.1 Hz, 2H), 6.93 (dd, J = 5.4, 3.1 Hz, 2H), 6.71 – 6.51 (m, 2H), 6.15 (s, 2H), 5.54 (s, 2H), 5.36 – 5.22 (m, 2H), 3.49 (ddd, J = 14.1, 9.7, 5.0 Hz, 2H), 3.11 (ddd, J = 13.6, 10.1, 3.9 Hz, 2H), 3.07 – 2.93 (m, 4H).

^{13}C NMR (126 MHz, Chloroform-d) δ 146.45, 144.88, 141.74, 138.83, 133.74, 132.25, 131.42, 130.62, 125.30, 124.90, 124.78, 123.56, 50.77, 35.42, 31.92.

HRMS (ESI) Calculated for $C_{30}H_{25}$ $[M+H]^+$: 385.1951; Found: 385.1966.



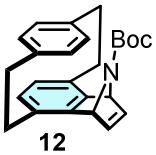
11

Yellow solid, 43.8 mg, 54% yield.

^{1}H NMR (500 MHz, Chloroform-d) δ 8.36 (s, 2H), 7.69 (d, J = 10.6 Hz, 2H), 7.54 (t, J = 7.4 Hz, 2H), 7.45 – 7.33 (m, 2H), 7.26 (s, 2H), 7.06 (s, 2H), 6.42 (s, 2H), 5.79 (s, 2H), 2.88 – 2.62 (m, 6H), 2.39 (ddd, J = 12.8, 9.3, 7.2 Hz, 2H).

^{13}C NMR (126 MHz, Chloroform-d) δ 156.90, 139.97, 138.86, 138.45, 136.79, 131.71, 129.29, 129.19, 128.35, 36.91, 35.02.

HRMS (ESI) Calculated for $C_{30}H_{25}N_2$ $[M+H]^+$: 413.2012; Found: 413.2103.



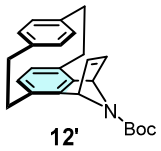
12

White solid, 13 mg, 17.4% yield.

^{1}H NMR (500 MHz, Chloroform-d) δ 6.95 (dd, J = 5.1, 1.8 Hz, 1H), 6.83 (dd, J = 5.1, 1.7 Hz, 1H), 6.62 (s, 2H), 6.54 (d, J = 7.6 Hz, 1H), 6.48 (d, J = 7.6 Hz, 1H), 6.02 (s, 2H), 5.53 (s, 1H), 5.41 (s, 1H), 3.21 – 3.09 (m, 4H), 2.98 (ddd, J = 23.8, 12.1, 3.1 Hz, 4H), 1.54 (s, 9H).

^{13}C NMR (126 MHz, Chloroform-d) δ 154.78, 146.17, 145.41, 145.19, 143.09, 139.35, 138.96, 132.53, 132.42, 132.26, 132.23, 132.06, 131.56, 80.50, 64.80, 63.93, 35.27, 35.11, 32.02, 28.63.

HRMS (ESI) Calculated for $C_{25}H_{28}NO_2$ $[M+H]^+$: 374.2115; Found: 374.2114.



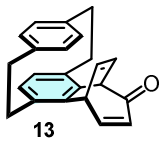
12'

White solid, 52 mg, 69.6% yield.

^{1}H NMR (500 MHz, Chloroform-d) δ 7.13 (d, J = 26.7 Hz, 2H), 6.79 – 6.57 (m, 2H), 6.02 (d, J = 1.5 Hz, 2H), 5.93 (s, 2H), 5.36 (d, J = 35.7 Hz, 2H), 3.24 – 3.04 (m, 4H), 2.91 (tdd, J = 12.6, 9.8, 5.2 Hz, 4H), 1.29 (s, 9H).

^{13}C NMR (126 MHz, Chloroform-d) δ 154.96, 144.52, 140.08, 139.14, 138.97, 138.73, 132.37, 131.39, 131.23, 80.36, 65.46, 64.77, 35.32, 32.26, 32.11, 28.17.

HRMS (ESI) Calculated for $C_{25}H_{28}NO_2$ $[M+H]^+$: 374.2115; Found: 374.2110.



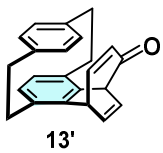
13

White solid, 21.5 mg, 34.4% yield.

^{1}H NMR (500 MHz, Chloroform-d) δ 7.08 (dd, J = 10.8, 8.7 Hz, 1H), 7.06 – 7.00 (m, 1H), 6.77 – 6.68 (m, 1H), 6.56 (s, 2H), 6.33 (s, 2H), 6.13 (d, J = 7.7 Hz, 1H), 6.09 (d, J = 7.8 Hz, 1H), 5.07 (dd, J = 10.8, 1.7 Hz, 1H), 4.88 – 4.74 (m, 1H), 4.47 (t, J = 7.6 Hz, 1H), 3.50 – 3.40 (m, 1H), 3.35 – 3.26 (m, 1H), 3.14 – 2.89 (m, 6H).

^{13}C NMR (126 MHz, Chloroform-d) δ 191.03, 153.10, 140.18, 139.12, 138.87, 137.51, 136.98, 134.49, 133.22, 133.16, 132.42, 132.32, 132.02, 131.94, 128.17, 125.04, 59.95, 42.01, 35.45, 35.30, 32.47, 31.87.

HRMS (ESI) Calculated for $C_{23}H_{21}O$ $[M+H]^+$: 313.1587; Found: 313.1587.



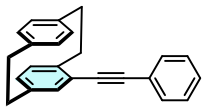
13'

White solid, 36.6 mg, 58.6% yield.

^{1}H NMR (500 MHz, Chloroform-d) δ 7.40 (dd, J = 10.9, 8.6 Hz, 1H), 6.84 – 6.78 (m, 1H), 6.77 – 6.70 (m, 2H), 6.52 – 6.43 (m, 1H), 6.38 (dd, J = 7.9, 1.4 Hz, 1H), 6.24 (s, 2H), 6.10 (dd, J = 7.9, 1.5 Hz, 1H), 5.83 – 5.60 (m, 1H), 4.73 (d, J = 7.0 Hz, 1H), 4.37 (t, J = 7.7 Hz, 1H), 3.41 – 3.27 (m, 1H), 3.24 – 2.95 (m, 7H).

^{13}C NMR (126 MHz, Chloroform-d) δ 191.86, 151.62, 140.60, 139.54, 139.45, 138.71, 138.43, 135.27, 134.10, 132.97, 132.83, 132.50, 132.45, 131.66, 130.97, 129.79, 127.07, 59.34, 41.02, 35.57, 35.09, 32.09, 31.83.

HRMS (ESI) Calculated for $C_{23}H_{21}O$ $[M+H]^+$: 313.1587; Found: 313.1590.



14

White solid, 56.5 mg, 92% yield, 95% e.e.

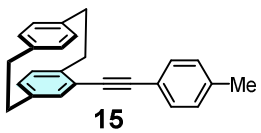
Chiral HPLC analysis of the product: Daicel Chiralpak OJ-H 250×4.6 mm 5u column; Hexane/ 2-propanol = 98/2, detected at 254 nm, Flow rate = 0.8 mL/min, Rentention times: 28.200 min (major), 23.040 min (minor).

^{1}H NMR (500 MHz, Chloroform-d) δ 7.65 – 7.57 (m, 2H), 7.45 – 7.35 (m, 3H), 7.05 (dd, J = 7.8, 1.7 Hz, 1H), 6.61 (d, J = 1.6 Hz, 1H), 6.56 (ddd, J = 7.8, 3.5, 1.8 Hz, 2H), 6.54 – 6.48 (m, 3H), 3.69 (ddd, J = 13.1, 10.4, 2.6 Hz, 1H), 3.28 (ddd, J = 13.0, 10.4, 5.5 Hz, 1H), 3.18 – 3.05 (m, 4H), 3.04 – 2.97 (m, 1H), 2.91 (ddd, J = 13.1, 10.6, 5.5 Hz, 1H).

^{13}C NMR (126 MHz, Chloroform-d) δ 142.61, 139.85, 139.65, 139.50, 137.14, 134.02, 133.44, 133.15, 132.90, 132.87, 132.58, 131.59, 130.20, 128.56, 128.23, 124.99, 124.01, 92.97, 89.87, 35.61, 35.27, 34.69, 34.47.

[α]D25 = 65.6 (c = 1.0, $CHCl_3$).

HRMS (EI) Calculated for $C_{24}H_{20}$ $[M]^+$: 308.1560; Found: 308.1568.



15

White solid, 58.6 mg, 91% yield, 96% e.e.

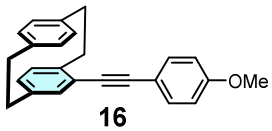
Chiral HPLC analysis of the product: Daicel Chiralpak OJ-H 250×4.6 mm 5u column; Hexane/ 2-propanol = 98/2, detected at 254 nm, Flow rate = 0.8 mL/min, Rentention times: 24.493 min (minor), 28.845 min (major).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.50 (d, *J* = 8.1 Hz, 2H), 7.21 (d, *J* = 7.8 Hz, 2H), 7.03 (dd, *J* = 7.8, 1.7 Hz, 1H), 6.58 (d, *J* = 1.6 Hz, 1H), 6.56 – 6.46 (m, 5H), 3.67 (ddd, *J* = 13.0, 10.4, 2.6 Hz, 1H), 3.26 (ddd, *J* = 13.0, 10.4, 5.5 Hz, 1H), 3.16 – 3.04 (m, 4H), 3.03 – 2.96 (m, 1H), 2.89 (ddd, *J* = 13.1, 10.6, 5.5 Hz, 1H), 2.41 (s, 3H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 142.52, 139.80, 139.68, 139.49, 138.36, 137.09, 133.99, 133.43, 132.85, 132.70, 132.58, 131.49, 130.18, 129.32, 125.21, 120.94, 93.15, 89.21, 35.62, 35.29, 34.71, 34.45, 21.68.

$[\alpha]_D^{25}$ = 90.6 (c = 1.0, $CHCl_3$).

HRMS (APCI) Calculated for $C_{25}H_{23}$ $[M+H]^+$: 323.1794; Found: 323.1796.



16

White solid, 89% yield, 98% e.e.

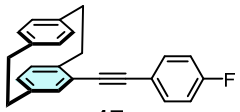
Chiral HPLC analysis of the product: Daicel Chiralpak OJ-H 250×4.6 mm 5u column; Hexane/ 2-propanol = 98/2, detected at 254 nm, Flow rate = 0.8 mL/min, Rentention times: 69.357 min (minor), 75.560 min (major).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.55 (d, *J* = 8.6 Hz, 2H), 7.10 – 7.02 (m, 1H), 6.95 (d, *J* = 8.6 Hz, 2H), 6.57 (dd, *J* = 6.9, 1.8 Hz, 2H), 6.56 – 6.48 (m, 4H), 3.87 (s, 3H), 3.68 (ddd, *J* = 12.9, 10.5, 2.3 Hz, 1H), 3.27 (ddd, *J* = 13.0, 10.5, 5.4 Hz, 1H), 3.18 – 3.05 (m, 4H), 3.04 – 2.97 (m, 1H), 2.90 (ddd, *J* = 13.0, 10.7, 5.4 Hz, 1H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 159.67, 142.35, 139.77, 139.66, 139.47, 136.99, 133.96, 133.42, 133.00, 132.84, 132.56, 132.55, 130.13, 125.33, 116.17, 114.22, 92.94, 88.54, 55.49, 35.61, 35.28, 34.71, 34.44.

$[\alpha]_D^{20}$ = 84.1 (c = 0.75, $CHCl_3$).

HRMS (ESI) Calculated for $C_{25}H_{23}O$ $[M+H]^+$: 339.1743; Found: 339.1745.



17

White solid, 53.5 mg, 82% yield, 95% e.e.

Chiral HPLC analysis of the product: Daicel Chiralpak OJ-H 250×4.6 mm 5u column; Hexane/ 2-propanol = 98.5/1.5, detected at 254 nm, Flow rate = 1 mL/min, Rentention times: 22.282 min (minor), 34.283 min (major).

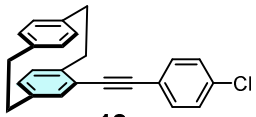
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.62 – 7.55 (m, 2H), 7.15 – 7.07 (m, 2H), 7.02 (dd, *J* = 7.8, 1.8 Hz, 1H), 6.59 (d, *J* = 1.8 Hz, 1H), 6.58 – 6.47 (m, 5H), 3.66 (ddd, *J* = 13.0, 10.3, 2.7 Hz, 1H), 3.26 (ddd, *J* = 13.0, 10.3, 5.5 Hz, 1H), 3.18 – 3.07 (m, 4H), 3.04 – 2.97 (m, 1H), 2.91 (ddd, *J* = 13.0, 10.4, 5.5 Hz, 1H).

^{19}F NMR (377 MHz, Chloroform-*d*) δ -111.23.

^{13}C NMR (101 MHz, Chloroform-*d*) δ 163.77, 161.30, 142.54, 139.88, 139.59, 139.52, 137.07, 134.04, 133.45, 133.44, 133.37, 133.14, 132.96, 132.89, 132.56, 130.16, 124.77, 120.07, 120.04, 115.94, 115.72, 91.80, 89.48, 35.59, 35.25, 34.65, 34.46.

$[\alpha]_D^{25}$ = 101.5 (c = 1.0, $CHCl_3$).

HRMS (APCI) Calculated for $C_{24}H_{20}F$ $[M+H]^+$: 327.1544; Found: 327.1541.



18

White solid, 51.3 mg, 75% yield, 96% e.e.

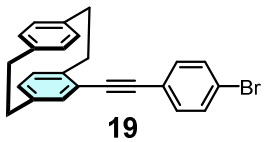
Chiral HPLC analysis of the product: Daicel Chiralpak OJ-H 250×4.6 mm 5u column; Hexane/ 2-propanol = 98/2, detected at 254 nm, Flow rate = 0.8 mL/min, Rentention times: 24.350 min (minor), 29.137 min (major).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.55 – 7.50 (m, 2H), 7.41 – 7.34 (m, 2H), 6.99 (dd, *J* = 7.8, 1.7 Hz, 1H), 6.59 (d, *J* = 1.7 Hz, 1H), 6.57 – 6.48 (m, 5H), 3.64 (ddd, *J* = 13.1, 10.4, 2.7 Hz, 1H), 3.24 (ddd, *J* = 13.1, 10.4, 5.5 Hz, 1H), 3.17 – 2.96 (m, 5H), 2.91 (ddd, *J* = 13.1, 10.6, 5.5 Hz, 1H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 142.65, 139.93, 139.58, 139.54, 137.11, 134.19, 134.08, 133.45, 133.15, 132.90, 132.78, 132.58, 130.22, 128.90, 124.63, 122.47, 91.77, 90.81, 35.60, 35.27, 34.67, 34.50.

$[\alpha]_D^{25}$ = 105.9 (c = 1.0, $CHCl_3$).

HRMS (APCI) Calculated for $C_{24}H_{20}Cl$ $[M+H]^+$: 343.1248; Found: 343.1261.



19

White solid, 52.0mg, 67% yield, 94% e.e.

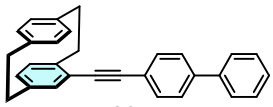
Chiral HPLC analysis of the product: Daicel Chiralpak OJ-H 250×4.6 mm 5u column; Hexane/ 2-propanol = 99.5/0.5, detected at 254 nm, Flow rate = 1 mL/min, Rentention times: 44.740 min (minor), 61.255 min (major).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.56 – 7.51 (m, 2H), 7.48 – 7.43 (m, 2H), 6.98 (dd, *J* = 7.8, 1.8 Hz, 1H), 6.59 (d, *J* = 1.8 Hz, 1H), 6.57 – 6.47 (m, 5H), 3.69 – 3.58 (m, 1H), 3.24 (ddd, *J* = 13.0, 10.2, 5.5 Hz, 1H), 3.17 – 2.96 (m, 5H), 2.90 (ddd, *J* = 13.0, 10.4, 5.5 Hz, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 142.65, 139.94, 139.57, 139.54, 137.10, 134.08, 133.45, 133.17, 133.15, 133.00, 132.90, 132.58, 131.81, 130.22, 124.61, 122.92, 122.37, 91.83, 91.00, 35.60, 35.26, 34.66, 34.49.

$[\alpha]_D^{25}$ = 71.1 (c = 2.1, $CHCl_3$).

HRMS (APCI) Calculated for $C_{24}H_{20}Br$ $[M+H]^+$: 387.0743, 389.0723; Found: 387.0743, 389.0726.



20

White solid, 55.4 mg, 72% yield, 98% e.e.

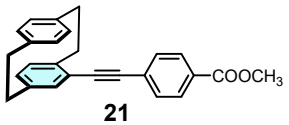
Chiral HPLC analysis of the product: Daicel Chiralpak OJ-H 250×4.6 mm 5u column; Hexane/ 2-propanol = 85/15, detected at 254 nm, Flow rate = 1 mL/min, Rentention times: 34.367 min (minor), 48.242 min (major).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.72 – 7.63 (m, 6H), 7.49 (t, *J* = 7.7 Hz, 2H), 7.43 – 7.36 (m, 1H), 7.06 (dd, *J* = 7.8, 1.7 Hz, 1H), 6.62 (d, *J* = 1.6 Hz, 1H), 6.59 – 6.50 (m, 5H), 3.71 (ddd, *J* = 13.1, 10.4, 2.6 Hz, 1H), 3.30 (ddd, *J* = 13.1, 10.4, 5.4 Hz, 1H), 3.20 – 2.99 (m, 5H), 2.93 (ddd, *J* = 13.1, 10.6, 5.4 Hz, 1H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 142.63, 140.99, 140.58, 139.88, 139.65, 139.51, 137.15, 134.04, 133.46, 132.93, 132.88, 132.60, 132.01, 130.23, 129.03, 127.77, 127.26, 127.19, 125.02, 122.92, 92.90, 90.61, 35.63, 35.29, 34.73, 34.50.

$[\alpha]_D^{25}$ = 61.4 (c = 1.0, $CHCl_3$).

HRMS (APCI) Calculated for $C_{30}H_{25}$ $[M+H]^+$: 385.1951; Found: 385.1955.



21

White solid, 46.2 mg, 63% yield, 94% e.e.

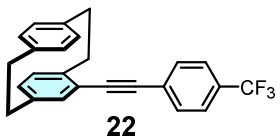
Chiral HPLC analysis of the product: Daicel Chiralpak IA 250×4.6 mm 5u column; Hexane/ 2-propanol = 96/4, detected at 254 nm, Flow rate = 1 mL/min, Rentention times: 7.293min (minor), 9.470 min (major).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.09 – 8.05 (m, 2H), 7.70 – 7.61 (m, 2H), 6.99 (dd, *J* = 7.8, 1.6 Hz, 1H), 6.62 (d, *J* = 1.7 Hz, 1H), 6.59 – 6.47 (m, 5H), 3.96 (s, 3H), 3.67 (ddd, *J* = 13.1, 10.4, 2.7 Hz, 1H), 3.26 (ddd, *J* = 13.1, 10.4, 5.4 Hz, 1H), 3.18 – 2.98 (m, 5H), 2.93 (ddd, *J* = 13.1, 10.6, 5.4 Hz, 1H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 166.74, 142.88, 140.00, 139.56, 139.54, 137.24, 134.12, 133.46, 132.90, 132.60, 131.46, 130.31, 129.75, 129.43, 128.71, 124.40, 92.95, 92.21, 52.38, 35.60, 35.27, 34.67, 34.54.

$[\alpha]_D^{25}$ = 83.0 (c = 1.0, $CHCl_3$).

HRMS (APCI) Calculated for $C_{26}H_{23}O_2$ $[M+H]^+$: 367.1693; Found: 367.1695.



22

White solid, 61 mg, 81% yield, 95% e.e.

Chiral HPLC analysis of the product: Daicel Chiralpak IA 250×4.6 mm 5u column; Hexane = 100%, detected at 254 nm, Flow rate = 1 mL/min, Rentention times: 14.320min (minor), 16.580 min (major).

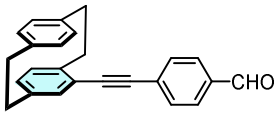
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.68 (q, *J* = 8.3 Hz, 4H), 6.98 (dd, *J* = 7.8, 1.6 Hz, 1H), 6.62 (d, *J* = 1.7 Hz, 1H), 6.60 – 6.47 (m, 5H), 3.66 (ddd, *J* = 13.1, 10.4, 2.7 Hz, 1H), 3.25 (ddd, *J* = 13.1, 10.4, 5.5 Hz, 1H), 3.18 – 3.06 (m, 4H), 3.05 – 2.98 (m, 1H), 2.93 (ddd, *J* = 13.2, 10.6, 5.5 Hz, 1H).

^{19}F NMR (471 MHz, Chloroform-*d*) δ -62.68;

^{13}C NMR (126 MHz, Chloroform-*d*) δ 142.89, 140.03, 139.57, 139.54, 137.24, 134.14, 133.52, 133.47, 132.93, 132.59, 131.77, 130.26, 125.52, 125.49, 124.24, 92.30, 91.51, 35.59, 35.26, 34.66, 34.53.

$[\alpha]_D^{25}$ = 86.7 (c = 1.0, $CHCl_3$).

HRMS (APCI) Calculated for $C_{25}H_{20}F_3$ $[M+H]^+$: 377.1512; Found: 377.1512.



23

White solid, 53.1 mg, 79% yield, 95% e.e.

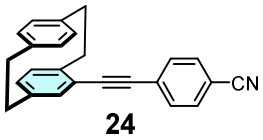
Chiral HPLC analysis of the product: Daicel Chiralpak OJ-H 250×4.6 mm 5u column; Hexane/ 2-propanol = 70/30, detected at 254 nm, Flow rate = 1 mL/min, Rentention times: 19.292 min (minor), 27.383 min (major).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 10.05 (s, 1H), 7.92 (d, *J* = 8.2 Hz, 2H), 7.74 (d, *J* = 8.0 Hz, 2H), 6.98 (dd, *J* = 7.9, 1.8 Hz, 1H), 6.64 (d, *J* = 1.9 Hz, 1H), 6.54 (dddd, *J* = 19.5, 11.6, 7.8, 1.9 Hz, 5H), 3.67 (ddd, *J* = 13.2, 10.3, 2.8 Hz, 1H), 3.26 (ddd, *J* = 13.0, 10.2, 5.4 Hz, 1H), 3.19 – 3.00 (m, 5H), 2.99 – 2.89 (m, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 191.57, 142.98, 140.05, 139.55, 139.49, 137.25, 135.36, 134.15, 133.68, 133.45, 132.91, 132.57, 132.03, 130.31, 130.27, 129.81, 124.14, 94.08, 92.09, 35.56, 35.23, 34.63, 34.53.

$[\alpha]_D^{25}$ = 97.7 (c = 1.0, $CHCl_3$).

HRMS (ESI) Calculated for $C_{25}H_{21}O$ $[M+H]^+$: 337.1587; Found: 337.1587.



24

White solid, 48.0 mg, 72% yield, 95% e.e.

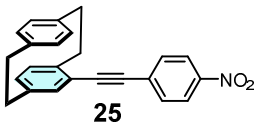
Chiral HPLC analysis of the product: Daicel Chiralpak OJ-H 250×4.6 mm 5u column; Hexane/ 2-propanol = 80/20, detected at 254 nm, Flow rate = 1 mL/min, Rentention times: 27.367 min (minor), 43.035 min (major).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.72 – 7.62 (m, 4H), 6.94 (dd, *J* = 7.9, 1.8 Hz, 1H), 6.62 (d, *J* = 1.9 Hz, 1H), 6.61 – 6.45 (m, 5H), 3.63 (ddd, *J* = 13.1, 10.2, 3.0 Hz, 1H), 3.23 (ddd, *J* = 13.1, 10.1, 5.5 Hz, 1H), 3.18 – 3.00 (m, 5H), 2.99 – 2.89 (m, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 142.99, 140.10, 139.57, 139.43, 137.23, 134.18, 133.83, 133.46, 132.93, 132.56, 132.25, 132.01, 130.28, 128.86, 123.87, 118.76, 111.31, 94.37, 91.26, 35.55, 35.22, 34.60, 34.53.

$[\alpha]_D^{25}$ = 89.8 (c = 1.0, $CHCl_3$).

HRMS (APCI) Calculated for $C_{25}H_{20}N$ $[M+H]^+$: 334.1591; Found: 334.1593.



25

Yellow solid, 61.3 mg, 87% yield, 95% e.e.

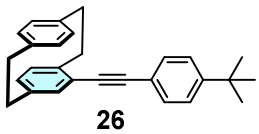
Chiral HPLC analysis of the product: Daicel Chiralpak OJ-H 250×4.6 mm 5u column; Hexane/ 2-propanol = 80/20, detected at 254 nm, Flow rate = 1 mL/min, Rentention times: 30.803 min (minor), 36.708 min (major).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.31 – 8.22 (m, 2H), 7.78 – 7.68 (m, 2H), 6.93 (dd, *J* = 7.8, 1.8 Hz, 1H), 6.64 (d, *J* = 1.9 Hz, 1H), 6.61 – 6.47 (m, 5H), 3.64 (ddd, *J* = 13.1, 10.2, 3.0 Hz, 1H), 3.28 – 3.19 (m, 1H), 3.19 – 3.03 (m, 5H), 3.02 – 2.90 (m, 1H);

^{13}C NMR (101 MHz, Chloroform-*d*) δ 146.97, 143.14, 140.19, 139.62, 139.45, 137.31, 134.25, 134.04, 133.49, 132.97, 132.61, 132.20, 130.94, 130.37, 123.90, 123.78, 95.41, 91.13, 35.58, 35.26, 34.64, 34.60.

$[\alpha]_D^{25}$ = 68.0 (c = 2.0, $CHCl_3$).

HRMS (APCI) Calculated for $C_{24}H_{20}NO_2$ $[M+H]^+$: 353.1489; Found: 354.1496.



26

White solid, 65.6 mg, 90% yield, 93% e.e.

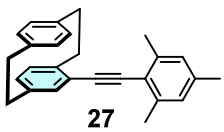
Chiral HPLC analysis of the product: Daicel Chiralpak OJ-H 250×4.6 mm 5u column; Hexane/ 2-propanol = 98/2, detected at 254 nm, Flow rate = 0.8 mL/min, Rentention times: 15.755 min (major), 30.502 min (minor).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.64 – 7.51 (m, 2H), 7.50 – 7.40 (m, 2H), 7.05 (dd, *J* = 7.8, 1.7 Hz, 1H), 6.59 (d, *J* = 1.7 Hz, 1H), 6.58 – 6.39 (m, 5H), 3.69 (ddd, *J* = 13.0, 10.4, 2.5 Hz, 1H), 3.27 (ddd, *J* = 13.0, 10.4, 5.5 Hz, 1H), 3.19 – 2.98 (m, 5H), 2.90 (ddd, *J* = 13.1, 10.6, 5.5 Hz, 1H), 1.38 (s, 9H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 151.51, 142.53, 139.79, 139.66, 139.48, 137.11, 133.97, 133.43, 133.14, 132.85, 132.69, 132.55, 131.32, 130.15, 125.57, 125.21, 120.98, 93.13, 89.24, 35.60, 35.26, 34.95, 34.71, 34.42, 31.36.

$[\alpha]_D^{25}$ = 65.0 (c = 1.0, $CHCl_3$).

HRMS (APCI) Calculated for $C_{28}H_{29}$ $[M+H]^+$: 365.2264; Found: 365.2264.



27

White solid, 68.7 mg, 98% yield, 86% e.e.

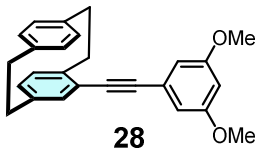
Chiral HPLC analysis of the product: Daicel Chiralpak IA 250×4.6 mm 5u column; Hexane = 100%, detected at 254 nm, Flow rate = 1 mL/min, Rentention times: 10.545 min (major), 12.137 min (minor).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.13 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.01 (s, 2H), 6.64 (d, *J* = 1.7 Hz, 1H), 6.62 – 6.47 (m, 5H), 3.76 (ddd, *J* = 13.0, 10.4, 2.6 Hz, 1H), 3.33 (ddd, *J* = 12.9, 10.4, 5.2 Hz, 1H), 3.19 – 3.03 (m, 5H), 2.96 (ddd, *J* = 13.0, 10.6, 5.2 Hz, 1H), 2.64 (s, 6H), 2.39 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 141.83, 140.09, 139.86, 139.58, 139.50, 137.75, 137.24, 133.96, 133.50, 133.12, 132.82, 132.62, 132.54, 130.02, 127.84, 125.74, 120.71, 97.69, 90.76, 35.58, 35.23, 34.64, 34.32, 21.47, 21.39.

$[\alpha]_D^{25}$ = 143.2 (c = 1.0, $CHCl_3$).

HRMS (ESI) Calculated for $C_{27}H_{27}$ $[M+H]^+$: 351.2108; Found: 351.2105.



28

White solid, 69.3 mg, 94% yield, 93% e.e.

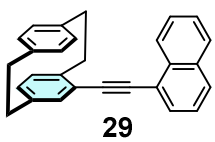
Chiral HPLC analysis of the product: Daicel Chiralpak IA 250×4.6 mm 5u column; Hexane/ 2-propanol = 98/2, detected at 254 nm, Flow rate = 1 mL/min, Rentention times: 7.687 min (minor), 9.793 min (major).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.04 (dd, *J* = 7.8, 1.8 Hz, 1H), 6.78 (d, *J* = 2.3 Hz, 2H), 6.61 (d, *J* = 1.9 Hz, 1H), 6.59 – 6.47 (m, 6H), 3.87 (s, 6H), 3.68 (ddd, *J* = 13.1, 10.3, 2.7 Hz, 1H), 3.28 (ddd, *J* = 13.0, 10.3, 5.4 Hz, 1H), 3.19 – 2.98 (m, 5H), 2.92 (ddd, *J* = 13.0, 10.5, 5.5 Hz, 1H);

^{13}C NMR (101 MHz, Chloroform-*d*) δ 160.74, 142.66, 139.83, 139.60, 139.46, 137.13, 134.00, 133.41, 132.97, 132.84, 132.55, 130.21, 125.25, 124.76, 109.41, 101.45, 92.90, 89.42, 55.58, 35.56, 35.23, 34.66, 34.45.

$[\alpha]_D^{25}$ = 85.9 (c = 1.0, $CHCl_3$).

HRMS (ESI) Calculated for $C_{26}H_{25}O_2$ $[M+H]^+$: 369.1849; Found: 369.1849.



29

White solid, 57.4 mg, 80% yield, 92% e.e.

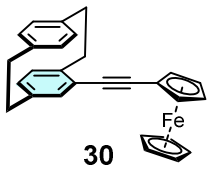
Chiral HPLC analysis of the product: Daicel Chiralpak OJ-H 250×4.6 mm 5u column; Hexane/ Ethanol = 99/1, detected at 254 nm, Flow rate = 0.8 mL/min, Rentention times: 23.827 min (major), 29.888 min (minor).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.57 (d, *J* = 8.3 Hz, 1H), 8.02 – 7.83 (m, 1H), 7.70 (ddd, *J* = 8.2, 6.9, 1.2 Hz, 1H), 7.61 (td, *J* = 7.5, 6.9, 1.1 Hz, 1H), 7.54 (dd, *J* = 8.1, 7.2 Hz, 1H), 7.12 (dd, *J* = 7.8, 1.5 Hz, 1H), 6.75 (d, *J* = 1.5 Hz, 1H), 6.65 – 6.53 (m, 5H), 3.84 (ddd, *J* = 13.1, 10.5, 2.6 Hz, 1H), 3.37 (ddd, *J* = 13.1, 10.5, 5.3 Hz, 1H), 3.25 – 3.06 (m, 5H), 3.06 – 2.97 (m, 1H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 142.49, 139.99, 139.63, 139.56, 137.35, 134.11, 133.50, 133.44, 133.41, 133.07, 132.90, 132.62, 130.43, 130.30, 128.69, 128.54, 126.98, 126.59, 126.34, 125.53, 125.14, 121.67, 94.79, 91.05, 35.63, 35.30, 34.85, 34.55.

$[\alpha]_D^{25}$ = 103.6 (c = 1.0, $CHCl_3$).

HRMS (APCI) Calculated for $C_{28}H_{23}$ $[M+H]^+$: 359.1794; Found: 359.1799.



30

Red solid, 68.3 mg, 82% yield, 95% e.e.

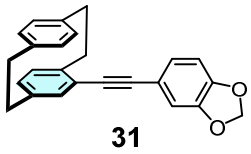
Chiral HPLC analysis of the product: Daicel Chiralpak IA 250×4.6 mm 5u column; Hexane/ 2-propanol = 98/2, detected at 254 nm, Flow rate = 0.8 mL/min, Rentention times: 8.452 min (minor), 14.162 min (major).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.08 (dd, *J* = 7.7, 1.7 Hz, 1H), 6.60 – 6.45 (m, 6H), 4.61 – 4.52 (m, 2H), 4.31 (s, 5H), 4.29 (t, *J* = 1.7 Hz, 2H), 3.65 (ddd, *J* = 13.0, 10.4, 2.5 Hz, 1H), 3.28 (ddd, *J* = 13.0, 10.4, 5.4 Hz, 1H), 3.17 – 3.10 (m, 2H), 3.09 – 3.04 (m, 2H), 3.03 – 2.96 (m, 1H), 2.88 (ddd, *J* = 13.0, 10.6, 5.4 Hz, 1H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 142.15, 139.77, 139.64, 139.52, 136.97, 133.94, 133.47, 132.88, 132.56, 132.26, 129.94, 125.70, 91.78, 86.17, 71.51, 71.43, 70.00, 68.93, 66.18, 35.63, 35.27, 34.74, 34.36.

$[\alpha]_D^{25}$ = 79.0 (c = 1.0, $CHCl_3$).

HRMS (ESI) Calculated for $C_{28}H_{25}Fe$ $[M+H]^+$: 417.1301; Found: 417.1300.



31

White solid, 63.4 mg, 90% yield, 92% e.e.

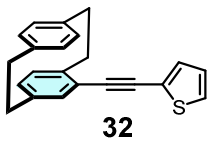
Chiral HPLC analysis of the product: Daicel Chiralpak IA 250×4.6 mm 5u column; Hexane/ 2-propanol = 99/1, detected at 254 nm, Flow rate = 1 mL/min, Rentention times: 11.480 min (minor), 17.168 min (major).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.13 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.05 (d, *J* = 1.6 Hz, 1H), 7.02 (dd, *J* = 7.8, 1.9 Hz, 1H), 6.85 (d, *J* = 8.0 Hz, 1H), 6.59 – 6.45 (m, 6H), 6.02 (s, 2H), 3.64 (ddd, *J* = 13.0, 10.2, 2.7 Hz, 1H), 3.24 (ddd, *J* = 13.0, 10.2, 5.5 Hz, 1H), 3.16 – 2.96 (m, 5H), 2.88 (ddd, *J* = 13.0, 10.4, 5.5 Hz, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 147.92, 147.67, 142.45, 139.82, 139.64, 139.50, 137.01, 134.00, 133.42, 132.86, 132.69, 132.55, 130.15, 126.13, 125.08, 117.28, 111.57, 108.71, 101.48, 92.89, 88.27, 35.61, 35.27, 34.69, 34.46.

$[\alpha]_D^{25}$ = 79.1 (c = 2.0, $CHCl_3$).

HRMS (ESI) Calculated for $C_{25}H_{21}O_2$ $[M+H]^+$: 353.1537; Found: 353.1537.



32

White solid, 53.4 mg, 85% yield, 95% e.e.

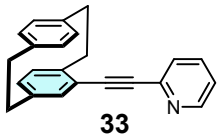
Chiral HPLC analysis of the product: Daicel Chiralpak IA 250×4.6 mm 5u column; Hexane/ Ethanol = 99/1, detected at 254 nm, Flow rate = 0.8 mL/min, Rentention times: 6.468 min (minor), 7.735 min (major).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.33 (d, *J* = 4.1 Hz, 2H), 7.07 (t, *J* = 4.2 Hz, 1H), 7.01 (d, *J* = 7.7 Hz, 1H), 6.58 (s, 1H), 6.56 – 6.46 (m, 5H), 3.67 – 3.58 (m, 1H), 3.25 (td, *J* = 11.8, 10.5, 5.4 Hz, 1H), 3.18 – 3.04 (m, 4H), 3.03 – 2.96 (m, 1H), 2.94 – 2.75 (m, 1H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 142.54, 139.90, 139.63, 139.49, 136.84, 134.06, 133.43, 133.14, 133.07, 132.85, 132.57, 131.51, 130.26, 127.33, 127.15, 124.63, 124.02, 93.57, 86.04, 35.58, 35.25, 34.67, 34.47.

$[\alpha]_D^{25}$ = 119.0 (c = 1.0, $CHCl_3$).

HRMS (APCI) Calculated for $C_{22}H_{19}S$ $[M+H]^+$: 315.1202; Found: 315.1212.



33

Brown solid, 41.5mg, 67% yield, 94% e.e.

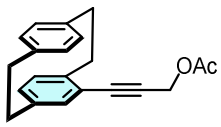
Chiral HPLC analysis of the product: Daicel Chiralpak IA 250×4.6 mm 5u column; Hexane/ Ethanol = 90/10, detected at 254 nm, Flow rate = 1 mL/min, Rentention times: 8.155 min (minor), 10.100 min (major).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.73 – 8.55 (m, 1H), 7.72 (td, *J* = 7.7, 1.8 Hz, 1H), 7.58 (d, *J* = 7.8 Hz, 1H), 7.27 (td, *J* = 5.1, 2.5 Hz, 1H), 7.02 (dd, *J* = 7.8, 1.5 Hz, 1H), 6.70 (d, *J* = 1.7 Hz, 1H), 6.64 – 6.41 (m, 5H), 3.71 (ddd, *J* = 13.2, 10.5, 2.8 Hz, 1H), 3.30 (ddd, *J* = 13.1, 10.5, 5.2 Hz, 1H), 3.18 – 2.98 (m, 5H), 2.98 – 2.90 (m, 1H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 150.30, 144.13, 143.21, 139.97, 139.62, 139.51, 137.54, 136.26, 134.09, 133.71, 133.40, 132.82, 132.70, 130.52, 127.32, 123.95, 122.67, 92.26, 89.73, 35.59, 35.27, 34.65, 34.57.

$[\alpha]_D^{25}$ = 125.8 (c = 1.0, $CHCl_3$).

HRMS (ESI) Calculated for $C_{23}H_{20}N$ $[M+H]^+$: 310.1591; Found: 310.1589.



34

White solid, 60.3 mg, 99% yield, 96% e.e.

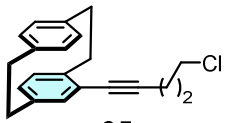
Chiral HPLC analysis of the product: Daicel Chiralpak OJ-H 250×4.6 mm 5u column; Hexane/ 2-propanol = 95/5, detected at 254 nm, Flow rate = 0.8 mL/min, Rentention times: 33.935 min (minor), 38.992 min (major).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 6.94 (dd, *J* = 7.8, 1.7 Hz, 1H), 6.60 – 6.42 (m, 6H), 5.00 (s, 2H), 3.60 – 3.47 (m, 1H), 3.20 (ddd, *J* = 13.0, 10.4, 5.3 Hz, 1H), 3.15 – 3.02 (m, 4H), 3.02 – 2.93 (m, 1H), 2.85 (ddd, *J* = 13.1, 10.6, 5.3 Hz, 1H), 2.19 (s, 3H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 170.56, 142.99, 139.81, 139.62, 139.46, 137.37, 133.98, 133.43, 133.38, 132.85, 132.57, 130.11, 123.86, 86.75, 86.34, 53.25, 35.54, 35.20, 34.44, 34.30, 20.99.

$[\alpha]_D^{25}$ = 112.0 (c = 1.0, $CHCl_3$).

HRMS (ESI) Calculated for $C_{21}H_{21}O_2$ $[M+H]^+$: 305.1537; Found: 305.1537.



35

White solid, 53.1 mg, 86% yield, 81% e.e.

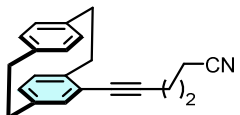
Chiral HPLC analysis of the product: Daicel Chiralpak IA 250×4.6 mm 5u column; Hexane/ 2-propanol = 99/1, detected at 254 nm, Flow rate = 1 mL/min, Rentention times: 5.997 min (minor), 7.640 min (major).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 6.97 (dd, *J* = 7.8, 1.8 Hz, 1H), 6.54 (dd, *J* = 7.8, 1.8 Hz, 1H), 6.51 – 6.43 (m, 5H), 3.82 (t, *J* = 6.3 Hz, 2H), 3.54 (ddd, *J* = 13.1, 10.4, 2.7 Hz, 1H), 3.19 (ddd, *J* = 13.0, 10.4, 5.4 Hz, 1H), 3.14 – 3.02 (m, 4H), 3.00 – 2.93 (m, 1H), 2.84 (ddd, *J* = 13.0, 10.5, 5.4 Hz, 1H), 2.74 (t, *J* = 6.8 Hz, 2H), 2.20 – 2.08 (m, 2H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 142.19, 139.68, 139.58, 139.47, 137.23, 133.85, 133.39, 133.13, 132.84, 132.52, 132.36, 129.89, 125.28, 91.25, 81.82, 43.99, 35.57, 35.21, 34.52, 34.35, 31.79, 17.24.

$[\alpha]_D^{25}$ = 91.9 (c = 1.0, $CHCl_3$).

HRMS (APCI) Calculated for $C_{21}H_{22}Cl$ $[M+H]^+$: 309.1405; Found: 309.1406.



36

White solid, 57.5 mg, 96% yield, 84% e.e.

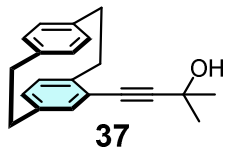
Chiral HPLC analysis of the product: Daicel Chiralpak IA 250×4.6 mm 5u column; Hexane/ 2-propanol = 95/5, detected at 254 nm, Flow rate = 1 mL/min, Rentention times: 8.912 min (minor), 12.282 min (major).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.93 (dd, *J* = 7.8, 1.9 Hz, 1H), 6.56 – 6.48 (m, 3H), 6.46 (d, *J* = 1.9 Hz, 2H), 6.45 – 6.43 (m, 1H), 3.51 (ddd, *J* = 13.1, 10.2, 3.0 Hz, 1H), 3.21 – 3.02 (m, 5H), 3.01 – 2.93 (m, 1H), 2.85 (ddd, *J* = 13.0, 10.3, 5.5 Hz, 1H), 2.72 (t, *J* = 6.8 Hz, 2H), 2.62 (t, *J* = 7.2 Hz, 2H), 2.11 – 2.00 (m, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 142.15, 139.74, 139.47, 137.20, 133.88, 133.37, 132.84, 132.60, 132.51, 129.87, 124.85, 119.30, 90.03, 82.59, 35.52, 35.17, 34.45, 34.36, 25.01, 18.89, 16.42.

$[\alpha]_D^{25}$ = 117.0 (c = 1.0, $CHCl_3$).

HRMS (APCI) Calculated for $C_{22}H_{22}N$ $[M+H]^+$: 300.1747; Found: 300.1758.



37

White solid, 52.8 mg, 91% yield, 95% e.e.

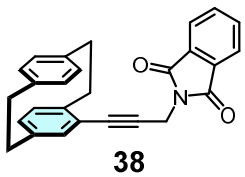
Chiral HPLC analysis of the product: Daicel Chiralpak OJ-H 250×4.6 mm 5u column; Hexane/ 2-propanol = 80/20, detected at 254 nm, Flow rate = 1 mL/min, Rentention times: 6.553 min (minor), 7.782 min (major).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.97 (dd, *J* = 7.8, 1.8 Hz, 1H), 6.56 – 6.42 (m, 6H), 3.54 (ddd, *J* = 13.0, 10.1, 2.8 Hz, 1H), 3.19 (ddd, *J* = 13.0, 10.1, 5.7 Hz, 1H), 3.14 – 3.01 (m, 4H), 3.00 – 2.91 (m, 1H), 2.83 (ddd, *J* = 13.0, 10.4, 5.7 Hz, 1H), 1.72 (d, *J* = 4.7 Hz, 6H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 142.48, 139.74, 139.54, 139.49, 137.11, 133.91, 133.43, 132.92, 132.80, 132.48, 129.82, 124.39, 97.39, 82.48, 65.95, 35.54, 35.19, 34.55, 34.28, 31.85, 31.81.

$[\alpha]_D^{25}$ = 113.6 (c = 1.0, $CHCl_3$).

HRMS (ESI) Calculated for $C_{21}H_{23}O$ $[M+H]^+$: 291.1744; Found: 291.1743.



38

White solid, 76.7 mg, 98% yield, 92% e.e.

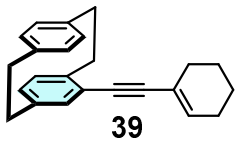
Chiral HPLC analysis of the product: Daicel Chiralpak IA 250×4.6 mm 5u column; Hexane/ 2-propanol = 95/5, detected at 254 nm, Flow rate = 1 mL/min, Rentention times: 17.493 min (minor), 19.278 min (major).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.93 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.76 (dd, *J* = 5.5, 3.0 Hz, 2H), 6.90 (dd, *J* = 7.8, 1.8 Hz, 1H), 6.48 (td, *J* = 7.6, 1.8 Hz, 4H), 6.45 – 6.36 (m, 2H), 4.78 (s, 2H), 3.52 (ddd, *J* = 13.0, 10.3, 2.7 Hz, 1H), 3.16 (ddd, *J* = 13.0, 10.3, 5.4 Hz, 1H), 3.11 – 2.98 (m, 4H), 2.97 – 2.88 (m, 1H), 2.80 (ddd, *J* = 13.0, 10.5, 5.4 Hz, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.35, 143.03, 139.69, 139.66, 139.37, 137.32, 134.34, 133.88, 133.35, 133.11, 132.78, 132.52, 132.20, 130.09, 124.00, 123.70, 86.08, 83.42, 35.50, 35.15, 34.46, 34.24, 28.31.

$[\alpha]_D^{25}$ = 87.5 (c = 2.0, $CHCl_3$).

HRMS (ESI) Calculated for $C_{27}H_{22}NO_2$ $[M+H]^+$: 392.1646; Found: 392.1647.



39

White solid, 41.9 mg, 67% yield, 88% e.e.

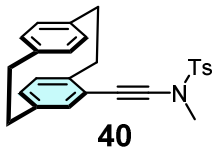
Chiral HPLC analysis of the product: Daicel Chiralpak OJ-H 250×4.6 mm 5u column; Hexane/ 2-propanol = 98/2, detected at 254 nm, Flow rate = 0.8 mL/min, Rentention times: 14.097 min (minor), 23.240 min (major).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.01 (dd, *J* = 7.8, 1.7 Hz, 1H), 6.52 (dd, *J* = 7.8, 1.8 Hz, 1H), 6.50 – 6.42 (m, 5H), 6.25 (dt, *J* = 4.1, 2.1 Hz, 1H), 3.57 (ddd, *J* = 13.0, 10.4, 2.6 Hz, 1H), 3.21 (ddd, *J* = 13.0, 10.4, 5.5 Hz, 1H), 3.13 – 3.01 (m, 4H), 3.01 – 2.91 (m, 1H), 2.82 (ddd, *J* = 13.0, 10.5, 5.5 Hz, 1H), 2.38 – 2.29 (m, 2H), 2.20 (ddt, *J* = 8.7, 6.2, 3.2 Hz, 2H), 1.80 – 1.71 (m, 2H), 1.68 (ddt, *J* = 8.3, 6.0, 2.6 Hz, 2H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 142.26, 139.69, 139.65, 139.46, 136.99, 134.42, 133.87, 133.40, 133.16, 132.82, 132.54, 132.31, 130.01, 125.54, 121.37, 94.96, 87.23, 35.61, 35.26, 34.65, 34.32, 29.63, 25.94, 22.57, 21.75.

$[\alpha]_D^{20}$ = 100.0 (c = 1.0, $CHCl_3$).

HRMS (APCI) Calculated for $C_{24}H_{25}$ $[M+H]^+$: 313.1951; Found: 313.1946.



40

White solid, 79.8 mg, 96% yield, 91% e.e.

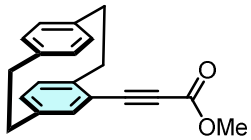
Chiral HPLC analysis of the product: Daicel Chiralpak IA 250×4.6 mm 5u column; Hexane/ Ethanol = 98/2, detected at 254 nm, Flow rate = 0.8 mL/min, Rentention times: 17.890 min (minor), 19.543 min (major).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.92 (d, *J* = 8.4 Hz, 2H), 7.51 – 7.36 (m, 2H), 6.92 (dd, *J* = 7.8, 1.9 Hz, 1H), 6.60 – 6.32 (m, 6H), 3.46 (ddd, *J* = 13.0, 10.2, 2.8 Hz, 1H), 3.24 (s, 3H), 3.20 – 3.01 (m, 5H), 3.00 – 2.90 (m, 1H), 2.81 (ddd, *J* = 13.0, 10.4, 5.5 Hz, 1H), 2.47 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 144.99, 142.15, 139.77, 139.66, 139.39, 136.83, 133.91, 133.66, 133.42, 132.82, 132.44, 132.42, 130.02, 129.99, 127.90, 124.37, 87.18, 69.30, 39.66, 35.57, 35.21, 34.50, 34.30, 21.82.

$[\alpha]_D^{25}$ = 61.9 (c = 1.0, $CHCl_3$).

HRMS (APCI) Calculated for $C_{26}H_{26}NO_2S$ $[M+H]^+$: 416.1679; Found: 416.1697.



41

White solid, 50.5 mg, 87% yield, 73% e.e.

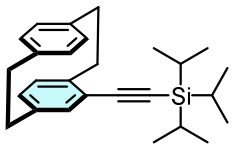
Chiral HPLC analysis of the product: Daicel Chiralpak IA 250×4.6 mm 5u column; Hexane/ 2-propanol = 96/4, detected at 254 nm, Flow rate = 1 mL/min, Rentention times: 6.042 min (minor), 7.597 min (major).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 6.89 (dd, *J* = 8.0, 1.4 Hz, 1H), 6.71 (d, *J* = 1.8 Hz, 1H), 6.62 (dd, *J* = 7.9, 1.8 Hz, 1H), 6.52 (d, *J* = 7.4 Hz, 3H), 6.46 (dd, *J* = 8.0, 1.6 Hz, 1H), 3.89 (s, 3H), 3.59 (ddd, *J* = 13.3, 10.5, 2.9 Hz, 1H), 3.25 (ddd, *J* = 13.1, 10.5, 5.1 Hz, 1H), 3.09 (dtd, *J* = 16.8, 10.5, 1.9 Hz, 4H), 3.04 – 2.98 (m, 1H), 2.98 – 2.89 (m, 1H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 154.95, 144.97, 140.30, 139.54, 139.48, 138.35, 135.46, 134.31, 133.47, 132.85, 132.66, 130.68, 121.16, 87.08, 83.88, 52.89, 35.48, 35.16, 34.52, 34.38.

$[\alpha]_D^{25}$ = 98.2 (c = 1.0, $CHCl_3$).

HRMS (APCI) Calculated for $C_{20}H_{19}O_2$ $[M+H]^+$: 291.1380; Found: 291.1391.



42

White solid, 49.7 mg, 64% yield, 92% e.e.

Chiral HPLC analysis of the product: Daicel Chiralpak IC 250×4.6 mm 5u column; Hexane/ 2-propanol = 99.5/0.5, detected at 254 nm, Flow rate = 1 mL/min, Rentention times: 7.210 min (minor), 7.900 min (major).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.05 (dd, *J* = 7.8, 1.9 Hz, 1H), 6.55 – 6.48 (m, 4H), 6.48 – 6.42 (m, 2H), 3.63 (ddd, *J* = 13.0, 10.4, 2.7 Hz, 1H), 3.23 (ddd, *J* = 12.9, 10.4, 5.2 Hz, 1H), 3.13 – 2.96 (m, 5H), 2.85 (ddd, *J* = 12.9, 10.6, 5.2 Hz, 1H), 1.22-1.20 (m, 21H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 142.83, 139.73, 139.64, 139.50, 137.83, 133.82, 133.52, 132.92, 132.83, 132.55, 129.97, 125.32, 107.47, 93.75, 35.57, 35.21, 34.58, 34.22, 18.96, 18.94, 11.65.

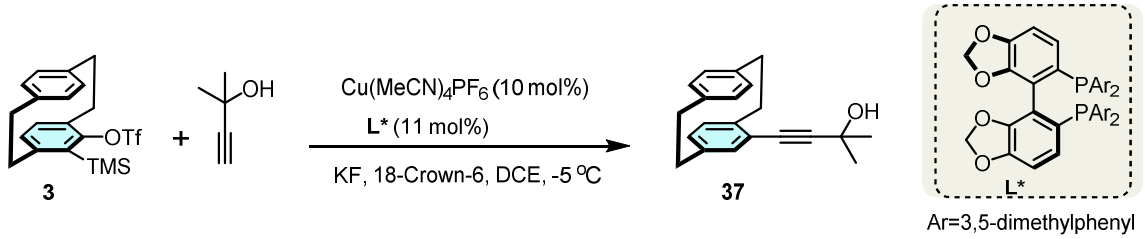
$[\alpha]_D^{25}$ = 105.2 (c = 1.0, $CHCl_3$).

HRMS (ESI) Calculated for $C_{27}H_{37}Si$ $[M+H]^+$: 389.2660; Found: 389.2665.

Note: The e.e. value of compound **42** was determined in the formation of compound **43**. **42** was treated with Tetrabutylammonium fluoride (2.0 equiv.) in THF at toom temperature for 10 minutes. In this reaction, **42** are quantitatively converted into **43**.

7. Large-scale experiments and synthetic application

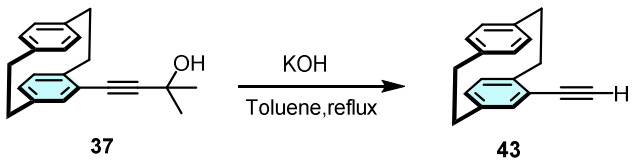
7.1 Gram-scale reaction



In a dried schlenk flask, $Cu(MeCN)_4PF_6$ (372.7 mg, 1.0 mmol, 10 mol %), L* (795.1 mg, 1.1 mmol, 11 mol %), KF (2.32 g , 40 mmol) and 18-Crown-6 (10.6 g, 40 mmol) were dissolved in DME (70 mL) under a nitrogen atmosphere, and the mixture was stirred at room temperature for 15 minutes. Then the reaction was cooled to -5 °C, a mixed solution of **3** (5.14 g, 12 mmol) and 2-Methyl-3-butyn-2-ol (841.2 mg, 10 mmol) in DME (30 mL) was added over a period of 30 minutes. The reaction was allowed to stirred at -5 °C for 24 h. After a full conversion, all volatiles were removed under reduced pressure, and the residue was purified by column chromatography on silica gel to afford the desired product **37** as a white solid (2.52g, 87%, 95% e.e.).

7.2 Synthetic transformation

7.2.1 The synthesis of 43



In a 100 mL round bottom flask, **37** (2.0 g, 6.9 mmol) and potassium hydroxide (0.77 g, 13.8 mmol) were suspended in 15 mL of Toluene. The mixture was heated at reflux for 1 h. The reaction was cooled to room temperature, treated with 50 mL water, and extracted (15mL × 3) with DCM. The combined organic extracts were dried over Na_2SO_4. The solvent was removed by rotary evaporation, and the raw product was purified by column chromatography (silica gel, dichloromethane) to afford **43** as a white solid (1.55 g, 97%, 95% e.e.).

Chiral HPLC analysis of the product: Daicel Chiralpak IC 250× 4.6 mm 5u column; Hexane/ 2-propanol = 99.5/0.5, detected at 254 nm, Flow rate = 1 mL/min, Rentention times: 6.940 min (minor), 7.935 min (major).

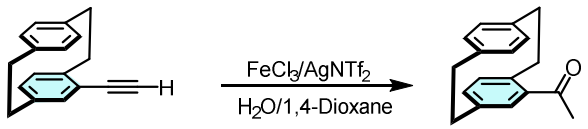
^{1}H NMR (400 MHz, Chloroform-d) δ 7.00 (dd, J = 7.8, 1.8 Hz, 1H), 6.56 (d, J = 1.9 Hz, 1H), 6.55 – 6.48 (m, 3H), 6.46 (dd, J = 7.9, 2.6 Hz, 2H), 3.59 (ddd, J = 13.1, 10.4, 2.8 Hz, 1H), 3.28 (s, 1H), 3.23 (ddd, J = 13.0, 10.4, 5.2 Hz, 1H), 3.14 – 3.02 (m, 4H), 3.02 – 2.94 (m, 1H), 2.86 (ddd, J = 13.1, 10.6, 5.2 Hz, 1H).

^{13}C NMR (101 MHz, Chloroform-d) δ 143.12, 139.83, 139.68, 139.50, 137.73, 133.99, 133.47, 133.40, 132.85, 132.64, 130.04, 123.84, 84.03, 80.39, 35.56, 35.22, 34.35, 34.24.

$[\alpha]_D^{25}$ = 68.1 (c = 2.0, $CHCl_3$).

HRMS (ESI) Calculated for $C_{18}H_{17}$ $[M+H]^+$: 233.1325; Found: 233.1329.

7.2.2 The synthesis of 44[3]



43 **44**

A dried Schlenk tube was charged with Ferric Chloride (12.1 mg, 0.075mmol, 5 mol %), Silver triflate (59.1 mg, 0.23mmol, 15 mol %) was added 1,4-Dioxane (1.0 mL). The mixture was stirred at room temperature for 20 min. Then a solution of **43** (348.5 mg, 1.5 mmol) in 1,4-Dioxane (2 mL) and water (135 mg, 7.5mmol) was added. After that, the reaction mixture was stirred at 80 ℃ for another 12 h, then quenched with water and extracted with DCM. The combined organic phase was dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel to afford **44** as white solid (281.8 mg, 75% yield, 95% e.e.).

Chiral HPLC analysis of the product: Daicel Chiralpak IC 250×4.6 mm 5u column; Hexane/ 2-propanol = 95/5, detected at 254 nm, Flow rate = 1 mL/min, Rentention times: 11.505 min (minor), 13.243 min (major).

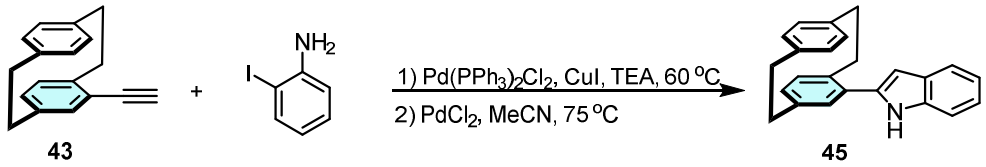
^{1}H NMR (400 MHz, Chloroform-d) δ 6.93 (d, J = 1.9 Hz, 1H), 6.66 (dd, J = 7.8, 1.9 Hz, 1H), 6.58 – 6.49 (m, 3H), 6.48 (dd, J = 7.8, 1.9 Hz, 1H), 6.38 (dd, J = 7.9, 1.9 Hz, 1H), 3.97 (ddd, J = 12.6, 7.0, 4.7 Hz, 1H), 3.23 – 3.11 (m, 4H), 3.09 – 2.97 (m, 2H), 2.90 – 2.78 (m, 1H), 2.47 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-d) δ 200.39, 141.69, 140.43, 139.86, 139.29, 138.02, 136.54, 136.47, 134.32, 133.16, 133.01, 132.16, 131.29, 36.18, 35.32, 35.29, 35.04, 28.86.

$[\alpha]_D^{25}$ = 69.2 (c = 1.0, $CHCl_3$).

HRMS (ESI) Calculated for $C_{18}H_{19}O$ $[M+H]^+$: 251.1431; Found: 251.1431.

7.2.3 The synthesis of 45[4]



43 45

To a mixture of **43** (46.4 mg, 0.2 mmol), 2-Iodoaniline (47.3 mg, 0.22 mmol), $Pd(PPh_3)_2Cl_2$ (2.8 mg, 0.04mmol, 2 mol%), CuI (1.9 , 0.01mmol, 5 mol%) was added TEA (2 mL) under nitrogen atmosphere. The mixture was stirred at 60 °C for 8 h. Then, the mixture was filtered and the filtrate was concentrated under reduced pressure to give the crude product which were used in step 2 without further purification. The residue was dissloved in MeCN (2 mL), then Palladium chloride (0.35 mg, 0.002 mmol, 1 mol%) was added under a nitrogen atmosphere. After stirred at 75 °C for 6 h. The reaction was quenched with H_2O (5.0 mL). The aqueous layer was extracted with DCM (3.0 mL × 3). The combined organic layers were washed with brine (3.0 mL), dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel to afford **45** as Yellow solid (56.3 mg, 87%, 95 % e.e.)

Chiral HPLC analysis of the product: Daicel Chiralpak IA 250×4.6 mm 5u column; Hexane/ 2-propanol = 90/10, detected at 254 nm, Flow rate = 1 mL/min, Rentention times: 18.385 min (minor), 20.548 min (major).

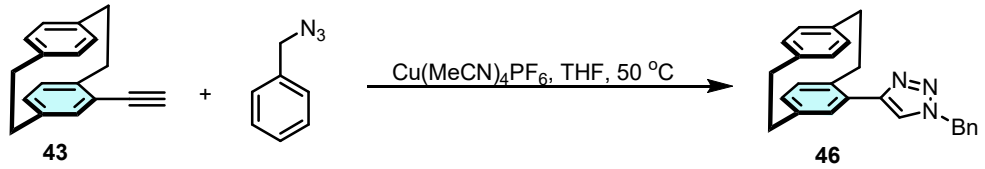
^{1}H NMR (500 MHz, Chloroform-d) δ 8.06 (s, 1H), 7.73 (d, J = 7.8 Hz, 1H), 7.43 (dd, J = 8.0, 1.1 Hz, 1H), 7.25 – 7.21 (m, 1H), 7.20 – 7.15 (m, 1H), 6.77 – 6.70 (m, 2H), 6.67 (d, J = 1.8 Hz, 1H), 6.64 (dd, J = 7.8, 1.9 Hz, 1H), 6.61 – 6.51 (m, 4H), 3.67 – 3.59 (m, 1H), 3.25 – 3.11 (m, 3H), 3.10 – 3.03 (m, 1H), 3.01 – 2.93 (m, 2H), 2.85 – 2.75 (m, 1H).

^{13}C NMR (126 MHz, Chloroform-d) δ 140.51, 139.61, 139.59, 139.31, 137.44, 136.78, 136.12, 133.53, 133.38, 132.84, 132.77, 132.75, 132.12, 130.04, 129.32, 122.14, 120.75, 120.17, 110.98, 101.85, 35.62, 35.39, 34.90, 34.88.

$[\alpha]_D^{25}$ = 212.2 (c = 1.0, $CHCl_3$).

HRMS (ESI) Calculated for $C_{24}H_{22}N$ $[M+H]^+$: 324.1747; Found: 324.1746.

7.2.4 The synthesis of 46



43 46

A dried Schlenk tube was charged with of $Cu(MeCN)_4PF_6$ (7.5 mg, 0.02 mmol, 10 mol%), **43** (46.4 mg, 0.20 mmol). The Schlenk tube was evacuated and filled with nitrogen for three times. A solution of benzyl azide in THF (2 mL) was added to the reaction mixture. The resulting mixture was stirred at 50 °C for 8 h. After the completion of the reaction, all volatiles were removed under reduced pressure, and the residue was purified by column chromatography on silica gel to afford the desired product **46** as a white solid (67.3 mg, 92%, 95% e.e.).

Chiral HPLC analysis of the product: Daicel Chiralpak OJ-H 250×4.6 mm 5u column; Hexane/2-propanol = 80/20, detected at 254 nm, Flow rate = 1 mL/min, Rentention times: 34.192 min (major), 49.450 min (minor).

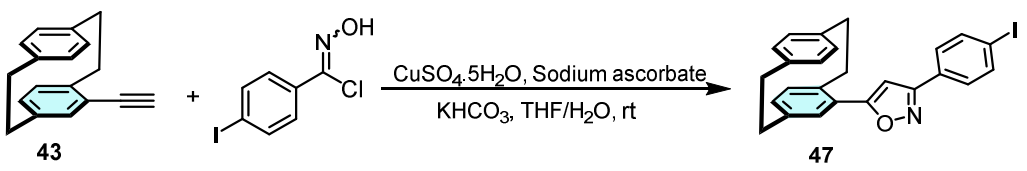
^{1}H NMR (400 MHz, Chloroform-d) δ 7.55 (s, 1H), 7.45 – 7.37 (m, 3H), 7.32 (dd, J = 7.8, 1.8 Hz, 2H), 6.80 (d, J = 1.3 Hz, 1H), 6.61 – 6.50 (m, 4H), 6.49 (t, J = 1.2 Hz, 2H), 5.64 (s, 2H), 3.79 (ddd, J = 13.0, 9.6, 2.3 Hz, 1H), 3.19 – 3.09 (m, 2H), 3.02 (dddd, J = 17.1, 14.6, 7.6, 2.7 Hz, 3H), 2.87 (ddd, J = 12.9, 9.8, 6.3 Hz, 1H), 2.77 (ddd, J = 12.7, 9.6, 6.3 Hz, 1H).

^{13}C NMR (101 MHz, Chloroform-d) δ 148.57, 140.06, 139.67, 139.49, 137.60, 135.91, 135.07, 133.05, 132.96, 132.68, 132.66, 132.39, 130.97, 130.33, 129.30, 128.87, 128.00, 121.49, 54.27, 35.51, 35.27, 34.93, 34.63.

$[\alpha]_D^{25}$ = 130.0 (c = 1.0, $CHCl_3$).

HRMS (ESI) Calculated for $C_{25}H_{24}N_3$ $[M+H]^+$: 366.1965; Found: 366.1965.

7.2.5 The synthesis of 47[5]



43 47

A dried Schlenk tube was charged with $CuSO_4{\cdot}5H_2O$ (1.0 mg, 0.004, 2 mol %), Sodium citrate (5.2 mg, 0.02 mmol, 10 mol %) and $KHCO_3$ (40 mg, 0.8 mmol, 4 equiv.) was added a mixed solvent of THF and water (v/v = 1:1, 1.0 mL) under a nitrogen atmosphere. The mixture was stirred at room temperature for 20 min. Then a solution of **43** (46.4 mg, 0.2 mmol) and N-Hydroxy-4-iodobenzenecarboximidoyl chloride (84.4 mg, 0.3 mmol, 1.5 equiv.) in above-mentioned solvent (1.5 mL) was added. After that, the reaction mixture was stirred at room temperature for another 6 h. The suspension was filtered through a pad of Celite, and the filter cake was washed with washed with DCM (15mL × 3). The combined organic extracts were dried over Na_2SO_4. The solvent was removed by rotary evaporation, and the crude product was purified by column chromatography (silica gel, dichloromethane) to afford **47** as a white solid (86 mg, 90%, 95% e.e.).

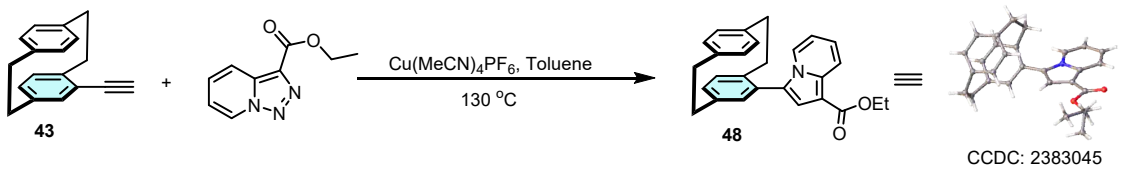
Chiral HPLC analysis of the product: Daicel Chiralpak OJ-H 250×4.6 mm 5u column; Hexane/ 2-propanol = 90/10, detected at 254 nm, Flow rate = 1 mL/min, Rentention times: 41.322 min (minor), 54.070 min (major).

^{1}H NMR (500 MHz, Chloroform-d) δ 7.88 – 7.84 (m, 2H), 7.71 – 7.63 (m, 2H), 6.85 (d, J = 1.8 Hz, 1H), 6.70 (s, 1H), 6.66 – 6.60 (m, 2H), 6.58 (d, J = 1.7 Hz, 2H), 6.51 (d, J = 1.7 Hz, 2H), 3.89 – 3.78 (m, 1H), 3.24 – 3.02 (m, 5H), 2.95 (dddd, J = 33.5, 12.9, 9.9, 6.4 Hz, 2H); **^{13}C NMR** (126 MHz, Chloroform-d) δ 172.02, 162.09, 140.52, 139.56, 139.54, 138.55, 138.29, 136.38, 134.75, 133.15, 133.12, 132.63, 132.31, 130.92, 128.92, 128.55, 128.17, 99.35, 96.27, 35.50, 35.37, 35.33, 34.92.

$[\alpha]_D^{25}$ = 132.0 (c = 1.0, $CHCl_3$).

HRMS (ESI) Calculated for $C_{25}H_{21}INO$ $[M+H]^+$: 478.0663; Found: 478.0667.

7.2.6 The synthesis of 48[6]



In a dried seal tube, **43** (46.4 mg, 0.2 mmol), Ethyl [1,2,3]triazolo[1,5-a]pyridine-3-carboxylate (57.4 mg, 0.3 mmol, 1.5 equiv.) and $Cu(MeCN)_4PF_6$ (7.5 mg, 0.02 mmol, 10 mol%) were

suspended in 3 mL of Toluene. The mixture was heated at 130 °C for 12 h. The reaction was cooled to room temperature, all volatiles were removed under reduced pressure, and the residue was purified by column chromatography on silica gel to afford the desired product **48** as a white solid (60.2 mg, 76%, 95% e.e.).

Chiral HPLC analysis of the product: Daicel Chiralpak IC 250×4.6 mm 5u column; Hexane/ 2-propanol = 95/5, detected at 254 nm, Flow rate = 1 mL/min, Rentention times: 14.542 min (minor), 18.950 min (major).

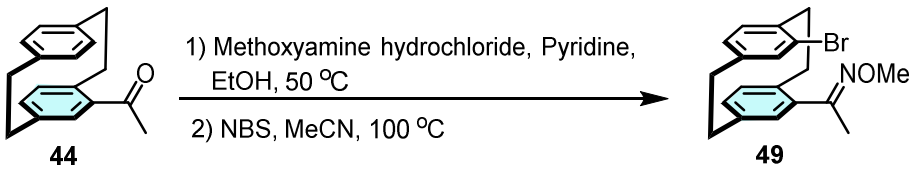
^{1}H NMR (400 MHz, Chloroform-d) δ 8.28 (dt, J = 9.1, 1.3 Hz, 1H), 7.96 (dt, J = 7.0, 1.2 Hz, 1H), 7.53 (s, 1H), 7.09 (ddd, J = 9.1, 6.5, 1.1 Hz, 1H), 6.82 (dd, J = 7.9, 1.9 Hz, 1H), 6.70 – 6.65 (m, 2H), 6.64 – 6.57 (m, 5H), 4.55 – 4.40 (m, 2H), 3.21 – 3.11 (m, 3H), 3.11 – 3.05 (m, 1H), 3.00 (ddd, J = 13.0, 10.2, 4.1 Hz, 1H), 2.85 (ddd, J = 13.7, 10.2, 3.8 Hz, 1H), 2.68 (ddd, J = 13.1, 9.9, 4.0 Hz, 1H), 2.58 (ddd, J = 13.6, 10.0, 3.8 Hz, 1H), 1.50 (t, J = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-d) δ 165.40, 141.17, 139.74, 139.52, 138.68, 136.16, 135.56, 134.37, 133.77, 133.41, 132.41, 130.22, 129.39, 128.44, 123.45, 122.61, 120.06, 116.28, 112.54, 104.41, 59.83, 35.56, 35.37, 35.10, 34.71, 14.92.

$[\alpha]_D^{25}$ = -299.0 (c = 1.0, $CHCl_3$).

HRMS (ESI) Calculated for $C_{27}H_{26}NO_2$ $[M+H]^+$: 396.1959; Found: 396.1957.

7.2.7 The synthesis of 49



44 **49**

To a mixture of **44** (50.6 mg, 0.2 mmol), Methoxyamine hydrochloride (16.7 mg, 0.2 mmol, 1.0 equiv.), Pyridine (32 mg, 0.4 mmol, 2.0 equiv.) was added EtOH (5 mL) under air. The mixture was stirred at 50 °C for 4 h. Then, the mixture was filtered and the filtrate was concentrated under reduced pressure to give the crude product which were used in step 2 without further purification. The residue was dissloved in MeCN (3 mL) equipped with a seal tube, then N-Bromosuccinimide (39.2 mg, 0.22 mmol, 1.1 equiv.) was added. After stirred at 100 °C for 8 h. The reaction was quenched with H_2O (5.0 mL). The aqueous layer was extracted with DCM (3.0

mL × 3). The combined organic layers were washed with brine (3.0 mL), dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel to afford **49** as White solid (63.8 mg, 89%, 95 % e.e.)

Chiral HPLC analysis of the product: Daicel Chiralpak IA 250×4.6 mm 5u column; Hexane/ 2-propanol = 98/2, detected at 254 nm, Flow rate = 1 mL/min, Rentention times: 13.620 min (minor), 16.510 min (major).

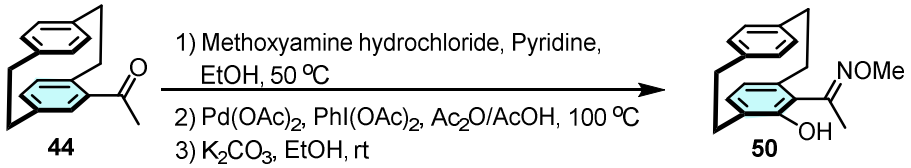
^{1}H NMR (500 MHz, Chloroform-d) δ 6.71 (d, J = 1.9 Hz, 1H), 6.66 – 6.58 (m, 2H), 6.57 – 6.52 (m, 1H), 6.52 – 6.47 (m, 2H), 4.09 – 4.02 (m, 1H), 4.00 (s, 3H), 3.47 (ddd, J = 13.6, 9.6, 2.4 Hz, 1H), 3.20 – 3.00 (m, 4H), 2.97 – 2.89 (m, 1H), 2.85 (ddd, J = 13.6, 10.0, 6.5 Hz, 1H), 2.33 (s, 3H).

^{13}C NMR (126 MHz, Chloroform-d) δ 155.67, 141.21, 139.54, 138.12, 137.91, 136.37, 136.30, 136.15, 135.05, 133.59, 131.29, 129.71, 126.21, 61.98, 36.61, 35.23, 34.78, 32.65, 15.27.

$[\alpha]_D^{25}$ = -44.0 (c = 1.0, $CHCl_3$).

HRMS (ESI) Calculated for $C_{19}H_{21}BrNO$ $[M+H]^+$: 358.0802, 360.0781; Found: 358.0803, 360.0784.

7.2.8 The synthesis of 50[7]



To a mixture of **44** (50.6 mg, 0.2 mmol), Methoxyamine hydrochloride (16.7 mg, 0.2 mmol, 1.0 equiv.), Pyridine (32 mg, 0.4 mmol, 2.0 equiv.) was added EtOH (5 mL) under air. The mixture was stirred at 50 ^oC for 4 h. Then, the mixture was filtered and the filtrate was concentrated under reduced pressure to give the crude product which were used in step 2 without further purification. The residue was dissloved in a mixed solvent of Acetic Acid and Acetic anhydride (v/v = 1:1, 2.0 mL) equipped with a schlenk tube, then Palladium(Ⅱ)acetate (2.2 mg, 0.1 mmol, 5 mol%.) and Iodobenzene diacetate (77.3 mg, 0.24 mmol, 1.2 equiv.) was added under a nitrogen atmosphere. The reaction was heated at 100 ^oC for 12 h. The suspension was filtered through a pad of Celite, and the filter cake was washed with washed with DCM (15mL × 3). The combined organic extracts were dried over Na_2SO_4. The solvent was removed by rotary evaporation. The residue was

dissolved in MeOH (10 mL) equipped with a 50 ml round-bottomed flask. K_2CO_3 (83 mg, 0.6 mmol, 3.0 equiv.) was added sequently. The reaction was allowed to stir at room temperature for 4 h, all volatiles were removed under reduced pressure, and the residue was purified by column chromatography on silica gel to afford the desired product **50** as a white solid (51.4 mg, 87%, 95% e.e.).

Chiral HPLC analysis of the product: Daicel Chiralpak IC 250×4.6 mm 5u column; Hexane/ 2-propanol = 99/1, detected at 254 nm, Flow rate = 1 mL/min, Rentention times: 5.523 min (minor), 6.193 min (major).

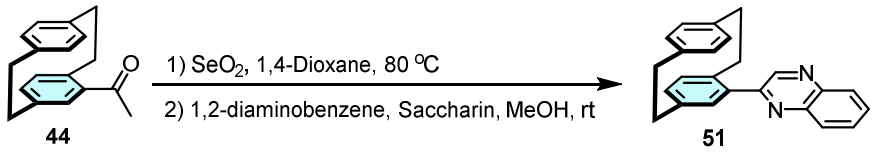
^{1}H NMR (500 MHz, Chloroform-d) δ 10.32 (s, 1H), 7.06 – 6.84 (m, 1H), 6.60 (ddd, J = 7.7, 5.2, 1.9 Hz, 2H), 6.50 (dd, J = 7.9, 1.9 Hz, 1H), 6.42 (d, J = 7.7 Hz, 1H), 6.28 (d, J = 7.7 Hz, 1H), 4.09 (s, 3H), 3.40 (dddd, J = 11.3, 10.1, 2.8, 1.4 Hz, 1H), 3.22 – 3.11 (m, 2H), 3.10 – 2.98 (m, 2H), 2.91 (ddd, J = 13.7, 9.8, 5.9 Hz, 1H), 2.78 (ddd, J = 12.8, 9.7, 5.8 Hz, 1H), 2.57 (ddd, J = 13.0, 10.6, 5.5 Hz, 1H), 2.18 (d, J = 1.1 Hz, 3H).

^{13}C NMR (126 MHz, Chloroform-d) δ 158.21, 154.53, 140.91, 140.11, 138.05, 135.74, 132.64, 132.45, 129.66, 128.03, 127.58, 127.04, 122.31, 62.50, 35.81, 35.17, 34.06, 30.88, 18.30.

$[\alpha]_D^{25}$ = 365.9 (c = 2.0, $CHCl_3$).

HRMS (ESI) Calculated for $C_{19}H_{22}NO_2$ $[M+H]^+$: 296.1651; Found: 296.1650.

7.2.9 The synthesis of 51[8]



To a mixture of **44** (50.6 mg, 0.2 mmol), Selenium dioxide (23.3 mg, 0.21 mmol, 1.05 equiv.), was added 1,4-Dioxane (2 mL) under air. The mixture was stirred at 80 °C for 12 h. After completion of the reaction, the reaction was cooled to room temperature. The dark solids were removed by filtration over a short pad of Celite,. The filtrate was dried over anhydrous Na_2SO_4, and the solvent was removed under vacuum to give the crude products 1,2-dione which were used in step 2 without further purification. A 100 mL Schlenk flask was charged with 1,2-dione, 1,2-diaminobenzene (32.4 mg, 0.3 mmol, 1.5equiv.) and saccharin (1.8 mg, 0.01 mmol, 5 mol%) in

10 mL of methanol. The reaction mixture was stirred at room temperature for 12 h. After completion of the reaction, solvent was removed under vacuum and the crude product was purified by flash column chromatography on silica gel to afford the desired product **51** as a pale yellow solid (49.8 mg, 74%, 95% e.e.).

Chiral HPLC analysis of the product: Daicel Chiralpak IA 250×4.6 mm 5u column; Hexane/ 2-propanol = 97/3, detected at 254 nm, Flow rate = 1 mL/min, Rentention times: 10.177 min (minor), 12.105 min (major).

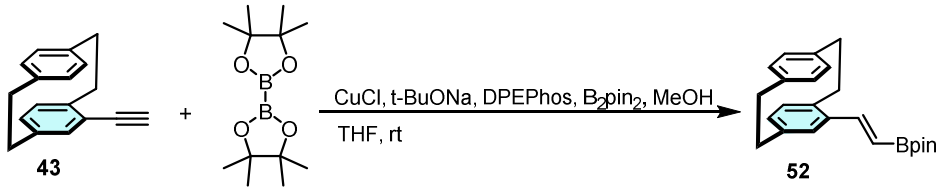
^{1}H NMR (500 MHz, Chloroform-d) δ 9.04 (s, 1H), 8.27 (dd, J = 8.2, 1.6 Hz, 1H), 8.17 (dd, J = 8.2, 1.6 Hz, 1H), 7.92 – 7.74 (m, 2H), 7.04 (d, J = 1.7 Hz, 1H), 6.72 – 6.65 (m, 2H), 6.65 – 6.56 (m, 4H), 3.86 – 3.65 (m, 1H), 3.30 – 3.18 (m, 2H), 3.17 – 3.08 (m, 2H), 3.08 – 2.97 (m, 2H), 2.86 – 2.72 (m, 1H).

^{13}C NMR (126 MHz, Chloroform-d) δ 153.83, 146.63, 142.67, 140.95, 140.34, 139.76, 139.57, 139.23, 137.42, 136.52, 134.39, 133.62, 133.08, 132.77, 132.73, 130.93, 130.13, 129.97, 129.57, 129.27, 35.55, 35.45, 35.39, 34.82.

$[\alpha]_D^{25}$ = -16.5 (c = 1.0, $CHCl_3$).

HRMS (ESI) Calculated for $C_{24}H_{21}N_2$ $[M+H]^+$: 337.1705; Found: 337.1699.

7.2.10 The synthesis of 52[9]



To a dried Schlenk tube charged with CuCl (1.0 mg, 0.01 mmol, 5 mol %), t-BuONa (1.9 mg, 0.02 mmol, 10 mol %) and DPEPhos (5.4 mg, 0.01 mmol, 5 mol %) was added anhydrous THF (1.0 mL) under a nitrogen atmosphere. The mixture was stirred at room temperature for 20 min. Then a solution of **43** (46.4 mg, 0.2 mmol), Bis(pinacolato)diboron (76.2 mg, 0.3 mmol, 1.5 equiv.) and MeOH (22.4 mg, 0.4 mmol, 2.0 equiv.) in THF (2 mL) was added via syringe. The mixture was stirred at room temperature for 16 h. The reaction was quenched with H_2O (5.0 mL). The aqueous layer was extracted with DCM (3.0 mL × 3). The combined organic layers were washed with brine

(3.0 mL), dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel to afford **52** as white solid (57.8 mg, 80%, 96 % e.e.)

Chiral HPLC analysis of the product: Daicel Chiralpak OD-H 250×4.6 mm 5u column; Hexane/ Ethanol = 98/2, detected at 254 nm, Flow rate = 1 mL/min, Rentention times: 8.397 min (minor), 12.557 min (major).

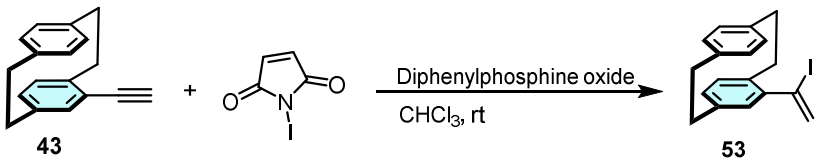
^{1}H NMR (500 MHz, Chloroform-d) δ 7.47 (d, J = 18.2 Hz, 1H), 6.67 (d, J = 1.8 Hz, 1H), 6.63 (dd, J = 7.9, 1.7 Hz, 1H), 6.51 (t, J = 2.2 Hz, 2H), 6.49 (dd, J = 7.7, 1.8 Hz, 1H), 6.43 (d, J = 7.7 Hz, 1H), 6.38 (dd, J = 7.8, 1.7 Hz, 1H), 5.95 (d, J = 18.1 Hz, 1H), 3.61 (ddd, J = 13.7, 10.0, 2.0 Hz, 1H), 3.17 – 3.06 (m, 3H), 2.98 (dddd, J = 24.5, 17.2, 11.6, 3.7 Hz, 3H), 2.83 (ddd, J = 13.7, 10.3, 6.6 Hz, 1H), 1.35 (s, 12H).

^{13}C NMR (126 MHz, Chloroform-d) δ 147.60, 139.99, 139.50, 139.26, 138.08, 135.03, 133.14, 133.07, 132.07, 130.79, 130.32, 83.42, 35.61, 35.41, 35.07, 33.82, 25.05, 24.98.

$[\alpha]_D^{25}$ = 186.2 (c = 1.0, $CHCl_3$).

HRMS (ESI) Calculated for $C_{24}H_{30}BO_2$ $[M+H]^+$: 361.2339; Found: 361.2335.

7.2.11 The synthesis of 53[10]



To a dried Schlenk tube charged with N-Iodosuccinimide (50 mg, 0.2 mmol, 1.0 equiv.), and Diphenylphosphine oxide (60.6 mg, 0.3 mmol, 1.5 equiv.) was added anhydrous Trichloromethane (2 mL) under a nitrogen atmosphere. The mixture was stirred at room temperature for 10 min. Then a solution of **43** (46.4 mg, 0.2 mmol) in Trichloromethane (1 mL) was added via syringe. The mixture was stirred at room temperature for 3 h. The reaction was quenched with H_2O (5.0 mL). The aqueous layer was extracted with DCM (3.0 mL × 3). The combined organic layers were washed with brine (3.0 mL), dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by flash columnchromatography on silica gel to afford **53** as white solid (70.7 mg, 98%, 96 % e.e.)

Chiral HPLC analysis of the product: Daicel Chiralpak IA 250×4.6 mm 5u column; Hexane/Ethanol = 99.9/0.1, detected at 254 nm, Flow rate = 1 mL/min, Rentention times: 13.872

min (minor), 16.405 min (major).

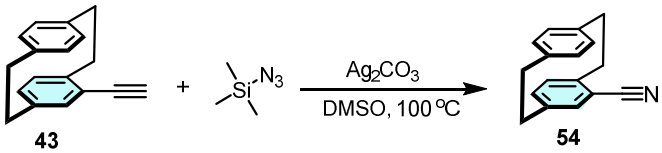
^{1}H NMR (400 MHz, Chloroform-d) δ 6.82 (dd, J = 7.9, 1.7 Hz, 1H), 6.66 – 6.55 (m, 3H), 6.45 – 6.39 (m, 3H), 6.28 (d, J = 1.2 Hz, 1H), 6.21 (d, J = 1.1 Hz, 1H), 3.65 – 3.51 (m, 1H), 3.21 – 3.03 (m, 4H), 3.03 – 2.90 (m, 3H).

^{13}C NMR (101 MHz, Chloroform-d) δ 141.76, 139.74, 139.61, 139.35, 137.50, 135.82, 134.03, 133.08, 132.61, 132.47, 130.55, 130.25, 107.10, 35.44, 35.13, 35.05, 34.22.

$[\alpha]_D^{25}$ = 144.8 (c = 1.0, $CHCl_3$).

HRMS (ESI) Calculated for $C_{18}H_{18}I$ $[M+H]^+$: 361.0453; Found: 361.0447.

7.2.12 The synthesis of 54[11]



43 **54**

In a dried seal tube, **43** (46.4 mg, 0.2 mmol), Ethyl [1,2,3]triazolo[1,5-a]pyridine-3-carboxylate (46.1 mg, 0.4 mmol, 2.0 equiv.) and Ag_2CO_3 (2.8 mg, 0.02 mmol, 10 mol%) were suspended in 3 mL of Dimethyl sulfoxide. The mixture was heated at 100 °C for 12 h. The reaction was quenched with H_2O (5.0 mL). The aqueous layer was extracted with DCM (3.0 mL × 3). The combined organic layers were washed with brine (3.0 mL), dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by flash columnchromatography on silica gel to afford **54** as gray solid (30.0 mg, 64%, 96 % e.e.)

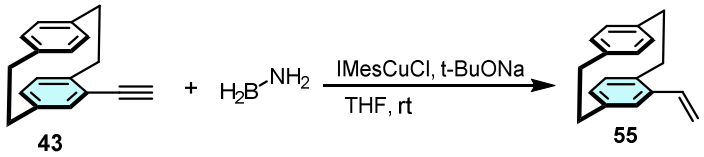
Chiral HPLC analysis of the product: Daicel Chiralpak IC 250×4.6 mm 5u column; Hexane/ Ethanol = 95/5, detected at 254 nm, Flow rate = 1 mL/min, Rentention times: 11.655 min (minor), 16.375 min (major).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 6.92 (d, *J* = 7.9 Hz, 1H), 6.77 (d, *J* = 1.9 Hz, 1H), 6.72 (dd, *J* = 7.9, 1.9 Hz, 1H), 6.59 (d, *J* = 7.9 Hz, 1H), 6.54 (s, 2H), 6.50 (d, *J* = 8.3 Hz, 1H), 3.53 (ddd, *J* = 13.6, 10.5, 3.0 Hz, 1H), 3.30 (ddd, *J* = 13.0, 10.5, 4.6 Hz, 1H), 3.21 – 2.99 (m, 6H); **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 144.33, 141.04, 139.63, 139.21, 137.23, 136.87, 134.62, 133.62, 133.11, 133.00, 132.80, 131.05, 119.04, 114.99, 35.41, 35.16, 34.55, 34.32.

$[\alpha]_D^{25}$ = 127.4 (c = 1.0, $CHCl_3$).

HRMS (ESI) Calculated for $C_{17}H_{16}N$ $[M+H]^+$: 234.1278; Found: 234.1276.

