

## Supporting Information

# Regio- and Stereoselective Electrochemical Synthesis of Sulfonylated Enethers from Alkynes and Sulfonyl Hydrazides

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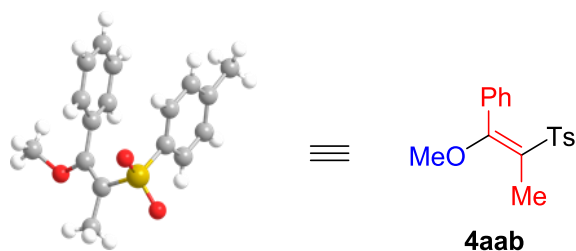
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## General methods

Unless noted, all commercial reagents and solvents were used without further purification. NMR spectra were recorded in  $\text{CDCl}_3$  on 400 MHz or 500 MHz spectrometers.  $^1\text{H}$  NMR chemical shifts ( $\delta$ ) are reported in parts per million relative to tetramethylsilane (0 ppm) or residual  $\text{CHCl}_3$  (7.26 ppm).  $^{13}\text{C}$  NMR chemical shifts are reported relative to the center line signal of the  $\text{CDCl}_3$  triplet at 77.0 ppm. The following abbreviations are used for multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, and m = multiplet. Mass spectra were obtained on an Ultima Global spectrometer with an ESI source. Silica gel (200–300 mesh) for column chromatography and silica GF254 for TLC were produced by Qingdao Marine Chemical Company (China). DC power supply DPS-305CF was used for all experiments.



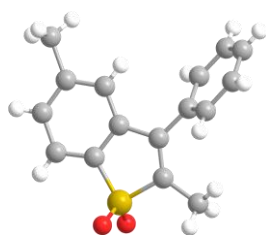
## Molecular structure and crystallographic data



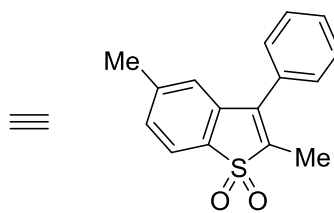
CCDC 2024060

**Table 1** Crystal data and structure refinement for **4aab**

Empirical formula	C <sub>17</sub> H <sub>18</sub> O <sub>3</sub> S
Formula weight	302.37
Temperature/K	170.00(15)
Crystal system	monoclinic
Space group	P2 <sub>1</sub> /n
a/Å	15.40316(12)
b/Å	7.20606(3)
c/Å	15.43887(9)
α/°	90
β/°	116.8711(9)
γ/°	90
Volume/Å <sup>3</sup>	1528.62(2)
Z	4
ρ <sub>calc</sub> /cm <sup>3</sup>	1.314
μ/mm <sup>-1</sup>	1.942
F(000)	640.0
Crystal size/mm <sup>3</sup>	0.34 × 0.28 × 0.19
Radiation	CuKα (λ = 1.54184)
2θ range for data collection/°	6.728 to 150.838
Index ranges	-17 ≤ h ≤ 18, -8 ≤ k ≤ 9, -19 ≤ l ≤ 19
Reflections collected	23298
Independent reflections	3042 [R <sub>int</sub> = 0.0148, R <sub>sigma</sub> = 0.0074]
Data/restraints/parameters	3042/0/193
Goodness-of-fit on F <sup>2</sup>	1.066
Final R indexes [I >= 2σ (I)]	R <sub>1</sub> = 0.0326, wR <sub>2</sub> = 0.0873
Final R indexes [all data]	R <sub>1</sub> = 0.0328, wR <sub>2</sub> = 0.0874
Largest diff. peak/hole / e Å <sup>-3</sup>	0.33/-0.38



CCDC 2032053



5

**Table 2** Crystal data and structure refinement for **5**

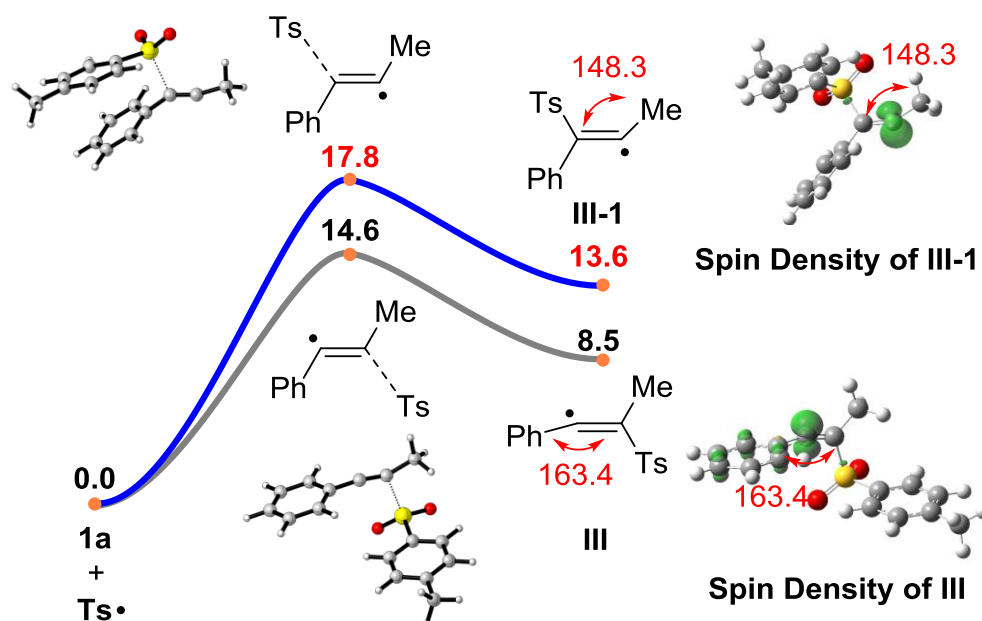
Empirical formula	$C_{16}H_{14}O_2S$
Formula weight	270.33
Temperature	298(2) K
Wavelength	0.71073 Å
Crystal system, space group	Orthorhombic, $P2(1)2(1)2(1)$
Unit cell dimensions	$a = 8.5976(8)$ Å $\alpha = 90$ deg. $b = 10.8141(9)$ Å $\beta = 90$ deg. $c = 15.2294(14)$ Å $\gamma = 90$ deg.
Volume	$1416.0(2)$ Å <sup>3</sup>
Z, Calculated density	4, 1.268 Mg/m <sup>3</sup>
Absorption coefficient	$0.223$ mm <sup>-1</sup>
F(000)	568
Crystal size	0.40 x 0.36 x 0.20 mm
Theta range for data collection	2.31 to 25.01 deg.
Limiting indices	$-10 \leq h \leq 9$ , $-10 \leq k \leq 12$ , $-18 \leq l \leq 18$
Reflections collected / unique	6668 / 2477 [R(int) = 0.1017]
Completeness to theta = 25.01	99.2 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9567 and 0.9161
Refinement method	Full-matrix least-squares on F <sup>2</sup>
Data / restraints / parameters	2477 / 0 / 174
Goodness-of-fit on F <sup>2</sup>	1.022
Final R indices [I > 2σ(I)]	R1 = 0.0577, wR2 = 0.1067
R indices (all data)	R1 = 0.0850, wR2 = 0.1143
Absolute structure parameter	0.09(12)
Largest diff. peak and hole	0.185 and -0.245 e.Å <sup>-3</sup>

## DFT calculations

### Computational methods

All calculations were performed using Gaussian 16, Revision A.03 package.<sup>1</sup> All structures were optimized in gas phase at the M062X/6-311G\* level of theory. Analytical frequency calculations were carried out at the same level of theory in order

to identify all stationary points as either intermediates (no imaginary frequencies) or transition states (only one imaginary frequency). The Gibbs free energy was then refined through single point calculations at the same functional with a larger basis set 6-311++G\*\*. This was carried out in the presence of solvent through the SMD<sup>ii</sup> method with dichloroethane. All reported energies are free energies at a concentration of 1 M. All the 3D molecular structures of the species were generated by using the CYLview program.<sup>iii</sup>



### Coordinates of the optimized structures

#### 1a

E = -347.650138 a.u.

C	-1.90604600	0.28384000	-0.00107800
C	-0.51670300	0.27923700	-0.00060700
C	0.19184700	1.48834200	0.00001700
C	-0.51577000	2.69801100	0.00013400
C	-1.90511100	2.69451200	-0.00033900
C	-2.60356900	1.48944700	-0.00093000
H	-2.44551700	-0.65660300	-0.00154100
H	0.02897900	-0.65761300	-0.00070200
H	0.03071400	3.63438900	0.00061800
H	-2.44385500	3.63537300	-0.00023100
H	-3.68778600	1.48987600	-0.00127500
C	1.62783200	1.48794400	0.00061300
C	2.83353900	1.48827100	0.00114800
C	4.29349500	1.48944900	0.00249400

H	4.68009100	1.98016600	-0.89300700
H	4.67841300	2.02152900	0.87475700
H	4.67949600	0.46886600	0.02632400

### TS1

E = -1167.085277 a.u.

C	0.23030600	-0.08839400	2.13106200
C	1.26843100	0.43943400	1.37909000
C	1.00318900	1.01445600	0.12098700
C	-0.31926500	1.04987500	-0.36028300
C	-1.34718900	0.51822400	0.40258200
C	-1.07726000	-0.05088500	1.64707000
H	0.43892600	-0.53146600	3.09810400
H	2.28765700	0.41494600	1.74791700
H	-0.52014200	1.49183500	-1.32939500
H	-2.36363800	0.54549900	0.02715300
H	-1.88532000	-0.46489200	2.23926400
C	2.06096000	1.54241500	-0.65240100
C	3.00413400	1.80934600	-1.40313900
C	4.04612700	2.68439200	-1.97129700
H	3.94888700	2.74845900	-3.05589100
H	3.95572000	3.68459400	-1.54616000
H	5.04051800	2.29438000	-1.73933500
C	6.44245700	-1.83736900	0.54130900
C	6.88771400	-1.17546800	-0.60420400
C	5.98800300	-0.68544500	-1.54558700
C	4.62999000	-0.88362400	-1.33357100
C	4.15071100	-1.53024400	-0.19654800
C	5.06505100	-2.00851000	0.72981000
H	7.95206200	-1.04037800	-0.76503700
H	6.33630600	-0.17506800	-2.43612900
H	3.08502300	-1.66963100	-0.05112300
H	4.70827000	-2.52604800	1.61472400
S	3.45325700	-0.17913000	-2.47355100
C	7.41200000	-2.35842800	1.56539200
H	7.26779700	-1.85268700	2.52373100
H	7.25778800	-3.42643600	1.73683200
H	8.44441200	-2.20526400	1.25022200
O	2.23720300	-1.00395200	-2.44099700
O	4.13952000	0.04540400	-3.75885800

III

E = -1167.098854 a.u.

C	-0.39825400	0.24624000	2.08686800
C	0.75466800	0.62732600	1.42566900
C	0.68402700	1.09534000	0.08729700
C	-0.58328100	1.17370600	-0.54634900
C	-1.72206200	0.78700000	0.13507600
C	-1.63993200	0.32299200	1.45072800
H	-0.33431100	-0.11482000	3.10711100
H	1.71985200	0.57274000	1.91608700
H	-0.64217100	1.53285900	-1.56716700
H	-2.68527300	0.84459900	-0.35911300
H	-2.53853100	0.02343700	1.97725400
C	1.83438000	1.49551600	-0.57617600
C	2.91538600	1.50614800	-1.28648400
C	3.87809100	2.62205100	-1.57969700
H	3.92426900	2.81168600	-2.65318200
H	3.55714800	3.52830000	-1.06828200
H	4.88315700	2.36276800	-1.23543700
C	6.80022200	-1.48903900	0.61078900
C	7.06560800	-0.84793900	-0.60074700
C	6.03177500	-0.42365700	-1.42875300
C	4.72133000	-0.65719000	-1.03173900
C	4.42260400	-1.28850200	0.17342900
C	5.46774800	-1.70217900	0.98503000
H	8.09378600	-0.67654900	-0.90134000
H	6.23898800	0.07071300	-2.37084700
H	3.39191400	-1.46086200	0.46429200
H	5.25039600	-2.19984000	1.92454300
S	3.38108000	-0.08821300	-2.05152600
C	7.91950100	-1.96868700	1.49206600
H	7.69395400	-1.79166200	2.54527000
H	8.06636200	-3.04531000	1.36587100
H	8.85873800	-1.47184100	1.24685500
O	2.26573300	-1.01891400	-1.90799100
O	3.91149700	0.20005800	-3.38435700

### TS1-1

E = -1167.098854 a.u.

C	1.42866400	1.28503400	-0.76474300
C	2.59469100	1.40520900	-1.18759000
C	6.99485600	-1.16791100	0.03973300
C	7.02933000	-0.57090100	-1.22652600
C	5.86948900	-0.39338600	-1.96595700
C	4.66287900	-0.83998500	-1.43255200

C	4.59220100	-1.42731000	-0.17544500
C	5.76717900	-1.59837400	0.54844900
H	7.97831400	-0.23411900	-1.63198300
H	5.89527500	0.07906300	-2.94118600
H	3.63923400	-1.75112500	0.22821800
H	5.72799500	-2.06692600	1.52608300
S	3.14394400	-0.42530500	-2.26385900
C	8.26361400	-1.32821000	0.83003000
H	8.69838000	-0.35194000	1.06016000
H	8.08404500	-1.85256500	1.76888300
H	9.00835900	-1.88754900	0.25872600
O	2.12155200	-1.42900600	-1.93969500
O	3.44976800	-0.15420100	-3.67715100
C	3.82907600	2.18735200	-1.20309700
C	4.29997300	2.74616700	-2.39385400
C	4.59475900	2.28170100	-0.03616600
C	5.52539400	3.40390100	-2.41160800
H	3.71051000	2.65664600	-3.29912100
C	5.82033200	2.93601000	-0.06304700
H	4.23035400	1.82898100	0.87946100
C	6.28913200	3.49403800	-1.25080600
H	5.88669400	3.84038300	-3.33580100
H	6.41325700	3.00332000	0.84217600
H	7.24834600	3.99888600	-1.27092200
C	0.09067100	0.82266500	-0.45256100
H	-0.06936200	0.80399700	0.62757300
H	-0.65922400	1.47453100	-0.90521300
H	-0.05114200	-0.19237500	-0.84100700

### III-1

E = -1167.098854 a.u.

C	1.67323800	1.68635400	-0.63794900
C	2.78004000	1.49507000	-1.30331500
C	6.86104100	-1.17026900	0.44399500
C	6.97202400	-0.64603600	-0.84506700
C	5.84074800	-0.36061700	-1.60225400
C	4.59024600	-0.61830300	-1.05525500
C	4.44475300	-1.13254300	0.23081700
C	5.58484800	-1.41043100	0.96886200
H	7.95476900	-0.45467800	-1.26257000
H	5.92871700	0.04843900	-2.60232200
H	3.45804400	-1.31711300	0.64153900
H	5.48796500	-1.81827700	1.96986300



S	3.13306600	-0.16295900	-1.96477600
C	8.08167100	-1.48655900	1.26224200
H	8.01777900	-1.02455200	2.24999300
H	8.17114100	-2.56556900	1.41432500
H	8.99048800	-1.13533200	0.77303500
O	2.03612200	-1.05121600	-1.58677500
O	3.49317100	-0.04485800	-3.37688800
C	3.88302900	2.47640700	-1.49325000
C	4.26452600	2.89785800	-2.76928300
C	4.57193300	2.94803500	-0.37288400
C	5.32247000	3.78884200	-2.91789100
H	3.73406500	2.52743300	-3.63854600
C	5.62843100	3.83911400	-0.52657700
H	4.27996100	2.60507400	0.61431700
C	6.00639400	4.25850600	-1.79937500
H	5.61190600	4.11760300	-3.90969300
H	6.15945100	4.20064700	0.34678700
H	6.83229400	4.95063300	-1.91974400
C	0.42151600	1.13902600	-0.12814600
H	0.26605600	1.44980100	0.90814600
H	-0.41731400	1.51750100	-0.71811000
H	0.41821100	0.04560500	-0.17677900

<sup>i</sup> Gaussian 16, Revision A.03, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2016.

<sup>ii</sup> A. V. Marenich, C. J. Cramer, D. G. Truhlar, J. Phys. Chem. B 2009, 113, 6378-6396.

<sup>iii</sup> CYLview, 1.0b; Legault, C. Y., Université de Sherbrooke, 2009 (<http://www.cylview.org>)

## Calculation for redox potential

The equation for the stand redox potential  $E^0$

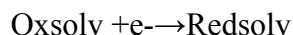
$$E^0 = -\frac{\Delta G_{solv}^{o,red}}{nF}$$

$\Delta G_{solv}^{o,red}$  is the calculated free energy of reduction;

F is the Faraday constant;

n is the number of electrons being transferred.

The reduction process for calculating  $\Delta G_{solv}^{o,red}$



where Oxsolv and Redsolv are the oxidized and reduced species in solution.

The effect of the electron on the free energy is -0.868 kcal/mol at 298.15 K.

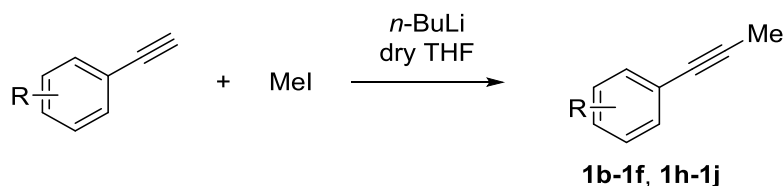
The Standard Hydrogen Electrode (SHE) potential in water was experimentally estimated to be 4.44 V.

The  $E^0$  versus SHE can be obtained via

$$E^0 \text{ vs SHE} = -\frac{\Delta G_{solv}^{o,red}}{nF} - 4.44V$$

## Preparation of the starting materials

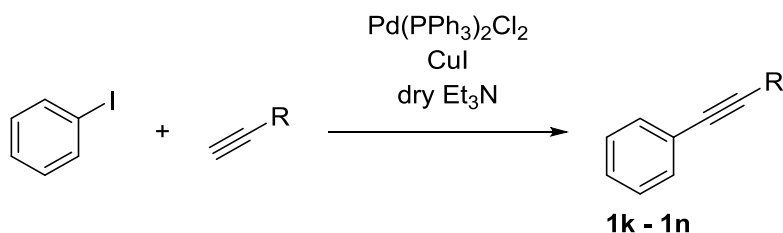
### Preparation of substrates 1



The compounds **1b** – **1f**, **1h** – **1j** were prepared according to previously described methods.<sup>[1]</sup>

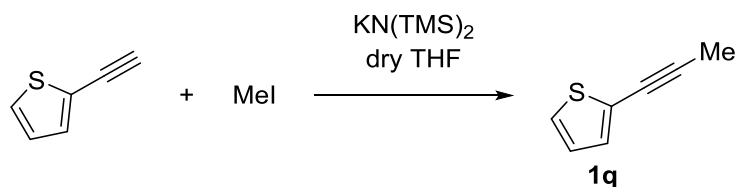
To a flame-dried round-bottom flask under  $N_2$  was added alkyne (10 mmol) followed by dry THF (50 mL, 0.2 M). Cool the flask to 0 °C. *n*-Butyllithium (8 mL, 2.5 M in hexanes, 20 mmol, 2 equiv.) was added slowly and the reaction was allowed to stir for 1 hour. Iodomethane (2 mL, 21 mmol, 2.1 equiv.) was added at -20 °C and the reaction was allowed to stir at room temperature for 3 ~ 5 hour (when most of alkyne was consumed as detected by TLC). The reaction was quenched with a saturated solution of ammonium chloride and extracted with ethyl acetate. The organics were dried over  $MgSO_4$  and the solvents were removed under reduced pressure. The residue was purified by silica chromatography to afford the corresponding compounds **1a** – **1i**.

The compounds **1k** – **1n** were prepared according to previously described methods.<sup>[2]</sup>



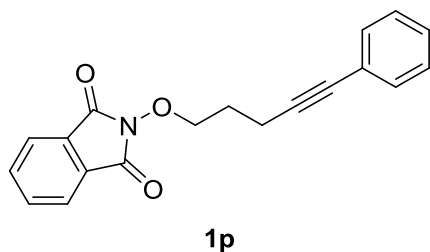
To a 50 mL flame-dried round-bottom flask, under  $\text{N}_2$ , was added  $\text{PdCl}_2(\text{PPh}_3)_2$  (0.05 mmol, 0.01 equiv.),  $\text{CuI}$  (0.1 mmol, 0.02 equiv.), iodobenzene (5 mmol, 1.0 equiv.), terminal alkynes (6 mmol, 1.2 equiv.) and dry  $\text{Et}_3\text{N}$  (10 mL), the reaction was allowed to stir at room temperature. The reaction was stirred overnight checked by TLC. The reaction is filtered over celite, washing with dichloromethane. The solvent was removed and the residue purified by flash column chromatography on silica gel to give compounds **1k – 1n**.

The compound **1q** were prepared according to previously described methods.<sup>[3]</sup>

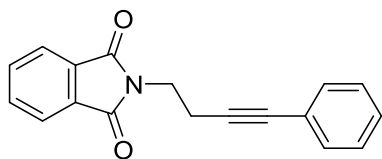


To a 50 mL flame-dried round-bottom flask under  $\text{N}_2$  was charged with thienylacetylene (5 mmol, 1 equiv.), THF (15 mL) and a stir bar. The reaction mixture was cooled to  $-78\text{ }^\circ\text{C}$  and a solution of  $\text{KN(TMS)}_2$  (1.0 M, 6.5 mmol, 1.3 equiv.) was added dropwise over a 10 min period. After allowing the reaction to stir at the temperature for 1 h, methyl iodide (6.5 mmol, 1.3 equiv.) was added. The reaction was slowly allowed to warm to room temperature. After stirring for 4 h, the reaction was quenched with water. The aqueous phase was extracted with ethyl acetate. The combined organic phase was dried with  $\text{MgSO}_4$ , filtered. The solvent was removed and the residue purified by flash column chromatography on silica gel to give compound **1q**.

The compound **1o – 1p** were prepared according to previously described methods.<sup>[4]</sup>



To a 50 mL Schlenk flask, under N<sub>2</sub>, was added *N*-Hydroxyphthalimide (6.5 mmol, 1.3 equiv.), triphenylphosphine (7.5 mmol, 1.5 equiv.), 30 mL of dry THF, and then pent-4-yn-1-ol (5 mmol, 1.0 equiv.) was added. The flask is immersed in an ice bath, and diisopropyl azodicarboxylate (7.5 mmol, 1.5 equiv.) was added dropwise, upon completion of the addition, the flask is removed from the ice bath and the solution is allowed to stir at room temperature overnight. The solvent was removed and the residue purified by flash column chromatography on silica gel to give compound 2-(pent-4-yn-1-yloxy)isoindoline-1,3-dione. Then, to a 50 mL Schlenk flask under N<sub>2</sub> was added PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (0.05 mmol, 0.01 equiv.), CuI (0.1 mmol, 0.02 equiv.), iodobenzene (6 mmol, 1.2 equiv.), compound 2-(pent-4-yn-1-yloxy)isoindoline-1,3-dione (5 mmol, 1.0 equiv.) and dry Et<sub>3</sub>N (10 mL), then the reaction was allowed to stir at room temperature for 10 h and checked by TLC. The reaction is filtered over celite, washing with dichloromethane. The solvent was removed and the residue purified by flash column chromatography on silica gel to give compound **1p**.

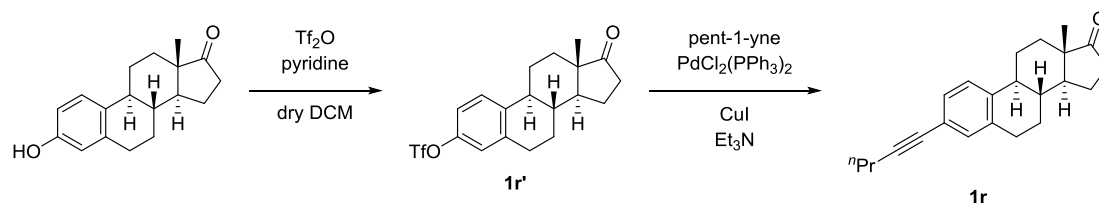


**1o**

To a 50 mL Schlenk flask, under N<sub>2</sub>, was added isoindoline-1,3-dione (6.5 mmol, 1.3 equiv.), triphenylphosphine (7.5 mmol, 1.5 equiv.), 30 mL of dry THF, and then but-3-yn-1-ol (5 mmol, 1.0 equiv.) was added. The flask is immersed in an ice bath, and diisopropyl azodicarboxylate (7.5 mmol, 1.5 equiv.) was added dropwise, upon completion of the addition, the flask is removed from the ice bath and the solution is allowed to stir at room temperature overnight. The solvent was removed and the residue purified by flash column chromatography on silica gel to give compound 2-(but-3-yn-1-yl)isoindoline-1,3-dione. Then, to a 50 mL Schlenk flask under N<sub>2</sub> was added PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (0.05 mmol, 0.01 equiv.), CuI (0.1 mmol, 0.02 equiv.), iodobenzene (6 mmol, 1.2 equiv.), compound 2-(but-3-yn-1-yl)isoindoline-1,3-dione (5 mmol, 1.0 equiv.) and dry Et<sub>3</sub>N (10 mL), then the reaction was allowed to stir at room temperature

for 10 h and checked by TLC. The reaction is filtered over celite, washing with dichloromethane. The solvent was removed and the residue purified by flash column chromatography on silica gel to give compound **1o**.

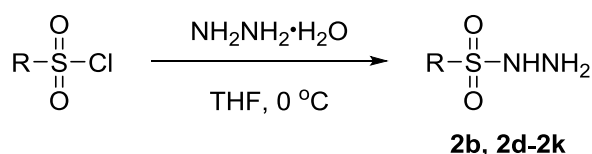
The compound **1r** were prepared according to previously described methods.<sup>[5]</sup>



To a solution of estrone (5 mmol, 1 equiv.) and pyridine (10 mmol, 2 equiv.) in dry DCM (50 mL) was added Tf<sub>2</sub>O (6 mmol, 1.2 equiv.) dropwise at 0 °C. After that, the mixture was warmed to rt, and stirred 3 h. The mixture was then quenched with 10% HCl and extracted with DCM. The combined organic layer was dried over anhydrous MgSO<sub>4</sub>. The filtrate was concentrated in vacuo and the residue was purified by flash column chromatography to afford **1r'**. A mixture of **1r'** (1.61 g, 4 mmol), pent-1-yne (0.5 mL, 5 mmol), trimethylamine (3.0 mL), Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (84 mg, 0.12 mmol) CuI (84 mg, 0.12 mmol) in 15 mL DMF was stirred at 90 °C for 4 h under nitrogen. The mixture was quenched with water and extracted with EtOAc. The combined organic phases are washed with brine and dried over MgSO<sub>4</sub>. The filtrate was concentrated in vacuo and the residue was purified by flash column chromatography to afford compound **1r**.

### Preparation of substrates **2**

The compound **2b** and **2d** – **2k** according to previously described methods.<sup>[6]</sup>

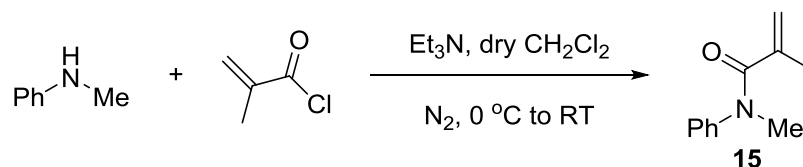


The hydrazine hydrate (80%, 30 mmol) was added dropwise into the solution of sulfonyl chloride (10 mmol) in THF (50 mL) under air at 0 °C. Subsequently, the mixture was further stirred at 0 °C for 5 minutes. After the completion of the reaction, the residue was extracted with dichloromethane, and the combined organic layer was washed with water, and brine, and dried over MgSO<sub>4</sub>. Concentration in vacuum followed by silicael column purification with petroleum ether/ethyl acetate eluent gave the

desired products **2b**, **2d** - **2k**.

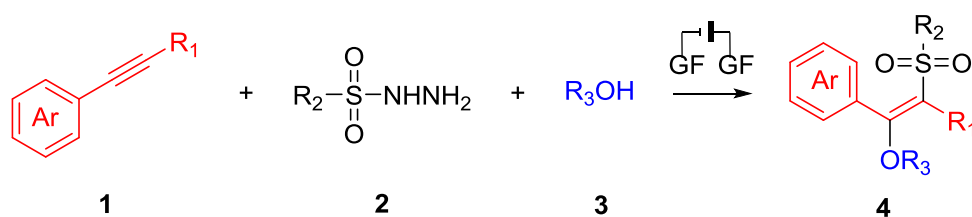
### Preparation of substrates **15**

The compound **15** according to previously described methods.<sup>[7]</sup>



Into a 250 mL Schlenk flask equipped with a magnetic stir-bar was added solution of *N*-methylaniline (1 equiv) in dry DCM (60 mL) and triethylamine (2 equiv). The mixture was stirred at 0 °C, and methacryloyl chloride (1.5 equiv) was added under nitrogen atmosphere. The resulting solution was allowed to warm up to room temperature and stirred for 6 hours, followed by the addition of saturated sodium bicarbonate solution (150 mL) to quench excess acyl chloride. The mixture was settled in a separation funnel, and the organic layer was extracted, and extracted with dichloromethane, and dried over MgSO<sub>4</sub>. The solvent was removed under reduced pressure and the crude product was purified by column chromatography gave the desired product **15**.

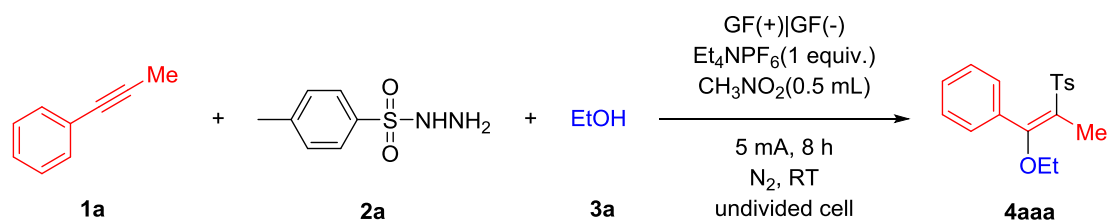
### General procedure for the synthesis of compounds **4**



In a undivided Schlenk flask (10 mL) equipped with a stir bar, sulfonyl hydrazides **2** (0.6 mmol, 3 equiv.), and Et<sub>4</sub>NPF<sub>6</sub> (0.2 mmol) were combined and added. The flask was equipped with a rubber stopper, a graphite felt anode (1 cm x 1 cm x 0.5 cm) and a graphite felt cathode (1 cm x 1 cm x 0.5 cm) and then flushed with nitrogen. Then alcohol **3** (4.5 mL), CH<sub>3</sub>NO<sub>2</sub> (0.5 mL) and alkyne **1** (0.2 mmol, 1 equiv.) were injected respectively into the flask via syringes. The reaction mixture was stirred and electrolyzed at a constant current of 5 mA at RT for 8 h. When the reaction was finished, the residue was chromatographed through silica gel eluting with petroleum ether

/EtOAc to give the product **4**.

## Optimization of reaction conditions

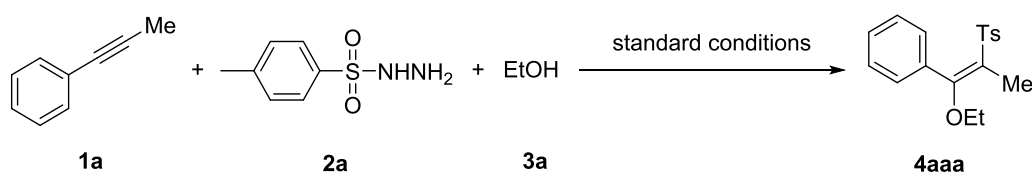


Entry	Variation from the standard conditions	Yield (%) <sup>b</sup>
1	none	78
2	3 mA, 13 h	71
3	10 mA, 4 h	68
4	Nickel foam cathode <sup>c</sup>	59
5	Pt plate cathode <sup>d</sup>	53
6	<sup>n</sup> Bu <sub>4</sub> NPF <sub>6</sub> instead of Et <sub>4</sub> NPF <sub>6</sub>	42
7	<sup>n</sup> Bu <sub>4</sub> NBF <sub>4</sub> instead of Et <sub>4</sub> NPF <sub>6</sub>	45
8	LiClO <sub>4</sub> instead of Et <sub>4</sub> NPF <sub>6</sub>	29
9	Me <sub>4</sub> NPF <sub>6</sub> instead of Et <sub>4</sub> NPF <sub>6</sub>	69
10	MeCN instead of CH <sub>3</sub> NO <sub>2</sub>	60
11	DCM instead of CH <sub>3</sub> NO <sub>2</sub>	trace
12	EA instead of CH <sub>3</sub> NO <sub>2</sub>	n.d.
13	DMF instead of CH <sub>3</sub> NO <sub>2</sub>	n.d.
14	THF instead of CH <sub>3</sub> NO <sub>2</sub>	trace
15	DMSO instead of CH <sub>3</sub> NO <sub>2</sub>	32
16	H <sub>2</sub> O instead of CH <sub>3</sub> NO <sub>2</sub>	42
17	1,4-dioxane instead of CH <sub>3</sub> NO <sub>2</sub>	25
18	add 10% Cp <sub>2</sub> Fe	71
19	add 10% TEMPO	55
20	50 °C	77
21	60 °C	73
22	air instead of N <sub>2</sub>	30

23	no electric current	n.r.
24	divided cell	5

<sup>a</sup>Standard conditions: **1a** (0.2mmol), **2a** (0.6 mmol), **3a** (4.5 mL), Et<sub>4</sub>NPF<sub>6</sub> (0.2 mmol), CH<sub>3</sub>NO<sub>2</sub> (0.5 mL), graphite felt anode (10 mm\*10mm\*5mm), graphite felt cathode (10 mm\*10mm\*5mm), constant current=5 mA, RT, 8 h, undivided cell (7.46 F, faradaic efficiency: 42%). <sup>b</sup>Isolated yield. <sup>c</sup>Nickel foam (10 mm\*10 mm\*1 mm). <sup>d</sup>Pt plate (10 mm\*10 mm\*0.1 mm). n.d. = not detected. n.r. = not reaction.

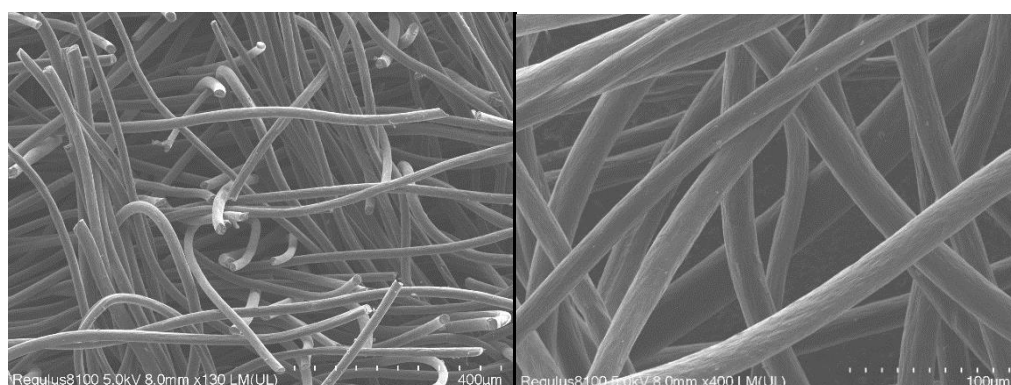
### The effect of anode materials



Entry	Variation from the standard conditions	Yield (%) <sup>b</sup>
1	Pt plate anode <sup>c</sup>	16
2	Ni foam anode <sup>d</sup>	27
3	Glassy carbon anode <sup>e</sup>	7
4	Carbon paper anode <sup>f</sup>	35
5	Carbon cloth anode <sup>g</sup>	42
6	Carbon felt anode <sup>h</sup>	78

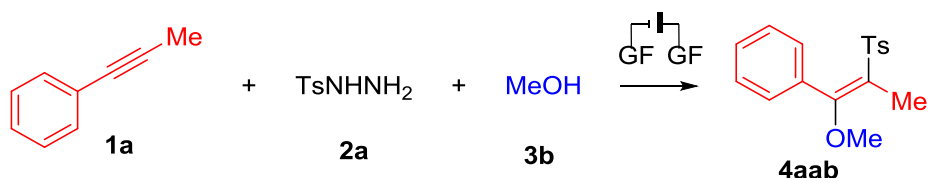
<sup>a</sup>Standard conditions: **1a** (0.2mmol), **2a** (0.6 mmol), **3a** (4.5 mL), Et<sub>4</sub>NPF<sub>6</sub> (0.2 mmol), CH<sub>3</sub>NO<sub>2</sub> (0.5 mL), graphite felt cathode (10 mm\*10mm\*5mm), constant current=5 mA, RT, 8 h, undivided cell. <sup>b</sup>Isolated yield. <sup>c</sup>Pt plate (10 mm\*10 mm\*0.1 mm). <sup>d</sup>Nickel foam (10 mm\*10 mm\*1 mm). <sup>e</sup>Glassy carbon (10 mm\*10 mm\*1mm). <sup>f</sup>Carbon paper (10 mm\*10 mm\*0.1 mm). <sup>g</sup>Carbon cloth (10 mm\*10 mm\*1mm). <sup>h</sup>Graphite felt anode (10 mm\*10mm\*5mm).

### SEM image of graphite felts:



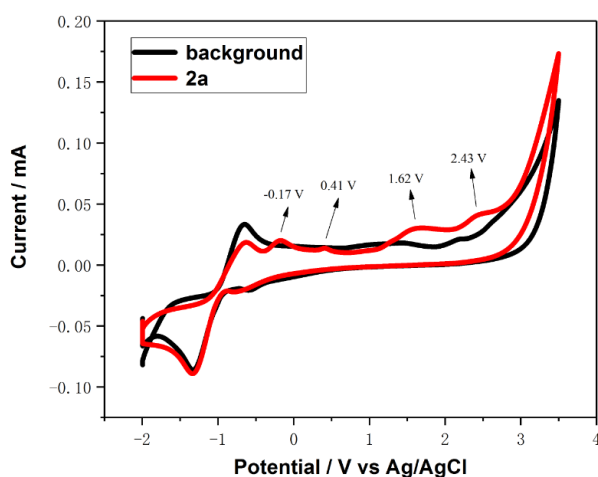


## Gram-scale reaction



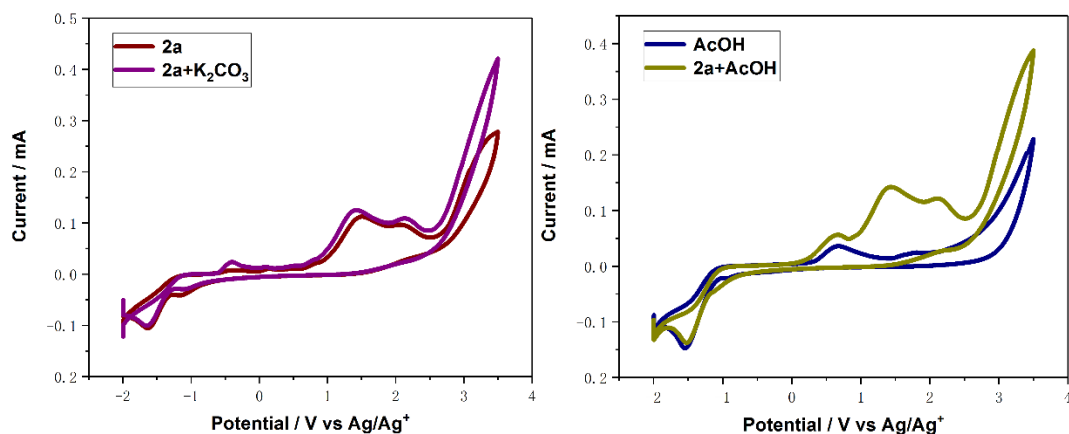
In a undivided Schlenk flask (250 mL) equipped with a stir bar, sulfonamide **2a** (15 mmol, 3 equiv.), and Et<sub>4</sub>NPF<sub>6</sub> (5 mmol) were combined and added. The flask was equipped with a rubber stopper, a graphite felt anode (1 cm x 5 cm x 1.5 cm) and a graphite felt cathode (1 cm x 5 cm x 1.5 cm) and then flushed with nitrogen. Then alcohol **3b** (112.5 mL), CH<sub>3</sub>NO<sub>2</sub> (12.5 mL) and alkyne **1a** (5 mmol, 1 equiv.) were injected respectively into the flask via syringes. The reaction mixture was stirred and electrolyzed at a constant voltage of 3.5 V at RT for 49 h. When the reaction was finished, the residue was chromatographed through silica gel eluting with petroleum ether /EtOAc to give the product **4aab** (1.41 g, 93%).

## Cyclic voltammetry study



**General procedure for cyclic voltammetry (CV):** Cyclic voltammograms of **2a** (0.1 mmol) were performed in a three-electrode cell at room temperature. The working electrode was a steady glassy carbon, the counter electrode was a platinum wire, and the reference was an Ag/AgCl electrode submerged in saturated aqueous KCl solution. A solvent (10 mL MeCN) containing Et<sub>4</sub>NPF<sub>6</sub> (0.1 mmol) were poured into the electrochemical cell in cyclic voltammetry experiments. The scan rate was 100 mV/s,

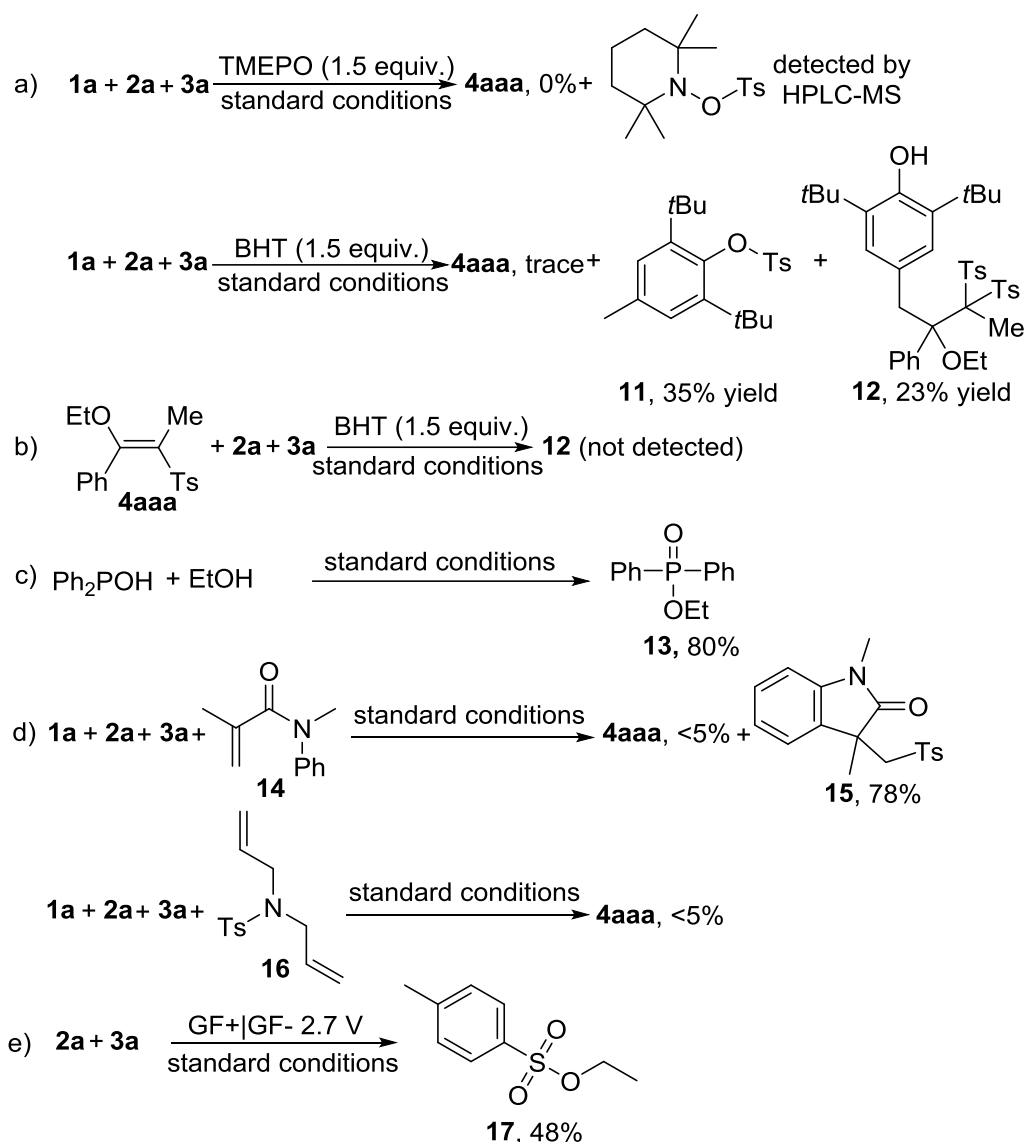
ranging from -2 V to 3.5 V.



**General procedure for cyclic voltammetry (CV):** Cyclic voltammograms of **1a** (0.2 mmol), and **2a** (0.1 mmol) were performed in a three-electrode cell at room temperature. The working electrode was a steady glassy carbon, the counter electrode was a platinum wire, and the reference was an Ag/Ag<sup>+</sup> electrode submerged in solution of 10 mM AgNO<sub>3</sub> and 10 mM Et<sub>4</sub>NPF<sub>6</sub> in CH<sub>3</sub>CN. A solvent (10 mL CH<sub>3</sub>NO<sub>2</sub>) containing Et<sub>4</sub>NPF<sub>6</sub> (0.1 mmol) were poured into the electrochemical cell in cyclic voltammetry experiments. The scan rate was 100 mV/s, ranging from 0 to 3.5 V. **1a** (0.02 M), **2a** (0.01 M), K<sub>2</sub>CO<sub>3</sub> (0.01 M), AcOH (0.01 M).

### Control experiments

1.

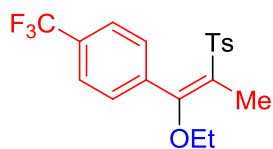
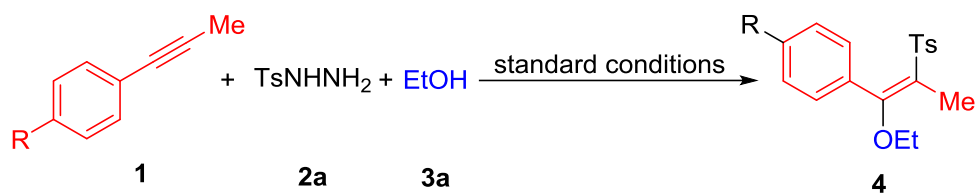


- a) In a undivided Schlenk flask (10 mL) equipped with a stir bar, sulfonyl hydrazides **2a** (0.6 mmol, 3 equiv.), TEMPO (0.3 mmol, 1.5 equiv.) or BHT (0.3 mmol, 1.5 equiv.), and  $\text{Et}_4\text{NPF}_6$  (0.2 mmol) were combined and added. The flask was equipped with a rubber stopper, a graphite felt anode (1 cm x 1 cm x 0.5 cm) and a graphite felt cathode (1 cm x 1 cm x 0.5 cm) and then flushed with nitrogen. Then alcohol **3a** (4.5 mL),  $\text{CH}_3\text{NO}_2$  (0.5 mL) and alkyne **1a** (0.2 mmol, 1 equiv.) were injected respectively into the flask via syringes. The reaction mixture was stirred and electrolyzed at a constant current of 5 mA at RT for 8 h.
- b) In a undivided Schlenk flask (10 mL) equipped with a stir bar, compound **4aaa** (0.2 mmol), sulfonyl hydrazides **2a** (0.6 mmol, 3 equiv.), and  $\text{Et}_4\text{NPF}_6$  (0.2 mmol) were combined and added. The flask was equipped with a rubber stopper, a graphite felt

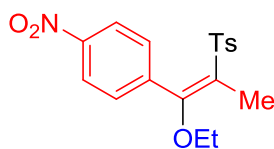
anode (1 cm x 1 cm x 0.5 cm) and a graphite felt cathode (1 cm x 1 cm x 0.5 cm) and then flushed with nitrogen. Then alcohol **3a** (4.5 mL), and CH<sub>3</sub>NO<sub>2</sub> (0.5 mL) were injected respectively into the flask via syringes. The reaction mixture was stirred and electrolyzed at a constant current of 5 mA at RT for 8 h.

- c) In a undivided Schlenk flask (10 mL) equipped with a stir bar, diphenylphosphine oxide (0.2 mmol), and Et<sub>4</sub>NPF<sub>6</sub> (0.2 mmol) were combined and added. The flask was equipped with a rubber stopper, a graphite felt anode (1 cm x 1 cm x 0.5 cm) and a graphite felt cathode (1 cm x 1 cm x 0.5 cm) and then flushed with nitrogen. Then alcohol (4.5 mL), and CH<sub>3</sub>NO<sub>2</sub> (0.5 mL) were injected respectively into the flask via syringes. The reaction mixture was stirred and electrolyzed at a constant current of 5 mA at RT for 8 h.
- d) In a undivided Schlenk flask (10 mL) equipped with a stir bar, sulfonyl hydrazides **2a** (0.6 mmol, 3 equiv.), **14** (0.3 mmol, 1.5 equiv.) or **16** (0.3 mmol, 1.5 equiv.), and Et<sub>4</sub>NPF<sub>6</sub> (0.2 mmol) were combined and added. The flask was equipped with a rubber stopper, a graphite felt anode (1 cm x 1 cm x 0.5 cm) and a graphite felt cathode (1 cm x 1 cm x 0.5 cm) and then flushed with nitrogen. Then alcohol **3a** (4.5 mL), CH<sub>3</sub>NO<sub>2</sub> (0.5 mL) and alkyne **1a** (0.2 mmol, 1 equiv.) were injected respectively into the flask via syringes. The reaction mixture was stirred and electrolyzed at a constant current of 5 mA at RT for 8 h.
- e) In a undivided Schlenk flask (10 mL) equipped with a stir bar, sulfonyl hydrazides **2a** (0.2 mmol.), and Et<sub>4</sub>NPF<sub>6</sub> (0.2 mmol) were combined and added. The flask was equipped with a rubber stopper, a graphite felt anode (1 cm x 1 cm x 0.5 cm) and a graphite felt cathode (1 cm x 1 cm x 0.5 cm) and then flushed with nitrogen. Then alcohol **3a** (4.5 mL), and CH<sub>3</sub>NO<sub>2</sub> (0.5 mL) were injected respectively into the flask via syringes. The reaction mixture was stirred and electrolyzed at a constant current of 2.7 V at RT for 8 h.

2.



$\mathbf{4\text{saa}}$ , <5%



$\mathbf{4\text{taa}}$ , <5%

## Experiments of divided cell

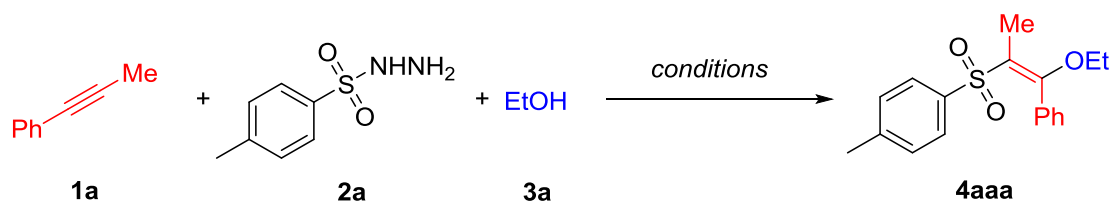


**A, C, E cell:** anode; **B, D, F cell:** cathode. Separation of anode and cathode cell using hydrogen proton exchange membranes.

**A, B, C, F cell:** In this cell equipped with a stir bar, sulfonyl hydrazides **2a** (0.3 mmol, 3 equiv.), and  $\text{Et}_4\text{NPF}_6$  (0.1 mmol) were combined and added. The cell was equipped with a rubber stopper, a graphite felt anode (1 cm x 1 cm x 0.5 cm) and then flushed with nitrogen. Then alcohol **3a** (2.25 mL),  $\text{CH}_3\text{NO}_2$  (0.25 mL) and alkyne **1a** (0.1 mmol, 1 equiv.) were injected respectively into the cell via syringes. The reaction mixture was stirred and electrolyzed at a constant current of 5 mA at RT for 8 h.

