

# Supporting Information

## Highly Regio- and Stereoselective Bromochlorination and Bromoazidation of 1,3- Dienes

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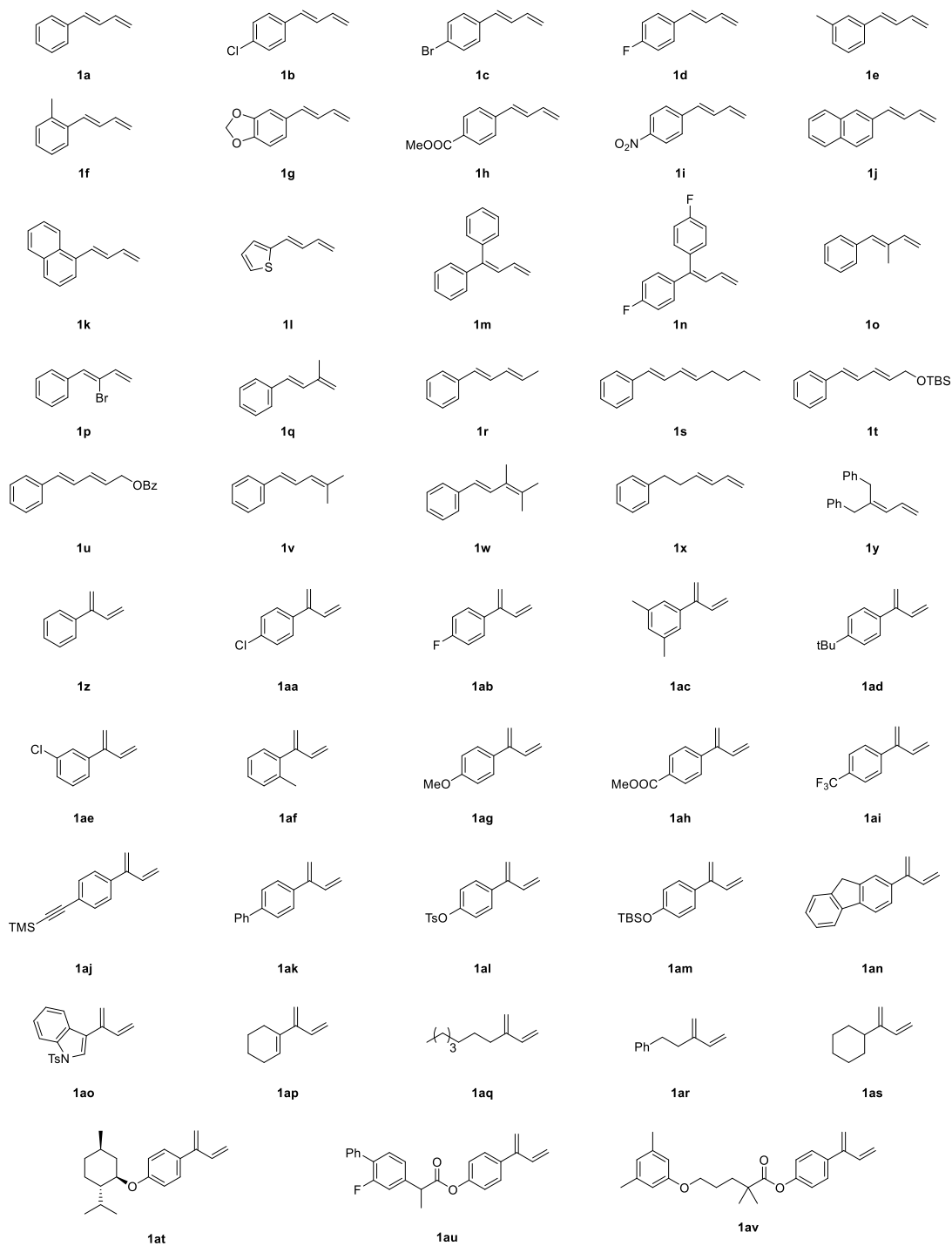
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## 1. General Information