7.2.13 The synthesis of 55[12]



To a oven-dried Schlenk tube charged with [1,3-Bis(2,4,6-trimethylphenyl)imidazol-2-ylidene]chlorocopper(I) (4.0 mg, 0.01 mmol, 5 mol %), t-BuONa (1.0 mg, 0.01 mmol, 5 mol %) was added anhydrous THF (1.0 mL) under a nitrogen atmosphere. The mixture was stirred at room temperature for 20 min. Then a solution of **43** (46.4 mg, 0.2 mmol), Ammonia borane (9.3 mg, 0.6 mmol, 3.0 equiv.) in THF (2 mL) was added via syringe. The mixture was stirred at room temperature for 16 h. The reaction was quenched with H_2O (5.0 mL). The aqueous layer was extracted with DCM (3.0 mL × 3). The combined organic layers were washed with brine (3.0 mL), dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel to afford **55** as white solid (40.3 mg, 86%, 95 % e.e.)

Note: Because this compound (**55**) was unabled to separate with Daicel Chiralpak IA, IC, AS-H, OJ-H, OD-H, AD-H and Phenomenex 00G-4457-E0 250X4.6 mm 5u column. And **55** was translated from **43** under mild reaction condition. So we reasonable speculate that there was no issue of e.e. decrease in the reaction.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.80 (dd, *J* = 17.4, 10.9 Hz, 1H), 6.72 (dd, *J* = 7.8, 1.8 Hz, 1H), 6.55 (d, *J* = 1.9 Hz, 1H), 6.54 – 6.46 (m, 3H), 6.43 (d, *J* = 7.8 Hz, 1H), 6.40 (dd, *J* = 7.8, 1.9 Hz, 1H), 5.54 (dd, *J* = 17.4, 1.4 Hz, 1H), 5.28 (dd, *J* = 10.9, 1.4 Hz, 1H), 3.48 (ddd, *J* = 13.6, 9.9, 1.9 Hz, 1H), 3.17 – 3.04 (m, 4H), 3.03 – 2.90 (m, 2H), 2.81 (ddd, *J* = 13.5, 10.4, 6.7 Hz, 1H).

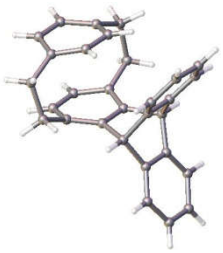
^{13}C NMR (101 MHz, Chloroform-*d*) δ 139.95, 139.48, 138.07, 137.91, 135.31, 134.89, 133.16, 132.06, 131.93, 130.26, 129.69, 114.36, 35.58, 35.34, 34.78, 33.79.

$[\alpha]_D^{25}$ = 337.1 (c = 1.0, $CHCl_3$).

HRMS (ESI) Calculated for $C_{18}H_{19}$ $[M+H]^+$: 235.1482; Found: 235.1478.

8. X-ray crystallography data

8.1 Crystal data of 10.

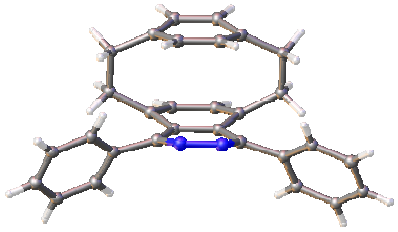


Crystal data have been deposited to CCDC with accession code of 2380667.

Table S3 Crystal data and structure refinement for cu_231216A_0m_a.

Identification code	cu_231216A_0m_a
Empirical formula	$C_{30}H_{24}$
Formula weight	384.49
Temperature/K	298.0
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	9.7881(6)
b/Å	8.4599(5)
c/Å	24.6781(17)
α/°	90
β/°	98.692(3)
γ/°	90
Volume/Å^3	2020.0(2)
Z	4
ρ_{calc}g/cm^3	1.264
μ/mm^{-1}	0.537
F(000)	816.0
Crystal size/mm^3	0.18 × 0.15 × 0.12
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	7.248 to 136.724
Index ranges	$-11 \le h \le 11$, $-10 \le k \le 10$, $-29 \le l \le 28$
Reflections collected	18405
Independent reflections	3698 [R_{int} = 0.0582, R_{sigma} = 0.0397]
Data/restraints/parameters	3698/0/272
Goodness-of-fit on F^2	1.055
Final R indexes [I>=2σ (I)]	R_1 = 0.0490, wR_2 = 0.1323
Final R indexes [all data]	R_1 = 0.0757, wR_2 = 0.1514
Largest diff. peak/hole / e Å^{-3}	0.27/-0.20

7.2 Crystal data of 11.

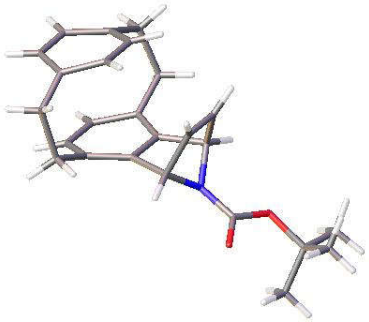


Crystal data have been deposited to CCDC with accession code of 2380679.

Table S4 Crystal data and structure refinement for cu_240130A_0m.

Identification code	cu_240130A_0m
Empirical formula	$C_{30}H_{24}N_2$
Formula weight	412.51
Temperature/K	291.00
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	12.694(7)
b/Å	12.292(7)
c/Å	15.177(9)
α/°	90
β/°	110.94(2)
γ/°	90
Volume/Å^3	2212(2)
Z	4
ρ_{calc}g/cm^3	1.239
μ/mm^{-1}	0.553
F(000)	872.0
Crystal size/mm^3	0.2 × 0.1 × 0.1
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	7.456 to 132.622
Index ranges	$-14 \leq h \leq 15$, $-14 \leq k \leq 14$, $-17 \leq l \leq 16$
Reflections collected	23375
Independent reflections	3851 [R_{int} = 0.0416, R_{sigma} = 0.0257]
Data/restraints/parameters	3851/0/290
Goodness-of-fit on F^2	1.042
Final R indexes [I>=2σ (I)]	R_1 = 0.0407, wR_2 = 0.1096
Final R indexes [all data]	R_1 = 0.0491, wR_2 = 0.1158
Largest diff. peak/hole / e Å^{-3}	0.21/-0.18

7.3 Crystal data of 12'.



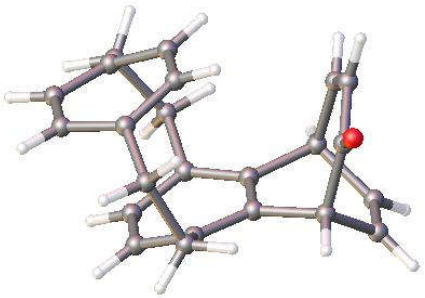
Crystal data have been deposited to CCDC with accession code of 2385577.

Table S5 Crystal data and structure refinement for cu_240429B_0m_a.

Identification code	cu_240429B_0m_a
Empirical formula	$C_{25}H_{27}NO_2$
Formula weight	373.47
Temperature/K	173.0
Crystal system	triclinic
Space group	P-1
a/Å	7.5962(11)
b/Å	11.8082(17)
c/Å	12.6318(19)
α/°	116.086(8)
β/°	105.328(9)
γ/°	94.776(9)
Volume/Å^3	955.0(3)
Z	2
ρ_{calc}g/cm^3	1.299
μ/mm^{-1}	0.638
F(000)	400.0
Crystal size/mm^3	0.16 × 0.15 × 0.12
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	8.568 to 136.4
Index ranges	$-9 \le h \le 9$, $-14 \le k \le 14$, $-14 \le l \le 15$
Reflections collected	9191
Independent reflections	3424 [R_{int} = 0.0687, R_{sigma} = 0.0785]
Data/restraints/parameters	3424/0/256
Goodness-of-fit on F^2	1.053
Final R indexes [I>=2σ (I)]	R_1 = 0.0509, wR_2 = 0.1281
Final R indexes [all data]	R_1 = 0.0715, wR_2 = 0.1437

Largest diff. peak/hole / e $Å^{-3}$ 0.18/-0.25

7.4 Crystal data of 13'.



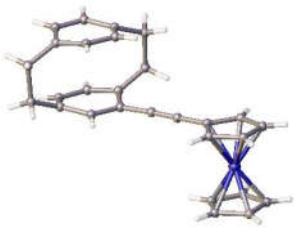
Crystal data have been deposited to CCDC with accession code of 2385578.

Table S6 Crystal data and structure refinement for cu_240628E_0m.

Identification code	cu_240628E_0m
Empirical formula	$C_{23}H_{20}O$
Formula weight	312.39
Temperature/K	173.0
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	12.7141(9)
b/Å	7.7931(6)
c/Å	16.4223(12)
α/°	90
β/°	102.423(3)
γ/°	90
Volume/$Å^3$	1589.1(2)
Z	4
$\rho_{calc}g/cm^3$	1.306
μ/mm^{-1}	0.600
F(000)	664.0
Crystal size/mm^3	0.02 × 0.01 × 0.01
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	7.12 to 133.508
Index ranges	$-15 \le h \le 14$, $-9 \le k \le 9$, $-19 \le l \le 19$
Reflections collected	24271
Independent reflections	2795 [R_{int} = 0.0569, R_{sigma} = 0.0276]
Data/restraints/parameters	2795/0/217
Goodness-of-fit on F^2	1.087

Final R indexes [I>=2σ (I)]	R_1 = 0.0432, wR_2 = 0.1097
Final R indexes [all data]	R_1 = 0.0462, wR_2 = 0.1123
Largest diff. peak/hole / e Å^{-3}	0.19/-0.24

7.5 Crystal data of 30.



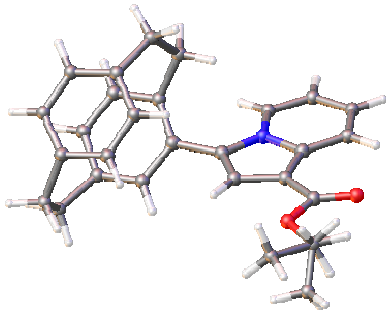
Crystal data have been deposited to CCDC with accession code of 2380683.

Table S7 Crystal data and structure refinement for cu_240229E_0m.

Identification code	cu_240229E_0m
Empirical formula	$C_{28}H_{24}Fe$
Formula weight	416.32
Temperature/K	298.0
Crystal system	monoclinic
Space group	$P2_1$
a/Å	7.5237(5)
b/Å	10.9183(7)
c/Å	12.4522(8)
α/°	90
β/°	90.177(3)
γ/°	90
Volume/Å^3	1022.89(12)
Z	2
ρ_{calc}g/cm^3	1.352
μ/mm^{-1}	5.970
F(000)	436.0
Crystal size/mm^3	0.18 × 0.16 × 0.15
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	7.098 to 136.468
Index ranges	-8 ≤ h ≤ 9, -13 ≤ k ≤ 12, -14 ≤ l ≤ 14
Reflections collected	8871
Independent reflections	3428 [R_{int} = 0.0508, R_{sigma} = 0.0729]
Data/restraints/parameters	3428/1/262
Goodness-of-fit on F^2	0.979

Final R indexes [I>=2σ (I)]	R_1 = 0.0418, wR_2 = 0.1014
Final R indexes [all data]	R_1 = 0.0510, wR_2 = 0.1055
Largest diff. peak/hole / e Å^{-3}	0.34/-0.29
Flack parameter	0.120(8)

7.6 Crystal data of 48.



Crystal data have been deposited to CCDC with accession code of 2383045 .

Table S8 Crystal data and structure refinement for cu_240905B_0m.

Identification code	cu_240905B_0m
Empirical formula	$C_{27}H_{25}NO_2$
Formula weight	395.48
Temperature/K	173.0
Crystal system	trigonal
Space group	$P3_121$
a/Å	10.8995(12)
b/Å	10.8995(12)
c/Å	30.934(6)
α/°	90
β/°	90
γ/°	120
Volume/Å^3	3182.6(9)
Z	6
ρ_{calc}g/cm^3	1.238
μ/mm^{-1}	0.608
F(000)	1260.0
Crystal size/mm^3	0.023 × 0.02 × 0.015
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	8.576 to 133.166
Index ranges	-12 ≤ h ≤ 12, -9 ≤ k ≤ 12, -34 ≤ l ≤ 36

Reflections collected	14473
Independent reflections	3691 [R_{int} = 0.0719, R_{sigma} = 0.0646]
Data/restraints/parameters	3691/97/260
Goodness-of-fit on F^2	1.097
Final R indexes [I>=2σ (I)]	R_1 = 0.0973, wR_2 = 0.2804
Final R indexes [all data]	R_1 = 0.1075, wR_2 = 0.2937
Largest diff. peak/hole / e $Å^{-3}$	0.58/-0.58
Flack parameter	0.1(12)

9. Density Functional Theory (DFT) calculation results

Computational Method

DFT calculations were performed with Gaussian 09[13] software package.Geometry optimizations of all the stationary points were carried out using the B3LYP[14] functional and 6-311+G(d,p)[15] or def2-SVP[16]basis set with Grimme's D3(BJ) dispersion correction in gas phase.[17] Frequency calculations at the same level were performed to validate each structure as either a minimum or a transition state. For the mechanism of asymmetric alkynylation reactions of [2,2]-paracyclophyne, solvation effects of DME were evaluatedusing SMD(THF) model[18] with modified ε (7.2) at B3LYP-D3(BJ)/def2-SVP level.Quasiharmonic corrections were applied with Grimme's quasi-RRHO correction[19] to obtain the thermal correction to Gibbs free energy at 298.15 K and 1 M using Shermo software package.[20] 3D structure was prepared with CYLview.[21] The molecular orbitals were prepared by VMD.[22]

Strain energy

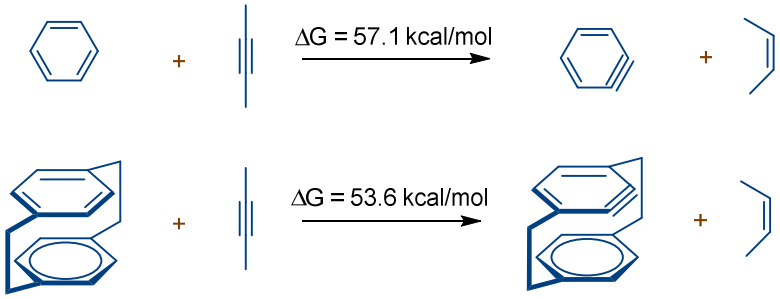


Figure S2. The strain energy of benzyne and [2,2]-paracyclophyneevaluated by homodesmoticreaction. Computed at B3LYP-D3(BJ)/6-311+G(d,p).

The interconversion between Int1-R and Int1-S

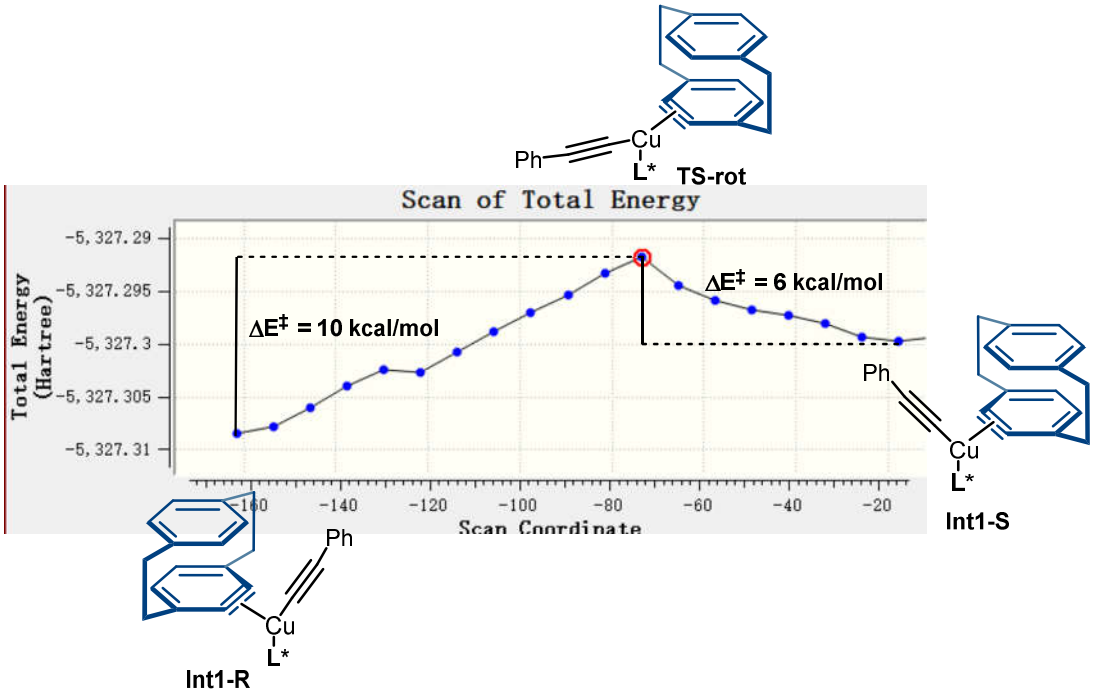


Figure S3. The energetic scanning for evaluating the activation energy of the interconversion between **Int1-R** and **Int1-S**.

We carried out energetic scanning of the dihedral angle to evaluate the activation energy of the interconversion between**Int1-R** and **Int1-S**(Figure S2). The results indicated that the activation electronic energy from **Int1-S** to **Int1-R** was evaluated to be 6 kcal/mol, indicating that **Int1-S** might be converted to **Int1-R** easily. The corresponding transition state was difficult to locate, probably due to the flat energy surface and very small imaginary frequency of this rotation transition state.

Distortion-interaction analysis

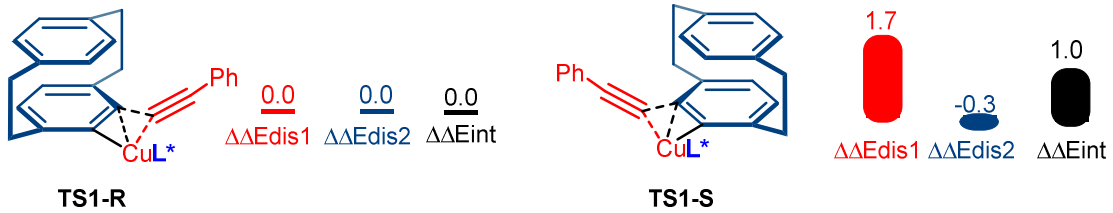


Figure S4. Distortion-interaction analysis of the enantioselective transition states.

We carried out distortion-interaction analysis to investigate the origin of the enantioselectivity (Figure S3, the [2,2]-paracyclophyne (blue) and copper acetylide (red) were selected as the two components). The calculations found that **TS1-S** has more distortion energy in copper acetylide by 1.7 kcal/mol compared to **TS1-R**. Also, **TS1-S** exhibited less interaction energy by 1.0

kcal/mol than **TS1-R**.Therefore, we attributed the origin of the enantioselectivity to the steric factor of the large chiral ligand **L***.

Table S9. Computed Energies for the Stationary Points.

Computed Energies for the Stationary Points. Thermal corrections to Gibbs energies (TCGs), single-point energies (SPEs) in gas phase and solvent.

	SPEs (in gas phase)[a] (hartree)	**TCGs (in gas phase)[b] (hartree)**	**SPEs (under SMD model)[c] (hartree)**
[2,2]-paracyclophyne	-4711.307858	0.210921	-617.608917
copper acetylide	-4709.615232	0.79472	-4709.664671
Int1-R	-5327.308492	1.038115	-5327.357742
Int1-S	-5327.30174	1.036326	-5327.35193
TS1-R	-5327.297161	1.038396	-5327.345925
TS1-S	-5327.292952	1.037684	-5327.34
Int2-R	-5327.391199	1.04262	-5327.441771
Int2-S	-5327.38692	1.040601	-5327.438881
TS0	-617.608912	0.213133	-617.623452

[a]Computed at B3LYP-D3(BJ)/def2-SVP.
[b]Computed at B3LYP-D3(BJ)/def2-SVP after Grimme's quasi-RRHO correction.
[c]Computed at SMD(DME)/B3LYP-D3(BJ)/def2-SVP//B3LYP-D3(BJ)/def2-SVP.

Cartesian coordinates for the stationary points

Int1-R

C	2.324653	-0.171606	1.912459
C	1.729258	-1.328696	1.851608
C	2.144996	-2.414299	2.632008
C	3.021689	-2.005872	3.671228
C	3.632692	-0.740485	3.695538
C	3.415104	0.215302	2.670159
H	3.373100	-2.758830	4.383825
H	4.427979	-0.559560	4.425787
C	4.409196	1.266238	2.254957
H	4.934541	1.660182	3.138268
H	3.864974	2.096905	1.786153
C	2.041697	-3.866094	2.226432
H	0.997655	-4.183623	2.087805
H	2.454151	-4.483524	3.039367
C	2.827382	-4.185466	0.886585
C	5.496548	0.735129	1.209859
C	5.245296	-0.685430	0.761677

C	4.394152	-0.972140	-0.314208
C	5.635216	-1.761170	1.575674
C	3.742121	-2.204210	-0.389642
H	4.103073	-0.174192	-0.999046
C	4.984096	-2.991278	1.498337
H	6.357470	-1.590776	2.379305
C	3.921063	-3.177655	0.602287
H	2.974030	-2.350559	-1.147428
H	5.204475	-3.758586	2.246247
H	3.217525	-5.214189	0.962955
H	2.113250	-4.173889	0.049118
H	6.489594	0.809716	1.679905
H	5.490298	1.414815	0.345502
C	5.002063	4.425356	-2.975923
C	4.368898	3.337001	-2.376499
C	3.207560	3.517965	-1.592831
C	2.713353	4.830951	-1.426453
C	3.351140	5.914206	-2.029273
C	4.496674	5.718738	-2.808259
H	5.899534	4.263366	-3.578588
H	4.764650	2.328072	-2.505437
H	1.822854	4.983220	-0.813907
H	2.952267	6.922224	-1.888450
H	4.994616	6.569843	-3.278858
C	2.548432	2.406425	-0.986981
C	1.957990	1.454518	-0.478321
Cu	1.127998	-0.050558	0.390913
P	-1.003565	1.005320	1.320421
C	-2.430632	-0.164221	1.258387
C	-2.908287	-0.811503	2.403421
C	-2.986158	-0.466405	-0.024559
C	-3.936486	-1.772071	2.352620
H	-2.480628	-0.558952	3.373394
C	-4.022655	-1.385708	-0.036007
C	-4.474093	-2.041285	1.111068
H	-4.292338	-2.278260	3.250440
C	-2.566335	0.180354	-1.302183
C	-1.327117	-0.032686	-1.985625
C	-3.439079	1.073605	-1.904868
C	-1.037276	0.671375	-3.160055
C	-3.130216	1.782541	-3.066326
C	-1.930123	1.601429	-3.722091

H	-0.090716	0.494441	-3.668088
H	-1.684039	2.154108	-4.628883
P	-0.060359	-1.147510	-1.248594
O	-5.446361	-2.939880	0.766912
O	-4.718425	-1.847169	-1.120186
O	-4.673994	1.455322	-1.460115
O	-4.154263	2.632129	-3.368925
C	-5.741743	-2.693098	-0.604297
C	-5.185963	2.376398	-2.418432
C	1.061444	-1.651865	-2.608410
C	2.002251	-0.709363	-3.055619
C	1.128597	-2.969714	-3.080723
C	2.994534	-1.067097	-3.974947
H	1.998086	0.299818	-2.638786
C	2.117672	-3.352093	-3.997839
H	0.423643	-3.718923	-2.719977
C	3.034431	-2.389441	-4.438500
H	3.812761	-2.681518	-5.150128
C	-1.043787	-2.635239	-0.837626
C	-1.883360	-3.224060	-1.789793
C	-1.034828	-3.114458	0.477325
C	-2.709754	-4.300547	-1.443311
H	-1.923077	-2.819881	-2.804023
C	-1.872650	-4.168195	0.856848
H	-0.408462	-2.614873	1.216435
C	-2.697599	-4.750816	-0.117528
H	-3.368882	-5.564303	0.173193
C	-0.817556	1.438857	3.093389
C	-0.247563	0.481567	3.945425
C	-1.109404	2.715930	3.599077
C	0.002819	0.769515	5.294688
H	0.030677	-0.498891	3.556133
C	-0.858669	3.032238	4.938897
H	-1.529527	3.478148	2.942218
C	-0.310580	2.046106	5.773463
H	-0.111625	2.285430	6.822768
C	-1.749623	2.493425	0.541373
C	-3.029967	2.930529	0.897042
C	-1.059666	3.126467	-0.502370
C	-3.631679	4.004557	0.227494
H	-3.579384	2.412200	1.686801
C	-1.652831	4.177888	-1.209254

H	-0.071375	2.763321	-0.787534
C	-2.933672	4.607472	-0.825697
H	-3.406731	5.425243	-1.378642
C	-1.900284	-4.657900	2.281406
H	-1.472134	-3.911812	2.965594
H	-2.930117	-4.870611	2.607036
H	-1.320159	-5.589911	2.394663
C	-3.604536	-4.928780	-2.481682
H	-3.016167	-5.475502	-3.237548
H	-4.310100	-5.642994	-2.031842
H	-4.181370	-4.158986	-3.019104
C	2.218319	-4.783037	-4.463436
H	2.547763	-4.845174	-5.511913
H	2.952993	-5.340399	-3.856927
H	1.254435	-5.305867	-4.373475
C	4.039846	-0.065044	-4.393800
H	4.423100	-0.274717	-5.403802
H	3.648025	0.962131	-4.373304
H	4.898926	-0.100038	-3.701202
C	0.630461	-0.275220	6.182074
H	0.726932	0.077783	7.219244
H	0.035566	-1.203224	6.190102
H	1.631942	-0.543627	5.809625
C	-1.159563	4.407813	5.480045
H	-1.811819	4.355943	6.367324
H	-0.235121	4.923598	5.789936
H	-1.657756	5.036555	4.727776
C	-0.953646	4.814624	-2.382901
H	-1.596008	4.787038	-3.278269
H	-0.715676	5.873466	-2.185650
H	-0.013784	4.297124	-2.618215
C	-5.013025	4.461756	0.624591
H	-5.022146	4.862374	1.651932
H	-5.389078	5.250939	-0.043704
H	-5.726340	3.621209	0.603981
H	-5.463198	3.316257	-1.916468
H	-6.060029	1.930778	-2.929435
H	-6.720766	-2.182223	-0.689658
H	-5.748506	-3.644185	-1.156926

Int1-S

C	-6.051063	3.812884	2.091577
C	-5.141289	2.772003	1.907583
C	-4.205594	2.809487	0.850488
C	-4.221703	3.924914	-0.016749
C	-5.134043	4.962009	0.173086
C	-6.052258	4.912794	1.227701
H	-6.766791	3.765572	2.916363
H	-5.139425	1.912727	2.581119
H	-3.507378	3.957126	-0.842158
H	-5.130146	5.816791	-0.508235
H	-6.765917	5.727003	1.374363
C	-3.260401	1.756325	0.665515
C	-2.409333	0.883364	0.503911
Cu	-1.124673	-0.495649	0.147349
P	0.988965	-0.021790	1.648676
C	2.021404	1.398833	1.078853
C	2.033919	2.623681	1.753904
C	2.756616	1.237037	-0.137183
C	2.749985	3.737783	1.274504
H	1.469081	2.723937	2.680987
C	3.468948	2.341250	-0.570029
C	3.453593	3.567126	0.100066
H	2.743337	4.693400	1.799601
C	2.817475	-0.046221	-0.895839
C	1.735621	-0.627604	-1.625750
C	3.983820	-0.797505	-0.849450
C	1.853629	-1.918745	-2.159934
C	4.092329	-2.075727	-1.397599
C	3.034577	-2.672662	-2.055068
H	0.996064	-2.364148	-2.664579
H	3.108861	-3.681931	-2.460402
P	0.094581	0.182354	-1.676675
O	4.189907	4.476814	-0.606815
O	4.219977	2.458662	-1.706688
O	5.153869	-0.477268	-0.221208
O	5.325552	-2.589096	-1.121117
C	4.832677	3.743579	-1.644713
C	6.050961	-1.560019	-0.449931
C	-0.675182	-0.178398	-3.300147
C	-2.052511	0.065923	-3.352961
C	0.002523	-0.593052	-4.455578
C	-2.773424	-0.124825	-4.540254

H	-2.571983	0.402960	-2.451357
C	-0.693243	-0.786620	-5.654951
H	1.079618	-0.767044	-4.428875
C	-2.078149	-0.554615	-5.676238
H	-2.629833	-0.715941	-6.607431
C	0.440125	1.975804	-1.858171
C	1.225096	2.440668	-2.921862
C	-0.091808	2.875863	-0.932788
C	1.504528	3.803713	-3.053484
H	1.641576	1.734310	-3.643628
C	0.181544	4.247258	-1.038367
H	-0.715033	2.504407	-0.119473
C	0.981630	4.689885	-2.098215
H	1.211694	5.756203	-2.181214
C	0.422170	0.472509	3.321572
C	-0.682900	1.340618	3.381554
C	0.975922	-0.017534	4.508174
C	-1.213213	1.745809	4.609014
H	-1.154788	1.679945	2.458168
C	0.451837	0.363062	5.754830
H	1.818771	-0.709619	4.473905
C	-0.631318	1.246951	5.786632
H	-1.044208	1.548627	6.754469
C	2.302114	-1.277586	1.934901
C	3.522637	-0.937862	2.528828
C	2.105099	-2.577422	1.450338
C	4.546929	-1.886008	2.656456
H	3.690579	0.085574	2.872460
C	3.121162	-3.534416	1.537153
H	1.161443	-2.831004	0.969350
C	4.330853	-3.174163	2.151727
H	5.132205	-3.916386	2.223746
C	-0.359162	5.198591	-0.002944
H	0.117823	5.014172	0.973949
H	-0.176552	6.248061	-0.276770
H	-1.442226	5.059565	0.141024
C	2.335226	4.306001	-4.207813
H	1.716437	4.451556	-5.110102
H	2.804939	5.274323	-3.976500
H	3.127042	3.587362	-4.470120
C	0.024043	-1.227818	-6.906329
H	-0.434678	-2.135506	-7.331364

H	-0.022153	-0.449311	-7.686252
H	1.084185	-1.443853	-6.709250
C	-4.266140	0.078962	-4.554016
H	-4.669174	0.074328	-5.577135
H	-4.767251	-0.723470	-3.986270
H	-4.543574	1.031108	-4.075258
C	-2.390156	2.687386	4.666539
H	-2.101265	3.660974	5.097920
H	-2.806381	2.871183	3.666334
H	-3.195021	2.281937	5.301134
C	1.042694	-0.197346	7.024855
H	2.142603	-0.132830	7.018463
H	0.674422	0.336271	7.913451
H	0.784121	-1.263440	7.144011
C	2.942503	-4.903819	0.934683
H	3.558312	-5.004653	0.024566
H	3.256993	-5.698403	1.630022
H	1.894334	-5.082230	0.655873
C	5.858255	-1.495606	3.290884
H	5.718149	-1.175106	4.336333
H	6.576637	-2.328921	3.289409
H	6.313669	-0.645691	2.755492
C	-1.925985	-1.916586	1.181873
C	-1.146679	-2.527853	0.334535
C	-2.873340	-2.444775	2.039630
C	-1.138043	-3.923298	0.220417
C	-2.655226	-3.839782	2.172412
C	-4.137127	-1.746161	2.462244
C	-1.816652	-4.548599	1.296538
C	-0.782990	-4.672115	-1.039669
H	-3.283179	-4.406058	2.867526
H	-4.590974	-2.289909	3.304608
H	-3.897044	-0.729671	2.806448
C	-5.207856	-1.624476	1.284091
H	-1.825619	-5.642214	1.347331
H	0.056635	-4.165994	-1.536029
H	-0.445200	-5.690800	-0.792304
C	-1.998406	-4.787272	-2.075179
C	-4.844528	-2.449905	0.070360
H	-6.188434	-1.926671	1.685033
H	-5.278966	-0.566058	0.996685
C	-3.232014	-4.043685	-1.620614

H	-2.230737	-5.854122	-2.216364
H	-1.659108	-4.399811	-3.048321
C	-4.141831	-1.875652	-0.999448
C	-4.943566	-3.849357	0.095039
C	-3.348628	-2.664054	-1.833946
C	-4.144440	-4.635709	-0.734933
H	-4.089827	-0.787547	-1.075665
H	-5.541556	-4.332729	0.873256
H	-2.694425	-2.180282	-2.560139
H	-4.130467	-5.720144	-0.592069
H	5.908850	3.628325	-1.408762
H	4.696747	4.264094	-2.604042
H	6.420939	-1.942437	0.513767
H	6.887687	-1.218765	-1.087507

Int2-R

C	-3.583124	1.168703	0.703274
C	-2.654417	1.527598	-0.311511
C	-3.105754	2.445542	-1.287914
C	-4.297523	3.153128	-1.076441
C	-5.208772	2.737765	-0.098742
C	-4.927898	1.632171	0.703904
H	-4.593465	3.941903	-1.776483
H	-6.207884	3.182009	-0.072809
C	-6.046357	0.803763	1.288102
H	-6.934988	1.439628	1.420087
H	-5.774568	0.412930	2.280311
C	-2.445352	2.494330	-2.649205
H	-1.352290	2.414497	-2.535819
H	-2.643592	3.464527	-3.132009
C	-2.938583	1.337224	-3.636540
C	-6.443609	-0.438831	0.362243
C	-5.797488	-0.393500	-1.003923
C	-4.582953	-1.052977	-1.237231
C	-6.225233	0.520380	-1.979133
C	-3.711272	-0.622231	-2.236761
H	-4.241819	-1.814449	-0.535929
C	-5.352217	0.956143	-2.975419
H	-7.198471	1.008011	-1.871713
C	-4.029974	0.488930	-3.028062
H	-2.711936	-1.056535	-2.289088

H	-5.656434	1.780120	-3.627453
H	-3.288546	1.805942	-4.569892
H	-2.079309	0.702273	-3.899230
H	-7.541894	-0.462387	0.279019
H	-6.139954	-1.364465	0.874123
C	-2.370493	-3.078713	5.260729
C	-2.932405	-2.131838	4.406192
C	-2.171831	-1.571300	3.356605
C	-0.834330	-1.994823	3.193823
C	-0.279398	-2.938234	4.054172
C	-1.041578	-3.485900	5.091535
H	-2.972836	-3.501757	6.068496
H	-3.967205	-1.810804	4.539052
H	-0.231407	-1.562570	2.397347
H	0.761650	-3.236367	3.915248
H	-0.603152	-4.224705	5.766484
C	-2.727479	-0.608261	2.469368
C	-3.156110	0.204052	1.660956
Cu	-0.891299	0.651144	-0.223767
P	0.975917	1.680300	0.668727
C	2.379358	1.468680	-0.499095
C	2.702154	2.543950	-1.342765
C	2.994360	0.194064	-0.703615
C	3.627390	2.433380	-2.395634
H	2.216560	3.505839	-1.179004
C	3.939459	0.132458	-1.717848
C	4.235675	1.205316	-2.559219
H	3.857412	3.276406	-3.047895
C	2.748079	-1.043679	0.090634
C	1.558526	-1.836122	0.063426
C	3.783979	-1.537927	0.867256
C	1.473940	-3.004395	0.833199
C	3.684632	-2.695800	1.639705
C	2.530833	-3.453289	1.647982
H	0.561091	-3.598116	0.797113
H	2.446818	-4.363359	2.242672
P	0.121180	-1.278033	-0.956087
O	5.145205	0.808944	-3.499036
O	4.669197	-0.957576	-2.110214
O	5.020436	-0.977380	1.062549
O	4.852685	-2.875940	2.333311
C	5.584119	-0.483584	-3.094074

C	5.780551	-1.971754	1.740108
C	-0.924310	-2.780564	-1.050300
C	-1.879524	-2.907624	-0.036206
C	-0.810671	-3.781822	-2.025400
C	-2.689005	-4.048959	0.058020
H	-2.011598	-2.097270	0.679845
C	-1.632702	-4.913565	-1.977706
H	-0.089878	-3.680370	-2.837628
C	-2.552150	-5.037233	-0.922490
H	-3.188221	-5.926437	-0.873871
C	0.905942	-1.055397	-2.596340
C	1.825999	-1.968288	-3.126659
C	0.641521	0.137078	-3.278021
C	2.469873	-1.706529	-4.341494
H	2.077760	-2.873023	-2.569287
C	1.293650	0.439955	-4.479249
H	-0.051957	0.854949	-2.837365
C	2.199420	-0.496096	-4.996476
H	2.721980	-0.268189	-5.929968
C	0.830699	3.498383	0.861497
C	-0.291542	4.122062	0.311372
C	1.788205	4.257528	1.553272
C	-0.469449	5.510522	0.428431
H	-1.050832	3.517555	-0.187178
C	1.633134	5.639801	1.687144
H	2.654644	3.763137	1.999391
C	0.499214	6.247119	1.116791
H	0.366955	7.328427	1.226532
C	1.524201	1.142415	2.328304
C	2.851240	0.878024	2.682111
C	0.504075	0.996811	3.280949
C	3.164169	0.436146	3.975541
H	3.651350	1.002475	1.951258
C	0.794886	0.588799	4.587346
H	-0.533392	1.193713	2.996395
C	2.129235	0.302163	4.910477
H	2.368493	-0.038019	5.923104
C	1.051102	1.763145	-5.156817
H	1.552345	2.574520	-4.602375
H	1.436268	1.770886	-6.186807
H	-0.022462	2.006200	-5.185584
C	3.432270	-2.712416	-4.920768

H	2.892735	-3.553350	-5.388964
H	4.071932	-2.263531	-5.695492
H	4.076719	-3.139537	-4.136454
C	-1.551218	-5.976155	-3.044792
H	-1.513464	-6.985782	-2.605362
H	-2.436436	-5.942836	-3.702598
H	-0.661534	-5.844572	-3.677848
C	-3.674138	-4.176630	1.191119
H	-4.299298	-5.075109	1.087333
H	-3.153668	-4.224134	2.161208
H	-4.336086	-3.296997	1.238375
C	-1.678318	6.168371	-0.187877
H	-1.913581	7.125773	0.300804
H	-1.508327	6.376322	-1.258787
H	-2.560042	5.512858	-0.125154
C	2.645678	6.471845	2.433864
H	3.095099	7.237316	1.779395
H	2.177953	7.005331	3.277841
H	3.459306	5.851152	2.836452
C	-0.299459	0.419104	5.608948
H	-0.037925	0.910770	6.559689
H	-1.249751	0.837806	5.250447
H	-0.470320	-0.648452	5.822946
C	4.581313	0.075318	4.345800
H	4.836900	0.424801	5.358193
H	4.716058	-1.019627	4.334196
H	5.302059	0.509711	3.637987
H	6.393509	-1.503089	2.521708
H	6.410740	-2.515406	1.008296
H	6.596978	-0.411733	-2.650899
H	5.582761	-1.162728	-3.958485

Int2-S

C	1.219433	6.062661	1.223572
C	1.579272	4.918704	0.513835
C	2.382496	3.922351	1.111731
C	2.846264	4.137884	2.426360
C	2.488545	5.289048	3.128327
C	1.664604	6.251876	2.536339
H	0.586718	6.814152	0.744612
H	1.239353	4.780075	-0.511453

H	3.489023	3.390001	2.891543
H	2.854513	5.434662	4.147752
H	1.379688	7.148776	3.091353
C	2.706128	2.732192	0.391296
C	2.982271	1.759314	-0.295505
Cu	0.676567	-0.409939	-1.106317
P	-0.508352	-1.872542	0.271593
C	-2.353771	-1.787634	0.257029
C	-3.139035	-2.853936	-0.198221
C	-2.969254	-0.556542	0.641730
C	-4.538525	-2.762776	-0.323016
H	-2.660077	-3.795256	-0.463217
C	-4.348752	-0.508013	0.534933
C	-5.117612	-1.565575	0.043685
H	-5.136147	-3.596748	-0.692360
C	-2.242368	0.625189	1.187546
C	-1.433483	1.525362	0.428766
C	-2.346335	0.904371	2.542201
C	-0.773830	2.582946	1.064273
C	-1.663712	1.951945	3.164165
C	-0.866081	2.820028	2.446207
H	-0.154924	3.247602	0.471368
H	-0.321917	3.640018	2.915490
P	-0.999632	1.160548	-1.317372
O	-6.429272	-1.183601	-0.008569
O	-5.170240	0.550823	0.812101
O	-3.046194	0.200336	3.483907
O	-1.906905	1.918633	4.508565
C	-6.498629	0.051480	0.698291
C	-2.853486	0.876188	4.723495
C	-0.470546	2.767838	-2.024836
C	0.797127	2.779667	-2.611209
C	-1.222157	3.954281	-1.968167
C	1.339016	3.963149	-3.140058
H	1.385732	1.859972	-2.625495
C	-0.712068	5.143338	-2.494503
H	-2.201614	3.962629	-1.487176
C	0.570196	5.128006	-3.076283
H	0.982892	6.061076	-3.472611
C	-2.604164	0.737604	-2.100169
C	-3.764904	1.504907	-1.936608
C	-2.665187	-0.463188	-2.814506

C	-4.981449	1.084582	-2.483297
H	-3.737402	2.414687	-1.334432
C	-3.875468	-0.922933	-3.350477
H	-1.760548	-1.069510	-2.913598
C	-5.018825	-0.134053	-3.178659
H	-5.973074	-0.487078	-3.580598
C	-0.137843	-3.652248	0.043347
C	-0.350489	-4.202486	-1.233601
C	0.457571	-4.439214	1.033978
C	-0.004516	-5.525853	-1.517540
H	-0.779355	-3.584447	-2.027142
C	0.829452	-5.767583	0.771369
H	0.654319	-4.017386	2.020519
C	0.579658	-6.296565	-0.498872
H	0.865976	-7.330717	-0.711488
C	-0.126918	-1.499812	2.022323
C	-0.821184	-2.106413	3.073406
C	0.825300	-0.506854	2.290247
C	-0.563657	-1.740645	4.401469
H	-1.587259	-2.854989	2.857161
C	1.084215	-0.107785	3.604678
H	1.343865	-0.018985	1.461625
C	0.384153	-0.739011	4.645147
H	0.577302	-0.429292	5.676812
C	-3.940191	-2.263562	-4.034455
H	-3.873305	-3.075126	-3.289341
H	-4.881008	-2.394869	-4.588672
H	-3.103829	-2.397416	-4.738372
C	-6.225007	1.922439	-2.328087
H	-7.131074	1.297420	-2.310486
H	-6.191063	2.516456	-1.402231
H	-6.334945	2.630408	-3.167650
C	-1.497879	6.428914	-2.425937
H	-0.944522	7.205481	-1.871917
H	-1.694066	6.832104	-3.433290
H	-2.466416	6.283288	-1.925851
C	2.728147	3.947789	-3.722253
H	3.087597	4.962817	-3.946028
H	3.433512	3.469477	-3.024173
H	2.759136	3.361009	-4.655402
C	-0.190861	-6.090535	-2.902502
H	0.731442	-5.969002	-3.496497

H	-0.423088	-7.165973	-2.874546
H	-0.998714	-5.576234	-3.444196
C	1.524310	-6.578474	1.834890
H	1.543793	-7.648834	1.582944
H	2.568220	-6.241788	1.953769
H	1.034047	-6.462762	2.814233
C	2.056928	1.003841	3.890221
H	1.522676	1.913668	4.209557
H	2.759813	0.731624	4.693503
H	2.631305	1.260361	2.990367
C	-1.312617	-2.408939	5.527029
H	-1.035978	-3.472969	5.614255
H	-1.103023	-1.931135	6.495539
H	-2.400197	-2.374708	5.351057
H	-6.916631	-0.121759	1.709831
H	-7.115497	0.765741	0.135520
H	-3.814237	1.308156	5.062053
H	-2.459207	0.170159	5.471122
C	3.451936	0.716210	-1.155064
C	2.582312	-0.309673	-1.617992
C	3.171233	-1.316809	-2.425417
C	4.442772	-1.116411	-2.976449
C	5.282874	-0.123665	-2.466474
C	4.850746	0.706041	-1.432443
H	4.847458	-1.838756	-3.693595
H	6.333610	-0.100150	-2.769314
C	5.860648	1.328503	-0.494163
H	6.840694	1.342894	-0.995563
H	5.606129	2.370671	-0.248499
C	2.560995	-2.701791	-2.478303
H	1.498806	-2.625774	-2.210234
H	2.611337	-3.131634	-3.493076
C	3.251800	-3.731712	-1.478434
C	6.003090	0.526212	0.872945
C	5.509493	-0.898231	0.753700
C	4.212374	-1.230494	1.171220
C	6.180403	-1.834418	-0.046828
C	3.519743	-2.293250	0.592760
H	3.680833	-0.557282	1.846356
C	5.482956	-2.888262	-0.637052
H	7.216382	-1.647081	-0.344616
C	4.103161	-3.046814	-0.434735

H	2.462992	-2.425063	0.824646
H	5.986751	-3.506762	-1.385579
H	3.882836	-4.422251	-2.059635
H	2.460028	-4.335061	-1.014991
H	7.059816	0.569273	1.184036
H	5.415806	1.044534	1.645766

TS0

C	-1.264312	1.376036	0.626584
C	-1.264312	1.376036	-0.626584
C	-1.394932	0.281852	-1.474006
C	-1.867445	-0.818112	-0.702756
C	-1.867445	-0.818112	0.702756
C	-1.394932	0.281852	1.474006
H	-2.065293	-1.763694	-1.217920
H	-2.065293	-1.763694	1.217920
C	-0.783715	0.115493	2.840816
H	-1.213592	-0.779549	3.314530
H	-1.040591	0.971770	3.481871
C	-0.783715	0.115493	-2.840816
H	-1.040591	0.971770	-3.481871
H	-1.213592	-0.779549	-3.314530
C	0.807165	-0.034177	-2.812713
C	0.807165	-0.034177	2.812713
C	1.360647	-0.170780	1.413607
C	1.791845	0.953990	0.698019
C	1.196895	-1.366357	0.696377
C	1.791845	0.953990	-0.698019
H	1.987339	1.888324	1.231299
C	1.196895	-1.366357	-0.696377
H	0.930325	-2.282376	1.231143
C	1.360647	-0.170780	-1.413607
H	1.987339	1.888324	-1.231299
H	0.930325	-2.282376	-1.231143
H	1.074187	-0.908658	-3.426273
H	1.250743	0.846516	-3.300318
H	1.074187	-0.908658	3.426273
H	1.250743	0.846516	3.300318

TS1-R

C	2.687023	0.079141	1.614127
C	1.912845	-0.920928	2.014168
C	2.386041	-1.815125	2.987526
C	3.542330	-1.383539	3.669813
C	4.328210	-0.334793	3.172628
C	4.000353	0.359406	1.984013
H	3.929212	-1.975184	4.505936
H	5.312551	-0.159660	3.616844
C	5.079766	0.964109	1.124438
H	5.979489	1.087238	1.745863
H	4.792067	1.960195	0.761752
C	1.893621	-3.239006	3.100001
H	0.798325	-3.264764	3.006416
H	2.139725	-3.639158	4.095992
C	2.514416	-4.218594	1.998840
C	5.442780	0.063431	-0.131556
C	5.000401	-1.374170	0.034339
C	3.836833	-1.828061	-0.600204
C	5.548704	-2.194781	1.031852
C	3.104227	-2.893072	-0.075749
H	3.418021	-1.248274	-1.420237
C	4.814063	-3.255488	1.559748
H	6.493127	-1.912635	1.506206
C	3.515574	-3.529570	1.101967
H	2.126930	-3.128863	-0.501292
H	5.196650	-3.784332	2.437471
H	2.982968	-5.067839	2.520588
H	1.694068	-4.626637	1.389542
H	6.529581	0.142045	-0.300069
H	4.940775	0.482474	-1.015864
C	4.745880	4.882371	-2.332774
C	4.280365	3.705251	-1.748157
C	3.101473	3.703569	-0.969527
C	2.414748	4.926204	-0.791633
C	2.885462	6.097740	-1.381381
C	4.050922	6.083257	-2.155836
H	5.659705	4.862782	-2.932062
H	4.823359	2.768914	-1.885148
H	1.506889	4.934829	-0.185783
H	2.339217	7.033073	-1.234455
H	4.417180	7.003867	-2.616216
C	2.602018	2.502928	-0.388335

C	2.100991	1.479005	0.077705
Cu	0.905187	0.019584	0.535057
P	-1.071345	0.926505	1.415955
C	-2.392698	-0.352771	1.263619
C	-2.784397	-1.114099	2.371692
C	-2.923866	-0.644235	-0.031868
C	-3.698897	-2.179476	2.271134
H	-2.376360	-0.871767	3.352641
C	-3.845916	-1.677615	-0.090872
C	-4.213234	-2.441042	1.017719
H	-3.990323	-2.768497	3.141294
C	-2.608071	0.101272	-1.285412
C	-1.381242	0.022006	-2.014442
C	-3.586754	0.914610	-1.834928
C	-1.210710	0.765867	-3.188714
C	-3.395219	1.668988	-2.993538
C	-2.211023	1.613228	-3.698906
H	-0.275463	0.685144	-3.740446
H	-2.058284	2.197210	-4.606771
P	-0.000096	-0.984552	-1.321803
O	-5.088942	-3.416178	0.629324
O	-4.495710	-2.151123	-1.197752
O	-4.837350	1.163763	-1.339155
O	-4.512681	2.414865	-3.240394
C	-5.402318	-3.146987	-0.734089
C	-5.497126	1.967625	-2.312376
C	1.185828	-1.185458	-2.700253
C	1.962040	-0.063111	-3.050426
C	1.461606	-2.421838	-3.289017
C	2.983469	-0.165962	-3.996863
H	1.801006	0.887359	-2.538850
C	2.500055	-2.555338	-4.226125
H	0.886619	-3.304124	-3.003556
C	3.238759	-1.421652	-4.574447
H	4.049858	-1.517323	-5.302663
C	-0.799110	-2.615456	-1.081272
C	-1.574976	-3.209120	-2.083544
C	-0.725681	-3.200525	0.188146
C	-2.283615	-4.389114	-1.829612
H	-1.658753	-2.727537	-3.060955
C	-1.443934	-4.368331	0.475556
H	-0.146140	-2.696392	0.964723

C	-2.214106	-4.945473	-0.544654
H	-2.793364	-5.846936	-0.324486
C	-0.993604	1.349002	3.197817
C	-0.331849	0.443245	4.038151
C	-1.463932	2.559941	3.728276
C	-0.154460	0.716055	5.401044
H	0.084315	-0.473003	3.618837
C	-1.294258	2.859352	5.085407
H	-1.955221	3.286349	3.080108
C	-0.644698	1.925269	5.907133
H	-0.504753	2.155158	6.967963
C	-1.836495	2.374196	0.592285
C	-3.151010	2.765949	0.868042
C	-1.110460	3.021361	-0.416998
C	-3.751673	3.806474	0.147814
H	-3.728582	2.232326	1.626668
C	-1.700223	4.039424	-1.174713
H	-0.094453	2.690300	-0.637703
C	-3.017886	4.419736	-0.875475
H	-3.492997	5.203468	-1.473252
C	-1.401767	-4.971200	1.855643
H	-1.502554	-4.191277	2.625365
H	-2.210356	-5.702240	2.000892
H	-0.444206	-5.487711	2.037183
C	-3.121487	-5.015412	-2.915527
H	-2.491563	-5.396022	-3.736806
H	-3.716191	-5.859487	-2.535770
H	-3.808889	-4.275201	-3.356485
C	2.821039	-3.909835	-4.804802
H	3.518085	-3.834953	-5.652142
H	3.287699	-4.555851	-4.041900
H	1.911299	-4.425005	-5.152132
C	3.834103	1.027312	-4.350341
H	3.932532	1.142261	-5.441741
H	3.417769	1.957217	-3.939272
H	4.853999	0.913317	-3.944814
C	0.574231	-0.274954	6.273257
H	0.745483	0.122249	7.284483
H	0.004130	-1.214244	6.370808
H	1.548526	-0.536685	5.830268
C	-1.770212	4.174520	5.650922
H	-2.271539	4.038002	6.622283

H	-0.923388	4.862355	5.817674
H	-2.473725	4.675416	4.969643
C	-0.941304	4.700697	-2.296298
H	-1.596320	4.893363	-3.160228
H	-0.520067	5.669936	-1.979588
H	-0.101611	4.075201	-2.629921
C	-5.162513	4.231636	0.469067
H	-5.203628	4.789365	1.420115
H	-5.578950	4.884933	-0.312483
H	-5.822084	3.356445	0.582401
H	-5.963239	2.834607	-1.822159
H	-6.257190	1.358959	-2.840280
H	-6.439325	-2.766169	-0.810054
H	-5.279687	-4.064711	-1.328835

TS1-S

C	0.561600	6.259114	1.624410
C	0.771738	5.007754	1.048430
C	1.273449	3.935204	1.822959
C	1.568759	4.169653	3.183648
C	1.355641	5.425793	3.750603
C	0.848071	6.475373	2.977142
H	0.172713	7.074876	1.009298
H	0.554187	4.841517	-0.006881
H	1.962649	3.349775	3.786408
H	1.587405	5.588148	4.806345
H	0.680940	7.457648	3.425424
C	1.442585	2.654632	1.227251
C	1.497350	1.565127	0.655643
Cu	1.044416	-0.026991	-0.377405
P	-0.076833	-1.748549	0.673208
C	-1.717852	-2.180651	-0.068926
C	-1.942790	-3.406511	-0.707226
C	-2.760668	-1.204926	-0.013096
C	-3.162959	-3.720731	-1.335218
H	-1.156121	-4.158299	-0.717216
C	-3.954940	-1.549956	-0.622072
C	-4.151921	-2.760106	-1.289210
H	-3.319513	-4.677220	-1.834776
C	-2.654428	0.096103	0.703855
C	-1.928488	1.232089	0.234559

C	-3.281353	0.232822	1.932588
C	-1.824322	2.374581	1.040158
C	-3.162401	1.373701	2.725682
C	-2.433137	2.467537	2.304362
H	-1.239958	3.222072	0.692488
H	-2.321059	3.358691	2.922362
P	-0.886578	1.077417	-1.269581
O	-5.404407	-2.783048	-1.830084
O	-5.088473	-0.792496	-0.721494
O	-4.029411	-0.702140	2.595646
O	-3.822197	1.177888	3.906776
C	-6.067171	-1.616053	-1.347716
C	-4.483447	-0.078748	3.793367
C	-0.615100	2.792373	-1.861029
C	0.662690	3.079834	-2.355376
C	-1.585470	3.804672	-1.824923
C	0.991546	4.367061	-2.802352
H	1.423576	2.299176	-2.369325
C	-1.281839	5.101840	-2.255017
H	-2.580532	3.596150	-1.426725
C	0.009851	5.363951	-2.738630
H	0.258280	6.378223	-3.066526
C	-1.987275	0.316187	-2.527673
C	-3.265356	0.803520	-2.825123
C	-1.517494	-0.837970	-3.163860
C	-4.085526	0.139521	-3.743495
H	-3.640546	1.693797	-2.316694
C	-2.326455	-1.536639	-4.069574
H	-0.518445	-1.207921	-2.917415
C	-3.605366	-1.034549	-4.343494
H	-4.250468	-1.577025	-5.040902
C	0.867753	-3.315919	0.618384
C	1.218350	-3.830789	-0.641951
C	1.351069	-3.939717	1.772873
C	1.986299	-4.993159	-0.755899
H	0.893453	-3.309711	-1.544971
C	2.175092	-5.073169	1.684516
H	1.103985	-3.533067	2.754920
C	2.466543	-5.593633	0.419065
H	3.094975	-6.485677	0.341377
C	-0.518190	-1.500401	2.435007
C	-1.347270	-2.405823	3.110338

C	-0.092015	-0.329662	3.070623
C	-1.750501	-2.154411	4.425907
H	-1.704990	-3.301825	2.596916
C	-0.499264	-0.045413	4.381470
H	0.518886	0.388617	2.519923
C	-1.321265	-0.968388	5.041350
H	-1.652490	-0.749074	6.060933
C	-1.833478	-2.815738	-4.694966
H	-1.765590	-3.614010	-3.936775
H	-2.505163	-3.165298	-5.492656
H	-0.826705	-2.689074	-5.123797
C	-5.448671	0.687819	-4.084209
H	-6.104480	-0.086946	-4.510000
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C	-2.302610	6.207240	-2.147539
H	-2.185581	6.758067	-1.197797
H	-2.196903	6.938222	-2.963775
H	-3.329352	5.812378	-2.170705
C	2.374224	4.652067	-3.330950
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H	3.123478	4.017873	-2.833545
H	2.433919	4.438511	-4.412309
C	2.272108	-5.600648	-2.105930
H	3.245473	-6.113484	-2.122578
H	1.504154	-6.349315	-2.367068
H	2.270145	-4.839587	-2.899690
C	2.760411	-5.685598	2.931138
H	3.032437	-6.740346	2.776861
H	3.676058	-5.147630	3.231383
H	2.057754	-5.628630	3.776506
C	-0.078380	1.243885	5.037098
H	-0.328983	2.104801	4.398080
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H	1.012517	1.270658	5.195905
C	-2.663665	-3.122543	5.135539
H	-2.206899	-4.122734	5.213874
H	-2.904884	-2.782737	6.153616
H	-3.609222	-3.245931	4.581261
H	-6.836944	-1.905598	-0.606502
H	-6.521404	-1.075598	-2.191147
H	-5.577584	0.079622	3.735879

H	-4.224920	-0.709794	4.657819
C	2.611716	-0.221725	-1.642142
C	2.852224	0.851229	-0.904603
C	3.985408	1.657243	-0.862975
C	4.787106	1.411063	-2.004733
C	4.594836	0.293563	-2.829339
C	3.589576	-0.656261	-2.551828
H	5.690453	2.013432	-2.139609
H	5.348419	0.075581	-3.593287
C	3.754685	-2.111731	-2.922872
H	4.074895	-2.227247	-3.971433
H	2.777577	-2.603446	-2.822380
C	4.535860	2.407350	0.323436
H	3.831929	3.171432	0.680776
H	5.448596	2.928782	-0.003300
C	4.894486	1.457260	1.537026
C	4.809708	-2.874945	-2.002595
C	5.135840	-2.129516	-0.728537
C	4.209852	-2.045846	0.320056
C	6.243498	-1.270019	-0.675970
C	4.232128	-0.963992	1.201310
H	3.370220	-2.737102	0.350520
C	6.278692	-0.202062	0.219445
H	7.022945	-1.351642	-1.439110
C	5.193478	0.049465	1.071969
H	3.396536	-0.827031	1.893123
H	7.082960	0.535301	0.138296
H	5.745107	1.905558	2.076819
H	4.038422	1.436232	2.226103
H	5.735146	-3.022186	-2.580840
H	4.408035	-3.874374	-1.781109

[2,2]-paracyclophyne(6-311+G(d,p))

C	0.675437	1.350480	-1.311881
C	-0.567548	1.339846	-1.362711
C	-1.465947	1.395207	-0.310867
C	-0.756556	1.816150	0.844881
C	0.643523	1.824706	0.908322
C	1.466997	1.419360	-0.177372
H	-1.312036	1.952840	1.768438
H	1.109619	1.965393	1.879180

C	2.818964	0.789205	0.026053
H	3.165372	1.037363	1.031802
H	3.555029	1.191284	-0.674398
C	-2.826884	0.751850	-0.266134
H	-3.277725	0.810562	-1.257489
H	-3.482314	1.295677	0.418428
C	-2.793027	-0.781374	0.190978
C	2.795873	-0.794409	-0.131652
C	1.413073	-1.373089	0.061461
C	0.637094	-1.740189	-1.041232
C	0.767455	-1.282445	1.298857
C	-0.753163	-1.739012	-0.968234
H	1.114614	-1.878589	-2.005348
C	-0.619993	-1.269919	1.369928
H	1.346382	-1.071186	2.192248
C	-1.398959	-1.359353	0.210612
H	-1.331182	-1.881439	-1.875460
H	-1.100493	-1.050166	2.317632
H	-3.228696	-0.848757	1.190449
H	-3.443109	-1.346028	-0.481630
H	3.514098	-1.208427	0.581659
H	3.152414	-1.050621	-1.131563

[2,2]-paracyclophyne(def2-SVP)

C	0.648462	1.271638	-1.364817
C	-0.604587	1.266388	-1.384166
C	-1.472683	1.389927	-0.305762
C	-0.723660	1.862415	0.809095
C	0.681645	1.866494	0.833561
C	1.474781	1.401275	-0.254462
H	-1.256325	2.055647	1.745985
H	1.179098	2.061162	1.789195
C	2.836726	0.787108	-0.058791
H	3.250492	1.153103	0.892765
H	3.529284	1.107254	-0.852102
C	-2.841578	0.775310	-0.173919
H	-3.423691	0.961309	-1.088004
H	-3.379012	1.261885	0.653705
C	-2.811404	-0.801956	0.097273
C	2.810613	-0.806882	-0.029527
C	1.416143	-1.364738	0.140573

C	0.675347	-1.790697	-0.970133
C	0.724977	-1.203193	1.351343
C	-0.720349	-1.789171	-0.941877
H	1.188824	-1.983260	-1.916055
C	-0.667577	-1.196989	1.378648
H	1.278226	-0.939088	2.257151
C	-1.410555	-1.357031	0.198270
H	-1.273118	-1.983230	-1.865245
H	-1.182990	-0.929788	2.305439
H	-3.367821	-0.997092	1.026828
H	-3.357612	-1.304145	-0.715011
H	3.476675	-1.138547	0.782764
H	3.240162	-1.184604	-0.969280

copper acetylide

C	-7.986066	1.233267	-1.317109
C	-6.607230	1.228376	-1.524053
C	-5.713854	1.530593	-0.470746
C	-6.264434	1.844276	0.793210
C	-7.644027	1.844288	0.993904
C	-8.514214	1.538179	-0.057915
H	-8.656990	0.993647	-2.146507
H	-6.195404	0.983316	-2.505052
H	-5.585351	2.081201	1.614845
H	-8.045958	2.085954	1.981619
H	-9.595121	1.538440	0.102025
C	-4.302519	1.472990	-0.661893
C	-3.084493	1.326394	-0.800305
Cu	-1.272627	0.746524	-0.778685
P	-0.659112	-1.461838	-0.420056
C	0.296948	-1.447298	1.154703
C	-0.338755	-1.810689	2.348672
C	1.635557	-0.941083	1.174069
C	0.296303	-1.712912	3.600899
H	-1.361345	-2.187555	2.308254
C	2.244013	-0.892461	2.418007
C	1.595420	-1.247015	3.602705
H	-0.209720	-1.994771	4.524761
C	2.412170	-0.517147	-0.028614
C	2.167202	0.661326	-0.800552
C	3.469173	-1.306619	-0.454190

C	2.919178	0.920024	-1.954219
C	4.214561	-1.036422	-1.604369
C	3.956145	0.072032	-2.385291
H	2.700555	1.813021	-2.540279
H	4.530754	0.280000	-3.288374
P	0.738157	1.732067	-0.372413
O	2.433551	-1.034102	4.660407
O	3.506307	-0.454220	2.711366
O	3.911973	-2.476700	0.099933
O	5.133961	-2.030244	-1.791485
C	3.700232	-0.701266	4.101177
C	5.107497	-2.809211	-0.599165
C	1.062230	3.355992	-1.157749
C	-0.028827	3.958044	-1.791510
C	2.294399	4.030181	-1.100675
C	0.090481	5.232905	-2.372281
H	-0.987512	3.430707	-1.818398
C	2.440929	5.294976	-1.673779
H	3.152240	3.564063	-0.612543
C	1.327081	5.879381	-2.304302
H	1.433509	6.871713	-2.753759
C	0.954265	2.019898	1.428643
C	2.190845	2.355833	1.989367
C	-0.159555	1.830097	2.256412
C	2.330068	2.502179	3.374079
H	3.068844	2.467614	1.350455
C	-0.039884	1.938304	3.647411
H	-1.122768	1.564845	1.811327
C	1.209799	2.276522	4.185789
H	1.315049	2.358289	5.271689
C	-2.069816	-2.590855	-0.090787
C	-3.304502	-1.976527	0.145224
C	-1.972185	-3.992033	-0.059119
C	-4.449429	-2.741886	0.425954
H	-3.386882	-0.888260	0.089381
C	-3.096006	-4.775711	0.215747
H	-1.018916	-4.482864	-0.257447
C	-4.323446	-4.133495	0.459739
H	-5.207132	-4.743300	0.673523
C	0.470808	-2.339662	-1.565263
C	1.192795	-3.479323	-1.187283
C	0.672101	-1.782768	-2.833213

C	2.095468	-4.080173	-2.070974
H	1.088314	-3.878888	-0.176575
C	1.594231	-2.344196	-3.726260
H	0.133479	-0.871957	-3.108126
C	2.288749	-3.494711	-3.330215
H	3.016185	-3.938306	-4.016282
C	-1.217371	1.642637	4.539081
H	-1.285239	0.558555	4.734662
H	-1.131603	2.151246	5.510909
H	-2.163874	1.947414	4.068095
C	3.659558	2.898355	3.965235
H	3.707030	2.680028	5.042837
H	4.488024	2.373045	3.464397
H	3.841474	3.979791	3.842607
C	3.756655	6.030210	-1.621210
H	4.131511	6.251909	-2.634246
H	3.652753	6.995758	-1.099025
H	4.525676	5.444212	-1.097090
C	-1.098634	5.867824	-3.046773
H	-0.864885	6.876222	-3.418050
H	-1.440372	5.260016	-3.900658
H	-1.950708	5.945685	-2.352375
C	-5.771921	-2.054640	0.653698
H	-6.557322	-2.768852	0.941575
H	-5.694969	-1.286936	1.439425
H	-6.103162	-1.523545	-0.253350
C	-3.008859	-6.281538	0.239358
H	-3.410326	-6.691801	1.180430
H	-3.595961	-6.727126	-0.581447
H	-1.970028	-6.627322	0.134000
C	1.867921	-1.686243	-5.053574
H	2.525654	-0.810298	-4.918619
H	2.366062	-2.372837	-5.753728
H	0.940169	-1.325638	-5.523700
C	2.835140	-5.331511	-1.670296
H	2.213073	-6.228666	-1.831923
H	3.755498	-5.464530	-2.259056
H	3.100609	-5.309646	-0.602075
H	4.399920	-1.549864	4.231011
H	4.090844	0.204848	4.586834
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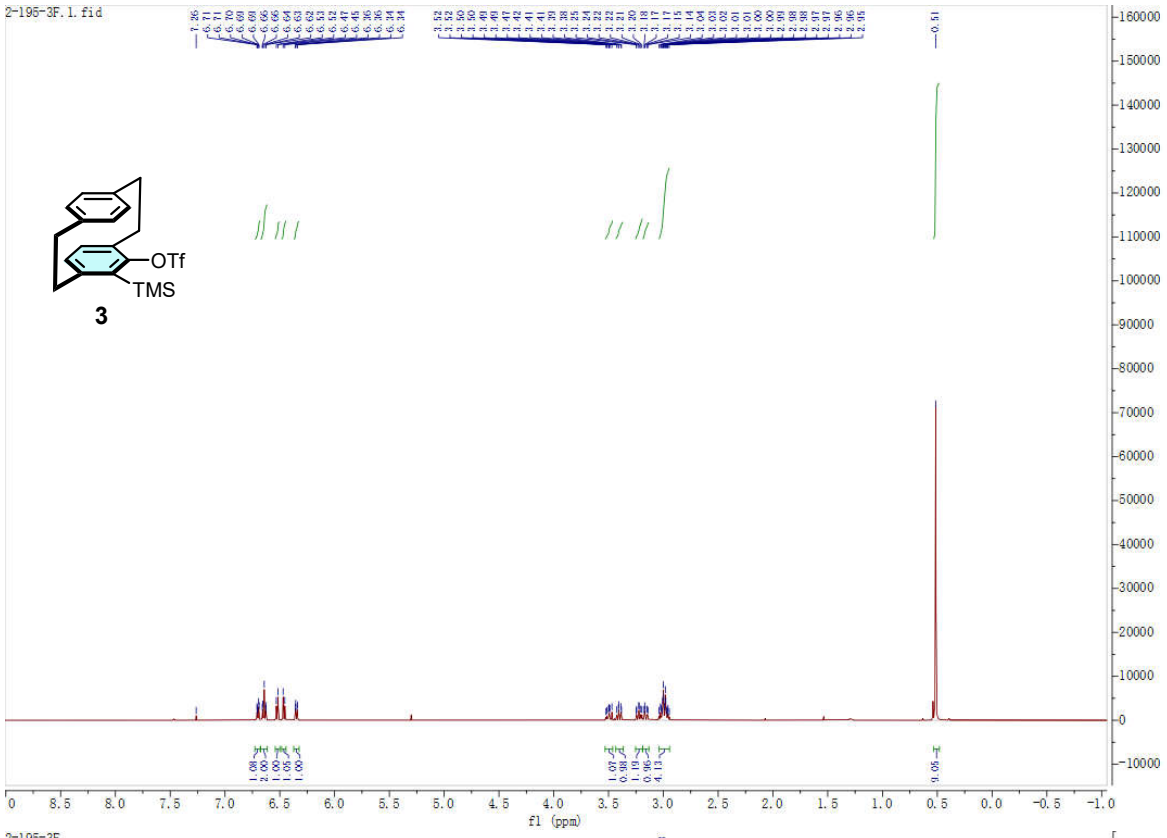
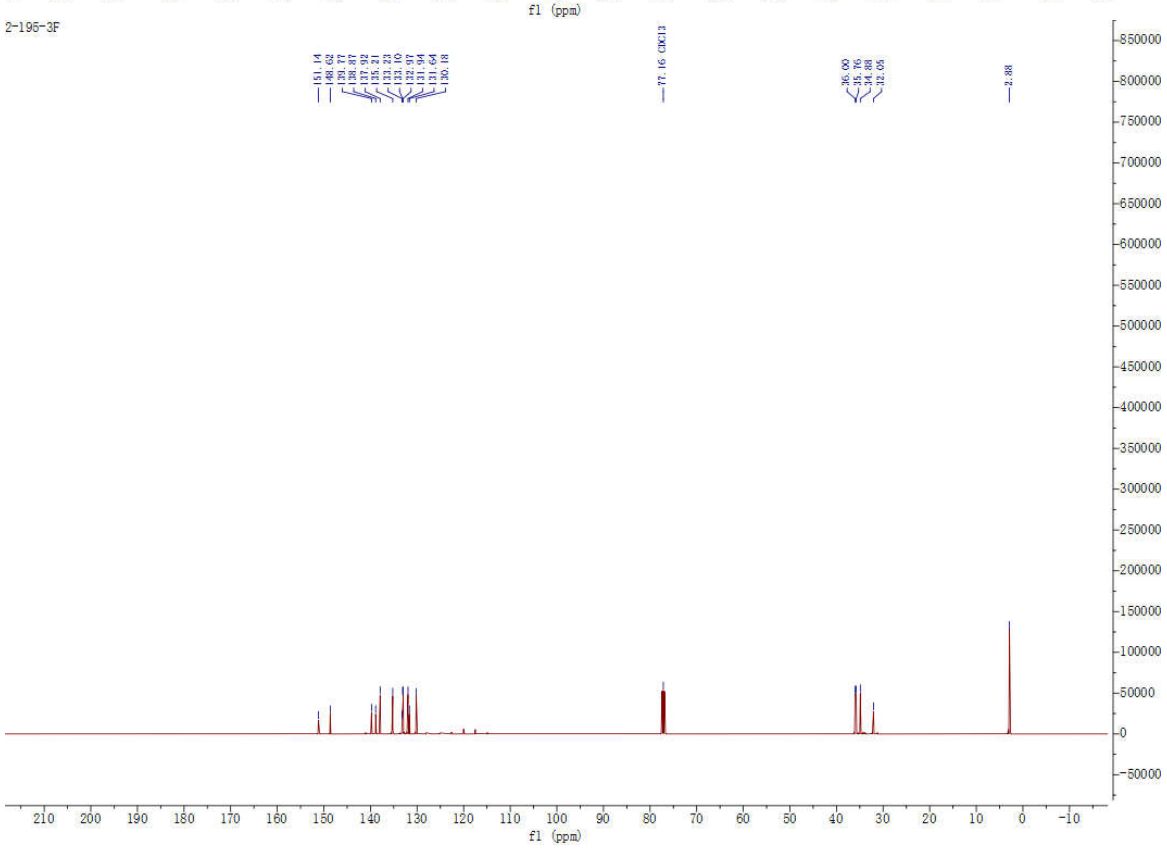
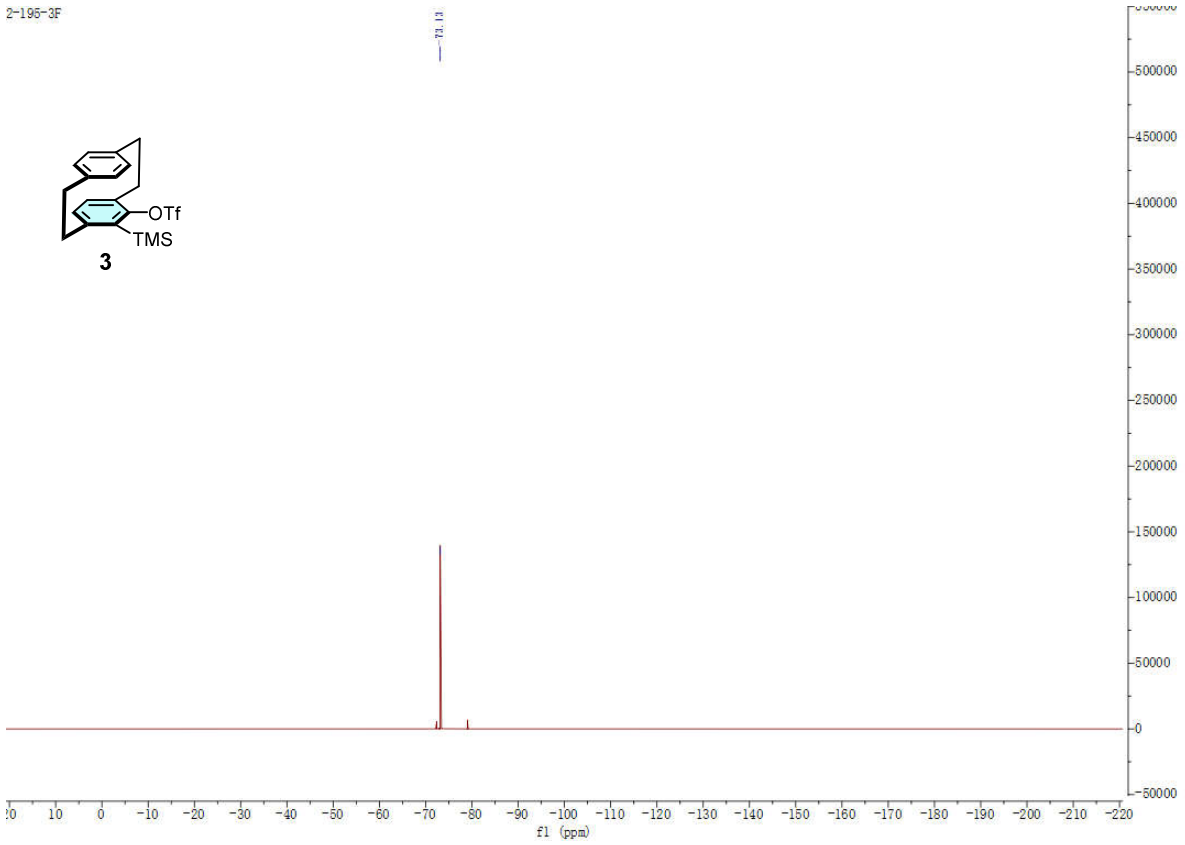
H	5.102519	-3.877751	-0.854821