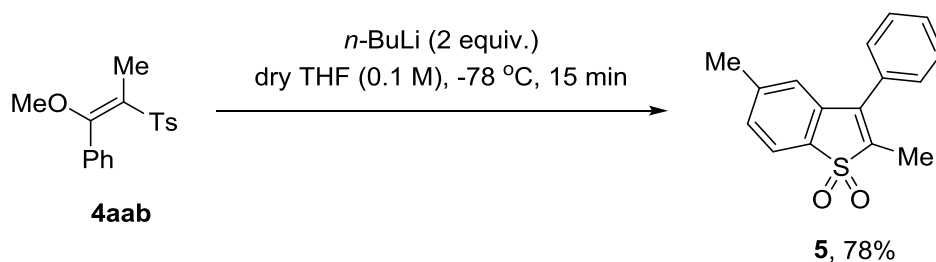
**D, E cell:** In this cell equipped with a stir bar,  $\text{Et}_4\text{NPF}_6$  (0.1 mmol) were combined and added. The cell was equipped with a rubber stopper, a graphite felt cathode (1 cm x 1 cm x 0.5 cm) and then flushed with nitrogen. Then alcohol (2.25 mL),  $\text{CH}_3\text{NO}_2$  (0.25 mL) were injected respectively into the cell via syringes. The reaction mixture was stirred and electrolyzed at a constant current of 5 mA at RT for 8 h.

## The sulfonylation of alkynes promoted by external oxidants

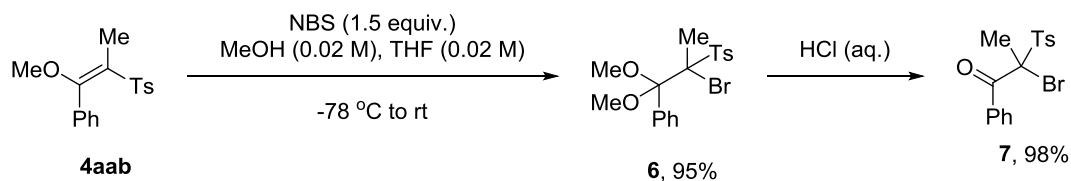


Entry	Conditions	Yield
1	TBAI (20 mol%), TBHP (2.0 eq.), CH <sub>3</sub> NO <sub>2</sub> , 80 °C	<5%
2	I <sub>2</sub> (50 mol%), TBHP (2.0 eq.), CH <sub>3</sub> NO <sub>2</sub> , 80 °C	<5%
3	FeCl <sub>3</sub> (10 mol%), air, CH <sub>3</sub> NO <sub>2</sub> , 80 °C	trace
4	CAN (2.0 equiv.), air, CH <sub>3</sub> NO <sub>2</sub> , RT	<5%
5	PCC (2.0 equiv.), air, CH <sub>3</sub> NO <sub>2</sub> , RT	N.R.
6	KMnO <sub>4</sub> (10 mol%), air, CH <sub>3</sub> NO <sub>2</sub> , RT	N.R.

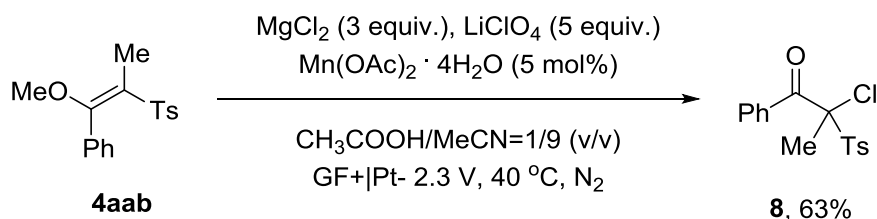
## Transformation of product 4aab



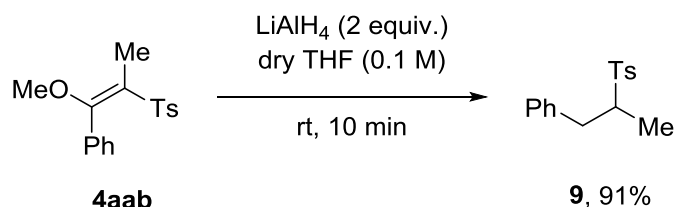
A solution of **4aab** (0.2 mmol) in dry THF (1 mL) was added to a cold solution (-78 °C) of *n*-BuLi (0.4 mmol, 2.5 M in hexanes) in THF (1 mL), under an argon atmosphere. After 10 min, the reaction mixture was quenched with a sat aq solution of NH<sub>4</sub>Cl (1 mL) and diluted with EtOAc (1 mL). The layers were separated and the aqueous phase was extracted with EtOAc. The combined organic layers were washed with brine, dried over MgSO<sub>4</sub>, filtered and concentrated. The residue was chromatographed through silica gel eluting with petroleum ether /EtOAc to give the product **5**.



To a 50 mL Schlenk flask, under  $\text{N}_2$ , was added **4aab** (0.2 mmol), dry THF (10 mL), and dry MeOH (10 mL). After the mixture cooled to  $-78\text{ }^\circ\text{C}$ , add the NBS (0.24 mmol) to the flask. Then the reaction was stirred overnight at RT and checked by TLC. The reaction is filtered over celite, washing with dichloromethane. The solvent was removed and the residue was purified by flash column chromatography on silica gel (petroleum ether: EtOAc = 20:1) to pure product **6**. **6** is further transformed to **7** under the action of HCl (aq.).

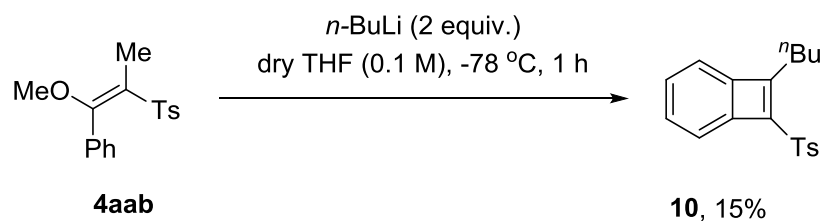


In a undivided Schlenk flask (10 mL) equipped with a stir bar, **4aab** (0.2 mmol),  $\text{MgCl}_2$  (3 equiv.),  $\text{LiClO}_4$  (5 equiv.), and  $\text{Mn(OAc)}_2 \cdot 4\text{H}_2\text{O}$  (5 mol%) were combined and added. The flask was equipped with a rubber stopper, a graphite felt anode (1 cm x 1 cm x 0.5 cm) and a platinum foil cathode (1 cm x 1 cm x 0.01 cm) and then flushed with nitrogen. Then AcOH (0.5 mL), and MeCN (4.5 mL) were injected respectively into the flask via syringes. Electrolysis was initiated at a cell potential of 2.3 V at  $40\text{ }^\circ\text{C}$  (oil bath temperature). When the reaction was finished, the residue was chromatographed through silica gel eluting with petroleum ether /EtOAc to give the product **8**.



To a 10 mL schlenk tube equipped with a magnetic stir bar was charged with **4aab** (0.2 mmol), and  $\text{LiAlH}_4$  (0.4 mmol) in 2 mL of THF. Then the mixture was stirred at RT for 10 min. The reaction mixture was quenched with  $\text{H}_2\text{SO}_4$  (1 M in  $\text{H}_2\text{O}$ ) and diluted with

EtOAc. The layers were separated and the aqueous phase was extracted with EtOAc. The combined organic layers were washed with brine, dried over MgSO<sub>4</sub>, filtered and concentrated. The residue was chromatographed through silica gel eluting with petroleum ether /EtOAc to give the product **9**.



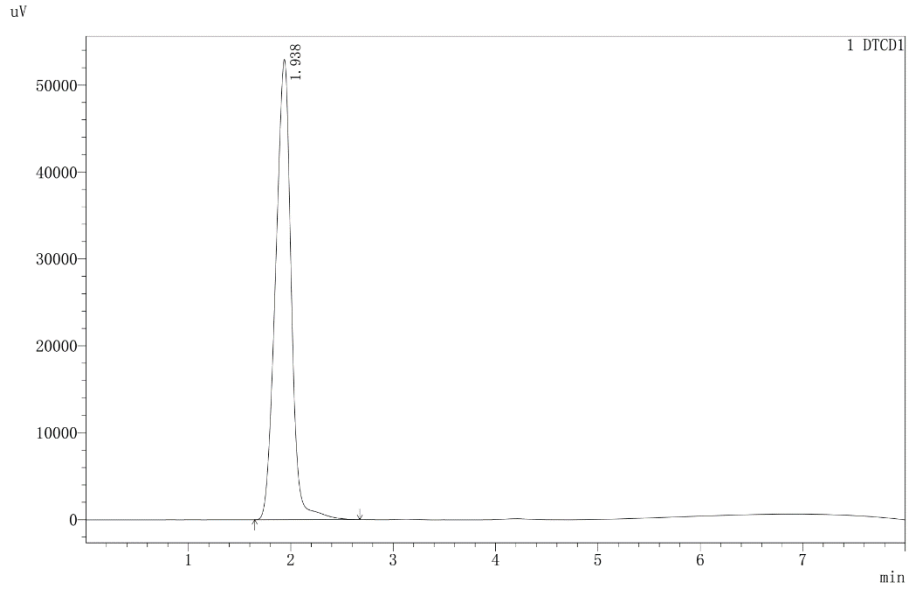
A solution of **4aab** (0.2 mmol) in dry THF (1 mL) was added to a cold solution (-78 °C) of *n*-BuLi (0.4 mmol, 2.5 M in hexanes) in THF (1 mL), under an argon atmosphere. After 1 h, the reaction mixture was quenched with a sat aq solution of NH<sub>4</sub>Cl (1 mL) and diluted with EtOAc (1 mL). The layers were separated and the aqueous phase was extracted with EtOAc. The combined organic layers were washed with brine, dried over MgSO<sub>4</sub>, filtered and concentrated. The residue was chromatographed through silica gel eluting with petroleum ether to give the product **10**.

## Detection of H<sub>2</sub> and N<sub>2</sub> by GC Analysis

Standard H<sub>2</sub> for reference:

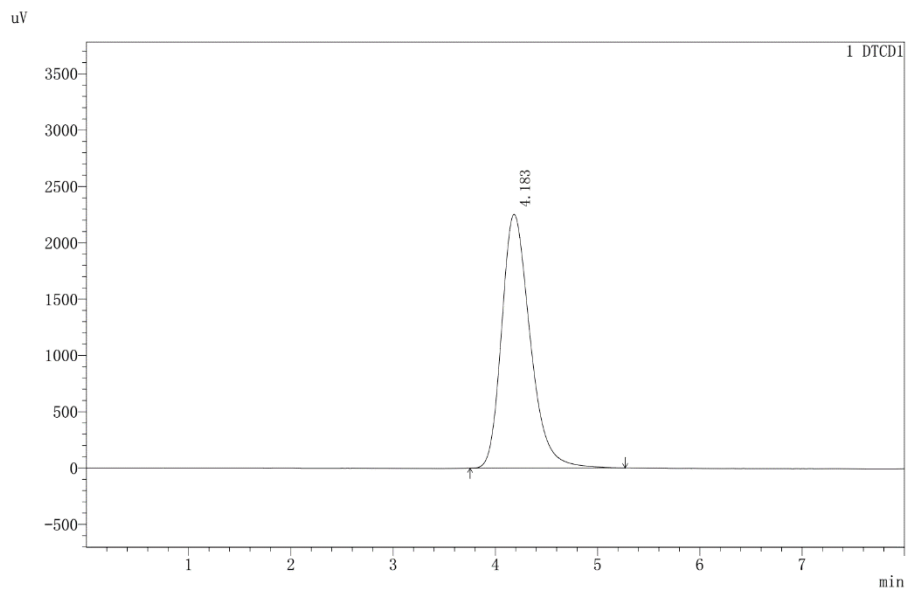


==== Shimadzu LabSolutions 分析报告 ====



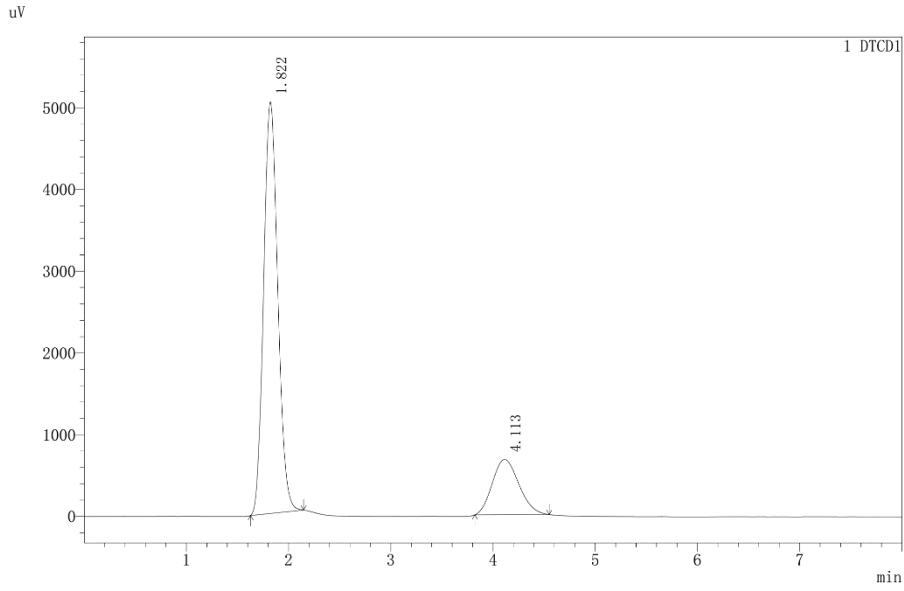
**Standard N<sub>2</sub> for reference:**

==== Shimadzu LabSolutions 分析报告 ====



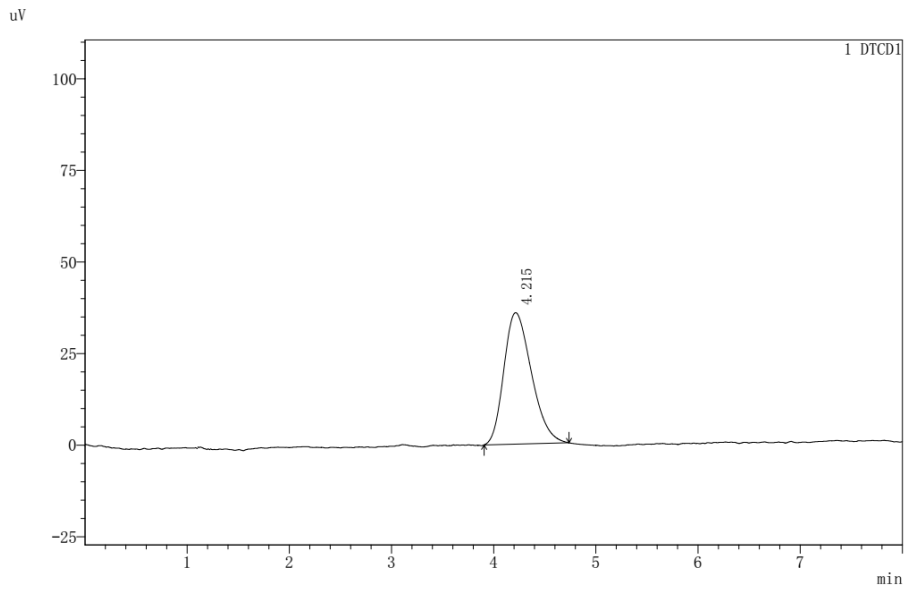
**Collected gas from gram-scale experiment :**

==== Shimadzu LabSolutions 分析报告 ====



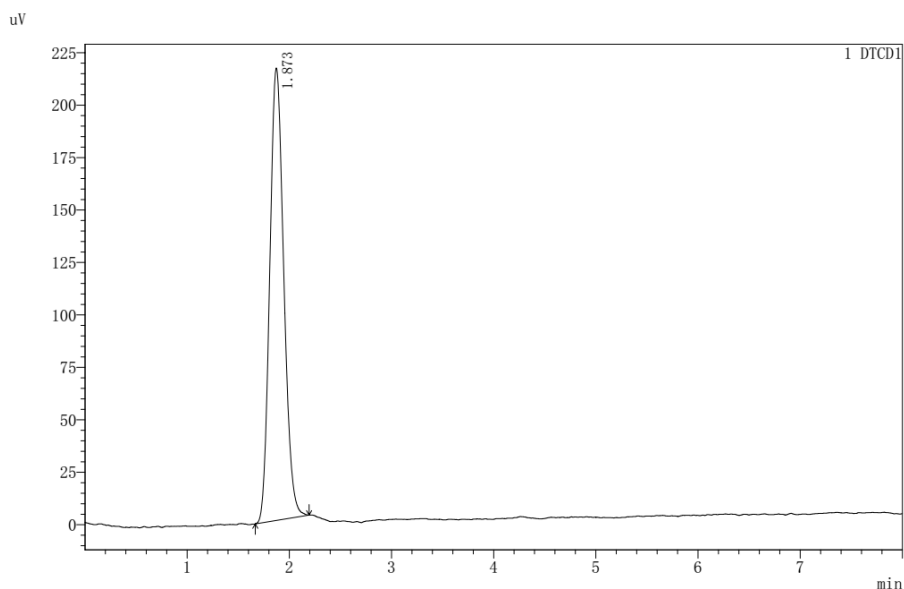
**N<sub>2</sub> from anode:**

==== Shimadzu LabSolutions 分析报告 ====



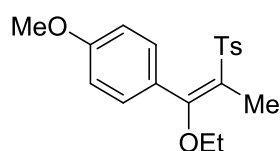
**H<sub>2</sub> from cathode:**

## ==== Shimadzu LabSolutions 分析报告 ====

**Characterization of products**

**(E)-1-((1-ethoxy-1-(4-methoxyphenyl)prop-1-en-2-yl)sulfonyl)-4-methylbenzene**

**(4baa)**



**4baa**

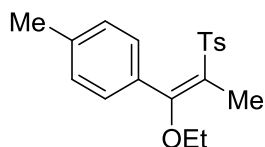
**4baa** was obtained in 80% (55.4 mg) as a colorless oil after column chromatography (eluent: petroleum ether/ethyl acetate = 20/1 v/v).

**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):** δ 7.40 (d, J = 8.3 Hz, 2H), 7.17 – 7.07 (m, 4H), 6.89 – 6.81 (m, 2H), 3.84 (s, 3H), 3.50 (q, J = 7.0, 7.0, 7.0 Hz, 2H), 2.37 (s, 3H), 2.09 (s, 3H), 1.14 (t, J = 7.0, 7.0 Hz, 3H).

**<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>):** δ = 162.86, 160.50, 142.89, 139.43, 131.31, 129.08, 127.23, 124.28, 118.79, 113.19, 77.34, 77.08, 76.83, 64.95, 55.25, 21.47, 15.18, 12.87.

**HRMS (ESI-TOF, [M + Na]<sup>+</sup>):** For C<sub>19</sub>H<sub>22</sub>NaO<sub>4</sub>S, 369.1136, Found: 369.1136.

**(E)-1-((1-ethoxy-1-(p-tolyl)prop-1-en-2-yl)sulfonyl)-4-methylbenzene (4caa)**



**4caa**

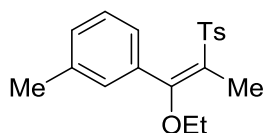
**4caa** was obtained in 75% (49.6 mg) as a colorless oil after column chromatography (eluent: petroleum ether/ethyl acetate = 20/1 v/v).

**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):** δ 7.42 (d, *J* = 8.4 Hz, 2H), 7.18 – 7.13 (m, 4H), 7.10 (d, *J* = 8.1 Hz, 2H), 3.49 (q, *J* = 7.0, 7.0, 7.1 Hz, 2H), 2.39 (s, 3H), 2.38 (s, 3H), 2.07 (s, 3H), 1.13 (t, *J* = 7.0, 7.0 Hz, 3H).

**<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>):** δ = 163.02, 142.92, 139.53, 139.35, 129.67, 129.30, 129.09, 128.49, 127.34, 118.41, 77.28, 77.03, 76.78, 64.97, 21.49, 15.19, 12.81.

**HRMS (ESI-TOF, [M + Na]<sup>+</sup>):** For C<sub>19</sub>H<sub>22</sub>NaO<sub>3</sub>S, 353.1187, Found: 353.1187.

**(*E*)-1-(1-ethoxy-2-tosylprop-1-en-1-yl)-3-methylbenzene (4daa)**



**4daa**

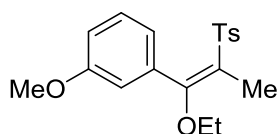
**4daa** was obtained in 36% (29.7 mg) as a colorless oil after column chromatography (eluent: petroleum ether/ethyl acetate = 20/1 v/v).

**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):** δ 7.38 (d, *J* = 8.3 Hz, 2H), 7.27 – 7.17 (m, 2H), 7.14 (d, *J* = 8.0 Hz, 2H), 7.02 (d, *J* = 7.4 Hz, 1H), 6.88 (s, 1H), 3.48 (q, *J* = 7.0, 7.0, 7.0 Hz, 2H), 2.37 (s, 3H), 2.31 (s, 3H), 2.11 (s, 3H), 1.14 (t, *J* = 7.0, 7.0 Hz, 3H).

**<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>):** δ = 163.05, 142.83, 139.47, 137.37, 132.07, 130.20, 130.17, 129.04, 127.67, 127.31, 127.06, 118.69, 77.29, 77.03, 76.78, 65.04, 21.46, 21.34, 15.19, 12.70.

**HRMS (ESI-TOF, [M + H]<sup>+</sup>):** For C<sub>19</sub>H<sub>23</sub>O<sub>3</sub>S, 331.1368, Found: 331.1372.

**(*E*)-1-(1-ethoxy-2-tosylprop-1-en-1-yl)-3-methoxybenzene (4eaa)**



**4eaa**

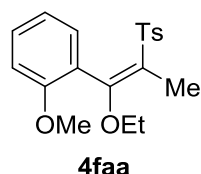
**4eaa** was obtained in 50% (34.6 mg) as a colorless oil after column chromatography (eluent: petroleum ether/ethyl acetate = 20/1 v/v).

**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):** δ 7.40 (d, *J* = 8.3 Hz, 2H), 7.29 – 7.23 (m, 1H), 7.14 (d, *J* = 8.0 Hz, 2H), 6.93 (dd, *J* = 2.6, 8.3 Hz, 1H), 6.81 (d, *J* = 7.7 Hz, 1H), 6.63 (dd, *J* = 1.5, 2.7 Hz, 1H), 3.76 (s, 3H), 3.50 (q, *J* = 7.0, 7.0, 7.0 Hz, 2H), 2.37 (s, 3H), 2.11 (s, 3H), 1.15 (t, *J* = 7.0, 7.0 Hz, 3H).

**<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>):** δ = 162.42, 158.96, 142.92, 139.32, 133.35, 129.08, 128.87, 127.34, 122.46, 118.97, 115.40, 114.87, 77.29, 77.04, 76.78, 65.07, 55.17, 21.45, 15.22, 12.68.

**HRMS (ESI-TOF, [M + H]<sup>+</sup>):** For C<sub>19</sub>H<sub>23</sub>O<sub>4</sub>S, 347.1317, Found: 347.1320.

**(*E*)-1-(1-ethoxy-2-tosylprop-1-en-1-yl)-2-methoxybenzene (4faa)**



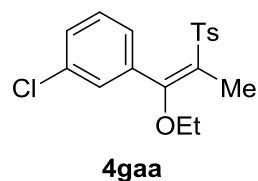
**4faa** was obtained in 91% (63.1 mg) as a colorless oil after column chromatography (eluent: petroleum ether/ethyl acetate = 20/1 v/v).

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 7.41 (d, *J* = 8.3 Hz, 2H), 7.37 (ddd, *J* = 1.8, 7.4, 8.3 Hz, 1H), 7.20 (dd, *J* = 1.8, 7.5 Hz, 1H), 7.12 (d, *J* = 8.0 Hz, 2H), 6.98 (td, *J* = 1.0, 7.4, 7.4 Hz, 1H), 6.76 (d, *J* = 8.3 Hz, 1H), 3.65 (s, 3H), 3.61 – 3.42 (m, 2H), 2.36 (s, 3H), 2.11 (s, 3H), 1.15 (t, *J* = 7.1, 7.1 Hz, 3H).

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>):** δ = 160.61, 156.76, 142.56, 139.45, 132.33, 131.33, 128.85, 127.30, 120.91, 120.00, 117.31, 110.14, 77.40, 77.08, 76.76, 64.27, 55.10, 21.47, 15.14, 12.47.

**HRMS (ESI-TOF, [M + Na]<sup>+</sup>):** For C<sub>19</sub>H<sub>22</sub>NaO<sub>4</sub>S, 369.1136, Found: 369.1141.

**(*E*)-1-chloro-3-(1-ethoxy-2-tosylprop-1-en-1-yl)benzene (4gaa)**



**4gaa** was obtained in 36% (25.3 mg) as a colorless oil after column chromatography

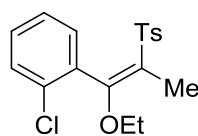
(eluent: petroleum ether/ethyl acetate = 20/1 v/v).

**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):** δ 7.39 (d, *J* = 8.3 Hz, 2H), 7.32 (t, *J* = 7.8, 7.8 Hz, 1H), 7.18 (dd, *J* = 4.5, 7.7 Hz, 4H), 7.03 (t, *J* = 1.9, 1.9 Hz, 1H), 3.49 (q, *J* = 7.0, 7.0, 7.0 Hz, 2H), 2.39 (s, 3H), 2.11 (s, 3H), 1.16 (t, *J* = 7.0, 7.0 Hz, 3H).

**<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>):** δ = 160.82, 143.37, 139.01, 136.28, 133.98, 129.65, 129.27, 129.14, 128.48, 127.88, 127.28, 120.19, 77.28, 77.03, 76.77, 65.37, 21.51, 15.16, 12.72.

**HRMS (ESI-TOF, [M + Na]<sup>+</sup>):** For C<sub>18</sub>H<sub>19</sub>ClNaO<sub>3</sub>S, 373.0641, Found: 373.0642.

**(*E*)-1-chloro-2-(1-ethoxy-2-tosylprop-1-en-1-yl)benzene (4haa)**



**4haa**

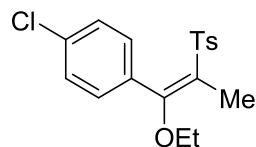
**4haa** was obtained in 45% (31.6 mg) as a colorless oil after column chromatography (eluent: petroleum ether/ethyl acetate = 20/1 v/v).

**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):** δ 7.55 (d, *J* = 8.3 Hz, 2H), 7.42 – 7.30 (m, 4H), 7.20 (d, *J* = 8.0 Hz, 2H), 3.53 (ddq, *J* = 7.0, 7.0, 7.0, 9.7, 69.1 Hz, 2H), 2.39 (s, 3H), 2.05 (s, 3H), 1.19 (t, *J* = 7.0, 7.0 Hz, 3H).

**<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>):** δ = 159.32, 143.27, 138.59, 133.35, 132.42, 131.69, 130.94, 129.25, 127.61, 126.30, 117.72, 77.29, 77.03, 76.78, 64.63, 21.53, 15.18, 12.49.

**HRMS (ESI-TOF, [M + H]<sup>+</sup>):** For C<sub>18</sub>H<sub>20</sub>ClO<sub>3</sub>S, 351.0822, Found: 351.0825.

**(*E*)-1-chloro-4-(1-ethoxy-2-tosylprop-1-en-1-yl)benzene (4iaa)**



**4iaa**

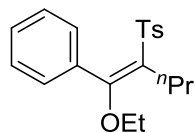
**4iaa** was obtained in 69% (48.4 mg) as a colorless oil after column chromatography (eluent: petroleum ether/ethyl acetate = 20/1 v/v).

**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):** δ 7.44 – 7.39 (m, 2H), 7.37 – 7.30 (m, 2H), 7.20 – 7.13 (m, 4H), 3.48 (q, *J* = 6.9, 7.0, 7.0 Hz, 2H), 2.38 (s, 3H), 2.08 (s, 3H), 1.15 (t, *J* = 7.0, 7.0 Hz, 3H).

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>):**  $\delta$  = 161.30, 143.32, 138.98, 135.75, 131.16, 130.74, 129.27, 128.16, 127.32, 119.70, 77.37, 77.05, 76.74, 65.27, 21.53, 15.18, 12.84.

**HRMS (ESI-TOF, [M + H]<sup>+</sup>):** For C<sub>18</sub>H<sub>20</sub>ClO<sub>3</sub>S, 351.0822, Found: 351.0823.

**(E)-1-((1-ethoxy-1-phenylpent-1-en-2-yl)sulfonyl)-4-methylbenzene (4jaa)**



**4jaa**

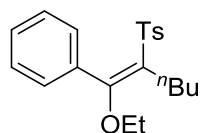
**4jaa** was obtained in 74% (51.0 mg) as a colorless oil after column chromatography (eluent: petroleum ether/ethyl acetate = 20/1 v/v).

**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):**  $\delta$  7.39 – 7.33 (m, 1H), 7.32 – 7.24 (m, 4H), 7.12 (d,  $J$  = 7.5 Hz, 2H), 7.07 (d,  $J$  = 8.0 Hz, 2H), 3.44 (q,  $J$  = 7.0, 7.0, 7.0 Hz, 2H), 2.60 – 2.54 (m, 2H), 2.35 (s, 3H), 1.69 – 1.56 (m, 2H), 1.13 (t,  $J$  = 7.0, 7.0 Hz, 3H), 0.99 (t,  $J$  = 7.4, 7.4 Hz, 3H).

**<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>):**  $\delta$  = 163.66, 142.63, 139.99, 132.17, 130.01, 129.35, 128.94, 127.72, 127.23, 124.22, 77.30, 77.05, 76.80, 65.06, 29.21, 22.69, 21.45, 15.15, 14.07.

**HRMS (ESI-TOF, [M + H]<sup>+</sup>):** For C<sub>20</sub>H<sub>24</sub>O<sub>3</sub>S, 345.1524, Found: 345.1525.

**(E)-1-((1-ethoxy-1-phenylhex-1-en-2-yl)sulfonyl)-4-methylbenzene (4kaa)**



**4kaa**

**4kaa** was obtained in 71% (50.9 mg) as a colorless oil after column chromatography (eluent: petroleum ether/ethyl acetate = 20/1 v/v).

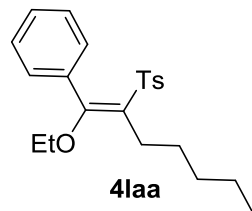
**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):**  $\delta$  7.36 (t,  $J$  = 7.4, 7.4 Hz, 1H), 7.28 (td,  $J$  = 3.7, 8.7, 9.3 Hz, 4H), 7.12 (d,  $J$  = 7.0 Hz, 2H), 7.07 (d,  $J$  = 7.9 Hz, 2H), 3.45 (q,  $J$  = 7.0, 7.0, 7.0 Hz, 2H), 2.61 – 2.55 (m, 2H), 2.35 (s, 3H), 1.65 – 1.57 (m, 2H), 1.40 (h,  $J$  = 7.2, 7.2, 7.2, 7.3, 7.3 Hz, 2H), 1.14 (t,  $J$  = 7.0, 7.0 Hz, 3H), 0.95 (t,  $J$  = 7.4, 7.4 Hz, 3H).

**<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>):**  $\delta$  = 163.42, 142.62, 139.95, 132.18, 129.99, 129.33, 128.92, 127.71, 127.25, 124.42, 77.28, 77.02, 76.77, 65.05, 31.57, 26.97, 22.68, 21.43,

15.14, 13.88.

**HRMS (ESI-TOF, [M + H]<sup>+</sup>):** For C<sub>21</sub>H<sub>27</sub>O<sub>3</sub>S, 359.1681, Found: 359.1679.

**(E)-1-((1-ethoxy-1-phenylhept-1-en-2-yl)sulfonyl)-4-methylbenzene (4laa)**



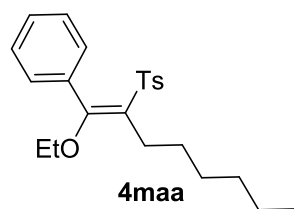
**4laa** was obtained in 71% (61.8 mg) as a colorless oil after column chromatography (eluent: petroleum ether/ethyl acetate = 20/1 v/v).

**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):** δ 7.36 (t, J = 7.3, 7.3 Hz, 1H), 7.33 – 7.24 (m, 4H), 7.15 – 7.05 (m, 4H), 3.44 (q, J = 7.0, 7.0, 7.0 Hz, 2H), 2.60 – 2.53 (m, 2H), 2.35 (s, 3H), 1.60 (t, J = 7.9, 7.9 Hz, 2H), 1.44 – 1.28 (m, 4H), 1.13 (t, J = 7.0, 7.0 Hz, 3H), 0.94 – 0.88 (m, 3H).

**<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>):** δ = 163.41, 142.64, 139.90, 132.17, 129.98, 129.34, 128.94, 127.72, 127.25, 124.35, 77.29, 77.04, 76.78, 65.06, 31.80, 29.00, 27.22, 22.37, 21.45, 15.16, 14.05.

**HRMS (ESI-TOF, [M + H]<sup>+</sup>):** For C<sub>22</sub>H<sub>29</sub>O<sub>3</sub>S, 373.1837, Found: 373.1836.

**(E)-1-((1-ethoxy-1-phenyloct-1-en-2-yl)sulfonyl)-4-methylbenzene (4maa)**



**4maa** was obtained in 87% (67.2 mg) as a colorless oil after column chromatography (eluent: petroleum ether/ethyl acetate = 20/1 v/v).

**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):** δ 7.40 – 7.33 (m, 1H), 7.33 – 7.25 (m, 4H), 7.16 – 7.10 (m, 2H), 7.08 (d, J = 8.0 Hz, 2H), 3.45 (q, J = 7.0, 7.0, 7.0 Hz, 2H), 2.60 – 2.53 (m, 2H), 2.35 (s, 3H), 1.65 – 1.56 (m, 3H), 1.40 – 1.27 (m, 5H), 1.14 (t, J = 7.0, 7.0 Hz, 3H), 0.95 – 0.88 (m, 3H).

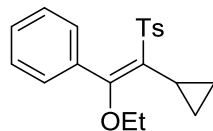
**<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>):** δ = 163.41, 142.64, 139.90, 132.17, 129.98, 129.34, 128.94, 127.72, 127.25, 124.35, 77.29, 77.04, 76.78, 65.06, 31.80, 29.00, 27.22, 22.37,



21.45, 15.16, 14.05.

**HRMS (ESI-TOF, [M + Na]<sup>+</sup>):** For C<sub>23</sub>H<sub>30</sub>NaO<sub>3</sub>S, 409.1813, Found 409.1807.

**(E)-1-((1-cyclopropyl-2-ethoxy-2-phenylvinyl)sulfonyl)-4-methylbenzene (4naa)**



**4naa**

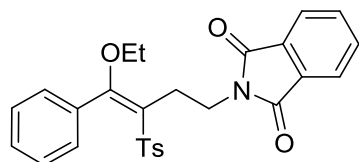
**4naa** was obtained in 49% (33.6 mg) as a colorless oil after column chromatography (eluent: petroleum ether/ethyl acetate = 20/1 v/v).

**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):** δ 7.52 – 7.46 (m, 2H), 7.43 – 7.36 (m, 1H), 7.33 (dd, *J* = 6.7, 8.4 Hz, 2H), 7.26 – 7.21 (m, 2H), 7.13 (d, *J* = 8.1 Hz, 2H), 3.54 (q, *J* = 7.0, 7.0, 7.0 Hz, 2H), 2.37 (s, 3H), 1.28 – 1.24 (m, 2H), 1.20 (t, *J* = 7.0, 7.0 Hz, 3H), 0.91 – 0.78 (m, 3H).

**<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>):** δ = 165.60, 142.75, 139.67, 132.87, 129.78, 129.68, 128.93, 127.85, 127.62, 124.85, 77.25, 77.00, 76.74, 65.65, 21.45, 15.21, 9.29, 8.22.

**HRMS (ESI-TOF, [M + Na]<sup>+</sup>):** For C<sub>20</sub>H<sub>22</sub>NaO<sub>3</sub>S, 365.1187, Found: 365.1188.

**(E)-2-(4-ethoxy-4-phenyl-3-tosylbut-3-en-1-yl)isoindoline-1,3-dione (4oaa)**



**4oaa**

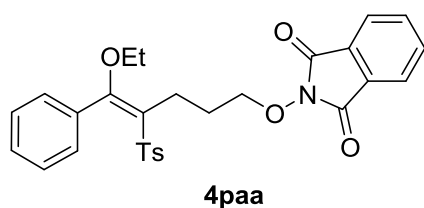
**4oaa** was obtained in 20% (19.0 mg) as a colorless oil after column chromatography (eluent: petroleum ether/ethyl acetate = 4/1 v/v).

**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):** δ 7.86 (dd, *J* = 3.0, 5.4 Hz, 2H), 7.69 (dd, *J* = 3.0, 5.4 Hz, 2H), 7.38 (dd, *J* = 7.2, 8.9 Hz, 3H), 7.31 (d, *J* = 7.7 Hz, 2H), 7.16 – 7.11 (m, 2H), 7.10 – 7.05 (m, 2H), 4.00 (t, *J* = 6.1, 6.1 Hz, 2H), 3.38 (q, *J* = 7.0, 7.0, 7.1 Hz, 2H), 2.96 (t, *J* = 6.1, 6.1 Hz, 2H), 2.31 (s, 3H), 1.04 (t, *J* = 7.0, 7.0 Hz, 3H).

**<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>):** δ = 168.34, 164.89, 142.60, 138.85, 133.40, 132.18, 129.41, 129.19, 128.77, 128.34, 127.53, 127.34, 126.98, 122.72, 119.28, 77.00, 76.75, 76.50, 65.15, 36.51, 26.03, 21.19, 14.59.

**HRMS (ESI-TOF, [M + H]<sup>+</sup>):** For C<sub>27</sub>H<sub>26</sub>NO<sub>5</sub>S, 476.1532, Found: 476.1531.

**(E)-2-((5-ethoxy-5-phenyl-4-tosylpent-4-en-1-yl)oxy)isoindoline-1,3-dione (4paa)**



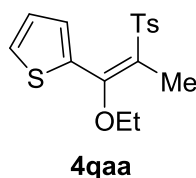
**4paa** was obtained in 75% (75.8 mg) as a colorless oil after column chromatography (eluent: petroleum ether/ethyl acetate = 4/1 v/v).

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 7.85 (dd, *J* = 3.1, 5.5 Hz, 2H), 7.75 (dd, *J* = 3.1, 5.5 Hz, 2H), 7.43 – 7.34 (m, 1H), 7.35 – 7.26 (m, 4H), 7.17 – 7.11 (m, 2H), 7.09 (d, *J* = 8.0 Hz, 2H), 4.31 (t, *J* = 6.7, 6.7 Hz, 2H), 3.49 (q, *J* = 7.0, 7.0, 7.1 Hz, 2H), 2.88 – 2.78 (m, 2H), 2.35 (s, 3H), 2.14 (dq, *J* = 6.9, 6.9, 6.9, 9.4 Hz, 2H), 1.14 (t, *J* = 7.0, 7.0 Hz, 3H).

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>):** δ = 164.44, 163.69, 142.92, 139.58, 134.48, 131.81, 129.86, 129.52, 129.10, 129.01, 127.81, 127.26, 123.49, 122.41, 78.27, 77.40, 77.09, 76.77, 65.34, 27.86, 23.64, 21.48, 15.17.

**HRMS (ESI-TOF, [M + Na]<sup>+</sup>):** For C<sub>28</sub>H<sub>27</sub>NNaO<sub>6</sub>S, 528.1457, 528.1461.

**(E)-2-(1-ethoxy-2-tosylprop-1-en-1-yl)thiophene (4qaa)**



**4qaa** was obtained in 74% (47.7 mg) as a yellow oil after column chromatography (eluent: petroleum ether/ethyl acetate = 20/1 v/v).

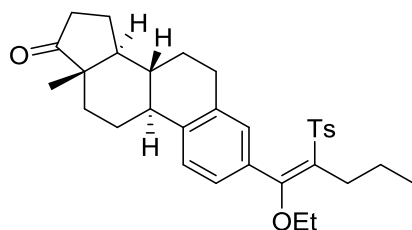
**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):** δ 7.46 – 7.39 (m, 3H), 7.21 (dd, *J* = 1.2, 3.6 Hz, 1H), 7.15 (d, *J* = 8.0 Hz, 2H), 7.02 (dd, *J* = 3.6, 5.1 Hz, 1H), 3.62 (q, *J* = 7.0, 7.0, 7.0 Hz, 2H), 2.37 (s, 3H), 2.14 (s, 3H), 1.19 (t, *J* = 7.0, 7.0 Hz, 3H).

**<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>):** δ = 154.41, 142.28, 137.94, 131.97, 131.01, 128.28, 128.16, 126.45, 125.65, 122.48, 76.45, 76.20, 75.94, 64.53, 20.65, 14.36, 12.49.

**HRMS (ESI-TOF, [M + Na]<sup>+</sup>):** For C<sub>16</sub>H<sub>18</sub>NaO<sub>3</sub>S<sub>2</sub>, 345.0595, Found: 345.0600.

**(8*R*,9*S*,13*S*,14*S*)-3-((*E*)-1-ethoxy-2-tosylpent-1-en-1-yl)-13-methyl-**

**6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta[*a*]phenanthren-17-one (4raa)**



**4raa**

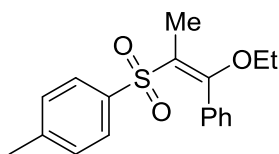
**4ara** was obtained in 71% (73.9 mg) as a colorless oil after column chromatography (eluent: petroleum ether/ethyl acetate = 4/1 v/v).

**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):** δ 7.28 (dd, *J* = 2.6, 9.4 Hz, 2H), 7.18 (d, *J* = 8.0 Hz, 1H), 7.05 (d, *J* = 8.0 Hz, 2H), 6.94 (dd, *J* = 1.9, 8.0 Hz, 1H), 6.69 (s, 1H), 3.47 (q, *J* = 7.0, 7.0, 7.1 Hz, 2H), 2.76 (dt, *J* = 4.5, 4.5, 7.2 Hz, 2H), 2.64 – 2.55 (m, 4H), 2.35 (s, 3H), 2.21 – 1.95 (m, 5H), 1.71 – 1.58 (m, 4H), 1.58 – 1.35 (m, 4H), 1.14 (t, *J* = 7.1, 7.1 Hz, 3H), 1.07 (t, *J* = 7.2, 7.2 Hz, 3H), 0.96 (s, 3H).

**<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>):** δ = 163.83, 142.28, 141.03, 140.10, 135.77, 130.25, 129.39, 128.69, 127.55, 127.22, 124.60, 124.09, 65.02, 50.54, 47.93, 44.48, 38.03, 35.83, 31.59, 29.17, 29.04, 26.40, 25.62, 22.74, 21.61, 21.46, 15.17, 14.08, 13.89.

**HRMS (ESI-TOF, [M + H]<sup>+</sup>):** For C<sub>32</sub>H<sub>41</sub>O<sub>4</sub>S, 521.2726, Found: 521.2729.

**(*E*)-1-((1-ethoxy-1-phenylprop-1-en-2-yl)sulfonyl)-4-methylbenzene (4aaa)**



**4aaa**

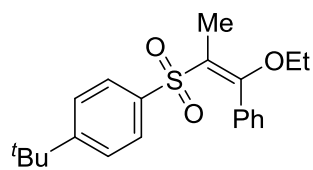
**4aaa** was obtained in 78% (49.4 mg) as a colorless oil after column chromatography (eluent: petroleum ether/ethyl acetate = 20/1 v/v).

**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):** δ 7.40 (d, *J* = 7.9 Hz, 3H), 7.38 – 7.28 (m, 2H), 7.23 – 7.17 (m, 2H), 7.14 (d, *J* = 8.0 Hz, 2H), 3.48 (q, *J* = 7.0, 7.0, 7.1 Hz, 2H), 2.37 (s, 3H), 2.10 (s, 3H), 1.14 (t, *J* = 7.0, 7.0 Hz, 3H).

**<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>):** δ = 162.78, 142.99, 139.29, 132.27, 129.78, 129.49, 129.16, 127.78, 127.31, 118.75, 77.31, 77.06, 76.80, 65.11, 21.49, 15.19, 12.78.

**HRMS (ESI-TOF, [M + Na]<sup>+</sup>):** For C<sub>18</sub>H<sub>20</sub>NaO<sub>3</sub>S, 339.1031, Found: 339.1038.

**(E)-1-(tert-butyl)-4-((1-ethoxy-1-phenylprop-1-en-2-yl)sulfonyl)benzene (4aba)**



**4aba**

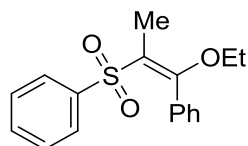
**4aba** was obtained in 67% (48.0 mg) as a colorless oil after column chromatography (eluent: petroleum ether/ethyl acetate = 20/1 v/v).

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 7.45 – 7.39 (m, 3H), 7.37 – 7.31 (m, 4H), 7.21 – 7.17 (m, 2H), 3.48 (q, *J* = 7.0, 7.0, 7.0 Hz, 2H), 2.13 (s, 3H), 1.30 (s, 9H), 1.14 (t, *J* = 7.1, 7.1 Hz, 3H).

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>):** δ = 162.67, 155.92, 139.13, 132.26, 129.81, 129.43, 127.78, 127.12, 125.49, 118.99, 77.36, 77.04, 76.73, 65.11, 35.04, 31.10, 15.20, 12.73.

**HRMS (ESI-TOF, [M + Na]<sup>+</sup>):** For C<sub>21</sub>H<sub>26</sub>NaO<sub>3</sub>S, 381.1500, Found: 381.1496.

**(E)-((1-ethoxy-1-phenylprop-1-en-2-yl)sulfonyl)benzene (4aca)**



**4aca**

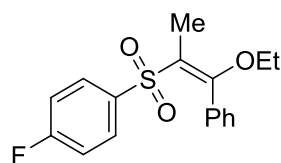
**4aca** was obtained in 67% (40.5 mg) as a colorless oil after column chromatography (eluent: petroleum ether/ethyl acetate = 20/1 v/v).

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 7.54 – 7.48 (m, 2H), 7.47 – 7.43 (m, 1H), 7.43 – 7.38 (m, 1H), 7.34 (ddd, *J* = 2.7, 6.9, 8.5 Hz, 4H), 7.21 – 7.17 (m, 2H), 3.49 (q, *J* = 7.0, 7.0, 7.0 Hz, 2H), 2.13 (s, 3H), 1.15 (t, *J* = 7.0, 7.0 Hz, 3H).

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>):** δ = 163.22, 142.20, 132.24, 132.10, 129.80, 129.55, 128.52, 127.84, 127.22, 118.55, 77.37, 77.06, 76.74, 65.20, 15.20, 12.76.

**HRMS (ESI-TOF, [M + Na]<sup>+</sup>):** For C<sub>17</sub>H<sub>18</sub>NaO<sub>3</sub>S, 325.0874, Found: 325.0872.

**(E)-1-((1-ethoxy-1-phenylprop-1-en-2-yl)sulfonyl)-4-fluorobenzene (4ada)**



**4ada**

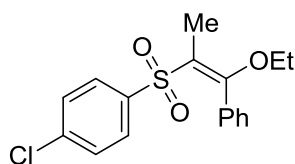
**4ada** was obtained in 81% (51.9 mg) as a colorless oil after column chromatography (eluent: petroleum ether/ethyl acetate = 20/1 v/v).

**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):** δ 7.50 – 7.46 (m, 2H), 7.43 – 7.38 (m, 1H), 7.34 (t, J = 7.4, 7.4 Hz, 2H), 7.20 – 7.14 (m, 2H), 7.00 (t, J = 8.6, 8.6 Hz, 2H), 3.49 (q, J = 7.0, 7.0, 7.0 Hz, 2H), 2.13 (s, 3H), 1.15 (t, J = 7.0, 7.0 Hz, 3H).

**<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>):** δ = 165.86, 163.84, 163.36, 138.37, 138.35, 132.00, 129.94, 129.87, 129.80, 129.66, 127.90, 118.66, 115.75, 115.57, 77.31, 77.06, 76.81, 65.29, 15.17, 12.68.

**HRMS (ESI-TOF, [M + Na]<sup>+</sup>):** For C<sub>17</sub>H<sub>17</sub>FN<sub>3</sub>O<sub>3</sub>S, 343.0780, Found: 343.0784.

**(E)-1-chloro-4-((1-ethoxy-1-phenylprop-1-en-2-yl)sulfonyl)benzene (4aea)**



**4aea**

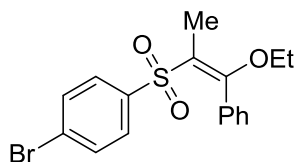
**4aea** was obtained in 78% (52.5 mg) as a colorless oil after column chromatography (eluent: petroleum ether/ethyl acetate = 20/1 v/v).

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 7.43 – 7.38 (m, 3H), 7.37 – 7.33 (m, 2H), 7.32 – 7.28 (m, 2H), 7.19 – 7.14 (m, 2H), 3.49 (q, J = 7.0, 7.0, 7.0 Hz, 2H), 2.13 (s, 3H), 1.15 (t, J = 7.1, 7.1 Hz, 3H).

**<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>):** δ = 163.64, 140.80, 138.72, 131.93, 129.78, 129.71, 128.76, 128.68, 127.91, 118.35, 77.30, 77.04, 76.79, 65.34, 15.18, 12.67.

**HRMS (ESI-TOF, [M + Na]<sup>+</sup>):** For C<sub>17</sub>H<sub>17</sub>ClNaO<sub>3</sub>S, 359.0485, Found: 359.0480.

**(E)-1-bromo-4-((1-ethoxy-1-phenylprop-1-en-2-yl)sulfonyl)benzene (4afa)**



**4afa**

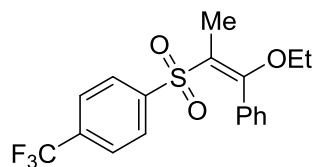
**4afa** was obtained in 72% (54.9 mg) as a colorless oil after column chromatography (eluent: petroleum ether/ethyl acetate = 20/1 v/v).

**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):** δ 7.50 – 7.44 (m, 2H), 7.44 – 7.40 (m, 1H), 7.37 –

7.30 (m, 4H), 7.19 – 7.14 (m, 2H), 3.49 (q,  $J = 7.0, 7.0, 7.0$  Hz, 2H), 2.13 (s, 3H), 1.15 (t,  $J = 7.0, 7.0$  Hz, 3H).

**$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ ):**  $\delta = 163.68, 141.33, 131.91, 131.74, 129.77, 129.72, 128.78, 127.92, 127.23, 118.28, 77.31, 77.05, 76.80, 65.34, 15.19, 12.67$ .

**HRMS (ESI-TOF,  $[\text{M} + \text{H}]^+$ ):** For  $\text{C}_{17}\text{H}_{18}\text{BrNaO}_3\text{S}$ , 381.0160, Found: 381.0162  
**(*E*)-1-((1-ethoxy-1-phenylprop-1-en-2-yl)sulfonyl)-4-(trifluoromethyl)benzene (4aga)**



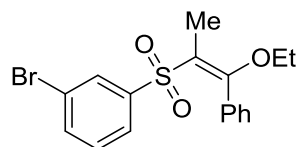
**4aga**

**4aga** was obtained in 65% (48.2 mg) as a colorless oil after column chromatography (eluent: petroleum ether/ethyl acetate = 20/1 v/v).

**$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):**  $\delta$  7.59 (s, 4H), 7.42 (t,  $J = 7.4, 7.4$  Hz, 1H), 7.33 (t,  $J = 7.6, 7.6$  Hz, 2H), 7.14 (d,  $J = 7.5$  Hz, 2H), 3.50 (q,  $J = 7.0, 7.0, 7.0$  Hz, 2H), 2.16 (s, 3H), 1.16 (t,  $J = 7.0, 7.0$  Hz, 3H).

**$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ ):**  $\delta = 164.28, 145.80, 133.97, 133.71, 131.72, 130.46, 129.81, 129.77, 128.85, 128.24, 127.96, 127.68, 125.63, 125.60, 125.57, 124.39, 122.22, 117.94, 77.29, 77.04, 76.78, 65.47, 15.16, 12.60$ .