Unless otherwise noted, reagents and solvents were purchased from commercial suppliers (such as Energy Chemical Corporation, J&K Scientific, Sinopharm Chemical Reagent Corporation etc.) and used without further purification. Dry toluene was used for bromochlorination of 1,3-dienes after distilled from CaH<sub>2</sub> while toluene was directly used for bromoazidation of 1,3-dienes without further purification. <sup>1</sup>H NMR, <sup>19</sup>F NMR and <sup>13</sup>C NMR spectra were recorded at 25 °C on a Bruker Advance 400 M NMR or 500 M NMR spectrometers (CDCl<sub>3</sub> as solvent). Chemical shifts of <sup>1</sup>H, <sup>19</sup>F and <sup>13</sup>C NMR spectra are reported as δ in units of parts per million (ppm) downfield from SiMe<sub>4</sub> (δ 0.00) and relative to the signal of SiMe<sub>4</sub> (δ 0.00 singlet). Multiplicities were given as: s (singlet); d (doublet); t (triplet); q (quartet); dd (doublet of doublets); dt (doublet of triplets); m (multiplets), etc. Coupling constants are reported as a *J* value in Hertz (Hz). The residual solvent signals were used as references and the chemical shifts were converted to the TMS scale (CDCl<sub>3</sub>: δ H = 7.26 ppm, δ C = 77.16 ppm). High resolution mass spectral analysis (HRMS) was performed on Waters XEVO G2 Q-TOF (Waters Corporation). Preparative high performance liquid chromatography (Preparative HPLC) was performed on Thermo Scientific UltiMate 3000 equipped with Shimadzu Shim-Pack PRC-ODS column, conditions: MeCN/H<sub>2</sub>O = 100:0, flow rate = 5 mL/min, column temperature = 25 °C, UV-Vis detection at λ = 214 nm. Flash chromatography was performed using 200-300 mesh silica gel with the indicated solvent system. Single crystal X-ray diffraction data was collected on the Rigaku Oxford Diffraction (ROD) SuperNova Diffraction System.

## 2. Synthesis of Starting Materials

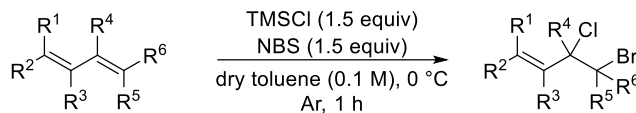
1,3-dienes (**1a-1r**, **1x**, **1y**)<sup>[1]</sup>, **1r**<sup>[2]</sup>, **1r**<sup>[3]</sup>, **1t**<sup>[4]</sup>, **1u**<sup>[5]</sup>, **1v**<sup>[6]</sup>, **1w**<sup>[7]</sup> (**11z-1av**)<sup>[8]</sup> were prepared according to published procedures. All 1,3-dienes were known compounds and those spectral data were in good agreement with literature values.



### 3. General Experimental Procedures

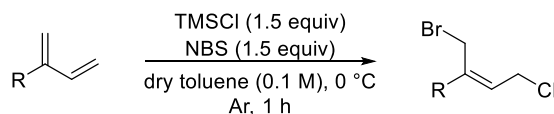
#### 3.1 General Procedure for Bromochlorination of 1,3-Dienes

Procedure A: Selective 4,3-bromochlorination of 1,3-dienes



An oven dried 15 mL sealed tube equipped with a magnetic stir bar was charged with the corresponding 1,3-diene (0.2 mmol, 1.0 equiv), dry toluene (2 mL) under argon atmosphere and cooled down to 0 °C. Then, TMSCl (0.3 mmol, 1.0 M in CH<sub>2</sub>Cl<sub>2</sub>) and NBS (0.3 mmol, 0.5 M in MeCN) were added dropwise in turn. The reaction mixture was stirred at 0 °C for 1 h. After that, the reaction mixture was quenched with saturated Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> aqueous solution, diluted with water and extracted with CH<sub>2</sub>Cl<sub>2</sub>. The combined organic layers were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure. The residue was purified by preparative HPLC to afford products.