10.NMR spectra



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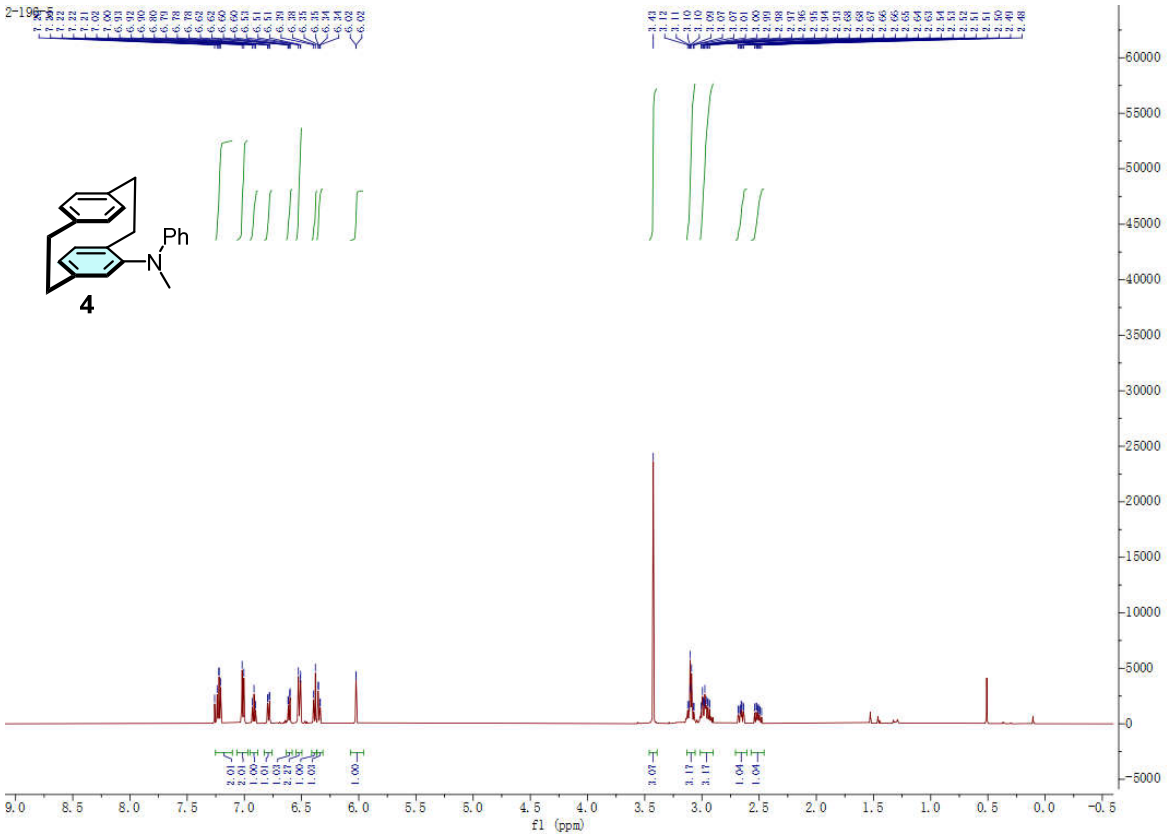
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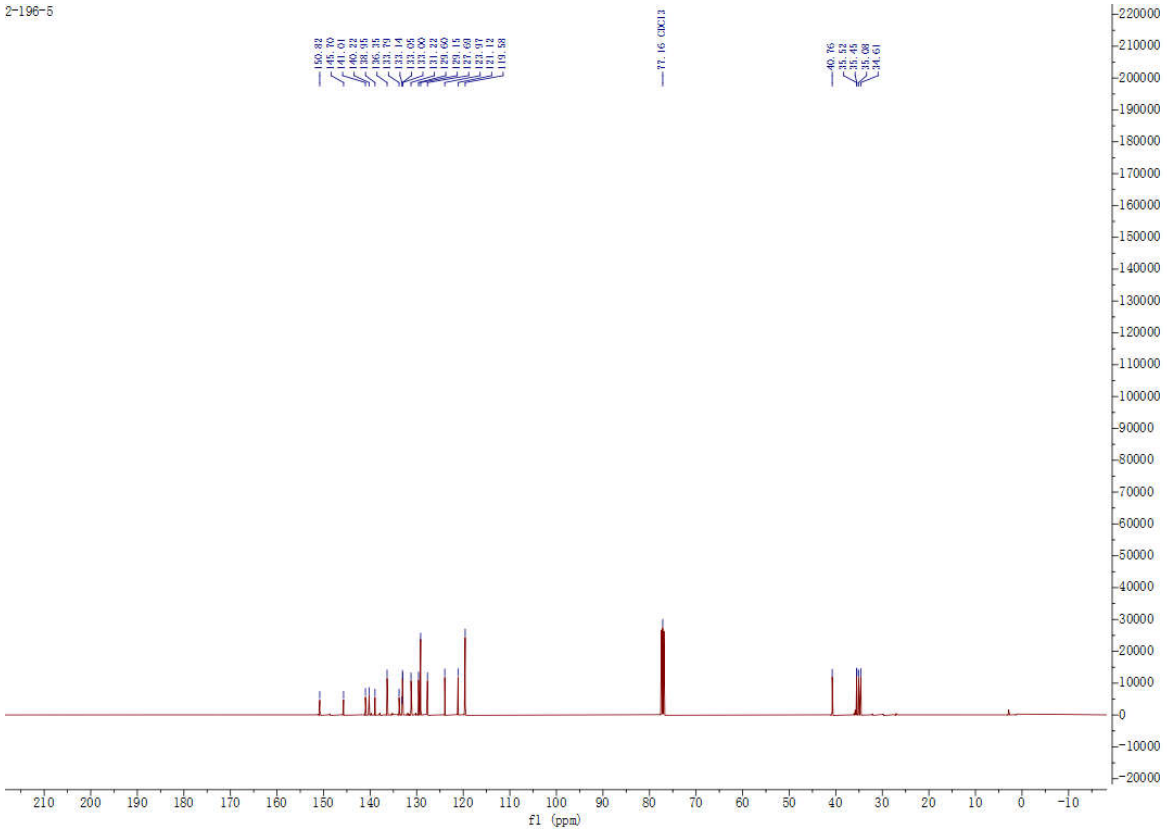
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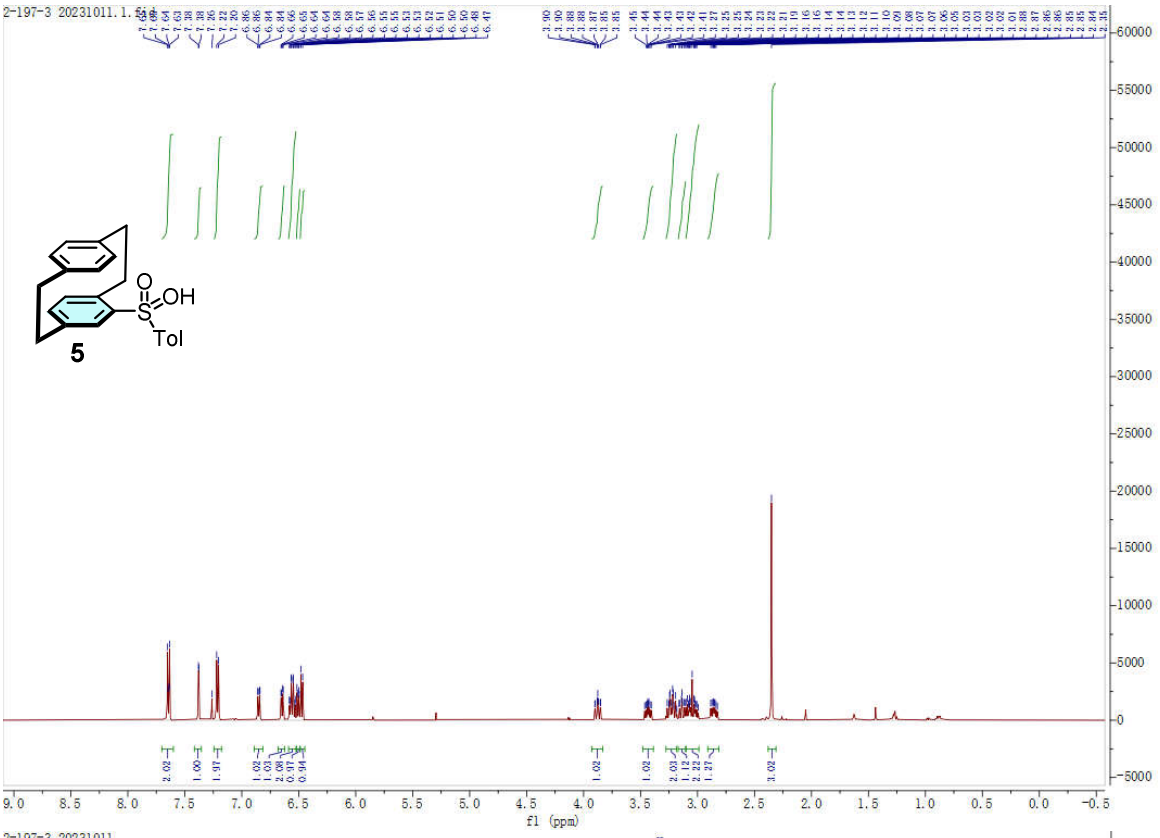
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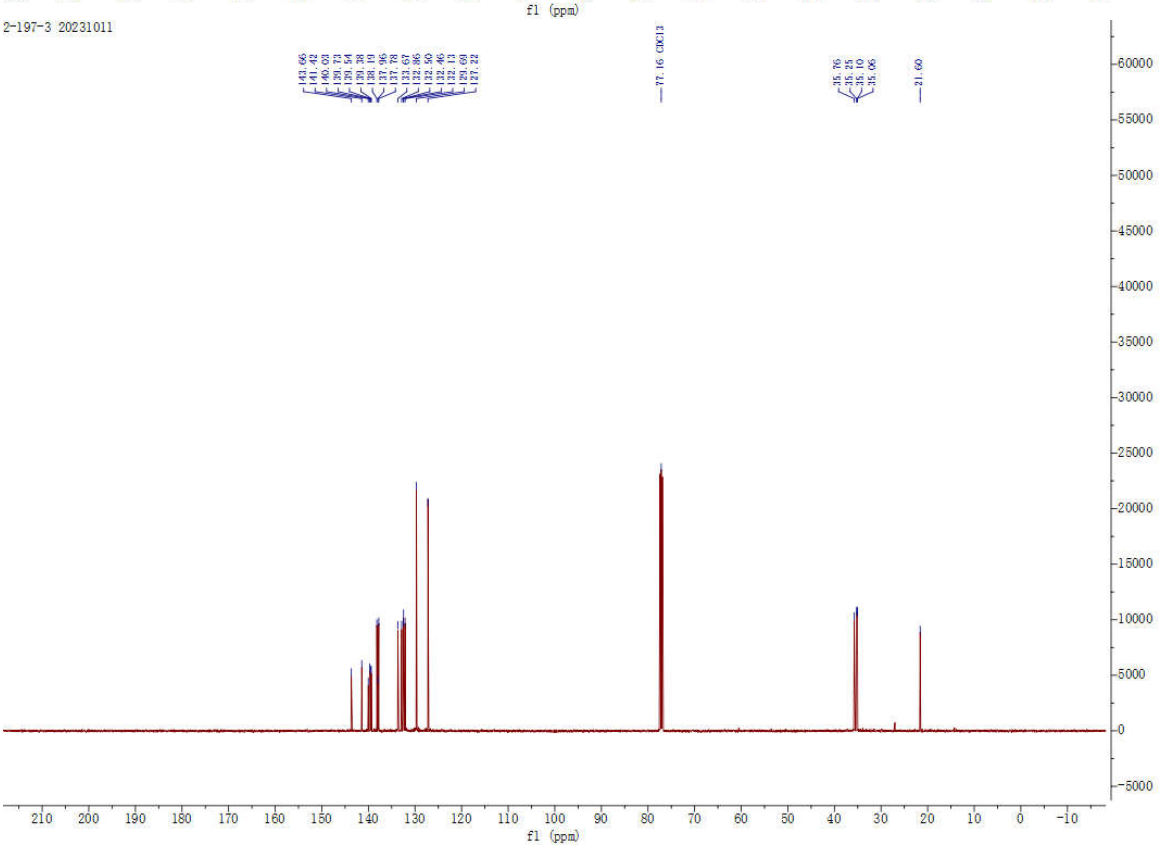
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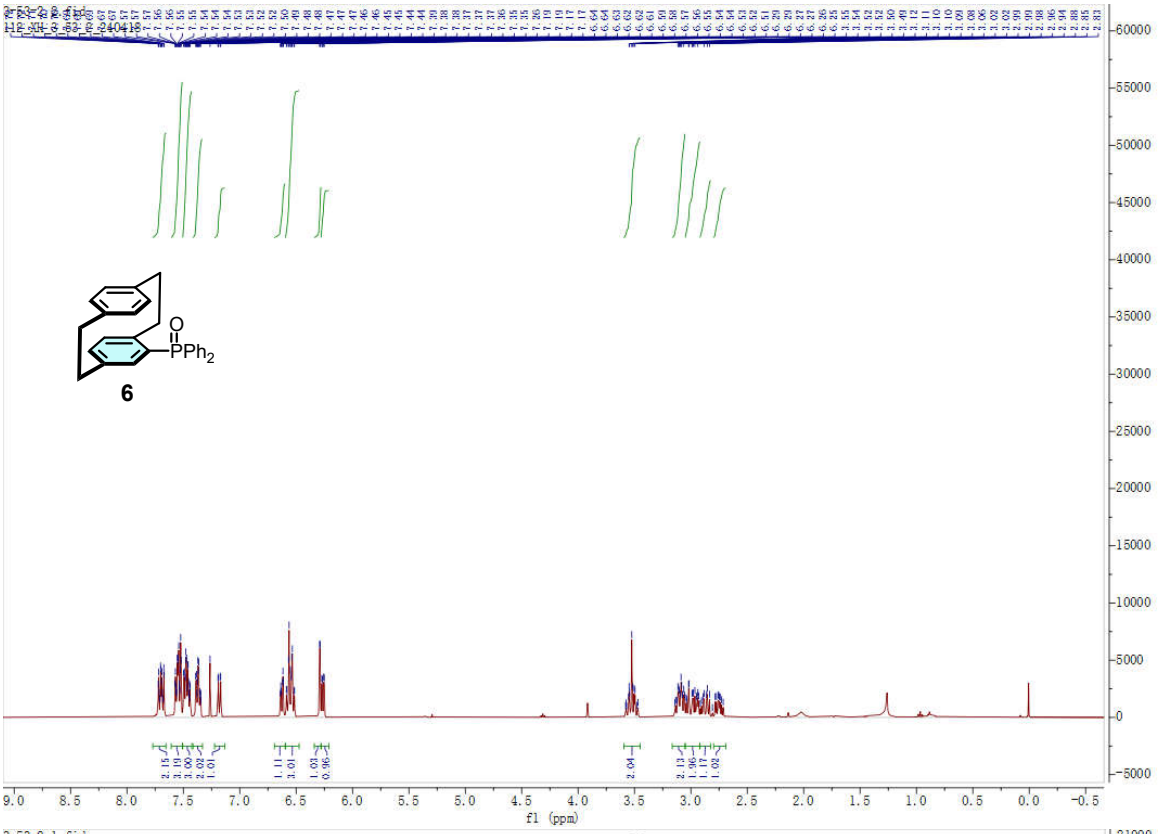
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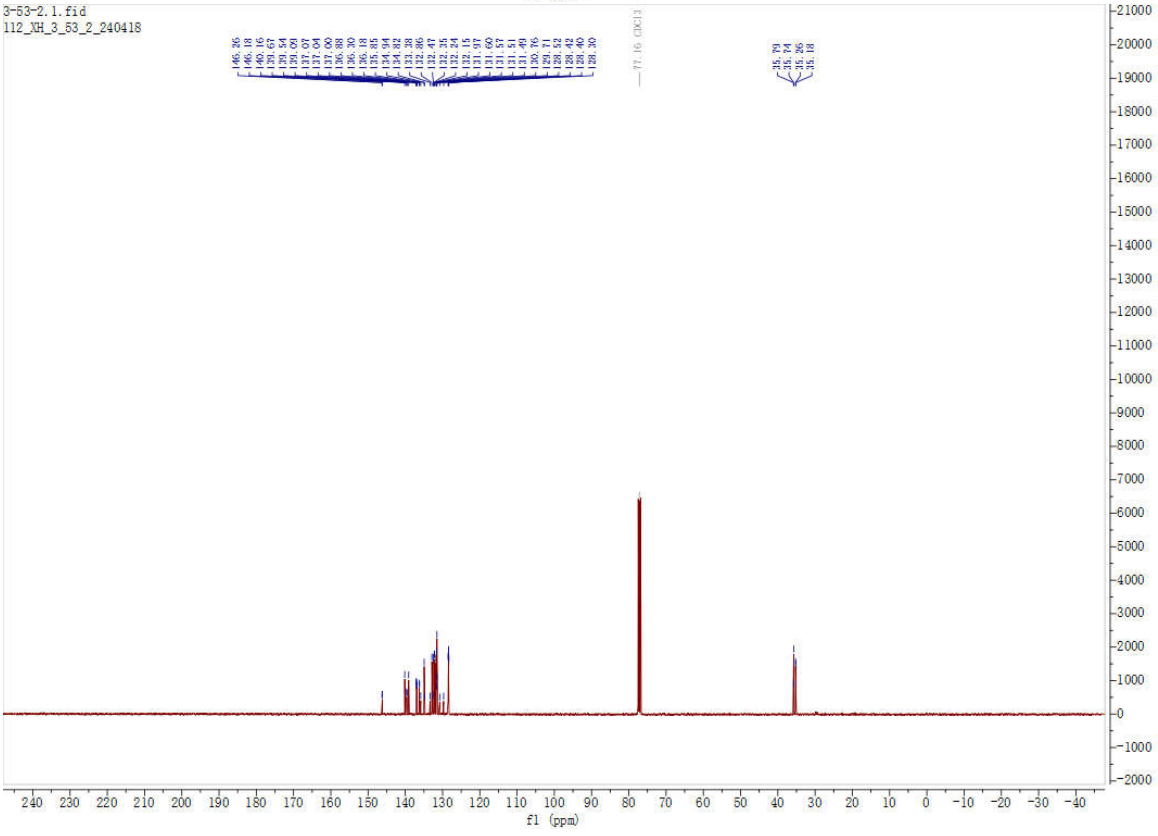
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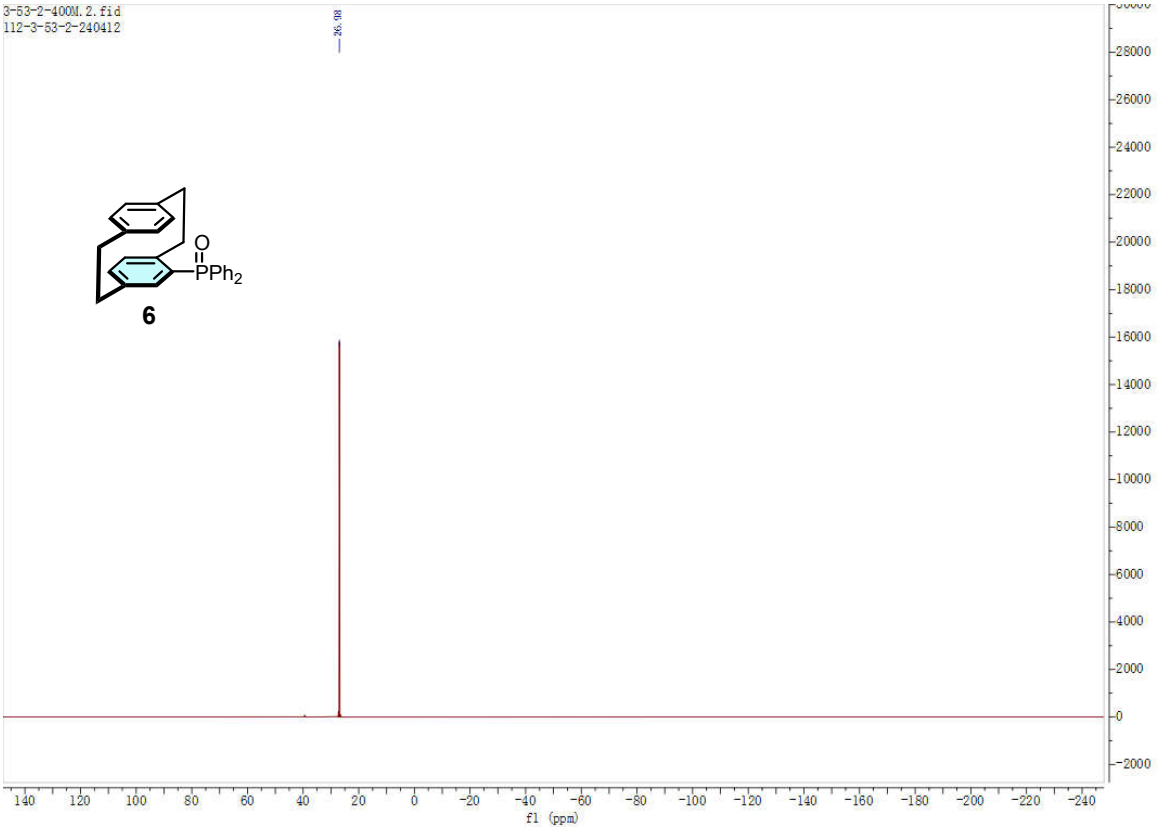
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26.98
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PPh2
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12000
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8000
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4000
2000
0
-2000
140
120
100
80
60
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-120
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-180
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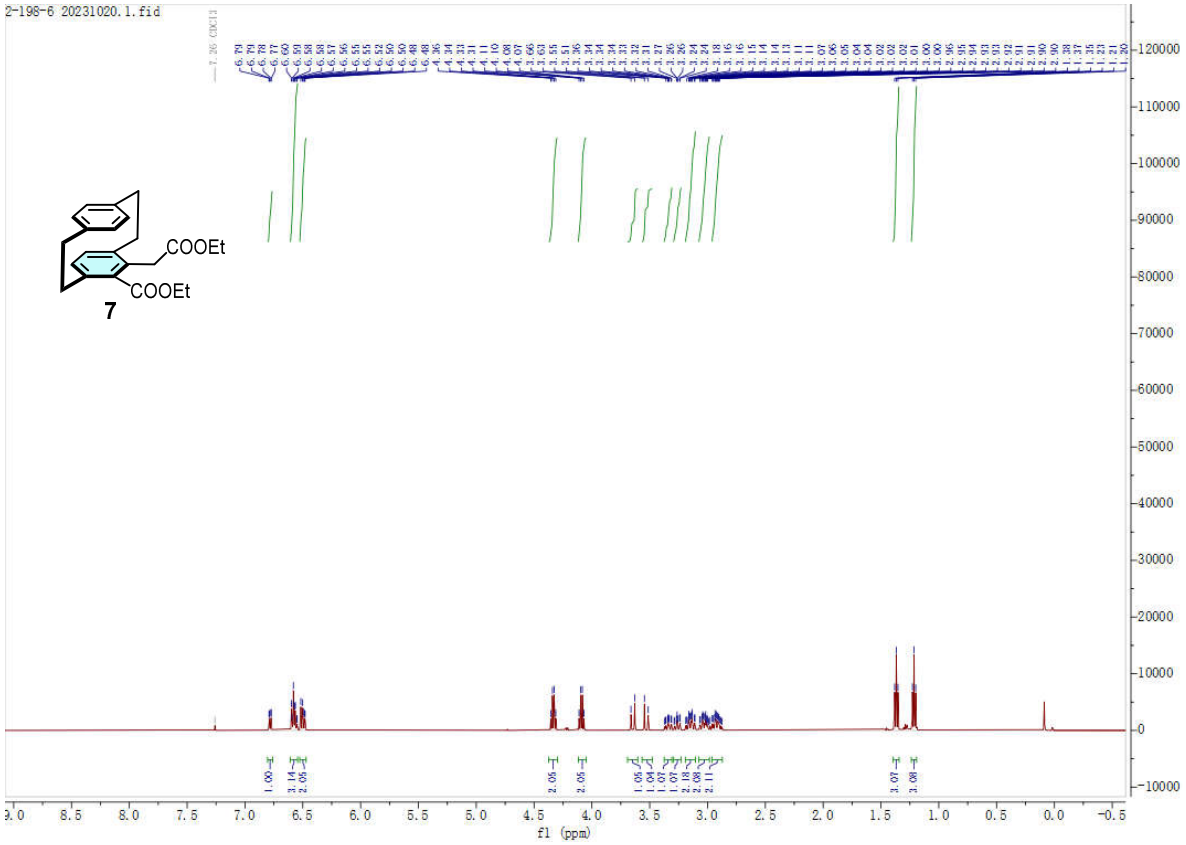
-240
f1 (ppm)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COOEt
7
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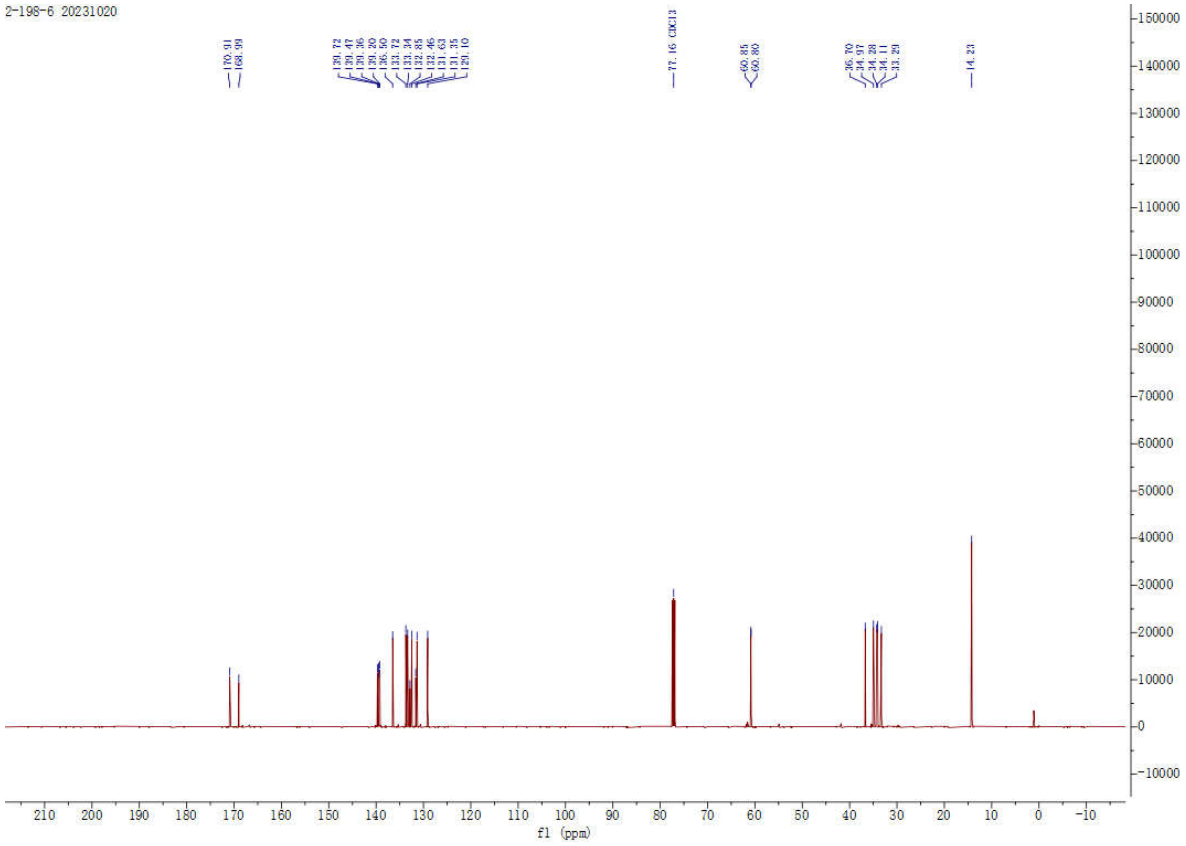
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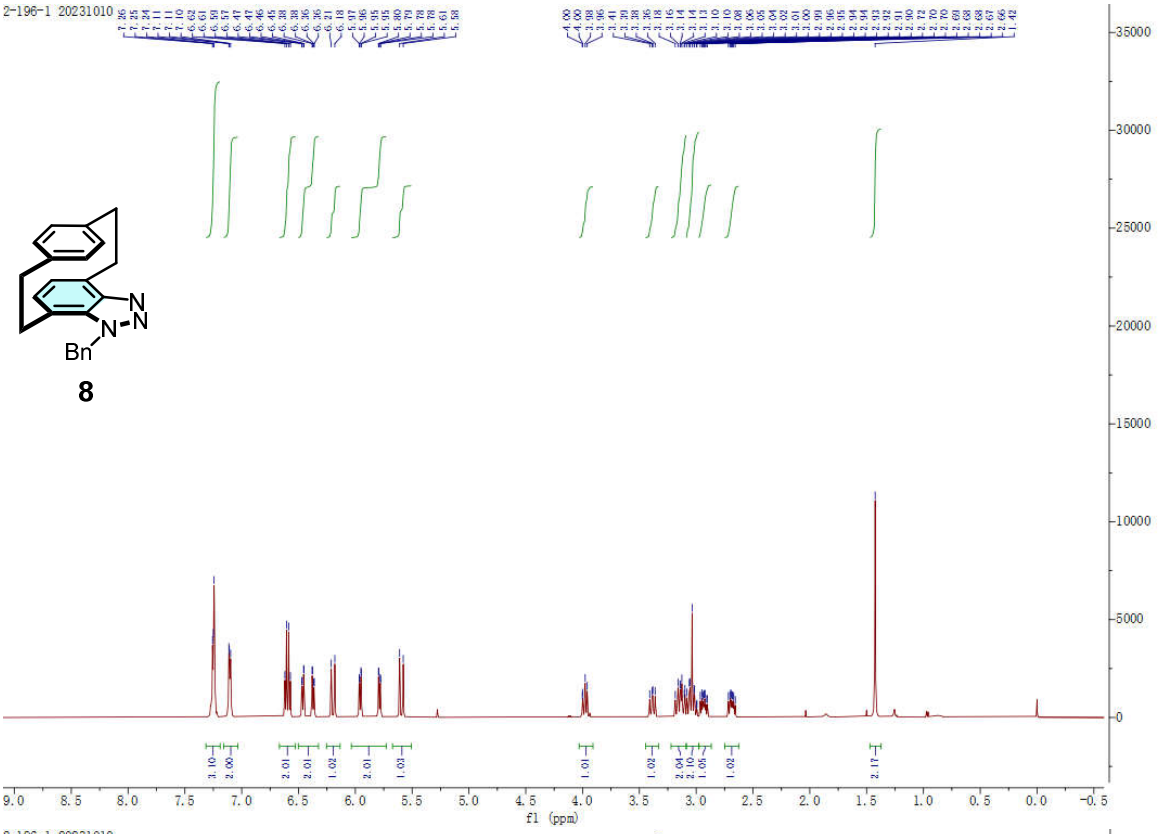
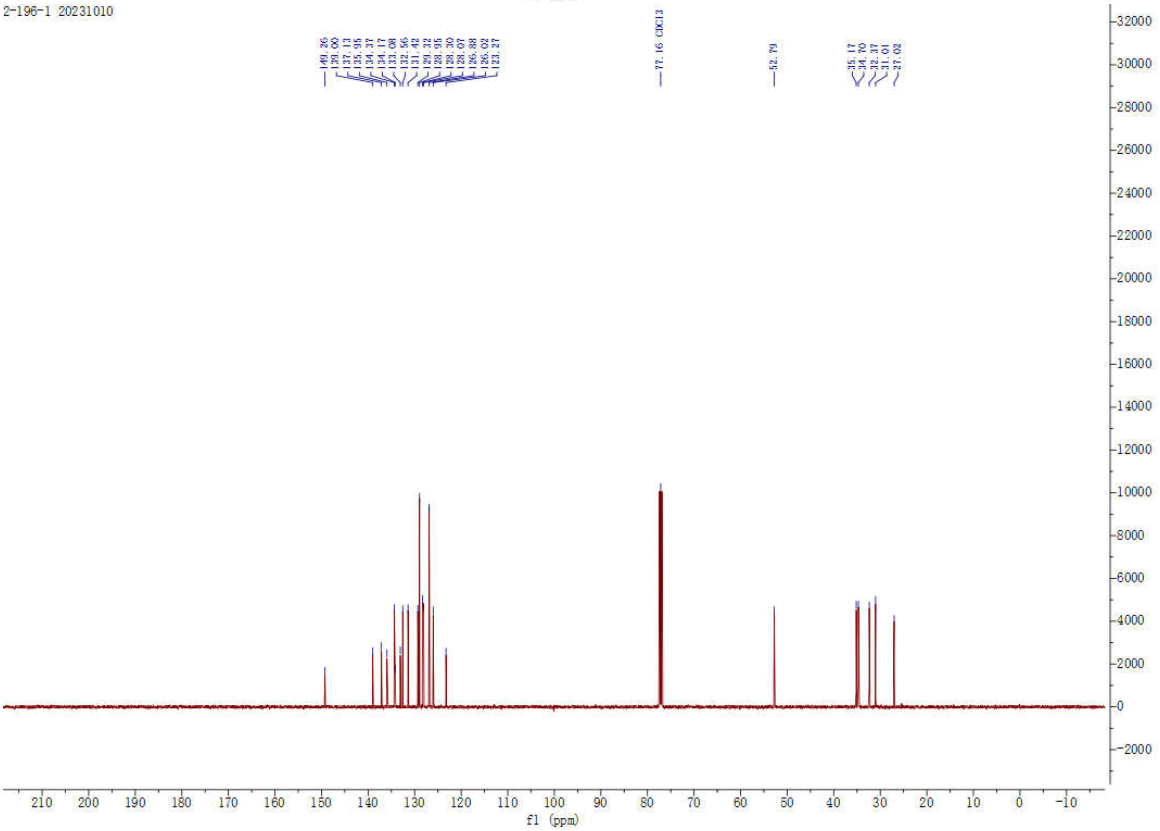
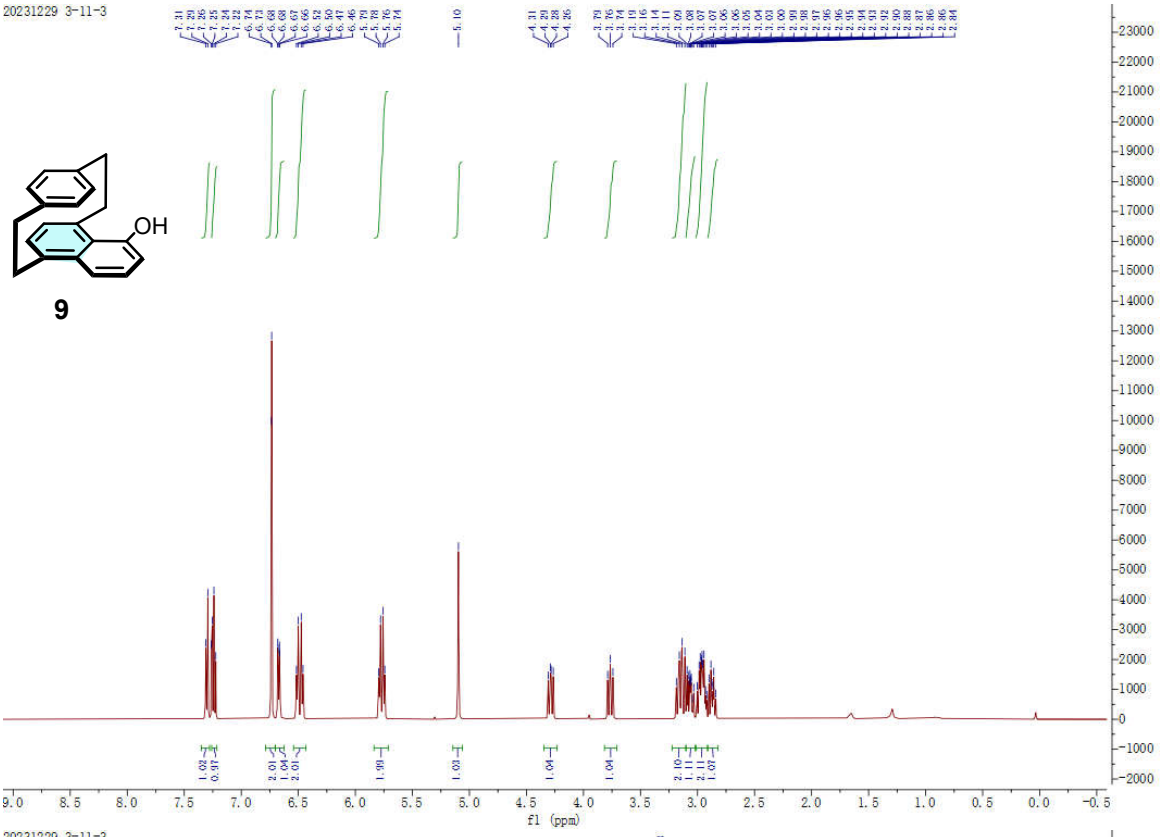
f1 (ppm)



8





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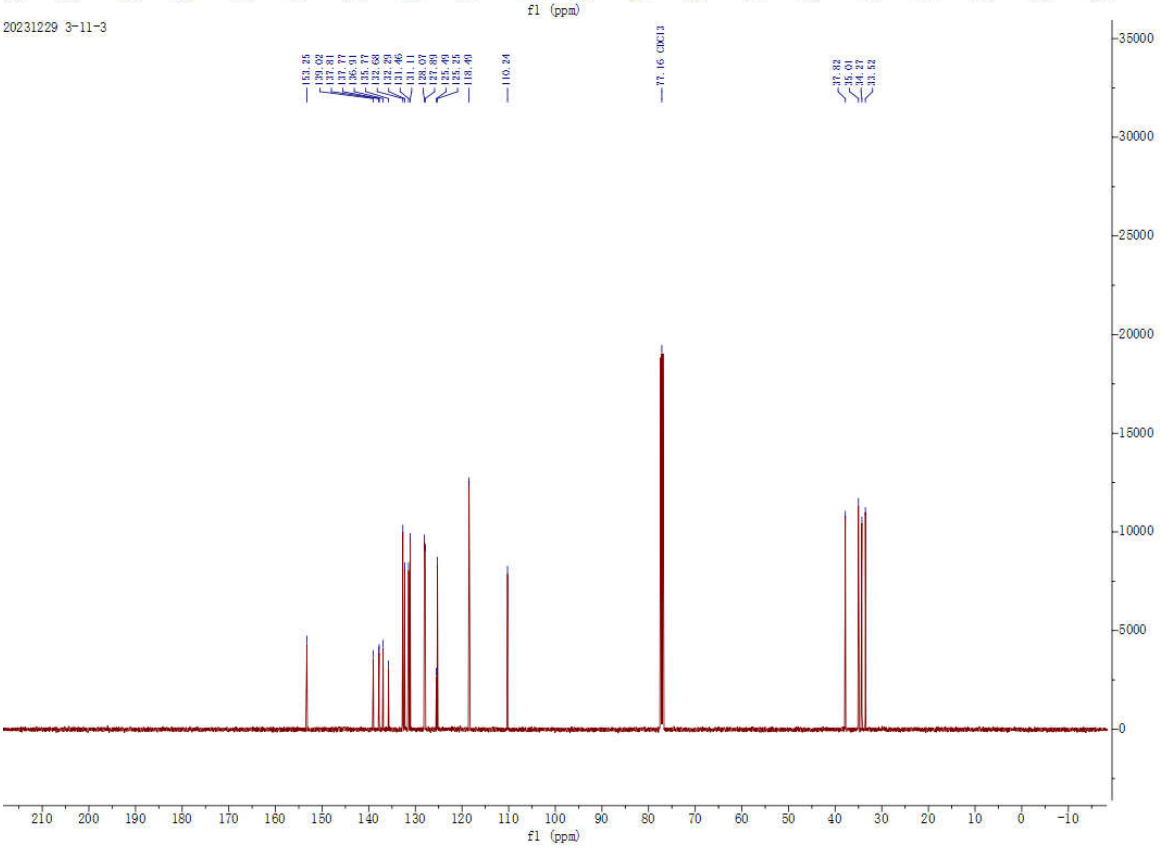

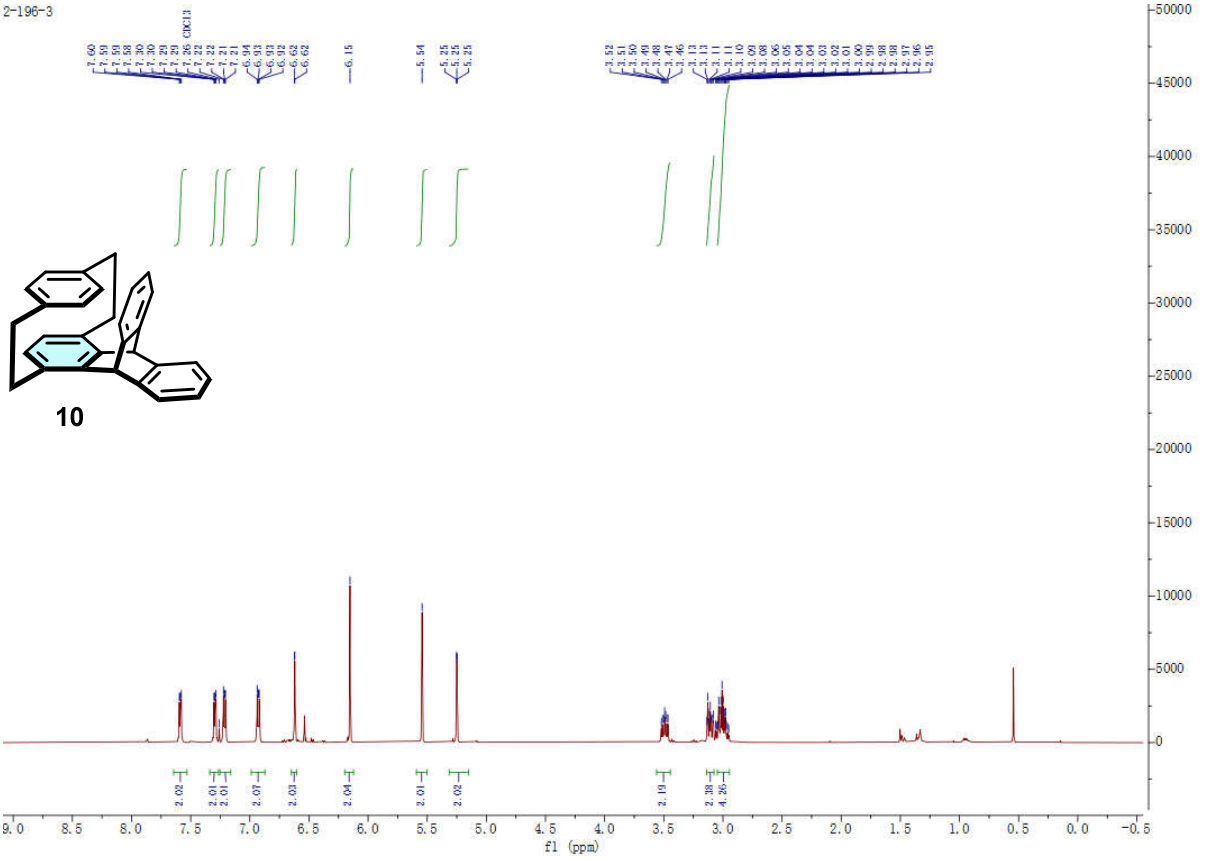
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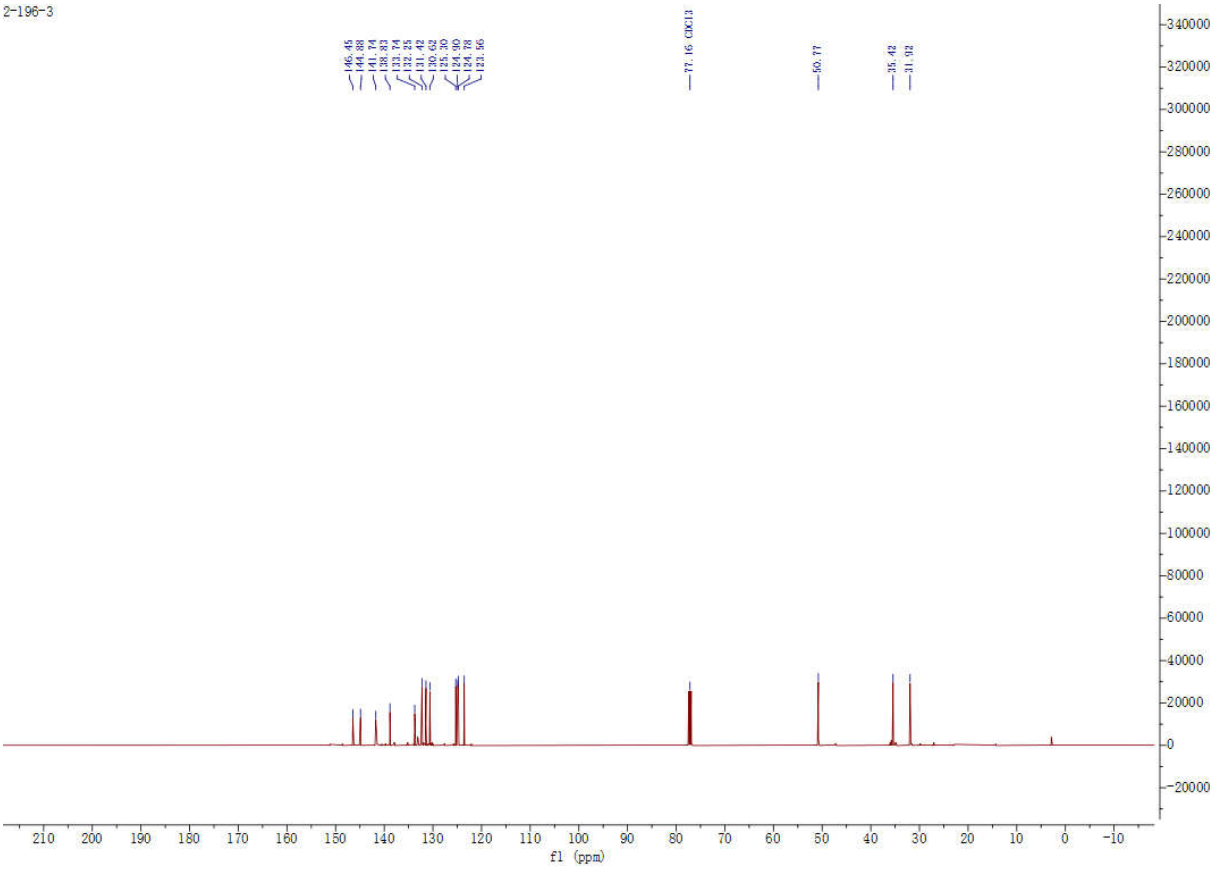
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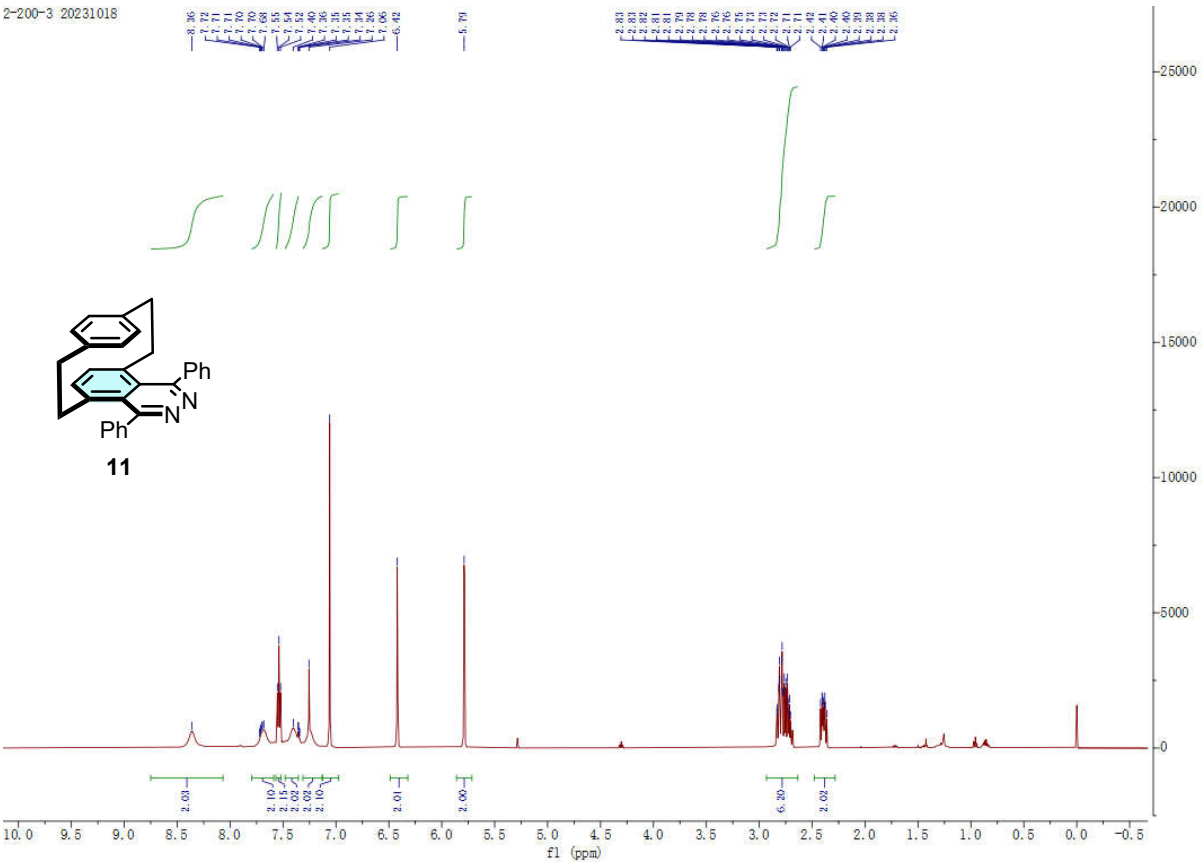
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N
Ph
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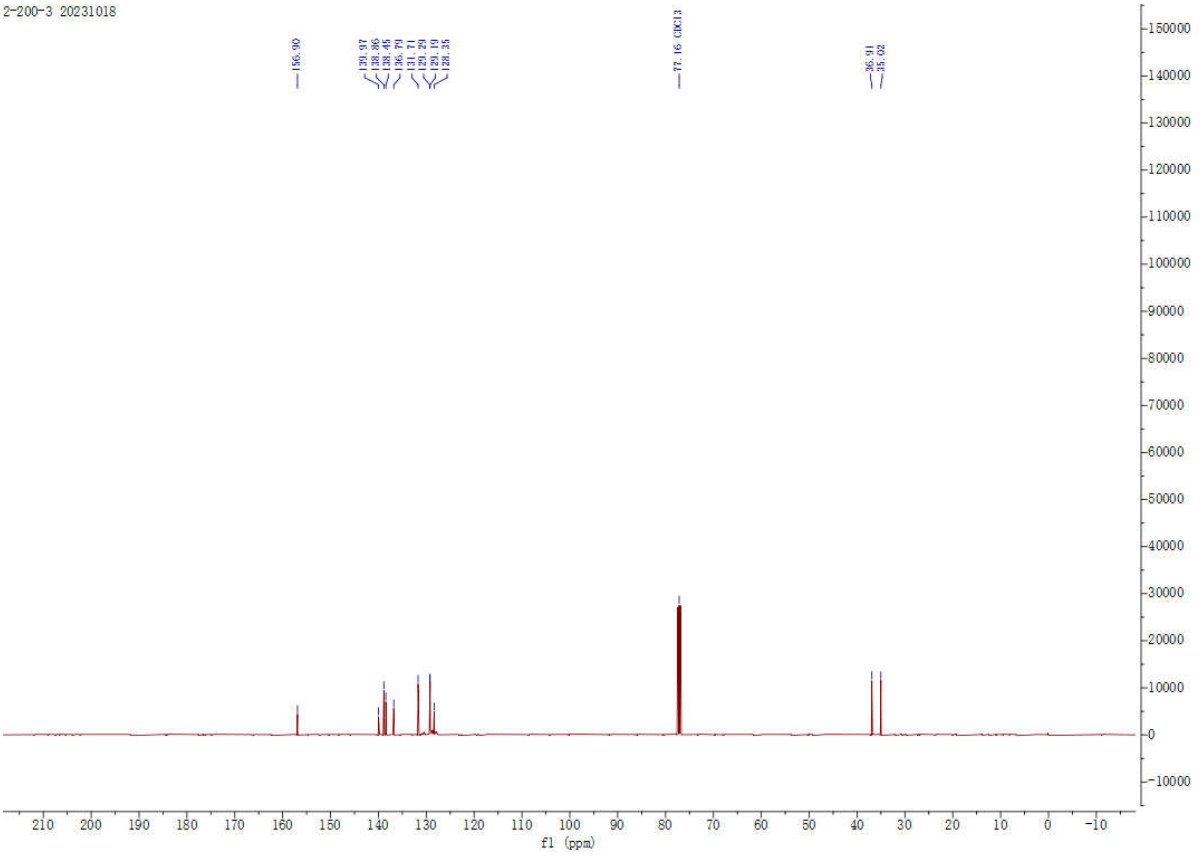
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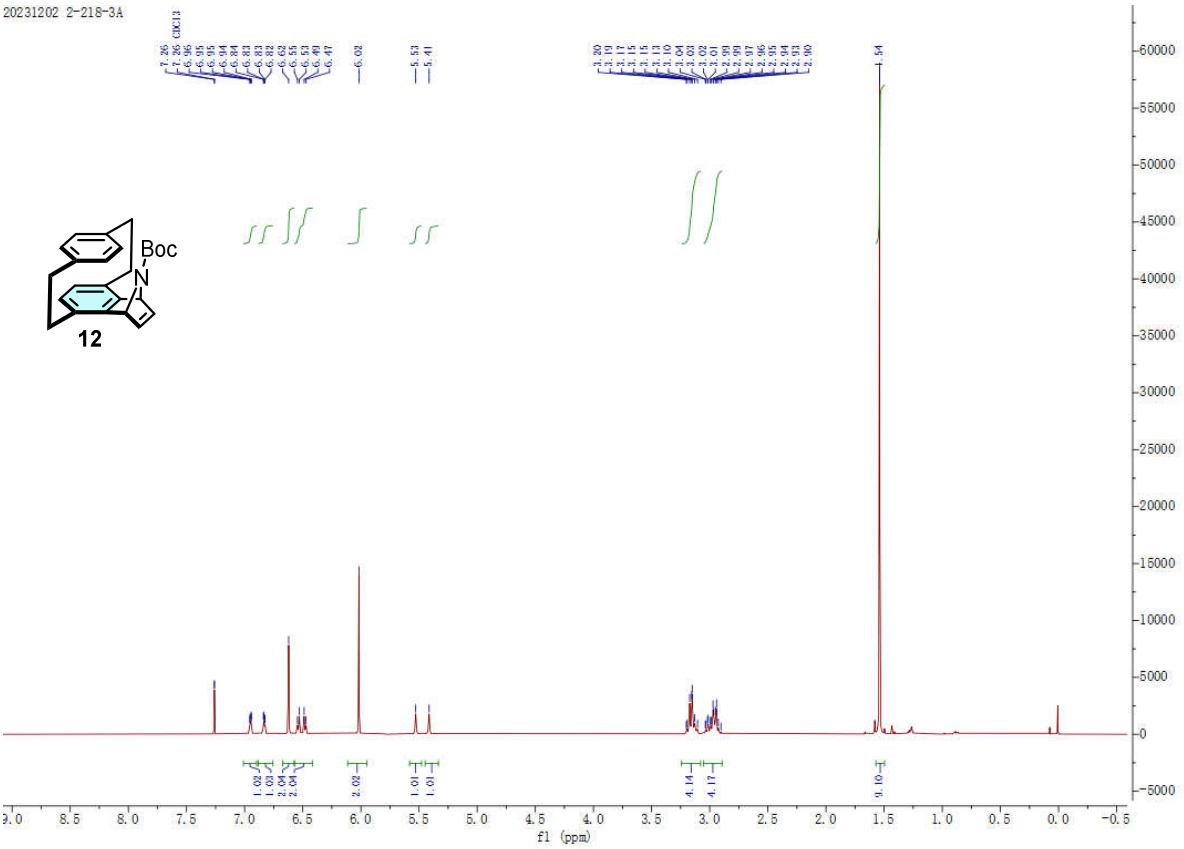
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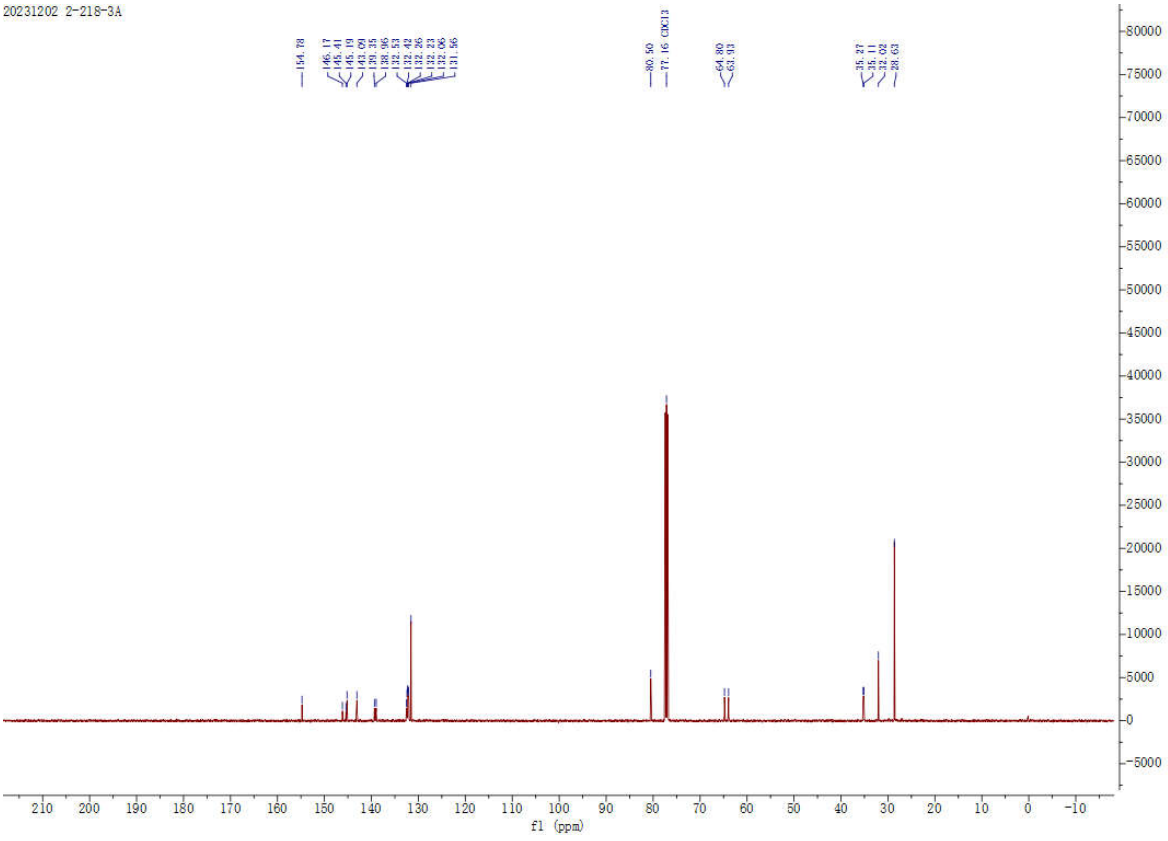
Boc
N
12
f1 (ppm)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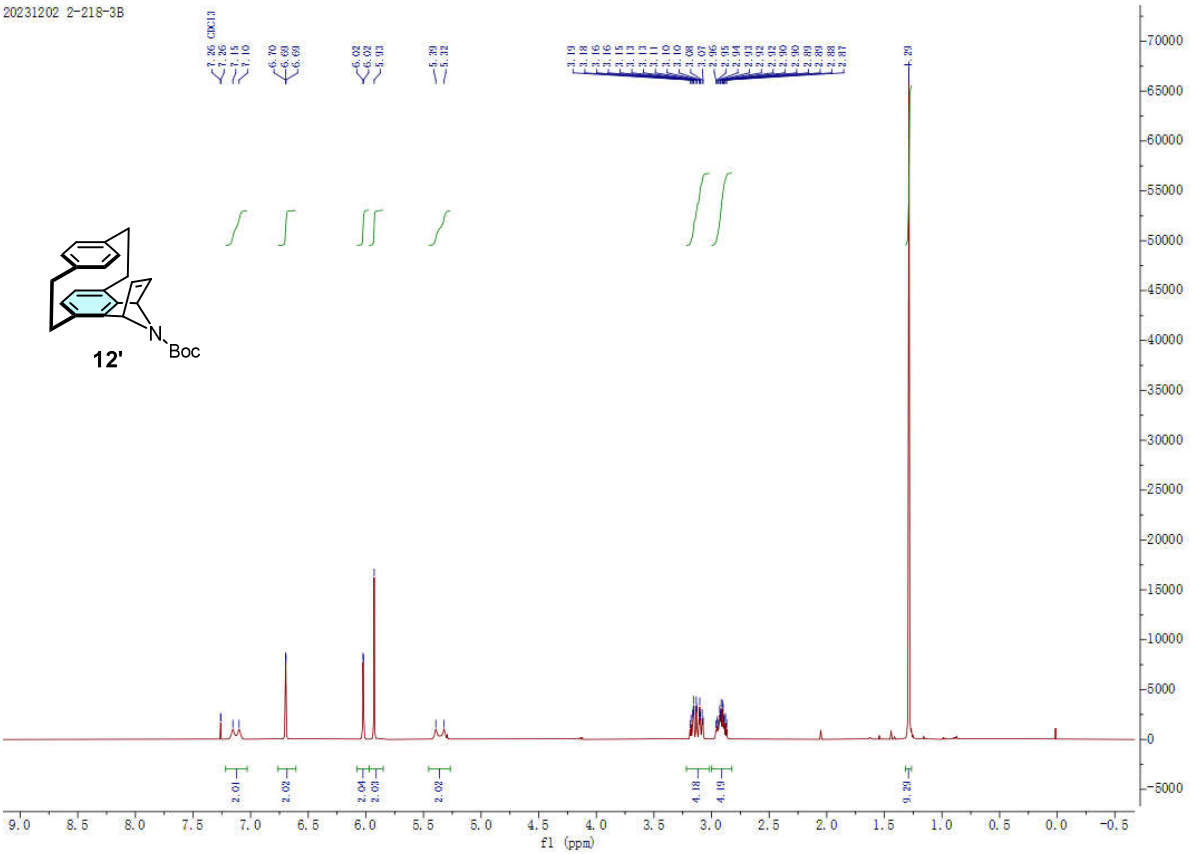
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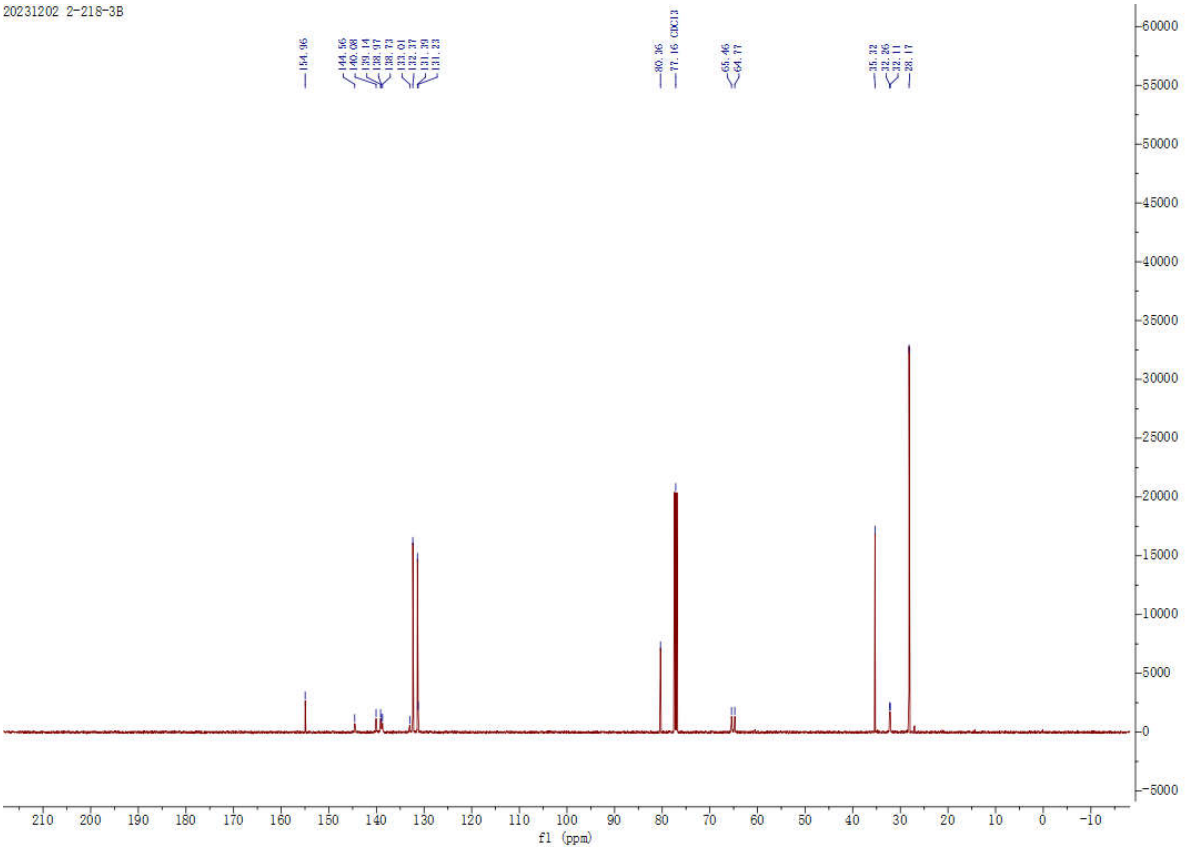
Boc
f1 (ppm)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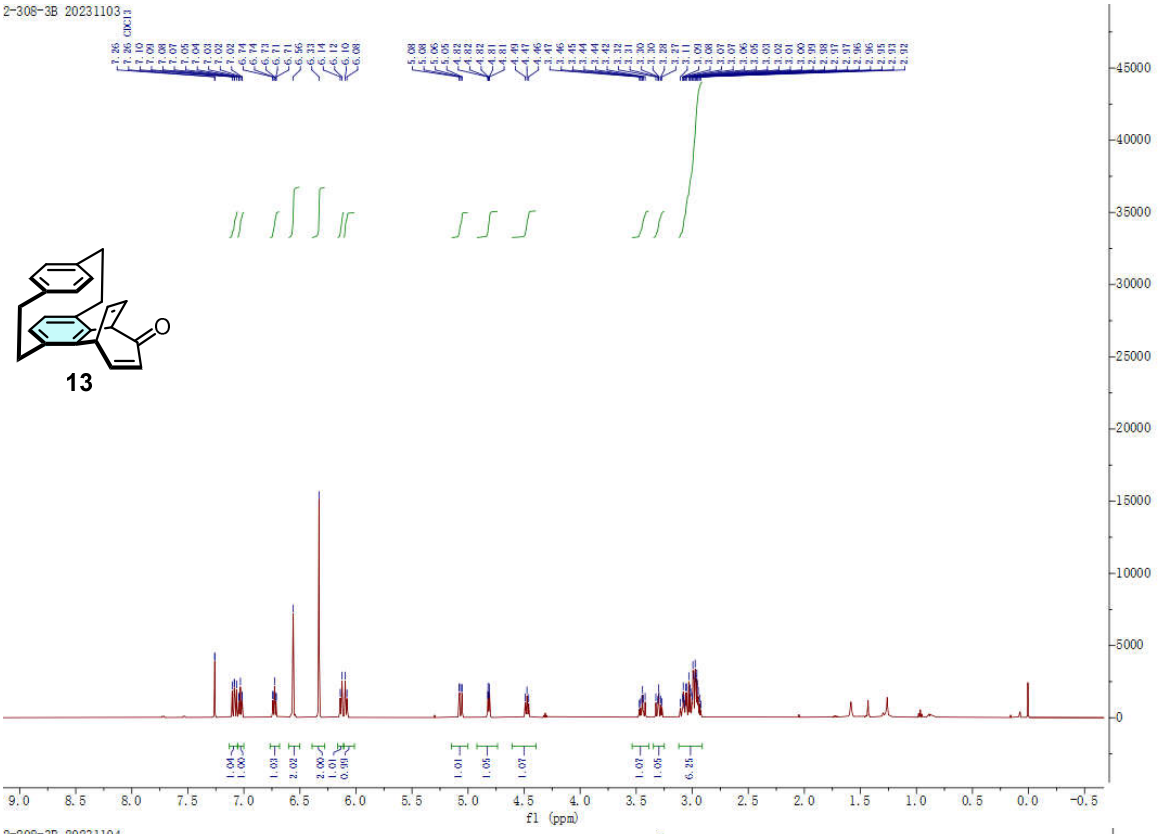
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13
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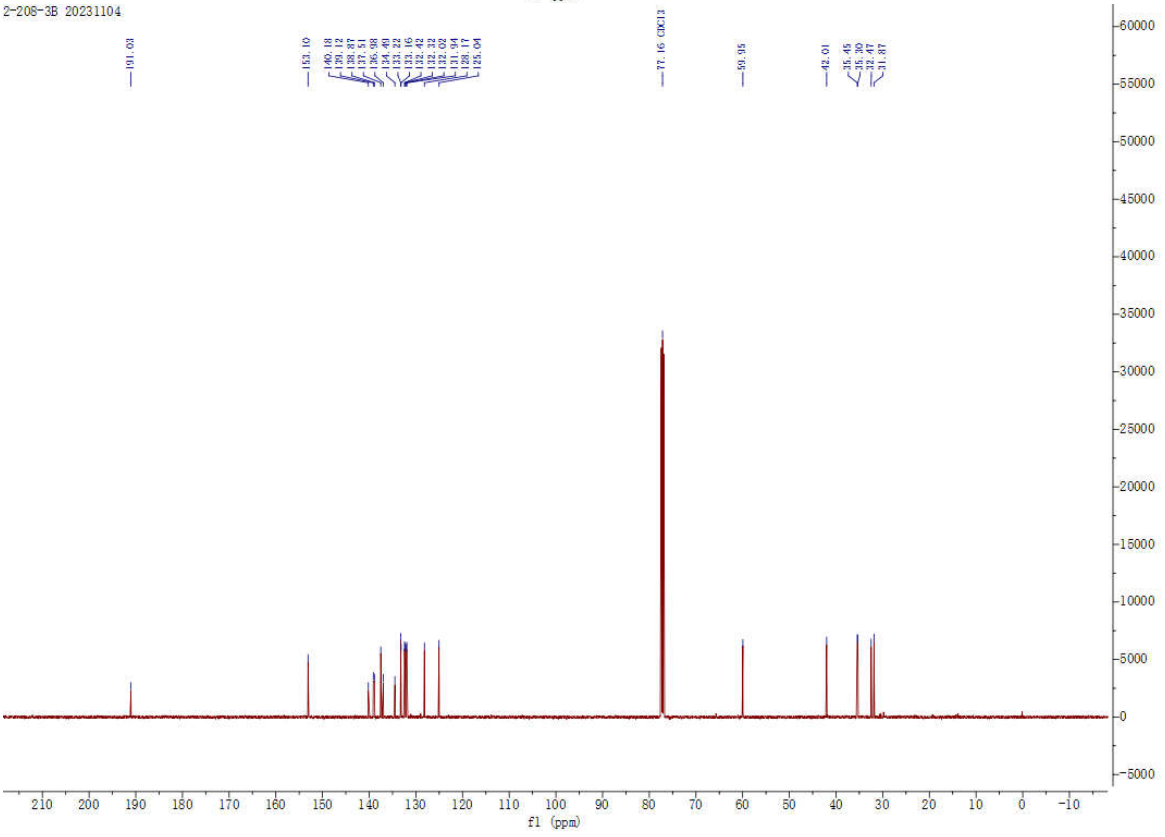
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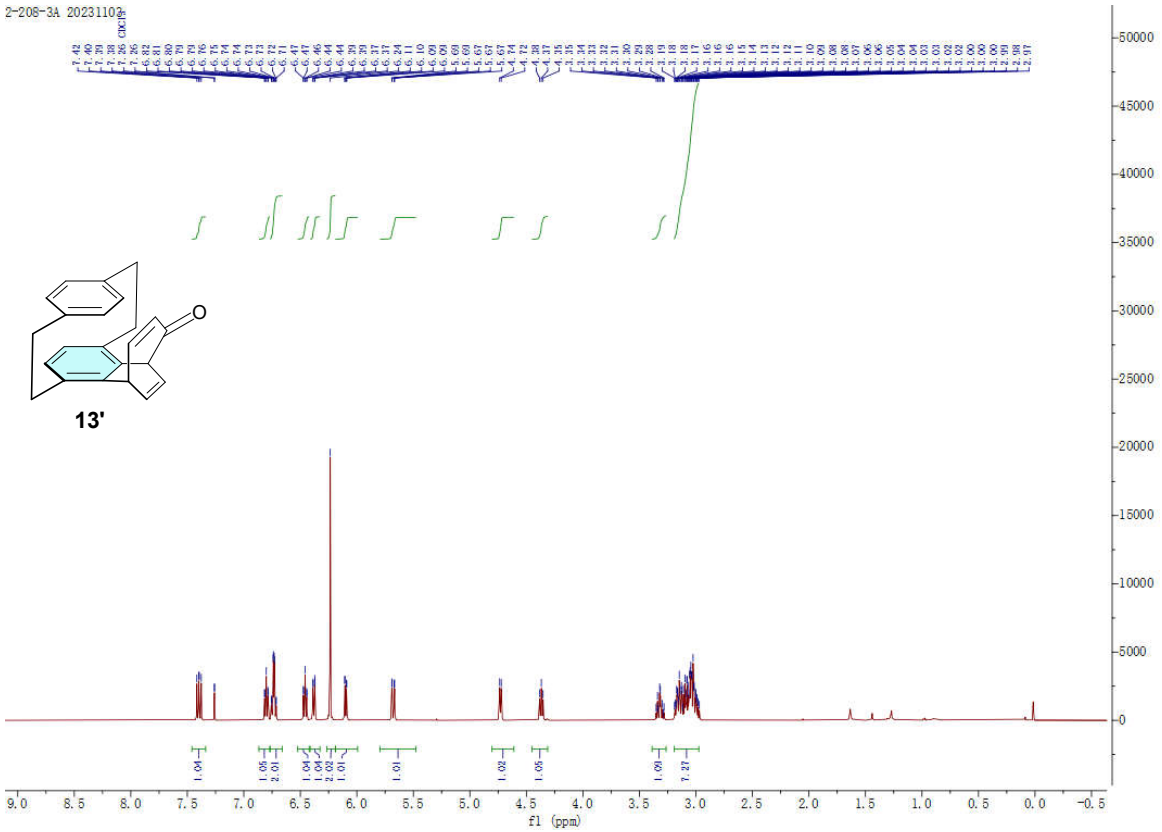
f1 (ppm)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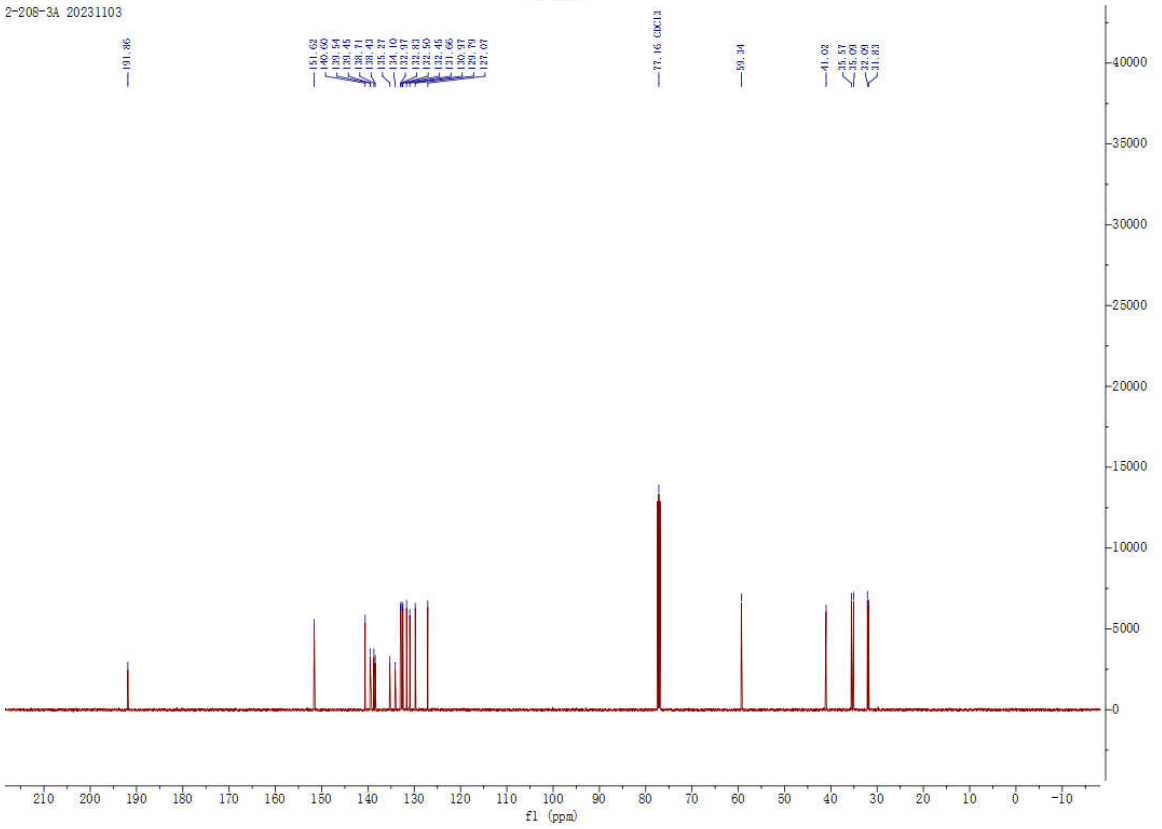
13'
f1 (ppm)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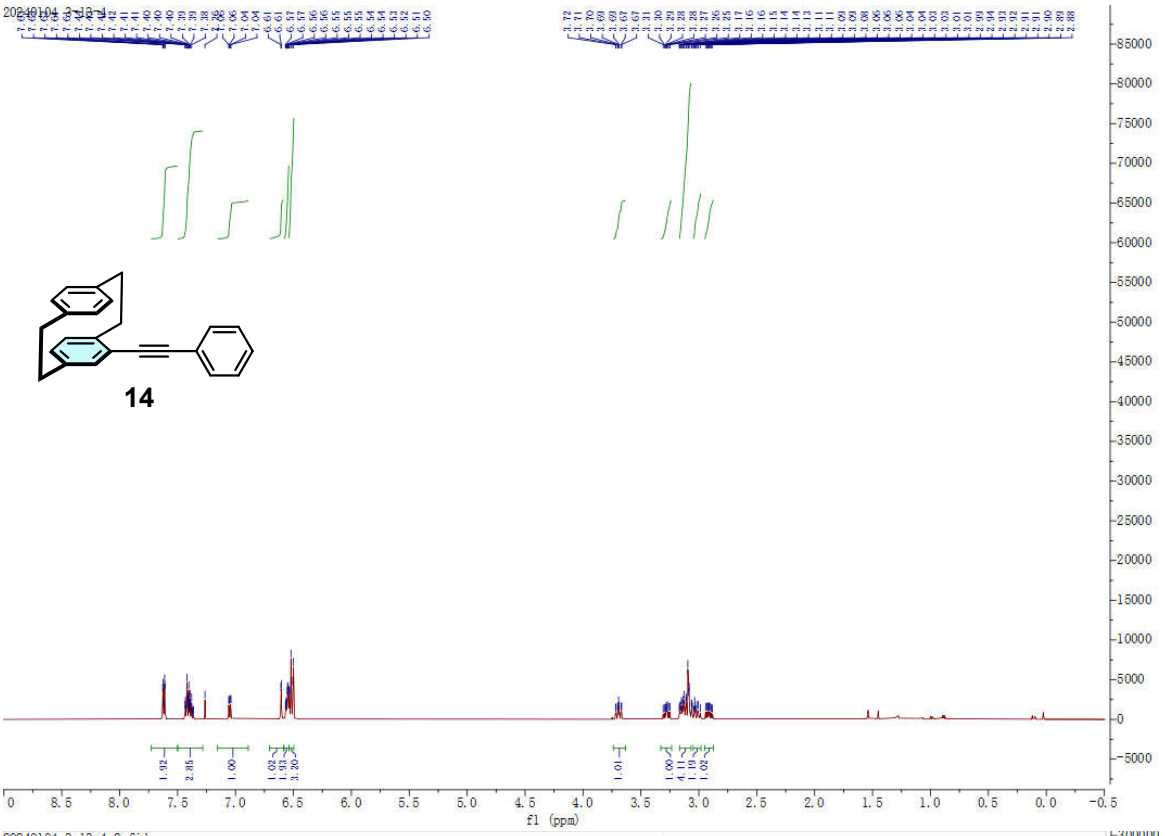
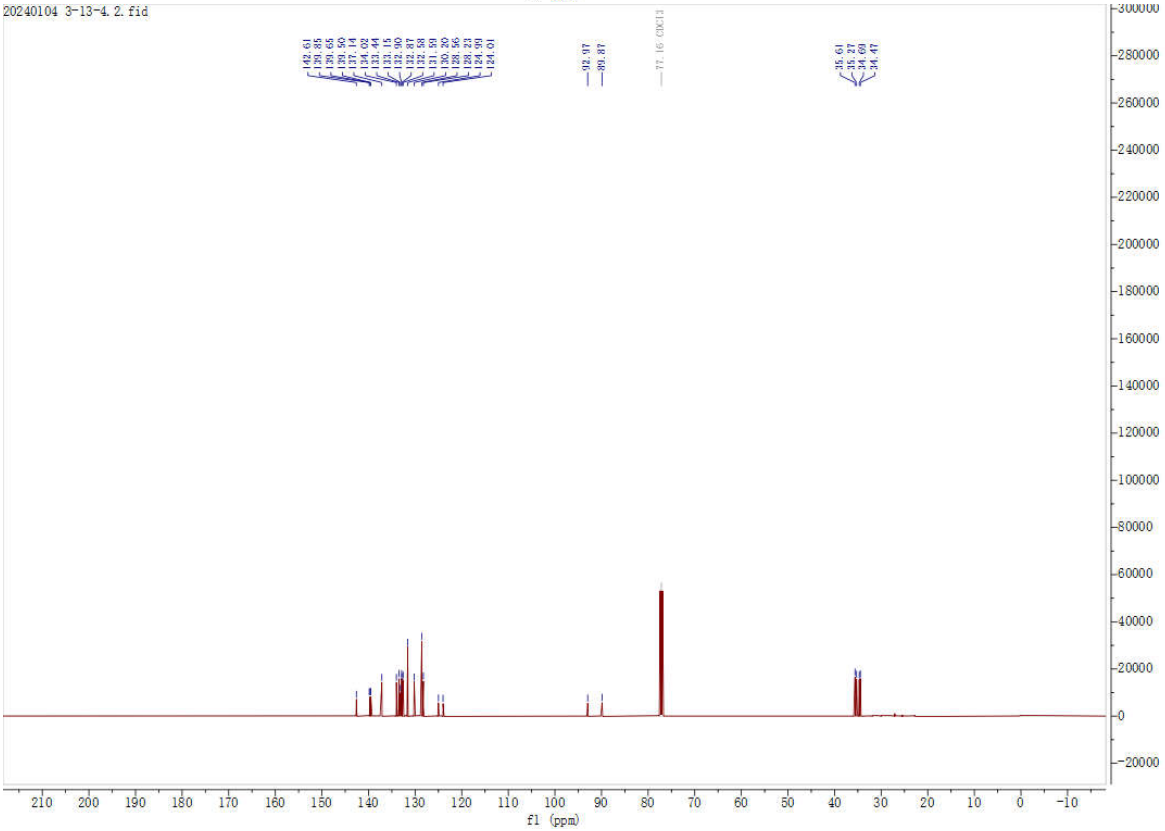
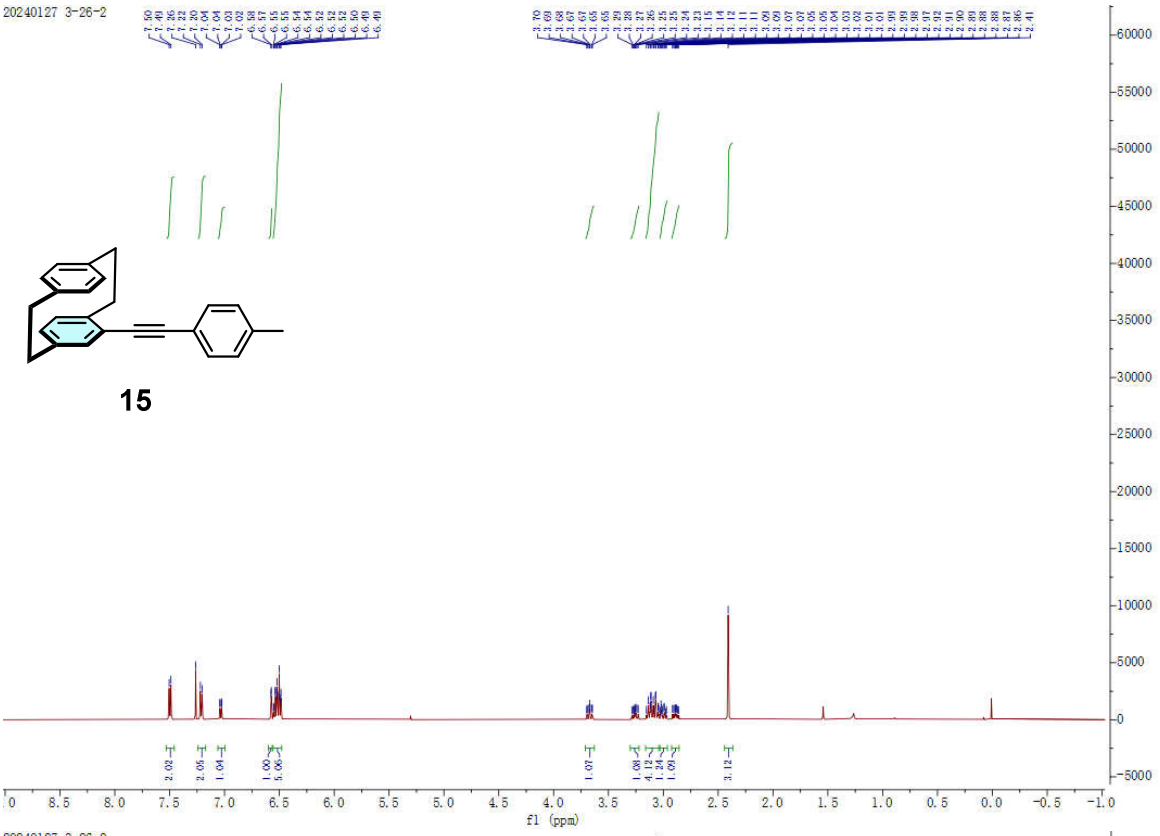


14

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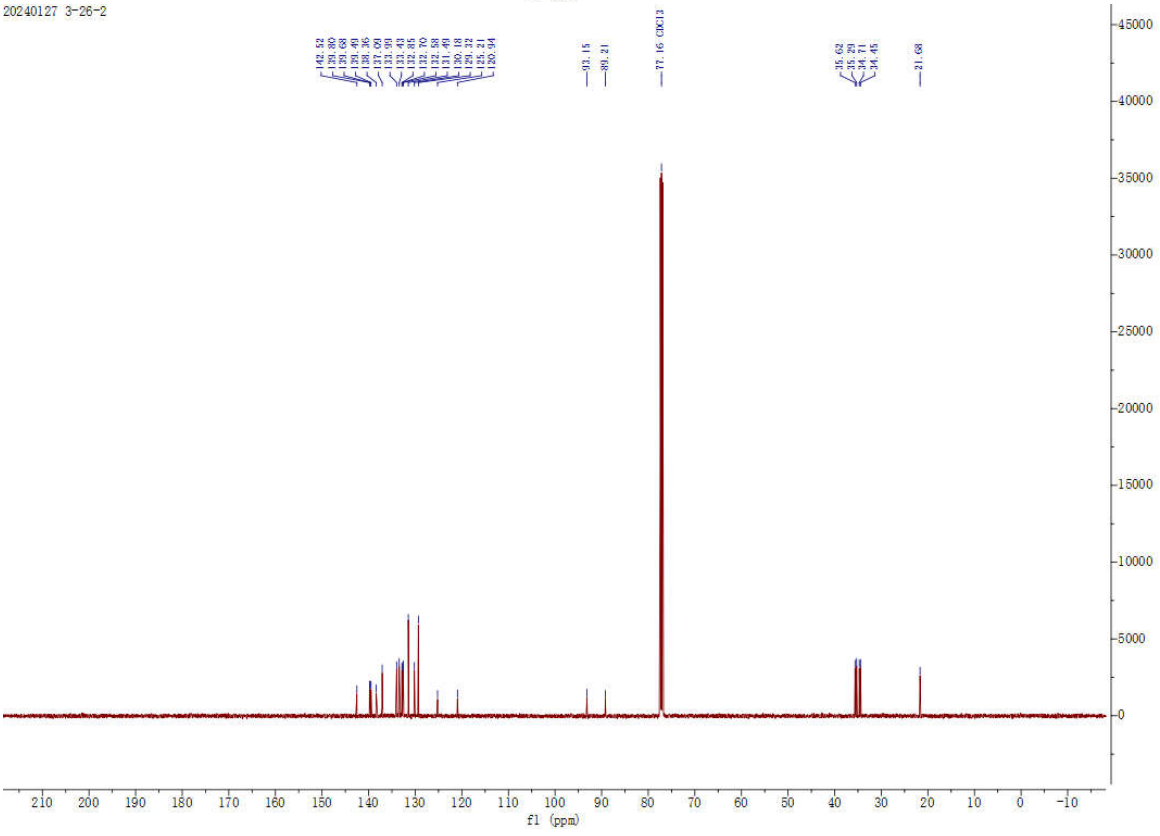
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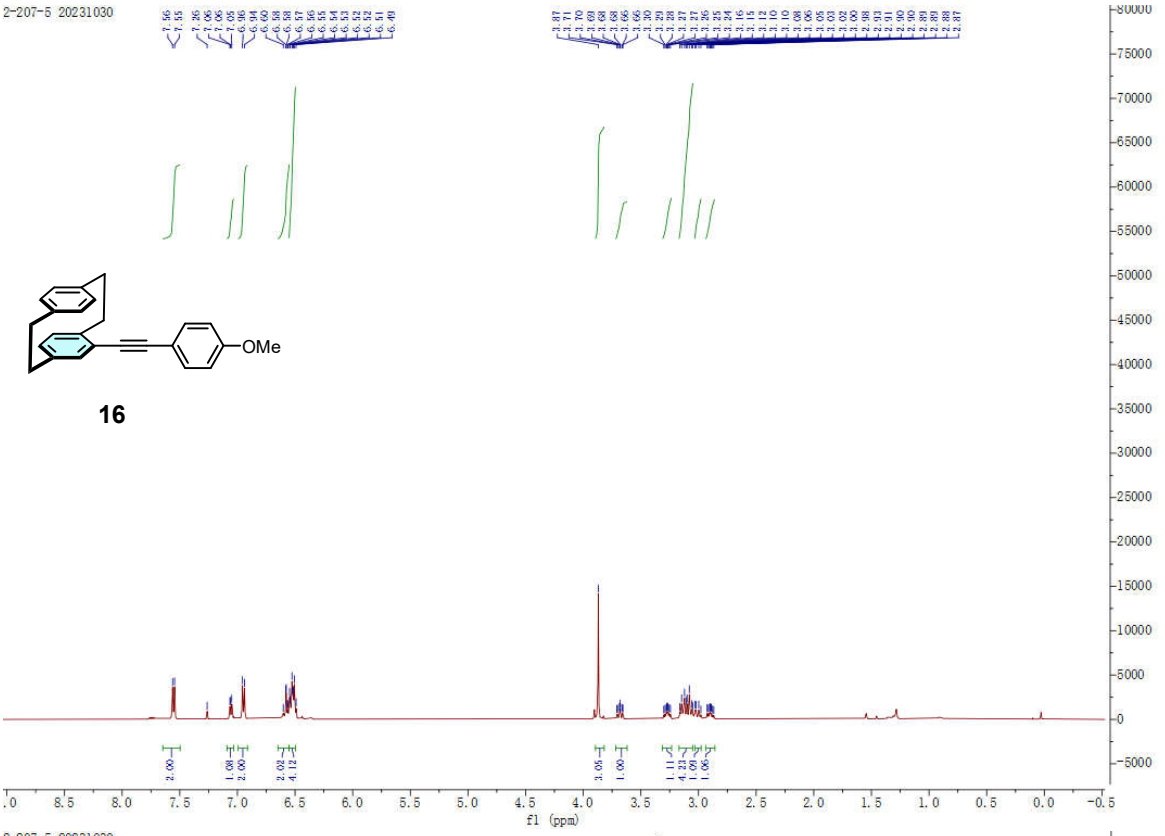

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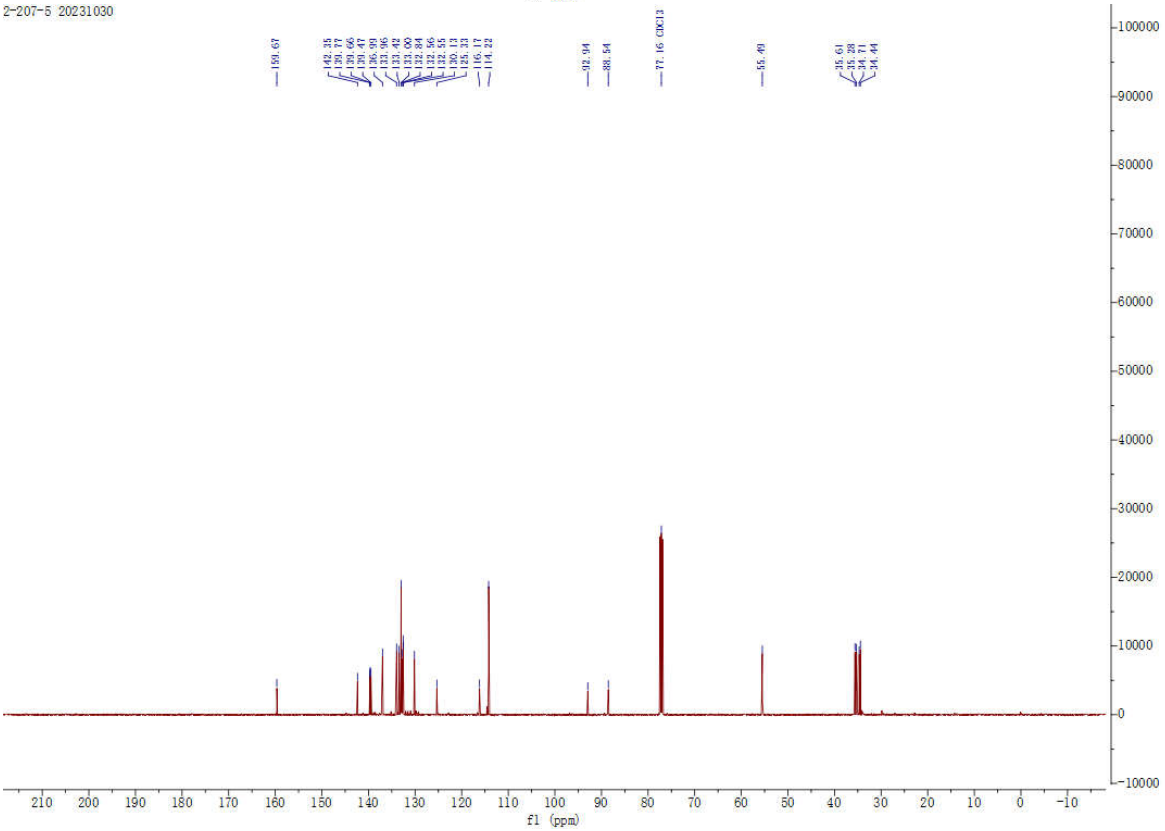

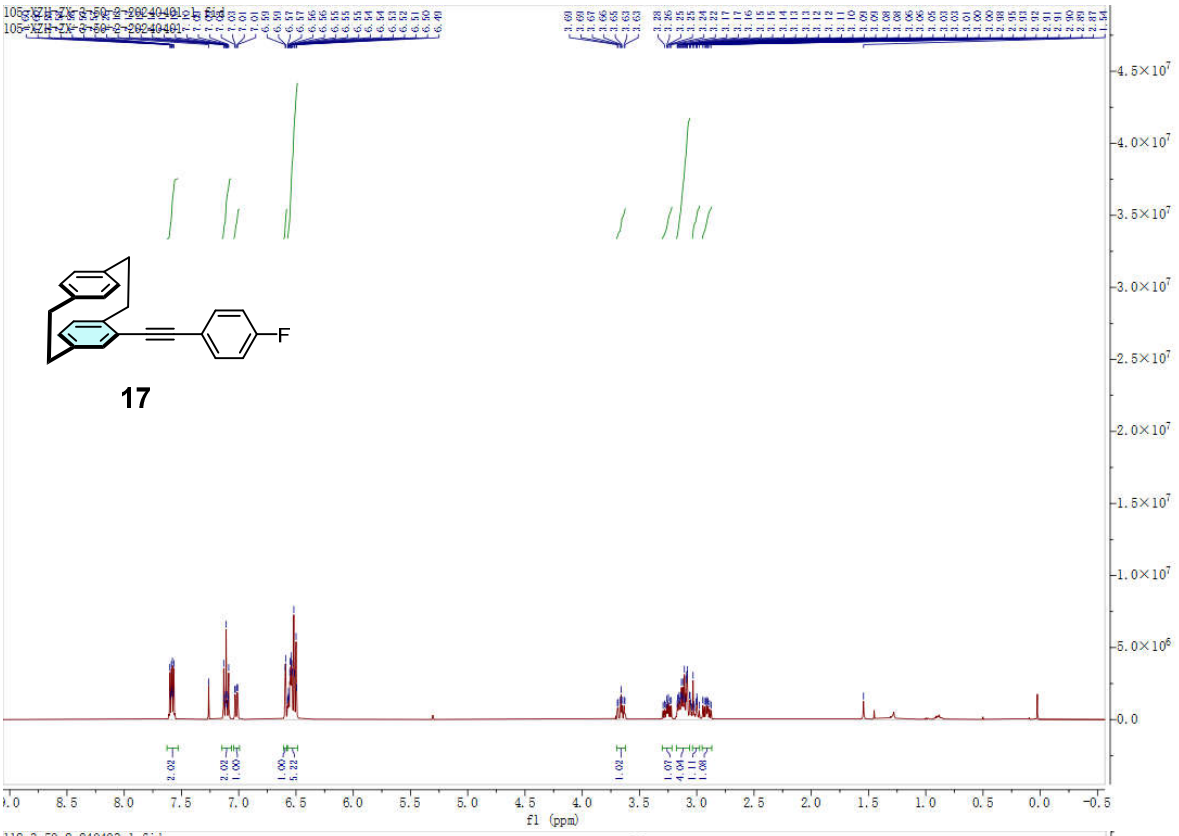

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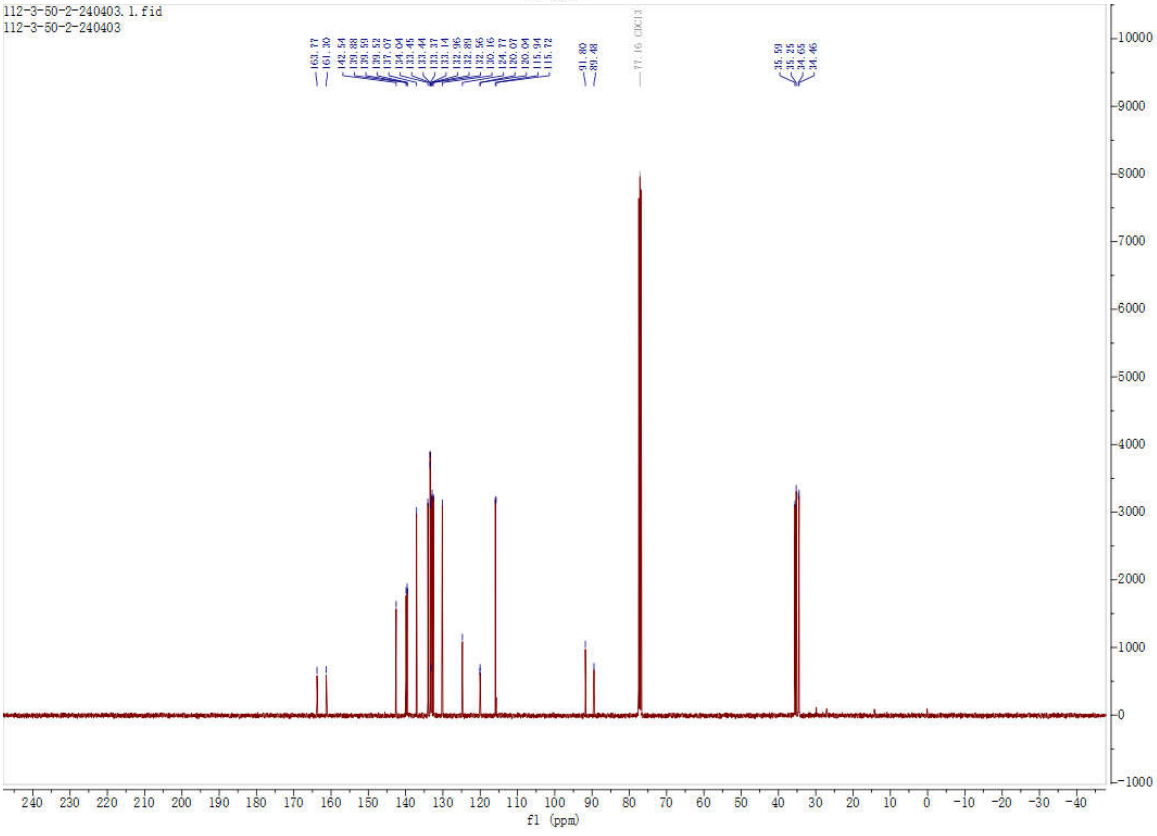

