
Copper-catalysed synthesis of chiral alkynyl cyclopropanes using enantioconvergent radical cross-coupling of cyclopropyl halides with terminal alkynes

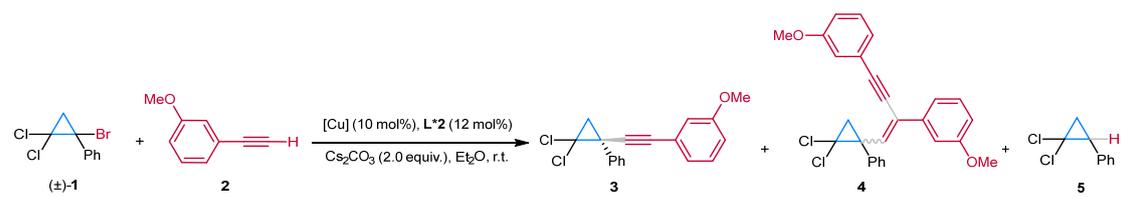
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Supplementary Tables for experiments

Supplementary Table 1 | Screening of copper salts^a

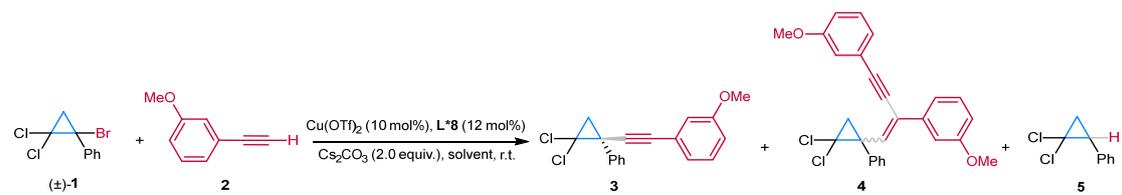


Entry	[Cu]	Yield (%) ^b			E.e. of 3 (%) ^c
		3 ^d	4	5	
1	CuTc	5 (22)	10	8	-68
2	CuSCN	8 (27)	14	8	-68
3	CuI	5 (29)	6	6	-68
4	Cu(PPh ₃) ₃ Br	8 (47)	6	3	-68
5	Cu(MeCN) ₄ PF ₆	5 (29)	5	7	-68
6	Cu(HCOO) ₂	30 (88)	2	2	-68
7	CuOAc	45 (68)	17	4	-68
8	Cu(OAc) ₂	44 (92)	4	ND	-68
9	CuOTf·1/2Ph	24 (69)	8	3	-68
10	Cu(OTf)₂	44 (96)	2	ND	-68

^aStandard reaction conditions: racemic cyclopropyl bromide **1** (0.10 mmol), 3-ethynylanisole **2** (1.5 equiv.), [Cu] (10 mol%), L***2** (12 mol%) and Cs₂CO₃ (2.0 equiv.) in Et₂O (1.0 mL) at room temperature (r.t.) for 3 d under argon. ^bYield was based on ¹H NMR analysis of the crude product using 1,3,5-trimethoxybenzene as an internal standard. ^cE.e. values were based on HPLC analysis.

^dThe percentage of **3** among the three products is shown in parenthesis. ND, not determined.

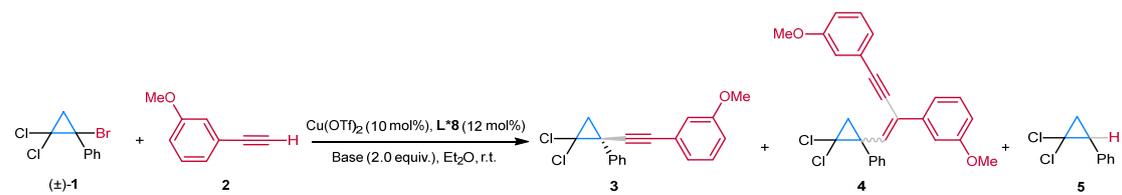
Supplementary Table 3 | Screening of solvents^a



Entry	Solvent	Yield (%) ^b			E.e. of 3 (%) ^c
		3	4	5	
1	CH ₂ Cl ₂	95	1	ND	80
2	EtOAc	95	ND	ND	84
3	Cyclohexane	67	1	ND	88
4	MeCN	95	1	ND	80
5	Toluene	95	1	ND	88
6	PhCF ₃	95	1	ND	88
7	THF	90	2	5	84
8	Et₂O	95	1	ND	90

^aStandard reaction conditions: racemic cyclopropyl bromide **1** (0.10 mmol), 3-ethynylanisole **2** (1.5 equiv.), Cu(OTf)₂ (10 mol%), L***8** (12 mol%) and Cs₂CO₃ (2.0 equiv.) in solvent (1.0 mL) at room temperature (r.t.) for 3 d under argon. ^bYield was based on ¹H NMR analysis of the crude product using 1,3,5-trimethoxybenzene as an internal standard. ^cE.e. values were based on HPLC analysis. ND, Not determined.

Supplementary Table 4 | Screening of base additives^a



Entry	Base	Yield (%) ^b			E.e. of 3 (%) ^c
		3	4	5	
1	LiO ^t Bu	27	2	ND	88
2	KO ^t Bu	50	2	3	90
3	NaOH	95	2	ND	88
4	Cs₂CO₃	95	1	ND	90
5	K ₂ CO ₃	27	4	ND	90
6	NaOAc	ND	ND	ND	ND
7	DIPEA	Trace	ND	ND	ND
8	DBU	Trace	ND	6	ND

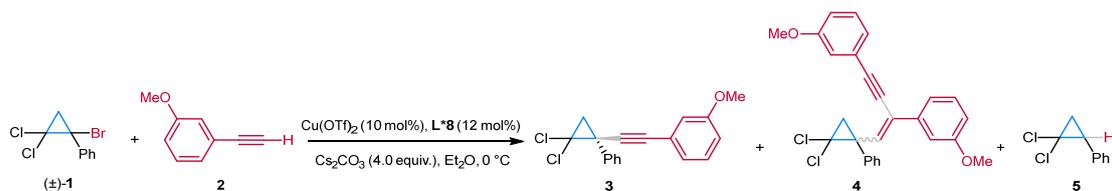
^aStandard reaction conditions: racemic cyclopropyl bromide **1** (0.10 mmol), 3-ethynylanisole **2** (1.5 equiv.), Cu(OTf)₂ (10 mol%), L***8** (12 mol%) and base (2.0 equiv.) in Et₂O (1.0 mL) at room temperature (r.t.) for 3 d under argon. ^bYield was based on ¹H NMR analysis of the crude product using 1,3,5-trimethoxybenzene as an internal standard. ^cE.e. values were based on HPLC analysis. ND, Not determined.

Supplementary Table 5 | Screening of reaction temperatures^a

Entry	Temp.	Yield (%) ^c			E.e. of 3 (%) ^d
		3	4	5	
1 ^b	r.t.	95	1	ND	90
2	0 °C	65	ND	ND	92
3	-10 °C	Trace	ND	ND	ND

^aStandard reaction conditions: racemic cyclopropyl bromide **1** (0.10 mmol), 3-ethynylanisole **2** (1.5 equiv.), Cu(OTf)₂ (10 mol%), L***8** (12 mol%) and Cs₂CO₃ (2.0 equiv.) in Et₂O (1.0 mL) for 6 d under argon. ^bFor 3 d. ^cYield was based on ¹H NMR analysis of the crude product using 1,3,5-trimethoxybenzene as an internal standard. ^dE.e. values were based on HPLC analysis. ND, not determined.

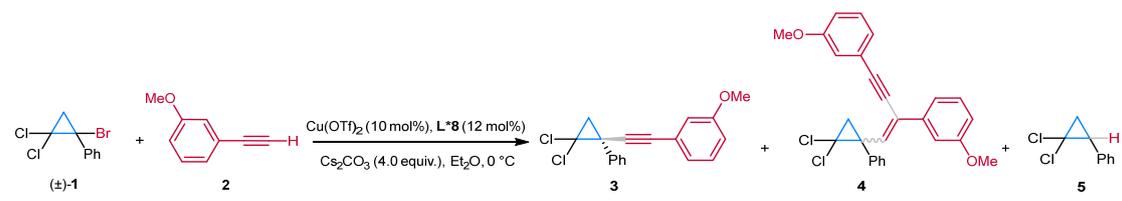
Supplementary Table 6 | Screening of substrate ratios^a



Entry	E1a/A1	Yield (%) ^c			E.e. of 3 (%) ^f
		3	4	5	
1 ^b	1.0:1.5	65	ND	ND	92
2	1.0:1.5	78	ND	ND	92
3 ^c	1.0:1.5	91	ND	ND	92
4 ^c	1.0:1.0	93	ND	ND	92
5	1.5:1.0	93	ND	ND	92
6 ^d	1.5:1.0	84	ND	ND	92

^aStandard reaction conditions: racemic cyclopropyl bromide **1** (0.10 mmol, entries 1–4), 3-ethynylanisole **2** (0.10 mmol, entry 5), Cu(OTf)₂ (10 mol%), **L*8** (12 mol%) and Cs₂CO₃ (4.0 equiv.) in Et₂O (1.0 mL) at 0 °C for 6 d under argon. ^bCs₂CO₃ (2.0 equiv.). ^cCu(OTf)₂ (15 mol%) and **L*8** (18 mol%). ^dWith NaOH (4.0 equiv.) instead of Cs₂CO₃. Although NaOH provided comparable results to Cs₂CO₃, we opted for Cs₂CO₃ to maximize the functional group tolerance of the cross-coupling reaction due to its milder basicity. ^eYield was based on ¹H NMR analysis of the crude product using 1,3,5-trimethoxybenzene as an internal standard. ^fE.e. values were based on HPLC analysis. ND, not determined.

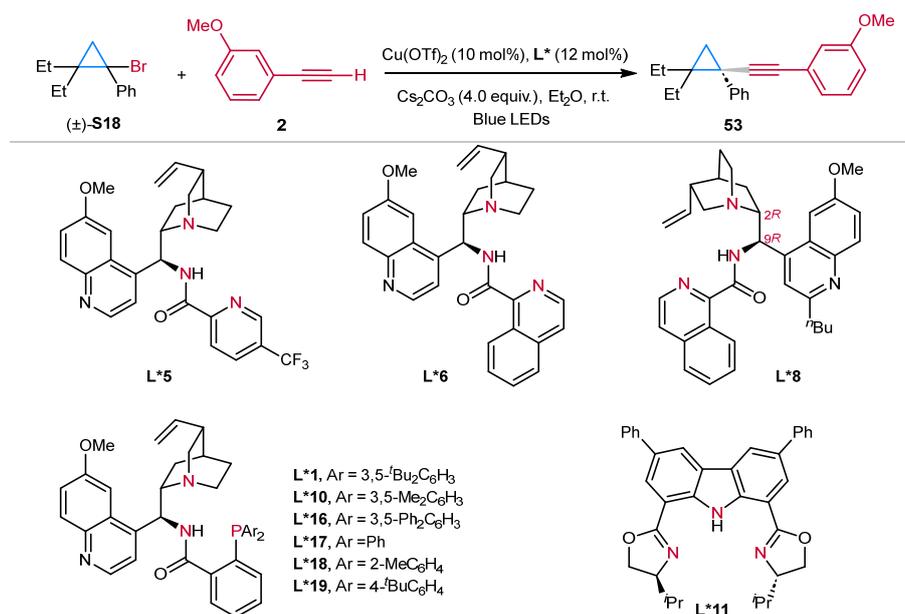
Supplementary Table 7 | Control experiments concerning catalysts and additives^a



Entry	Variations	Yield (%) ^b			E.e. of 3 (%) ^c
		3	4	5	
1	None	93	ND	ND	92
2	Without $\text{Cu}(\text{OTf})_2$	0	0	0	ND
3	Without L*8	4	0	0	0
4	Without Cs_2CO_3	0	0	0	ND

^aStandard reaction conditions: racemic cyclopropyl bromide **1** (1.5 equiv.), 3-ethynylanisole **2** (0.050 mmol), $\text{Cu}(\text{OTf})_2$ (10 mol%), **L*8** (12 mol%) and Cs_2CO_3 (4.0 equiv.) in Et_2O (0.50 mL) for 6 d under argon. ^bYield was based on ^1H NMR analysis of the crude product using 1,3,5-trimethoxybenzene as an internal standard. ^cE.e. values were based on HPLC analysis. ND, not determined.

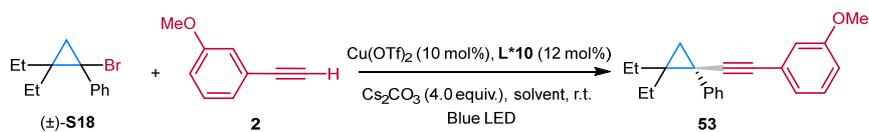
Supplementary Table 8 | Reaction condition optimizations for racemic **S18**^a



Entry	L^*	Yield (%) ^b	E.e. (%) ^c
1	L*5	12	−4
2	L*6	60	−28
3	L*8	46	18
4	L*1	25	32
5	L*10	72	42
6	L*16	56	37
7	L*17	24	25
8	L*18	ND	ND
9	L*19	18	24
10	L*11	90	−34

^aStandard reaction conditions: racemic cyclopropyl bromide **S18** (0.050 mmol), 3-ethynylanisole **2** (1.5 equiv.), $\text{Cu}(\text{OTf})_2$ (10 mol%), L^* (12 mol%), and Cs_2CO_3 (4.0 equiv.) in Et_2O (0.50 mL) at r.t. under the irradiation of blue LEDs (5 W) and argon for 5 d. ^bYield was based on ¹H NMR analysis of the crude product using mesitylene as an internal standard. ^cE.e. values were based on HPLC analysis. ND, not determined.

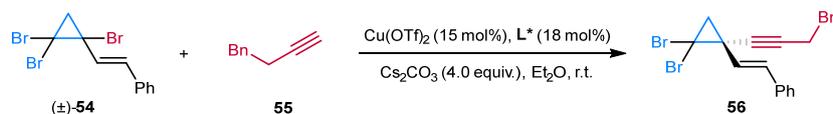
Supplementary Table 9 | Reaction condition optimizations for racemic **S18**^a



Entry	Solvent	Yield (%) ^b	E.e. (%) ^c
1	Et ₂ O	72	42
2	CH ₂ Cl ₂	30	42
3	EtOAc	58	44
4	Cyclohexane	15	40
5	MeCN	30	44
6	Toluene	65	33
7	PhCF ₃	40	36
8	THF	70	42
9	1,4-dioxane	75	47

^aStandard reaction conditions: racemic cyclopropyl bromide **S18** (0.050 mmol), 3-ethynylanisole **2** (1.5 equiv.), Cu(OTf)₂ (10 mol%), L***10** (12 mol%), and Cs₂CO₃ (4.0 equiv.) in solvent (0.50 mL) at r.t. under the irradiation of blue LEDs (5 W) and argon for 5 d. ^bYield was based on ¹H NMR analysis of the crude product using mesitylene as an internal standard. ^cE.e. values were based on HPLC analysis.

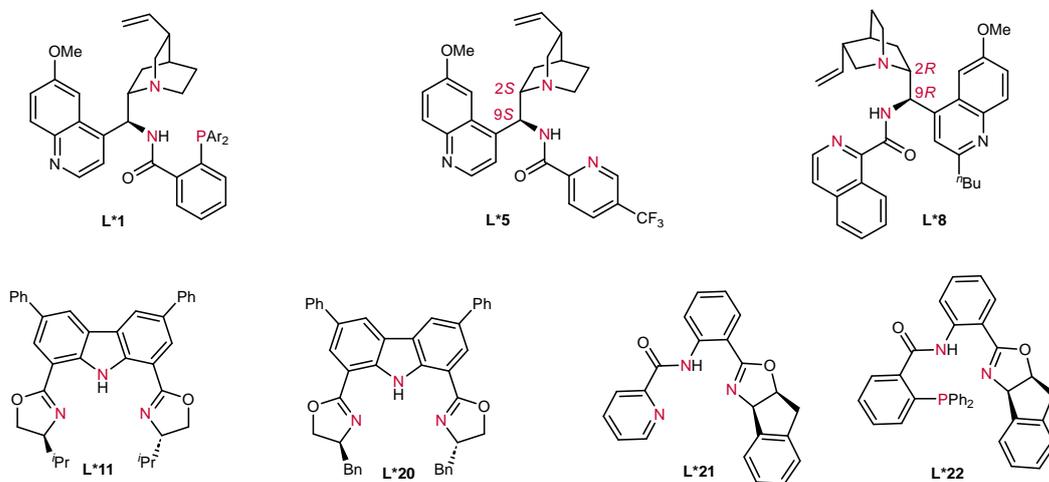
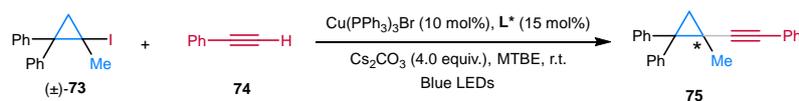
Supplementary Table 10 | Reaction condition optimizations for racemic **54**^a



Entry	L*	[Cu]	Solvent	Yield (%) ^b	E.e. (%) ^c
1 ^d	L*8	Cu(OTf) ₂	Et ₂ O	11	-79
2	L*8	Cu(OTf) ₂	Et ₂ O	18	-79
3	L*2	Cu(OTf) ₂	Et ₂ O	10	84
4	L*3	Cu(OTf) ₂	Et ₂ O	12	90
5	L*4	Cu(OTf) ₂	Et ₂ O	15	76
6	L*5	Cu(OTf) ₂	Et ₂ O	30	92
7	L*5	CuI	Et ₂ O	15	90
8	L*5	Cu(MeCN) ₄ PF ₆	Et ₂ O	21	89
9	L*5	CuTc	Et ₂ O	48	92
10	L*5	CuTc	THF	38	89
11	L*5	CuTc	MTBE	69	92
12^e	L*5	CuTc	MTBE	93	92

^aStandard reaction conditions: racemic cyclopropyl bromide **54** (1.5 equiv.), 4-phenyl-1-butyne **55** (0.050 mmol), [Cu] (15 mol%), ligand L* (18 mol%) and Cs₂CO₃ (4.0 equiv.) in solvent (1.0 mL) at r.t. for 4 d under argon. ^bYield was based on ¹H NMR analysis of the crude product using mesitylene as an internal standard. ^cE.e. values were based on HPLC analysis. ^dCu(OTf)₂ (10 mol%) and ligand L*8 (12 mol%). ^eThe reaction was conducted for 7 d.

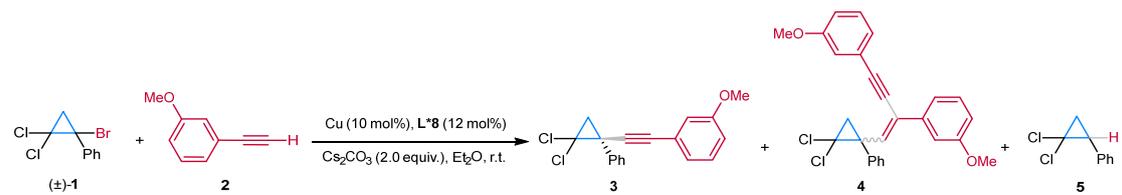
Supplementary Table 11 | Reaction condition optimizations for racemic **73**^a



Entry	L^*	Yield of 75 (%) ^b	E.e. of 75 (%) ^c
1 ^d	L^*8	0	ND
2 ^e	L^*5	0	ND
3	L^*1	Trace	ND
4	L^*5	Trace	ND
5	L^*8	Trace	ND
6	L^*11	56	52
7	L^*20	32	30
8	L^*21	Trace	ND
9	L^*22	Trace	ND

^aStandard reaction conditions: racemic cyclopropyl halide **73** (1.5 equiv.), phenylacetylene **74** (0.10 mmol), $\text{Cu}(\text{PPh}_3)_3\text{Br}$ (10 mol%), ligand L^* (15 mol%) and Cs_2CO_3 (4.0 equiv.) in MTBE (2.0 mL) at r.t. under the irradiation of blue LEDs (5 W) and argon for 7 d. ^bIsolated yield is shown. ^cE.e. is based on chiral HPLC analysis. ^dPhenylacetylene (0.10 mmol), racemic cyclopropyl halide **73** (1.5 equiv.), $\text{Cu}(\text{OTf})_2$ (10 mol%), L^*8 (12 mol%), and Cs_2CO_3 (4.0 equiv.) in Et_2O (1.0 mL) under argon at 0 °C for 6 d. ^ePhenylacetylene (0.10 mmol), racemic cyclopropyl halide **73** (1.5 equiv.), CuTc (15 mol%), L^*5 (18 mol%), and Cs_2CO_3 (4.0 equiv.) in MTBE (2.0 mL) at r.t. for 7 d under argon. ND, not determined.

Supplementary Table 12 | The effect of mixed Cu(OTf)₂ and CuOTf·1/2Ph

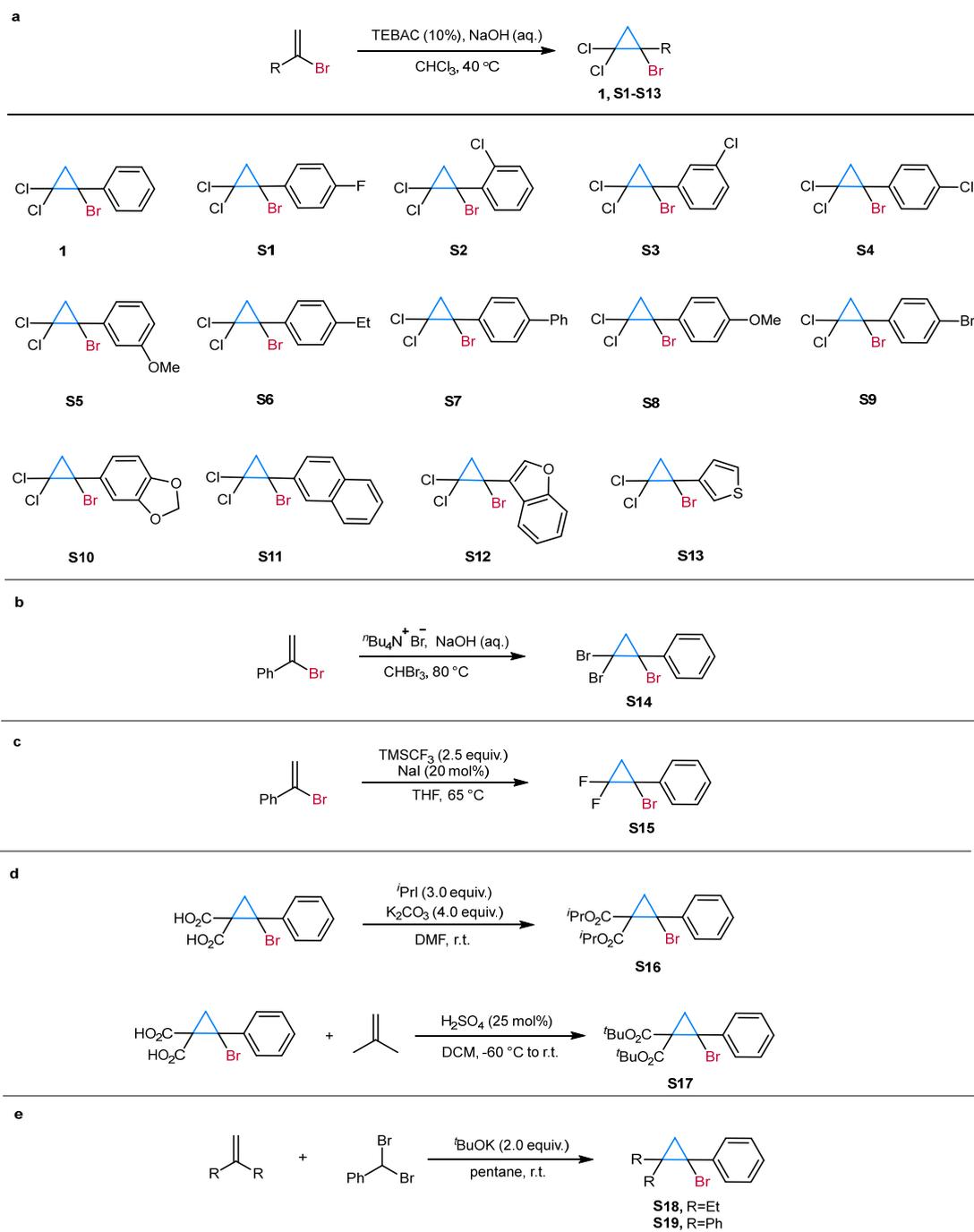


Entry	Cu(OTf) ₂ :CuOTf·1/2Ph	Yield (%) ^b			E.e. of 3 (%) ^c
		3 ^d	4	5	
1	10:0	95 (97)	1	2	90
2	8:2	87 (91)	4	5	90
3	6:4	85 (89)	6	5	90
4	4:6	81 (85)	8	6	90
5	2:8	75 (82)	10	7	90
6	0:10	75 (82)	10	7	90

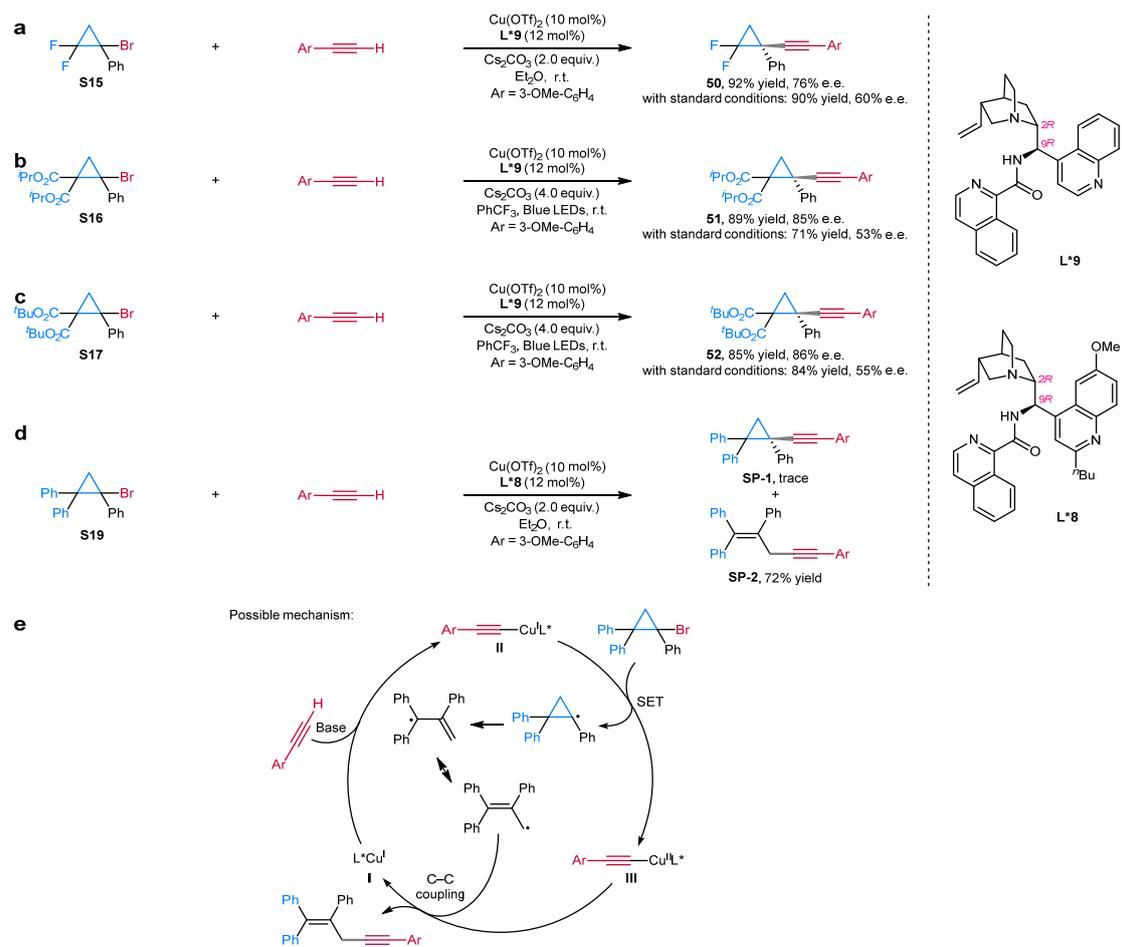
^aStandard reaction conditions: racemic cyclopropyl bromide **1** (0.30 mmol), 3-ethynylanisole **2** (1.5 equiv.), Cu (10 mol%), L***8** (12 mol%) and Cs₂CO₃ (2.0 equiv.) in Et₂O (3.0 mL) at room temperature (r.t.) for 3 d under argon. ^bYield was based on ¹H NMR analysis of the crude product using 1,3,5-trimethoxybenzene as an internal standard. ^cE.e. values were based on HPLC analysis.

^dThe percentage of **3** among the three products is shown in parenthesis.

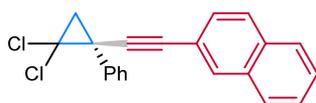
Supplementary figures for experiments



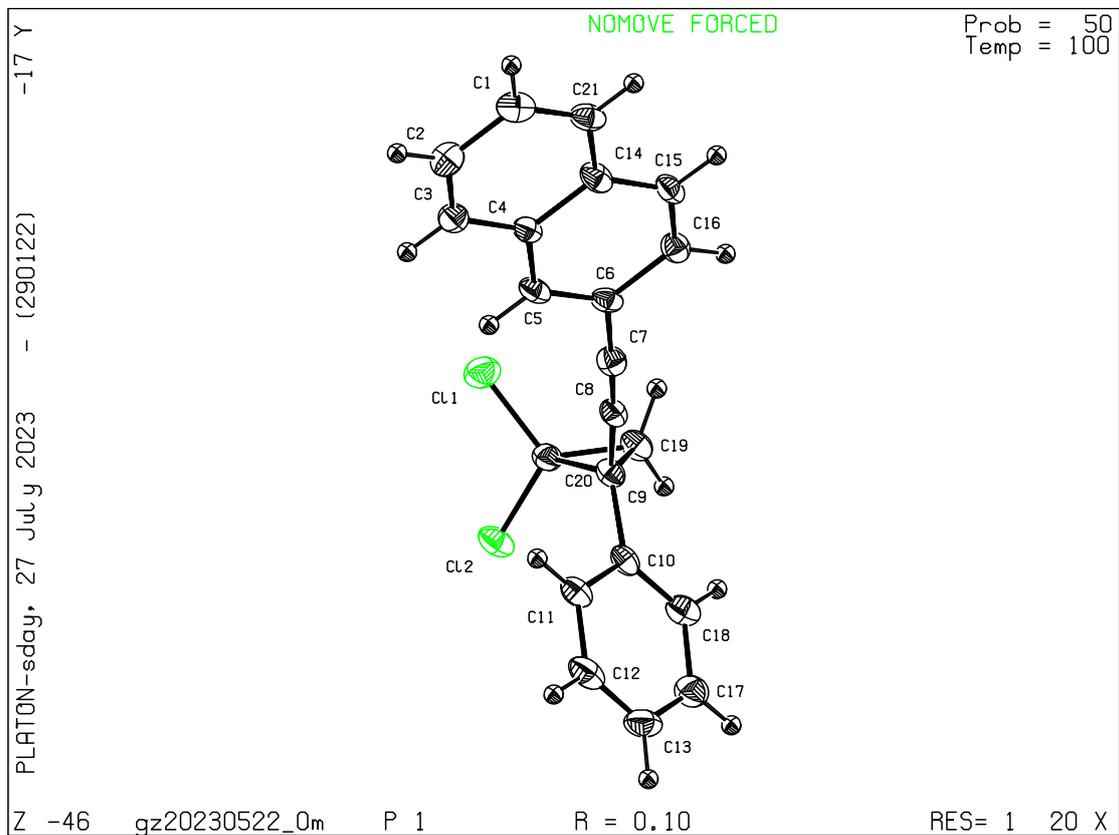
Supplementary Fig. 1 | The structures and synthesis of racemic cyclopropyl bromides.



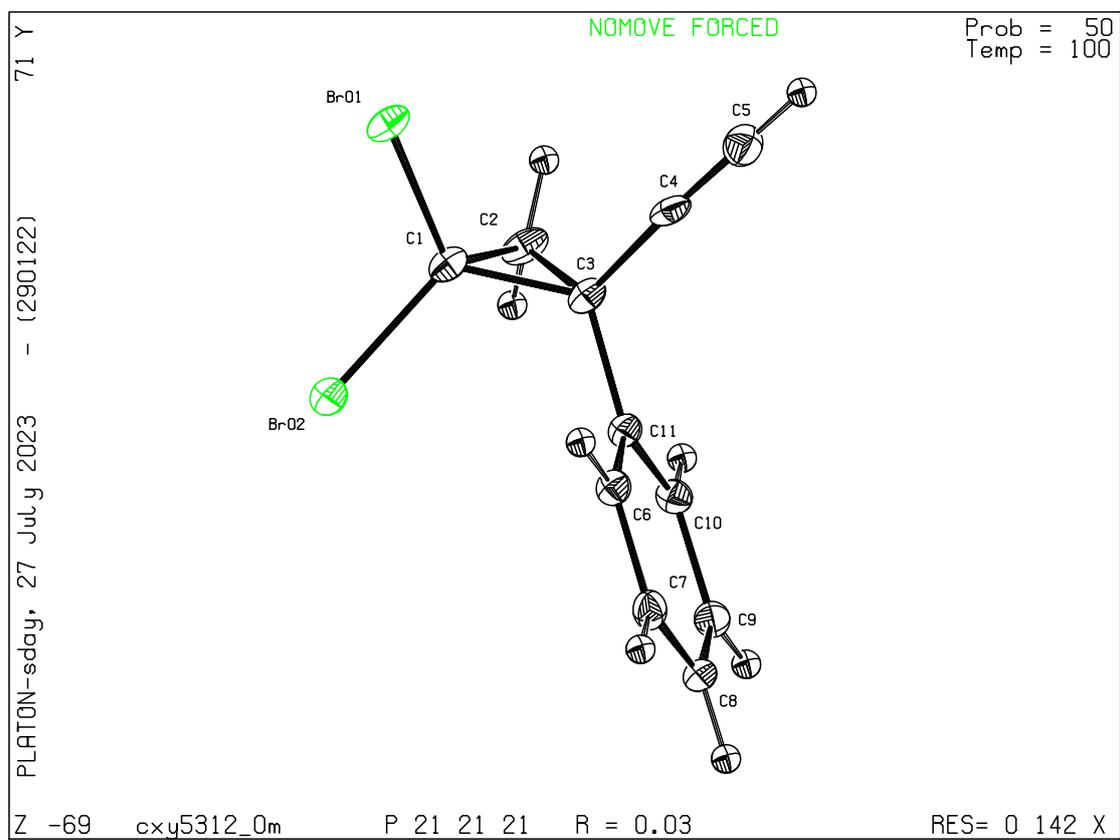
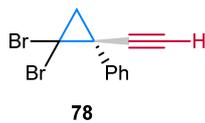
Supplementary Fig. 2 | Detailed results of additional 1-phenyl-cyclopropyl bromides.



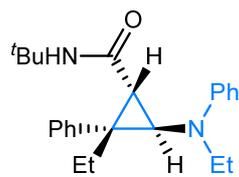
20



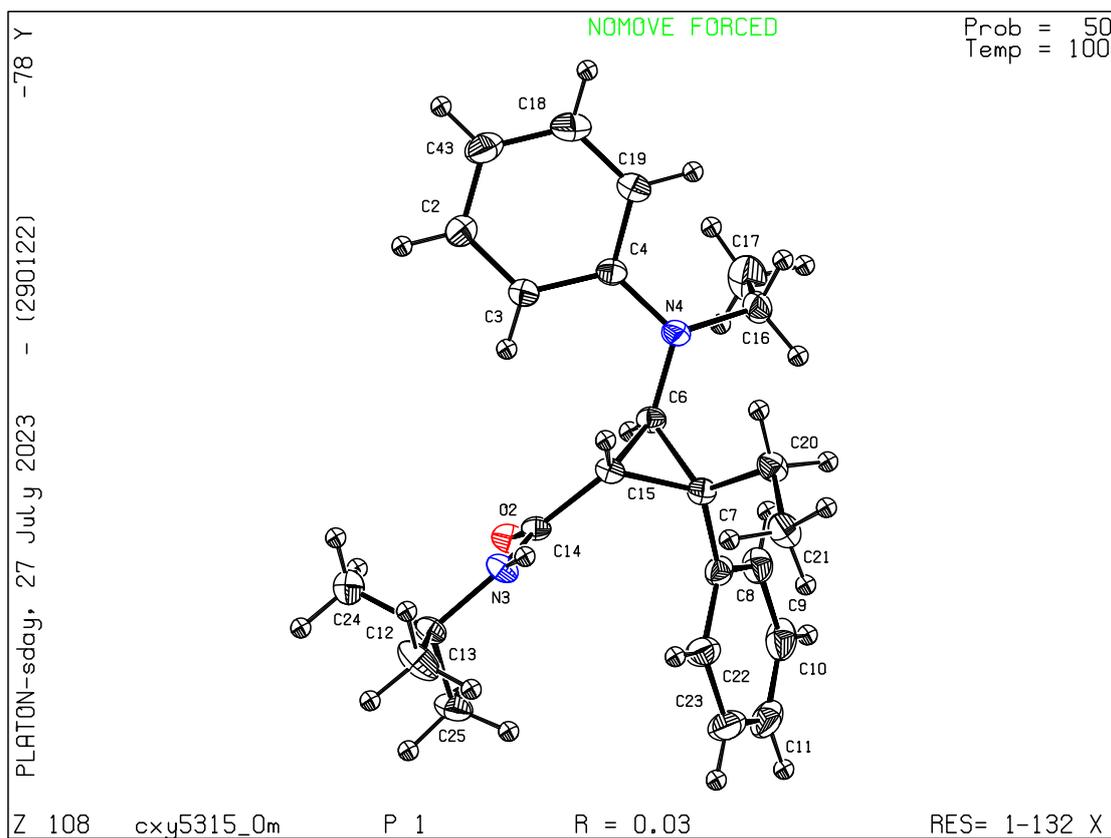
Supplementary Fig. 3 | The X-ray structure of 20 (CCDC 2264730).



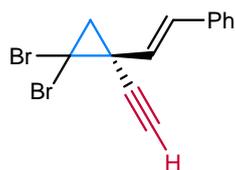
Supplementary Fig. 4 | The X-ray structure of 78 (CCDC 2267172).



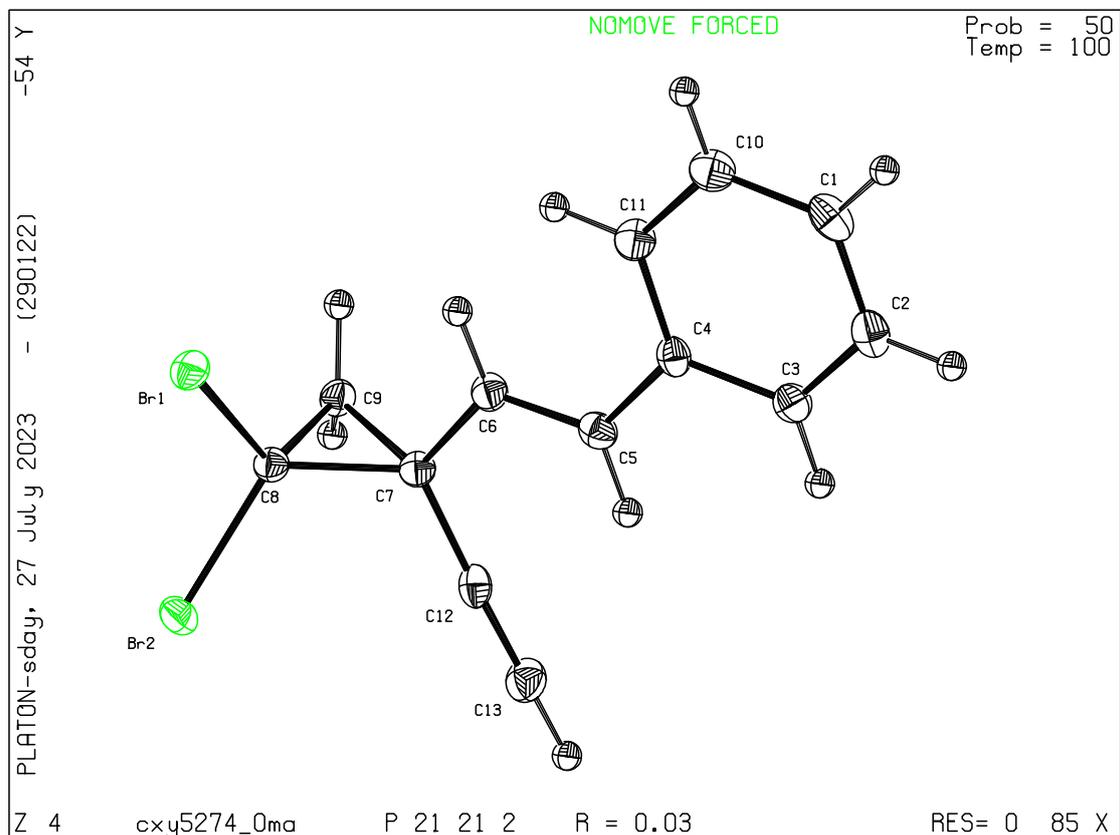
86



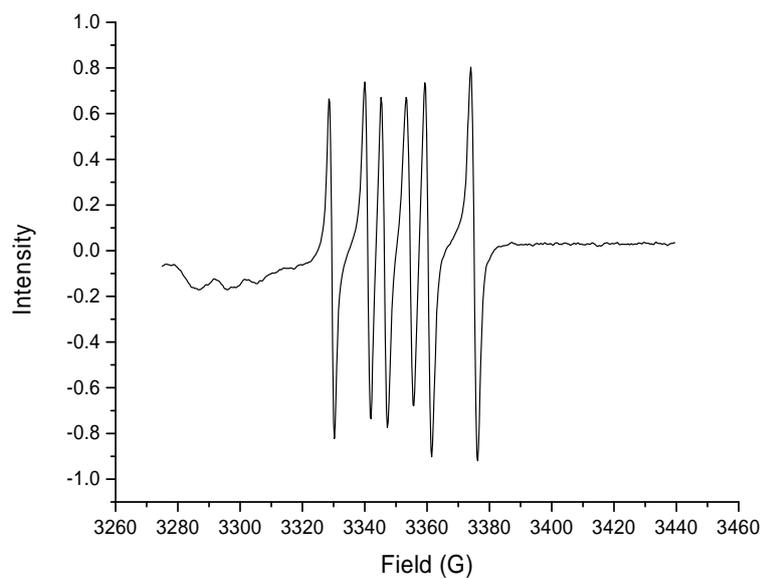
Supplementary Fig. 5 | The X-ray structure of 86 (CCDC 2267173).



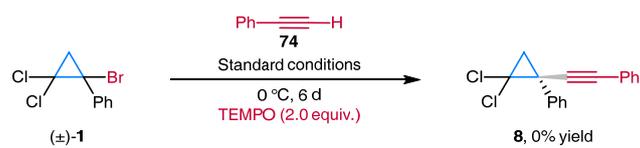
88



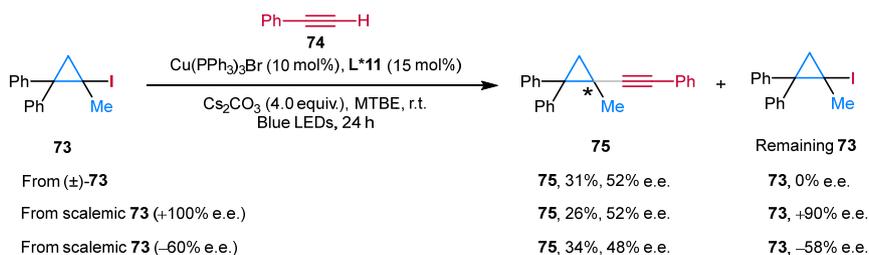
Supplementary Fig. 6 | The X-ray structure of 88 (CCDC 2264731).



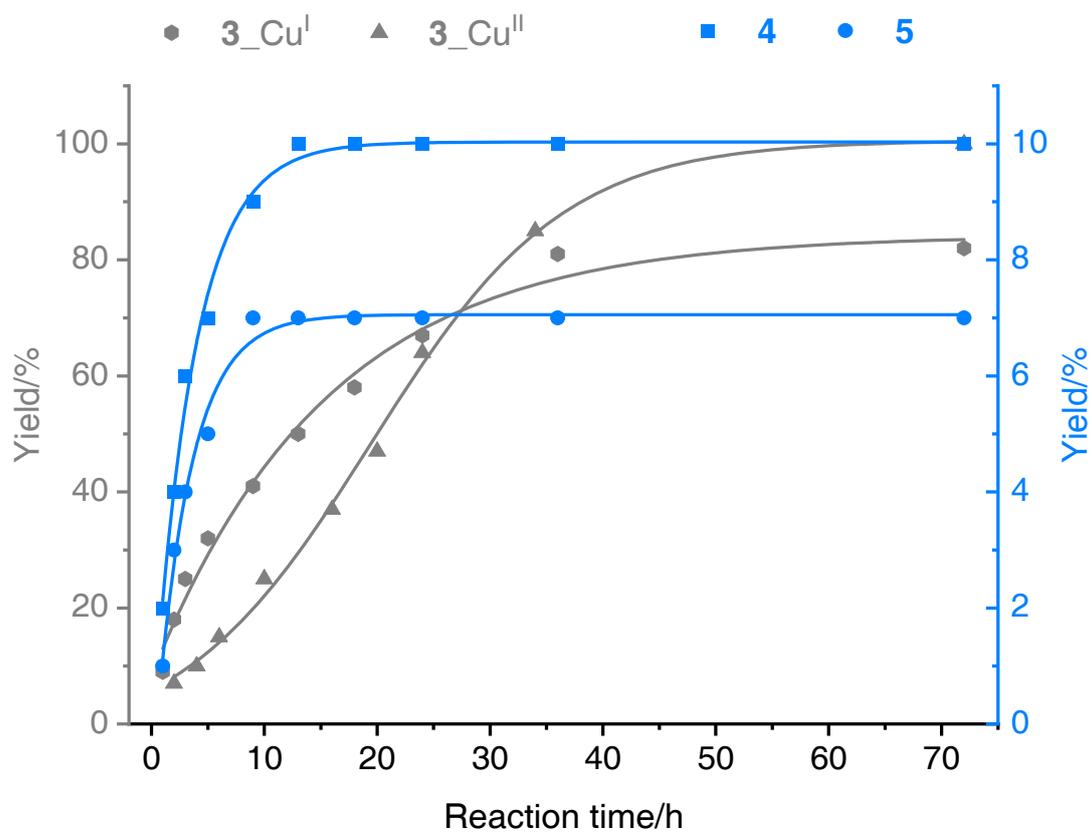
Supplementary Fig. 7 | Room temperature Q-band CW-EPR spectrum of the spin trap study. $g = 2.0071$; $a_H = 18.90$ G; $a_N = 13.37$ G. EPR acquisition parameters: temperature = 298 K; MW power = 40 dB; modulation amplitude = 1 G; conversion time = 20 ms.



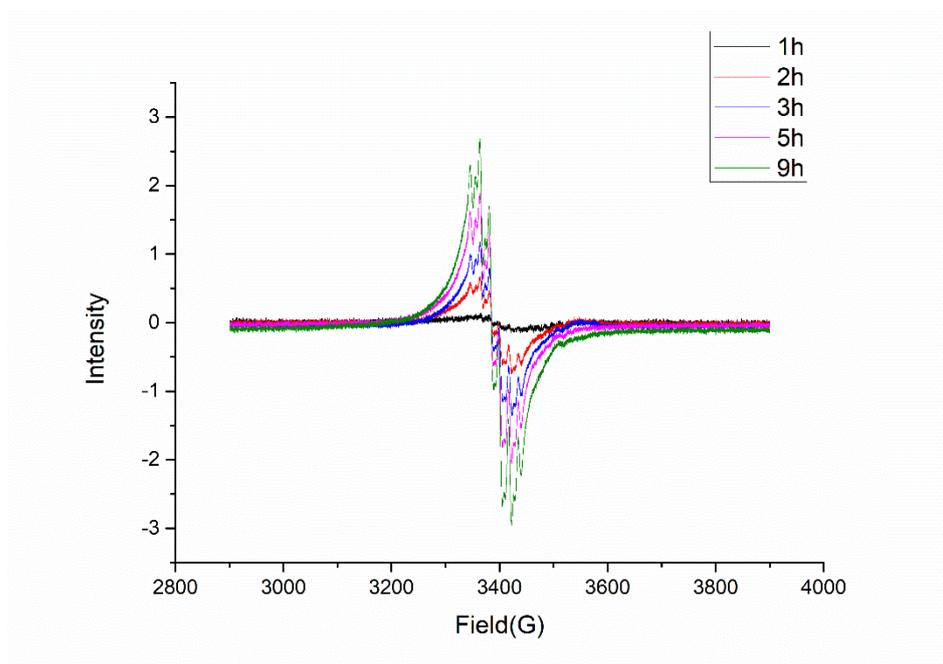
Supplementary Fig. 8 | Results of the radical inhibition control experiment with TEMPO.



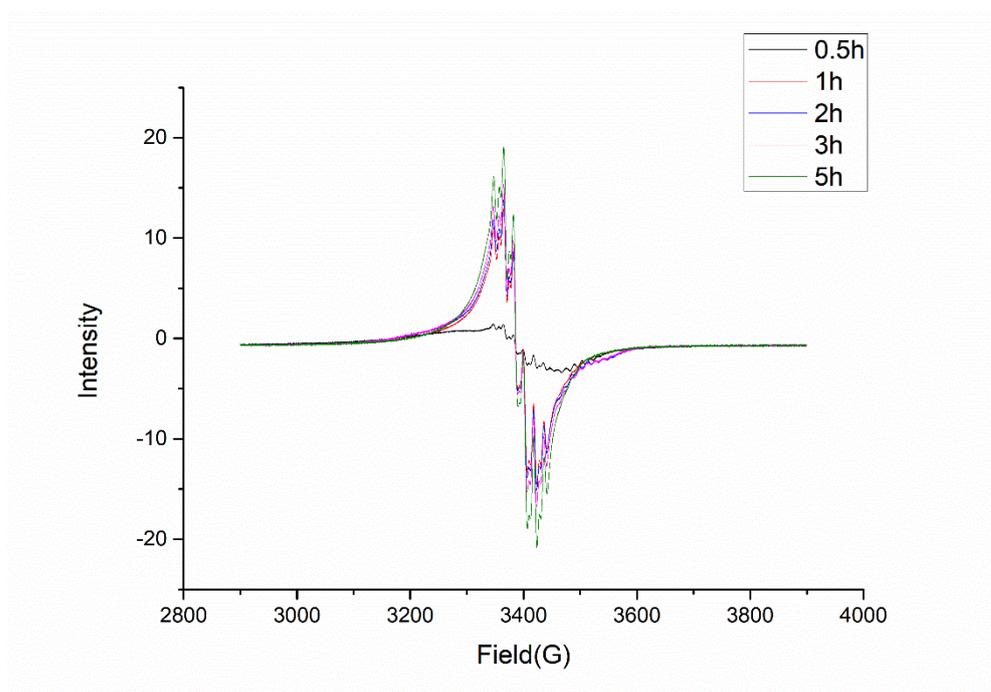
Supplementary Fig. 9 | Control experiments concerning the enantiopurity of 73. No changes to the enantiopurities of the recovered **73** were observed in the reactions of either racemic or scalemic **73**, respectively, thus excluding pathways that involve kinetic resolution or fast racemization of **73**. Values aligned horizontally belong to one experiment.



Supplementary Fig. 10 | Time-course experiment results using Cu(OTf)₂ and CuOTf catalyst precursors. The formation of side products was monitored when CuOTf was employed, as it was completely suppressed when Cu(OTf)₂ was used. Solid lines for compounds 4 and 5 represent exponential decay fits to the experimental data. The solid line for compound 3 with CuOTf as the precatalyst is a dose-response fit, while the solid line for compound 3 with Cu(OTf)₂ is a Boltzmann fit to the experimental data.



Supplementary Fig. 11 | Time-course X-band EPR spectra of the reaction mixtures with CuOTf as the catalyst precursor. EPR acquisition parameters: solvent = toluene; temperature = 298 K; frequency = 9.838739 GHz; MW power = 20 dB; modulation amplitude = 1 G; conversion time = 12 ms.



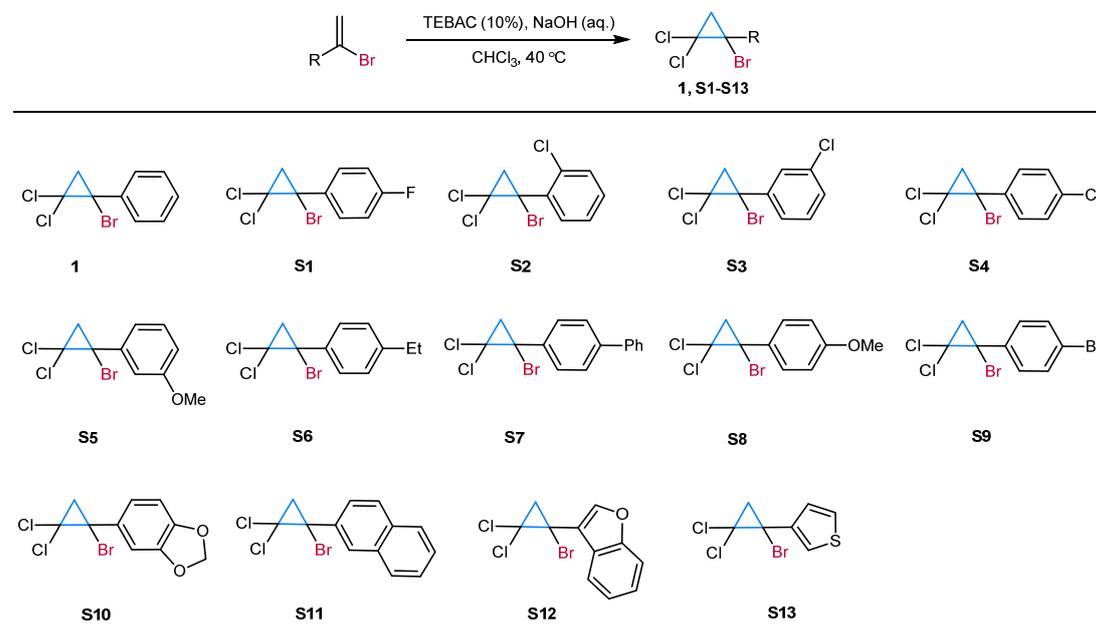
Supplementary Fig. 12 | Time-course X-band EPR spectra of the reaction mixtures with $\text{Cu}(\text{OTf})_2$ as the catalyst precursor. EPR acquisition parameters: solvent = toluene; temperature = 298 K; frequency = 9.837637 GHz; MW power = 20 dB; modulation amplitude = 1 G; conversion time = 12 ms.

General information

Reactions were carried out under argon atmosphere using Schlenk techniques. Reagents were purchased at the highest commercial quality and used without further purification, unless otherwise stated. $\text{Cu}(\text{OTf})_2$ was purchased from TCI. CuTc was purchased from Adamas. $\text{Cu}(\text{PPh}_3)_3\text{Br}$ was purchased from Adamas. Anhydrous diethyl ether (Et_2O) was distilled from sodium (Na) and stored under argon. Anhydrous methyl *tert*-butyl ether (MTBE) was purchased from Titan, which was distilled after refluxing with sodium and benzophenone. Cs_2CO_3 were purchased from Bide Pharmatech Ltd., which was dried at 200 °C for 3 h in vacuum. Analytical thin layer chromatography (TLC) was performed on precoated silica gel 60 GF254 plates. Flash column chromatography was performed using Tsingdao silica gel (60, particle size 0.040–0.063 mm). As the eluent, the petroleum ether (PE) and EtOAc were purchased from Shanghai Titan Scientific Co. Ltd. without further purification. Visualization on TLC was achieved by use of UV light (254 nm), iodine or basic KMnO_4 indicator. NMR spectra were recorded on Bruker DRX-400 spectrometers at 400 MHz for ^1H NMR, 100 MHz for ^{13}C NMR and 376 MHz for ^{19}F NMR, respectively, in CDCl_3 with tetramethylsilane (TMS) as internal standard. The chemical shifts were expressed in ppm and coupling constants were given in Hz. Data for ^1H NMR are recorded as follows: chemical shift (ppm), multiplicity (s, singlet; d, doublet; t, triplet; q, quartet; p, pentet, m, multiplet; br, broad), coupling constant (Hz), integration. Data for ^{13}C NMR were reported in terms of chemical shift (δ , ppm). Mass spectrometric data were obtained using Bruker Apex IV RTMS. Enantiomeric excess (e.e.) was determined by Agilent and Shimadzu high-performance liquid chromatography (HPLC) with a Hatachi detector (at an appropriate wavelength). Column conditions were reported in the experimental section below. X-ray diffraction was measured on a 'Bruker APEX-II CCD' diffractometer with $\text{Cu-K}\alpha$ radiation.

General procedures for the synthesis of substrates

The structures and synthesis of 1-(hetero)aryl-substituted cyclopropyl bromides:

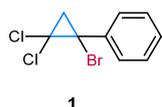


General procedure 1:

To a mixture of 1-(hetero)aryl-substituted vinyl bromide (5.0 mmol, 1.0 equiv.) and benzyltriethylammonium chloride (TEBAC) (113.5 mg 0.50 mmol, 10 mol%) in chloroform (20 mL) was added dropwise NaOH (50% aq., 2.0 g, 50 mmol, 10 equiv.) within 2 h under heating at 40 °C with vigorous stirring. Then the mixture was stirred for 1 h at 40 °C. After completion of the reaction (monitored by TLC), the mixture was quenched with water and extracted with CH₂Cl₂. The combined organic solution was concentrated under reduced pressure to afford the residue, which was purified by column chromatography on silica gel to provide the corresponding cyclopropyl bromide.

Note: Substrate **1** was a known compound and was synthesized according to reported literature¹.

(1-Bromo-2,2-dichlorocyclopropyl)benzene (**1**)



According to **General procedure 1** with (1-bromovinyl)benzene (1.83 g, 10.0 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 100/1) to yield the product **1** as a white solid (2.07 g, 78% yield).

m.p. 45–47 °C

¹H NMR (400 MHz, CDCl₃) δ 7.51 – 7.43 (m, 2H), 7.42 – 7.28 (m, 3H), 2.39 (d, *J* =

9.0 Hz, 1H), 2.15 (d, $J = 9.0$ Hz, 1H).

^{13}C NMR (100 MHz, CDCl_3) δ 138.9, 129.3, 129.1, 128.8, 63.0, 43.1, 35.5.

HRMS (ESI) m/z calcd. for $\text{C}_9\text{H}_8\text{BrCl}_2$ $[\text{M} + \text{H}]^+$ 264.9181, found 264.9186.

1-(1-Bromo-2,2-dichlorocyclopropyl)-4-fluorobenzene (S1)



S1

According to **General procedure 1** with 1-(1-bromovinyl)-4-fluorobenzene (1.00 g, 5.0 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 100/1) to yield the product **S1** as a colorless liquid (0.60 g, 42% yield).

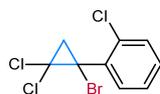
^1H NMR (400 MHz, CDCl_3) δ 7.52 – 7.39 (m, 2H), 7.12 – 7.00 (m, 2H), 2.34 (d, $J = 9.0$ Hz, 1H), 2.15 (d, $J = 9.1$ Hz, 1H).

^{13}C NMR (100 MHz, CDCl_3) δ 162.8 (d, $J = 249.5$ Hz), 134.9 (d, $J = 3.4$ Hz), 131.3 (d, $J = 8.7$ Hz), 115.9 (d, $J = 22.0$ Hz), 62.9, 42.3, 35.7.

^{19}F NMR (376 MHz, CDCl_3) δ -111.5.

HRMS (ESI) m/z calcd. for $\text{C}_9\text{H}_7\text{BrCl}_2\text{F}$ $[\text{M} + \text{H}]^+$ 282.9087, found 282.9098.

1-(1-Bromo-2,2-dichlorocyclopropyl)-2-chlorobenzene (S2)



S2

According to **General procedure 1** with 1-(1-bromovinyl)-2-chlorobenzene (0.87 g, 4.0 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 100/1) to yield the product **S2** as a white solid (0.60 g, 50% yield). The compound is a mixture of atropisomers (ratio: 1/0.27).

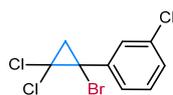
m.p. 61–64 °C

^1H NMR (400 MHz, CDCl_3) δ 7.50 – 7.45 (m, 1H), 7.36 – 7.24 (m, 3H), 2.36 (d, $J = 8.9$ Hz, 2H), 2.21 (d, $J = 8.9$ Hz, 1H).

^{13}C NMR (100 MHz, CDCl_3) δ 136.9, 136.3, 130.7, 130.6, 129.9, 127.2, 63.1, 42.0, 36.1.

HRMS (ESI) m/z calcd. for $\text{C}_9\text{H}_7\text{BrCl}_3$ $[\text{M} + \text{H}]^+$ 298.8791, found 298.8780.

1-(1-Bromo-2,2-dichlorocyclopropyl)-3-chlorobenzene (S3)



S3

According to **General procedure 1** with 1-(1-bromovinyl)-3-chlorobenzene (1.08 g, 5.0 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on

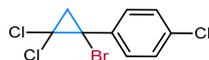
silica gel (petroleum ether/EtOAc = 100/1) to yield the product **S3** as a colorless liquid (0.79 g, 53% yield).

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.44 (s, 1H), 7.41 – 7.28 (m, 3H), 2.37 (d, $J = 9.1$ Hz, 1H), 2.15 (d, $J = 9.1$ Hz, 1H).

$^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 140.7, 134.6, 130.1, 129.4, 129.3, 127.6, 62.7, 42.0, 35.5.

HRMS (ESI) m/z calcd. for $\text{C}_9\text{H}_7\text{BrCl}_3$ $[\text{M} + \text{H}]^+$ 298.8791, found 298.8787.

1-(1-Bromo-2,2-dichlorocyclopropyl)-4-chlorobenzene (**S4**)



S4

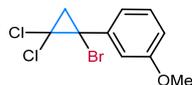
According to **General procedure 1** with 1-(1-bromovinyl)-4-chlorobenzene (1.08 g, 5.0 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 100/1) to yield the product **S4** as a colorless liquid (0.65 g, 43% yield).

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.47 – 7.28 (m, 4H), 2.33 (d, $J = 9.1$ Hz, 1H), 2.13 (d, $J = 9.0$ Hz, 1H).

$^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 137.4, 135.0, 130.7, 129.1, 62.7, 42.1, 35.5.

HRMS (ESI) m/z calcd. for $\text{C}_9\text{H}_7\text{BrCl}_3$ $[\text{M} + \text{H}]^+$ 298.8791, found 298.8797.

1-(1-Bromo-2,2-dichlorocyclopropyl)-3-methoxybenzene (**S5**)



S5

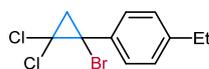
According to **General procedure 1** with 1-(1-bromovinyl)-3-methoxybenzene (0.75 g, 3.5 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 100/1) to yield the product **S5** as a colorless liquid (0.39 g, 38% yield).

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.28 (t, $J = 8.0$ Hz, 1H), 7.06 – 7.00 (m, 1H), 6.99 (t, $J = 2.1$ Hz, 1H), 6.87 (ddd, $J = 8.3, 2.5, 0.9$ Hz, 1H), 3.82 (s, 3H), 2.37 (d, $J = 9.0$ Hz, 1H), 2.12 (d, $J = 9.0$ Hz, 1H).

$^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 159.7, 140.1, 129.8, 121.4, 115.0, 114.7, 63.0, 55.5, 43.0, 35.5.

HRMS (ESI) m/z calcd. for $\text{C}_{10}\text{H}_{10}\text{OBrCl}_2$ $[\text{M} + \text{H}]^+$ 294.9287, found 294.9282.

1-(1-Bromo-2,2-dichlorocyclopropyl)-4-ethylbenzene (**S6**)



S6

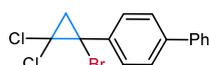
According to **General procedure 1** with 1-(1-bromovinyl)-4-ethylbenzene (1.05 g, 3.5 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 100/1) to yield the product **S6** as a colorless liquid (0.94 g, 64% yield).

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.42 – 7.31 (m, 2H), 7.25 – 7.14 (m, 2H), 2.64 (q, J = 7.6 Hz, 2H), 2.34 (d, J = 8.9 Hz, 1H), 2.11 (d, J = 8.9 Hz, 1H), 1.23 (t, J = 7.6 Hz, 3H).

$^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 145.3, 136.1, 129.2, 128.3, 63.1, 43.3, 35.5, 28.7, 15.3.

HRMS (ESI) m/z calcd. for $\text{C}_{11}\text{H}_{12}\text{BrCl}_2$ [$\text{M} + \text{H}$] $^+$ 292.9494, found 292.9488.

4-(1-Bromo-2,2-dichlorocyclopropyl)-1,1'-biphenyl (**S7**)



S7

According to **General procedure 1** with 4-(1-bromovinyl)-1,1'-biphenyl (0.93 g, 3.6 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 100/1) to yield the product **S7** as a white solid (0.85 g, 69% yield).

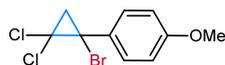
m.p. 130–132 °C

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.68 – 7.59 (m, 4H), 7.58 – 7.52 (m, 2H), 7.50 – 7.42 (m, 2H), 7.42 – 7.35 (m, 1H), 2.44 (d, J = 9.0 Hz, 1H), 2.20 (d, J = 9.0 Hz, 1H).

$^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 142.0, 140.3, 137.8, 129.7, 129.0, 127.9, 127.5, 127.3, 63.0, 43.0, 35.6.

HRMS (ESI) m/z calcd. for $\text{C}_{15}\text{H}_{12}\text{BrCl}_2$ [$\text{M} + \text{H}$] $^+$ 340.9494, found 340.9501.

1-(1-Bromo-2,2-dichlorocyclopropyl)-4-methoxybenzene (**S8**)



S8

According to **General procedure 1** with 1-(1-bromovinyl)-4-methoxybenzene (0.64 g, 3.0 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 50/1) to yield the product **S8** as a white solid (0.43 g, 48% yield).

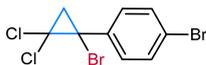
m.p. 51–55 °C

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.45 – 7.33 (m, 2H), 6.96 – 6.82 (m, 2H), 3.81 (s, 3H), 2.33 (d, J = 8.9 Hz, 1H), 2.12 (d, J = 9.0 Hz, 1H).

$^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 160.0, 131.1, 130.7, 114.1, 63.2, 55.5, 43.3, 35.7.

HRMS (ESI) m/z calcd. for $\text{C}_{10}\text{H}_{10}\text{OBrCl}_2$ [$\text{M} + \text{H}$] $^+$ 294.9287, found 294.9283.

1-Bromo-4-(1-bromo-2,2-dichlorocyclopropyl)benzene (**S9**)



S9

According to **General procedure 1** with 1-bromo-4-(1-bromovinyl)benzene (1.30 g, 5.0 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 100/1) to yield the product **S9** as a white solid (0.69 g, 40% yield).

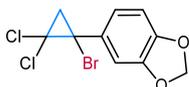
m.p. 40–42 °C

¹H NMR (400 MHz, CDCl₃) δ 7.57 – 7.46 (m, 2H), 7.39 – 7.28 (m, 2H), 2.33 (d, *J* = 9.0 Hz, 1H), 2.14 (d, *J* = 9.1 Hz, 1H).

¹³C NMR (100 MHz, CDCl₃) δ 137.9, 132.0, 130.9, 123.3, 62.6, 42.2, 35.5.

HRMS (ESI) *m/z* calcd. for C₉H₇Br₂Cl₂ [M + H]⁺ 342.8286, found 342.8290.

5-(1-Bromo-2,2-dichlorocyclopropyl)benzo[d][1,3]dioxole (S10)



S10

According to **General procedure 1** with 5-(1-bromovinyl)benzo[d][1,3]dioxole (0.68 g, 3.0 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 100/1) to yield the product **S10** as a white solid (0.35 g, 38% yield).

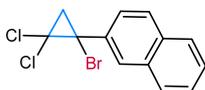
m.p. 103–107 °C

¹H NMR (400 MHz, CDCl₃) δ 6.96 (s, 1H), 6.90 (dd, *J* = 8.1, 1.8 Hz, 1H), 6.77 (d, *J* = 8.1 Hz, 1H), 5.98 (brs, 2H), 2.31 (d, *J* = 9.0 Hz, 1H), 2.11 (d, *J* = 9.0 Hz, 1H).

¹³C NMR (100 MHz, CDCl₃) δ 148.3, 147.9, 132.7, 122.9, 110.0, 108.2, 101.7, 63.2, 43.4, 35.9.

HRMS (ESI) *m/z* calcd. for C₁₀H₈O₂BrCl₂ [M + H]⁺ 308.9079, found 308.9082.

2-(1-Bromo-2,2-dichlorocyclopropyl)naphthalene (S11)



S11

According to **General procedure 1** with 2-(1-bromovinyl)naphthalene (0.93 g, 4.0 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 100/1) to yield the product **S11** as a white solid (0.69 g, 55% yield).

m.p. 82–84 °C

¹H NMR (400 MHz, CDCl₃) δ 7.88 – 7.77 (m, 4H), 7.61 (dd, *J* = 8.6, 1.9 Hz, 1H), 7.52 – 7.45 (m, 2H), 2.50 (d, *J* = 9.0 Hz, 1H), 2.20 (d, *J* = 9.0 Hz, 1H).

¹³C NMR (100 MHz, CDCl₃) δ 136.3, 133.4, 133.0, 128.8, 128.3, 127.9, 127.8, 127.3,

127.2, 126.8, 63.0, 43.6, 35.5.

HRMS (ESI) m/z calcd. for $C_{13}H_{10}BrCl_2$ $[M + H]^+$ 314.9337, found 314.9336.

3-(1-Bromo-2,2-dichlorocyclopropyl)benzofuran (S12)



According to **General procedure 1** with 3-(1-bromovinyl)benzofuran (0.23 g, 1.0 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 100/1) to yield the product **S12** as a white solid (0.21 g, 68% yield).

m.p. 60–63 °C

1H NMR (400 MHz, $CDCl_3$) δ 7.86 – 7.79 (m, 1H), 7.66 (s, 1H), 7.54 – 7.47 (m, 1H), 7.41 – 7.33 (m, 2H), 2.38 (d, J = 8.8 Hz, 1H), 2.23 (d, J = 8.8 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 155.6, 143.8, 126.0, 125.5, 123.5, 121.4, 121.2, 111.9, 62.7, 35.6, 34.8.

HRMS (ESI) m/z calcd. for $C_{11}H_8OBrCl_2$ $[M + H]^+$ 304.9130, found 304.9131.

3-(1-Bromo-2,2-dichlorocyclopropyl)thiophene (S13)

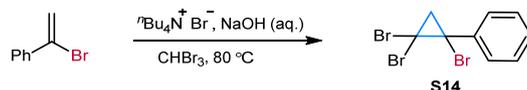


According to **General procedure 1** with 3-(1-bromovinyl)thiophene (0.57 g, 3.0 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 100/1) to yield the product **S13** as a colorless oil (0.42 g, 51% yield).

1H NMR (400 MHz, $CDCl_3$) δ 7.33 (dd, J = 5.0, 3.0 Hz, 1H), 7.29 (dd, J = 3.0, 1.4 Hz, 1H), 7.22 (dd, J = 5.0, 1.4 Hz, 1H), 2.38 (d, J = 9.0 Hz, 1H), 2.14 (d, J = 9.0 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 139.7, 128.5, 126.6, 125.1, 63.1, 38.6, 36.0.

HRMS (ESI) m/z calcd. for $C_7H_6BrCl_2S$ $[M + H]^+$ 270.8745, found 270.8741.



To a reaction flask were added (1-bromovinyl)benzene (1.83 g, 10 mmol, 1.0 equiv.), bromoform (3.5 mL, 40 mmol, 4.0 equiv.), NaOH (50% aq., 4.0 g, 100 mmol, 10 equiv.), and *n*-tetrabutylammonium bromide (32.2 mg, 0.10 mmol, 1.0 mol%). The mixture was stirred for 20 h at 80 °C and then CH_2Cl_2 (30 mL) and water (30 mL) were added. The water layer was extracted with CH_2Cl_2 . The combined organic solution was concentrated under reduced pressure to afford the residue, which was purified by column chromatography on silica gel (petroleum ether/EtOAc = 100/1) to provide **S14**

as a white solid (2.48 g, 70% yield).

Note: Substrate **S14** was a known compound and was synthesized according to reported literature².

(1,2,2-Tribromocyclopropyl)benzene (**S14**)



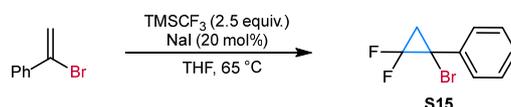
S14

m.p. 85–88 °C

¹H NMR (400 MHz, CDCl₃) δ 7.52 – 7.43 (m, 2H), 7.42 – 7.28 (m, 3H), 2.50 (d, *J* = 9.3 Hz, 1H), 2.24 (d, *J* = 9.3 Hz, 1H).

¹³C NMR (100 MHz, CDCl₃) δ 140.1, 129.3, 129.1, 128.7, 43.0, 37.2, 32.0.

HRMS (ESI) *m/z* calcd. for C₉H₈Br₂⁸¹Br [M + H]⁺ 354.8150, found 354.8135.



(1-bromovinyl)benzene (0.92 g, 5.0 mmol, 1.0 equiv.) was added to a 100 mL three-necked flask that was charged with anhydrous NaI (0.15 g, 0.2 equiv.) and dry THF (20 mL). Then, TMSCF₃ (1.78 g, 2.5 equiv.) was added to the solution. Then the reaction mixture was refluxed at 65 °C for 12 h under argon atmosphere. After completion of the reaction, the reaction mixture was filtered, evaporated and purified by column chromatography on silica gel (PE as eluent) to afford the product **S15** as a colorless oil (0.76 g, 65% yield).

Note: Substrate **S15** was a known compound and was synthesized according to reported literature³.

(1-Bromo-2,2-difluorocyclopropyl)benzene (**S15**)



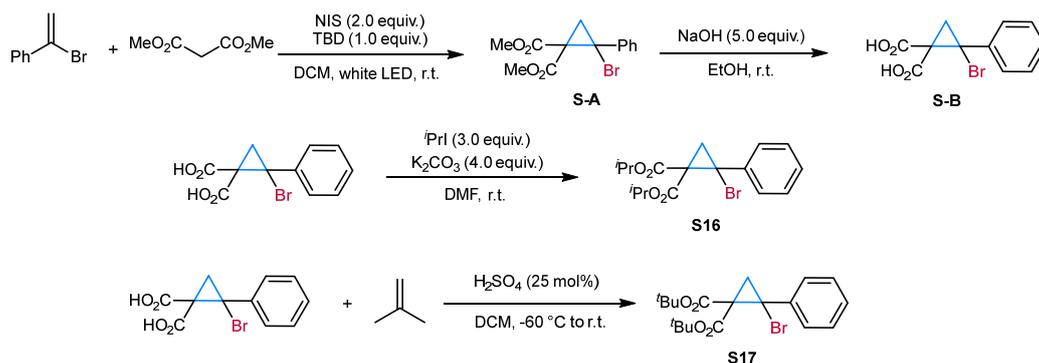
S15

¹H NMR (400 MHz, CDCl₃) δ 7.52 – 7.43 (m, 2H), 7.41 – 7.29 (m, 3H), 2.23 (ddd, *J* = 13.6, 9.5, 4.6 Hz, 1H), 2.06 (ddd, *J* = 10.8, 9.5, 4.9 Hz, 1H).

¹³C NMR (100 MHz, CDCl₃) δ 136.3 (t, *J* = 2.0 Hz), 129.38, 129.35, 129.0, 109.7 (dd, *J* = 292.0, 290.5 Hz), 34.3 (t, *J* = 11.9 Hz), 27.1 (t, *J* = 10.7 Hz).

¹⁹F NMR (376 MHz, CDCl₃) δ –127.1 (d, *J* = 149.1 Hz), –132.1 (d, *J* = 148.8 Hz).

HRMS (ESI) *m/z* calcd. for C₉H₈BrF₂ [M + H]⁺ 232.9772, found 232.9769.



Into an oven-dried reaction vial flushed with argon was added dimethyl malonate (1.2 mL, 10 mmol), (1-bromovinyl)benzene (3.68 g, 2.0 equiv.), NIS (4.50 g, 2.0 equiv.), TBD (1.39 g, 1.0 equiv.), and CH₂Cl₂ (30 mL). Then the reaction mixture was stirred for 24 h at r.t. under argon atmosphere in the presence of white LED light. After the reaction was complete, the mixture was poured into H₂O and extracted with CH₂Cl₂. The combined organic layer was dried with anhydrous Na₂SO₄ and evaporated under vacuum. The crude mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 10/1) to afford the corresponding product **S-A**.

To a round-bottomed flask were added **S-A** (1.0 equiv.), sodium hydroxide (5.0 equiv.) and EtOH (20 mL). The reaction mixture was stirred for 12 h at r.t.. After completion of the reaction (monitored by TLC), the mixture was partitioned between water and EtOAc and acidified with 4 N HCl to pH < 1. The combined organic solution was concentrated under reduced pressure to afford **S-B** as a white solid (1.20 g, 42% yield over two steps).

Into an oven-dried reaction was added **S-B** (0.29 g, 1.0 mmol), K₂CO₃ (0.55 g, 4.0 equiv.) and DMF (10 mL). Then, 2-iodopropane (0.51 g, 3.0 equiv.) was added to the solution. The reaction mixture was stirred for 12 h at r.t.. The mixture was poured into H₂O and extracted with CH₂Cl₂. The combined organic layer was dried with anhydrous Na₂SO₄ and evaporated under vacuum. The crude mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 10/1) to afford the product **S16** as a colorless oil (0.20 g, 54% yield).

A solution of **S-B** (0.29 g, 1.0 mmol) in CH₂Cl₂ (5.0 mL) was stirred at -60 °C, and isobutene (30 equiv.) in CH₂Cl₂ was added. Sulfuric acid (25 mol%) was then added, and the mixture was stirred at r.t. until reaction completed. The mixture was washed with aqueous NaHCO₃ and CH₂Cl₂. The combined organic layer was dried with anhydrous Na₂SO₄ and evaporated under vacuum. The crude mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 20/1) to afford the product **S17** as a white solid (0.31 g, 76% yield).

Diisopropyl 2-bromo-2-phenylcyclopropane-1,1-dicarboxylate (**S16**)



¹H NMR (400 MHz, CDCl₃) δ 7.47 – 7.42 (m, 2H), 7.33 – 7.24 (m, 3H), 5.23 (hept, *J* = 6.3 Hz, 1H), 4.70 (hept, *J* = 6.3 Hz, 1H), 2.48 (d, *J* = 7.0 Hz, 1H), 2.27 (d, *J* = 7.0 Hz,

1H), 1.45 – 1.35 (m, 6H), 1.01 (d, $J = 6.2$ Hz, 3H), 0.84 (d, $J = 6.3$ Hz, 3H).
 ^{13}C NMR (100 MHz, CDCl_3) δ 165.7, 165.2, 139.4, 129.0, 128.8, 128.5, 70.2, 69.7, 42.1, 40.6, 26.7, 22.0, 21.9, 21.6, 21.1.
 HRMS (ESI) m/z calcd. for $\text{C}_{17}\text{H}_{22}\text{O}_4\text{Br}$ [$\text{M} + \text{H}$] $^+$ 369.0696, found 369.0691.

Di-*tert*-butyl 2-bromo-2-phenylcyclopropane-1,1-dicarboxylate (S17)

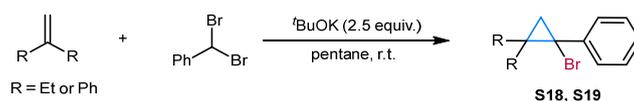


m.p. 60–64 °C

^1H NMR (400 MHz, CDCl_3) δ 7.47 – 7.39 (m, 2H), 7.35 – 7.25 (m, 3H), 2.38 (d, $J = 6.9$ Hz, 1H), 2.16 (d, $J = 6.9$ Hz, 1H), 1.59 (s, 9H), 1.15 (s, 9H).

^{13}C NMR (100 MHz, CDCl_3) δ 165.2, 164.7, 139.7, 129.0, 128.6, 128.4, 82.7, 82.4, 43.4, 40.6, 28.2, 27.7, 26.5.

HRMS (ESI) m/z calcd. for $\text{C}_{19}\text{H}_{26}\text{O}_4\text{Br}$ [$\text{M} + \text{H}$] $^+$ 397.1009, found 397.0994.



General procedure 2:

A solution of α,α -dibromotoluene (1.25 g, 5.0 mmol, 1.0 equiv.) in pentane (5.0 mL) at 0 °C was added dropwise within 1 h to a suspension of $t\text{BuOK}$ (1.40 g, 2.5 equiv.) in anhydrous pentane (20 mL) containing alkenes (2.2 equiv.). The resulting mixture was vigorously stirred at r.t. over a period of 2 days. After completion of the reaction (monitored by TLC), the mixture was quenched with H_2O and extracted with CH_2Cl_2 . The combined organic solution was concentrated under reduced pressure to afford the residue, which was purified by column chromatography on silica gel provide provide the corresponding cyclopropyl bromide **S18** or **S19**.

(1-bromo-2,2-diethylcyclopropyl)benzene (S18)



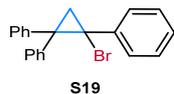
According to **General procedure 2** with 2-ethyl-1-butene (1.34 mL, 11.0 mmol), the crude product was purified by column chromatography on silica gel (petroleum ether) to yield **S18** as a colorless oil (0.99 g, 78% yield).

^1H NMR (400 MHz, CDCl_3) δ 7.41 – 7.33 (m, 2H), 7.32 – 7.27 (m, 2H), 7.25 – 7.19 (m, 1H), 2.03 (dq, $J = 14.6, 7.4$ Hz, 1H), 1.71 (dq, $J = 14.6, 7.4, 1.1$ Hz, 1H), 1.47 (dq, $J = 14.5, 7.3, 1.3$ Hz, 1H), 1.30 (d, $J = 6.2$ Hz, 1H), 1.18 – 1.06 (m, 4H), 0.80 (t, $J = 7.4$ Hz, 3H), 0.44 (dq, $J = 14.3, 7.4, 1.1$ Hz, 1H).

^{13}C NMR (100 MHz, CDCl_3) δ 142.5, 129.5, 128.4, 127.7, 47.5, 32.9, 27.8, 26.7, 25.0, 10.79, 10.76.

HRMS (ESI) m/z calcd. for $\text{C}_{13}\text{H}_{18}\text{Br}$ [$\text{M} + \text{H}$] $^+$ 253.0586, found 253.0585.

(2-Bromocyclopropane-1,1,2-triyl)tribenzene (S19)



According to **General procedure 2** with 1,1-diphenylethylene (1.98 g, 11.0 mmol), the crude product was purified by column chromatography on silica gel (petroleum ether/EtOAc = 100/1) to yield **S19** as a white solid (1.26 g, 72% yield).

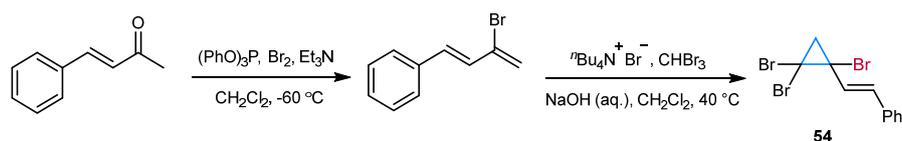
m.p. 101–104 °C

¹H NMR (400 MHz, CDCl₃) δ 7.69 – 7.58 (m, 2H), 7.44 – 7.32 (m, 4H), 7.30 – 7.24 (m, 1H), 7.19 – 7.13 (m, 2H), 7.12 – 7.05 (m, 3H), 7.01 – 6.88 (m, 3H), 2.71 (d, *J* = 6.9 Hz, 1H), 2.22 (d, *J* = 7.0 Hz, 1H).

¹³C NMR (100 MHz, CDCl₃) δ 143.6, 140.5, 140.2, 130.6, 129.4, 129.2, 128.3, 128.1, 127.9, 127.7, 127.1, 126.3, 45.2, 43.8, 27.5.

HRMS (ESI) *m/z* calcd. for C₂₁H₁₈Br [M + H]⁺ 349.0586, found 349.0577.

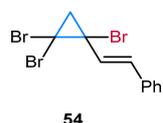
The structures and synthesis of 1-alkenyl-substituted cyclopropyl bromides:



According to the reported literature⁴, to a cold solution of triphenyl phosphite (5.8 mL, 22.0 mmol, 1.1 equiv.) in anhydrous CH₂Cl₂ (60 mL) maintained at -60 °C under Ar was added bromine (3.52 g, 22.0 mmol, 1.1 equiv.) dropwise. Then anhydrous triethylamine (3.1 mL, 22.0 mmol, 1.1 equiv.) and (*E*)-4-phenyl-3-buten-2-one (2.92 g, 20.0 mmol, 1.0 equiv.) were added to the faint orange solution. The reaction mixture was stirred for 18 h while warmed to r.t. and then was heated to reflux for a further 2 h. The reaction mixture was cooled to r.t. and concentrated in vacuo. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 100/1) to give (*E*)-(3-bromobuta-1,3-dien-1-yl)benzene.

To a round-bottomed flask were added (*E*)-(3-bromobuta-1,3-dien-1-yl)benzene (1.0 equiv.), bromoform (4.0 equiv.), sodium hydroxide (50% aq., 10 equiv.), *n*-tetrabutylammonium bromide (10 mol%) and CH₂Cl₂ (40 mL). The reaction mixture was stirred for 24 h at 40 °C. After completion of the reaction (monitored by TLC), the mixture was quenched with water and extracted with CH₂Cl₂. The combined organic solution was concentrated under reduced pressure to afford the residue, which was purified by column chromatography on silica gel to provide **54** as a white solid (4.27 g, 56% yield over two steps).

(*E*)-(2-(1,2,2-Tribromocyclopropyl)vinyl)benzene (**54**)

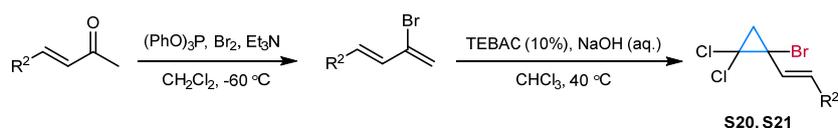


m.p. 89–91 °C

¹H NMR (400 MHz, CDCl₃) δ 7.46 – 7.39 (m, 2H), 7.38 – 7.27 (m, 3H), 6.71 (d, *J* = 15.4 Hz, 1H), 6.50 (d, *J* = 15.5 Hz, 1H), 2.36 (d, *J* = 9.3 Hz, 1H), 2.17 (d, *J* = 9.3 Hz, 1H).

¹³C NMR (100 MHz, CDCl₃) δ 135.4, 135.0, 128.9, 128.81, 128.79, 127.0, 42.6, 37.3, 32.9.

HRMS (ESI) *m/z* calcd. for C₁₁H₁₀Br₃ [M + H]⁺ 378.8327, found 378.8318.



General procedure 3:

According to the reported literature⁴, to a cold solution of triphenyl phosphite (5.8 mL, 22.0 mmol, 1.1 equiv.) in anhydrous CH₂Cl₂ (60 mL) maintained at -60 °C under Ar flow was added bromine (3.52 g, 22.0 mmol, 1.1 equiv.) dropwise. Then anhydrous

triethylamine (3.1 mL, 22.0 mmol, 1.1 equiv.) and (*E*)-4-phenyl-3-buten-2-one (2.92 g, 20.0 mmol, 1.0 equiv.) were added to the faint orange solution. The reaction mixture was stirred for 18 h while warmed to r.t. and then was heated to reflux for a further 2 h. The reaction mixture was cooled to r.t. and concentrated in vacuo. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 100/1) to give the corresponding 1-alkenyl-substituted vinyl bromide.

To a mixture of 1-alkenyl-substituted vinyl bromide (1.0 equiv.) and benzyltriethylammonium chloride (10 mol%) in chloroform (40 mL) was added dropwise NaOH (50% aq., 10 equiv.) within 2 h under heating at 40 °C with vigorous stirring. Then the mixture was stirred for 12 h at 40 °C. After completion of the reaction (monitored by TLC), the mixture was quenched with water and extracted with CH₂Cl₂. The combined organic solution was concentrated under reduced pressure to afford the residue, which was purified by column chromatography on silica gel to provide the corresponding cyclopropyl bromide **S20** or **S21**.

(*E*)-(2-(1-Bromo-2,2-dichlorocyclopropyl)vinyl)benzene (**S20**)



According to **General procedure 3** with (*E*)-4-phenyl-3-buten-2-one (1.46 g, 10.0 mmol, 1.0 equiv.), the crude product was purified by column chromatography on silica gel (petroleum ether/EtOAc = 100/1) to yield **S20** as a white solid (1.31 g, 45% yield over two steps).

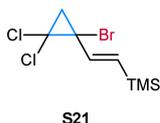
m.p. 61–63 °C

¹H NMR (400 MHz, CDCl₃) δ 7.43 – 7.35 (m, 2H), 7.36 – 7.24 (m, 3H), 6.74 (d, *J* = 15.5 Hz, 1H), 6.44 (d, *J* = 15.5 Hz, 1H), 2.22 (d, *J* = 9.0 Hz, 1H), 2.04 (d, *J* = 9.0 Hz, 1H).

¹³C NMR (100 MHz, CDCl₃) δ 135.44, 135.36, 128.9, 128.8, 127.01, 126.99, 63.7, 42.9, 35.5.

HRMS (ESI) *m/z* calcd. for C₁₁H₁₀BrCl₂ [M + H]⁺ 290.9337, found 290.9335.

(*E*)-(2-(1-Bromo-2,2-dichlorocyclopropyl)vinyl)trimethylsilane (**S21**)

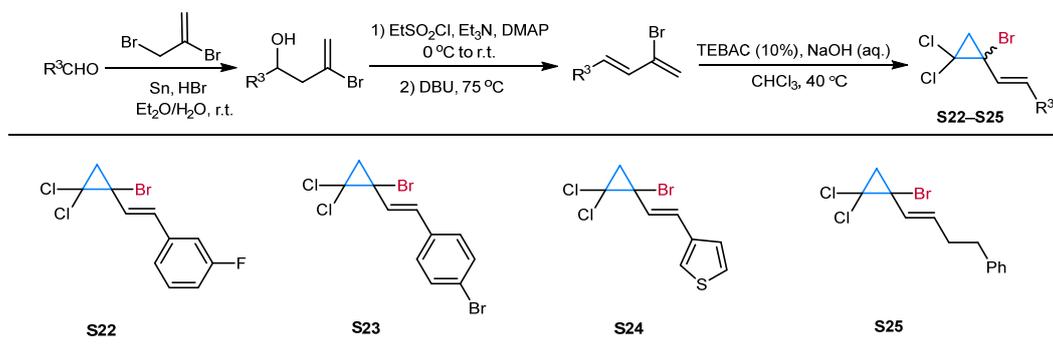


According to **General procedure 3** with (*E*)-4-(trimethylsilyl)but-3-en-2-one (0.71 g, 5.0 mmol, 1.0 equiv.), the crude product was purified by column chromatography on silica gel (petroleum ether) to yield **S21** as a colorless oil (0.59 g, 41% yield over two steps).

¹H NMR (400 MHz, CDCl₃) δ 6.03 (d, *J* = 18.1 Hz, 1H), 5.96 (d, *J* = 18.1 Hz, 1H), 2.03 (d, *J* = 8.9 Hz, 1H), 1.86 (d, *J* = 8.9 Hz, 1H), 0.00 (s, 9H).

^{13}C NMR (100 MHz, CDCl_3) δ 142.6, 137.6, 64.8, 46.4, 36.4, 0.0.

HRMS (ESI) m/z calcd. for $\text{C}_8\text{H}_{14}\text{BrCl}_2\text{Si}$ $[\text{M} + \text{H}]^+$ 286.9420, found 286.9408.



General procedure 4:

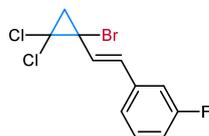
According to the reported literature⁵, tin powder (1.75 g, 15.0 mmol, 1.5 equiv.) was suspended in a biphasic mixture of Et_2O - H_2O (1:1 v/v, 60 mL). 2,3-Dibromopropene (3.0 mL, 30.0 mmol, 3.0 equiv.) and aldehyde (10.0 mmol, 1.0 equiv.) were then added at r.t. and the resulting mixture was vigorously stirred for 5 min. After that time, HBr (48% aq., 2.2 mL, 20.0 mmol, 2.0 equiv.) [Caution! Corrosive on skin or eye contact and toxic by inhalation. Use with appropriate protective equipment and in a well-ventilated fume hood] was added slowly, not letting the reaction temperature exceed $30\text{ }^\circ\text{C}$ (with a temperature probe). The suspension was stirred vigorously for 4 hours until complete as indicated by TLC. Water, Et_2O , and brine were then added, the organic layer was separated, and the aqueous layer was further extracted with Et_2O . The combined organic layers were dried over anhydrous Na_2SO_4 , filtered through celite (the drying/filtration sequence was repeated twice), and concentrated in vacuo. The residue was purified by column chromatography on silica gel to give the product alcohols which were submitted directly to the next step.

To a solution of an appropriate alcohol (1.0 equiv.) in CH_2Cl_2 (40 mL) at $0\text{ }^\circ\text{C}$ were added ethanesulfonyl chloride (2.0 equiv.), Et_3N (3.0 equiv.), and DMAP (10 mol%). The resulting mixture was warmed to r.t., stirred for 3 h, quenched with saturated aqueous NH_4Cl , and extracted with CH_2Cl_2 . The combined organic layers were washed with brine, dried over anhydrous MgSO_4 , and concentrated in vacuo. The crude product was dissolved in toluene (20 mL) and DBU (5.0 equiv.) was added. The resulting mixture was stirred at $75\text{ }^\circ\text{C}$ for 3 h, cooled to r.t., and quenched with saturated aqueous NH_4Cl . The aqueous layer was extracted with Et_2O and the combined organic layers dried over anhydrous MgSO_4 and concentrated in vacuo. The residue was purified by column chromatography on silica gel to give the 2-bromodiene products as single alkene regioisomers.

To a mixture of 2-bromodiene (1.0 equiv.) and benzyltriethylammonium chloride (10 mol%) in chloroform (20 mL) was added dropwise of NaOH (50% aq., 10 equiv.) within 2 h under heating at $40\text{ }^\circ\text{C}$ with vigorous stirring. Then the mixture was stirred for 12 h at $40\text{ }^\circ\text{C}$. After completion of the reaction (monitored by TLC), the mixture was quenched with water and extracted with CH_2Cl_2 . The combined organic solution was dried over anhydrous MgSO_4 and concentrated under reduced pressure to afford

the residue, which was purified by column chromatography on silica gel to provide the corresponding cyclopropyl bromide.

(*E*)-1-(2-(1-Bromo-2,2-dichlorocyclopropyl)vinyl)-3-fluorobenzene (S22)



S22

According to **General procedure 4** with 3-fluorobenzaldehyde (1.24 g, 10.0 mmol, 1.0 equiv.), the crude product was purified by column chromatography on silica gel (petroleum ether) to yield **S22** as a colorless oil (0.96 g, 31% yield over three steps).

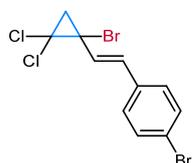
$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.35 – 7.27 (m, 1H), 7.21 – 7.14 (m, 1H), 7.13 – 7.09 (m, 1H), 6.99 (td, $J = 8.4, 2.5$ Hz, 1H), 6.73 (d, $J = 15.5$ Hz, 1H), 6.43 (d, $J = 15.5$ Hz, 1H), 2.24 (d, $J = 9.0$ Hz, 1H), 2.08 (d, $J = 9.0$ Hz, 1H).

$^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 163.2 (d, $J = 246.2$ Hz), 137.8 (d, $J = 7.8$ Hz), 134.3 (d, $J = 2.6$ Hz), 130.4 (d, $J = 8.4$ Hz), 128.5, 122.9 (d, $J = 2.9$ Hz), 115.6 (d, $J = 21.4$ Hz), 113.5 (d, $J = 22.0$ Hz), 63.6, 42.5, 35.7.

$^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ -112.9.

HRMS (ESI) m/z calcd. for $\text{C}_{11}\text{H}_9\text{BrCl}_2\text{F}$ $[\text{M} + \text{H}]^+$ 308.9243, found 308.9239.

(*E*)-1-Bromo-4-(2-(1-bromo-2,2-dichlorocyclopropyl)vinyl)benzene (S23)



S23

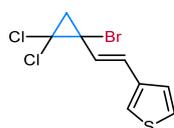
According to **General procedure 4** with 4-bromobenzaldehyde (1.85 g, 10.0 mmol, 1.0 equiv.), the crude product was purified by column chromatography on silica gel (petroleum ether) to yield **S23** as a colorless oil (1.37 g, 37% yield over three steps).

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.47 (d, $J = 8.2$ Hz, 2H), 7.27 (d, $J = 8.4$ Hz, 2H), 6.70 (d, $J = 15.5$ Hz, 1H), 6.42 (d, $J = 15.4$ Hz, 1H), 2.23 (d, $J = 9.0$ Hz, 1H), 2.07 (d, $J = 9.0$ Hz, 1H).

$^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 134.4, 134.2, 132.0, 128.5, 127.8, 122.7, 63.6, 42.6, 35.6.

HRMS (ESI) m/z calcd. for $\text{C}_{11}\text{H}_9\text{Br}_2\text{Cl}_2$ $[\text{M} + \text{H}]^+$ 368.8443, found 368.8432.

(*E*)-3-(2-(1-Bromo-2,2-dichlorocyclopropyl)vinyl)thiophene (S24)



S24

According to **General procedure 4** with thiophene-3-carbaldehyde (0.56 g, 5.0 mmol, 1.0 equiv.), the crude product was purified by column chromatography on silica gel (petroleum ether) to yield **S24** as a white solid (0.45 g, 30% yield over three steps).

m.p. 70–72 °C

¹H NMR (400 MHz, CDCl₃) δ 7.30 (dd, *J* = 5.0, 3.1 Hz, 1H), 7.26 (d, *J* = 3.4 Hz, 1H), 7.22 (dd, *J* = 5.0, 1.2 Hz, 1H), 6.75 (d, *J* = 15.5 Hz, 1H), 6.32 (d, *J* = 15.4 Hz, 1H), 2.20 (d, *J* = 8.9 Hz, 1H), 2.04 (d, *J* = 9.0 Hz, 1H).

¹³C NMR (100 MHz, CDCl₃) δ 138.1, 129.5, 126.8, 126.7, 125.1, 124.2, 63.6, 42.9, 35.5.

HRMS (ESI) *m/z* calcd. for C₉H₈BrCl₂S [M + H]⁺ 296.8902, found 296.8898.

(E)-(4-(1-Bromo-2,2-dichlorocyclopropyl)but-3-en-1-yl)benzene (**S25**)



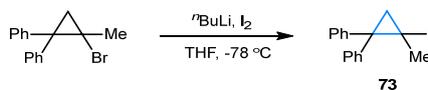
According to **General procedure 4** with 3-phenylpropanal (1.34 g, 10.0 mmol, 1.0 equiv.), the crude product was purified by column chromatography on silica gel (petroleum ether) to yield **S25** as a colorless liquid (1.34 g, 42% yield over three steps).

¹H NMR (400 MHz, CDCl₃) δ 7.32 – 7.24 (m, 2H), 7.21 – 7.11 (m, 3H), 5.89 (dt, *J* = 15.1, 6.5 Hz, 1H), 5.79 (d, *J* = 14.9 Hz, 1H), 2.75 – 2.66 (m, 2H), 2.48 – 2.37 (m, 2H), 2.03 (d, *J* = 8.9 Hz, 1H), 1.91 (d, *J* = 9.0 Hz, 1H).

¹³C NMR (100 MHz, CDCl₃) δ 141.2, 136.2, 128.7, 128.6, 128.5, 126.1, 63.4, 42.7, 35.3, 35.1, 33.7.

HRMS (ESI) *m/z* calcd. for C₁₃H₁₄BrCl₂ [M + H]⁺ 318.9650, found 318.9639.

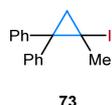
The structures and synthesis of 1-alkyl-substituted cyclopropyl halide



An oven-dried two-necked flask was charged under nitrogen atmosphere with a solution of (2-bromo-2-methylcyclopropane-1,1-diyl)dibenzene (2.87 g, 10.0 mmol, 1.0 equiv.) in anhydrous THF (20 mL). The solution was cooled to $-78\text{ }^{\circ}\text{C}$ and $n\text{BuLi}$ (2.5 M in hexanes, 4.0 mL, 10.0 mmol, 1.0 equiv.) was added dropwise. The reaction mixture was stirred for 30 min before the addition of iodine (2.5 g, 10 mmol, 1.0 equiv.). The stirring was continued for 12 h. After completion of the reaction (monitored by TLC), the mixture was quenched with water. Saturated aqueous $\text{Na}_2\text{S}_2\text{O}_3$ and CH_2Cl_2 were then added, the organic layer was separated, and the aqueous layer was further extracted with CH_2Cl_2 . The combined organic solution was dried over anhydrous MgSO_4 and concentrated under reduced pressure to afford the residue, which was purified by column chromatography on silica gel to provide **73** as a white solid (2.61 g, 78% yield).

Note: (2-bromo-2-methylcyclopropane-1,1-diyl)dibenzene was synthesized according to literature⁶.

(2-Iodo-2-methylcyclopropane-1,1-diyl)dibenzene (**73**)



m.p. 87–89 $^{\circ}\text{C}$

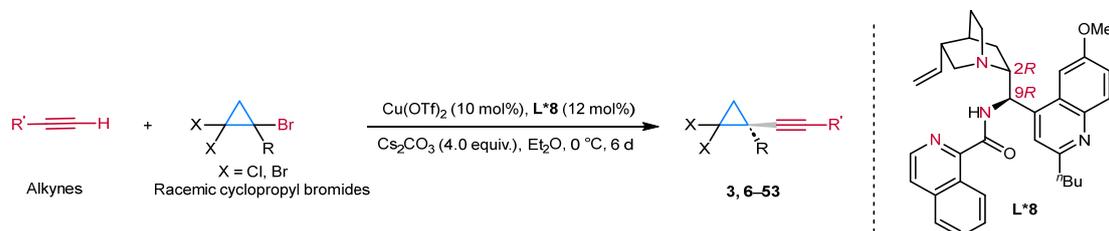
^1H NMR (400 MHz, CDCl_3) δ 7.56 – 7.46 (m, 4H), 7.37 – 7.28 (m, 4H), 7.27 – 7.19 (m, 2H), 1.99 (s, 3H), 1.98 (d, $J = 6.4$ Hz, 1H), 1.75 (d, $J = 6.4$ Hz, 1H).

^{13}C NMR (100 MHz, CDCl_3) δ 146.9, 141.0, 129.6, 129.5, 128.7, 128.2, 126.9, 126.8, 42.3, 33.7, 30.8, 15.5.

HRMS (ESI) m/z calcd. for $\text{C}_{16}\text{H}_{16}\text{I}$ $[\text{M} + \text{H}]^+$ 335.0291, found 335.0286.

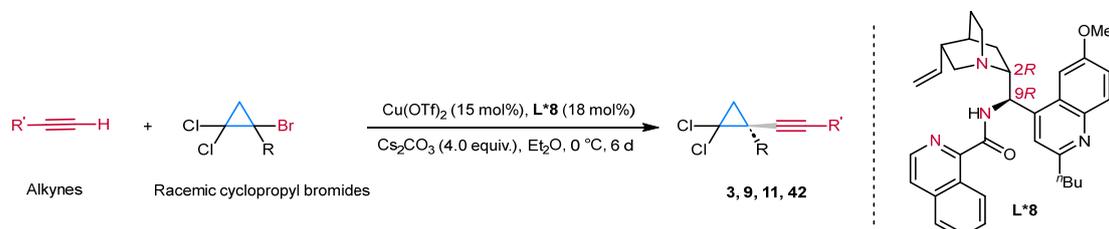
Enantioconvergent cross-coupling of alkynes with 1-(hetero)aryl-substituted cyclopropyl bromides

General procedure A:



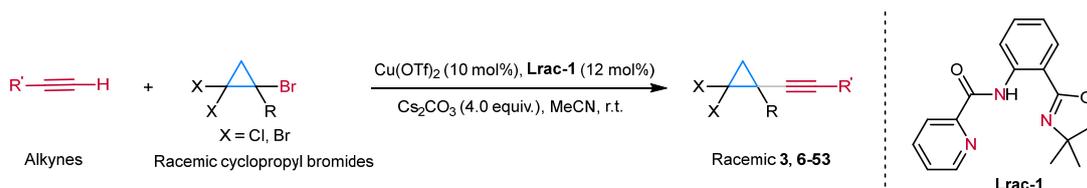
An oven-dried resealable Schlenk tube equipped with a magnetic stirring bar was charged with $\text{Cu}(\text{OTf})_2$ (7.20 mg, 0.020 mmol, 10 mol%), chiral ligand **L*8** (12.80 mg, 0.024 mmol, 12 mol%), and Cs_2CO_3 (256.0 mg, 0.80 mmol, 4.0 equiv.). The tube was evacuated and backfilled with argon three times. Then racemic 1-(hetero)aryl-substituted cyclopropyl bromide (0.30 mmol, 1.5 equiv.), alkyne (0.20 mmol, 1.0 equiv.), and Et_2O (2.0 mL) were sequentially added into the mixture under argon. The tube was sealed and the reaction mixture was allowed to stir at 0 °C for 6 d. Upon completion of the reaction (monitored by TLC), the mixture was then filtered through a pad of celite and rinsed with EtOAc . The filtrate was evaporated and the residue was purified by column chromatography on silica gel to afford the desired product.

General procedure B:



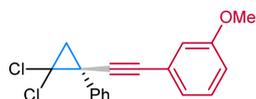
An oven-dried resealable Schlenk tube equipped with a magnetic stirring bar was charged with $\text{Cu}(\text{OTf})_2$ (10.85 mg, 0.030 mmol, 15 mol%), chiral ligand **L*8** (19.20 mg, 0.036 mmol, 18 mol%), and Cs_2CO_3 (256.0 mg, 0.80 mmol, 4.0 equiv.). The tube was evacuated and backfilled with argon three times. Then racemic 1-(hetero)aryl-substituted cyclopropyl bromide (0.20 mmol, 1.0 equiv.), alkyne (0.20 mmol, 1.0 equiv.), and Et_2O (2.0 mL) were sequentially added into the mixture under argon. The tube was sealed and the reaction mixture was allowed to stir at 0 °C for 6 d. Upon completion of the reaction (monitored by TLC), the mixture was then filtered through a pad of celite and rinsed with EtOAc . The filtrate was evaporated and the residue was purified by column chromatography on silica gel to afford the desired product.

The preparation of racemic products (\pm)-**3** and (\pm)-**6-53**:



Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with $\text{Cu}(\text{OTf})_2$ (3.60 mg, 0.010 mmol, 10 mol%), **Lrac-1** (3.54 mg, 0.012 mmol, 12 mol%), Cs_2CO_3 (128.0 mg, 0.40 mmol, 4.0 equiv.), and MeCN (1.0 mL). Then, racemic 1-(hetero)aryl-substituted cyclopropyl bromide (0.15 mmol, 1.5 equiv.) and alkyne (0.10 mmol, 1.0 equiv.) were sequentially added into the mixture and the reaction mixture was stirred at r.t. for 3 d. Upon completion, the precipitate was filtered off and washed by EtOAc. The filtrate was evaporated and the residue was purified by column chromatography on silica gel to afford the desired product.

(*R*)-1-((2,2-Dichloro-1-phenylcyclopropyl)ethynyl)-3-methoxybenzene (**3**)



3

According to **General procedure A** with 1-ethynyl-3-methoxybenzene (25.6 μL , 0.20 mmol) and (1-bromo-2,2-dichlorocyclopropyl)benzene **1** (79.8 mg, 0.30 mmol), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 50/1) to yield the product **3** as a colorless oil (58.4 mg, 92% yield, 92% e.e.).

According to **General procedure B** with 1-ethynyl-3-methoxybenzene (25.6 μL , 0.20 mmol) and (1-bromo-2,2-dichlorocyclopropyl)benzene **1** (53.2 mg, 0.20 mmol), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 50/1) to yield the product **3** as a colorless oil (58.3 mg, 92% yield, 92% e.e.).

$[\alpha]_{\text{D}}^{27} = -96$ (c 0.5, CHCl_3).

HPLC analysis: Chiralcel IA (*n*-hexane/*i*-PrOH = 99.5/0.5, flow rate 0.5 mL/min, $\lambda = 254$ nm), t_{R} (minor) = 11.79 min, t_{R} (major) = 13.65 min.

^1H NMR (400 MHz, CDCl_3) δ 7.50 – 7.45 (m, 2H), 7.42 – 7.31 (m, 3H), 7.18 (t, $J = 7.9$ Hz, 1H), 7.02 (dt, $J = 7.6, 1.2$ Hz, 1H), 6.94 (dd, $J = 2.7, 1.4$ Hz, 1H), 6.85 (ddd, $J = 8.3, 2.7, 1.0$ Hz, 1H), 3.76 (s, 3H), 2.40 (d, $J = 7.6$ Hz, 1H), 2.20 (d, $J = 7.6$ Hz, 1H).

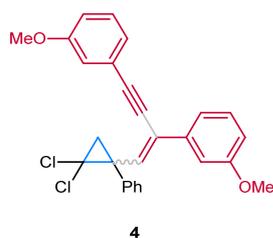
^{13}C NMR (100 MHz, CDCl_3) δ 159.4, 136.3, 129.4, 129.1, 128.6, 128.3, 124.5, 123.8, 116.7, 115.1, 89.2, 82.1, 64.9, 55.4, 34.1, 33.2.

HRMS (ESI) m/z calcd. for $\text{C}_{18}\text{H}_{15}\text{Cl}_2\text{O}$ $[\text{M} + \text{H}]^+$ 317.0494, found 317.0490.

Side products **4** and **5** were obtained under indicated conditions according to similar protocols as described above.

3,3'-(4-(2,2-Dichloro-1-phenylcyclopropyl)but-3-en-1-yne)-1,3-

diyl)bis(methoxybenzene) (4)

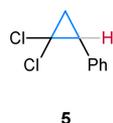


$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.41 – 7.35 (m, 2H), 7.33 – 7.27 (m, 3H), 7.25 (d, $J = 8.2$ Hz, 1H), 7.23 – 7.17 (m, 1H), 7.04 (dt, $J = 7.6, 1.2$ Hz, 1H), 6.96 (dd, $J = 2.6, 1.4$ Hz, 1H), 6.92 – 6.84 (m, 4H), 6.82 (dd, $J = 2.6, 1.5$ Hz, 1H), 3.79 (s, 3H), 3.76 (s, 3H), 2.04 (dd, $J = 8.1, 1.2$ Hz, 1H), 1.40 (d, $J = 8.2$ Hz, 1H).

$^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 159.5, 159.4, 139.1, 138.2, 136.7, 129.5, 129.3, 128.8, 128.7, 127.8, 127.6, 124.4, 124.1, 121.2, 116.4, 115.3, 114.14, 114.09, 90.3, 89.7, 66.3, 55.4, 55.4, 39.5, 31.7.

HRMS (ESI) m/z calcd. for $\text{C}_{27}\text{H}_{23}\text{O}_2\text{Cl}_2$ $[\text{M} + \text{H}]^+$ 449.1070, found 449.1063.

(2,2-Dichlorocyclopropyl)benzene (5)

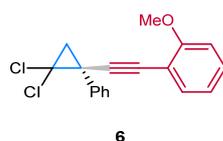


$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.37 – 7.26 (m, 3H), 7.25 – 7.20 (m, 2H), 2.89 (dd, $J = 10.6, 8.5$ Hz, 1H), 1.94 (dd, $J = 10.7, 7.4$ Hz, 1H), 1.83 (t, $J = 7.9$ Hz, 1H).

$^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 134.7, 129.0, 128.4, 127.7, 60.9, 35.6, 25.8.

HRMS (ESI) m/z calcd. for $\text{C}_9\text{H}_9\text{Cl}_2$ $[\text{M} + \text{H}]^+$ 187.0076, found 187.0080.

(*R*)-1-((2,2-Dichloro-1-phenylcyclopropyl)ethynyl)-2-methoxybenzene (6)



According to **General procedure A** with 1-ethynyl-2-methoxybenzene (25.8 μL , 0.20 mmol) and (1-bromo-2,2-dichlorocyclopropyl)benzene **1** (79.8 mg, 0.30 mmol), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 50/1) to yield the product **6** as a pale-yellow solid (50.8 mg, 80% yield, 92% e.e.).

m.p. 102–105 $^\circ\text{C}$

$[\alpha]_{\text{D}}^{27} = -88$ (c 0.5, CHCl_3).

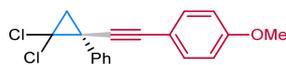
HPLC analysis: Chiralcel OD3 (*n*-hexane/*i*-PrOH = 99/1, flow rate 0.5 mL/min, $\lambda = 254$ nm), t_{R} (minor) = 11.60 min, t_{R} (major) = 13.92 min.

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.56 – 7.46 (m, 2H), 7.44 – 7.28 (m, 4H), 7.27 – 7.20 (m, 1H), 6.86 (t, $J = 7.5$ Hz, 1H), 6.82 (d, $J = 8.3$ Hz, 1H), 3.80 (s, 3H), 2.41 (d, $J = 7.6$ Hz, 1H), 2.21 (d, $J = 7.6$ Hz, 1H).

^{13}C NMR (100 MHz, CDCl_3) δ 160.5, 136.4, 133.9, 129.9, 129.1, 128.5, 128.1, 120.4, 112.0, 110.9, 93.2, 78.7, 65.1, 55.9, 34.4, 33.2

HRMS (ESI) m/z calcd. for $\text{C}_{18}\text{H}_{15}\text{Cl}_2\text{O}$ $[\text{M} + \text{H}]^+$ 317.0494, found 317.0491.

(*R*)-1-((2,2-Dichloro-1-phenylcyclopropyl)ethynyl)-4-methoxybenzene (7)



7

According to **General procedure A** with 1-ethynyl-4-methoxybenzene (26.4 mg, 0.20 mmol) and (1-bromo-2,2-dichlorocyclopropyl)benzene **1** (79.8 mg, 0.30 mmol), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 50/1) to yield the product **7** as a white solid (57.7 mg, 91% yield, 92% e.e.).

m.p. 56–59 °C

$[\alpha]_{\text{D}}^{27} = -114$ (c 0.5, CHCl_3).

HPLC analysis: Chiralcel IG (*n*-hexane/*i*-PrOH = 98/2, flow rate 1.0 mL/min, $\lambda = 254$ nm), t_{R} (minor) = 5.68 min, t_{R} (major) = 7.04 min.

^1H NMR (400 MHz, CDCl_3) δ 7.52 – 7.43 (m, 2H), 7.42 – 7.28 (m, 5H), 6.88 – 6.72 (m, 2H), 3.77 (s, 3H), 2.37 (d, $J = 7.5$ Hz, 1H), 2.17 (d, $J = 7.7$ Hz, 1H).

^{13}C NMR (100 MHz, CDCl_3) δ 159.8, 136.6, 133.4, 129.0, 128.6, 128.2, 114.9, 114.0, 87.9, 82.1, 65.0, 55.4, 34.2, 33.2.

HRMS (ESI) m/z calcd. for $\text{C}_{18}\text{H}_{15}\text{Cl}_2\text{O}$ $[\text{M} + \text{H}]^+$ 317.0494, found 317.0492.

(*R*)-(2,2-Dichloro-1-(phenylethynyl)cyclopropyl)benzene (8)



8

According to **General procedure A** with ethynylbenzene (21.9 μL , 0.20 mmol) and (1-bromo-2,2-dichlorocyclopropyl)benzene **1** (79.8 mg, 0.30 mmol), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 50/1) to yield the product **8** as a colorless oil (47.1 mg, 82% yield, 92% e.e.).

$[\alpha]_{\text{D}}^{27} = -102$ (c 0.5, CHCl_3).

HPLC analysis: Chiralcel IG (*n*-hexane/*i*-PrOH = 98/2, flow rate 1.0 mL/min, $\lambda = 254$ nm), t_{R} (minor) = 4.10 min, t_{R} (major) = 4.62 min.

^1H NMR (400 MHz, CDCl_3) δ 7.51 – 7.45 (m, 2H), 7.44 – 7.30 (m, 5H), 7.29 – 7.23 (m, 3H), 2.39 (d, $J = 7.6$ Hz, 1H), 2.19 (d, $J = 7.6$ Hz, 1H).

^{13}C NMR (100 MHz, CDCl_3) δ 136.4, 132.0, 129.1, 128.6, 128.5, 128.4, 128.2, 122.8, 89.3, 82.2, 64.9, 34.1, 33.2.

HRMS (ESI) m/z calcd. for $\text{C}_{17}\text{H}_{13}\text{Cl}_2$ $[\text{M} + \text{H}]^+$ 287.0389, found 287.0385.

(*R*)-1-((2,2-Dichloro-1-phenylcyclopropyl)ethynyl)-4-methylbenzene (9)



9

According to **General procedure A** with 1-ethynyl-4-methylbenzene (25.3 μ L, 0.20 mmol) and (1-bromo-2,2-dichlorocyclopropyl)benzene **1** (79.8 mg, 0.30 mmol), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 50/1) to yield the product **9** as a white solid (52.9 mg, 88% yield, 90% e.e.).

According to **General procedure B** with 1-ethynyl-4-methylbenzene (25.3 μ L, 0.20 mmol) and (1-bromo-2,2-dichlorocyclopropyl)benzene **1** (53.2 mg, 0.20 mmol), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 50/1) to yield the product **9** as a white solid (51.8 mg, 86% yield, 90% e.e.).

m.p. 54–57 °C

$[\alpha]_D^{27} = -105$ (c 0.5, CHCl₃).

HPLC analysis: Chiralcel IG (*n*-hexane/*i*-PrOH = 98/2, flow rate 0.5 mL/min, $\lambda = 254$ nm), t_R (minor) = 9.06 min, t_R (major) = 10.44 min.

¹H NMR (400 MHz, CDCl₃) δ 7.53 – 7.42 (m, 2H), 7.41 – 7.35 (m, 2H), 7.34 – 7.25 (m, 3H), 7.12 – 7.01 (m, 2H), 2.38 (d, $J = 7.5$ Hz, 1H), 2.31 (s, 3H), 2.17 (d, $J = 7.5$ Hz, 1H).

¹³C NMR (100 MHz, CDCl₃) δ 138.6, 136.5, 131.8, 129.11, 129.06, 128.6, 128.2, 119.7, 88.6, 82.4, 65.0, 34.2, 33.2, 21.6.

HRMS (ESI) m/z calcd. for C₁₈H₁₅Cl₂ [M + H]⁺ 301.0545, found 301.0535.

(*R*)-4-((2,2-Dichloro-1-phenylcyclopropyl)ethynyl)-1,1'-biphenyl (**10**)



10

According to **General procedure A** with 4-ethynyl-1,1'-biphenyl (35.6 mg, 0.20 mmol) and (1-bromo-2,2-dichlorocyclopropyl)benzene **1** (79.8 mg, 0.30 mmol), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 50/1) to yield the product **10** as a white solid (62.4 mg, 86% yield, 92% e.e.).

m.p. 140–142 °C

$[\alpha]_D^{27} = -124$ (c 0.5, CHCl₃).

HPLC analysis: Chiralcel IG (*n*-hexane/*i*-PrOH = 98/2, flow rate 0.5 mL/min, $\lambda = 254$ nm), t_R (minor) = 14.02 min, t_R (major) = 16.54 min.

¹H NMR (400 MHz, CDCl₃) δ 7.66 – 7.52 (m, 8H), 7.51 – 7.42 (m, 4H), 7.41 – 7.35 (m, 2H), 2.46 (d, $J = 7.5$ Hz, 1H), 2.26 (d, $J = 7.7$ Hz, 1H).

¹³C NMR (100 MHz, CDCl₃) δ 141.2, 140.4, 136.4, 132.4, 129.1, 129.0, 128.6, 128.3, 127.8, 127.1, 127.0, 121.7, 90.0, 82.1, 64.9, 34.2, 33.3.

HRMS (ESI) m/z calcd. for C₂₃H₁₇Cl₂ [M + H]⁺ 363.0702, found 363.0692.

(*R*)-1-((2,2-Dichloro-1-phenylcyclopropyl)ethynyl)-4-fluorobenzene (**11**)



11

According to **General procedure A** with 1-ethynyl-4-fluorobenzene (23.0 μ L, 0.20 mmol) and (1-bromo-2,2-dichlorocyclopropyl)benzene **1** (79.8 mg, 0.30 mmol) for 8 d, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 50/1) to yield the product **11** as a colorless oil (43.1 mg, 71% yield, 92% e.e.).

According to **General procedure B** with 1-ethynyl-4-fluorobenzene (23.0 μ L, 0.20 mmol) and (1-bromo-2,2-dichlorocyclopropyl)benzene **1** (53.2 mg, 0.20 mmol), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 50/1) to yield the product **11** as a colorless oil (45.8 mg, 75% yield, 92% e.e.).

$[\alpha]_D^{27} = -103$ (c 0.5, CHCl_3).

HPLC analysis: Chiralcel IG (*n*-hexane/*i*-PrOH = 98/2, flow rate 0.5 mL/min, $\lambda = 254$ nm), t_R (minor) = 8.56 min, t_R (major) = 9.67 min.

^1H NMR (400 MHz, CDCl_3) δ 7.53 – 7.44 (m, 2H), 7.44 – 7.29 (m, 5H), 7.03 – 6.89 (m, 2H), 2.39 (d, $J = 7.5$ Hz, 1H), 2.18 (d, $J = 7.6$ Hz, 1H).

^{13}C NMR (100 MHz, CDCl_3) δ 162.6 (d, $J = 249.6$ Hz), 136.3, 133.9 (d, $J = 8.4$ Hz), 129.1, 128.7, 128.3, 118.9 (d, $J = 3.5$ Hz), 115.7 (d, $J = 22.1$ Hz), 89.0 (d, $J = 1.5$ Hz), 81.2, 64.8, 34.1, 33.2.

^{19}F NMR (376 MHz, CDCl_3) δ -110.6.

HRMS (ESI) m/z calcd. for $\text{C}_{17}\text{H}_{12}\text{Cl}_2\text{F}$ $[\text{M} + \text{H}]^+$ 305.0295, found 305.0287.

(*R*)-1-Chloro-4-((2,2-dichloro-1-phenylcyclopropyl)ethynyl)benzene (**12**)



12

According to **General procedure A** with 1-chloro-4-ethynylbenzene (27.2 mg, 0.20 mmol) and (1-bromo-2,2-dichlorocyclopropyl)benzene **1** (79.8 mg, 0.30 mmol) for 8 d, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 50/1) to yield the product **12** as a white solid (45.6 mg, 71% yield, 92% e.e.).

m.p. 46–49 $^\circ\text{C}$

$[\alpha]_D^{27} = -109$ (c 0.5, CHCl_3).

HPLC analysis: Chiralcel IG (*n*-hexane/*i*-PrOH = 98/2, flow rate 0.5 mL/min, $\lambda = 214$ nm), t_R (minor) = 9.15 min, t_R (major) = 10.85 min.

^1H NMR (400 MHz, CDCl_3) δ 7.52 – 7.42 (m, 2H), 7.41 – 7.29 (m, 5H), 7.28 – 7.19 (m, 2H), 2.39 (d, $J = 7.6$ Hz, 1H), 2.18 (d, $J = 7.5$ Hz, 1H).

^{13}C NMR (100 MHz, CDCl_3) δ 136.2, 134.5, 133.2, 129.1, 128.69, 128.68, 128.3, 121.3, 90.3, 81.1, 64.8, 34.1, 33.2.

HRMS (ESI) m/z calcd. for $\text{C}_{17}\text{H}_{12}\text{Cl}_3$ $[\text{M} + \text{H}]^+$ 320.9999, found 320.9991.

(*R*)-1-Bromo-4-((2,2-dichloro-1-phenylcyclopropyl)ethynyl)benzene (**13**)



13

According to **General procedure A** with 1-bromo-4-ethynylbenzene (36.2 mg, 0.20 mmol) and (1-bromo-2,2-dichlorocyclopropyl)benzene **1** (79.8 mg, 0.30 mmol) for 8 d, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 50/1) to yield the product **13** as a white solid (60.1 mg, 82% yield, 92% e.e.).

m.p. 75–77 °C

$[\alpha]_D^{27} = -115$ (c 0.5, CHCl₃).

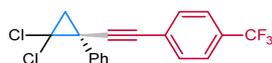
HPLC analysis: Chiralcel OD3 (*n*-hexane/*i*-PrOH = 99.5/0.5, flow rate 0.5 mL/min, $\lambda = 254$ nm), t_R (minor) = 9.36 min, t_R (major) = 10.10 min.

¹H NMR (400 MHz, CDCl₃) δ 7.49 – 7.43 (m, 2H), 7.43 – 7.31 (m, 5H), 7.30 – 7.23 (m, 2H), 2.39 (d, $J = 7.5$ Hz, 1H), 2.19 (d, $J = 7.5$ Hz, 1H).

¹³C NMR (100 MHz, CDCl₃) δ 136.1, 133.4, 131.6, 129.1, 128.7, 128.3, 122.7, 121.7, 90.5, 81.2, 64.7, 34.1, 33.2.

HRMS (ESI) m/z calcd. for C₁₇H₁₂BrCl₂ [M + H]⁺ 364.9494, found 364.9484.

(R)-1-((2,2-Dichloro-1-phenylcyclopropyl)ethynyl)-4-(trifluoromethyl)benzene (14)



14

According to **General procedure A** with 1-ethynyl-4-(trifluoromethyl)benzene (32.5 μ L, 0.20 mmol) and (1-bromo-2,2-dichlorocyclopropyl)benzene **1** (79.8 mg, 0.30 mmol) for 8 d, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 50/1) to yield the product **14** as a colorless oil (60.5 mg, 85% yield, 90% e.e.).

$[\alpha]_D^{27} = -118$ (c 0.5, CHCl₃).

HPLC analysis: Chiralcel ODH (*n*-hexane/*i*-PrOH = 98/2, flow rate 1.0 mL/min, $\lambda = 254$ nm), t_R (minor) = 9.11 min, t_R (major) = 10.14 min.

¹H NMR (400 MHz, CDCl₃) δ 7.56 – 7.48 (m, 4H), 7.48 – 7.43 (m, 2H), 7.43 – 7.32 (m, 3H), 2.41 (d, $J = 7.6$ Hz, 1H), 2.21 (d, $J = 7.6$ Hz, 1H).

¹³C NMR (100 MHz, CDCl₃) δ 136.0, 132.2, 130.2 (q, $J = 32.7$ Hz), 129.1, 128.8, 128.5, 126.7 (q, $J = 1.3$ Hz), 125.3 (q, $J = 3.9$ Hz), 124.0 (q, $J = 272.7$ Hz), 91.9, 80.9, 64.7, 34.1, 33.3.

¹⁹F NMR (376 MHz, CDCl₃) δ –62.8.

HRMS (ESI) m/z calcd. for C₁₈H₁₂Cl₂F₃ [M + H]⁺ 355.0263, found 355.0258.

(R)-4-((2,2-Dichloro-1-phenylcyclopropyl)ethynyl)benzaldehyde (15)



15

According to **General procedure A** with 4-ethynylbenzaldehyde (26.0 mg, 0.20 mmol) and (1-bromo-2,2-dichlorocyclopropyl)benzene **1** (79.8 mg, 0.30 mmol) at r.t., the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 20/1) to yield the product **15** as a colorless oil (50.5 mg, 80% yield, 86% e.e.).

$[\alpha]_D^{27} = -148$ (c 0.5, CHCl₃).

HPLC analysis: Chiralcel OJH (*n*-hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, $\lambda = 214$ nm), t_R (minor) = 6.71 min, t_R (major) = 9.00 min.

¹H NMR (400 MHz, CDCl₃) δ 9.98 (s, 1H), 7.85 – 7.74 (m, 2H), 7.62 – 7.52 (m, 2H), 7.51 – 7.44 (m, 2H), 7.43 – 7.33 (m, 3H), 2.44 (d, $J = 7.6$ Hz, 1H), 2.24 (d, $J = 7.6$ Hz, 1H).

¹³C NMR (100 MHz, CDCl₃) δ 191.5, 135.9, 135.6, 132.5, 129.6, 129.10, 129.08, 128.7, 128.5, 93.6, 81.4, 64.7, 34.1, 33.4.

HRMS (ESI) m/z calcd. for C₁₈H₁₃Cl₂O [M + H]⁺ 315.0338, found 315.0334.

Methyl (*R*)-4-((2,2-dichloro-1-phenylcyclopropyl)ethynyl)benzoate (**16**)



16

According to **General procedure A** with methyl 4-ethynylbenzoate (32.0 mg, 0.20 mmol) and (1-bromo-2,2-dichlorocyclopropyl)benzene **1** (79.8 mg, 0.30 mmol) for 8 d, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 20/1) to yield the product **16** as a colorless oil (48.8 mg, 71% yield, 92% e.e.).

$[\alpha]_D^{27} = -114$ (c 0.5, CHCl₃).

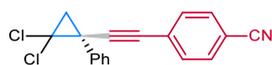
HPLC analysis: Chiralcel IG (*n*-hexane/*i*-PrOH = 95/5, flow rate 1.0 mL/min, $\lambda = 254$ nm), t_R (minor) = 7.59 min, t_R (major) = 10.12 min.

¹H NMR (400 MHz, CDCl₃) δ 8.01 – 7.91 (m, 2H), 7.55 – 7.44 (m, 4H), 7.43 – 7.33 (m, 3H), 3.91 (s, 3H), 2.43 (d, $J = 7.6$ Hz, 1H), 2.23 (d, $J = 7.6$ Hz, 1H).

¹³C NMR (100 MHz, CDCl₃) δ 166.6, 136.0, 131.9, 129.7, 129.5, 129.1, 128.7, 128.4, 127.5, 92.4, 81.5, 64.7, 52.4, 34.1, 33.3.

HRMS (ESI) m/z calcd. for C₁₉H₁₅Cl₂O₂ [M + H]⁺ 345.0444, found 345.0438.

(*R*)-4-((2,2-Dichloro-1-phenylcyclopropyl)ethynyl)benzotrile (**17**)



17

According to **General procedure A** with 4-ethynylbenzotrile (26.0 mg, 0.20 mmol) and (1-bromo-2,2-dichlorocyclopropyl)benzene **1** (79.8 mg, 0.30 mmol) at r.t., the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 20/1) to yield the product **17** as a colorless oil (46.2 mg, 74% yield, 84% e.e.).

$[\alpha]_D^{27} = -140$ (c 0.5, CHCl₃).

HPLC analysis: Chiralcel IG (*n*-hexane/*i*-PrOH = 95/5, flow rate 1.0 mL/min, λ = 214 nm), t_R (minor) = 8.34 min, t_R (major) = 11.97 min.

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.63 – 7.54 (m, 2H), 7.53 – 7.32 (m, 7H), 2.45 (d, J = 7.6 Hz, 1H), 2.24 (d, J = 7.6 Hz, 1H).

$^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 135.7, 132.5, 132.1, 129.1, 128.8, 128.5, 127.7, 118.5, 111.8, 94.0, 80.6, 64.6, 34.0, 33.4.

HRMS (ESI) m/z calcd. for $\text{C}_{18}\text{H}_{12}\text{NCl}_2$ $[\text{M} + \text{H}]^+$ 312.0341, found 312.0337.

(*R*)-1-((2,2-Dichloro-1-phenylcyclopropyl)ethynyl)-4-nitrobenzene (**18**)



18

According to **General procedure A** with 1-ethynyl-4-nitrobenzene (29.4 mg, 0.20 mmol) and (1-bromo-2,2-dichlorocyclopropyl)benzene **1** (79.8 mg, 0.30 mmol) at r.t., the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 30/1) to yield the product **18** as a colorless oil (62.1 mg, 93% yield, 80% e.e.).

$[\alpha]_D^{27} = -141$ (c 0.5, CHCl_3).

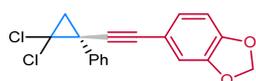
HPLC analysis: Chiralcel IG (*n*-hexane/*i*-PrOH = 95/5, flow rate 0.5 mL/min, λ = 214 nm), t_R (minor) = 19.89 min, t_R (major) = 26.65 min.

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.26 – 8.07 (m, 2H), 7.61 – 7.52 (m, 2H), 7.52 – 7.32 (m, 5H), 2.47 (d, J = 7.7 Hz, 1H), 2.27 (d, J = 7.6 Hz, 1H).

$^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 147.2, 135.6, 132.7, 129.7, 129.1, 128.8, 128.6, 123.6, 94.9, 80.4, 64.6, 34.0, 33.4.

HRMS (ESI) m/z calcd. for $\text{C}_{17}\text{H}_{12}\text{O}_2\text{NCl}_2$ $[\text{M} + \text{H}]^+$ 332.0240, found 332.0233.

(*R*)-5-((2,2-Dichloro-1-phenylcyclopropyl)ethynyl)benzo[*d*][1,3]dioxole (**19**)



19

According to **General procedure A** with 5-ethynylbenzo[*d*][1,3]dioxole (29.2 mg, 0.20 mmol) and (1-bromo-2,2-dichlorocyclopropyl)benzene **1** (79.8 mg, 0.30 mmol), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 50/1) to yield the product **19** as a colorless oil (56.2 mg, 85% yield, 92% e.e.).

$[\alpha]_D^{27} = -112$ (c 0.5, CHCl_3).

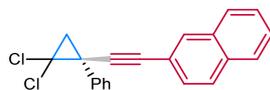
HPLC analysis: Chiralcel ODH (*n*-hexane/*i*-PrOH = 98/2, flow rate 0.5 mL/min, λ = 254 nm), t_R (minor) = 11.86 min, t_R (major) = 13.44 min.

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.52 – 7.45 (m, 2H), 7.43 – 7.33 (m, 3H), 6.97 (dd, J = 8.1, 1.6 Hz, 1H), 6.89 (d, J = 1.6 Hz, 1H), 6.73 (d, J = 8.0 Hz, 1H), 5.95 (s, 2H), 2.40 (d, J = 7.6 Hz, 1H), 2.19 (d, J = 7.5 Hz, 1H).

$^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 148.0, 147.4, 136.5, 129.0, 128.6, 128.2, 126.6, 116.0, 111.9, 108.5, 101.4, 87.7, 82.1, 64.9, 34.1, 33.2.

HRMS (ESI) m/z calcd. for $C_{18}H_{13}O_2Cl_2$ $[M + H]^+$ 331.0287, found 331.0283.

(R)-2-((2,2-Dichloro-1-phenylcyclopropyl)ethynyl)naphthalene (20)



20

According to **General procedure A** with 2-ethynyl naphthalene (30.4 mg, 0.20 mmol) and (1-bromo-2,2-dichlorocyclopropyl)benzene **1** (79.8 mg, 0.30 mmol), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 50/1) to yield the product **20** as a white solid (54.4 mg, 81% yield, 90% e.e.).

m.p. 109–112 °C

$[\alpha]_D^{27} = -146$ (c 0.5, $CHCl_3$).

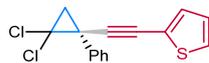
HPLC analysis: Chiralcel IG (*n*-hexane/*i*-PrOH = 95/5, flow rate 1.0 mL/min, $\lambda = 254$ nm), t_R (minor) = 4.95 min, t_R (major) = 5.90 min.

1H NMR (400 MHz, $CDCl_3$) δ 8.01 (s, 1H), 7.88 – 7.71 (m, 3H), 7.67 – 7.32 (m, 8H), 2.47 (d, $J = 7.5$ Hz, 1H), 2.29 (d, $J = 7.5$ Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 136.4, 133.0, 132.9, 131.9, 129.1, 128.7, 128.6, 128.3, 128.0, 127.85, 127.79, 126.8, 126.6, 120.1, 89.7, 82.6, 64.9, 34.2, 33.3.

HRMS (ESI) m/z calcd. for $C_{21}H_{15}Cl_2$ $[M + H]^+$ 337.0545, found 337.0540.

(R)-2-((2,2-Dichloro-1-phenylcyclopropyl)ethynyl)thiophene (21)



21

According to **General procedure A** with 2-ethynylthiophene (19.6 μ L, 0.20 mmol) and (1-bromo-2,2-dichlorocyclopropyl)benzene **1** (79.8 mg, 0.30 mmol), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 50/1) to yield the product **21** as a colorless oil (43.9 mg, 75% yield, 92% e.e.).

$[\alpha]_D^{27} = -112$ (c 0.5, $CHCl_3$).

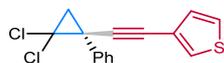
HPLC analysis: Chiralcel ODH (*n*-hexane/*i*-PrOH = 98/2, flow rate 0.5 mL/min, $\lambda = 254$ nm), t_R (minor) = 10.96 min, t_R (major) = 11.98 min.

1H NMR (400 MHz, $CDCl_3$) δ 7.53 – 7.46 (m, 2H), 7.44 – 7.33 (m, 3H), 7.27 – 7.18 (m, 2H), 6.96 (dd, $J = 5.1, 3.6$ Hz, 1H), 2.42 (d, $J = 7.6$ Hz, 1H), 2.23 (d, $J = 7.6$ Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 136.1, 132.5, 129.1, 128.7, 128.3, 127.3, 127.0, 122.8, 93.1, 75.5, 64.8, 34.3, 33.3.

HRMS (ESI) m/z calcd. for $C_{15}H_{11}Cl_2S$ $[M + H]^+$ 292.9953, found 292.9949.

(R)-3-((2,2-Dichloro-1-phenylcyclopropyl)ethynyl)thiophene (22)



22

According to **General procedure A** with 3-ethynylthiophene (19.7 μL , 0.20 mmol) and (1-bromo-2,2-dichlorocyclopropyl)benzene **1** (79.8 mg, 0.30 mmol), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 50/1) to yield the product **22** as a colorless oil (51.8 mg, 85% yield, 92% e.e.).

$[\alpha]_{\text{D}}^{27} = -101$ (c 0.5, CHCl_3).

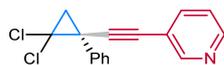
HPLC analysis: Chiralcel ODH (*n*-hexane/*i*-PrOH = 99/1, flow rate 0.5 mL/min, $\lambda = 270$ nm), t_{R} (minor) = 10.32 min, t_{R} (major) = 11.24 min.

^1H NMR (400 MHz, CDCl_3) δ 7.50 – 7.44 (m, 2H), 7.43 – 7.30 (m, 4H), 7.22 (dd, $J = 5.0, 3.0$ Hz, 1H), 7.08 (dd, $J = 5.0, 1.2$ Hz, 1H), 2.38 (d, $J = 7.5$ Hz, 1H), 2.18 (d, $J = 7.5$ Hz, 1H).

^{13}C NMR (100 MHz, CDCl_3) δ 136.4, 130.1, 129.3, 129.1, 128.6, 128.3, 125.4, 121.8, 88.8, 77.4, 64.8, 34.2, 33.2.

HRMS (ESI) m/z calcd. for $\text{C}_{15}\text{H}_{11}\text{Cl}_2\text{S}$ $[\text{M} + \text{H}]^+$ 292.9953, found 292.9943.

(*R*)-3-((2,2-Dichloro-1-phenylcyclopropyl)ethynyl)pyridine (**23**)



23

According to **General procedure A** with 3-ethynylpyridine (20.2 μL , 0.20 mmol) and (1-bromo-2,2-dichlorocyclopropyl)benzene **1** (79.8 mg, 0.30 mmol) at r.t., the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 20/1) to yield the product **23** as a white solid (53.5 mg, 93% yield, 86% e.e.).

m.p. 54–57 $^{\circ}\text{C}$

$[\alpha]_{\text{D}}^{27} = -104$ (c 0.5, CHCl_3).

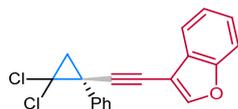
HPLC analysis: Chiralcel IG (*n*-hexane/*i*-PrOH = 95/5, flow rate 0.5 mL/min, $\lambda = 254$ nm), t_{R} (minor) = 24.13 min, t_{R} (major) = 30.85 min.

^1H NMR (400 MHz, CDCl_3) δ 8.66 (d, $J = 2.3$ Hz, 1H), 8.51 (dd, $J = 4.9, 1.7$ Hz, 1H), 7.70 (dt, $J = 7.9, 1.9$ Hz, 1H), 7.53 – 7.44 (m, 2H), 7.44 – 7.31 (m, 3H), 7.21 (dd, $J = 7.8, 4.9$ Hz, 1H), 2.42 (d, $J = 7.6$ Hz, 1H), 2.23 (d, $J = 7.6$ Hz, 1H).

^{13}C NMR (100 MHz, CDCl_3) δ 152.5, 148.7, 138.8, 135.9, 129.0, 128.7, 128.4, 123.0, 119.9, 92.7, 78.9, 64.6, 34.0, 33.2.

HRMS (ESI) m/z calcd. for $\text{C}_{16}\text{H}_{12}\text{NCl}_2$ $[\text{M} + \text{H}]^+$ 288.0341, found 288.0338.

(*R*)-3-((2,2-Dichloro-1-phenylcyclopropyl)ethynyl)benzofuran (**24**)



24

According to **General procedure A** with 3-ethynylbenzofuran (28.4 mg, 0.20 mmol) and (1-bromo-2,2-dichlorocyclopropyl)benzene **1** (79.8 mg, 0.30 mmol), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 50/1) to yield the product **24** as a colorless oil (44.5 mg, 68% yield, 92% e.e.).

$[\alpha]_{\text{D}}^{27} = -119$ (c 0.5, CHCl_3).

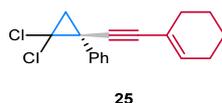
HPLC analysis: Chiralcel ODH (*n*-hexane/*i*-PrOH = 99/1, flow rate 1.0 mL/min, λ = 230 nm), t_R (minor) = 10.75 min, t_R (major) = 11.63 min.

^1H NMR (400 MHz, CDCl_3) δ 7.79 (s, 1H), 7.70 – 7.64 (m, 1H), 7.55 – 7.51 (m, 2H), 7.51 – 7.47 (m, 1H), 7.46 – 7.40 (m, 2H), 7.39 – 7.28 (m, 3H), 2.46 (d, J = 7.6 Hz, 1H), 2.26 (d, J = 7.7 Hz, 1H).

^{13}C NMR (100 MHz, CDCl_3) δ 154.6, 148.0, 136.3, 129.1, 128.7, 128.4, 127.9, 125.4, 123.5, 120.7, 111.7, 104.1, 93.9, 71.9, 64.7, 34.4, 33.4.

HRMS (ESI) m/z calcd. for $\text{C}_{19}\text{H}_{13}\text{OCl}_2$ $[\text{M} + \text{H}]^+$ 327.0338, found 327.0336.

(*R*)-(2,2-dichloro-1-(cyclohex-1-en-1-ylethynyl)cyclopropyl)benzene (**25**)



According to **General procedure A** with 1-ethynylcyclohex-1-ene (23.5 μL , 0.20 mmol) and (1-bromo-2,2-dichlorocyclopropyl)benzene **1** (79.8 mg, 0.30 mmol), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 50/1) to yield the product **25** as a colorless oil (44.9 mg, 77% yield, 92% e.e.).

$[\alpha]_D^{27} = -33$ (c 0.5, CHCl_3).

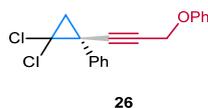
HPLC analysis: Chiralcel ODH (*n*-hexane/*i*-PrOH = 99.5/0.5, flow rate 0.5 mL/min, λ = 254 nm), t_R (minor) = 9.26 min, t_R (major) = 10.40 min.

^1H NMR (400 MHz, CDCl_3) δ 7.45 – 7.39 (m, 2H), 7.38 – 7.33 (m, 2H), 7.33 – 7.28 (m, 1H), 6.11 (tt, J = 3.8, 1.8 Hz, 1H), 2.32 (d, J = 7.5 Hz, 1H), 2.13 – 2.03 (m, 5H), 1.63 – 1.52 (m, 4H).

^{13}C NMR (100 MHz, CDCl_3) δ 136.8, 135.6, 129.0, 128.5, 128.0, 120.3, 86.6, 84.1, 65.0, 34.1, 33.2, 29.2, 25.7, 22.3, 21.6.

HRMS (ESI) m/z calcd. for $\text{C}_{17}\text{H}_{17}\text{Cl}_2$ $[\text{M} + \text{H}]^+$ 291.0702, found 291.0696.

(*R*)-(2,2-Dichloro-1-(3-phenoxyprop-1-yn-1-yl)cyclopropyl)benzene (**26**)



According to **General procedure A** with (prop-2-yn-1-yloxy)benzene (26.4 mg, 0.20 mmol) and (1-bromo-2,2-dichlorocyclopropyl)benzene **1** (79.8 mg, 0.30 mmol), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 50/1) to yield the product **26** as a colorless oil (48.2 mg, 76% yield, 92% e.e.).

$[\alpha]_D^{27} = -40$ (c 0.5, CHCl_3).

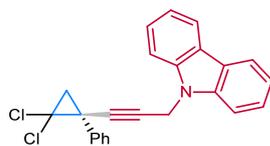
HPLC analysis: Chiralcel ODH (*n*-hexane/*i*-PrOH = 99/1, flow rate 0.8 mL/min, λ = 230 nm), t_R (minor) = 15.55 min, t_R (major) = 18.71 min.

^1H NMR (400 MHz, CDCl_3) δ 7.44 – 7.17 (m, 7H), 7.08 – 6.84 (m, 3H), 4.71 (s, 2H), 2.28 (d, J = 7.6 Hz, 1H), 2.06 (d, J = 7.6 Hz, 1H).

^{13}C NMR (100 MHz, CDCl_3) δ 157.7, 135.9, 129.5, 129.0, 128.6, 128.3, 121.5, 115.2, 87.2, 77.3, 64.4, 56.3, 33.5, 32.9.

HRMS (ESI) m/z calcd. for $C_{18}H_{15}OCl_2$ $[M + H]^+$ 317.0494, found 317.0490.

(R)-9-(3-(2,2-Dichloro-1-phenylcyclopropyl)prop-2-yn-1-yl)-9H-carbazole (27)



27

According to **General procedure A** with 9-(prop-2-yn-1-yl)-9H-carbazole (41.0 mg, 0.20 mmol) and (1-bromo-2,2-dichlorocyclopropyl)benzene **1** (79.8 mg, 0.30 mmol), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 20/1) to yield the product **27** as a white solid (73.7 mg, 94% yield, 92% e.e.).

m.p. 101–103 °C

$[\alpha]_D^{27} = -12$ (c 0.5, $CHCl_3$).

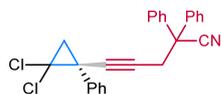
HPLC analysis: Chiralcel ODH (*n*-hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, $\lambda = 254$ nm), t_R (minor) = 10.78 min, t_R (major) = 12.92 min.

1H NMR (400 MHz, $CDCl_3$) δ 8.21 – 8.10 (m, 2H), 7.57 – 7.46 (m, 4H), 7.43 – 7.28 (m, 7H), 5.08 (s, 2H), 2.26 (d, $J = 7.5$ Hz, 1H), 2.01 (d, $J = 7.6$ Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 140.0, 135.9, 128.9, 128.6, 128.3, 125.9, 123.3, 120.5, 119.6, 109.1, 84.0, 76.6, 64.3, 33.4, 32.9, 32.8.

HRMS (ESI) m/z calcd. for $C_{24}H_{18}NCl_2$ $[M + H]^+$ 390.0811, found 390.0806.

(R)-5-(2,2-Dichloro-1-phenylcyclopropyl)-2,2-diphenylpent-4-ynenitrile (28)



28

According to **General procedure A** with 2,2-diphenylpent-4-ynenitrile (46.2 mg, 0.20 mmol) and (1-bromo-2,2-dichlorocyclopropyl)benzene **1** (79.8 mg, 0.30 mmol), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 20/1) to yield the product **28** as a white solid (64.4 mg, 77% yield, 93% e.e.).

m.p. 128–130 °C

$[\alpha]_D^{27} = -18$ (c 0.5, $CHCl_3$).

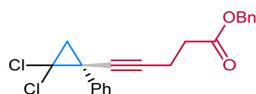
HPLC analysis: Chiralcel IG (*n*-hexane/*i*-PrOH = 95/5, flow rate 1.0 mL/min, $\lambda = 230$ nm), t_R (minor) = 13.54 min, t_R (major) = 15.26 min.

1H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.25 (m, 13H), 7.25 – 7.19 (m, 2H), 3.27 (s, 2H), 2.20 (d, $J = 7.5$ Hz, 1H), 1.90 (d, $J = 7.5$ Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 139.0, 138.9, 136.0, 128.9, 128.8, 128.4, 128.3, 128.1, 127.30, 127.26, 121.8, 84.9, 76.9, 64.4, 51.4, 33.5, 32.6, 31.5.

HRMS (ESI) m/z calcd. for $C_{26}H_{20}NCl_2$ $[M + H]^+$ 416.0967, found 416.0962.

Benzyl (*R*)-5-(2,2-dichloro-1-phenylcyclopropyl)pent-4-ynoate (**29**)



29

According to **General procedure A** with benzyl pent-4-ynoate (37.6 mg, 0.20 mmol) and (1-bromo-2,2-dichlorocyclopropyl)benzene **1** (79.8 mg, 0.30 mmol), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 50/1) to yield the product **29** as a pale yellow oil (62.9 mg, 84% yield, 92% e.e.).

$[\alpha]_D^{27} = -39$ (c 0.5, CHCl₃).

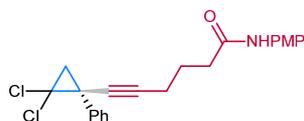
HPLC analysis: Chiralcel ODH (*n*-hexane/*i*-PrOH = 99/1, flow rate 1.0 mL/min, $\lambda = 230$ nm), t_R (minor) = 11.00 min, t_R (major) = 12.06 min.

¹H NMR (400 MHz, CDCl₃) δ 7.41 – 7.30 (m, 10H), 5.13 (s, 2H), 2.67 – 2.51 (m, 4H), 2.27 (d, $J = 7.5$ Hz, 1H), 2.00 (d, $J = 7.5$ Hz, 1H).

¹³C NMR (100 MHz, CDCl₃) δ 171.7, 136.6, 135.8, 128.9, 128.7, 128.5, 128.4, 128.3, 128.1, 80.9, 80.8, 66.6, 64.5, 33.7, 33.6, 32.7, 15.0.

HRMS (ESI) m/z calcd. for C₂₁H₁₉O₂Cl₂ [M + H]⁺ 373.0757, found 373.0755.

(*R*)-6-(2,2-Dichloro-1-phenylcyclopropyl)-*N*-(4-methoxyphenyl)hex-5-ynamide (**30**)



30

According to **General procedure A** with *N*-(4-methoxyphenyl)hex-5-ynamide (43.4 mg, 0.20 mmol) and (1-bromo-2,2-dichlorocyclopropyl)benzene **1** (79.8 mg, 0.30 mmol), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 5/1) to yield the product **30** as a pale-yellow oil (64.2 mg, 80% yield, 92% e.e.).

$[\alpha]_D^{27} = -27$ (c 0.5, CHCl₃).

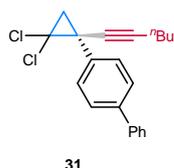
HPLC analysis: Chiralcel OD3 (*n*-hexane/*i*-PrOH = 75/25, flow rate 1.0 mL/min, $\lambda = 214$ nm), t_R (minor) = 15.58 min, t_R (major) = 19.87 min.

¹H NMR (400 MHz, CDCl₃) δ 7.56 – 7.26 (m, 8H), 6.88 – 6.77 (m, 2H), 3.77 (s, 3H), 2.43 (t, $J = 7.3$ Hz, 2H), 2.32 (t, $J = 6.8$ Hz, 2H), 2.27 (d, $J = 7.5$ Hz, 1H), 2.04 (d, $J = 7.5$ Hz, 1H), 1.90 (p, $J = 7.0$ Hz, 2H).

¹³C NMR (100 MHz, CDCl₃) δ 170.7, 156.4, 136.8, 131.0, 128.8, 128.5, 128.1, 121.9, 114.1, 81.9, 81.2, 64.8, 55.5, 35.9, 33.7, 32.8, 24.3, 18.2.

HRMS (ESI) m/z calcd. for C₂₂H₂₂O₂NCl₂ [M + H]⁺ 402.1022, found 402.1017.

(*R*)-4-(2,2-Dichloro-1-(hex-1-yn-1-yl)cyclopropyl)-1,1'-biphenyl (**31**)



According to **General procedure A** with 1-hexyne (22.9 μL , 0.20 mmol) and 4-(1-bromo-2,2-dichlorocyclopropyl)-1,1'-biphenyl **S7** (102.6 mg, 0.30 mmol), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 100/1) to yield the product **31** as a white solid (59.2 mg, 88% yield, 94% e.e.).

m.p. 90–93 $^{\circ}\text{C}$

$[\alpha]_{\text{D}}^{27} = -17$ (c 0.5, CHCl_3).

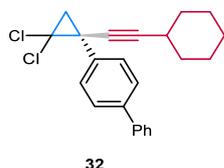
HPLC analysis: Chiralcel OJH (*n*-hexane/*i*-PrOH = 98/2, flow rate 1.0 mL/min, $\lambda = 254$ nm), t_{R} (major) = 8.93 min, t_{R} (minor) = 11.54 min.

^1H NMR (400 MHz, CDCl_3) δ 7.67 – 7.59 (m, 4H), 7.54 – 7.43 (m, 4H), 7.41 – 7.35 (m, 1H), 2.34 (d, $J = 7.5$ Hz, 1H), 2.27 (t, $J = 6.9$ Hz, 2H), 2.08 (d, $J = 7.5$ Hz, 1H), 1.60 – 1.39 (m, 4H), 0.95 (t, $J = 7.2$ Hz, 3H).

^{13}C NMR (100 MHz, CDCl_3) δ 140.8, 140.6, 136.1, 129.3, 128.9, 127.5, 127.21, 127.18, 83.2, 79.9, 64.9, 33.6, 33.0, 30.8, 22.0, 18.7, 13.7.

HRMS (ESI) m/z calcd. for $\text{C}_{21}\text{H}_{21}\text{Cl}_2$ $[\text{M} + \text{H}]^+$ 343.1015, found 343.1011.

(*R*)-4-(2,2-Dichloro-1-(cyclohexylethynyl)cyclopropyl)-1,1'-biphenyl (32)



According to **General procedure A** with ethynylcyclohexane (26.0 μL , 0.20 mmol) and 4-(1-bromo-2,2-dichlorocyclopropyl)-1,1'-biphenyl **S7** (102.6 mg, 0.30 mmol), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 100/1) to yield the product **32** as a white solid (63.9 mg, 87% yield, 94% e.e.).

m.p. 90–92 $^{\circ}\text{C}$

$[\alpha]_{\text{D}}^{27} = -19$ (c 0.5, CHCl_3).

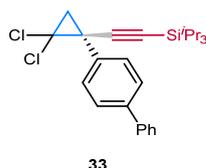
HPLC analysis: Chiralcel OJH (*n*-hexane/*i*-PrOH = 98/2, flow rate 1.0 mL/min, $\lambda = 254$ nm), t_{R} (major) = 7.52 min, t_{R} (minor) = 14.44 min.

^1H NMR (400 MHz, CDCl_3) δ 7.68 – 7.57 (m, 4H), 7.53 – 7.42 (m, 4H), 7.41 – 7.32 (m, 1H), 2.47 (tt, $J = 8.2, 3.8$ Hz, 1H), 2.35 (d, $J = 7.6$ Hz, 1H), 2.07 (d, $J = 7.6$ Hz, 1H), 1.85 – 1.67 (m, 4H), 1.56 – 1.46 (m, 3H), 1.39 – 1.28 (m, 3H).

^{13}C NMR (100 MHz, CDCl_3) δ 140.8, 140.6, 136.1, 129.3, 128.9, 127.5, 127.2, 127.1, 87.2, 80.1, 65.0, 33.6, 33.0, 32.6, 29.1, 26.1, 24.7.

HRMS (ESI) m/z calcd. for $\text{C}_{23}\text{H}_{23}\text{Cl}_2$ $[\text{M} + \text{H}]^+$ 369.1171, found 369.1165.

(*R*)-((1-([1,1'-Biphenyl]-4-yl)-2,2-dichlorocyclopropyl)ethynyl)triisopropylsilane (33)



According to **General procedure A** with ethynyltriisopropylsilane (22.0 μL , 0.10 mmol) and 4-(1-bromo-2,2-dichlorocyclopropyl)-1,1'-biphenyl **S7** (51.3 mg, 0.15 mmol), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 100/1) to yield the product **33** as a colorless oil (23.2 mg, 52% yield, 94% e.e.).

$[\alpha]_{\text{D}}^{27} = -12$ (c 0.5, CHCl_3).

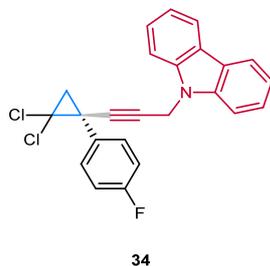
HPLC analysis: Chiralcel ODH (*n*-hexane/*i*-PrOH = 100/0, flow rate 0.5 mL/min, $\lambda = 254$ nm), t_{R} (minor) = 17.47 min, t_{R} (major) = 23.90 min.

^1H NMR (400 MHz, CDCl_3) δ 7.66 – 7.54 (m, 4H), 7.52 – 7.47 (m, 2H), 7.47 – 7.40 (m, 2H), 7.38 – 7.31 (m, 1H), 2.39 (d, $J = 7.6$ Hz, 1H), 2.11 (d, $J = 7.6$ Hz, 1H), 1.07 (s, 21H).

^{13}C NMR (100 MHz, CDCl_3) δ 140.9, 140.6, 135.2, 129.3, 128.9, 127.6, 127.2, 127.1, 106.7, 83.9, 64.9, 34.3, 33.3, 18.8, 11.4.

HRMS (ESI) m/z calcd. for $\text{C}_{26}\text{H}_{33}\text{Cl}_2\text{Si}$ $[\text{M} + \text{H}]^+$ 443.1723, found 443.1718.

(*R*)-9-(3-(2,2-Dichloro-1-(4-fluorophenyl)cyclopropyl)prop-2-yn-1-yl)-9*H*-carbazole (34)



According to **General procedure A** with 9-(prop-2-yn-1-yl)-9*H*-carbazole (41.0 mg, 0.20 mmol) and 1-(1-bromo-2,2-dichlorocyclopropyl)-4-fluorobenzene **S1** (85.2 mg, 0.30 mmol), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 20/1) to yield the product **34** as a white solid (56.3 mg, 69% yield, 90% e.e.).

m.p. 86–88 $^{\circ}\text{C}$

$[\alpha]_{\text{D}}^{27} = -10$ (c 0.5, CHCl_3).

HPLC analysis: Chiralcel ODH (*n*-hexane/*i*-PrOH = 95/5, flow rate 0.5 mL/min, $\lambda = 254$ nm), t_{R} (minor) = 32.81 min, t_{R} (major) = 35.49 min.

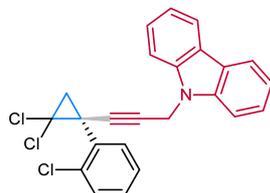
^1H NMR (400 MHz, CDCl_3) δ 8.15 (d, $J = 7.7$ Hz, 2H), 7.56 – 7.45 (m, 4H), 7.36 – 7.25 (m, 4H), 7.11 – 6.98 (m, 2H), 5.10 (s, 2H), 2.20 (d, $J = 7.6$ Hz, 1H), 2.02 (d, $J = 7.6$ Hz, 1H).

^{13}C NMR (100 MHz, CDCl_3) δ 162.5 (d, $J = 247.6$ Hz), 140.0, 131.8 (d, $J = 3.2$ Hz), 130.7 (d, $J = 8.4$ Hz), 125.9, 123.3, 120.5, 119.6, 115.5 (d, $J = 21.7$ Hz), 109.0, 83.8, 76.8, 64.2, 33.1, 32.9, 32.8.

^{19}F NMR (376 MHz, CDCl_3) δ -113.3.

HRMS (ESI) m/z calcd. for $\text{C}_{24}\text{H}_{17}\text{NCl}_2\text{F}$ $[\text{M} + \text{H}]^+$ 408.0717, found 408.0715.

(S)-9-(3-(2,2-Dichloro-1-(2-chlorophenyl)cyclopropyl)prop-2-yn-1-yl)-9H-carbazole (35)



35

According to **General procedure A** with 9-(prop-2-yn-1-yl)-9H-carbazole (41.0 mg, 0.20 mmol) and 1-(1-bromo-2,2-dichlorocyclopropyl)-2-chlorobenzene **S2** (85.2 mg, 0.30 mmol), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 20/1) to yield the product **35** as a white solid (76.3 mg, 90% yield, 93% e.e.).

m.p. 106–109 °C

$[\alpha]_{\text{D}}^{27} = -14$ (c 0.5, CHCl_3).

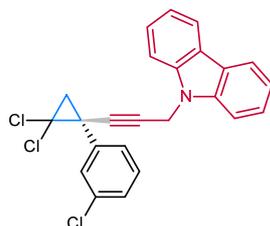
HPLC analysis: Chiralcel ODH (*n*-hexane/*i*-PrOH = 97/3, flow rate 0.5 mL/min, $\lambda = 254$ nm), t_{R} (minor) = 47.10 min, t_{R} (major) = 50.99 min.