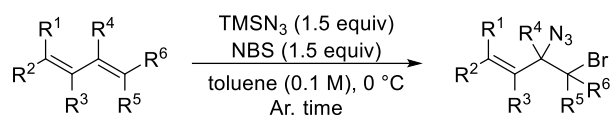
Procedure B: Selective 1,4-bromochlorination of 2-substituted 1,3-dienes



An oven dried 15 mL sealed tube equipped with a magnetic stir bar was charged with the corresponding 1,3-diene (0.2 mmol, 1.0 equiv), dry toluene (2 mL) under argon atmosphere and cooled down to 0 °C. Then, TMSCl (0.3 mmol, 1.0 M in CH<sub>2</sub>Cl<sub>2</sub>) and NBS (0.3 mmol, 0.5 M in MeCN) were added dropwise in turn. The reaction mixture was stirred at 0 °C for 1 h. After that, the reaction mixture was quenched with saturated Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> aqueous solution, diluted with water and extracted with CH<sub>2</sub>Cl<sub>2</sub>. The combined organic layers were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel or preparative HPLC to afford products.

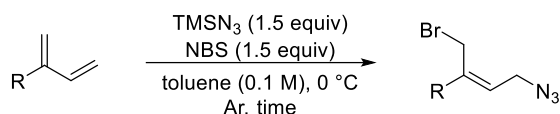
#### 3.2 General Procedure for Bromoazidation of 1,3-Dienes

Procedure C: Selective 4,3-bromoazidation of 1,3-dienes



An oven dried 15 mL sealed tube equipped with a magnetic stir bar was charged with the corresponding 1,3-diene (0.2 mmol, 1.0 equiv), toluene (2 mL) under argon atmosphere and cooled down to 0 °C. Then, TMSN<sub>3</sub> (0.3 mmol, 1.0 M in CH<sub>2</sub>Cl<sub>2</sub>) and NBS (0.3 mmol, 0.5 M in MeCN) were added dropwise in turn. The reaction mixture was stirred at 0 °C until completion of the reaction (monitored by TLC). After that, the reaction mixture was quenched with saturated Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> aqueous solution, diluted with water and extracted with CH<sub>2</sub>Cl<sub>2</sub>. The combined organic layers were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate to afford products.

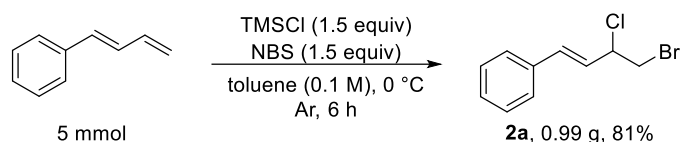
Procedure D: Selective 1,4-bromoazidation of 2-substituted 1,3-dienes



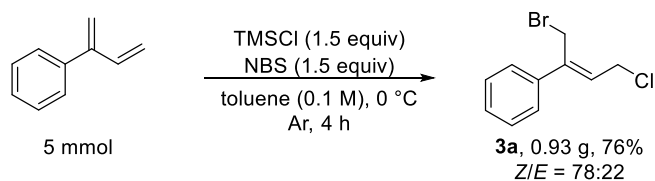
An oven dried 15 mL sealed tube equipped with a magnetic stir bar was charged with the corresponding 1,3-diene (0.2 mmol, 1.0 equiv), toluene (2 mL) under argon atmosphere and cooled down to 0 °C. Then, TMSN<sub>3</sub> (0.3 mmol, 1.0 M in CH<sub>2</sub>Cl<sub>2</sub>) and NBS (0.3 mmol, 0.5 M in MeCN) were added dropwise in turn. The reaction mixture was stirred at 0 °C until completion of the reaction (monitored by TLC). After that, the reaction mixture was quenched with saturated Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> aqueous solution, diluted with water and extracted with CH<sub>2</sub>Cl<sub>2</sub>. The combined organic layers were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate to afford products.

