

Supporting Information

Highly convergent modular access to poly-carbon substituted cyclopropanes *via* Cu(I)-catalyzed multicomponent cyclopropene carboallylation

Hexin Li,^a Mengru Zhang,^a Haroon Mehfooz,^a Dongxia Zhu,^a Jinbo Zhao^{a,*} and Qian Zhang^{a,b,*}

^a *Key Laboratory of Functional Molecule Synthesis of Jilin Province, Department of Chemistry, Northeast Normal University, Changchun, 130024 P. R. China*

^b *State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, 345 Lingling Rd, Shanghai 200032 P. R. China*
zhaojb100@nenu.edu.cn; zhangq651@nenu.edu.cn

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1. General information.

Instrumentation and software.

All ^1H NMR and ^{13}C NMR spectra were recorded at 25 °C on a Bruker 600 MHz spectrometer. Chemical shifts (δ) are given in parts per million (ppm) relative to internal standards (TMS, ^1H -NMR: δ 0 ppm and ^{13}C -NMR: δ 77.0 ppm for CDCl_3). The multiplicity of the NMR signals is assigned as follows: s = singlet, brs = broad singlet, d = doublet, t = triplet, q = quadruplet, m = multiplet, or combinations thereof. NMR yields were determined by addition of a known amount, approximately 20.5 μl , of nitromethane to the crude product and dissolving everything in CDCl_3 , followed by ^1H NMR-analysis. Flash chromatography was performed on silica gel 60 (particle size 300-400 mesh ASTM, purchased from Taizhou, China). Enantioselectivities were determined by Agilent 1260 HPLC system with Darcel Chiralpak columns.

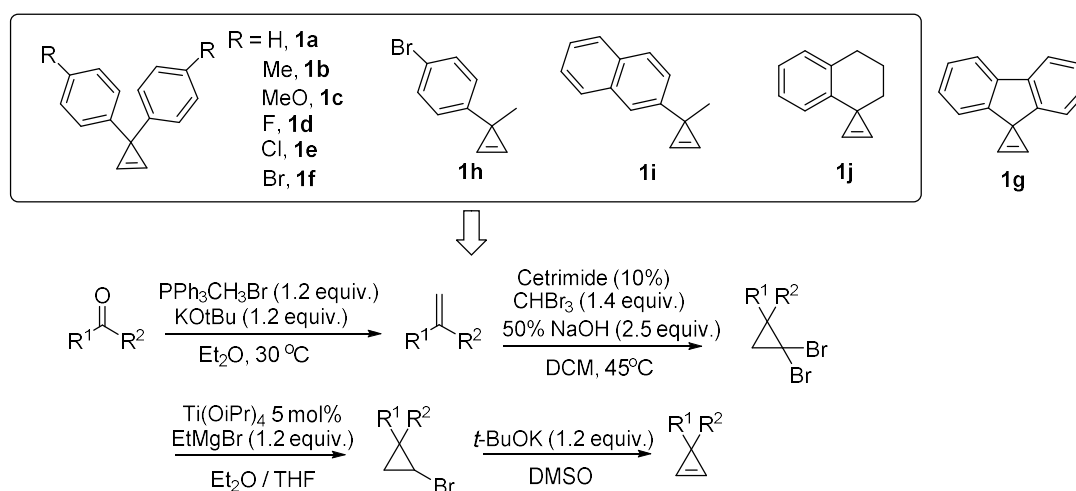
Solvents and reagents.

Unless otherwise noted, all reactions were conducted under a nitrogen atmosphere. Copper salts and other commercial chemicals were used without further purification. Ether was distilled from sodium with benzophenone as indicator. Cyclopropenes **1a-1f**, **1h-1j**,^[1a-1b] **1g**^[1c] and aryl boronic esters^[2] were synthesized according to literature; the structure of existing compounds were verified by comparison with reported ^1H NMR data. Allyl bromides were purchased from commercial sources or prepared from the literature [2-(bromomethyl)but-1-ene].^[3]

Experimental procedures

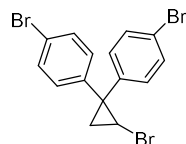
2.1 Preparation of starting materials

Cyclopropenes **1a-1f** and **1h-1j** used in this study (Scheme S1) were synthesized according to literature [1a-1b] by a 4-step procedure typically from the corresponding ketones; cyclopropene **1g** was synthesized according to literature by a 3-step procedure from Tosylhydrazone.^[1c]



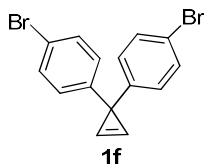
Scheme S1.

Substrates Preparation:



4,4'-(2-bromocyclopropane-1,1-diyl)bis(bromobenzene): $\text{Ti}(\text{O}^i\text{Pr})_4$ (548 μL , 1.9 mmol) was added to a solution of 4,4'-(2,2-dibromocyclopropane-1,1-diyl)bis(bromobenzene) (9.36 g, 18.5 mmol) in and Et_2O (40 mL) at 0 °C. EtMgBr (7.5 mL, 22.2 mmol; 3.0 M solution in Et_2O) was added dropwise to it over 2 h and the mixture was further stirred for 1 h while gradually raising the temperature to room temperature. The reaction was slowly quenched with saturated NH_4Cl aq and 1 M HCl aq was added to it. After extraction with Et_2O , the organic layer was washed with saturated NaCl aq, dried over MgSO_4 , filtered, and concentrated *in vacuo*. The residue was chromatographed on silica gel with petroleum ether to afford the title compound (6.17 g, 78% yield) as a yellow solid.

M.p. = 73 - 75°C. ^1H NMR (600 MHz, CDCl_3) δ 7.50 - 7.46 (m, 2H), 7.40 - 7.36 (m, 2H), 7.25 - 7.21 (m, 2H), 7.08 - 7.05 (m, 2H), 3.64 - 3.60 (m, 1H), 1.87 - 1.82 (m, 1H), 1.80 - 1.76 (m, 1H). ^{13}C NMR (151 MHz, CDCl_3) δ 142.53, 139.18, 132.03, 131.79, 131.54, 129.36, 121.46, 120.85, 35.33, 27.50, 23.99. HRMS (ESI-TOF) (m/z): Calcd for $\text{C}_{15}\text{H}_{12}\text{Br}_3$ ($[\text{M} + \text{H}]^+$), 428.8484; found 428.8486.



4,4'-(cycloprop-2-ene-1,1-diyl)bis(bromobenzene) (1f): KO^tBu (0.67 g, 6.0 mmol) was added portionwise to a solution of 4,4'-(2-bromocyclopropane-1,1-diyl)bis(bromobenzene) (2.14 g, 5.0 mmol) in DMSO (10 mL), and the mixture was stirred for 18 h. The reaction was quenched with H₂O aq and extracted with Et₂O. The organic layer was washed with saturated NaCl aq, dried over MgSO₄, and concentrated *in vacuo*. The residue was chromatographed on silica gel with petroleum ether to afford **1f** (1.50 g, 86% yield) as a yellow solid.

M.p. = 83 - 88°C. ¹H NMR (600 MHz, CDCl₃) δ 7.47–7.44 (m, 1H), 7.40 (s, 2H), 7.27–7.24 (m, 1H), 7.23 – 7.19 (m, 1H), 7.17 – 7.12 (m, 2H), 7.07–7.00 (m, 1H), 6.90–6.86 (m, 2H). ¹³C NMR (151 MHz, CDCl₃) δ 146.93, 145.09, 133.10, 131.34, 128.17, 127.83, 126.58, 125.33, 124.96, 113.02, 32.89. HRMS (ESI-TOF) (*m/z*): Calcd for C₁₅H₁₀Br₂ ([M+H]⁺), 348.9222; found 348.9225.

2.2 Reaction optimization

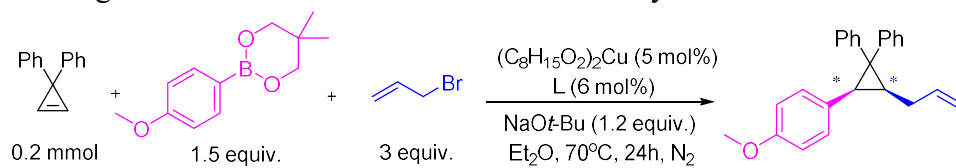
Table S1. Optimization of the cyclopropene carboallylation (I): solvent screening.

Entry	Solvent	Yield/%
1	THF	trace
2	dioxane	trace
3	Et ₂ O	40
4	Toluene	40
5	cyclohexane	20

Table S2. Optimization of the cyclopropene carboallylation (II): evaluation of ligands.

Entry	Ligand	Yield/%
1	IMes	trace
2	dcype	trace
3	IPr	25
4	dppf	40
5	PPh ₃	20
6	Phen	trace
7	P(4-CF ₃ C ₆ H ₄) ₃	30
8	P(4-FC₆H₄)₃	55
9	P(4-ClC ₆ H ₄) ₃	50
10	P(3,5-di-CF ₃ C ₆ H ₃) ₃	16
11	P(<i>o</i> -tol) ₃	trace
12	PCy ₃	trace
13	P(<i>n</i> -Bu) ₃	trace
14	P(<i>t</i> -Bu) ₃	trace

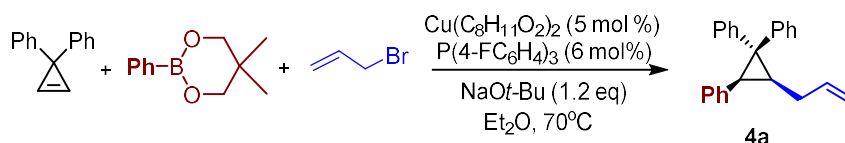
Table S3. Ligand effect on the enantioselective carboallylation.



Entry	Ligand	Yield/%	ee/%
1	(<i>R, R</i>)-DTBMSEgPhos	38	– 69
2	(<i>R</i>)-H ₈ -BINAP	40	– 65
3	(<i>R</i>)-MeO-Tol-BIPHEP	28	– 69
4	(<i>R</i>)-SegPhos	50	– 60
5	(<i>R</i>)-BINAP	25	– 66
6	(<i>R, R</i>)-Ph-BPE	11	88

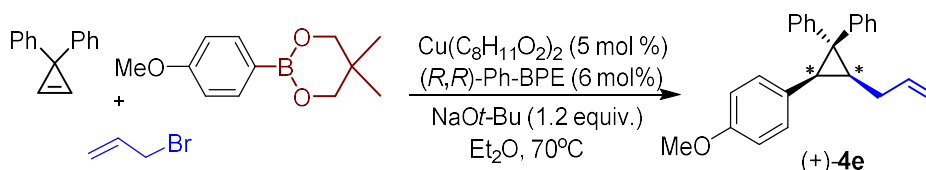
2.3 Procedures

Typical procedure for Cu-catalyzed biscarbonation of cyclopropenes.



In a nitrogen filled glovebox, $\text{Cu}(\text{C}_8\text{H}_{11}\text{O}_2)_2$ (0.01 mmol, 5 mol%) and $\text{P}(\text{4-FC}_6\text{H}_4)_3$ (0.012 mmol, 6 mol%) were dissolved in anhydrous Et_2O (3 mL). The mixture was stirred at room temperature for ca. 2 min before NaOt-Bu (0.3 mmol, 1.5 equiv., 23 mg), boronic ester (0.30 mmol, 1.5 equiv.) and allyl bromide (0.6 mmol, 3.0 equiv.) were successively added. Then cyclopropene (0.20 mmol) was added dropwise into the solution. The resulting mixture was stirred at 70 °C for 24 h. After complete conversion, the solvent was removed *in vacuo* and residue was subjected to flash chromatography (eluent: petroleum ether/ EtOAc = 200:1) to afford the title compound **4a** (46.2 mg, 75% yield) as a colorless oil.

Catalytic enantioselective three-component arylallylation of cyclopropene:



In a nitrogen filled glovebox, $\text{Cu}(\text{C}_8\text{H}_{11}\text{O}_2)_2$ (0.01 mmol, 5 mol%) and $(R,R)\text{-Ph-BPE}$ (0.012 mmol, 6 mol%) were dissolved in anhydrous Et_2O (3 mL) in a screw-cap tube. The mixture was stirred at room temperature for ca. 2 min before NaOt-Bu (0.3 mmol, 1.5 equiv., 23 mg), boronic ester (0.30 mmol, 1.5 equiv.) and allyl bromide (0.6 mmol, 3.0 equiv.) were successively added. Then cyclopropene (0.20 mmol) was added dropwise into the solution. The tube was sealed, taken out of the glovebox. The tube was stirred for 24 h in a 70 °C oil bath. After complete conversion, the solvent was removed *in vacuo* and residue was subjected to flash chromatography (eluent: petroleum ether/ EtOAc = 200:1) to afford **(+)-4e** (7.5 mg, 11% yield, 94:6 e.r.) $[\alpha]_{\text{D}}^{20} = 19.7$ ($c = 0.5$, CHCl_3)

2.4. Crystal structure of compound (\pm)-4e (CCDC# 1935679).

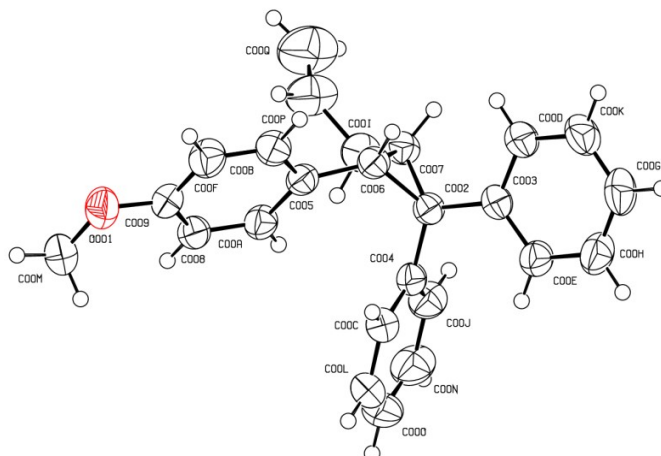
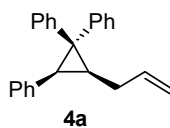


Figure S1. ORTEP representation of compound (\pm)-**4e**.

Bond precision: C-C = 0.0034 Å		Wavelength=1.54178	
Cell:	a=10.220 (2)	b=9.550 (2)	c=20.071 (5)
	alpha=90	beta=93.737 (13)	gamma=90
Temperature:	273 K		
	Calculated	Reported	
Volume	1954.8 (7)	1954.8 (8)	
Space group	P 21/c	P 1 21/c 1	
Hall group	-P 2ybc	-P 2ybc	
Moiety formula	C25 H24 O	C25 H24 O	
Sum formula	C25 H24 O	C25 H24 O	
Mr	340.44	338.42	
Dx, g cm-3	1.157	1.150	
Z	4	4	
Mu (mm-1)	0.525	0.525	
F000	728.0	720.0	
F000'	729.92		
h, k, lmax	12, 11, 24	12, 11, 24	
Nref	3685	3594	
Tmin, Tmax			
Tmin'			
Correction method= Not given			
Data completeness= 0.975		Theta(max)= 69.671	
R(reflections)= 0.0624 (2969)		wR2(reflections)= 0.1530 (3594)	
S = 1.081		Npar= 236	

Figure S2. Crystal structure parameters.

3. Compound Characterization

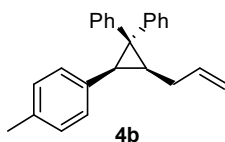


((2S*,3S*)-3-Allylcyclopropane-1,1,2-triyl)tribenzene (4a): following the general procedure, the reaction of 5,5-dimethyl-2-phenyl-1,3,2-dioxaborinane (0.30 mmol, 1.5 equiv., 57.0 mg), 3-bromoprop-1-ene (0.60 mmol, 3.0 equiv., 72.0 mg) and 3,3-diphenyl cyclopropene (0.20 mmol, 1.0 equiv., 38.4 mg) afforded **4a** (46.2 mg, 75% yield) as a colorless oil.

¹H NMR (600 MHz, CDCl₃) δ 7.28–7.24 (m, 2H), 7.19–7.13 (m, 4H), 7.13–7.09 (m, 3H), 7.08–7.03 (m, 4H), 6.77–6.72 (m, 2H), 5.79–5.71 (m, 1H), 5.06–4.99 (m, 1H), 4.93–4.89 (m, 1H), 2.74 (d, *J* = 10.2 Hz, 1H), 2.59–2.51 (m, 1H), 2.26–2.18 (m, 1H), 2.04–1.97 (m, 1H).

¹³C NMR (151 MHz, CDCl₃) δ 149.07, 138.16, 137.77, 137.56, 132.01, 129.75, 128.42, 128.23, 127.57, 127.45, 126.55, 125.85, 125.37, 115.22, 40.82, 35.27, 31.79, 30.08.

HRMS (ESI-TOF) (*m/z*): Calcd for C₂₄H₂₂ ([M+H]⁺), 311.1794; found 311.1782.

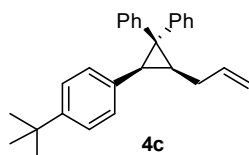


((2S*,3S*)-2-Allyl-3-(p-tolyl)cyclopropane-1,1-diyl)dibenzene (4b): following the general procedure, the reaction of 5,5-dimethyl-2-(p-tolyl)-1,3,2-dioxaborinane (0.30 mmol, 1.5 equiv., 61.2 mg), 3-bromoprop-1-ene (0.60 mmol, 3.0 equiv., 0.0720 g) and 3,3-diphenyl cyclopropene (0.20 mmol, 1.0 equiv., 38.4 mg) afforded **4b** (46.6 mg, 72% yield) as a colorless oil.

¹H NMR (600 MHz, CDCl₃) δ 7.33–7.31 (m, 2H), 7.26–7.21 (m, 4H), 7.21–7.16 (m, 3H), 7.14–7.09 (m, 1H), 6.97–6.92 (m, 2H), 6.72–6.68 (m, 2H), 5.87–5.79 (m, 1H), 5.14–5.07 (m, 1H), 5.01–4.96 (m, 1H), 2.78 (d, *J* = 10.2 Hz, 1H), 2.63–2.56 (m, 1H), 2.31–2.24 (m, 4H), 2.08–2.01 (m, 1H).

¹³C NMR (151 MHz, CDCl₃) δ 149.18, 137.90, 137.69, 134.92, 134.83, 132.06, 129.63, 128.39, 128.22, 128.19, 127.55, 126.50, 125.78, 115.15, 40.52, 35.04, 31.66, 30.12, 20.91.

HRMS (ESI-TOF) (*m/z*): Calcd for C₂₅H₂₄ ([M + H]⁺), 325.1950; found 325.1955.

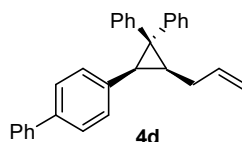


((2S*,3S*)-2-Allyl-3-(4-(tert-butyl)phenyl)cyclopropane-1,1-diyl)dibenzene (4c): following the general procedure, the reaction of 2-(4-(tert-butyl)phenyl)-5,5-dimethyl-1,3,2-dioxaborinane (0.30 mmol, 1.5 equiv., 73.8 mg), 3-bromoprop-1-ene (0.60 mmol, 3.0 equiv., 72.0 mg) and 3,3-diphenyl cyclopropene (0.20 mmol, 1.0 equiv., 38.4 mg) afforded **4c** (38.1 mg, 52% yield) as a colorless oil.

¹H NMR (600 MHz, CDCl₃) δ 7.27–7.24 (m, 2H), 7.18–7.10 (m, 7H), 7.09–7.05 (m, 2H), 7.05–7.01 (m, 1H), 5.81–5.73 (m, 1H), 5.05–5.00 (m, 1H), 4.94–4.89 (m, 1H), 2.71 (d, *J* = 9.6 Hz, 1H), 2.53–2.46 (m, 1H), 2.22–2.16 (m, 1H), 1.99–1.93 (m, 1H), 1.20 (s, 9H).

¹³C NMR (151 MHz, CDCl₃) δ 149.25, 148.12, 138.00, 137.83, 134.89, 132.06, 129.40, 128.39, 128.16, 127.64, 126.45, 125.77, 124.34, 115.12, 77.21, 77.00, 76.79, 40.62, 34.83, 34.25, 31.56, 31.34, 30.24.

HRMS (ESI-TOF) (*m/z*): Calcd for C₂₈H₃₀ ([M+H]⁺), 367.2420; found 367.2418.

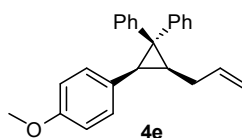


4-((1S*,3S*)-3-Allyl-2,2-diphenylcyclopropyl)-1,1'-biphenyl (4d): following the general procedure, the reaction of 2-([1,1'-biphenyl]-4-yl)-5,5-dimethyl-1,3,2-dioxaborinane (0.30 mmol, 1.5 equiv., 79.8 mg), 3-bromoprop-1-ene (0.60 mmol, 3.0 equiv., 72.0 mg) and 3,3-diphenyl cyclopropene (0.20 mmol, 1.0 equiv., 38.4 mg) afforded **4d** (67.5 mg, 87% yield) as a colorless oil.

¹H NMR (600 MHz, CDCl₃) δ 7.59–7.55 (m, 2H), 7.43–7.37 (m, 4H), 7.37–7.33 (m, 2H), 7.32–7.28 (m, 1H), 7.26–7.23 (m, 4H), 7.23–7.20 (m, 3H), 7.16–7.12 (m, 1H), 6.90–6.86 (m, 2H), 5.90–5.82 (m, 1H), 5.16–5.10 (m, 1H), 5.03–4.99 (m, 1H), 2.855 (d, *J* = 10.2 Hz, 1H), 2.69–2.61 (m, 1H), 2.37–2.29 (m, 1H), 2.15–2.08 (m, 1H).

¹³C NMR (151 MHz, CDCl₃) δ 149.02, 140.76, 138.01, 137.74, 137.56, 137.40, 132.07, 130.15, 128.69, 128.45, 128.30, 127.56, 126.99, 126.80, 126.63, 126.02, 125.89, 115.31, 41.05, 35.10, 32.03, 30.14.

HRMS (ESI-TOF) (*m/z*): Calcd for C₃₀H₂₆ ([M+H]⁺), 387.2107; found 387.2102.

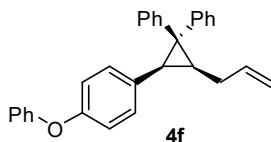


((2S*,3S*)-2-Allyl-3-(4-methoxyphenyl)cyclopropane-1,1-diyl)dibenzene (4e): following the general procedure, the reaction of 2-(4-methoxyphenyl)-5,5-dimethyl-1,3,2-dioxaborinane (0.30 mmol, 1.5 equiv., 66.0 mg), 3-bromoprop-1-ene (0.60 mmol, 3.0 equiv., 72.0 mg) and 3,3-diphenyl cyclopropene (0.20 mmol, 1.0 equiv., 38.4 mg) afforded **4e** (61.5 mg, 91% yield) as a yellow solid. M.p. = 87 - 89°C.

¹H NMR (600 MHz, CDCl₃) δ 7.25–7.21 (m, 2H), 7.18–7.13 (m, 4H), 7.13–7.08 (m, 3H), 7.06–7.02 (m, 1H), 6.68–6.64 (m, 2H), 5.63–5.59 (m, 2H), 5.80–5.71 (m, 1H), 5.06–4.99 (m, 1H), 4.93–4.89 (m, 1H), 3.64 (s, 3H), 2.69 (d, *J* = 9.6 Hz, 1H), 2.55–2.48 (m, 1H), 2.22–2.15 (m, 1H), 1.99–1.92 (m, 1H).

¹³C NMR (151 MHz, CDCl₃) δ 157.46, 149.15, 137.88, 137.65, 132.10, 130.63, 129.98, 128.38, 128.20, 127.50, 126.49, 125.75, 115.17, 112.96, 55.09, 40.14, 34.67, 31.43, 30.12.

HRMS (ESI-TOF) (*m/z*): Calcd for C₂₅H₂₄O ([M + H]⁺), 341.1899; found 341.1892.

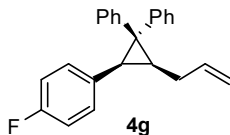


((2S*,3S*)-2-Allyl-3-(4-phenoxyphenyl)cyclopropane-1,1-diyl)dibenzene (4f): following the general procedure, the reaction of 5,5-dimethyl-2-(4-phenoxyphenyl)-1,3,2-dioxaborinane (0.30 mmol, 1.5 equiv., 84.6 mg), 3-bromoprop-1-ene (0.60 mmol, 3.0 equiv., 72.0 mg) and 3,3-diphenyl cyclopropene (0.20 mmol, 1.0 equiv., 38.4 mg) afforded **4f** (72.7 mg, 90% yield) as a colorless oil.

¹H NMR (600 MHz, CDCl₃) δ 7.34–7.28 (m, 4H), 7.27–7.21 (m, 4H), 7.21–7.16 (m, 3H), 7.15–7.10 (m, 1H), 7.09–7.04 (m, 1H), 7.00–6.96 (m, 2H), 6.82–6.76 (m, 4H), 5.90–5.80 (m, 1H), 5.14–5.07 (m, 1H), 5.04–4.98 (m, 1H), 2.81 (d, *J* = 9.6 Hz, 1H), 2.67–2.59 (m, 1H), 2.34–2.27 (m, 1H), 2.12–2.05 (m, 1H).

¹³C NMR (151 MHz, CDCl₃) δ 157.38, 154.98, 149.01, 137.74, 137.53, 133.00, 132.03, 130.87, 129.63, 128.43, 128.25, 127.54, 126.59, 125.85, 123.00, 118.68, 118.00, 115.28, 40.50, 34.68, 31.59, 30.12.

HRMS (ESI-TOF) (*m/z*): Calcd for C₃₀H₂₆O ([M + H]⁺), 403.2056; found 403.2048.



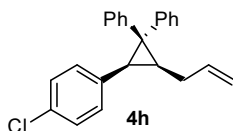
((2S*,3S*)-2-Allyl-3-(4-fluorophenyl)cyclopropane-1,1-diyl)dibenzene (4g): following the general procedure, the reaction of 2-(4-fluorophenyl)-5,5-dimethyl-1,3,2-dioxaborinane (0.30 mmol, 1.5 equiv., 62.4 mg), 3-bromoprop-1-ene (0.60 mmol, 3.0 equiv., 72.0 mg) and 3,3-diphenyl cyclopropene (0.20 mmol, 1.0 equiv., 38.4 mg) afforded **4g** (46.3 mg, 71% yield) as a yellow solid. M.p. = 79 - 81°C.

¹H NMR (600 MHz, CDCl₃) δ 7.34–7.29 (m, 2H), 7.27–7.18 (m, 5H), 7.18–7.10 (m, 3H), 6.85–6.80 (m, 2H), 6.79–6.74 (m, 2H), 5.86–5.77 (m, 1H), 5.12–5.06 (m, 1H), 2.80 (d, *J* = 10.2 Hz, 1H), 2.65–2.58 (m, 1H), 2.28–2.21 (m, 1H), 2.09–2.03 (m, 1H).

¹³C NMR (151 MHz, CDCl₃) δ 161.05 (d, *J* = 242.7 Hz), 148.85, 137.55, 137.30, 133.75 (d, *J* = 3.2 Hz), 131.99, 130.95 (d, *J* = 7.5 Hz), 128.45, 128.32, 127.49, 126.67, 125.91, 115.35, 114.31 (d, *J* = 20.9 Hz), 40.53, 34.51, 31.57, 29.97.

¹⁹F NMR (470 MHz, CDCl₃) δ –117.99 (tt, *J* = 8.9, 5.2 Hz).

HRMS (ESI-TOF) (*m/z*): Calcd for C₂₄H₂₁F ([M + H]⁺), 329.1700; found 329.1708.



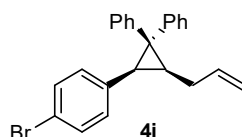
((2S*,3S*)-2-Allyl-3-(4-chlorophenyl)cyclopropane-1,1-diyl)dibenzene (4h): following the general procedure, the reaction of 2-(4-chlorophenyl)-5,5-dimethyl-1,3,2-dioxaborinane (0.30 mmol, 1.5 equiv., 67.3 mg), 3-bromoprop-1-ene (0.60 mmol, 3.0

equiv., 72.0 mg) and 3,3-diphenyl cyclopropene (0.20 mmol, 1.0 equiv., 38.4 mg) afforded **4h** (59.5 mg, 87% yield) as a colorless oil.

¹H NMR (600 MHz, CDCl₃) δ 7.32–7.30 (m, 2H), 7.27–7.18 (m, 5H), 7.18–7.14 (m, 2H), 7.14–7.11 (m, 1H), 7.01–7.08 (m, 2H), 6.75–6.69 (m, 2H), 5.85–5.75 (m, 1H), 5.12–5.06 (m, 1H), 5.02–4.98 (m, 1H), 2.78 (d, *J* = 9.6 Hz, 1H), 2.66–2.58 (m, 1H), 2.27–2.22 (m, 1H), 2.12–2.05 (m, 1H).

¹³C NMR (151 MHz, CDCl₃) δ 148.70, 137.36, 137.18, 136.75, 131.93, 131.25, 130.90, 128.47, 128.39, 127.57, 127.45, 126.76, 125.98, 115.44, 34.67, 31.90, 30.32, 29.90.

HRMS (ESI-TOF) (*m/z*): Calcd for C₂₄H₂₁Cl ([M+H]⁺), 345.1404; found 345.1406.

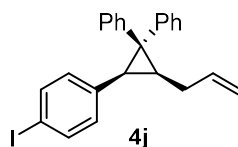


((2S*,3S*)-2-Allyl-3-(4-bromophenyl)cyclopropane-1,1-diyl)dibenzene (4i**)**: following the general procedure, the reaction of 2-(4-bromophenyl)- 5,5- dimethyl- 1,3,2-dioxaborinane (0.30 mmol, 1.5 equiv., 80.7 mg), 3-bromoprop-1-ene (0.60 mmol, 3.0 equiv., 72.0 mg) and 3,3-diphenyl cyclopropene (0.20 mmol, 1.0 equiv., 38.4 mg) afforded **4i** (63.5 mg, 82% yield) as a colorless oil.

¹H NMR (600 MHz, CDCl₃) δ 7.32–7.28 (m, 2H), 7.27–7.18 (m, 7H), 7.18–7.10 (m, 3H), 6.68–6.64 (m, 2H), 5.85–5.75 (m, 1H), 5.12–5.06 (m, 1H), 5.02–4.97 (m, 1H), 2.76 (d, *J* = 9.6 Hz, 1H), 2.66–2.57 (m, 1H), 2.26–1.90 (m, 1H), 2.12–2.05 (m, 1H).

¹³C NMR (151 MHz, CDCl₃) δ 148.66, 137.30, 137.15, 131.92, 131.29, 130.50, 128.47, 128.40, 127.45, 126.77, 125.99, 119.34, 115.45, 41.02, 34.73, 31.92, 29.87.

HRMS (ESI-TOF) (*m/z*): Calcd for C₂₄H₂₁Br([M + H]⁺), 389.0899; found 389.0901.

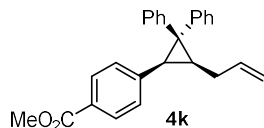


((2S*,3S*)-2-Allyl-3-(4-iodophenyl)cyclopropane-1,1-diyl)dibenzene (4j**)**: following the general procedure, the reaction of 2-(4-iodophenyl)-5,5- dimethyl- 1,3,2-dioxaborinane (0.30 mmol, 1.5 equiv., 91.1 mg), 3-bromoprop-1-ene (0.60 mmol, 3.0 equiv., 72.0 mg) and 3,3-diphenyl cyclopropene (0.20 mmol, 1.0 equiv., 38.4 mg) afforded **4j** (65.7 mg, 75% yield) as a colorless oil.

¹H NMR (600 MHz, CDCl₃) δ 7.46 – 7.41 (m, 2H), 7.32 – 7.28 (m, 2H), 7.27 – 7.18 (m, 5H), 7.18 – 7.10 (m, 3H), 6.52 – 6.51 (m, 2H), 5.84 – 5.76 (m, 1H), 5.12 – 5.06 (m, 1H), 5.02 – 4.97 (m, 1H), 2.74 (d, *J* = 9.6 Hz, 1H), 2.65 – 2.57 (m, 1H), 2.26 – 2.18 (m, 1H), 2.12 – 2.05 (m, 1H).

¹³C NMR (151 MHz, CDCl₃) δ 148.66, 138.03, 137.28, 137.16, 136.45, 131.90, 131.66, 128.48, 128.42, 127.45, 126.78, 126.00, 125.51, 115.46, 34.84, 32.00, 30.32, 29.86.

HRMS (ESI-TOF) (*m/z*): Calcd for C₂₄H₂₁I ([M + H]⁺), 437.0760; found 437.0762.



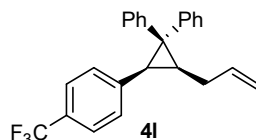
Methyl 4-((1S*,3S*)-3-allyl-2,2-diphenylcyclopropyl)benzoate (4k):

following the general procedure, the reaction of methyl 4-(5,5-dimethyl-1,3,2-dioxaborinan-2-yl)benzoate (0.30 mmol, 1.5 equiv., 74.4 mg), 3-bromoprop-1-ene (0.60 mmol, 3.0 equiv., 72.0 mg) and 3,3-diphenyl cyclopropene (0.20 mmol, 1.0 equiv., 38.4 mg) afforded **4k** (27.4 mg, 37% yield) as a white solid. M.p. = 84 - 88°C.

¹H NMR (600 MHz, CDCl₃) δ 7.81–7.78 (m, 2H), 7.34–7.31 (m, 2H), 7.27–7.20 (m, 5H), 7.18–7.12 (m, 3H), 6.88–6.85 (m, 2H), 5.83–5.75 (m, 1H), 5.11–5.06 (m, 1H), 5.00–4.98 (m, 1H), 3.87 (s, 3H), 2.86 (d, *J* = 9.6 Hz, 1H), 2.71–2.64 (m, 1H), 2.32–2.25 (m, 1H), 2.20–2.13 (m, 1H).

¹³C NMR (151 MHz, CDCl₃) δ 167.16, 148.55, 144.19, 137.22, 137.04, 131.84, 129.59, 128.64, 128.51, 128.44, 127.46, 127.15, 126.84, 126.07, 115.51, 51.91, 41.98, 35.38, 32.67, 29.92.

HRMS (ESI-TOF) (*m/z*): Calcd for C₂₆H₂₄O₂ ([M + H]⁺), 369.1849; found 369.1856.



((2S*,3S*)-2-Allyl-3-(4-(trifluoromethyl)phenyl)cyclopropane-1,1-diyl)dibenzene (4l):

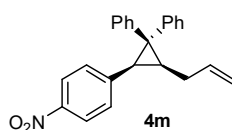
following the general procedure, the reaction of 5,5-dimethyl-2-(4-(trifluoromethyl)phenyl)-1,3,2-dioxaborinane (0.30 mmol, 1.5 equiv., 77.4 mg), 3-bromoprop-1-ene (0.60 mmol, 3.0 equiv., 72.0 mg) and 3,3-diphenyl cyclopropene (0.20 mmol, 1.0 equiv., 0.0384 g) afforded **4l** (29.4 mg, 39% yield) as a white solid. M.p. = 236 - 240°C.

¹H NMR (600 MHz, CDCl₃) δ 7.39 - 7.36 (m, 2H), 7.34 - 7.31 (m, 2H), 7.28 - 7.20 (m, 5H), 7.19 - 7.12 (m, 3H), 6.91 - 6.87 (m, 2H), 5.83 - 5.75 (m, 1H), 5.12 - 5.06 (m, 1H), 5.02 - 4.97 (m, 1H), 2.86 (d, *J* = 9.6 Hz, 1H), 2.70 - 2.63 (m, 1H), 2.29 - 2.21 (m, 1H), 2.18 - 2.12 (m, 1H).

¹³C NMR (151 MHz, CDCl₃) δ 148.49, 142.68, 137.15, 136.97, 131.84, 129.80, 128.54, 128.50, 127.52 (q, *J* = 32.5 Hz), 127.48, 126.91, 126.12, 124.38 (q, ¹*J*_{C-F} = 271.8 Hz), 124.25 (q, ¹*J*_{C-F} = 4.5 Hz), 115.57, 41.75, 34.98, 32.40, 29.84.

¹⁹F NMR (470 MHz, CDCl₃) δ - 62.22 (s).

HRMS (ESI-TOF) (*m/z*): Calcd for C₂₅H₂₁F₃Na ([M + Na]⁺), 401.1481; found 401.1488.

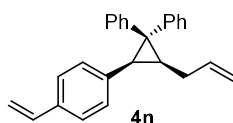


((2S*,3S*)-2-Allyl-3-(4-nitrophenyl)cyclopropane-1,1-diyl)dibenzene (4m): following the general procedure, the reaction of 5,5-dimethyl-2-(4-nitrophenyl)-1,3,2-dioxaborinane (0.30 mmol, 1.5 equiv., 70.5 mg), 3-bromoprop-1-ene (0.60 mmol, 3.0 equiv., 72.0 mg) and 3,3-diphenylcyclopropene (0.20 mmol, 1.0 equiv., 38.4 mg) afforded **4m** (30.8 mg, 43% yield) as a colorless oil.

¹H NMR (600 MHz, CDCl₃) δ 7.93 – 7.89 (m, 2H), 7.27 – 7.24 (m, 2H), 7.22 – 7.17 (m, 5H), 7.12 – 7.07 (m, 3H), 6.87 – 6.83 (m, 2H), 5.76 – 5.66 (m, 1H), 5.04 – 4.98 (m, 1H), 4.95 – 4.90 (m, 1H), 2.87 – 2.82 (m, 1H), 2.69 – 2.60 (m, 1H), 2.23 – 2.14 (m, 2H).

¹³C NMR (151 MHz, CDCl₃) δ 148.03, 146.95, 145.71, 136.71, 136.52, 131.69, 130.07, 128.68, 128.62, 127.39, 127.17, 126.33, 122.57, 115.82, 42.86, 35.25, 33.25, 29.72.

HRMS (ESI-TOF) (*m/z*): Calcd for C₂₄H₂₁NO₂ ([M + H]⁺), 356.1645; found 356.1641.

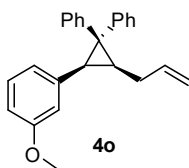


((2S*,3S*)-2-Allyl-3-(4-vinylphenyl)cyclopropane-1,1-diyl)dibenzene (4n): following the general procedure, the reaction of 5,5-dimethyl-2-(4-vinylphenyl)-1,3,2-dioxaborinane (0.30 mmol, 1.5 equiv., 64.8 mg), 3-bromoprop-1-ene (0.60 mmol, 3.0 equiv., 72.0 mg) and 3,3-diphenylcyclopropene (0.20 mmol, 1.0 equiv., 38.4 mg) afforded **4n** (45.4 mg, 68% yield) as a colorless oil.

¹H NMR (600 MHz, CDCl₃) δ 7.26–7.23 (m, 2H), 7.20–7.15 (m, 5H), 7.13–7.10 (m, 4H), 7.07–7.03 (m, 1H), 6.71–6.68 (m, 2H), 6.61–6.54 (m, 1H), 5.79–5.71 (m, 1H), 5.63–5.58 (m, 1H), 5.12–5.08 (m, 1H), 5.06–5.00 (m, 1H), 4.94–4.90 (m, 1H), 2.73 (d, *J* = 9.6 Hz, 1H), 2.59 – 2.52 (m, 1H), 2.24–2.17 (m, 1H), 2.05–1.98 (m, 1H).

¹³C NMR (151 MHz, CDCl₃) δ 148.96, 137.99, 137.66, 137.49, 136.54, 134.65, 132.01, 129.85, 128.43, 128.28, 127.50, 126.62, 125.87, 125.31, 115.28, 112.91, 41.04, 35.24, 32.07, 30.08.

HRMS (ESI-TOF) (*m/z*): Calcd for C₂₆H₂₄ ([M + H]⁺), 337.1950; found 337.1952.



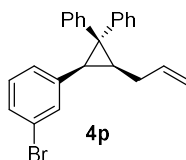
((2S*,3S*)-2-Allyl-3-(3-methoxyphenyl)cyclopropane-1,1-diyl)dibenzene (4o): following the general procedure, the reaction of 2-(3-methoxyphenyl)-5,5-dimethyl-1,3,2-dioxaborinane (0.30 mmol, 1.5 equiv., 66.0 mg), 3-bromoprop-1-ene (0.60 mmol, 3.0 equiv., 72.0 mg) and 3,3-diphenylcyclopropene (0.20 mmol, 1.0 equiv., 38.4 mg) afforded **4o** (40.9 mg, 60% yield) as a colorless oil.

¹H NMR (600 MHz, CDCl₃) δ 7.28–7.24 (m, 2H), 7.19–7.09 (m, 7H), 7.07–7.03 (m, 1H), 7.01–6.96 (m, 1H), 6.30–6.59 (m, 1H), 6.45–6.41 (m, 1H), 6.23–6.20 (m, 1H), 5.81–5.72 (m, 1H), 5.07–5.01 (m, 1H), 4.95–4.90 (m, 1H), 3.49 (s, 3H), 2.72 (d, *J* = 10.2 Hz, 1H), 2.59–2.52

(m, 1H), 2.26–2.19 (m, 1H), 2.02–1.96 (m, 1H).