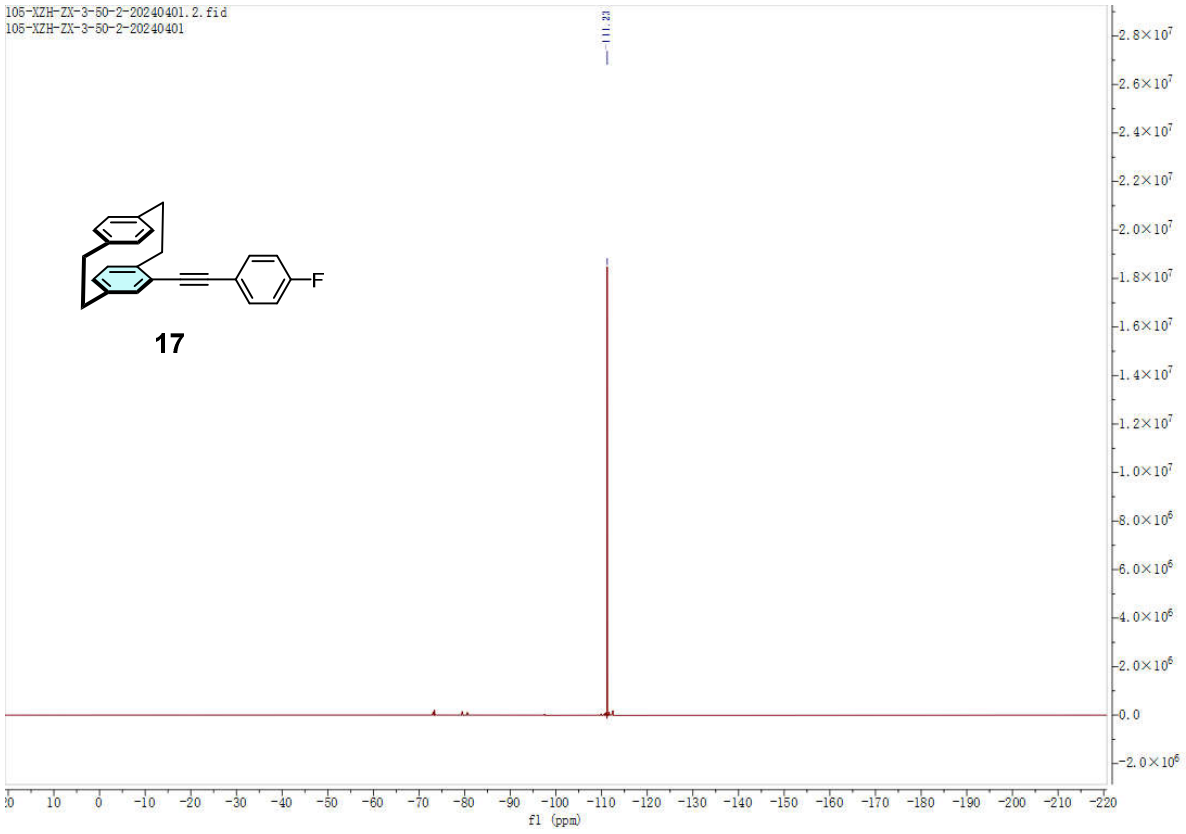
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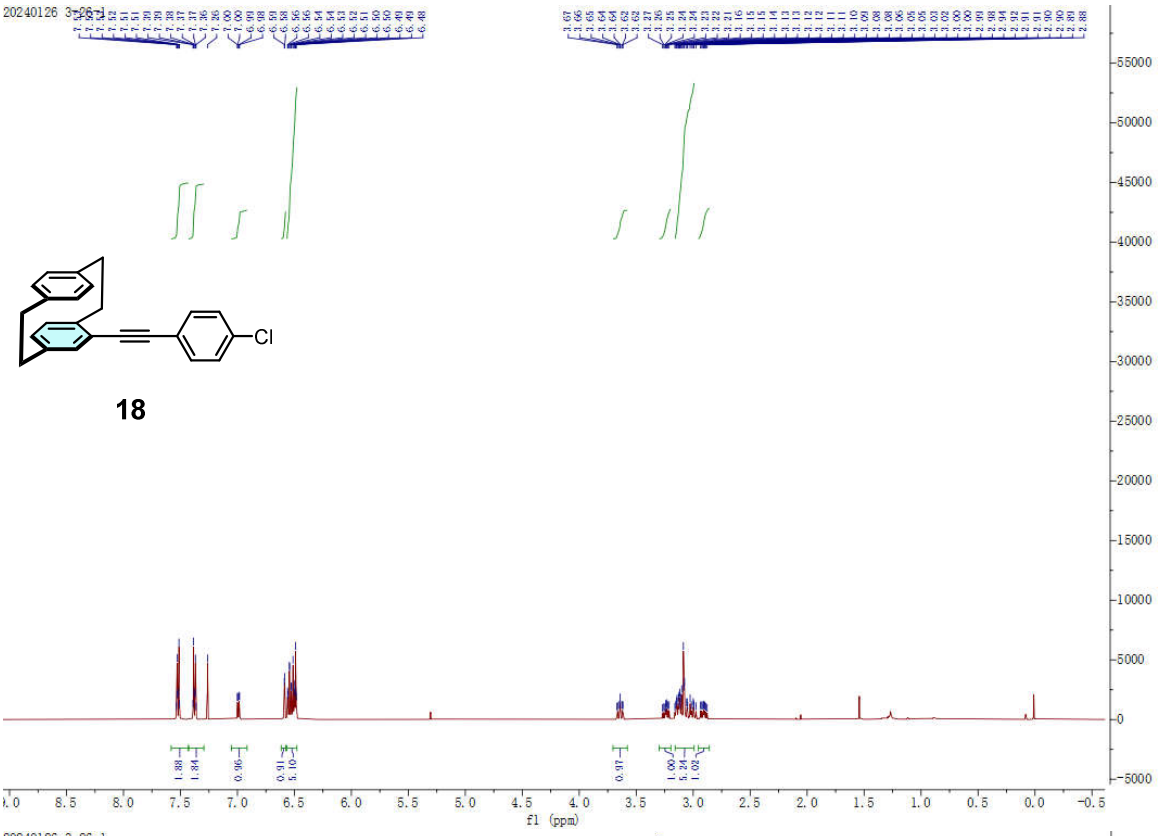
F
17
f1 (ppm)



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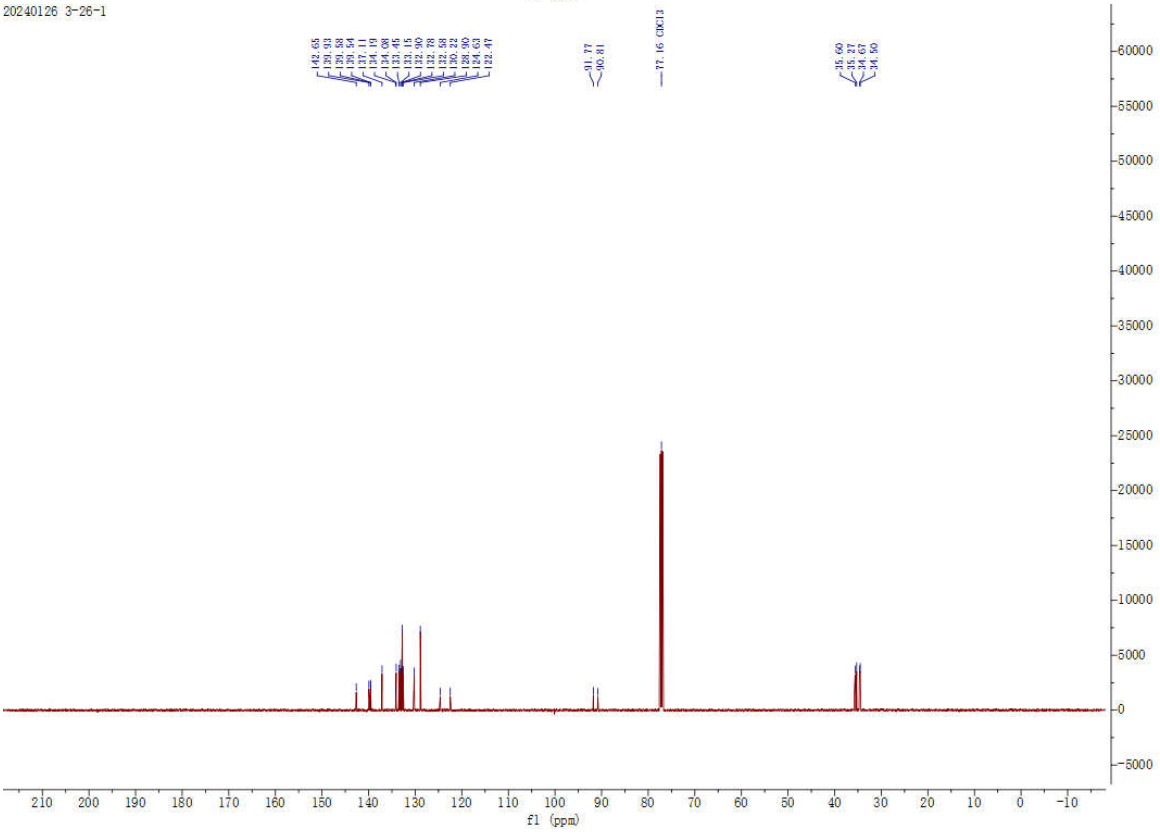

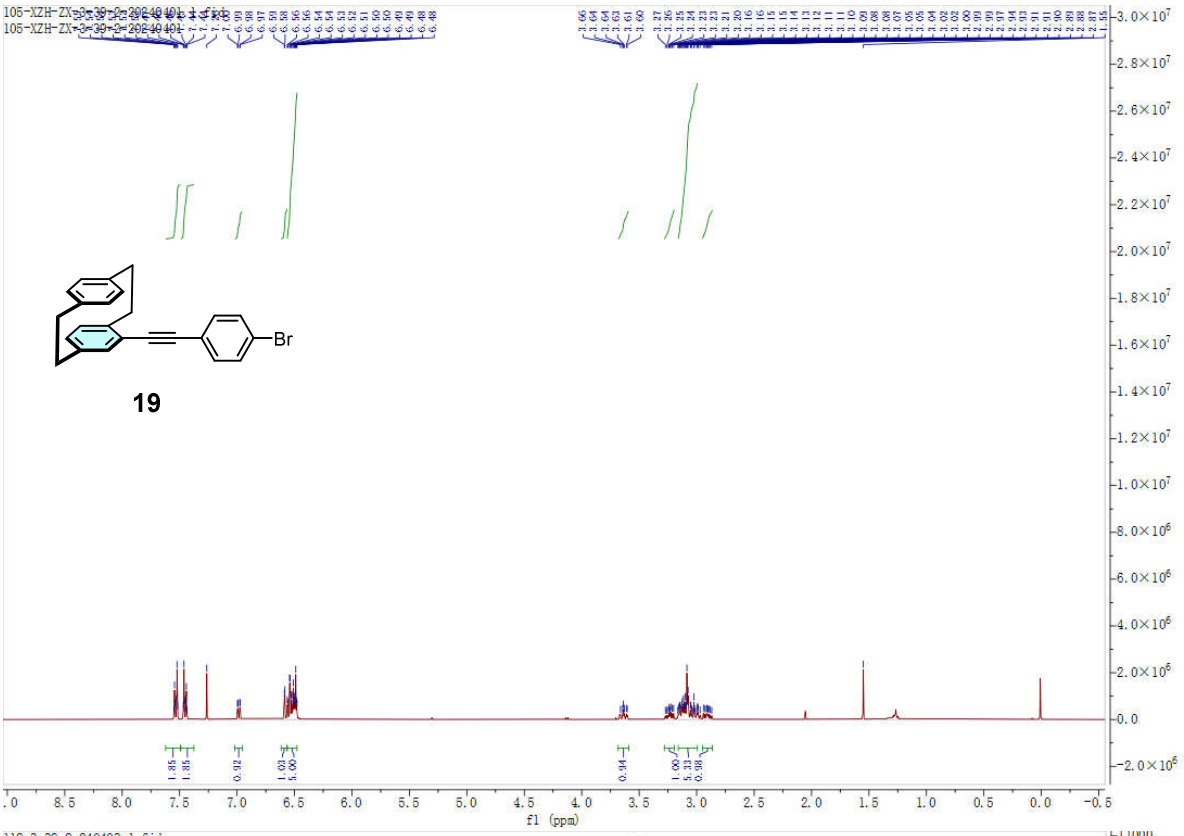

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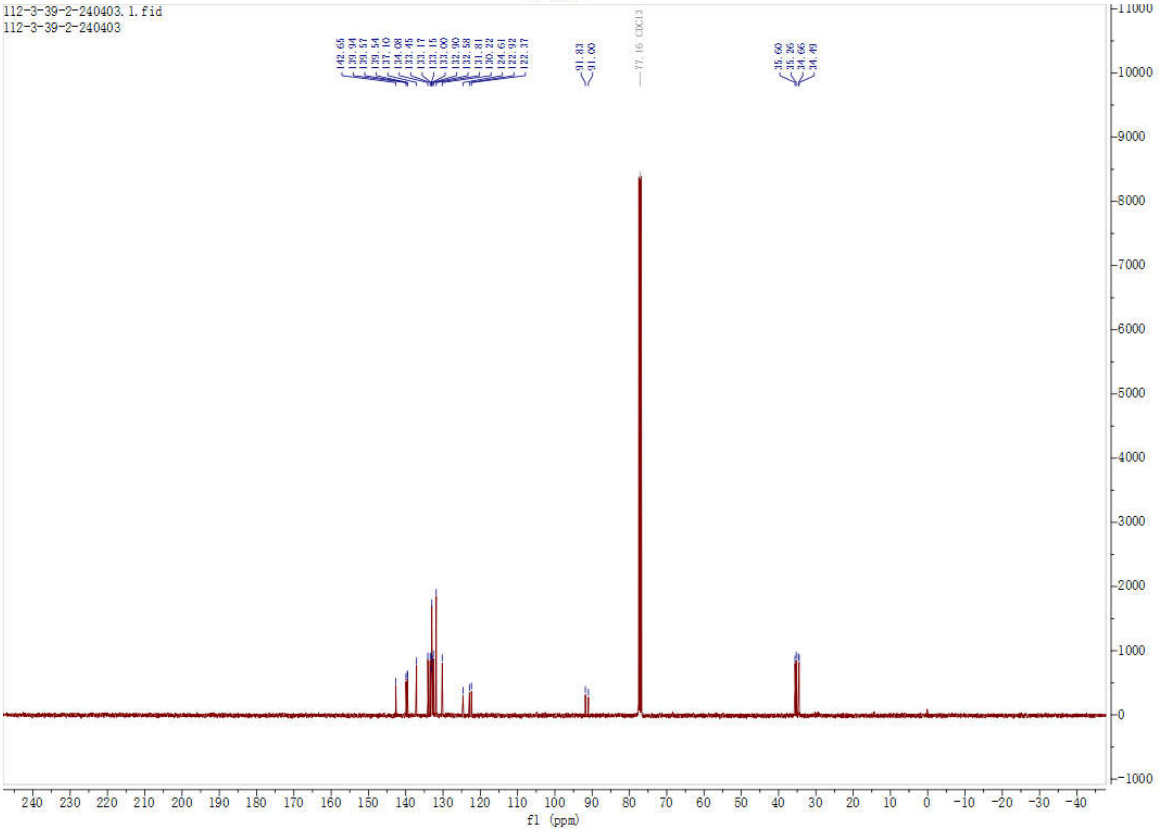

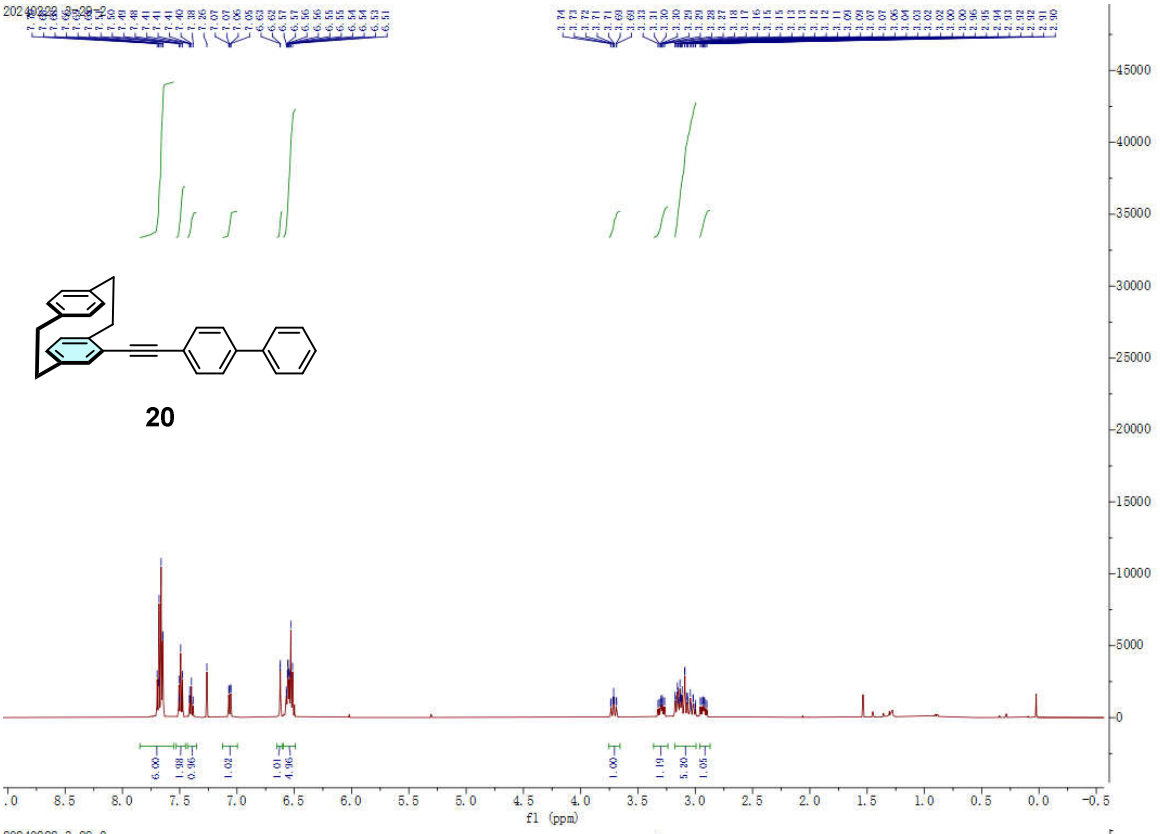

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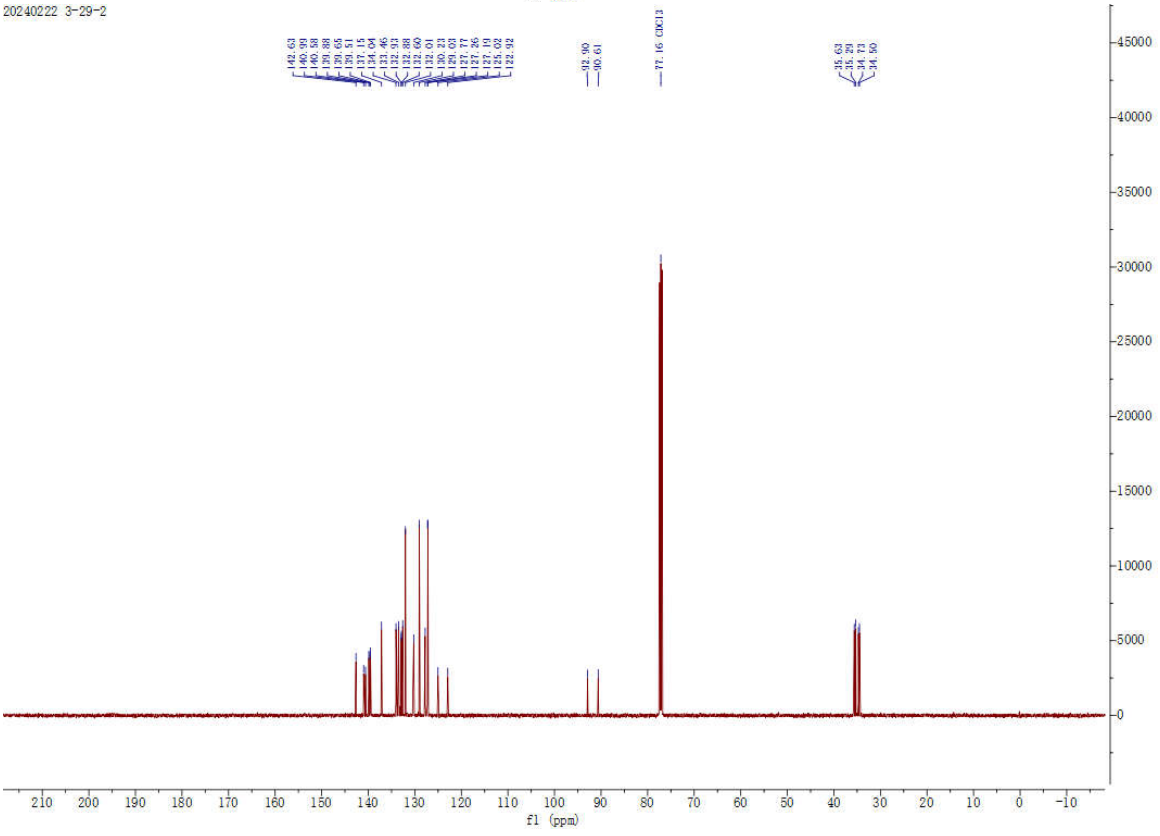

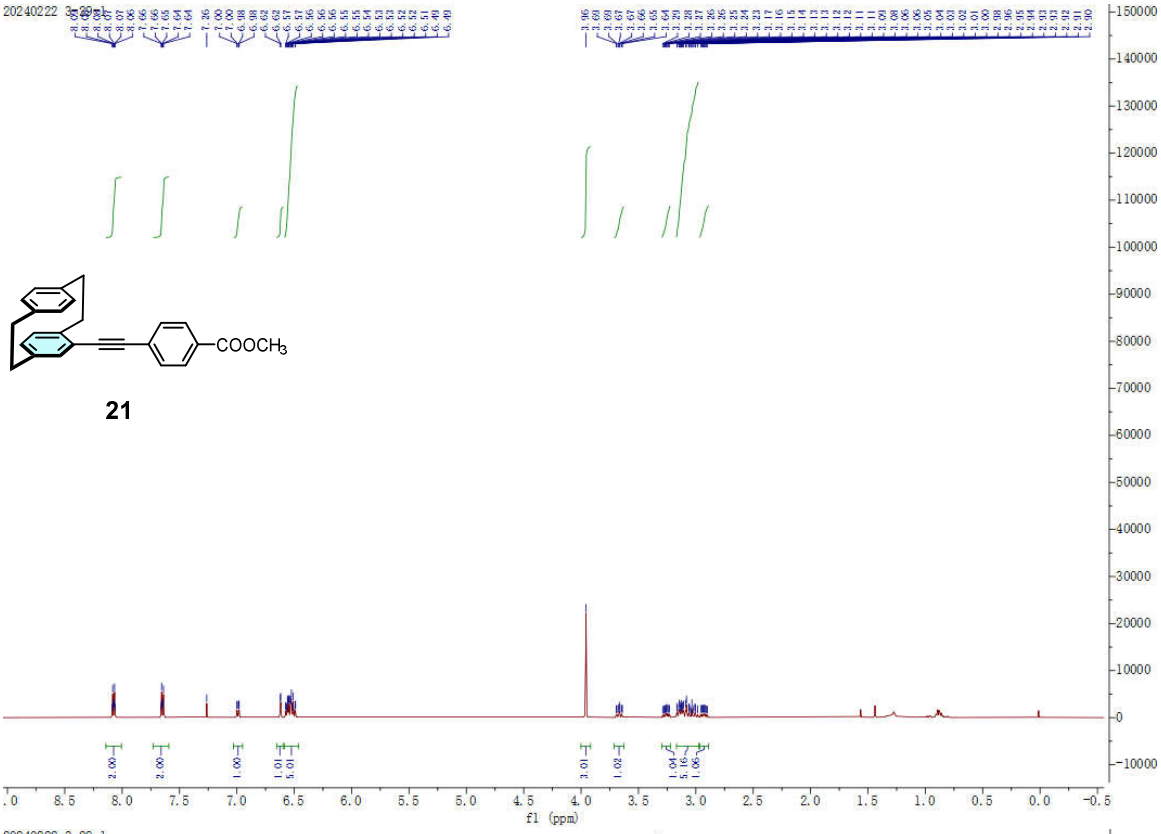

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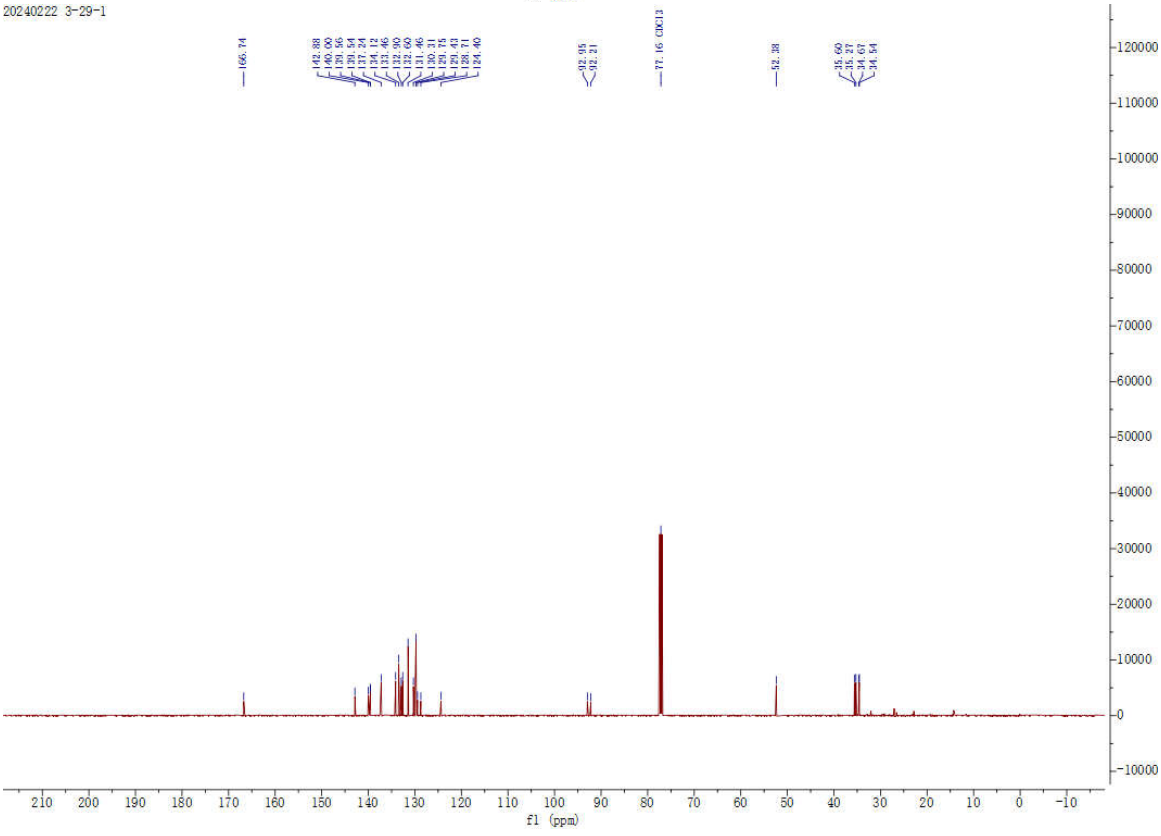

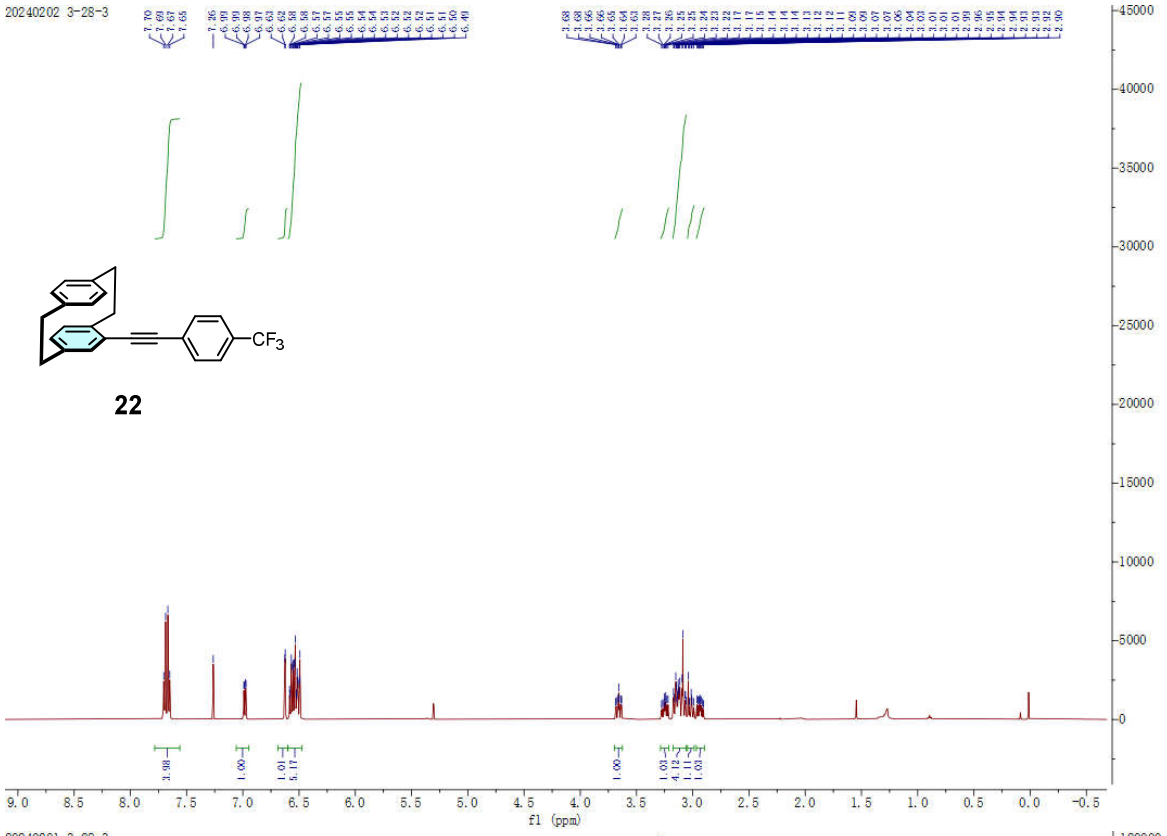

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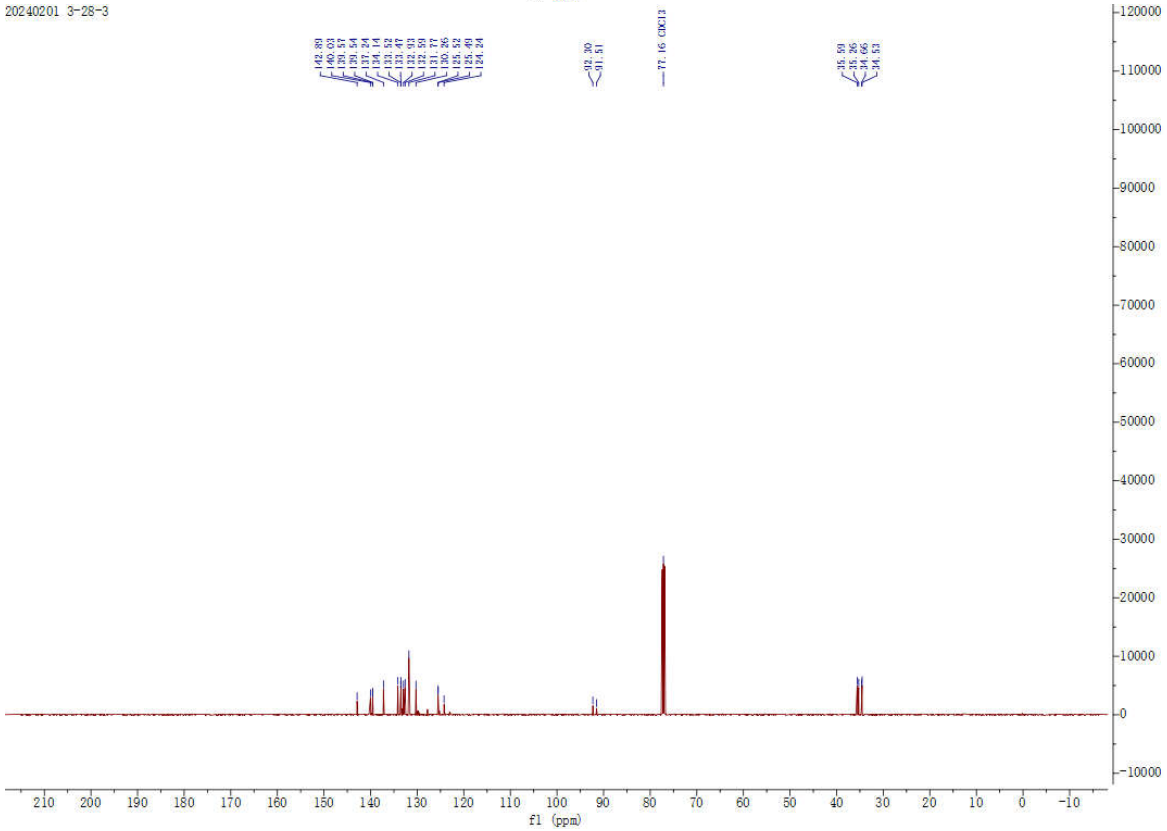

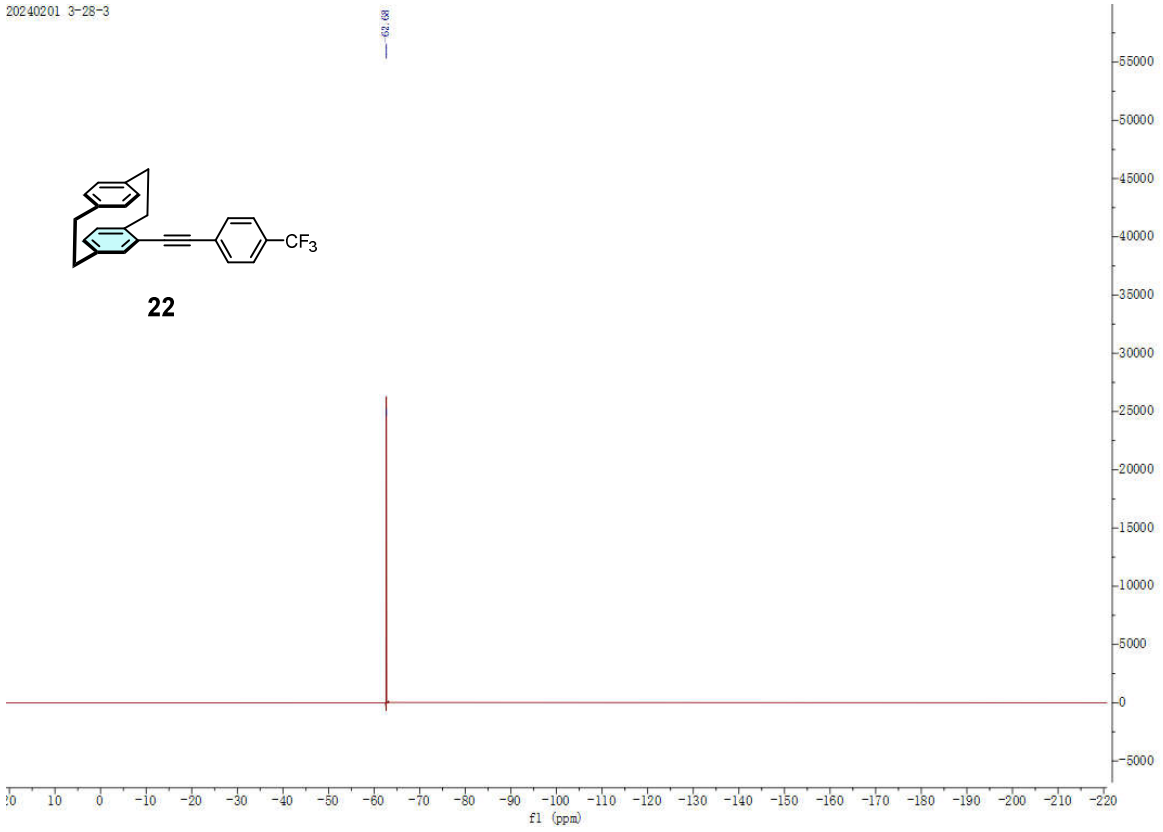
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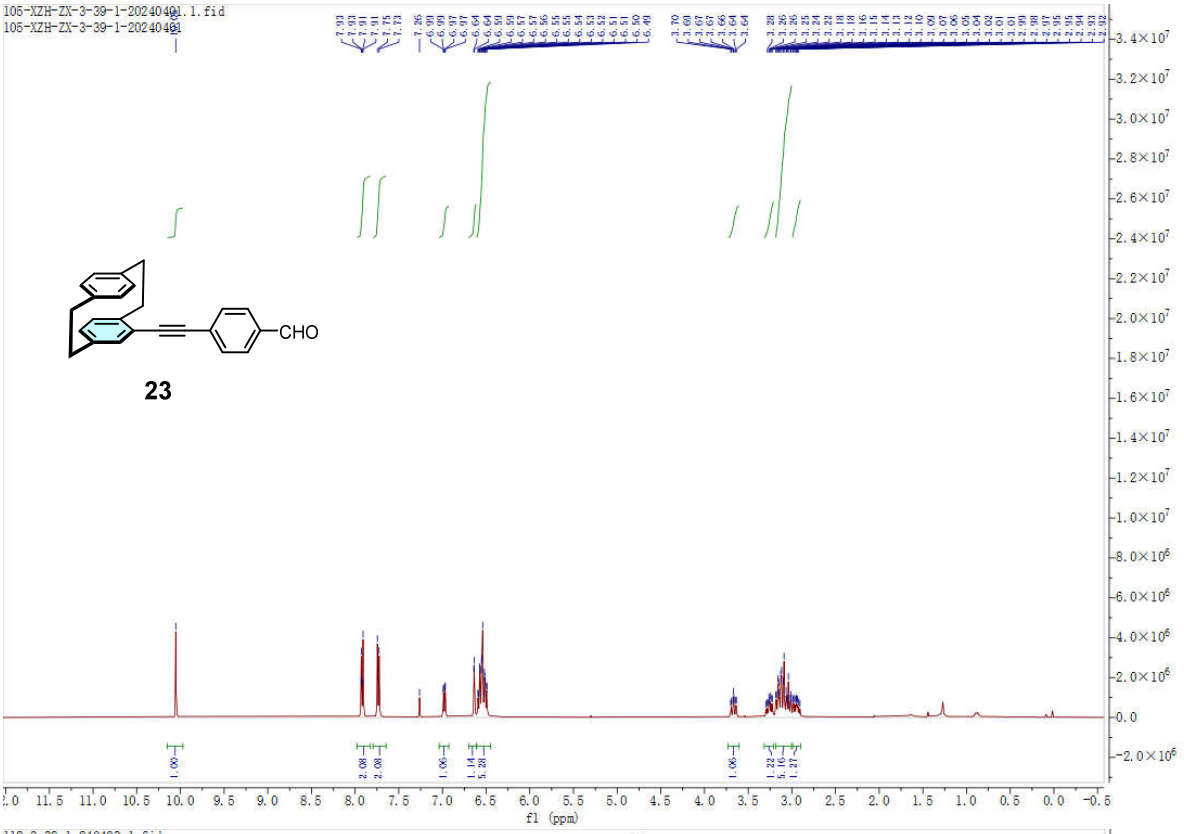
f1 (ppm)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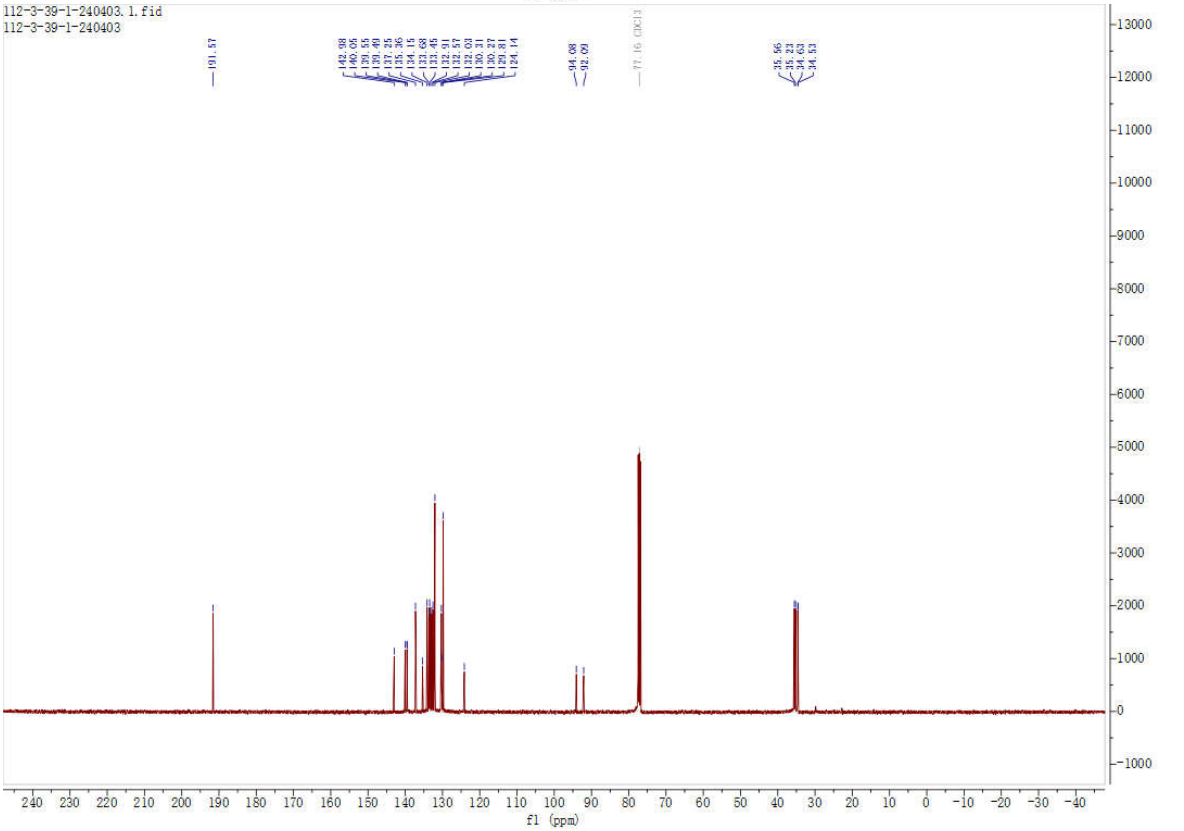
CHO
f1 (ppm)

23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112-3-39-1-240403
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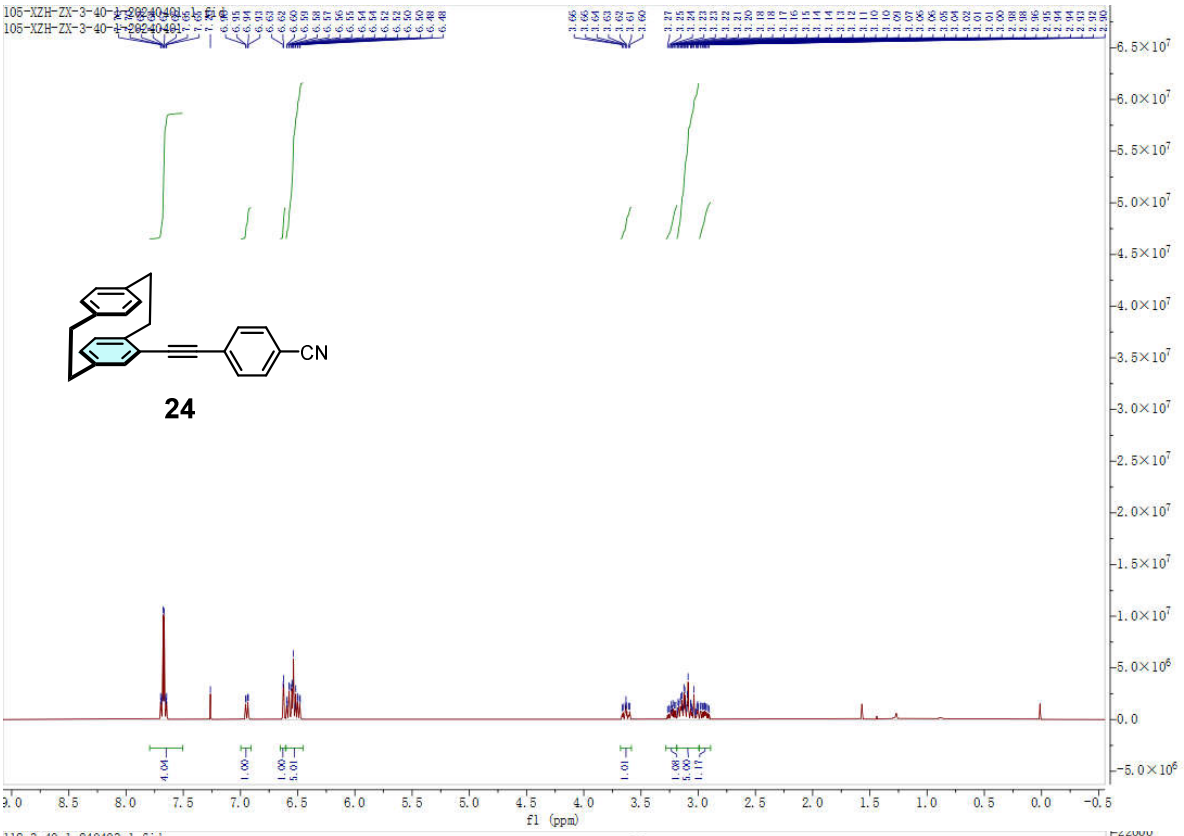
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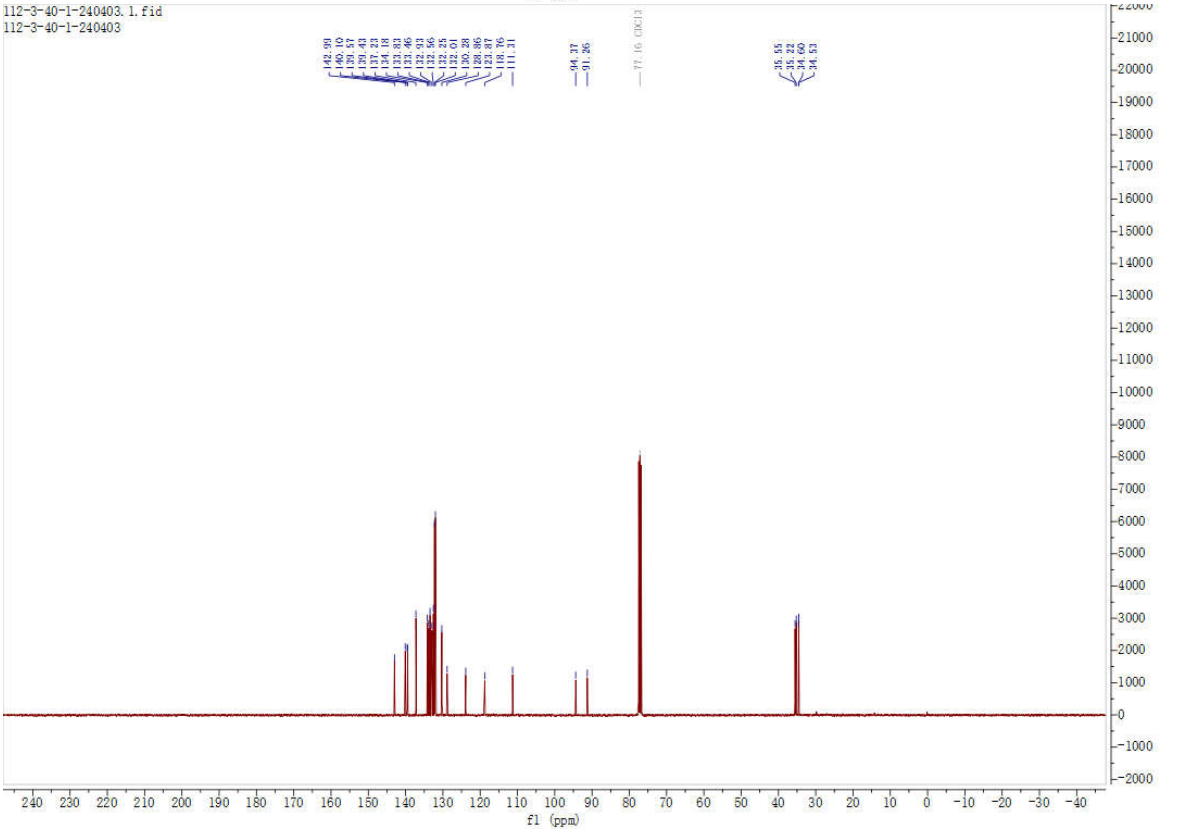
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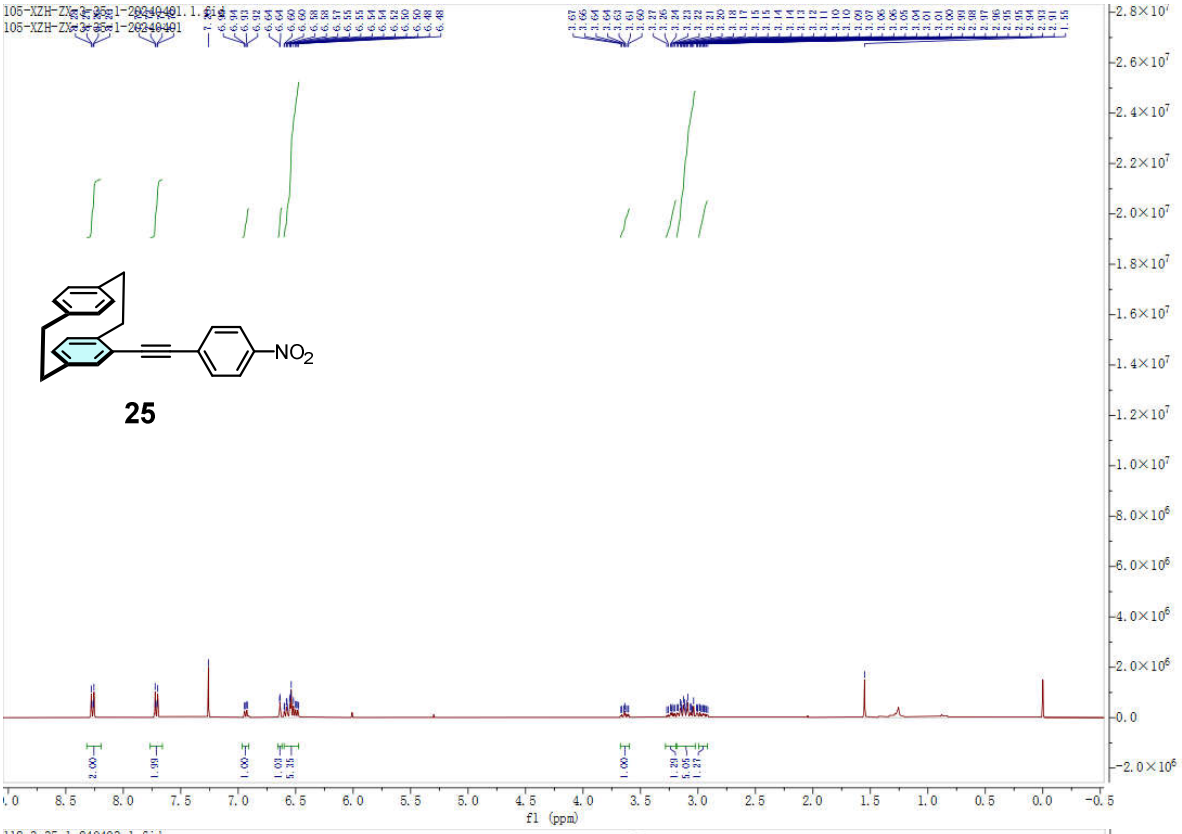
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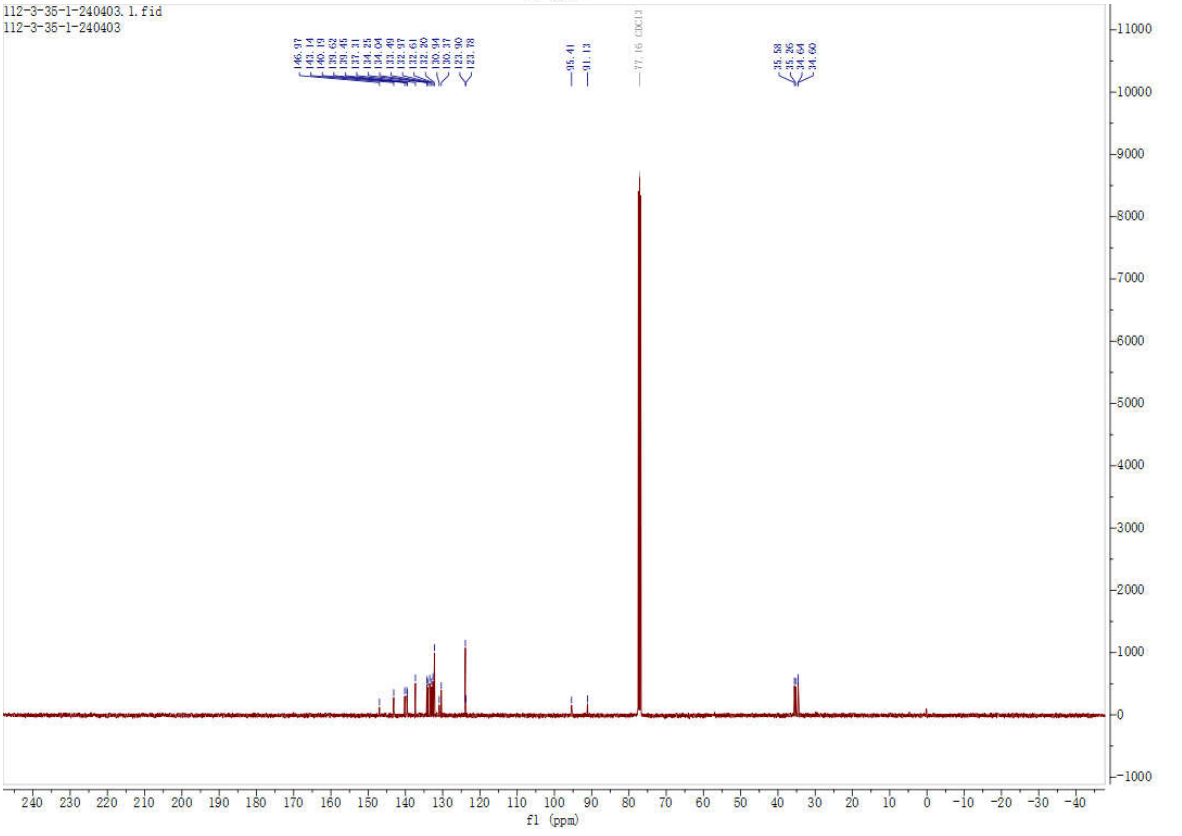
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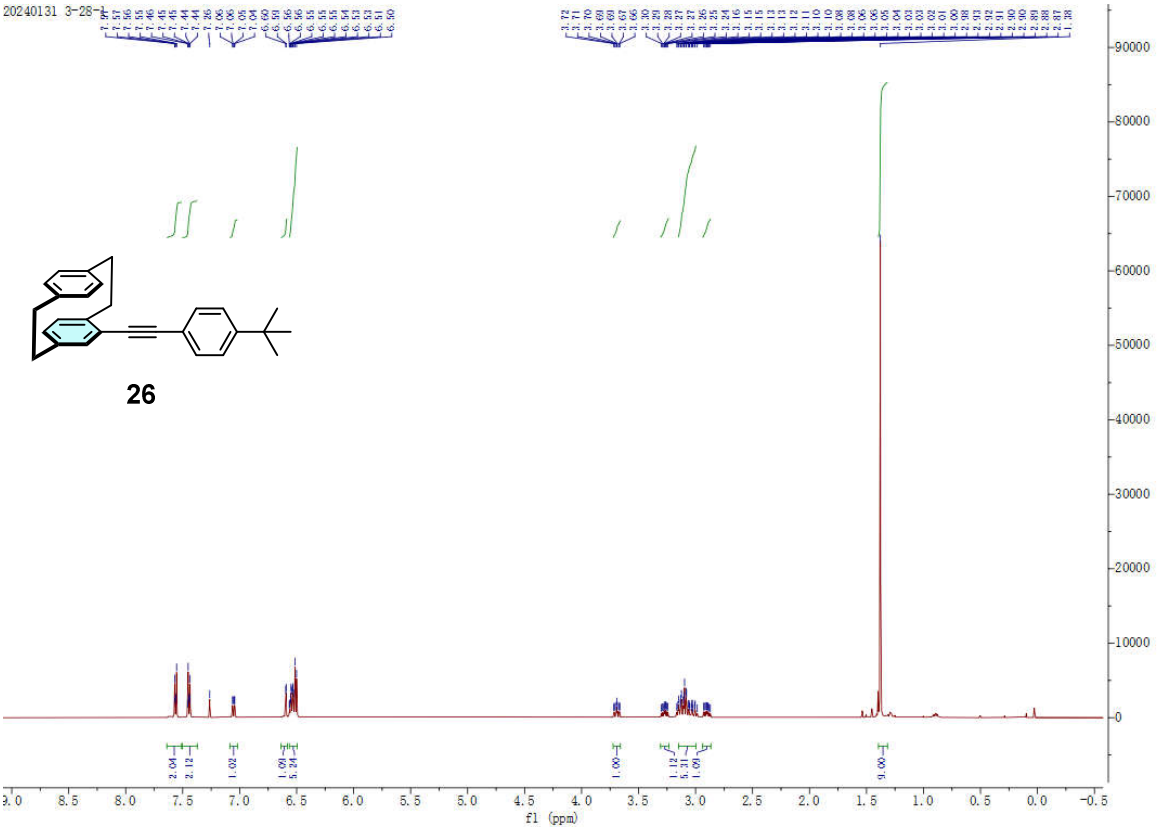
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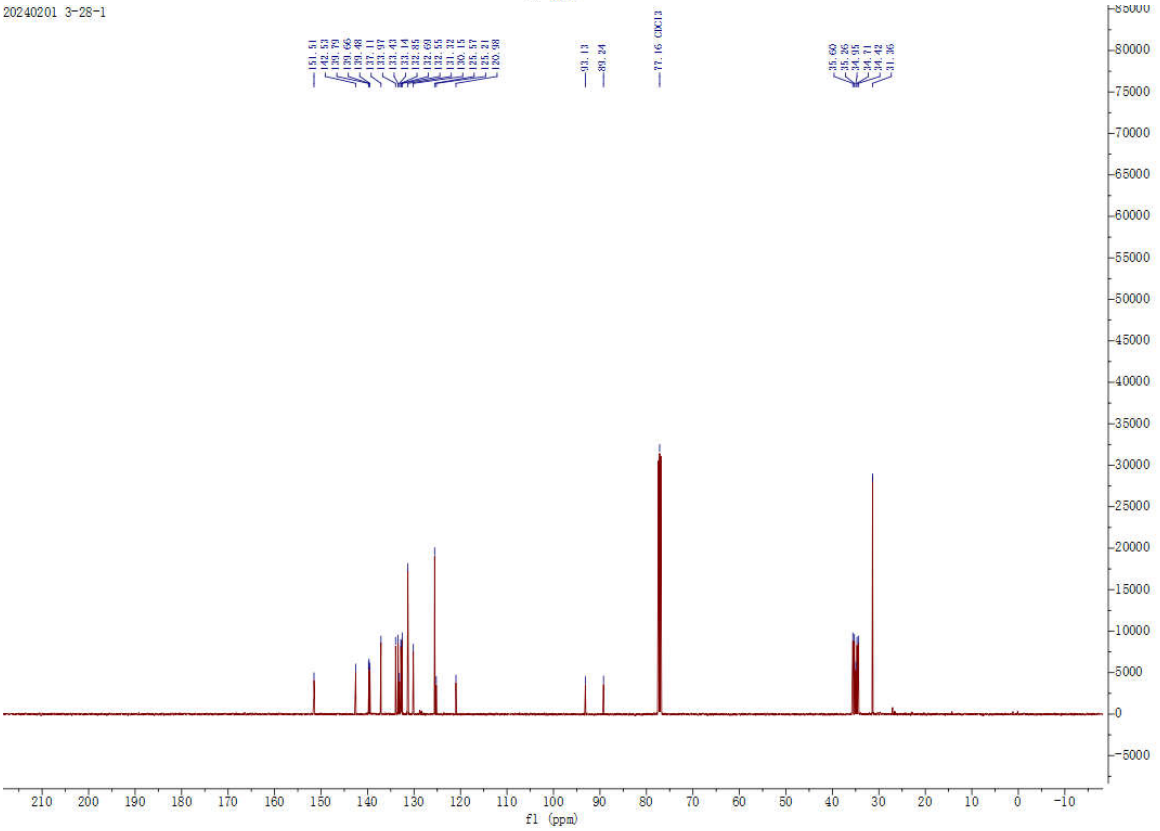
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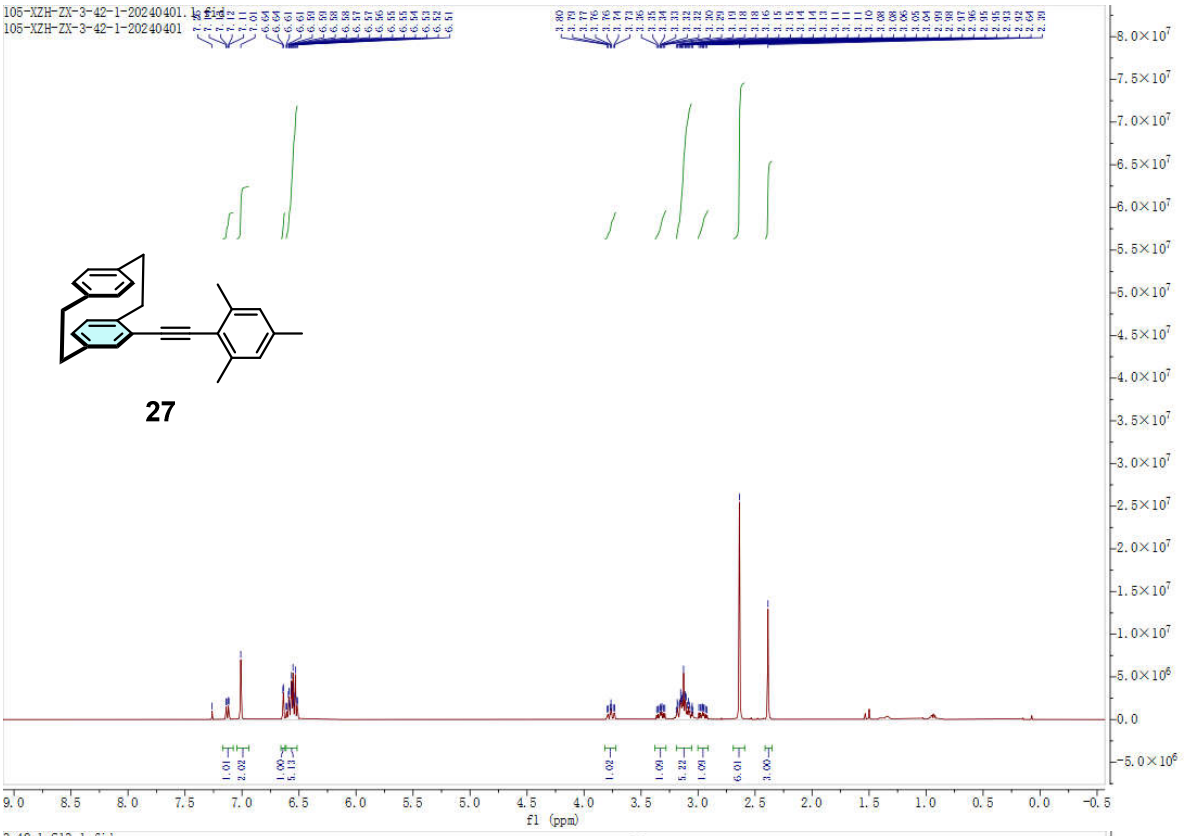
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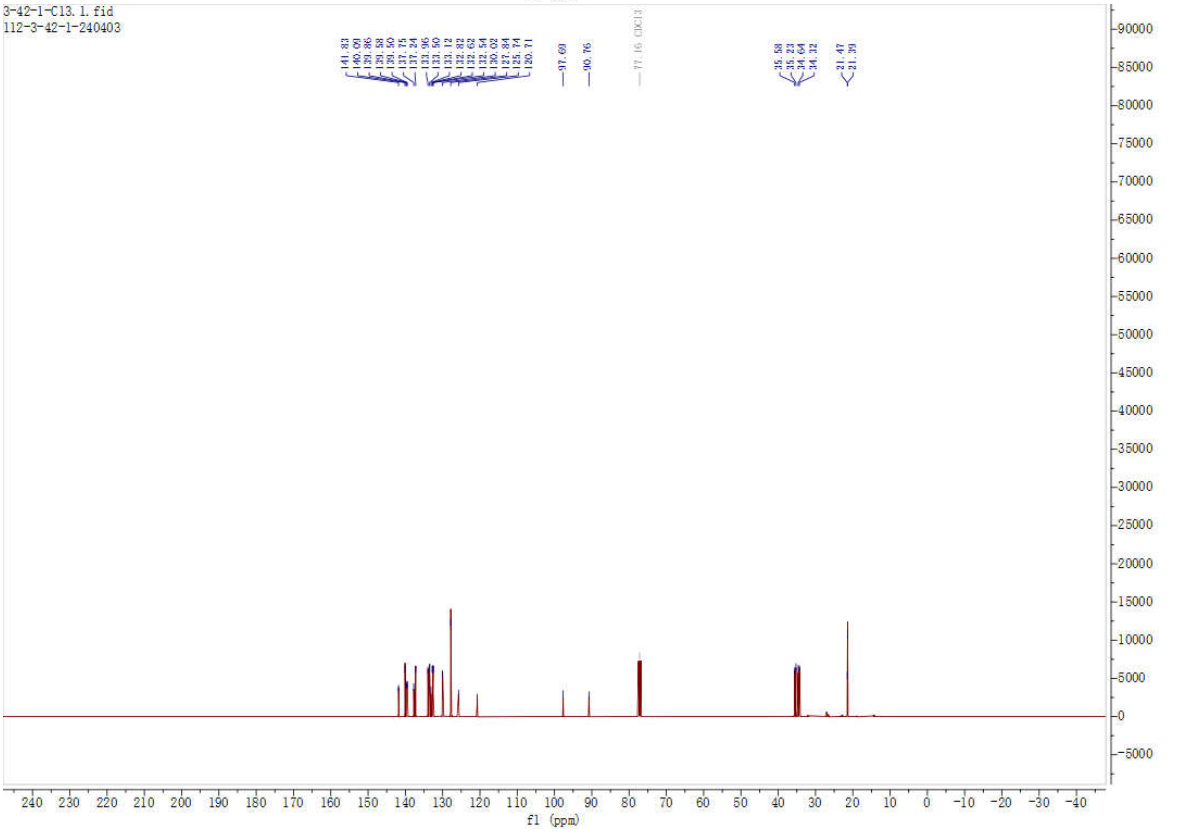
f1 (ppm)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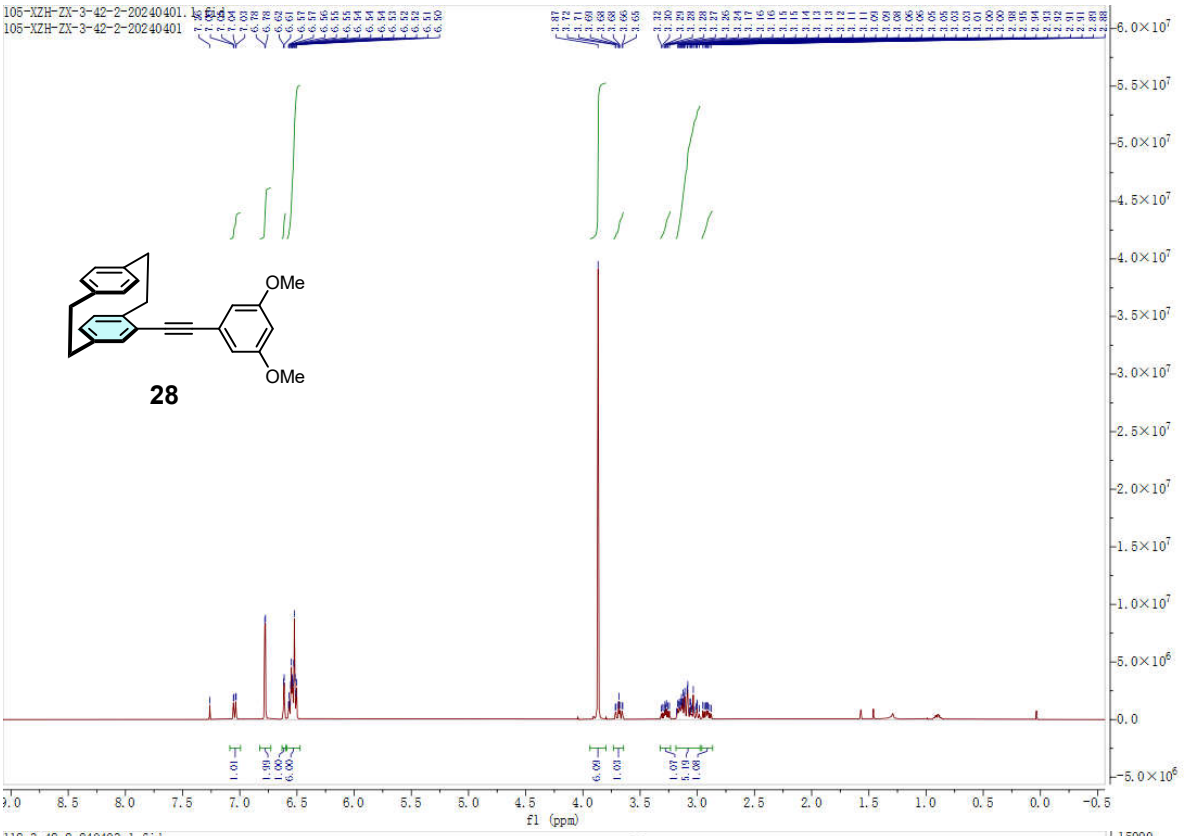
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OMe
OMe
28
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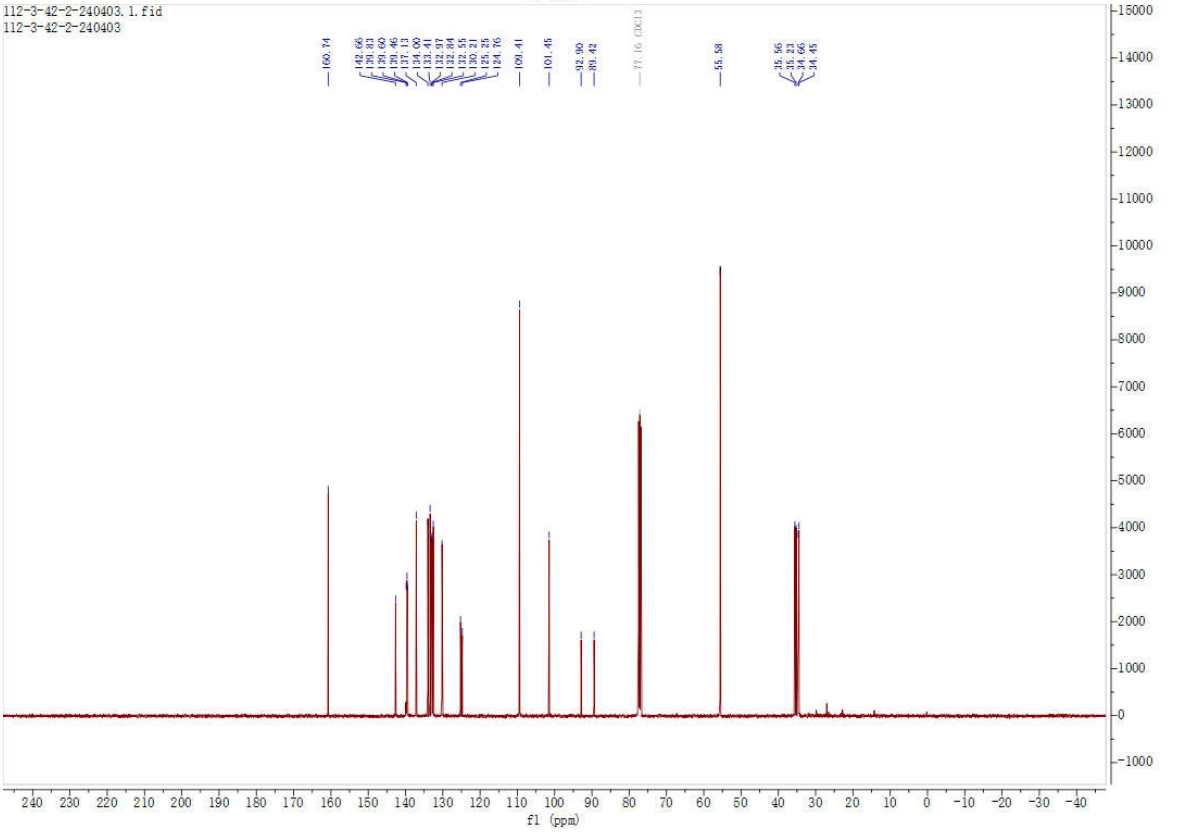
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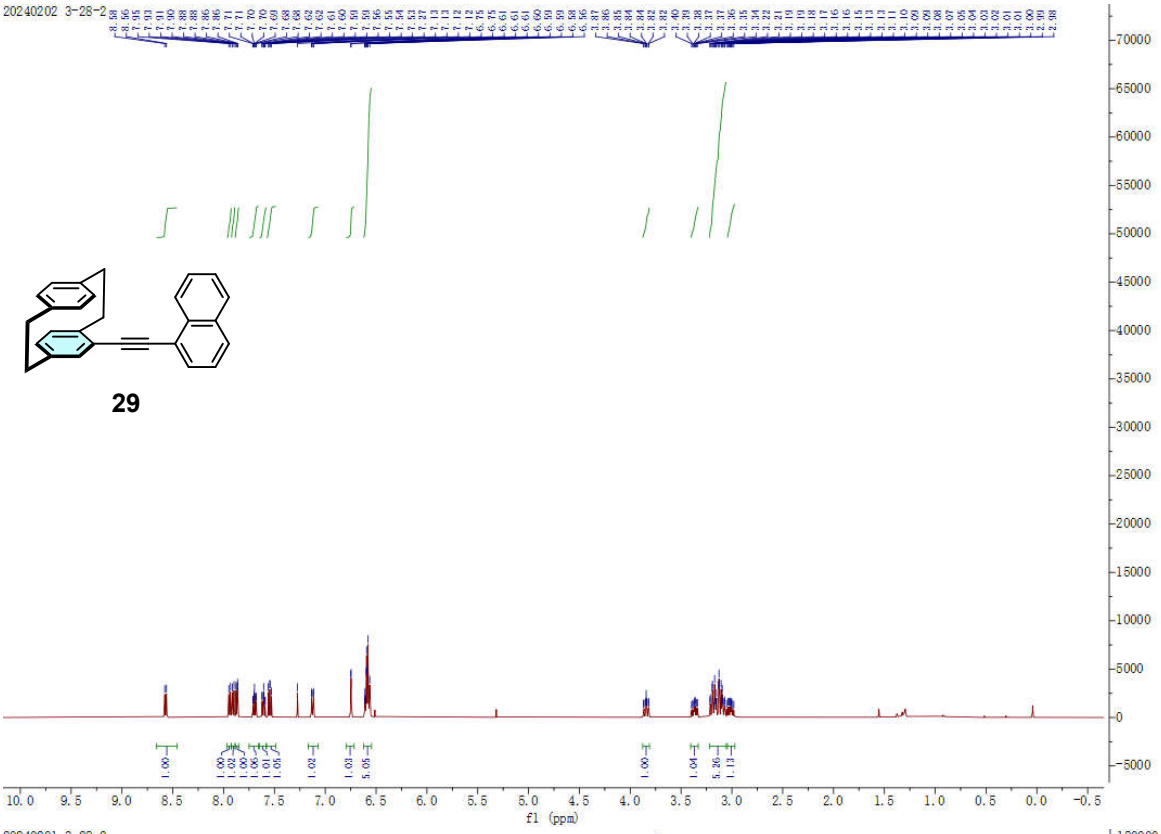
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29
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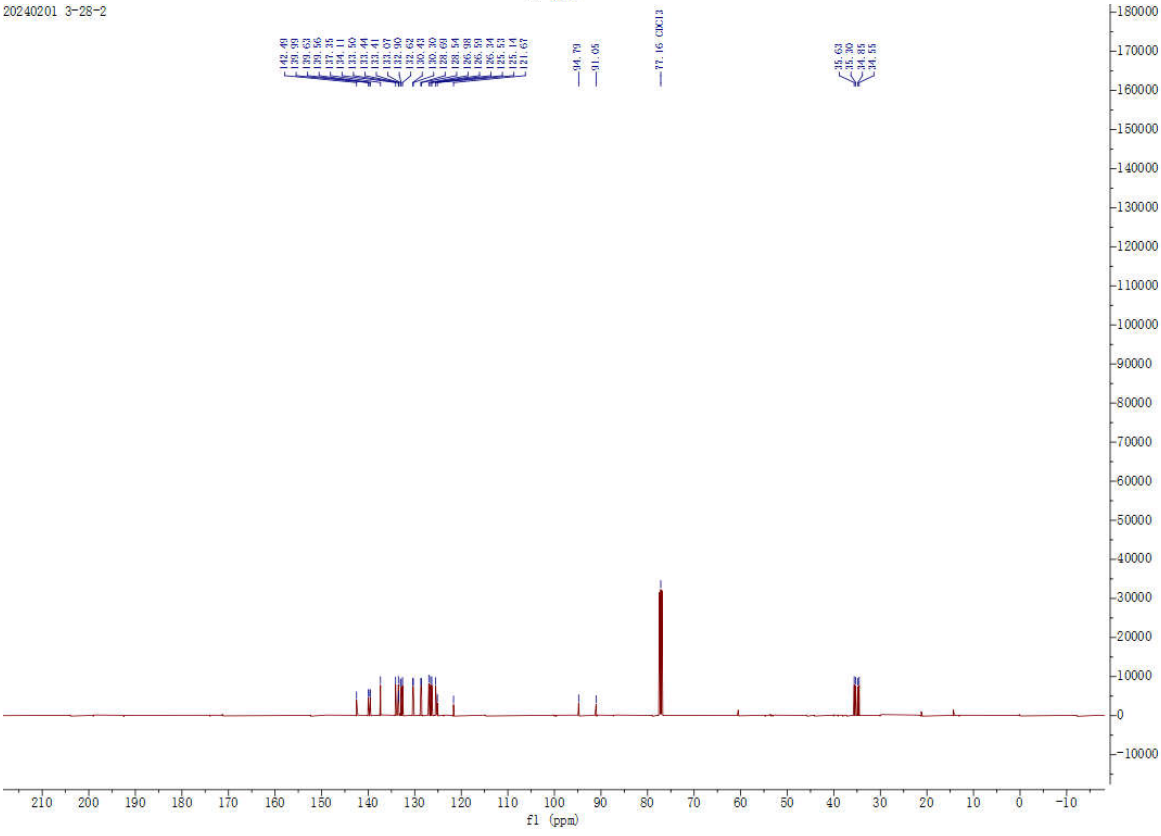
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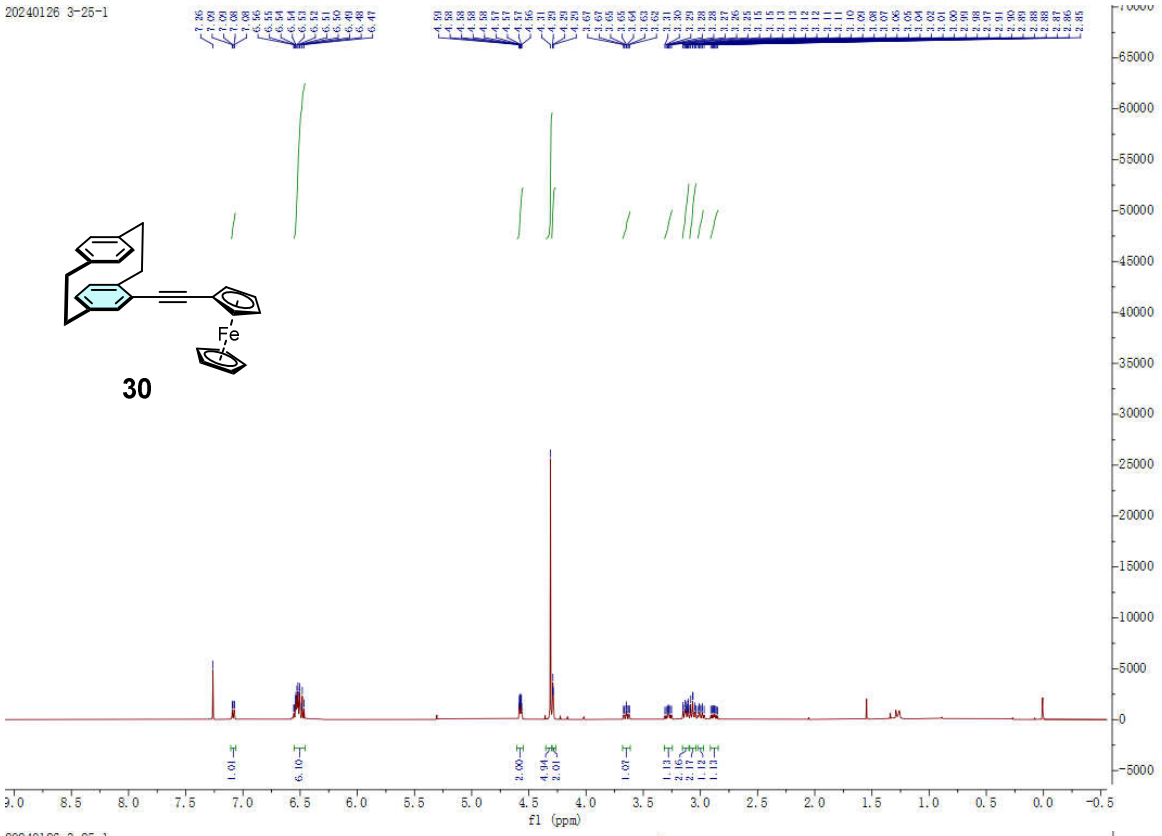
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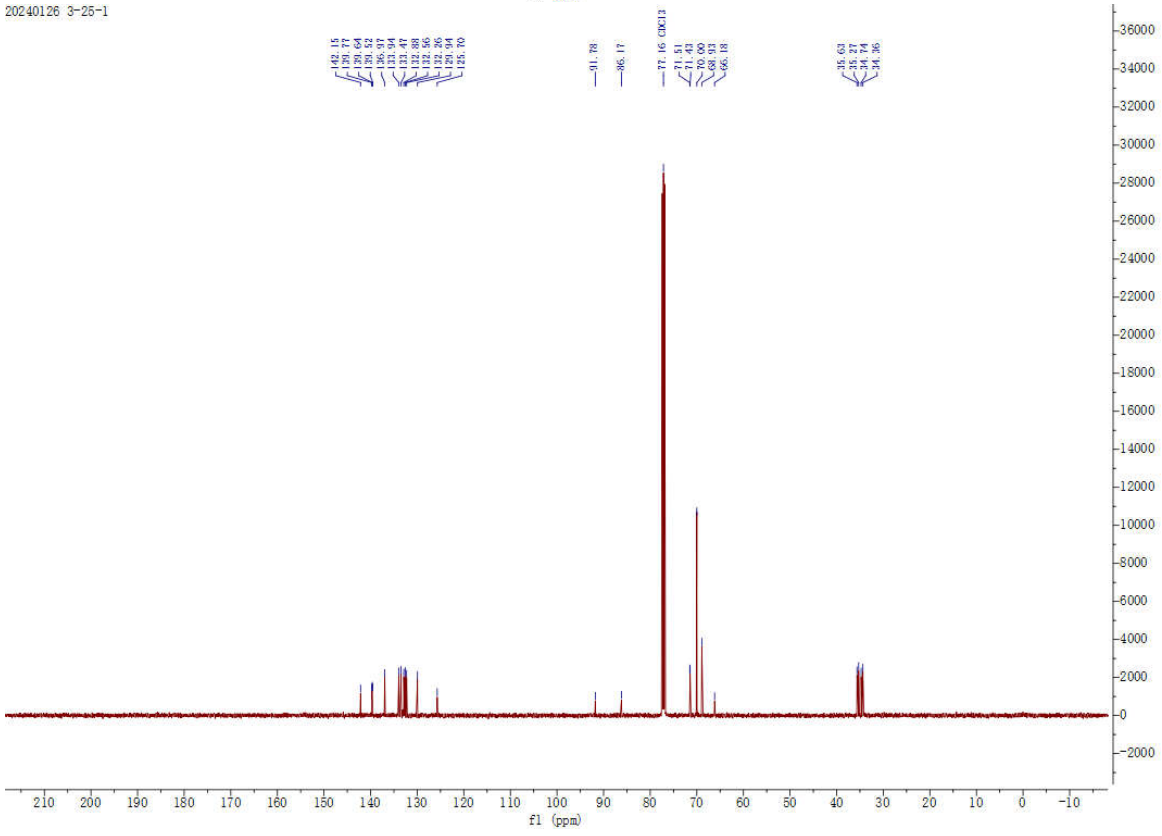
Fe
30
f1 (ppm)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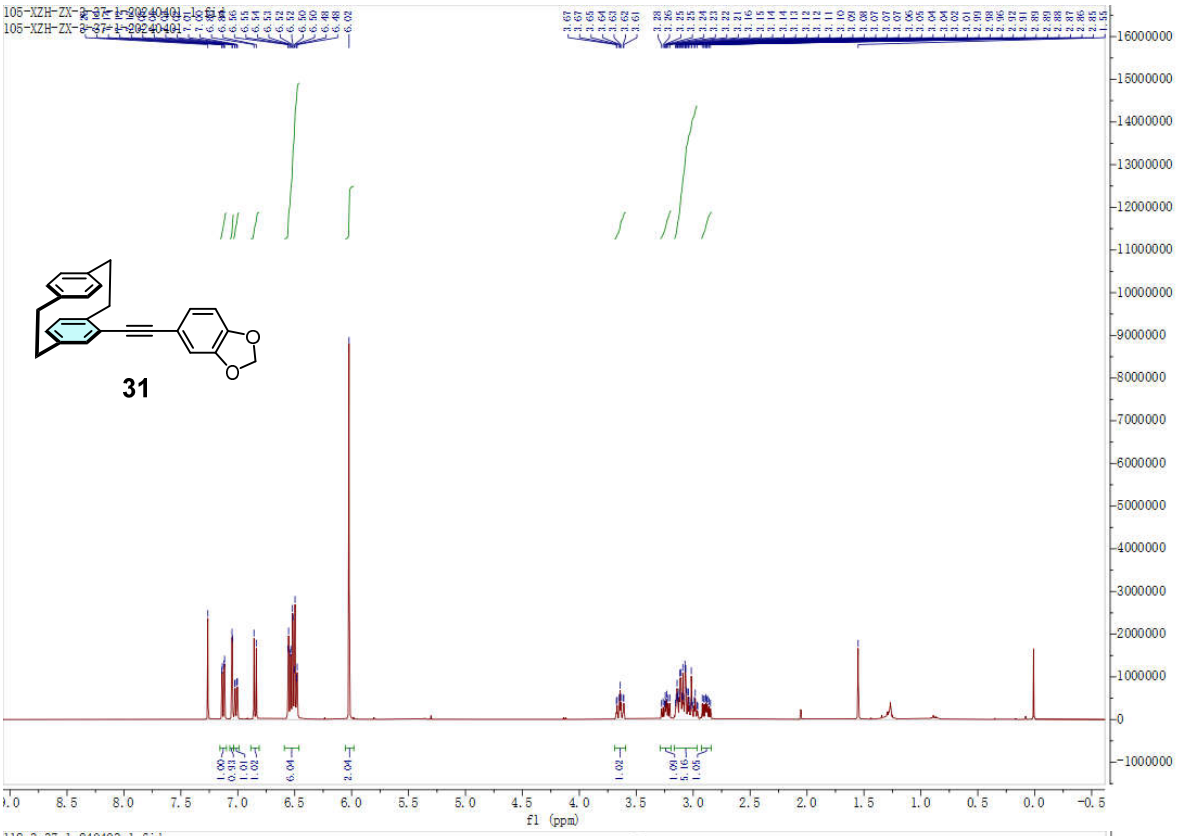
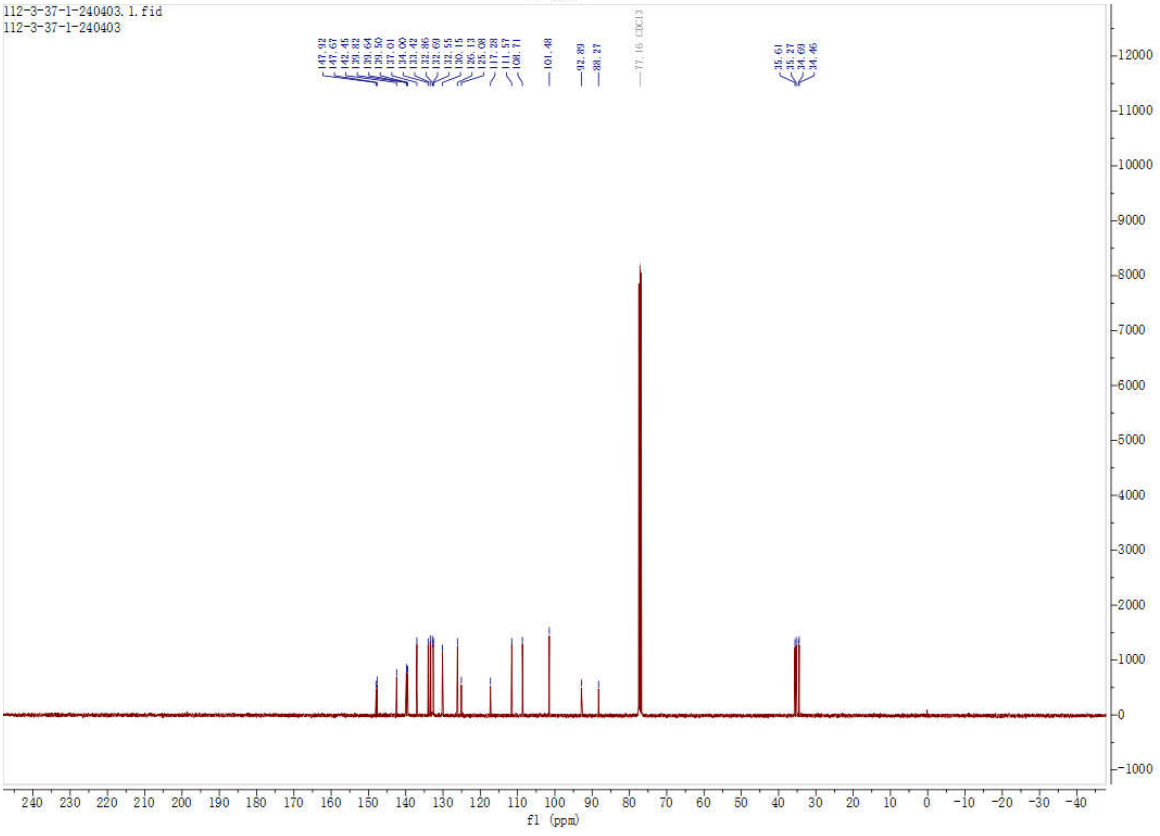