^1H NMR (400 MHz, CDCl_3) δ 8.05 (dt, $J = 7.7, 1.0$ Hz, 2H), 7.46 – 7.36 (m, 5H), 7.25 – 7.00 (m, 5H), 5.01 (s, 2H), 2.06 (d, $J = 7.3$ Hz, 1H), 1.98 (d, $J = 7.3$ Hz, 1H).

^{13}C NMR (100 MHz, CDCl_3) δ 140.1, 136.4, 134.9, 130.3, 130.1, 129.8, 127.0, 125.9, 123.3, 120.4, 119.5, 109.1, 82.3, 76.4, 64.1, 33.9, 33.0, 29.8.

HRMS (ESI) m/z calcd. for $\text{C}_{24}\text{H}_{17}\text{NCl}_3$ $[\text{M} + \text{H}]^+$ 424.0421, found 424.0420.

(R)-9-(3-(2,2-Dichloro-1-(3-chlorophenyl)cyclopropyl)prop-2-yn-1-yl)-9H-carbazole (36)



36

According to **General procedure A** with 9-(prop-2-yn-1-yl)-9H-carbazole (41.0 mg, 0.20 mmol) and 1-(1-bromo-2,2-dichlorocyclopropyl)-3-chlorobenzene **S3** (85.2 mg, 0.30 mmol), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 20/1) to yield the product **36** as a colorless oil (80.6 mg, 95% yield, 92% e.e.).

$[\alpha]_{\text{D}}^{27} = -19$ (c 0.5, CHCl_3).

HPLC analysis: Chiralcel ODH (*n*-hexane/*i*-PrOH = 97/3, flow rate 0.5 mL/min, $\lambda =$

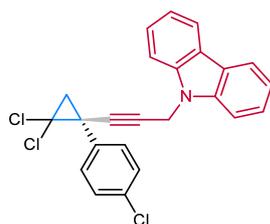
254 nm), t_R (minor) = 37.27 min, t_R (major) = 39.69 min.

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.22 – 8.06 (m, 2H), 7.58 – 7.43 (m, 4H), 7.38 (t, J = 1.9 Hz, 1H), 7.35 – 7.27 (m, 4H), 7.24 – 7.19 (m, 1H), 5.11 (s, 2H), 2.23 (d, J = 7.7 Hz, 1H), 2.02 (d, J = 7.7 Hz, 1H).

$^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 139.9, 137.8, 134.4, 129.7, 129.1, 128.4, 127.1, 125.9, 123.3, 120.4, 119.5, 108.9, 83.3, 77.1, 63.9, 33.0, 32.9, 32.8.

HRMS (ESI) m/z calcd. for $\text{C}_{24}\text{H}_{17}\text{NCl}_3$ $[\text{M} + \text{H}]^+$ 424.0421, found 424.0416.

(*R*)-9-(3-(2,2-Dichloro-1-(4-chlorophenyl)cyclopropyl)prop-2-yn-1-yl)-9*H*-carbazole (37)



37

According to **General procedure A** with 9-(prop-2-yn-1-yl)-9*H*-carbazole (41.0 mg, 0.20 mmol) and 1-(1-bromo-2,2-dichlorocyclopropyl)-4-chlorobenzene **S4** (85.2 mg, 0.30 mmol), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 20/1) to yield the product **37** as a white solid (87.8 mg, 97% yield, 91% e.e.).

m.p. 103–105 °C

$[\alpha]_D^{27} = -16$ (c 0.5, CHCl_3).

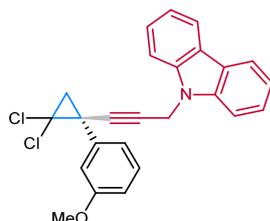
HPLC analysis: Chiralcel ODH (*n*-hexane/*i*-PrOH = 95/5, flow rate 1.0 mL/min, λ = 230 nm), t_R (minor) = 16.17 min, t_R (major) = 17.99 min.

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.16 (d, J = 7.7 Hz, 2H), 7.58 – 7.45 (m, 4H), 7.38 – 7.30 (m, 4H), 7.30 – 7.23 (m, 2H), 5.09 (s, 2H), 2.20 (d, J = 7.7 Hz, 1H), 2.02 (d, J = 7.7 Hz, 1H).

$^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 140.0, 134.4, 134.2, 130.3, 128.7, 125.9, 123.3, 120.5, 119.6, 109.0, 83.5, 77.0, 64.1, 32.9, 32.8.

HRMS (ESI) m/z calcd. for $\text{C}_{24}\text{H}_{17}\text{NCl}_3$ $[\text{M} + \text{H}]^+$ 424.0421, found 424.0418.

(*R*)-9-(3-(2,2-Dichloro-1-(3-methoxyphenyl)cyclopropyl)prop-2-yn-1-yl)-9*H*-carbazole (38)



38

According to **General procedure A** with 9-(prop-2-yn-1-yl)-9*H*-carbazole (41.0 mg,

0.20 mmol) and 1-(1-bromo-2,2-dichlorocyclopropyl)-3-methoxybenzene **S5** (88.8 mg, 0.30 mmol), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 20/1) to yield the product **38** as a white solid (75.4 mg, 90% yield, 92% e.e.).

m.p. 115–118 °C

$[\alpha]_D^{27} = -11$ (c 0.5, CHCl₃).

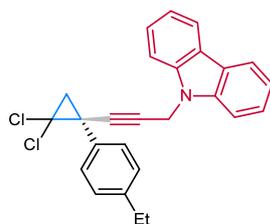
HPLC analysis: Chiralcel ODH (*n*-hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, $\lambda = 230$ nm), t_R (minor) = 15.31 min, t_R (major) = 25.19 min.

¹H NMR (400 MHz, CDCl₃) δ 8.07 (d, $J = 7.8$ Hz, 2H), 7.52 – 7.37 (m, 4H), 7.27 – 7.16 (m, 3H), 6.93 – 6.67 (m, 3H), 5.04 (s, 2H), 3.66 (s, 3H), 2.19 (d, $J = 7.6$ Hz, 1H), 1.94 (d, $J = 7.6$ Hz, 1H).

¹³C NMR (100 MHz, CDCl₃) δ 159.7, 140.0, 137.3, 129.5, 125.9, 123.3, 121.0, 120.5, 119.6, 114.7, 114.0, 109.0, 84.0, 76.6, 64.3, 55.3, 33.4, 33.0, 32.9.

HRMS (ESI) m/z calcd. for C₂₅H₂₀ONCl₂ [M + H]⁺ 420.0916, found 420.0914.

(*R*)-9-(3-(2,2-Dichloro-1-(4-ethylphenyl)cyclopropyl)prop-2-yn-1-yl)-9H-carbazole (39)



39

According to **General procedure A** with 9-(prop-2-yn-1-yl)-9H-carbazole (41.0 mg, 0.20 mmol) and 1-(1-bromo-2,2-dichlorocyclopropyl)-4-ethylbenzene **S6** (88.2 mg, 0.30 mmol), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 20/1) to yield the product **39** as a colorless oil (80.6 mg, 96% yield, 91% e.e.).

$[\alpha]_D^{27} = -15$ (c 0.5, CHCl₃).

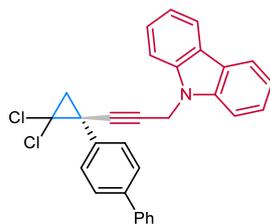
HPLC analysis: Chiralcel ODH (*n*-hexane/*i*-PrOH = 95/5, flow rate 1.0 mL/min, $\lambda = 230$ nm), t_R (minor) = 10.88 min, t_R (major) = 13.66 min.

¹H NMR (400 MHz, CDCl₃) δ 8.14 (dt, $J = 7.8, 0.9$ Hz, 2H), 7.55 – 7.47 (m, 4H), 7.35 – 7.26 (m, 4H), 7.24 – 7.17 (m, 2H), 5.08 (s, 2H), 2.70 (q, $J = 7.6$ Hz, 2H), 2.23 (d, $J = 7.5$ Hz, 1H), 1.99 (d, $J = 7.5$ Hz, 1H), 1.29 (t, $J = 7.6$ Hz, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 144.3, 140.0, 133.1, 128.8, 128.0, 125.9, 123.3, 120.4, 119.5, 109.1, 84.2, 76.4, 64.4, 33.2, 32.9, 32.8, 28.6, 15.4.

HRMS (ESI) m/z calcd. for C₂₆H₂₂NCl₂ [M + H]⁺ 418.1124, found 418.1119.

(*R*)-9-(3-(1-([1,1'-Biphenyl]-4-yl)-2,2-dichlorocyclopropyl)prop-2-yn-1-yl)-9H-carbazole (40)



40

According to **General procedure A** with 9-(prop-2-yn-1-yl)-9*H*-carbazole (41.0 mg, 0.20 mmol) and 4-(1-bromo-2,2-dichlorocyclopropyl)-1,1'-biphenyl **S7** (102.6 mg, 0.30 mmol), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 20/1) to yield the product **40** as a white solid (88.3 mg, 95% yield, 92% e.e.).

m.p. 157–159 °C

$[\alpha]_D^{27} = +15$ (c 0.5, CHCl₃).

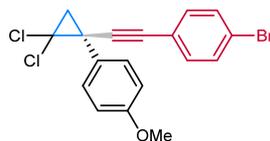
HPLC analysis: Chiralcel ODH (*n*-hexane/*i*-PrOH = 95/5, flow rate 1.0 mL/min, $\lambda = 254$ nm), t_R (minor) = 23.52 min, t_R (major) = 28.01 min.

¹H NMR (400 MHz, CDCl₃) δ 8.16 (d, $J = 7.7$ Hz, 2H), 7.67 – 7.57 (m, 4H), 7.56 – 7.46 (m, 6H), 7.45 – 7.38 (m, 3H), 7.37 – 7.29 (m, 2H), 5.10 (s, 2H), 2.29 (d, $J = 7.6$ Hz, 1H), 2.04 (d, $J = 7.6$ Hz, 1H).

¹³C NMR (100 MHz, CDCl₃) δ 141.0, 140.4, 140.0, 134.8, 129.3, 128.9, 127.6, 127.2, 127.2, 125.9, 123.3, 120.5, 119.6, 109.0, 84.0, 76.7, 64.4, 33.2, 32.9, 32.9.

HRMS (ESI) m/z calcd. for C₃₀H₂₂NCl₂ [M + H]⁺ 466.1124, found 466.1123.

(*R*)-1-Bromo-4-((2,2-dichloro-1-(4-methoxyphenyl)cyclopropyl)ethynyl)benzene (41)



41

According to **General procedure A** with 1-bromo-4-ethynylbenzene (36.2 mg, 0.20 mmol) and 1-(1-bromo-2,2-dichlorocyclopropyl)-4-methoxybenzene **S8** (88.8 mg, 0.30 mmol), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 50/1) to yield the product **41** as a colorless oil (56.5 mg, 72% yield, 90% e.e.).

$[\alpha]_D^{27} = -111$ (c 0.5, CHCl₃).

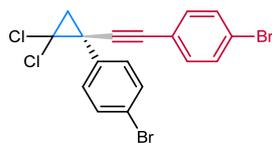
HPLC analysis: Chiralcel ODH (*n*-hexane/*i*-PrOH = 98/2, flow rate 0.5 mL/min, $\lambda = 254$ nm), t_R (minor) = 11.71 min, t_R (major) = 13.74 min.

¹H NMR (400 MHz, CDCl₃) δ 7.56 – 7.32 (m, 4H), 7.27 (d, $J = 8.5$ Hz, 2H), 6.91 (d, $J = 8.3$ Hz, 2H), 3.81 (s, 3H), 2.34 (d, $J = 7.5$ Hz, 1H), 2.16 (d, $J = 7.6$ Hz, 1H).

¹³C NMR (100 MHz, CDCl₃) δ 159.6, 133.4, 131.6, 130.2, 128.3, 122.7, 121.9, 114.1, 90.8, 65.0, 55.4, 33.5, 33.4.

HRMS (ESI) m/z calcd. for C₁₈H₁₄OBrCl₂ [M + H]⁺ 394.9600, found 394.9599.

(R)-1-Bromo-4-((1-(4-bromophenyl)-2,2-dichlorocyclopropyl)ethynyl)benzene (42)



42

According to **General procedure A** with 1-bromo-4-ethynylbenzene (36.2 mg, 0.20 mmol) and 1-bromo-4-(1-bromo-2,2-dichlorocyclopropyl)benzene **S9** (103.5 mg, 0.30 mmol), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 50/1) to yield the product **42** as a colorless oil (66.8 mg, 75% yield, 91% e.e.).

According to **General procedure B** with 1-bromo-4-ethynylbenzene (36.2 mg, 0.20 mmol) and 1-bromo-4-(1-bromo-2,2-dichlorocyclopropyl)benzene **S9** (69.0 mg, 0.20 mmol), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 50/1) to yield the product **42** as a colorless oil (75.6 mg, 85% yield, 91% e.e.).

$[\alpha]_D^{27} = -64$ (c 0.5, CHCl₃).

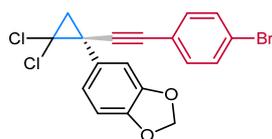
HPLC analysis: Chiralcel IG (*n*-hexane/*i*-PrOH = 99.5/0.5, flow rate 0.5 mL/min, $\lambda = 214$ nm), t_R (minor) = 12.51 min, t_R (major) = 13.11 min.

¹H NMR (400 MHz, CDCl₃) δ 7.55 – 7.49 (m, 2H), 7.45 – 7.39 (m, 2H), 7.35 – 7.30 (m, 2H), 7.28 – 7.25 (m, 2H), 2.35 (d, $J = 7.7$ Hz, 1H), 2.20 (d, $J = 7.6$ Hz, 1H).

¹³C NMR (100 MHz, CDCl₃) δ 135.3, 133.4, 131.9, 131.7, 130.8, 122.9, 122.5, 121.5, 89.9, 81.6, 64.4, 33.7, 33.4.

HRMS (ESI) m/z calcd. for C₁₇H₁₁Br₂Cl₂ [M + H]⁺ 442.8599, found 442.8587.

(R)-5-(1-((4-Bromophenyl)ethynyl)-2,2-dichlorocyclopropyl)benzo[d][1,3]dioxole (43)



43

According to **General procedure A** with 1-bromo-4-ethynylbenzene (36.2 mg, 0.20 mmol) and 5-(1-bromo-2,2-dichlorocyclopropyl)benzo[d][1,3]dioxole **S10** (93.0 mg, 0.30 mmol), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 50/1) to yield the product **43** as a colorless oil (71.6 mg, 87% yield, 84% e.e.).

$[\alpha]_D^{27} = -86$ (c 0.5, CHCl₃).

HPLC analysis: Chiralcel ODH (*n*-hexane/*i*-PrOH = 98/2, flow rate 0.5 mL/min, $\lambda = 254$ nm), t_R (minor) = 14.41 min, t_R (major) = 16.42 min.

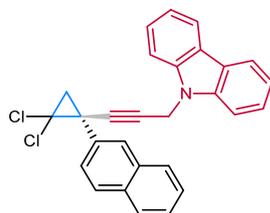
¹H NMR (400 MHz, CDCl₃) δ 7.50 – 7.20 (m, 4H), 7.03 – 6.71 (m, 3H), 5.97 (s, 2H), 2.29 (d, $J = 7.6$ Hz, 1H), 2.15 (d, $J = 7.6$ Hz, 1H).

¹³C NMR (100 MHz, CDCl₃) δ 147.9, 147.7, 133.4, 131.6, 130.0, 122.7, 122.4, 121.7,

109.8, 108.3, 101.5, 90.5, 81.1, 64.8, 33.8, 33.6.

HRMS (ESI) m/z calcd. for $C_{18}H_{12}O_2BrCl_2$ $[M + H]^+$ 408.9392, found 408.9371.

(R)-9-(3-(2,2-Dichloro-1-(naphthalen-2-yl)cyclopropyl)prop-2-yn-1-yl)-9H-carbazole (44)



44

According to **General procedure A** with 9-(prop-2-yn-1-yl)-9H-carbazole (41.0 mg, 0.20 mmol) and 2-(1-bromo-2,2-dichlorocyclopropyl)naphthalene **S11** (94.8 mg, 0.30 mmol), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 20/1) to yield the product **44** as a white solid (74.9 mg, 85% yield, 83% e.e.).

m.p. 158–160 °C

$[\alpha]_D^{27} = +8.2$ (c 0.5, $CHCl_3$).

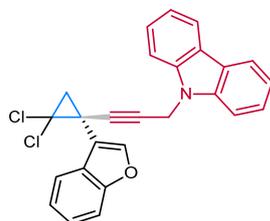
HPLC analysis: Chiralcel IA (*n*-hexane/*i*-PrOH = 98/2, flow rate 0.5 mL/min, $\lambda = 254$ nm), t_R (major) = 24.71 min, t_R (minor) = 27.61 min.

1H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, $J = 7.7$ Hz, 2H), 7.83 – 7.76 (m, 2H), 7.75 – 7.69 (m, 1H), 7.67 (d, $J = 1.8$ Hz, 1H), 7.50 – 7.39 (m, 7H), 7.26 – 7.22 (m, 2H), 5.05 (s, 2H), 2.34 (d, $J = 7.6$ Hz, 1H), 2.03 (d, $J = 7.5$ Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 140.1, 133.5, 133.15, 133.06, 128.4, 128.1, 127.81, 127.79, 126.9, 126.6, 126.5, 125.9, 123.4, 120.5, 119.6, 109.1, 84.0, 76.9, 64.3, 33.7, 33.0.

HRMS (ESI) m/z calcd. for $C_{28}H_{20}NCl_2$ $[M + H]^+$ 440.0967, found 440.0963.

(S)-9-(3-(1-(Benzofuran-3-yl)-2,2-dichlorocyclopropyl)prop-2-yn-1-yl)-9H-carbazole (45)



45

According to **General procedure A** with 9-(prop-2-yn-1-yl)-9H-carbazole (41.0 mg, 0.20 mmol) and 3-(1-bromo-2,2-dichlorocyclopropyl)benzofuran **S12** (91.8 mg, 0.30 mmol), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 20/1) to yield the product **45** as a colorless oil (80.1 mg, 93% yield, 81% e.e.).

$[\alpha]_D^{27} = +11$ (c 0.5, CHCl₃).

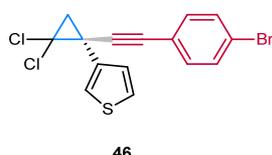
HPLC analysis: Chiralcel ODH (*n*-hexane/*i*-PrOH = 97/3, flow rate 0.5 mL/min, $\lambda = 254$ nm), t_R (minor) = 53.27 min, t_R (major) = 59.26 min.

¹H NMR (400 MHz, CDCl₃) δ 8.07 (dt, $J = 7.8, 1.0$ Hz, 2H), 7.62 (dt, $J = 7.7, 1.0$ Hz, 1H), 7.45 (dt, $J = 8.3, 0.9$ Hz, 1H), 7.43 – 7.35 (m, 5H), 7.29 (ddd, $J = 8.4, 7.2, 1.3$ Hz, 1H), 7.26 – 7.21 (m, 2H) 7.15 (td, $J = 7.6, 1.0$ Hz, 1H), 5.03 (s, 2H), 2.10 (d, $J = 7.3$ Hz, 1H), 2.02 (d, $J = 7.3$ Hz, 1H).

¹³C NMR (100 MHz, CDCl₃) δ 155.5, 143.6, 140.0, 126.7, 125.9, 125.0, 123.3, 123.1, 120.8, 120.5, 119.6, 118.0, 111.7, 109.0, 82.0, 76.8, 64.1, 33.5, 32.9, 25.2.

HRMS (ESI) m/z calcd. for C₂₆H₁₈ONCl₂ [M + H]⁺ 430.0760, found 430.0757.

(*S*)-3-(1-((4-Bromophenyl)ethynyl)-2,2-dichlorocyclopropyl)thiophene (**46**)



According to **General procedure A** with 1-bromo-4-ethynylbenzene (36.2 mg, 0.20 mmol) and 3-(1-bromo-2,2-dichlorocyclopropyl)thiophene **S13** (81.6 mg, 0.30 mmol), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 50/1) to yield the product **46** as a pale-yellow oil (66.7 mg, 89% yield, 90% e.e.).

$[\alpha]_D^{27} = -109$ (c 0.5, CHCl₃).

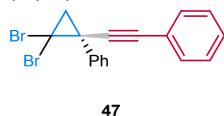
HPLC analysis: Chiralcel ODH (*n*-hexane/*i*-PrOH = 98/2, flow rate 0.5 mL/min, $\lambda = 254$ nm), t_R (minor) = 11.77 min, t_R (major) = 12.95 min.

¹H NMR (400 MHz, CDCl₃) δ 7.48 – 7.37 (m, 2H), 7.36 – 7.22 (m, 4H), 7.18 (d, $J = 5.1$ Hz, 1H), 2.32 (d, $J = 7.6$ Hz, 1H), 2.21 (d, $J = 7.6$ Hz, 1H).

¹³C NMR (100 MHz, CDCl₃) δ 137.0, 133.4, 131.7, 128.2, 126.0, 124.3, 122.8, 121.6, 89.6, 81.3, 64.9, 34.7, 30.3.

HRMS (ESI) m/z calcd. for C₁₅H₁₀BrCl₂S [M + H]⁺ 370.9058, found 370.9057.

(*R*)-(2,2-dibromo-1-(phenylethynyl)cyclopropyl)benzene (**47**)



According to **General procedure A** with ethynylbenzene (21.9 μ L, 0.20 mmol) and (1,2,2-tribromocyclopropyl)benzene **S14** (106.5 mg, 0.30 mmol) at -10 °C, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 50/1) to yield the product **47** as a colorless oil (60.8 mg, 81% yield, 91% e.e.).

$[\alpha]_D^{27} = -162$ (c 0.5, CHCl₃).

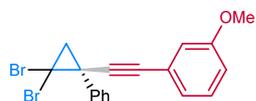
HPLC analysis: Chiralcel OJ-RH (MeCN/H₂O = 70/30, flow rate 0.7 mL/min, $\lambda = 254$ nm), t_R (minor) = 15.36 min, t_R (major) = 18.65 min.

¹H NMR (400 MHz, CDCl₃) δ 7.49 – 7.45 (m, 2H), 7.45 – 7.41 (m, 2H), 7.40 – 7.36 (m, 2H), 7.36 – 7.31 (m, 1H), 7.30 – 7.23 (m, 3H), 2.57 (d, $J = 7.9$ Hz, 1H), 2.34 (d, $J = 7.9$ Hz, 1H).

^{13}C NMR (100 MHz, CDCl_3) δ 137.7, 131.9, 129.1, 128.6, 128.5, 128.4, 128.3, 122.9, 90.9, 82.1, 35.3, 34.7, 33.5.

HRMS (ESI) m/z calcd. for $\text{C}_{17}\text{H}_{13}\text{Br}_2$ $[\text{M} + \text{H}]^+$ 374.9379, found 374.9372.

(*R*)-1-((2,2-Dibromo-1-phenylcyclopropyl)ethynyl)-3-methoxybenzene (**48**)



48

According to **General procedure A** with 1-ethynyl-3-methoxybenzene (25.6 μL , 0.20 mmol) and (1,2,2-tribromocyclopropyl)benzene **S14** (106.5 mg, 0.30 mmol) at $-10\text{ }^\circ\text{C}$, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 50/1) to yield the product **48** as a colorless oil (70.7 mg, 87% yield, 92% e.e.).

$[\alpha]_{\text{D}}^{27} = -139$ (c 0.5, CHCl_3).

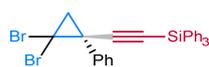
HPLC analysis: Chiralcel ODH (*n*-hexane/*i*-PrOH = 95/5, flow rate 0.5 mL/min, $\lambda = 230$ nm), t_{R} (minor) = 11.72 min, t_{R} (major) = 12.56 min.

^1H NMR (400 MHz, CDCl_3) δ 7.56 – 7.46 (m, 2H), 7.45 – 7.34 (m, 3H), 7.21 (t, $J = 7.9$ Hz, 1H), 7.06 (d, $J = 7.6$ Hz, 1H), 6.98 (t, $J = 1.9$ Hz, 1H), 6.88 (dd, $J = 8.1, 2.5$ Hz, 1H), 3.79 (s, 3H), 2.61 (d, $J = 7.9$ Hz, 1H), 2.38 (d, $J = 7.9$ Hz, 1H).

^{13}C NMR (100 MHz, CDCl_3) δ 159.3, 137.7, 129.4, 129.1, 128.6, 128.3, 124.5, 123.8, 116.7, 115.1, 90.6, 81.9, 55.4, 35.2, 34.6, 33.4.

HRMS (ESI) m/z calcd. for $\text{C}_{18}\text{H}_{15}\text{OBr}_2$ $[\text{M} + \text{H}]^+$ 404.9484, found 404.9479.

(*R*)-((2,2-Dibromo-1-phenylcyclopropyl)ethynyl)triphenylsilane (**49**)



49

According to **General procedure A** with ethynyltriphenylsilane (56.9 mg, 0.20 mmol) and (1,2,2-tribromocyclopropyl)benzene **S14** (106.5 mg, 0.30 mmol) at $-10\text{ }^\circ\text{C}$, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 50/1) to yield the product **49** as a colorless oil (82.6 mg, 74% yield, 92% e.e.).

$[\alpha]_{\text{D}}^{27} = -45$ (c 0.5, CHCl_3).

HPLC analysis: Chiralcel ODH (*n*-hexane/*i*-PrOH = 99.5/0.5, flow rate 0.5 mL/min, $\lambda = 230$ nm), t_{R} (minor) = 13.58 min, t_{R} (major) = 17.83 min.

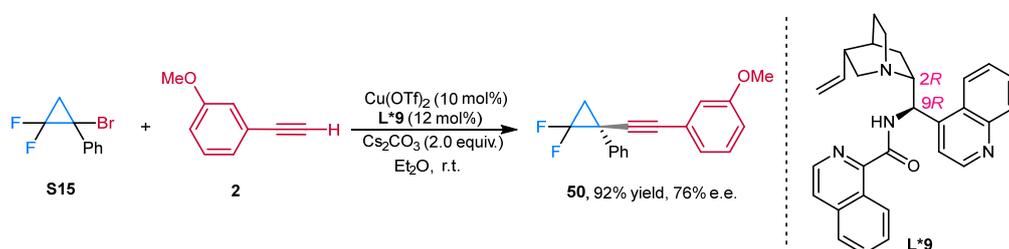
^1H NMR (400 MHz, CDCl_3) δ 7.75 – 7.64 (m, 6H), 7.56 – 7.50 (m, 2H), 7.49 – 7.36 (m, 12H), 2.63 (d, $J = 8.0$ Hz, 1H), 2.43 (d, $J = 7.9$ Hz, 1H).

^{13}C NMR (100 MHz, CDCl_3) δ 137.1, 135.7, 133.5, 130.0, 129.1, 128.6, 128.4, 128.0, 110.8, 82.3, 35.1, 33.9, 33.8.

HRMS (ESI) m/z calcd. for $\text{C}_{29}\text{H}_{23}\text{Br}_2\text{Si}$ $[\text{M} + \text{H}]^+$ 556.9930, found 556.9926.

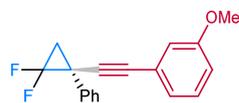
Gram-scale reaction

An oven-dried Schlenk tube equipped with a magnetic stirring bar was charged with Cu(OTf)₂ (108.0 mg, 0.30 mmol, 10 mol%), chiral ligand **L*8** (192.0 mg, 0.36 mmol, 12 mol%), and Cs₂CO₃ (3.91 g, 12.0 mmol, 4.0 equiv.). The tube was evacuated and backfilled with argon three times. Then racemic (1,2,2-tribromocyclopropyl)benzene **S14** (1.60 g, 4.5 mmol, 1.5 equiv.), ethynyltriphenylsilane (0.85 g, 3.0 mmol, 1.0 equiv.), and Et₂O (30 mL) were sequentially added into the mixture under argon. The tube was sealed and the mixture was allowed to stir at -10 °C for 8 d. Upon completion of the reaction (monitored by TLC), the mixture was quenched with water and extracted with CH₂Cl₂. The combined organic phase was dried over anhydrous Na₂SO₄, filtered, and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (petroleum ether/EtOAc = 50/1) to afford the desired product **49** as a colorless oil (1.04 g, 62% yield, 92% e.e.).



An oven-dried resealable Schlenk tube equipped with a magnetic stirring bar was charged with Cu(OTf)₂ (3.61 mg, 0.010 mmol, 10 mol%), chiral ligand **L*9** (5.38 mg, 0.012 mmol, 12 mol%), and Cs₂CO₃ (64.2 mg, 0.20 mmol, 2.0 equiv.). The tube was evacuated and backfilled with argon three times. Then racemic (1-bromo-2,2-difluorocyclopropyl)benzene **S15** (23.3 mg, 0.10 mmol, 1.0 equiv.), 1-ethynyl-3-methoxybenzene (19.2 μL, 0.15 mmol, 1.5 equiv.), and Et₂O (1.0 mL) were sequentially added into the mixture under argon. The tube was sealed and the reaction mixture was allowed to stir at r.t. for 3 d. Upon completion of the reaction (monitored by TLC), the mixture was then filtered through a pad of celite and rinsed with EtOAc. The filtrate was evaporated and the residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 50/1) to yield the product **50** as a colorless oil (26.1 mg, 92% yield, 76% e.e.).

(*R*)-1-((2,2-difluoro-1-phenylcyclopropyl)ethynyl)-3-methoxybenzene (**50**)



50

$[\alpha]_D^{27} = -17$ (c 0.5, CHCl₃).

HPLC analysis: Chiralcel ODH (*n*-hexane/*i*-PrOH = 98/2, flow rate 0.5 mL/min, λ = 254 nm), *t*_R (major) = 12.35 min, *t*_R (minor) = 14.36 min.

¹H NMR (400 MHz, CDCl₃) δ 7.53 – 7.44 (m, 2H), 7.43 – 7.29 (m, 3H), 7.19 (t, *J* = 8.0 Hz, 1H), 7.03 (d, *J* = 7.6 Hz, 1H), 6.99 – 6.92 (m, 1H), 6.85 (dd, *J* = 8.4, 2.7 Hz, 1H), 3.77 (s, 3H), 2.25 – 2.05 (m, 2H).

¹³C NMR (100 MHz, CDCl₃) δ 159.4, 134.2 (d, *J* = 2.2 Hz), 129.4, 128.8, 128.4, 128.3,

128.0, 124.5, 123.7, 116.7, 115.2, 111.9 (t, $J = 292.7$ Hz), 86.1, 82.1, 55.4, 28.4 (dd, $J = 14.5, 10.4$ Hz), 24.9 (t, $J = 9.1$ Hz).

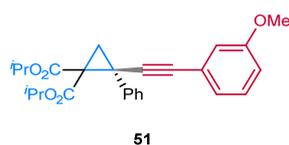
^{19}F NMR (376 MHz, CDCl_3) $\delta -129.7$ (d, $J = 142.9$ Hz), -134.8 (d, $J = 143.0$ Hz).

HRMS (ESI) m/z calcd. for $\text{C}_{18}\text{H}_{15}\text{OF}_2$ $[\text{M} + \text{H}]^+$ 285.1085, found 285.1081.



General procedure C: An oven-dried resealable Schlenk tube equipped with a magnetic stirring bar was charged with $\text{Cu}(\text{OTf})_2$ (3.61 mg, 0.010 mmol, 10 mol%), chiral ligand **L*9** (5.38 mg, 0.012 mmol, 12 mol%), and Cs_2CO_3 (128.4 mg, 0.40 mmol, 4.0 equiv.). The tube was evacuated and backfilled with argon three times. Then racemic cyclopropyl bromide (0.10 mmol, 1.0 equiv.), 1-ethynyl-3-methoxybenzene (19.2 μL , 0.15 mmol, 1.5 equiv.), and PhCF_3 (1.0 mL) were sequentially added into the mixture under argon. The tube was sealed and the reaction mixture was allowed to stir under the irradiation of blue LEDs (5 W) at r.t. for 3 d. Upon completion of the reaction (monitored by TLC), the mixture was then filtered through a pad of celite and rinsed with EtOAc. The filtrate was evaporated and the residue was purified by column chromatography on silica gel to afford the desired product.

Diisopropyl (*R*)-2-((3-methoxyphenyl)ethynyl)-2-phenylcyclopropane-1,1-dicarboxylate (**51**)



According to **General procedure C** with diisopropyl 2-bromo-2-phenylcyclopropane-1,1-dicarboxylate **S16** (36.9 mg, 0.10 mmol, 1.0 equiv.) and 1-ethynyl-3-methoxybenzene (19.2 μL , 1.5 equiv.) at r.t., the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 10/1) to yield the product **51** as a colorless oil (37.3 mg, 89% yield, 85% e.e.).

$[\alpha]_{\text{D}}^{27} = -121$ (c 0.5, CHCl_3).

HPLC analysis: Chiralcel ODH (*n*-hexane/*i*-PrOH = 99/1, flow rate 0.5 mL/min, $\lambda = 254$ nm), t_{R} (minor) = 19.78 min, t_{R} (major) = 21.91 min.

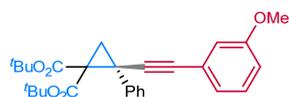
^1H NMR (400 MHz, CDCl_3) δ 7.51 – 7.44 (m, 2H), 7.34 – 7.24 (m, 3H), 7.15 (t, $J = 7.9$ Hz, 1H), 6.96 (dt, $J = 7.6, 1.2$ Hz, 1H), 6.88 (dd, $J = 2.7, 1.4$ Hz, 1H), 6.82 (ddd, $J = 8.3, 2.6, 1.0$ Hz, 1H), 5.14 (hept, $J = 6.3$ Hz, 1H), 4.66 (hept, $J = 6.3$ Hz, 1H), 3.75 (s, 3H), 2.51 (d, $J = 5.6$ Hz, 1H), 2.26 (d, $J = 5.5$ Hz, 1H), 1.33 – 1.27 (m, 6H), 0.93 (d, $J = 6.3$ Hz, 3H), 0.86 (d, $J = 6.2$ Hz, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 166.3, 165.5, 159.3, 136.4, 129.3, 129.0, 128.3, 127.9,

124.4, 124.0, 116.5, 114.9, 89.4, 81.6, 69.6, 69.3, 55.3, 43.8, 32.4, 24.2, 22.0, 21.9, 21.3, 21.3.

HRMS (ESI) m/z calcd. for $C_{26}H_{29}O_5$ $[M + H]^+$ 421.2009, found 421.2001.

Di-*tert*-butyl (*R*)-2-((3-methoxyphenyl)ethynyl)-2-phenylcyclopropane-1,1-dicarboxylate (**52**)



52

According to **General procedure C** with di-*tert*-butyl 2-bromo-2-phenylcyclopropane-1,1-dicarboxylate **S17** (39.7 mg, 0.10 mmol, 1.0 equiv.) and 1-ethynyl-3-methoxybenzene (19.2 μ L, 1.5 equiv.) at r.t., the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 20/1) to yield the product **52** as a colorless oil (38.2 mg, 85% yield, 86% e.e.).

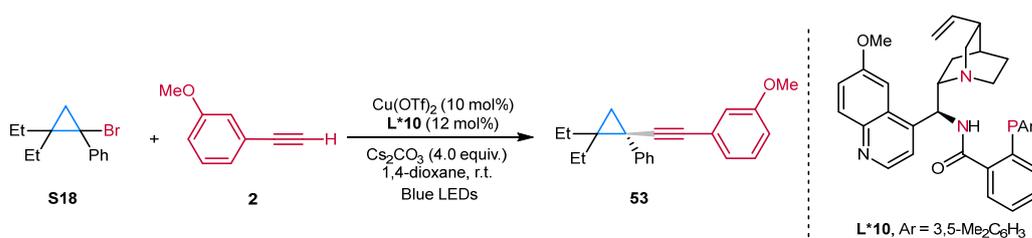
$[\alpha]_D^{27} = -46$ (c 0.5, $CHCl_3$).

HPLC analysis: Chiralcel IG (*n*-hexane/*i*-PrOH = 98/2, flow rate 0.5 mL/min, $\lambda = 254$ nm), t_R (minor) = 22.48 min, t_R (major) = 24.74 min.

1H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.44 (m, 2H), 7.34 – 7.24 (m, 3H), 7.15 (t, $J = 8.0$ Hz, 1H), 6.97 (dt, $J = 7.6, 1.2$ Hz, 1H), 6.89 (dd, $J = 2.8, 1.4$ Hz, 1H), 6.82 (ddd, $J = 8.4, 2.7, 1.0$ Hz, 1H), 3.75 (s, 3H), 2.41 (d, $J = 5.5$ Hz, 1H), 2.15 (d, $J = 5.5$ Hz, 1H), 1.52 (s, 9H), 1.10 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.8, 165.0, 159.2, 136.7, 129.3, 129.2, 128.3, 127.7, 124.4, 124.2, 116.4, 114.9, 89.9, 82.0, 81.8, 81.2, 55.3, 45.1, 31.9, 28.2, 27.5, 23.9.

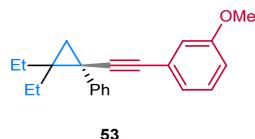
HRMS (ESI) m/z calcd. for $C_{28}H_{33}O_5$ $[M + H]^+$ 449.2322, found 449.2311.



An oven-dried resealable Schlenk tube equipped with a magnetic stirring bar was charged with $Cu(OTf)_2$ (7.22 mg, 0.020 mmol, 10 mol%), chiral ligand **L*10** (15.93 mg, 0.024 mmol, 12 mol%), and Cs_2CO_3 (256.8 mg, 0.80 mmol, 4.0 equiv.). The tube was evacuated and backfilled with argon three times. Then racemic cyclopropyl bromide **S18** (50.6 mg, 0.20 mmol, 1.0 equiv.), 1-ethynyl-3-methoxybenzene (38.4 μ L, 0.30 mmol, 1.5 equiv.), and 1,4-dioxane (2.0 mL) were sequentially added into the mixture under argon. The tube was sealed and the reaction mixture was allowed to stir under the irradiation of blue LEDs (5 W) at r.t. for 5 d. Upon completion of the reaction (monitored by TLC), the mixture was then filtered through a pad of celite and rinsed with EtOAc. The filtrate was evaporated and the residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 100/1) to afford the desired

product **53** as a colorless oil (45.7 mg, 75% yield, 47% e.e.).

(*R*)-1-((2,2-diethyl-1-phenylcyclopropyl)ethynyl)-3-methoxybenzene (**53**)



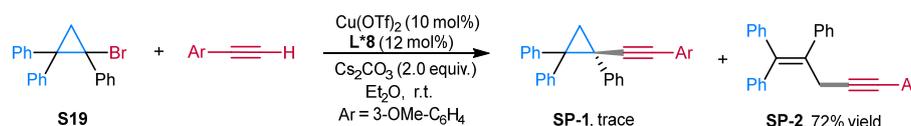
$[\alpha]_D^{27} = -26$ (c 0.5, CHCl₃).

HPLC analysis: Chiralcel OJ-RH (MeCN/ H₂O = 70/30, flow rate 0.7 mL/min, $\lambda = 254$ nm), t_R (minor) = 15.72 min, t_R (major) = 18.00 min.

¹H NMR (400 MHz, CDCl₃) δ 7.40 – 7.35 (m, 2H), 7.33 – 7.26 (m, 2H), 7.24 – 7.18 (m, 1H), 7.13 (t, $J = 7.9$ Hz, 1H), 6.95 (dt, $J = 7.6, 1.2$ Hz, 1H), 6.88 (dd, $J = 2.6, 1.4$ Hz, 1H), 6.78 (dd, $J = 8.2, 2.6$ Hz, 1H), 3.73 (s, 3H), 1.94 (dq, $J = 14.6, 7.3$ Hz, 1H), 1.71 (dq, $J = 14.5, 7.4$ Hz, 1H), 1.39 (d, $J = 4.8$ Hz, 1H), 1.30 (dt, $J = 14.2, 7.2$ Hz, 1H), 1.14 (t, $J = 7.4$ Hz, 3H), 1.10 (d, $J = 4.7$ Hz, 1H), 0.79 (t, $J = 7.3$ Hz, 3H), 0.58 (dq, $J = 14.8, 7.4$ Hz, 1H).

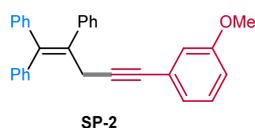
¹³C NMR (100 MHz, CDCl₃) δ 159.3, 140.0, 129.5, 129.2, 128.2, 126.5, 125.4, 124.3, 116.6, 114.0, 94.6, 78.1, 55.3, 36.1, 28.5, 26.4, 26.0, 24.0, 10.8, 10.6.

HRMS (ESI) m/z calcd. for C₂₂H₂₅O [M + H]⁺ 305.1900, found 305.1892.



An oven-dried resealable Schlenk tube equipped with a magnetic stirring bar was charged with Cu(OTf)₂ (3.61 mg, 0.010 mmol, 10 mol%), chiral ligand **L*8** (6.40 mg, 0.012 mmol, 12 mol%), and Cs₂CO₃ (64.2 mg, 0.20 mmol, 2.0 equiv.). The tube was evacuated and backfilled with argon three times. Then racemic (2-bromocyclopropane-1,1,2-triyl)tribenzene **S19** (34.9 mg, 0.10 mmol, 1.0 equiv.), 1-ethynyl-3-methoxybenzene (19.2 μ L, 0.15 mmol, 1.5 equiv.), and Et₂O (1.0 mL) were sequentially added into the mixture under argon. The tube was sealed and the reaction mixture was allowed to stir at r.t. for 5 d. Upon completion of the reaction (monitored by TLC), the mixture was then filtered through a pad of celite and rinsed with EtOAc. The filtrate was evaporated and the residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 50/1) to yield the ring-opening side product **SP-2** as a colorless oil (28.9 mg, 72% yield), the desired product **SP-1** is rarely provided.

(5-(3-methoxyphenyl)pent-1-en-4-yne-1,1,2-triyl)tribenzene (**SP-2**)



¹H NMR (400 MHz, CDCl₃) δ 7.42 – 7.34 (m, 4H), 7.32 – 7.27 (m, 1H), 7.25 – 7.11 (m, 6H), 7.07 – 6.98 (m, 3H), 6.96 – 6.90 (m, 2H), 6.87 (dt, $J = 7.6, 1.2$ Hz, 1H), 6.82

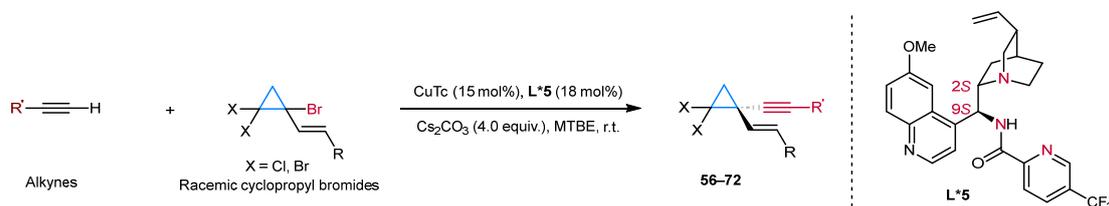
– 6.75 (m, 2H), 3.74 (s, 3H), 3.56 (s, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 159.3, 142.7, 142.5, 141.6, 141.2, 135.0, 130.8, 129.9, 129.8, 129.3, 128.5, 128.0, 127.6, 127.3, 126.7, 126.4, 125.1, 124.2, 116.7, 114.2, 88.3, 81.8, 55.3, 27.5.

HRMS (ESI) *m/z* calcd. for C₃₀H₂₅O [M + H]⁺ 401.1900, found 401.1892.

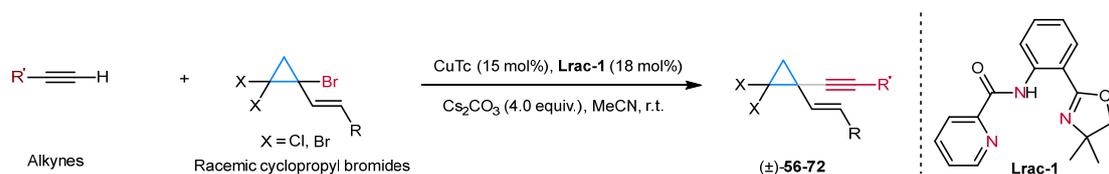
Enantioconvergent cross-coupling of alkynes with 1-alkenyl-substituted cyclopropyl bromides

General procedure D:



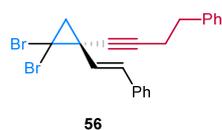
An oven-dried resealable Schlenk tube equipped with a magnetic stirring bar was charged with $CuTc$ (2.85 mg, 0.015 mmol, 15 mol%), L^*5 (8.90 mg, 0.018 mmol, 18 mol%), and Cs_2CO_3 (128.0 mg, 0.40 mmol, 4.0 equiv.). The tube was evacuated and backfilled with argon three times. Then racemic 1-alkenyl-substituted cyclopropyl bromide (0.15 mmol, 1.5 equiv.), alkyne (0.10 mmol, 1.0 equiv.), and MTBE (2.0 mL) were sequentially added into the mixture under argon. The tube was sealed and the reaction mixture was allowed to stir at r.t. for 7 d. Upon completion of the reaction (monitored by TLC), the mixture was then filtered through a pad of celite and rinsed with EtOAc. The filtrate was evaporated and the residue was purified by column chromatography on silica gel to afford the desired product.

The preparation of racemic products (\pm)-**56-72**:



Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with $CuTc$ (2.85 mg, 0.015 mmol, 15 mol%), $Lrac-1$ (5.31 mg, 0.018 mmol, 18 mol%), Cs_2CO_3 (128.0 mg, 0.40 mmol, 4.0 equiv.), and MeCN (1.0 mL). Then 1-alkenyl-substituted cyclopropyl bromide (0.15 mmol, 1.5 equiv.) and alkyne (0.10 mmol, 1.0 equiv.) were sequentially added into the mixture and the reaction mixture was stirred at r.t. for 3 d. Upon completion, the precipitate was filtered off and washed by EtOAc. The filtrate was evaporated and the residue was purified by column chromatography on silica gel to afford the desired product.

(*S,E*)-(2-(2,2-Dibromo-1-(4-phenylbut-1-yn-1-yl)cyclopropyl)vinyl)benzene (**56**)



According to **General procedure D** with 4-phenyl-1-butyne (14.0 μ L, 0.10 mmol) and (*E*)-(2-(1,2,2-tribromocyclopropyl)vinyl)benzene **54** (57.1 mg, 0.15 mmol), the reaction mixture was purified by column chromatography on silica gel (petroleum

ether/EtOAc = 100/1) to yield the product **56** as a colorless oil (40.2 mg, 93% yield, 92% e.e.).

$[\alpha]_D^{27} = -27$ (c 1.0, CHCl₃).

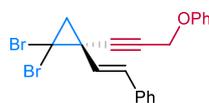
HPLC analysis: Chiralcel OJH (*n*-hexane/*i*-PrOH = 95/5, flow rate 1.0 mL/min, $\lambda = 254$ nm), t_R (major) = 16.26 min, t_R (minor) = 18.65 min.

¹H NMR (400 MHz, CDCl₃) δ 7.37 – 7.20 (m, 10H), 6.89 (d, $J = 15.5$ Hz, 1H), 6.01 (d, $J = 15.5$ Hz, 1H), 2.90 (t, $J = 7.4$ Hz, 2H), 2.63 (t, $J = 7.4$ Hz, 2H), 2.13 (d, $J = 7.5$ Hz, 1H), 2.06 (d, $J = 7.6$ Hz, 1H).

¹³C NMR (100 MHz, CDCl₃) δ 140.6, 136.6, 133.7, 128.9, 128.73, 128.67, 128.5, 127.9, 126.7, 126.5, 84.8, 78.9, 38.2, 35.4, 35.1, 30.4, 21.1.

HRMS (ESI) m/z calcd. for C₂₁H₁₉Br₂ [M + H]⁺ 428.9848, found 428.9837.

(*S,E*)-(2-(2,2-Dibromo-1-(3-phenoxyprop-1-yn-1-yl)cyclopropyl)vinyl)benzene (**57**)



57

According to **General procedure D** with phenyl propargyl ether (12.8 μ L, 0.10 mmol) and (*E*)-(2-(1,2,2-tribromocyclopropyl)vinyl)benzene **54** (57.1 mg, 0.15 mmol), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 100/1) to yield the product **57** as a colorless oil (32.1 mg, 74% yield, 87% e.e.).

$[\alpha]_D^{27} = -36$ (c 0.5, CHCl₃).

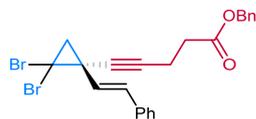
HPLC analysis: Chiralcel ODH (*n*-hexane/*i*-PrOH = 95/5, flow rate 1.0 mL/min, $\lambda = 254$ nm), t_R (minor) = 13.77 min, t_R (major) = 18.74 min.

¹H NMR (400 MHz, CDCl₃) δ 7.35 – 7.22 (m, 7H), 7.09 – 6.95 (m, 3H), 6.90 (d, $J = 15.6$ Hz, 1H), 5.98 (d, $J = 15.6$ Hz, 1H), 4.83 (s, 2H), 2.21 (d, $J = 7.7$ Hz, 1H), 2.09 (d, $J = 7.7$ Hz, 1H).

¹³C NMR (100 MHz, CDCl₃) δ 157.7, 136.3, 134.2, 129.6, 128.8, 128.1, 127.7, 126.6, 121.6, 115.2, 85.5, 79.7, 56.2, 38.2, 34.2, 30.2.

HRMS (ESI) m/z calcd. for C₂₀H₁₇OBr₂ [M + H]⁺ 430.9641, found 430.9636.

Benzyl (*S,E*)-5-(2,2-dibromo-1-styrylcyclopropyl)pent-4-ynoate (**58**)



58

According to **General procedure D** with benzyl pent-4-ynoate (18.8 mg, 0.10 mmol) and (*E*)-(2-(1,2,2-tribromocyclopropyl)vinyl)benzene **54** (57.1 mg, 0.15 mmol), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 50/1) to yield the product **58** as a colorless oil (35.2 mg, 72% yield, 90% e.e.).

$[\alpha]_D^{27} = -29$ (c 1.0, CHCl₃).

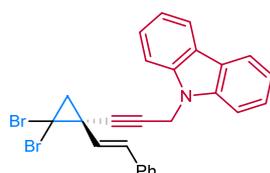
HPLC analysis: Chiralcel IG (*n*-hexane/*i*-PrOH = 98/2, flow rate 0.5 mL/min, λ = 254 nm), t_R (minor) = 23.94 min, t_R (major) = 27.17 min.

^1H NMR (400 MHz, CDCl_3) δ 7.41 – 7.29 (m, 9H), 7.27 – 7.22 (m, 1H), 6.98 (d, J = 15.5 Hz, 1H), 6.01 (d, J = 15.6 Hz, 1H), 5.15 (s, 2H), 2.70 – 2.62 (m, 4H), 2.12 (d, J = 7.6 Hz, 1H), 2.05 (d, J = 7.6 Hz, 1H).

^{13}C NMR (100 MHz, CDCl_3) δ 171.8, 136.6, 135.8, 133.8, 128.8, 128.7, 128.6, 128.44, 128.38, 128.0, 126.6, 83.4, 79.1, 66.7, 38.1, 35.1, 33.8, 30.3, 15.1.

HRMS (ESI) m/z calcd. for $\text{C}_{23}\text{H}_{21}\text{O}_2\text{Br}_2$ $[\text{M} + \text{H}]^+$ 486.9903, found 486.9898.

(*S,E*)-9-(3-(2,2-Dibromo-1-styrylcyclopropyl)prop-2-yn-1-yl)-9*H*-carbazole (**59**)



59

According to **General procedure D** with 9-(prop-2-yn-1-yl)-9*H*-carbazole (20.5 mg, 0.10 mmol) and (*E*)-(2-(1,2,2-tribromocyclopropyl)vinyl)benzene **54** (57.1 mg, 0.15 mmol), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 20/1) to yield the product **59** as a colorless oil (45.9 mg, 91% yield, 84% e.e.).

$[\alpha]_D^{27} = -53$ (c 0.5, CHCl_3).

HPLC analysis: Chiralcel ODH (*n*-hexane/*i*-PrOH = 95/5, flow rate 1.0 mL/min, λ = 254 nm), t_R (minor) = 20.41 min, t_R (major) = 23.79 min.

^1H NMR (400 MHz, CDCl_3) δ 8.10 (dt, J = 7.8, 1.0 Hz, 2H), 7.57 – 7.42 (m, 4H), 7.29 – 7.19 (m, 5H), 7.17 – 7.12 (m, 2H), 6.73 (d, J = 15.6 Hz, 1H), 5.89 (d, J = 15.7 Hz, 1H), 5.14 (s, 2H), 2.09 (d, J = 7.7 Hz, 1H), 1.99 (d, J = 7.7 Hz, 1H).

^{13}C NMR (100 MHz, CDCl_3) δ 140.1, 136.2, 134.1, 128.7, 128.0, 127.6, 126.6, 126.0, 123.5, 120.6, 119.7, 109.0, 82.2, 79.1, 38.1, 34.2, 32.9, 30.2.

HRMS (ESI) m/z calcd. for $\text{C}_{26}\text{H}_{20}\text{NBr}_2$ $[\text{M} + \text{H}]^+$ 503.9957, found 503.9952.

(*S,E*)-((2,2-Dibromo-1-styrylcyclopropyl)ethynyl)triisopropylsilane (**60**)



60

According to **General procedure D** with ethynyltriisopropylsilane (22.0 μL , 0.10 mmol) and (*E*)-(2-(1,2,2-tribromocyclopropyl)vinyl)benzene **54** (57.1 mg, 0.15 mmol), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 100/1) to yield the product **60** as a colorless oil (39.9 mg, 83% yield, 91% e.e.). The e.e. value of **60** was determined by converting it to the corresponding terminal alkyne **88**.

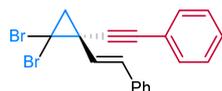
$[\alpha]_D^{27} = -17$ (c 0.5, CHCl_3).

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.40 – 7.36 (m, 2H), 7.35 – 7.30 (m, 2H), 7.29 – 7.23 (m, 1H), 7.14 (d, $J = 15.6$ Hz, 1H), 6.03 (d, $J = 15.5$ Hz, 1H), 2.23 (d, $J = 7.6$ Hz, 1H), 2.12 (d, $J = 7.6$ Hz, 1H), 1.13 (s, 21H).

$^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 136.6, 134.2, 128.8, 128.4, 128.0, 126.6, 104.7, 86.6, 39.0, 34.8, 31.2, 18.8, 11.4.

HRMS (ESI) m/z calcd. for $\text{C}_{22}\text{H}_{31}\text{Br}_2\text{Si}$ $[\text{M} + \text{H}]^+$ 481.0556, found 481.0551.

(*S,E*)-(2-(2,2-Dibromo-1-(phenylethynyl)cyclopropyl)vinyl)benzene (61)



61

According to **General procedure D** with ethynylbenzene (11.0 μL , 0.10 mmol) and (*E*)-(2-(1,2,2-tribromocyclopropyl)vinyl)benzene **54** (57.1 mg, 0.15 mmol) at 10 $^\circ\text{C}$ for 10 d, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 50/1) to yield the product **61** as a colorless oil (29.6 mg, 74% yield, 92% e.e.).

$[\alpha]_{\text{D}}^{27} = +13$ (c 1.0, CHCl_3).

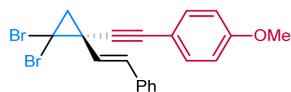
HPLC analysis: Chiralcel OJH (*n*-hexane/*i*-PrOH = 95/5, flow rate 1.0 mL/min, $\lambda = 254$ nm), t_{R} (major) = 8.82 min, t_{R} (minor) = 11.52 min.

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.56 – 7.49 (m, 2H), 7.45 – 7.40 (m, 2H), 7.37 – 7.30 (m, 5H), 7.27 (d, $J = 7.2$ Hz, 1H), 7.09 (d, $J = 15.6$ Hz, 1H), 6.12 (d, $J = 15.6$ Hz, 1H), 2.34 (d, $J = 7.7$ Hz, 1H), 2.21 (d, $J = 7.6$ Hz, 1H).

$^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 136.5, 134.2, 132.0, 128.8, 128.7, 128.5, 128.3, 128.1, 126.7, 122.8, 87.7, 84.7, 38.6, 35.2, 30.8.

HRMS (ESI) m/z calcd. for $\text{C}_{19}\text{H}_{15}\text{Br}_2$ $[\text{M} + \text{H}]^+$ 400.9535, found 400.9523.

(*S,E*)-1-((2,2-Dibromo-1-styrylcyclopropyl)ethynyl)-4-methoxybenzene (62)



62

According to **General procedure D** with 1-ethynyl-4-methoxybenzene (13.2 mg, 0.10 mmol) and (*E*)-(2-(1,2,2-tribromocyclopropyl)vinyl)benzene **54** (57.1 mg, 0.15 mmol) at 10 $^\circ\text{C}$ for 10 d, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 30/1) to yield the product **62** as a colorless oil (30.1 mg, 70% yield, 92% e.e.).

$[\alpha]_{\text{D}}^{27} = +19$ (c 1.0, CHCl_3).

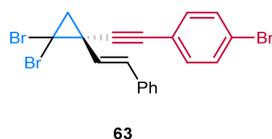
HPLC analysis: Chiralcel ODH (*n*-hexane/*i*-PrOH = 99/1, flow rate 0.5 mL/min, $\lambda = 254$ nm), t_{R} (minor) = 16.04 min, t_{R} (major) = 17.16 min.

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.48 – 7.39 (m, 4H), 7.35 – 7.30 (m, 2H), 7.27 – 7.23 (m, 1H), 7.08 (d, $J = 15.6$ Hz, 1H), 6.86 (d, $J = 8.8$ Hz, 2H), 6.12 (d, $J = 15.5$ Hz, 1H), 3.81 (s, 3H), 2.32 (d, $J = 7.6$ Hz, 1H), 2.20 (d, $J = 7.6$ Hz, 1H).

^{13}C NMR (100 MHz, CDCl_3) δ 159.9, 136.6, 134.1, 133.5, 128.8, 128.5, 128.0, 126.7, 114.8, 114.1, 86.3, 84.6, 55.5, 38.6, 35.5, 30.9.

HRMS (ESI) m/z calcd. for $\text{C}_{20}\text{H}_{17}\text{OBr}_2$ $[\text{M} + \text{H}]^+$ 430.9641, found 430.9636.

(*S,E*)-1-Bromo-4-((2,2-dibromo-1-styrylcyclopropyl)ethynyl)benzene (**63**)



According to **General procedure D** with 1-bromo-4-ethynylbenzene (17.8 mg, 0.10 mmol) and (*E*)-(2-(1,2,2-tribromocyclopropyl)vinyl)benzene **54** (57.1 mg, 0.15 mmol) at 10 °C for 10 d, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 50/1) to yield the product **63** as a colorless oil (25.0 mg, 52% yield, 88% e.e.).

$[\alpha]_{\text{D}}^{27} = +23$ (c 1.0, CHCl_3).

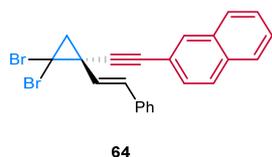
HPLC analysis: Chiralcel ODH (*n*-hexane/*i*-PrOH = 99.5/0.5, flow rate 0.5 mL/min, $\lambda = 254$ nm), t_{R} (major) = 14.92 min, t_{R} (minor) = 17.02 min.

^1H NMR (400 MHz, CDCl_3) δ 7.50 – 7.45 (m, 2H), 7.44 – 7.40 (m, 2H), 7.39 – 7.30 (m, 4H), 7.28 (d, $J = 7.2$ Hz, 1H), 7.04 (d, $J = 15.6$ Hz, 1H), 6.11 (d, $J = 15.6$ Hz, 1H), 2.34 (d, $J = 7.7$ Hz, 1H), 2.22 (d, $J = 7.7$ Hz, 1H).

^{13}C NMR (100 MHz, CDCl_3) δ 136.4, 134.2, 133.4, 131.8, 128.8, 128.2, 128.0, 126.7, 122.9, 121.7, 89.0, 83.6, 38.5, 34.9, 30.7.

HRMS (ESI) m/z calcd. for $\text{C}_{19}\text{H}_{14}\text{Br}_3$ $[\text{M} + \text{H}]^+$ 478.8640, found 478.8630.

(*S,E*)-2-((2,2-Dibromo-1-styrylcyclopropyl)ethynyl)naphthalene (**64**)



According to **General procedure D** with 2-ethynyl naphthalene (15.2 mg, 0.10 mmol) and (*E*)-(2-(1,2,2-tribromocyclopropyl)vinyl)benzene **54** (57.1 mg, 0.15 mmol) at 10 °C for 10 d, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 50/1) to yield the product **64** as a colorless oil (29.3 mg, 65% yield, 92% e.e.).

$[\alpha]_{\text{D}}^{27} = +29$ (c 1.0, CHCl_3).

HPLC analysis: Chiralcel ODH (*n*-hexane/*i*-PrOH = 98/2, flow rate 0.5 mL/min, $\lambda = 254$ nm), t_{R} (minor) = 16.14 min, t_{R} (major) = 18.77 min.

^1H NMR (400 MHz, CDCl_3) δ 8.04 (s, 1H), 7.84 – 7.76 (m, 3H), 7.55 (dd, $J = 8.5, 1.6$ Hz, 1H), 7.51 – 7.41 (m, 4H), 7.36 – 7.30 (m, 2H), 7.30 – 7.24 (m, 1H), 7.13 (d, $J = 15.6$ Hz, 1H), 6.15 (d, $J = 15.6$ Hz, 1H), 2.38 (d, $J = 7.7$ Hz, 1H), 2.23 (d, $J = 7.7$ Hz, 1H).

^{13}C NMR (100 MHz, CDCl_3) δ 136.5, 134.2, 133.1, 131.9, 128.8, 128.6, 128.33, 128.28, 128.2, 128.1, 127.92, 127.86, 126.9, 126.8, 126.7, 120.0, 88.1, 85.0, 38.6, 35.3, 30.9.

HRMS (ESI) m/z calcd. for $C_{23}H_{17}Br_2$ $[M + H]^+$ 450.9691, found 450.9689.

(*S,E*)-3-((2,2-Dibromo-1-styrylcyclopropyl)ethynyl)thiophene (65)



65

According to **General procedure D** with 3-ethynylthiophene (10.0 μ L, 0.10 mmol) and (*E*)-(2-(1,2,2-tribromocyclopropyl)vinyl)benzene **54** (57.1 mg, 0.15 mmol) at 10 °C for 10 d, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 50/1) to yield the product **65** as a colorless oil (31.6 mg, 78% yield, 92% e.e.).

$[\alpha]_D^{27} = +12$ (c 1.0, $CHCl_3$).

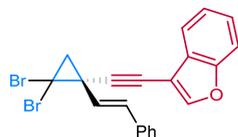
HPLC analysis: Chiralcel OJH (*n*-hexane/*i*-PrOH = 95/5, flow rate 1.0 mL/min, $\lambda = 254$ nm), t_R (major) = 13.33 min, t_R (minor) = 17.83 min.

1H NMR (400 MHz, $CDCl_3$) δ 7.52 (dd, $J = 3.0, 1.2$ Hz, 1H), 7.45 – 7.39 (m, 2H), 7.35 – 7.30 (m, 2H), 7.29 – 7.24 (m, 2H), 7.18 (dd, $J = 5.0, 1.2$ Hz, 1H), 7.06 (d, $J = 15.6$ Hz, 1H), 6.11 (d, $J = 15.6$ Hz, 1H), 2.32 (d, $J = 7.7$ Hz, 1H), 2.20 (d, $J = 7.7$ Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 136.5, 134.1, 130.2, 129.4, 128.8, 128.2, 128.1, 126.7, 125.5, 121.7, 87.2, 79.8, 38.5, 35.1, 30.8.

HRMS (ESI) m/z calcd. for $C_{17}H_{13}Br_2S$ $[M + H]^+$ 406.9099, found 406.9097.

(*S,E*)-3-((2,2-Dibromo-1-styrylcyclopropyl)ethynyl)benzofuran (66)



66

According to **General procedure D** with 3-ethynylbenzofuran (14.2 mg, 0.10 mmol) and (*E*)-(2-(1,2,2-tribromocyclopropyl)vinyl)benzene **54** (57.1 mg, 0.15 mmol) at 10 °C for 10 d, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 50/1) to yield the product **66** as a colorless oil (33.8 mg, 76% yield, 90% e.e.).

$[\alpha]_D^{27} = +7.1$ (c 0.5, $CHCl_3$).

HPLC analysis: Chiralcel ODH (*n*-hexane/*i*-PrOH = 99.5/0.5, flow rate 0.5 mL/min, $\lambda = 254$ nm), t_R (major) = 16.85 min, t_R (minor) = 21.21 min.

1H NMR (400 MHz, $CDCl_3$) δ 7.87 (s, 1H), 7.74 (d, $J = 7.3$ Hz, 1H), 7.51 (d, $J = 7.8$ Hz, 1H), 7.45 – 7.40 (m, 2H), 7.37 – 7.24 (m, 5H), 7.12 (d, $J = 15.6$ Hz, 1H), 6.15 (d, $J = 15.6$ Hz, 1H), 2.38 (d, $J = 7.7$ Hz, 1H), 2.26 (d, $J = 7.7$ Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 154.7, 148.1, 136.4, 134.2, 128.8, 128.2, 128.1, 127.9, 126.7, 125.4, 123.6, 120.7, 111.8, 104.1, 92.2, 74.3, 38.7, 34.8, 31.0.

HRMS (ESI) m/z calcd. for $C_{21}H_{15}OBr_2$ $[M + H]^+$ 440.9484, found 440.9479.

(*S,E*)-2-(2,2-Dichloro-1-(4-phenylbut-1-yn-1-yl)cyclopropyl)vinyl)benzene (67)



67

According to **General procedure D** with 4-phenyl-1-butyne (14.0 μ L, 0.10 mmol) and (*E*)-2-(1-bromo-2,2-dichlorocyclopropyl)vinyl)benzene **S20** (43.8 mg, 0.15 mmol) at r.t., the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 50/1) to yield the product **67** as a colorless oil (32.0 mg, 94% yield, 90% e.e.).

$[\alpha]_D^{27} = -17$ (c 0.5, CHCl₃).

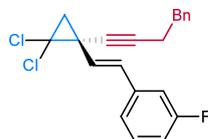
HPLC analysis: Chiralcel OJH (*n*-hexane/*i*-PrOH = 95/5, flow rate 1.0 mL/min, $\lambda = 254$ nm), t_R (major) = 10.94 min, t_R (minor) = 13.72 min.

¹H NMR (400 MHz, CDCl₃) δ 7.39 – 7.16 (m, 10H), 6.88 (d, $J = 15.6$ Hz, 1H), 5.97 (d, $J = 15.7$ Hz, 1H), 2.89 (t, $J = 7.4$ Hz, 2H), 2.62 (t, $J = 7.4$ Hz, 2H), 1.95 (d, $J = 7.3$ Hz, 1H), 1.85 (d, $J = 7.2$ Hz, 1H).

¹³C NMR (100 MHz, CDCl₃) δ 140.6, 136.6, 133.8, 128.70, 128.66, 128.5, 127.9, 127.0, 126.6, 126.5, 84.8, 77.6, 65.7, 36.0, 35.1, 31.6, 21.1.

HRMS (ESI) m/z calcd. for C₂₁H₁₉Cl₂ [M + H]⁺ 341.0858, found 341.0856.

(*S,E*)-1-(2-(2,2-Dichloro-1-(4-phenylbut-1-yn-1-yl)cyclopropyl)vinyl)-3-fluorobenzene (68)



68

According to **General procedure D** with 4-phenyl-1-butyne (14.0 μ L, 0.10 mmol) and (*E*)-1-(2-(1-bromo-2,2-dichlorocyclopropyl)vinyl)-3-fluorobenzene **S22** (46.5 mg, 0.15 mmol) at r.t., the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 50/1) to yield the product **68** as a colorless oil (32.6 mg, 91% yield, 90% e.e.).

$[\alpha]_D^{27} = -15$ (c 0.5, CHCl₃).

HPLC analysis: Chiralcel IG (*n*-hexane/*i*-PrOH = 99.5/0.5, flow rate 0.5 mL/min, $\lambda = 254$ nm), t_R (minor) = 16.73 min, t_R (major) = 21.79 min.

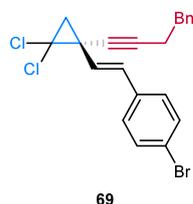
¹H NMR (400 MHz, CDCl₃) δ 7.33 – 7.20 (m, 6H), 7.10 (dt, $J = 7.8, 1.2$ Hz, 1H), 7.02 (dt, $J = 10.2, 2.1$ Hz, 1H), 6.93 (tdd, $J = 8.4, 2.6, 1.0$ Hz, 1H), 6.82 (d, $J = 15.6$ Hz, 1H), 5.97 (d, $J = 15.5$ Hz, 1H), 2.89 (t, $J = 7.3$ Hz, 2H), 2.63 (t, $J = 7.3$ Hz, 2H), 1.97 (d, $J = 7.3$ Hz, 1H), 1.86 (d, $J = 7.3$ Hz, 1H).

¹³C NMR (100 MHz, CDCl₃) δ 163.2 (d, $J = 245.4$ Hz), 140.5, 138.9 (d, $J = 7.7$ Hz), 132.7 (d, $J = 2.6$ Hz), 130.1 (d, $J = 8.4$ Hz), 128.7, 128.5, 128.4, 126.5, 122.5 (d, $J = 2.8$ Hz), 114.7 (d, $J = 21.4$ Hz), 113.2 (d, $J = 21.8$ Hz), 85.1, 77.3, 65.6, 36.1, 35.0, 31.5, 21.0.

^{19}F NMR (376 MHz, CDCl_3) δ -113.4.

HRMS (ESI) m/z calcd. for $\text{C}_{21}\text{H}_{18}\text{Cl}_2\text{F}$ $[\text{M} + \text{H}]^+$ 359.0764, found 359.0758.

(*S,E*)-1-Bromo-4-(2-(2,2-dichloro-1-(4-phenylbut-1-yn-1-yl)cyclopropyl)vinyl)benzene (69)



According to **General procedure D** with 4-phenyl-1-butyne (14.0 μL , 0.10 mmol) and (*E*)-1-bromo-4-(2-(1-bromo-2,2-dichlorocyclopropyl)vinyl)benzene **S23** (55.6 mg, 0.15 mmol) at r.t., the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 50/1) to yield the product **69** as a colorless oil (38.6 mg, 92% yield, 90% e.e.).

$[\alpha]_{\text{D}}^{27} = -34$ (c 0.5, CHCl_3).

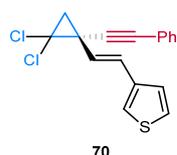
HPLC analysis: Chiralcel OJH (*n*-hexane/*i*-PrOH = 95/5, flow rate 1.0 mL/min, $\lambda = 254$ nm), t_{R} (major) = 14.21 min, t_{R} (minor) = 19.79 min.

^1H NMR (400 MHz, CDCl_3) δ 7.45 – 7.40 (m, 2H), 7.31 – 7.17 (m, 7H), 6.79 (d, $J = 15.6$ Hz, 1H), 5.94 (d, $J = 15.6$ Hz, 1H), 2.88 (t, $J = 7.3$ Hz, 2H), 2.62 (t, $J = 7.3$ Hz, 2H), 1.96 (d, $J = 7.2$ Hz, 1H), 1.85 (d, $J = 7.3$ Hz, 1H).

^{13}C NMR (100 MHz, CDCl_3) δ 140.5, 135.5, 132.6, 131.8, 128.7, 128.5, 128.1, 127.8, 126.5, 121.7, 85.0, 77.4, 65.6, 36.1, 35.0, 31.5, 21.0.

HRMS (ESI) m/z calcd. for $\text{C}_{21}\text{H}_{18}\text{BrCl}_2$ $[\text{M} + \text{H}]^+$ 418.9963, found 418.9954.

(*S,E*)-3-(2-(2,2-Dichloro-1-(phenylethynyl)cyclopropyl)vinyl)thiophene (70)



According to **General procedure D** with ethynylbenzene (11.0 μL , 0.10 mmol) and (*E*)-3-(2-(1-bromo-2,2-dichlorocyclopropyl)vinyl)thiophene **S24** (44.7 mg, 0.15 mmol) at 10 $^{\circ}\text{C}$ for 10 d, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 50/1) to yield the product **70** as a colorless oil (29.1 mg, 91% yield, 88% e.e.).

$[\alpha]_{\text{D}}^{27} = +90$ (c 0.5, CHCl_3).

HPLC analysis: Chiralcel ODH (*n*-hexane/*i*-PrOH = 99/1, flow rate 1.0 mL/min, $\lambda = 254$ nm), t_{R} (major) = 5.85 min, t_{R} (minor) = 6.47 min.

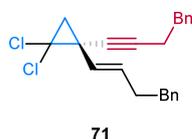
^1H NMR (400 MHz, CDCl_3) δ 7.56 – 7.47 (m, 2H), 7.37 – 7.31 (m, 3H), 7.30 – 7.26 (m, 1H), 7.24 – 7.19 (m, 2H), 7.06 (d, $J = 15.6$ Hz, 1H), 5.94 (d, $J = 15.6$ Hz, 1H), 2.15 (d, $J = 7.3$ Hz, 1H), 1.98 (d, $J = 7.3$ Hz, 1H).

^{13}C NMR (100 MHz, CDCl_3) δ 139.0, 132.1, 128.7, 128.5, 128.3, 126.4, 126.1, 125.1,

122.9, 122.7, 86.3, 84.7, 65.7, 36.3, 31.8.

HRMS (ESI) m/z calcd. for $C_{17}H_{13}Cl_2S$ $[M + H]^+$ 319.0109, found 319.0103.

(*S,E*)-(4-(2,2-Dichloro-1-(4-phenylbut-1-en-1-yl)cyclopropyl)but-3-yn-1-yl)benzene (71)



According to **General procedure D** with 4-phenyl-1-butyne (14.0 μ L, 0.10 mmol) and (*E*)-(4-(1-bromo-2,2-dichlorocyclopropyl)but-3-en-1-yl)benzene **S25** (48 mg, 0.15 mmol) at r.t., the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 50/1) to yield the product **71** as a colorless oil (30.0 mg, 81% yield, 84% e.e.).

$[\alpha]_D^{27} = +44$ (c 0.5, $CHCl_3$).

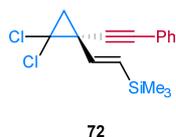
HPLC analysis: Chiralcel OJH (*n*-hexane/*i*-PrOH = 95/5, flow rate 1.0 mL/min, $\lambda = 214$ nm), t_R (minor) = 13.30 min, t_R (major) = 19.27 min.

1H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.25 (m, 4H), 7.24 – 7.14 (m, 6H), 5.99 (dt, $J = 15.1, 6.8$ Hz, 1H), 5.28 (d, $J = 15.1$ Hz, 1H), 2.83 (t, $J = 7.5$ Hz, 2H), 2.69 (t, $J = 7.9$ Hz, 2H), 2.56 (t, $J = 7.5$ Hz, 2H), 2.41 – 2.35 (m, 2H), 1.81 (d, $J = 7.2$ Hz, 1H), 1.66 (d, $J = 7.1$ Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 141.8, 140.6, 134.4, 128.65, 128.56, 128.5, 128.4, 127.4, 126.4, 126.0, 84.1, 78.0, 65.3, 35.7, 35.3, 35.1, 34.2, 30.9, 21.0.

HRMS (ESI) m/z calcd. for $C_{23}H_{23}Cl_2$ $[M + H]^+$ 369.1171, found 369.1168.

(*S,E*)-(2-(2,2-Dichloro-1-(phenylethynyl)cyclopropyl)vinyl)trimethylsilane (72)



According to **General procedure D** with ethynylbenzene (11.0 μ L, 0.10 mmol) and (*E*)-(2-(1-bromo-2,2-dichlorocyclopropyl)vinyl)trimethylsilane **S21** (43.2 mg, 0.15 mmol) at 10 $^\circ$ C for 10 d, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 100/1) to yield the product **72** as a colorless oil (15.5 mg, 50% yield, 86% e.e.).

$[\alpha]_D^{27} = -26$ (c 0.5, $CHCl_3$).

HPLC analysis: Chiralcel OJH (*n*-hexane/*i*-PrOH = 100/0, flow rate 1.0 mL/min, $\lambda = 254$ nm), t_R (major) = 4.65 min, t_R (minor) = 6.38 min.

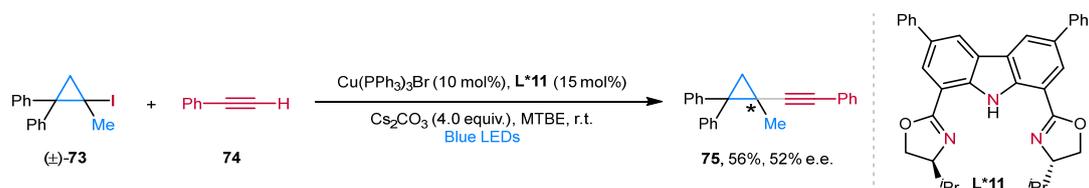
1H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.31 (m, 2H), 7.28 – 7.14 (m, 3H), 6.34 (d, $J = 18.3$ Hz, 1H), 5.69 (d, $J = 18.3$ Hz, 1H), 1.98 (d, $J = 7.3$ Hz, 1H), 1.83 (d, $J = 7.3$ Hz, 1H), 0.00 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 142.0, 136.3, 133.2, 129.7, 129.6, 124.0, 87.5, 86.2, 66.6, 37.1, 34.8, 0.0.

HRMS (ESI) m/z calcd. for $C_{16}H_{19}Cl_2Si$ $[M + H]^+$ 309.0628, found 309.0625.

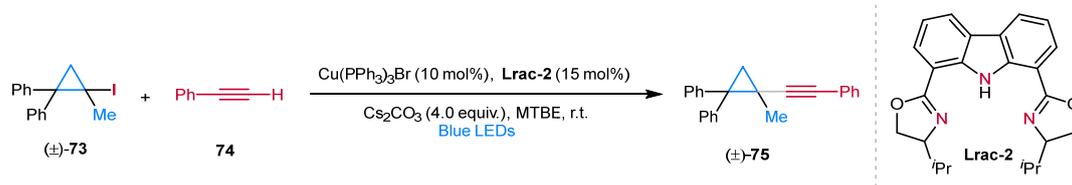
Enantioconvergent cross-coupling of alkynes with 1-alkyl-2,2-diphenylcyclopropyl iodide

General procedure E:



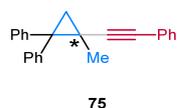
An oven-dried resealable Schlenk tube equipped with a magnetic stirring bar was charged with $\text{Cu(PPh}_3)_3\text{Br}$ (9.30 mg, 0.010 mmol, 10 mol%), **L*11** (8.12 mg, 0.015 mmol, 15 mol%), and Cs_2CO_3 (128.0 mg, 0.40 mmol, 4.0 equiv.). The tube was evacuated and backfilled with argon three times. Then racemic 1-alkyl-substituted cyclopropyl iodine **73** (50.1 mg, 0.15 mmol, 1.5 equiv.), phenylacetylene (11.0 μL , 0.10 mmol, 1.0 equiv.), and MTBE (2.0 mL) were sequentially added into the mixture under argon. The tube was sealed and the reaction mixture was allowed to stir under the irradiation of blue LEDs (5 W) at r.t. for 7 d. Upon completion of the reaction (monitored by TLC), the mixture was then filtered through a pad of celite and rinsed with EtOAc. The filtrate was evaporated and the residue was purified by column chromatography on silica gel to afford the desired product **75** as a colorless oil (17.3 mg, 56% yield, 52% e.e.).

The preparation of racemic products (\pm)-**75**:



Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with $\text{Cu(PPh}_3)_3\text{Br}$ (9.30 mg, 0.010 mmol, 10 mol%), **Lrac-2** (5.80 mg, 0.015 mmol, 15 mol%), Cs_2CO_3 (128.0 mg, 0.40 mmol, 4.0 equiv.), and MTBE (1.0 mL). Then 1-alkyl-substituted cyclopropyl iodine **73** (50.1 mg, 0.15 mmol, 1.5 equiv.) and phenylacetylene (11.0 μL , 0.10 mmol, 1.0 equiv.) were sequentially added into the mixture and the reaction mixture was stirred at r.t. for 7 d. Upon completion, the precipitate was filtered off and washed by EtOAc. The filtrate was evaporated and the residue was purified by column chromatography on silica gel to afford the desired product.

(2-Methyl-2-(phenylethynyl)cyclopropane-1,1-diyl)dibenzene (**75**)



$[\alpha]_{\text{D}}^{27} = -59$ (c 0.5, CHCl_3).

HPLC analysis: Chiralcel ODH (*n*-hexane/*i*-PrOH = 99/1, flow rate 0.5 mL/min, $\lambda =$

254 nm), t_R (major) = 9.41 min, t_R (minor) = 10.79 min.

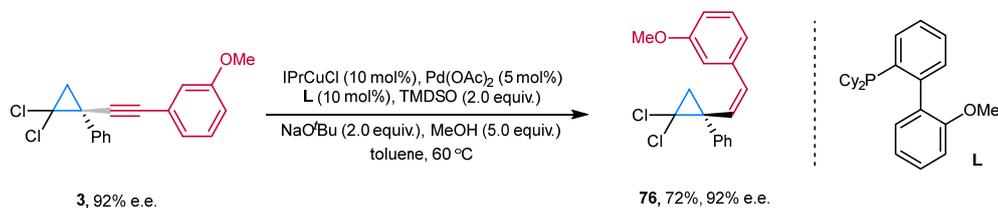
^1H NMR (400 MHz, CDCl_3) δ 7.60 – 7.56 (m, 2H), 7.47 – 7.43 (m, 2H), 7.30 – 7.24 (m, 4H), 7.20 – 7.15 (m, 5H), 7.09 – 7.04 (m, 2H), 1.85 (d, J = 4.7 Hz, 1H), 1.60 (d, J = 4.7 Hz, 1H), 1.28 (s, 3H).

^{13}C NMR (100 MHz, CDCl_3) δ 143.9, 142.1, 131.4, 130.1, 129.9, 128.6, 128.1, 128.0, 127.4, 126.7, 126.5, 124.0, 94.7, 81.6, 43.3, 28.7, 22.9, 19.7.

HRMS (ESI) m/z calcd. for $\text{C}_{24}\text{H}_{21}$ $[\text{M} + \text{H}]^+$ 309.1638, found 309.1633.

Synthetic applications

Synthesis of 76



To a flamed Schlenk tube charged with a stir bar were added NaO^tBu (19.2 mg, 0.20 mmol, 2.0 equiv.), **3** (31.7 mg, 0.10 mmol, 1.0 equiv., 92% e.e.), Pd(OAc)₂ (1.1 mg, 0.0050 mmol, 5.0 mol%), **L** (3.8 mg, 0.010 mmol, 10 mol%), IPrCuCl (4.9 mg, 0.010 mmol, 10 mol%), TMSO (1,1,3,3-tetramethyldisiloxane) (26.8 mg, 0.20 mmol, 2.0 equiv.), MeOH (16.0 mg, 0.50 mmol, 5.0 equiv.) and toluene (1.0 mL). The reaction mixture was stirred at 60 °C for 12 h. Upon completion (monitored by TLC), the reaction mixture was filtered through a short plug of silica gel eluted with EtOAc and purified by column chromatography (petroleum ether/EtOAc = 100/1) to afford **76** as a colorless oil (22.8 mg, 72% yield, 92% e.e.).

(*S,Z*)-1-(2-(2,2-Dichloro-1-phenylcyclopropyl)vinyl)-3-methoxybenzene (**76**)



$[\alpha]_D^{27} = +196$ (c 0.5, CHCl₃).

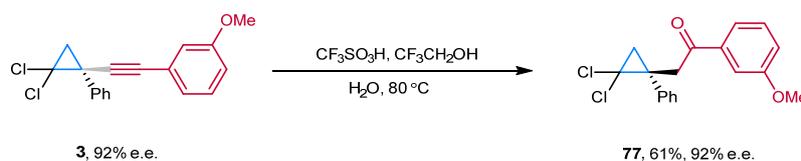
HPLC analysis: Chiralcel OJH (*n*-hexane/*i*-PrOH = 95/5, flow rate 1.0 mL/min, $\lambda = 230$ nm), t_R (minor) = 10.17 min, t_R (major) = 20.38 min.

¹H NMR (400 MHz, CDCl₃) δ 7.43 – 7.36 (m, 4H), 7.32 – 7.26 (m, 1H), 7.21 (t, $J = 7.9$ Hz, 1H), 6.85 – 6.73 (m, 3H), 6.63 (d, $J = 11.6$ Hz, 1H), 6.40 (dd, $J = 11.5, 1.1$ Hz, 1H), 3.75 (s, 3H), 2.22 (dd, $J = 8.0, 1.2$ Hz, 1H), 1.51 (d, $J = 8.0$ Hz, 1H).

¹³C NMR (100 MHz, CDCl₃) δ 159.4, 139.2, 137.2, 132.7, 130.4, 129.1, 128.6, 128.5, 127.5, 121.6, 114.2, 113.4, 66.9, 55.4, 38.6, 31.5.

HRMS (ESI) m/z calcd. for C₁₈H₁₇OCl₂ [M + H]⁺ 319.0651, found 319.0643.

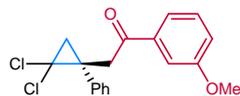
Synthesis of 77



To a solution of **3** (31.7 mg, 0.10 mmol, 1.0 equiv., 92% e.e.) in CF₃CH₂OH (0.50

mL) were added CF₃SO₃H (3.0 mg, 0.020 mmol, 20 mol%) and water (3.6 mg, 0.20 mmol, 2.0 equiv.). The reaction mixture was stirred at 80 °C for 24 h. After evaporation under reduced pressure, the residue was purified with column chromatography on silica gel (petroleum ether/EtOAc = 30/1) to yield the product **77** as a colorless oil (20.5 mg, 61% yield, 92% e.e.).

(R)-2-(2,2-Dichloro-1-phenylcyclopropyl)-1-(3-methoxyphenyl)ethan-1-one (77)



77

$[\alpha]_D^{27} = -35$ (c 0.5, CHCl₃).

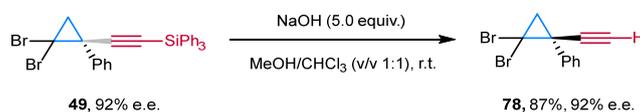
HPLC analysis: Chiralcel ODH (*n*-hexane/*i*-PrOH = 95/5, flow rate 1.0 mL/min, $\lambda = 254$ nm), t_R (major) = 8.59 min, t_R (minor) = 13.61 min.

¹H NMR (400 MHz, CDCl₃) δ 7.47 – 7.41 (m, 2H), 7.38 (dt, $J = 7.6, 1.2$ Hz, 1H), 7.34 – 7.25 (m, 4H), 7.25 – 7.20 (m, 1H), 7.05 (dd, $J = 8.1, 2.3$ Hz, 1H), 4.00 (dd, $J = 17.5, 1.4$ Hz, 1H), 3.79 (s, 3H), 3.45 (d, $J = 17.5$ Hz, 1H), 2.22 (dd, $J = 7.9, 1.3$ Hz, 1H), 1.88 (d, $J = 8.0$ Hz, 1H).

¹³C NMR (100 MHz, CDCl₃) δ 196.4, 159.9, 139.3, 138.2, 129.9, 129.7, 128.4, 127.6, 120.7, 120.0, 112.1, 65.1, 55.5, 46.7, 37.2, 31.7.

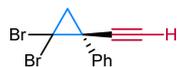
HRMS (ESI) m/z calcd. for C₁₈H₁₇O₂Cl₂ [M + H]⁺ 335.0600, found 335.0592.

Synthesis of 78



To a solution of **49** (1.12 g, 2.0 mmol, 1.0 equiv., 92% e.e.) in MeOH/CHCl₃ (v/v 1:1, 20 mL) was added NaOH (0.40 g, 10.0 mmol, 5.0 equiv.) and the resulting mixture was stirred at r.t. for 1 h. After completion of the reaction (monitored by TLC), the mixture was concentrated under reduced pressure and purified by column chromatography (petroleum ether/EtOAc = 100/1) to yield **78** as a white solid (0.52 g, 87% yield, 92% e.e.).

(S)-2-(2,2-Dibromo-1-ethynylcyclopropyl)benzene (78)



78

m.p. 69–71 °C

$[\alpha]_D^{27} = -15$ (c 0.5, CHCl₃).

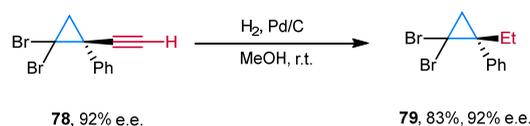
HPLC analysis: Chiralcel ODH (*n*-hexane/*i*-PrOH = 99/1, flow rate 0.5 mL/min, $\lambda = 254$ nm), t_R (minor) = 12.63 min, t_R (major) = 14.09 min.

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.46 – 7.31 (m, 5H), 2.50 (d, $J = 7.9$ Hz, 1H), 2.36 (s, 1H), 2.27 (d, $J = 7.9$ Hz, 1H).

$^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 137.3, 129.0, 128.6, 128.4, 84.8, 70.5, 34.7, 33.0, 32.6.

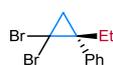
HRMS (ESI) m/z calcd. for $\text{C}_{11}\text{H}_9\text{Br}_2$ $[\text{M} + \text{H}]^+$ 298.9065, found 298.9062.

Synthesis of 79



To a mixture of Pd/C (10% w/w Pd on carbon, 79.5 mg, 0.075 mmol, 5 mol%), in MeOH (20 mL) was added **78** (0.45 g, 1.5 mmol, 1.0 equiv., 92% e.e.) under argon atmosphere. Then the reaction flask was evacuated and refilled with hydrogen through a balloon. The resulting reaction mixture was stirred under the hydrogen atmosphere at r.t. for 2 h. After completion, the reaction mixture was filtered and rinsed with EtOAc. The filtrate was concentrated under reduced pressure and the residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 100/1) to afford **79** as a pale-yellow liquid (0.38 g, 83% yield, 92% e.e.).

(*R*)-(2,2-Dibromo-1-ethylcyclopropyl)benzene (**79**)



79

$[\alpha]_D^{27} = -87$ (c 0.5, CHCl_3).

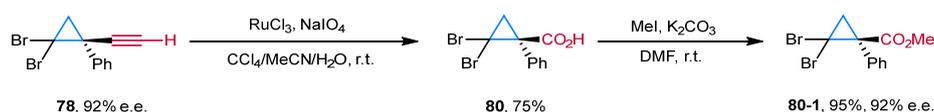
HPLC analysis: Chiralcel OJH (n -hexane/ i -PrOH = 99/1, flow rate 0.5 mL/min, $\lambda = 230$ nm), t_R (major) = 11.81 min, t_R (minor) = 15.14 min.

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.45 – 7.12 (m, 5H), 2.15 (dt, $J = 14.7, 7.3$ Hz, 1H), 2.04 (d, $J = 7.5$ Hz, 1H), 1.79 (dt, $J = 14.7, 7.3$ Hz, 1H), 1.72 (d, $J = 7.6$ Hz, 1H), 0.85 (t, $J = 7.4$ Hz, 3H).

$^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 140.3, 129.6, 128.3, 127.4, 41.1, 36.9, 33.8, 32.9, 11.5.

HRMS (ESI) m/z calcd. for $\text{C}_{11}\text{H}_{13}\text{Br}_2$ $[\text{M} + \text{H}]^+$ 302.9378, found 302.9368.

Synthesis of 80

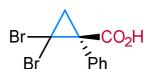


To a mixture of RuCl_3 (1.5 mg, 0.010 mmol, 5 mol%) and sodium periodate (171.0 mg, 0.80 mmol, 4.0 equiv.) in a mixed solvent of CCl_4 (0.40 mL) and water (0.60 mL) was added a solution of **78** (60.0 mg, 0.20 mmol, 1.0 equiv., 92% e.e.) in MeCN (0.40 mL) in one portion. The reaction mixture was stirred at r.t. for 8 h, and then, was concentrated. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 2/1) to afford the product **80** as a white solid (48.3 mg, 75%

yield). The e.e. value of **80** was determined by converting it to the corresponding ester **80-1**.

To a solution of **80** (32.0 mg, 0.10 mmol, 1.0 equiv.) in anhydrous DMF (1.0 mL) were added MeI (28.4 mg, 0.20 mmol, 2.0 equiv.) and K₂CO₃ (27.6 mg, 0.20 mmol, 2.0 equiv.) at r.t. Then it was stirred for 2 h. Upon completion (monitored by TLC), the reaction was quenched with water and extracted with EtOAc. The organic phase was concentrated and purified with by column chromatography on silica gel (petroleum ether/EtOAc = 10/1) to afford the product **80-1** as a white solid (31.9 mg, 95% yield, 92% e.e.).

(*R*)-2,2-Dibromo-1-phenylcyclopropane-1-carboxylic acid (**80**)



80

m.p. 75–78 °C

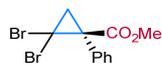
[α]_D²⁷ = +32 (c 0.5, CHCl₃).

¹H NMR (400 MHz, CDCl₃) δ 8.63 (s, 1H), 7.51 – 7.45 (m, 2H), 7.40 – 7.35 (m, 3H), 2.76 (d, *J* = 8.0 Hz, 1H), 2.24 (d, *J* = 8.0 Hz, 1H).

¹³C NMR (100 MHz, CDCl₃) δ 173.3, 135.2, 131.0, 128.8, 128.4, 44.2, 32.4, 28.0.

HRMS (ESI) *m/z* calcd. for C₁₀H₉O₂Br₂ [M + H]⁺ 318.8964, found 318.8964.

Methyl (*R*)-2,2-dibromo-1-phenylcyclopropane-1-carboxylate (**80-1**)



80-1

m.p. 88–90 °C

[α]_D²⁷ = +20 (c 0.5, CHCl₃).

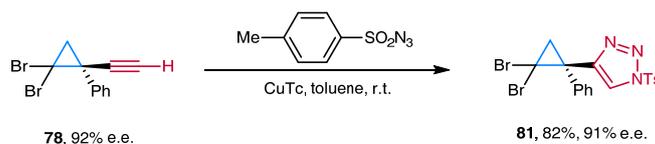
HPLC analysis: Chiralcel OJH (*n*-hexane/*i*-PrOH = 95/5, flow rate 1.0 mL/min, λ = 254 nm), *t_R* (major) = 13.22 min, *t_R* (minor) = 16.27 min.

¹H NMR (400 MHz, CDCl₃) δ 7.55 – 7.46 (m, 2H), 7.42 – 7.32 (m, 3H), 3.75 (s, 3H), 2.78 (d, *J* = 8.0 Hz, 1H), 2.22 (d, *J* = 7.9 Hz, 1H).

¹³C NMR (100 MHz, CDCl₃) δ 168.3, 135.6, 130.9, 128.7, 128.3, 53.4, 44.6, 32.3, 28.3.

HRMS (ESI) *m/z* calcd. for C₁₁H₁₁O₂Br₂ [M + H]⁺ 332.9120, found 332.9114.

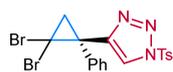
Synthesis of **81**



To a solution of **78** (30.0 mg, 0.10 mmol, 1.0 equiv., 92% e.e.) in toluene (1.0 mL) were added 4-methylbenzenesulfonyl azide (23.6 mg, 0.12 mmol, 1.2 equiv.) and

copper thiophene-2-carboxylate (0.95 mg, 0.0050 mmol, 5 mol%) under argon atmosphere. The reaction mixture was stirred at r.t. for 8 h, and then, was concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 10/1) to yield the product **81** as a colorless oil (40.7 mg, 82% yield, 91% e.e.).

(R)-4-(2,2-Dibromo-1-phenylcyclopropyl)-1-tosyl-1H-1,2,3-triazole (81)



81

$[\alpha]_D^{27} = +52$ (c 0.5, CHCl₃).

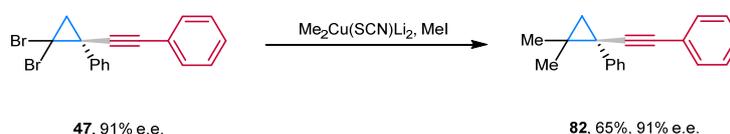
HPLC analysis: Chiralcel ODH (*n*-hexane/*i*-PrOH = 70/30, flow rate 1.0 mL/min, $\lambda = 254$ nm), t_R (minor) = 7.65 min, t_R (major) = 10.24 min.

¹H NMR (400 MHz, CDCl₃) δ 8.00 (s, 1H), 7.99 – 7.88 (m, 2H), 7.54 – 7.46 (m, 2H), 7.44 – 7.32 (m, 5H), 3.01 (d, $J = 8.0$ Hz, 1H), 2.48 (d, $J = 7.9$ Hz, 1H), 2.43 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 147.7, 147.6, 139.1, 132.8, 130.6, 129.8, 128.92, 128.87, 128.4, 123.1, 36.7, 33.2, 33.0, 22.0.

HRMS (ESI) m/z calcd. for C₁₈H₁₆O₂N₃Br₂S [M + H]⁺ 495.9324, found 495.9314.

Synthesis of 82

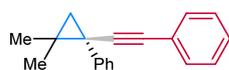


47, 91% e.e.

82, 65%, 91% e.e.

To a flamed Schlenk tube charged with a stir bar were added cuprous thiocyanate (134.9 mg, 1.1 mmol) and dry ether (1.0 mL). Methyl lithium (2.0 mmol) was added to the suspension at -78 °C under argon atmosphere and the mixture was gradually warmed up to 0 °C in 30 min. Then the mixture was cooled to -20 °C and a solution of **47** (37.6 mg, 0.10 mmol, 1.0 equiv., 91% e.e.) in dry ether (1.0 mL) and HMPA (43.5 μ L, 0.25 mmol) was added dropwise to the mixture at -20 °C. The reaction mixture was stirred for 1h and much excess of methyl iodide (0.50 mL) was added at -40 °C. After 1 h, the reaction mixture was quenched with aqueous NH₄Cl at -78 °C and precipitates were filtrated off on a celite bed. The filtrated was extracted with ether and the organic layer was washed with brine. The organic layer was concentrated under reduced pressure and the residue was purified by column chromatography on silica gel (petroleum ether) to afford **82** as a colorless oil (16.1 mg, 65% yield, 91% e.e.).

(R)-(2,2-dimethyl-1-(phenylethynyl)cyclopropyl)benzene (82)



82

$[\alpha]_D^{27} = -96$ (c 0.5, CHCl₃).

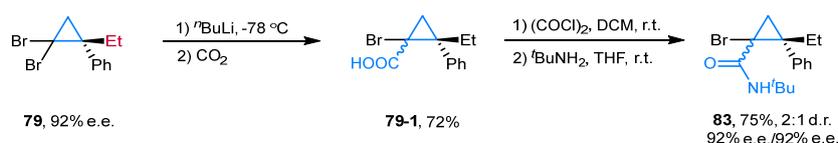
HPLC analysis: Chiralcel OJ-RH (MeCN/H₂O = 70/30, flow rate 0.7 mL/min, $\lambda = 254$ nm), t_R (minor) = 15.36 min, t_R (major) = 18.65 min.

¹H NMR (400 MHz, CDCl₃) δ 7.44 – 7.38 (m, 4H), 7.36 – 7.31 (m, 2H), 7.29 – 7.24 (m, 4H), 1.54 (s, 3H), 1.47 (d, $J = 4.8$ Hz, 1H), 1.18 (d, $J = 4.8$ Hz, 1H), 0.83 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 140.3, 131.7, 129.4, 128.3, 128.2, 127.5, 126.6, 124.3, 94.6, 78.6, 27.8, 27.6, 26.4, 24.1, 22.3.

HRMS (ESI) m/z calcd. for C₁₉H₁₉ [M + H]⁺ 247.1481, found 247.1477.

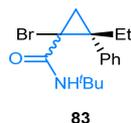
Synthesis of **83**



An oven-dried two-necked flask was charged under nitrogen atmosphere with a solution of **79** (300.0 mg, 1.0 mmol, 1.0 equiv.) in anhydrous THF (10 mL). The solution was cooled to -78 °C and *t*-BuLi (2.5 M in hexanes, 0.38 mL, 0.95 mmol, 0.95 equiv.) was added dropwise over the course of 15 min. After the addition was complete, the reaction mixture was warmed to -61 °C and stirred for 20 min. The cold solution was then cannulated into a 1-L flask containing freshly condensed CO₂. The reaction mixture was stirred for 2 h under constant flow of dry CO₂ gas while allowed to warm to r.t.. The mixture was partitioned between water and CHCl₃ and acidified with 4 N HCl. The aqueous layer was extracted with CHCl₃. The combined organic phases were then back-extracted with saturated NaHCO₃. The combined aqueous extracts were washed with CHCl₃, acidified to pH < 1, and extracted with CHCl₃. The combined organic phases were dried with anhydrous MgSO₄ and concentrated in vacuum. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 2/1) to afford **79-1** as a colorless oil (193.8 mg, 72% yield).

A flame-dried round-bottom flask equipped with a dried magnetic stir bar was charged with **79-1** obtained above, DMF (2 drops), and CH₂Cl₂ (10 mL). The mixture was then treated with oxalyl chloride (0.10 mL, 1.1 mmol, 1.5 equiv.) at 0 °C, stirred for 15 min, warmed to r.t. and additionally stirred for 2 h. The solvent was then removed in vacuum and the crude acyl chloride was dissolved in dry THF (5.0 mL), followed by the addition of a solution of *tert*-butyl amine (0.20 mL, 2.2 mmol, 3.0 equiv.) in THF (5.0 mL). The reaction mixture was stirred overnight. After the reaction was complete, the solvent was removed in vacuum and the resulting residue was partitioned between EtOAc and water. The combined organic phases were dried over anhydrous Na₂SO₄ and concentrated. The residue was purified by chromatography on silica gel (petroleum ether/EtOAc = 20/1) to afford **83** as a white solid (175.3 mg, 75% yield, 2:1 d.r., 92% e.e./92% e.e.).

(2*R*)-1-Bromo-*N*-(*tert*-butyl)-2-ethyl-2-phenylcyclopropane-1-carboxamide (**83**)



m.p. 44–46 °C

$[\alpha]_D^{27} = +12$ (c 0.5, CHCl₃).

HPLC analysis: Chiralcel IG and IC (*n*-hexane/*i*-PrOH = 95/5, flow rate 0.5 mL/min, $\lambda = 230$ nm), t_R (minor1) = 19.14 min, t_R (major1) = 20.62 min, t_R (minor2) = 22.84 min, t_R (major2) = 23.94 min.

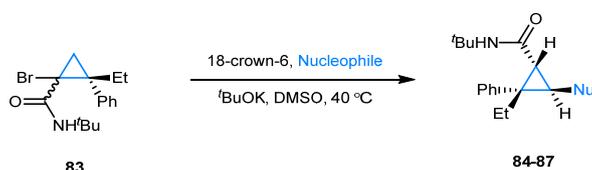
¹H NMR (400 MHz, CDCl₃) δ 7.39 – 7.32 (m, 1H), 7.31 – 7.21 (m, 2H+3H×0.50), 7.20 – 7.14 (m, 2H+2H×0.50), 6.31 (s, 1H×0.50), 6.25 (s, 1H), 2.49 (dd, $J = 6.2, 1.7$ Hz, 1H), 2.16 – 2.05 (m, 1H+1H×0.50), 1.95 – 1.77 (m, 1H+1H×0.50), 1.65 – 1.52 (m, 2H×0.50), 1.41 (s, 9H×0.50), 1.19 (d, $J = 6.2$ Hz, 1H), 1.10 (s, 9H), 0.84 (t, $J = 7.4$ Hz, 3H), 0.77 (t, $J = 7.3$ Hz, 3H×0.50).

¹³C NMR (100 MHz, CDCl₃) (major) δ 165.3, 138.4, 129.0, 128.0, 126.9, 51.5, 45.7, 40.1, 33.8, 28.3, 25.2, 11.4.

¹³C NMR (100 MHz, CDCl₃) (minor) δ 166.8, 141.3, 129.8, 128.1, 127.1, 52.0, 42.9, 41.1, 28.7, 27.3, 24.8, 11.6.

HRMS (ESI) m/z calcd. for C₁₆H₂₃ONBr [M + H]⁺ 324.0957, found 324.0953.

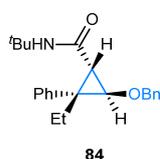
Synthesis of 84–87



General procedure F:

An oven-dried 10-mL Weaton vial was charged with 18-crown-6 (2.7 mg, 0.010 mmol, 10 mol%), ^tBuOK (67.0 mg, 0.60 mmol, 6.0 equiv.), nucleophile (0.30 mmol, 3.0 equiv.), and anhydrous DMSO (2.0 mL). The mixture was stirred at r.t. for 1 min and **83** (32.4 mg, 0.10 mmol, 1.0 equiv.) was added in a single portion. The reaction mixture was stirred at 40 °C for 24 h. Then the reaction mixture was poured into a separatory funnel and was partitioned between water and EtOAc. The organic layers were washed with brine, dried over MgSO₄, filtered and evaporated. The residue was purified by chromatography on silica gel to afford the desired product.

(1*S*,2*S*,3*R*)-3-(Benzyloxy)-*N*-(*tert*-butyl)-2-ethyl-2-phenylcyclopropane-1-carboxamide (**84**)



According to **General procedure F** with benzyl alcohol (31.0 μ L, 0.30 mmol, 3.0

equiv.), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 10/1) to yield the product **84** as a white solid (28.6 mg, 81% yield, 92% e.e., > 20:1 d.r.).

m.p. 62–64 °C

$[\alpha]_D^{27} = -8.5$ (c 0.5, CHCl₃).

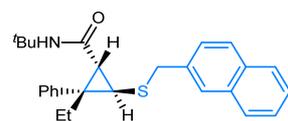
HPLC analysis: Chiralcel ODH (*n*-hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, $\lambda = 230$ nm), t_R (major) = 4.48 min, t_R (minor) = 7.62 min.

¹H NMR (400 MHz, CDCl₃) δ 7.45 – 7.24 (m, 7H), 7.23 – 7.15 (m, 3H), 4.96 (s, 1H), 4.75 – 4.62 (m, 2H), 4.09 (d, $J = 3.3$ Hz, 1H), 1.97 (dq, $J = 14.6, 7.4$ Hz, 1H), 1.76 (dq, $J = 14.3, 7.3$ Hz, 1H), 1.64 (d, $J = 3.4$ Hz, 1H), 1.15 (s, 9H), 0.88 (t, $J = 7.4$ Hz, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 168.2, 139.2, 137.8, 129.8, 128.6, 128.2, 128.1, 127.9, 127.0, 73.4, 67.2, 51.1, 43.0, 36.3, 28.8, 28.4, 11.6.

HRMS (ESI) m/z calcd. for C₂₃H₃₀O₂N [M + H]⁺ 352.2271, found 352.2266.

(1*R*,2*S*,3*R*)-*N*-(*tert*-Butyl)-2-ethyl-3-((naphthalen-2-ylmethyl)thio)-2-phenylcyclopropane-1-carboxamide (**85**)



85

According to **General procedure F** with naphthalen-2-ylmethanethiol (52.2 mg, 0.30 mmol, 3.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 10/1) to yield the product **85** as a colorless oil (28.6 mg, 72% yield, 90% e.e., > 20:1 d.r.).

$[\alpha]_D^{27} = -9.8$ (c 0.5, CHCl₃).

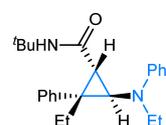
HPLC analysis: Chiralcel ODH (*n*-hexane/*i*-PrOH = 95/5, flow rate 1.0 mL/min, $\lambda = 254$ nm), t_R (major) = 8.68 min, t_R (minor) = 10.88 min.

¹H NMR (400 MHz, CDCl₃) δ 7.96 – 7.66 (m, 4H), 7.59 – 7.35 (m, 3H), 7.24 – 6.95 (m, 5H), 4.74 (s, 1H), 4.15 – 3.87 (m, 2H), 2.89 (d, $J = 5.0$ Hz, 1H), 2.02 (dq, $J = 15.1, 7.6$ Hz, 1H), 1.74 (dq, $J = 15.1, 7.6$ Hz, 1H), 1.51 (d, $J = 5.0$ Hz, 1H), 1.04 (s, 9H), 0.79 (t, $J = 7.4$ Hz, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 167.6, 139.8, 136.0, 133.4, 132.6, 129.6, 128.5, 128.1, 127.9, 127.7, 127.6, 127.3, 126.9, 126.3, 125.9, 51.1, 42.8, 39.1, 38.4, 31.5, 30.8, 28.7, 11.6.

HRMS (ESI) m/z calcd. for C₂₇H₃₂ONS [M + H]⁺ 418.2199, found 418.2192.

(1*S*,2*S*,3*R*)-*N*-(*tert*-Butyl)-2-ethyl-3-(ethyl(phenyl)amino)-2-phenylcyclopropane-1-carboxamide (**86**)



86

According to **General procedure F** with *N*-ethylaniline (36.3 mg, 0.30 mmol, 3.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 10/1) to yield the product **86** as a white solid (29.2 mg, 80% yield, 92% e.e., > 20:1 d.r.).

m.p. 65–68 °C

$[\alpha]_D^{27} = -12$ (c 0.5, CHCl₃).

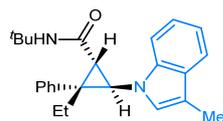
HPLC analysis: Chiralcel ODH (*n*-hexane/*i*-PrOH = 95/5, flow rate 1.0 mL/min, $\lambda = 254$ nm), t_R (major) = 9.02 min, t_R (minor) = 12.14 min.

¹H NMR (400 MHz, CDCl₃) δ 7.31 – 7.19 (m, 7H), 7.06 – 6.90 (m, 2H), 6.85 – 6.76 (m, 1H), 5.24 (s, 1H), 3.74 (dq, $J = 14.1, 7.0$ Hz, 1H), 3.56 – 3.36 (m, 2H), 1.88 – 1.73 (m, 2H), 1.53 (d, $J = 4.4$ Hz, 1H), 1.24 (s, 9H), 1.17 (t, $J = 7.1$ Hz, 3H), 0.88 (t, $J = 7.4$ Hz, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 168.3, 149.3, 140.1, 129.6, 129.0, 128.2, 126.9, 118.6, 116.9, 51.3, 48.5, 46.9, 45.4, 37.4, 28.9, 27.7, 11.9, 10.9.

HRMS (ESI) m/z calcd. for C₂₄H₃₃ON₂ [M + H]⁺ 365.2587, found 365.2582.

(1*S*,2*S*,3*R*)-*N*-(*tert*-Butyl)-2-ethyl-3-(3-methyl-1*H*-indol-1-yl)-2-phenylcyclopropane-1-carboxamide (**87**)



87

According to **General procedure F** with 3-methyl-1*H*-indole (39.3 mg, 0.30 mmol, 3.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 10/1) to yield the product **87** as a white solid (26.4 mg, 70% yield, 92% e.e., > 20:1 d.r.).

m.p. 70–73 °C

$[\alpha]_D^{27} = -62$ (c 0.5, CHCl₃).

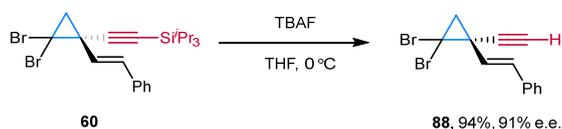
HPLC analysis: Chiralcel IA (*n*-hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, $\lambda = 230$ nm), t_R (minor) = 3.75 min, t_R (major) = 6.22 min.

¹H NMR (400 MHz, CDCl₃) δ 7.64 – 7.53 (m, 2H), 7.49 – 7.42 (m, 2H), 7.41 – 7.33 (m, 2H), 7.32 – 7.26 (m, 2H), 7.15 (t, $J = 7.5$ Hz, 1H), 6.94 (s, 1H), 5.35 (s, 1H), 4.30 (d, $J = 4.3$ Hz, 1H), 2.33 (s, 3H), 2.27 (d, $J = 4.3$ Hz, 1H), 1.56 – 1.44 (m, 2H), 1.26 (s, 9H), 0.77 (t, $J = 7.3$ Hz, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 167.1, 138.8, 137.9, 129.7, 129.5, 128.5, 127.4, 125.7, 122.0, 119.3, 119.2, 111.0, 110.4, 51.5, 44.0, 43.1, 35.3, 28.8, 28.5, 11.5, 9.7.

HRMS (ESI) m/z calcd. for C₂₅H₃₁ON₂ [M + H]⁺ 375.2431, found 375.2426.

Synthesis of **88**



60

88, 94%, 91% e.e.

Compound **60** (289.2 mg, 0.60 mmol, 1.0 equiv.) was dissolved in anhydrous THF (10.0 mL) under argon atmosphere in a 25-mL Schlenk flask. Then TBAF (1 M in THF, 1.2 mL, 1.2 mmol, 2.0 equiv.) was added into the solution, and the mixture was stirred at 0 °C for 3 h. Upon completion of the reaction, the reaction mixture was poured into water and extracted with CH₂Cl₂. The combined organic layers were dried over MgSO₄, filtered, and concentrated under reduced pressure. The thus-obtained crude product was purified by column chromatography on silica gel (petroleum ether/ EtOAc = 100/1) to yield the product **88** as a white solid (183.9 mg, 94% yield, 91% e.e.).

(*S,E*)-(2-(2,2-Dibromo-1-ethynylcyclopropyl)vinyl)benzene (88**)**



m.p. 83–85 °C

[α]_D²⁷ = –98 (c 0.5, CHCl₃).

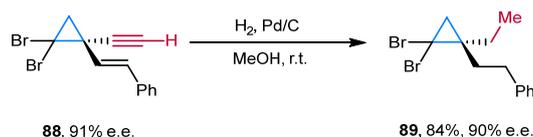
HPLC analysis: Chiralcel OJH (*n*-hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm), *t_R* (major) = 9.56 min, *t_R* (minor) = 14.80 min.

¹H NMR (400 MHz, CDCl₃) δ 7.44 – 7.37 (m, 2H), 7.36 – 7.30 (m, 2H), 7.29 – 7.24 (m, 1H), 7.04 (d, *J* = 15.6 Hz, 1H), 6.03 (d, *J* = 15.6 Hz, 1H), 2.52 (s, 1H), 2.25 (d, *J* = 7.7 Hz, 1H), 2.12 (d, *J* = 7.7 Hz, 1H).

¹³C NMR (100 MHz, CDCl₃) δ 136.4, 134.2, 128.8, 128.2, 127.7, 126.7, 81.8, 73.0, 38.1, 33.6, 30.0.

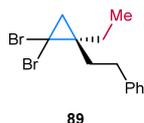
HRMS (ESI) *m/z* calcd. for C₁₃H₁₁Br₂ [M + H]⁺ 324.9222, found 324.9224.

Synthesis of **89**



To a mixture of Pd/C (10% w/w Pd on carbon, 5.0 mg, 0.0050 mmol, 5 mol%) in MeOH (2.0 mL) was added **88** (32.6 mg, 0.10 mmol, 1.0 equiv., 91% e.e.) under argon atmosphere. Then, the reaction flask was evacuated and refilled with hydrogen through a balloon. The resulting reaction mixture was stirred under the hydrogen atmosphere at r.t. for 4 h. After completion, the reaction mixture was filtered and rinsed with EtOAc. The filtrate was concentrated under reduced pressure and the residue was purified by column chromatography on silica gel (petroleum ether) to afford **89** as a colorless oil (27.9 mg, 84% yield, 90% e.e.).

(*R*)-(2-(2,2-Dibromo-1-ethylcyclopropyl)ethyl)benzene (89**)**



$[\alpha]_D^{27} = -39$ (c 0.5, CHCl_3).

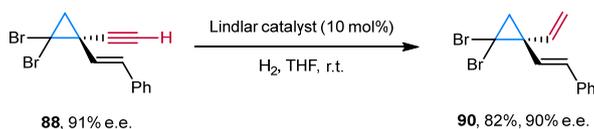
HPLC analysis: Chiralcel OJ3 (*n*-hexane/*i*-PrOH = 99.5/0.5, flow rate 0.5 mL/min, $\lambda = 254$ nm), t_R (major) = 13.50 min, t_R (minor) = 14.32 min.

^1H NMR (400 MHz, CDCl_3) δ 7.32 – 7.26 (m, 2H), 7.25 – 7.16 (m, 3H), 2.83 (ddd, $J = 13.4, 10.3, 6.4$ Hz, 1H), 2.67 (ddd, $J = 13.5, 10.5, 6.9$ Hz, 1H), 2.04 – 1.89 (m, 2H), 1.84 (dq, $J = 14.7, 7.5$ Hz, 1H), 1.71 (dq, $J = 14.7, 7.5$ Hz, 1H), 1.44 – 1.35 (m, 2H), 1.08 (t, $J = 7.4$ Hz, 3H).

^{13}C NMR (100 MHz, CDCl_3) δ 141.9, 128.6, 128.4, 126.2, 39.5, 36.7, 34.1, 33.9, 32.5, 28.0, 10.7.

HRMS (ESI) m/z calcd. for $\text{C}_{13}\text{H}_{17}\text{Br}_2$ $[\text{M} + \text{H}]^+$ 330.9691, found 330.9683.

Synthesis of 90



A flask containing a magnetic stirrer was charged with **88** (32.6 mg, 0.10 mmol, 1.0 equiv., 91% e.e.), Lindlar catalyst (21.1 mg, 0.010 mmol, 10 mol%), and THF (2.0 mL). Then the reaction flask was evacuated and refilled with hydrogen through a balloon. The mixture was stirred at r.t. under the hydrogen atmosphere for 4 h. Upon completion as monitored by TLC, EtOAc was added, and the mixture was passed through a membrane filter. After filtration and evaporation in vacuo, the thus-obtained residue was purified by column chromatography on silica gel (petroleum ether) to afford **90** as a colorless oil (26.9 mg, 82% yield, 90% e.e.).

(*R,E*)-(2-(2,2-Dibromo-1-vinylcyclopropyl)vinyl)benzene (**90**)



$[\alpha]_D^{27} = -34$ (c 0.5, CHCl_3).

HPLC analysis: Chiralcel OJ3 (*n*-hexane/*i*-PrOH = 99/1, flow rate 0.5 mL/min, $\lambda = 254$ nm), t_R (major) = 19.56 min, t_R (minor) = 22.40 min.

^1H NMR (400 MHz, CDCl_3) δ 7.43 – 7.37 (m, 2H), 7.35 – 7.30 (m, 2H), 7.27 – 7.24 (m, 1H), 6.51 (d, $J = 15.9$ Hz, 1H), 6.39 (d, $J = 15.9$ Hz, 1H), 6.10 (dd, $J = 17.1, 10.3$ Hz, 1H), 5.40 (dd, $J = 10.3, 1.0$ Hz, 1H), 5.26 (dd, $J = 17.1, 1.0$ Hz, 1H), 2.09 (q, $J = 7.7$ Hz, 2H).

^{13}C NMR (100 MHz, CDCl_3) δ 138.0, 136.7, 133.8, 129.5, 128.8, 128.0, 126.5, 118.9, 38.3, 36.5, 33.7.

HRMS (ESI) m/z calcd. for $C_{13}H_{13}Br_2$ $[M + H]^+$ 326.9378, found 326.9380.

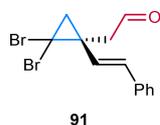
Synthesis of **91** and **92**



Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with 5,5'-bis(trifluoromethyl)-2,2'-bipyridine (11.7 mg, 0.040 mmol, 0.20 equiv.), tris(acetonitrile) (η^5 -cyclopentadienyl)ruthenium hexafluorophosphate (18.4 mg, 0.040 mmol, 0.20 equiv.), a mixture of water and *N*-methyl-2-pyrrolidinone (20% v/v, 1.0 mL), and **88** (65.2 mg, 0.20 mmol, 1.0 equiv., 91% e.e.). The mixture was stirred at $40\text{ }^\circ\text{C}$ for 48 h. Upon completion of the reaction, the reaction mixture was poured into water and extracted with CH_2Cl_2 . The combined organic layers were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The thus-obtained crude product was purified by column chromatography on silica gel (petroleum ether/EtOAc = 20/1) to yield the product **91** as a colorless oil (48.8 mg, 71% yield). The e.e. value of **91** was determined by converting it to the corresponding alcohol **92**.

To a vial equipped with a magnetic stirring bar was added aldehyde **91** (34.4 mg, 0.10 mmol, 1.0 equiv.) in MeOH (1.0 mL) at r.t. Then $NaBH_4$ (7.6 mg, 0.20 mmol, 2.0 equiv.) was added and the reaction was stirred under the same conditions. Upon completion as monitored by TLC, the reaction was quenched by the addition of water and extracted with CH_2Cl_2 . The combined organic layers were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The thus-obtained crude product was purified by column chromatography on silica gel (petroleum ether/ EtOAc = 5/1) to yield the product **92** as a colorless oil (32.9 mg, 95% yield, 90% e.e.).

(*S,E*)-2-(2,2-Dibromo-1-styrylcyclopropyl)acetaldehyde (**91**)



$[\alpha]_D^{27} = +28$ (c 0.5, $CHCl_3$).

1H NMR (400 MHz, $CDCl_3$) δ 9.84 (s, 1H), 7.38 – 7.24 (m, 5H), 6.48 (d, $J = 16.0$ Hz, 1H), 6.32 (d, $J = 16.0$ Hz, 1H), 3.09 (d, $J = 17.9$ Hz, 1H), 2.96 (d, $J = 17.8$ Hz, 1H), 2.11 (d, $J = 8.0$ Hz, 1H), 1.89 (d, $J = 8.0$ Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 199.5, 136.2, 133.7, 129.6, 128.8, 128.3, 126.5, 50.2, 35.0, 34.0, 31.7.

HRMS (ESI) m/z calcd. for $C_{13}H_{13}OBr_2$ $[M + H]^+$ 342.9328, found 342.9323.

(*S,E*)-2-(2,2-Dibromo-1-styrylcyclopropyl)ethan-1-ol (**92**)



92

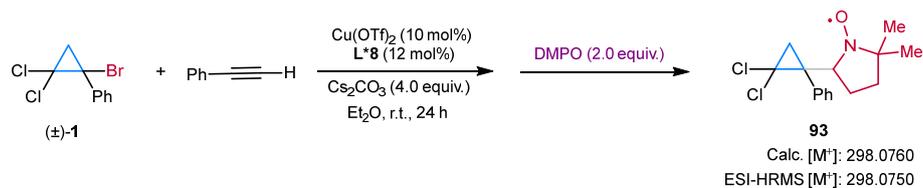
$[\alpha]_D^{27} = +12$ (c 0.5, CHCl_3).

HPLC analysis: Chiralcel ODH (*n*-hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, $\lambda = 254$ nm), t_R (minor) = 15.50 min, t_R (major) = 23.01 min.

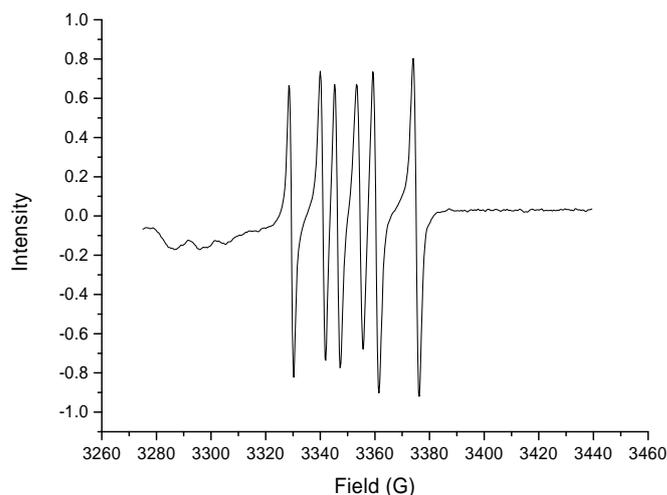
^1H NMR (400 MHz, CDCl_3) δ 7.44 – 7.36 (m, 2H), 7.36 – 7.29 (m, 2H), 7.28 – 7.24 (m, 1H), 6.48 (d, $J = 15.9$ Hz, 1H), 6.32 (d, $J = 15.9$ Hz, 1H), 3.96 – 3.72 (m, 2H), 2.27 (dt, $J = 13.4, 6.5$ Hz, 1H), 2.04 (dt, $J = 13.4, 6.5$ Hz, 1H) 2.00 (d, $J = 7.5$ Hz, 1H), 1.77 (d, $J = 7.7$ Hz, 1H).

^{13}C NMR (100 MHz, CDCl_3) δ 136.4, 133.6, 129.7, 128.8, 128.1, 126.5, 60.9, 39.9, 37.0, 34.2, 33.1.

HRMS (ESI) m/z calcd. for $\text{C}_{13}\text{H}_{15}\text{OBr}_2$ $[\text{M} + \text{H}]^+$ 344.9484, found 344.9473.

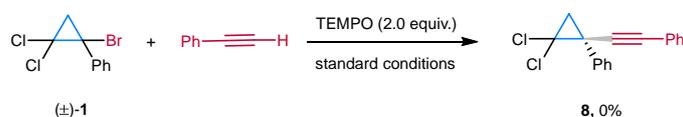


An oven-dried resealable Schlenk tube equipped with a magnetic stirring bar was charged with Cu(OTf)₂ (3.6 mg, 0.010 mmol, 10 mol%), chiral ligand L*8 (6.4 mg, 0.012 mmol, 12 mol%), and Cs₂CO₃ (128.0 mg, 0.40 mmol, 4.0 equiv.). The tube was evacuated and backfilled with argon three times. Then racemic **1** (39.9 mg, 0.15 mmol, 1.5 equiv.), phenylacetylene (11.0 μL, 0.10 mmol, 1.0 equiv.), and Et₂O (1.0 mL) were sequentially added into the mixture under argon. The tube was sealed and the reaction mixture was allowed to stir at r.t. for 24 h. Next, 5,5-dimethyl-1-pyrroline *N*-oxide (DMPO) (22.6 mg, 0.20 mmol, 2.0 equiv.) was added and the reaction mixture was stirred at r.t. for another 1 h. The resulting reaction mixture was analyzed by EPR. The EPR results revealed the likely formation of persistent radical **93**, a DMPO-trapped cyclopropyl radical, in the reaction, which was further supported by the ESI-HRMS results. Therefore, we concluded the formation of cyclopropyl radicals in this reaction.



Supplementary Fig. 7' | Room Temperature Q-band CW-EPR spectrum of the spin trap study. $g = 2.0071$; $A_H = 18.90$ G; $A_N = 13.37$ G. EPR acquisition parameters: temperature = 298 K; MW power = 40 dB; modulation amplitude = 1 G; conversion time = 20 ms.

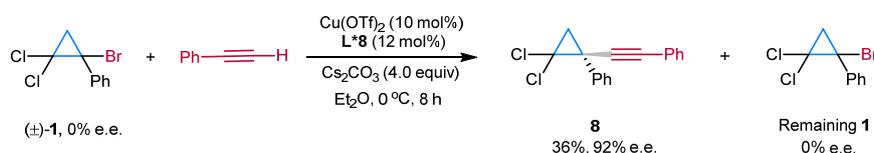
Radical inhibition experiment with TEMPO



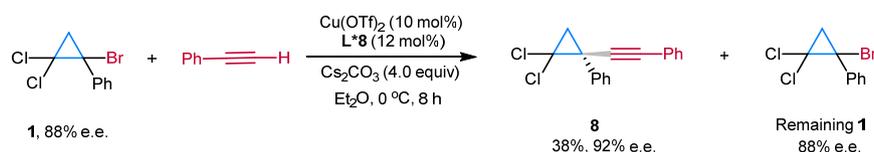
An oven-dried resealable Schlenk tube equipped with a magnetic stirring bar was charged with Cu(OTf)₂ (3.6 mg, 0.010 mmol, 10 mol%), chiral ligand L*8 (6.4 mg,

0.012 mmol, 12 mol%), and Cs₂CO₃ (128.0 mg, 0.40 mmol, 4.0 equiv.). The tube was evacuated and backfilled with argon three times. Then racemic **1** (39.9 mg, 0.15 mmol, 1.5 equiv.), phenylacetylene (11.0 μL, 0.1 mmol, 1.0 equiv.), TEMPO (31.3 mg, 0.20 mmol, 2.0 equiv.) and Et₂O (1.0 mL) were sequentially added into the mixture under argon. The tube was sealed and the reaction mixture was allowed to stir at 0 °C for 6 d. The reaction mixture was filtered and washed by EtOAc. After evaporation under reduced pressure, the residue was analyzed by ¹H NMR spectroscopy using 1,3,5-trimethylbenzene as an internal standard.

Control experiments with racemic and scalemic cyclopropyl bromide **1**

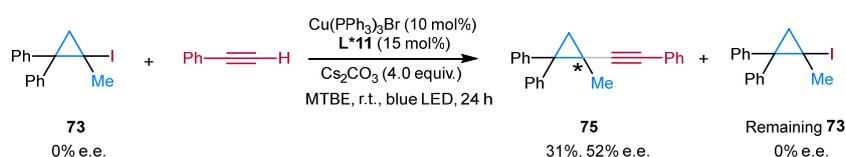


According to **General procedure A** with racemic (1-bromo-2,2-dichlorocyclopropyl)benzene **1** (13.3 mg, 0.050 mmol, 1.0 equiv.) and ethynylbenzene (5.5 μL, 0.05 mmol, 1.0 equiv.) at 0 °C for 8 h, the reaction mixture was filtered and washed by EtOAc. After evaporation, the thus-obtained residue was analyzed by ¹H NMR spectroscopy using 1,3,5-trimethylbenzene as an internal standard. The product was then separated by preparative TLC. The e.e. values of **8** and the remaining **1** were determined by chiral HPLC analysis.

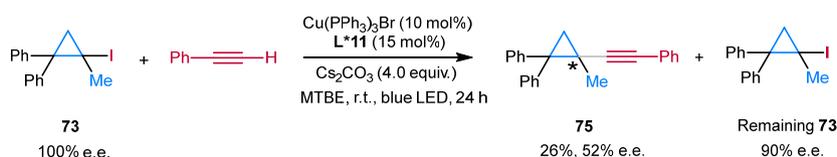


The procedure for the reaction with scalemic (1-bromo-2,2-dichlorocyclopropyl)benzene **1** was the same with that described above except that enantioenriched **1** (13.3 mg, 0.050 mmol, 1.0 equiv., 88% e.e.) was used instead of racemic **1**.

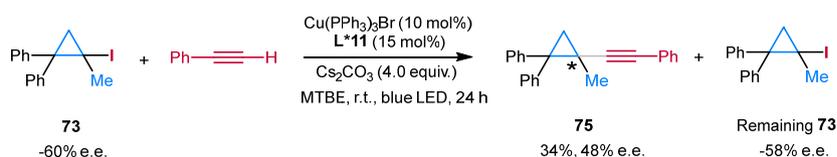
Control experiments with racemic and scalemic 1-alkyl-substituted cyclopropyl iodine **73**



According to **General procedure E** with racemic (2-iodo-2-methylcyclopropane-1,1-diyl)dibenzene **73** (25.1 mg, 0.075 mmol, 1.5 equiv.) and ethynylbenzene (5.5 μ L, 0.05 mmol, 1.0 equiv.) at r.t. for 24 h, the reaction mixture was filtered and washed by EtOAc. After evaporation, the thus-obtained residue was analyzed by ^1H NMR spectroscopy using 1,3,5-trimethylbenzene as an internal standard. The product was then separated by preparative TLC. The e.e. values of **75** and remaining **73** were determined by chiral HPLC analysis.

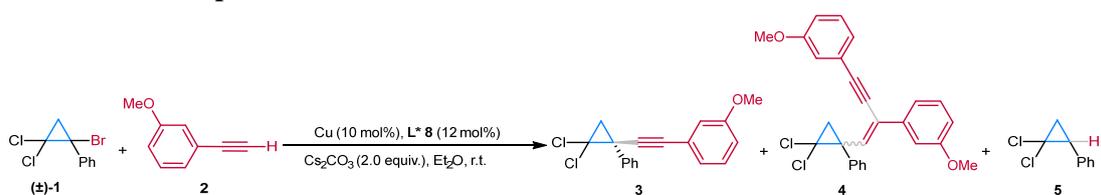


The procedure for the reaction with scalemic (2-iodo-2-methylcyclopropane-1,1-diyl)dibenzene **73** was the same with that described above except that enantioenriched **73** (25.1 mg, 0.075 mmol, 1.5 equiv., 100% e.e.) was used instead of racemic **73**.



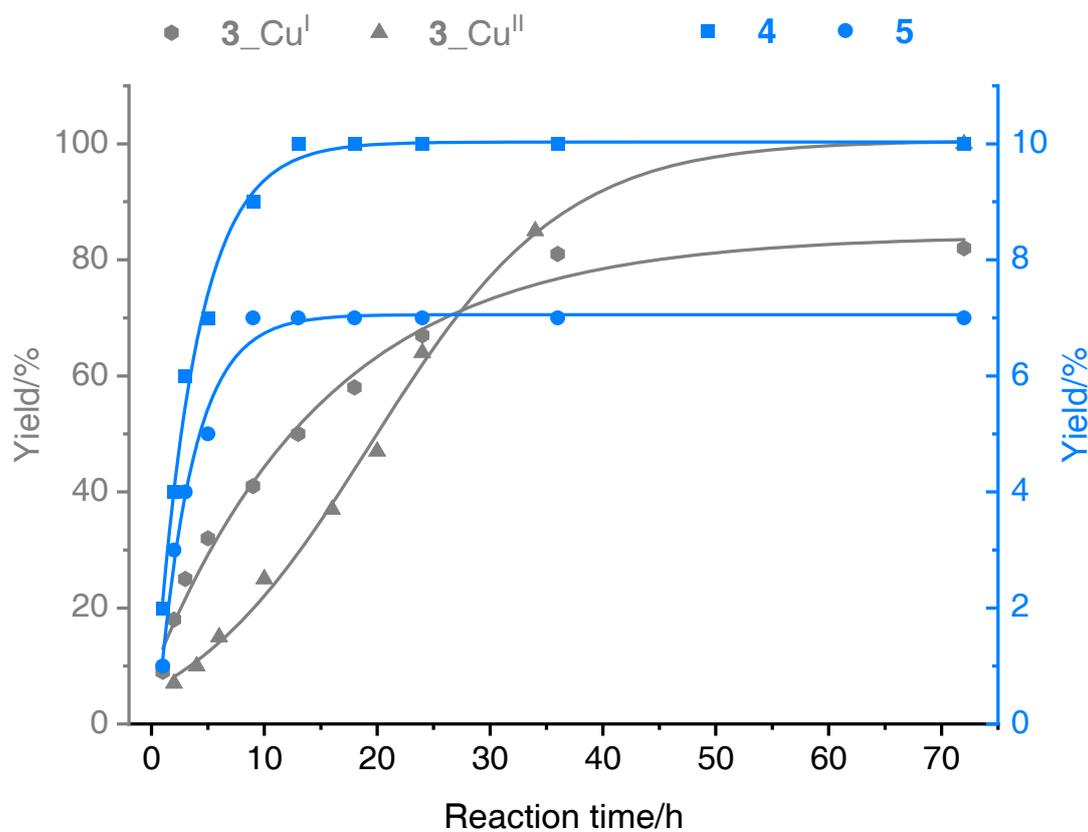
The procedure for the reaction with scalemic (2-iodo-2-methylcyclopropane-1,1-diyl)dibenzene **73** was the same with that described above except that enantioenriched **73** (25.1 mg, 0.075 mmol, 1.5 equiv., -60% e.e.) was used instead of racemic **73**.

Time-course experiment



The time-course experiment sample were prepared following the general procedure: an oven-dried resealable Schlenk tube equipped with a magnetic stirring bar was charged with $\text{CuOTf}\cdot\text{1/2Ph}$ (2.51 mg, 0.010 mmol, 10 mol%) or $\text{Cu}(\text{OTf})_2$ (3.61 mg, 0.010 mmol, 10 mol%), chiral ligand $\text{L}^*\mathbf{8}$ (6.40 mg, 0.012 mmol, 12 mol%), and Cs_2CO_3 (65.2 mg, 0.20 mmol, 2.0 equiv.). The tube was evacuated and backfilled with argon three times. Then (1-bromo-2,2-dichlorocyclopropyl)benzene **1** (26.6 mg, 0.10 mmol, 1.0 equiv.), 1-ethynyl-3-methoxybenzene (19.2 μ L, 0.15 mmol, 1.5 equiv.), and Et_2O (1.0 mL) were sequentially added into the mixture under argon. The tube was sealed and the reaction mixture was stirred at r.t. for appropriate time. Upon completion, the precipitate was then filtered through a pad of celite and rinsed with EtOAc. The filtrate was evaporated and the residue was analyzed by ^1H NMR spectroscopy using

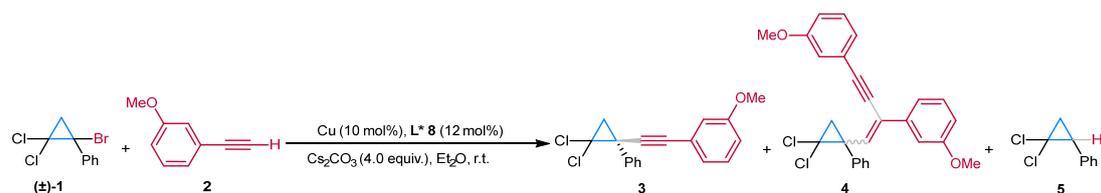
1,3,5-trimethoxybenzene as an internal standard.



Supplementary Fig. 10' | Time-course experiment results using Cu(OTf)₂ and CuOTf catalyst precursors. The formation of side products was monitored when CuOTf was employed, as it was substantially suppressed when Cu(OTf)₂ was used. Solid lines for compounds **4** and **5** represent exponential decay fits to the experimental data. The solid line for compound **3** with CuOTf as the precatalyst is a dose-response fit, while the solid line for compound **3** with Cu(OTf)₂ is a Boltzmann fit to the experimental data.

EPR experiments for the Cu(II) concentration during reaction

Sample Prepare

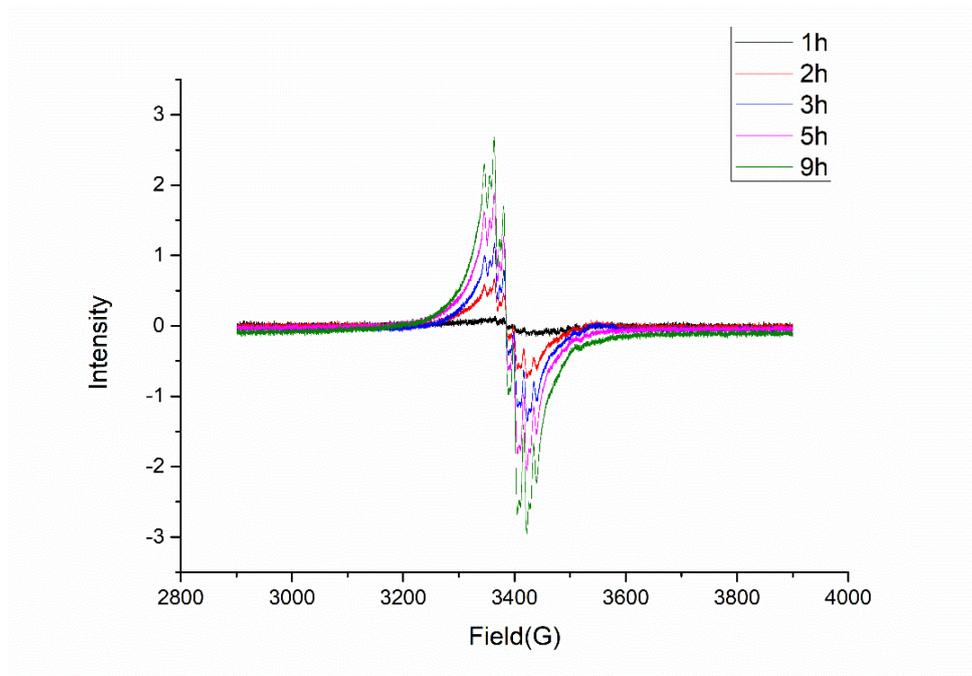


The EPR sample were prepared following the general procedure: an oven-dried resealable Schlenk tube equipped with a magnetic stirring bar was charged with CuOTf·1/2Ph (7.53 mg, 0.030 mmol, 10 mol%) or Cu(OTf)₂ (10.83 mg, 0.030 mmol, 10 mol%), chiral ligand L*8 (19.20 mg, 0.036 mmol, 12 mol%), and Cs₂CO₃ (391.2

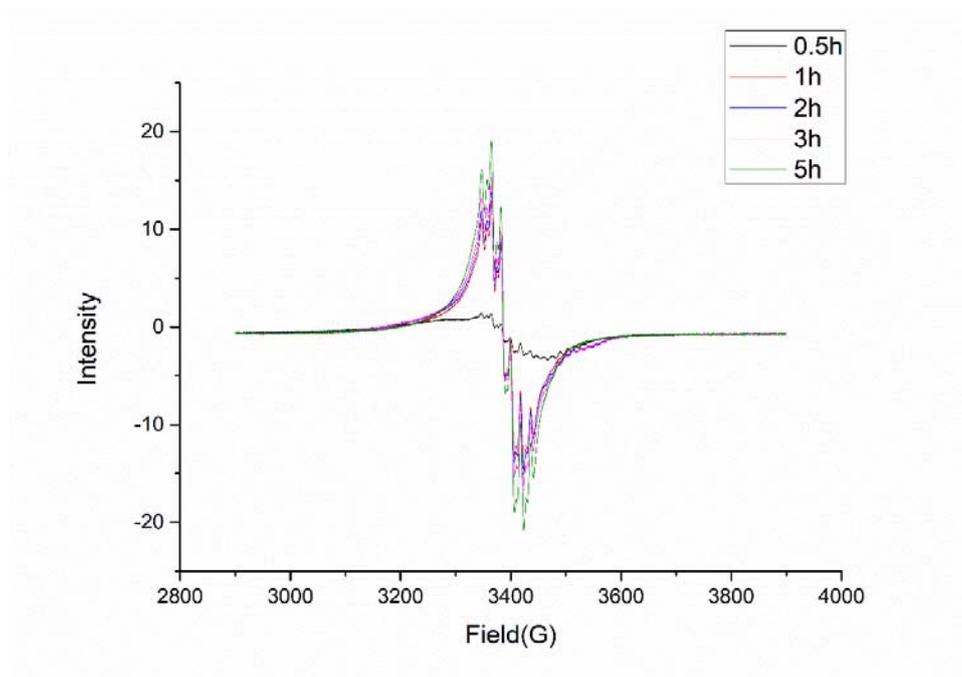
mg, 1.20 mmol, 4.0 equiv.). The tube was evacuated and backfilled with argon three times. Then (1-bromo-2,2-dichlorocyclopropyl)benzene **1** (119.7 mg, 0.45 mmol, 1.5 equiv.), 1-ethynyl-3-methoxybenzene (38.4 μ L, 0.30 mmol, 1.0 equiv.), and Et₂O (3.0 mL) were sequentially added into the mixture under argon. The tube was sealed and the reaction mixture was stirred at r.t.. Samples were transferred into quartz tubes in glovebox and sealed for EPR test.

X-Band EPR Details

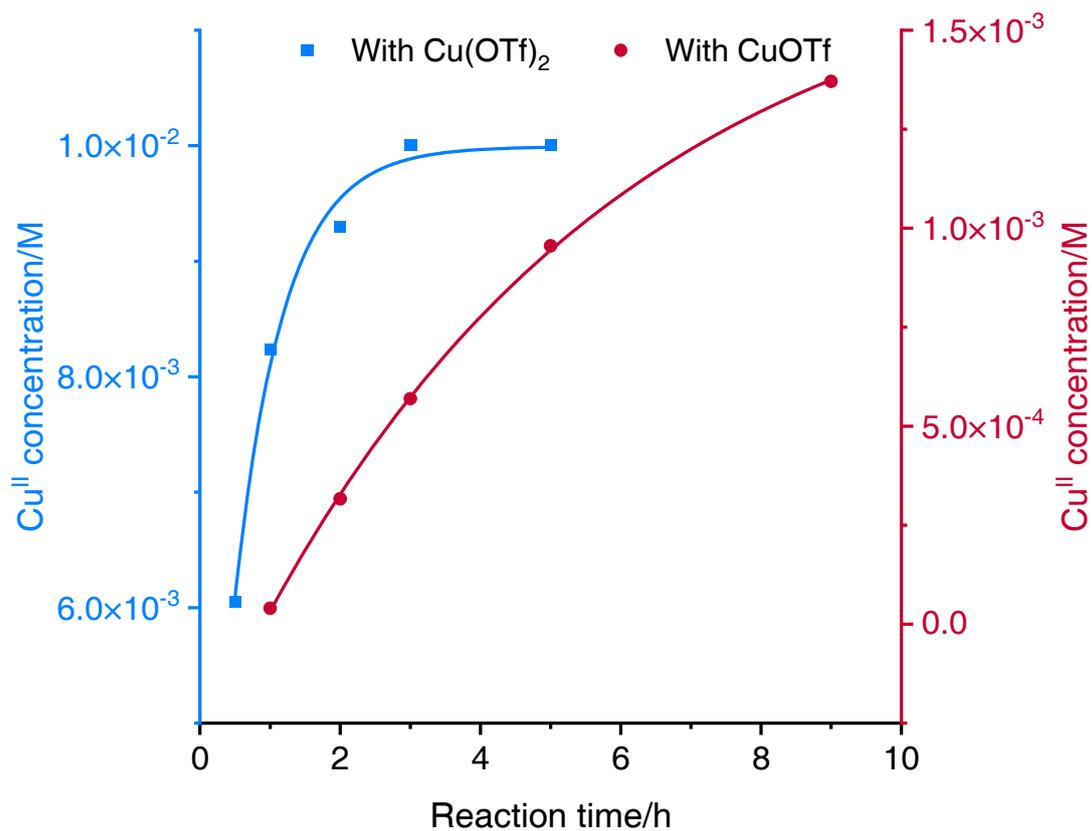
EPR measurements were performed in 4mm quartz tubes. All spectra were baseline-corrected. EPR spectra were recorded on a Bruker EMXPlus-10/12 EPR X-band spectrometer at room temperature.



Supplementary Fig. 11' | Time-course X-band EPR spectra of the reaction mixtures with CuOTf-1/2Ph as the catalyst precursor. EPR acquisition parameters: solvent = toluene; temperature = 298 K; frequency = 9.838739 GHz; MW power = 20 dB; modulation amplitude = 1 G; conversion time = 12 ms.



Supplementary Fig. 12' | Time-course X-band EPR spectra of the reaction mixtures with $\text{Cu}(\text{OTf})_2$ as the catalyst precursor. EPR acquisition parameters: solvent = toluene; temperature = 298 K; frequency = 9.837637 GHz; MW power = 20 dB; modulation amplitude = 1 G; conversion time = 12 ms.



Supplementary Fig. 13 | Calculated Cu^{II} concentrations based on EPR spectroscopy. Spin quantification was conducted using an internal standard of Cu(edta)₂ with a known concentration, employing the Bruker Xenon software. Following region definition and double integration, the Cu^{II} concentrations of the respective samples were plotted against time. The solid lines represent exponential decay fits to the experimental data.

Computational studies

1. Computational Details

All density functional theory (DFT) calculation results are obtained with Gaussian 16 program⁸. Default G16 SCF convergence criteria, optimization convergence criteria and integral grid parameters for Gaussian 16 are applied unless otherwise stated. (5d,7f) keyword in Gaussian 16 was used.

Geometry optimizations are conducted with B3LYP functional⁹⁻¹⁰, employing the D3 version of Grimme's dispersion corrections¹¹ with Becke-Johnson damping¹². LANL2DZ basis set¹³⁻¹⁸ is used for copper and 6-31G(d) basis set is used for all other light elements (C, H, N, O, Cl).

Single-point energies and solvent effects at diethyl ether are also evaluated with B3LYP functional with Grimme's dispersion corrections and Becke-Johnson damping. SDD basis set^{13,17-20} is used for copper and 6-311+G(d,p) basis set is used for all other light elements (C, H, N, O, Cl). The solvation energies are calculated with a self-consistent reaction field (SCRF) using the SMD implicit solvent model²¹.

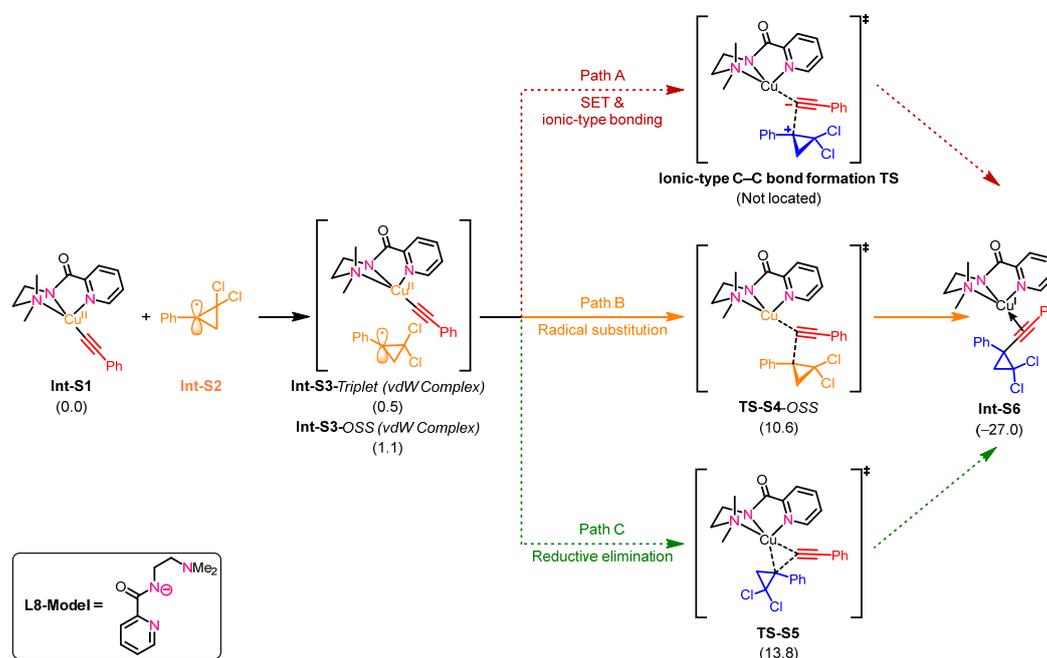
Frequency analysis is also performed at the same level of theory as geometry optimization using harmonic oscillator model to confirm whether optimized stationary points are either local minimum or transition state, as well as to evaluate zero-point vibrational energies and thermal corrections for enthalpies and free energies at 298.15 K. Mulliken spin population analysis is obtained at the same level of theory as geometry optimization.

In addition, geometry optimization, frequency analysis and single point energy of open-shell transition states and local minimums are calculated with unrestricted open-shell DFT methods, while same computations for closed-shell structures were performed with restricted closed-shell DFT methods. Wavefunction stability test at the same level of theory as geometry optimizations is employed to ensure that the SCF converged wavefunction was stable.

To correct the Gibbs free energies under 1 atm to the standard state in solution (1 mol/L), a correction of $RT\ln(c_s/c_g)$ is added to energies of all species. c_s stands for the standard molar concentration in solution (1 mol/L), c_g stands for the standard molar concentration in gas phase (about 0.040876 mol/L), and R is the gas constant. For calculated intermediates at the standard state of 1 mol/L at 298.15 K, the correction value equaling to 1.89 kcal/mol is used.

The 3D diagrams of optimized structures shown in this supplementary information for computations are generated with CYLview software ²².

2. Discussion on the Cu-Mediated C–C Bonding Mechanism of Cyclopropyl Radicals and Alkynyl Nucleophiles



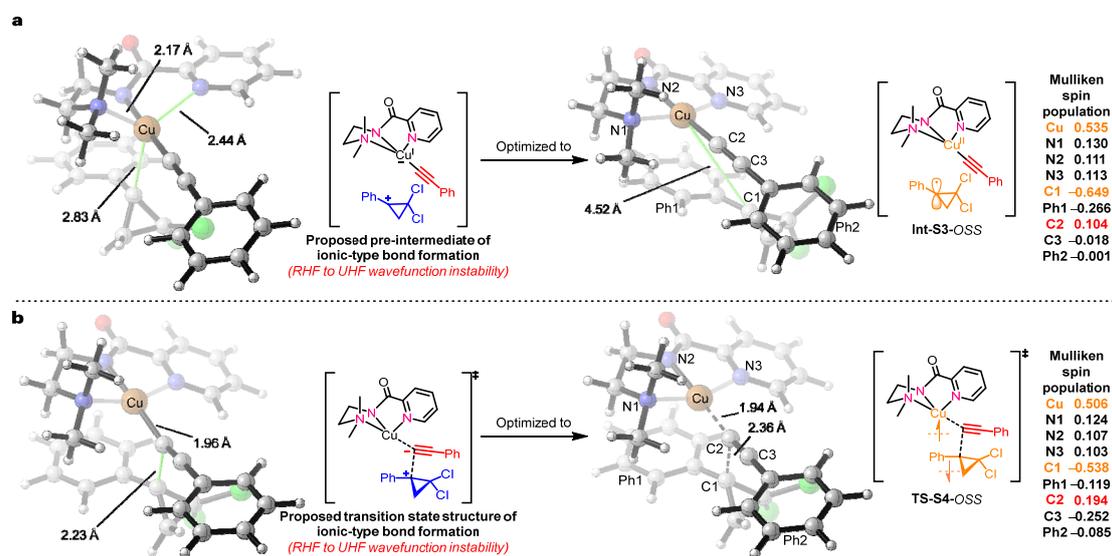
Supplementary Fig. 14 | DFT exploration on the C–C bond formation mechanism of (L8-Model)Cu(II)(alkynyl) species Int-S1 and cyclopropyl radical Int-S2. Free energies in kcal/mol shown in parentheses are compared to the sum of Int-S1 and Int-S2.

DFT calculations in model systems are performed to study the Cu-mediated C–C bond formation pathway for cyclopropyl radicals and alkynyl nucleophiles. Simplified N,N,N-ligand based on **L*8** is used for calculations in this section.

The proposed C–C bond formation pathways between (**L8-Model**)Cu(II)(alkynyl) species **Int-S1** and tertiary cyclopropyl radical **Int-S2** include three major possibilities: sequential SET (single-electron transfer) and ionic-type C–C bond formation (Path A in **Supplementary Fig. 14**), outer-sphere radical-substitution-type C–C bond formation via **TS-S4-OSS** (Path B in **Supplementary Fig. 14**), and reductive elimination via **TS-S5** (Path C in **Supplementary Fig. 14**).

For Path A (SET and ionic-type C–C bonding), despite our considerable efforts, the ionic-type C–C bond formation transition state could not be identified. Furthermore, we conducted a detailed examination of the pre-intermediates of this transition state and found them to exhibit an RHF (restricted Hartree–Fock) to UHF (unrestricted Hartree–Fock) wavefunction instability. Upon employing stable wavefunctions and subsequent geometry structure optimization, we obtained a radical substitution-type

transition state pre-intermediate, **Int-S3-OSS**. Mulliken spin population analysis indicated that **Int-S3-OSS** is an open-shell singlet (**Supplementary Fig. 15a**). Similarly, the proposed transition state structure also demonstrated an RHF to UHF wavefunction instability, and further optimization yielded an open-shell singlet radical substitution-type transition state **TS-S4-OSS**. (**Supplementary Fig. 15b**) Therefore, the ionic-type C–C bond formation reaction pathway is likely not operative.

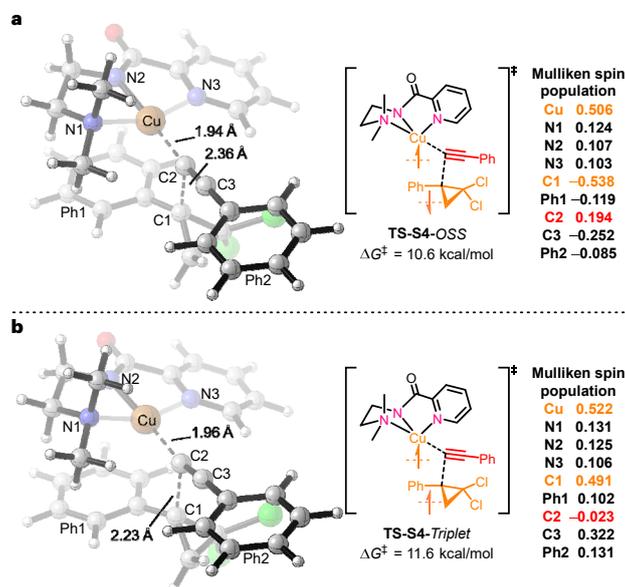


Supplementary Fig. 15 | Detailed investigations on the sequential SET and ionic-type C–C bond formation pathway. a, The proposed pre-intermediate structure. **b**, The proposed transition state structure. These structures have an RHF to UHF wavefunction instability, and further optimizations using UHF wavefunctions lead to a radical substitution pathway.

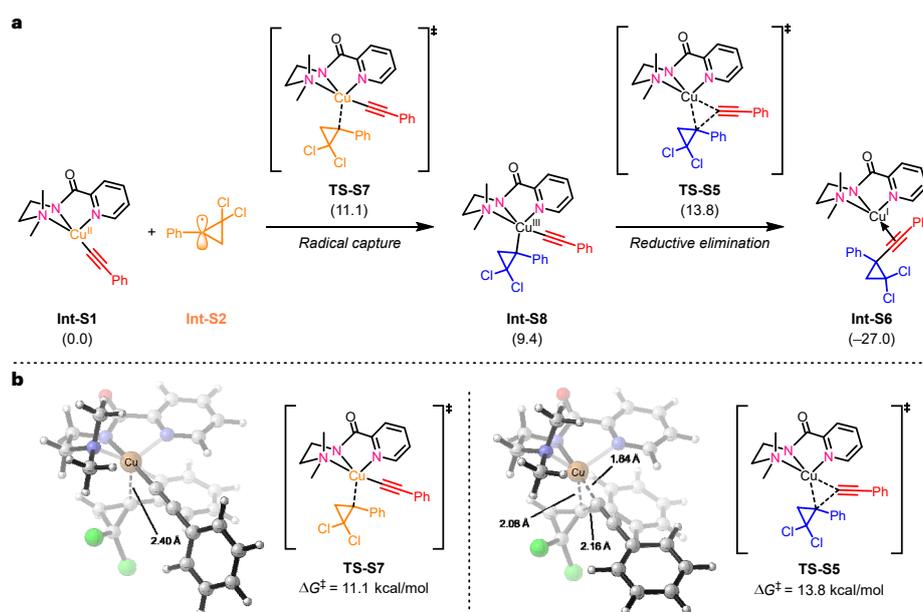
For Path B (radical substitution), both the open-shell singlet transition state **TS-S4-OSS** (**Supplementary Fig. 16a**) and the triplet transition state **TS-S4-Triplet** (**Supplementary Fig. 16b**) were located. Mulliken spin population analysis confirmed their respective open-shell singlet and triplet nature. The free energy barrier of radical substitution via **TS-S4-OSS** is favored by 1.0 kcal/mol compared to **TS-S4-Triplet**. The overall free energy barrier of C–C via the radical substitution pathway is 10.6 kcal/mol.

For Path (C–C reductive elimination), the pathway involves the radical capture via **TS-S7** to form a Cu(III) intermediate **Int-S8** and the following reductive elimination of **Int-S8** via **TS-S5**, presenting an overall free energy barrier of 13.8 kcal/mol (**Supplementary Fig. 17**). Compared to the radical substitution process, this pathway exhibits a higher energy barrier (10.6 kcal/mol via **TS-S4** vs 13.8 kcal/mol via **TS-S5**). Thus, the C–C reductive elimination pathway is not favored.

To sum up, the calculation results mentioned above support a radical substitution pathway with an open-shell singlet transition state **TS-S4-OSS**, resulting in a free energy barrier of 10.6 kcal/mol for the Cu-mediated C–C bond formation between tertiary cyclopropyl radical **Int-S2** and the phenylacetylene nucleophile.



Supplementary Fig. 16 | Details of the located transition states in the radical substitution pathway. a, Located open-shell singlet radical substitution transition state. b, Located triplet radical substitution transition state. Free energy barriers in kcal/mol are compared to the sum of **Int-S1 and **Int-S2**.**



Supplementary Fig. 17 | Detailed investigations on the sequential radical capture and reductive elimination pathway. **a**, Located C–C reductive elimination pathway. **b**, Key radical capture and reductive elimination transition states. Free energies in kcal/mol shown in parentheses are compared to the sum of **Int-S1** and **Int-S2**.

3. Table of Energies

Supplementary Table 13 | Energies in **Supplementary Figs. 14, 15, 16, and 17**. Zero-point correction (*ZPE*), thermal correction to enthalpy (*TCH*), thermal correction to Gibbs free energy (*TCG*), energies (*E*), enthalpies (*H*), and Gibbs free energies (*G*) (in Hartree) of the structures calculated at B3LYP-D3(BJ)/6-311+G(d,p)-SDD-SMD(Ether)//B3LYP-D3(BJ)/6-31G(d)-LANL2DZ level of theory.