¹³C NMR (151 MHz, CDCl₃) δ 158.72, 149.02, 139.75, 137.83, 137.55, 131.99, 128.43, 128.30, 128.25, 127.59, 126.57, 125.88, 122.54, 115.25, 115.02, 111.33, 54.84, 40.94, 35.11, 31.90, 30.18.

HRMS (ESI-TOF) (*m/z*): Calcd for C₂₅H₂₄O ([M + H]⁺), 341.1899; found 341.1893.

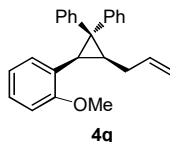


((2S*,3S*)-2-Allyl-3-(3-bromophenyl)cyclopropane-1,1-diyl)dibenzene (4p): following the general procedure, the reaction of 2-(3-bromophenyl)-5,5-dimethyl-1,3,2-dioxaborinane (0.30 mmol, 1.5 equiv., 80.4 mg), 3-bromoprop-1-ene (0.60 mmol, 3.0 equiv., 72.0 mg) and 3,3-diphenyl cyclopropene (0.20 mmol, 1.0 equiv., 38.4 mg) afforded **4p** (38.9 mg, 50% yield) as a colorless oil.

¹H NMR (600 MHz, CDCl₃) δ 7.34–7.30 (m, 2H), 7.27–7.19 (m, 6H), 7.18–7.11 (m, 3H), 7.07–7.05 (m, 1H), 6.92 (t, *J* = 7.8 Hz, 1H), 6.63–6.60 (m, 1H), 5.86–5.78 (m, 1H), 5.13–5.07 (m, 1H), 5.03–4.99 (m, 1H), 2.75 (d, *J* = 9.6 Hz, 1H), 2.66–2.59 (m, 1H), 2.28–2.21 (m, 1H), 2.12–2.07 (m, 1H).

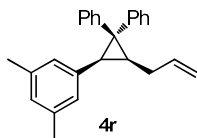
¹³C NMR (151 MHz, CDCl₃) δ 148.58, 140.75, 137.23, 137.15, 132.85, 131.85, 128.81, 128.50, 128.42, 128.37, 127.96, 127.50, 126.82, 126.04, 121.60, 115.50, 41.28, 34.74, 32.05, 29.89.

HRMS (ESI-TOF) (*m/z*): Calcd for C₂₄H₂₁Br ([M + H]⁺), 389.0899; found 389.0902.



((2S*,3S*)-2-Allyl-3-(2-methoxyphenyl)cyclopropane-1,1-diyl)dibenzene (4q): following the general procedure, the reaction of 2-(2-methoxyphenyl)-5,5-dimethyl-1,3,2-dioxaborinane (0.30 mmol, 1.5 equiv., 66.0 mg), 3-bromoprop-1-ene (0.60 mmol, 3.0 equiv., 72.0 mg) and 3,3-diphenyl cyclopropene (0.20 mmol, 1.0 equiv., 38.4 mg) afforded **4q** (10.9 mg, 16% yield) as a colorless oil.

¹H NMR (600 MHz, CDCl₃) δ 7.48 (d, *J* = 7.8 Hz, 2H), 7.29–7.26 (m, 2H), 7.17–7.08 (m, 7H), 6.91 (d, *J* = 7.8 Hz, 1H), 6.66 (t, *J* = 7.8 Hz, 1H), 6.60 (d, *J* = 7.2 Hz, 1H), 5.99–5.91 (m, 1H), 5.19–5.04 (m, 2H), 3.91 (s, 3H), 3.15 (d, *J* = 9.6 Hz, 1H), 2.64–2.54 (m, 1H), 2.43–2.35 (m, 1H), 2.13–2.06 (m, 1H). **¹³C NMR** (150 MHz, CDCl₃) δ 159.15, 149.51, 139.27, 138.01, 131.32, 128.81, 128.28, 127.93, 127.06, 126.56, 126.06, 125.74, 119.63, 115.22, 110.04, 77.21, 77.00, 76.79, 55.53, 39.66, 30.82, 30.27, 27.59. **HRMS** (ESI-TOF) (*m/z*): Calcd for C₂₅H₂₅O ([M + H]⁺), 341.1900; found 341.1904.



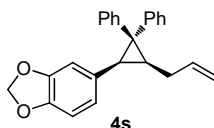
((2S*,3S*)-2-Allyl-3-(3,5-dimethylphenyl)cyclopropane-1,1-diyl)dibenzene (4r):

following the general procedure, the reaction of 2-(3,5-dimethylphenyl)-5,5-dimethyl-1,3,2-dioxaborinane (0.30 mmol, 1.5 equiv., 65.0 mg), 3-bromoprop-1-ene (0.60 mmol, 3.0 equiv., 72.0 mg) and 3,3-diphenyl cyclopropene (0.20 mmol, 1.0 equiv., 83.4 mg) afforded **4r** (39.2 mg, 58% yield) as a colorless oil.

¹H NMR (600 MHz, CDCl₃) δ 7.27–7.24 (m, 2H), 7.18–7.13 (m, 4H), 7.13–7.09 (m, 3H), 7.06–7.03 (m, 1H), 6.70 (s, 1H), 6.34 (s, 2H), 5.82–5.74 (m, 1H), 5.07–5.01 (m, 1H), 4.95–4.91 (m, 1H), 2.66 (d, *J* = 9.6 Hz, 1H), 2.54–2.47 (m, 1H), 2.25–2.17 (m, 1H), 2.08 (s, 6H), 2.00–1.93 (m, 1H).

¹³C NMR (151 MHz, CDCl₃) δ 149.24, 137.99, 137.97, 137.88, 136.71, 132.10, 128.44, 128.09, 127.85, 127.66, 127.07, 126.50, 125.83, 115.19, 40.72, 35.24, 31.82, 30.24, 21.40.

HRMS (ESI-TOF) (*m/z*): Calcd for C₂₆H₂₆ ([M + H]⁺), 339.2107; found 339.2105.

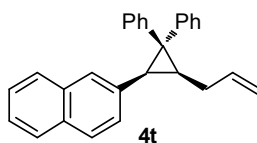


5-((1S*,3S*)-3-Allyl-2,2-diphenylcyclopropyl)benzo[d][1,3]dioxole (4s): following the general procedure, the reaction of 2-(benzo[d][1,3]dioxol-5-yl)-5,5-dimethyl-1,3,2-dioxaborinane (0.30 mmol, 1.5 equiv., 70.2 mg), 3-bromoprop-1-ene (0.60 mmol, 3.0 equiv., 72.0 mg) and 3,3-diphenylcyclopropene (0.20 mmol, 1.0 equiv., 38.4 mg) afforded **4s** (28.4 mg, 40% yield) as a colorless oil.

¹H NMR (600 MHz, CDCl₃) δ 7.25–7.22 (m, 2H), 7.19–7.14 (m, 4H), 7.14–7.09 (m, 3H), 7.07–7.03 (m, 1H), 6.56 (d, *J* = 7.8 Hz, 1H), 6.37–6.34 (m, 1H), 6.16–6.14 (m, 1H), 5.82–5.79 (m, 2H), 5.79–5.73 (m, 1H), 5.07–5.02 (m, 1H), 4.96–4.92 (m, 1H), 2.68 (d, *J* = 9.6 Hz, 1H), 2.55–2.48 (m, 1H), 2.23–2.15 (m, 1H), 1.98–1.91 (m, 1H).

¹³C NMR (151 MHz, CDCl₃) δ 149.06, 146.85, 145.34, 137.75, 137.55, 131.96, 131.82, 128.41, 128.25, 127.54, 126.61, 125.83, 123.07, 115.25, 109.94, 107.55, 100.71, 40.34, 35.07, 31.43, 30.11.

HRMS (ESI-TOF) (*m/z*): Calcd for C₂₅H₂₂O₂ ([M + H]⁺), 355.1692; found 355.1699.



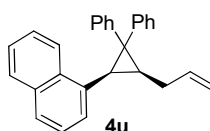
2-((1S*,3S*)-3-Allyl-2,2-diphenylcyclopropyl)naphthalene (4t): following the general procedure, the reaction of 5,5-dimethyl-2-(naphthalen-2-yl)-1,3,2-dioxaborinane (0.30

mmol, 1.5 equiv., 72.0 mg), 3-bromoprop-1-ene (0.60 mmol, 3.0 equiv., 72.0 mg) and 3,3-diphenyl cyclopropene (0.20 mmol, 1.0 equiv., 38.4 mg) afforded **4t** (49.4 mg, 69% yield) as a colorless oil.

¹H NMR (600 MHz, CDCl₃) δ 7.69–7.64 (m, 1H), 7.54–7.50 (m, 1H), 7.50–7.46 (m, 1H), 7.32–7.27 (m, 4H), 7.21–7.16 (m, 3H), 7.15–7.11 (m, 5H), 7.08–7.04 (m, 1H), 6.92–6.88 (m, 1H), 5.79–5.70 (m, 1H), 5.06–5.00 (m, 1H), 4.91–4.87 (m, 1H), 2.90 (d, *J* = 9.6 Hz, 1H), 2.67–2.59 (m, 1H), 2.34–2.27 (m, 1H), 2.12–2.05 (m, 1H).

¹³C NMR (151 MHz, CDCl₃) δ 148.99, 137.77, 137.51, 135.86, 132.99, 132.06, 131.56, 128.60, 128.46, 128.28, 128.12, 127.58, 127.57, 127.35, 126.63, 125.91, 125.71, 125.13, 115.31, 41.08, 35.52, 32.22, 30.22.

HRMS (ESI-TOF) (*m/z*): Calcd for C₂₈H₂₄ ([M + H]⁺), 361.1950; found 361.1948.

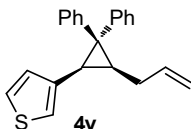


1-((1S*,3S*)-3-Allyl-2,2-diphenylcyclopropyl)naphthalene (4u**)**: following the general procedure, the reaction of 5,5-dimethyl-2-(naphthalen-1-yl)-1,3,2-dioxaborinane (0.30 mmol, 1.5 equiv., 72.0 mg), 3-bromoprop-1-ene (0.60 mmol, 3.0 equiv., 72.0 mg) and 3,3-diphenyl cyclopropene (0.20 mmol, 1.0 equiv., 38.4 mg) afforded **4u** (12.3 mg, 17% yield) as a colorless oil.

¹H NMR (600 MHz, CDCl₃) δ 8.22–8.18 (m, 1H), 7.89–7.85 (m, 1H), 7.71–7.67 (m, 1H), 7.52–7.47 (m, 2H), 7.37–7.30 (m, 4H), 7.24–7.18 (m, 2H), 7.14–7.10 (m, 1H), 7.09–7.01 (m, 3H), 6.96–6.92 (m, 2H), 6.07–5.98 (m, 1H), 5.25–5.20 (m, 1H), 5.12–5.08 (m, 1H), 3.23–3.19 (m, 1H), 2.59–2.52 (m, 1H), 2.51–2.43 (m, 2H).

¹³C NMR (151 MHz, CDCl₃) δ 148.62, 138.84, 137.97, 134.61, 134.42, 133.62, 131.64, 128.82, 128.51, 127.85, 127.31, 126.66, 126.20, 126.14, 125.81, 125.49, 125.08, 124.69, 115.60, 39.30, 33.36, 31.60, 30.19.

HRMS (ESI-TOF) (*m/z*): Calcd for C₂₈H₂₄ ([M + H]⁺), 361.1950; found 361.1958.



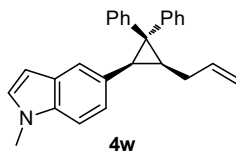
3-((1R*,3S*)-3-Allyl-2,2-diphenylcyclopropyl)thiophene (4v**)**: following the general procedure, the reaction of 5,5-dimethyl-2-(thiophen-3-yl)-1,3,2-dioxaborinane (0.30 mmol, 1.5 equiv., 58.8 mg), 3-bromoprop-1-ene (0.60 mmol, 3.0 equiv., 72.0 mg) and 3,3-diphenyl cyclopropene (0.20 mmol, 1.0 equiv., 38.4 mg) afforded **4v** (11.2 mg, 18% yield) as a white solid. M.p. 54–56 °C.

¹H NMR (600 MHz, CDCl₃) δ 7.23 – 7.20 (m, 2H), 7.19 – 7.16 (m, 4H), 7.15 – 7.13 (m, 3H), 7.07 – 7.03 (m, 2H), 6.55 (dd, *J* = 4.8, 1.2 Hz, 1H), 6.34 (dd, *J* = 3.0, 1.2 Hz, 1H), 5.74 (dddd, *J* = 17.1, 10.3, 6.7, 5.4 Hz, 1H), 5.01 (dq, *J* = 17.2, 1.7 Hz, 1H), 4.94 – 4.90 (m, 1H), 2.90 (d,

$J = 9.6$ Hz, 1H), 2.51 (dt, $J = 16.1, 6.8, 1.4$ Hz, 1H), 2.13 (dddt, $J = 15.2, 7.3, 5.4, 1.7$ Hz, 1H), 1.96 – 1.91 (m, 1H).

^{13}C NMR (151 MHz, CDCl_3) δ 148.62, 138.00, 137.97, 137.44, 132.08, 129.97, 128.40, 128.21, 127.37, 126.65, 125.84, 123.50, 120.92, 115.20, 40.22, 31.30, 31.15, 30.74.

HRMS (ESI-TOF) (m/z): Calcd for $\text{C}_{22}\text{H}_{20}\text{S}$ ($[\text{M} + \text{H}]^+$), 317.1358; found 317.1350.

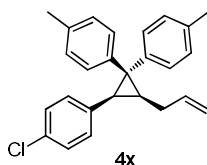


5-((1S*, 3S*)-3-Allyl-2,2-diphenylcyclopropyl)-1-methyl-1H-indole (4w): following the general procedure, the reaction of 5-(5,5-dimethyl-1,3,2-dioxaborinan-2-yl)-1-methyl-1H-indole (0.30 mmol, 1.5 equiv., 72.9 mg), 3-bromoprop-1-ene (0.60 mmol, 3.0 equiv., 72.0 mg) and 3,3-diphenyl cyclopropene (0.20 mmol, 1.0 equiv., 38.4 mg) afforded **4w** (43.2 mg, 60% yield) as a colorless oil.

^1H NMR (600 MHz, CDCl_3) δ 7.29–7.25 (m, 2H), 7.17–7.13 (m, 2H), 7.12–7.06 (m, 5H), 7.05–6.98 (m, 3H), 6.86–6.84 (m, 1H), 6.68–6.64 (m, 1H), 6.22–6.19 (m, 1H), 5.81–5.72 (m, 1H), 5.05–5.01 (m, 1H), 4.91–4.85 (m, 1H), 3.59 (s, 3H), 2.85 (d, $J = 10.2$ Hz, 1H), 2.59–2.51 (m, 1H), 2.34–2.26 (m, 1H), 2.03–1.95 (m, 1H).

^{13}C NMR (151 MHz, CDCl_3) δ 149.55, 138.31, 138.01, 135.07, 132.16, 128.66, 128.45, 128.34, 128.04, 127.65, 126.27, 125.63, 124.12, 121.63, 115.00, 108.13, 100.61, 40.00, 35.69, 32.71, 31.47, 30.35.

HRMS (ESI-TOF) (m/z): Calcd for $\text{C}_{27}\text{H}_{25}\text{N}$ ($[\text{M} + \text{H}]^+$), 364.2059; found 364.2052.

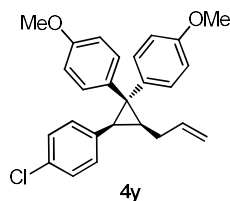


4,4'-((2S*, 3S*)-2-Allyl-3-(4-chlorophenyl)cyclopropane-1,1-diyl)bis(methylbenzene) (4x): following the general procedure, the reaction of 2-(4-chlorophenyl)-5,5-dimethyl-1,3,2-dioxaborinane (0.20 mmol, 1.0 equiv., 44.8 mg), 3-bromoprop-1-ene (0.60 mmol, 3.0 equiv., 72.0 mg) and 4,4'-(cycloprop-2-ene-1,1-diyl)bis(methylbenzene) (0.30 mmol, 1.5 equiv., 66.0 mg) afforded **4x** (37.6 mg, 50% yield) as a colorless oil.

^1H NMR (600 MHz, CDCl_3) δ 7.20–7.16 (m, 2H), 7.11–7.08 (m, 2H), 7.06–7.01 (m, 6H), 6.76–6.72 (m, 2H), 5.8–5.75 (m, 1H), 5.11–5.05 (m, 1H), 5.00–4.95 (m, 1H), 2.71 (d, $J = 9.6$ Hz, 1H), 2.64–2.56 (m, 1H), 2.31–2.25 (m, 6H), 2.25–2.18 (m, 1H), 2.07–2.01 (m, 1H).

^{13}C NMR (151 MHz, CDCl_3) δ 146.11, 137.33, 136.99, 136.21, 135.47, 134.42, 131.67, 131.09, 130.90, 129.12, 127.50, 127.24, 115.30, 40.28, 34.64, 31.80, 29.90, 21.11, 20.88.

HRMS (ESI-TOF) (m/z): Calcd for $\text{C}_{26}\text{H}_{26}\text{Cl}$ ($[\text{M} + \text{H}]^+$), 373.1718; found 373.1719.



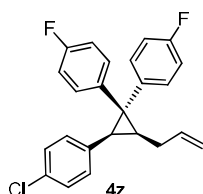
4,4'-((2S*,3S*)-2-Allyl-3-(4-chlorophenyl)cyclopropane-1,1-diyl)bis(methoxybenzene)

(4y): following the general procedure, the reaction of 2-(4-chlorophenyl)-5,5-dimethyl-1,3,2-dioxaborinane (0.20 mmol, 1.0 equiv., 44.8 mg), 3-bromoprop-1-ene (0.60 mmol, 3.0 equiv., 72.0 mg) and 4,4'-(cycloprop-2-ene-1,1-diyl) bis (methoxybenzene) (0.30 mmol, 1.5 equiv., 75.6 mg) afforded **4y** (46.5 mg, 58% yield) as a yellow solid. M.p. 38–40 °C.

¹H NMR (600 MHz, CDCl₃) δ 7.22–7.18 (m, 2H), 7.12–7.08 (m, 2H), 7.06–7.03 (m, 2H), 6.80–6.76 (m, 4H), 6.75–6.72 (m, 2H), 5.84–5.76 (m, 1H), 5.11–5.06 (m, 1H), 5.01–4.97 (m, 1H), 3.77 (s, 3H), 3.74 (s, 3H), 2.69 (d, *J* = 9.6 Hz, 1H), 2.61–2.54 (m, 1H), 2.25–2.18 (m, 1H), 2.04–1.99 (m, 1H).

¹³C NMR (151 MHz, CDCl₃) δ 146.13, 137.34, 137.01, 136.22, 135.48, 134.45, 131.69, 131.11, 130.91, 129.13, 127.51, 127.25, 115.31, 40.29, 34.66, 31.82, 29.91, 21.11, 20.88.

HRMS (ESI-TOF) (*m/z*): Calcd for C₂₆H₂₆ClO₂ ([M + H]⁺), 405.1616; found 405.1625.



4,4'-((2S*,3S*)-2-Allyl-3-(4-chlorophenyl)cyclopropane-1,1-diyl)bis(fluorobenzene) (4z):

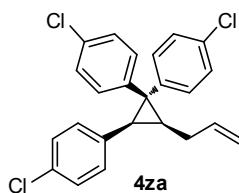
following the general procedure, the reaction of 2-(4-chlorophenyl)-5,5-dimethyl-1,3,2-dioxaborinane (0.30 mmol, 1.5 equiv., 67.3 mg), 3-bromoprop-1-ene (0.60 mmol, 3.0 equiv., 72.0 mg) and 4,4'-(cycloprop-2-ene-1,1-diyl)bis(fluorobenzene) (0.20 mmol, 1.0 equiv., 45.6 mg) afforded **4z** (57 mg, 75% yield) as a colorless oil.

¹H NMR (600 MHz, CDCl₃) δ 7.26 – 7.22 (m, 2H), 7.14 – 7.07 (m, 4H), 6.97 – 6.90 (m, 4H), 6.75 – 6.70 (m, 2H), 5.85 – 5.76 (m, 1H), 5.13 – 5.07 (m, 1H), 5.05 – 4.99 (m, 1H), 2.72 (d, *J* = 9.6 Hz, 1H), 2.61 – 2.52 (m, 1H), 2.28 – 2.20 (m, 1H), 2.07 – 2.01 (m, 1H).

¹³C NMR (151 MHz, CDCl₃) δ 161.69 (d, *J* = 245.0 Hz), 161.11 (d, *J* = 243.6 Hz), 144.30 (d, *J* = 3.0 Hz), 136.91, 136.24, 133.30 (d, *J* = 7.8 Hz), 133.14 (d, *J* = 3.5 Hz), 131.55, 130.80, 128.94 (d, *J* = 8.0 Hz), 127.76, 115.56 (d, *J* = 29.3 Hz), 115.47 (d, *J* = 28.2 Hz), 115.24, 39.51, 34.67, 31.89, 29.78.

¹⁹F NMR (470 MHz, CDCl₃) δ – 115.07 (tt, *J* = 8.5, 5.6 Hz, 1F), – 116.66 (tt, *J* = 8.5, 5.2 Hz, 1F).

HRMS (ESI-TOF) (*m/z*): Calcd for C₂₄H₁₉ClF₂ ([M + H]⁺), 381.1216; found 381.1208.

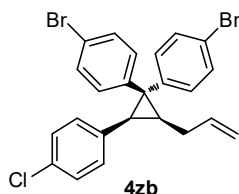


4,4',4''-((2S*,3S*)-3-Allylcyclopropane-1,1,2-triyl)tris(chlorobenzene) (4za): following the general procedure, the reaction of 2-(4-chlorophenyl)-5,5-dimethyl-1,3,2-dioxaborinane (0.30 mmol, 1.5 equiv., 67.3 mg), 3-bromoprop-1-ene (0.60 mmol, 3.0 equiv., 72.0 mg) and 4,4'-(cycloprop-2-ene-1,1-diyl)bis(chlorobenzene) (0.20 mmol, 1.0 equiv., 52.0 mg) afforded **4za** (55.4 mg, 67% yield) as a yellow solid. M.p. 98-100 °C.

¹H NMR (600 MHz, CDCl₃) δ 7.25–7.18 (m, 6H), 7.15–7.11 (m, 2H), 7.07–7.03 (m, 2H), 6.75–6.72 (m, 2H), 5.84–5.76 (m, 1H), 5.12–5.07 (m, 1H), 5.04–5.00 (m, 1H), 2.72 (d, *J* = 10.2 Hz, 1H), 2.59–2.52 (m, 1H), 2.27–2.21 (m, 1H), 2.08–2.03 (m, 1H).

¹³C NMR (151 MHz, CDCl₃) δ 146.60, 136.75, 135.92, 135.57, 133.12, 133.01, 131.98, 131.69, 130.80, 128.81, 128.76, 128.69, 127.84, 115.81, 39.62, 34.77, 31.82, 29.74.

HRMS (ESI-TOF) (*m/z*): Calcd for C₂₄H₁₉Cl₃ ([*M* + *H*]⁺), 413.0625; found 413.0620.

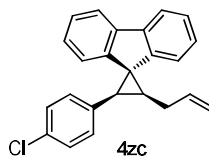


4,4'-((2S*,3S*)-2-Allyl-3-(4-chlorophenyl)cyclopropane-1,1-diyl)bis(bromobenzene) (4zb): following the general procedure, the reaction of 2-(4-chlorophenyl)-5,5-dimethyl-1,3,2-dioxaborinane (0.30 mmol, 1.5 equiv., 67.3 mg), 3-bromoprop-1-ene (0.60 mmol, 3.0 equiv., 72.0 mg) and 4,4'-(cycloprop-2-ene-1,1-diyl)bis(bromobenzene) (0.20 mmol, 1.0 equiv., 69.5 mg) afforded **4zb** (79 mg, 79% yield) as a colorless oil.

¹H NMR (600 MHz, CDCl₃) δ 7.40–7.34 (m, 4H), 7.15–7.11 (m, 4H), 7.01–6.96 (m, 2H), 6.76–6.72 (m, 2H), 5.84–5.75 (m, 1H), 5.12–5.06 (m, 1H), 5.05–5.00 (m, 1H), 2.72 (d, *J* = 9.6 Hz, 1H), 2.58–2.51 (m, 1H), 2.28–2.20 (m, 1H), 2.08–2.02 (m, 1H).

¹³C NMR (151 MHz, CDCl₃) δ 147.02, 136.70, 136.00, 135.85, 133.48, 131.77, 131.71, 131.64, 130.79, 129.14, 127.85, 121.23, 120.04, 115.83, 39.74, 34.73, 31.74, 29.72.

HRMS (ESI-TOF) (*m/z*): Calcd for C₂₄H₁₉Br₂Cl ([*M* + *H*]⁺), 500.9614; found 500.9606.

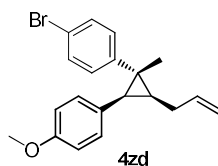


(2S*,3S*)-2-Allyl-3-(4-chlorophenyl)spiro[cyclopropane-1,9'-fluorene] (4zc): following the general procedure, the reaction of 2-(4-chlorophenyl)-5,5-dimethyl-1,3,2-dioxaborinane (0.30 mmol, 1.5 equiv., 67.3 mg), 3-bromoprop-1-ene (0.60 mmol, 3.0 equiv., 72.0 mg) and spiro[cyclopropane-1,9'-fluorene]-2-ene (0.20 mmol, 1.0 equiv., 38.0 mg) afforded **4zc** (44.7 mg, 65% yield) as a white solid. M.p. 45-47°C.

¹H NMR (600 MHz, CDCl₃) δ 7.89–7.83 (m, 2H), 7.41–7.30 (m, 3H), 7.26–7.21 (m, 2H), 7.16–7.12 (m, 1H), 7.05–6.97 (m, 3H), 6.25 (d, *J* = 7.8 Hz, 1H), 5.70–5.61 (m, 1H), 4.94–4.89 (m, 1H), 4.89–4.85 (m, 1H), 3.42 (d, *J* = 8.4 Hz, 1H), 2.70–2.62 (m, 1H), 2.38–2.31 (m, 2H).

¹³C NMR (151 MHz, CDCl₃) δ 148.82, 141.44, 141.41, 139.12, 136.57, 132.82, 132.77, 132.73, 128.35, 127.01, 126.07, 125.90, 125.53, 125.09, 119.93, 119.63, 118.37, 115.52, 37.74, 35.87, 33.60, 29.51.

HRMS (ESI-TOF) (*m/z*): Calcd for C₂₄H₁₉Cl ([M + H]⁺), 343.1248; found 343.1256.



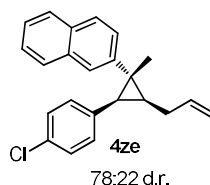
1-((1S*,2R*,3S*)-3-allyl-2-(4-bromophenyl)-2-methylcyclopropyl)-4-methoxybenzene

(4zd): following the general procedure, the reaction of 2-(4-methoxyphenyl)-5,5-dimethyl-1,3,2-dioxaborinane (0.30 mmol, 1.5 equiv., 66.6 mg), 3-bromoprop-1-ene (0.60 mmol, 3.0 equiv., 72.0 mg) and 1-bromo-4-(1-methylcycloprop-2-en-1-yl)benzene (0.20 mmol, 1.0 equiv., 41.5 mg) afforded **4zd** (28.5 mg, 40% yield, 84:16 d.r.) as a colorless oil.

¹H NMR (600 MHz, CDCl₃) δ 7.46–7.41 (m, 2H), 7.40–7.37 (0.48H, ArH of the minor isomer), 7.28–7.23 (m, 2H), 7.22–7.17 (m, 2H), 7.01–6.97 (m, 0.44H, ArH of the minor isomer), 6.91–6.84 (m, 2H), 6.68–6.63 (m, 0.38H), 6.62–6.58 (m, 0.36H, ArH of the minor isomer), 6.00 (ddt, *J* = 17.4, 10.8, 6.0 Hz, 1H), 5.71 (ddt, *J* = 17.4, 10.8, 6.0 Hz, 0.19H, C=CH of the minor isomer), 5.18–5.10 (m, 1H), 5.10–5.05 (m, 1H), 5.04–4.99 (m, 0.23H, C=CH of the minor isomer), 4.96–4.91 (m, 0.19H, C=CH of the minor isomer), 3.80 (s, 3H), 3.93 (s, 0.54H, OMe of the minor isomer), 2.45–2.36 (m, 2H), 2.36–2.30 (m, 0.21H), 2.20 (d, *J* = 9.6 Hz, 0.20H), 2.08–1.96 (m, 1.22H), 1.51–1.46 (m, 1H), 1.46 (s, 0.6H, Me of the minor isomer), 1.19 (s, 3H);

¹³C NMR (151 MHz, CDCl₃) δ (peaks of isomers were recorded together and not assigned to each isomer) 158.09, 157.23, 148.42, 139.23, 137.99, 137.82, 132.84, 131.81, 131.40, 131.39, 130.26, 130.20, 129.22, 128.82, 120.18, 119.36, 115.10, 114.79, 113.73, 112.92, 55.21, 55.08, 33.37, 33.13, 30.93, 30.71, 30.59, 30.22, 29.78, 27.91, 27.68, 17.47.

HRMS (ESI-TOF) (*m/z*): Calcd for C₂₀H₂₁BrO ([M + H]⁺), 357.0849; found 357.0856.



2-((1R*,2S*,3S*)-2-allyl-3-(4-chlorophenyl)-1-methylcyclopropyl)naphthalene (4ze):

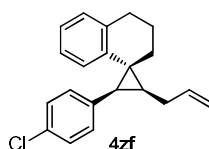
following the general procedure, the reaction of 2-(4-chlorophenyl)-5,5-dimethyl-1,3,2-dioxaborinane (0.30 mmol, 1.5 equiv., 66.6 mg), 3-bromoprop-1-ene (0.60 mmol, 3.0 equiv., 72.0 mg) and 2-(1-methylcycloprop-2-en-1-yl)naphthalene (0.20 mmol, 1.0 equiv.,

36.0 mg) afforded **4ze** (15.7 mg, 24% yield, 78:22 d.r.) as a colorless oil.

¹H NMR (600 MHz, CDCl₃) δ (overlapped peaks of isomers were assigned together) 7.86-7.77 (m, 4.3H), 7.77-7.71 (m, 0.6H), 7.63 (s, 0.3H), 7.55-7.50 (m, 1H), 7.50-7.41 (m, 2.6H), 7.36-7.27 (m, 4H), 7.22-7.17 (m, 0.3H), 7.02-6.97 (m, 0.6H), 6.64-6.58 (m, 0.6H), 6.06 (ddt, *J* = 17.4, 10.8, 6.0 Hz, 1H), 5.72 (ddt, *J* = 17.4, 10.8, 6.0 Hz, 0.3H), 5.24-5.17 (m, 1H), 5.16-5.09 (m, 1H), 5.07-5.01 (m, 0.3H), 4.99-4.93 (m, 0.3H), 2.54 (d, *J* = 9.6 Hz, 1H), 2.51 (t, *J* = 6.0 Hz, 0.3H), 2.47-2.37 (m, 1H), 2.32-2.24 (m, 0.3H), 2.13-2.01 (m, 1.3H); 1.67 (dt, *J* = 9.0, 6.0 Hz, 1H), 1.60-1.56 (m, 0.3H), 1.56 (s, 1H, methyl of the minor isomer), 1.30 (s, 3H, methyl of the major isomer);

¹³C NMR (151 MHz, CDCl₃) δ (peaks correspond to both isomers and are not assigned to each isomer) 146.29, 137.87, 137.62, 137.36, 137.23, 135.80, 133.55, 133.52, 132.31, 132.13, 132.10, 131.96, 130.72, 130.50, 129.53, 129.16, 128.46, 128.14, 127.95, 127.71, 127.64, 127.58, 127.55, 127.40, 126.26, 126.07, 125.82, 125.66, 125.45, 125.40, 115.30, 114.98, 33.63, 33.31, 32.55, 31.60, 30.57, 30.28, 29.73, 28.54, 27.61, 17.68.

HRMS (ESI-TOF) (*m/z*): Calcd for C₂₃H₂₁Cl ([M + H]⁺), 333.1405; found 333.1412.

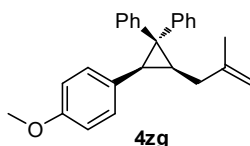


(1R,2S*,3S*)-2-Allyl-3-(4-chlorophenyl)-3',4'-dihydro-2'H-spiro[cyclopropane-1,1'-naphthalene] (4zf): following the general procedure, the reaction of 2-(4-chlorophenyl)-5,5-dimethyl-1,3,2-dioxaborinane (0.30 mmol, 1.5 equiv., 67.3 mg), 3-bromoprop-1-ene (0.60 mmol, 3.0 equiv., 72.0 mg) and 3',4'-dihydro-2'H-spiro [cyclopropane-1,1'-naphthalen]-2-ene (0.20 mmol, 1.0 equiv., 31.2 mg) afforded **4zf** (27 mg, 44% yield) as a colorless oil.

¹H NMR (600 MHz, CDCl₃) δ 7.28–7.25 (m, 2H), 7.23–7.19 (m, 2H), 7.19–7.14 (m, 1H), 7.11–7.06 (m, 2H), 6.85 (d, *J* = 7.8 Hz, 1H), 6.03–5.94 (m, 1H), 5.14–5.08 (m, 1H), 5.07–5.03 (m, 1H), 2.93–2.80 (m, 2H), 2.57 (d, *J* = 9.6 Hz, 1H), 2.40–2.33 (m, 1H), 2.21–2.14 (m, 1H), 1.87–1.81 (m, 2H), 1.68–1.62 (m, 1H), 1.55–1.52 (m, 2H).

¹³C NMR (151 MHz, CDCl₃) δ 142.42, 137.79, 137.45, 135.55, 132.06, 132.01, 128.82, 128.39, 126.37, 124.75, 121.83, 115.24, 35.35, 32.16, 30.82, 29.77, 25.37, 25.11, 22.16.

HRMS (ESI-TOF) (*m/z*): Calcd for C₂₁H₂₁Cl ([M + H]⁺), 309.1404; found 309.1409.



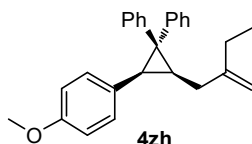
((2S*,3S*)-2-(4-Methoxyphenyl)-3-(2-methylallyl)cyclopropane-1,1-diyl)dibenzene (4zg): following the general procedure, the reaction of 2-(4-methoxyphenyl)-5,5-dimethyl-1,3,2-dioxaborinane (0.30 mmol, 1.5 equiv., 66.0 mg), 3-bromo-2-methylprop-1-ene (0.60 mmol, 3.0 equiv., 81.0 mg) and 3,3-diphenyl cyclopropene (0.20 mmol, 1.0 equiv., 38.4 mg)

afforded **4zg** (47.5 mg, 67% yield) as a colorless oil.

¹H NMR (600 MHz, CDCl₃) δ 7.27–7.23 (m, 2H), 7.18–7.09 (m, 7H), 7.06–7.01 (m, 1H), 6.67–6.59 (m, 4H), 4.80 (s, 1H), 4.71 (s, 1H), 3.66 (s, 3H), 2.73 (d, *J* = 9.6 Hz, 1H), 2.49–2.40 (m, 1H), 2.12–2.01 (m, 2H), 1.61 (s, 3H).

¹³C NMR (151 MHz, CDCl₃) δ 157.43, 149.29, 145.27, 138.03, 132.05, 130.73, 130.11, 128.39, 128.18, 127.45, 126.44, 125.72, 112.89, 110.33, 55.08, 39.68, 34.79, 33.39, 30.63, 23.48.

HRMS (ESI-TOF) (*m/z*): Calcd for C₂₆H₂₆NaO ([M + Na]⁺), 377.1863; found 377.1876.

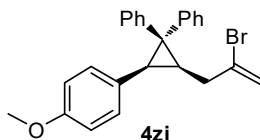


((2S*,3S*)-2-(4-Methoxyphenyl)-3-(2-methylenebutyl)cyclopropane-1,1-diyl)dibenzene (4zh): following the general procedure, the reaction of 2-(4-methoxyphenyl)- 5,5-dimethyl-1,3,2-dioxaborinane (0.30 mmol, 1.5 equiv., 66.0 mg), 2-(bromomethyl) but-1-ene (0.60 mmol, 3.0 equiv., 88.8 mg) and 3,3-diphenyl cyclopropene (0.20 mmol, 1.0 equiv., 38.4 mg) afforded **4zh** (51.4 mg, 70% yield) as a colorless oil.

¹H NMR (600 MHz, CDCl₃) δ 7.27–7.23 (m, 2H), 7.1–7.13 (m, 4H), 7.13–7.09 (m, 3H), 7.07–7.03 (m, 1H), 6.67–6.63 (m, 2H), 6.63–6.59 (m, 2H), 4.85 (s, 1H), 4.73 (s, 1H), 3.67 (s, 3H), 2.74 (d, *J* = 9.6 Hz, 1H), 2.48–2.41 (m, 1H), 2.13–2.04 (m, 2H), 1.97–1.86 (m, 2H), 0.92–0.87 (t, *J* = 7.8 Hz, 3H).

¹³C NMR (151 MHz, CDCl₃) δ 157.41, 151.87, 149.30, 138.02, 132.07, 130.73, 130.13, 128.38, 128.16, 127.43, 126.44, 125.70, 112.87, 108.22, 55.09, 39.68, 34.84, 31.88, 30.61, 29.84, 12.51.

HRMS (ESI-TOF) (*m/z*): Calcd for C₂₇H₂₈NaO ([M + Na]⁺), 391.2032; found 391.2033.

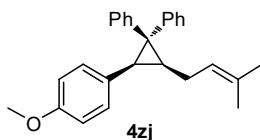


((2S*,3S*)-2-(2-Bromoallyl)-3-(4-methoxyphenyl)cyclopropane-1,1-diyl)dibenzene (4zi): following the general procedure, the reaction of 2-(4-methoxyphenyl)- 5,5-dimethyl-1,3,2-dioxaborinane (0.30 mmol, 1.5 equiv., 66.0 mg), 2,3- dibromoprop-1-ene (0.60 mmol, 3.0 equiv., 118.7 mg) and 3,3-diphenyl cyclopropene (0.20 mmol, 1.0 equiv., 84.0 mg) afforded **4zi** (56.0 mg, 67% yield) as a colorless oil.

¹H NMR (600 MHz, CDCl₃) δ 7.30–7.26 (m, 2H), 7.20–7.15 (m, 4H), 7.15–7.10 (m, 3H), 7.08–7.04 (m, 1H), 6.62 (s, 4H), 5.45 (s, 1H), 5.31 (s, 1H), 3.67 (s, 3H), 2.95– 2.89 (m, 1H), 2.76 (d, *J* = 9.6 Hz, 1H), 2.57–2.51 (m, 1H), 2.21–2.15 (m, 1H).

¹³C NMR (151 MHz, CDCl₃) δ 157.62, 148.68, 137.51, 132.92, 131.82, 130.63, 129.17, 128.49, 128.37, 127.56, 126.70, 126.00, 117.02, 113.04, 55.11, 39.93, 37.77, 34.35, 30.35.

HRMS (ESI-TOF) (*m/z*): Calcd for C₂₅H₂₃BrO ([M + H]⁺), 419.1005; found 419.1012.

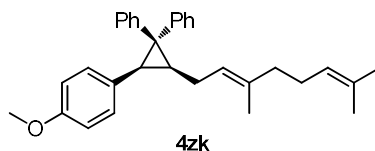


((2S*,3S*)-2-(4-methoxyphenyl)-3-(3-methylbut-2-en-1-yl)cyclopropane-1,1-diyl)dibenzene (4zj): following the general procedure, the reaction of 2-(4-methoxyphenyl)-5,5-dimethyl-1,3,2-dioxaborinane (0.30 mmol, 1.5 equiv., 66.0 mg, 1-bromo-3-methylbut-2-ene (0.60 mmol, 3.0 equiv., 89.4 mg) and 3,3-diphenyl cyclopropene (0.20 mmol, 1.0 equiv., 38.4 mg) afforded **4zj** (44.2 mg, 60% yield) as a colorless oil.

¹H NMR (600 MHz, CDCl₃) δ 7.22–7.19 (m, 2H), 7.17–7.12 (m, 4H), 7.12–7.06 (m, 3H), 7.05–7.00 (m, 1H), 6.70–6.65 (m, 2H), 6.64–6.60 (m, 2H), 5.15–5.10 (m, 1H), 3.67 (s, 3H), 2.64 (d, *J* = 9.6 Hz, 1H), 2.47–2.40 (m, 1H), 2.11–2.03 (m, 1H), 1.91–1.85 (m, 1H), 1.61 (s, 3H), 1.49 (s, 3H).

¹³C NMR (151 MHz, CDCl₃) δ 157.40, 149.40, 138.00, 132.25, 131.97, 130.68, 130.29, 128.32, 128.16, 127.50, 126.37, 125.64, 123.59, 112.96, 55.10, 40.24, 34.92, 33.07, 25.79, 24.77, 18.05.

