

Supplementary Information

Nickel-Catalyzed Regiodivergent Sulfonylarylation of 1,3- Enynes to Access Allenes and Dienes

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1. General Information

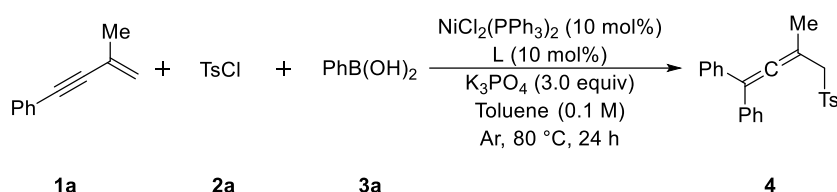
Unless otherwise noted, commercially available reagents were purchased from commercial suppliers (such as Innochem, Alfa Aesar, J&K Chemical, Energy Chemical, Bidepharm and Adamas) and used as received without further purification. Solvents were generally dried over 4 Å molecular sieves (water <50ppm, resealable bottle). Purification of products was performed by flash chromatography (FC) using silica gel or preparative thin layer chromatography. ¹H and ¹³C NMR spectra were recorded on a Bruker AVANCE III spectrometer (400 MHz and 101 MHz, respectively). Chemical shifts are reported parts per million (ppm) referenced to CDCl₃ (δ = 7.26 ppm), tetramethylsilane (TMS, δ = 0.00 ppm) for ¹H NMR and CDCl₃ (δ = 77.0 ppm) for ¹³C NMR. Multiplicities are given as s (singlet), d (doublet), t (triplet), dd (doublet of doublets), td (triplet of doublets) or m (multiplet). High-resolution mass spectra (HRMS) were obtained using a Q-TOF instrument equipped with an ESI source. Data collection for crystal structure was performed on a Bruker APEXII diffractometer.

2. Experimental Section

2.1 Optimization of reaction conditions

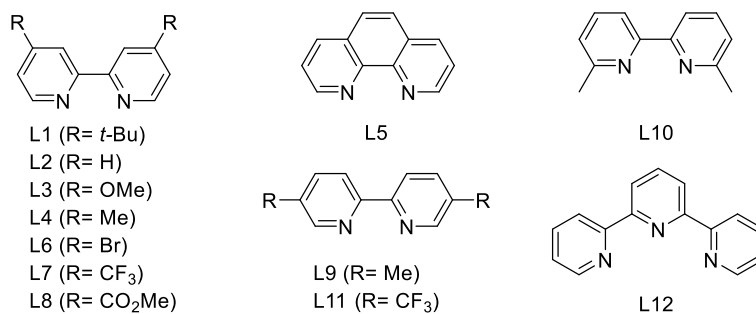
The oven-dried Schlenk sealed tube (15 mL) containing a stirring bar was charged with 1,3-enyne substrate, arylboronic acid, sulfonyl chloride, Ni-catalyst, ligand, base and solvent under argon atmosphere. Then the tube was placed into a preheated oil bath with stirring for 24 h. Upon completion of the reaction, the crude reaction mixture was diluted with DCM, and filtrated. After the solvent was concentrated under reduced pressure, the crude ¹H NMR spectrum was taken using CH₂Br₂ as internal standard. Yield was determined by ¹H NMR with CH₂Br₂ as internal standard.

2.1.1 Ligand screening

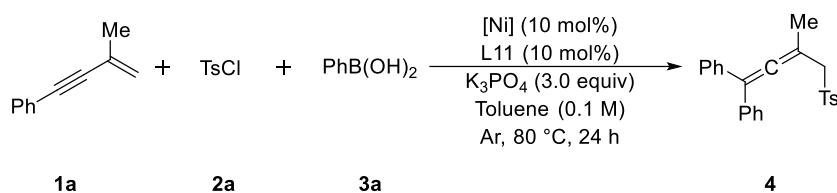


Entry	Ligand	Yield
1	L1	21%
2	L2	4%
3	L3	4%
4	L4	Trace
5	L5	Trace
6	L6	20%
7	L7	25%
8	L8	21%
9	L9	Trace
10	L10	N.D.
11	L11	25%
12	L12	Trace

Reaction conditions: 1,3-enyne (0.1 mmol, 1.0 equiv), arylboronic acids (0.2 mmol, 2.0 equiv), sulfonyl chlorides (0.2 mmol, 2.0 equiv), Ni-catalyst (10 mol%), ligand (10 mol%), base (0.3 mmol, 3.0 equiv) and solvent (1.0 mL), Ar, 80 °C, 24 h.



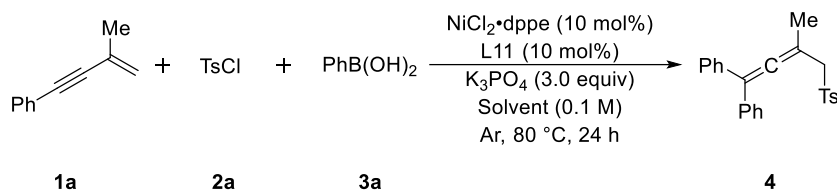
2.1.2 Ni-catalyst screening



Entry	[Ni]	Yield
1	NiBr ₂ (PPh ₃) ₂	30%
2	NiCl ₂ ·dppe	38%
3	NiCl ₂ ·dppp	34%
4	NiCl ₂ ·dppf	24%
5	NiCl ₂ (Py) ₄	14%
6	NiCl ₂ ·DME	26%
7	Ni(OTf) ₂	33%
8	Ni(COD) ₂	37%
9	Ni(NO ₃) ₂ ·6H ₂ O	16%

Reaction conditions: 1,3-enyne (0.1 mmol, 1.0 equiv), arylboronic acids (0.2 mmol, 2.0 equiv), sulfonyl chlorides (0.2 mmol, 2.0 equiv), Ni-catalyst (10 mol%), ligand (10 mol%), base (0.3 mmol, 3.0 equiv) and solvent (1.0 mL), Ar, 80 °C, 24 h.

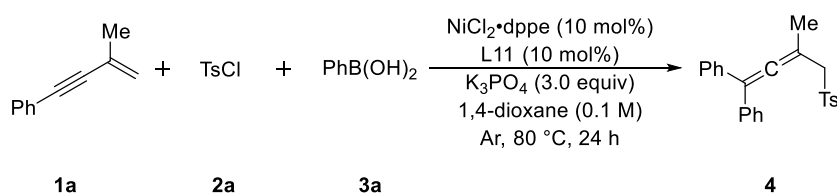
2.1.3 Solvent screening



Entry	Solvent	Yield
1	1,4-Dioxane	46%
2	DCE	35%
3	DMF	N.D.
4	MeCN	N.D.
5	Acetone	N.D.
6	Xylene	35%
7	Mesitylene	30%
8	THF	N.D.
9	DME	N.D.
10	Tetrahydropyran	N.D.

Reaction conditions: 1,3-enyne (0.1 mmol, 1.0 equiv), arylboronic acids (0.2 mmol, 2.0 equiv), sulfonyl chlorides (0.2 mmol, 2.0 equiv), Ni-catalyst (10 mol%), ligand (10 mol%), base (0.3 mmol, 3.0 equiv) and solvent (1.0 mL), Ar, 80 °C, 24 h.

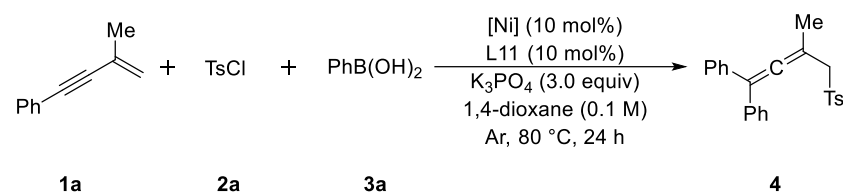
2.1.4 Relative ratios screening



Entry	1a(mmol)	2a(mmol)	3a(mmol)	Yield
1	0.1	0.1	0.1	11%
2	0.1	0.15	0.15	26%
3	0.1	0.25	0.25	52%
4	0.1	0.3	0.3	52%
5	0.1	0.2	0.3	51%
6	0.1	0.3	0.2	24%
7	0.2	0.1	0.2	31%
8	0.2	0.2	0.1	15%

Reaction conditions: 1,3-enyne, arylboronic acids, sulfonyl chlorides, Ni-catalyst (10 mol%), ligand (10 mol%), base (0.3 mmol, 3.0 equiv) and solvent (1.0 mL), Ar, 80 °C, 24 h.

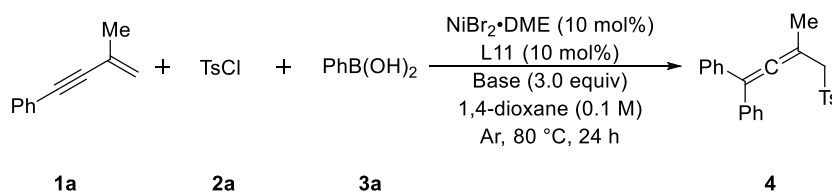
2.1.5 Ni-catalyst screening



Entry	[Ni]	Yield
1	$NiCl_2(PPh_3)_2$	51%
2	$NiBr_2(PPh_3)_2$	40%
3	$NiCl_2 \cdot dppe$	58%
4	$NiCl_2 \cdot dppp$	31%
5	$NiCl_2 \cdot dppf$	48%
6	$NiCl_2(PCy_3)_2$	44%
7	$NiCl_2(Py)_4$	20%
8	$Ni(PPh_3)_4$	53%
9	$Ni(OTf)_2$	57%
10	$Ni(COD)_2$	51%
11	$NiCl_2 \cdot DME$	50%
12	$NiBr_2 \cdot DME$	62%
13	$NiBr_2 \cdot diglyme$	45%
14	$Ni(acac)_2$	trace
15	NiF_2	N.D.
16	$NiCl_2$	14%
17	NiI_2	50%
18	$Ni(NO_3)_2 \cdot 6H_2O$	41%
19	$Ni(PO_4)_2 \cdot 8H_2O$	N.D.

Reaction conditions: 1,3-enyne (0.1 mmol, 1.0 equiv), arylboronic acids (0.25 mmol, 2.5 equiv), sulfonyl chlorides (0.25 mmol, 2.5 equiv), Ni-catalyst (10 mol%), ligand (10 mol%), base (0.3 mmol, 3.0 equiv) and solvent (1.0 mL), Ar, 80 °C, 24 h.

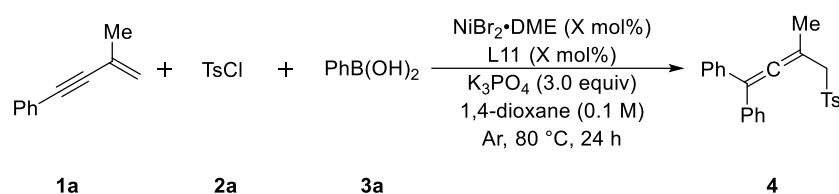
2.1.6 Base screening



Entry	Base	Yield
1	K ₂ CO ₃	57%
2	K ₂ HPO ₄	35%
3	<i>t</i> -BuOK	16
4	AcOK	N.D.
5	KHCO ₃	N.D.
6	Na ₃ PO ₄	40%
7	Na ₂ CO ₃	31%
8	Cs ₂ CO ₃	N.D.

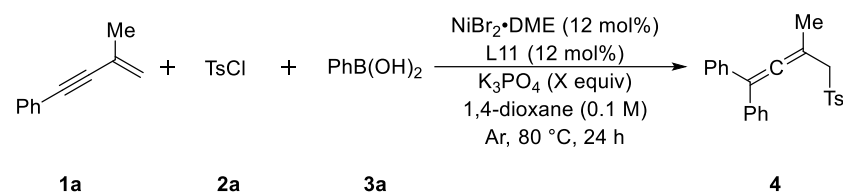
Reaction conditions: 1,3-enyne (0.1 mmol, 1.0 equiv), arylboronic acids (0.25 mmol, 2.5 equiv), sulfonyl chlorides (0.25 mmol, 2.5 equiv), Ni-catalyst (10 mol%), ligand (10 mol%), base (0.3 mmol, 3.0 equiv) and solvent (1.0 mL), Ar, 80 °C, 24 h.

2.1.7 Relative ratios screening



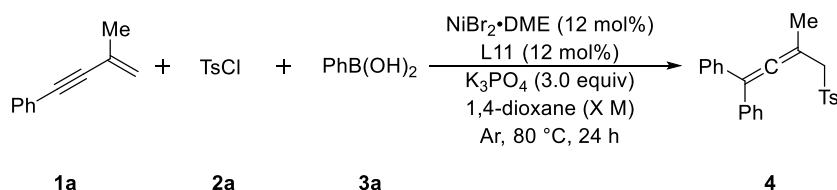
Entry	NiBr ₂ ·DME	L11	Yield
1	5.0%	7.5%	46%
2	10%	15%	44%
3	10%	20%	36%
4	12%	12%	69%
5	12%	15%	56%
6	15%	15%	65%
7	15%	20%	63%

Reaction conditions: 1,3-enyne (0.1 mmol, 1.0 equiv), arylboronic acids (0.25 mmol, 2.5 equiv), sulfonyl chlorides (0.25 mmol, 2.5 equiv), Ni-catalyst, ligand, base (0.3 mmol, 3.0 equiv) and solvent (1.0 mL), Ar, 80 °C, 24 h.



Entry	$\text{K}_3\text{PO}_4(\text{eq})$	Yield
1	1.5	55%
2	2.0	65%
3	2.5	66%
4	3.5	57%
5	4.0	50%

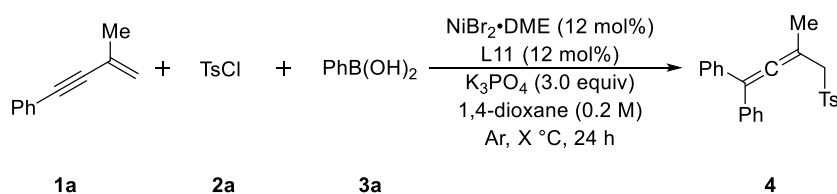
Reaction conditions: 1,3-enyne (0.1 mmol, 1.0 equiv), arylboronic acids (0.25 mmol, 2.5 equiv), sulfonyl chlorides (0.25 mmol, 2.5 equiv), Ni-catalyst (12 mol%), ligand (12 mol%), base and solvent (1.0 mL), Ar, 80 °C, 24 h.



Entry	1,4-dioxane(mL)	Yield
1	0.5	82%
2	1.5	69%
3	2.0	69%

Reaction conditions: 1,3-enyne (0.1 mmol, 1.0 equiv), arylboronic acids (0.25 mmol, 2.5 equiv), sulfonyl chlorides (0.25 mmol, 2.5 equiv), Ni-catalyst (12 mol%), ligand (12 mol%), base (0.3 mmol, 3.0 equiv) and solvent, Ar, 80 °C, 24 h.

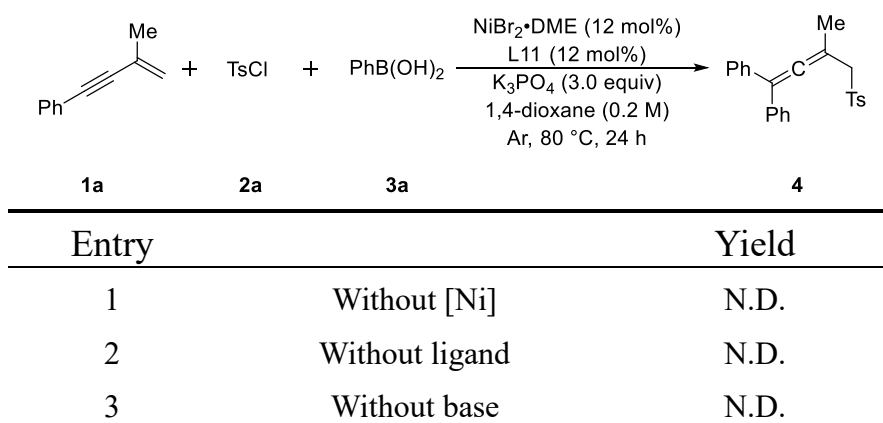
2.1.8 Temperature screening



Entry	T(°C)	Yield
1	40	38%
2	50	63%
3	60	71%
4	70	75%
5	90	58%
6	100	53%

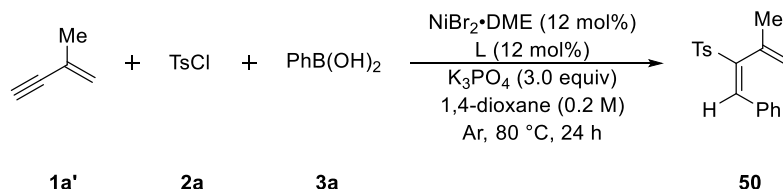
Reaction conditions: 1,3-enyne (0.1 mmol, 1.0 equiv), arylboronic acids (0.25 mmol, 2.5 equiv), sulfonyl chlorides (0.25 mmol, 2.5 equiv), Ni-catalyst (12 mol%), ligand (12 mol%), base (0.3 mmol, 3.0 equiv) and solvent (0.5 mL), Ar, 24 h.

2.1.9 Control reactions



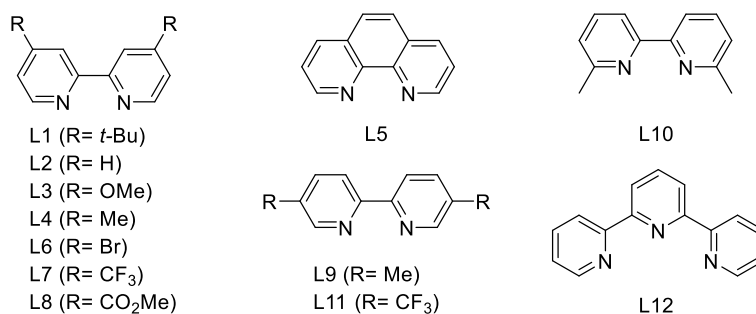
Reaction conditions: 1,3-enyne (0.1 mmol, 1.0 equiv), arylboronic acids (0.25 mmol, 2.5 equiv), sulfonyl chlorides (0.25 mmol, 2.5 equiv), Ni-catalyst (12 mol%), ligand (12 mol%), base (0.3 mmol, 3.0 equiv) and solvent (0.5 mL), Ar, 80 °C, 24 h.

2.1.10 Ligand screening



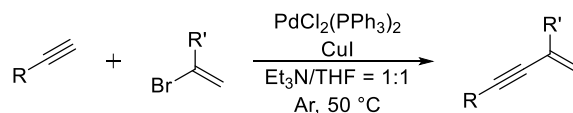
Entry	Ligand	Yield
1	L1	33%
2	L2	Trace
3	L3	Trace
4	L4	N.D.
5	L5	Trace
6	L6	16%
7	L7	55%
8	L8	26%
9	L9	5%
10	L10	N.D.
11	L11	60%
12	L12	N.D.

Reaction conditions: 1,3-enyne (0.1 mmol, 1.0 equiv), arylboronic acids (0.25 mmol, 2.5 equiv), sulfonyl chlorides (0.25 mmol, 2.5 equiv), Ni-catalyst (12 mol%), ligand (12 mol%), base (0.3 mmol, 3.0 equiv) and solvent (0.5 mL), Ar, 80 °C, 24 h.



2.2 General procedures for synthesis of substrates

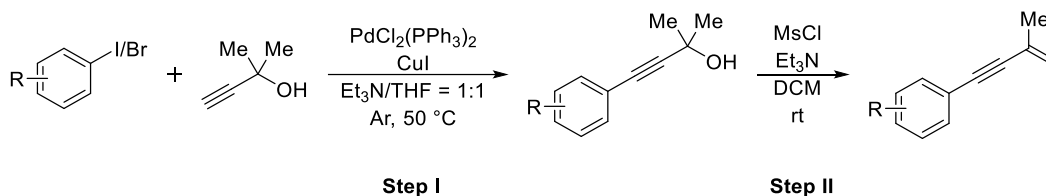
2.2.1 General procedure A



The oven-dried Schlenk flask containing a stirring bar was charged with PdCl₂(PPh₃)₂ (2.0 mmol%) and CuI (5.0 mmol%). The mixture was evacuated and back-filled with Ar for 3 times. Dry THF and Et₃N was respectively added under a stream of argon, and the substituted alkyne (1.0 equiv) and substituted 2-Bromopropene (1.2 equiv) was successively added carefully at room temperature. Then, the reaction mixture was stirred and heated to 50 °C under argon atmosphere. After completion (monitored by TLC), the reaction was cooled to room temperature and diluted with ethyl acetate and washed with brine. The

organic layer was dried over anhydrous Na_2SO_4 and filtrated. After the solvent was concentrated under reduced pressure, the crude product was purified by flash silica gel column chromatography (PE) to afford the desired products.^[1]

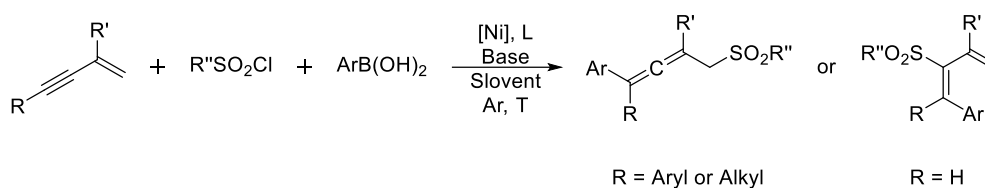
2.2.2 General procedure B



Step I: The oven-dried Schlenk flask containing a stirring bar was charged with $\text{PdCl}_2(\text{PPh}_3)_2$ (2.0 mmol%) and CuI (5.0 mmol%). The mixture was evacuated and back-filled with Ar for 3 times. Dry THF and Et_3N was respectively added under a stream of argon, and the substituted aryl halides (1.0 equiv) and 2-methyl-3-butyn-2-ol (1.2 equiv) was added carefully at room temperature. Then, the reaction mixture was stirred and heated to 50 °C under argon atmosphere. After completion (monitored by TLC), the reaction was cooled to room temperature and diluted with ethyl acetate and washed with brine. The organic layer was dried over anhydrous Na_2SO_4 and filtrated. After the solvent was concentrated under reduced pressure, the crude product was purified by flash silica gel column chromatography (PE:EA=5:1-1:1) to afford the desired products.

Step II: The resulting propargyl alcohol (1.0 equiv) was dissolved in DCM, and the mixture was cooled to 0 °C. After Et_3N (5.0 equiv) was added to this solution, methylsulfonyl chloride (2.0 equiv) was added carefully at 0 °C. Then, the reaction mixture was stirred at room temperature. After completion (monitored by TLC), the reaction was diluted with dichloromethane and washed with brine. The organic layer was dried over anhydrous Na_2SO_4 and filtrated. After the solvent was concentrated under reduced pressure, the crude product was purified by flash silica gel column chromatography (PE:EA=100:1-10:1) to afford the desired products.^[2]

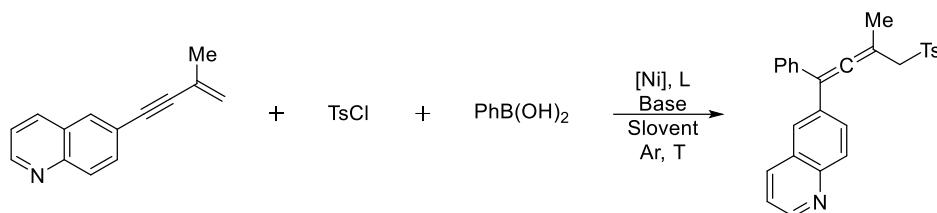
2.3 General procedures for synthesis of products



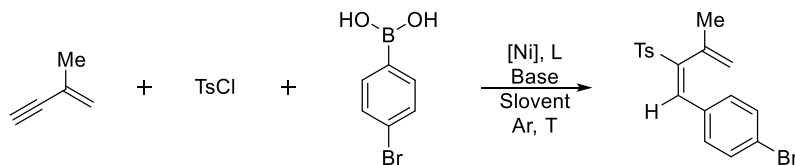
The oven-dried Schlenk sealed tube (15 mL) containing a stirring bar was charged with 1,3-enyne

substrates (0.1 mmol, 1.0 equiv), arylboronic acids (0.25 mmol, 2.5 equiv), sulfonyl chlorides (0.25 mmol, 2.5 equiv), NiBr₂•DME (12 mol%), 5,5'-Bis(trifluoromethyl)-2,2'-bipyridine (12 mol%), K₃PO₄ (0.3 mmol, 3.0 equiv) and 1,4-dioxane (0.5 mL) under argon atmosphere. Then the tube was placed into a preheated oil bath at 80 °C with stirring for 24 h. Upon completion of the reaction, the crude reaction mixture was diluted with DCM, and filtrated. After the solvent was concentrated under reduced pressure, the crude ¹H NMR spectrum was taken using CH₂Br₂ as internal standard. The resulting residue was purified by flash silica gel column chromatography or preparative thin layer chromatography to give the desired products.

2.4 Large-scale experiments



The oven-dried Schlenk sealed tube (100 mL) containing a stirring bar was charged with 1,3-enyne substrates (3.0 mmol, 1.0 equiv), arylboronic acids (7.5 mmol, 2.5 equiv), sulfonyl chlorides (7.5 mmol, 2.5 equiv), NiBr₂•DME (12 mol%), 5,5'-Bis(trifluoromethyl)-2,2'-bipyridine (12 mol%), K₃PO₄ (9 mmol, 3.0 equiv) and 1,4-dioxane (15 mL) under argon atmosphere. Then the tube was placed into a preheated oil bath at 80 °C with stirring for 24 h. Upon completion of the reaction, the crude reaction mixture was diluted with DCM, and filtrated. After the solvent was concentrated under reduced pressure, the resulting residue was purified by flash silica gel column chromatography (PE:EA=5:1-1:1) to give the desired products in 68%.

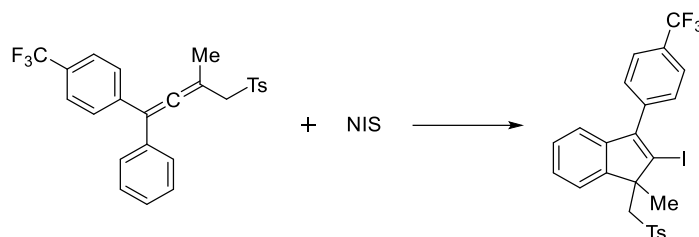


The oven-dried Schlenk sealed tube (100 mL) containing a stirring bar was charged with 1,3-enyne substrates (5.0 mmol, 1.0 equiv), arylboronic acids (12.5 mmol, 2.5 equiv), sulfonyl chlorides (12.5 mmol, 2.5 equiv), NiBr₂•DME (12 mol%), 5,5'-Bis(trifluoromethyl)-2,2'-bipyridine (12 mol%), K₃PO₄ (15 mmol, 3.0 equiv) and 1,4-dioxane (25 mL) under argon atmosphere. Then the tube was placed into a preheated oil bath at 80 °C with stirring for 24 h. Upon completion of the reaction, the crude reaction

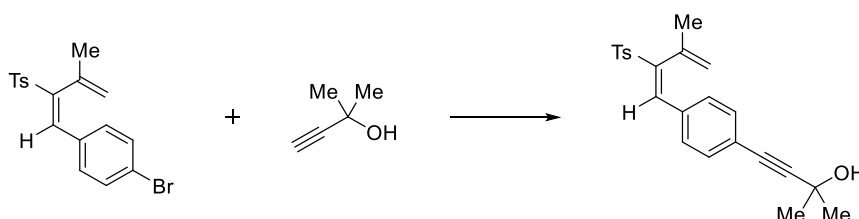
mixture was diluted with DCM, and filtrated. After the solvent was concentrated under reduced pressure, the resulting residue was purified by flash silica gel column chromatography (PE:EA=20:1-10:1) to give the desired products in 60%.

2.5 Synthetic application

2.5.1 Synthetic transformations

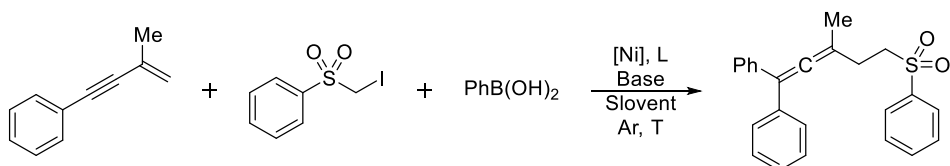


The oven-dried Schlenk sealed tube (15 mL) containing a stirring bar was charged with **26** substrate (0.1 mmol, 1.0 equiv), NIS (0.2 mmol, 2.0 equiv), and MeNO₂ (1.5 mL) under air atmosphere. Then, the reaction mixture was stirred at room temperature for 30 min. After completion (monitored by TLC), the solvent was concentrated under reduced pressure. The crude product was purified by flash silica gel column chromatography (PE:EA=15:1-10:1) to afford the desired products.^[3]



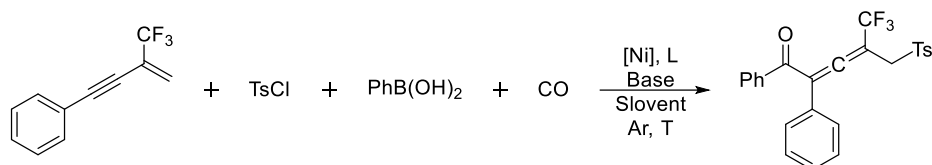
The oven-dried Schlenk flask containing a stirring bar was charged with **54** substrate (0.1 mmol, 1.0 equiv), Pd(OAc)₂ (2.0 mmol%), PPh₃ (2.0 mmol%) and CuI (5.0 mmol%). The mixture was evacuated and back-filled with Ar for 3 times. Dry Et₃N was added under a stream of argon, and 2-methyl-3-butyn-2-ol (1.2 equiv) was added carefully at room temperature. Then, the reaction mixture was stirred and heated to 50 °C under argon atmosphere. After completion (monitored by TLC), the reaction was cooled to room temperature and diluted with ethyl acetate and washed with brine. The organic layer was dried over anhydrous Na₂SO₄ and filtrated. After the solvent was concentrated under reduced pressure, the crude product was purified by flash silica gel column chromatography (PE:EA=5:1-1:1) to afford the desired products.^[4]

2.5.2 Utilization of another type of radical precursor



The oven-dried Schlenk sealed tube (15 mL) containing a stirring bar was charged with 1,3-enyne substrates (0.1 mmol, 1.0 equiv), arylboronic acids (0.25 mmol, 2.5 equiv), ((iodomethyl)sulfonyl)benzene (0.25 mmol, 2.5 equiv), NiBr₂•DME (12 mol%), 5,5'-Bis(trifluoromethyl)-2,2'-bipyridine (12 mol%), K₃PO₄ (0.3 mmol, 3.0 equiv) and 1,4-dioxane (0.5 mL) under argon atmosphere. Then the tube was placed into a preheated oil bath at 80 °C with stirring for 24 h. Upon completion of the reaction, the crude reaction mixture was diluted with DCM, and filtrated. After the solvent was concentrated under reduced pressure, the crude ¹H NMR spectrum was taken using CH₂Br₂ as internal standard. The resulting residue was purified by flash silica gel column chromatography (PE:EA=20:1-10:1) to give the desired products.

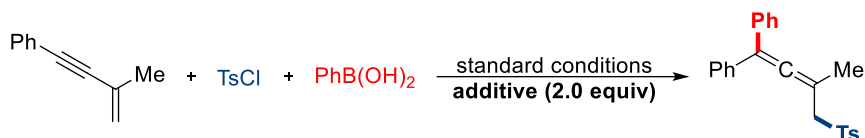
2.5.3 Utilization of CO



The oven-dried Schlenk sealed tube (15 mL) containing a stirring bar was charged with 1,3-enyne substrates (0.1 mmol, 1.0 equiv), arylboronic acids (0.25 mmol, 2.5 equiv), sulfonyl chlorides (0.25 mmol, 2.5 equiv), NiBr₂•DME (12 mol%), 5,5'-Bis(trifluoromethyl)-2,2'-bipyridine (12 mol%), K₃PO₄ (0.3 mmol, 3.0 equiv) and 1,4-dioxane (0.5 mL) under argon atmosphere. The mixture was evacuated and back-filled with CO (1atm) for 3 times. Then the tube was placed into a preheated oil bath at 80 °C with stirring for 24 h. Upon completion of the reaction, the crude reaction mixture was diluted with DCM, and filtrated. After the solvent was concentrated under reduced pressure, the crude ¹H NMR spectrum was taken using CH₂Br₂ as internal standard. The resulting residue was purified by preparative thin layer chromatography (PE:EA=20:1-10:1) to give the desired products.

2.6 Mechanistic Studies

2.6.1 Radical inhibition experiments

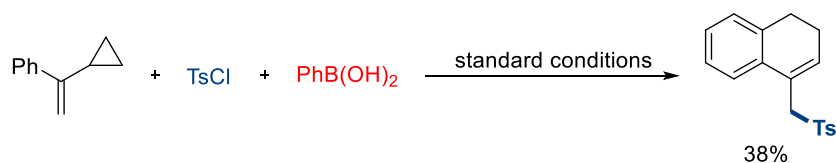


The oven-dried Schlenk sealed tube (15 mL) containing a stirring bar was charged with **TEMPO** (0.2 mmol, 2.0 equiv) 1,3-enyne substrates (0.1 mmol, 1.0 equiv), arylboronic acids (0.25 mmol, 2.5 equiv), sulfonyl chlorides (0.25 mmol, 2.5 equiv), NiBr₂•DME (12 mol%), 5,5'-Bis(trifluoromethyl)-2,2'-bipyridine (12 mol%), K₃PO₄ (0.3 mmol, 3.0 equiv) and 1,4-dioxane (0.5 mL) under argon atmosphere. Then the tube was placed into a preheated oil bath at 80 °C with stirring for 24 h. Upon completion of the reaction, the crude reaction mixture was diluted with DCM, and filtrated. After the solvent was concentrated under reduced pressure, the crude ¹H NMR spectrum was taken using CH₂Br₂ as internal standard. No expected product was observed.

The oven-dried Schlenk sealed tube (15 mL) containing a stirring bar was charged with **1,1-diphenylethylene** (0.2 mmol, 2.0 equiv) 1,3-enyne substrates (0.1 mmol, 1.0 equiv), arylboronic acids (0.25 mmol, 2.5 equiv), sulfonyl chlorides (0.25 mmol, 2.5 equiv), NiBr₂•DME (12 mol%), 5,5'-Bis(trifluoromethyl)-2,2'-bipyridine (12 mol%), K₃PO₄ (0.3 mmol, 3.0 equiv) and 1,4-dioxane (0.5 mL) under argon atmosphere. Then the tube was placed into a preheated oil bath at 80 °C with stirring for 24 h. Upon completion of the reaction, the crude reaction mixture was diluted with DCM, and filtrated. After the solvent was concentrated under reduced pressure, the crude ¹H NMR spectrum was taken using CH₂Br₂ as internal standard. The resulting residue was purified by preparative thin layer chromatography to give the desired products in 20% yield. Fortunately, **78** product was detected in 30% yield.

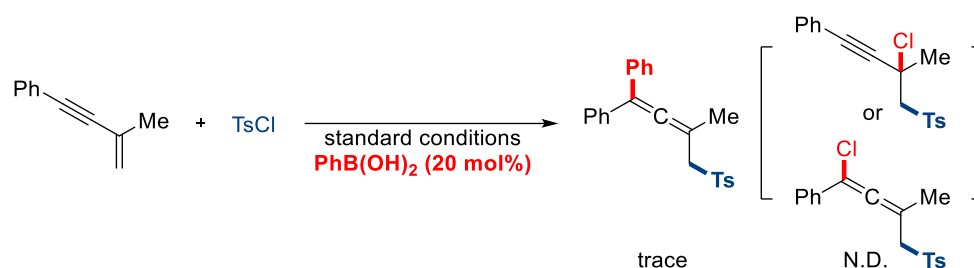
The oven-dried Schlenk sealed tube (15 mL) containing a stirring bar was charged with 1,3-enyne substrates (0.1 mmol, 1.0 equiv), arylboronic acids (0.25 mmol, 2.5 equiv), sulfonyl chlorides (0.25 mmol, 2.5 equiv), NiBr₂•DME (12 mol%), 5,5'-Bis(trifluoromethyl)-2,2'-bipyridine (12 mol%), K₃PO₄ (0.3 mmol, 3.0 equiv) and 1,4-dioxane (0.5 mL) under **air** atmosphere. Then the tube was placed into a preheated oil bath at 80 °C with stirring for 24 h. Upon completion of the reaction, the crude reaction mixture was diluted with DCM, and filtrated. After the solvent was concentrated under reduced pressure, the crude ¹H NMR spectrum was taken using CH₂Br₂ as internal standard. No expected product was observed.

2.6.2 Radical clock experiment



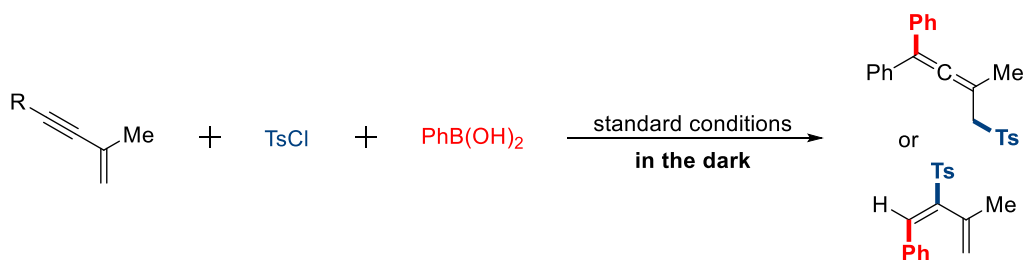
The oven-dried Schlenk sealed tube (15 mL) containing a stirring bar was charged with (1-cyclopropylvinyl)benzene (0.1 mmol, 1.0 equiv), arylboronic acids (0.25 mmol, 2.5 equiv), sulfonyl chlorides (0.25 mmol, 2.5 equiv), $\text{NiBr}_2 \cdot \text{DME}$ (12 mol%), 5,5'-Bis(trifluoromethyl)-2,2'-bipyridine (12 mol%), K_3PO_4 (0.3 mmol, 3.0 equiv) and 1,4-dioxane (0.5 mL) under argon atmosphere. Then the tube was placed into a preheated oil bath at 80 °C with stirring for 24 h. Upon completion of the reaction, the crude reaction mixture was diluted with DCM, and filtrated. After the solvent was concentrated under reduced pressure, the crude ^1H NMR spectrum was taken using CH_2Br_2 as internal standard. The resulting residue was purified by preparative thin layer chromatography to give the **79** product in 38% yield.

2.6.3 Probe for putative intermediates



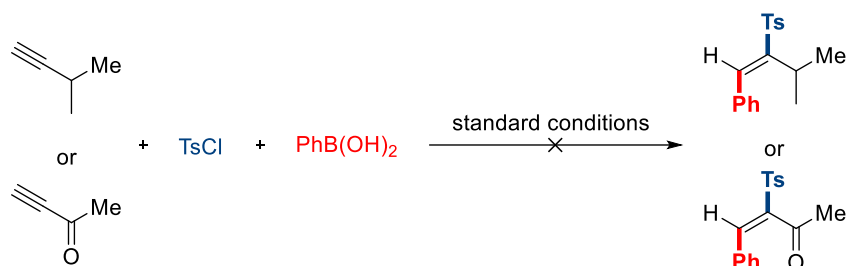
The oven-dried Schlenk sealed tube (15 mL) containing a stirring bar was charged with 1,3-enyne substrates (0.1 mmol, 1.0 equiv), **arylboronic acids (20 mol%)**, sulfonyl chlorides (0.25 mmol, 2.5 equiv), $\text{NiBr}_2 \cdot \text{DME}$ (12 mol%), 5,5'-Bis(trifluoromethyl)-2,2'-bipyridine (12 mol%), K_3PO_4 (0.3 mmol, 3.0 equiv) and 1,4-dioxane (0.5 mL) under argon atmosphere. Then the tube was placed into a preheated oil bath at 80 °C with stirring for 24 h. Upon completion of the reaction, the crude reaction mixture was diluted with DCM, and filtrated. After the solvent was concentrated under reduced pressure, the crude ^1H NMR spectrum was taken using CH_2Br_2 as internal standard. The resulting residue was purified by preparative thin layer chromatography to give the desired products in 5% yield.

2.6.4 Control experiments in the dark:



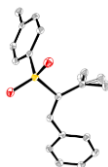
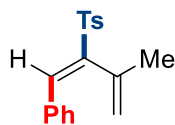
The oven-dried Schlenk sealed tube (15 mL) containing a stirring bar was charged with 1,3-enyne substrates (0.1 mmol, 1.0 equiv), arylboronic acids (0.25 mmol, 2.5 equiv), sulfonyl chlorides (0.25 mmol, 2.5 equiv), NiBr₂·DME (12 mol%), 5,5'-Bis(trifluoromethyl)-2,2'-bipyridine (12 mol%), K₃PO₄ (0.3 mmol, 3.0 equiv) and 1,4-dioxane (0.5 mL) under argon atmosphere. Then the tube was placed into a preheated oil bath at 80 °C with stirring for 24 h **in the dark**. Upon completion of the reaction, the crude reaction mixture was diluted with DCM, and filtrated. After the solvent was concentrated under reduced pressure, the crude ¹H NMR spectrum was taken using CH₂Br₂ as internal standard. The resulting residue was purified by preparative thin layer chromatography to give the desired products.

2.6.5 Control experiments with other terminal alkynes:



The oven-dried Schlenk sealed tube (15 mL) containing a stirring bar was charged with terminal alkynes substrates (0.1 mmol, 1.0 equiv), arylboronic acids (0.25 mmol, 2.5 equiv), sulfonyl chlorides (0.25 mmol, 2.5 equiv), NiBr₂·DME (12 mol%), 5,5'-Bis(trifluoromethyl)-2,2'-bipyridine (12 mol%), K₃PO₄ (0.3 mmol, 3.0 equiv) and 1,4-dioxane (0.5 mL) under argon atmosphere. Then the tube was placed into a preheated oil bath at 80 °C with stirring for 24 h. Upon completion of the reaction, the crude reaction mixture was diluted with DCM, and filtrated. The solvent was concentrated under reduced pressure and no expected product was observed.

3. X-Ray Crystallographic Spectrum



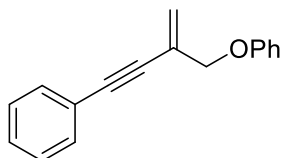
The CCDC number of this compound is **2344342**.

Table 1. Crystal data and structure refinement for **50**.

Identification code	50
Empirical formula	C ₁₈ H ₁₈ O ₂ S
Formula weight	298.38
Temperature/K	150.00(10)
Crystal system	Triclinic
Space group	P-1
a/Å	9.12295(12)
b/Å	9.29509(14)
c/Å	10.32066(17)
α/°	66.4462(15)
β/°	78.6780(13)
γ/°	73.4692(12)
Volume/Å ³	765.70(2)
Z	2
ρ _{calc} /cm ³	1.294
μ/mm ⁻¹	1.883
F(000)	316.0
Crystal size/mm ³	0.12 × 0.07 × 0.06
Radiation	Cu Kα (λ = 1.54184)
Theta range for data collection/°	9.39 to 133.18
Index ranges	-10 ≤ h ≤ 10, -11 ≤ k ≤ 11, -12 ≤ l ≤ 12
Reflections collected	12187
Independent reflections	2674 [R _{int} = 0.0281, R _{sigma} = 0.0175]
Data/restraints/parameters	2674/61/212
Goodness-of-fit on F ²	1.052
Final R indexes [I ≥ 2σ(I)]	R1 = 0.0313, wR2 = 0.0855
Final R indexes [all data]	R1 = 0.0317, wR2 = 0.0859
Largest diff. peak/hole / e Å ⁻³	0.32/-0.33

4. Characterization of unknown substrates and products

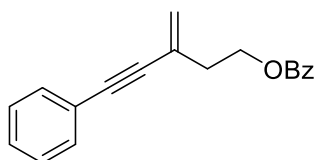
4.1 Characterization of unknown substrates



(2-methylene-4-phenylbut-3-yn-1-yl)oxybenzene

$^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.41 – 7.35 (m, 2H), 7.27 – 7.18 (m, 5H), 6.93 – 6.85 (m, 3H), 5.61 (q, $J = 1.7$ Hz, 1H), 5.59 (q, $J = 1.5$ Hz, 1H), 4.58 – 4.52 (m, 2H).

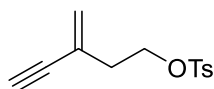
$^{13}\text{C NMR}$ (101 MHz, CDCl_3): δ 158.2, 131.6, 129.4, 128.5, 128.3, 127.0, 122.7, 122.1, 121.1, 114.9, 90.7, 86.8, 69.4.



3-methylene-5-phenylpent-4-yn-1-yl benzoate

$^1\text{H NMR}$ (400 MHz, CDCl_3): δ 8.08 – 8.03 (m, 2H), 7.57 – 7.51 (m, 1H), 7.45 – 7.38 (m, 4H), 7.34 – 7.27 (m, 3H), 5.56 (d, $J = 1.6$ Hz, 1H), 5.45 (d, $J = 1.7$ Hz, 1H), 4.57 (t, $J = 6.5$ Hz, 2H), 2.72 (t, $J = 6.5$ Hz, 2H).

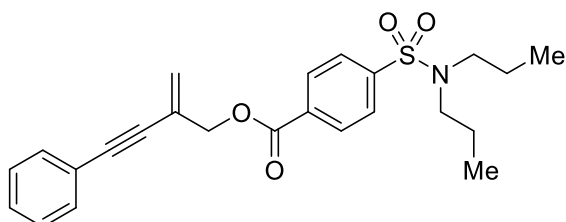
$^{13}\text{C NMR}$ (101 MHz, CDCl_3): δ 166.4, 132.8, 131.5, 130.1, 129.5, 128.3, 128.2, 128.2, 127.6, 123.4, 122.8, 89.8, 88.8, 63.1, 36.5.



3-methylenepent-4-yn-1-yl 4-methylbenzenesulfonate

$^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.79 (d, $J = 8.3$ Hz, 2H), 7.34 (d, $J = 8.1$ Hz, 2H), 5.48 (s, 1H), 5.35 (s, 1H), 4.20 (t, $J = 6.5$ Hz, 2H), 2.83 (s, 1H), 2.49 (t, $J = 6.6$ Hz, 2H), 2.45 (s, 3H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3): δ 144.7, 133.0, 129.7, 127.9, 125.8, 125.0, 82.3, 78.1, 67.8, 36.3, 21.6.

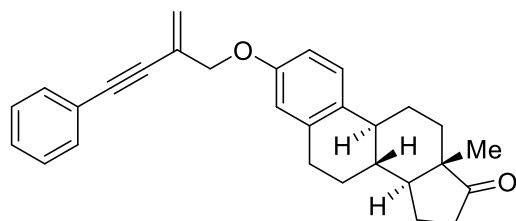


2-methylene-4-phenylbut-3-yn-1-yl 4-(N,N-dipropylsulfamoyl)benzoate

$^1\text{H NMR}$ (400 MHz, CDCl_3): δ 8.23 (d, $J = 8.5$ Hz, 2H), 7.89 (d, $J = 8.5$ Hz, 2H), 7.47 – 7.40 (m, 2H), 7.36 – 7.29 (m, 3H), 5.72 – 5.69 (m, 1H), 5.68 – 5.65 (m, 1H), 4.96 (s, 2H), 3.14 – 3.06 (m, 4H), 1.60 – 1.48 (m, 4H), 0.87 (t, $J = 7.4$ Hz, 6H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3): δ 164.6, 144.3, 133.1, 131.6, 130.3, 128.6, 128.3, 127.0, 126.1, 123.2,

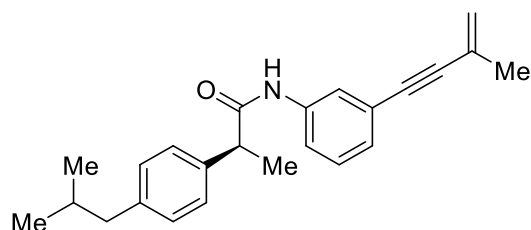
122.4, 90.9, 86.4, 66.6, 49.8, 21.9, 11.1.



(8R,9S,13S,14S)-13-methyl-3-((2-methylene-4-phenylbut-3-yn-1-yl)oxy)-6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta[a]phenanthren-17-one

¹H NMR (400 MHz, CDCl₃): δ 7.50 – 7.42 (m, 2H), 7.36 – 7.28 (m, 3H), 7.21 (d, J = 8.6 Hz, 1H), 6.78 (dd, J = 8.9, 2.7 Hz, 1H), 6.71 (d, J = 2.7 Hz, 1H), 5.70 (t, J = 1.7 Hz, 1H), 5.66 (t, J = 1.6 Hz, 1H), 4.60 (d, J = 1.8 Hz, 2H), 2.94 – 2.85 (m, 2H), 2.55 – 2.44 (m, 1H), 2.43 – 2.35 (m, 1H), 2.25 (td, J = 10.7, 3.9 Hz, 1H), 2.16 – 1.93 (m, 4H), 1.62 – 1.42 (m, 6H), 0.90 (s, 3H).

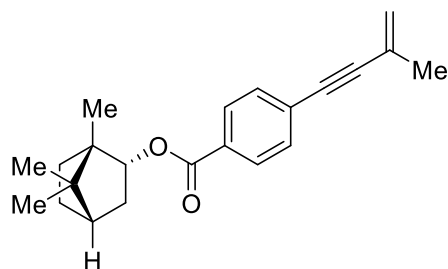
¹³C NMR (101 MHz, CDCl₃): δ 156.2, 137.7, 132.4, 131.6, 128.4, 128.3, 127.0, 126.3, 122.6, 121.9, 114.8, 112.4, 90.6, 86.8, 69.4, 50.3, 47.9, 43.9, 38.2, 35.8, 31.5, 29.6, 26.4, 25.8, 21.5, 13.8.



(S)-2-(4-isobutylphenyl)-N-(3-(3-methylbut-3-en-1-yn-1-yl)phenyl)propanamide

¹H NMR (400 MHz, CDCl₃): δ 7.52 (t, J = 1.9 Hz, 1H), 7.40 (dt, J = 8.2, 1.6 Hz, 1H), 7.24 (d, J = 7.9 Hz, 2H), 7.21 – 7.11 (m, 5H), 5.38 – 5.34 (m, 1H), 5.30 – 5.25 (m, 1H), 3.68 (q, J = 7.1 Hz, 1H), 2.47 (d, J = 7.2 Hz, 2H), 1.95 (s, 3H), 1.90 – 1.81 (m, 1H), 1.57 (d, J = 7.2 Hz, 3H), 0.91 (d, J = 6.6 Hz, 6H).

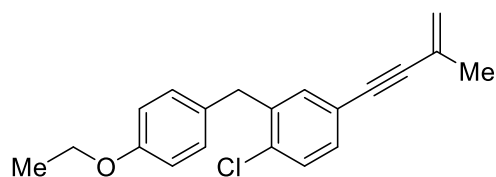
¹³C NMR (101 MHz, CDCl₃): δ 172.7, 141.1, 137.8, 137.8, 129.8, 128.8, 127.3, 127.2, 126.6, 123.8, 122.5, 122.1, 119.5, 90.7, 87.8, 47.6, 45.0, 30.1, 23.4, 22.3, 18.4.



(1S,2R,4S)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl 4-(3-methylbut-3-en-1-yn-1-yl)benzoate

¹H NMR (400 MHz, CDCl₃): δ 8.00 (d, J = 8.4 Hz, 2H), 7.50 (d, J = 8.4 Hz, 2H), 5.45 (s, 1H), 5.36 (s, 1H), 5.15 – 5.07 (m, 1H), 2.55 – 2.41 (m, 1H), 2.18 – 2.07 (m, 1H), 2.01 (s, 3H), 1.86 – 1.77 (m, 1H), 1.74 (t, J = 4.5 Hz, 1H), 1.46 – 1.36 (m, 1H), 1.36 – 1.27 (m, 1H), 1.12 (dd, J = 13.8, 3.5 Hz, 1H), 0.97 (s, 3H), 0.91 (s, 6H).

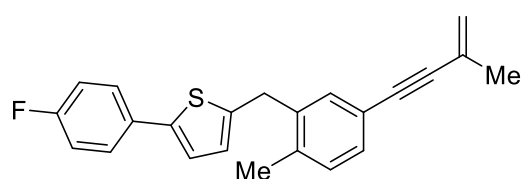
¹³C NMR (101 MHz, CDCl₃): δ 166.2, 131.4, 130.0, 129.3, 127.8, 126.5, 123.0, 93.3, 87.6, 80.7, 49.1, 47.9, 44.9, 36.8, 28.1, 27.4, 23.3, 19.7, 18.9, 13.6.



1-chloro-2-(4-ethoxybenzyl)-4-(3-methylbut-3-en-1-yn-1-yl)benzene

¹H NMR (400 MHz, CDCl₃): δ 7.32 – 7.27 (m, 1H), 7.25 – 7.19 (m, 2H), 7.09 (d, *J* = 8.7 Hz, 2H), 6.82 (d, *J* = 8.6 Hz, 2H), 5.39 – 5.35 (m, 1H), 5.30 – 5.27 (m, 1H), 4.04 – 3.96 (m, 4H), 1.95 (s, 3H), 1.39 (t, *J* = 7.0 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃): δ 157.5, 139.3, 134.2, 133.8, 130.8, 130.6, 129.9, 129.5, 126.6, 122.3, 122.0, 114.5, 91.2, 87.4, 63.4, 38.2, 23.4, 14.9.



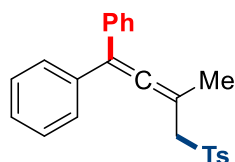
2-(4-fluorophenyl)-5-(2-methyl-5-(3-methylbut-3-en-1-yn-1-yl)benzyl)thiophene

¹H NMR (400 MHz, CDCl₃): δ 7.48 – 7.43 (m, 2H), 7.31 (s, 1H), 7.26 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.11 (d, *J* = 7.8 Hz, 1H), 7.04 – 6.98 (m, 3H), 6.65 (d, *J* = 3.6 Hz, 1H), 5.39 – 5.35 (m, 1H), 5.28 – 5.25 (m, 1H), 4.07 (s, 2H), 2.30 (s, 3H), 1.97 (s, 3H).

¹³C NMR (101 MHz, CDCl₃): δ 162.0 (d, *J* = 247.7 Hz), 142.8, 141.6, 138.2, 136.8, 132.5, 130.7 (d, *J* = 3.4 Hz), 130.5, 130.1, 127.1 (d, *J* = 7.9 Hz), 126.9, 126.0, 122.6, 121.7, 121.0, 115.7 (d, *J* = 22.0 Hz), 90.1, 88.4, 33.9, 23.5, 19.4.

¹⁹F NMR (376 MHz, CDCl₃): δ -115.08.

4.2 Characterization of products



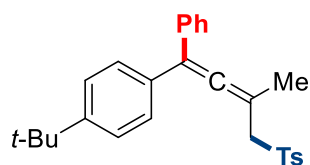
(3-methyl-4-tosylbuta-1,2-diene-1,1-diyl)dibenzene (4)

Colorless oil, 27.5 mg, 73% yield. (PE/EtOAc = 20/1)

¹H NMR (400 MHz, CDCl₃): δ 7.67 (d, *J* = 8.4 Hz, 2H), 7.30 – 7.23 (m, 6H), 7.14 – 7.04 (m, 4H), 3.92 (s, 2H), 2.32 (s, 3H), 2.06 (s, 3H).

¹³C NMR (101 MHz, CDCl₃): δ 207.5, 144.3, 136.1, 135.3, 129.6, 128.5, 128.2, 128.1, 127.4, 110.1, 92.8, 61.4, 21.6, 19.2.

HRMS (m/z, ESI-TOF): Calcd for C₂₄H₂₂SO₂Na⁺ [M+Na⁺] 397.1233, found 397.1241.



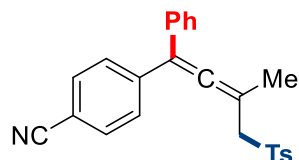
1-(tert-butyl)-4-(3-methyl-1-phenyl-4-tosylbuta-1,2-dien-1-yl)benzene (5)

Colorless oil, 30.5mg, **71%** yield. (PE/EtOAc = 20/1)

¹H NMR (400 MHz, CDCl₃): δ 7.69 (d, *J* = 8.0 Hz, 2H), 7.30 (d, *J* = 8.2 Hz, 2H), 7.28 – 7.22 (m, 3H), 7.15 – 7.02 (m, 6H), 3.91 (s, 2H), 2.34 (s, 3H), 2.05 (s, 3H), 1.33 (s, 9H).

¹³C NMR (101 MHz, CDCl₃): δ 207.5, 150.4, 144.3, 136.3, 135.5, 133.0, 129.6, 128.7, 128.2, 128.1, 127.3, 125.1, 109.9, 92.6, 61.6, 34.5, 31.3, 21.6, 19.3.

HRMS (m/z, ESI-TOF): Calcd for C₂₈H₃₀SO₂Na⁺ [M+Na⁺] 453.1859, found 453.1852.



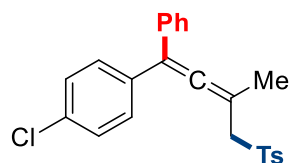
4-(3-methyl-1-phenyl-4-tosylbuta-1,2-dien-1-yl)benzonitrile (6)

Colorless oil, 29.5mg, **74%** yield. (PE/EtOAc = 10/1)

¹H NMR (400 MHz, CDCl₃): δ 7.70 (d, *J* = 7.9 Hz, 2H), 7.55 (d, *J* = 8.1 Hz, 2H), 7.37 – 7.24 (m, 5H), 7.20 – 7.05 (m, 4H), 3.93 (d, *J* = 4.9 Hz, 2H), 2.36 (s, 3H), 2.06 (s, 3H).

¹³C NMR (101 MHz, CDCl₃): δ 207.9, 144.5, 141.2, 135.4, 134.8, 131.9, 129.6, 128.9, 128.5, 128.4, 127.9, 127.8, 118.7, 110.6, 109.2, 93.9, 60.8, 21.5, 19.0.

HRMS (m/z, ESI-TOF): Calcd for C₂₅H₂₁NSO₂Na⁺ [M+Na⁺] 422.1185, found 422.1184.



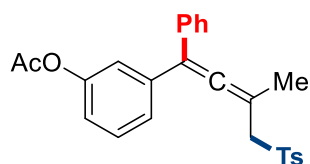
1-chloro-4-(3-methyl-1-phenyl-4-tosylbuta-1,2-dien-1-yl)benzene (7)

Colorless oil, 28.5mg, **70%** yield. (PE/EtOAc = 20/1)

¹H NMR (400 MHz, CDCl₃): δ 7.67 (d, *J* = 7.9 Hz, 2H), 7.33 – 7.25 (m, 3H), 7.22 (d, *J* = 8.4 Hz, 2H), 7.14 – 7.07 (m, 4H), 7.04 (d, *J* = 8.2 Hz, 2H), 3.98 – 3.86 (m, 2H), 2.34 (s, 3H), 2.05 (s, 3H).

¹³C NMR (101 MHz, CDCl₃): δ 207.4, 144.5, 135.7, 135.3, 134.7, 133.1, 129.8, 129.6, 128.4, 128.3, 128.3, 128.0, 127.6, 109.2, 93.2, 61.3, 21.6, 19.1.

HRMS (m/z, ESI-TOF): Calcd for C₂₄H₂₁ClSO₂Na⁺ [M+Na⁺] 431.0843, found 431.0848.



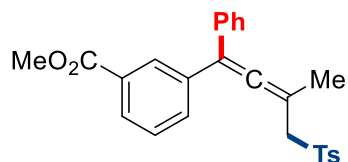
3-(3-methyl-1-phenyl-4-tosylbuta-1,2-dien-1-yl)phenyl acetate (8)

Colorless oil, 29.7mg, **69%** yield. (PE/EtOAc = 20/1)

¹H NMR (400 MHz, CDCl₃): δ 7.66 (d, *J* = 8.0 Hz, 2H), 7.31 – 7.23 (m, 4H), 7.15 – 7.05 (m, 4H), 6.99 (dt, *J* = 7.8, 2.2 Hz, 2H), 6.91 (t, *J* = 2.0 Hz, 1H), 3.92 (s, 2H), 2.31 (s, 3H), 2.26 (s, 3H), 2.04 (s, 3H).

¹³C NMR (101 MHz, CDCl₃): δ 207.4, 169.2, 150.5, 144.3, 137.8, 135.6, 135.2, 129.5, 129.0, 128.5, 128.2, 127.9, 127.4, 125.9, 121.5, 120.6, 109.4, 93.1, 61.2, 21.5, 21.0, 19.1.

HRMS (m/z, ESI-TOF): Calcd for C₂₆H₂₄SO₄Na⁺ [M+Na⁺] 455.1288, found 455.1288.



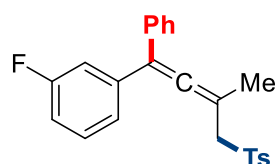
methyl 3-(3-methyl-1-phenyl-4-tosylbuta-1,2-dien-1-yl)benzoate (9)

Colorless oil, 32.4mg, 75% yield. (PE/EtOAc = 20/1)

¹H NMR (400 MHz, CDCl₃): δ 7.95 (d, *J* = 6.4 Hz, 1H), 7.83 (s, 1H), 7.67 (d, *J* = 7.9 Hz, 2H), 7.40 – 7.32 (m, 2H), 7.32 – 7.22 (m, 3H), 7.15 – 7.01 (m, 4H), 3.95 (s, 2H), 3.89 (s, 3H), 2.28 (s, 3H), 2.06 (s, 3H).

¹³C NMR (101 MHz, CDCl₃): δ 207.5, 166.7, 144.3, 136.7, 135.6, 135.2, 133.0, 130.2, 129.5, 129.4, 128.4, 128.3, 127.9, 127.5, 109.4, 93.2, 61.2, 52.0, 21.5, 19.1.

HRMS (m/z, ESI-TOF): Calcd for C₂₆H₂₄SO₄Na⁺ [M+Na⁺] 455.1288, found 455.1289.



1-fluoro-3-(3-methyl-1-phenyl-4-tosylbuta-1,2-dien-1-yl)benzene (10)

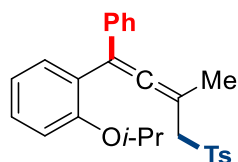
Colorless oil, 30.0mg, 76% yield. (PE/EtOAc = 20/1)

¹H NMR (400 MHz, CDCl₃): δ 7.68 (d, *J* = 7.9 Hz, 2H), 7.33 – 7.17 (m, 4H), 7.16 – 7.05 (m, 4H), 7.00 – 6.87 (m, 2H), 6.80 (d, *J* = 10.0 Hz, 1H), 3.93 (d, *J* = 2.7 Hz, 2H), 2.32 (s, 3H), 2.06 (s, 3H).

¹³C NMR (101 MHz, CDCl₃): δ 207.4, 162.6 (d, *J* = 246.5 Hz), 144.5, 138.6 (d, *J* = 7.5 Hz), 135.4 (d, *J* = 32.2 Hz), 129.6, 129.6, 129.6, 128.5, 128.3, 128.0, 127.6, 124.2 (d, *J* = 2.9 Hz), 115.3 (d, *J* = 22.2 Hz), 114.2 (d, *J* = 21.4 Hz), 109.3 (d, *J* = 2.4 Hz), 93.3, 61.2, 21.5, 19.1.

¹⁹F NMR (376 MHz, CDCl₃): δ -112.99.

HRMS (m/z, ESI-TOF): Calcd for C₂₄H₂₁FSO₂Na⁺ [M+Na⁺] 415.1138, found 415.1154.



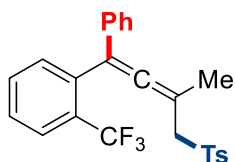
1-isopropoxy-2-(3-methyl-1-phenyl-4-tosylbuta-1,2-dien-1-yl)benzene (11)

Colorless oil, 24.0mg, 55% yield. (PE/EtOAc = 20/1)

¹H NMR (400 MHz, CDCl₃): δ 7.65 (d, *J* = 8.1 Hz, 2H), 7.25 (td, *J* = 7.6, 7.1, 1.9 Hz, 1H), 7.19 – 7.13 (m, 3H), 7.02 (d, *J* = 8.1 Hz, 2H), 6.99 – 6.91 (m, 3H), 6.86 (dd, *J* = 8.0, 4.9 Hz, 2H), 4.43 – 4.33 (m, 1H), 3.97 (d, *J* = 13.9 Hz, 1H), 3.87 (d, *J* = 13.9 Hz, 1H), 2.29 (s, 3H), 2.03 (s, 3H), 1.06 (dd, *J* = 6.0, 2.3 Hz, 6H).

¹³C NMR (101 MHz, CDCl₃): δ 207.4, 155.3, 144.1, 136.9, 135.2, 131.4, 129.5, 128.7, 128.0, 127.8, 127.2, 126.6, 126.2, 120.2, 113.8, 106.1, 91.5, 70.1, 61.6, 21.9, 21.8, 21.6, 18.8.

HRMS (m/z, ESI-TOF): Calcd for C₂₇H₂₈SO₃Na⁺ [M+Na⁺] 455.1651, found 455.1663.



1-(3-methyl-1-phenyl-4-tosylbuta-1,2-dien-1-yl)-2-(trifluoromethyl)benzene (12)

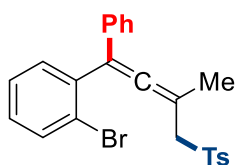
Colorless oil, 19.7mg, **45%** yield. (PE/EtOAc = 20/1)

¹H NMR (400 MHz, CDCl₃): δ 7.69 (d, *J* = 7.6 Hz, 1H), 7.64 (d, *J* = 8.2 Hz, 2H), 7.53 – 7.41 (m, 2H), 7.22 – 7.12 (m, 4H), 7.05 (d, *J* = 7.9 Hz, 2H), 6.91 – 6.81 (m, 2H), 3.95 (d, *J* = 13.9 Hz, 1H), 3.83 (d, *J* = 13.9 Hz, 1H), 2.30 (s, 3H), 2.01 (s, 3H).

¹³C NMR (101 MHz, CDCl₃): δ 205.4, 144.3, 136.1, 135.1, 134.6 (q, *J* = 2.0 Hz), 132.2, 131.6, 129.5, 129.0 (q, *J* = 30.3 Hz), 128.1, 128.1, 127.7, 127.1, 126.9, 126.2 (q, *J* = 5.1 Hz), 123.8 (q, *J* = 275.2 Hz), 106.0, 93.9, 61.1, 21.6, 18.5.

¹⁹F NMR (376 MHz, CDCl₃): δ -59.29.

HRMS (m/z, ESI-TOF): Calcd for C₂₅H₂₁F₃SO₂Na⁺ [M+Na⁺] 465.1107, found 465.1120.



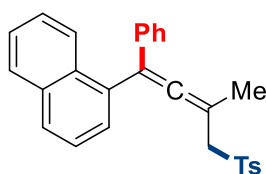
1-bromo-2-(3-methyl-1-phenyl-4-tosylbuta-1,2-dien-1-yl)benzene (13)

Colorless oil, 27.6mg, **61%** yield. (PE/EtOAc = 20/1)

¹H NMR (400 MHz, CDCl₃): δ 7.65 (d, *J* = 7.9 Hz, 2H), 7.56 (d, *J* = 7.9 Hz, 1H), 7.30 – 7.23 (m, 1H), 7.23 – 7.14 (m, 4H), 7.10 (d, *J* = 7.4 Hz, 1H), 7.04 (d, *J* = 8.0 Hz, 2H), 6.96 – 6.86 (m, 2H), 4.02 (d, *J* = 13.9 Hz, 1H), 3.88 (d, *J* = 13.9 Hz, 1H), 2.29 (s, 3H), 2.07 (s, 3H).

¹³C NMR (101 MHz, CDCl₃): δ 206.2, 144.2, 136.8, 135.3, 134.9, 132.8, 131.6, 129.5, 129.0, 128.2, 128.0, 127.2, 127.1, 126.9, 124.0, 108.3, 93.7, 60.9, 21.6, 18.4.

HRMS (m/z, ESI-TOF): Calcd for C₂₄H₂₁BrSO₂Na⁺ [M+Na⁺] 475.0338, found 475.0358.



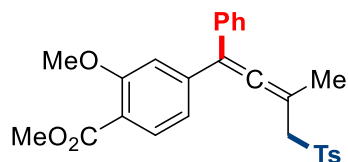
1-(3-methyl-1-phenyl-4-tosylbuta-1,2-dien-1-yl)naphthalene (14)

Colorless oil, 22.4mg, **53%** yield. (PE/EtOAc = 20/1)

¹H NMR (400 MHz, CDCl₃): δ 7.83 (dd, *J* = 11.7, 8.2 Hz, 2H), 7.60 (d, *J* = 8.5 Hz, 1H), 7.54 (d, *J* = 8.3 Hz, 2H), 7.47 – 7.39 (m, 2H), 7.33 – 7.27 (m, 1H), 7.23 (dd, *J* = 7.2, 1.3 Hz, 1H), 7.19 – 7.11 (m, 3H), 7.01 – 6.93 (m, 2H), 6.80 (d, *J* = 8.0 Hz, 2H), 3.98 – 3.85 (m, 2H), 2.15 (s, 3H), 2.08 (s, 3H).

¹³C NMR (101 MHz, CDCl₃): δ 207.0, 144.1, 136.4, 134.9, 133.6, 133.5, 131.7, 129.2, 128.3, 128.2, 128.0, 127.9, 127.5, 127.1, 127.1, 125.9, 125.8, 125.8, 125.4, 107.3, 92.5, 61.5, 21.5, 18.8.

HRMS (m/z, ESI-TOF): Calcd for C₂₈H₂₄SO₂Na⁺ [M+Na⁺] 447.1389, found 447.1405.



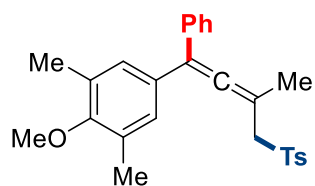
methyl 2-methoxy-4-(3-methyl-1-phenyl-4-tosylbuta-1,2-dien-1-yl)benzoate (15)

Colorless oil, 34.3mg, **74%** yield. (PE/EtOAc = 15/1)

¹H NMR (400 MHz, CDCl₃): δ 7.77 – 7.64 (m, 3H), 7.35 – 7.24 (m, 3H), 7.20 – 7.09 (m, 4H), 6.99 (s, 1H), 6.72 (d, *J* = 8.0 Hz, 1H), 4.02 – 3.81 (m, 8H), 2.34 (s, 3H), 2.05 (s, 3H).

¹³C NMR (101 MHz, CDCl₃): δ 207.7, 166.2, 159.1, 144.5, 141.8, 135.4, 135.4, 131.4, 129.6, 128.4, 128.3, 127.9, 127.6, 120.2, 118.6, 112.2, 109.7, 93.2, 61.0, 56.0, 51.9, 21.4, 19.1.

HRMS (m/z, ESI-TOF): Calcd for C₂₇H₂₆SO₅Na⁺ [M+Na⁺] 485.1393, found 485.1400.



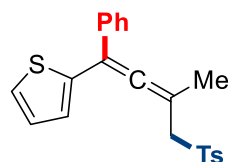
2-methoxy-1,3-dimethyl-5-(3-methyl-1-phenyl-4-tosylbuta-1,2-dien-1-yl)benzene (16)

Colorless oil, 17.3mg, **40%** yield. (PE/EtOAc = 20/1)

¹H NMR (400 MHz, CDCl₃): δ 7.67 (d, *J* = 7.9 Hz, 2H), 7.31 – 7.23 (m, 3H), 7.13 – 7.01 (m, 4H), 6.84 (s, 2H), 3.92 (d, *J* = 3.4 Hz, 2H), 3.73 (s, 3H), 2.31 (s, 3H), 2.25 (s, 6H), 2.03 (s, 3H).

¹³C NMR (101 MHz, CDCl₃): δ 207.4, 156.4, 144.3, 136.4, 135.4, 131.4, 130.6, 129.5, 129.0, 128.6, 128.1, 128.0, 127.2, 109.8, 92.2, 61.6, 59.6, 21.6, 19.4, 16.1.

HRMS (m/z, ESI-TOF): Calcd for C₂₇H₂₈SO₃Na⁺ [M+Na⁺] 455.1651, found 455.1657.



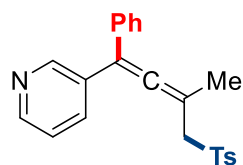
2-(3-methyl-1-phenyl-4-tosylbuta-1,2-dien-1-yl)thiophene (17)

Colorless oil, 18.5mg, **49%** yield. (PE/EtOAc = 10/1)

¹H NMR (400 MHz, CDCl₃): δ 7.67 (d, *J* = 8.1 Hz, 2H), 7.32 – 7.26 (m, 3H), 7.24 – 7.18 (m, 3H), 7.08 (d, *J* = 7.9 Hz, 2H), 6.94 (dd, *J* = 5.1, 3.6 Hz, 1H), 6.79 (dd, *J* = 3.6, 1.2 Hz, 1H), 3.97 – 3.85 (m, 2H), 2.33 (s, 3H), 2.05 (s, 3H).

¹³C NMR (101 MHz, CDCl₃): δ 207.0, 144.4, 139.4, 135.7, 135.3, 129.6, 128.3, 128.2, 128.1, 127.8, 127.3, 126.4, 125.4, 104.9, 93.4, 61.3, 21.6, 19.2.

HRMS (m/z, ESI-TOF): Calcd for C₂₂H₂₀S₂O₂Na⁺ [M+Na⁺] 403.0797, found 403.0802.



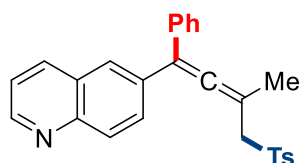
3-(3-methyl-1-phenyl-4-tosylbuta-1,2-dien-1-yl)pyridine (18)

Colorless oil, 23.0mg, **61%** yield. (PE/EtOAc = 5/1)

¹H NMR (400 MHz, CDCl₃): δ 8.52 (dd, *J* = 4.8, 1.6 Hz, 1H), 8.38 (d, *J* = 2.3 Hz, 1H), 7.68 (d, *J* = 8.0 Hz, 2H), 7.47 (dt, *J* = 8.0, 2.0 Hz, 1H), 7.32 – 7.27 (m, 3H), 7.22 (dd, *J* = 7.9, 4.8 Hz, 1H), 7.16 – 7.06 (m, 4H), 3.93 (d, *J* = 1.6 Hz, 2H), 2.33 (s, 3H), 2.06 (s, 3H).

¹³C NMR (101 MHz, CDCl₃): δ 207.5, 149.3, 148.1, 144.5, 135.8, 135.1, 134.9, 132.2, 129.6, 128.4, 128.2, 127.9, 127.7, 123.1, 107.2, 93.7, 61.0, 21.6, 19.1.

HRMS (m/z, ESI-TOF): Calcd for C₂₃H₂₁NSO₂H⁺ [M+H⁺] 376.1366, found 376.1375.



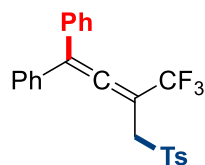
6-(3-methyl-1-phenyl-4-tosylbuta-1,2-dien-1-yl)quinolone (19)

Colorless oil, 32.5mg, **76%** yield. (PE/EtOAc = 3/1)

¹H NMR (400 MHz, CDCl₃): δ 8.89 (dd, *J* = 4.1, 1.9 Hz, 1H), 8.06 (d, *J* = 8.3 Hz, 1H), 8.00 (d, *J* = 8.8 Hz, 1H), 7.67 (d, *J* = 7.9 Hz, 2H), 7.59 (d, *J* = 2.0 Hz, 1H), 7.48 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.42 – 7.36 (m, 1H), 7.35 – 7.29 (m, 3H), 7.23 – 7.14 (m, 2H), 6.98 (d, *J* = 7.9 Hz, 2H), 4.07 – 3.91 (m, 2H), 2.16 (s, 3H), 2.11 (s, 3H).

¹³C NMR (101 MHz, CDCl₃): δ 208.0, 150.3, 147.5, 144.4, 135.9, 135.7, 135.1, 134.4, 130.1, 129.5, 129.2, 128.5, 128.3, 128.0, 127.9, 127.6, 127.0, 121.3, 109.7, 93.3, 61.2, 21.3, 19.1.

HRMS (m/z, ESI-TOF): Calcd for C₃₃H₂₇NSO₃Na⁺ [M+Na⁺] 540.1604, found 540.1616.



(4,4,4-trifluoro-3-(tosylmethyl)buta-1,2-diene-1,1-diyl)dibenzene (20)

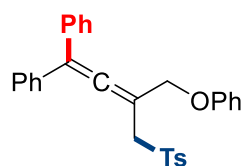
Colorless oil, 21.4mg, **50%** yield. (PE/EtOAc = 20/1)

¹H NMR (400 MHz, CDCl₃): δ 7.60 (d, *J* = 8.0 Hz, 2H), 7.42 – 7.33 (m, 6H), 7.33 – 7.25 (m, 4H), 7.08 (d, *J* = 8.0 Hz, 2H), 4.06 (s, 2H), 2.32 (s, 3H).

¹³C NMR (101 MHz, CDCl₃): δ 208.3 (q, *J* = 3.6 Hz), 144.9, 134.8, 133.4, 129.7, 128.9, 128.6, 128.3, 122.4 (q, *J* = 276.2 Hz), 118.9, 91.6 (q, *J* = 37.2 Hz), 54.1, 21.6.

¹⁹F NMR (376 MHz, CDCl₃): δ -62.35.

HRMS (m/z, ESI-TOF): Calcd for C₂₄H₁₉F₃SO₂Na⁺ [M+Na⁺] 451.0950, found 451.0945.



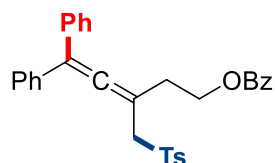
(4-phenoxy-3-(tosylmethyl)buta-1,2-diene-1,1-diyl)dibenzene (21)

Colorless oil, 33.5mg, **72%** yield. (PE/EtOAc = 20/1)

¹H NMR (400 MHz, CDCl₃): δ 7.64 (d, *J* = 8.1 Hz, 2H), 7.31 – 7.22 (m, 6H), 7.17 – 7.08 (m, 6H), 7.00 (d, *J* = 8.0 Hz, 2H), 6.90 – 6.79 (m, 3H), 4.81 (s, 2H), 4.05 (s, 2H), 2.26 (s, 3H).

¹³C NMR (101 MHz, CDCl₃): δ 207.6, 157.8, 144.4, 135.2, 135.0, 129.6, 129.3, 128.7, 128.2, 128.0, 127.7, 121.1, 115.0, 113.1, 94.2, 67.5, 56.6, 21.5.

HRMS (m/z, ESI-TOF): Calcd for C₃₀H₂₆SO₃Na⁺ [M+Na⁺] 489.1495, found 489.1515.



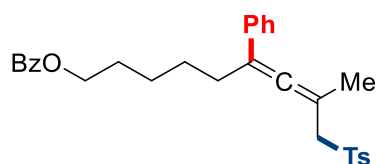
5,5-diphenyl-3-(tosylmethyl)penta-3,4-dien-1-yl benzoate (22)

Colorless oil, 32.8mg, **64%** yield. (PE/EtOAc = 20/1)

¹H NMR (400 MHz, CDCl₃): δ 7.80 (d, *J* = 6.8 Hz, 2H), 7.66 (d, *J* = 8.3 Hz, 2H), 7.48 (t, *J* = 7.4 Hz, 1H), 7.30 (t, *J* = 7.8 Hz, 2H), 7.22 – 7.12 (m, 6H), 7.12 – 7.06 (m, 4H), 7.02 (d, *J* = 8.1 Hz, 2H), 4.52 (t, *J* = 6.0 Hz, 2H), 4.03 (s, 2H), 2.89 (t, *J* = 6.0 Hz, 2H), 2.28 (s, 3H).

¹³C NMR (101 MHz, CDCl₃): δ 206.9, 166.3, 144.4, 135.5, 135.1, 132.6, 129.8, 129.6, 129.4, 128.4, 128.1, 128.1, 127.9, 127.4, 112.3, 94.2, 62.2, 60.1, 31.6, 21.5.

HRMS (m/z, ESI-TOF): Calcd for C₃₂H₂₈SO₄Na⁺ [M+Na⁺] 531.1601, found 531.1598.