105-XZH-ZX-3-37-1-20240401
31
f1 (ppm)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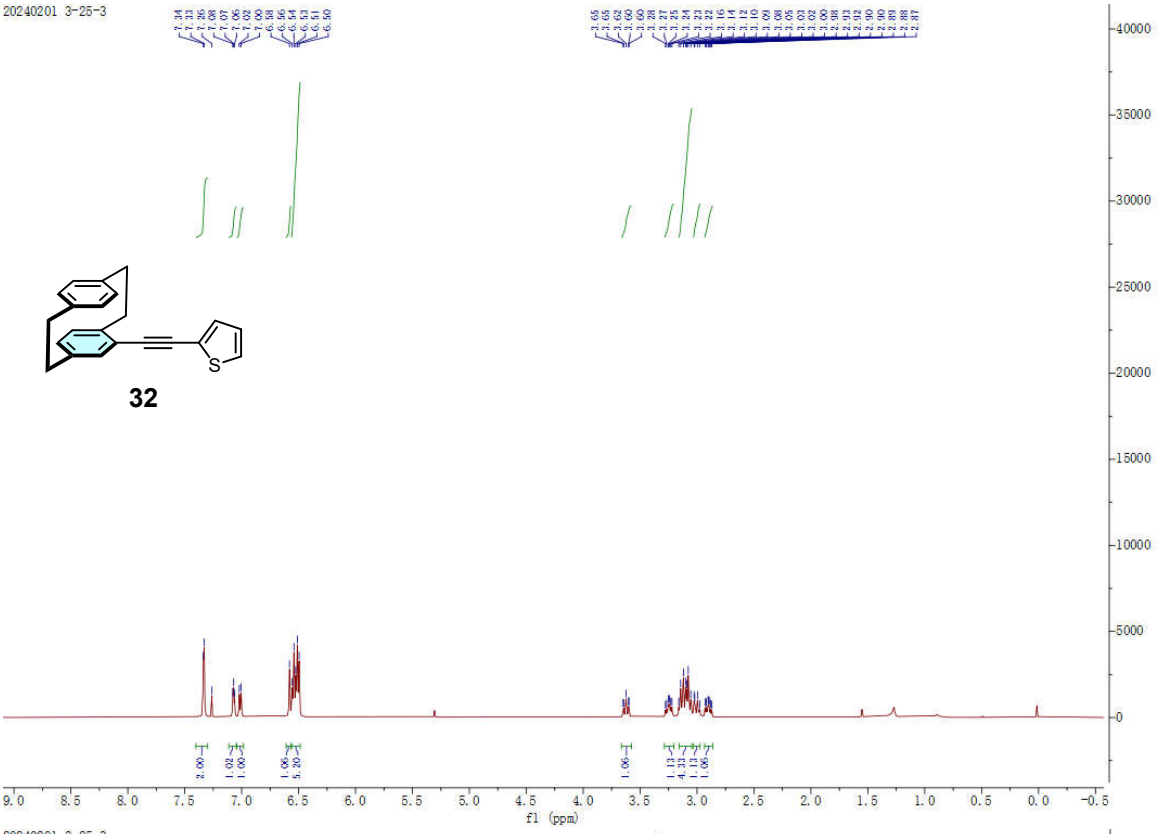
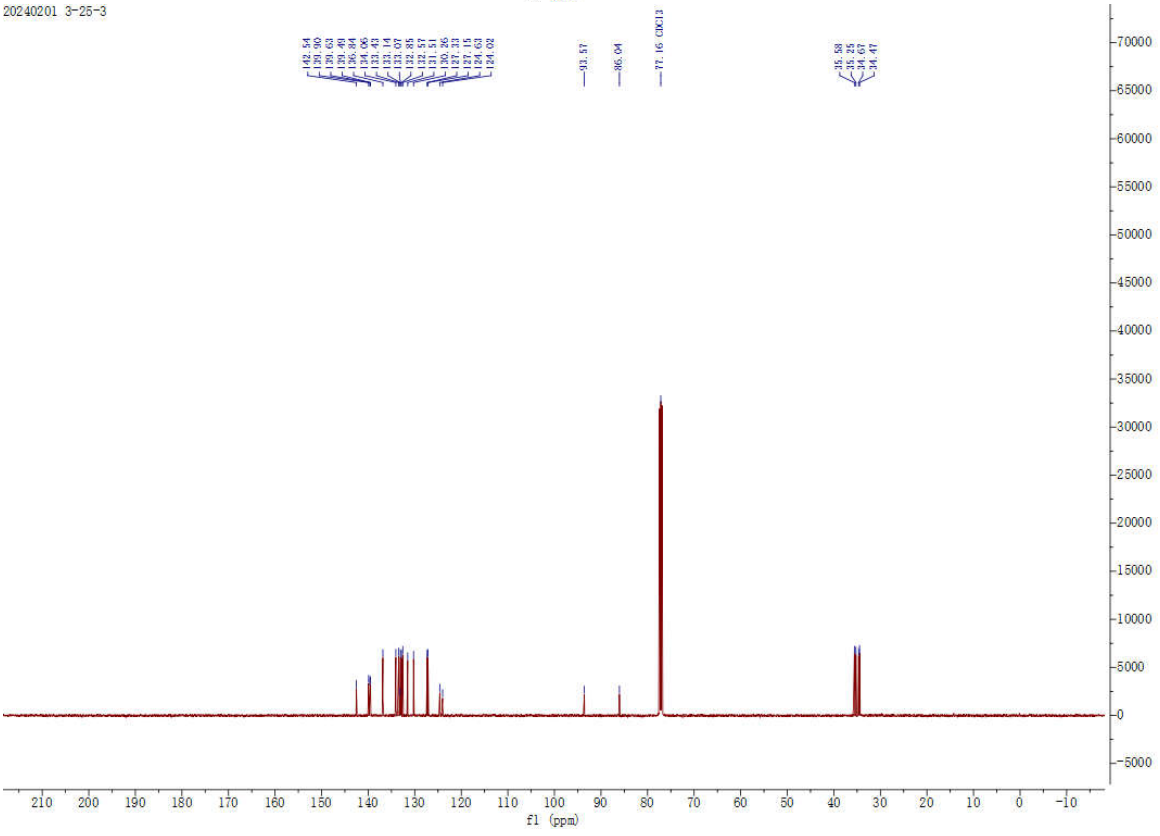
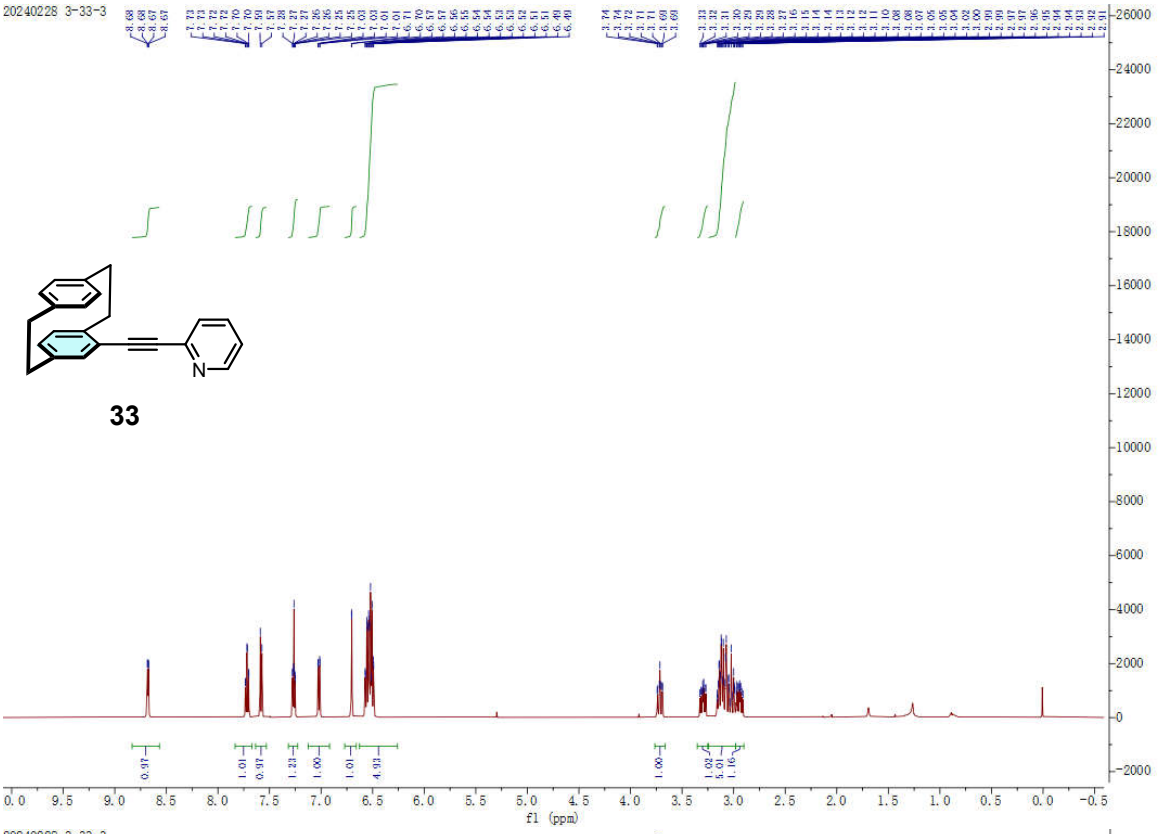
112-3-37-1-240403
f1 (ppm)



32





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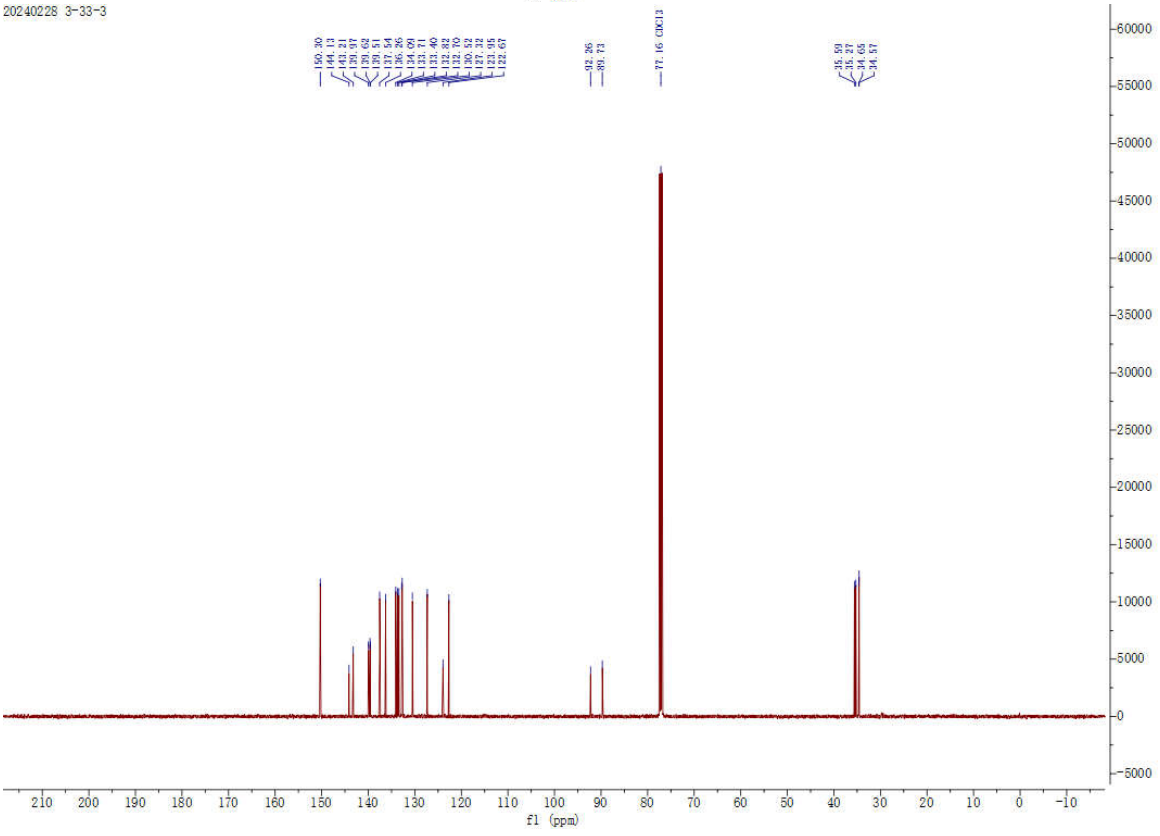

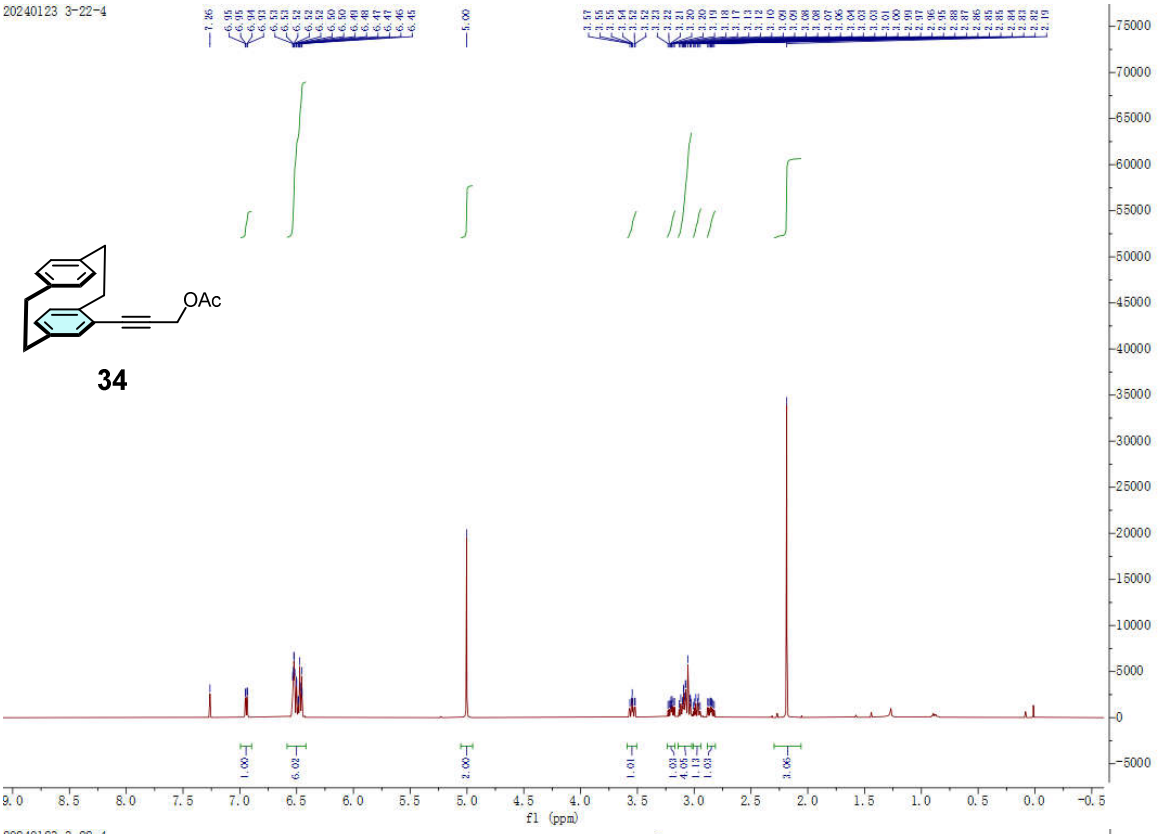
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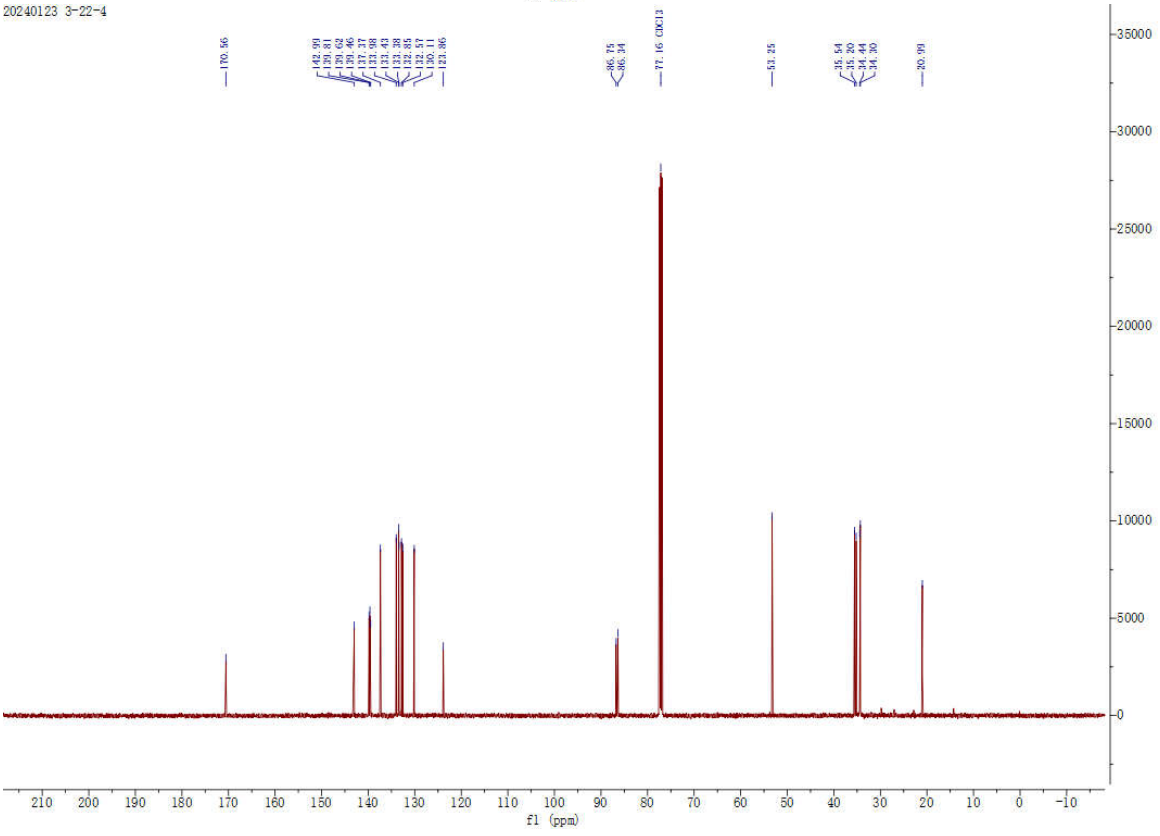
OAc
34
f1 (ppm)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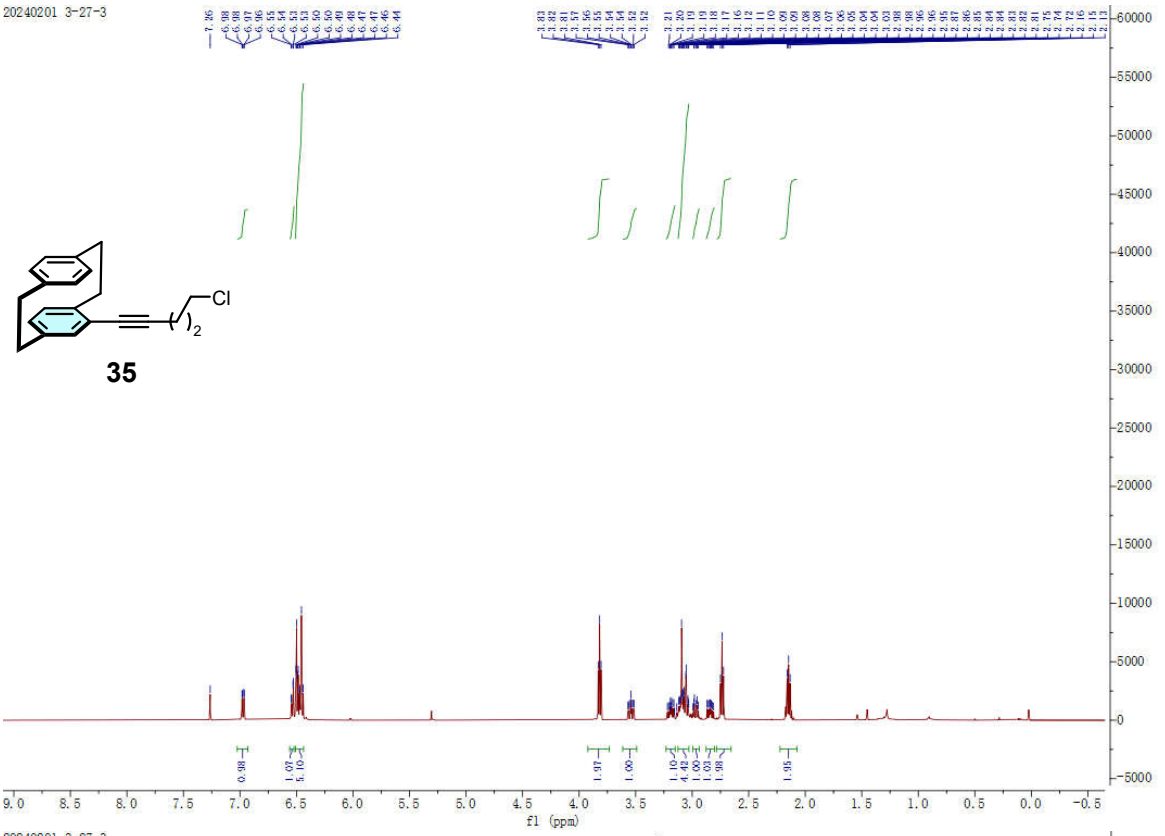
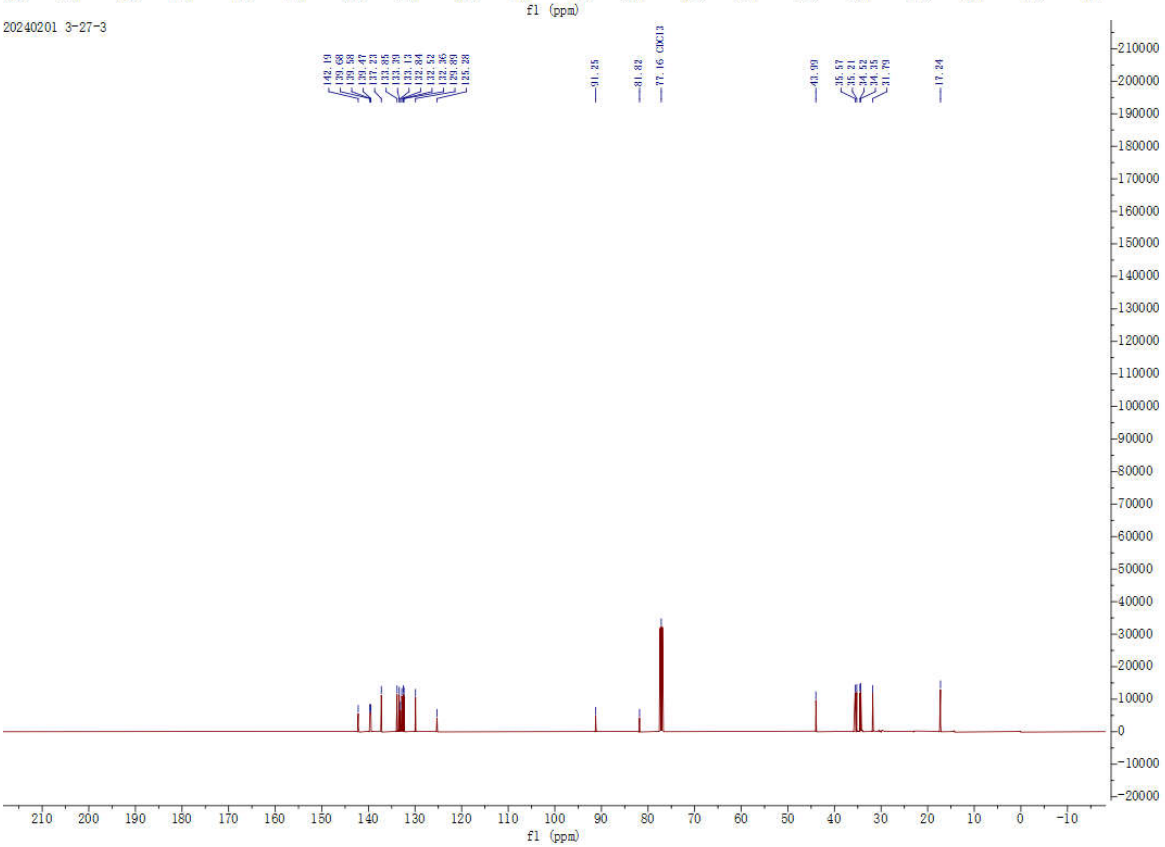
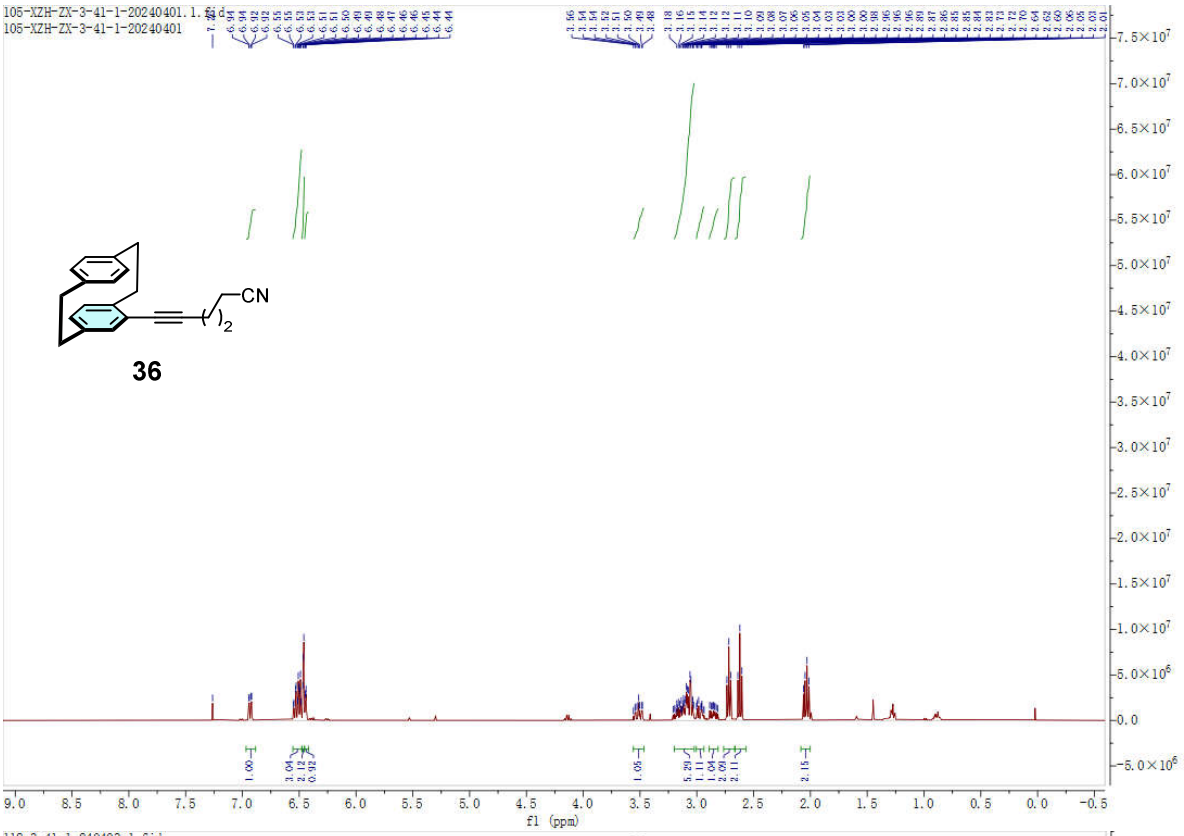


35

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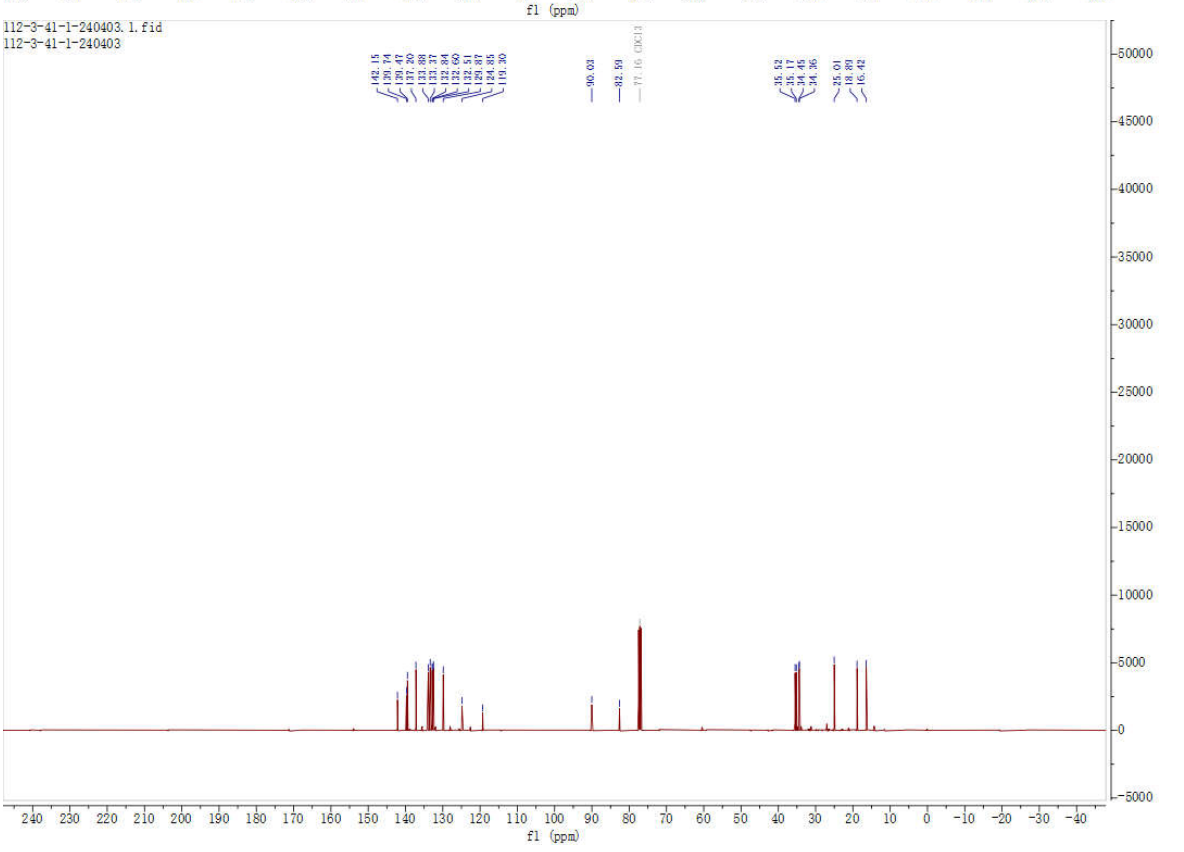
105-XZH-ZX-3-41-1-20240401
CN
2
36
f1 (ppm)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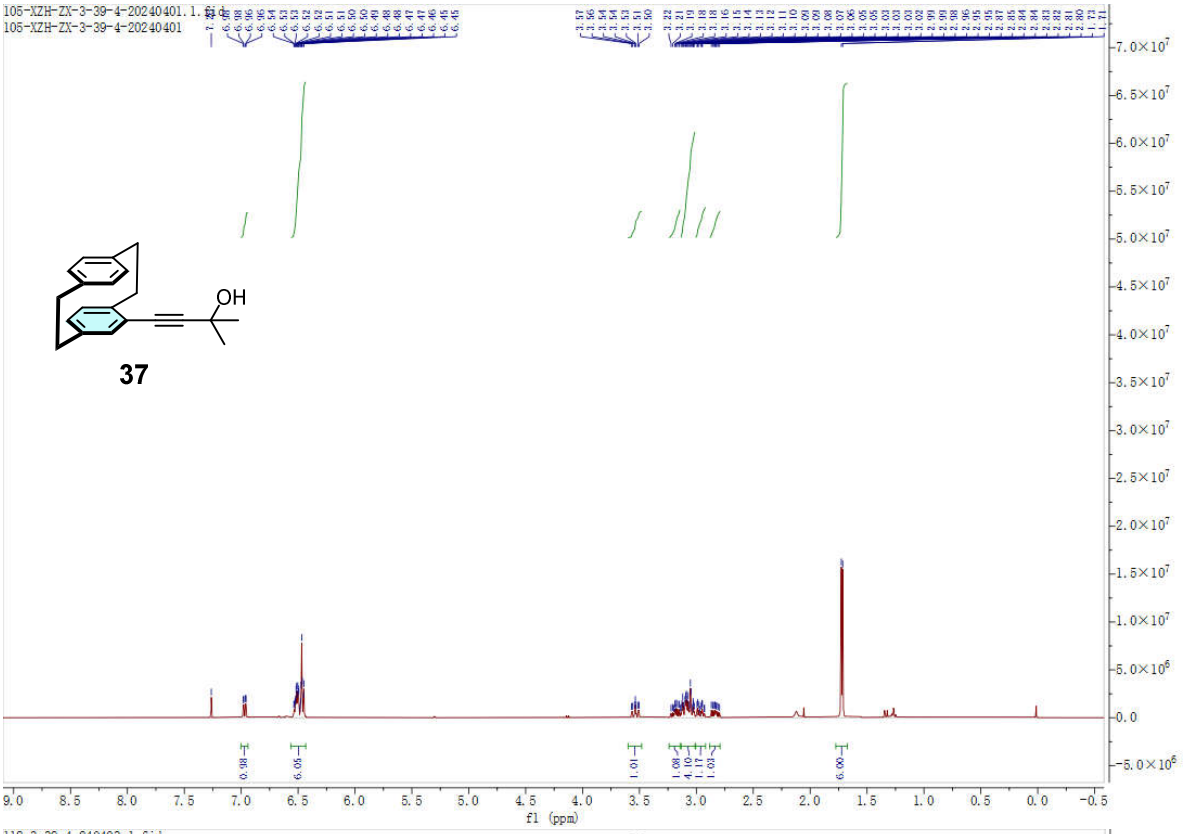
f1 (ppm)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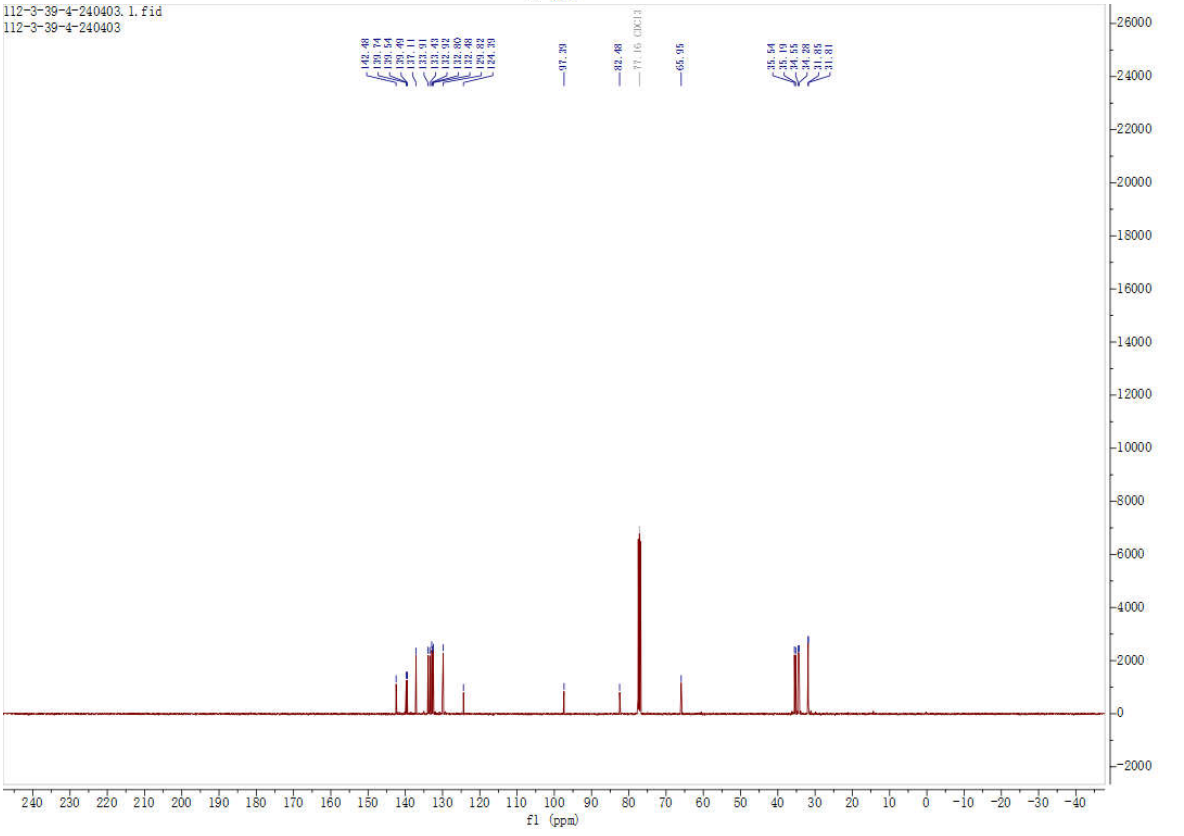
OH
37
f1 (ppm)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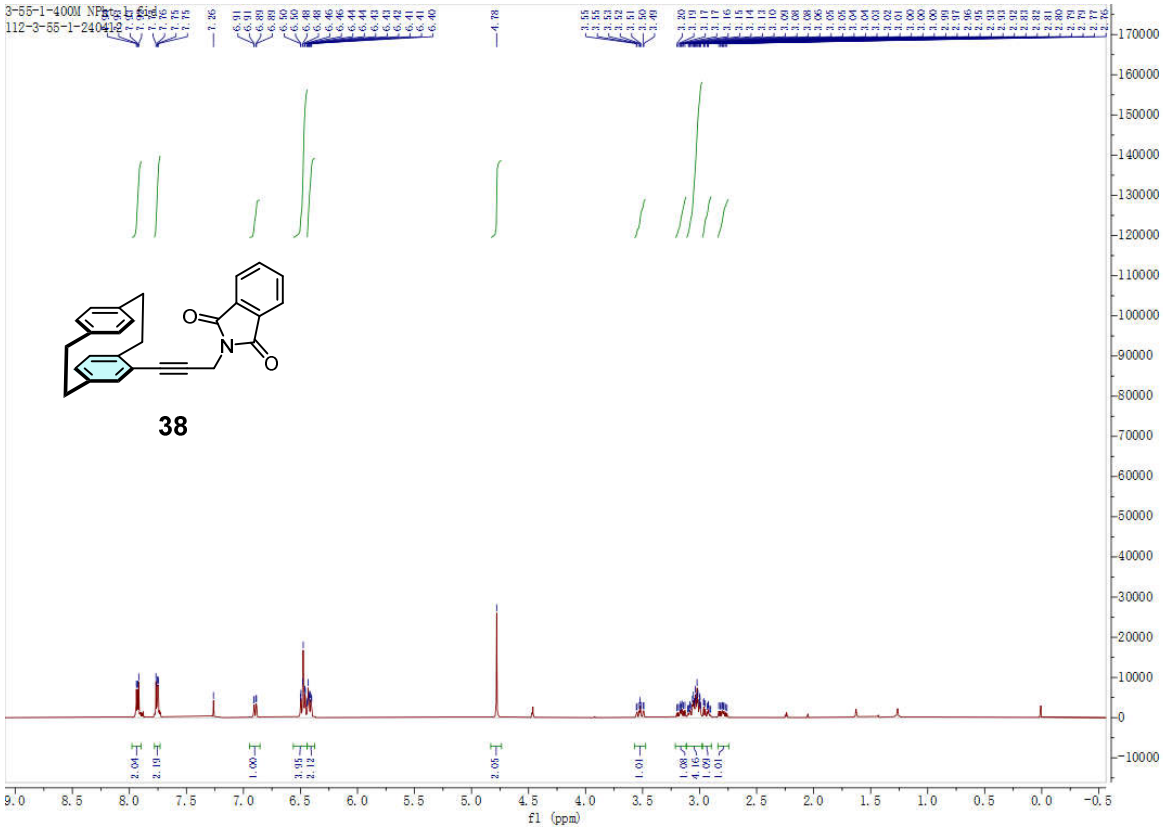
f1 (ppm)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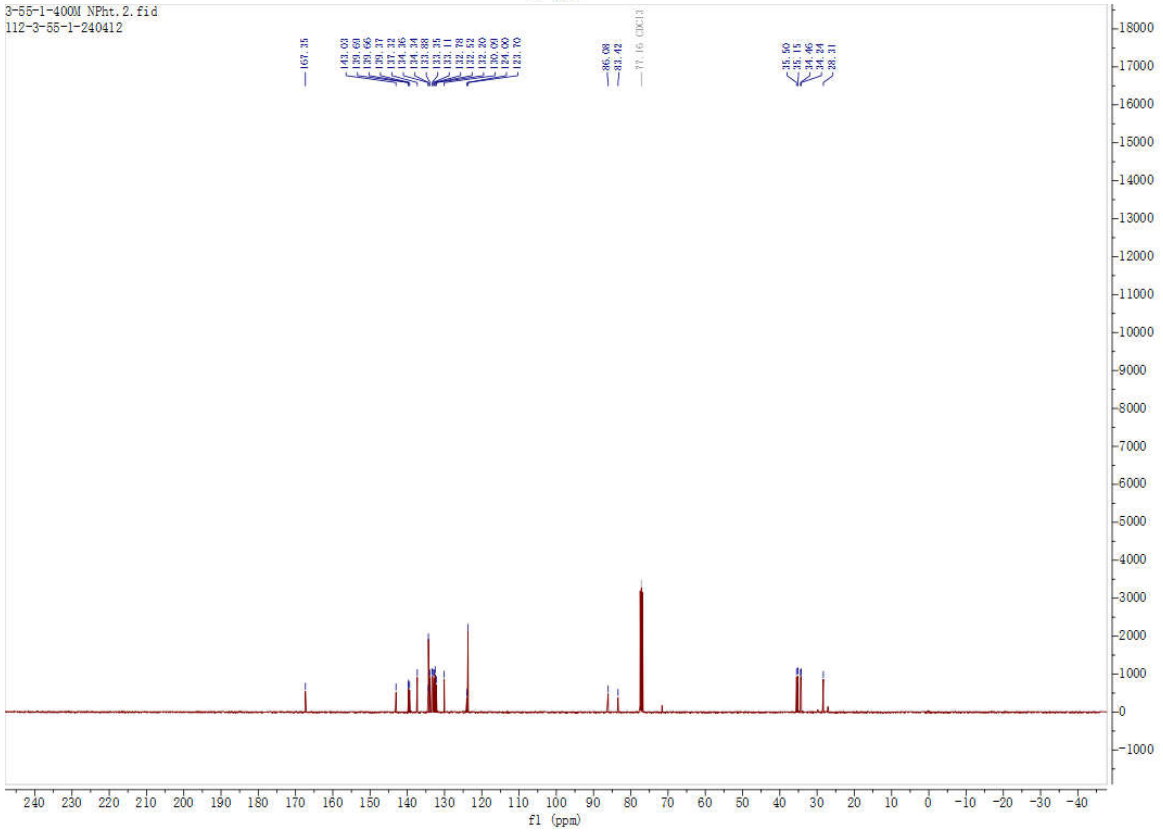
112-3-55-1-240412
38
f1 (ppm)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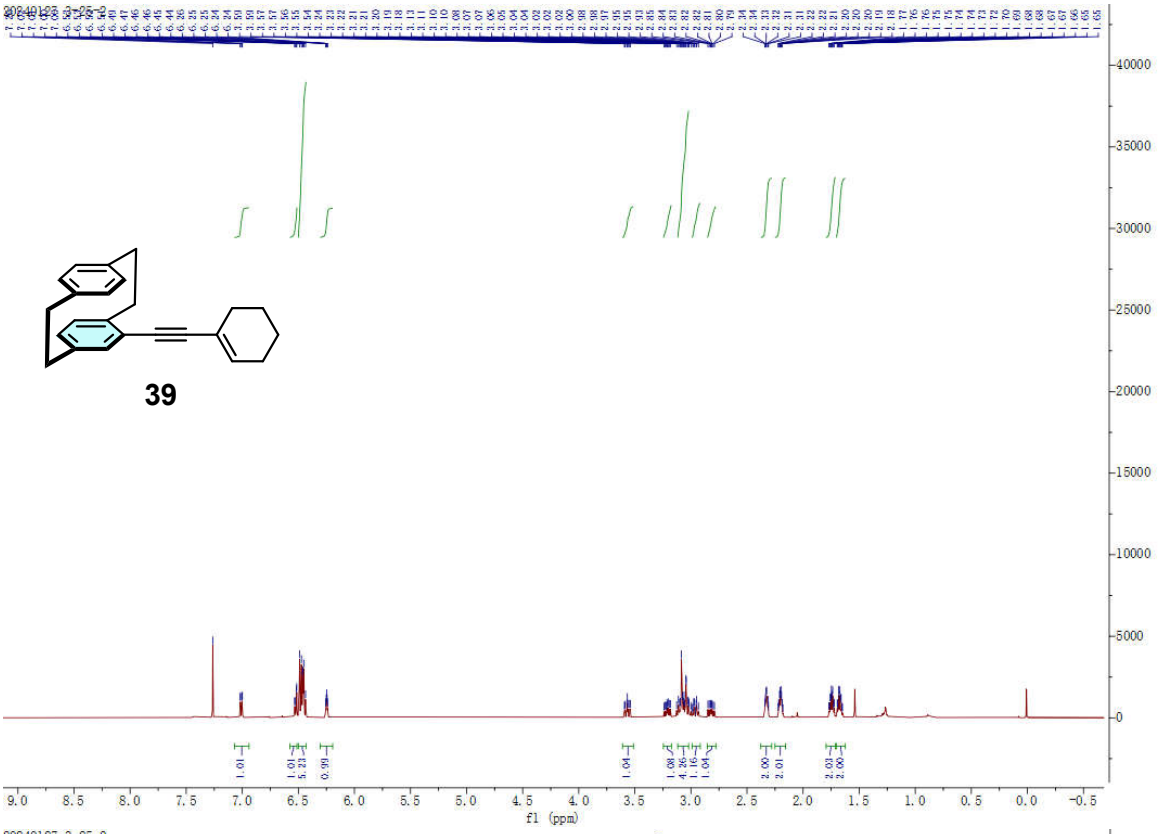
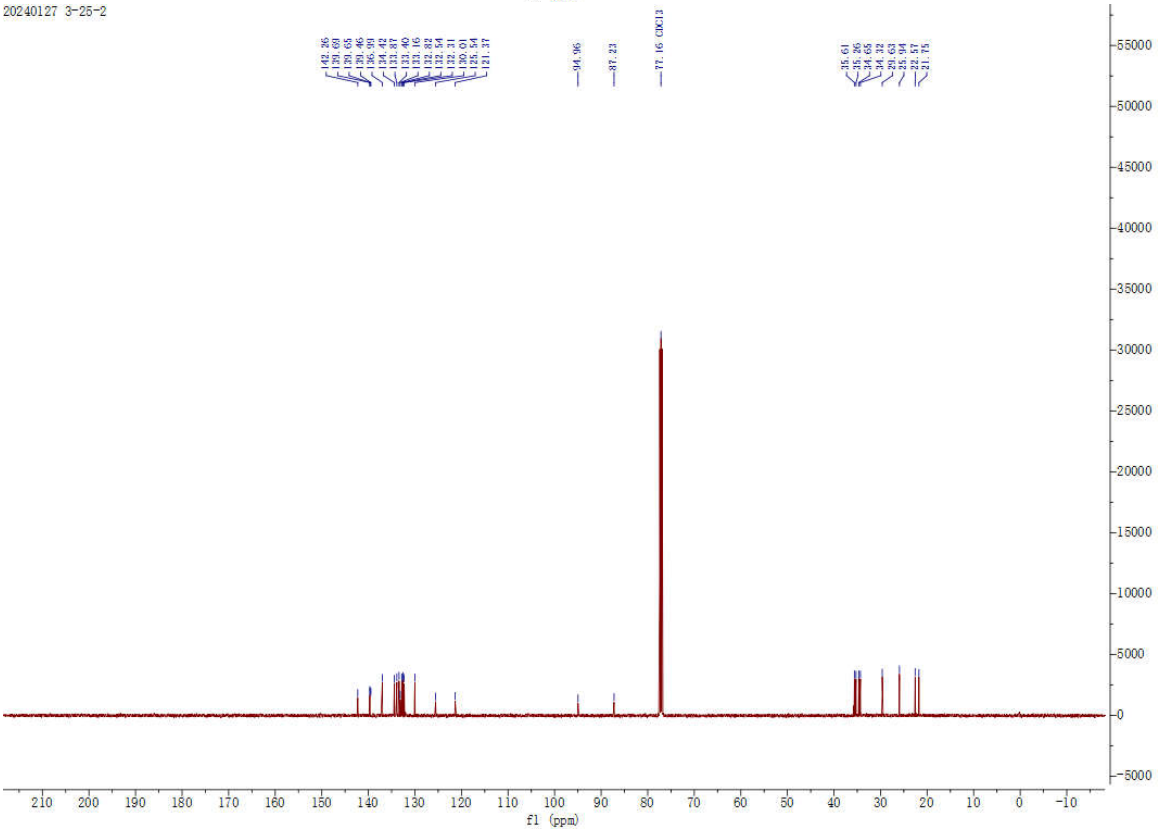
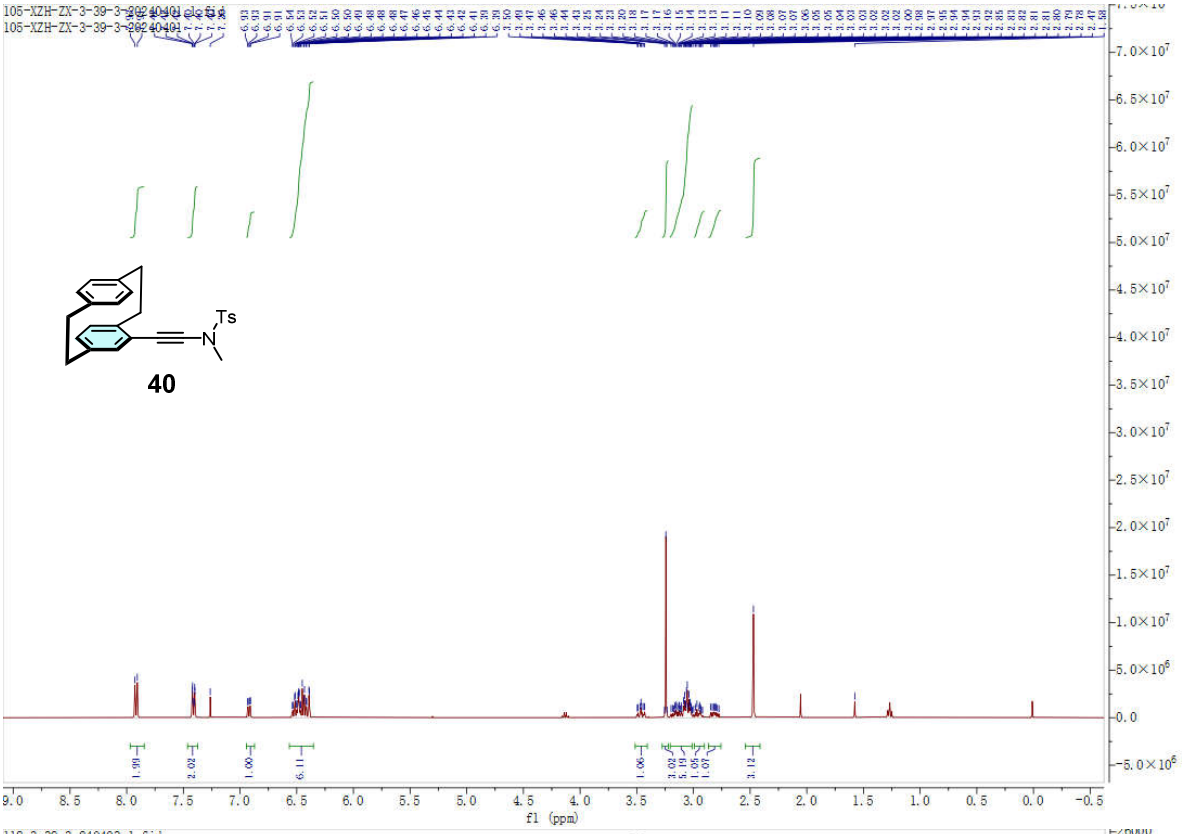


39

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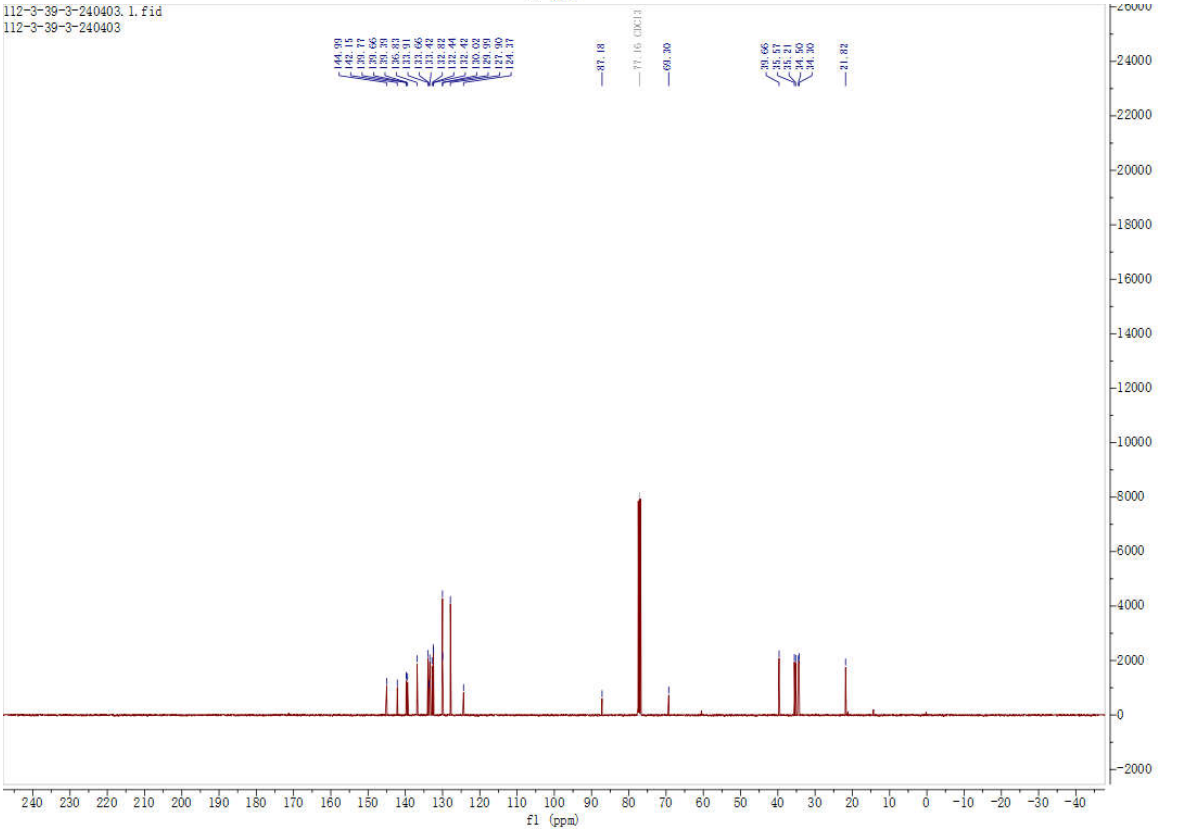
Ts
N
40
f1 (ppm)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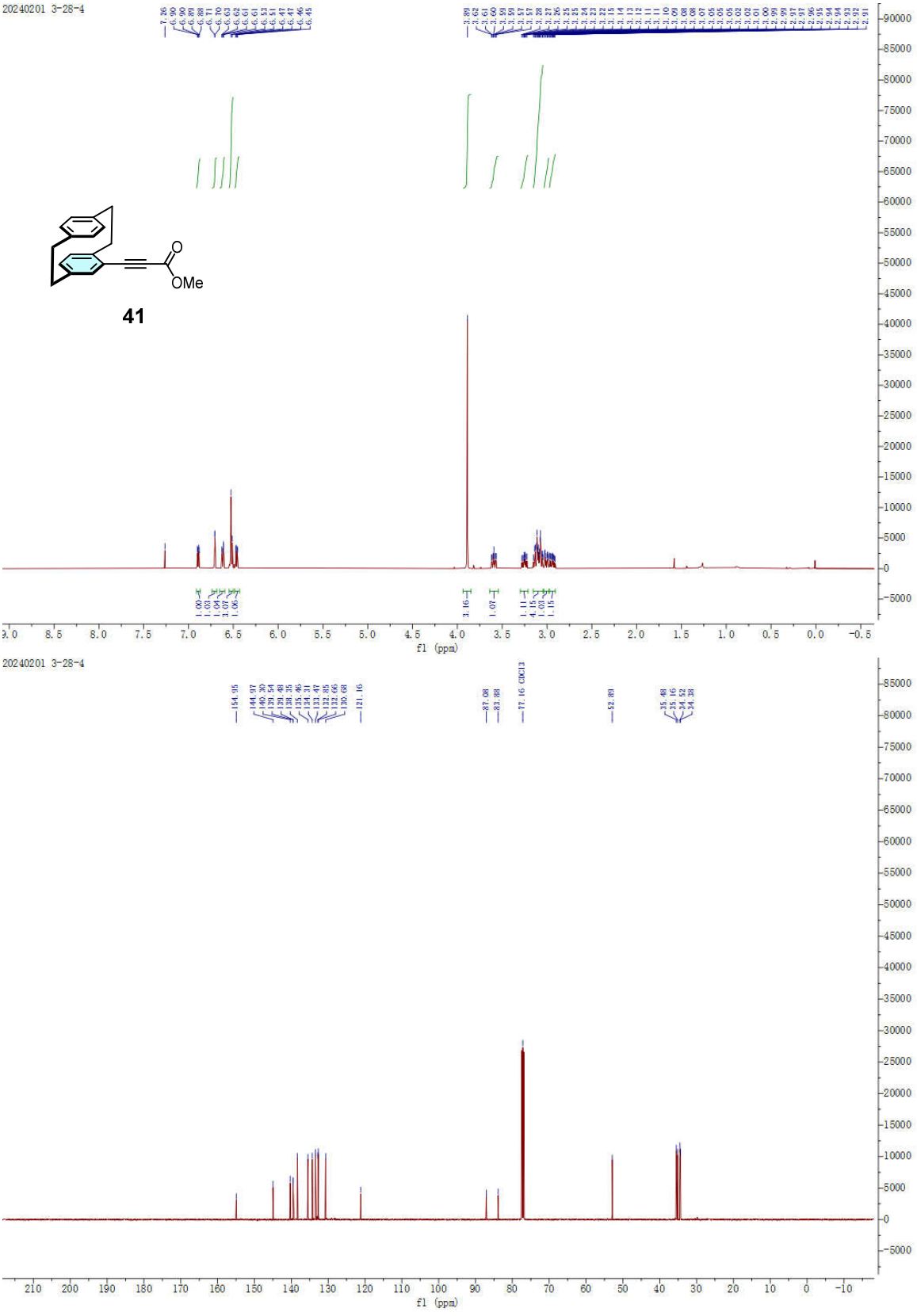
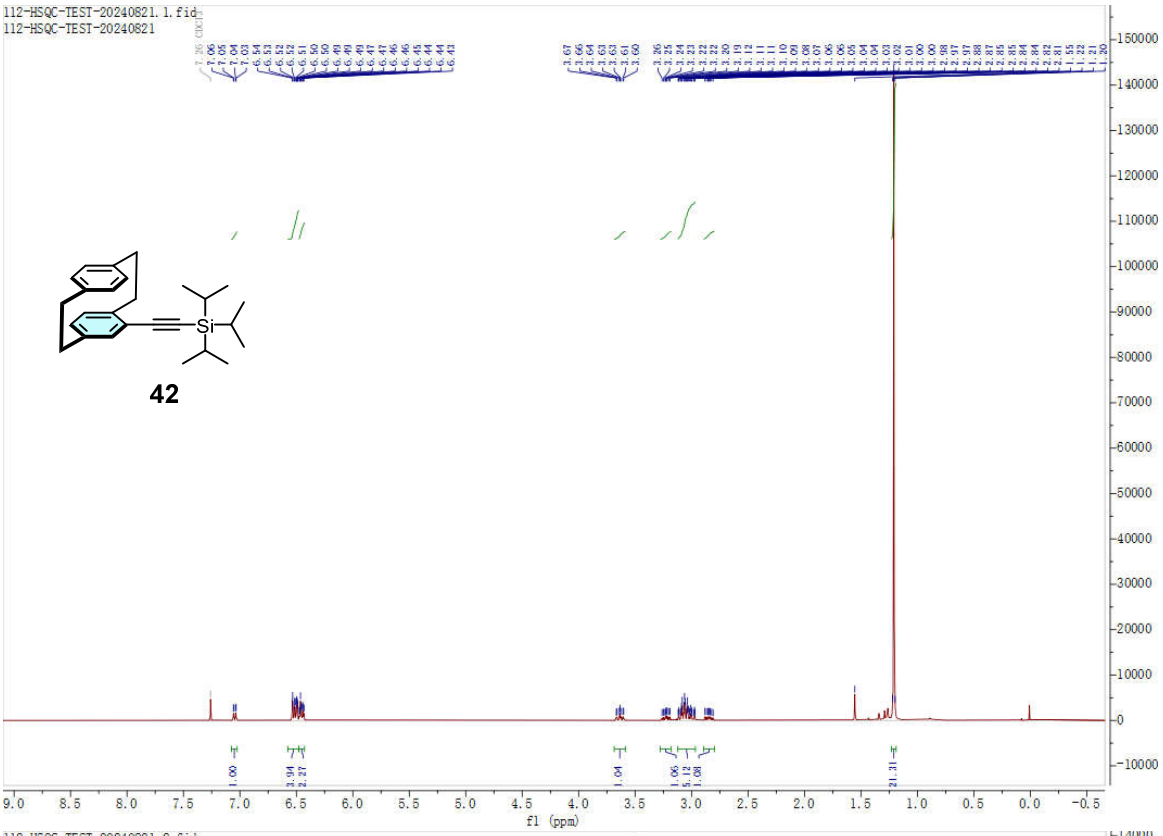
112-3-39-3-240403
f1 (ppm)


20240201 3-28-4
OMe
41
f1 (ppm)
20240201 3-28-4
f1 (ppm)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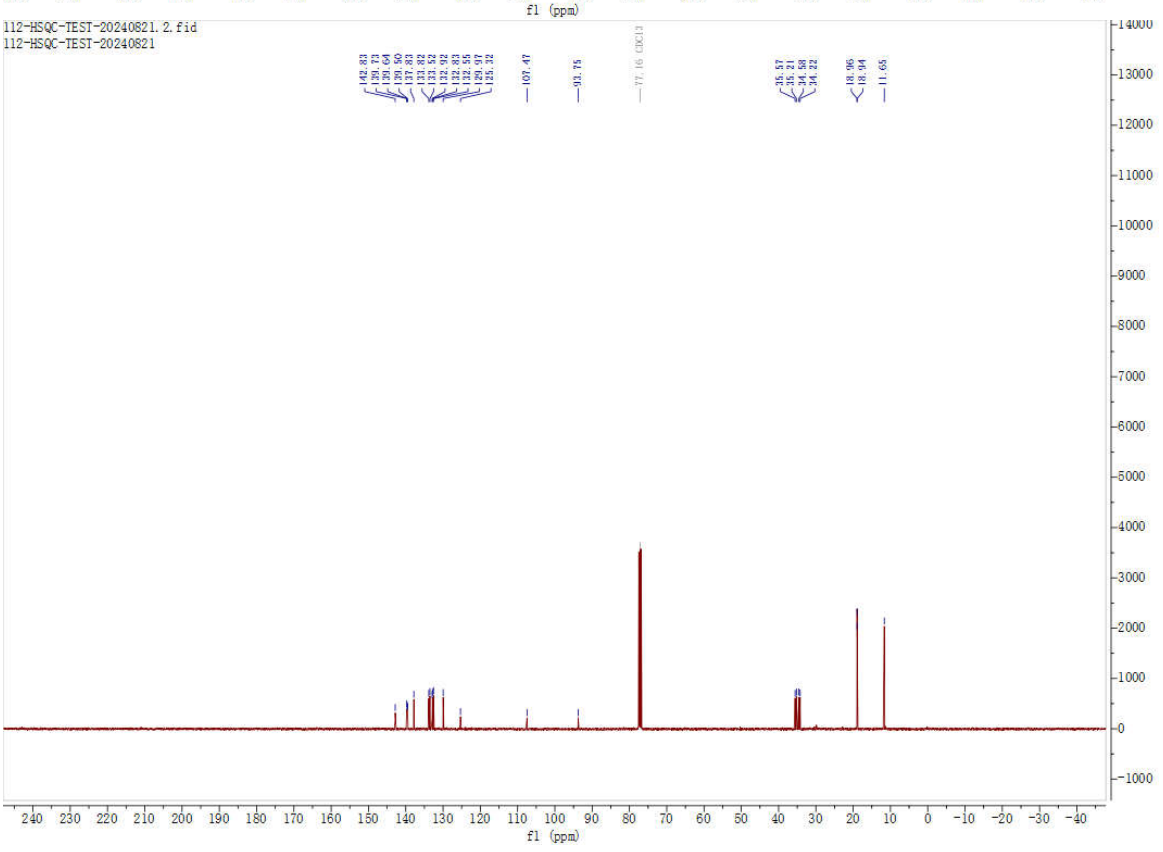
Si
f1 (ppm)

42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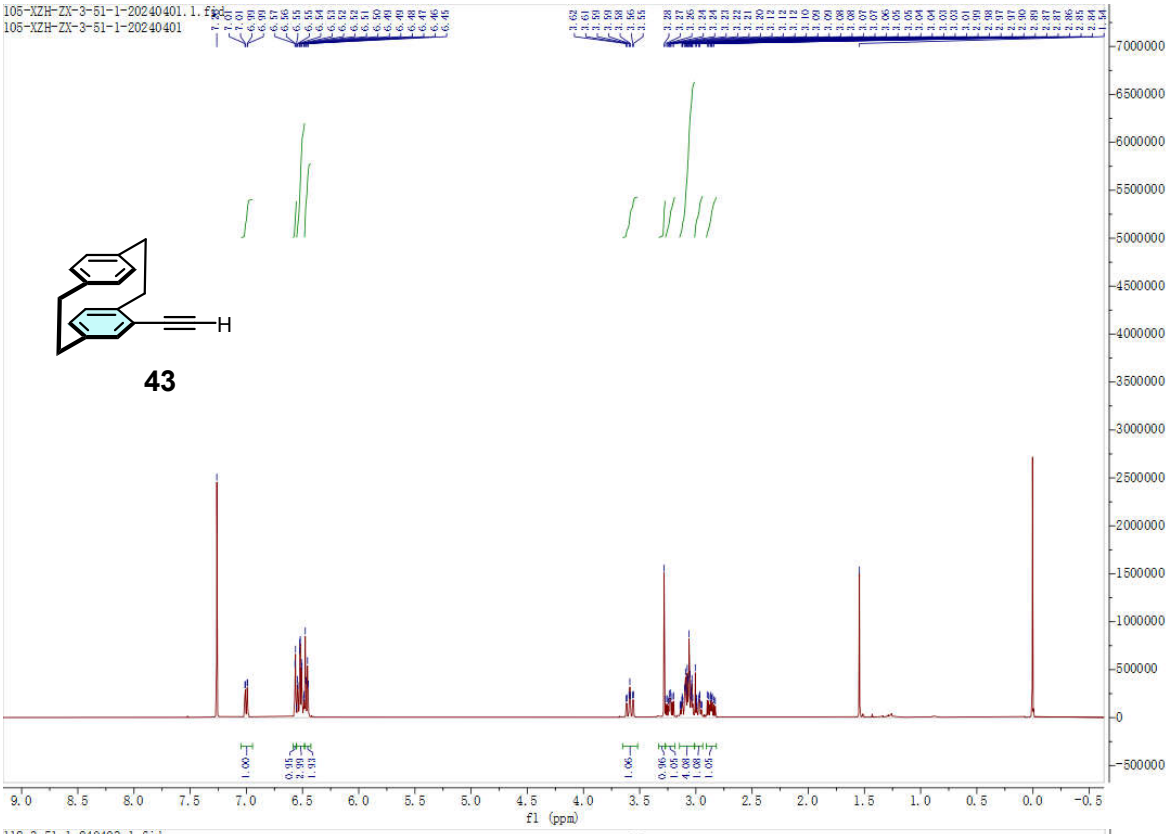
f1 (ppm)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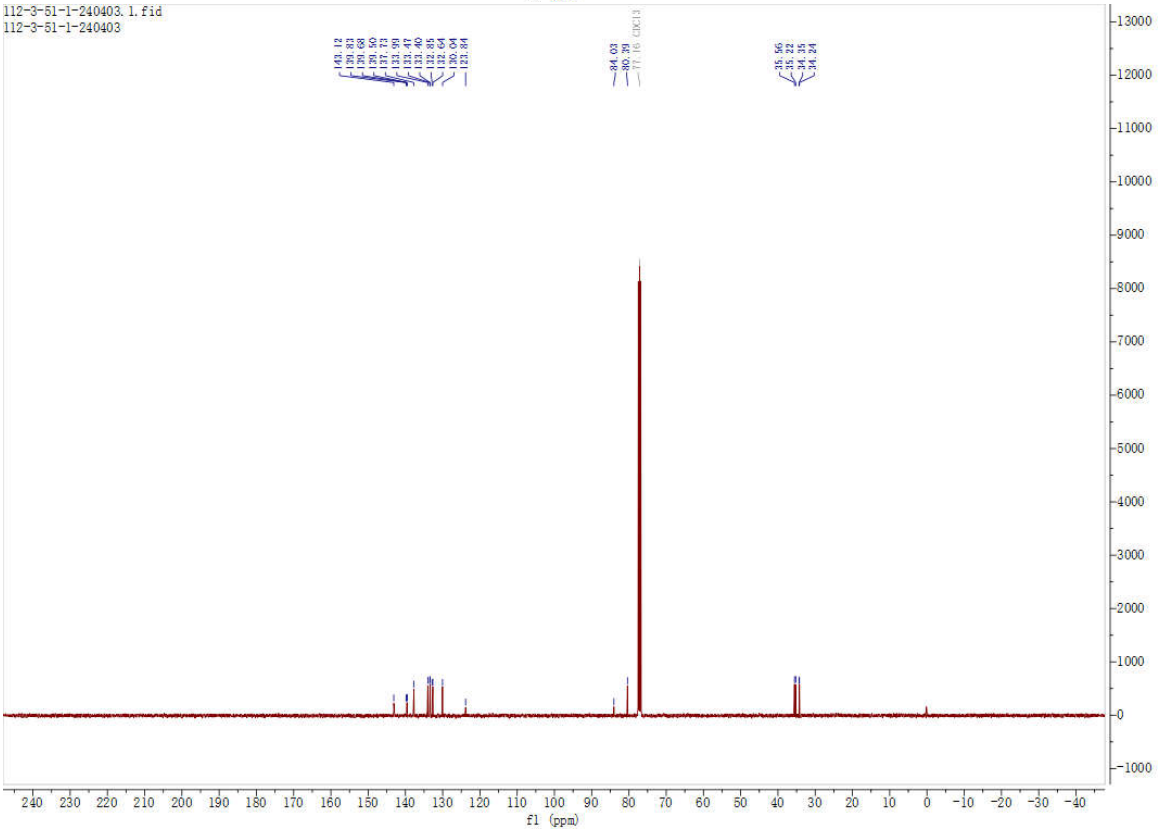
105-XZH-ZX-3-51-1-20240401
H
43
f1 (ppm)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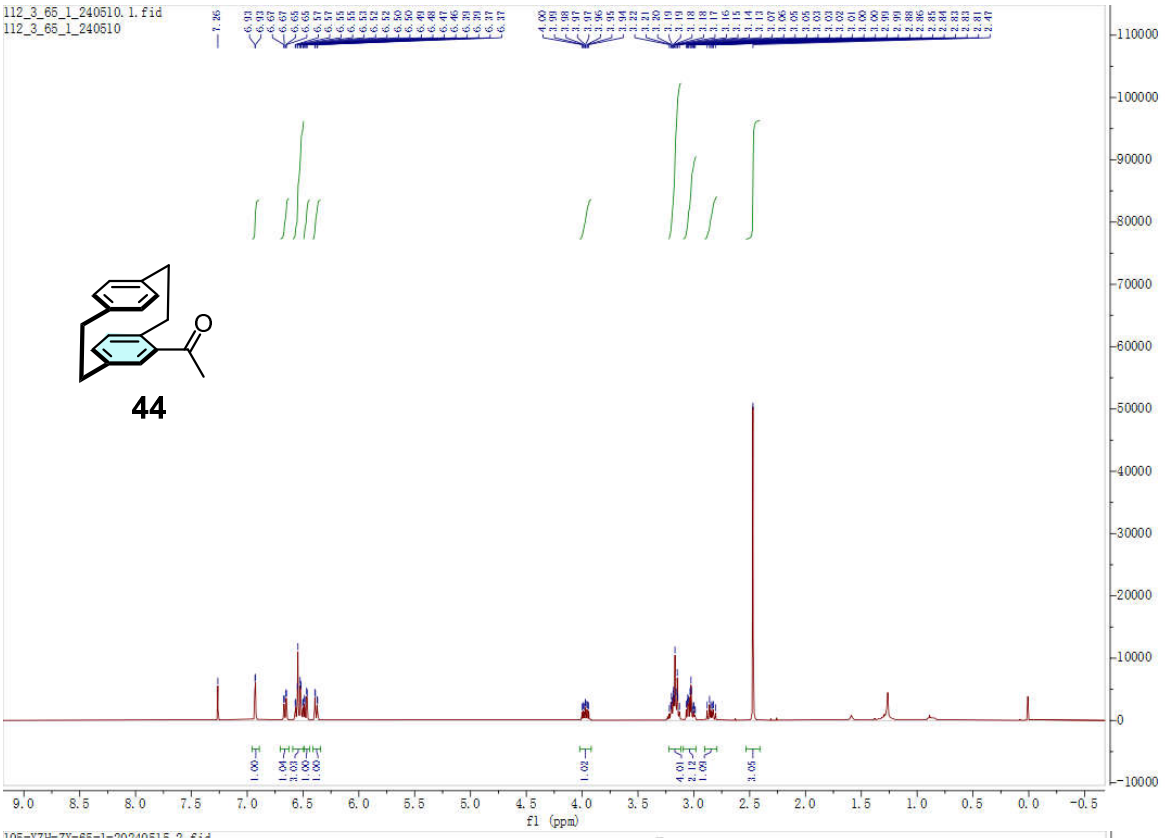
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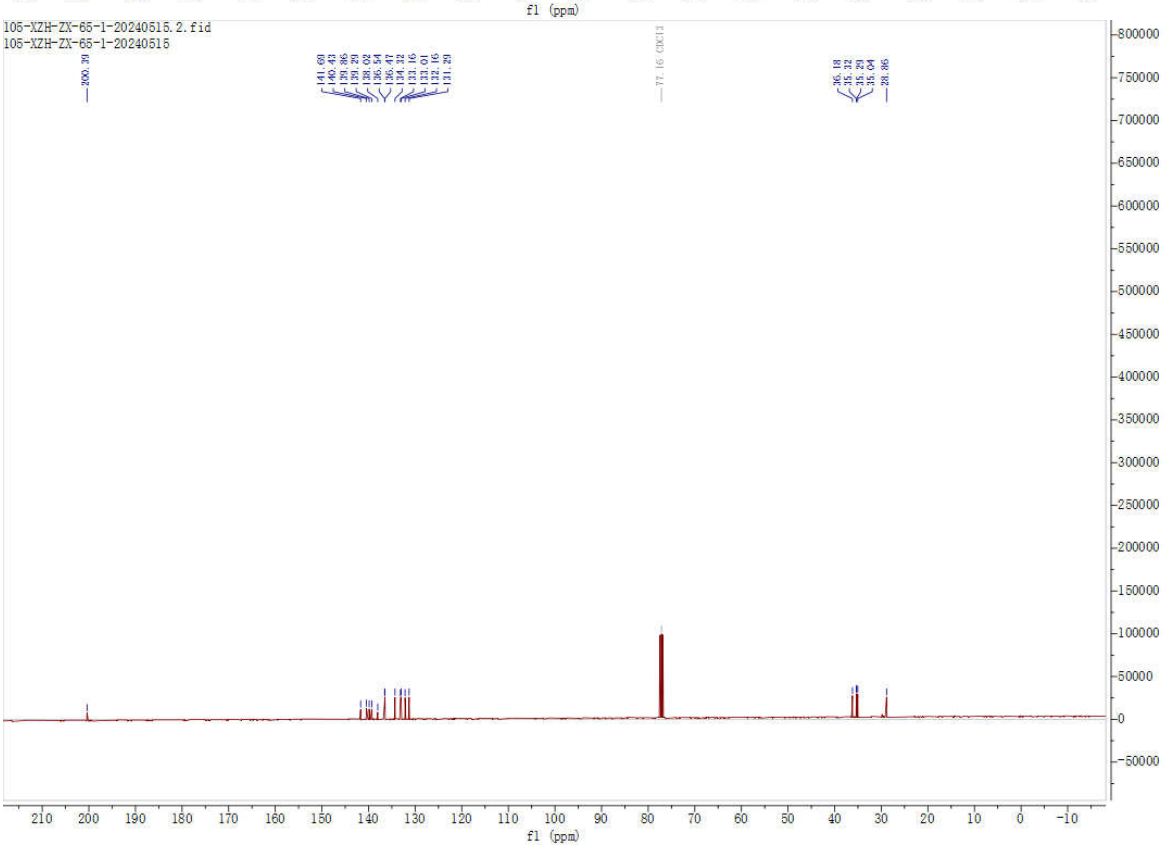
f1 (ppm)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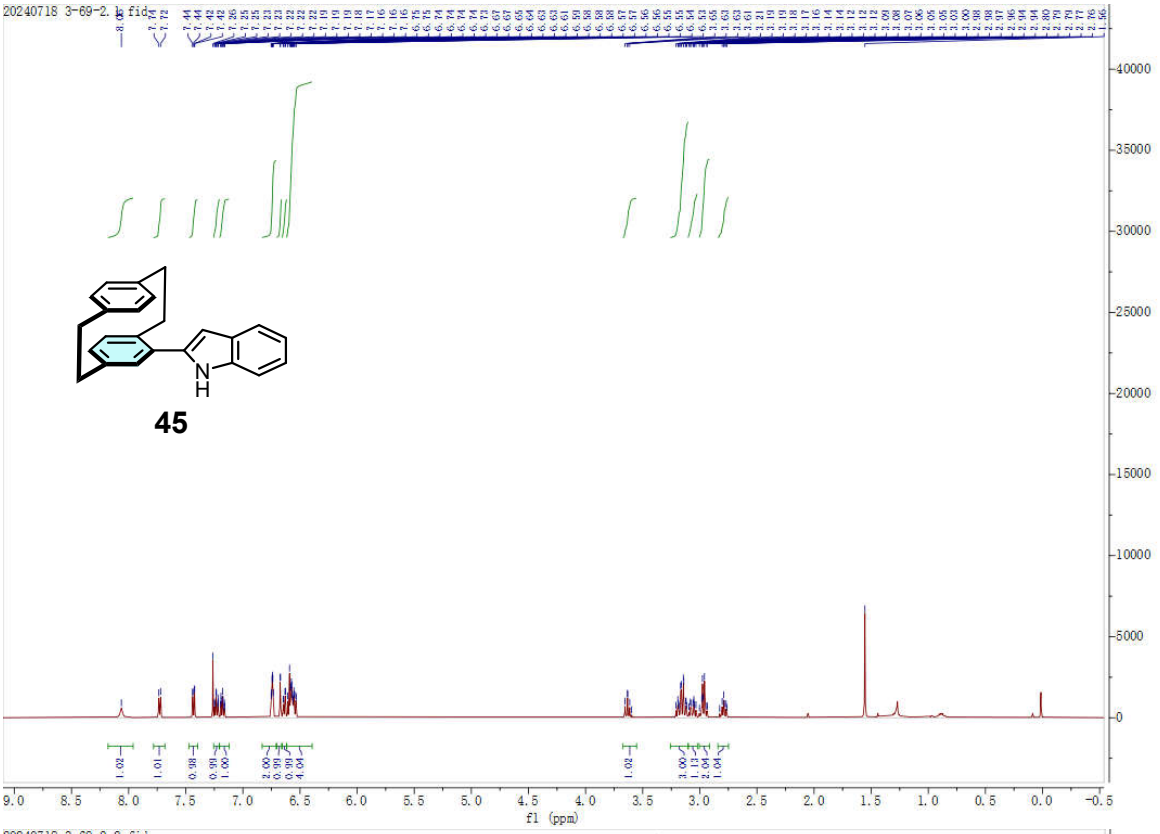

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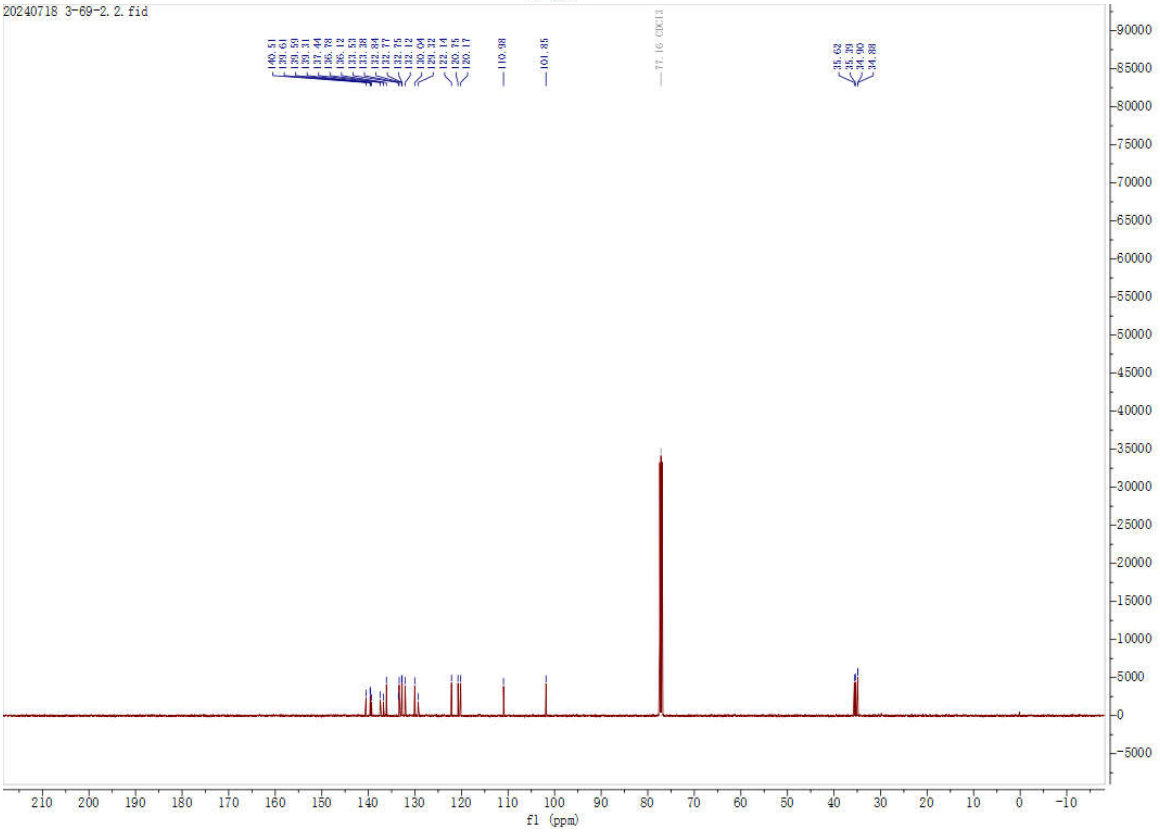

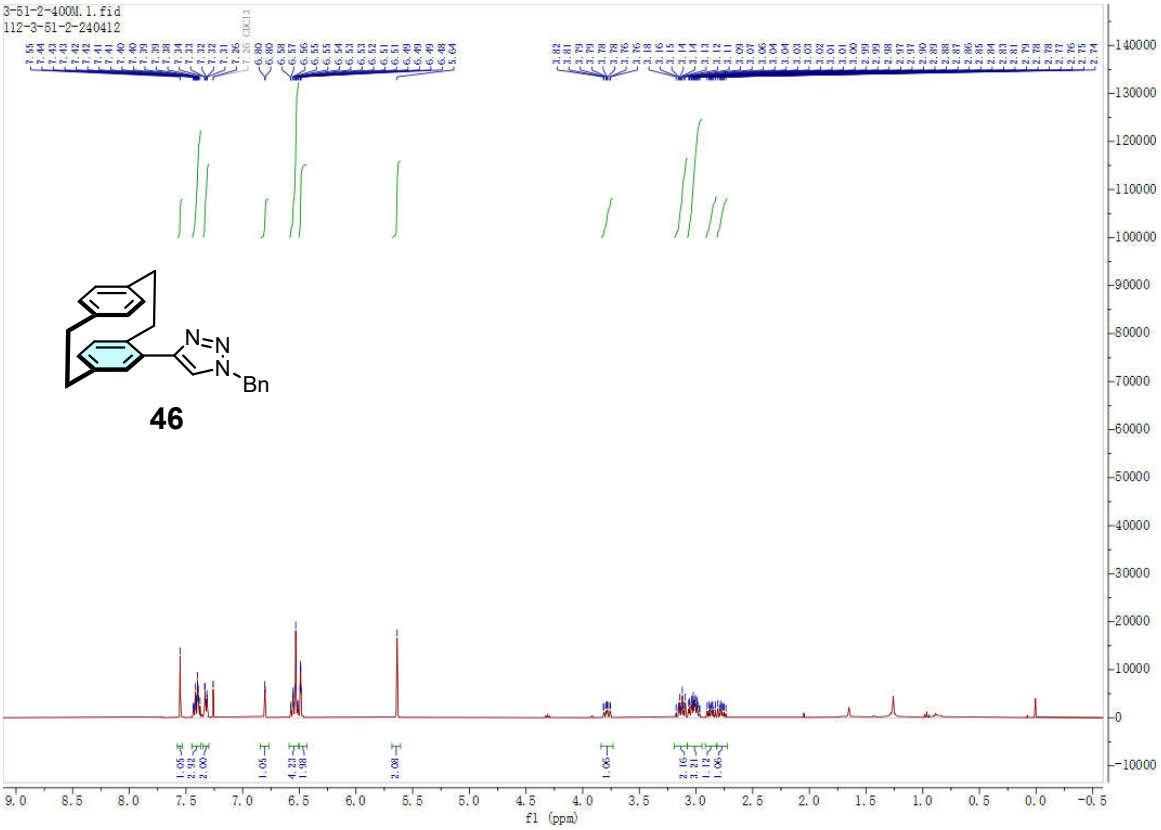
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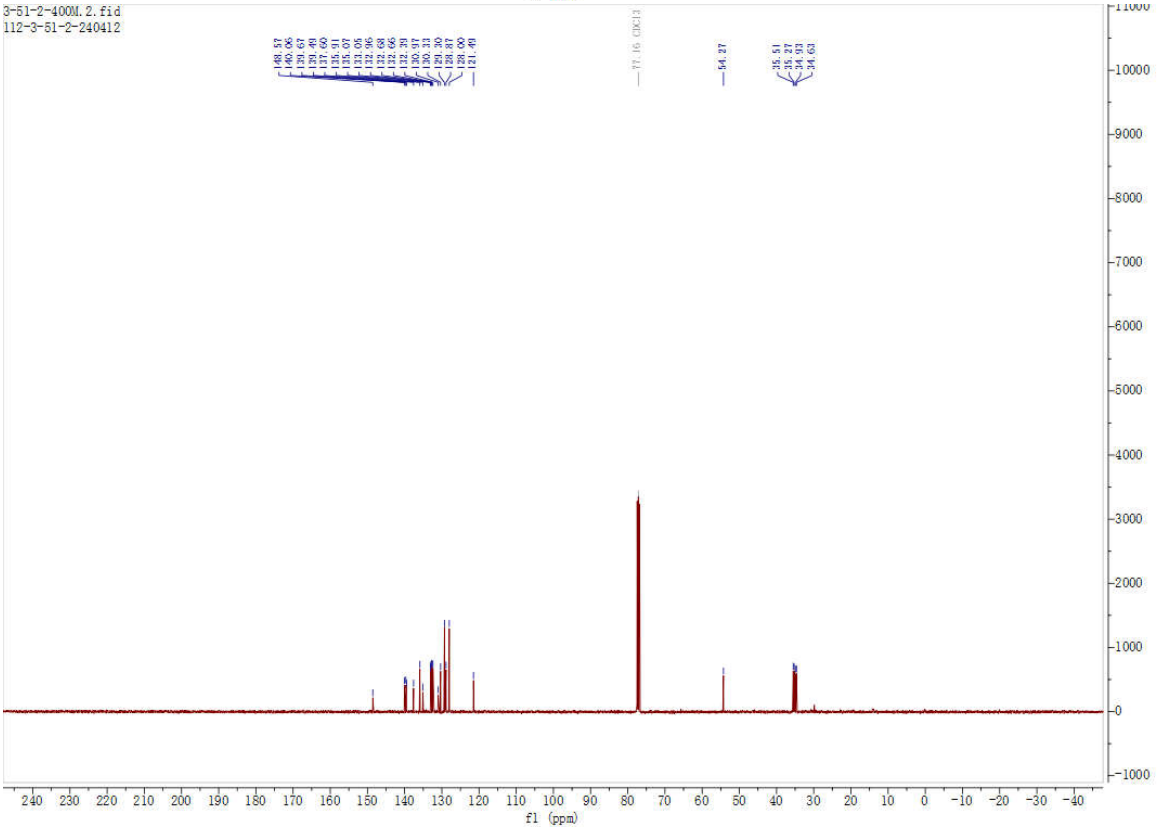
N
N
Bn