Structure	<i>ZPE</i>	<i>TCH</i>	<i>TCG</i>	<i>E</i>	<i>H</i>	<i>G</i>	Imaginary Frequency
Int-S1	0.339674	0.362490	0.284300	-1134.555782	-1134.193292	-1134.271482	
Int-S2	0.130367	0.141298	0.092211	-1267.675745	-1267.534447	-1267.583534	
Int-S3-OSS	0.471441	0.506022	0.401859	-2402.252078	-2401.746056	-2401.850219	
Int-S3-Triplet	0.471447	0.506026	0.400844	-2402.252096	-2401.746070	-2401.851252	
TS-S4-OSS	0.471630	0.505136	0.405097	-2402.240211	-2401.735075	-2401.835114	247.9i
TS-S4-Triplet	0.471367	0.504911	0.403442	-2402.236924	-2401.732013	-2401.833482	275.1i
TS-S5	0.472434	0.505608	0.406174	-2402.236131	-2401.730523	-2401.829957	178.5i
Int-S6	0.472862	0.507061	0.403664	-2402.298748	-2401.791687	-2401.895084	
TS-S7	0.471717	0.505267	0.404748	-2402.239124	-2401.733857	-2401.834376	102.6i
Int-S8	0.473359	0.507056	0.406563	-2402.243643	-2401.736587	-2401.837080	

4. Cartesian Coordinates of Computed Species

Int-S1

Charge = 0, Multiplicity = 2

Cu	-0.79033000	-0.47292100	-0.06526300
N	-2.69143000	-0.74044500	0.01052300
C	-2.75445100	1.61823500	0.00025800
C	-3.52096100	0.31266000	0.07406900
O	-4.75241300	0.31169700	0.18030800
C	-3.39475800	2.85272800	0.01647200
C	-0.65585000	2.62210700	-0.12272300
C	-2.61557000	4.00757900	-0.04407100
H	-4.47693700	2.86853600	0.07773600
C	-1.22534100	3.89441700	-0.11440600
H	0.41538400	2.45071300	-0.16969500
H	-3.08510700	4.98706300	-0.03467700
C	-3.21162800	-2.08575000	0.09999600
C	-2.15198400	-3.00839900	-0.50265800
H	-3.42778000	-2.36237700	1.14381800
H	-2.15450400	-2.88641200	-1.59007300
N	-0.79257100	-2.62618700	-0.03913700
C	0.25518300	-3.21096200	-0.89002200
H	0.08850400	-2.90832900	-1.92657700
H	1.22485200	-2.82605300	-0.57096700
H	0.24431100	-4.30997300	-0.82813100
C	-0.56239800	-2.98321600	1.37156200
H	-0.59849300	-4.07445600	1.51181400
H	0.41936300	-2.60917500	1.67026900
H	-1.32342000	-2.51798300	2.00160800
N	-1.41428400	1.52254600	-0.06825500
C	1.12140400	-0.20585700	-0.05175500
C	2.33330700	-0.01787300	-0.02388800
C	3.74407000	0.19535200	0.00988900
C	4.41290000	0.40420800	1.23252700
C	4.50165700	0.20176000	-1.17830800
C	5.78945400	0.61118100	1.26236800

H	3.83564700	0.40123200	2.15199400
C	5.87785500	0.41000200	-1.14162100
H	3.99312100	0.04220300	-2.12411700
C	6.52877600	0.61538500	0.07716800
H	6.28810700	0.77039000	2.21474700
H	6.44562000	0.41203600	-2.06826400
H	7.60264900	0.77737500	0.10310400
H	-0.58961100	4.77220700	-0.16042500
H	-2.34855800	-4.06754200	-0.27525000
H	-4.15626900	-2.19104400	-0.44780000

Int-S2

Charge = 0, Multiplicity = 2

C	1.27751400	1.74849300	0.00097300
C	0.26537700	0.68298900	-0.00032600
C	1.63351800	0.26680700	0.00011900
H	1.47540100	2.31054900	-0.91454600
H	1.47441800	2.30911600	0.91758500
C	-1.07552400	0.28906700	-0.00030300
C	-1.41700200	-1.09181000	-0.00105100
C	-2.12147300	1.25136100	0.00041700
C	-2.74666000	-1.48171300	-0.00106000
H	-0.61945200	-1.82797600	-0.00159100
C	-3.44627700	0.84426100	0.00039700
H	-1.86332000	2.30600200	0.00098900
C	-3.76764000	-0.52051400	-0.00034400
H	-2.99829700	-2.53826300	-0.00161900
H	-4.23907900	1.58674000	0.00095900
H	-4.80751300	-0.83307400	-0.00036600
Cl	2.35294300	-0.44753500	-1.48425800
Cl	2.35098900	-0.44933200	1.48459000

Int-S3-OSS

Charge = 0, Multiplicity = 1

Cu	-1.67968300	1.02081800	-0.40519200
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N	-3.49129200	0.36670800	-0.37009300
C	-2.50708000	-1.56390900	-1.29984400
C	-3.74900600	-0.89284400	-0.75108900
O	-4.82134200	-1.50747600	-0.69063800
C	-2.52389100	-2.86981300	-1.77794900
C	-0.22968200	-1.35429100	-1.73310600
C	-1.33314000	-3.42263500	-2.24801100
H	-3.46366800	-3.40989400	-1.76039200
C	-0.16555500	-2.65777000	-2.22293100
H	0.63852600	-0.70798500	-1.66974000
H	-1.31231900	-4.44136800	-2.62470900
C	-4.53758500	1.19264800	0.18617000
C	-3.86795900	2.20748900	1.11554000
H	-5.10270900	1.70544300	-0.60760900
H	-3.58214200	1.70431000	2.04297900
N	-2.61340400	2.73085800	0.51704500
C	-1.76353400	3.38325700	1.52254500
H	-1.55603700	2.67876100	2.33142100
H	-0.81618800	3.65992200	1.05734300
H	-2.25565000	4.27522000	1.93994100
C	-2.87414900	3.64919900	-0.60548700
H	-3.40960000	4.54785000	-0.26248600
H	-1.91926400	3.94067700	-1.04868700
H	-3.47439400	3.14413000	-1.36499200
N	-1.37820600	-0.83380700	-1.29195000
C	0.12056500	1.71587200	-0.52445100
C	1.29360500	2.07067300	-0.57947600
C	2.66842800	2.44603600	-0.62298700
C	3.18955100	3.39545500	0.27924100
C	3.55069000	1.84102300	-1.54210500
C	4.54281000	3.72266800	0.26377800
H	2.51785400	3.86382900	0.99226000
C	4.90336200	2.17091300	-1.55056500
H	3.16064400	1.10101600	-2.23283000
C	5.40636800	3.11200100	-0.64903900
H	4.92666700	4.45523500	0.96866400
H	5.56837200	1.68752200	-2.26072100

H	6.46242800	3.36584100	-0.65620300
H	0.78437200	-3.05672900	-2.56002200
H	-4.54375200	3.03786800	1.37314600
H	-5.26680600	0.59489900	0.74714500
C	3.15308700	-0.49299500	1.34469300
C	1.88786700	-1.22665700	1.20621500
C	3.06108300	-1.86406700	0.69292300
H	3.36274000	0.35764500	0.69592800
H	3.63359700	-0.43827800	2.32450900
C	0.54190300	-1.38198800	1.55014600
C	-0.14230300	-2.59332600	1.25966200
C	-0.17432100	-0.32836400	2.17951100
C	-1.48620500	-2.73191300	1.57145700
H	0.40342000	-3.40069700	0.78342300
C	-1.51491600	-0.48948500	2.49378300
H	0.34171900	0.60355200	2.38201500
C	-2.18306700	-1.68316700	2.18551600
H	-2.00395700	-3.65484000	1.33062800
H	-2.05387000	0.31677700	2.98209000
H	-3.24042100	-1.78952100	2.40513300
Cl	3.31931600	-1.98228700	-1.09181500
Cl	3.75484500	-3.29156400	1.53402700

Int-S3-Triplet

Charge = 0, Multiplicity = 3

Cu	-1.68148900	1.01906400	-0.40550600
N	-3.49186900	0.36168000	-0.36944200
C	-2.50451800	-1.56758600	-1.29868600
C	-3.74745300	-0.89849300	-0.74985300
O	-4.81868200	-1.51497400	-0.68873300
C	-2.51917700	-2.87375200	-1.77614400
C	-0.22761100	-1.35421200	-1.73260400
C	-1.32758900	-3.42471800	-2.24627100
H	-3.45799200	-3.41548600	-1.75801800
C	-0.16133800	-2.65780300	-2.22186000
H	0.63953200	-0.70642900	-1.66958100

H	-1.30509000	-4.44359300	-2.62248500
C	-4.53957600	1.18581400	0.18688800
C	-3.87150300	2.20322500	1.11455500
H	-5.10660300	1.69638900	-0.60695900
H	-3.58402100	1.70182400	2.04246900
N	-2.61857200	2.72863100	0.51454700
C	-1.76961400	3.38456500	1.51849700
H	-1.56011000	2.68188000	2.32842800
H	-0.82312400	3.66256300	1.05233800
H	-2.26345600	4.27613400	1.93470500
C	-2.88210300	3.64455900	-0.60927500
H	-3.41952300	4.54247900	-0.26743100
H	-1.92815400	3.93765600	-1.05343400
H	-3.48150300	3.13687200	-1.36769800
N	-1.37692300	-0.83552100	-1.29144700
C	0.11754800	1.71699000	-0.52595200
C	1.29059400	2.07177700	-0.58094300
C	2.66547600	2.44688600	-0.62382300
C	3.18701800	3.39395000	0.28064200
C	3.54749800	1.84357300	-1.54428500
C	4.54045400	3.72048400	0.26605800
H	2.51550800	3.86096500	0.99472500
C	4.90034300	2.17277600	-1.55187100
H	3.15713600	1.10536500	-2.23675400
C	5.40377300	3.11148100	-0.64809900
H	4.92463700	4.45119600	0.97268900
H	5.56516400	1.69066700	-2.26307300
H	6.45997300	3.36475400	-0.65455600
H	0.78920300	-3.05527200	-2.55896800
H	-4.54898000	3.03240300	1.37164100
H	-5.26691600	0.58699000	0.74916500
C	3.15555500	-0.48862700	1.34386400
C	1.89011200	-1.22191900	1.20507700
C	3.06343200	-1.85998100	0.69277900
H	3.36603600	0.36158700	0.69482400
H	3.63543800	-0.43361300	2.32397300
C	0.54442200	-1.37759300	1.54990600

C	-0.13931400	-2.58961500	1.26104800
C	-0.17207400	-0.32375000	2.17858500
C	-1.48289000	-2.72871100	1.57395100
H	0.40655800	-3.39714600	0.78525700
C	-1.51238300	-0.48534900	2.49391400
H	0.34350900	0.60871300	2.37971900
C	-2.18000600	-1.67974000	2.18738400
H	-2.00025600	-3.65219800	1.33443700
H	-2.05147200	0.32116300	2.98166700
H	-3.23713000	-1.78657000	2.40786500
Cl	3.32267700	-1.97929600	-1.09171600
Cl	3.75622600	-3.28725000	1.53513300

TS-S4-OSS

Charge = 0, Multiplicity = 1

Cu	0.86618400	-0.99897400	-0.57078900
N	2.76755000	-1.29689200	-0.73201100
C	2.72549400	0.84369500	-1.71798700
C	3.54941400	-0.32798800	-1.22415900
O	4.78436500	-0.30055000	-1.30119800
C	3.31595000	1.99586500	-2.22557500
C	0.58815400	1.71862500	-2.01752400
C	2.49184100	3.04559700	-2.63129800
H	4.39802200	2.03588000	-2.27710900
C	1.10607000	2.90706000	-2.52960600
H	-0.47482900	1.55251700	-1.88993300
H	2.92359400	3.96308700	-3.02084900
C	3.35114800	-2.51069700	-0.21299400
C	2.31427900	-3.15256500	0.71127800
H	3.63303800	-3.19694800	-1.02664100
H	2.30282100	-2.61166300	1.66027000
N	0.94397200	-3.03043000	0.14905700
C	-0.07159300	-3.38864500	1.14804200
H	0.06688700	-2.77007300	2.03537000
H	-1.06159300	-3.18680100	0.73664600
H	0.00987400	-4.45059900	1.42720600

C	0.76354000	-3.84090500	-1.06830200
H	0.88340100	-4.91303300	-0.84846600
H	-0.24097100	-3.66497700	-1.46173000
H	1.49478600	-3.54562300	-1.82280300
N	1.38886200	0.72515300	-1.62021400
C	-1.04147400	-0.68628200	-0.35679100
C	-2.26069600	-0.84295400	-0.49852300
C	-3.66596000	-0.98244900	-0.59996800
C	-4.37176600	-1.82406200	0.28976200
C	-4.39741500	-0.27763300	-1.58176100
C	-5.75383000	-1.95106200	0.19932200
H	-3.81613700	-2.36738900	1.04835400
C	-5.77864800	-0.41190700	-1.66505800
H	-3.86153900	0.37381900	-2.26351500
C	-6.46396800	-1.24706300	-0.77734900
H	-6.28109900	-2.60063500	0.89258200
H	-6.32682000	0.13909300	-2.42418000
H	-7.54324900	-1.34755000	-0.84573200
H	0.43286600	3.70322900	-2.82821300
H	2.54747000	-4.20998300	0.91321300
H	4.27054400	-2.30614200	0.35056800
C	-2.07797200	1.05697200	2.05203400
C	-0.78060300	0.92906200	1.33745500
C	-1.55596300	2.15369200	1.15526500
H	-2.93409500	0.49649000	1.67895400
H	-2.08216000	1.24534600	3.12599700
C	0.55287000	0.73675100	1.85071100
C	1.64733100	1.48238800	1.36399900
C	0.79496900	-0.24740200	2.83167400
C	2.93825100	1.21489300	1.80558600
H	1.46966900	2.26366100	0.63459600
C	2.08746600	-0.50096200	3.28077100
H	-0.04892200	-0.79924900	3.23546000
C	3.16797100	0.21652200	2.75662800
H	3.77261400	1.77825500	1.39902500
H	2.25556400	-1.25802200	4.04242400
H	4.17874300	0.00742400	3.09345800

Cl	-2.44853500	2.54452700	-0.35409300
Cl	-0.96996900	3.66773400	1.92855800

TS-S4-Triplet

Charge = 0, Multiplicity = 3

Cu	0.90399500	-0.92526900	-0.62144000
N	2.80226000	-1.21334900	-0.78518800
C	2.76894000	0.95720000	-1.70710400
C	3.58742500	-0.22786200	-1.24096000
O	4.82286100	-0.20143600	-1.30040800
C	3.36203900	2.12437400	-2.17510500
C	0.63248000	1.83853900	-1.99272400
C	2.53901800	3.18452000	-2.55583900
H	4.44438400	2.16776000	-2.21770000
C	1.15308100	3.04205600	-2.46592100
H	-0.43100300	1.66874500	-1.87487100
H	2.97214700	4.11342300	-2.91553200
C	3.38651200	-2.43461500	-0.28122400
C	2.33368100	-3.10790200	0.60014400
H	3.69605200	-3.09657600	-1.10445900
H	2.28898100	-2.59054800	1.56152700
N	0.97864300	-2.98680700	0.00052700
C	-0.05762000	-3.38984400	0.96100500
H	0.03567100	-2.78074400	1.86059400
H	-1.04000000	-3.21071700	0.52252000
H	0.04737000	-4.45354800	1.22496200
C	0.84628000	-3.76020900	-1.24662100
H	0.98471700	-4.83615200	-1.05881600
H	-0.15214900	-3.59455600	-1.65933400
H	1.58846000	-3.42441800	-1.97281800
N	1.43187200	0.83331900	-1.62256700
C	-1.00373100	-0.58589300	-0.34767600
C	-2.21832100	-0.78284700	-0.54542900
C	-3.61285700	-0.94783900	-0.67510800
C	-4.30549700	-1.88988900	0.12419500
C	-4.35455600	-0.18179000	-1.60599200

C	-5.67942100	-2.05360500	-0.00464900
H	-3.74396900	-2.47792900	0.84398200
C	-5.72780600	-0.35457000	-1.72643000
H	-3.83089100	0.54600600	-2.21583900
C	-6.39802400	-1.28870100	-0.92935800
H	-6.19570900	-2.77887600	0.61824100
H	-6.28309400	0.24356900	-2.44352100
H	-7.47184200	-1.41854200	-1.02706000
H	0.48115600	3.84678900	-2.74357500
H	2.57240500	-4.16752700	0.78298300
H	4.28915600	-2.23341700	0.30937900
C	-2.20108000	1.00472900	2.04700900
C	-0.88400400	0.82867200	1.37278600
C	-1.58461400	2.10220800	1.22008300
H	-3.07019700	0.50497300	1.61951300
H	-2.24022700	1.15143500	3.12661200
C	0.41100300	0.56854000	1.96218700
C	1.56776600	1.24212600	1.51878100
C	0.55283700	-0.41879500	2.95798100
C	2.82062200	0.91434800	2.02788300
H	1.46791600	2.02347800	0.77495300
C	1.80691200	-0.73366700	3.47534900
H	-0.33710000	-0.92322500	3.32391400
C	2.94916300	-0.07788400	3.00365800
H	3.70219600	1.42807500	1.65604600
H	1.89567200	-1.49094800	4.25007900
H	3.92845600	-0.33164700	3.39836700
Cl	-2.40204900	2.60427500	-0.30669600
Cl	-0.95254400	3.55448200	2.07198600

TS-S5

Charge = 0, Multiplicity = 1

Cu	0.85633700	-0.85851900	-0.27693900
N	2.72720700	-1.10107100	0.24030400
C	3.05395100	1.00828500	-0.84305700
C	3.64981700	-0.24867000	-0.24194600

O	4.87937800	-0.41089400	-0.28639000
C	3.82659000	2.15517700	-1.02383900
C	1.19259600	2.02868100	-1.76991300
C	3.22779800	3.28143100	-1.58193700
H	4.86670300	2.13031900	-0.71983700
C	1.88375900	3.22290800	-1.95785200
H	0.14463000	1.92154500	-2.03489400
H	3.79711400	4.19647300	-1.71966600
C	3.14287100	-2.48516400	0.40018100
C	1.99543900	-3.40345600	-0.07020500
H	4.06027000	-2.66454000	-0.17336700
H	1.27066300	-3.55371700	0.73733900
N	1.23858000	-2.79718900	-1.19295100
C	0.01881700	-3.55940500	-1.48624100
H	-0.59185000	-3.62751500	-0.58403300
H	-0.55915300	-3.03104000	-2.24788400
H	0.25681600	-4.57324800	-1.84604900
C	2.06214300	-2.65319200	-2.40222700
H	2.38272300	-3.63667400	-2.78220100
H	1.47372800	-2.14927600	-3.17340100
H	2.94232900	-2.04796000	-2.18535100
N	1.76882700	0.94900700	-1.23264300
C	-0.94265400	-0.55622100	-0.54383500
C	-2.08612100	-0.30527400	-0.90204600
C	-3.41422900	-0.00564900	-1.30580600
C	-4.45666100	-0.92918200	-1.08778000
C	-3.71749200	1.23416500	-1.90485500
C	-5.76017900	-0.61827400	-1.46176200
H	-4.22500100	-1.87851000	-0.61595400
C	-5.02453800	1.53679700	-2.27454100
H	-2.91593000	1.94793700	-2.06868200
C	-6.04972300	0.61285200	-2.05662400
H	-6.55548600	-1.33721000	-1.28635700
H	-5.24548300	2.49587300	-2.73463800
H	-7.06883600	0.85145500	-2.34676800
H	1.37937200	4.08279100	-2.38605200
H	2.38089400	-4.39635800	-0.35542800

H	3.38132800	-2.73842100	1.44362200
C	0.48764700	-0.84904100	2.56085100
C	-0.11701400	-0.07638600	1.39030100
C	-0.99095400	-0.83917100	2.34302300
H	1.00719400	-1.78400200	2.39167800
H	0.89197200	-0.24758500	3.37173600
C	-0.02282100	1.39897100	1.37007400
C	-1.11356300	2.20706600	1.01494000
C	1.20656700	2.00355400	1.66938200
C	-0.97201500	3.59084700	0.96513000
H	-2.06351500	1.74479900	0.77643500
C	1.34907000	3.38760900	1.60698500
H	2.05555100	1.37491200	1.91805800
C	0.25968100	4.18571200	1.25419800
H	-1.82525000	4.20800400	0.69773700
H	2.31235200	3.83961100	1.82337900
H	0.36828500	5.26554100	1.20456100
Cl	-1.73370100	-2.38797500	1.86454100
Cl	-2.03484100	0.06362000	3.46203500

Int-S6

Charge = 0, Multiplicity = 1

Cu	-0.68719000	0.61981500	0.24101500
N	0.19843200	2.21245200	0.93506500
C	1.27781600	0.81170500	2.54804300
C	1.13443700	2.17449800	1.88088100
O	1.89864600	3.09317000	2.23753700
C	2.34681200	0.60044500	3.42285000
C	0.56306700	-1.37085200	2.80862700
C	2.51517900	-0.65759800	3.99580000
H	3.01342400	1.43241900	3.61651000
C	1.60791200	-1.67047700	3.68204600
H	-0.16462700	-2.12855900	2.52725800
H	3.34348800	-0.84919600	4.67255500
C	-0.03167800	3.46522900	0.25683900
C	-0.89349800	3.21128300	-0.98721000

H	-0.51908800	4.19098200	0.92681500
H	-0.26559400	2.75128300	-1.75837000
N	-2.00647900	2.27216500	-0.73471600
C	-2.65372800	1.88204100	-1.98349200
H	-1.91304400	1.42176400	-2.64487400
H	-3.43598200	1.14600000	-1.77497900
H	-3.10997300	2.74046600	-2.50859900
C	-2.97801000	2.79987600	0.22309700
H	-3.45524700	3.72943600	-0.13572900
H	-3.75610400	2.04901600	0.39321000
H	-2.47979500	3.00059500	1.17390100
N	0.39338900	-0.16401500	2.25742300
C	-0.34802500	-1.09613200	-1.00971800
C	-1.50160300	-1.12416400	-0.57367100
C	-2.87515300	-1.29152500	-0.20069100
C	-3.83351500	-1.66801300	-1.15929300
C	-3.28285700	-1.03611200	1.12308500
C	-5.17314900	-1.78413200	-0.79753400
H	-3.51620100	-1.85836000	-2.17955300
C	-4.62470500	-1.15552500	1.47395400
H	-2.53906600	-0.73949700	1.85685800
C	-5.57228600	-1.52684600	0.51651800
H	-5.90806700	-2.07343000	-1.54297700
H	-4.93178400	-0.95605500	2.49628800
H	-6.61863800	-1.61559400	0.79325700
H	1.70458000	-2.66840600	4.09770400
H	-1.27529600	4.16712500	-1.38929500
H	0.90850700	3.93819900	-0.06119800
C	1.11936200	-2.46582700	-2.57440700
C	0.96017800	-1.28692400	-1.60263000
C	1.72579600	-2.55834000	-1.21668500
H	0.24531800	-3.07667900	-2.77395400
H	1.79735600	-2.31938800	-3.40916400
C	1.70486800	-0.00225100	-1.85930300
C	2.35812000	0.64271700	-0.80528700
C	1.63108500	0.61504200	-3.11059000
C	2.92395000	1.90175900	-0.99299800

H	2.40258900	0.16686900	0.16703100
C	2.20188000	1.87439000	-3.30283300
H	1.11533400	0.11690000	-3.92745900
C	2.84216100	2.52035900	-2.24194800
H	3.37848600	2.41208200	-0.14981200
H	2.14049600	2.35213500	-4.27655400
H	3.27250400	3.50701100	-2.38754500
Cl	1.00253800	-3.67342100	-0.04277600
Cl	3.48816100	-2.48122900	-1.07346900

TS-S7

Charge = 0, Multiplicity = 1

Cu	0.83802000	-0.79623900	-0.53598300
N	2.64523300	-1.06732100	0.06457400
C	3.01265800	1.11910400	-0.80981400
C	3.58633100	-0.14446400	-0.21022900
O	4.80970300	-0.26365300	-0.06007600
C	3.78783000	2.26134100	-0.98937700
C	1.14297800	2.14369400	-1.72725200
C	3.19005300	3.38573700	-1.55560000
H	4.82662100	2.23475600	-0.68066800
C	1.84499900	3.33147200	-1.92599300
H	0.09384800	2.03145600	-1.98251300
H	3.76284600	4.29697400	-1.70293500
C	3.08315800	-2.43360800	0.29116600
C	1.94133500	-3.38020300	-0.11296500
H	3.99495600	-2.63030900	-0.28701800
H	1.22112600	-3.48001900	0.70453000
N	1.18425000	-2.83680400	-1.26422800
C	-0.03531500	-3.61152600	-1.52584800
H	-0.64471700	-3.64391900	-0.62323100
H	-0.61360800	-3.11311000	-2.30579100
H	0.20988100	-4.63763900	-1.84294000
C	2.00417500	-2.74855500	-2.48238100
H	2.33292200	-3.74774700	-2.81012200
H	1.40694900	-2.29366000	-3.27676500

H	2.87851400	-2.12288800	-2.30097200
N	1.72550100	1.06925900	-1.19017600
C	-0.97326900	-0.51630400	-1.03532900
C	-2.15269800	-0.25874000	-1.24101100
C	-3.53663800	0.05501800	-1.37382400
C	-4.38841500	-0.06014300	-0.25532600
C	-4.08179600	0.50138100	-2.59307200
C	-5.73811900	0.26566100	-0.35824500
H	-3.97329900	-0.40986000	0.68514500
C	-5.43342700	0.82255900	-2.68838500
H	-3.43114200	0.59097100	-3.45764700
C	-6.26719700	0.70785000	-1.57330200
H	-6.38038000	0.17230900	0.51332100
H	-5.83879300	1.16482800	-3.63684000
H	-7.32093900	0.96025600	-1.65107100
H	1.34444600	4.19078000	-2.35951400
H	2.32846300	-4.38664900	-0.34166000
H	3.34739000	-2.62183500	1.34189600
C	0.68475100	-0.93418000	2.76132200
C	0.13131900	-0.10430500	1.65342200
C	-0.78748500	-0.97269000	2.40050400
H	1.25962800	-1.82684000	2.53330400
H	0.97461900	-0.43345100	3.68484400
C	0.14964900	1.32757000	1.51649800
C	-0.98553500	2.03881200	1.07072800
C	1.33466400	2.03659100	1.80510200
C	-0.93192400	3.41920000	0.93467400
H	-1.88631800	1.49183900	0.82303400
C	1.38316200	3.41709200	1.65543700
H	2.21060800	1.48388600	2.12990200
C	0.25045400	4.11310200	1.22118900
H	-1.81154200	3.96010900	0.59785800
H	2.30347300	3.95185000	1.86991600
H	0.28881700	5.19237900	1.10363400
Cl	-1.43661300	-2.48544100	1.71573200
Cl	-1.96595500	-0.22156100	3.51442600

Int-S8

Charge = 0, Multiplicity = 1

Cu	0.77135300	-0.85755700	-0.27791000
N	2.66194100	-0.97739000	0.01565800
C	2.79859600	1.20330600	-0.99348000
C	3.49513700	-0.02553600	-0.45837000
O	4.72852400	-0.11167000	-0.53570700
C	3.49058000	2.40035000	-1.17508700
C	0.83729400	2.11629500	-1.80836500
C	2.79536500	3.49640100	-1.67987700
H	4.54206300	2.43916200	-0.91459900
C	1.44203000	3.35808400	-1.99559500
H	-0.21266800	1.94577900	-2.02868600
H	3.29755500	4.44943900	-1.82024600
C	3.17104700	-2.34103500	0.06460900
C	2.08878900	-3.28892700	-0.49115200
H	4.09988800	-2.39350900	-0.51401800
H	1.43165600	-3.62331300	0.31623900
N	1.21694100	-2.59191500	-1.47040400
C	0.03281200	-3.40337500	-1.79091000
H	-0.51842300	-3.61642400	-0.87388600
H	-0.62054700	-2.83499200	-2.45443000
H	0.32638500	-4.34678700	-2.27658200
C	1.93432300	-2.22404700	-2.70149200
H	2.24601100	-3.12465000	-3.25295400
H	1.26983700	-1.62867400	-3.33187400
H	2.81370800	-1.62799000	-2.46144700
N	1.50675500	1.06498700	-1.32913000
C	-1.05917300	-0.71102400	-0.62402500
C	-2.23666600	-0.49811500	-0.87123000
C	-3.59748500	-0.17960600	-1.14865500
C	-4.59219500	-1.17577500	-1.17321800
C	-3.97435300	1.15805400	-1.38475700
C	-5.91975900	-0.84180700	-1.42679400
H	-4.30738500	-2.20627700	-0.98589400
C	-5.30393800	1.48471800	-1.63613900

H	-3.20955800	1.92870800	-1.36224100
C	-6.28181300	0.48730200	-1.65960100
H	-6.67653600	-1.62130200	-1.44089900
H	-5.57924300	2.52060400	-1.81493300
H	-7.31874000	0.74400000	-1.85652800
H	0.86425600	4.19307000	-2.37789000
H	2.53963600	-4.18340300	-0.94966900
H	3.42388100	-2.65953200	1.08568800
C	1.11468400	-0.69471800	2.68425200
C	0.33201500	-0.07900400	1.54819500
C	-0.34924400	-0.99237900	2.50872400
H	1.81065300	-1.50223800	2.48905500
H	1.39986200	-0.03572200	3.50202300
C	0.11919700	1.37235700	1.46976900
C	-1.14105100	1.92795900	1.19022400
C	1.21759700	2.22911000	1.64429000
C	-1.29094200	3.30704500	1.08813300
H	-1.98829700	1.27056900	1.04793000
C	1.06752100	3.60855800	1.52698400
H	2.19242800	1.79990300	1.85322500
C	-0.18777000	4.15201900	1.24750600
H	-2.27247200	3.72520200	0.88236700
H	1.92993900	4.25715700	1.64895800
H	-0.30785800	5.22809300	1.15758000
Cl	-0.77992700	-2.65518600	2.02048100
Cl	-1.51939600	-0.33783800	3.67612100

Proposed Pre-intermediate of Ion-type Bond Formation

Charge = 0, Multiplicity = 1

Cu	0.90399500	-0.92526900	-0.62144000
N	2.80226000	-1.21334900	-0.78518800
C	2.76894000	0.95720000	-1.70710400
C	3.58742500	-0.22786200	-1.24096000
O	4.82286100	-0.20143600	-1.30040800
C	3.36203900	2.12437400	-2.17510500
C	0.63248000	1.83853900	-1.99272400

C	2.53901800	3.18452000	-2.55583900
H	4.44438400	2.16776000	-2.21770000
C	1.15308100	3.04205600	-2.46592100
H	-0.43100300	1.66874500	-1.87487100
H	2.97214700	4.11342300	-2.91553200
C	3.38651200	-2.43461500	-0.28122400
C	2.33368100	-3.10790200	0.60014400
H	3.69605200	-3.09657600	-1.10445900
H	2.28898100	-2.59054800	1.56152700
N	0.97864300	-2.98680700	0.00052700
C	-0.05762000	-3.38984400	0.96100500
H	0.03567100	-2.78074400	1.86059400
H	-1.04000000	-3.21071700	0.52252000
H	0.04737000	-4.45354800	1.22496200
C	0.84628000	-3.76020900	-1.24662100
H	0.98471700	-4.83615200	-1.05881600
H	-0.15214900	-3.59455600	-1.65933400
H	1.58846000	-3.42441800	-1.97281800
N	1.43187200	0.83331900	-1.62256700
C	-1.00373100	-0.58589300	-0.34767600
C	-2.21832100	-0.78284700	-0.54542900
C	-3.61285700	-0.94783900	-0.67510800
C	-4.30549700	-1.88988900	0.12419500
C	-4.35455600	-0.18179000	-1.60599200
C	-5.67942100	-2.05360500	-0.00464900
H	-3.74396900	-2.47792900	0.84398200
C	-5.72780600	-0.35457000	-1.72643000
H	-3.83089100	0.54600600	-2.21583900
C	-6.39802400	-1.28870100	-0.92935800
H	-6.19570900	-2.77887600	0.61824100
H	-6.28309400	0.24356900	-2.44352100
H	-7.47184200	-1.41854200	-1.02706000
H	0.48115600	3.84678900	-2.74357500
H	2.57240500	-4.16752700	0.78298300
H	4.28915600	-2.23341700	0.30937900
C	-2.20108000	1.00472900	2.04700900
C	-0.88400400	0.82867200	1.37278600

C	-1.58461400	2.10220800	1.22008300
H	-3.07019700	0.50497300	1.61951300
H	-2.24022700	1.15143500	3.12661200
C	0.41100300	0.56854000	1.96218700
C	1.56776600	1.24212600	1.51878100
C	0.55283700	-0.41879500	2.95798100
C	2.82062200	0.91434800	2.02788300
H	1.46791600	2.02347800	0.77495300
C	1.80691200	-0.73366700	3.47534900
H	-0.33710000	-0.92322500	3.32391400
C	2.94916300	-0.07788400	3.00365800
H	3.70219600	1.42807500	1.65604600
H	1.89567200	-1.49094800	4.25007900
H	3.92845600	-0.33164700	3.39836700
Cl	-2.40204900	2.60427500	-0.30669600
Cl	-0.95254400	3.55448200	2.07198600

Proposed Transition State Structure of Ion-type Bond Formation

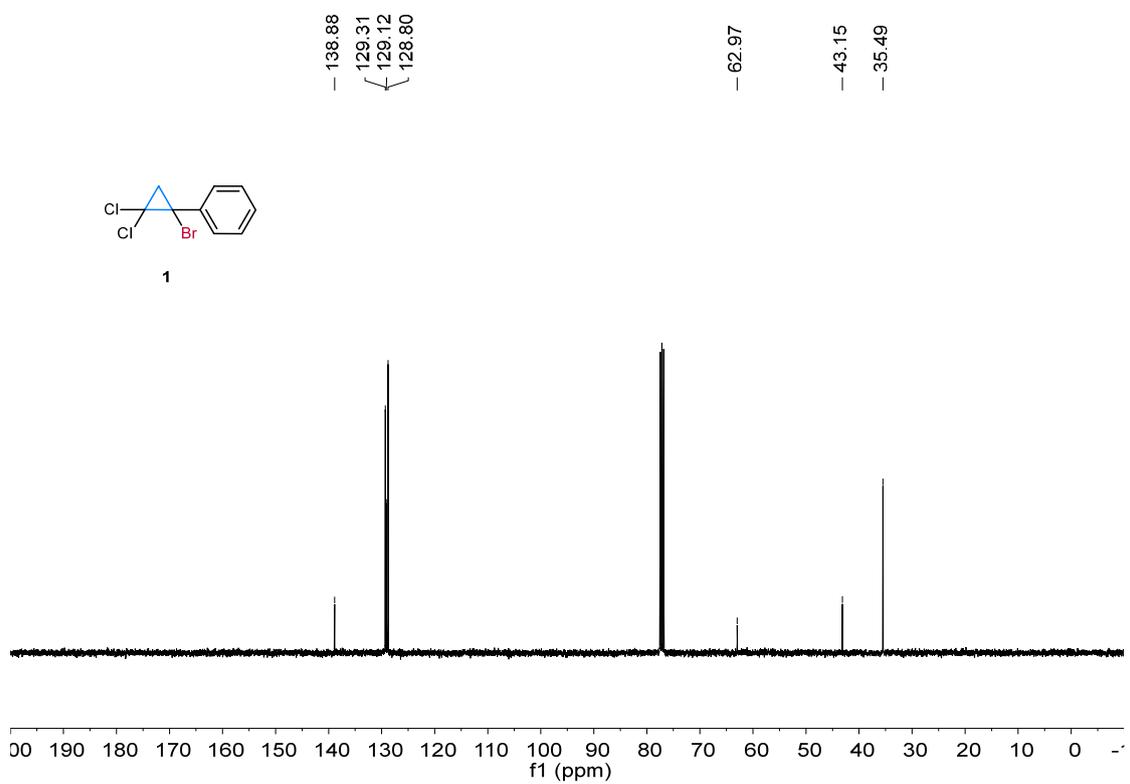
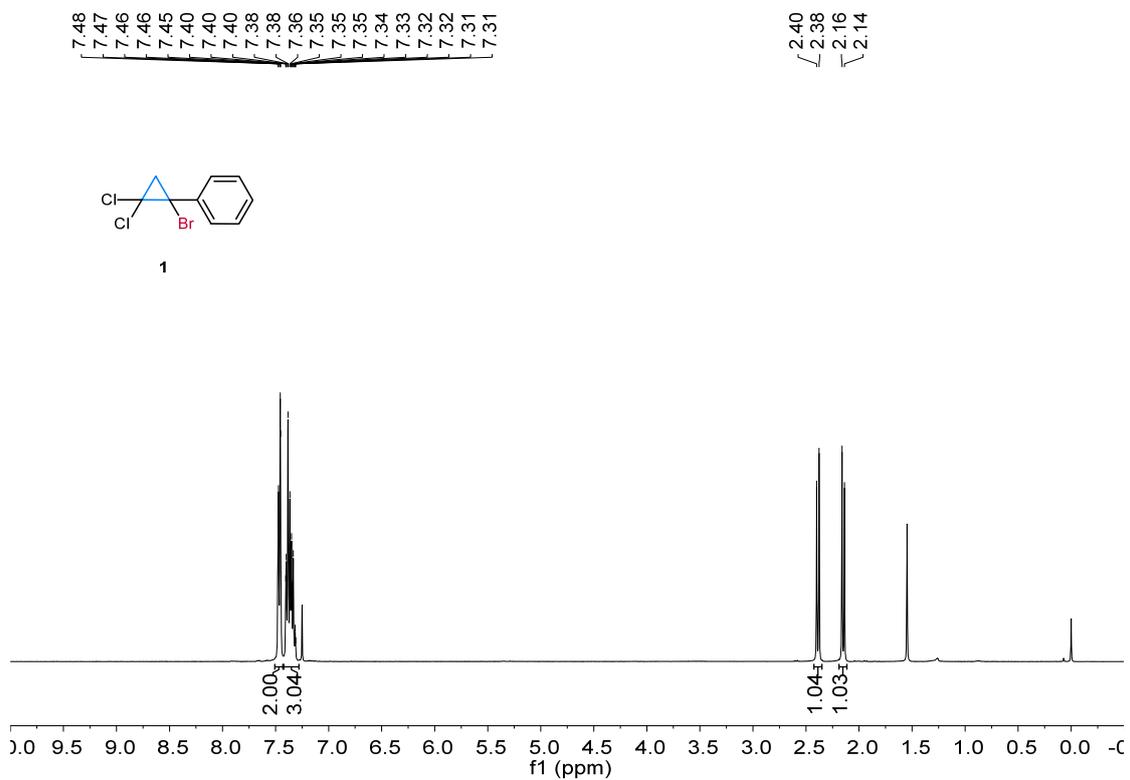
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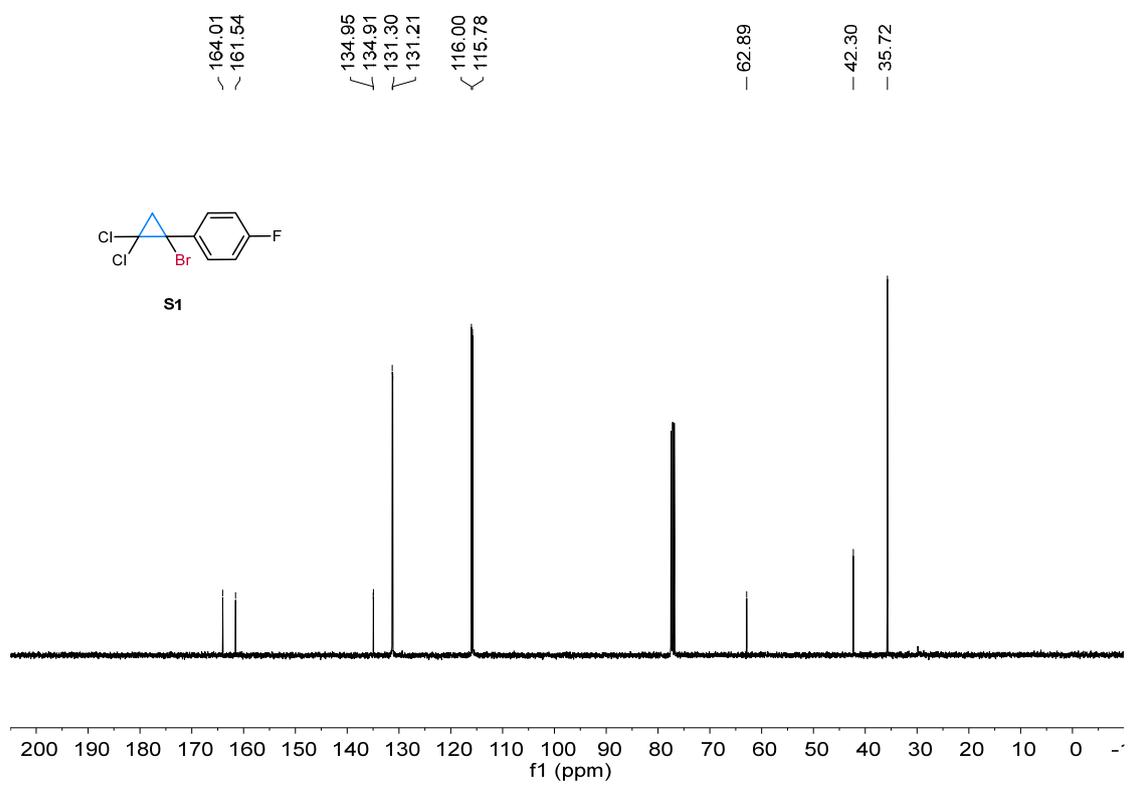
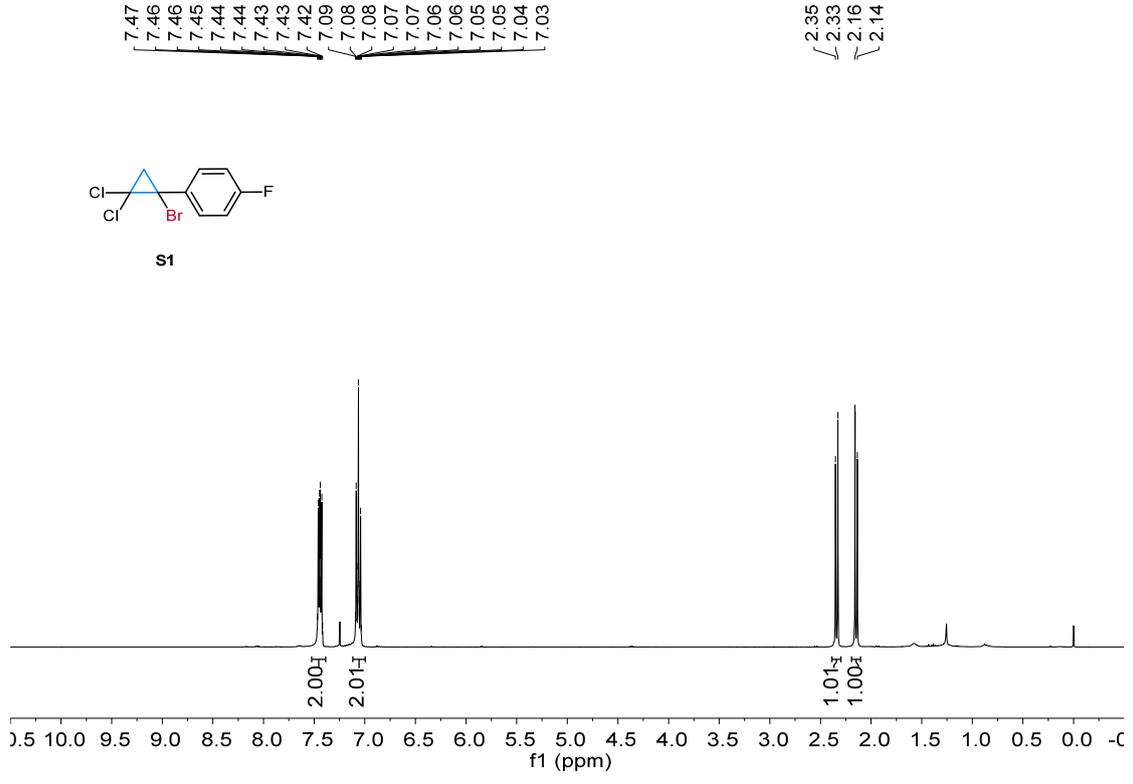
Cu	-0.12402800	-0.83132200	-0.55555700
N	-2.02189600	-1.18121800	-0.78312800
C	-2.02237900	-2.16276300	1.42559200
C	-2.73657800	-1.87538100	0.12287600
O	-3.87779200	-2.33768900	-0.04371000
C	-2.75220600	-2.47394700	2.57575400
C	-0.01652900	-2.48586000	2.52114400
C	-2.05847700	-2.78152900	3.74279100
H	-3.83462100	-2.47412500	2.51985400
C	-0.66134300	-2.78952600	3.71952700
H	1.06840300	-2.47961700	2.44351900
H	-2.59520200	-3.01667000	4.65763800
C	-2.47012400	-1.30739100	-2.16567700
C	-1.26884400	-1.05414800	-3.08423500
H	-2.82458100	-2.33910300	-2.31681200
H	-1.02980800	0.01687000	-3.03080100
N	-0.05215300	-1.72852200	-2.53198200

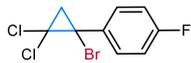
C	1.16366100	-1.36046700	-3.27228100
H	1.21184100	-0.27277600	-3.36482700
H	2.03696400	-1.68955900	-2.70782200
H	1.18083000	-1.81281000	-4.27410200
C	-0.15727500	-3.19088000	-2.41272000
H	-0.24700000	-3.67797800	-3.39447800
H	0.74689800	-3.55797900	-1.92031000
H	-1.01600300	-3.45461200	-1.79535900
N	-0.67978100	-2.18032700	1.40053700
C	1.71877400	-0.54905400	-0.31725300
C	2.92899300	-0.40256200	-0.20357900
C	4.33833900	-0.21631100	-0.09374800
C	5.06314300	-0.76939300	0.98029900
C	5.03788600	0.53591500	-1.05884700
C	6.43793400	-0.57482300	1.08301400
H	4.53101700	-1.35087900	1.72684400
C	6.41232000	0.72805500	-0.94963100
H	4.48533100	0.96331500	-1.89019800
C	7.11915800	0.17404900	0.12044900
H	6.98102700	-1.00912400	1.91803900
H	6.93509600	1.31159700	-1.70269600
H	8.19175600	0.32443700	0.20334700
H	-0.08368500	-3.02978100	4.60653600
H	-1.52219900	-1.28329200	-4.09824000
H	-3.28416000	-0.67541500	-2.45351600
C	0.32417400	3.15195900	-0.81909300
C	-0.48496000	1.97035300	-0.36914100
C	0.25503100	2.80096600	0.63873200
H	1.26619200	2.97935000	-1.36855000
H	-0.19927300	4.05501600	-1.17907200
C	-2.02188400	2.05174900	-0.42242300
C	-2.77369000	1.80535200	0.72672800
C	-2.66233200	2.37190100	-1.61945200
C	-4.16565400	1.87845100	0.67860800
H	-2.26850600	1.55222100	1.67010300
C	-4.05467000	2.44602900	-1.66752000
H	-2.06993800	2.56630500	-2.52521400

C	-4.80638100	2.19923900	-0.51879800
H	-4.75832900	1.68363500	1.58419000
H	-4.55934300	2.69887900	-2.61136600
H	-5.90390300	2.25687300	-0.55648200
Cl	1.67811200	2.12600900	1.42414500
Cl	-0.65807500	3.84079500	1.72620300

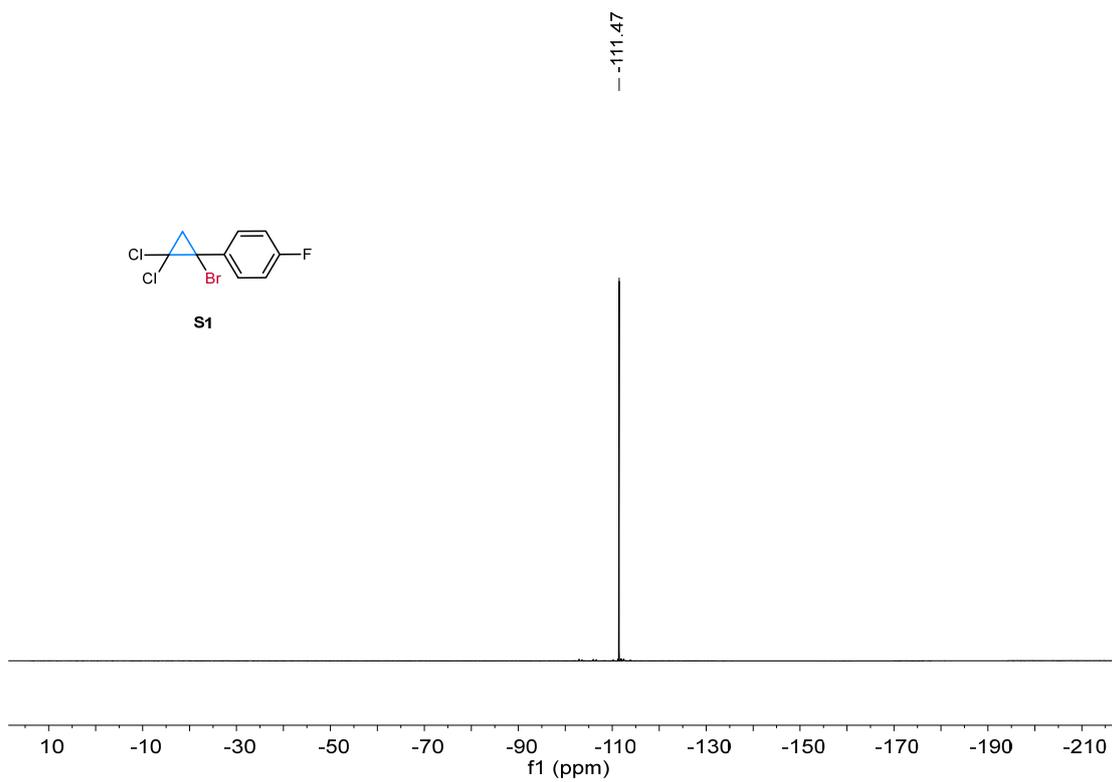
NMR spectra

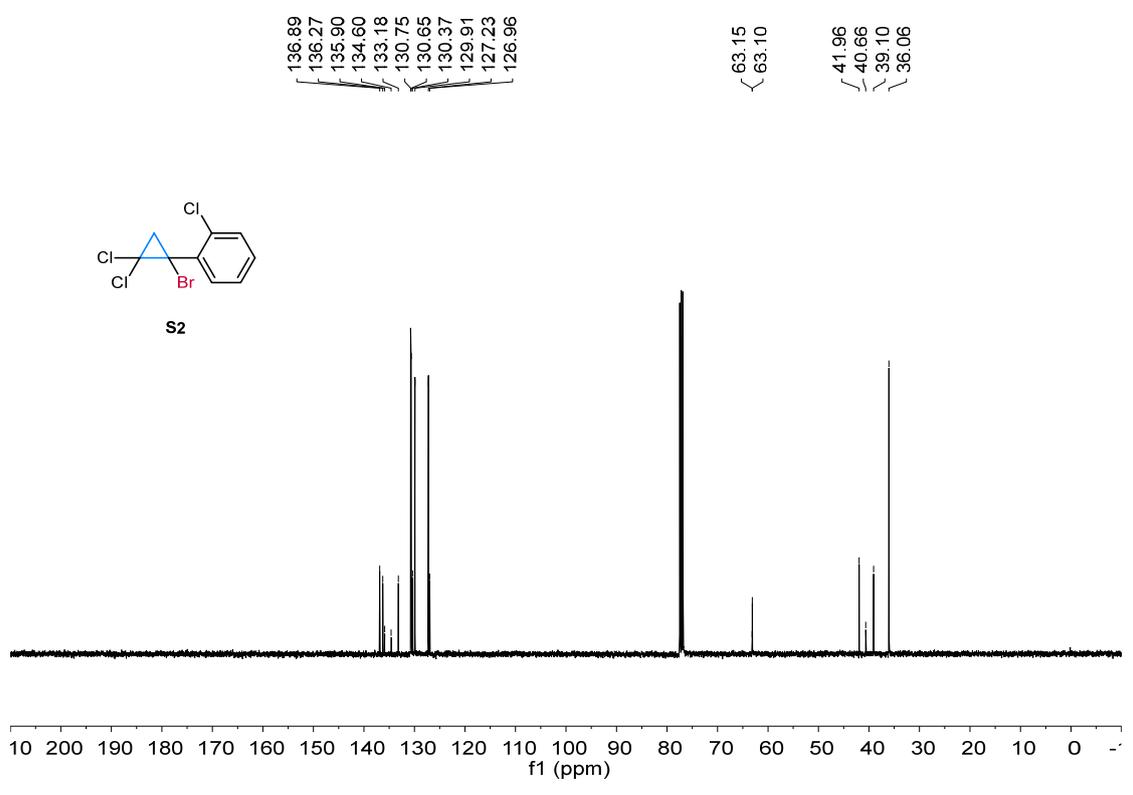
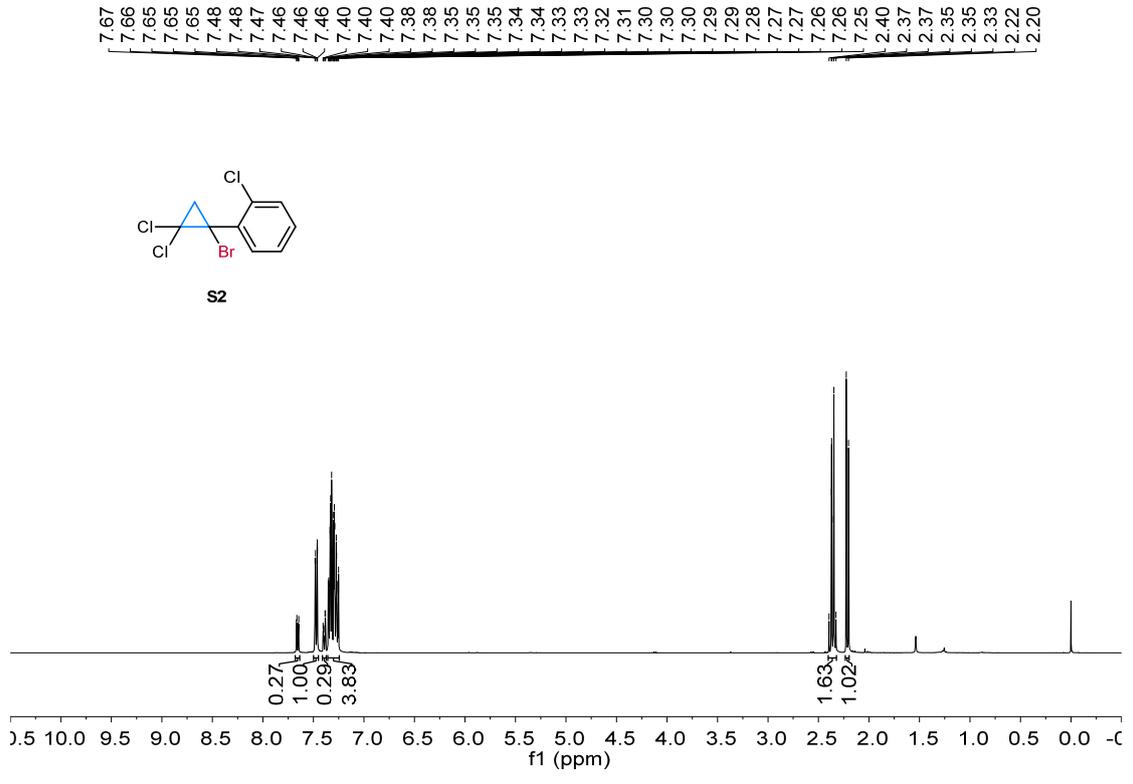


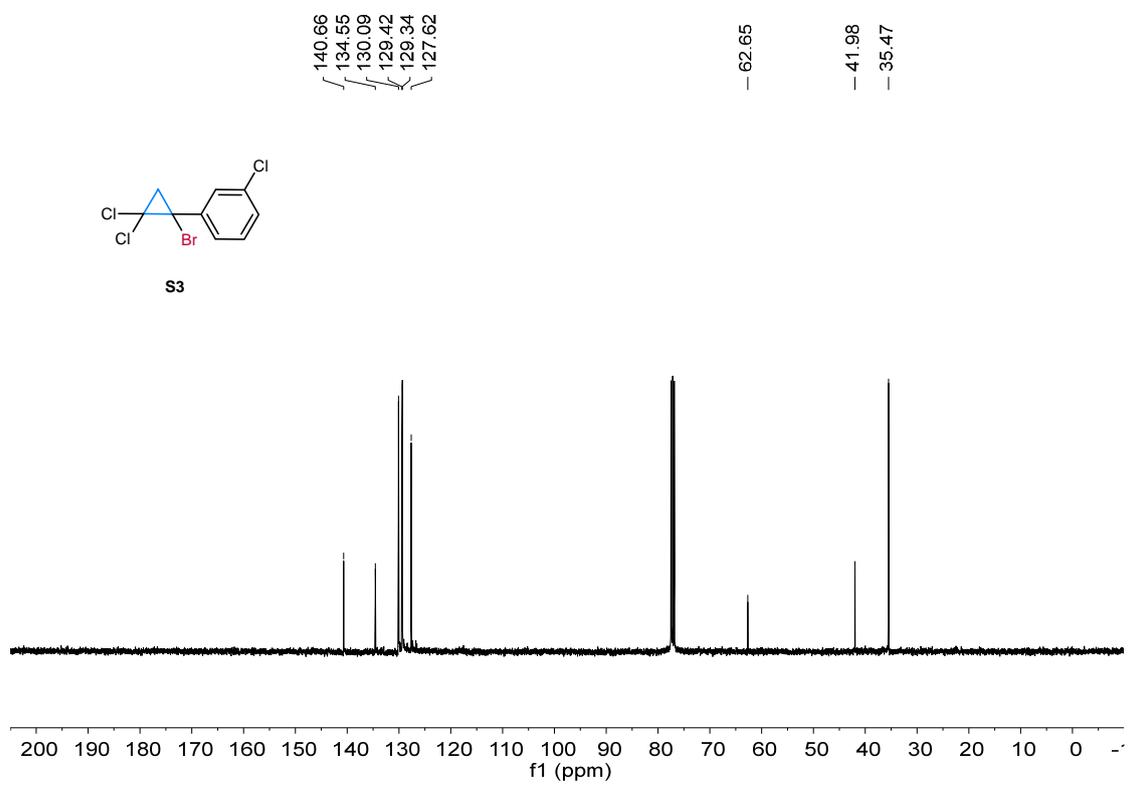
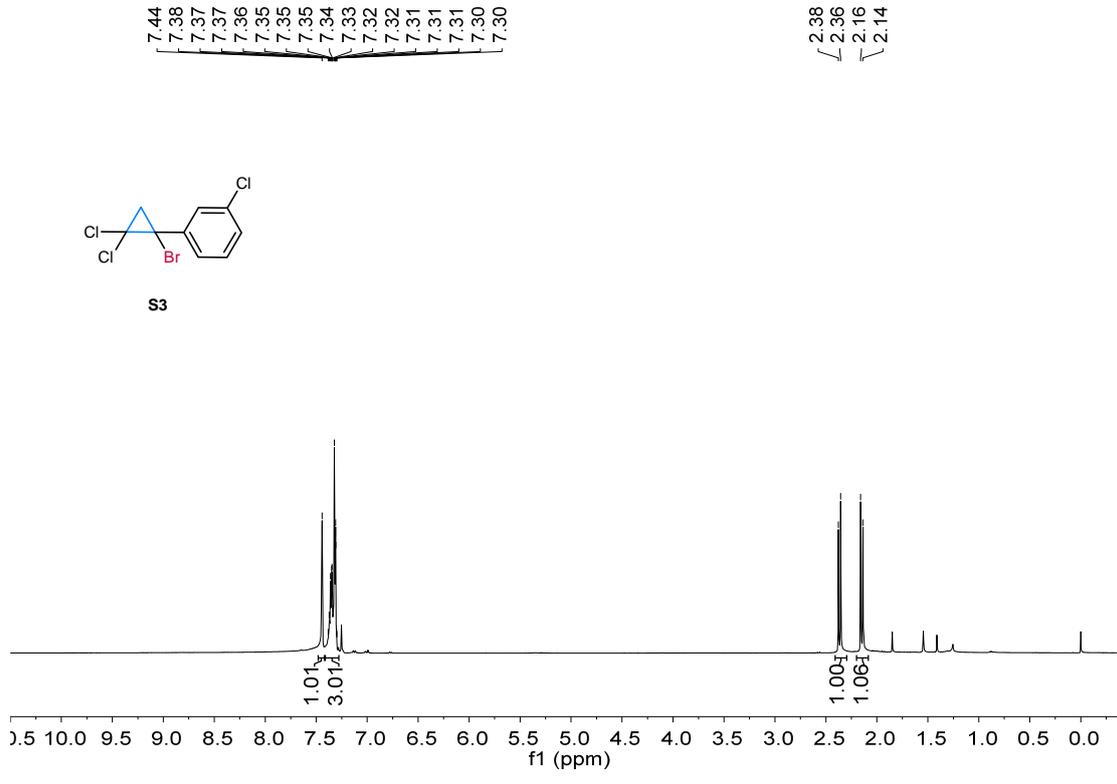


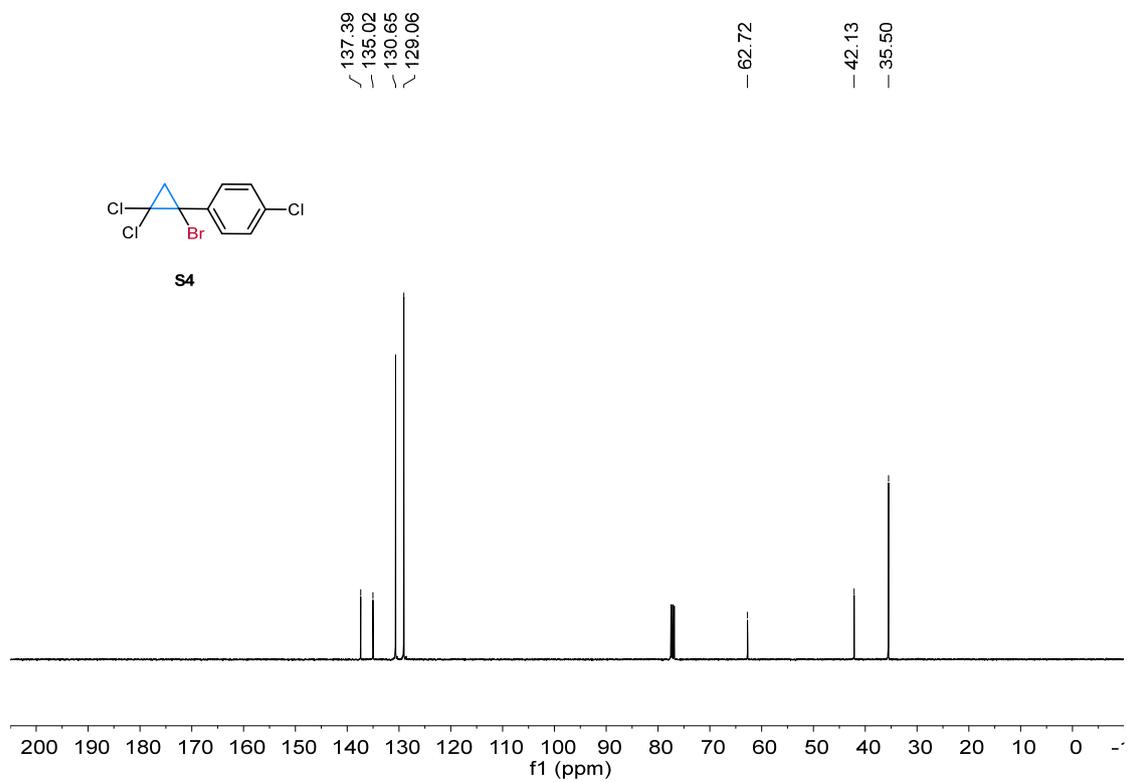
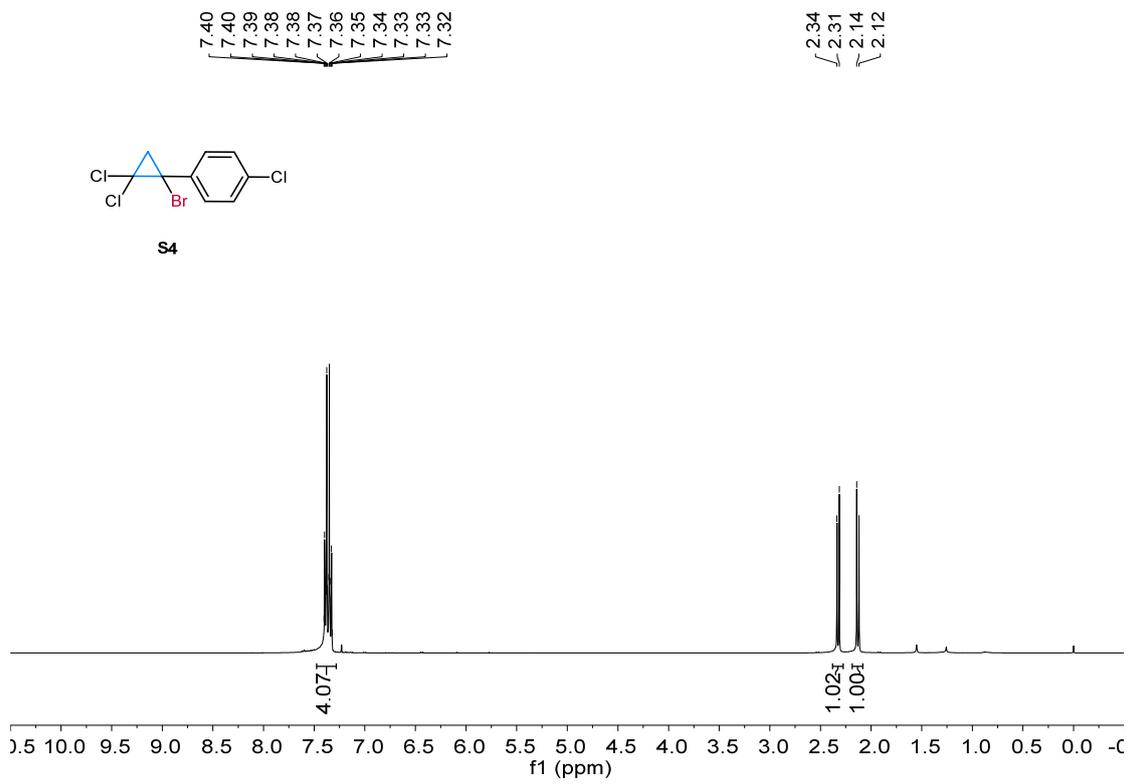


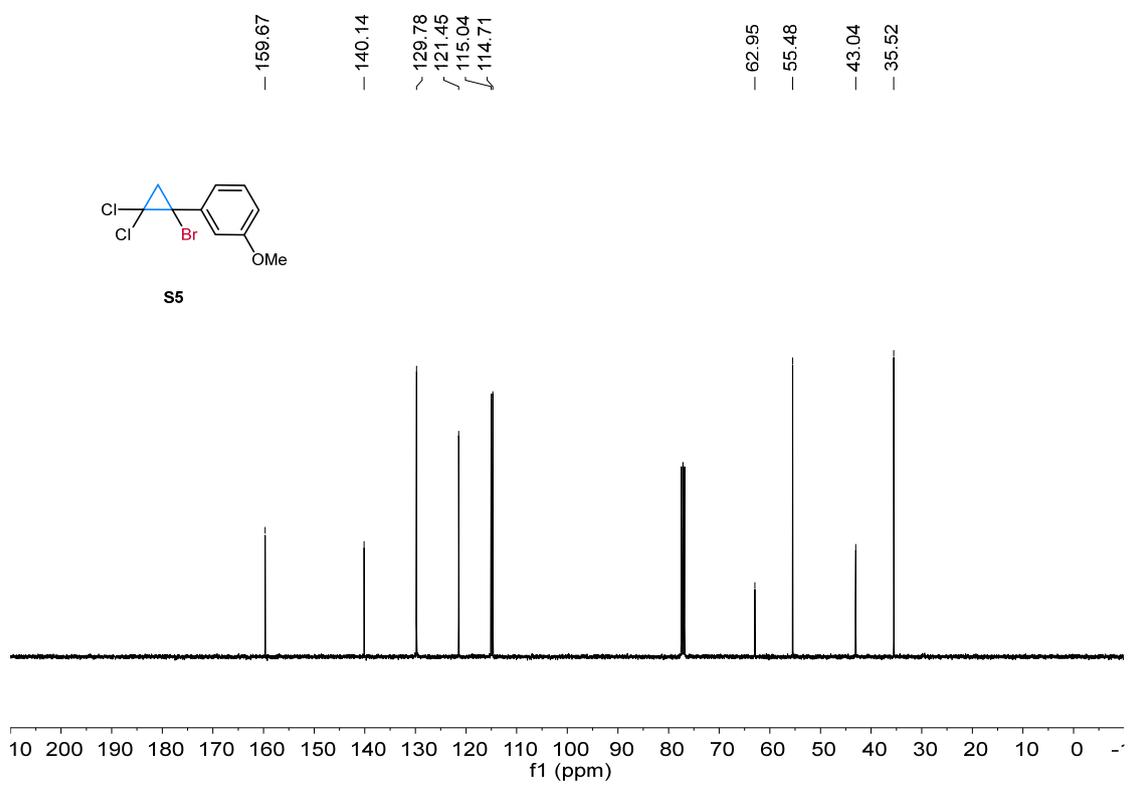
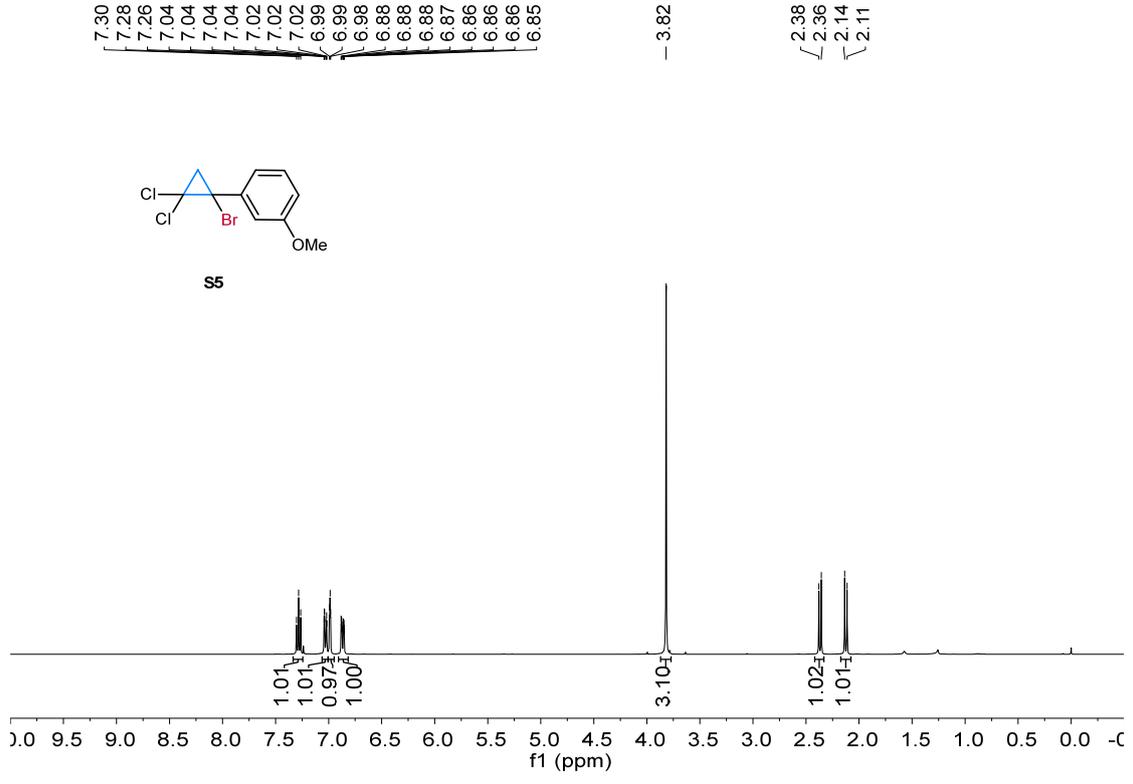
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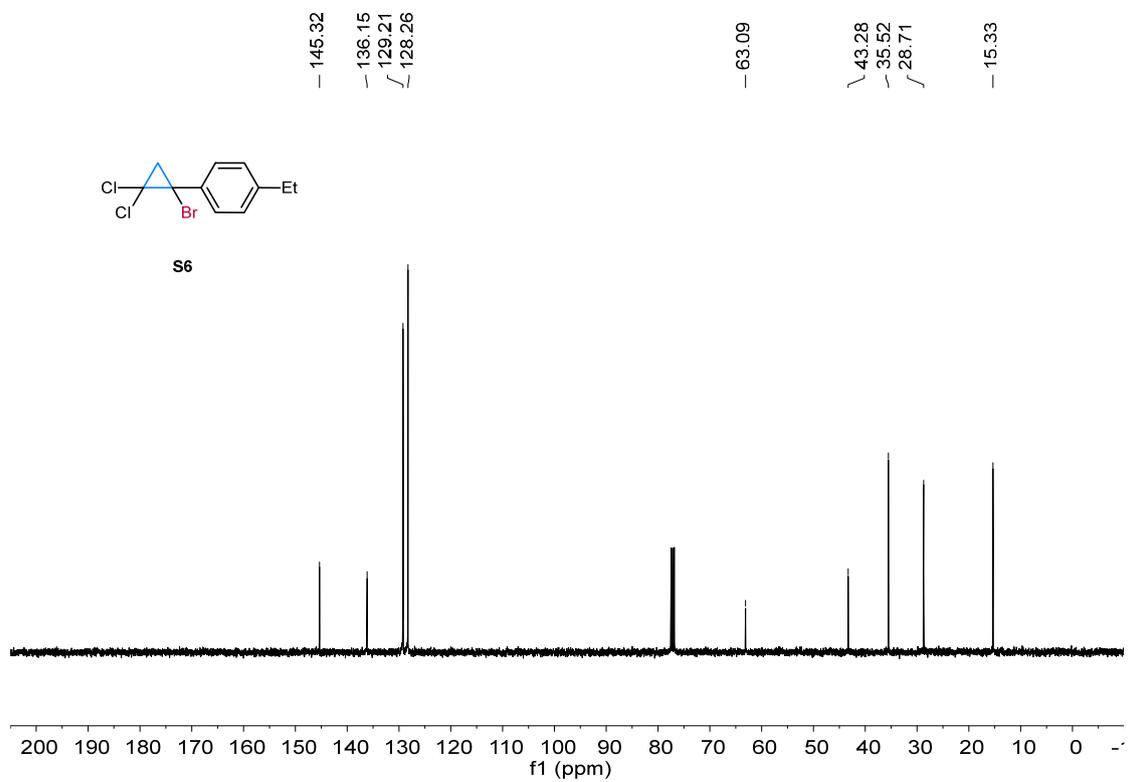
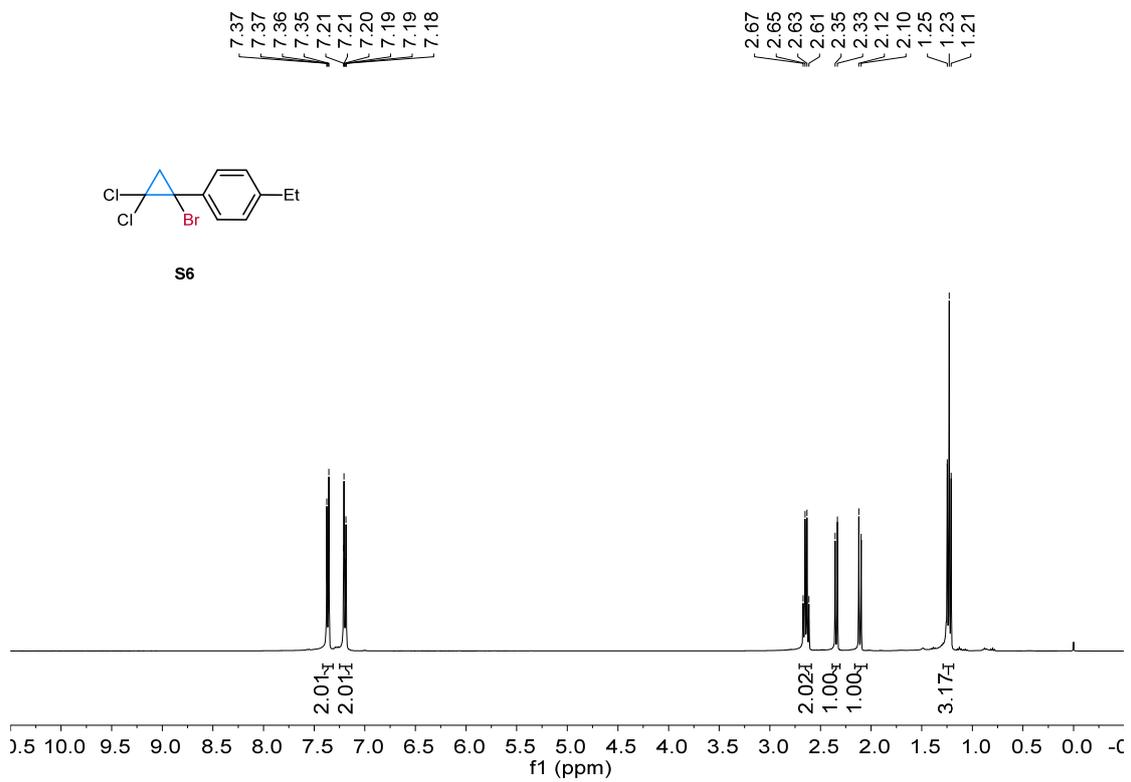


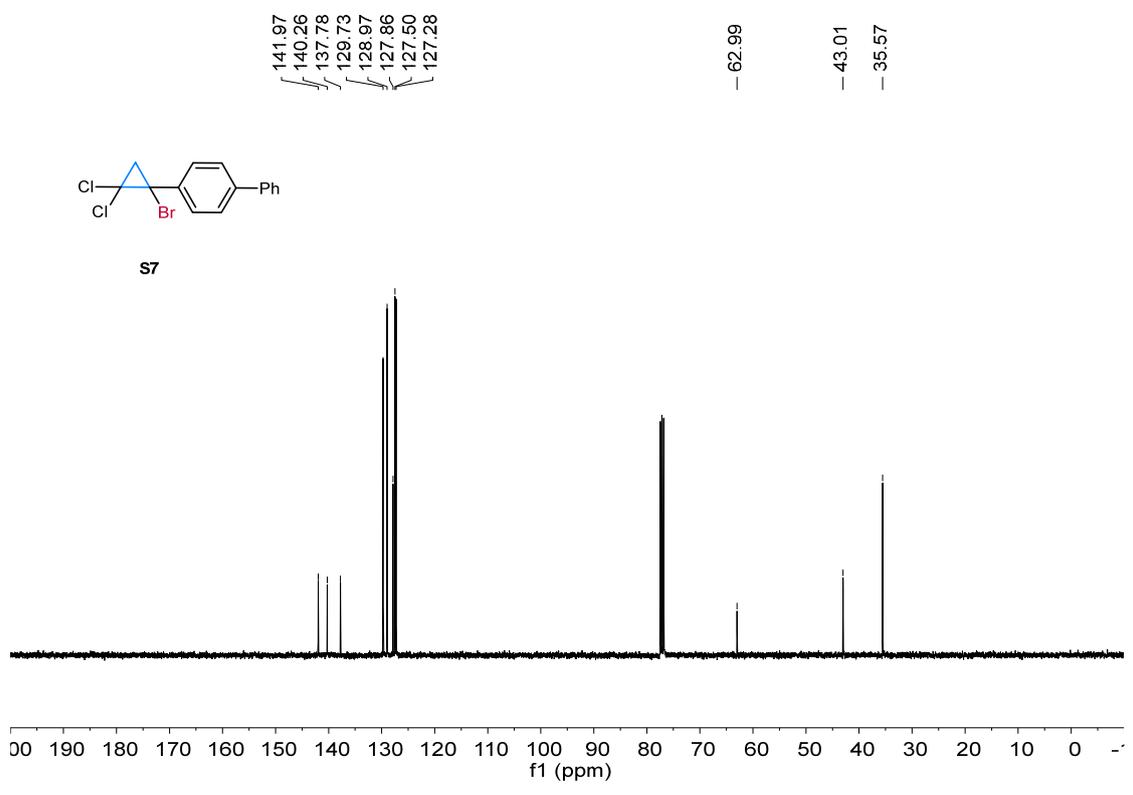
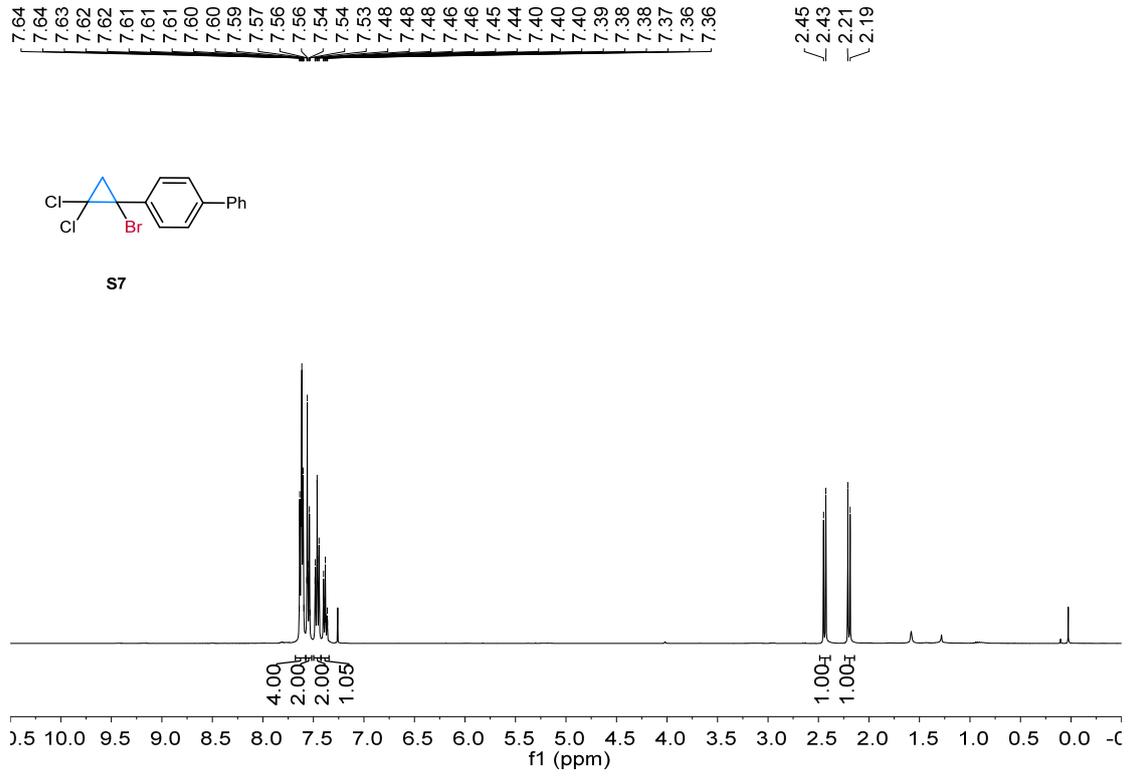


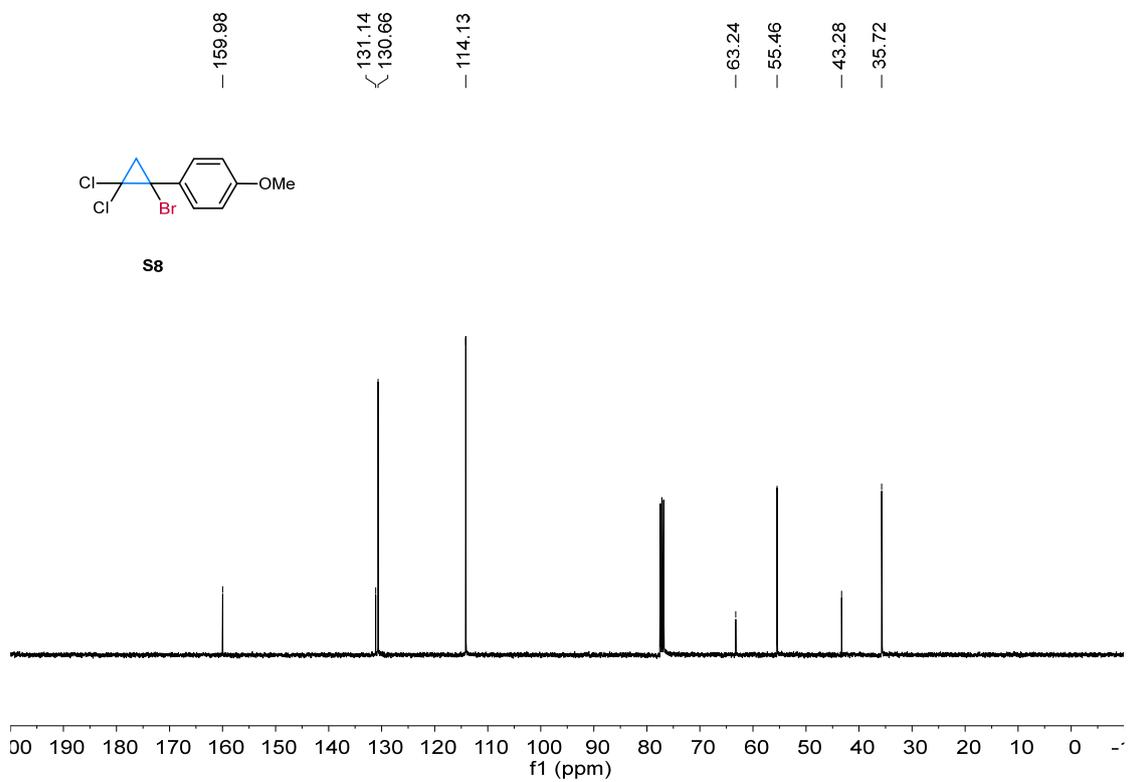
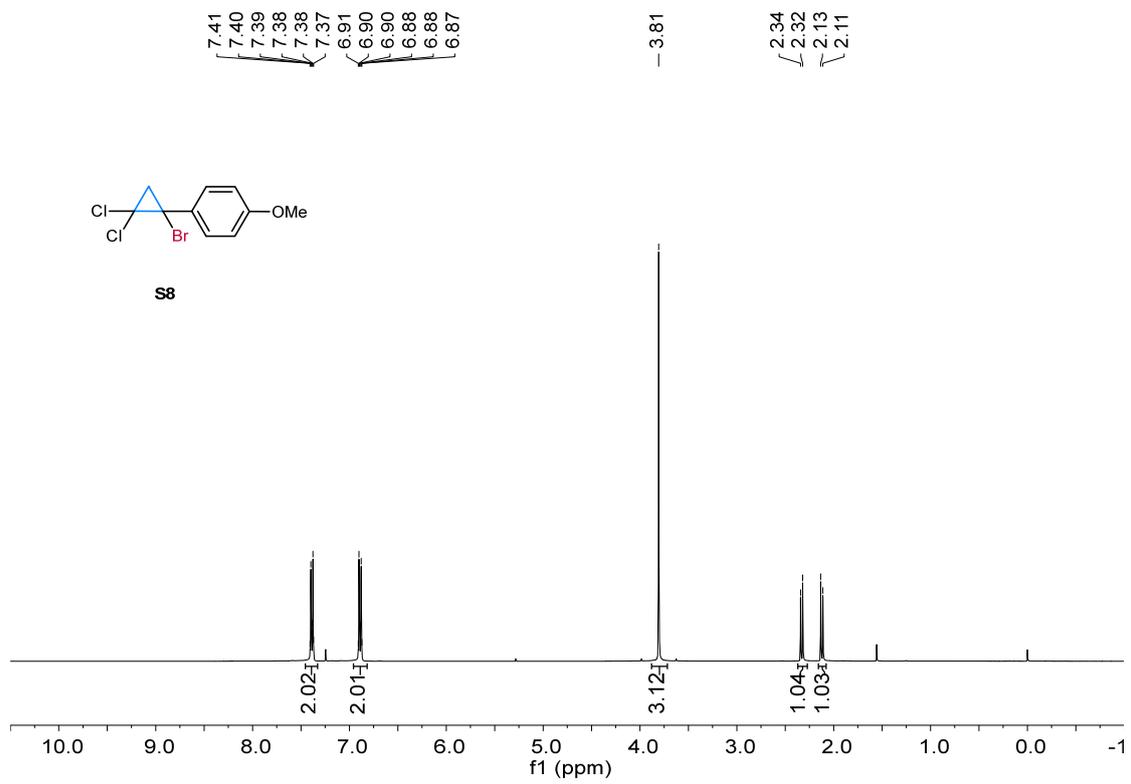


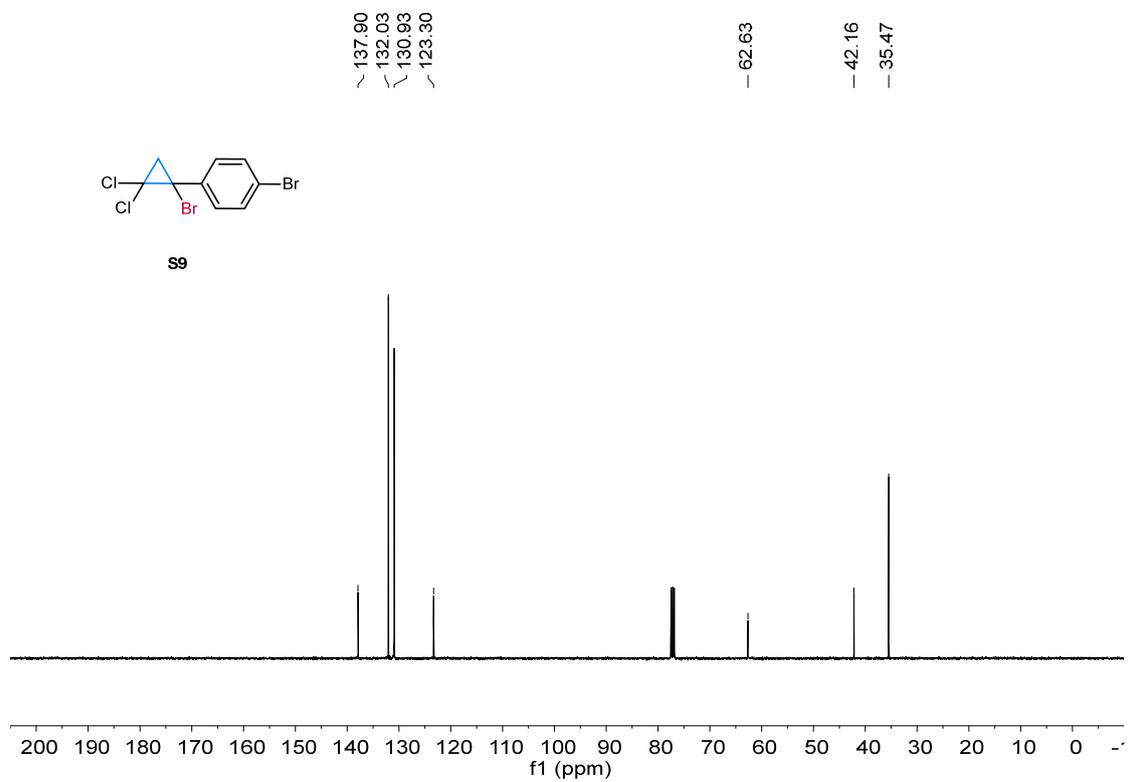
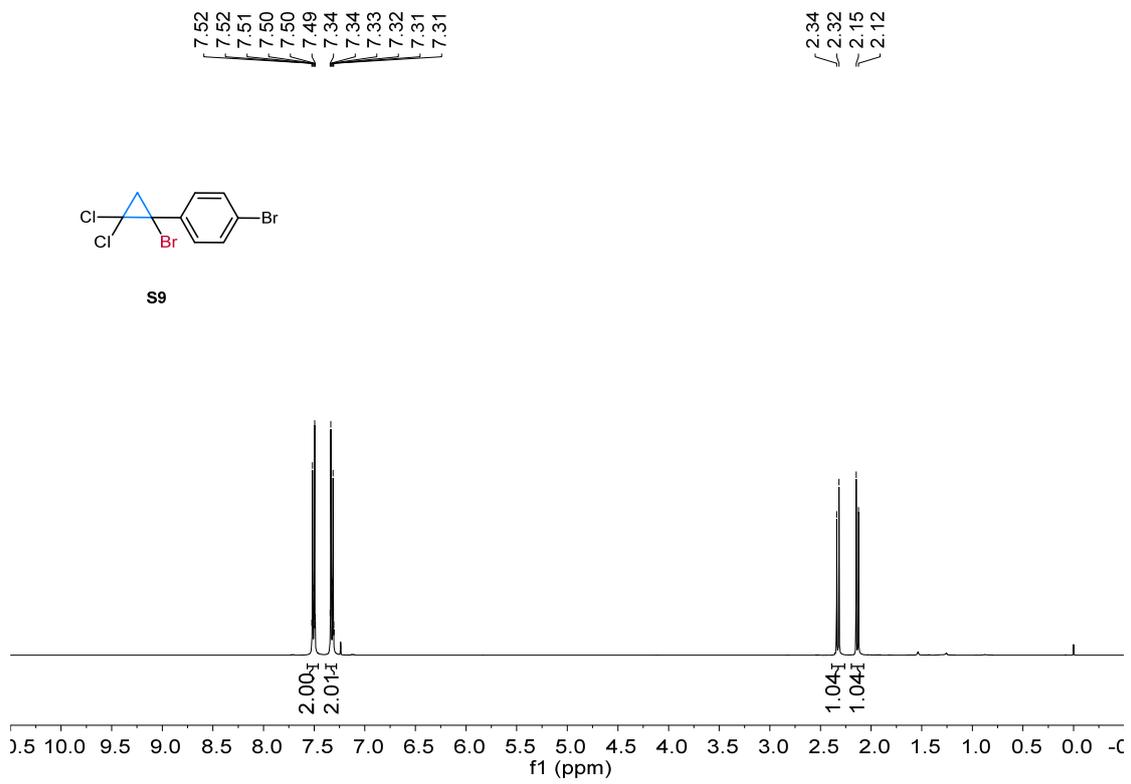


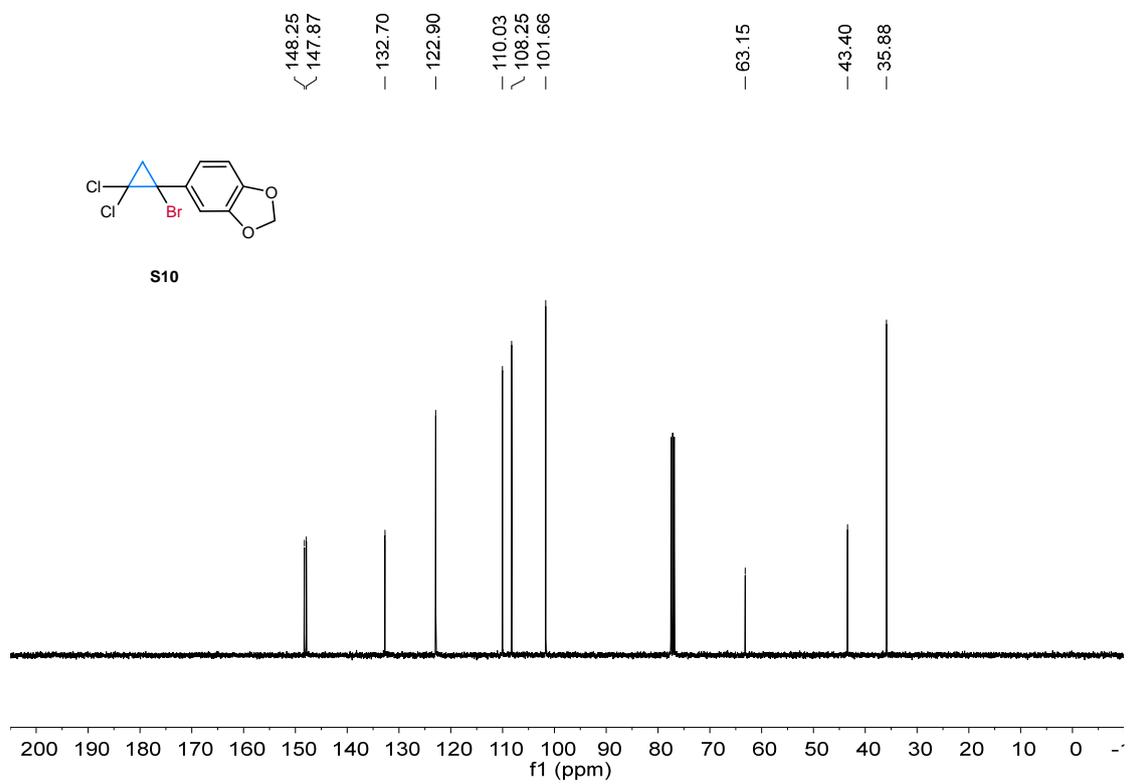
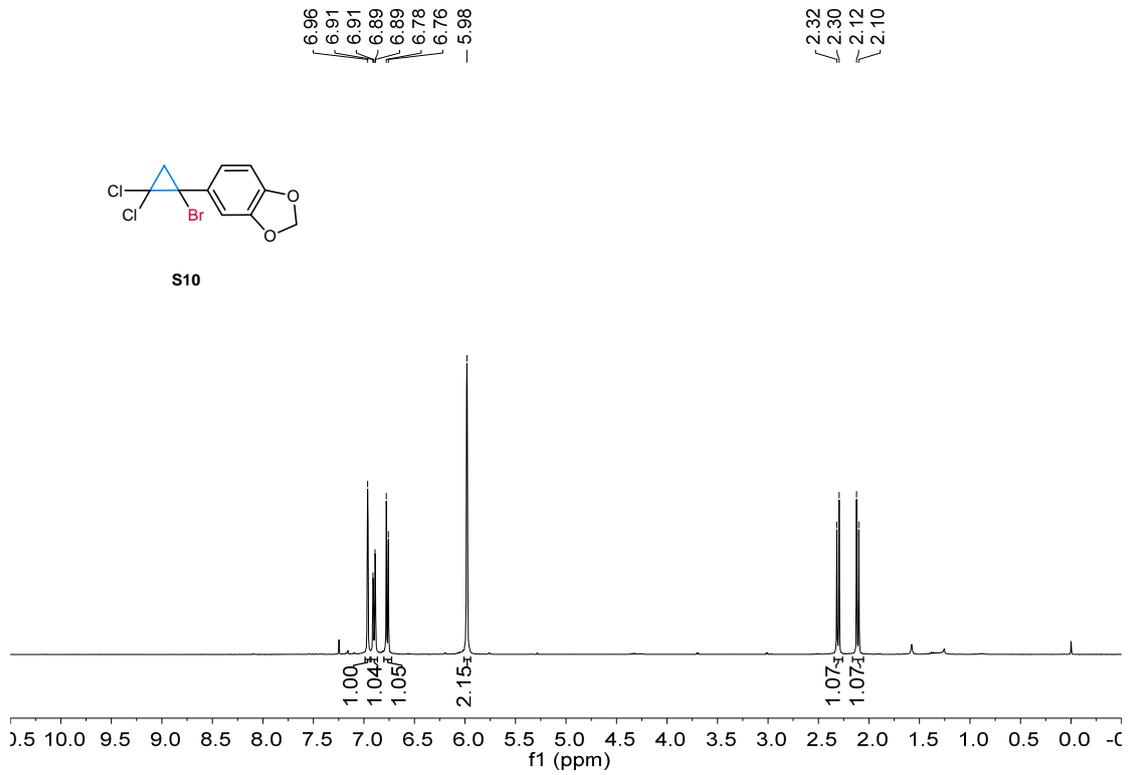


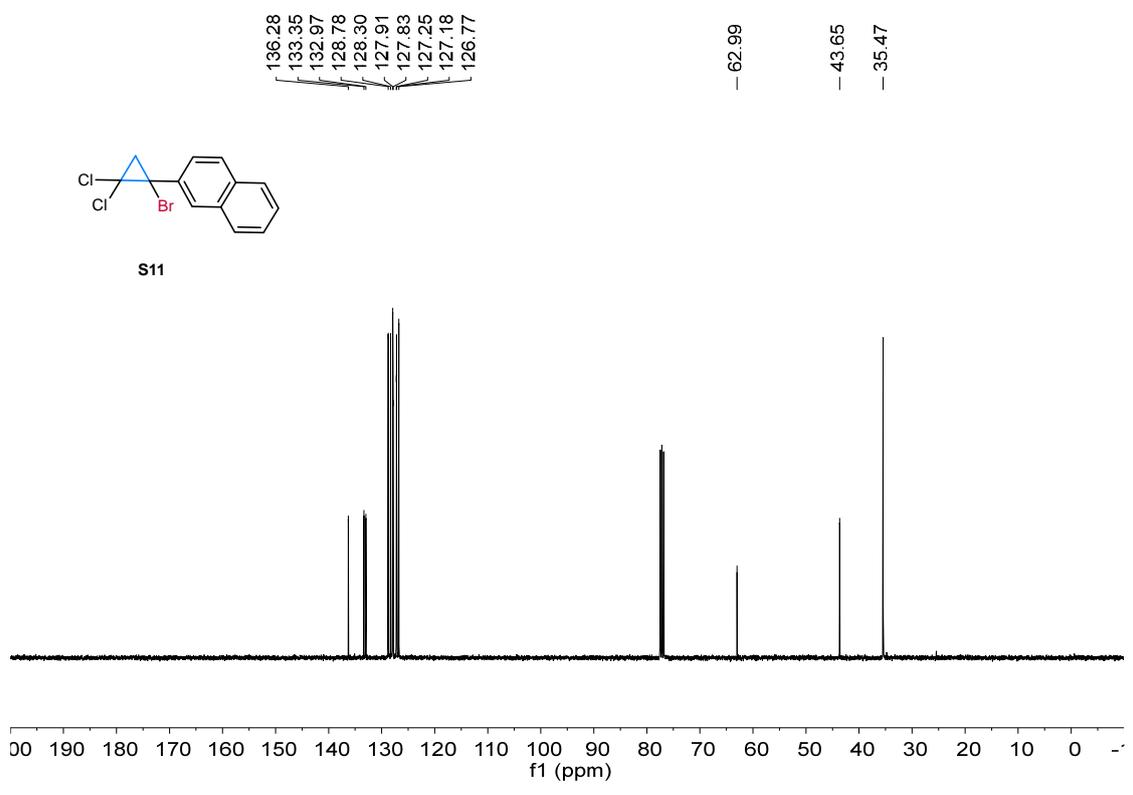
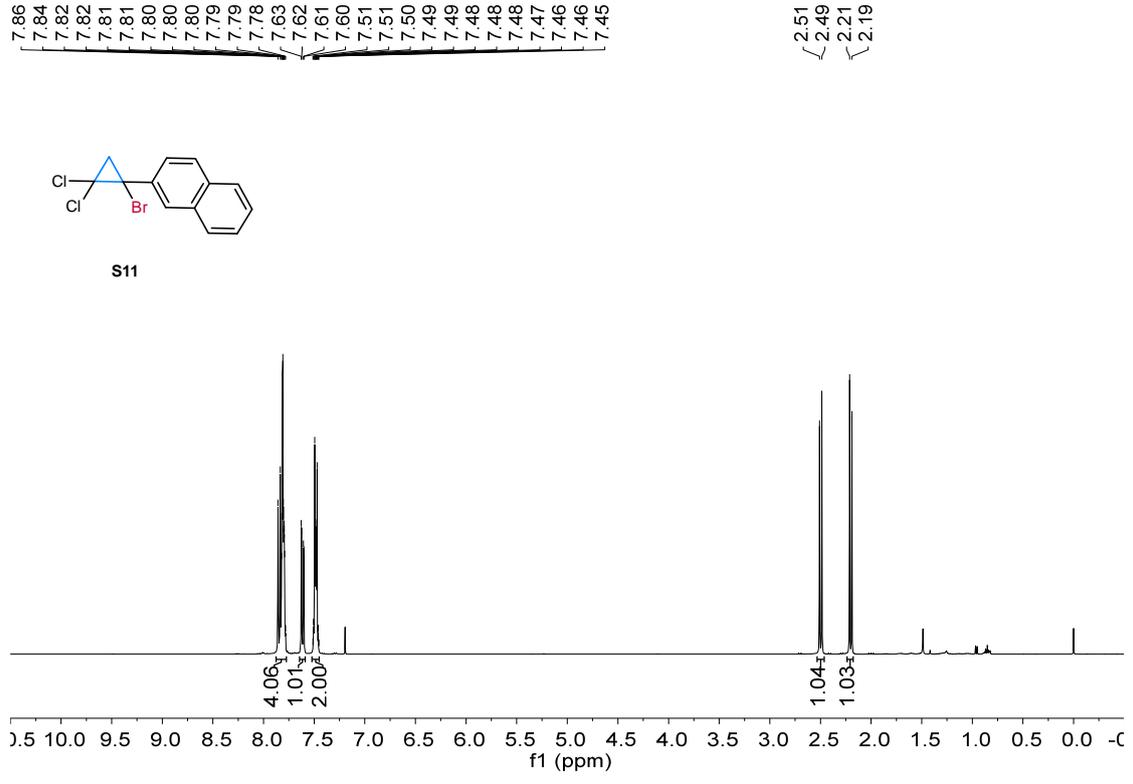


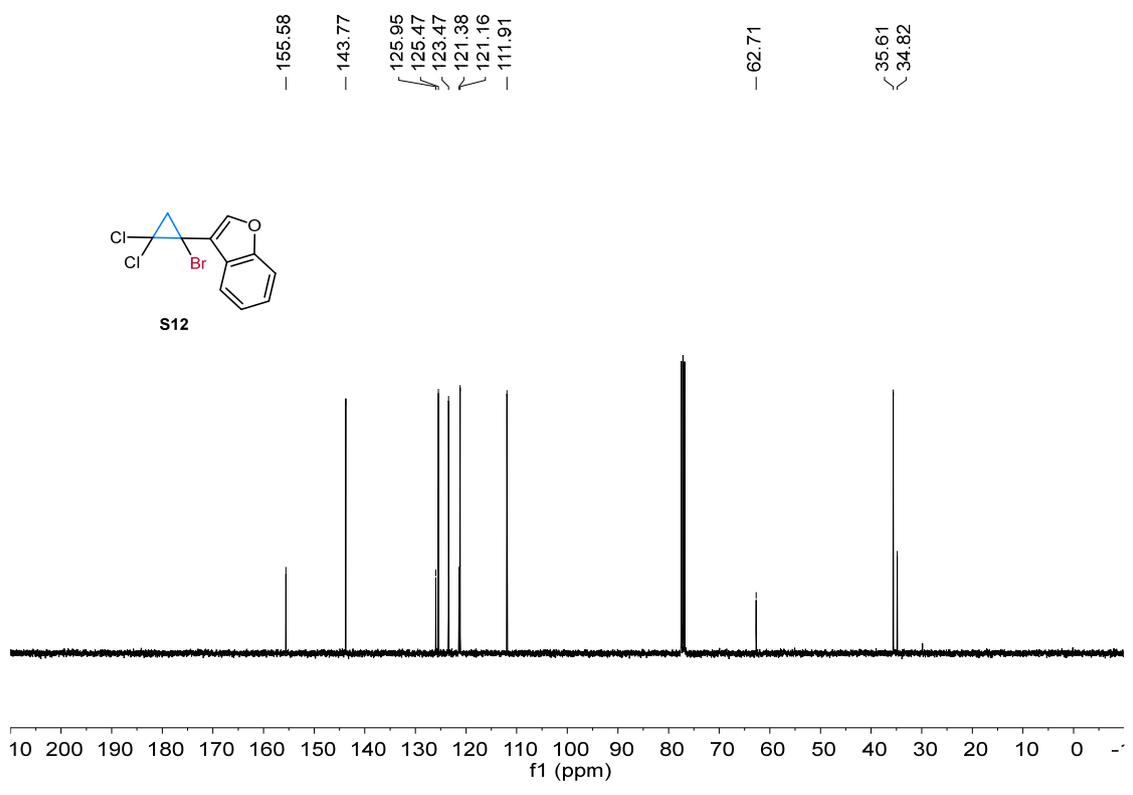
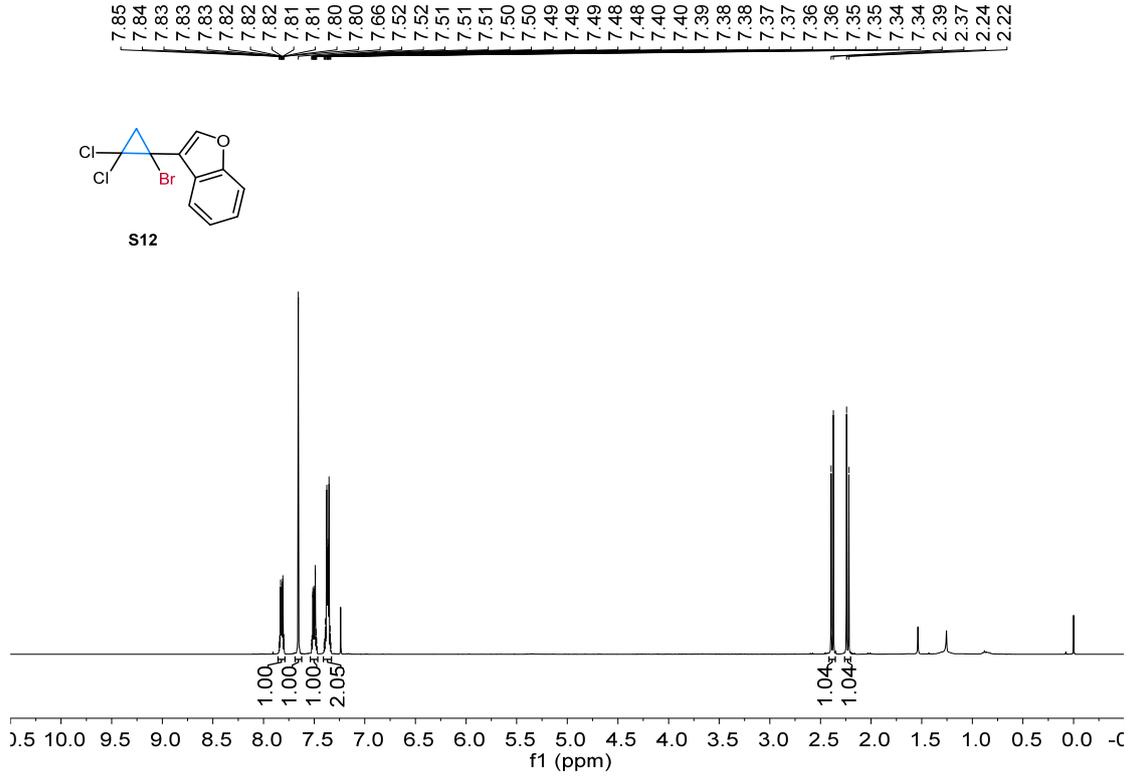


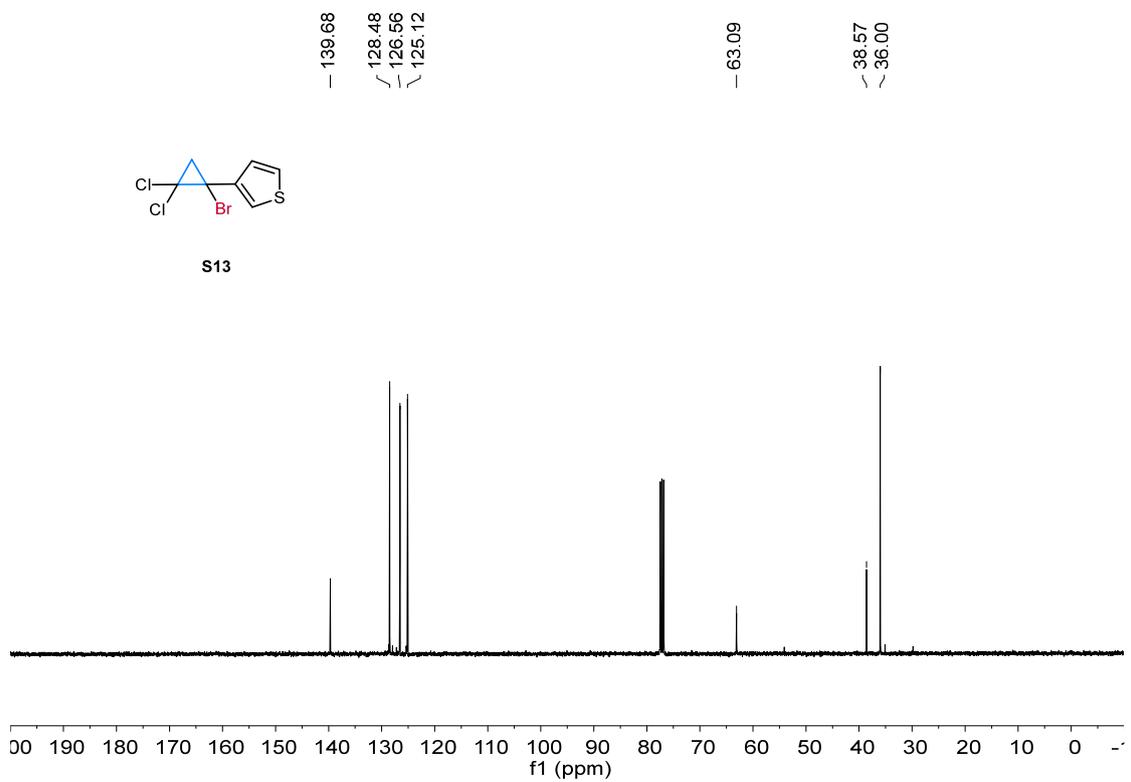
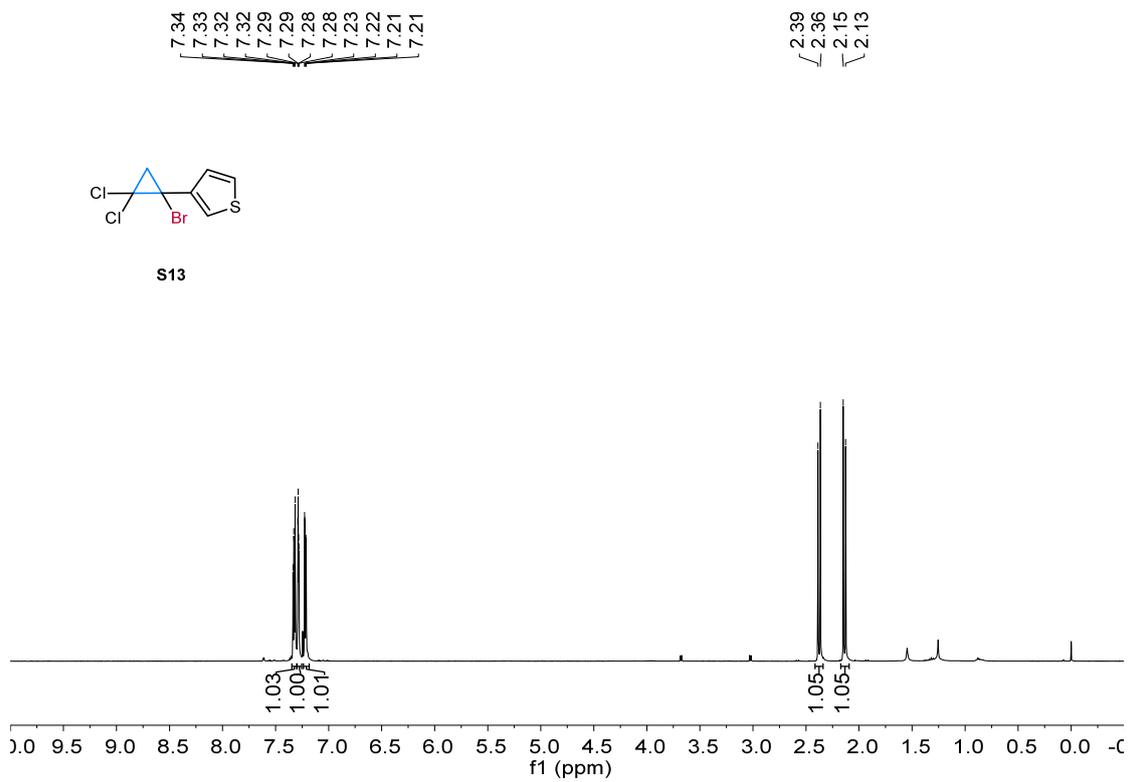


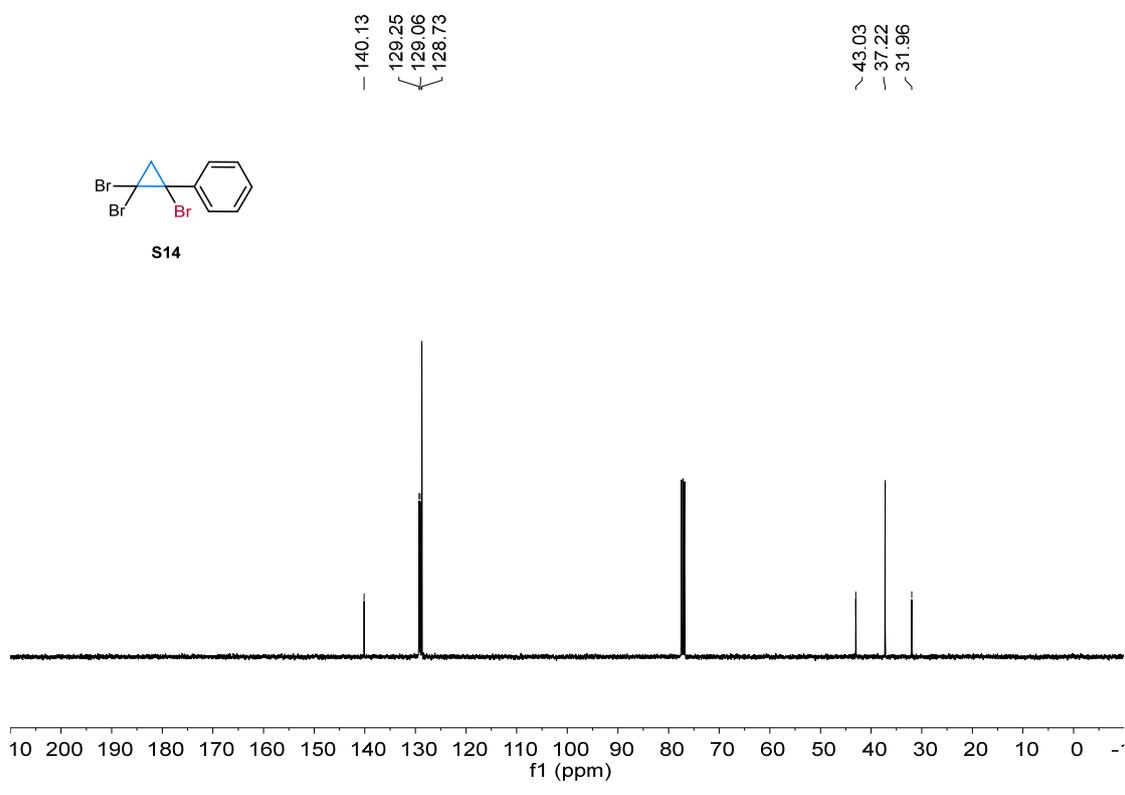
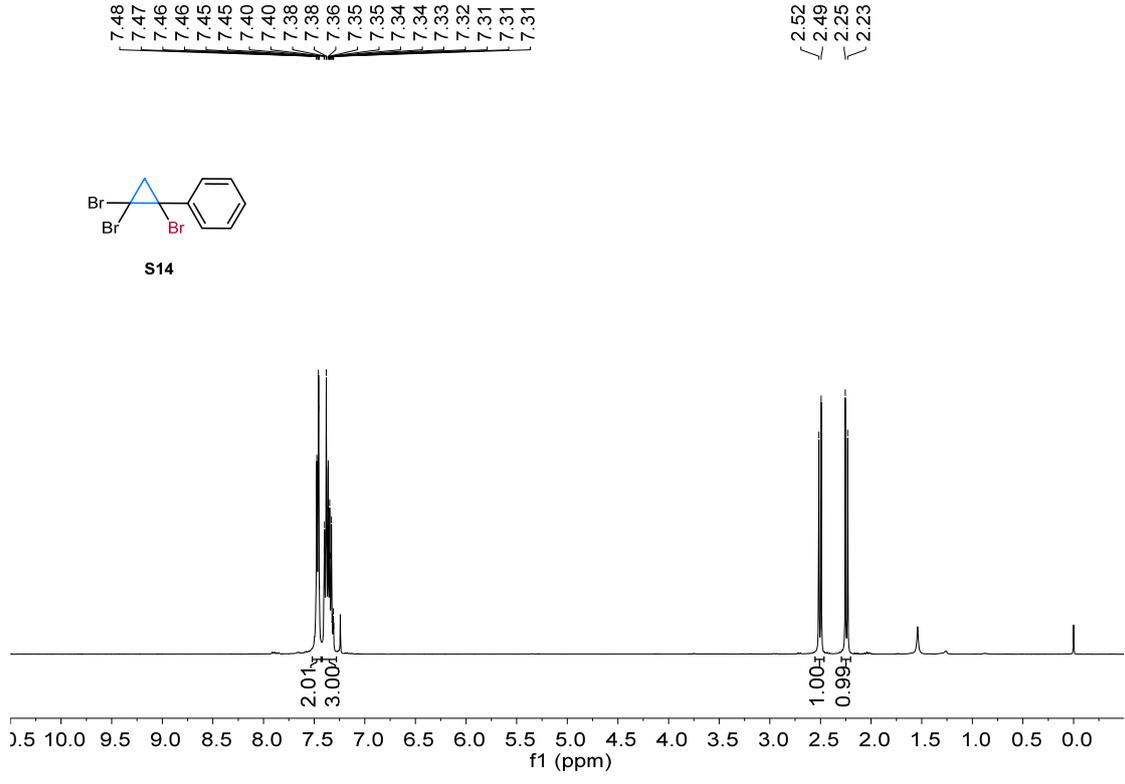


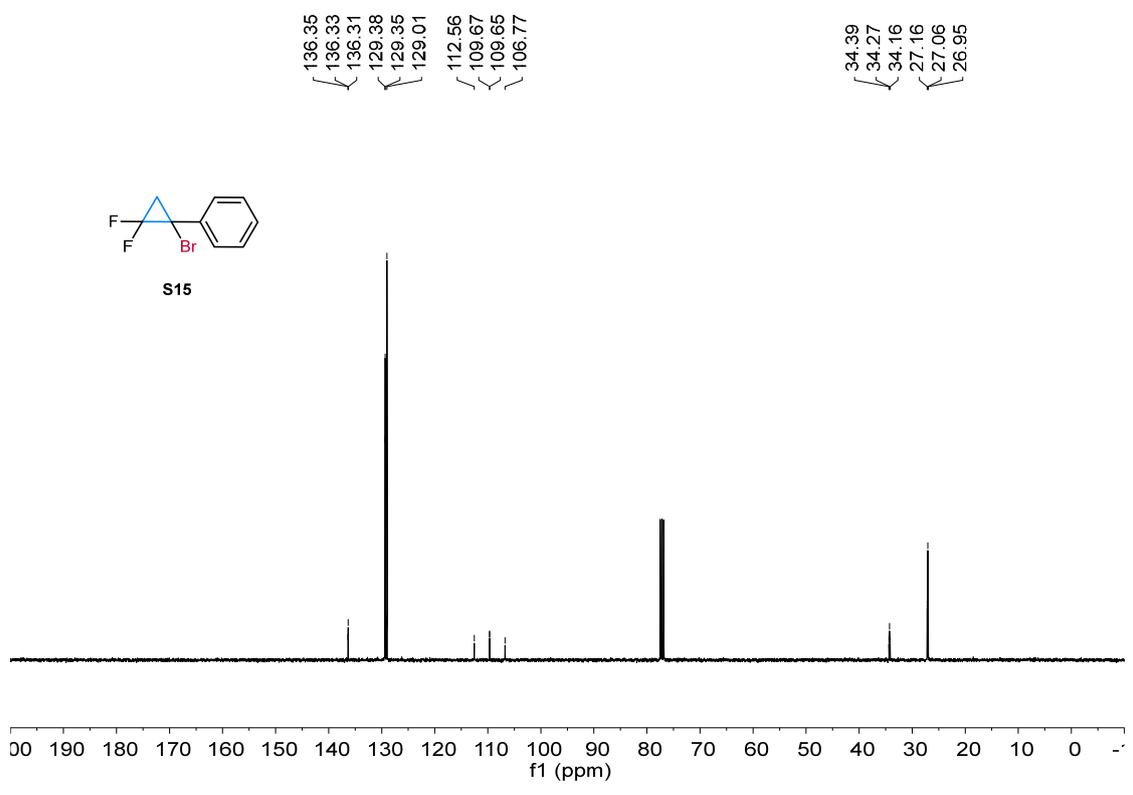
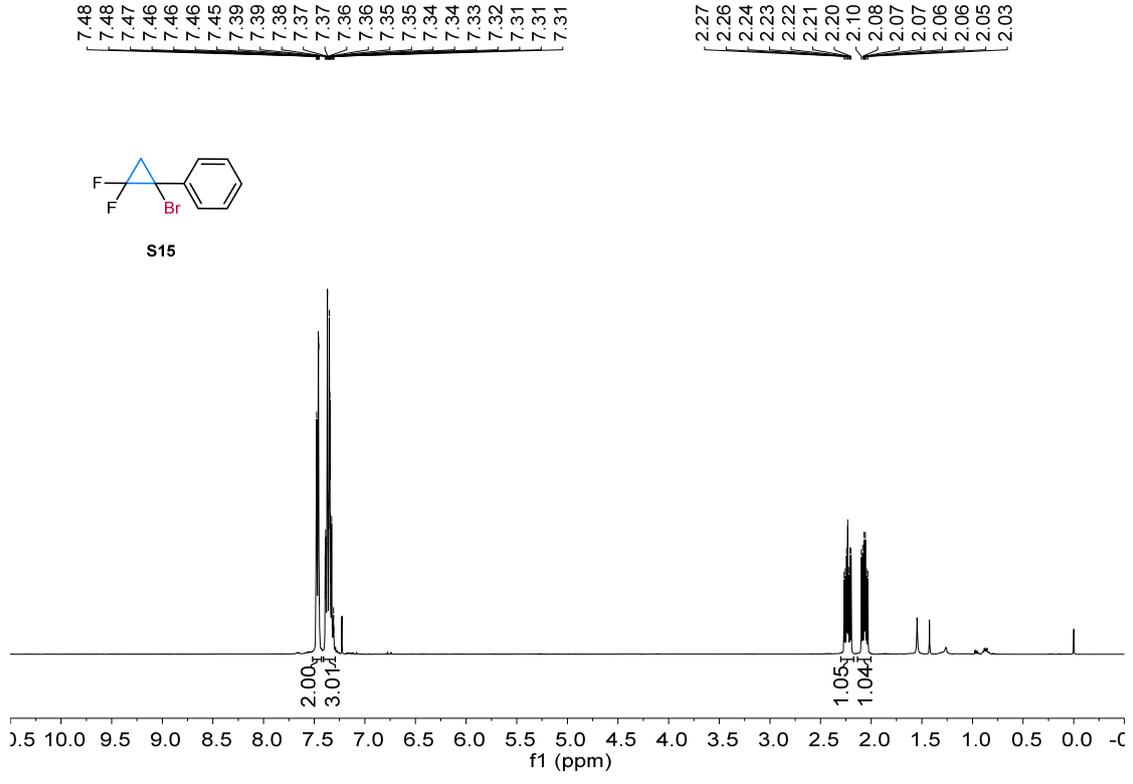








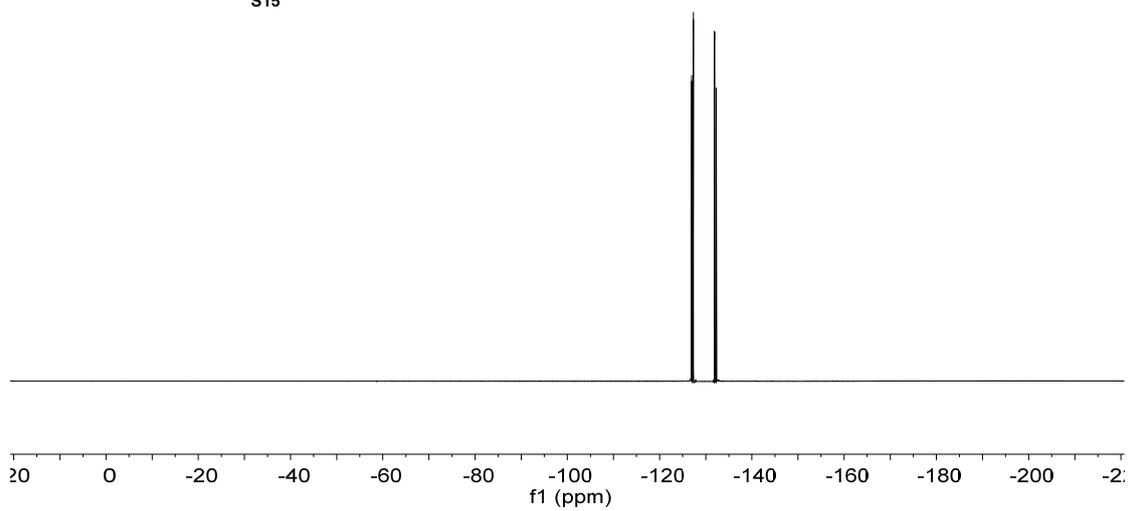


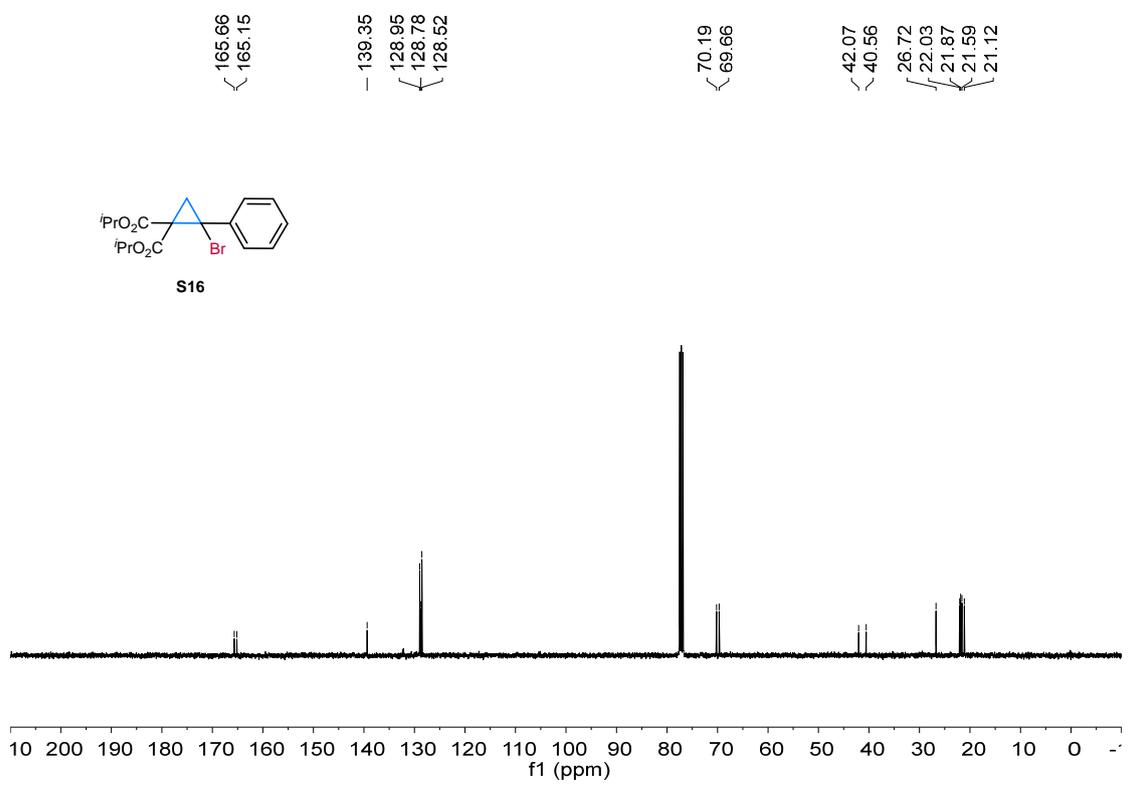
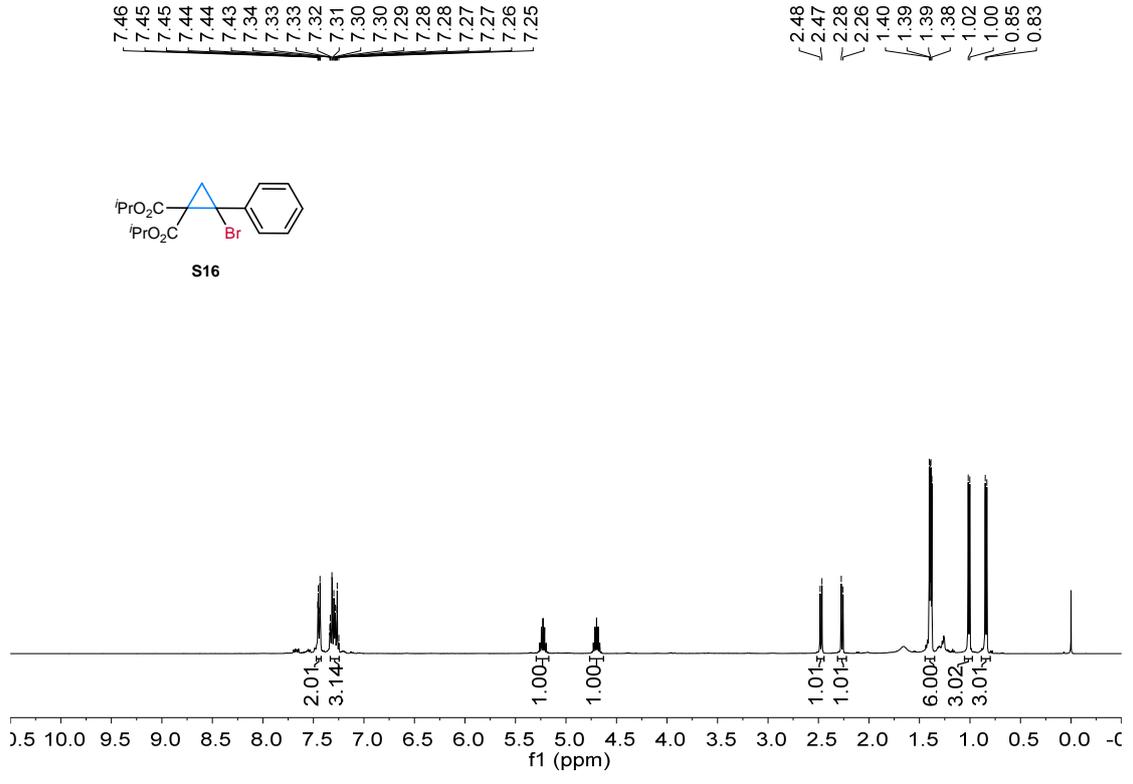


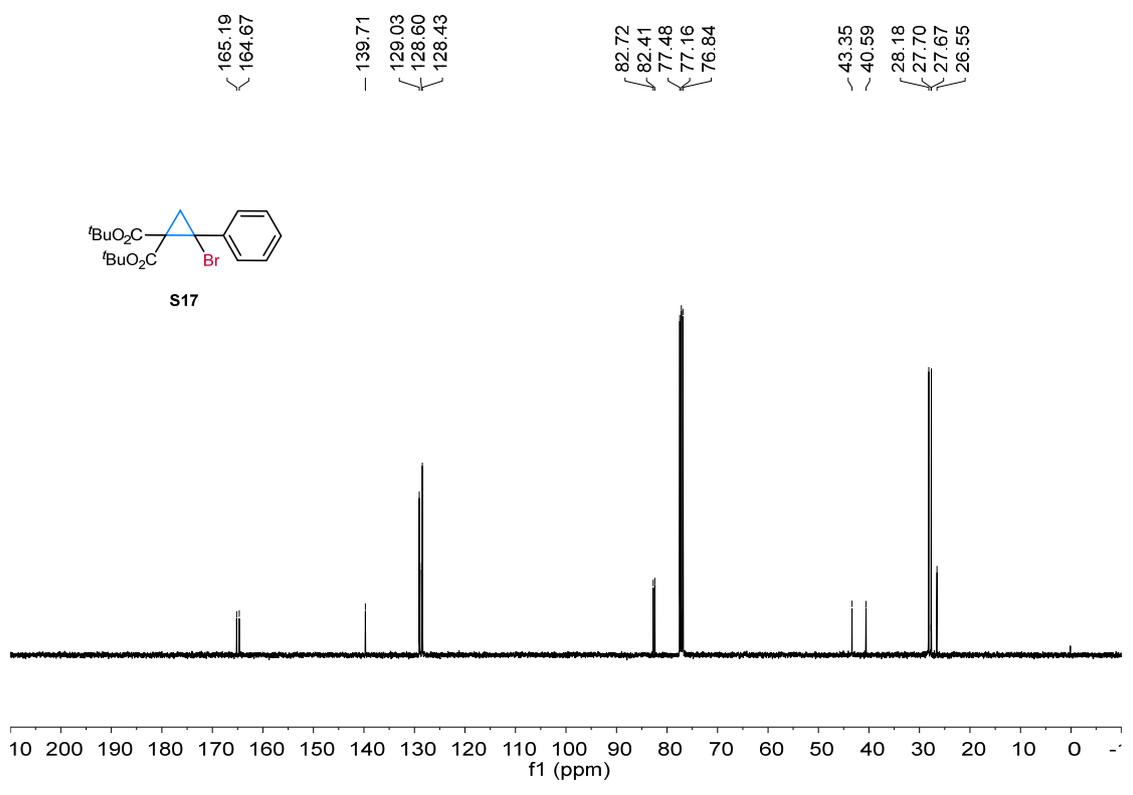
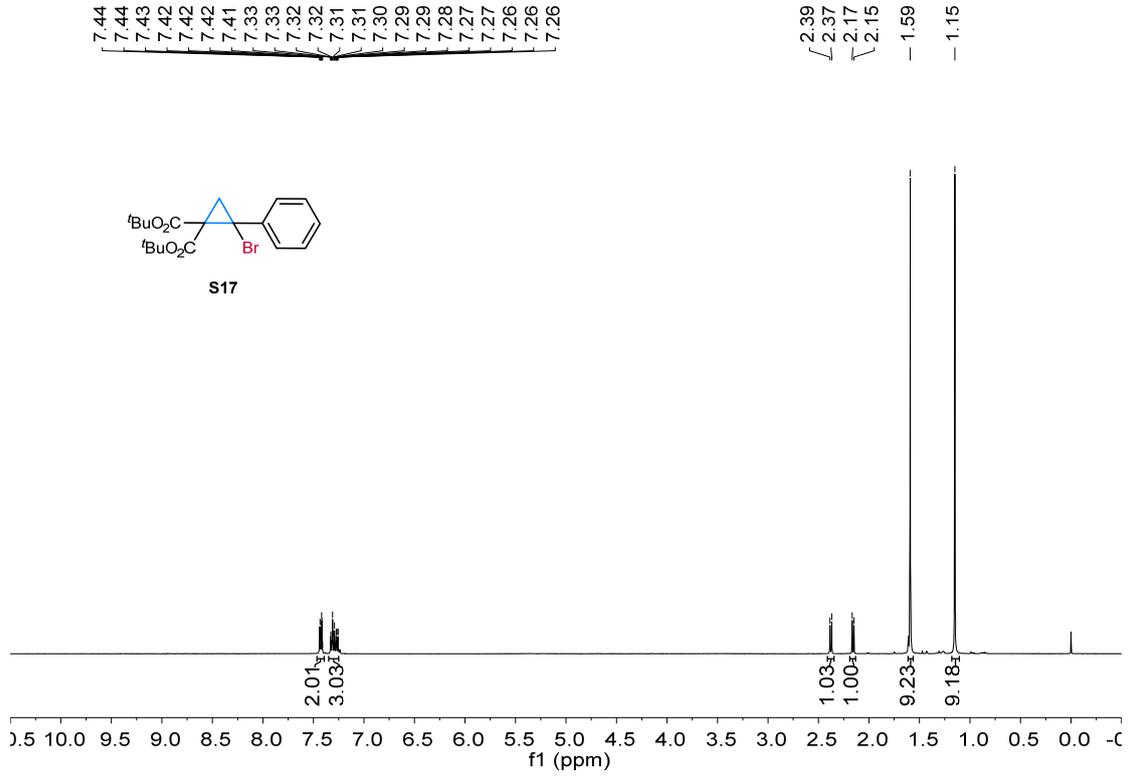


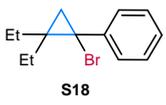
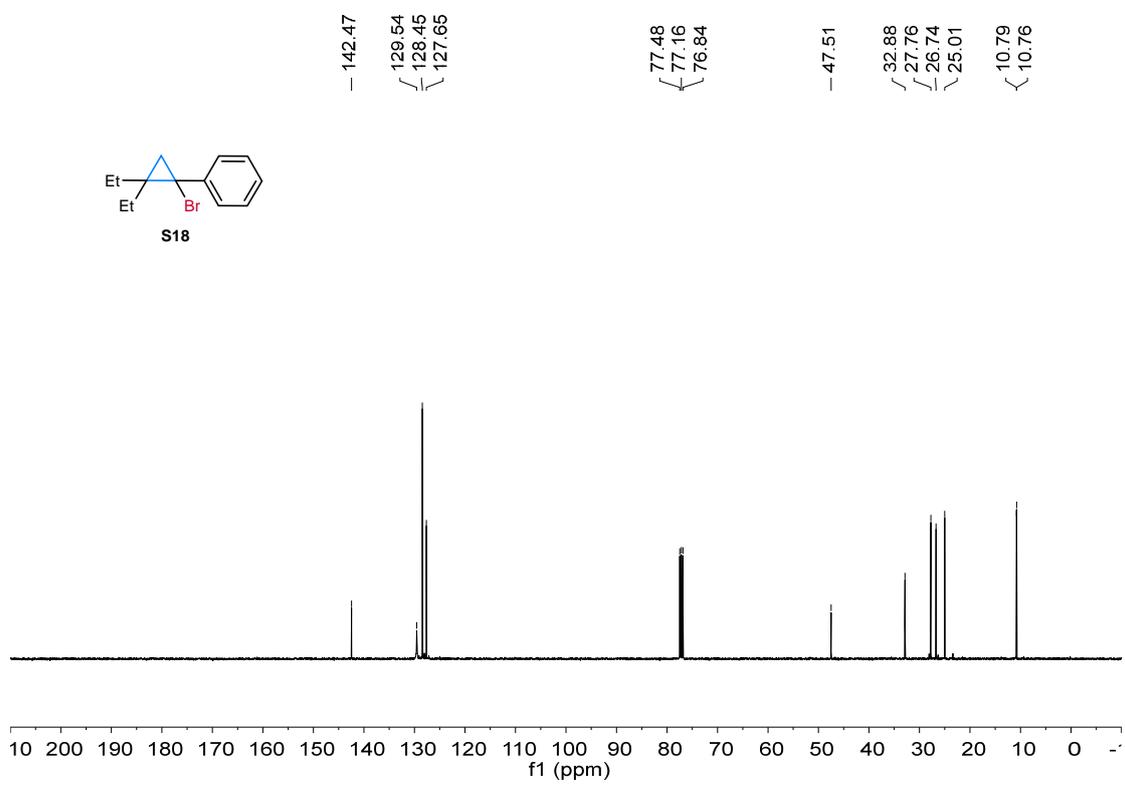
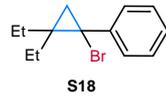
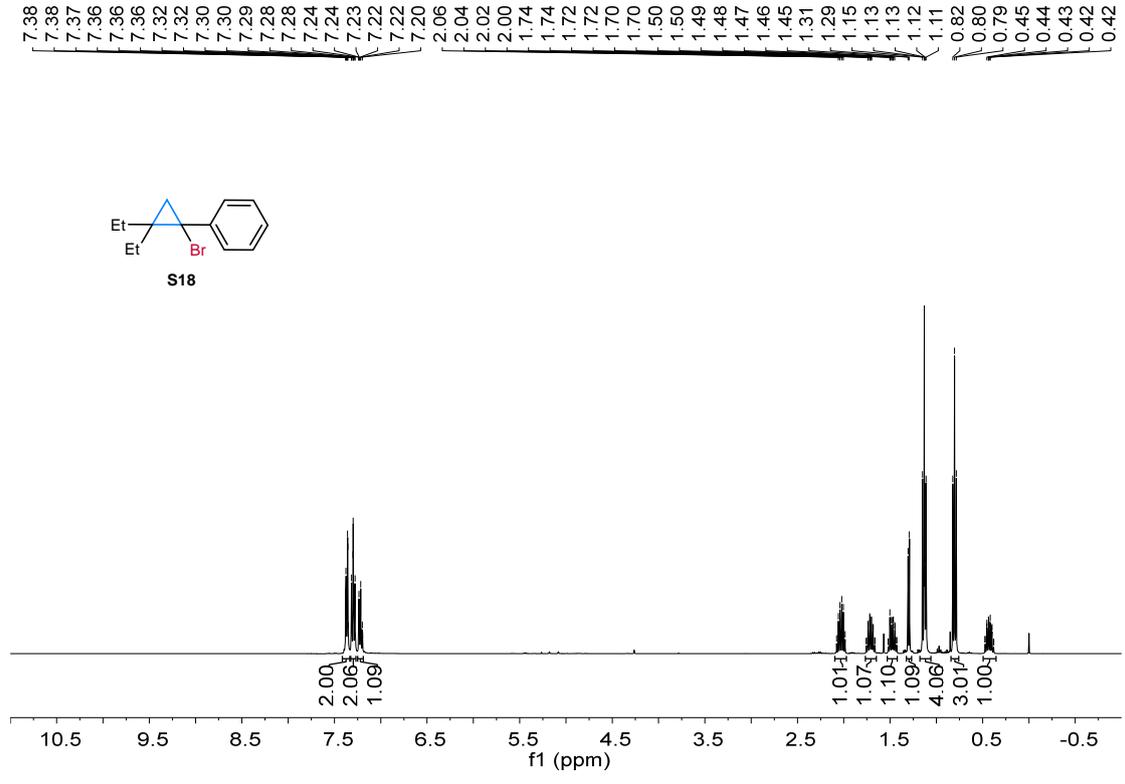
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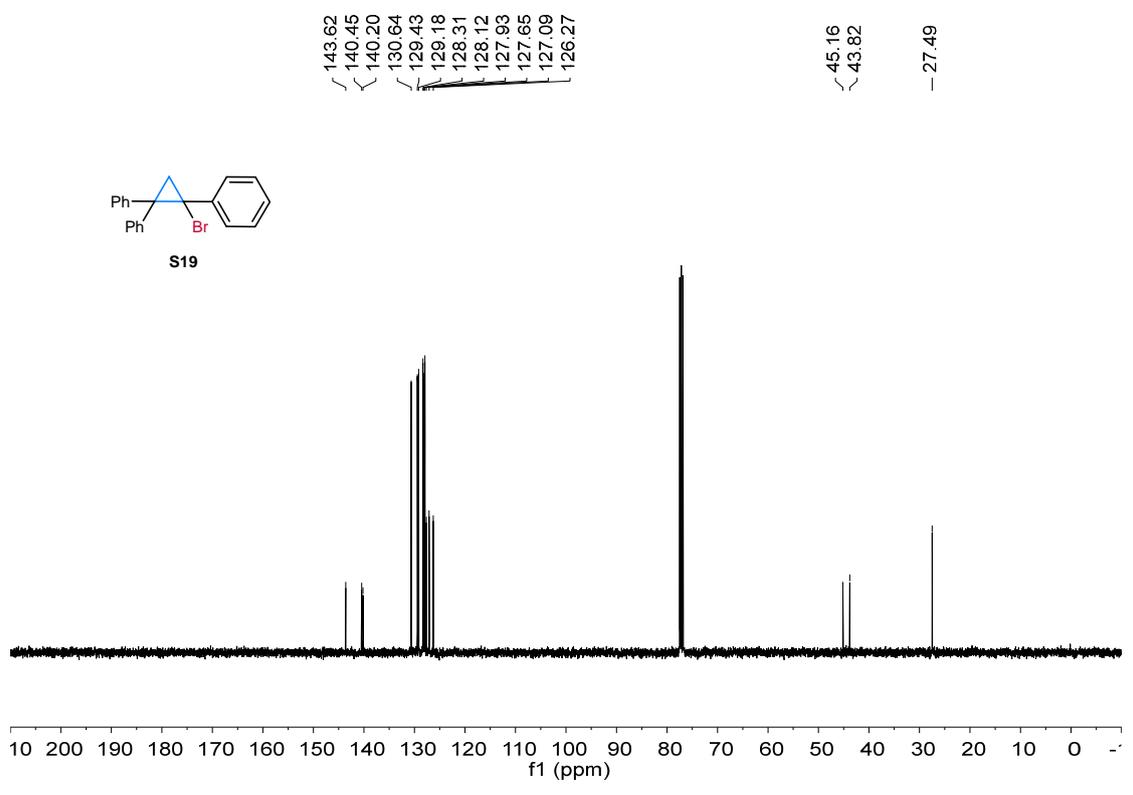
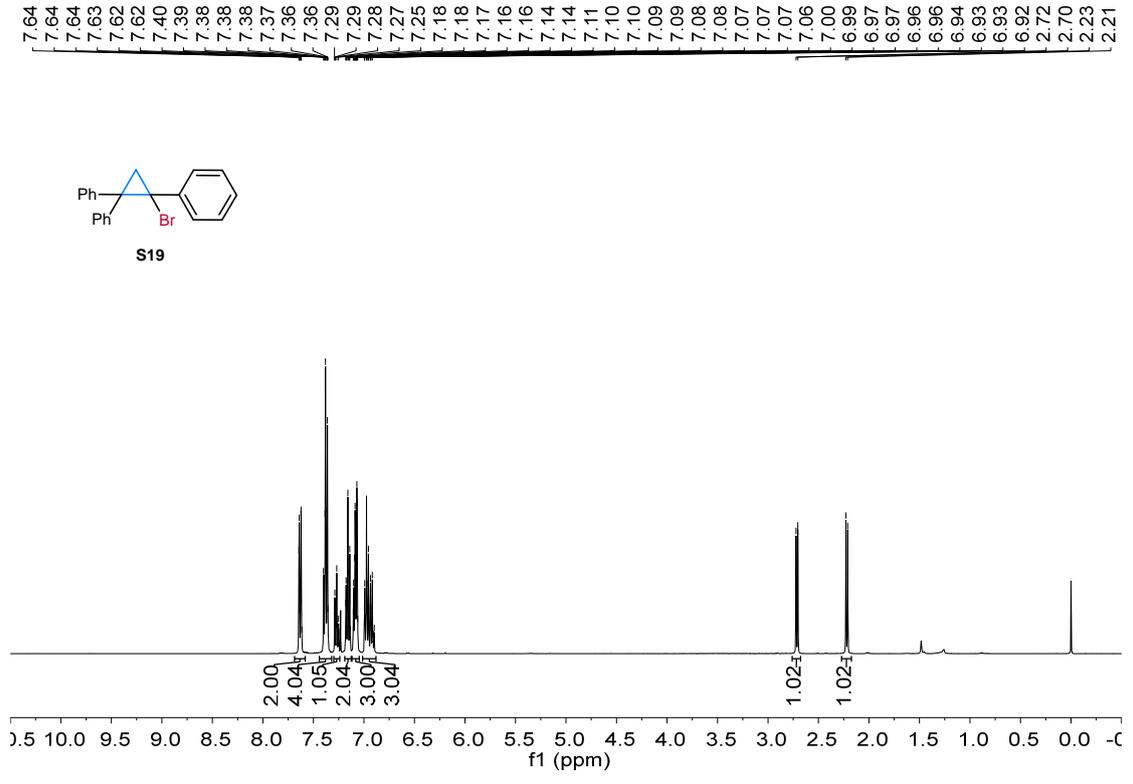
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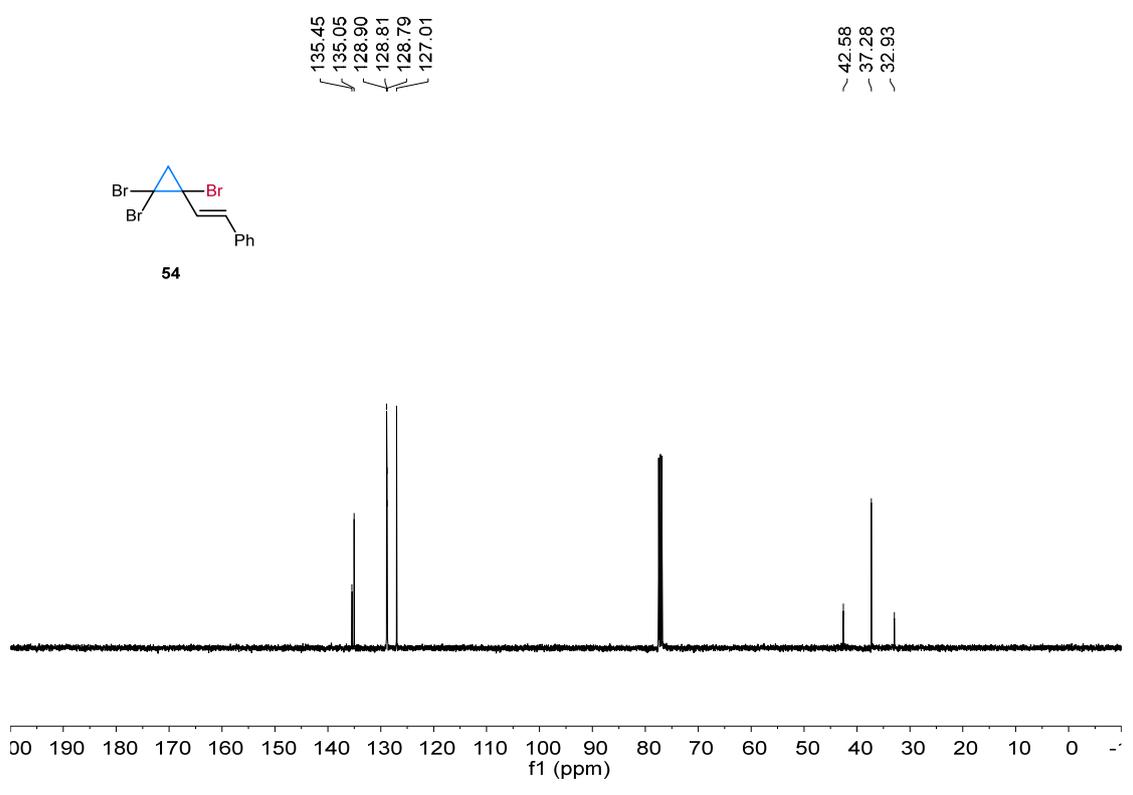
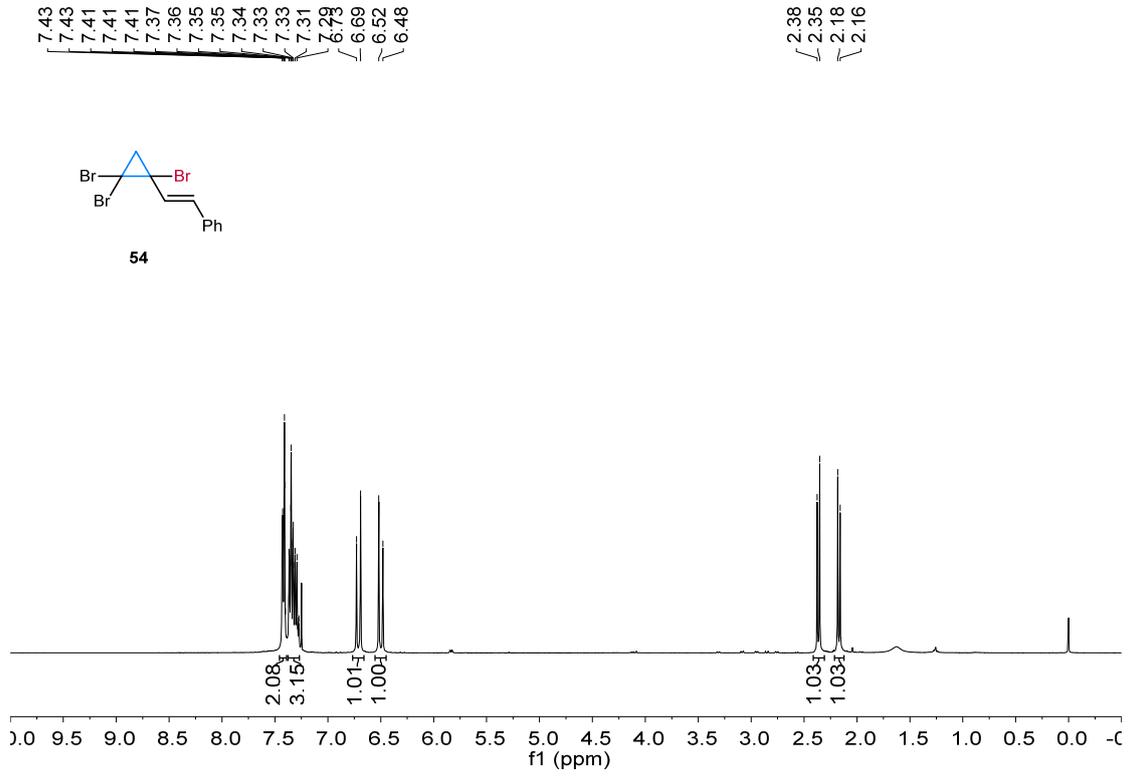


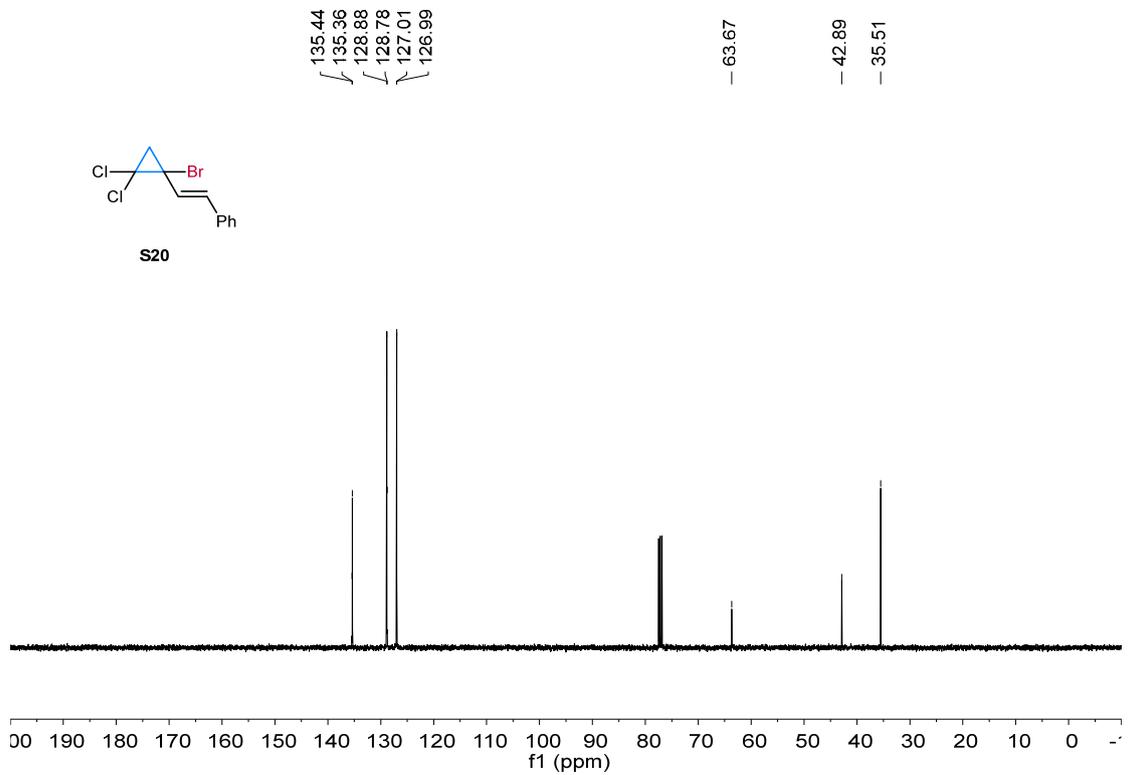
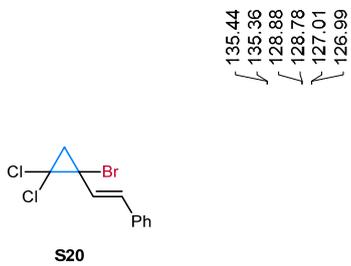
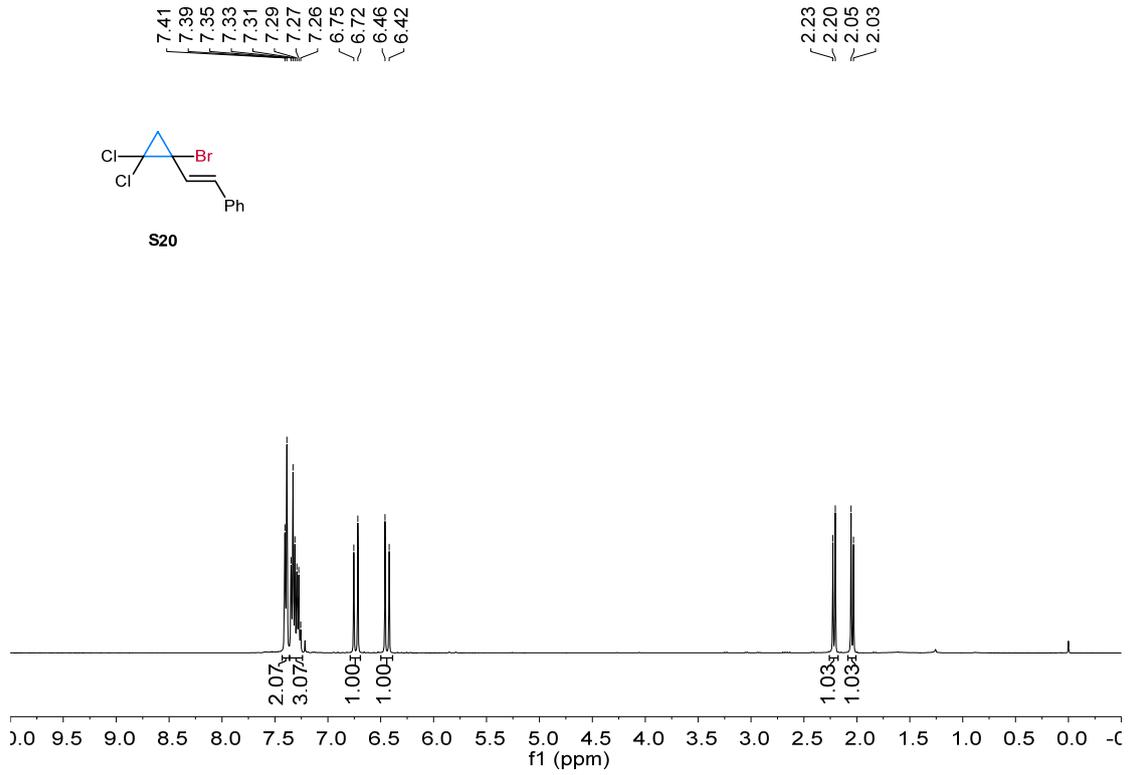
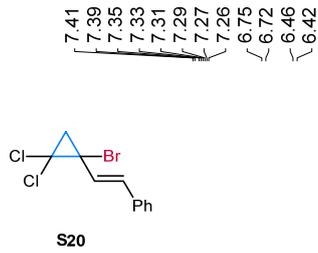