HRMS (ESI-TOF) (*m/z*): Calcd for C₂₇H₂₈O ([M + H]⁺), 369.2212; found 369.2220.

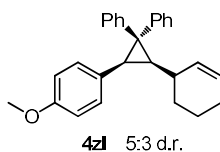


((2S*,3S*)-2-((E)-3,7-Dimethylocta-2,6-dien-1-yl)-3-(4-methoxyphenyl)cyclopropane-1,1-diyl)dibenzene (4zk): following the general procedure, the reaction of 2-(4-methoxyphenyl)-5,5-dimethyl-1,3,2-dioxaborinane (0.30 mmol, 1.5 equiv., 66.0 mg), (*E*)-1-bromo-3,7-dimethylocta-2,6-diene (0.60 mmol, 1.5 equiv., 64.8 mg) and 3,3-diphenyl cyclopropene (0.20 mmol, 1.0 equiv., 38.4 mg) afforded **4zk** (35.8 mg, 41% yield) as a white solid. M.p. 116–119°C.

¹H NMR (600 MHz, CDCl₃) δ 7.32–7.29 (m, 2H), 7.25–7.20 (m, 4H), 7.19–7.15 (m, 3H), 7.13–7.09 (m, 1H), 6.78–6.74 (m, 2H), 6.71–6.68 (m, 2H), 5.26–5.22 (m, 1H), 5.12–5.07 (m, 1H), 3.75 (s, 3H), 2.72 (d, *J* = 10.2 Hz, 1H), 2.53–2.46 (m, 1H), 2.20–2.13 (m, 1H), 2.12–2.04 (m, 2H), 2.04–1.92 (m, 3H), 1.68–1.66 (m, 3H), 1.61–1.59 (m, 3H), 1.57–1.54 (m, 3H).

¹³C NMR (151 MHz, CDCl₃) δ 157.39, 149.45, 138.08, 135.55, 132.20, 131.34, 130.68, 130.30, 128.33, 128.16, 127.60, 126.34, 125.65, 124.26, 123.68, 112.95, 55.10, 40.34, 39.67, 34.78, 32.99, 26.59, 25.70, 24.67, 17.71, 16.34.

HRMS (ESI-TOF) (*m/z*): Calcd for C₃₂H₃₆O ([M + H]⁺), 437.2838; found 437.2846.



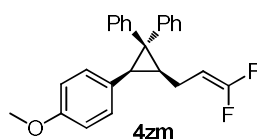
((2S*,3S*)-2-((S)-Cyclohex-2-en-1-yl)-3-(4-methoxyphenyl)cyclopropane-1,1-diyl)dibenzene

ene (4zl): following the general procedure, the reaction of 2-(4-methoxyphenyl)-5,5-dimethyl-1,3,2-dioxaborinane (0.30 mmol, 1.5 equiv., 66.0 mg), 1-(bromomethyl)cyclohex-1-ene (0.60 mmol, 3.0 equiv., 96.6 mg) and 3,3-diphenylcyclopropene (0.20 mmol, 1.0 equiv., 38.4 mg) afforded **4zl** (47.7 mg, 63% yield, 5:3 d.r.) as a colorless oil.

¹H NMR (600 MHz, CDCl₃) δ (most peaks of the two diastereomers overlap and have been integrated and assigned together) 7.31-7.21 (m, 3.51H), 7.18-7.06 (m, 11.7H), 7.06-7.00 (m, 1.72H), 6.69-6.64 (m, 1.25H), 6.63-6.57 (m, 5.20H), 6.19-6.14 (m, 1H, H_a (vinyl) of the major isomer), 5.82-5.76 (m, 1H, H_b (vinyl) of the major isomer), 5.50-5.44 (m, m, 1H, H_b (vinyl) of the minor isomer), 5.07-5.02 (m, 1H, H_a (vinyl) of the major isomer), 3.67 (s, 5H), 2.65 (d, *J* = 10.2 Hz, 0.60H), 2.63 (d, *J* = 9.6 Hz, 1H), 2.43-2.35 (m, 0.6H), 2.35-2.27 (m, 1H), 2.27-2.21 (m, 0.6H), 2.04-1.83 (m, 3.6H), 1.83-1.72 (m, 2H), 1.72-1.65 (m, 1H), 1.64-1.55 (m, 0.8H), 1.55-1.47 (m, 1.2H), 1.31-1.21 (m, 2.3H), 1.11-1.00 (m, 1H), 0.84-0.76 (m, 0.50H);

¹³C NMR (151 MHz, CDCl₃) δ (peaks of each diastereomer were not assigned) δ 157.42, 157.37, 149.48, 149.47, 138.36, 138.23, 132.03, 131.89, 131.71, 130.62, 130.60, 130.52, 130.35, 130.23, 128.36, 128.25, 128.22, 128.20, 127.81, 127.72, 127.57, 126.40, 126.38, 125.71, 125.69, 112.98, 112.91, 55.07, 41.28, 41.13, 39.01, 38.90, 34.46, 34.18, 31.50, 30.95, 30.72, 28.10, 25.26, 25.07, 21.33, 21.11.

HRMS (ESI-TOF) (*m/z*): Calcd for C₂₉H₃₀O ([M + H]⁺), 395.2369; found 395.2377.



((2S*,3S*)-2-(3,3-Difluoroallyl)-3-(4-methoxyphenyl)cyclopropane-1,1-diyl)dibenzene

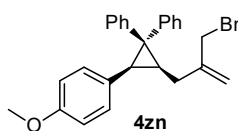
(4zm): following the general procedure, the reaction of 2-(4-methoxyphenyl)-5,5-dimethyl-1,3,2-dioxaborinane (0.30 mmol, 1.5 equiv., 66.0 mg), 3-bromo-3,3-difluoroprop-1-ene (0.60 mmol, 3.0 equiv., 93.5 mg) and 3,3-diphenylcyclopropene (0.20 mmol, 1.0 equiv., 38.4 mg) afforded **4zm** (34.6mg, 46% yield) as a colorless oil.

¹H NMR (600 MHz, CDCl₃) δ 7.23–7.20 (m, 2H), 7.19–7.11 (m, 5H), 7.09–7.03 (m, 3H), 6.66–6.61 (m, 4H), 3.98–3.89 (m, 1H), 3.67 (s, 3H), 2.67 (d, *J* = 9.6 Hz, 1H), 2.59–2.52 (m, 1H), 2.09–2.01 (m, 1H), 1.93–1.87 (m, 1H).

¹³C NMR (151 MHz, CDCl₃) δ 157.60, 156.06 (t, ¹*J*_{C-F} = 286.9 Hz), 148.76, 137.46, 131.92, 130.53, 129.35, 128.44, 128.35, 127.46, 126.67, 125.91, 113.13, 77.26 (t, ²*J*_{C-F} = 21.1 Hz), 55.12, 40.43, 34.45, 31.81 (t, ⁴*J*_{C-F} = 2.3 Hz), 19.43 (d, ³*J*_{C-F} = 4.5 Hz).

¹⁹F NMR (470 MHz, CDCl₃) δ – 88.67 (d, ²*J*_{F-F} = 47.0 Hz, 1F); – 90.35 (dd, ²*J*_{F-F} = 47.0 Hz, ³*J*_{F-H (trans)} = 25.6 Hz, 1F).

HRMS (ESI-TOF) (*m/z*): Calcd for C₂₅H₂₂F₂O ([M + H]⁺), 377.1711; found 377.1719.



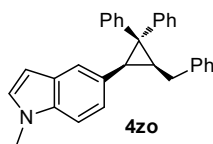
((2S*,3S*)-2-(3,3-Difluoroallyl)-3-(4-methoxyphenyl)cyclopropane-1,1-diyl)dibenzene

(4zn): following the general procedure, the reaction of 2-(4-methoxyphenyl)-5,5-dimethyl-1,3,2-dioxaborinane (0.30 mmol, 1.5 equiv., 66.0 mg), 3-bromo-2-(bromomethyl)prop-1-ene (0.60 mmol, 3.0 equiv., 127.1mg) and 3,3-diphenylcyclopropene (0.20 mmol, 1.0 equiv., 38.4 mg) afforded **4zn** (32.0mg, 37%yield) as a pair of atropisomeric isomers (ratio: 3:2).

¹H NMR (600 MHz, C₆D₆) δ (overlapped peaks of the isomers are assigned together) 7.31-7.22 (m, 4H), 7.16 (s, 4H), 7.14-7.07 (m, 4H), 7.04-6.97 (m, 2H), 6.76-6.70 (m, 2H), 6.65-6.59 (m, 2H), 4.98 (s, 0.4H), 4.96 (s, 0.6H), 4.89 (s, 0.4H), 4.87 (s, 0.6H), 3.64 (d, J = 11.4 Hz, 0.4H), 3.55 (d, J = 10.2 Hz, 0.6H), 3.53 (d, J = 11.4 Hz, 0.4H), 3.44 (d, J = 10.2 Hz, 0.6H), 3.24 (s, 3H), 2.91 (dd, J = 17.4, 6.0 Hz, 0.6H), 2.85 (dd, J = 16.2, 6.0 Hz, 0.4H), 2.74 (d, J = 9.6 Hz, 1H), 2.40-2.28 (m, 1H), 2.07-2.00 (m, 1H);

¹³C NMR (151 MHz, CDCl₃): (peaks of two isomers were not assigned and recorded together) 157.56, 148.98, 144.72, 144.45, 137.70, 137.68, 131.94, 130.64, 129.63, 128.45, 128.31, 127.39, 127.38, 126.63, 125.86, 115.74, 115.11, 113.01, 113.00, 55.11, 48.89, 39.75, 39.73, 37.33, 34.64, 34.62, 30.24, 30.18, 29.57, 29.21.

HRMS (ESI-TOF) (m/z): Calcd for C₂₅H₂₂F₂O ([M + H]⁺), 433.1162; found 433.1170.



5-((1S*,3S*)-3-benzyl-2,2-diphenylcyclopropyl)-1-methyl-1H-indole (4zo): following the general procedure, the reaction of 5-(5,5-dimethyl-1,3,2-dioxaborinane-2-yl)-1-methyl-1H-indole (0.30 mmol, 1.5 equiv., 72.9 mg), benzyl bromide (0.60 mmol, 3.0 equiv., 51.0 mg) and 3,3-diphenylcyclopropene (0.20 mmol, 1.0 equiv., 38.4 mg) afforded **4zo** (19.8 mg, 24% yield) as a colorless oil.

¹H NMR (600 MHz, C₆D₆) δ 7.38-7.30 (m, 2H), 7.30-7.17 (m, 9H), 7.17-7.07 (m, 6H), 7.02-6.94 (m, 1H), 6.85-6.77 (m, 1H), 6.31 (d, J = 3.0 Hz, 1H), 3.74 (s, 3H), 3.23 (dd, J = 15.6, 6.6 Hz, 1H), 3.08-2.96 (m, 2H), 2.38-2.30 (m, 1H);

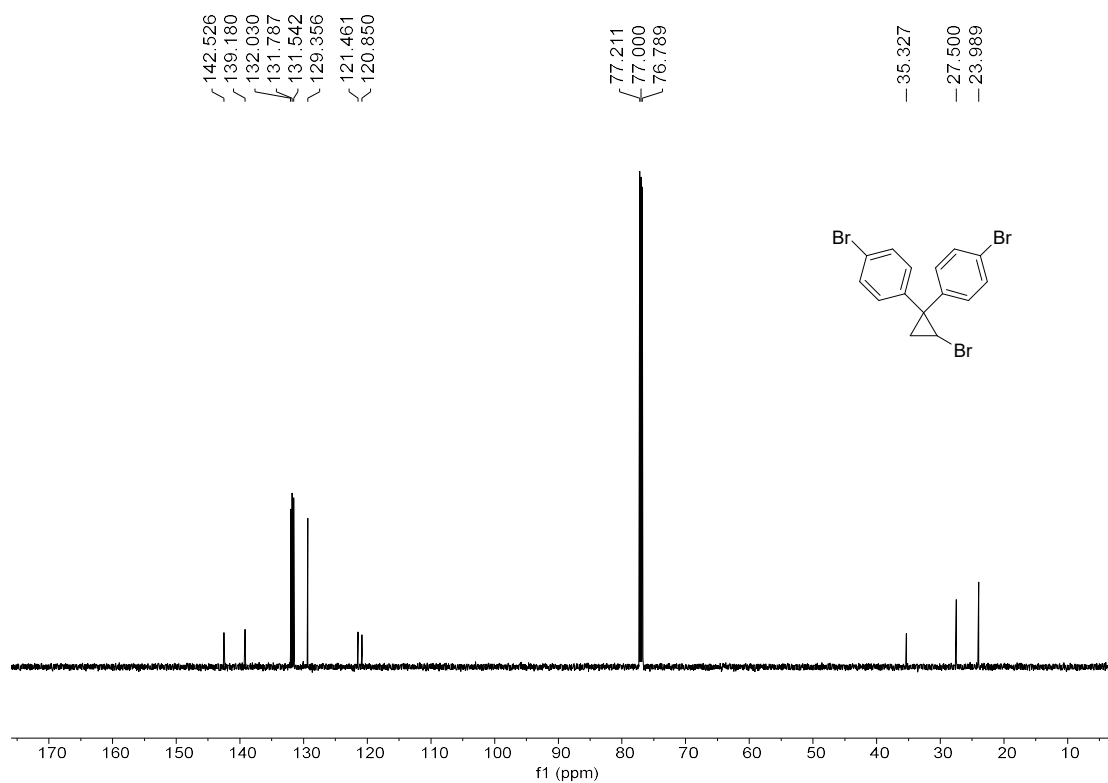
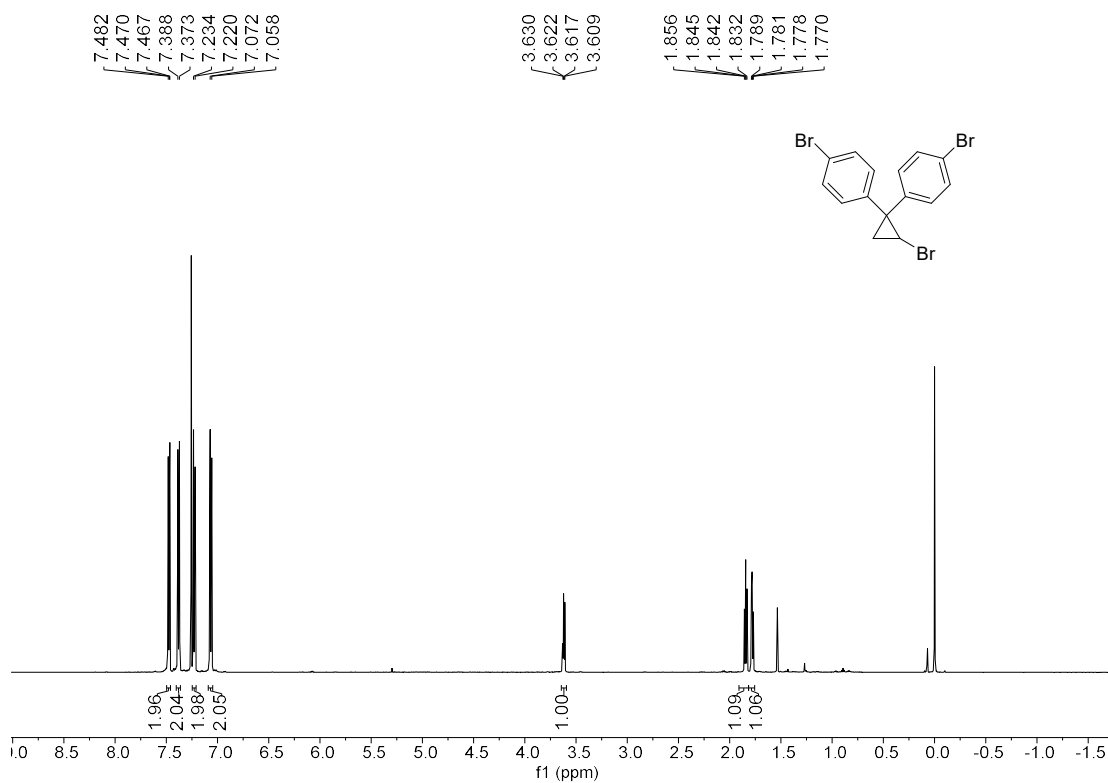
¹³C NMR (151 MHz, CDCl₃): δ 149.50, 141.88, 138.34, 135.19, 132.28, 128.70, 128.48, 128.43, 128.36, 128.26, 128.10, 128.08, 127.60, 126.33, 125.70, 125.64, 124.43, 121.99, 108.22, 100.71, 39.89, 36.25, 33.43, 32.79, 31.60.

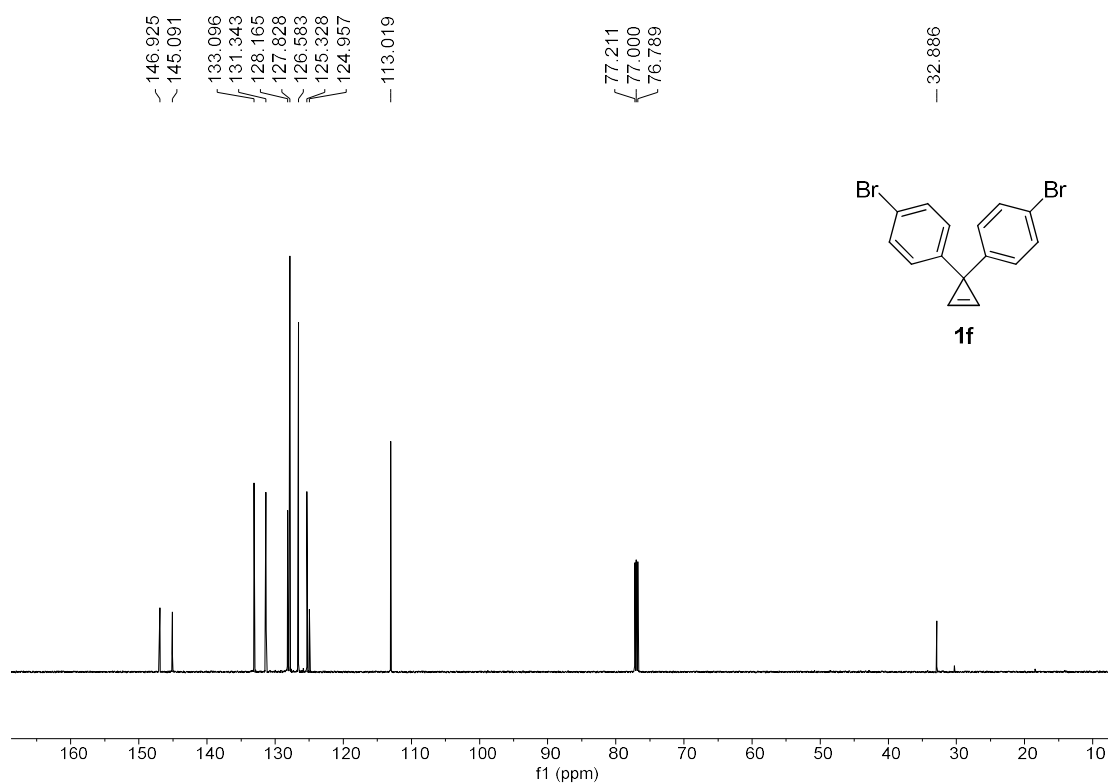
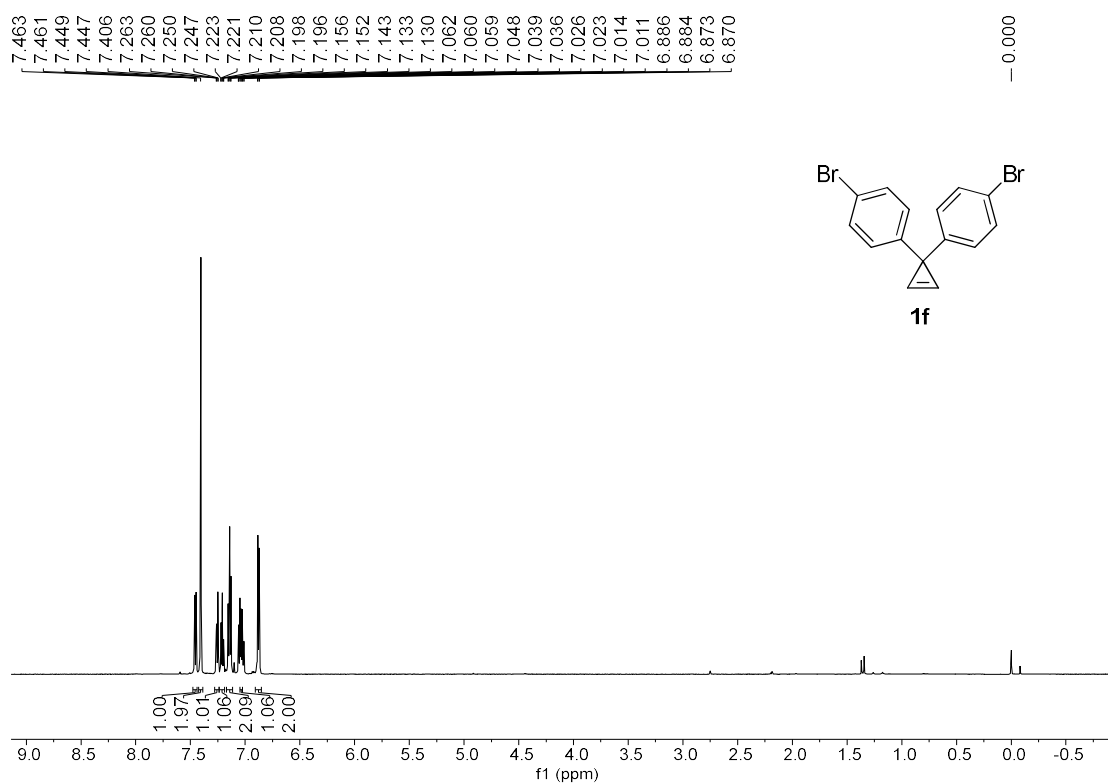
HRMS (ESI-TOF) (m/z): Calcd for C₂₅H₂₂F₂O ([M + H]⁺), 414.2216; found 414.2223.

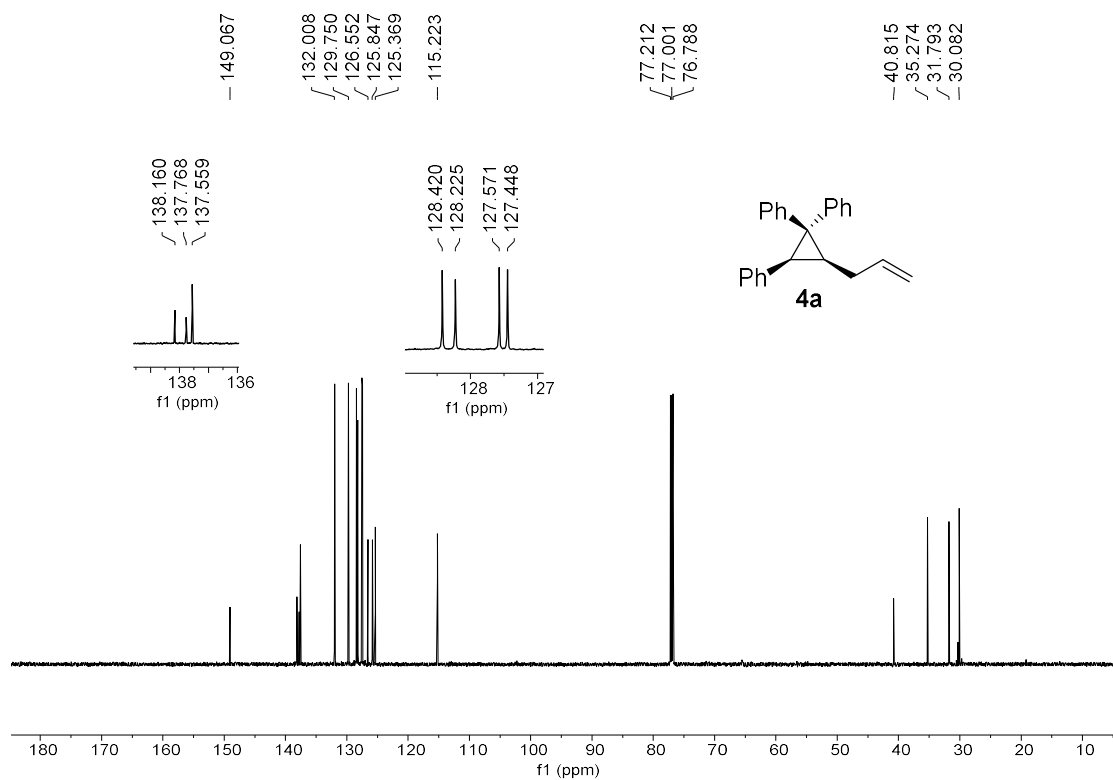
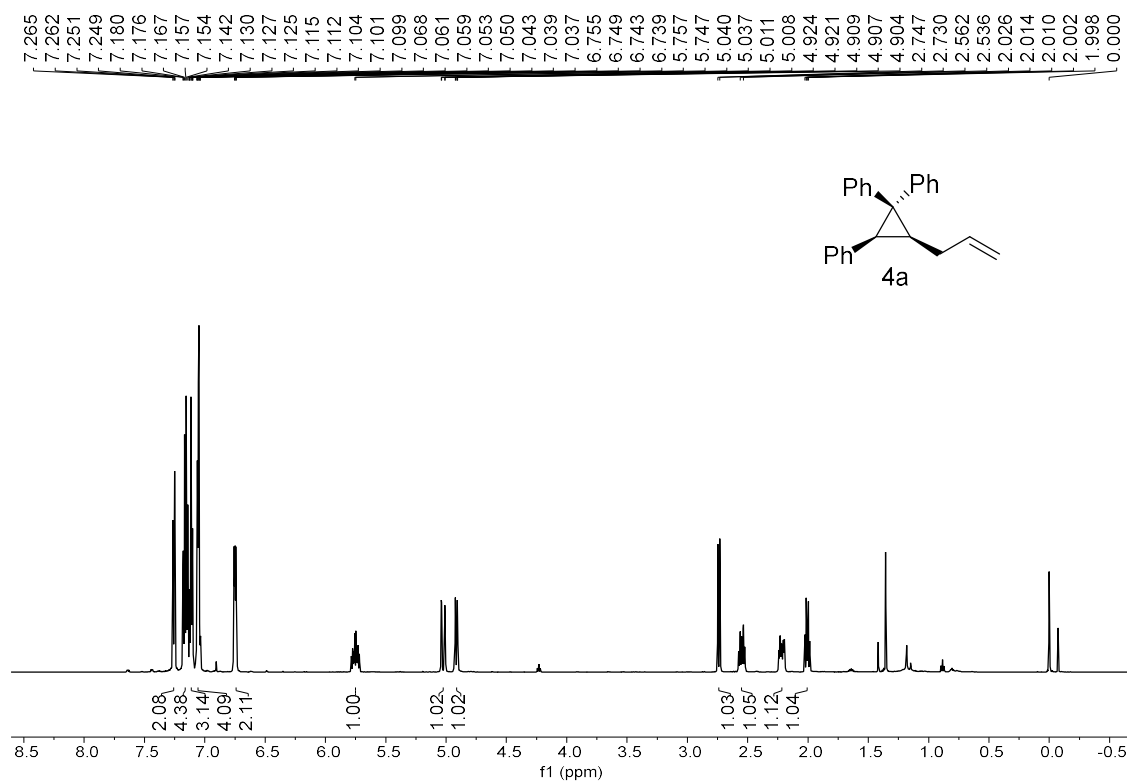
References

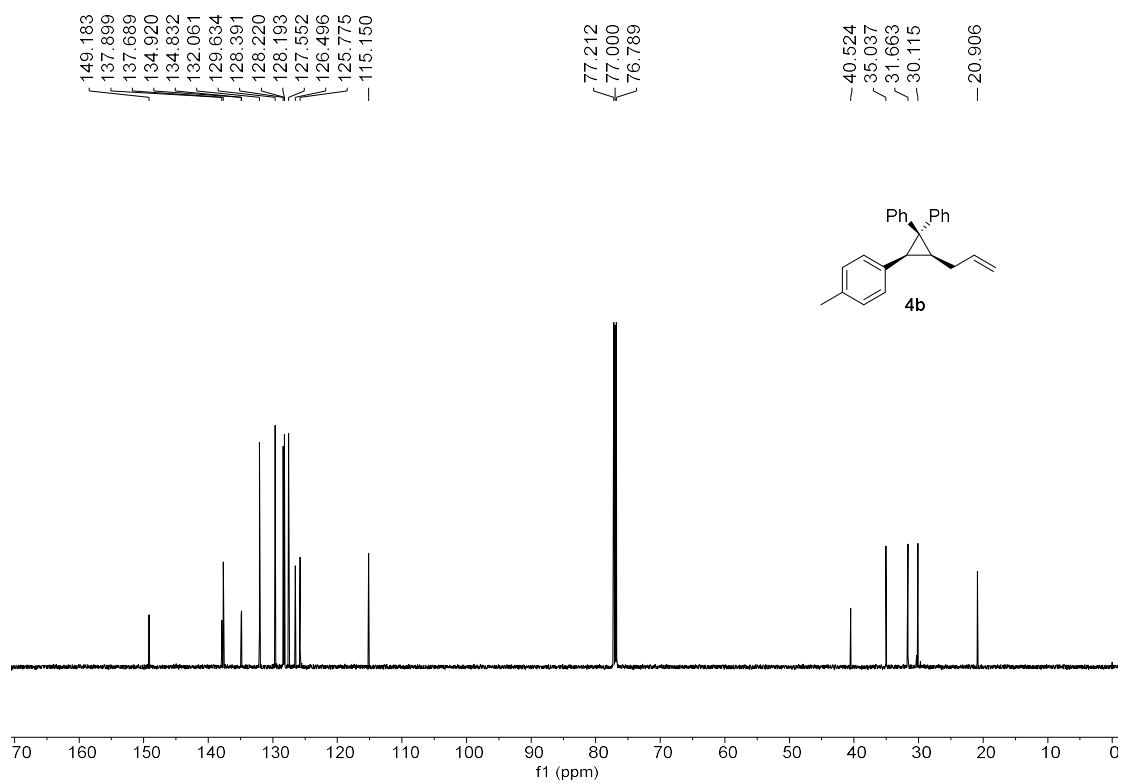
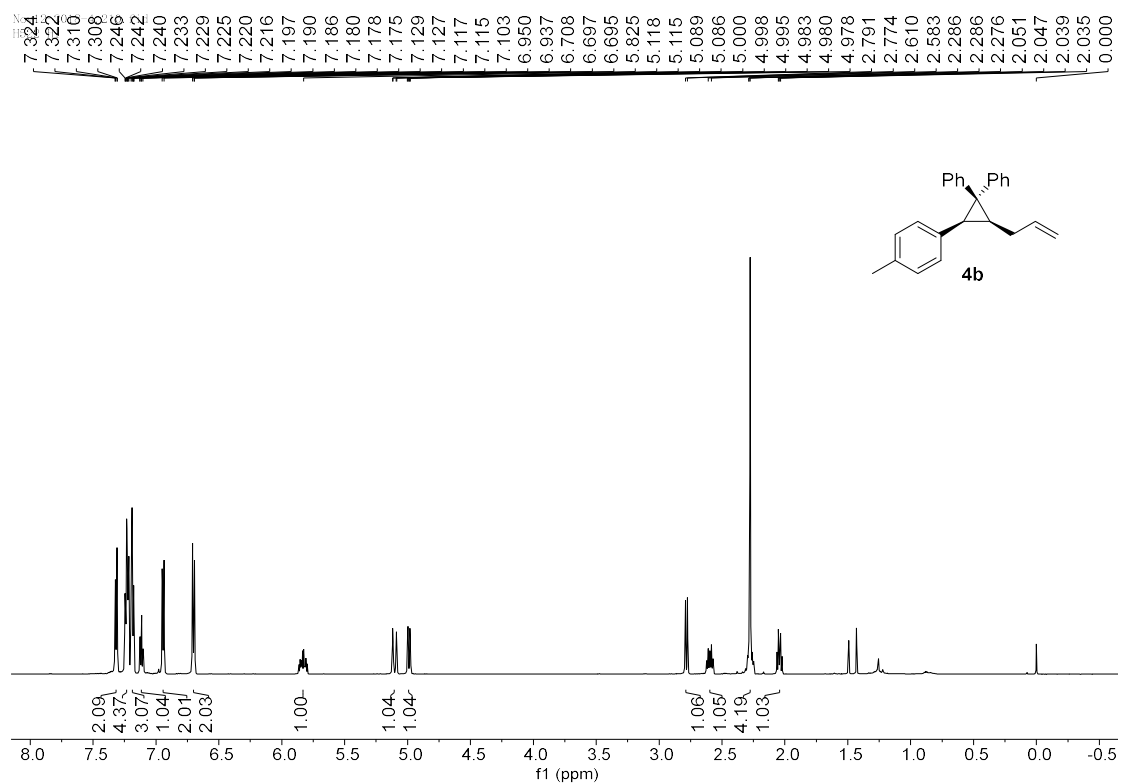
- [1] (a) Sherrill, W. M.; Kim, R.; Rubin, M. *Tetrahedron* **2008**, *64*, 8610 – 8617. (b) Phan, D. H. T.; Kou, K. G. M.; Dong, V. M. *J. Am. Chem. Soc* **2010**, *132*, 16354–16355. (c) Krämer, K.; Leong, P.; Lautens, M. *Org. Lett.* **2011**, *13*, 819-821. (c). Zhang, H.; Wang, B.; Yi, H.; Wang, J. *Org. Lett.* **2015**, *17*, 3322 – 3325.
- [2] Liu, X. Y.; Yang, C. T.; Zhang, Z. Q.; Lu, X.; Luo, X.; Xiao, B.; Fu, Y. *Chem. Commun.* **2015**, *51*, 2388 – 2391.
- [3] Zhao, H.; Chen, X. W.; Jiang, H. F.; Zhang, M. *Org. Chem. Front.* **2018**, *5*, 539–543.

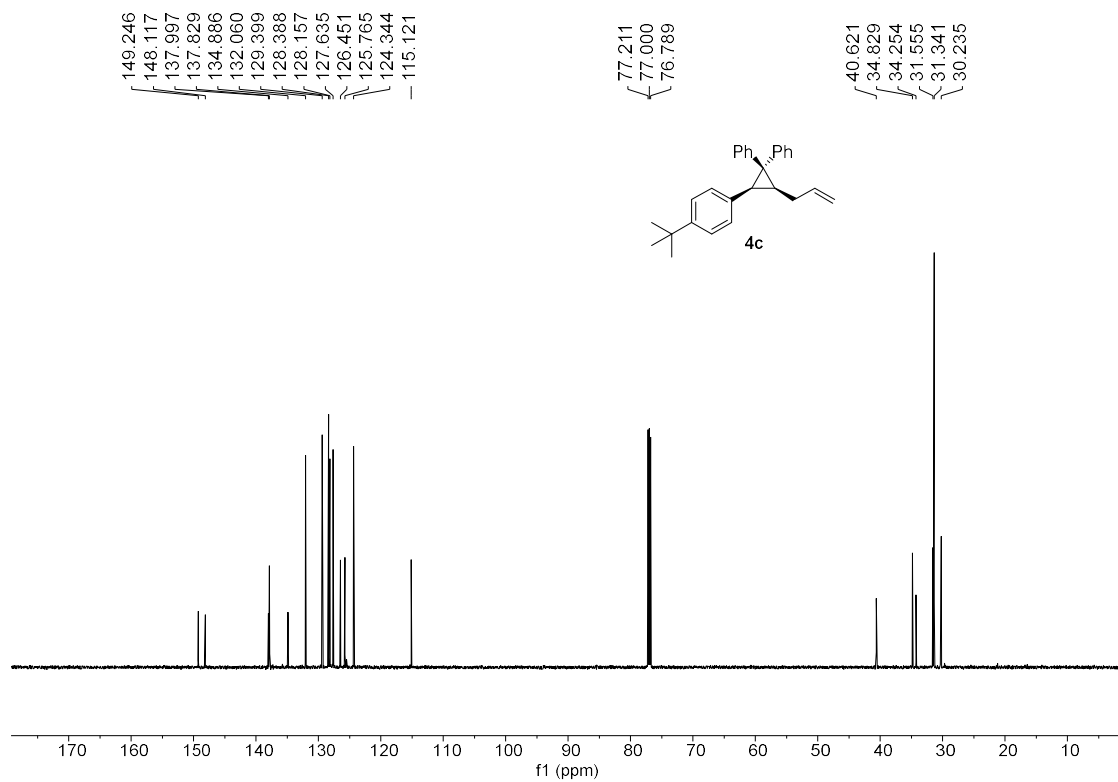
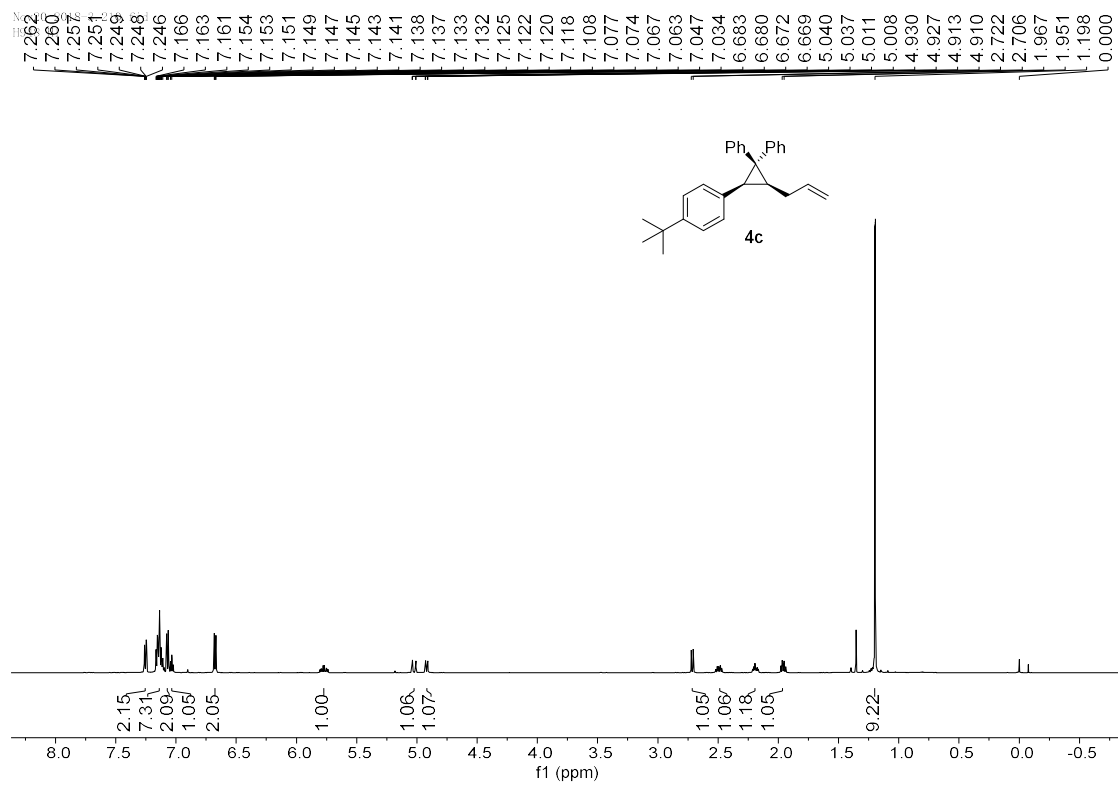
4. NMR spectra and HPLC chromatographs of new compounds