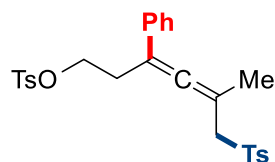
8-methyl-6-phenyl-9-tosylnona-6,7-dien-1-yl benzoate (23)

Colorless oil, 16.9mg, **35%** yield. (PE/EtOAc = 20/1)

¹H NMR (400 MHz, CDCl₃): δ 8.04 (d, *J* = 7.7 Hz, 2H), 7.76 (d, *J* = 7.9 Hz, 2H), 7.60 – 7.51 (m, 1H), 7.44 (t, *J* = 7.6 Hz, 2H), 7.29 – 7.18 (m, 5H), 7.14 (d, *J* = 7.5 Hz, 2H), 4.31 (t, *J* = 6.6 Hz, 2H), 3.83 (s, 2H), 2.39 (s, 3H), 2.34 – 2.24 (m, 1H), 2.24 – 2.14 (m, 1H), 1.95 (s, 3H), 1.82 – 1.71 (m, 2H), 1.49 – 1.39 (m, 4H).

¹³C NMR (101 MHz, CDCl₃): δ 206.4, 166.6, 144.5, 135.9, 135.9, 132.9, 130.3, 129.7, 129.5, 128.3, 128.3, 128.2, 126.9, 126.3, 106.0, 92.1, 64.9, 61.7, 30.0, 28.5, 27.4, 25.8, 21.6, 19.0.

HRMS (m/z, ESI-TOF): Calcd for C₃₀H₃₂SO₄Na⁺ [M+Na⁺] 511.1914, found 511.1917.



5-methyl-3-phenyl-6-tosylhexa-3,4-dien-1-yl 4-methylbenzenesulfonate (24)

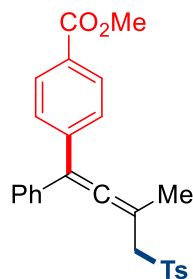
Colorless oil, 12.5mg, **25%** yield. (PE/EtOAc = 15/1)

¹H NMR (400 MHz, CDCl₃): δ 7.76 (d, *J* = 8.0 Hz, 4H), 7.34 – 7.25 (m, 5H), 7.24 – 7.20 (m, 2H), 7.11 – 7.05 (m, 2H), 4.14 – 4.03 (m, 2H), 3.86 – 3.73 (m, 2H), 2.67 – 2.54 (m, 2H), 2.43 (d, *J* = 6.4 Hz, 6H), 1.91 (s, 3H).

¹³C NMR (101 MHz, CDCl₃): δ 206.4, 144.8, 144.8, 135.8, 134.8, 132.8, 129.8, 129.8, 128.4, 128.2,

127.8, 127.3, 126.1, 101.4, 93.9, 68.2, 61.3, 29.7, 21.7, 21.6, 19.0.

HRMS (m/z, ESI-TOF): Calcd for $C_{27}H_{28}S_2O_5Na^+$ [$M+Na^+$] 519.1270, found 519.1261.



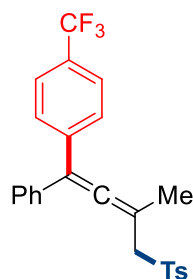
methyl 4-(3-methyl-1-phenyl-4-tosylbuta-1,2-dien-1-yl)benzoate (25)

Colorless oil, 35.9mg, **83%** yield. (PE/EtOAc = 20/1)

1H NMR (400 MHz, $CDCl_3$): δ 7.93 (d, $J = 8.5$ Hz, 2H), 7.68 (d, $J = 8.2$ Hz, 2H), 7.32 – 7.27 (m, 3H), 7.16 (d, $J = 8.4$ Hz, 2H), 7.14 – 7.07 (m, 4H), 3.95 (d, $J = 3.1$ Hz, 2H), 3.92 (s, 3H), 2.33 (s, 3H), 2.07 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 207.8, 166.6, 144.5, 141.0, 135.4, 135.2, 129.6, 129.4, 128.8, 128.3, 128.0, 127.6, 109.6, 93.4, 61.1, 52.0, 21.5, 18.9.

HRMS (m/z, ESI-TOF): Calcd for $C_{26}H_{24}SO_4Na^+$ [$M+Na^+$] 455.1288, found 455.1304.



1-methyl-4-((2-methyl-4-phenyl-4-(trifluoromethyl)phenyl)buta-2,3-dien-1-yl)sulfonylbenzene (26)

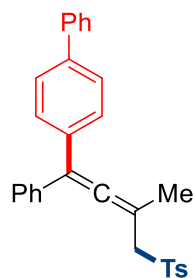
Colorless oil, 28.3mg, **64%** yield. (PE/EtOAc = 20/1)

1H NMR (400 MHz, $CDCl_3$): δ 7.69 (d, $J = 8.0$ Hz, 2H), 7.52 (d, $J = 8.1$ Hz, 2H), 7.34 – 7.27 (m, 3H), 7.24 (d, $J = 7.9$ Hz, 2H), 7.16 – 7.05 (m, 4H), 4.02 – 3.86 (m, 2H), 2.33 (s, 3H), 2.07 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 207.7, 144.6, 140.1 (q, $J = 1.5$ Hz), 135.4, 135.4, 129.7, 129.3 (q, $J = 32.4$ Hz), 128.8, 128.5, 128.4, 128.1, 127.8, 125.1 (q, $J = 3.8$ Hz), 124.7 (q, $J = 272.9$ Hz), 109.3, 93.6, 61.1, 21.5, 19.1.

^{19}F NMR (376 MHz, $CDCl_3$): δ -62.40.

HRMS (m/z, ESI-TOF): Calcd for $C_{25}H_{21}F_3SO_2Na^+$ [$M+Na^+$] 465.1107, found 465.1093.



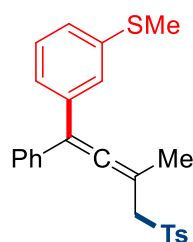
4-(3-methyl-1-phenyl-4-tosylbuta-1,2-dien-1-yl)-1,1'-biphenyl (27)

Colorless oil, 28.0mg, **62%** yield. (PE/EtOAc = 20/1)

¹H NMR (400 MHz, CDCl₃): δ 7.69 (d, *J* = 7.9 Hz, 2H), 7.59 (d, *J* = 7.0 Hz, 2H), 7.51 (d, *J* = 8.2 Hz, 2H), 7.44 (t, *J* = 7.5 Hz, 2H), 7.35 (d, *J* = 7.4 Hz, 1H), 7.33 – 7.25 (m, 3H), 7.23 – 7.13 (m, 4H), 7.08 (d, *J* = 8.0 Hz, 2H), 3.94 (s, 2H), 2.29 (s, 3H), 2.07 (s, 3H).

¹³C NMR (101 MHz, CDCl₃): δ 207.6, 144.4, 140.5, 140.2, 136.1, 135.4, 135.1, 129.6, 128.9, 128.8, 128.6, 128.3, 128.1, 127.4, 127.4, 126.9, 126.8, 109.9, 92.9, 61.4, 21.6, 19.2.

HRMS (m/z, ESI-TOF): Calcd for C₃₀H₂₆SO₂Na⁺ [M+Na⁺] 473.1546, found 473.1569.



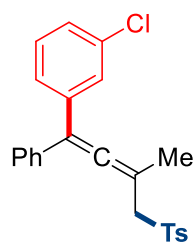
methyl(3-(3-methyl-1-phenyl-4-tosylbuta-1,2-dien-1-yl)phenyl)sulfane (28)

Colorless oil, 24.0mg, **57%** yield. (PE/EtOAc = 20/1)

¹H NMR (400 MHz, CDCl₃): δ 7.67 (d, *J* = 7.9 Hz, 2H), 7.31 – 7.23 (m, 3H), 7.22 – 7.05 (m, 7H), 6.88 (dt, *J* = 7.4, 1.7 Hz, 1H), 3.92 (d, *J* = 2.4 Hz, 2H), 2.45 (s, 3H), 2.32 (s, 3H), 2.04 (s, 3H).

¹³C NMR (101 MHz, CDCl₃): δ 207.4, 144.4, 138.5, 136.9, 135.8, 135.3, 129.6, 128.6, 128.5, 128.2, 128.0, 127.4, 126.4, 125.3, 125.3, 109.8, 92.9, 61.3, 21.6, 19.2, 15.6.

HRMS (m/z, ESI-TOF): Calcd for C₂₅H₂₄S₂O₂Na⁺ [M+Na⁺] 443.1110, found 443.1125.



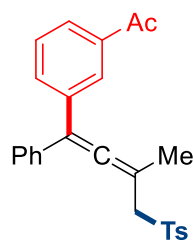
1-chloro-3-(3-methyl-1-phenyl-4-tosylbuta-1,2-dien-1-yl)benzene (29)

Colorless oil, 29.0mg, **71%** yield. (PE/EtOAc = 20/1)

¹H NMR (400 MHz, CDCl₃): δ 7.66 (d, *J* = 8.3 Hz, 2H), 7.31 – 7.26 (m, 3H), 7.25 – 7.17 (m, 2H), 7.14 – 7.06 (m, 5H), 7.02 (dt, *J* = 7.2, 1.6 Hz, 1H), 3.92 (d, *J* = 3.9 Hz, 2H), 2.31 (s, 3H), 2.05 (s, 3H).

¹³C NMR (101 MHz, CDCl₃): δ 207.4, 144.4, 138.2, 135.5, 135.2, 134.1, 129.6, 129.4, 128.4, 128.4, 128.0, 127.6, 127.4, 126.8, 109.2, 93.4, 61.2, 21.6, 19.2.

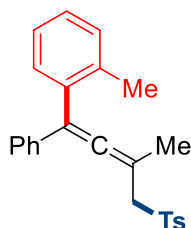
HRMS (m/z, ESI-TOF): Calcd for C₂₄H₂₁ClSO₂H⁺ [M+H⁺] 409.1024, found 409.1023.



1-(3-(3-methyl-1-phenyl-4-tosylbuta-1,2-dien-1-yl)phenyl)ethan-1-one (30)

Colorless oil, 30.8mg, **74%** yield. (PE/EtOAc = 20/1)

¹H NMR (400 MHz, CDCl₃): δ 7.91 – 7.84 (m, 2H), 7.69 (d, *J* = 8.1 Hz, 2H), 7.42 – 7.35 (m, 2H), 7.33 – 7.27 (m, 3H), 7.16 – 7.08 (m, 4H), 3.93 (d, *J* = 5.4 Hz, 2H), 2.59 (s, 3H), 2.32 (s, 3H), 2.05 (s, 3H).
¹³C NMR (101 MHz, CDCl₃): δ 207.6, 198.0, 144.4, 137.2, 136.9, 135.6, 135.5, 133.1, 129.6, 128.5, 128.5, 128.4, 128.0, 127.6, 127.2, 109.6, 93.2, 61.2, 26.7, 21.5, 19.3.
HRMS (m/z, ESI-TOF): Calcd for C₂₆H₂₄SO₃Na⁺ [M+Na⁺] 439.1338, found 439.1353.



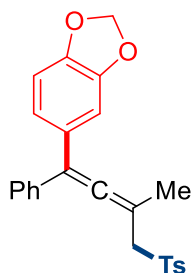
1-methyl-2-(3-methyl-1-phenyl-4-tosylbuta-1,2-dien-1-yl)benzene (31)

Colorless oil, 7.5mg, 19% yield. (PE/EtOAc = 20/1)

¹H NMR (400 MHz, CDCl₃): δ 7.63 (d, *J* = 8.3 Hz, 2H), 7.27 – 7.24 (m, 1H), 7.23 – 7.17 (m, 4H), 7.16 – 7.13 (m, 1H), 7.04 (d, *J* = 8.0 Hz, 2H), 6.99 (dd, *J* = 7.8, 1.4 Hz, 1H), 6.96 – 6.91 (m, 2H), 3.89 (d, *J* = 4.0 Hz, 2H), 2.33 (s, 3H), 2.04 (s, 3H), 1.98 (s, 3H).

¹³C NMR (101 MHz, CDCl₃): δ 206.2, 144.3, 136.5, 136.1, 135.3, 135.1, 130.2, 130.1, 129.6, 128.3, 128.1, 127.7, 127.1, 127.0, 125.8, 108.1, 92.3, 61.6, 21.7, 20.0, 18.8.

HRMS (m/z, ESI-TOF): Calcd for C₂₅H₂₄SO₂Na⁺ [M+Na⁺] 411.1389, found 411.1395.



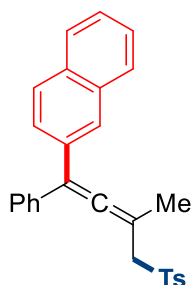
5-(3-methyl-1-phenyl-4-tosylbuta-1,2-dien-1-yl)benzo[d][1,3]dioxole (32)

Colorless oil, 26.3mg, 63% yield. (PE/EtOAc = 20/1)

¹H NMR (400 MHz, CDCl₃): δ 7.68 (d, *J* = 8.3 Hz, 2H), 7.29 – 7.24 (m, 3H), 7.15 – 7.06 (m, 4H), 6.71 (dd, *J* = 7.8, 0.8 Hz, 1H), 6.62 – 6.56 (m, 2H), 5.95 (q, *J* = 1.4 Hz, 2H), 3.91 (d, *J* = 1.2 Hz, 2H), 2.34 (s, 3H), 2.03 (s, 3H).

¹³C NMR (101 MHz, CDCl₃): δ 207.2, 147.5, 147.0, 144.4, 136.3, 135.4, 130.0, 129.6, 128.6, 128.2, 128.1, 127.4, 122.2, 109.9, 108.9, 108.0, 101.1, 92.6, 61.5, 21.6, 19.2.

HRMS (m/z, ESI-TOF): Calcd for C₂₅H₂₂SO₄Na⁺ [M+Na⁺] 441.1131, found 441.1142.



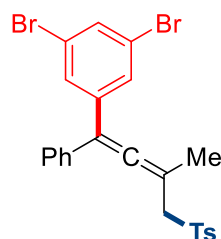
2-(3-methyl-1-phenyl-4-tosylbuta-1,2-dien-1-yl)naphthalene (33)

Colorless oil, 27.3mg, **64%** yield. (PE/EtOAc = 20/1)

¹H NMR (400 MHz, CDCl₃): δ 7.84 – 7.78 (m, 1H), 7.72 (d, *J* = 8.3 Hz, 2H), 7.65 (d, *J* = 7.9 Hz, 2H), 7.56 (s, 1H), 7.49 – 7.42 (m, 2H), 7.33 – 7.27 (m, 3H), 7.24 (dd, *J* = 8.5, 1.8 Hz, 1H), 7.17 (dd, *J* = 6.6, 3.0 Hz, 2H), 6.92 (d, *J* = 7.9 Hz, 2H), 3.96 (d, *J* = 4.3 Hz, 2H), 2.10 (d, *J* = 1.8 Hz, 6H).

¹³C NMR (101 MHz, CDCl₃): δ 207.9, 144.3, 136.1, 135.2, 133.5, 133.2, 132.6, 129.5, 128.6, 128.3, 128.0, 127.8, 127.5, 127.5, 127.4, 126.7, 126.2, 126.0, 110.2, 92.9, 61.4, 21.3, 19.2.

HRMS (m/z, ESI-TOF): Calcd for C₂₈H₂₄SO₂Na⁺ [M+Na⁺] 447.1389, found 447.1395.

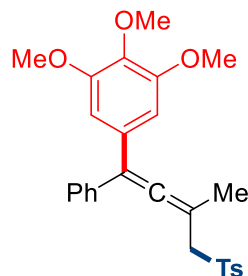
**1,3-dibromo-5-(3-methyl-1-phenyl-4-tosylbuta-1,2-dien-1-yl)benzene (34)**

Colorless oil, 37.8mg, **71%** yield. (PE/EtOAc = 20/1)

¹H NMR (400 MHz, CDCl₃): δ 7.66 (d, *J* = 8.0 Hz, 2H), 7.55 (s, 1H), 7.34 – 7.27 (m, 3H), 7.24 (d, *J* = 1.8 Hz, 2H), 7.14 – 7.05 (m, 4H), 4.01 – 3.85 (m, 2H), 2.32 (s, 3H), 2.03 (s, 3H).

¹³C NMR (101 MHz, CDCl₃): δ 207.4, 144.5, 140.2, 135.2, 134.9, 132.8, 130.1, 129.6, 128.5, 128.3, 127.9, 127.9, 122.7, 108.3, 94.0, 61.0, 21.6, 19.2.

HRMS (m/z, ESI-TOF): Calcd for C₂₄H₂₀Br₂SO₂Na⁺ [M+Na⁺] 552.9443, found 552.9426.

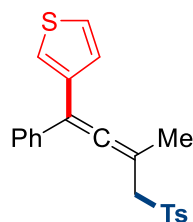
**1,2,3-trimethoxy-5-(3-methyl-1-phenyl-4-tosylbuta-1,2-dien-1-yl)benzene (35)**

Colorless oil, 26.4mg, **57%** yield. (PE/EtOAc = 10/1)

¹H NMR (400 MHz, CDCl₃): δ 7.71 (d, *J* = 8.3 Hz, 2H), 7.33 – 7.26 (m, 3H), 7.19 (dd, *J* = 7.6, 2.0 Hz, 2H), 7.16 (d, *J* = 8.0 Hz, 2H), 6.57 (s, 2H), 3.97 – 3.91 (m, 2H), 3.88 (s, 3H), 3.81 (s, 6H), 2.36 (s, 3H), 2.01 (s, 3H).

¹³C NMR (101 MHz, CDCl₃): δ 207.4, 153.0, 144.6, 137.4, 136.1, 135.9, 131.6, 129.6, 128.6, 128.2, 127.9, 127.5, 110.3, 105.9, 92.4, 61.5, 60.8, 56.1, 21.5, 19.5.

HRMS (m/z, ESI-TOF): Calcd for C₂₇H₂₈SO₅Na⁺ [M+Na⁺] 487.1550, found 487.1551.



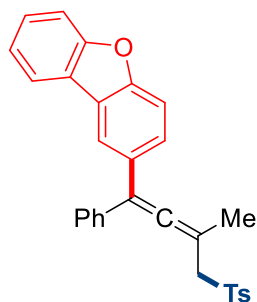
3-(3-methyl-1-phenyl-4-tosylbuta-1,2-dien-1-yl)thiophene (36)

Colorless oil, 25.2mg, **66%** yield. (PE/EtOAc = 20/1)

$^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.70 (d, J = 8.4 Hz, 2H), 7.32 – 7.26 (m, 3H), 7.24 (dd, J = 5.0, 3.0 Hz, 1H), 7.21 – 7.17 (m, 2H), 7.14 (d, J = 8.0 Hz, 2H), 6.94 (dd, J = 3.0, 1.3 Hz, 1H), 6.90 (dt, J = 5.0, 1.1 Hz, 1H), 3.90 (d, J = 2.8 Hz, 2H), 2.36 (s, 3H), 2.04 (s, 3H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3): δ 207.5, 144.5, 136.7, 136.1, 135.5, 129.7, 128.3, 128.2, 128.1, 127.9, 127.5, 125.3, 123.0, 105.5, 92.4, 61.5, 21.6, 19.2.

HRMS (m/z , ESI-TOF): Calcd for $\text{C}_{22}\text{H}_{20}\text{S}_2\text{O}_2\text{H}^+$ [$\text{M}+\text{H}^+$] 381.0977, found 381.0985.



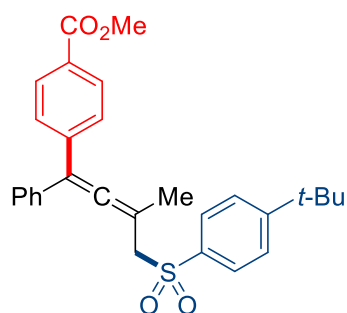
2-(3-methyl-1-phenyl-4-tosylbuta-1,2-dien-1-yl)dibenzo[b,d]furan (37)

Colorless oil, 29.4mg, **63%** yield. (PE/EtOAc = 15/1)

$^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.89 (d, J = 7.6 Hz, 1H), 7.75 (s, 1H), 7.67 (d, J = 7.9 Hz, 2H), 7.56 (d, J = 8.2 Hz, 1H), 7.46 (d, J = 8.3 Hz, 2H), 7.36 – 7.26 (m, 4H), 7.24 – 7.15 (m, 3H), 6.98 (d, J = 7.9 Hz, 2H), 4.05 – 3.90 (m, 2H), 2.10 (d, J = 10.0 Hz, 6H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3): δ 207.6, 156.5, 155.5, 144.3, 136.5, 135.4, 131.0, 129.5, 128.5, 128.3, 128.0, 127.5, 127.3, 124.3, 123.9, 122.8, 120.8, 120.7, 111.6, 111.3, 110.1, 92.7, 61.6, 21.3, 19.3.

HRMS (m/z , ESI-TOF): Calcd for $\text{C}_{30}\text{H}_{24}\text{SO}_3\text{Na}^+$ [$\text{M}+\text{Na}^+$] 487.1338, found 487.1340.



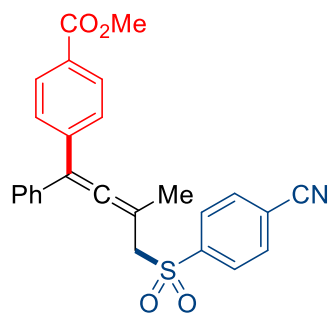
methyl 4-(4-((tert-butyl)phenyl)sulfonyl)-3-methyl-1-phenylbuta-1,2-dien-1-yl)benzoate (38)

Colorless oil, 32.3mg, **68%** yield. (PE/EtOAc = 20/1)

$^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.97 (d, J = 8.5 Hz, 2H), 7.76 (d, J = 8.5 Hz, 2H), 7.36 (d, J = 8.6 Hz, 2H), 7.34 – 7.28 (m, 5H), 7.25 – 7.21 (m, 2H), 3.94 (d, J = 3.0 Hz, 2H), 3.91 (s, 3H), 2.07 (s, 3H), 1.27 (s, 9H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3): δ 207.9, 166.7, 157.5, 141.1, 135.9, 135.5, 129.6, 128.9, 128.6, 128.4, 127.9, 127.7, 126.0, 109.8, 93.3, 61.2, 52.0, 35.1, 30.9, 19.5.

HRMS (m/z , ESI-TOF): Calcd for $\text{C}_{29}\text{H}_{30}\text{SO}_4\text{Na}^+$ [$\text{M}+\text{Na}^+$] 497.1757, found 497.1753.



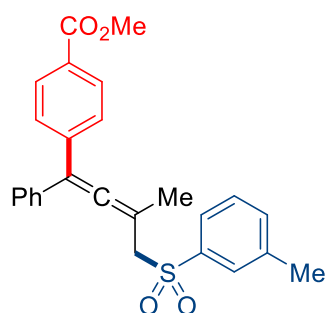
methyl 4-((4-cyanophenyl)sulfonyl)-3-methyl-1-phenylbuta-1,2-dien-1-ylbenzoate (39)

Colorless oil, 25.8mg, **58%** yield. (PE/EtOAc = 5/1)

¹H NMR (400 MHz, CDCl₃): δ 7.96 (d, *J* = 8.1 Hz, 2H), 7.83 (d, *J* = 8.1 Hz, 2H), 7.41 (d, *J* = 8.1 Hz, 2H), 7.38 – 7.30 (m, 3H), 7.14 (d, *J* = 8.1 Hz, 2H), 7.06 – 6.99 (m, 2H), 4.09 – 3.99 (m, 2H), 3.93 (s, 3H), 2.12 (s, 3H).

¹³C NMR (101 MHz, CDCl₃): δ 207.8, 166.5, 141.7, 140.5, 135.1, 132.4, 129.6, 129.4, 128.6, 128.5, 128.5, 128.2, 128.2, 117.1, 116.9, 110.1, 92.8, 60.9, 52.1, 19.0.

HRMS (m/z, ESI-TOF): Calcd for C₂₆H₂₁NSO₄Na⁺ [*M*+Na⁺] 466.1083, found 466.1092.



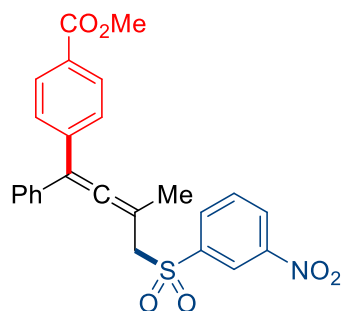
methyl 4-(3-methyl-1-phenyl-4-(m-tolylsulfonyl)buta-1,2-dien-1-yl)benzoate (40)

Colorless oil, 32.1mg, **74%** yield. (PE/EtOAc = 20/1)

¹H NMR (400 MHz, CDCl₃): δ 7.93 (d, *J* = 8.1 Hz, 2H), 7.68 – 7.60 (m, 2H), 7.33 – 7.26 (m, 4H), 7.24 (d, *J* = 7.6 Hz, 1H), 7.18 (d, *J* = 8.1 Hz, 2H), 7.14 – 7.07 (m, 2H), 3.96 (d, *J* = 3.1 Hz, 2H), 3.92 (s, 3H), 2.31 (s, 3H), 2.07 (s, 3H).

¹³C NMR (101 MHz, CDCl₃): δ 207.9, 166.7, 141.0, 139.3, 138.3, 135.4, 134.4, 129.5, 128.9, 128.9, 128.4, 128.4, 128.3, 128.1, 127.6, 125.2, 109.6, 93.3, 61.1, 52.0, 21.1, 18.9.

HRMS (m/z, ESI-TOF): Calcd for C₂₆H₂₄SO₄Na⁺ [*M*+Na⁺] 455.1288, found 455.1289.



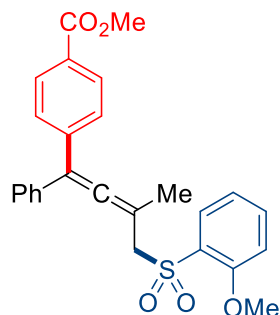
methyl 4-(3-methyl-4-((3-nitrophenyl)sulfonyl)-1-phenylbuta-1,2-dien-1-yl)benzoate (41)

Colorless oil, 18.7mg, **40%** yield. (PE/EtOAc = 10/1)

¹H NMR (400 MHz, CDCl₃): δ 8.59 (t, *J* = 2.0 Hz, 1H), 8.12 – 8.02 (m, 2H), 7.90 (d, *J* = 8.4 Hz, 2H), 7.37 (t, *J* = 8.0 Hz, 1H), 7.31 – 7.22 (m, 3H), 7.11 (d, *J* = 8.5 Hz, 2H), 7.02 – 6.96 (m, 2H), 4.09 (d, *J* = 2.3 Hz, 2H), 3.94 (s, 3H), 2.14 (s, 3H).

¹³C NMR (101 MHz, CDCl₃): δ 208.0, 166.6, 147.7, 140.5, 139.9, 135.0, 133.3, 130.1, 129.6, 129.3, 128.5, 128.4, 128.2, 128.0, 127.9, 123.2, 110.1, 92.9, 61.0, 52.2, 18.9.

HRMS (m/z, ESI-TOF): Calcd for C₂₅H₂₁NSO₆Na⁺ [M+Na⁺] 486.0982, found 486.0982.



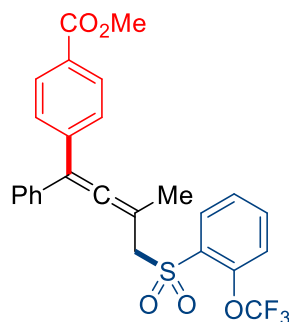
methyl 4-((2-methoxyphenyl)sulfonyl)-3-methyl-1-phenylbuta-1,2-dien-1-ylbenzoate (42)

Colorless oil, 35.0mg, **78%** yield. (PE/EtOAc = 20/1)

¹H NMR (400 MHz, CDCl₃): δ 7.90 (d, *J* = 8.4 Hz, 2H), 7.86 (dd, *J* = 7.9, 1.8 Hz, 1H), 7.33 – 7.24 (m, 4H), 7.14 (d, *J* = 8.4 Hz, 2H), 7.09 (dd, *J* = 6.6, 3.0 Hz, 2H), 6.90 (t, *J* = 7.5 Hz, 1H), 6.63 (d, *J* = 8.4 Hz, 1H), 4.31 (d, *J* = 13.8 Hz, 1H), 4.20 (d, *J* = 14.0 Hz, 1H), 3.92 (s, 3H), 3.77 (s, 3H), 2.04 (s, 3H).

¹³C NMR (101 MHz, CDCl₃): δ 207.8, 166.6, 156.7, 141.1, 135.5, 130.1, 129.5, 128.7, 128.4, 128.4, 128.2, 127.5, 125.8, 120.4, 111.8, 109.4, 93.7, 59.2, 55.9, 52.0, 18.9.

HRMS (m/z, ESI-TOF): Calcd for C₂₆H₂₄SO₅Na⁺ [M+Na⁺] 471.1237, found 471.1245.



methyl 4-((2-(trifluoromethoxy)phenyl)sulfonyl)-3-methyl-1-phenylbuta-1,2-dien-1-ylbenzoate (43)

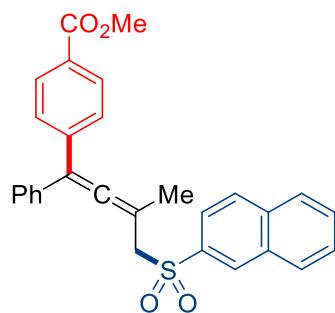
Colorless oil, 26.0mg, **52%** yield. (PE/EtOAc = 20/1)

¹H NMR (400 MHz, CDCl₃): δ 7.95 – 7.88 (m, 3H), 7.36 – 7.30 (m, 1H), 7.30 – 7.26 (m, 3H), 7.19 – 7.11 (m, 3H), 7.11 – 7.06 (m, 2H), 7.04 (dt, *J* = 8.4, 1.6 Hz, 1H), 4.25 – 4.13 (m, 2H), 3.93 (s, 3H), 2.07 (s, 3H).

¹³C NMR (101 MHz, CDCl₃): δ 207.8, 166.7, 146.4 (q, *J* = 1.7 Hz), 140.9, 135.4, 135.3, 131.1, 129.8, 129.6, 129.0, 128.5, 128.5, 128.3, 127.7, 126.3, 120.1 (q, *J* = 262.6 Hz), 119.2 (q, *J* = 2.2 Hz), 110.0, 93.0, 60.2, 52.1, 19.2.

¹⁹F NMR (376 MHz, CDCl₃): δ -56.18.

HRMS (m/z, ESI-TOF): Calcd for C₂₆H₂₁F₃SO₅Na⁺ [M+Na⁺] 525.0954, found 525.0971.



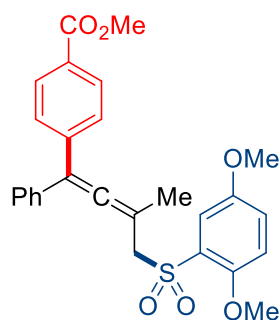
methyl 4-(3-methyl-4-(naphthalen-2-ylsulfonyl)-1-phenylbuta-1,2-dien-1-yl)benzoate (44)

Colorless oil, 31.5mg, **67%** yield. (PE/EtOAc = 20/1)

¹H NMR (400 MHz, CDCl₃): δ 8.41 (s, 1H), 7.85 (d, *J* = 8.1 Hz, 1H), 7.82 – 7.71 (m, 3H), 7.68 – 7.59 (m, 3H), 7.59 – 7.53 (m, 1H), 7.19 – 7.08 (m, 3H), 6.98 (dd, *J* = 8.1, 6.1 Hz, 4H), 4.15 – 4.00 (m, 2H), 3.91 (s, 3H), 2.11 (s, 3H).

¹³C NMR (101 MHz, CDCl₃): δ 208.0, 166.6, 140.7, 135.3, 135.2, 135.2, 132.0, 130.0, 129.5, 129.5, 129.4, 129.2, 128.9, 128.4, 128.2, 128.1, 127.8, 127.6, 122.6, 109.7, 93.5, 61.1, 52.1, 19.1.

HRMS (m/z, ESI-TOF): Calcd for C₂₉H₂₄SO₄Na⁺ [M+Na⁺] 491.1288, found 491.1297.



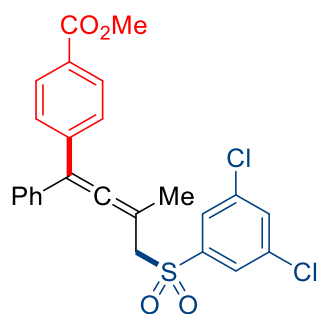
methyl 4-(4-((2,5-dimethoxyphenyl)sulfonyl)-3-methyl-1-phenylbuta-1,2-dien-1-yl)benzoate (45)

Colorless oil, 38.5mg, **80%** yield. (PE/EtOAc = 20/1)

¹H NMR (400 MHz, CDCl₃): δ 7.90 (d, *J* = 8.3 Hz, 2H), 7.38 (d, *J* = 3.2 Hz, 1H), 7.31 – 7.25 (m, 3H), 7.14 (d, *J* = 8.3 Hz, 2H), 7.09 (dd, *J* = 6.7, 3.0 Hz, 2H), 6.77 (dd, *J* = 9.0, 3.2 Hz, 1H), 6.56 (d, *J* = 9.0 Hz, 1H), 4.35 (d, *J* = 13.9 Hz, 1H), 4.20 (d, *J* = 13.9 Hz, 1H), 3.93 (s, 3H), 3.75 (s, 3H), 3.73 (s, 3H), 2.06 (s, 3H).

¹³C NMR (101 MHz, CDCl₃): δ 207.9, 166.7, 153.0, 150.7, 141.0, 135.5, 129.5, 128.8, 128.4, 128.4, 128.2, 127.6, 126.3, 121.2, 114.2, 113.4, 109.5, 93.6, 58.9, 56.5, 55.6, 52.0, 19.1.

HRMS (m/z, ESI-TOF): Calcd for C₂₇H₂₆SO₆Na⁺ [M+Na⁺] 501.1342, found 501.1340.



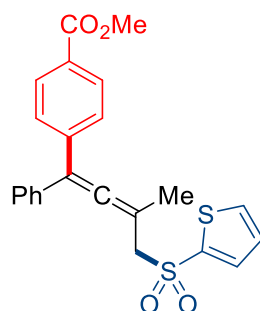
methyl 4-(4-((3,5-dichlorophenyl)sulfonyl)-3-methyl-1-phenylbuta-1,2-dien-1-yl)benzoate (46)

Colorless oil, 24.8mg, **51%** yield. (PE/EtOAc = 20/1)

¹H NMR (400 MHz, CDCl₃): δ 7.97 (d, *J* = 8.0 Hz, 2H), 7.66 (d, *J* = 1.9 Hz, 2H), 7.36 – 7.28 (m, 3H), 7.23 (t, *J* = 1.9 Hz, 1H), 7.17 (d, *J* = 8.1 Hz, 2H), 7.11 – 7.04 (m, 2H), 4.02 (s, 2H), 3.93 (s, 3H), 2.10 (s, 3H).

¹³C NMR (101 MHz, CDCl₃): δ 208.1, 166.6, 140.9, 140.6, 135.9, 135.0, 133.6, 129.7, 129.2, 128.5, 128.3, 128.2, 127.9, 126.2, 110.0, 92.7, 61.0, 52.1, 18.8.

HRMS (m/z, ESI-TOF): Calcd for C₂₅H₂₀Cl₂SO₄Na⁺ [M+Na⁺] 509.0352, found 509.0346.



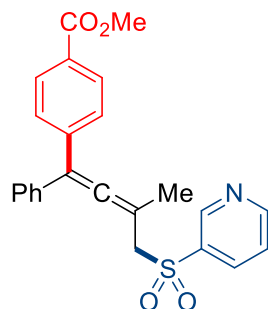
methyl 4-(3-methyl-1-phenyl-4-(thiophen-2-ylsulfonyl)buta-1,2-dien-1-yl)benzoate (47)

Colorless oil, 21.2mg, **50%** yield. (PE/EtOAc = 20/1)

¹H NMR (400 MHz, CDCl₃): δ 7.96 (d, *J* = 8.0 Hz, 2H), 7.56 (d, *J* = 3.7 Hz, 1H), 7.51 (d, *J* = 5.0 Hz, 1H), 7.32 (d, *J* = 6.7 Hz, 3H), 7.23 (d, *J* = 8.1 Hz, 2H), 7.15 (dd, *J* = 7.3, 2.2 Hz, 2H), 6.88 (t, *J* = 4.4 Hz, 1H), 4.07 – 4.01 (m, 2H), 3.92 (s, 3H), 2.09 (s, 3H).

¹³C NMR (101 MHz, CDCl₃): δ 208.0, 166.7, 141.0, 139.0, 135.5, 134.5, 134.1, 129.6, 129.0, 128.6, 128.5, 127.8, 127.7, 109.9, 93.4, 62.8, 52.1, 19.0.

HRMS (m/z, ESI-TOF): Calcd for C₂₃H₂₀S₂O₄Na⁺ [M+Na⁺] 447.0695, found 447.0696.



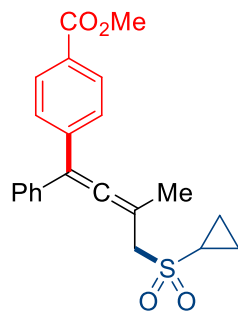
methyl 4-(3-methyl-1-phenyl-4-(pyridin-3-ylsulfonyl)buta-1,2-dien-1-yl)benzoate (48)

Colorless oil, 23.8mg, **57%** yield. (PE/EtOAc = 5/1)

¹H NMR (400 MHz, CDCl₃): δ 9.03 (d, *J* = 2.3 Hz, 1H), 8.59 (dd, *J* = 4.9, 1.6 Hz, 1H), 8.00 (dt, *J* = 8.1, 2.0 Hz, 1H), 7.95 (d, *J* = 8.4 Hz, 2H), 7.34 – 7.29 (m, 3H), 7.17 (d, *J* = 8.4 Hz, 2H), 7.11 – 7.04 (m, 3H), 4.03 (s, 2H), 3.93 (s, 3H), 2.11 (s, 3H).

¹³C NMR (101 MHz, CDCl₃): δ 207.9, 166.6, 154.0, 148.8, 140.6, 135.7, 135.1, 134.6, 129.6, 129.2, 128.5, 128.5, 128.3, 127.9, 123.3, 110.1, 92.9, 61.6, 52.1, 19.1.

HRMS (m/z, ESI-TOF): Calcd for C₂₄H₂₁NSO₄Na⁺ [M+Na⁺] 442.1083, found 442.1092.



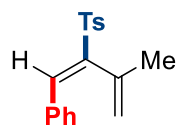
methyl 4-(4-(cyclopropylsulfonyl)-3-methyl-1-phenylbuta-1,2-dien-1-yl)benzoate (49)

Colorless oil, 22.9mg, **60%** yield. (PE/EtOAc = 20/1)

¹H NMR (400 MHz, CDCl₃): δ 8.01 (d, *J* = 8.0 Hz, 2H), 7.42 (d, *J* = 8.1 Hz, 2H), 7.39 – 7.28 (m, 5H), 3.92 (s, 3H), 3.83 (s, 2H), 2.28 – 2.11 (m, 4H), 1.11 (td, *J* = 4.8, 2.4 Hz, 2H), 0.67 (dd, *J* = 8.1, 2.4 Hz, 2H).

¹³C NMR (101 MHz, CDCl₃): δ 208.0, 166.6, 140.9, 135.4, 129.7, 129.2, 128.6, 128.5, 128.3, 127.9, 109.9, 93.6, 58.5, 52.1, 28.9, 19.1, 4.8, 4.8.

HRMS (m/z, ESI-TOF): Calcd for C₂₂H₂₂SO₄Na⁺ [*M*+Na⁺] 405.1131, found 405.1143.



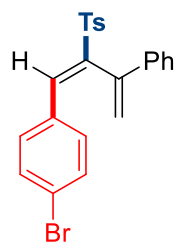
(*E*)-1-methyl-4-((3-methyl-1-phenylbuta-1,3-dien-2-yl)sulfonyl)benzene (50)

White solid, 15.1mg, **51%** yield. (PE/EtOAc = 20/1)

¹H NMR (400 MHz, CDCl₃): δ 7.77 (d, *J* = 8.0 Hz, 2H), 7.71 (s, 1H), 7.63 – 7.57 (m, 2H), 7.40 – 7.33 (m, 3H), 7.30 (d, *J* = 8.0 Hz, 2H), 5.26 (s, 1H), 4.81 (s, 1H), 2.42 (s, 3H), 1.78 (s, 3H).

¹³C NMR (101 MHz, CDCl₃): δ 144.1, 142.3, 136.5, 135.7, 135.7, 133.0, 130.0, 130.0, 129.4, 128.8, 128.6, 121.9, 22.6, 21.6.

HRMS (m/z, ESI-TOF): Calcd for C₁₈H₁₈SO₂Na⁺ [*M*+Na⁺] 321.0920, found 321.0914.



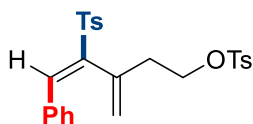
(*E*)-1-bromo-4-(3-phenyl-2-tosylbuta-1,3-dien-1-yl)benzene (51)

White solid, 17.0mg, **39%** yield. (PE/EtOAc = 20/1)

¹H NMR (400 MHz, CDCl₃): δ 7.93 (s, 1H), 7.65 (d, *J* = 7.9 Hz, 2H), 7.41 (d, *J* = 8.4 Hz, 2H), 7.36 (d, *J* = 8.4 Hz, 2H), 7.25 – 7.20 (m, 2H), 7.20 – 7.11 (m, 5H), 5.89 (s, 1H), 5.12 (s, 1H), 2.34 (s, 3H).

¹³C NMR (101 MHz, CDCl₃): δ 144.2, 141.7, 139.3, 137.0, 136.2, 135.4, 131.8, 131.7, 131.5, 129.3, 129.0, 128.4, 128.3, 126.1, 124.7, 120.7, 21.5.

HRMS (m/z, ESI-TOF): Calcd for C₂₃H₁₉BrSO₂Na⁺ [*M*+Na⁺] 461.0181, found 461.0201.



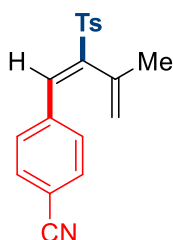
(E)-3-methylene-5-phenyl-4-tosylpent-4-en-1-yl 4-methylbenzenesulfonate (52)

White solid, 19.3mg, **40%** yield. (PE/EtOAc = 15/1)

$^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.76 – 7.64 (m, 5H), 7.56 (d, J = 6.8 Hz, 2H), 7.39 – 7.25 (m, 7H), 5.31 (s, 1H), 4.89 (s, 1H), 4.02 (t, J = 6.5 Hz, 2H), 2.50 – 2.39 (m, 8H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3): δ 144.8, 144.5, 140.9, 137.2, 135.4, 135.1, 132.7, 132.4, 130.4, 130.1, 129.8, 129.5, 128.8, 128.7, 127.7, 122.9, 67.2, 34.6, 21.6.

HRMS (m/z , ESI-TOF): Calcd for $\text{C}_{26}\text{H}_{26}\text{S}_2\text{O}_5\text{Na}^+$ [$\text{M}+\text{Na}^+$] 505.1114, found 505.1111.



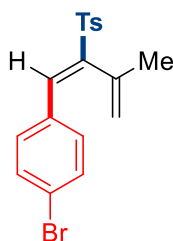
(E)-4-(3-methyl-2-tosylbuta-1,3-dien-1-yl)benzonitrile (53)

White solid, 19.2mg, **59%** yield. (PE/EtOAc = 8/1)

$^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.76 (d, J = 7.9 Hz, 2H), 7.73 – 7.61 (m, 5H), 7.33 (d, J = 7.9 Hz, 2H), 5.30 (s, 1H), 4.82 (s, 1H), 2.44 (s, 3H), 1.75 (s, 3H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3): δ 146.0, 144.6, 137.4, 135.7, 134.8, 133.1, 132.3, 130.1, 129.5, 129.0, 122.6, 118.2, 113.1, 22.6, 21.6.

HRMS (m/z , ESI-TOF): Calcd for $\text{C}_{19}\text{H}_{17}\text{NSO}_2\text{Na}^+$ [$\text{M}+\text{Na}^+$] 346.0872, found 346.0876.



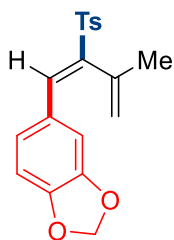
(E)-1-bromo-4-(3-methyl-2-tosylbuta-1,3-dien-1-yl)benzene (54)

White solid, 24.4mg, **65%** yield. (PE/EtOAc = 20/1)

$^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.76 (d, J = 8.0 Hz, 2H), 7.64 (s, 1H), 7.52 – 7.43 (m, 4H), 7.31 (d, J = 7.9 Hz, 2H), 5.27 (s, 1H), 4.80 (s, 1H), 2.43 (s, 3H), 1.75 (s, 3H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3): δ 144.3, 143.0, 136.2, 135.3, 134.2, 131.9, 131.9, 131.3, 129.4, 128.9, 124.4, 122.2, 22.6, 21.6.

HRMS (m/z , ESI-TOF): Calcd for $\text{C}_{18}\text{H}_{17}\text{BrSO}_2\text{Na}^+$ [$\text{M}+\text{Na}^+$] 399.0025, found 399.0021.



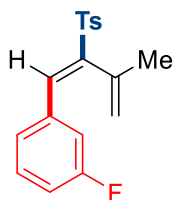
(E)-5-(3-methyl-2-tosylbuta-1,3-dien-1-yl)benzo[d][1,3]dioxole (55)

White solid, 16.9mg, 49% yield. (PE/EtOAc = 20/1)

¹H NMR (400 MHz, CDCl₃): δ 7.75 (d, *J* = 7.9 Hz, 2H), 7.61 (s, 1H), 7.29 (d, *J* = 8.0 Hz, 2H), 7.18 (s, 1H), 7.09 (d, *J* = 7.7 Hz, 1H), 6.81 (d, *J* = 8.1 Hz, 1H), 5.99 (s, 2H), 5.26 (s, 1H), 4.78 (s, 1H), 2.42 (s, 3H), 1.78 (s, 3H).

¹³C NMR (101 MHz, CDCl₃): δ 149.2, 147.9, 144.0, 139.8, 136.6, 135.8, 135.3, 129.3, 128.7, 127.0, 126.5, 122.0, 108.6, 108.4, 101.5, 22.6, 21.6.

HRMS (m/z, ESI-TOF): Calcd for C₁₉H₁₈SO₄Na⁺ [M+Na⁺] 365.0818, found 365.0819.



(E)-1-fluoro-3-(3-methyl-2-tosylbuta-1,3-dien-1-yl)benzene (56)

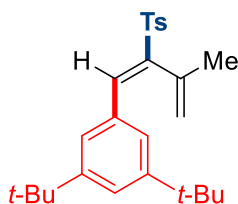
White solid, 17.5mg, 55% yield. (PE/EtOAc = 20/1)

¹H NMR (400 MHz, CDCl₃): δ 7.76 (d, *J* = 8.3 Hz, 2H), 7.67 (s, 1H), 7.40 – 7.28 (m, 5H), 7.12 – 7.02 (m, 1H), 5.28 (s, 1H), 4.81 (s, 1H), 2.43 (s, 3H), 1.77 (s, 3H).

¹³C NMR (101 MHz, CDCl₃): δ 162.6 (d, *J* = 247.3 Hz), 144.3, 143.7, 136.1, 135.3, 135.0 (d, *J* = 7.9 Hz), 134.1 (d, *J* = 2.7 Hz), 130.2 (d, *J* = 8.4 Hz), 129.4, 128.9, 126.1 (d, *J* = 2.6 Hz), 122.2, 116.9 (d, *J* = 21.4 Hz), 116.0 (d, *J* = 22.6 Hz), 22.6, 21.6.

¹⁹F NMR (376 MHz, CDCl₃): δ -112.19.

HRMS (m/z, ESI-TOF): Calcd for C₁₈H₁₇FSO₂Na⁺ [M+Na⁺] 339.0825, found 339.0826.



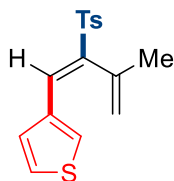
(E)-1,3-di-tert-butyl-5-(3-methyl-2-tosylbuta-1,3-dien-1-yl)benzene (57)

White solid, 18.1mg, 44% yield. (PE/EtOAc = 20/1)

¹H NMR (400 MHz, CDCl₃): δ 7.77 (d, *J* = 8.0 Hz, 2H), 7.74 (s, 1H), 7.51 (d, *J* = 1.8 Hz, 2H), 7.43 (s, 1H), 7.30 (d, *J* = 7.9 Hz, 2H), 5.28 (s, 1H), 4.75 (s, 1H), 2.43 (s, 3H), 1.83 (s, 3H), 1.30 (s, 18H).

¹³C NMR (101 MHz, CDCl₃): δ 151.1, 144.0, 140.8, 137.4, 136.9, 135.9, 132.1, 129.4, 128.8, 124.8, 124.4, 121.2, 34.9, 31.3, 22.7, 21.6.

HRMS (m/z, ESI-TOF): Calcd for C₂₆H₃₄SO₂Na⁺ [M+Na⁺] 433.2172, found 433.2167.

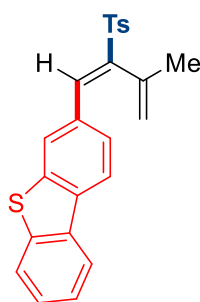


(E)-3-(3-methyl-2-tosylbuta-1,3-dien-1-yl)thiophene (58)

White solid, 10.2mg, **33%** yield. (PE/EtOAc = 20/1)

¹H NMR (400 MHz, CDCl₃): δ 7.75 (d, *J* = 8.3 Hz, 2H), 7.71 (s, 1H), 7.66 (dd, *J* = 3.1, 1.3 Hz, 1H), 7.35 (dd, *J* = 5.1, 1.3 Hz, 1H), 7.33 – 7.27 (m, 3H), 5.26 (s, 1H), 4.70 (s, 1H), 2.43 (s, 3H), 1.85 (s, 3H).
¹³C NMR (101 MHz, CDCl₃): δ 144.1, 140.5, 137.0, 135.8, 134.8, 129.7, 129.6, 129.4, 128.8, 127.6, 126.3, 121.7, 22.7, 21.6.

HRMS (m/z, ESI-TOF): Calcd for C₁₆H₁₆S₂O₂Na⁺ [M+Na⁺] 327.0484, found 327.0478.



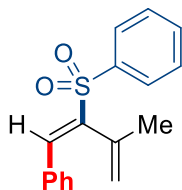
(E)-3-(3-methyl-2-tosylbuta-1,3-dien-1-yl)dibenzo[b,d]thiophene (59)

White solid, 15.8mg, **39%** yield. (PE/EtOAc = 20/1)

¹H NMR (400 MHz, CDCl₃): δ 8.21 – 8.04 (m, 3H), 7.90 – 7.83 (m, 2H), 7.79 (d, *J* = 8.0 Hz, 2H), 7.71 (d, *J* = 8.3 Hz, 1H), 7.53 – 7.44 (m, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 5.34 (s, 1H), 4.89 (s, 1H), 2.43 (s, 3H), 1.81 (s, 3H).

¹³C NMR (101 MHz, CDCl₃): δ 144.2, 142.4, 140.3, 139.7, 136.7, 136.6, 135.6, 135.3, 134.7, 131.5, 129.4, 128.9, 127.4, 126.1, 124.6, 124.4, 122.9, 122.3, 122.0, 121.6, 22.7, 21.6.

HRMS (m/z, ESI-TOF): Calcd for C₂₄H₂₀S₂O₂Na⁺ [M+Na⁺] 427.0797, found 427.0792.



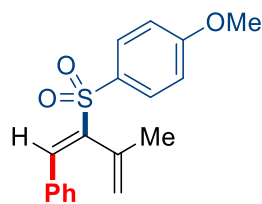
(E)-((3-methyl-1-phenylbuta-1,3-dien-2-yl)sulfonyl)benzene (60)

White solid, 12.8mg, **45%** yield. (PE/EtOAc = 20/1)

¹H NMR (400 MHz, CDCl₃): δ 7.90 (d, *J* = 7.3 Hz, 2H), 7.74 (s, 1H), 7.66 – 7.56 (m, 3H), 7.51 (t, *J* = 7.6 Hz, 2H), 7.41 – 7.33 (m, 3H), 5.26 (s, 1H), 4.79 (s, 1H), 1.78 (s, 3H).

¹³C NMR (101 MHz, CDCl₃): δ 141.9, 138.6, 136.5, 136.1, 133.2, 132.9, 130.2, 130.0, 128.8, 128.7, 128.7, 122.0, 22.6.

HRMS (m/z, ESI-TOF): Calcd for C₁₇H₁₆SO₂Na⁺ [M+Na⁺] 307.0763, found 307.0766.



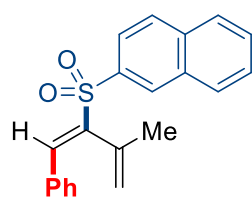
(E)-1-methoxy-4-((3-methyl-1-phenylbuta-1,3-dien-2-yl)sulfonyl)benzene (61)

White solid, 12.8mg, 41% yield. (PE/EtOAc = 20/1)

¹H NMR (400 MHz, CDCl₃): δ 7.81 (d, *J* = 8.9 Hz, 2H), 7.69 (s, 1H), 7.63 – 7.57 (m, 2H), 7.40 – 7.32 (m, 3H), 6.97 (d, *J* = 8.9 Hz, 2H), 5.27 (s, 1H), 4.81 (s, 1H), 3.87 (s, 3H), 1.78 (s, 3H).

¹³C NMR (101 MHz, CDCl₃): δ 163.3, 142.4, 136.7, 135.2, 133.0, 131.0, 130.1, 130.0, 130.0, 128.6, 121.8, 113.9, 55.6, 22.7.

HRMS (*m/z*, ESI-TOF): Calcd for C₁₈H₁₈SO₃Na⁺ [*M*+Na⁺] 337.0869, found 337.0866.



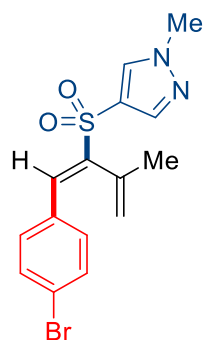
(E)-2-((3-methyl-1-phenylbuta-1,3-dien-2-yl)sulfonyl)naphthalene (62)

White solid, 15.6mg, 47% yield. (PE/EtOAc = 20/1)

¹H NMR (400 MHz, CDCl₃): δ 8.49 (s, 1H), 8.00 – 7.88 (m, 3H), 7.86 – 7.80 (m, 2H), 7.68 – 7.58 (m, 4H), 7.40 – 7.33 (m, 3H), 5.23 (s, 1H), 4.76 (s, 1H), 1.79 (s, 3H).

¹³C NMR (101 MHz, CDCl₃): δ 141.8, 136.5, 136.4, 135.5, 135.0, 132.9, 131.9, 130.6, 130.2, 130.1, 129.4, 129.0, 129.0, 128.7, 127.9, 127.5, 123.5, 122.0, 22.7.

HRMS (*m/z*, ESI-TOF): Calcd for C₂₁H₁₈SO₂Na⁺ [*M*+Na⁺] 357.0920, found 357.0915.



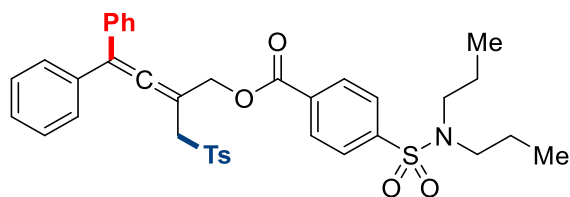
(E)-4-((1-(4-bromophenyl)-3-methylbuta-1,3-dien-2-yl)sulfonyl)-1-methyl-1H-pyrazole (63)

White solid, 19.1mg, 52% yield. (PE/EtOAc = 10/1)

¹H NMR (400 MHz, CDCl₃): δ 7.83 (s, 1H), 7.76 (s, 1H), 7.57 (s, 1H), 7.53 – 7.43 (m, 4H), 5.39 (s, 1H), 5.01 (s, 1H), 3.96 (s, 3H), 1.85 (s, 3H).

¹³C NMR (101 MHz, CDCl₃): δ 143.5, 140.1, 136.4, 133.5, 133.3, 131.9, 131.7, 131.3, 124.4, 122.2, 120.7, 39.6, 22.8.

HRMS (*m/z*, ESI-TOF): Calcd for C₁₅H₁₅BrN₂SO₂Na⁺ [*M*+Na⁺] 388.9930, found 388.9938.



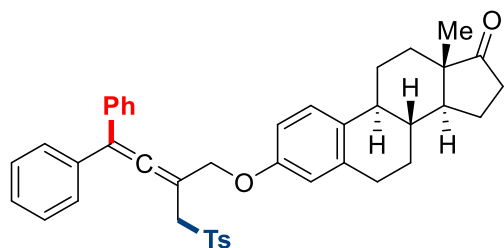
4,4-diphenyl-2-(tosylmethyl)buta-2,3-dien-1-yl 4-(N,N-dipropylsulfamoyl)benzoate (64)

Colorless oil, 43.4mg, **66%** yield. (PE/EtOAc = 10/1)

¹H NMR (400 MHz, CDCl₃): δ 8.05 (d, *J* = 8.1 Hz, 2H), 7.80 (d, *J* = 8.1 Hz, 2H), 7.70 (d, *J* = 7.9 Hz, 2H), 7.33 – 7.20 (m, 6H), 7.17 – 7.02 (m, 6H), 5.15 (s, 2H), 4.11 (s, 2H), 3.08 (t, *J* = 7.7 Hz, 4H), 2.31 (s, 3H), 1.61 – 1.45 (m, 4H), 0.85 (t, *J* = 7.4 Hz, 6H).

¹³C NMR (101 MHz, CDCl₃): δ 207.4, 164.4, 144.6, 144.1, 134.8, 134.7, 132.8, 130.1, 129.6, 128.4, 128.2, 128.0, 127.8, 126.7, 113.9, 93.6, 64.1, 57.7, 49.7, 21.7, 21.5, 11.0.

HRMS (m/z, ESI-TOF): Calcd for C₃₇H₃₉NS₂O₆Na⁺ [M+Na⁺] 680.2111, found 680.2091.



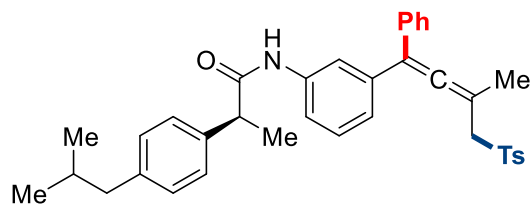
(8R,9S,13S,14S)-3-((4,4-diphenyl-2-(tosylmethyl)buta-2,3-dien-1-yl)oxy)-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta[a]phenanthren-17-one (65)

Colorless oil, 32.7mg, **51%** yield. (PE/EtOAc = 10/1)

¹H NMR (400 MHz, CDCl₃): δ 7.65 (d, *J* = 7.9 Hz, 2H), 7.33 – 7.25 (m, 6H), 7.16 – 7.08 (m, 4H), 7.07 – 6.99 (m, 3H), 6.65 (dd, *J* = 8.6, 2.7 Hz, 1H), 6.55 (d, *J* = 2.7 Hz, 1H), 4.82 (s, 2H), 4.05 (s, 2H), 2.75 – 2.55 (m, 2H), 2.53 – 2.44 (m, 1H), 2.35 – 2.25 (m, 4H), 2.19 – 2.14 (m, 1H), 2.13 – 1.99 (m, 2H), 1.97 – 1.87 (m, 2H), 1.67 – 1.56 (m, 1H), 1.53 – 1.43 (m, 4H), 1.37 – 1.29 (m, 1H), 0.90 (s, 3H).

¹³C NMR (101 MHz, CDCl₃): δ 207.5, 155.7, 144.4, 137.6, 135.1, 135.1, 135.1, 132.3, 129.5, 128.7, 128.2, 128.0, 127.7, 126.2, 114.7, 113.1, 112.8, 94.2, 67.3, 56.5, 50.2, 47.9, 43.8, 38.1, 35.8, 31.4, 29.3, 26.4, 25.7, 21.6, 21.5, 13.7.

HRMS (m/z, ESI-TOF): Calcd for C₄₂H₄₂SO₄Na⁺ [M+Na⁺] 665.2696, found 665.2678.

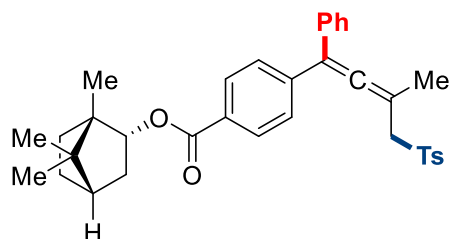


(2S)-2-(4-isobutylphenyl)-N-(3-(3-methyl-1-phenyl-4-tosylbuta-1,2-dien-1-yl)phenyl)propanamide (66) White solid, 42.4mg, **73%** yield. (PE/EtOAc = 8/1)

¹H NMR (400 MHz, CDCl₃): δ 7.67 – 7.58 (m, 3H), 7.48 (s, 1H), 7.28 – 7.21 (m, 5H), 7.20 – 7.14 (m, 2H), 7.13 – 7.04 (m, 4H), 7.02 (d, *J* = 8.1 Hz, 2H), 6.80 (d, *J* = 7.5 Hz, 1H), 3.88 (d, *J* = 1.9 Hz, 2H), 3.69 – 3.61 (m, 1H), 2.41 (dd, *J* = 7.2, 1.8 Hz, 2H), 2.26 (s, 3H), 1.99 (d, *J* = 3.2 Hz, 3H), 1.86 – 1.77 (m, 1H), 1.53 (d, *J* = 7.1 Hz, 3H), 0.87 (d, *J* = 6.6 Hz, 6H).

^{13}C NMR (101 MHz, CDCl_3): δ 207.5, 172.6, 144.4, 140.7, 138.2, 138.0, 138.0, 136.8, 136.8, 135.8, 135.7, 135.1, 129.5, 129.5, 128.6, 128.4, 128.1, 127.9, 127.9, 127.3, 127.2, 124.2, 119.6, 118.8, 109.8, 92.6, 61.3, 61.3, 47.4, 44.8, 30.0, 22.2, 21.5, 19.1, 19.0, 18.5.

HRMS (m/z, ESI-TOF): Calcd for $\text{C}_{37}\text{H}_{39}\text{NSO}_3\text{Na}^+$ [$\text{M}+\text{Na}^+$] 600.2543, found 600.2556.

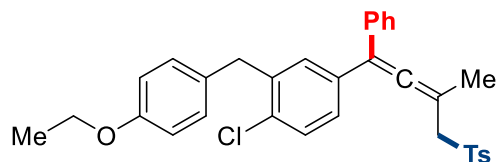


(1S,2R,4S)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl 4-(3-methyl-1-phenyl-4-tosylbuta-1,2-dien-1-yl)benzoate (67) Colorless oil, 35.7mg, 64% yield. (PE/EtOAc = 20/1)

^1H NMR (400 MHz, CDCl_3): δ 7.96 (d, J = 8.0 Hz, 2H), 7.70 (d, J = 7.9 Hz, 2H), 7.33 – 7.25 (m, 3H), 7.21 – 7.07 (m, 6H), 5.13 (d, J = 9.8 Hz, 1H), 4.04 – 3.87 (m, 2H), 2.56 – 2.44 (m, 1H), 2.34 (s, 3H), 2.20 – 2.04 (m, 4H), 1.89 – 1.78 (m, 1H), 1.77 – 1.70 (m, 1H), 1.48 – 1.37 (m, 1H), 1.36 – 1.26 (m, 1H), 1.12 (dd, J = 13.9, 3.5 Hz, 1H), 0.98 (s, 3H), 0.92 (s, 6H).

^{13}C NMR (101 MHz, CDCl_3): δ 207.8, 166.4, 144.4, 140.8, 135.4, 135.1, 129.6, 129.6, 129.4, 128.5, 128.4, 128.3, 128.0, 127.6, 109.6, 93.4, 80.4, 61.1, 49.0, 47.8, 44.8, 36.8, 28.0, 27.3, 21.6, 19.6, 19.0, 18.8, 13.5.

HRMS (m/z, ESI-TOF): Calcd for $\text{C}_{35}\text{H}_{38}\text{SO}_4\text{Na}^+$ [$\text{M}+\text{Na}^+$] 577.2383, found 577.2387.



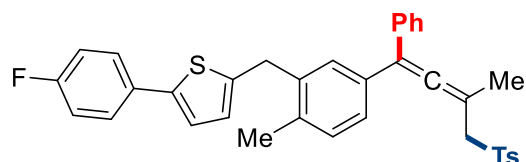
1-chloro-2-(4-ethoxybenzyl)-4-(3-methyl-1-phenyl-4-tosylbuta-1,2-dien-1-yl)benzene (68)

Colorless oil, 21.1mg, 39% yield. (PE/EtOAc = 10/1)

^1H NMR (400 MHz, CDCl_3): δ 7.63 (d, J = 7.9 Hz, 2H), 7.29 – 7.20 (m, 4H), 7.14 – 6.99 (m, 7H), 6.88 (d, J = 8.4 Hz, 1H), 6.81 (d, J = 8.2 Hz, 2H), 4.03 – 3.93 (m, 4H), 3.86 (d, J = 3.0 Hz, 2H), 2.30 (s, 3H), 1.98 (s, 3H), 1.38 (t, J = 7.0 Hz, 3H).

^{13}C NMR (101 MHz, CDCl_3): δ 207.5, 157.4, 144.4, 139.0, 135.6, 135.3, 134.9, 133.1, 131.1, 129.8, 129.5, 129.2, 128.4, 128.2, 128.0, 127.6, 127.5, 114.4, 109.3, 93.1, 63.3, 61.2, 38.3, 21.6, 19.1, 14.8.

HRMS (m/z, ESI-TOF): Calcd for $\text{C}_{33}\text{H}_{31}\text{ClSO}_3\text{Na}^+$ [$\text{M}+\text{Na}^+$] 565.1575, found 565.1586.



2-(4-fluorophenyl)-5-(2-methyl-5-(3-methyl-1-phenyl-4-tosylbuta-1,2-dien-1-yl)benzyl)thiophene (69)

Colorless oil, 14.6mg, 25% yield. (PE/EtOAc = 10/1)

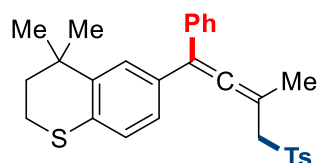
^1H NMR (400 MHz, CDCl_3): δ 7.67 (d, J = 8.0 Hz, 2H), 7.50 – 7.43 (m, 2H), 7.28 – 7.23 (m, 3H), 7.14

– 6.99 (m, 9H), 6.93 (dd, $J = 7.7, 1.9$ Hz, 1H), 6.67 (d, $J = 3.6$ Hz, 1H), 4.08 (s, 2H), 3.89 (d, $J = 3.9$ Hz, 2H), 2.32 (d, $J = 9.0$ Hz, 6H), 2.01 (s, 3H).

^{13}C NMR (101 MHz, CDCl_3): δ 207.6, 162.0 (d, $J = 247.7$ Hz), 144.3, 143.1, 141.5, 138.2, 136.1, 135.7, 135.4, 134.0, 130.7 (d, $J = 3.3$ Hz), 130.4, 129.7, 129.6, 128.6, 128.2, 128.1, 127.3, 127.1, 127.0 (d, $J = 8.0$ Hz), 126.0, 122.6, 115.7 (d, $J = 21.9$ Hz), 109.9, 92.6, 61.5, 34.1, 21.6, 19.2, 19.2.

^{19}F NMR (376 MHz, CDCl_3): δ -115.03.

HRMS (m/z, ESI-TOF): Calcd for $\text{C}_{36}\text{H}_{31}\text{FS}_2\text{O}_2\text{Na}^+$ [$\text{M}+\text{Na}^+$] 601.1642, found 601.1626.



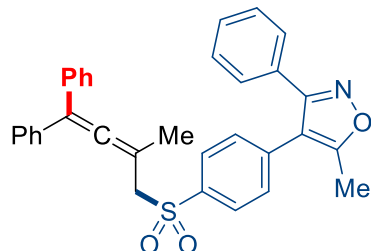
4,4-dimethyl-6-(3-methyl-1-phenyl-4-tosylbuta-1,2-dien-1-yl)thiochromane (70)

Colorless oil, 16.9mg, 35% yield. (PE/EtOAc = 20/1)

^1H NMR (400 MHz, CDCl_3): δ 7.68 (d, $J = 7.9$ Hz, 2H), 7.29 – 7.23 (m, 4H), 7.16 – 7.06 (m, 4H), 6.98 (d, $J = 8.2$ Hz, 1H), 6.74 (dd, $J = 8.2, 2.0$ Hz, 1H), 3.91 (d, $J = 2.4$ Hz, 2H), 3.07 – 2.99 (m, 2H), 2.36 (s, 3H), 2.04 (s, 3H), 1.99 – 1.93 (m, 2H), 1.28 (d, $J = 5.1$ Hz, 6H).

^{13}C NMR (101 MHz, CDCl_3): δ 207.5, 144.4, 141.8, 136.1, 135.5, 131.6, 131.2, 129.6, 128.5, 128.2, 128.1, 127.4, 126.9, 126.3, 126.3, 110.1, 92.6, 61.5, 37.6, 33.0, 30.1, 30.1, 23.1, 21.7, 19.4.

HRMS (m/z, ESI-TOF): Calcd for $\text{C}_{29}\text{H}_{30}\text{S}_2\text{O}_2\text{Na}^+$ [$\text{M}+\text{Na}^+$] 497.1579, found 497.1567.



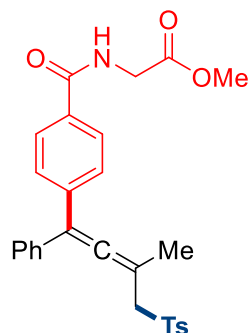
5-methyl-4-(4-((2-methyl-4,4-diphenylbuta-2,3-dien-1-yl)sulfonyl)phenyl)-3-phenylisoxazole (71)

Colorless oil, 22.9mg, 44% yield. (PE/EtOAc = 8/1)

^1H NMR (400 MHz, CDCl_3): δ 7.80 (d, $J = 8.5$ Hz, 2H), 7.37 – 7.20 (m, 16H), 7.10 (d, $J = 8.4$ Hz, 2H), 3.95 (s, 2H), 2.40 (s, 3H), 2.05 (s, 3H).

^{13}C NMR (101 MHz, CDCl_3): δ 207.5, 167.2, 160.9, 137.7, 136.0, 136.0, 130.0, 129.6, 128.6, 128.6, 128.5, 128.3, 128.3, 127.5, 114.2, 110.5, 92.4, 61.5, 19.7, 11.8.

HRMS (m/z, ESI-TOF): Calcd for $\text{C}_{33}\text{H}_{27}\text{NSO}_3\text{Na}^+$ [$\text{M}+\text{Na}^+$] 540.1604, found 540.1616.



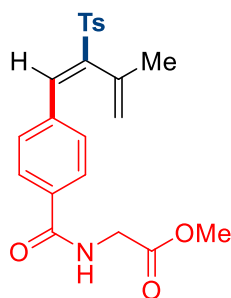
methyl (4-(3-methyl-1-phenyl-4-tosylbuta-1,2-dien-1-yl)benzoyl)glycinate (72)

White solid, 36.3mg, 74% yield. (PE/EtOAc = 5/1)

¹H NMR (400 MHz, CDCl₃): δ 7.74 (d, *J* = 8.0 Hz, 2H), 7.67 (d, *J* = 7.9 Hz, 2H), 7.32 – 7.25 (m, 4H), 7.17 (d, *J* = 8.0 Hz, 3H), 7.10 (d, *J* = 7.4 Hz, 5H), 4.22 (d, *J* = 5.3 Hz, 2H), 4.00 – 3.87 (m, 2H), 3.76 (s, 3H), 2.33 (s, 3H), 2.05 (s, 3H).

¹³C NMR (101 MHz, CDCl₃): δ 207.7, 170.3, 166.9, 144.6, 139.7, 135.4, 135.0, 132.3, 129.6, 128.5, 128.4, 128.3, 127.9, 127.6, 127.0, 109.5, 93.2, 61.0, 52.2, 41.5, 21.5, 19.0.

HRMS (m/z, ESI-TOF): Calcd for C₂₈H₂₇NSO₅Na⁺ [M+Na⁺] 512.1502, found 512.1506.



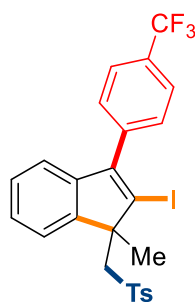
methyl (*E*)-(4-(3-methyl-2-tosylbuta-1,3-dien-1-yl)benzoyl)glycinate (73)

White solid, 8.2mg, 20% yield. (PE/EtOAc = 8/1)

¹H NMR (400 MHz, CDCl₃): δ 7.80 (d, *J* = 8.2 Hz, 2H), 7.77 (d, *J* = 8.0 Hz, 2H), 7.72 (s, 1H), 7.66 (d, *J* = 8.2 Hz, 2H), 7.32 (d, *J* = 7.9 Hz, 2H), 6.72 (t, *J* = 5.0 Hz, 1H), 5.28 (s, 1H), 4.83 (s, 1H), 4.25 (d, *J* = 5.0 Hz, 2H), 3.81 (s, 3H), 2.44 (s, 3H), 1.75 (s, 3H).

¹³C NMR (101 MHz, CDCl₃): δ 170.3, 166.5, 144.4, 136.4, 136.2, 135.2, 134.6, 134.2, 130.0, 129.5, 129.0, 127.4, 122.3, 52.5, 41.7, 22.7, 21.6.

HRMS (m/z, ESI-TOF): Calcd for C₂₂H₂₃NSO₅Na⁺ [M+Na⁺] 436.1189, found 436.1183.



2-iodo-1-methyl-1-(tosylmethyl)-3-(4-(trifluoromethyl)phenyl)-1H-indene (74)

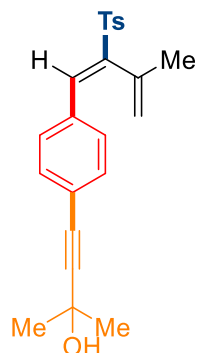
White solid, 49.8mg, 88% yield. (PE/EtOAc = 8/1)

¹H NMR (400 MHz, CDCl₃): δ 7.75 (d, *J* = 8.0 Hz, 2H), 7.60 (d, *J* = 8.0 Hz, 2H), 7.31 (d, *J* = 8.4 Hz, 2H), 7.16 (d, *J* = 7.5 Hz, 2H), 7.12 – 7.02 (m, 3H), 6.96 (td, *J* = 7.4, 1.2 Hz, 1H), 3.76 (q, *J* = 14.8 Hz, 2H), 2.35 (s, 3H), 1.34 (s, 3H).

¹³C NMR (101 MHz, CDCl₃): δ 146.6, 146.2, 144.0, 142.4, 138.8 (q, *J* = 1.8 Hz), 137.0, 130.2 (q, *J* = 32.7 Hz), 129.4, 127.7, 127.4, 125.7, 125.4 (q, *J* = 3.8 Hz), 123.5, 124.1 (q, *J* = 273.1 Hz), 120.1, 112.9, 62.3, 54.4, 26.5, 21.5.

¹⁹F NMR (376 MHz, CDCl₃): δ -62.50.

HRMS (m/z, ESI-TOF): Calcd for C₂₅H₂₀F₃ISO₂Na⁺ [M+Na⁺] 591.0073, found 591.0073.



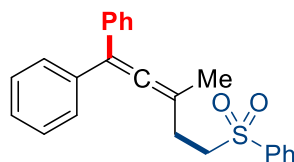
(E)-2-methyl-4-(4-(3-methyl-2-tosylbuta-1,3-dien-1-yl)phenyl)but-3-yn-2-ol (75)

White solid, 35.0mg, **92%** yield. (PE/EtOAc = 5/1)

¹H NMR (400 MHz, CDCl₃): δ 7.76 (d, *J* = 8.0 Hz, 2H), 7.66 (s, 1H), 7.52 (d, *J* = 8.1 Hz, 2H), 7.38 (d, *J* = 8.1 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 5.26 (s, 1H), 4.81 (s, 1H), 2.42 (s, 3H), 2.24 (s, 1H), 1.74 (s, 3H), 1.61 (s, 6H).

¹³C NMR (101 MHz, CDCl₃): δ 144.2, 143.0, 136.4, 135.5, 134.7, 132.8, 131.8, 129.7, 129.4, 128.9, 124.5, 122.1, 96.0, 81.5, 65.6, 31.4, 31.0, 22.6, 21.6.

HRMS (m/z, ESI-TOF): Calcd for C₂₃H₂₄SO₃Na⁺ [M+Na⁺] 403.1338, found 403.1345.



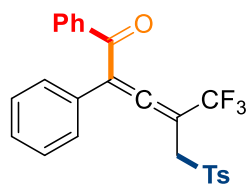
(3-methyl-5-(phenylsulfonyl)penta-1,2-diene-1,1-diyl)dibenzene (76)

Colorless oil, 17.4mg, **46%** yield. (PE/EtOAc = 20/1)

¹H NMR (400 MHz, CDCl₃): δ 7.93 – 7.86 (m, 2H), 7.66 (t, *J* = 7.4 Hz, 1H), 7.55 (t, *J* = 7.7 Hz, 2H), 7.36 – 7.21 (m, 10H), 3.34 – 3.22 (m, 2H), 2.56 – 2.45 (m, 2H), 1.87 (s, 3H).

¹³C NMR (101 MHz, CDCl₃): δ 201.8, 138.6, 136.9, 133.8, 129.3, 128.3, 128.3, 128.1, 127.3, 111.3, 100.3, 54.2, 27.2, 19.3.

HRMS (m/z, ESI-TOF): Calcd for C₂₄H₂₂SO₂Na⁺ [M+Na⁺] 397.1233, found 397.1233.



5,5,5-trifluoro-1,2-diphenyl-4-(tosylmethyl)penta-2,3-dien-1-one (77)

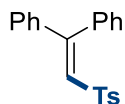
Colorless oil, 9.5mg, **21%** yield. (PE/EtOAc = 15/1)

¹H NMR (400 MHz, CDCl₃): δ 7.95 (d, *J* = 7.7 Hz, 2H), 7.65 (t, *J* = 7.4 Hz, 1H), 7.55 – 7.47 (m, 4H), 7.45 – 7.35 (m, 5H), 7.13 (d, *J* = 7.9 Hz, 2H), 3.94 (s, 2H), 2.37 (s, 3H).

¹³C NMR (101 MHz, CDCl₃): δ 209.3 (q, *J* = 3.5 Hz), 189.6, 145.3, 136.8, 134.6, 134.2, 130.0, 129.8, 129.7, 129.5, 129.0, 128.8, 128.3, 128.3, 121.9 (q, *J* = 276.5 Hz), 115.8, 94.5 (q, *J* = 37.5 Hz), 53.6, 21.7.

¹⁹F NMR (376 MHz, CDCl₃): δ -62.15.

HRMS (m/z, ESI-TOF): Calcd for C₂₅H₁₉F₃SO₃Na⁺ [M+Na⁺] 479.0899, found 479.0902.



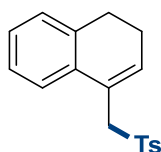
(2-tosylethene-1,1-diyl)dibenzene (78)

Colorless oil, 10.0mg, **30%** yield. (PE/EtOAc = 15/1)

¹H NMR (400 MHz, CDCl₃): δ 7.47 (d, *J* = 8.3 Hz, 2H), 7.40 – 7.34 (m, 2H), 7.33 – 7.27 (m, 4H), 7.22 – 7.18 (m, 2H), 7.15 (d, *J* = 8.1 Hz, 2H), 7.12 – 7.07 (m, 2H), 6.99 (s, 1H), 2.38 (s, 3H).

¹³C NMR (101 MHz, CDCl₃): δ 154.7, 143.7, 139.2, 138.5, 135.5, 130.2, 129.7, 129.3, 128.9, 128.8, 128.5, 128.2, 127.8, 127.7, 21.5.

HRMS (m/z, ESI-TOF): Calcd for C₂₁H₁₈SO₂Na⁺ [M+Na⁺] 357.0920, found 357.0922.