### 3.3 Gram-Scale Reactions and Product Transformations

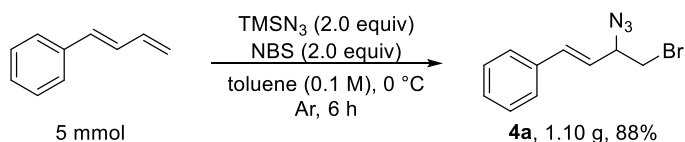
#### (1) Gram-Scale Reactions



An oven dried round bottom flask equipped with a magnetic stir bar was charged with the corresponding 1,3-diene (5.0 mmol, 1.0 equiv), dry toluene (50 mL) under argon atmosphere and cooled down to 0 °C. Then, TMSCl (7.5 mmol, 1.0 M in CH<sub>2</sub>Cl<sub>2</sub>) and NBS (7.5 mmol, 0.5 M in MeCN) were added dropwise in turn. The reaction mixture was vigorously stirred at 0 °C for 6 h. After that, the reaction mixture was quenched with saturated Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> aqueous solution, diluted with water and extracted with CH<sub>2</sub>Cl<sub>2</sub>. The combined organic layers were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure. The residue was purified by preparative HPLC to afford product **2a** in 81% yield (0.99 g).

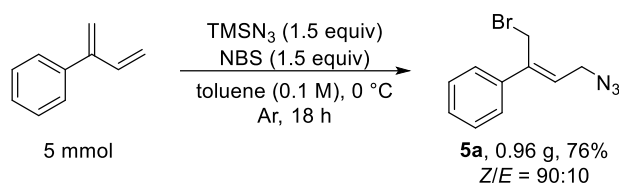


An oven dried round bottom flask equipped with a magnetic stir bar was charged with the corresponding 1,3-diene (5.0 mmol, 1.0 equiv), dry toluene (50 mL) under argon atmosphere and cooled down to 0 °C. Then, TMSCl (7.5 mmol, 1.0 M in CH<sub>2</sub>Cl<sub>2</sub>) and NBS (7.5 mmol, 0.5 M in MeCN) were added dropwise in turn. The reaction mixture was vigorously stirred at 0 °C for 4 h. After that, the reaction mixture was quenched with saturated Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> aqueous solution, diluted with water and extracted with CH<sub>2</sub>Cl<sub>2</sub>. The combined organic layers were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel and eluted with petroleum ether to afford product **3a** in 76% yield (0.93 g, *Z/E* = 78:22).



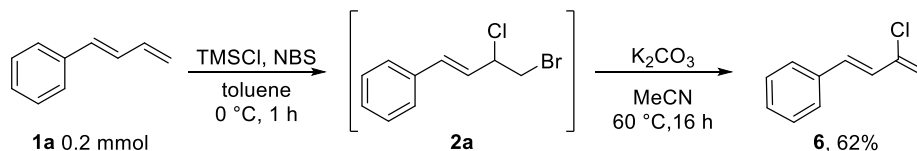
An oven dried round bottom flask equipped with a magnetic stir bar was charged with the corresponding 1,3-diene (5.0 mmol, 1.0 equiv), toluene (50 mL) under argon atmosphere and cooled down to 0 °C. Then, TMSN<sub>3</sub> (10.0 mmol, 1.0 M in CH<sub>2</sub>Cl<sub>2</sub>) and

NBS (10.0 mmol, 0.5 M in MeCN) were added dropwise in turn. The reaction mixture was vigorously stirred at 0 °C for 6 h. After that, the reaction mixture was quenched with saturated Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> aqueous solution, diluted with water and extracted with CH<sub>2</sub>Cl<sub>2</sub>. The combined organic layers were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel and eluted with ethyl acetate/petroleum ether (1:20) to afford product **4a** in 88% yield (1.10 g).