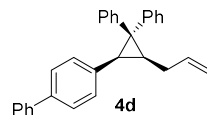
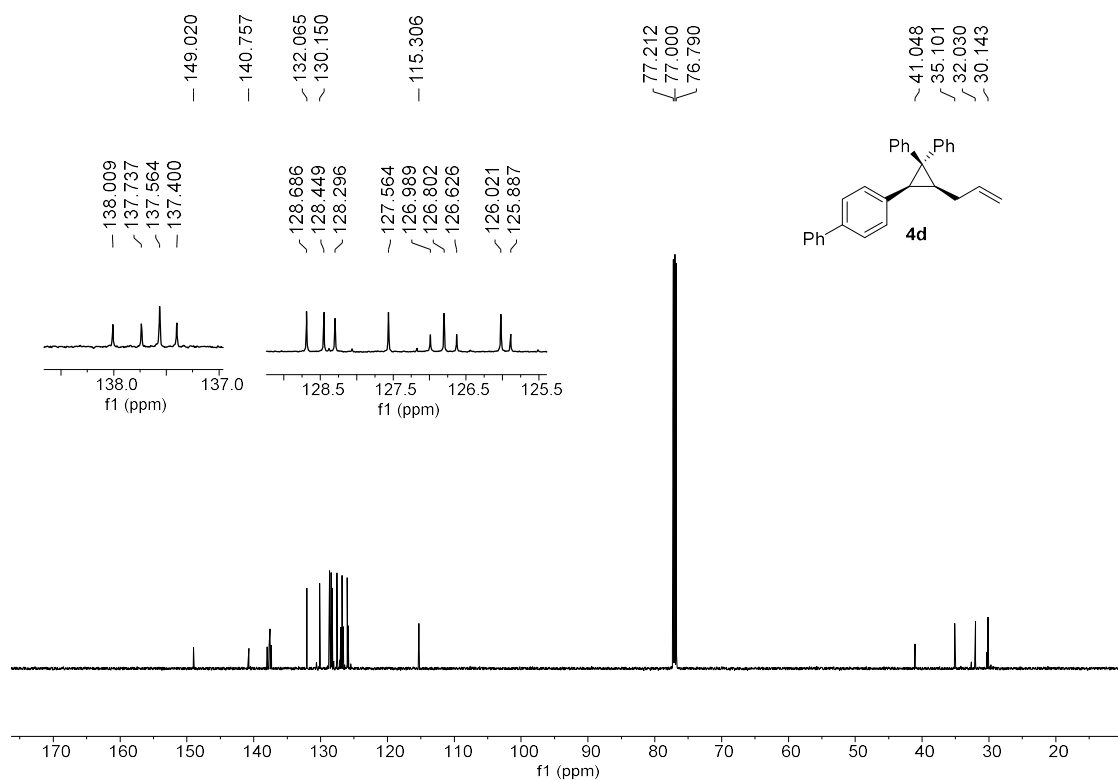
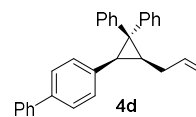
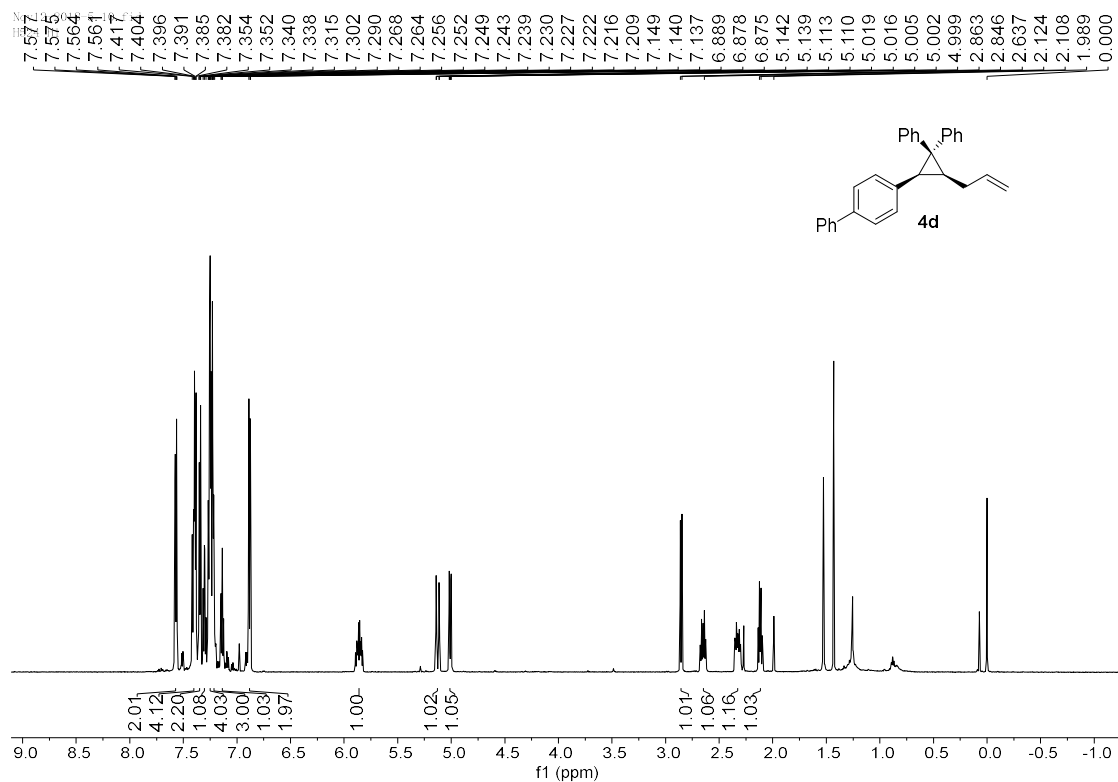


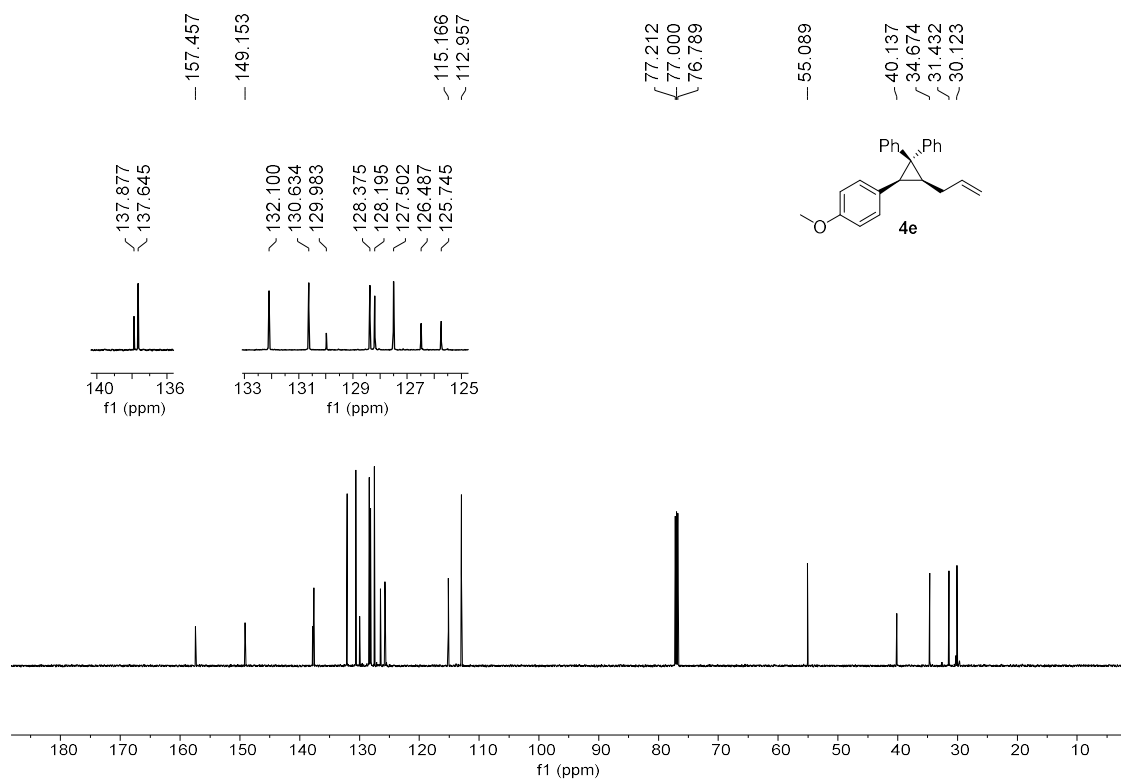
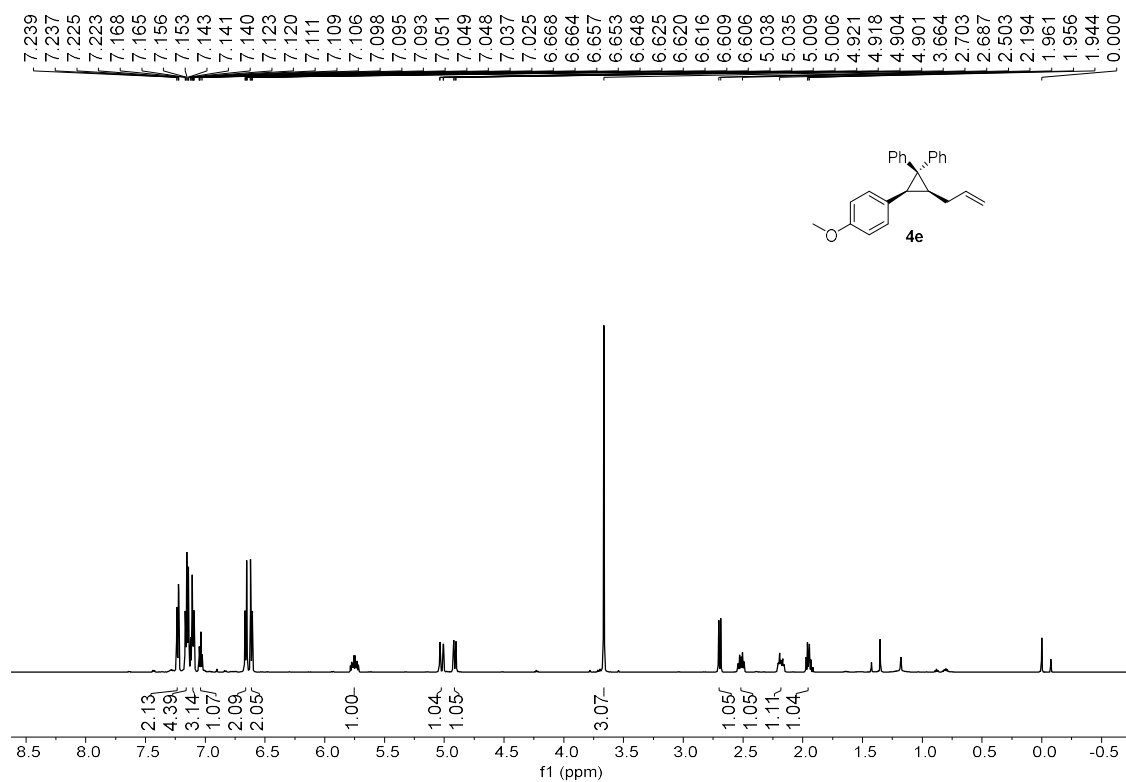


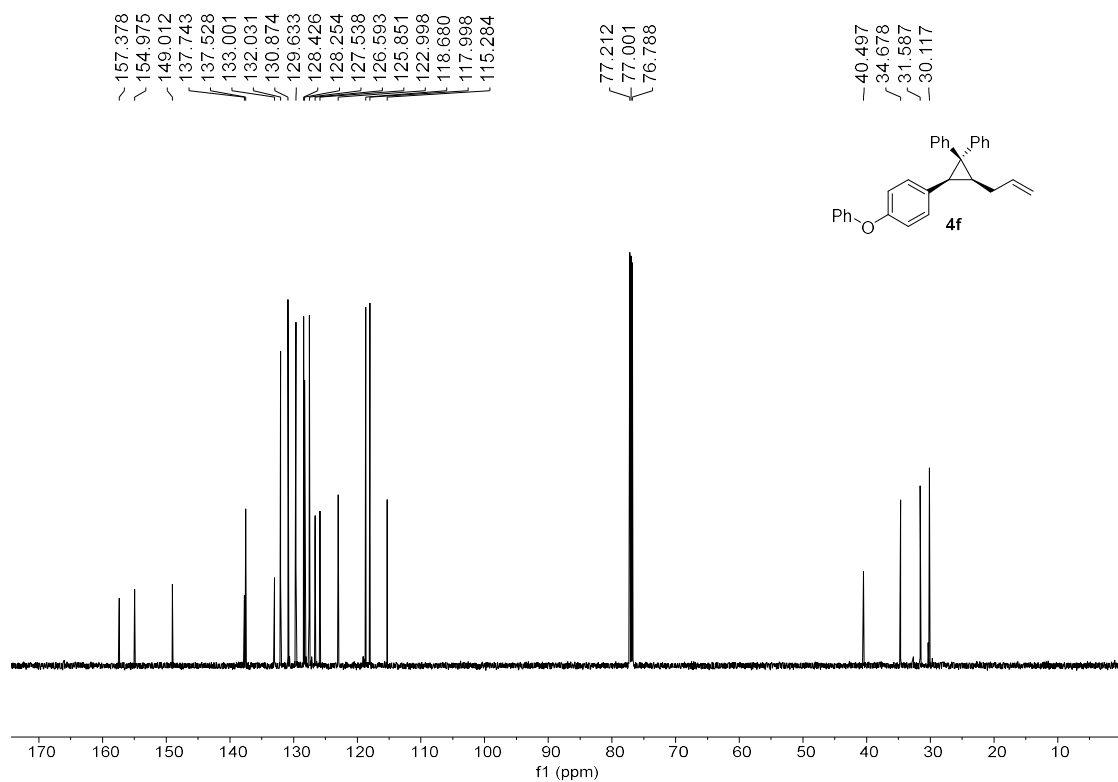
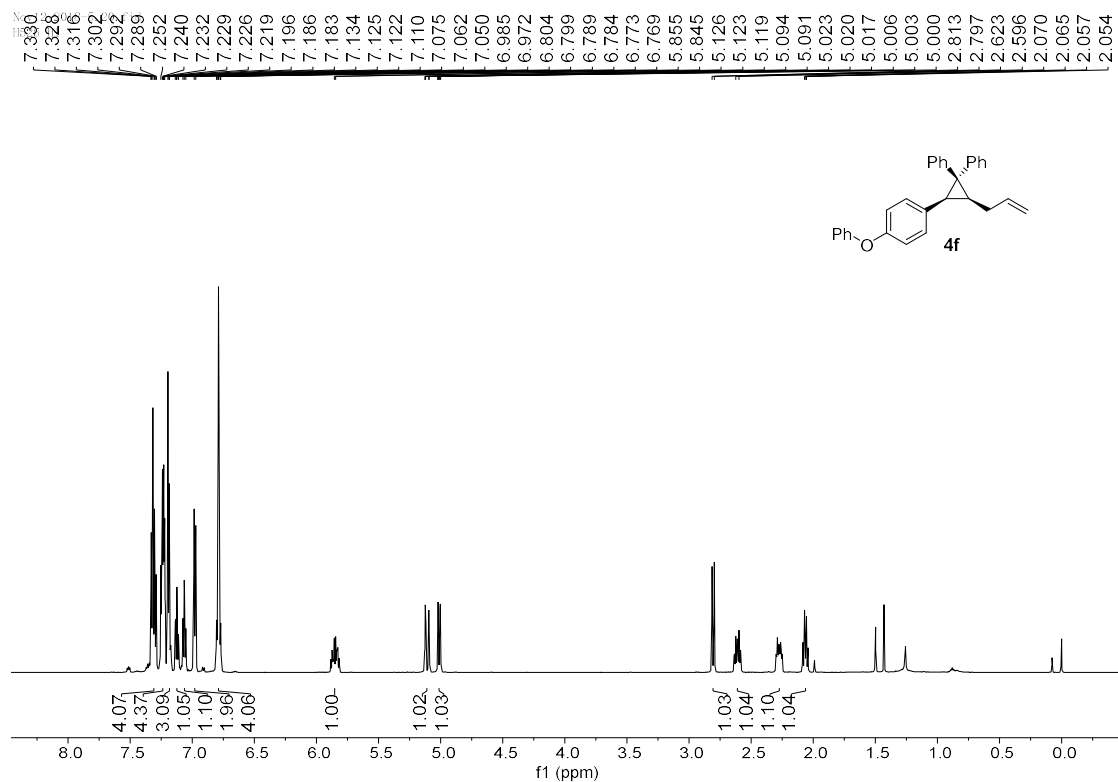


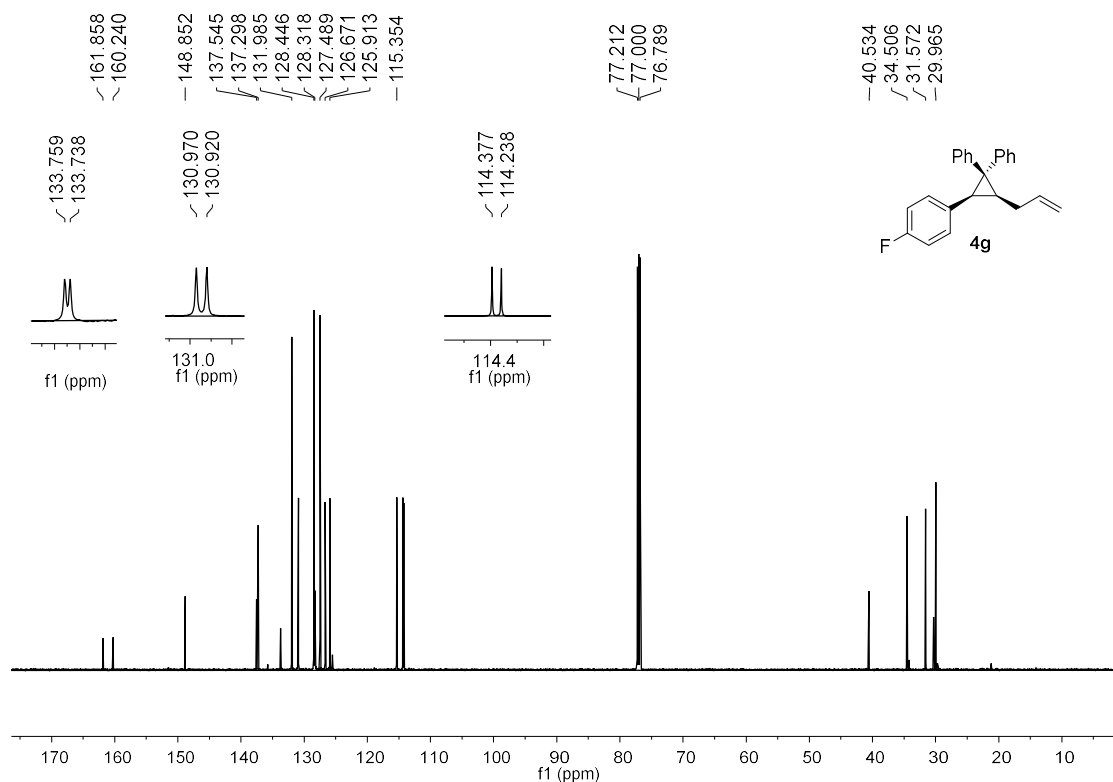
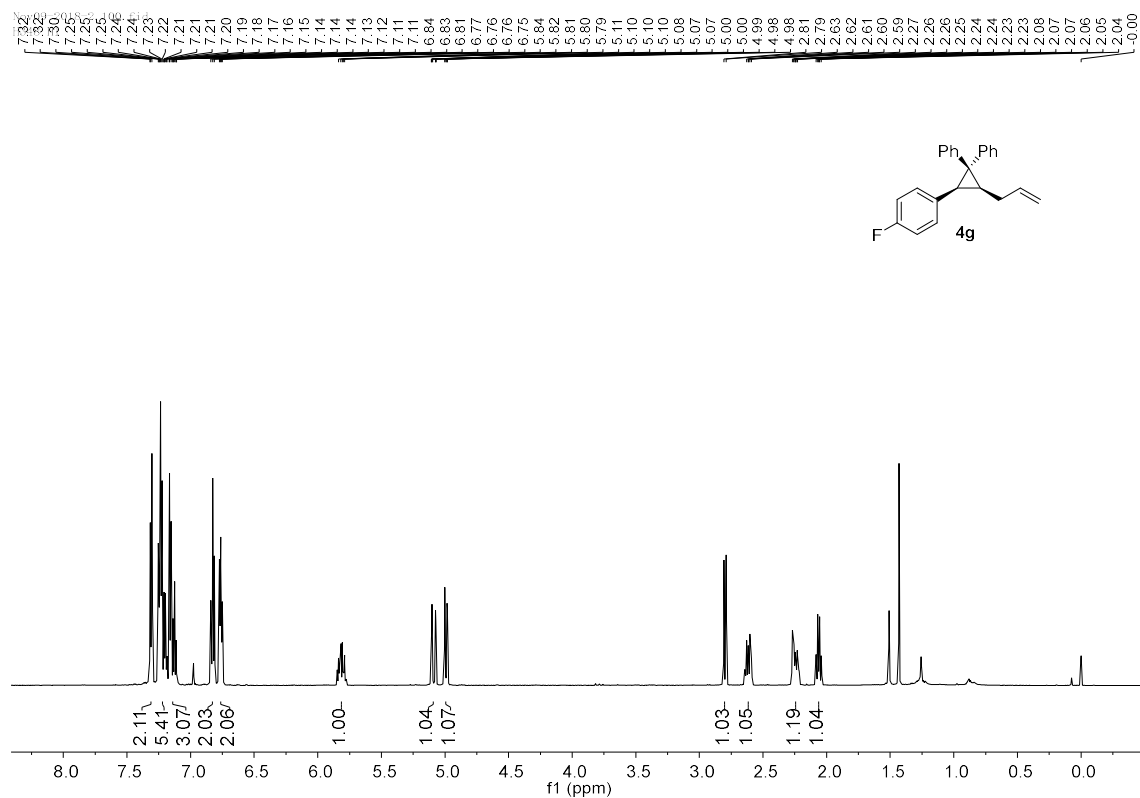


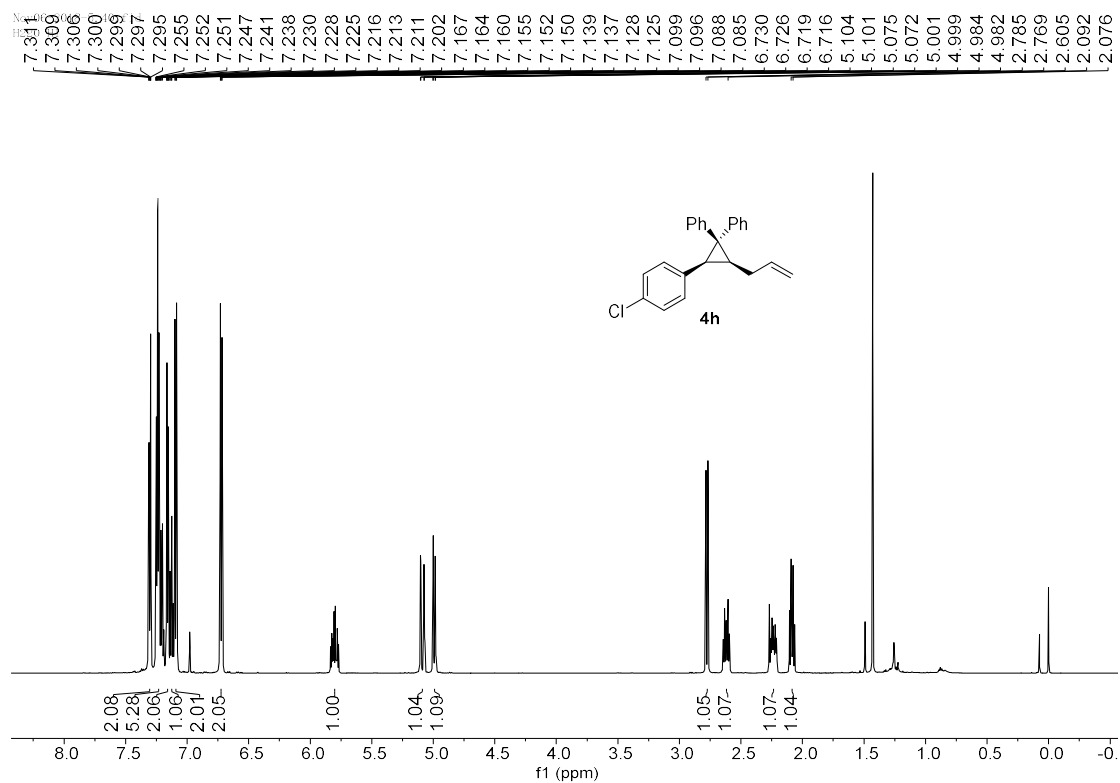
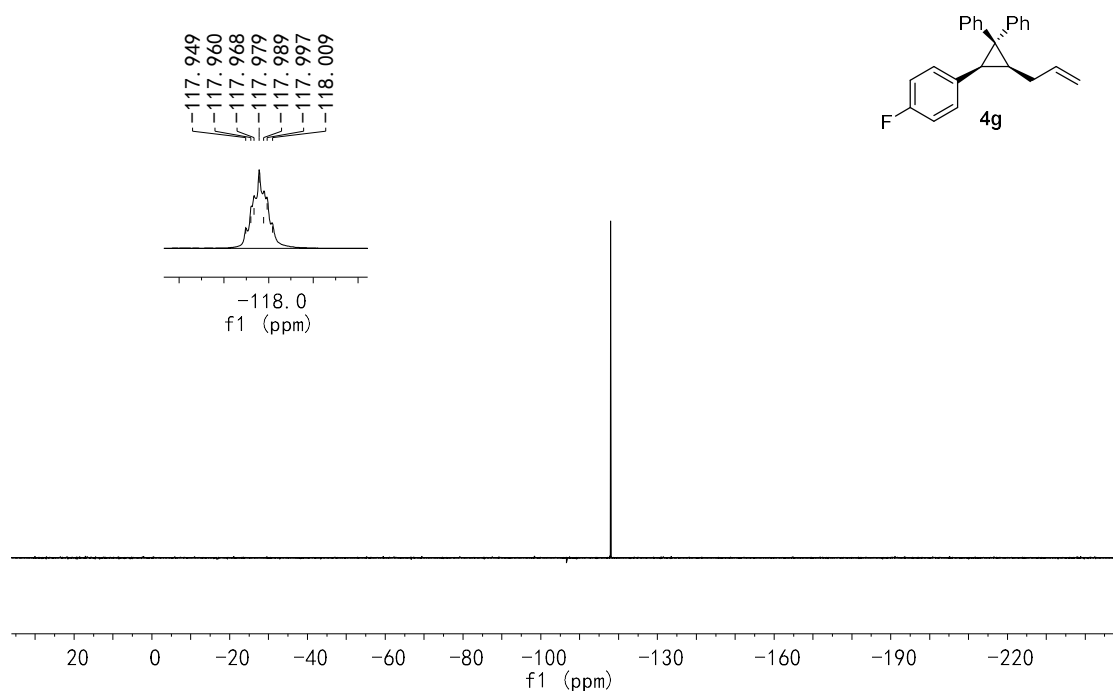


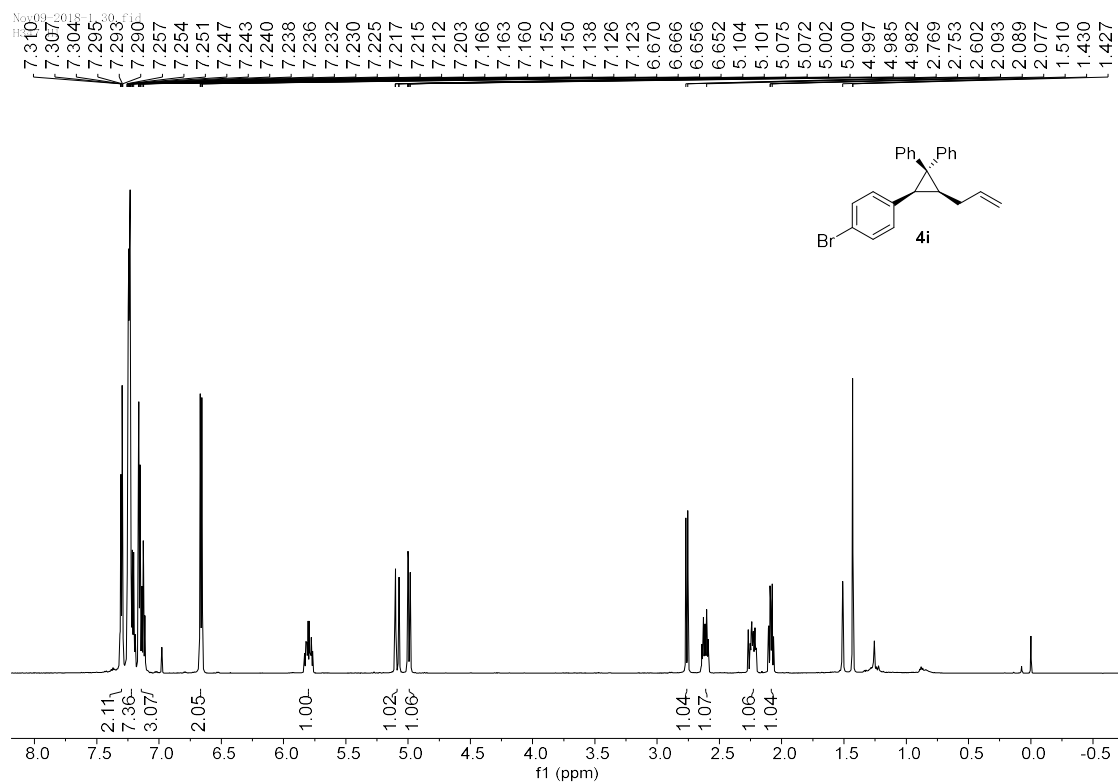
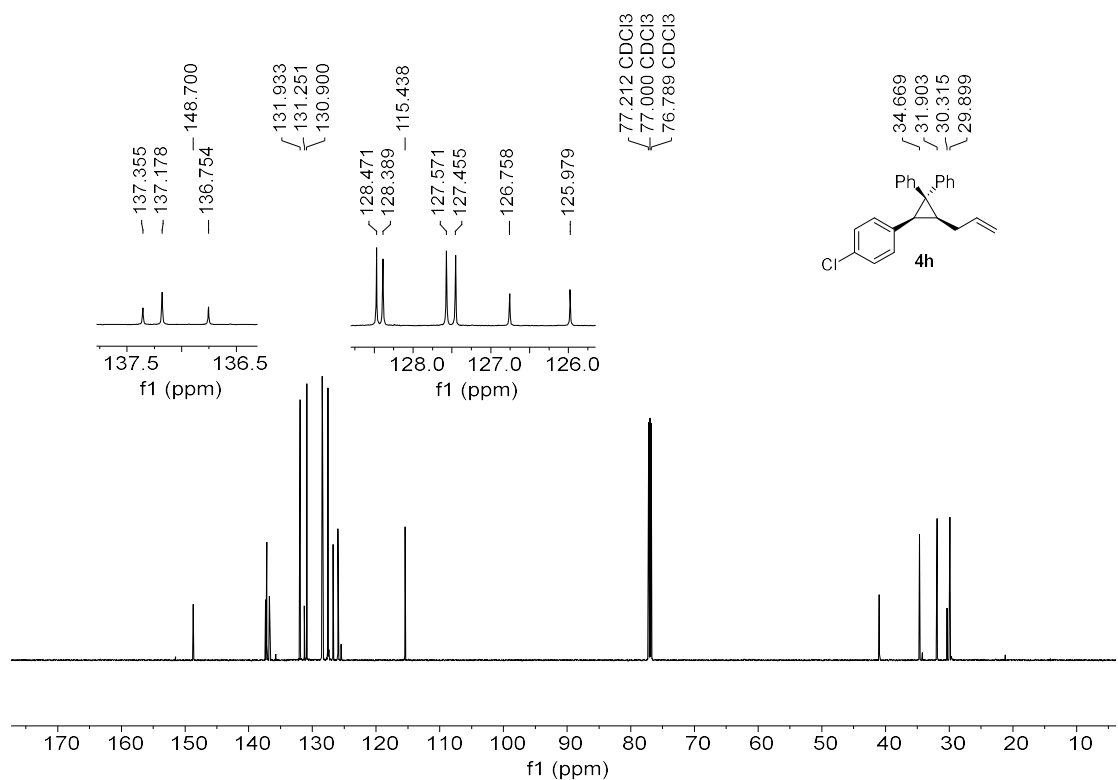


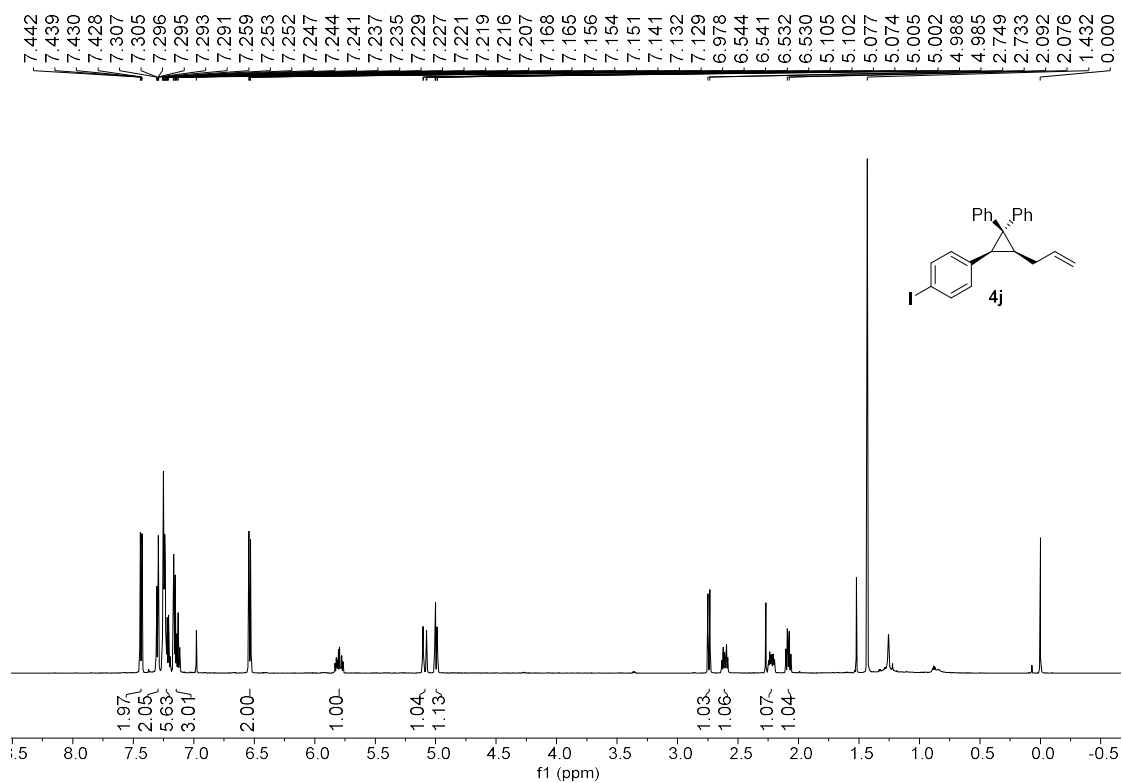
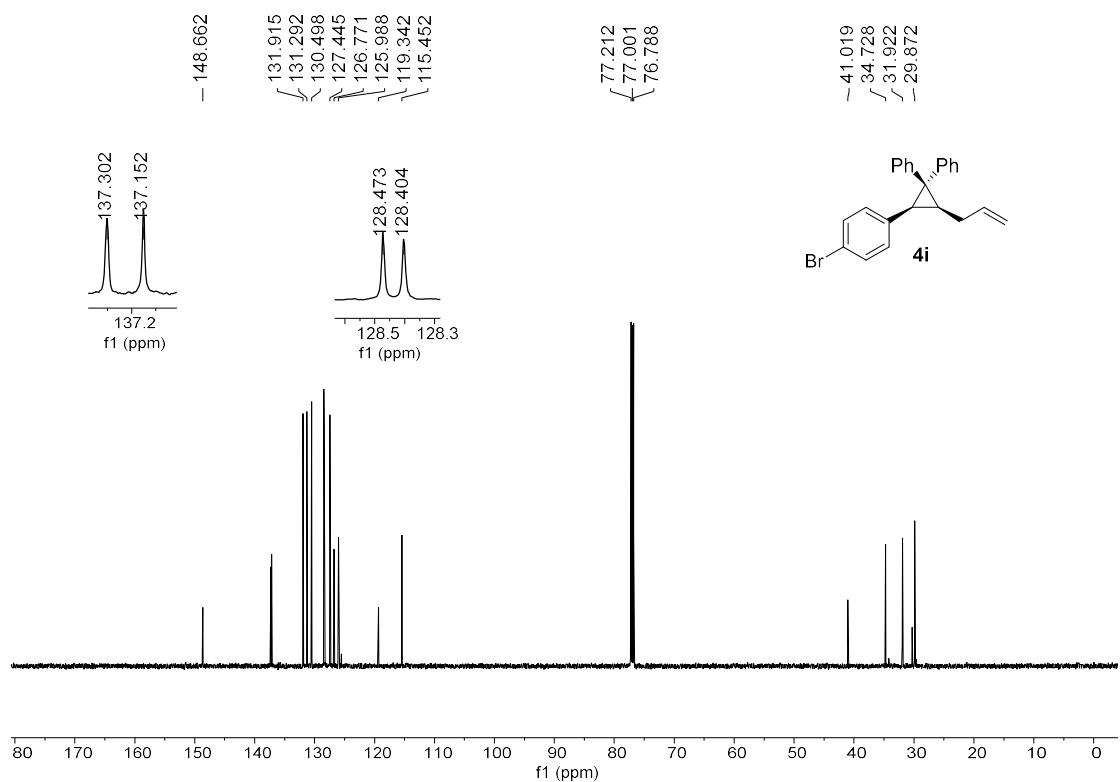


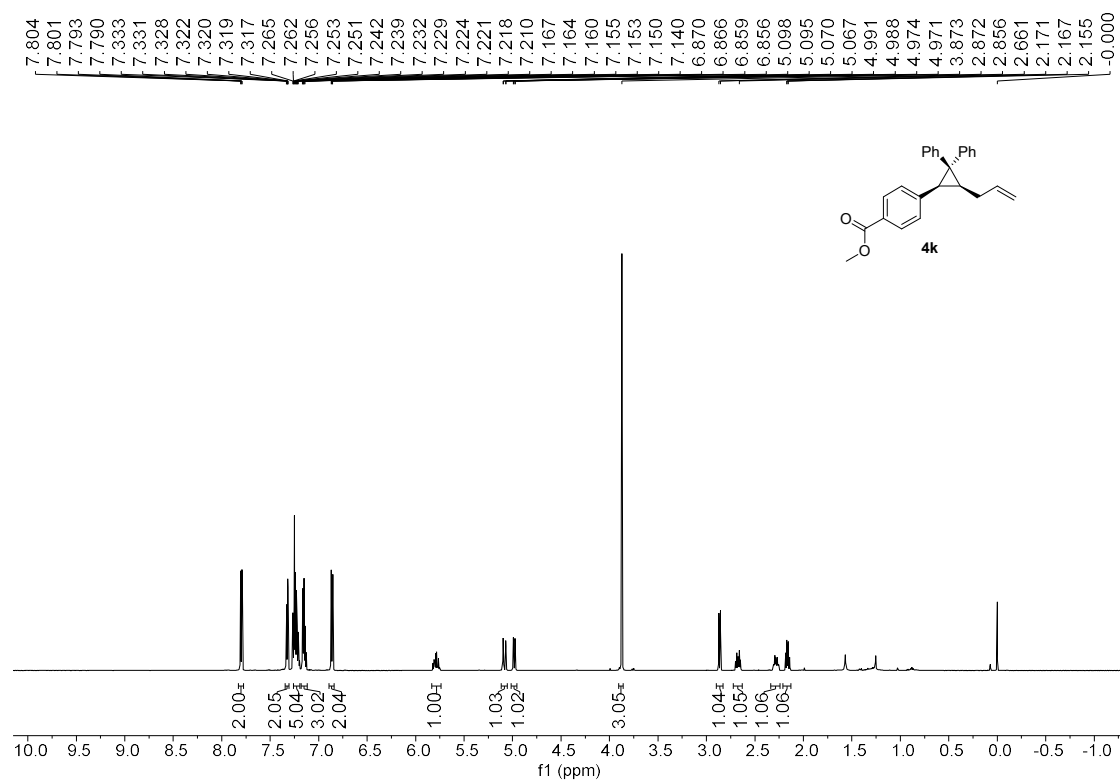
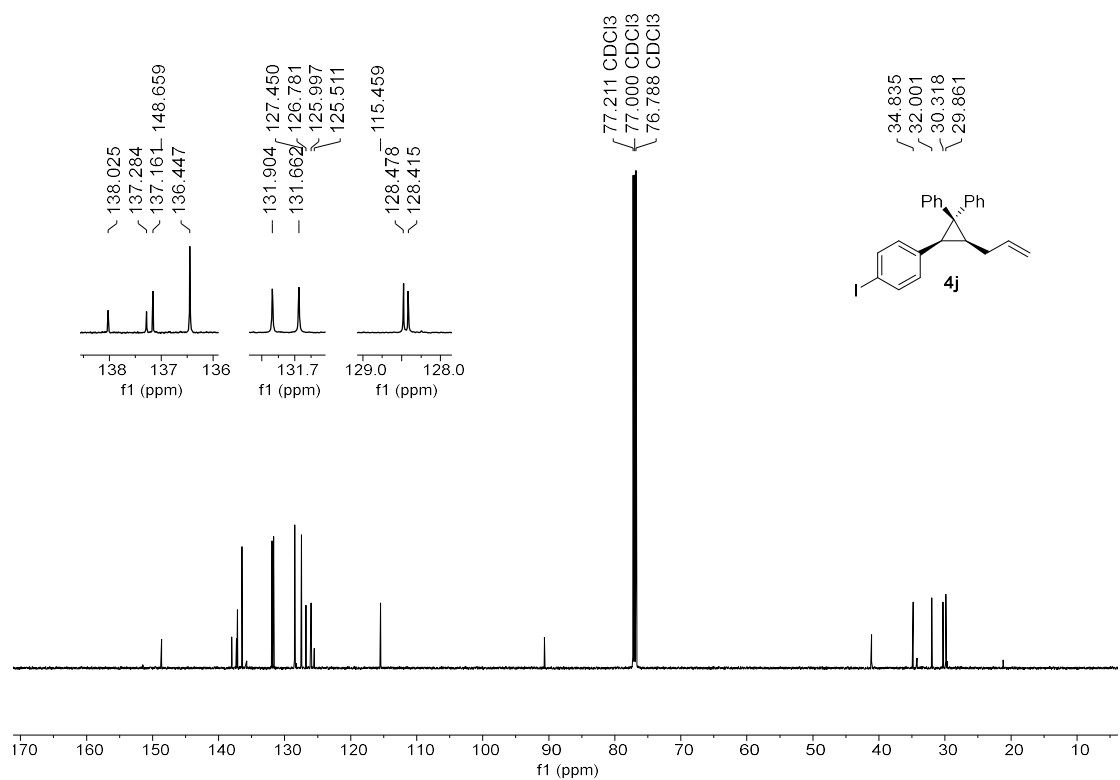