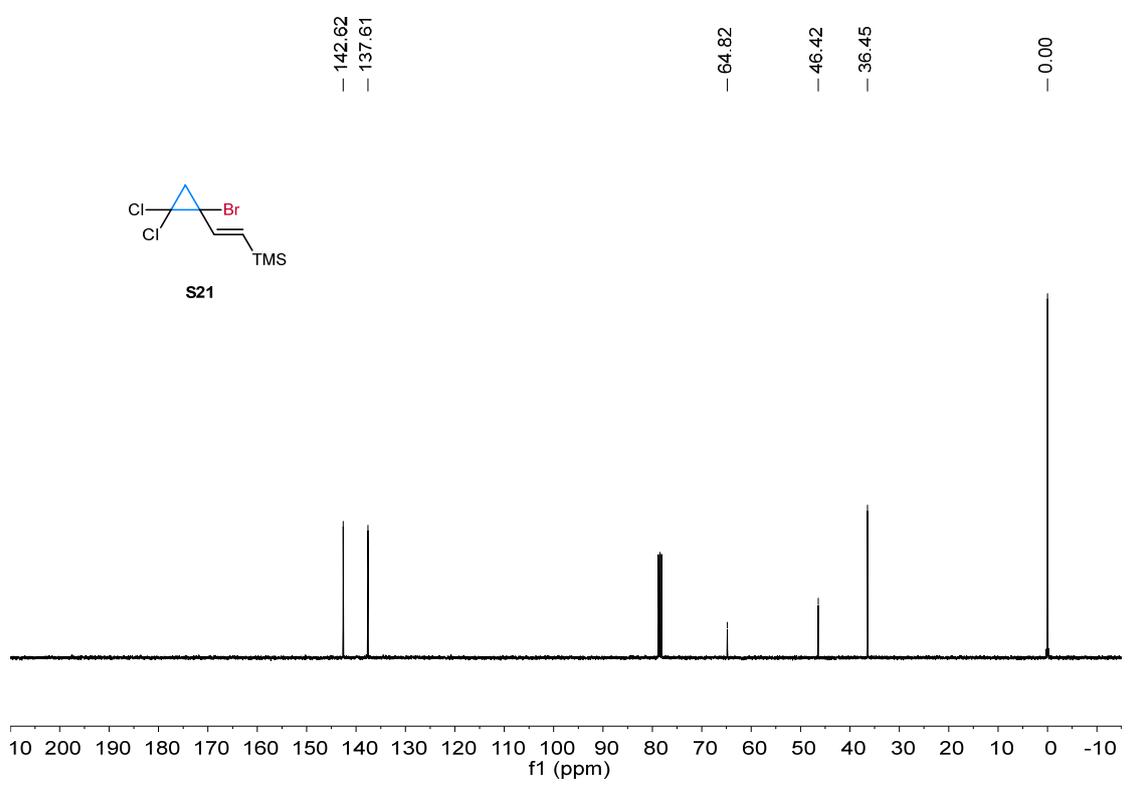
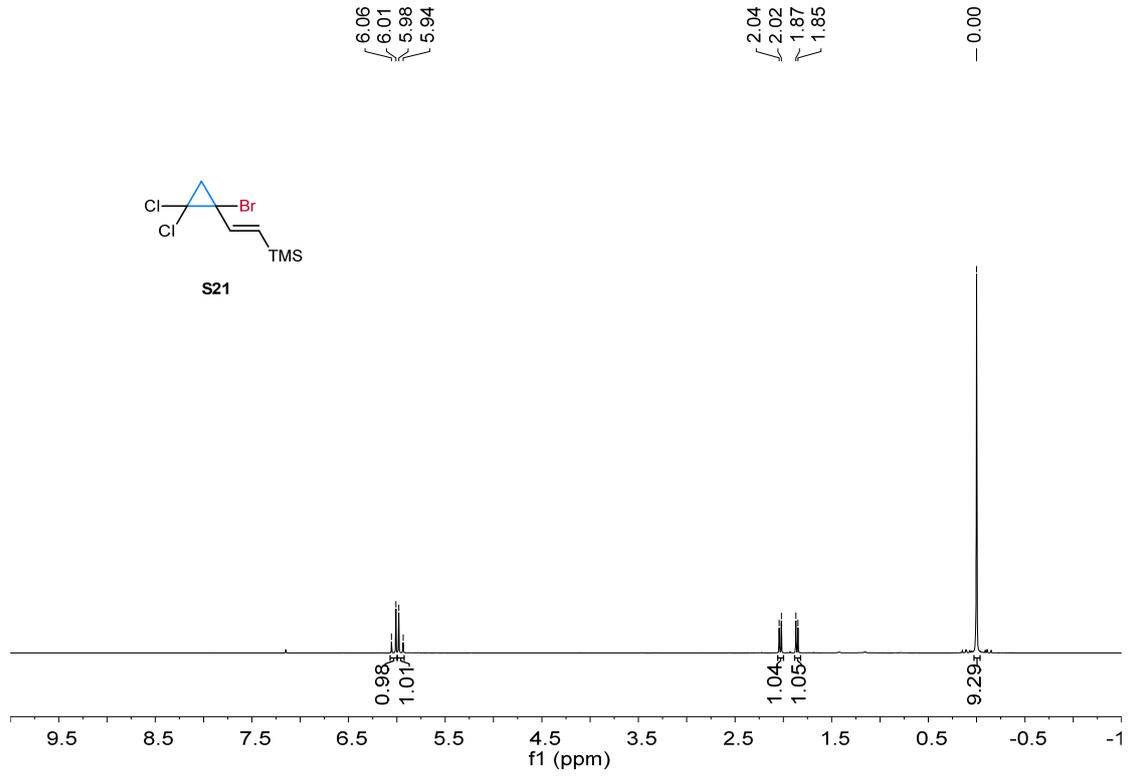


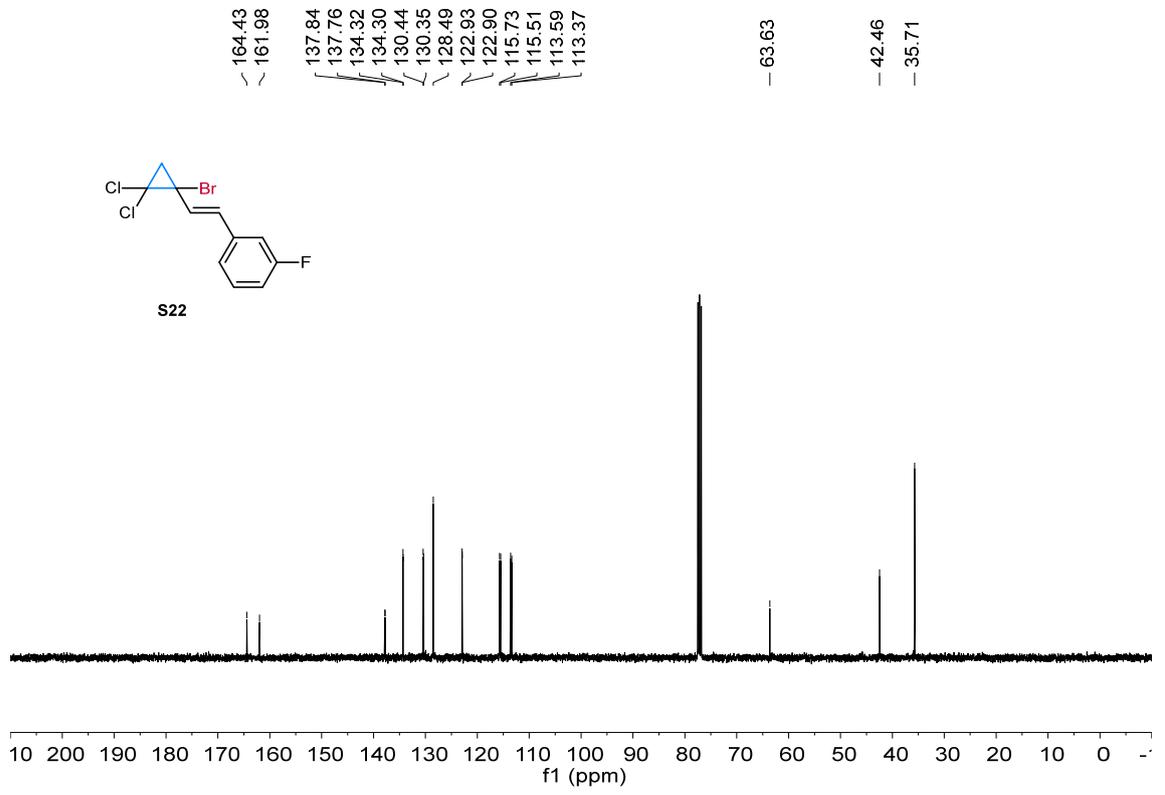
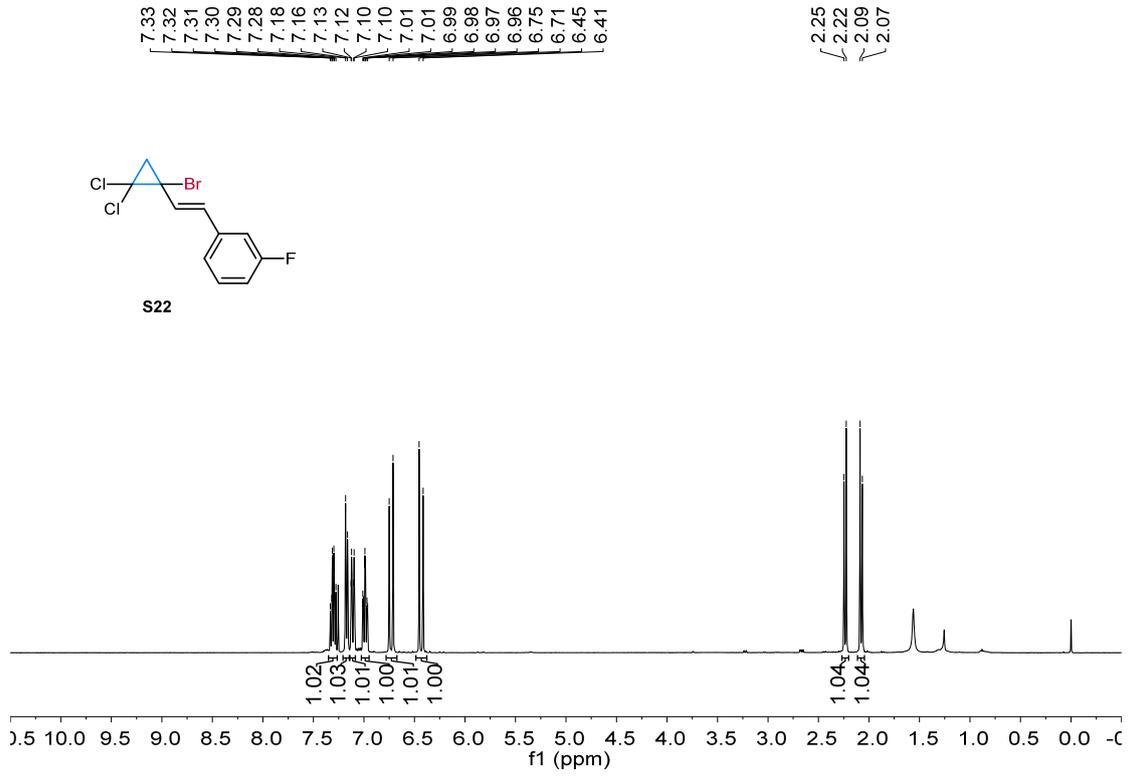


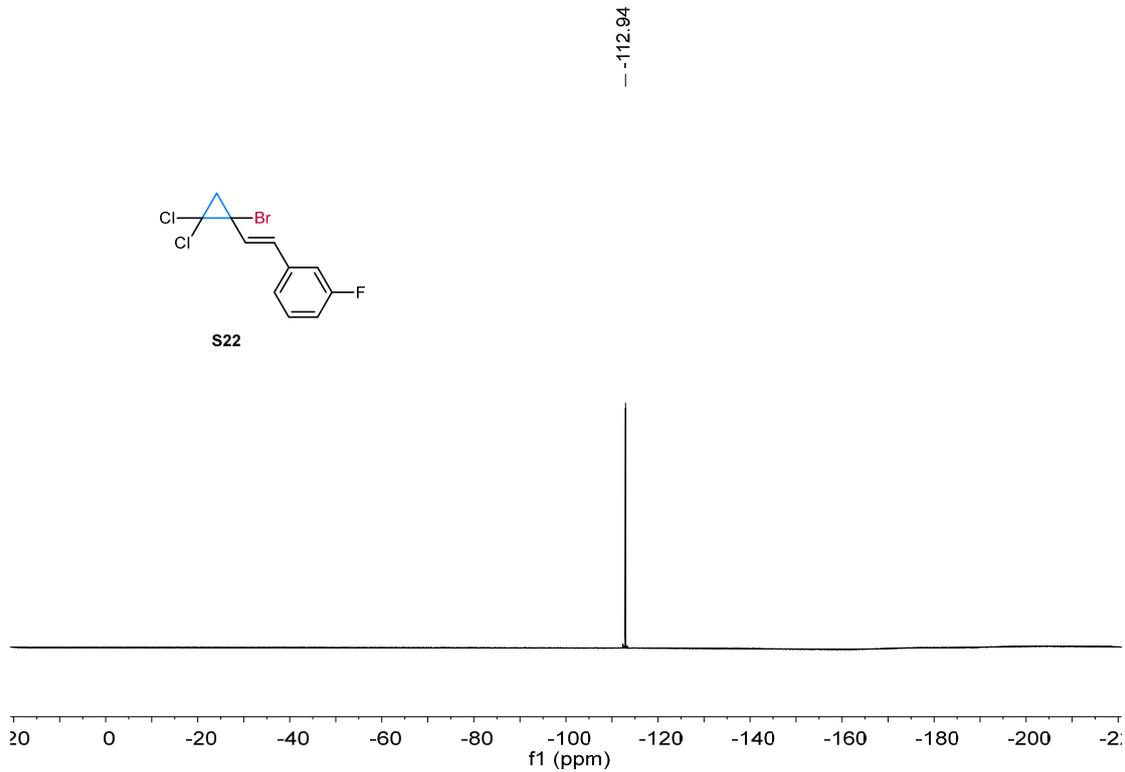
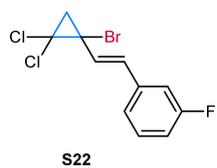


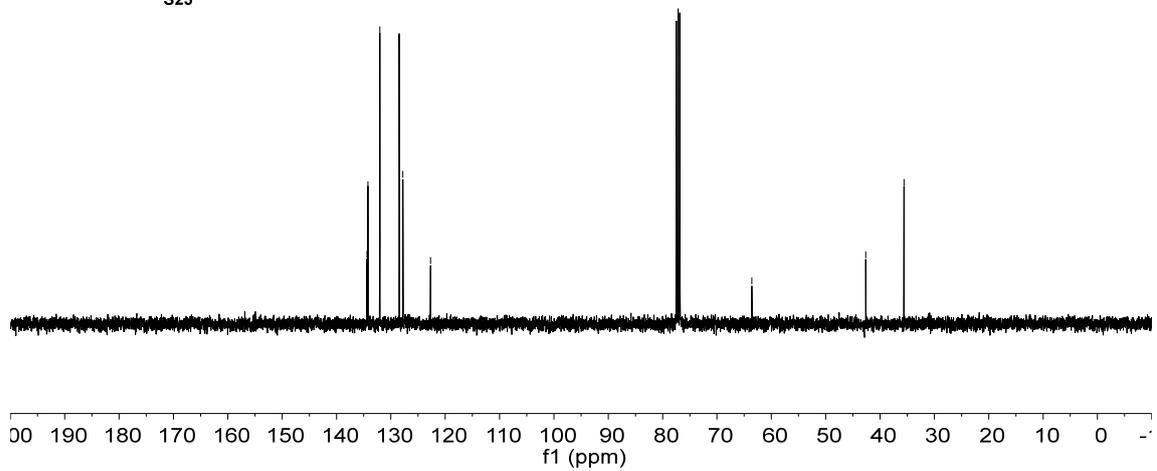
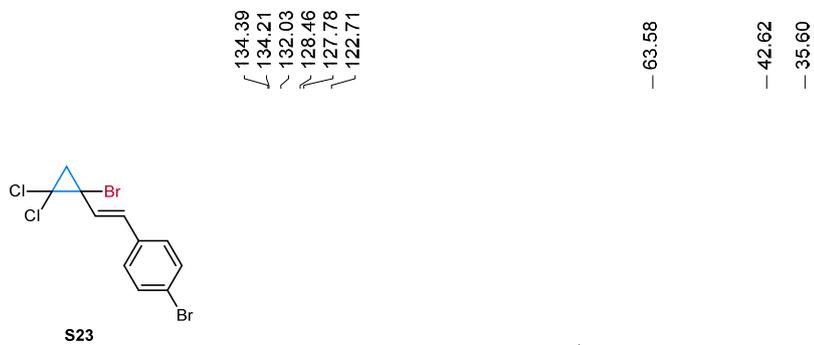
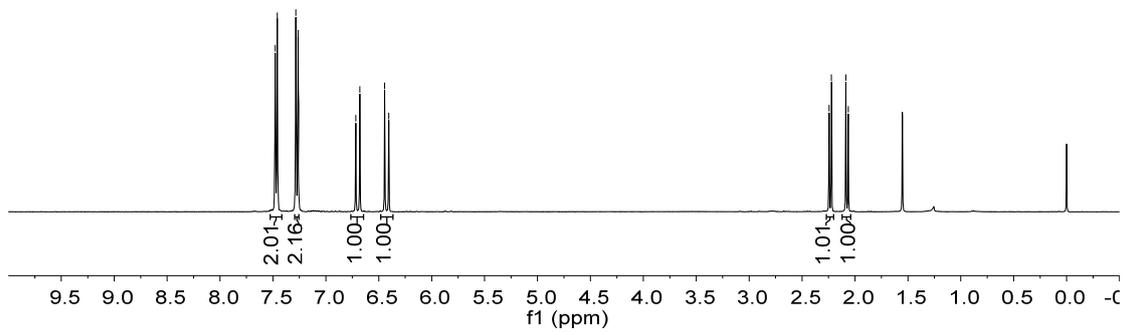
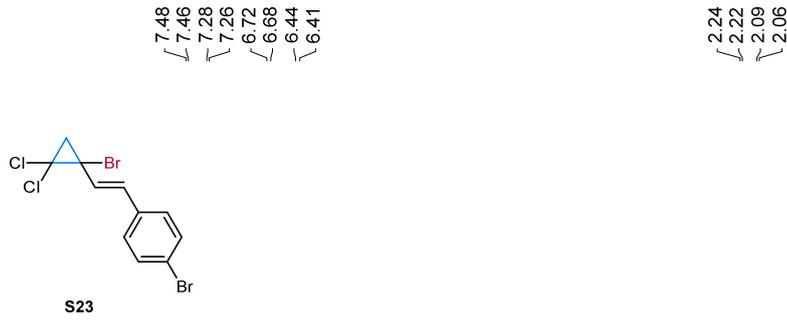


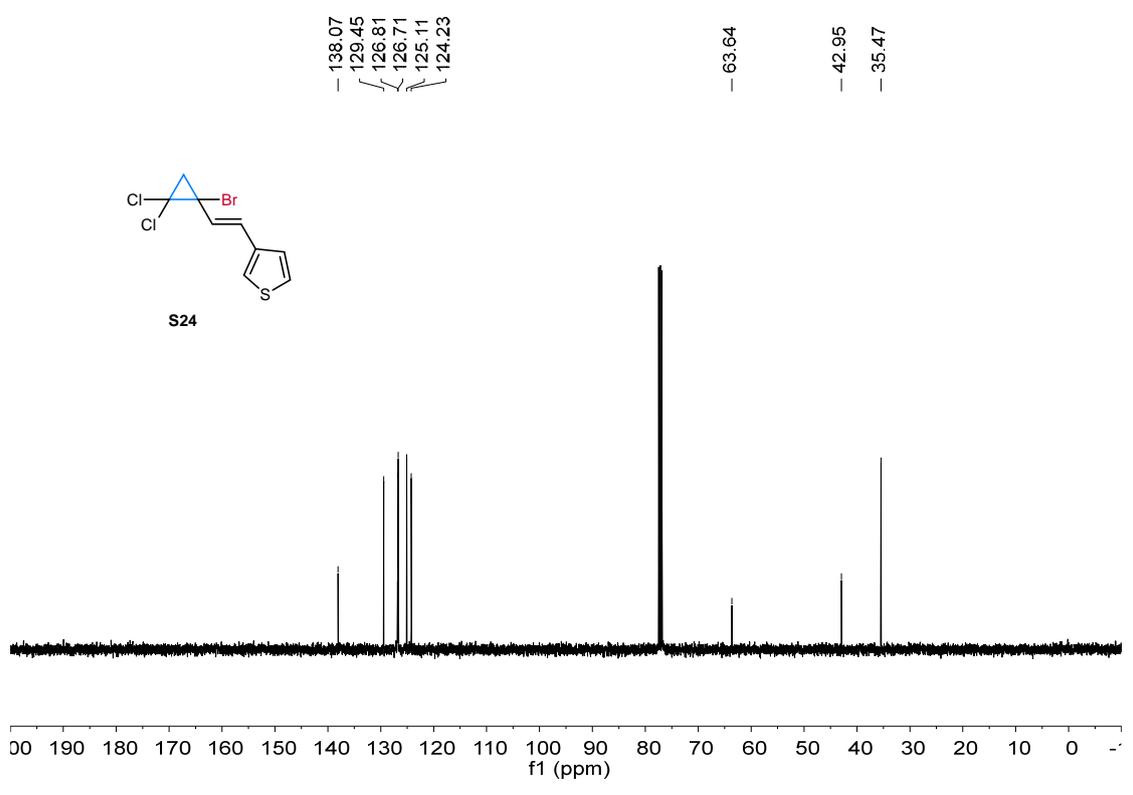
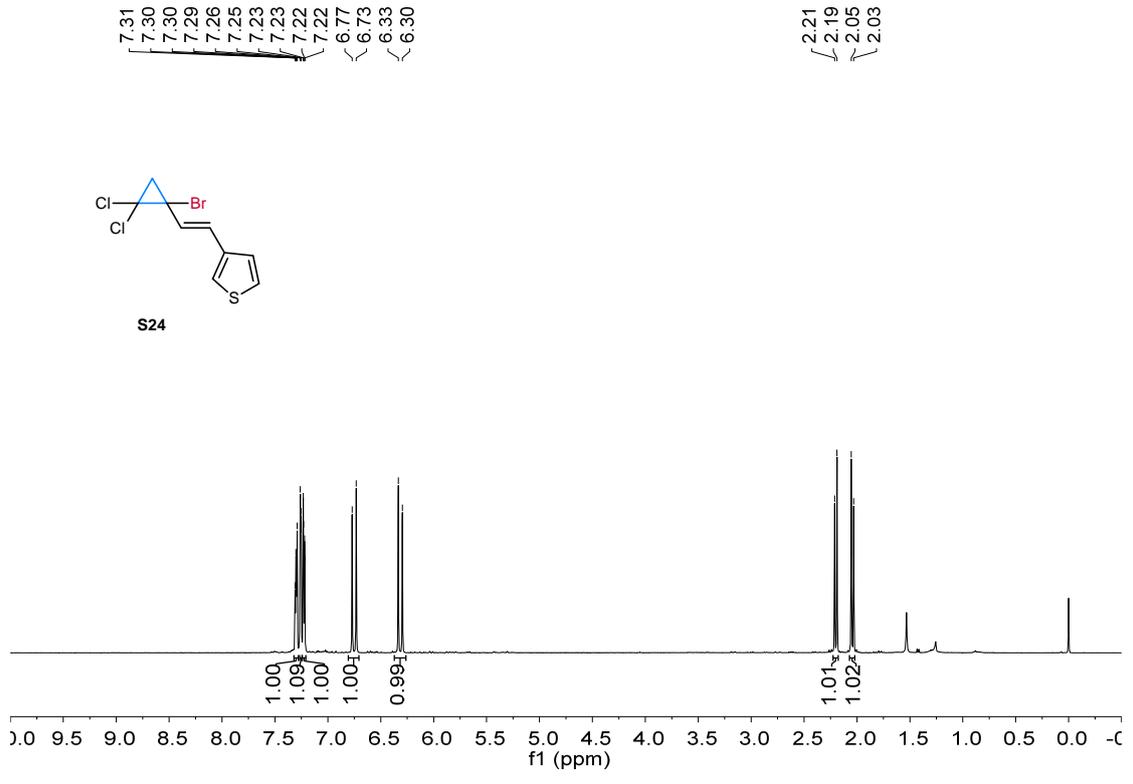


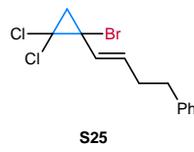
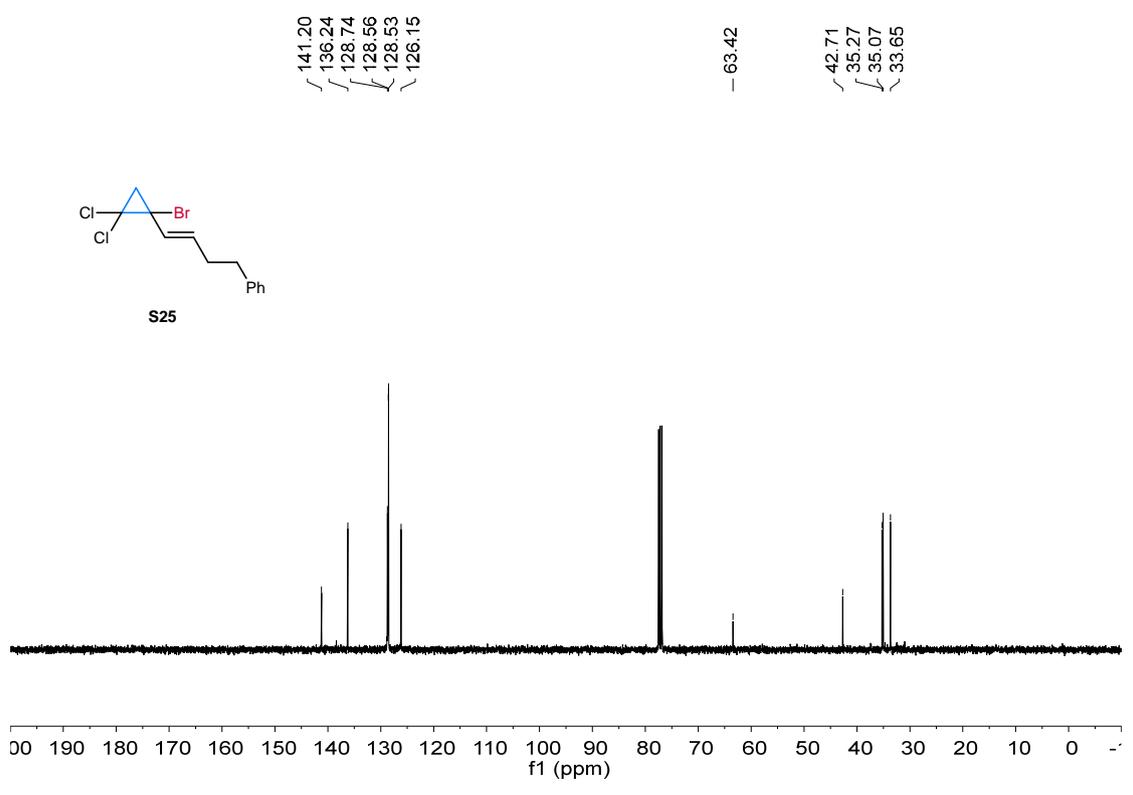
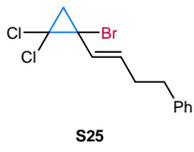
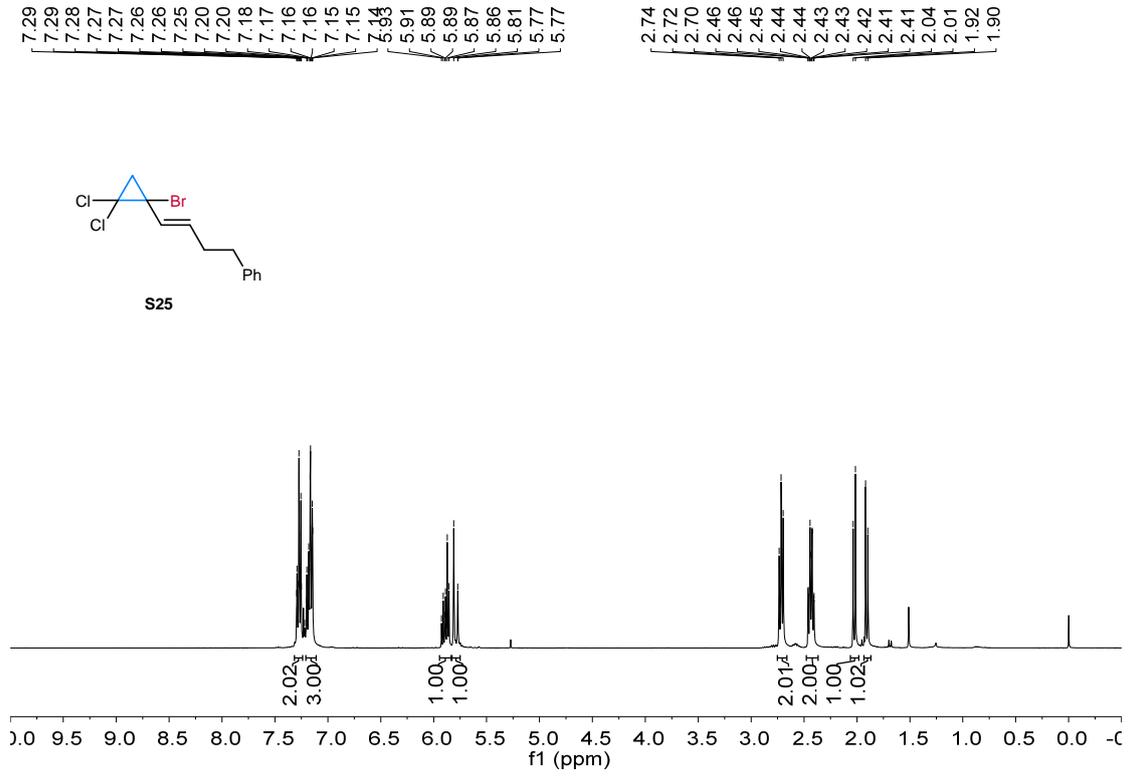


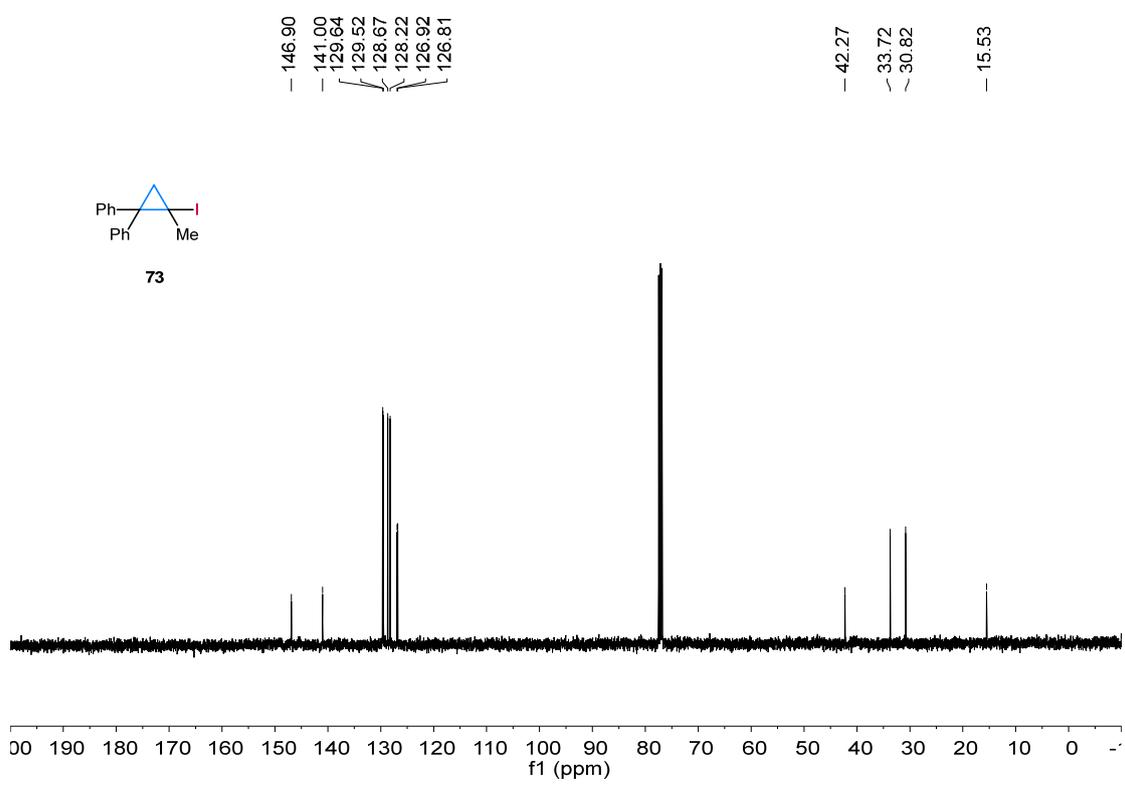
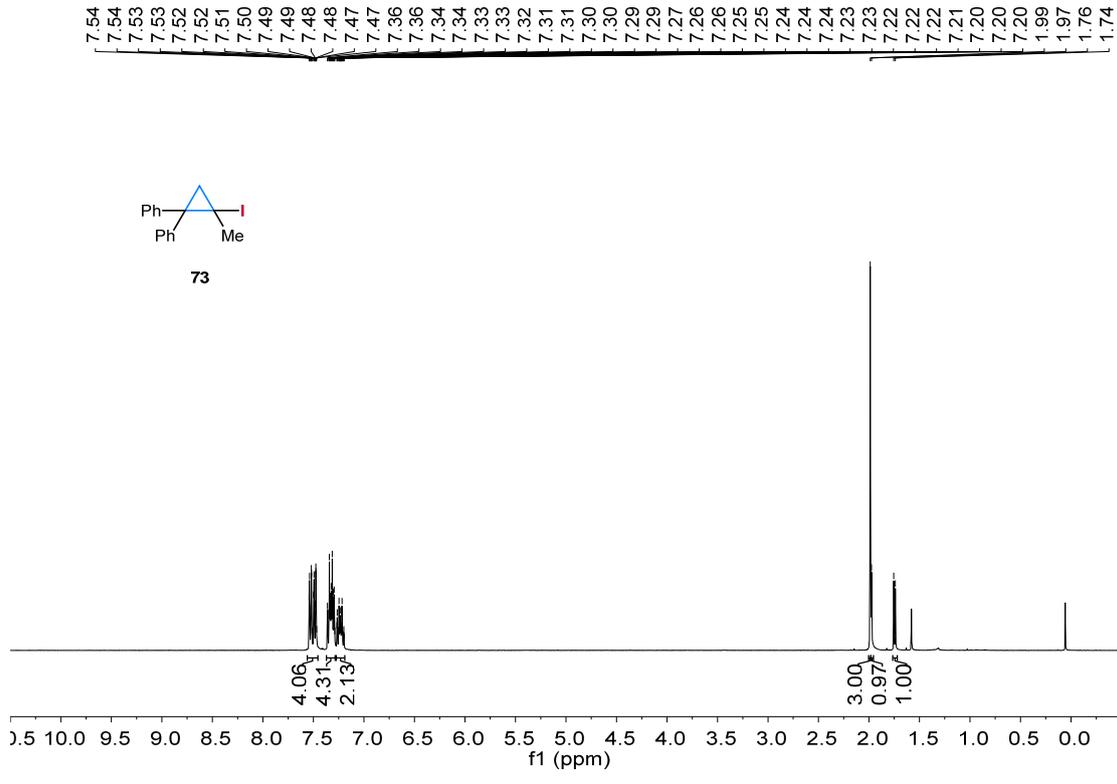


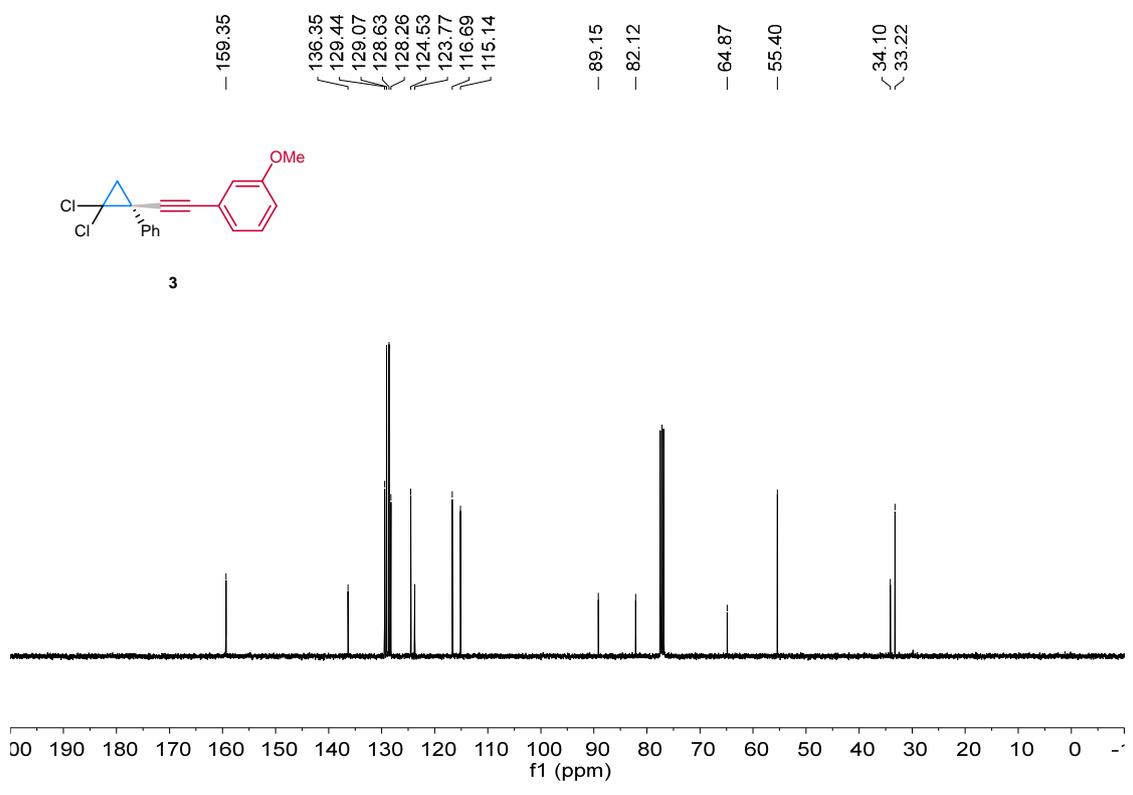
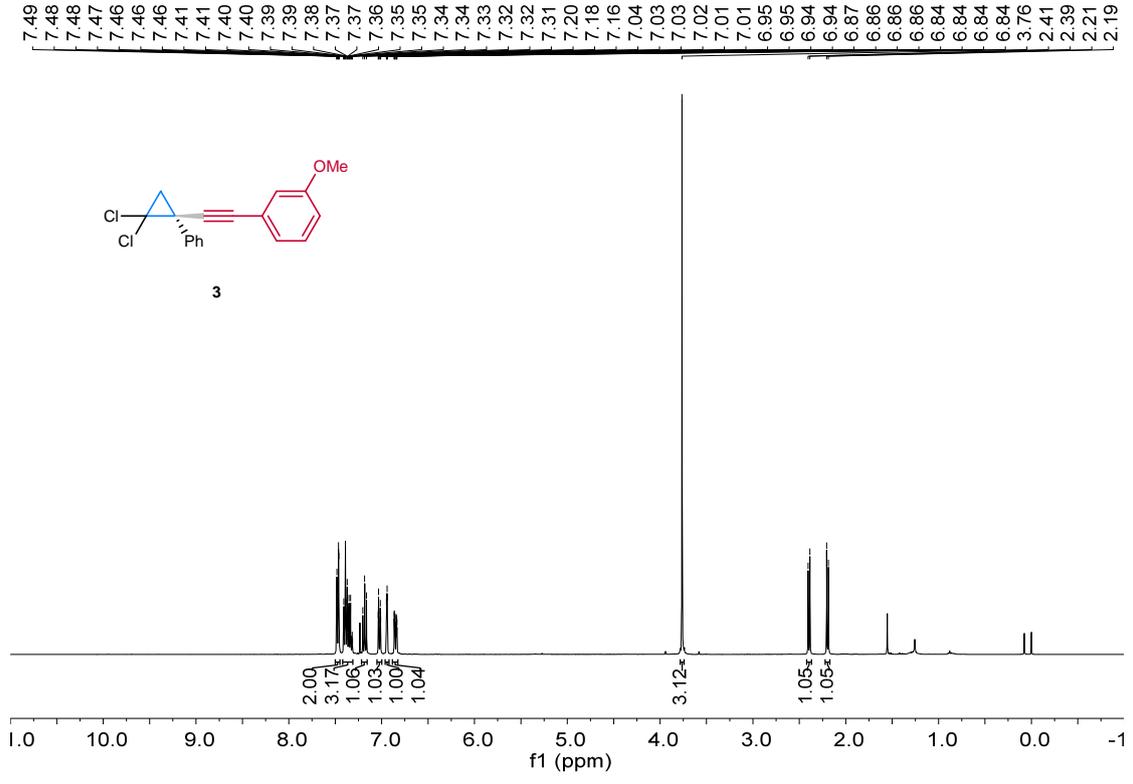


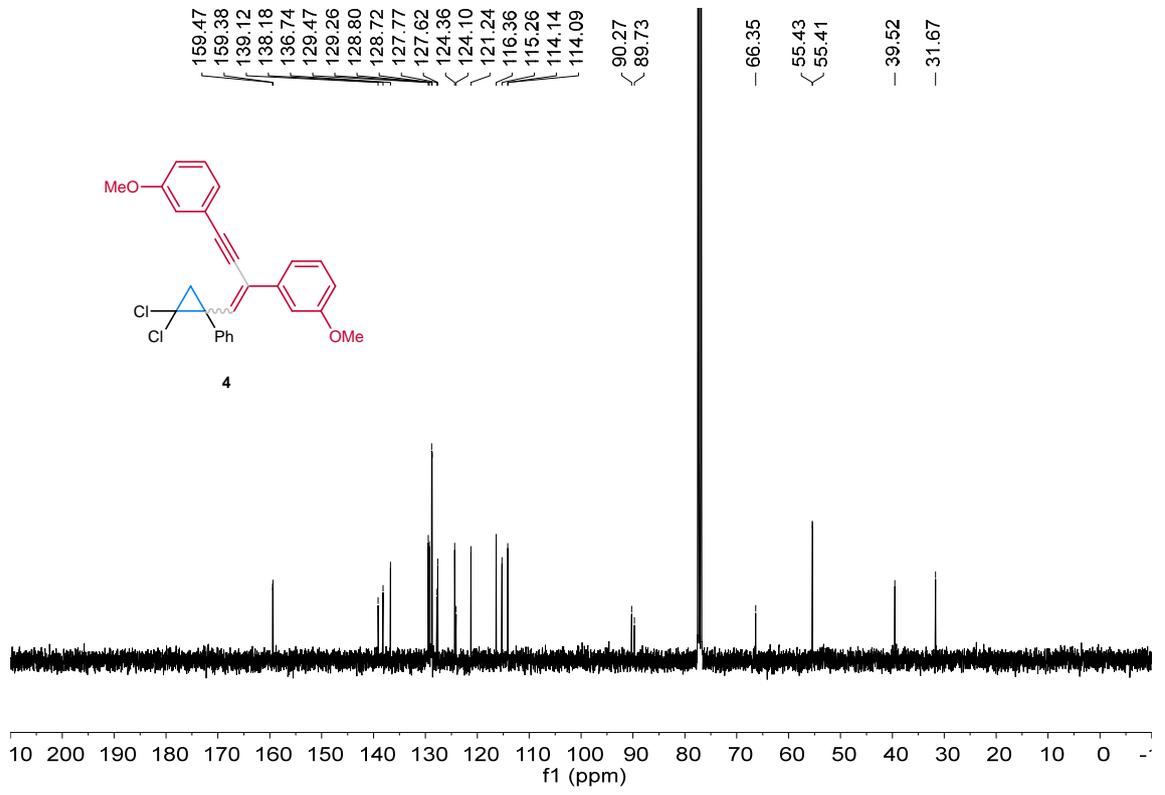
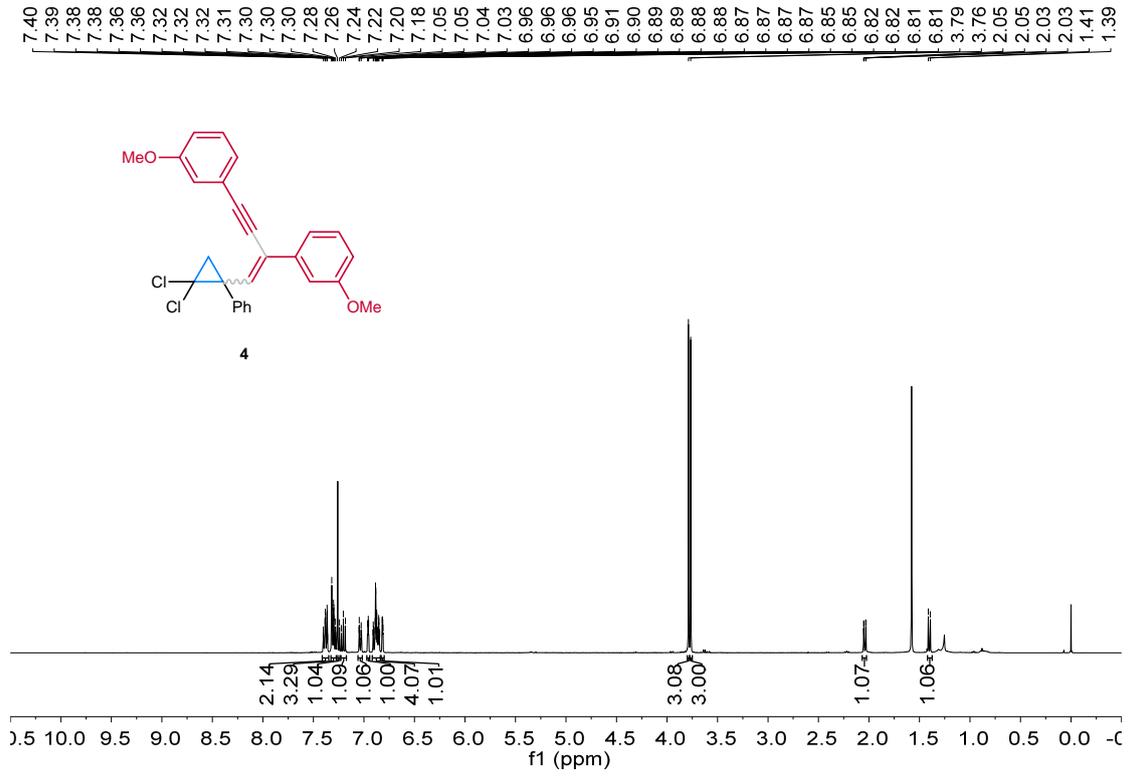


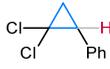




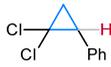
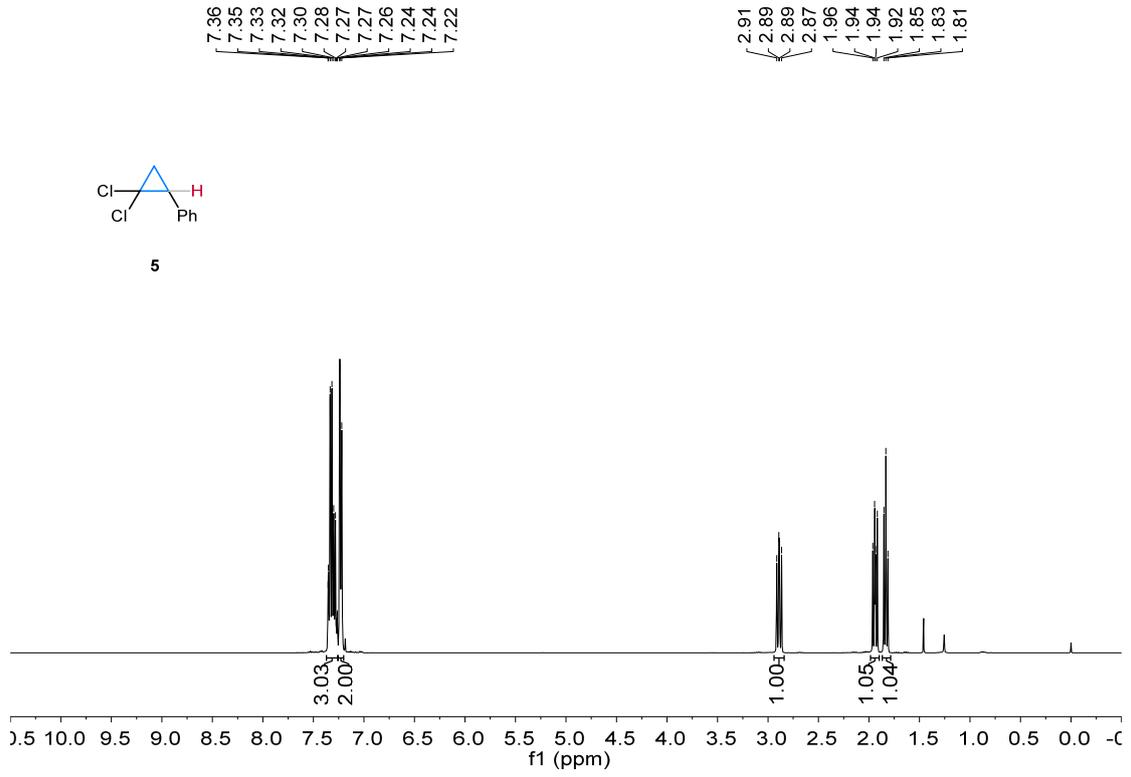




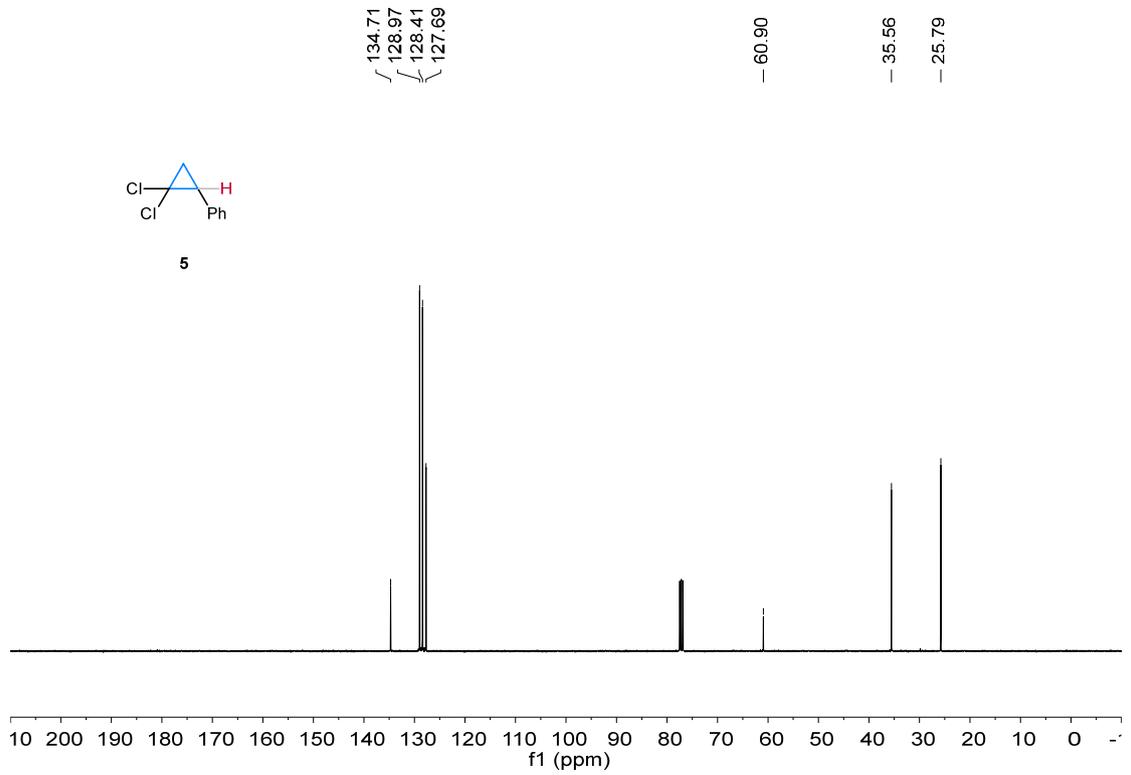


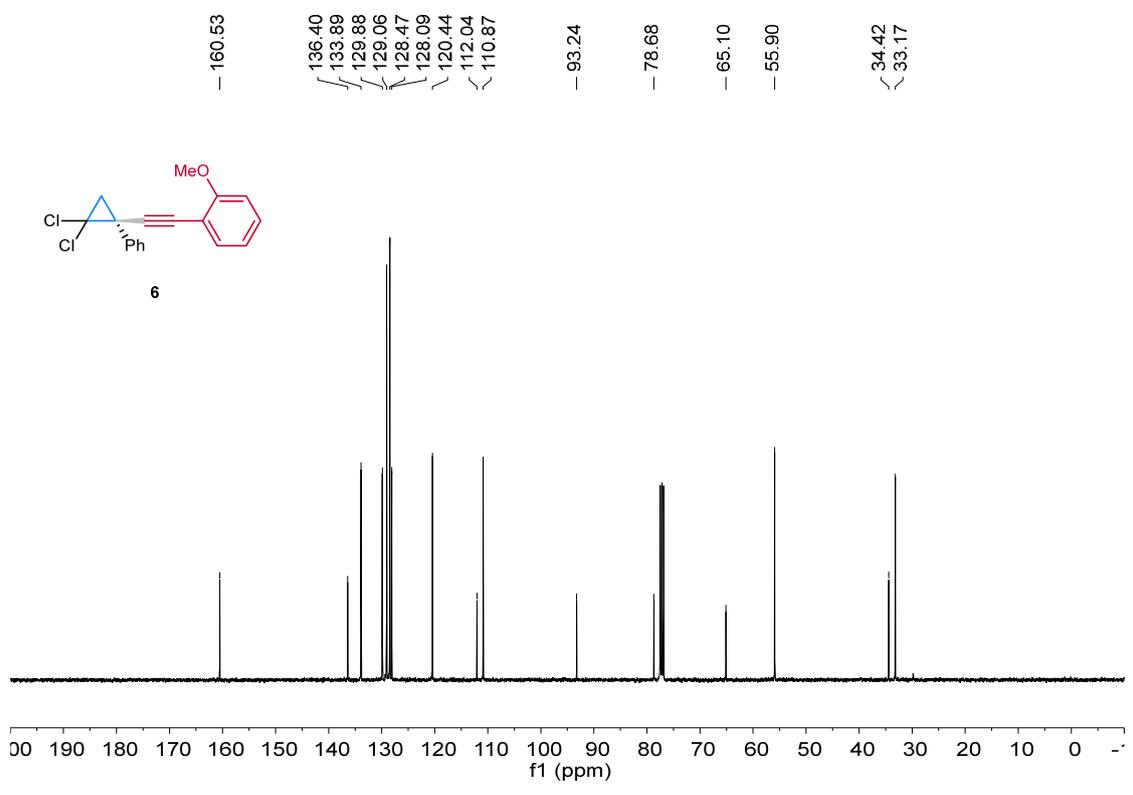
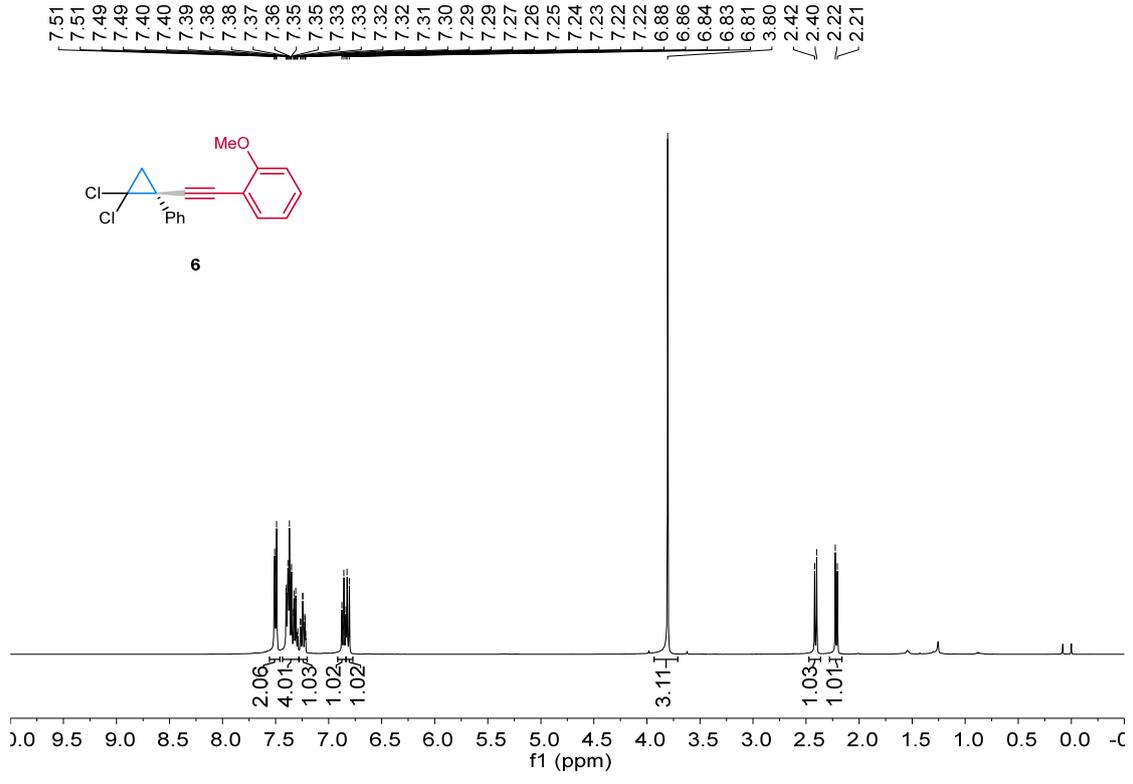


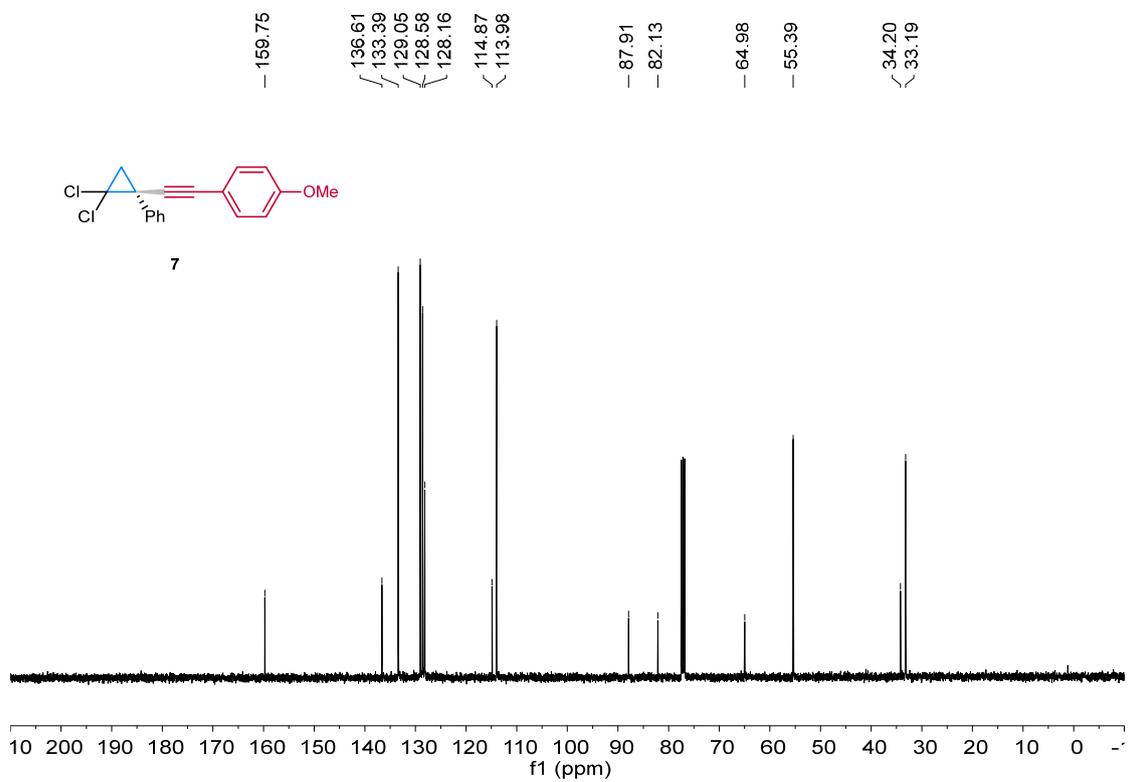
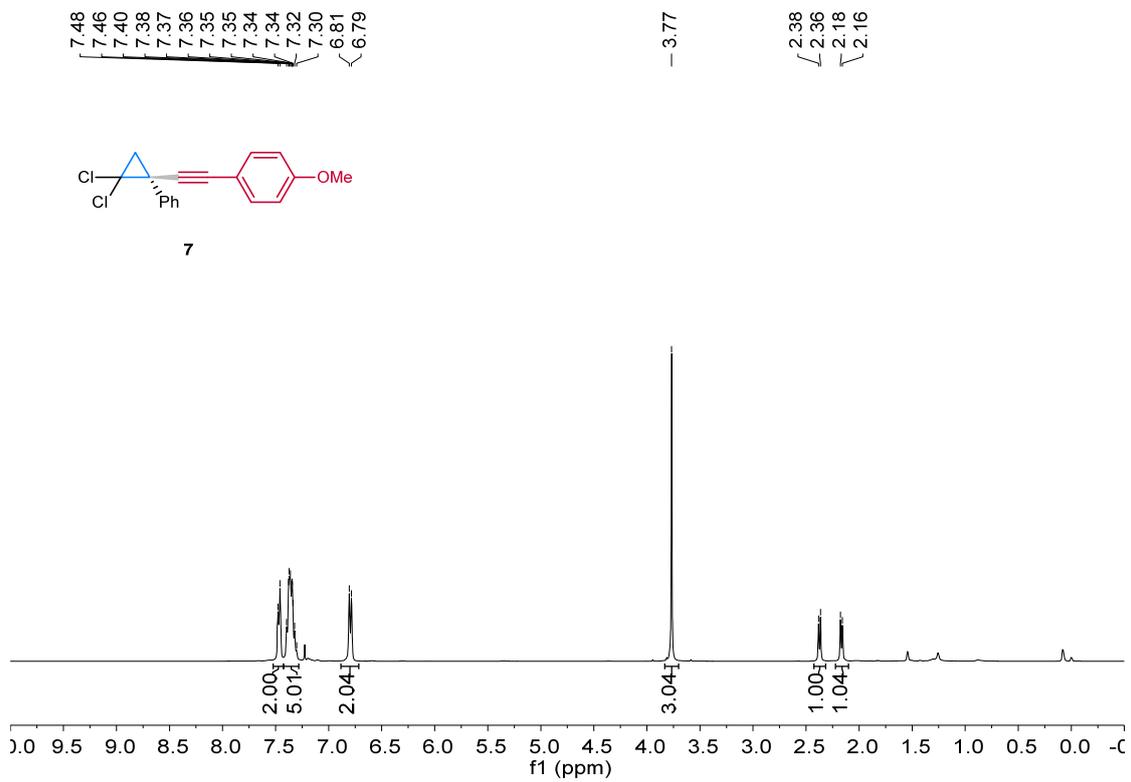
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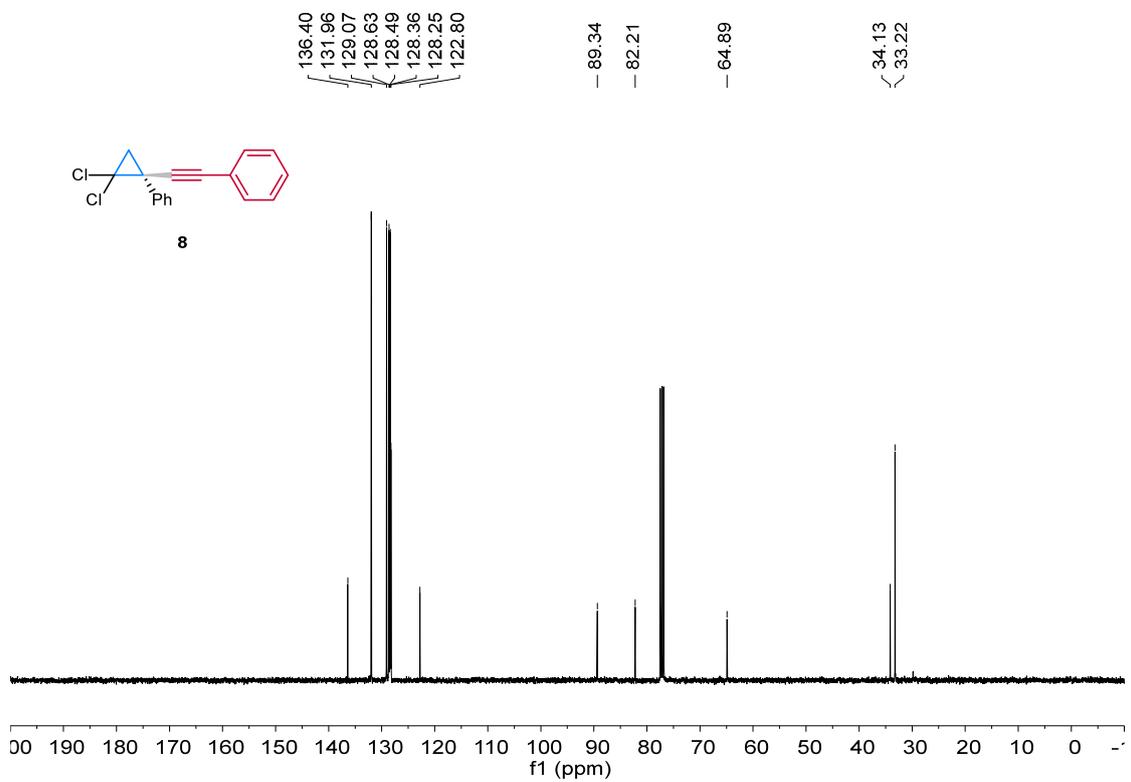
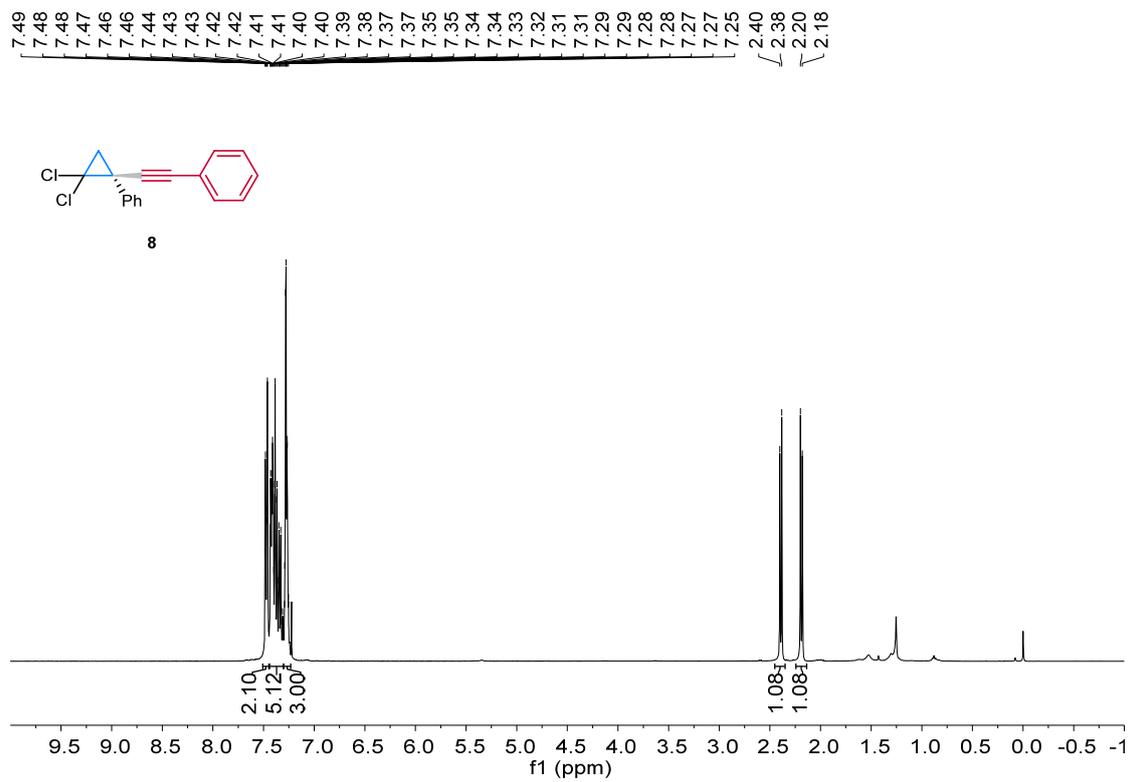


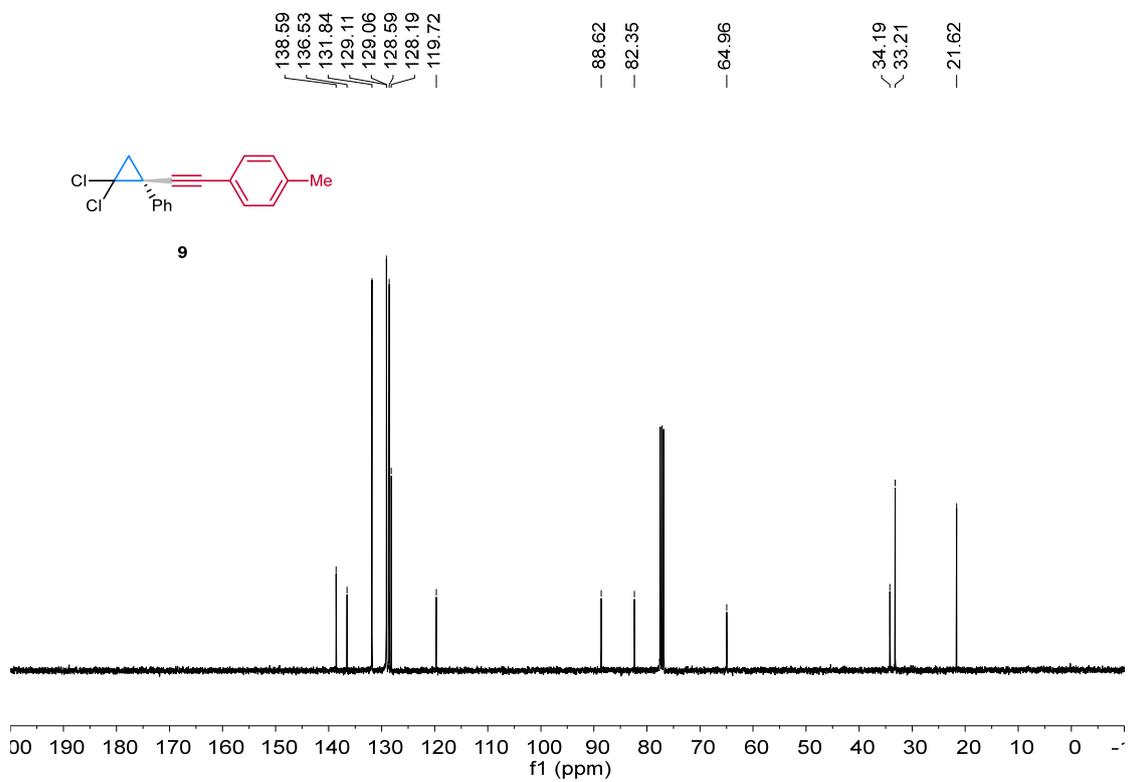
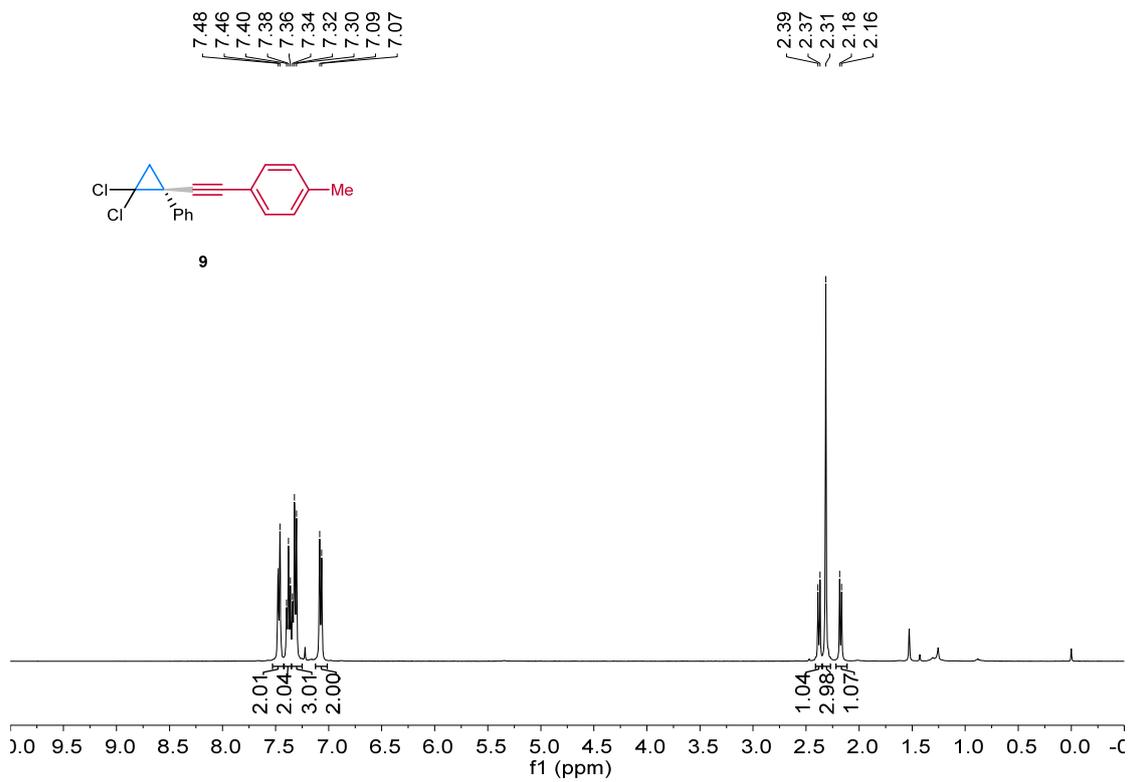
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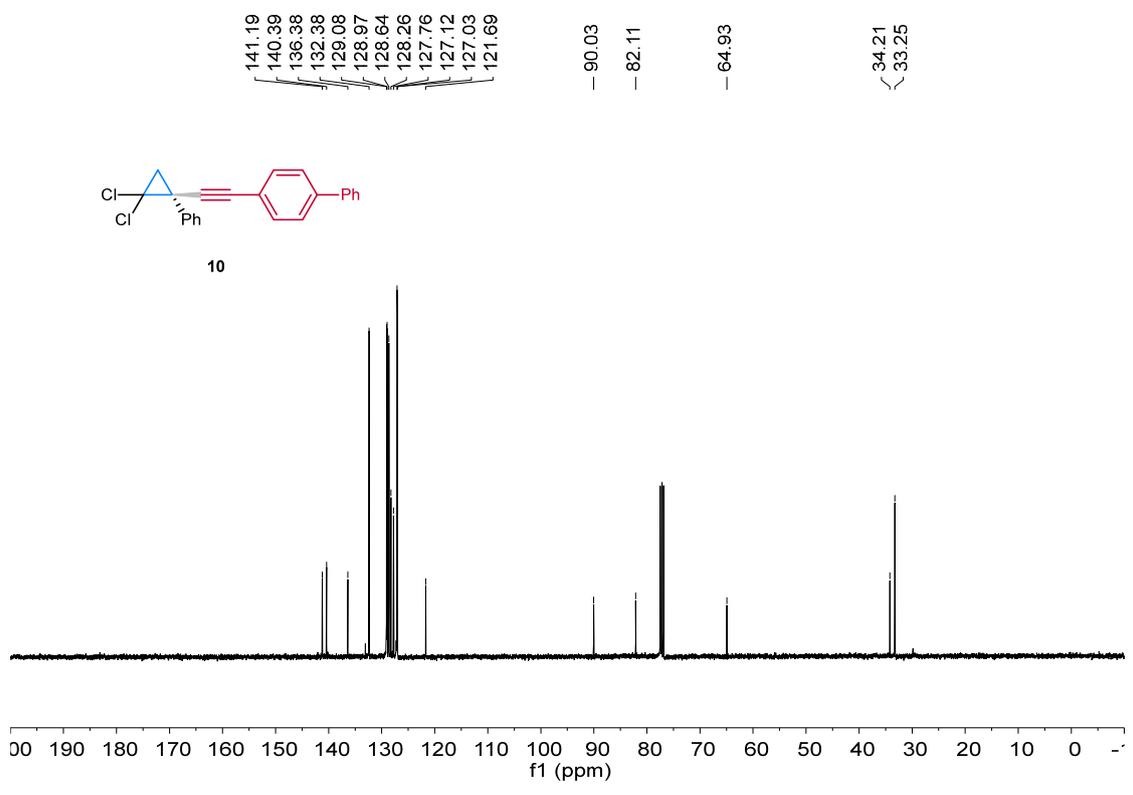
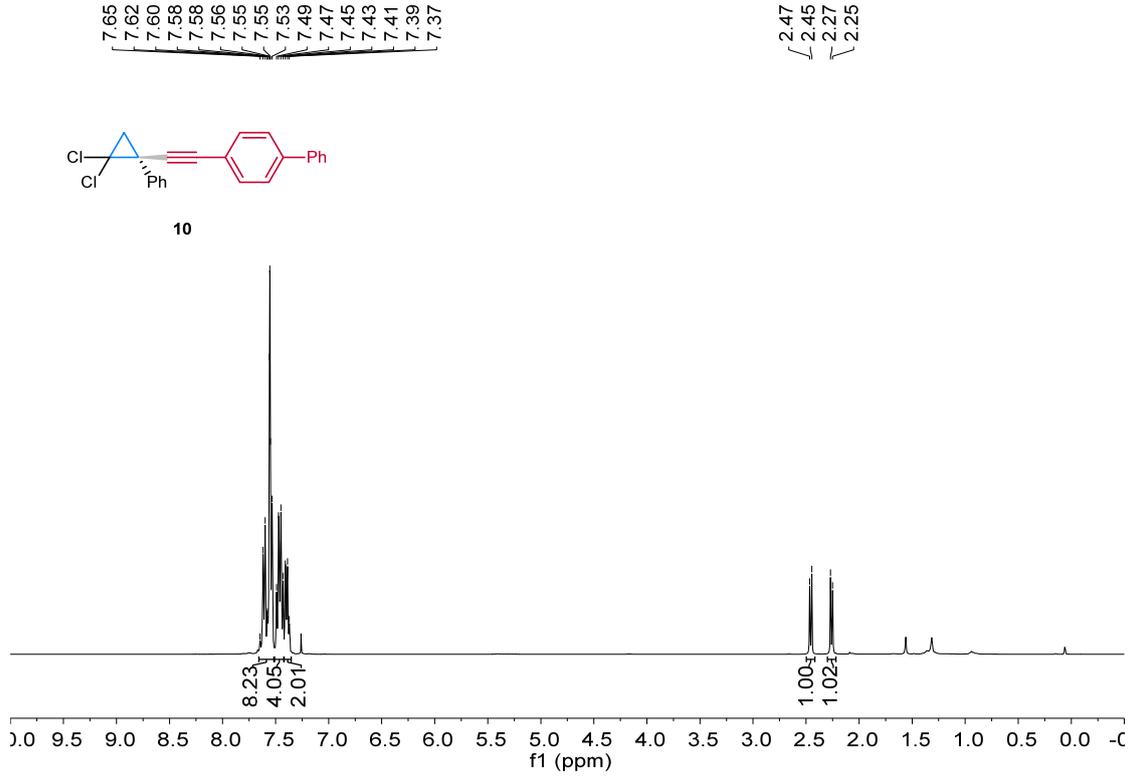


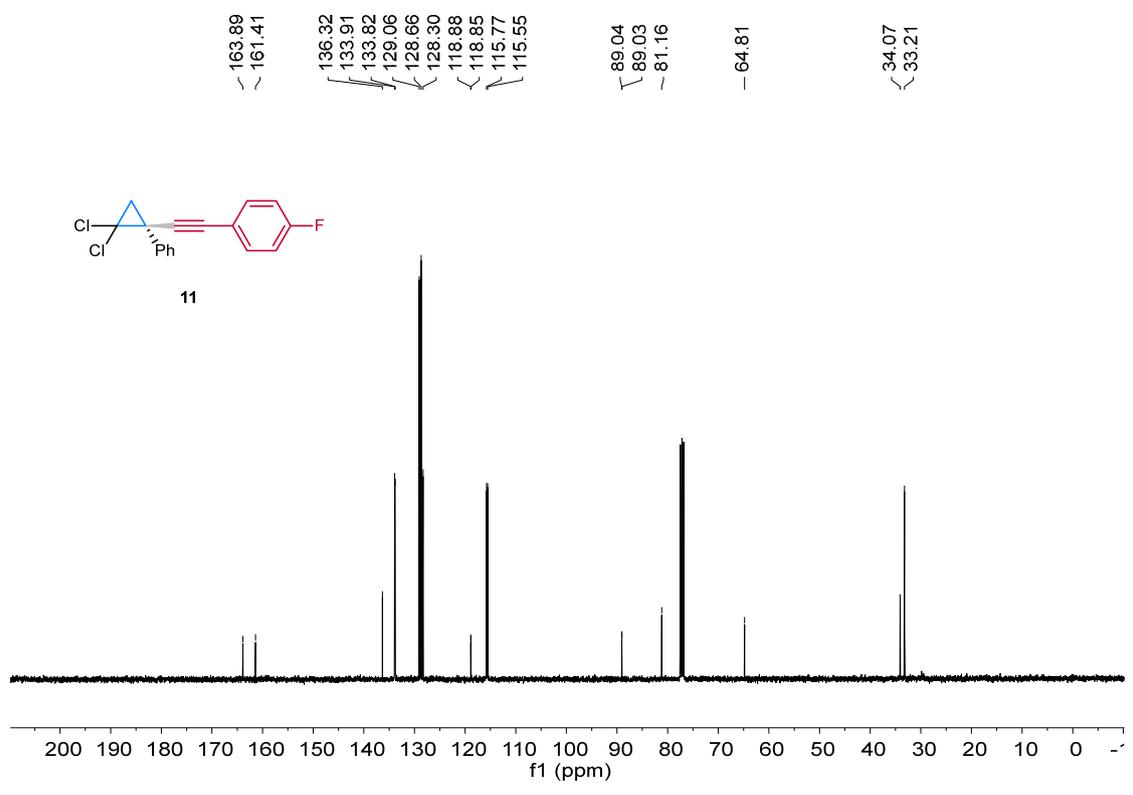
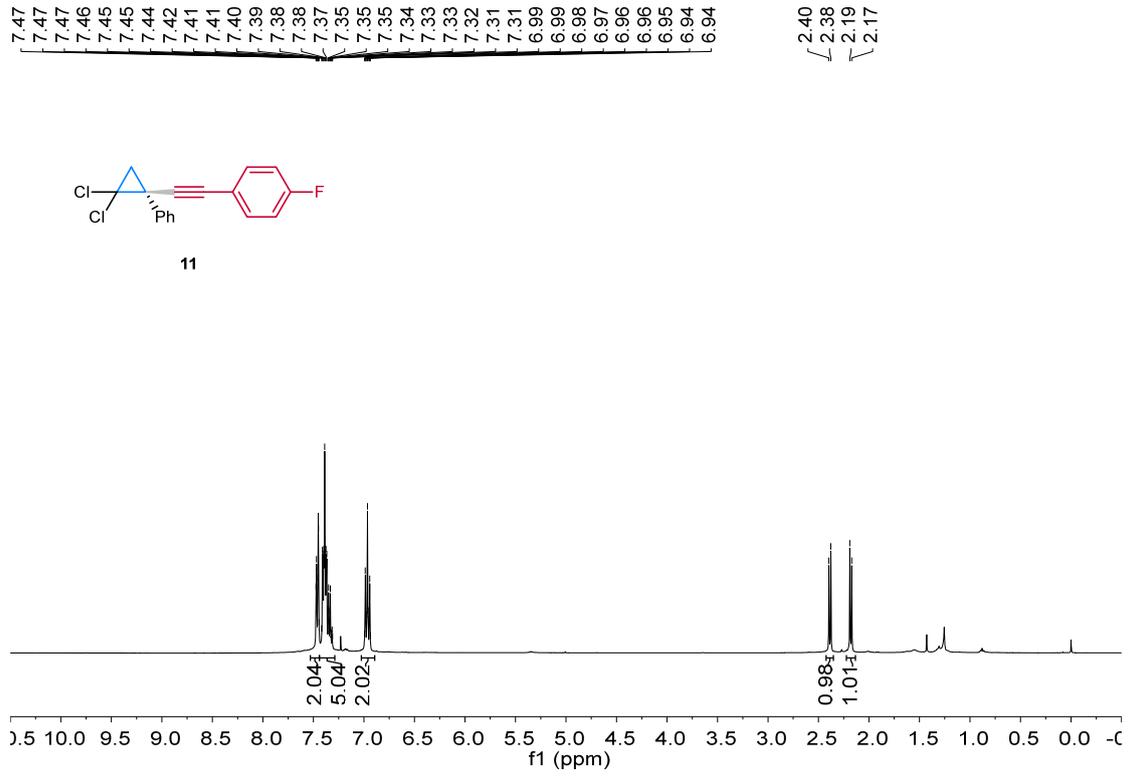


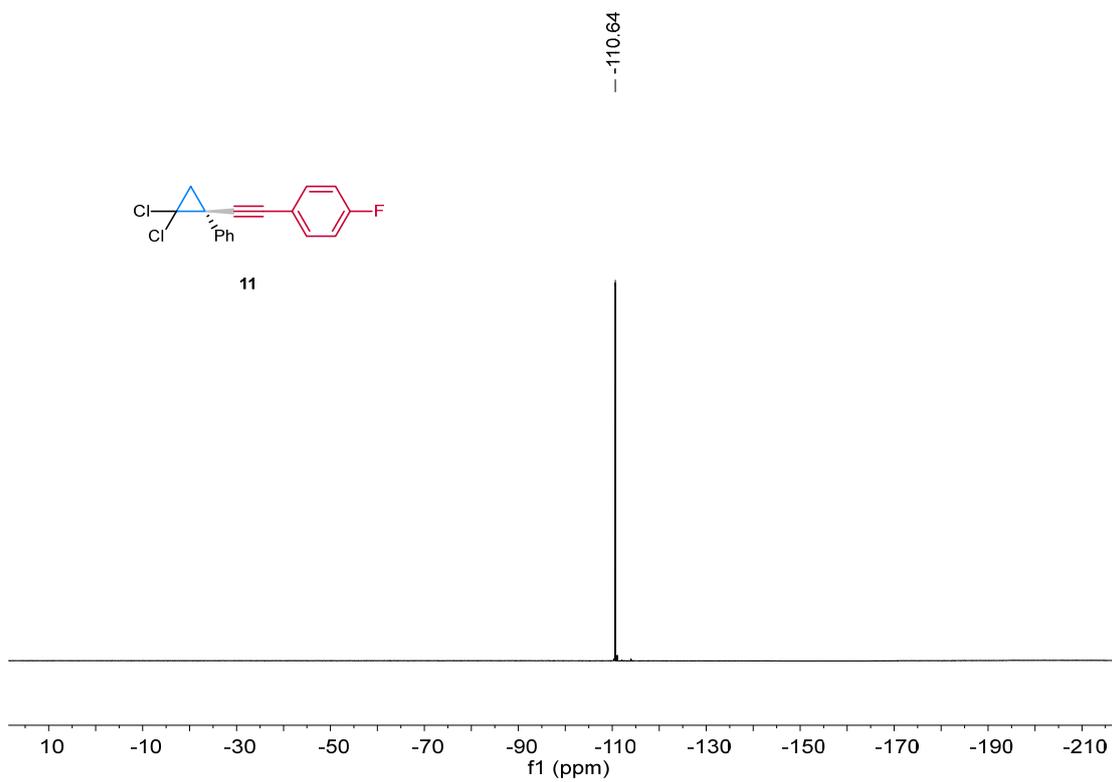


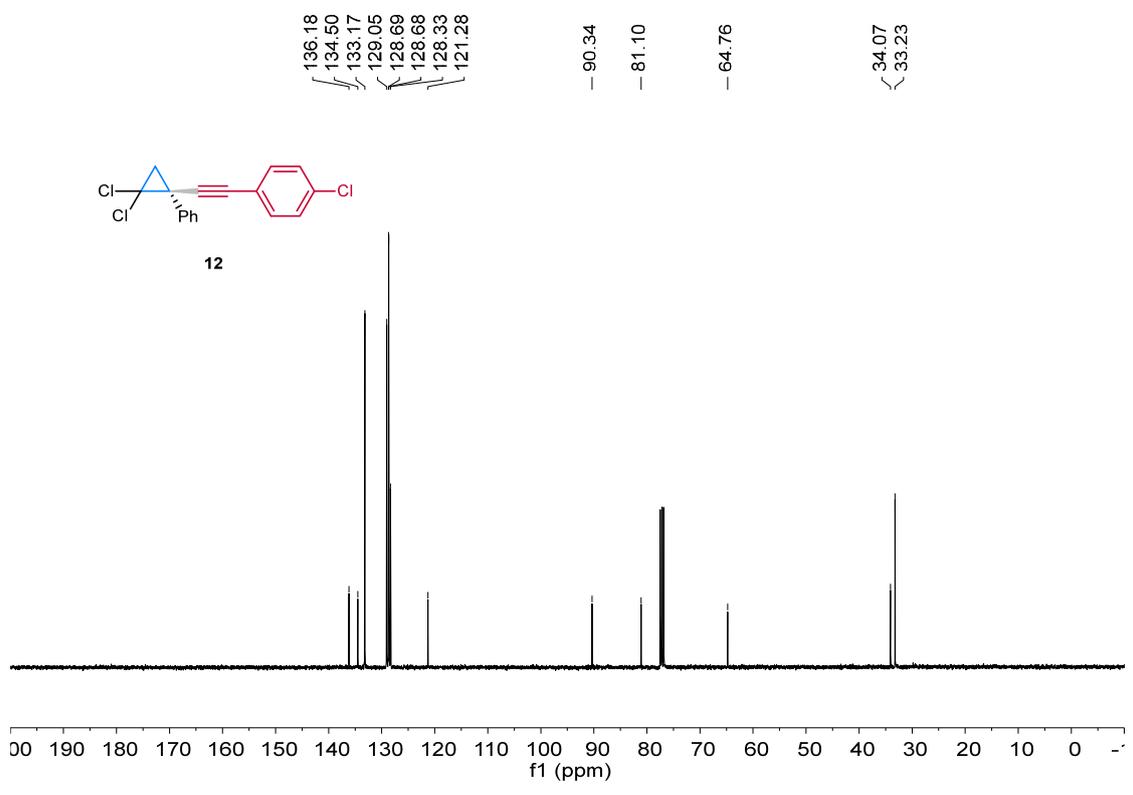
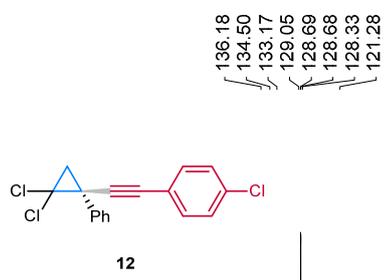
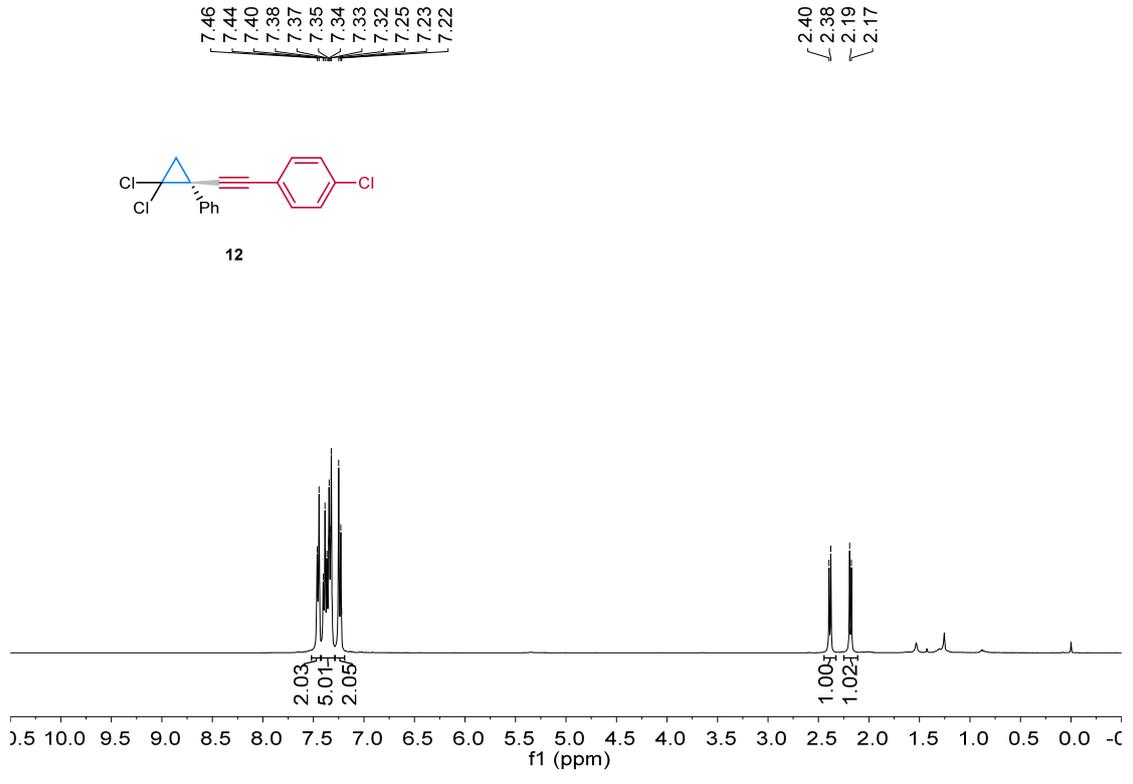
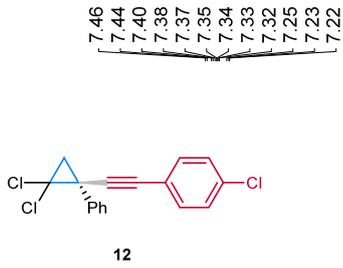


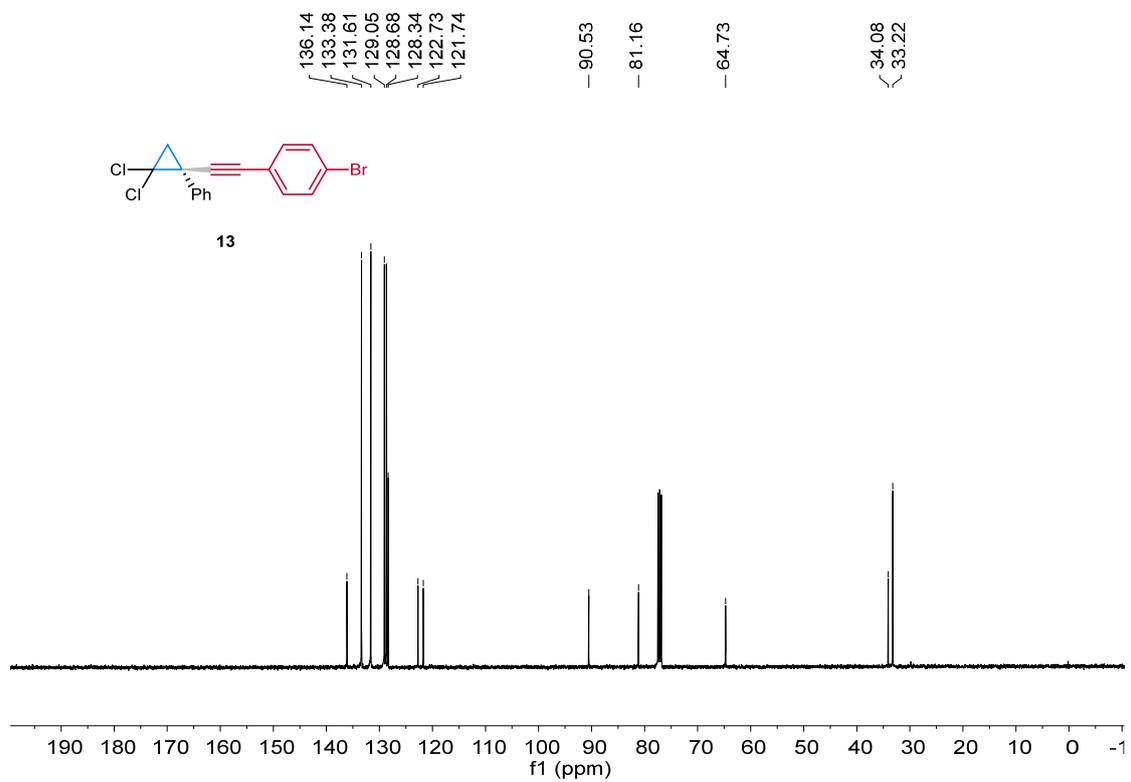
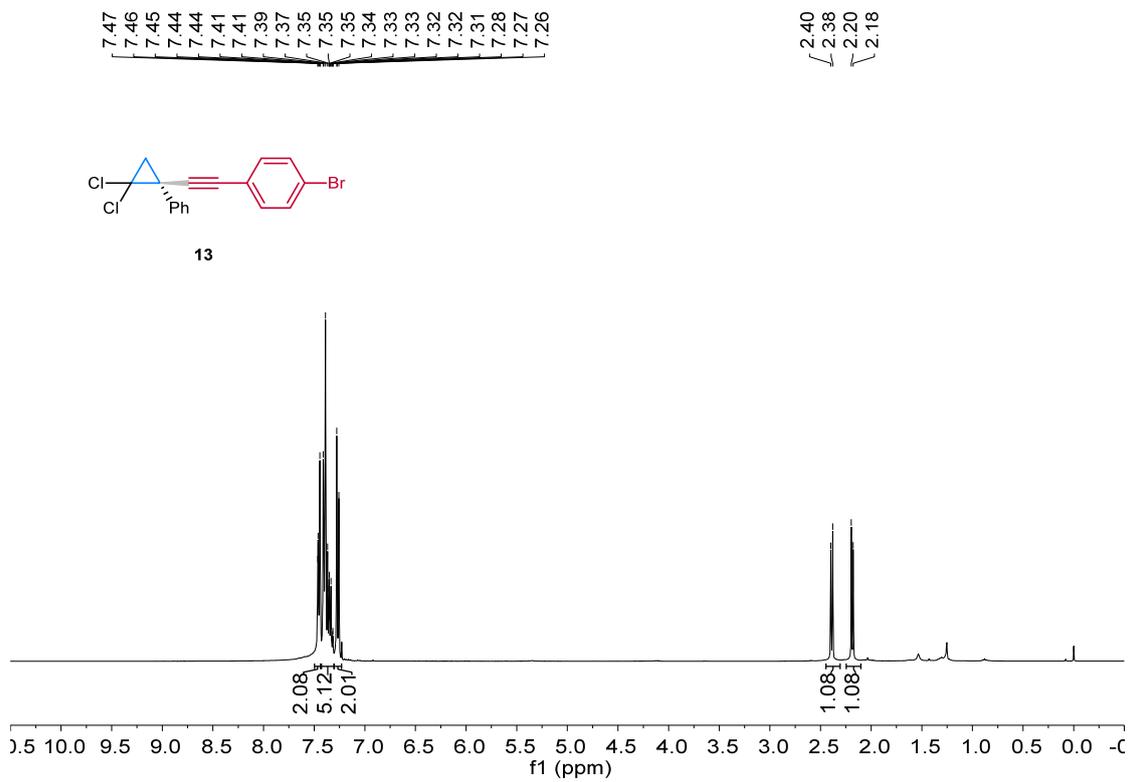


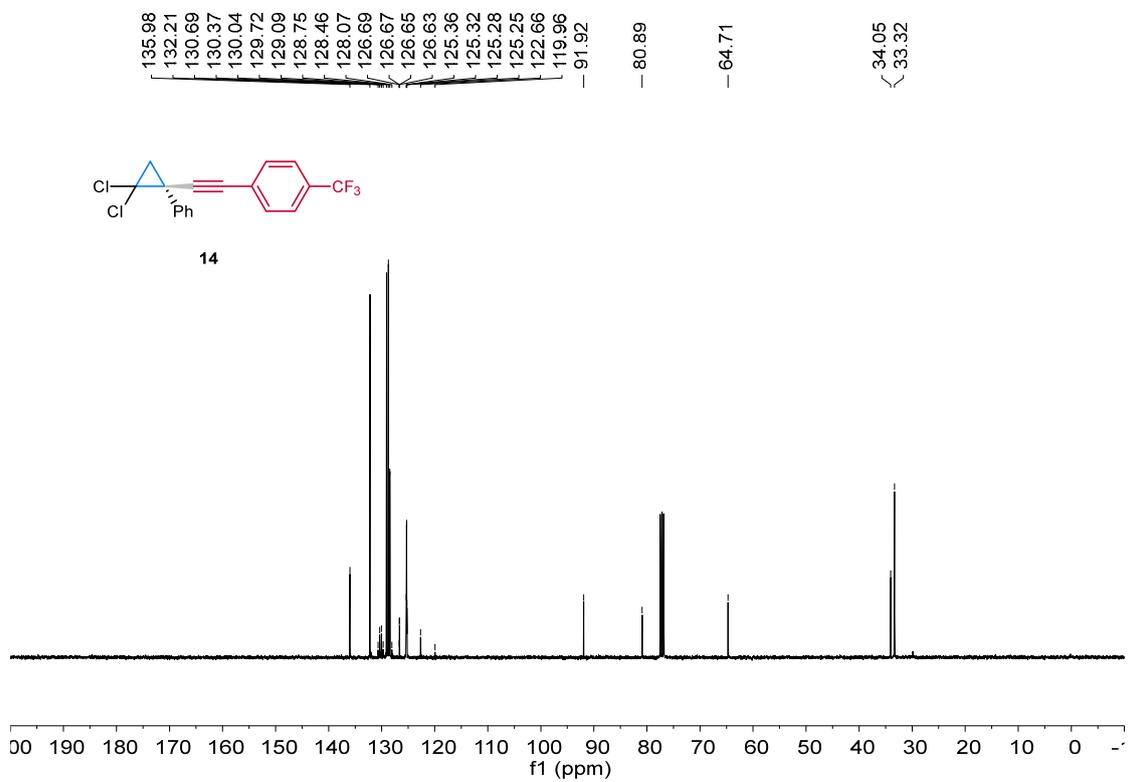
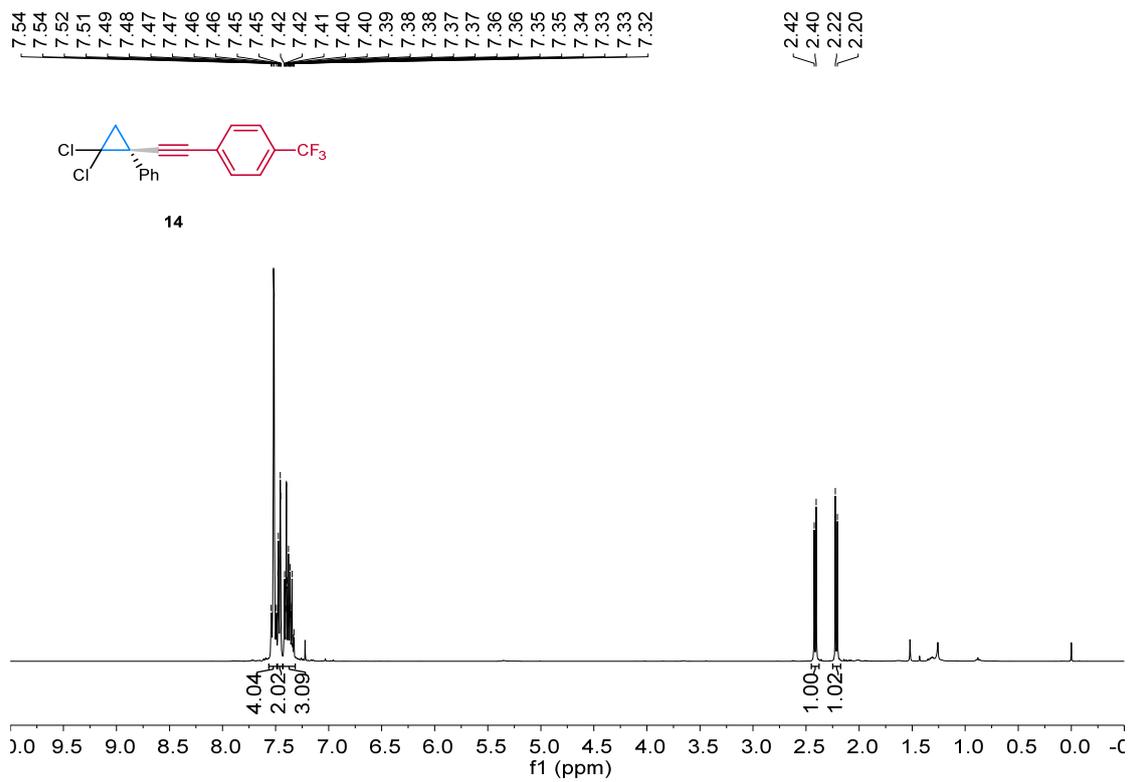


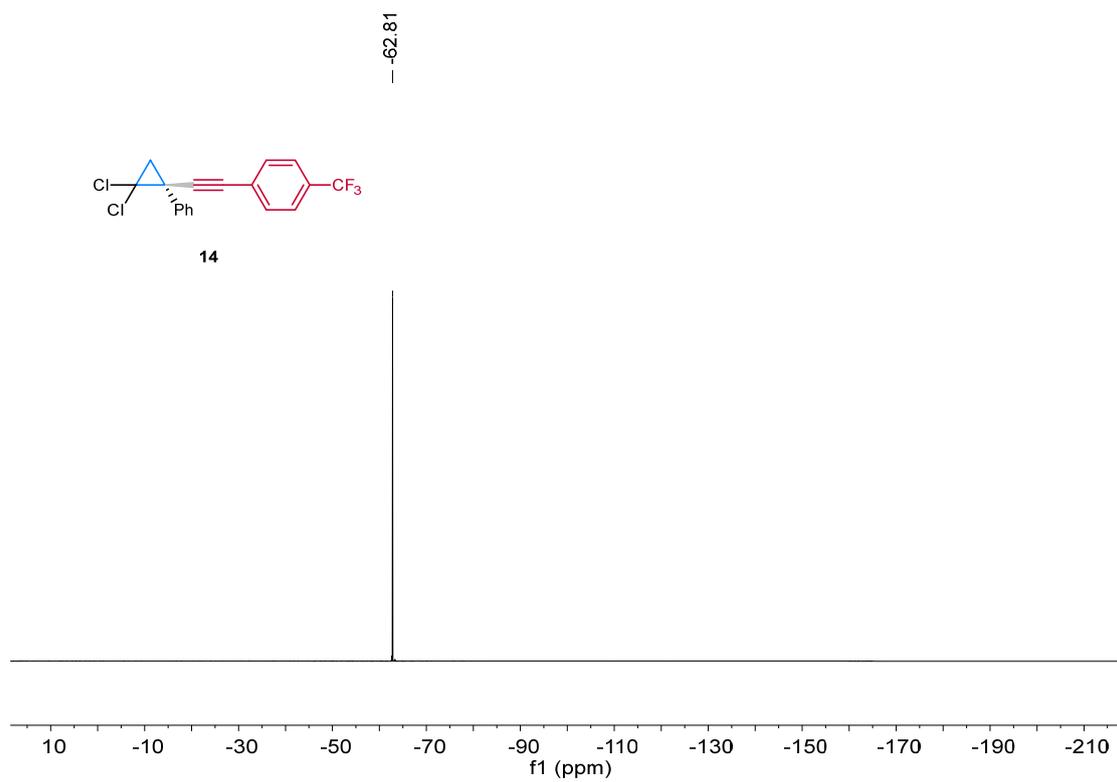


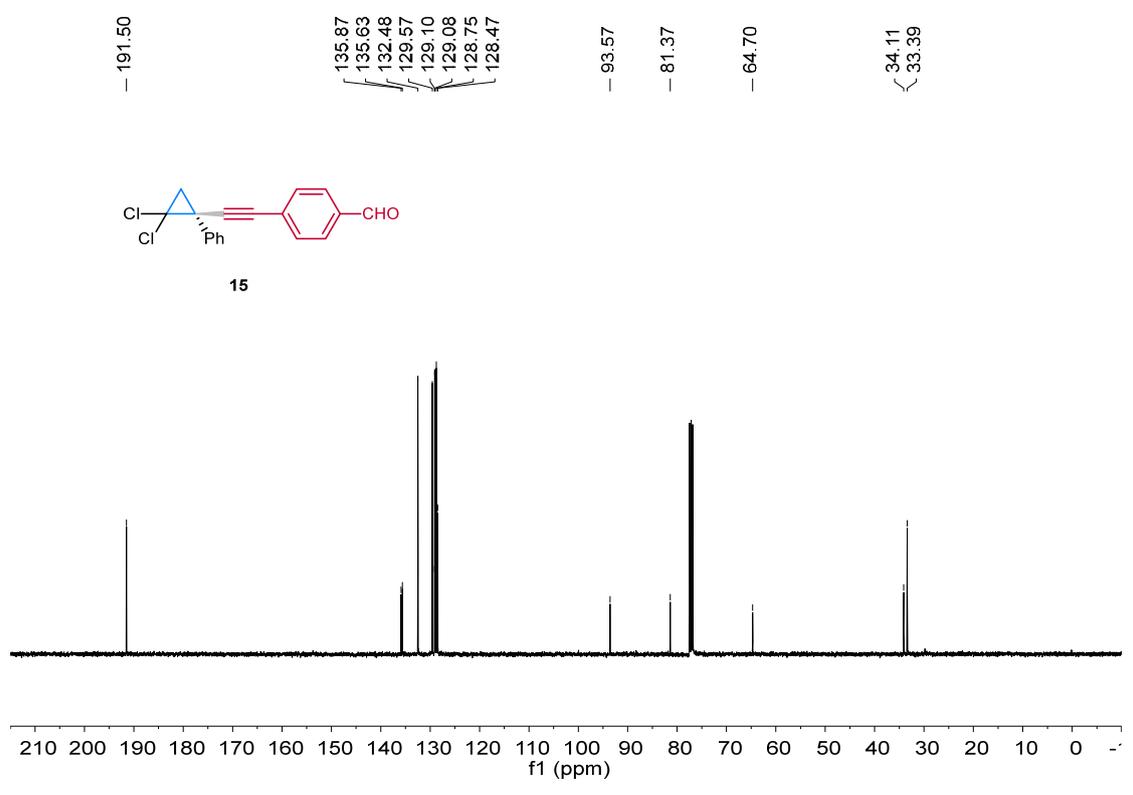
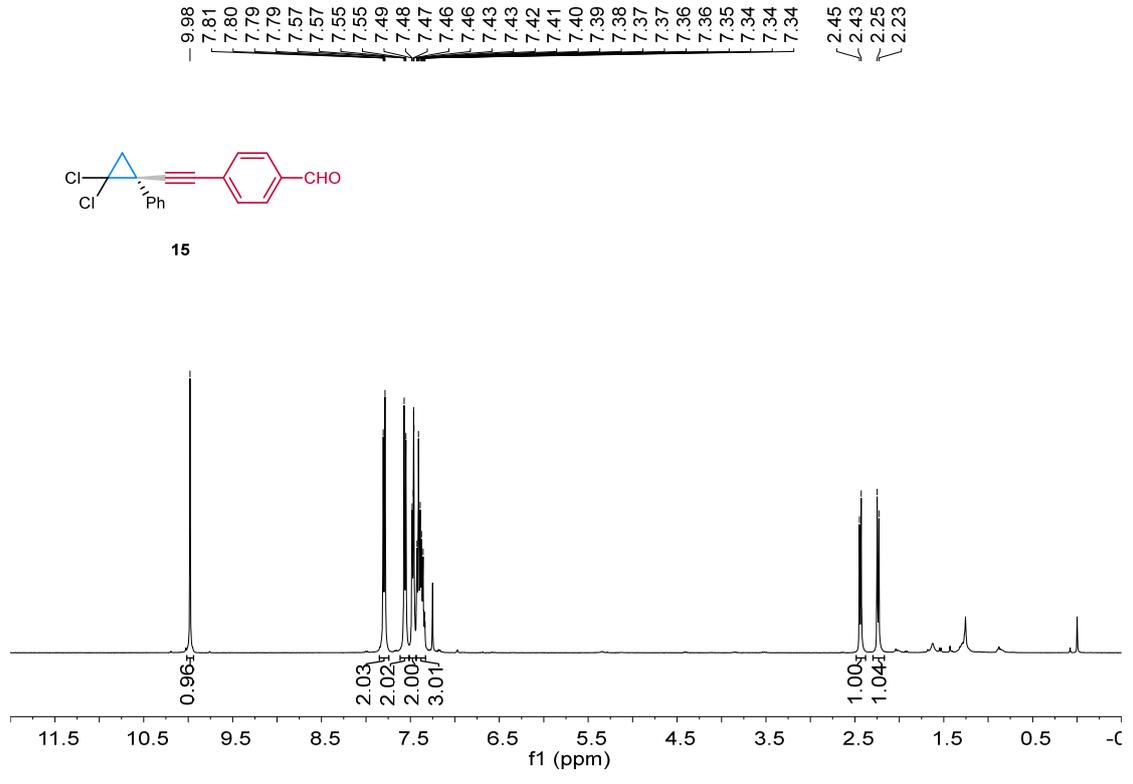


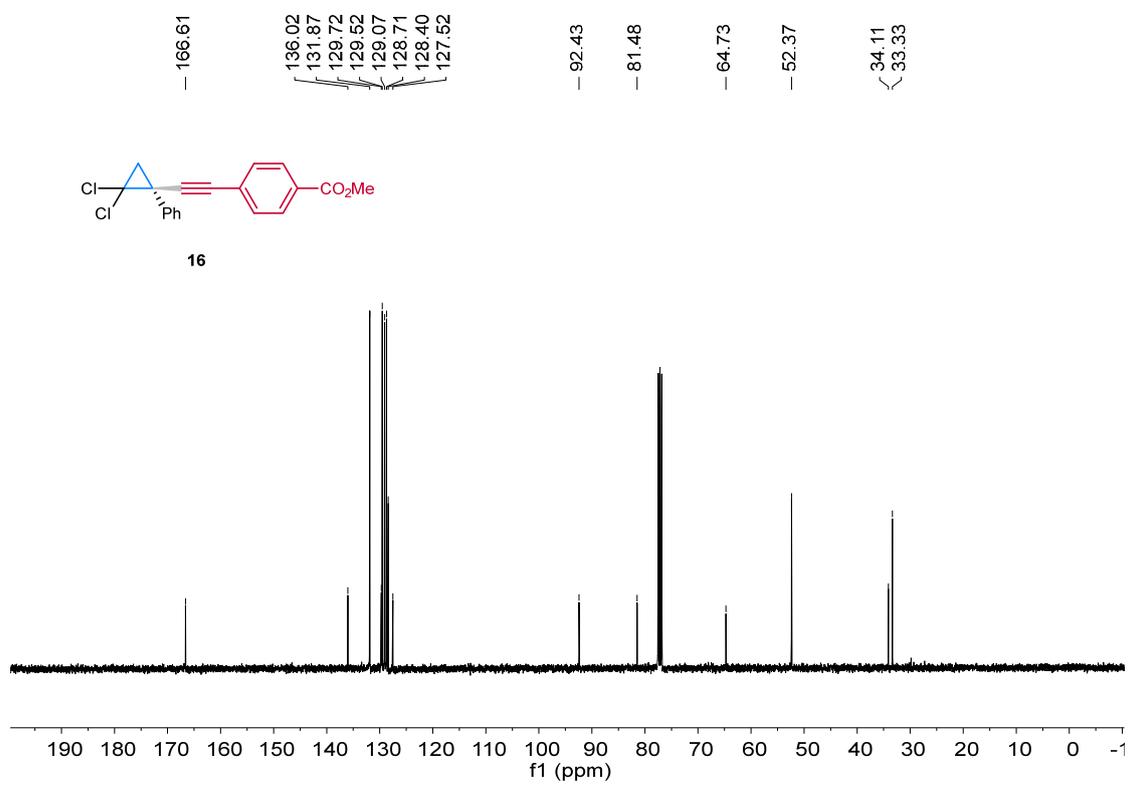
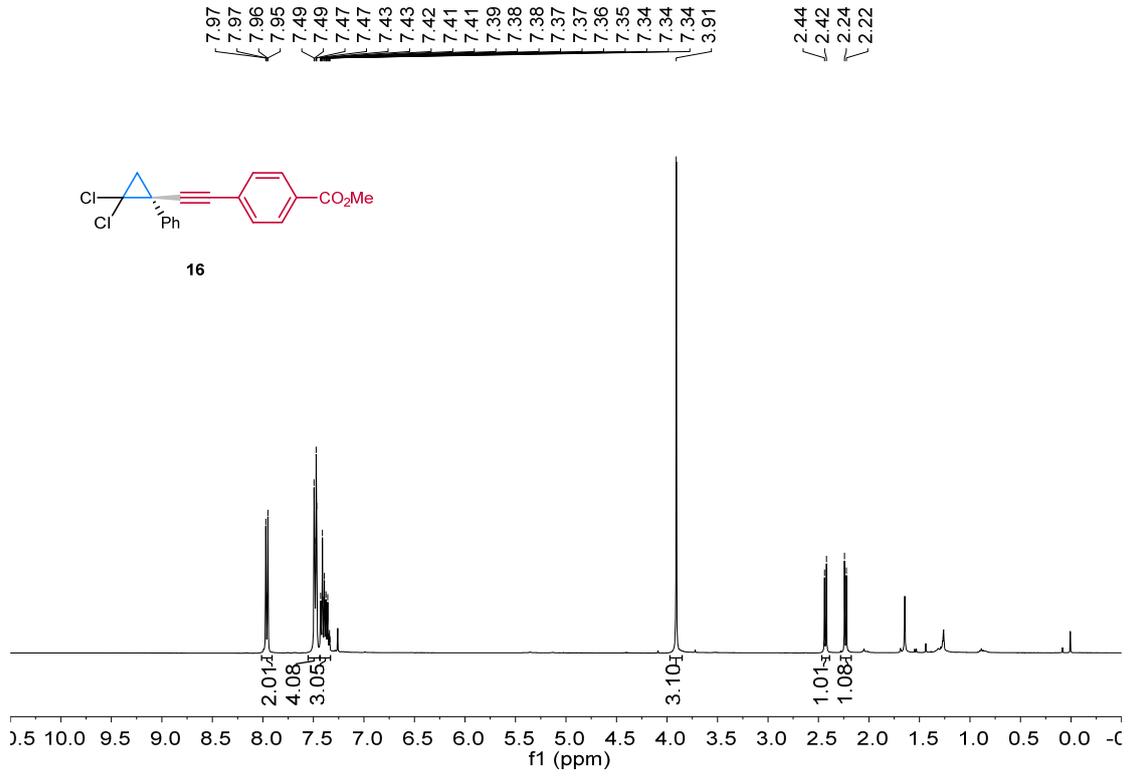


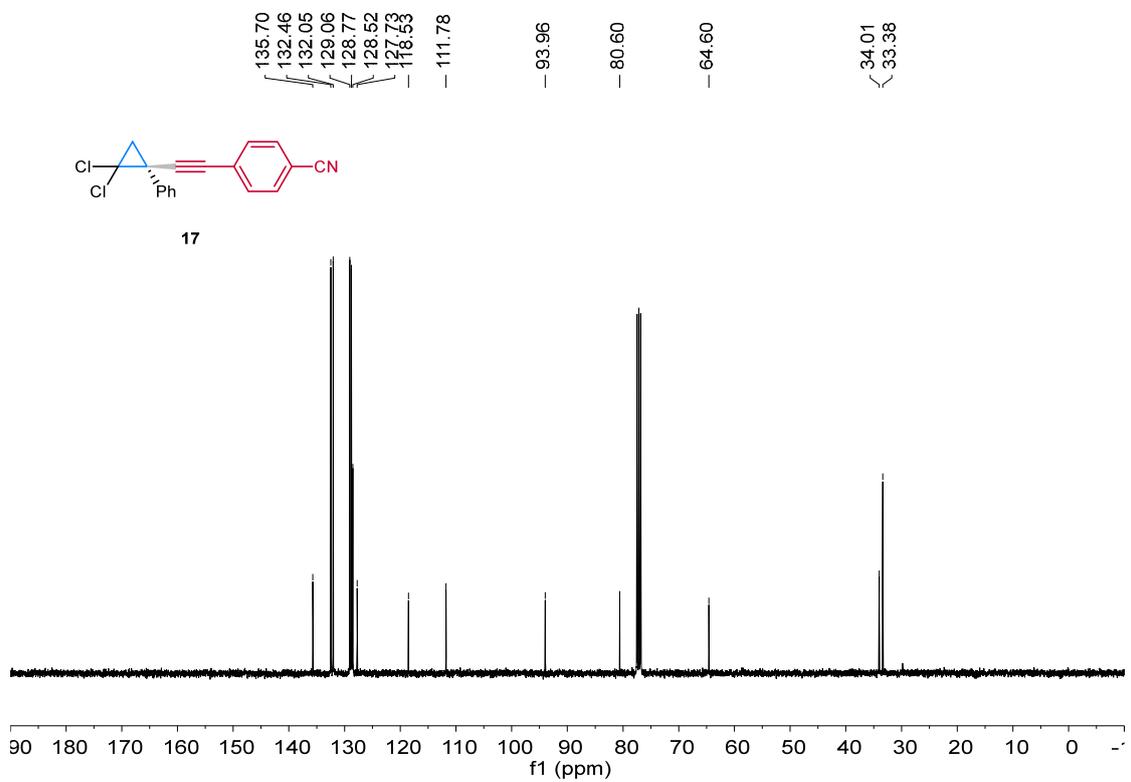
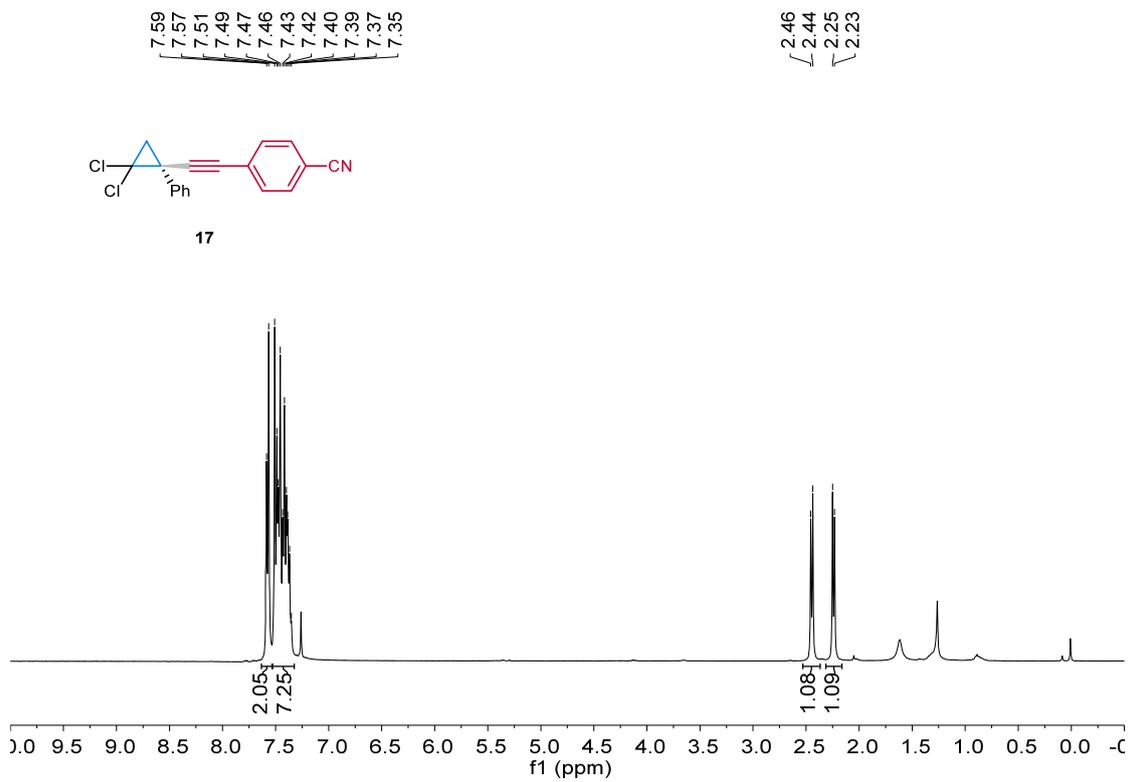


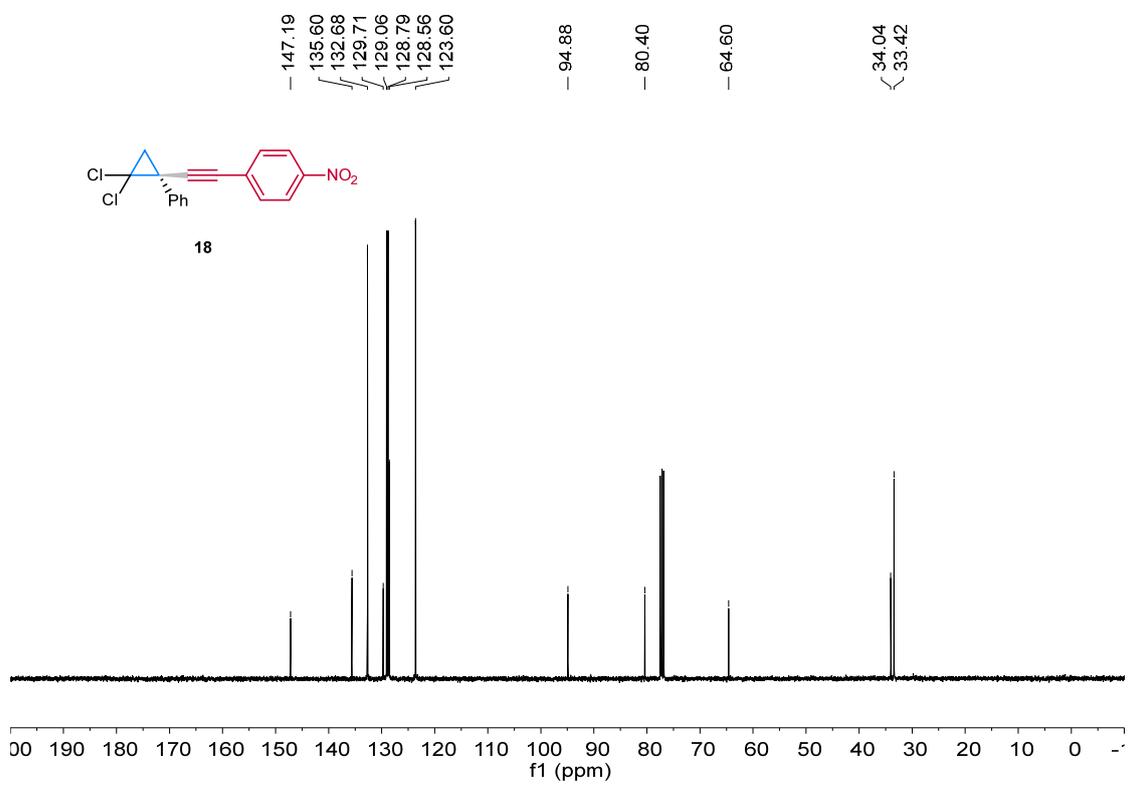
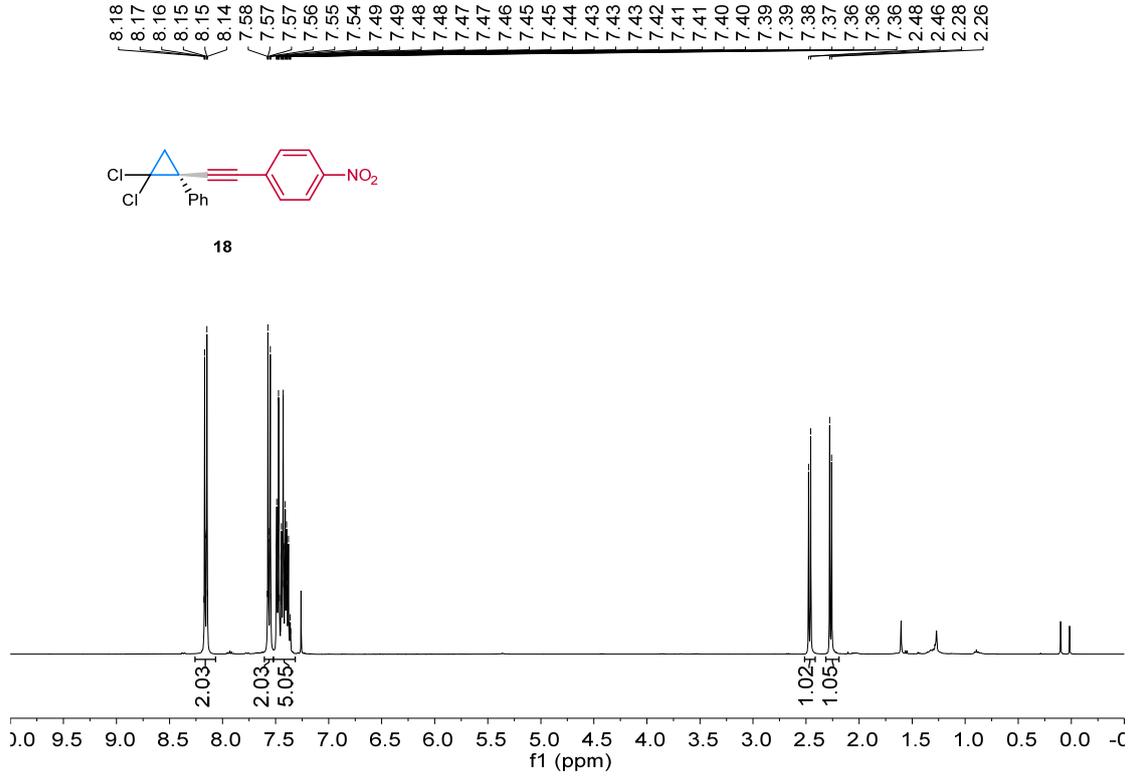


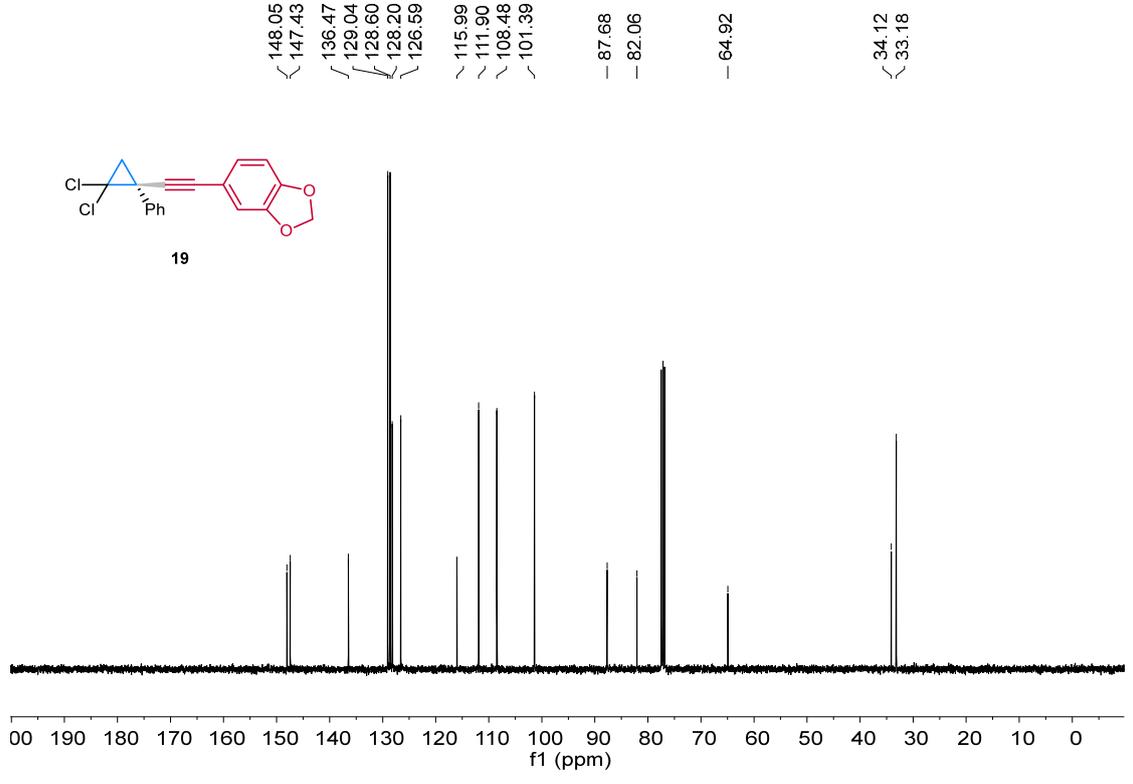
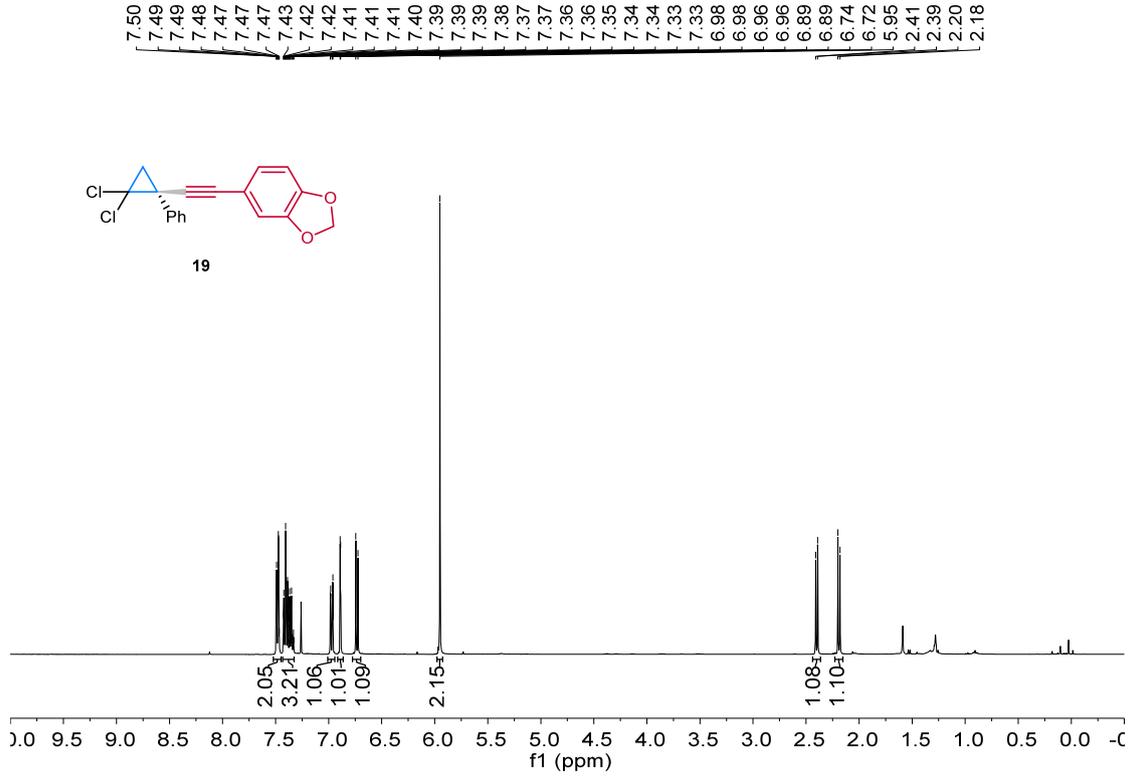


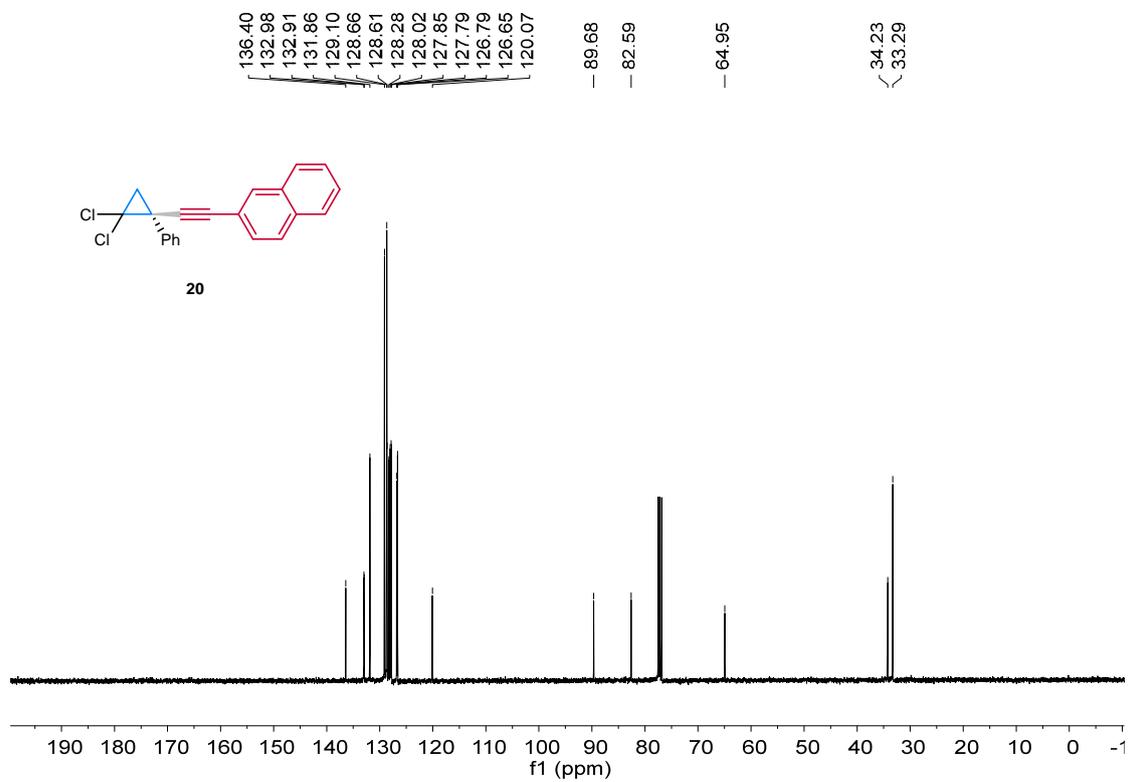
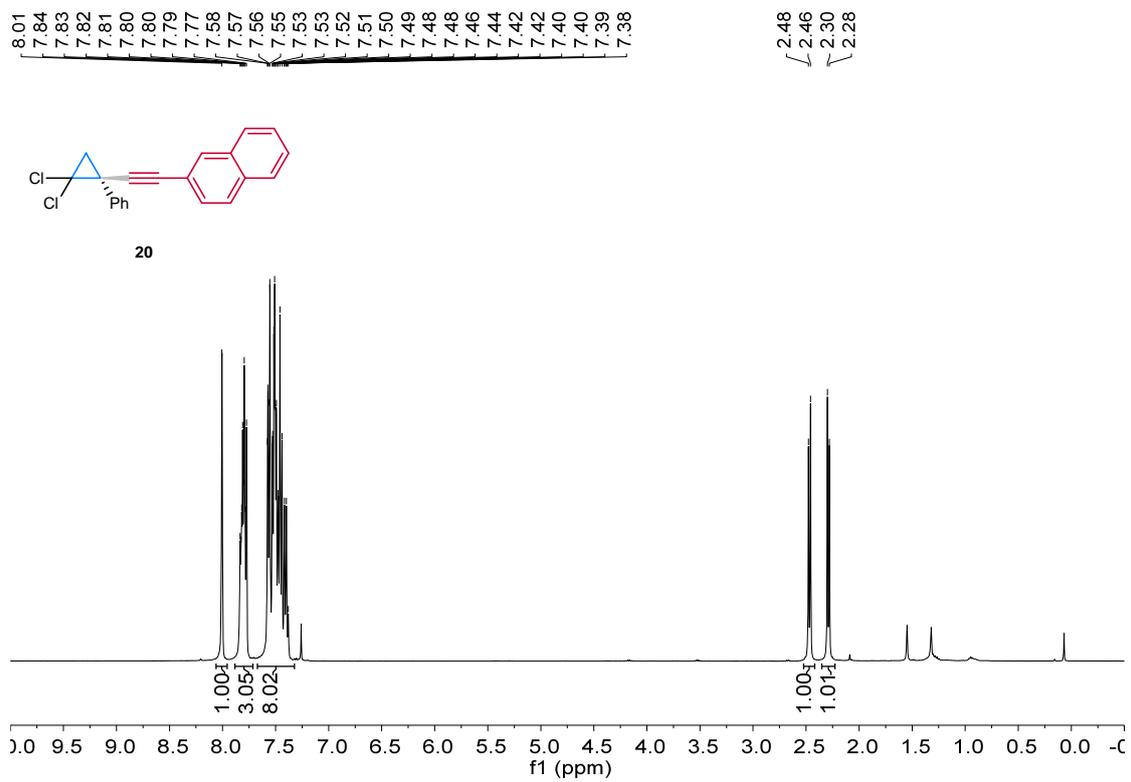


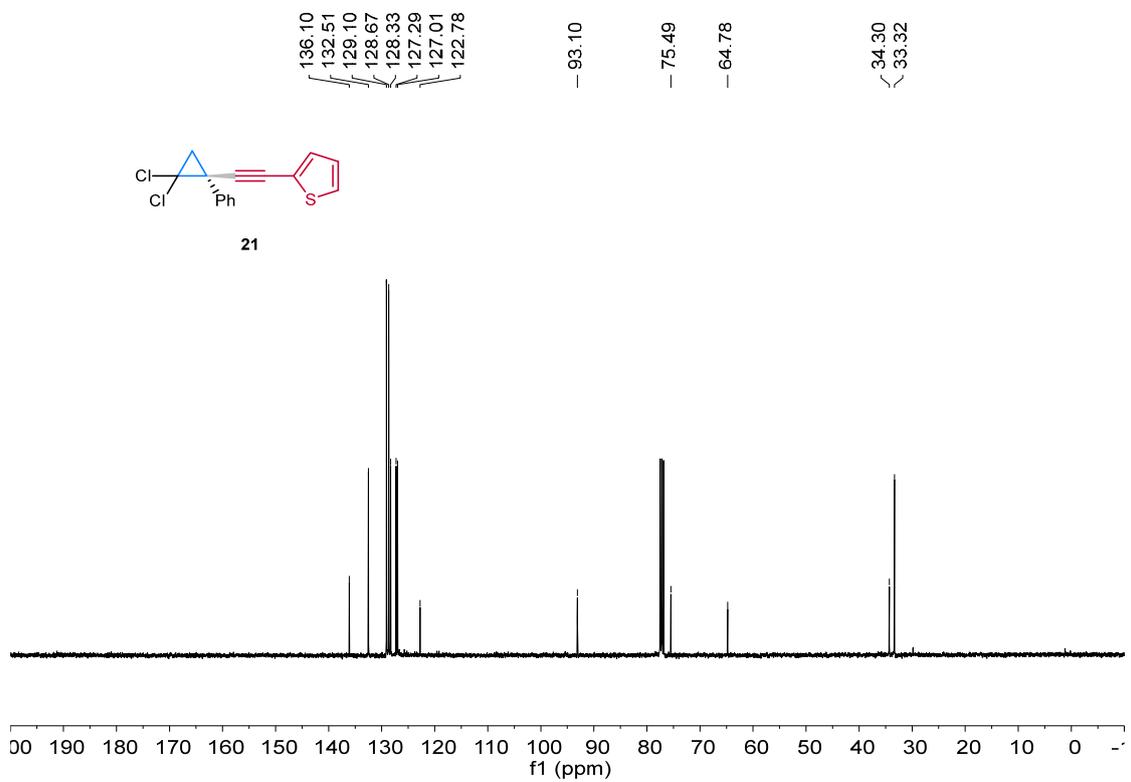
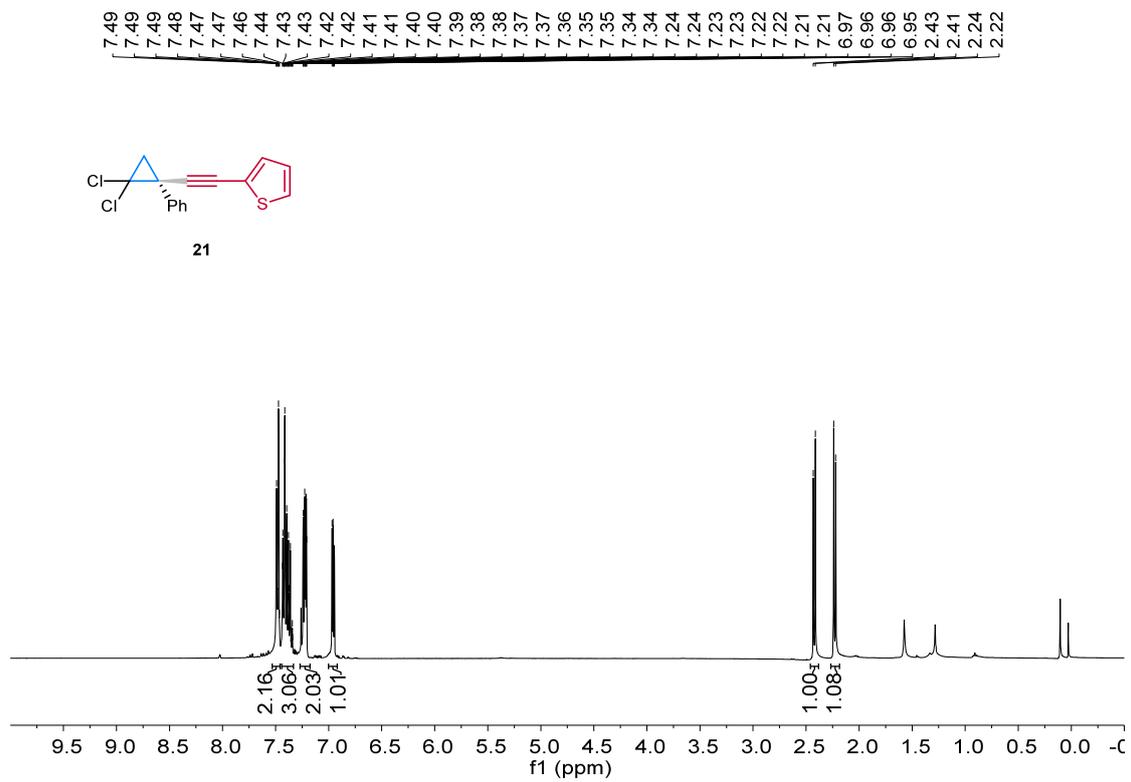


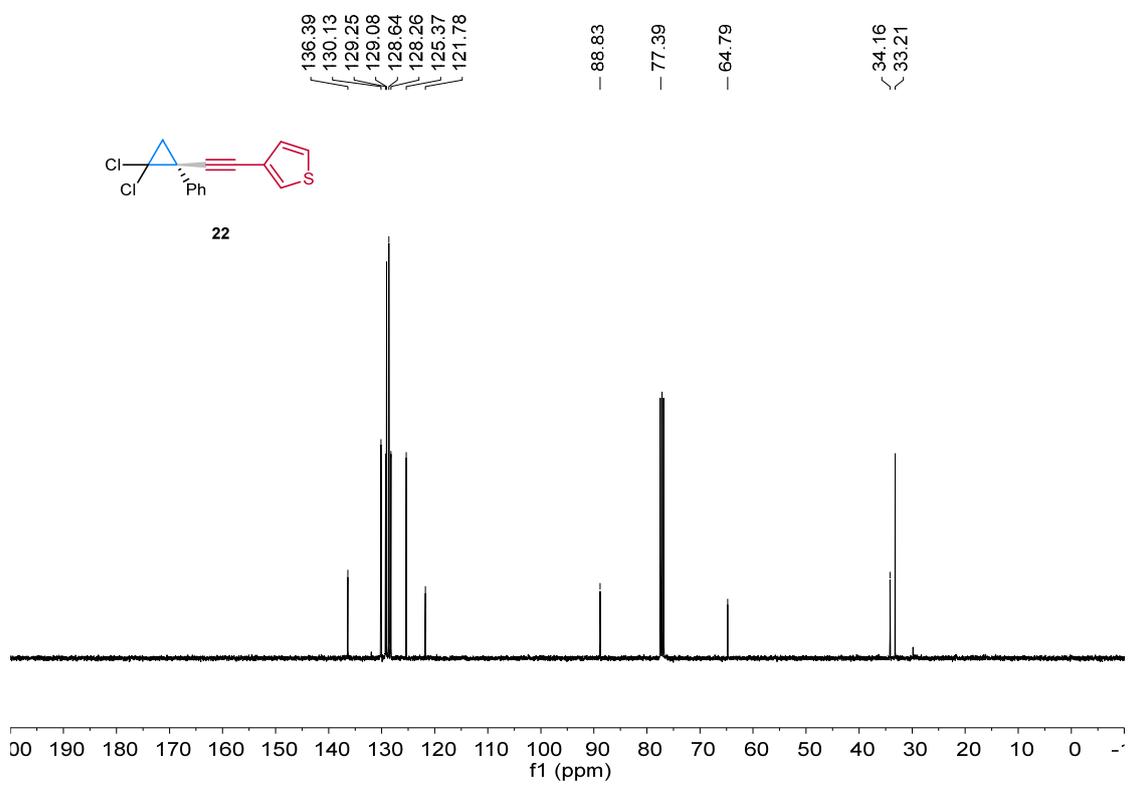
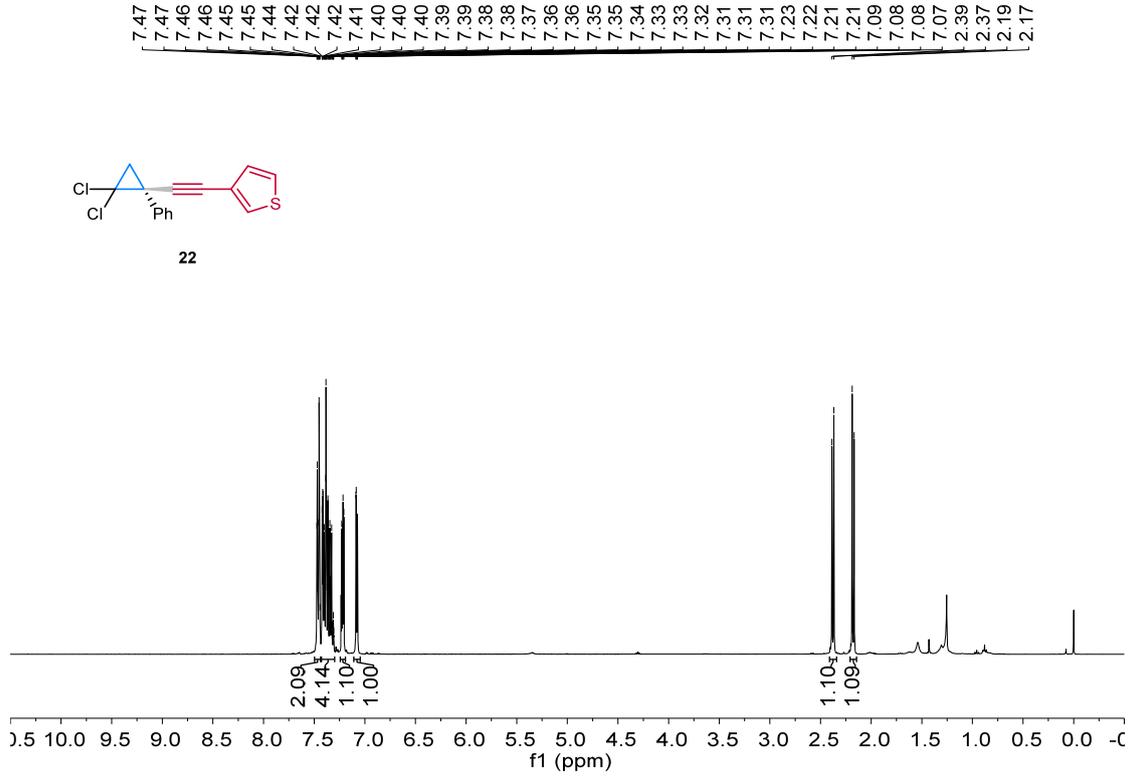


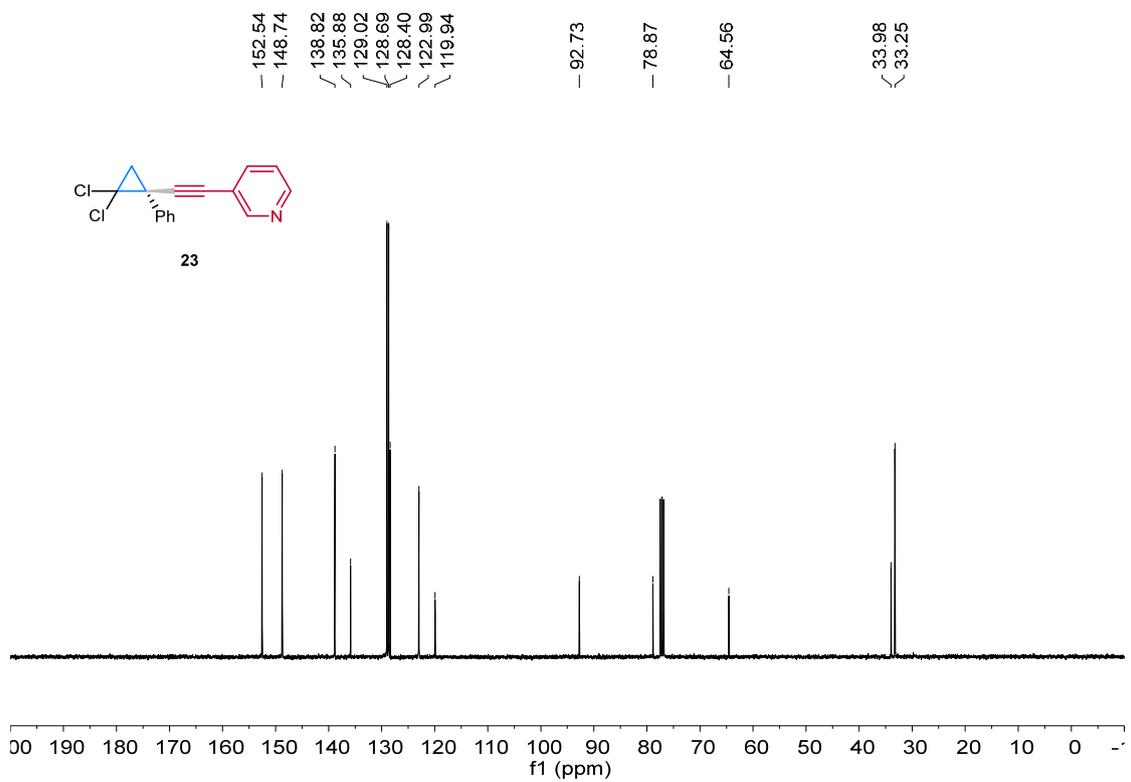
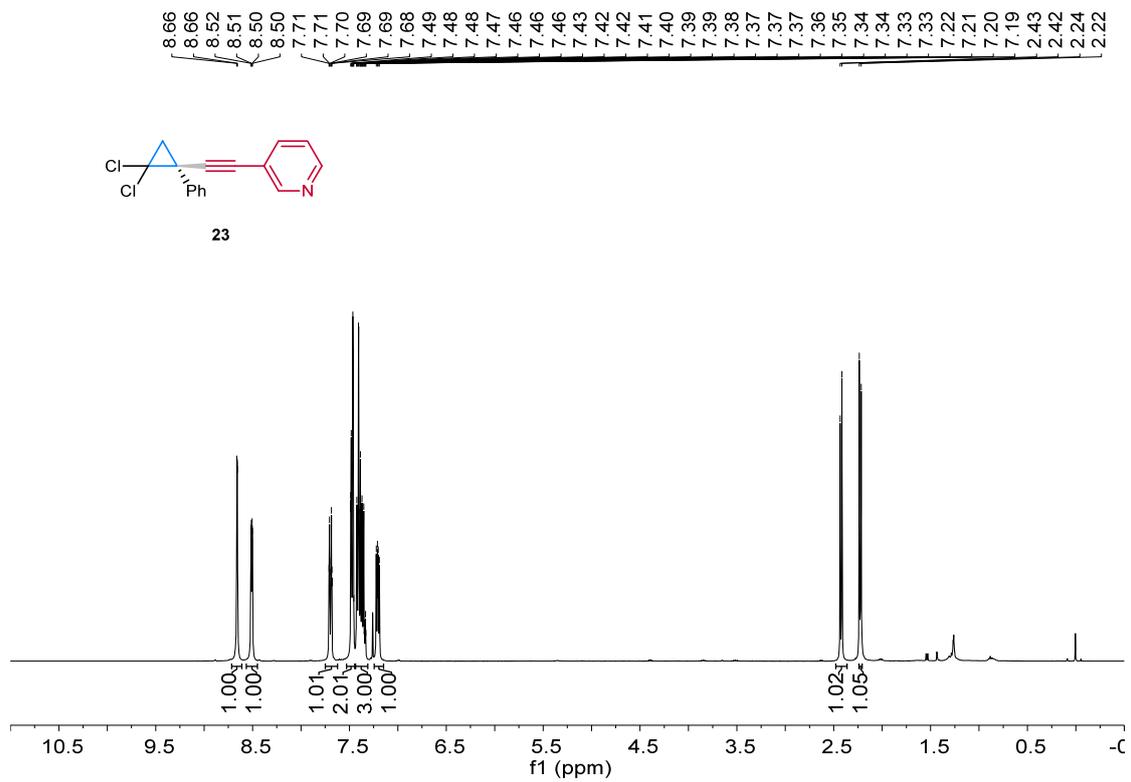