4-(tosylmethyl)-1,2-dihydronaphthalene (79)

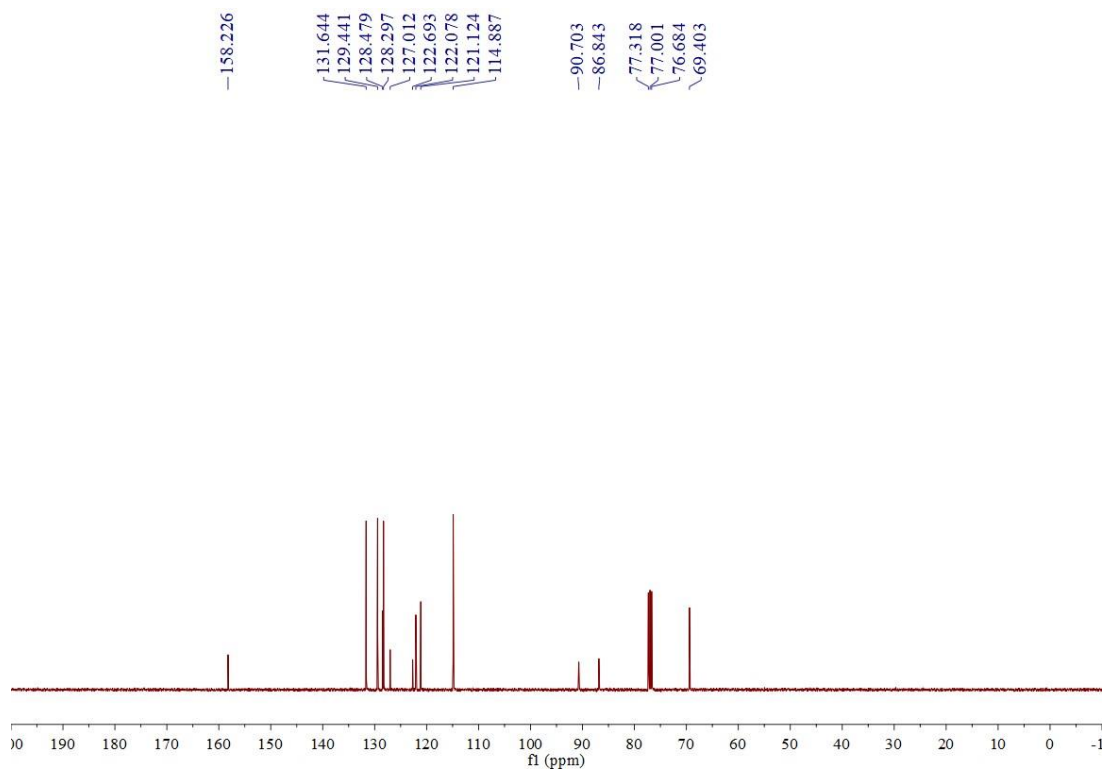
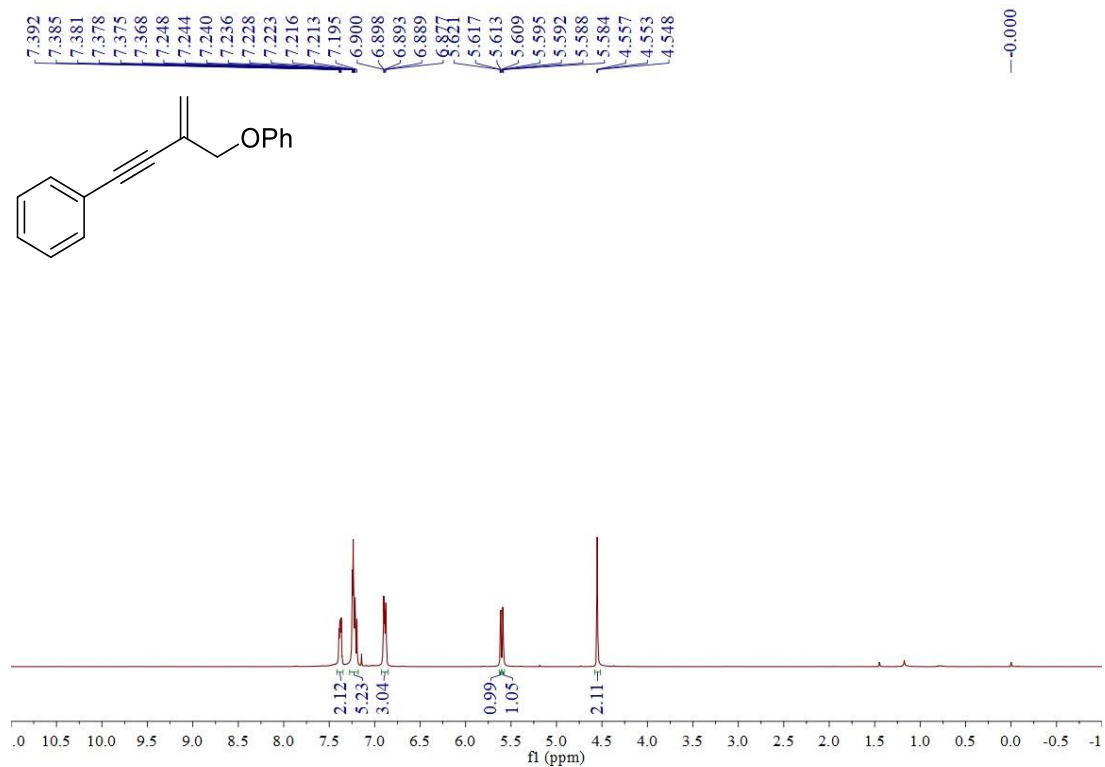
Colorless oil, 11.4mg, **38%** yield. (PE/EtOAc = 20/1)

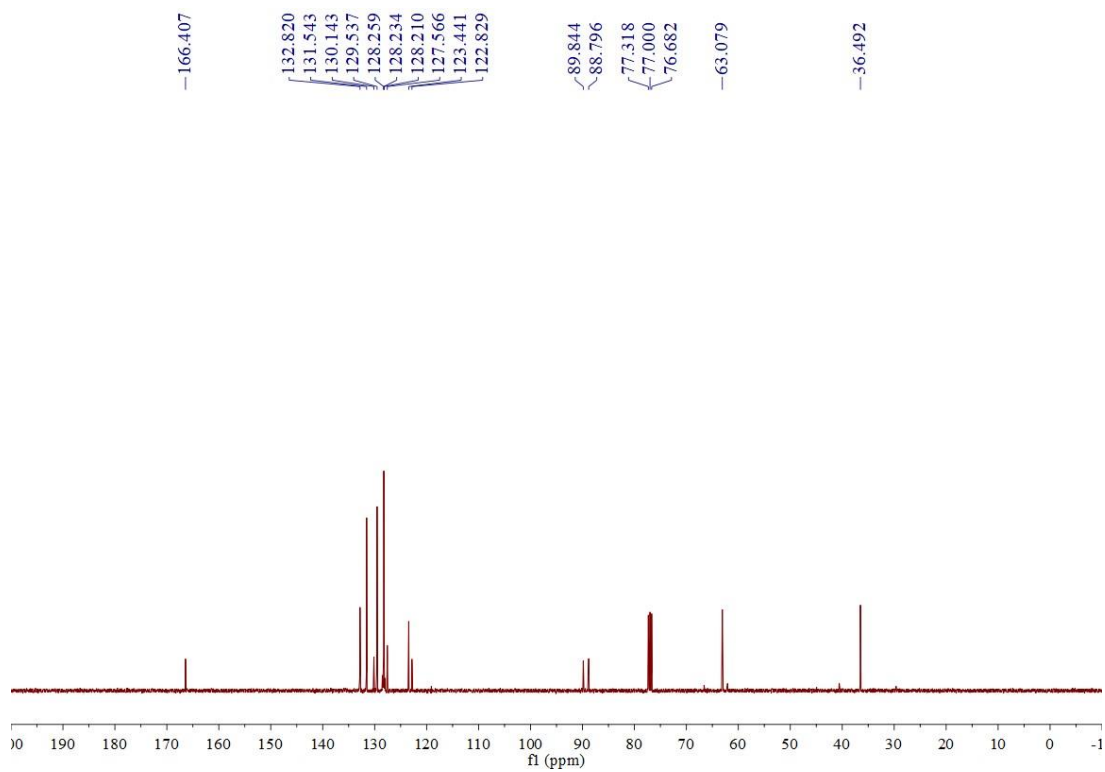
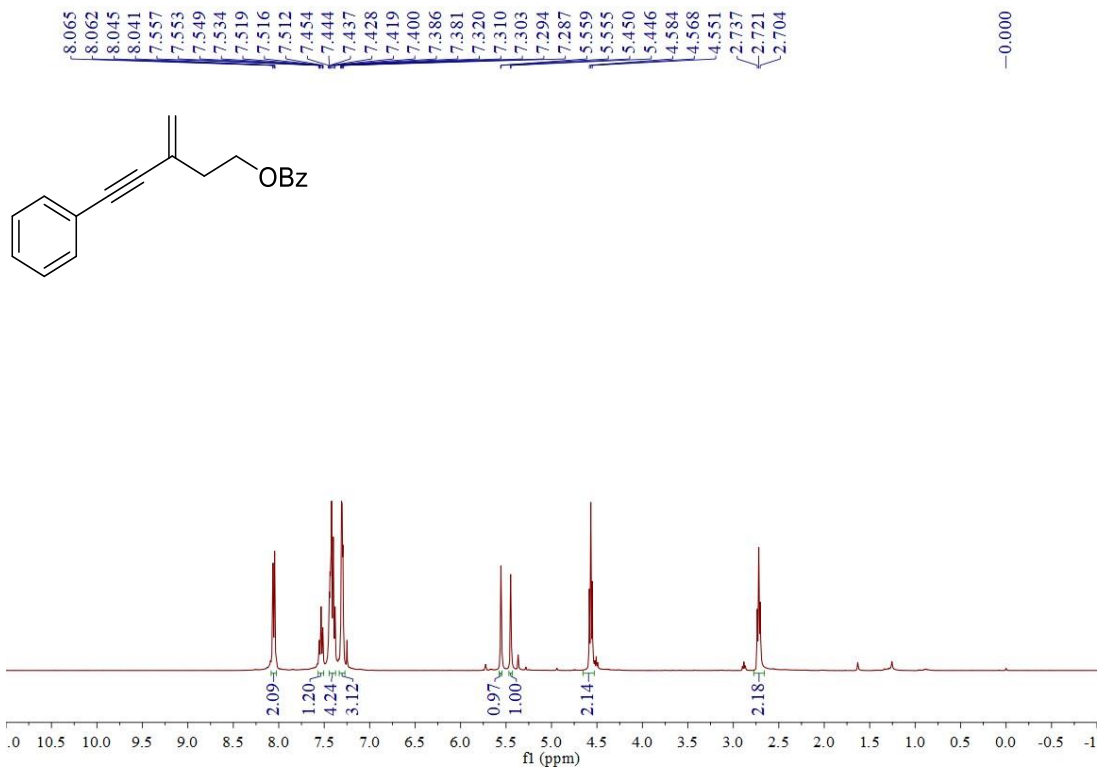
¹H NMR (400 MHz, CDCl₃): δ 7.67 (d, *J* = 8.0 Hz, 2H), 7.22 (d, *J* = 8.0 Hz, 2H), 7.17 – 7.05 (m, 4H), 5.90 (t, *J* = 4.7 Hz, 1H), 4.20 (s, 2H), 2.69 (t, *J* = 8.1 Hz, 2H), 2.38 (s, 3H), 2.28 – 2.17 (m, 2H).

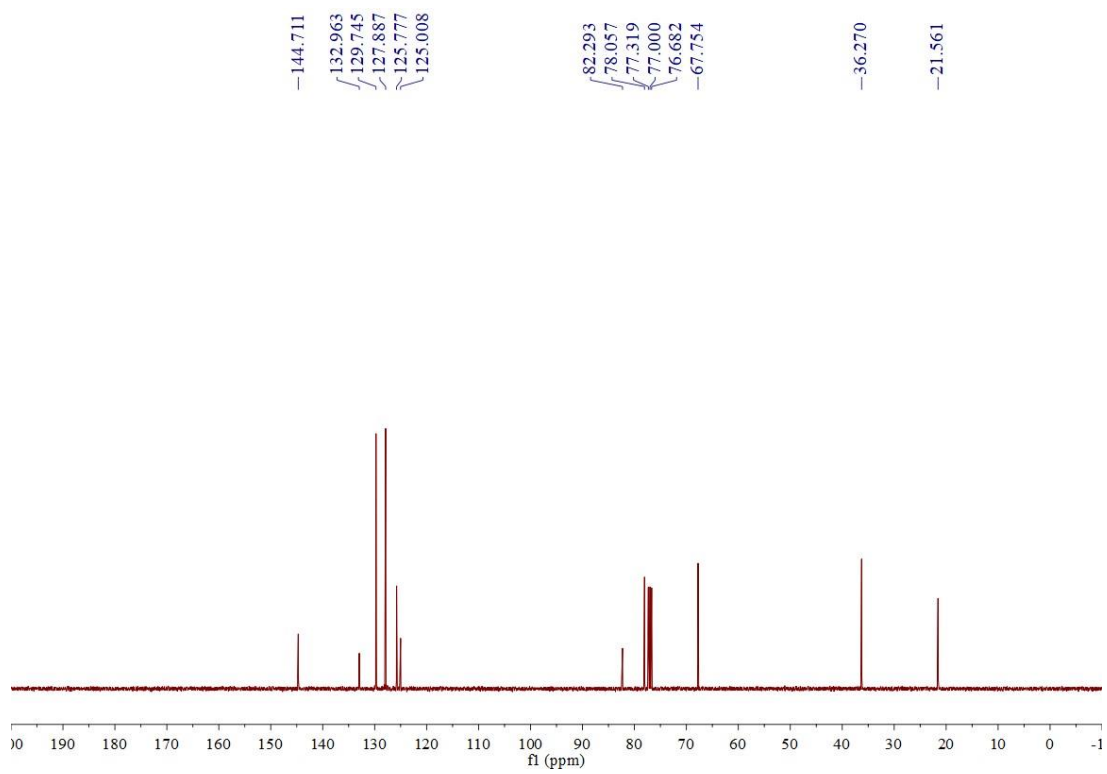
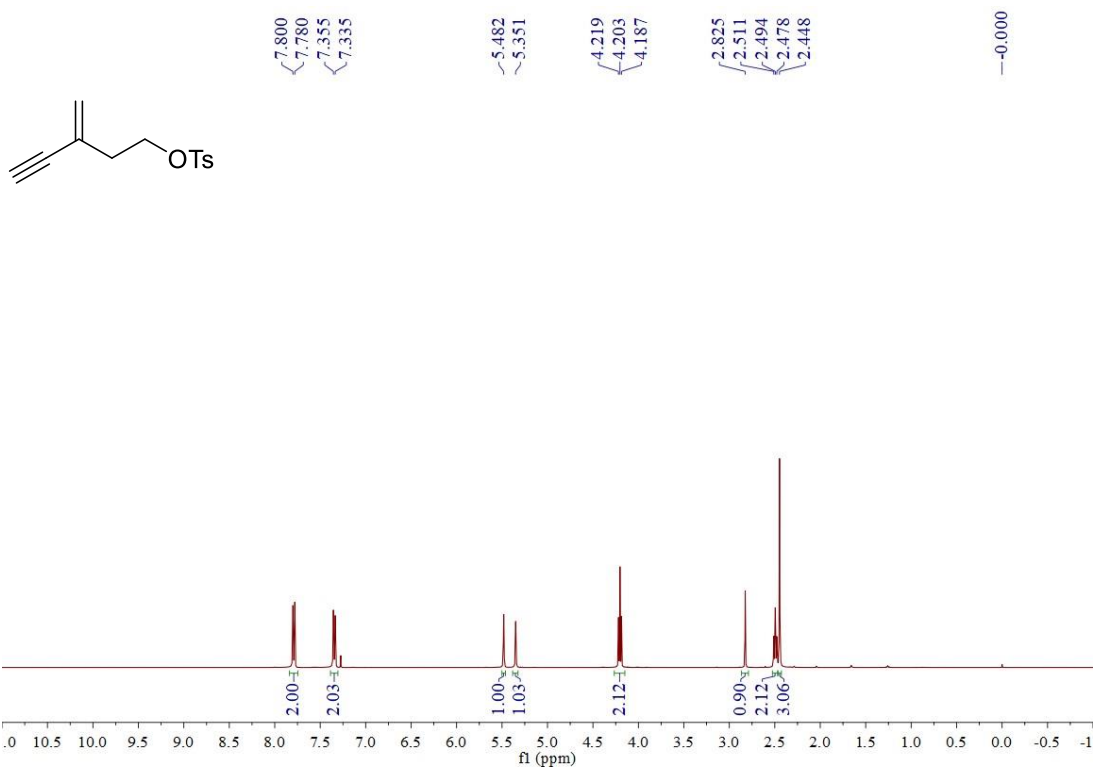
¹³C NMR (101 MHz, CDCl₃): δ 144.5, 135.9, 135.3, 134.8, 132.6, 129.4, 128.7, 127.5, 127.2, 126.3, 125.8, 123.1, 59.9, 27.7, 23.3, 21.5.

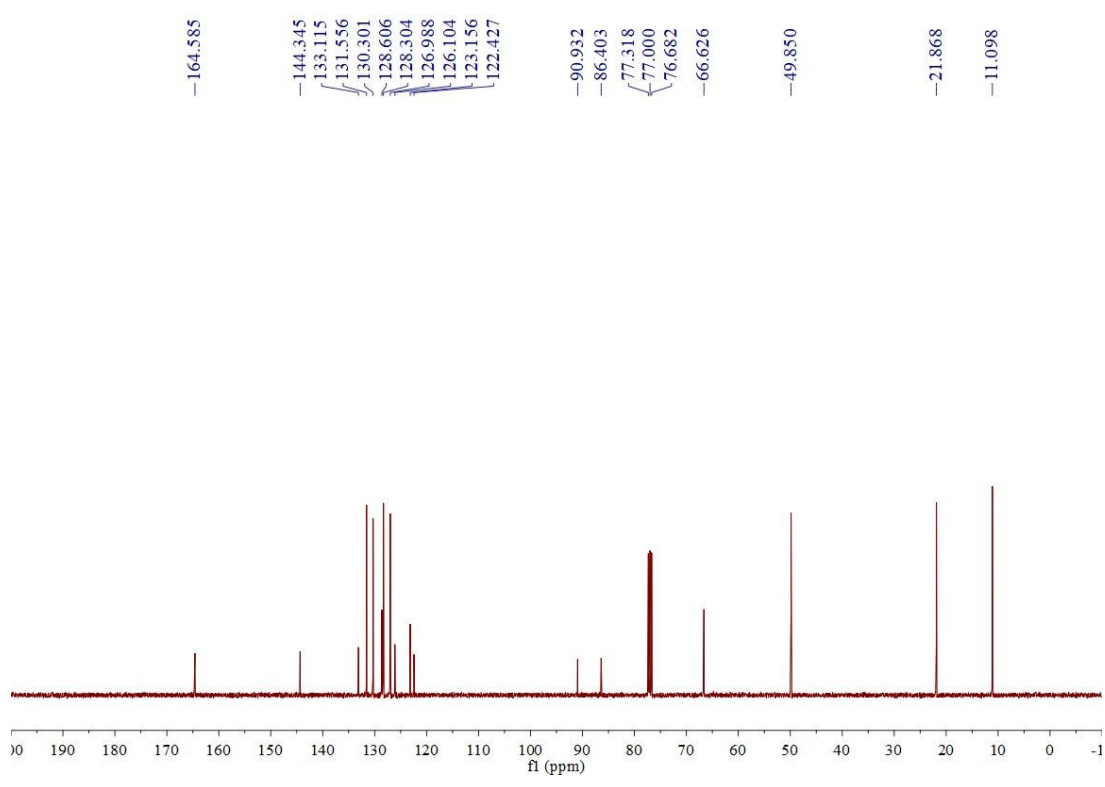
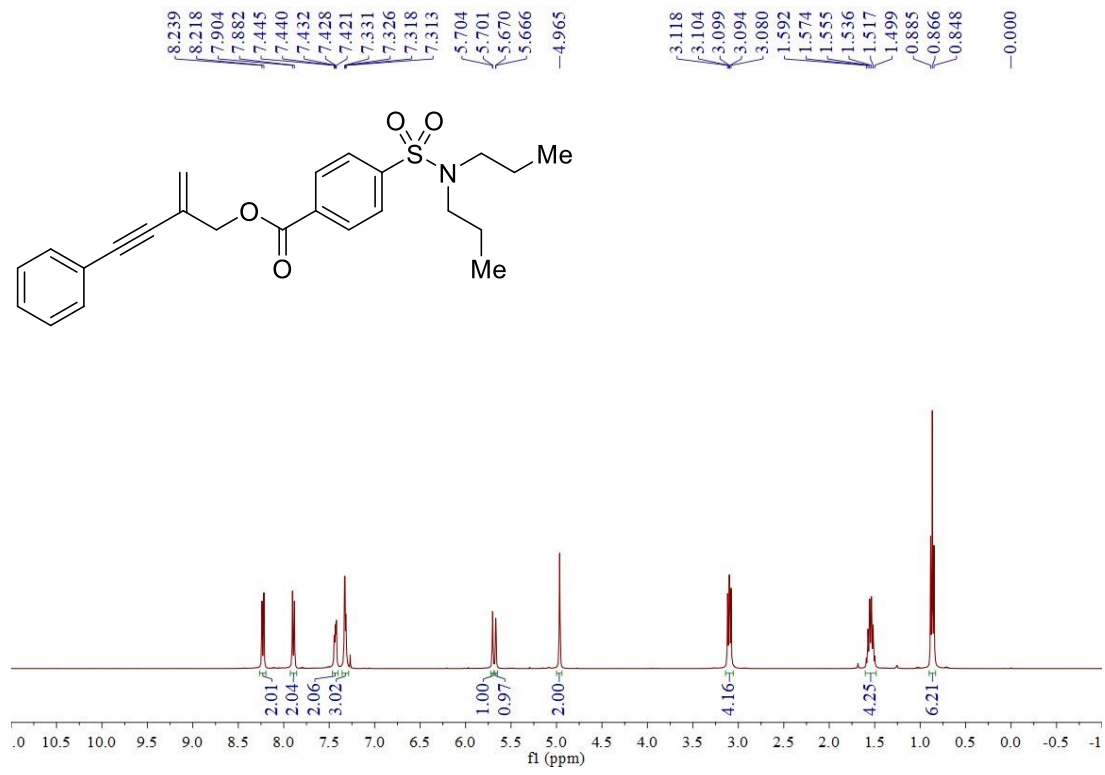
HRMS (m/z, ESI-TOF): Calcd for C₁₈H₁₈SO₂Na⁺ [M+Na⁺] 321.0920, found 321.0925.

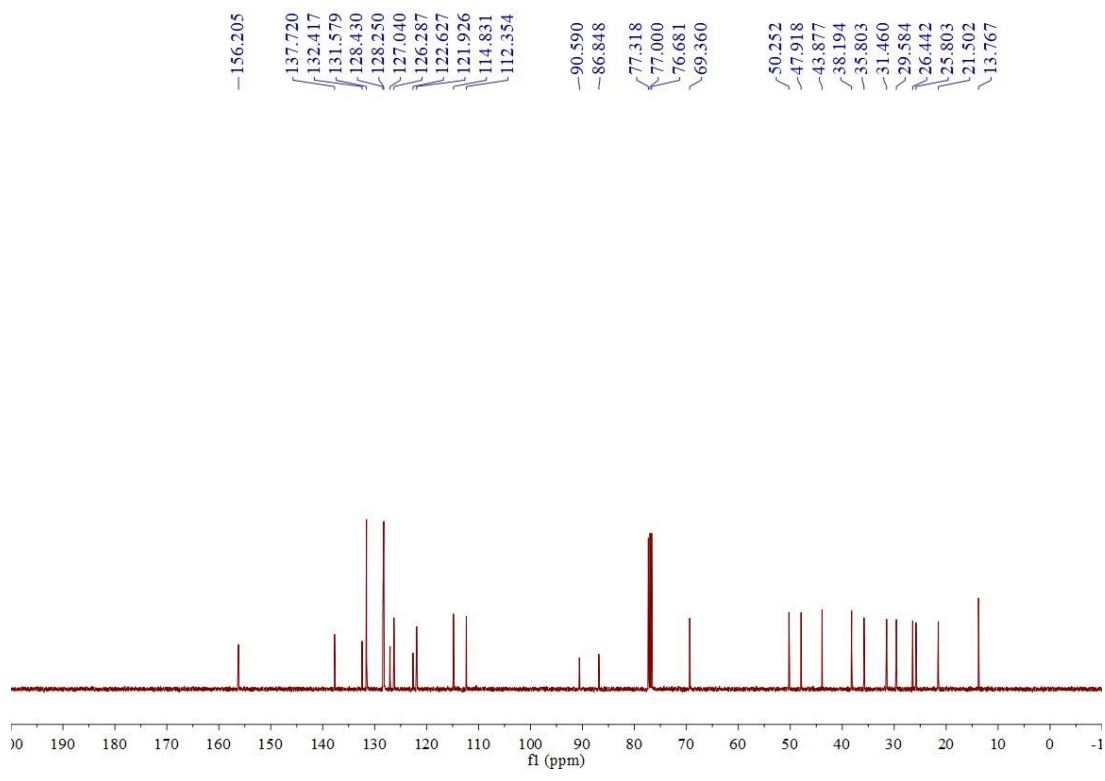
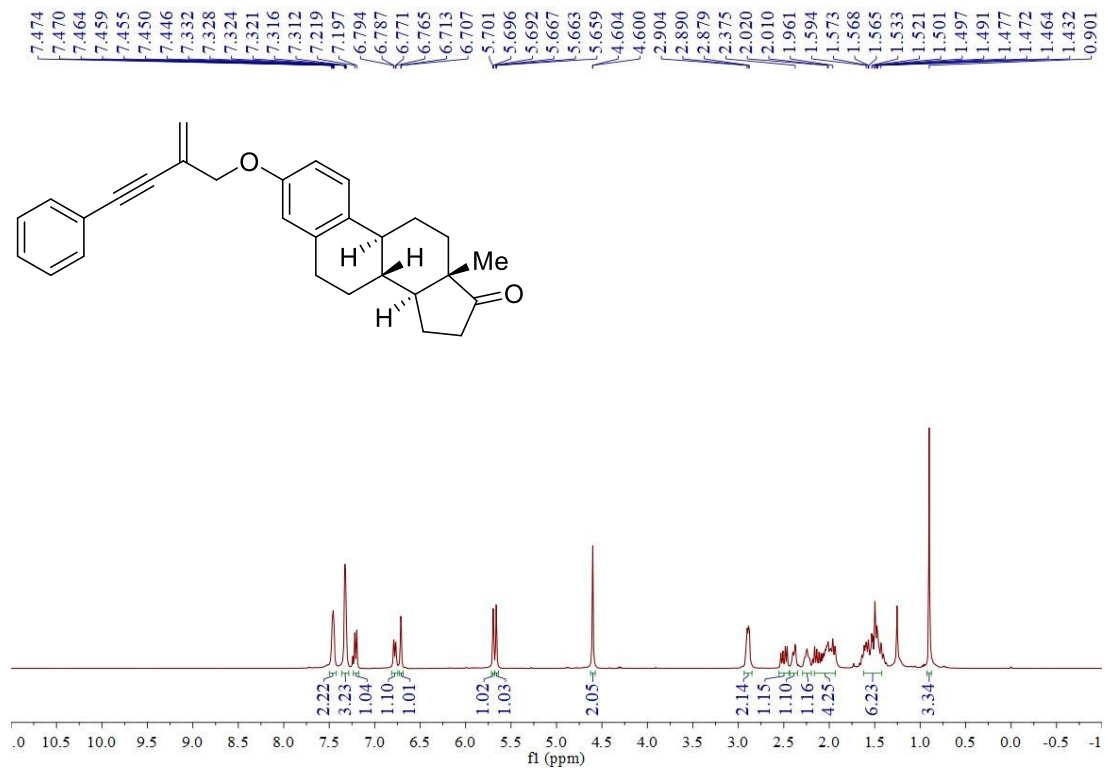
5. NMR Spectra of Compounds

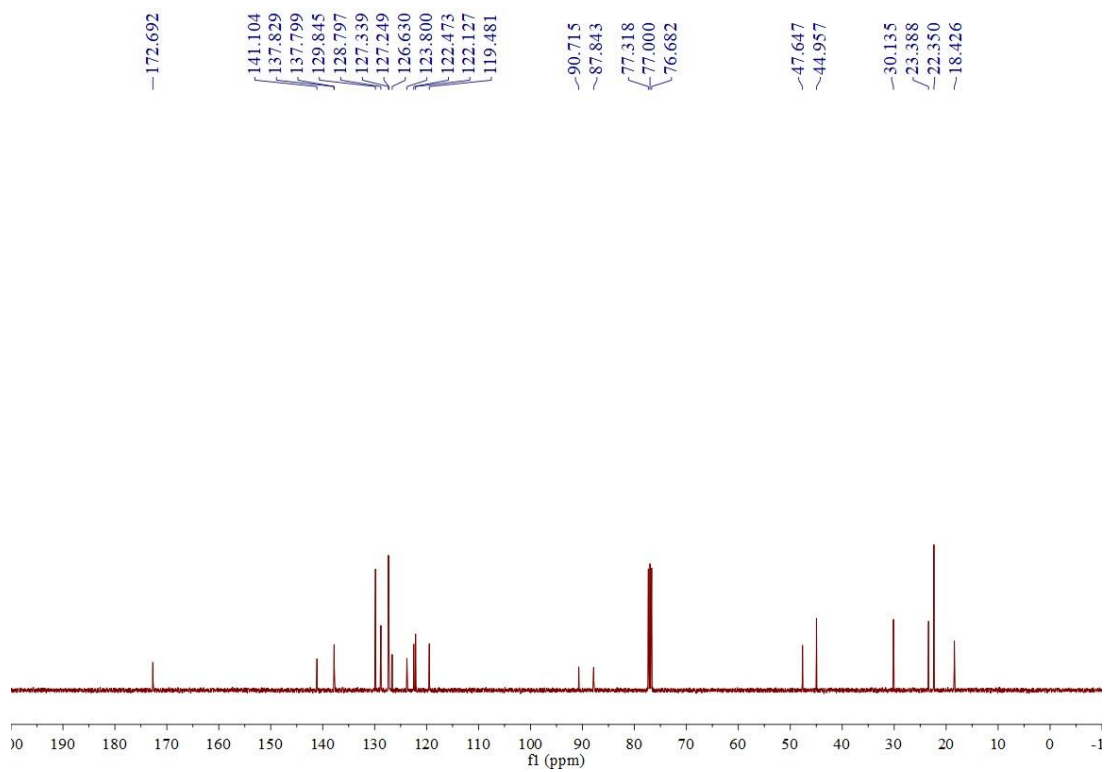
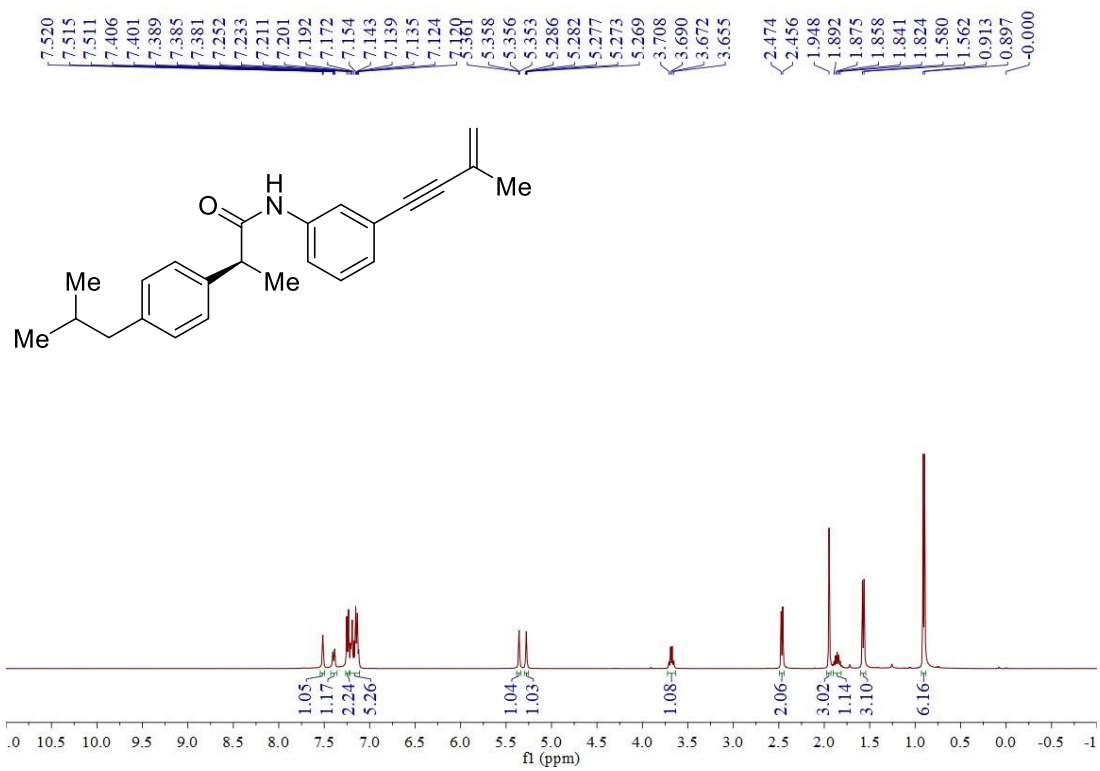


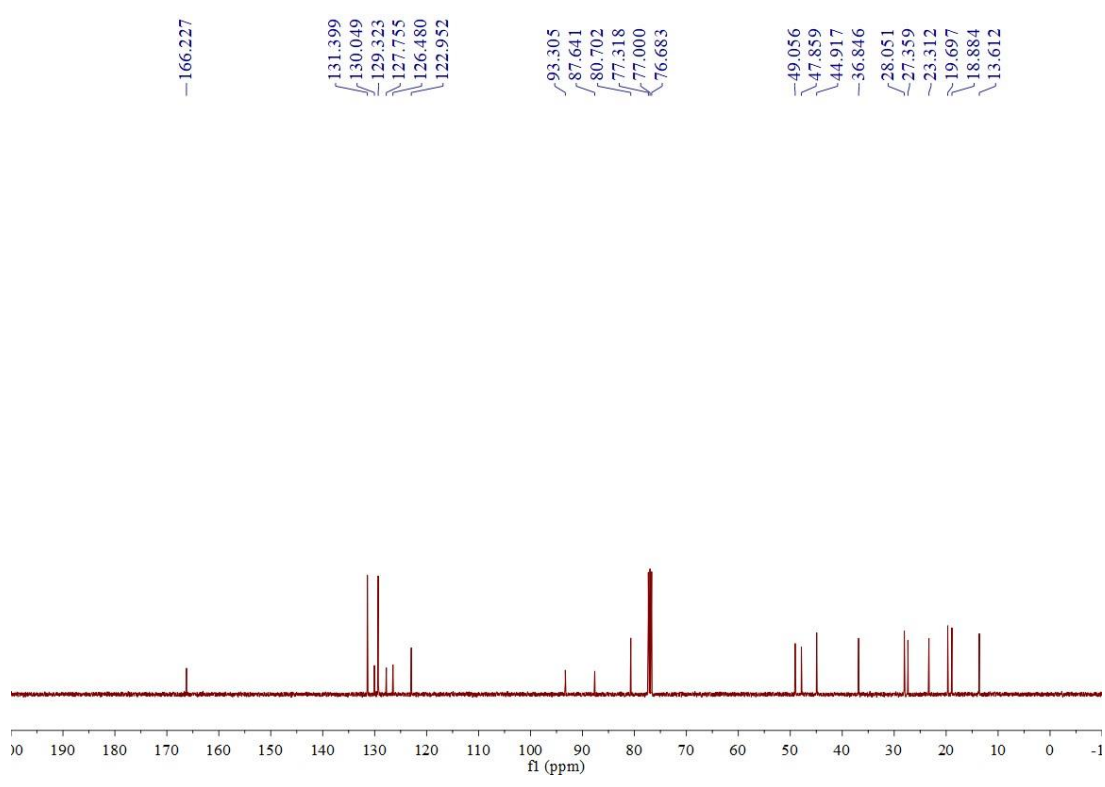
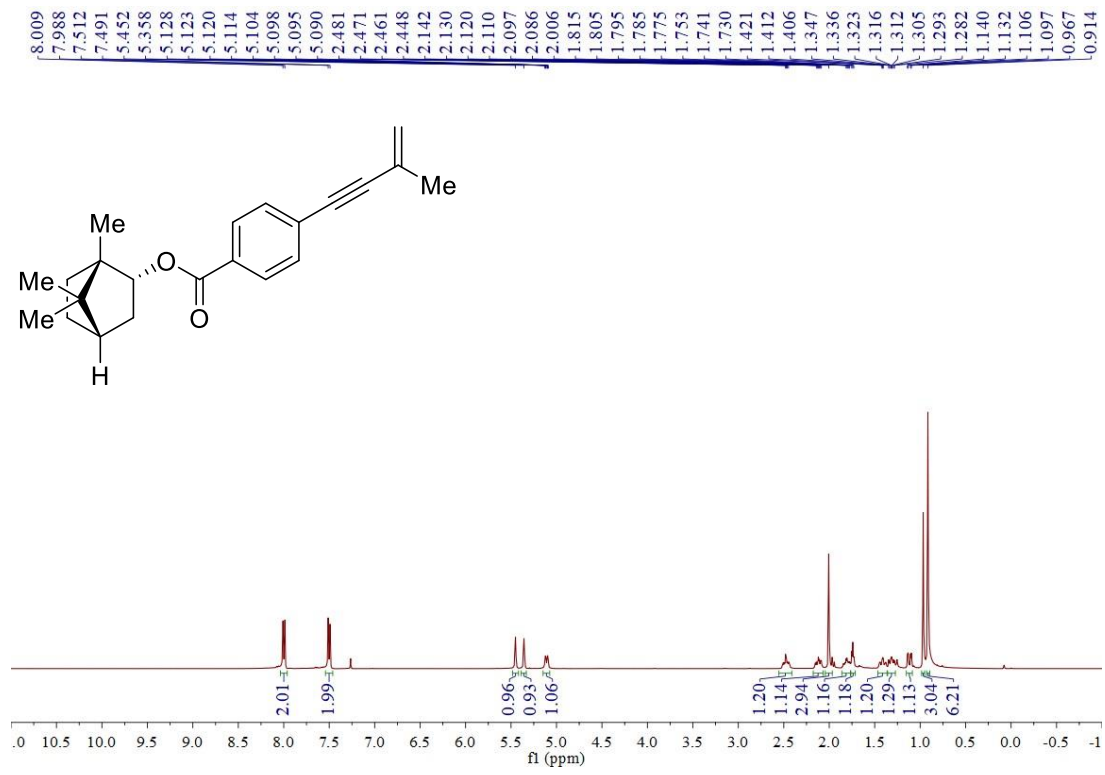


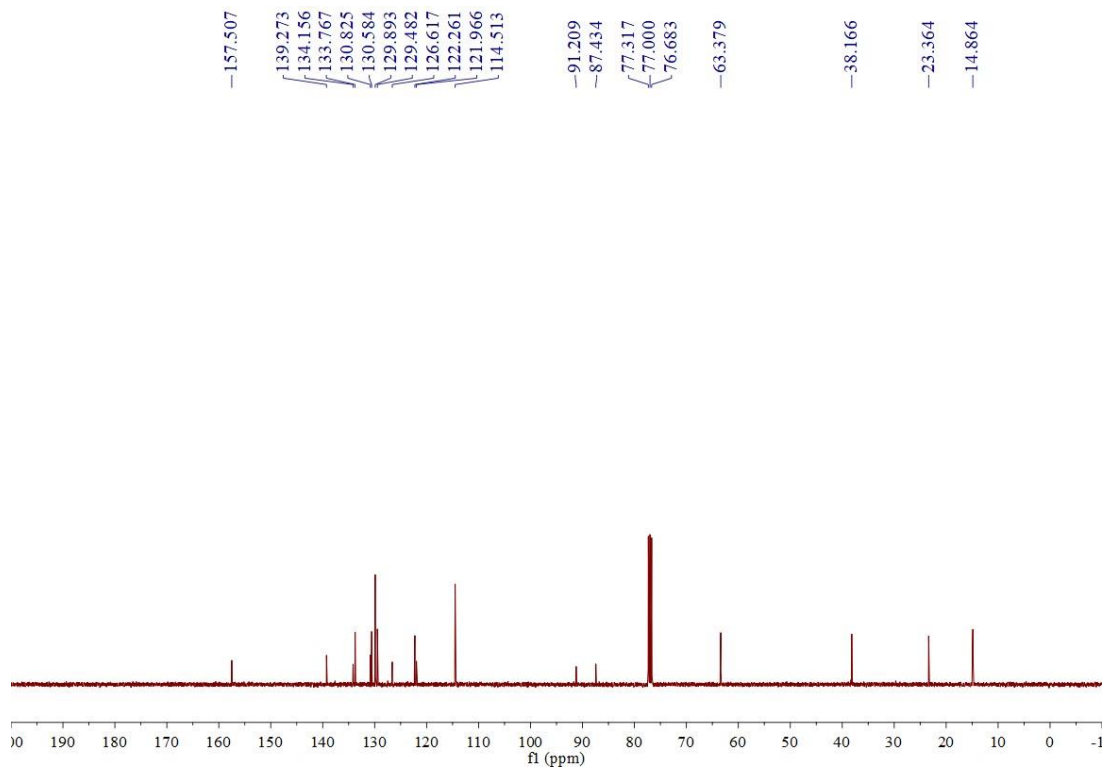
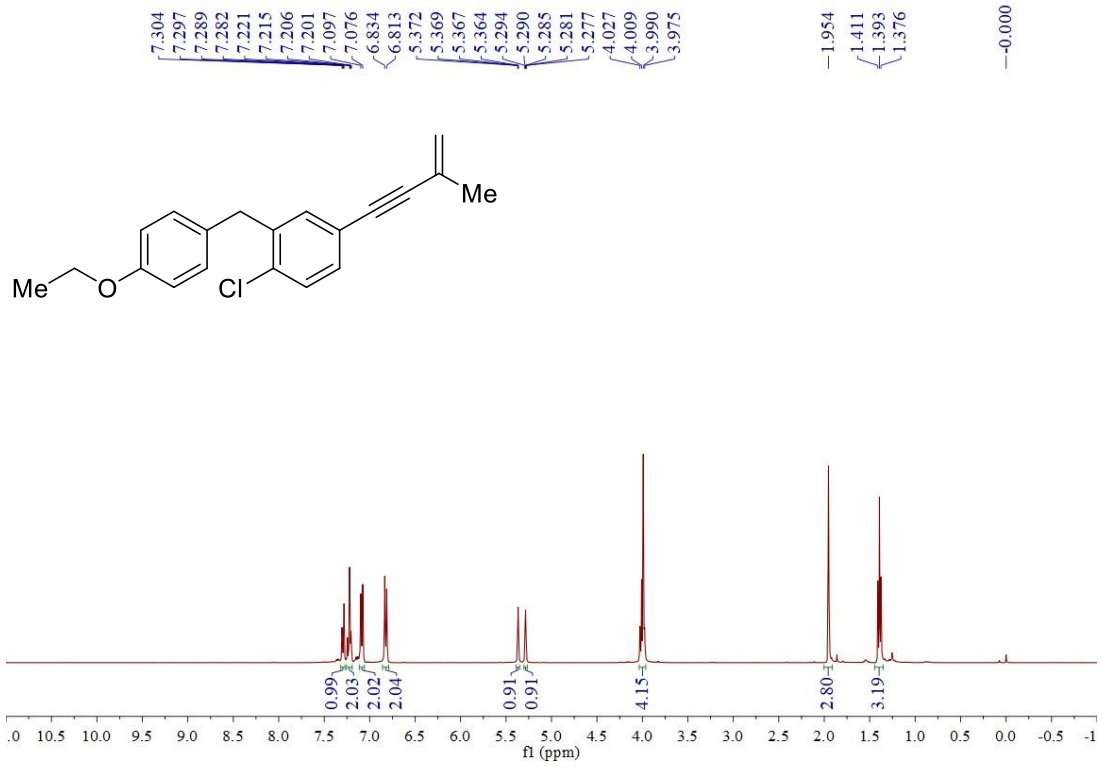


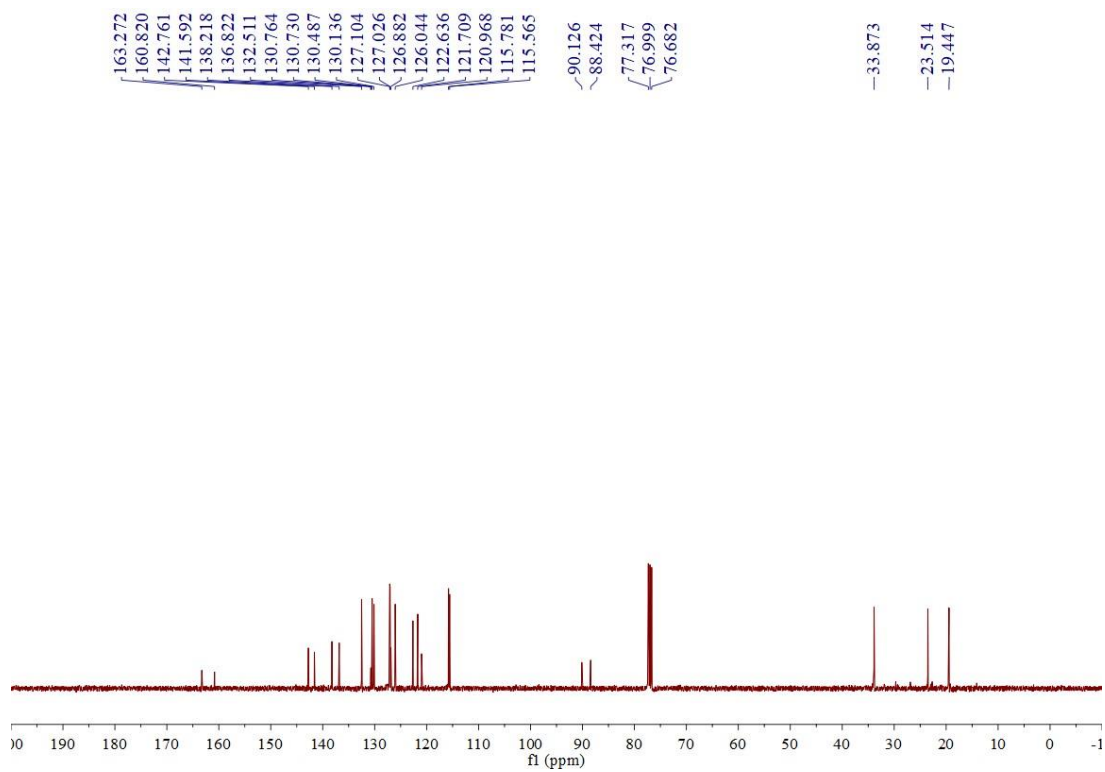
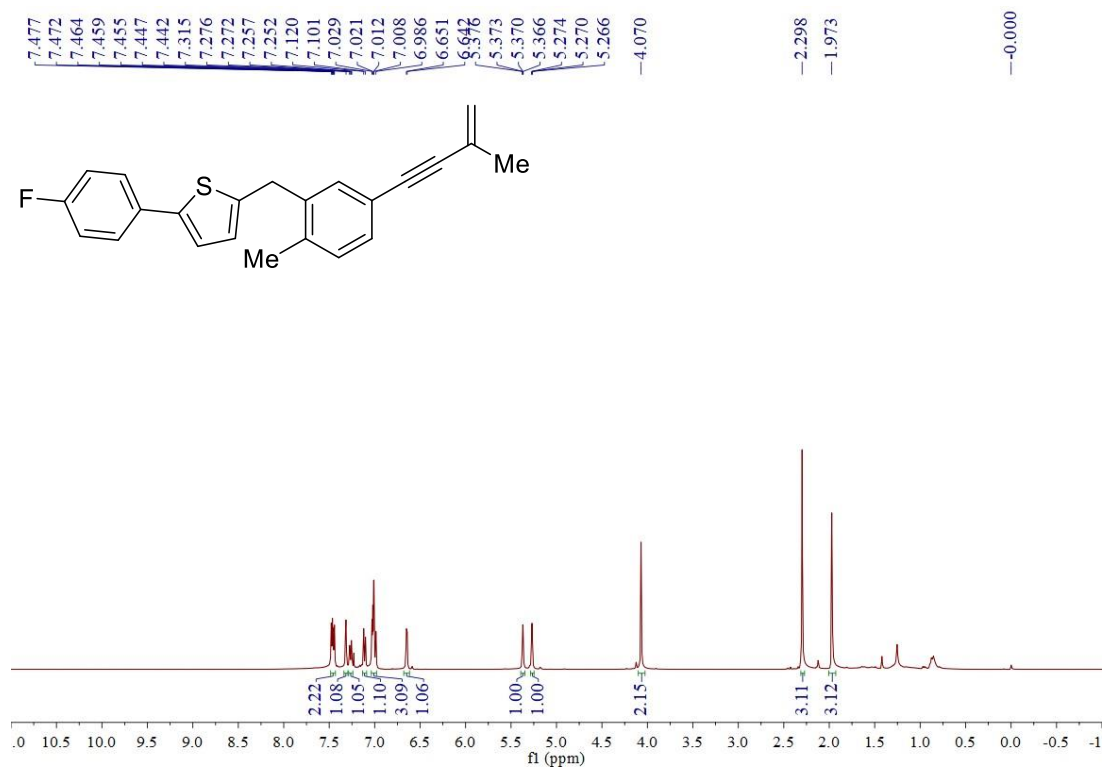


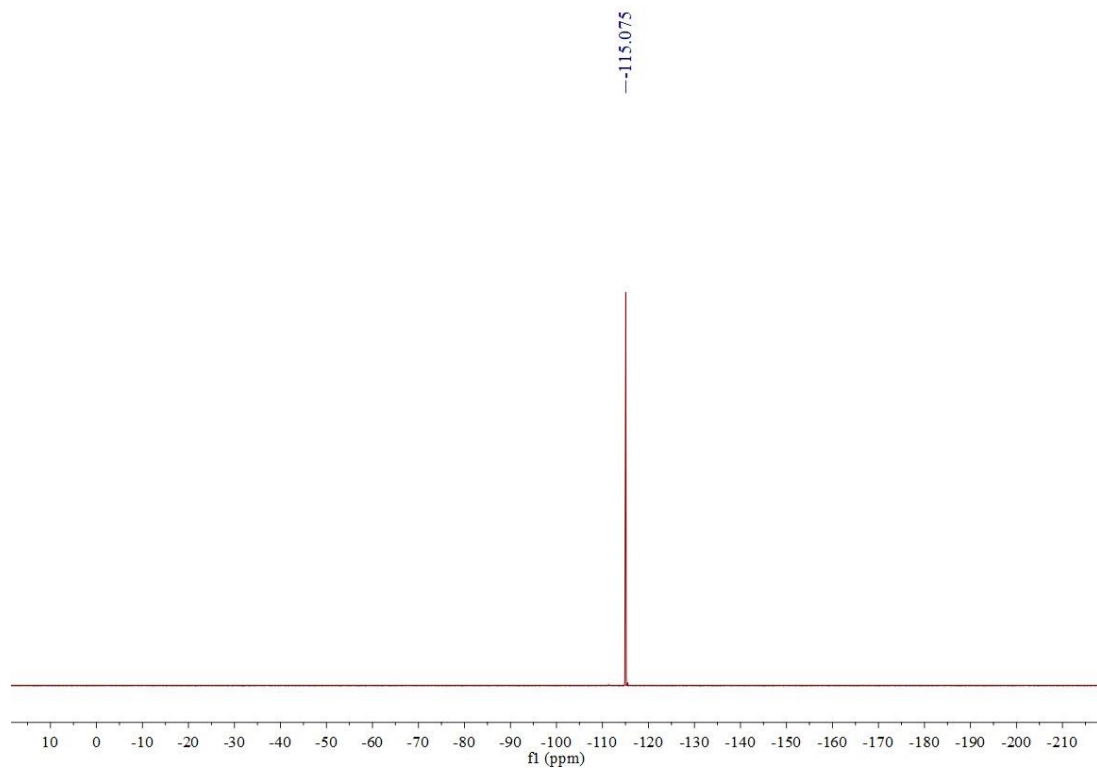




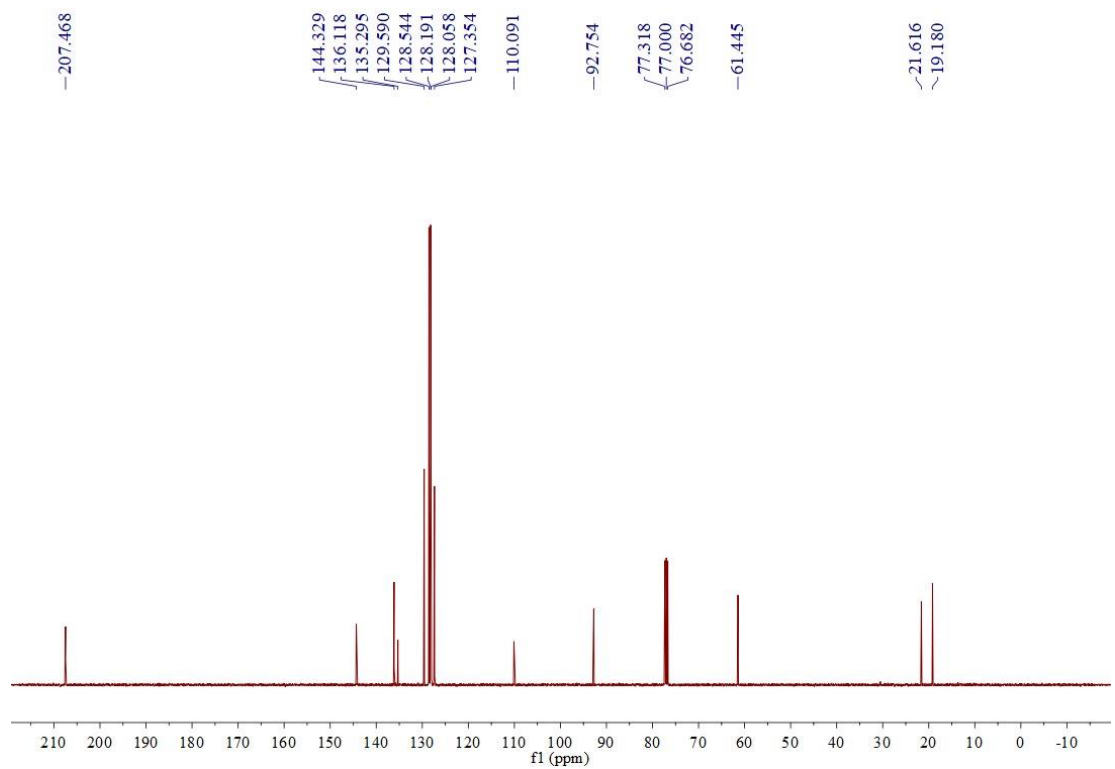
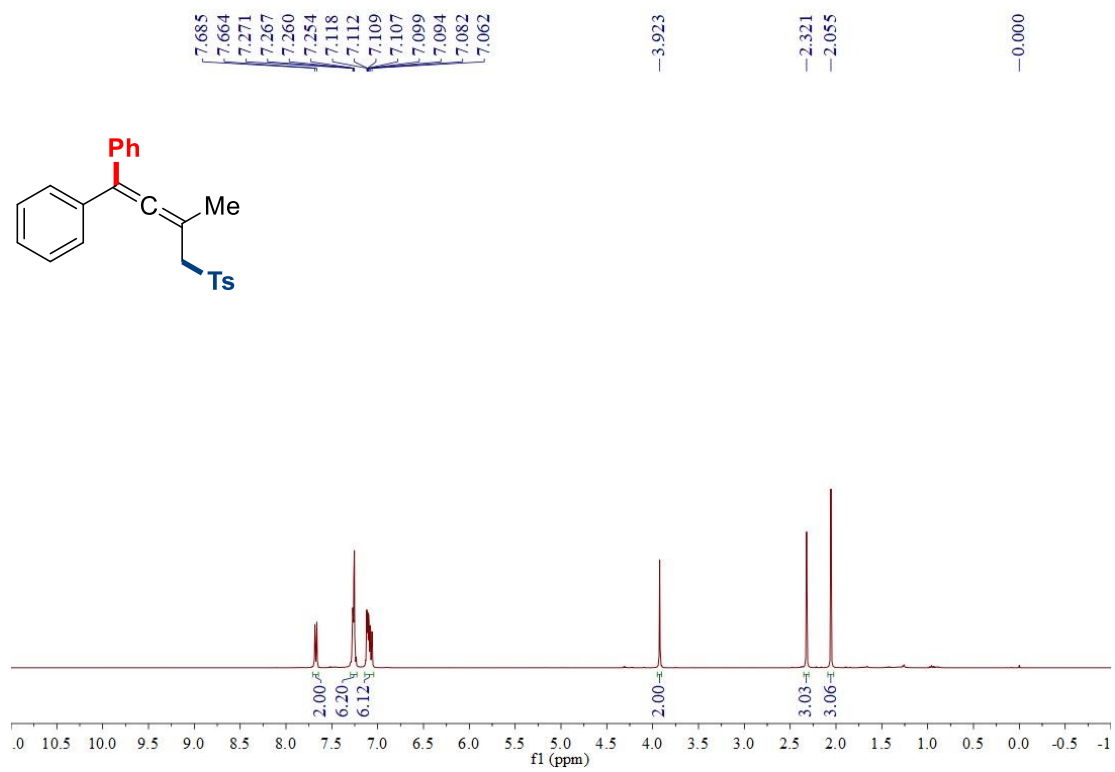


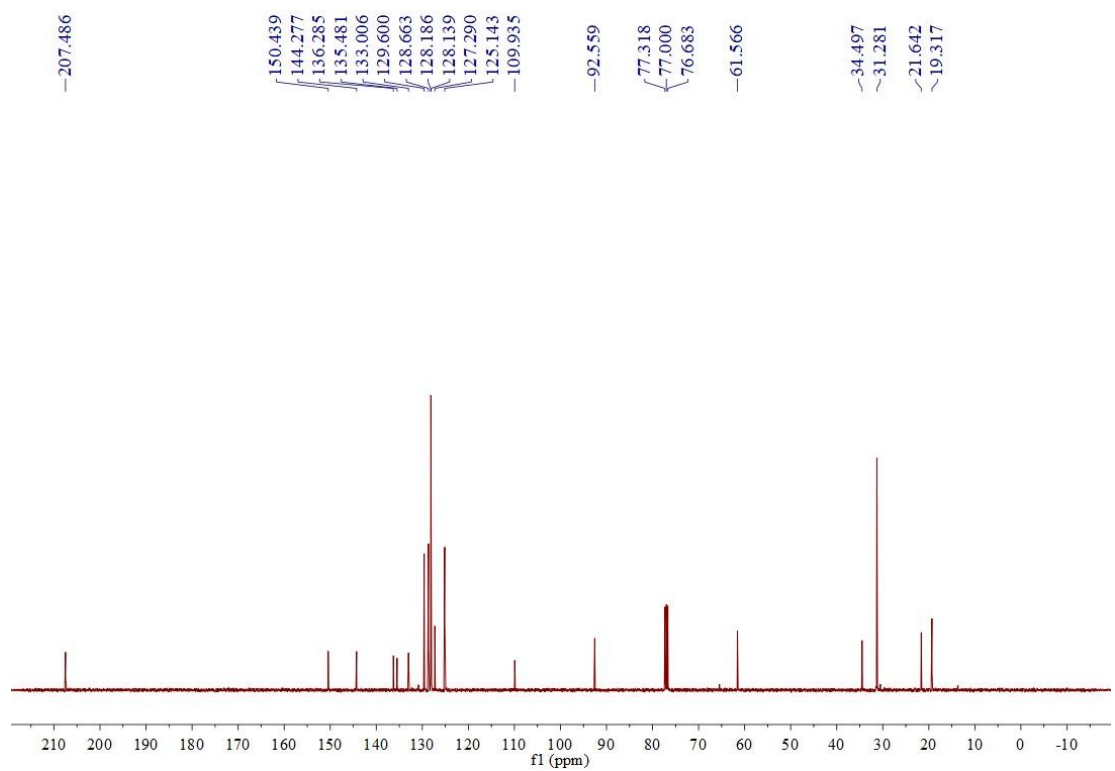
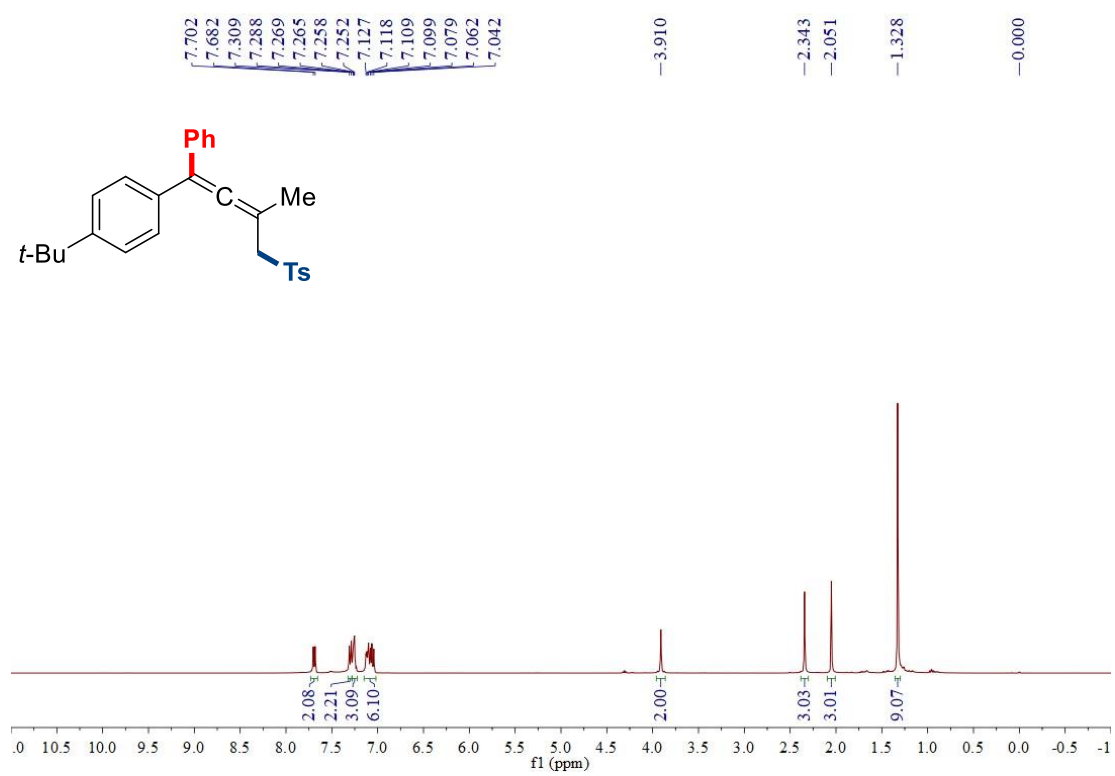




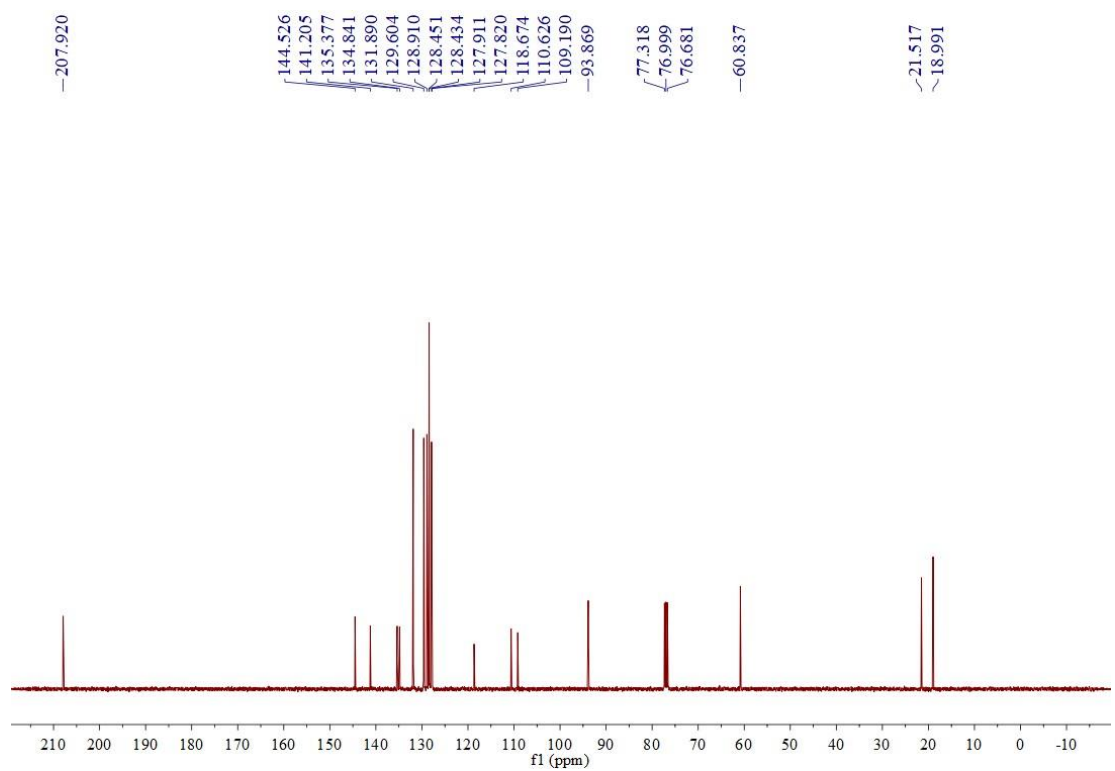
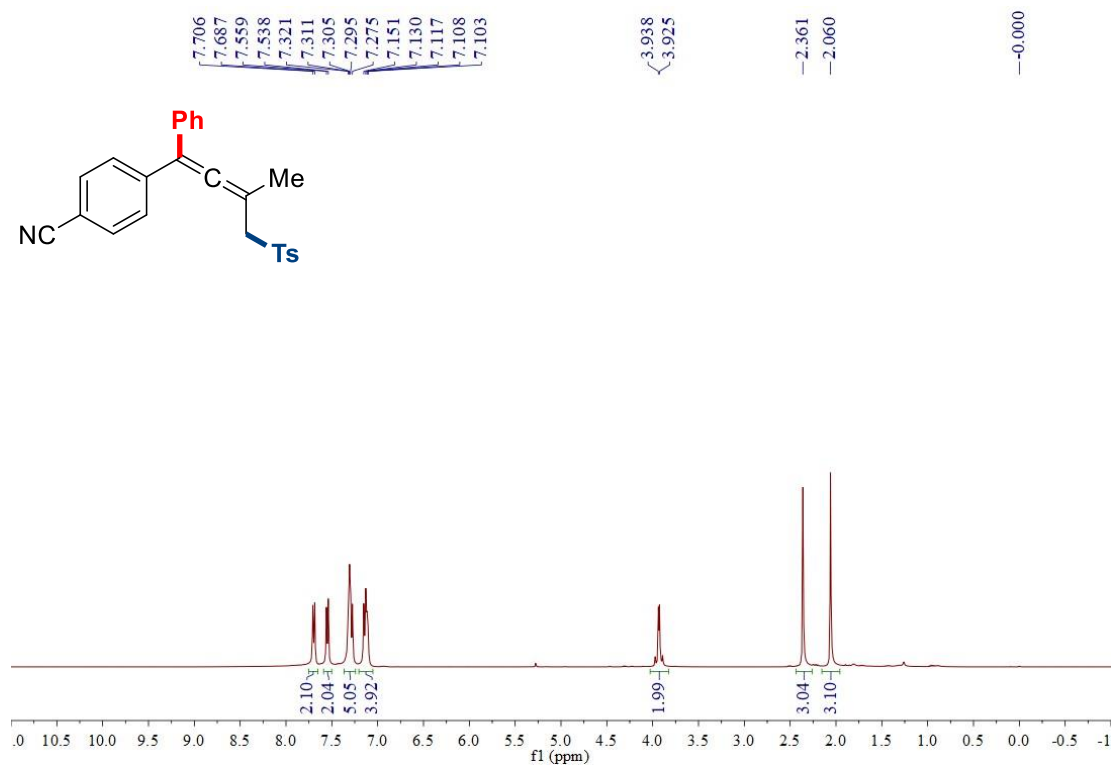


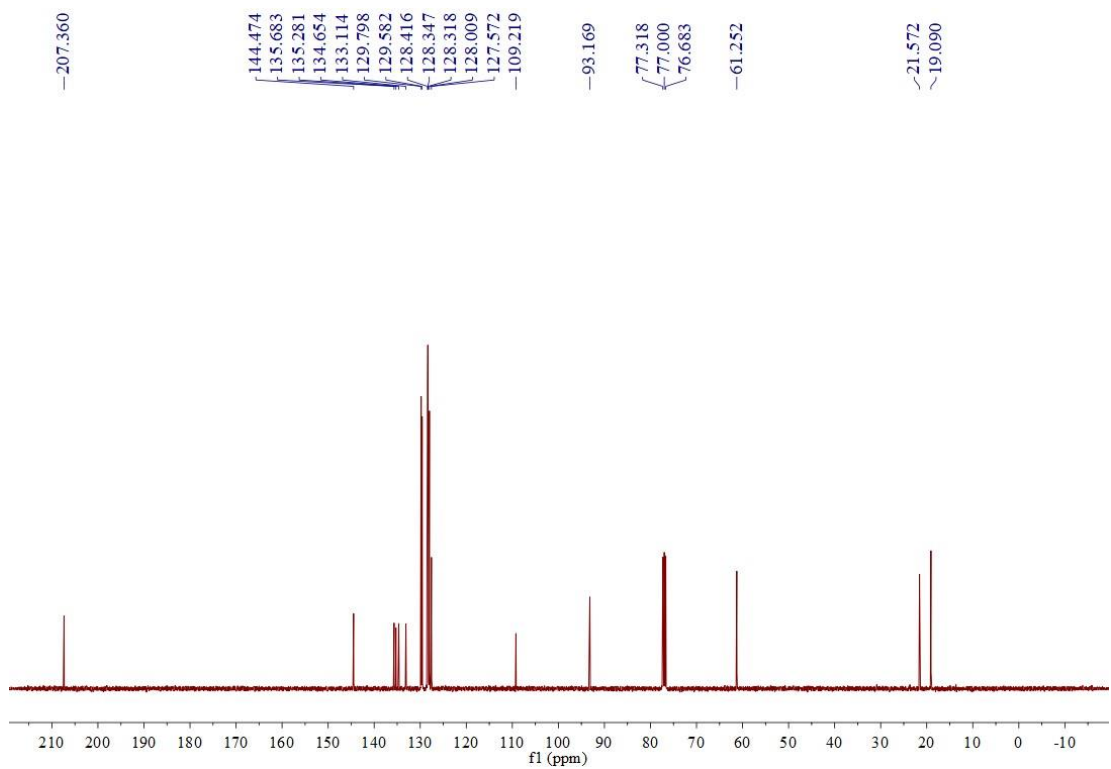
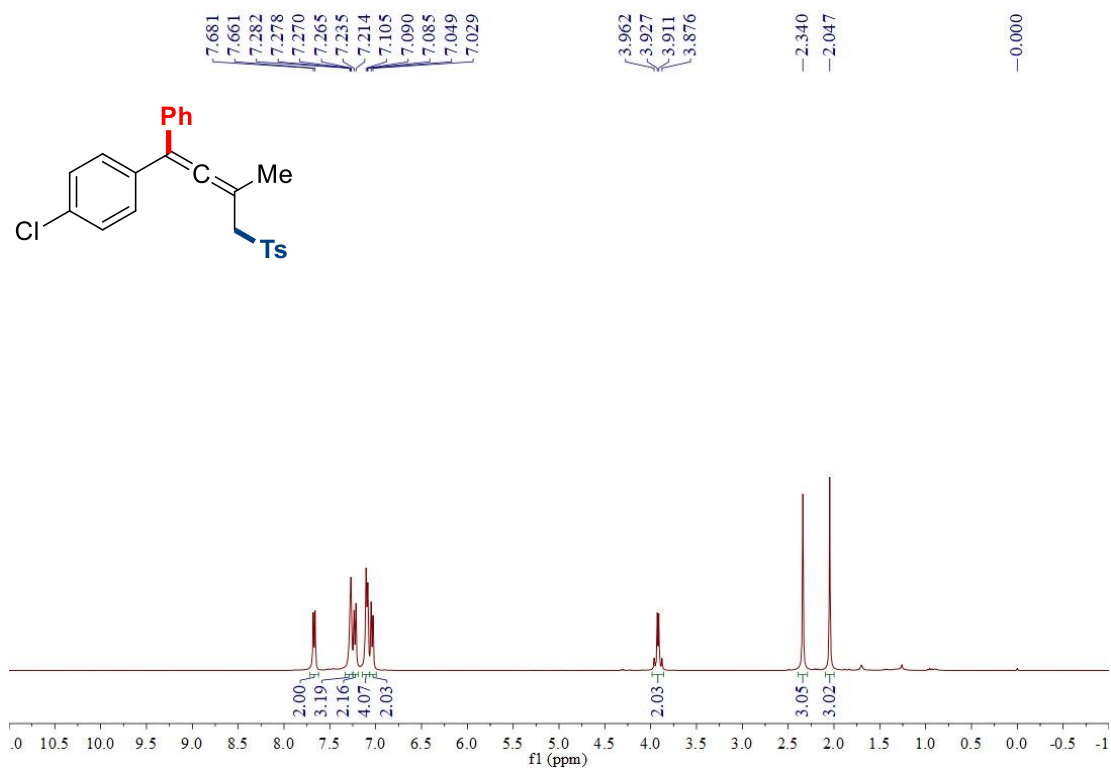
4

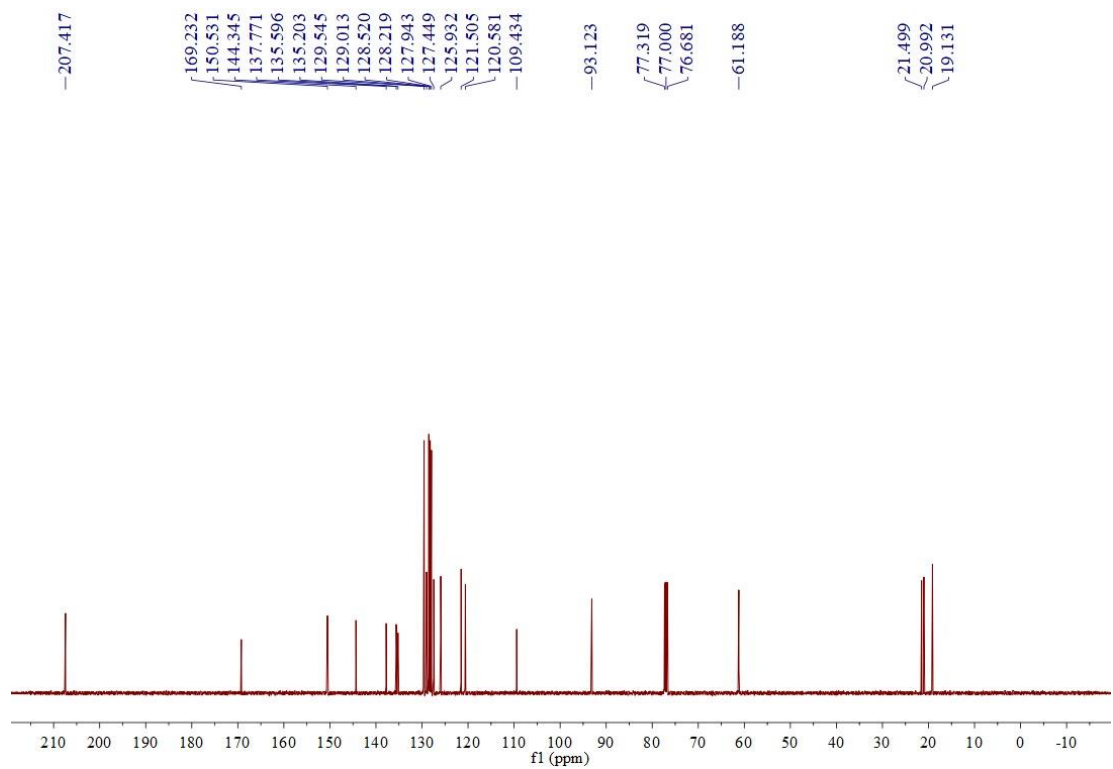
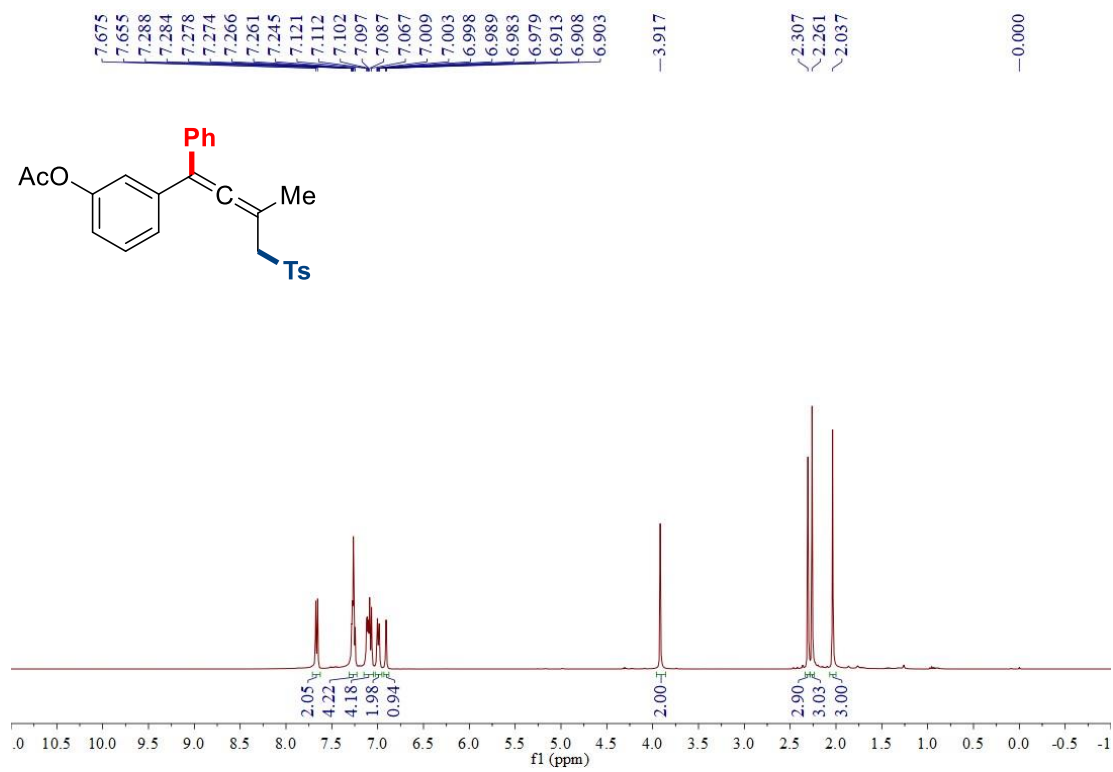