46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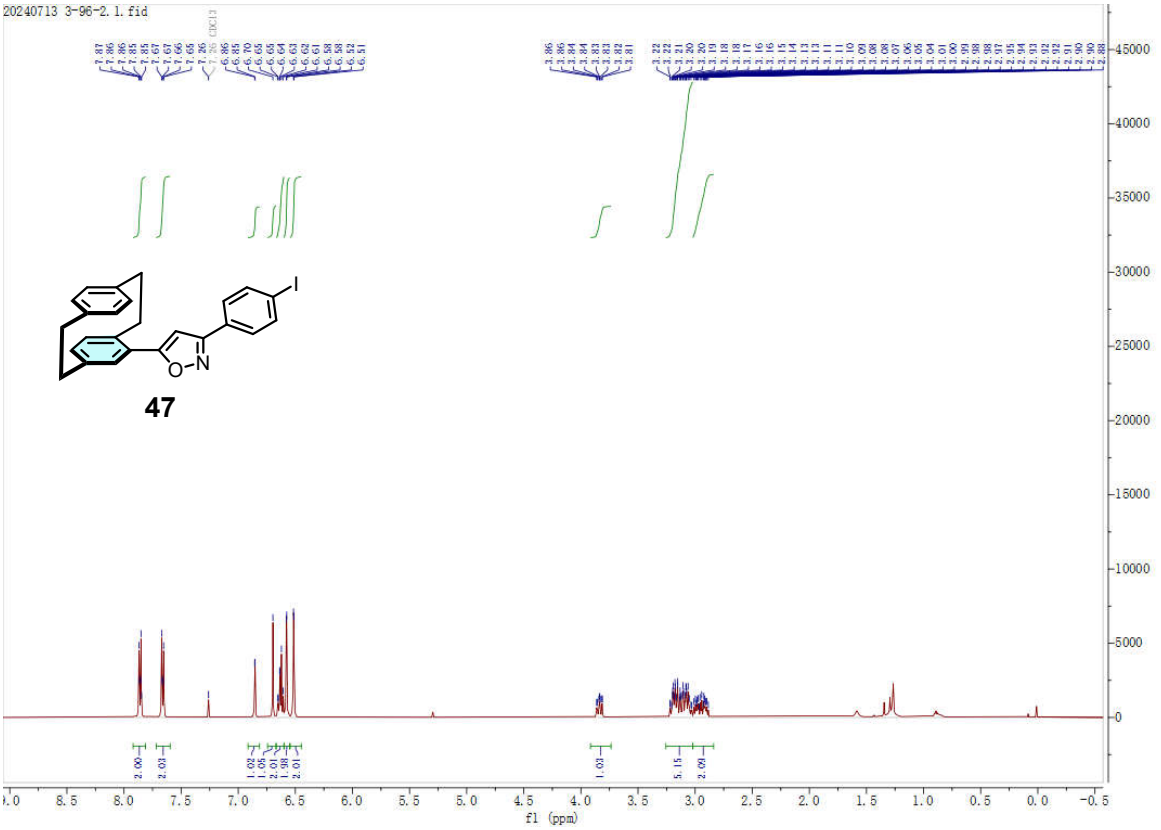
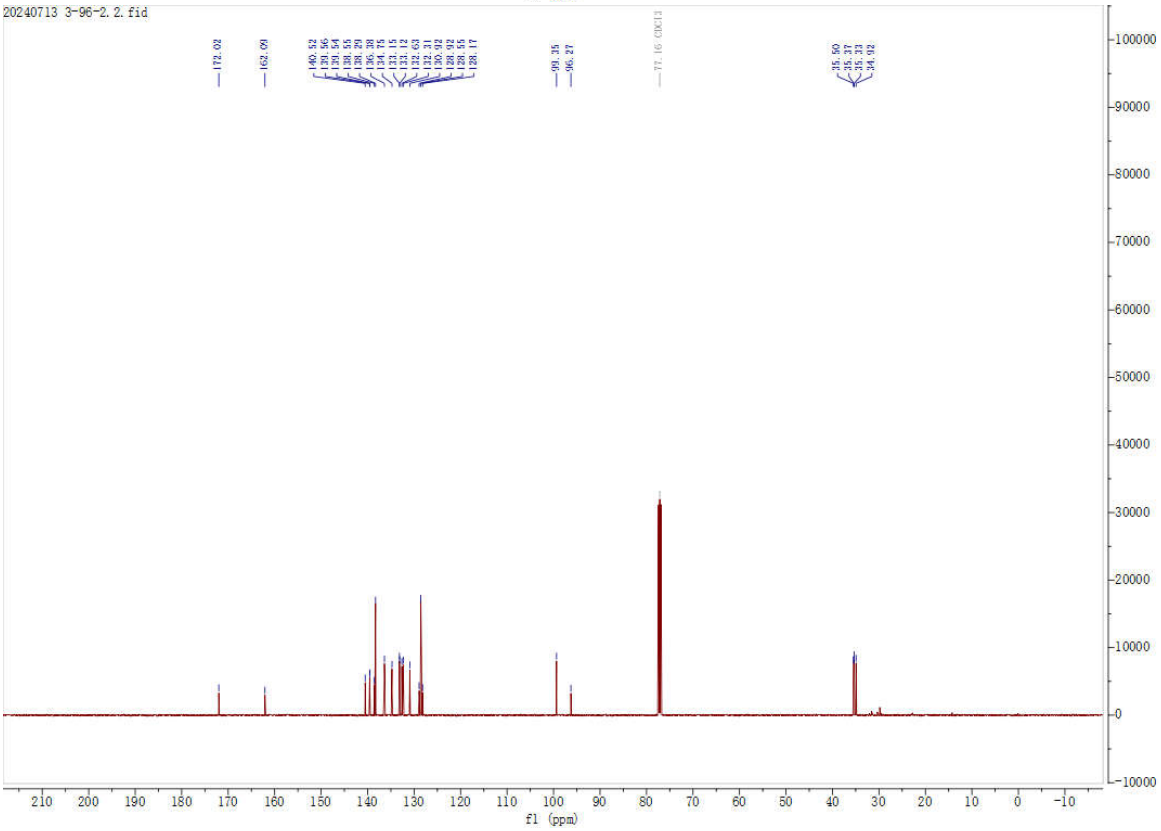
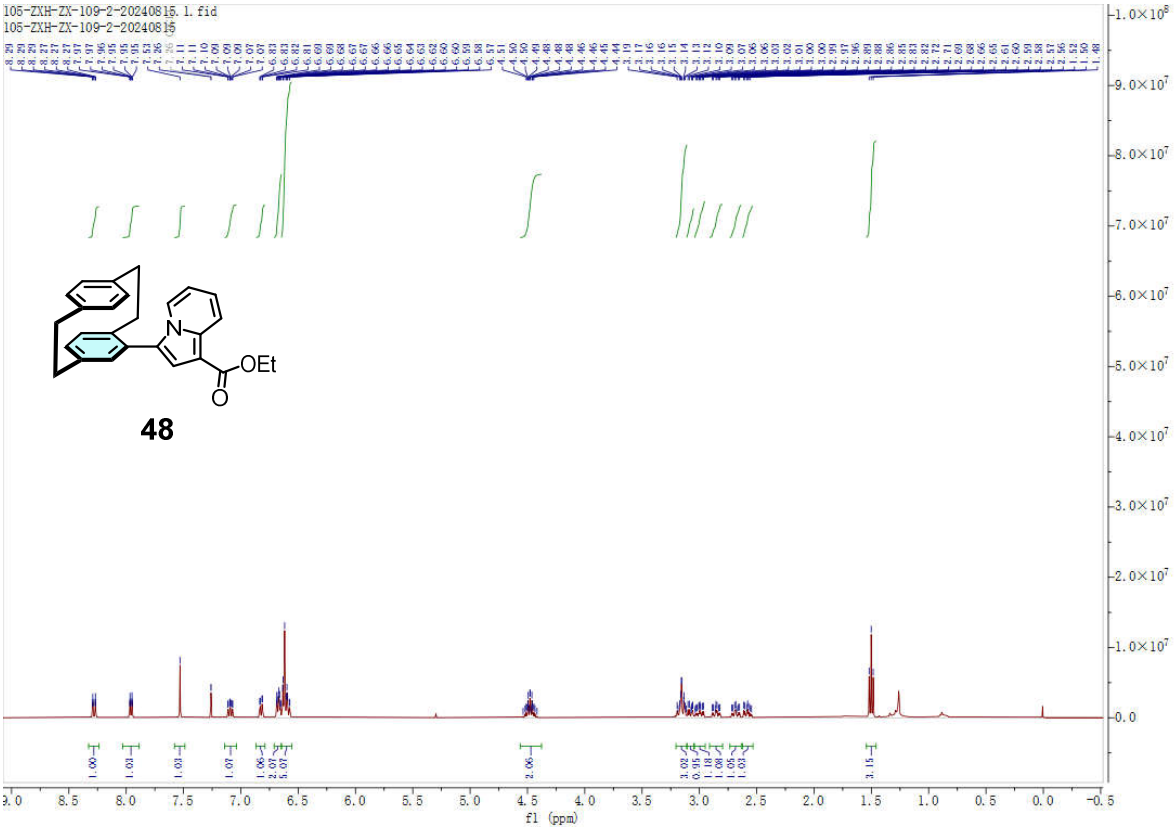
f1 (ppm)



47

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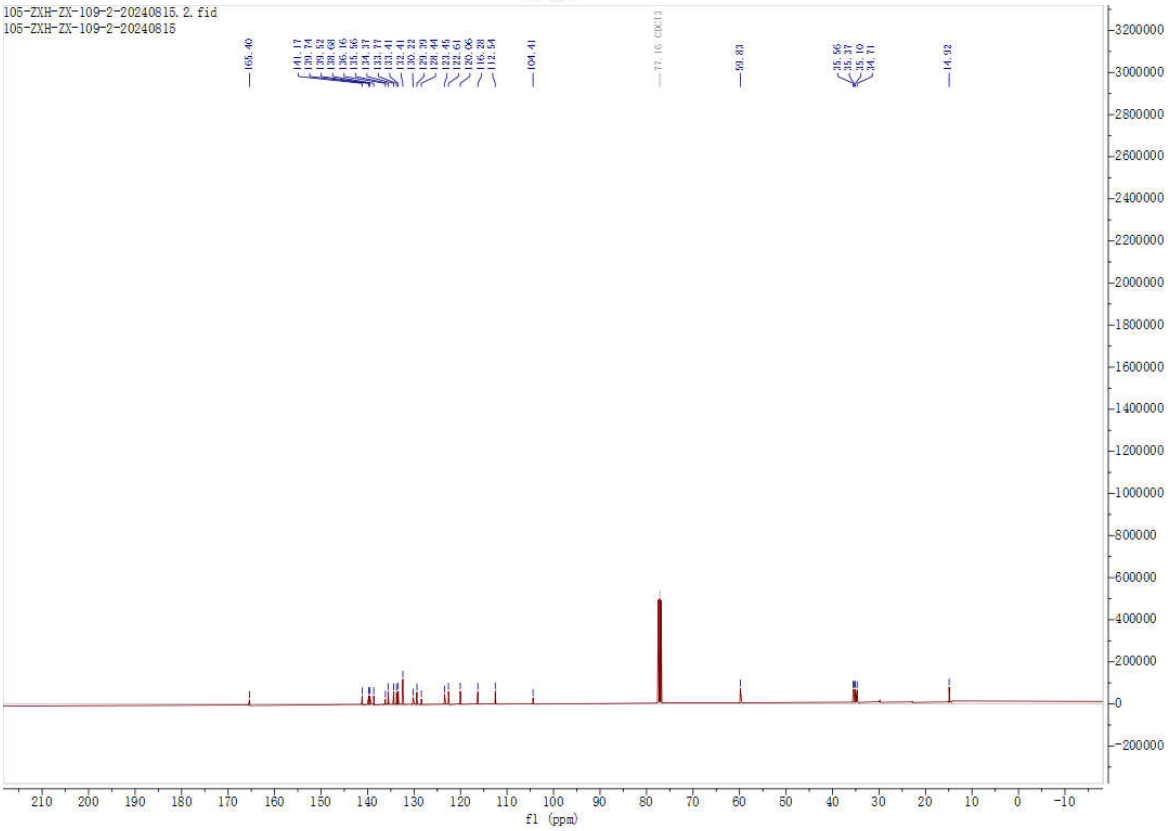
OEt
O
f1 (ppm)

48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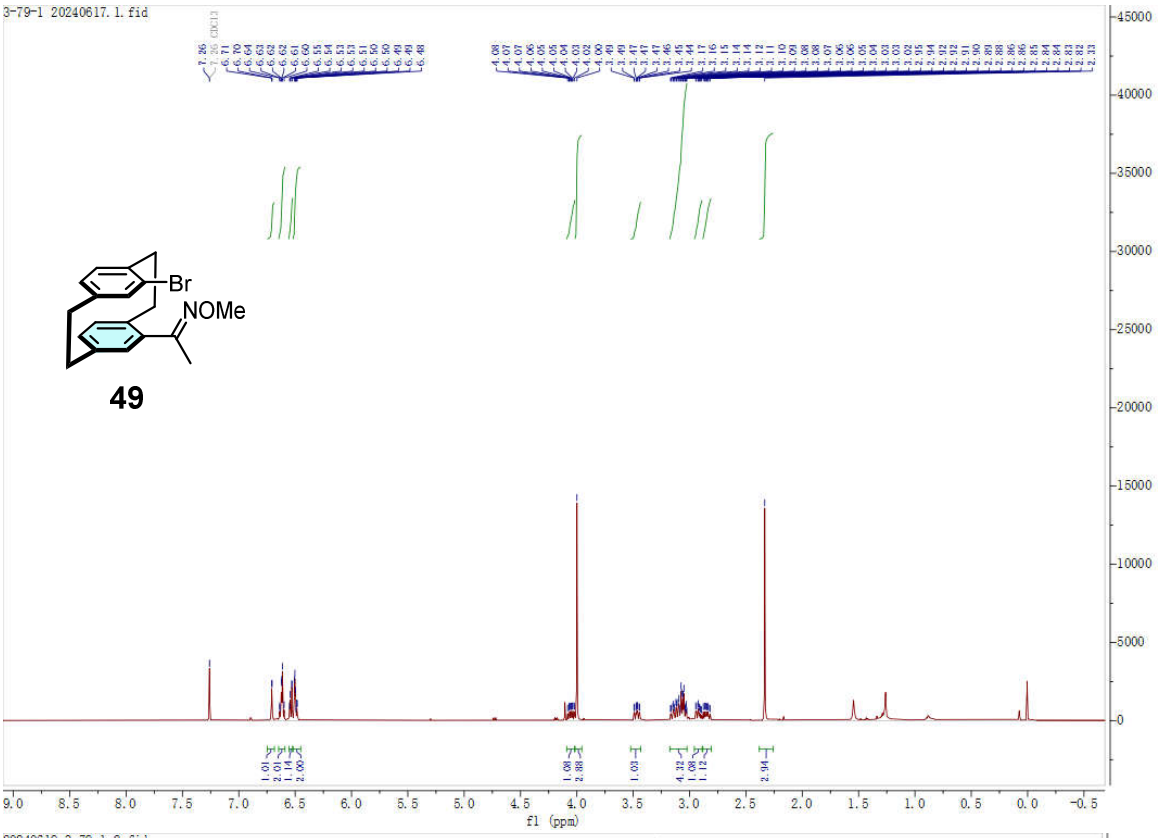
f1 (ppm)



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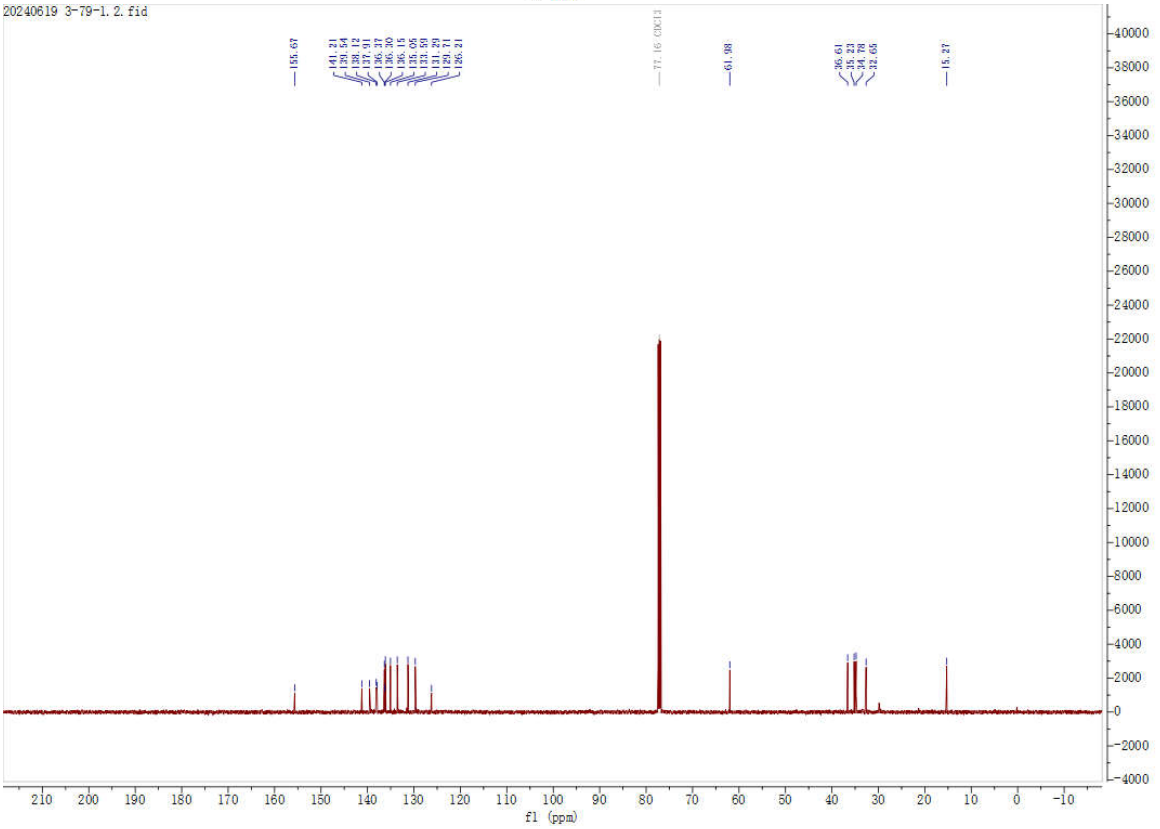

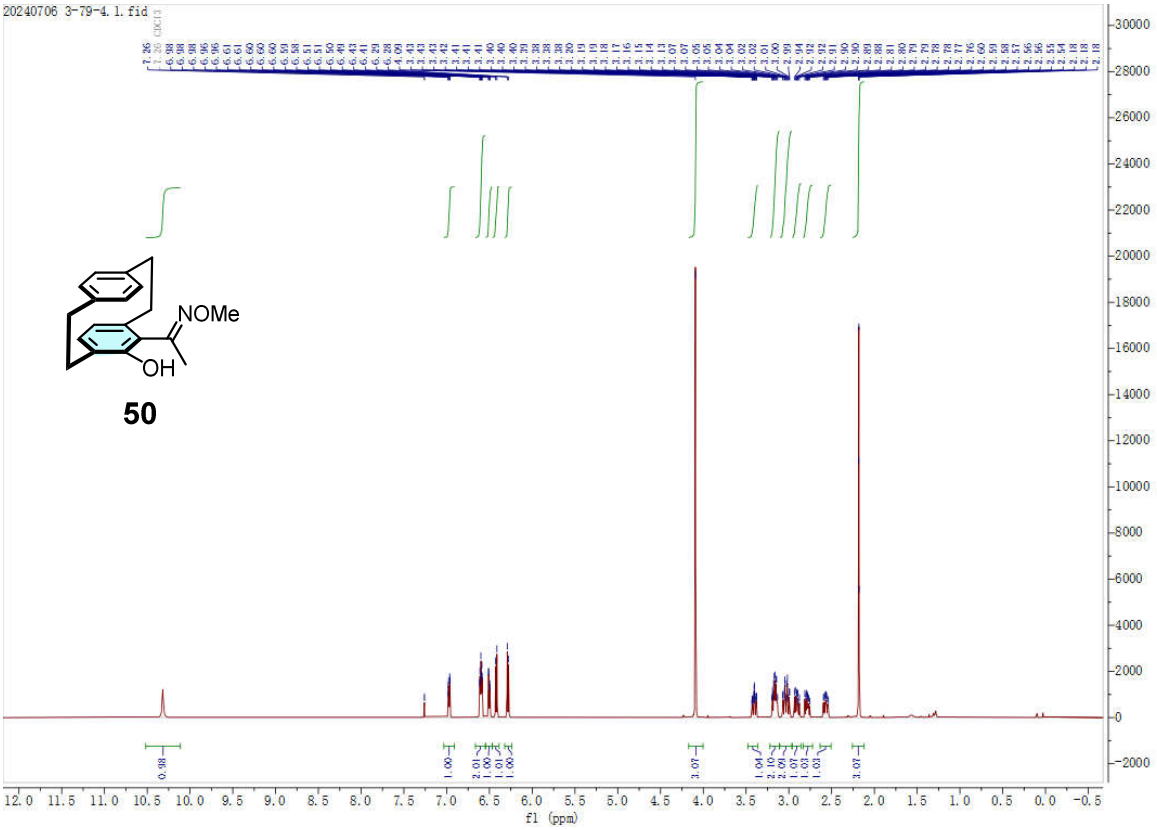

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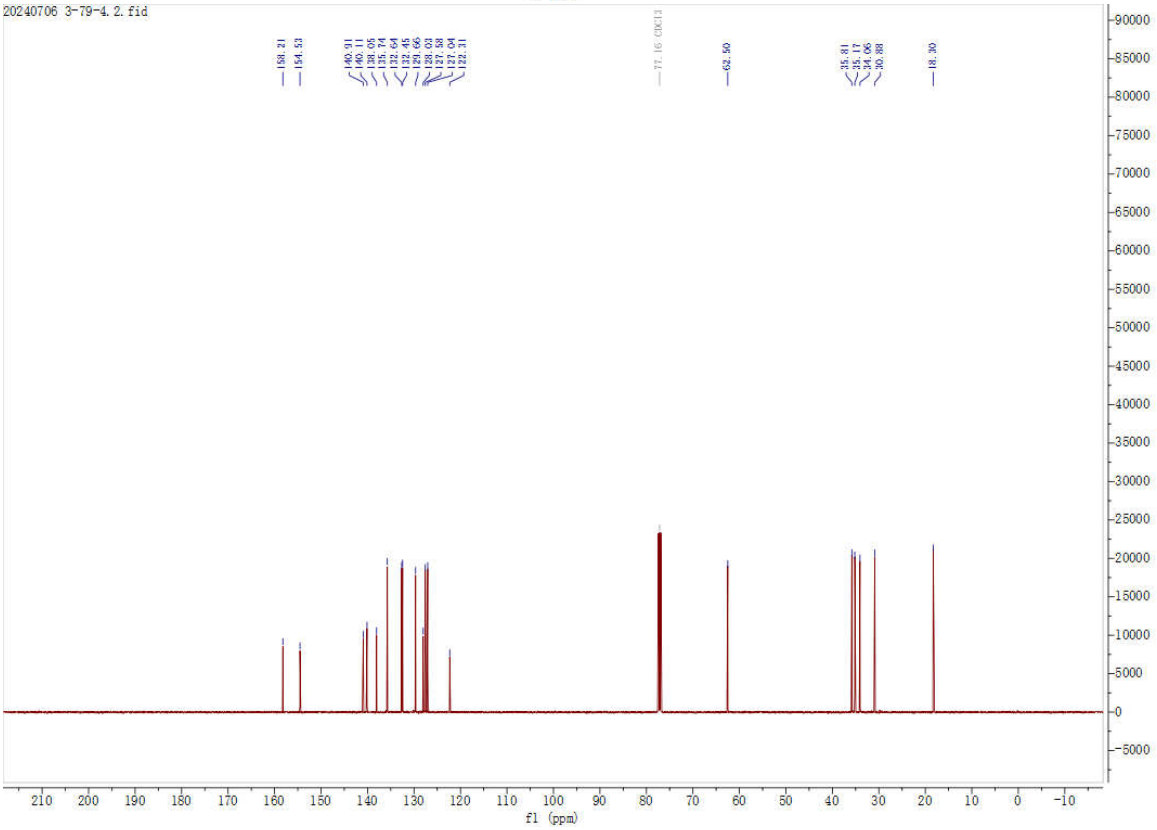

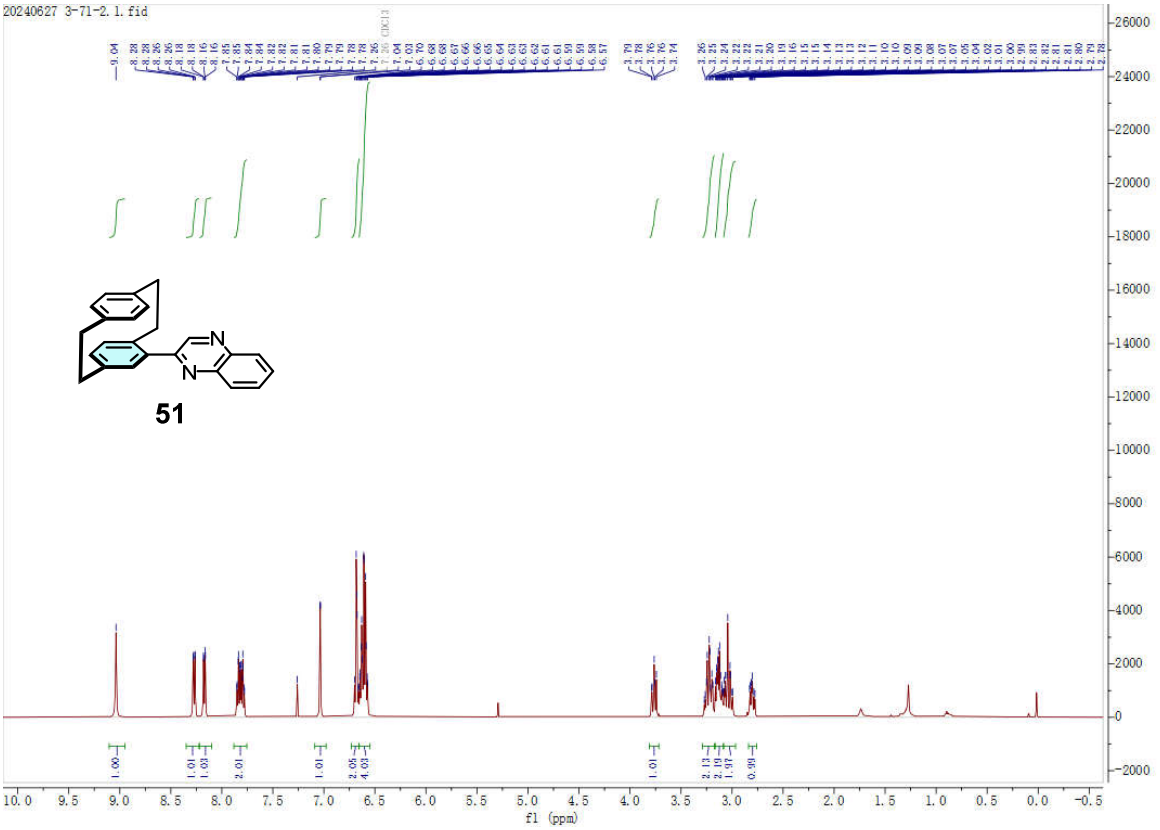
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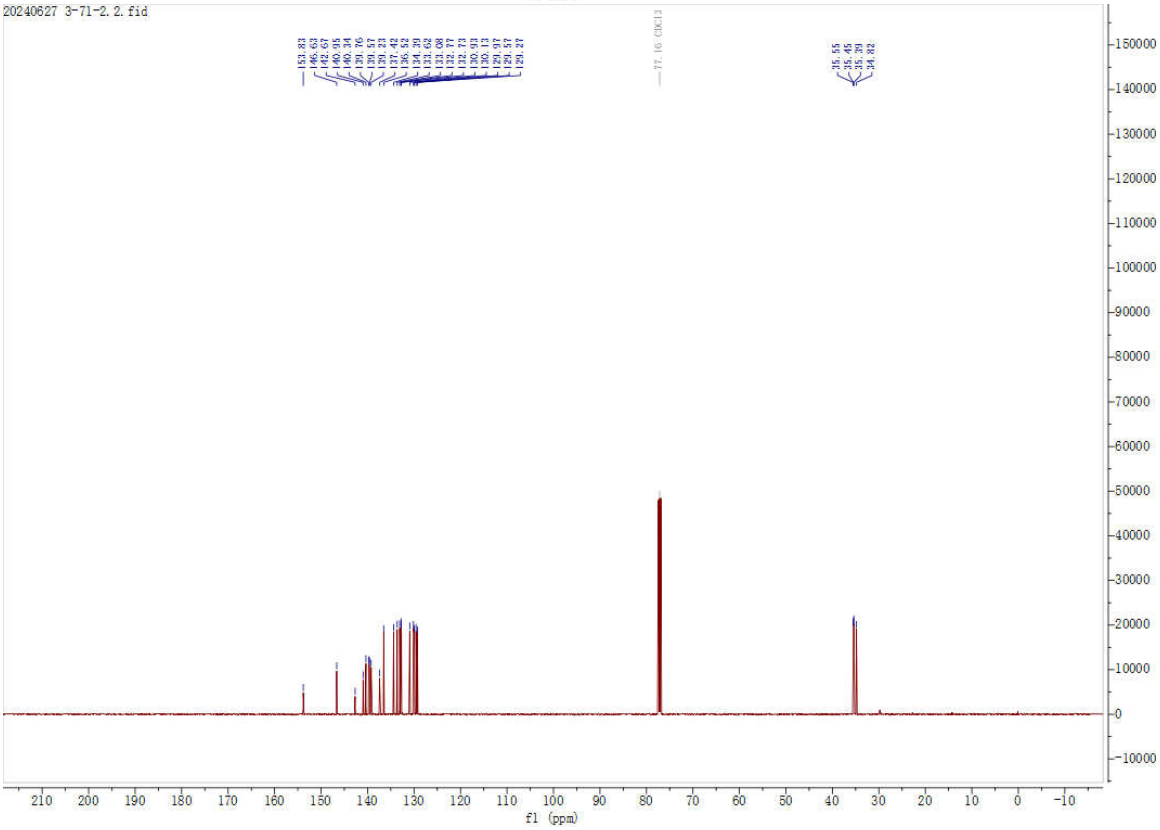
51
f1 (ppm)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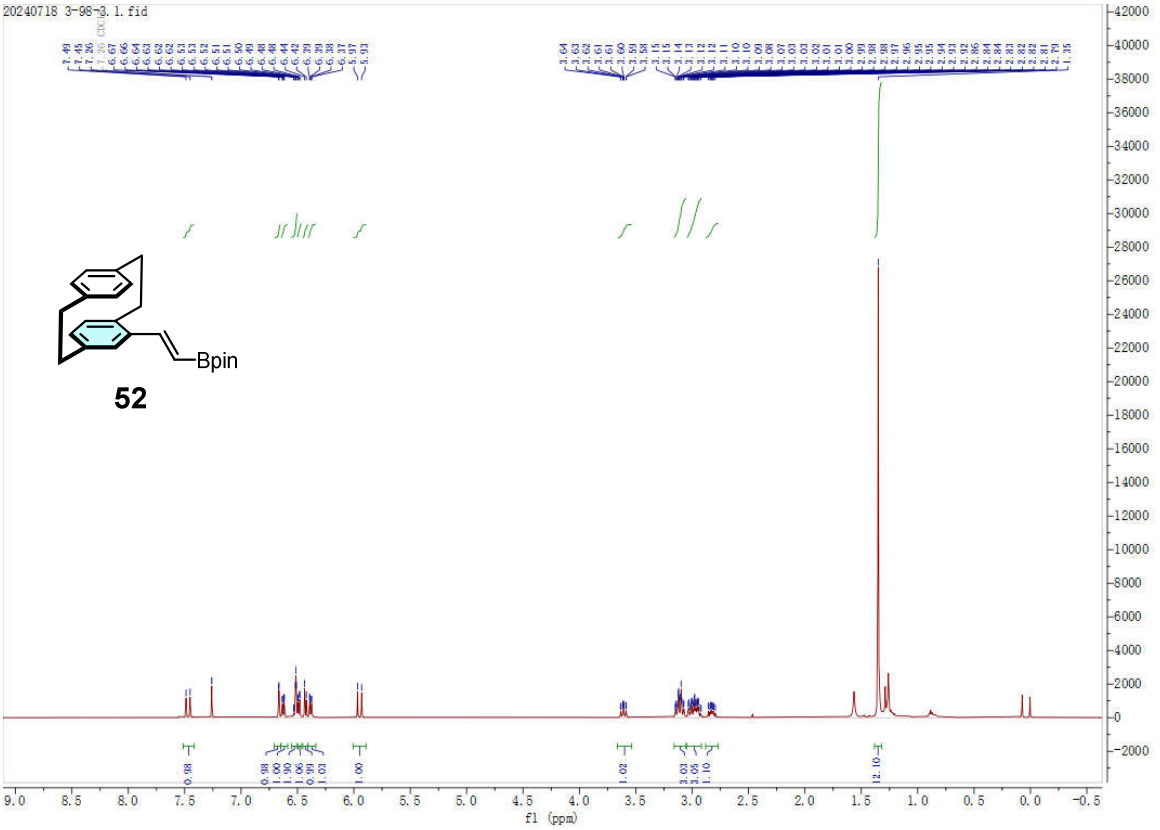
f1 (ppm)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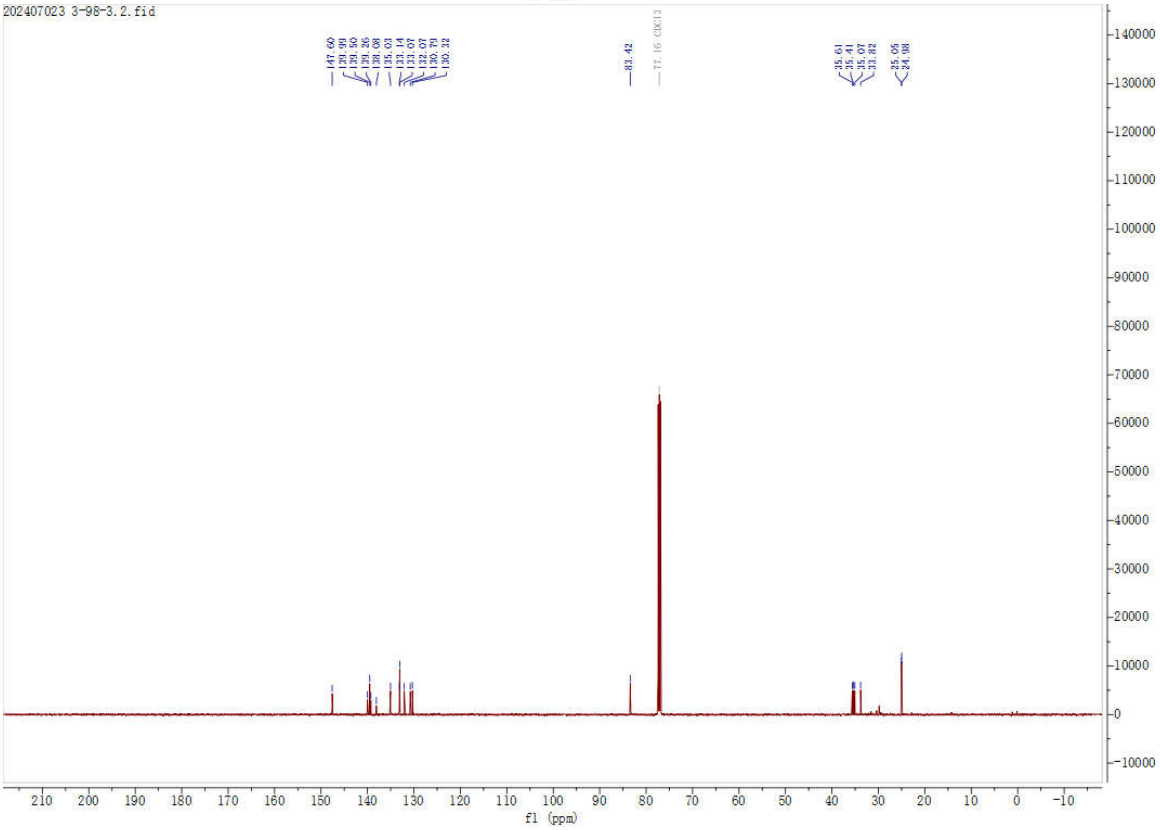
Bpin
52
f1 (ppm)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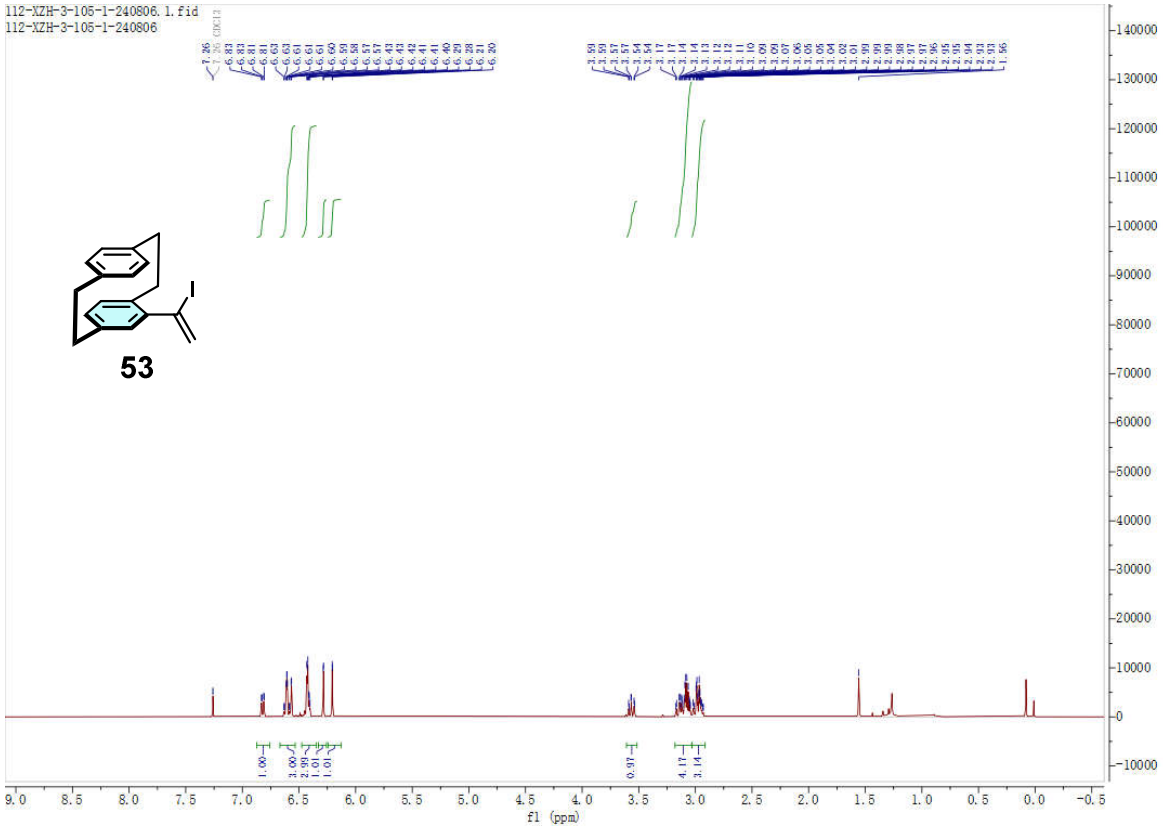
f1 (ppm)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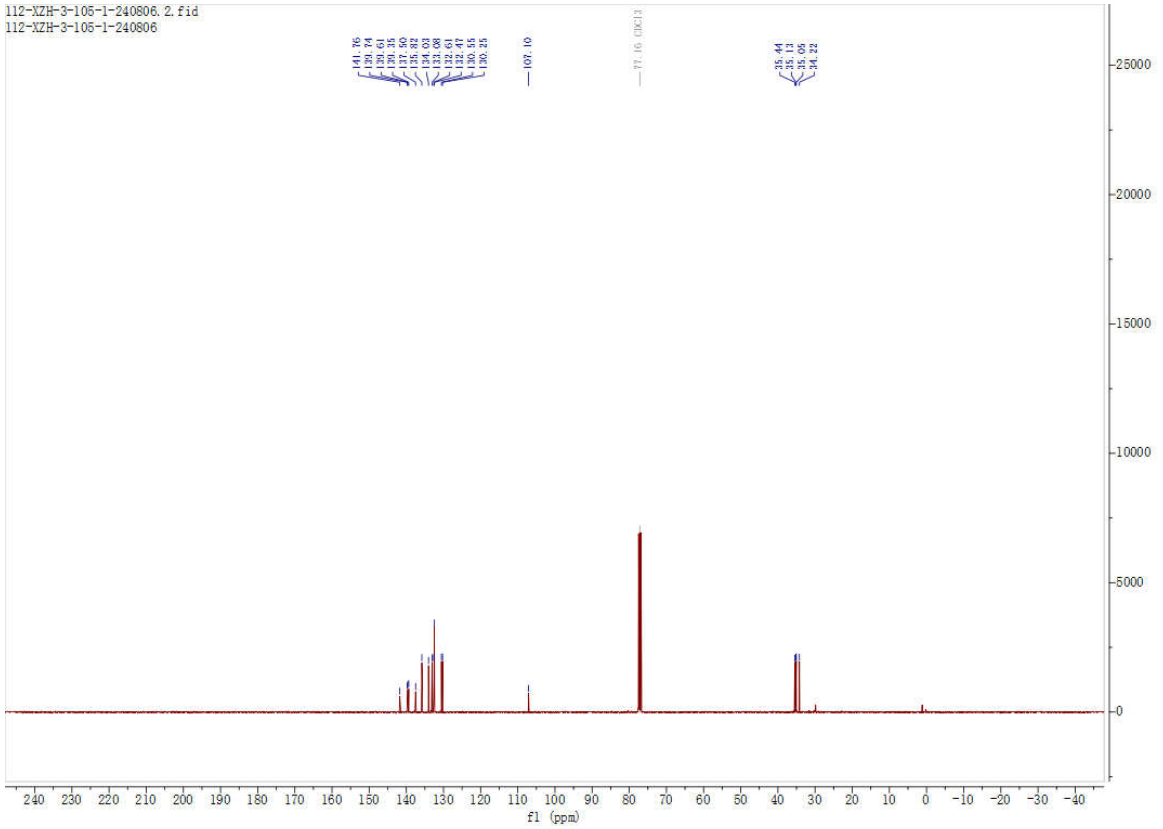
112-XZH-3-105-1-240806
I
53
f1 (ppm)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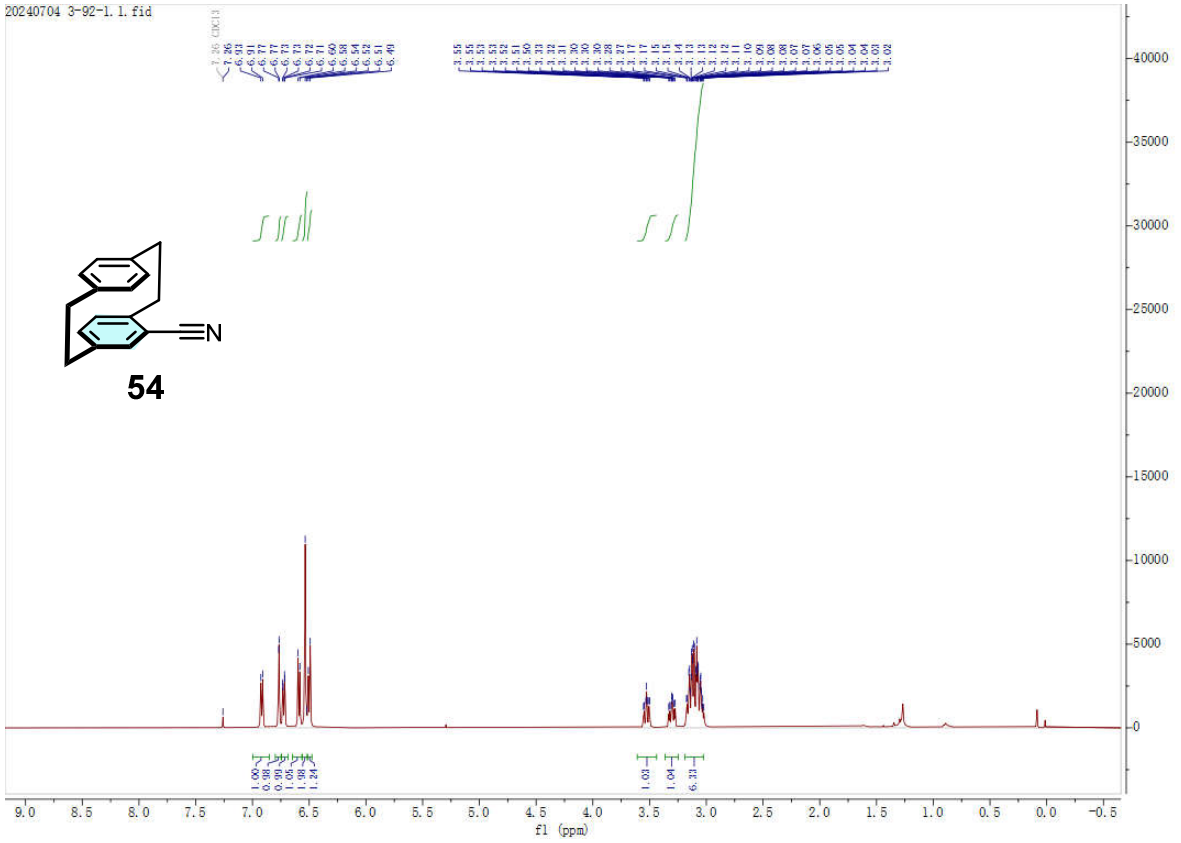
f1 (ppm)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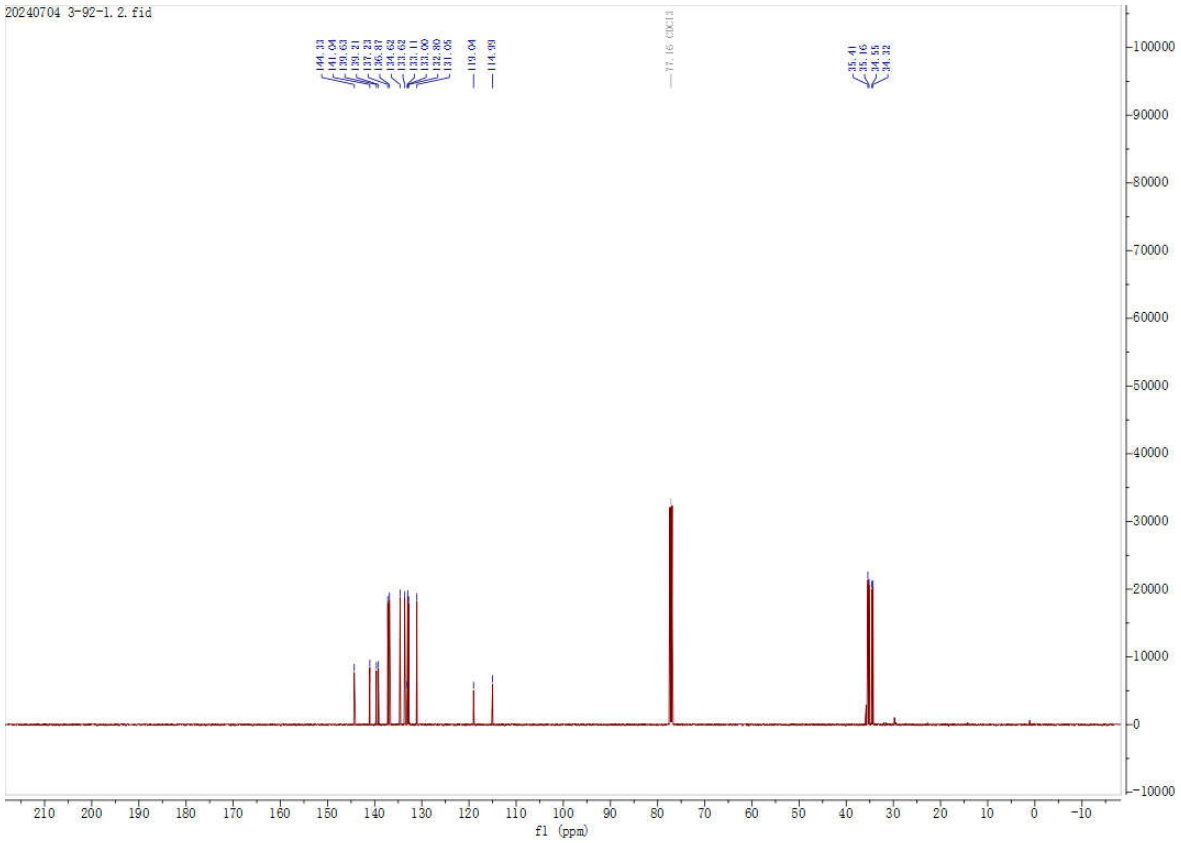
N
54
f1 (ppm)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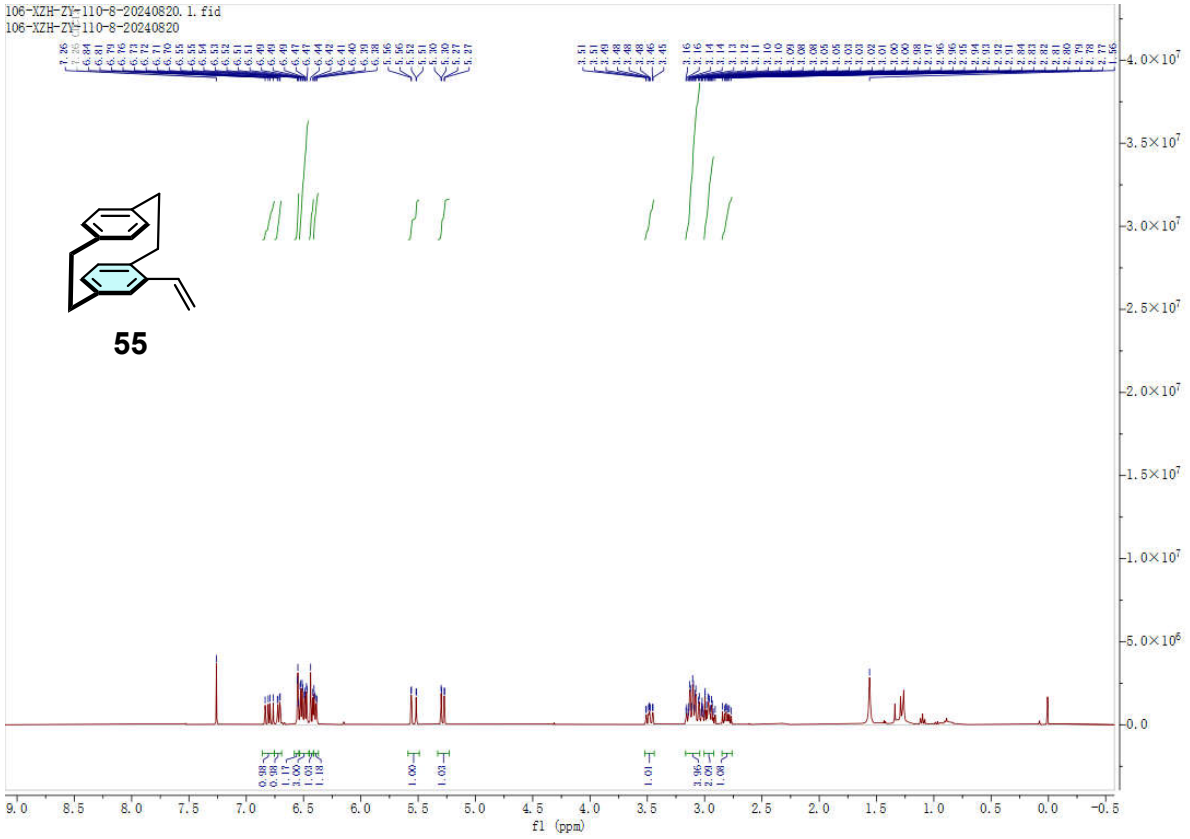
f1 (ppm)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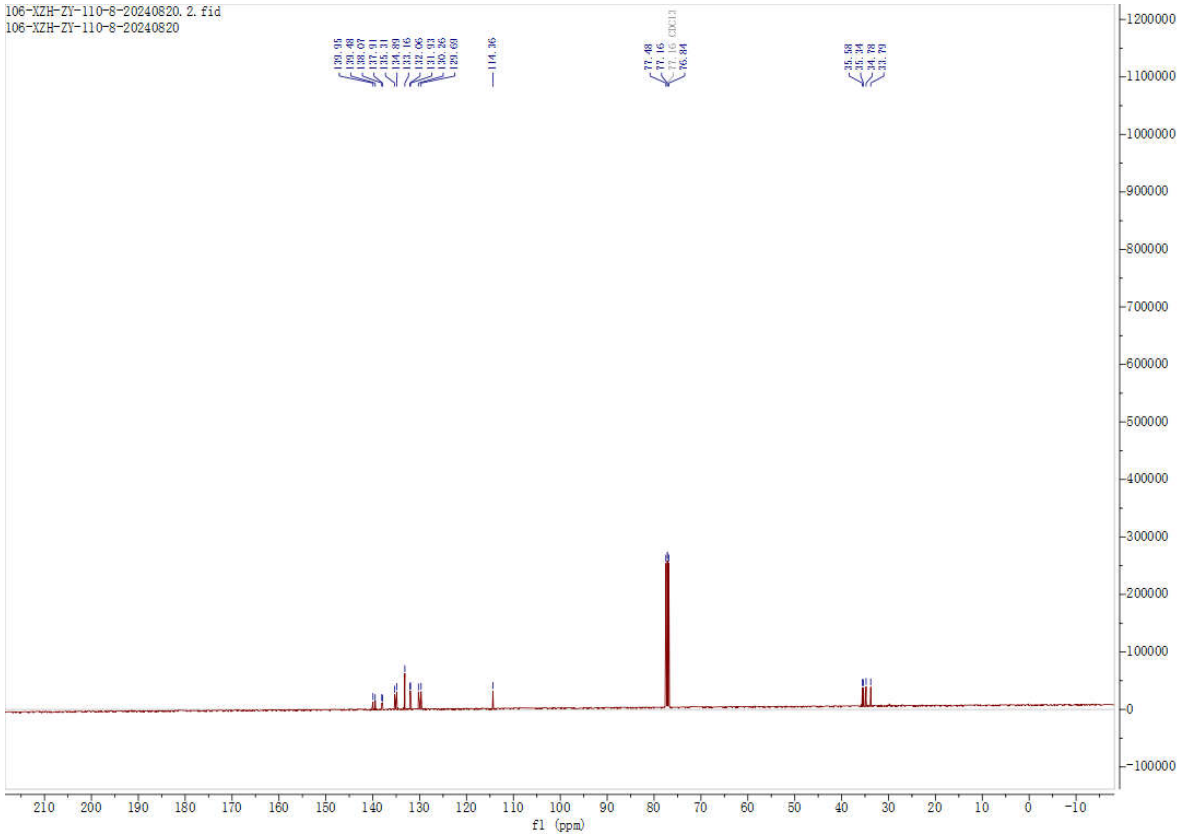
55
f1 (ppm)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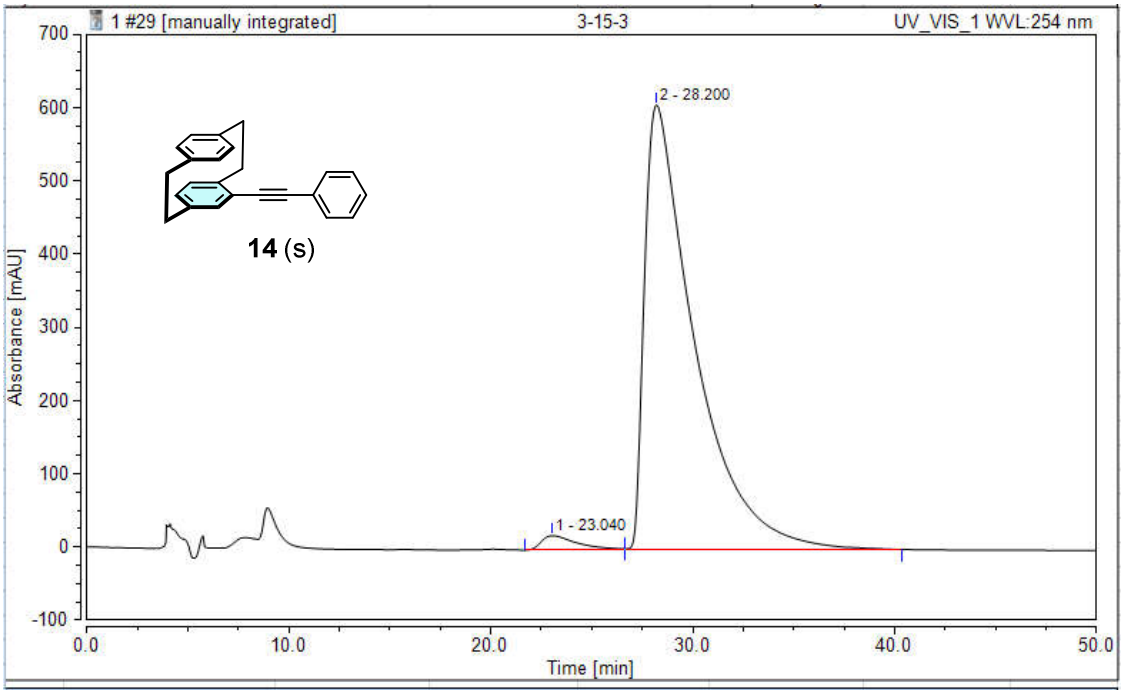
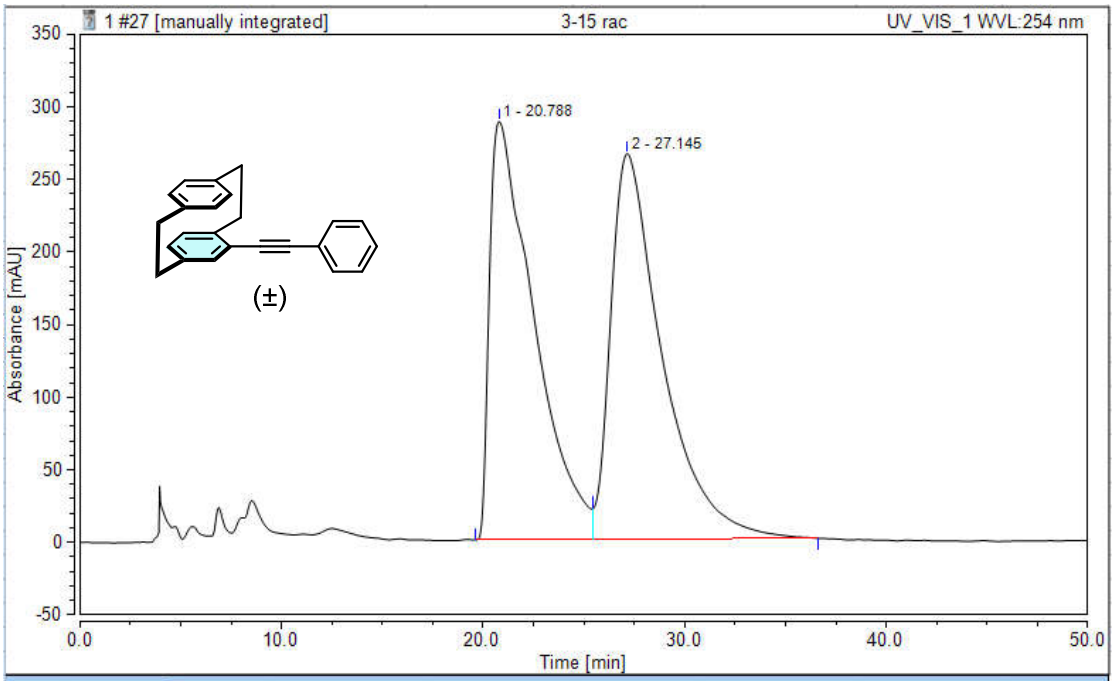
11. HPLC spectra



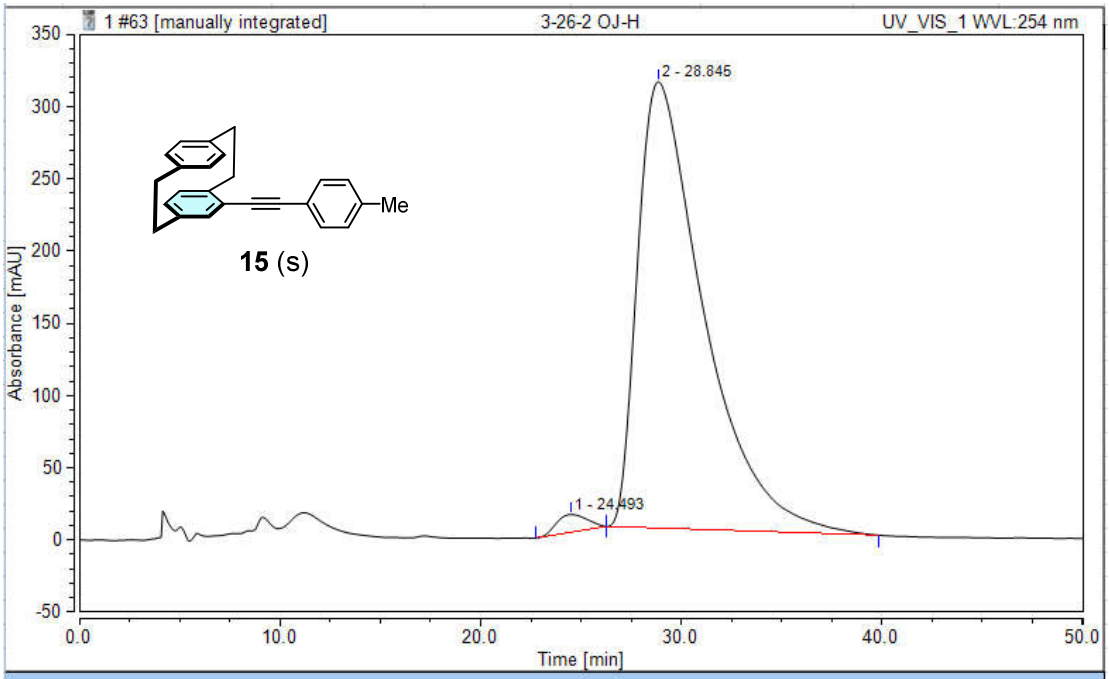
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		23.040	40.918	19.609	2.29	3.12	n.a.
2		28.200	1743.784	607.905	97.71	96.88	n.a.
Total:			**1784.702**	**627.514**	**100.00**	**100.00**	



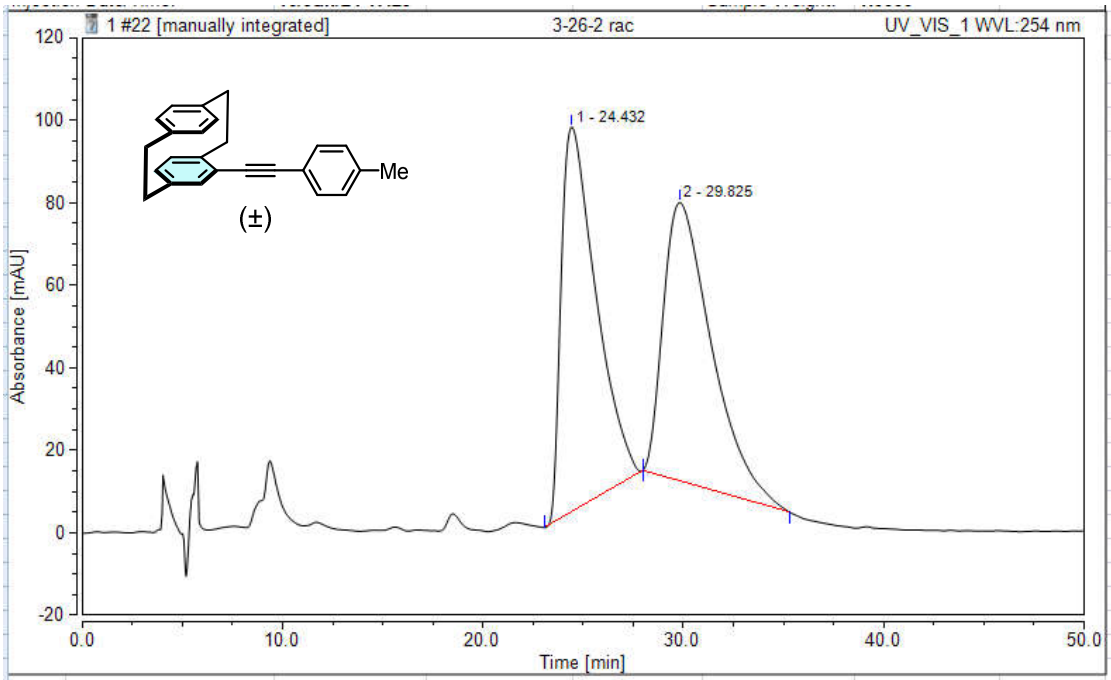
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		20.788	736.969	288.111	48.46	52.03	n.a.
2		27.145	783.840	265.583	51.54	47.97	n.a.



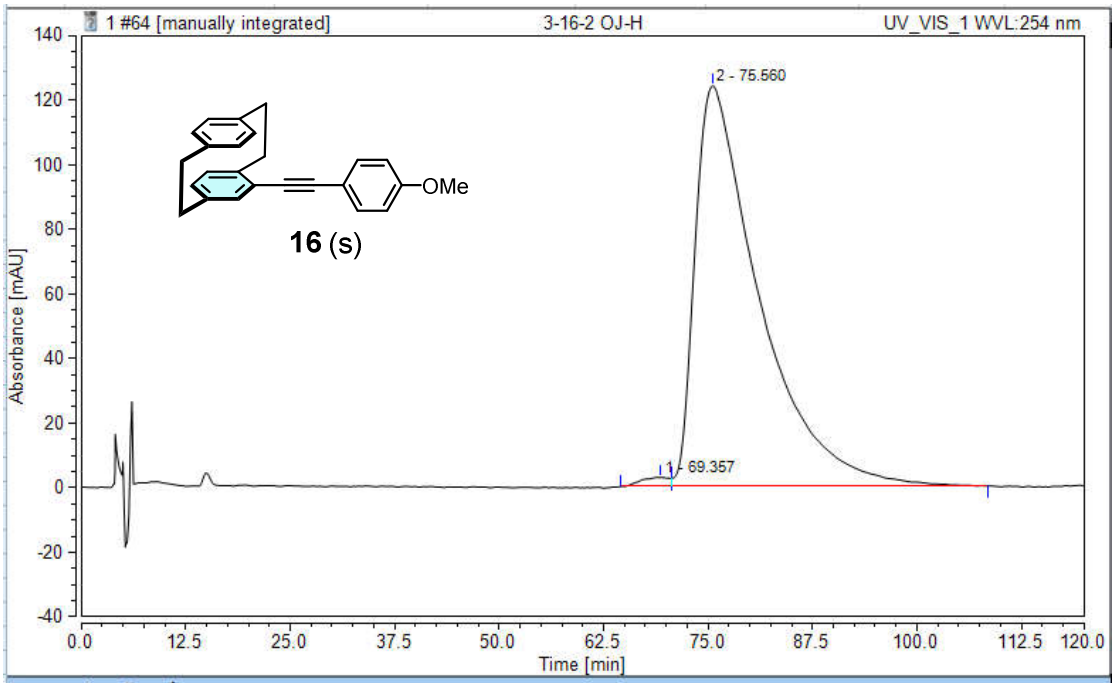
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		24.493	21.953	12.361	1.83	3.85	n.a.
2		28.845	1179.808	308.981	98.17	96.15	n.a.
Total:			**1201.761**	**321.342**	**100.00**	**100.00**	



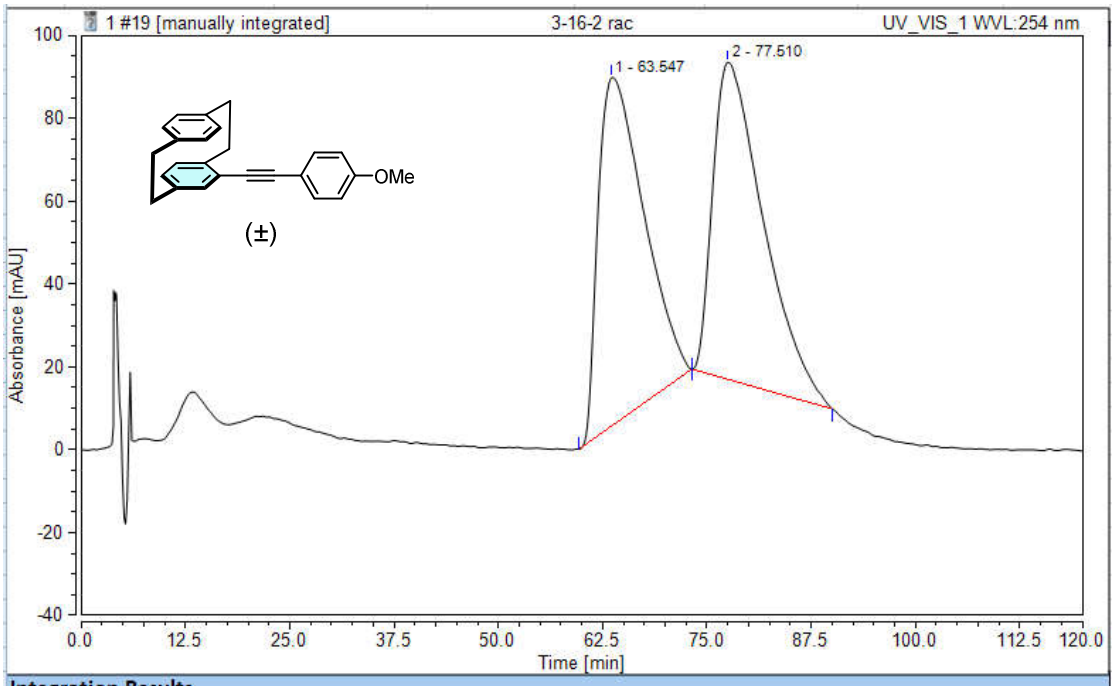
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		24.432	186.747	93.219	49.72	58.00	n.a.
2		29.825	188.851	67.490	50.28	42.00	n.a.
Total:			**375.598**	**160.709**	**100.00**	**100.00**	



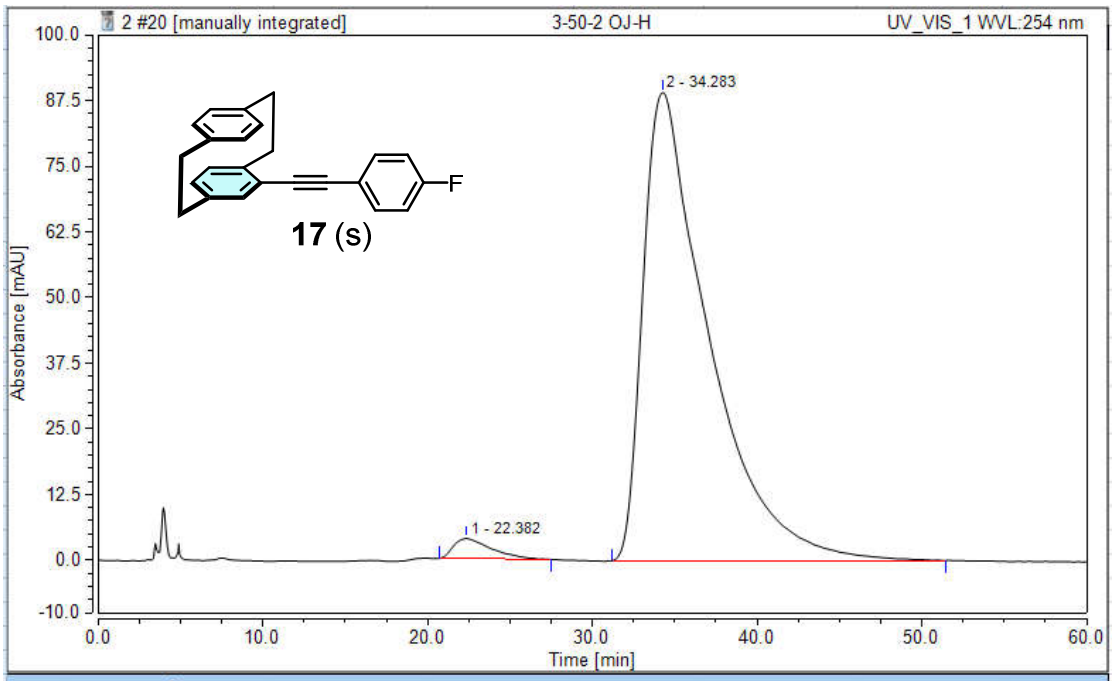
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		69.357	11.129	2.801	1.00	2.21	n.a.
2		75.560	1103.000	124.001	99.00	97.79	n.a.
Total:			**1114.129**	**126.802**	**100.00**	**100.00**	



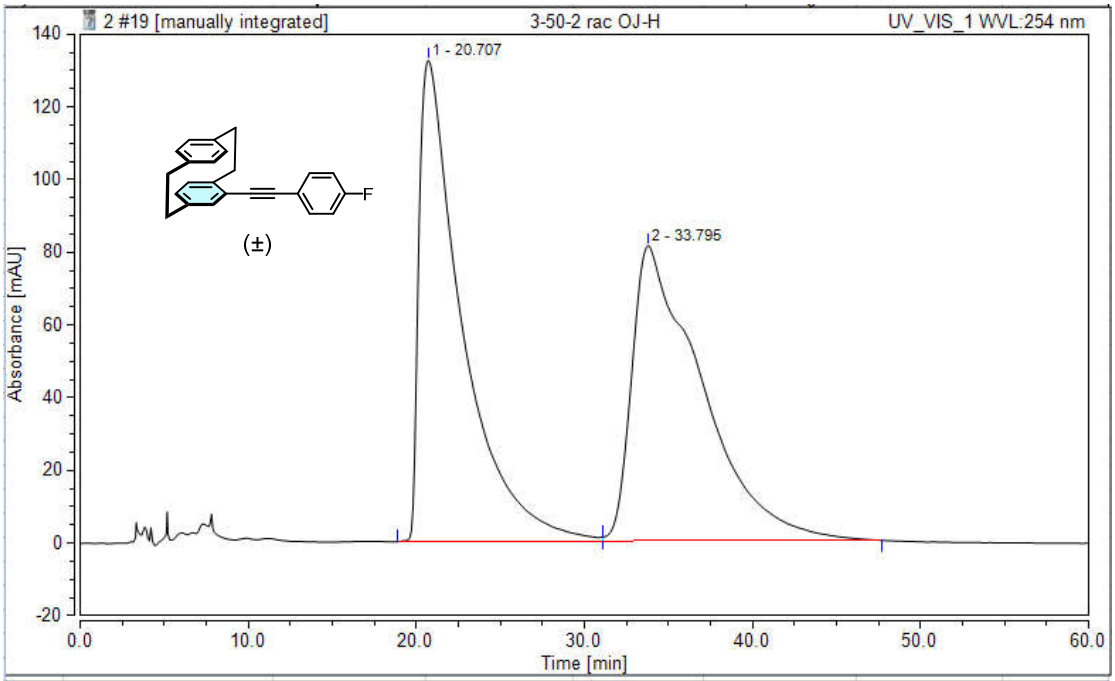
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		63.547	529.879	84.129	49.51	52.34	n.a.
2		77.510	540.447	76.600	50.49	47.66	n.a.
Total:			**1070.326**	**160.728**	**100.00**	**100.00**	



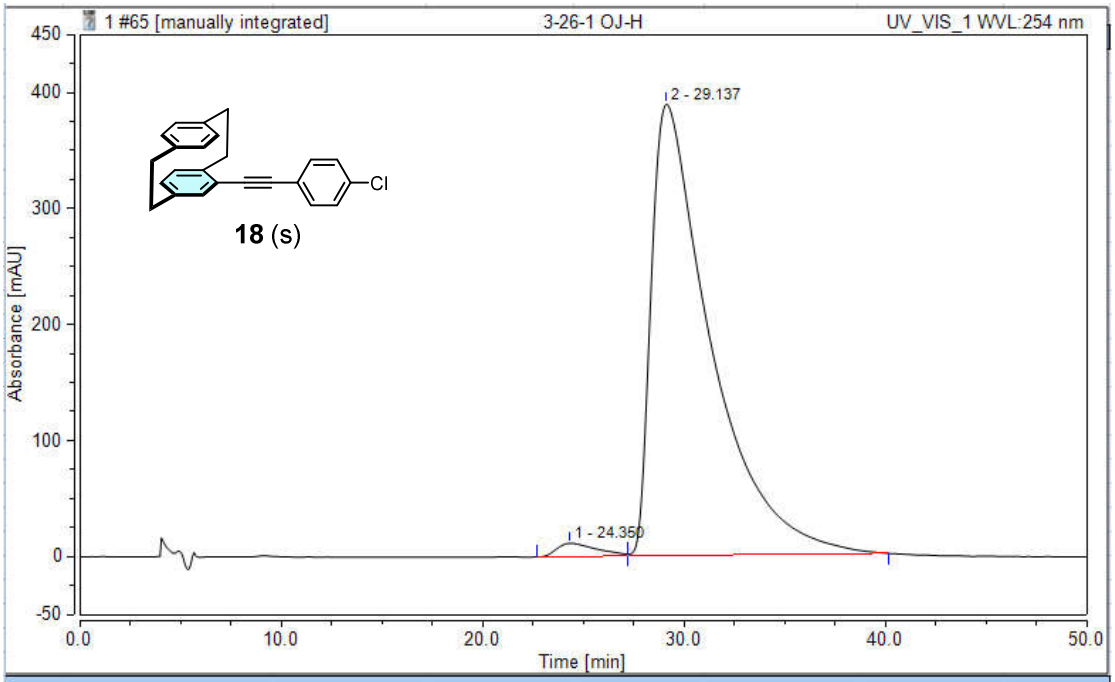
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		22.382	10.251	3.856	2.43	4.15	n.a.
2		34.283	411.024	89.127	97.57	95.85	n.a.
Total:			**421.274**	**92.983**	**100.00**	**100.00**	



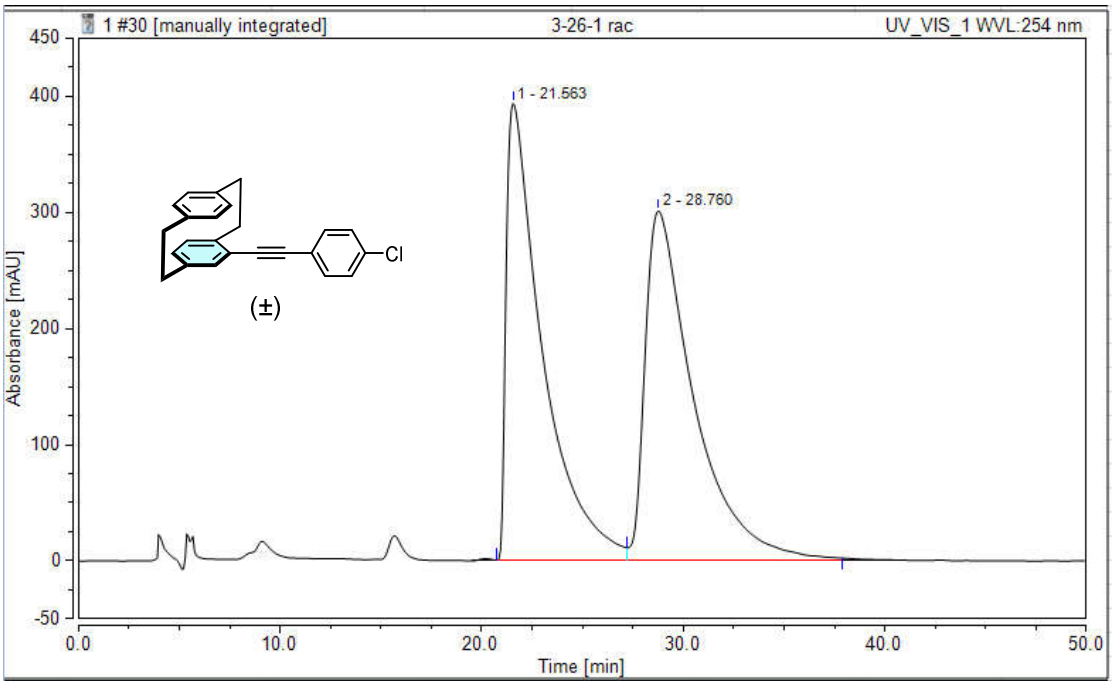
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		20.707	392.109	132.399	50.08	61.97	n.a.
2		33.795	390.818	81.263	49.92	38.03	n.a.
Total:			**782.927**	**213.662**	**100.00**	**100.00**	



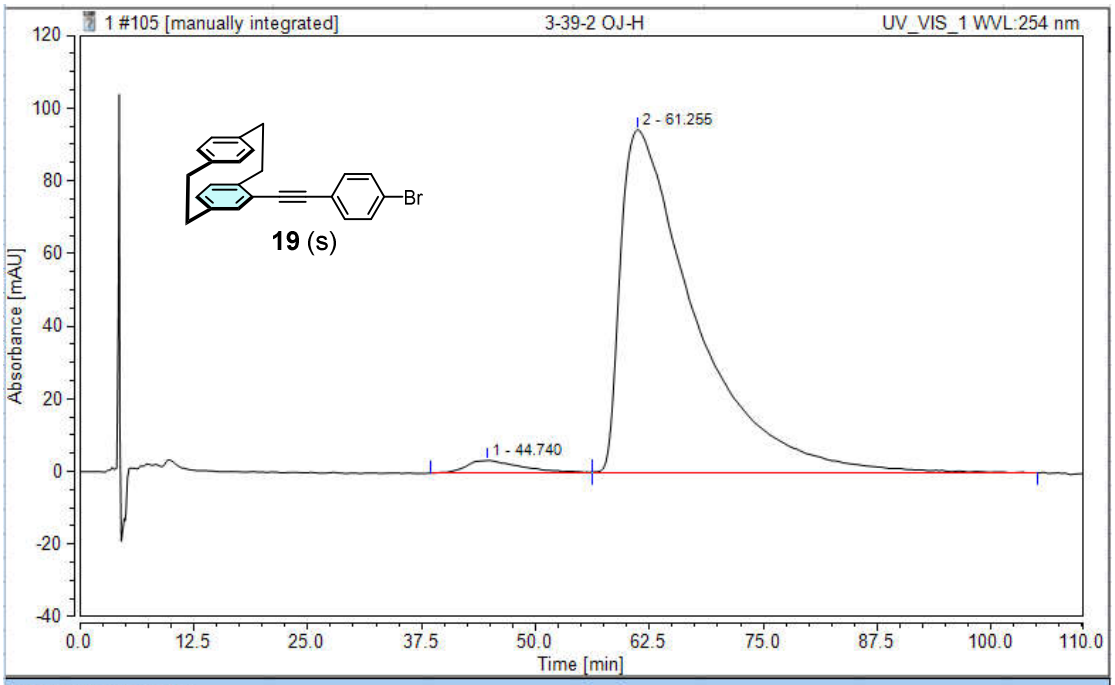
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		24.350	26.604	11.487	1.96	2.87	n.a.
2		29.137	1332.698	389.175	98.04	97.13	n.a.
Total:			**1359.302**	**400.662**	**100.00**	**100.00**	



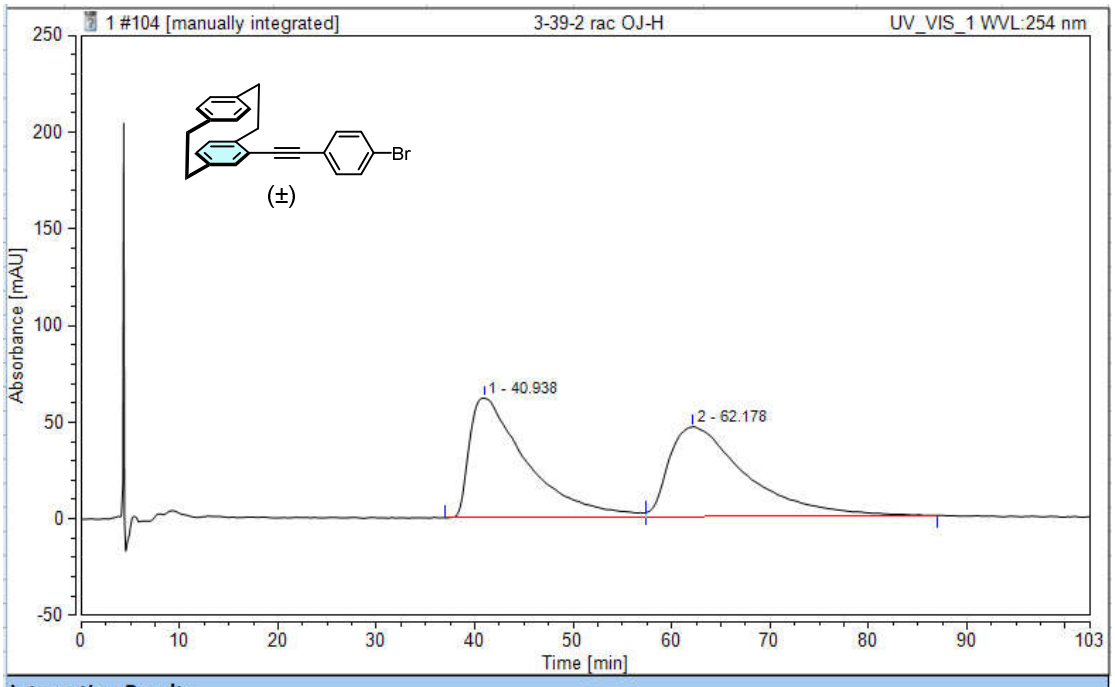
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		21.563	818.829	393.669	49.32	56.68	n.a.
2		28.760	841.388	300.928	50.68	43.32	n.a.
Total:			**1660.217**	**694.596**	**100.00**	**100.00**	



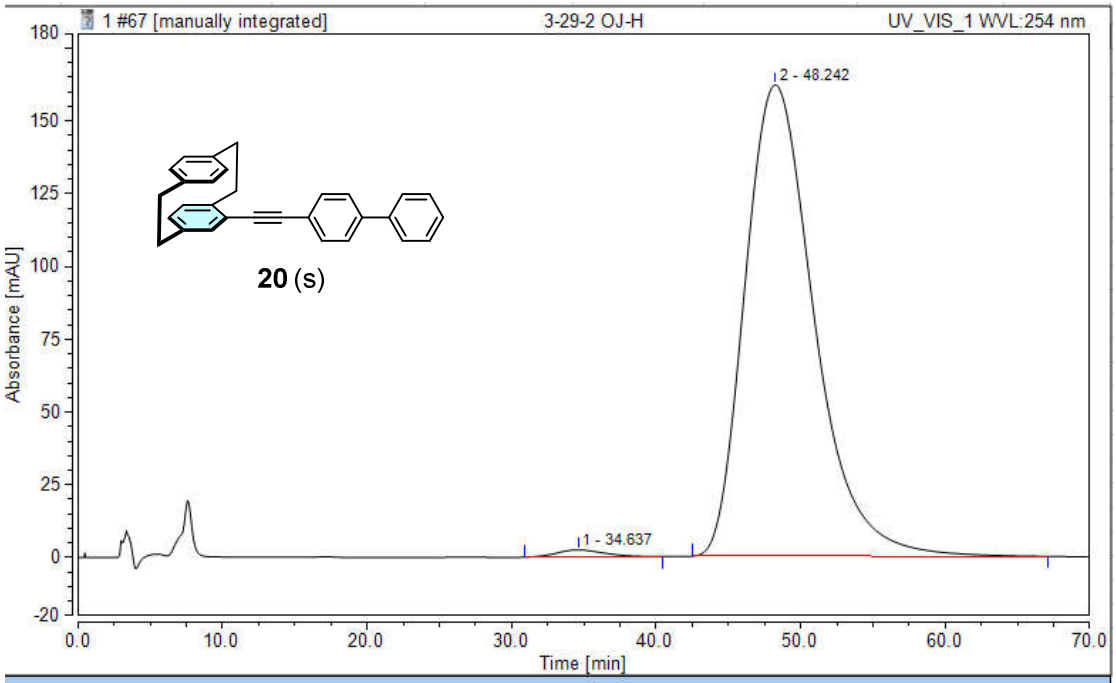
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		44.740	25.507	3.514	2.75	3.59	n.a.
2		61.255	900.431	94.507	97.25	96.41	n.a.
Total:			**925.938**	**98.021**	**100.00**	**100.00**	