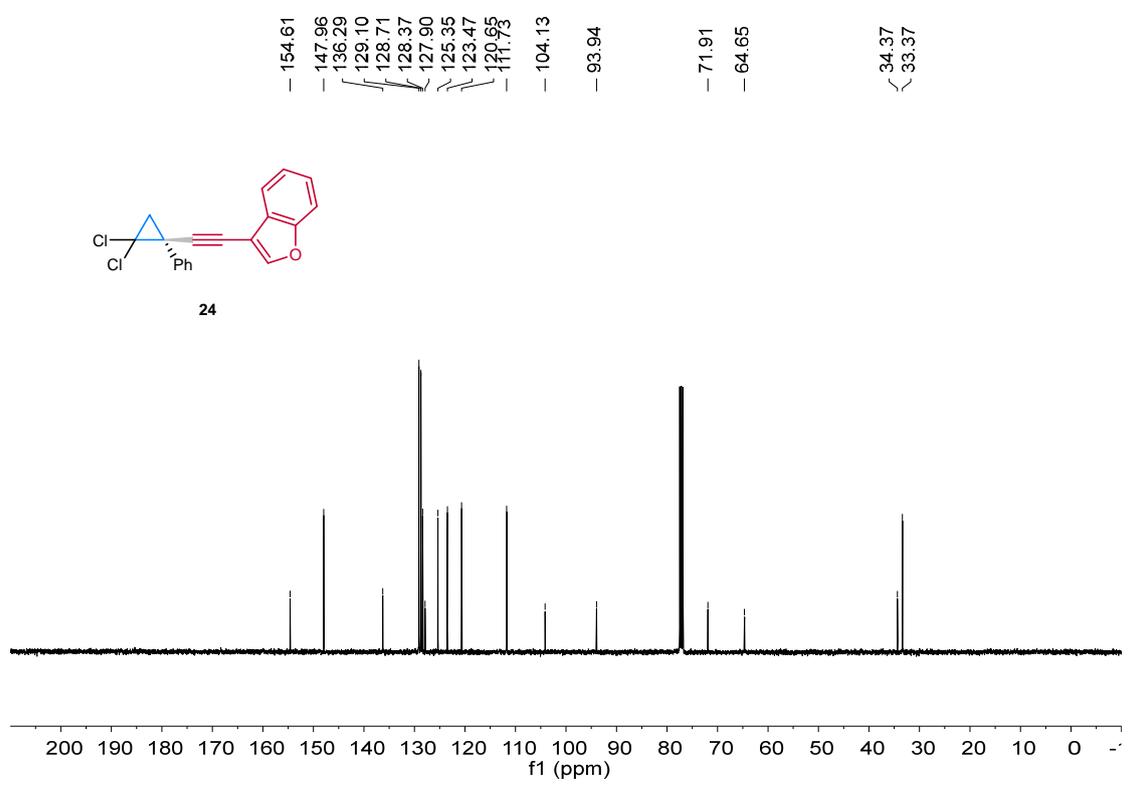
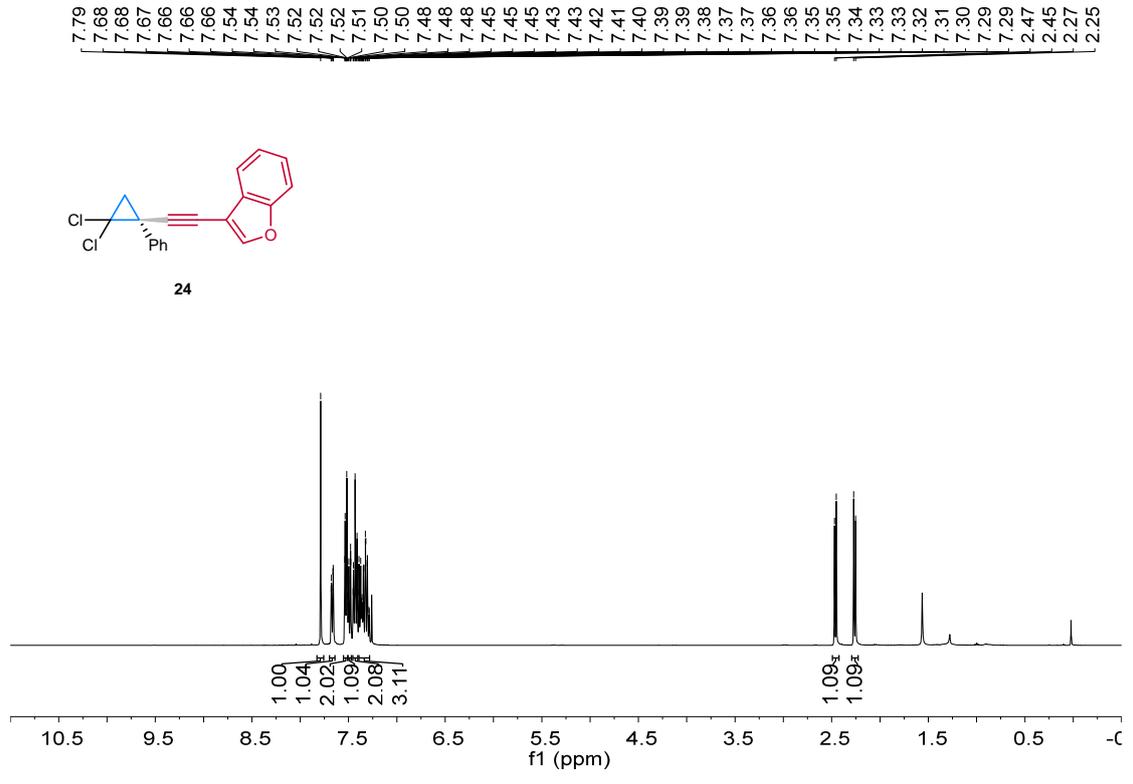


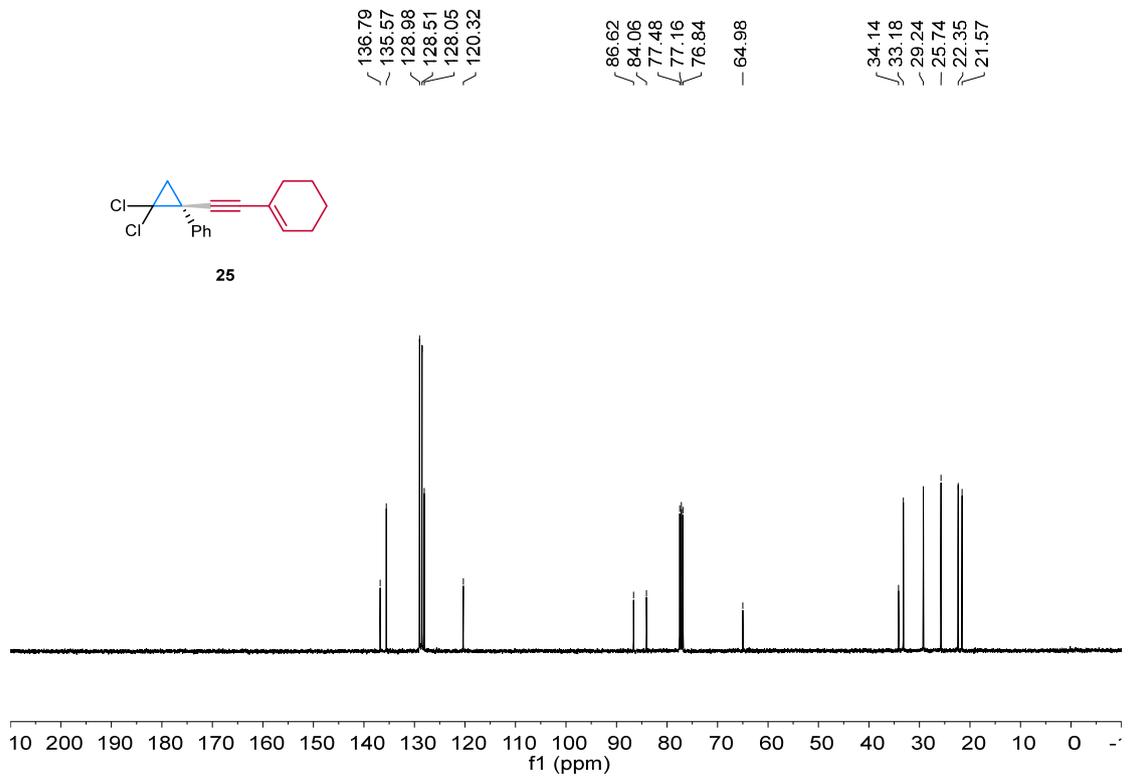
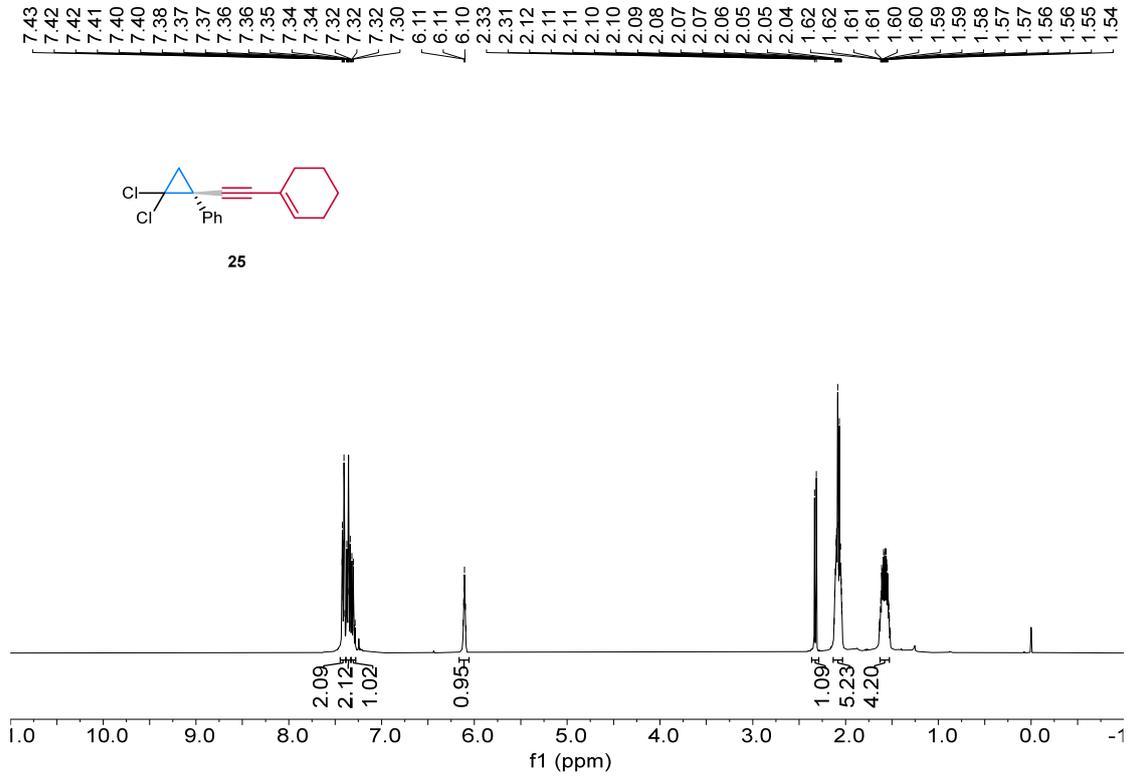


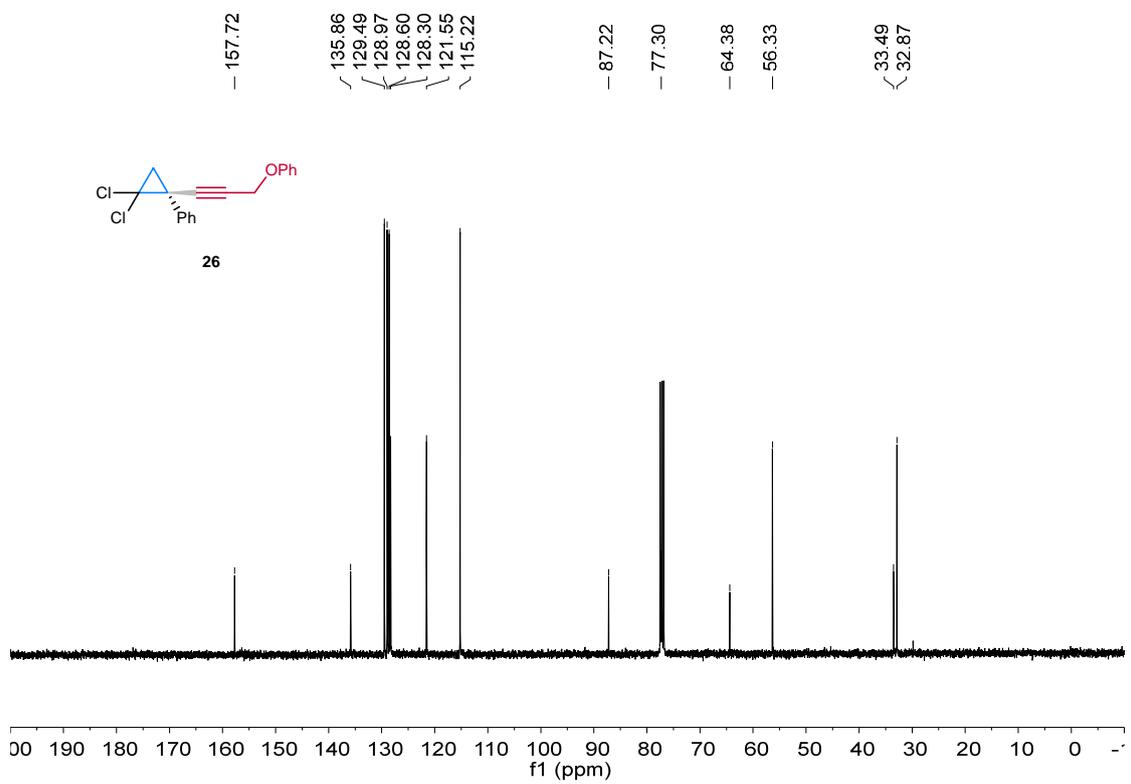
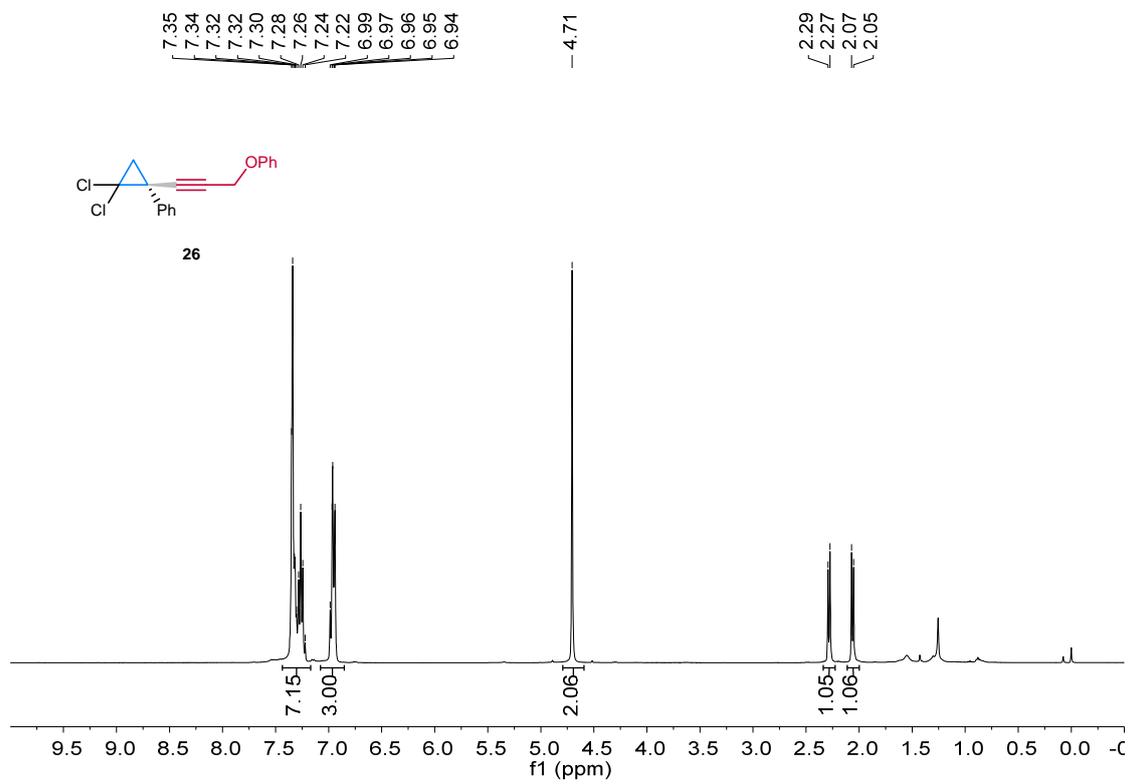


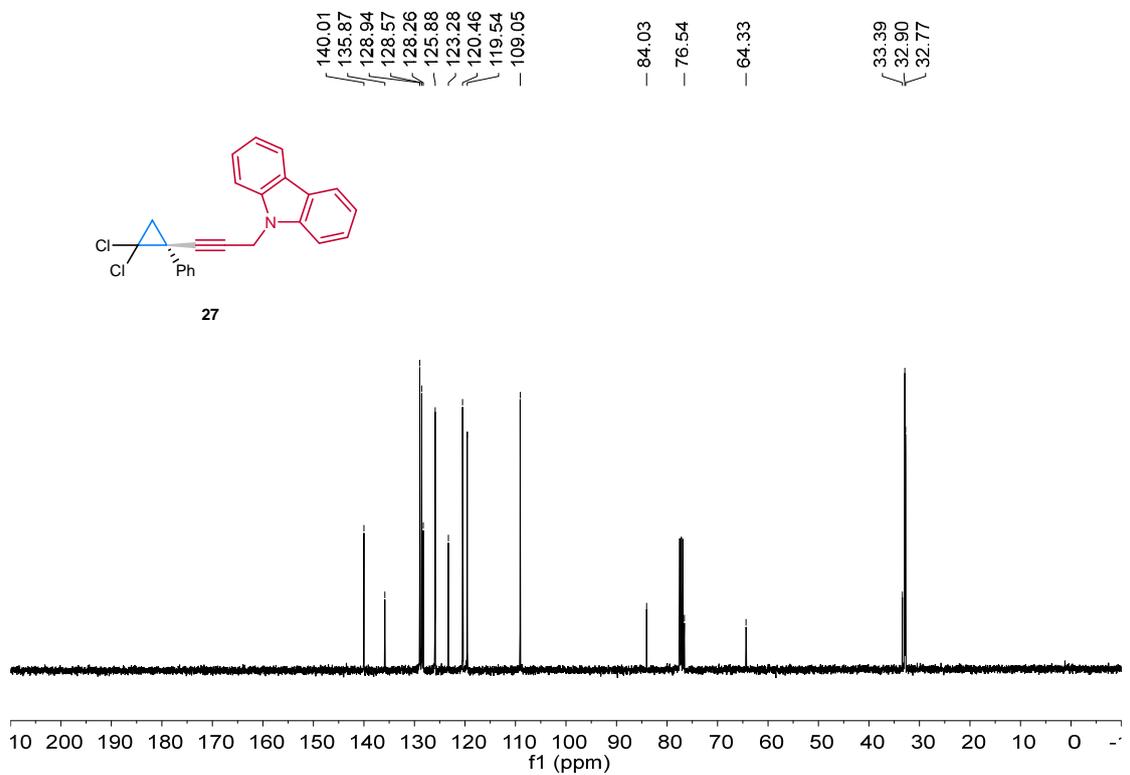
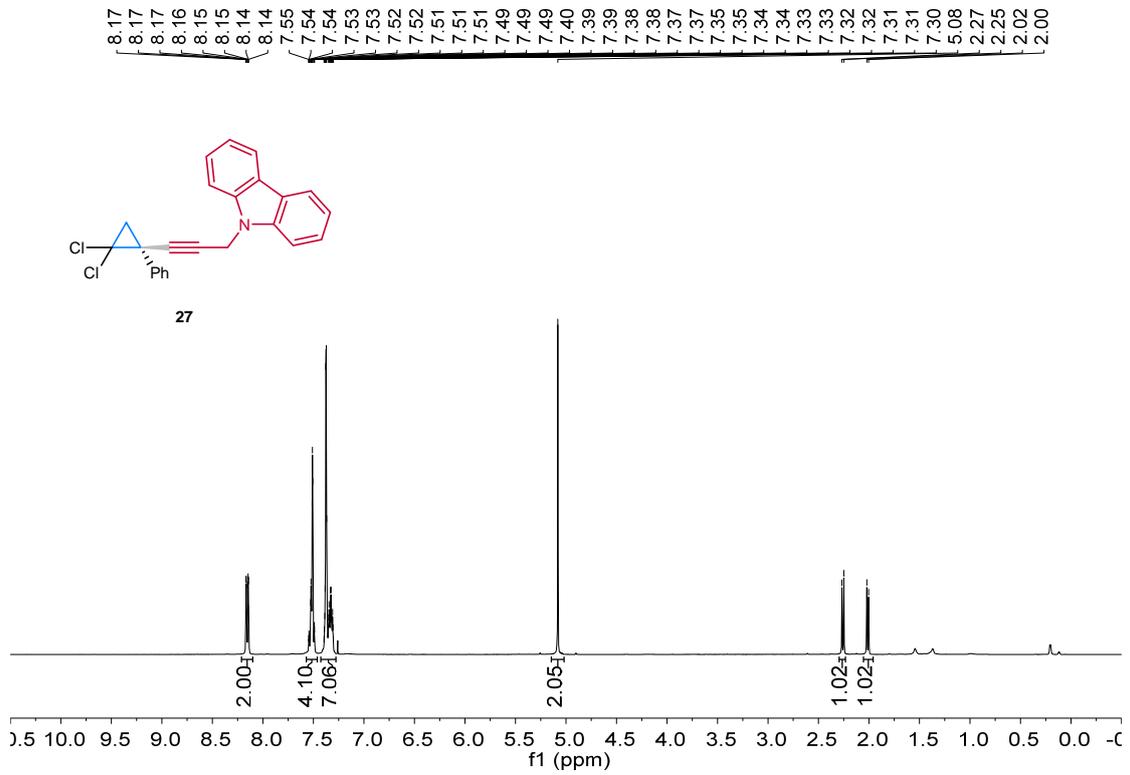


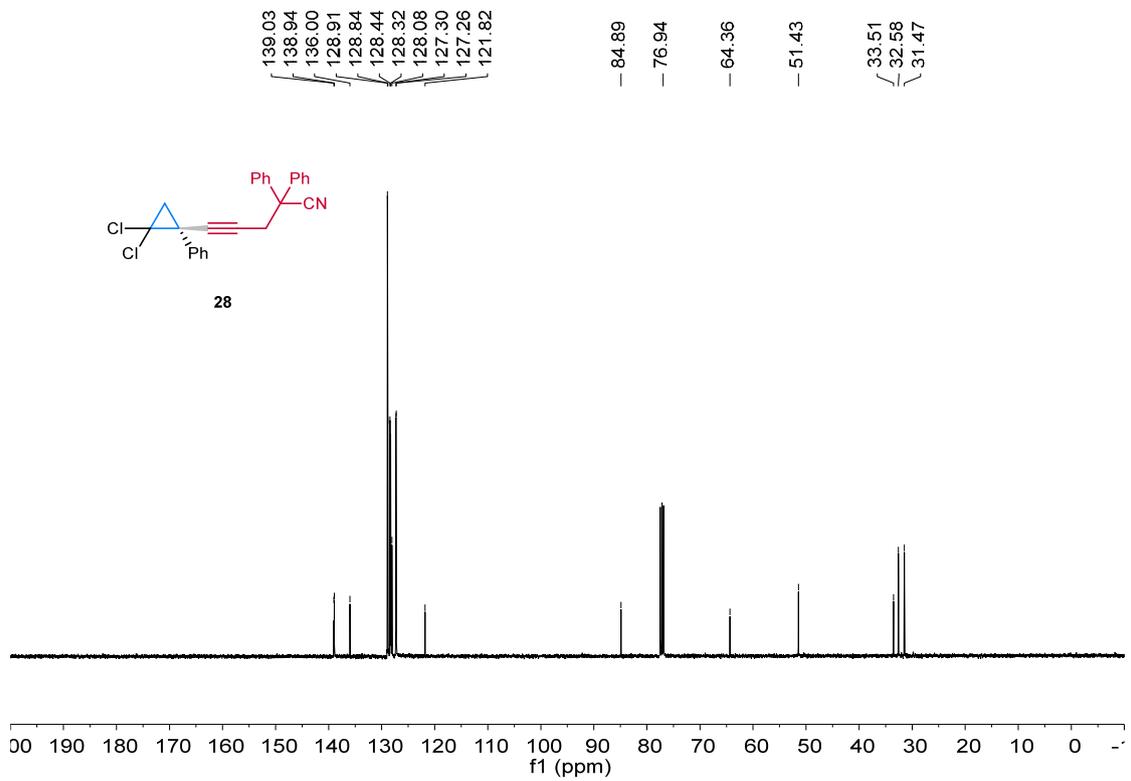
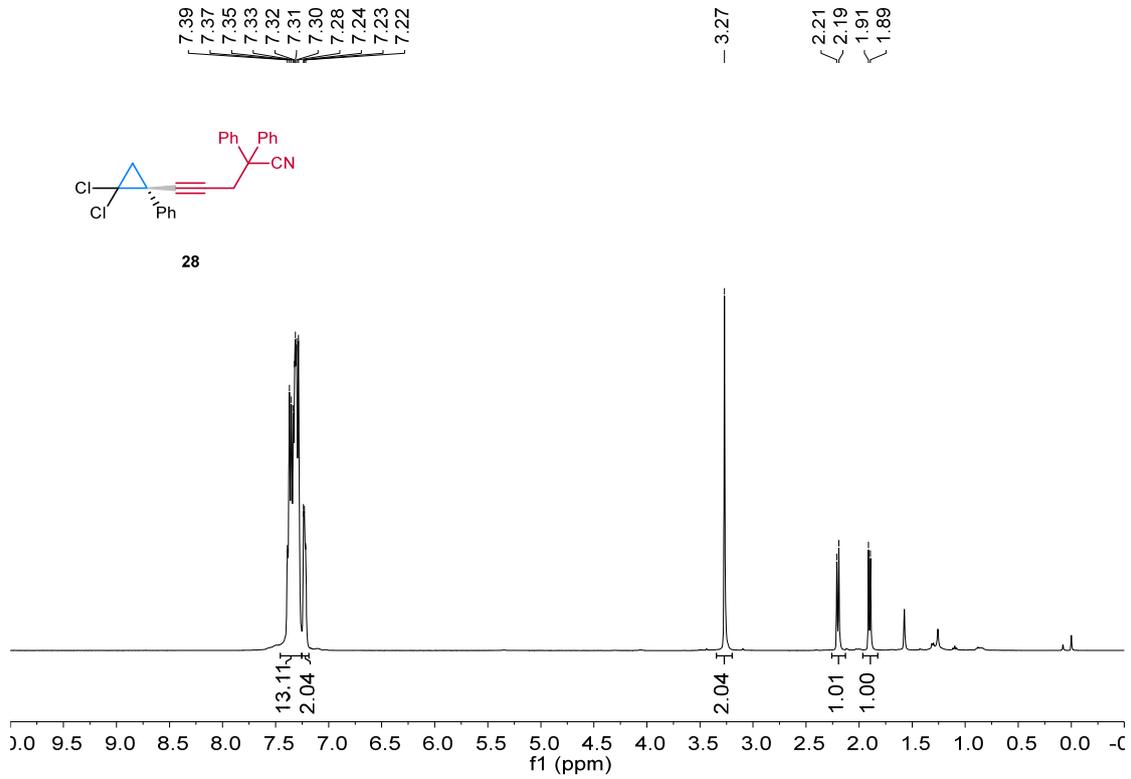


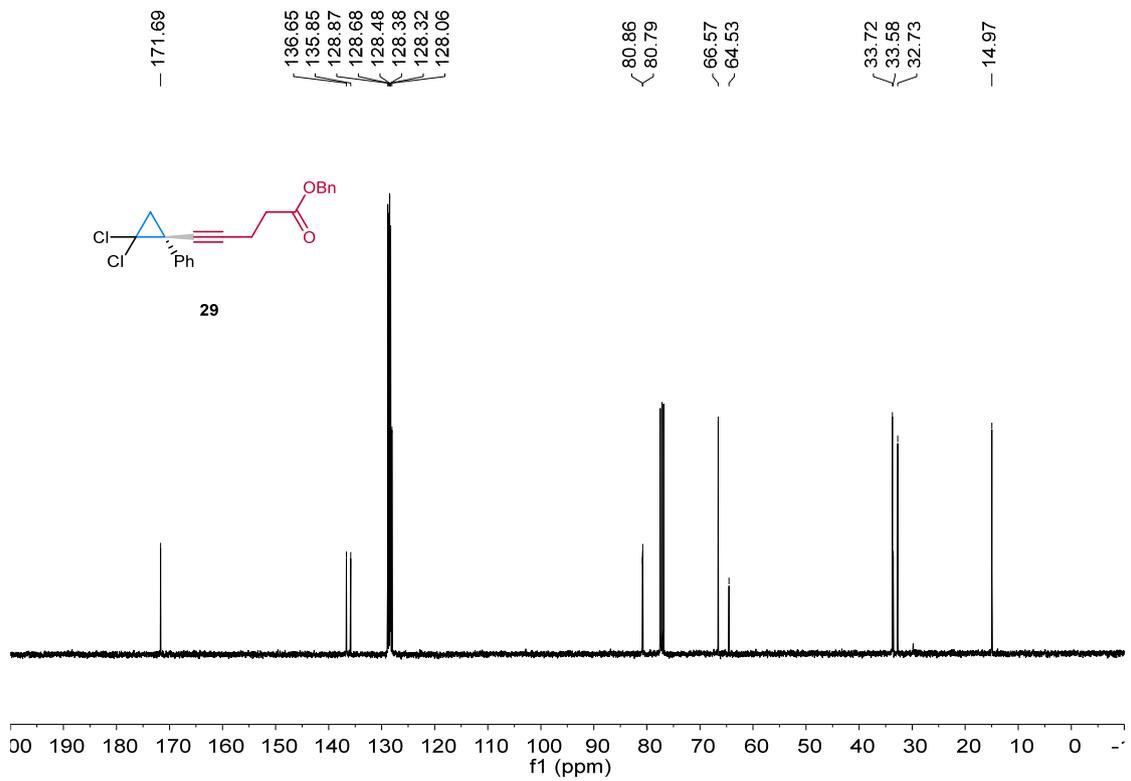
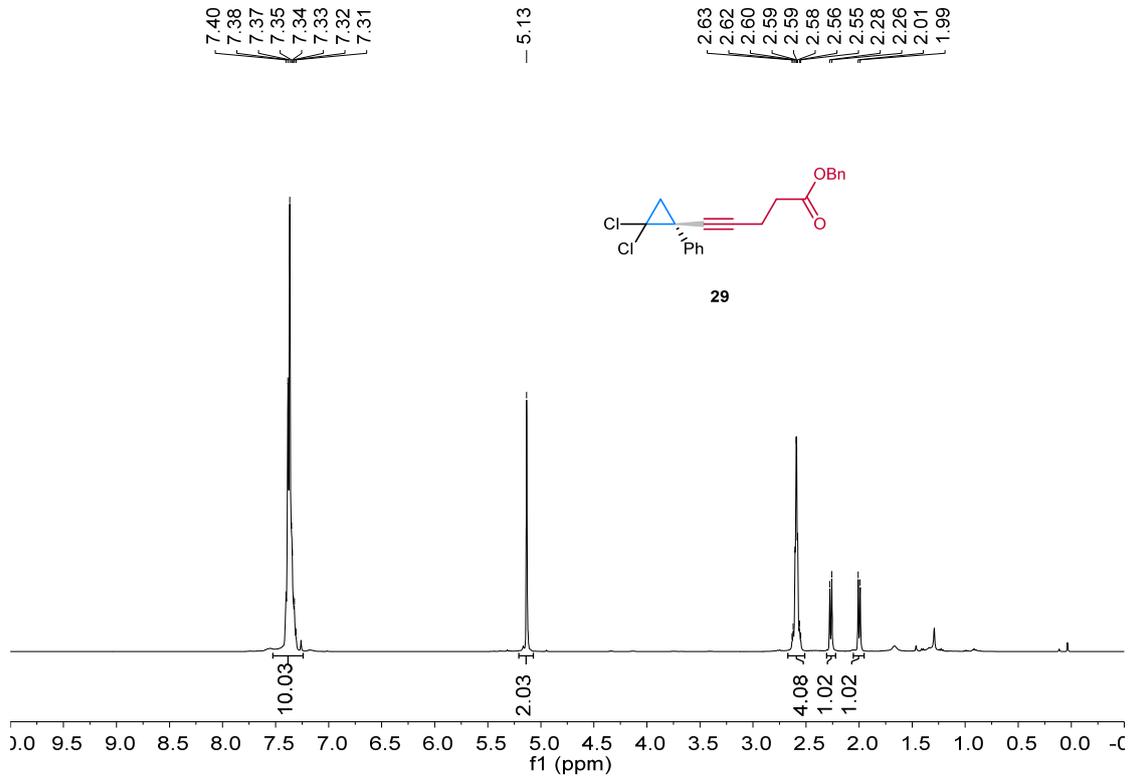


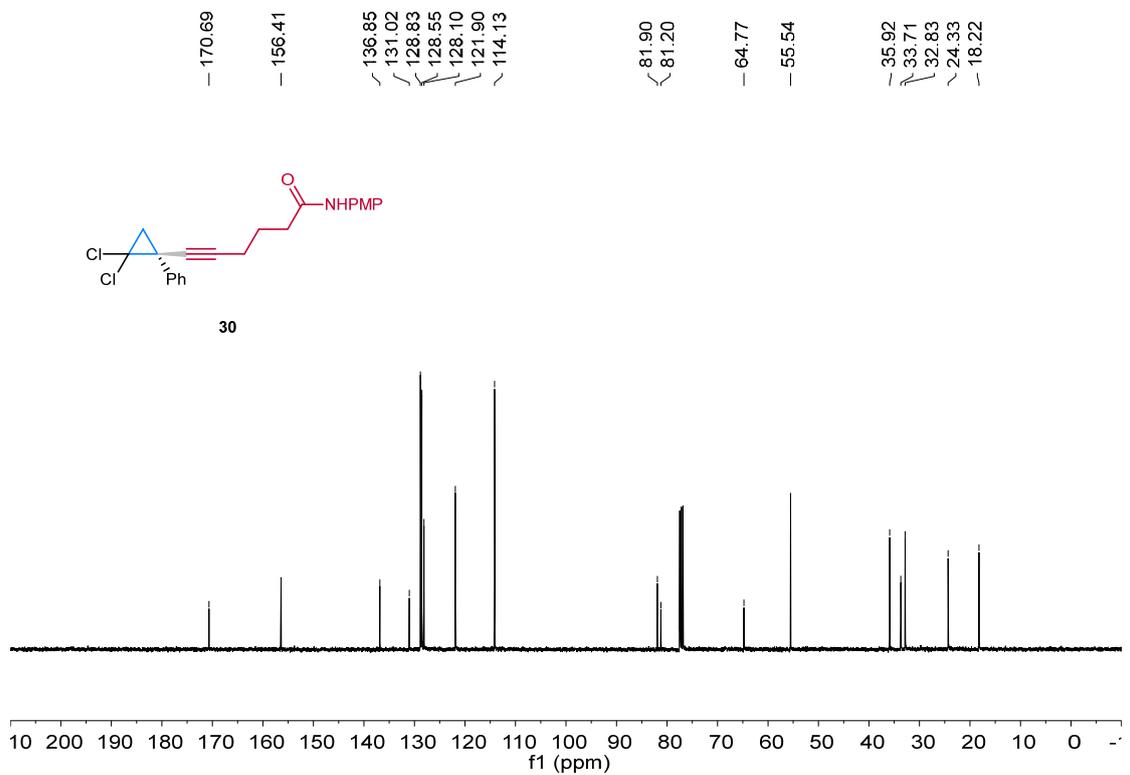
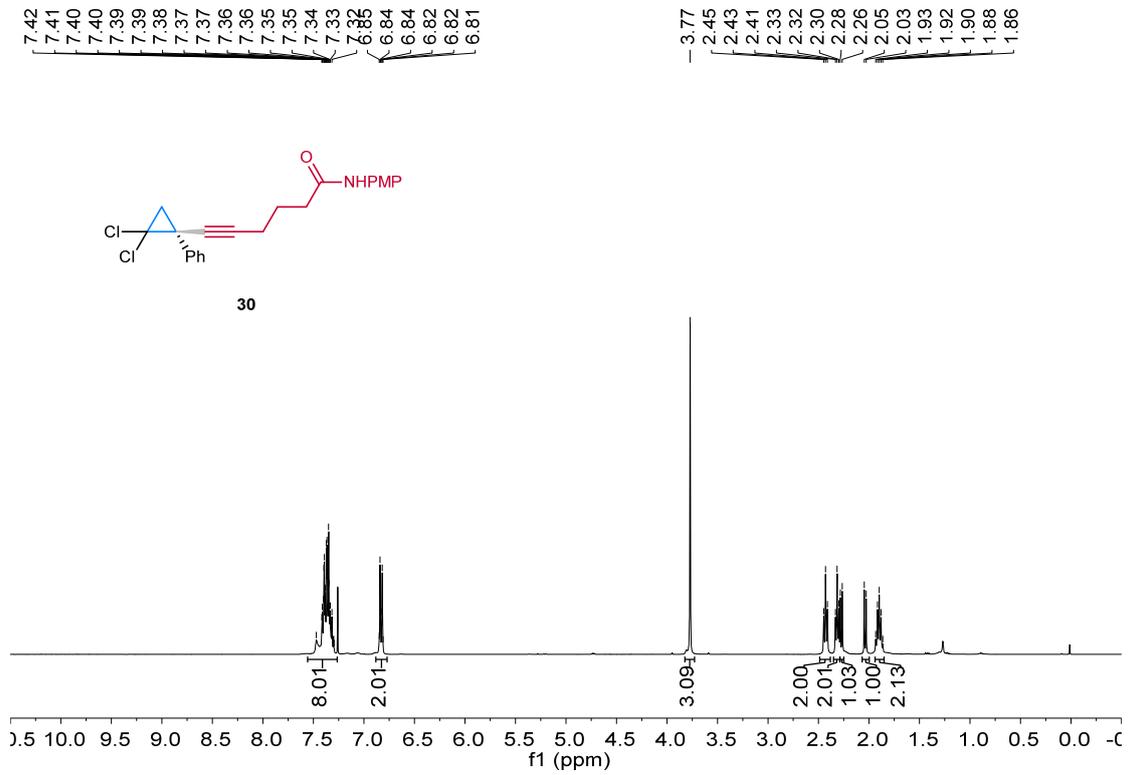


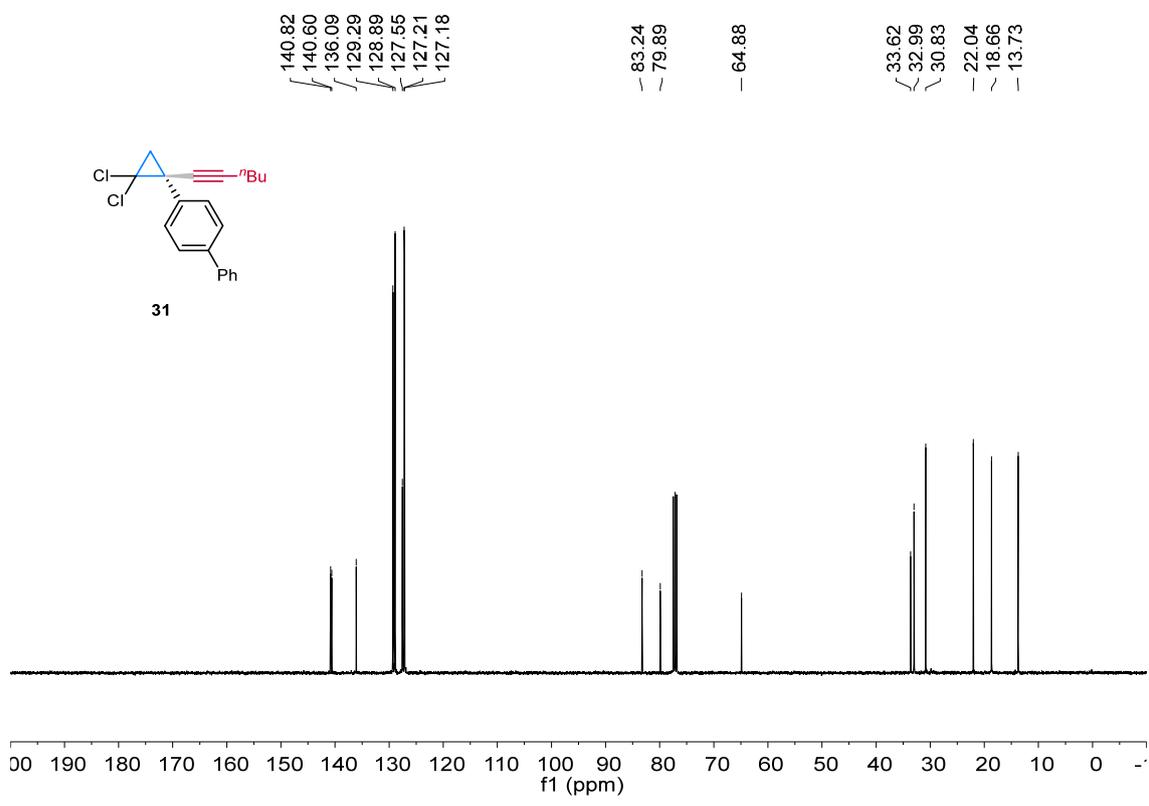
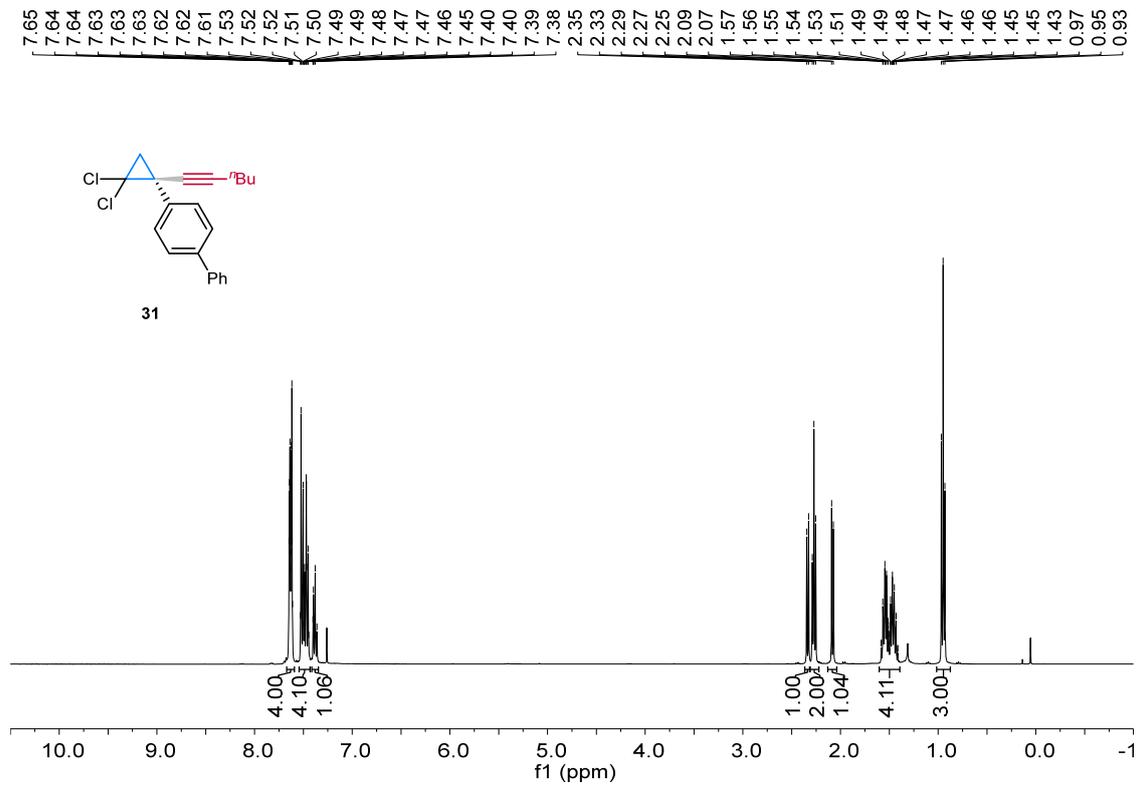


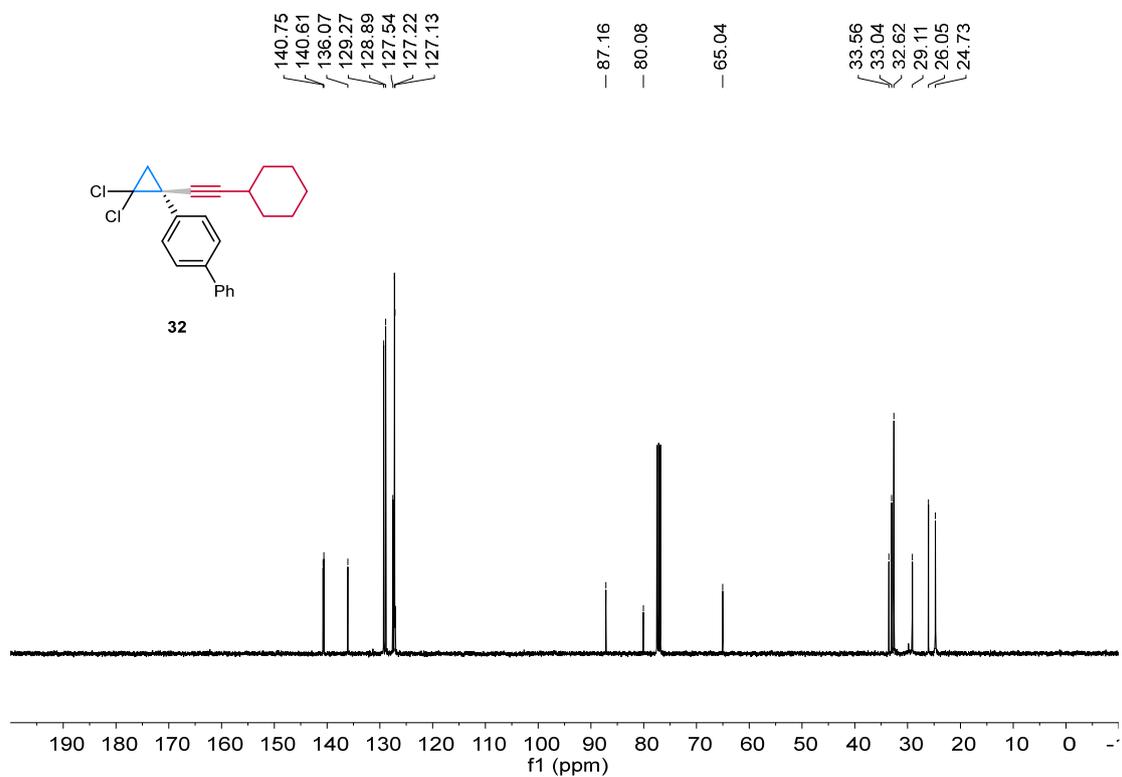
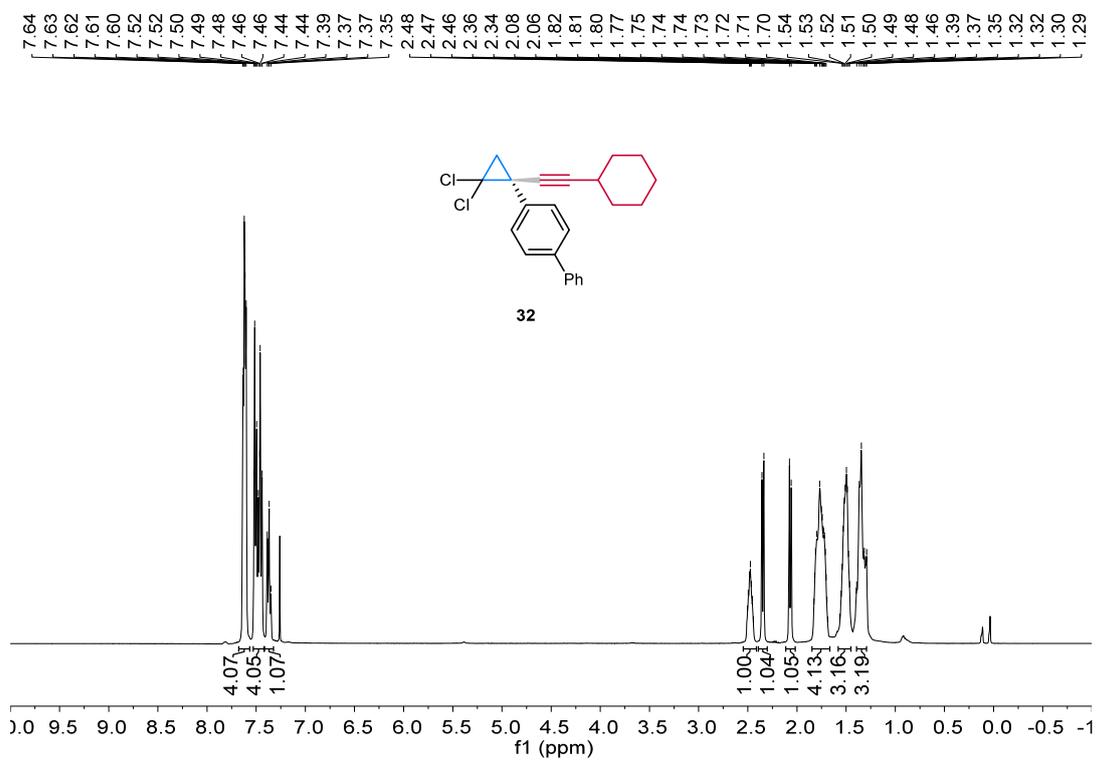


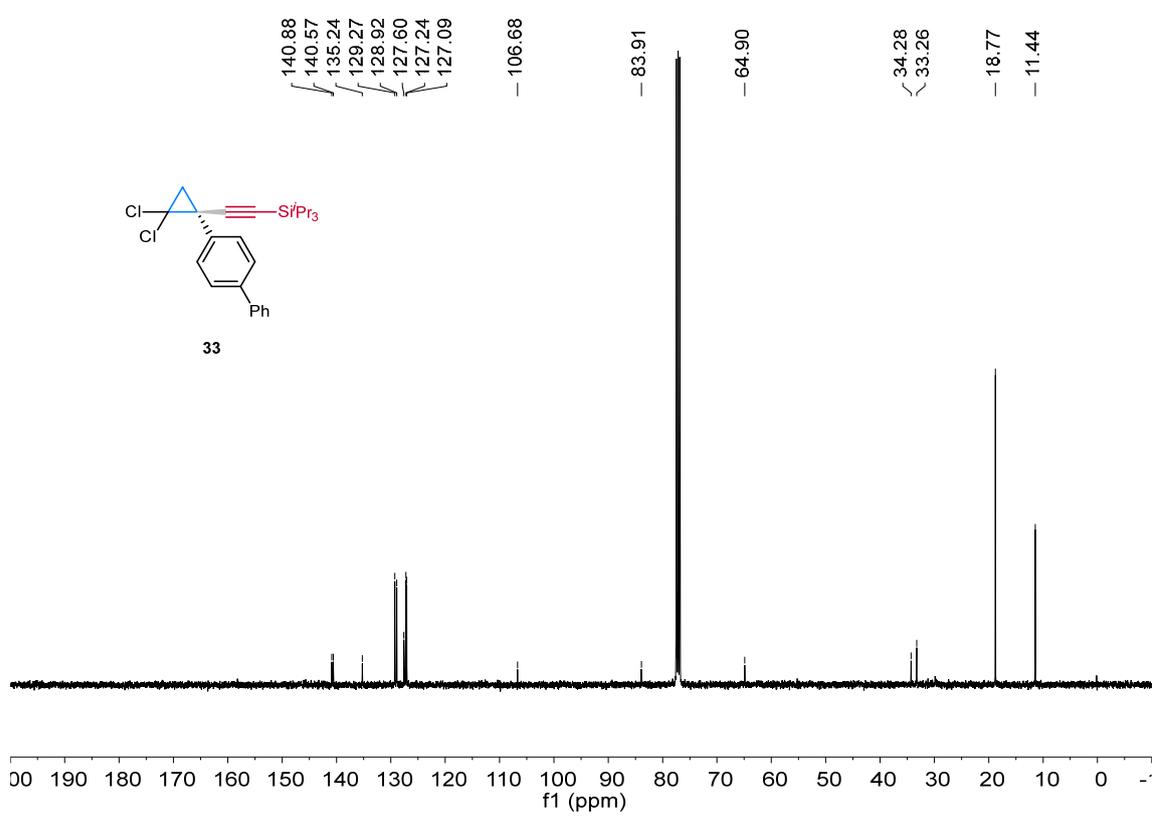
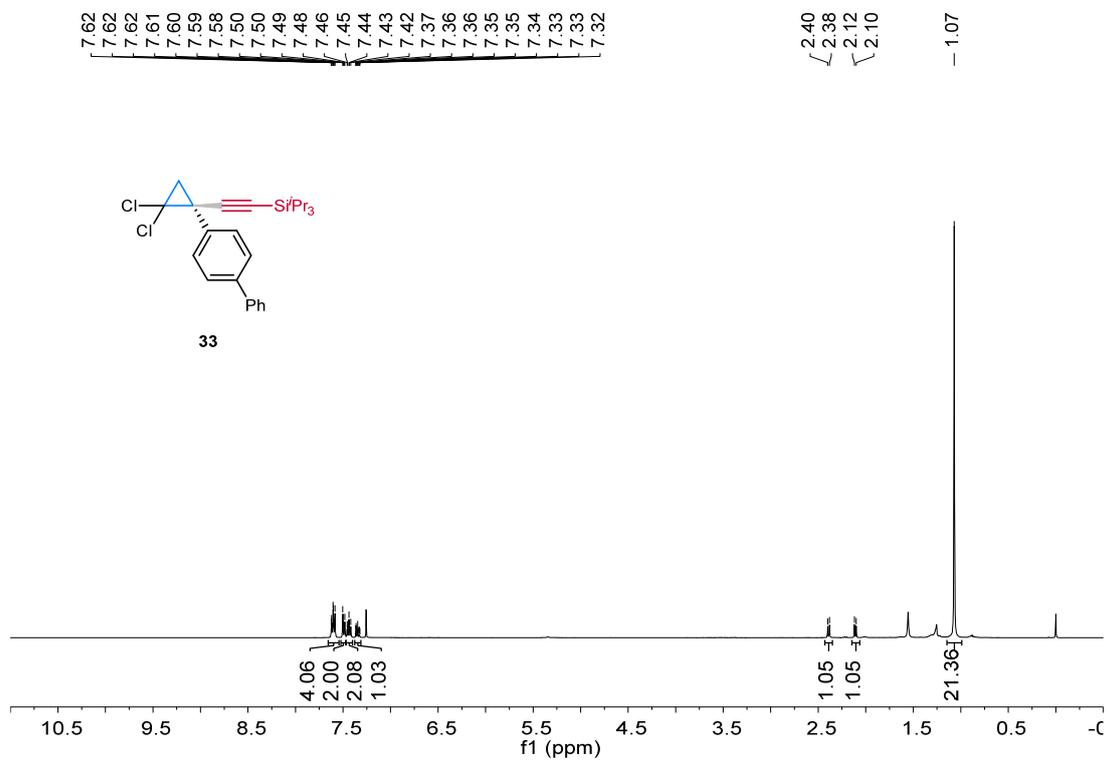


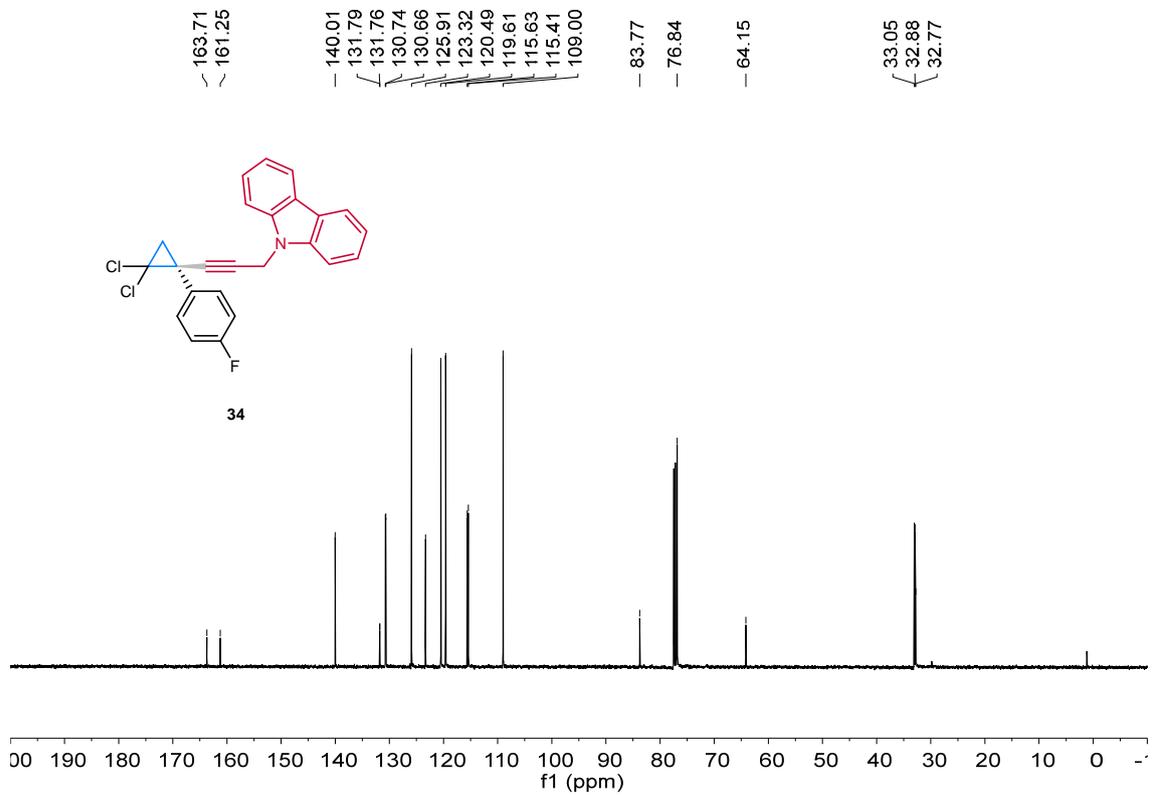
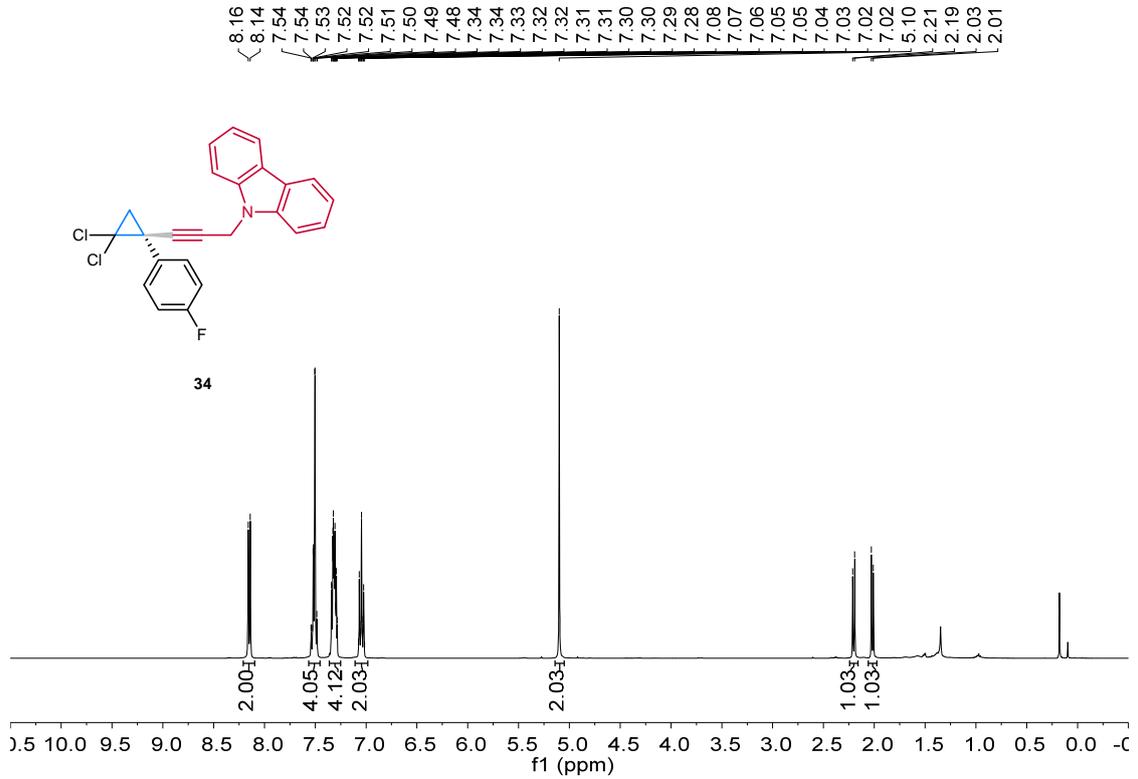


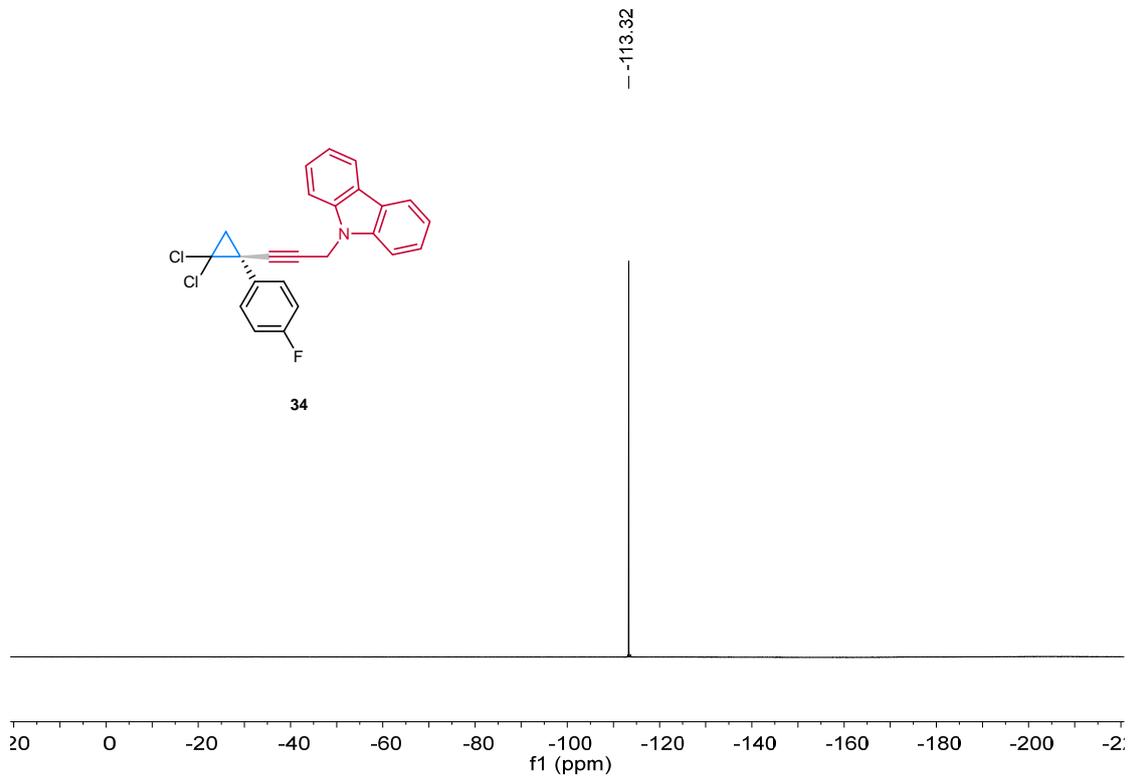


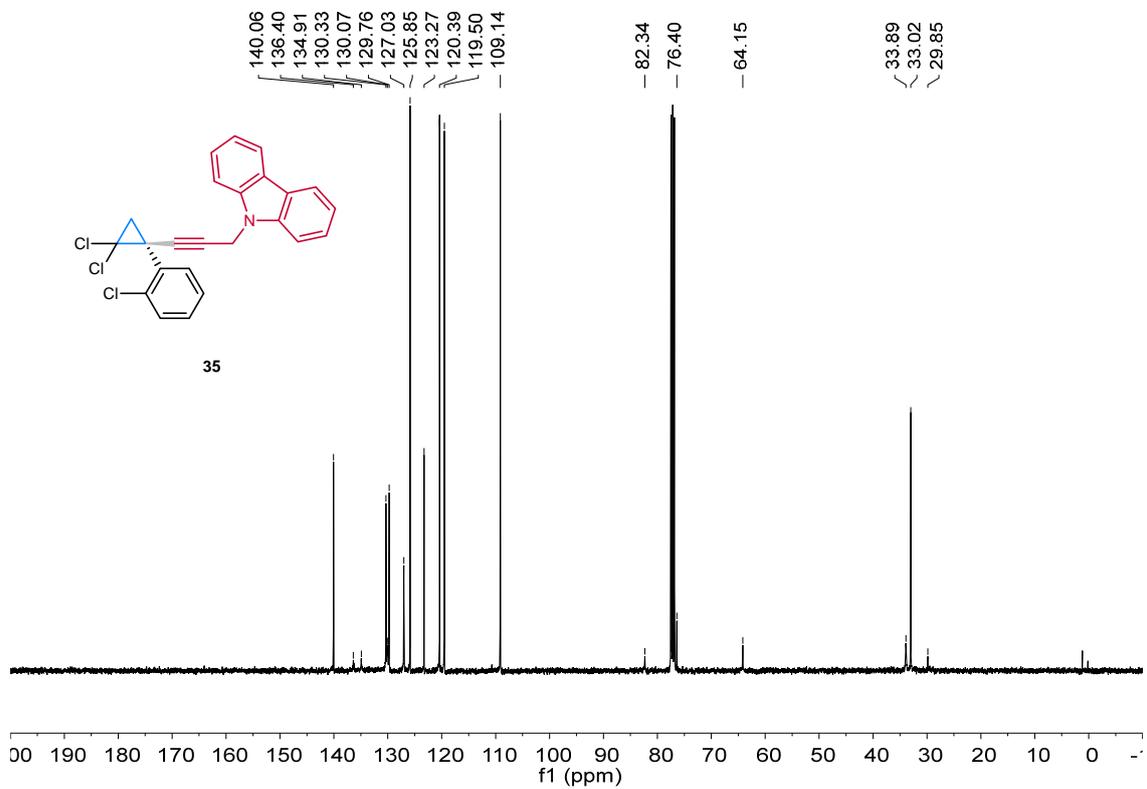
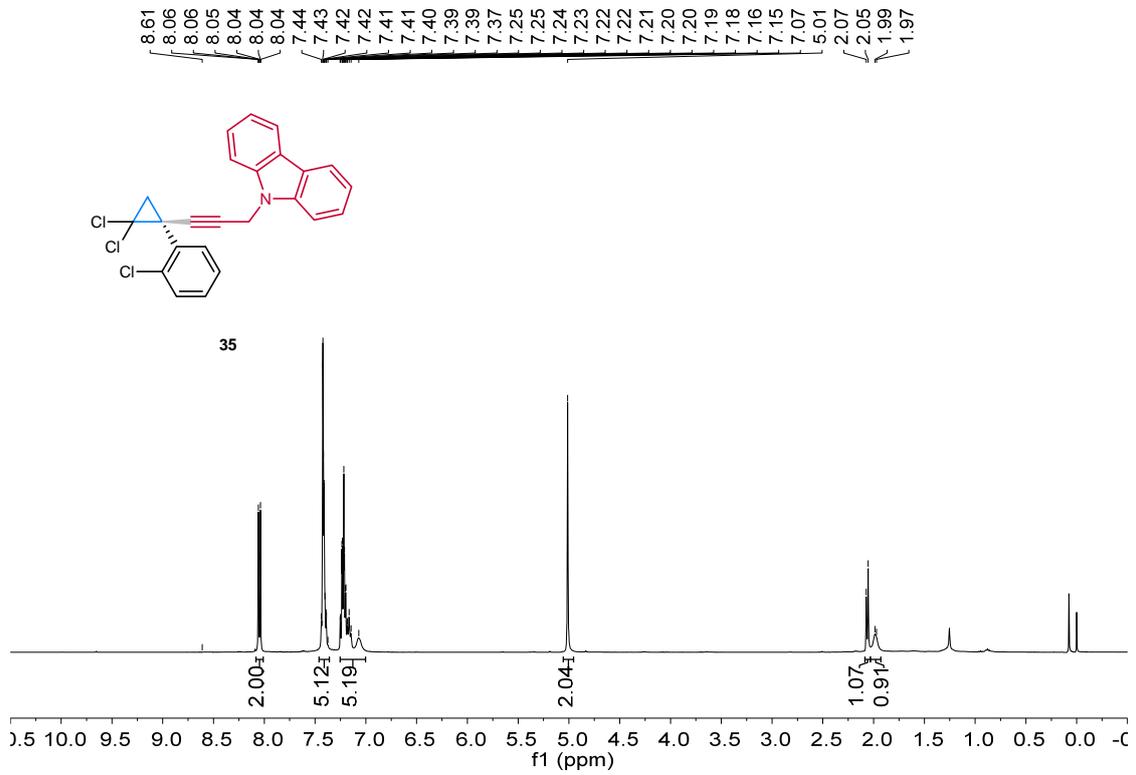


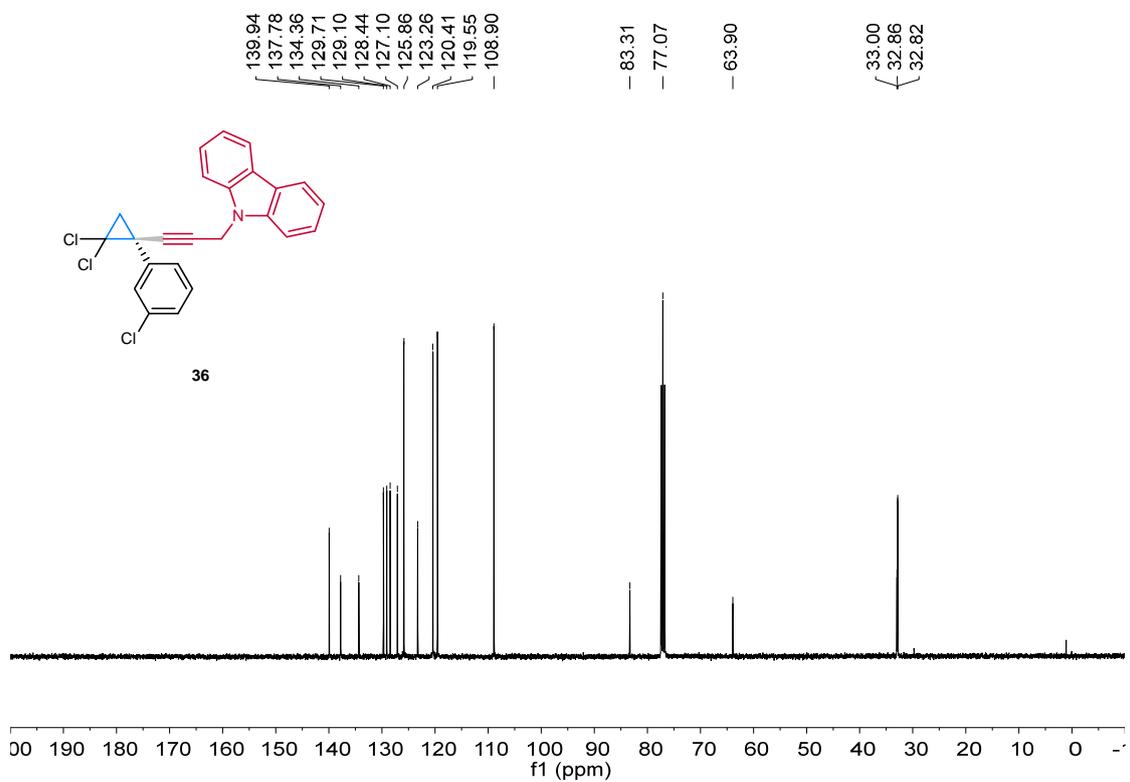
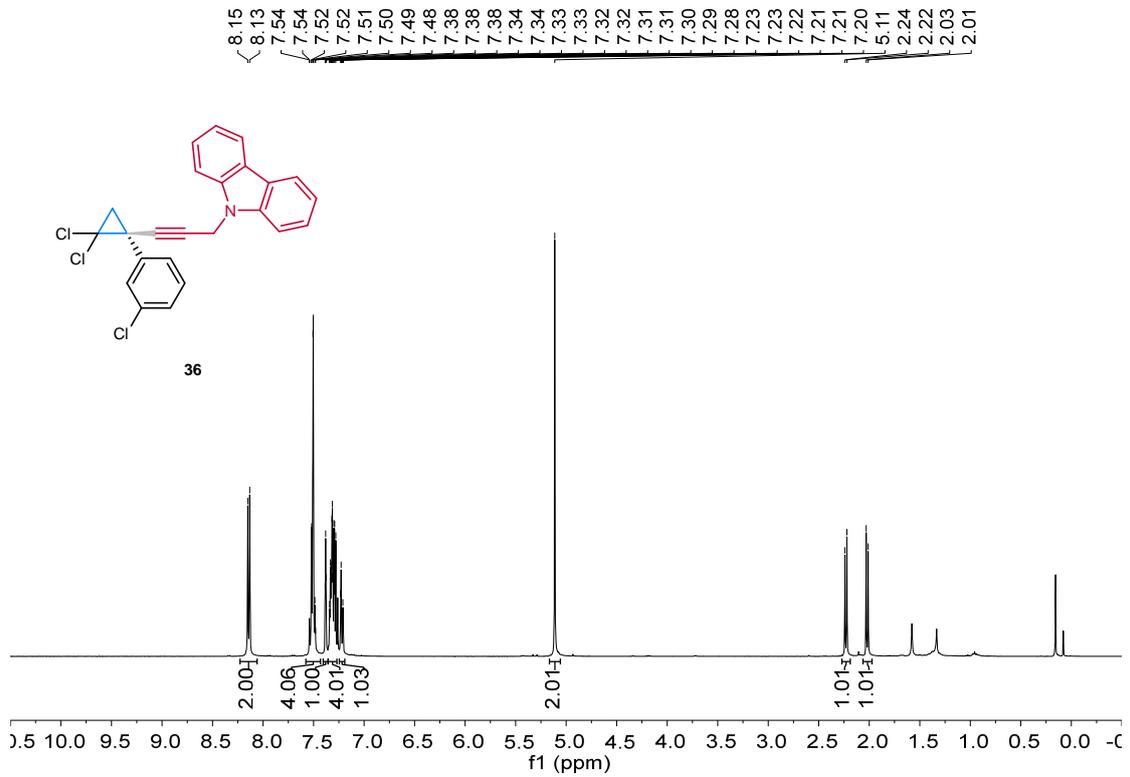


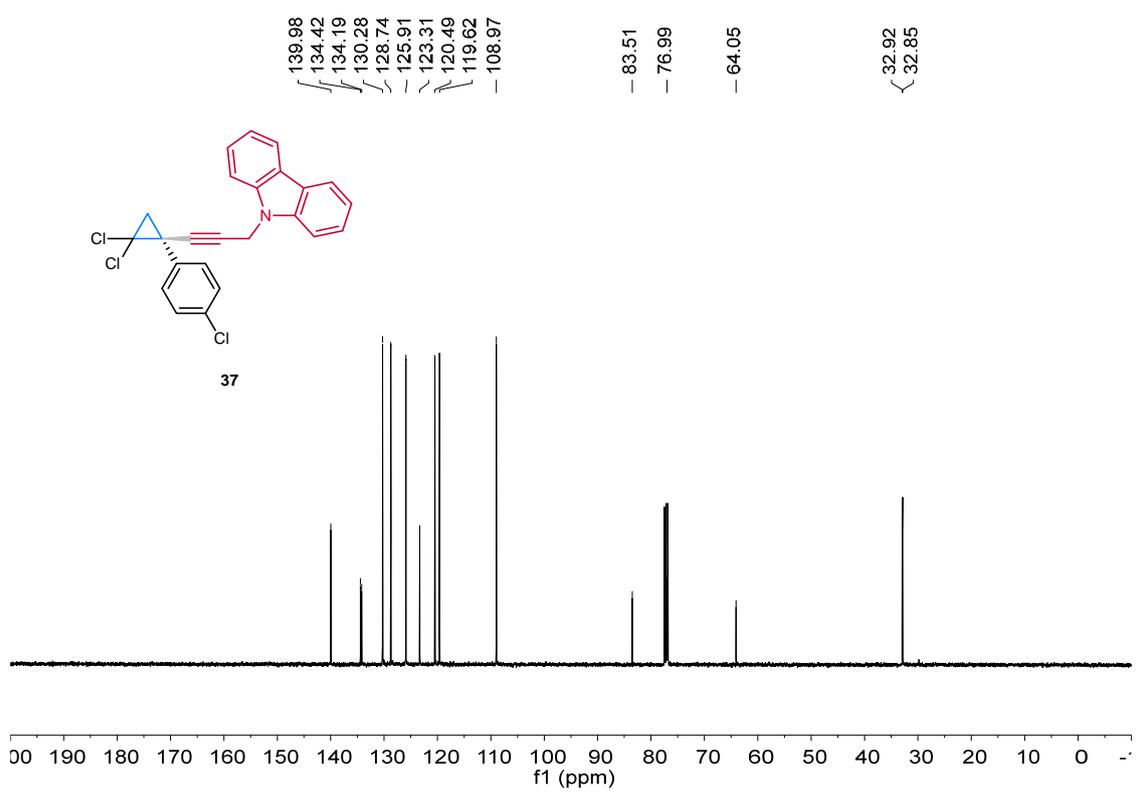
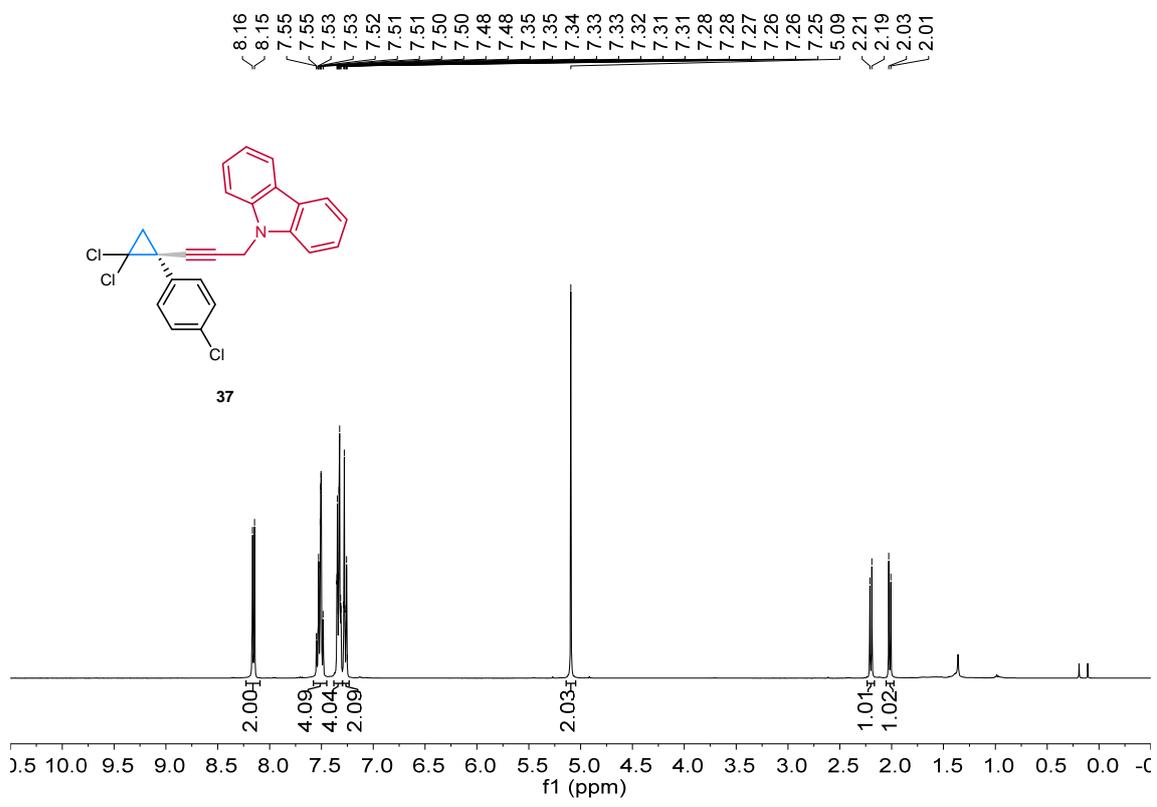


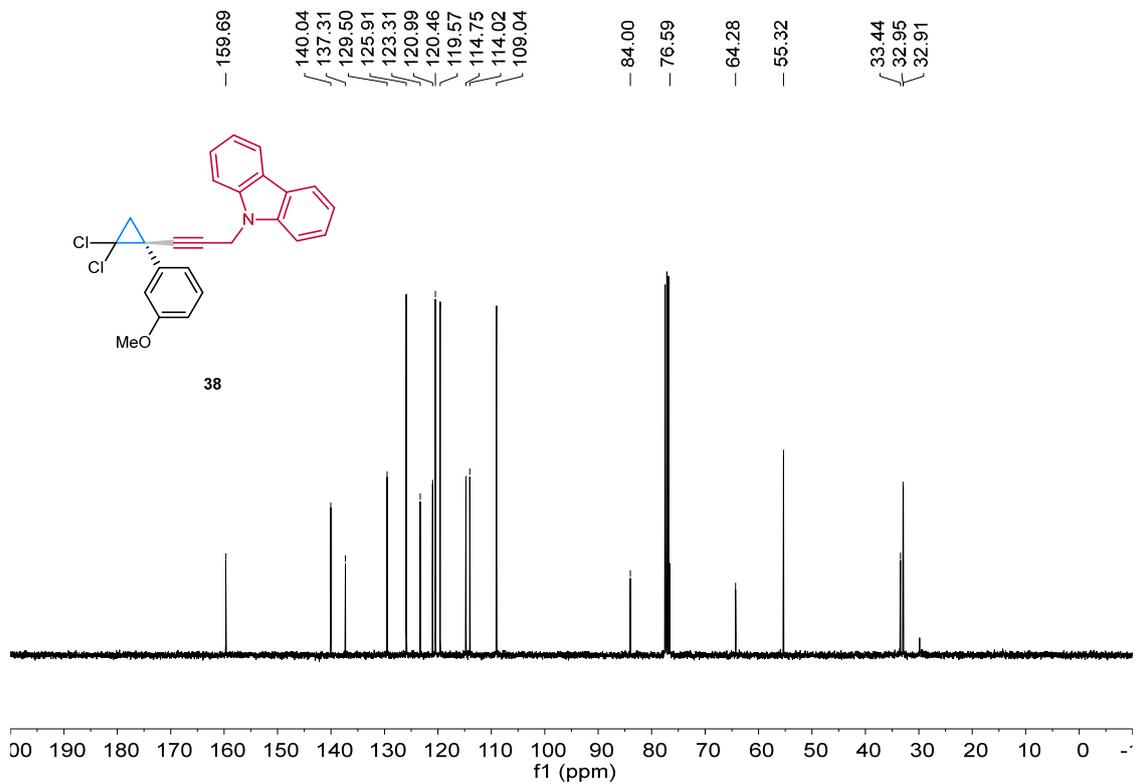
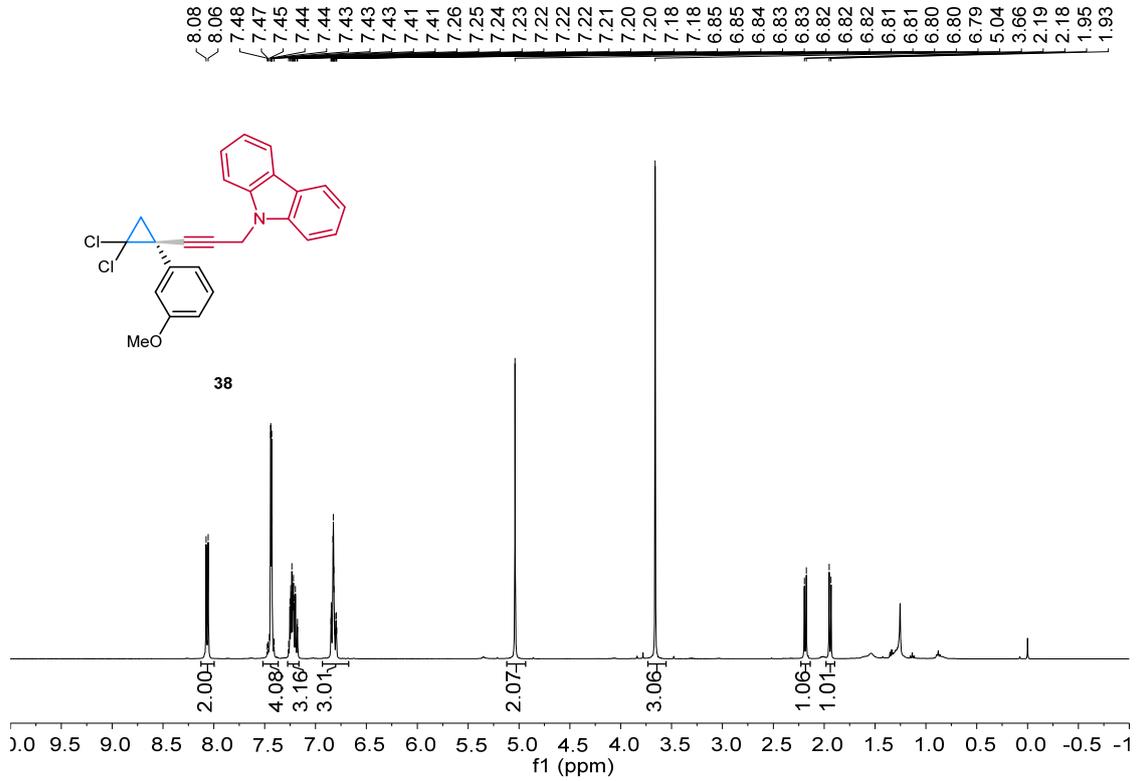


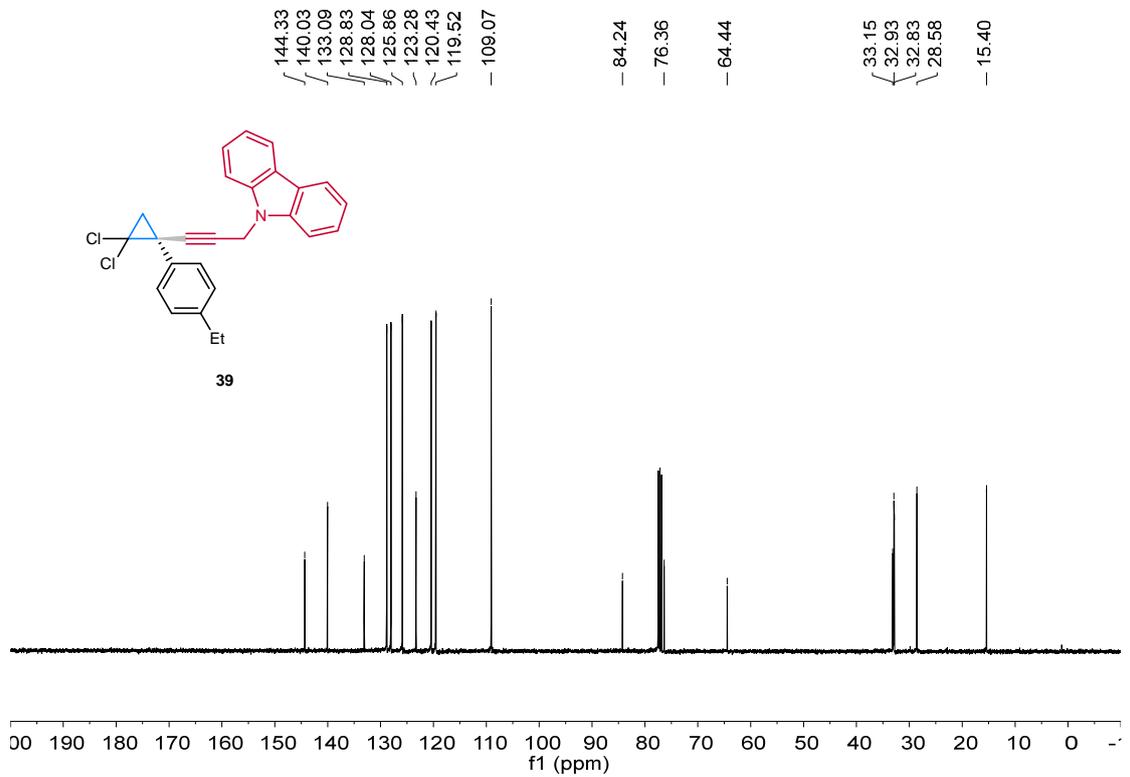
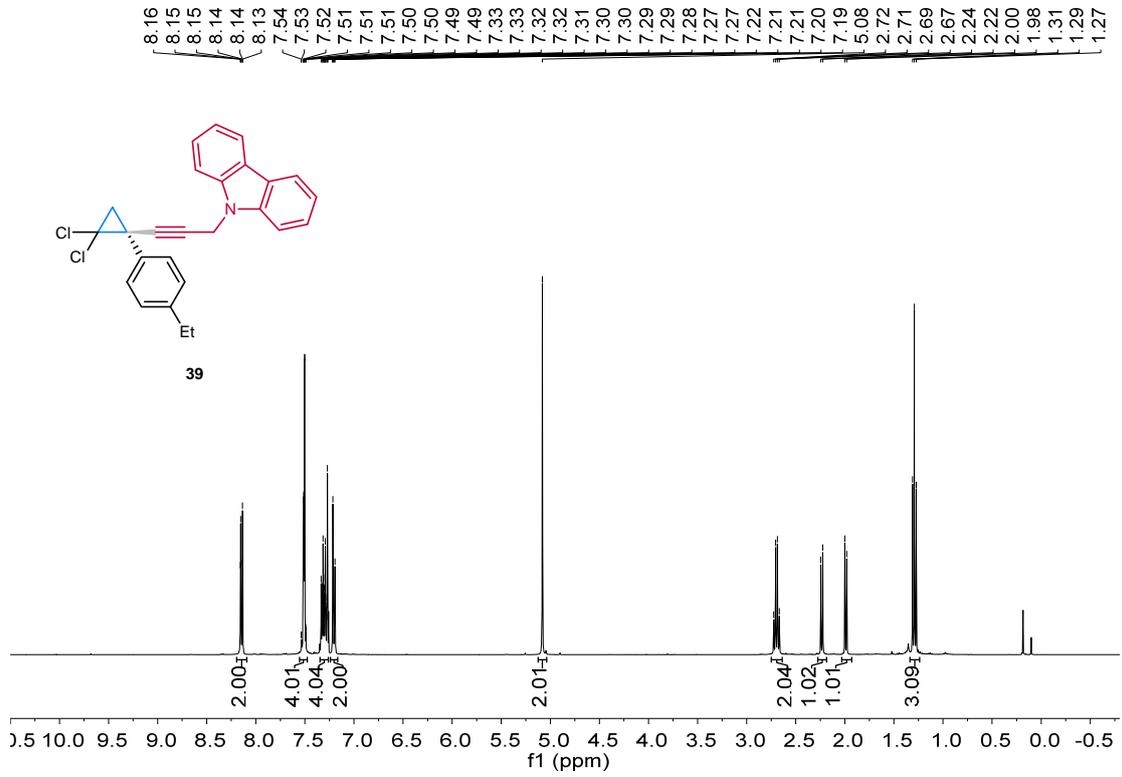


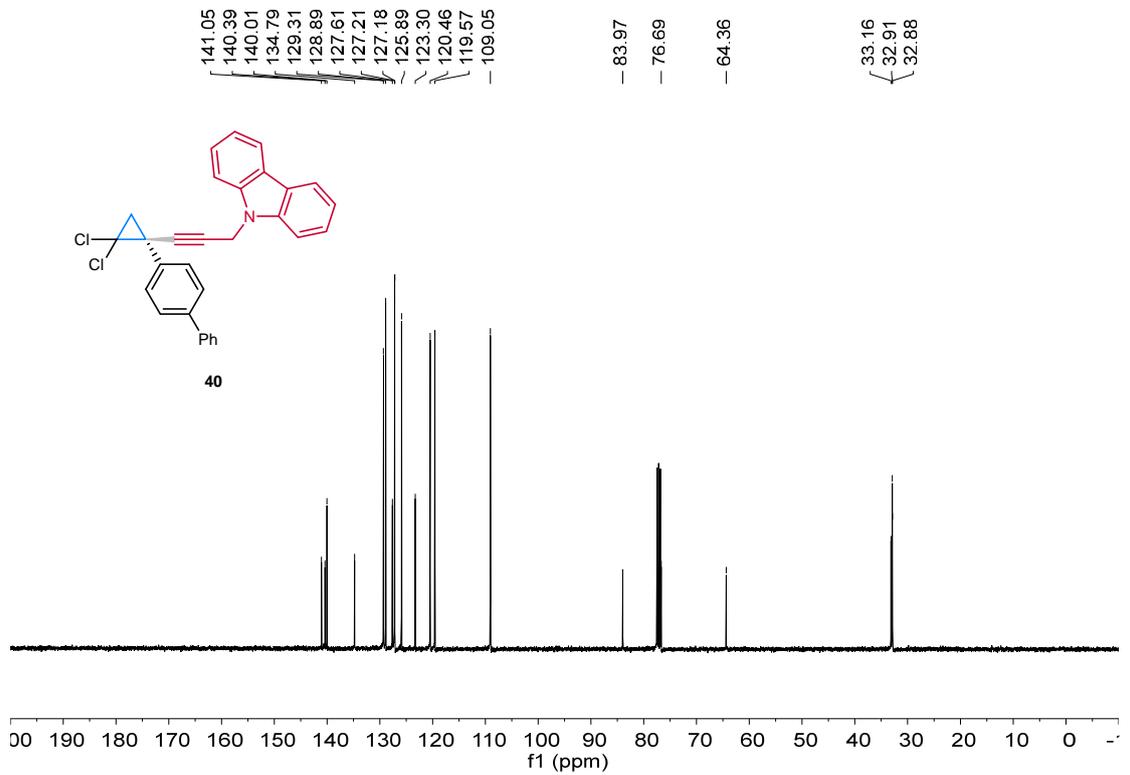
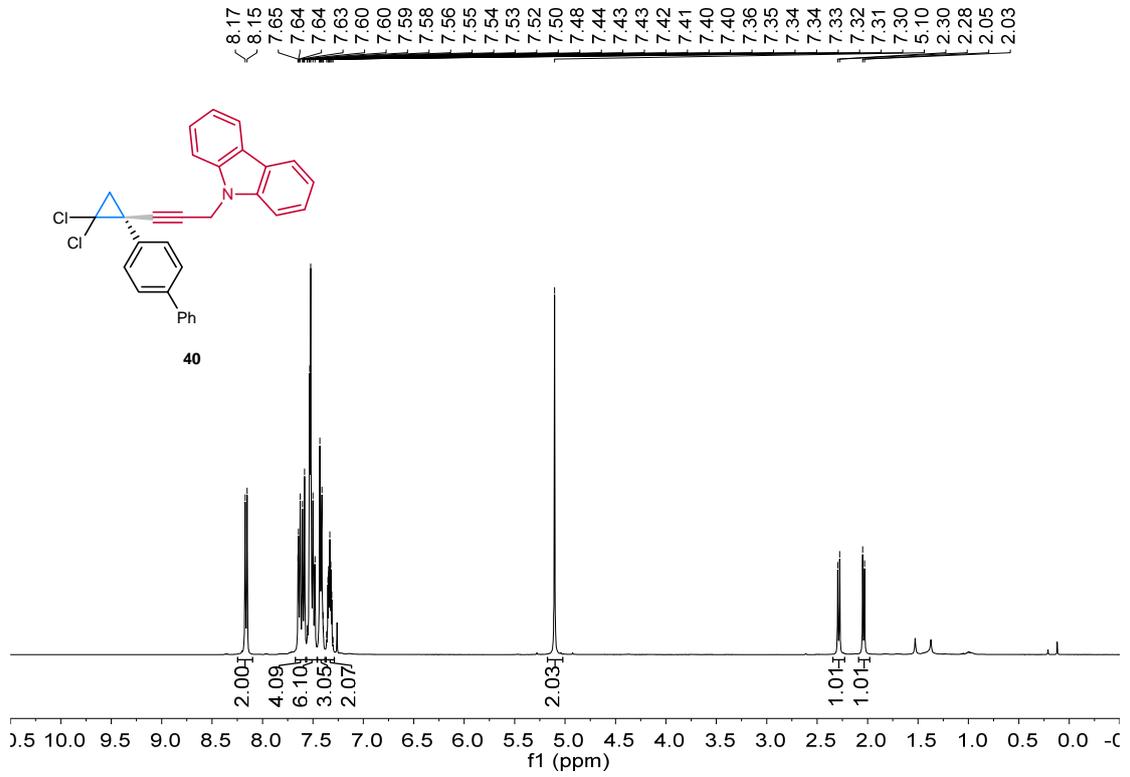


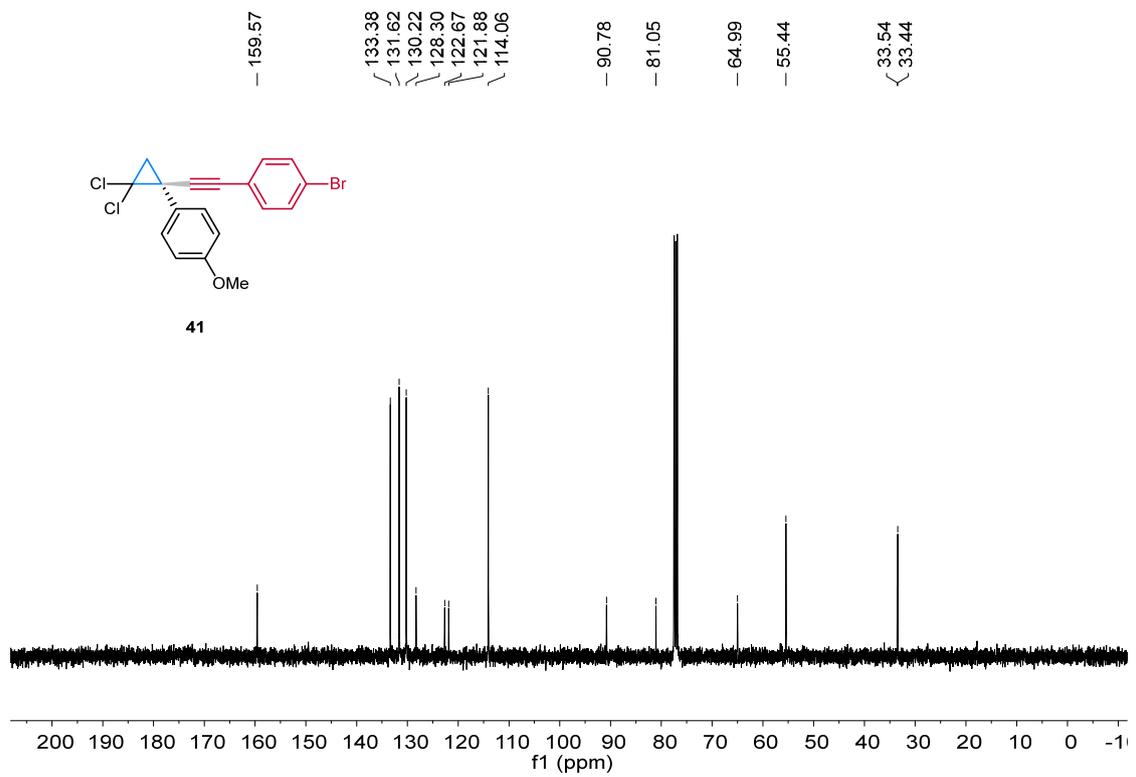
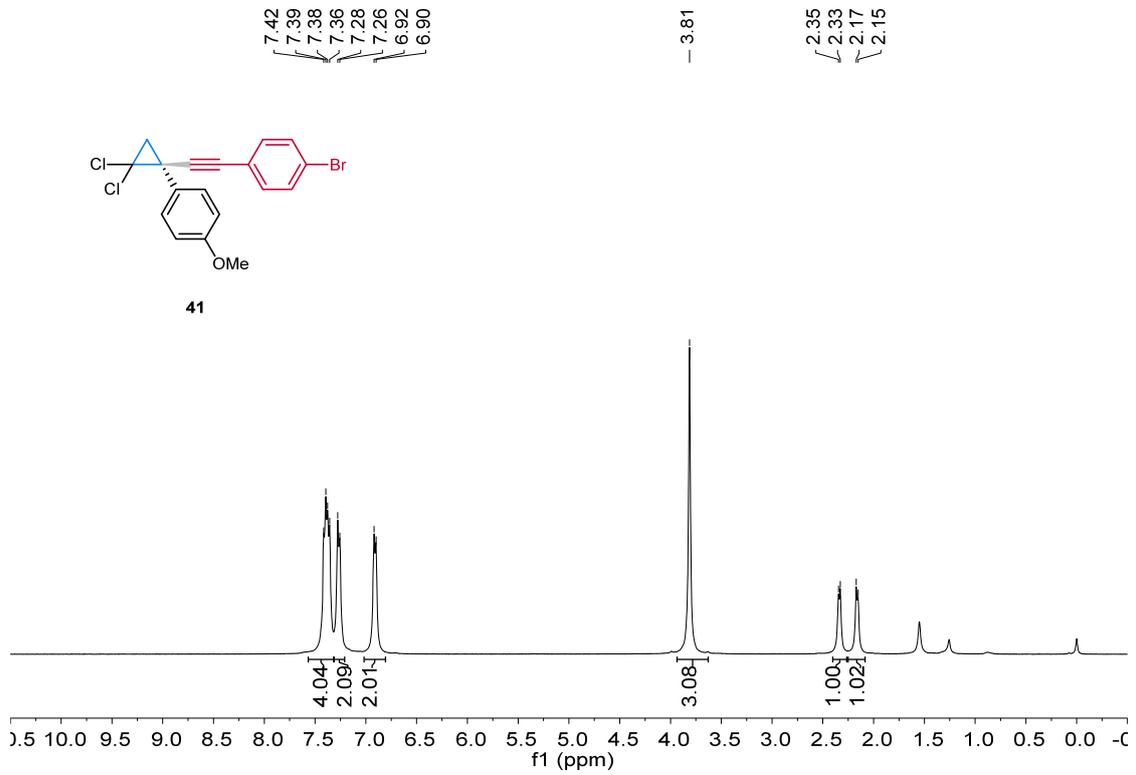


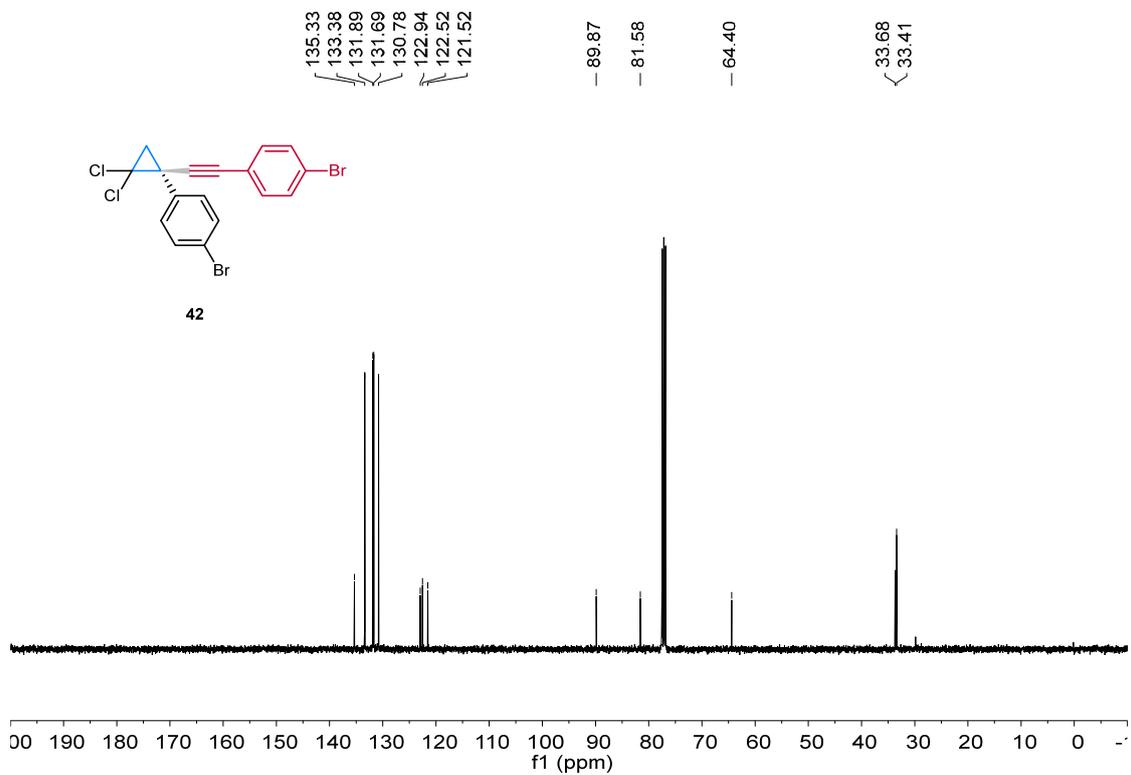
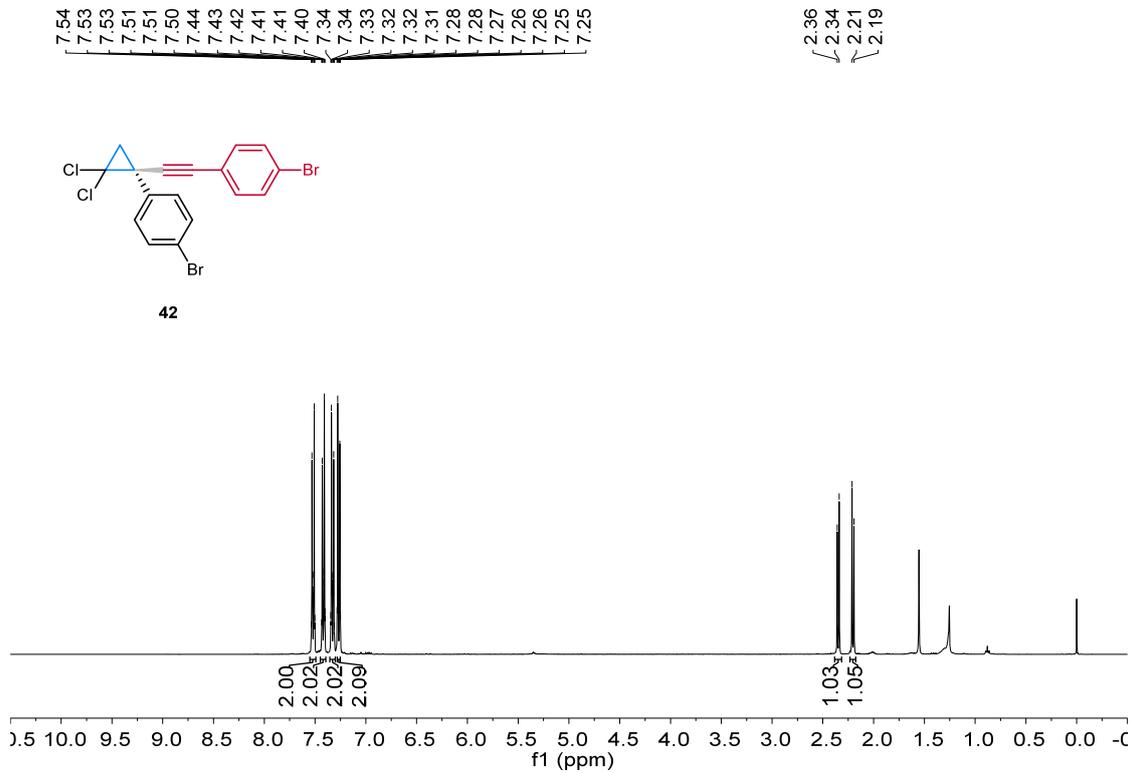


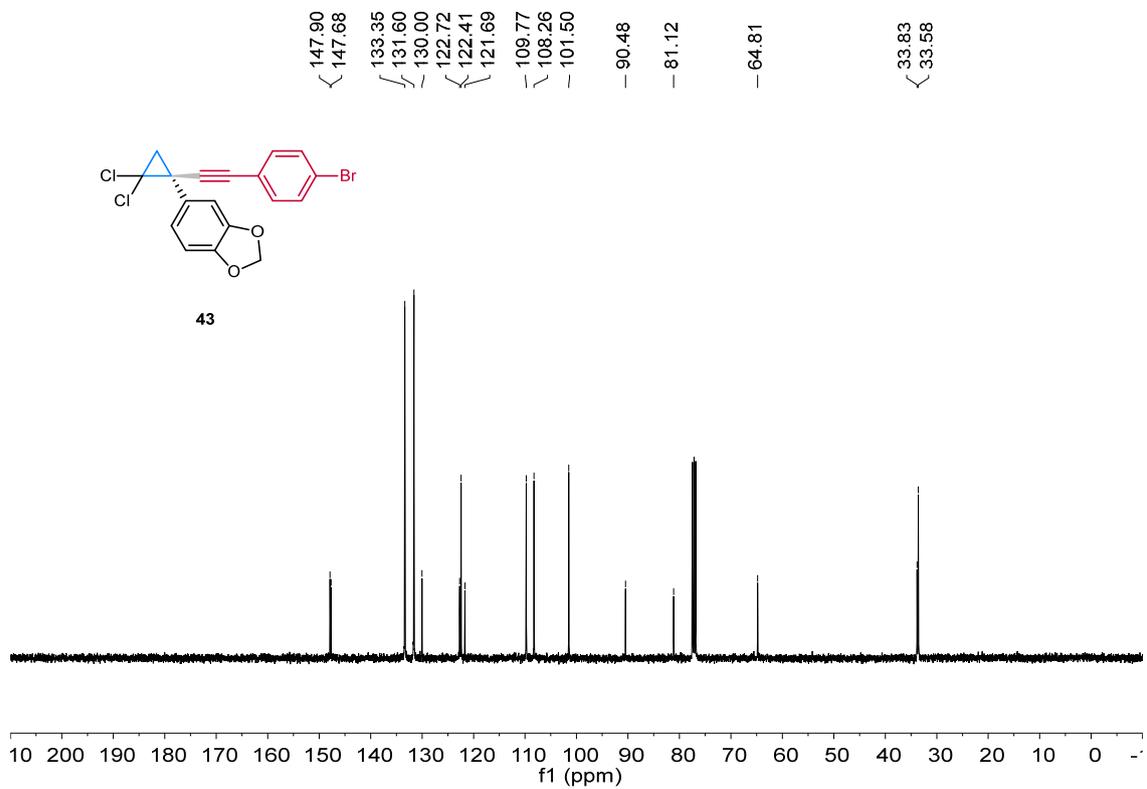
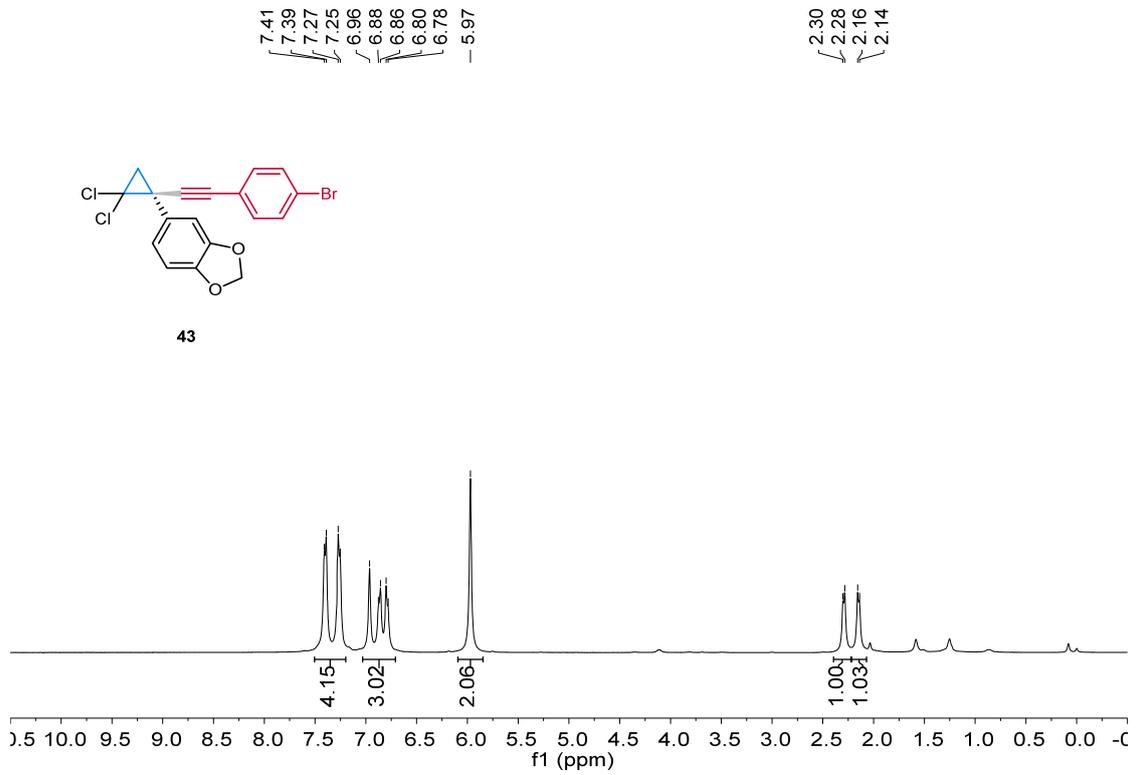


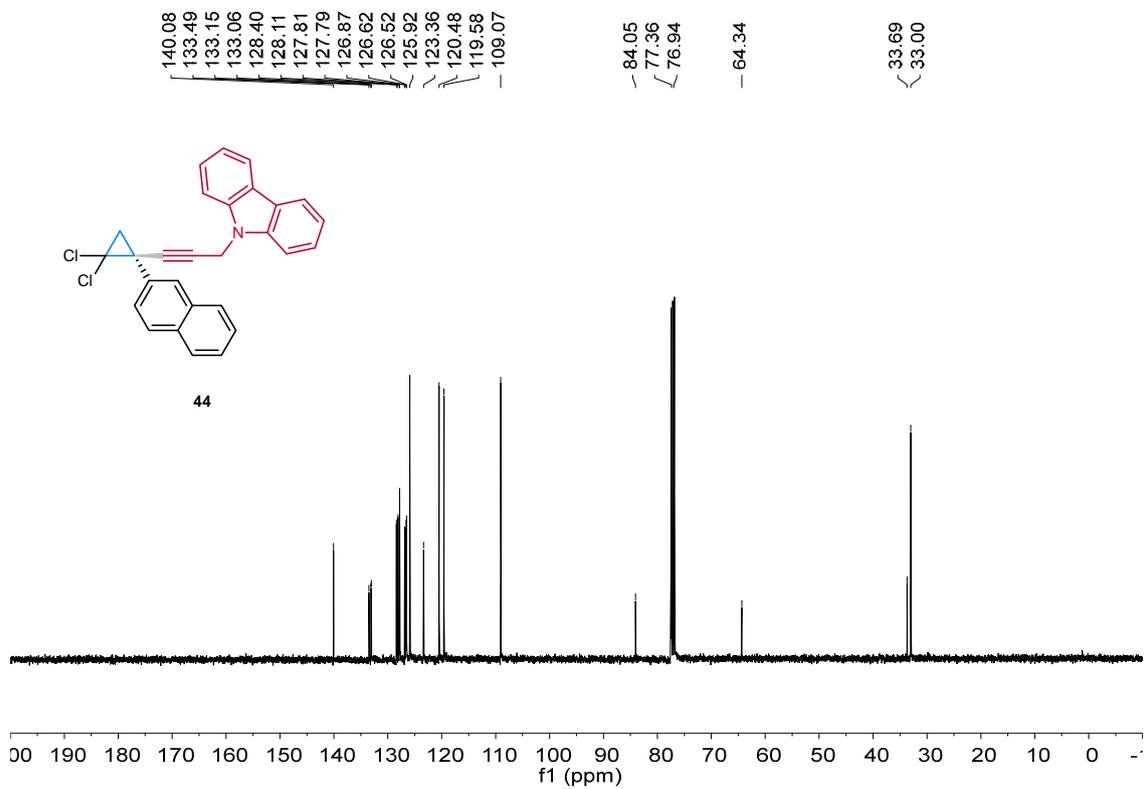
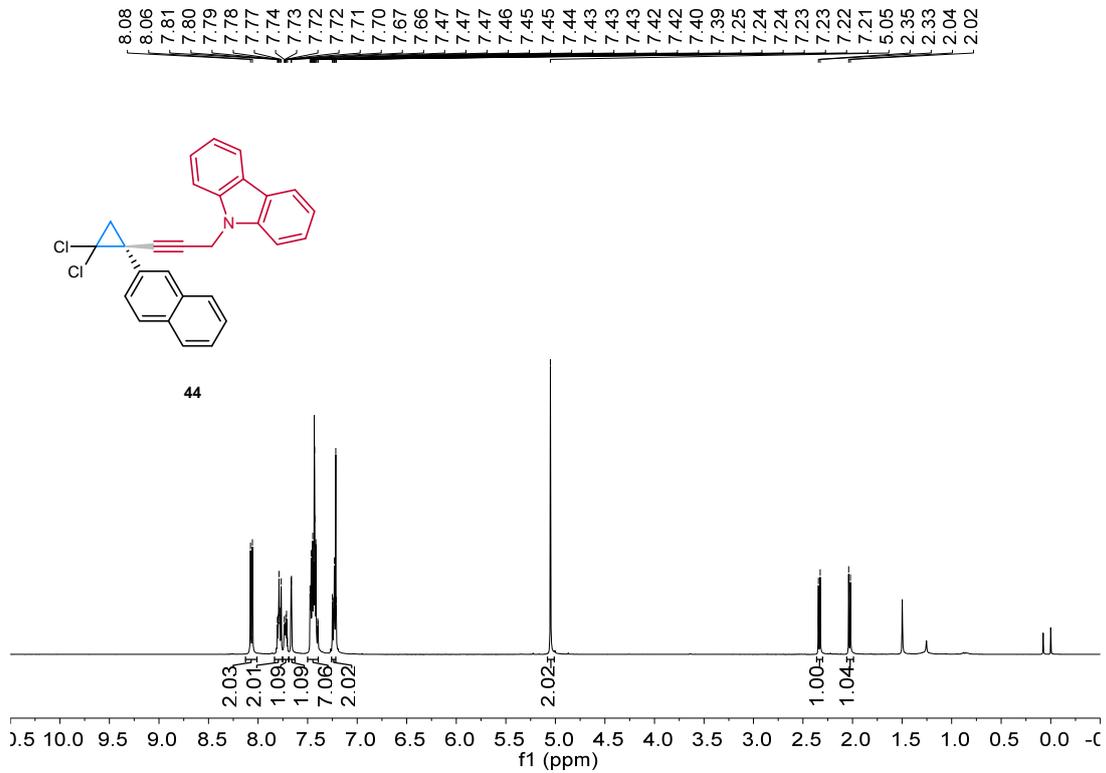


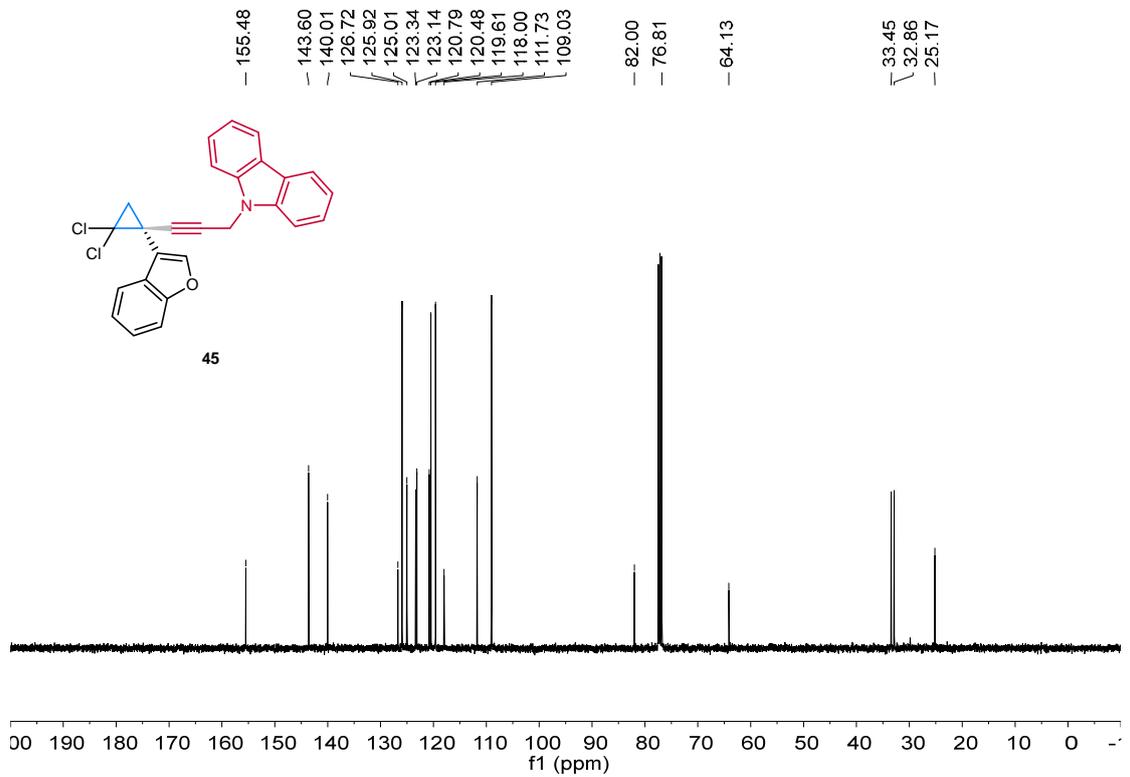
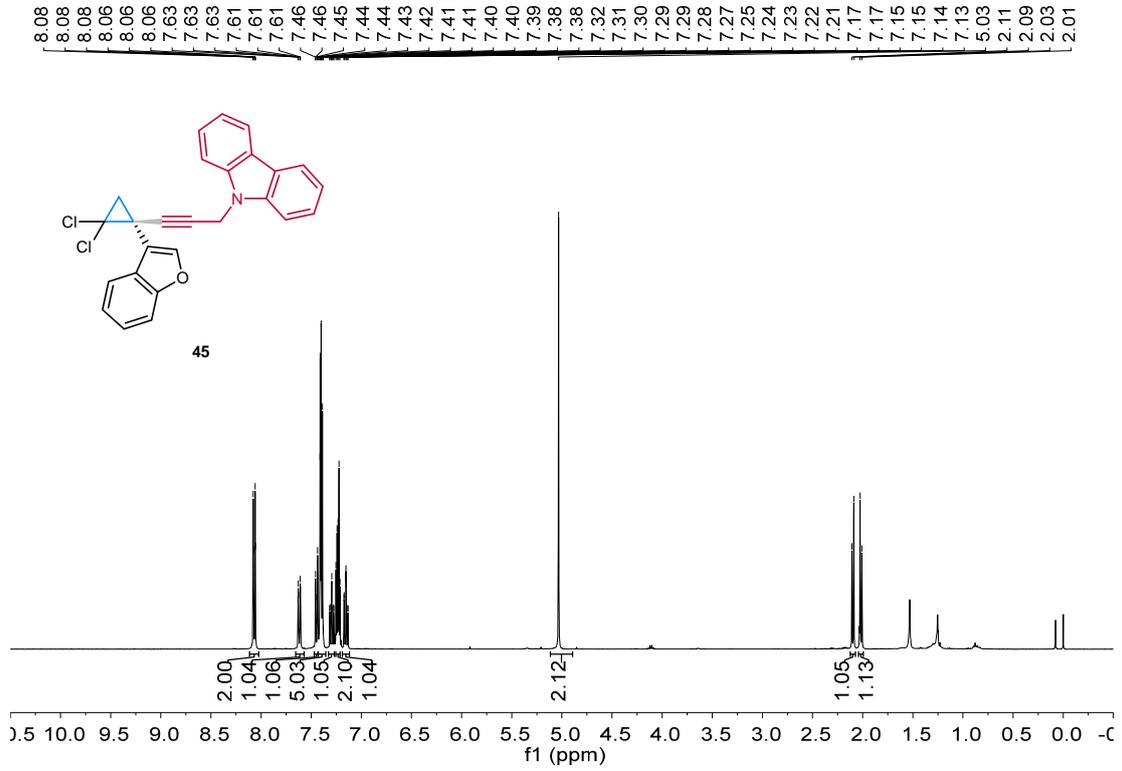


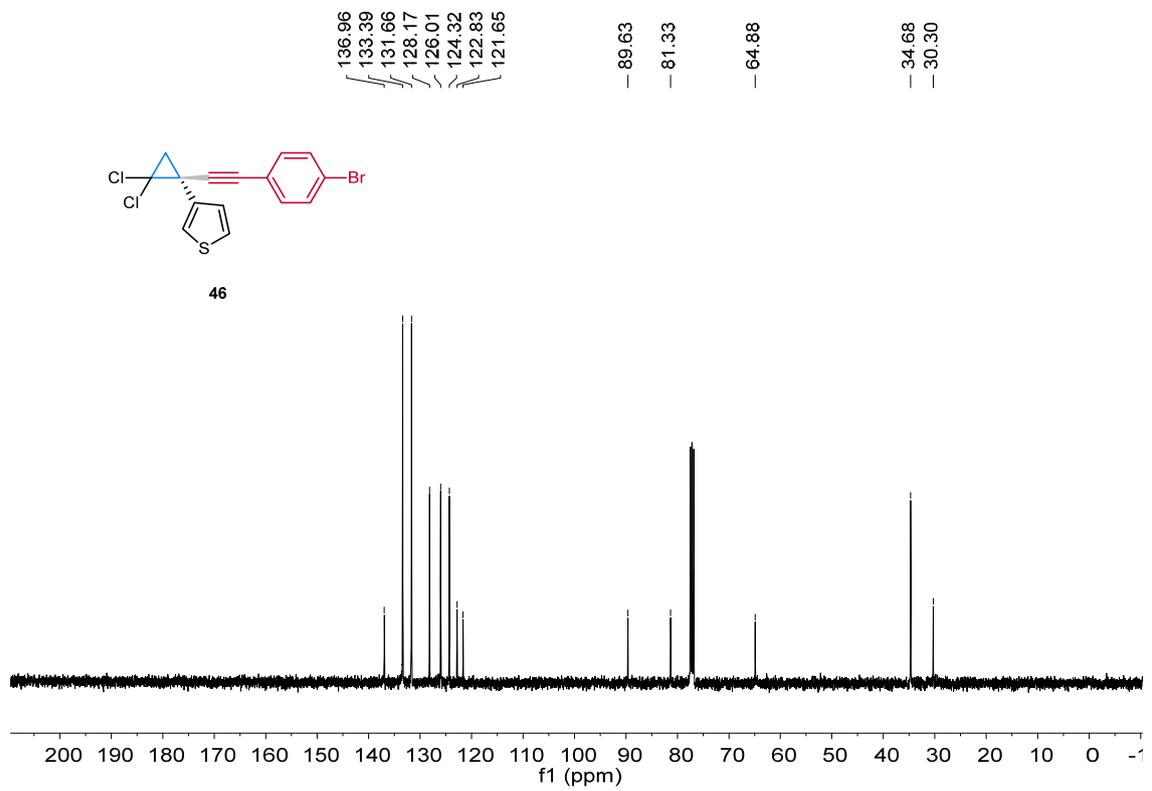
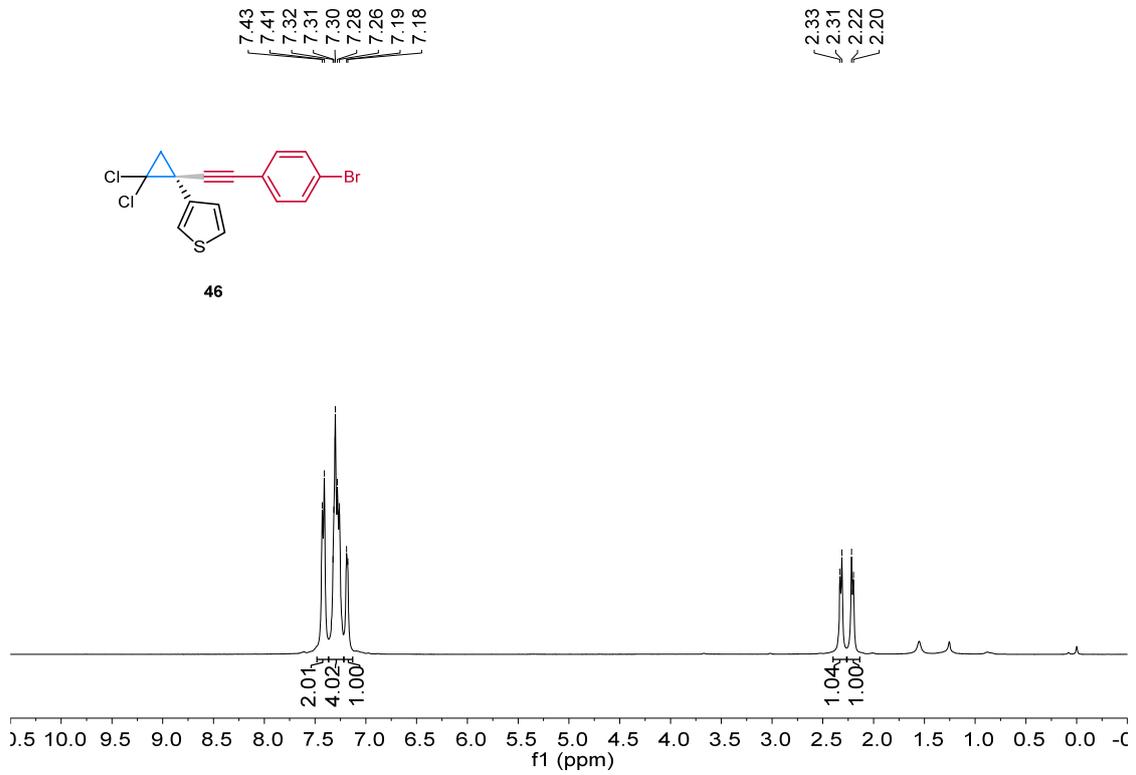


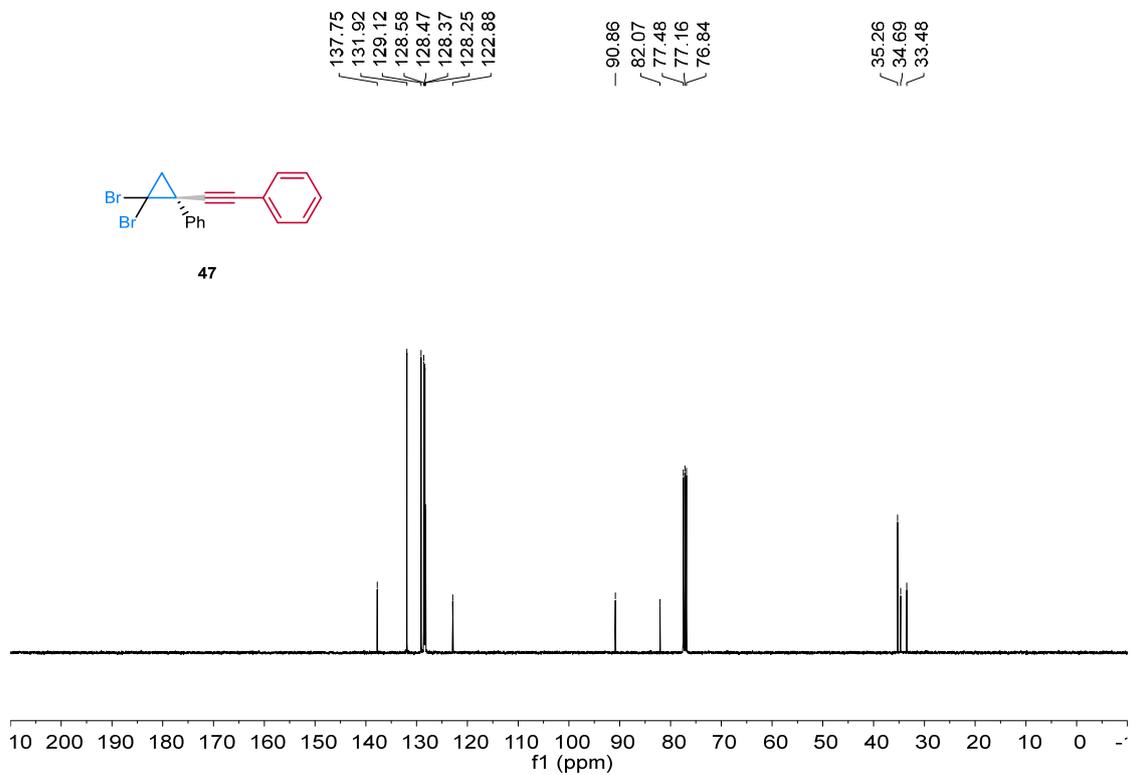
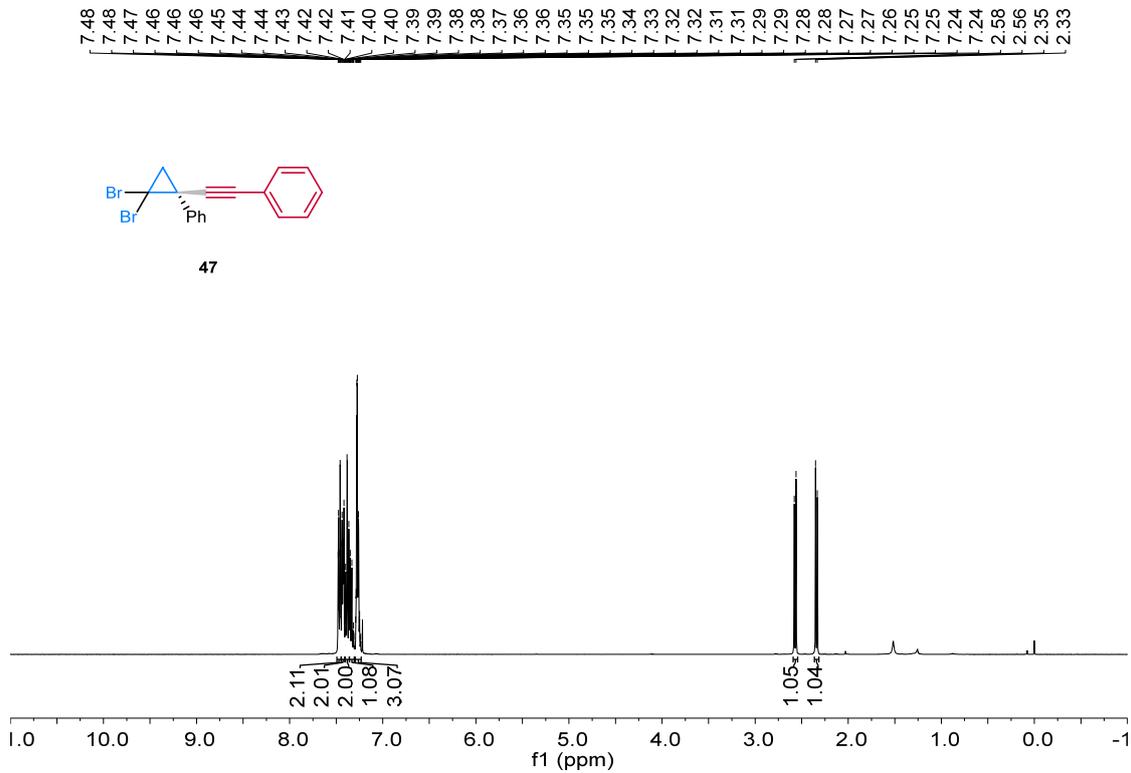


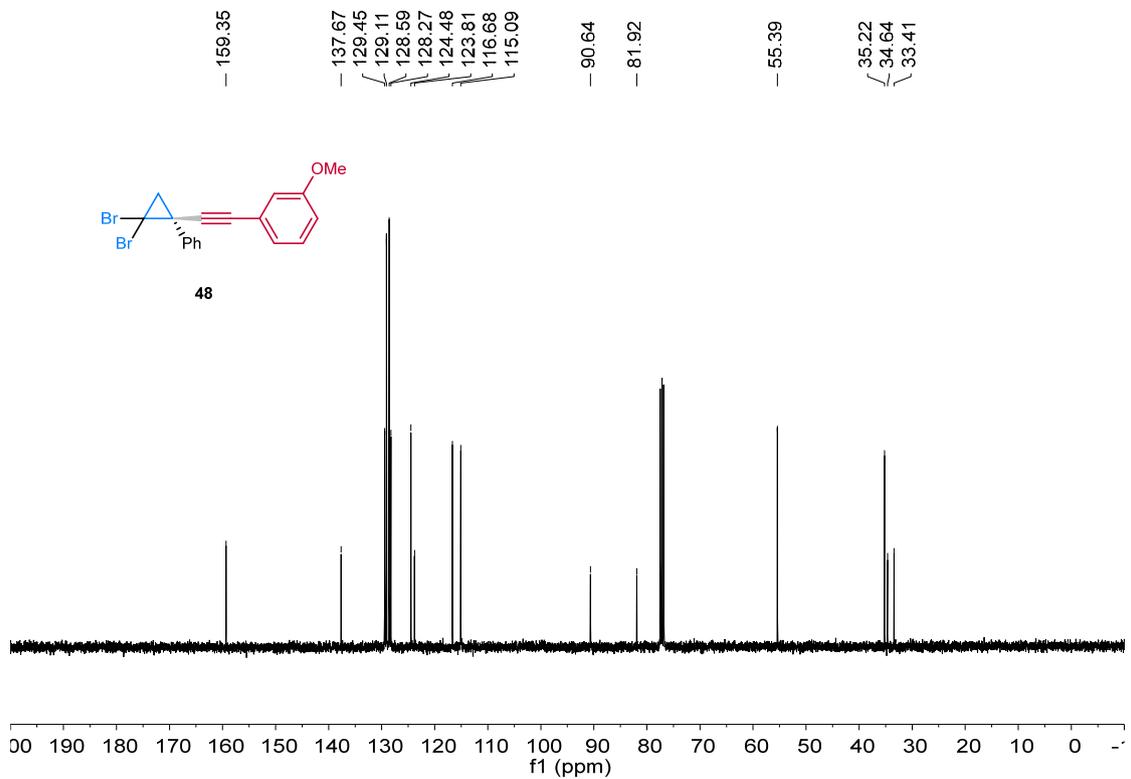
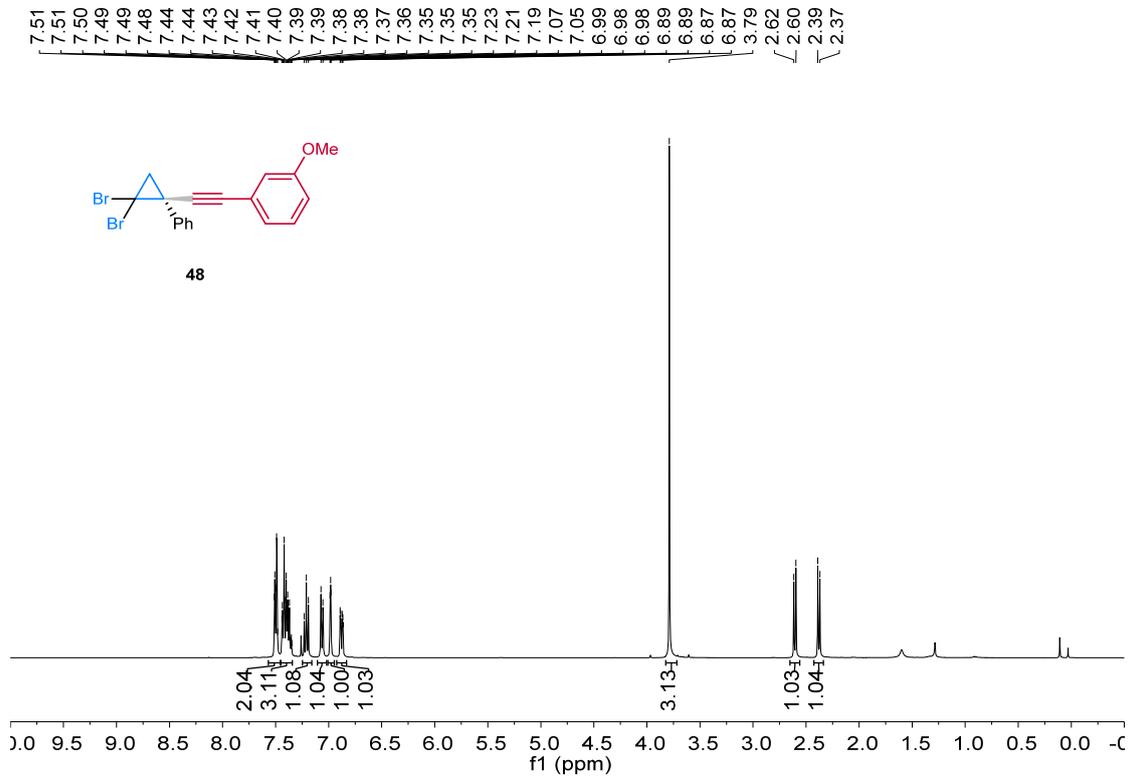


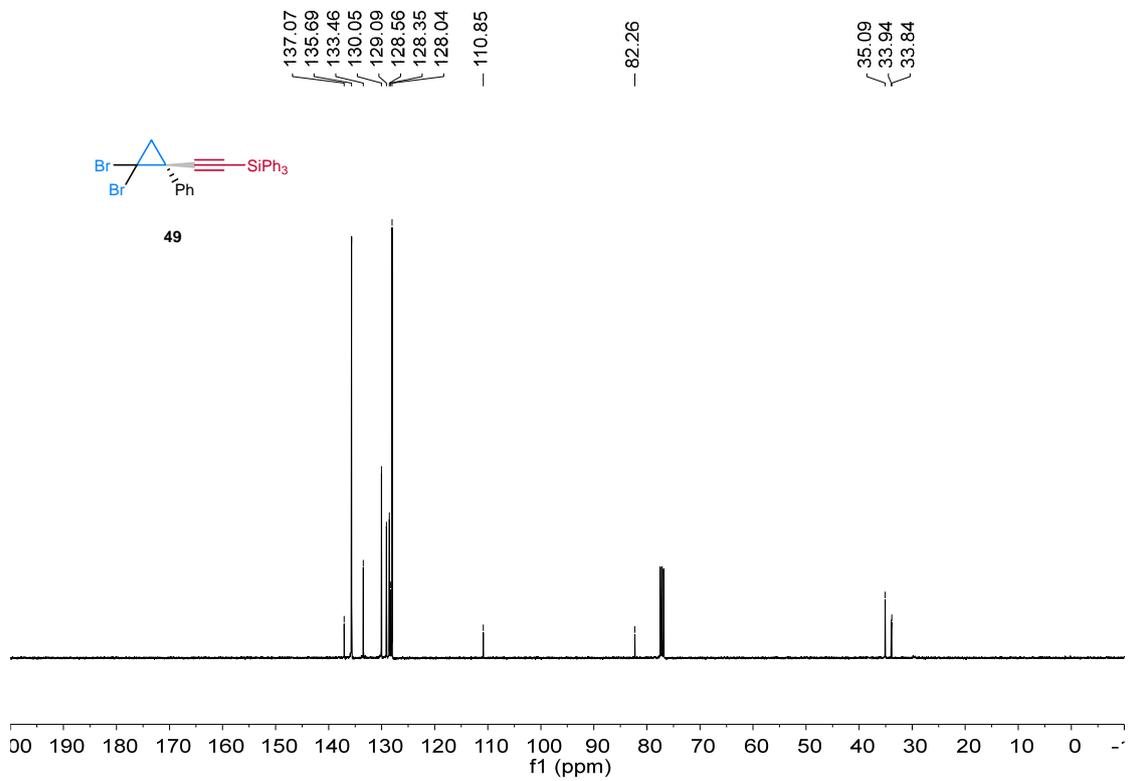
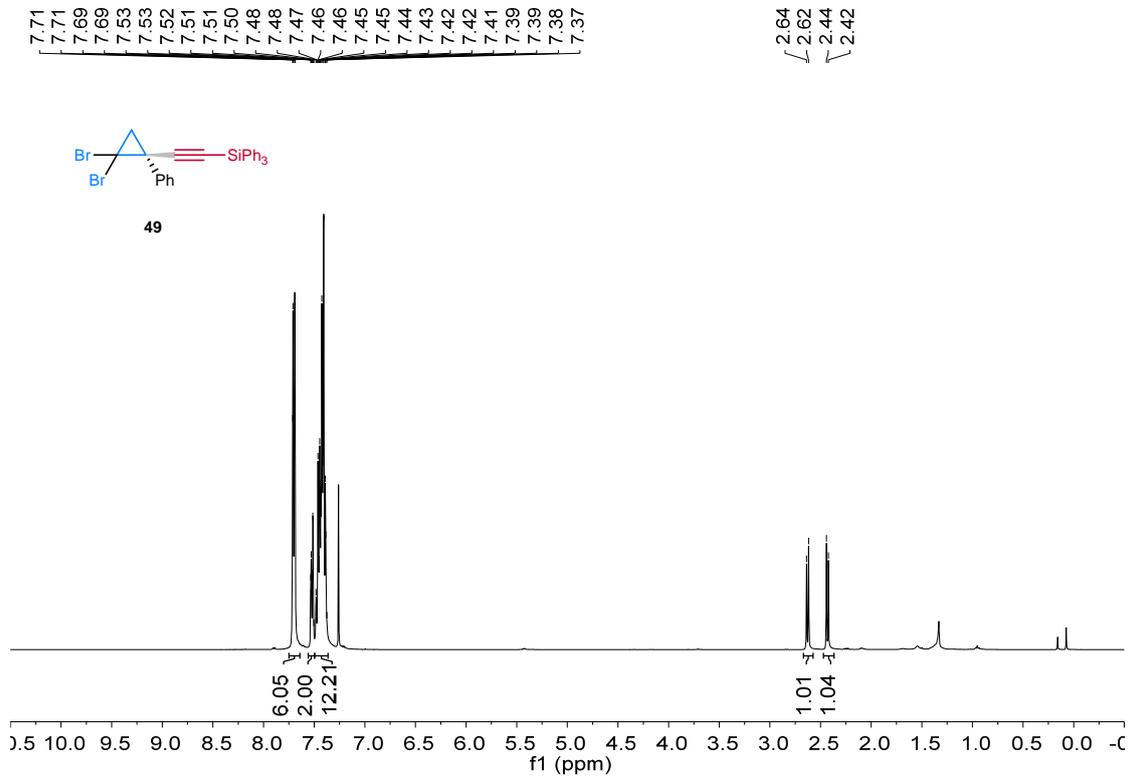


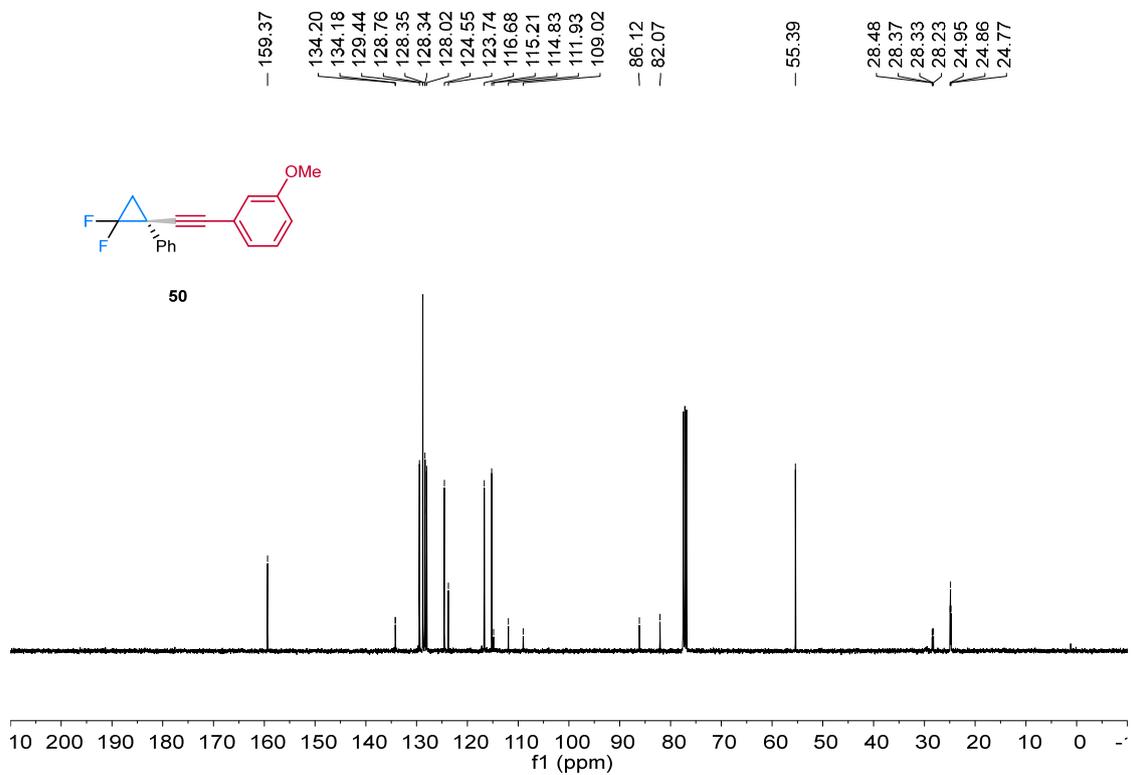
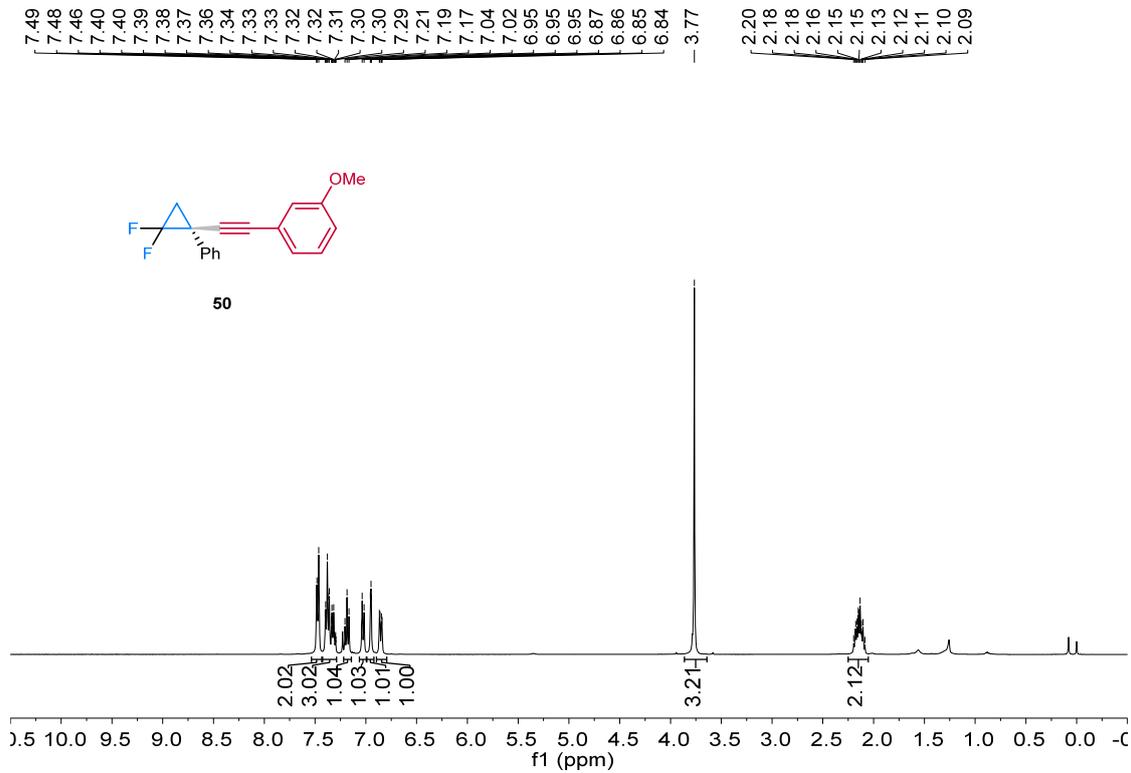


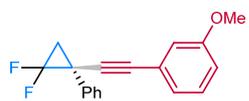






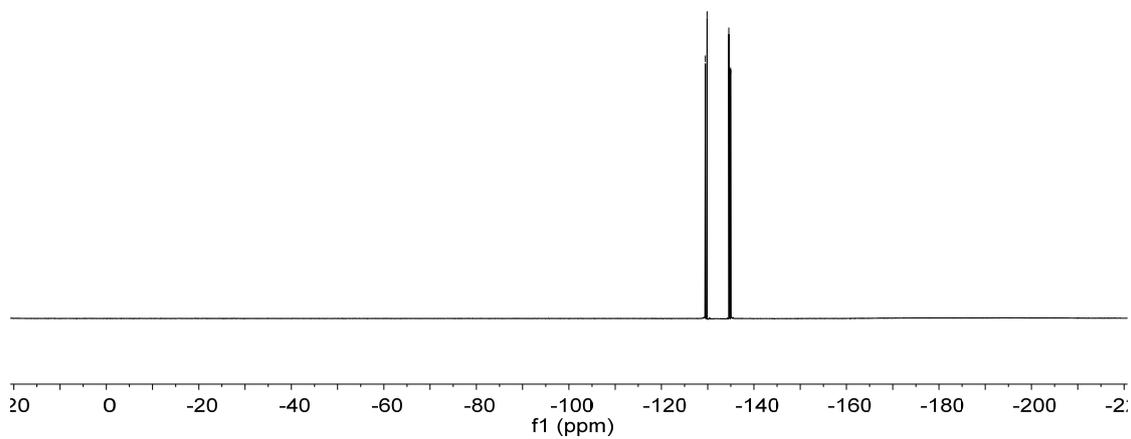


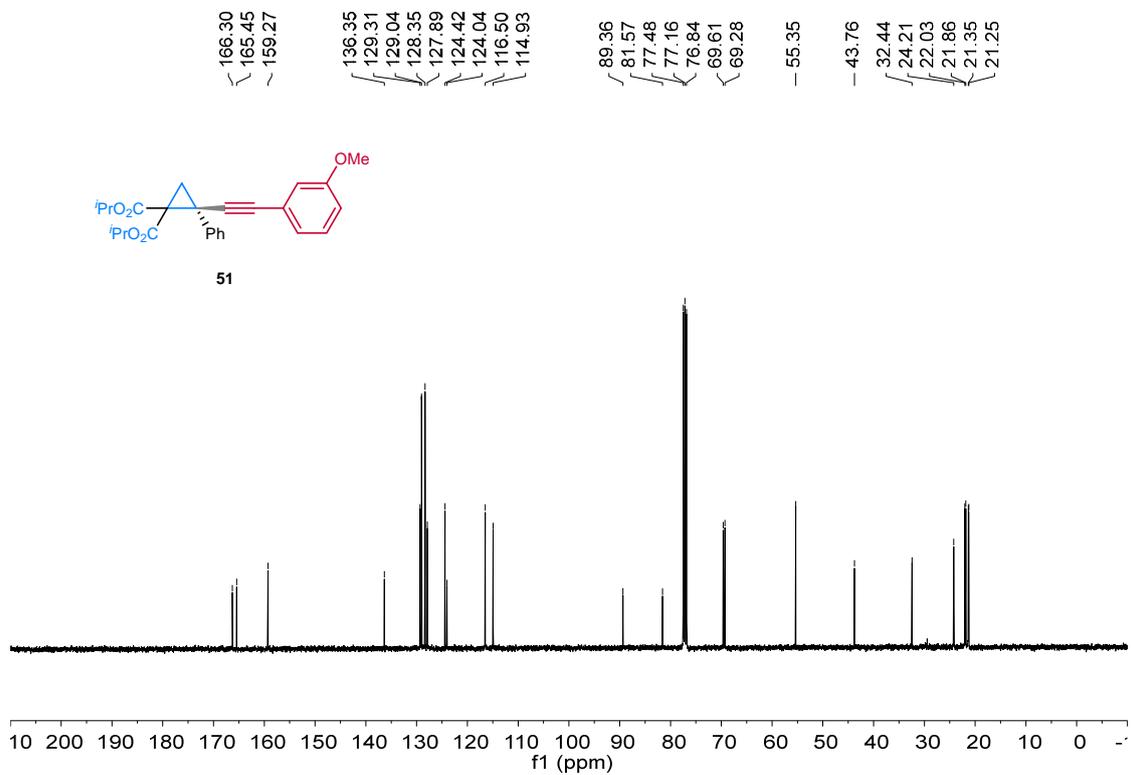
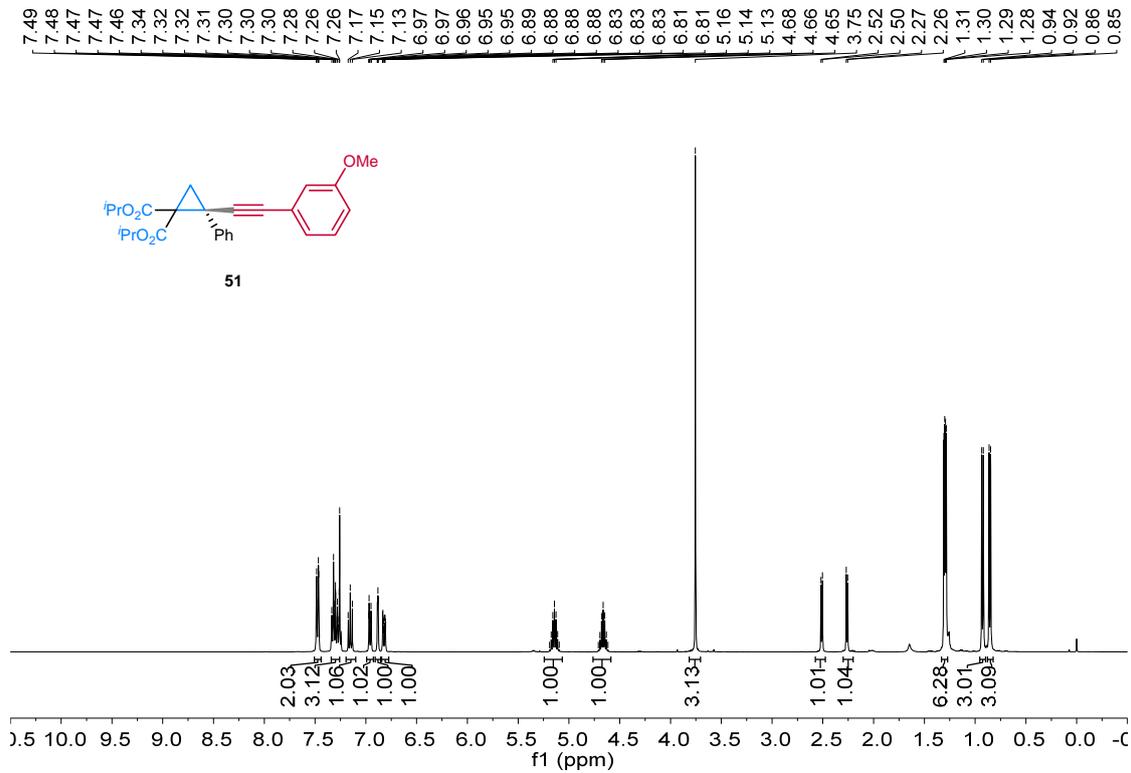