**HRMS (ESI-TOF,  $[\text{M} + \text{H}]^+$ ):** For  $\text{C}_{18}\text{H}_{18}\text{F}_3\text{O}_3\text{S}$ , 371.0929, Found: 371.0932  
**(*E*)-1-bromo-3-((1-ethoxy-1-phenylprop-1-en-2-yl)sulfonyl)benzene (4aha)**



**4aha**

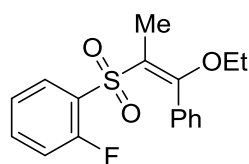
**4aha** was obtained in 42% (32.0 mg) as a colorless oil after column chromatography (eluent: petroleum ether/ethyl acetate = 20/1 v/v).

**$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):**  $\delta$  7.57 (dt,  $J = 1.3, 1.3, 8.0$  Hz, 1H), 7.49 (t,  $J = 1.9, 1.9$  Hz, 1H), 7.43 (dtd,  $J = 1.8, 3.4, 3.5, 6.6$  Hz, 2H), 7.35 (t,  $J = 7.7, 7.7$  Hz, 2H), 7.22 (t,  $J = 7.9, 7.9$  Hz, 1H), 7.17 – 7.13 (m, 2H), 3.50 (q,  $J = 7.0, 7.0, 7.0$  Hz, 2H), 2.15 (s, 3H), 1.16 (t,  $J = 7.0, 7.0$  Hz, 3H).

**<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>):**  $\delta$  = 163.99, 144.14, 135.23, 131.59, 130.26, 130.03, 129.88, 129.80, 127.92, 125.68, 122.45, 118.35, 77.29, 77.03, 76.78, 65.40, 15.18, 12.62.

**HRMS (ESI-TOF, [M + H]<sup>+</sup>):** For C<sub>17</sub>H<sub>18</sub>BrO<sub>3</sub>S, 381.0160, Found: 381.0161.

**(E)-1-((1-ethoxy-1-phenylprop-1-en-2-yl)sulfonyl)-2-fluorobenzene (4aia)**



**4aia**

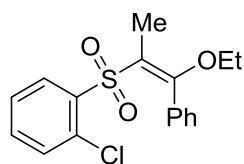
**4aia** was obtained in 67% (42.9 mg) as a colorless oil after column chromatography (eluent: petroleum ether/ethyl acetate = 20/1 v/v).

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):**  $\delta$  7.45 – 7.37 (m, 1H), 7.34 – 7.28 (m, 1H), 7.22 (td,  $J$  = 1.9, 7.4, 7.7 Hz, 3H), 7.12 – 7.02 (m, 3H), 6.93 (td,  $J$  = 1.1, 7.7, 7.7 Hz, 1H), 3.50 (q,  $J$  = 7.0, 7.0, 7.0 Hz, 2H), 2.20 (s, 3H), 1.17 (t,  $J$  = 7.0, 7.0 Hz, 3H).

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>):**  $\delta$  = 163.85, 160.30, 157.77, 134.51, 134.43, 131.45, 130.20, 130.06, 129.90, 129.77, 129.51, 127.73, 123.72, 123.68, 119.25, 116.57, 116.36, 77.38, 77.06, 76.74, 65.32, 15.19, 12.10, 12.07.

**HRMS (ESI-TOF, [M + H]<sup>+</sup>):** For C<sub>17</sub>H<sub>18</sub>FO<sub>3</sub>S, 321.0961, Found: 321.0968.

**(E)-1-chloro-2-((1-ethoxy-1-phenylprop-1-en-2-yl)sulfonyl)benzene (4aja)**



**4aja**

**4aja** was obtained in 47% (31.7 mg) as a colorless oil after column chromatography (eluent: petroleum ether/ethyl acetate = 20/1 v/v).

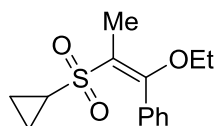
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):**  $\delta$  7.33 (dd,  $J$  = 1.4, 8.3 Hz, 1H), 7.30 – 7.22 (m, 3H), 7.10 (dd,  $J$  = 6.9, 8.5 Hz, 2H), 7.07 – 7.00 (m, 2H), 6.97 – 6.88 (m, 1H), 3.49 (q,  $J$  = 7.0, 7.0, 7.0 Hz, 2H), 2.26 (s, 3H), 1.17 (t,  $J$  = 7.0, 7.0 Hz, 3H).

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>):**  $\delta$  = 162.82, 139.60, 132.85, 131.97, 131.18, 130.84,

130.34, 129.96, 129.54, 127.69, 126.35, 119.53, 77.36, 77.04, 76.72, 65.38, 15.22, 12.13.

**HRMS (ESI-TOF, [M + H]<sup>+</sup>):** For C<sub>17</sub>H<sub>18</sub>ClO<sub>3</sub>S, 337.0665, Found: 337.0669

**(E)-(2-(cyclopropylsulfonyl)-1-ethoxyprop-1-en-1-yl)benzene (4aka)**



**4aka**

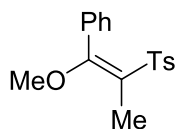
**4aka** was obtained in 46% (24.5 mg) as a colorless oil after column chromatography (eluent: petroleum ether/ethyl acetate = 20/1 v/v).

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 7.48 – 7.32 (m, 5H), 3.55 (q, J = 7.0, 7.0, 7.0 Hz, 2H), 2.19 (s, 3H), 2.15 (dt, J = 4.8, 4.8, 8.0 Hz, 1H), 1.19 (t, J = 7.0, 7.0 Hz, 3H), 1.12 – 0.97 (m, 2H), 0.92 – 0.75 (m, 2H).

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>):** δ = 162.20, 132.44, 129.82, 129.68, 127.88, 118.46, 77.29, 77.03, 76.78, 65.09, 31.63, 15.23, 12.91, 4.97.

**HRMS (ESI-TOF, [M + Na]<sup>+</sup>):** For C<sub>14</sub>H<sub>18</sub>NaO<sub>3</sub>S, 289.0874, Found: 289.0876.

**(E)-1-((1-methoxy-1-phenylprop-1-en-2-yl)sulfonyl)-4-methylbenzene (4aab)**



**4aab**

**4aab** was obtained in 90% (54.4 mg) as a white solid after column chromatography (eluent: petroleum ether/ethyl acetate = 20/1 v/v).

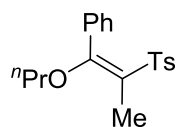
**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):** δ 7.44 – 7.33 (m, 5H), 7.22 – 7.13 (m, 4H), 3.28 (s, 3H), 2.37 (s, 3H), 2.08 (s, 3H).

**<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>):** δ = 163.29, 143.05, 139.27, 131.60, 129.77, 129.58, 129.19, 127.91, 127.32, 118.16, 77.38, 77.06, 76.74, 56.64, 21.51, 12.54.

**HRMS (ESI-TOF, [M + H]<sup>+</sup>):** For C<sub>17</sub>H<sub>19</sub>O<sub>3</sub>S, 303.1055, Found: 303.1061.

**(E)-1-methyl-4-((1-phenyl-1-propoxyprop-1-en-2-yl)sulfonyl)benzene (4aac)**





**4aac**

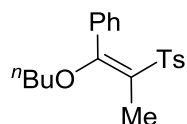
**4aac** was obtained in 35% (23.1 mg) as a colorless oil after column chromatography (eluent: petroleum ether/ethyl acetate = 20/1 v/v).

**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):** δ 7.43 – 7.30 (m, 5H), 7.22 – 7.12 (m, 4H), 3.36 (t, *J* = 6.5, 6.5 Hz, 2H), 2.37 (s, 3H), 2.11 (s, 3H), 1.54 (h, *J* = 7.1, 7.1, 7.1, 7.1, 7.1 Hz, 2H), 0.86 (t, *J* = 7.4, 7.4 Hz, 3H).

**<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>):** δ = 162.97, 142.97, 139.33, 132.31, 129.79, 129.46, 129.15, 127.78, 127.31, 118.46, 77.31, 77.06, 76.81, 70.99, 22.99, 21.50, 12.67, 10.37.

**HRMS (ESI-TOF, [M + H]<sup>+</sup>):** For C<sub>19</sub>H<sub>23</sub>O<sub>3</sub>S, 331.1368, Found: 331.1371.

**(*E*)-1-((1-butoxy-1-phenylprop-1-en-2-yl)sulfonyl)-4-methylbenzene (4aad)**



**4aad**

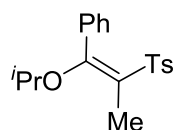
**4aad** was obtained in 26% (17.9 mg) as a colorless oil after column chromatography (eluent: petroleum ether/ethyl acetate = 20/1 v/v).

**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):** δ 7.43 – 7.30 (m, 5H), 7.22 – 7.12 (m, 4H), 3.40 (t, *J* = 6.5, 6.5 Hz, 2H), 2.37 (s, 3H), 2.10 (s, 3H), 1.49 (dq, *J* = 6.4, 6.5, 6.5, 8.3 Hz, 2H), 1.35 – 1.24 (m, 2H), 0.84 (t, *J* = 7.4, 7.4 Hz, 3H).

**<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>):** δ = 162.99, 142.96, 139.32, 132.31, 129.77, 129.45, 129.14, 127.77, 127.30, 118.45, 77.30, 77.05, 76.79, 69.14, 31.68, 21.49, 18.98, 13.65, 12.68.

**HRMS (ESI-TOF, [M + H]<sup>+</sup>):** For C<sub>20</sub>H<sub>25</sub>O<sub>3</sub>S, 345.1524, Found: 345.1528.

**(*E*)-1-((1-isopropoxy-1-phenylprop-1-en-2-yl)sulfonyl)-4-methylbenzene (4aae)**



**4aae**

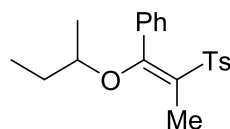
**4aae** was obtained in 53% (35.0 mg) as a colorless oil after column chromatography (eluent: petroleum ether/ethyl acetate = 20/1 v/v).

**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):** δ 7.44 – 7.29 (m, 5H), 7.27 – 7.22 (m, 2H), 7.13 (d, *J* = 8.1 Hz, 2H), 3.79 (p, *J* = 6.1, 6.1, 6.1, 6.1 Hz, 1H), 2.36 (s, 3H), 2.10 (s, 3H), 1.11 (s, 3H), 1.10 (s, 3H).

**<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>):** δ = 162.14, 142.96, 139.17, 132.74, 129.97, 129.53, 129.12, 127.69, 127.31, 120.58, 77.31, 77.06, 76.80, 71.62, 22.44, 21.48, 13.13.

**HRMS (ESI-TOF, [M + Na]<sup>+</sup>):** For C<sub>19</sub>H<sub>22</sub>NaO<sub>3</sub>S, 353.1187, Found: 353.1189.

**(*E*)-1-((1-(sec-butoxy)-1-phenylprop-1-en-2-yl)sulfonyl)-4-methylbenzene (4aaf)**



**4aaf**

**4aaf** was obtained in 50% (34.4 mg) as a colorless oil after column chromatography (eluent: petroleum ether/ethyl acetate = 20/1 v/v).

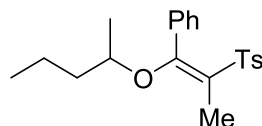
**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):** δ 7.39 (dd, *J* = 6.5, 8.1 Hz, 3H), 7.34 (dd, *J* = 6.7, 8.2 Hz, 2H), 7.25 – 7.19 (m, 2H), 7.13 (d, *J* = 8.0 Hz, 2H), 3.59 (h, *J* = 6.2, 6.2, 6.2, 6.2, 6.2 Hz, 1H), 2.36 (s, 3H), 2.11 (s, 3H), 1.53 (dp, *J* = 7.3, 7.3, 7.3, 7.3, 14.3 Hz, 1H), 1.46 – 1.37 (m, 1H), 1.05 (d, *J* = 6.2 Hz, 3H), 0.80 (t, *J* = 7.4, 7.4 Hz, 3H).

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>):** δ = 162.57, 142.93, 139.27, 132.73, 130.01, 129.47, 129.13, 127.68, 127.30, 119.98, 77.38, 77.06, 76.74, 76.30, 29.43, 21.50, 19.98, 13.05, 9.60.

**HRMS (ESI-TOF, [M + Na]<sup>+</sup>):** For C<sub>20</sub>H<sub>24</sub>NaO<sub>3</sub>S, 367.1344, Found: 367.1346

**(*E*)-1-methyl-4-((1-(pentan-2-yloxy)-1-phenylprop-1-en-2-yl)sulfonyl)benzene**

**(4aag)**



**4aag**

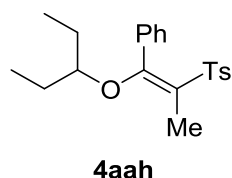
**4aag** was obtained in 38% (27.2 mg) as a colorless oil after column chromatography (eluent: petroleum ether/ethyl acetate = 20/1 v/v).

**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):** δ 7.38 (dd, *J* = 6.5, 8.3 Hz, 3H), 7.33 (t, *J* = 7.3, 7.3 Hz, 2H), 7.24 – 7.19 (m, 2H), 7.13 (d, *J* = 8.0 Hz, 2H), 3.69 – 3.59 (m, 1H), 2.36 (s, 3H), 2.10 (s, 3H), 1.58 – 1.46 (m, 1H), 1.39 – 1.27 (m, 2H), 1.20 (dddd, *J* = 1.9, 5.2, 7.4, 15.0 Hz, 1H), 1.05 (d, *J* = 6.2 Hz, 3H), 0.80 (t, *J* = 7.1, 7.1 Hz, 3H).

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>):** δ = 162.57, 142.92, 139.27, 132.74, 130.00, 129.48, 129.12, 127.67, 127.31, 119.99, 77.37, 77.05, 76.73, 74.97, 38.82, 21.50, 20.53, 18.52, 13.94, 13.06.

**HRMS (ESI-TOF, [M + Na]<sup>+</sup>):** For C<sub>21</sub>H<sub>26</sub>NaO<sub>3</sub>S, 381.1500, Found: 381.1500.

**(*E*)-1-methyl-4-((1-(pentan-3-yloxy)-1-phenylprop-1-en-2-yl)sulfonyl)benzene (4aah)**



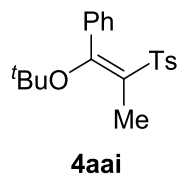
**4aah** was obtained in 38% (25.8 mg) as a colorless oil after column chromatography (eluent: petroleum ether/ethyl acetate = 20/1 v/v).

**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):** δ 7.43 – 7.35 (m, 3H), 7.36 – 7.30 (m, 2H), 7.22 – 7.17 (m, 2H), 7.14 (d, *J* = 8.0 Hz, 2H), 3.43 (p, *J* = 5.9, 5.9, 5.9, 5.9 Hz, 1H), 2.37 (s, 3H), 2.11 (s, 3H), 1.53 – 1.31 (m, 4H), 0.78 (t, *J* = 7.4, 7.4 Hz, 6H).

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>):** δ = 163.04, 142.88, 139.39, 132.69, 130.09, 129.40, 129.13, 127.64, 127.29, 119.29, 80.84, 77.36, 77.05, 76.73, 26.63, 21.50, 12.94, 9.41.

**HRMS (ESI-TOF, [M + Na]<sup>+</sup>):** For C<sub>21</sub>H<sub>26</sub>NaO<sub>3</sub>S, 381.1500, Found: 381.1501.

**(*E*)-1-((1-(*tert*-butoxy)-1-phenylprop-1-en-2-yl)sulfonyl)-4-methylbenzene (4aai)**



**4aai** was obtained in 30% (20.7 mg) as a colorless oil after column chromatography (eluent: petroleum ether/ethyl acetate = 20/1 v/v).

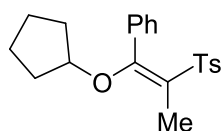
**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):** δ 7.38 – 7.28 (m, 4H), 7.28 (d, *J* = 1.7 Hz, 2H), 7.24 (d, *J* = 7.8 Hz, 1H), 7.08 (d, *J* = 8.1 Hz, 2H), 2.34 (s, 3H), 2.17 (s, 3H), 1.10 (s, 9H).

**<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>):**  $\delta$  = 161.16, 142.99, 138.76, 135.77, 130.82, 129.37, 129.00, 127.29, 127.14, 127.08, 82.34, 77.28, 77.03, 76.77, 29.55, 21.47, 14.36.

**HRMS (ESI-TOF, [M + Na]<sup>+</sup>):** For C<sub>20</sub>H<sub>24</sub>NaO<sub>3</sub>S, 367.1344, Found: 367.1343.

**(E)-1-((1-(cyclopentyloxy)-1-phenylprop-1-en-2-yl)sulfonyl)-4-methylbenzene**

**(4aaj)**



**4aaj**

**4aaj** was obtained in 47% (33.5 mg) as a colorless oil after column chromatography (eluent: petroleum ether/ethyl acetate = 20/1 v/v).

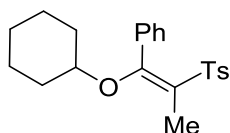
**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):**  $\delta$  7.41 – 7.30 (m, 5H), 7.24 – 7.19 (m, 2H), 7.13 (d,  $J$  = 8.3 Hz, 2H), 4.13 – 4.06 (m, 1H), 2.36 (s, 3H), 2.08 (s, 3H), 1.77 – 1.64 (m, 5H), 1.51 – 1.47 (m, 3H).

**<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>):**  $\delta$  = 162.21, 142.96, 139.24, 132.77, 130.09, 129.39, 129.14, 127.68, 127.31, 120.40, 81.04, 77.38, 77.06, 76.74, 32.99, 23.74, 21.50, 12.94.

**HRMS (ESI-TOF, [M + Na]<sup>+</sup>):** For C<sub>21</sub>H<sub>24</sub>NaO<sub>3</sub>S, 379.1344, Found: 379.1344

**(E)-1-((1-(cyclohexyloxy)-1-phenylprop-1-en-2-yl)sulfonyl)-4-methylbenzene**

**(4aak)**



**4aak**

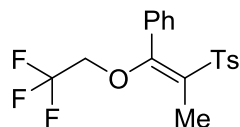
**4aak** was obtained in 43% (31.9 mg) as a colorless oil after column chromatography (eluent: petroleum ether/ethyl acetate = 20/1 v/v).

**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):**  $\delta$  7.44 – 7.29 (m, 5H), 7.25 – 7.20 (m, 2H), 7.13 (d,  $J$  = 8.0 Hz, 2H), 3.51 (tt,  $J$  = 3.4, 3.4, 8.7, 8.7 Hz, 1H), 2.36 (s, 3H), 2.12 (s, 3H), 1.68 – 1.59 (m, 4H), 1.45 – 1.33 (m, 3H), 1.25 – 1.18 (m, 1H), 1.16 – 1.05 (m, 2H).

**<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>):**  $\delta$  = 162.24, 142.91, 139.25, 132.66, 129.96, 129.47, 129.10, 127.66, 127.29, 120.20, 77.30, 77.05, 76.79, 76.42, 32.25, 25.24, 23.35, 21.48, 13.15.

**HRMS (ESI-TOF, [M + Na]<sup>+</sup>):** For C<sub>22</sub>H<sub>26</sub>NaO<sub>3</sub>S, 393.1500, Found: 393.1500.

**(E)-1-methyl-4-((1-phenyl-1-(2,2,2-trifluoroethoxy)prop-1-en-2-yl)sulfonyl)benzene (4aal)**



**4aal**

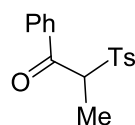
**4aal** was obtained in 43% (38.5 mg) as a colorless oil after column chromatography (eluent: petroleum ether/ethyl acetate = 20/1 v/v).

**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):** δ 7.52 – 7.43 (m, 1H), 7.40 (ddt, *J* = 1.4, 1.4, 6.8, 8.3 Hz, 4H), 7.27 – 7.21 (m, 2H), 7.18 (d, *J* = 8.0 Hz, 2H), 3.76 (q, *J* = 8.2, 8.2, 8.2 Hz, 2H), 2.38 (s, 3H), 2.14 (s, 3H).

**<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>):** δ = 160.11, 143.60, 138.38, 130.45, 130.31, 130.22, 129.34, 128.35, 127.49, 126.35, 124.12, 122.66, 121.90, 119.69, 77.30, 77.04, 76.79, 65.41, 65.13, 64.85, 64.56, 21.52, 12.73.

**HRMS (ESI-TOF, [M + Na]<sup>+</sup>):** For C<sub>18</sub>H<sub>17</sub>F<sub>3</sub>NaO<sub>3</sub>S, 393.0748, Found: 393.0750.

**1-phenyl-2-tosylpropan-1-one (4aam)**



**4aam**

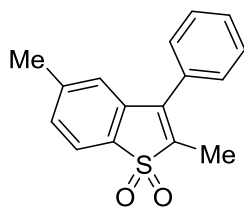
**4aam** was obtained in 62% (35.8 mg) as a colorless oil after column chromatography (eluent: petroleum ether/ethyl acetate = 20/1 v/v).

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 8.01 – 7.94 (m, 2H), 7.66 (d, *J* = 8.4 Hz, 2H), 7.65 – 7.56 (m, 1H), 7.52 – 7.43 (m, 2H), 7.31 (d, *J* = 8.1 Hz, 2H), 5.16 (q, *J* = 6.9, 6.9, 6.9 Hz, 1H), 2.43 (s, 3H), 1.56 (d, *J* = 6.9 Hz, 3H).

**<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>):** δ = 192.66, 145.38, 136.27, 134.03, 133.02, 129.84, 129.55, 129.20, 128.75, 77.38, 77.06, 76.74, 64.99, 21.70, 13.23.

**HRMS (ESI-TOF, [M + H]<sup>+</sup>):** For C<sub>16</sub>H<sub>17</sub>O<sub>3</sub>S, 289.0898, Found: 289.0900.

**2,5-dimethyl-3-phenylbenzo[*b*]thiophene 1,1-dioxide (5)**



5

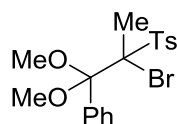
5 was obtained in 78% (42.2 mg) as a white solid after column chromatography (eluent: petroleum ether/ethyl acetate = 20/1 v/v).

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 7.68 (d, *J* = 7.7 Hz, 1H), 7.59 – 7.46 (m, 3H), 7.39 – 7.32 (m, 2H), 7.30 – 7.24 (m, 1H), 6.98 (s, 1H), 2.36 (s, 3H), 2.13 (s, 3H).

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>):** δ = 144.43, 137.89, 135.74, 133.89, 133.44, 130.58, 129.72, 129.39, 129.07, 128.70, 124.13, 121.40, 77.36, 77.05, 76.73, 21.86, 7.55.

**HRMS (ESI-TOF, [M + H]<sup>+</sup>):** For C<sub>16</sub>H<sub>15</sub>O<sub>2</sub>S, 271.0793, Found: 271.0795.

#### 1-((2-bromo-1,1-dimethoxy-1-phenylpropan-2-yl)sulfonyl)-4-methylbenzene (6)



6

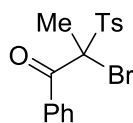
6 was obtained in 95% (78.5 mg) as a white solid after column chromatography (eluent: petroleum ether/ethyl acetate = 20/1 v/v).

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 7.90 (d, *J* = 8.4 Hz, 1H), 7.65 – 7.57 (m, 1H), 7.40 – 7.36 (m, 2H), 7.31 (d, *J* = 8.1 Hz, 1H), 3.39 (s, 2H), 3.33 (s, 2H), 2.44 (s, 2H), 2.00 (s, 2H).

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>):** δ = 144.63, 135.23, 135.00, 131.84, 130.32, 129.04, 128.70, 127.27, 104.84, 86.53, 77.41, 77.09, 76.78, 53.33, 52.88, 26.51, 21.67.

**HRMS (ESI-TOF, [M + H]<sup>+</sup>):** For C<sub>18</sub>H<sub>22</sub>BrO<sub>4</sub>S, 413.0422, Found: 413.0422.

#### 2-bromo-1-phenyl-2-tosylpropan-1-one (7)



7

7 was obtained in 98% (35.9 mg) as a white solid after column chromatography (eluent:

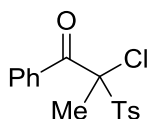
petroleum ether/ethyl acetate = 20/1 v/v).

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 8.23 – 8.17 (m, 2H), 7.79 (d, *J* = 8.4 Hz, 2H), 7.64 – 7.54 (m, 1H), 7.45 (t, *J* = 7.8, 7.8 Hz, 2H), 7.34 (d, *J* = 8.1 Hz, 2H), 2.46 (s, 3H), 2.23 (s, 3H).

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>):** δ = 191.20, 146.22, 135.13, 133.25, 131.31, 131.05, 130.81, 130.17, 129.76, 129.52, 127.99, 77.73, 77.35, 77.03, 76.71, 27.45, 21.80.

**HRMS (ESI-TOF, [M + H]<sup>+</sup>):** For C<sub>16</sub>H<sub>16</sub>BrO<sub>3</sub>S, 367.0004, Found: 367.0004.

### 2-chloro-1-phenyl-2-tosylpropan-1-one (**8**)



**8**

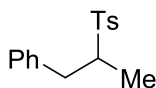
**8** was obtained in 63% (40.7 mg) as a white solid after column chromatography (eluent: petroleum ether/ethyl acetate = 20/1 v/v).

**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):** δ 8.14 (dd, *J* = 1.4, 8.4 Hz, 2H), 7.81 (d, *J* = 8.4 Hz, 2H), 7.60 – 7.53 (m, 1H), 7.44 (t, *J* = 7.9, 7.9 Hz, 2H), 7.35 (d, *J* = 8.1 Hz, 2H), 2.47 (s, 3H), 2.06 (s, 3H).

**<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>):** δ = 191.55, 146.32, 134.84, 133.25, 131.25, 131.04, 130.64, 129.60, 128.01, 86.50, 77.29, 77.03, 76.78, 26.26, 21.79.

**HRMS (ESI-TOF, [M + H]<sup>+</sup>):** For C<sub>16</sub>H<sub>16</sub>ClO<sub>3</sub>S, 323.0509, Found: 323.0511.

### 1-methyl-4-((1-phenylpropan-2-yl)sulfonyl)benzene (**9**)



**9**

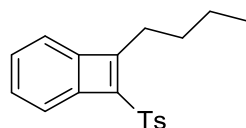
**9** was obtained in 91% (49.7 mg) as a colorless oil after column chromatography (eluent: petroleum ether/ethyl acetate = 20/1 v/v).

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 7.81 (d, *J* = 8.3 Hz, 2H), 7.38 (d, *J* = 8.0 Hz, 2H), 7.31 – 7.19 (m, 3H), 7.12 – 7.06 (m, 2H), 3.42 (dd, *J* = 3.1, 13.3 Hz, 1H), 3.24 (dq, *J* = 3.2, 6.9, 6.9, 6.9, 13.8 Hz, 1H), 2.52 (dd, *J* = 11.5, 13.3 Hz, 1H), 2.46 (s, 3H), 1.14 (d, *J* = 6.8 Hz, 3H).

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>):**  $\delta$  = 144.77, 137.08, 134.16, 129.86, 129.12, 129.08, 128.71, 126.89, 77.40, 77.08, 76.77, 61.67, 35.43, 21.67, 12.71.

**HRMS (ESI-TOF, [M + H]<sup>+</sup>):** For C<sub>16</sub>H<sub>19</sub>O<sub>2</sub>S, 275.1106, Found: 275.1106.

**7-butyl-8-tosylbicyclo[4.2.0]octa-1,3,5,7-tetraene (10)**



**10**

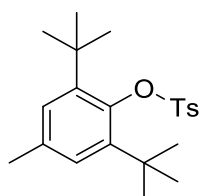
**10** was obtained in 15% (6.8 mg) as a colorless oil after column chromatography (petroleum ether).

**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):**  $\delta$  7.68 (d,  $J$  = 8.1 Hz, 1H), 7.49 (dd,  $J$  = 6.9, 8.1 Hz, 2H), 7.43 – 7.32 (m, 3H), 7.23 (s, 1H), 7.11 (dd,  $J$  = 1.7, 8.2 Hz, 1H), 2.81 (t,  $J$  = 7.7, 7.7 Hz, 2H), 2.38 (s, 3H), 1.66 (p,  $J$  = 7.3, 7.3, 7.4, 7.4 Hz, 2H), 0.90 – 0.81 (m, 5H).

**<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>):**  $\delta$  = 142.80, 140.76, 135.81, 135.33, 133.81, 133.20, 130.13, 128.50, 127.22, 125.39, 122.48, 121.72, 77.27, 77.02, 76.76, 31.32, 29.71, 28.79, 22.34, 21.44.

**HRMS (ESI-TOF, [M + H]<sup>+</sup>):** For C<sub>19</sub>H<sub>21</sub>O<sub>2</sub>S, 313.1262, Found: 313.1269.

**2,6-di-*tert*-butyl-4-methylphenyl 4-methylbenzenesulfonate (11)**



**11**

**11** was obtained in 35% (26.2 mg) as a white solid after column chromatography (eluent: petroleum ether/ethyl acetate = 20/1 v/v).

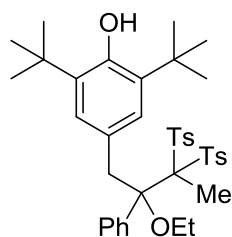
**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):**  $\delta$ . 7.51 (d,  $J$  = 8.2 Hz, 2H), 7.18 (d,  $J$  = 8.0 Hz, 2H), 6.63 (s, 2H), 2.36 (s, 3H), 1.81 (s, 3H), 1.10 (s, 18H).

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>):**  $\delta$  = 183.70, 151.21, 145.30, 135.71, 130.61, 130.26, 128.80, 77.35, 77.03, 76.71, 65.81, 35.19, 28.97, 21.61, 18.53.

**HRMS (ESI-TOF, [M + Na]<sup>+</sup>):** For C<sub>22</sub>H<sub>30</sub>NaO<sub>3</sub>S, 397.1813, Found: 397.1814.

**2,6-di-*tert*-butyl-4-(2-ethoxy-2-phenyl-3,3-ditosylbutyl)phenol (12)**





**12**

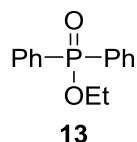
**12** was obtained in 23% (31.7 mg) as a colorless oil after column chromatography (eluent: petroleum ether/ethyl acetate = 20/1 v/v).

**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):** δ 7.42 (dd, *J* = 8.0, 18.7 Hz, 5H), 7.38 – 7.31 (m, 2H), 7.20 (dt, *J* = 2.7, 2.7, 6.8 Hz, 4H), 7.15 (d, *J* = 8.0 Hz, 2H), 6.73 (s, 2H), 5.24 (s, 1H), 4.19 (s, 2H), 3.48 (q, *J* = 7.0, 7.0, 7.1 Hz, 2H), 2.40 (s, 3H), 2.37 (s, 3H), 2.10 (s, 3H), 1.32 (s, 18H), 1.14 (t, *J* = 7.0, 7.0 Hz, 3H).

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>):** δ = 162.77, 154.20, 144.33, 142.99, 139.28, 135.99, 134.91, 132.27, 129.79, 129.49, 129.30, 129.16, 128.90, 127.78, 127.67, 127.32, 118.94, 118.76, 77.37, 77.05, 76.73, 65.11, 63.26, 34.13, 30.05, 21.54, 21.50, 15.20, 12.78.

**HRMS (ESI-TOF, [M + Na]<sup>+</sup>):** For C<sub>40</sub>H<sub>50</sub>NaO<sub>6</sub>S<sub>2</sub>, 713.2947, Found: 713.2955.

### ethyl diphenylphosphinate (**13**)



**13**

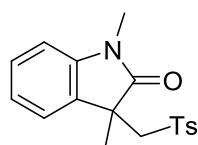
**13** was obtained in 80% (39.4 mg) as a colorless oil after column chromatography (eluent: petroleum ether/ethyl acetate = 1/2 v/v).

**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):** δ 7.80 (ddd, *J* = 1.4, 8.2, 12.3 Hz, 4H), 7.53 – 7.46 (m, 2H), 7.43 (ddd, *J* = 3.6, 6.8, 8.6 Hz, 4H), 4.09 (p, *J* = 7.1, 7.1, 7.1, 7.1 Hz, 2H), 1.35 (t, *J* = 7.0, 7.0 Hz, 3H).

**<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>):** δ = 132.13, 131.68, 131.59, 131.08, 128.58, 128.48, 77.36, 77.10, 76.85, 61.18, 61.14, 16.54, 16.49.

**HRMS (ESI-TOF, [M + Na]<sup>+</sup>):** For C<sub>14</sub>H<sub>15</sub>NaO<sub>2</sub>P, 269.0707, Found: 269.0703.

### 1,3-dimethyl-3-(tosylmethyl)indolin-2-one (**15**)



**15**

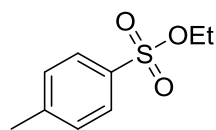
**15** was obtained in 78% (77.1 mg) as a white solid after column chromatography (eluent: petroleum ether/ethyl acetate = 2/1 v/v).

**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):** δ 7.37 (d, *J* = 8.2 Hz, 2H), 7.29 – 7.24 (m, 1H), 7.16 (d, *J* = 7.9 Hz, 2H), 7.08 (d, *J* = 7.3 Hz, 1H), 6.92 (t, *J* = 7.5, 7.5 Hz, 1H), 6.84 (d, *J* = 7.8 Hz, 1H), 3.84 (d, *J* = 14.5 Hz, 1H), 3.65 (d, *J* = 14.6 Hz, 1H), 3.15 (s, 3H), 2.39 (s, 3H), 1.38 (s, 3H).

**<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>):** δ = 177.66, 144.35, 143.25, 136.99, 129.60, 129.51, 128.59, 127.86, 124.16, 122.48, 108.39, 77.31, 77.05, 76.80, 61.89, 45.65, 26.54, 25.51, 21.59.

**HRMS (ESI-TOF, [M + Na]<sup>+</sup>):** For C<sub>18</sub>H<sub>19</sub>NNaO<sub>3</sub>S, 352.0983, Found: 352.0984.

#### **ethyl 4-methylbenzenesulfonate (17)**



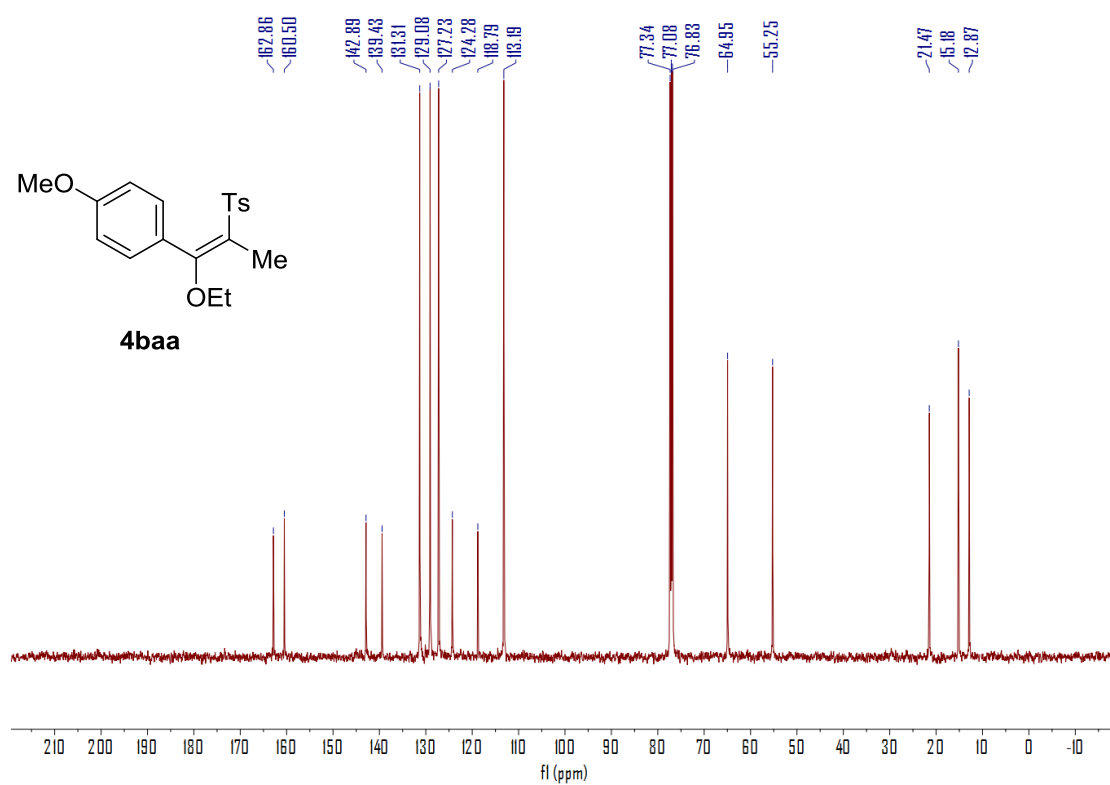
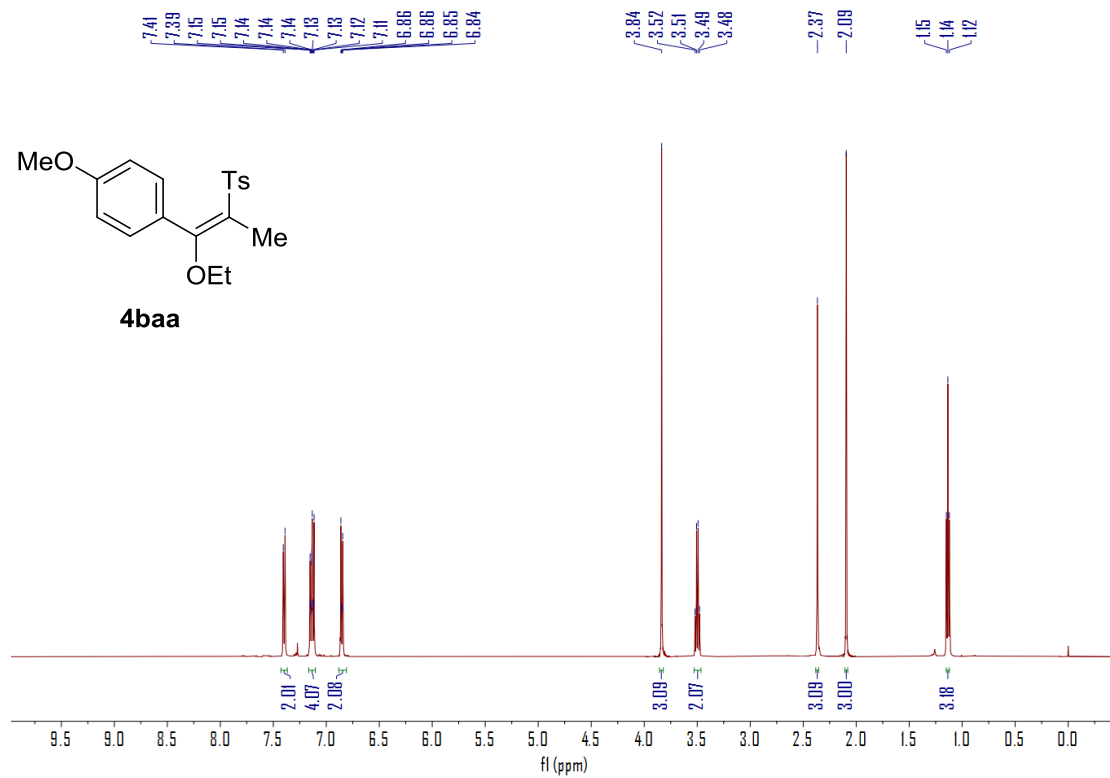
**17**

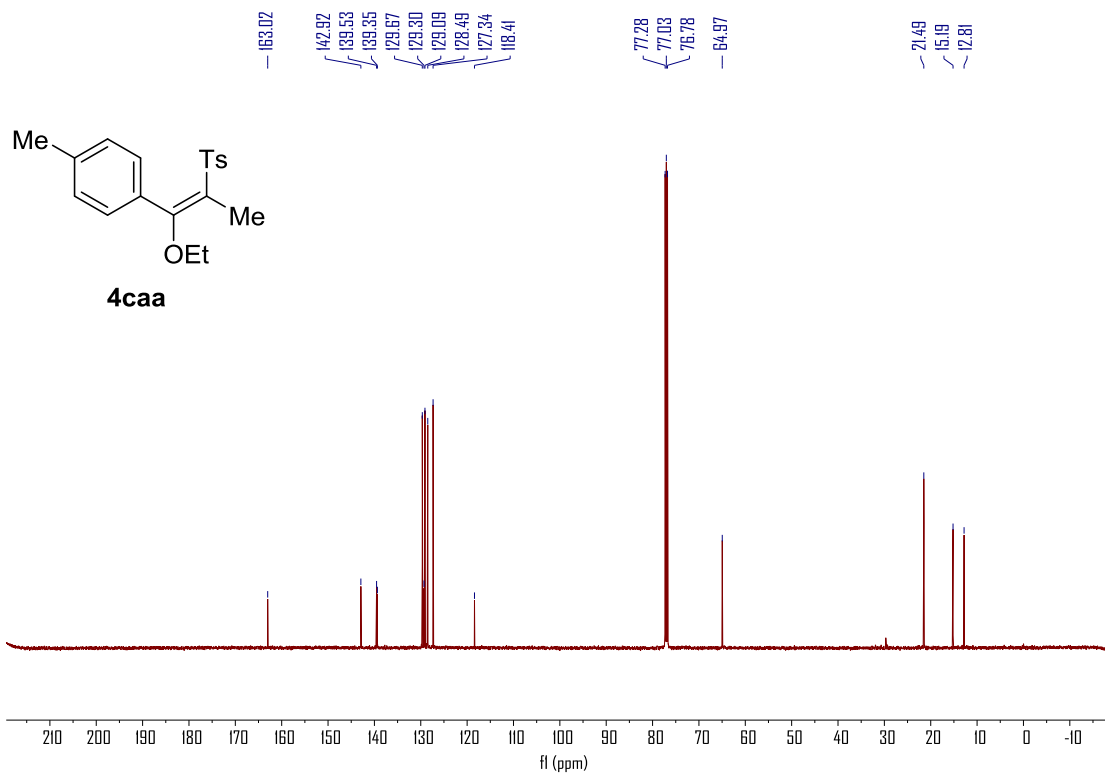
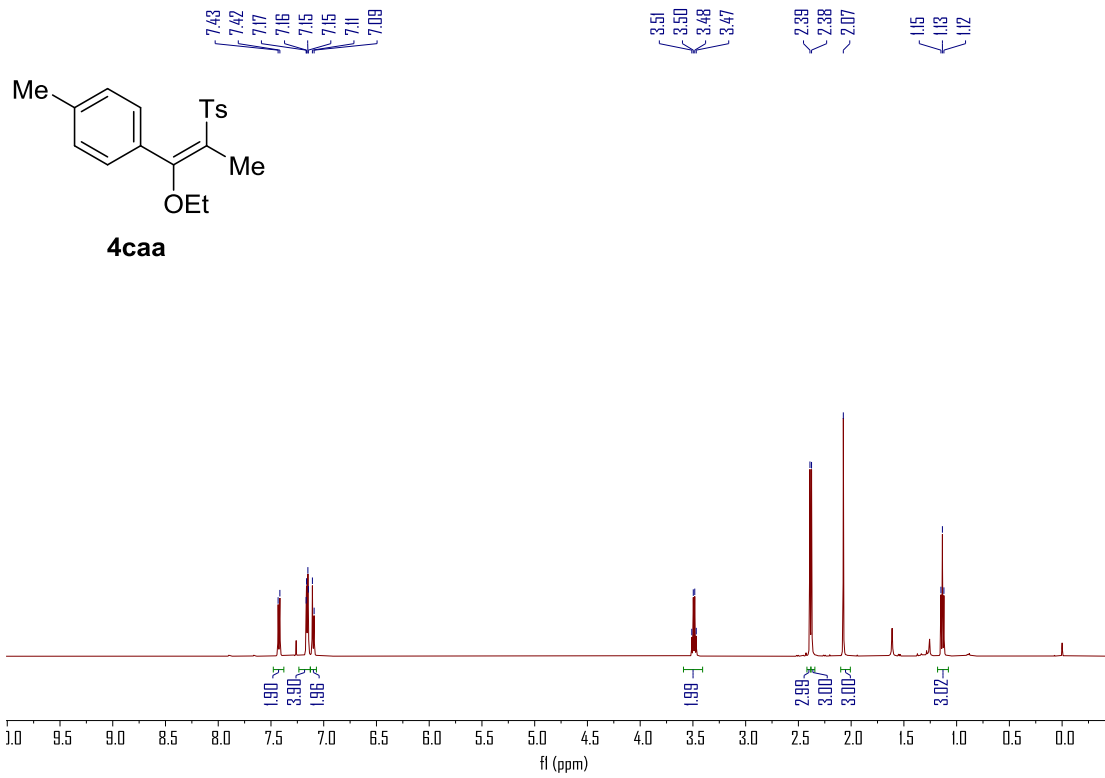
**17** was obtained in 48% (19.2 mg) as a colorless oil after column chromatography (eluent: petroleum ether/ethyl acetate = 20/1 v/v).

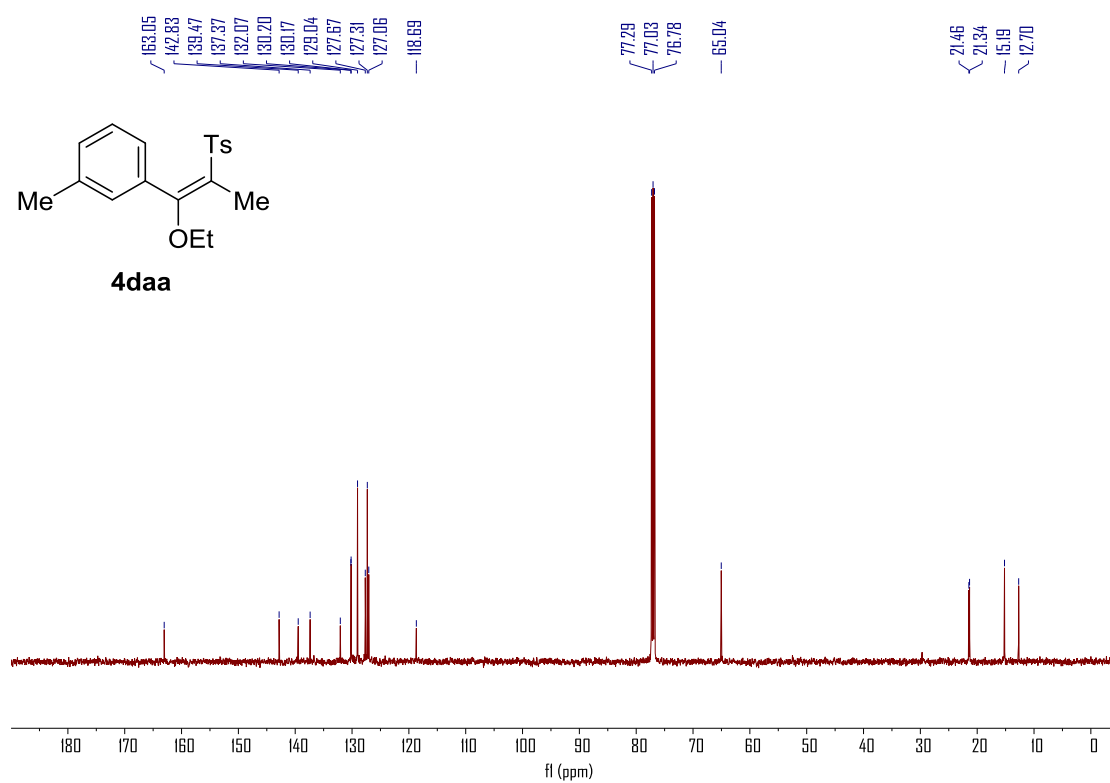
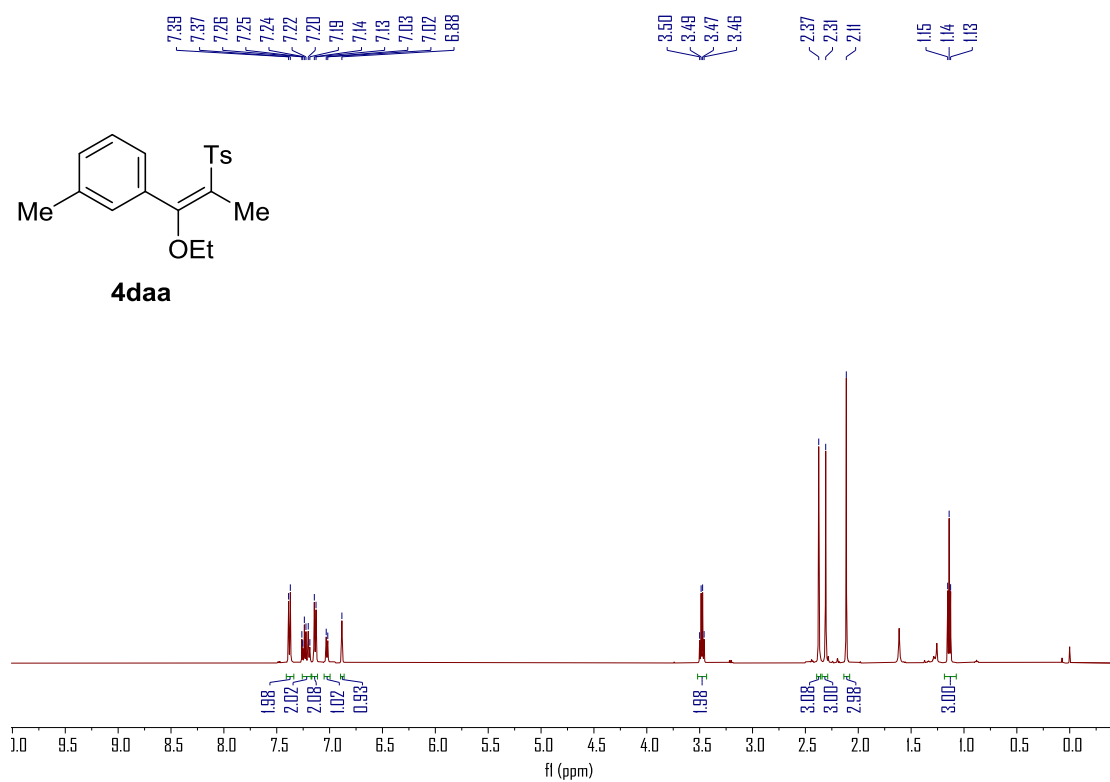
**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):** δ 7.83 (d, *J* = 8.8 Hz, 2H), 7.00 (d, *J* = 8.9 Hz, 2H), 4.08 (q, *J* = 7.1, 7.1, 7.1 Hz, 2H), 3.88 (s, 3H), 1.29 (t, *J* = 7.1, 7.1 Hz, 3H).