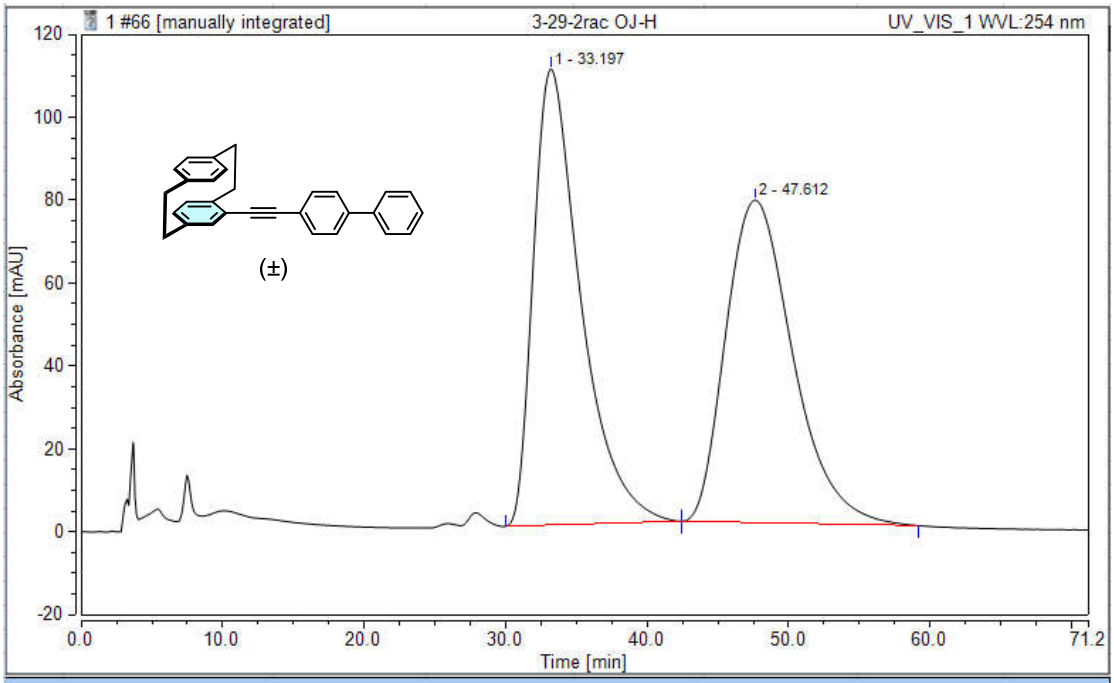
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		40.938	417.409	61.743	49.72	57.04	n.a.
2		62.178	422.182	46.510	50.28	42.96	n.a.
Total:			**839.591**	**108.253**	**100.00**	**100.00**	



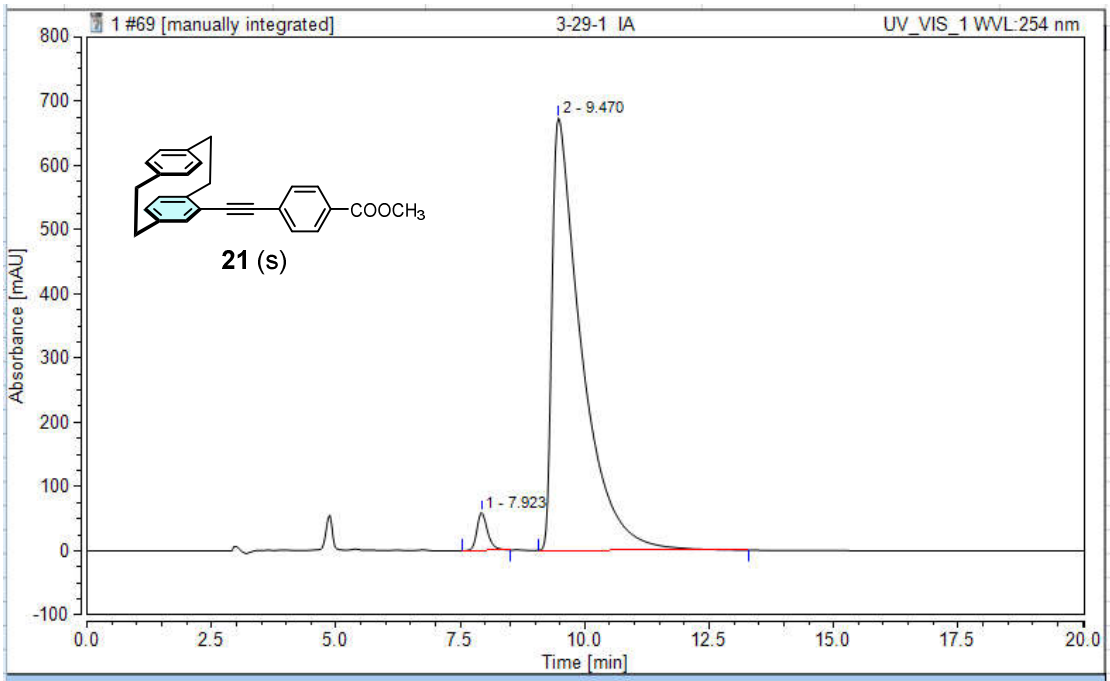
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		34.637	9.206	2.432	1.02	1.48	n.a.
2		48.242	896.715	161.940	98.98	98.52	n.a.
Total:			**905.921**	**164.372**	**100.00**	**100.00**	



Integration Results

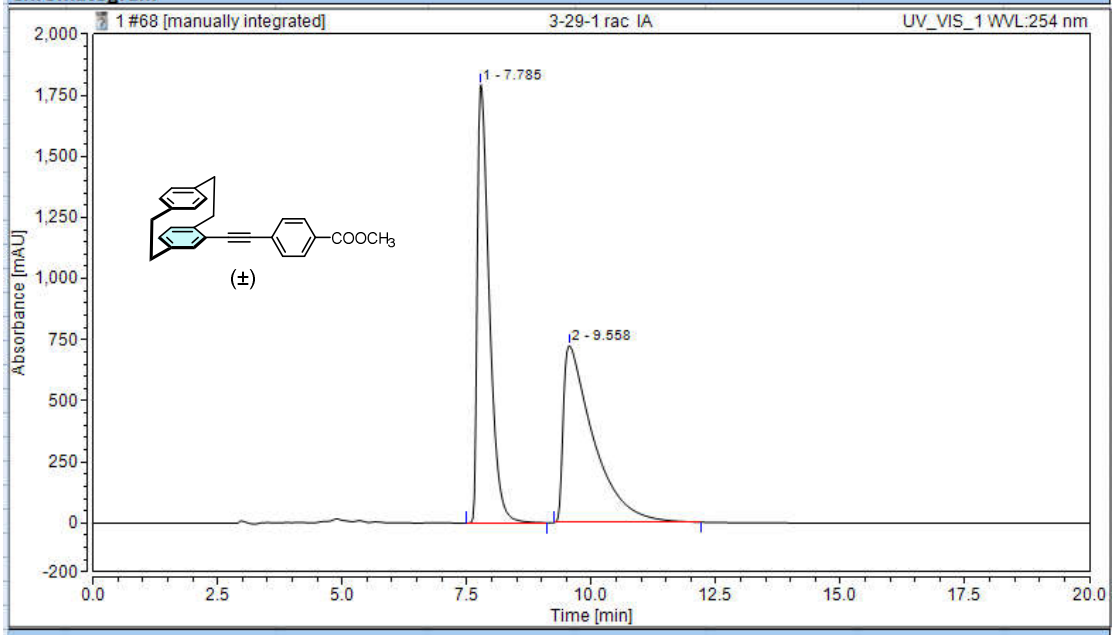
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		33.197	426.186	110.075	49.96	58.58	n.a.
2		47.612	426.934	77.817	50.04	41.42	n.a.
Total:			**853.119**	**187.892**	**100.00**	**100.00**	



Integration Results

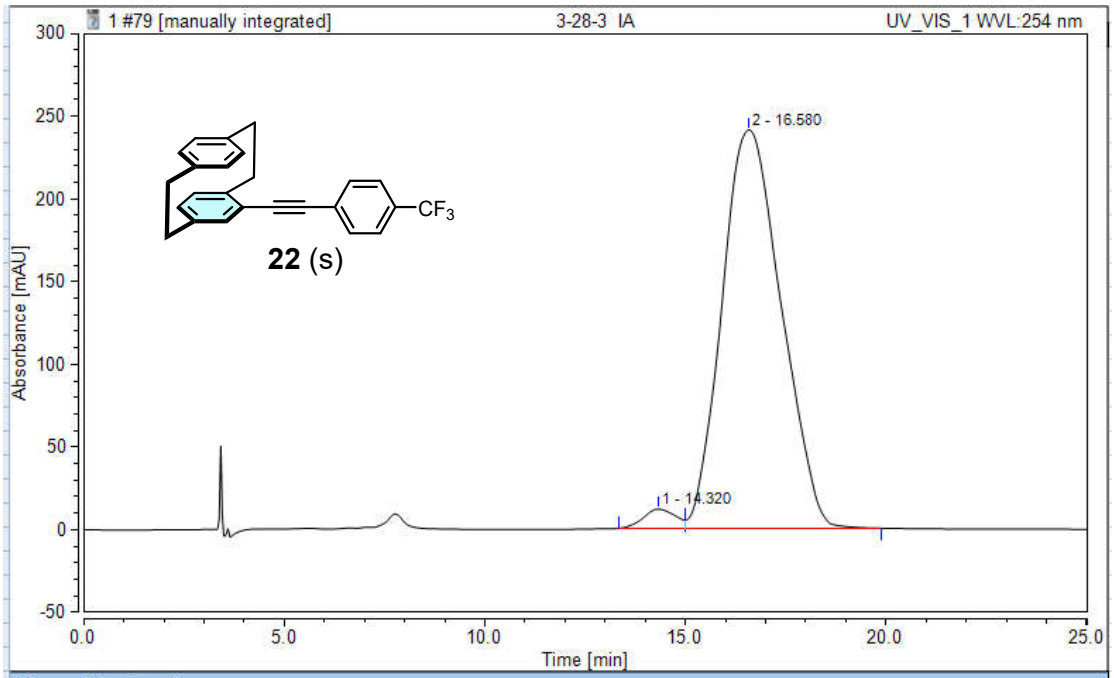
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		7.923	14.661	59.054	3.08	8.06	n.a.
2		9.470	461.087	673.357	96.92	91.94	n.a.
Total:			**475.747**	**732.411**	**100.00**	**100.00**	

Chromatogram



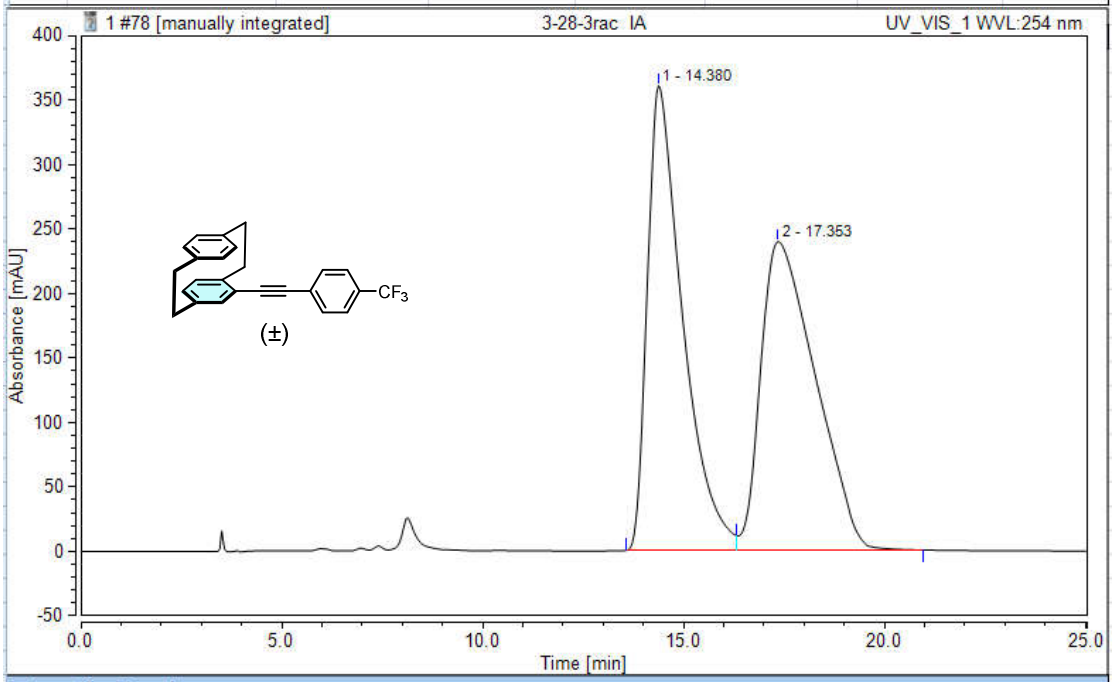
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		7.785	500.940	1793.876	49.76	71.28	n.a.
2		9.558	505.758	722.905	50.24	28.72	n.a.
Total:			**1006.698**	**2516.782**	**100.00**	**100.00**	



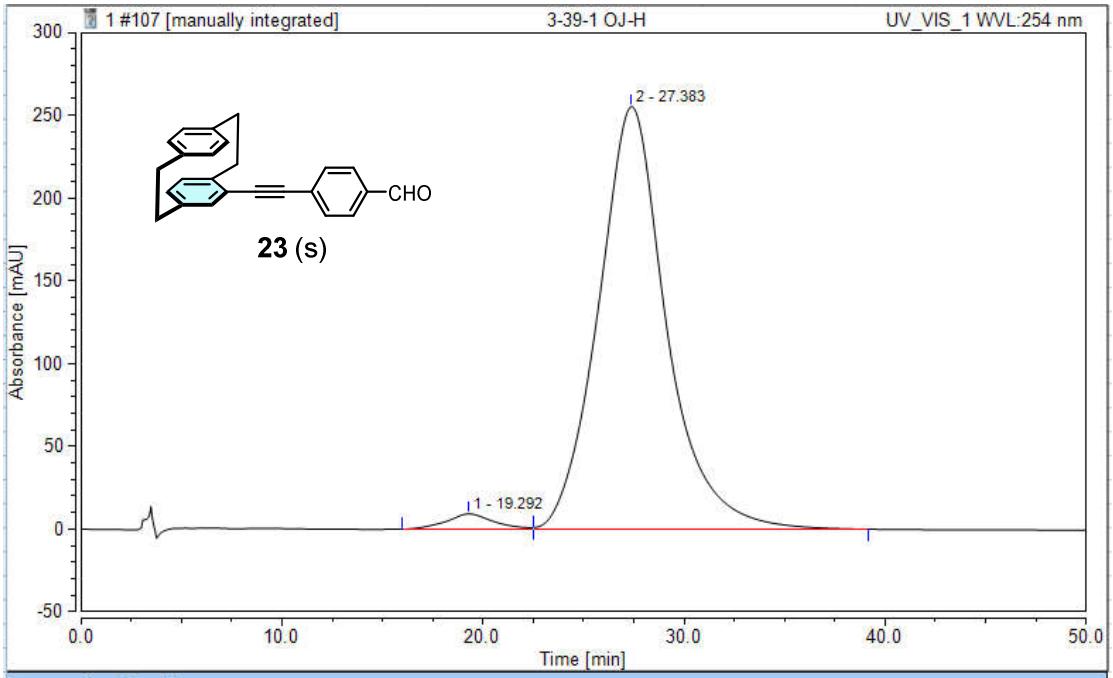
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		14.320	10.838	11.613	2.56	4.60	n.a.
2		16.580	412.203	240.884	97.44	95.40	n.a.
Total:			**423.041**	**252.497**	**100.00**	**100.00**	



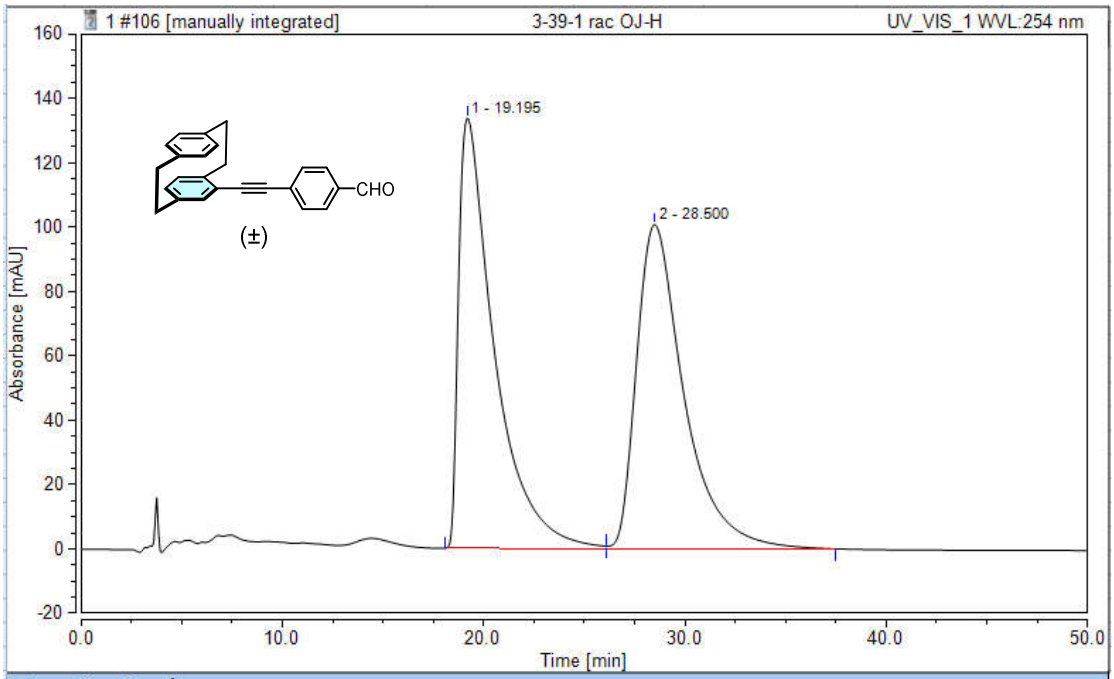
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		14.380	366.577	360.294	49.32	60.09	n.a.
2		17.353	376.720	239.300	50.68	39.91	n.a.
Total:			**743.296**	**599.593**	**100.00**	**100.00**	



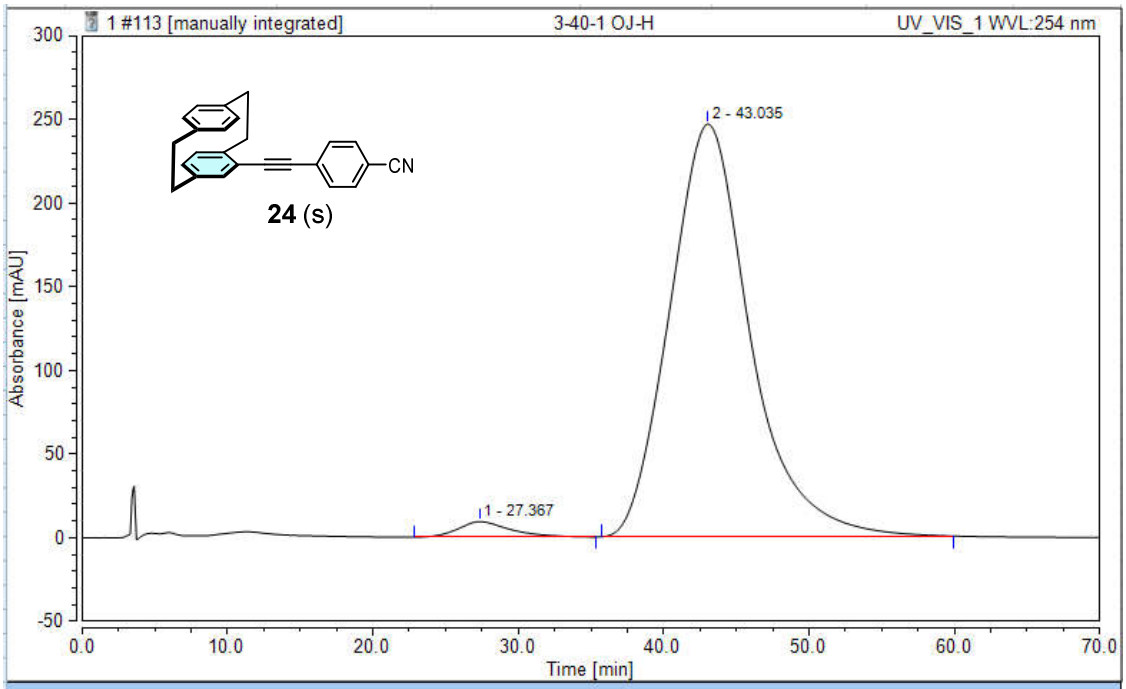
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		19.292	25.548	9.316	2.48	3.52	n.a.
2		27.383	1002.744	255.367	97.52	96.48	n.a.
Total:			**1028.292**	**264.683**	**100.00**	**100.00**	



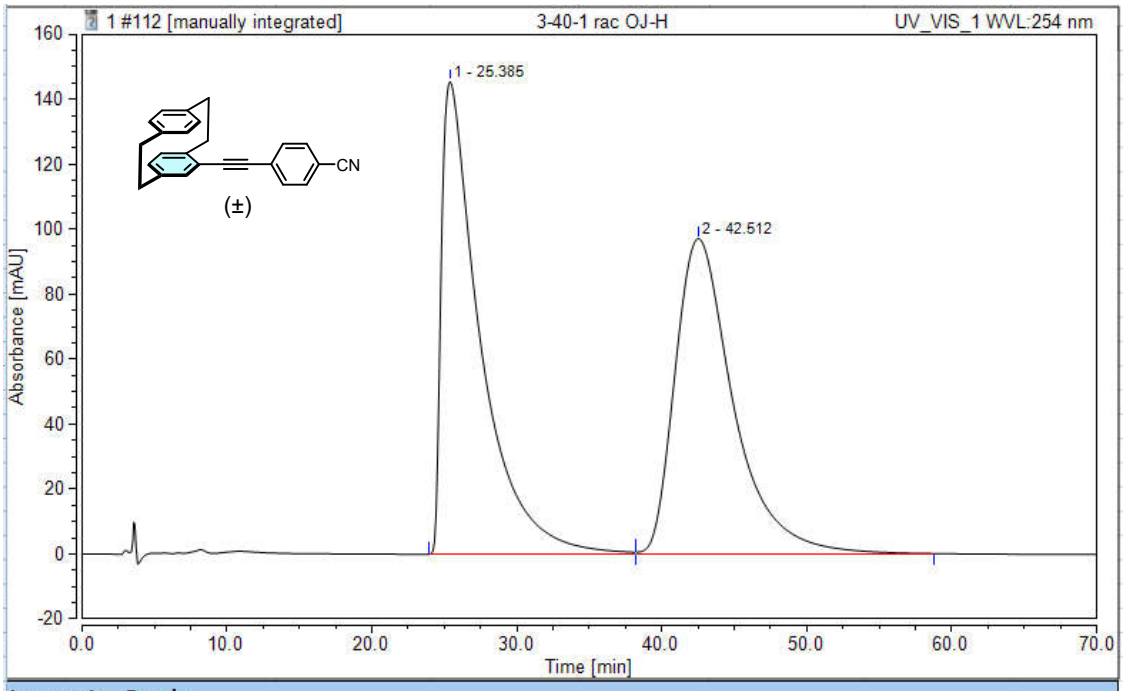
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		19.195	274.130	133.731	49.96	57.05	n.a.
2		28.500	274.566	100.676	50.04	42.95	n.a.
Total:			**548.696**	**234.408**	**100.00**	**100.00**	



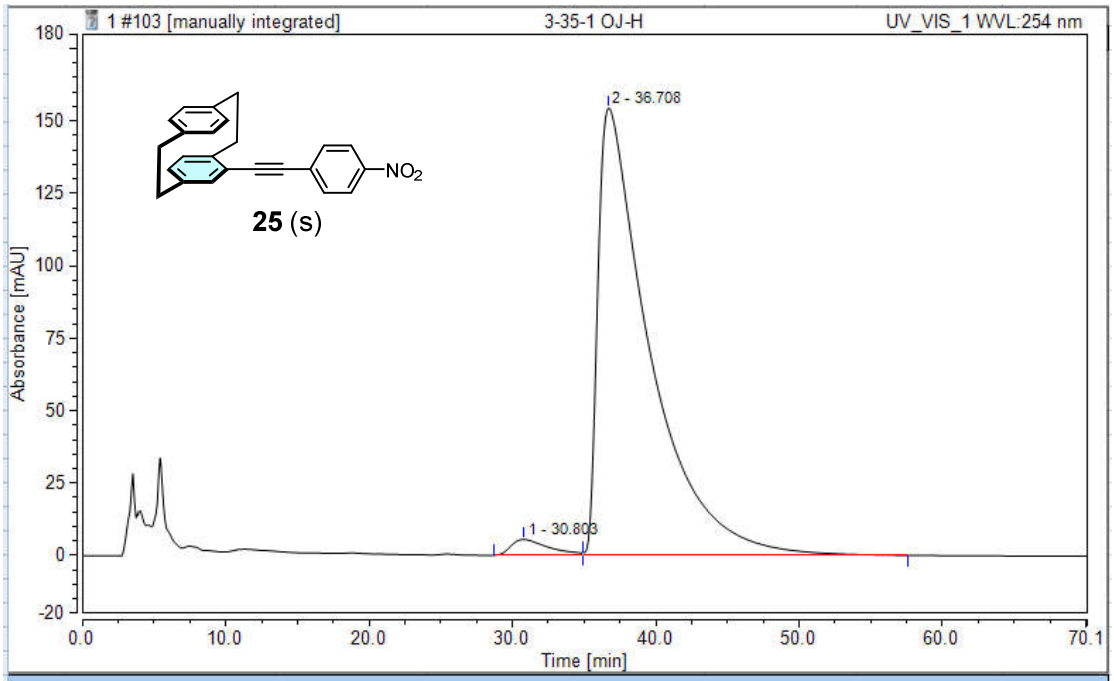
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		27.367	38.432	9.261	2.38	3.62	n.a.
2		43.035	1576.512	246.484	97.62	96.38	n.a.
Total:			**1614.944**	**255.746**	**100.00**	**100.00**	



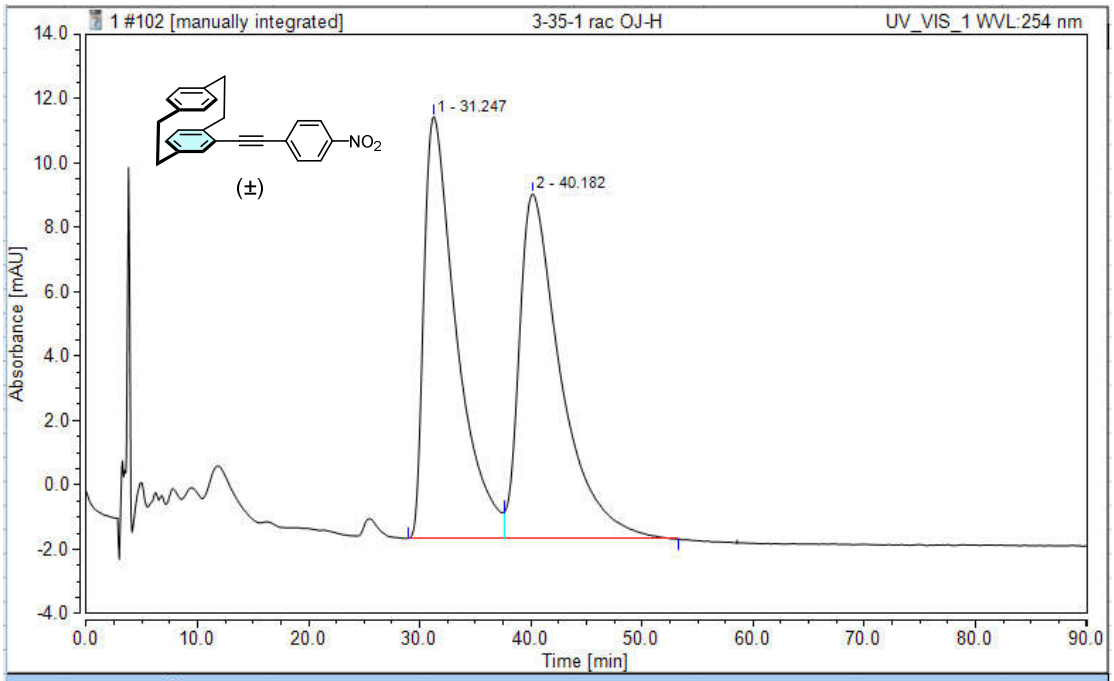
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		25.385	451.496	145.506	50.00	59.99	n.a.
2		42.512	451.532	97.030	50.00	40.01	n.a.
Total:			**903.027**	**242.536**	**100.00**	**100.00**	



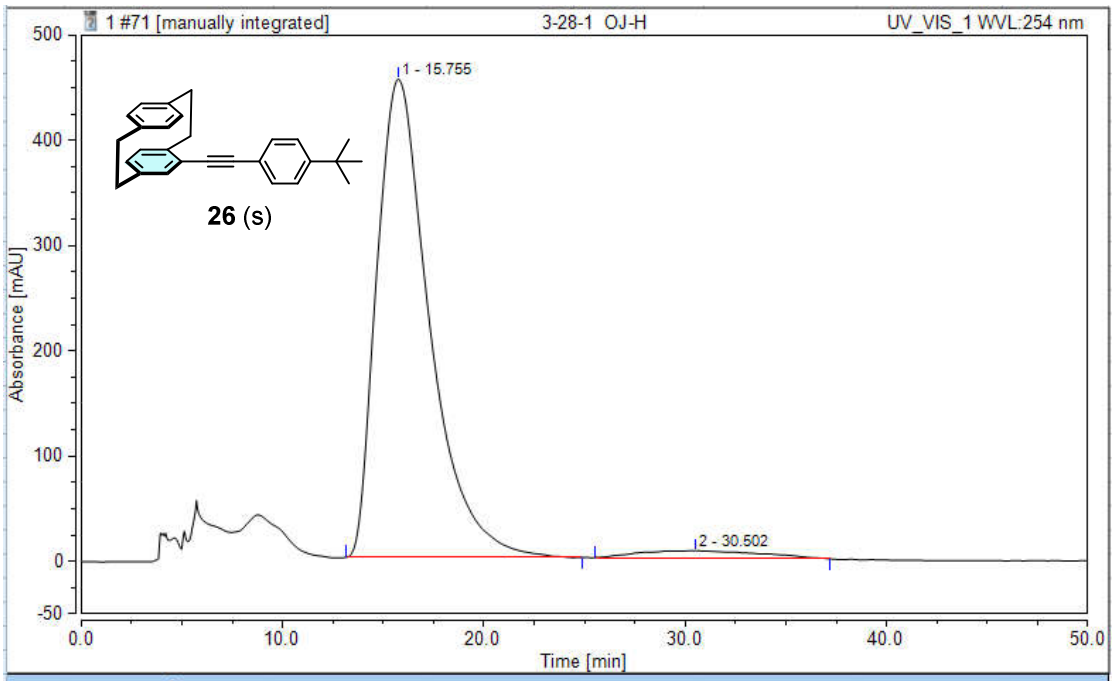
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		30.803	16.441	5.445	2.48	3.41	n.a.
2		36.708	646.271	154.401	97.52	96.59	n.a.
Total:			**662.712**	**159.846**	**100.00**	**100.00**	



Integration Results

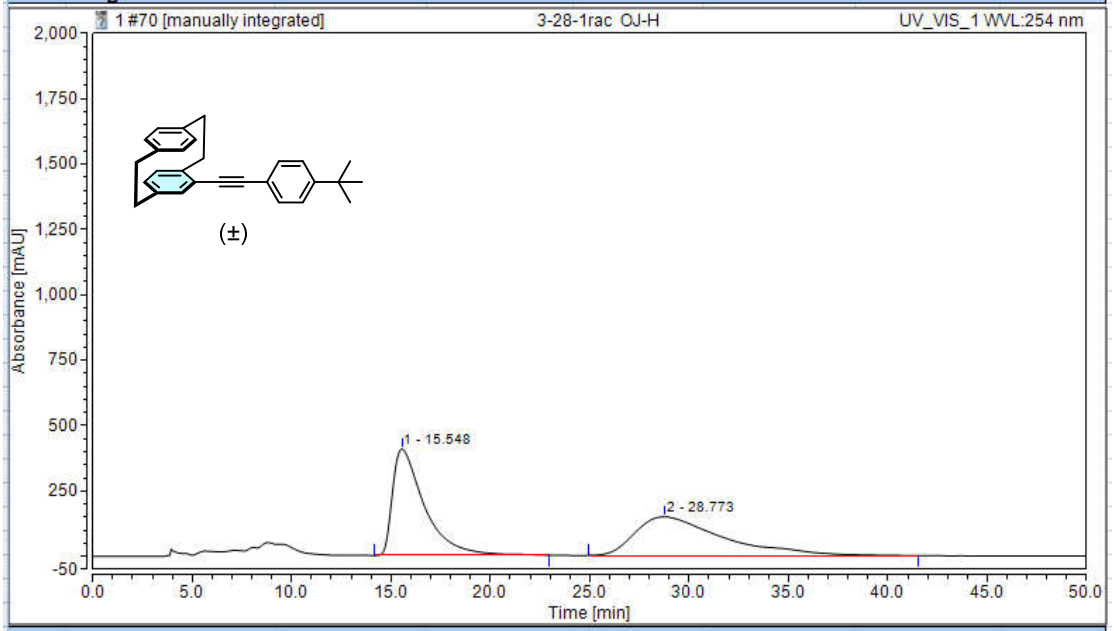
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		31.247	44.461	13.108	48.99	55.04	n.a.
2		40.182	46.293	10.709	51.01	44.96	n.a.
Total:			**90.754**	**23.816**	**100.00**	**100.00**	



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		15.755	1378.163	454.099	96.49	98.49	n.a.
2		30.502	50.118	6.959	3.51	1.51	n.a.
Total:			**1428.282**	**461.058**	**100.00**	**100.00**	

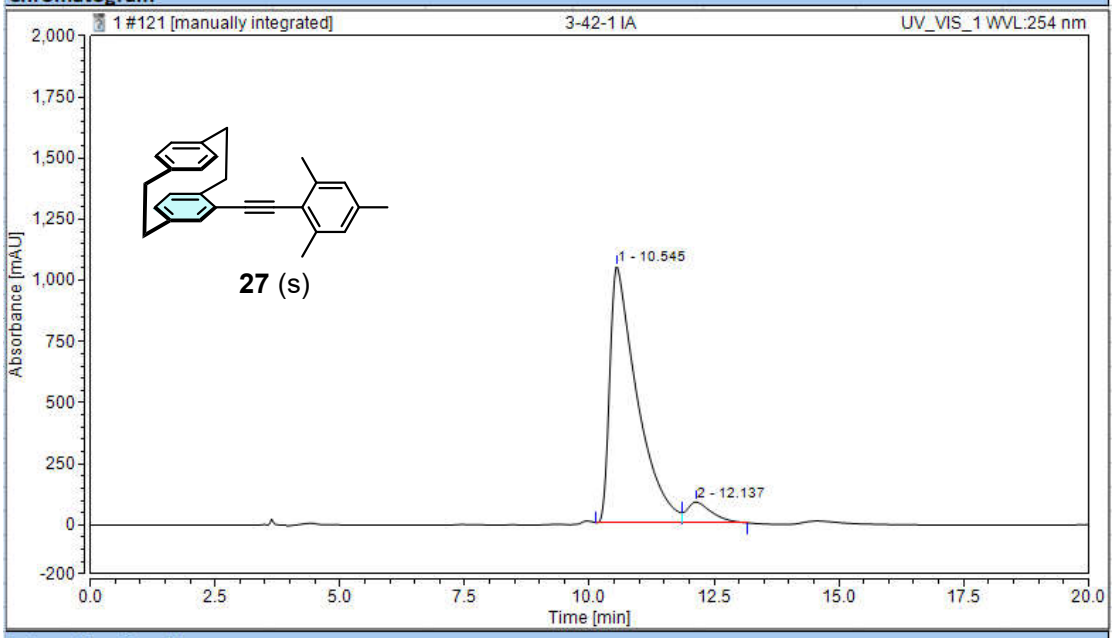
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		15.548	759.515	407.229	50.12	73.33	n.a.
2		28.773	755.849	148.111	49.88	26.67	n.a.
Total:			**1515.363**	**555.340**	**100.00**	**100.00**	

Chromatogram

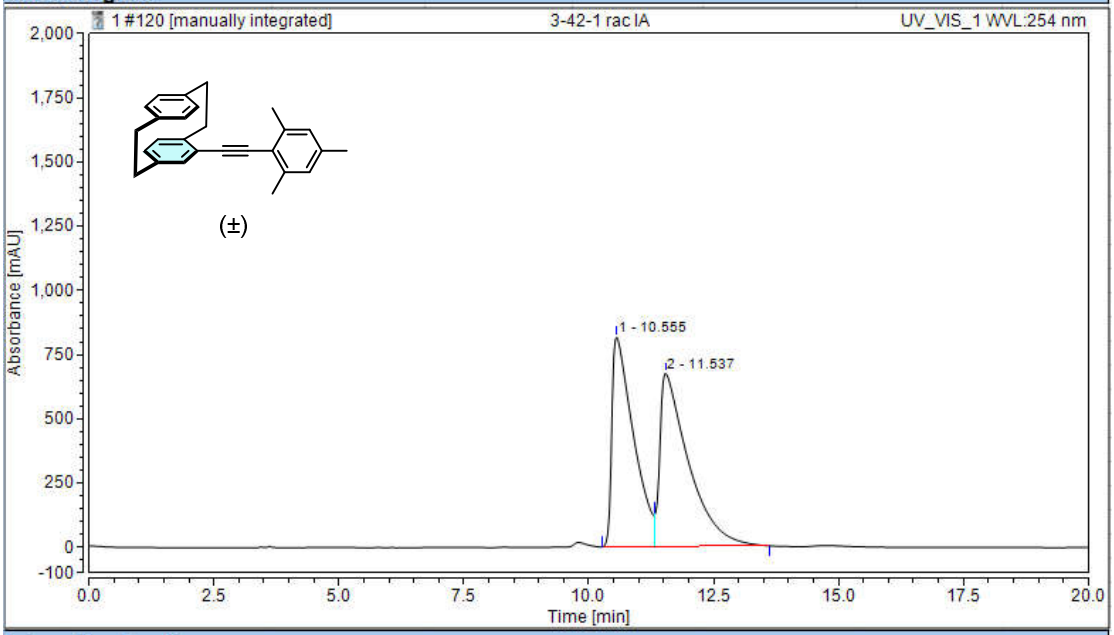


27 (s)

Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		10.545	662.324	1048.150	93.08	92.49	n.a.
2		12.137	49.211	85.076	6.92	7.51	n.a.
Total:			**711.534**	**1133.226**	**100.00**	**100.00**	

Chromatogram

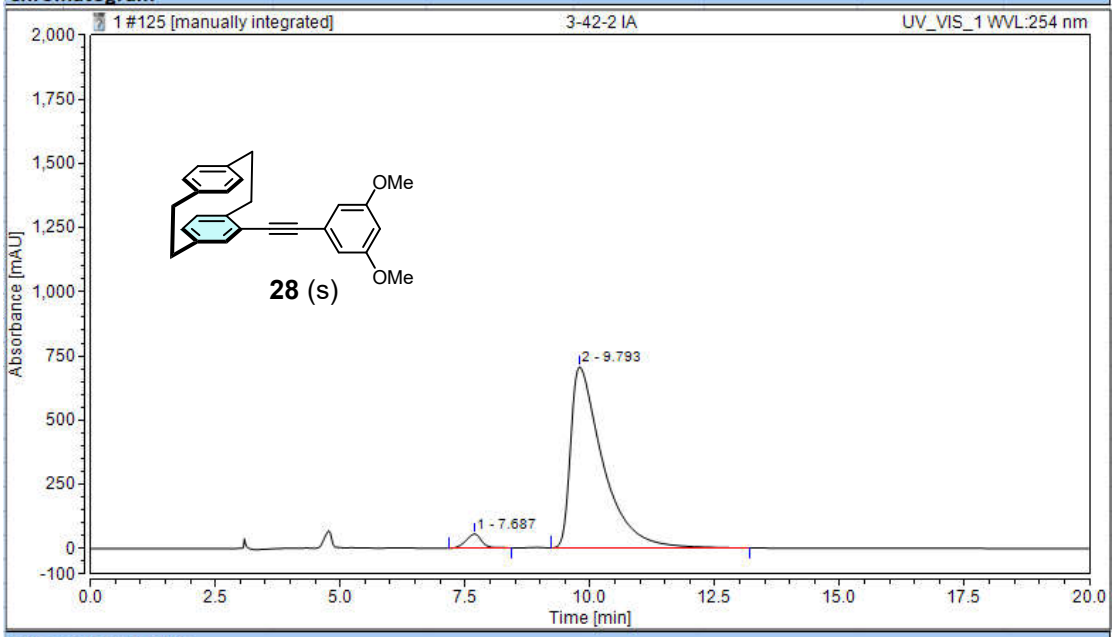


(±)

Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		10.555	409.234	816.272	47.85	54.77	n.a.
2		11.537	445.932	673.957	52.15	45.23	n.a.
Total:			**855.166**	**1490.229**	**100.00**	**100.00**	

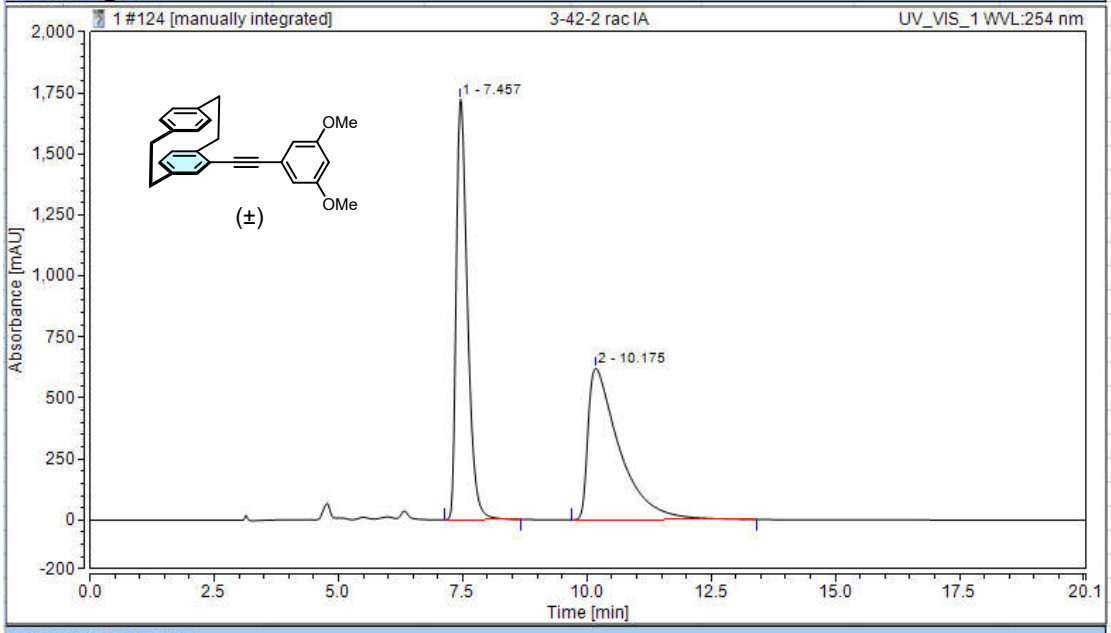
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		7.687	19.855	55.001	3.62	7.24	n.a.
2		9.793	528.052	704.684	96.38	92.76	n.a.
Total:			**547.907**	**759.685**	**100.00**	**100.00**	

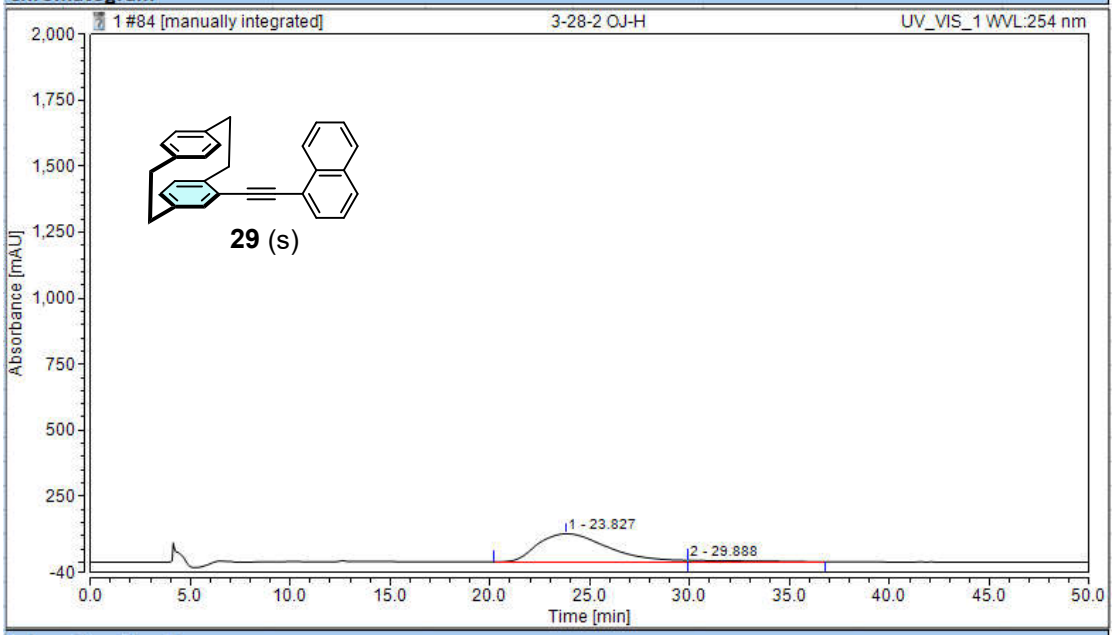
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		7.457	451.850	1722.984	49.77	73.51	n.a.
2		10.175	455.947	620.881	50.23	26.49	n.a.
Total:			**907.797**	**2343.865**	**100.00**	**100.00**	

Chromatogram

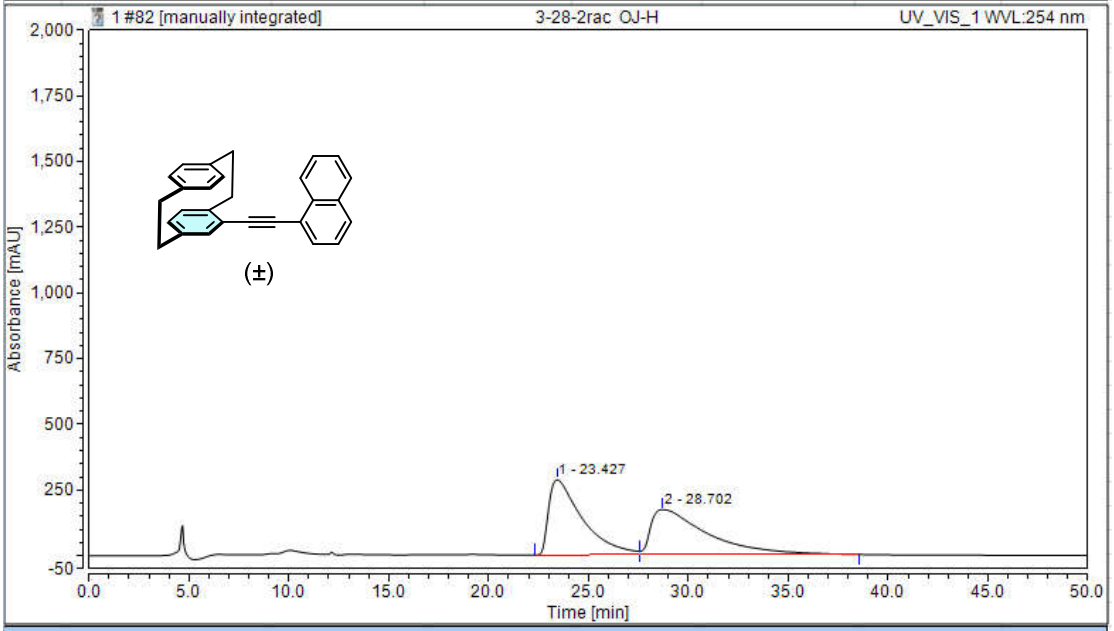


29 (s)

Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		23.827	435.285	106.794	96.03	94.98	n.a.
2		29.888	17.988	5.640	3.97	5.02	n.a.
Total:			**453.273**	**112.434**	**100.00**	**100.00**	

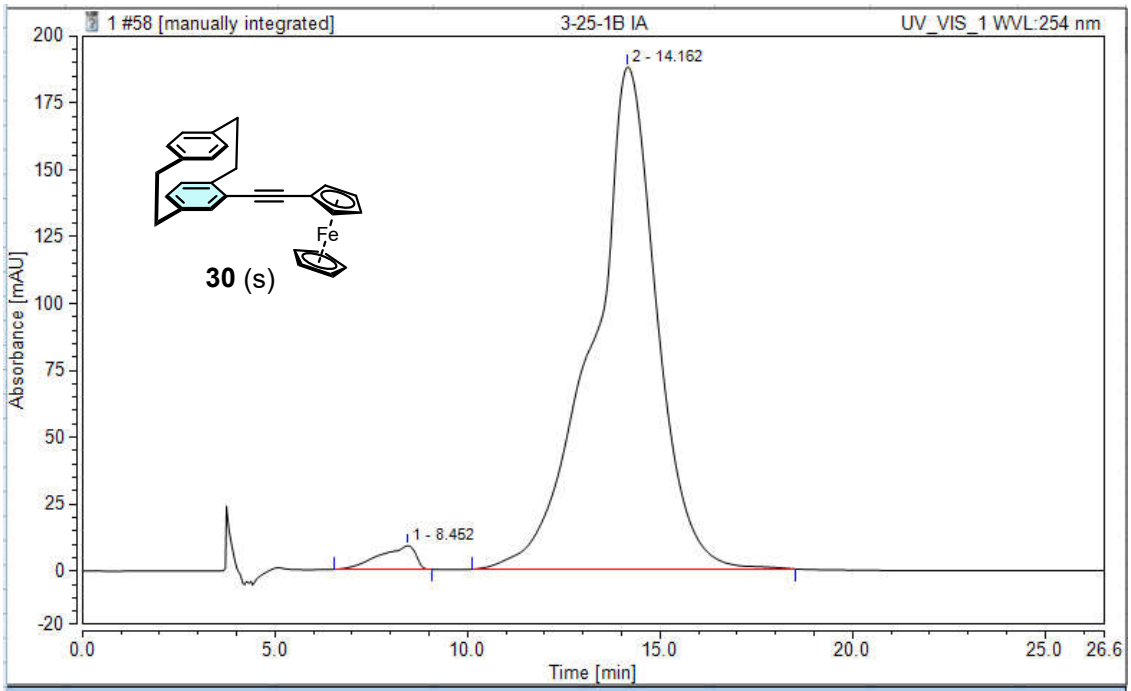
Chromatogram



(±)

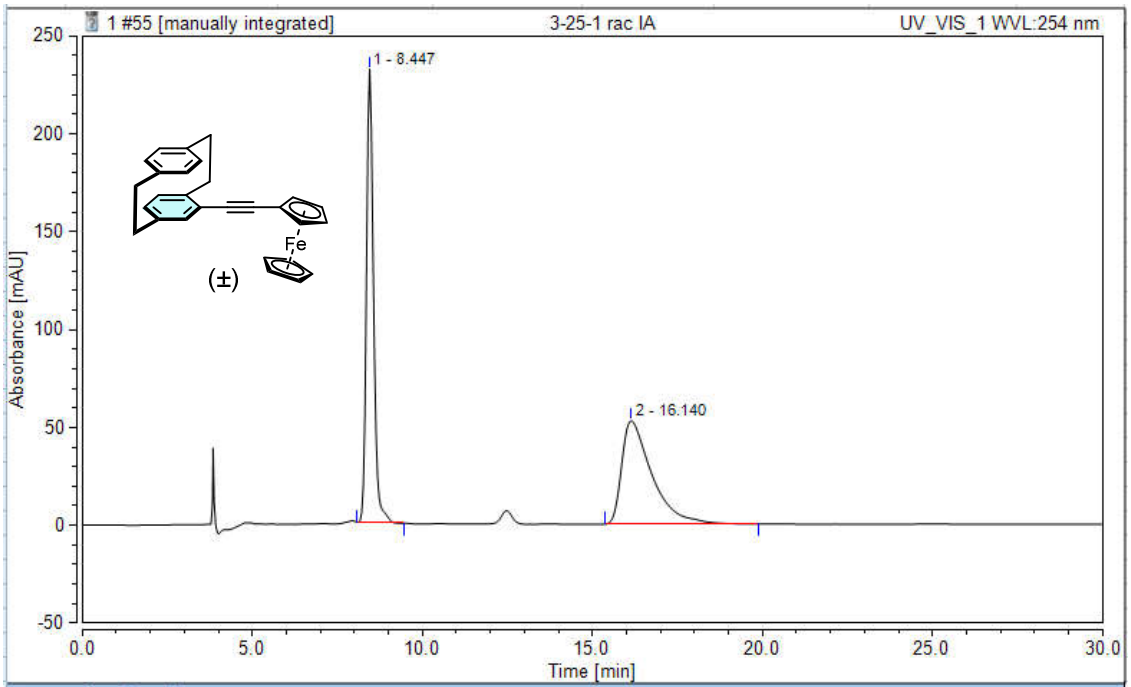
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		23.427	563.653	286.364	49.90	62.45	n.a.
2		28.702	565.985	172.200	50.10	37.55	n.a.
Total:			**1129.638**	**458.564**	**100.00**	**100.00**	



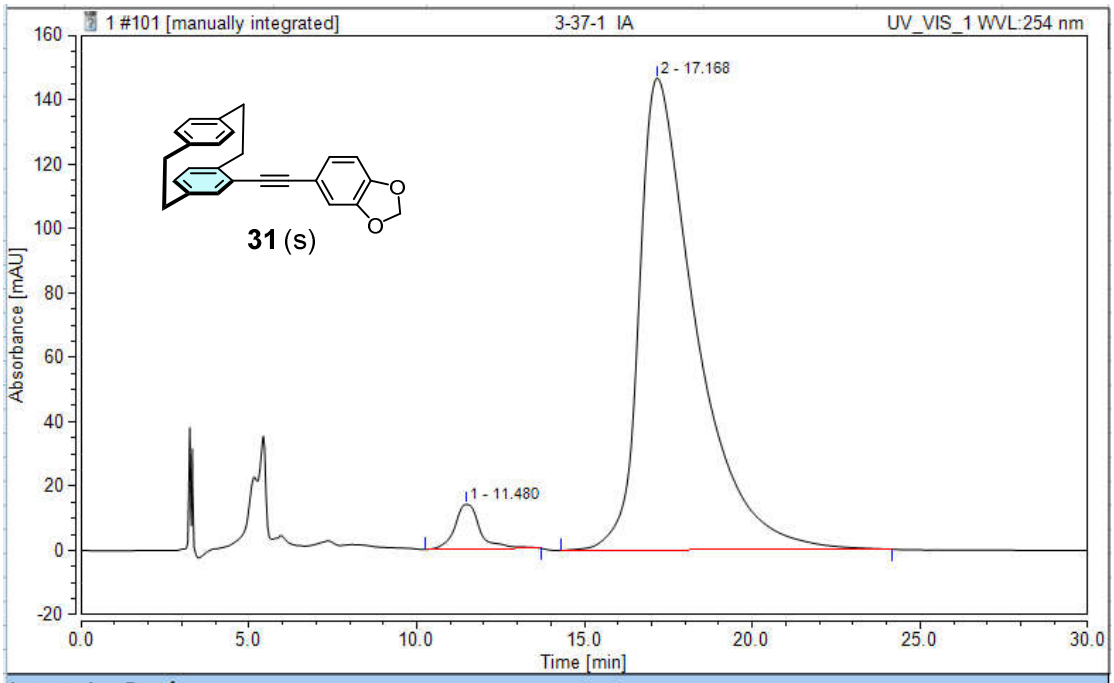
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		8.452	9.546	8.835	2.59	4.50	n.a.
2		14.162	359.499	187.691	97.41	95.50	n.a.
Total:			**369.045**	**196.526**	**100.00**	**100.00**	



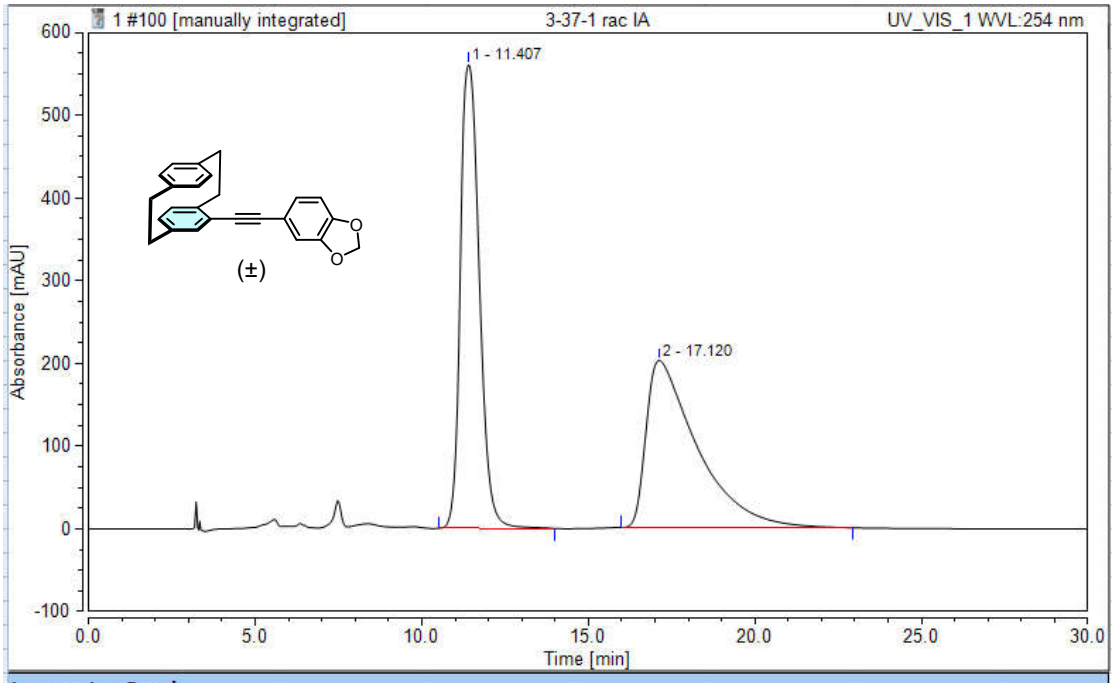
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		8.447	55.482	231.661	50.60	81.45	n.a.
2		16.140	54.156	52.777	49.40	18.55	n.a.
Total:			**109.638**	**284.438**	**100.00**	**100.00**	



Integration Results

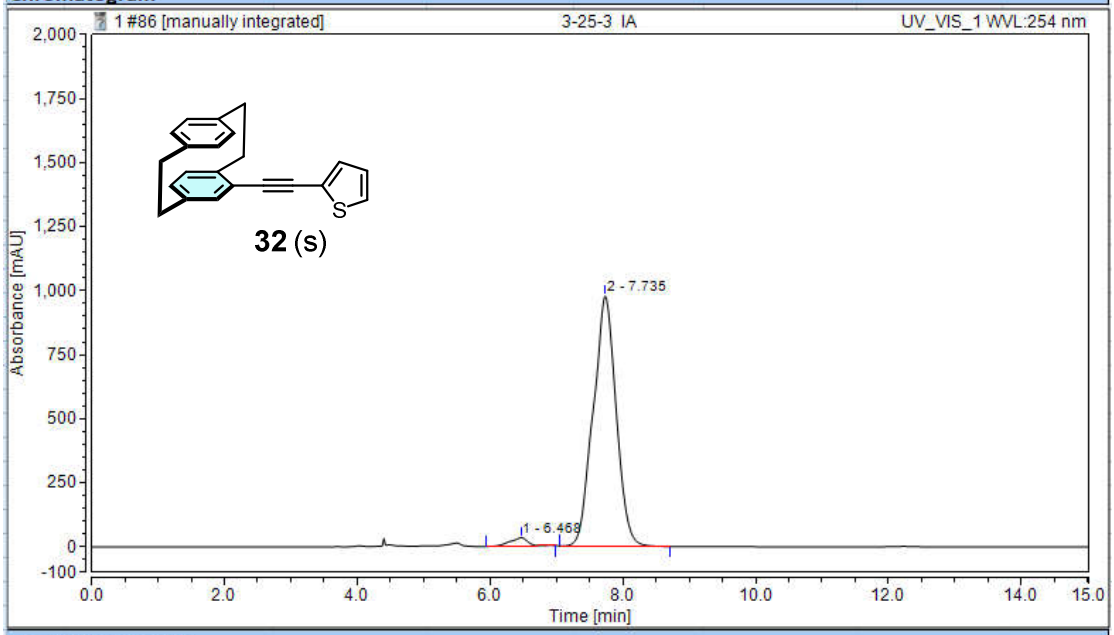
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		11.480	12.204	13.904	4.07	8.66	n.a.
2		17.168	287.461	146.670	95.93	91.34	n.a.
Total:			**299.666**	**160.574**	**100.00**	**100.00**	



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		11.407	370.241	560.664	50.78	73.50	n.a.
2		17.120	358.874	202.121	49.22	26.50	n.a.
Total:			**729.115**	**762.785**	**100.00**	**100.00**	

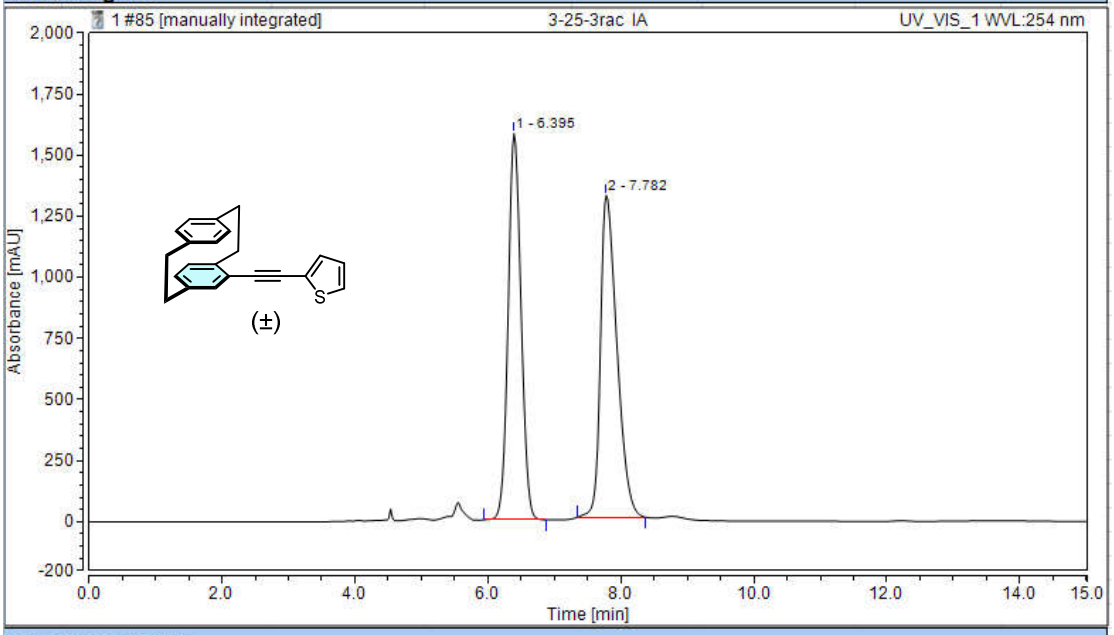
Chromatogram



Integration Results

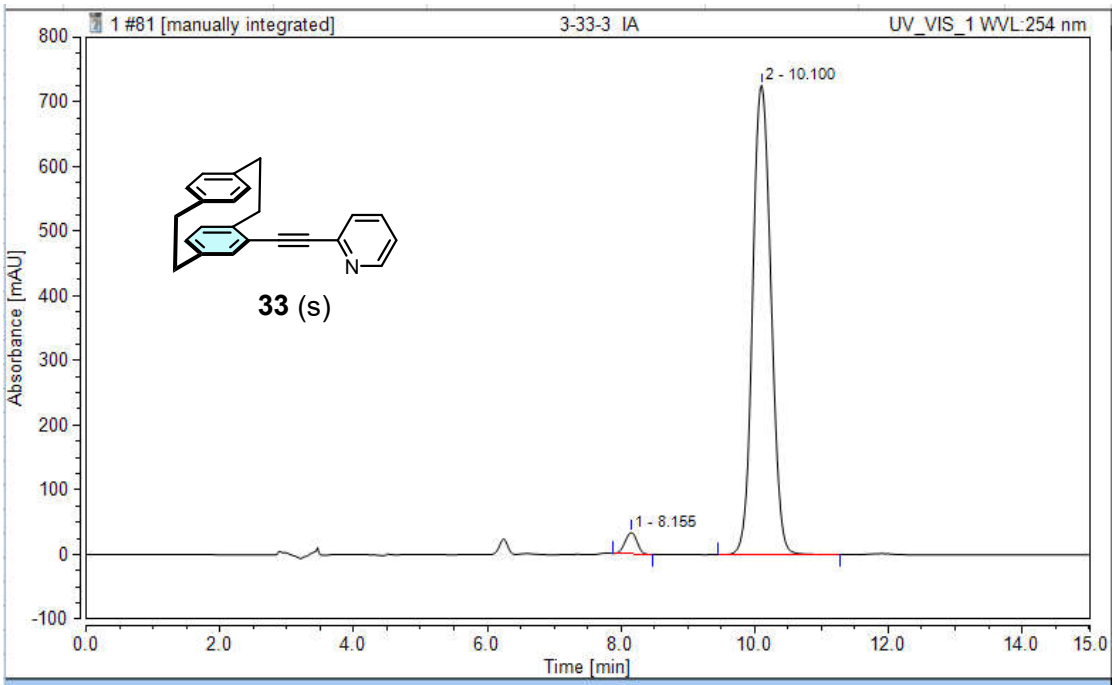
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		6.468	9.996	32.448	2.50	3.22	n.a.
2		7.735	390.470	976.328	97.50	96.78	n.a.
Total:			**400.467**	**1008.777**	**100.00**	**100.00**	

Chromatogram



Integration Results

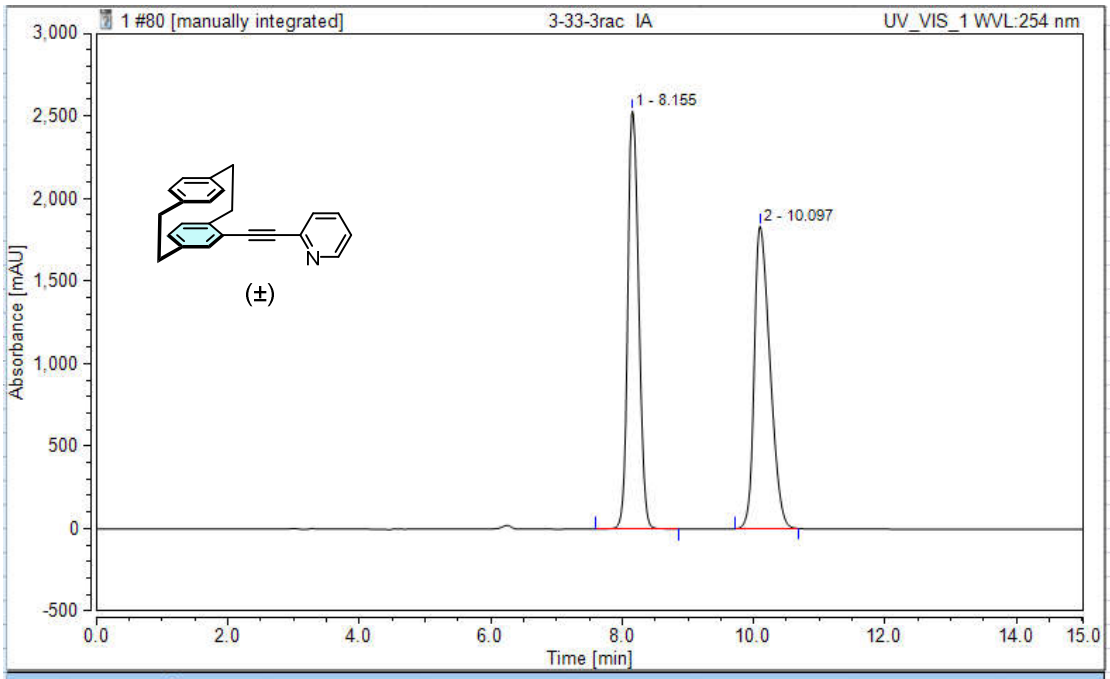
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		6.395	354.724	1580.761	48.49	54.55	n.a.
2		7.782	376.822	1317.232	51.51	45.45	n.a.
Total:			**731.546**	**2897.994**	**100.00**	**100.00**	



33 (s)

Integration Results

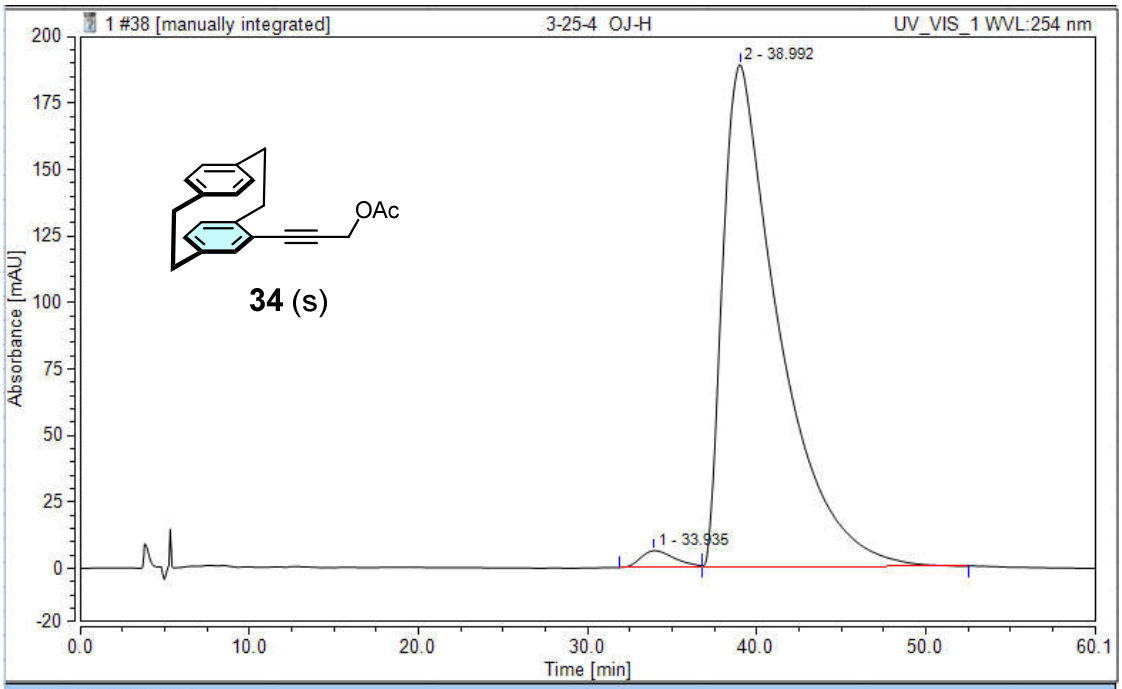
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		8.155	6.828	32.903	2.88	4.33	n.a.
2		10.100	230.349	726.455	97.12	95.67	n.a.
Total:			**237.177**	**759.358**	**100.00**	**100.00**	



(±)

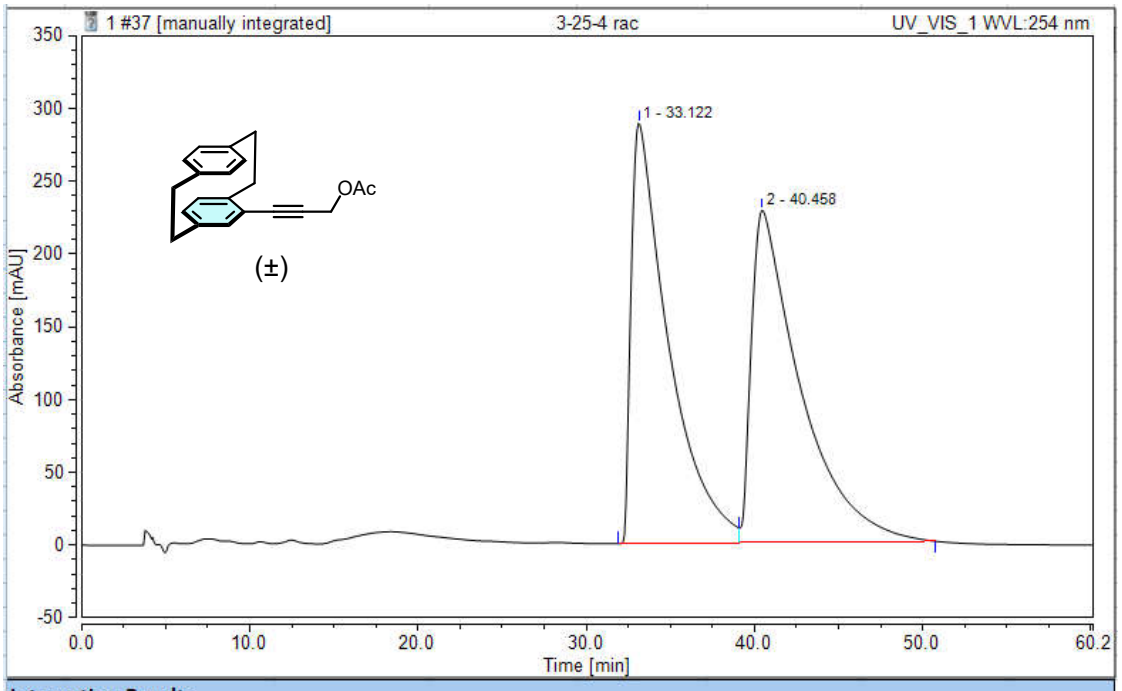
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		8.155	489.934	2533.534	49.10	58.01	n.a.
2		10.097	507.946	1833.528	50.90	41.99	n.a.
Total:			**997.880**	**4367.063**	**100.00**	**100.00**	



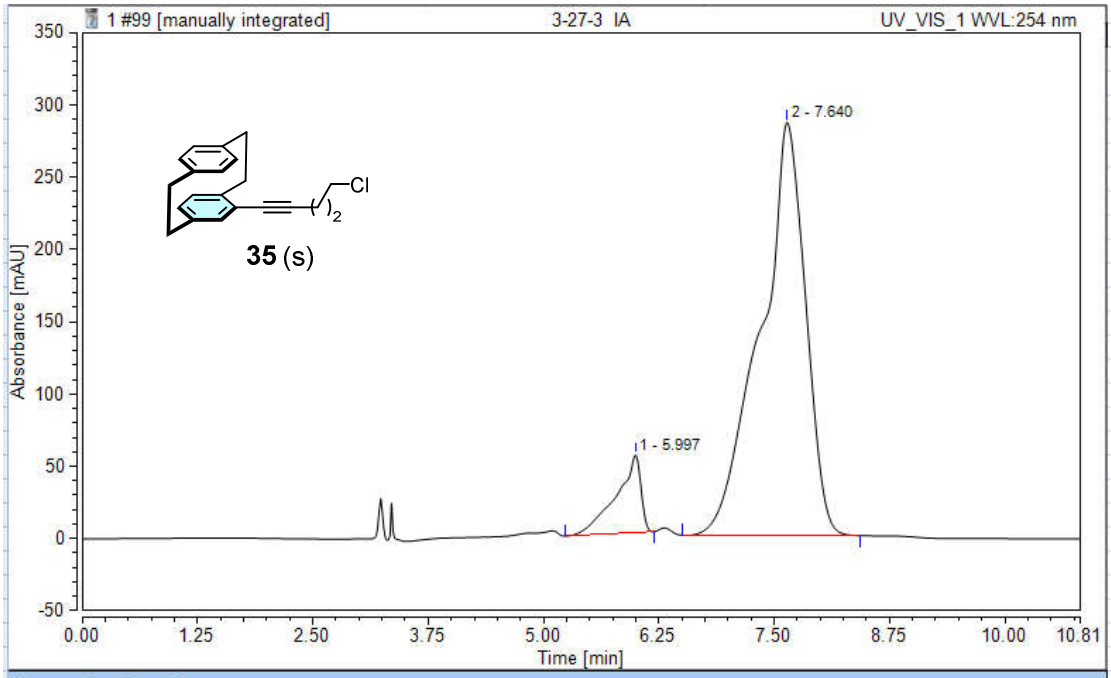
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		33.935	14.547	6.284	1.97	3.22	n.a.
2		38.992	725.662	188.956	98.03	96.78	n.a.
Total:			**740.209**	**195.240**	**100.00**	**100.00**	



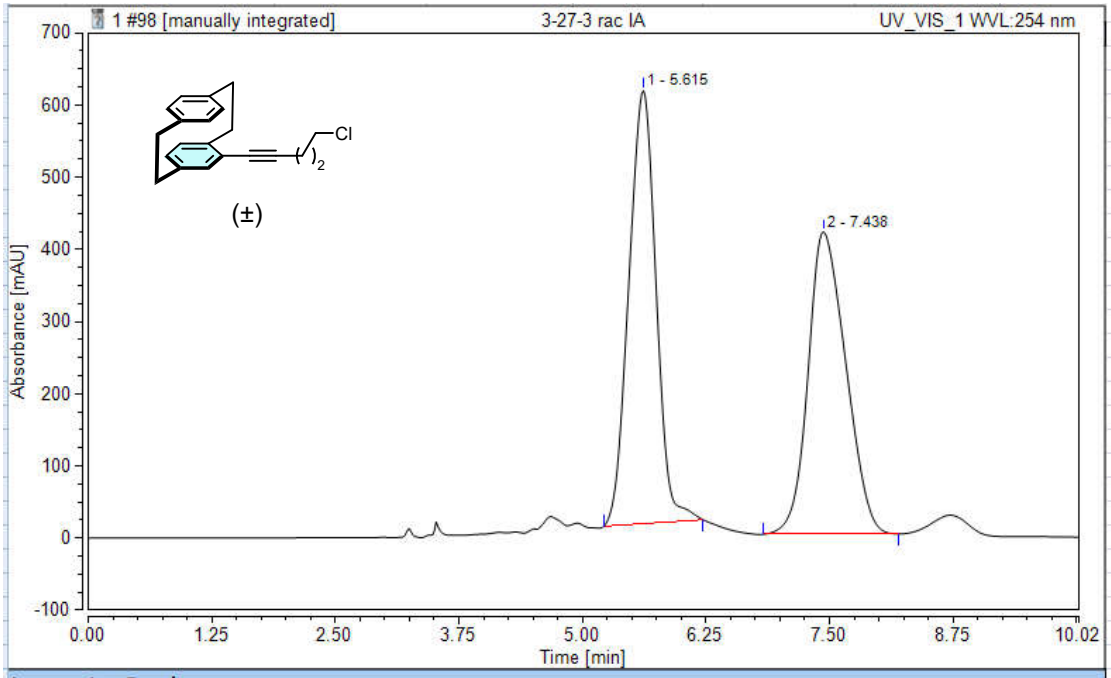
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		33.122	741.392	288.945	49.20	55.86	n.a.
2		40.458	765.600	228.289	50.80	44.14	n.a.
Total:			**1506.991**	**517.234**	**100.00**	**100.00**	



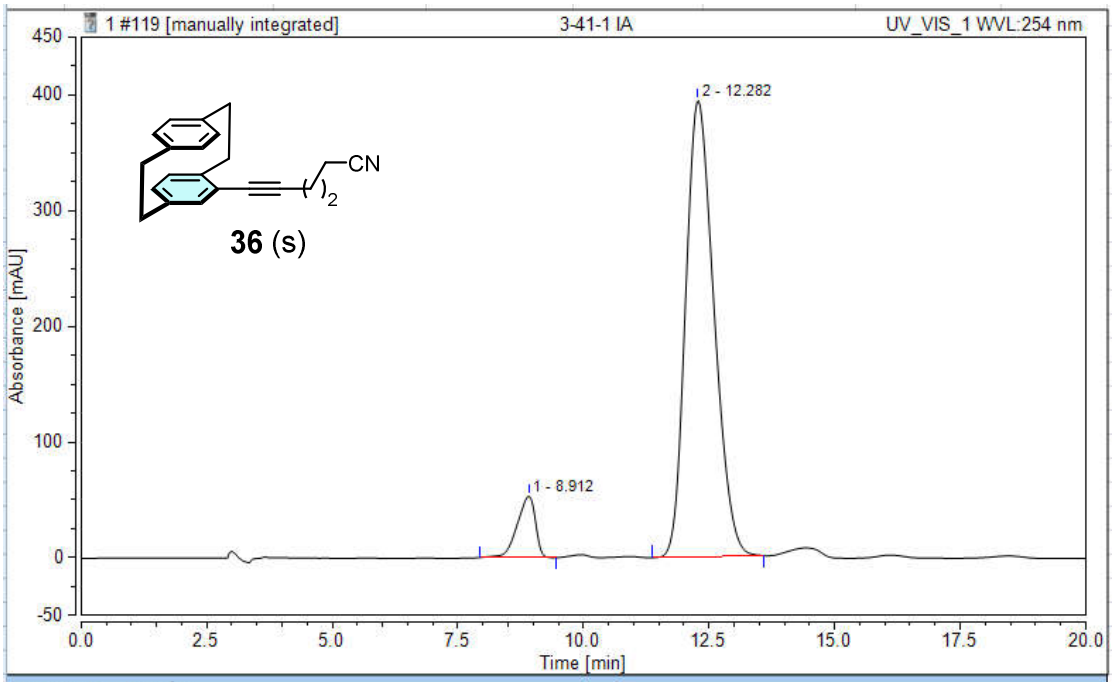
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		5.997	16.662	53.912	9.36	15.87	n.a.
2		7.640	161.330	285.828	90.64	84.13	n.a.
Total:			**177.992**	**339.740**	**100.00**	**100.00**	



Integration Results

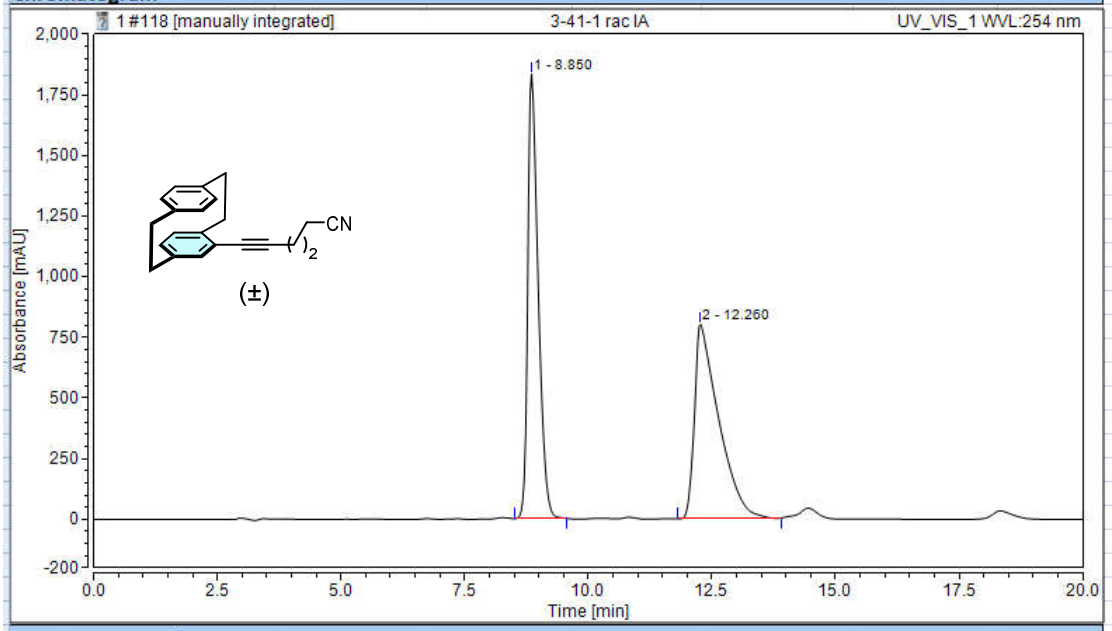
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		5.615	191.731	600.680	50.87	58.91	n.a.
2		7.438	185.156	418.989	49.13	41.09	n.a.
Total:			**376.887**	**1019.668**	**100.00**	**100.00**	



Integration Results

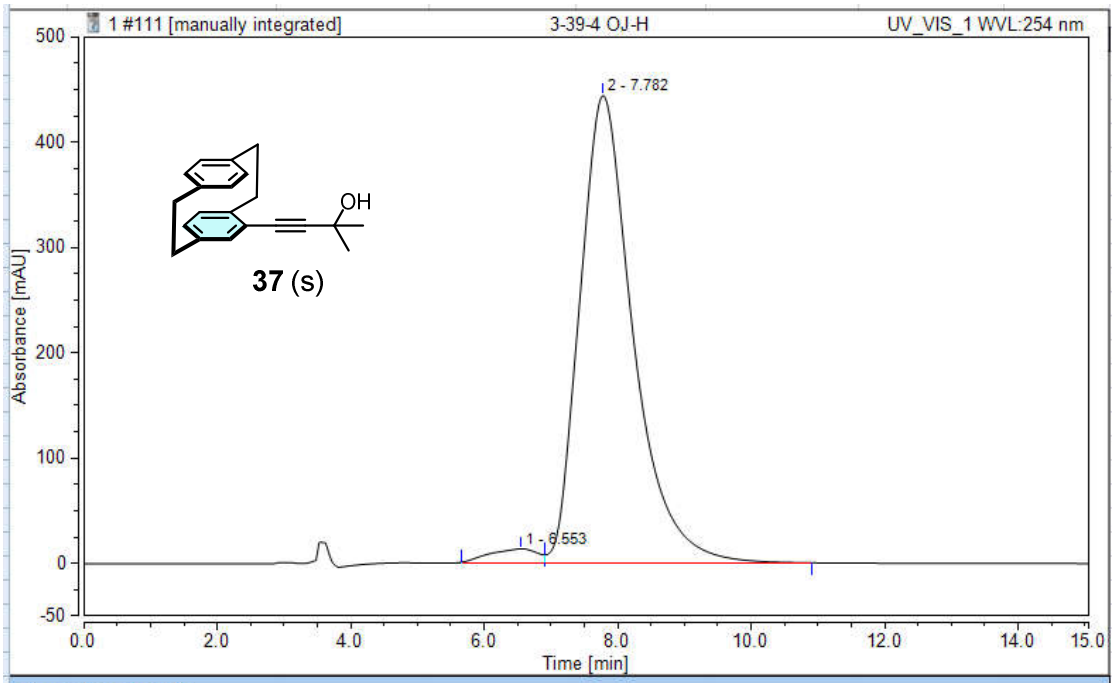
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		8.912	22.292	53.048	7.96	11.86	n.a.
2		12.282	257.687	394.241	92.04	88.14	n.a.
Total:			**279.979**	**447.289**	**100.00**	**100.00**	

Chromatogram



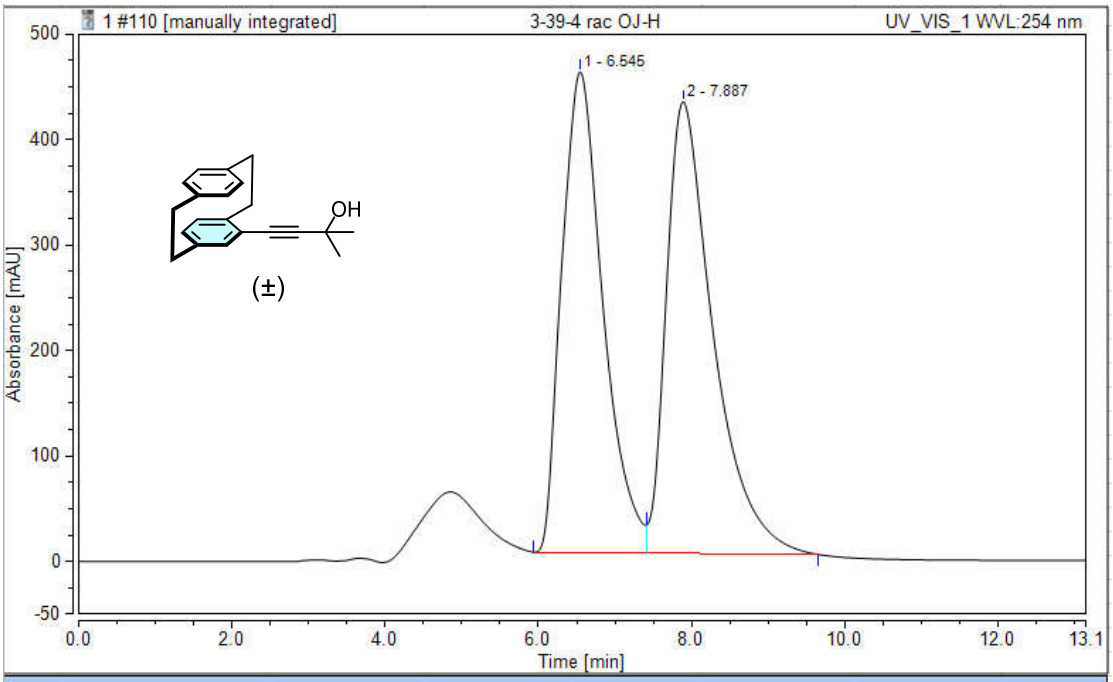
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		8.850	447.758	1832.472	49.71	69.54	n.a.
2		12.260	453.023	802.488	50.29	30.46	n.a.
Total:			**900.781**	**2634.959**	**100.00**	**100.00**	