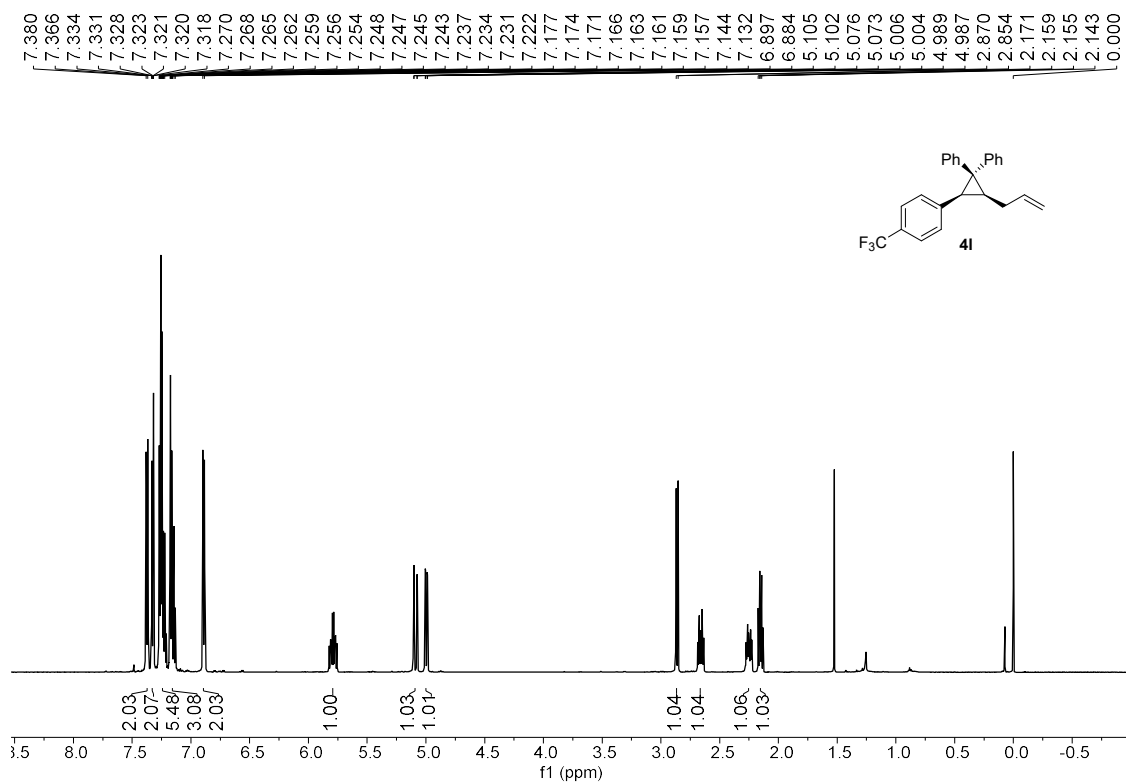
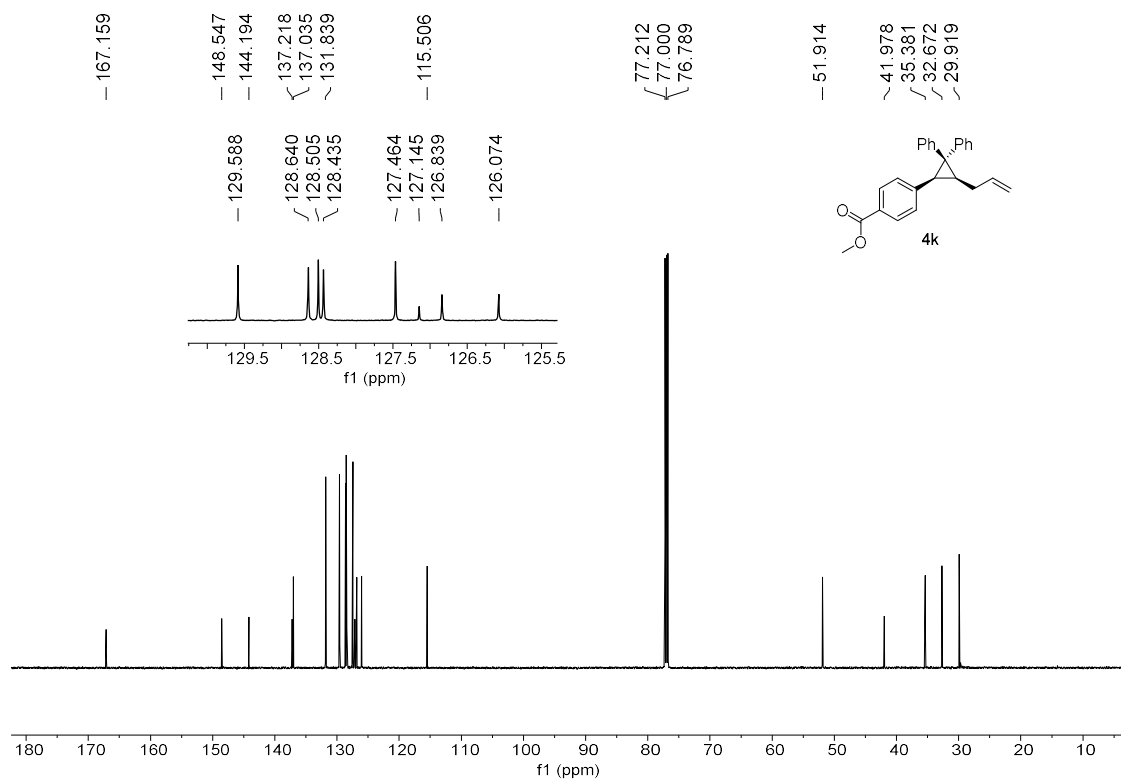


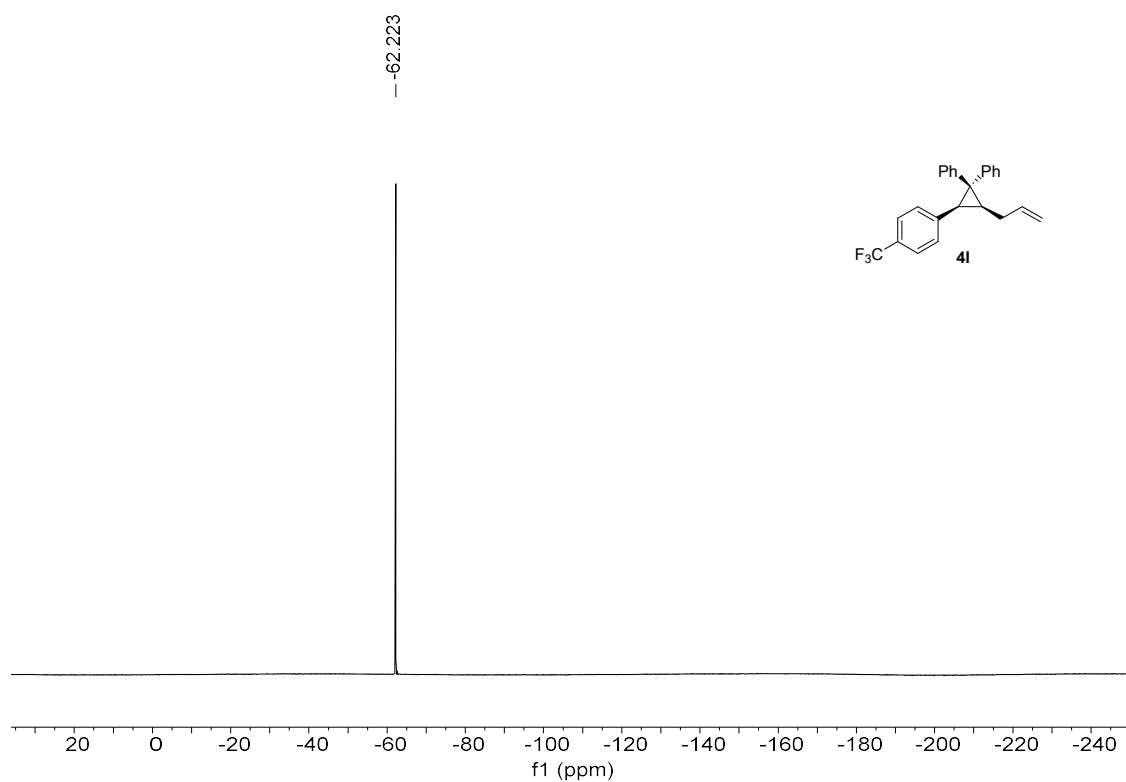
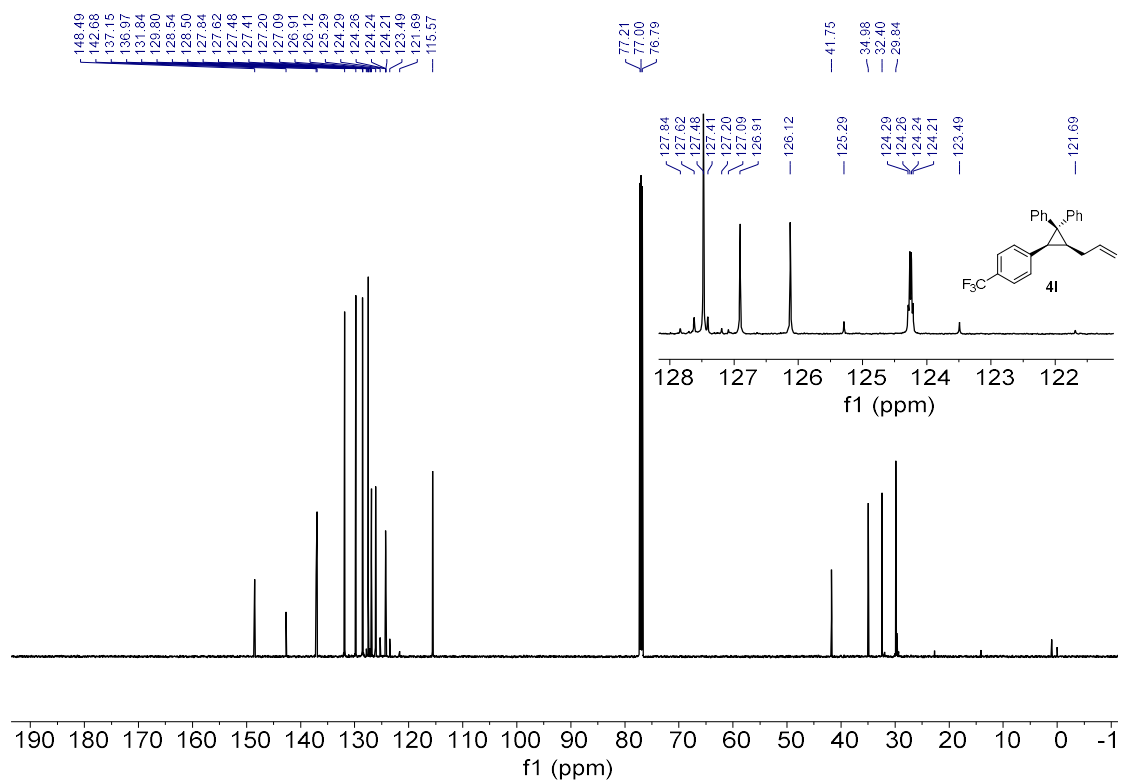


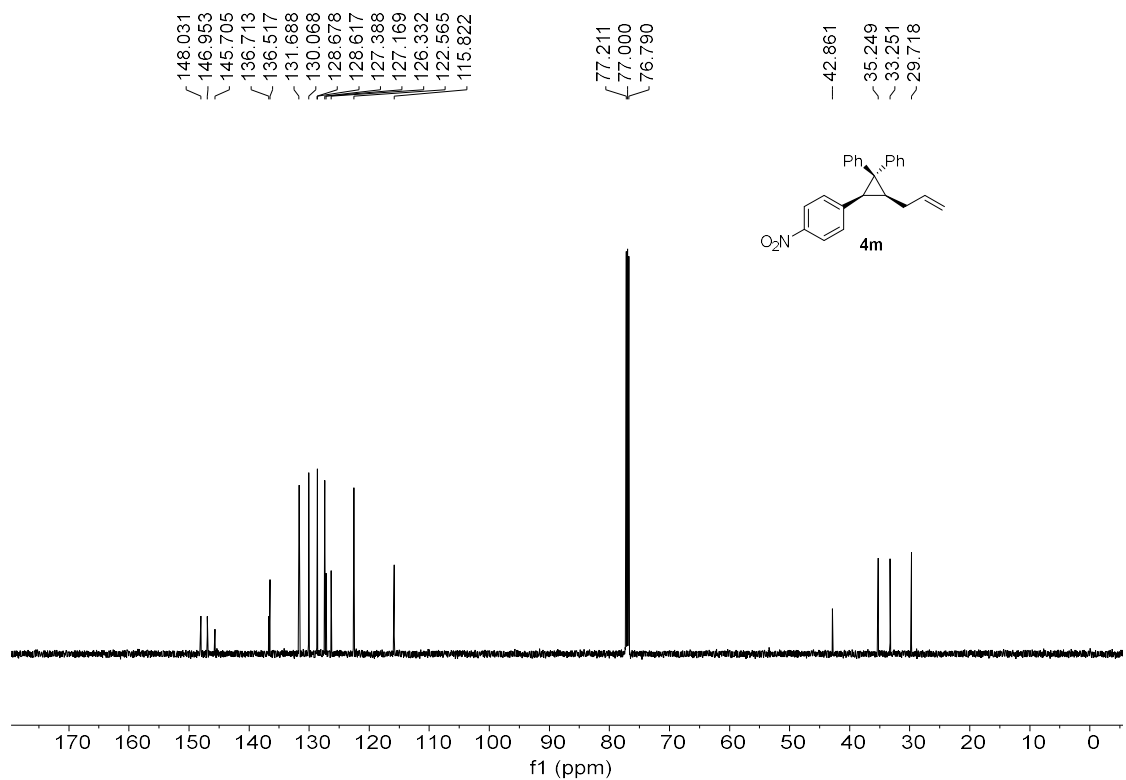
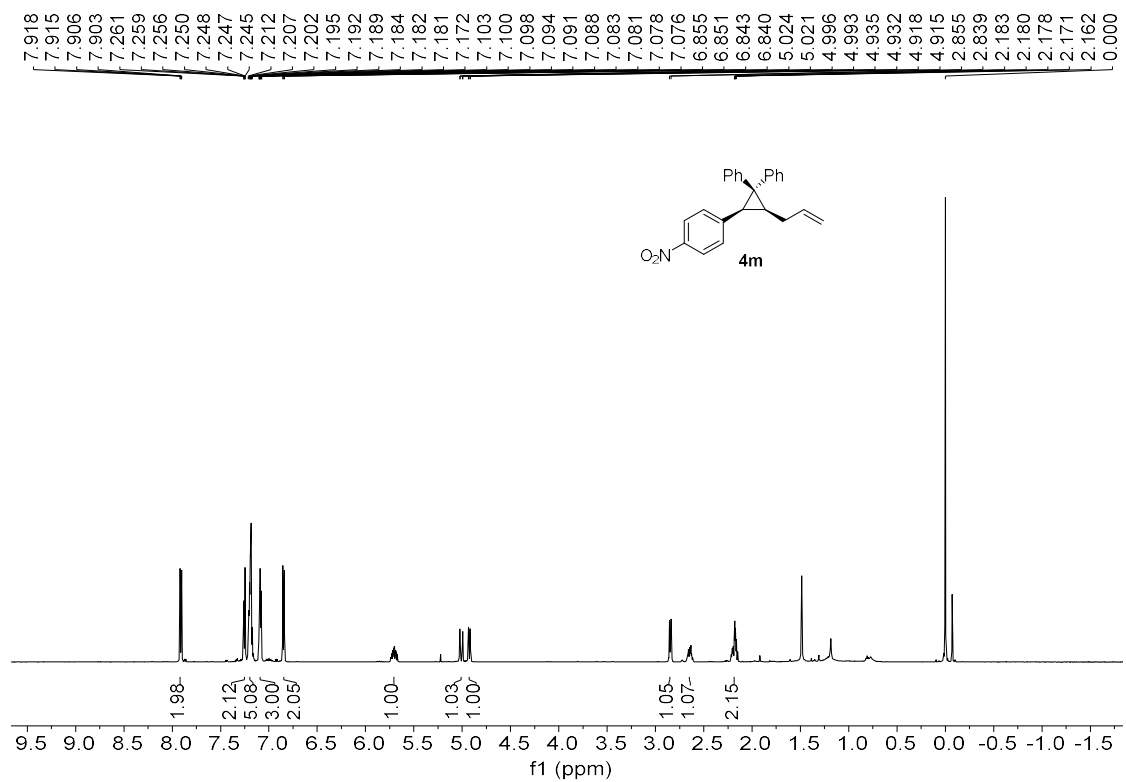


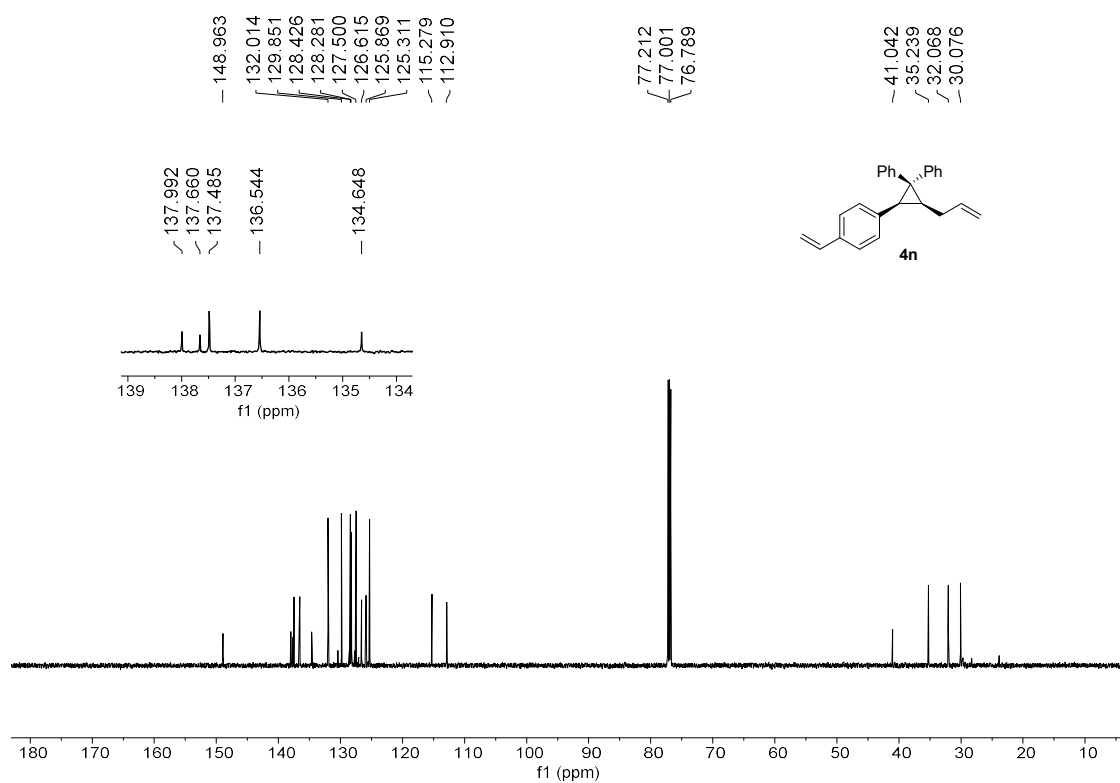
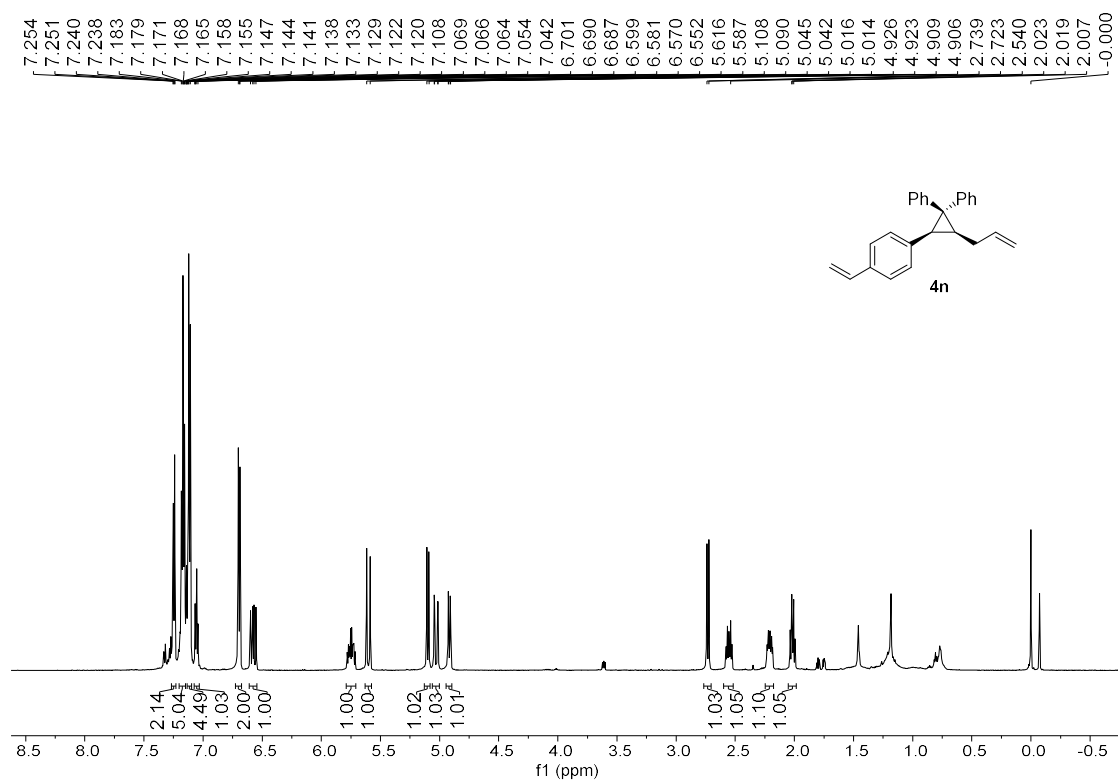


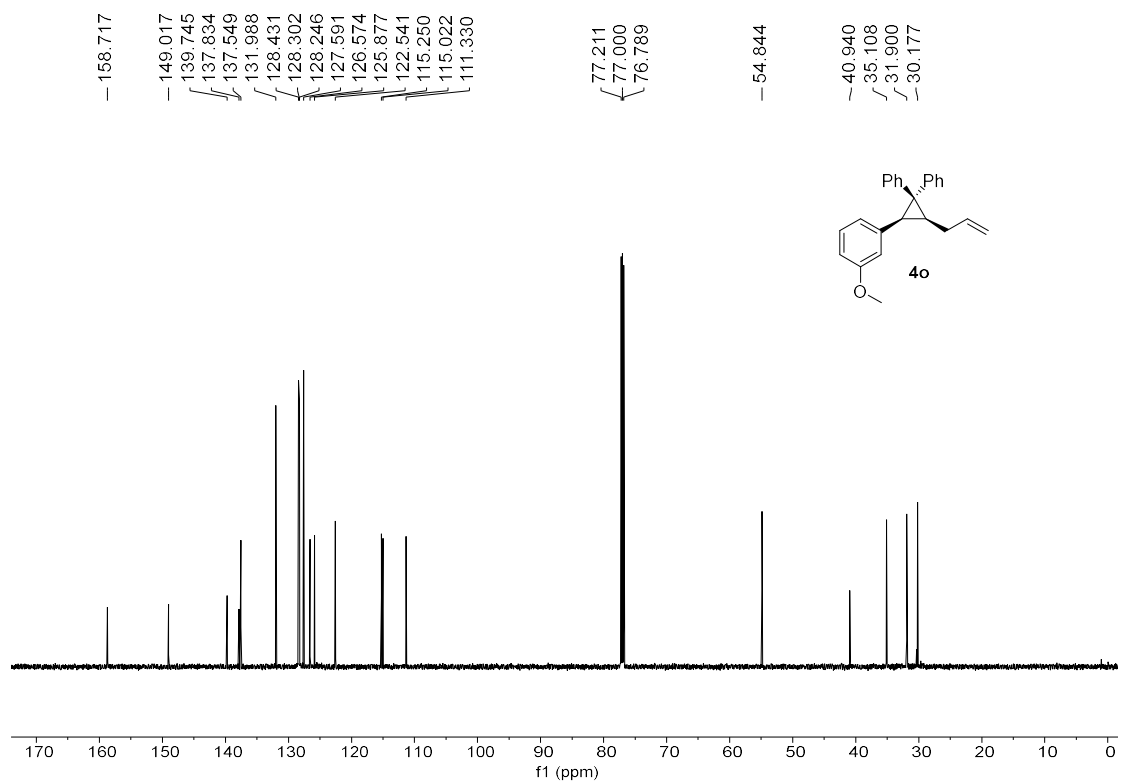
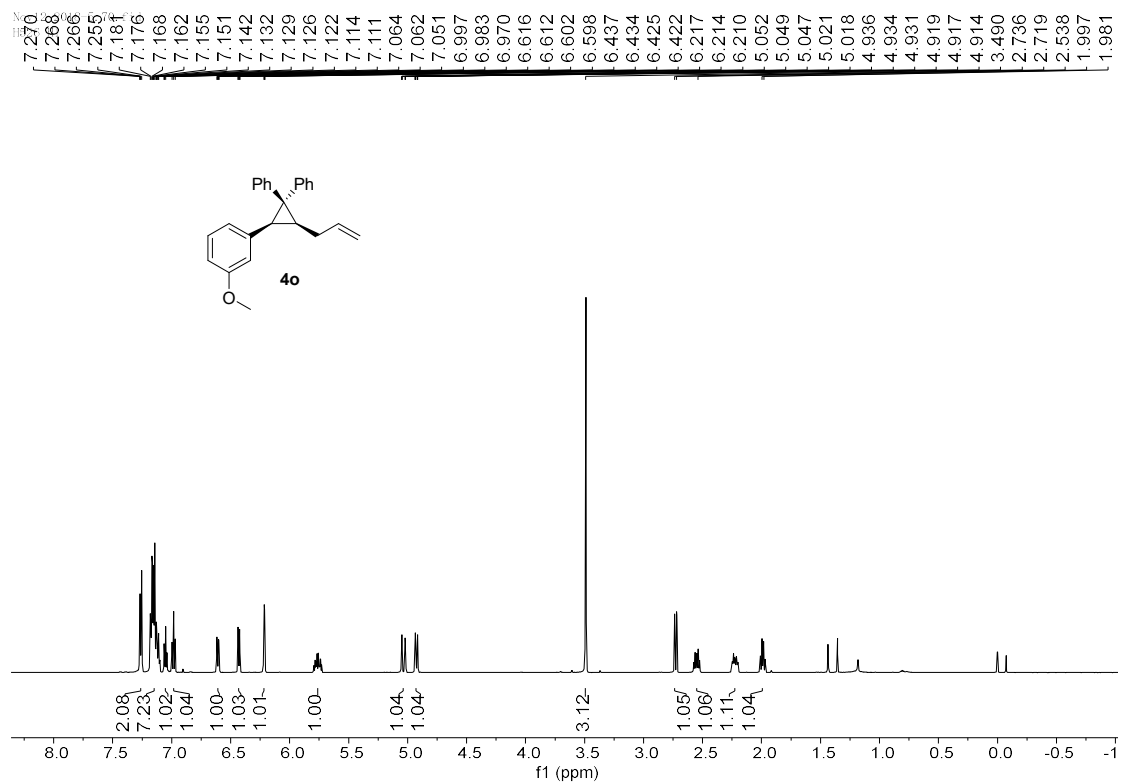


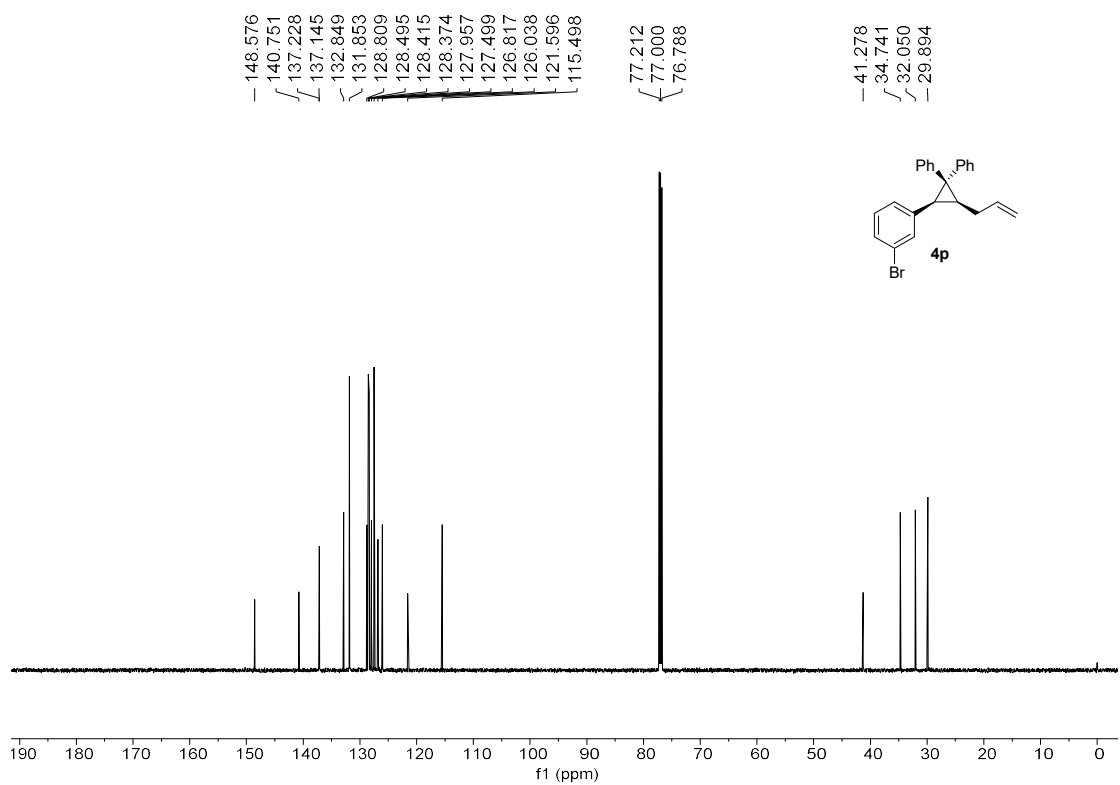
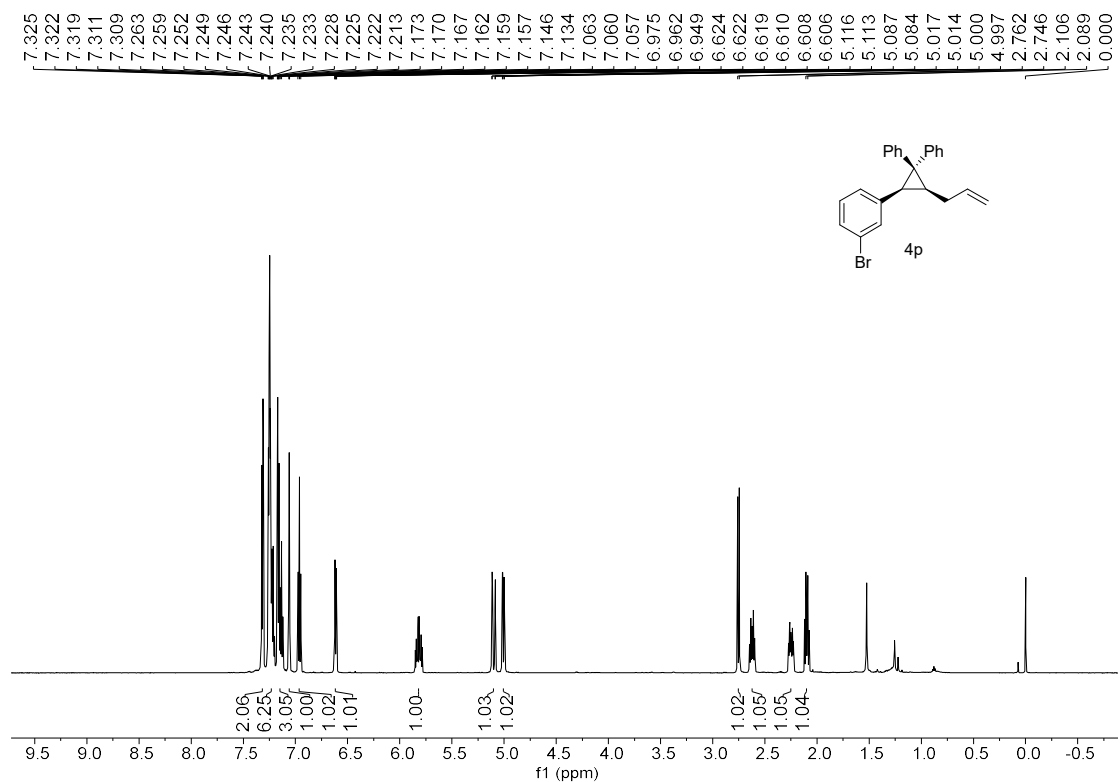


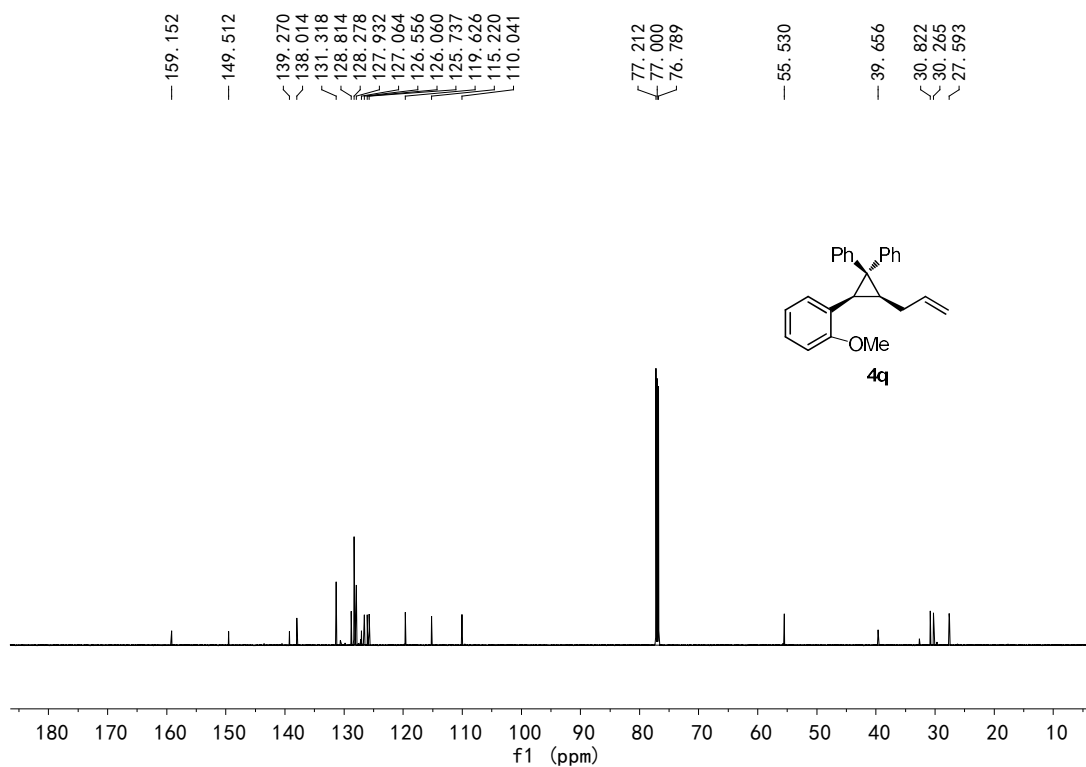
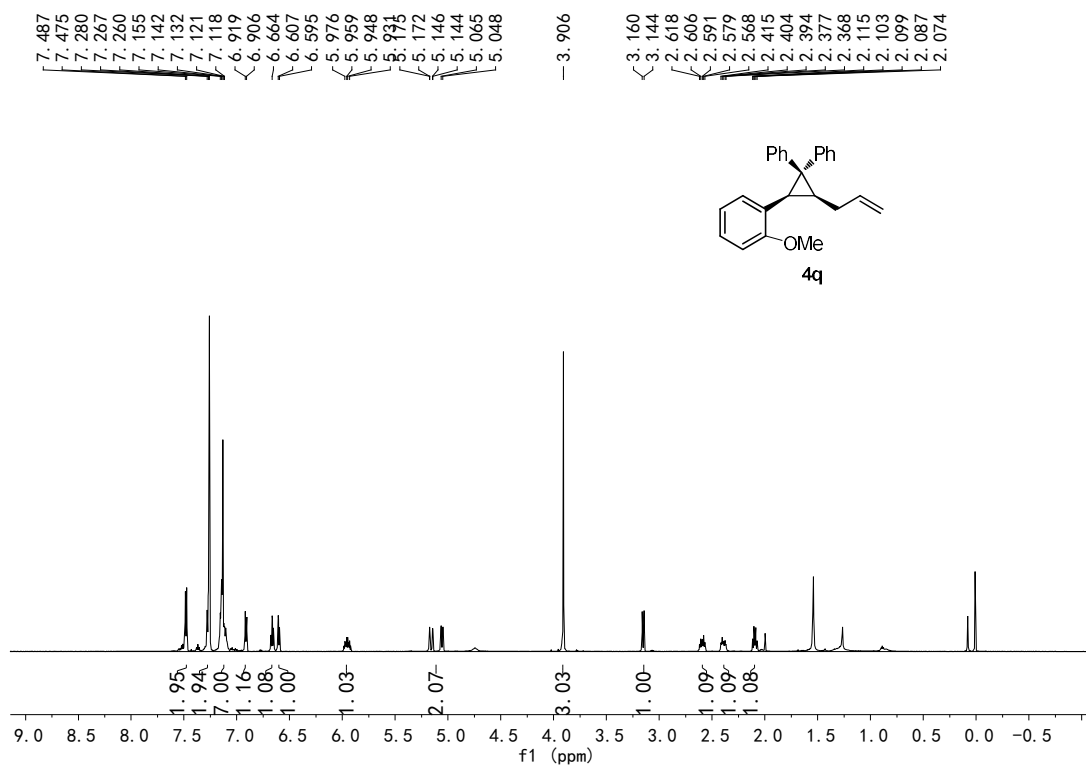