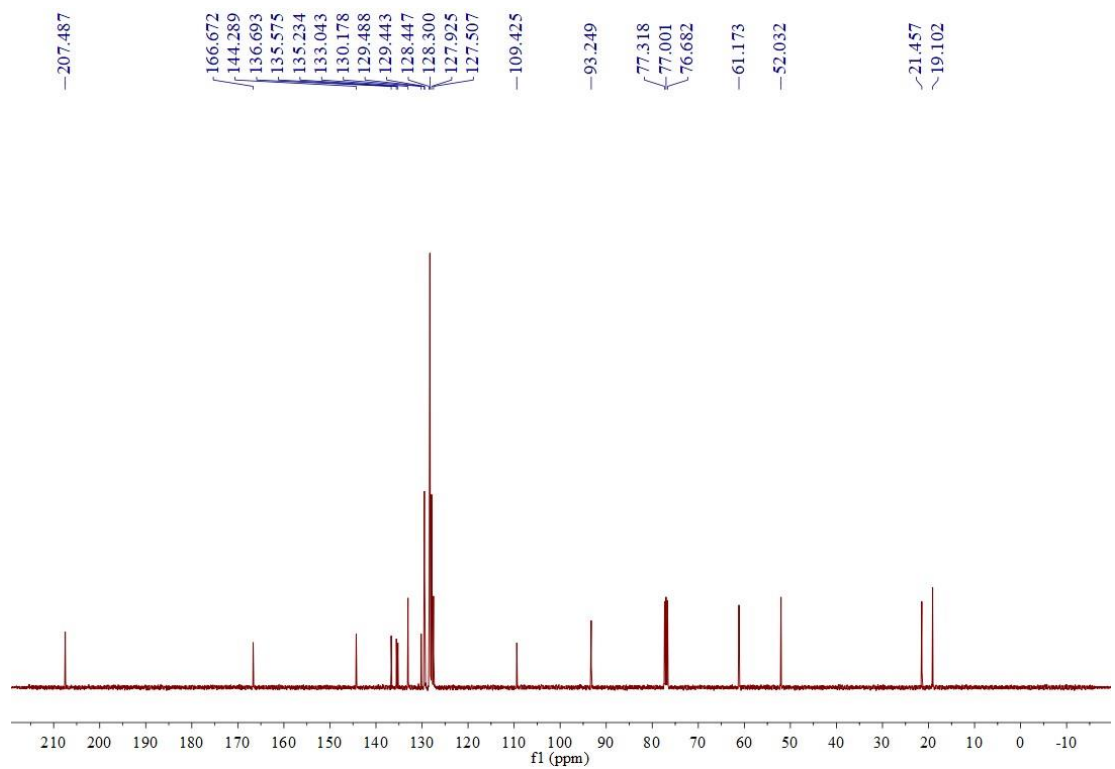
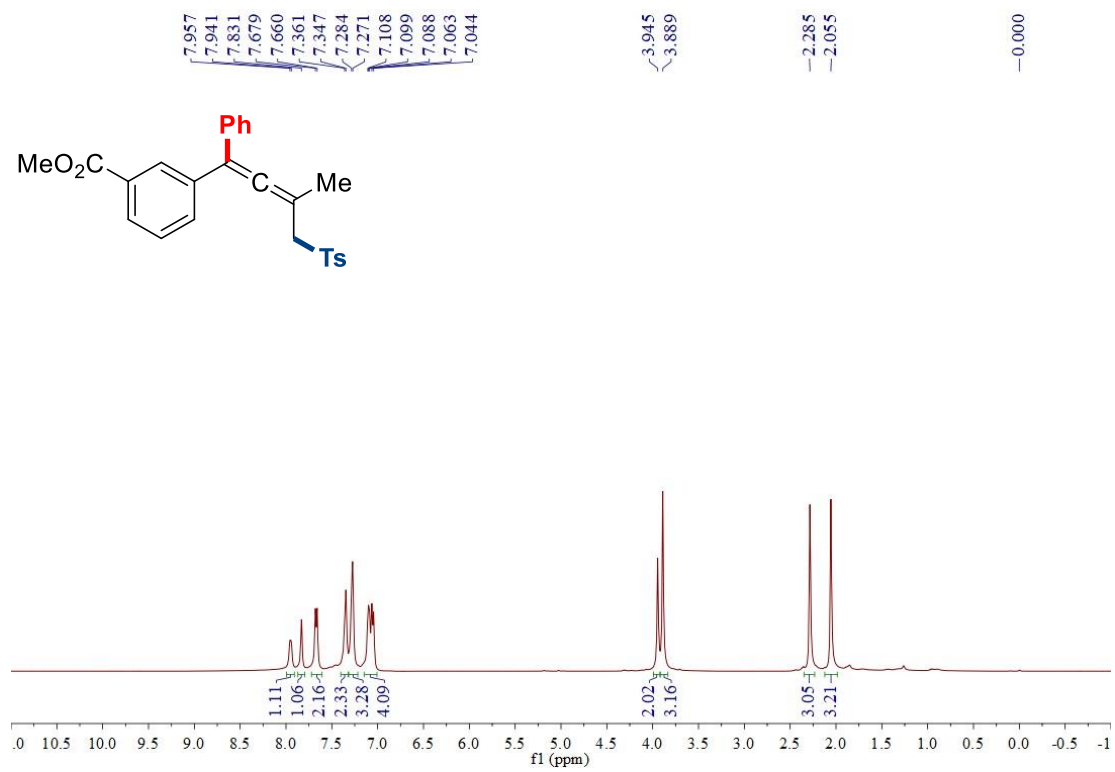


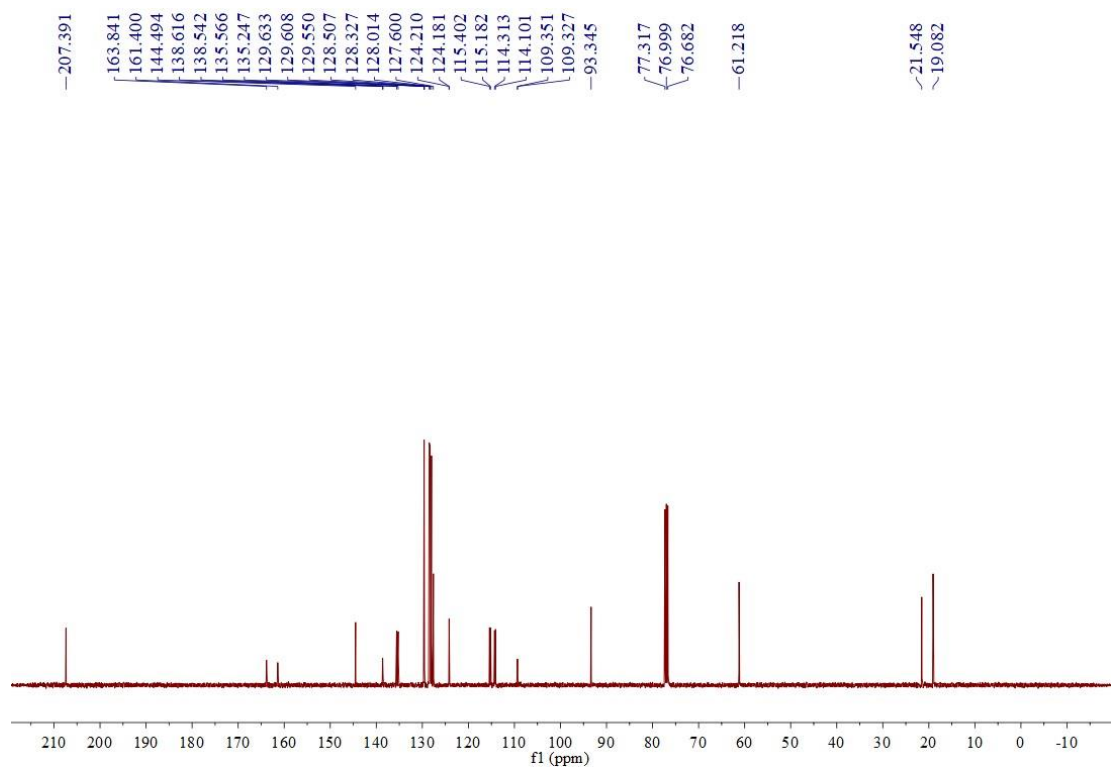
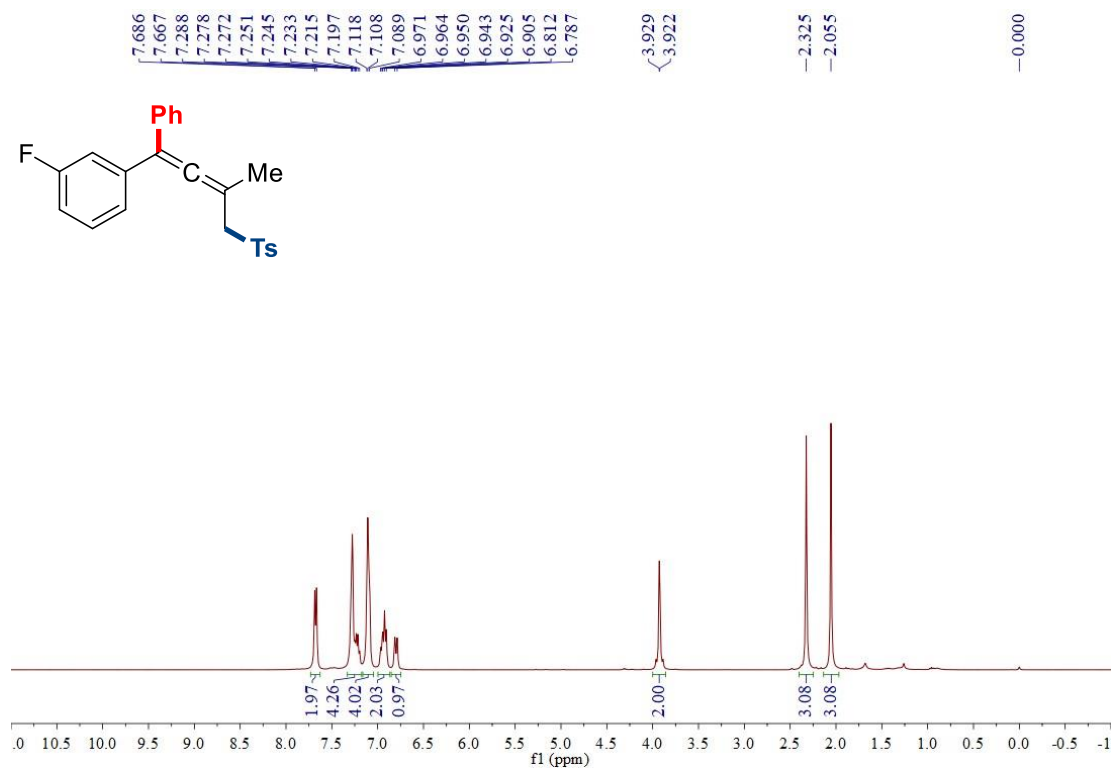
6

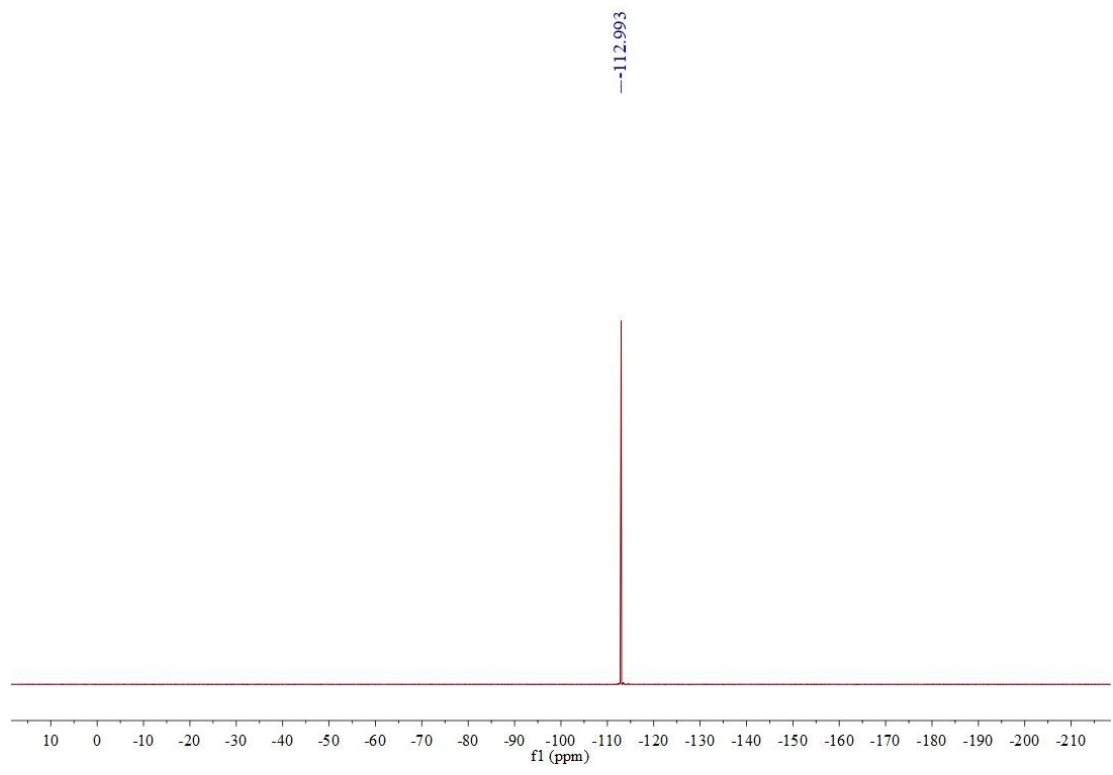


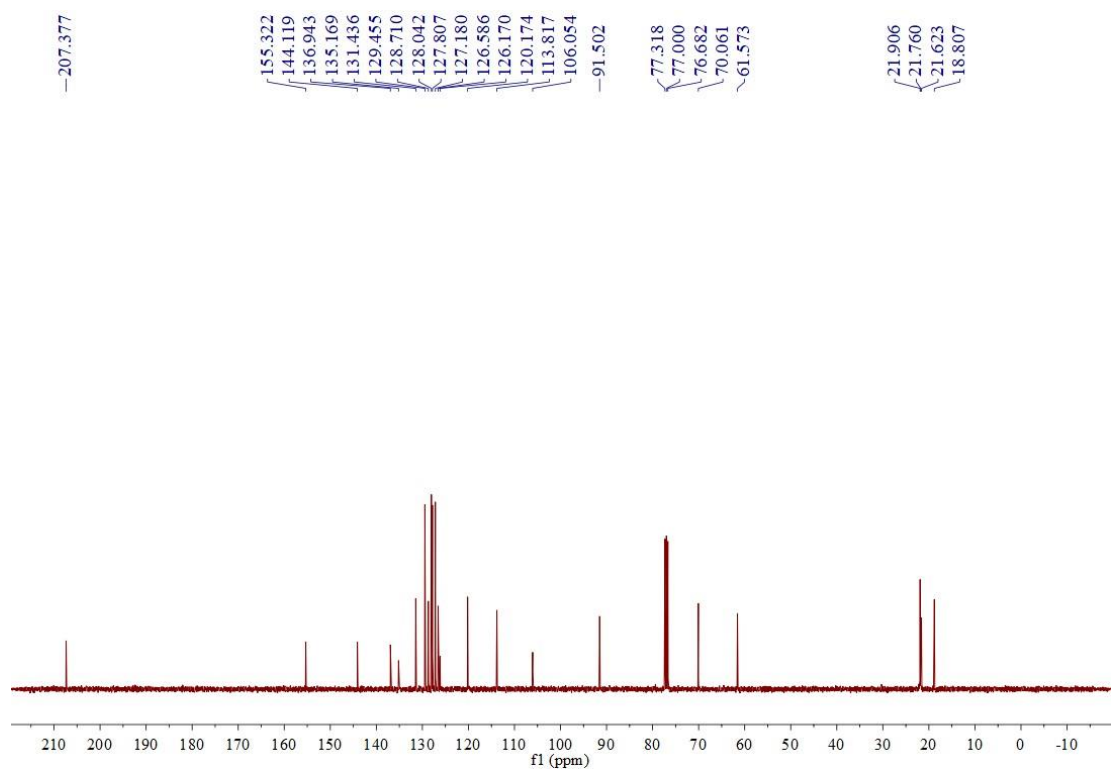
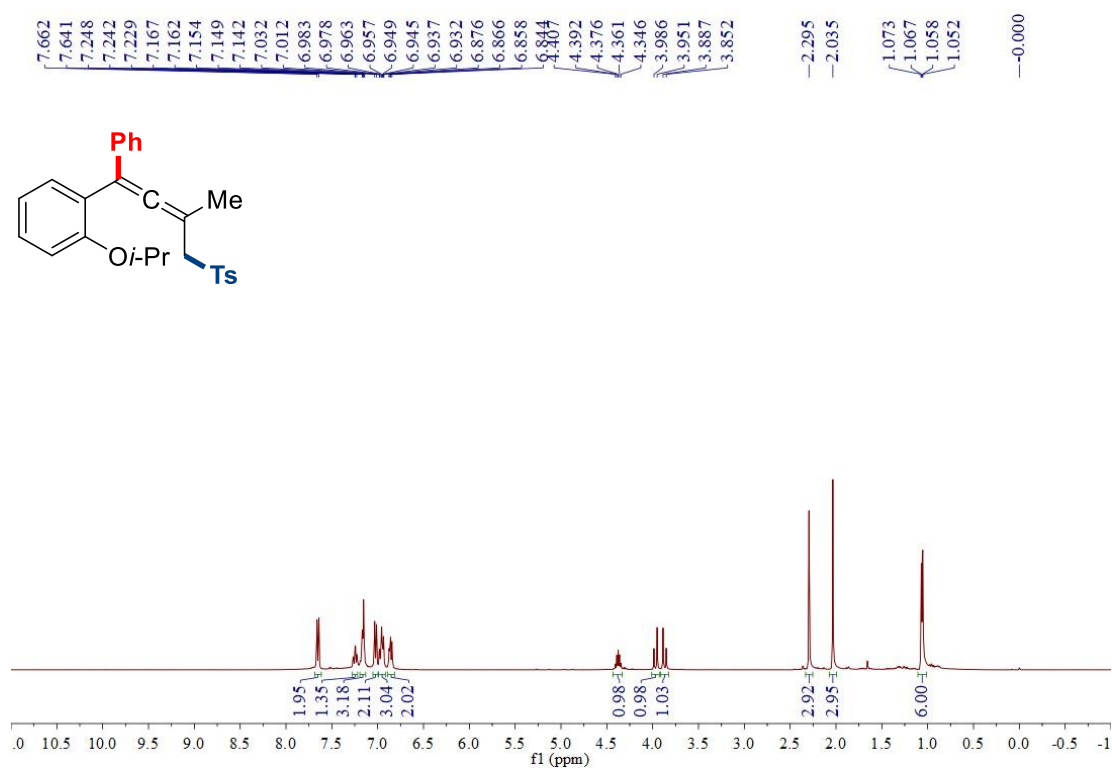


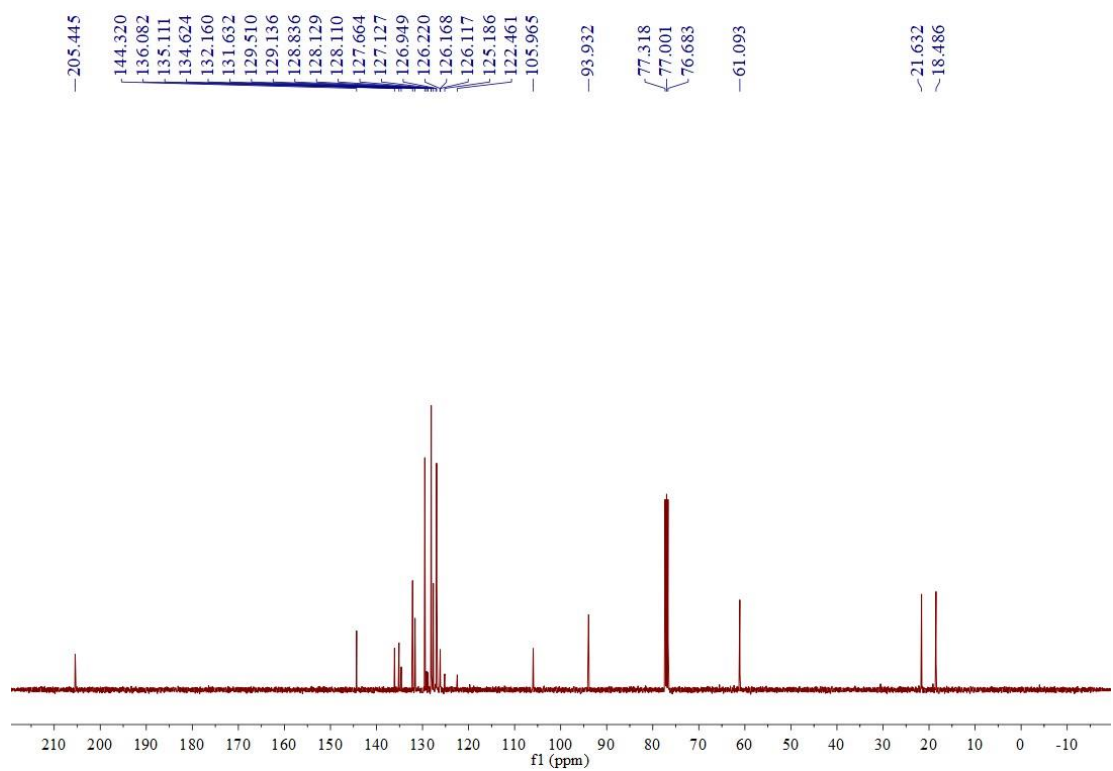
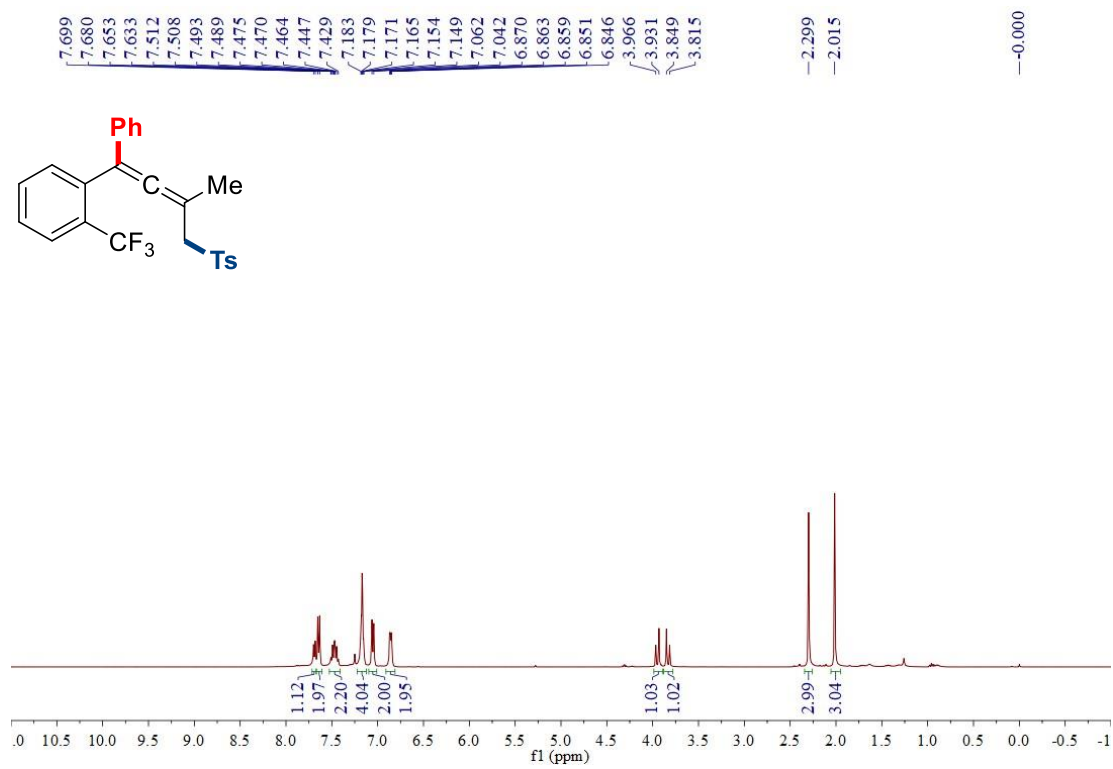


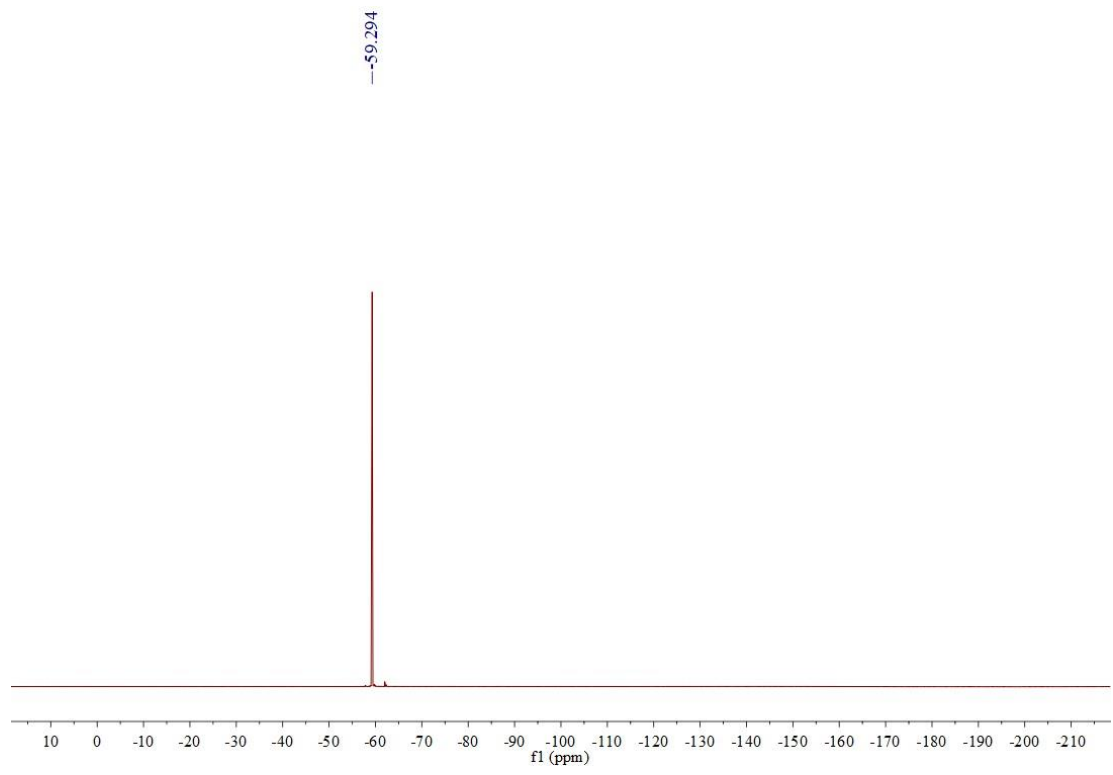


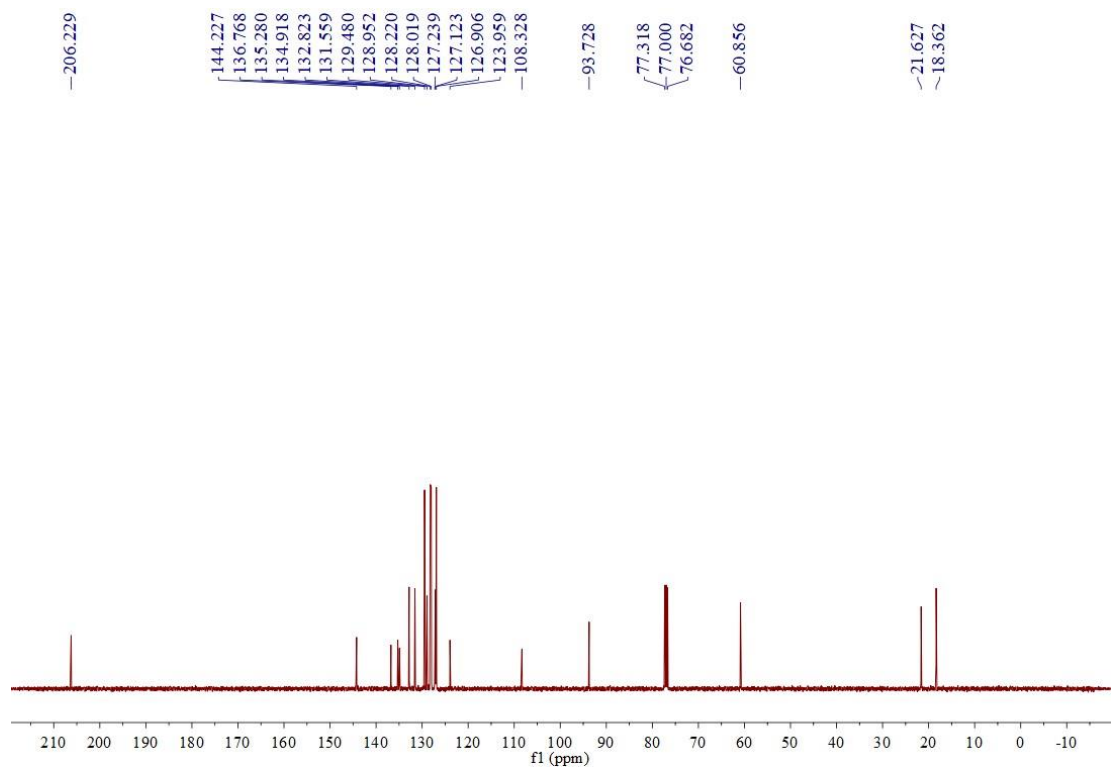
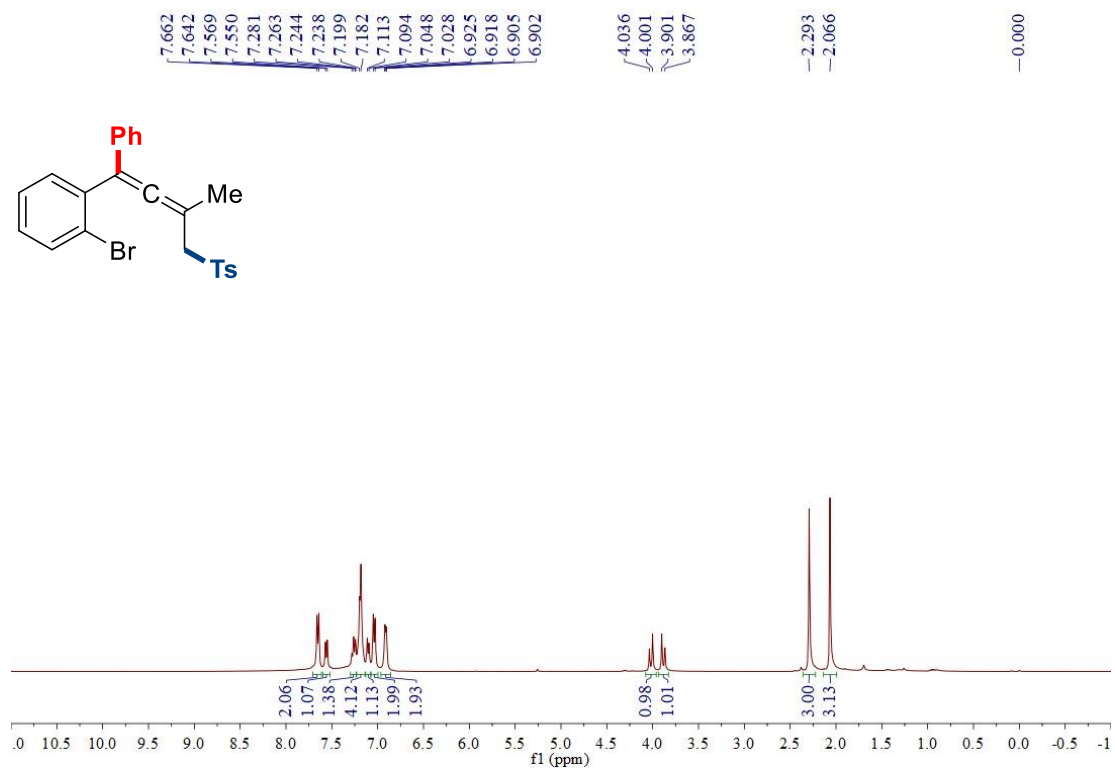


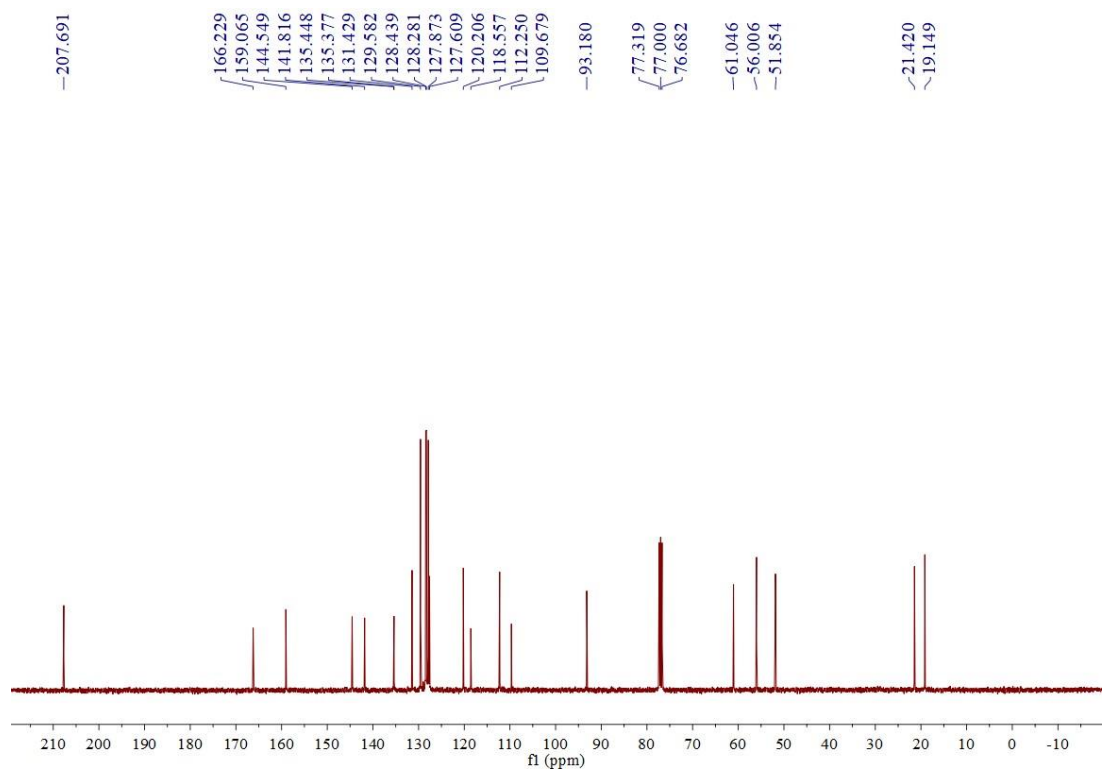
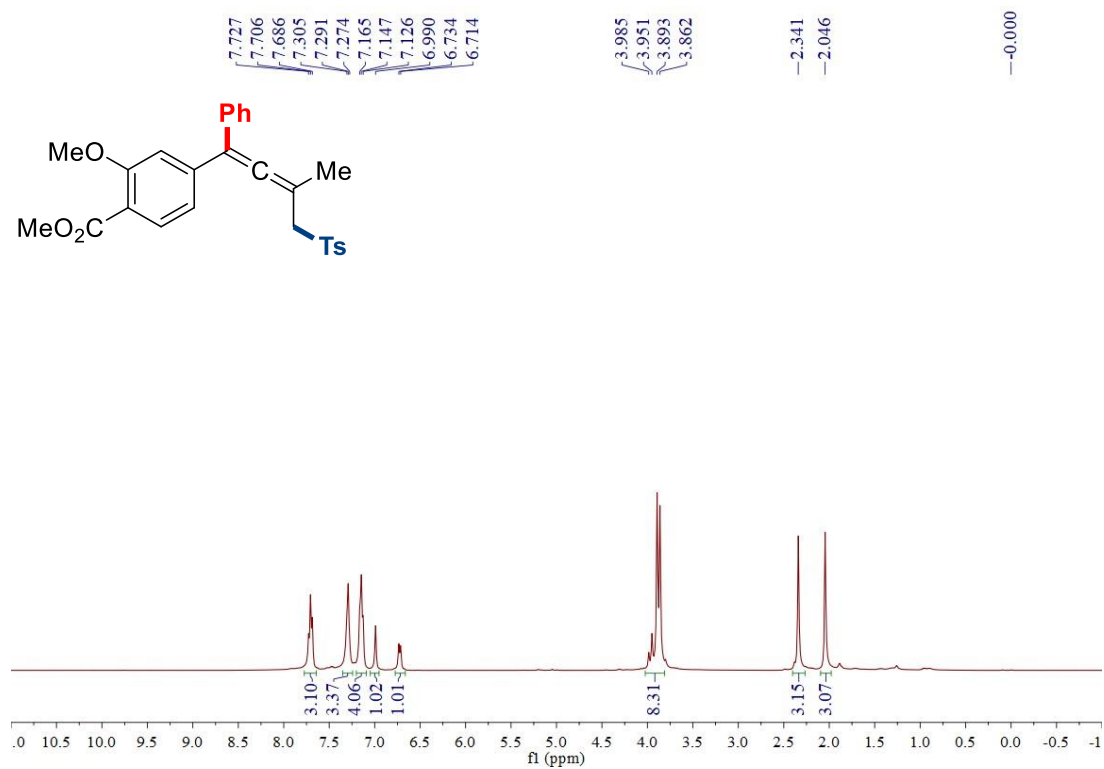


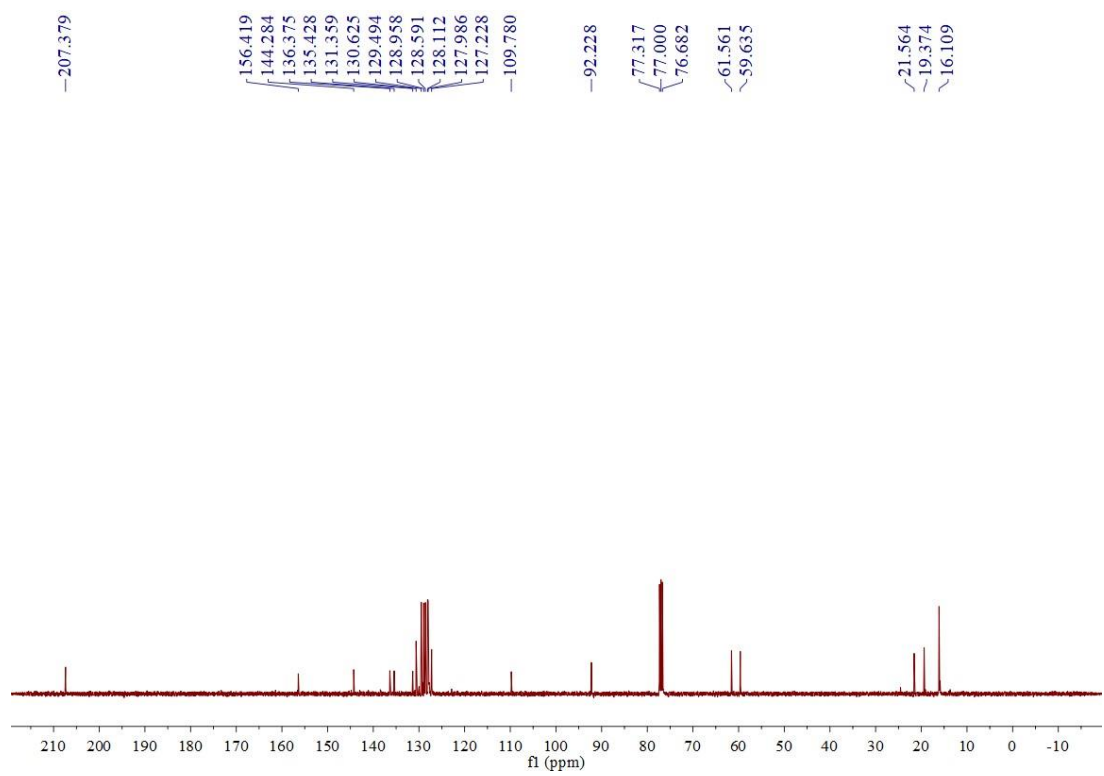
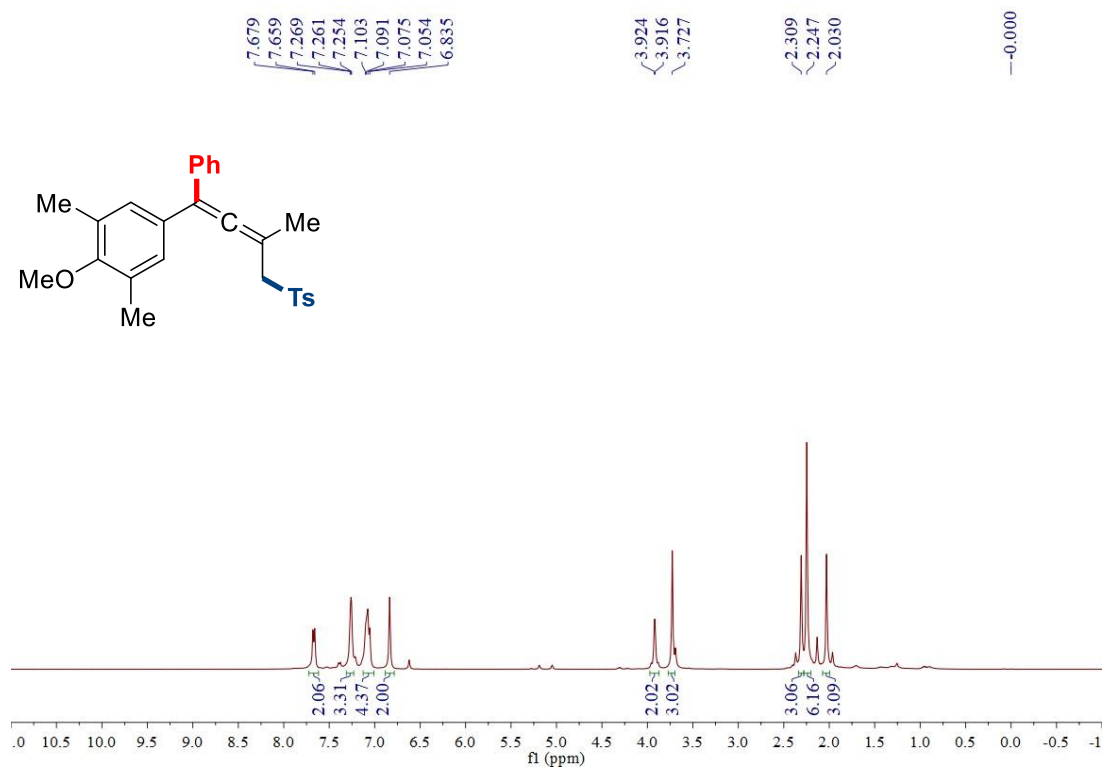


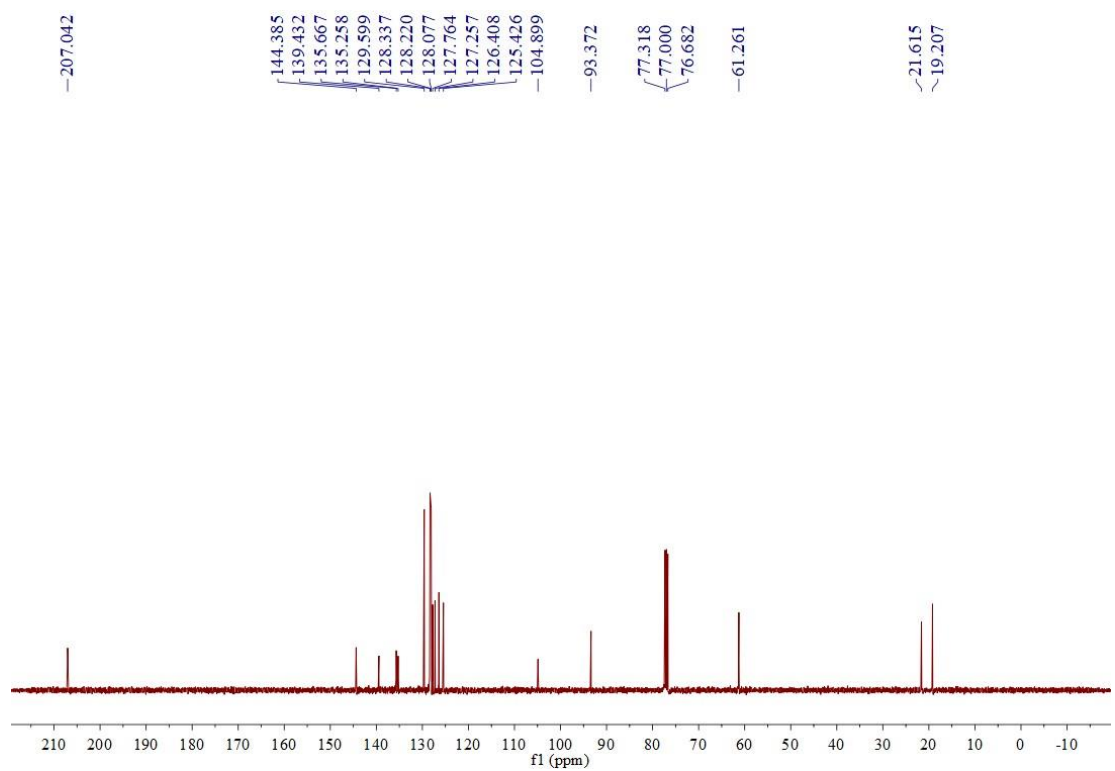
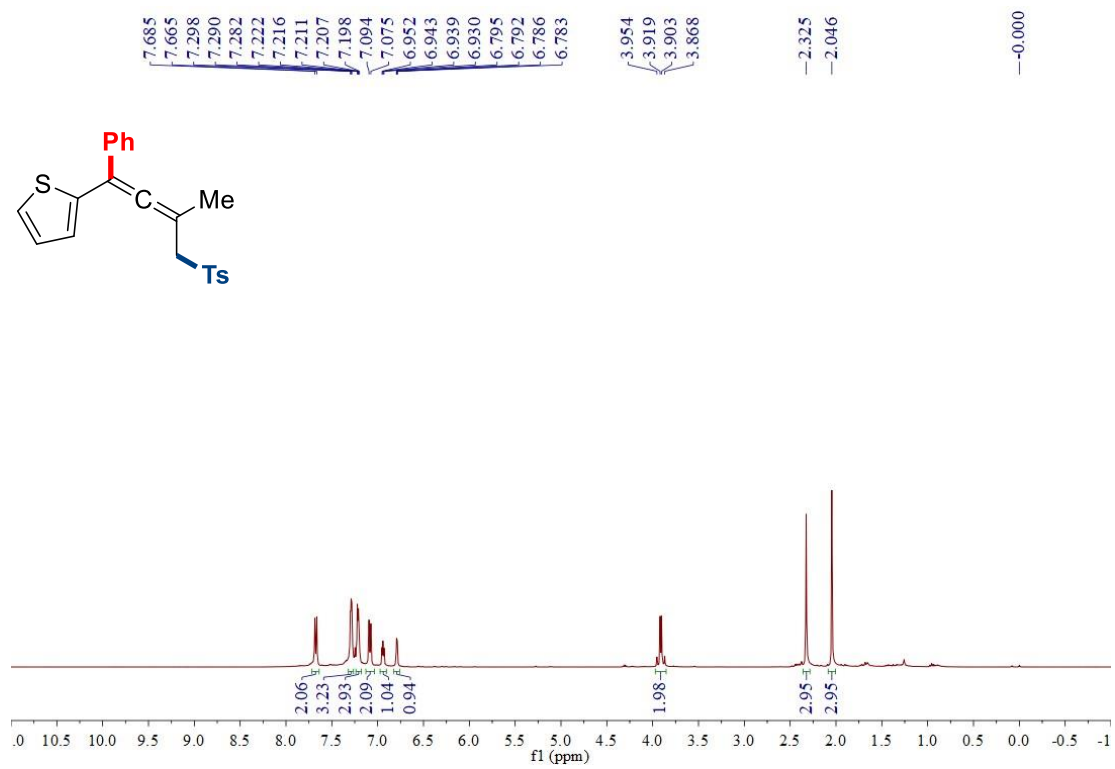


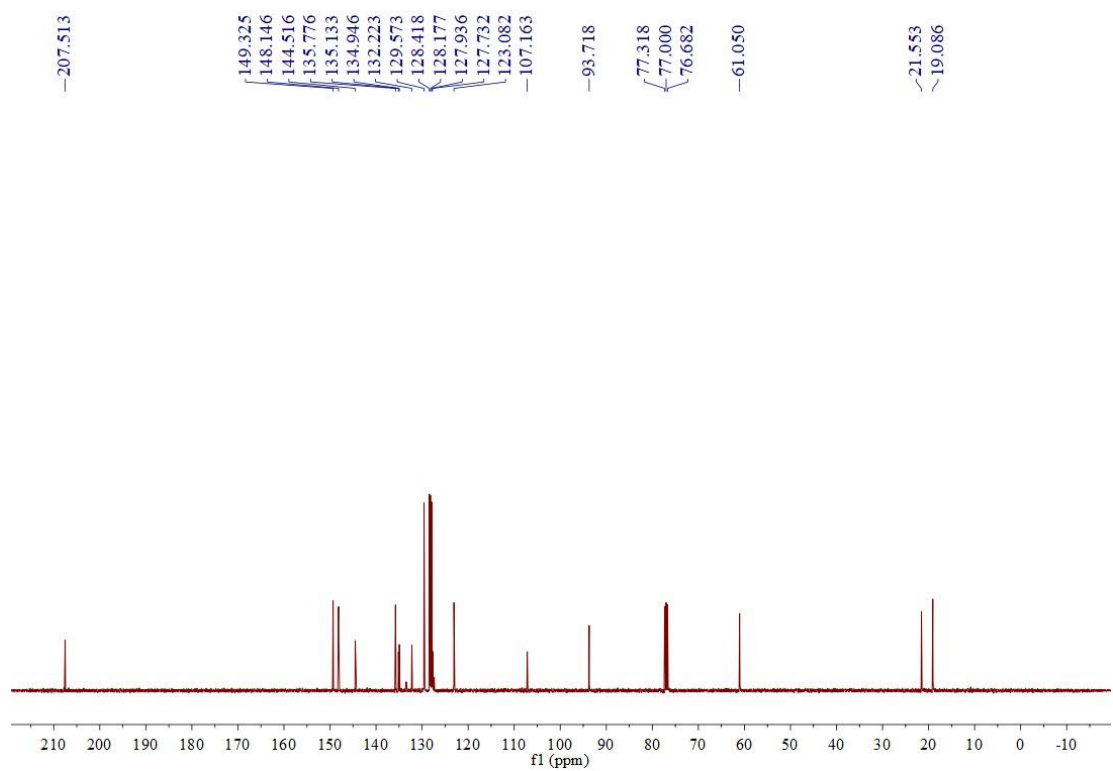
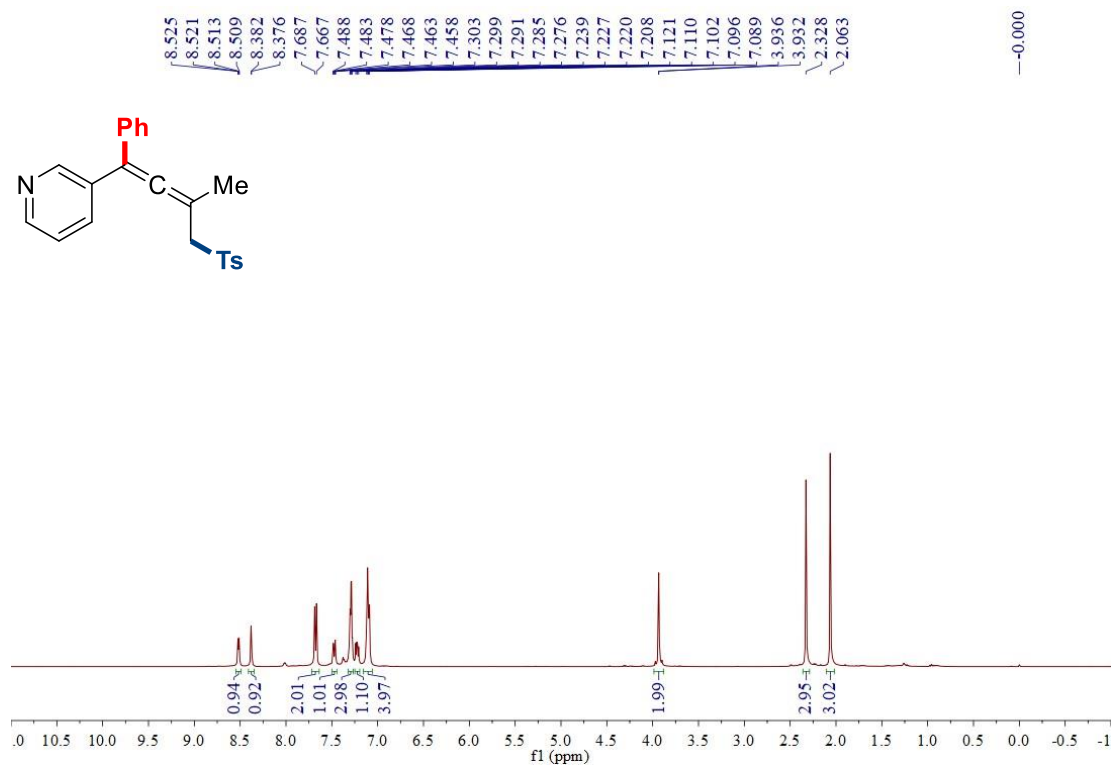


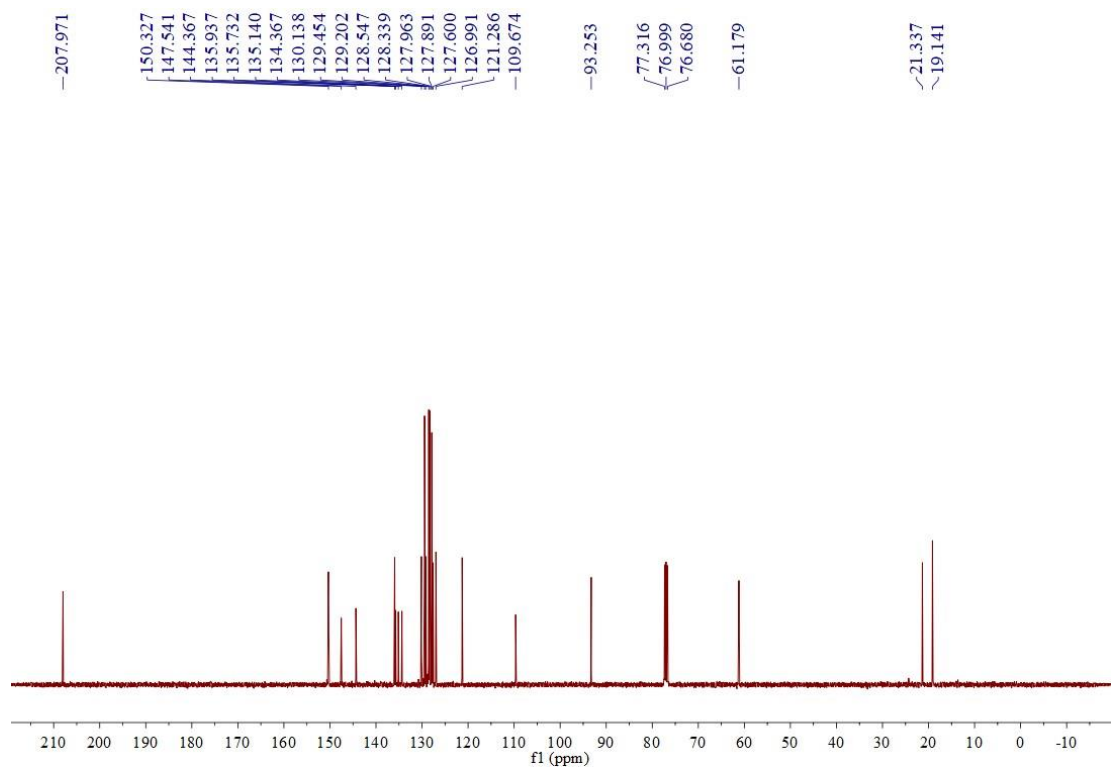
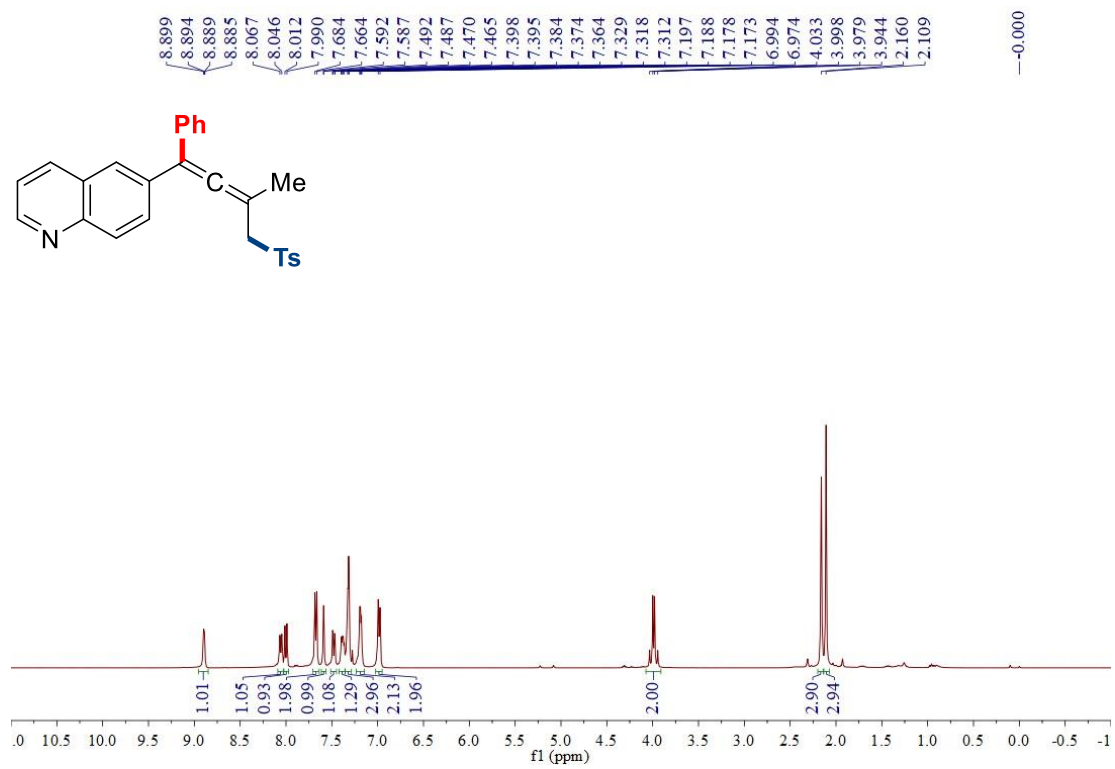


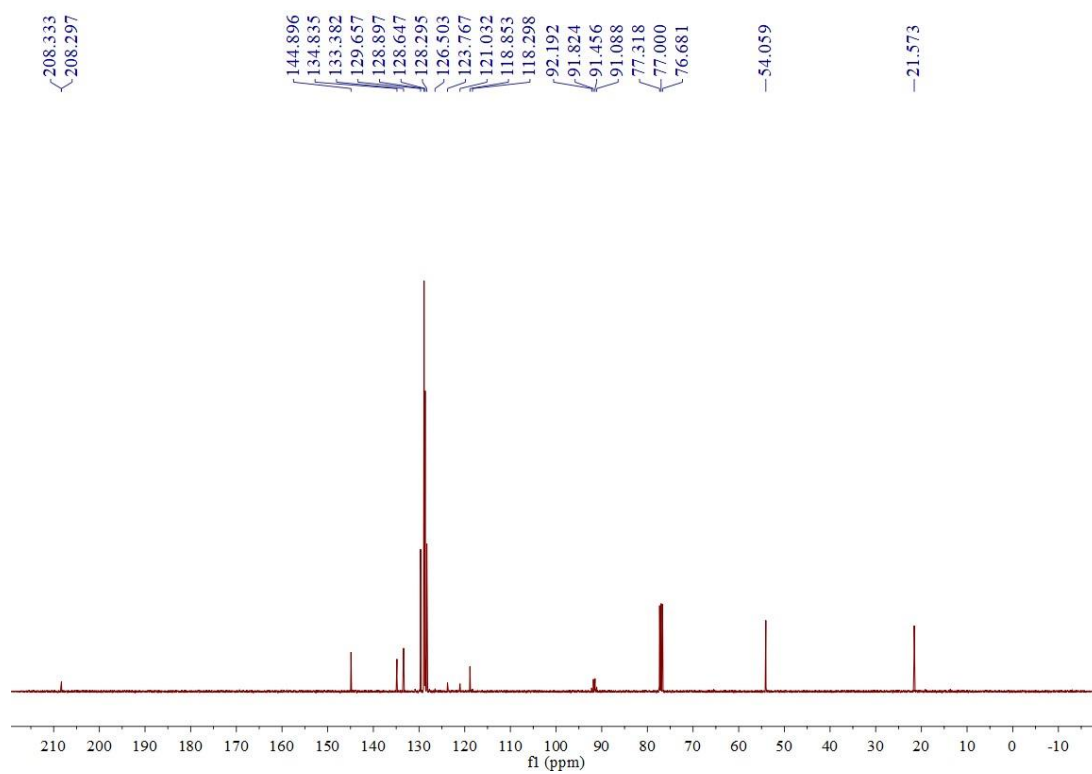
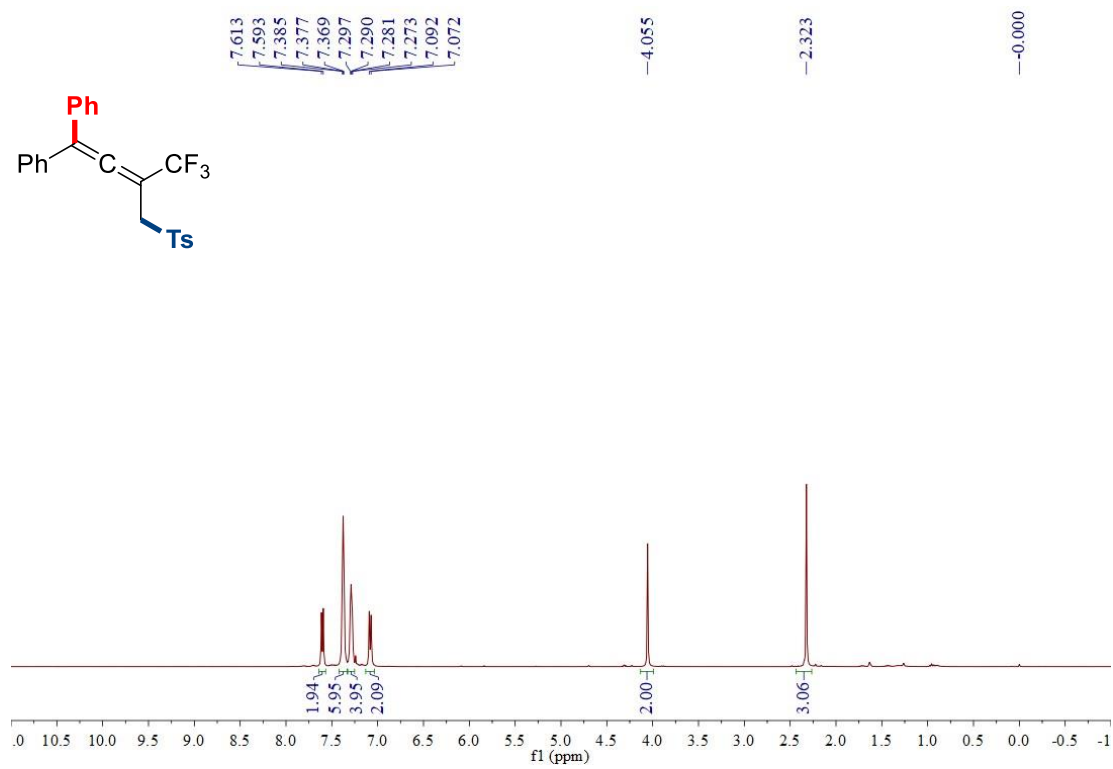


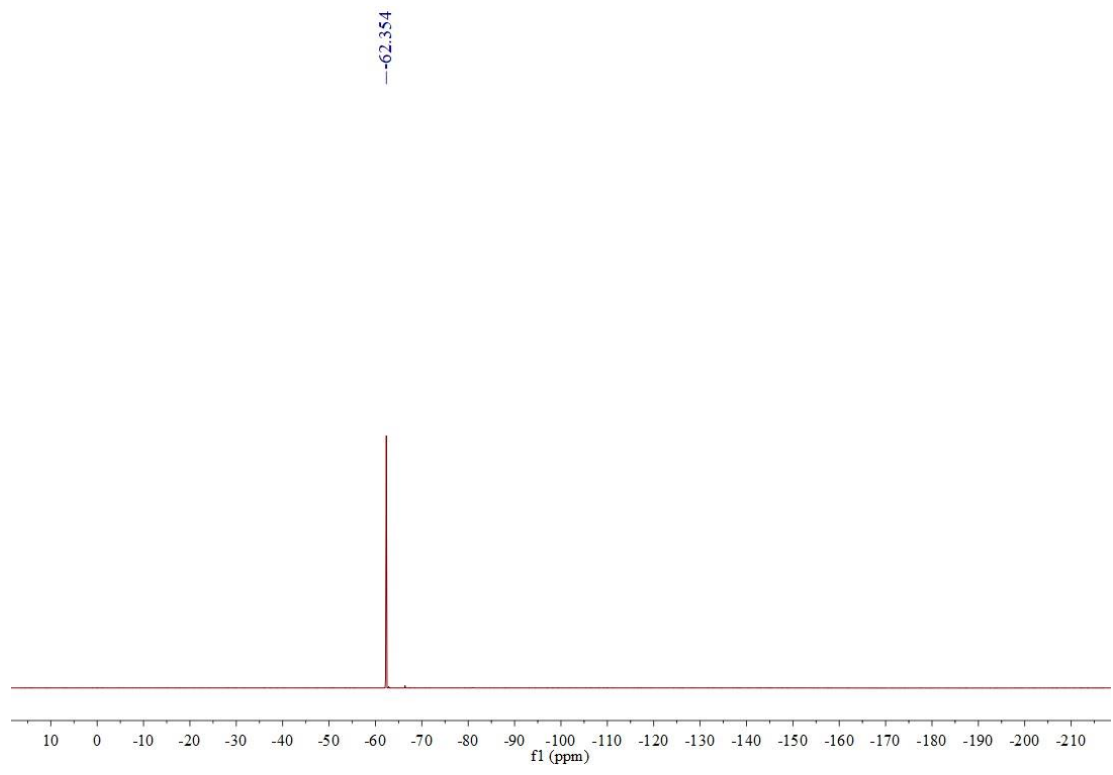


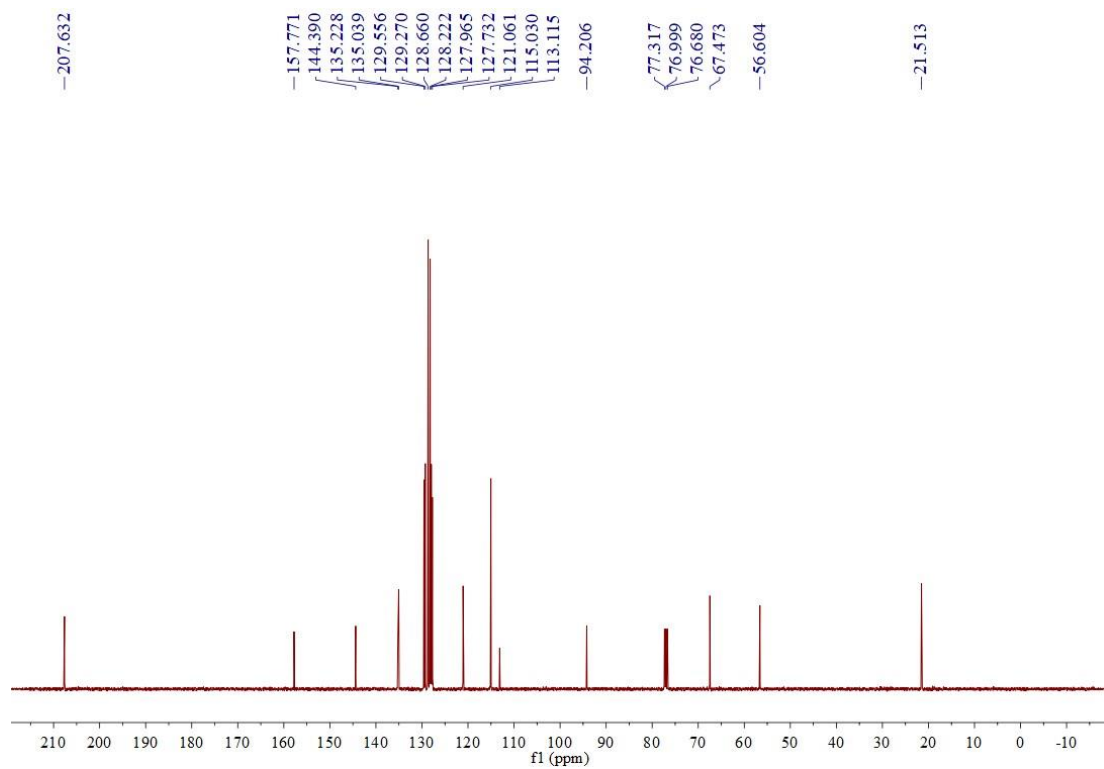
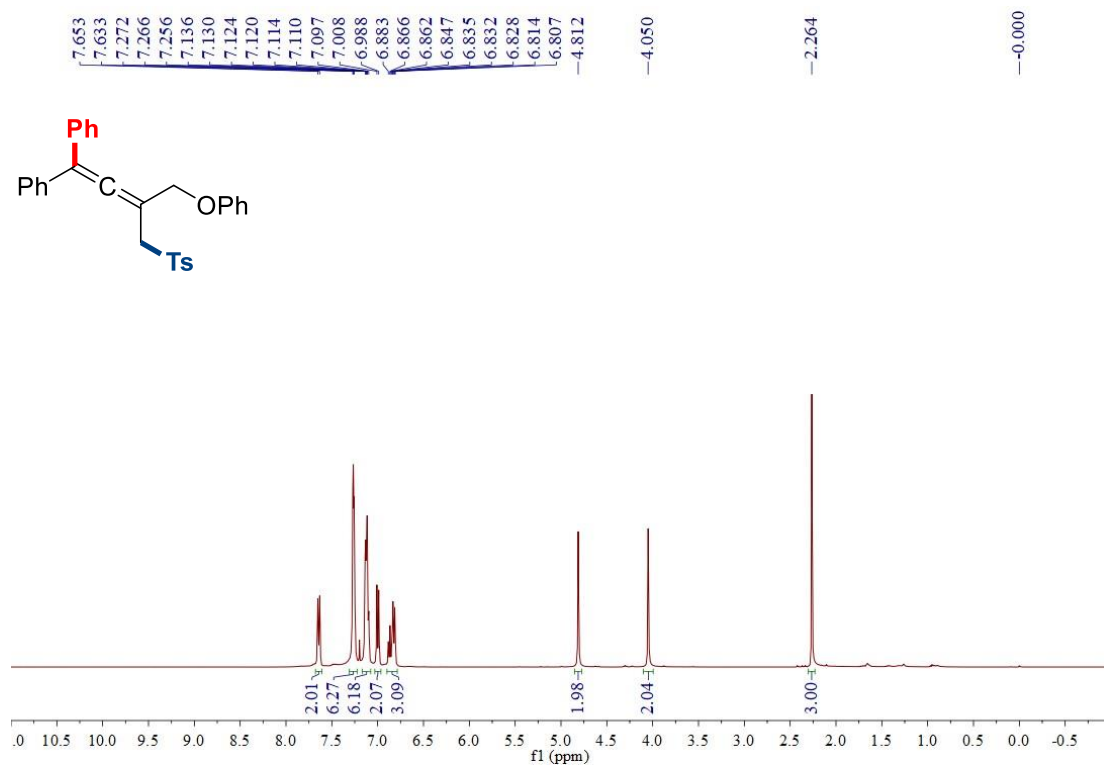


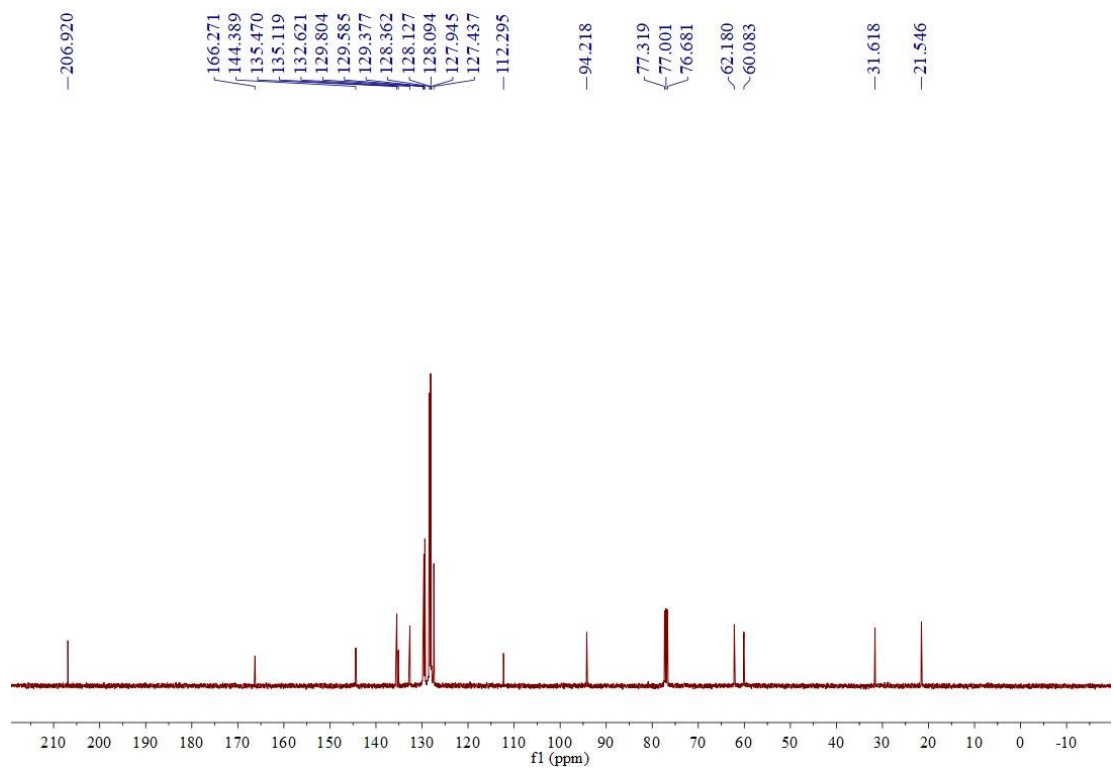
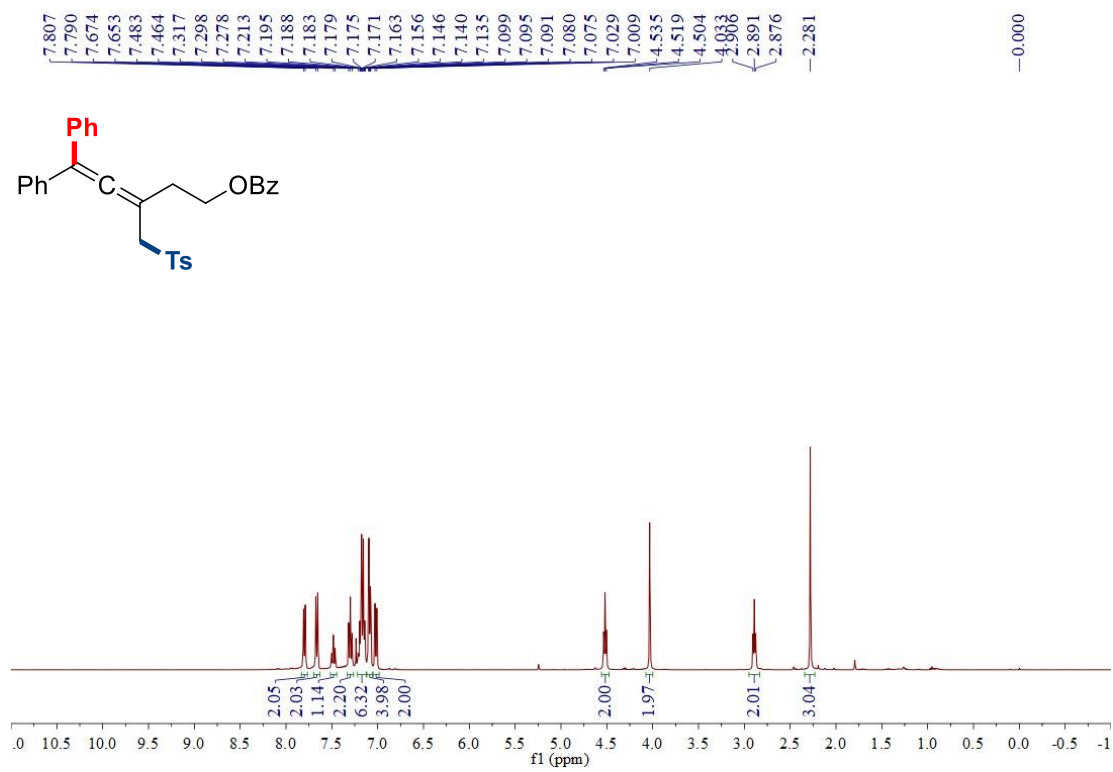


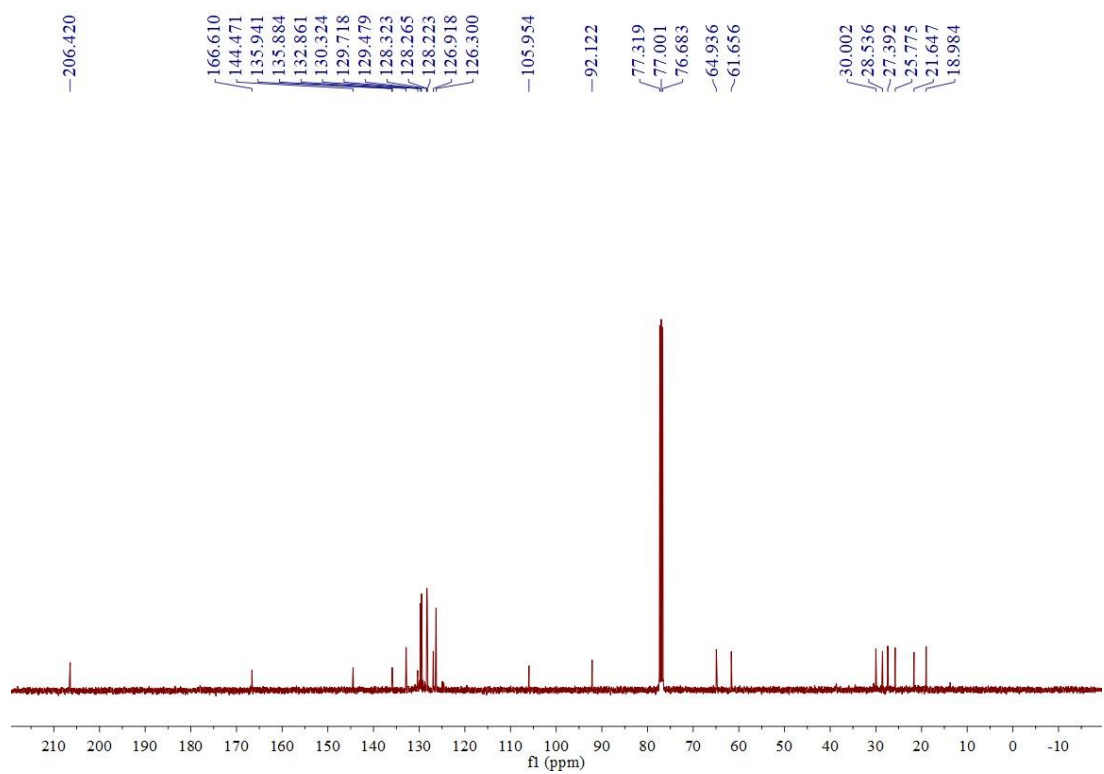
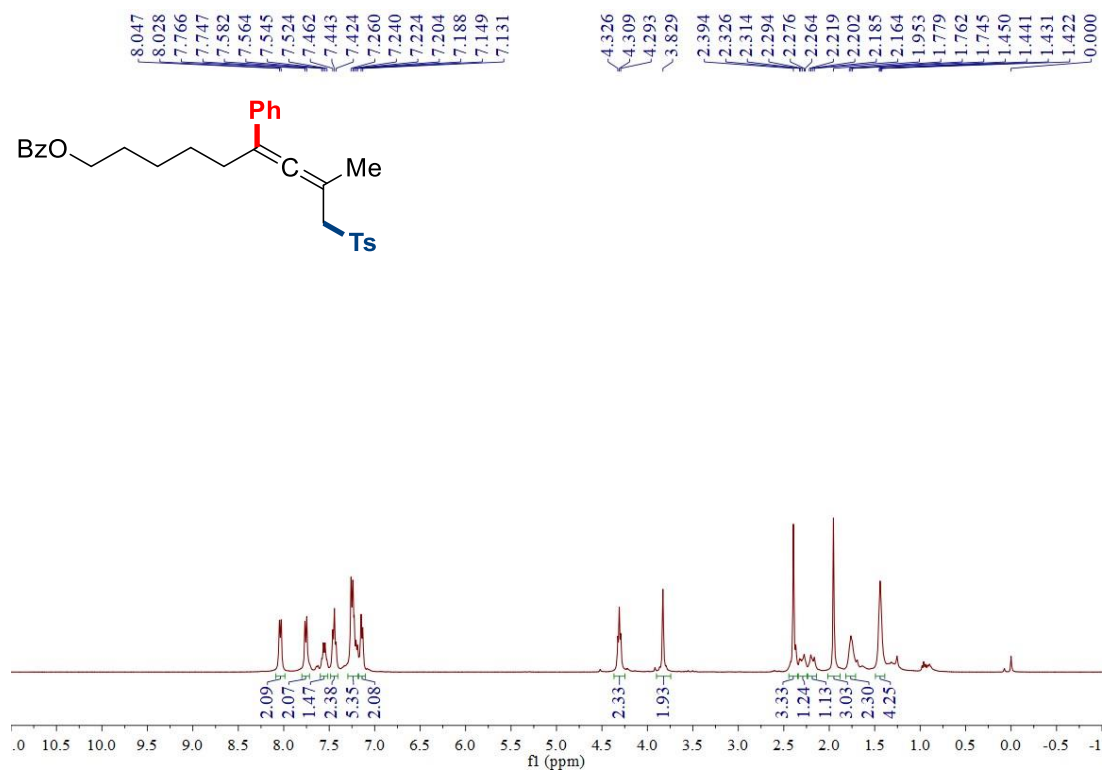