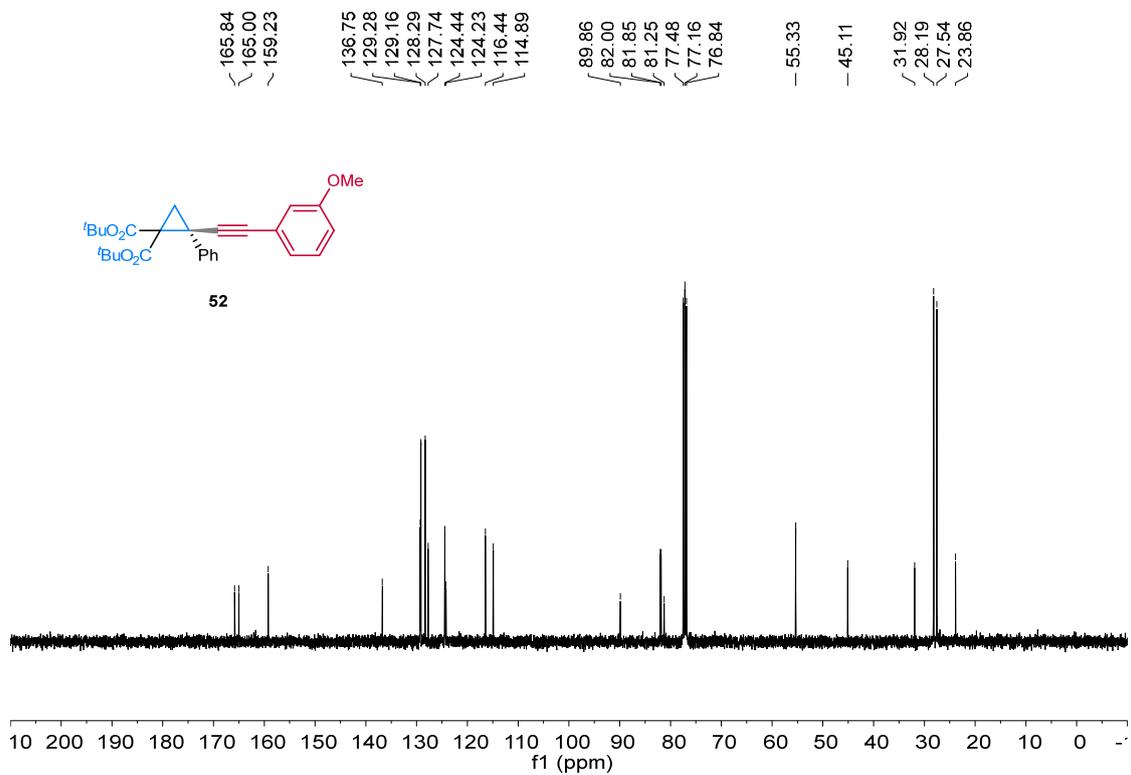
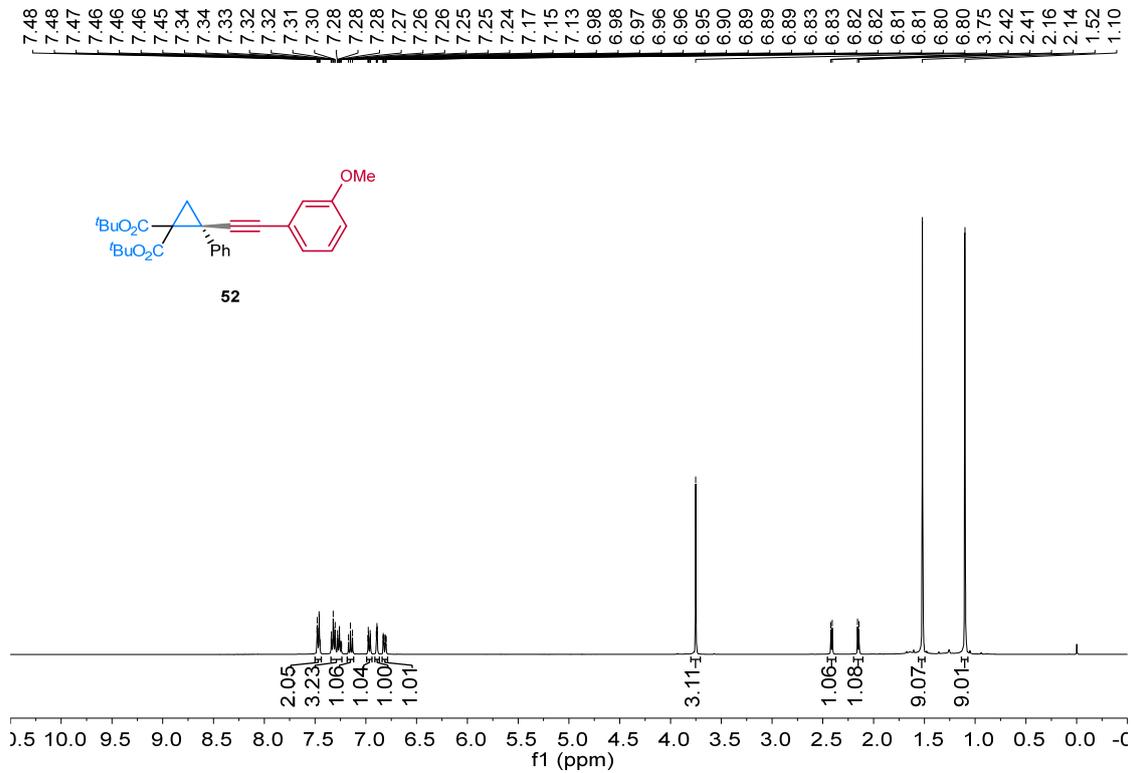


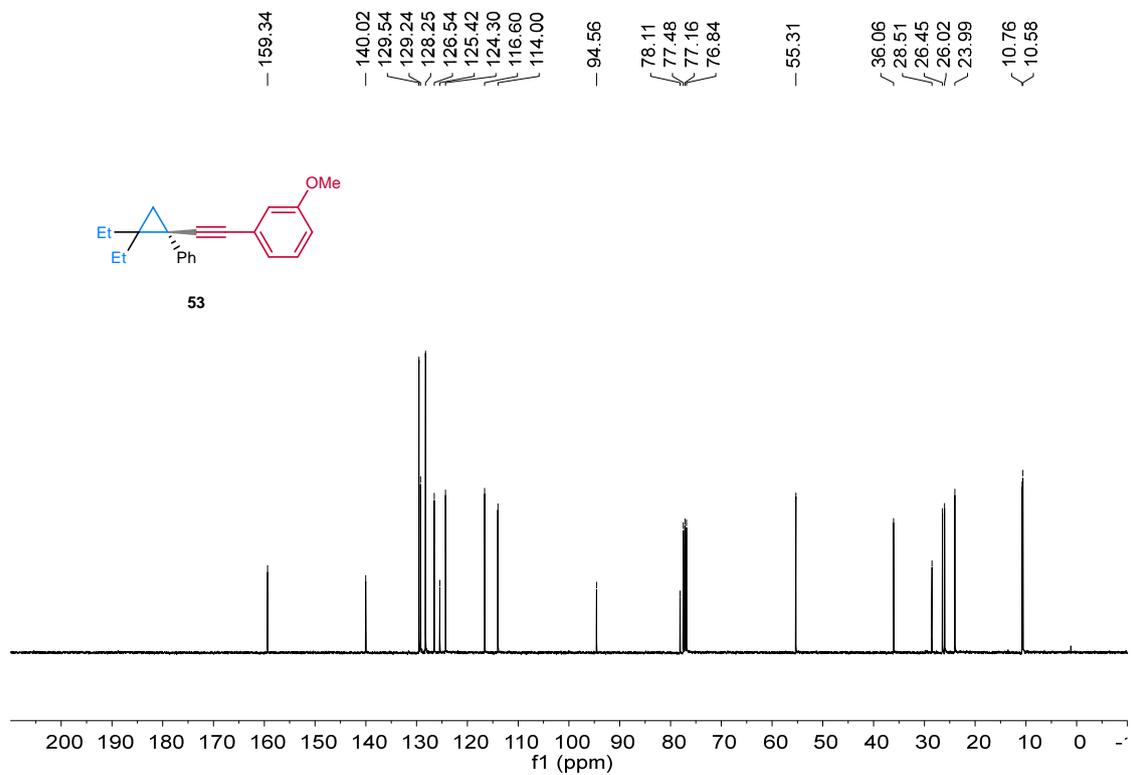
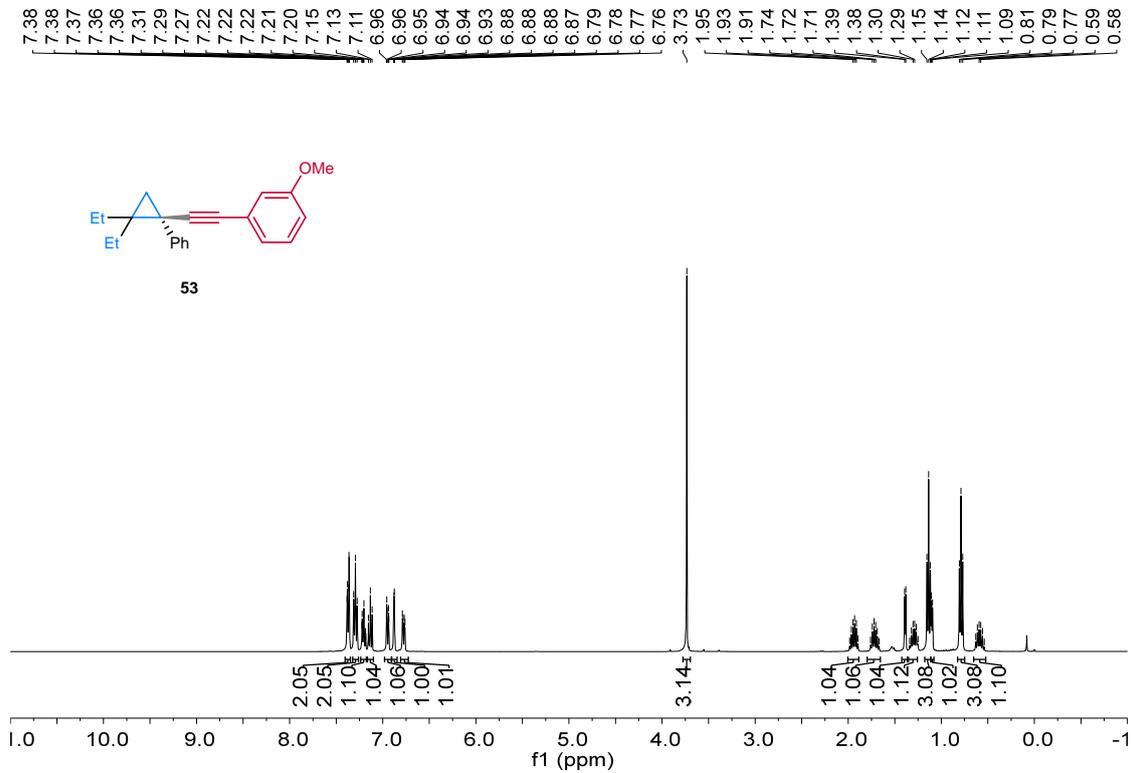
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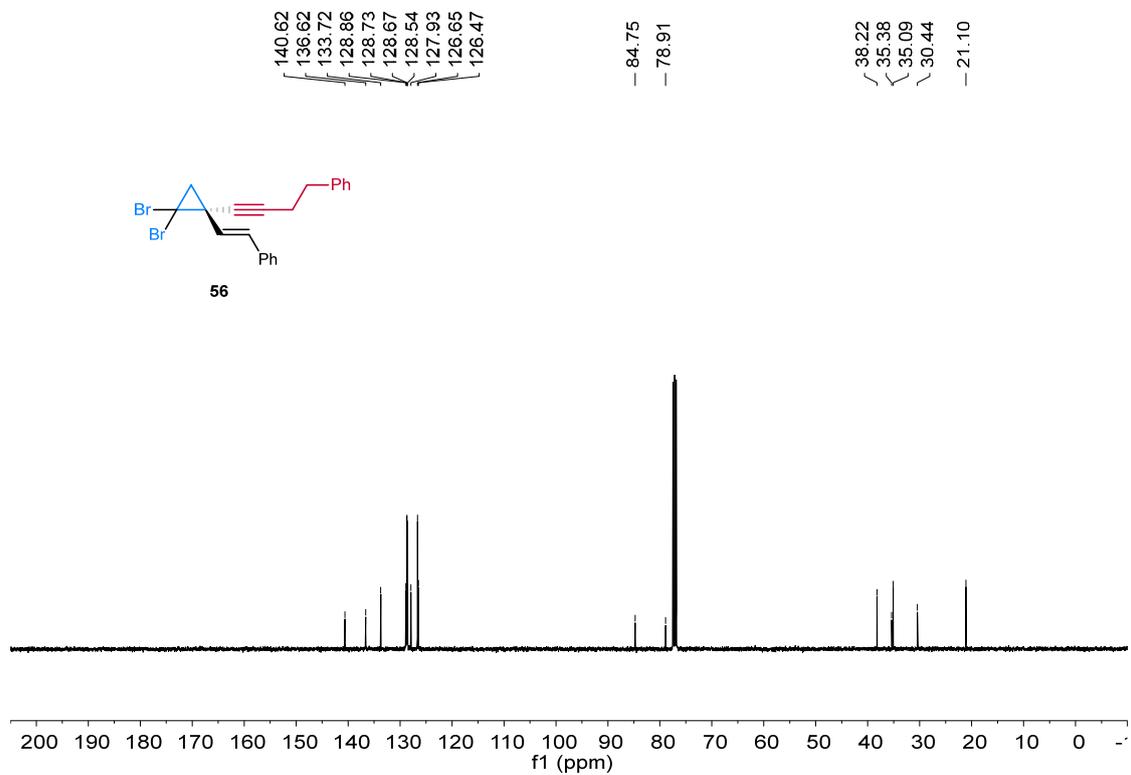
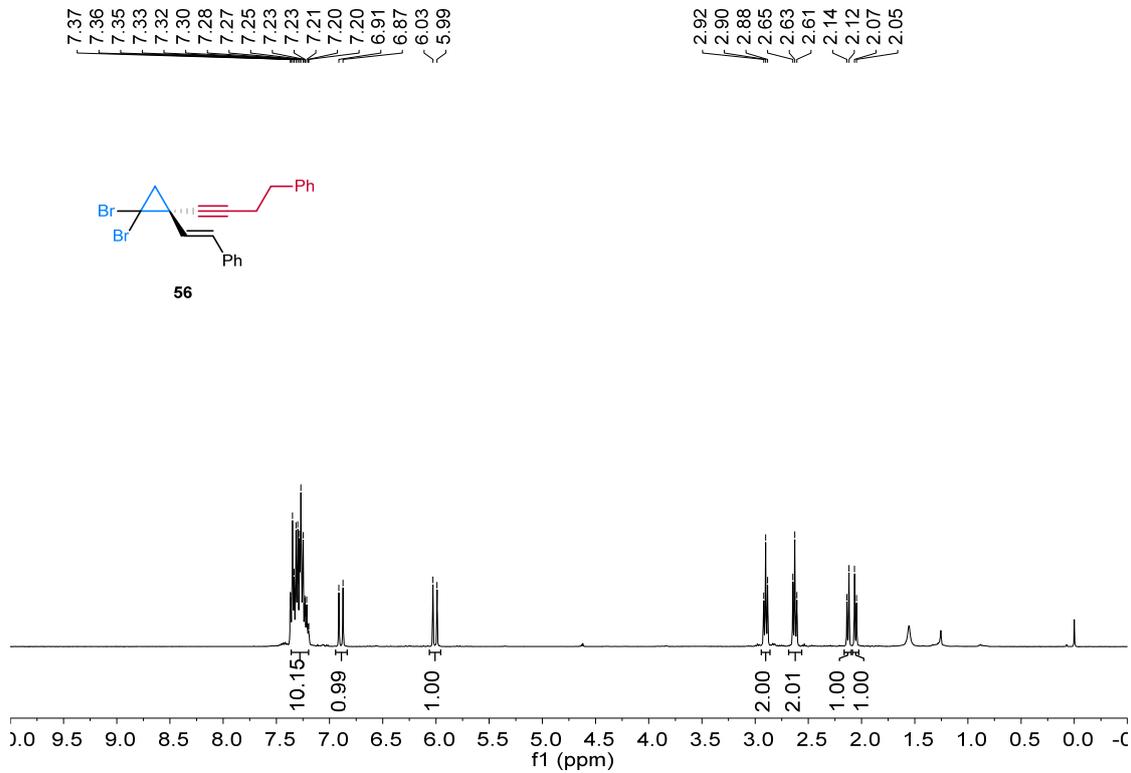
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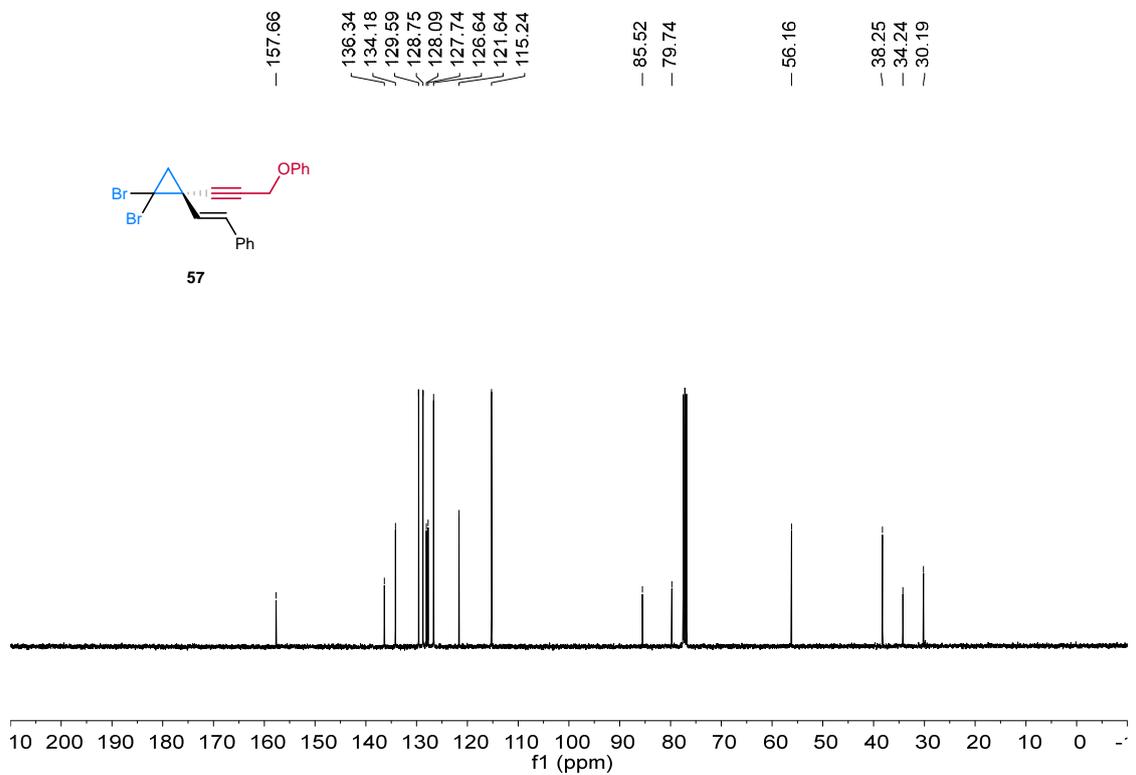
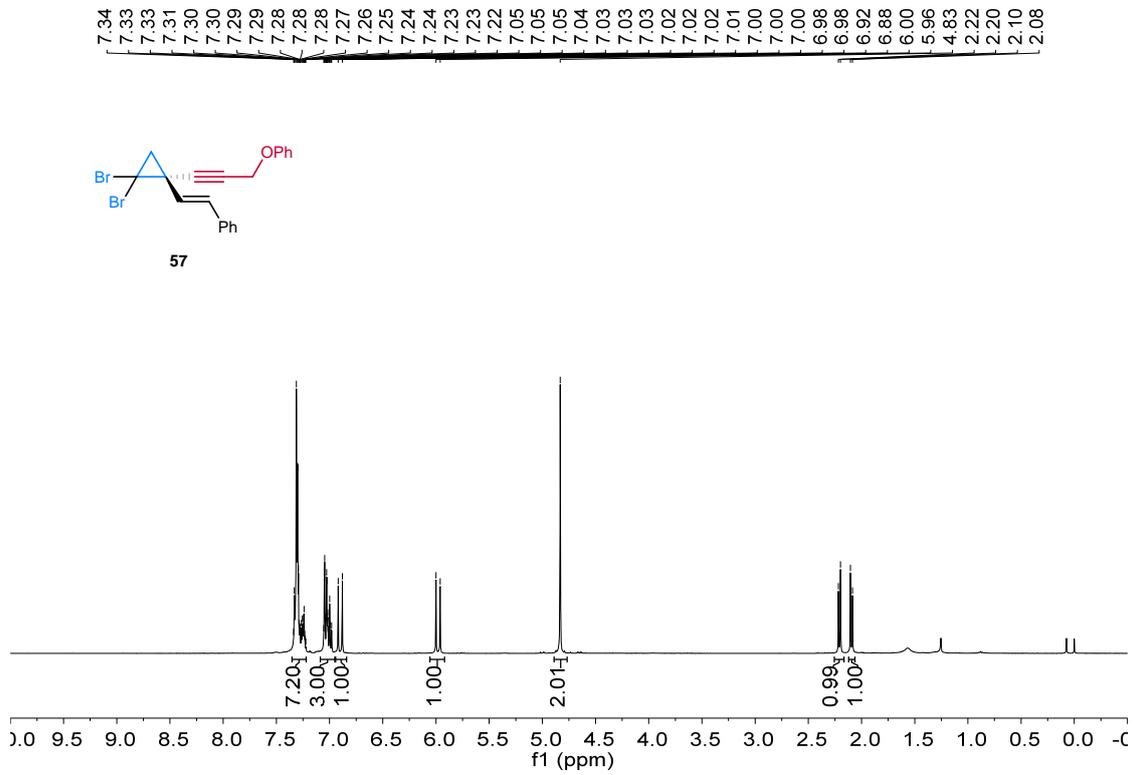


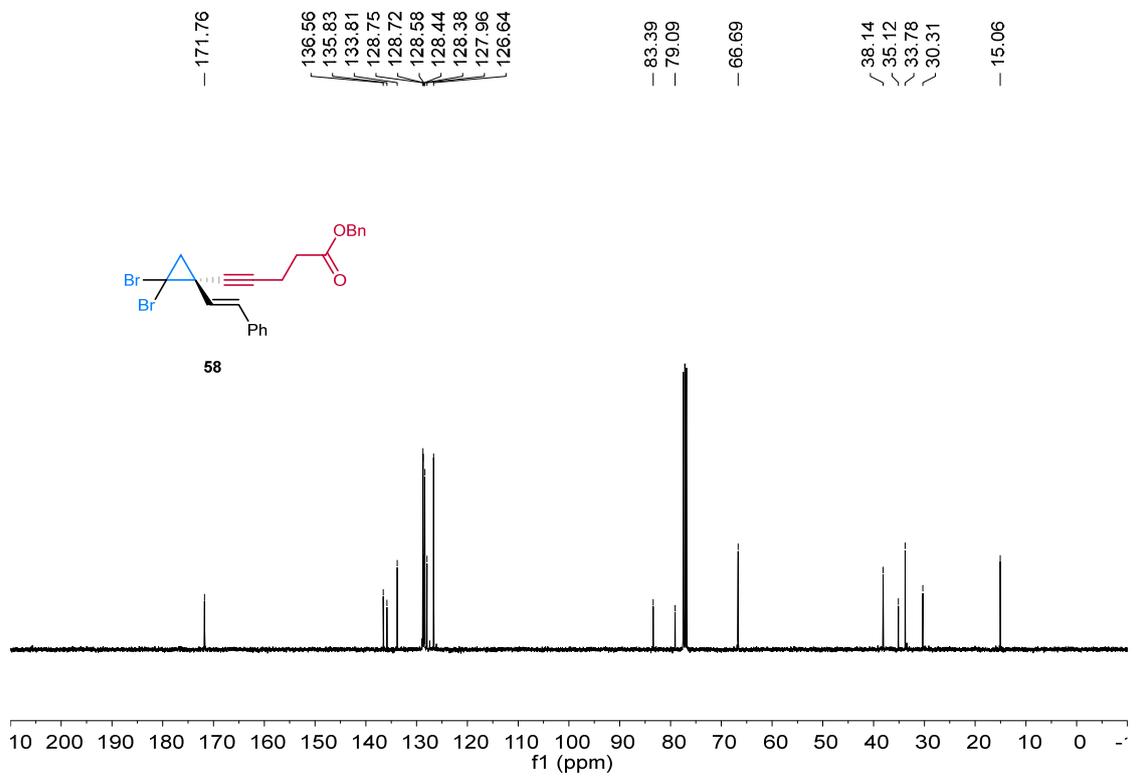
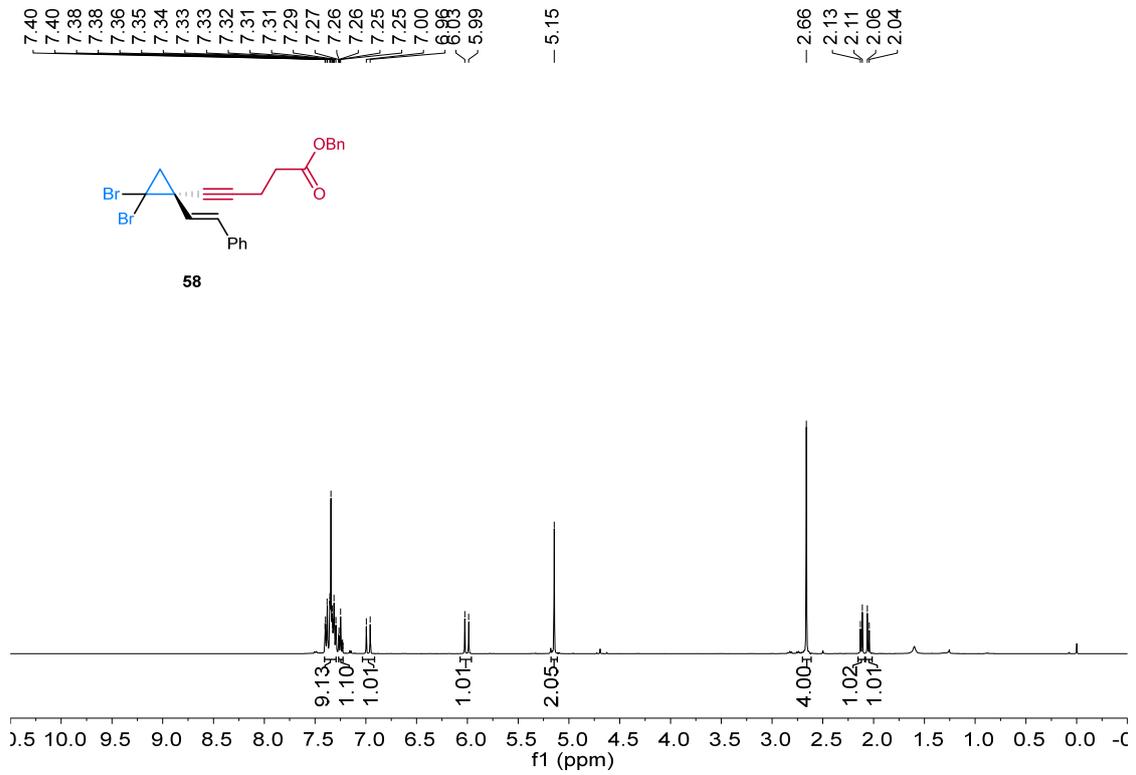


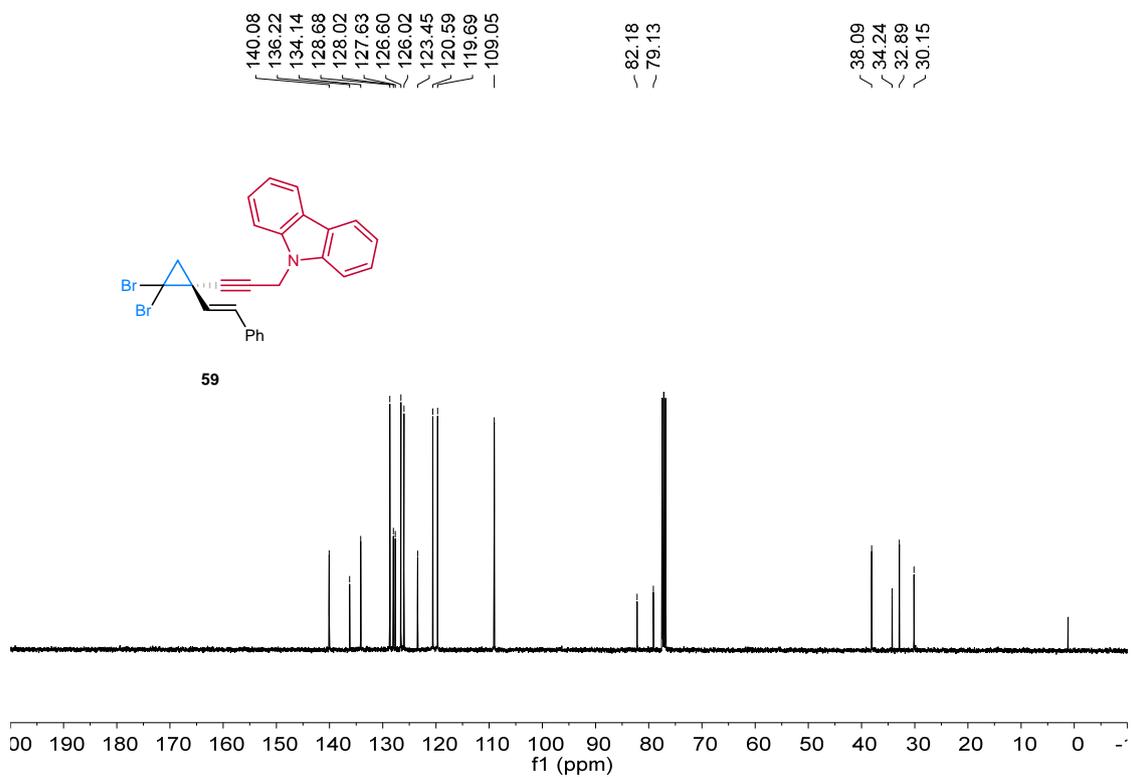
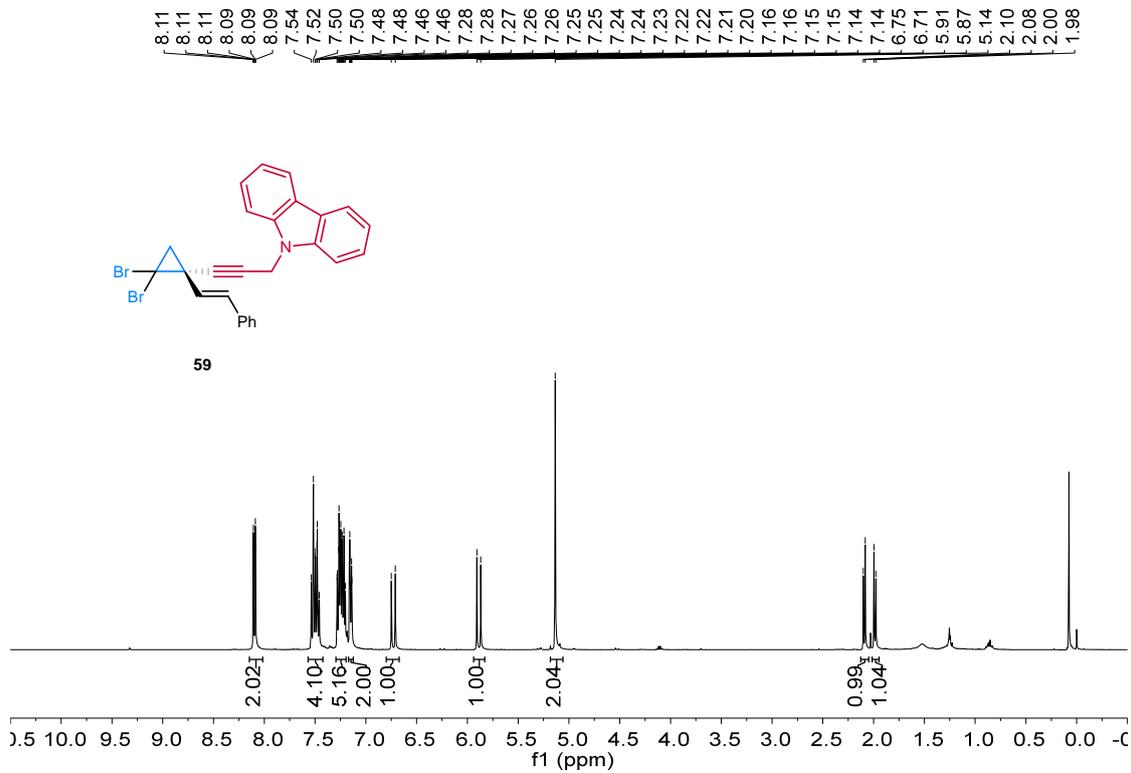


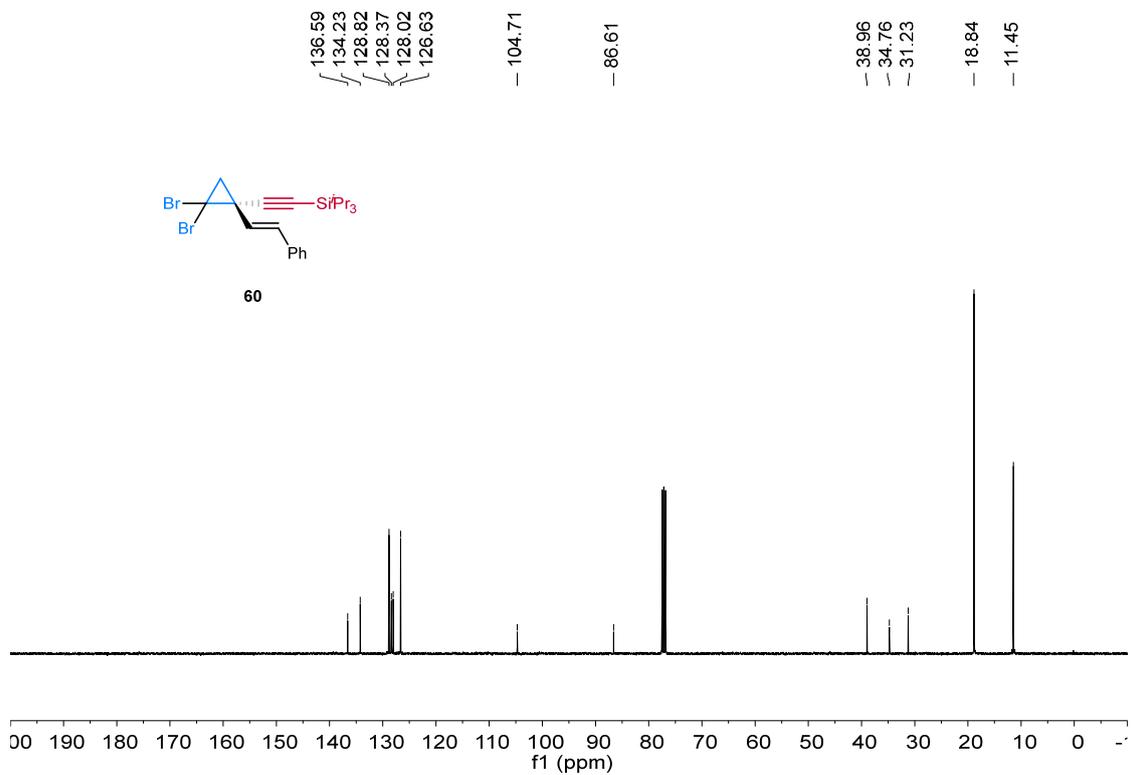
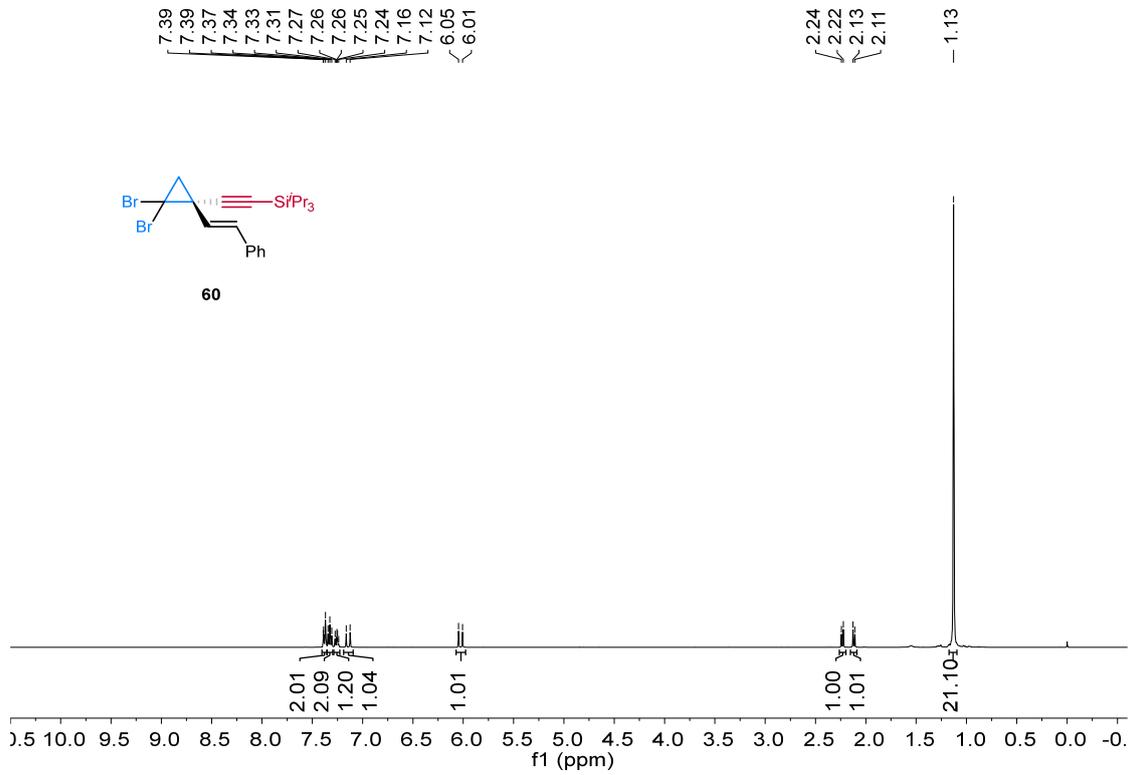


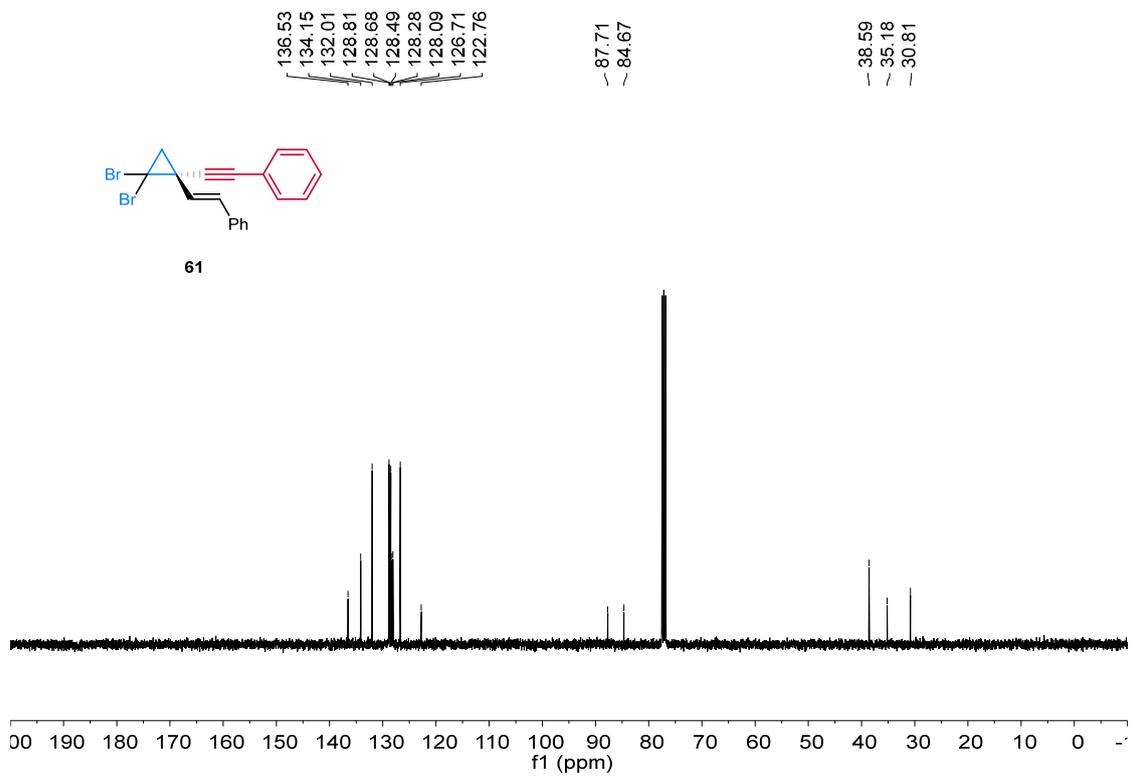
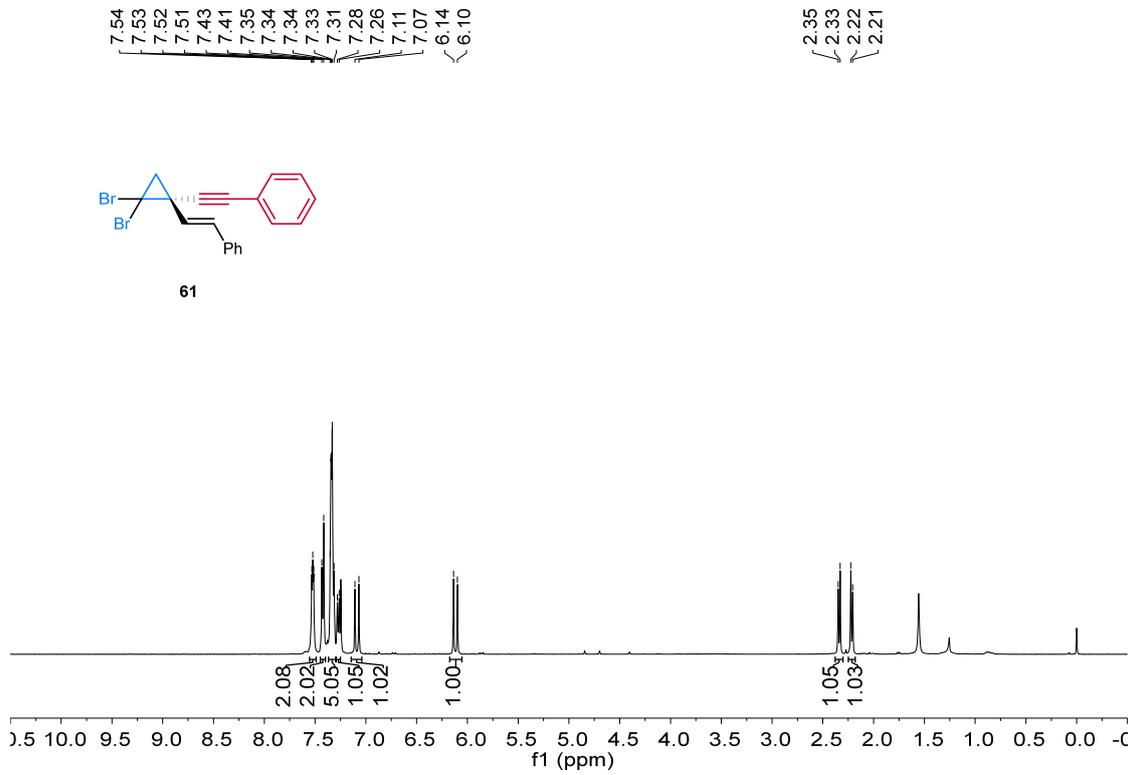


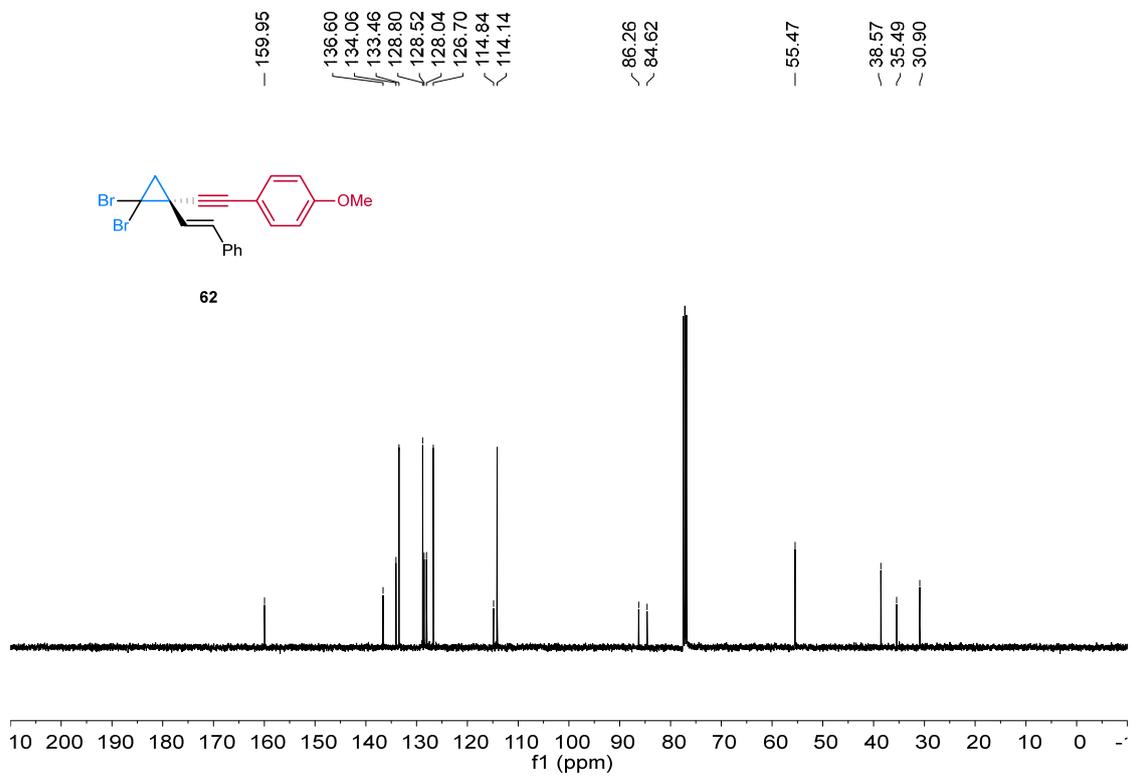
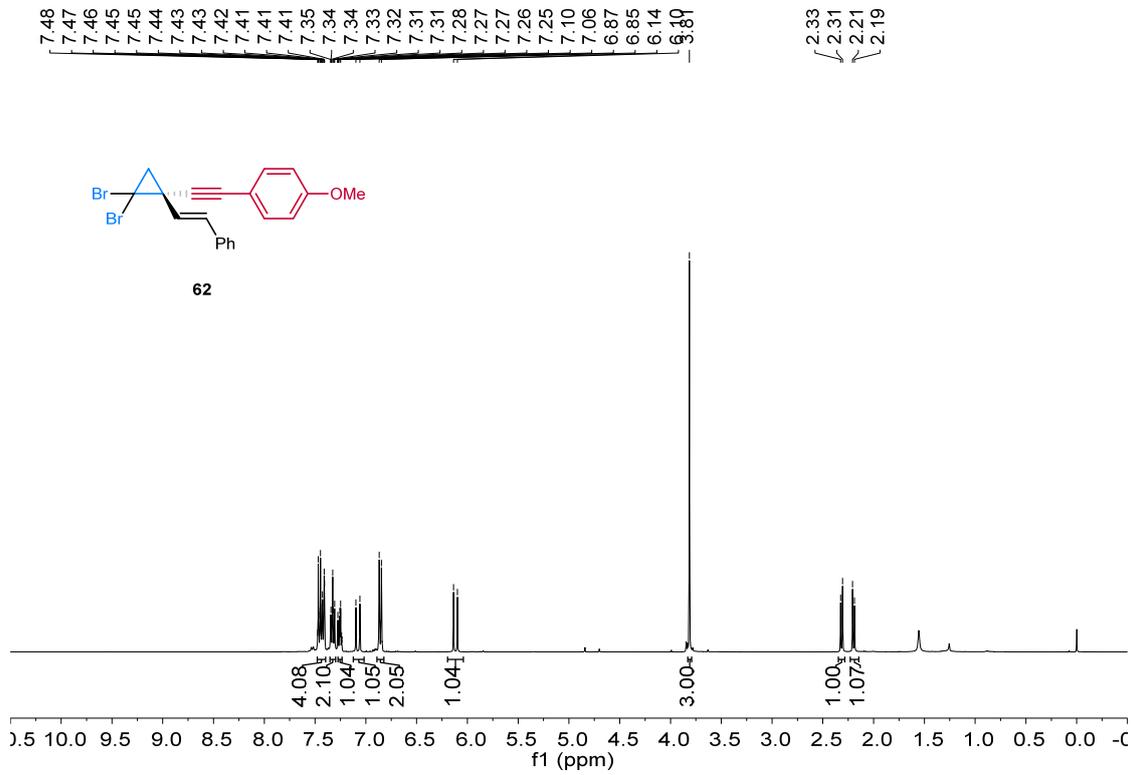


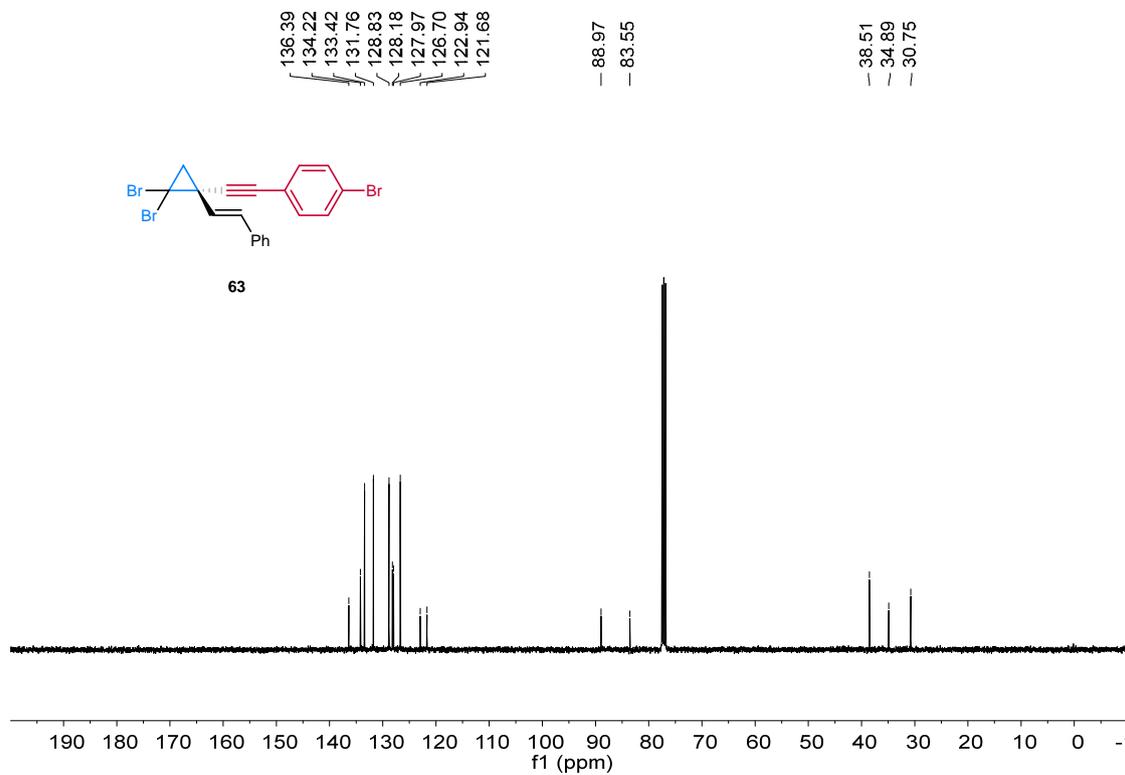
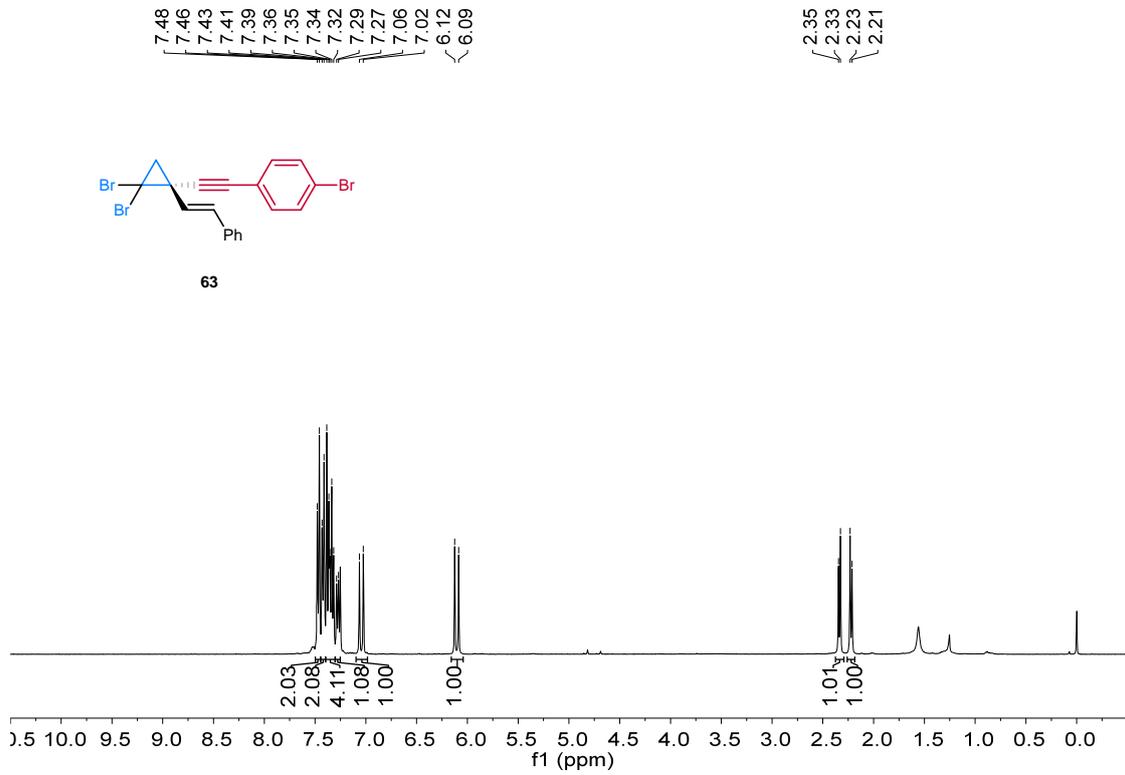


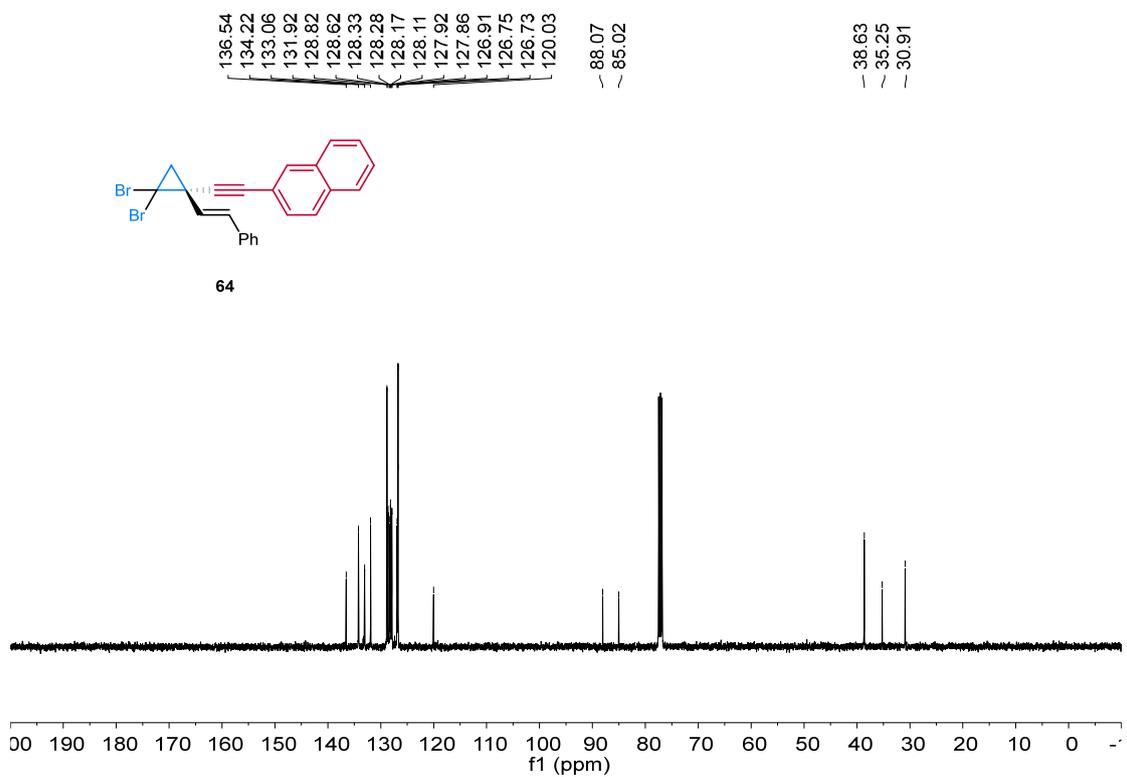
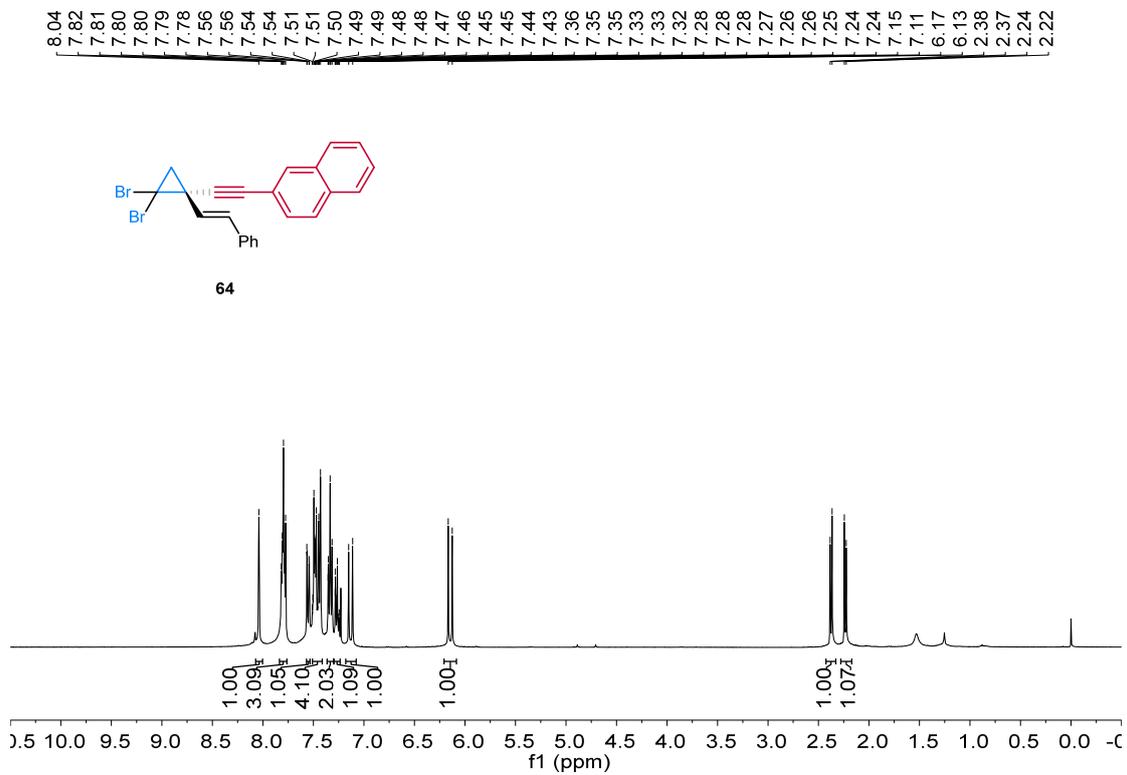








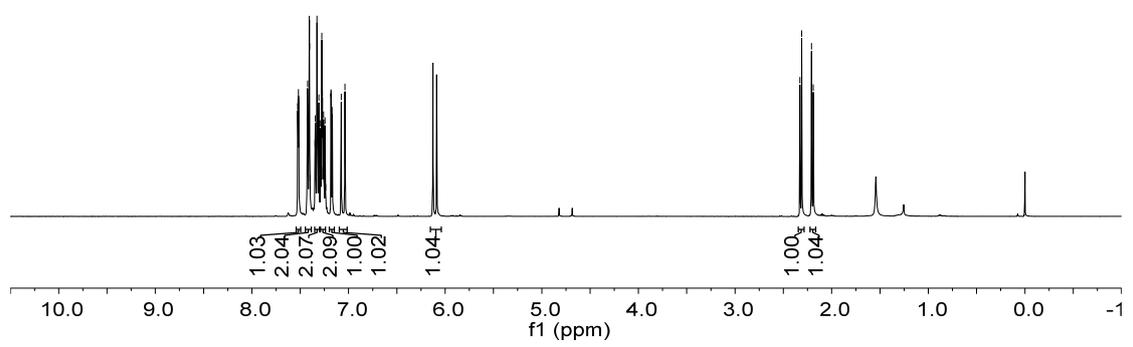




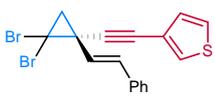
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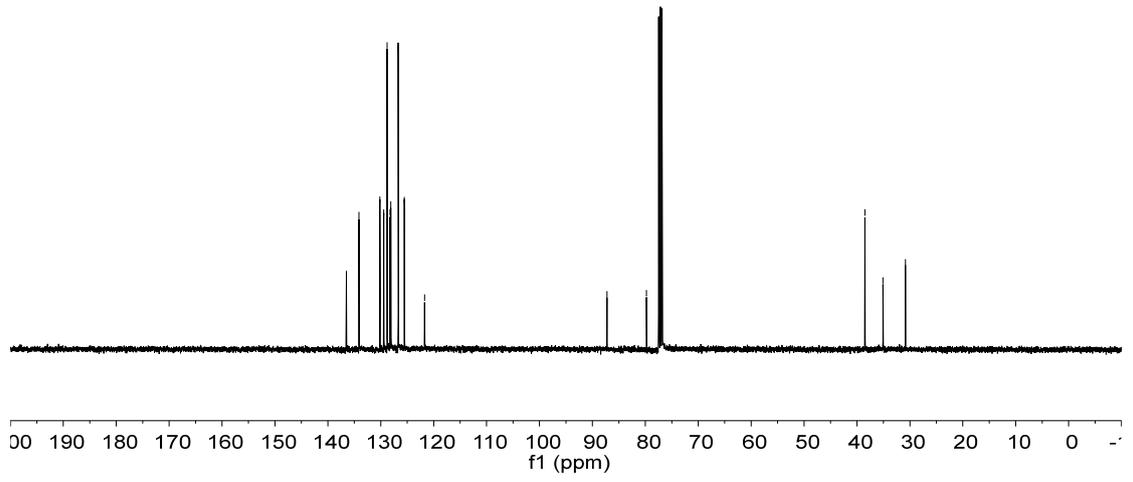
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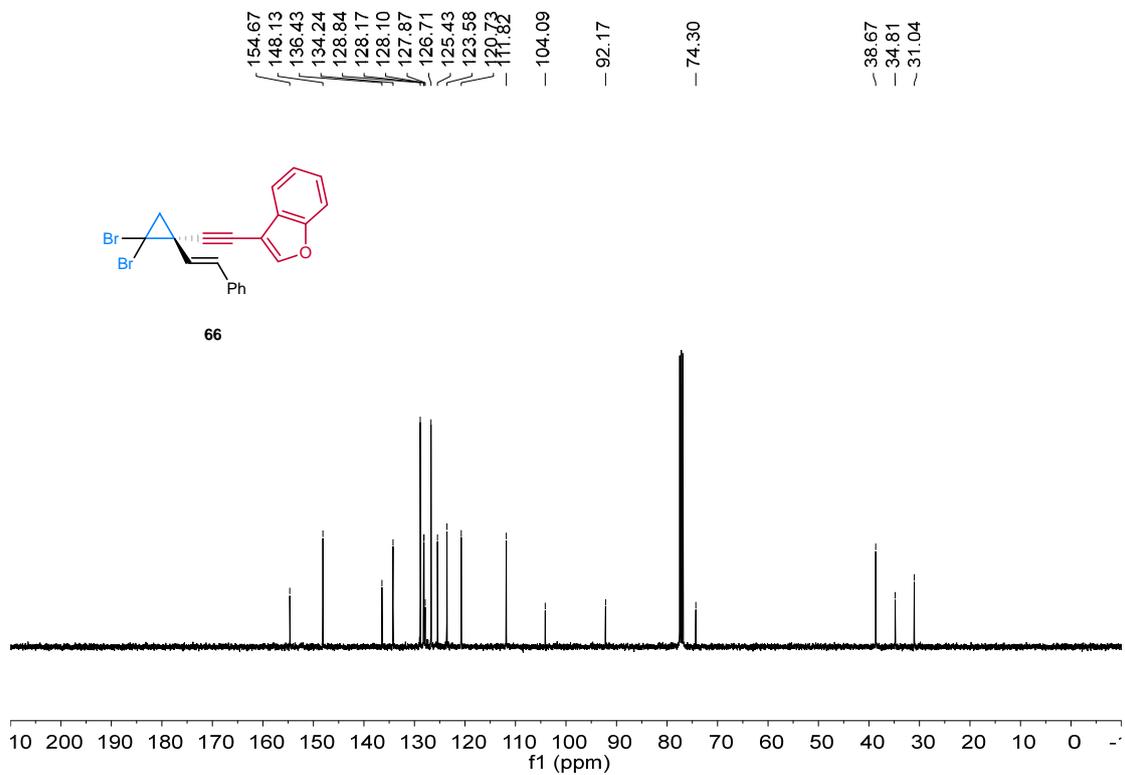
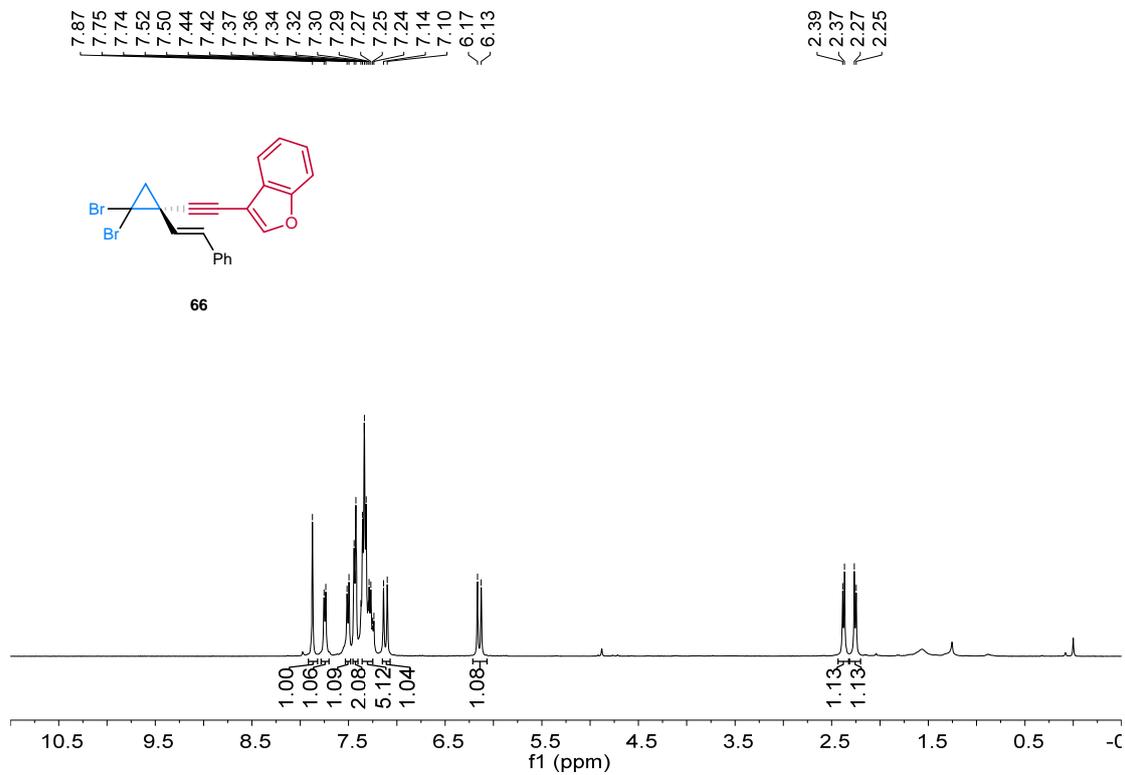


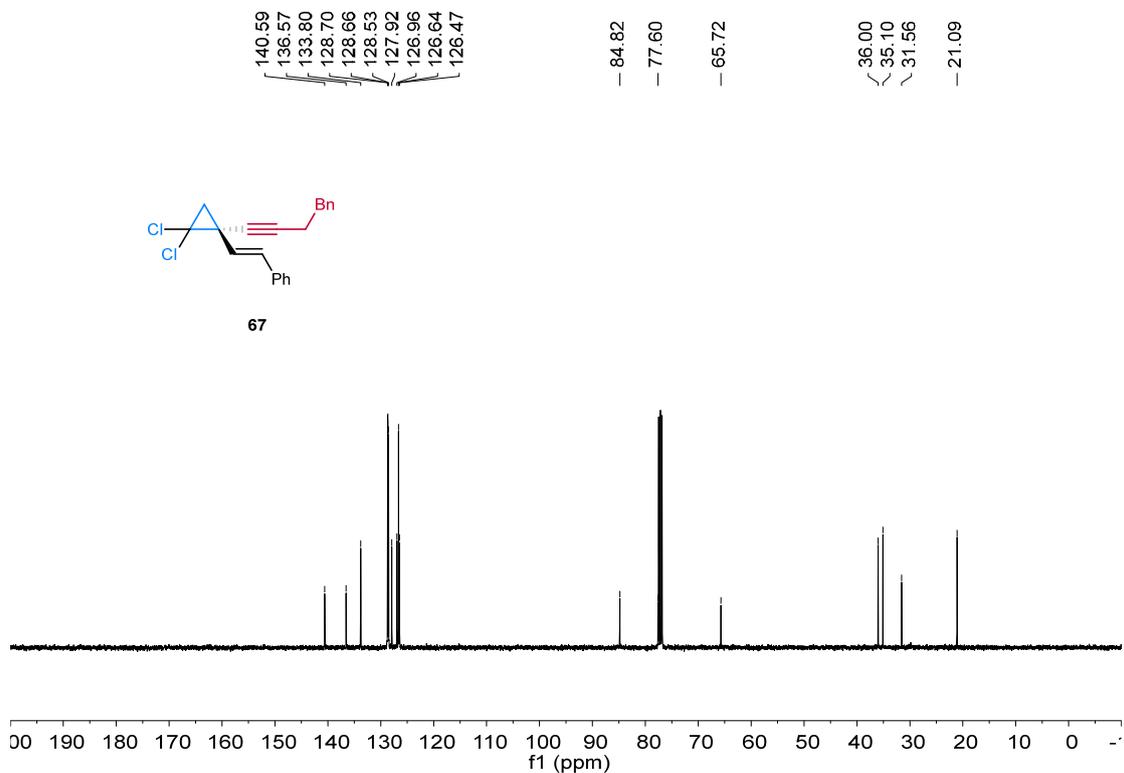
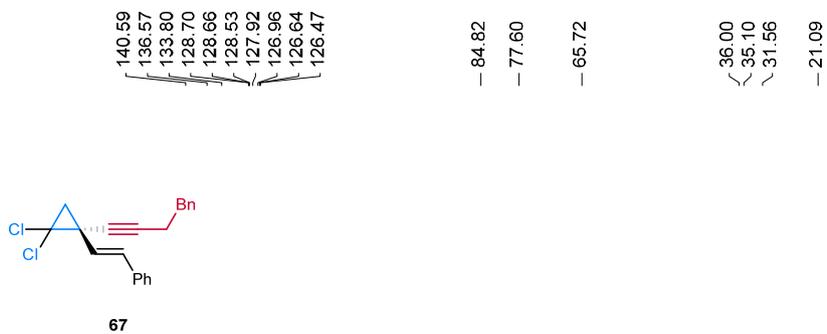
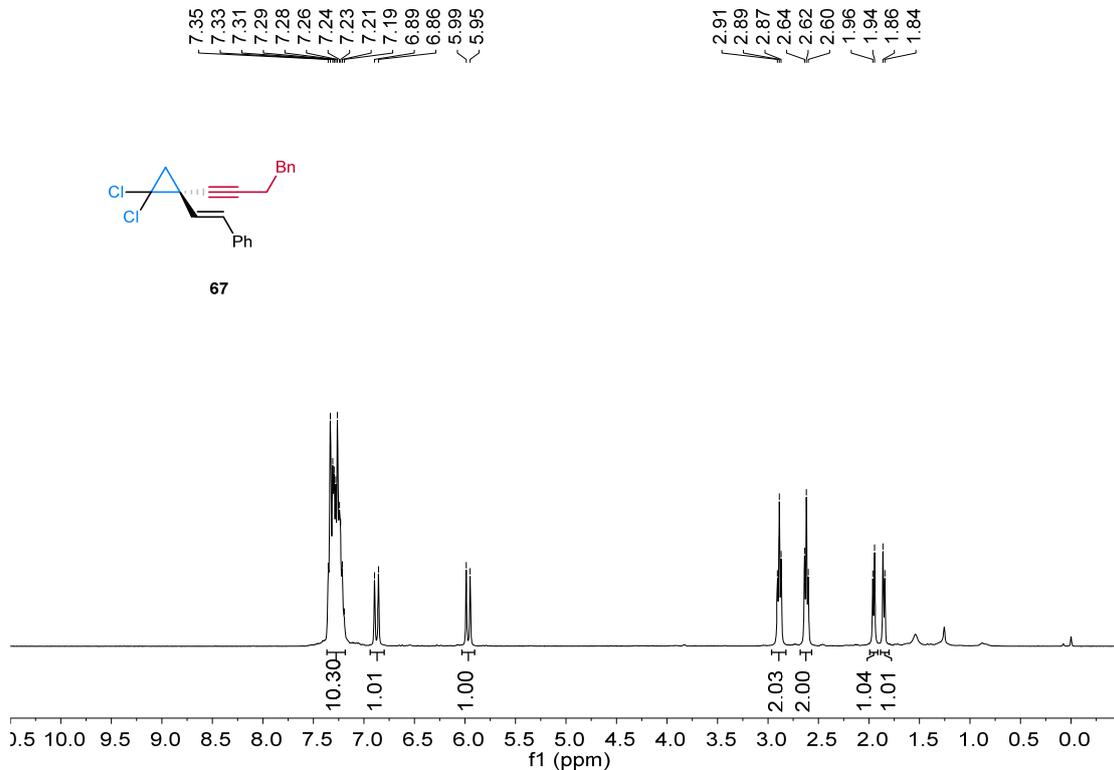
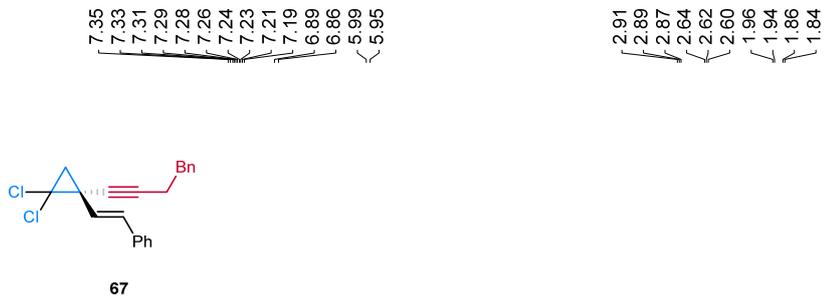
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30.85

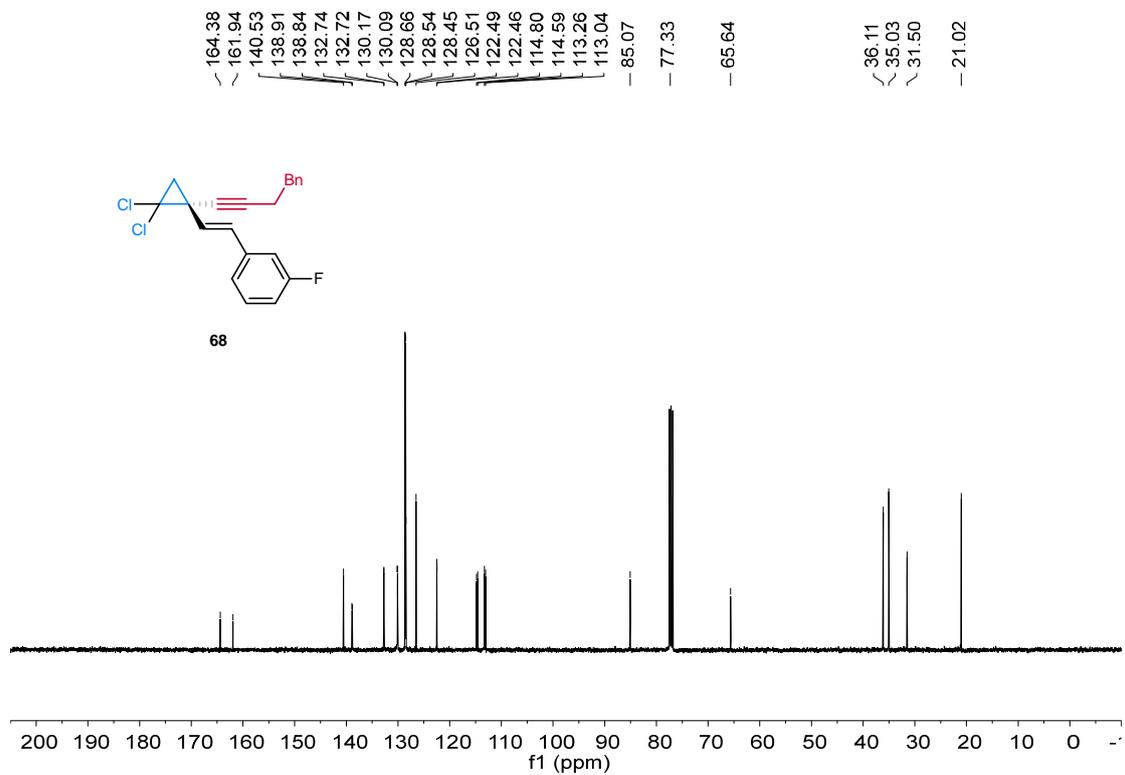
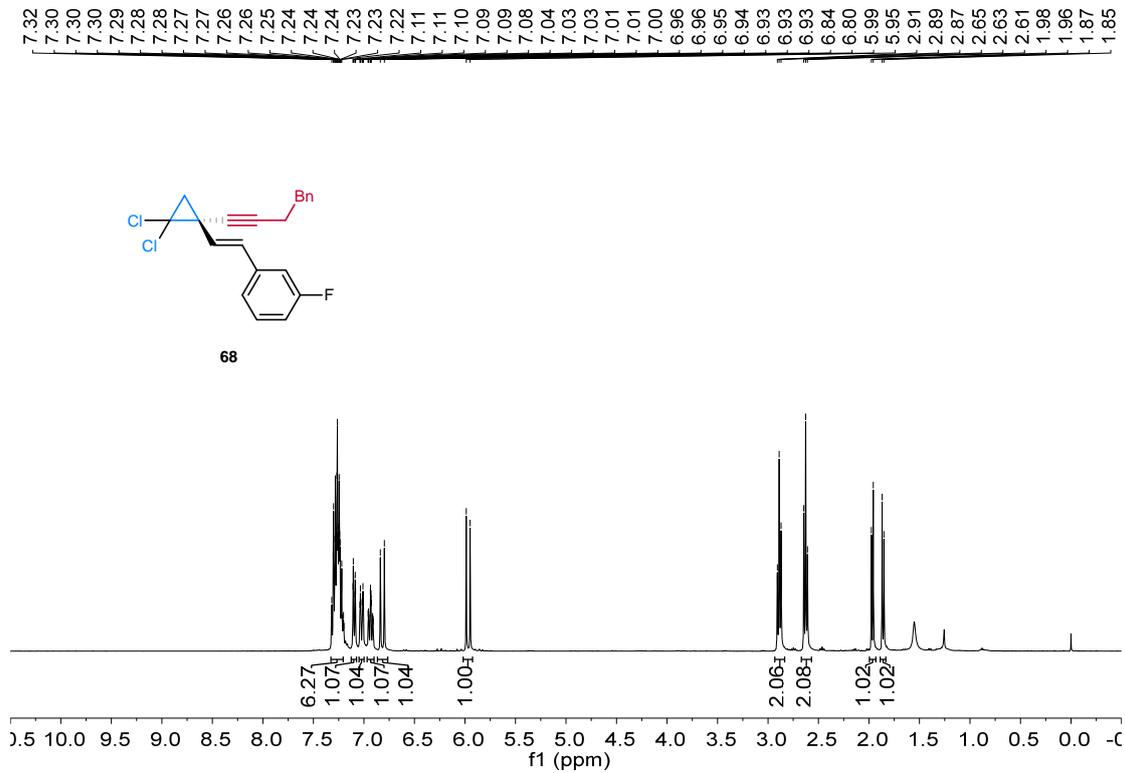


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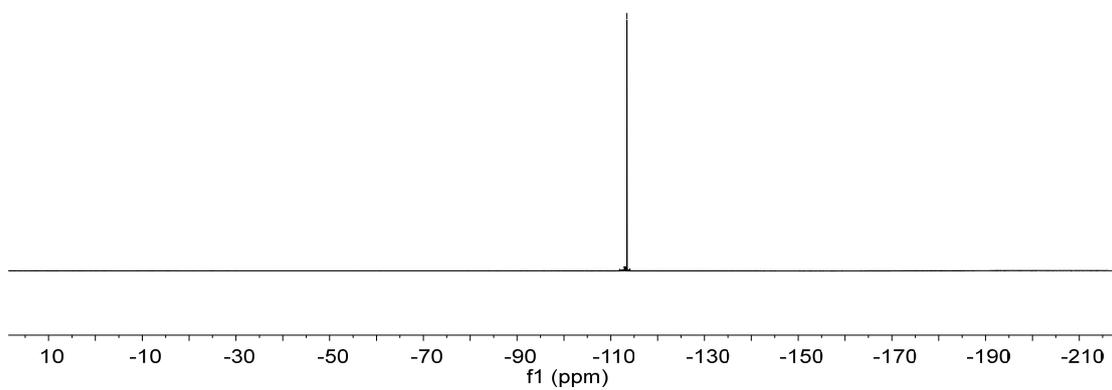


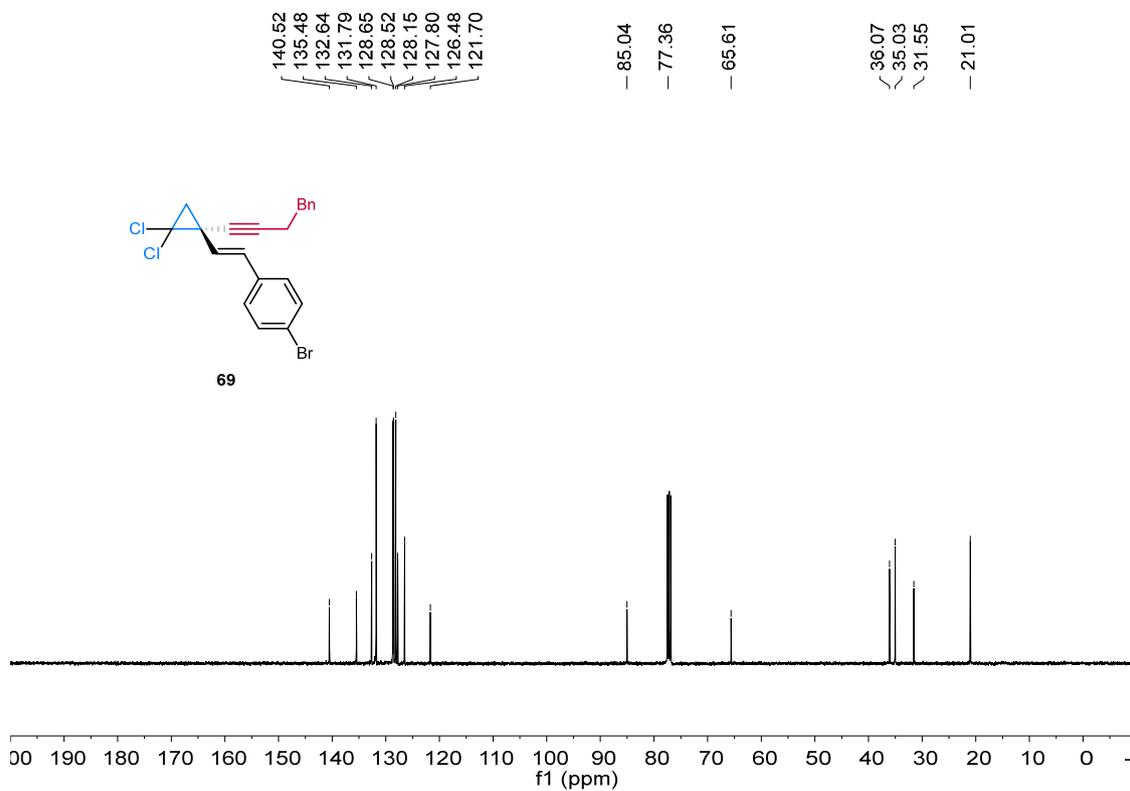
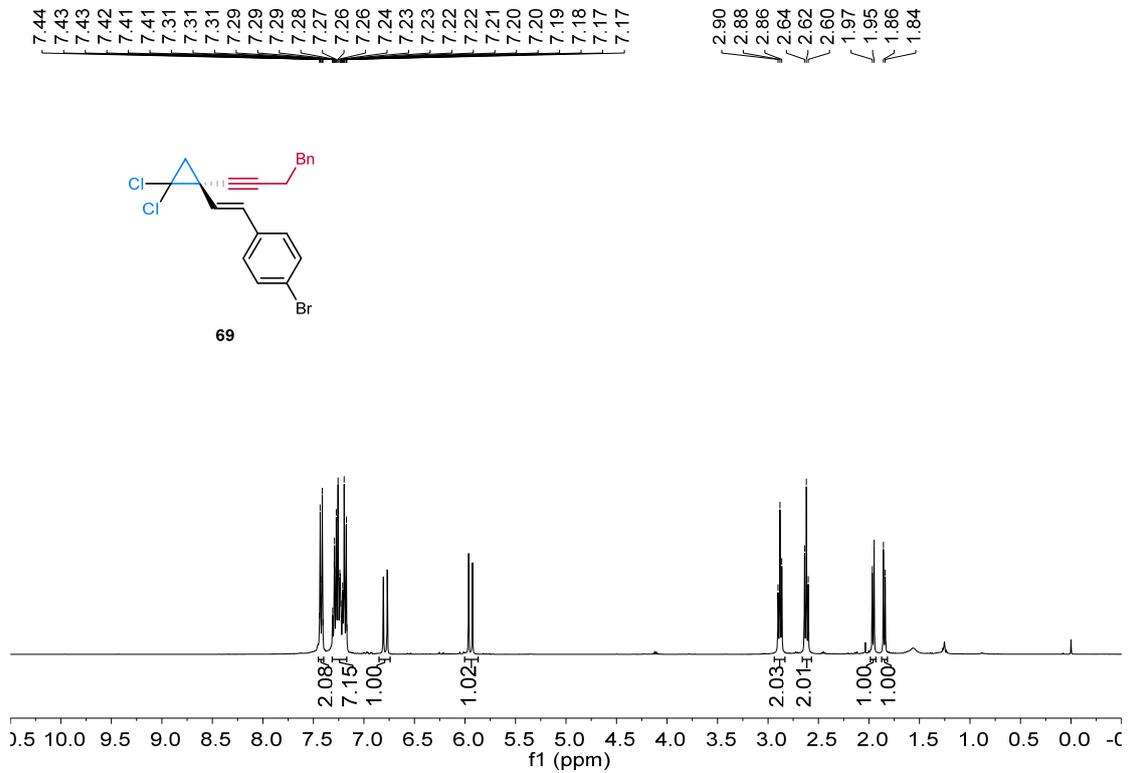


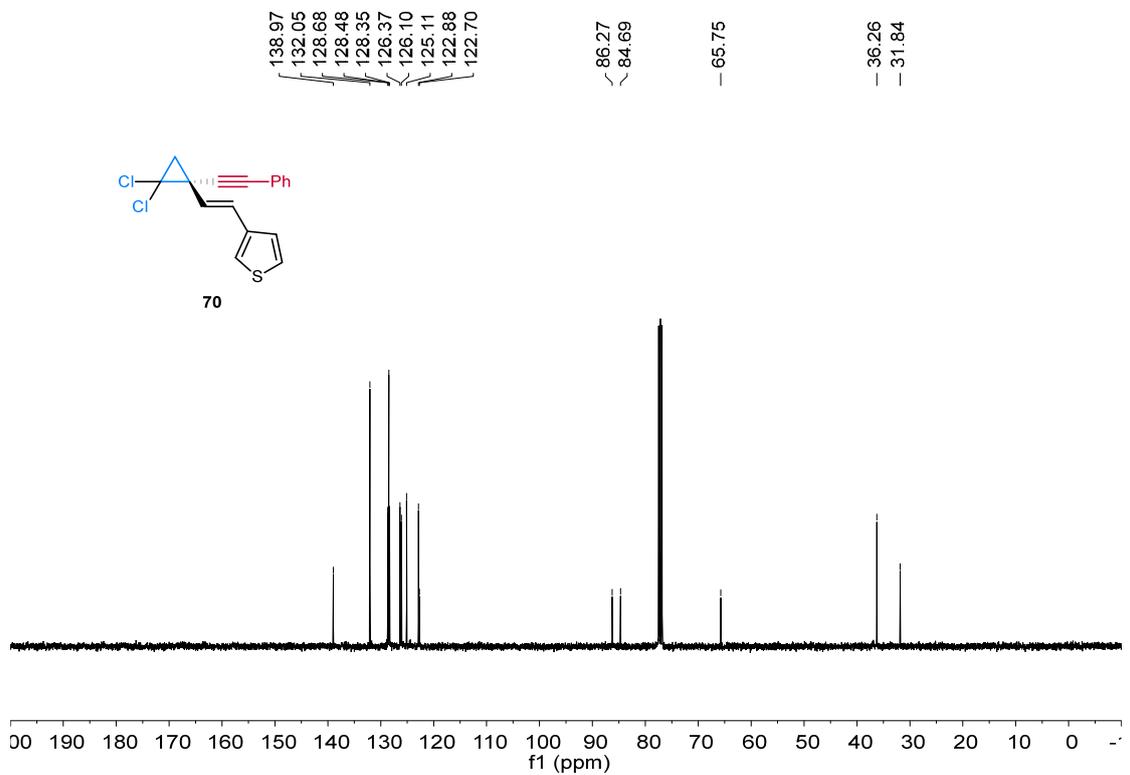
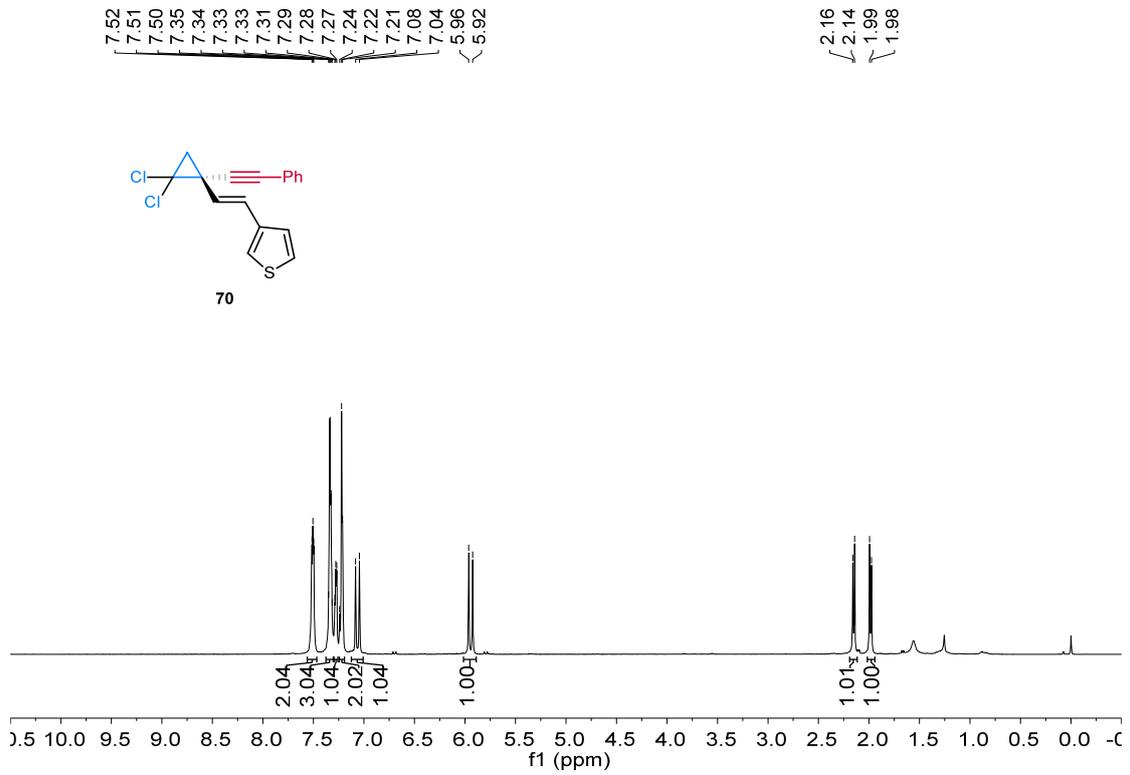


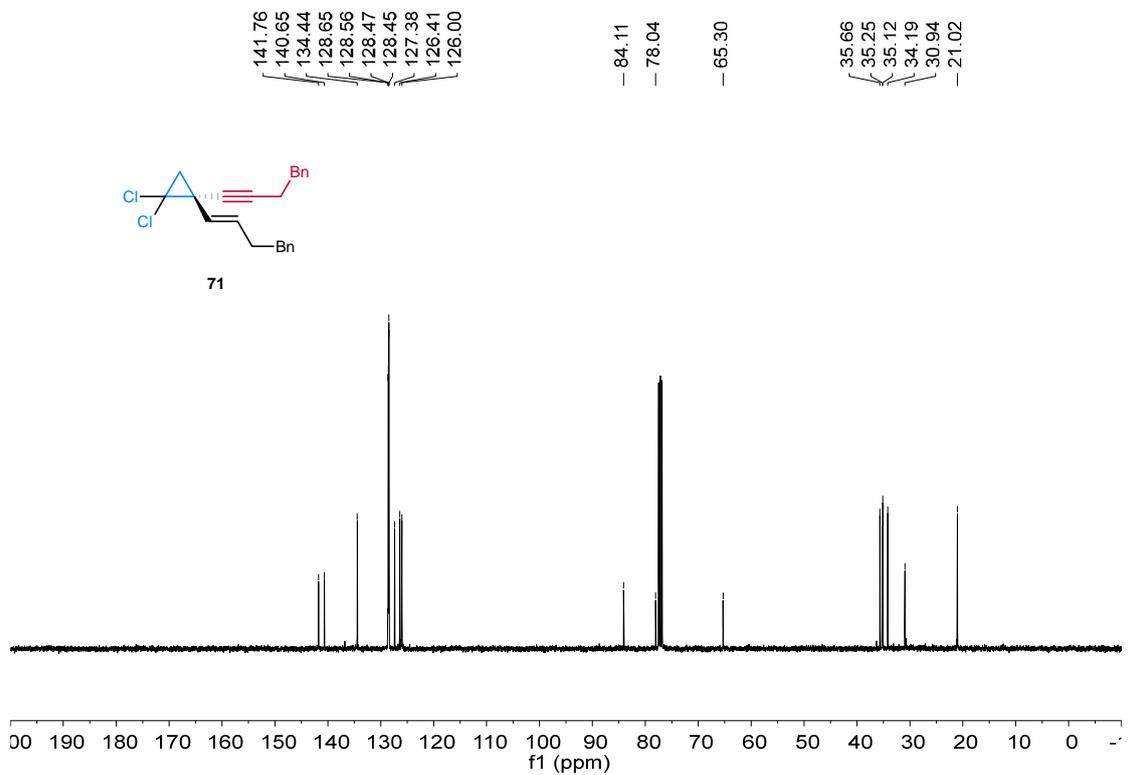
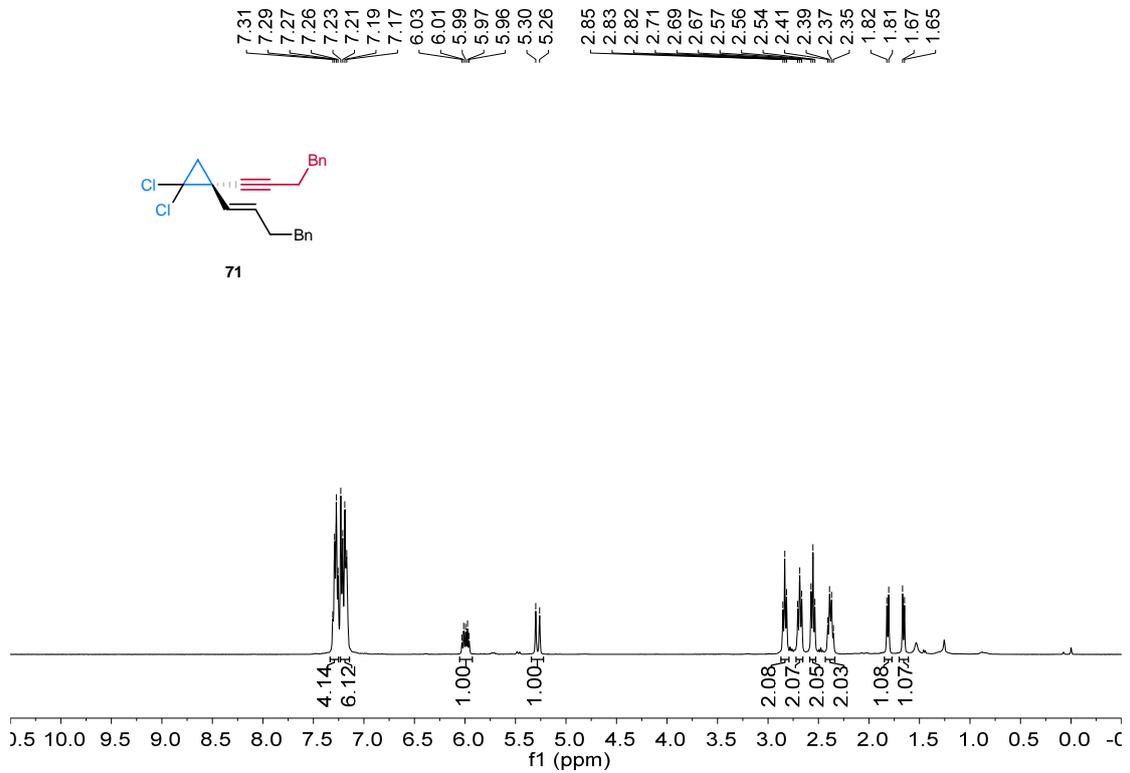
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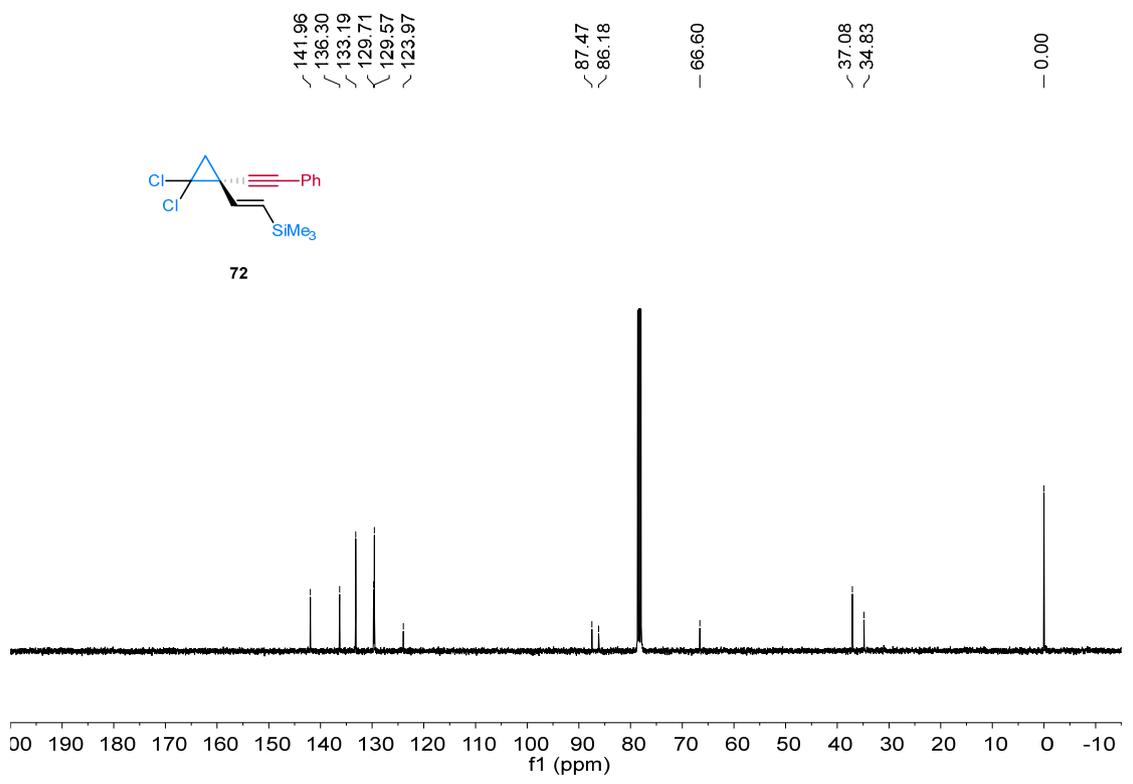
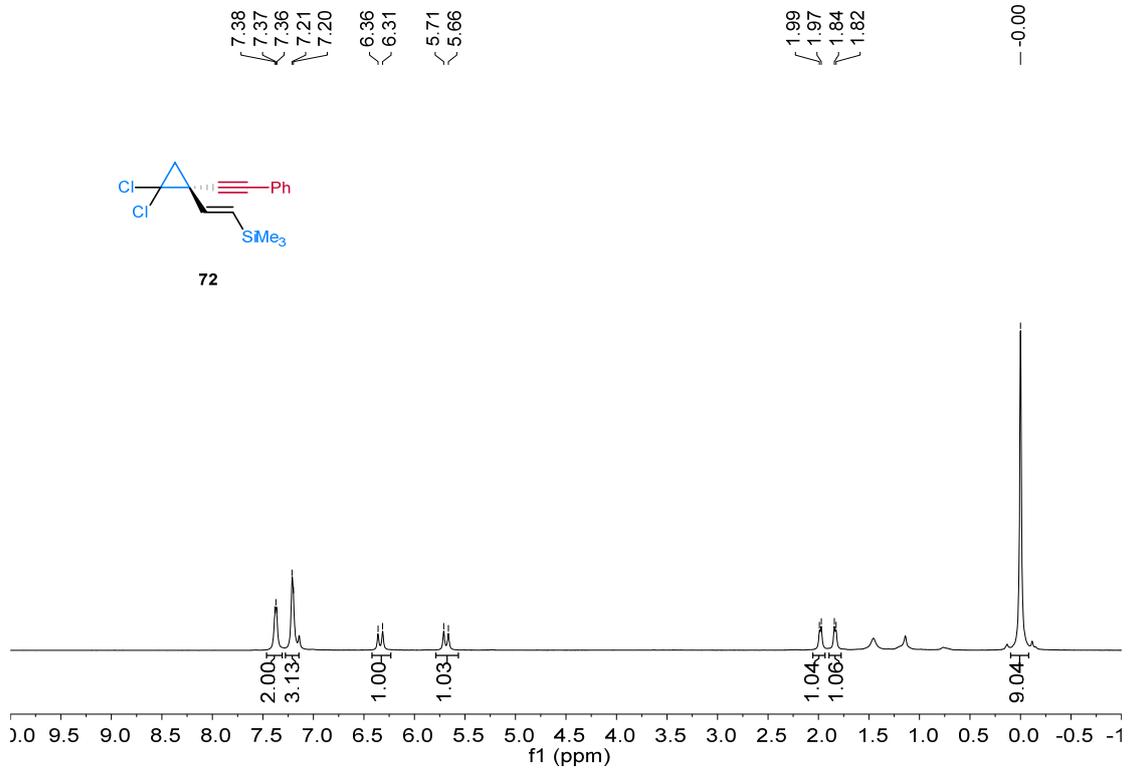
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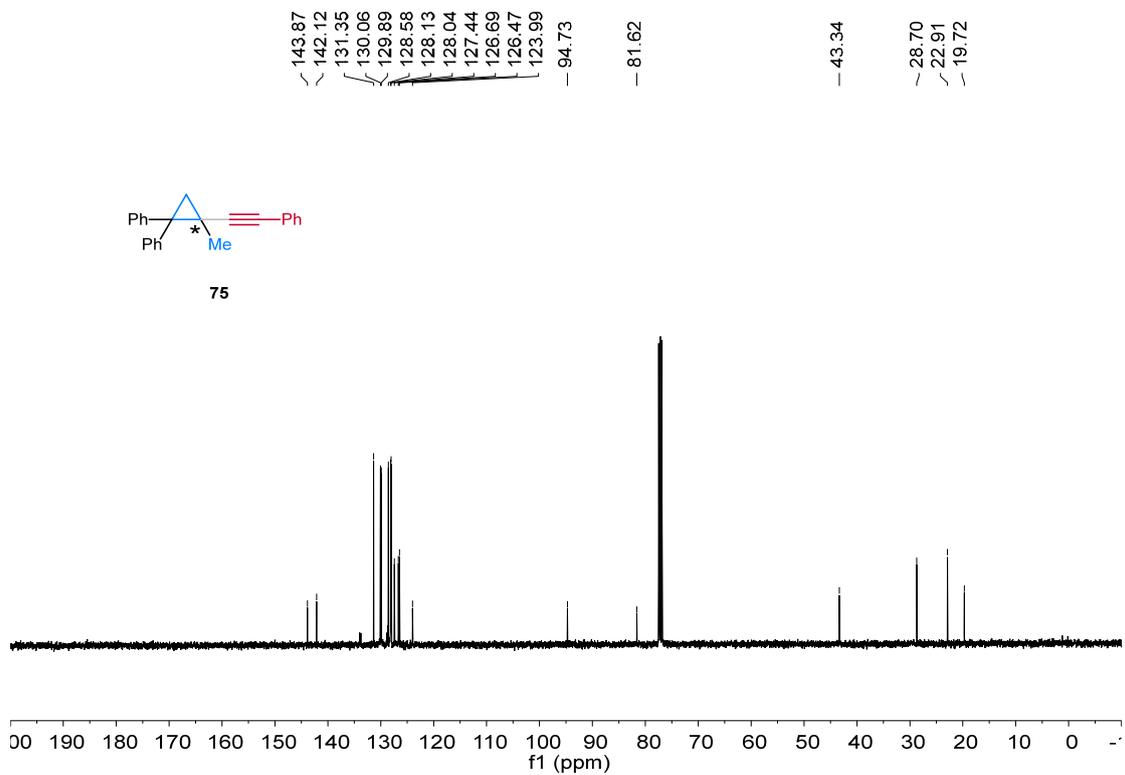
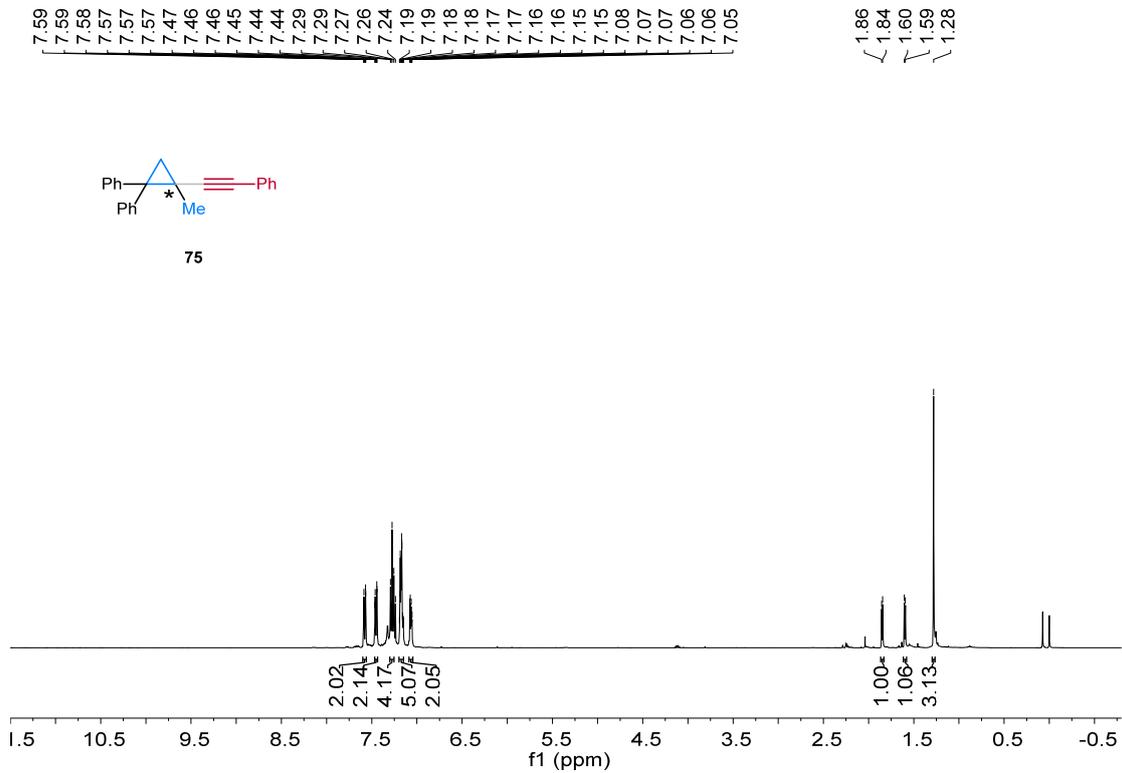


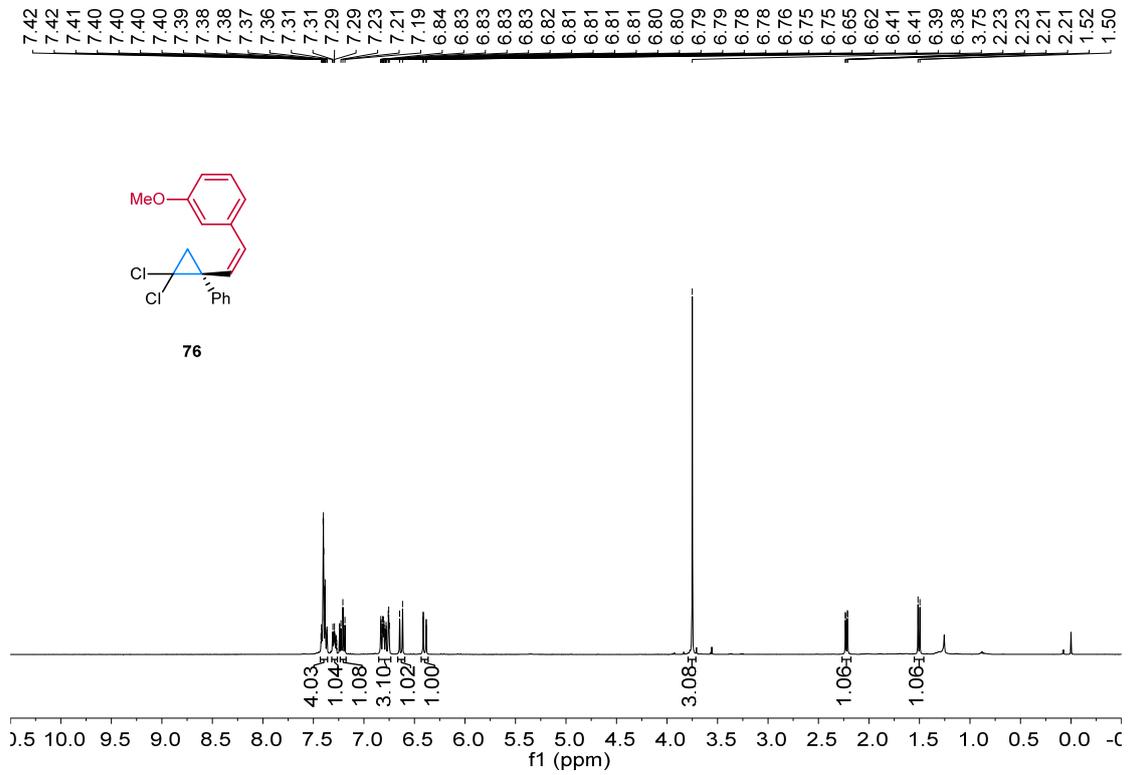




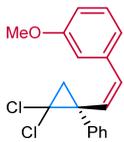
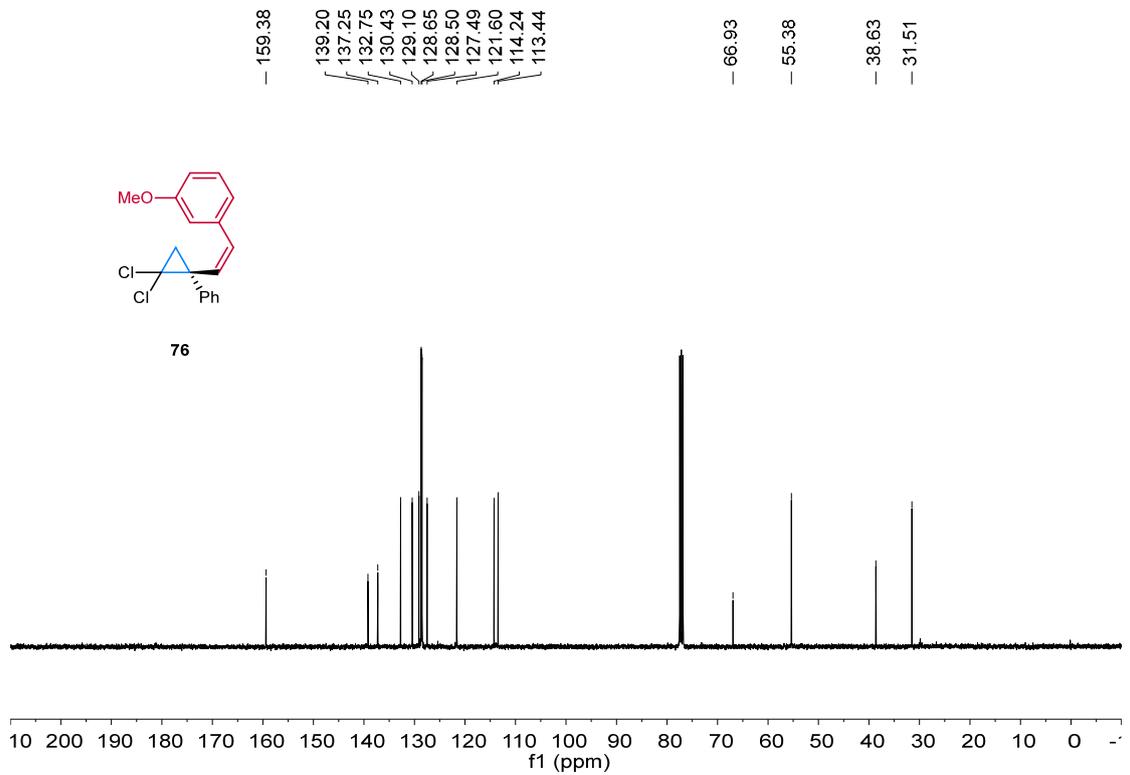




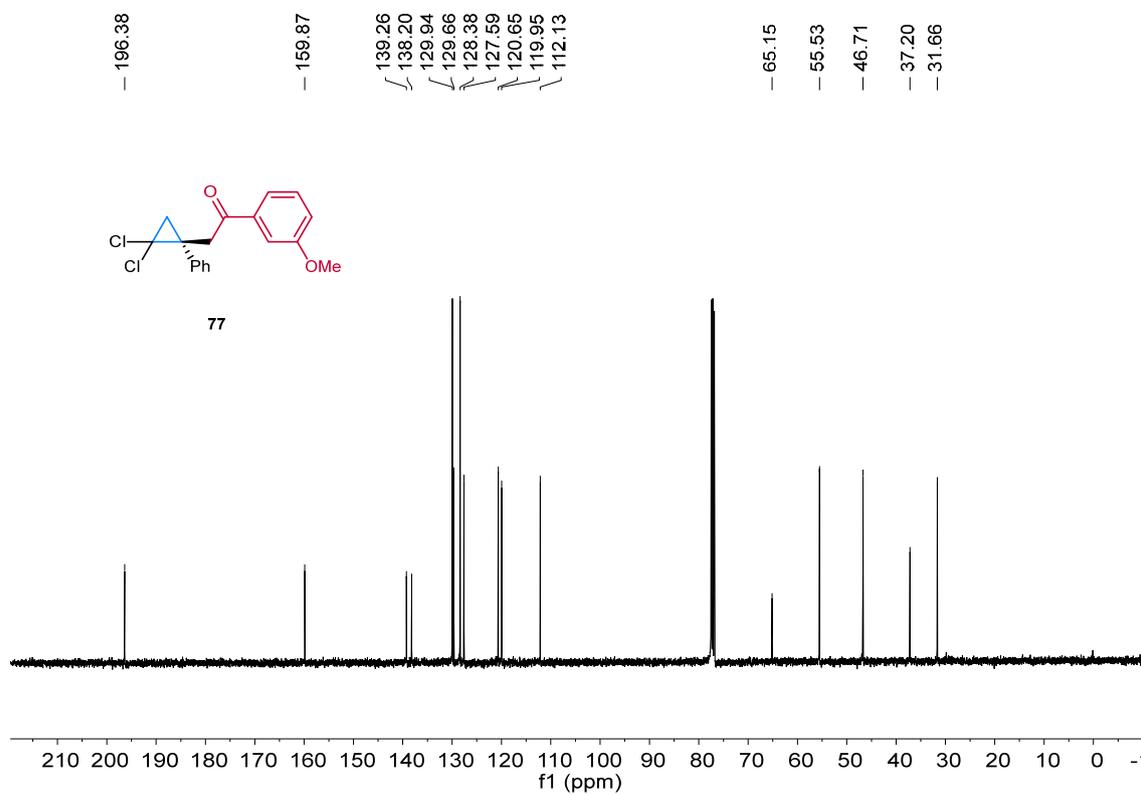
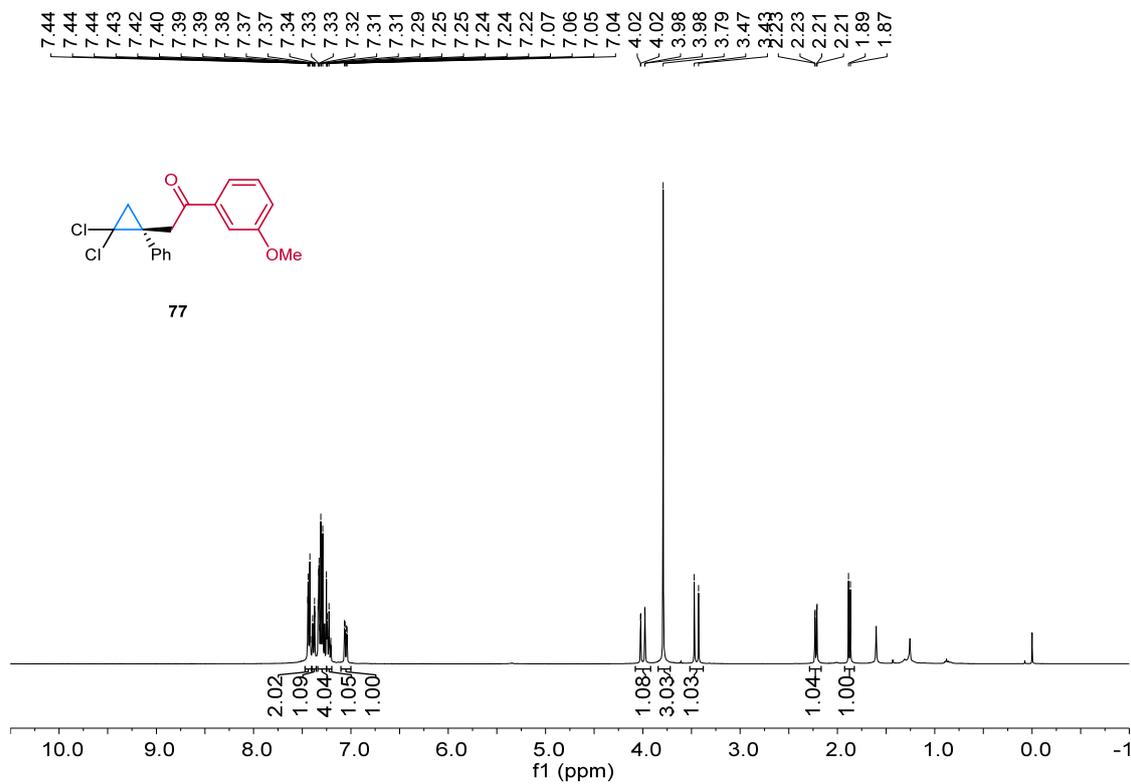


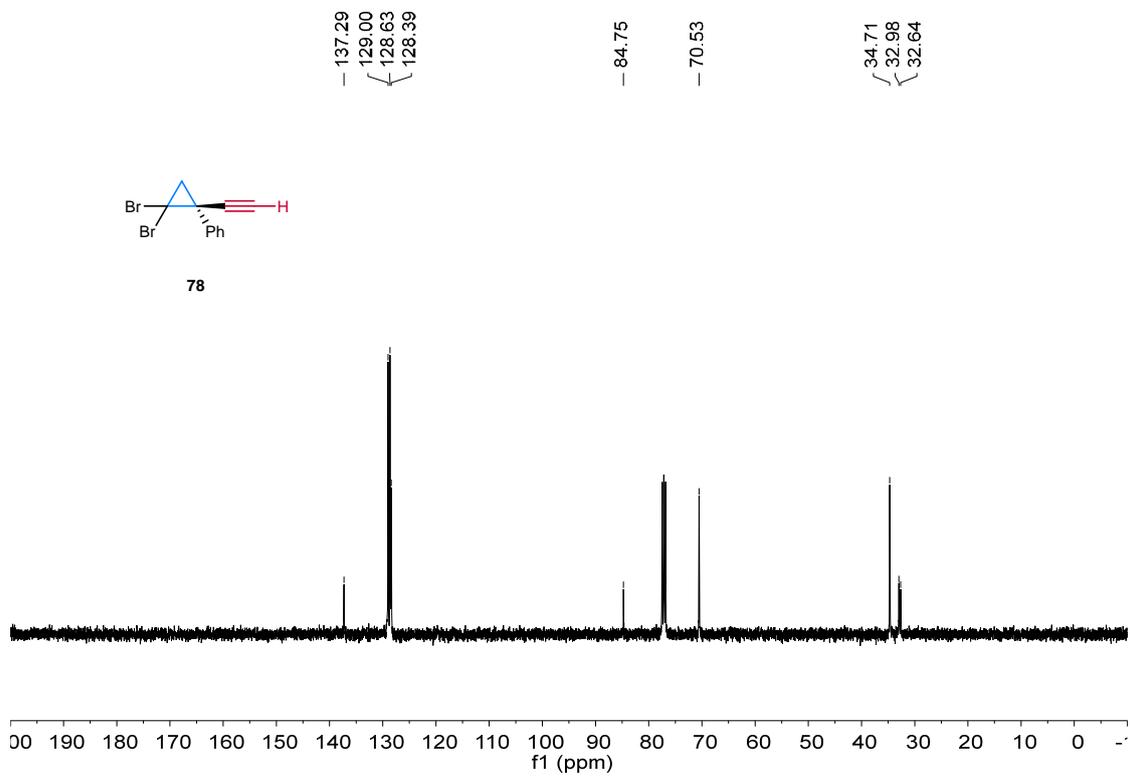
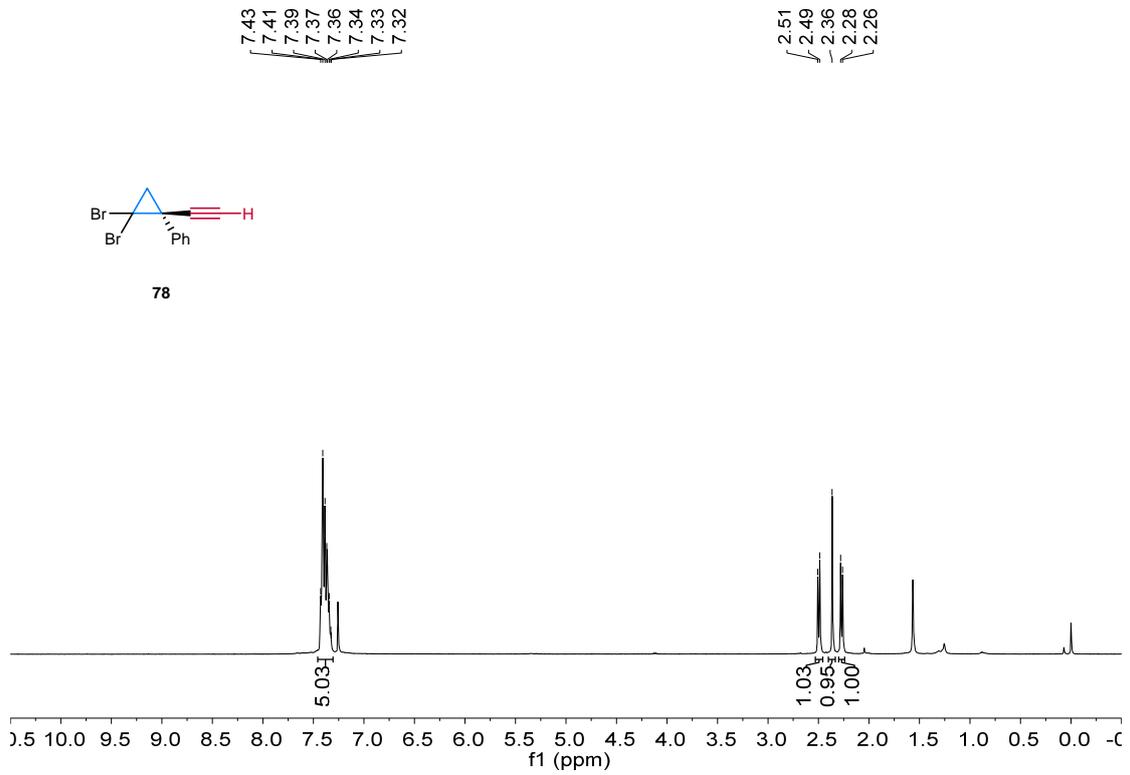


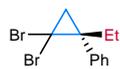
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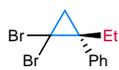
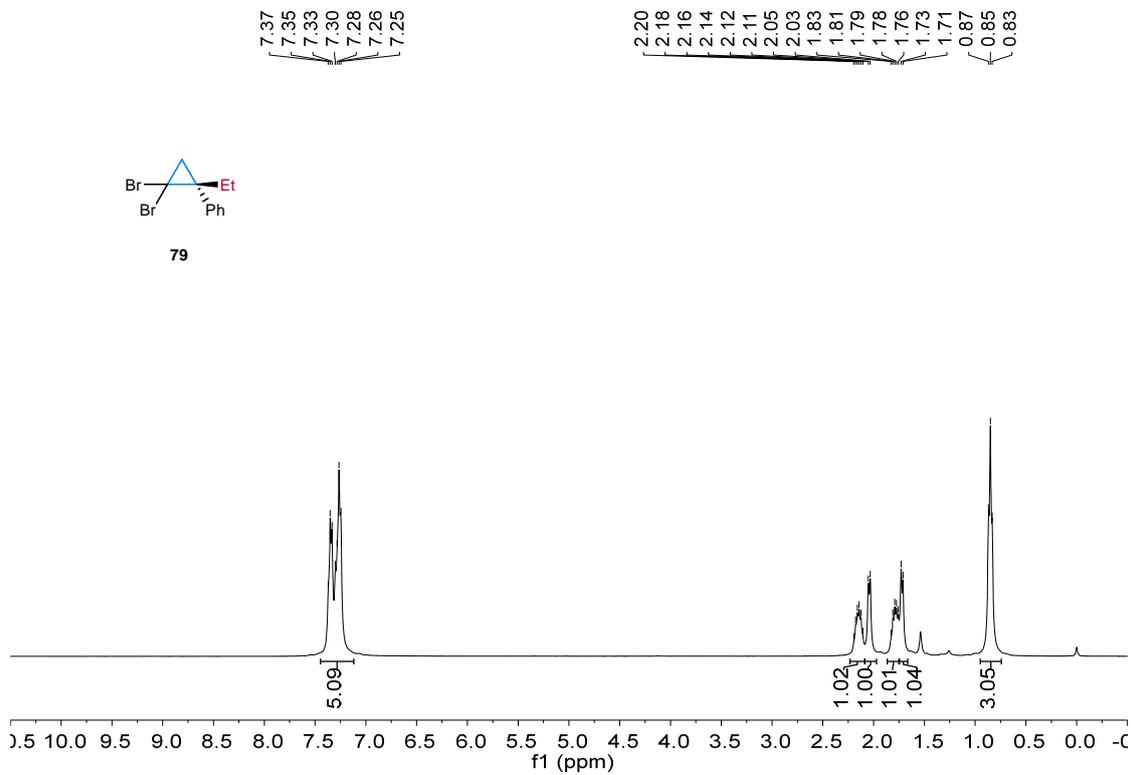
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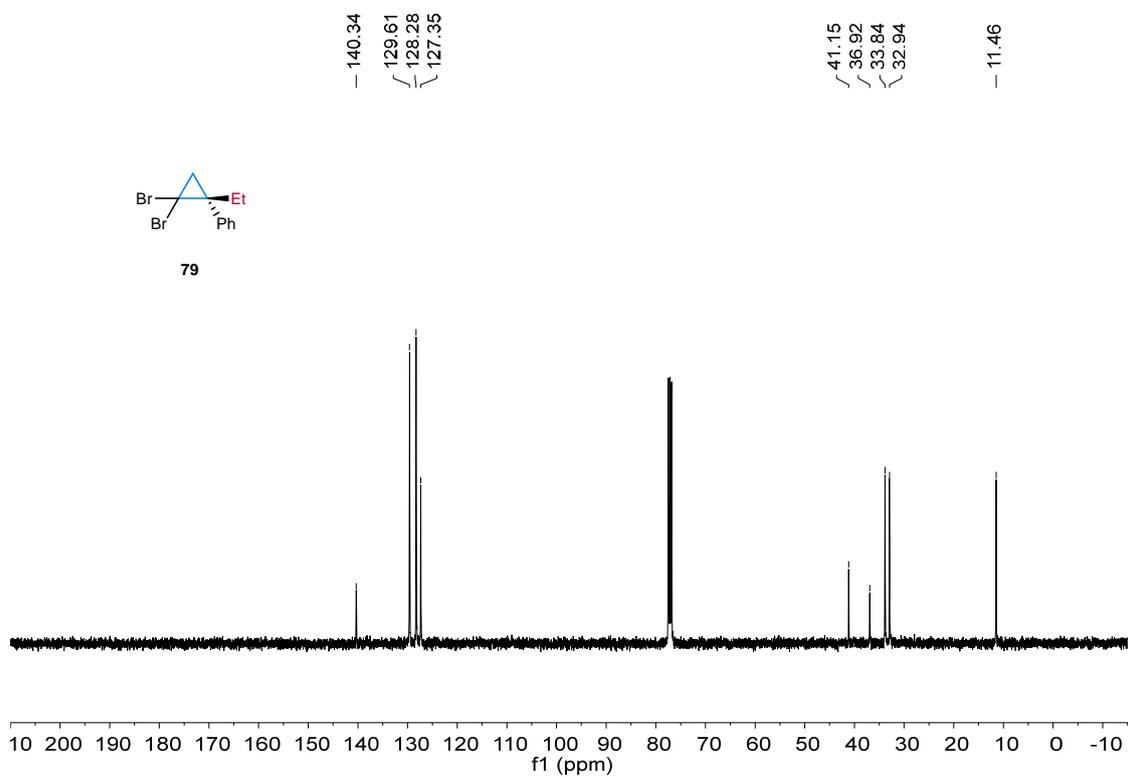


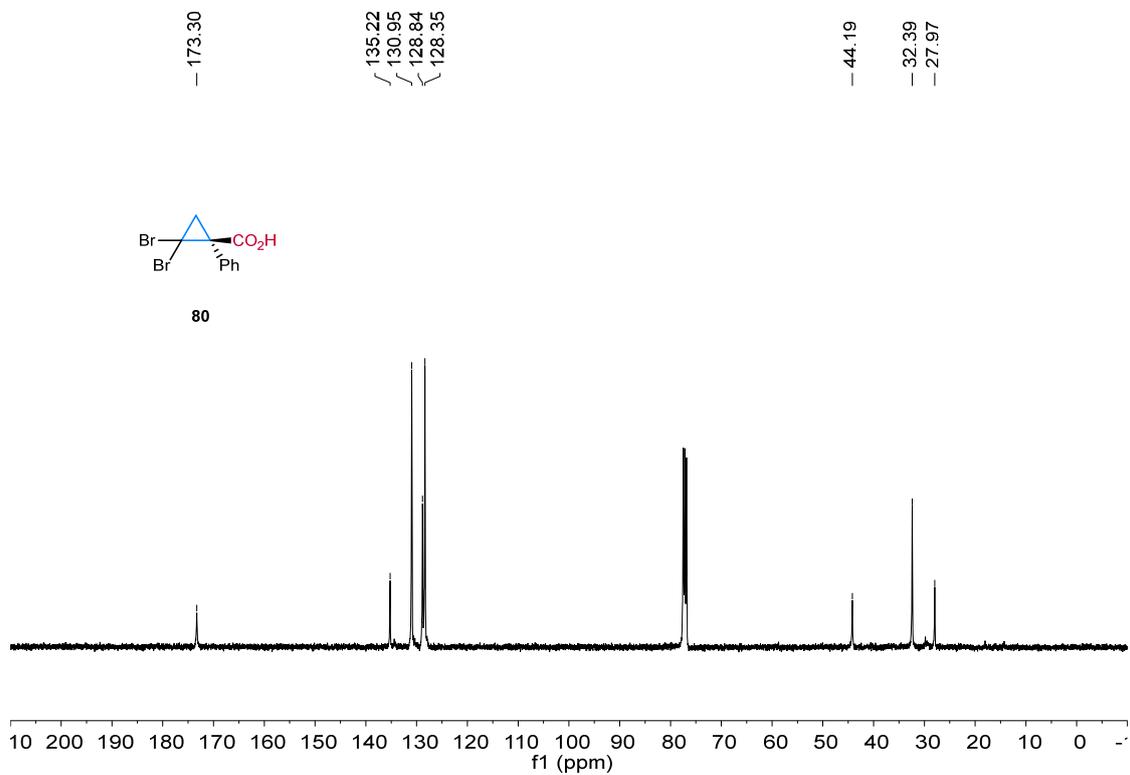
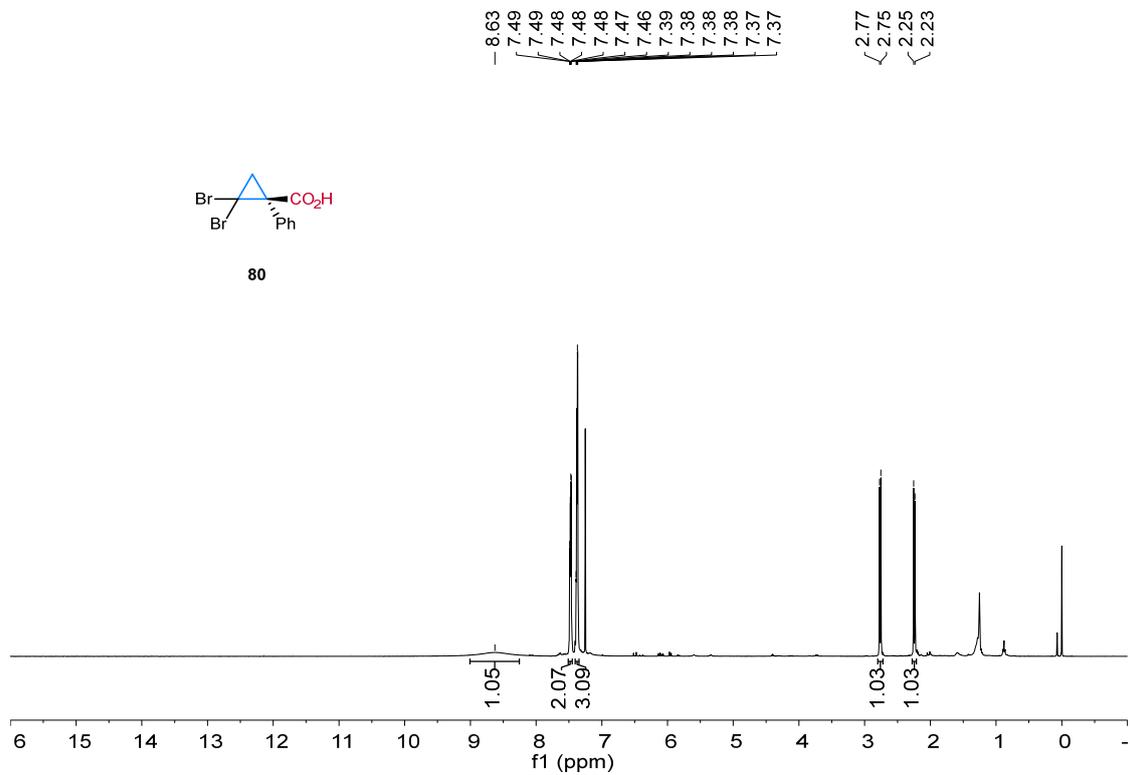


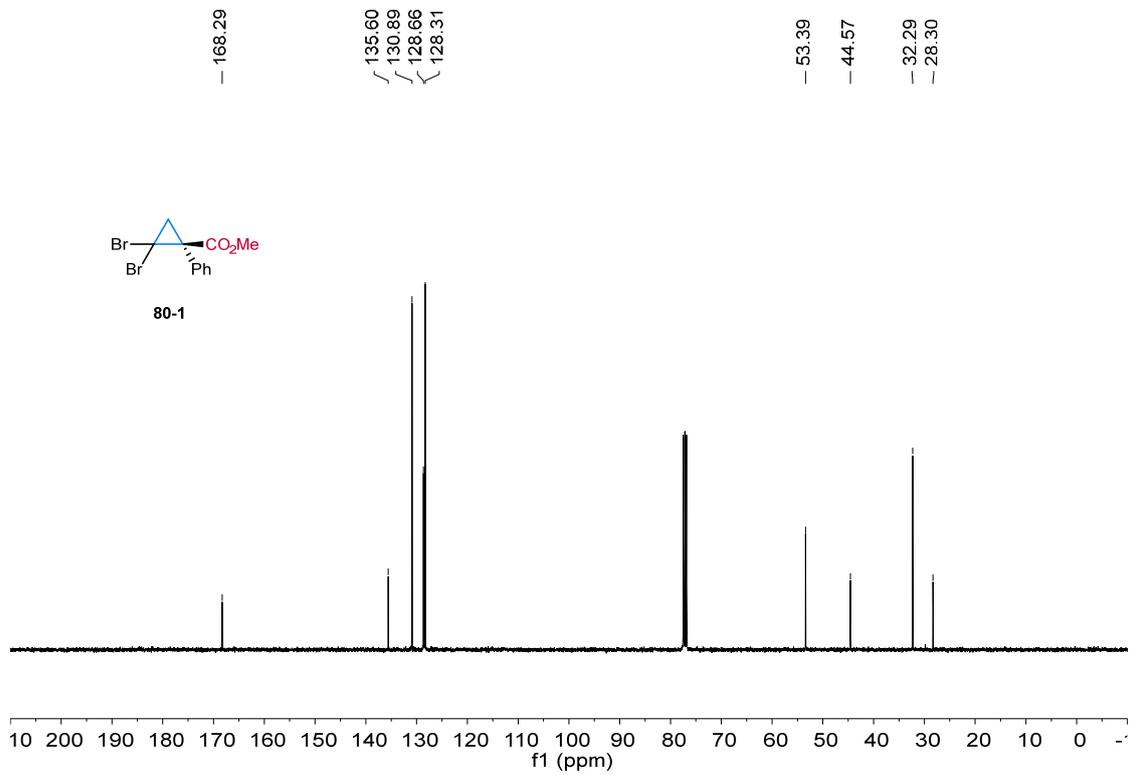
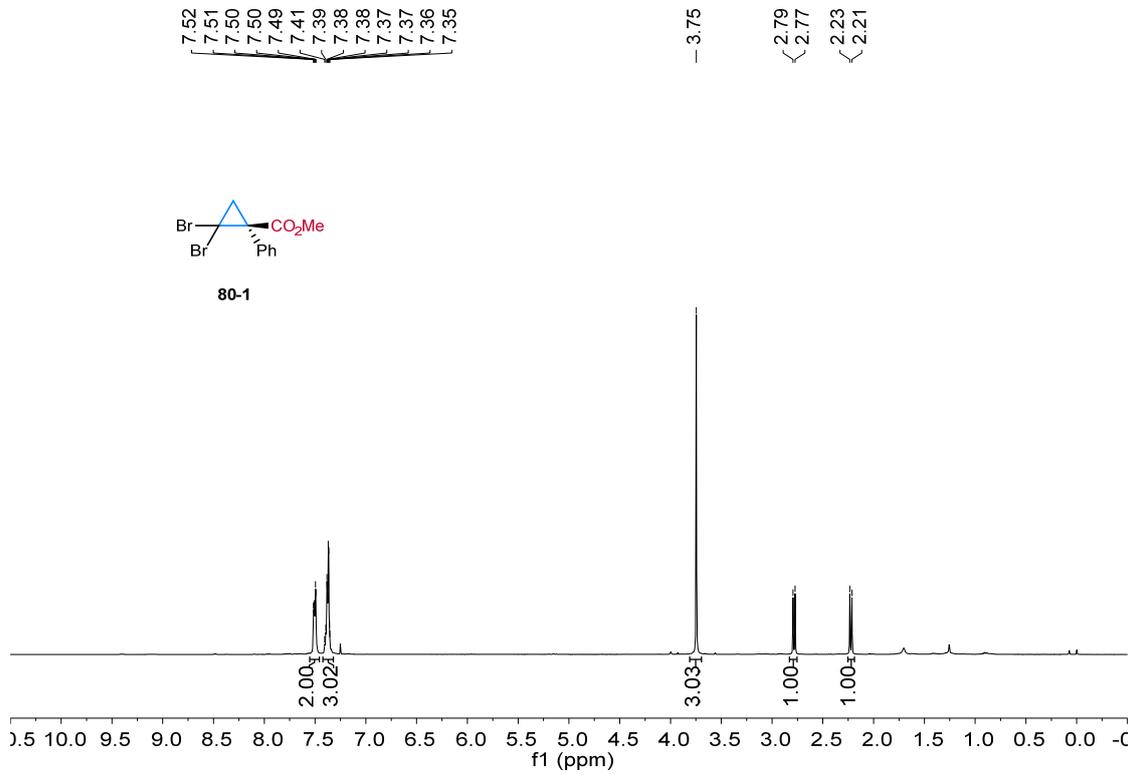
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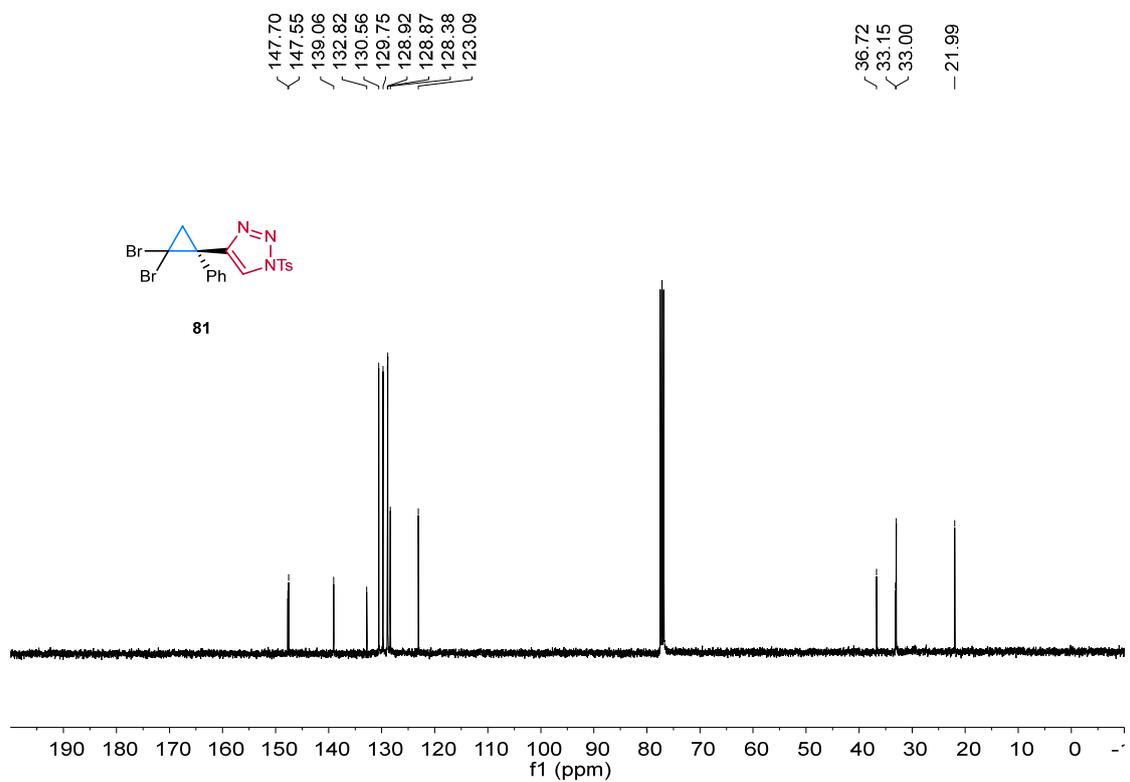
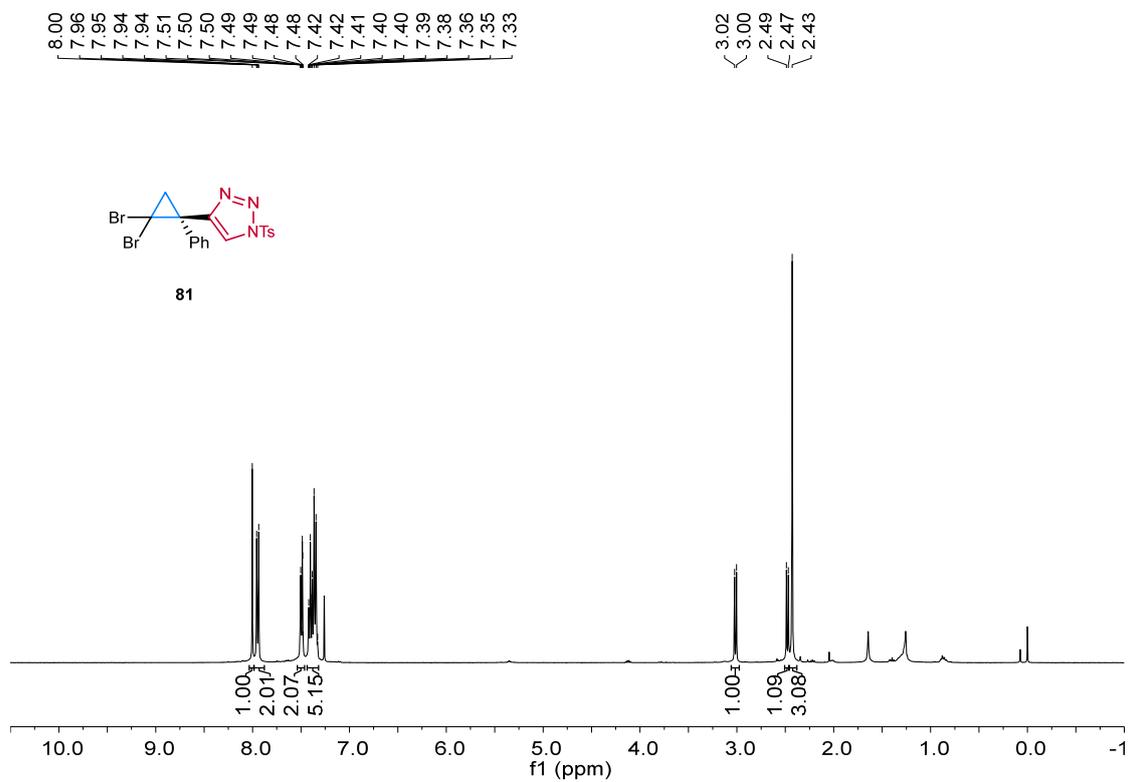


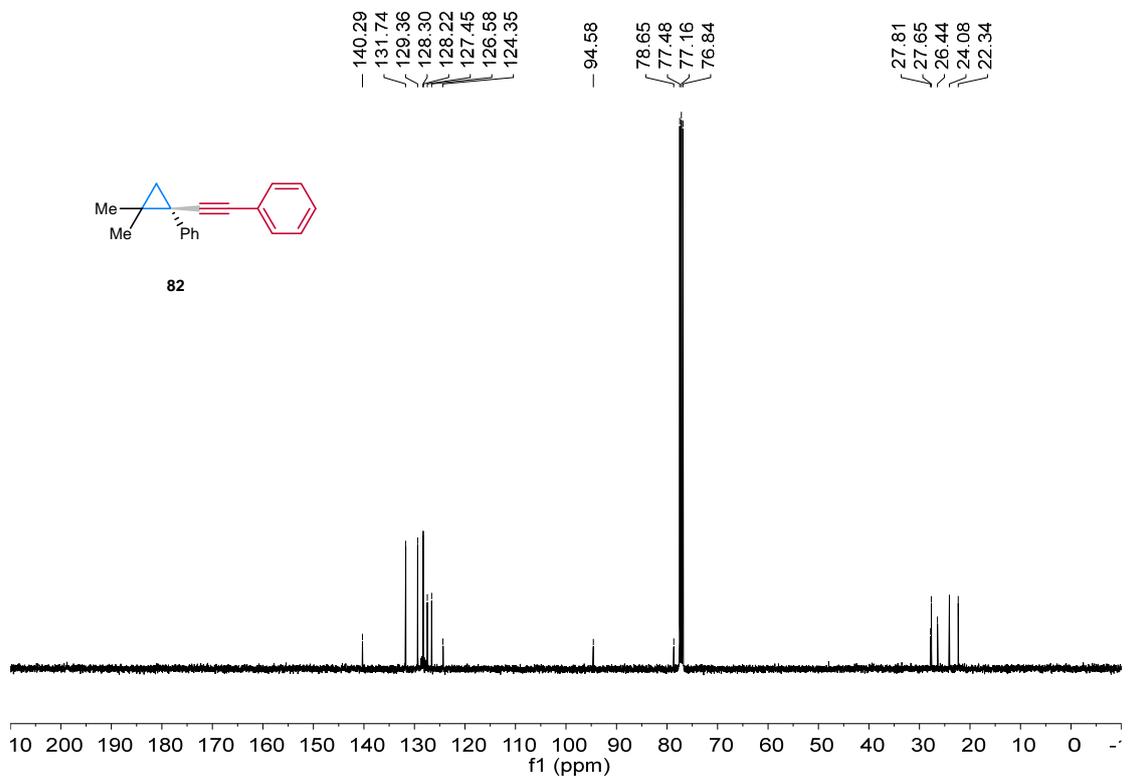
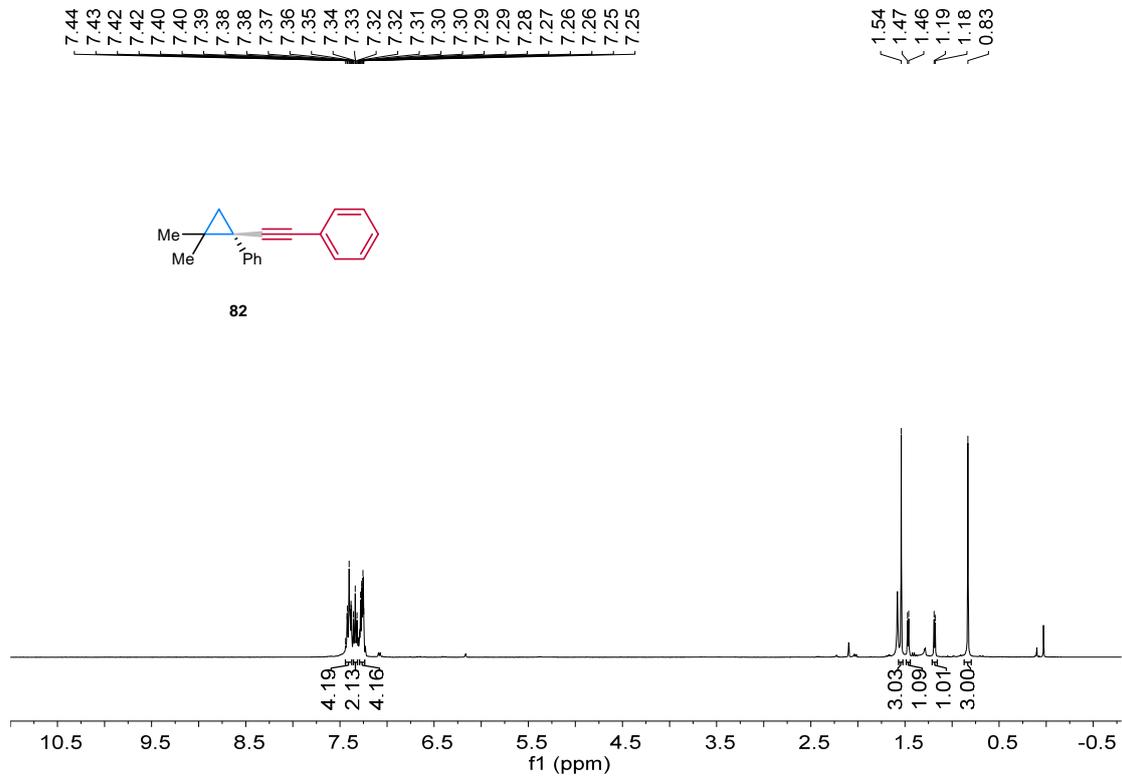
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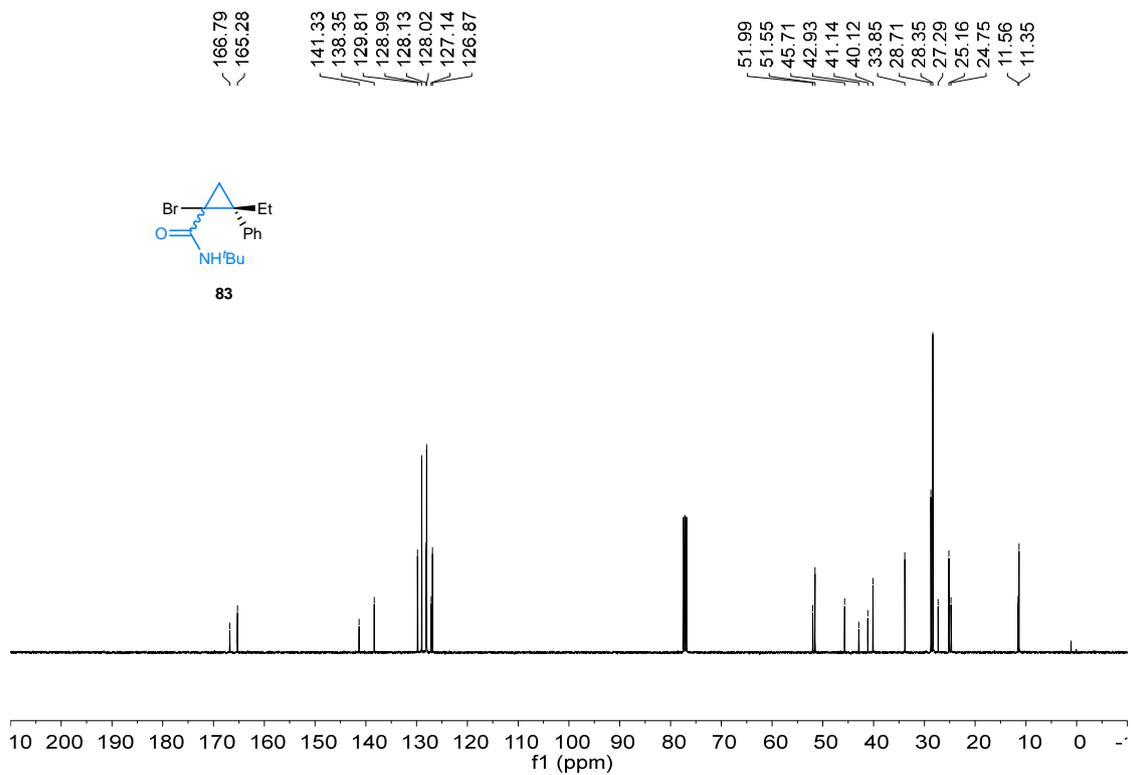
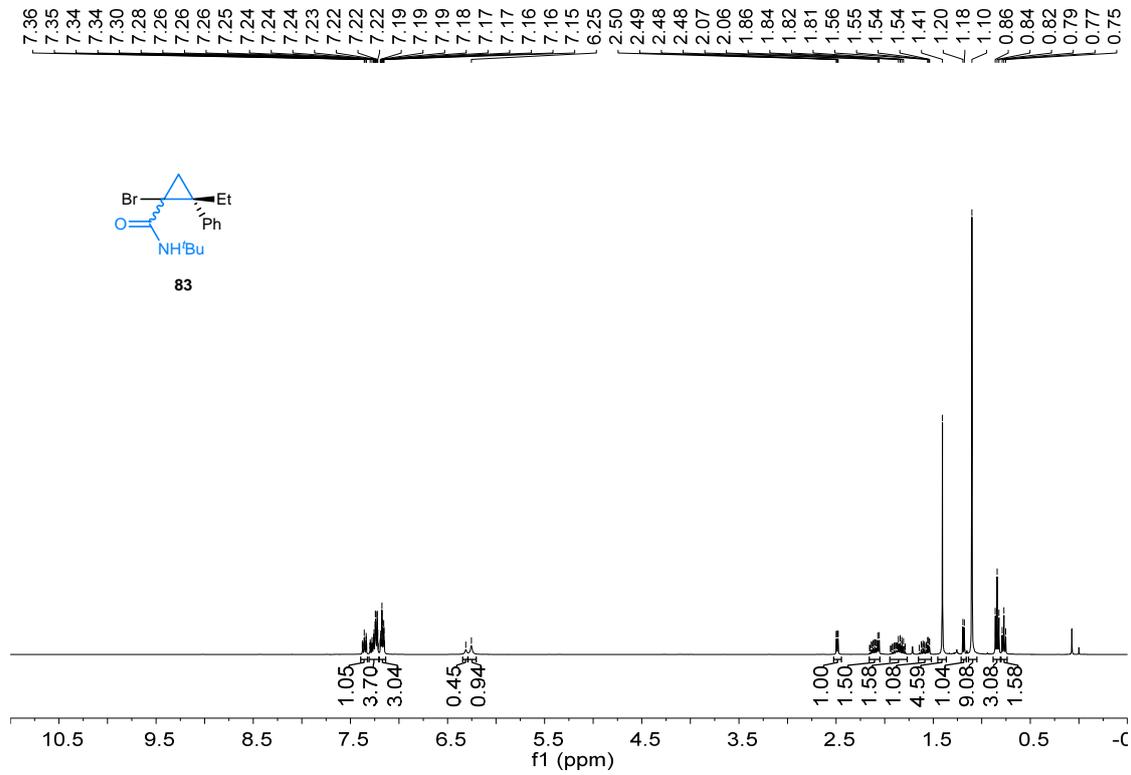