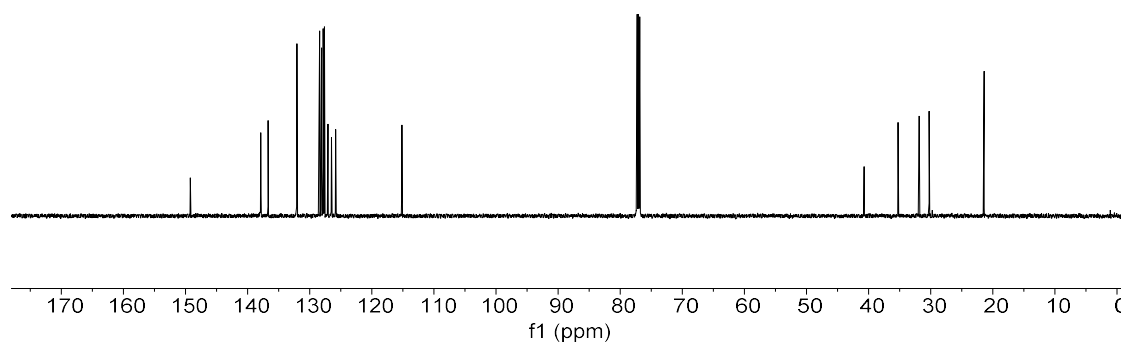
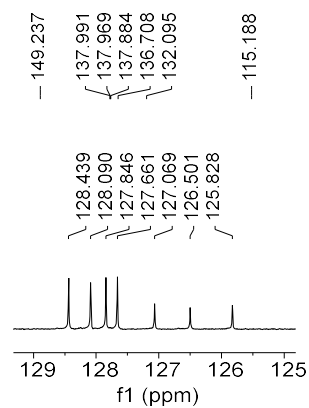
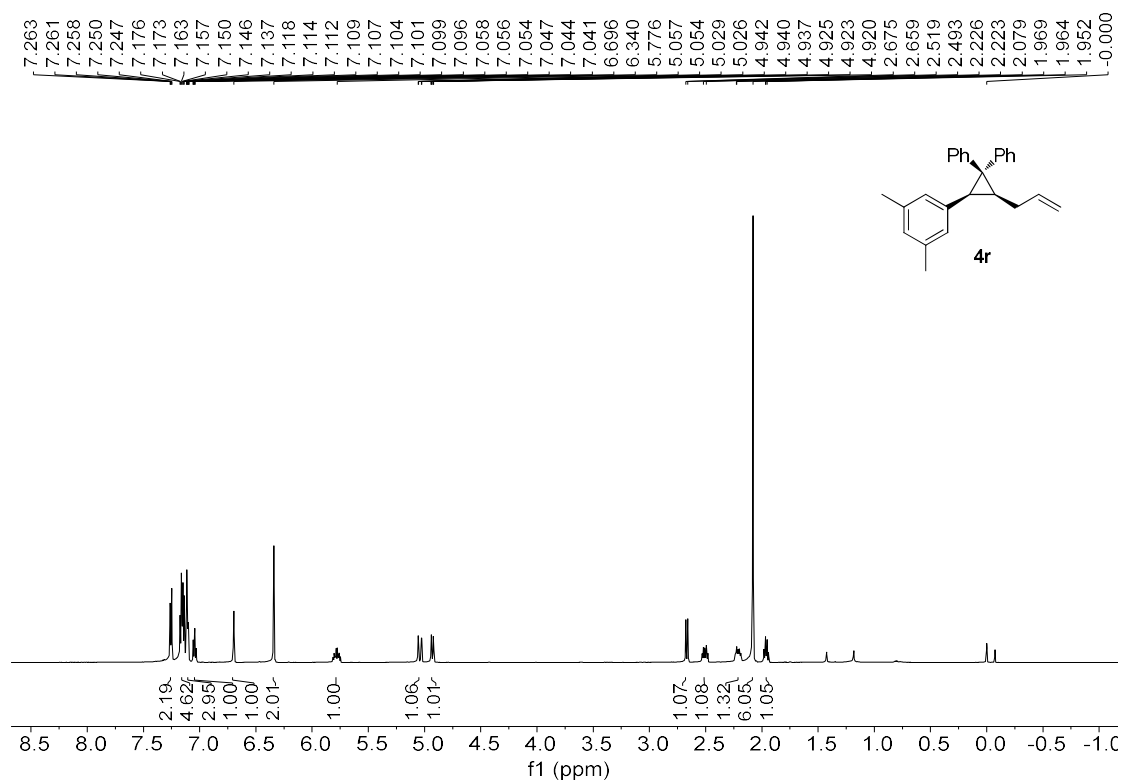


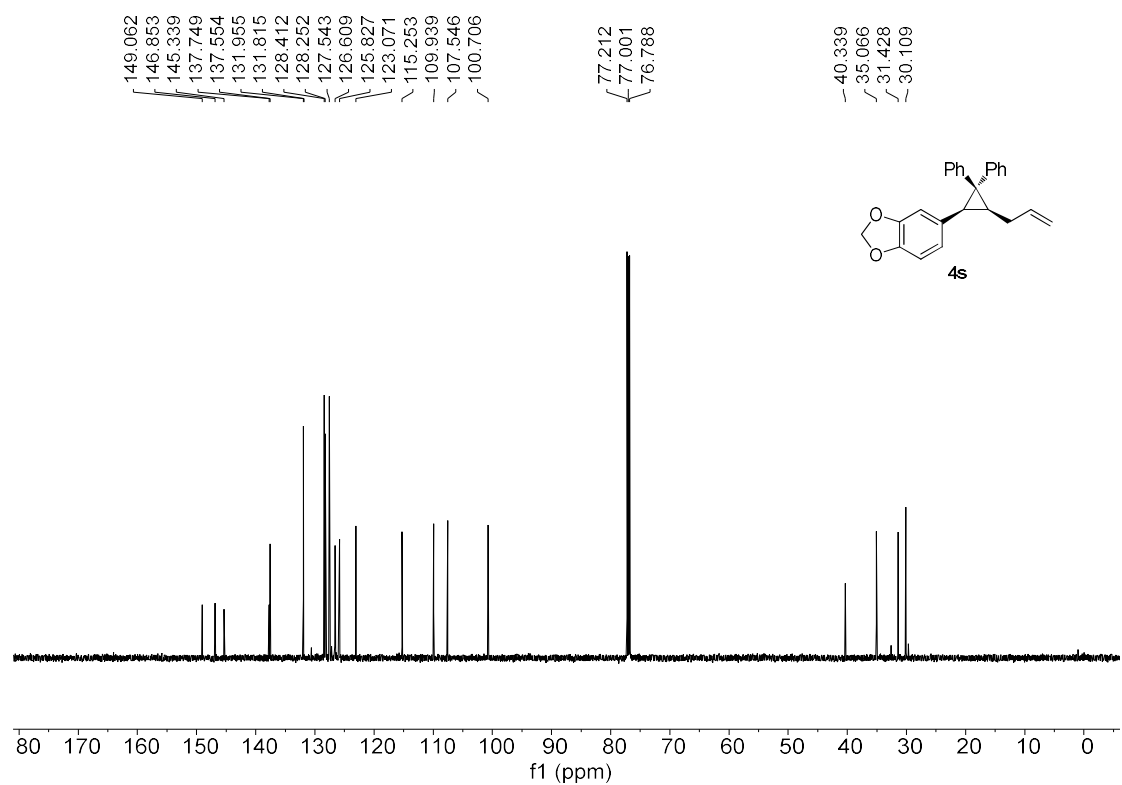
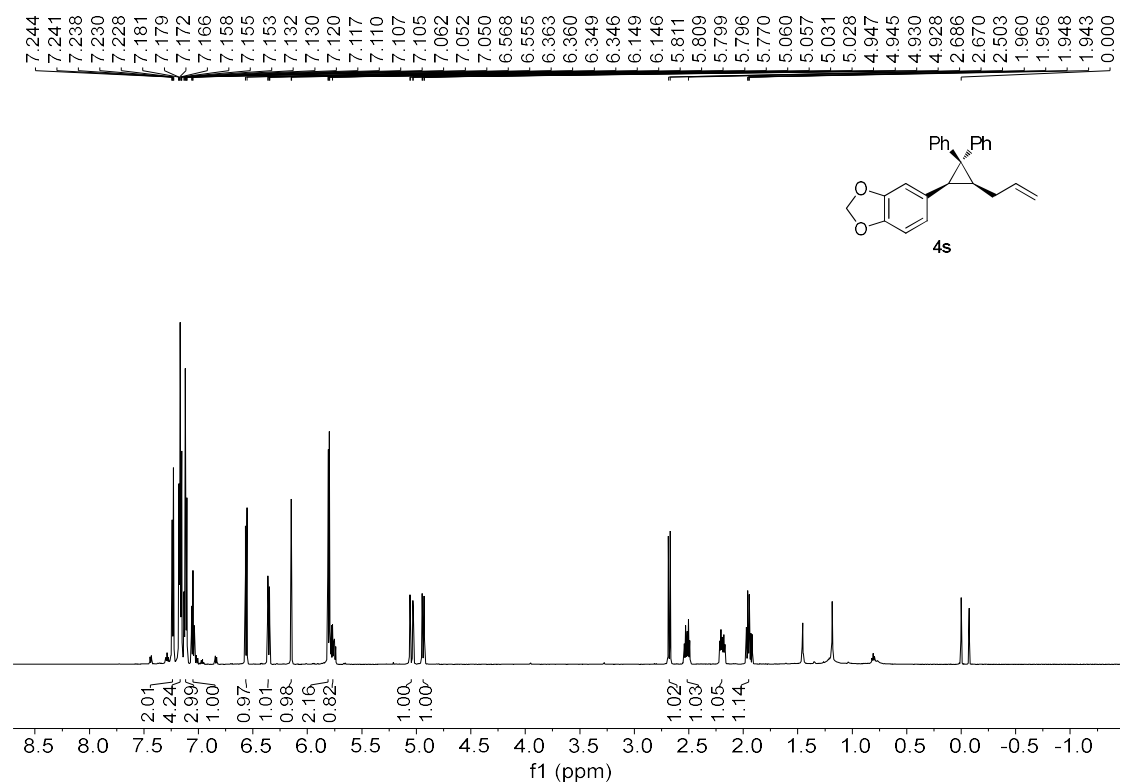


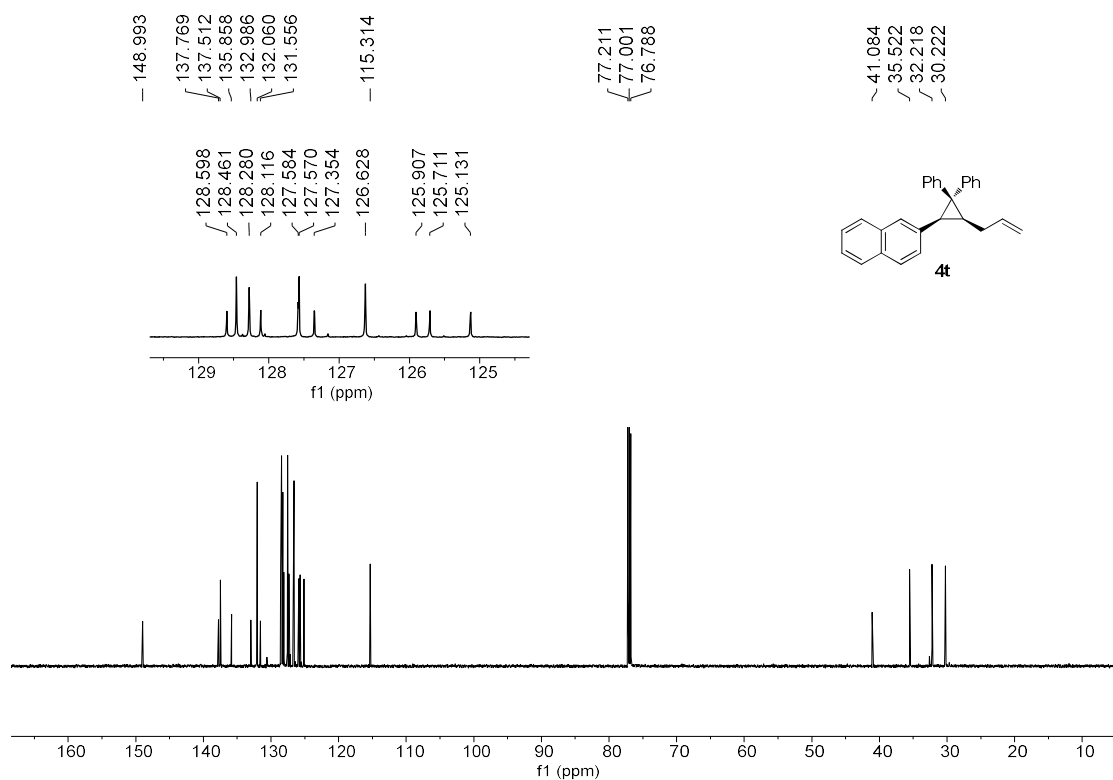
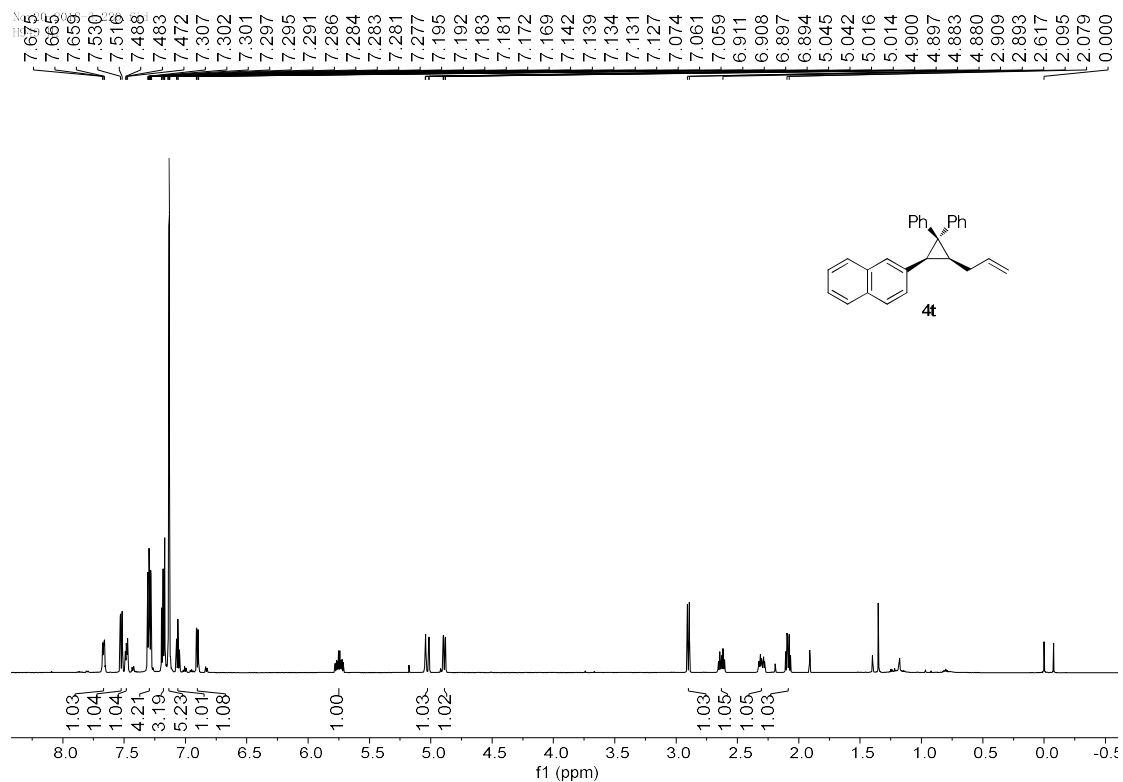


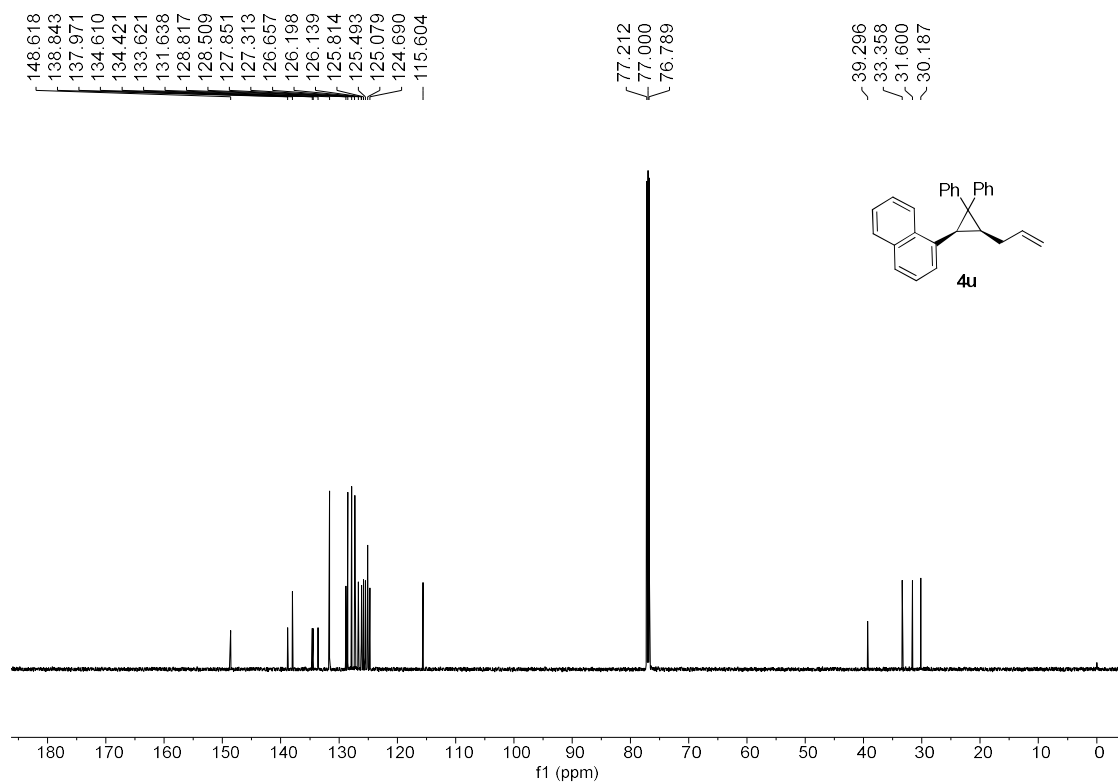
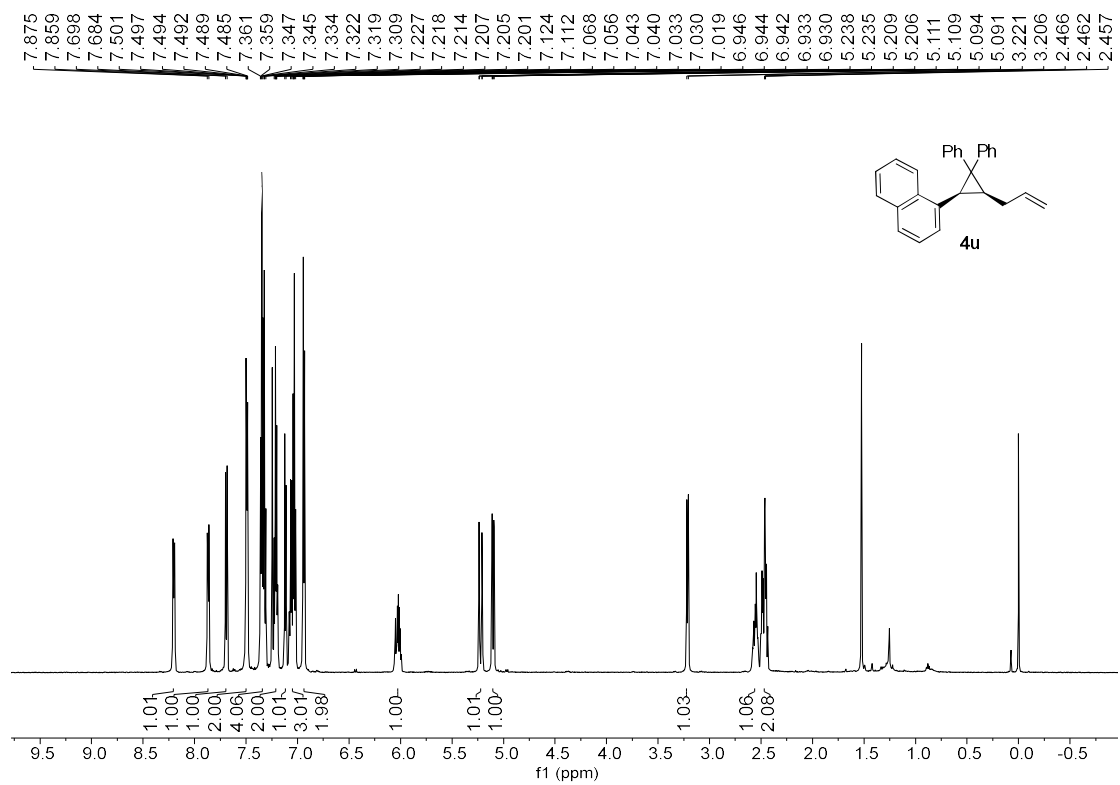


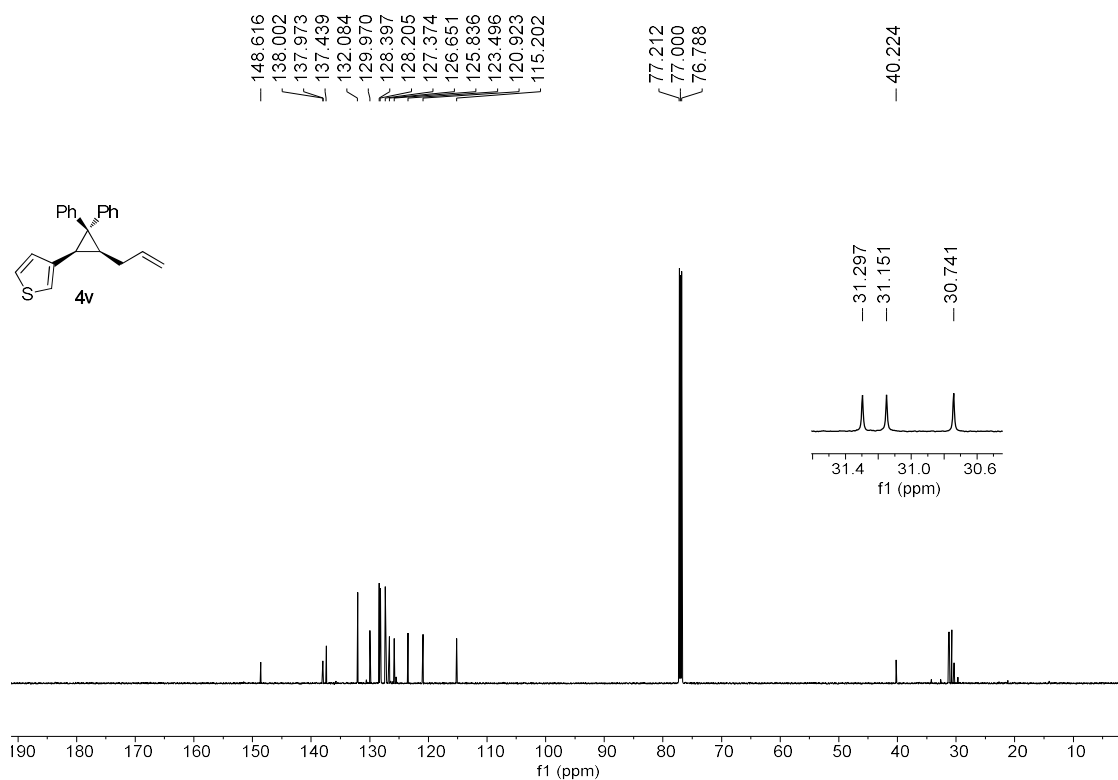
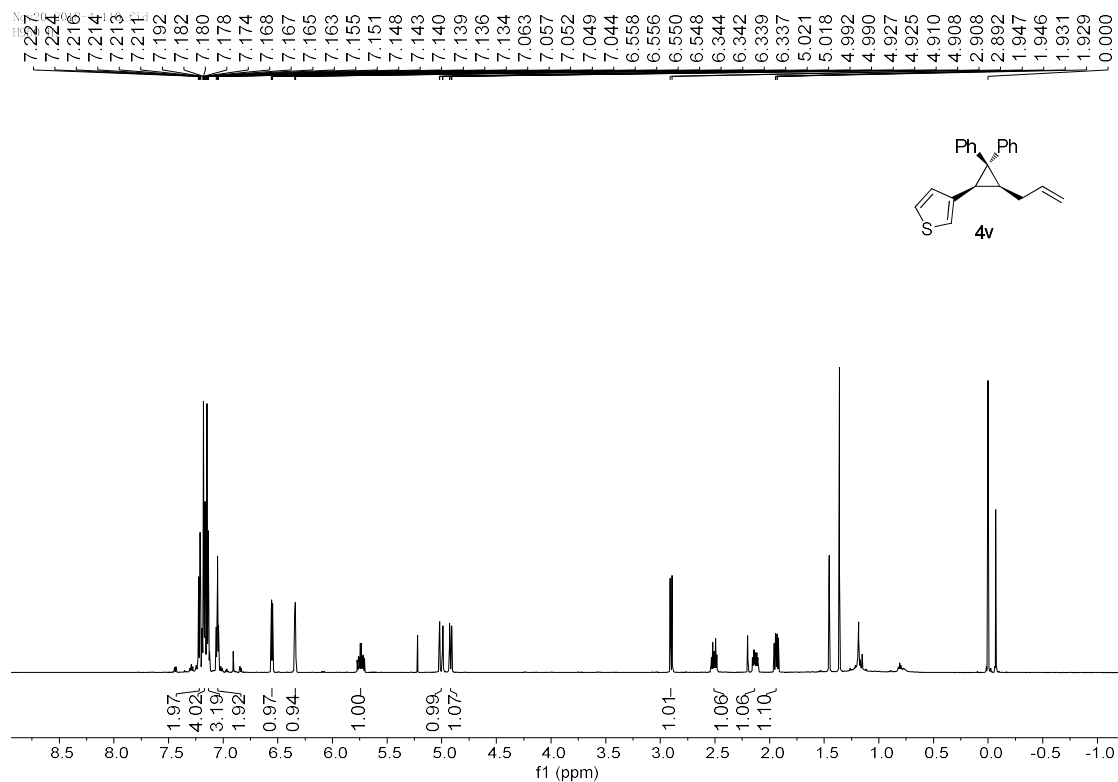


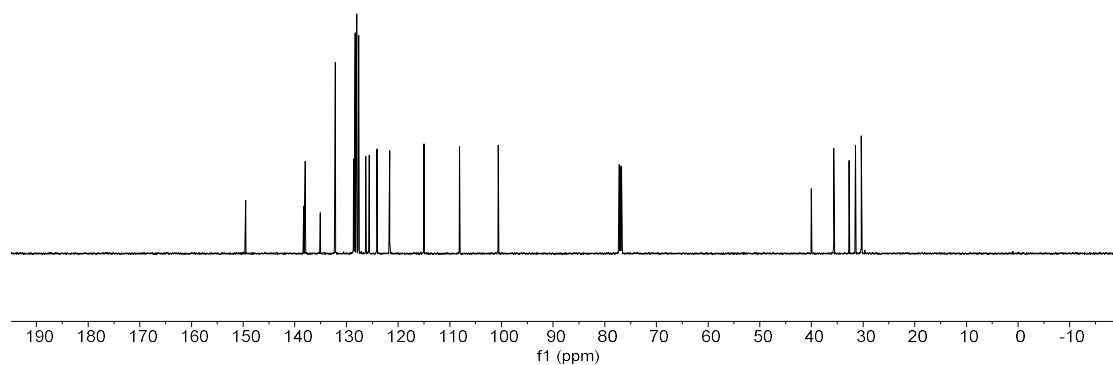
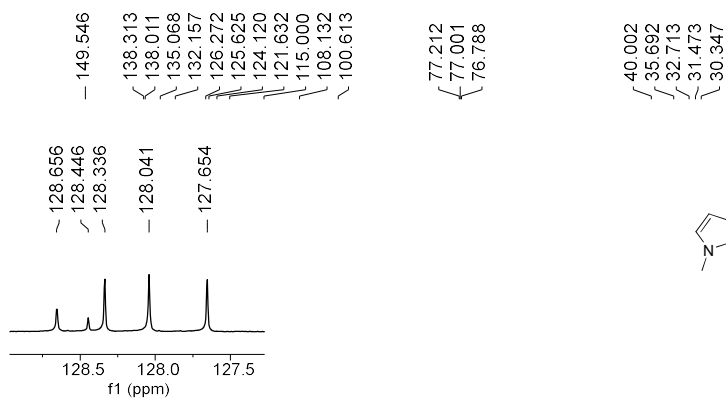
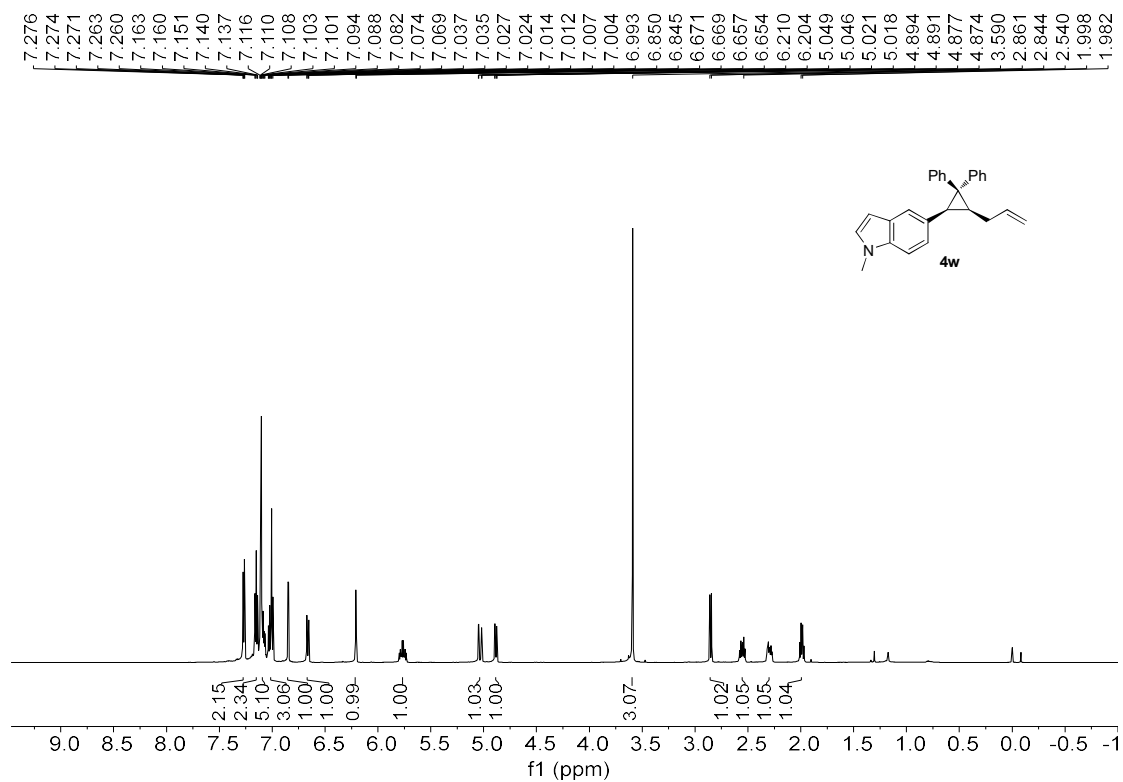


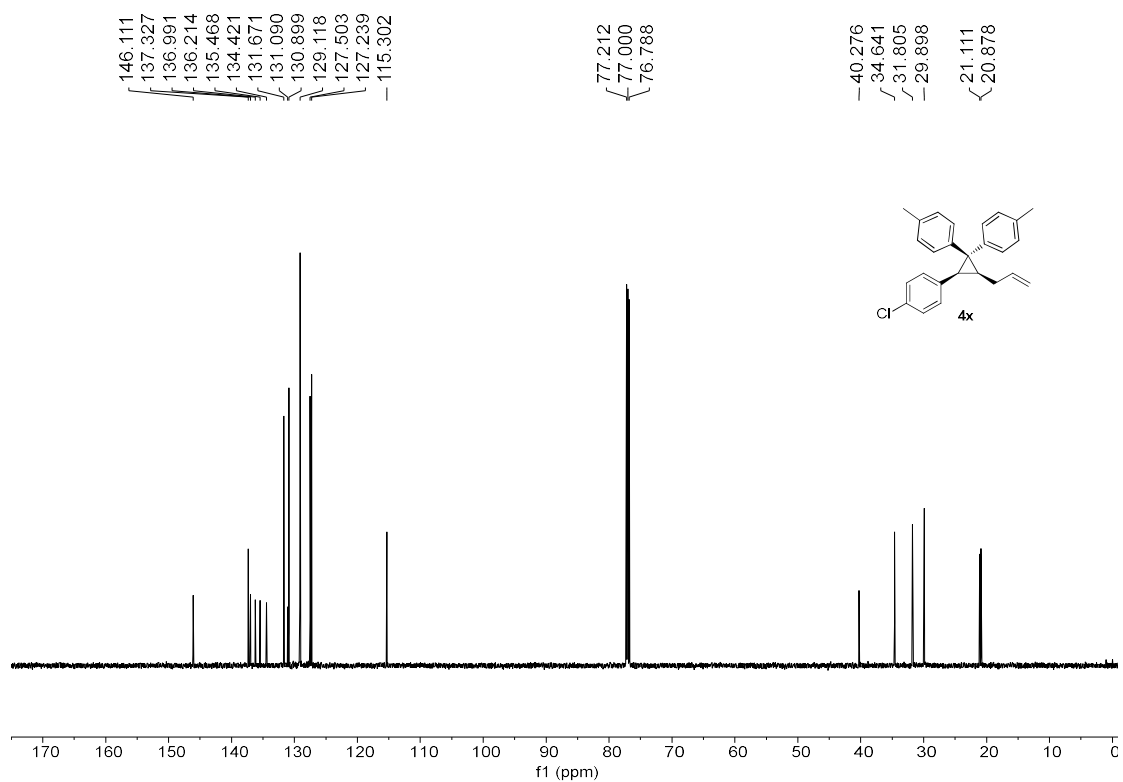
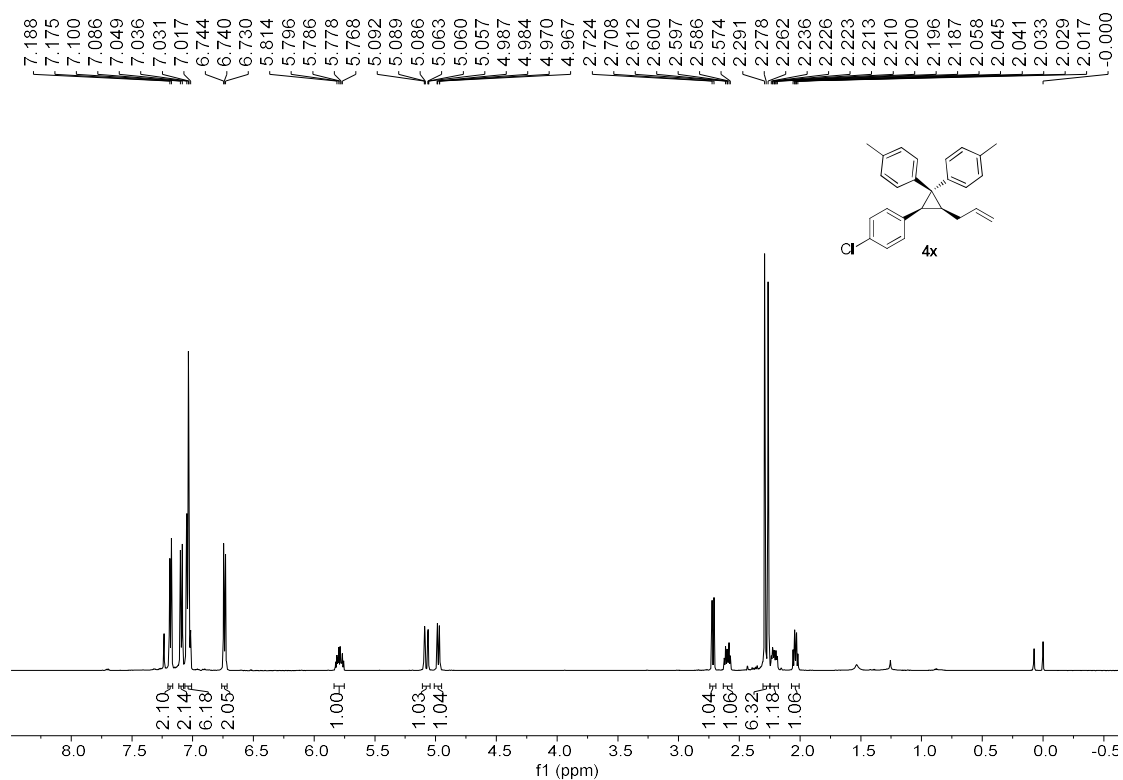


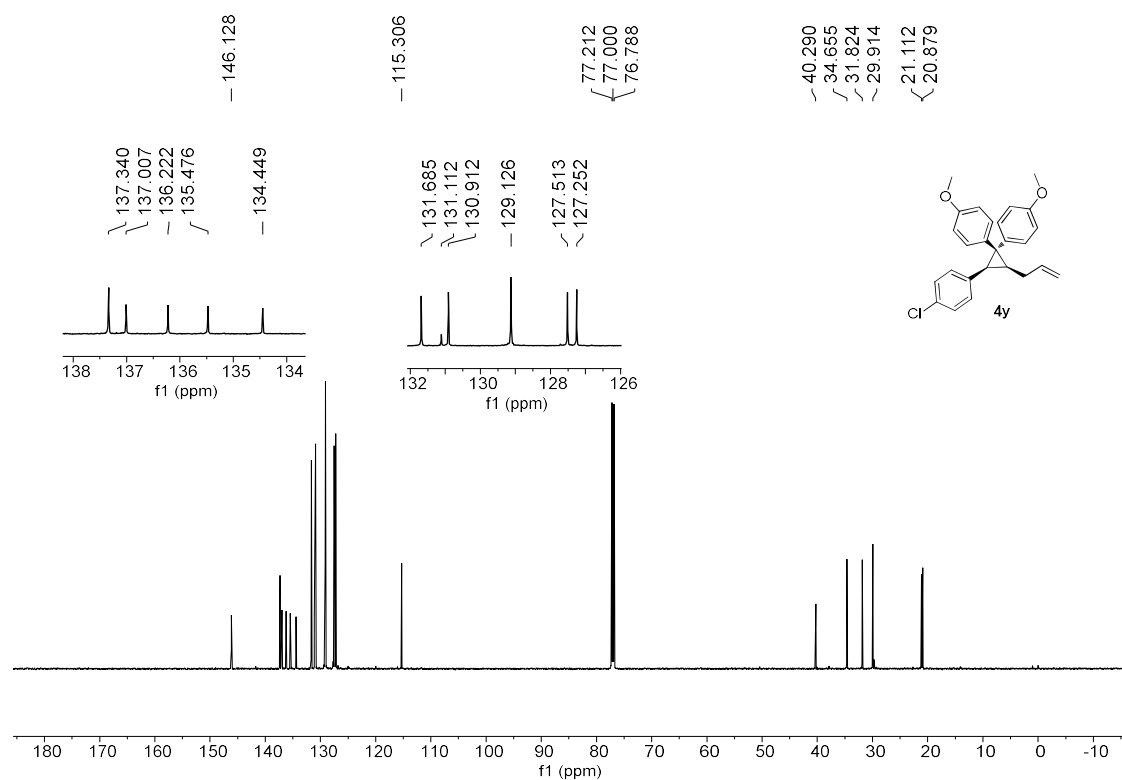
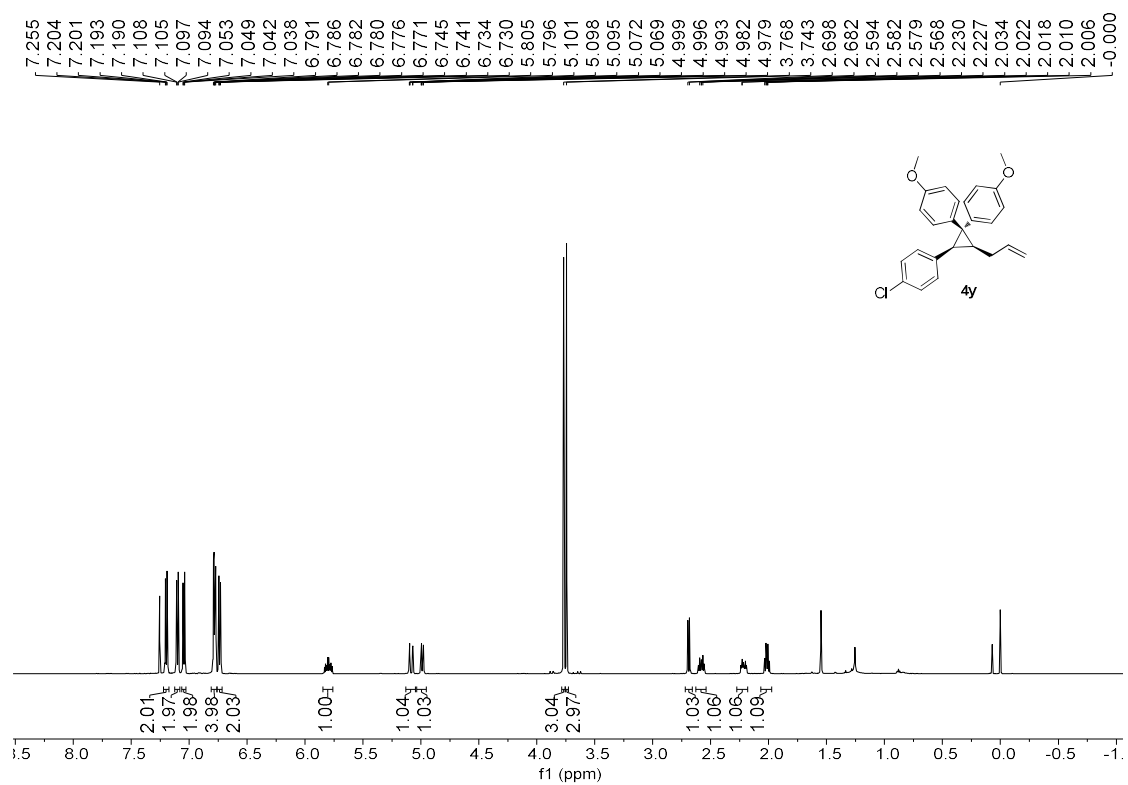