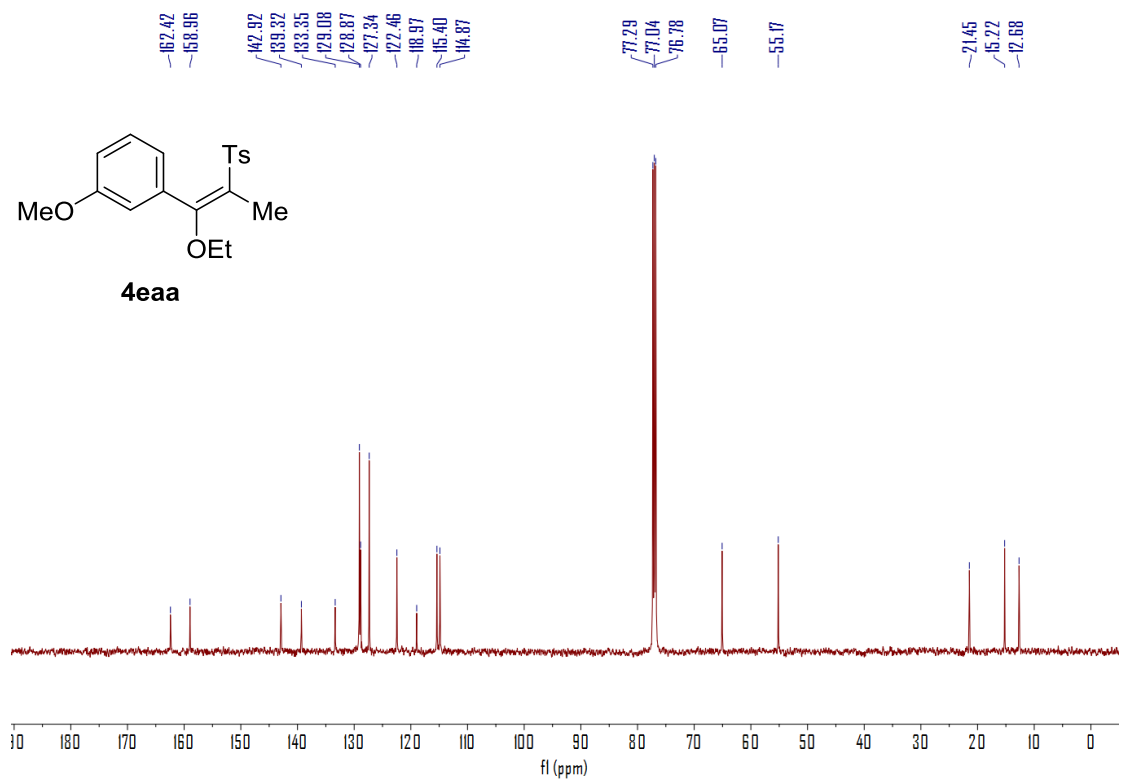
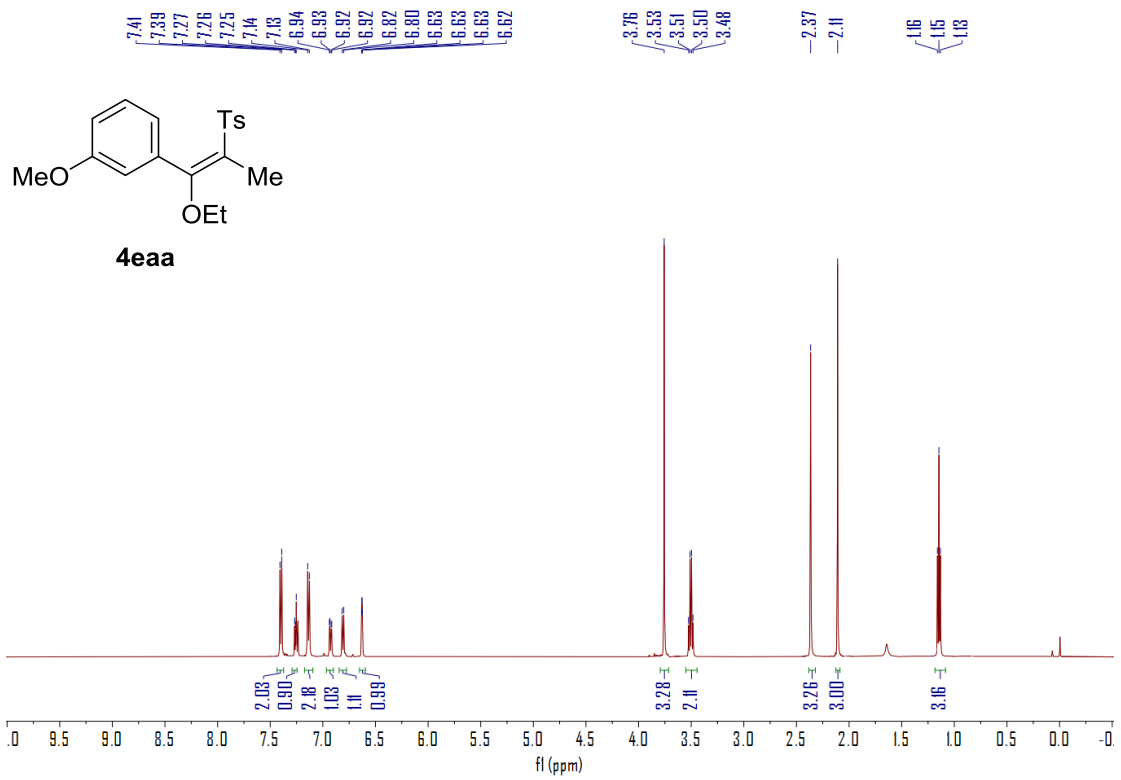
**<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>):** δ = 163.69, 130.03, 127.75, 114.40, 77.30, 77.04, 76.79, 66.60, 55.70, 14.70.

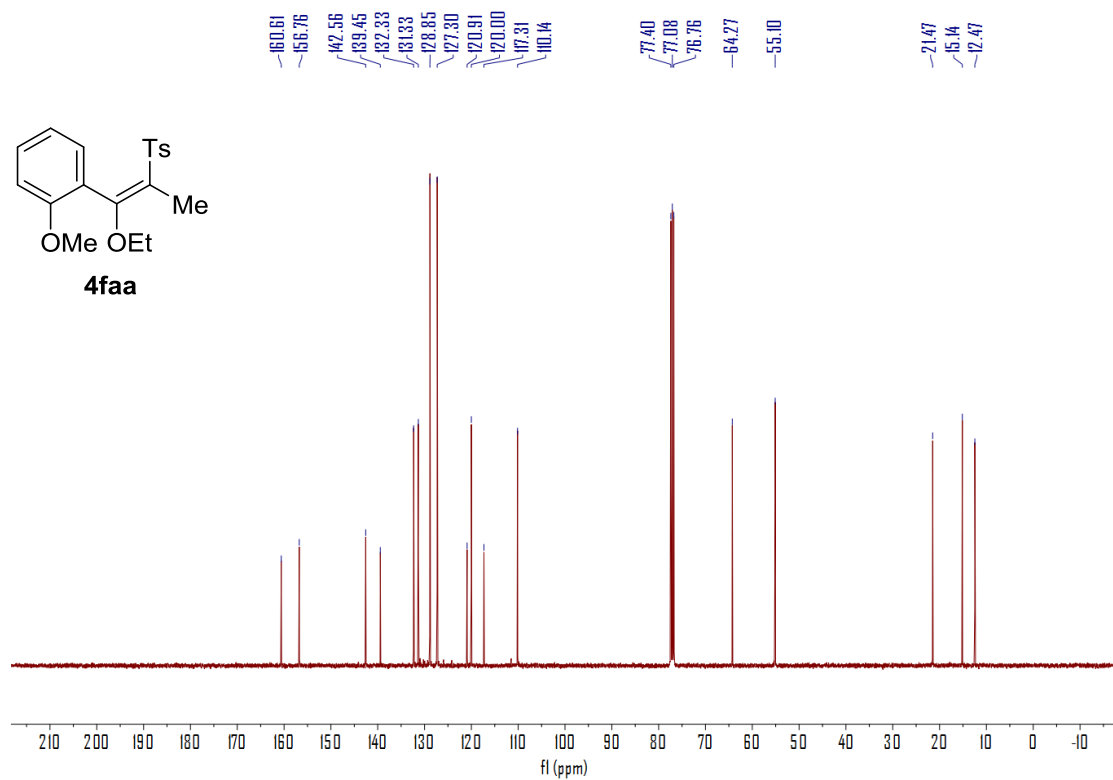
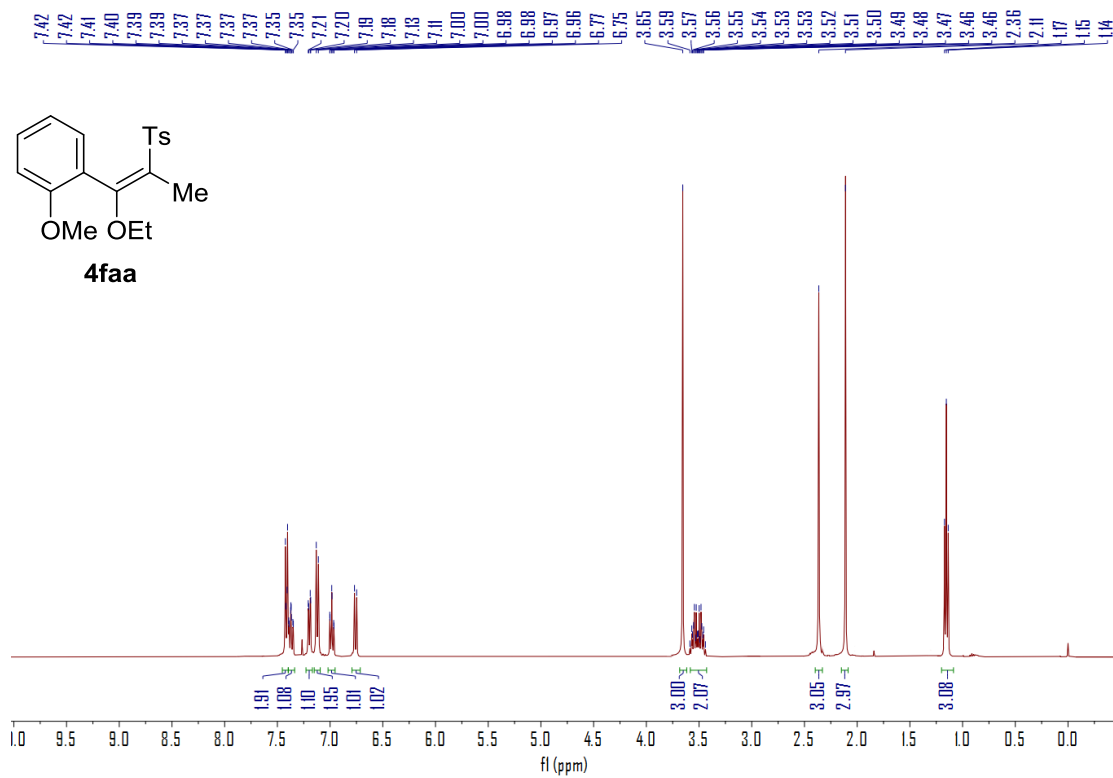
**HRMS (ESI-TOF, [M + Na]<sup>+</sup>):** For C<sub>9</sub>H<sub>12</sub>NaO<sub>3</sub>S, 223.0405, Found: 223.0406.

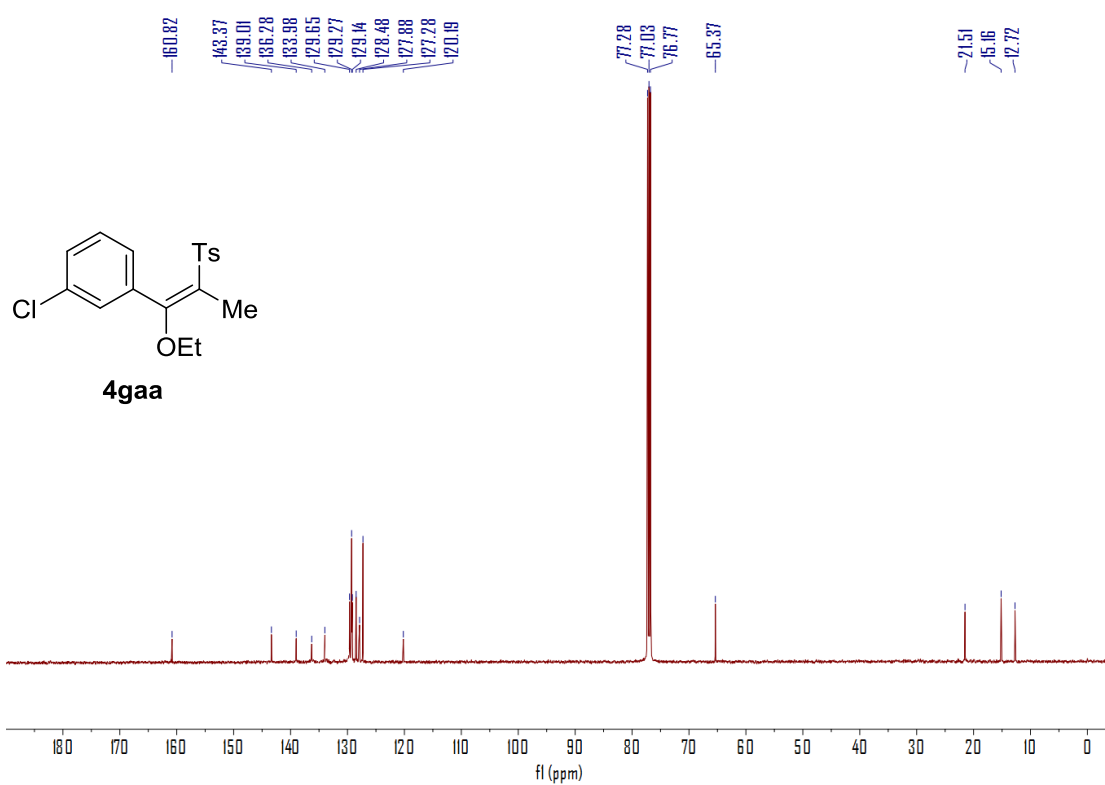
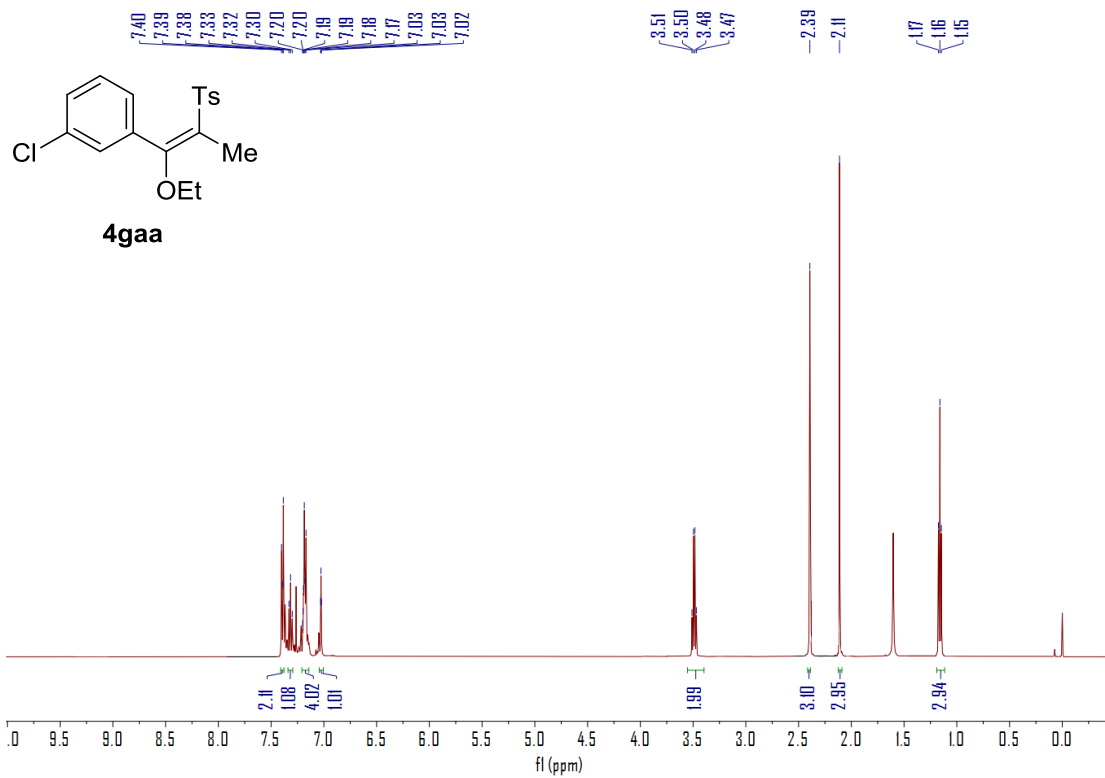




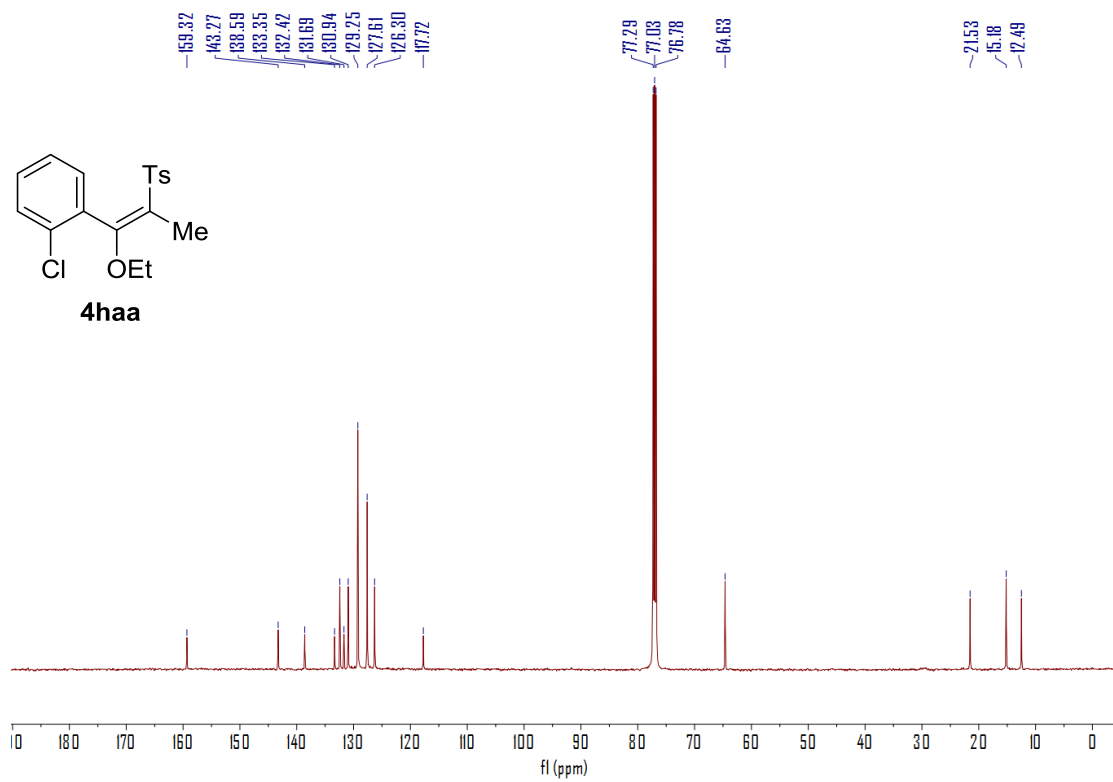
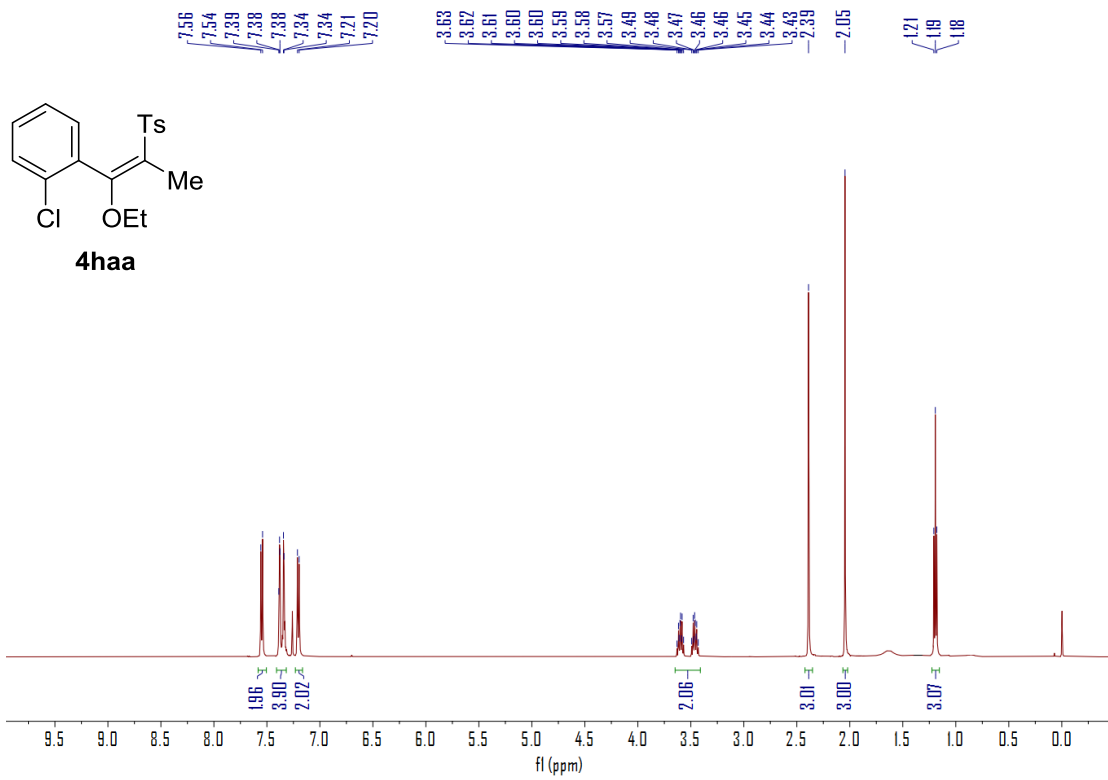


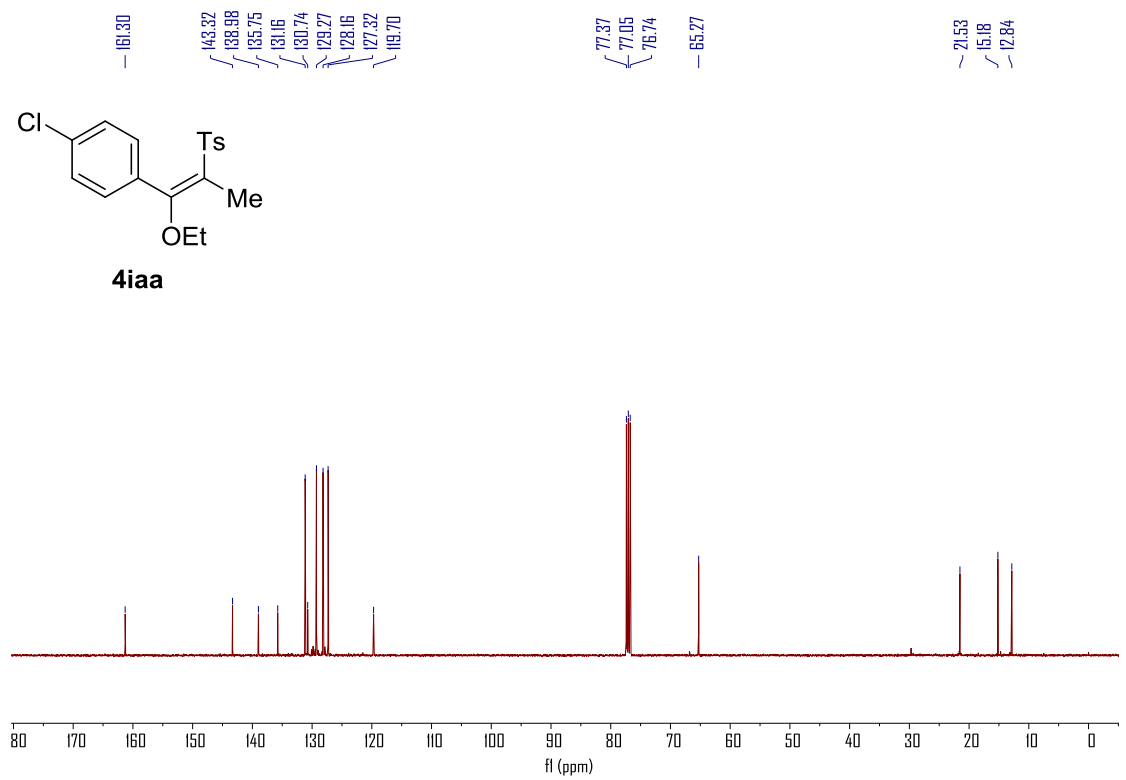
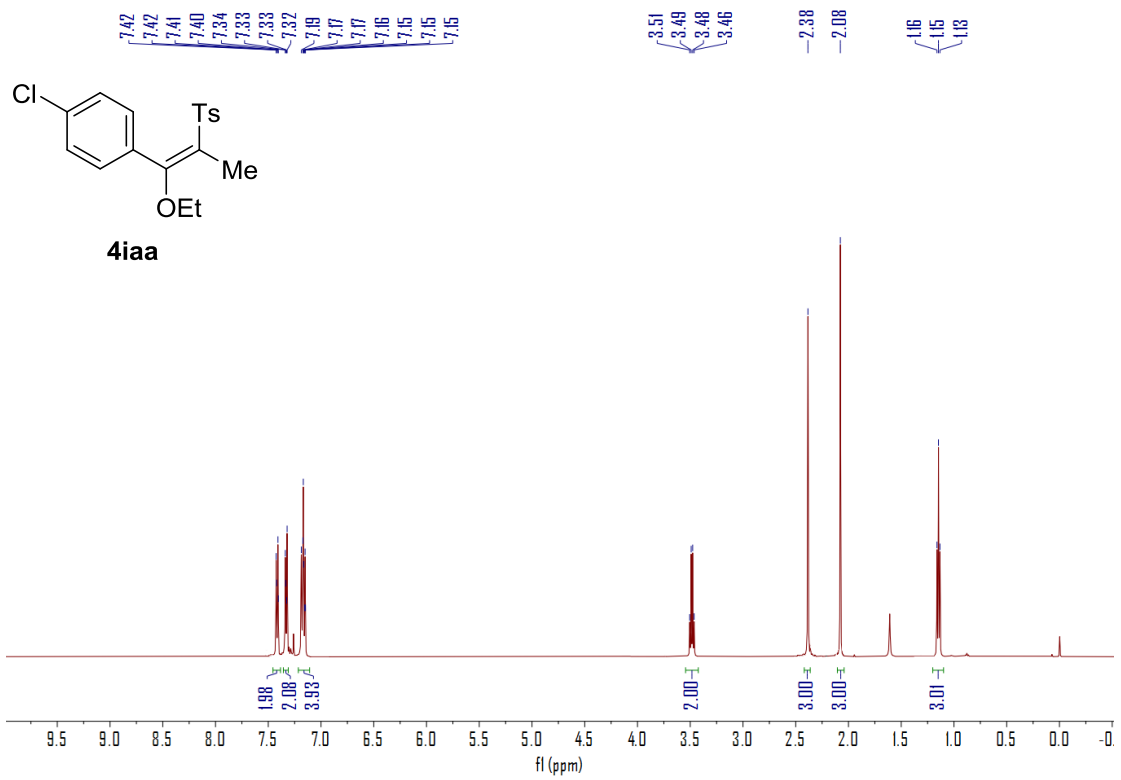


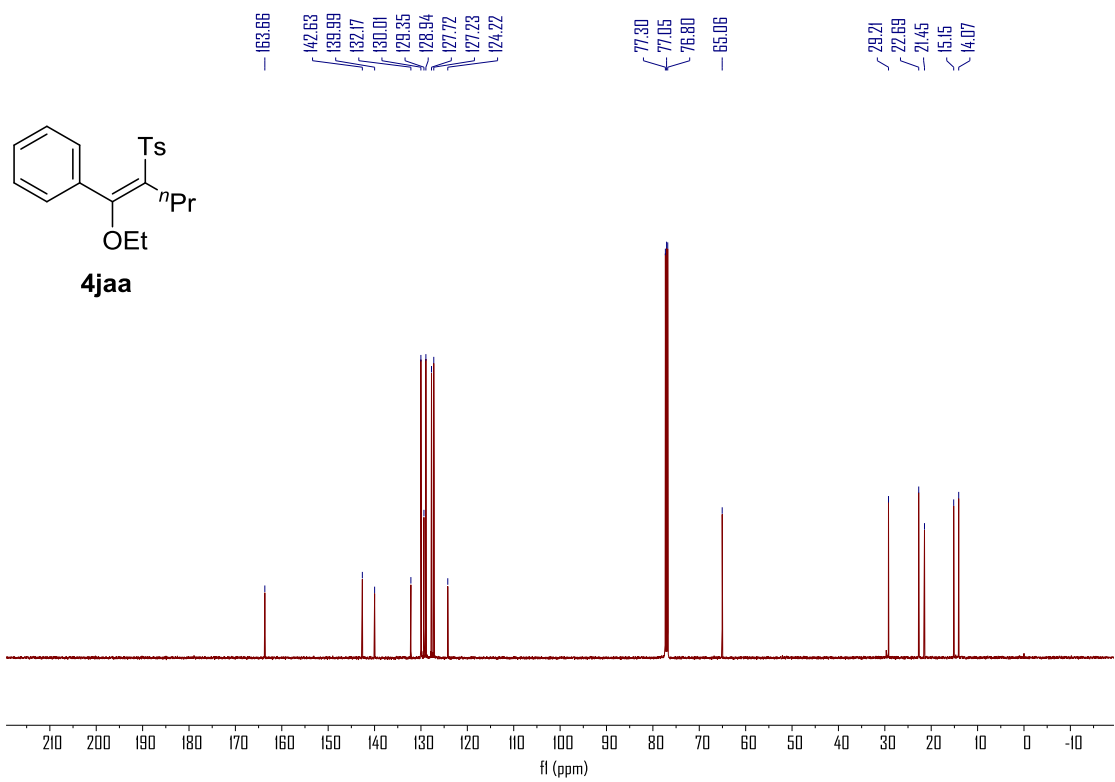
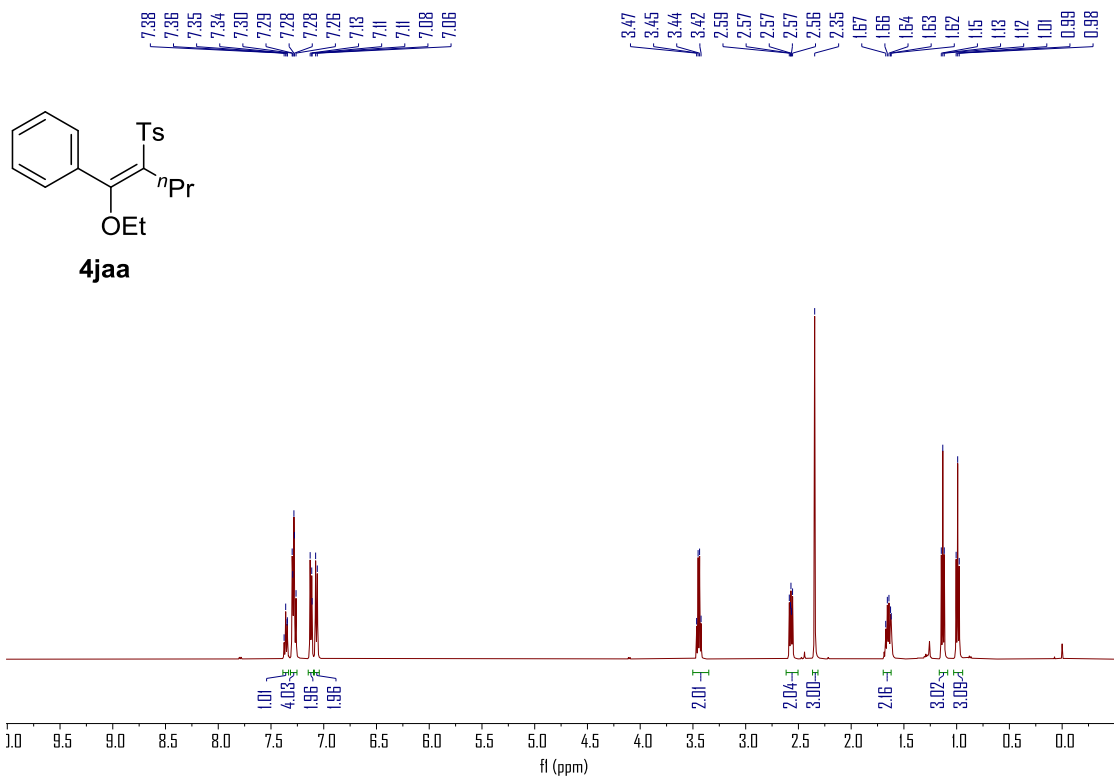


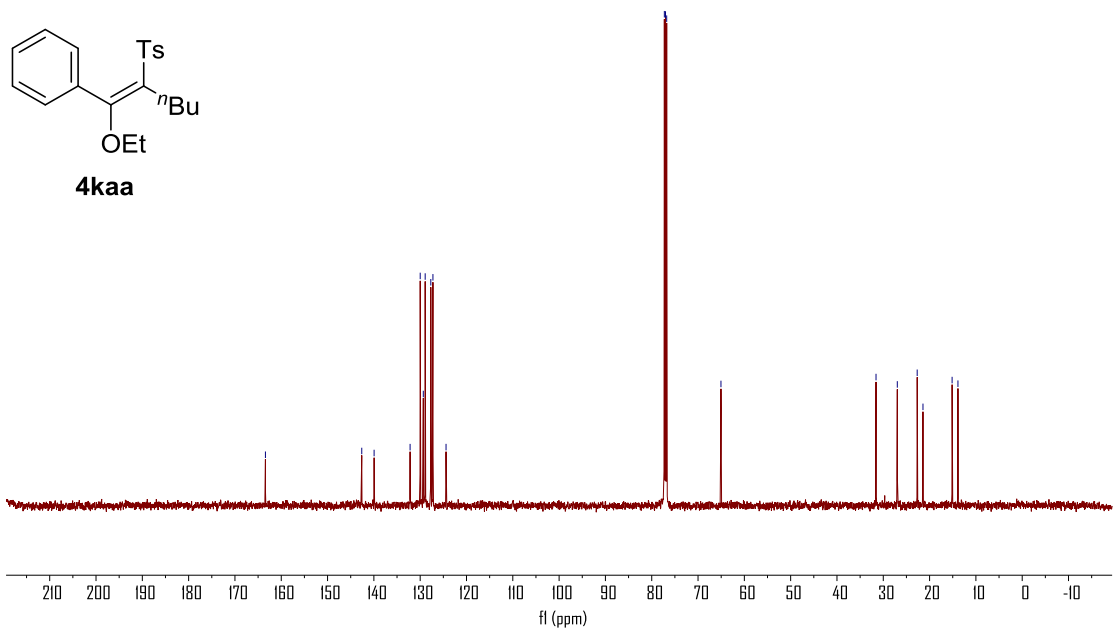
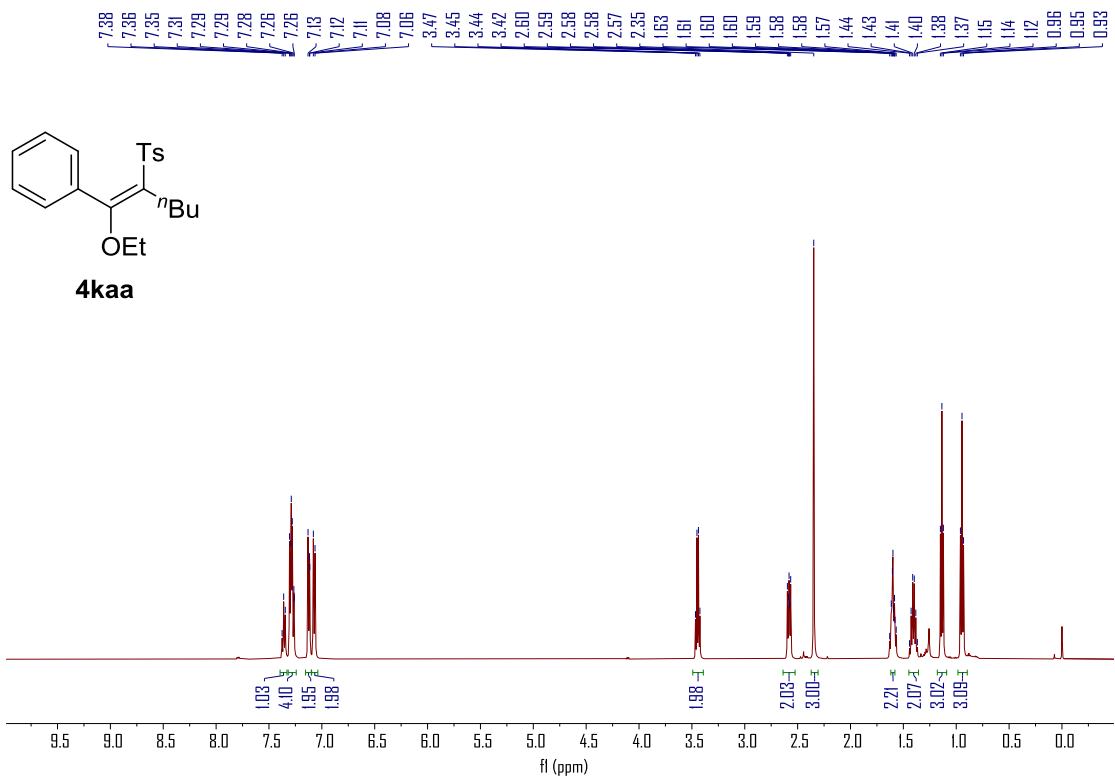


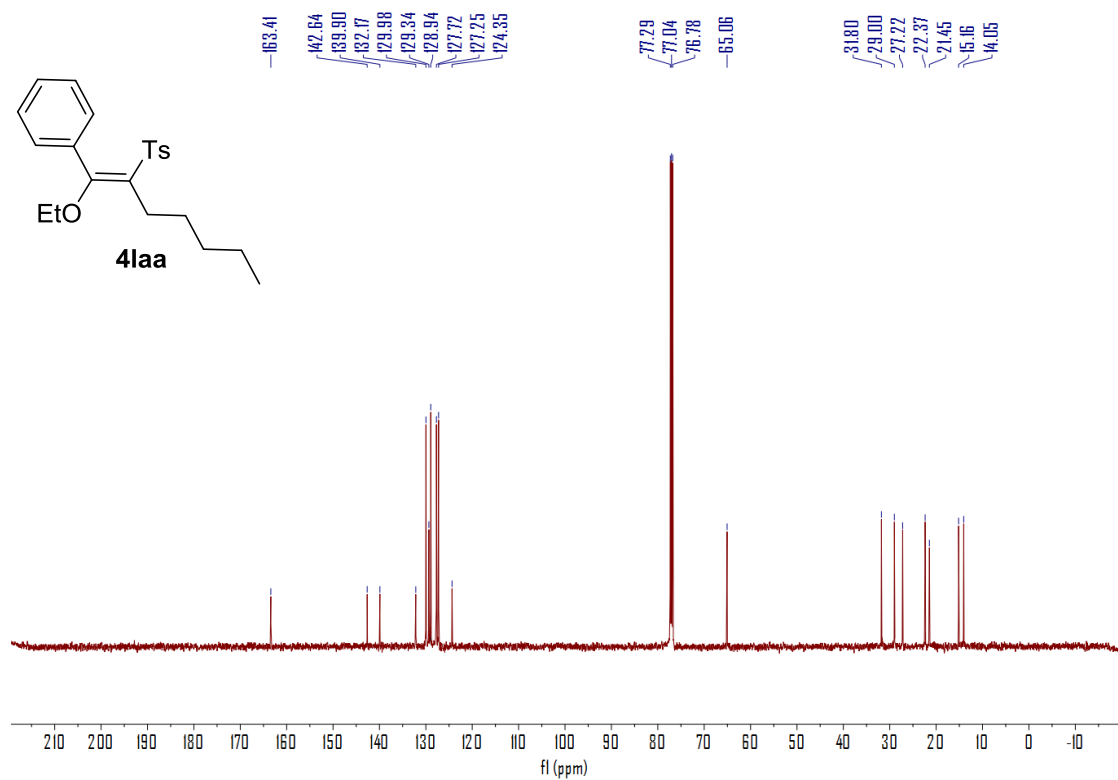
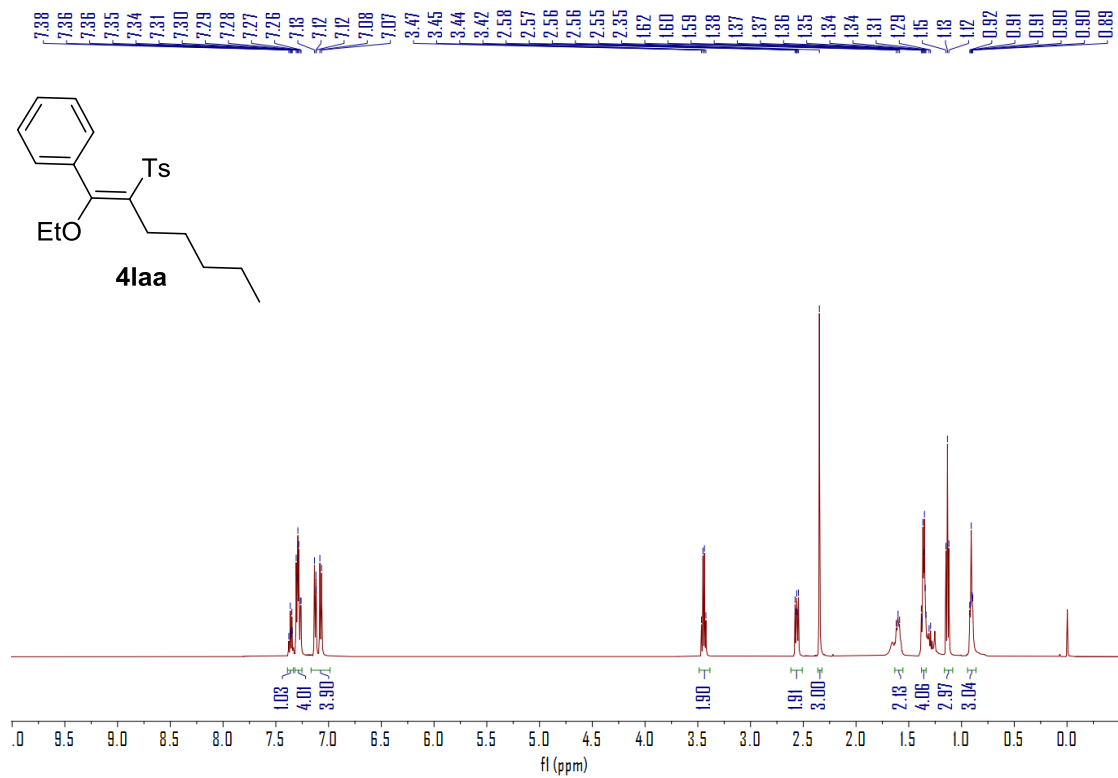


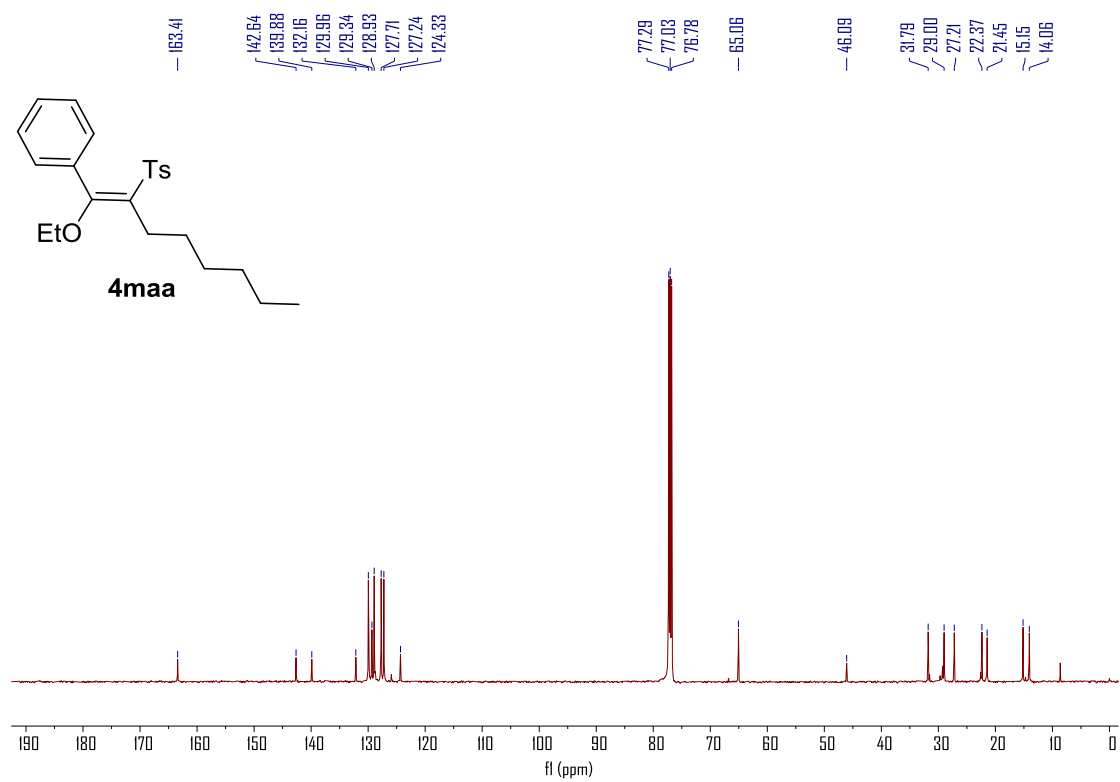
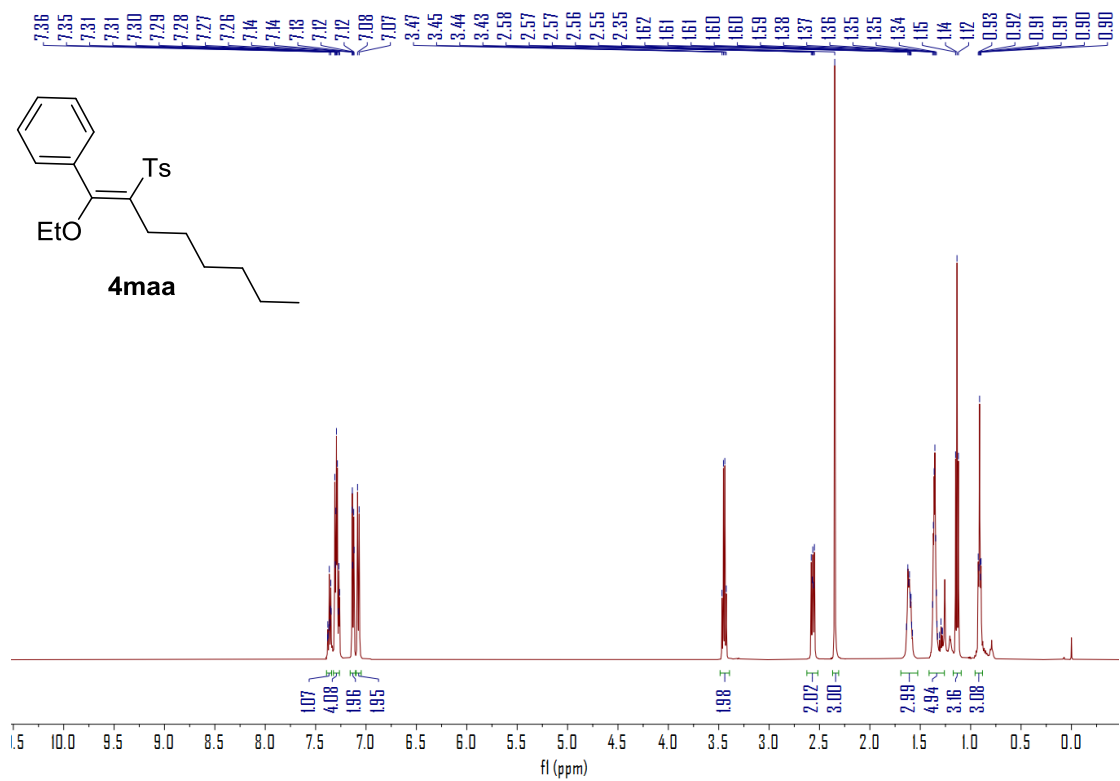


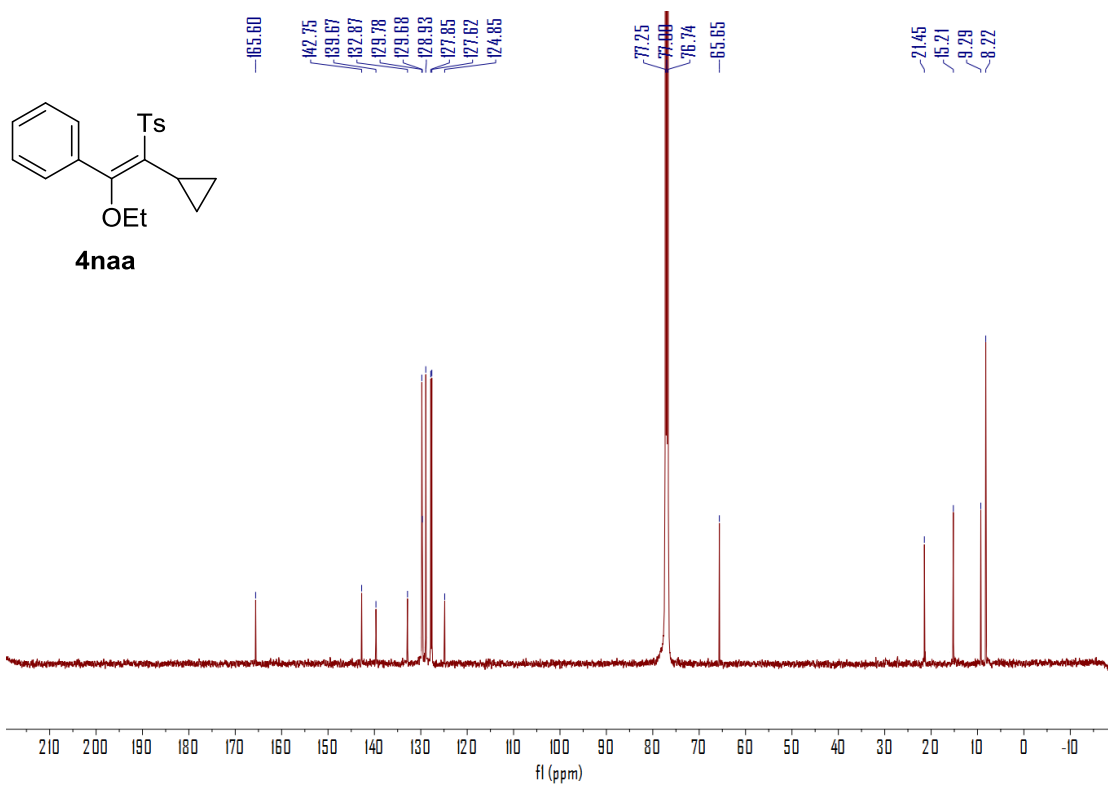
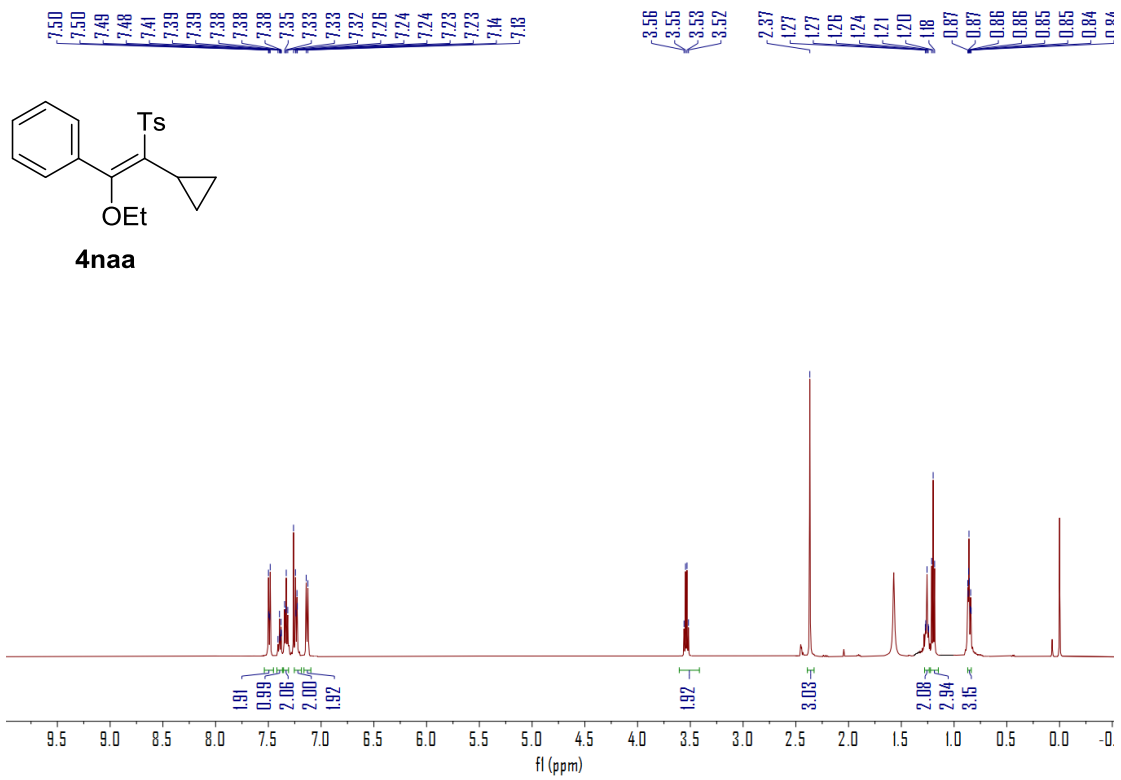