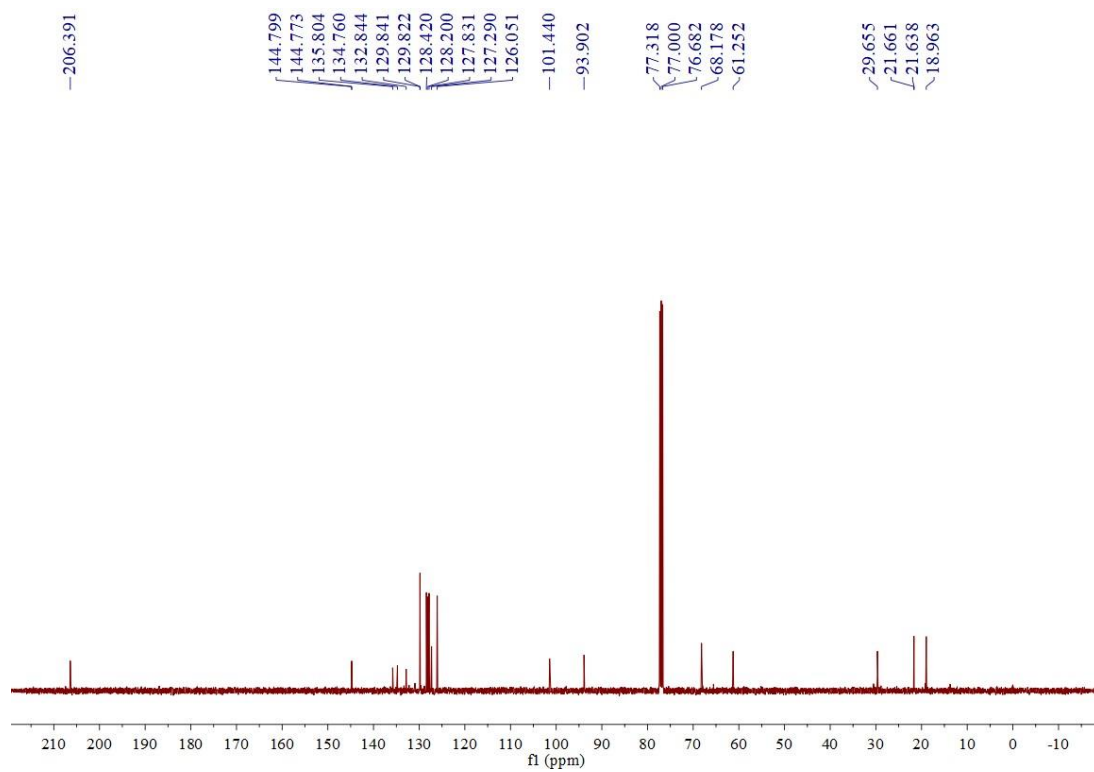
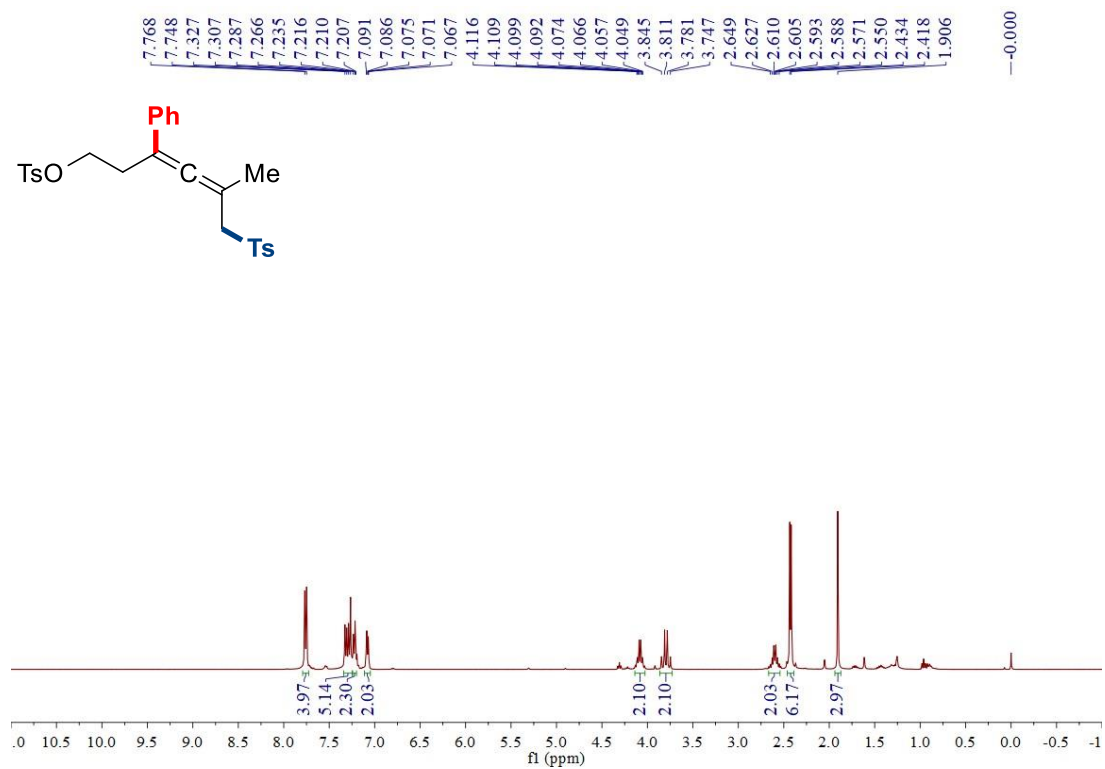


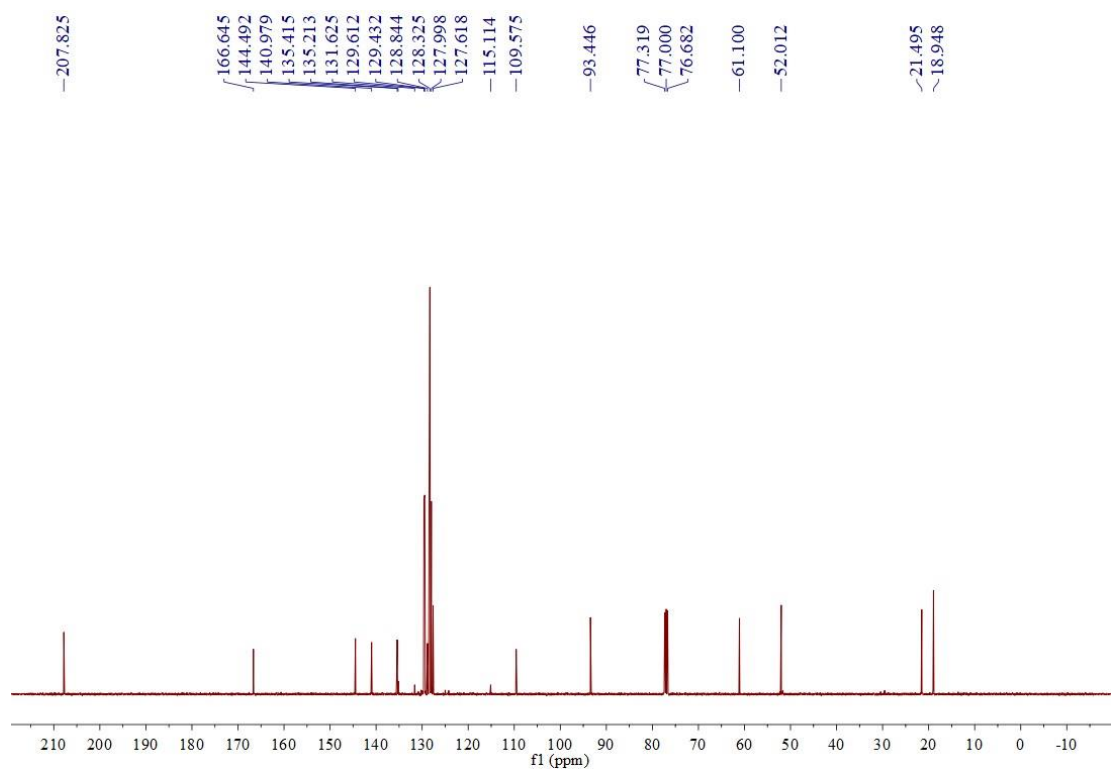
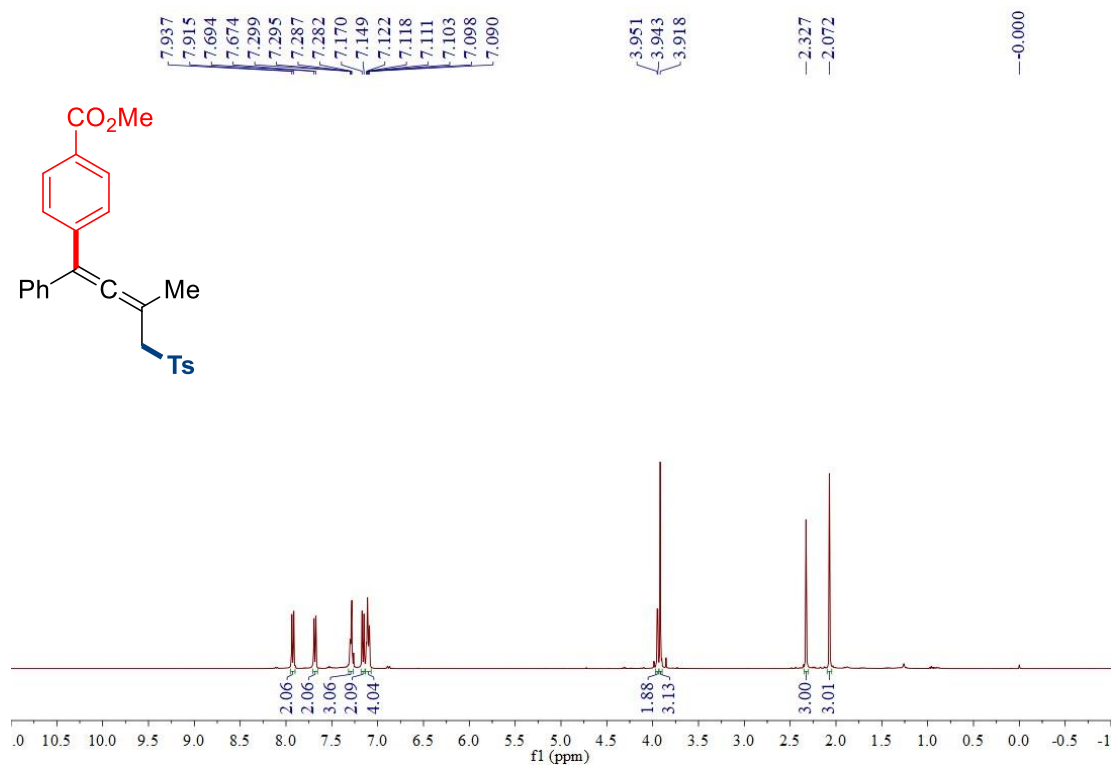


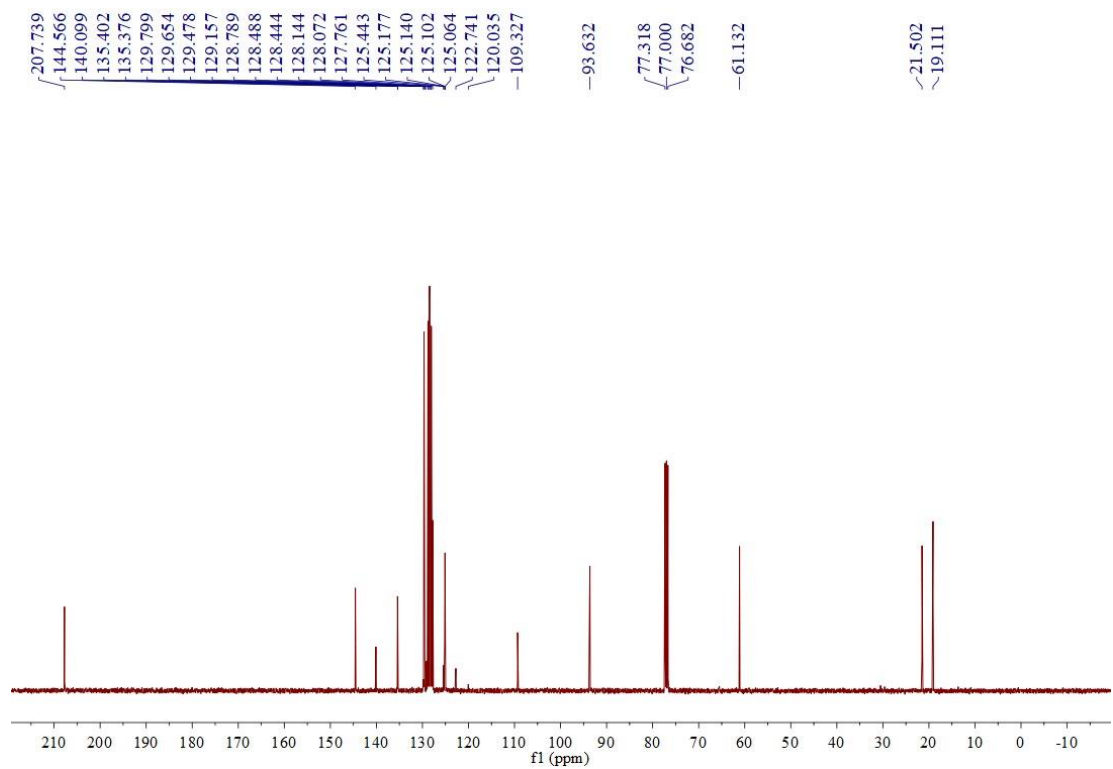
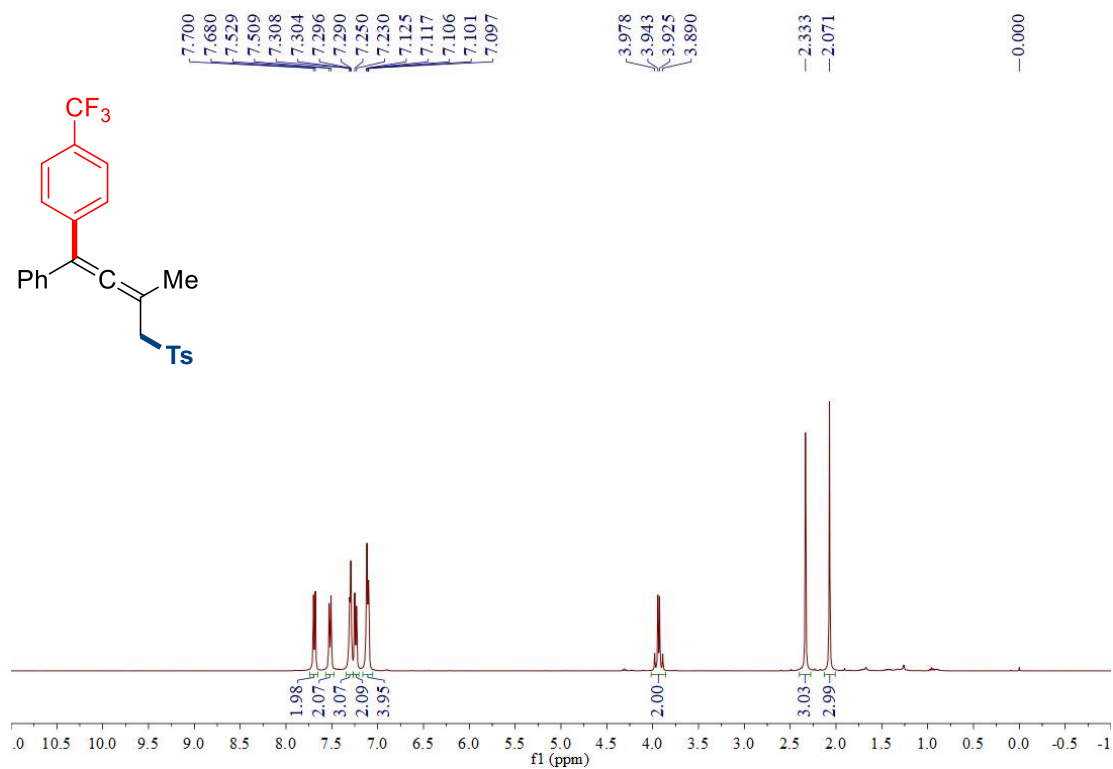


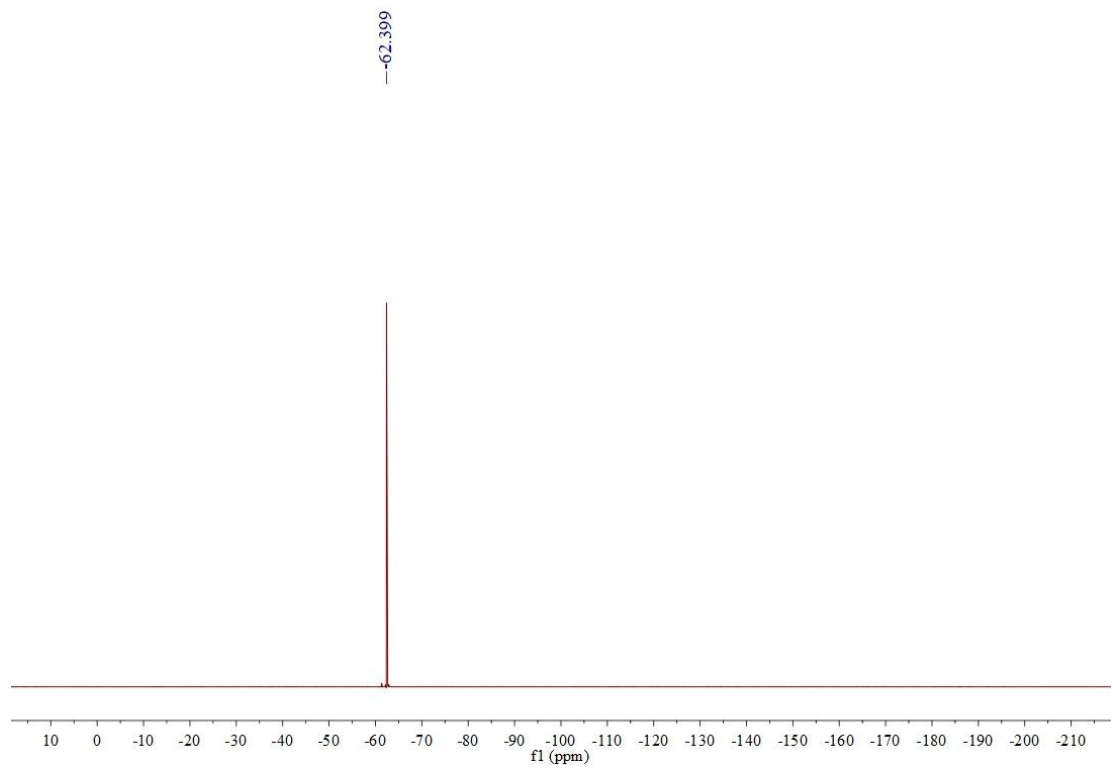


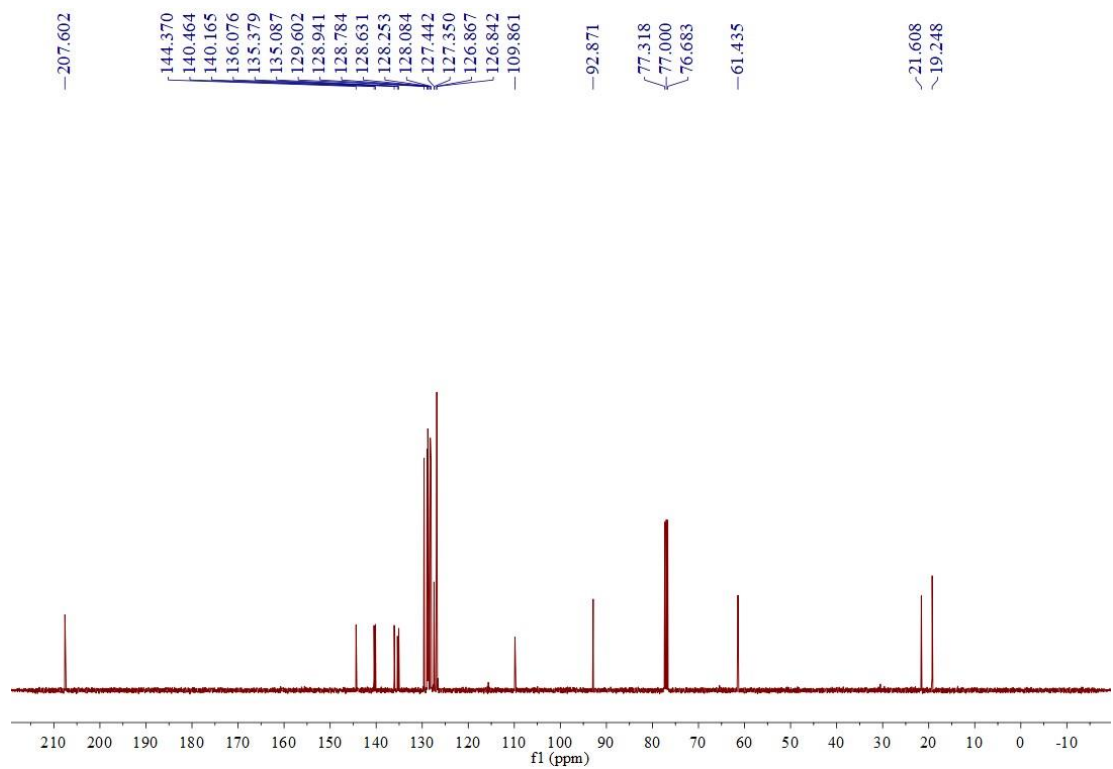
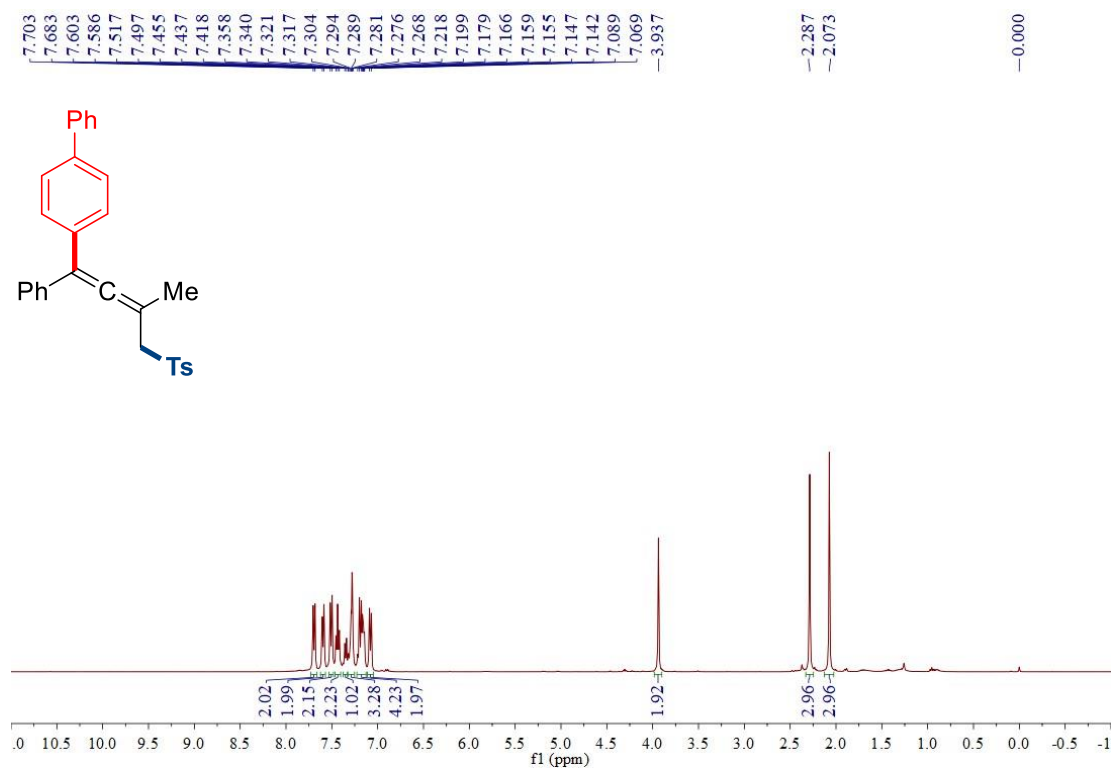


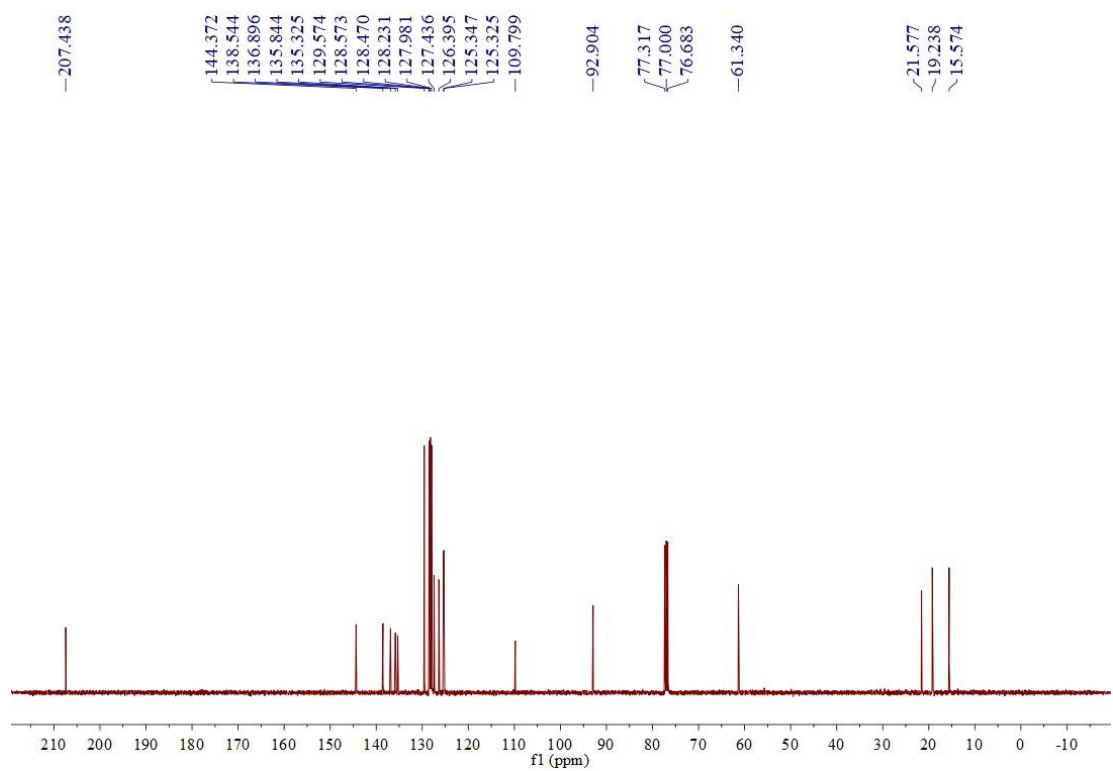
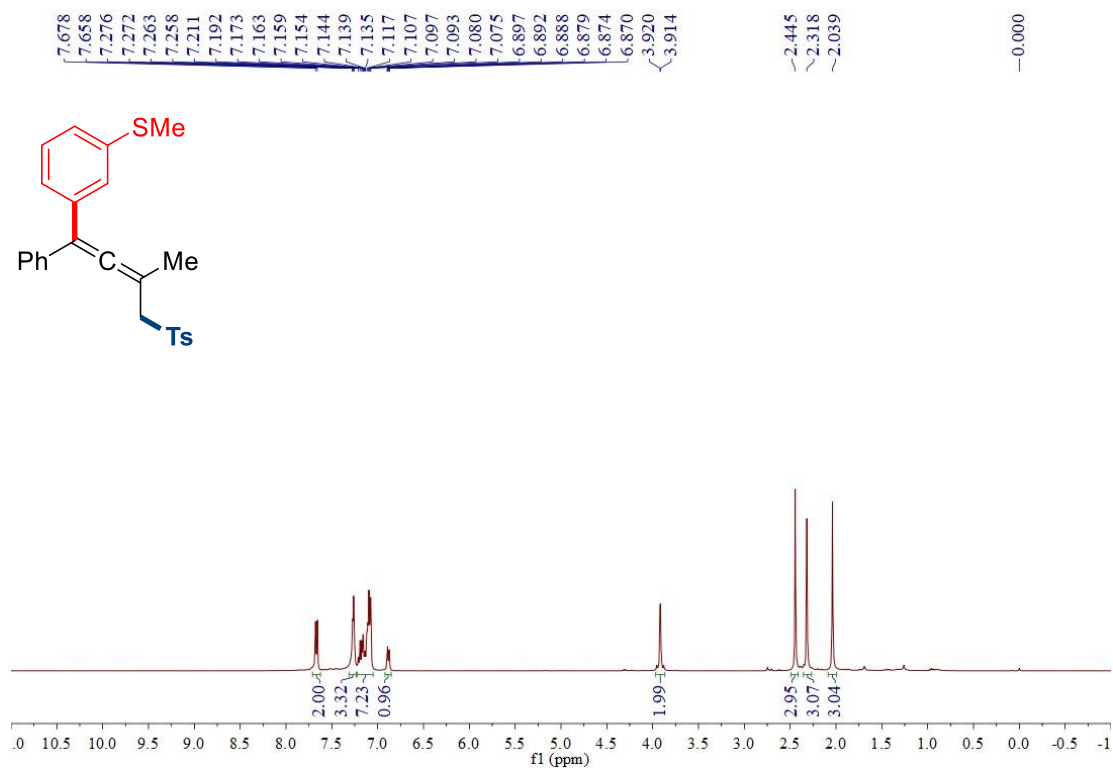


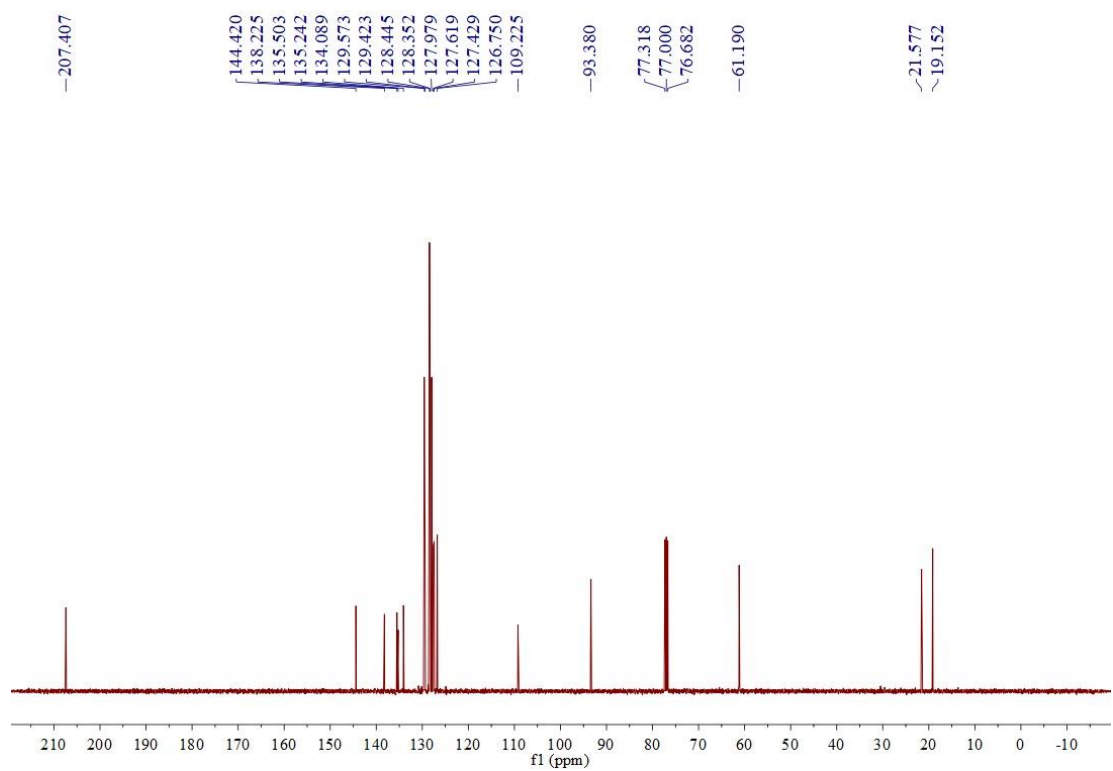
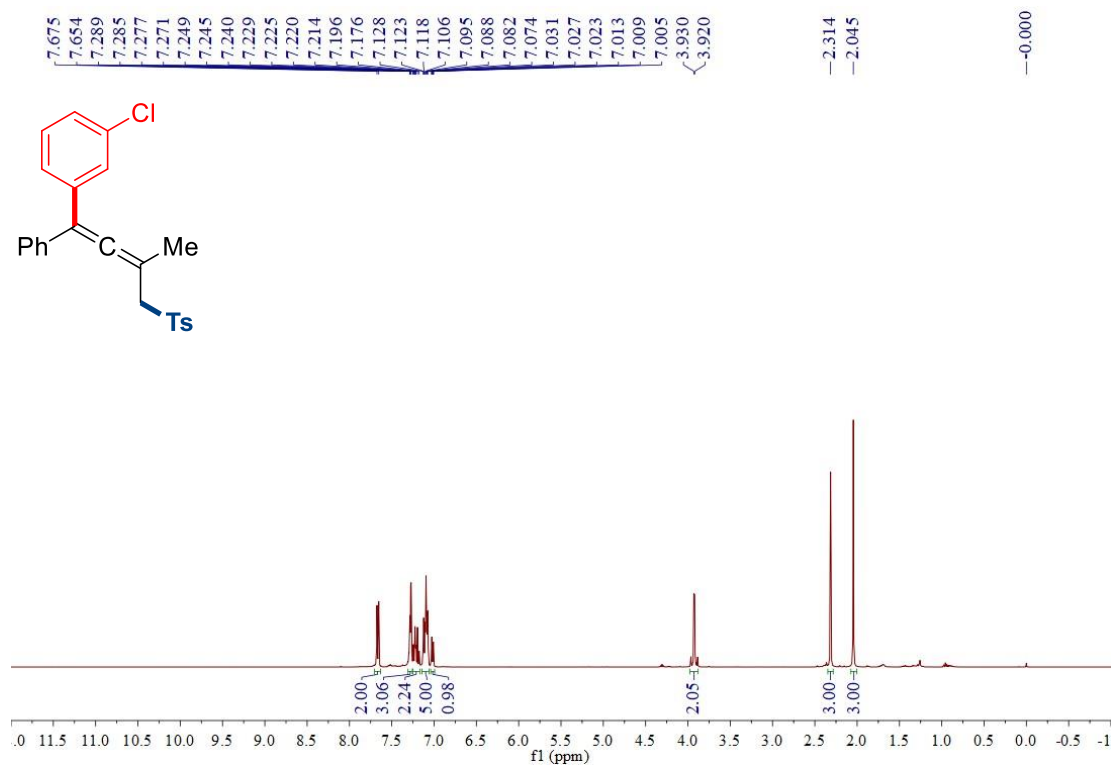


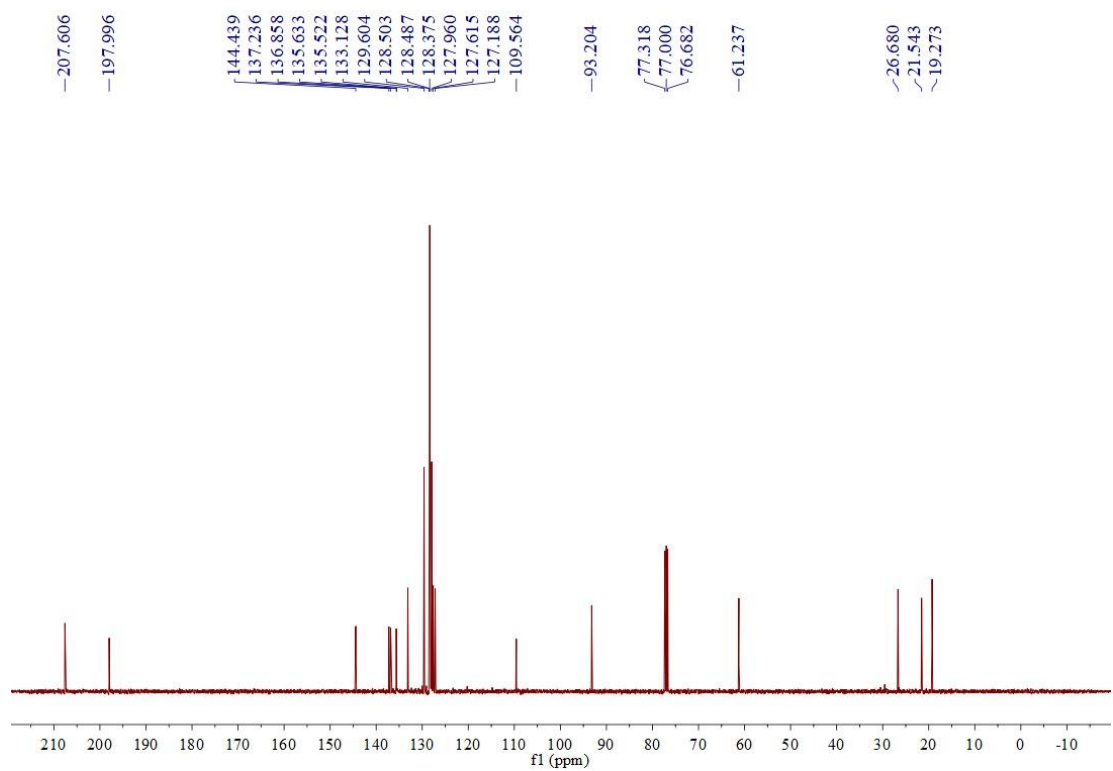
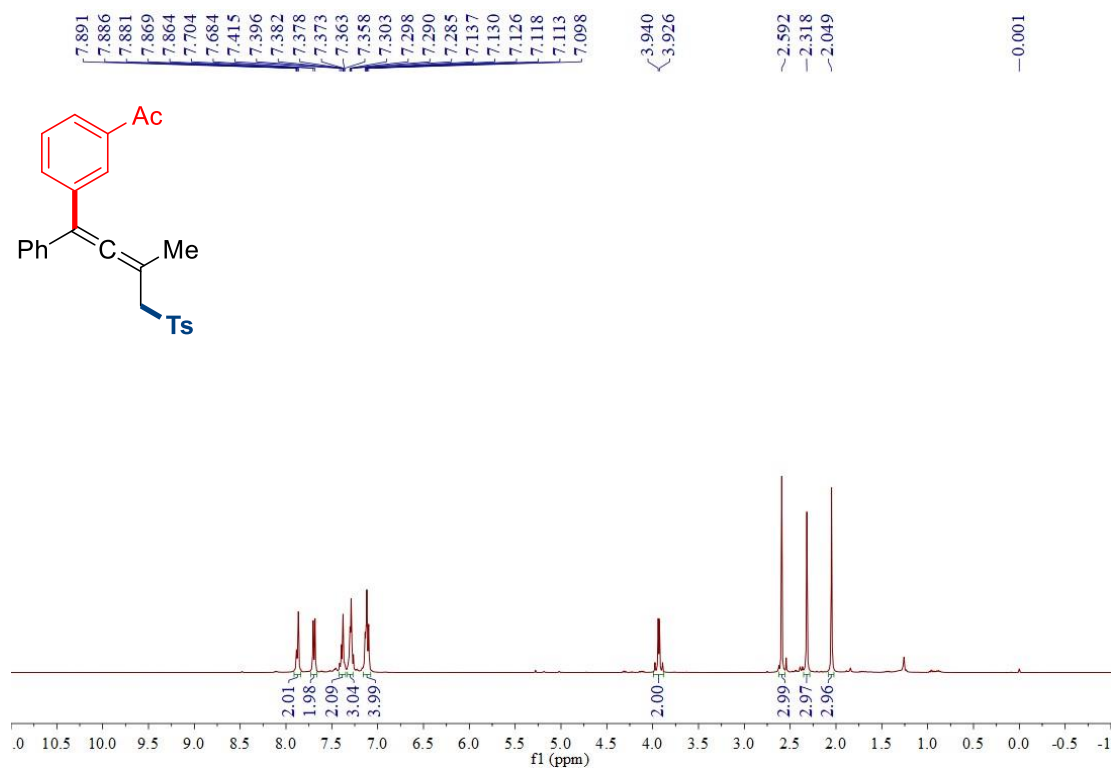


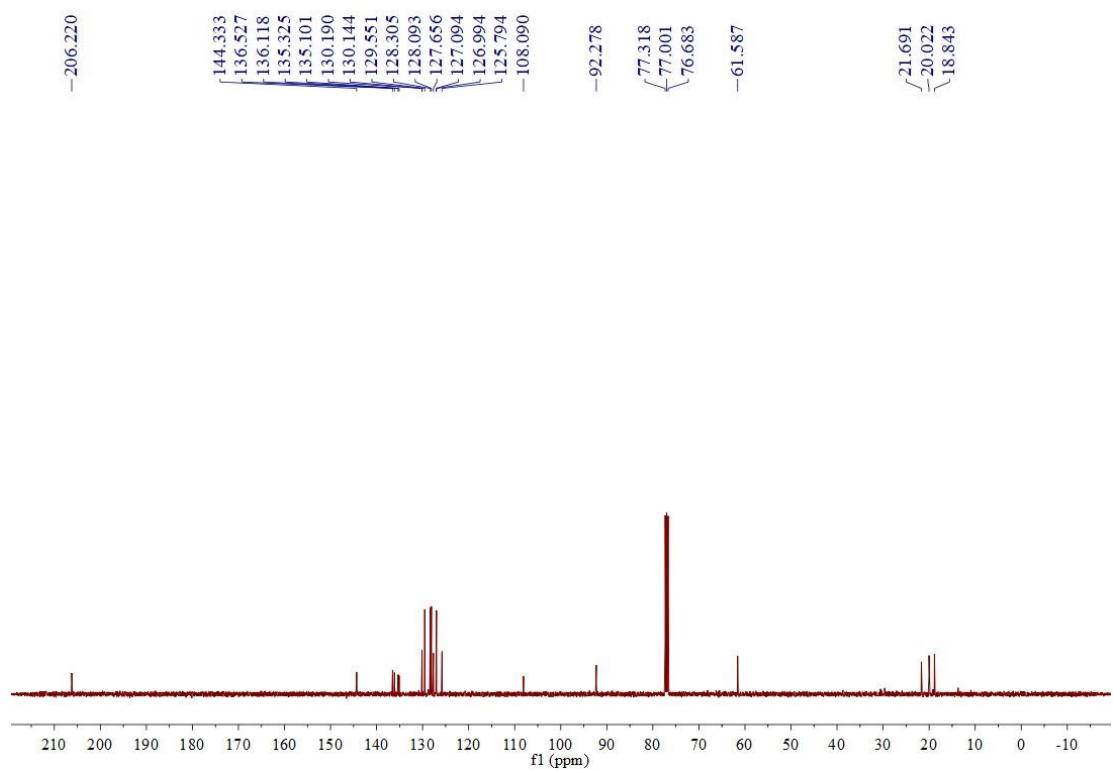
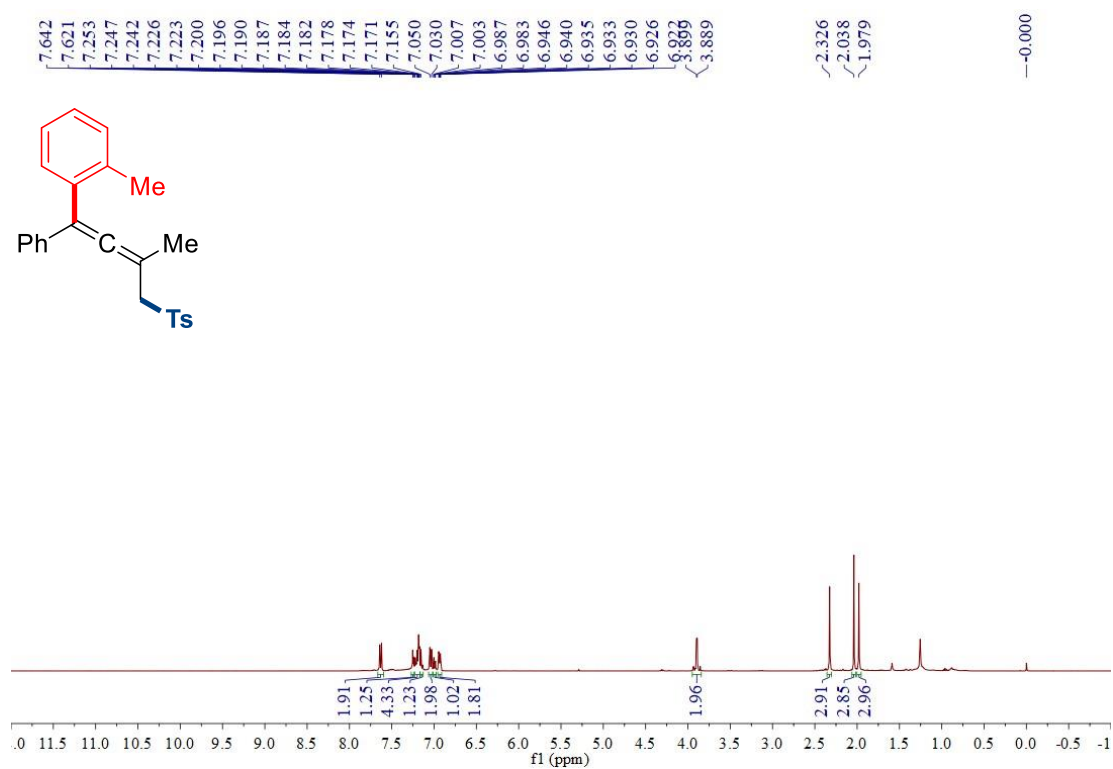


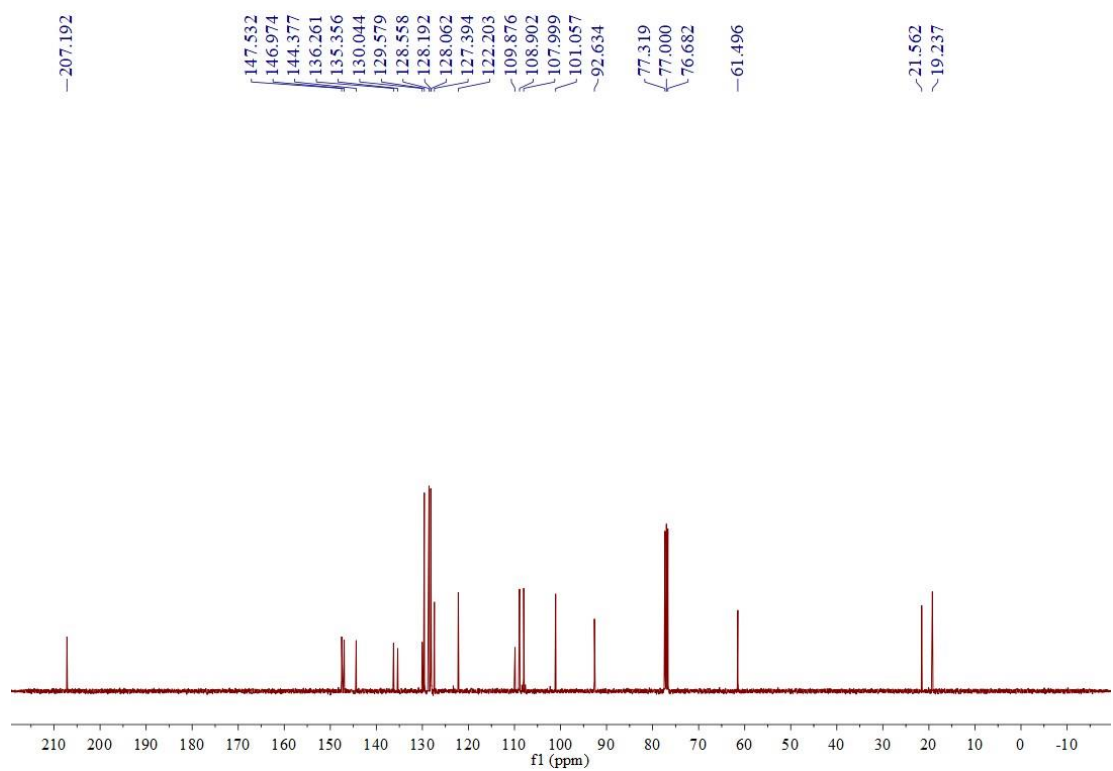
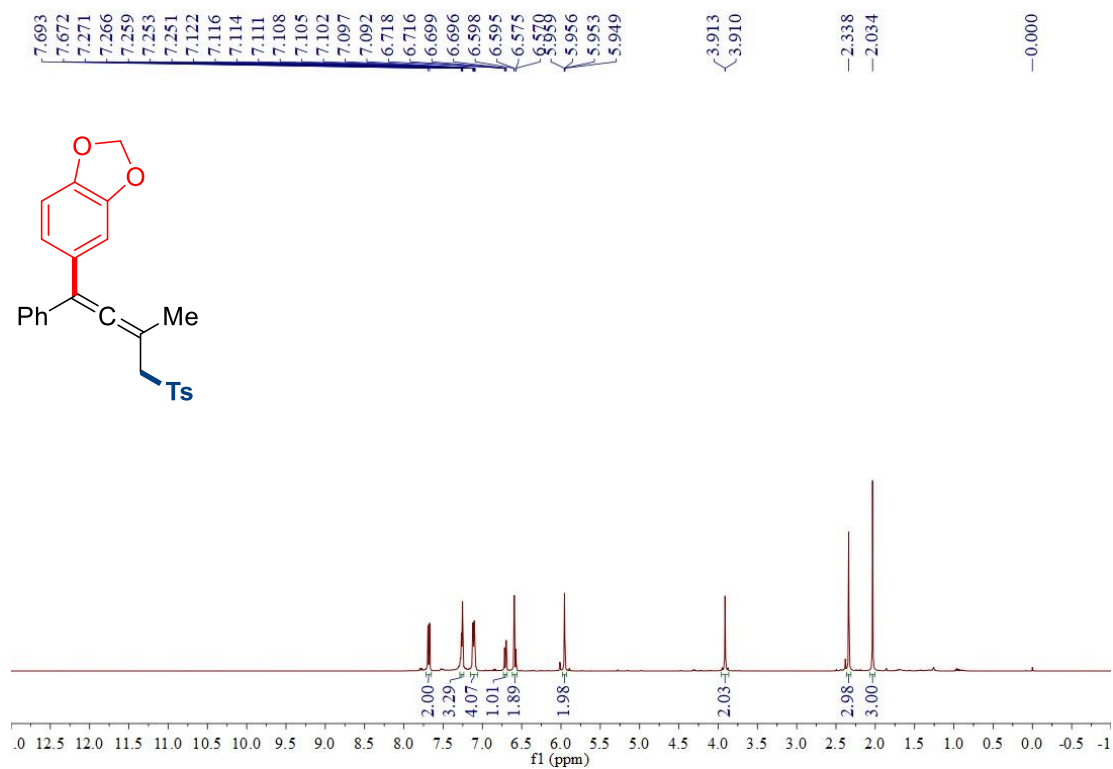


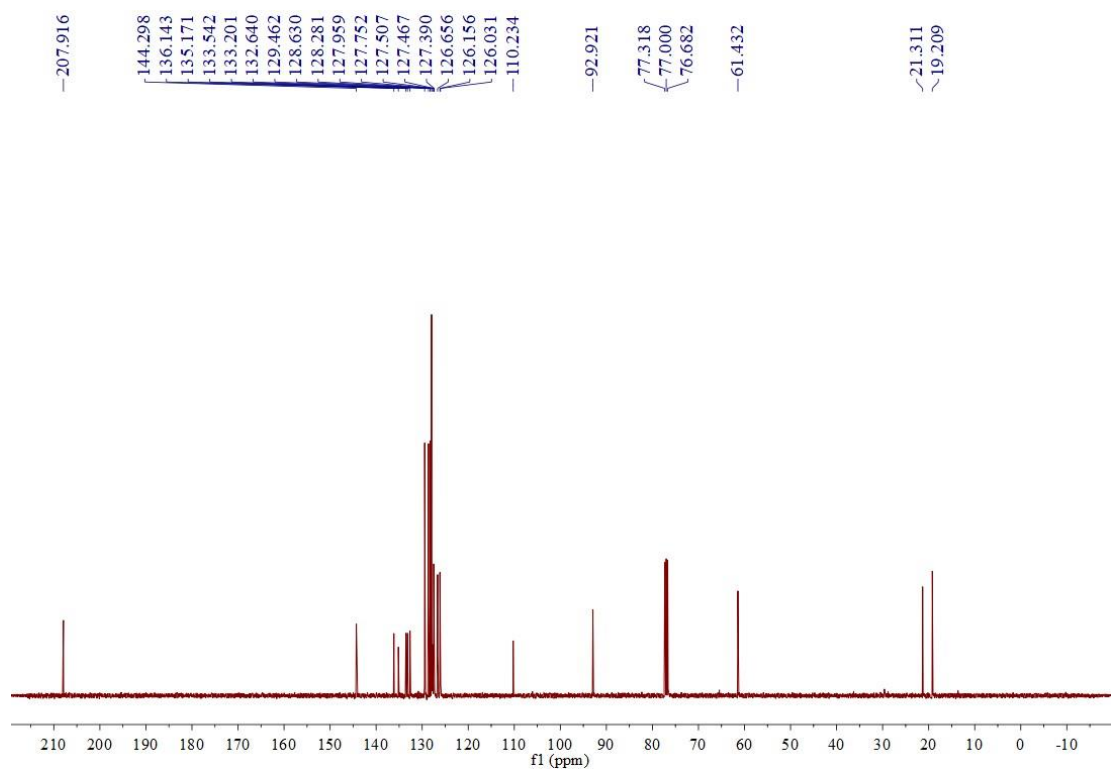
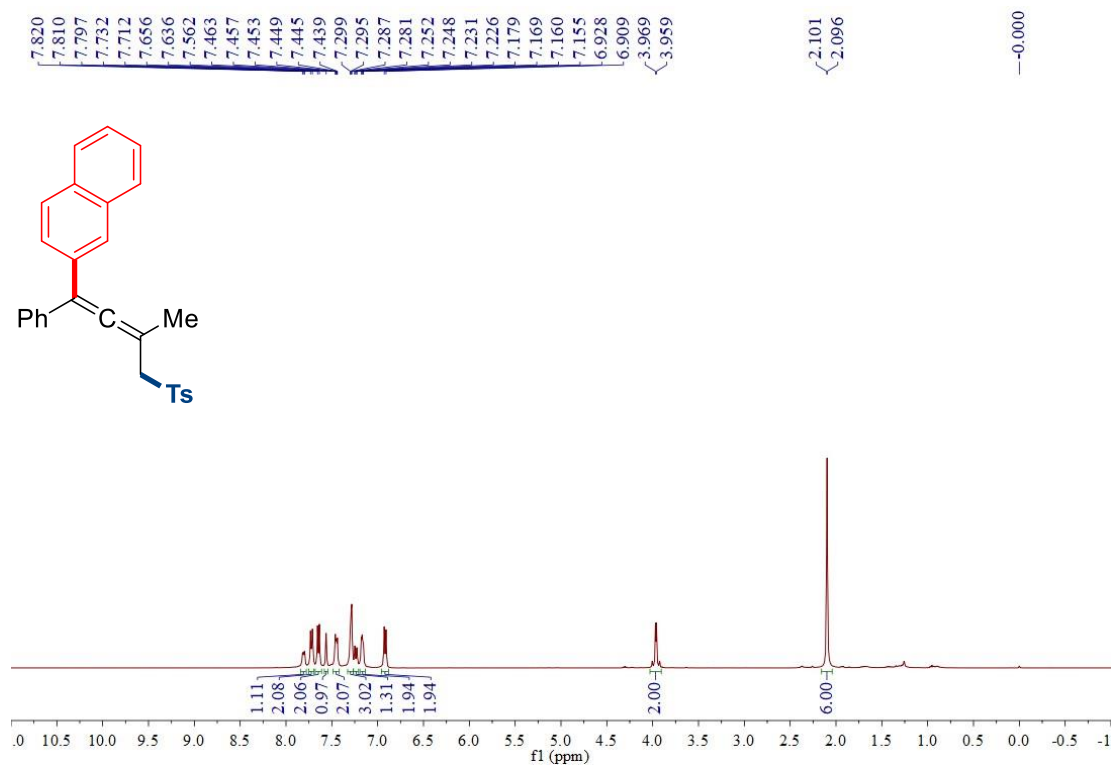


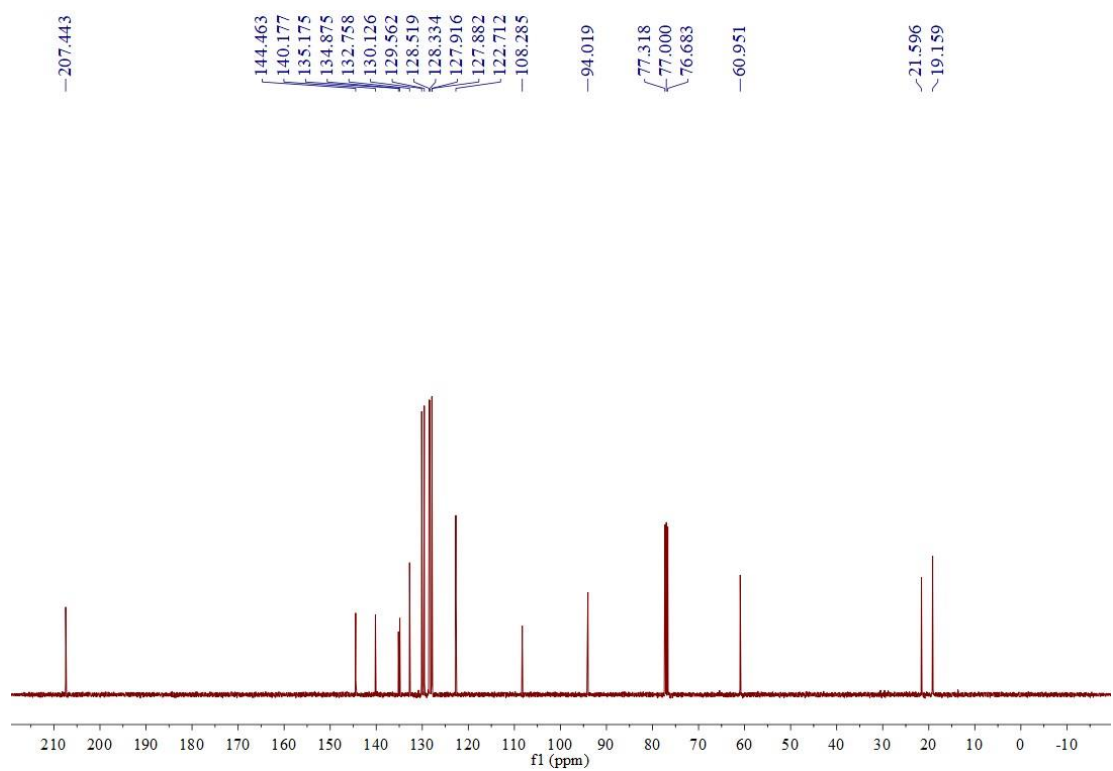
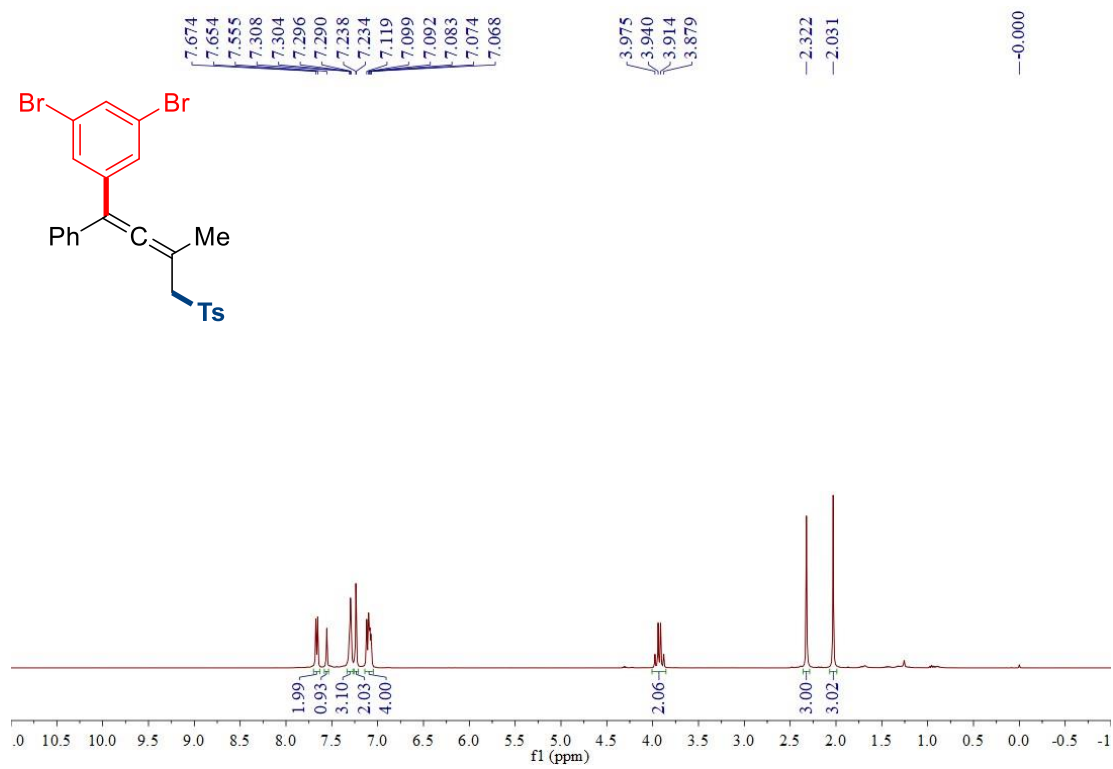


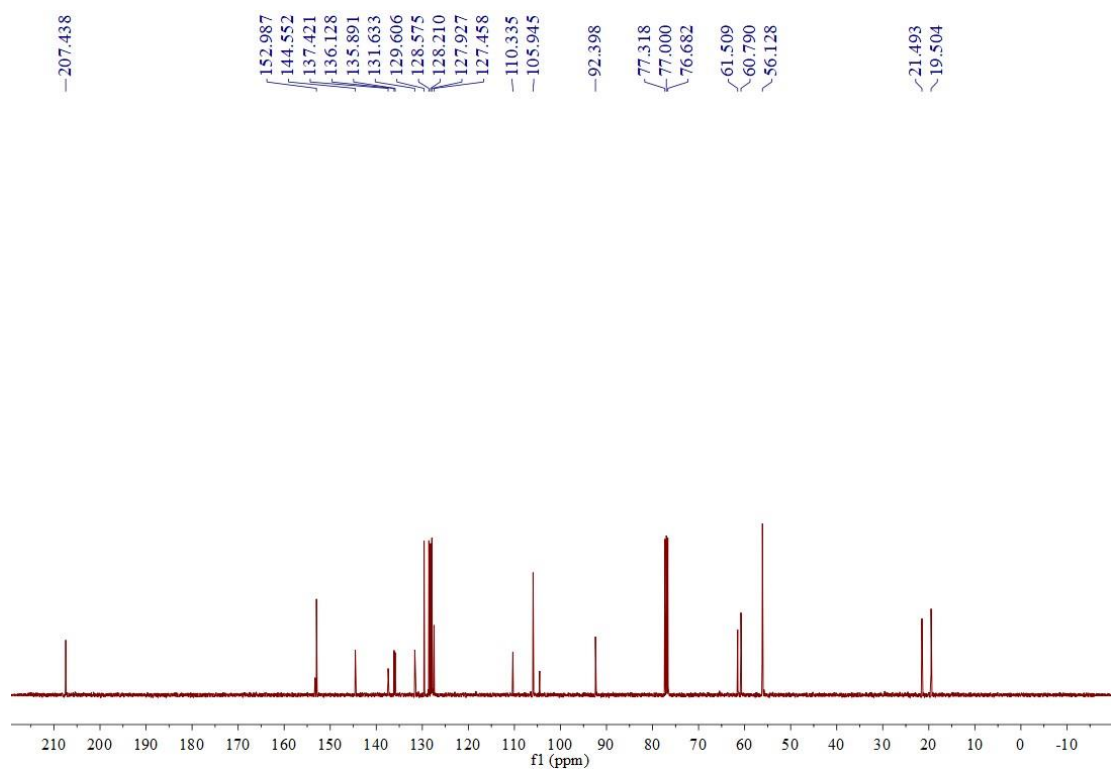
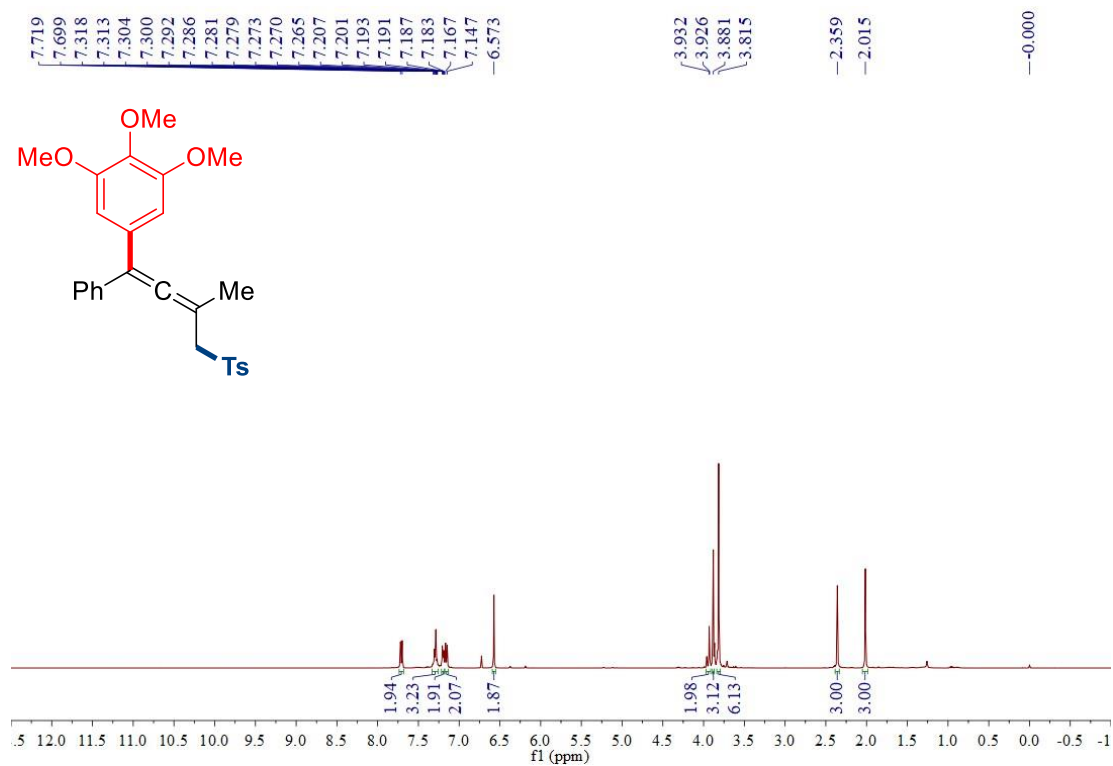


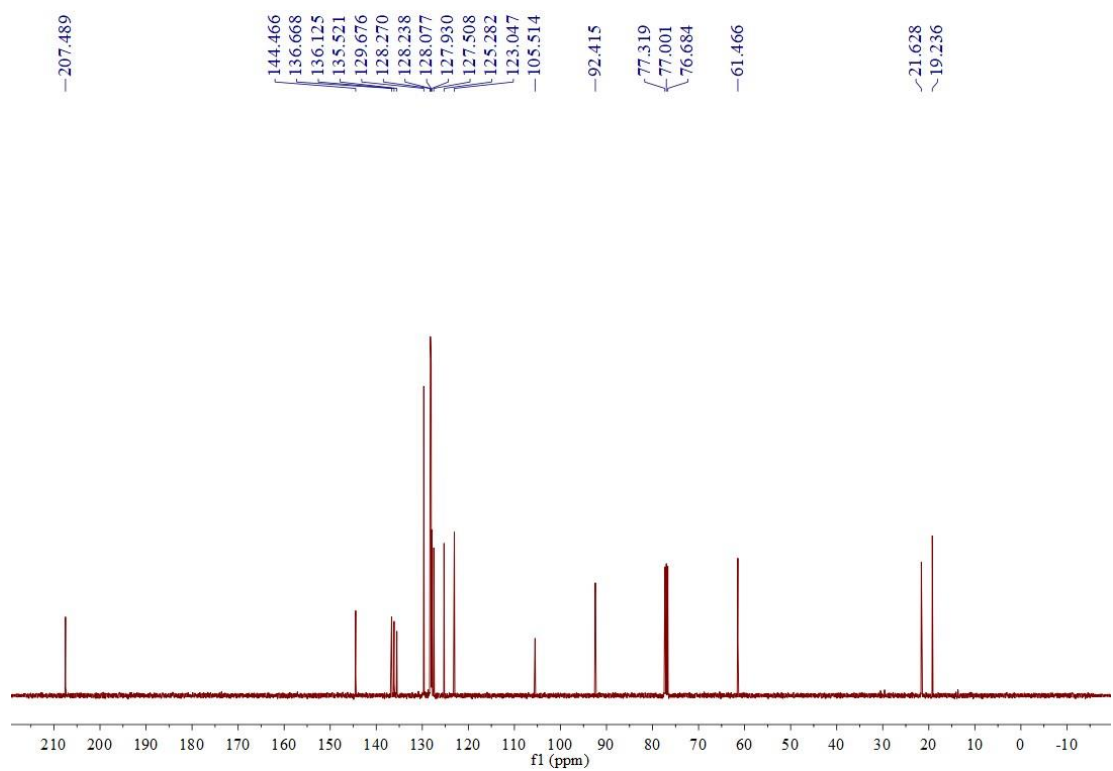
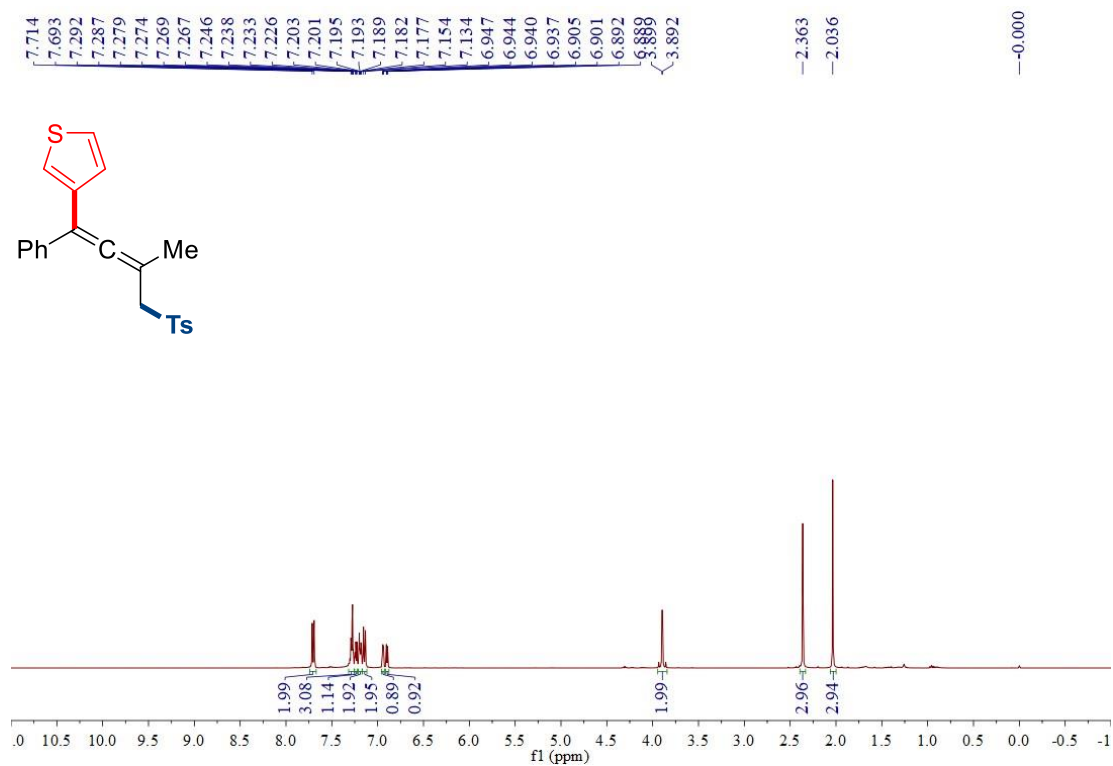


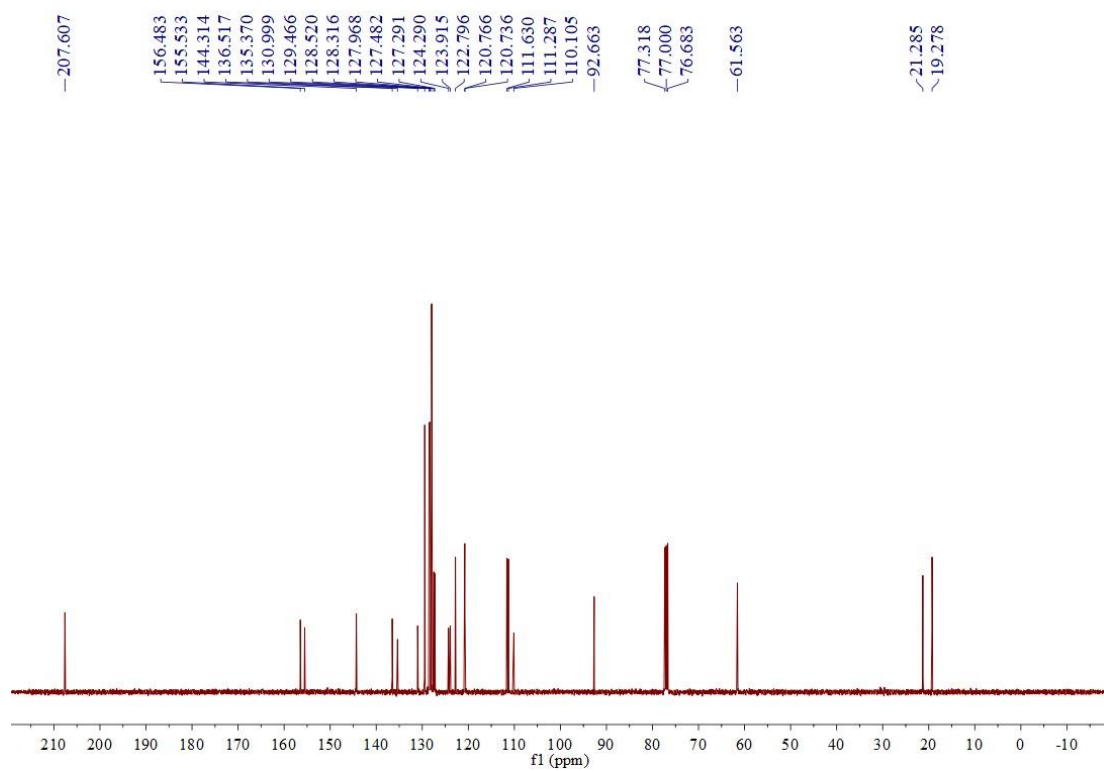
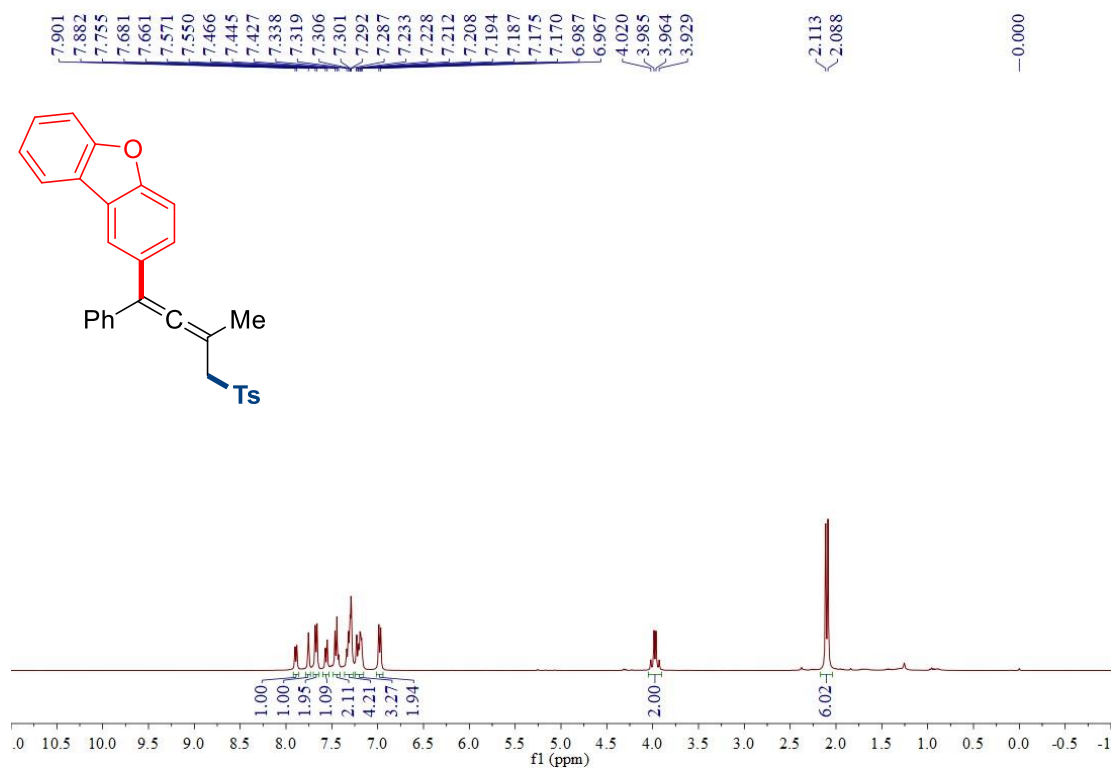