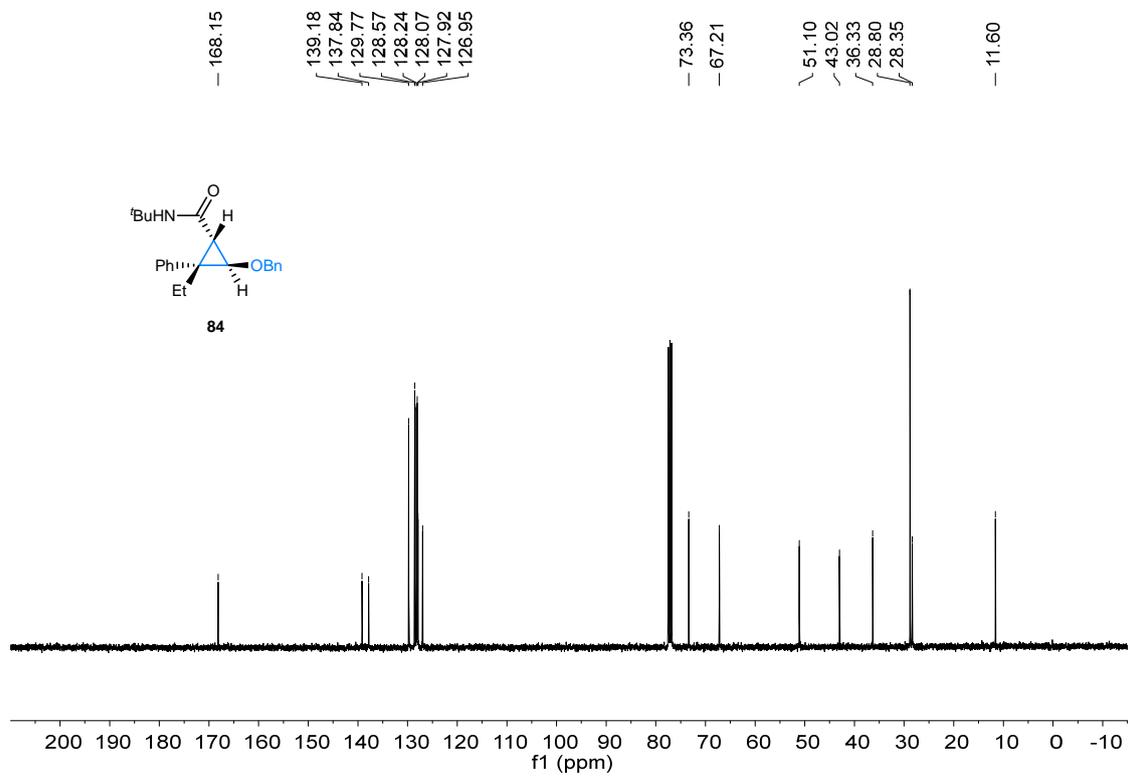
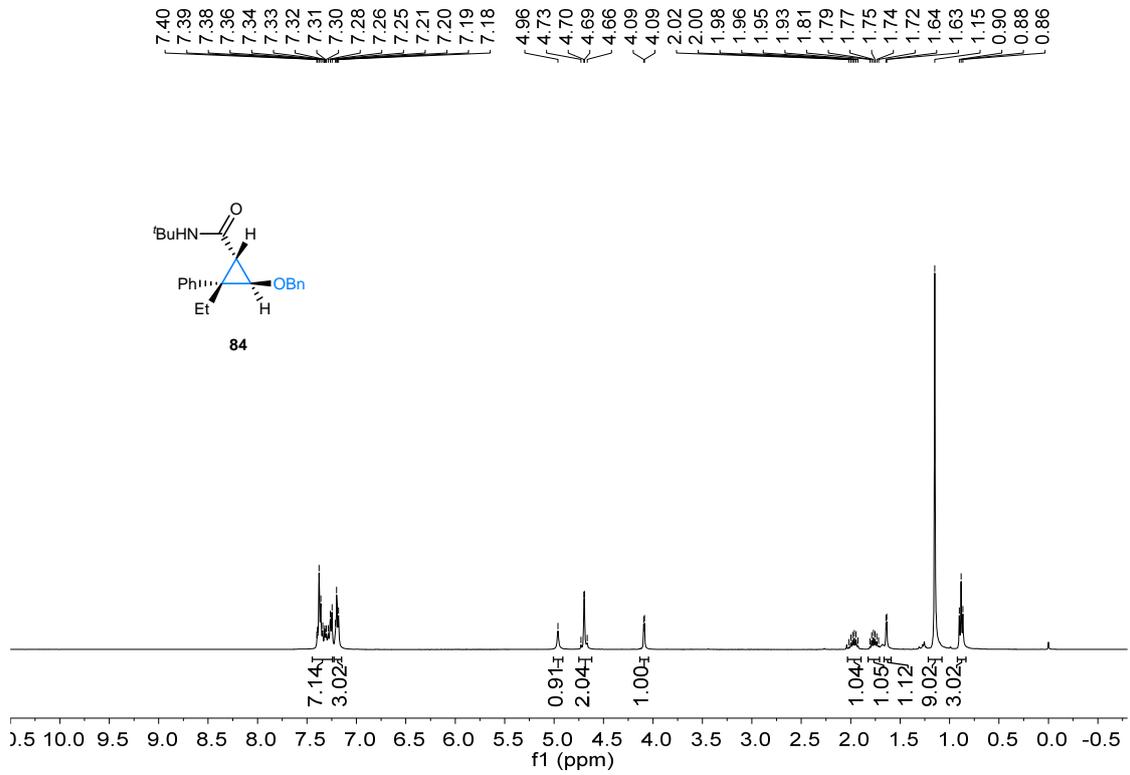


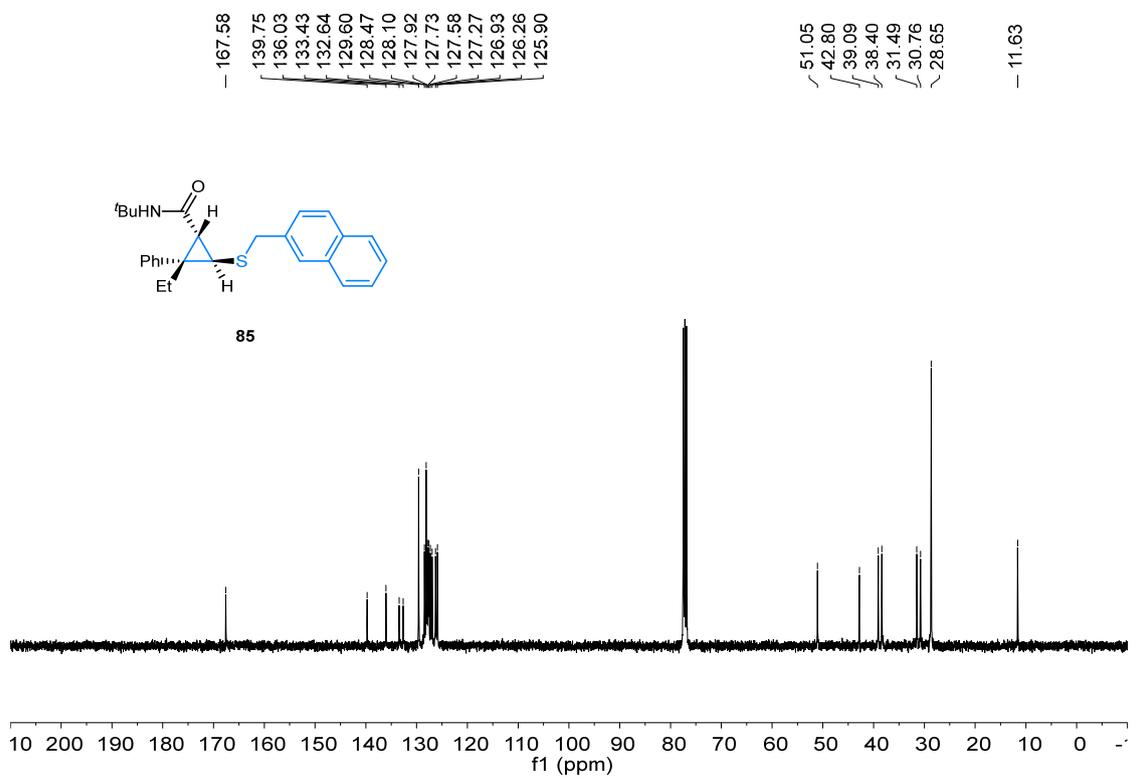
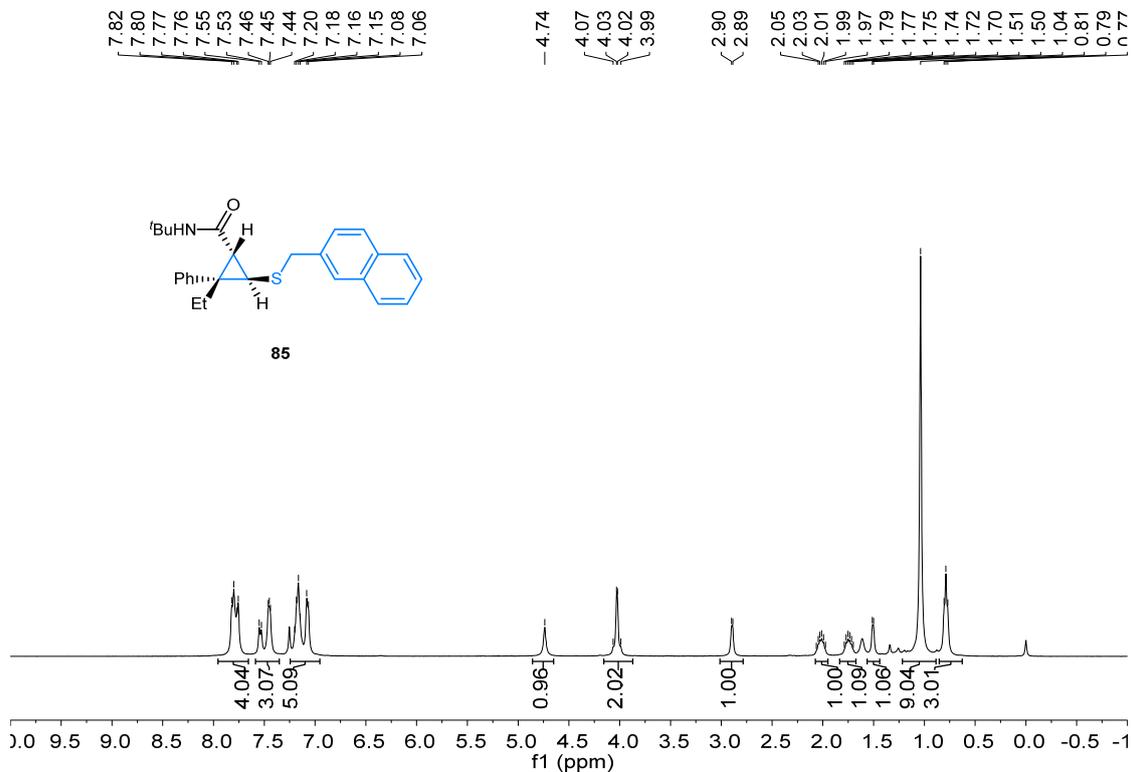


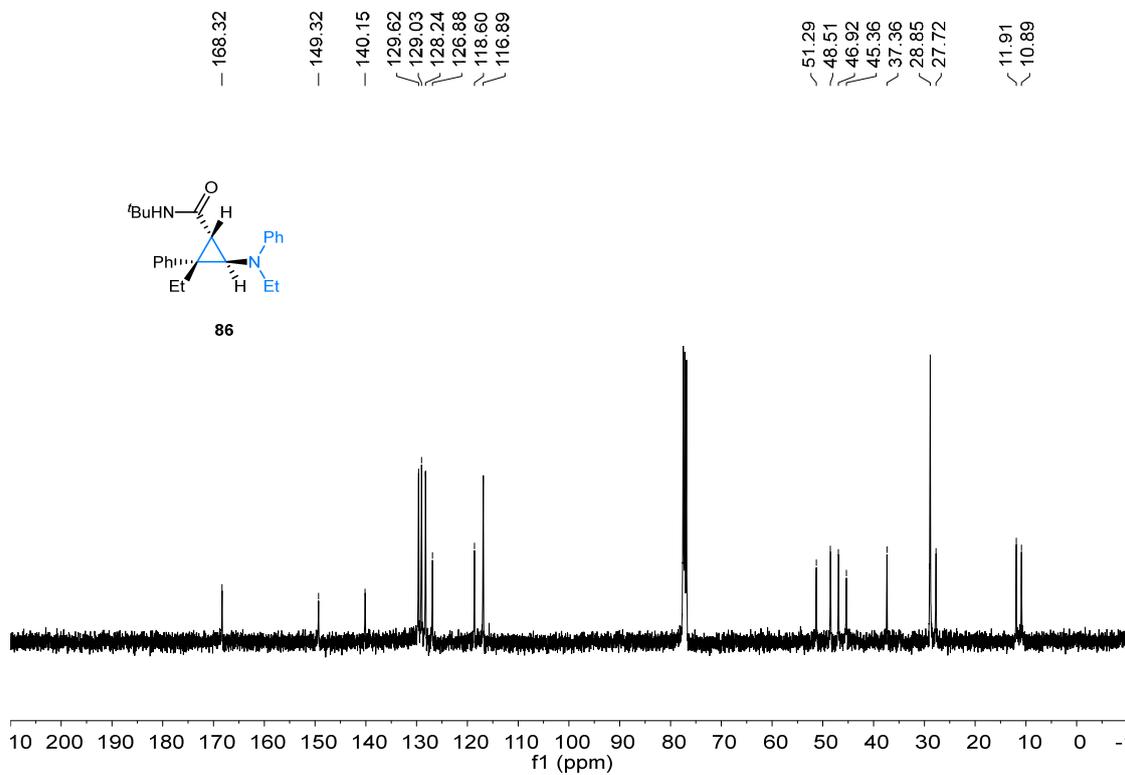
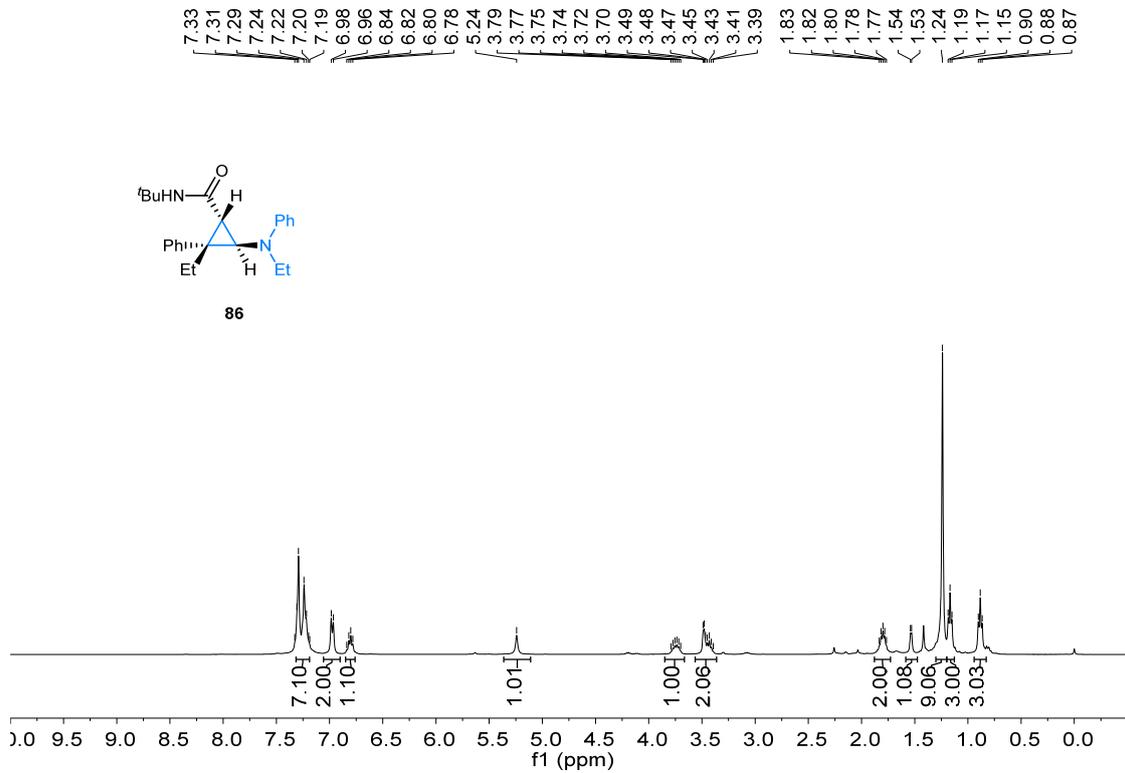


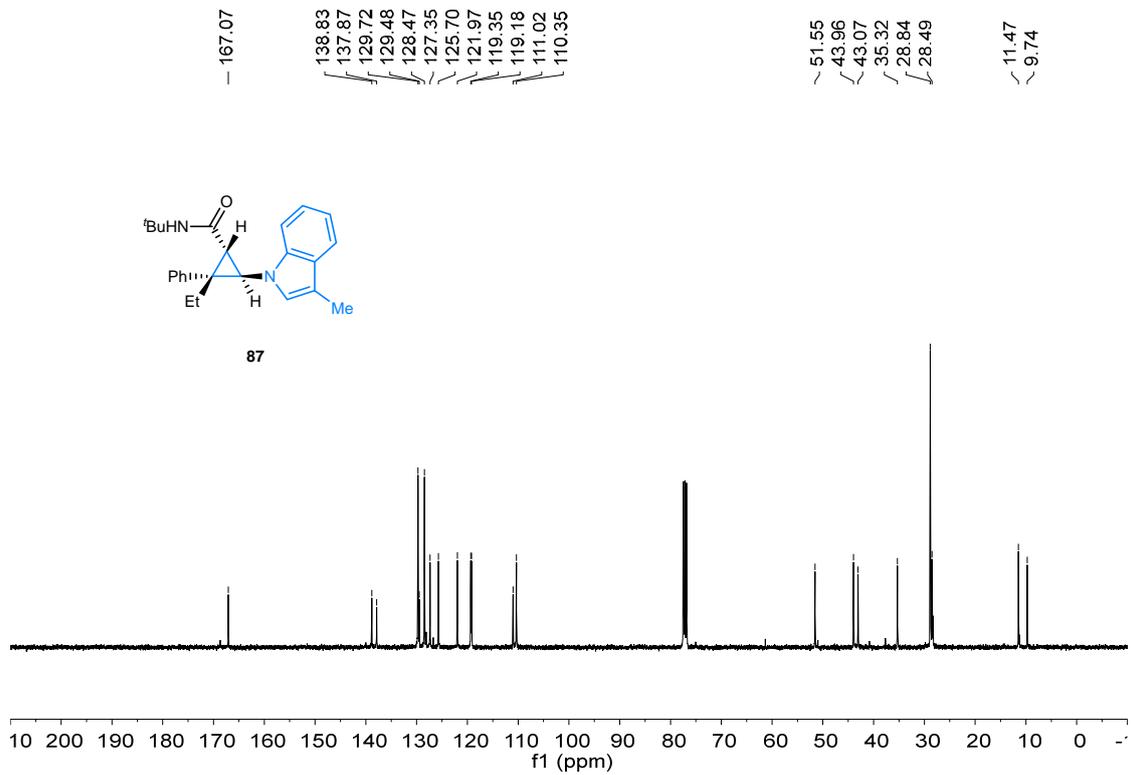
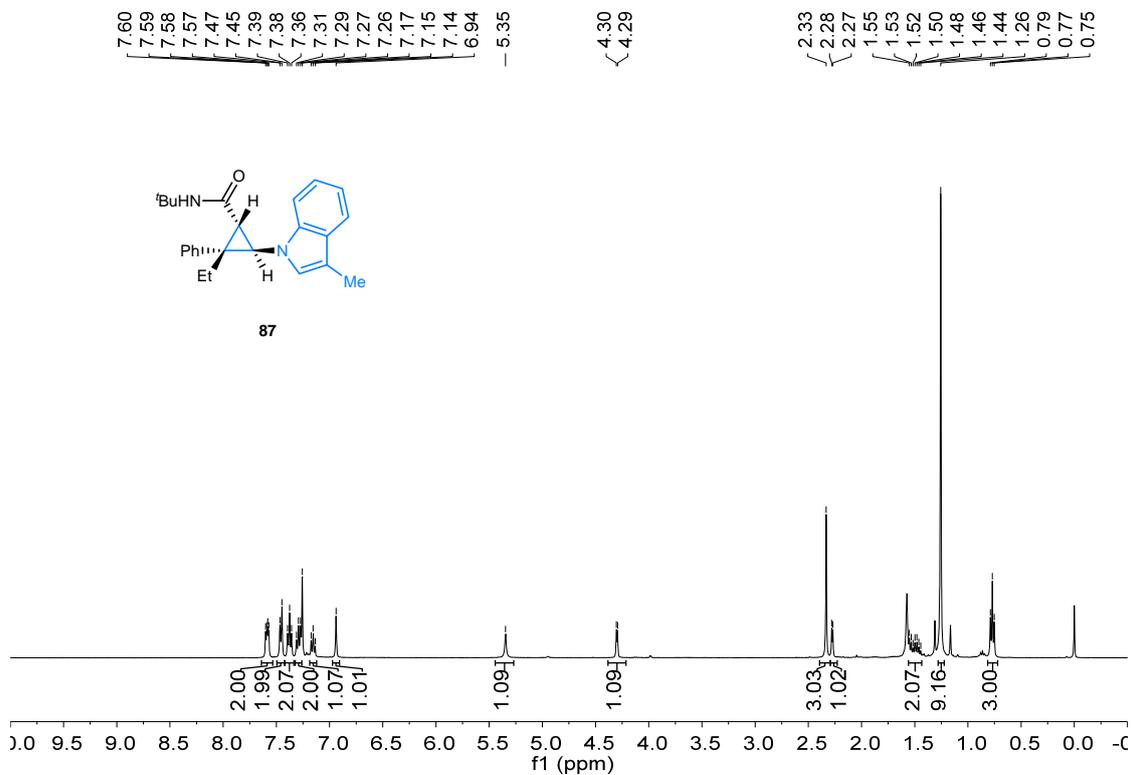


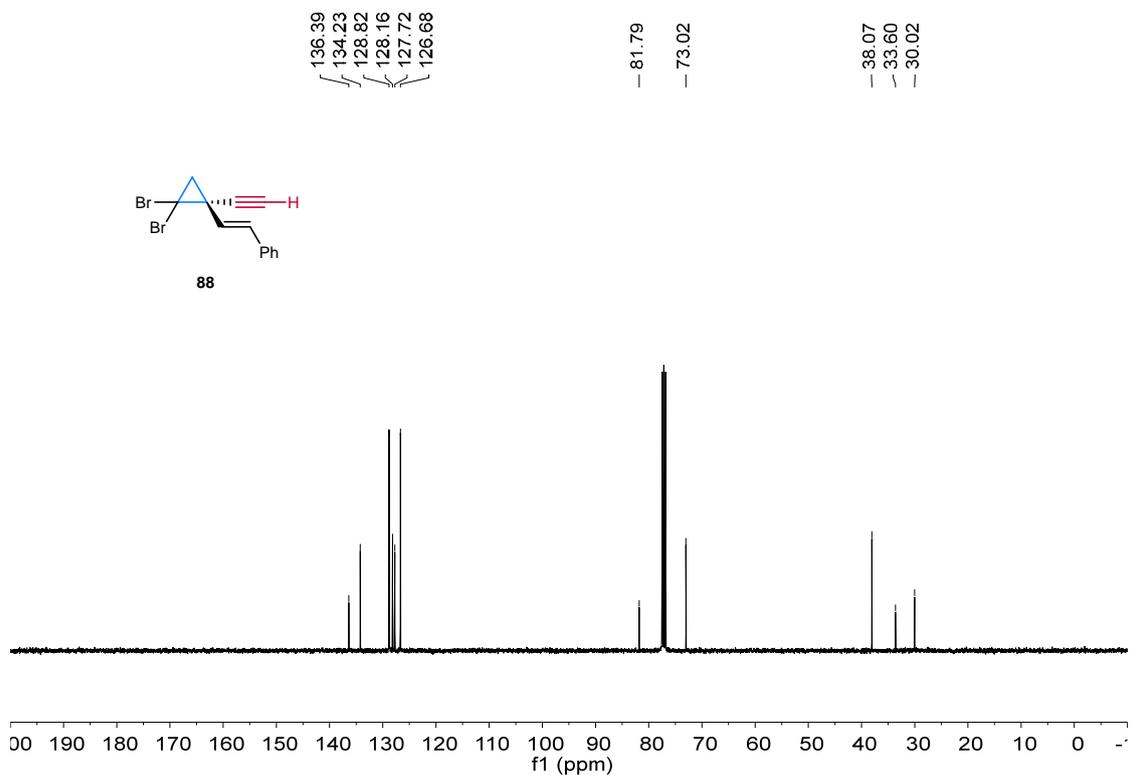
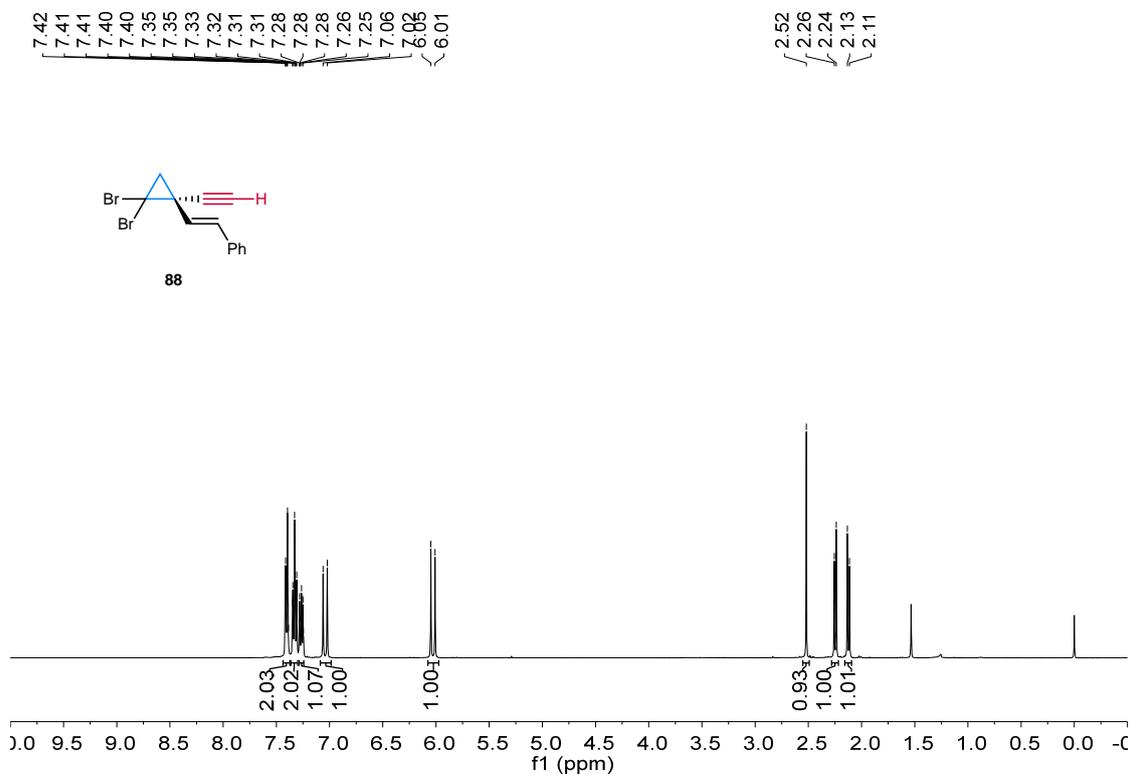


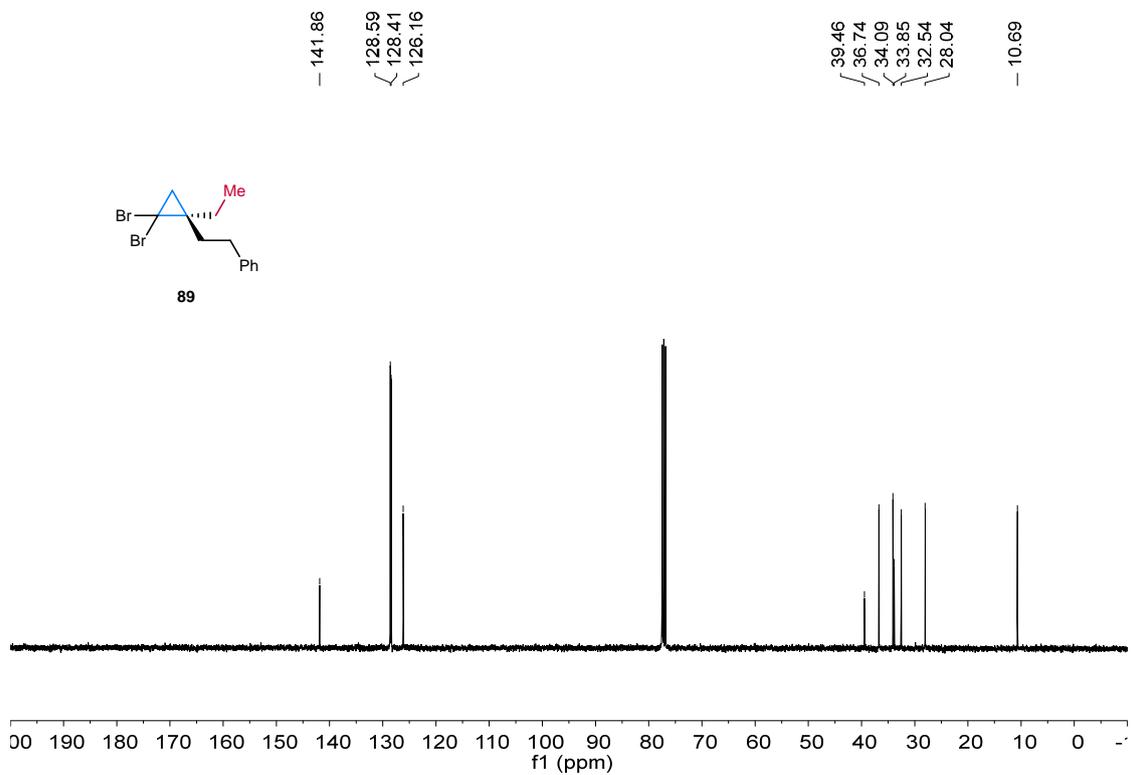
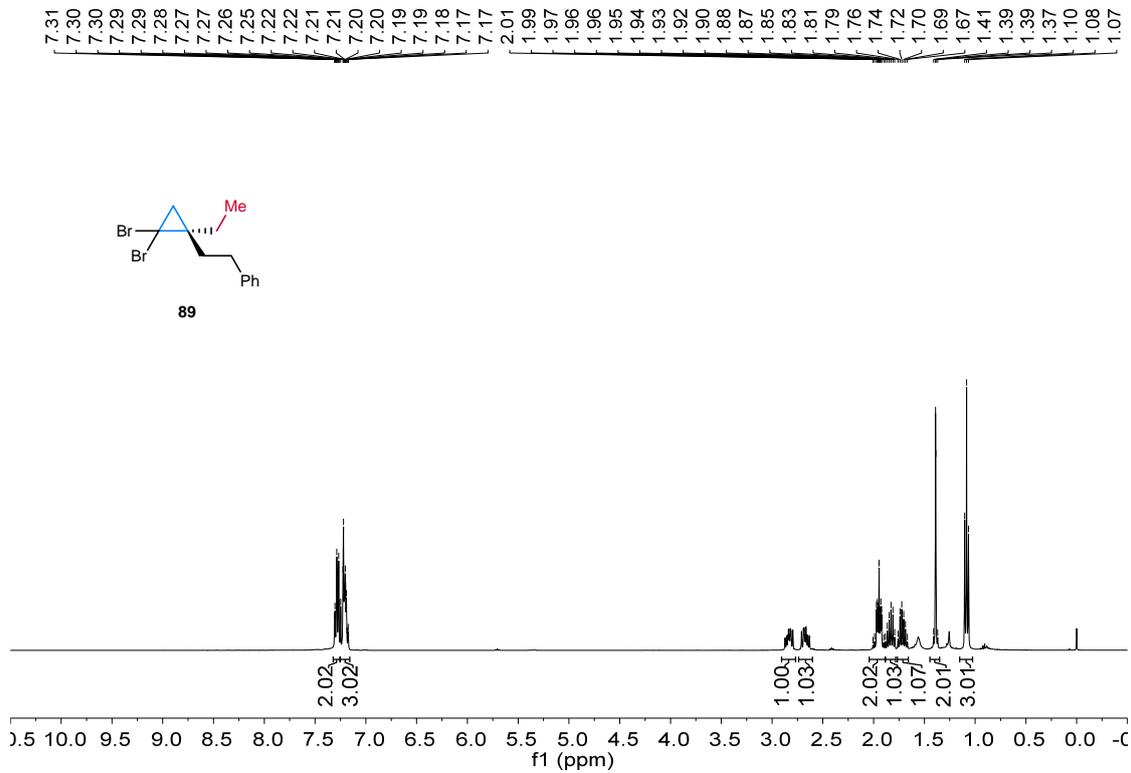


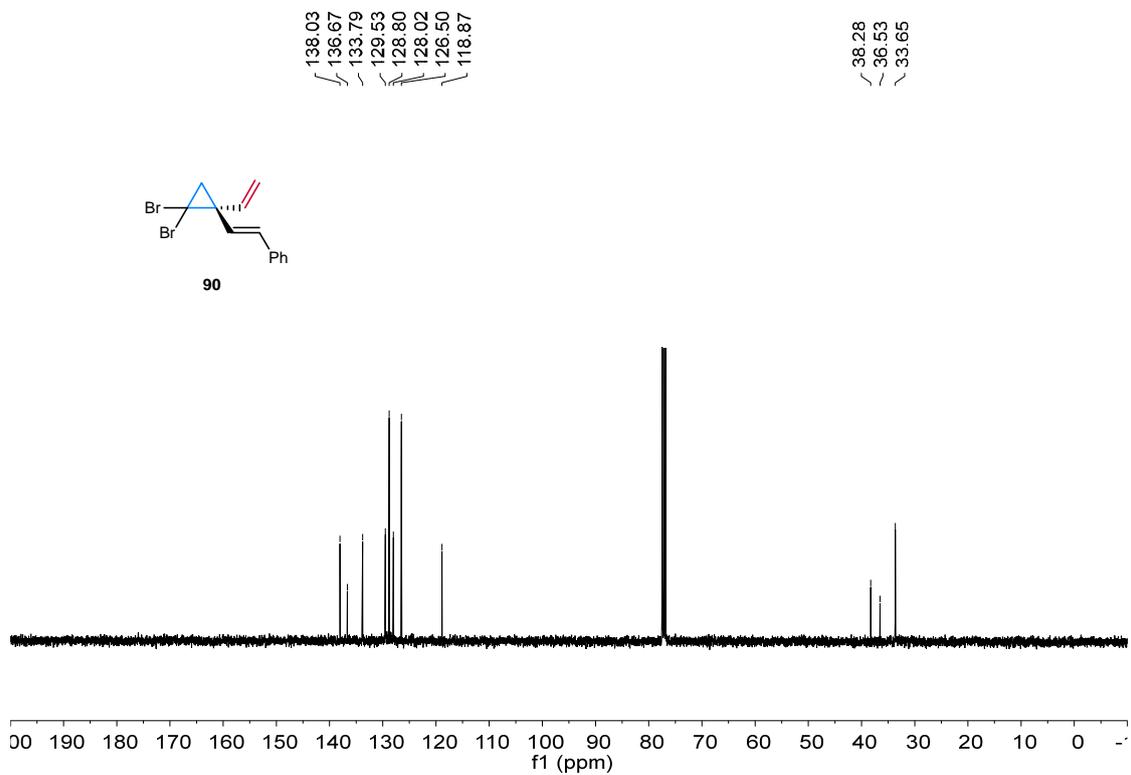
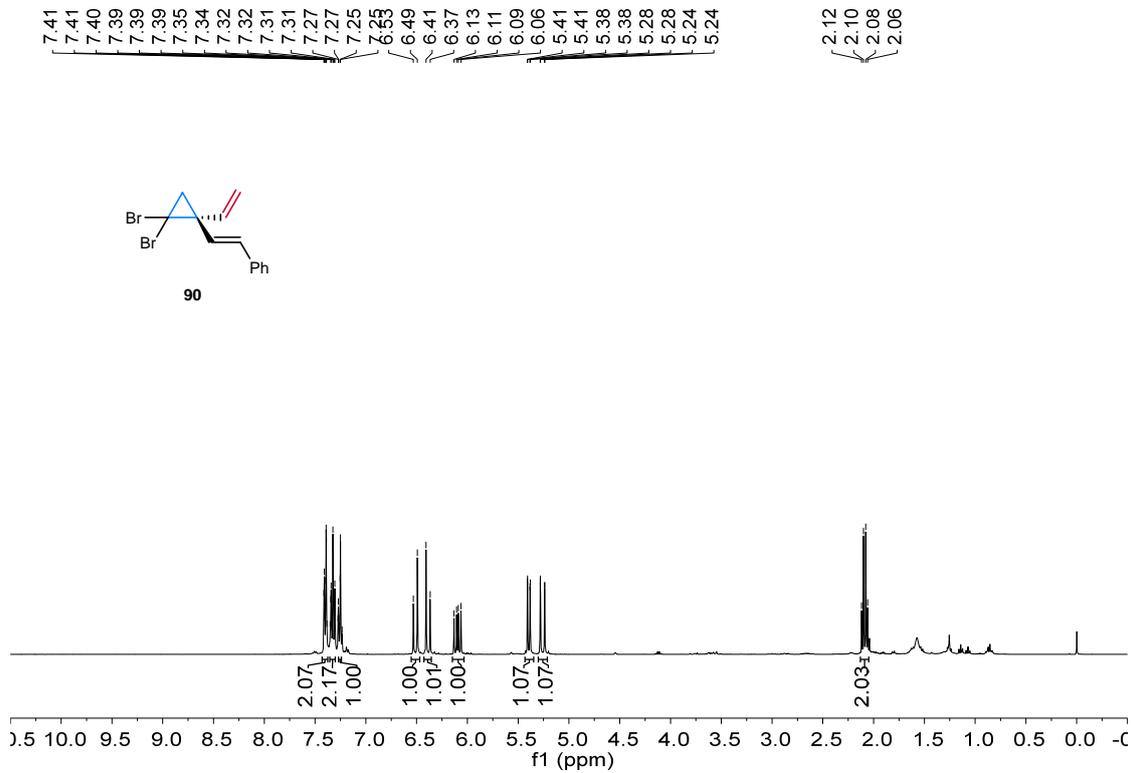


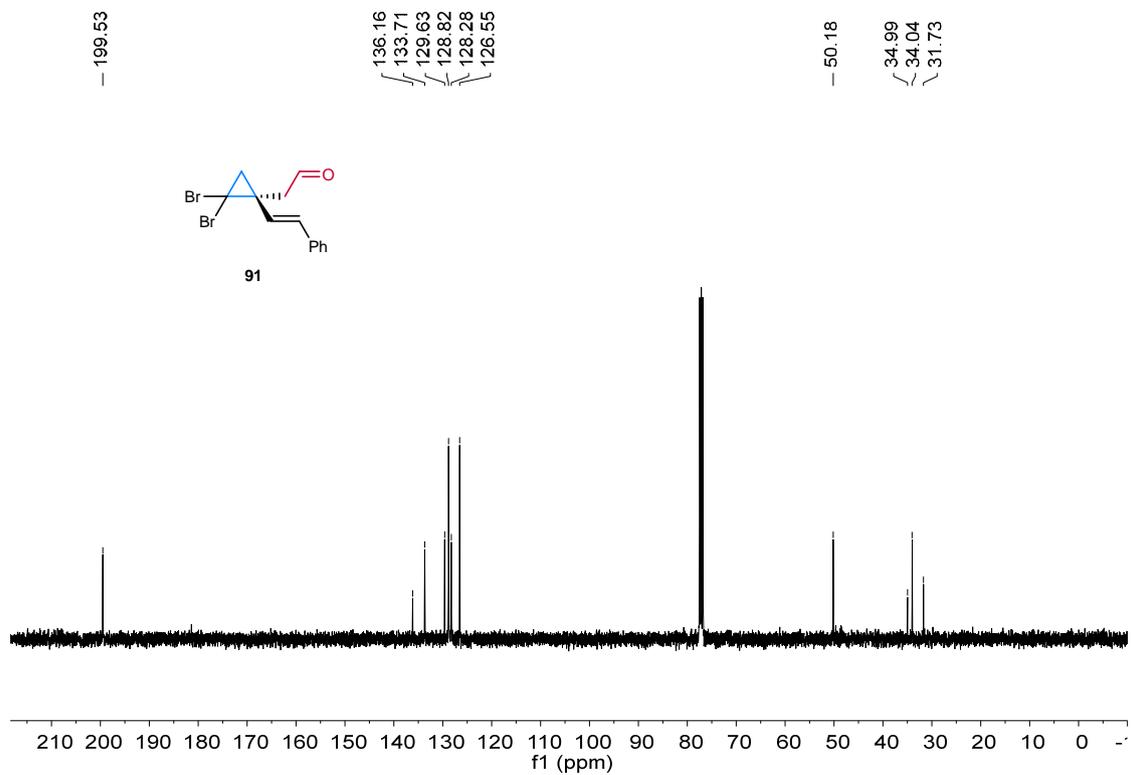
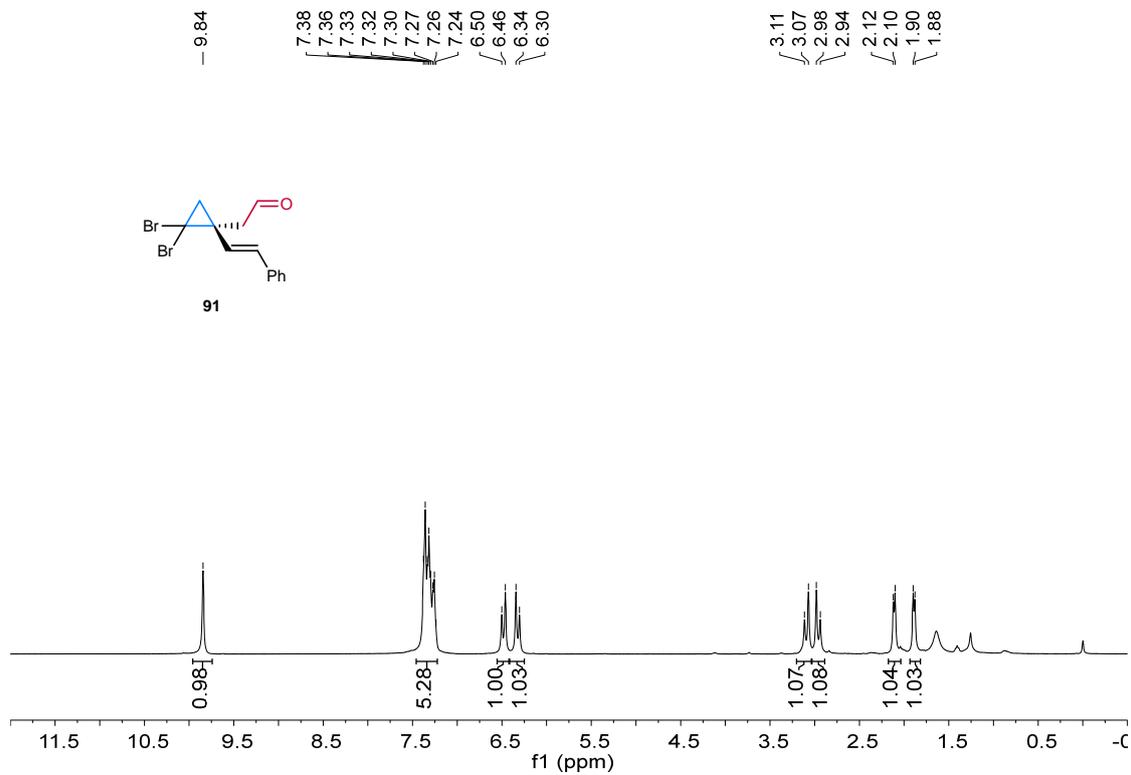


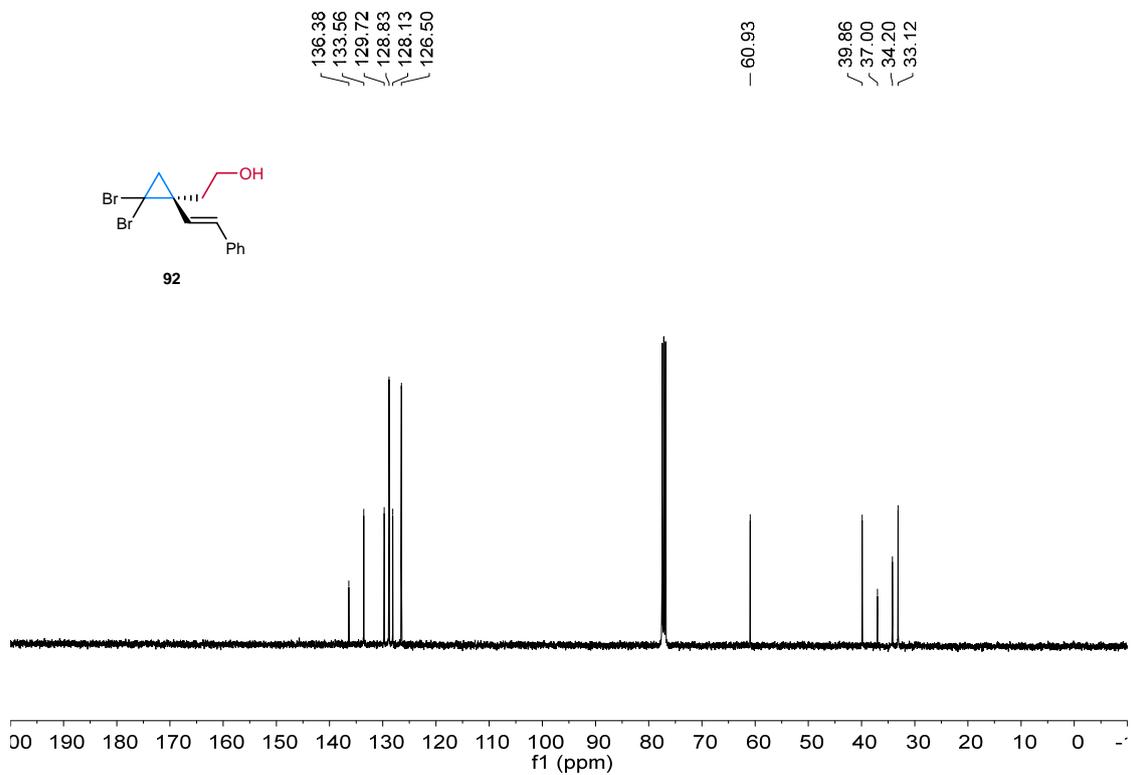
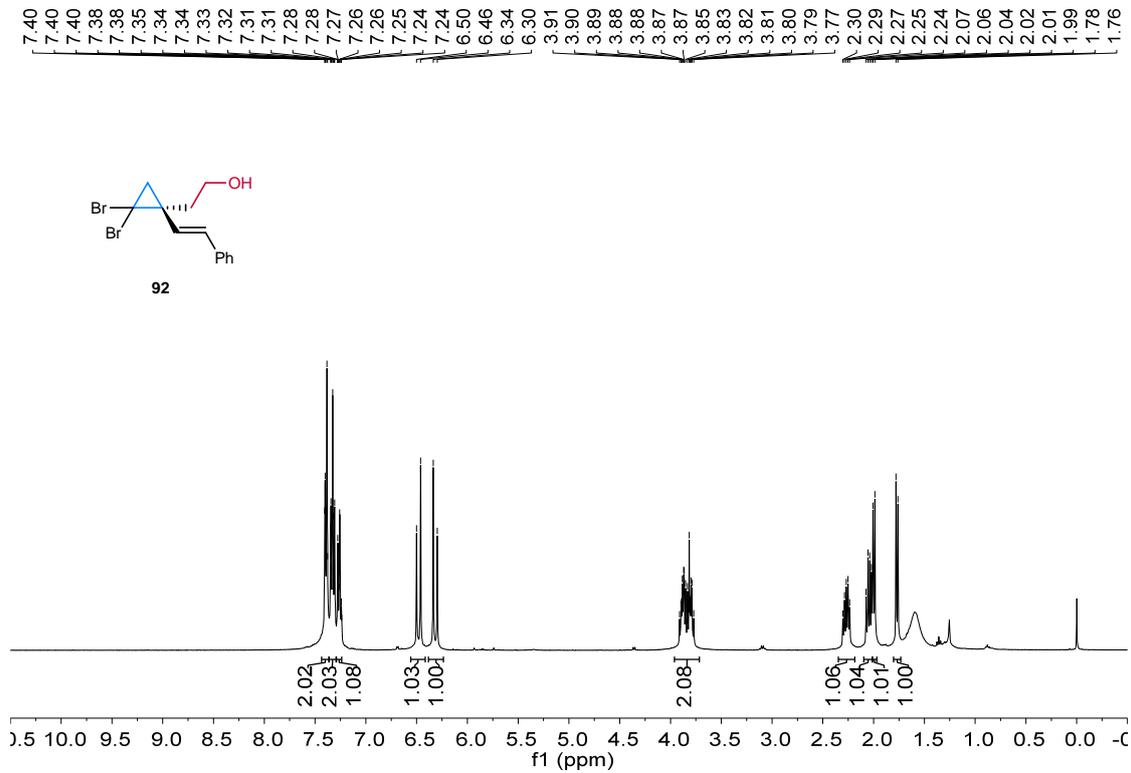


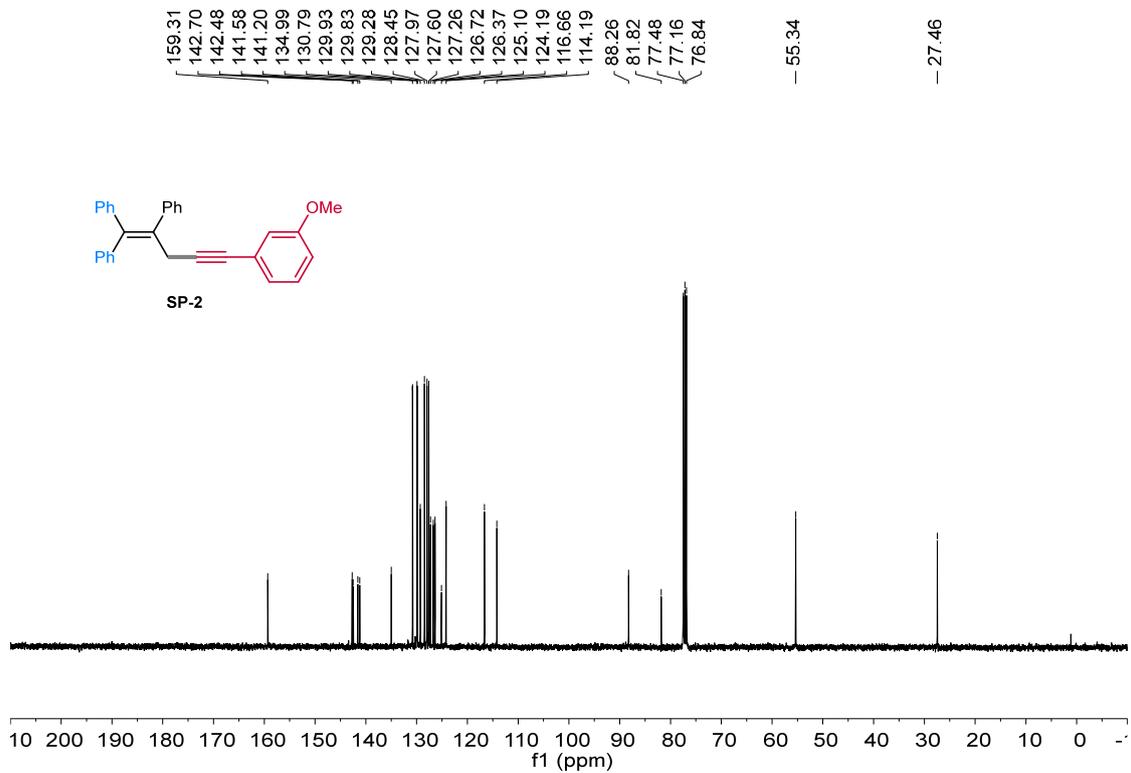
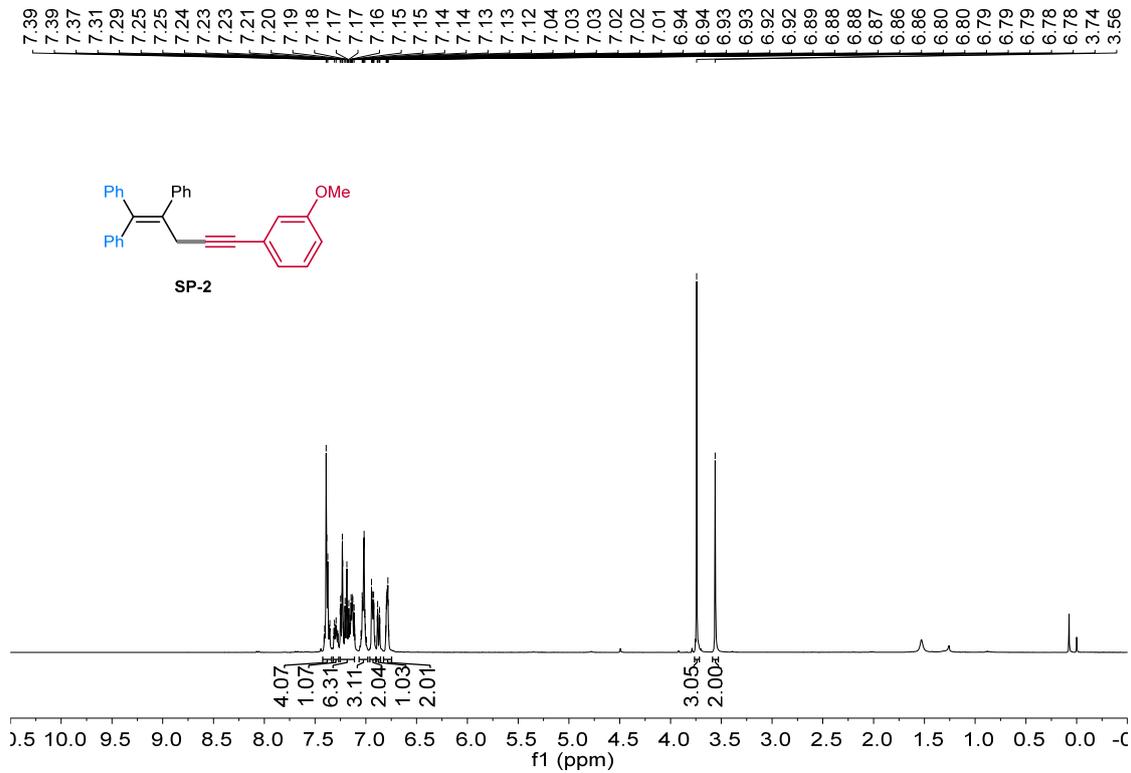




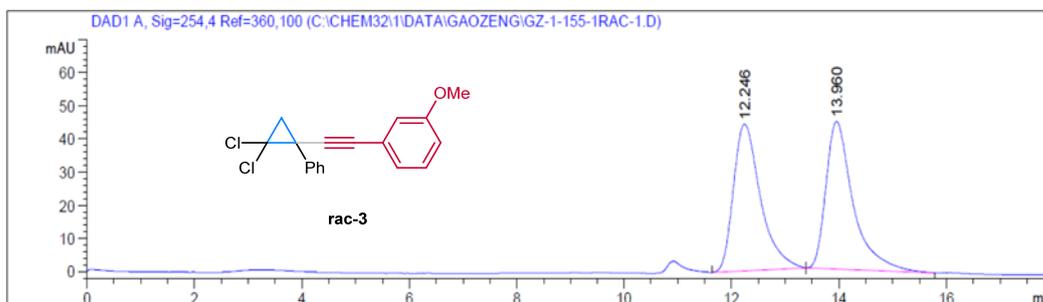








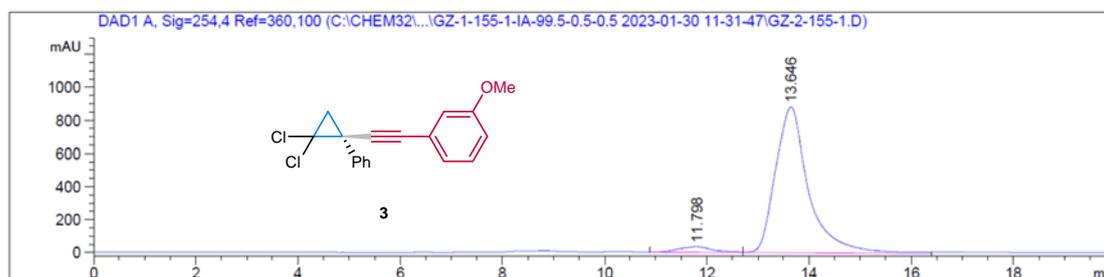
HPLC spectra



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.246	BB	0.5260	1544.36060	44.16593	49.6701
2	13.960	BB	0.5227	1564.87415	44.45662	50.3299

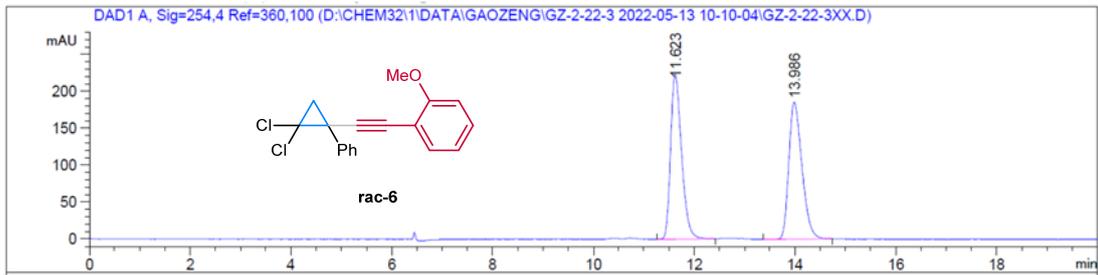
Totals : 3109.23474 88.62255



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.798	MF R	0.7599	1536.05957	33.68901	3.7116
2	13.646	MF R	0.7511	3.98491e4	884.19171	96.2884

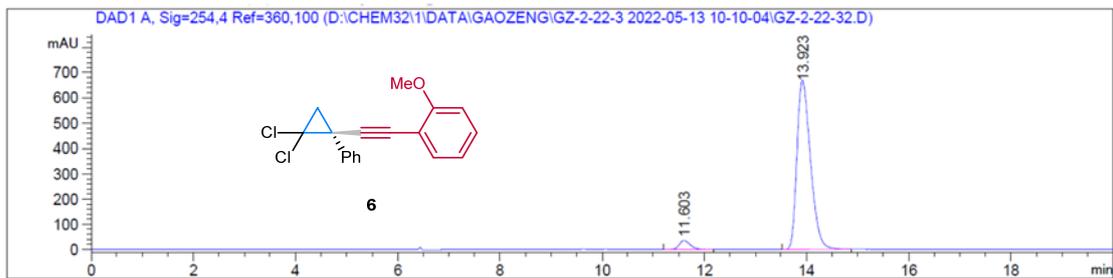
Totals : 4.13851e4 917.88072



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.623	BV R	0.2307	3378.04517	223.04590	50.0734
2	13.986	VV R	0.2780	3368.13892	185.33647	49.9266

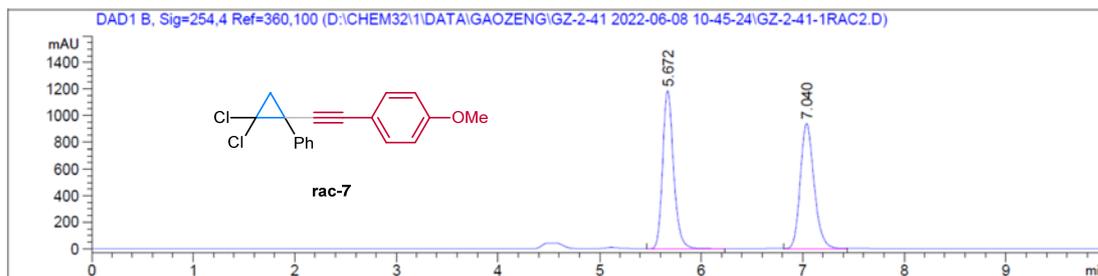
Totals : 6746.18408 408.38237



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.603	VV R	0.2291	530.98621	35.37651	4.1355
2	13.923	BV R	0.2844	1.23087e4	669.72052	95.8645

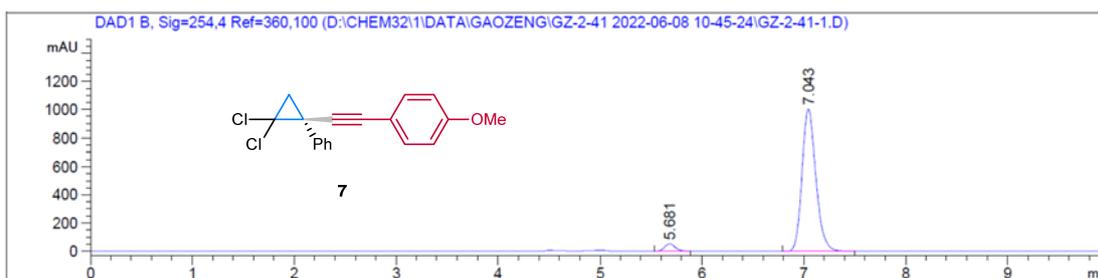
Totals : 1.28397e4 705.09703



Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.672	BB	0.1155	8890.93164	1185.70374	49.9534
2	7.040	VV	0.1466	8907.52246	939.64233	50.0466

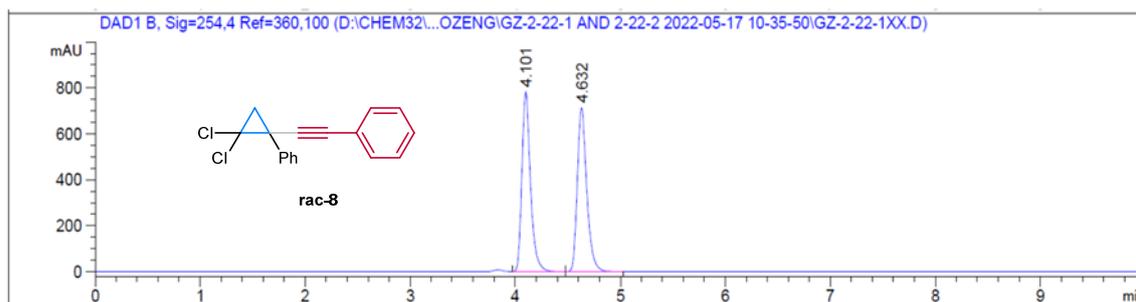
Totals : 1.77985e4 2125.34607



Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.681	FM R	0.1227	395.08945	53.67612	3.9998
2	7.043	MF R	0.1574	9482.63281	1004.31403	96.0002

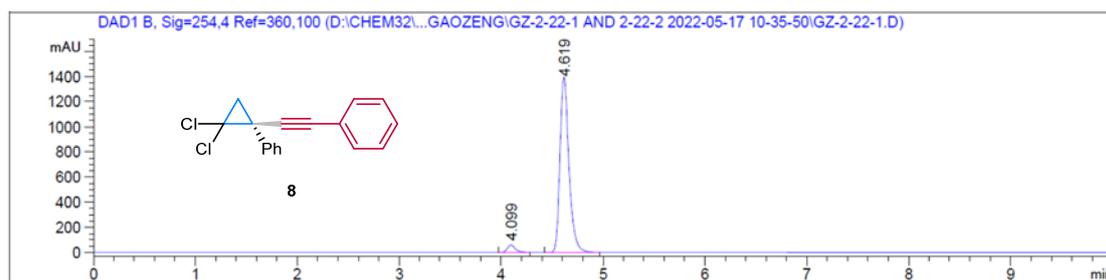
Totals : 9877.72226 1057.99015



Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.101	VB	0.0865	4453.23535	781.27679	49.9748
2	4.632	BV	0.0949	4457.73389	713.66992	50.0252

Totals : 8910.96924 1494.94672



Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.099	MF R	0.0920	331.92282	60.11448	3.7390
2	4.619	MF R	0.1017	8545.46777	1400.56592	96.2610

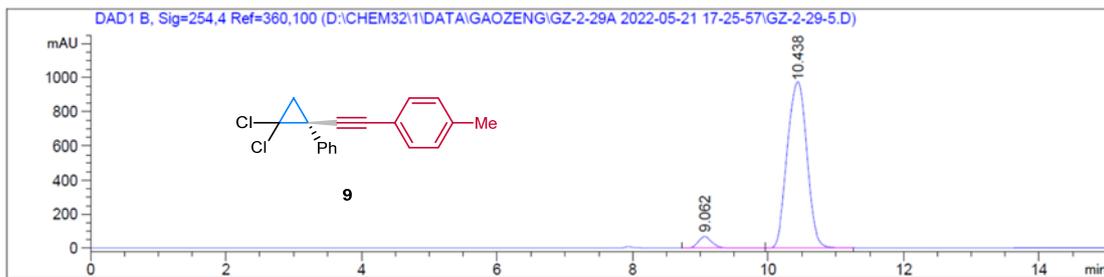
Totals : 8877.39059 1460.68039



Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.034	BB	0.2302	8008.40332	536.19440	50.2294
2	10.387	MF R	0.3388	7935.24414	390.34964	49.7706

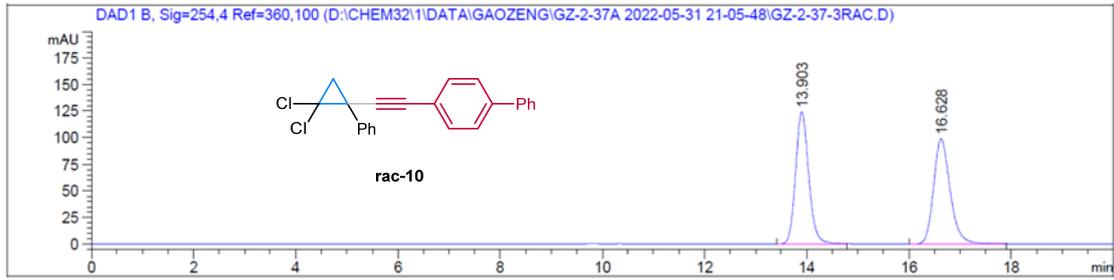
Totals : 1.59436e4 926.54404



Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.062	BV	0.2254	1015.55902	69.12321	4.8637
2	10.438	MF R	0.3386	1.98649e4	977.88190	95.1363

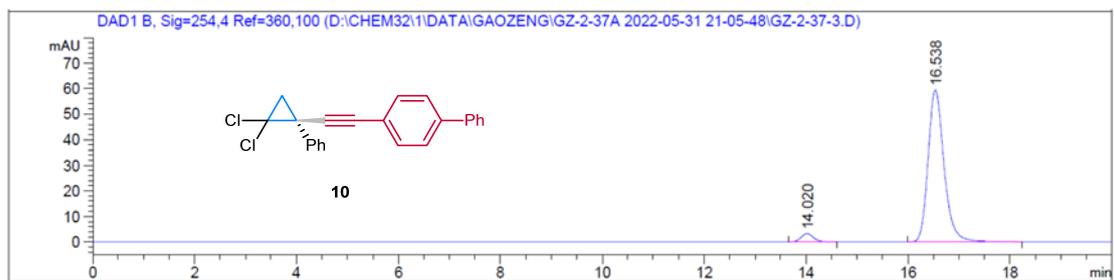
Totals : 2.08805e4 1047.00511



Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.903	MF R	0.2996	2225.51001	123.81416	49.8069
2	16.628	MF R	0.3782	2242.76685	98.84414	50.1931

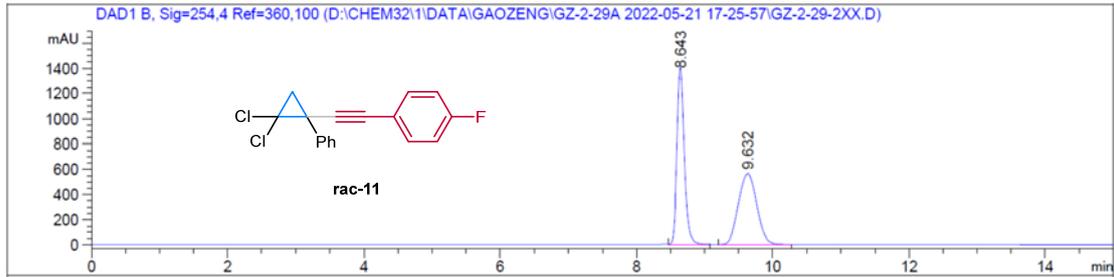
Totals : 4468.27686 222.65830



Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.020	BB	0.2674	55.24406	3.23214	4.0889
2	16.538	BB	0.3321	1295.81409	59.48830	95.9111

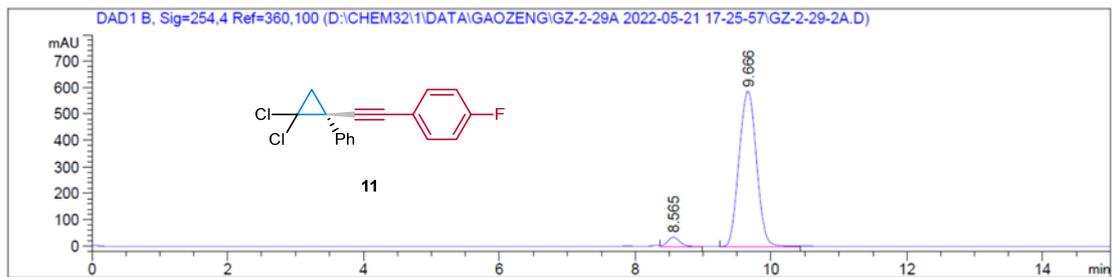
Totals : 1351.05815 62.72044



Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.643	VV	0.1161	1.06235e4	1407.34534	49.8001
2	9.632	VB	0.3023	1.07087e4	567.00201	50.1999

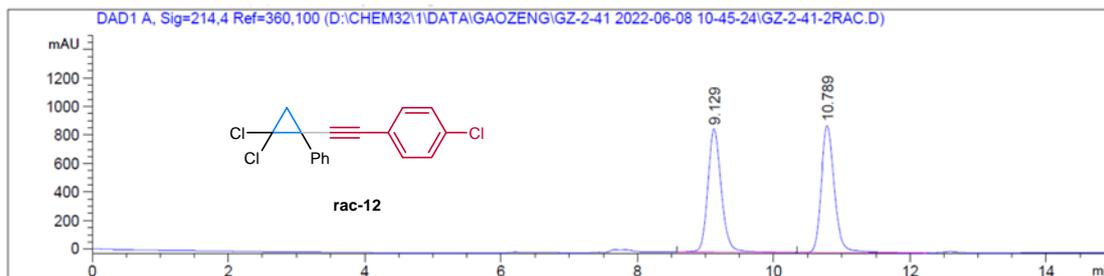
Totals : 2.13322e4 1974.34735



Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.565	VB	0.1882	443.37091	35.86748	4.0536
2	9.666	MF R	0.2977	1.04944e4	587.56189	95.9464

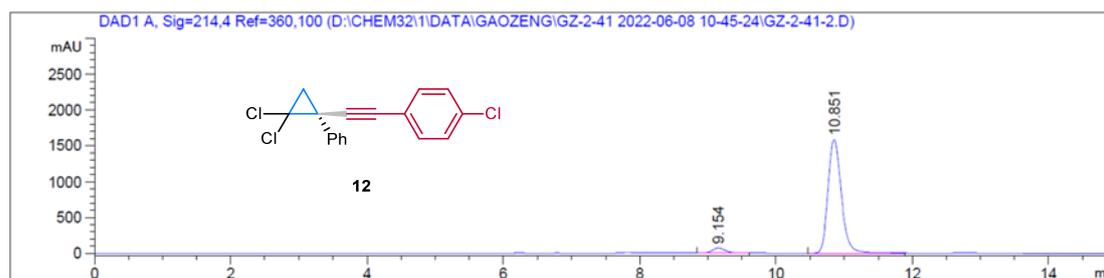
Totals : 1.09378e4 623.42937



Signal 1: DAD1 A, Sig=214,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.129	BB	0.2121	1.20356e4	866.39014	50.1464
2	10.789	BB	0.2067	1.19653e4	890.60474	49.8536

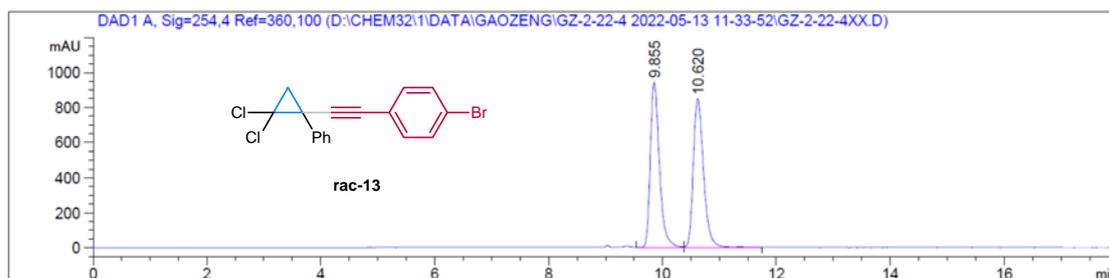
Totals : 2.40010e4 1756.99487



Signal 1: DAD1 A, Sig=214,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.154	BB	0.2073	940.32690	70.63223	4.1462
2	10.851	MF R	0.2292	2.17391e4	1581.00220	95.8538

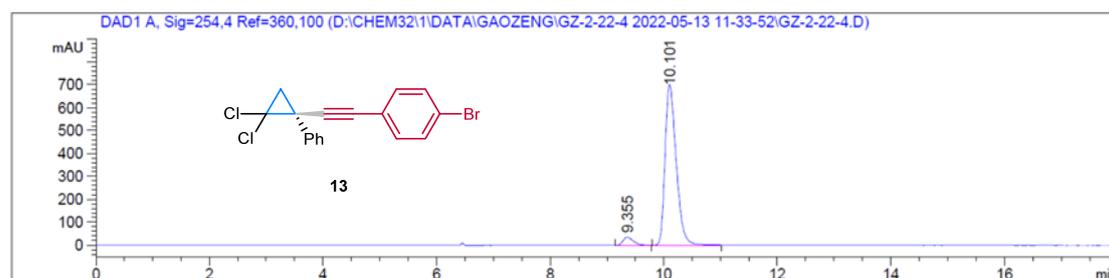
Totals : 2.26794e4 1651.63442



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.855	BV	0.1699	1.04786e4	941.27509	49.7612
2	10.620	VV R	0.1911	1.05792e4	848.33759	50.2388

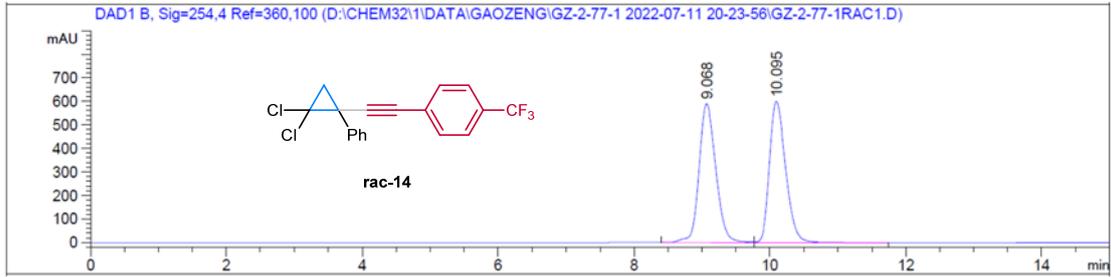
Totals : 2.10578e4 1789.61267



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.355	BV R	0.1824	427.42328	35.00928	4.2972
2	10.101	BV R	0.2062	9519.17578	701.82184	95.7028

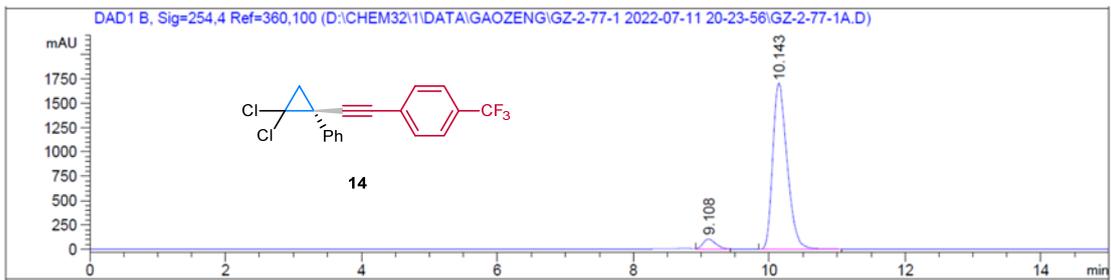
Totals : 9946.59906 736.83112



Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.068	BV	0.2661	1.01106e4	589.37531	50.5256
2	10.095	VB	0.2544	9900.25781	600.27911	49.4744

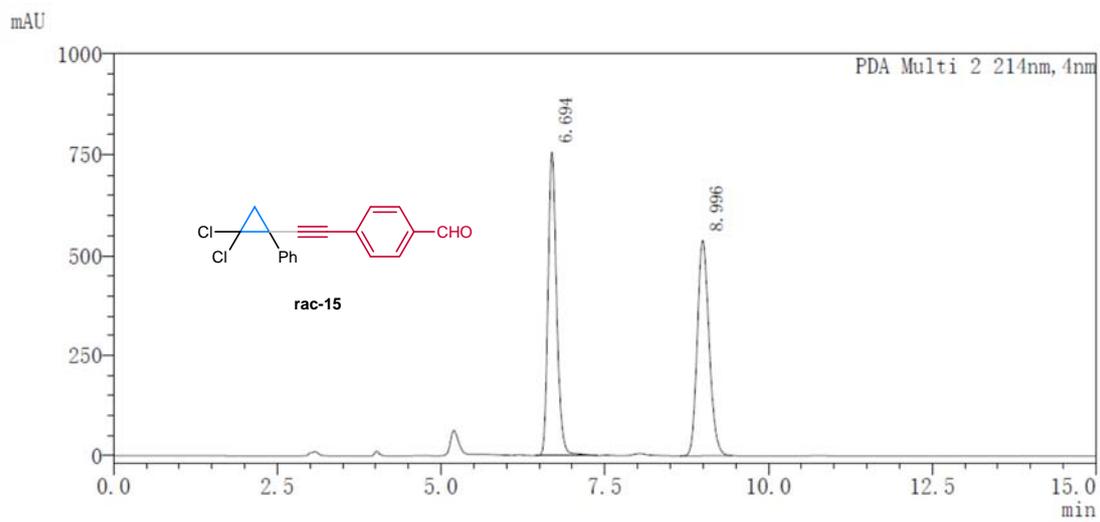
Totals : 2.00109e4 1189.65442



Signal 2: DAD1 B, Sig=254,4 Ref=360,100

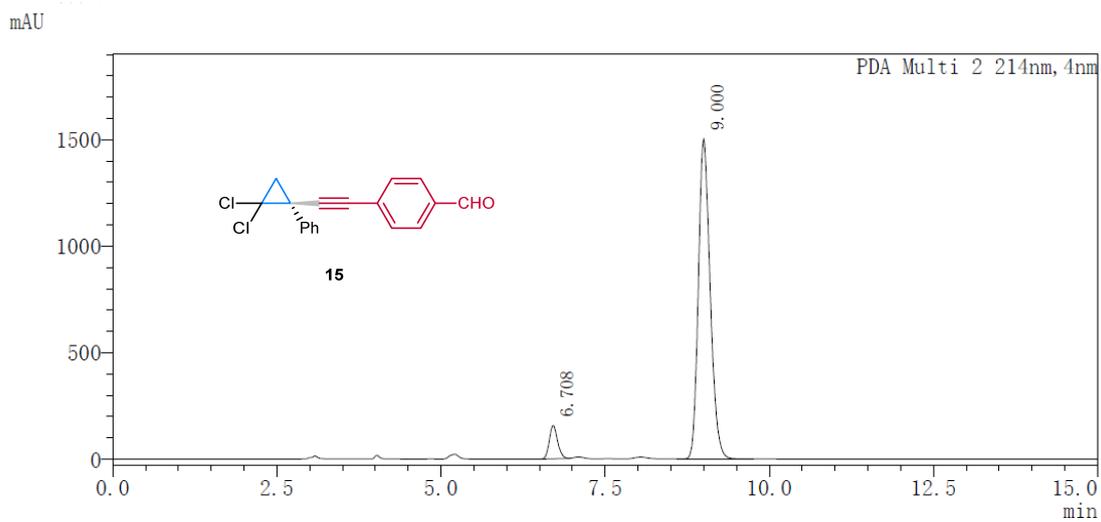
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.108	FM R	0.2221	1416.50110	106.29203	5.3095
2	10.143	MF R	0.2471	2.52622e4	1704.01721	94.6905

Totals : 2.66787e4 1810.30924



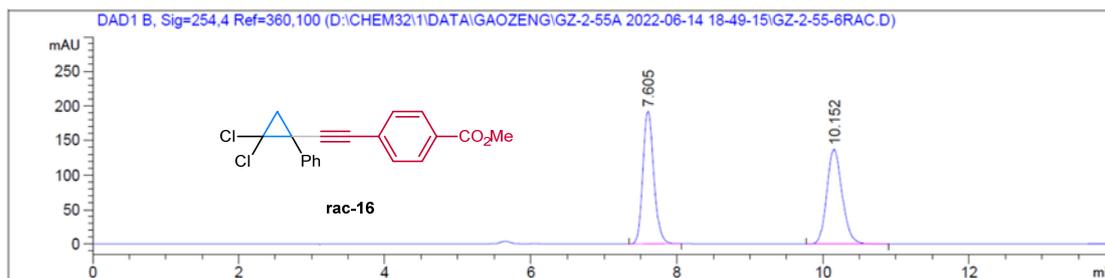
PDA Ch2 214nm

T	Hight	Area	Area%
6.694	755012	6927562	50.567
8.996	538555	6772306	49.433



PDA Ch2 214nm

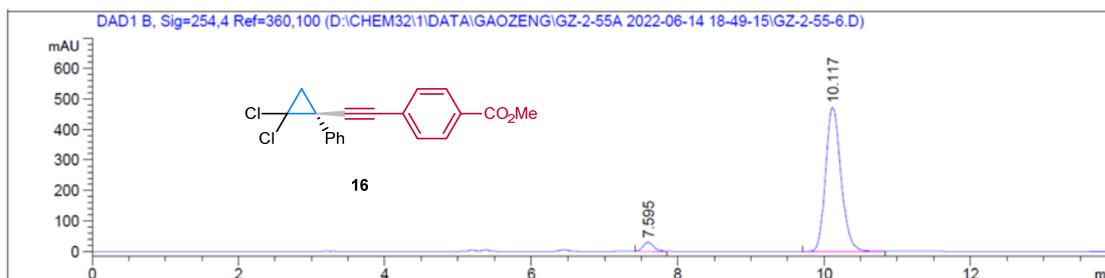
T	Hight	Area	Area%
6.708	156293	1367955	6.808
9.000	1500689	18725663	93.192



Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.605	BB	0.1618	1998.87427	191.40591	49.9494
2	10.152	BB	0.2266	2002.92603	136.94254	50.0506

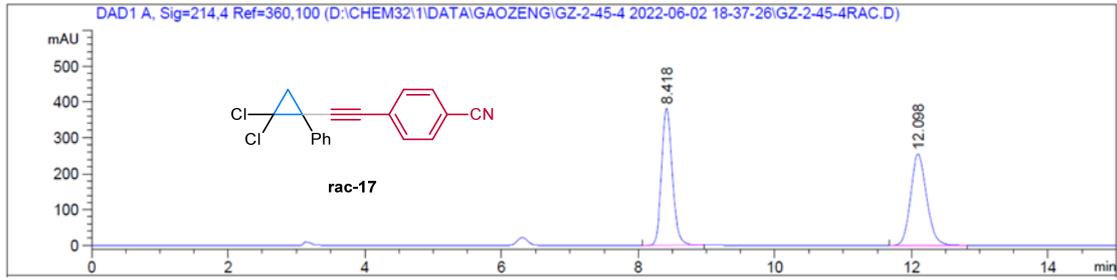
Totals : 4001.80029 328.34845



Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.595	FM R	0.1722	305.55423	29.57558	4.2214
2	10.117	MF R	0.2445	6932.65039	472.51431	95.7786

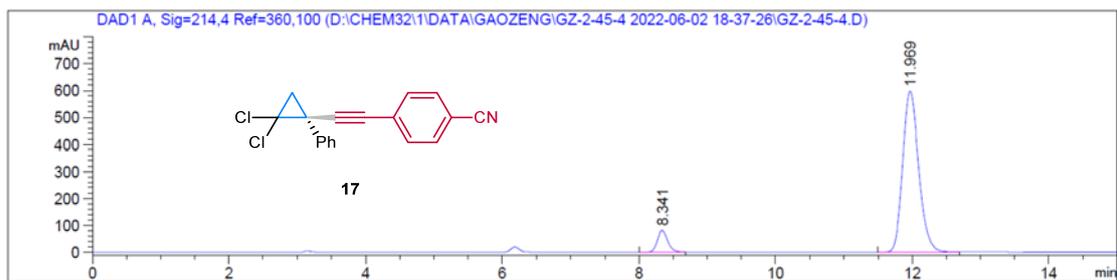
Totals : 7238.20462 502.08990



Signal 1: DAD1 A, Sig=214,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.418	BB	0.1673	4161.02100	381.34067	50.0351
2	12.098	BB	0.2496	4155.18896	255.62955	49.9649

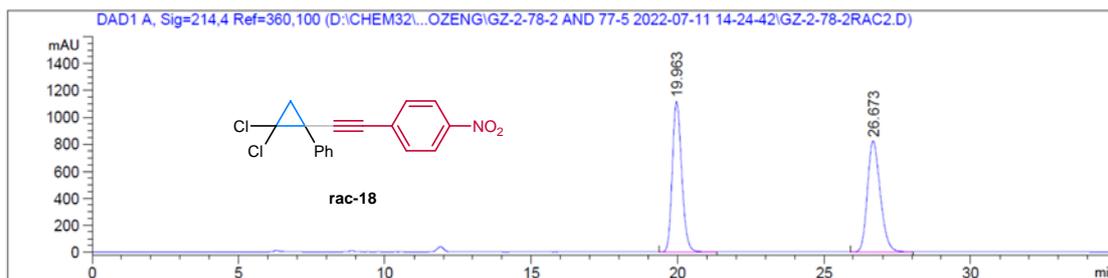
Totals : 8316.20996 636.97021



Signal 1: DAD1 A, Sig=214,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.341	MF R	0.1772	867.84839	81.61297	8.1570
2	11.969	MF R	0.2723	9771.45020	598.05707	91.8430

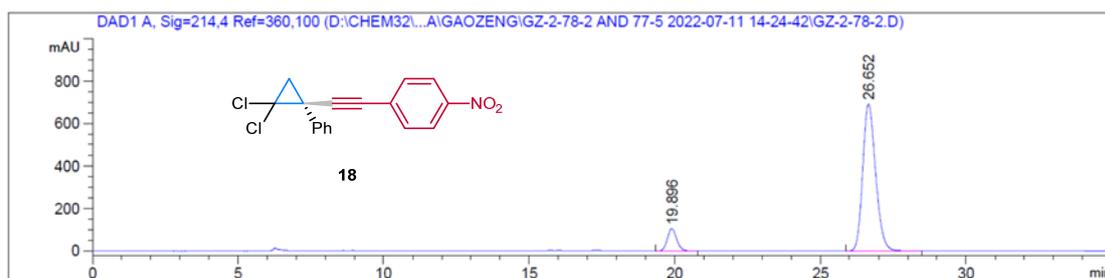
Totals : 1.06393e4 679.67004



Signal 1: DAD1 A, Sig=214,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.963	BB	0.3471	2.49516e4	1115.09436	49.8167
2	26.673	MF R	0.5102	2.51352e4	821.10950	50.1833

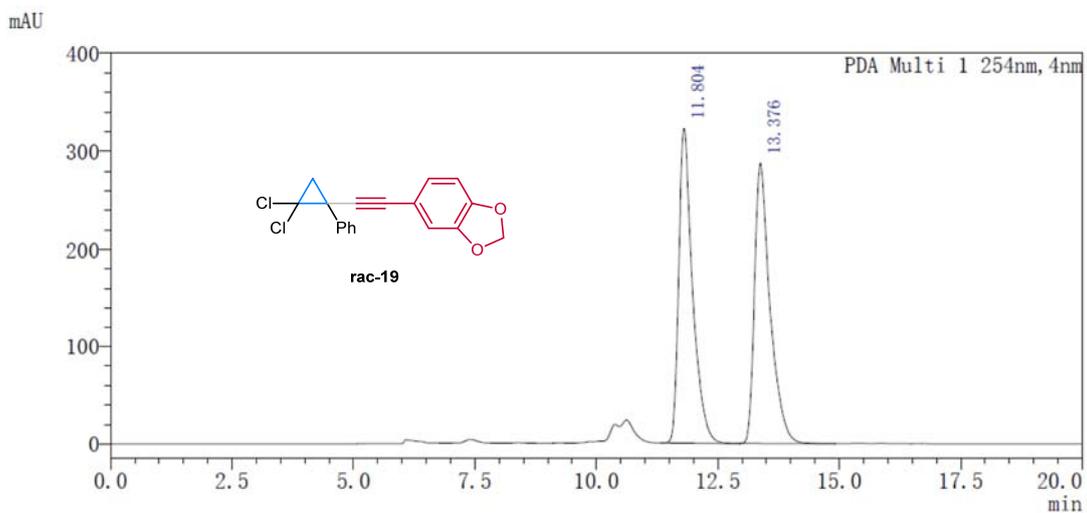
Totals : 5.00868e4 1936.20386



Signal 1: DAD1 A, Sig=214,4 Ref=360,100

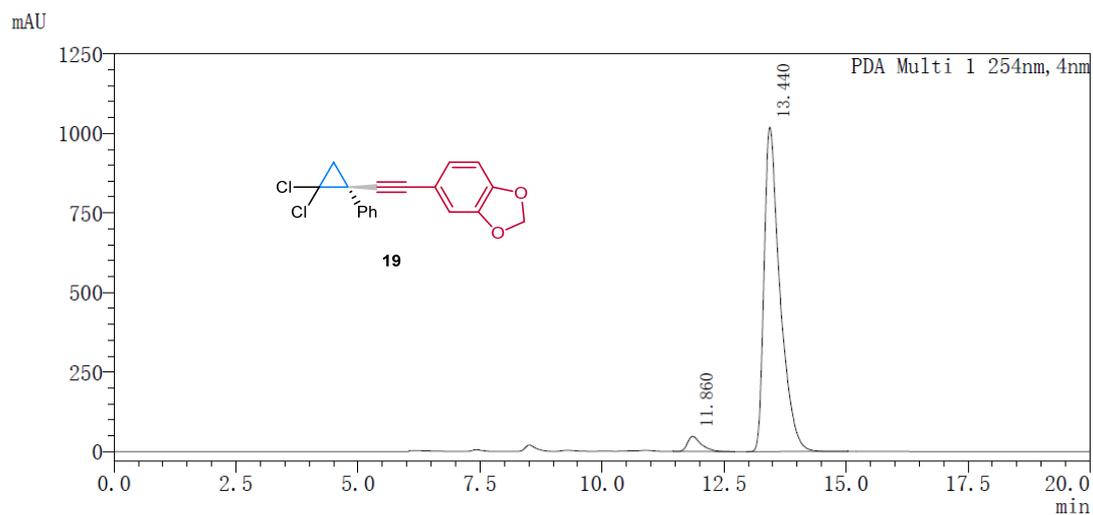
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.896	BB	0.3398	2333.91699	105.63633	9.8744
2	26.652	BB	0.4698	2.13021e4	690.78723	90.1256

Totals : 2.36360e4 796.42356



PDA Ch1 254nm

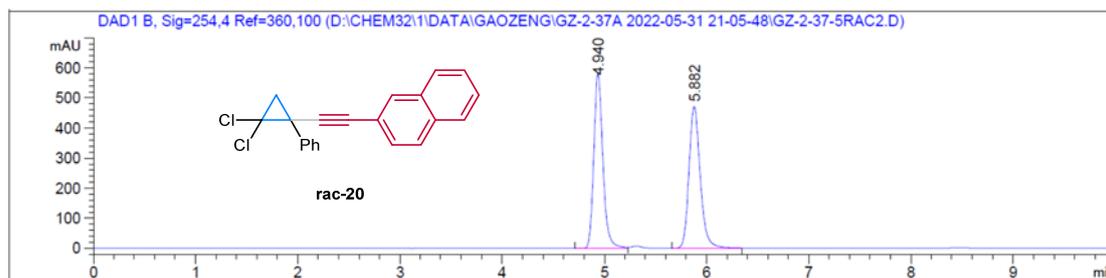
T	Hight	Area	Area%
11.804	322858	6400967	49.983
13.376	287602	6405426	50.017



Peak Table

PDA Ch1 254nm

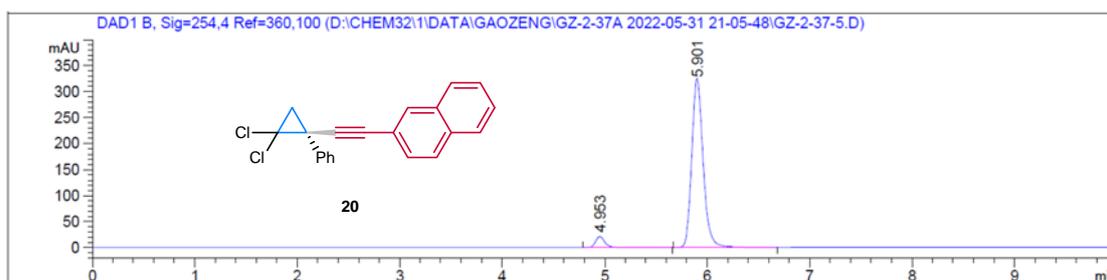
Peak#	Ret. Time	Area	Area%
1	11.860	935572	3.892
2	13.440	23104116	96.108



Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.940	BV	0.0962	3594.59644	581.17987	49.6953
2	5.882	MF R	0.1285	3638.67065	471.80038	50.3047

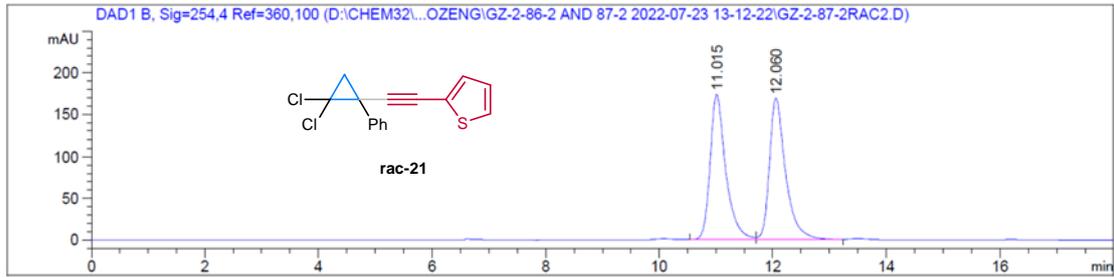
Totals : 7233.26709 1052.98026



Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.953	BB	0.0954	133.12120	21.16086	5.0352
2	5.901	BB	0.1180	2510.66895	325.41650	94.9648

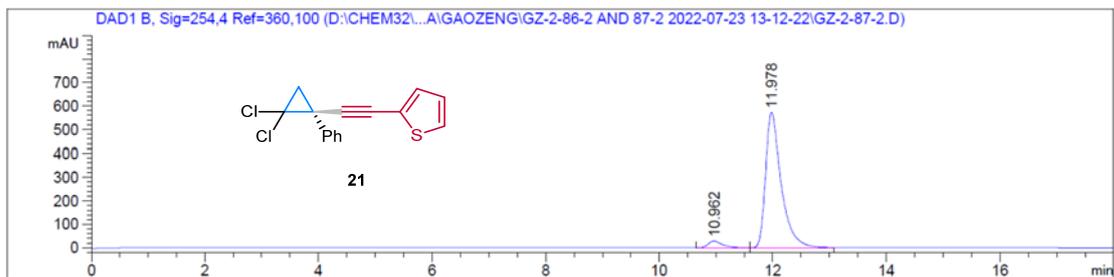
Totals : 2643.79015 346.57736



Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.015	BV	0.2810	3312.56641	173.28084	49.8823
2	12.060	VB	0.2921	3328.20093	168.77985	50.1177

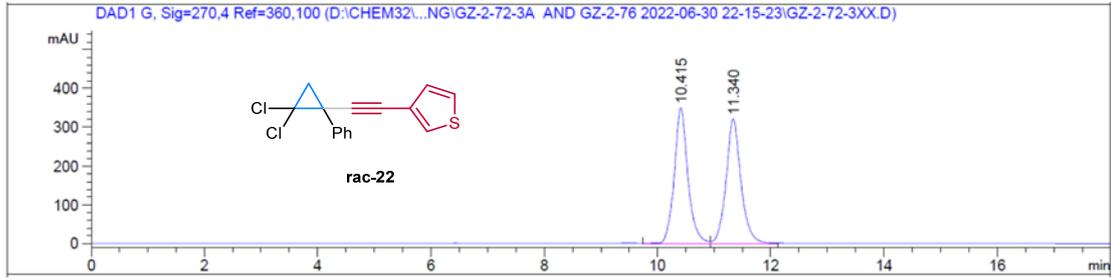
Totals : 6640.76733 342.06068



Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.962	BB	0.2477	474.59125	28.29502	4.1625
2	11.978	MF R	0.3180	1.09270e4	572.77887	95.8375

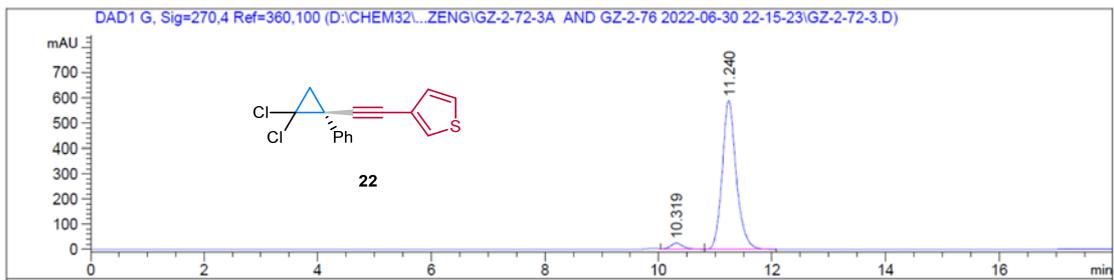
Totals : 1.14016e4 601.07389



Signal 7: DAD1 G, Sig=270,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.415	BV	0.2453	5848.51855	349.40112	49.8032
2	11.340	MF R	0.3068	5894.73926	320.22665	50.1968

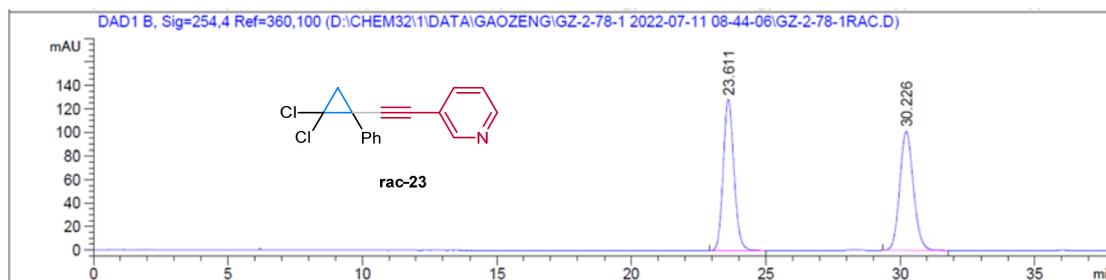
Totals : 1.17433e4 669.62778



Signal 7: DAD1 G, Sig=270,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.319	VV	0.2321	391.79510	24.83173	3.7141
2	11.240	MF R	0.2874	1.01570e4	588.96472	96.2859

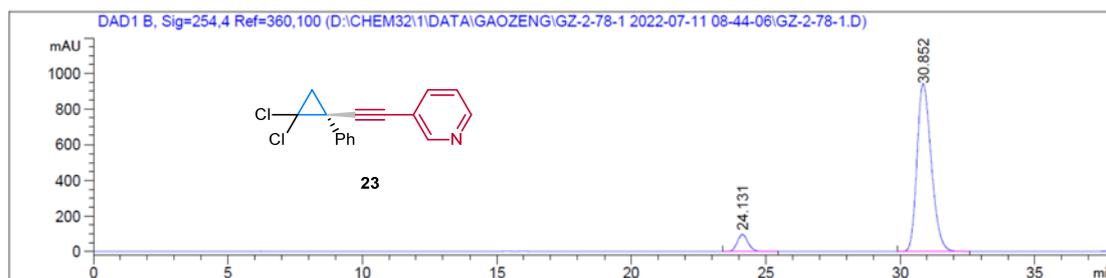
Totals : 1.05488e4 613.79645



Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	23.611	BB	0.4337	3580.63330	128.24510	49.9928
2	30.226	BB	0.5400	3581.66211	100.93671	50.0072

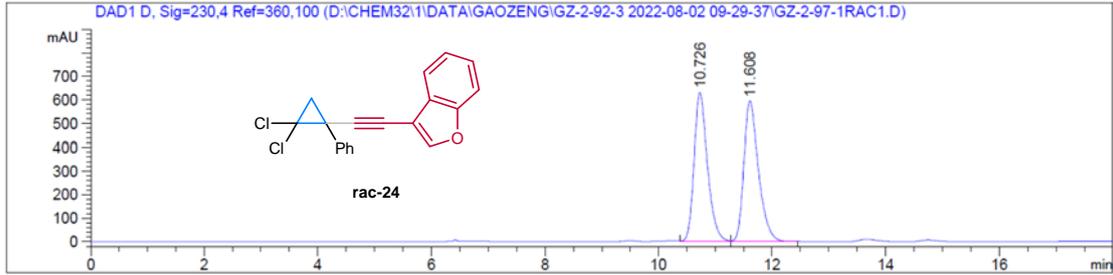
Totals : 7162.29541 229.18182



Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	24.131	BB	0.4366	2704.75928	96.02908	7.1992
2	30.852	MF R	0.6158	3.48656e4	943.59320	92.8008

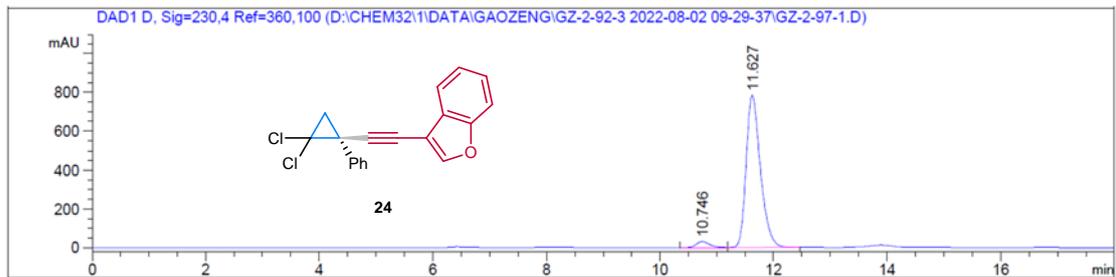
Totals : 3.75704e4 1039.62228



Signal 4: DAD1 D, Sig=230,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.726	VV	0.2476	1.03642e4	631.07007	49.2113
2	11.608	MF R	0.2998	1.06964e4	594.60132	50.7887

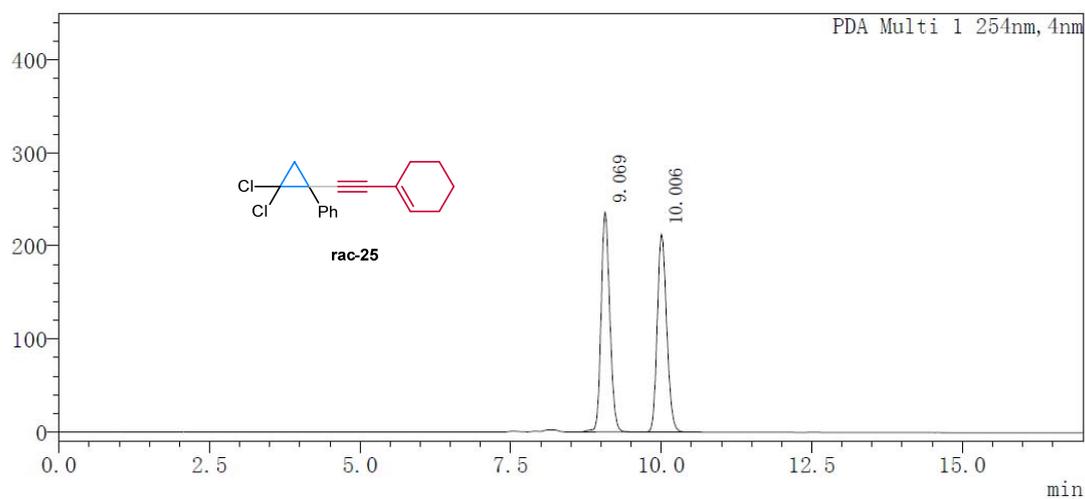
Totals : 2.10607e4 1225.67139



Signal 4: DAD1 D, Sig=230,4 Ref=360,100

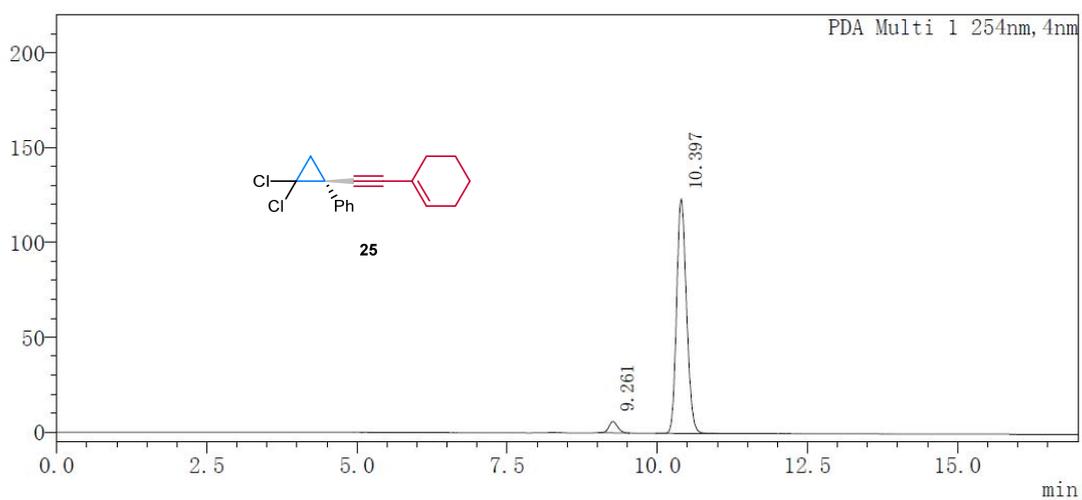
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.746	BV	0.2426	507.47772	31.72584	3.5705
2	11.627	VB	0.2639	1.37057e4	784.37036	96.4295

Totals : 1.42132e4 816.09620



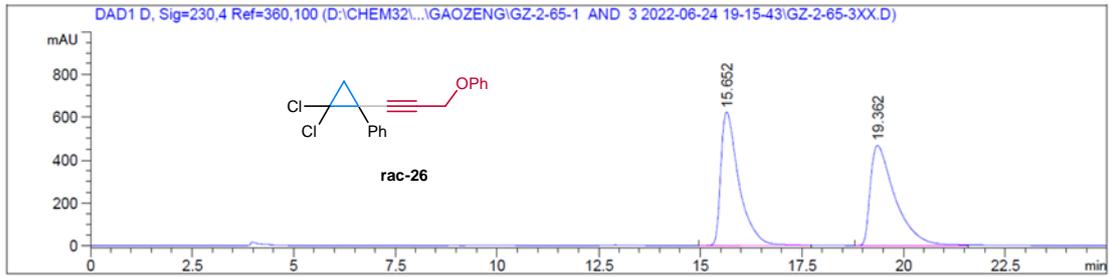
PDA Ch1 254nm

T	Hight	Area	Area%
9.069	236183	2374659	50.324
10.006	212694	2344054	49.676



PDA Ch1 254nm

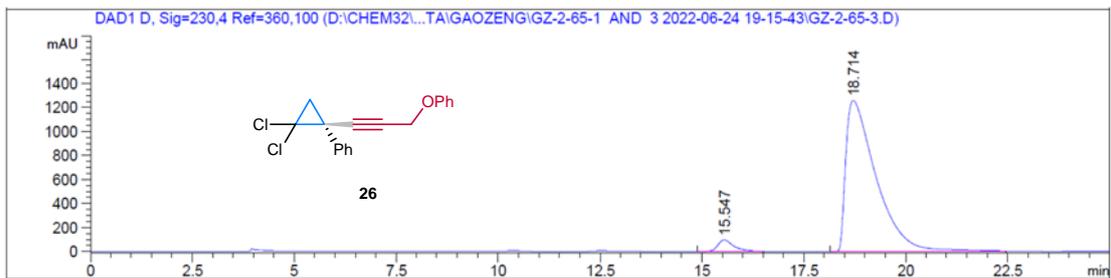
T	Hight	Area	Area%
9.261	5942	59729	4.052
10.397	123548	1414240	95.948



Signal 4: DAD1 D, Sig=230,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.652	BB	0.4630	1.92373e4	621.77954	49.2746
2	19.362	MF R	0.7041	1.98037e4	468.79950	50.7254

Totals : 3.90409e4 1090.57904

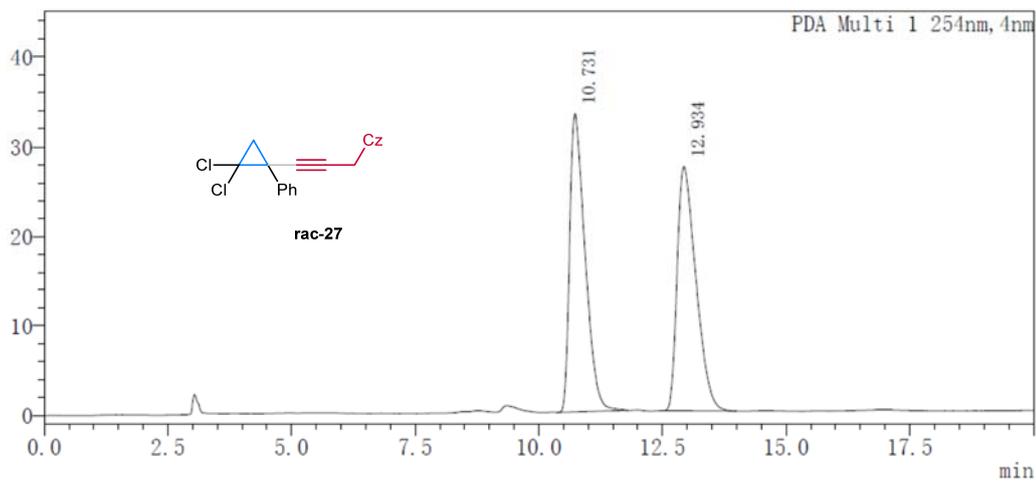


Signal 4: DAD1 D, Sig=230,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.547	MF R	0.4576	2659.13770	96.85825	3.9168
2	18.714	MF R	0.8629	6.52316e4	1259.90015	96.0832

Totals : 6.78907e4 1356.75839

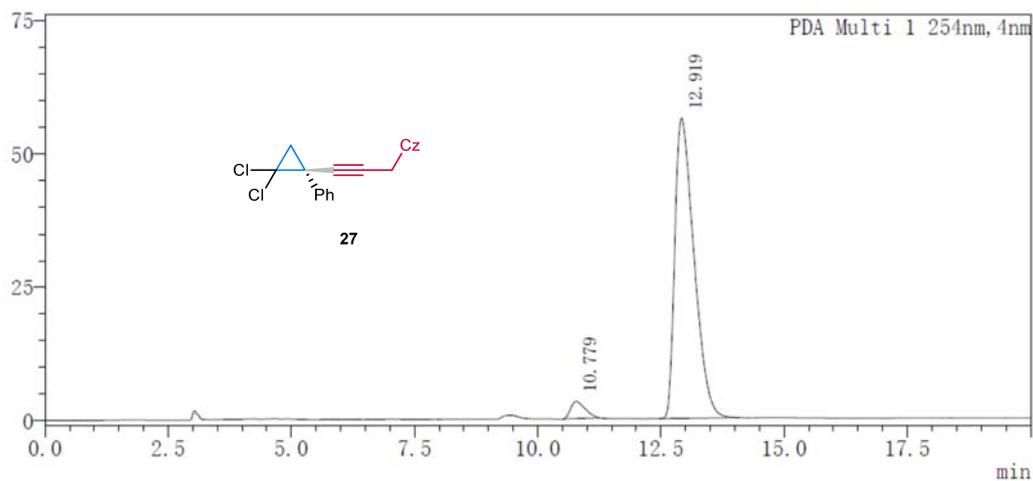
mAU



PDA Ch1 254nm

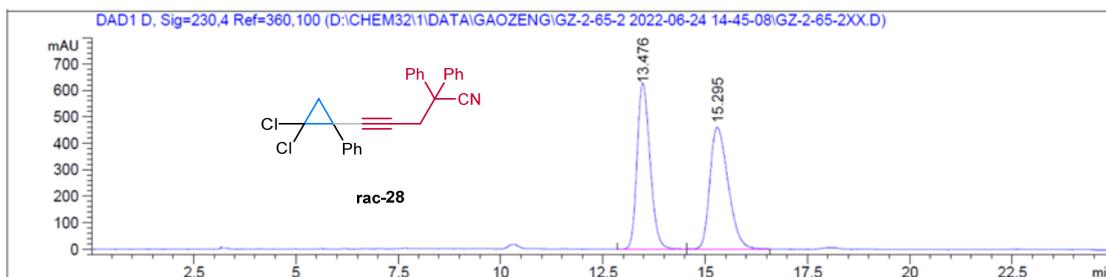
T	Hight	Area	Area%
10.731	33253	721882	50.044
12.934	27320	720625	49.956

mAU



PDA Ch1 254nm

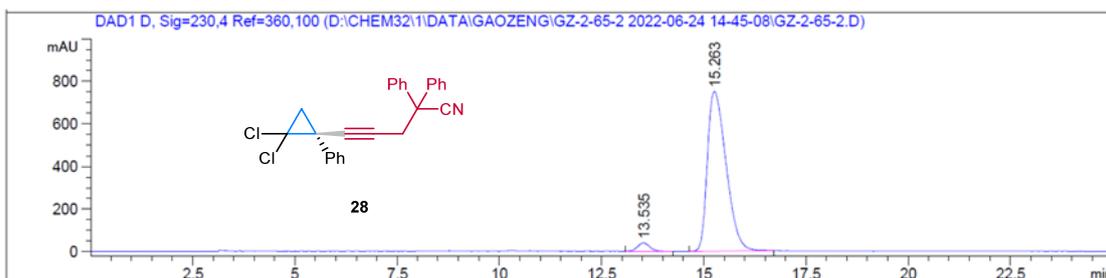
T	Hight	Area	Area%
10.779	3165	64161	4.033
12.919	56312	1526703	95.967



Signal 4: DAD1 D, Sig=230,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.476	VV R	0.3429	1.38426e4	628.26355	49.2037
2	15.295	VV R	0.4419	1.42906e4	460.22842	50.7963

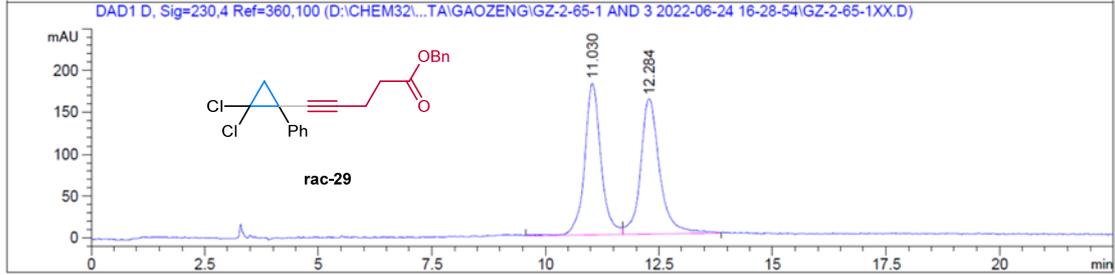
Totals : 2.81332e4 1088.49197



Signal 4: DAD1 D, Sig=230,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.535	VV R	0.2862	855.11780	40.20064	3.4617
2	15.263	BV R	0.4494	2.38469e4	748.90234	96.5383

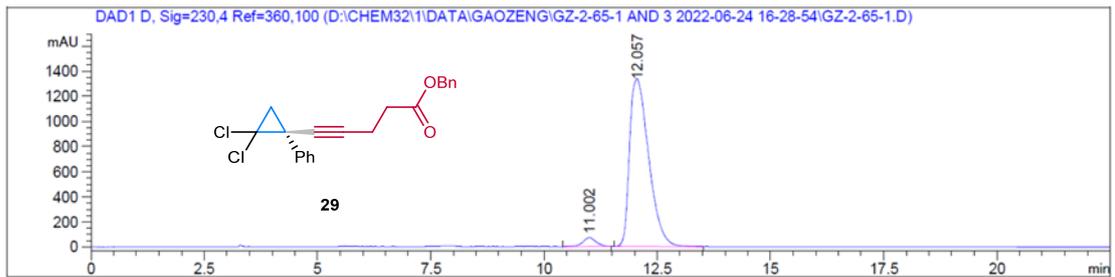
Totals : 2.47021e4 789.10299



Signal 4: DAD1 D, Sig=230,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.030	MF R	0.4202	4555.41504	180.66690	48.8934
2	12.284	FM R	0.4918	4761.61377	161.35999	51.1066

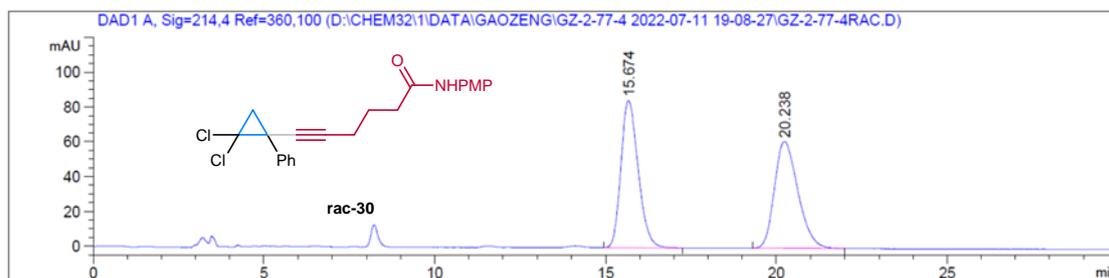
Totals : 9317.02881 342.02689



Signal 4: DAD1 D, Sig=230,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.002	VB R	0.2955	1485.90344	71.77244	3.6485
2	12.057	BV R	0.4119	3.92408e4	1338.95984	96.3515

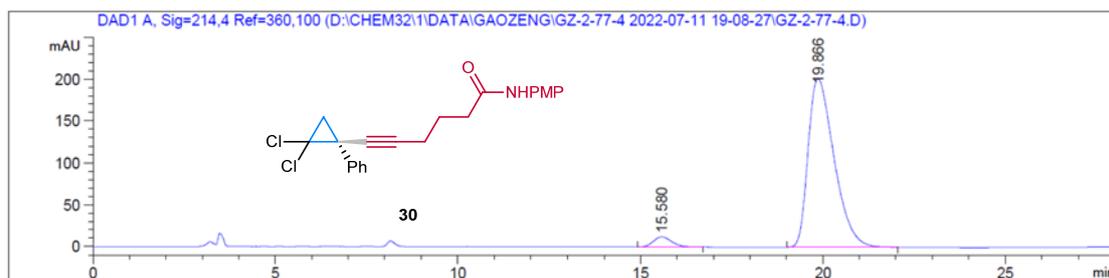
Totals : 4.07267e4 1410.73228



Signal 1: DAD1 A, Sig=214,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.674	BB	0.5416	2968.71240	84.56567	50.2925
2	20.238	BB	0.7115	2934.18091	61.40513	49.7075

Totals : 5902.89331 145.97080

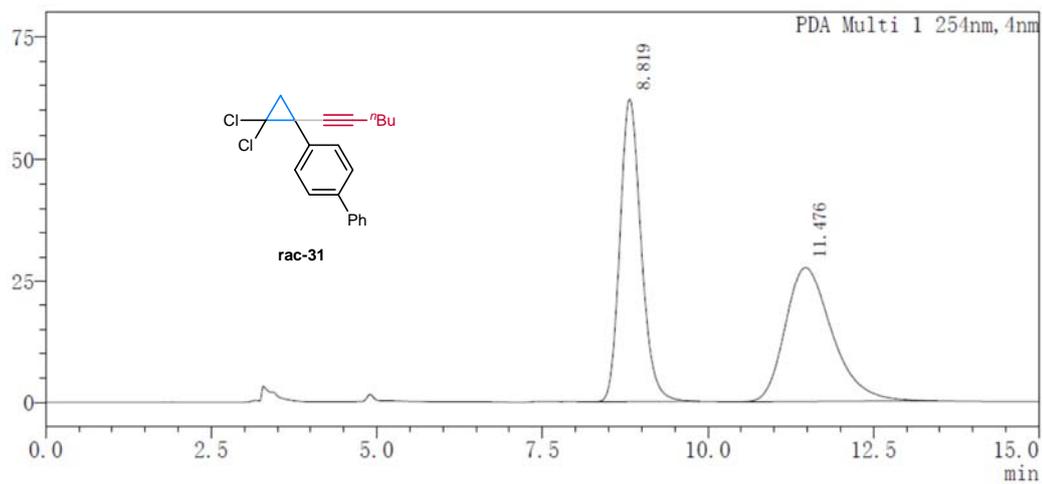


Signal 1: DAD1 A, Sig=214,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.580	BB	0.4281	421.89581	12.11939	4.0628
2	19.866	BB	0.7491	9962.40820	201.40533	95.9372

Totals : 1.03843e4 213.52473

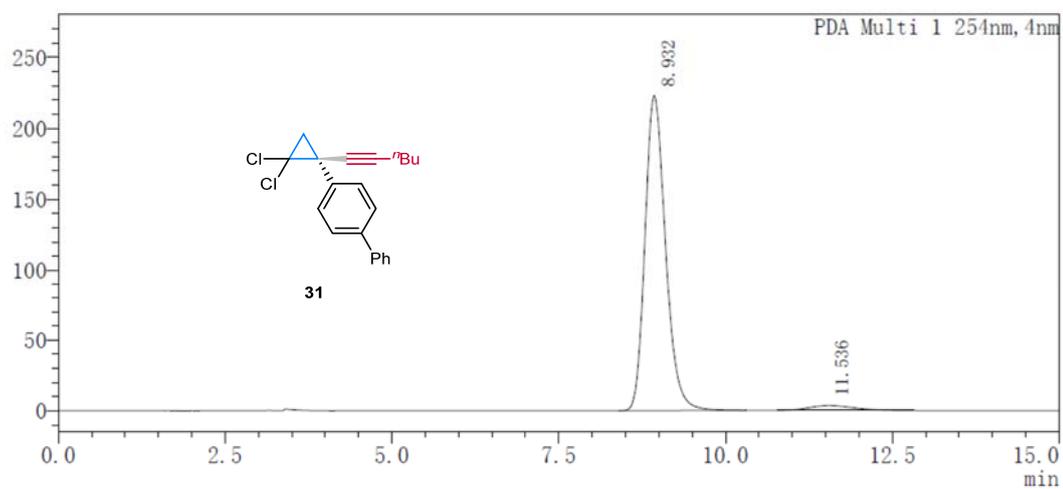
mAU



PDA Ch1 254nm

T	Hight	Area	Area%
8.819	62112	1386377	50.533
11.476	27680	1357110	49.467

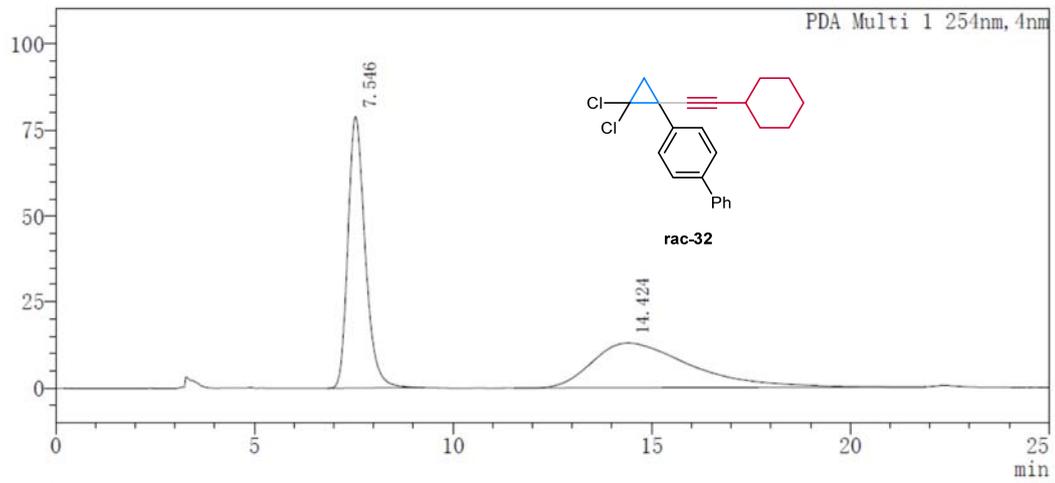
mAU



PDA Ch1 254nm

T	Hight	Area	Area%
8.932	222927	4784706	96.776
11.536	3449	159408	3.224

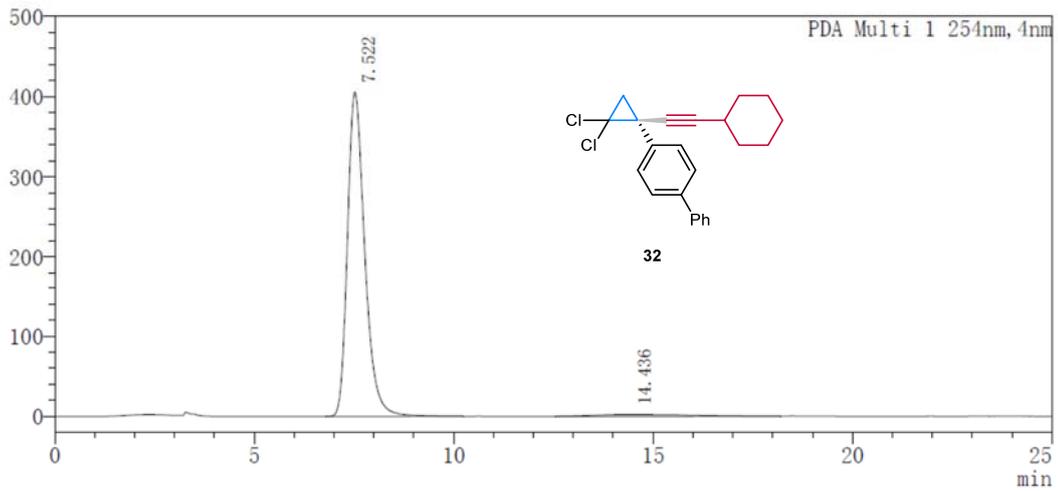
mAU



PDA Ch1 254nm

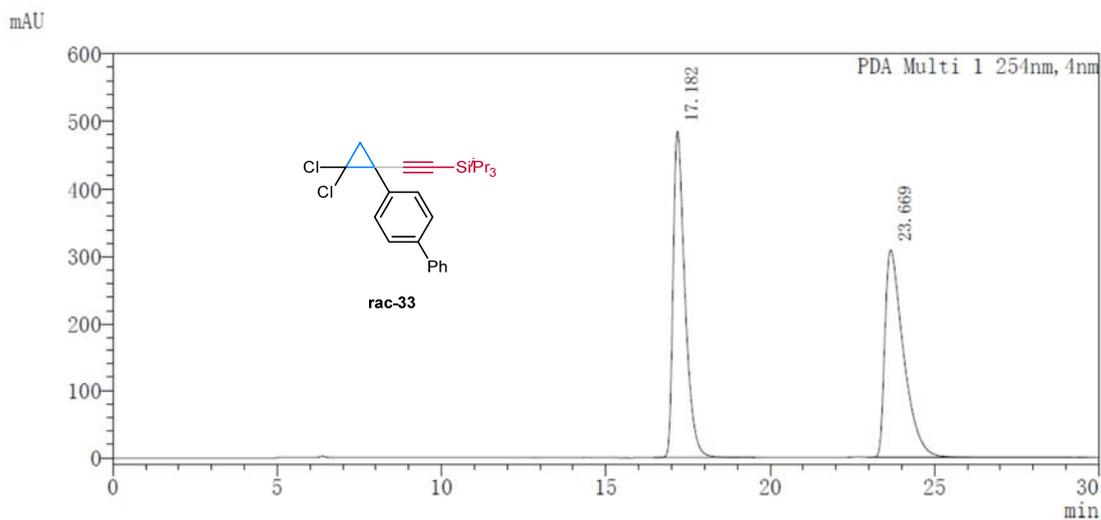
T	Hight	Area	Area%
7.546	78659	2375238	51.578
14.424	12909	2229910	48.422

mAU



PDA Ch1 254nm

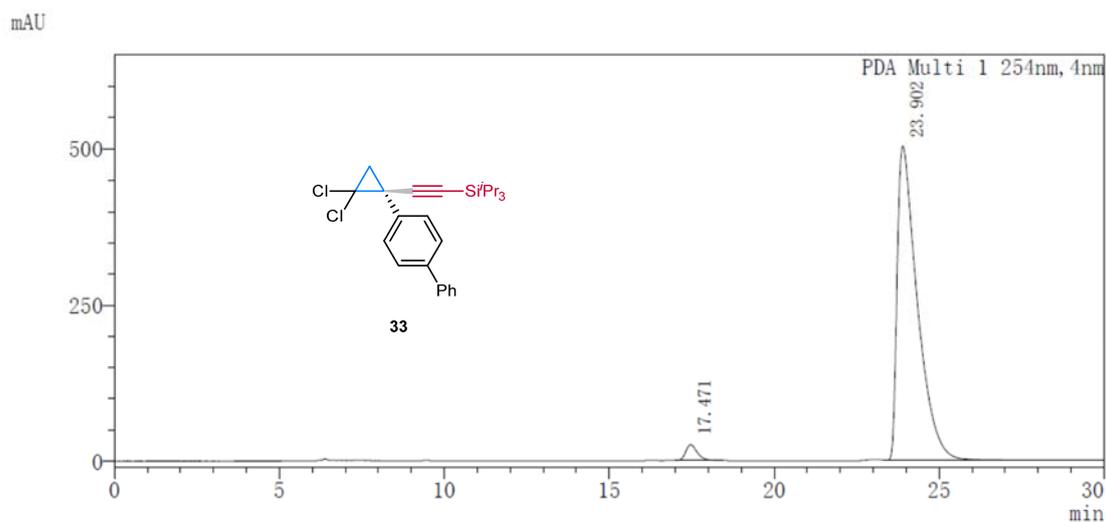
T	Hight	Area	Area%
7.522	405322	12274748	97.228
14.436	2303	349907	2.772



Peak Table

PDA Ch1 254nm

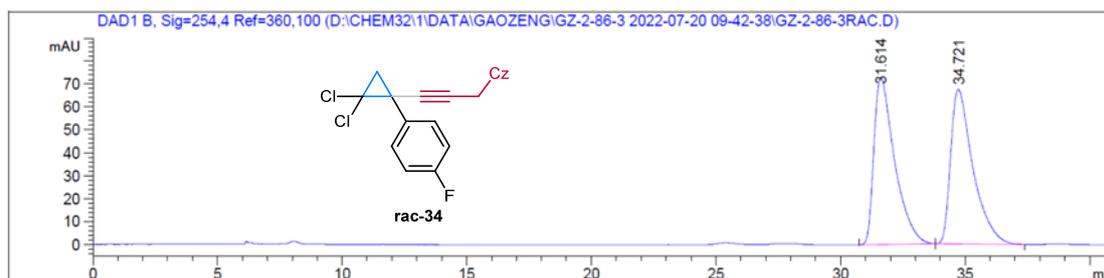
Peak#	Ret. Time	Area	Area%
1	17.182	12185673	50.014
2	23.669	12178614	49.986



Peak Table

PDA Ch1 254nm

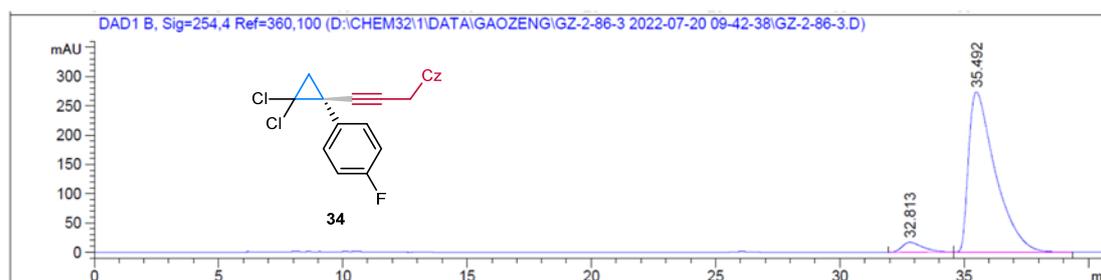
Peak#	Ret. Time	Area	Area%
1	17.471	617729	2.813
2	23.902	21344312	97.187



Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	31.614	BB	0.8395	4211.40234	72.73378	50.0280
2	34.721	BB	0.9164	4206.68799	67.37827	49.9720

Totals : 8418.09033 140.11205

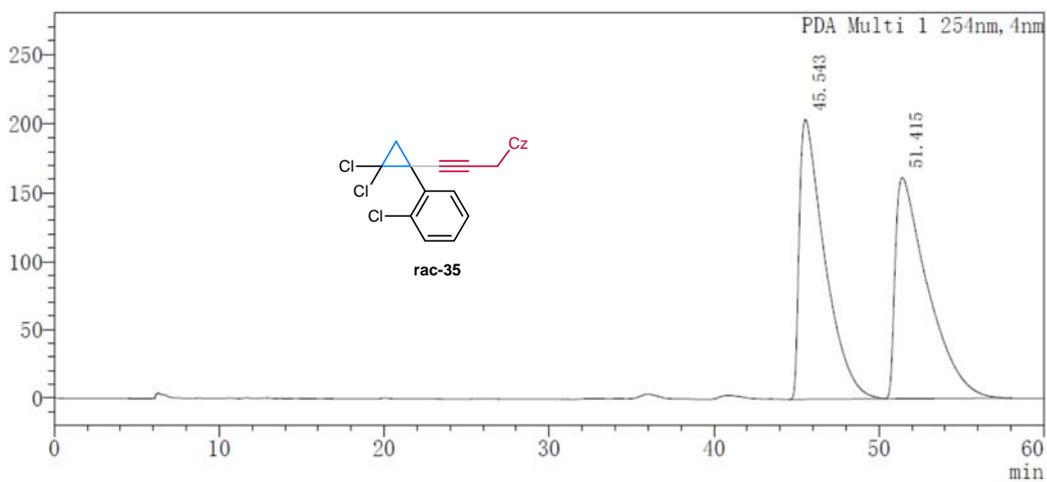


Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	32.813	BB	0.8030	981.45569	16.91350	4.5862
2	35.492	BB	1.0785	2.04189e4	273.03793	95.4138

Totals : 2.14003e4 289.95144

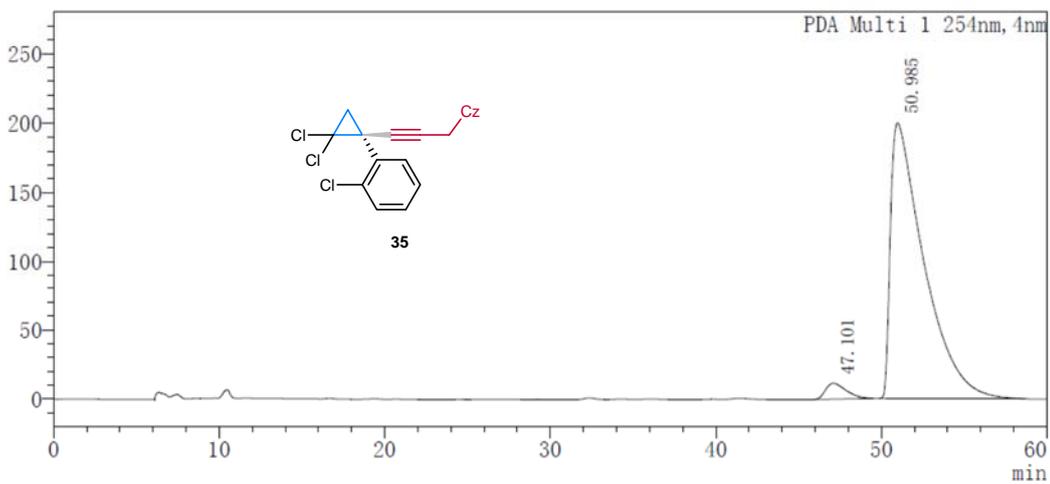
mAU



PDA Ch1 254nm

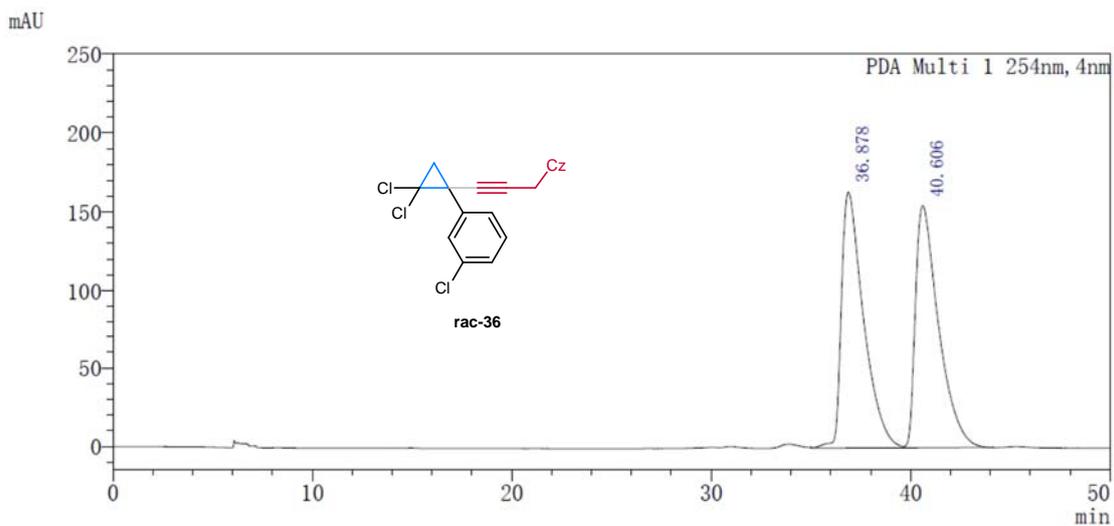
T	Hight	Area	Area%
45.543	203625	21912104	49.746
51.415	161614	22135794	50.254

mAU



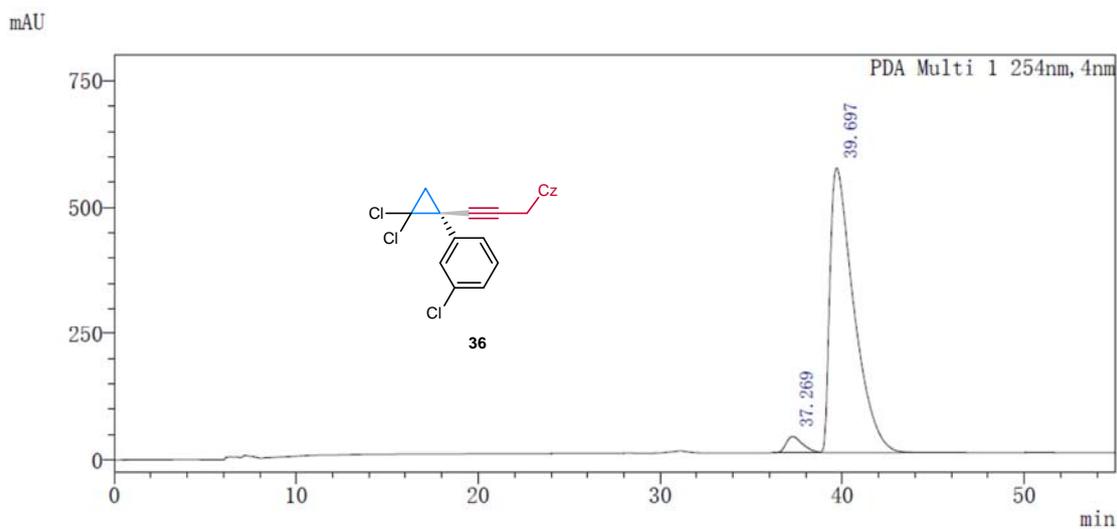
PDA Ch1 254nm

T	Hight	Area	Area%
47.101	11369	983887	3.394
50.985	199500	28001496	96.606



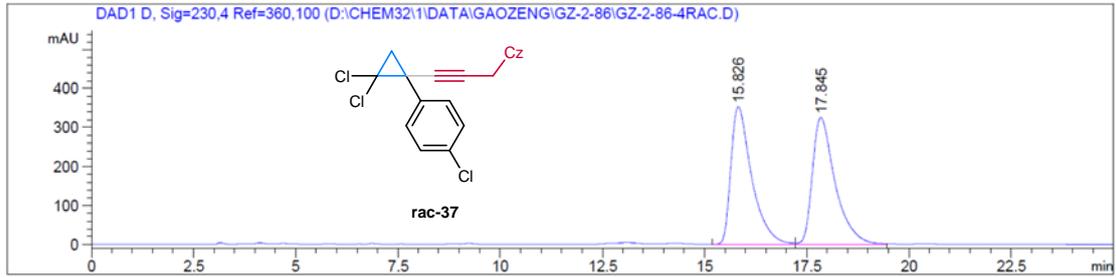
PDA Ch1 254nm

T	Hight	Area	Area%
36.878	163629	12638279	50.319
40.606	154858	12477867	49.681



PDA Ch1 254nm

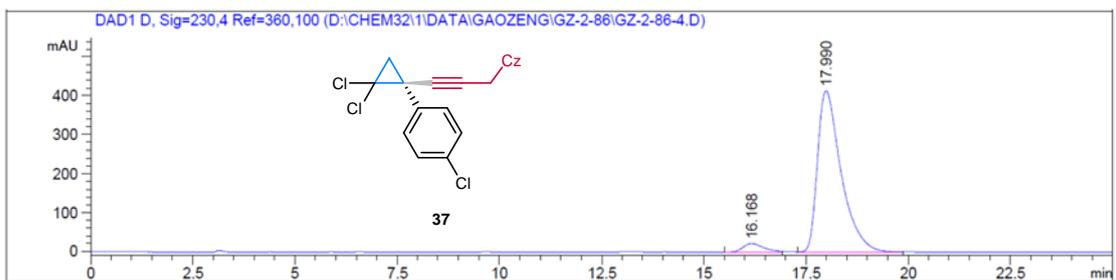
T	Hight	Area	Area%
37.269	32395	2067511	3.859
39.697	564436	51512568	96.141



Signal 4: DAD1 D, Sig=230,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.826	BV	0.5281	1.25280e4	352.94241	49.8711
2	17.845	MF R	0.6463	1.25928e4	324.73535	50.1289

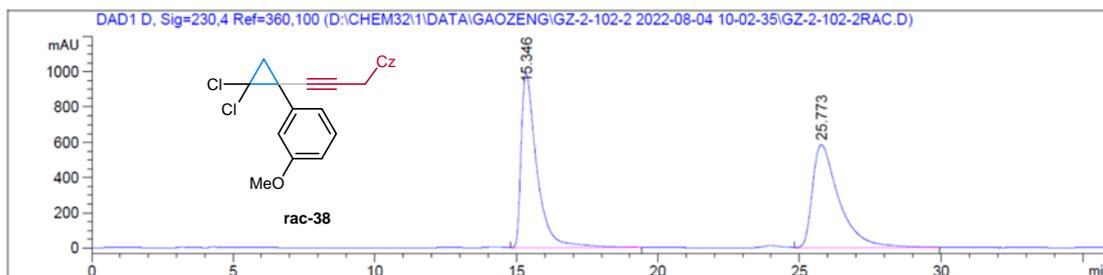
Totals : 2.51208e4 677.67776



Signal 4: DAD1 D, Sig=230,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.168	MF R	0.5791	768.17157	22.10682	4.4119
2	17.990	MF R	0.6694	1.66432e4	414.38925	95.5881

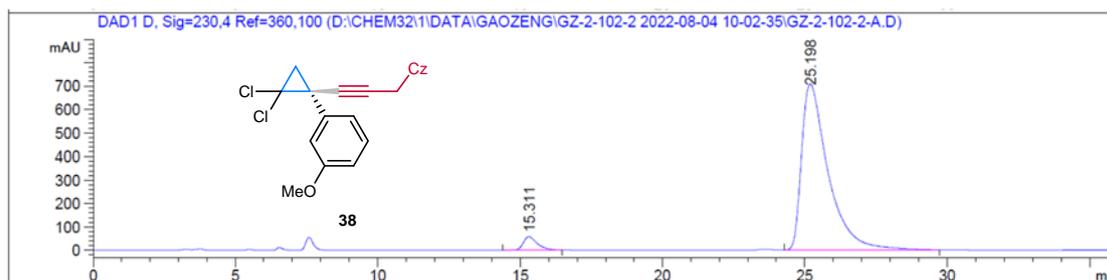
Totals : 1.74114e4 436.49607



Signal 4: DAD1 D, Sig=230,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.346	MF R	0.6486	3.86042e4	991.91559	50.2093
2	25.773	MF R	1.0924	3.82824e4	584.07513	49.7907

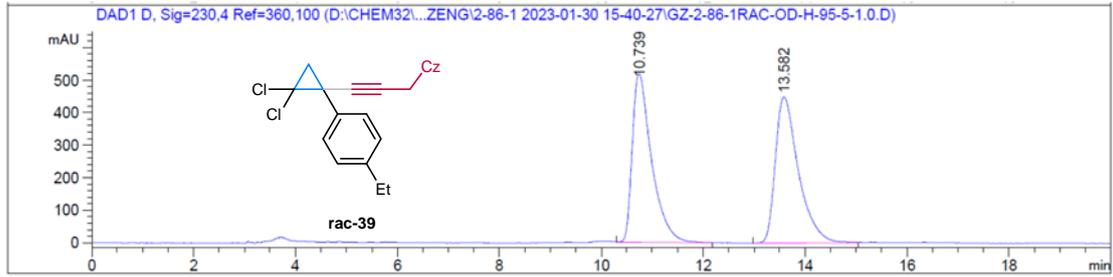
Totals : 7.68866e4 1575.99072



Signal 4: DAD1 D, Sig=230,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.311	MF R	0.5897	2072.41333	58.57244	4.3058
2	25.198	MF R	1.0860	4.60582e4	706.84021	95.6942

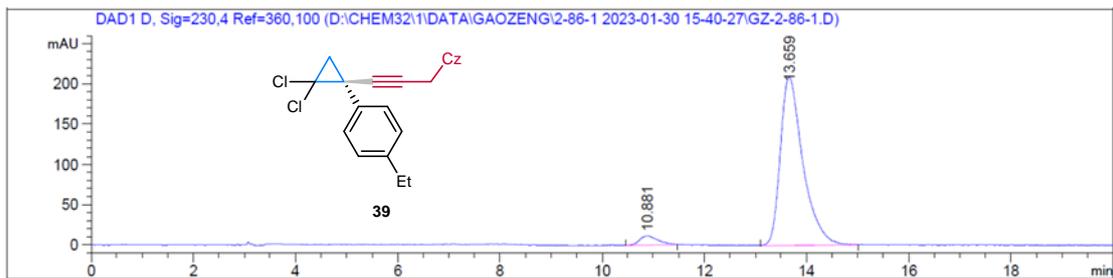
Totals : 4.81306e4 765.41265



Signal 4: DAD1 D, Sig=230,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.739	FM R	0.4392	1.36710e4	518.77765	49.1694
2	13.582	BV R	0.4754	1.41329e4	448.82864	50.8306

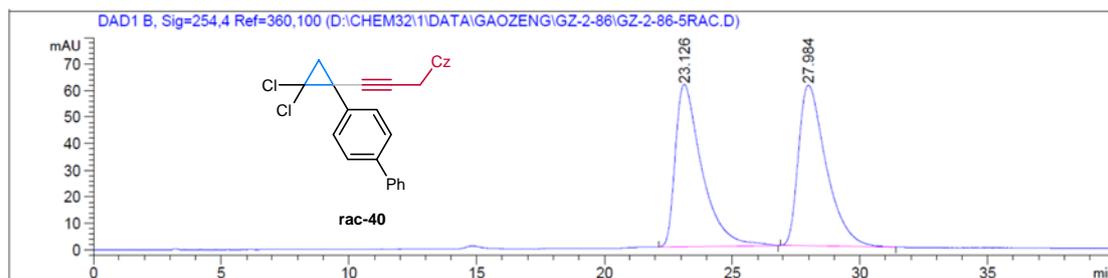
Totals : 2.78039e4 967.60629



Signal 4: DAD1 D, Sig=230,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.881	MF R	0.4284	303.02078	11.78842	4.5049
2	13.659	BV R	0.4504	6423.44873	209.11108	95.4951

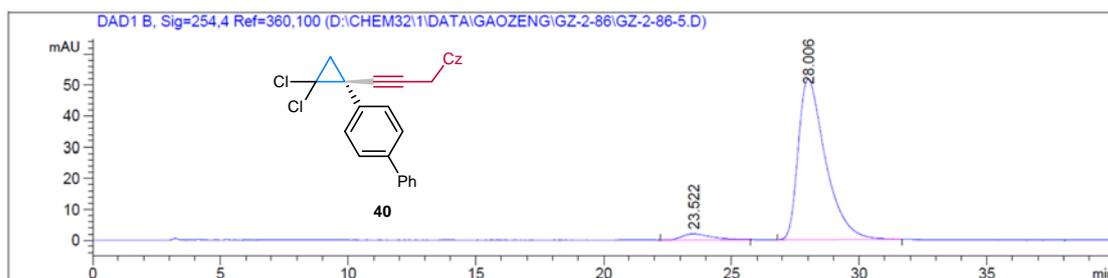
Totals : 6726.46951 220.89951



Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	23.126	BB	1.0305	4416.49414	61.15915	49.1628
2	27.984	BB	1.0566	4566.91309	60.50277	50.8372

Totals : 8983.40723 121.66192

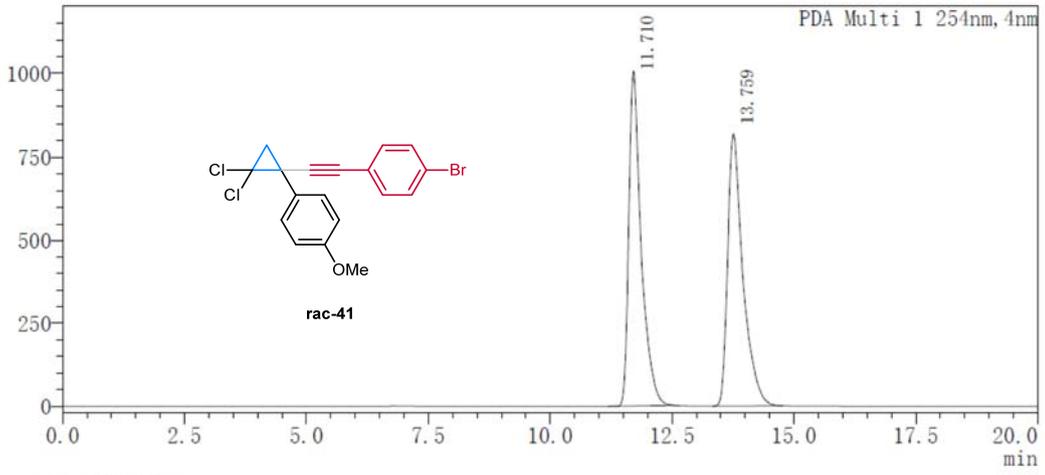


Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	23.522	MM R	1.3645	164.24826	2.00627	4.0999
2	28.006	BB	1.0869	3841.87012	51.70651	95.9001

Totals : 4006.11838 53.71278

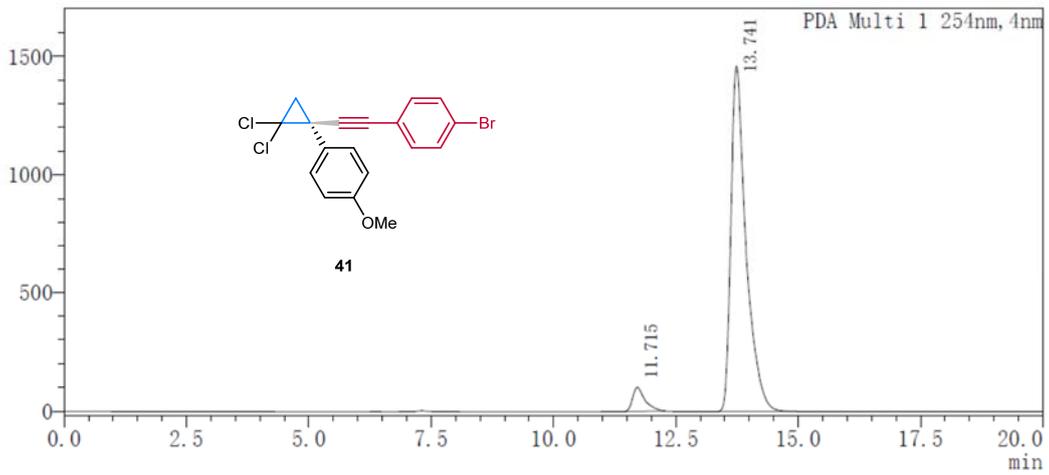
mAU



PDA Ch1 254nm

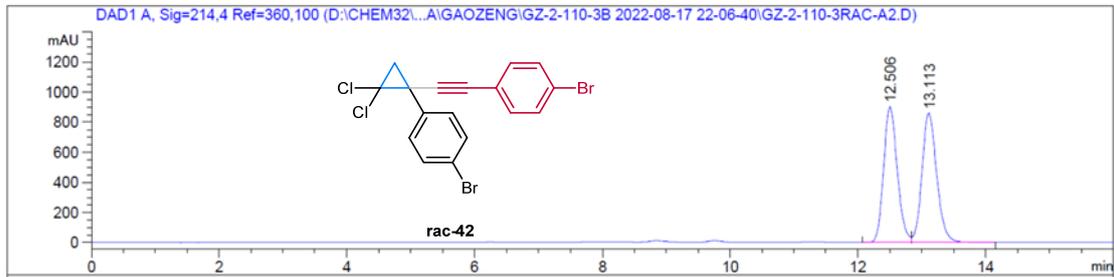
T	Hight	Area	Area%
11.710	1004689	17818102	49.974
13.759	818970	17836339	50.026

mAU



PDA Ch1 254nm

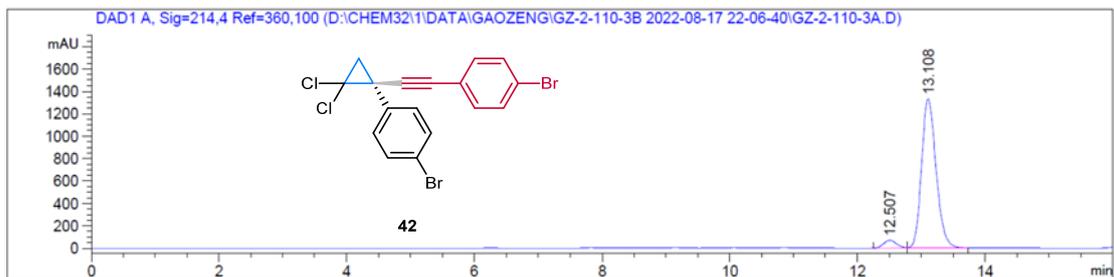
T	Hight	Area	Area%
11.715	101325	1777797	5.365
13.741	1459106	31360879	94.635



Signal 1: DAD1 A, Sig=214,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.506	BV	0.2292	1.33692e4	900.31714	49.2261
2	13.113	VB	0.2472	1.37896e4	859.48138	50.7739

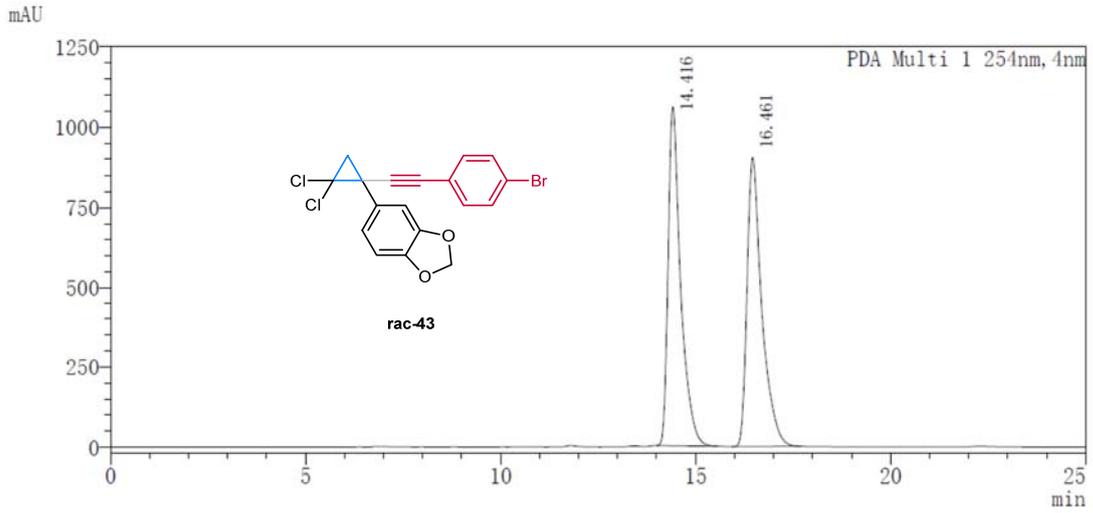
Totals : 2.71589e4 1759.79852



Signal 1: DAD1 A, Sig=214,4 Ref=360,100

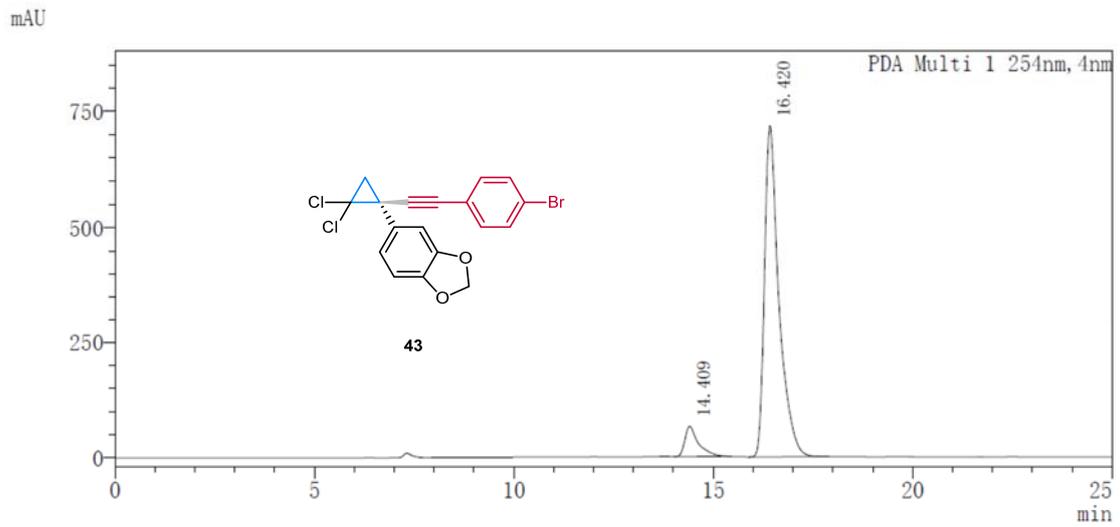
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.507	FM R	0.2396	1015.90656	70.65785	4.5983
2	13.108	MF R	0.2637	2.10770e4	1332.22119	95.4017

Totals : 2.20929e4 1402.87904



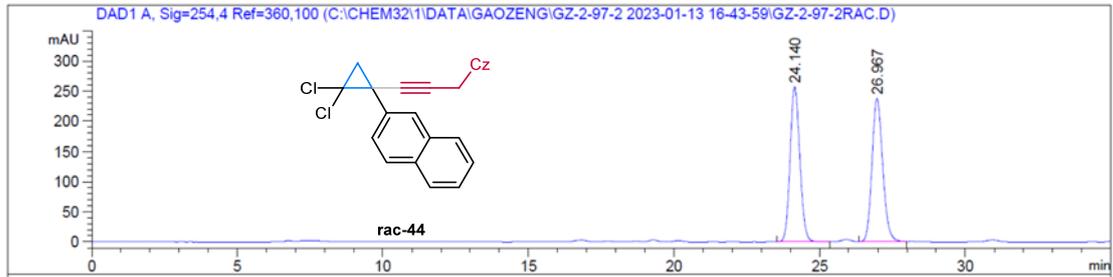
PDA Ch1 254nm

T	Hight	Area	Area%
14.416	1059226	23648655	49.840
16.461	903476	23800441	50.160



PDA Ch1 254nm

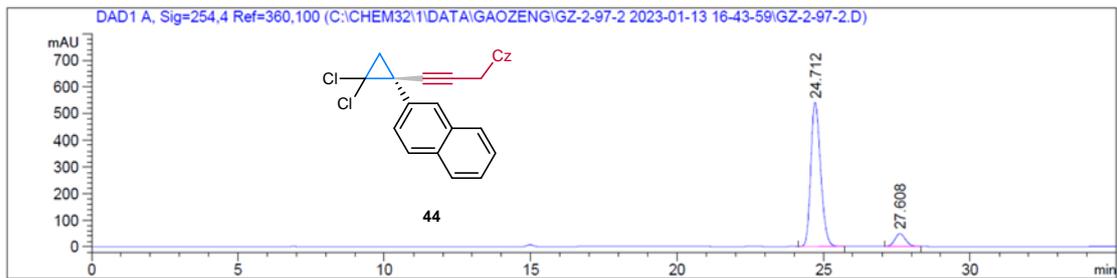
T	Hight	Area	Area%
14.409	65664	1551481	7.915
16.420	717425	18051391	92.085



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	24.140	BB	0.3622	5993.90088	256.88849	49.6025
2	26.967	BB	0.3954	6089.97119	237.29114	50.3975