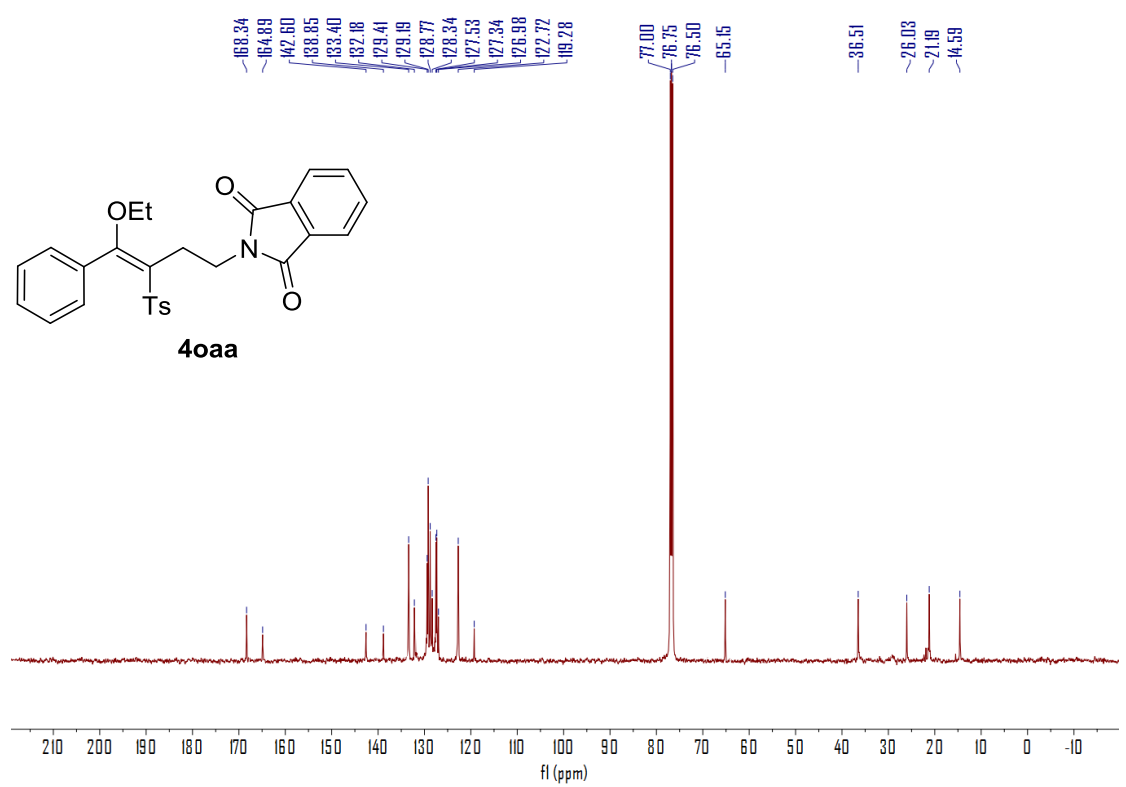
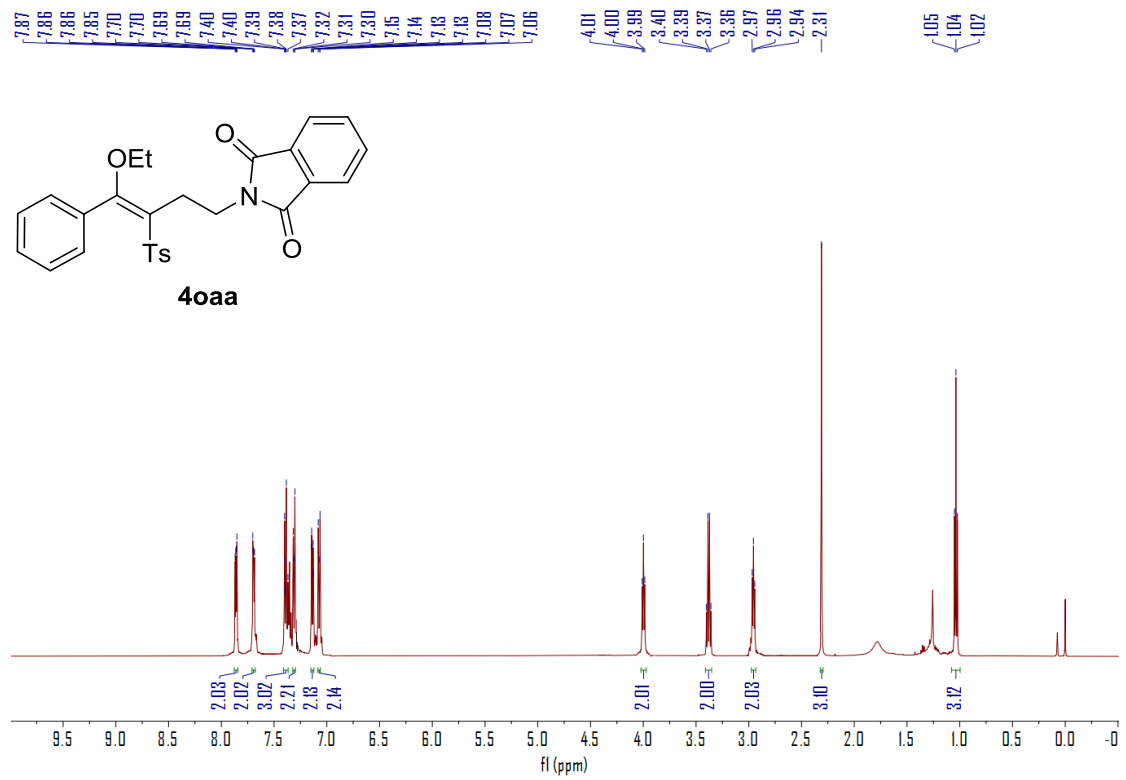




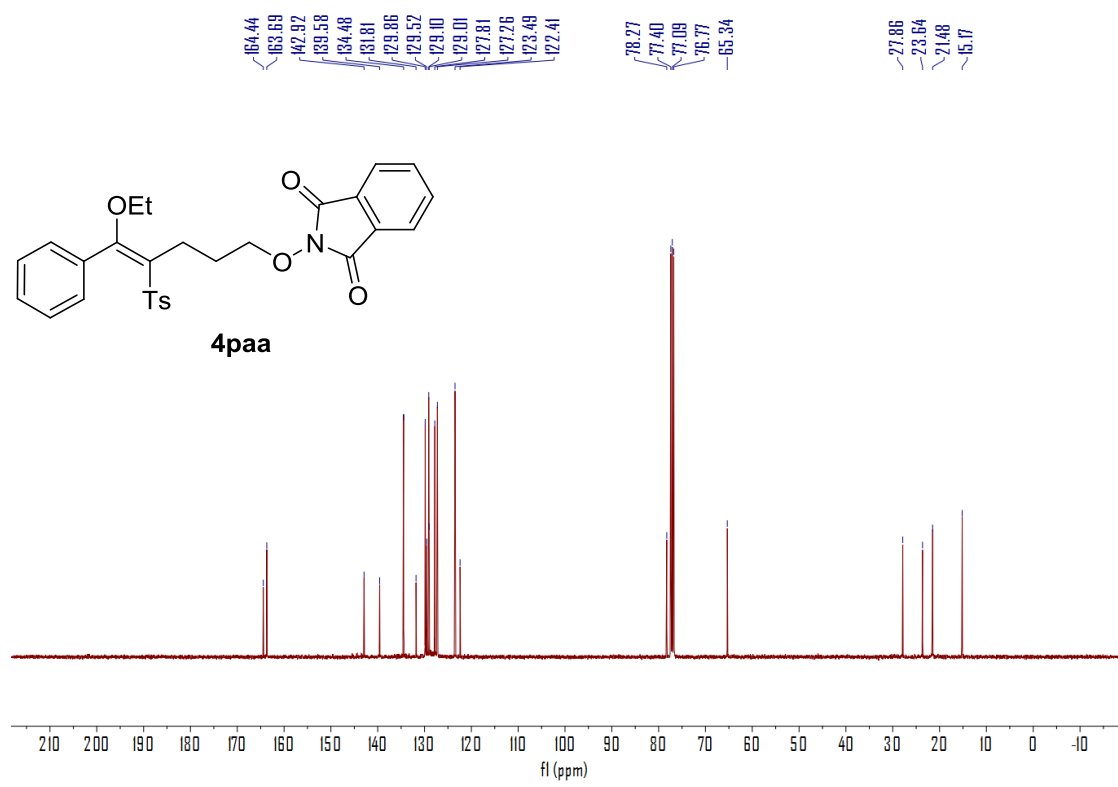
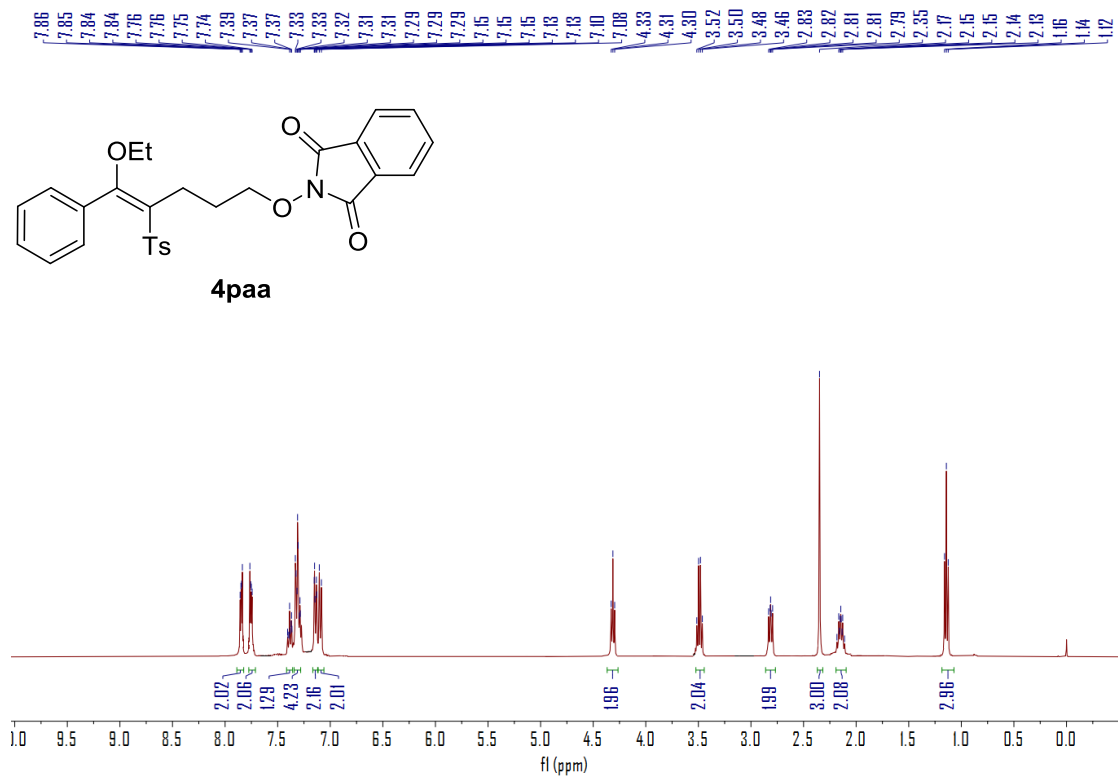


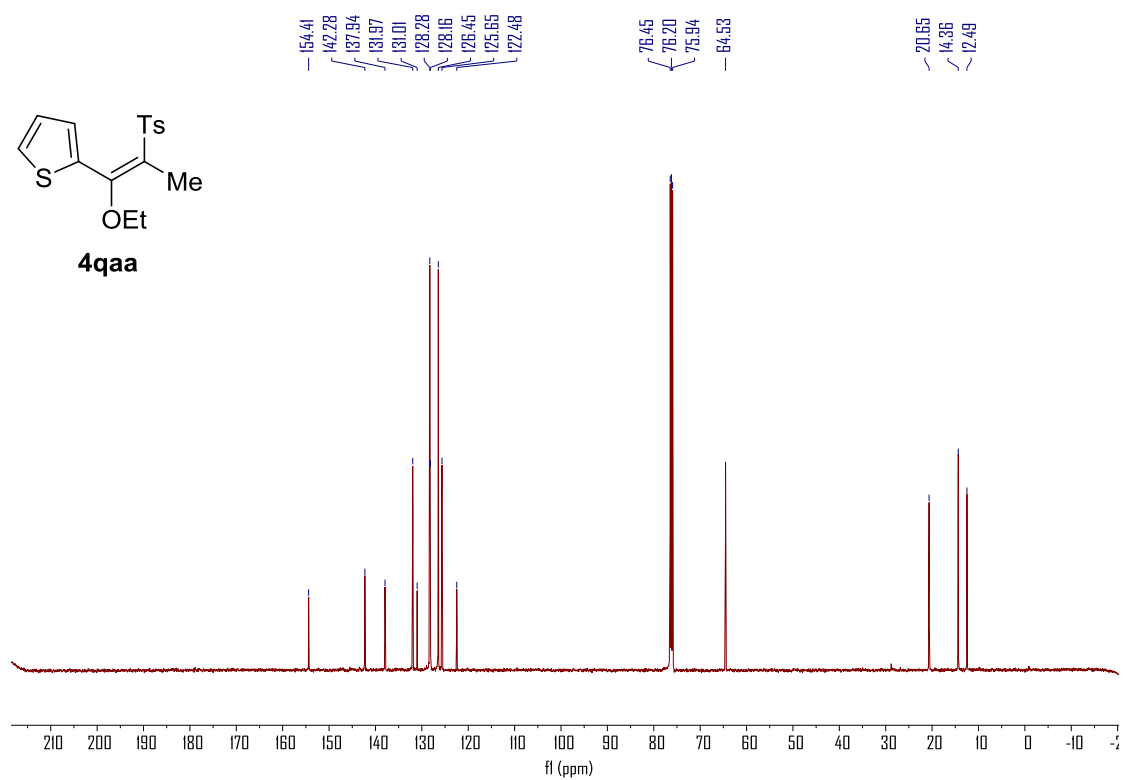
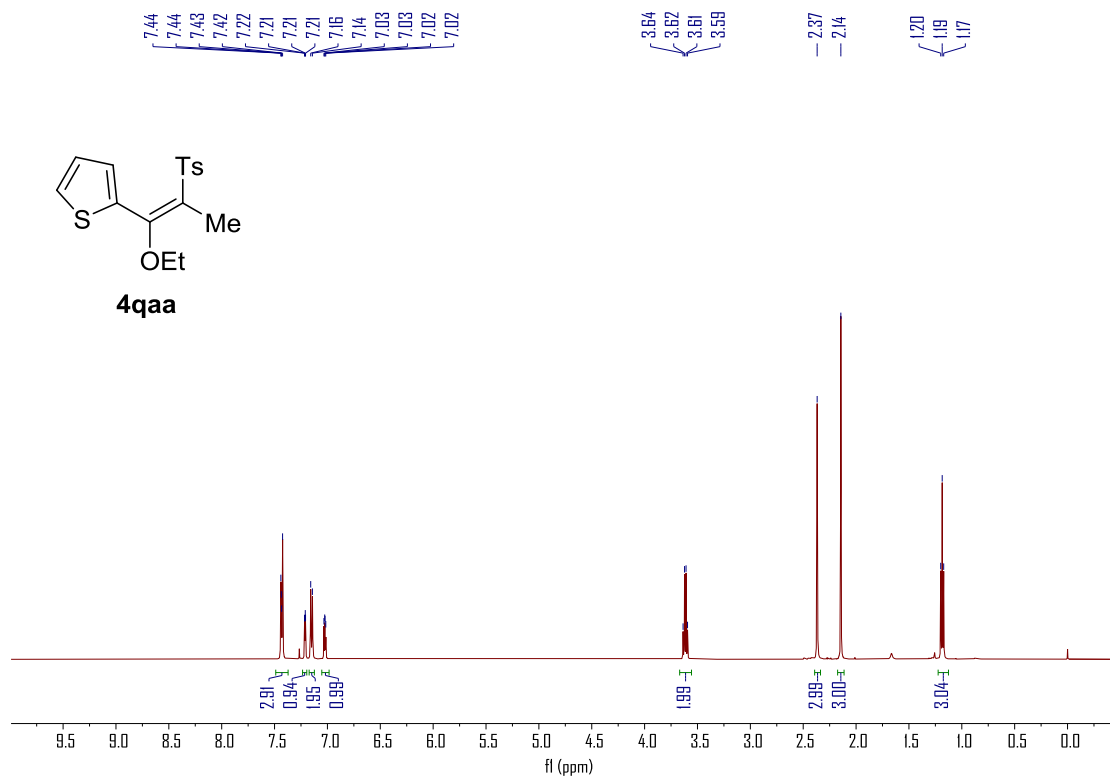


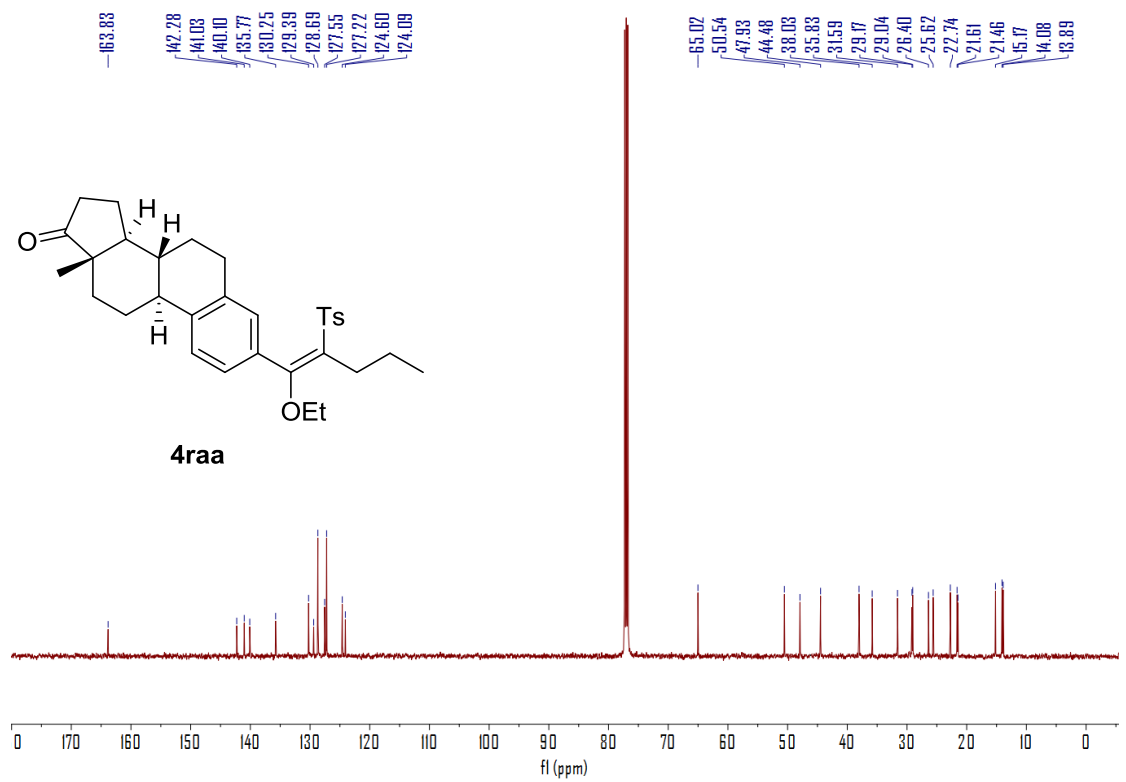
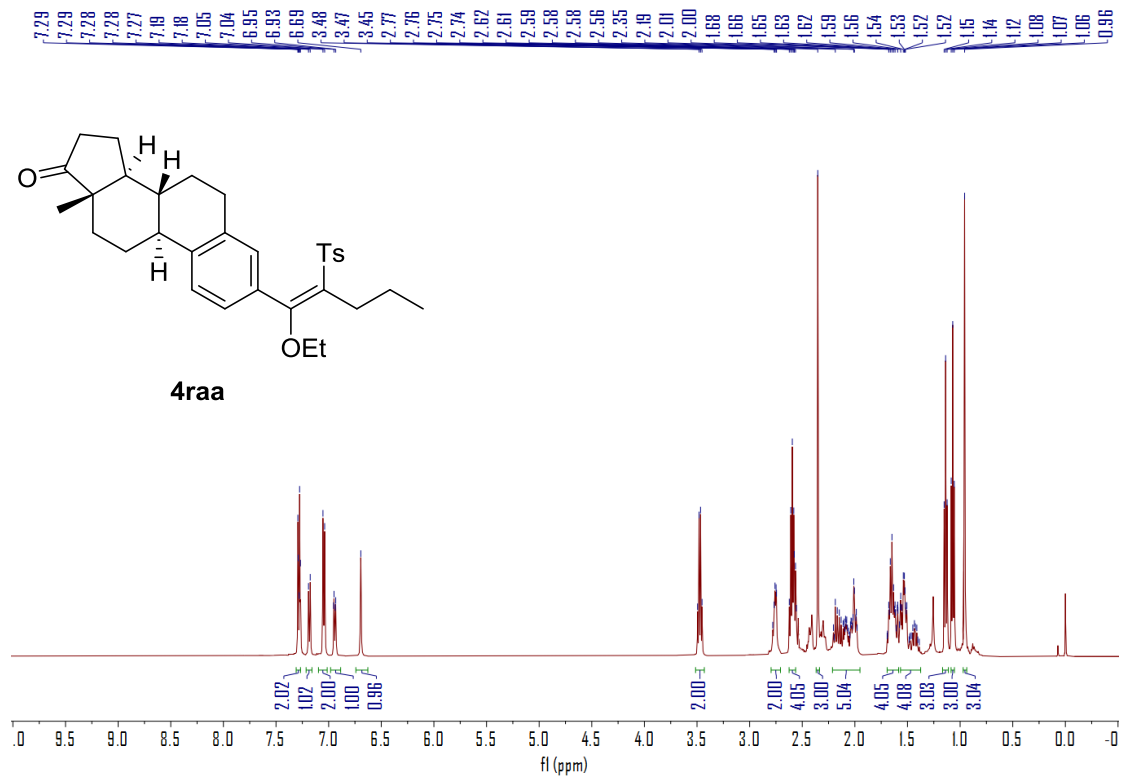


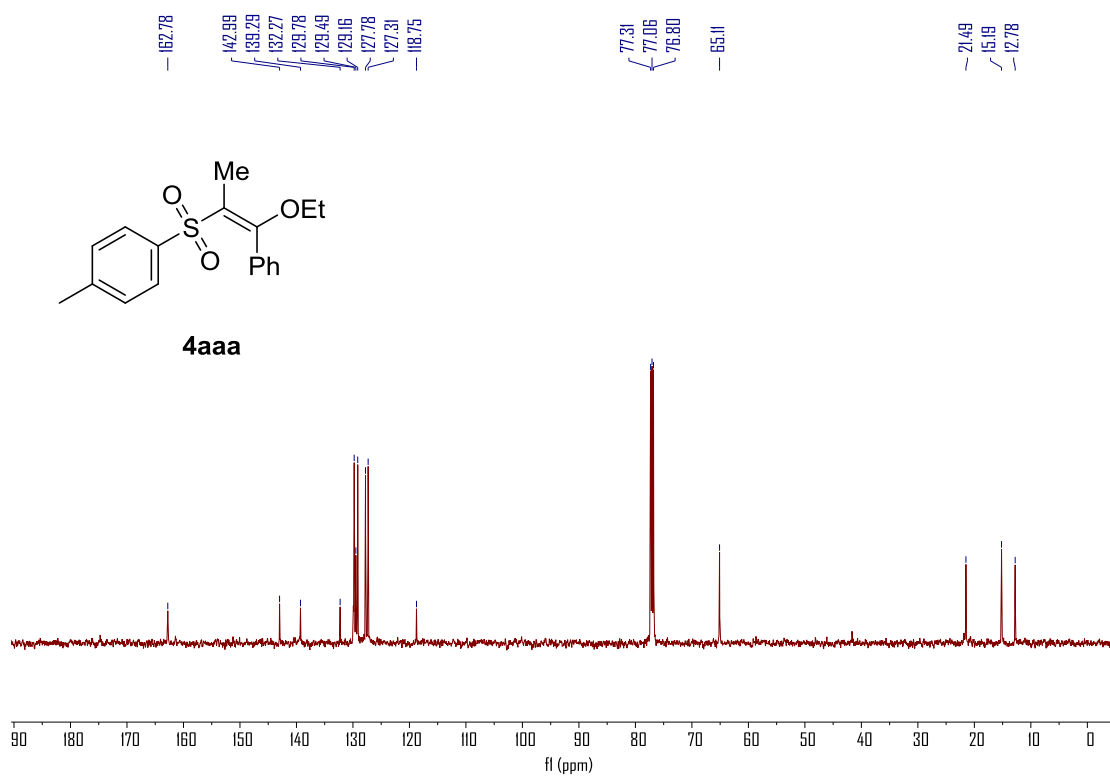
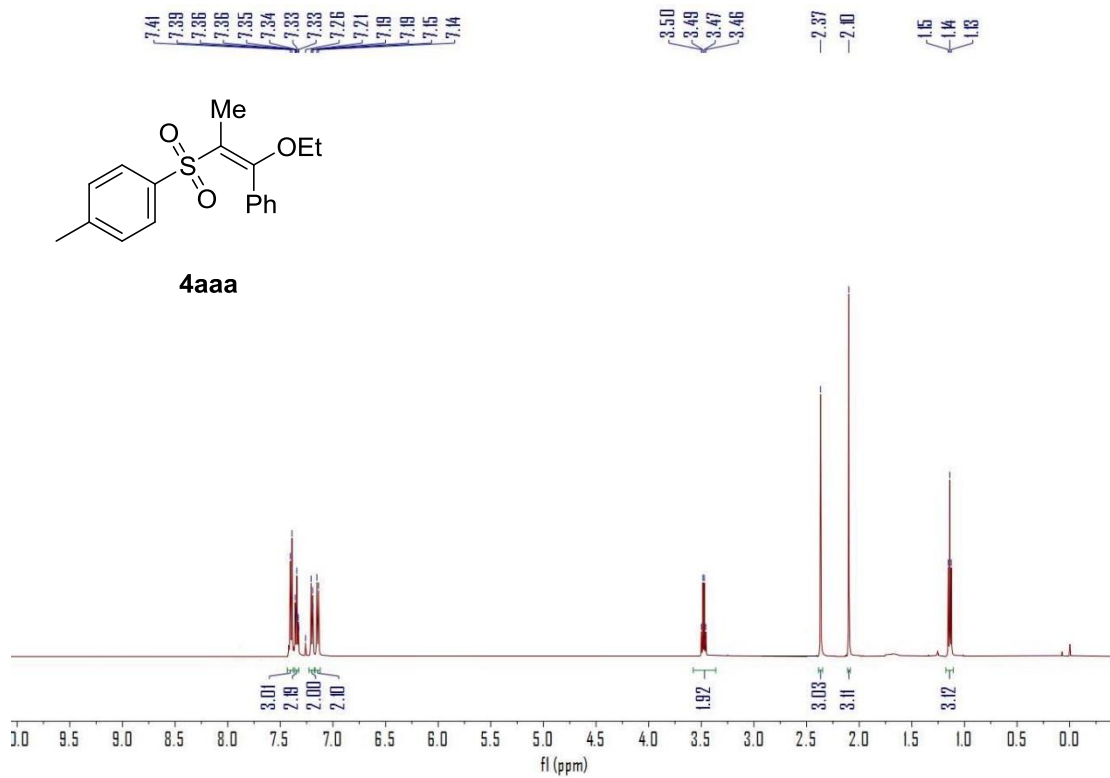


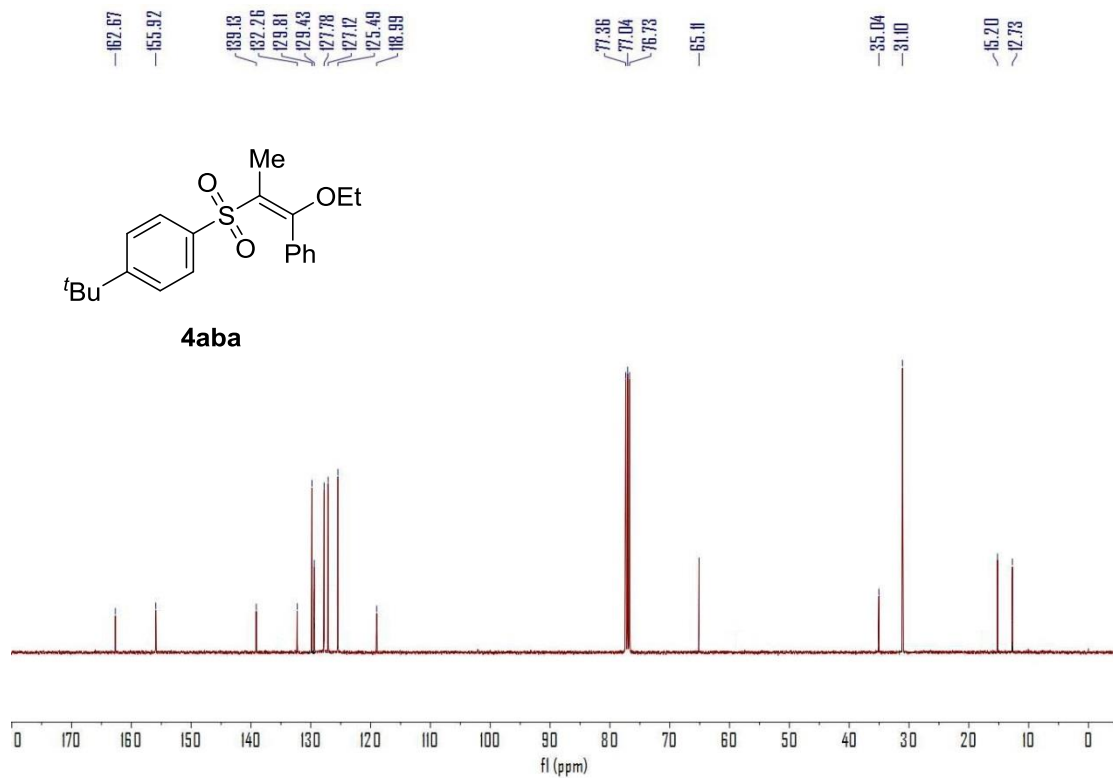
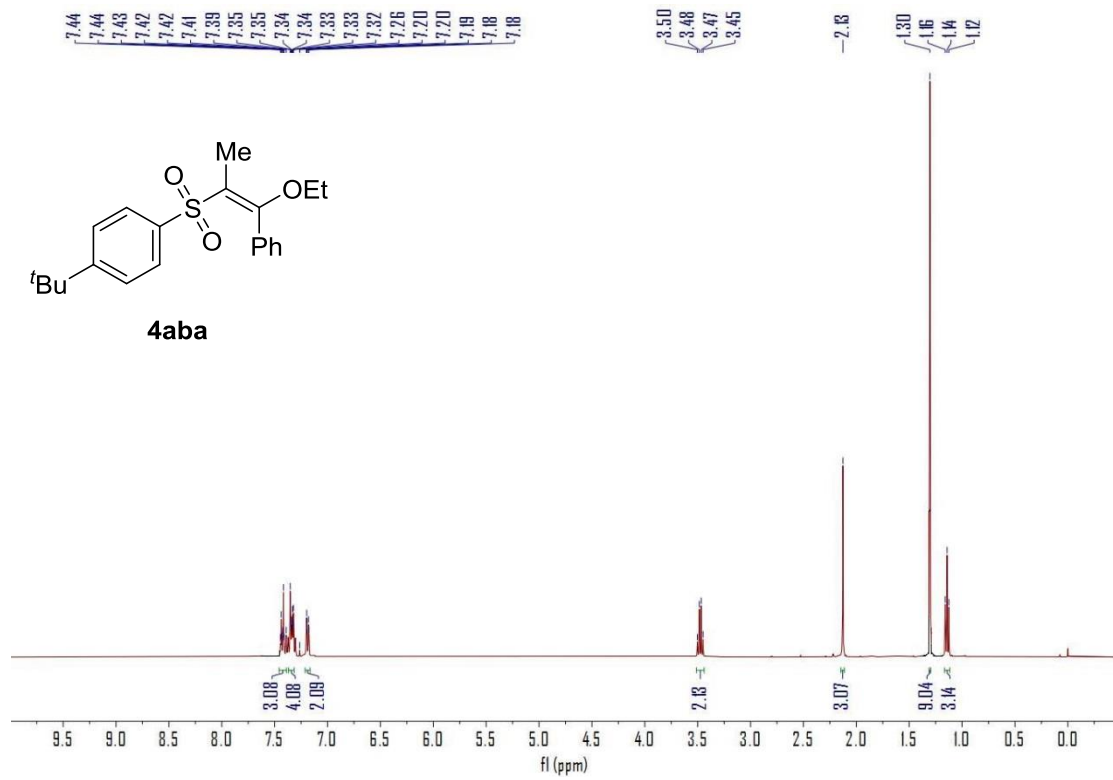


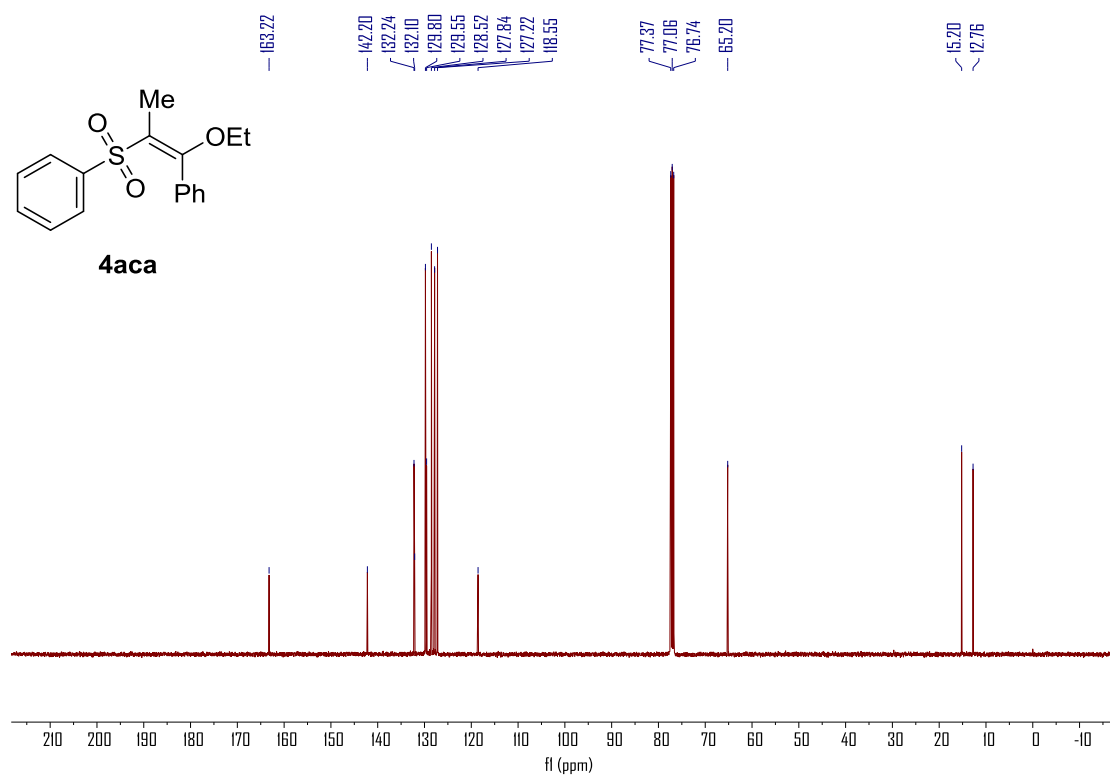
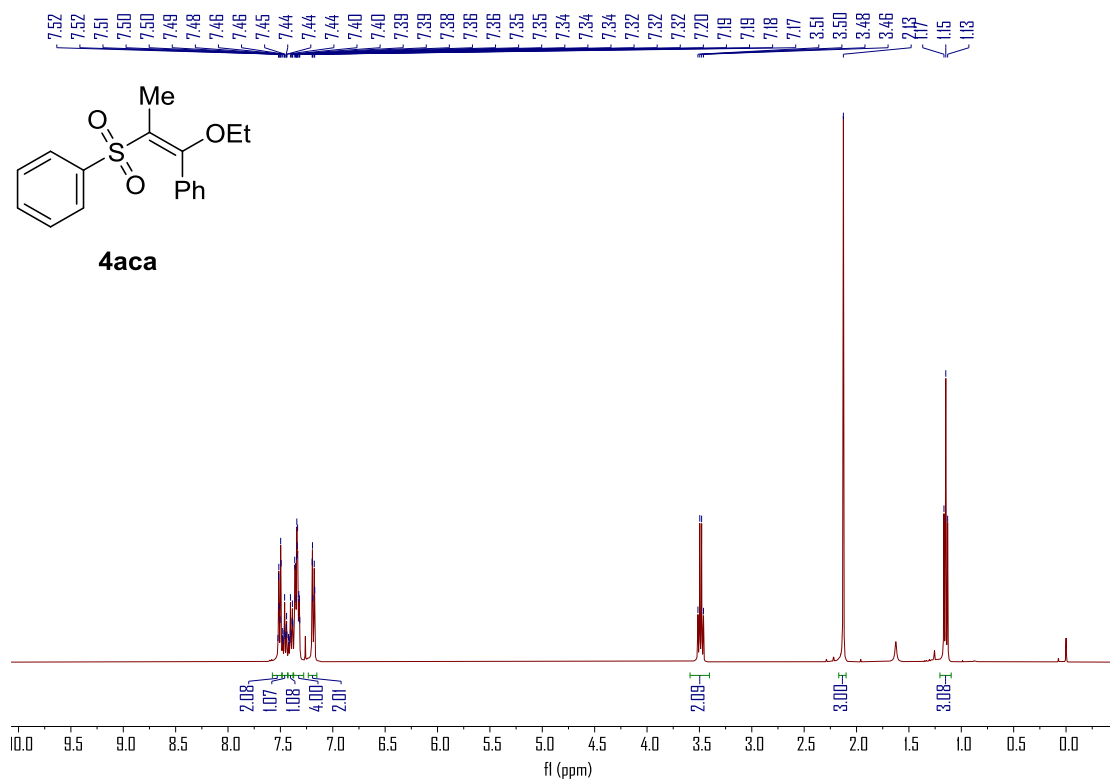


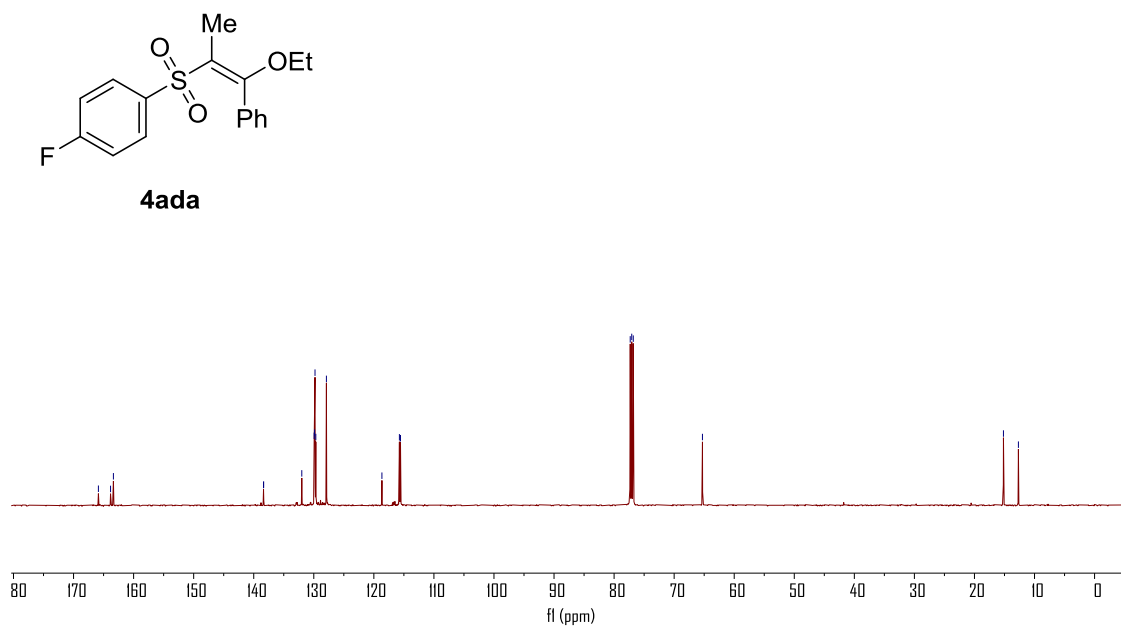
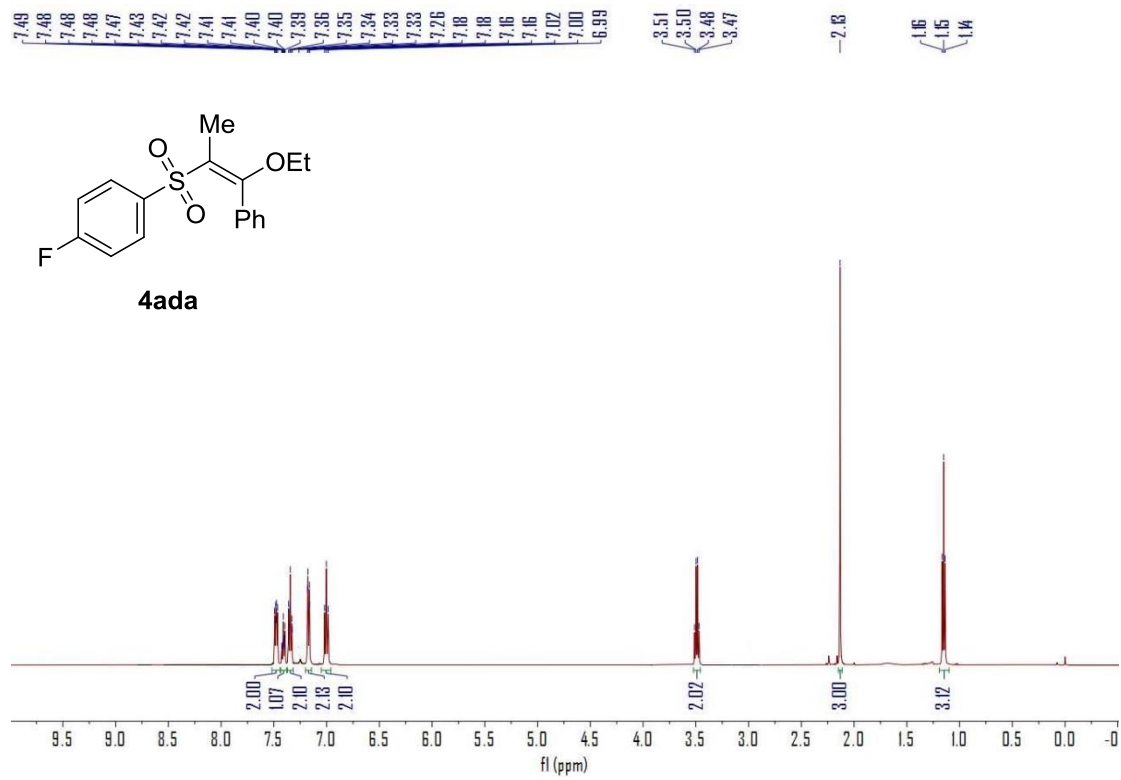


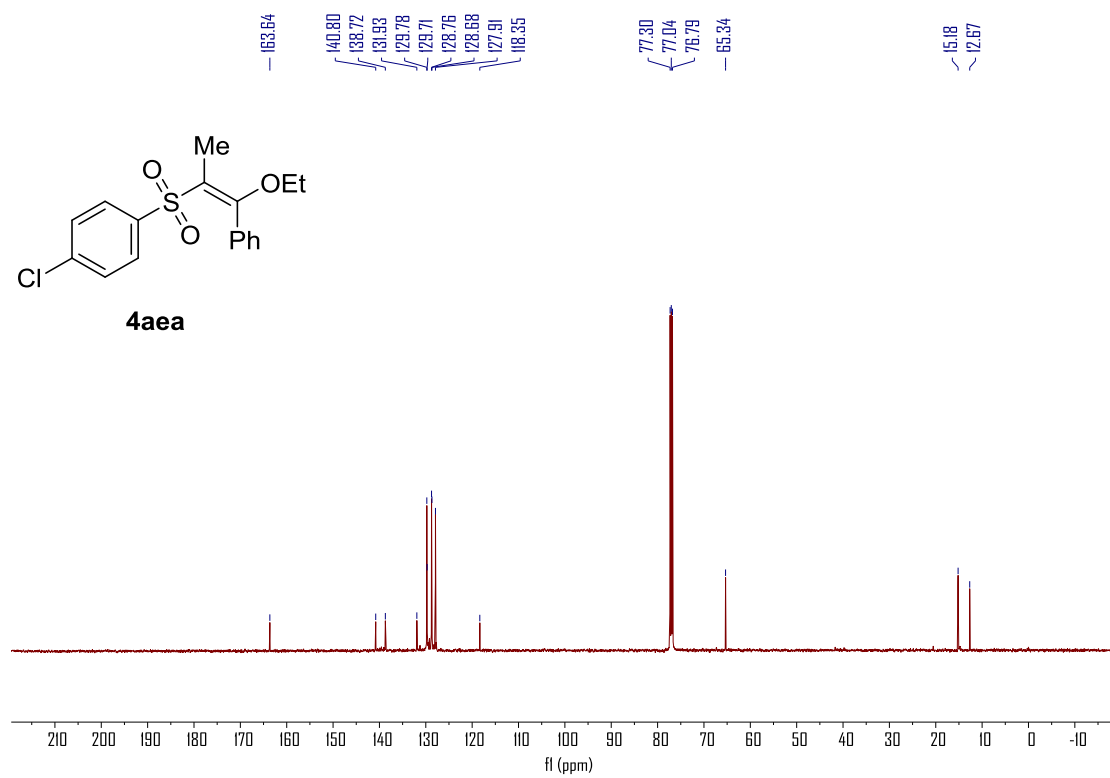
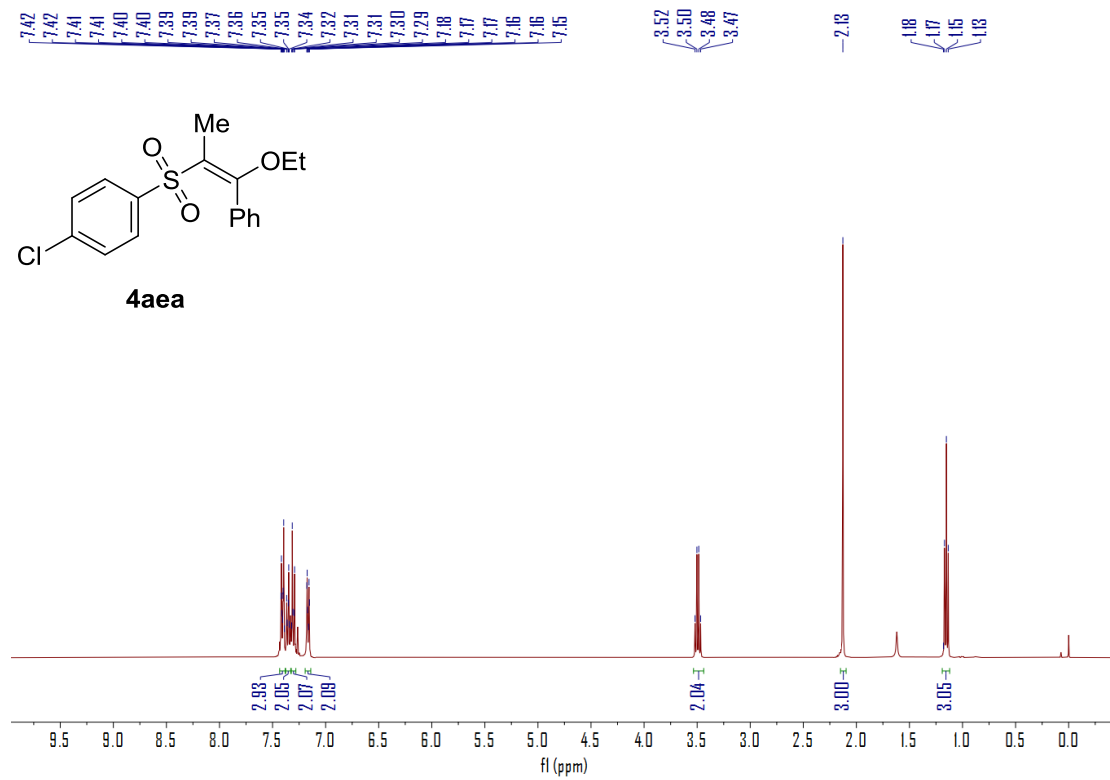




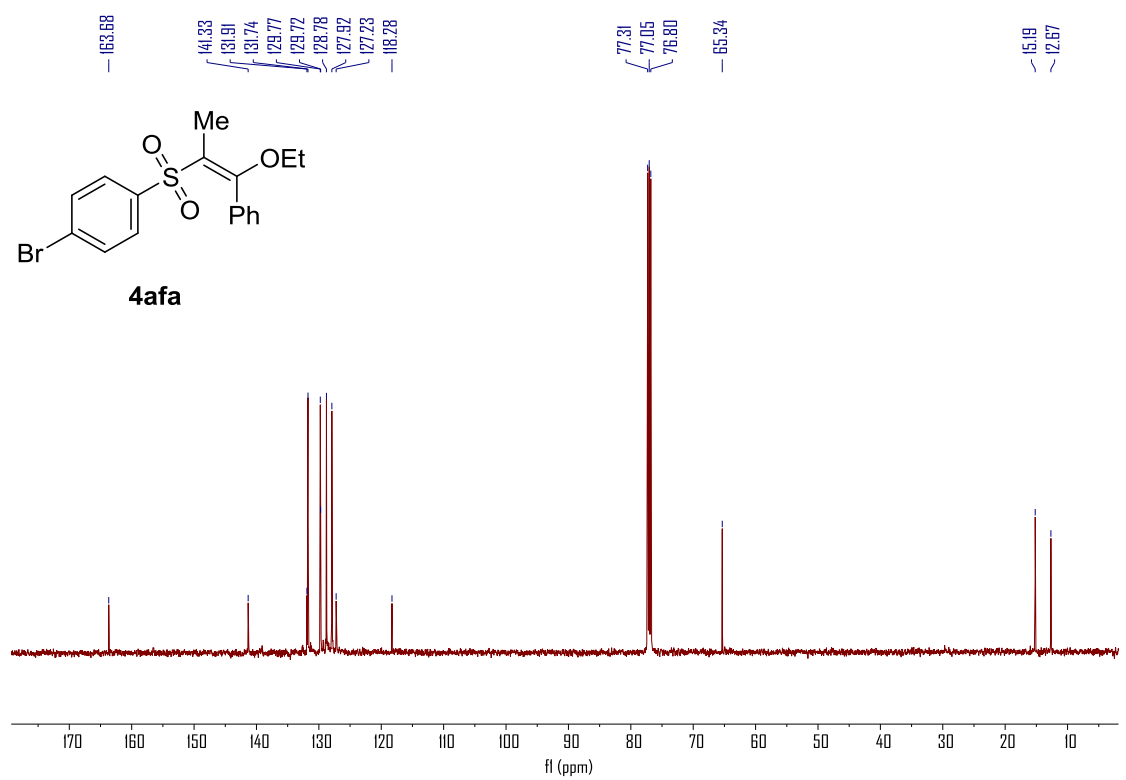
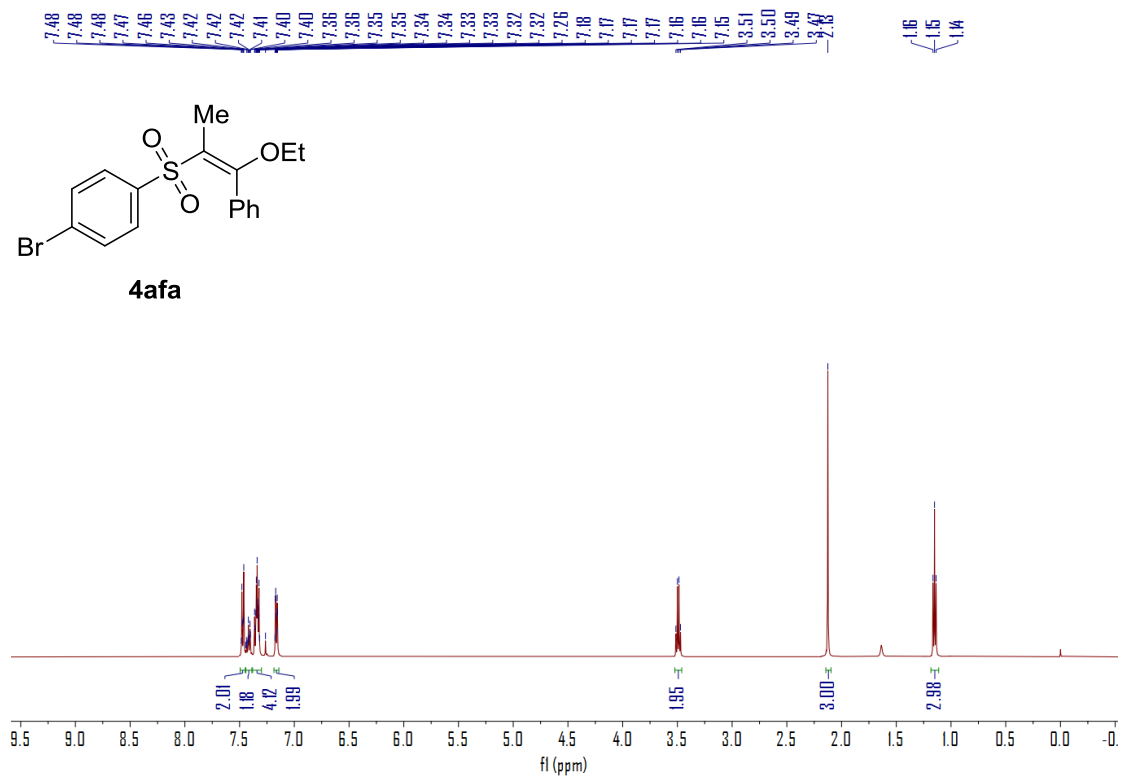