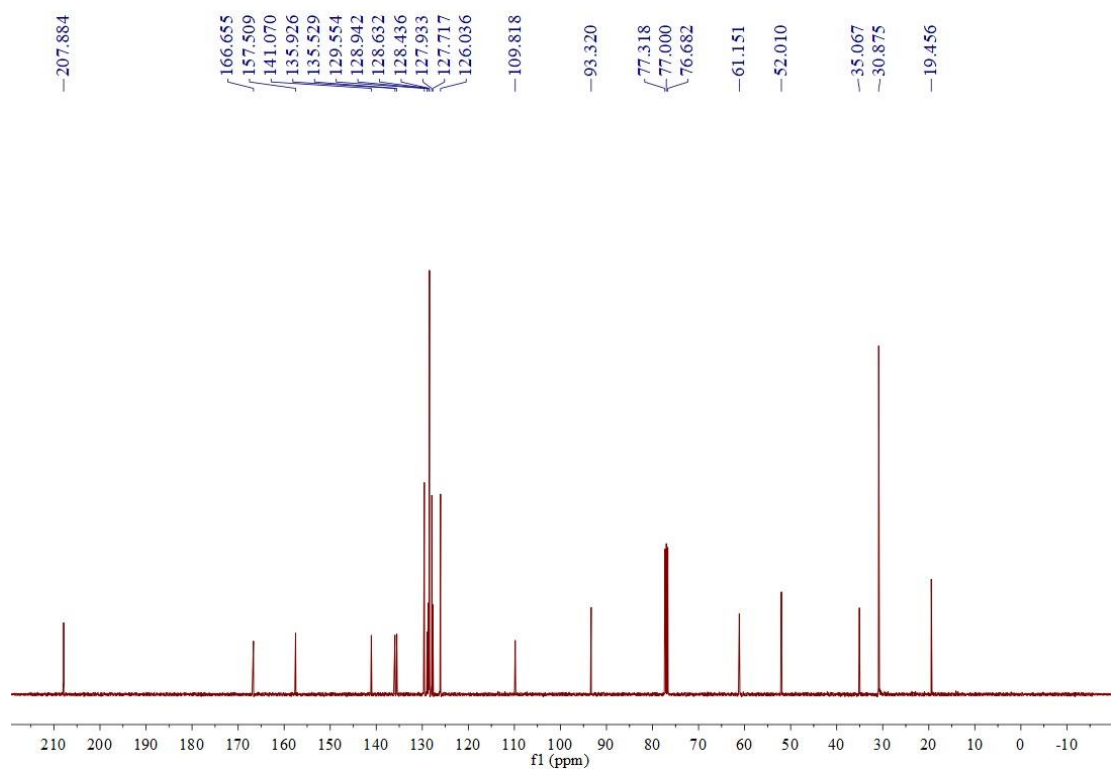
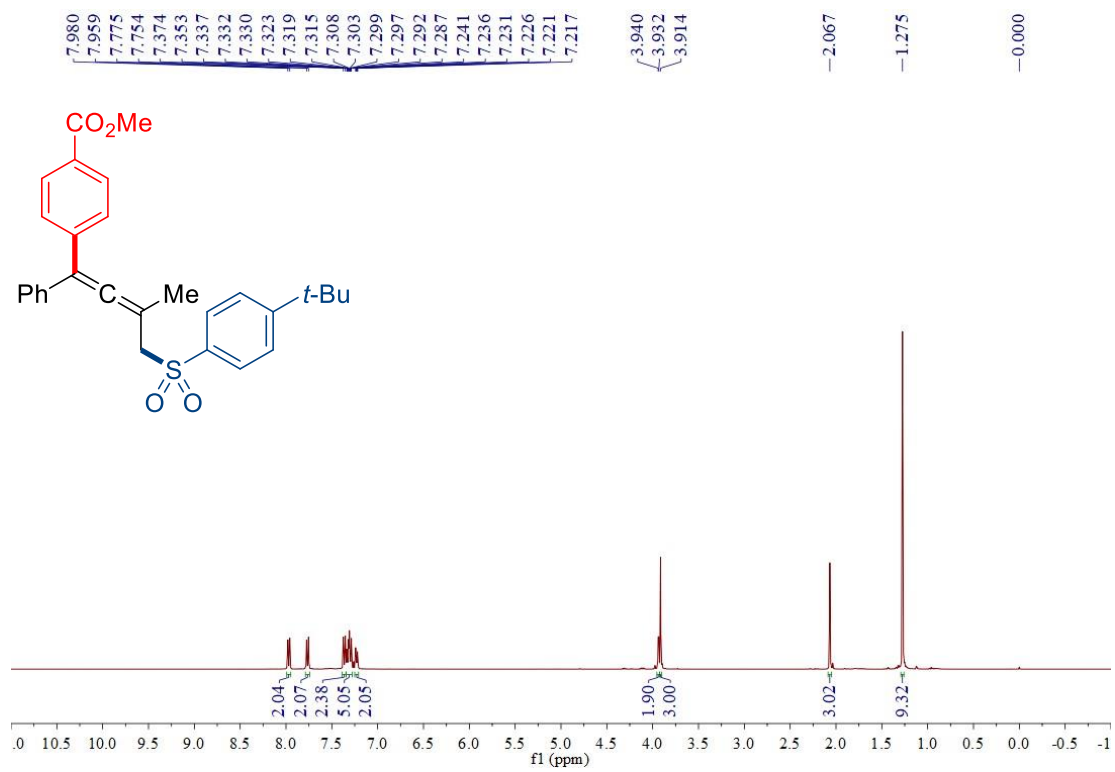


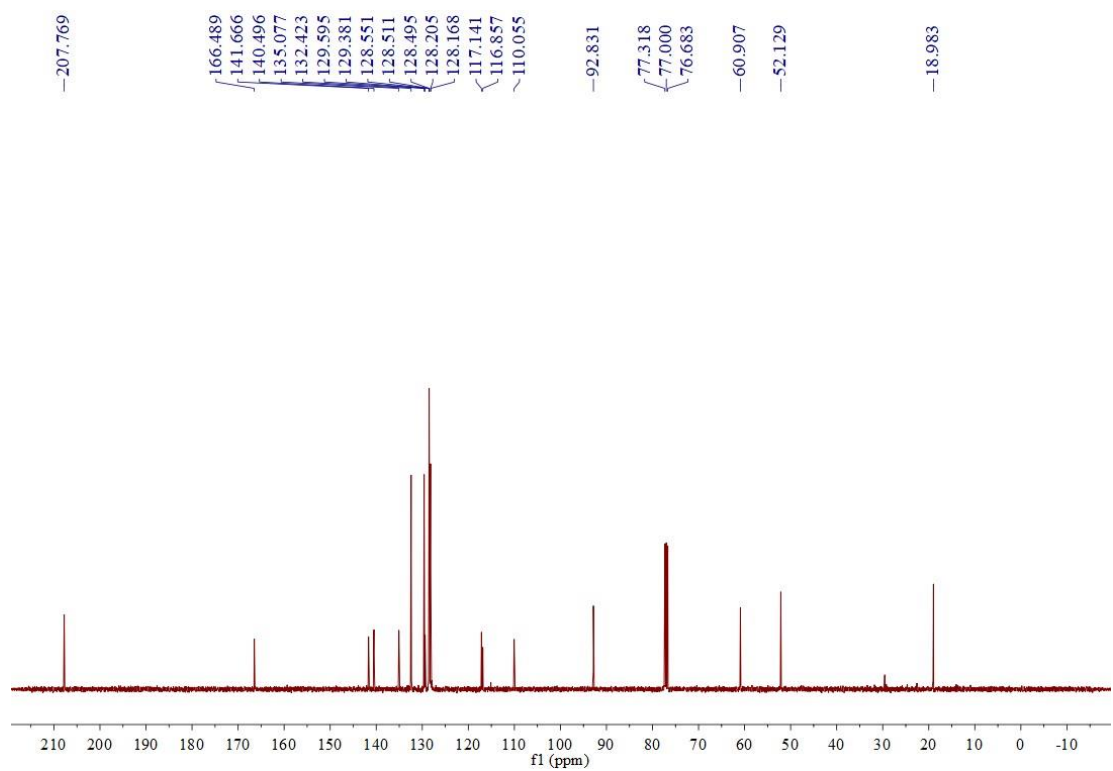
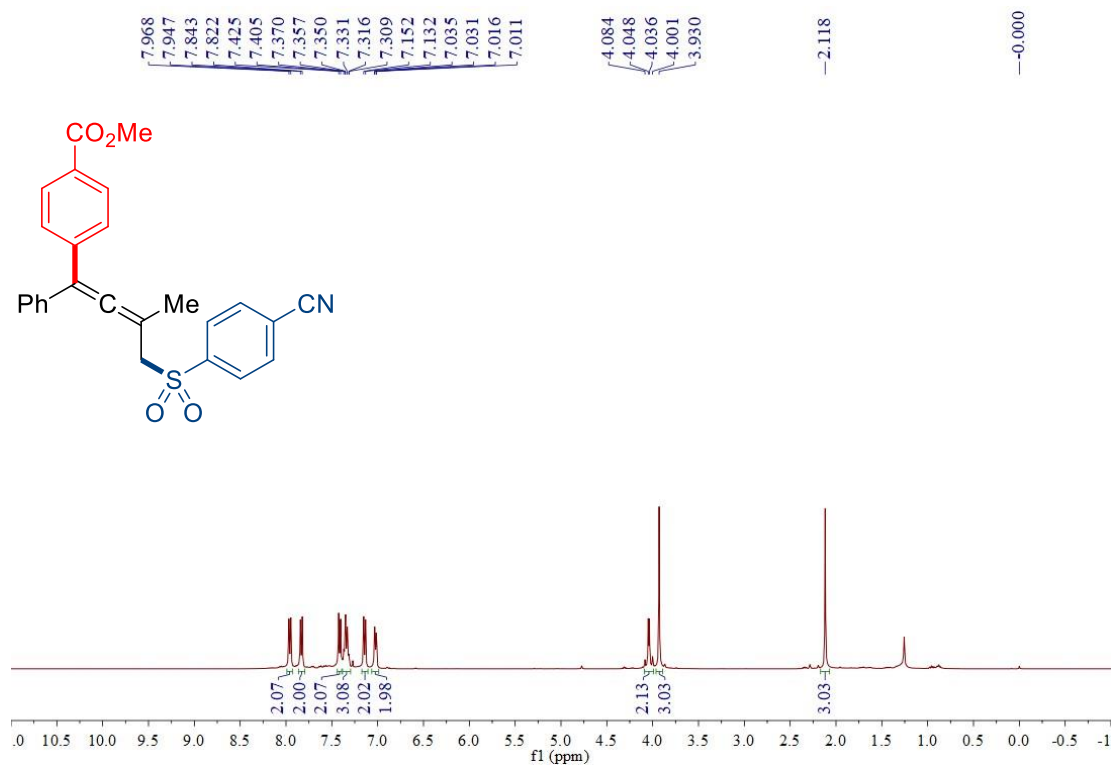


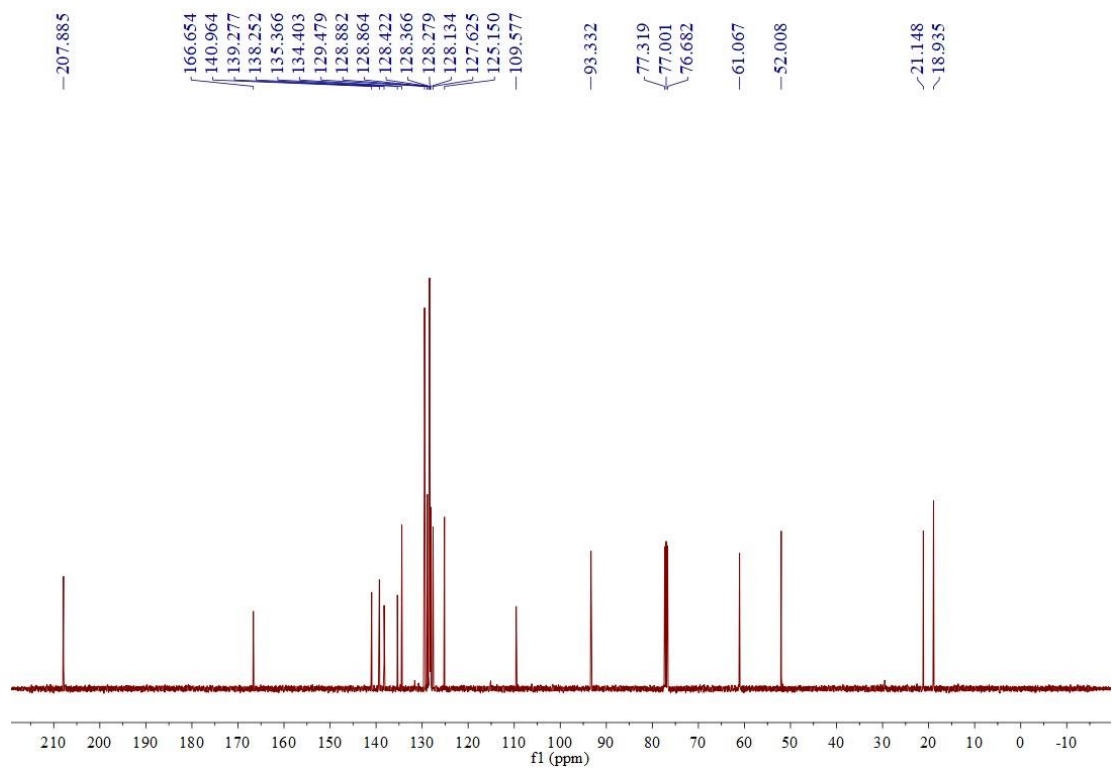
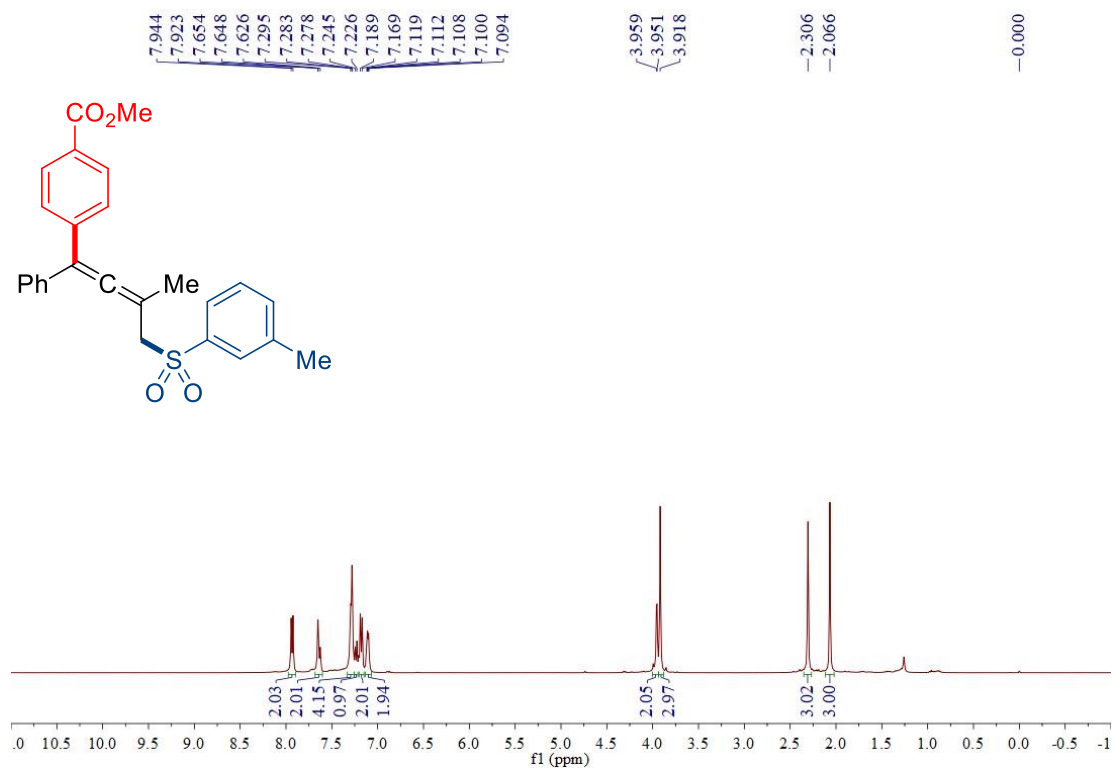


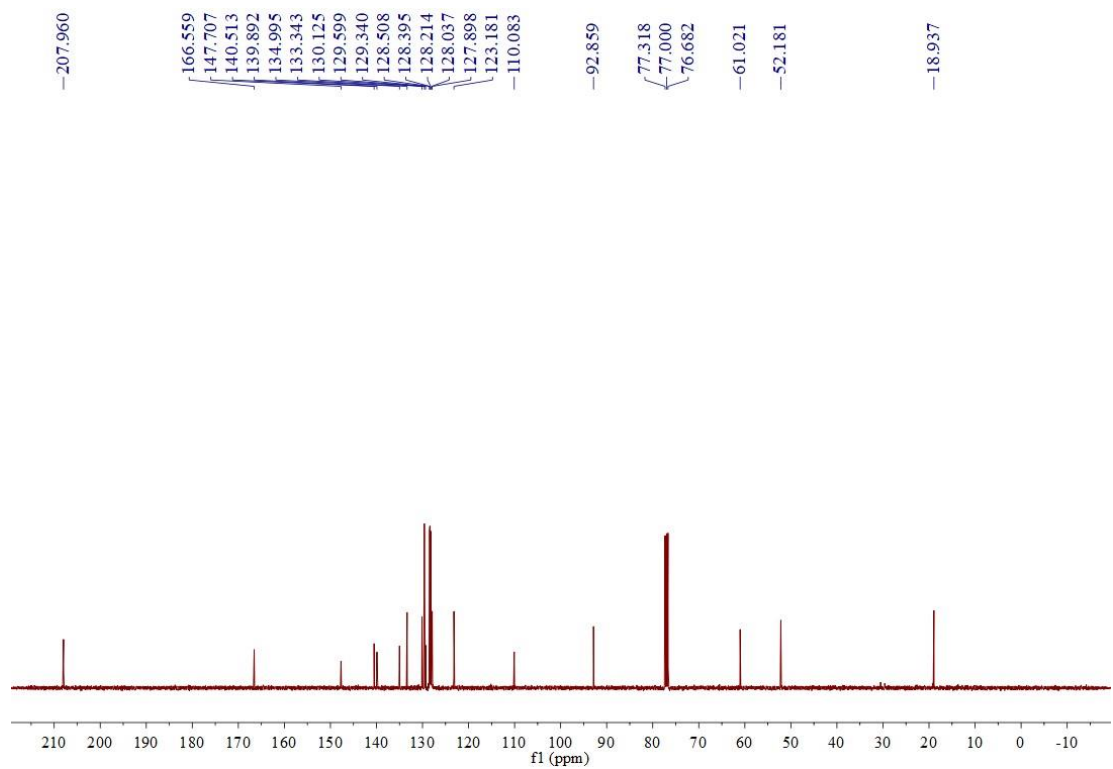
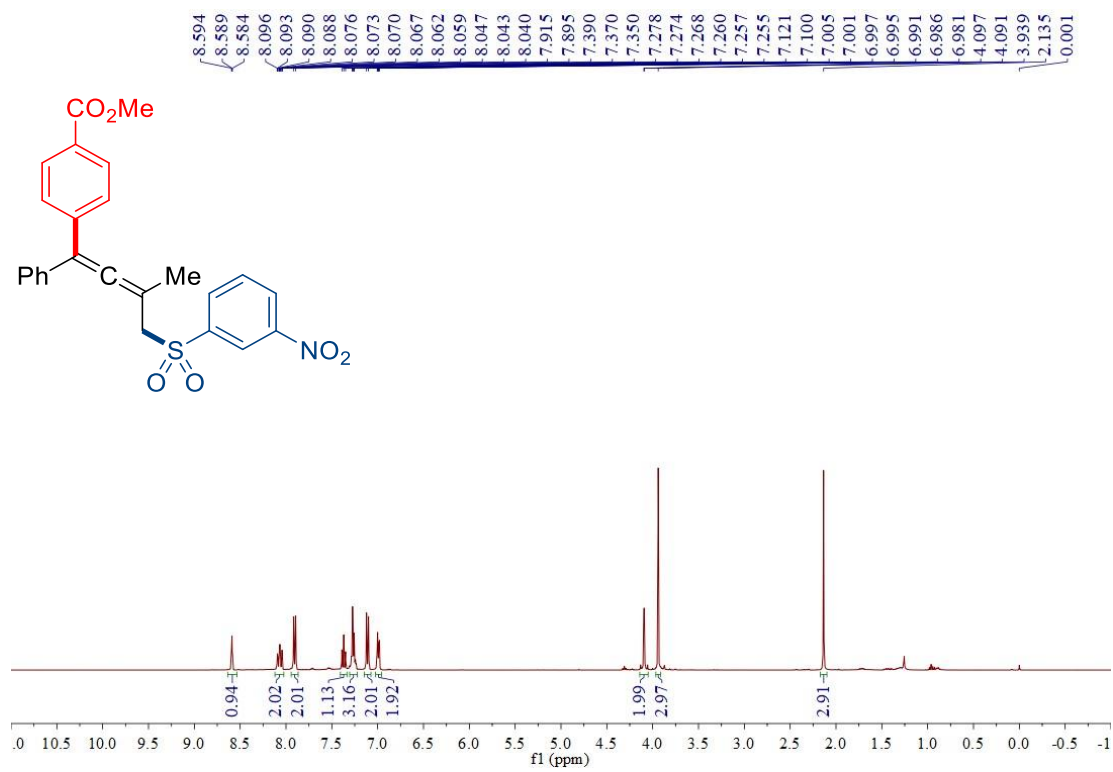


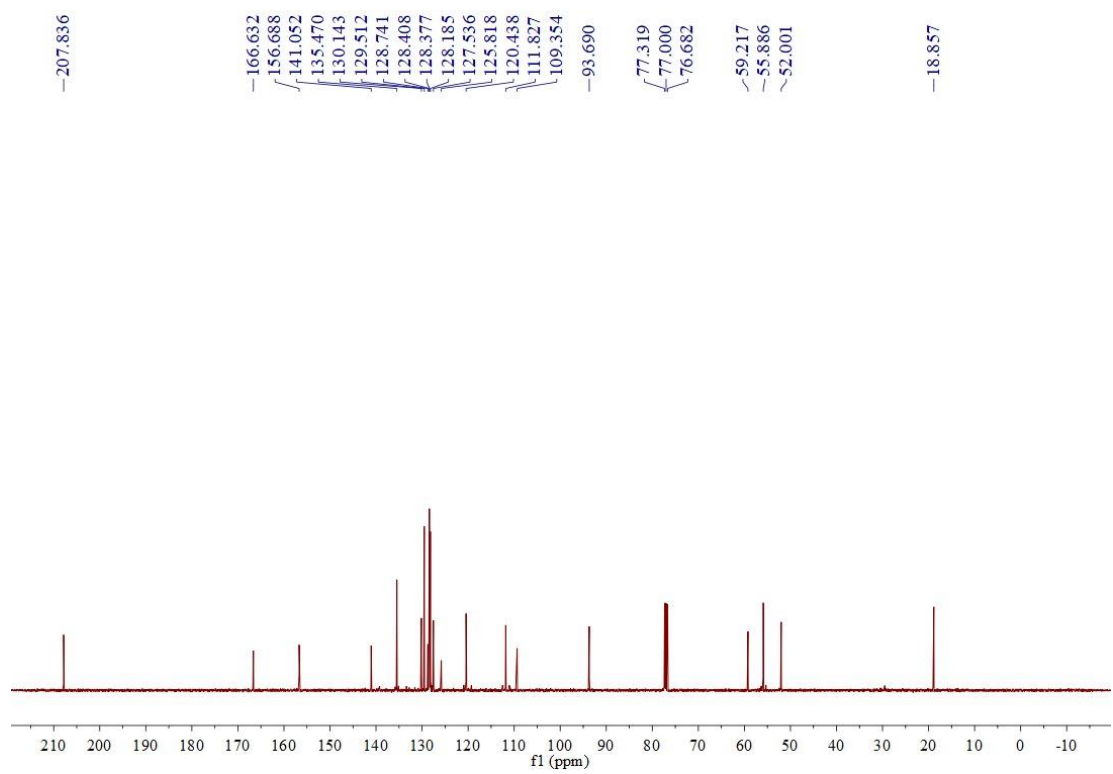
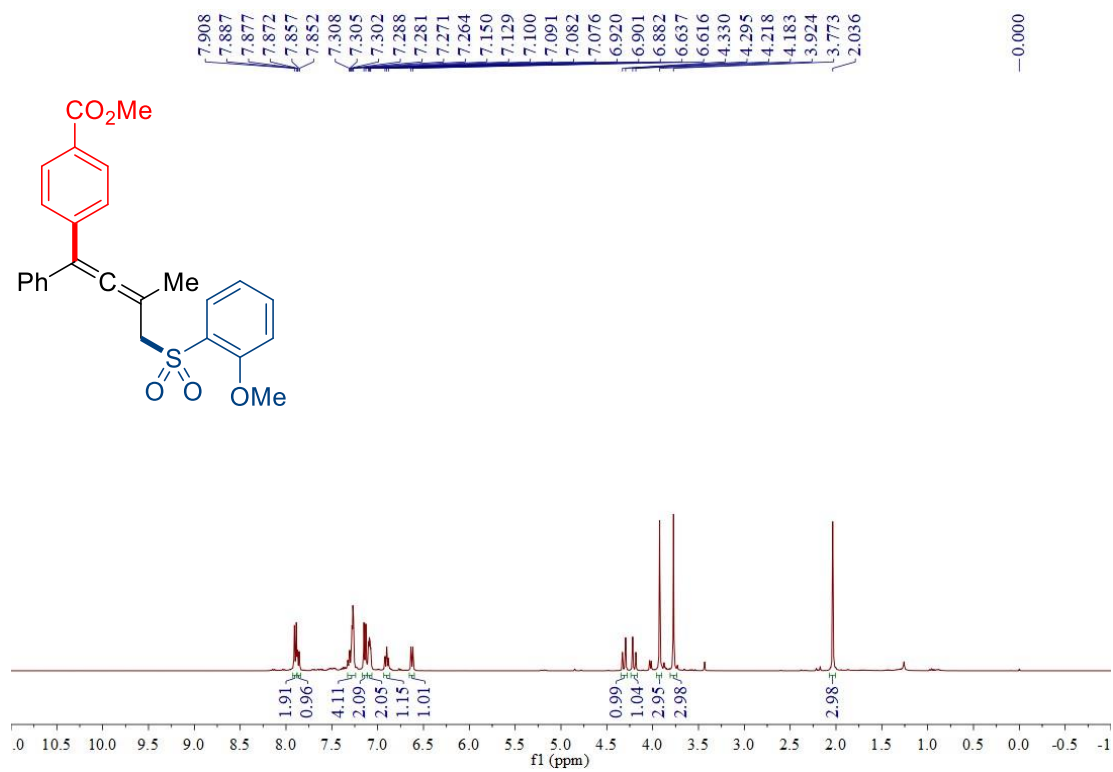


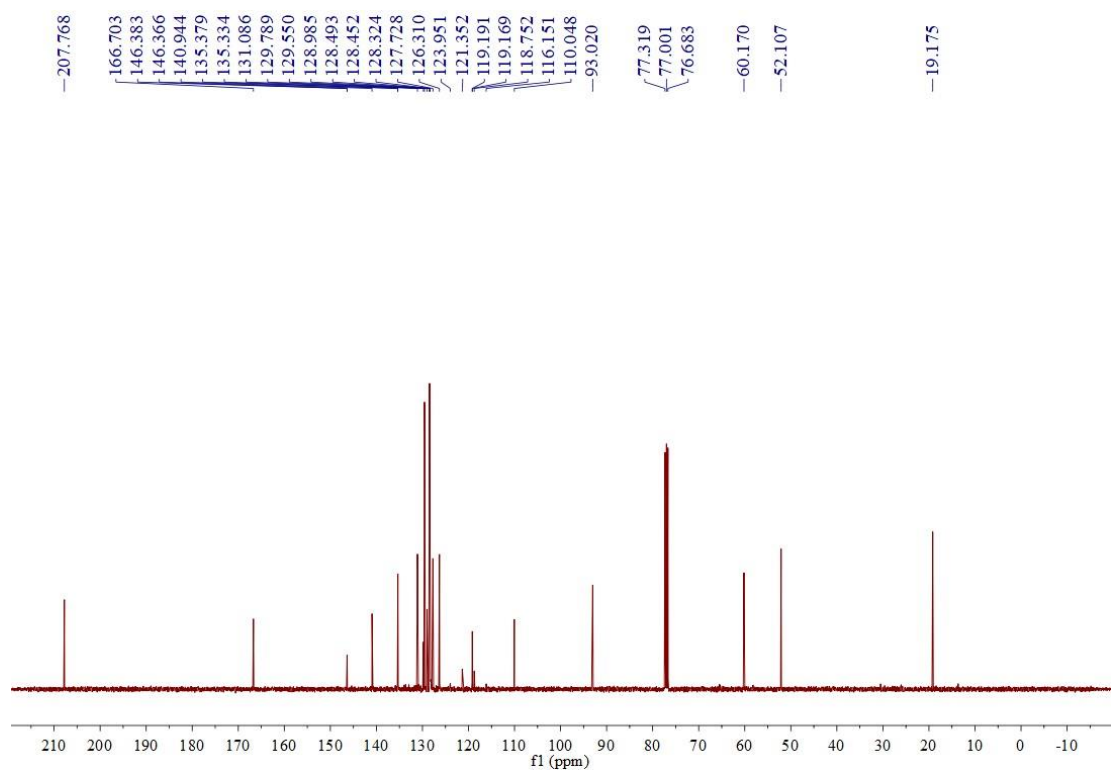
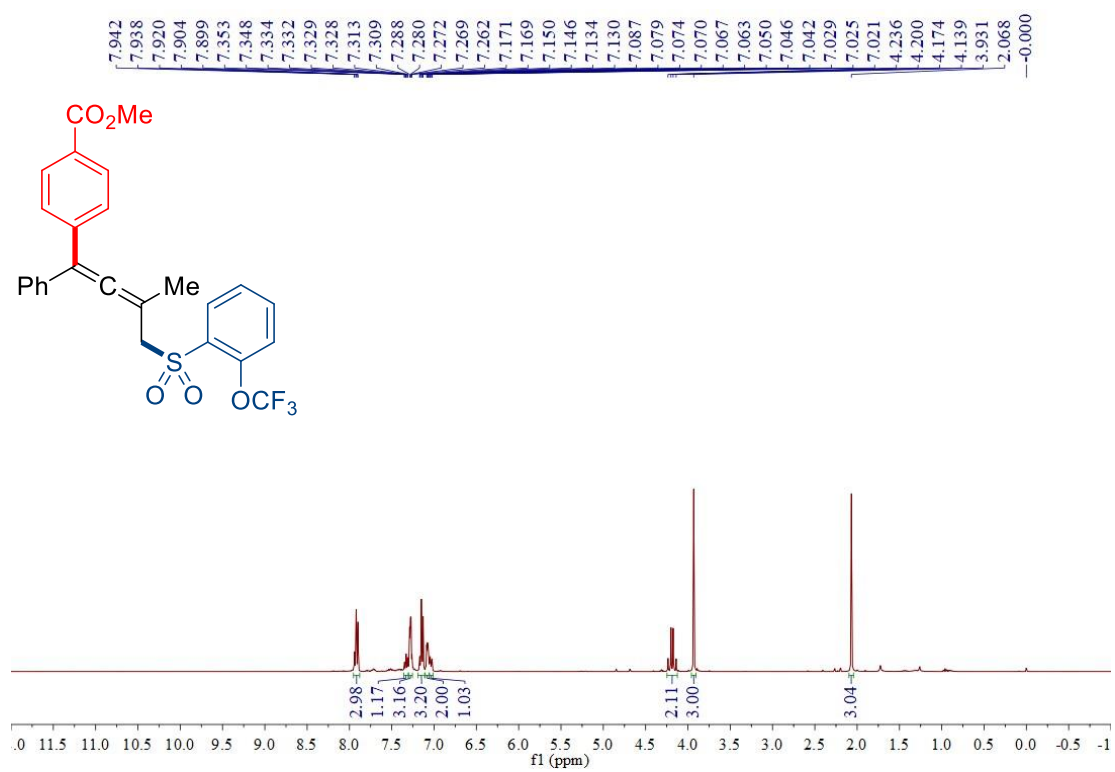


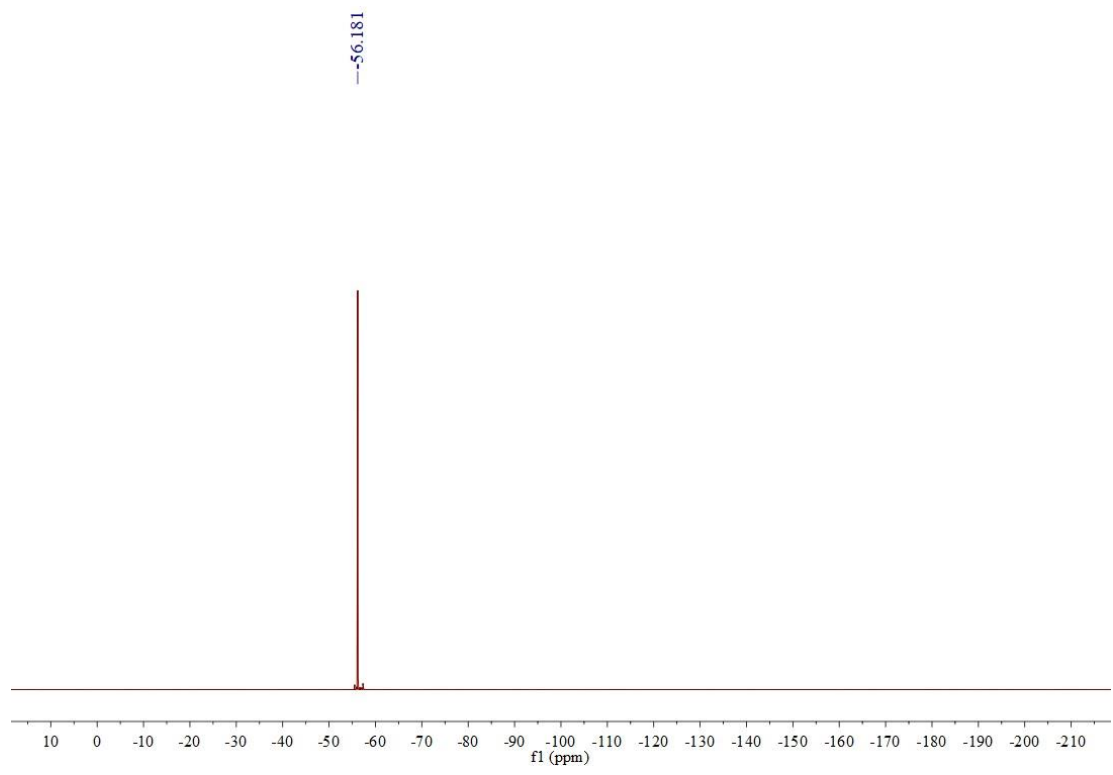


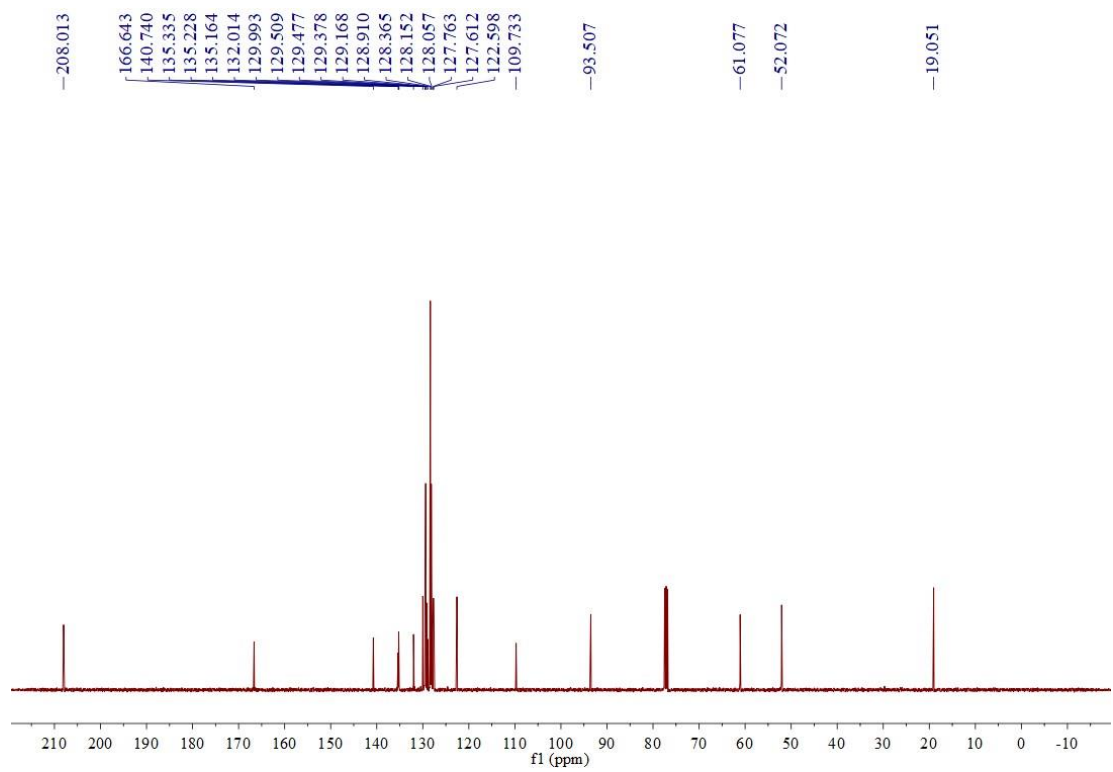
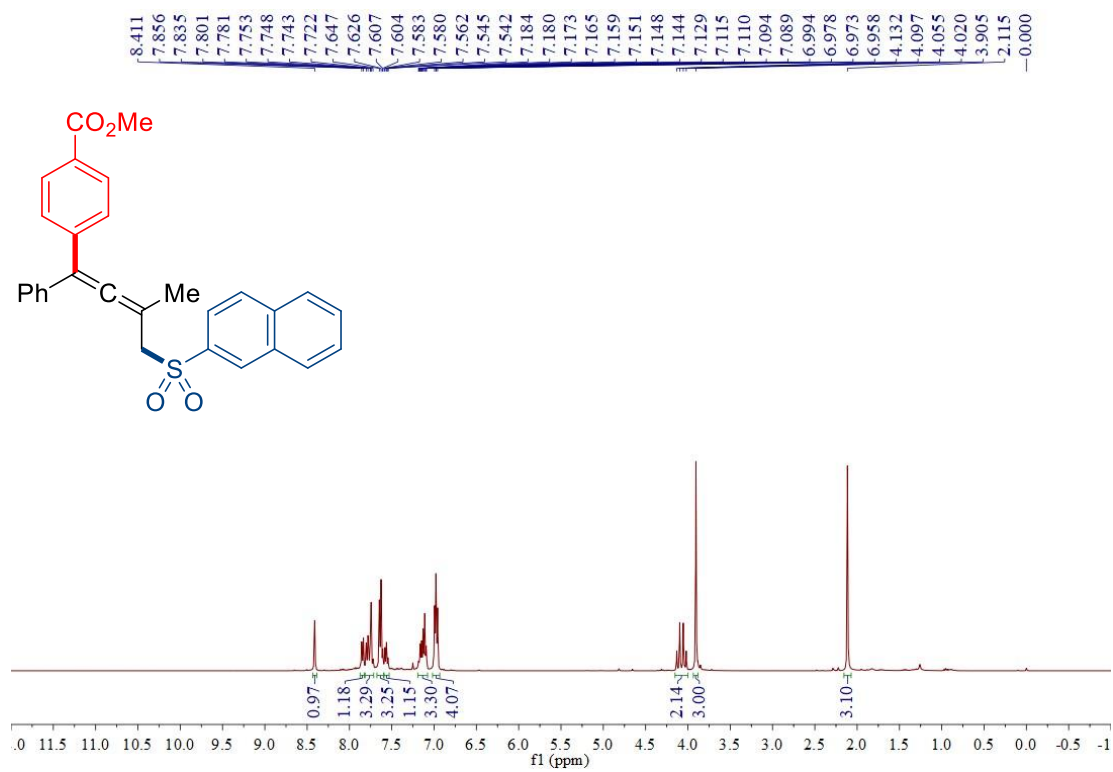


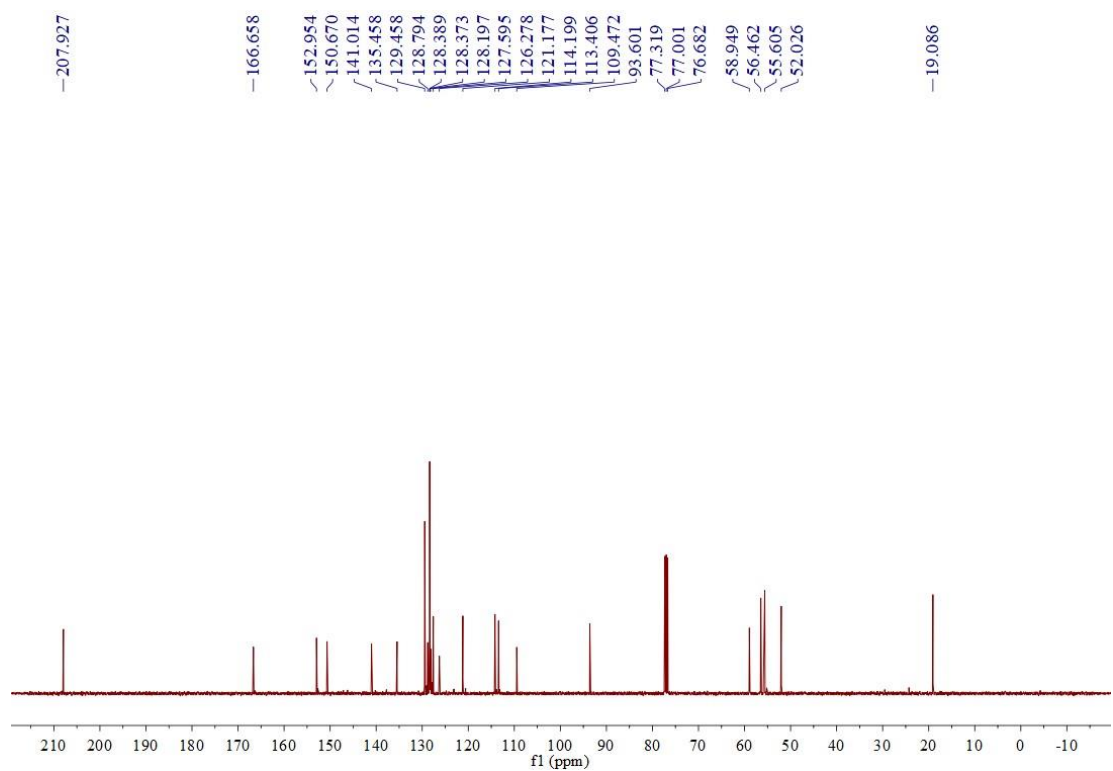
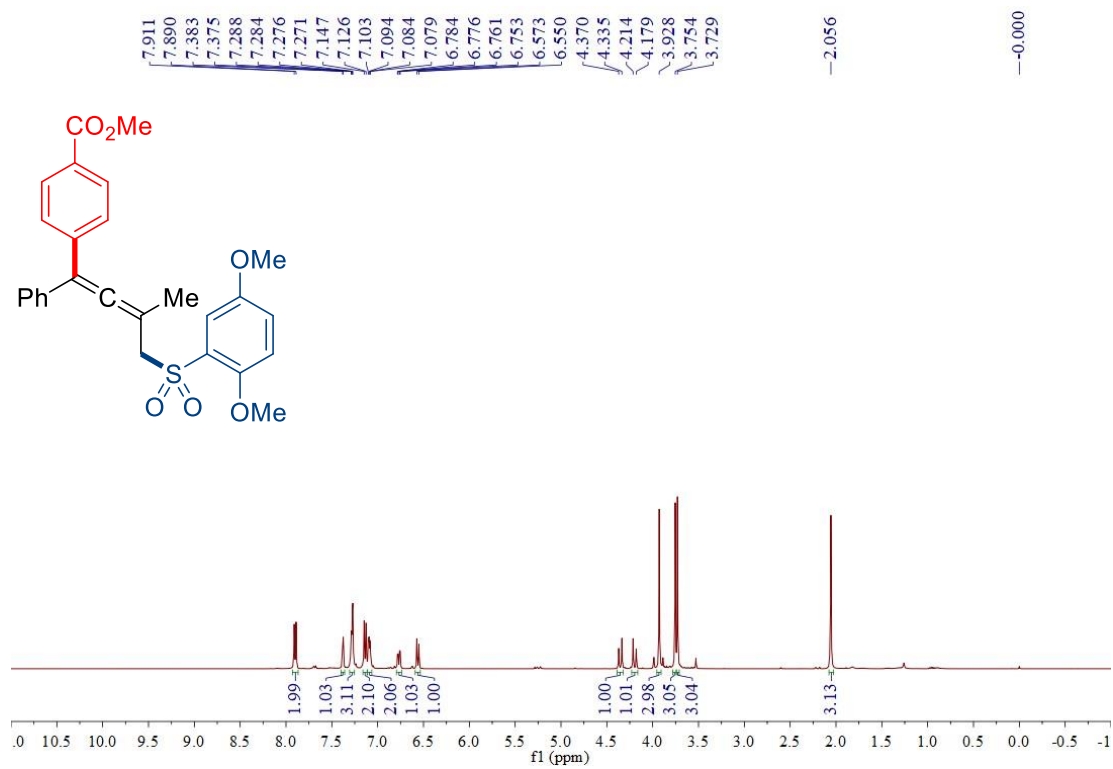


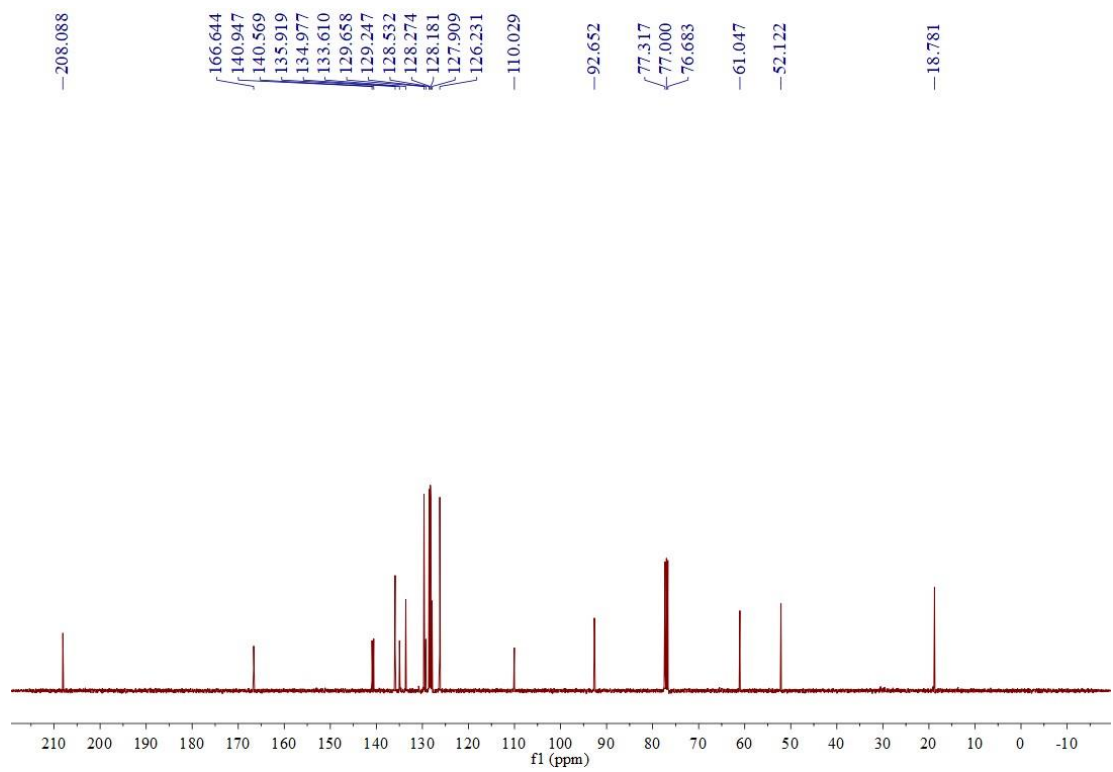
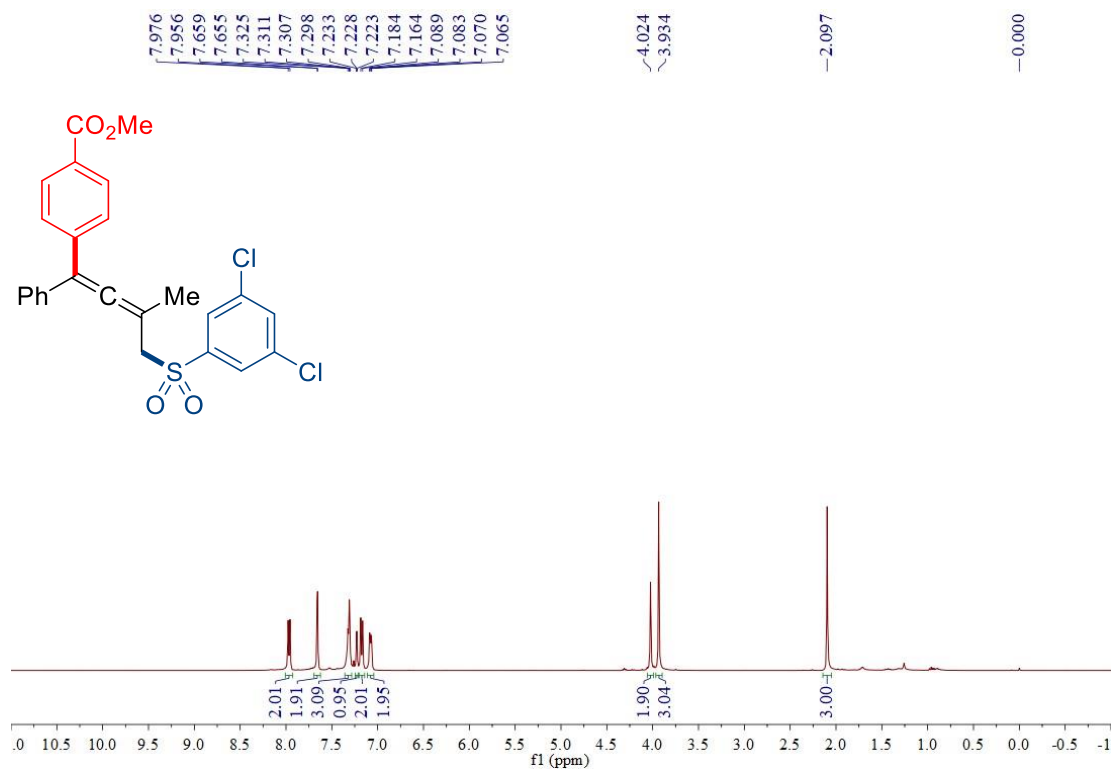


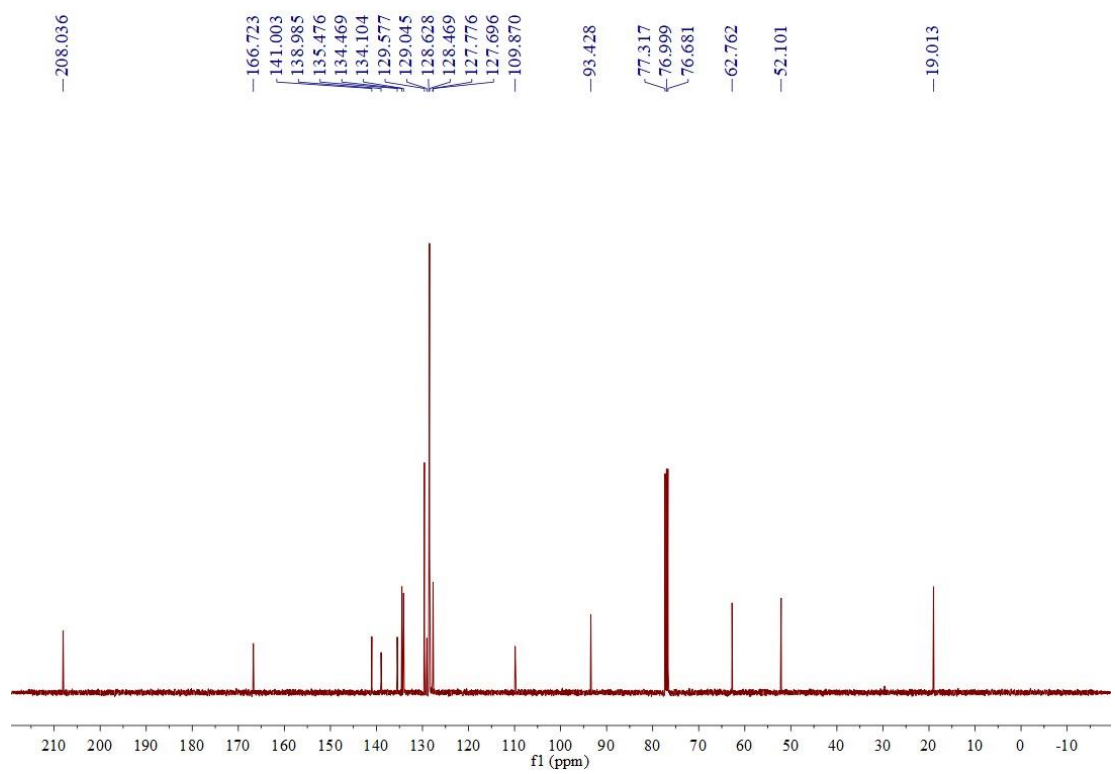
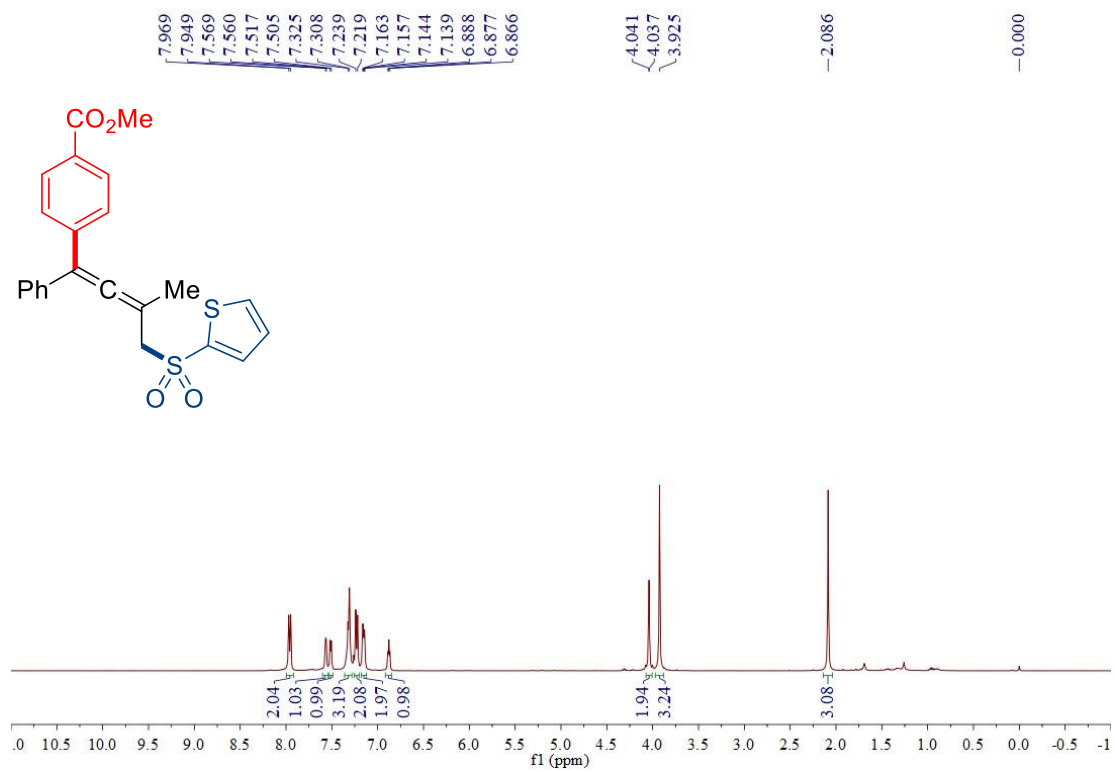


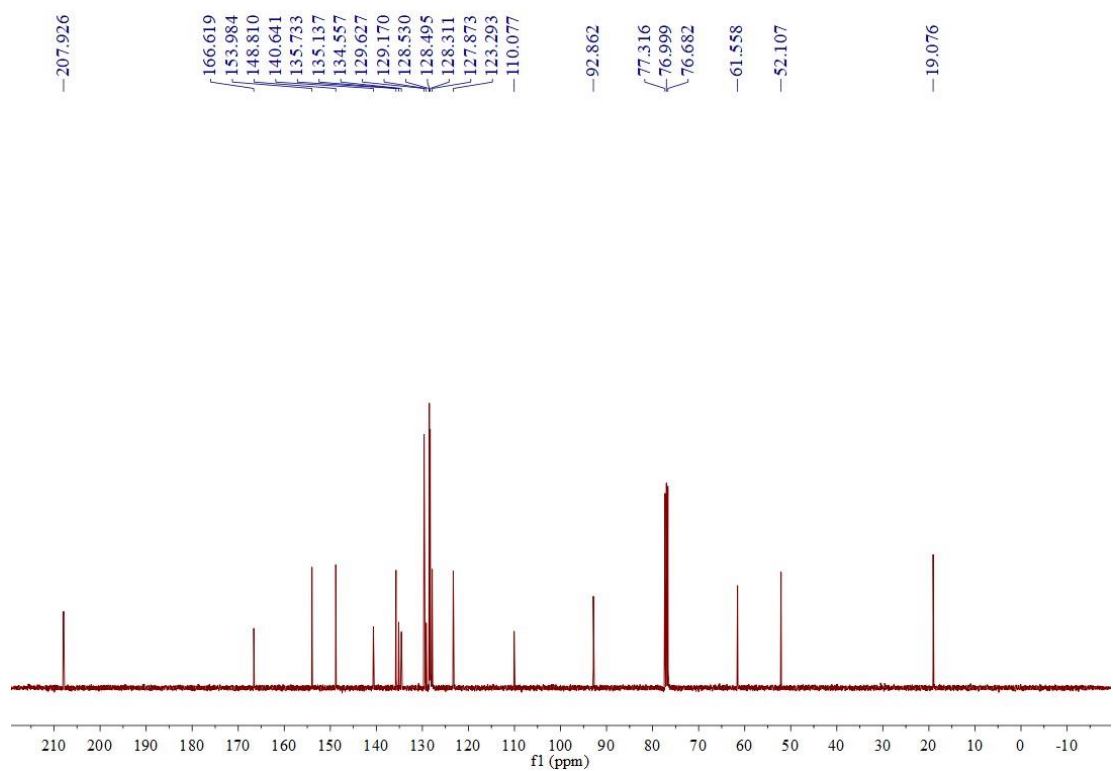
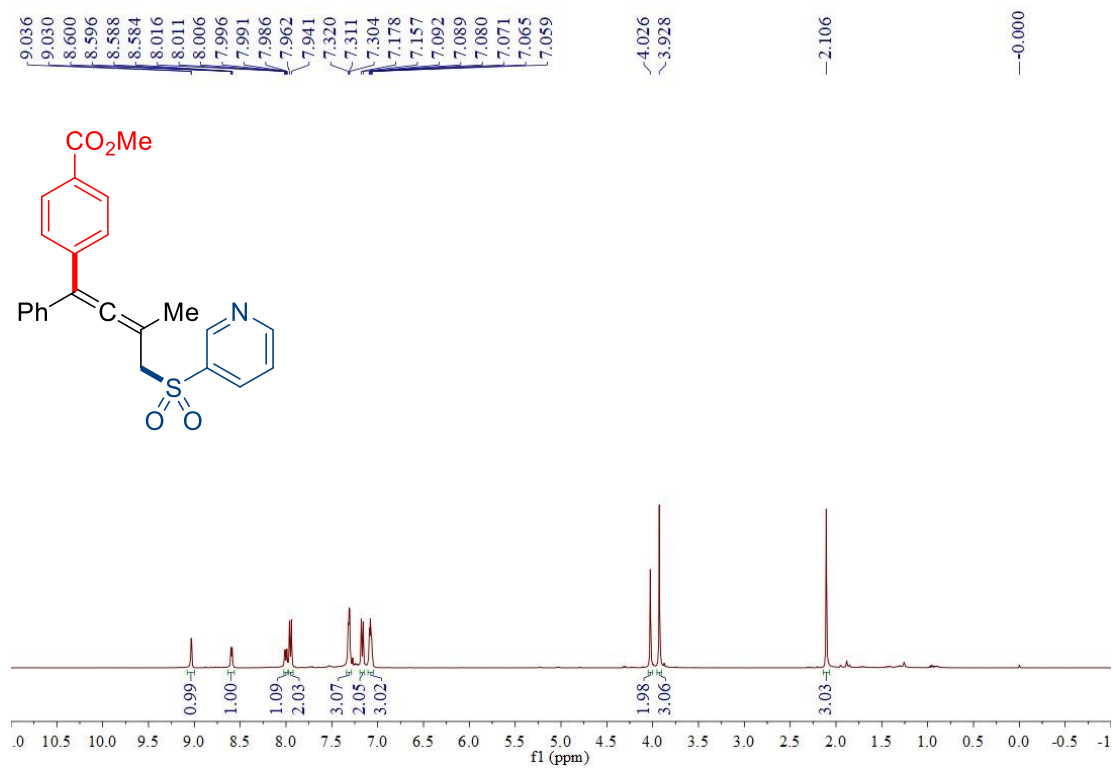


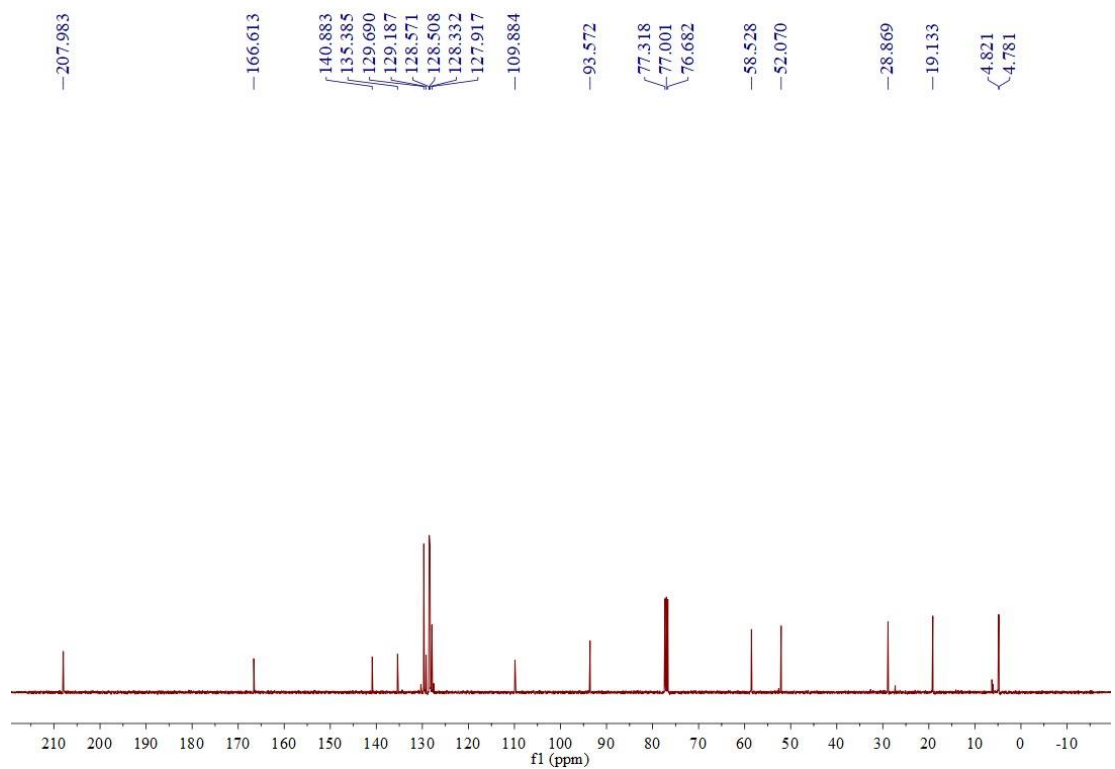
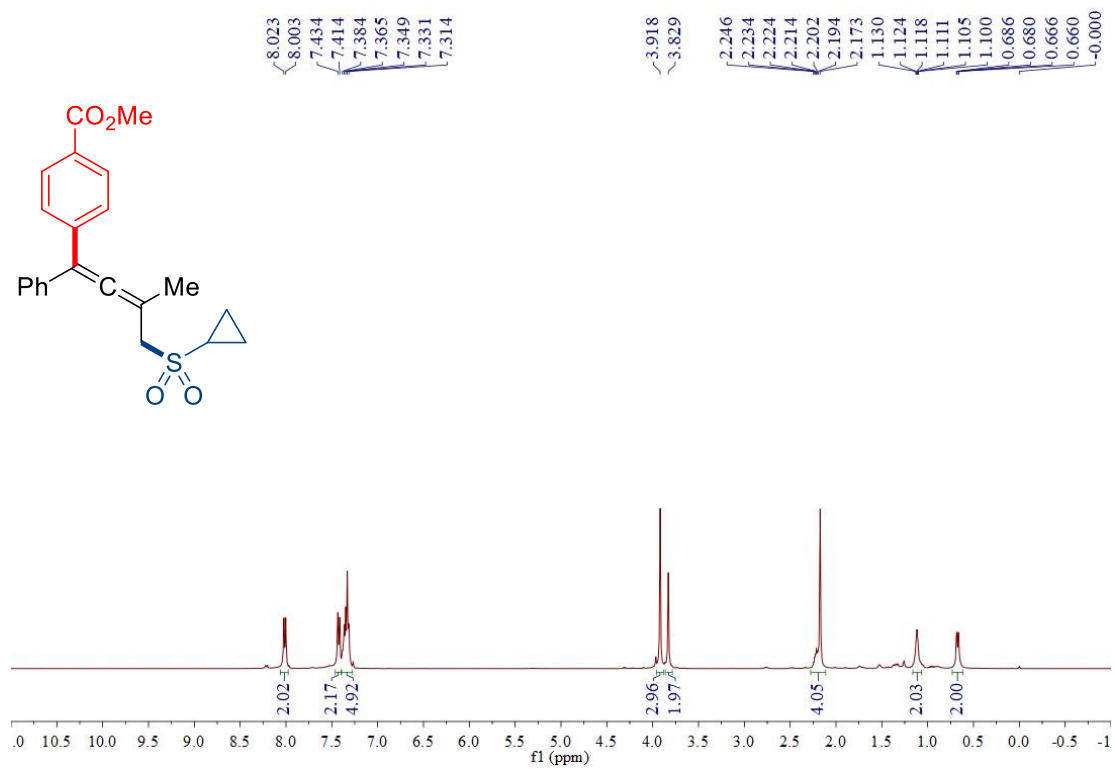


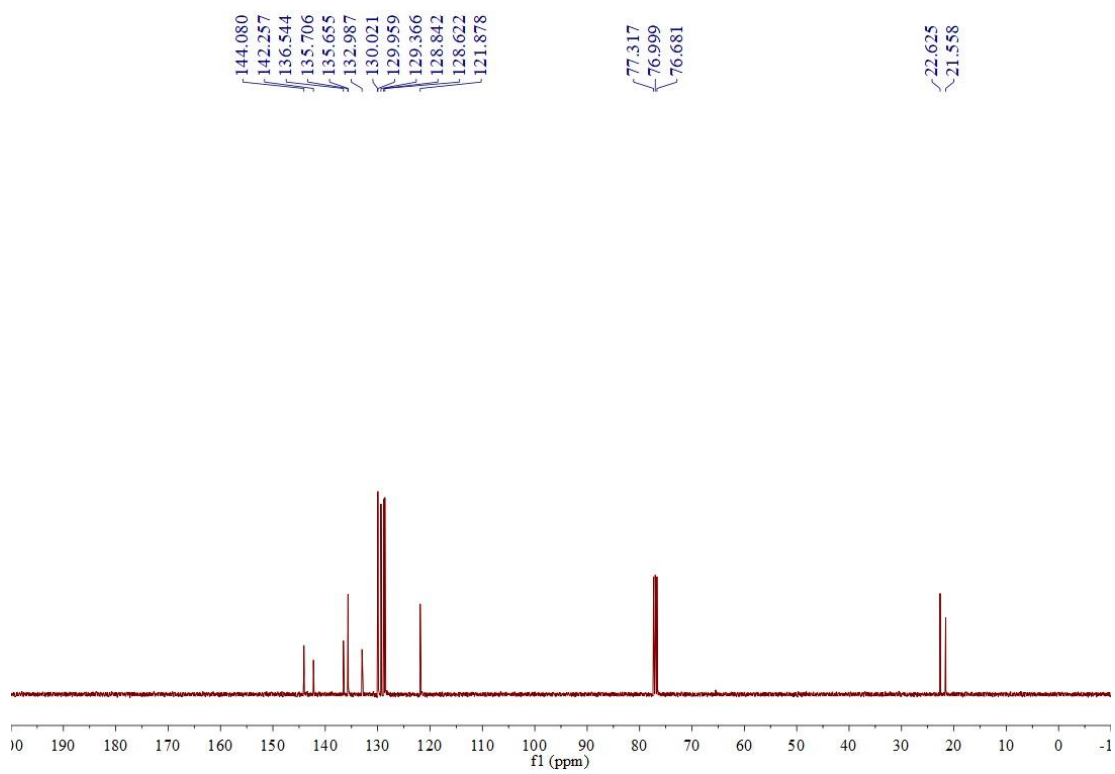
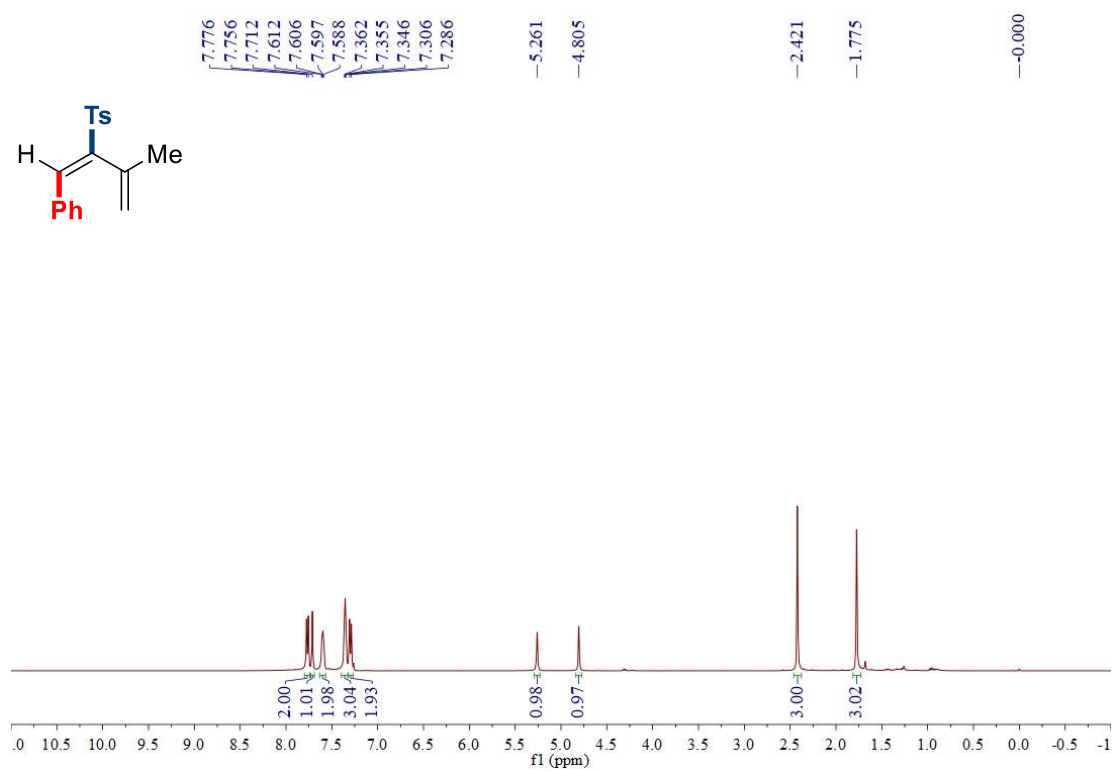


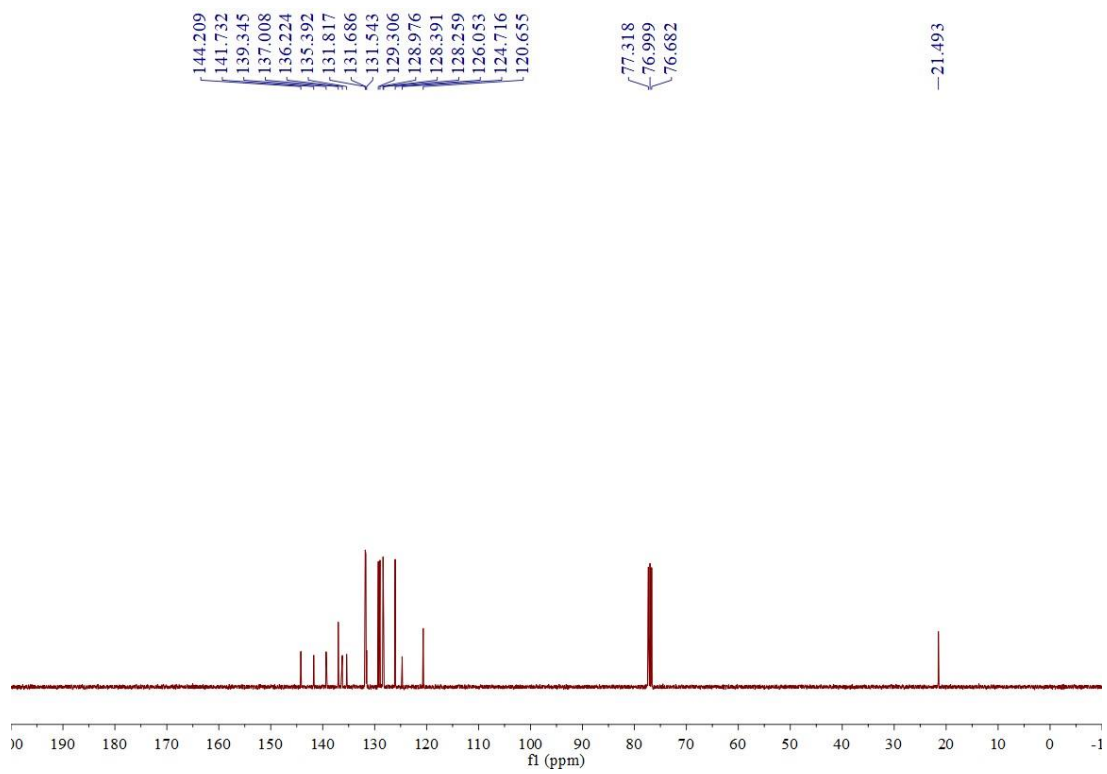
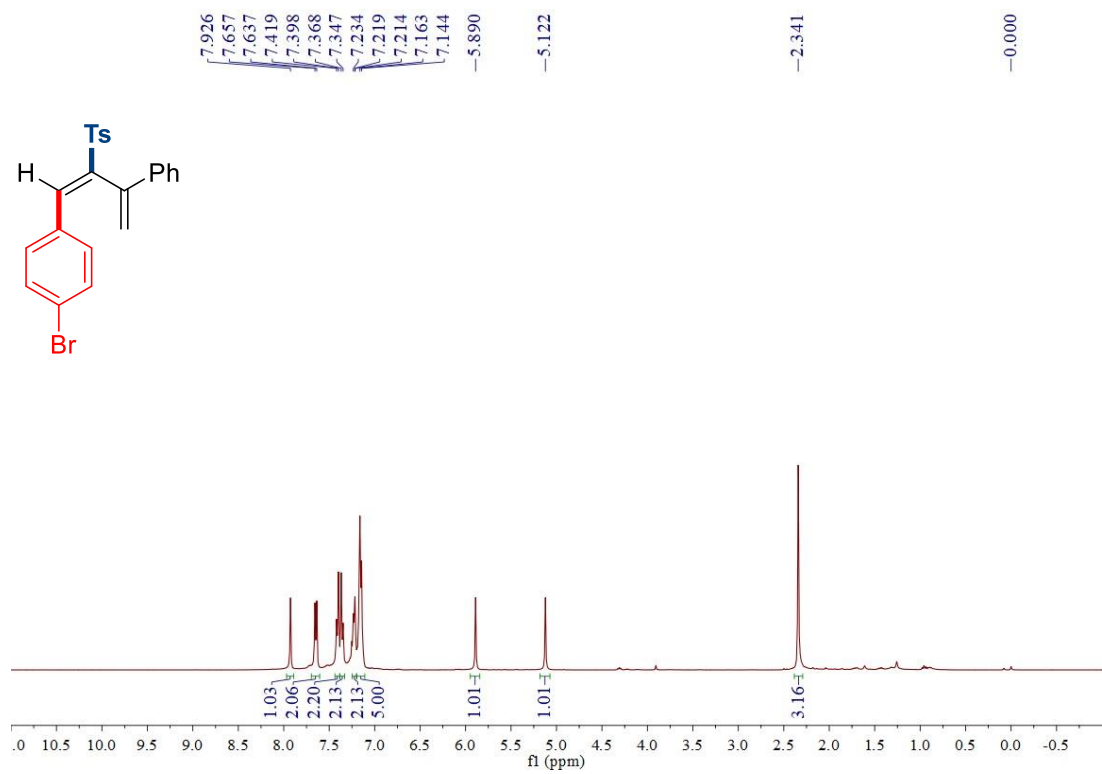