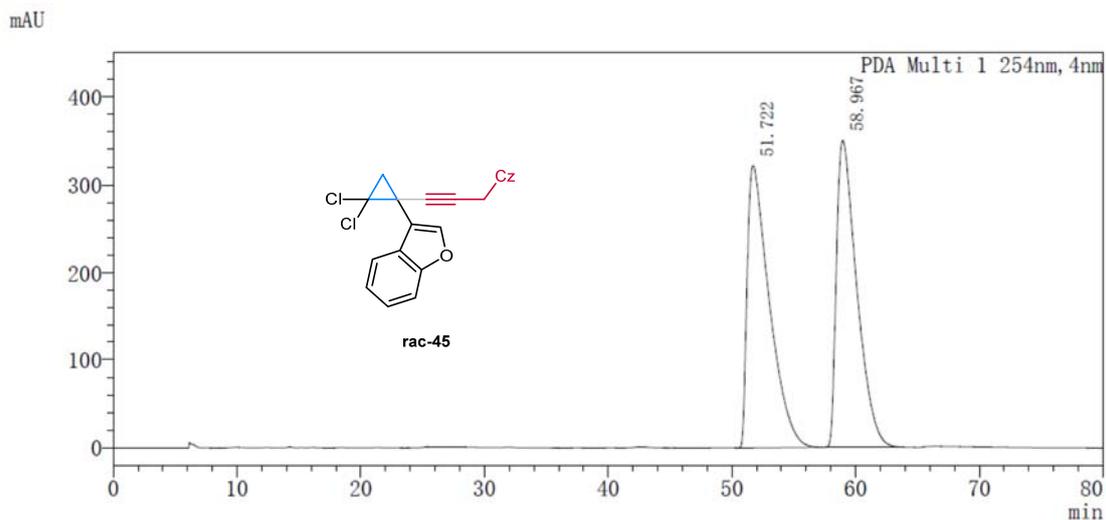
Totals : 1.20839e4 494.17963



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	24.712	MF R	0.3884	1.25875e4	540.09961	91.4907
2	27.608	BB	0.3844	1170.72900	47.36433	8.5093

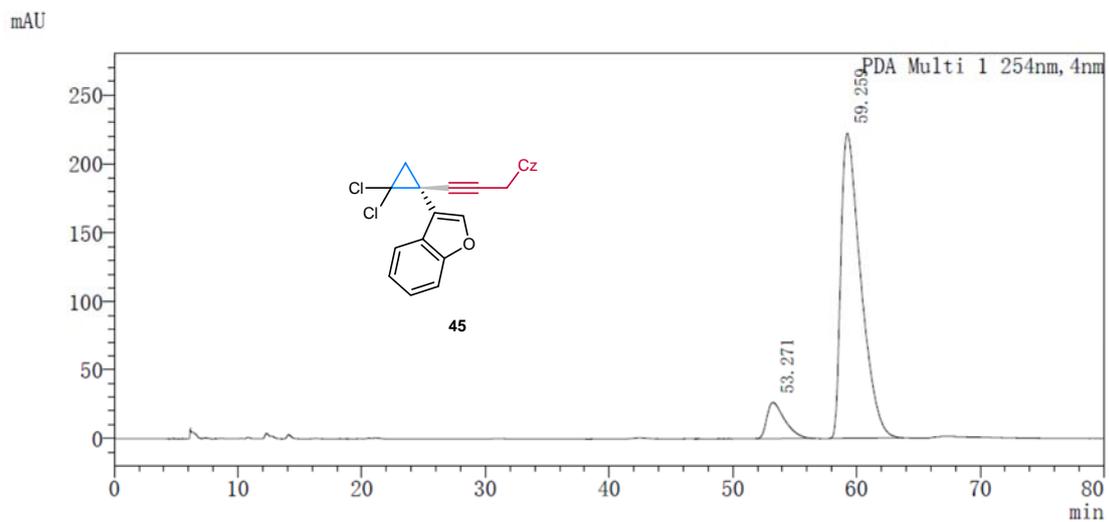
Totals : 1.37582e4 587.46394



Peak Table

PDA Ch1 254nm

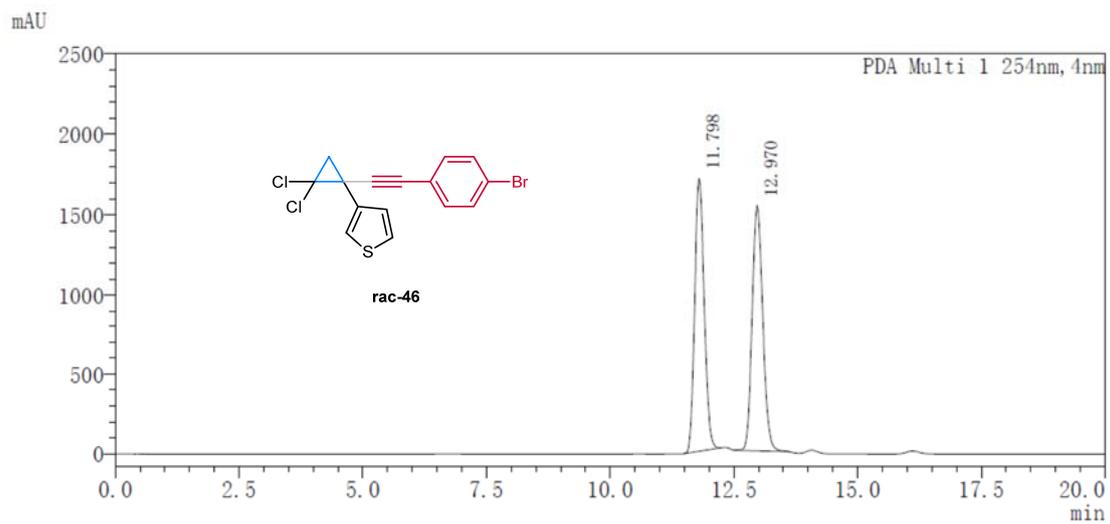
Peak#	Ret. Time	Area	Area%
1	51.722	39978442	50.015
2	58.967	39954579	49.985



Peak Table

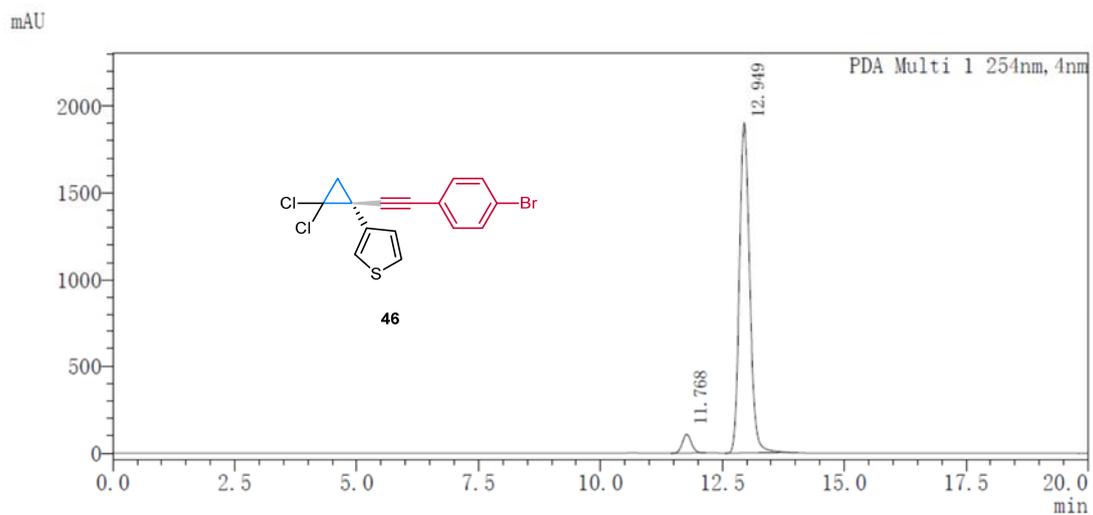
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	53.271	2633111	9.565
2	59.259	24895374	90.435



PDA Ch1 254nm

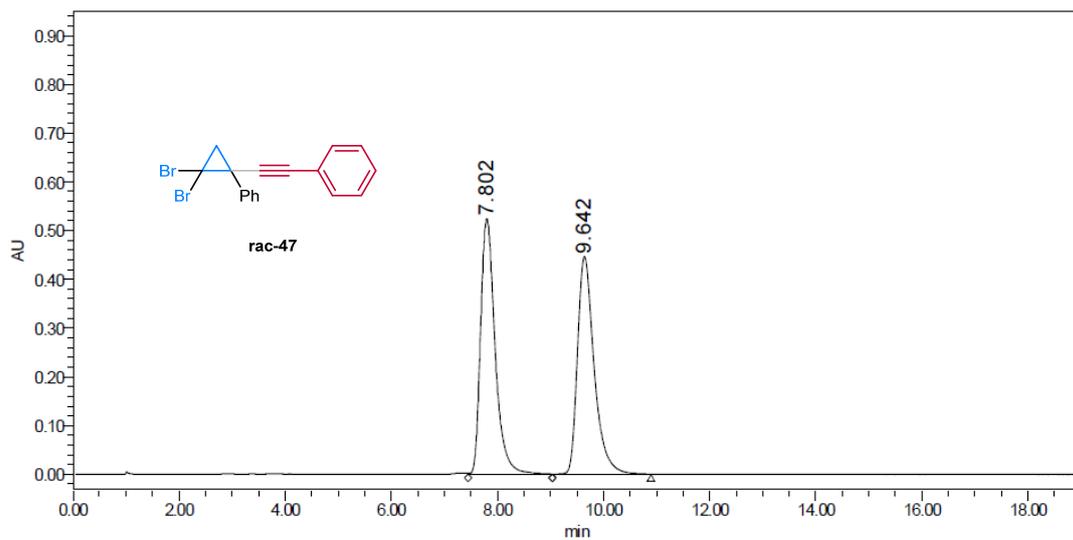
T	Hight	Area	Area%
11.798	1708944	22869419	49.790
12.970	1537100	23062216	50.210



PDA Ch1 254nm

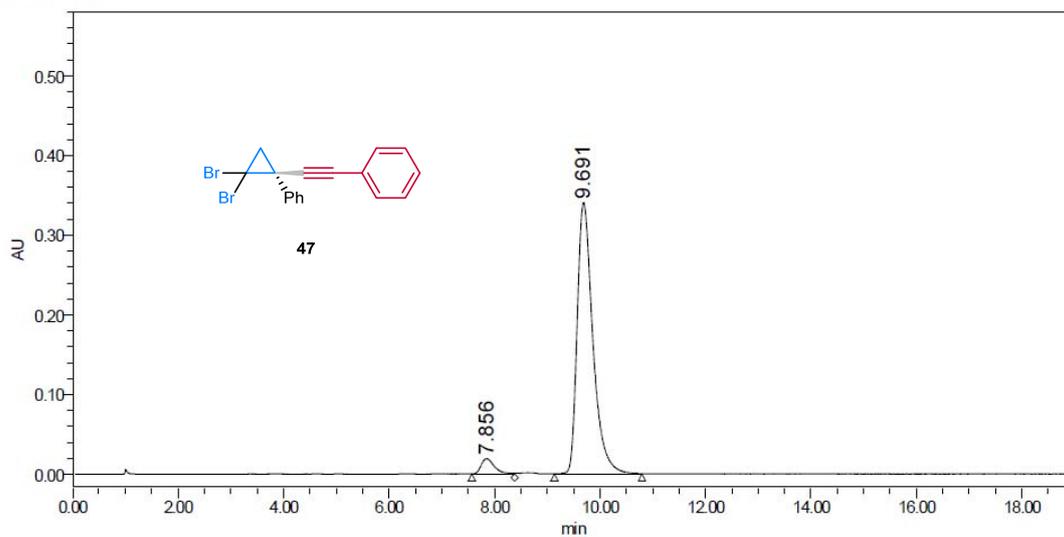
T	Hight	Area	Area%
11.768	106964	1380695	4.705
12.949	1899972	27962181	95.295

PDA 254nm

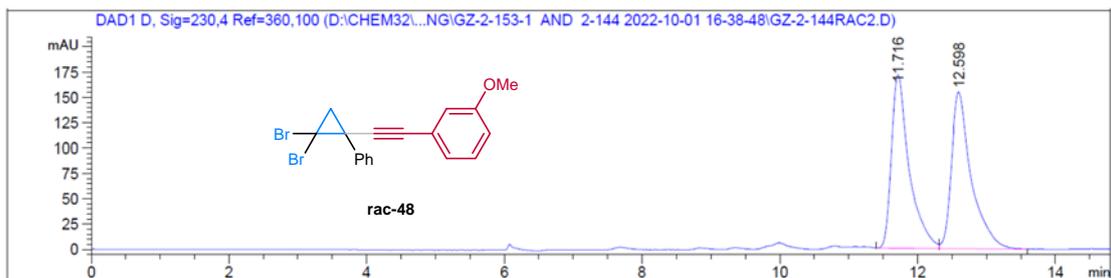


	RT	Area	% Area	Height
1	7.802	9843194	50.13	524688
2	9.642	9792247	49.87	446638

PDA 254nm



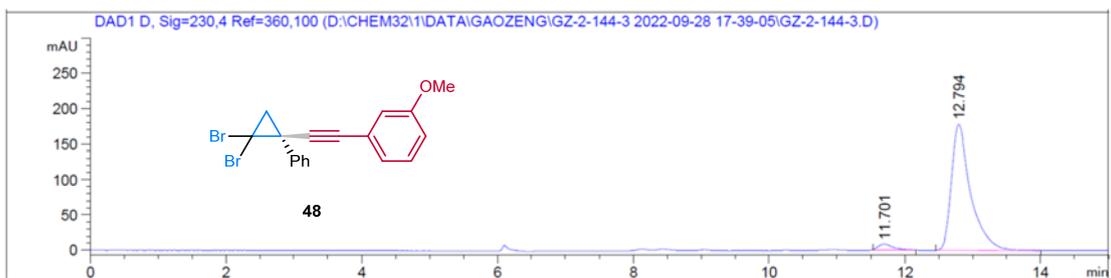
	RT	Area	% Area	Height
1	7.856	333823	4.52	19066
2	9.691	7049473	95.48	340040



Signal 4: DAD1 D, Sig=230,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.716	BV	0.2575	3046.78857	171.31827	49.6249
2	12.598	VB	0.2894	3092.85229	154.57343	50.3751

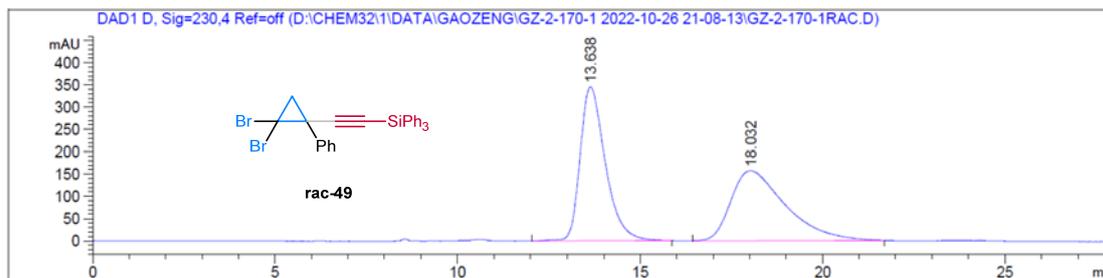
Totals : 6139.64087 325.89169



Signal 4: DAD1 D, Sig=230,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.701	MM R	0.2619	135.46072	8.61915	3.7101
2	12.794	MM R	0.3296	3515.65723	177.79204	96.2899

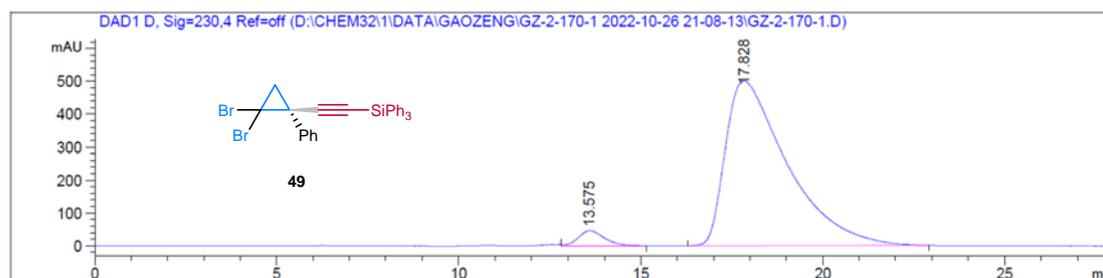
Totals : 3651.11795 186.41119



Signal 4: DAD1 D, Sig=230,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.638	VV R	0.7095	1.66404e4	345.77271	50.3982
2	18.032	BB	1.2408	1.63775e4	157.55028	49.6018

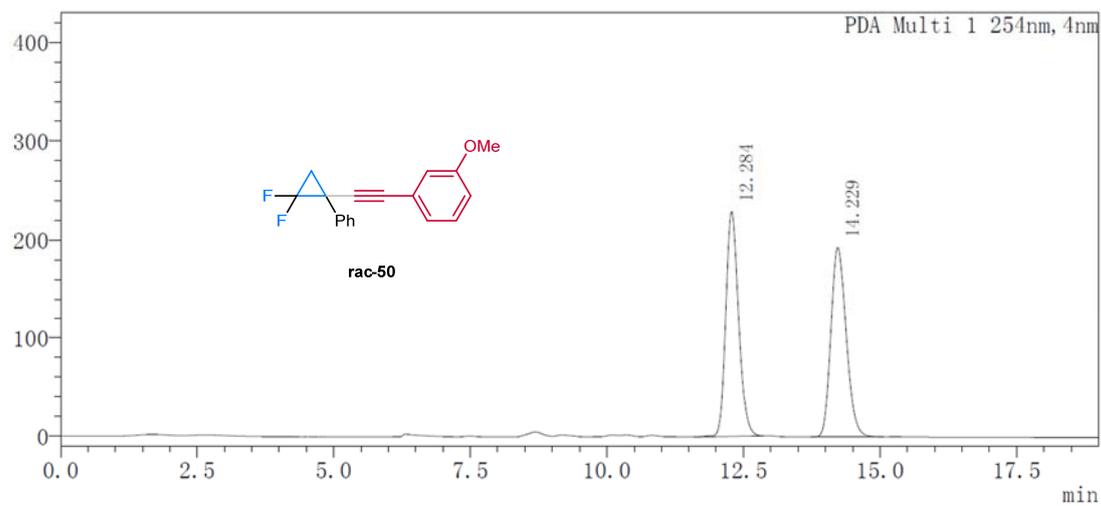
Totals : 3.30179e4 503.32298



Signal 4: DAD1 D, Sig=230,4 Ref=off

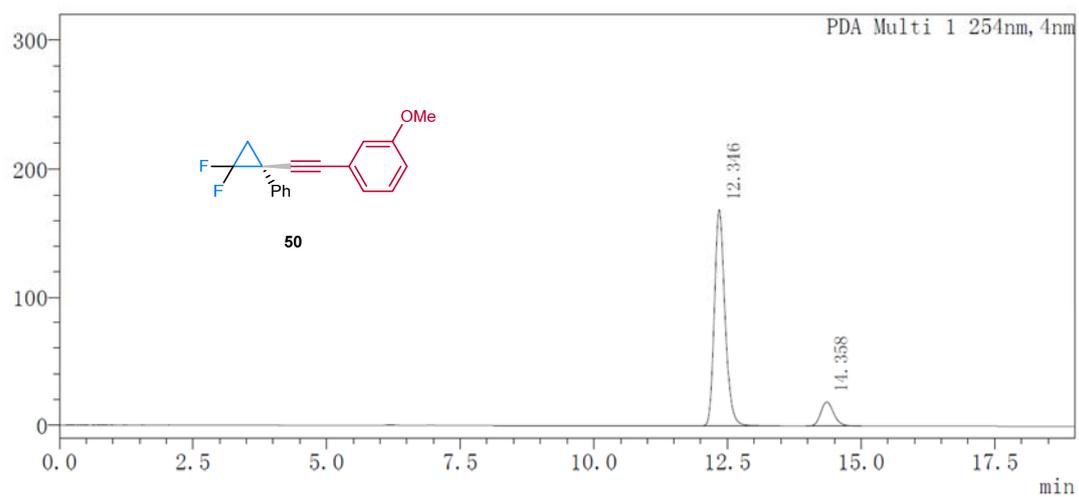
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.575	FM R	0.8214	2249.65308	45.64775	3.6577
2	17.828	VV R	1.3989	5.92545e4	500.60257	96.3423

Totals : 6.15042e4 546.25032



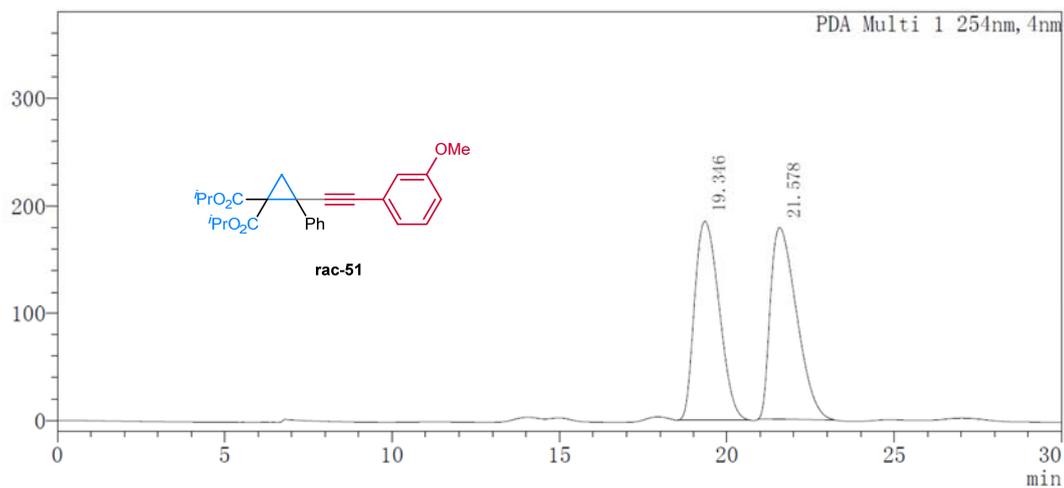
PDA Ch1 254nm

T	Hight	Area	Area%
12.284	228899	3765998	49.982
14.229	193344	3768778	50.018



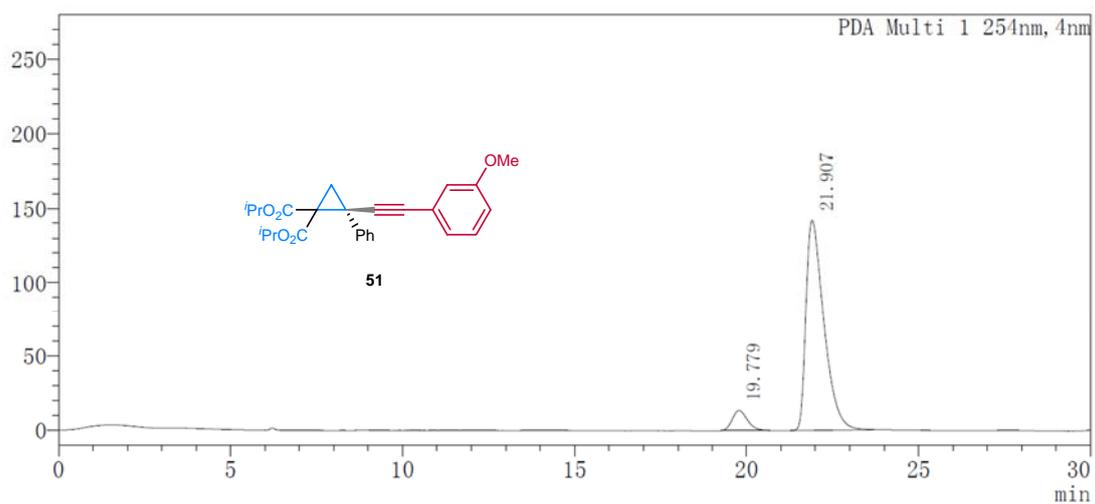
PDA Ch1 254nm

T	Hight	Area	Area%
12.346	168853	2344934	88.253
14.358	18712	312139	11.747



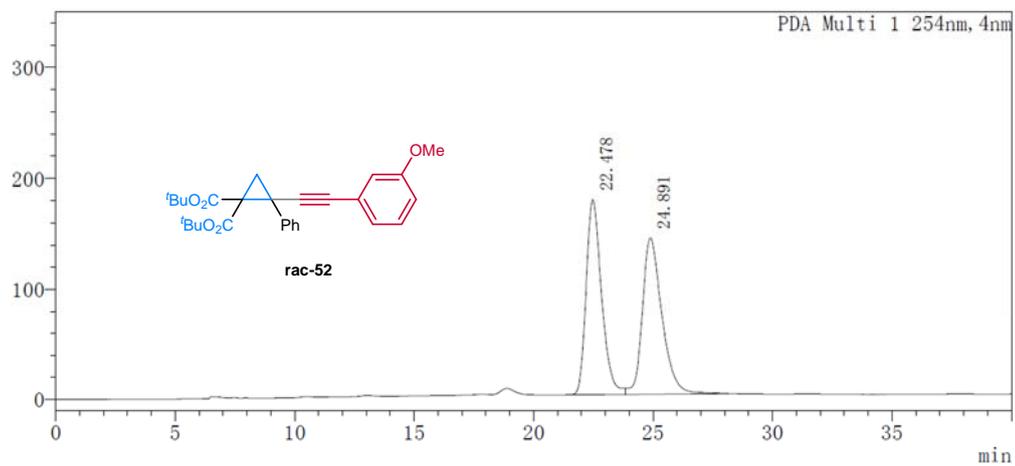
PDA Ch1 254nm

T	Hight	Area	Area%
19.346	185686	9499032	49.321
21.578	178785	9760726	50.679



PDA Ch1 254nm

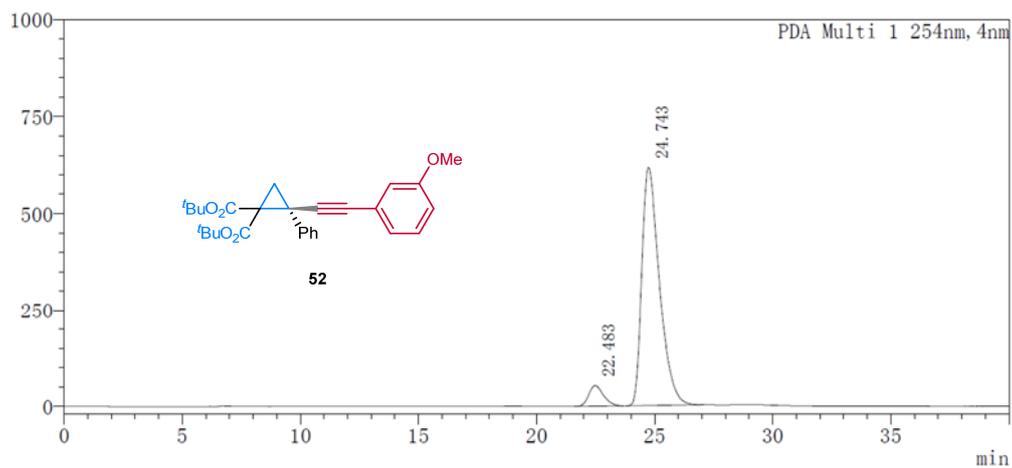
T	Hight	Area	Area%
19.779	13623	415907	7.485
21.907	142068	5140657	92.515



Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	22.478	7915233	49.538
2	24.891	8062942	50.462

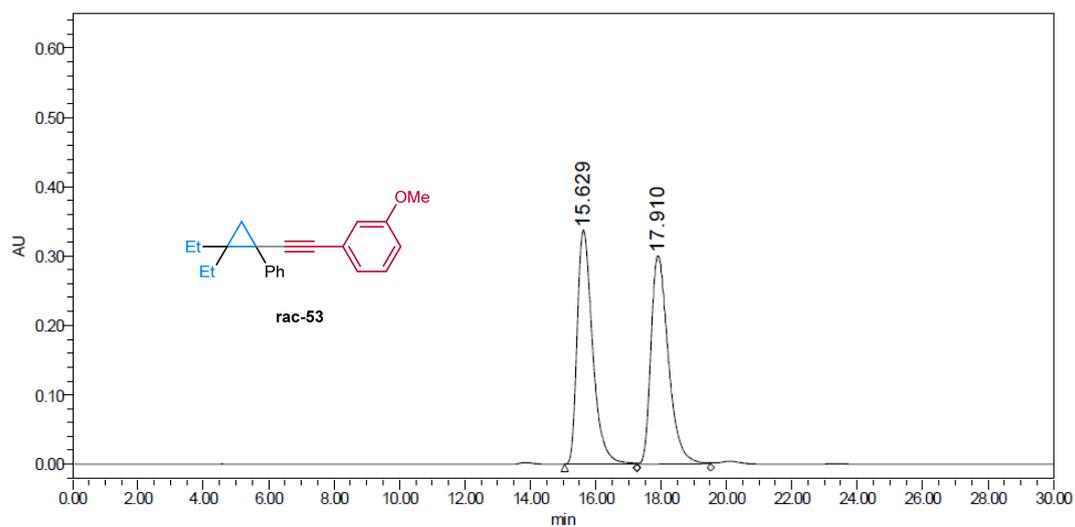


Peak Table

PDA Ch1 254nm

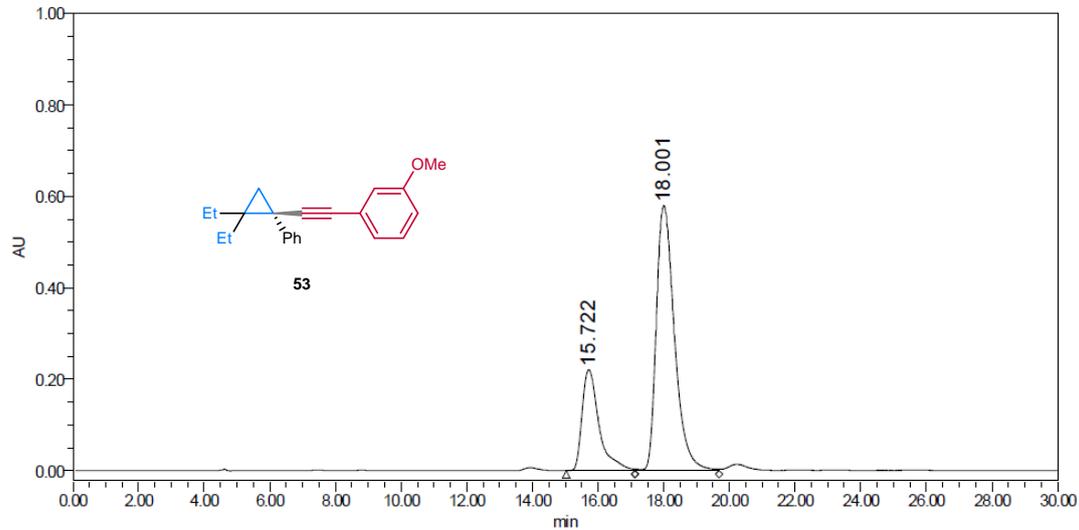
Peak#	Ret. Time	Area	Area%
1	22.483	2304047	6.709
2	24.743	32038821	93.291

PDA 254nm

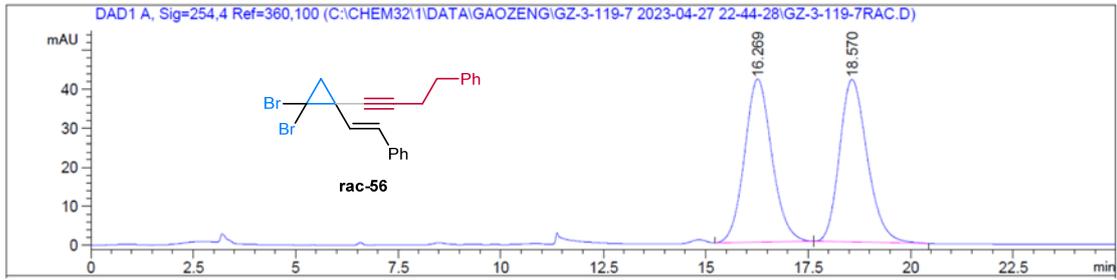


	RT	Area	% Area	Height
1	15.629	11057312	50.16	337071
2	17.910	10984757	49.84	300573

PDA 254nm



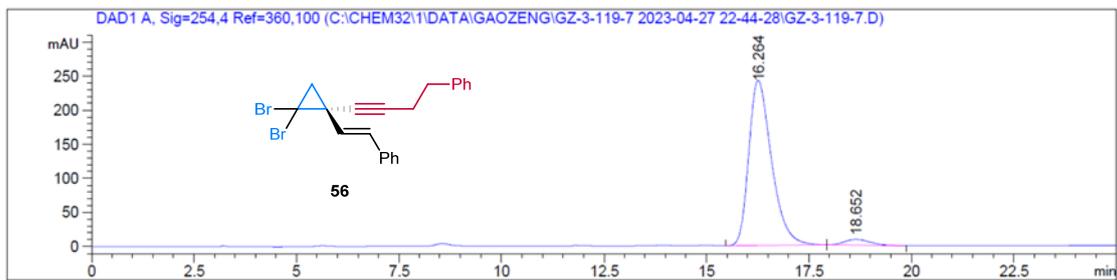
	RT	Area	% Area	Height
1	15.722	7938040	26.52	220752
2	18.001	21994050	73.48	578724



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.269	BB	0.7137	1944.04089	41.86842	49.6874
2	18.570	MF R	0.7870	1968.49829	41.68915	50.3126

Totals : 3912.53918 83.55756

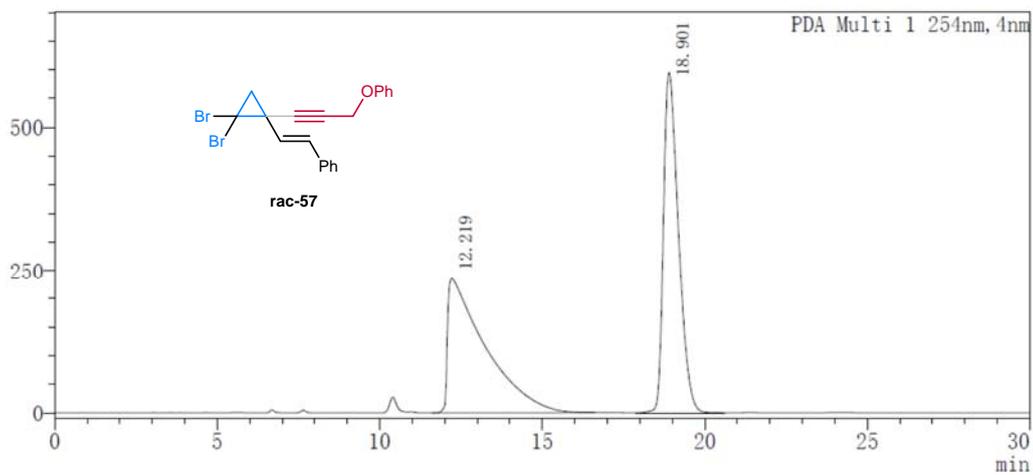


Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.264	BB	0.5913	9374.26074	242.35936	96.2334
2	18.652	BB	0.6747	366.91513	8.51500	3.7666

Totals : 9741.17587 250.87436

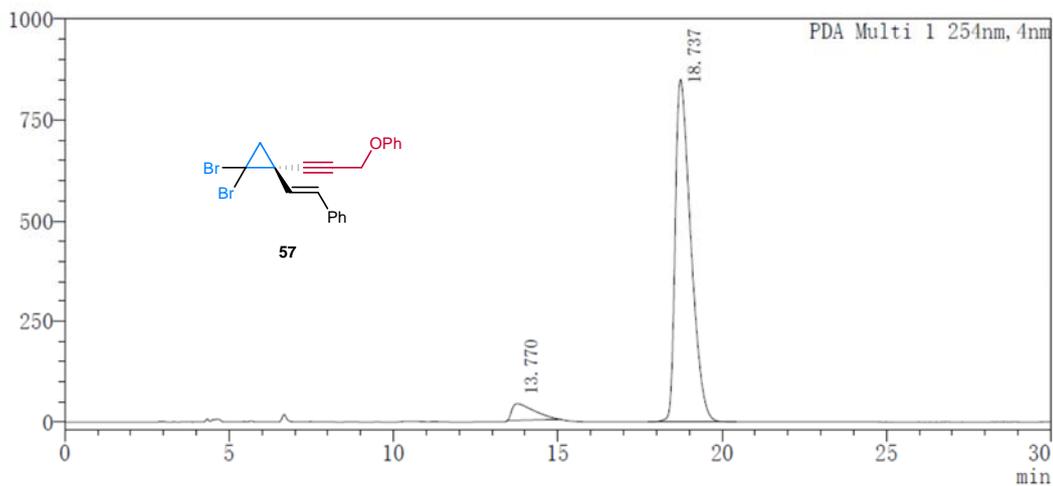
mAU



PDA Ch1 254nm

T	Hight	Area	Area%
12.219	234716	18945511	49.774
18.901	595081	19117369	50.226

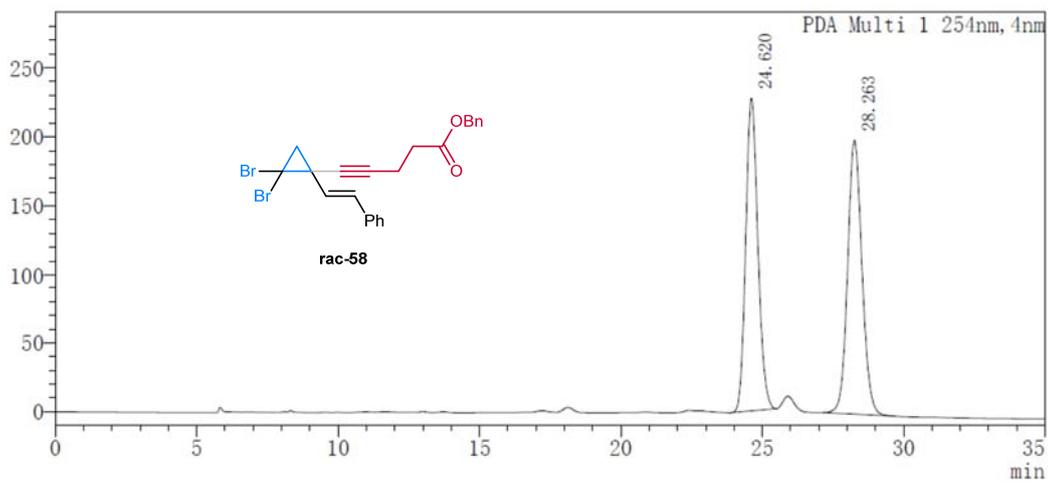
mAU



PDA Ch1 254nm

T	Hight	Area	Area%
13.770	41311	1956001	6.519
18.737	850446	28047385	93.481

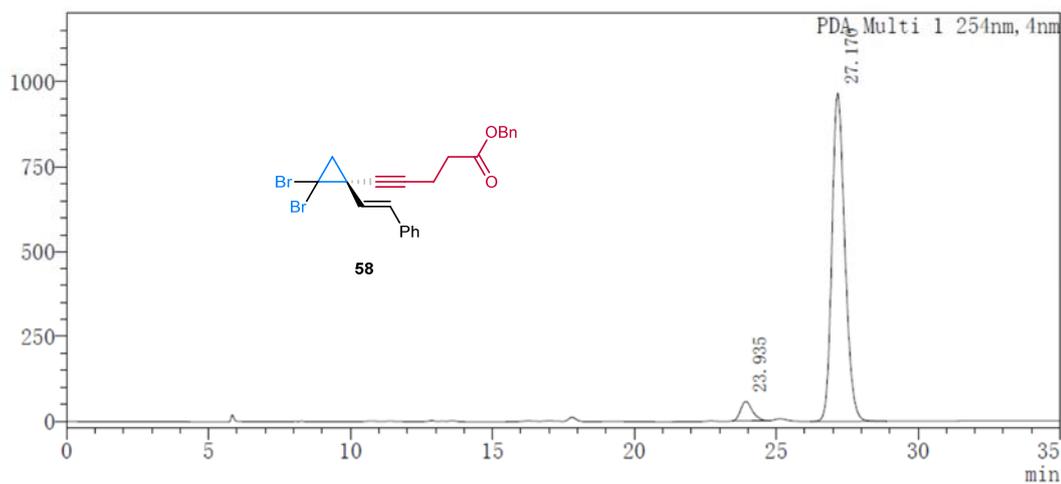
mAU



PDA Ch1 254nm

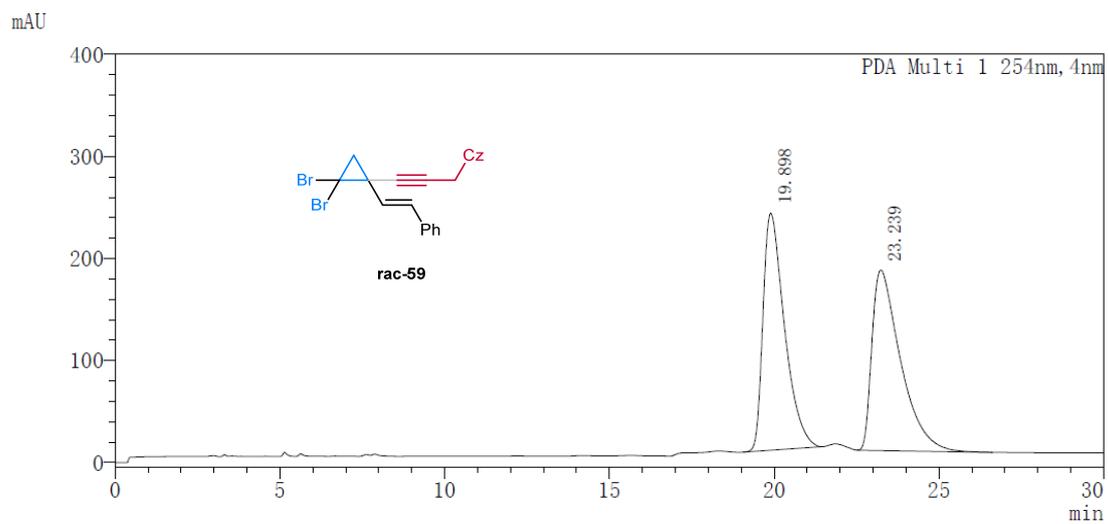
T	Hight	Area	Area%
24.620	227597	6810328	49.139
28.263	199360	7048916	50.861

mAU



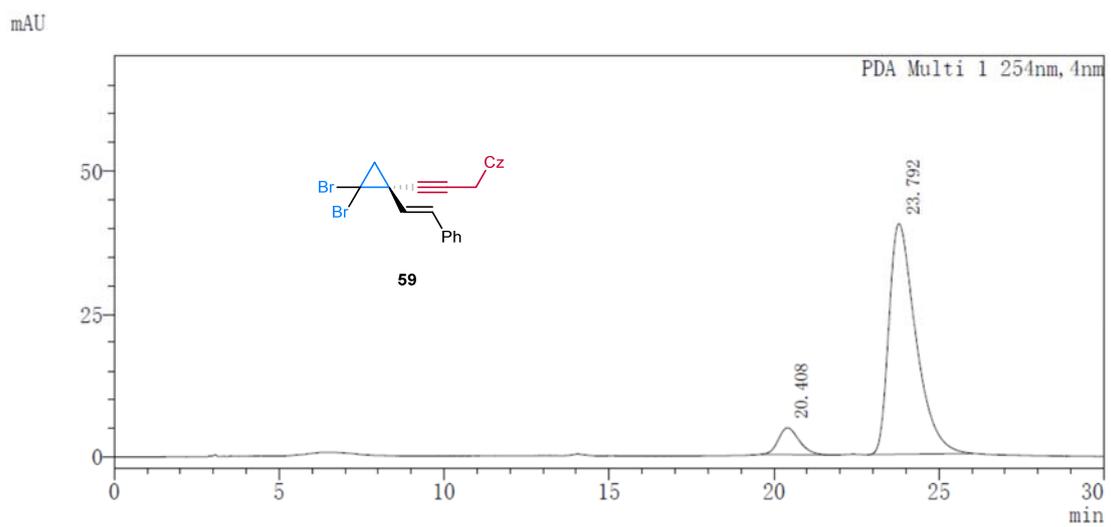
PDA Ch1 254nm

T	Hight	Area	Area%
23.935	57261	1655643	5.129
27.170	966127	30621966	94.871



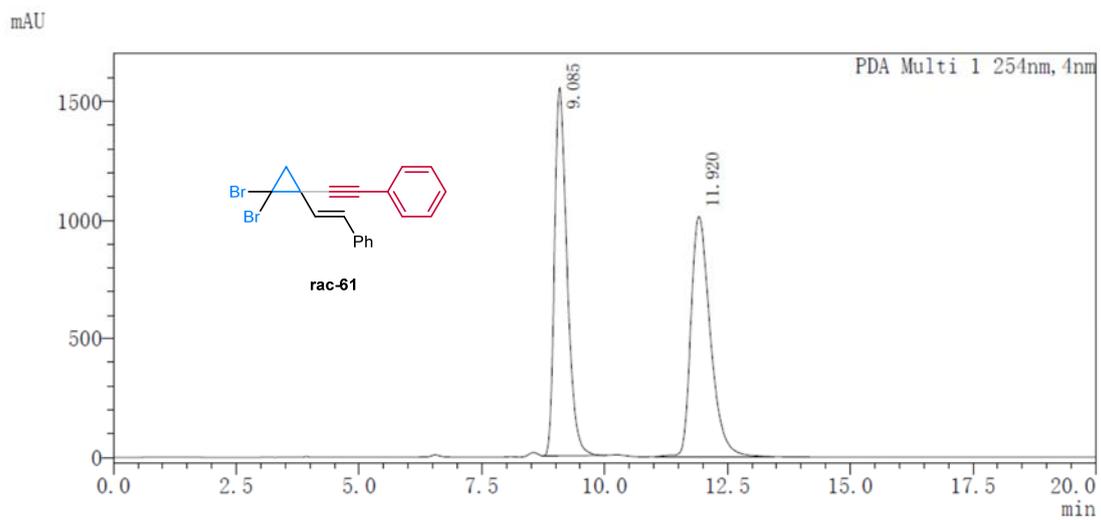
PDA Ch1 254nm

T	Hight	Area	Area%
19.898	232374	10555523	49.692
23.239	176952	10686185	50.308



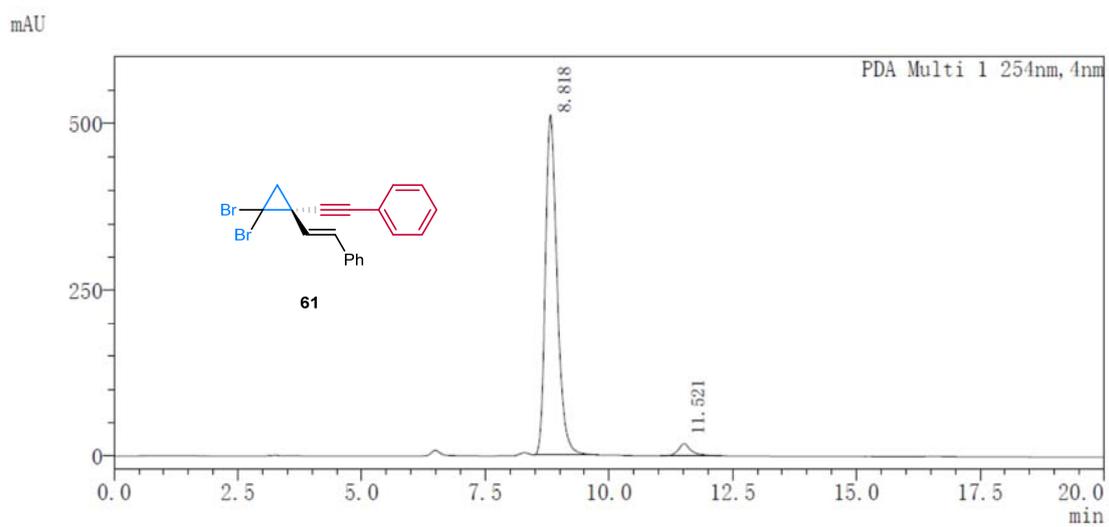
PDA Ch1 254nm

T	Hight	Area	Area%
20.408	4648	202568	8.126
23.792	40352	2290210	91.874



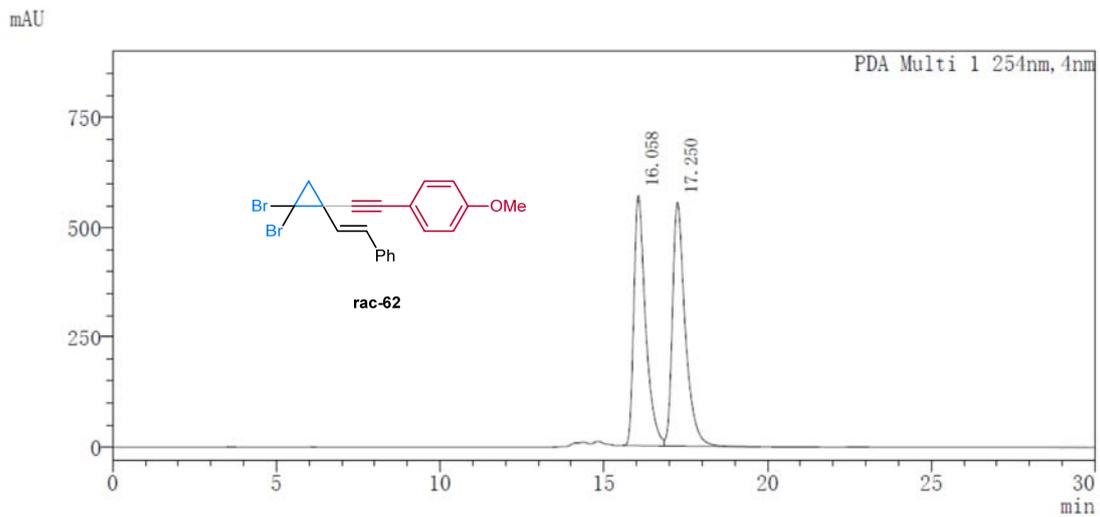
PDA Ch1 254nm

T	Hight	Area	Area%
9.085	1551242	27546234	49.684
11.920	1012713	27896798	50.316



PDA Ch1 254nm

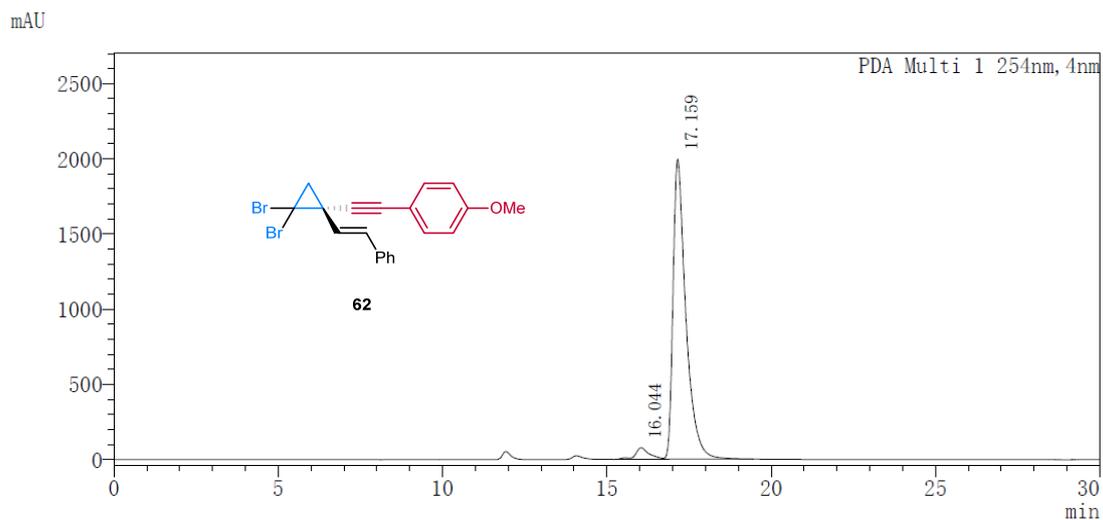
T	Hight	Area	Area%
8.818	511149	8408799	96.264
11.521	18196	326317	3.736



Peak Table

PDA Ch1 254nm

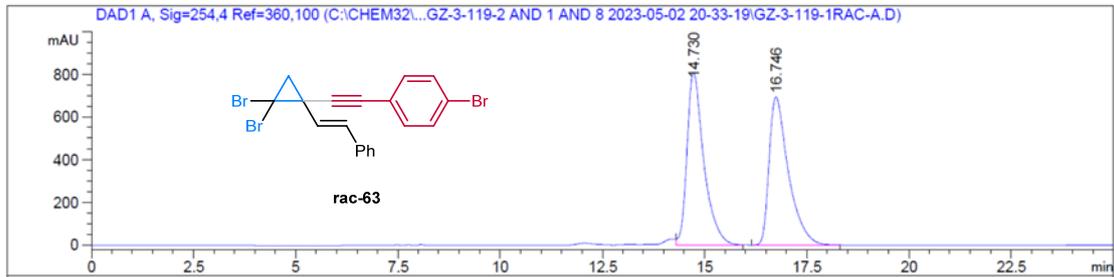
Peak#	Ret. Time	Area	Area%
1	16.058	14189895	48.504
2	17.250	15065385	51.496



Peak Table

PDA Ch1 254nm

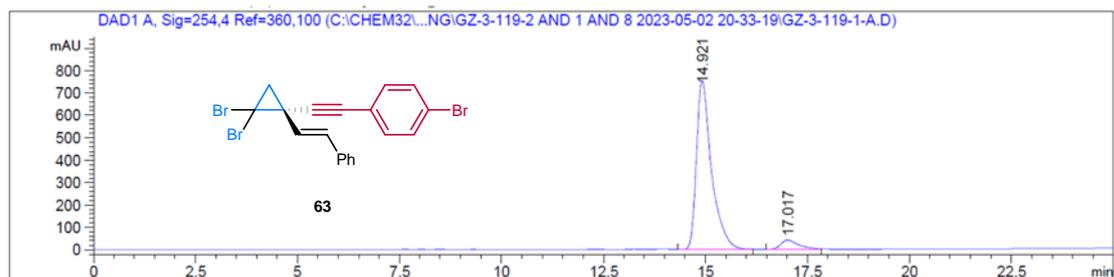
Peak#	Ret. Time	Area	Area%
1	16.044	2246226	3.998
2	17.159	53939471	96.002



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.730	MF R	0.4773	2.31847e4	809.56775	50.2729
2	16.746	MF R	0.5508	2.29330e4	693.98761	49.7271

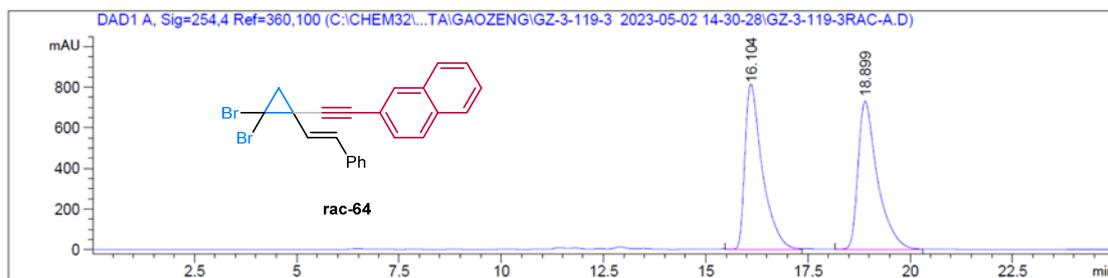
Totals : 4.61178e4 1503.55536



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.921	MF R	0.4257	1.92792e4	754.73895	93.9676
2	17.017	MF R	0.4973	1237.65125	41.48273	6.0324

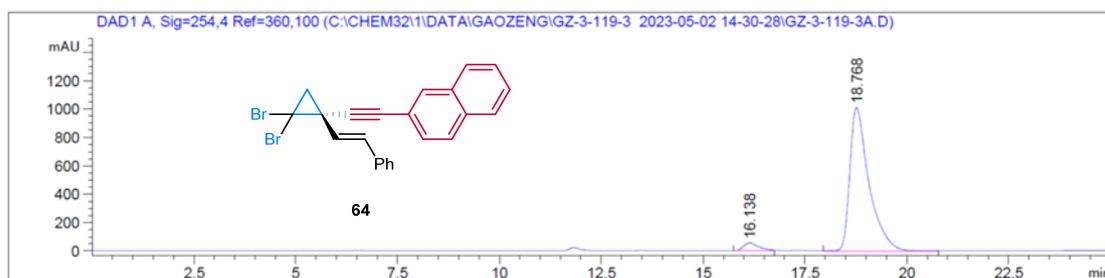
Totals : 2.05169e4 796.22168



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.104	FM R	0.4938	2.41761e4	815.91705	49.9974
2	18.899	FM R	0.5514	2.41786e4	730.85938	50.0026

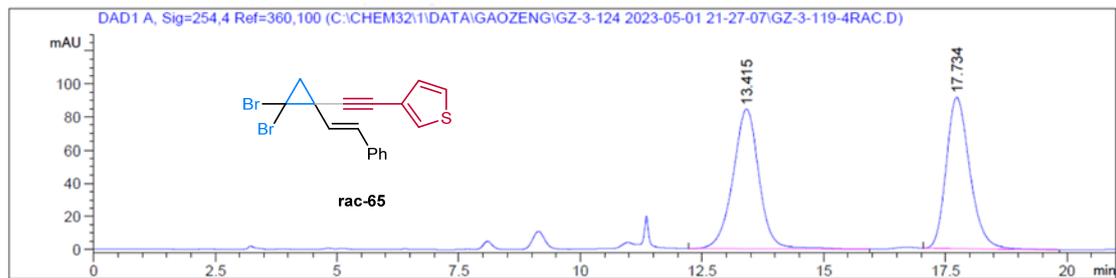
Totals : 4.83547e4 1546.77643



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.138	MM R	0.4422	1474.19019	55.56740	4.2096
2	18.768	MM R	0.5521	3.35453e4	1012.71283	95.7904

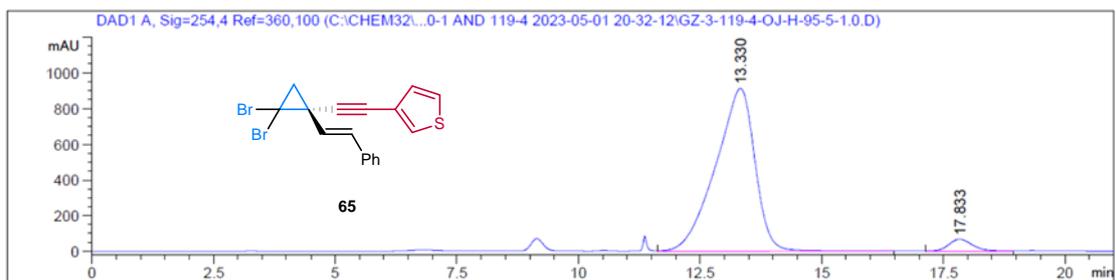
Totals : 3.50195e4 1068.28023



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.415	BB	0.5682	3155.50928	84.40516	50.5428
2	17.734	BB	0.5198	3087.73828	91.47199	49.4572

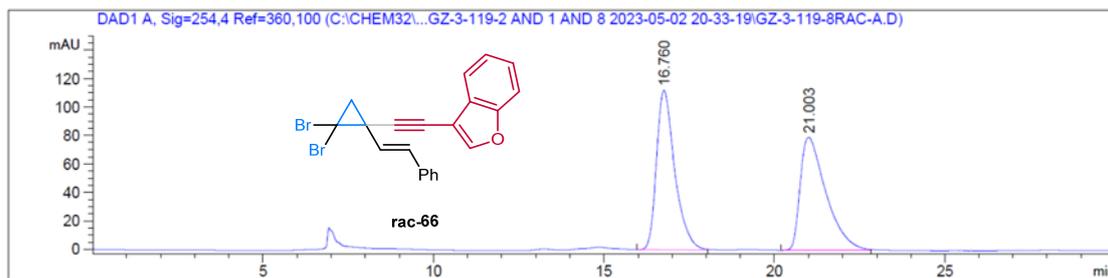
Totals : 6243.24756 175.87715



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.330	VB	0.8117	5.12696e4	912.16748	95.9131
2	17.833	BB	0.5082	2184.61230	65.99548	4.0869

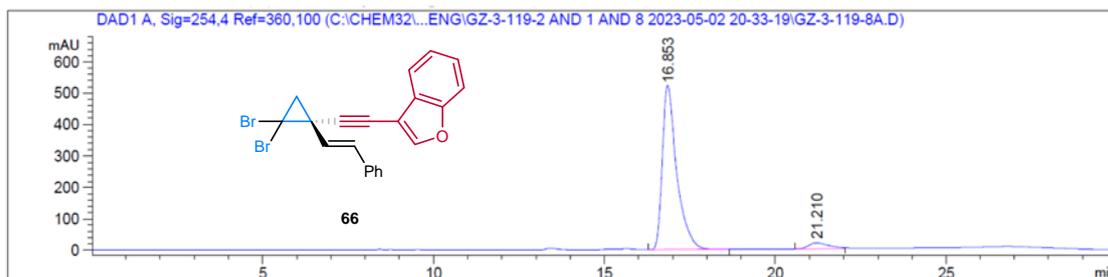
Totals : 5.34543e4 978.16296



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.760	MF R	0.6206	4180.24316	112.25492	49.9308
2	21.003	MF R	0.8810	4191.82861	79.29884	50.0692

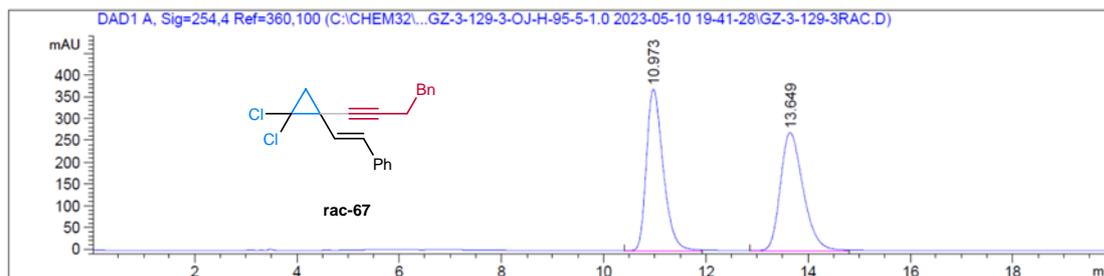
Totals : 8372.07178 191.55376



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.853	BB	0.4313	1.52880e4	522.61011	95.3272
2	21.210	FM R	0.6873	749.40558	18.17309	4.6728

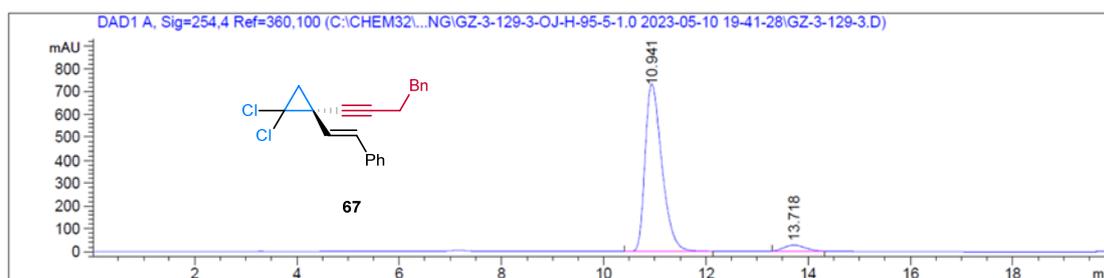
Totals : 1.60375e4 540.78320



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.973	MF R	0.3788	8414.79785	370.27197	50.1266
2	13.649	MF R	0.5157	8372.29883	270.60547	49.8734

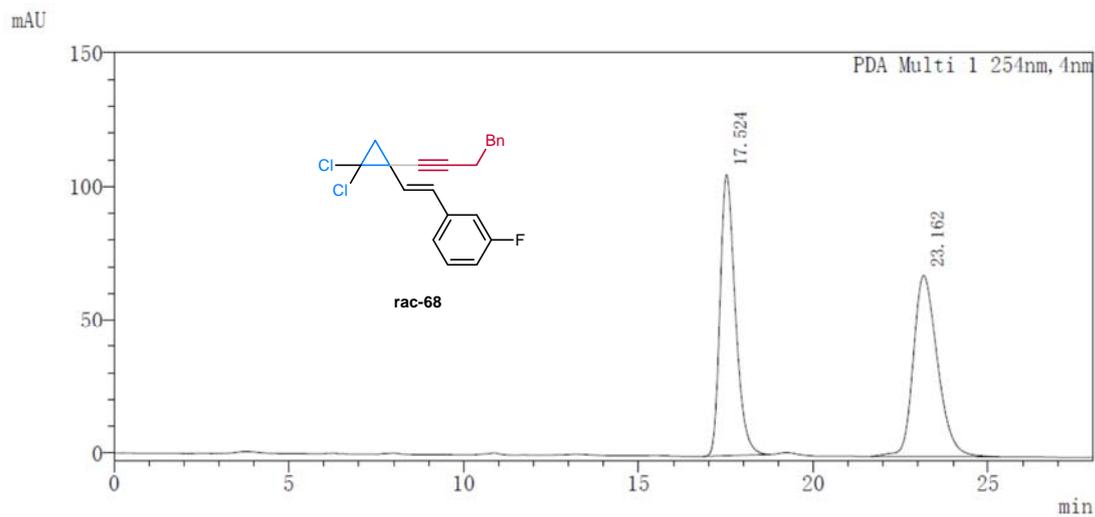
Totals : 1.67871e4 640.87744



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

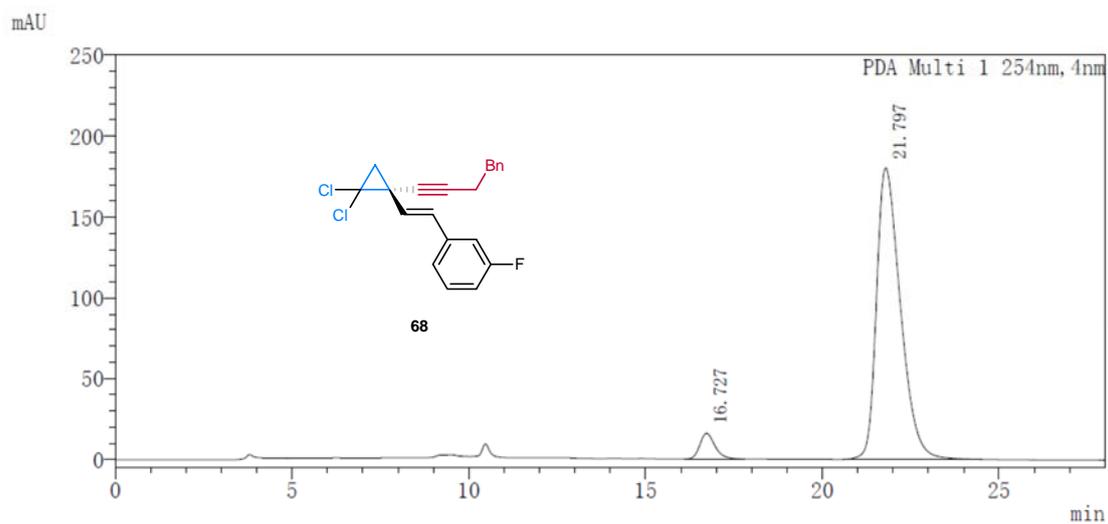
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.941	MF R	0.3809	1.67404e4	732.52246	95.2343
2	13.718	MF R	0.5094	837.72638	27.40740	4.7657

Totals : 1.75781e4 759.92986



PDA Ch1 254nm

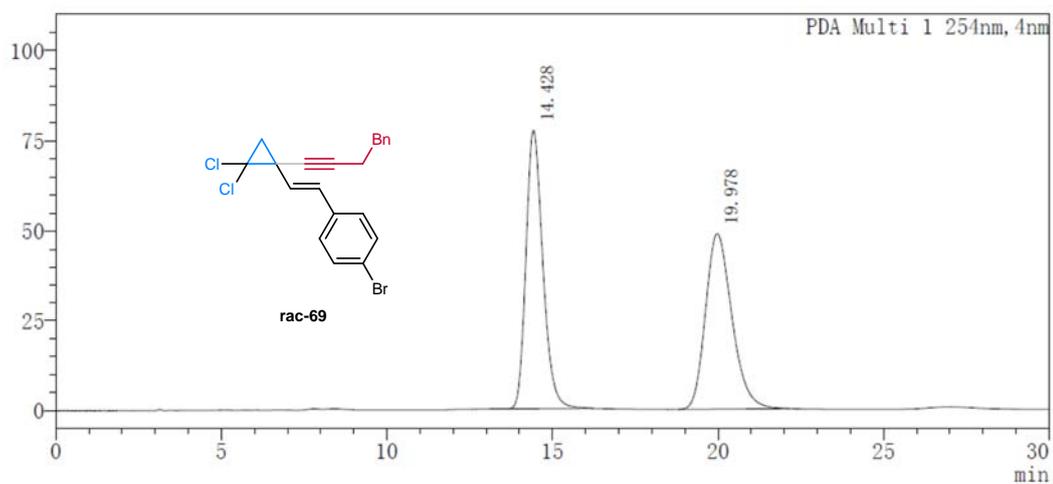
T	Hight	Area	Area%
17.524	105474	3206114	49.513
23.162	68032	3269184	50.487



PDA Ch1 254nm

T	Hight	Area	Area%
16.727	15742	464992	5.196
21.797	180224	8483691	94.804

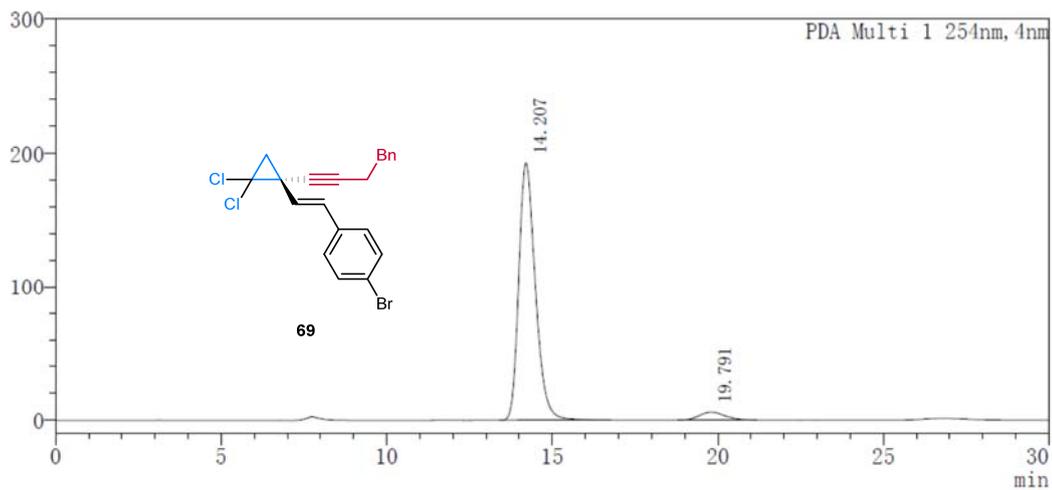
mAU



PDA Ch1 254nm

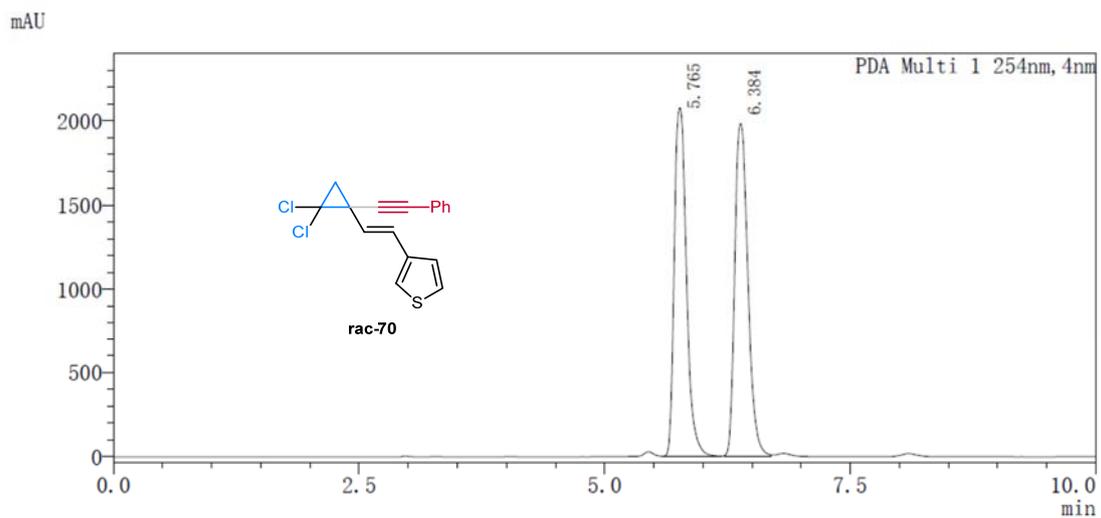
T	Hight	Area	Area%
14.428	77376	2748660	50.262
19.978	48959	2719977	49.738

mAU



PDA Ch1 254nm

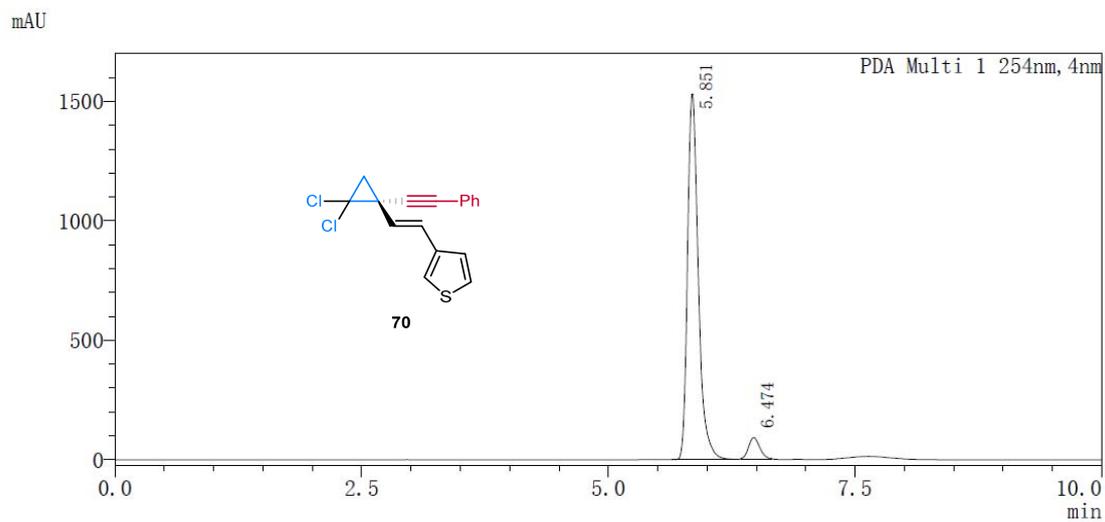
T	Hight	Area	Area%
14.207	192787	6696638	95.393
19.791	5953	323416	4.607



Peak Table

PDA Ch1 254nm

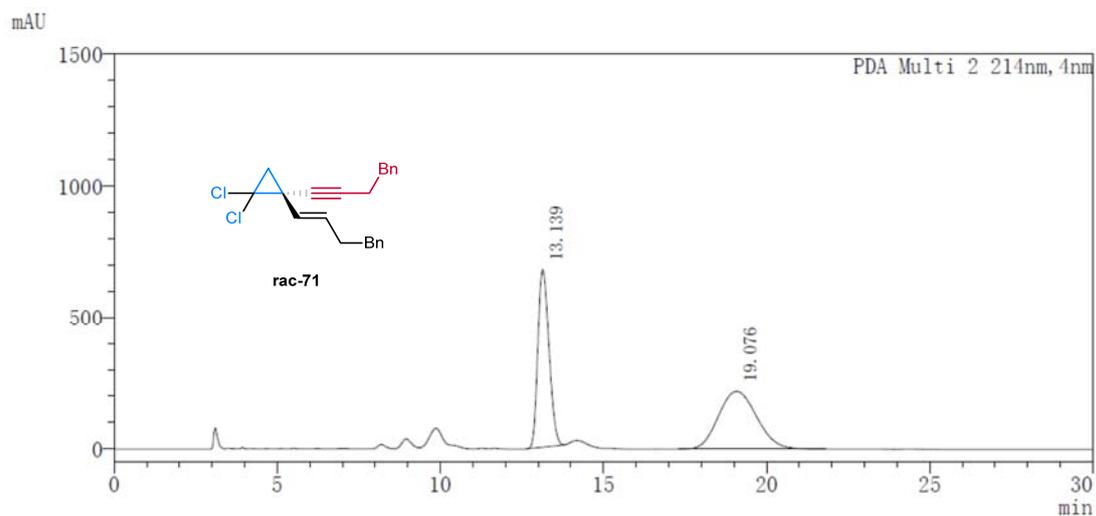
Peak#	Ret. Time	Area	Area%
1	5.765	17993793	49.297
2	6.384	18507089	50.703



Peak Table

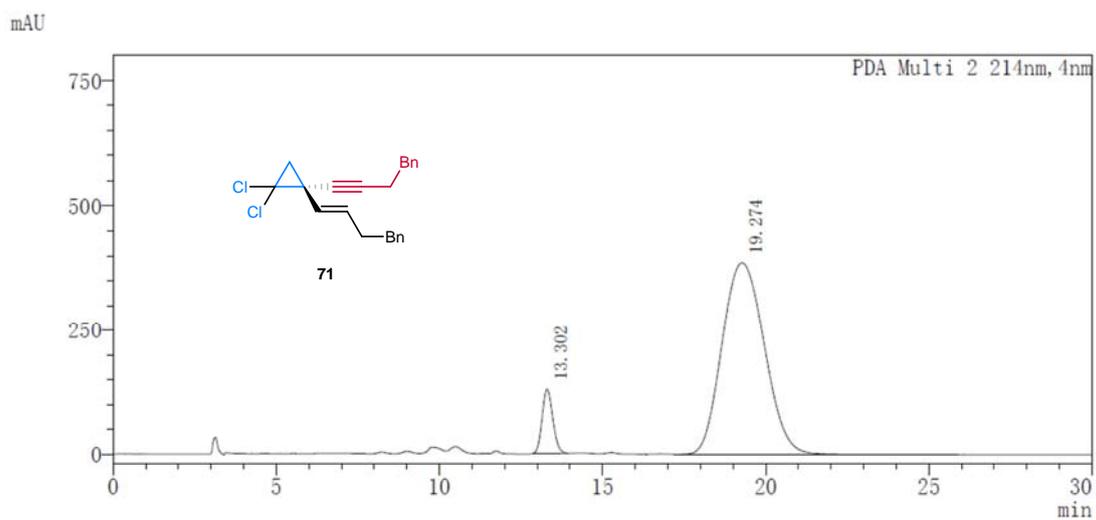
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	5.851	11604836	93.978
2	6.474	743580	6.022



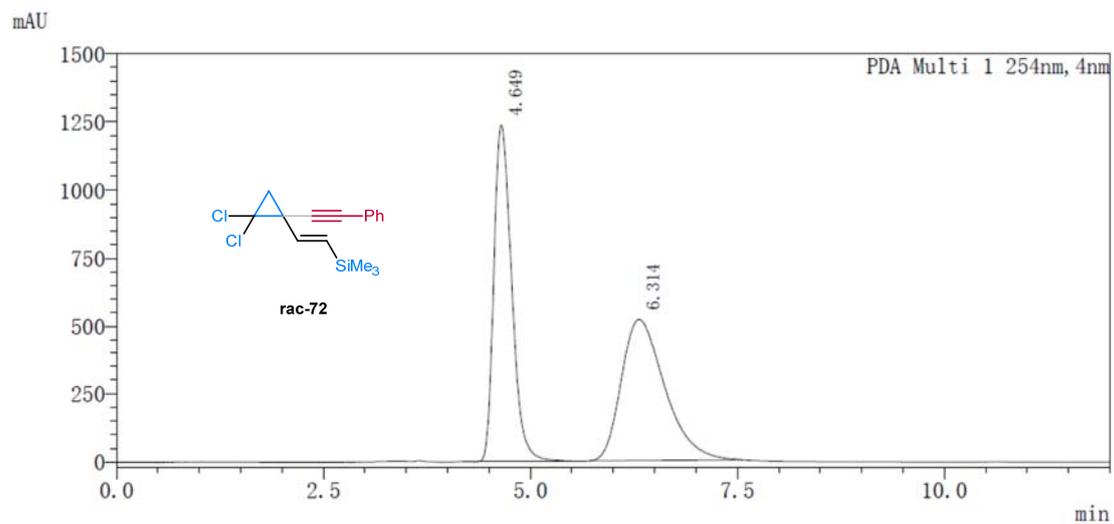
PDA Ch2 214nm

T	Hight	Area	Area%
13.139	675572	16087953	47.413
19.076	218525	17843866	52.587



PDA Ch2 214nm

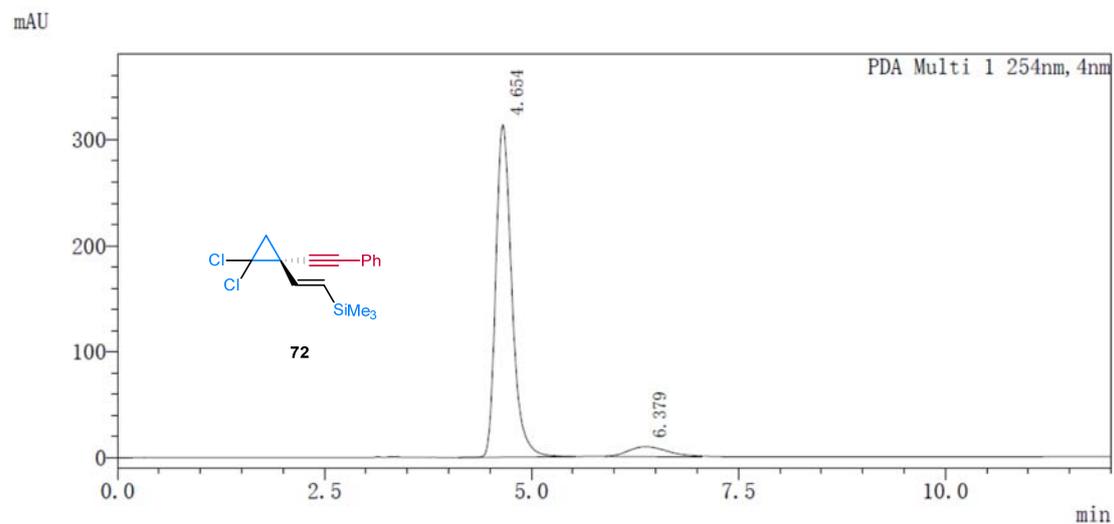
T	Hight	Area	Area%
13.302	129934	2962018	7.832
19.274	386926	34856516	92.168



Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	4.649	18482556	49.415
2	6.314	18919850	50.585

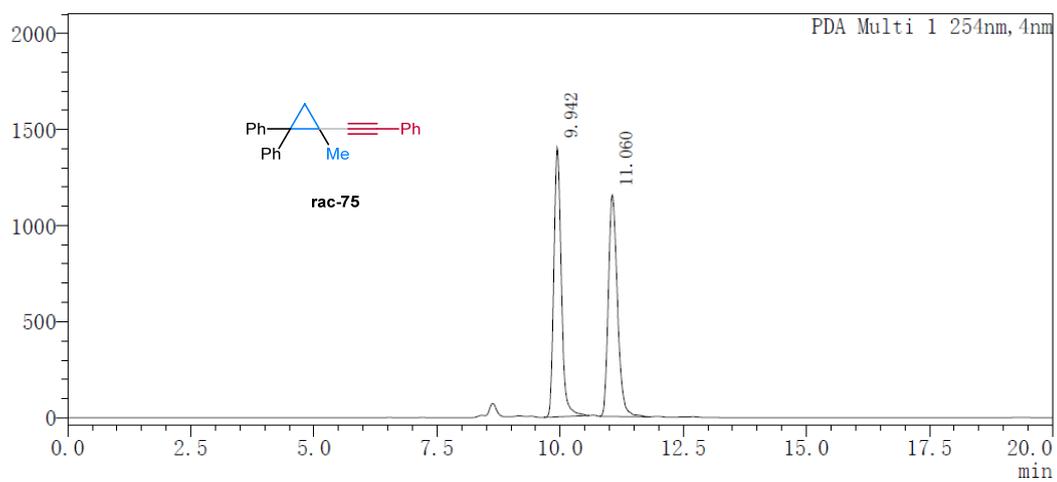


Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	4.654	4217850	93.197
2	6.379	307889	6.803

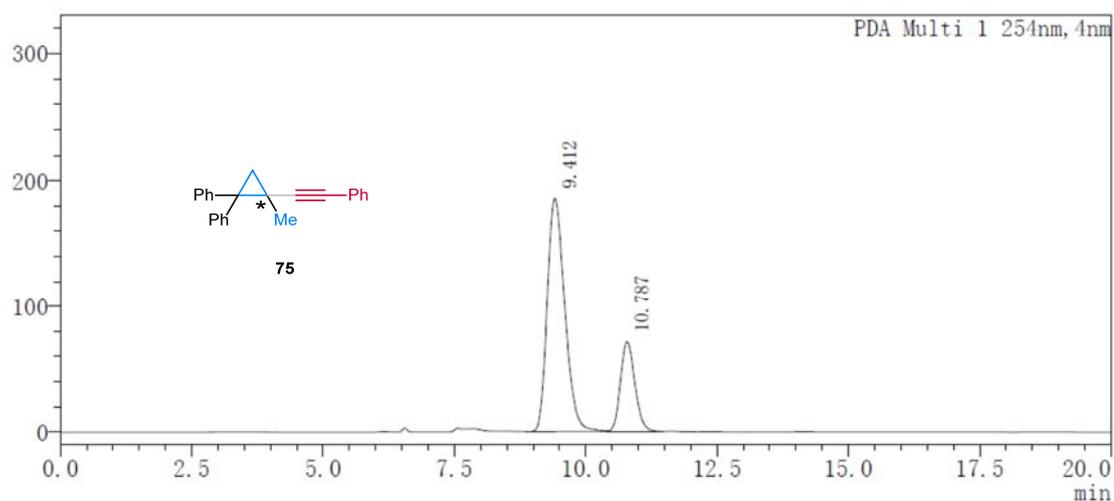
mAU



PDA Ch1 254nm

T	Hight	Area	Area%
9.942	1402210	14934785	50.314
11.060	1151799	14748238	49.686

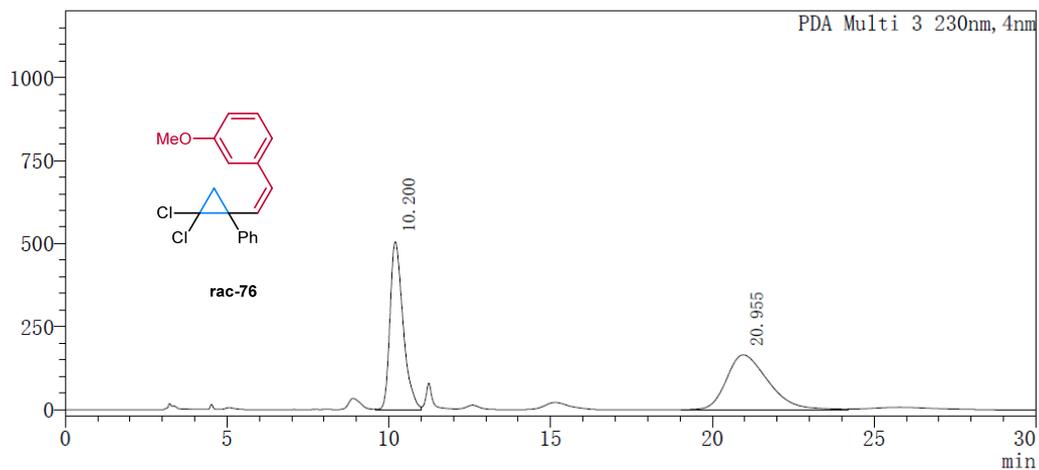
mAU



PDA Ch1 254nm

T	Hight	Area	Area%
9.412	185701	4313143	76.051
10.787	71332	1358264	23.949

mAU

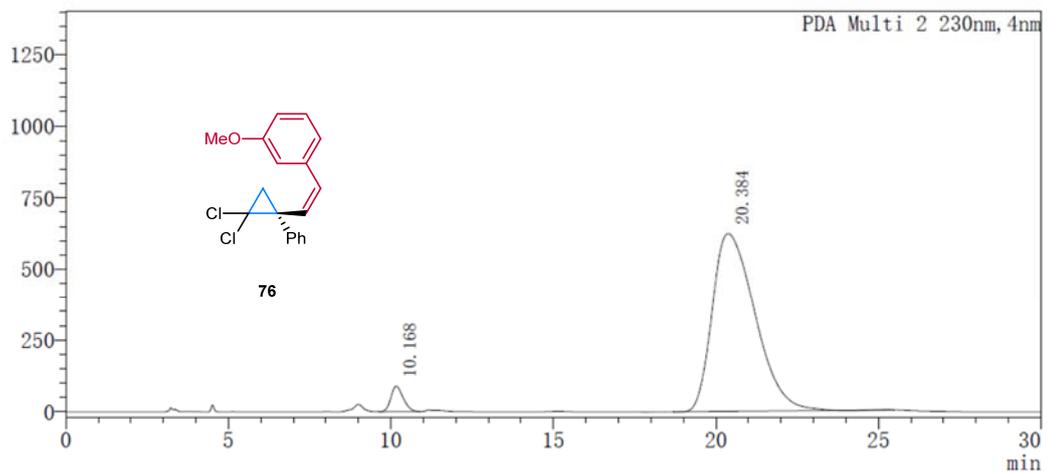


Peak Table

PDA Ch3 230nm

Peak#	Ret. Time	Area	Area%
1	10.200	14213112	49.125
2	20.955	14719539	50.875

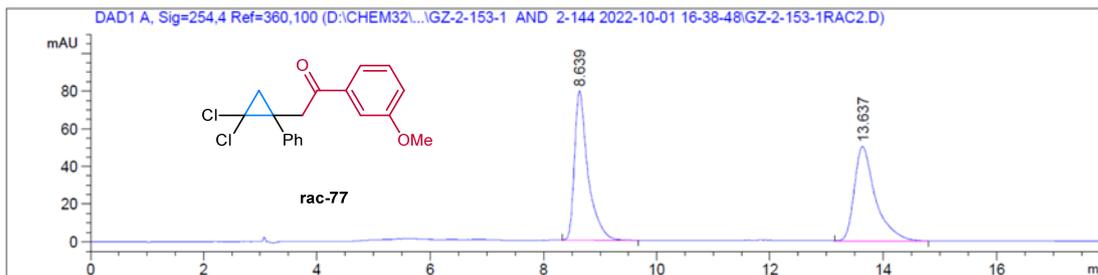
mAU



Peak Table

PDA Ch2 230nm

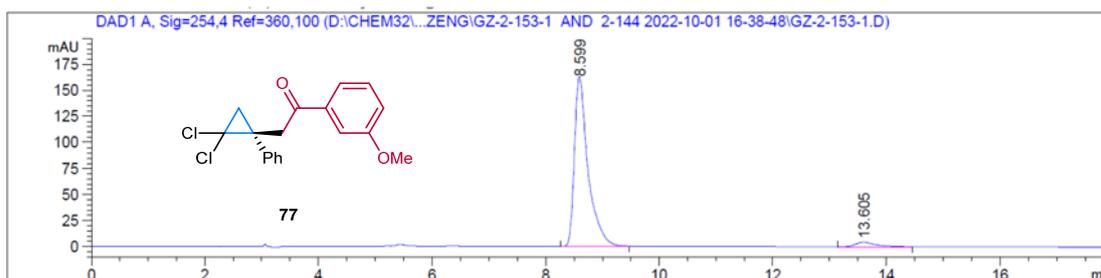
Peak#	Ret. Time	Area	Area%
1	10.168	2355249	3.976
2	20.384	56882947	96.024



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.639	BB	0.2426	1303.38879	78.94127	50.1596
2	13.637	BB	0.3801	1295.09631	50.02019	49.8404

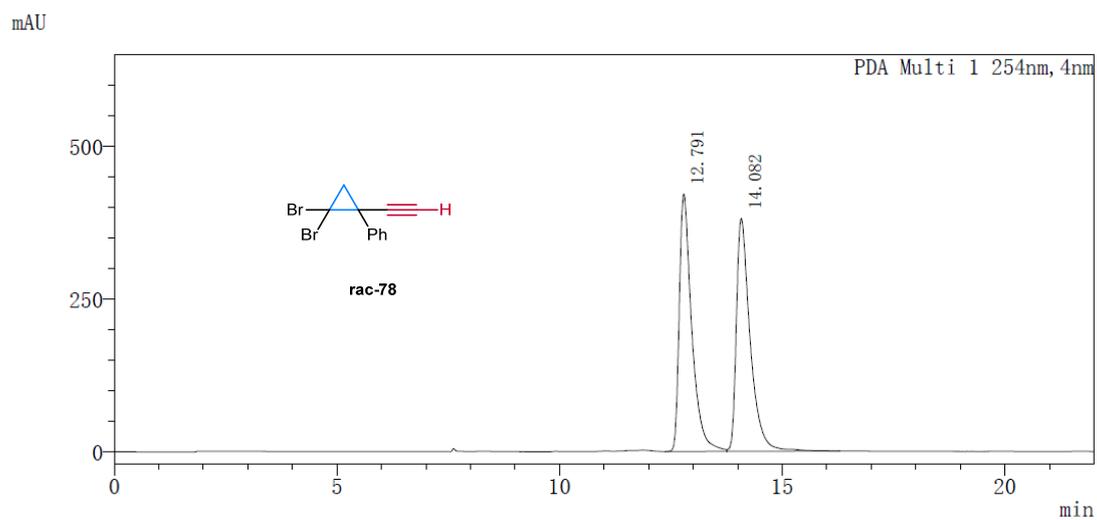
Totals : 2598.48511 128.96146



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.599	BB	0.2430	2708.05469	163.74033	95.9767
2	13.605	BB	0.3703	113.52175	4.35294	4.0233

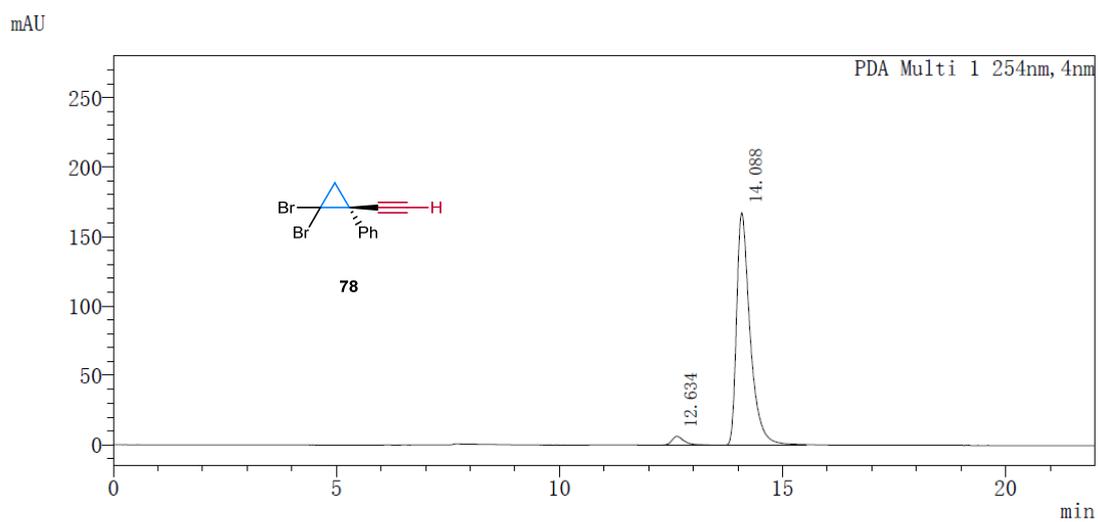
Totals : 2821.57644 168.09326



Peak Table

PDA Ch1 254nm

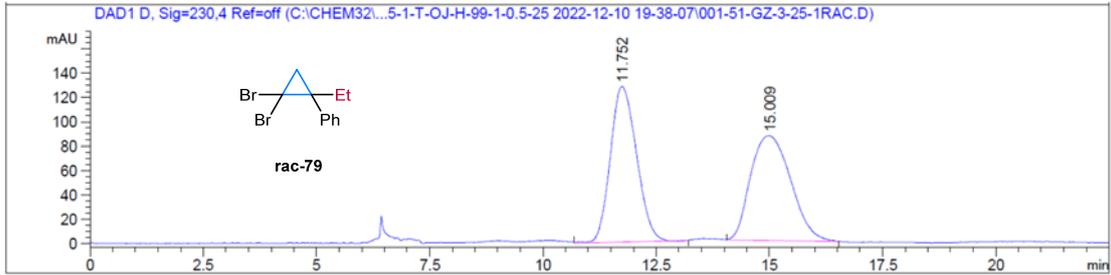
Peak#	Ret. Time	Area	Area%
1	12.791	8183539	49.914
2	14.082	8211605	50.086



Peak Table

PDA Ch1 254nm

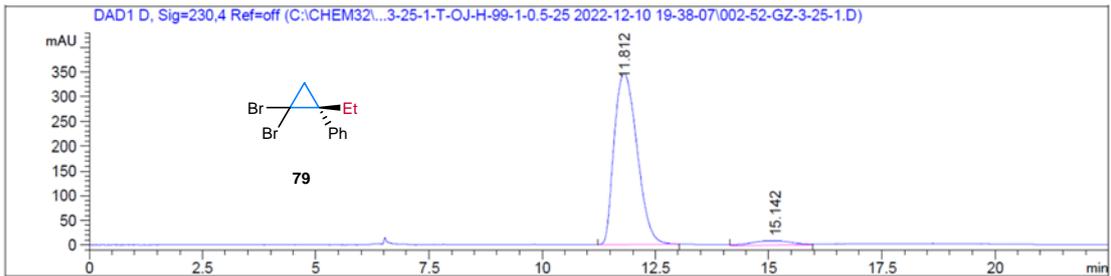
Peak#	Ret. Time	Area	Area%
1	12.634	129166	3.521
2	14.088	3539765	96.479



Signal 4: DAD1 D, Sig=230,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.752	MM R	0.6704	5140.88184	127.80561	49.1224
2	15.009	MM R	1.0321	5324.57373	85.98619	50.8776

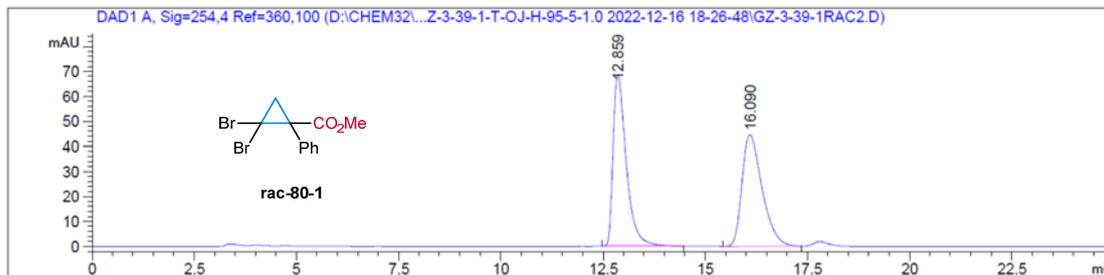
Totals : 1.04655e4 213.79180



Signal 4: DAD1 D, Sig=230,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.812	BV R	0.5667	1.21818e4	346.03873	95.9357
2	15.142	MF R	1.0091	516.08777	8.52367	4.0643

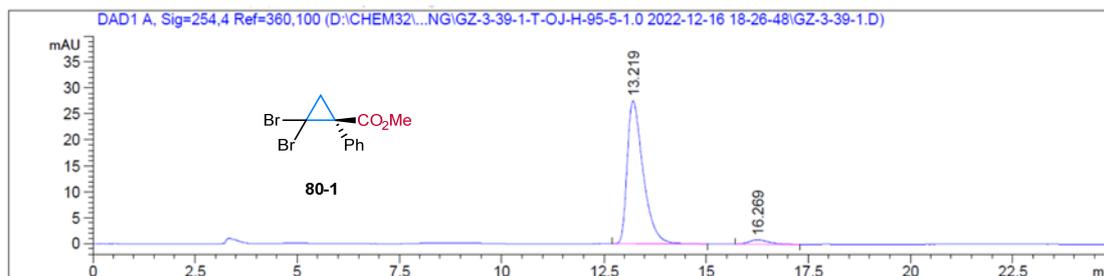
Totals : 1.26979e4 354.56239



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.859	BB	0.3414	1534.81714	68.50484	50.1324
2	16.090	BB	0.5239	1526.71118	44.53648	49.8676

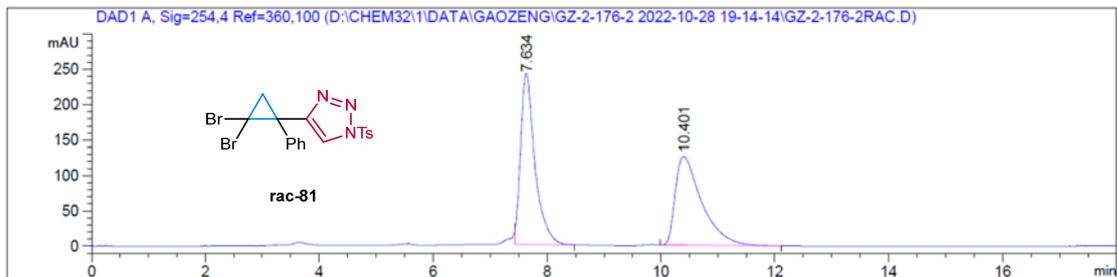
Totals : 3061.52832 113.04132



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.219	BB	0.4093	748.70435	27.53009	96.4218
2	16.269	MM R	0.5523	27.78392	8.38436e-1	3.5782

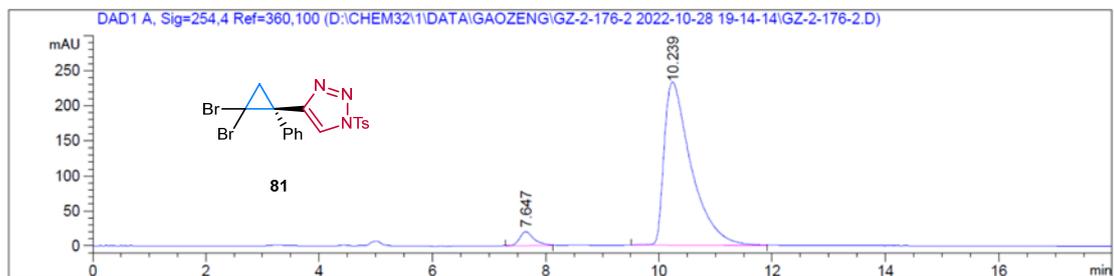
Totals : 776.48826 28.36853



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.634	FM R	0.2911	4235.69629	242.48491	51.0057
2	10.401	BB	0.4714	4068.65649	125.79124	48.9943

Totals : 8304.35278 368.27615

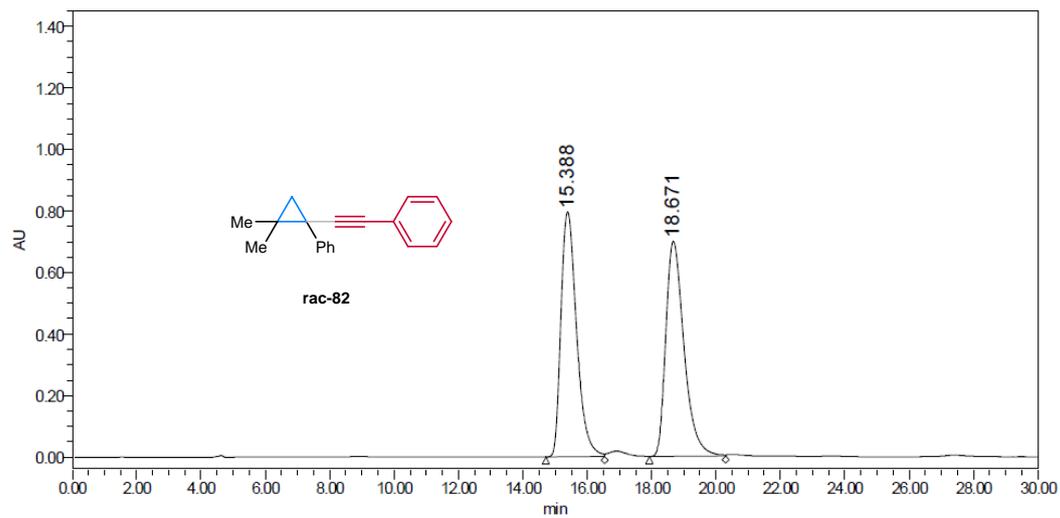


Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.647	FM R	0.2963	357.52658	20.11223	4.4023
2	10.239	MF R	0.5555	7763.85498	232.94995	95.5977

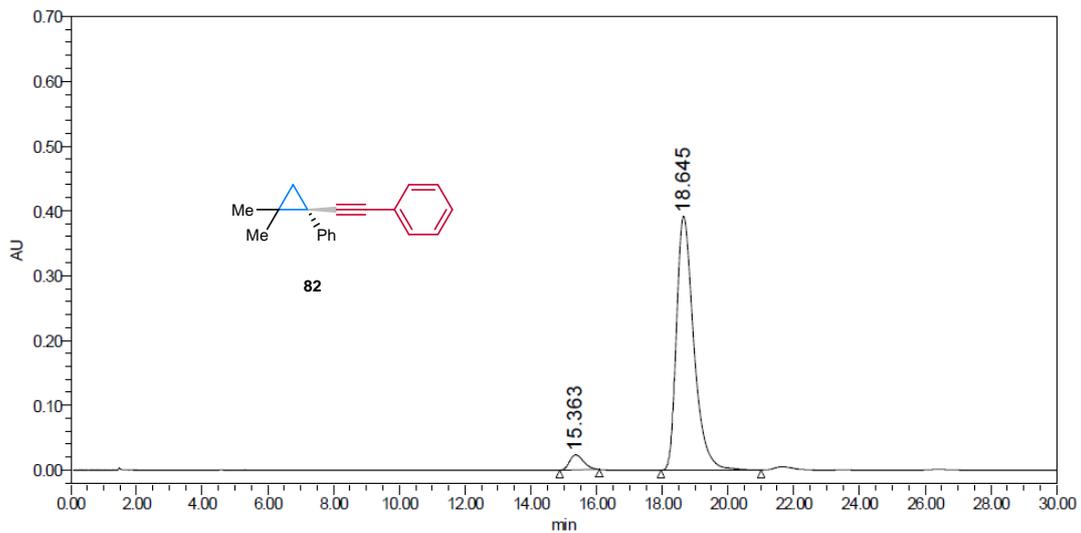
Totals : 8121.38156 253.06219

PDA 254nm

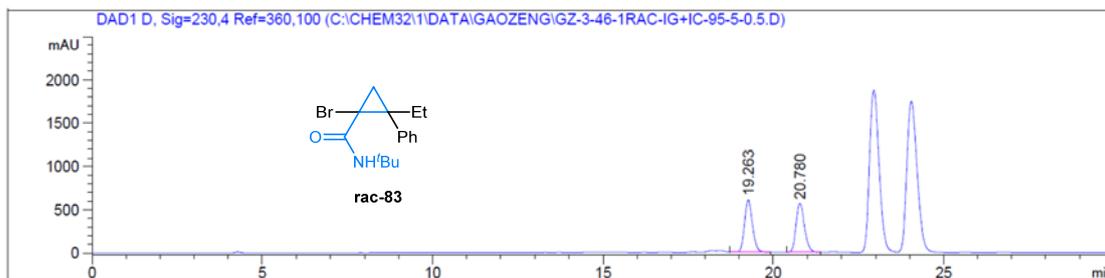


	RT	Area	% Area	Height
1	15.388	26958722	49.43	796031
2	18.671	27581950	50.57	698387

PDA 254nm



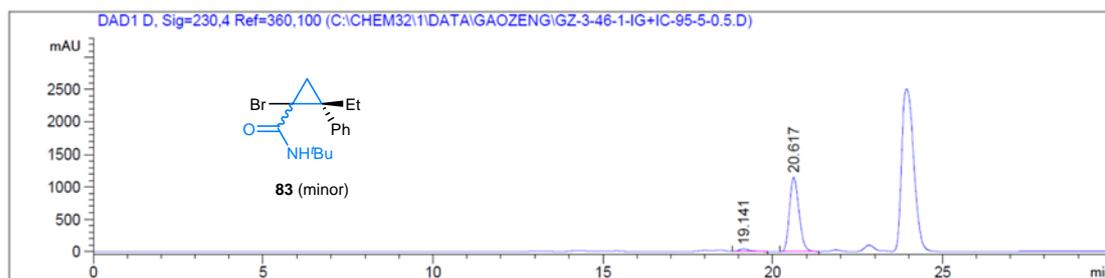
	RT	Area	% Area	Height
1	15.363	682736	4.53	23220
2	18.645	14397750	95.47	391988



Signal 4: DAD1 D, Sig=230,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.263	VB R	0.2501	9776.22852	604.66412	49.9673
2	20.780	MF R	0.2879	9789.02051	566.61035	50.0327

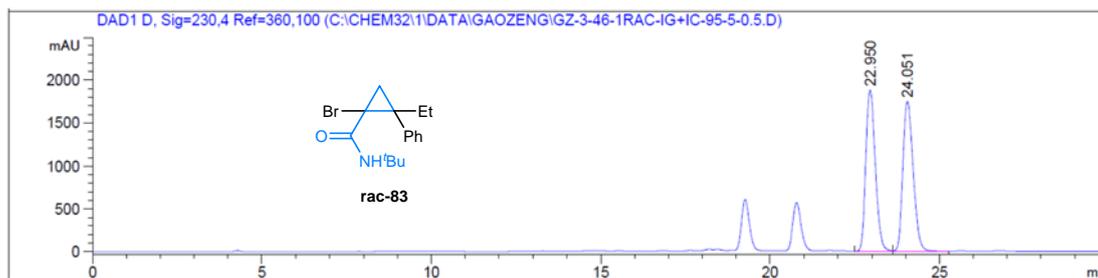
Totals : 1.95652e4 1171.27448



Signal 4: DAD1 D, Sig=230,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.141	VB	0.3118	804.18414	38.47950	3.4646
2	20.617	MF R	0.3249	2.24074e4	1149.60327	96.5354

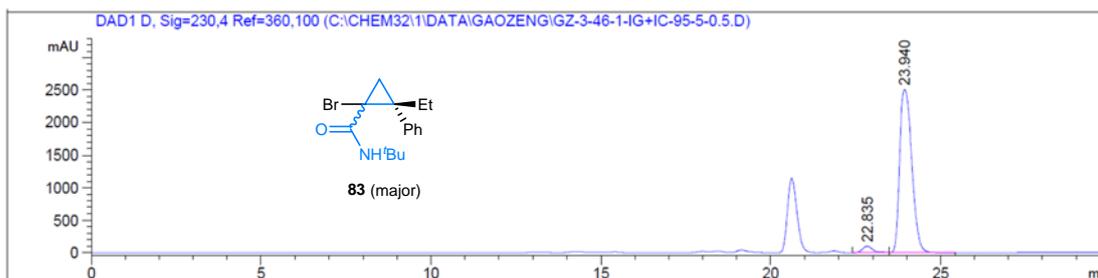
Totals : 2.32115e4 1188.08277



Signal 4: DAD1 D, Sig=230,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.950	BV	0.3079	3.66847e4	1877.72131	49.8516
2	24.051	VB	0.3328	3.69031e4	1744.74841	50.1484

Totals : 7.35878e4 3622.46973

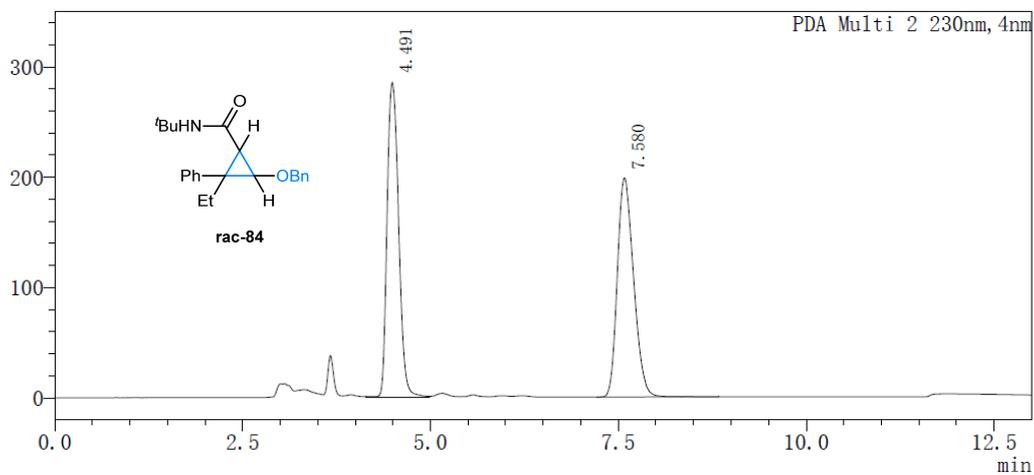


Signal 4: DAD1 D, Sig=230,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.835	BV	0.3290	2216.36816	102.20673	3.4426
2	23.940	VB	0.3932	6.21638e4	2507.36914	96.5574

Totals : 6.43802e4 2609.57587

mAU

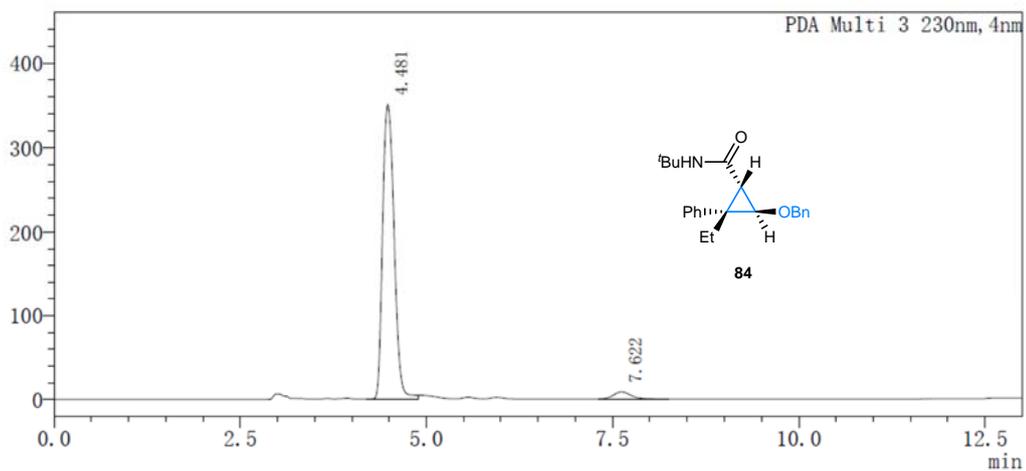


Peak Table

PDA Ch2 230nm

Peak#	Ret. Time	Area	Area%
1	4.491	3037100	50.431
2	7.580	2985129	49.569

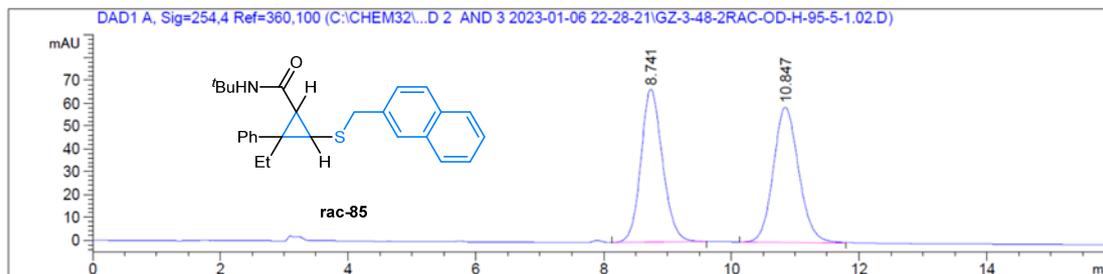
mAU



Peak Table

PDA Ch3 230nm

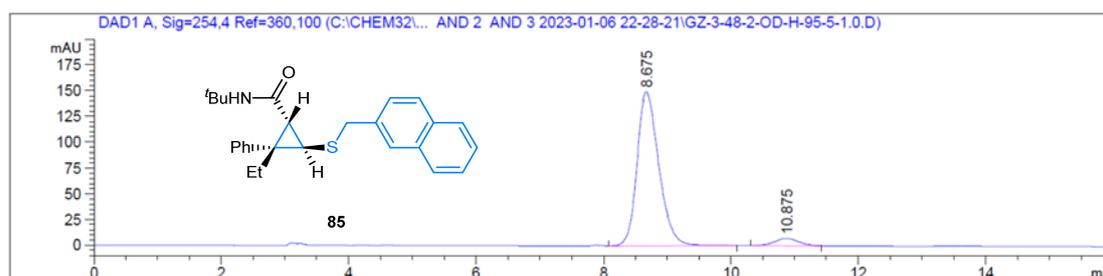
Peak#	Ret. Time	Area	Area%
1	4.481	3772044	96.402
2	7.622	140791	3.598



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.741	BB	0.3603	1575.42773	67.00132	48.9959
2	10.847	MF R	0.4613	1639.99915	59.25490	51.0041

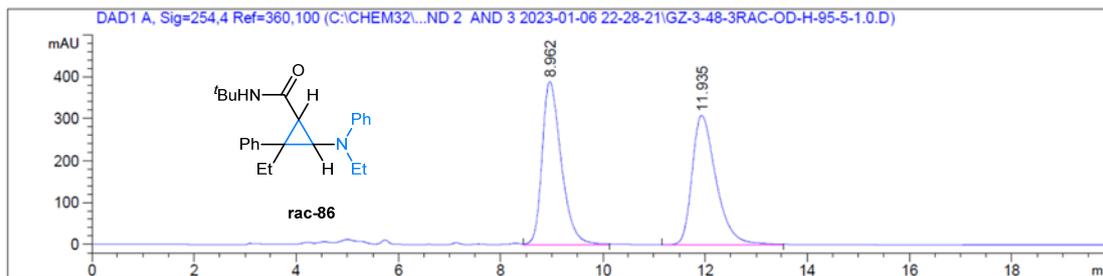
Totals : 3215.42688 126.25622



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.675	BB	0.3623	3540.07471	149.45584	95.0604
2	10.875	MF R	0.4366	183.95291	7.02285	4.9396

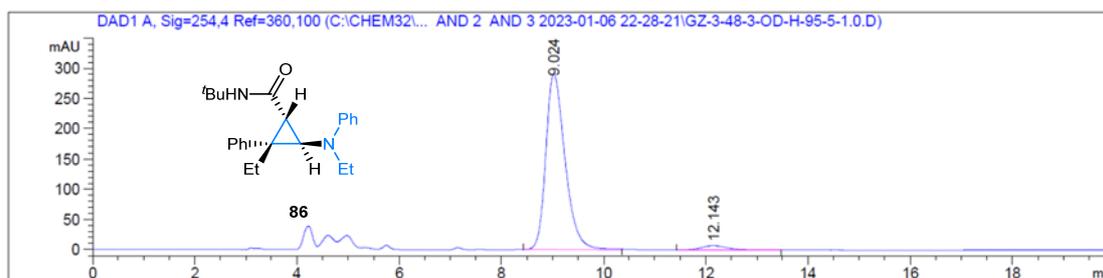
Totals : 3724.02762 156.47869



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.962	MF R	0.4338	1.01135e4	388.57239	50.0728
2	11.935	MF R	0.5454	1.00841e4	308.14670	49.9272

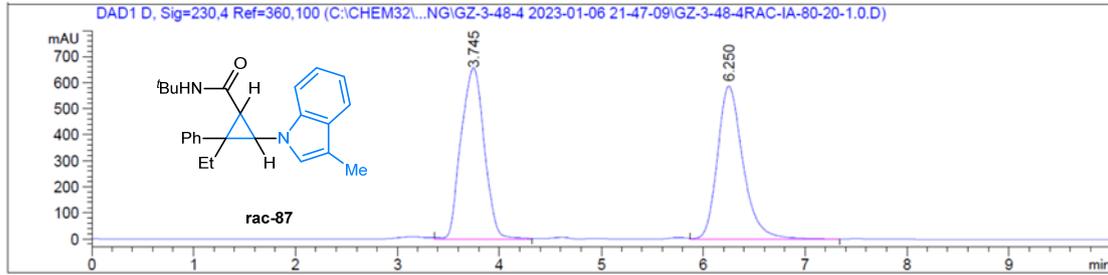
Totals : 2.01976e4 696.71909



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.024	MF R	0.4367	7620.42285	290.82623	96.9401
2	12.143	BB	0.5227	240.53670	6.90020	3.0599

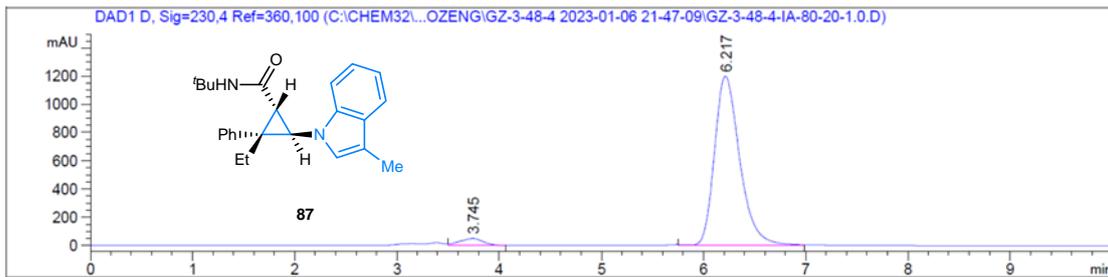
Totals : 7860.95955 297.72643



Signal 4: DAD1 D, Sig=230,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.745	MF R	0.2642	1.04384e4	658.44598	50.5230
2	6.250	FM R	0.2898	1.02223e4	587.94098	49.4770

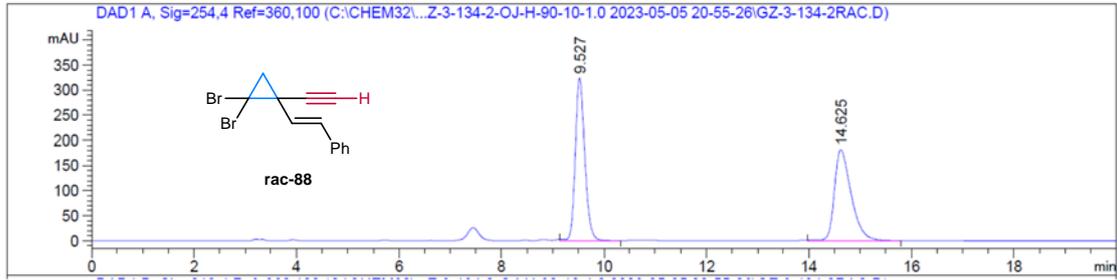
Totals : 2.06607e4 1246.38696



Signal 4: DAD1 D, Sig=230,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.745	VB	0.2353	776.95667	48.92669	3.6129
2	6.217	FM R	0.2880	2.07284e4	1199.61401	96.3871

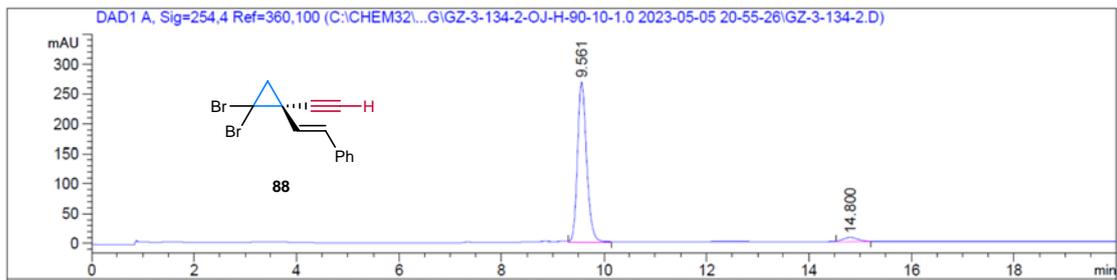
Totals : 2.15053e4 1248.54070



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.527	FM R	0.2142	4160.56885	323.70178	50.2183
2	14.625	MF R	0.3790	4124.39063	181.37109	49.7817

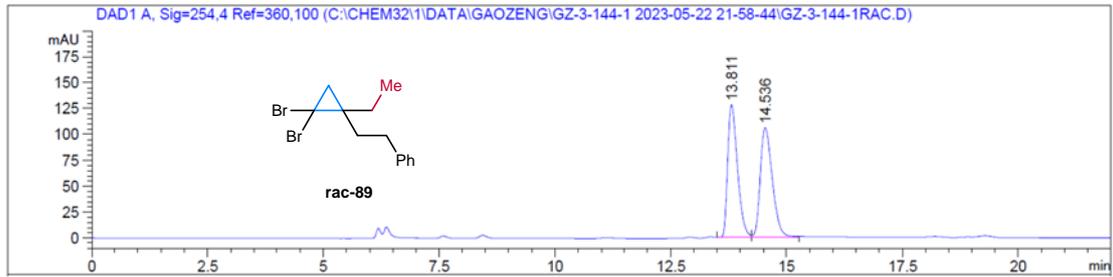
Totals : 8284.95947 505.07288



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.561	MF R	0.2066	3318.20947	267.62881	95.5100
2	14.800	FM R	0.3571	155.99007	7.28092	4.4900

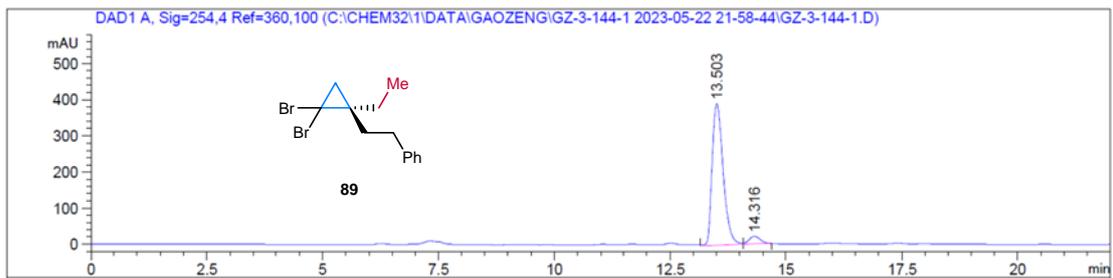
Totals : 3474.19954 274.90973



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.811	BV	0.2275	1886.90088	128.35933	49.4674
2	14.536	MF R	0.3027	1927.53076	106.13022	50.5326

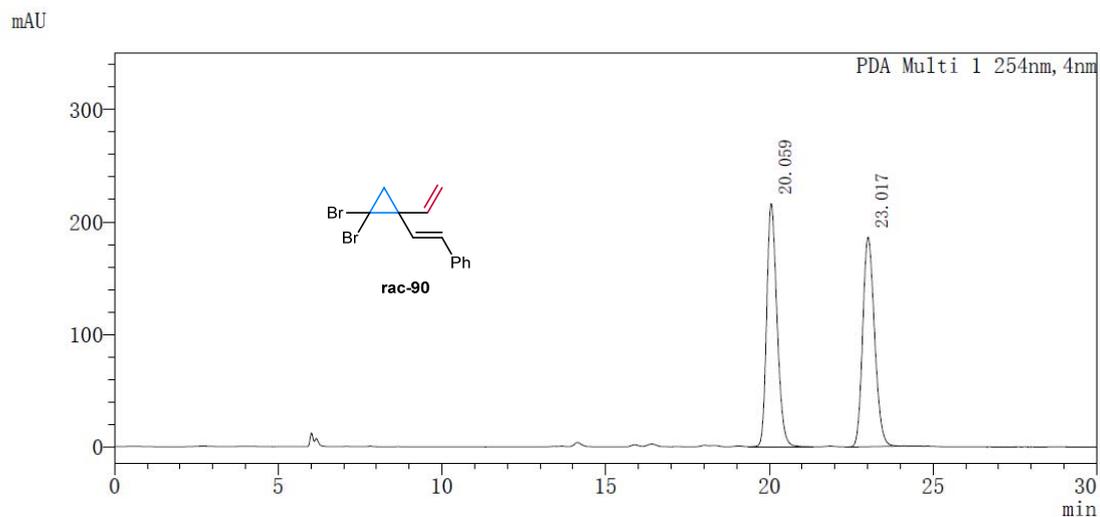
Totals : 3814.43164 234.48955



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.503	MF R	0.2770	6516.35303	392.06116	95.0988
2	14.316	FM R	0.2706	335.84055	20.68396	4.9012

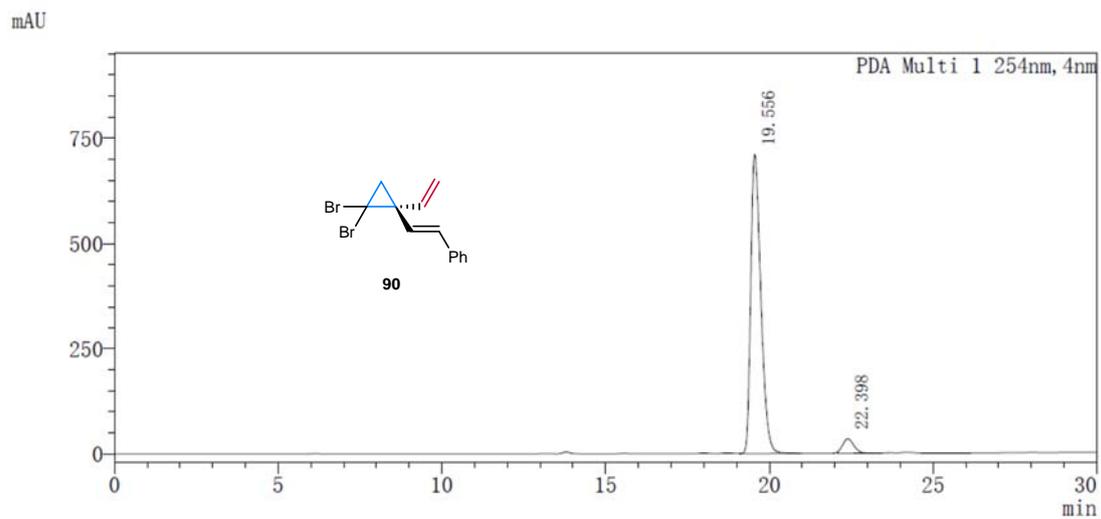
Totals : 6852.19357 412.74512



Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	20.059	4741868	50.320
2	23.017	4681615	49.680

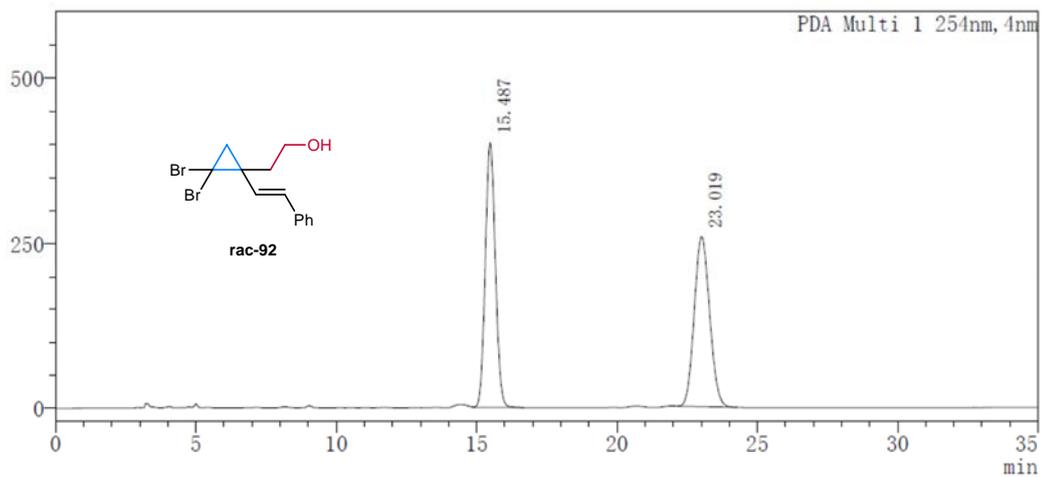


Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	19.556	15187257	94.839
2	22.398	826524	5.161

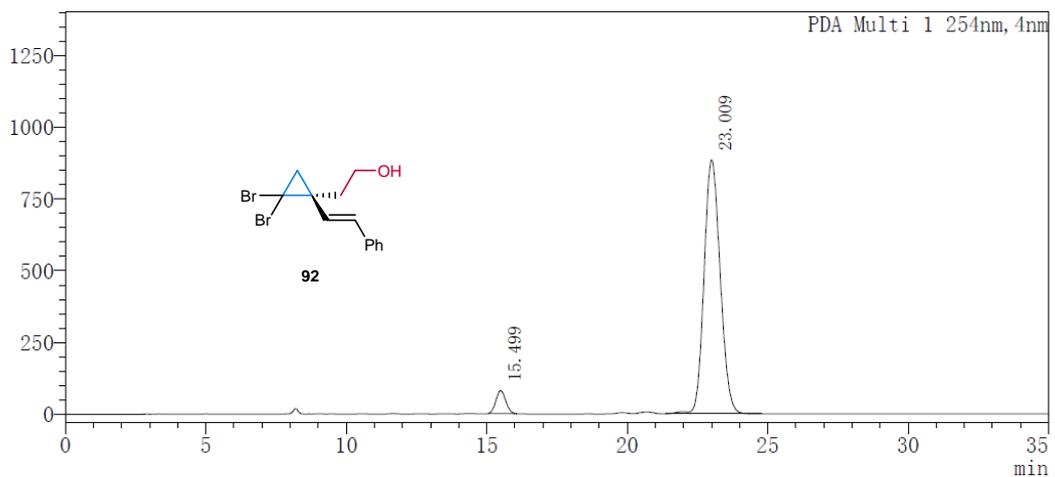
mAU



PDA Ch1 254nm

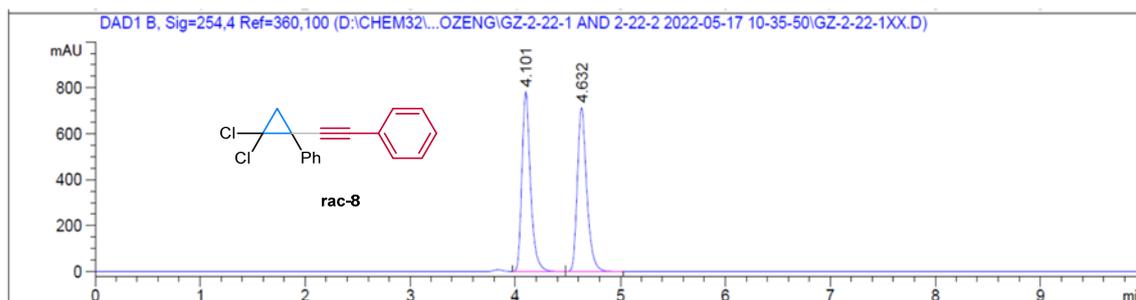
T	Hight	Area	Area%
15.487	401198	9972998	50.298
23.019	258776	9854837	49.702

mAU



PDA Ch1 254nm

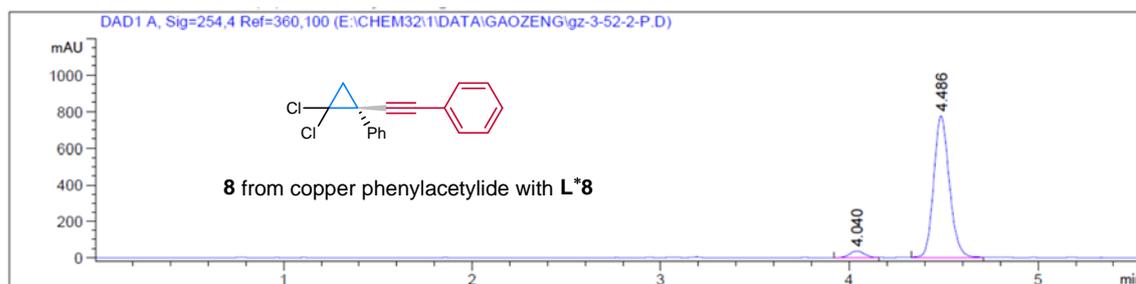
T	Hight	Area	Area%
15.499	79727	1935217	5.189
23.009	884526	35360022	94.811



Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.101	VB	0.0865	4453.23535	781.27679	49.9748
2	4.632	BV	0.0949	4457.73389	713.66992	50.0252

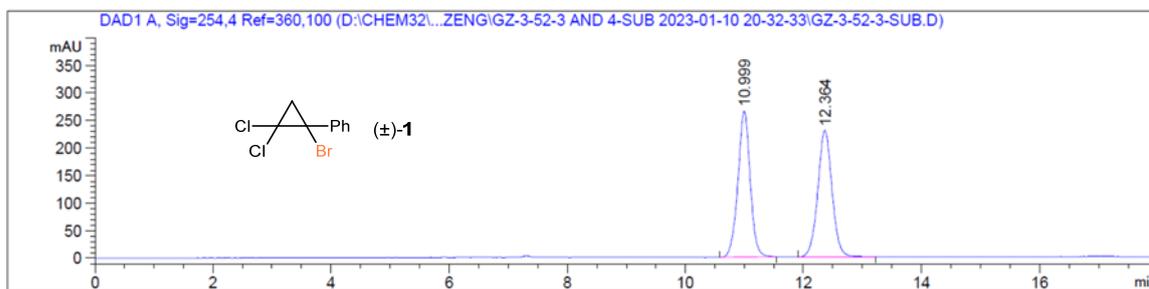
Totals : 8910.96924 1494.94672



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.040	FM R	0.0918	202.39581	36.75843	4.3008
2	4.486	MF R	0.0964	4503.58398	778.42743	95.6992

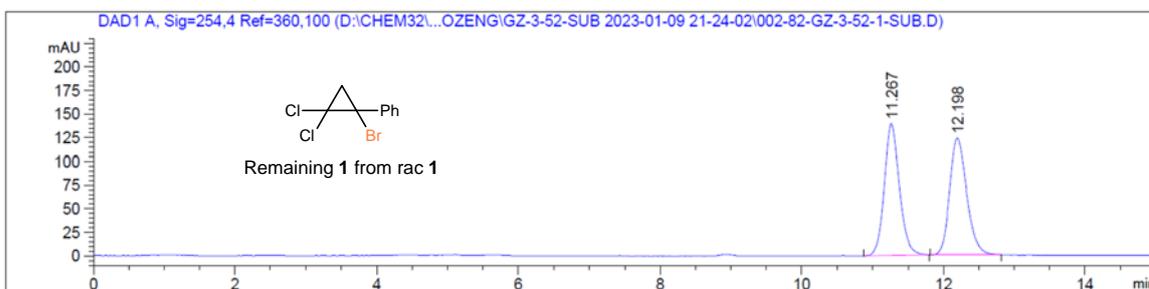
Totals : 4705.97980 815.18586



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.999	BB	0.2193	3838.51709	264.57318	49.9694
2	12.364	BB	0.2555	3843.21069	229.33238	50.0306

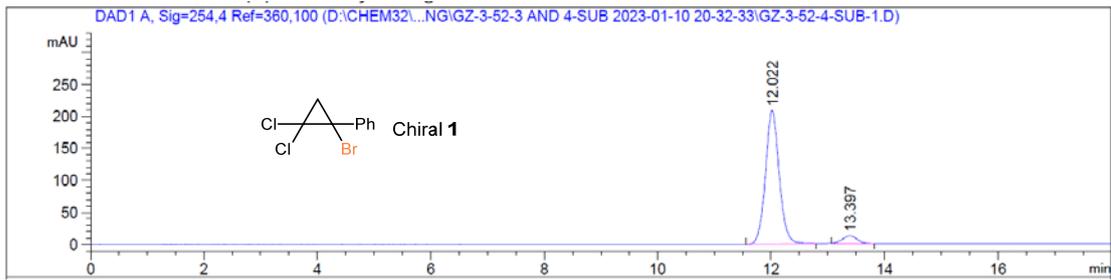
Totals : 7681.72778 493.90556



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.267	BB	0.2261	2083.58594	139.66383	50.1119
2	12.198	BB	0.2558	2074.27686	123.58104	49.8881

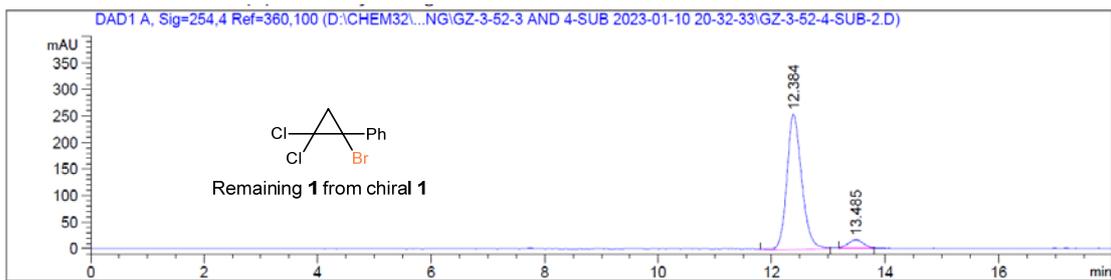
Totals : 4157.86279 263.24487



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.022	BV R	0.2555	3499.64331	208.83693	93.8747
2	13.397	FM R	0.3020	228.34953	12.60070	6.1253

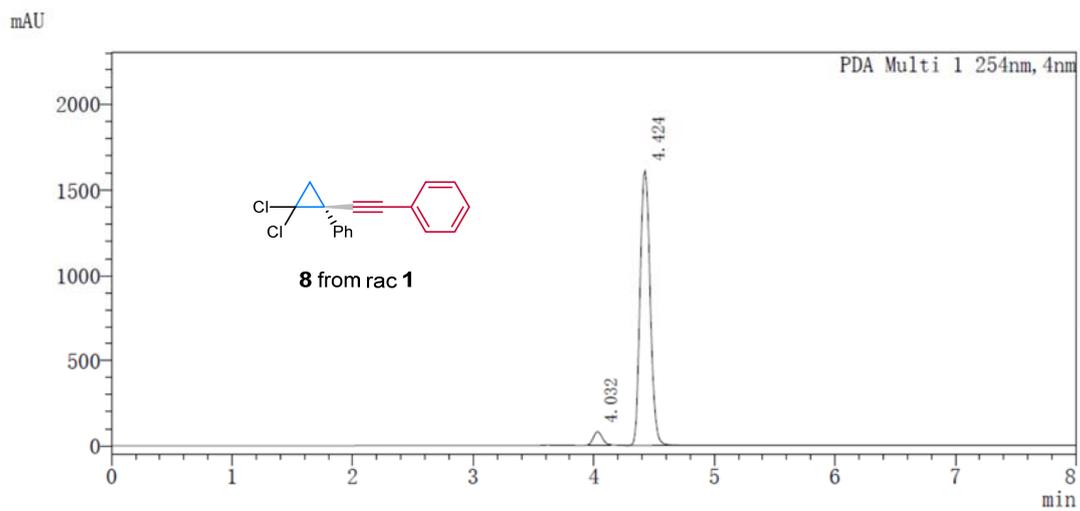
Totals : 3727.99284 221.43763



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.384	MM R	0.3020	4605.14111	254.15686	93.6414
2	13.485	MM R	0.3197	312.70697	16.30370	6.3586

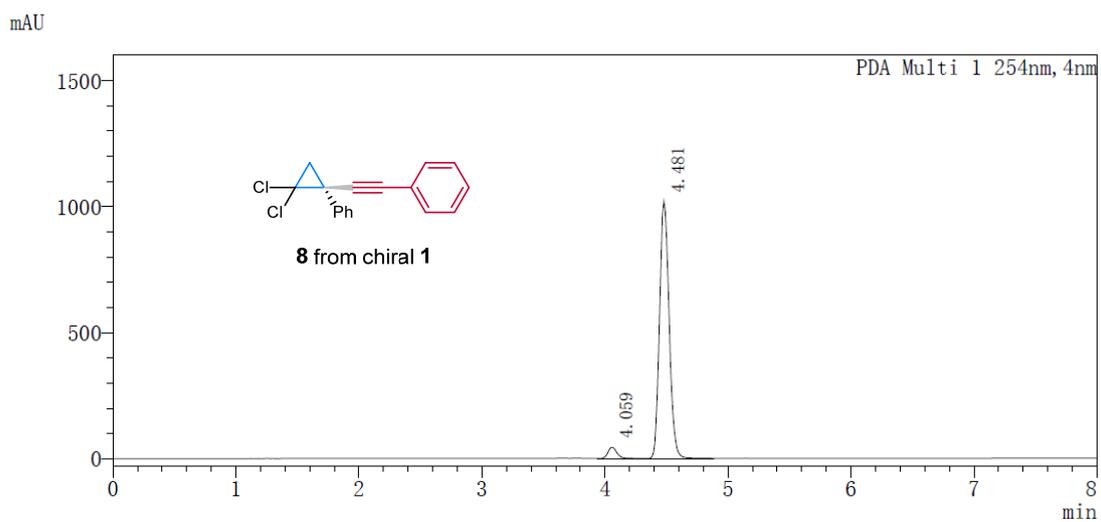
Totals : 4917.84808 270.46056



Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	4.032	423389	4.310
2	4.424	9401149	95.690

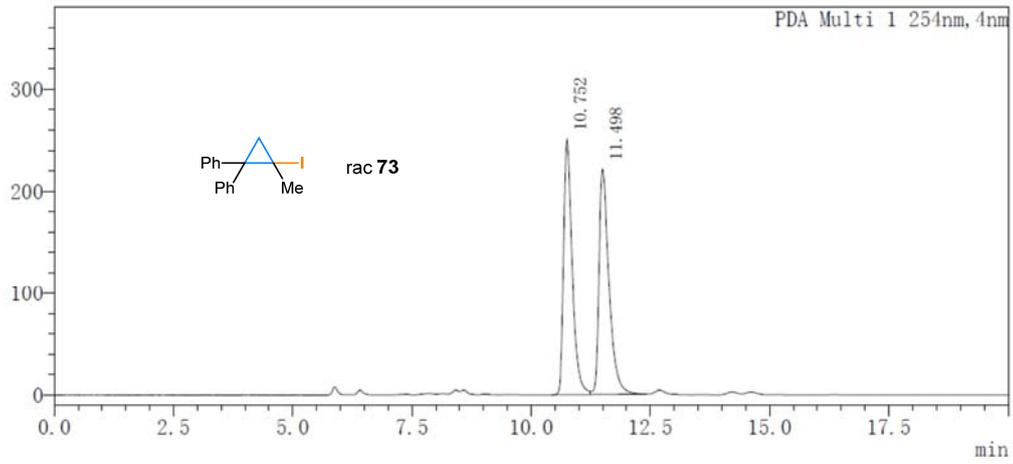


Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	4.059	229834	4.016
2	4.481	5493351	95.984

mAU

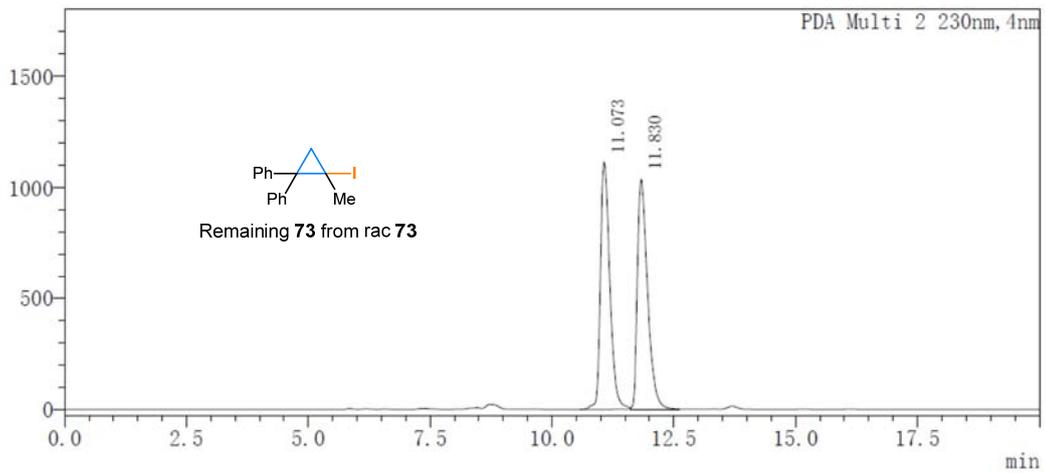


Peak Table

PDA Ch1 254nm

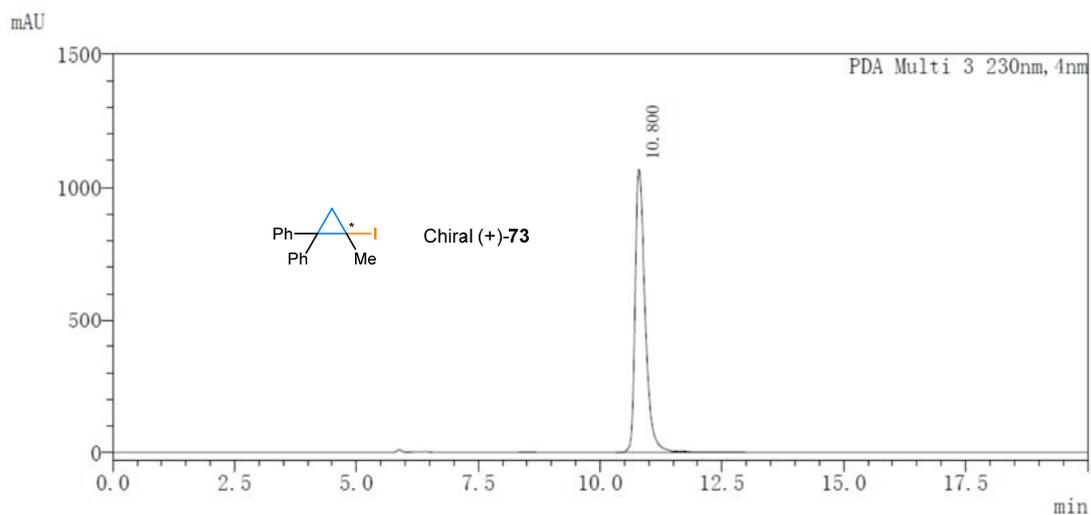
Peak#	Ret. Time	Area	Area%
1	10.752	3167127	49.436
2	11.498	3239398	50.564

mAU



PDA Ch2 230nm

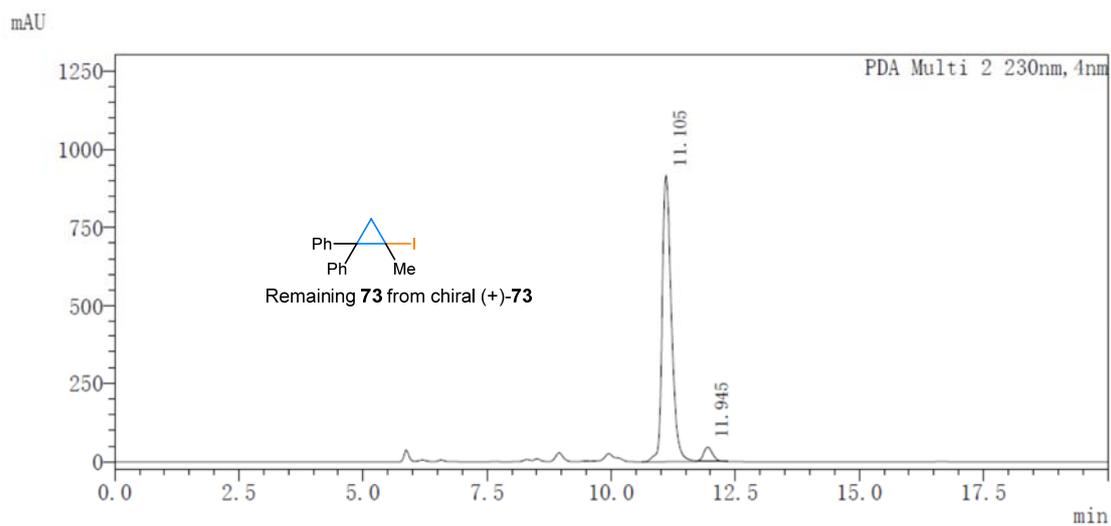
T	Hight	Area	Area%
11.073	1113892	14982229	49.911
11.830	1037101	15035610	50.089



Peak Table

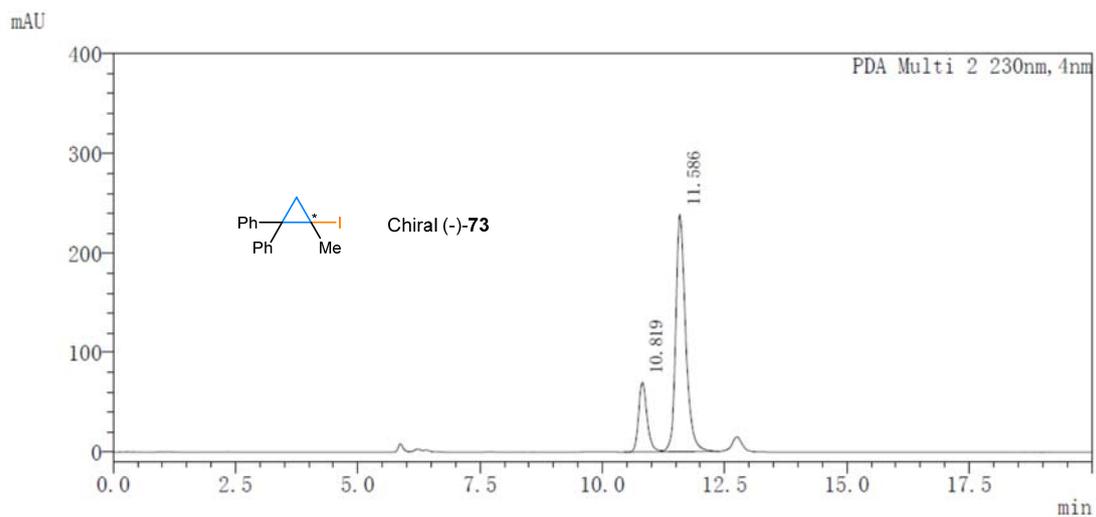
PDA Ch3 230nm

Peak#	Ret. Time	Area	Area%
1	10.800	15370428	100.000



PDA Ch2 230nm

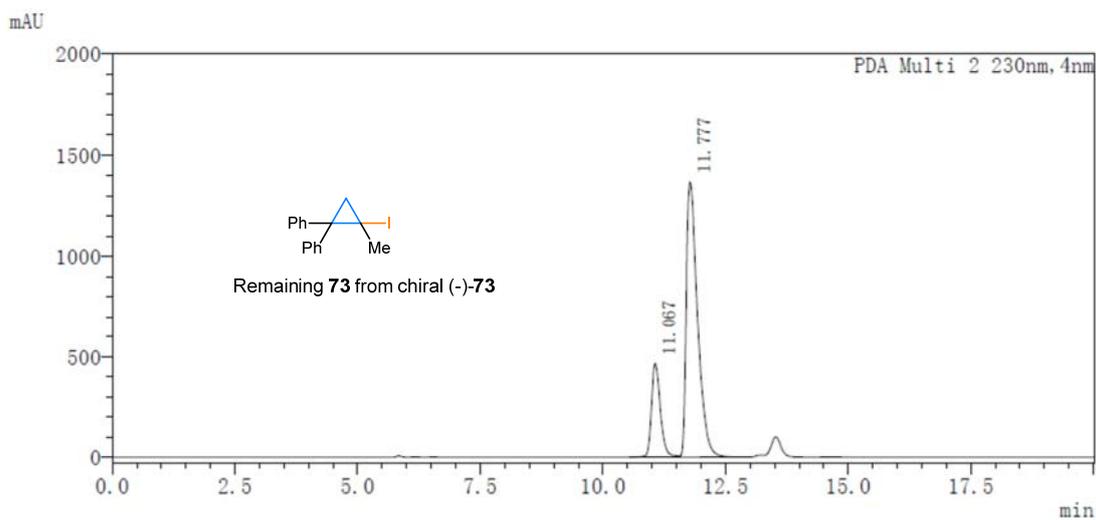
T	Hight	Area	Area%
11.105	915138	11833499	95.230
11.945	46126	592685	4.770



Peak Table

PDA Ch2 230nm

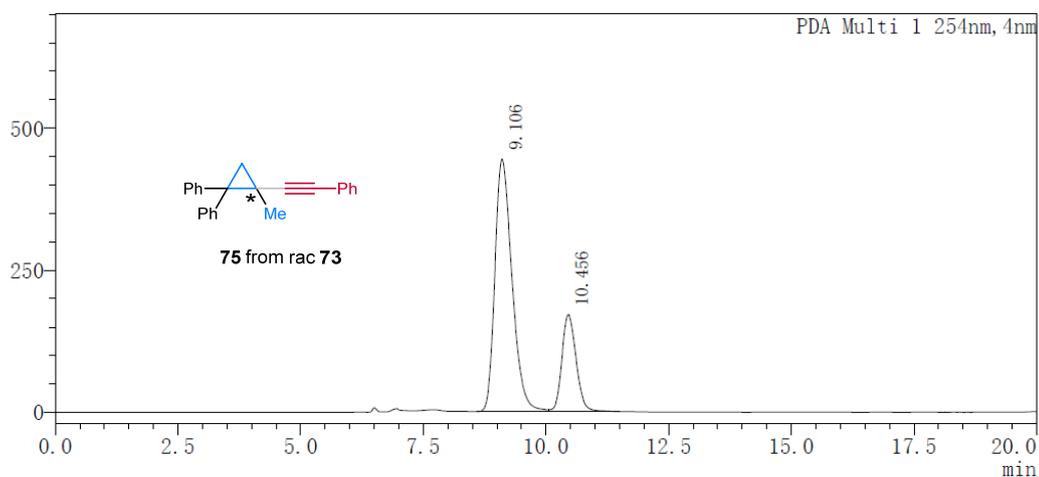
Peak#	Ret. Time	Area	Area%
1	10.819	842523	20.042
2	11.586	3361294	79.958



PDA Ch2 230nm

T	Hight	Area	Area%
11.067	464727	5863524	21.114
11.777	1367370	21906689	78.886

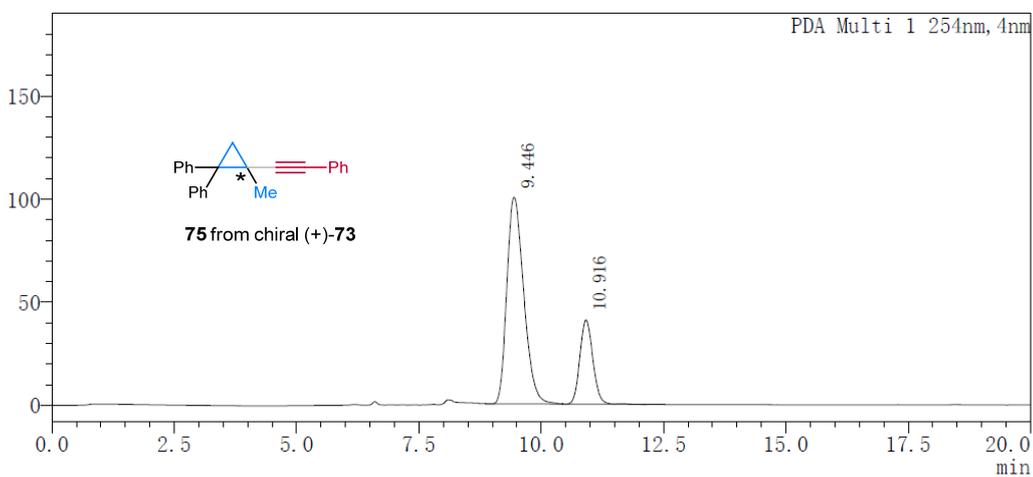
mAU



PDA Ch1 254nm

T	Hight	Area	Area%
9.106	444356	10808823	75.856
10.456	170693	3440377	24.144

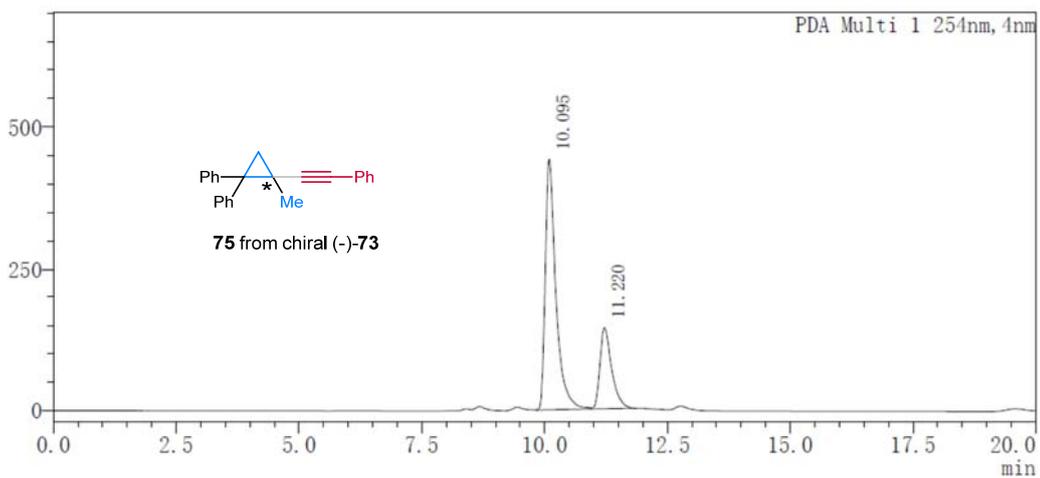
mAU



PDA Ch1 254nm

T	Hight	Area	Area%
9.446	100226	2408480	76.035
10.916	40808	759099	23.965

mAU



PDA Ch1 254nm

T	Height	Area	Area%
10.095	442319	6639745	73.725
11.220	142476	2366402	26.275

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