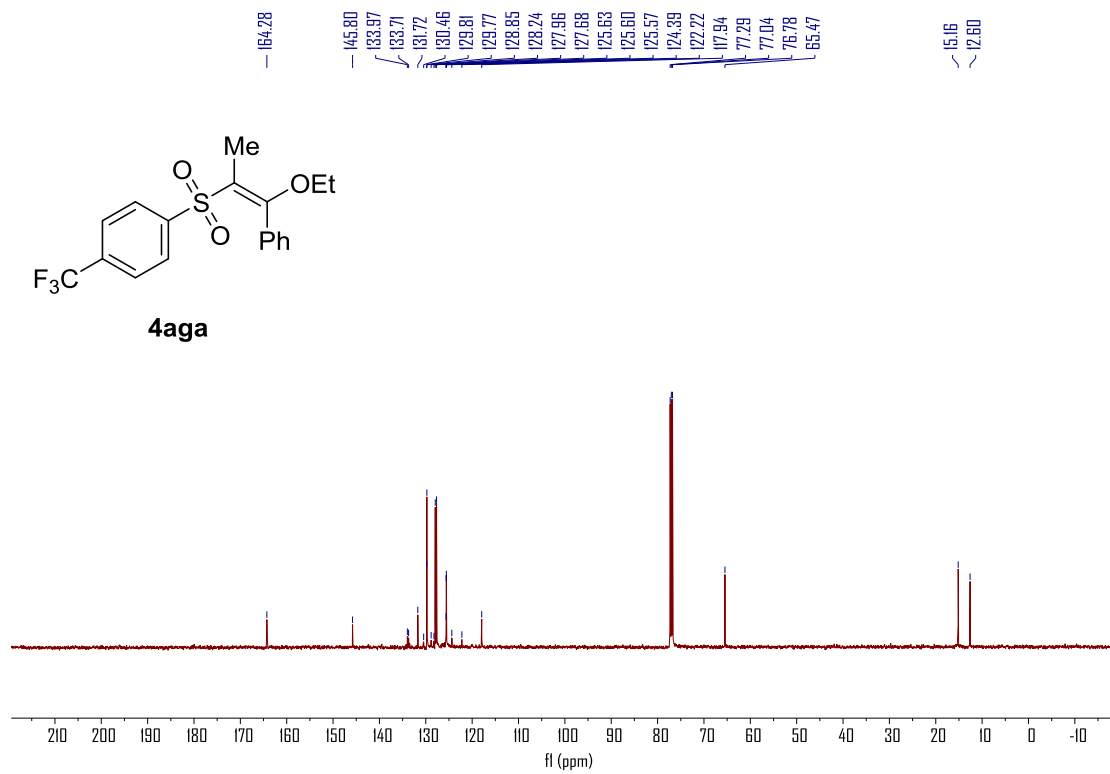
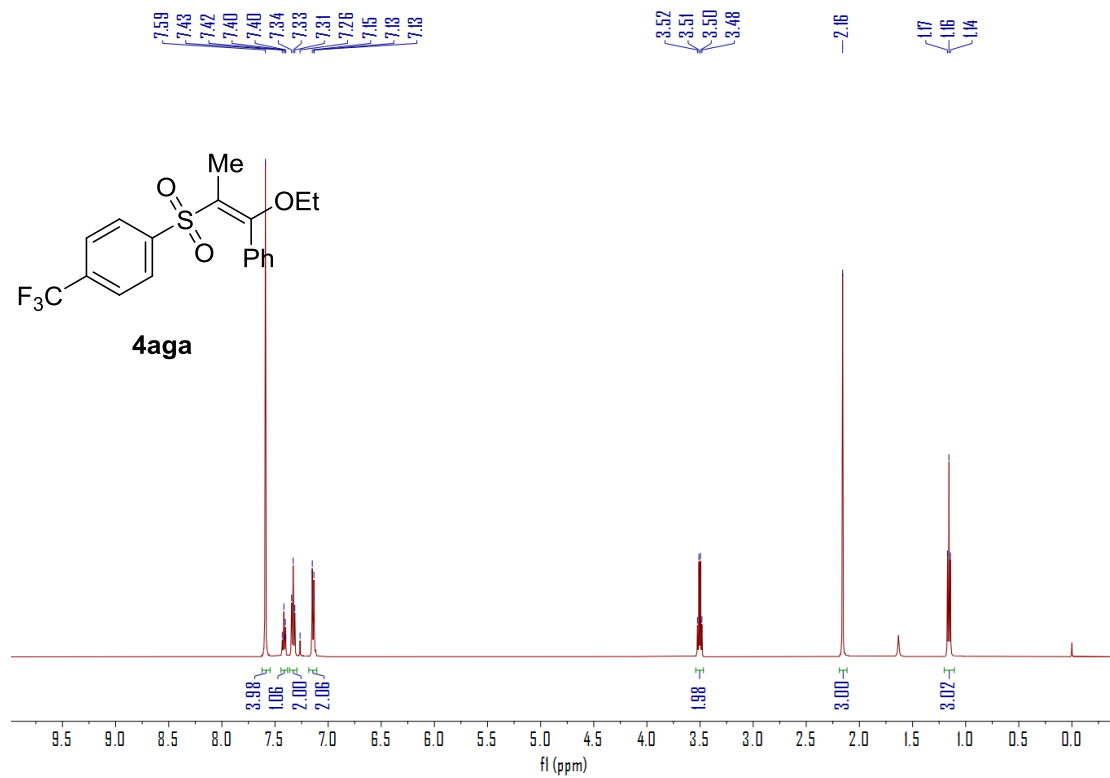


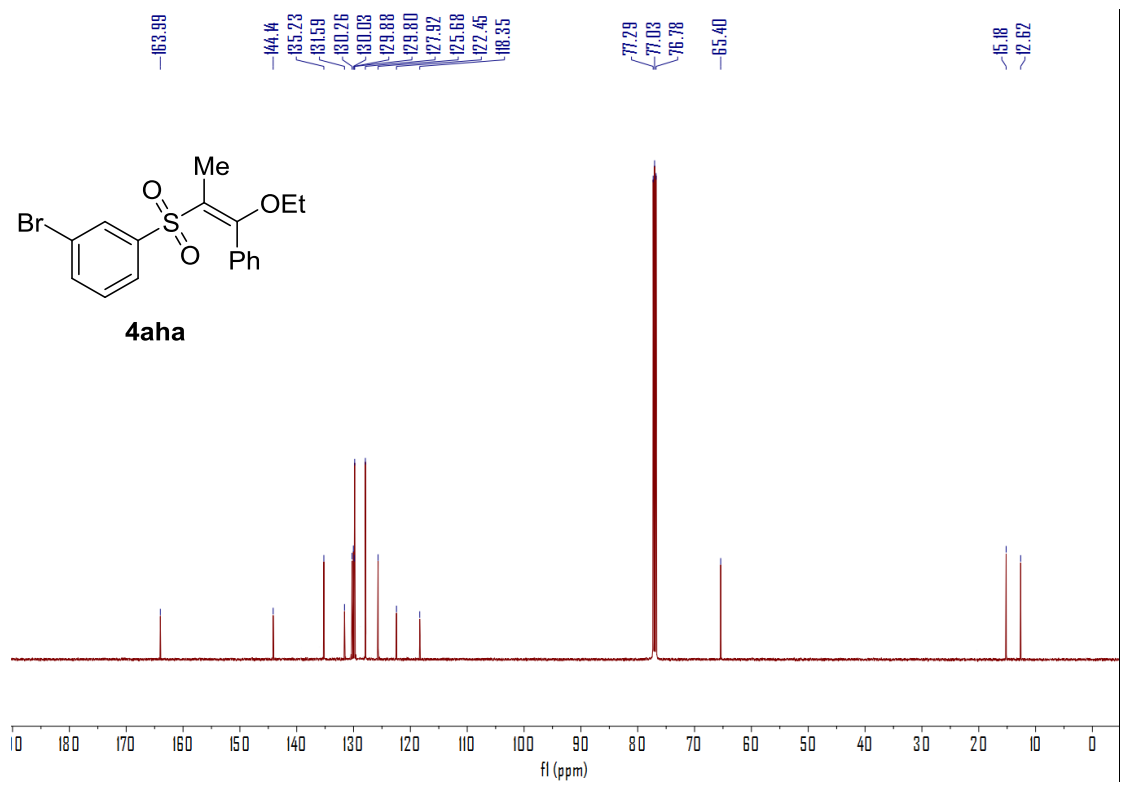
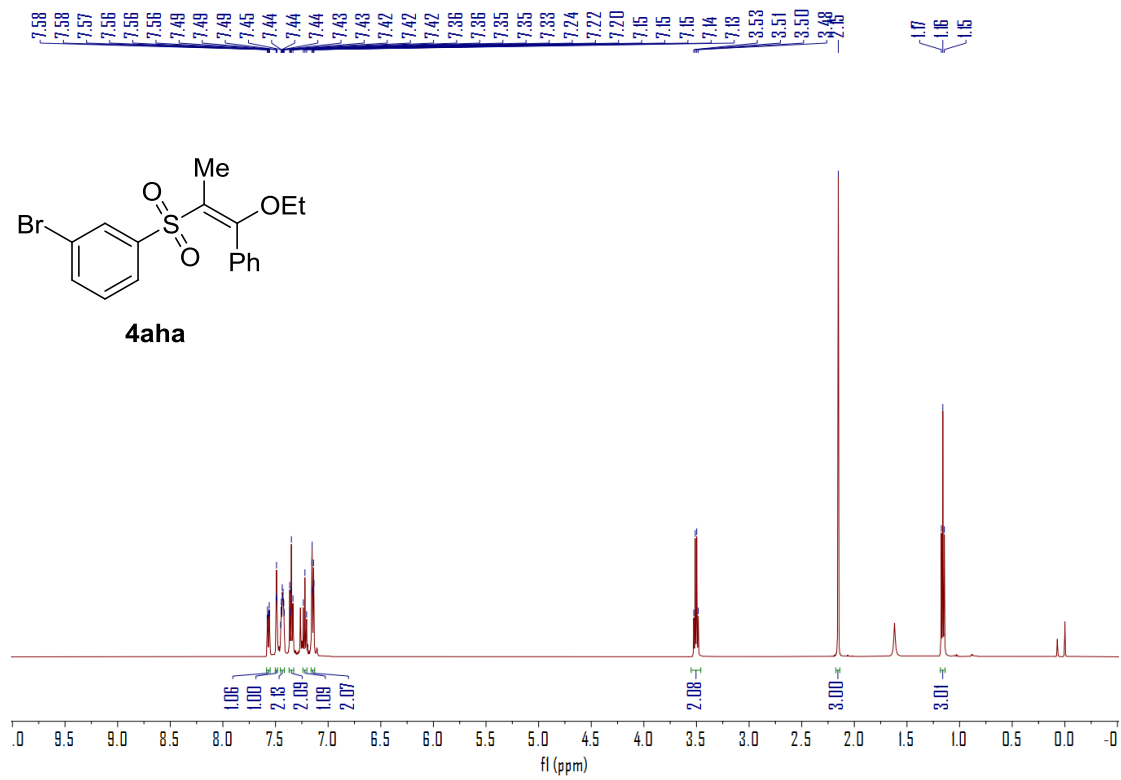


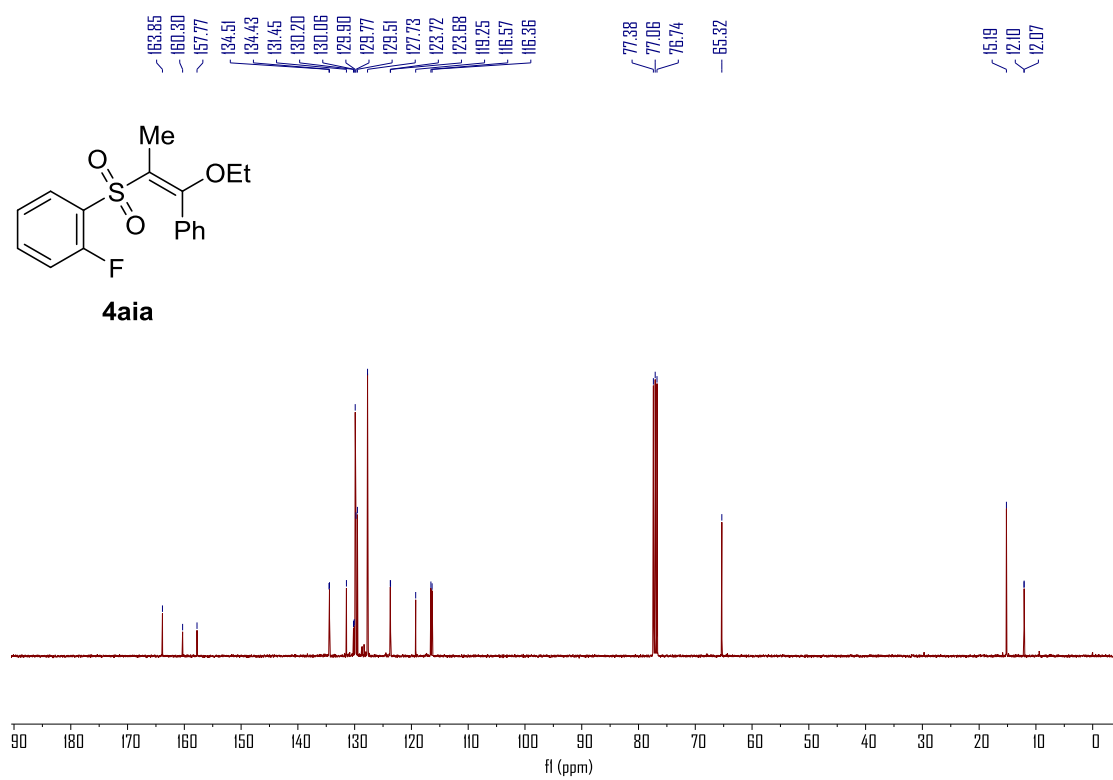
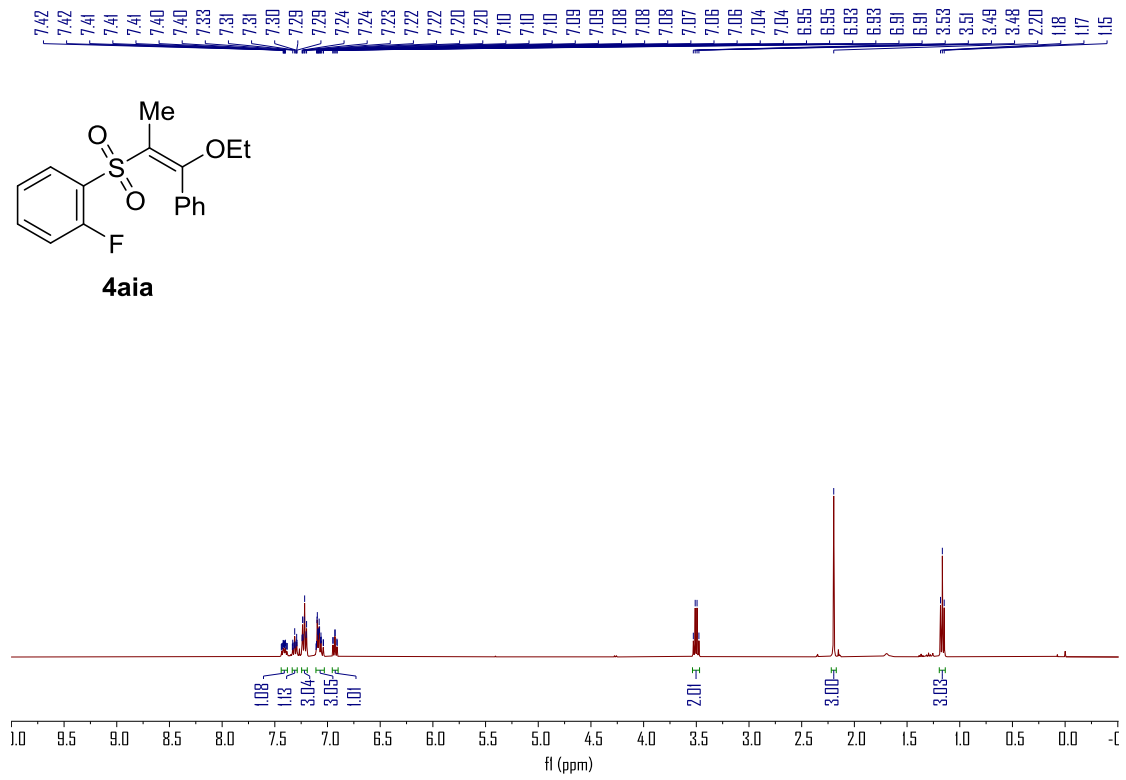


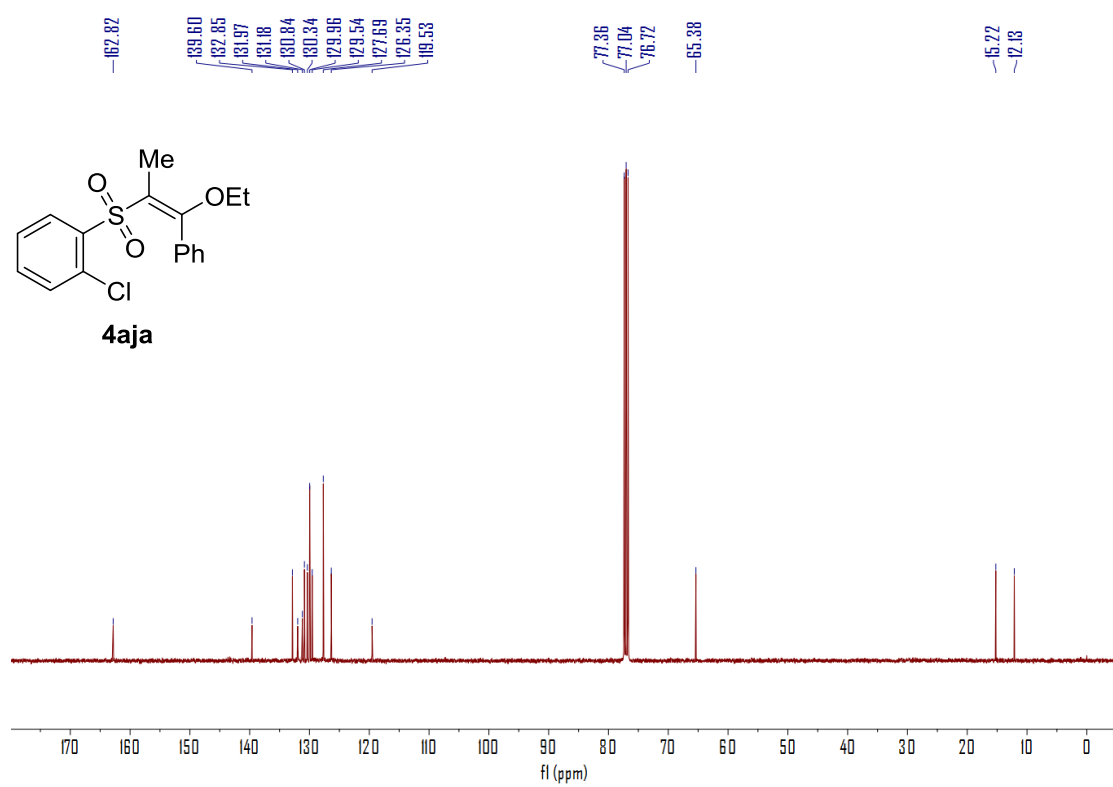
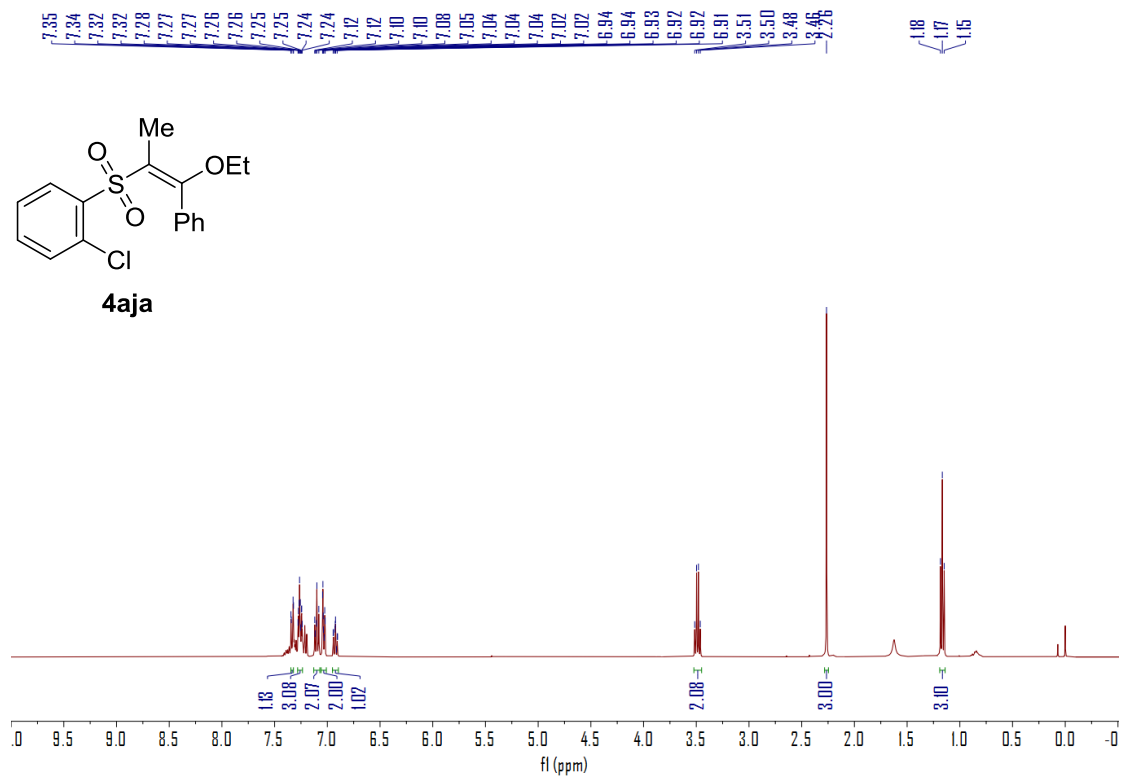


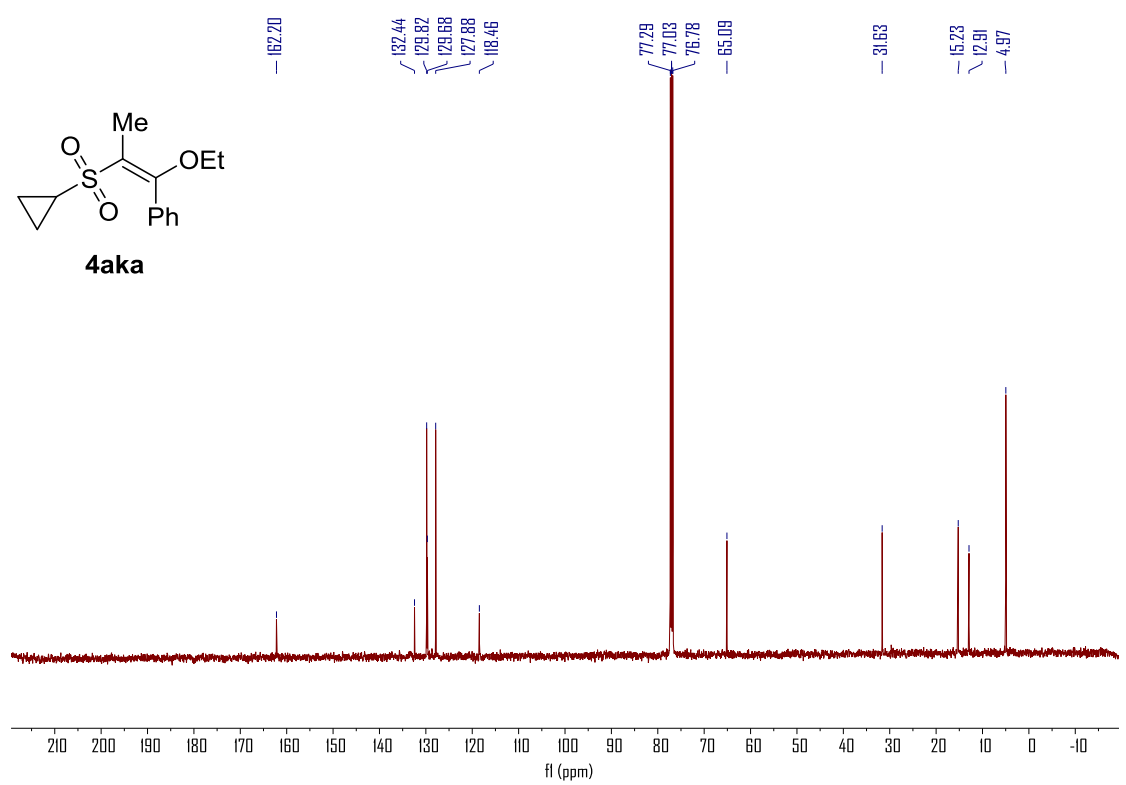
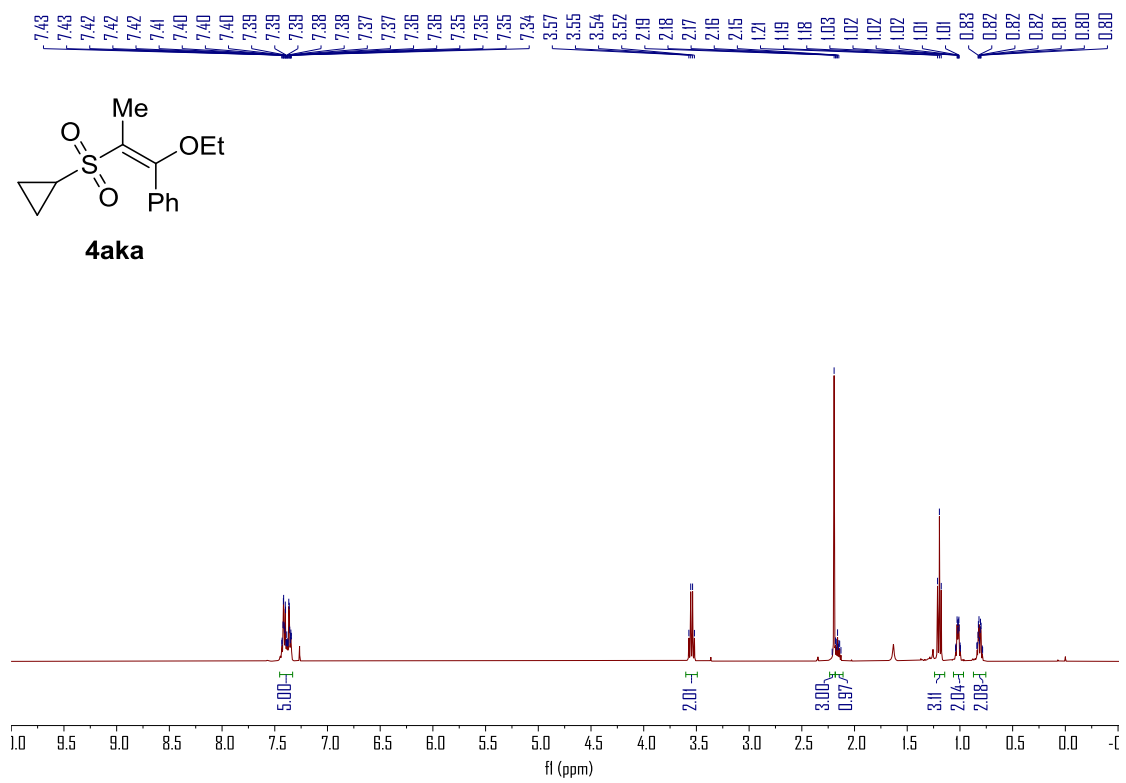


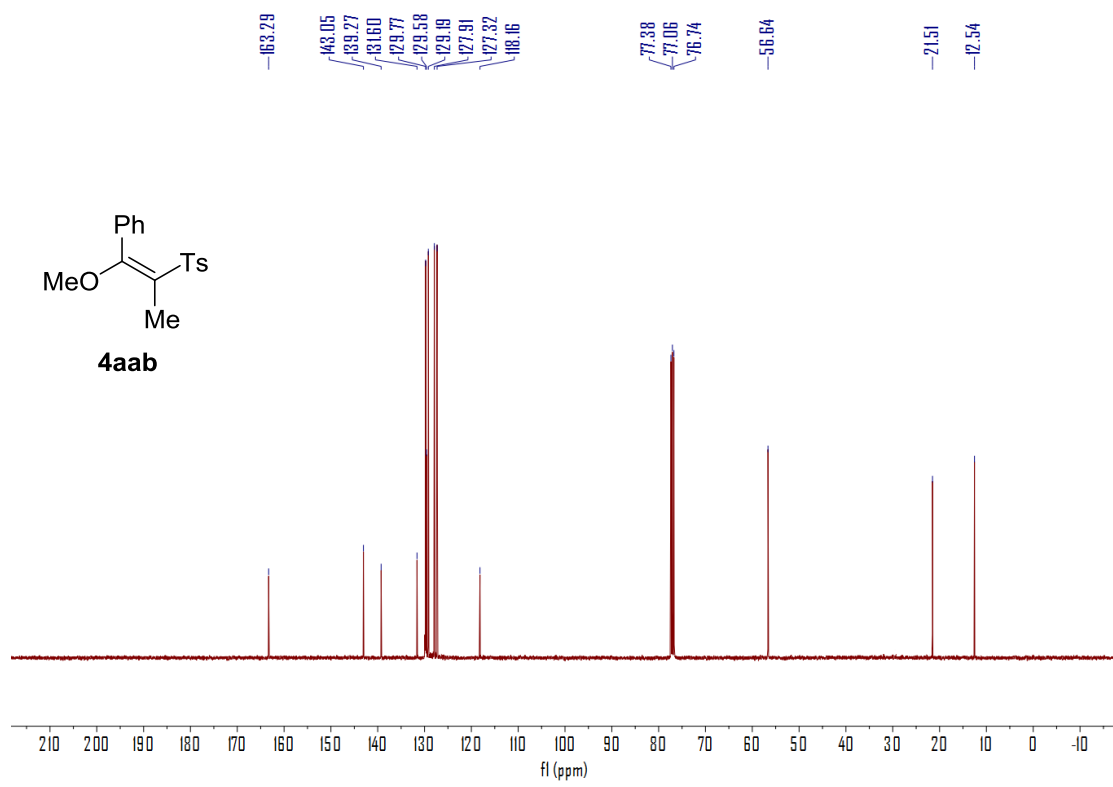
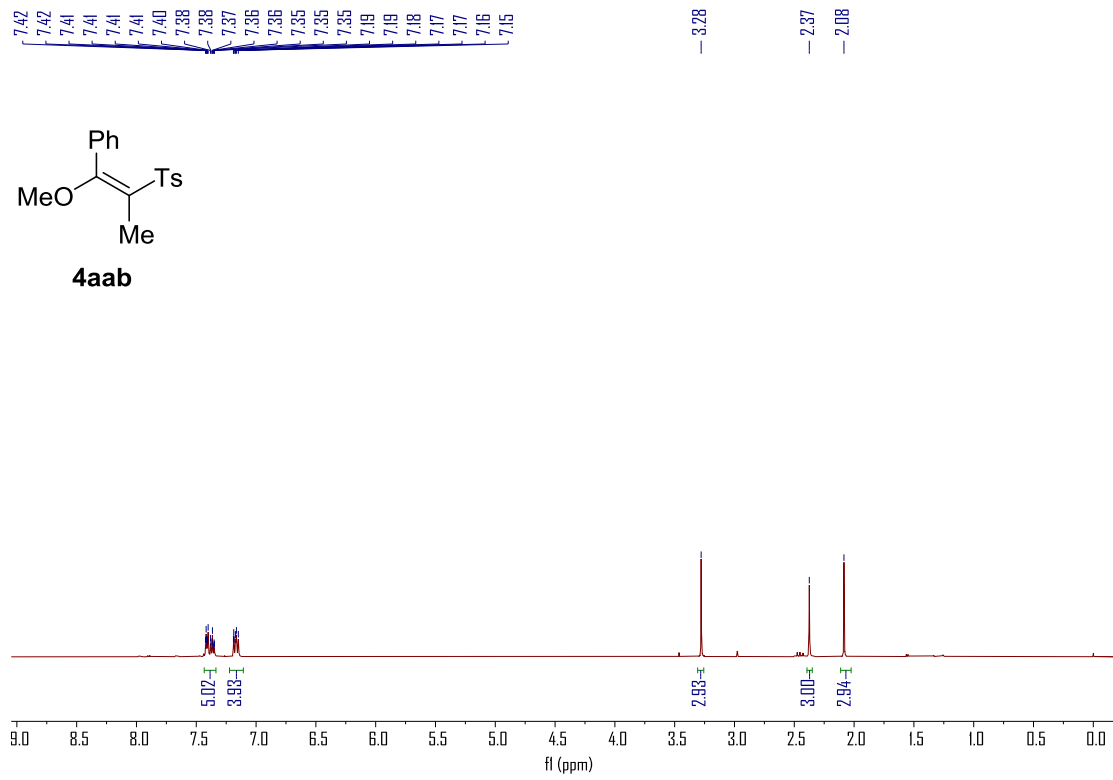


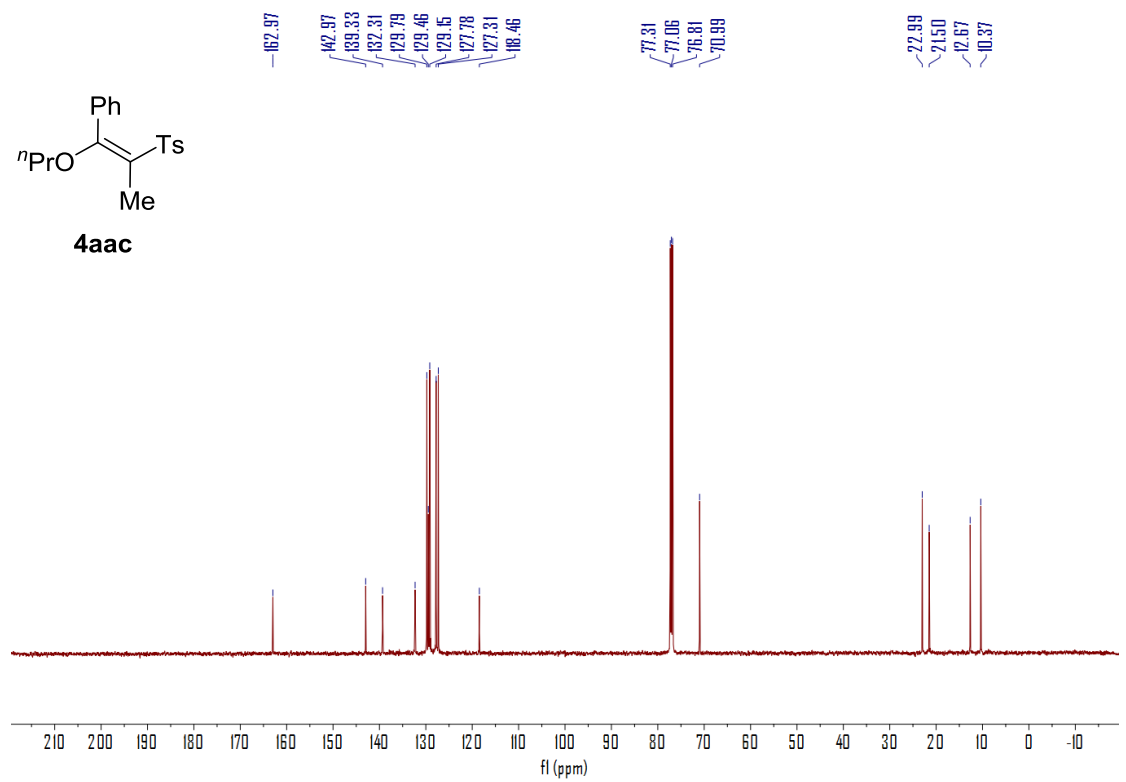
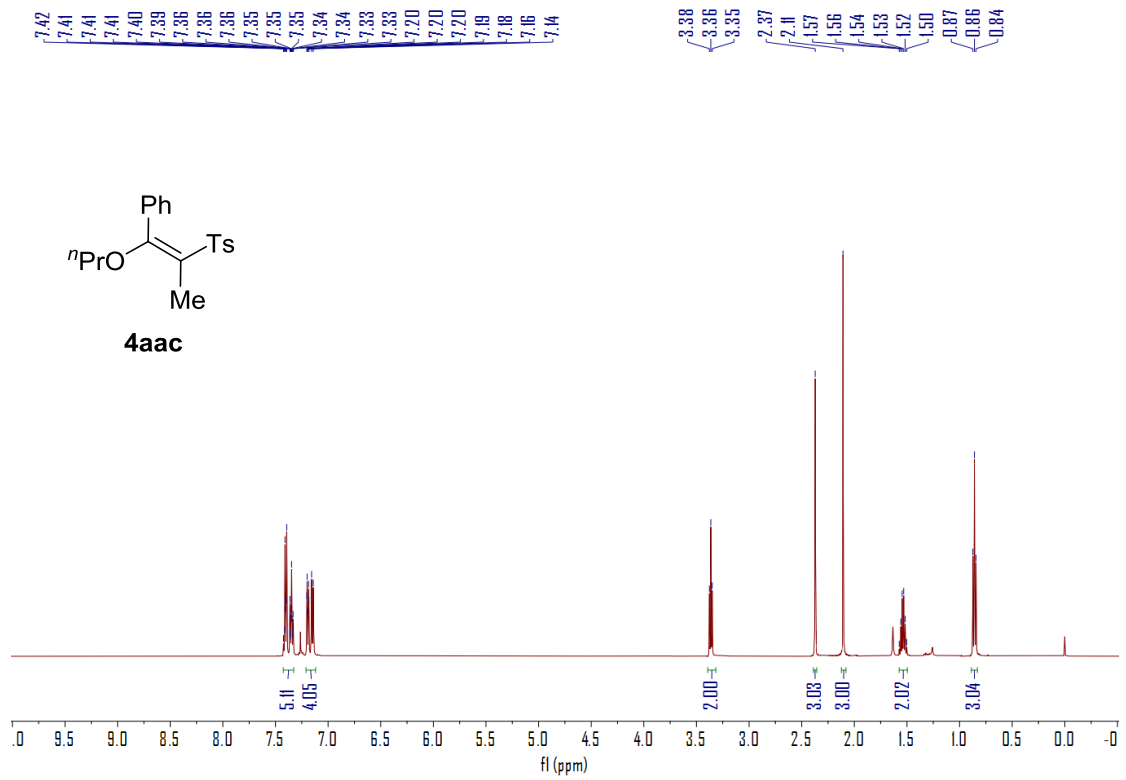




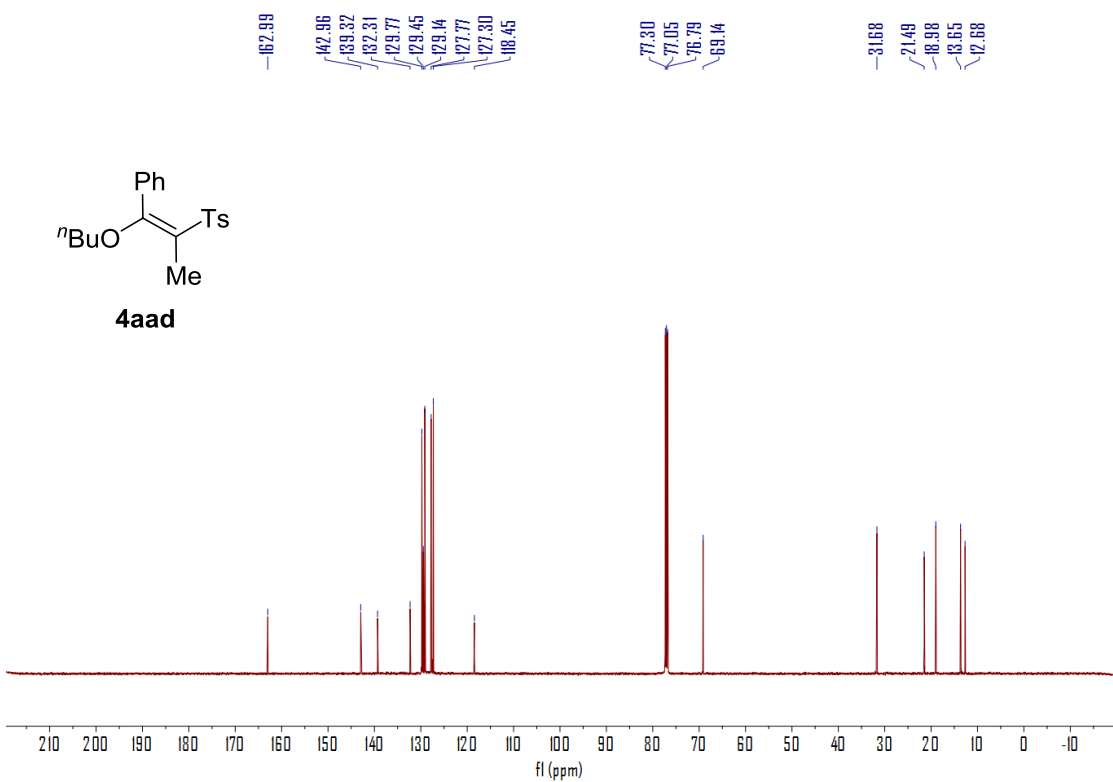
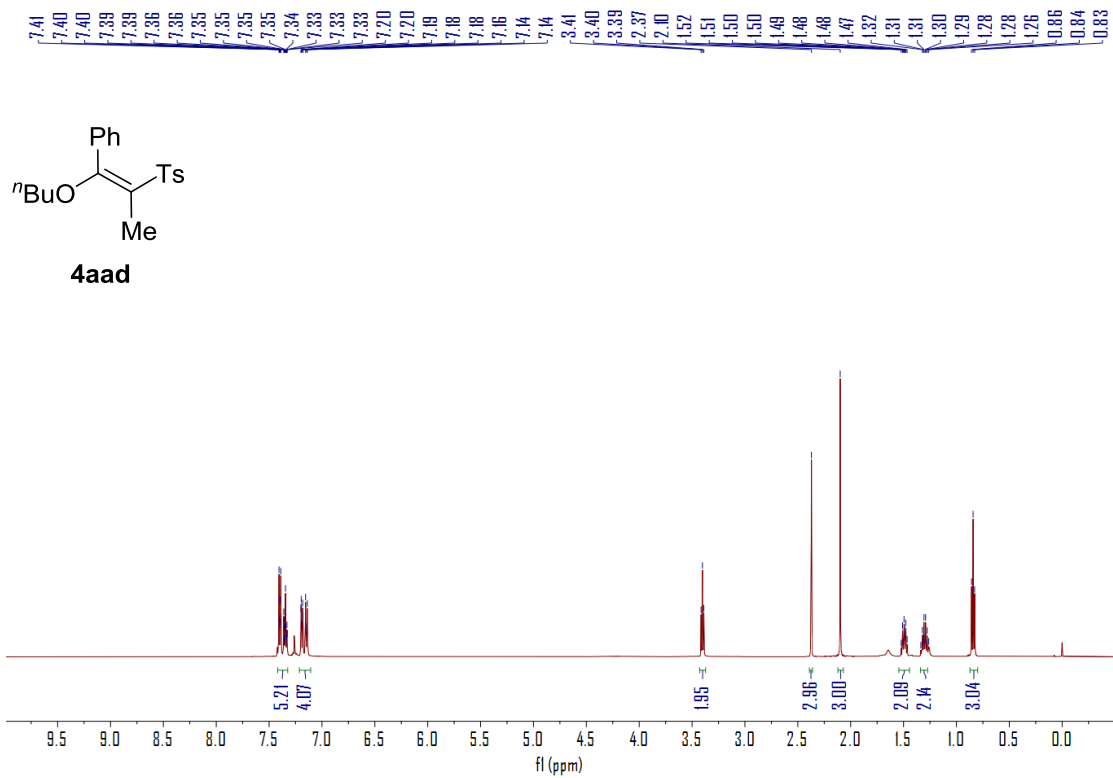


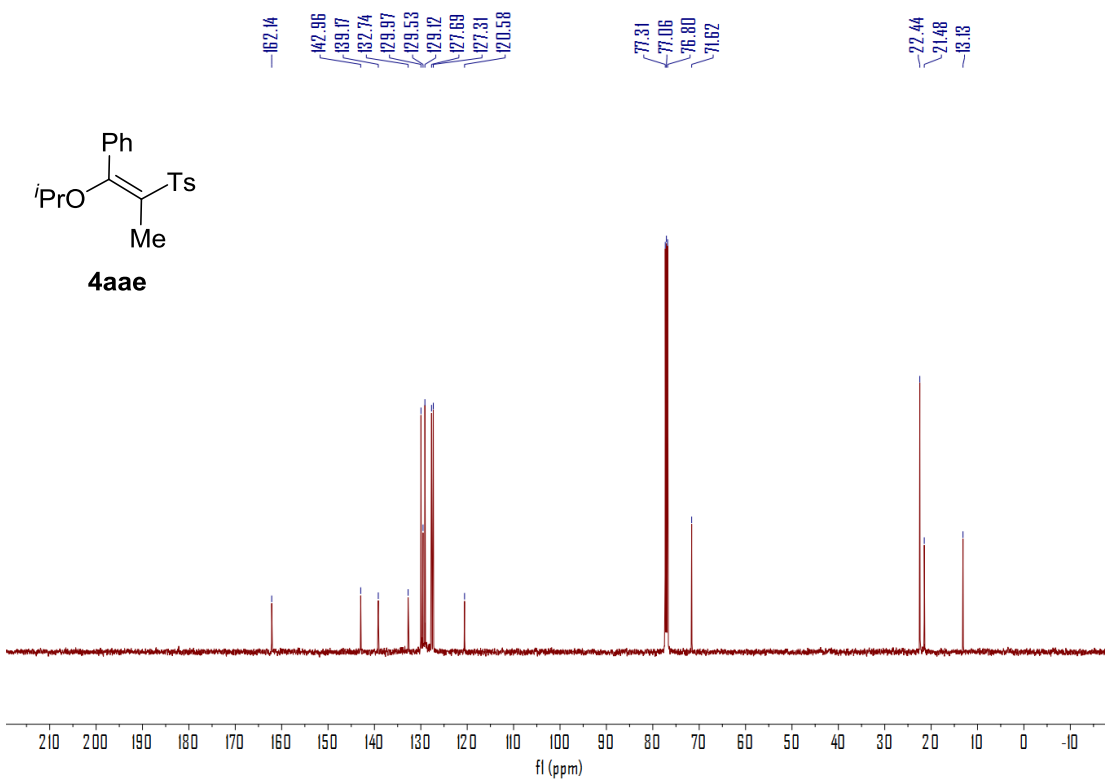
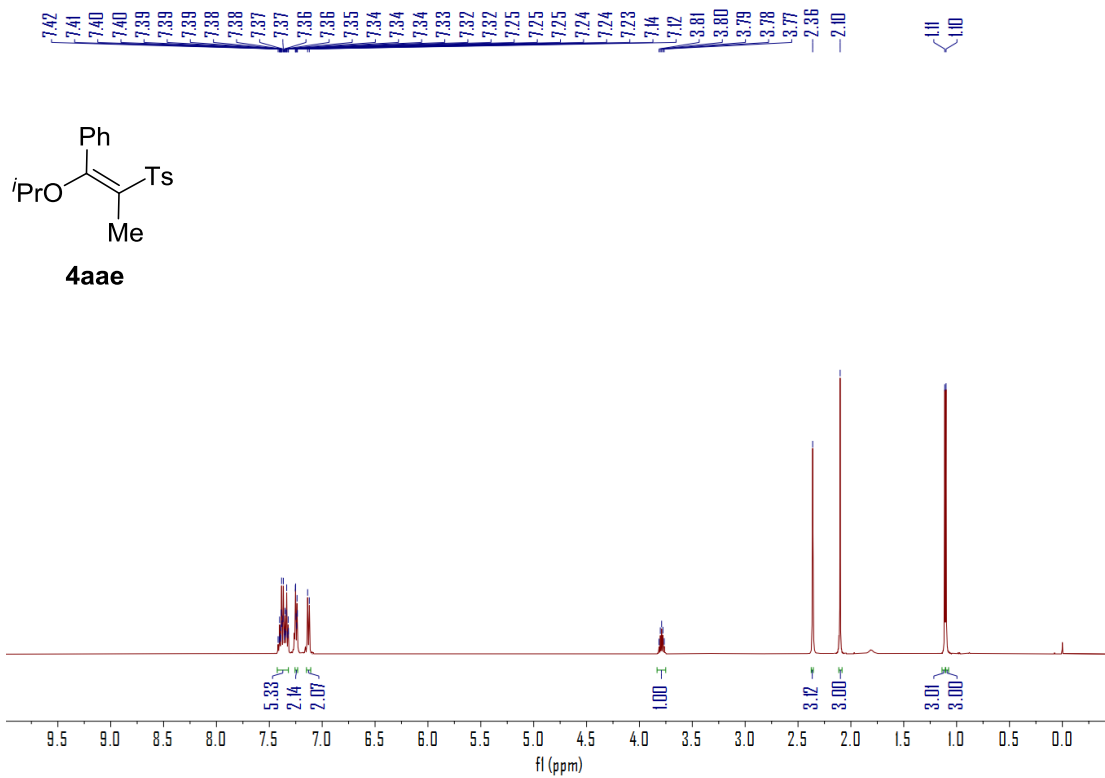