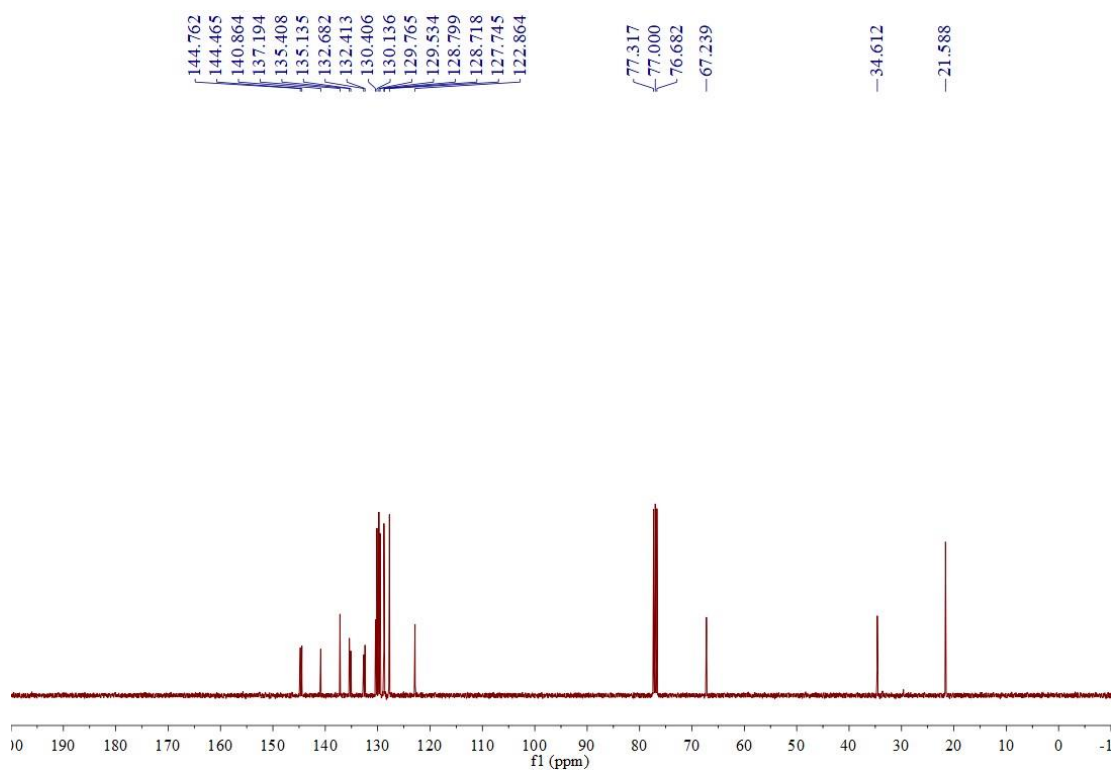
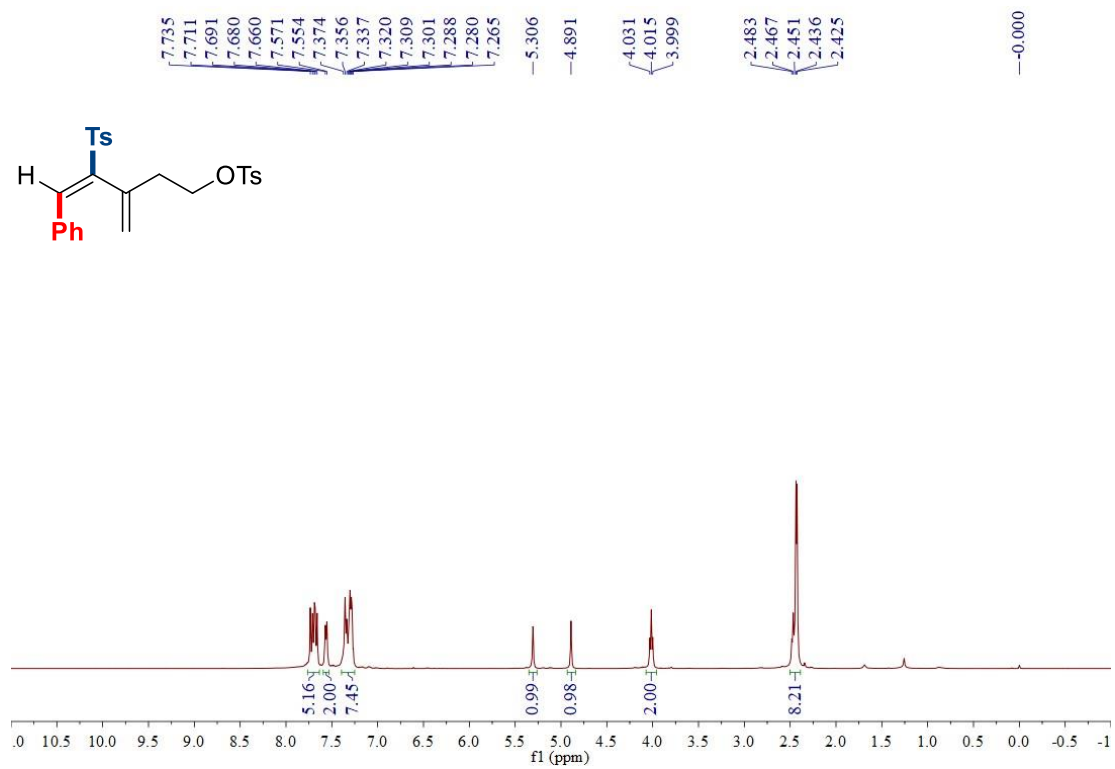


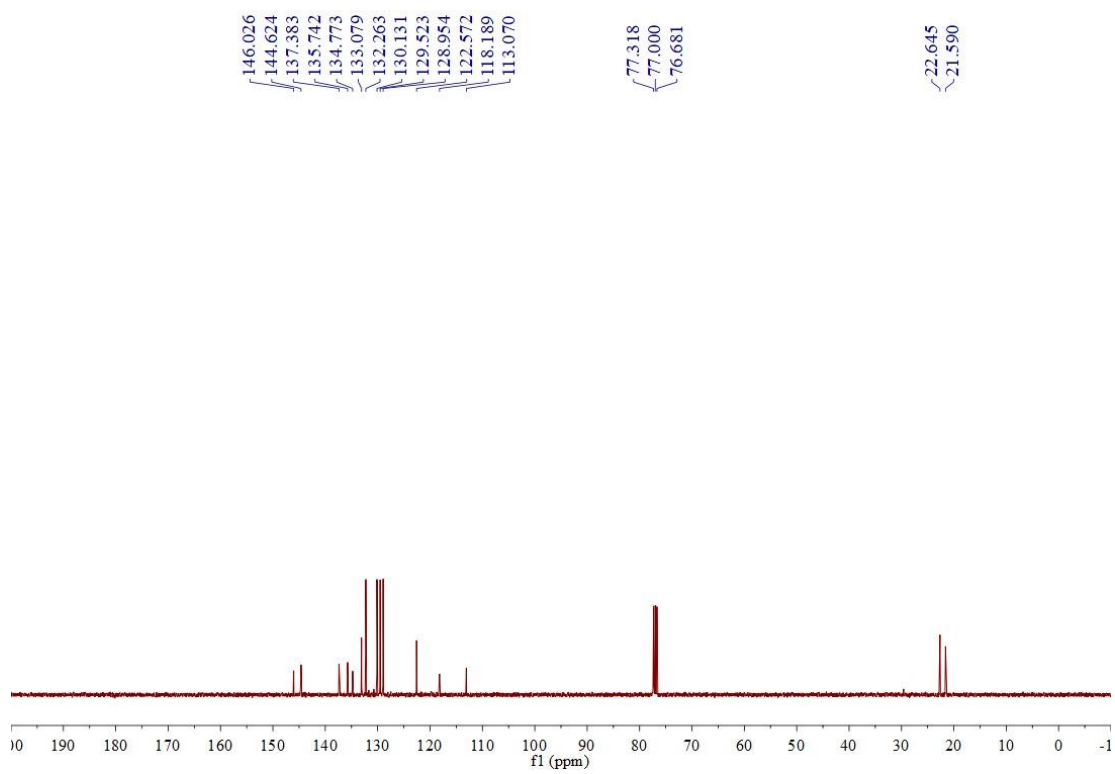
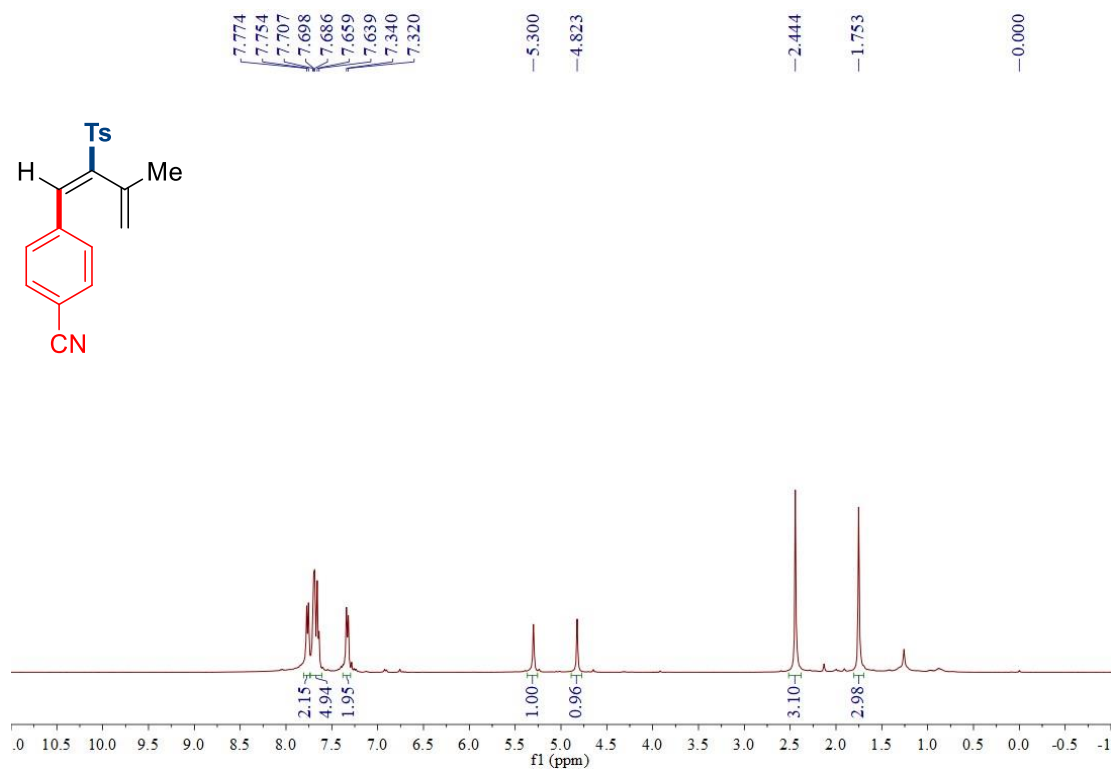


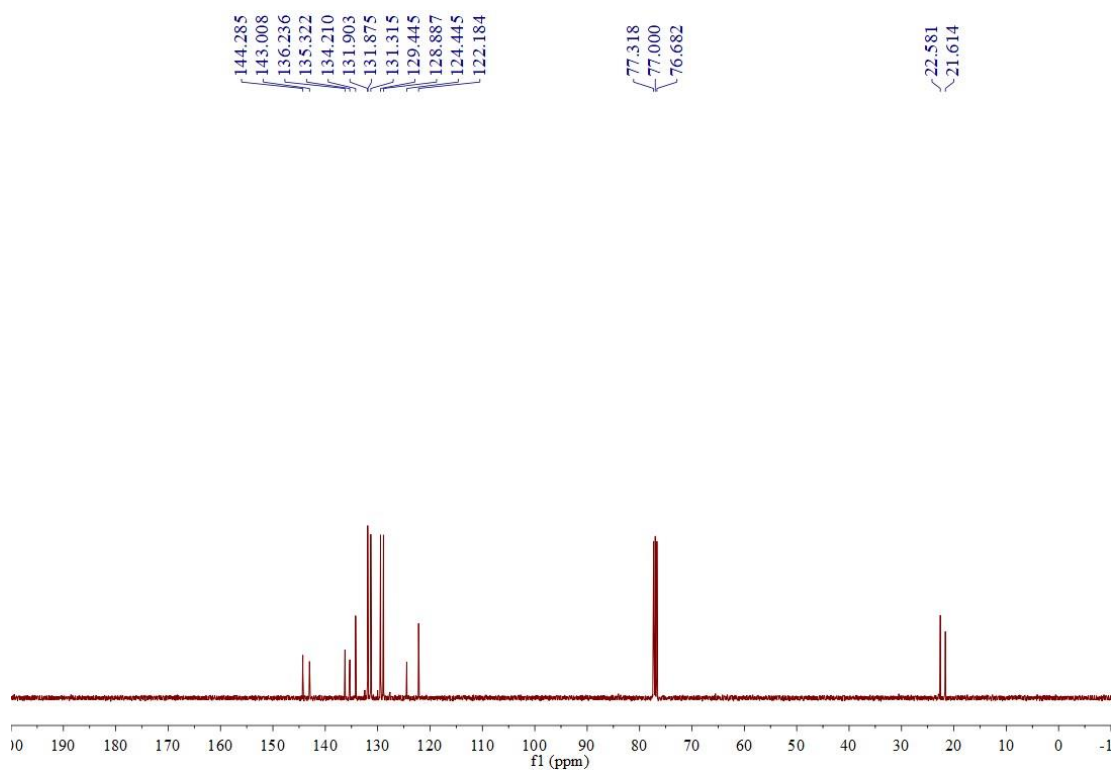
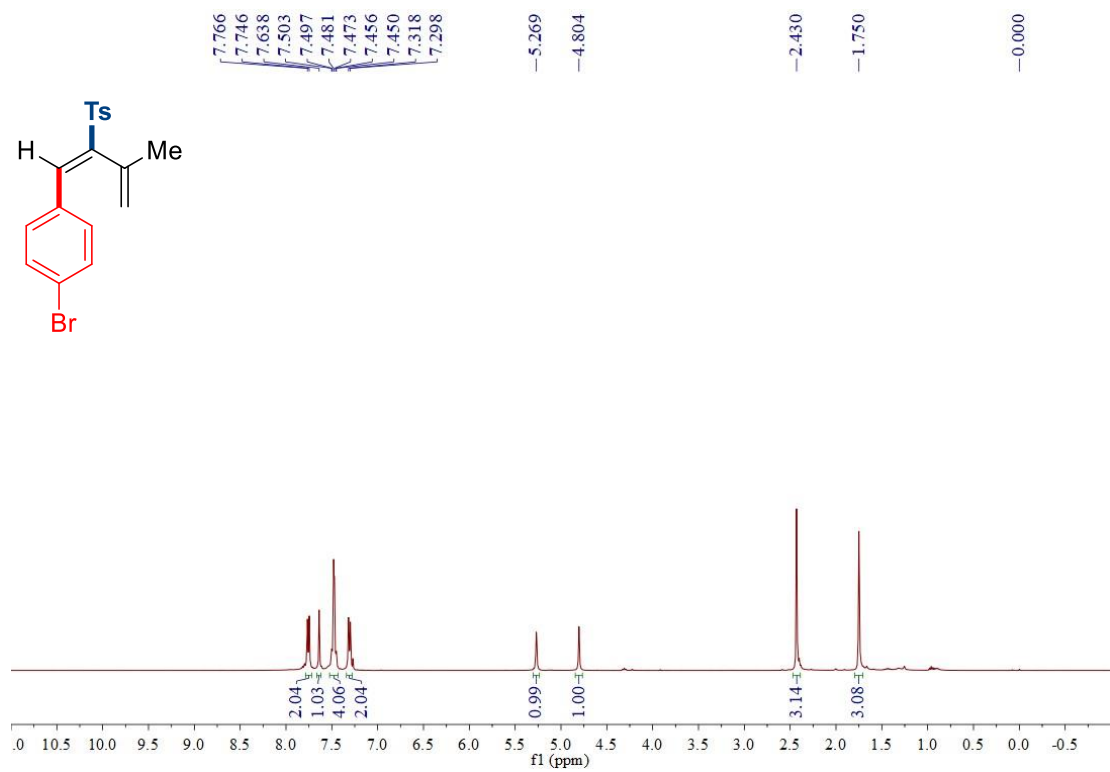


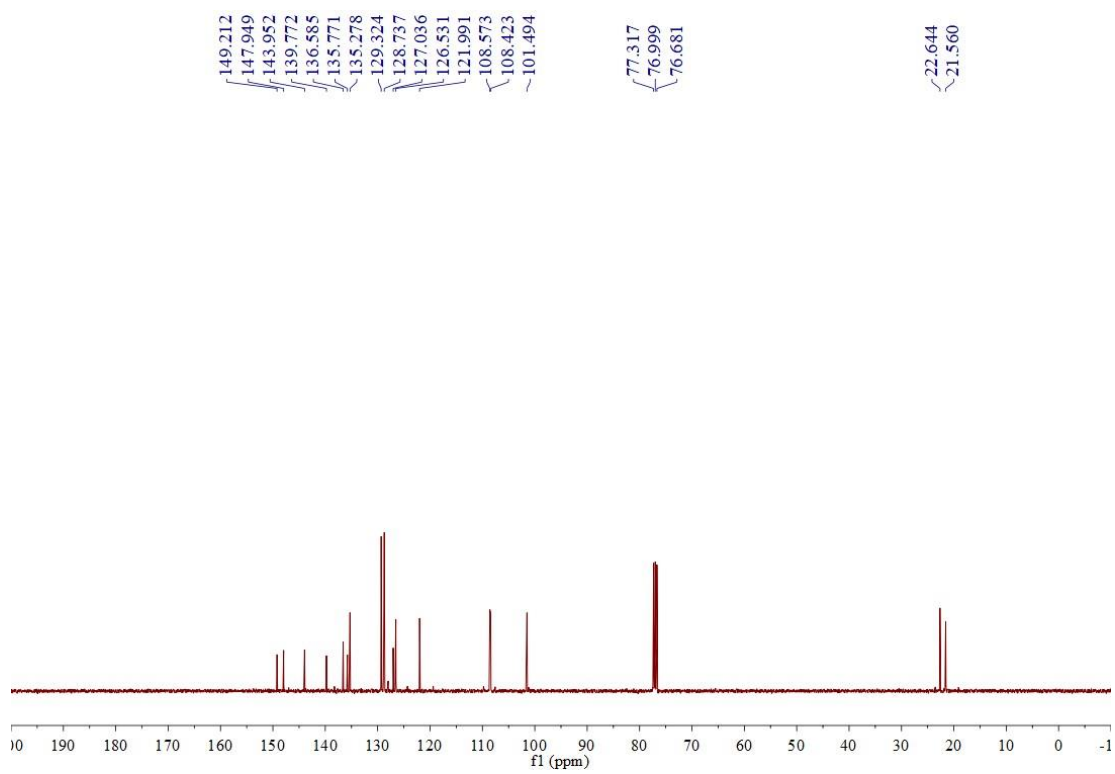
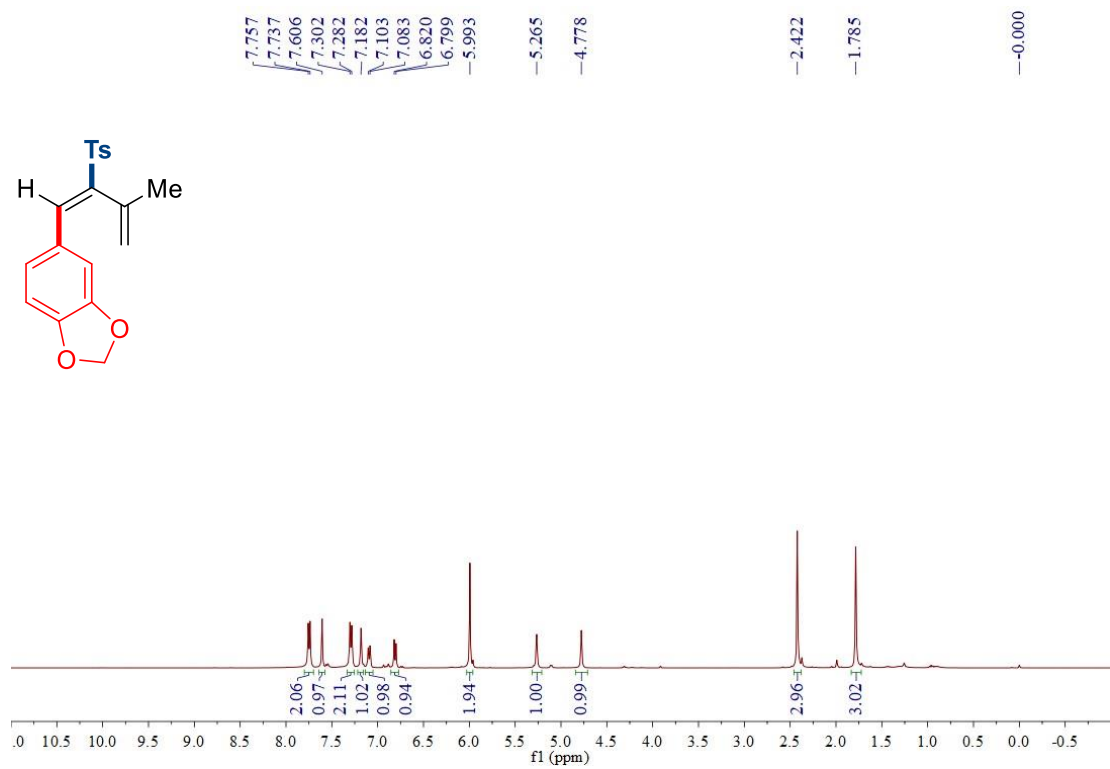


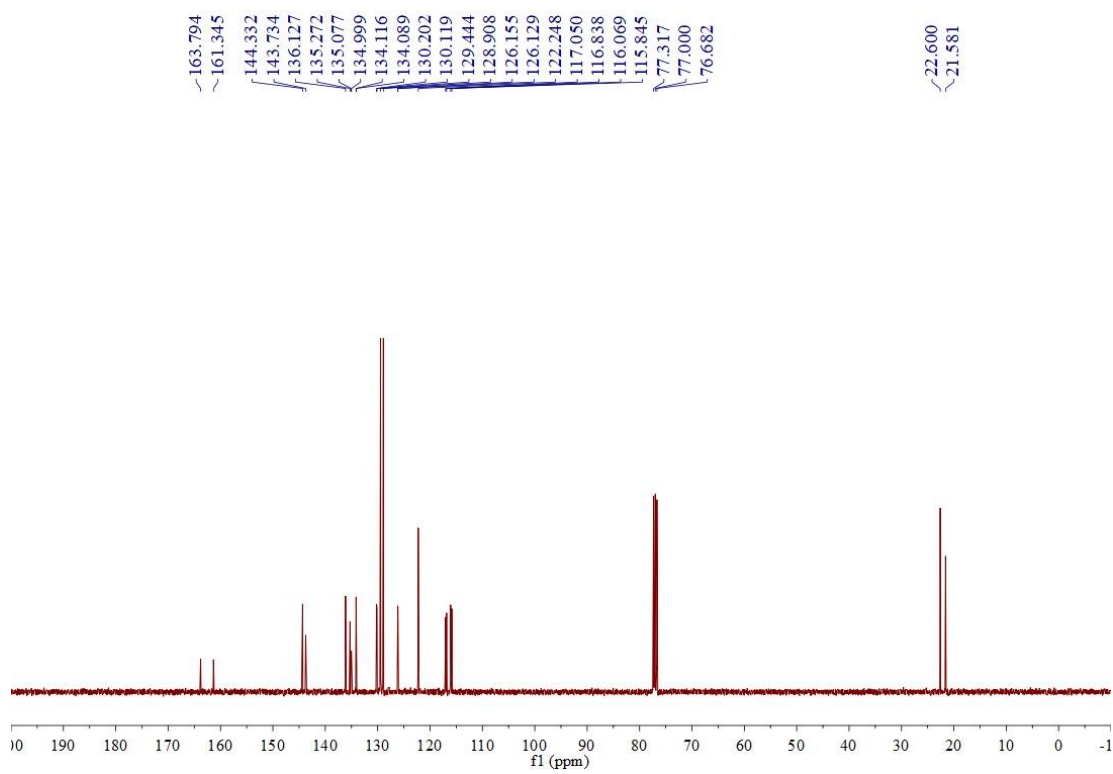
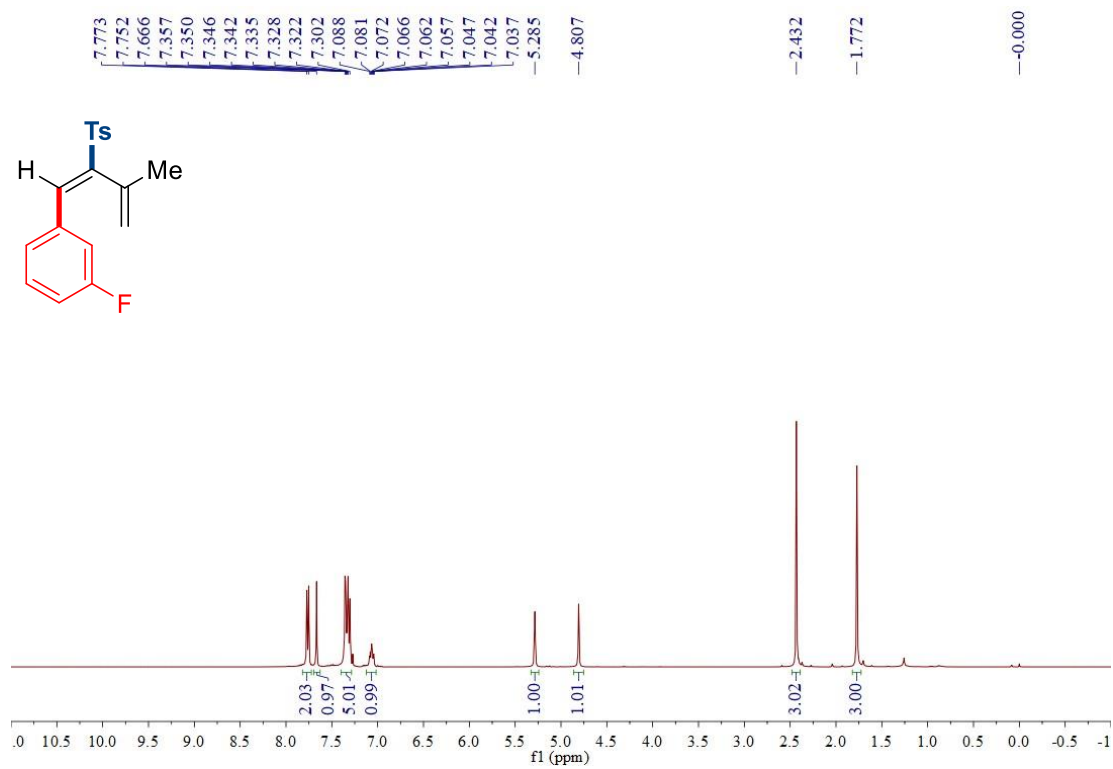


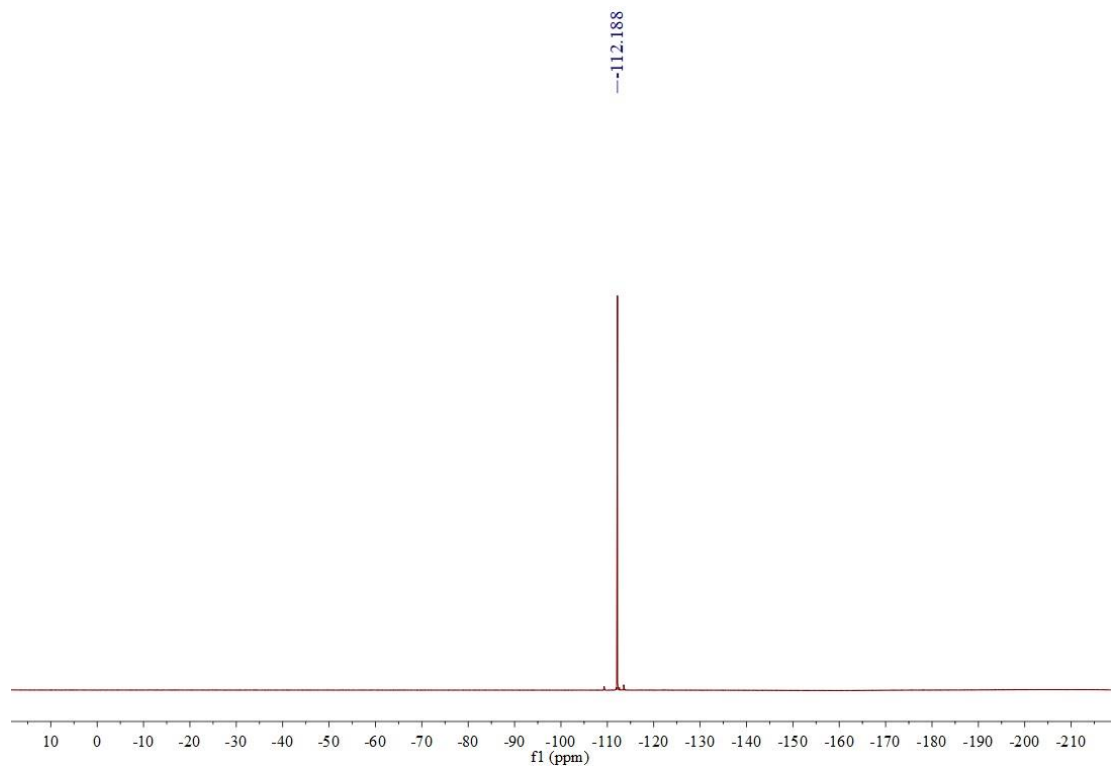


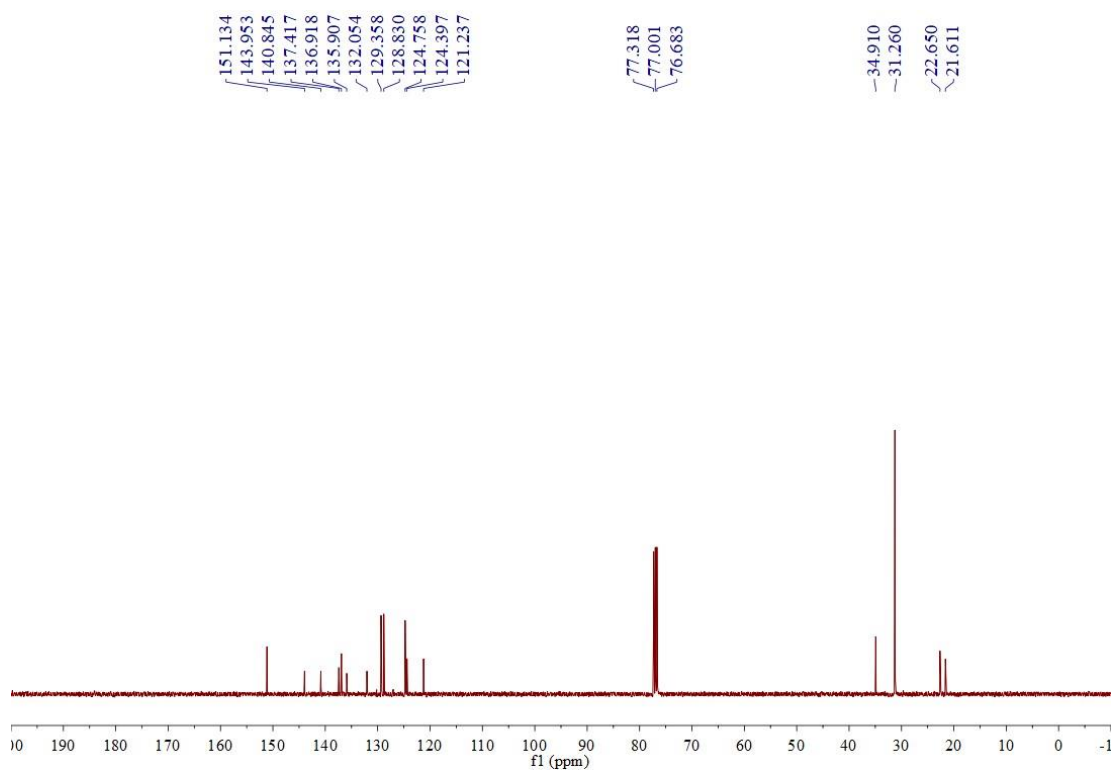
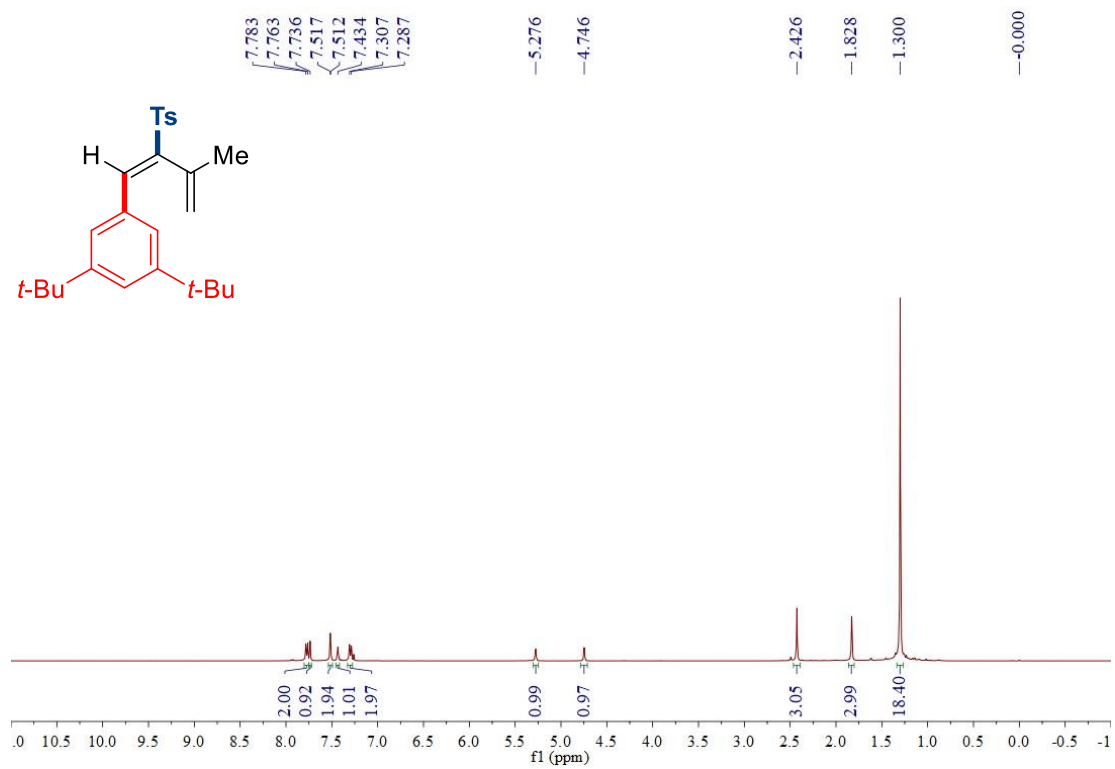


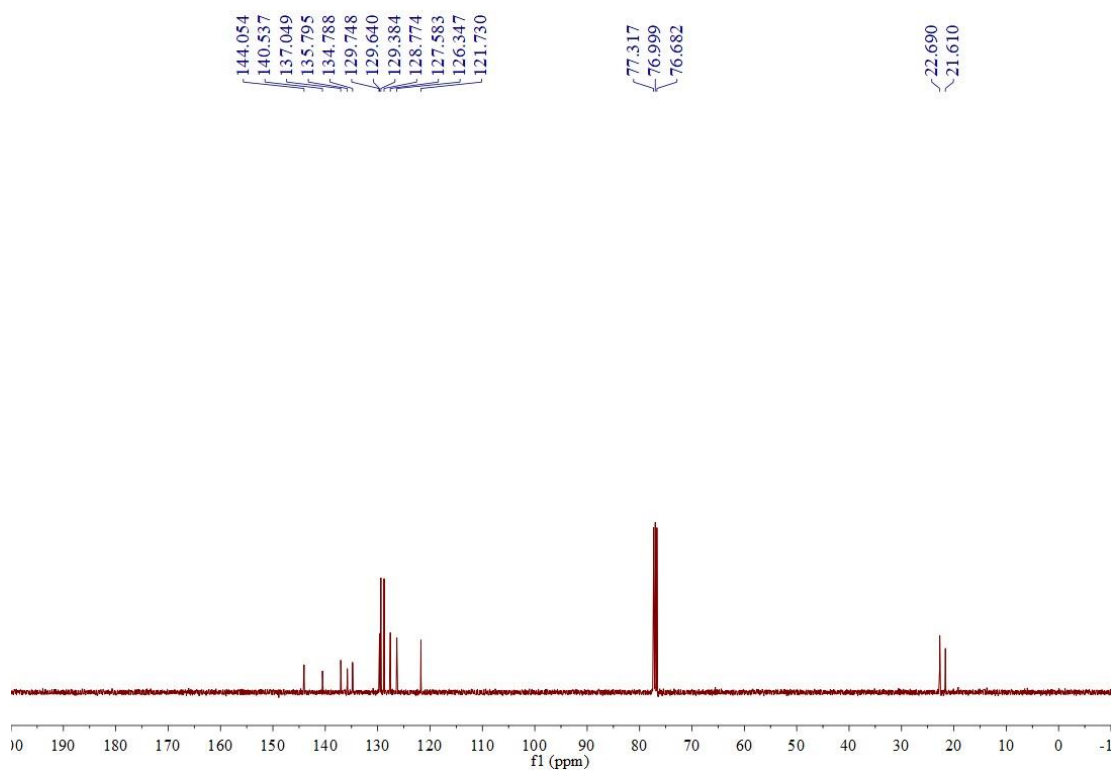
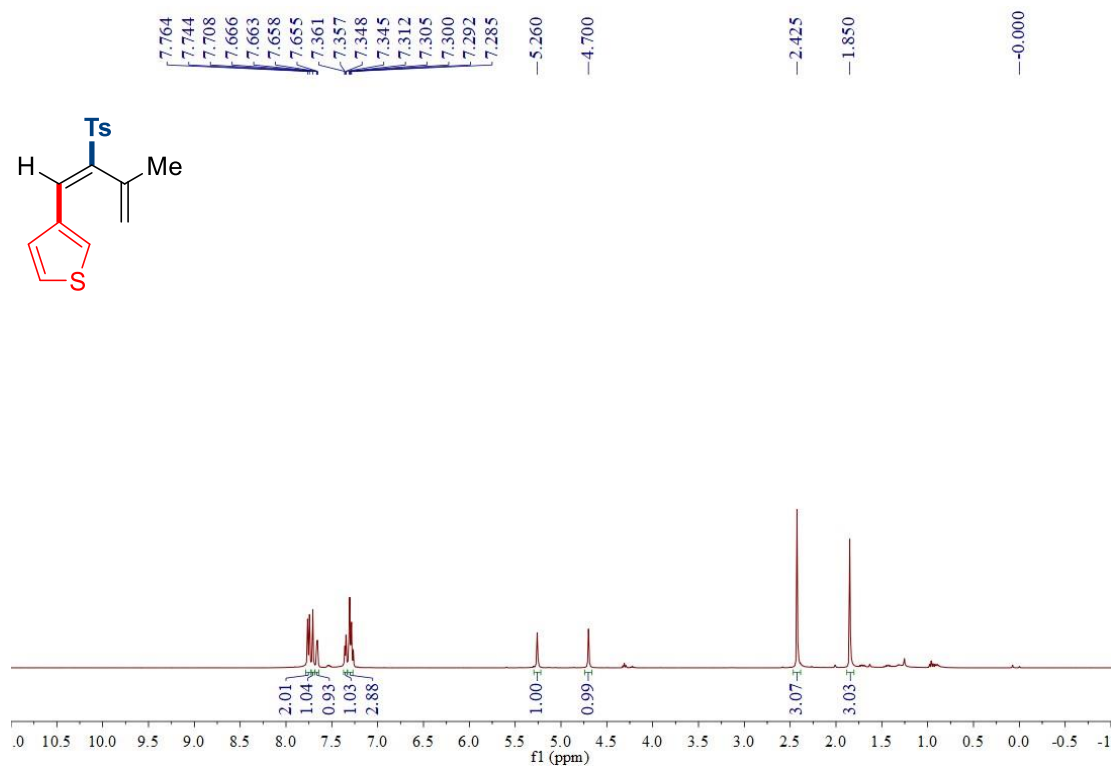


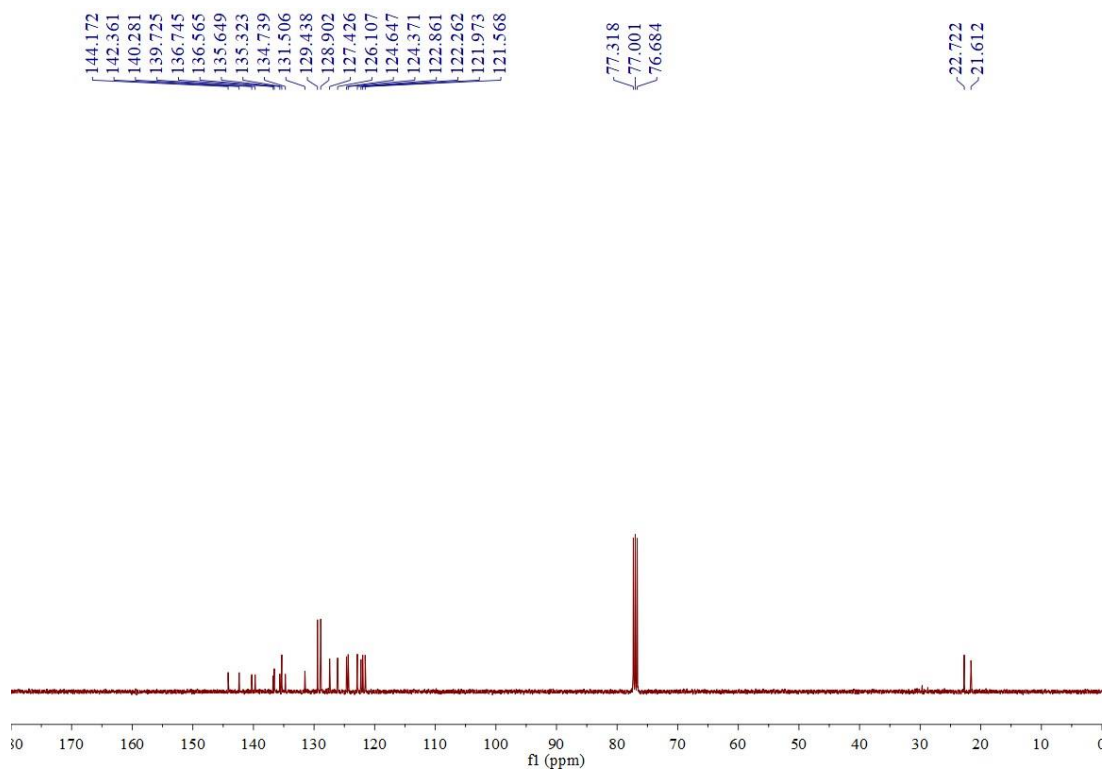
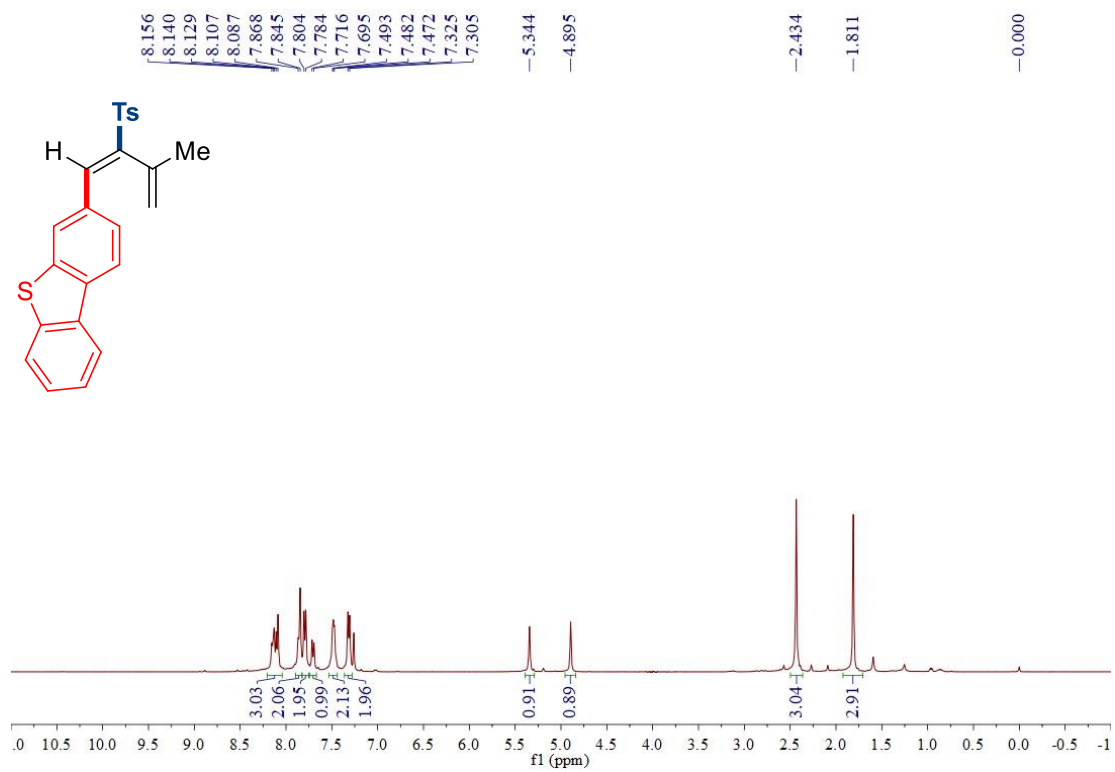


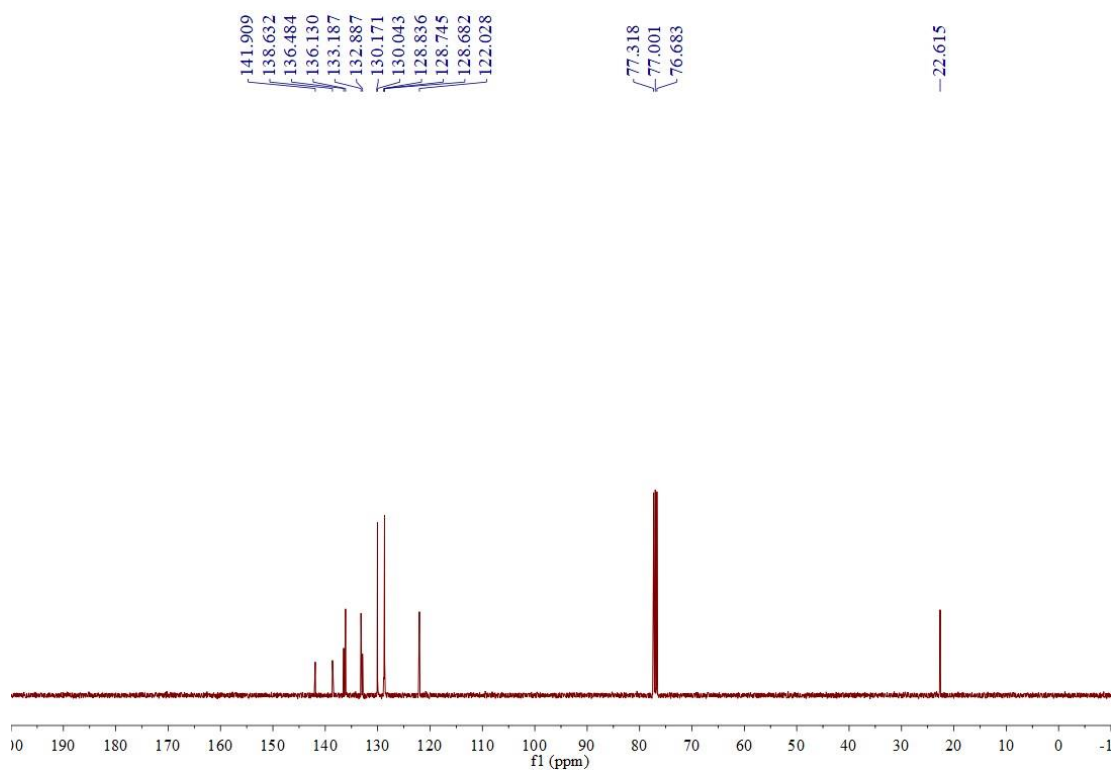
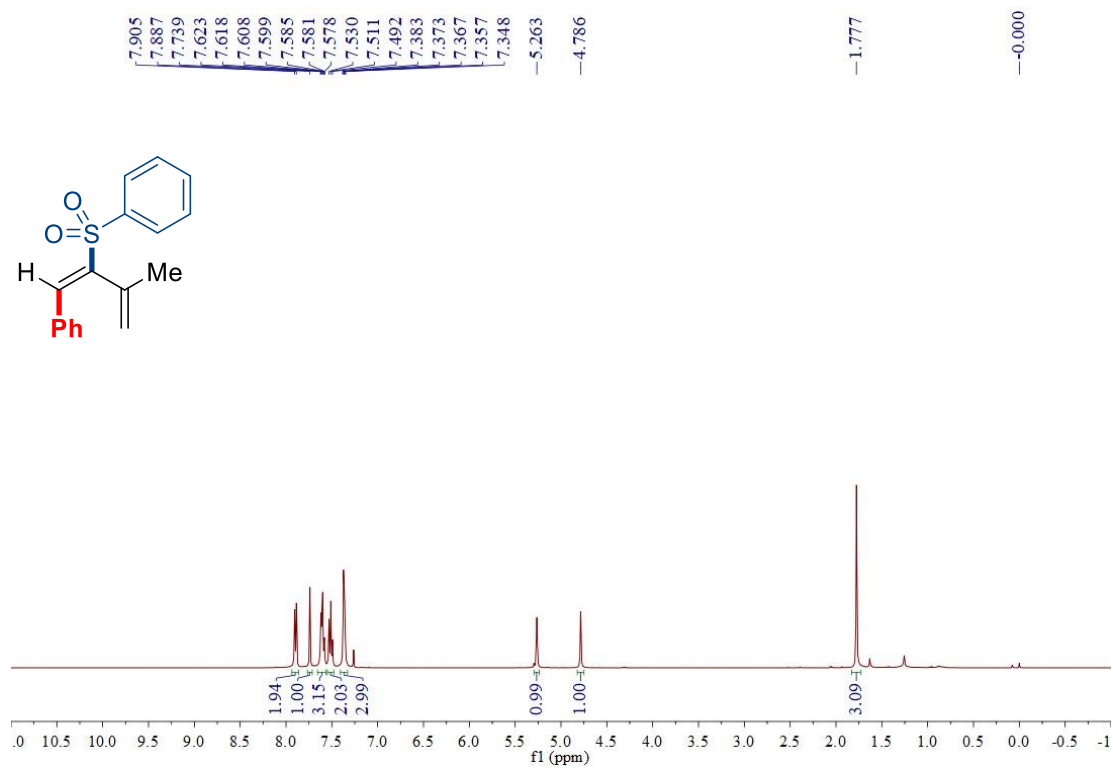


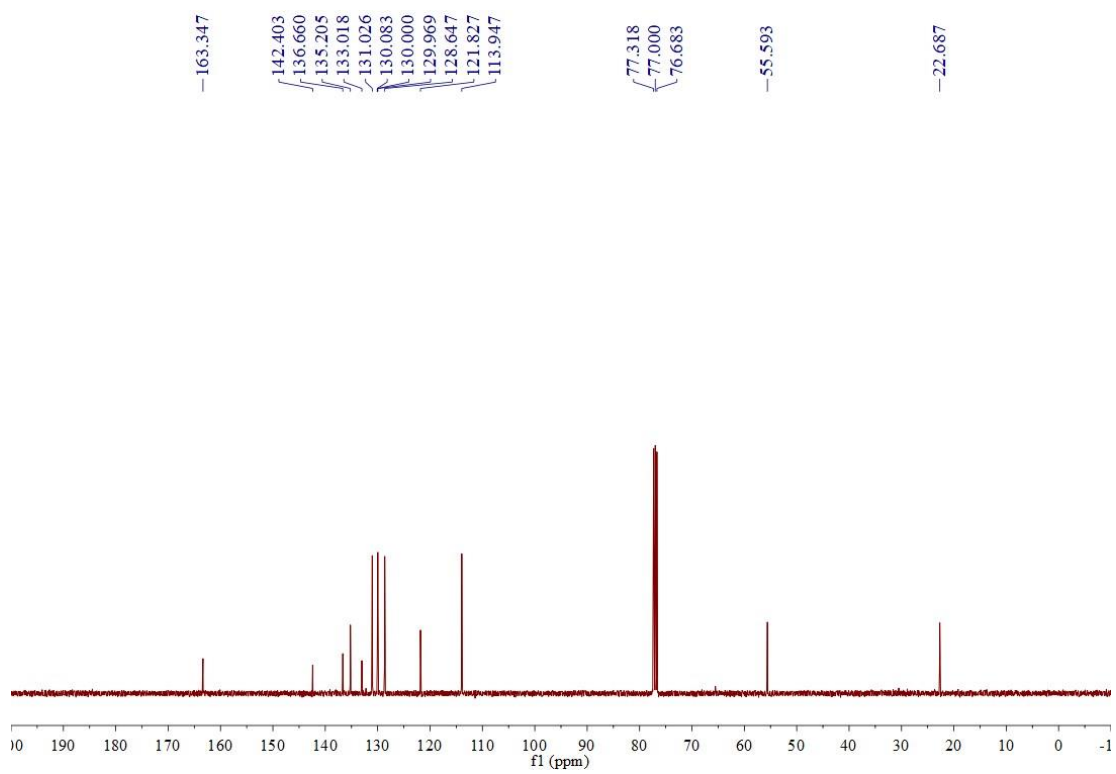
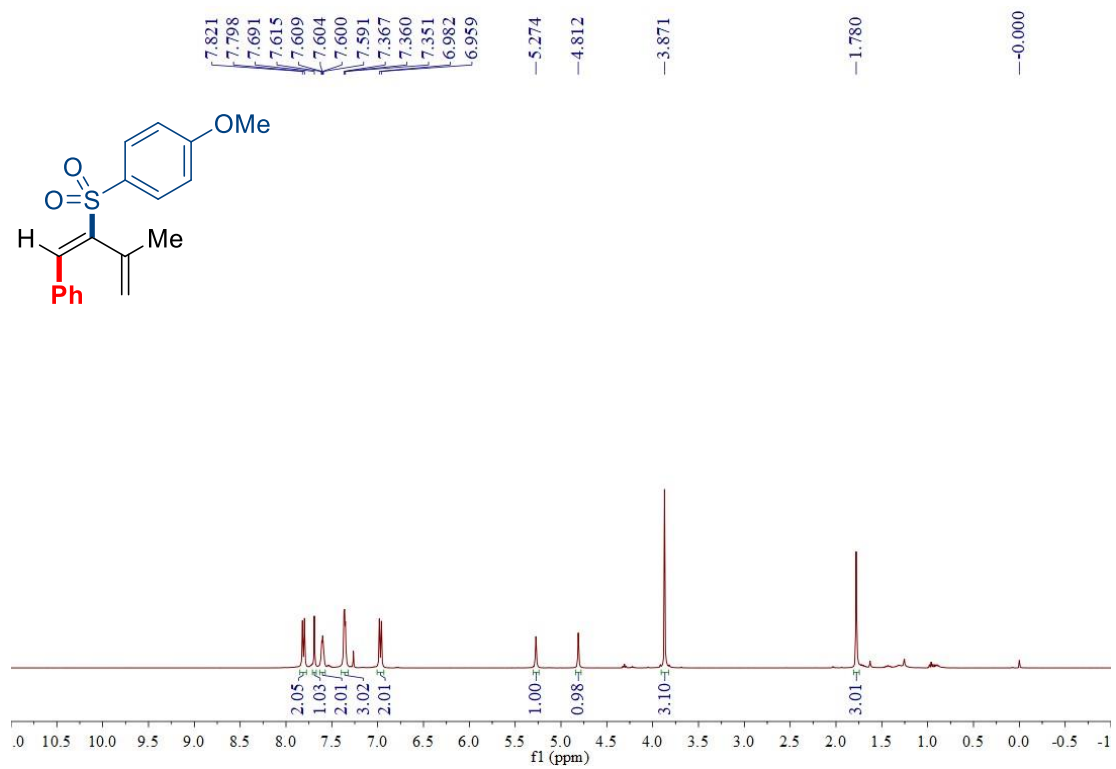


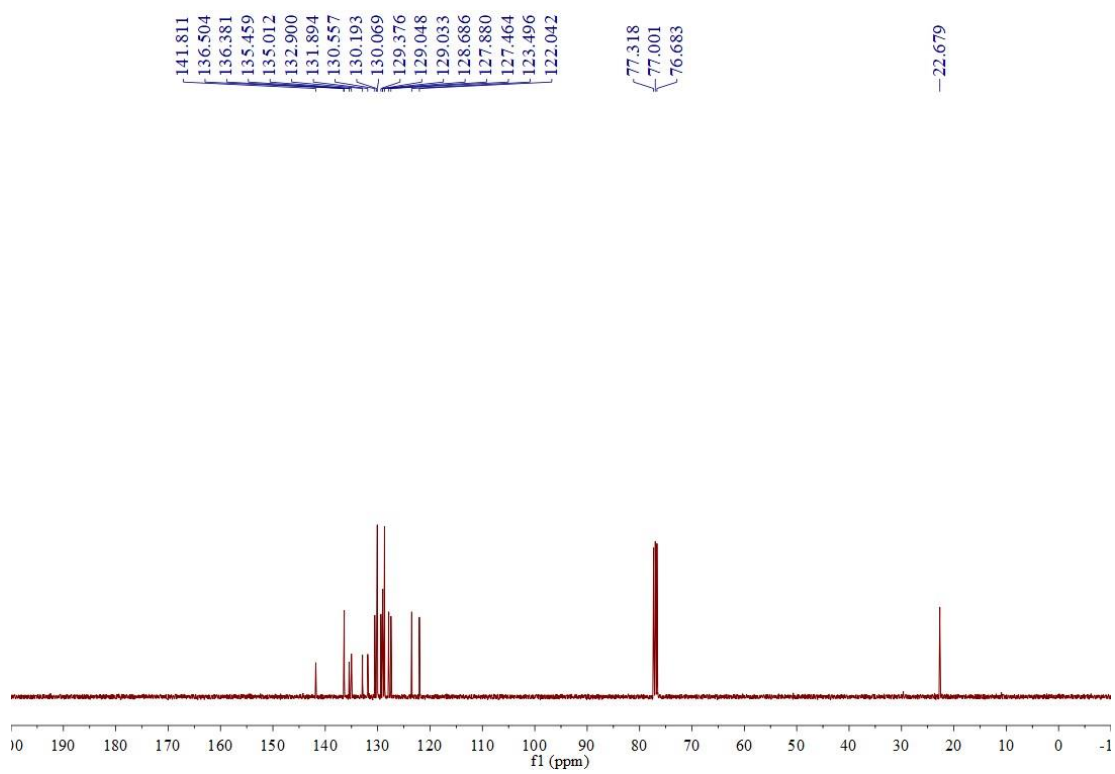
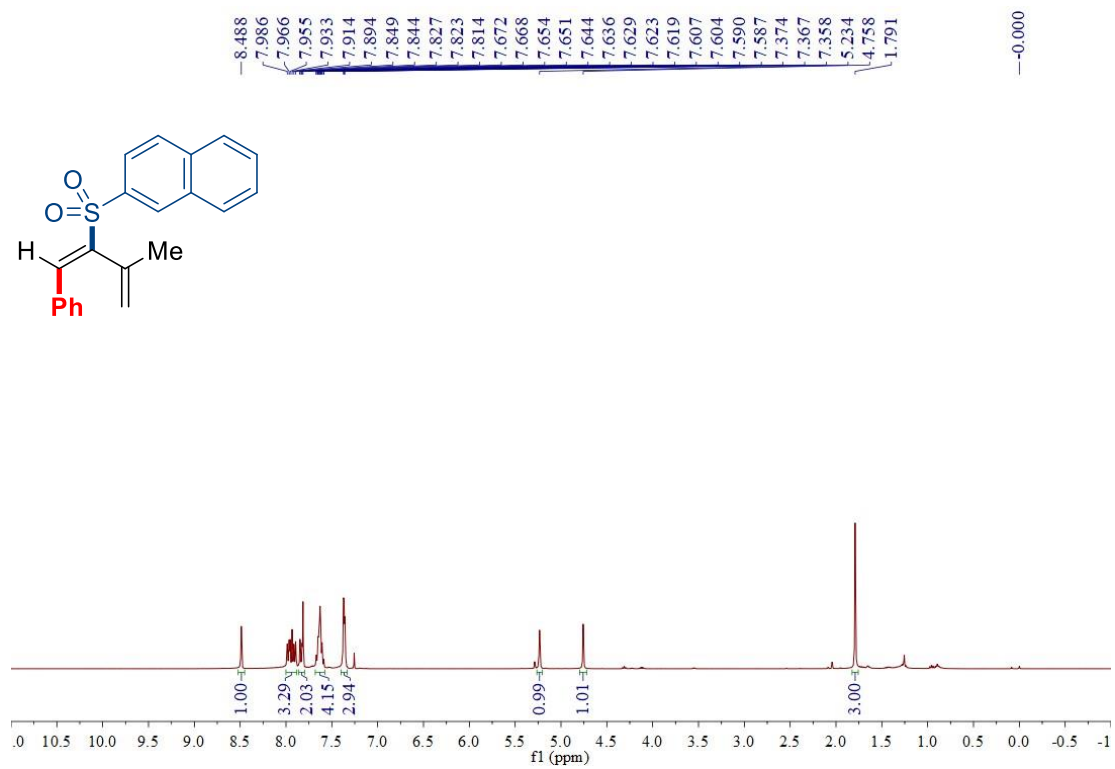


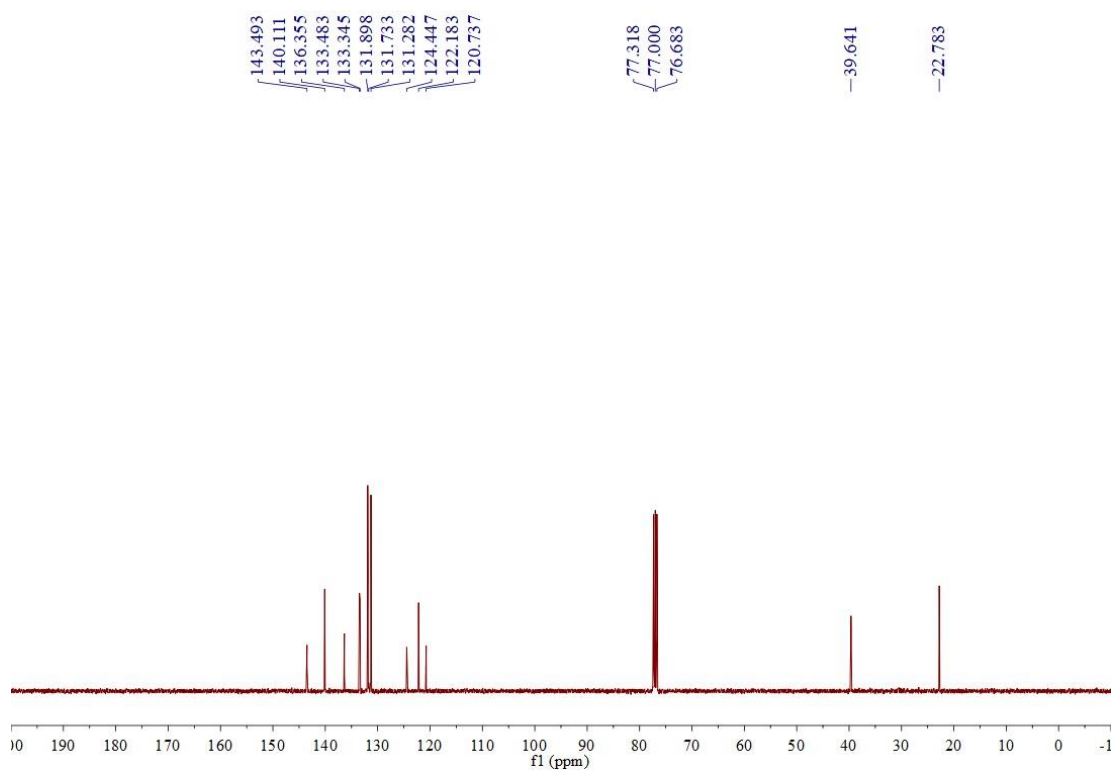
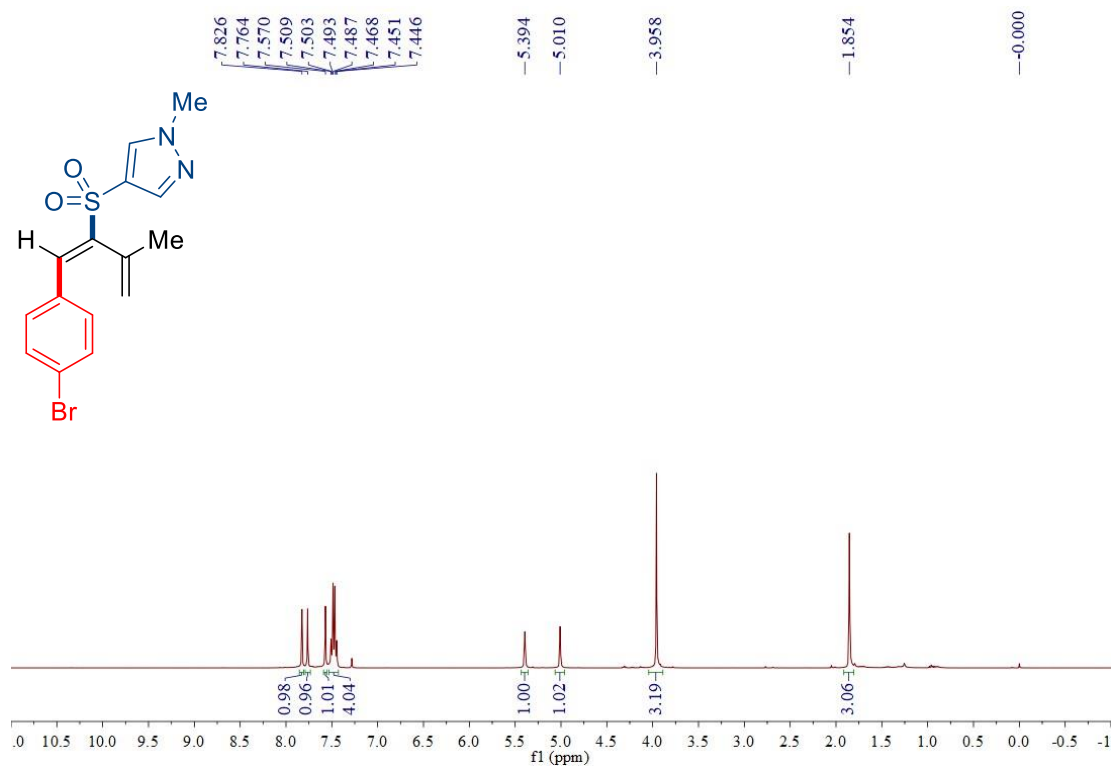


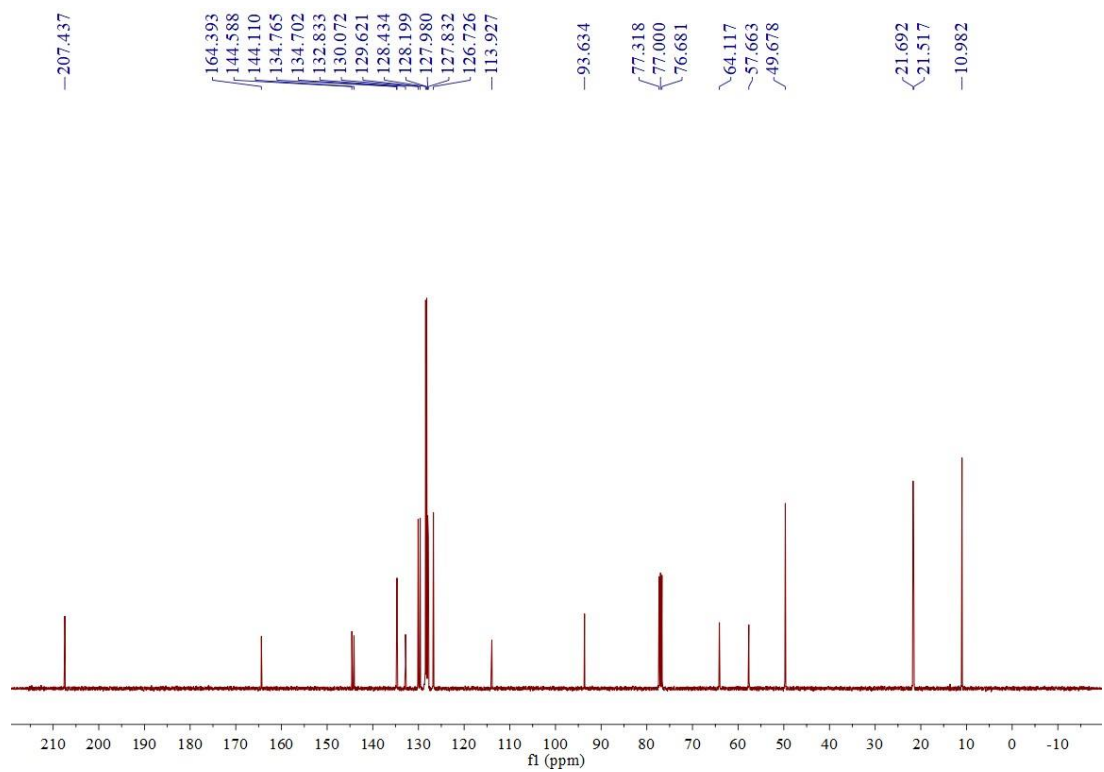
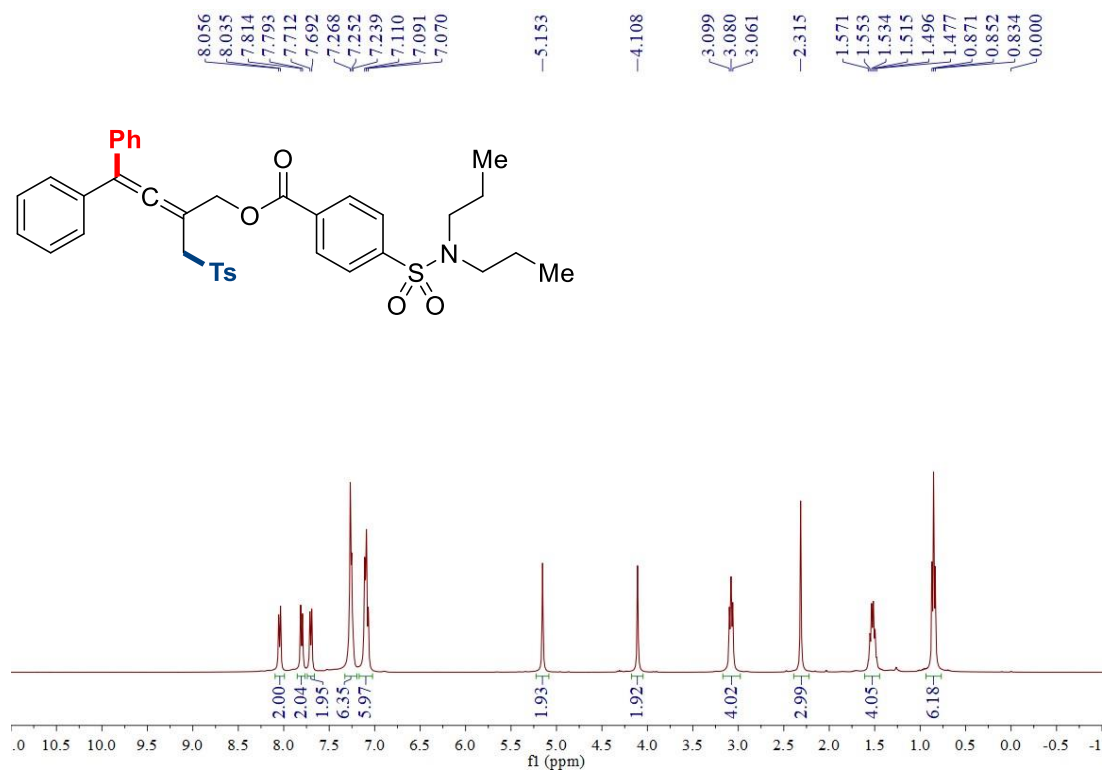


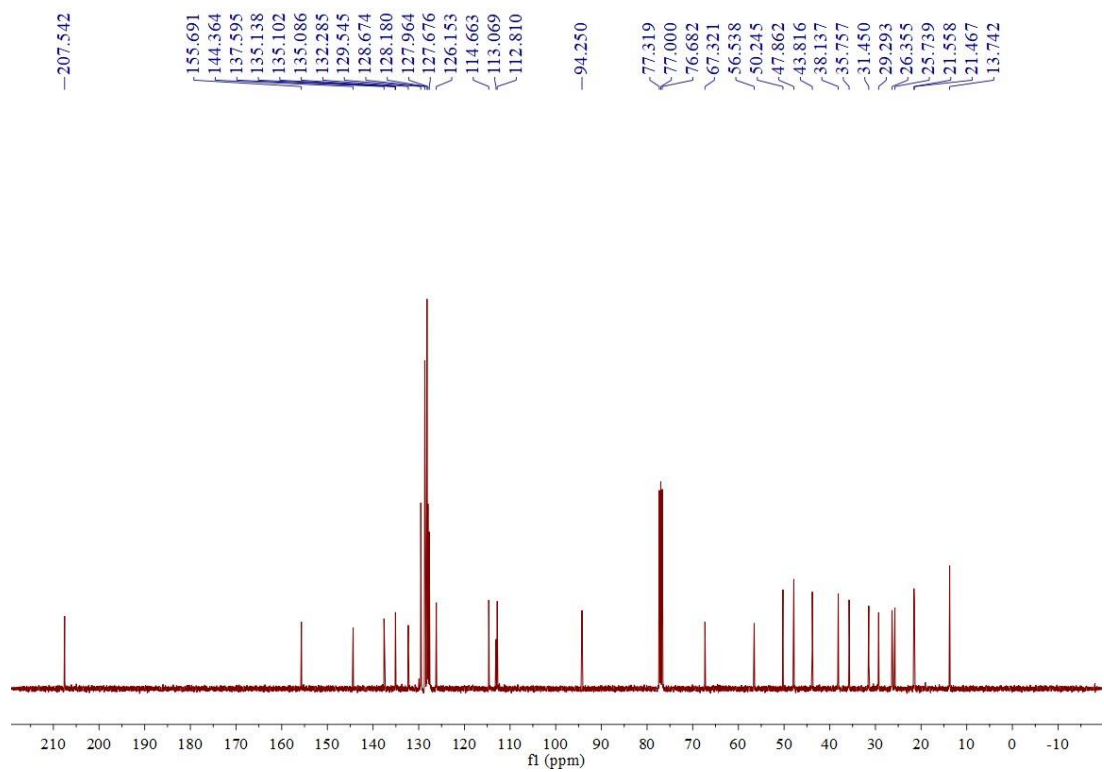
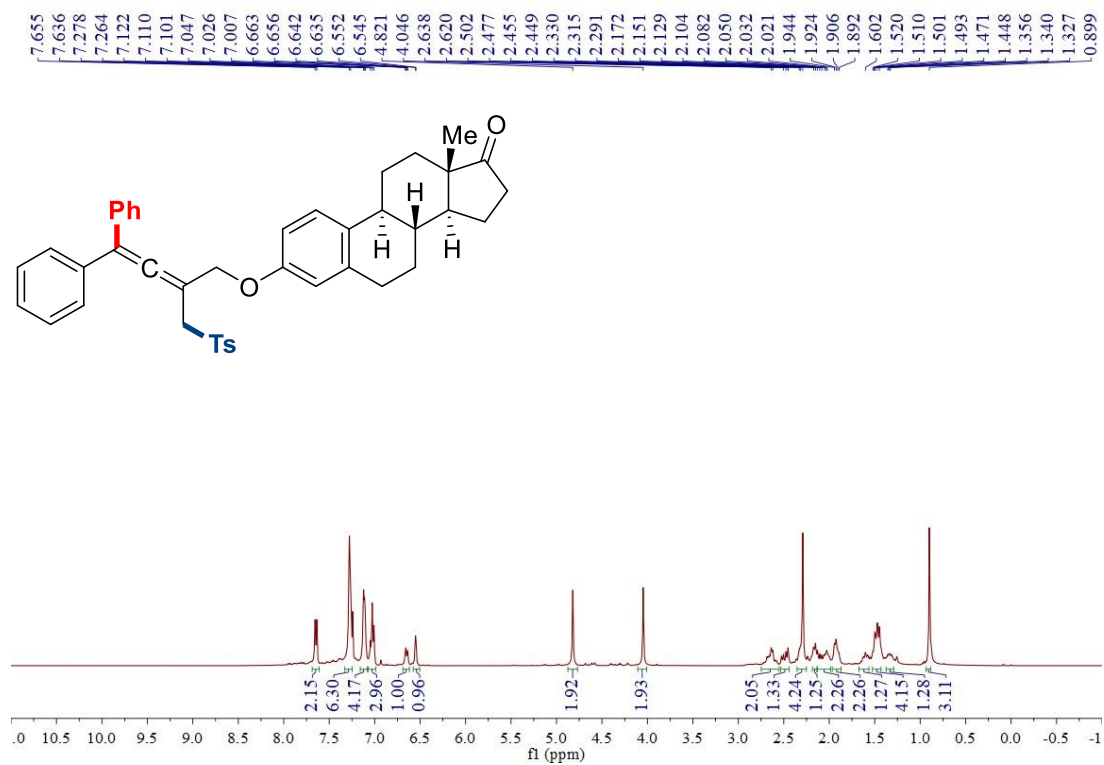


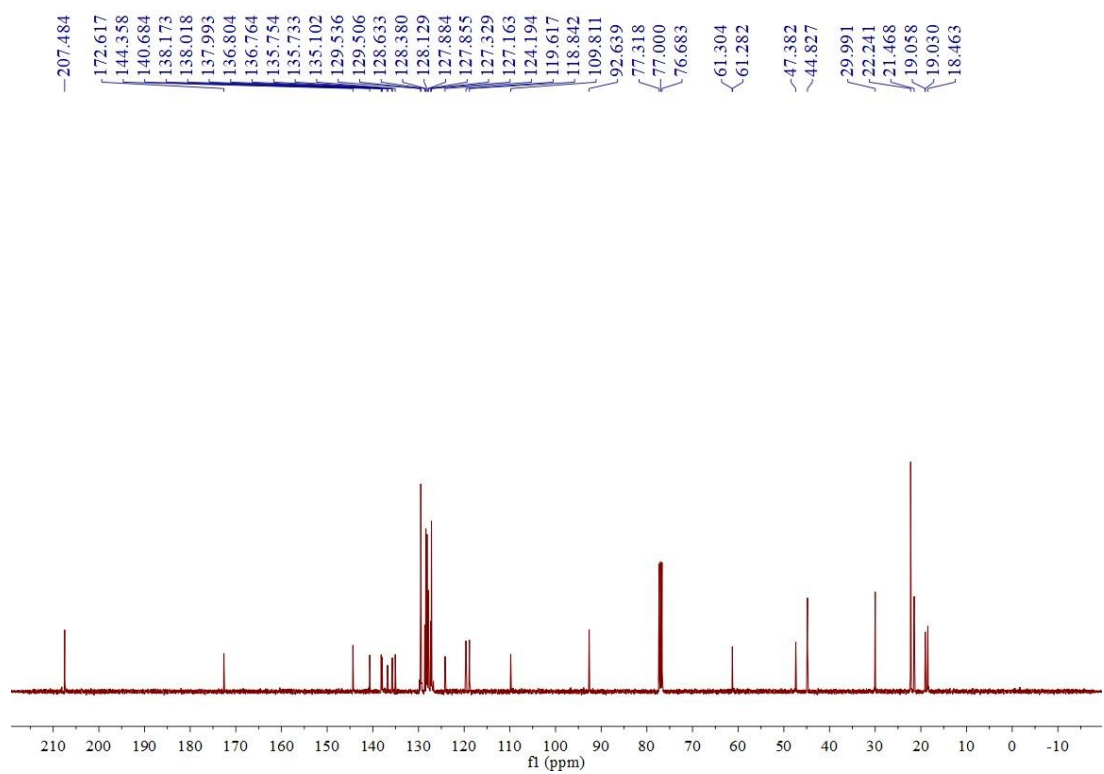
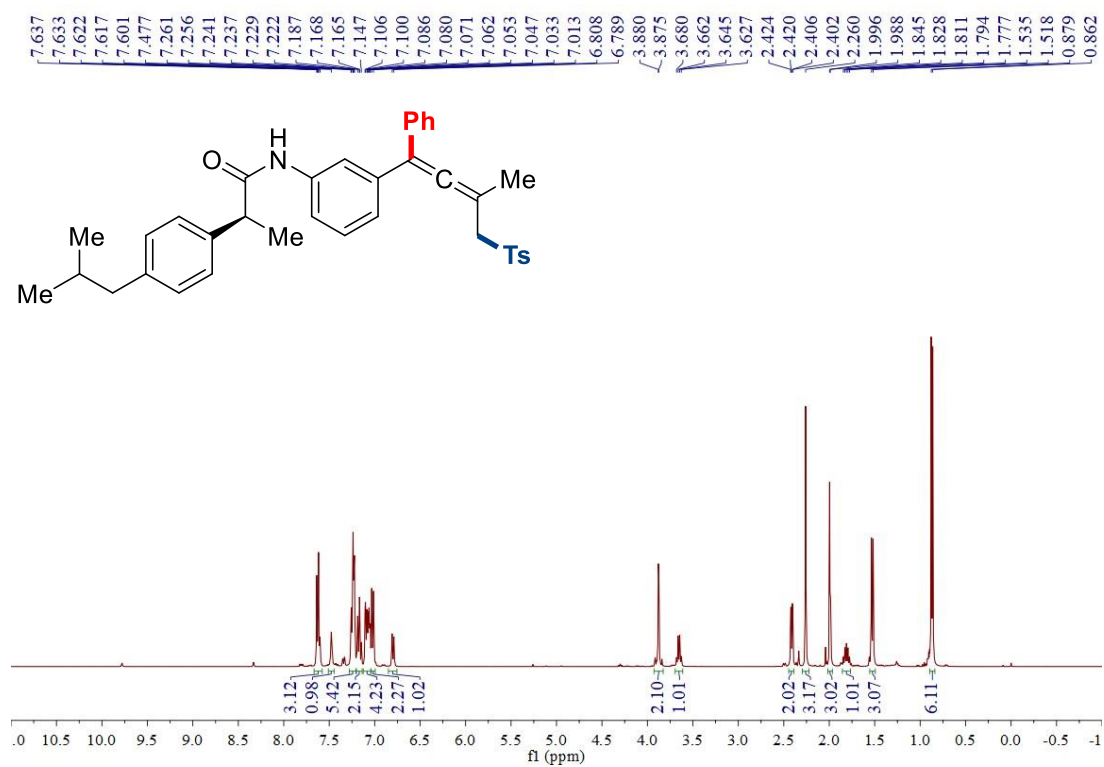