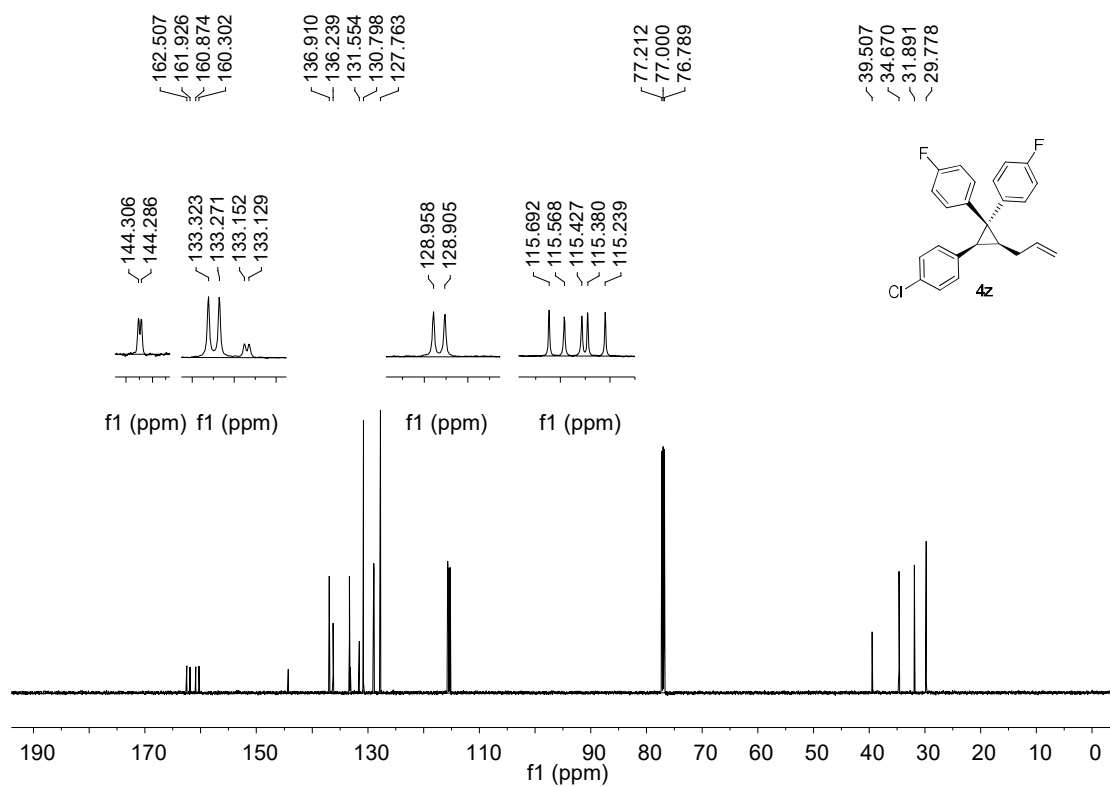
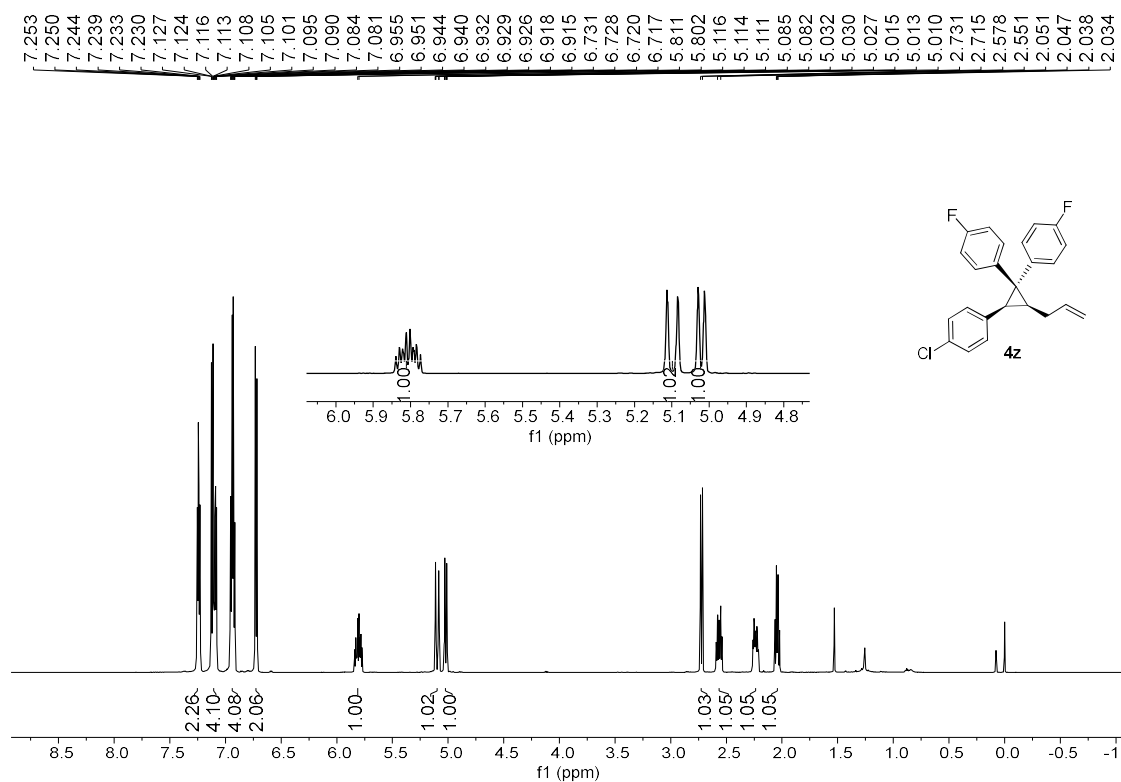


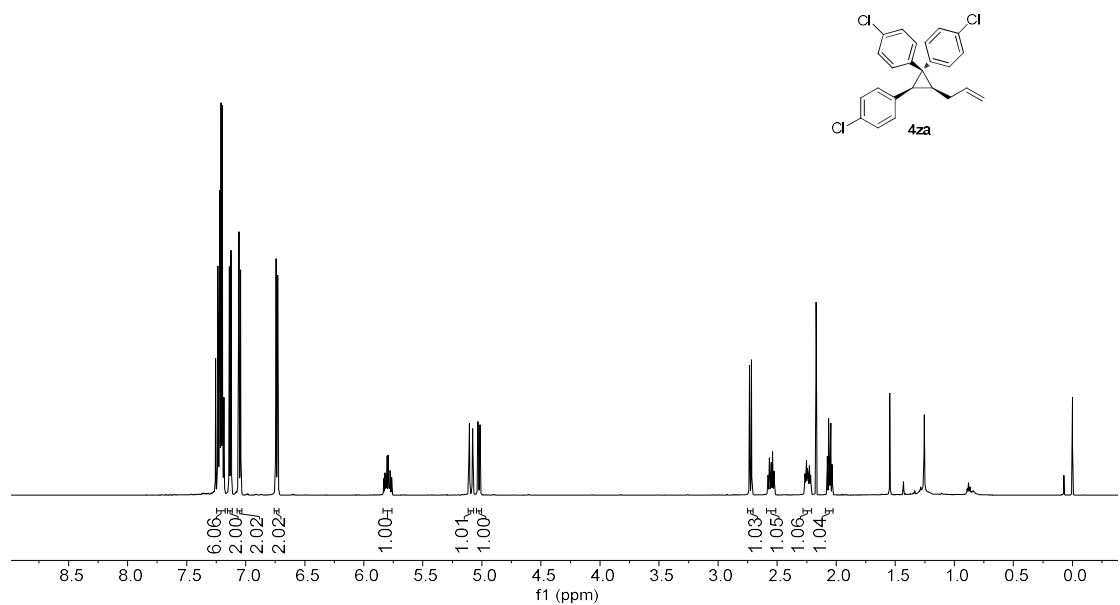
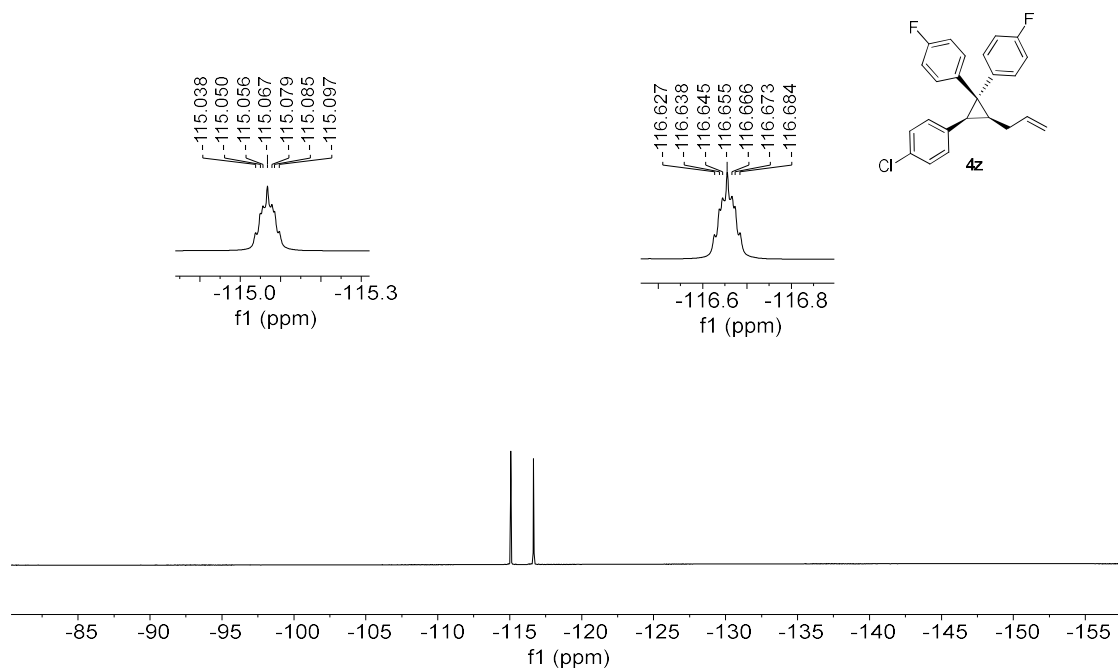


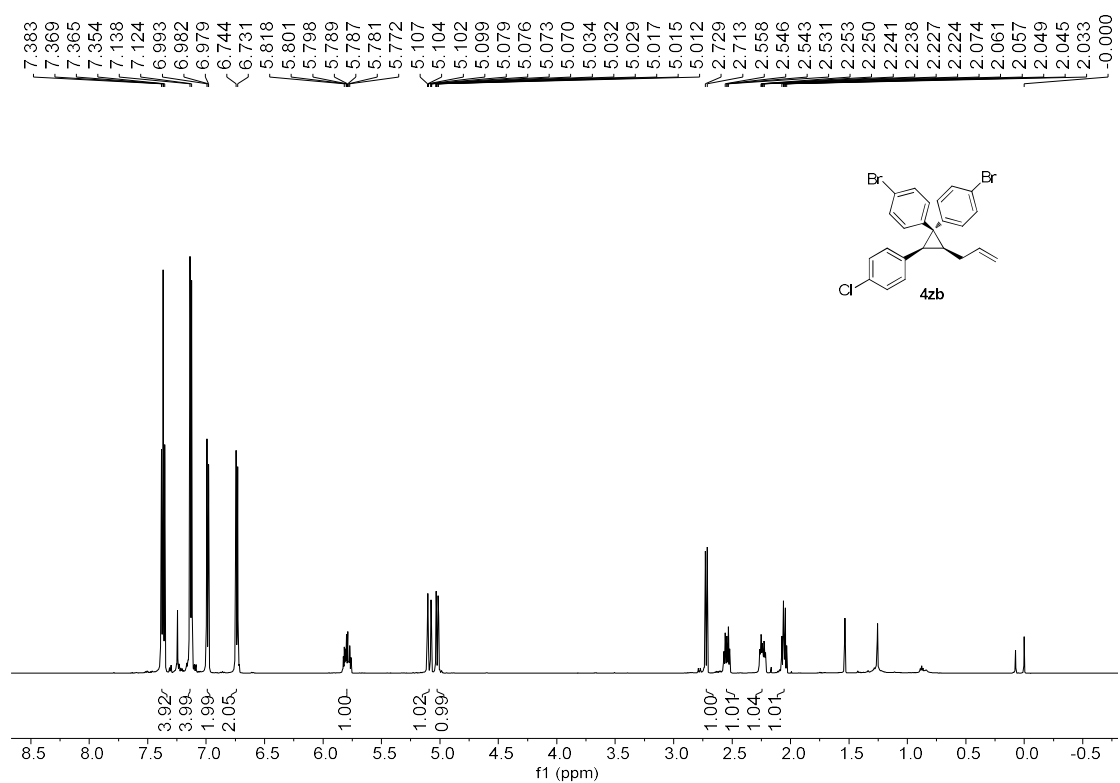
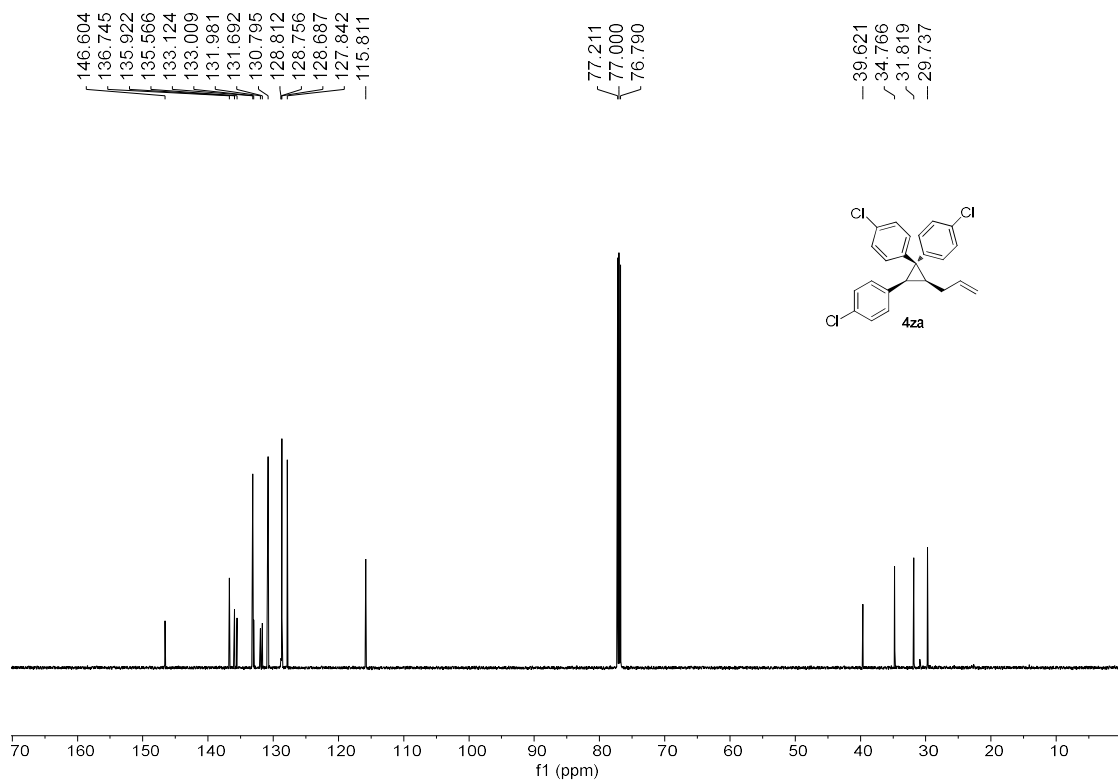


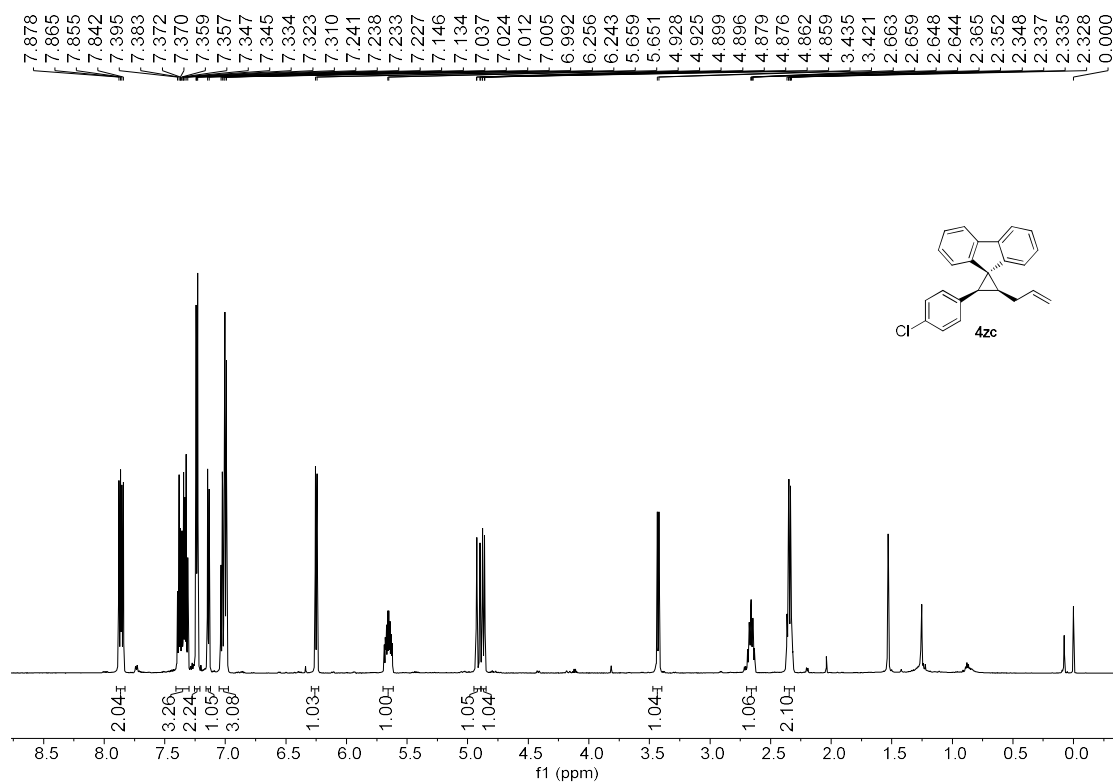
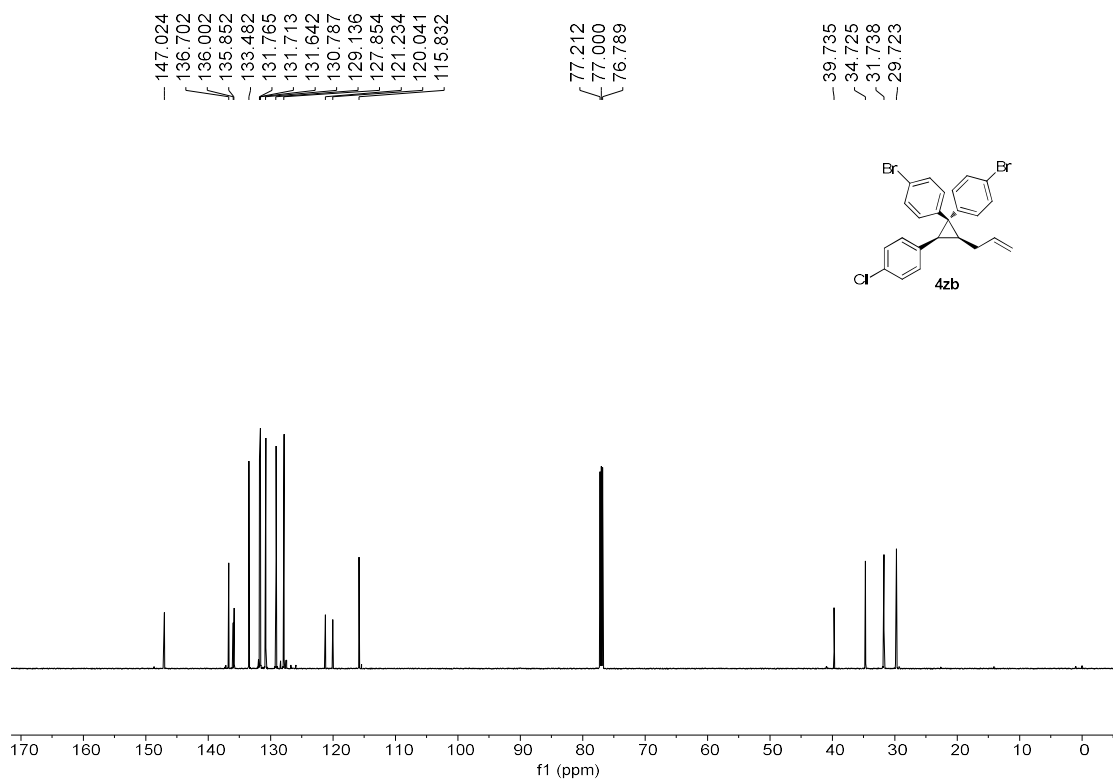


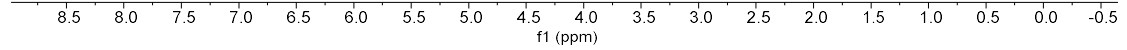


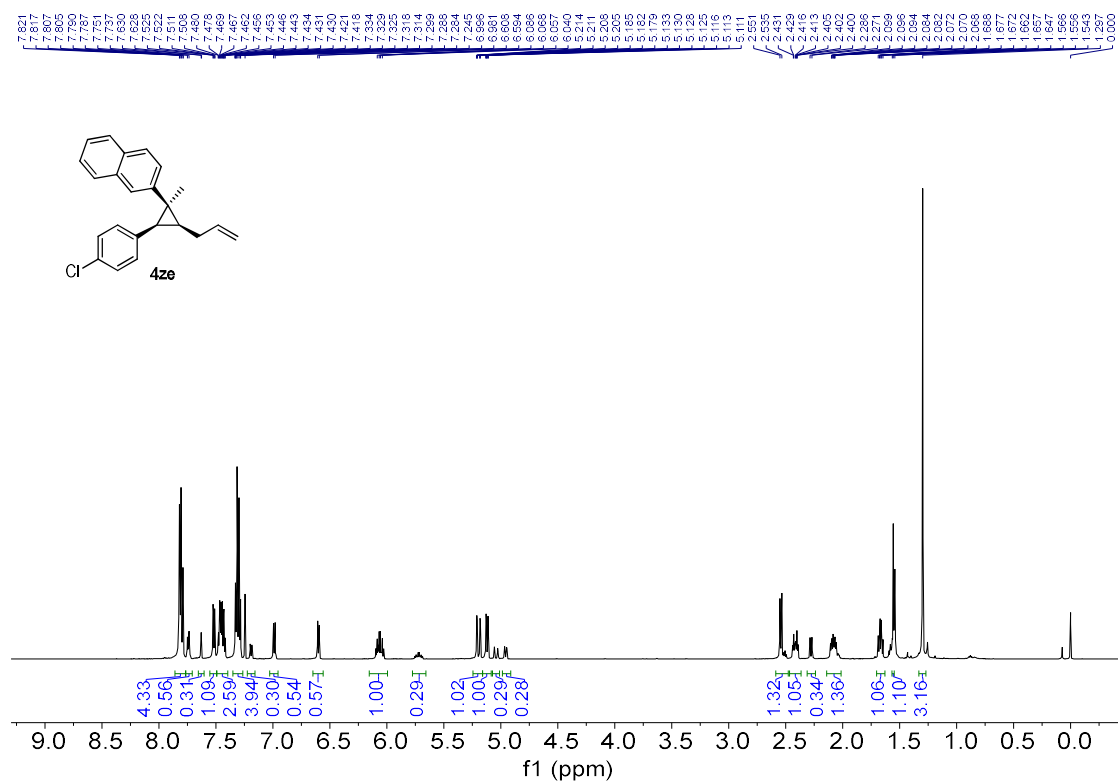
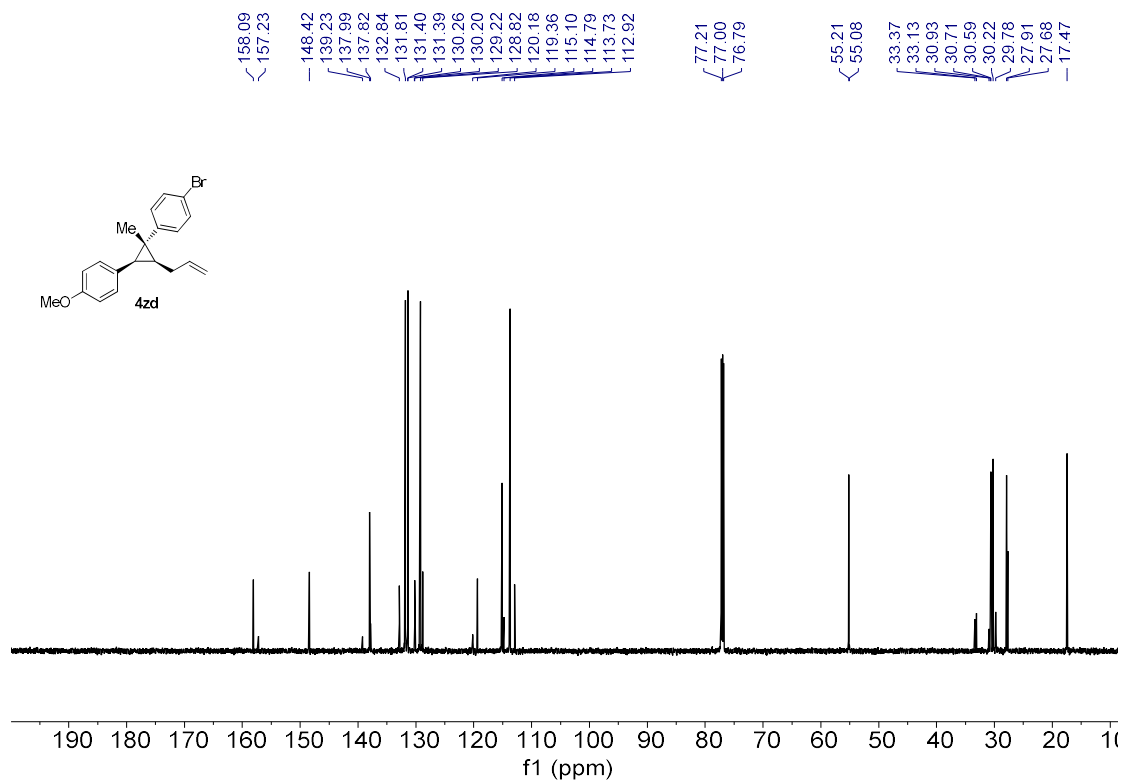


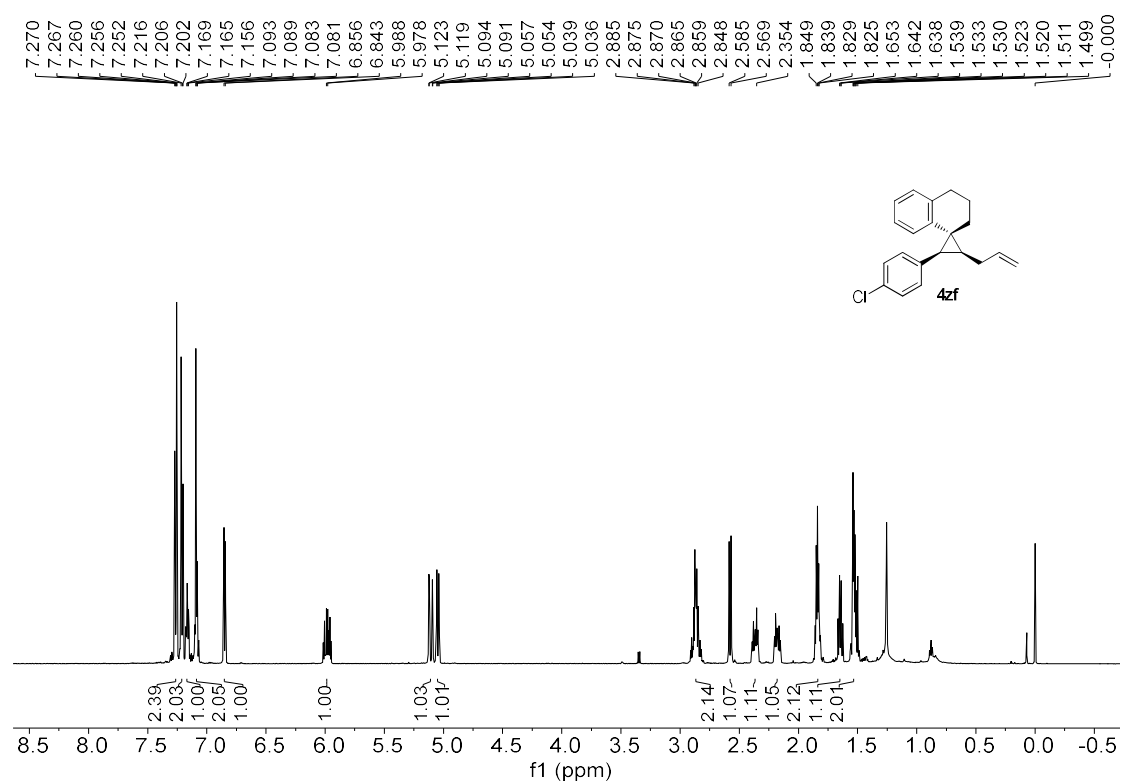
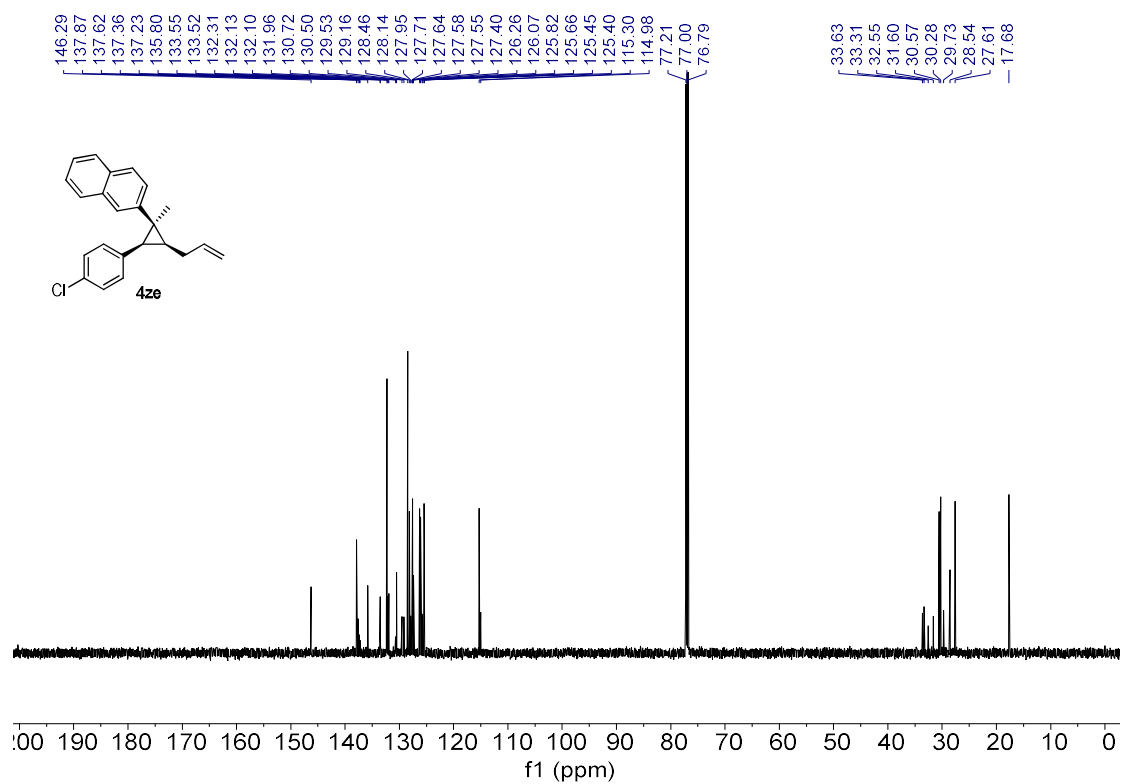


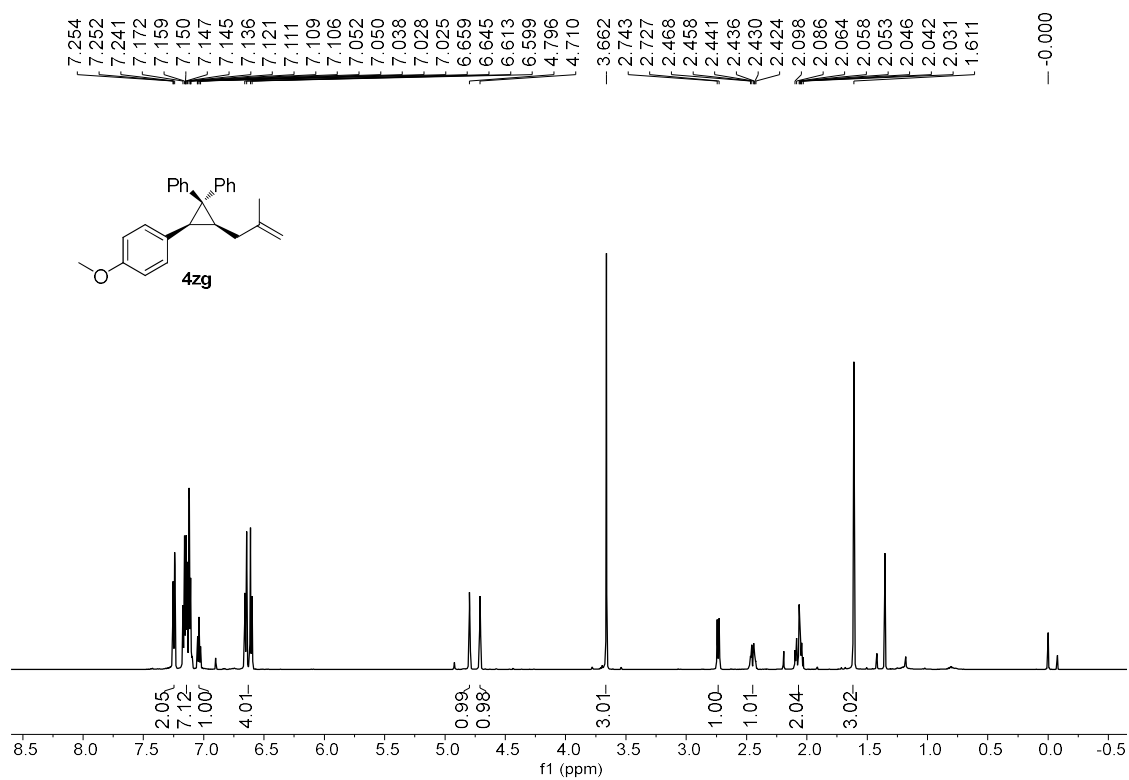
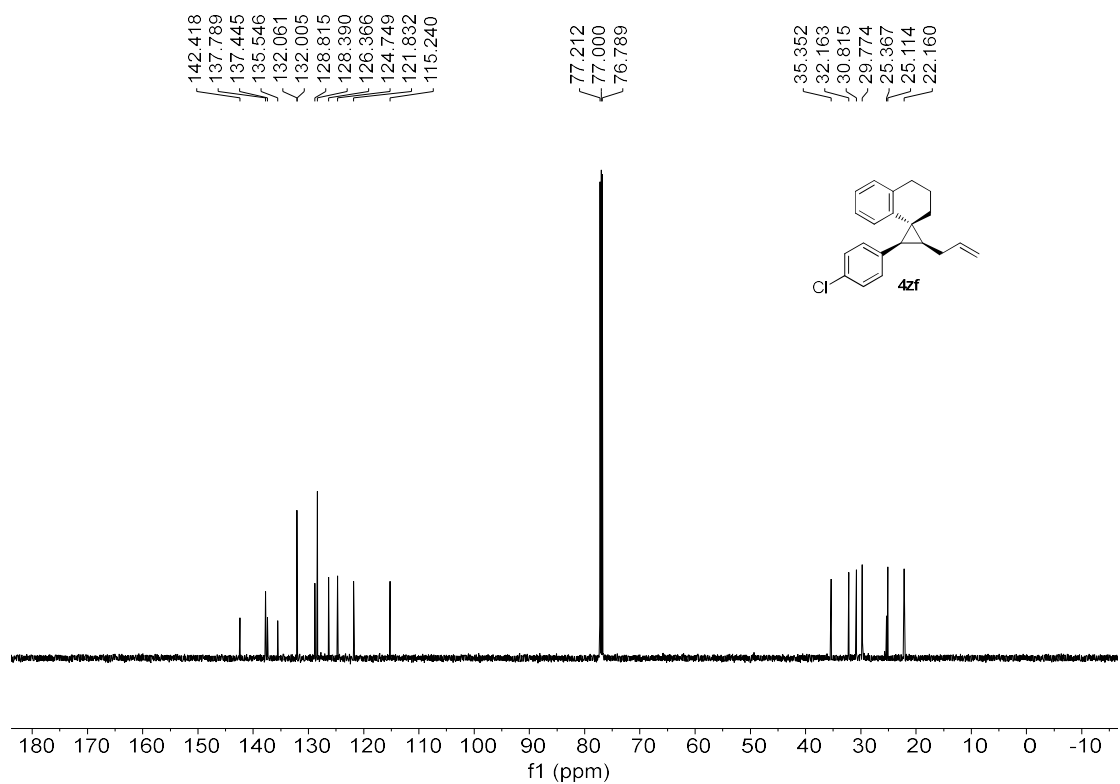


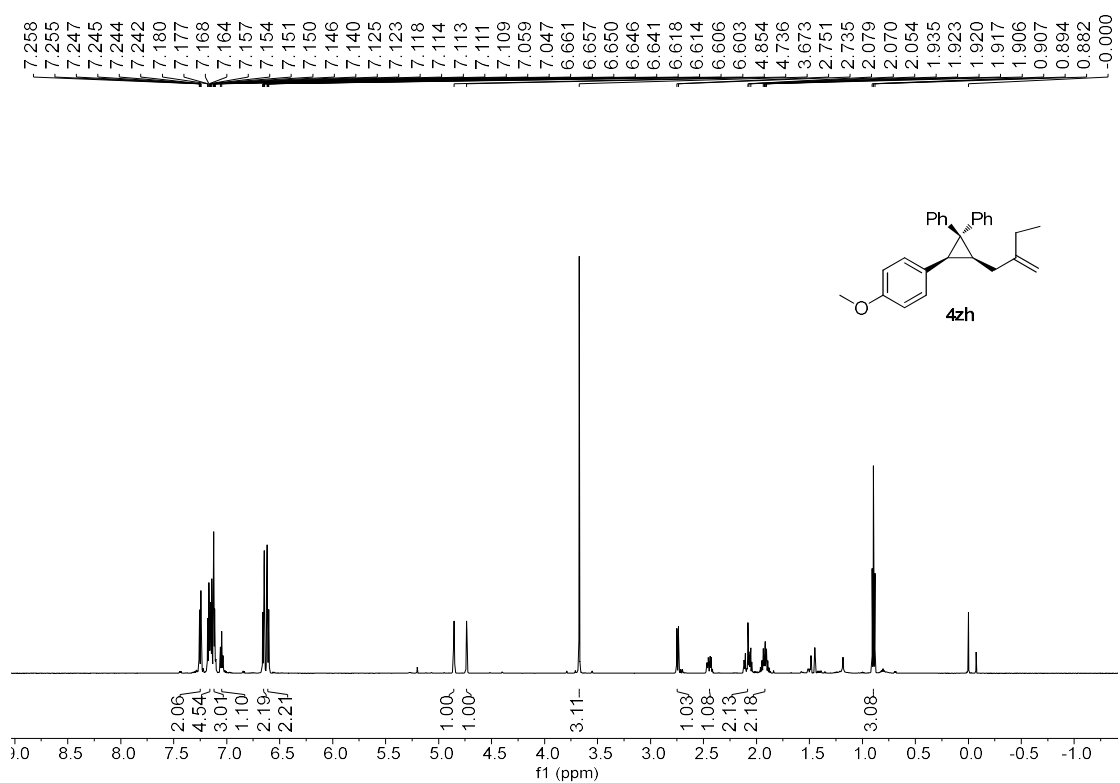
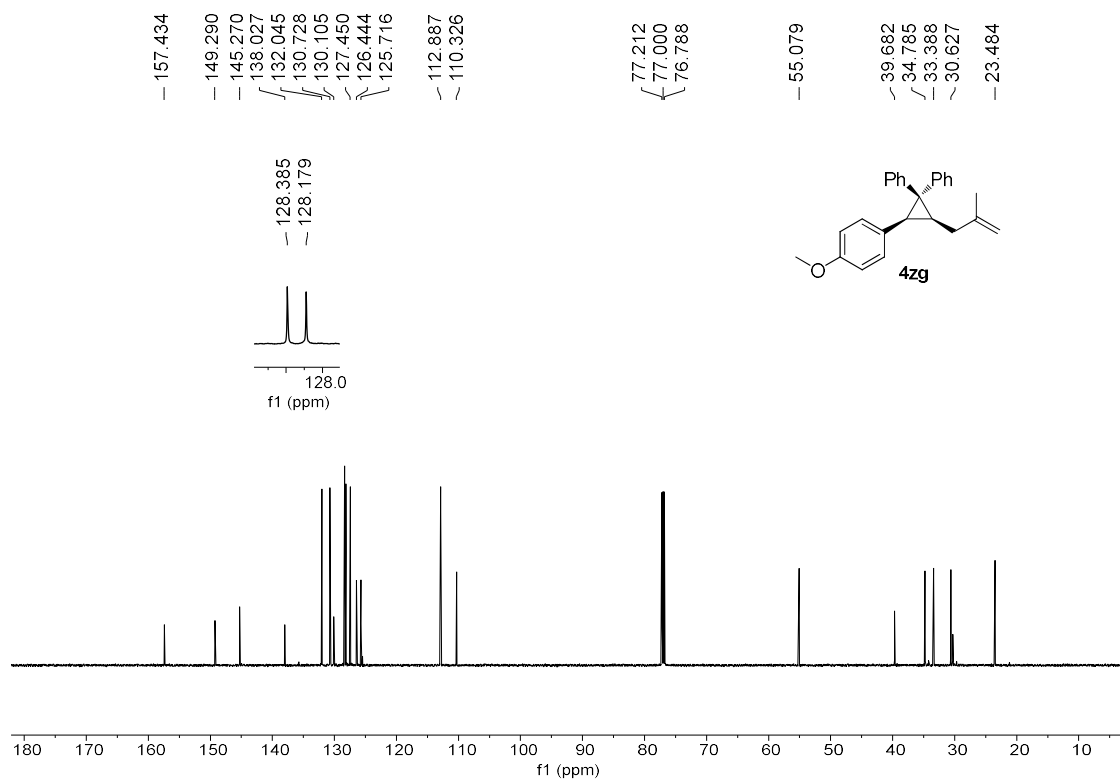