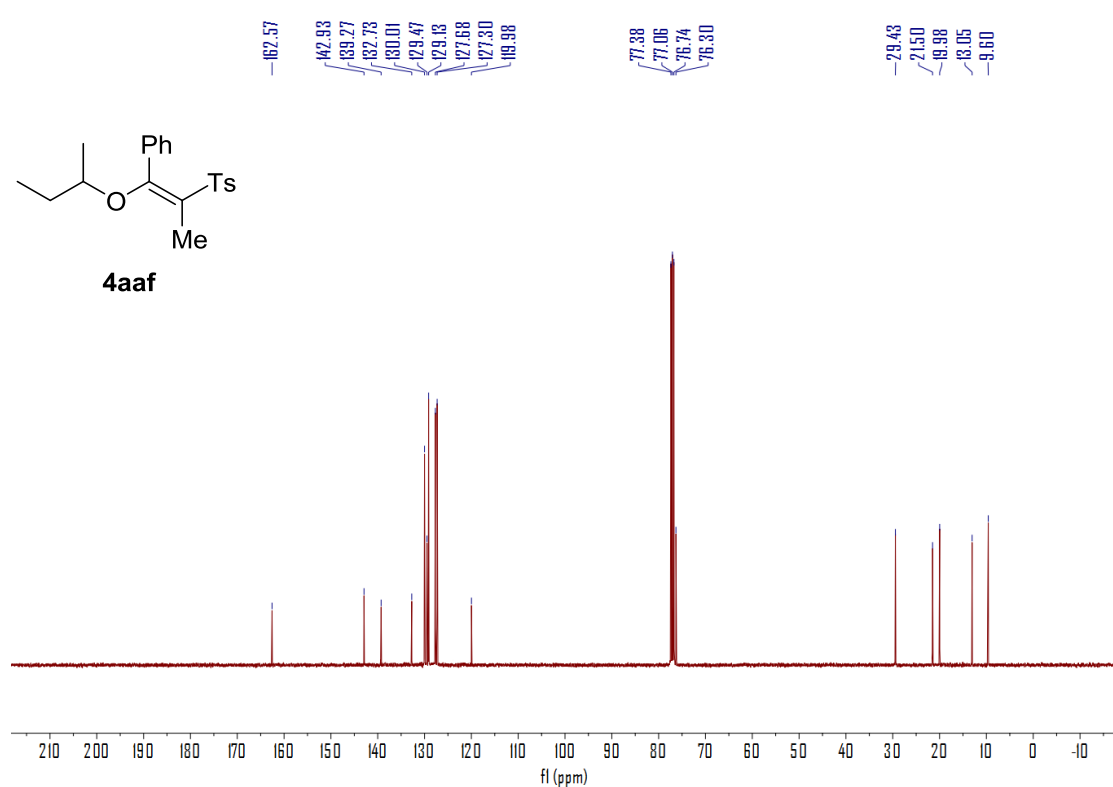
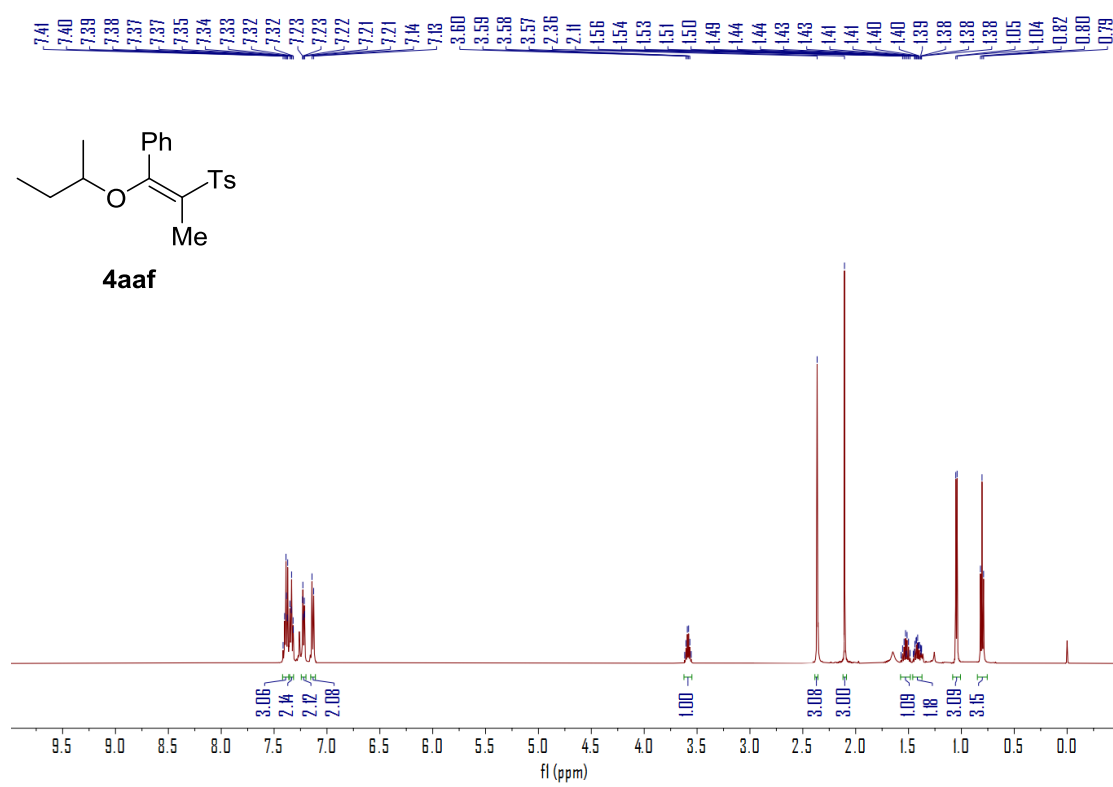


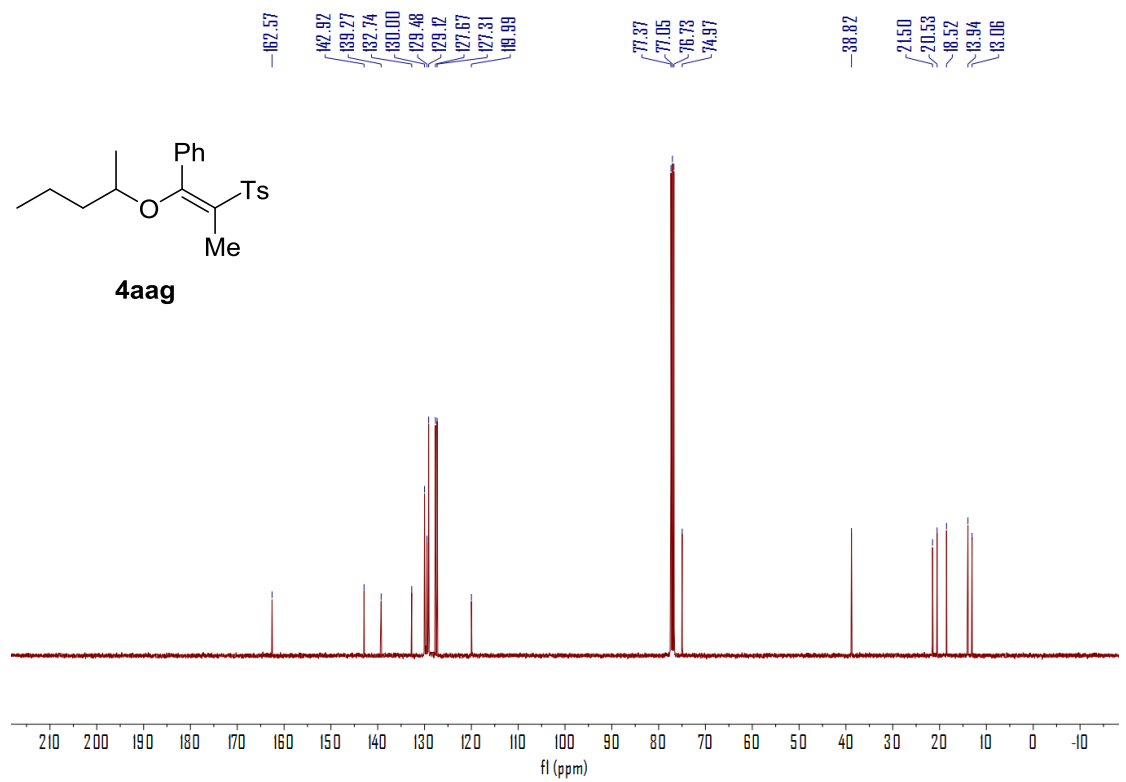
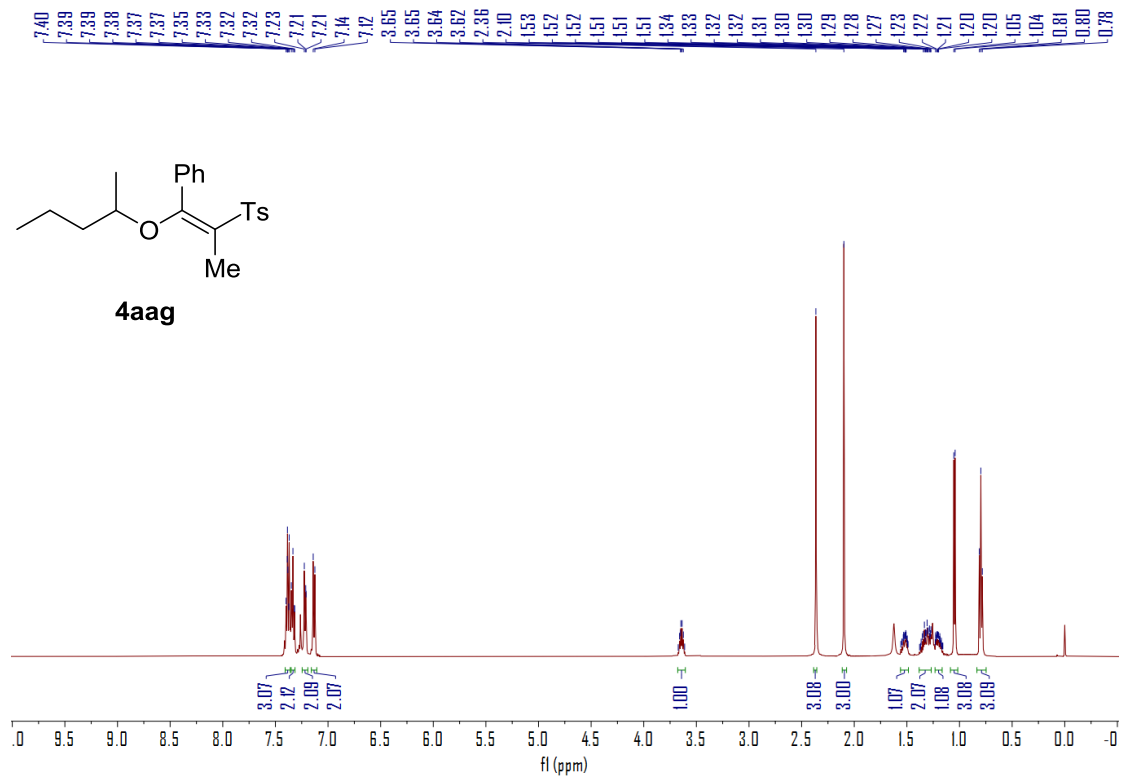


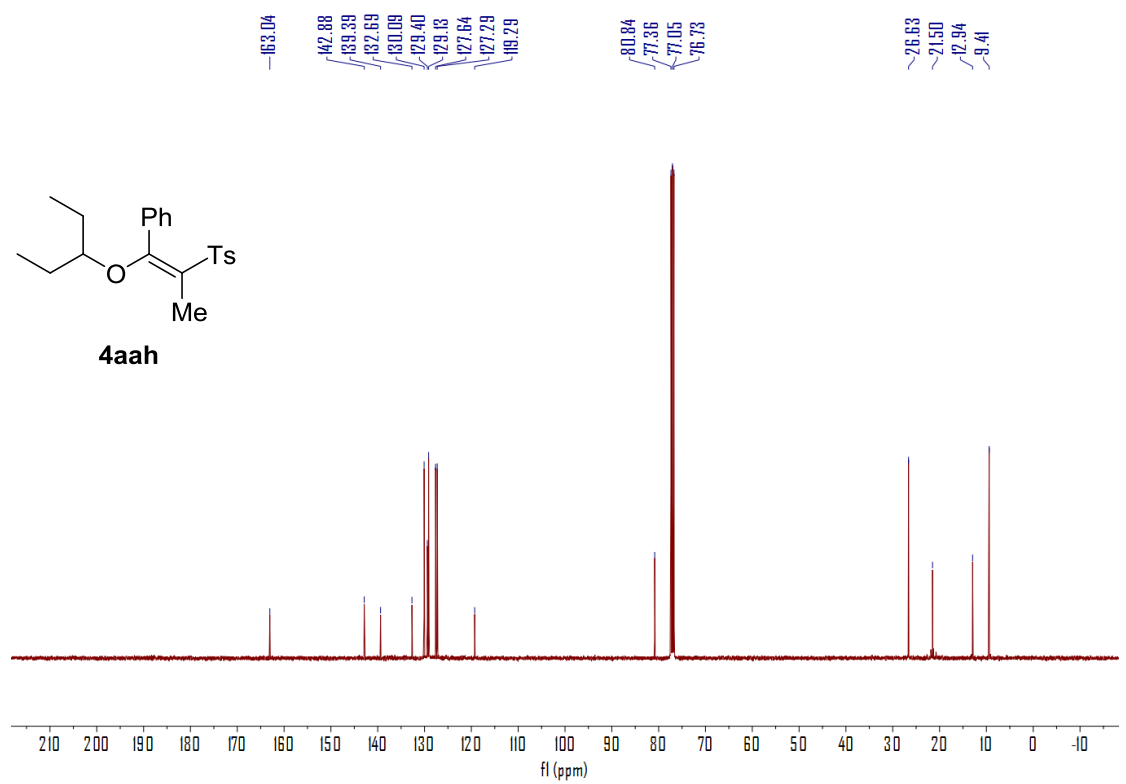
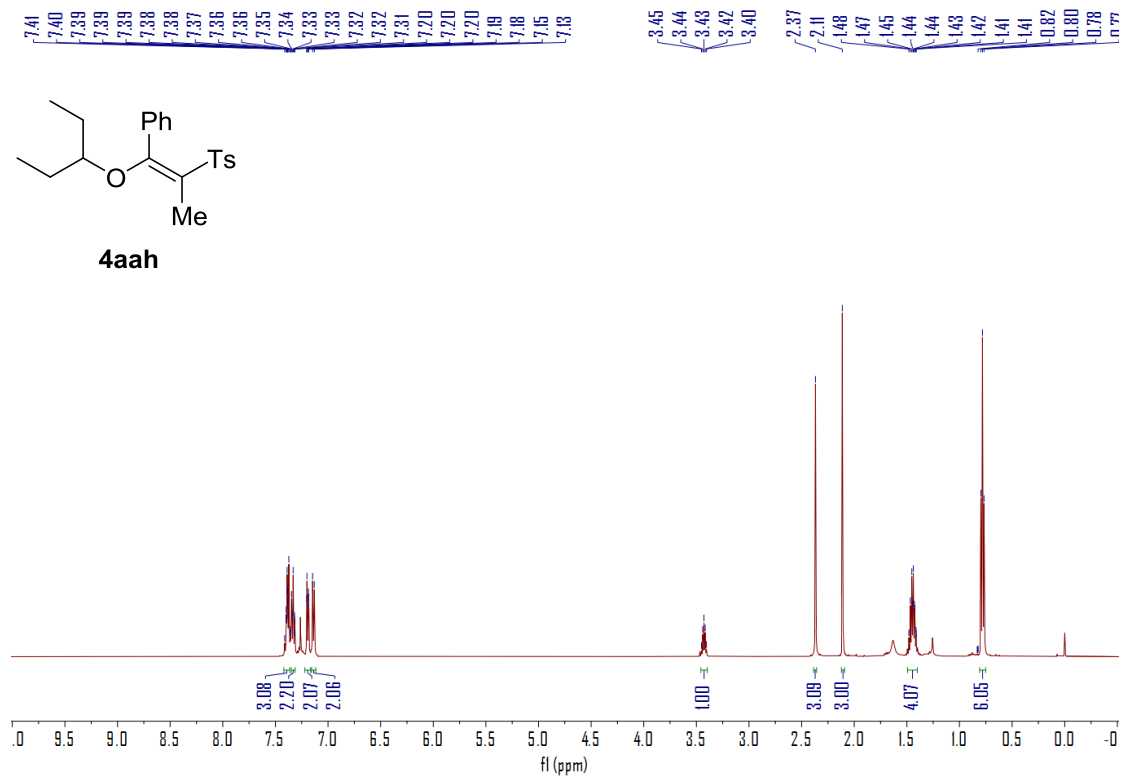


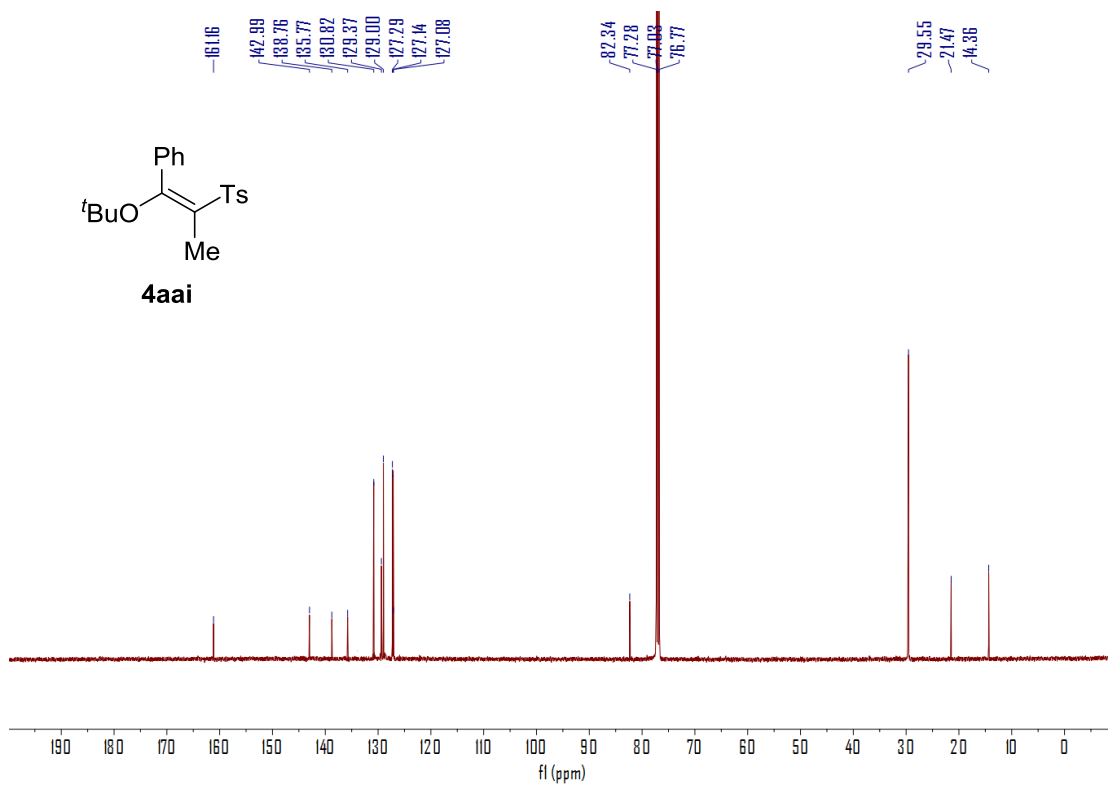
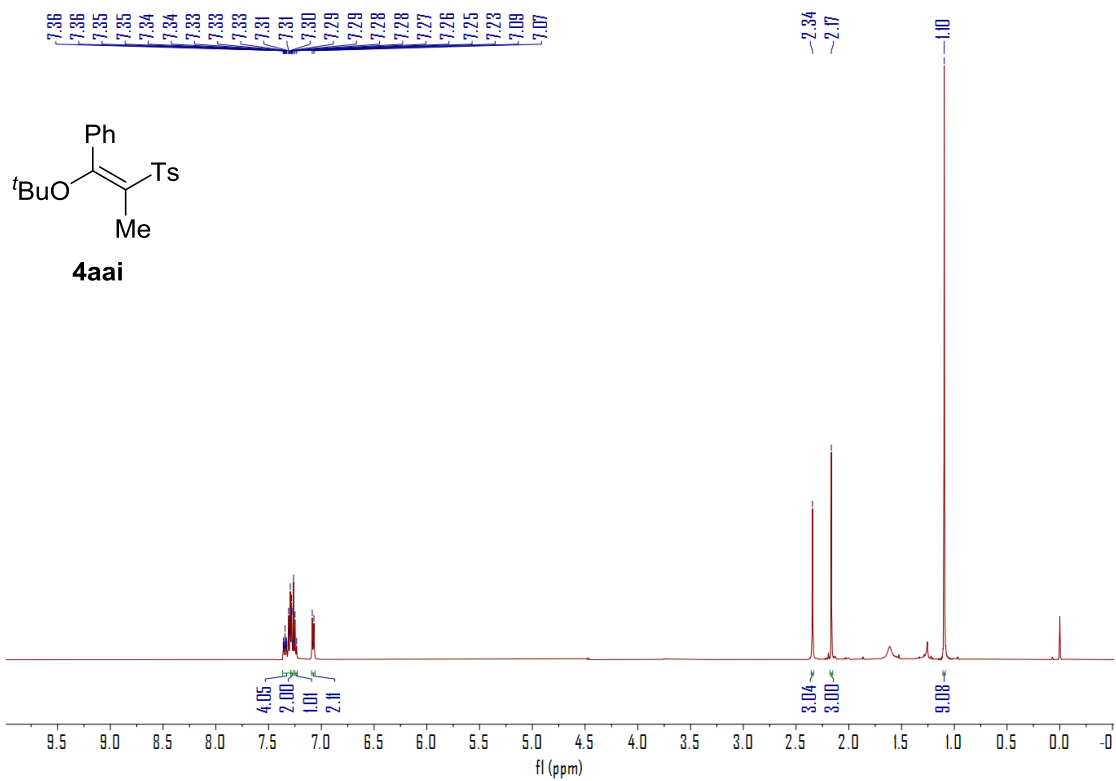


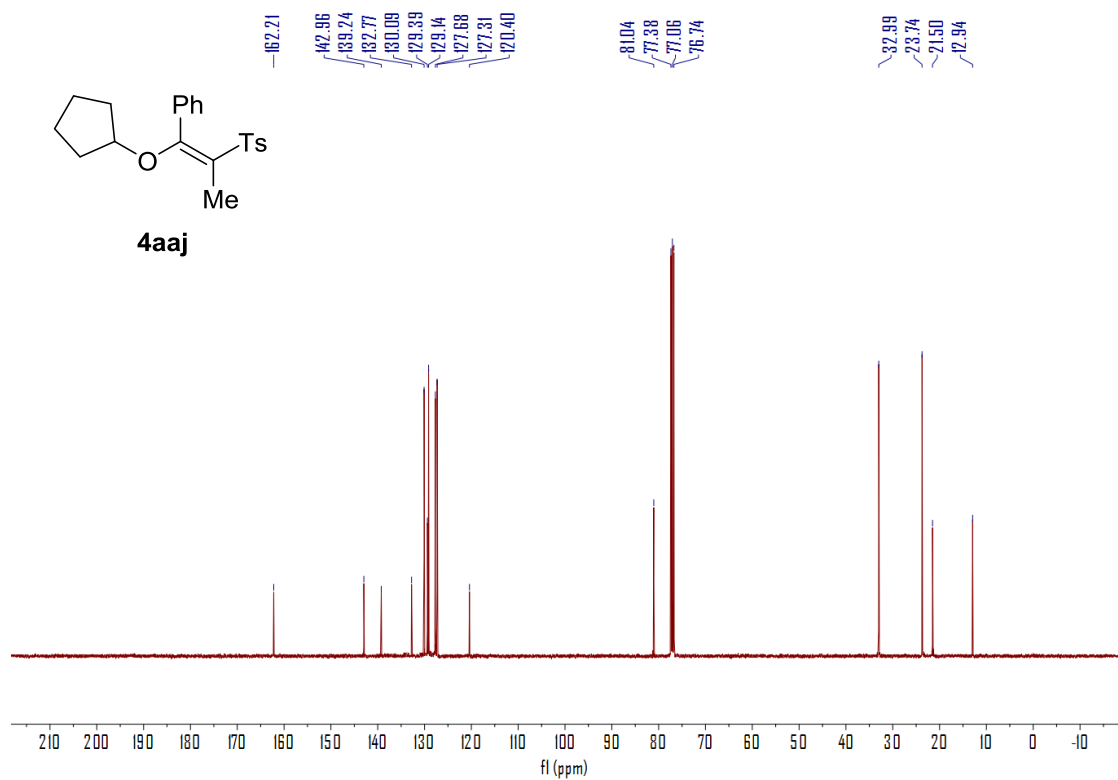
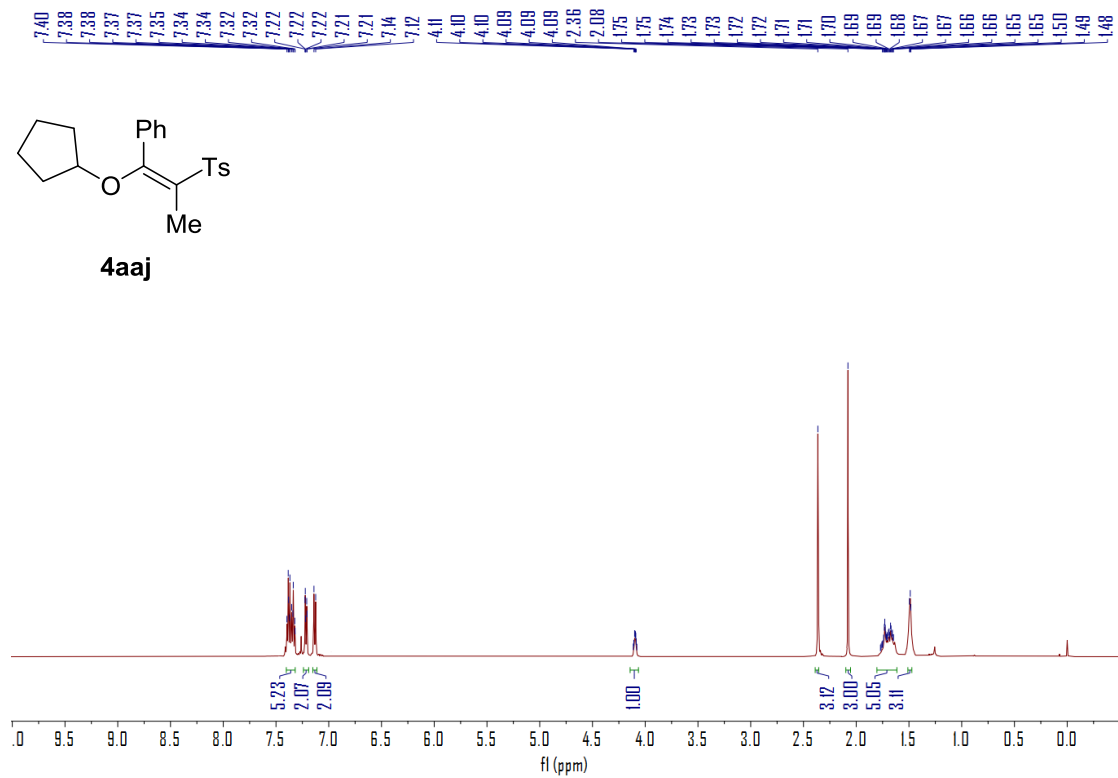


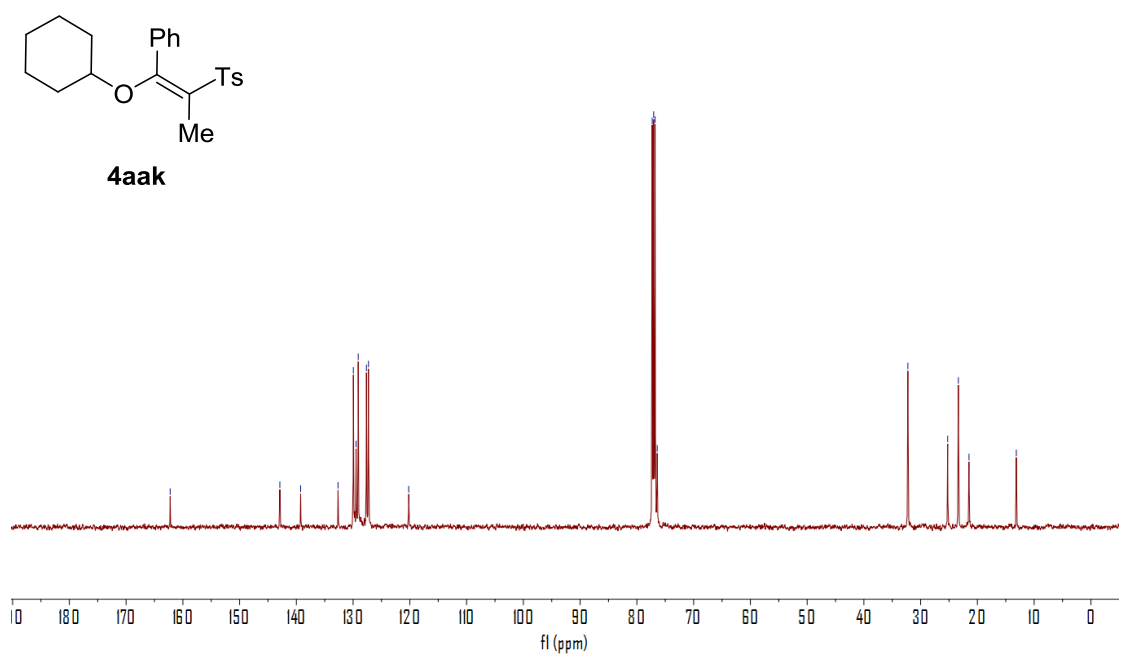
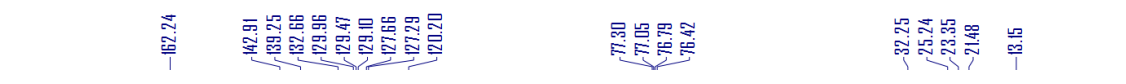
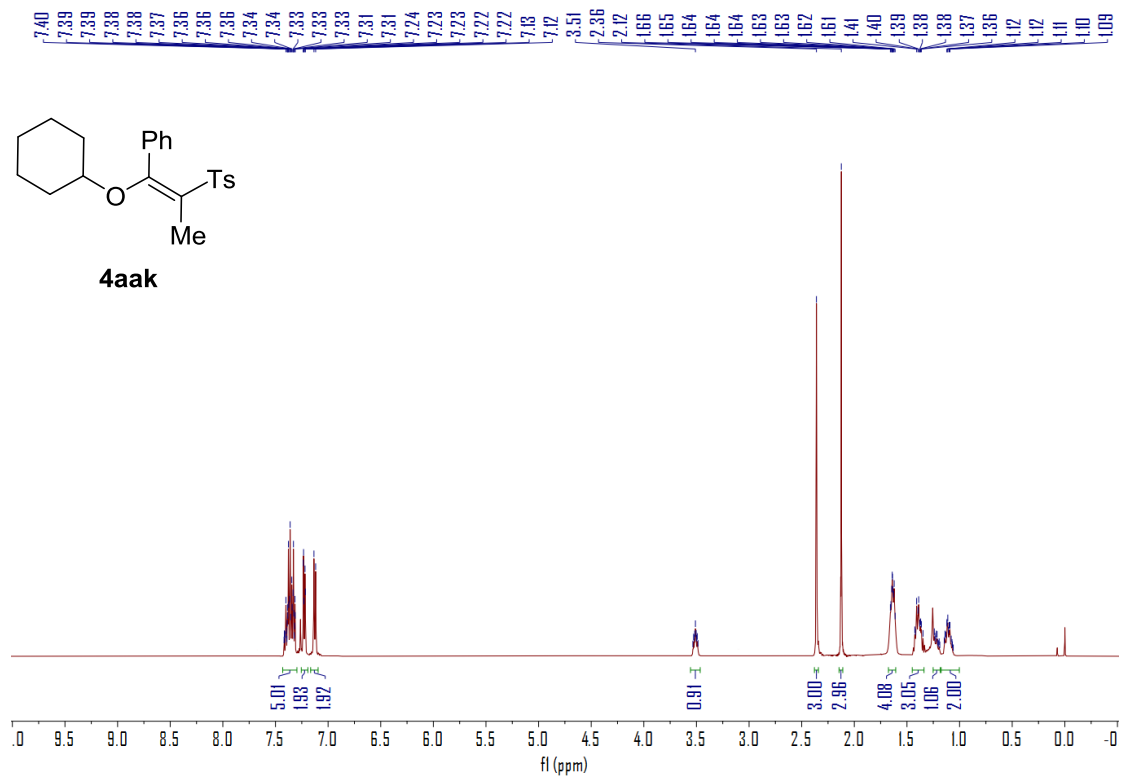




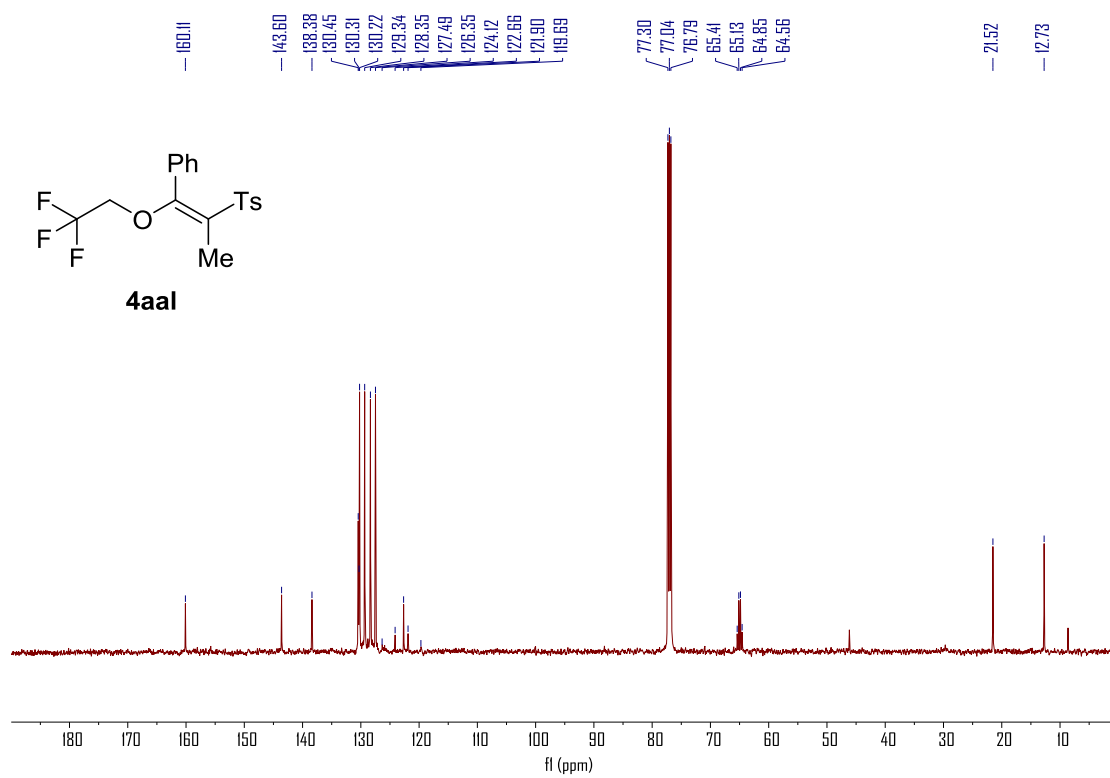
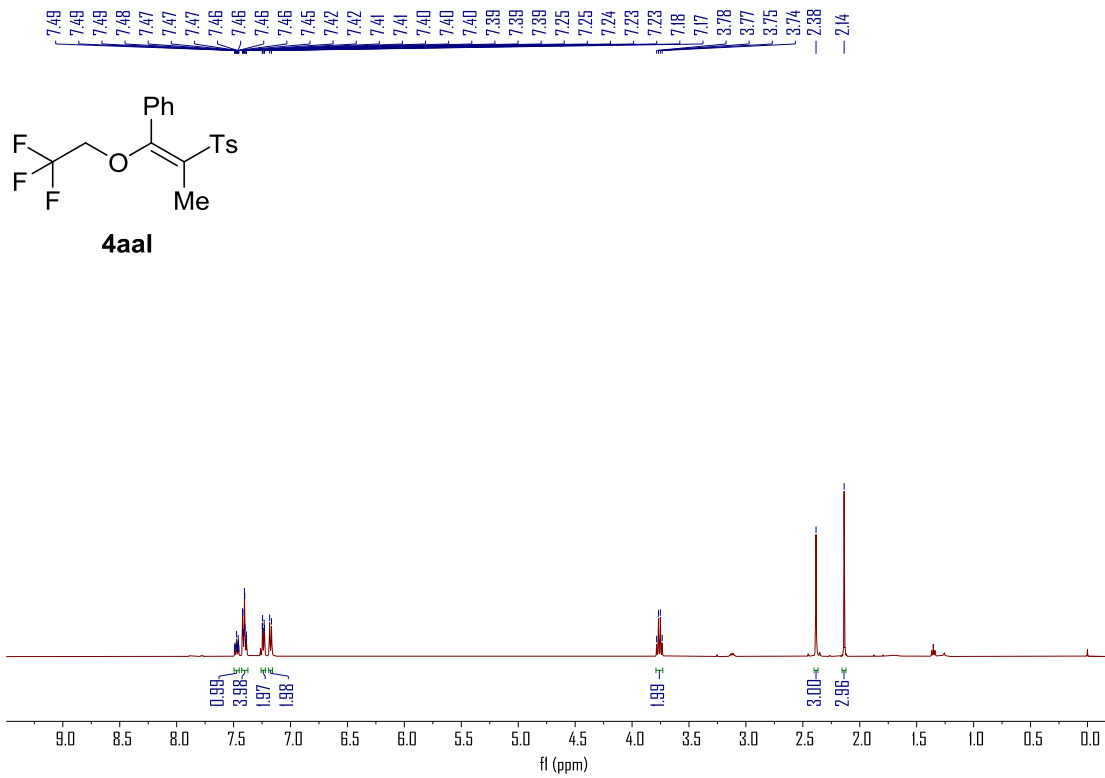


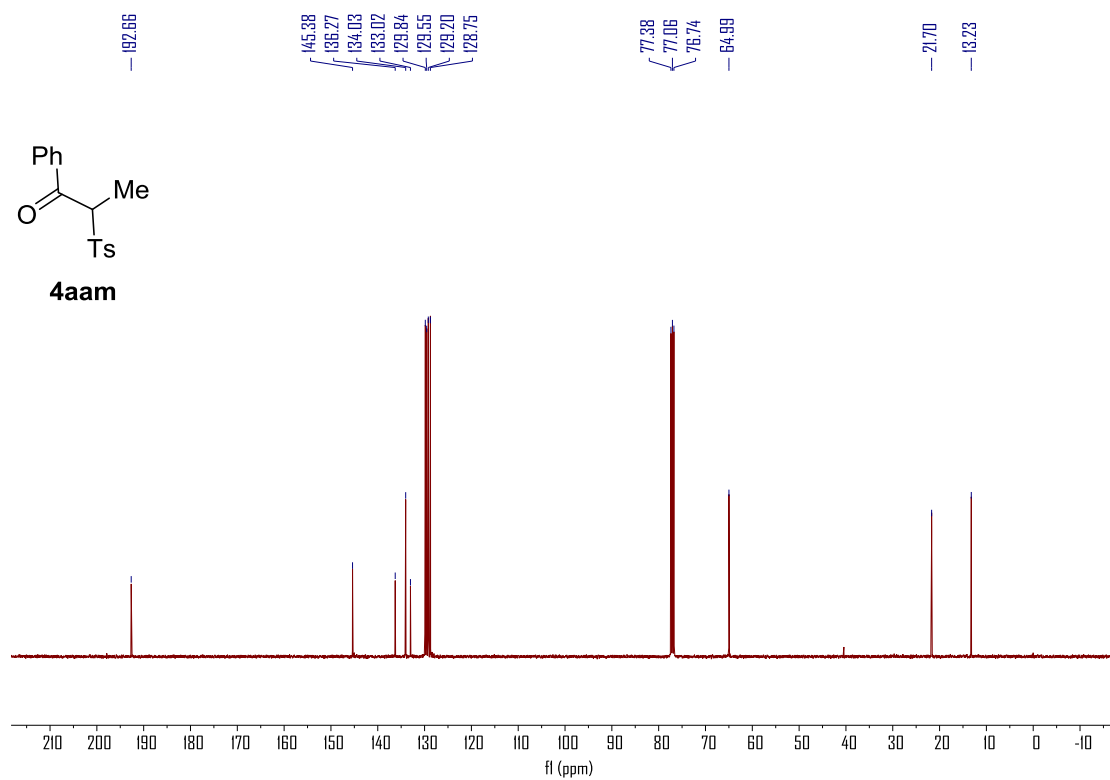
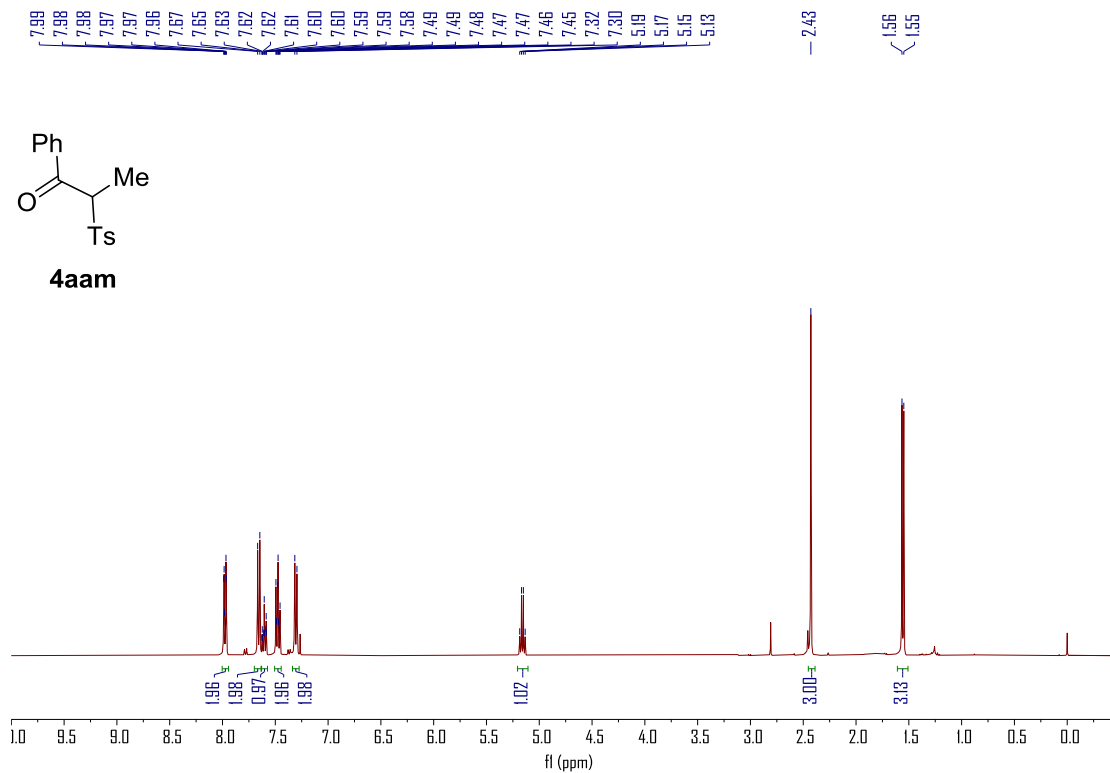


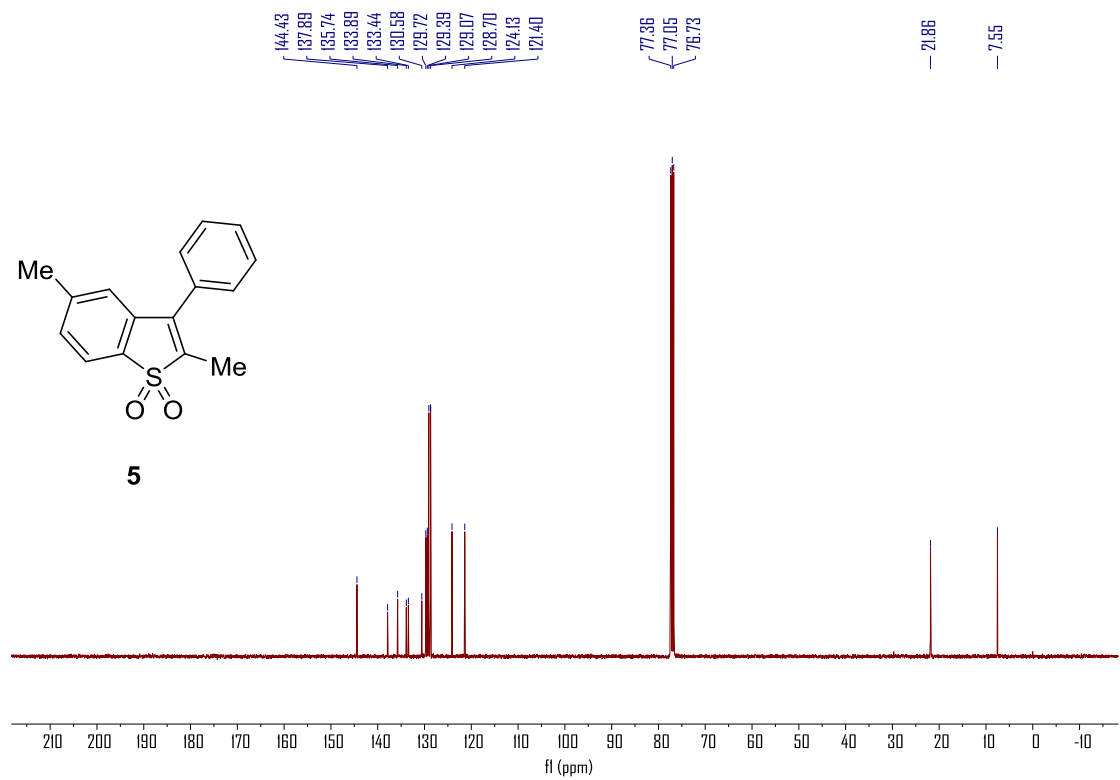
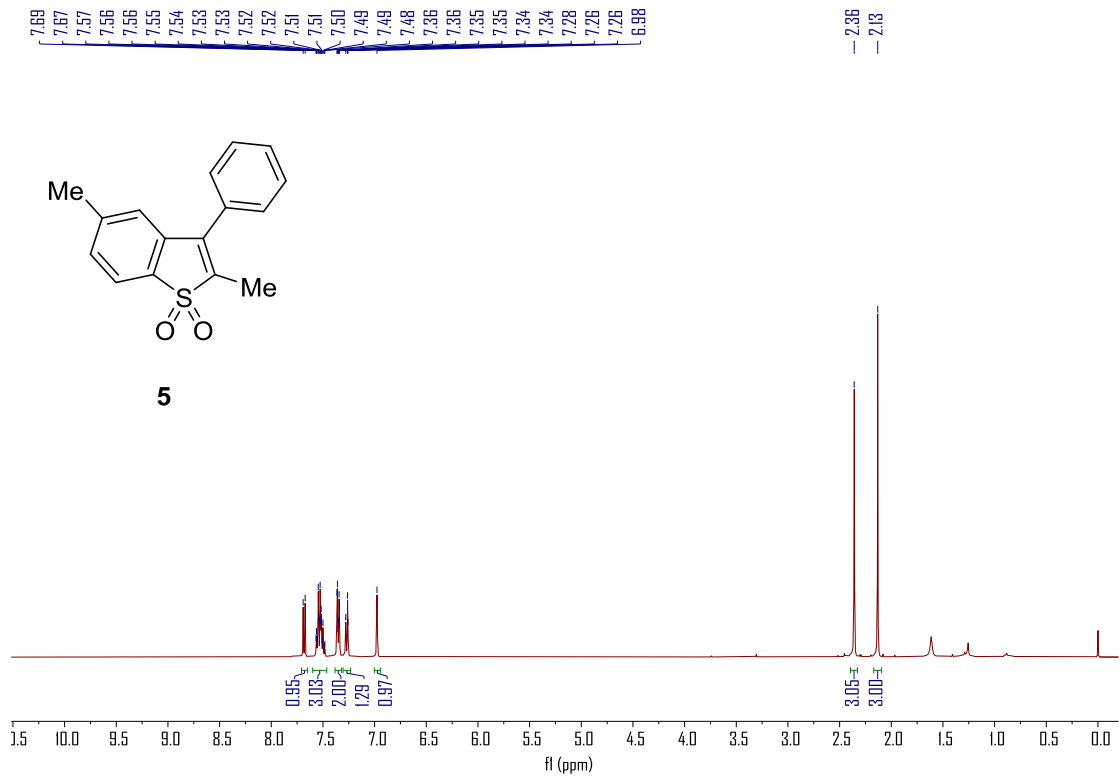


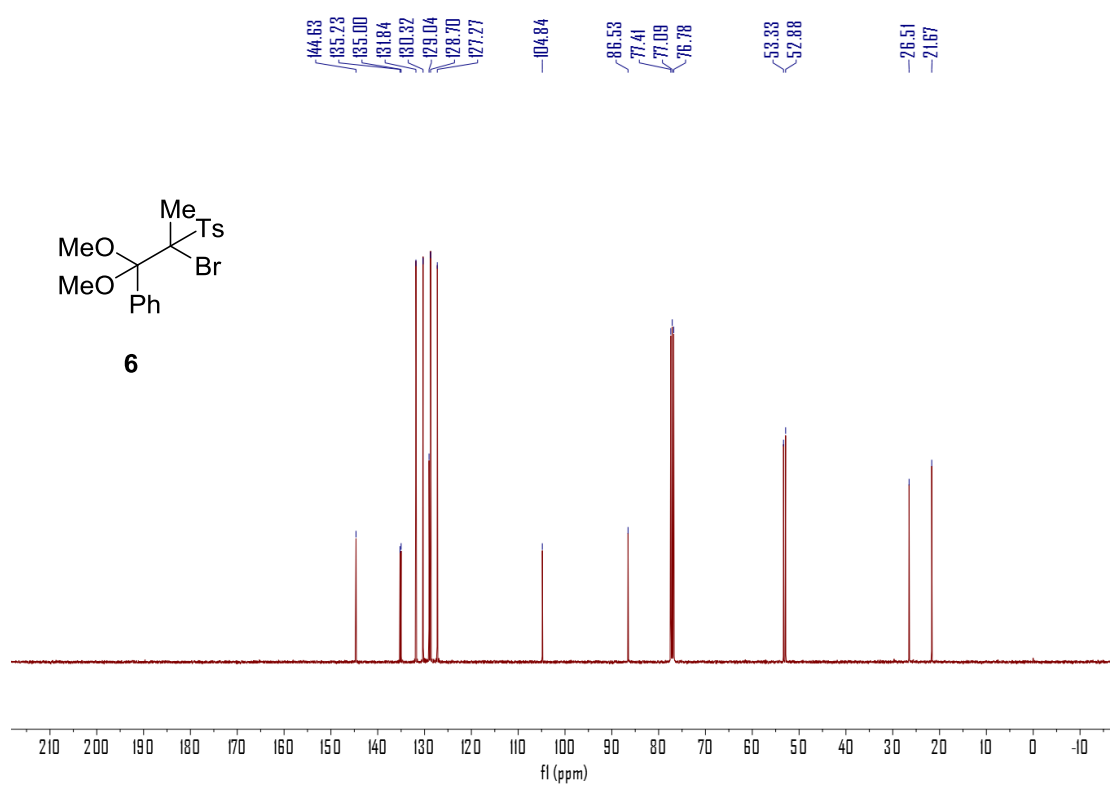
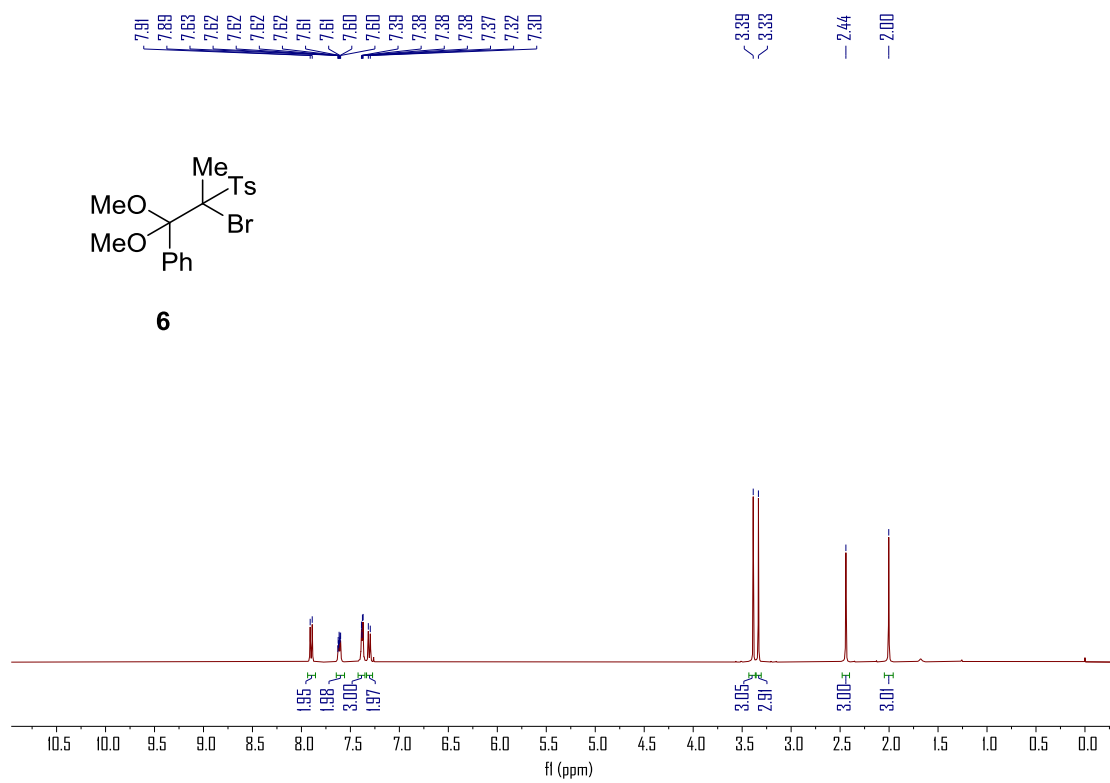