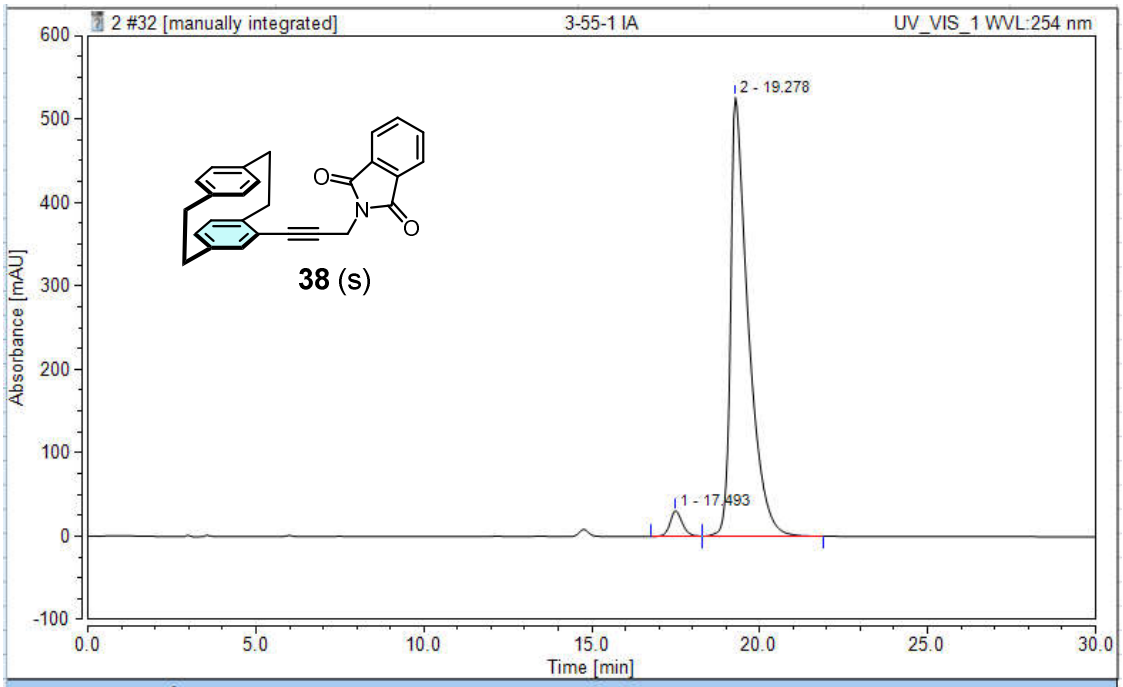
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		6.553	10.976	13.240	2.61	2.90	n.a.
2		7.782	409.423	443.655	97.39	97.10	n.a.
Total:			**420.399**	**456.895**	**100.00**	**100.00**	



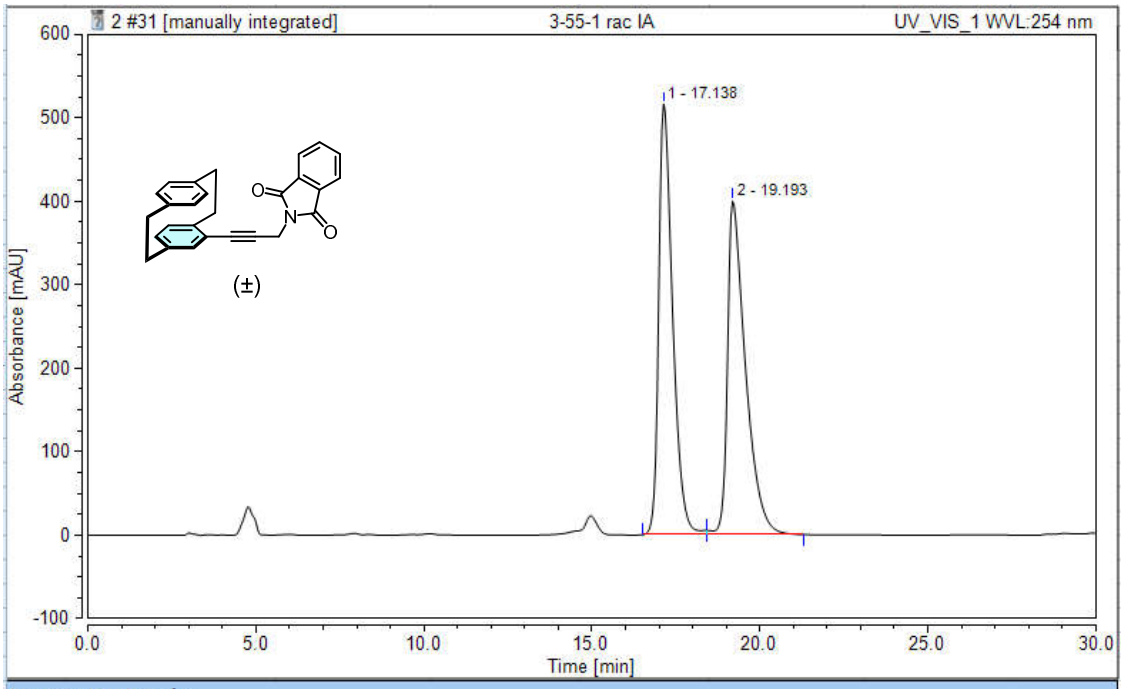
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		6.545	283.464	455.916	48.32	51.57	n.a.
2		7.887	303.163	428.141	51.68	48.43	n.a.
Total:			**586.628**	**884.056**	**100.00**	**100.00**	



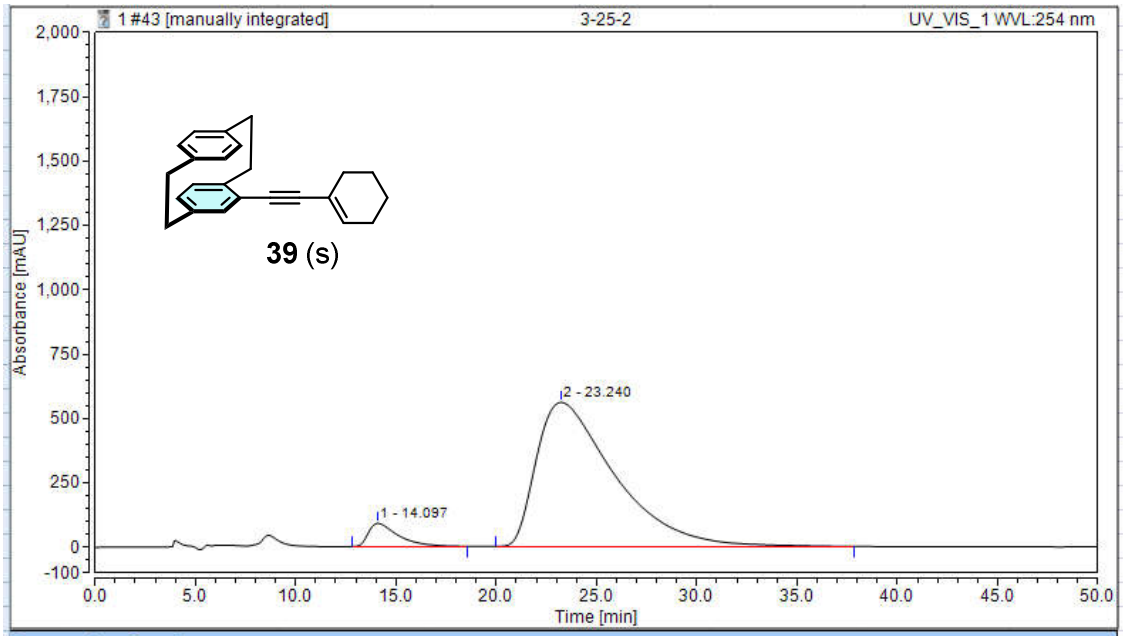
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		17.493	13.220	30.834	3.94	5.53	n.a.
2		19.278	321.970	526.461	96.06	94.47	n.a.
Total:			**335.190**	**557.294**	**100.00**	**100.00**	



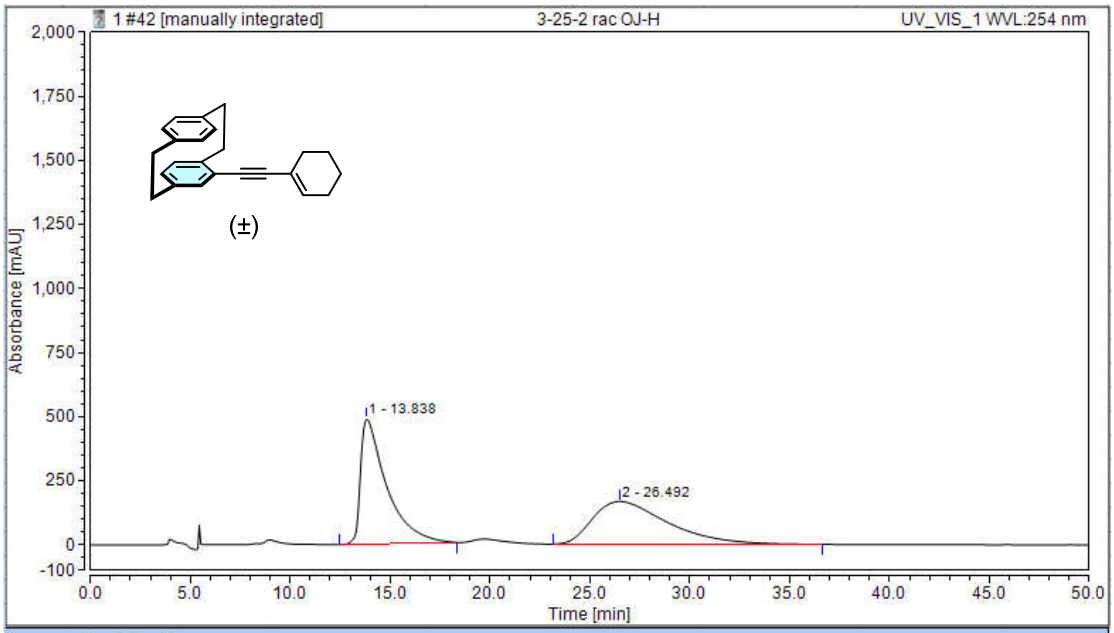
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		17.138	248.394	515.896	50.04	56.31	n.a.
2		19.193	248.022	400.224	49.96	43.69	n.a.
Total:			**496.416**	**916.121**	**100.00**	**100.00**	



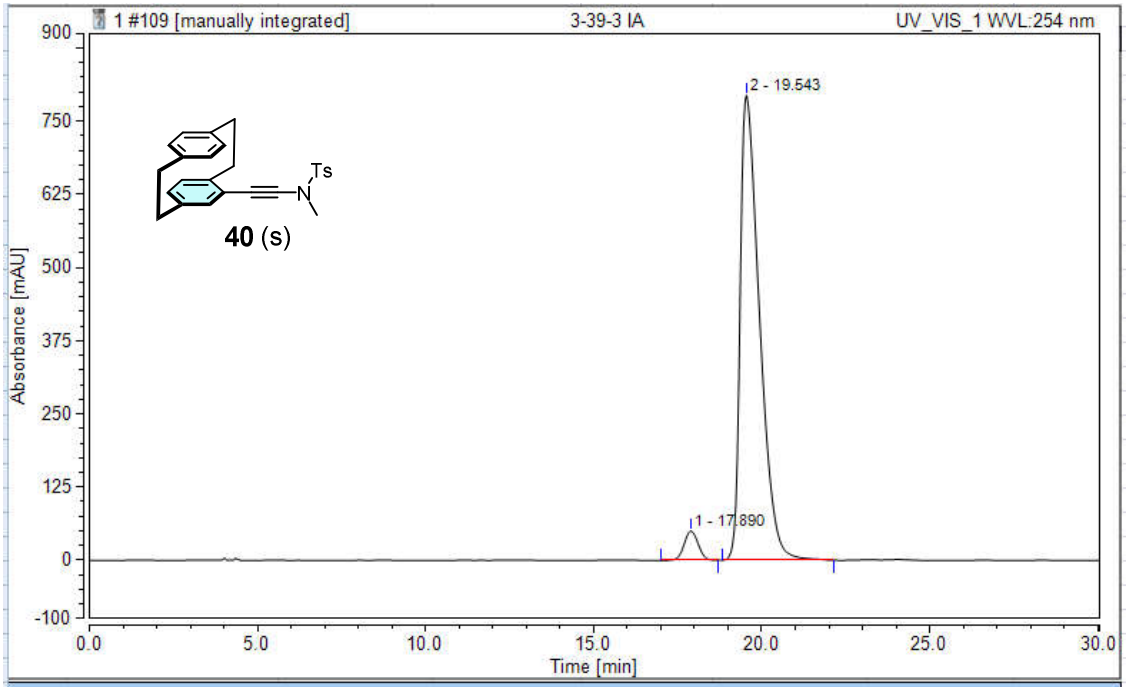
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		14.097	153.689	89.691	5.74	13.83	n.a.
2		23.240	2523.787	559.048	94.26	86.17	n.a.
Total:			**2677.475**	**648.739**	**100.00**	**100.00**	



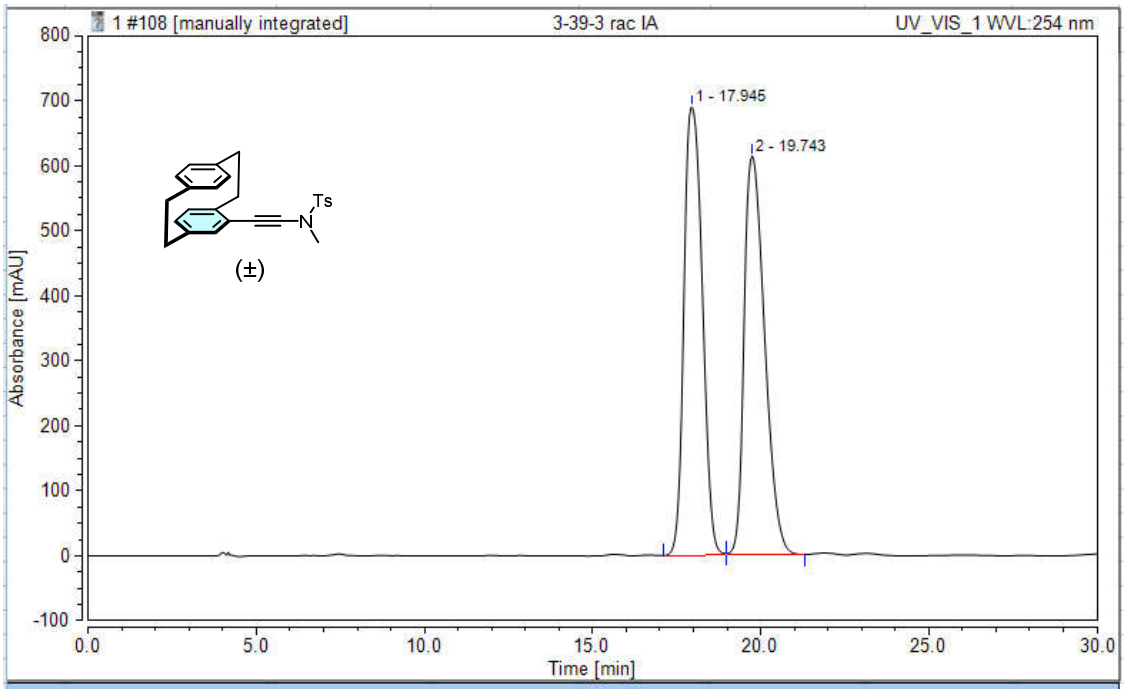
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		13.838	739.132	487.804	50.46	74.54	n.a.
2		26.492	725.682	166.584	49.54	25.46	n.a.
Total:			**1464.814**	**654.387**	**100.00**	**100.00**	



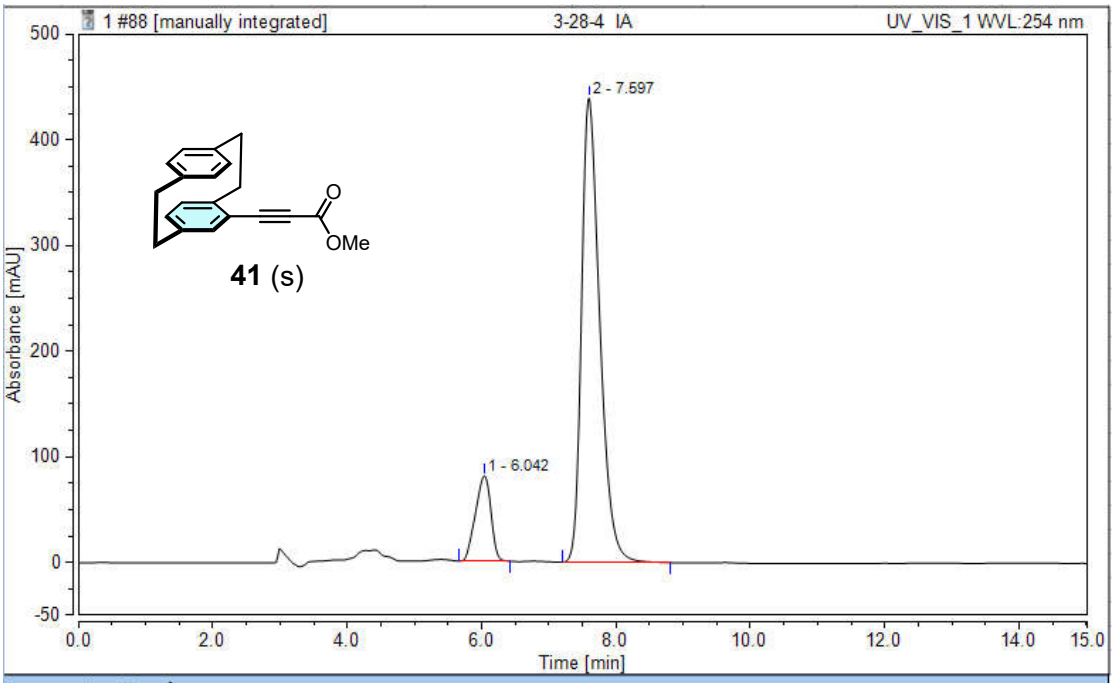
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		17.890	24.191	49.963	4.37	5.92	n.a.
2		19.543	529.447	793.975	95.63	94.08	n.a.
Total:			**553.638**	**843.939**	**100.00**	**100.00**	



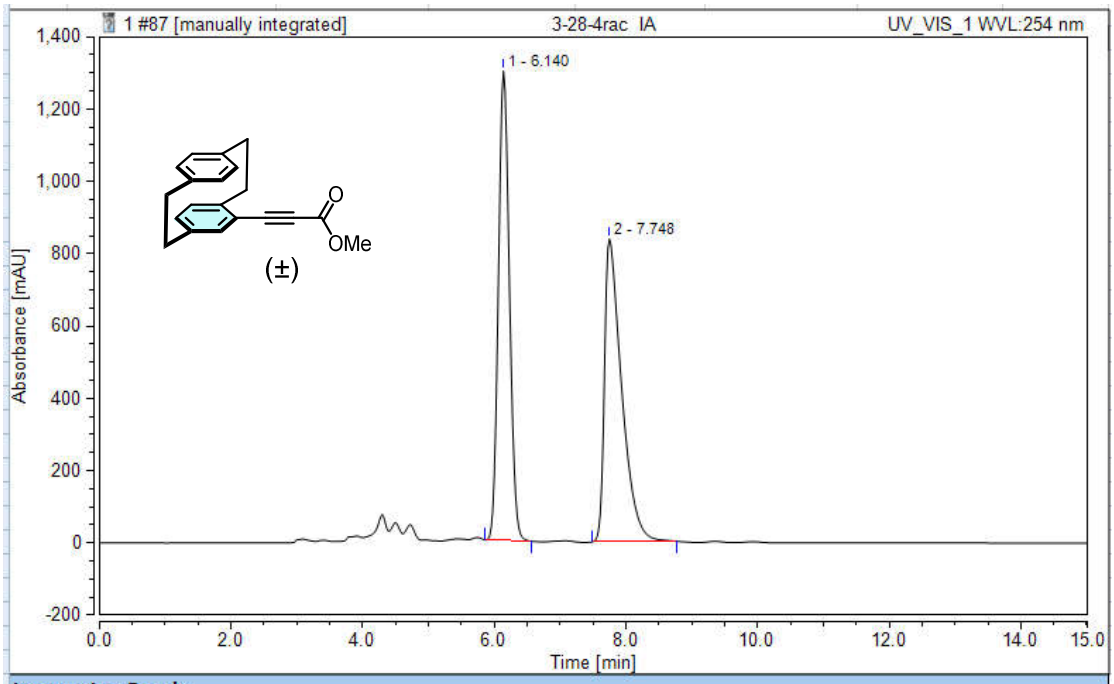
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		17.945	435.908	689.975	50.16	52.91	n.a.
2		19.743	433.206	613.979	49.84	47.09	n.a.
Total:			**869.114**	**1303.953**	**100.00**	**100.00**	



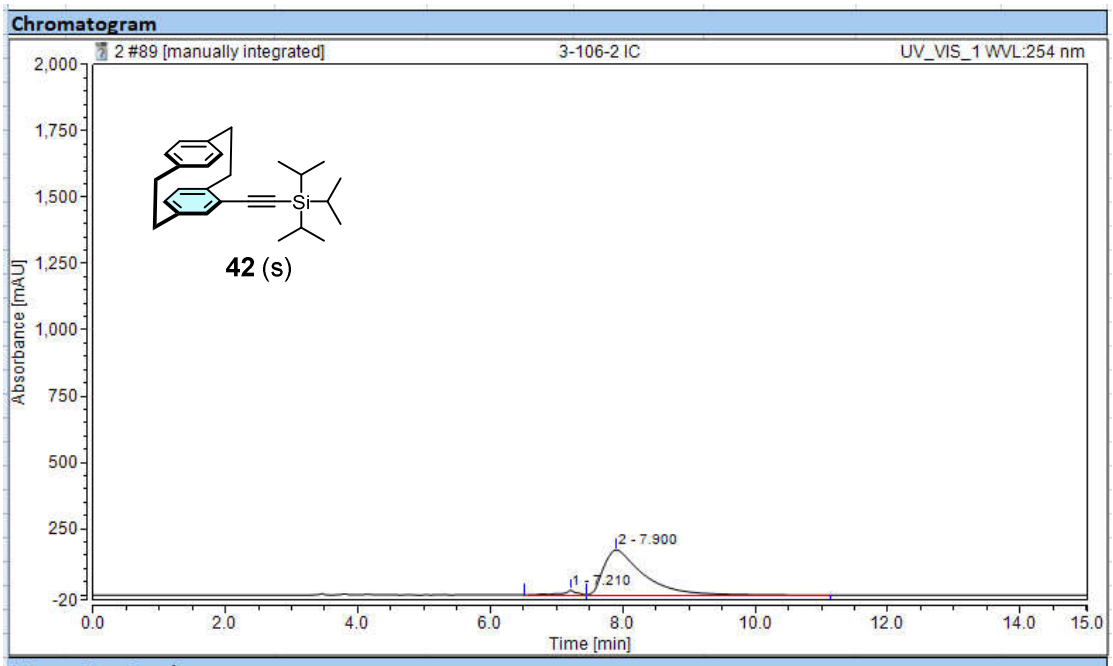
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		6.042	21.568	80.914	13.53	15.55	n.a.
2		7.597	137.807	439.335	86.47	84.45	n.a.
Total:			**159.375**	**520.249**	**100.00**	**100.00**	



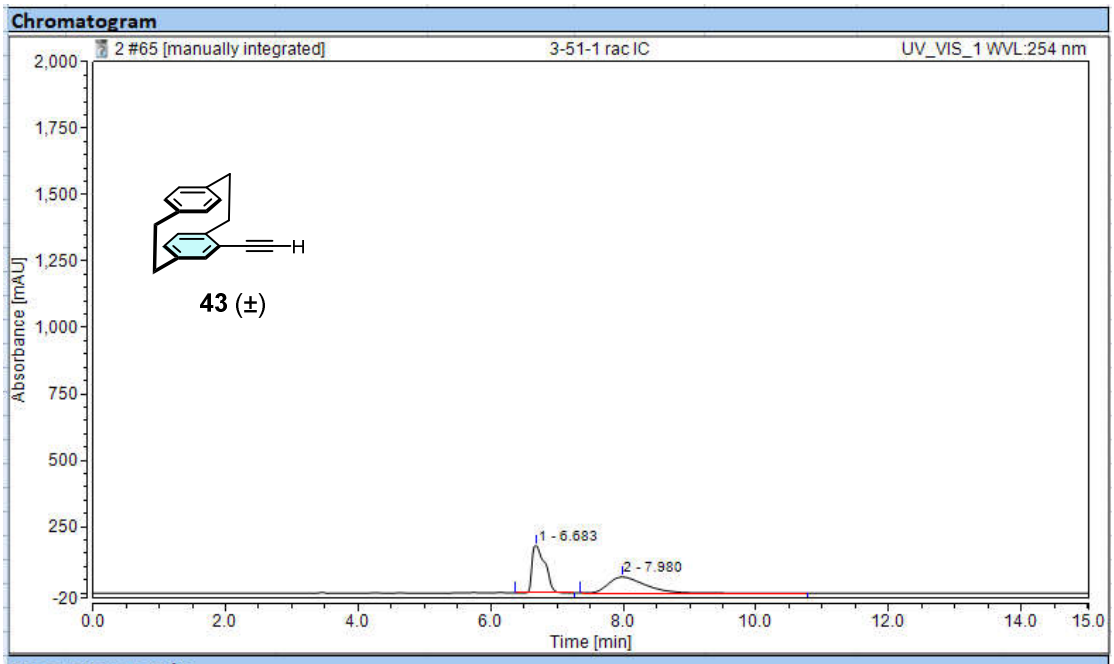
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		6.140	251.399	1298.908	49.87	60.79	n.a.
2		7.748	252.692	837.860	50.13	39.21	n.a.
Total:			**504.091**	**2136.769**	**100.00**	**100.00**	



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		7.210	4.514	18.237	3.67	9.68	n.a.
2		7.900	118.548	170.178	96.33	90.32	n.a.
Total:			**123.062**	**188.414**	**100.00**	**100.00**	

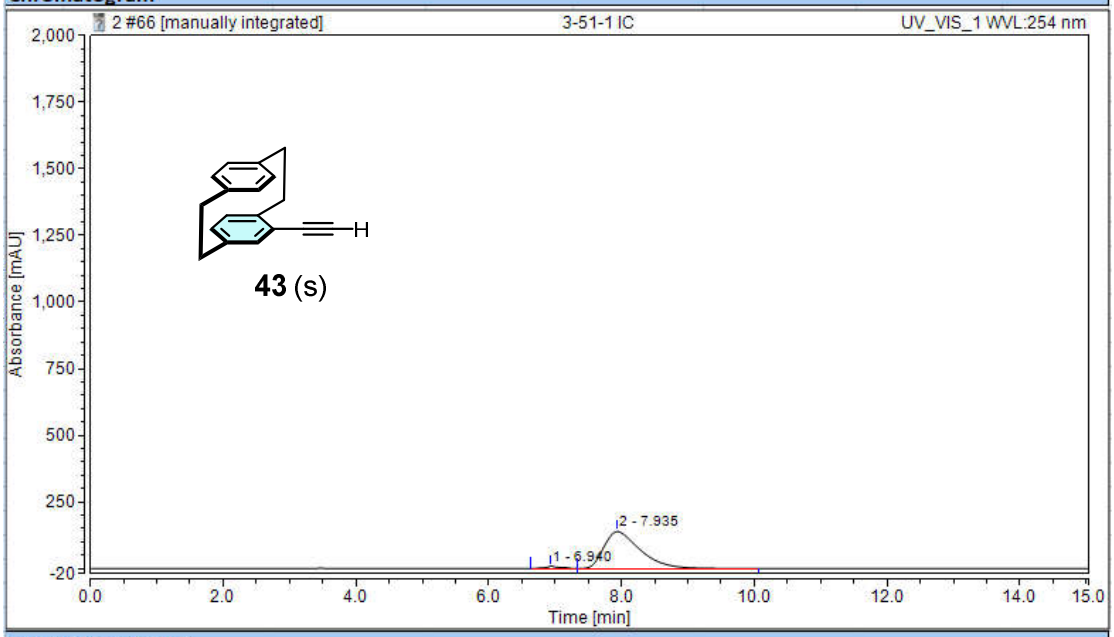


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		6.683	40.409	177.416	51.03	74.60	n.a.
2		7.980	38.774	60.393	48.97	25.40	n.a.
Total:			**79.184**	**237.809**	**100.00**	**100.00**	

Note: The e.e. value of compound **42** was determined in the formation of compound **43**.

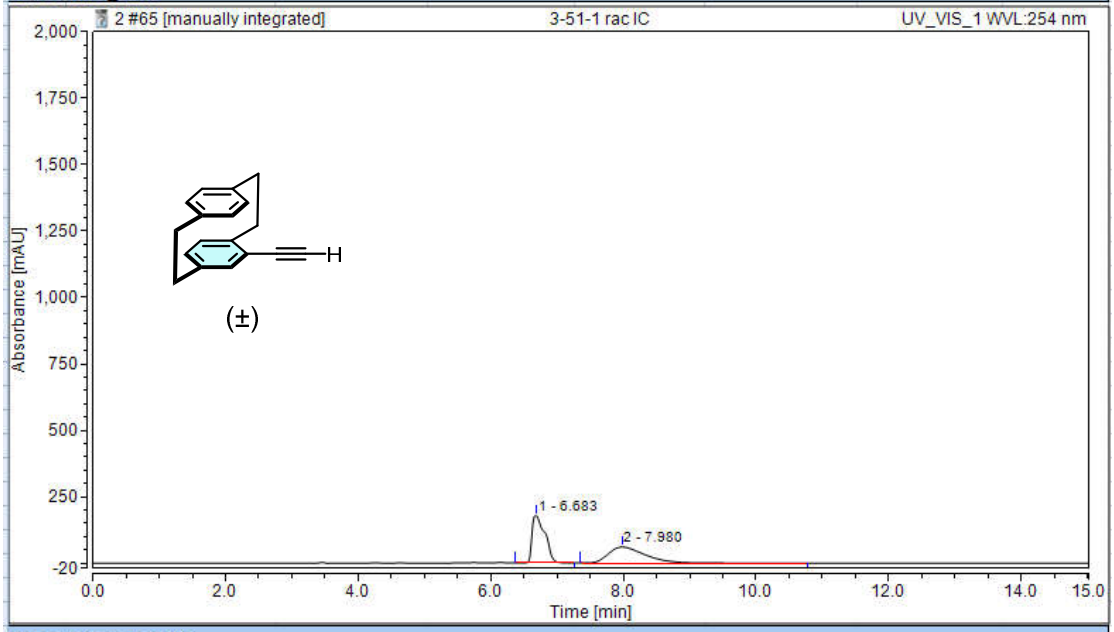
Chromatogram



Integration Results

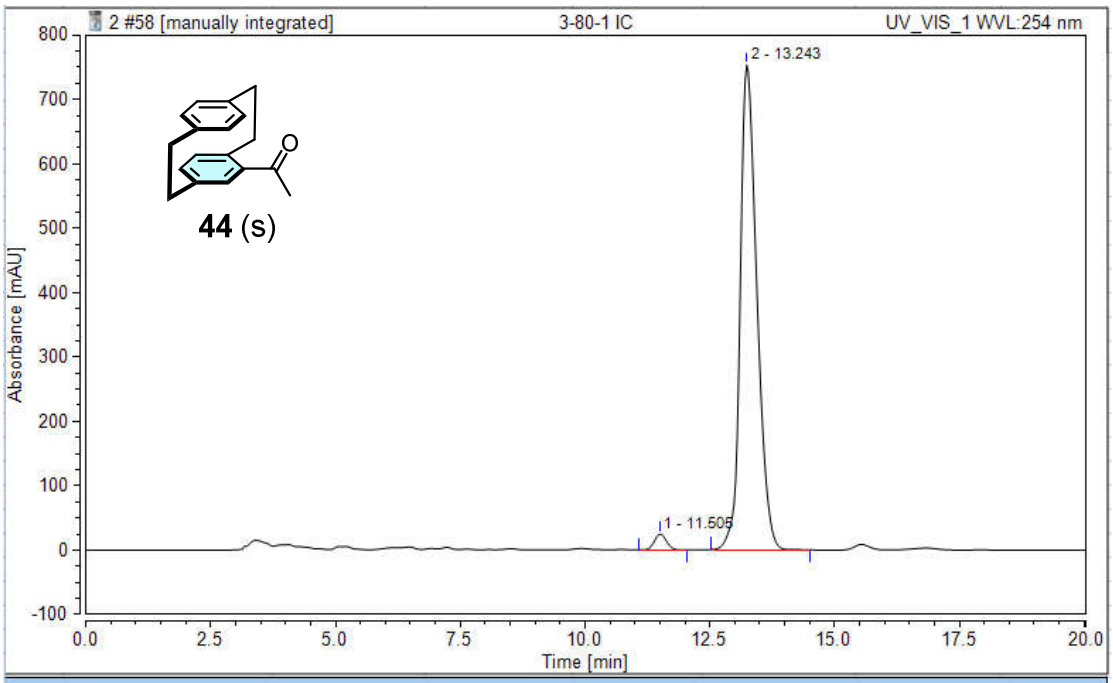
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		6.940	2.112	9.245	2.35	6.25	n.a.
2		7.935	87.813	138.789	97.65	93.75	n.a.
Total:			**89.925**	**148.035**	**100.00**	**100.00**	

Chromatogram



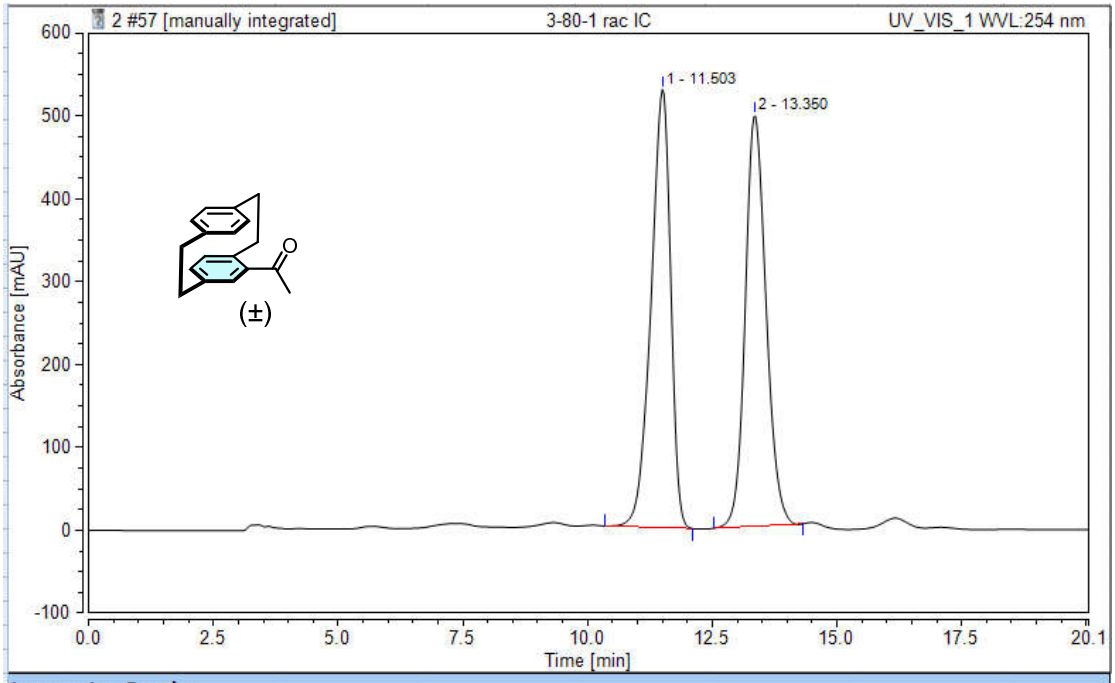
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		6.683	40.409	177.416	51.03	74.60	n.a.
2		7.980	38.774	60.393	48.97	25.40	n.a.
Total:			**79.184**	**237.809**	**100.00**	**100.00**	



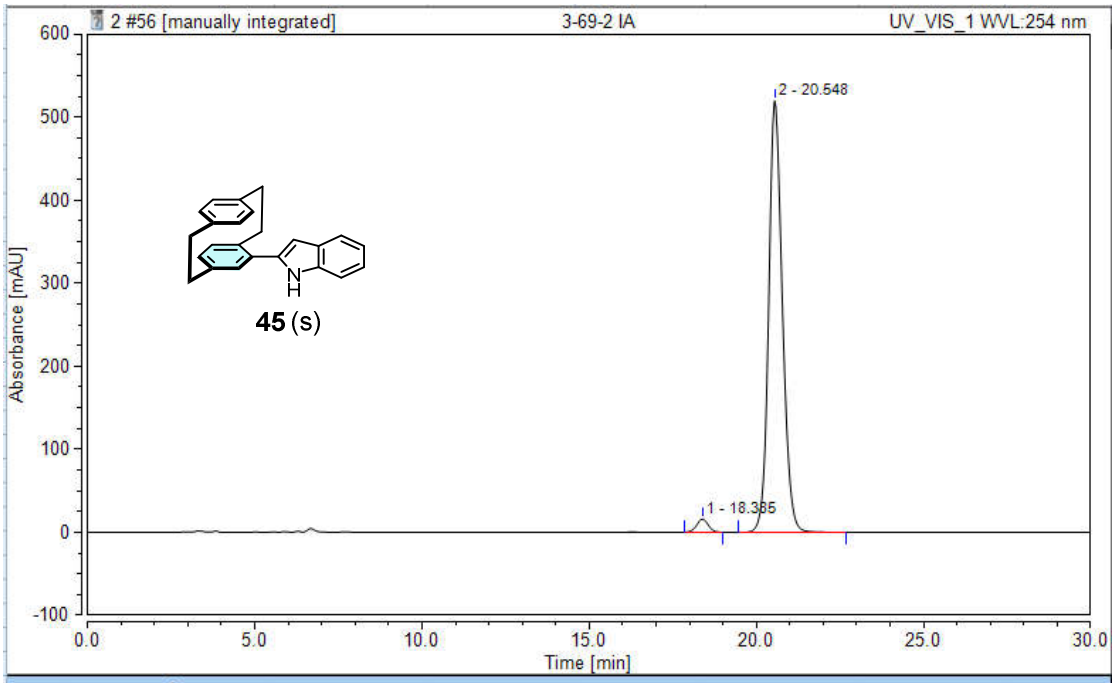
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		11.505	6.965	24.702	2.33	3.17	n.a.
2		13.243	292.070	753.520	97.67	96.83	n.a.
Total:			**299.035**	**778.222**	**100.00**	**100.00**	



Integration Results

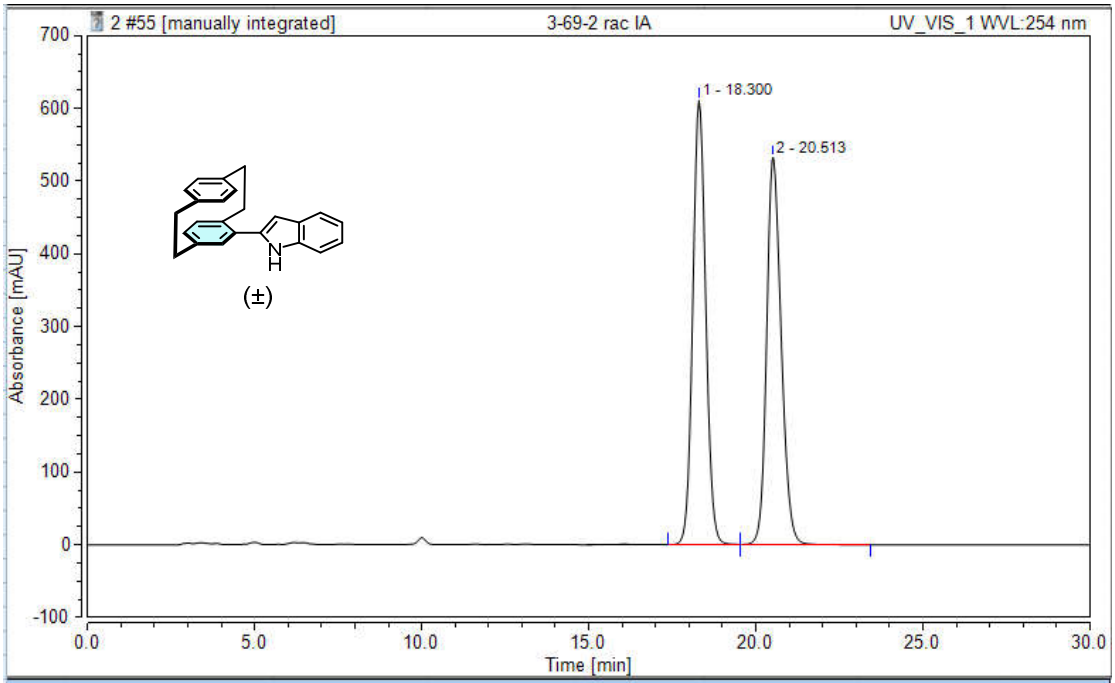
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		11.503	240.864	529.384	50.11	51.61	n.a.
2		13.350	239.809	496.405	49.89	48.39	n.a.
Total:			**480.672**	**1025.789**	**100.00**	**100.00**	



45 (s)

Integration Results

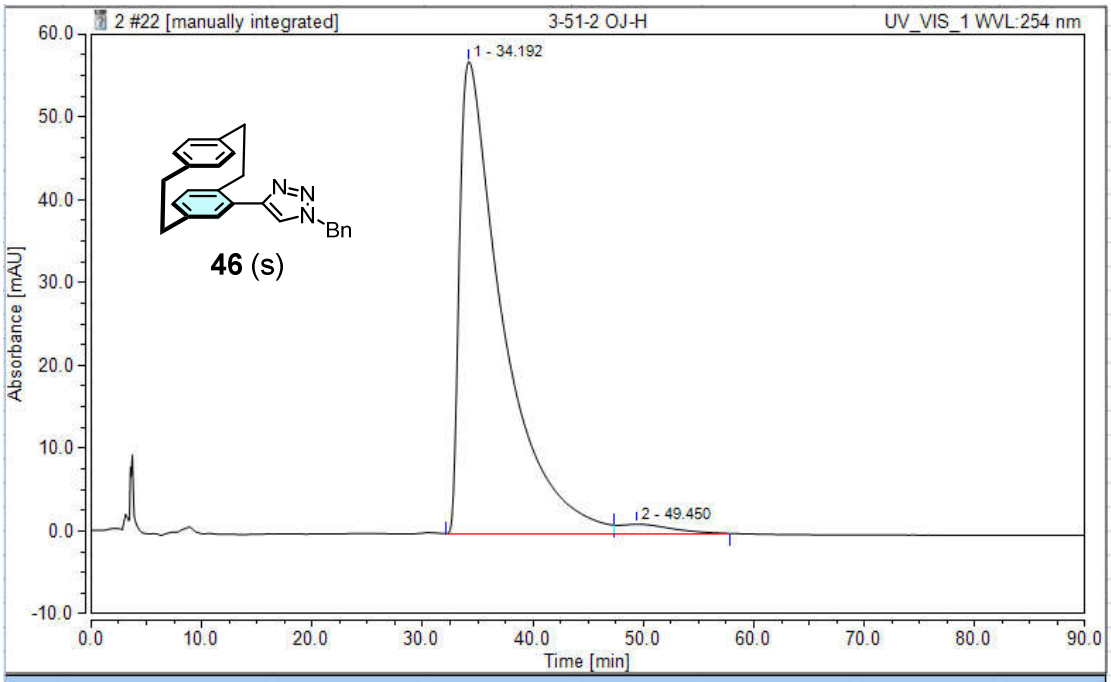
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		18.385	6.575	16.070	2.60	3.00	n.a.
2		20.548	246.671	519.946	97.40	97.00	n.a.
Total:			**253.246**	**536.015**	**100.00**	**100.00**	



(±)

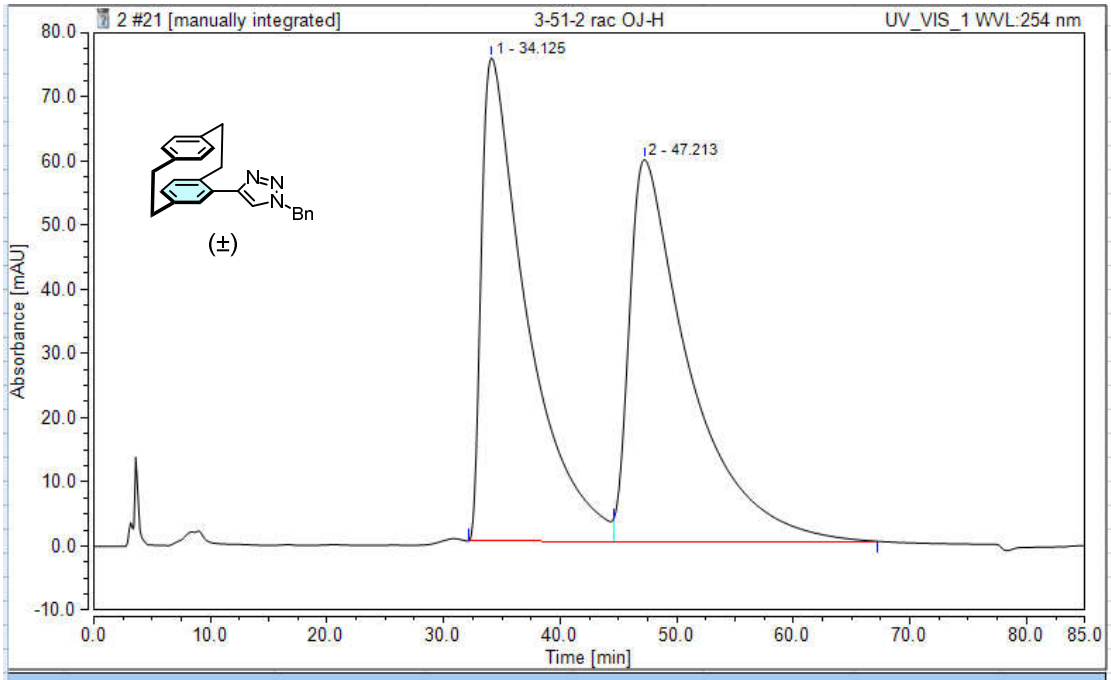
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		18.300	275.203	611.489	50.58	53.45	n.a.
2		20.513	268.859	532.582	49.42	46.55	n.a.
Total:			**544.062**	**1144.071**	**100.00**	**100.00**	



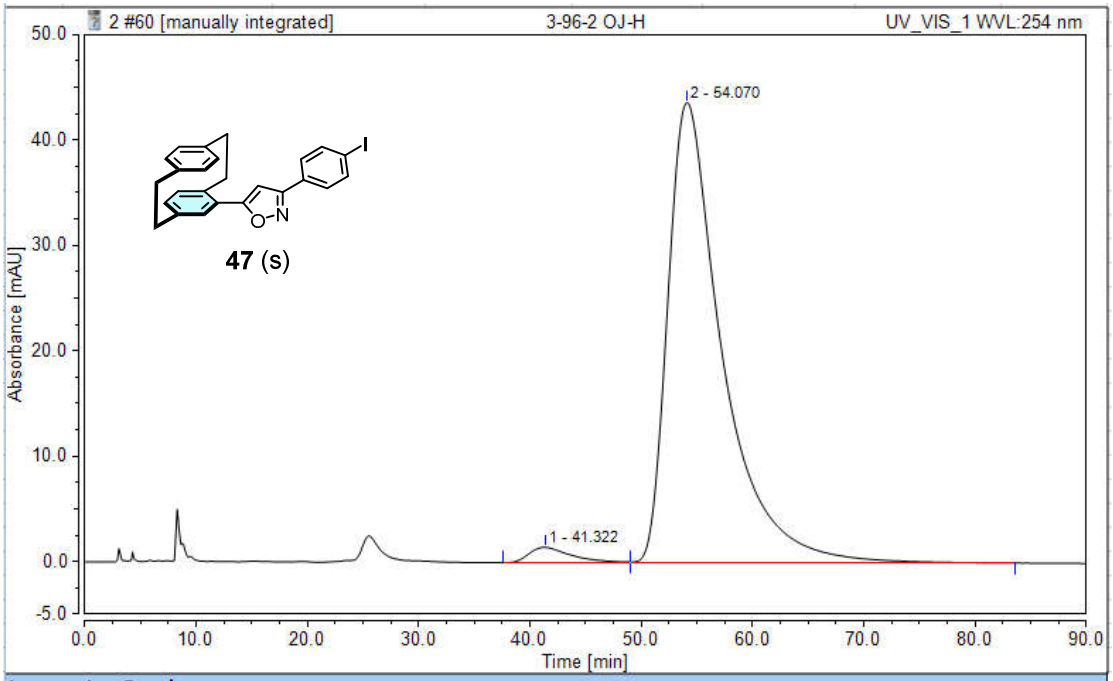
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		34.192	256.196	56.996	97.63	98.06	n.a.
2		49.450	6.219	1.129	2.37	1.94	n.a.
Total:			**262.415**	**58.126**	**100.00**	**100.00**	



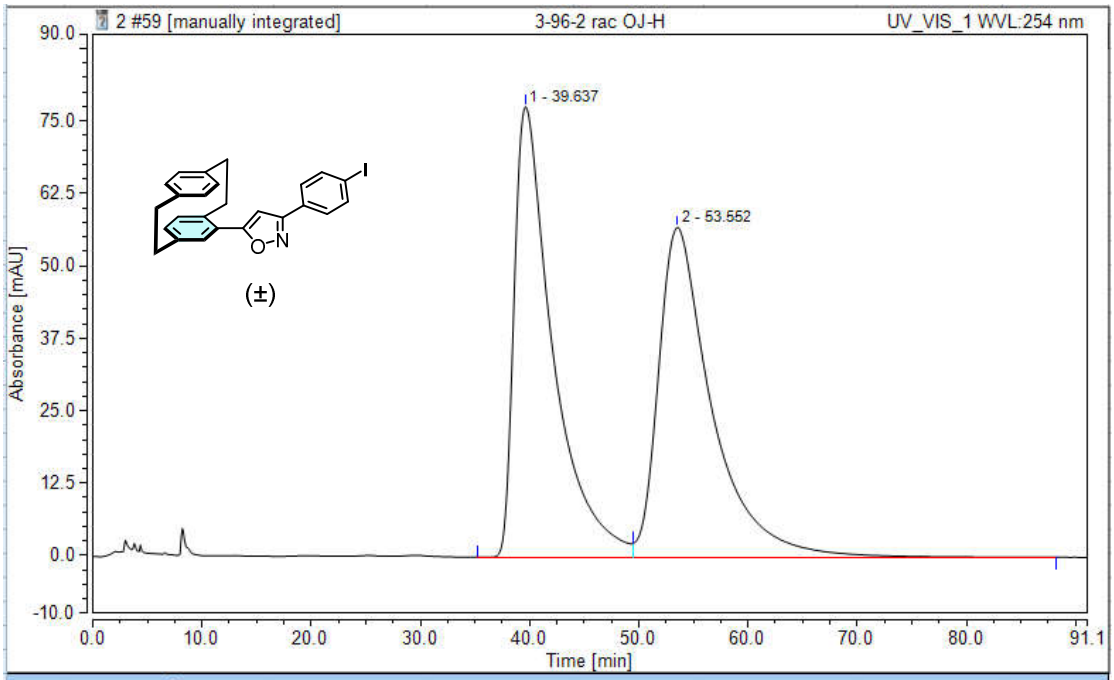
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		34.125	339.393	75.285	48.97	55.86	n.a.
2		47.213	353.631	59.493	51.03	44.14	n.a.
Total:			**693.024**	**134.777**	**100.00**	**100.00**	



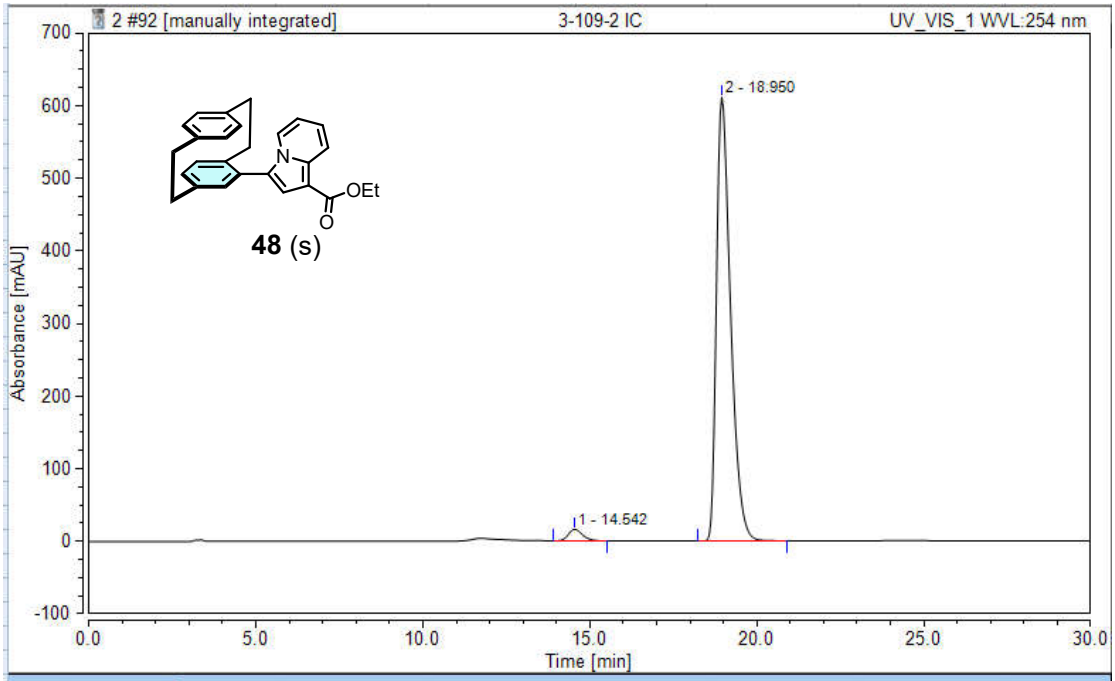
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		41.322	6.463	1.461	2.55	3.24	n.a.
2		54.070	246.895	43.665	97.45	96.76	n.a.
Total:			**253.359**	**45.126**	**100.00**	**100.00**	



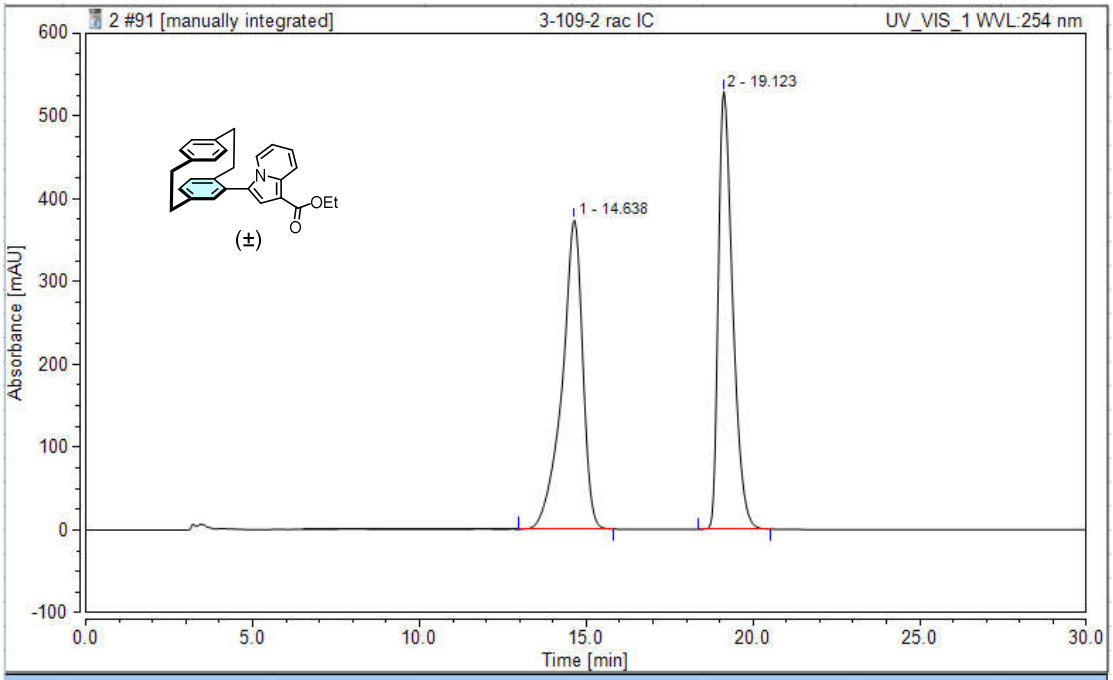
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		39.637	318.056	77.805	49.67	57.74	n.a.
2		53.552	322.315	56.938	50.33	42.26	n.a.
Total:			**640.370**	**134.743**	**100.00**	**100.00**	



Integration Results

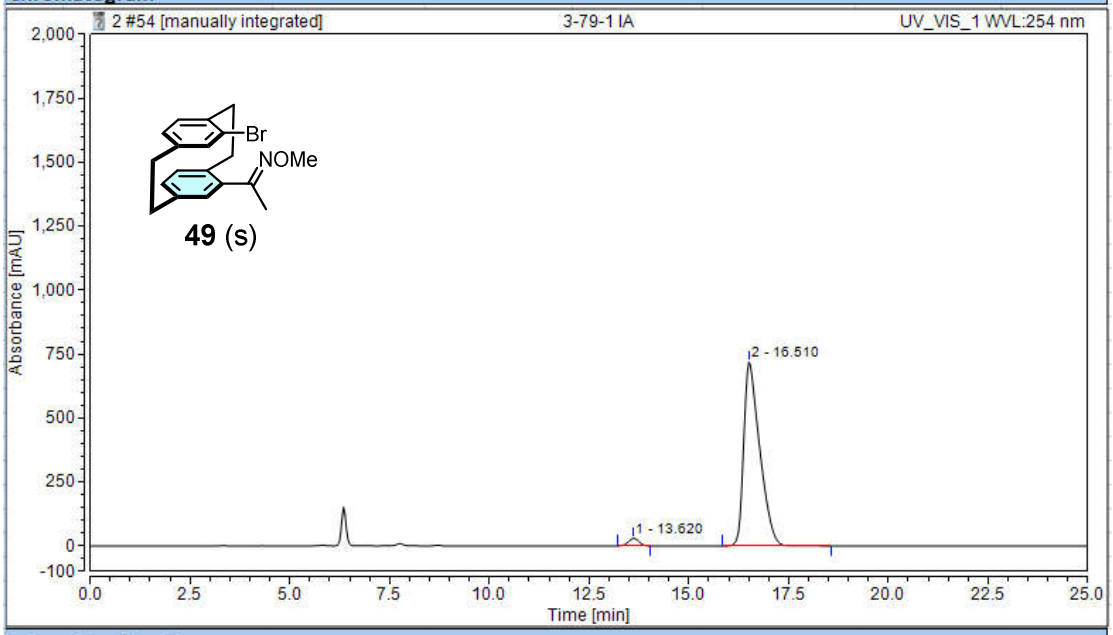
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		14.542	7.824	15.946	2.55	2.54	n.a.
2		18.950	298.494	611.247	97.45	97.46	n.a.
Total:			**306.318**	**627.193**	**100.00**	**100.00**	



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		14.638	266.501	373.878	50.25	41.43	n.a.
2		19.123	263.832	528.585	49.75	58.57	n.a.
Total:			**530.333**	**902.463**	**100.00**	**100.00**	

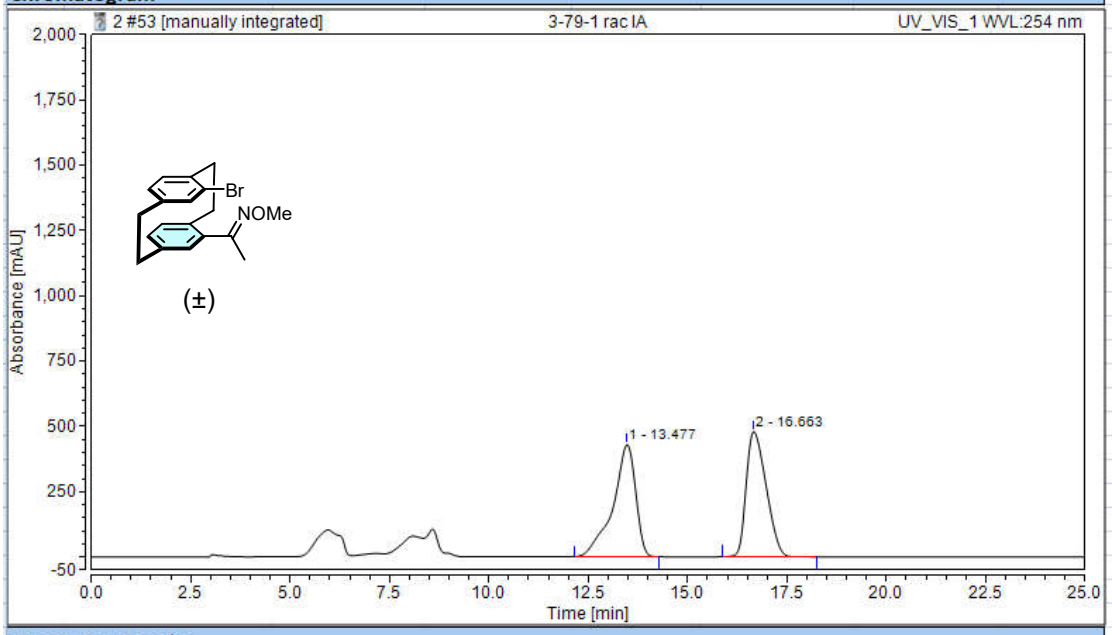
Chromatogram



Integration Results

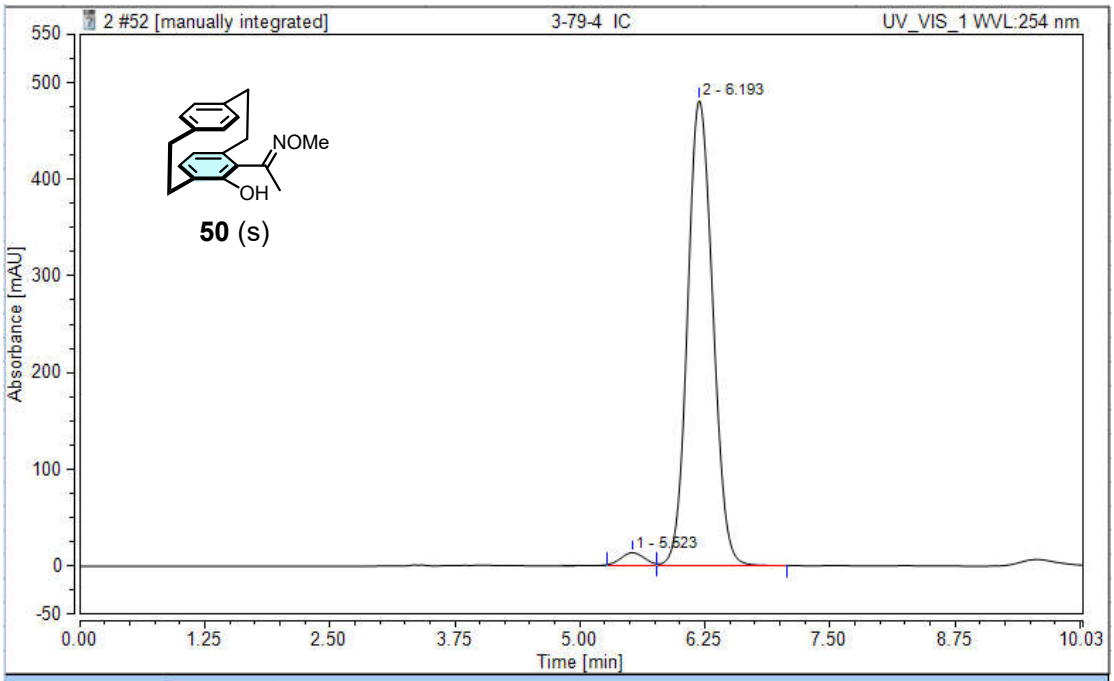
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		13.620	9.204	29.677	2.68	3.96	n.a.
2		16.510	334.412	720.437	97.32	96.04	n.a.
Total:			**343.616**	**750.114**	**100.00**	**100.00**	

Chromatogram



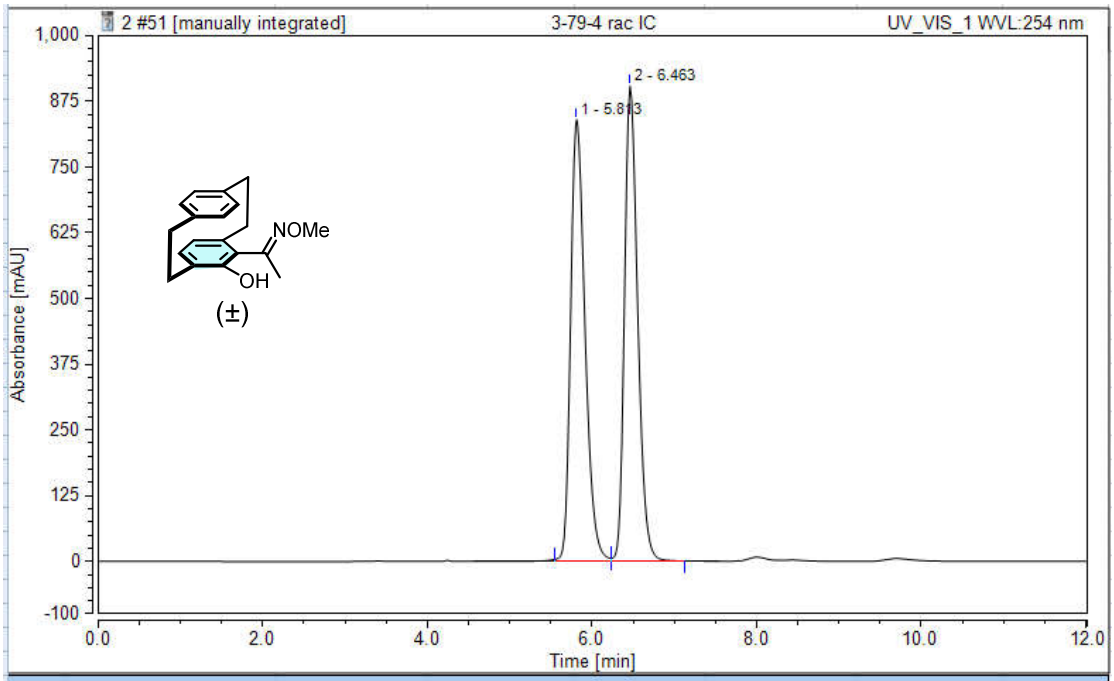
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		13.477	284.723	429.795	50.55	47.24	n.a.
2		16.663	278.516	480.074	49.45	52.76	n.a.
Total:			**563.240**	**909.868**	**100.00**	**100.00**	



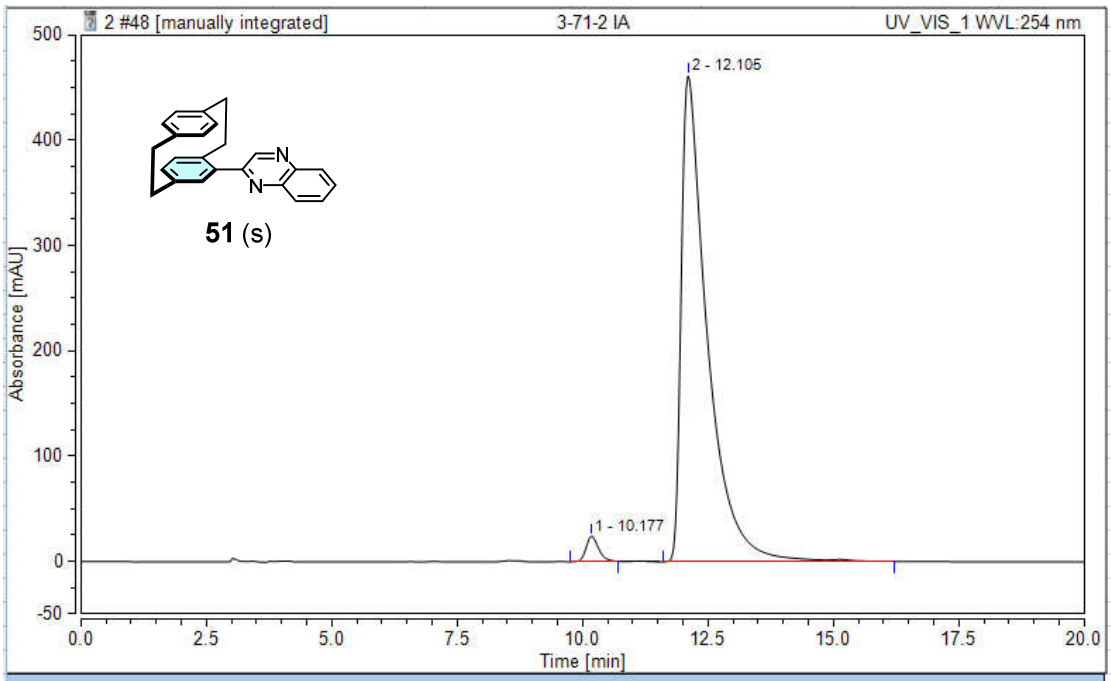
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		5.523	3.754	13.511	2.60	2.73	n.a.
2		6.193	140.402	481.169	97.40	97.27	n.a.
Total:			**144.157**	**494.679**	**100.00**	**100.00**	



Integration Results

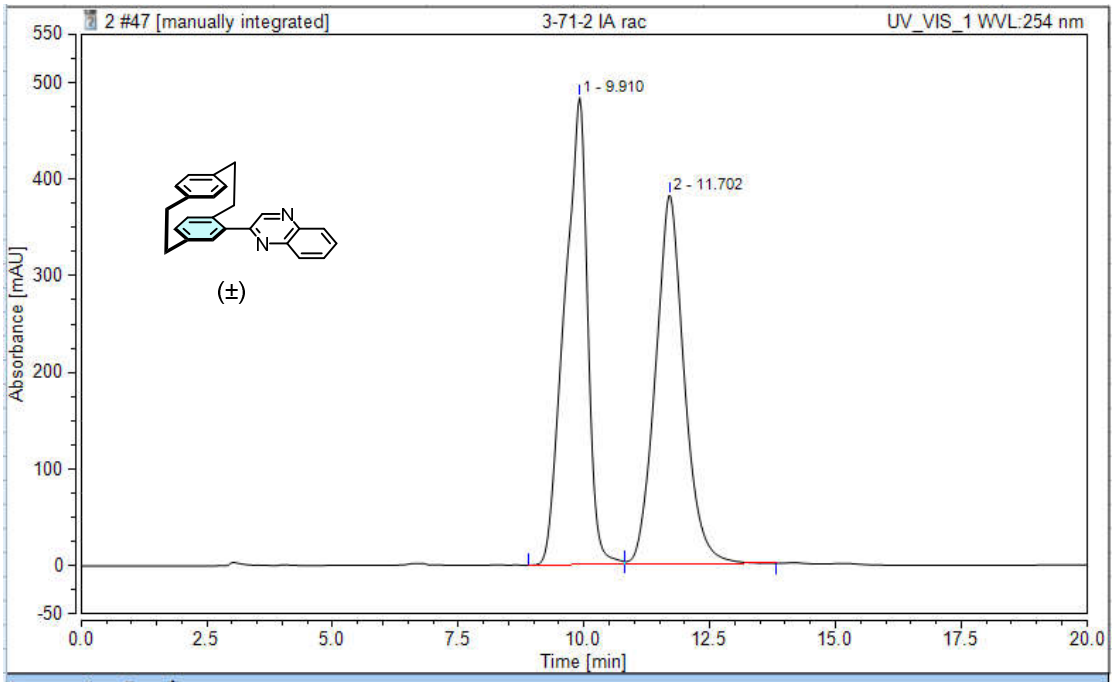
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		5.813	170.095	839.896	50.33	48.16	n.a.
2		6.463	167.840	904.023	49.67	51.84	n.a.
Total:			**337.935**	**1743.919**	**100.00**	**100.00**	



51 (s)

Integration Results

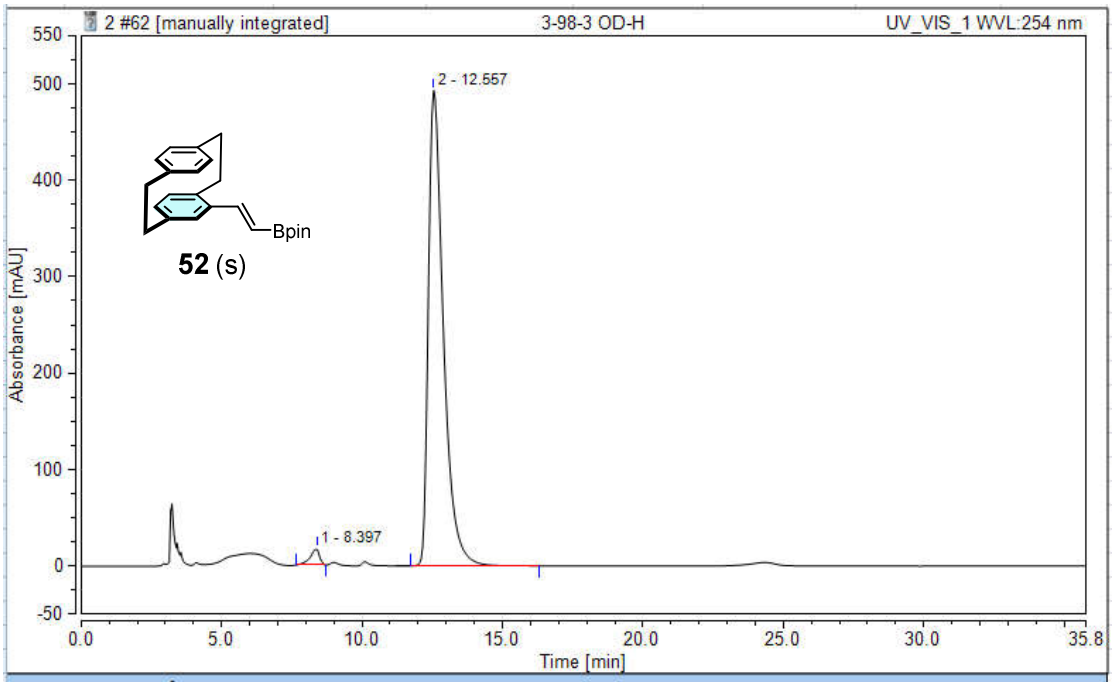
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		10.177	7.120	24.336	2.49	5.00	n.a.
2		12.105	278.534	462.076	97.51	95.00	n.a.
Total:			**285.654**	**486.412**	**100.00**	**100.00**	



(±)

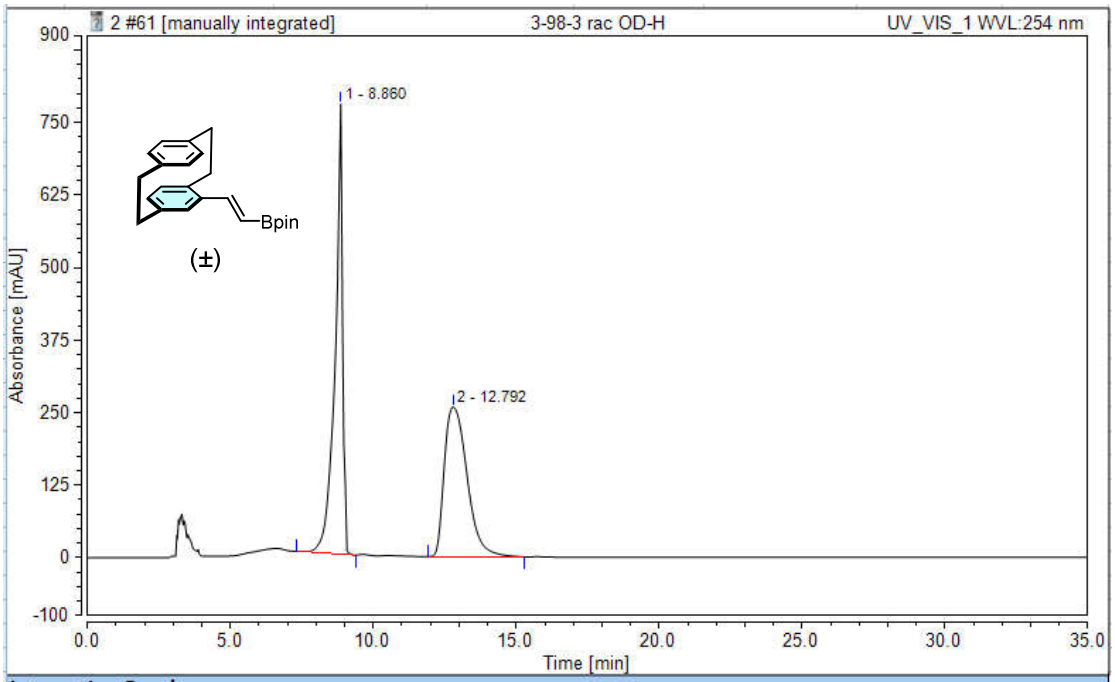
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		9.910	257.252	483.464	50.52	55.87	n.a.
2		11.702	252.005	381.928	49.48	44.13	n.a.
Total:			**509.256**	**865.392**	**100.00**	**100.00**	



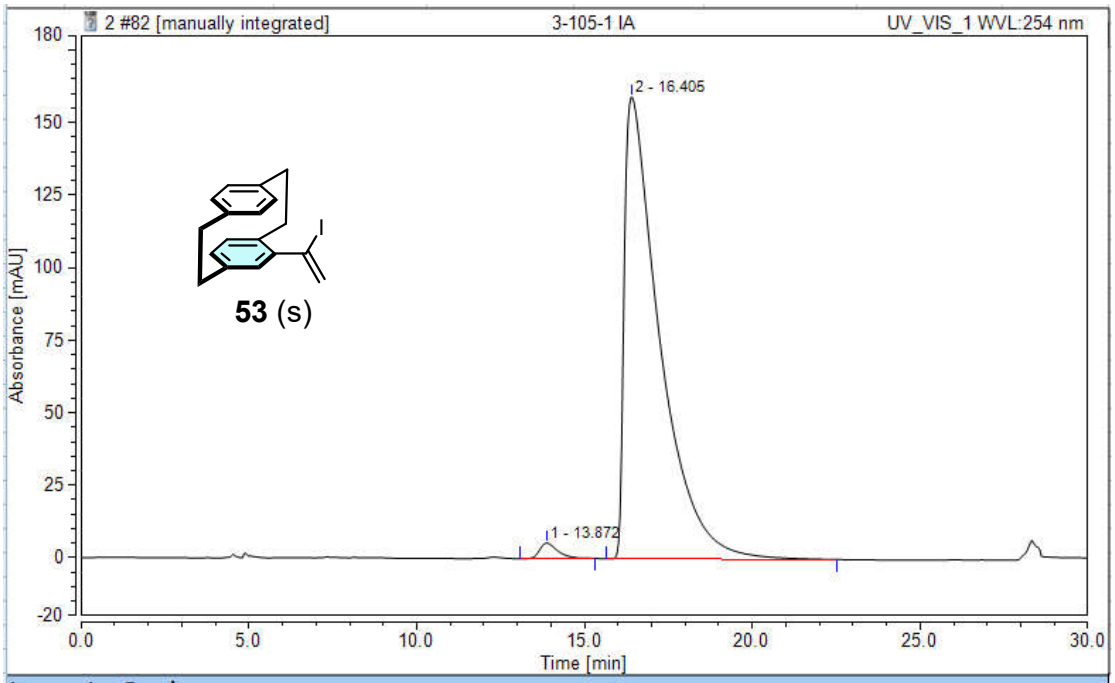
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		8.397	6.415	17.329	2.06	3.40	n.a.
2		12.557	305.587	492.960	97.94	96.60	n.a.
Total:			**312.002**	**510.288**	**100.00**	**100.00**	



Integration Results

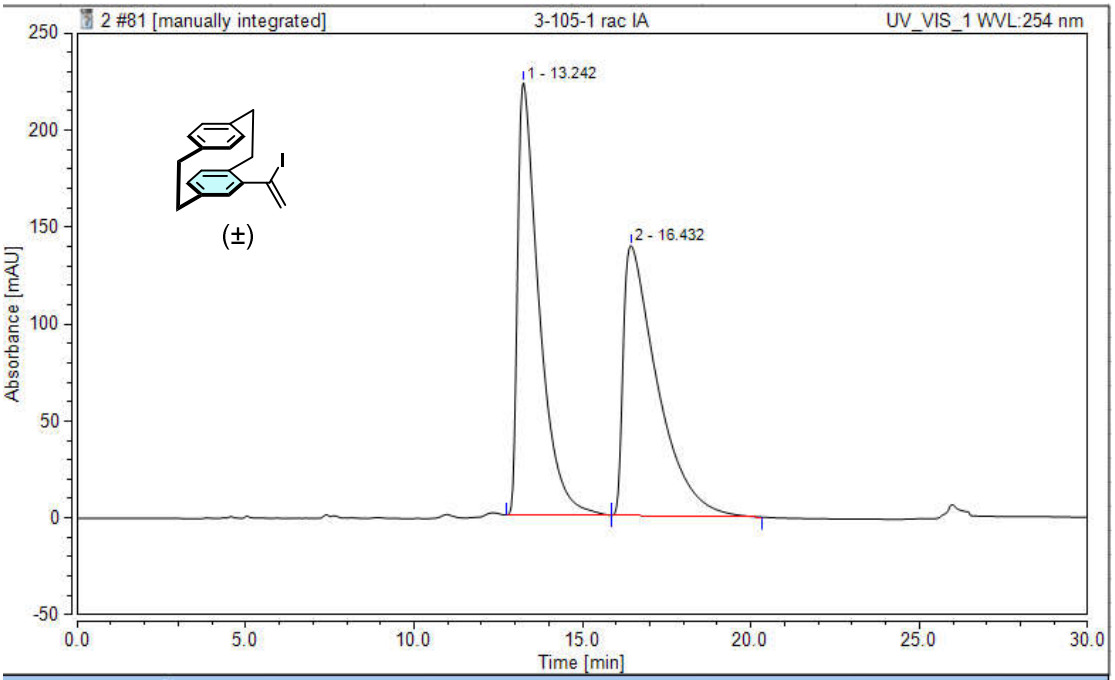
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		8.860	232.209	775.993	49.31	75.05	n.a.
2		12.792	238.713	258.028	50.69	24.95	n.a.
Total:			**470.922**	**1034.021**	**100.00**	**100.00**	



53 (s)

Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		13.872	3.341	5.350	1.69	3.25	n.a.
2		16.405	194.028	159.325	98.31	96.75	n.a.
Total:			**197.369**	**164.675**	**100.00**	**100.00**	

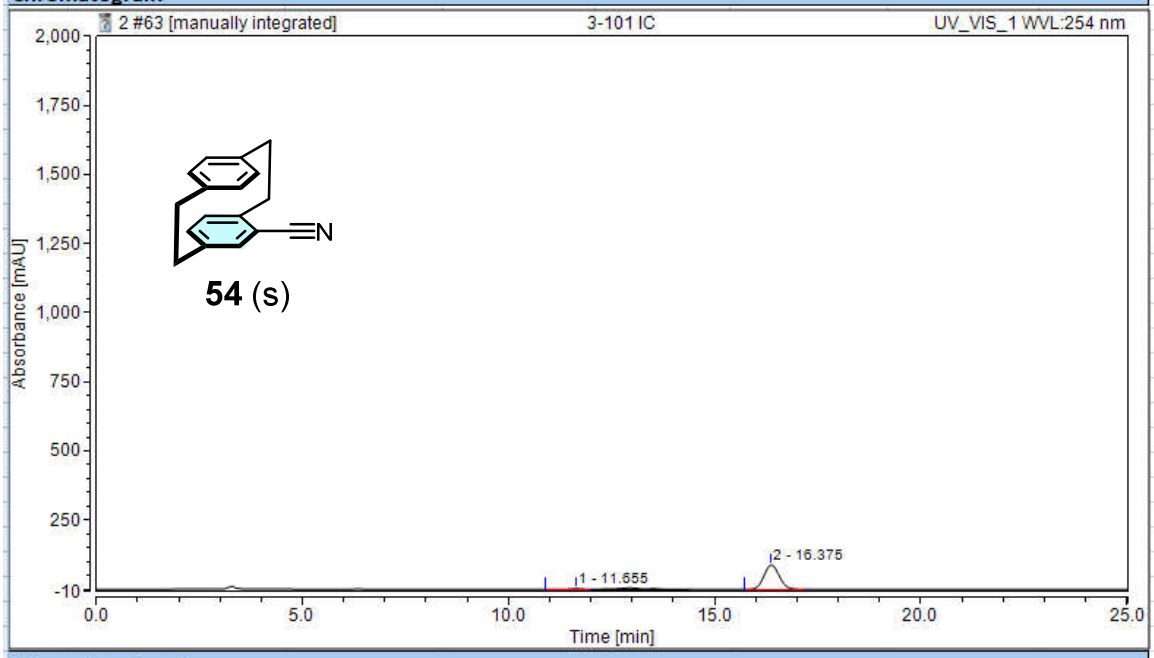


(±)

Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		13.242	164.318	222.854	50.24	61.55	n.a.
2		16.432	162.768	139.215	49.76	38.45	n.a.
Total:			**327.086**	**362.069**	**100.00**	**100.00**	

Chromatogram

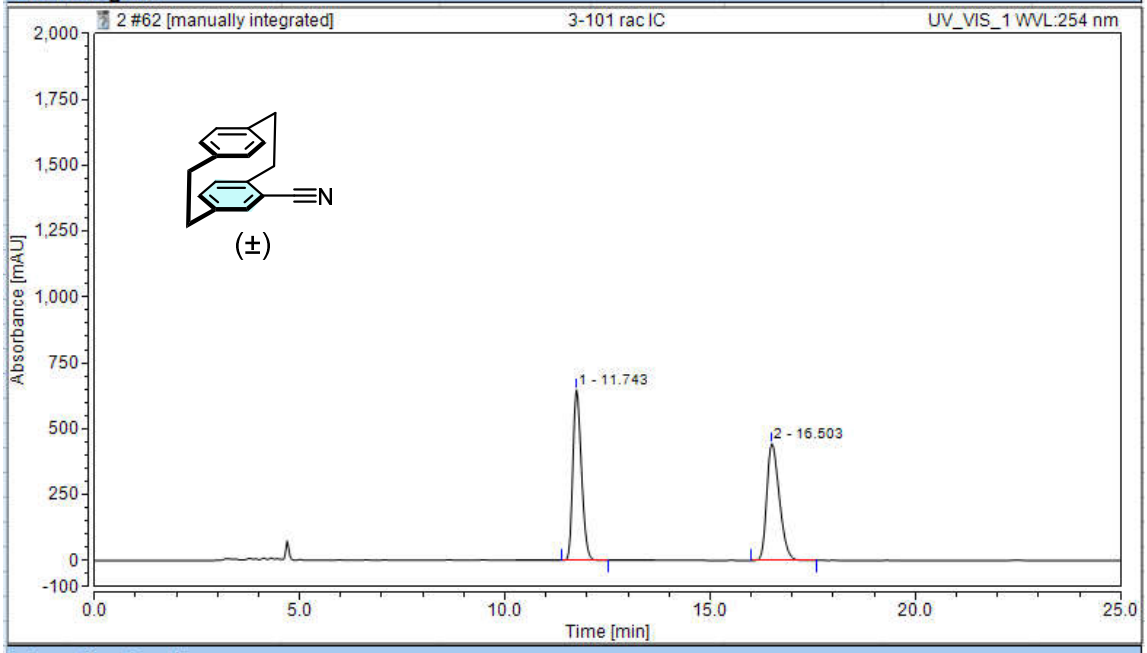


54 (s)

Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		11.655	0.695	2.165	1.83	2.41	n.a.
2		16.375	37.377	87.612	98.17	97.59	n.a.
Total:			**38.073**	**89.777**	**100.00**	**100.00**	

Chromatogram



(±)

Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		11.743	156.628	647.540	49.93	59.32	n.a.
2		16.503	157.089	444.108	50.07	40.68	n.a.
Total:			**313.717**	**1091.648**	**100.00**	**100.00**	

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