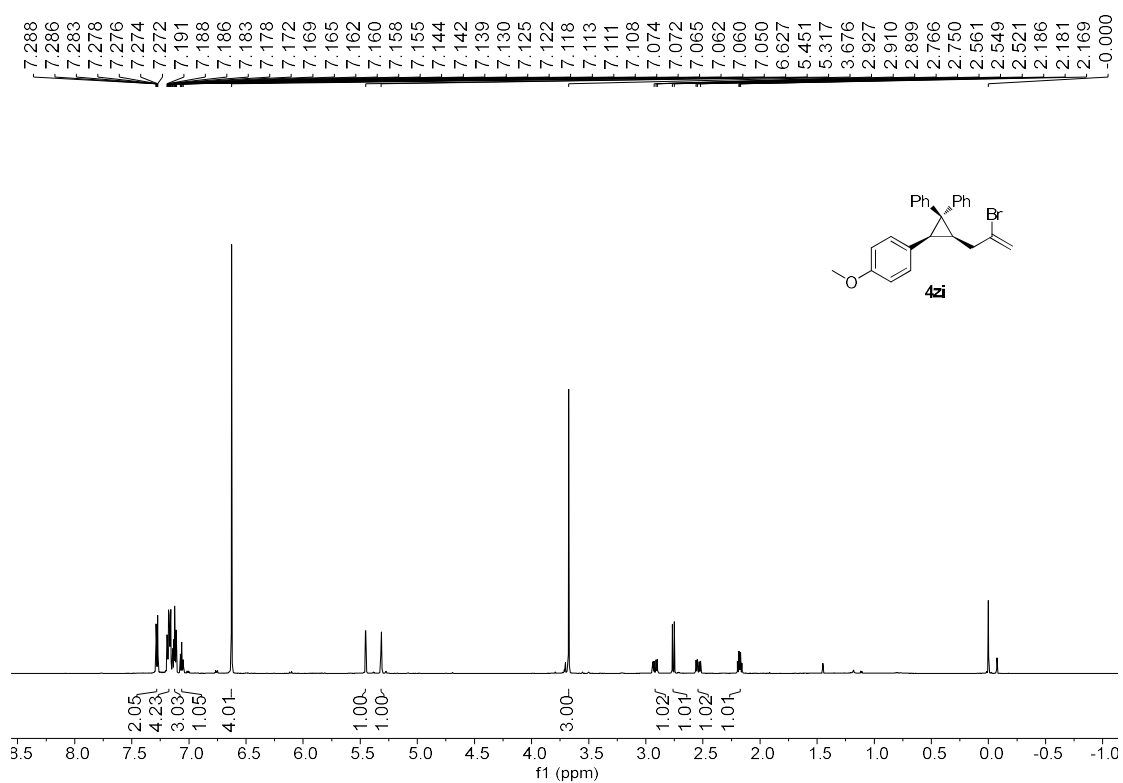
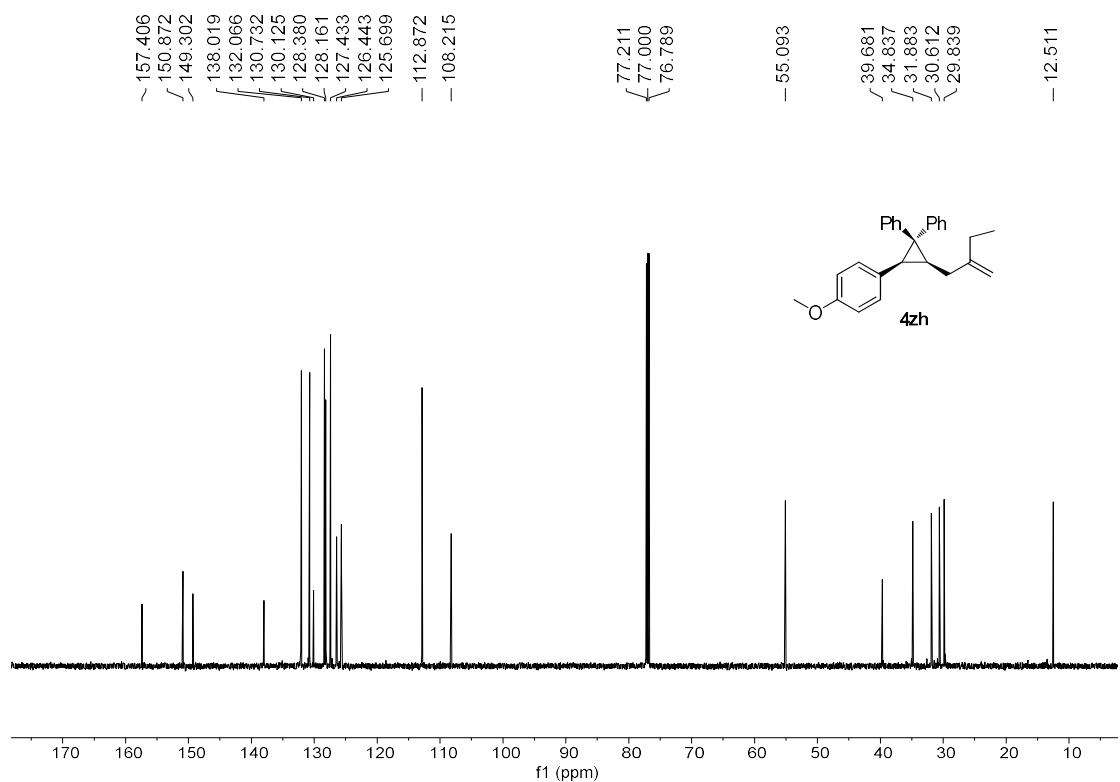


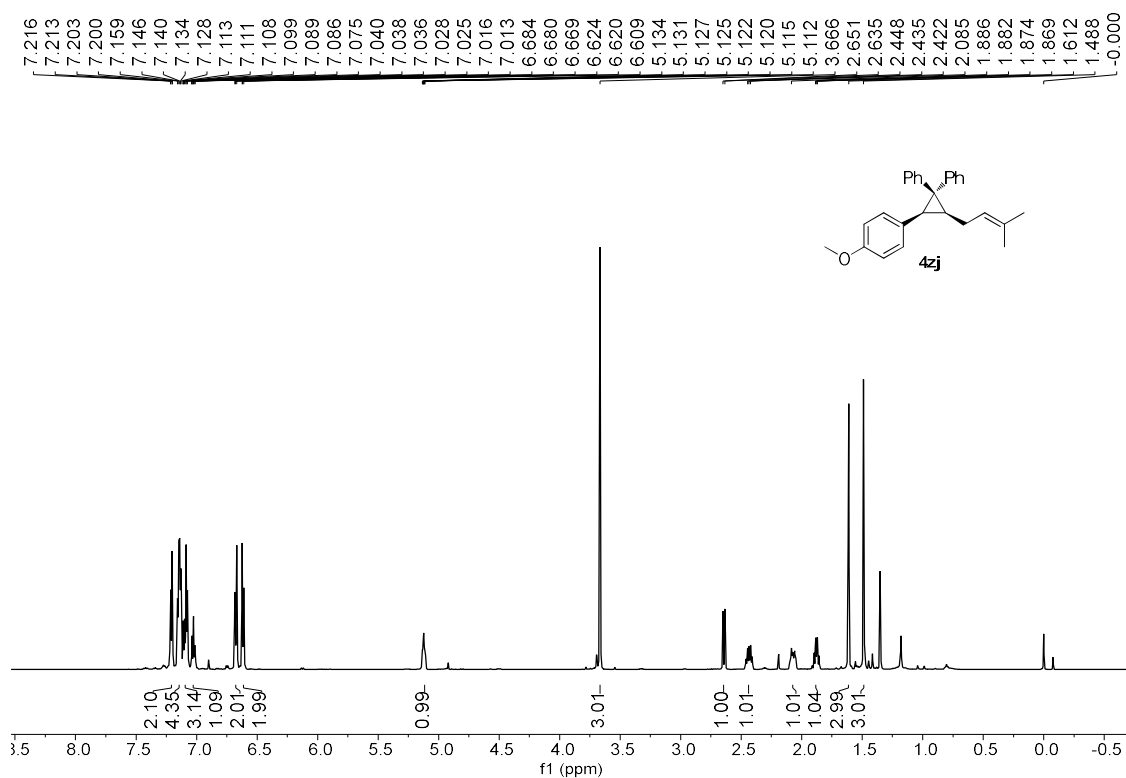
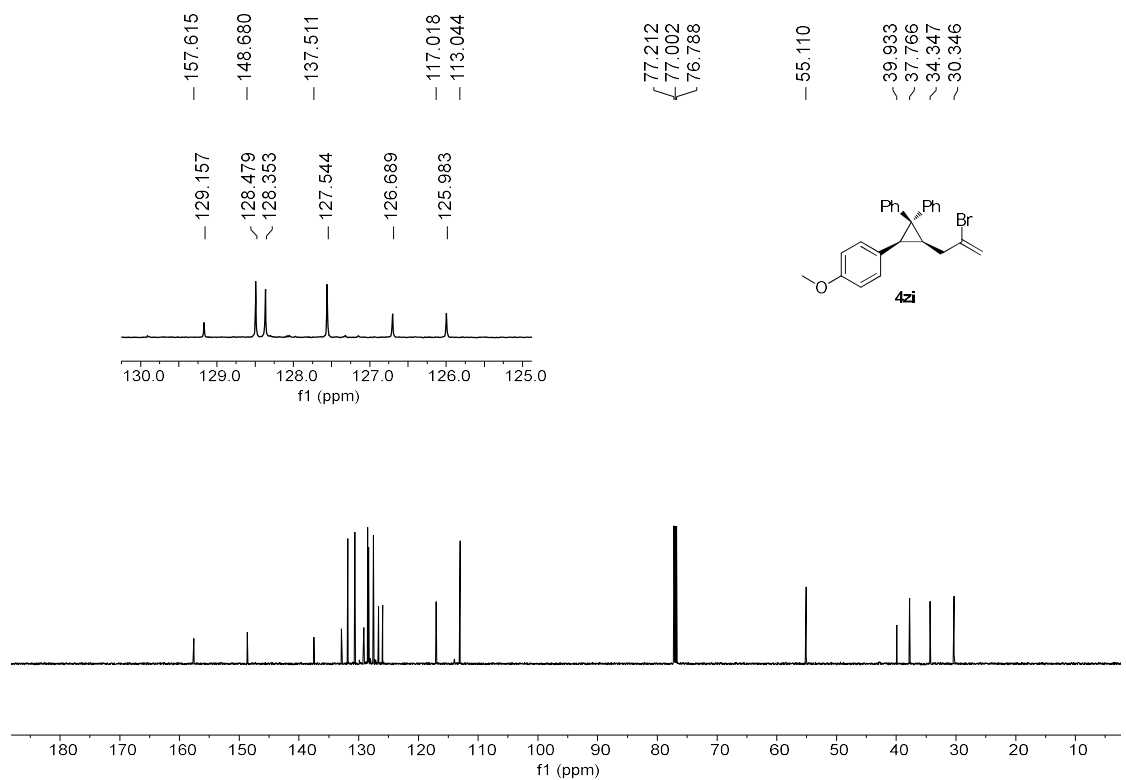


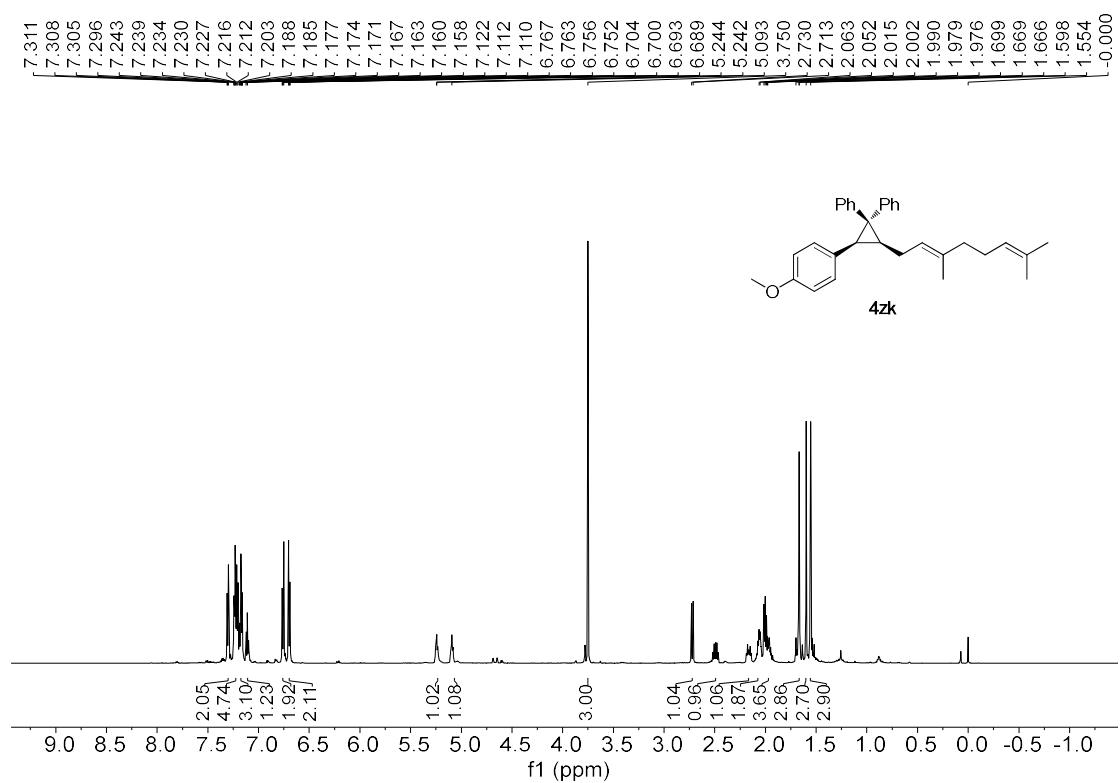
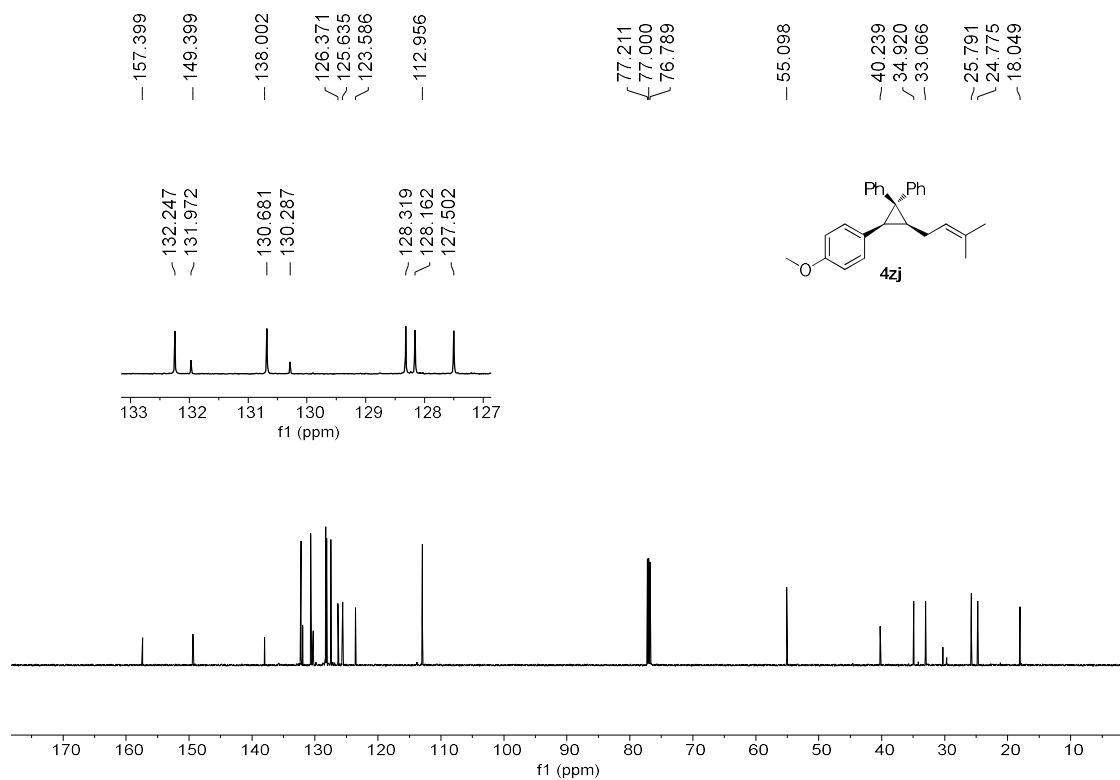


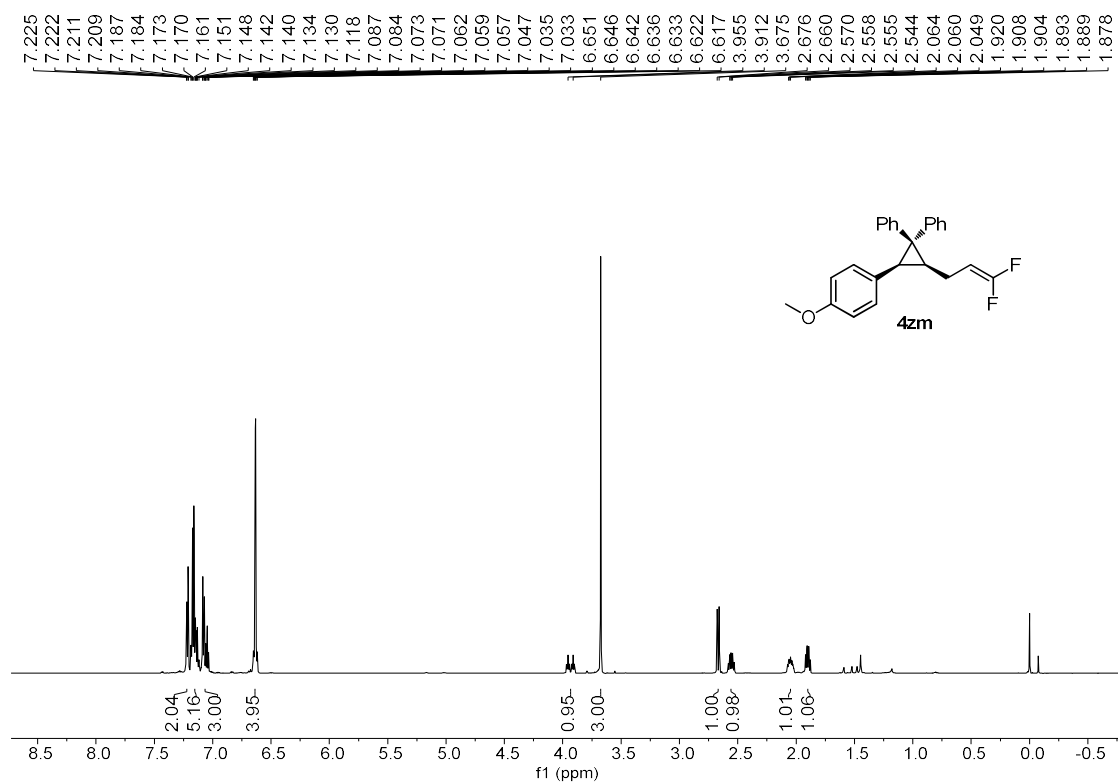
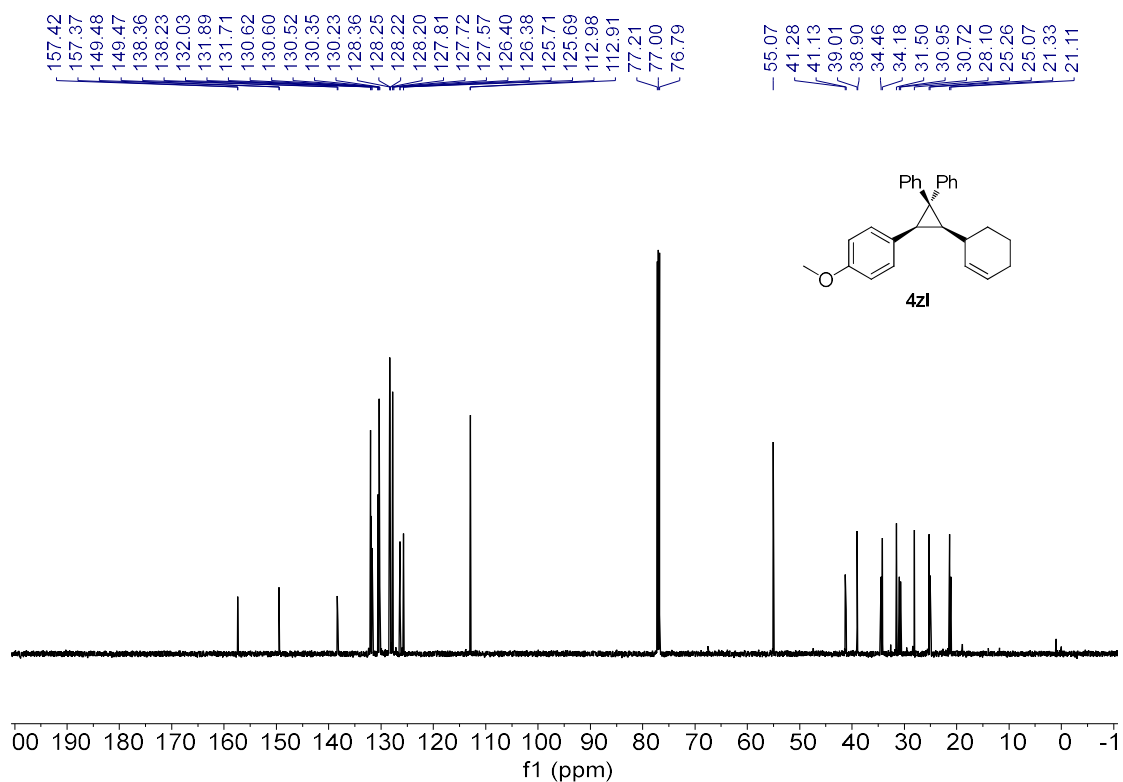


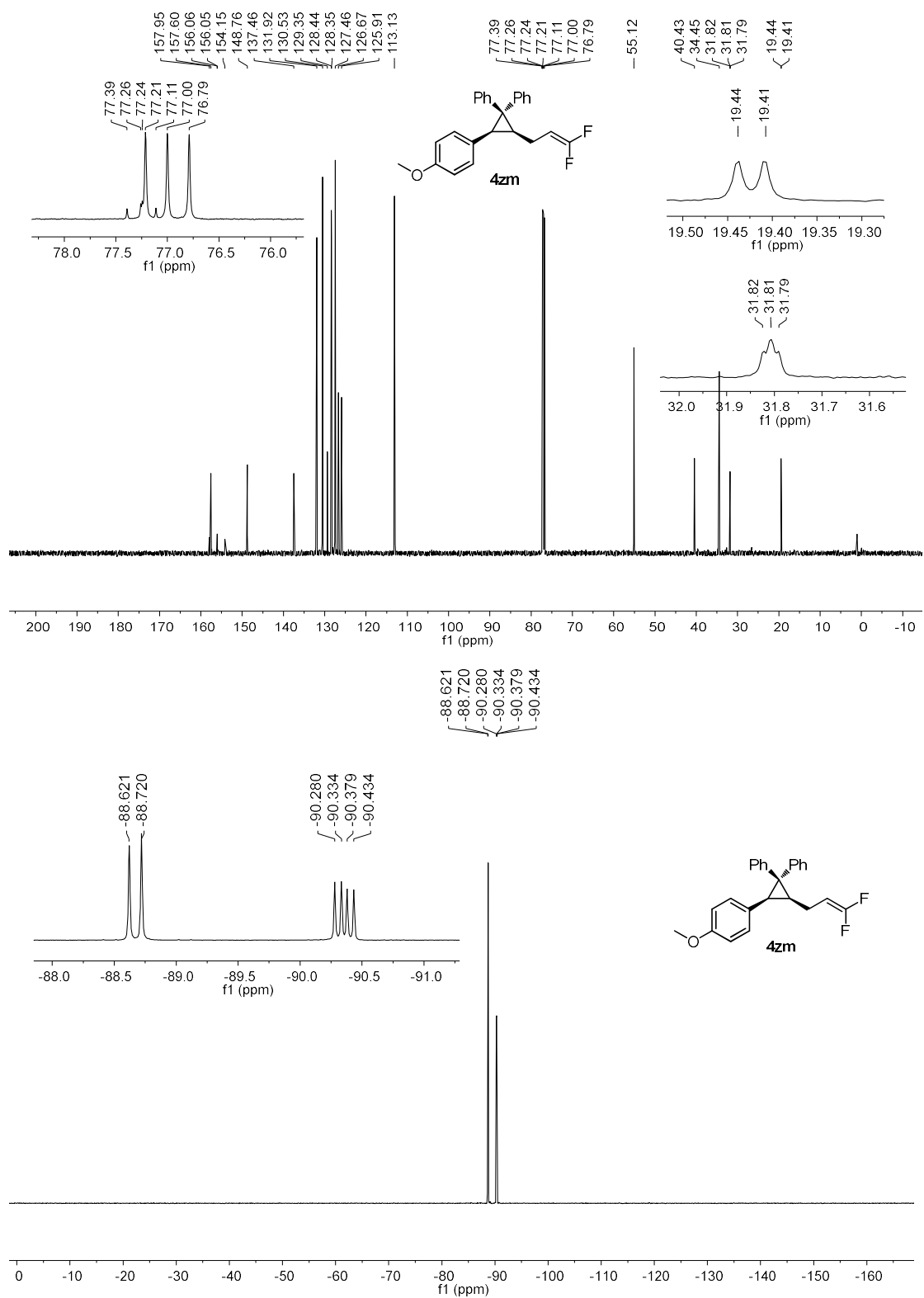


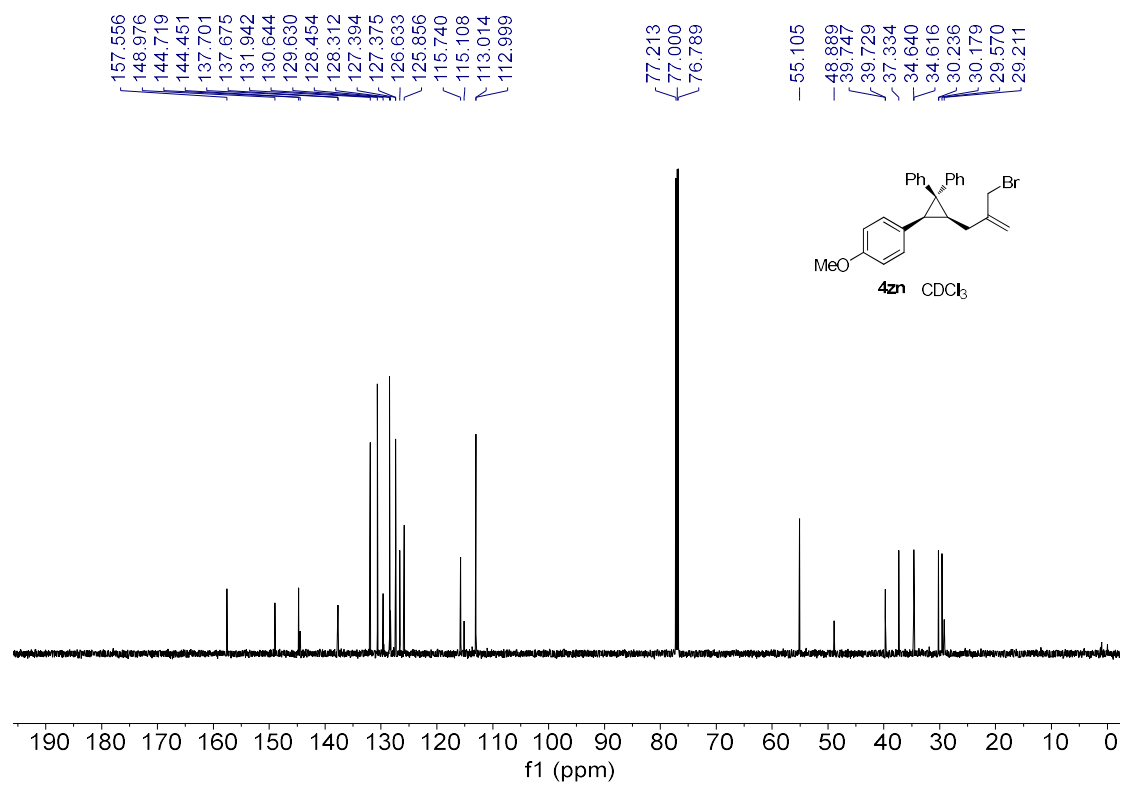
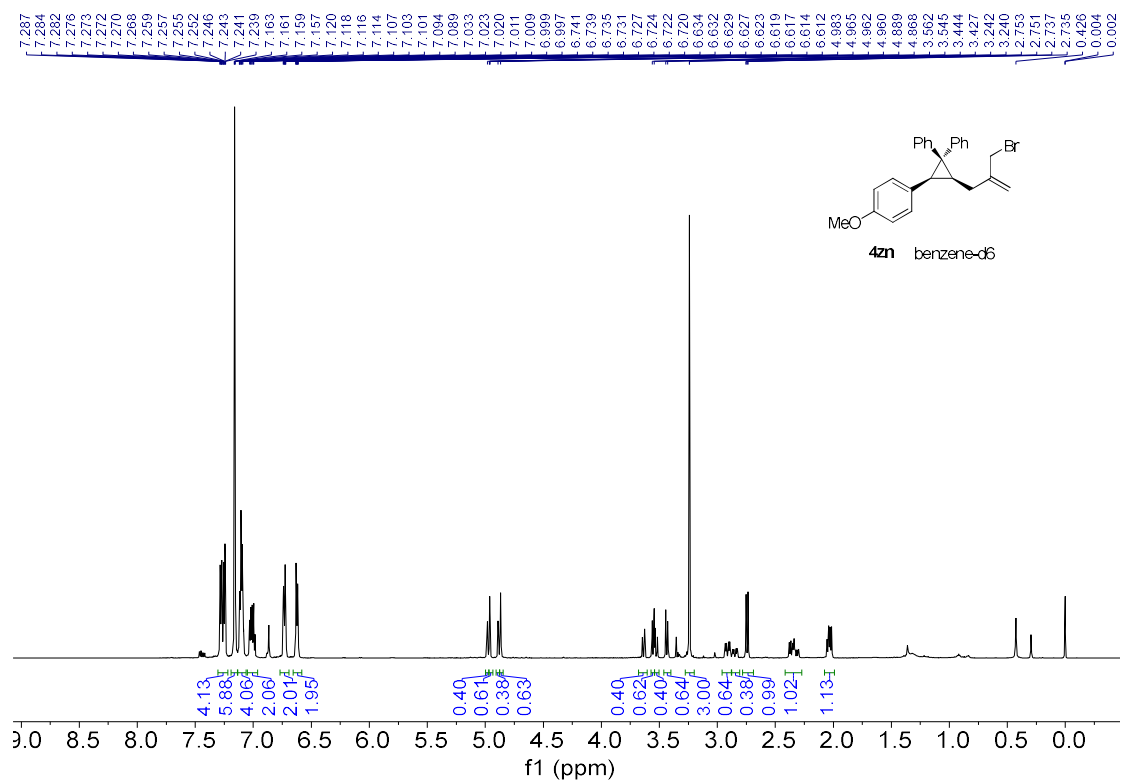


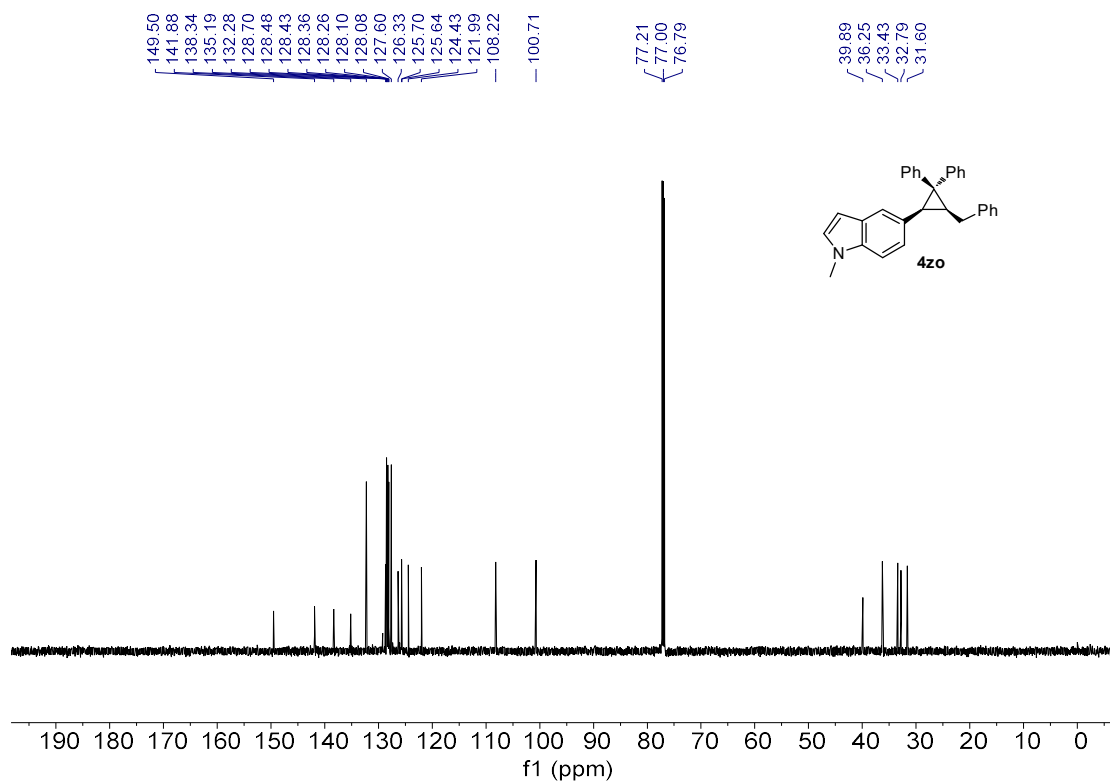
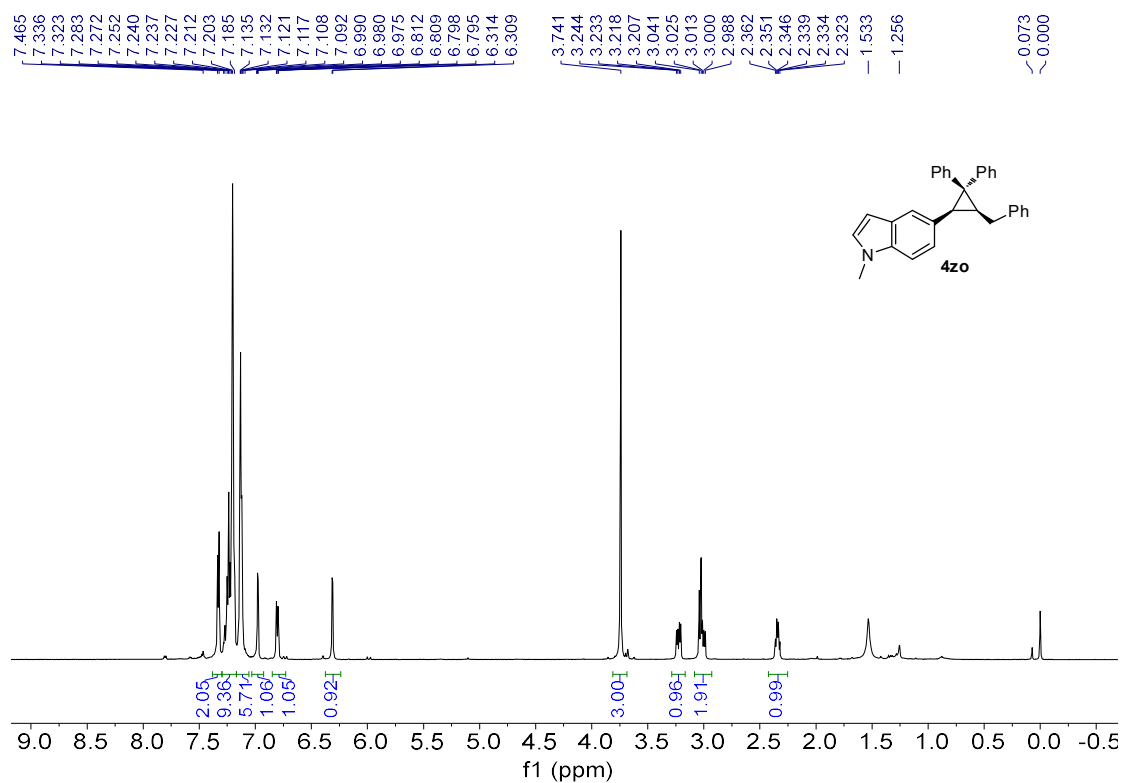






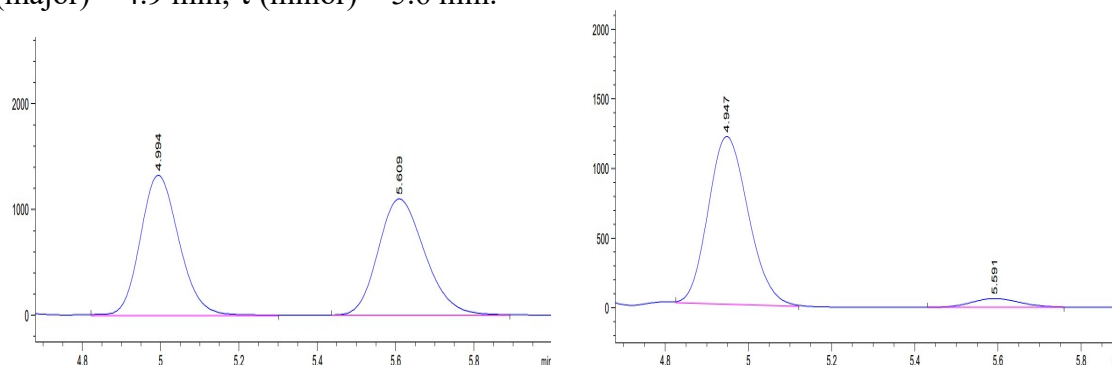






HPLC traces of (+)-4e.

HPLC conditions: chiralpak OD-H column, hexanes/i-PrOH = 99/1, 1 mL/min, τ (major) = 4.9 min; τ (minor) = 5.6 min.



Racemic:

Peak	PetTime	Type	Width(min)	Area(mAu*S)	Hight(mAu)	Area%
1	4.994	MM R	0.1148	9141.33008	1327.40552	50.1945
2	5.609	MM R	0.1376	9070.47559	1098.53735	49.8055

Chiral:

Peak	PetTime	Type	Width(min)	Area(mAu*S)	Hight(mAu)	Area%
1	4.947	MM R	0.1095	8078.30518	1204.73352	94.0192
2	5.591	MM R	0.1261	513.88239	63.11434	5.9808