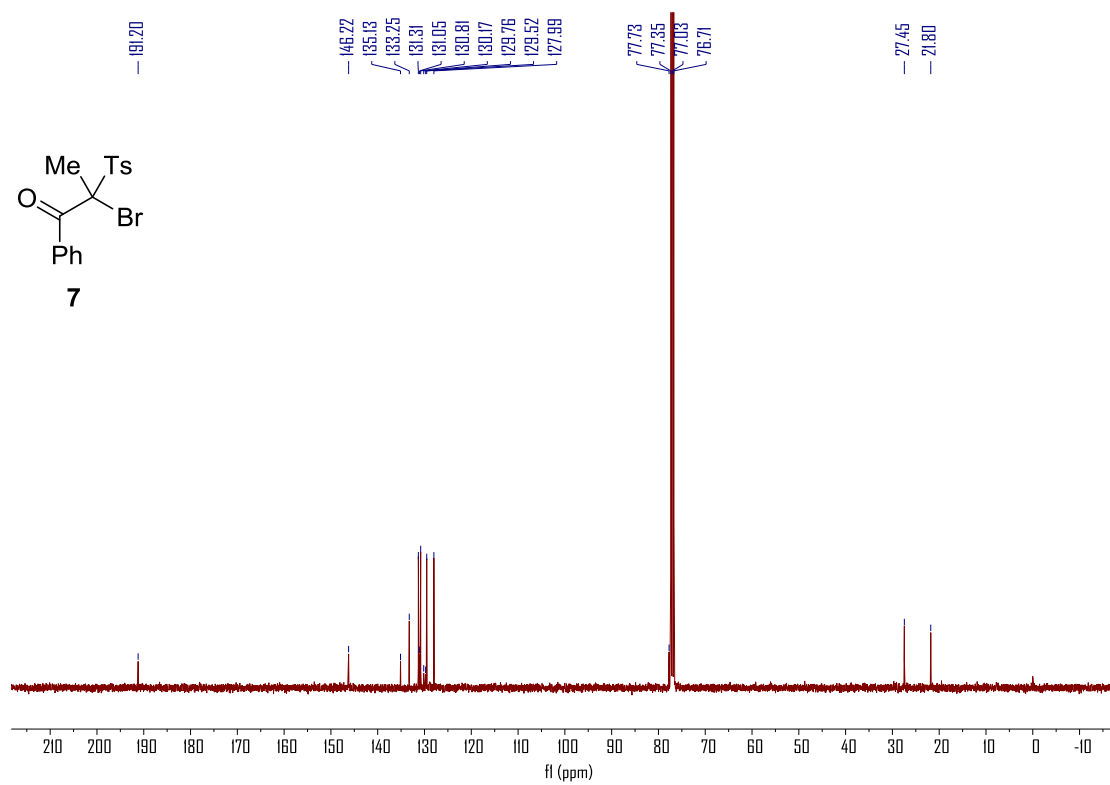
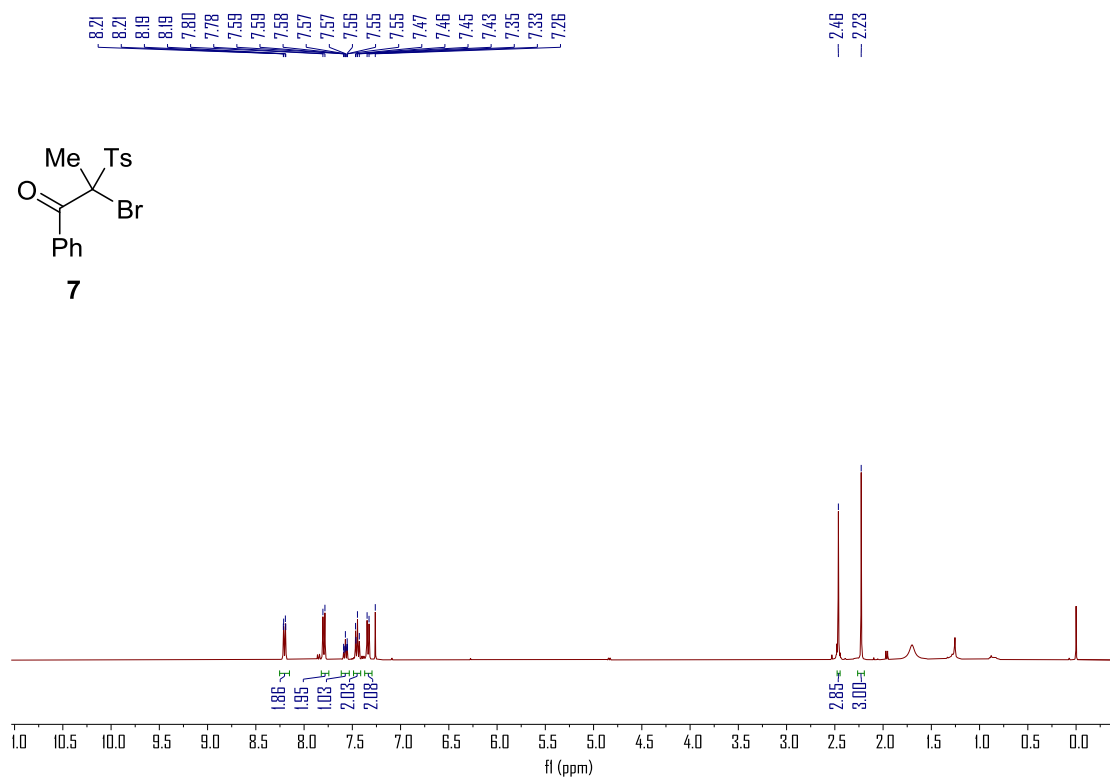


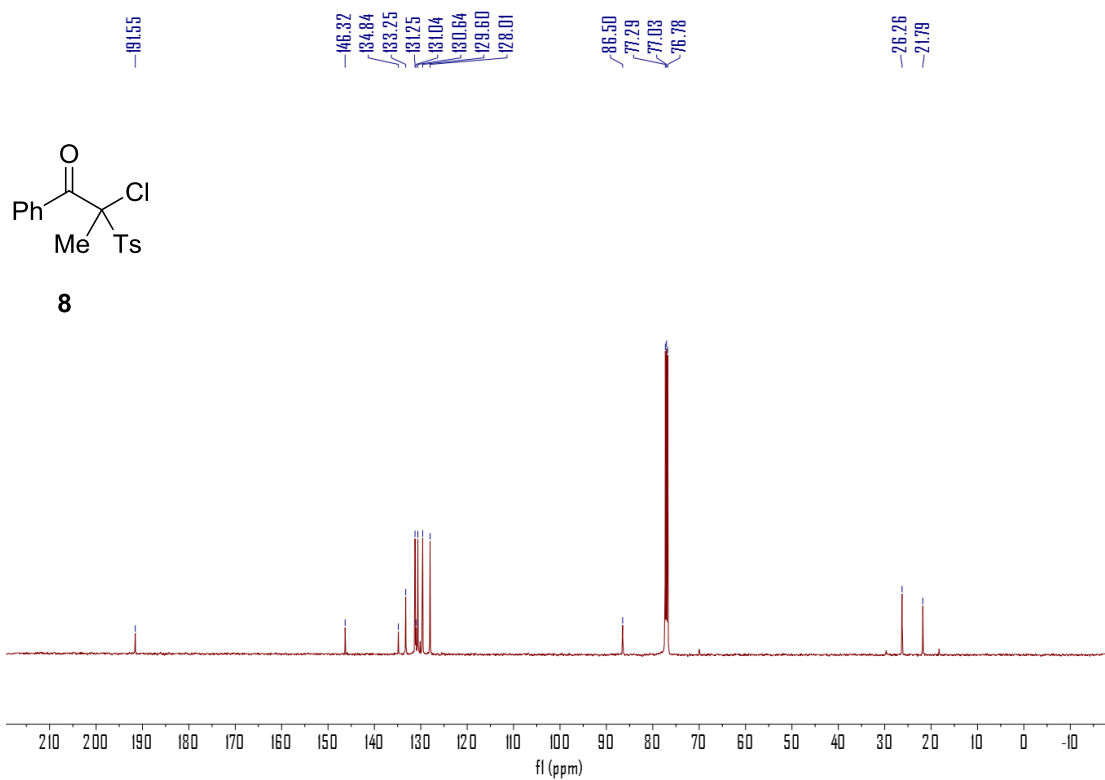
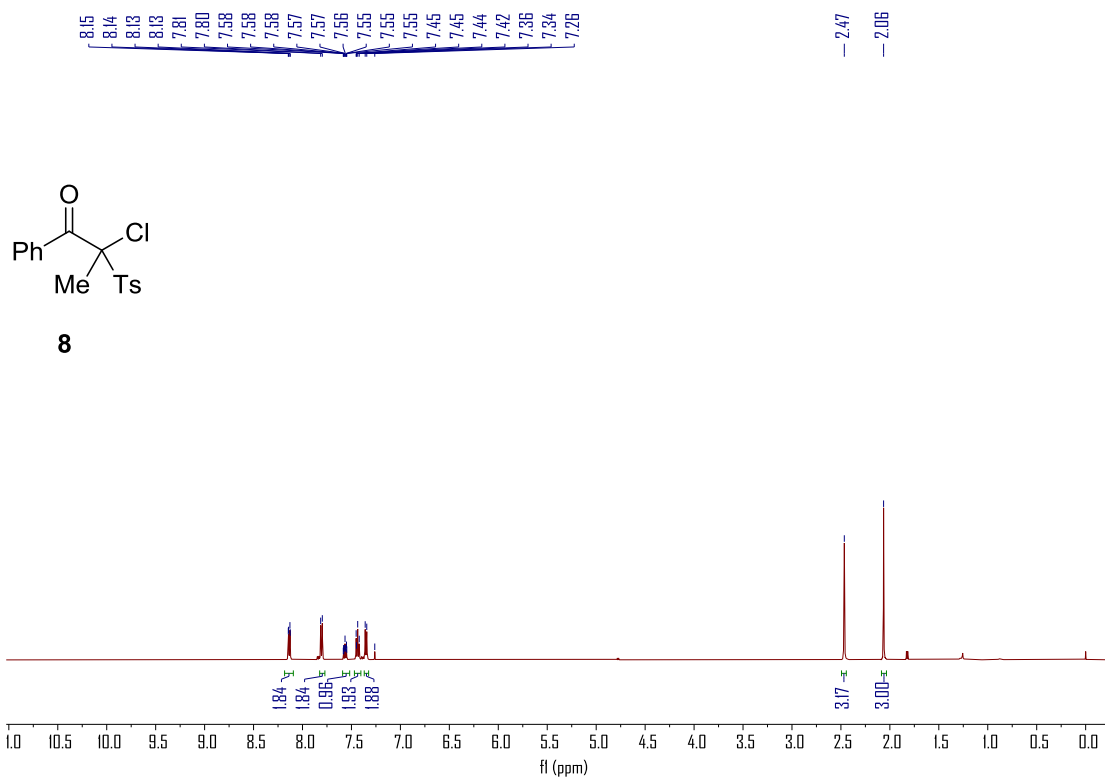


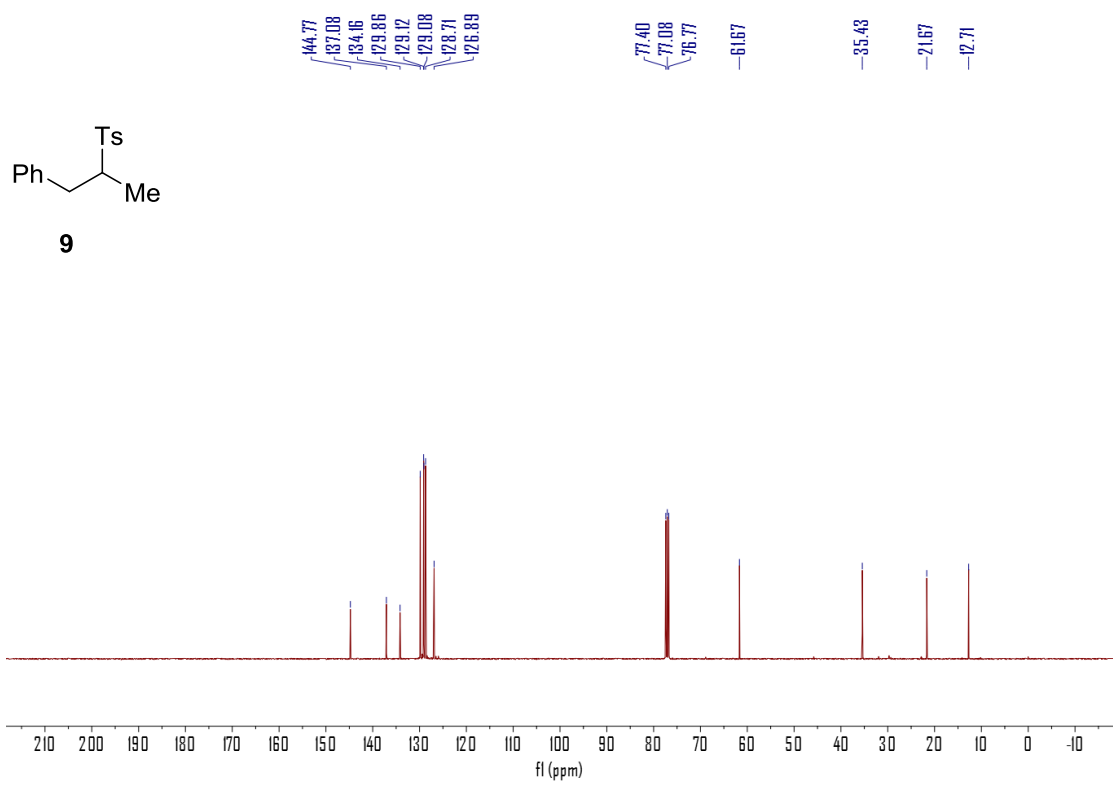
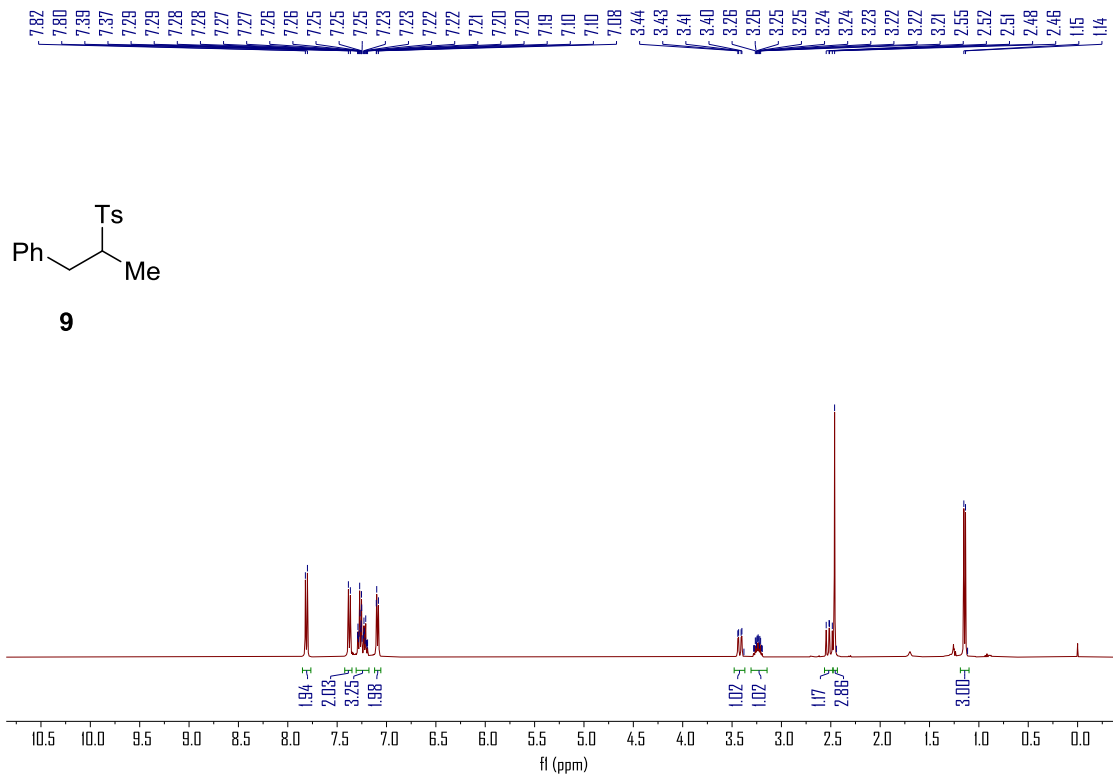


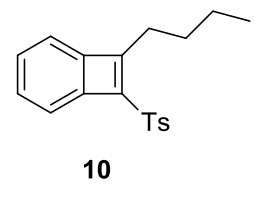
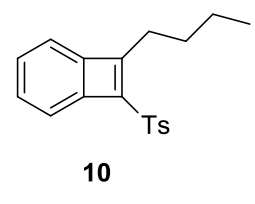
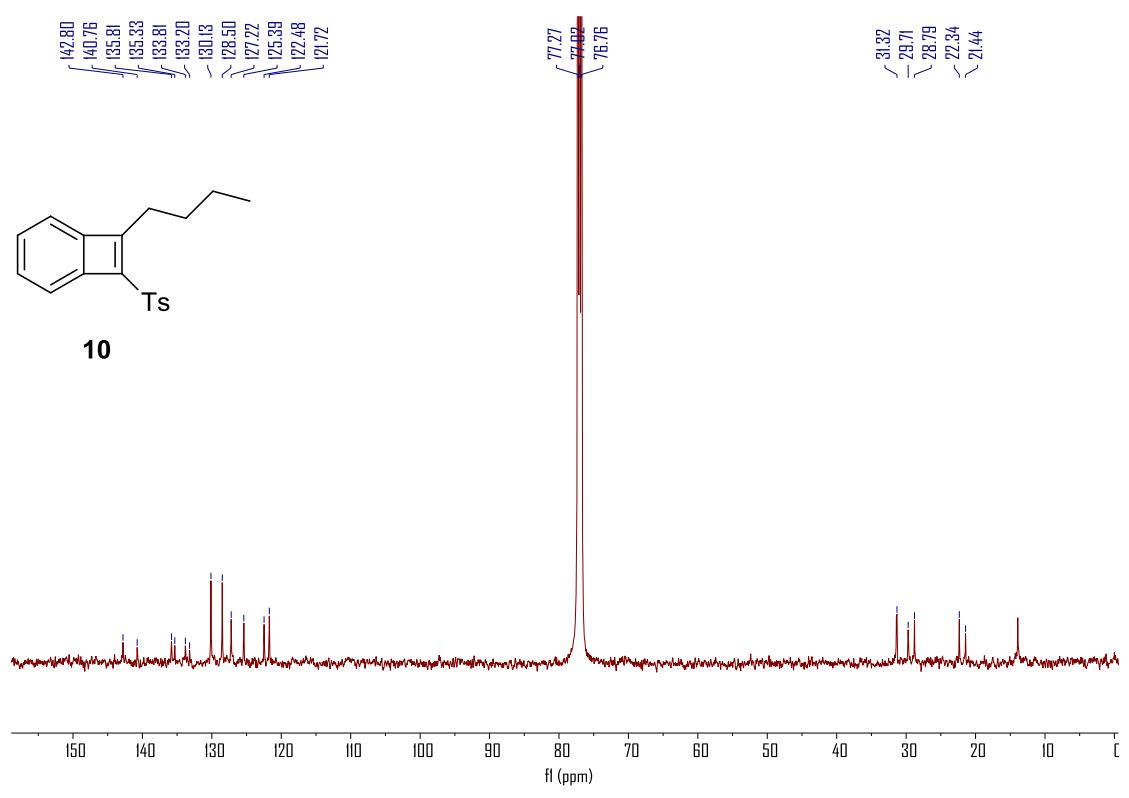
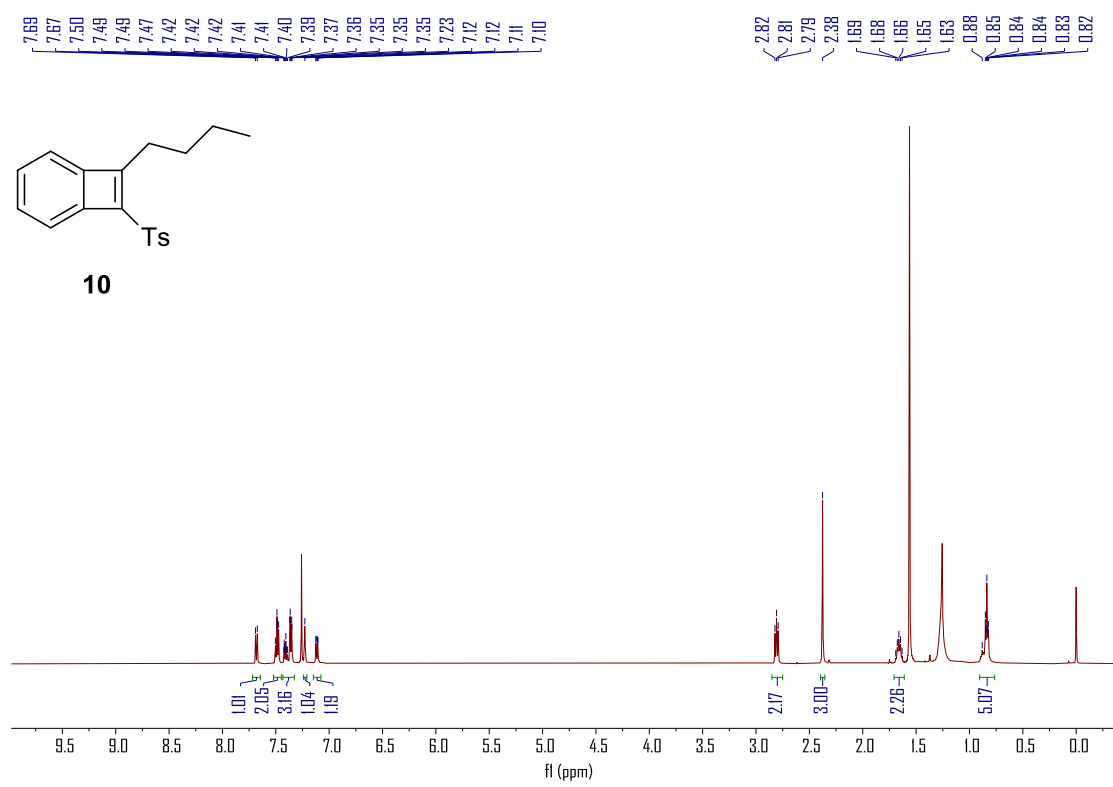




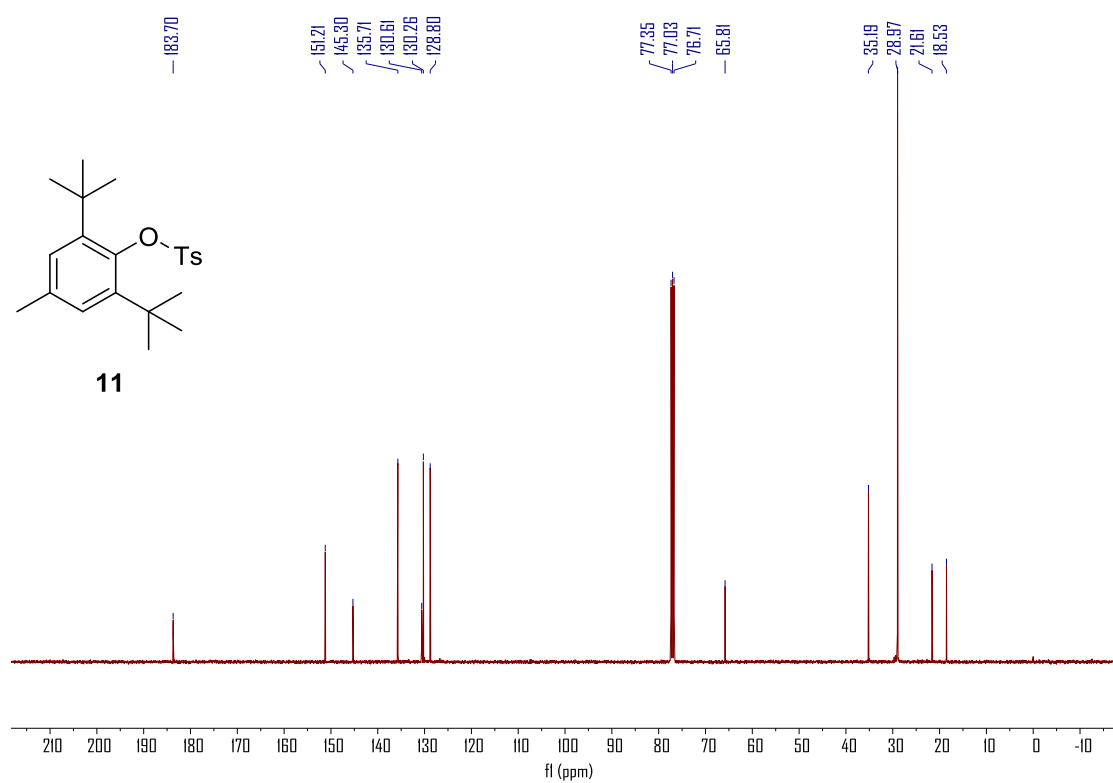
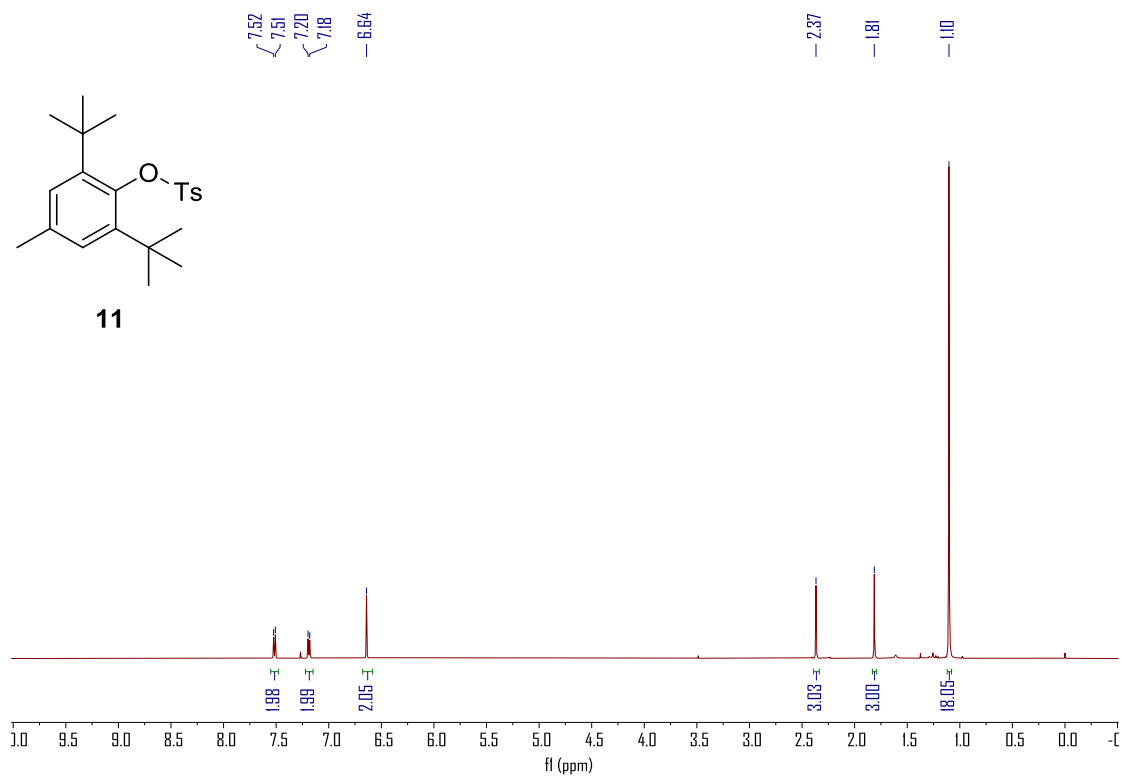


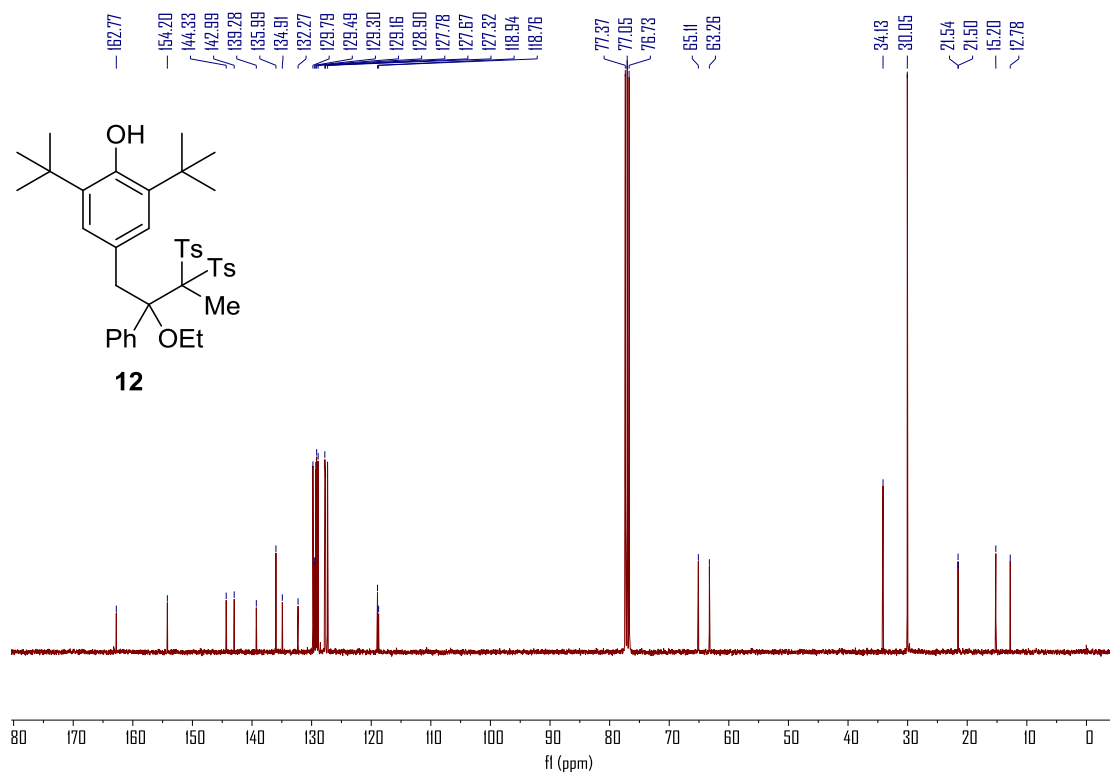
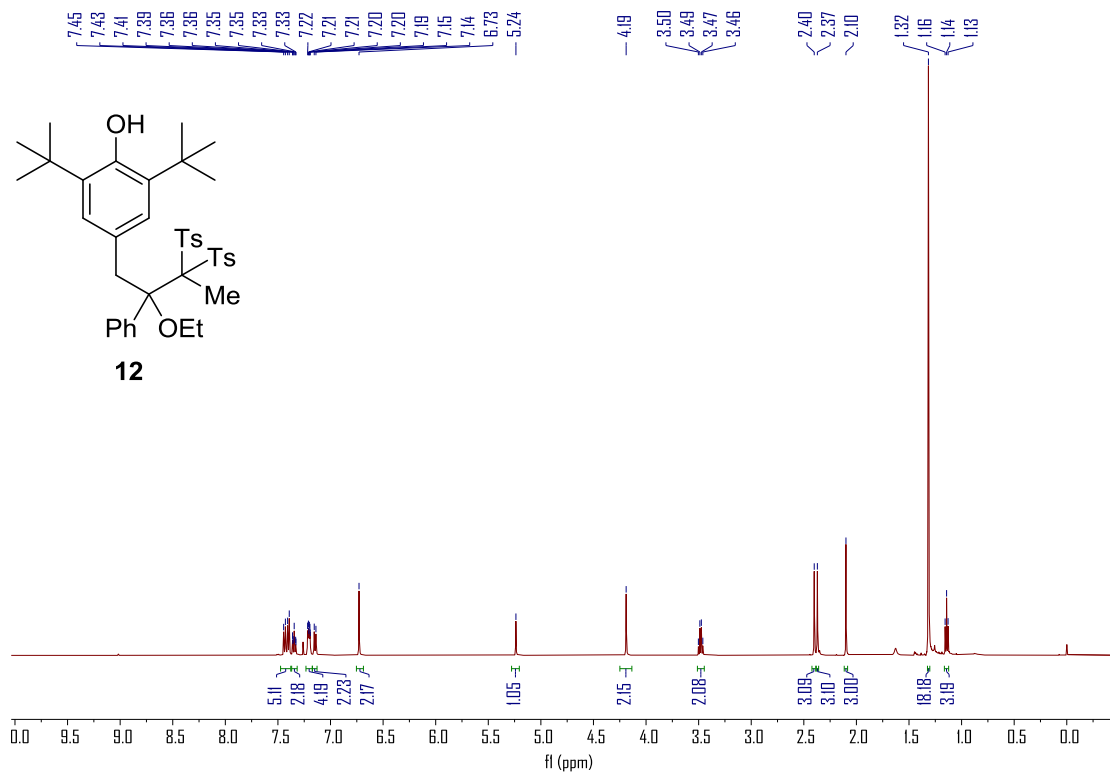


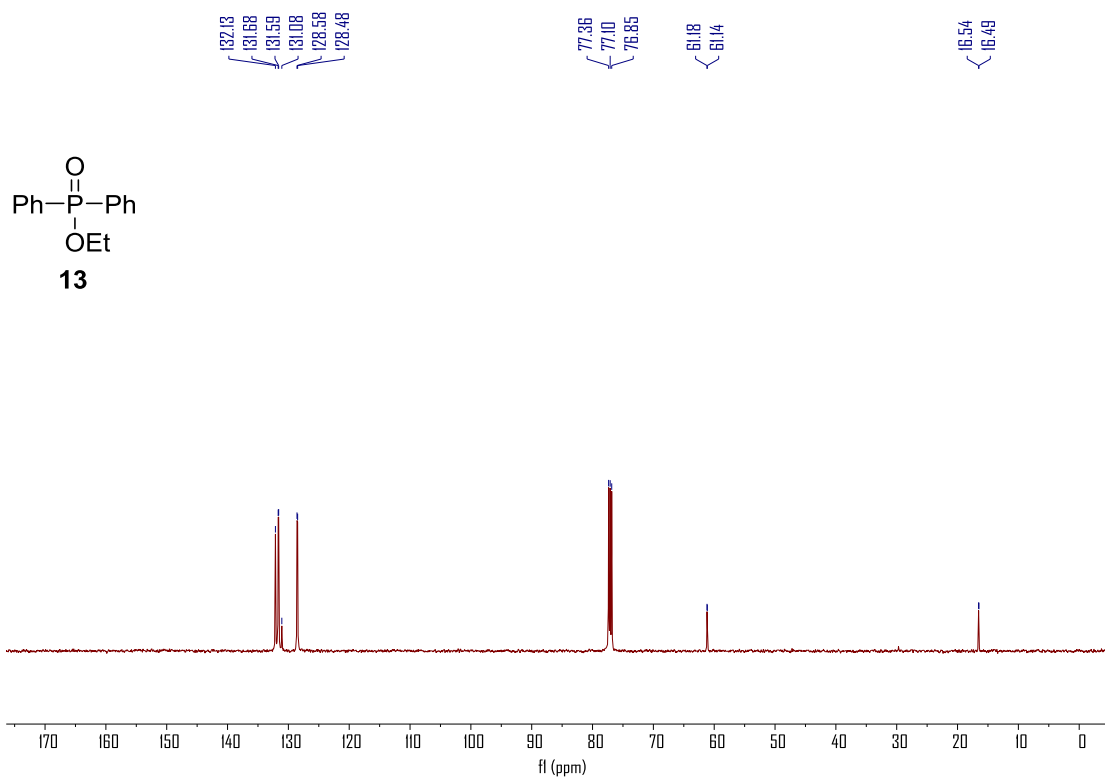
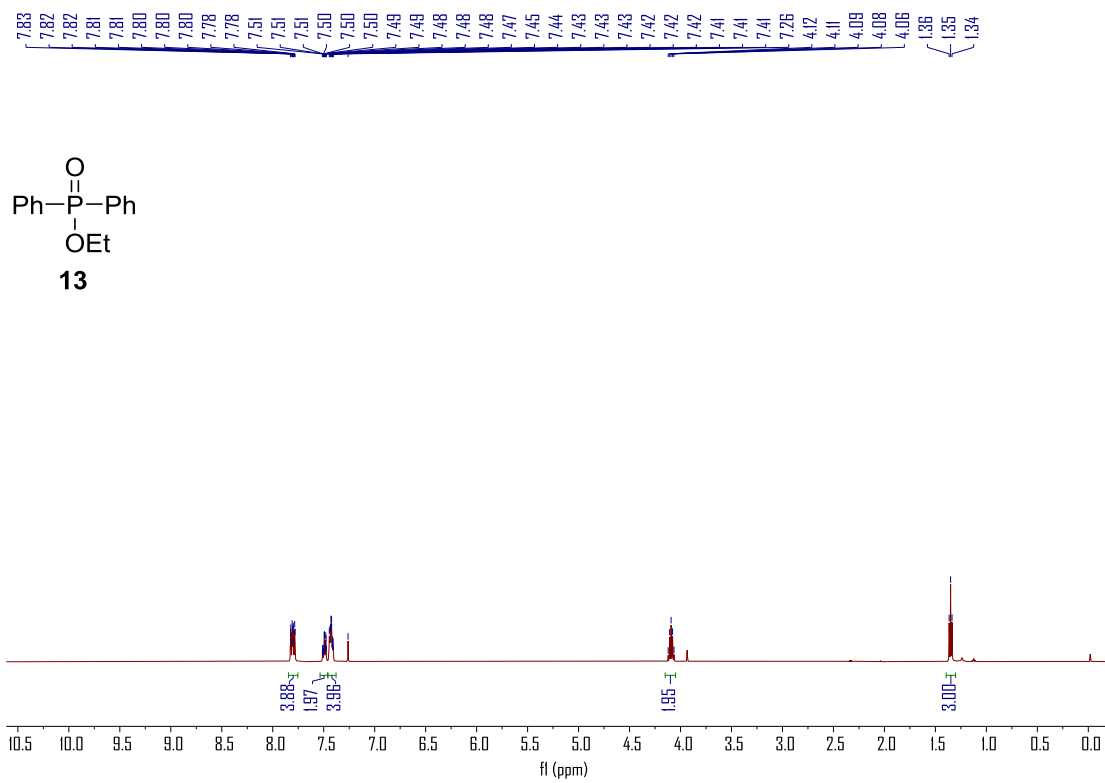


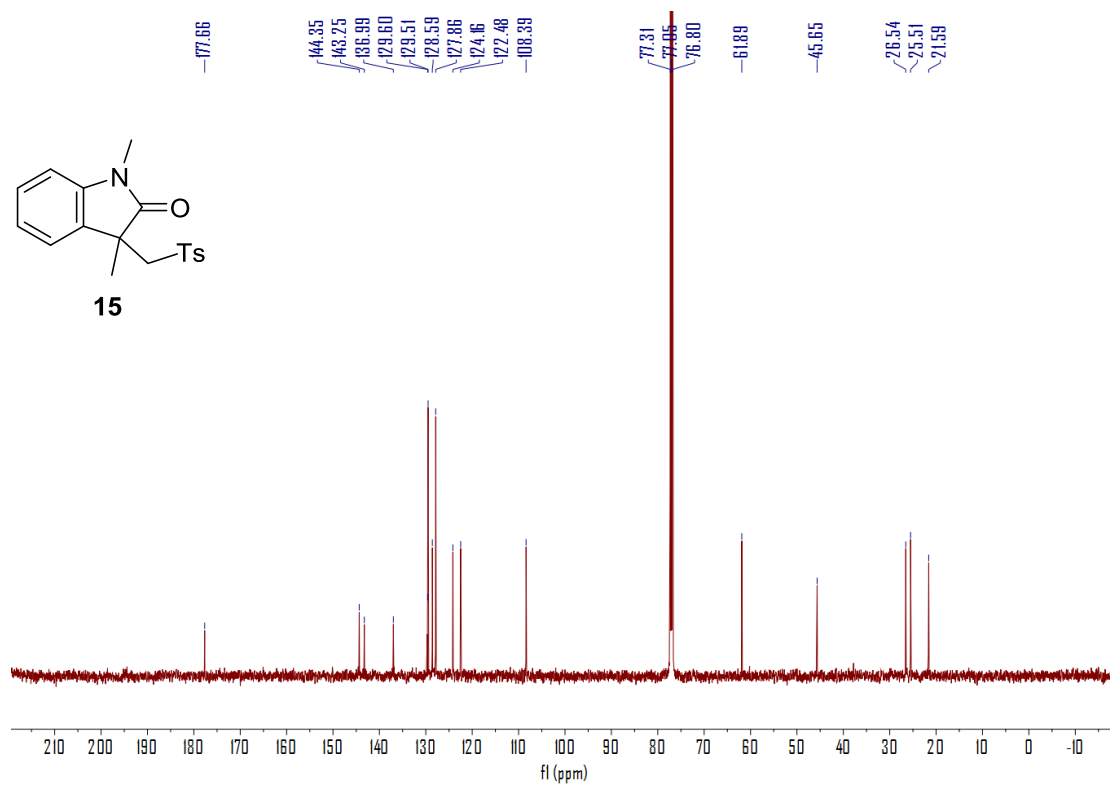
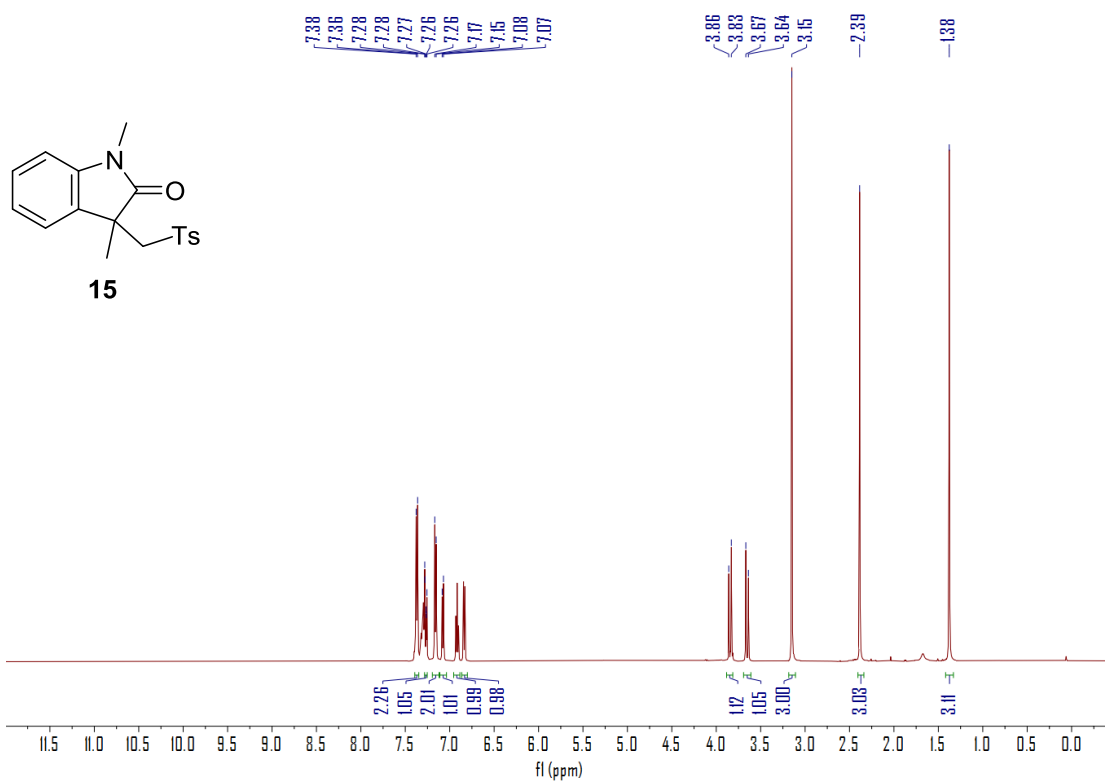


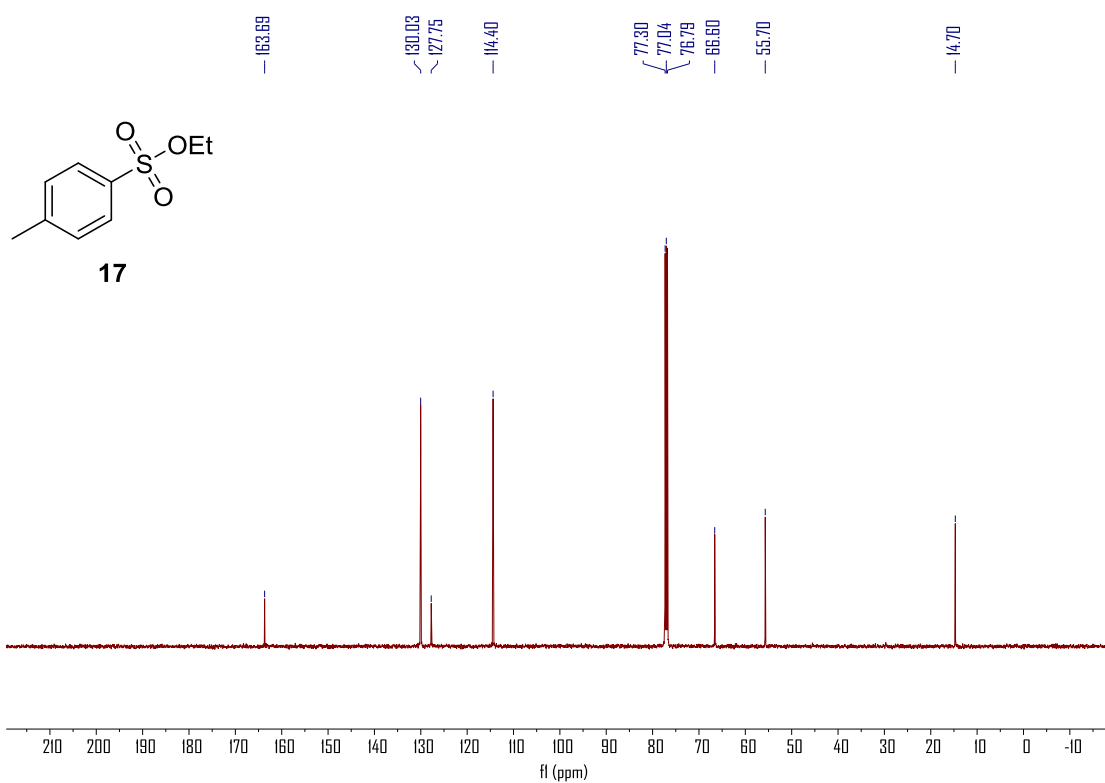
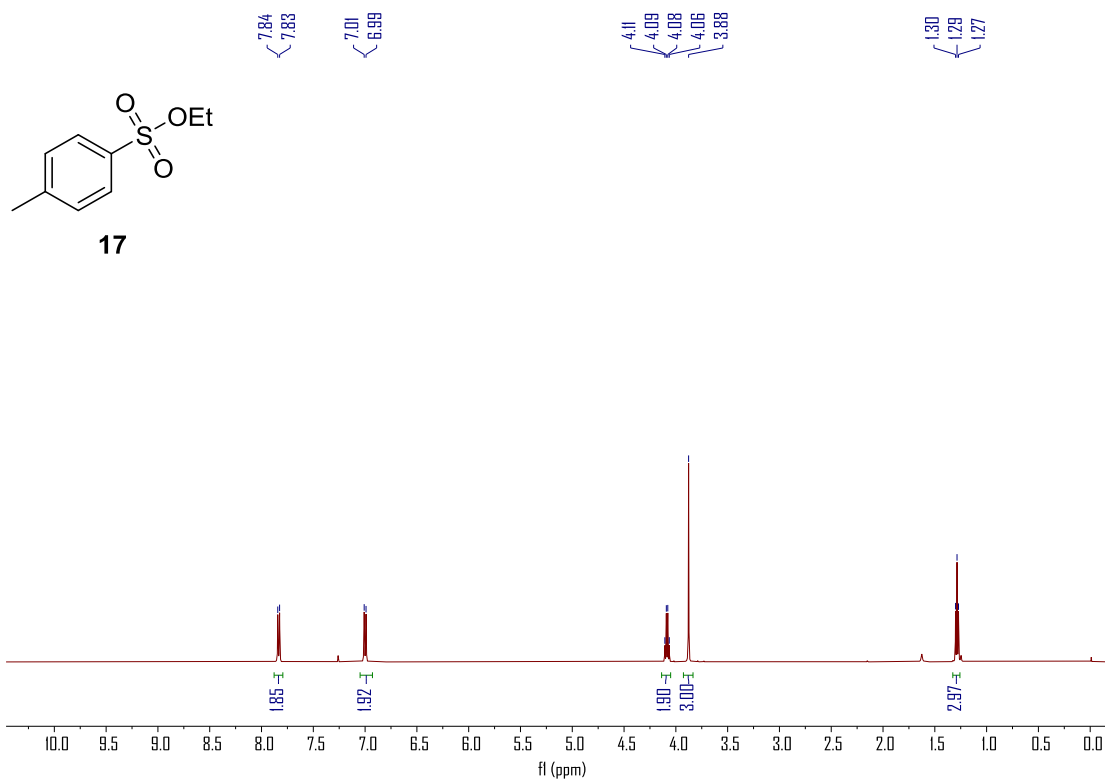












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