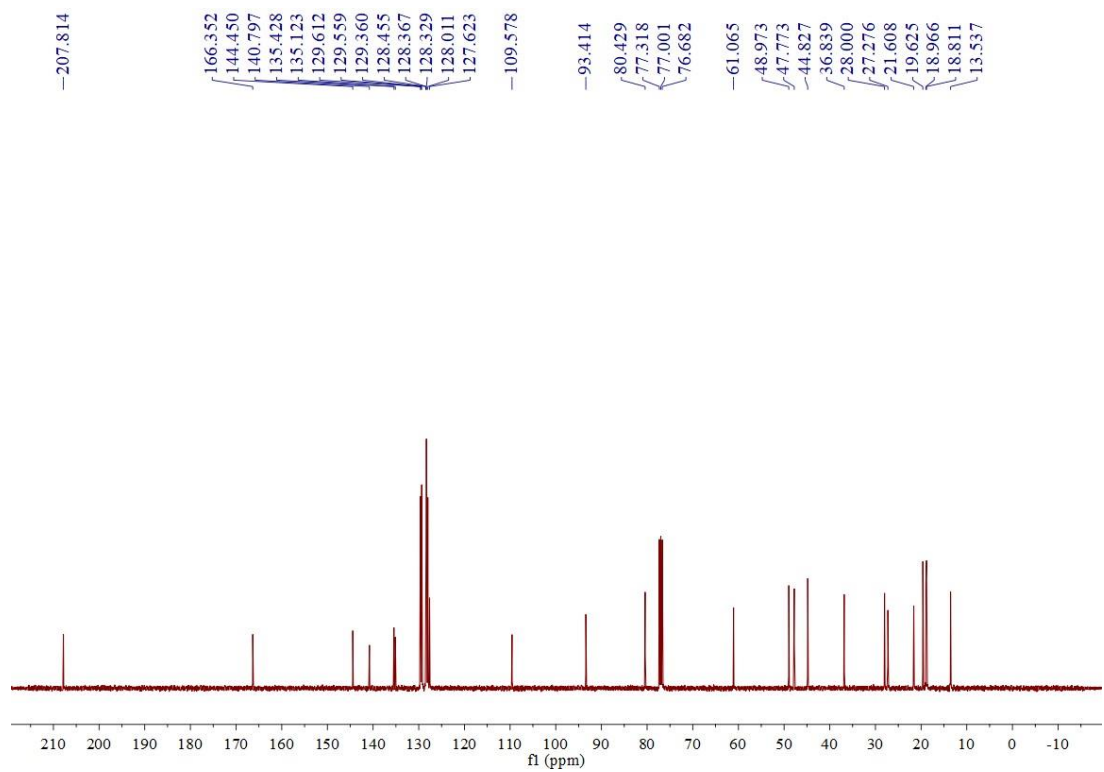
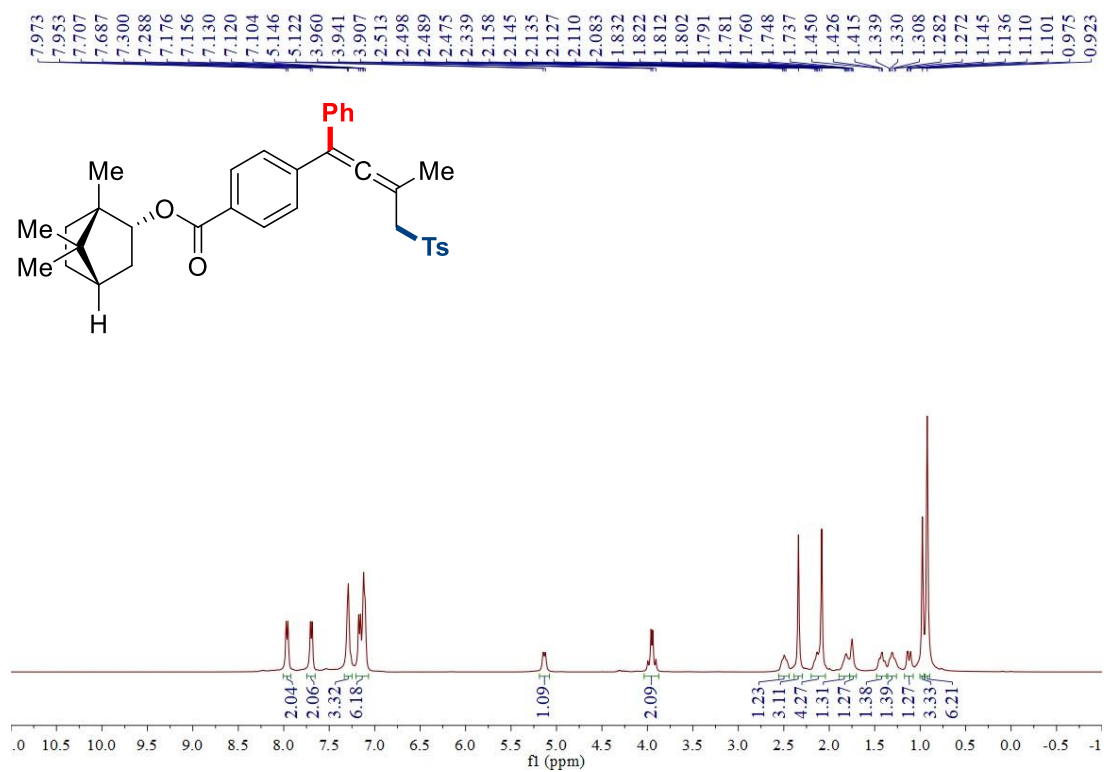


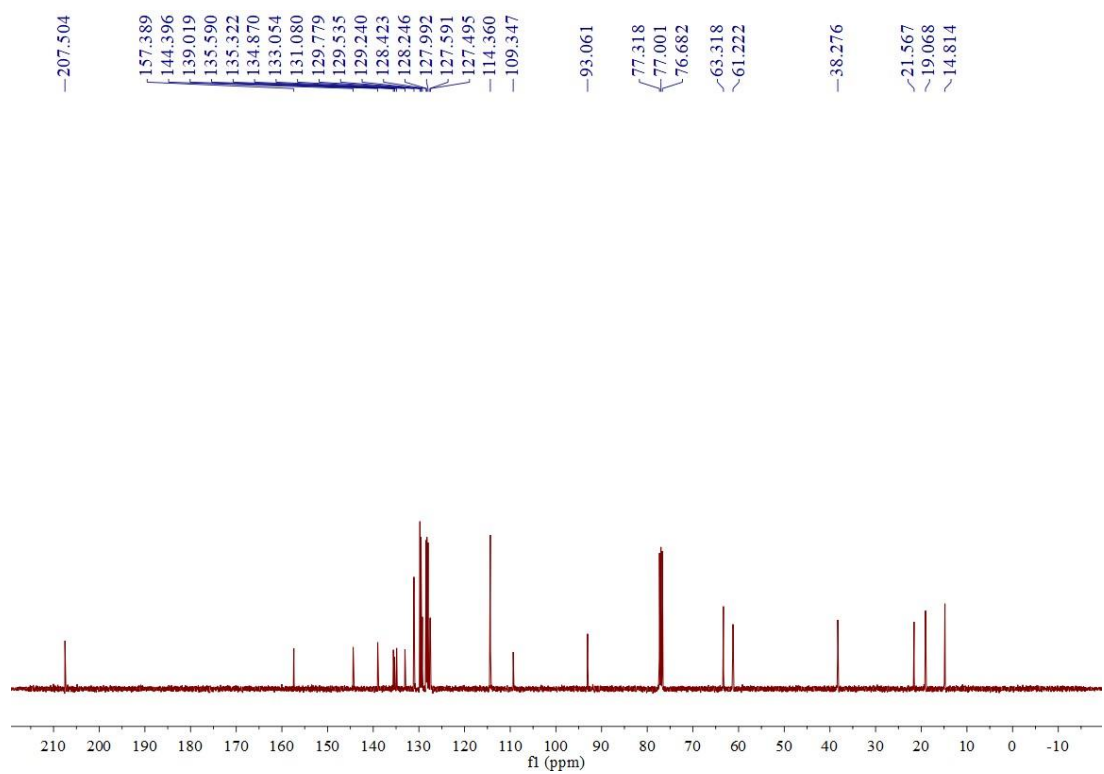
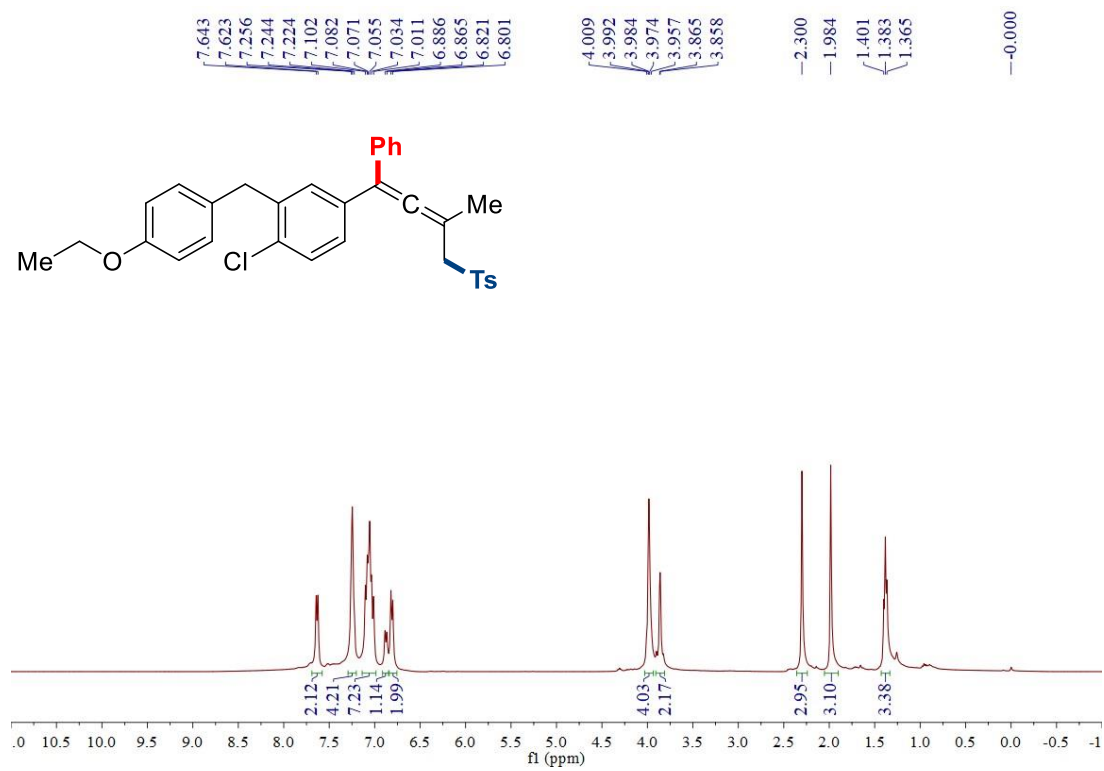


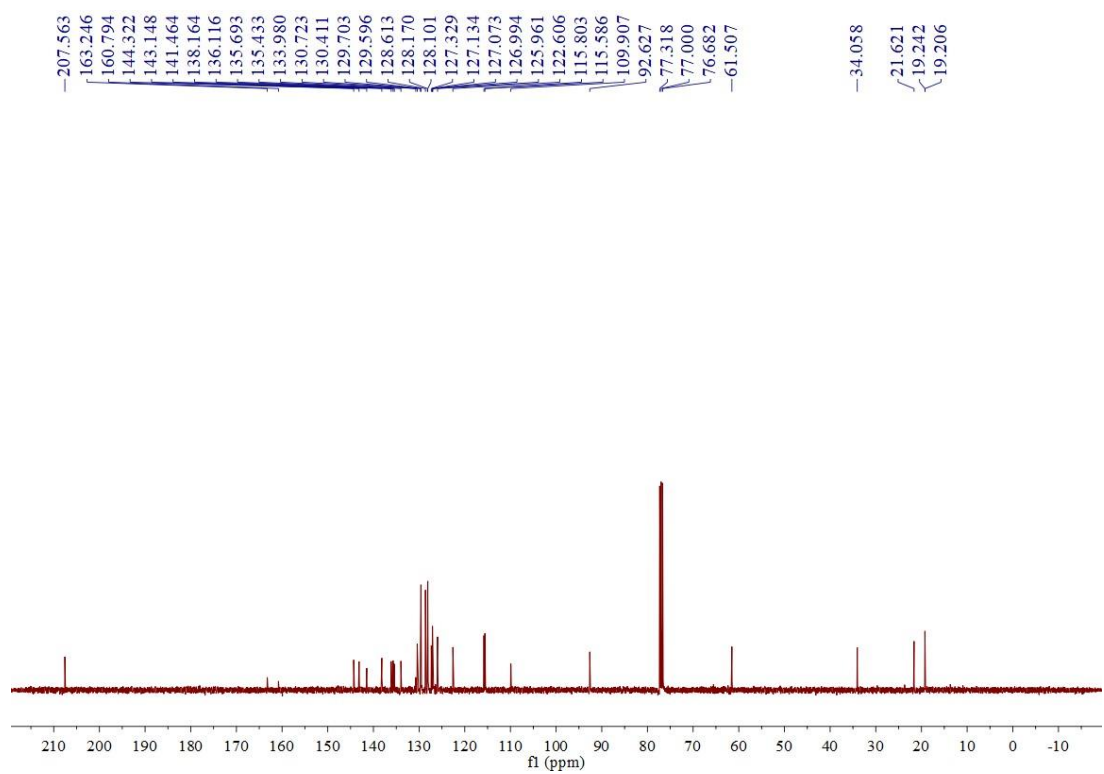
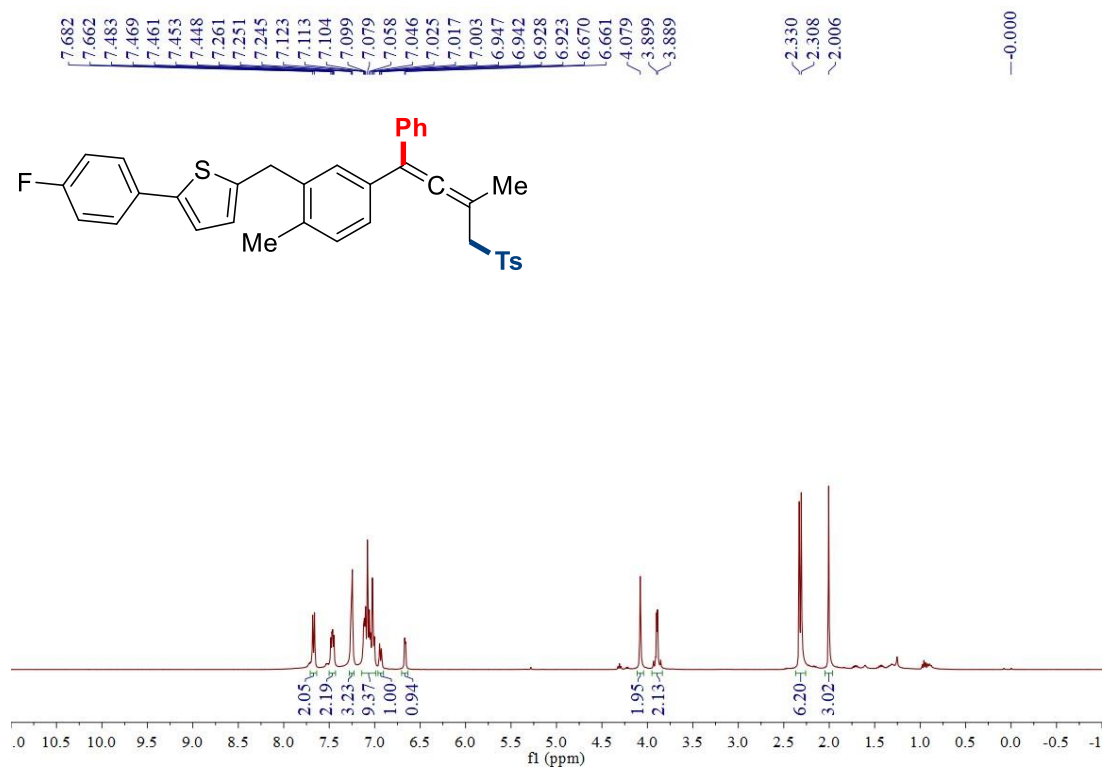


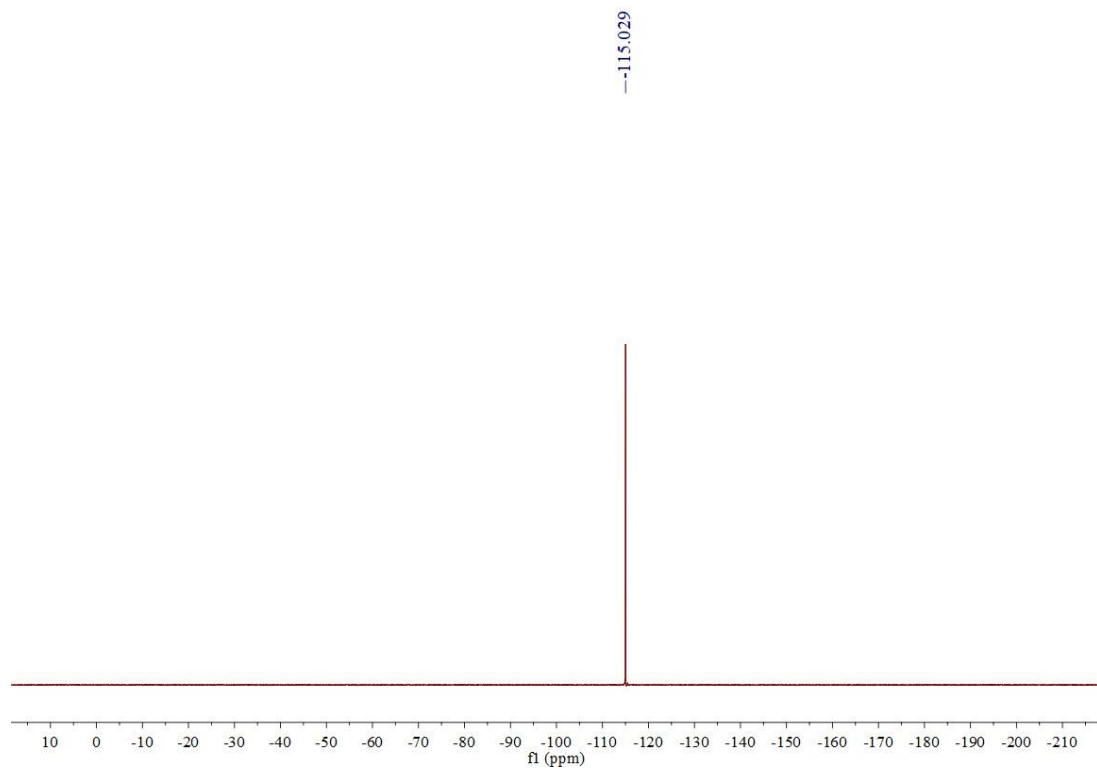


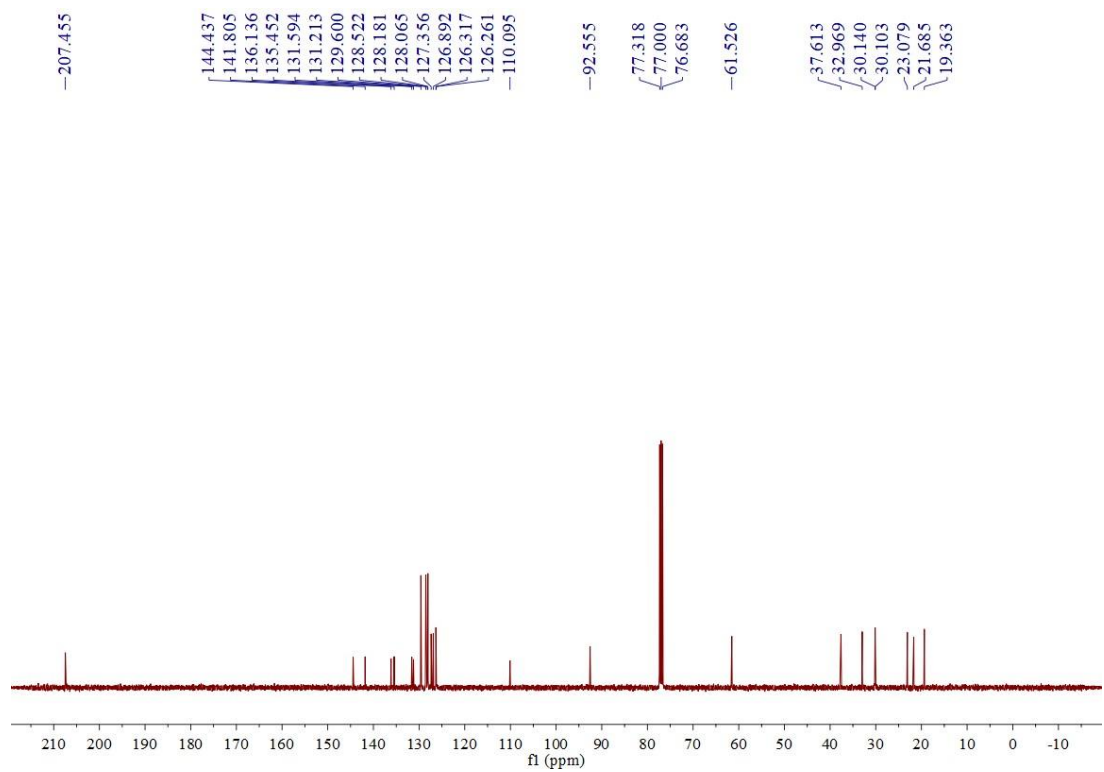
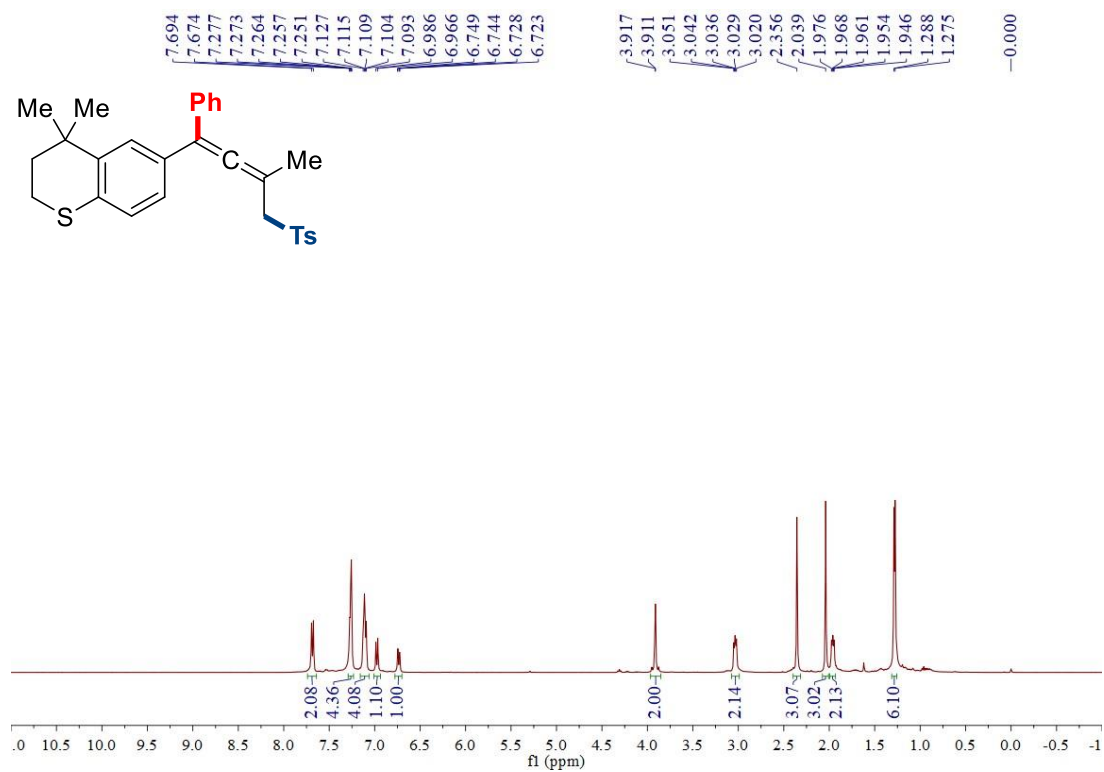


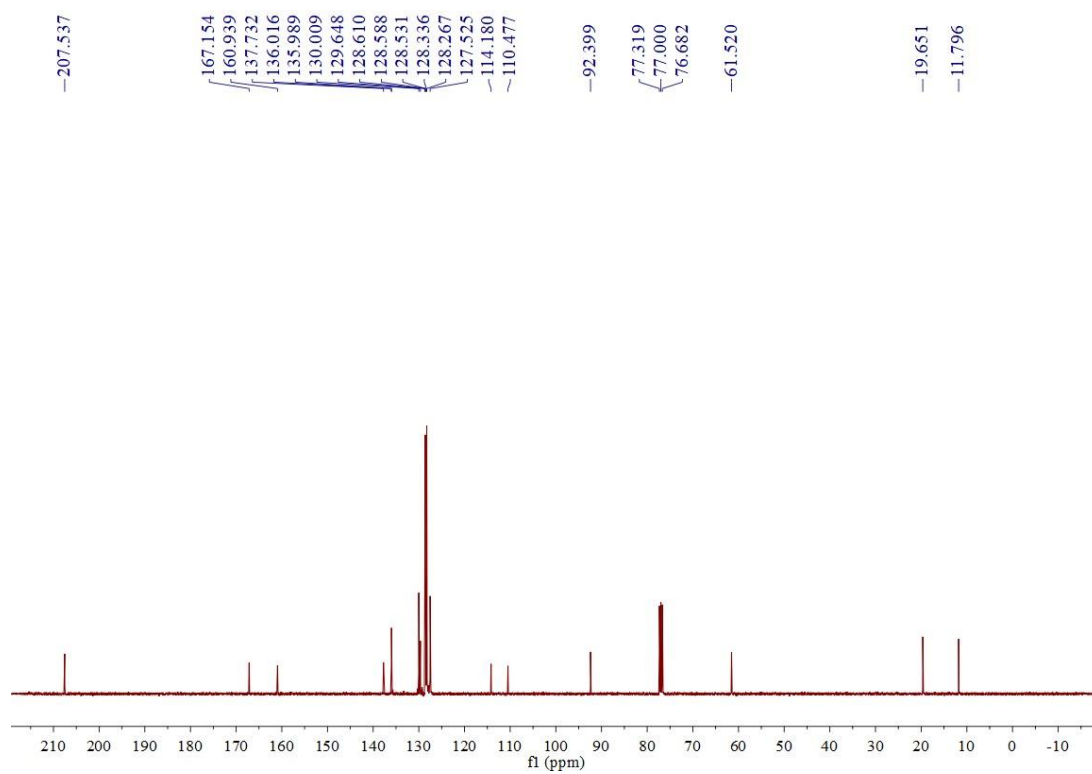
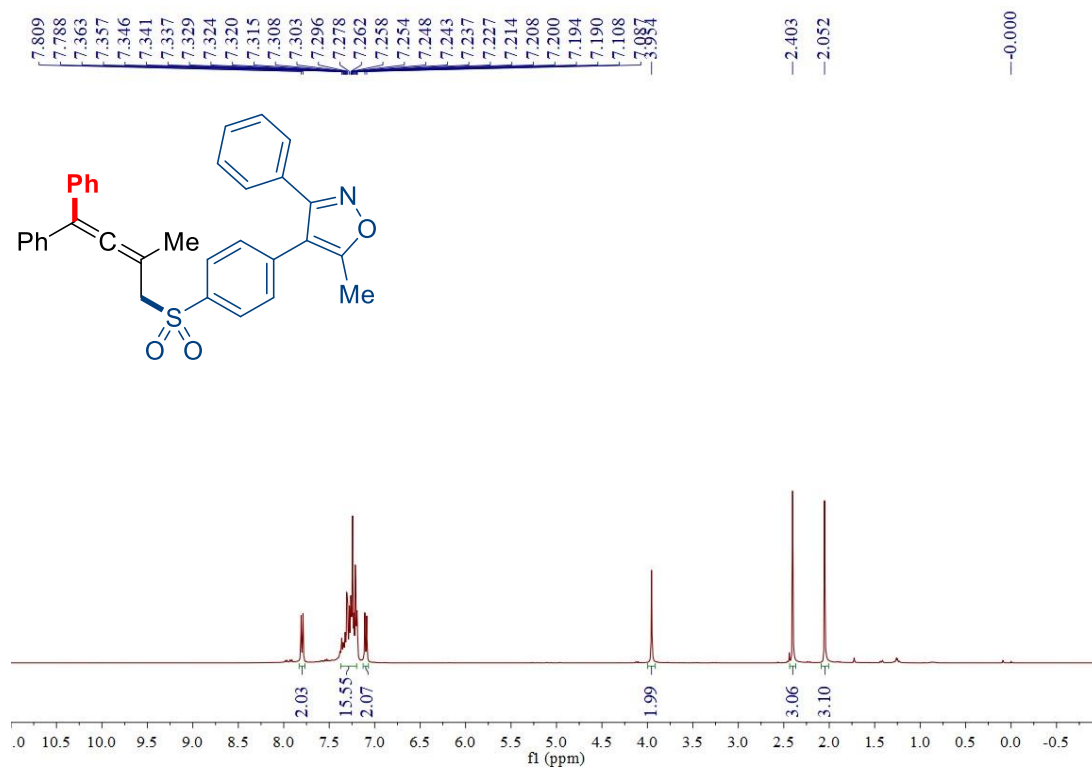


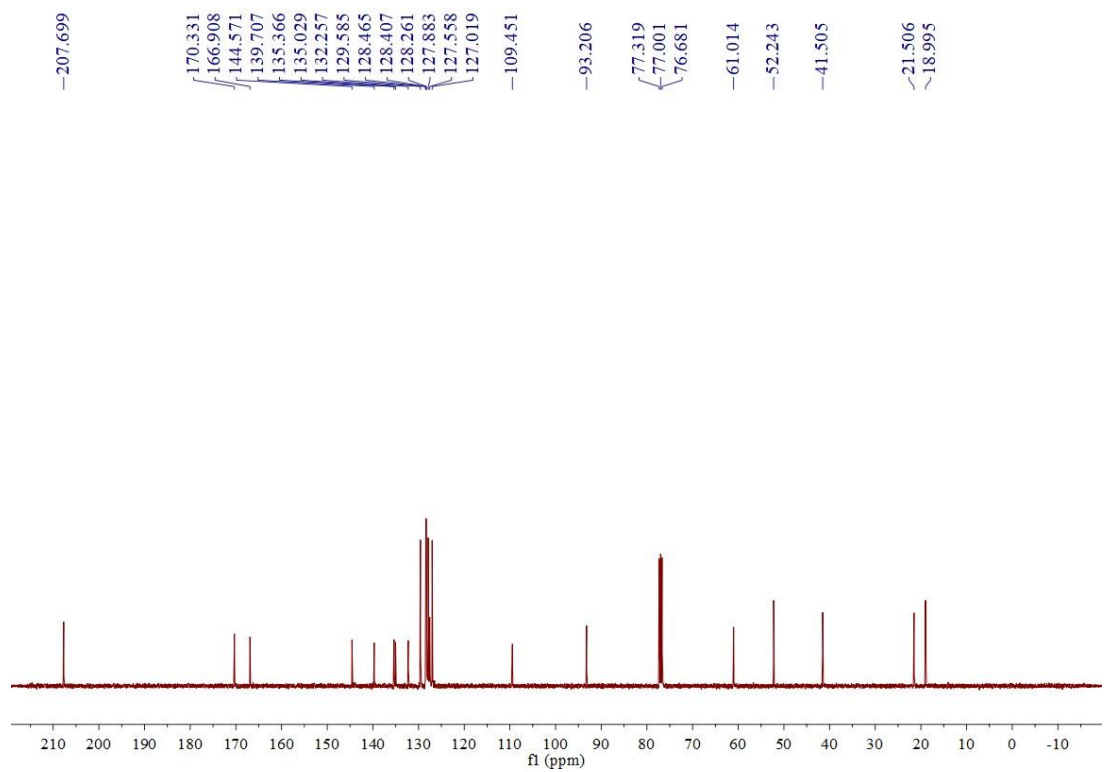
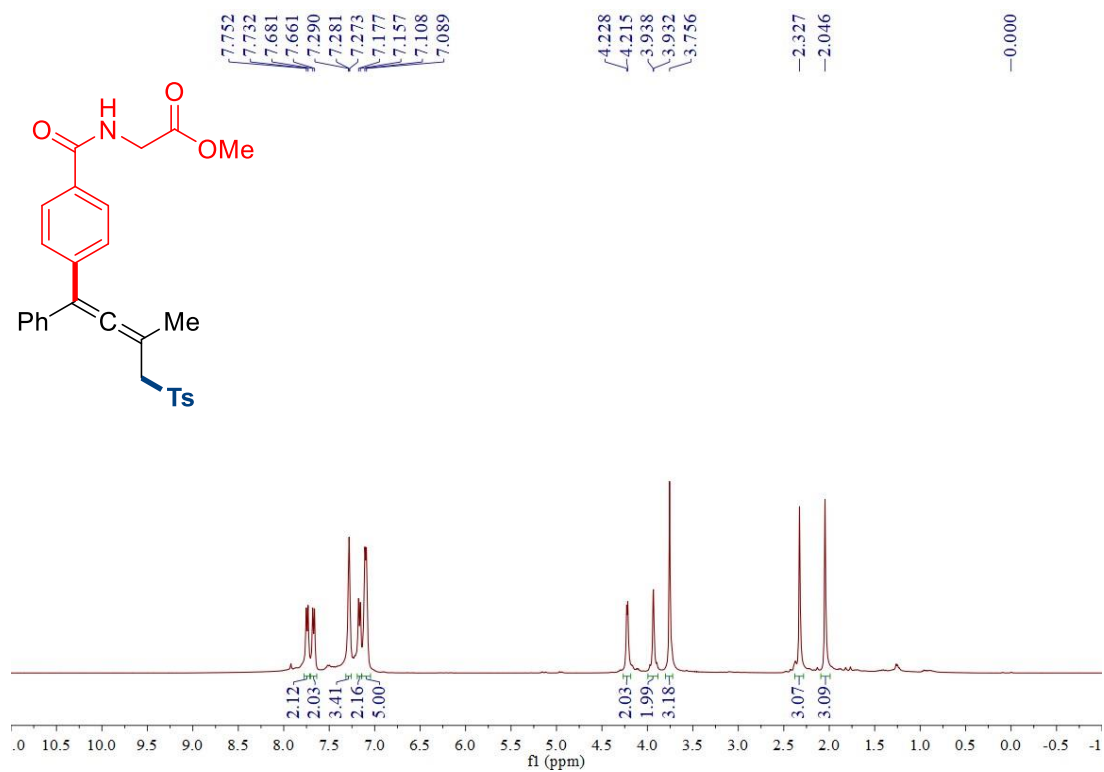


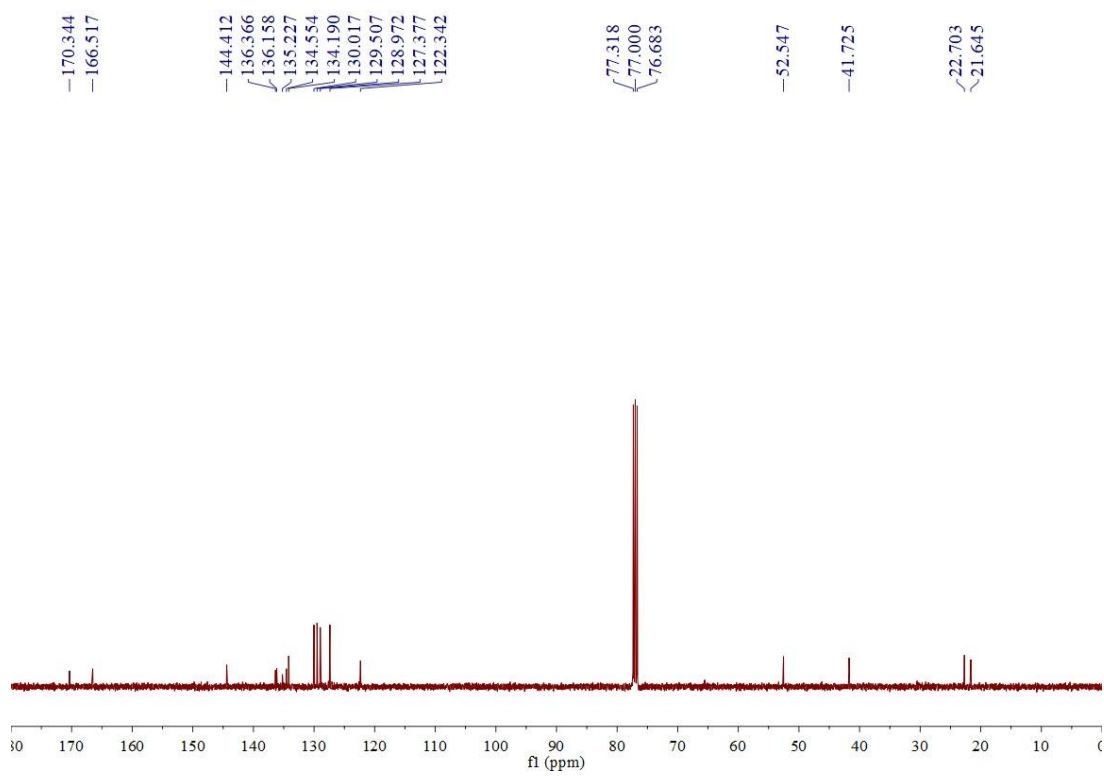
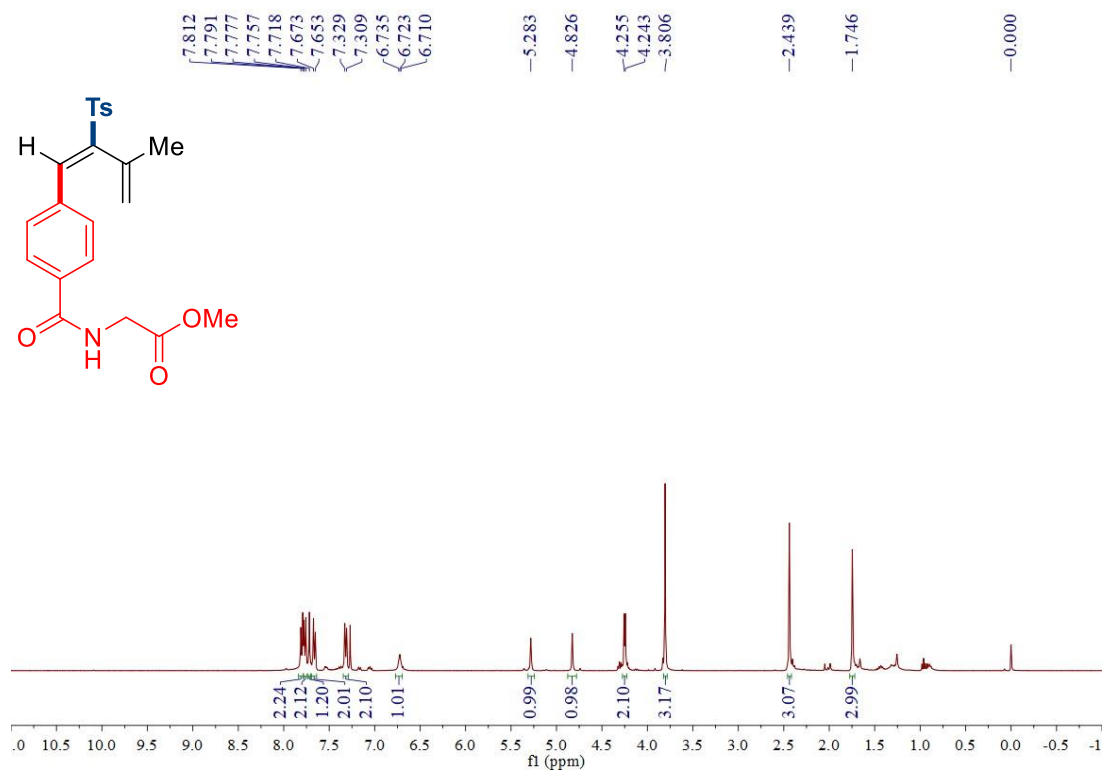


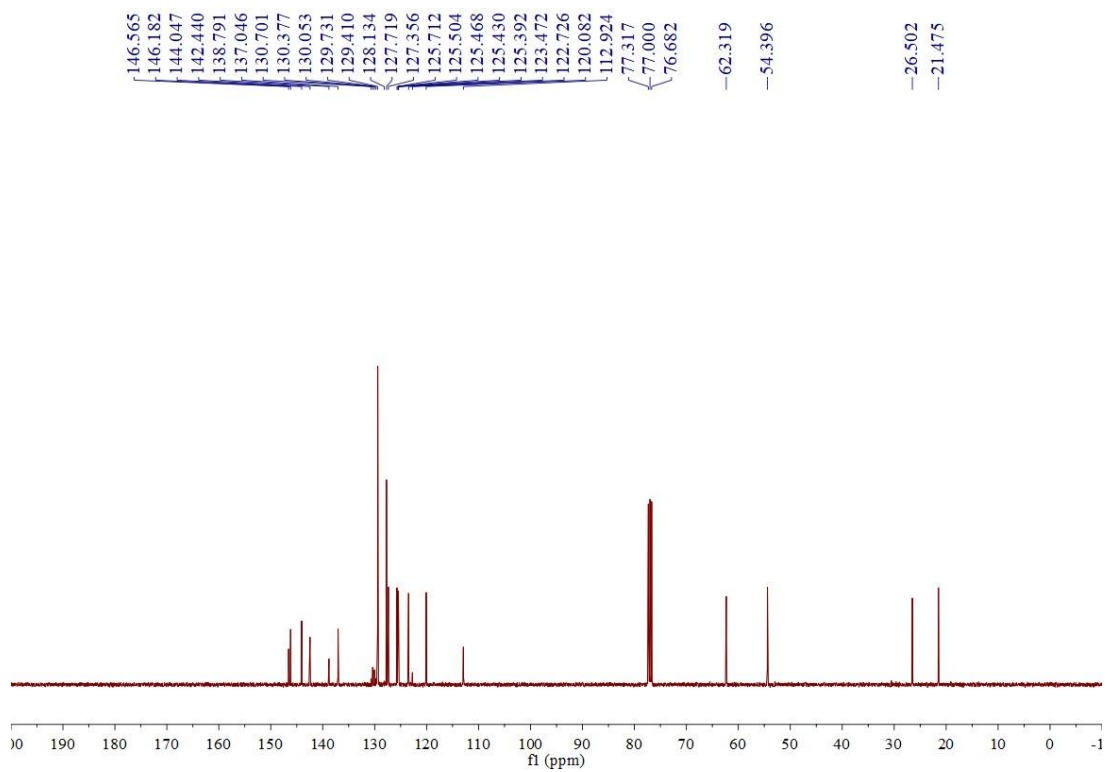
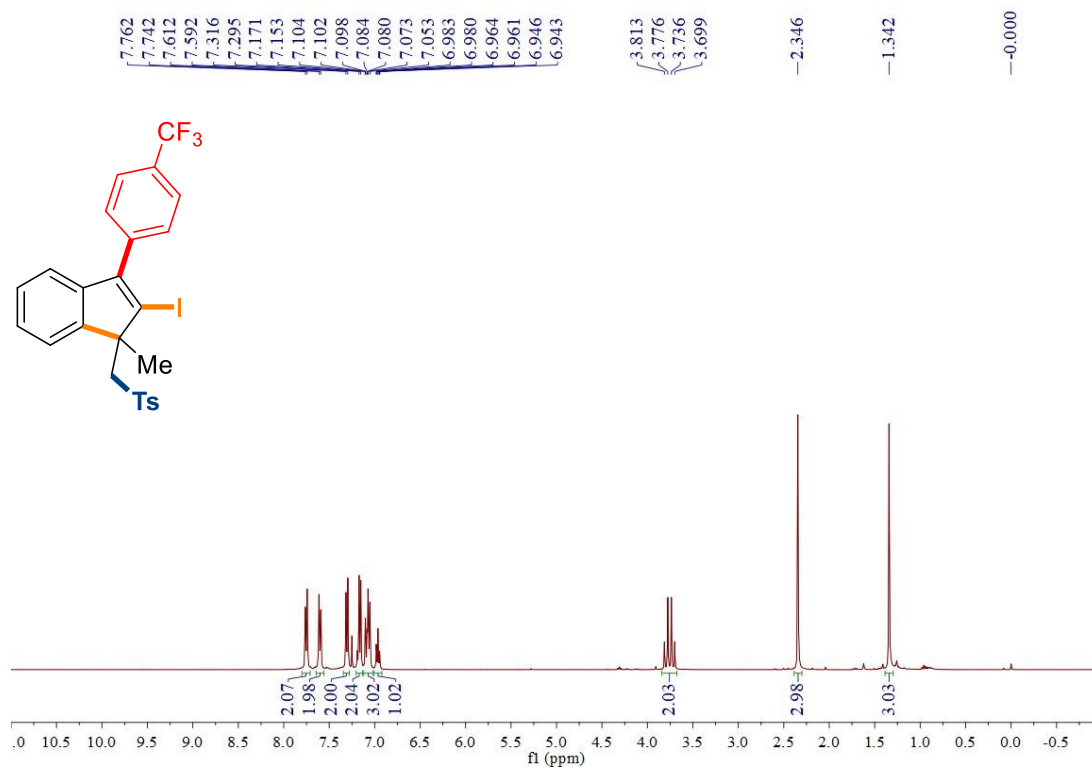


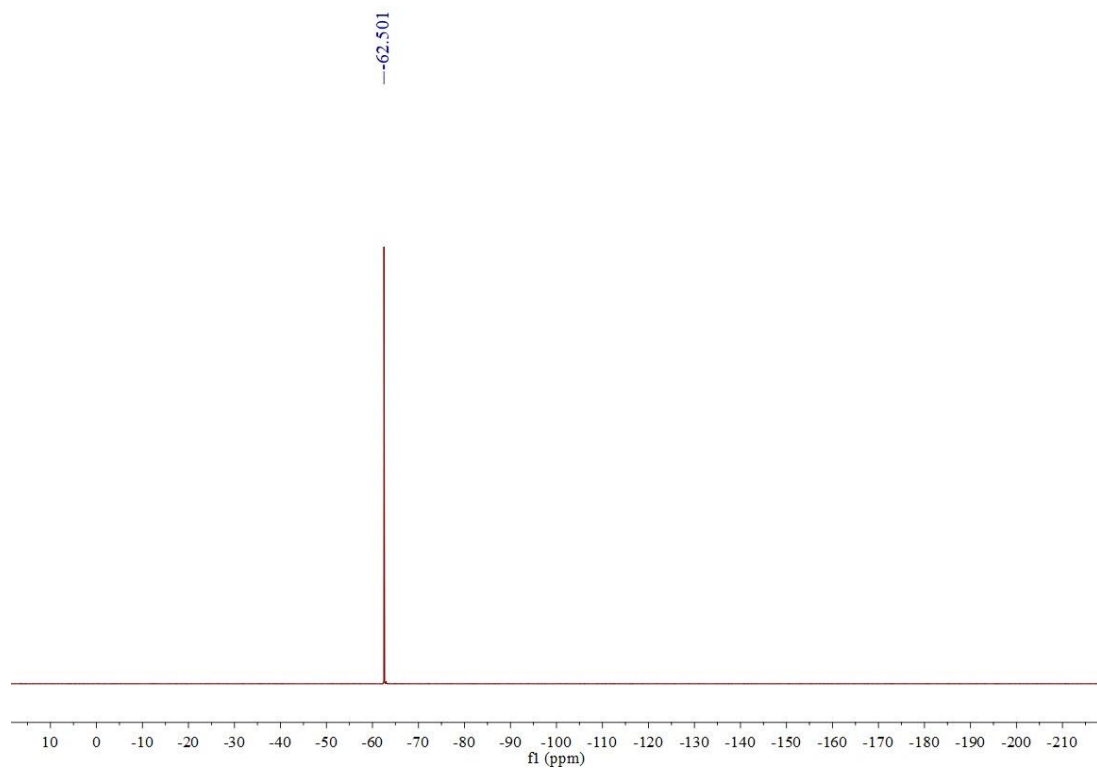


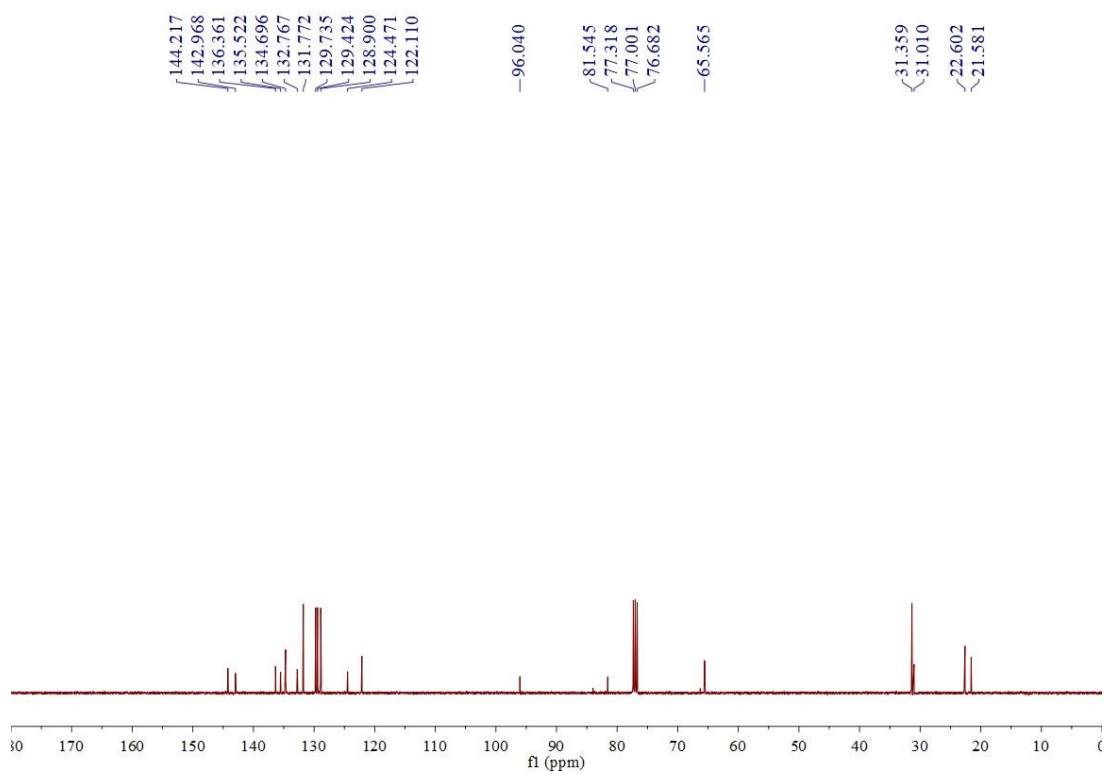
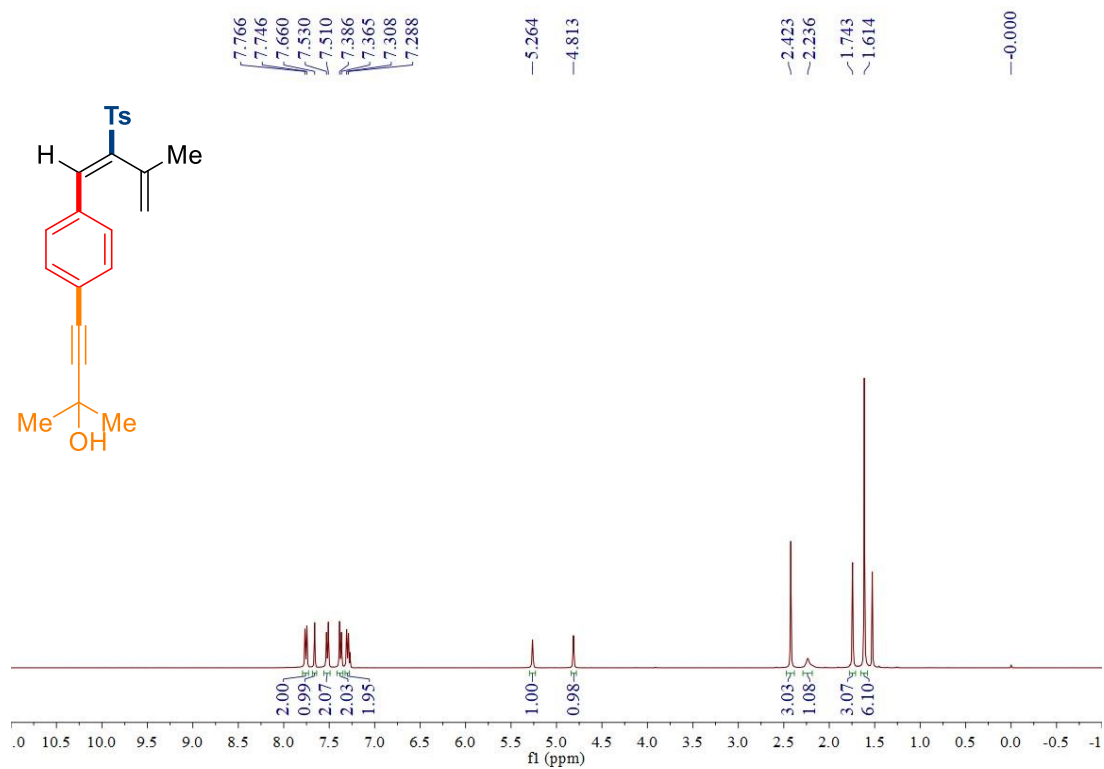


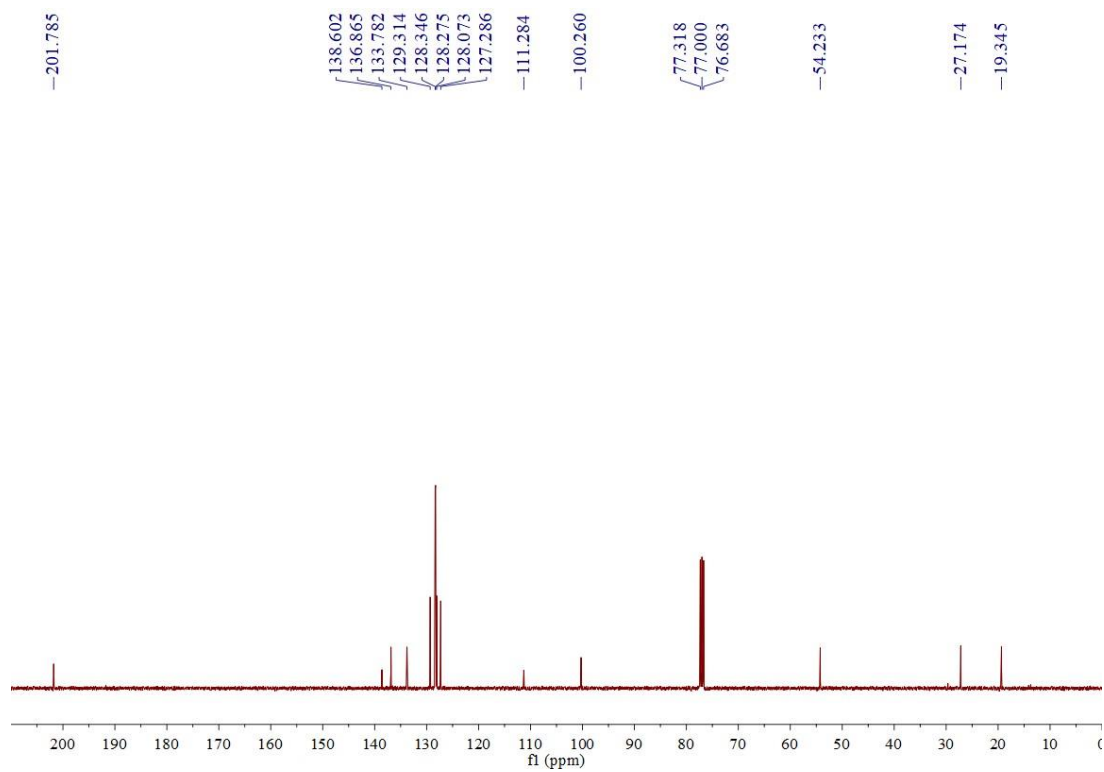
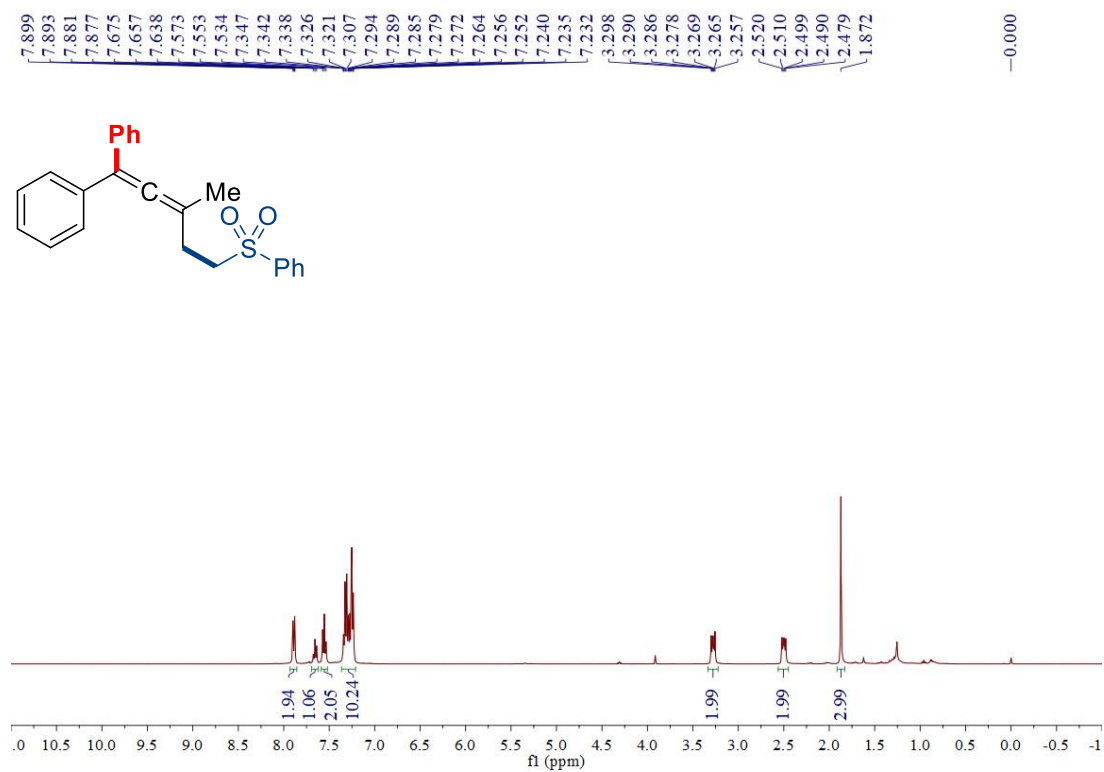


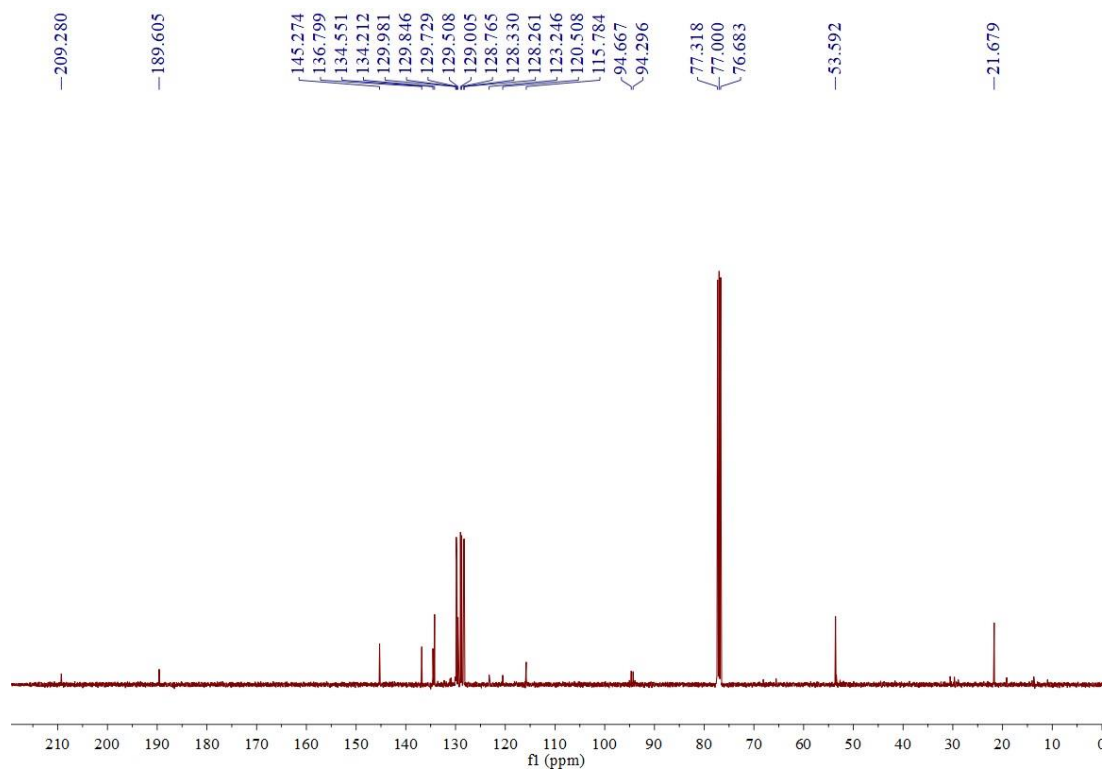
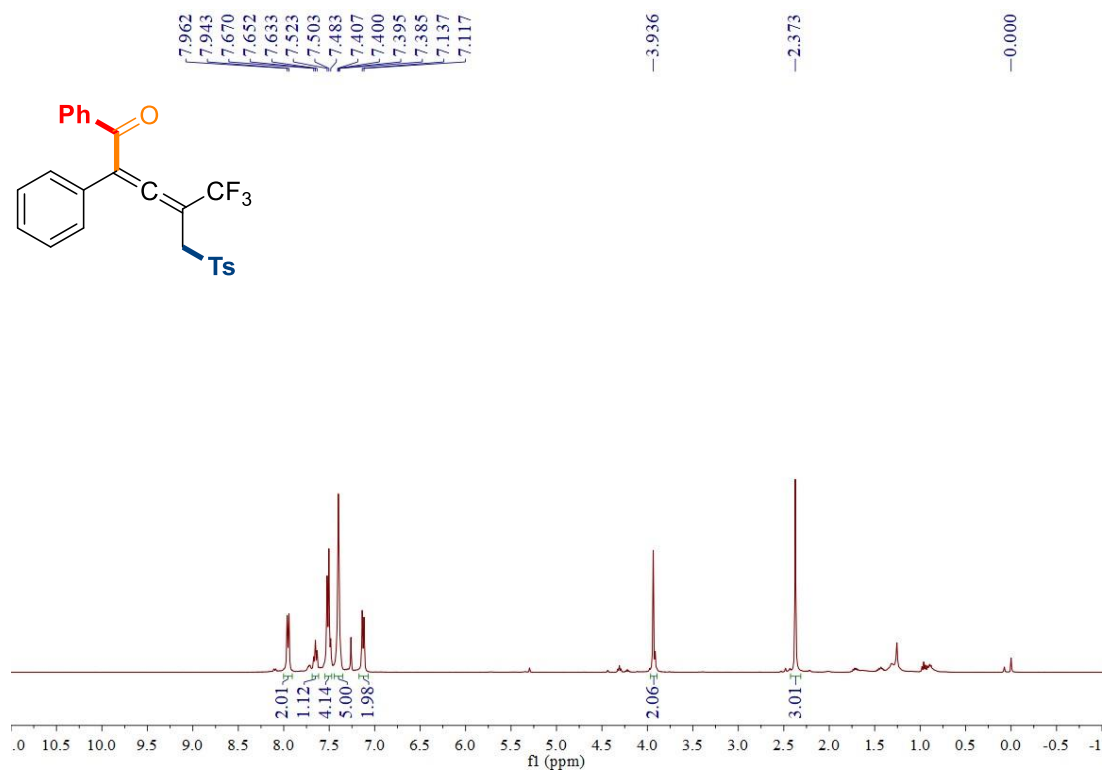


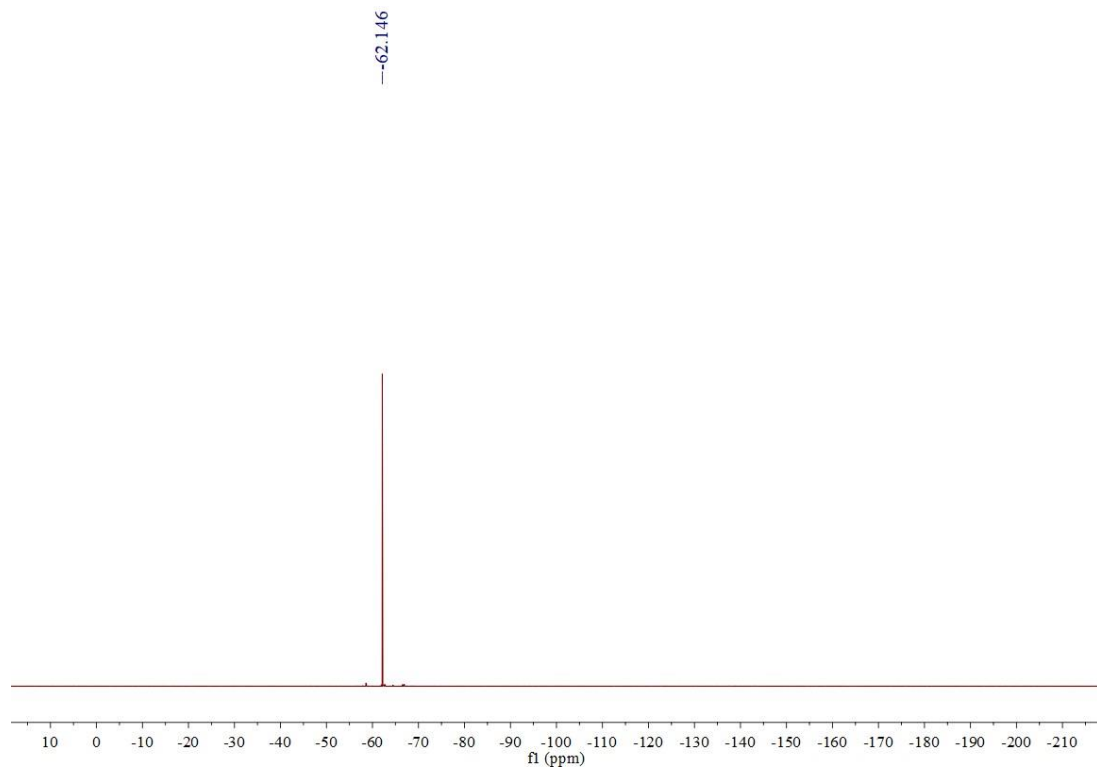


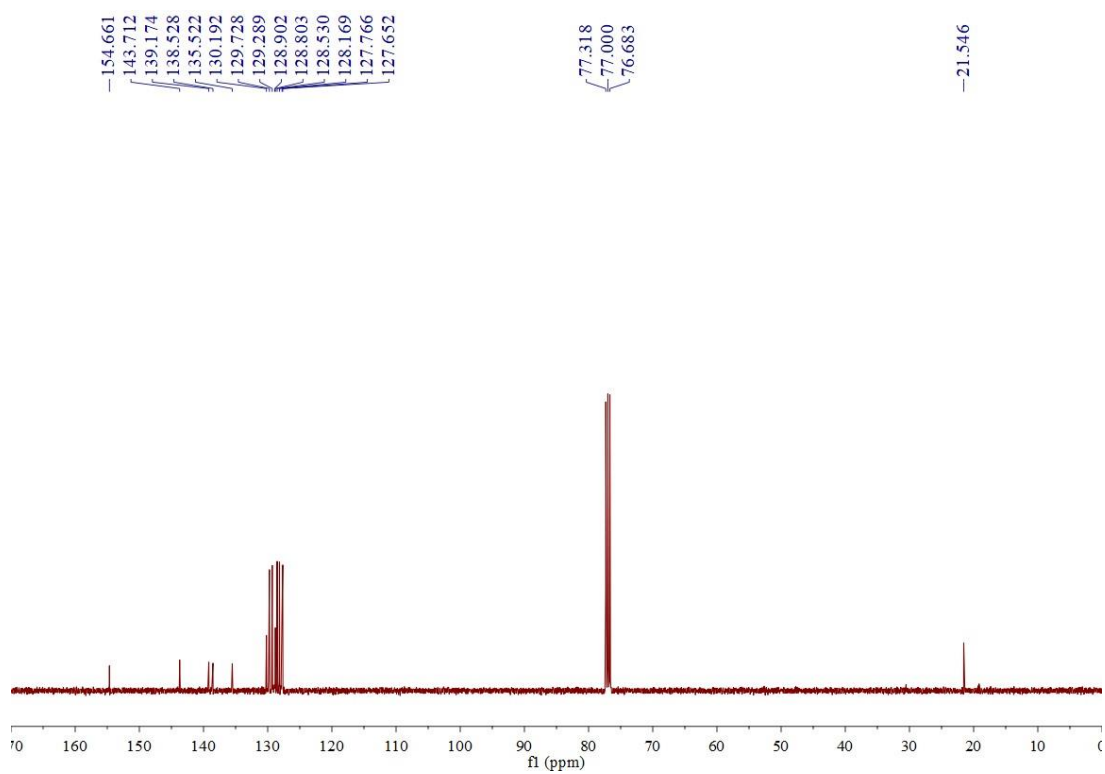
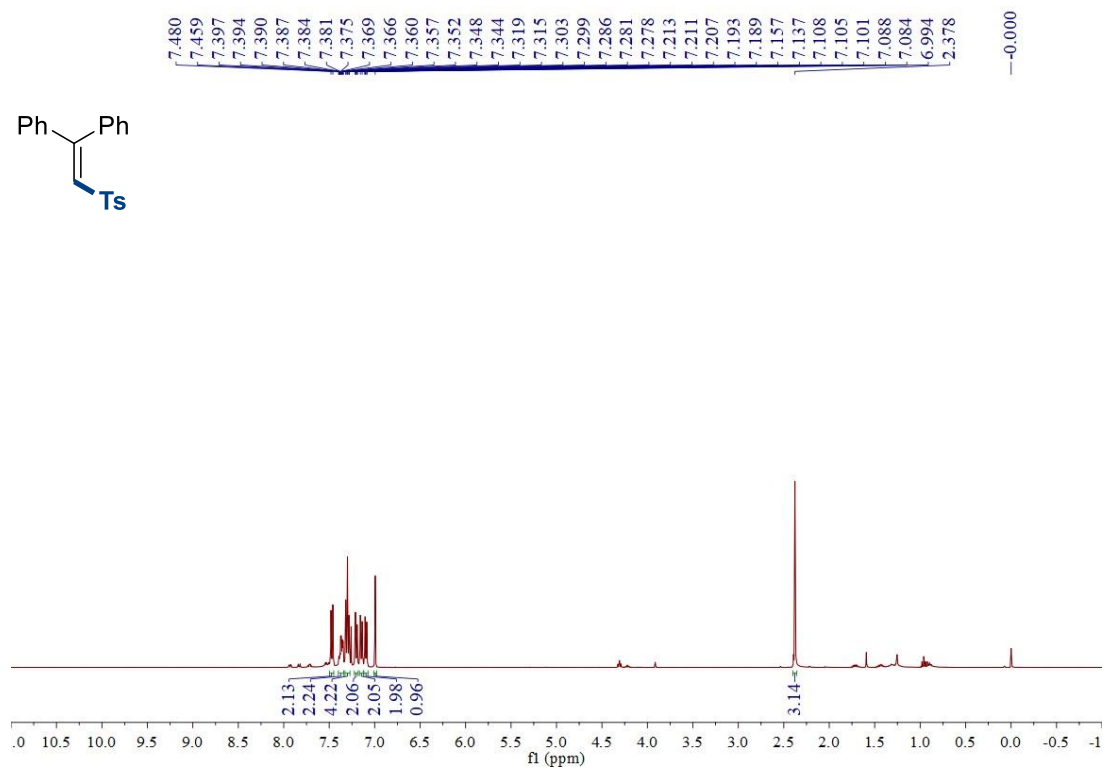


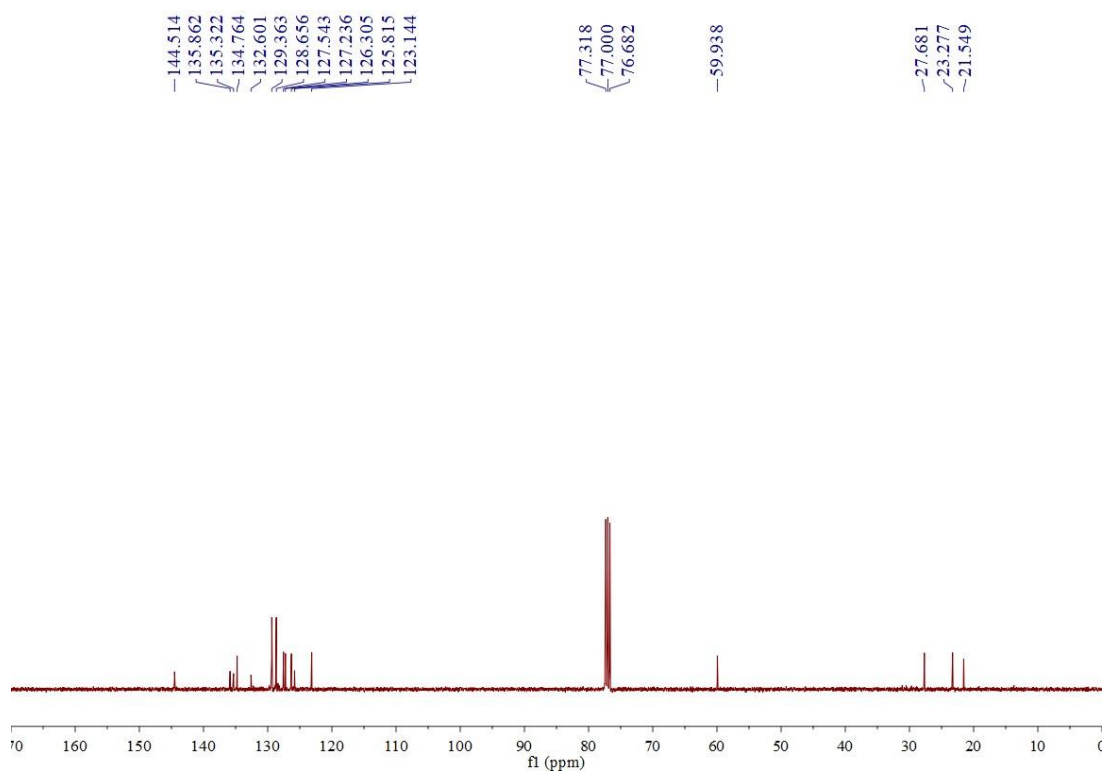
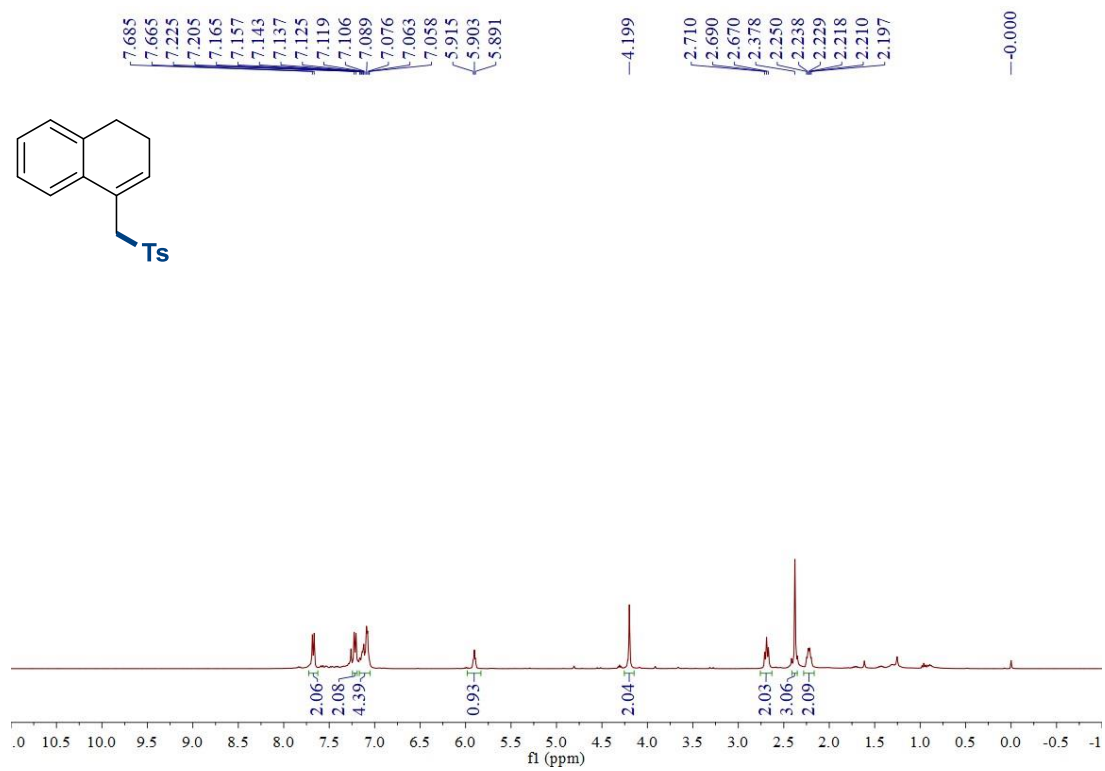












6. References

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