An oven dried round bottom flask equipped with a magnetic stir bar was charged with the corresponding 1,3-diene (5.0 mmol, 1.0 equiv), toluene (50 mL) under argon atmosphere and cooled down to 0 °C. Then, TMSN<sub>3</sub> (7.5 mmol, 1.0 M in CH<sub>2</sub>Cl<sub>2</sub>) and NBS (7.5 mmol, 0.5 M in MeCN) were added dropwise in turn. The reaction mixture was vigorously stirred at 0 °C for 18 h. After that, the reaction mixture was quenched with saturated Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> aqueous solution, diluted with water and extracted with CH<sub>2</sub>Cl<sub>2</sub>. The combined organic layers were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel and eluted with ethyl acetate/petroleum ether (1:20) to afford product **5a** in 76% yield (0.96 g, *Z/E* = 90:10).

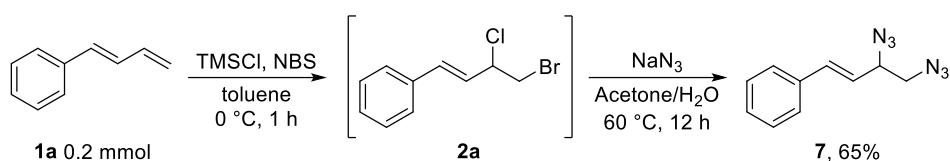
## (2) One-pot synthesis of (*E*)-(3-chlorobuta-1,3-dien-1-yl)benzene



The crude product **2a** was prepared according to the procedure A. Then, K<sub>2</sub>CO<sub>3</sub> (2.0 equiv), MeCN (1 mL) were added to the residue and the mixture was stirred at 60 °C for 16 h. After that, the reaction mixture was quenched with H<sub>2</sub>O, extracted with CH<sub>2</sub>Cl<sub>2</sub>, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated under vacuum. The residue was purified by column chromatography on silica gel and eluted with petroleum ether to afford product **6** in 62% yield (20.4 mg).

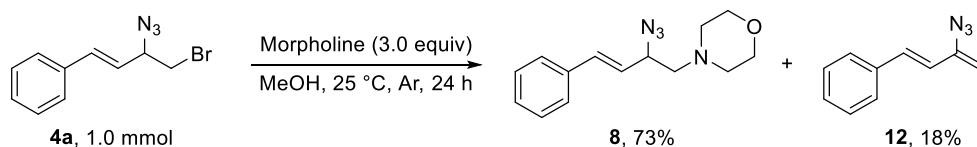


### (3) One-pot synthesis of (*E*)-(3,4-diazidobut-1-en-1-yl)benzene

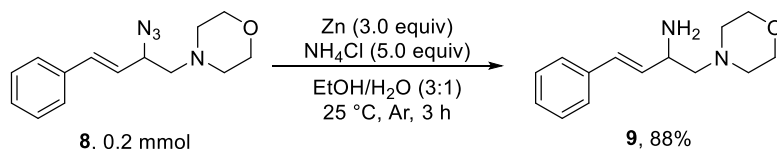


The crude product **2a** was prepared according to the procedure A. Then, NaN<sub>3</sub> (1.5 equiv), acetone (0.8 mL) and H<sub>2</sub>O (0.2 mL) were added to the residue and the mixture was stirred at 60 °C for 12 h. After that, the reaction mixture was quenched with H<sub>2</sub>O, extracted with CH<sub>2</sub>Cl<sub>2</sub>, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated under vacuum. The residue was purified by column chromatography on silica gel and eluted with ethyl acetate/petroleum ether (1:20) to afford product **7** in 65% yield (27.9 mg).

### (4) Synthesis of (*E*)-(3-azidobuta-1,3-dien-1-yl)benzene and (*E*)-1-morpholino-4-phenylbut-3-en-2-amine



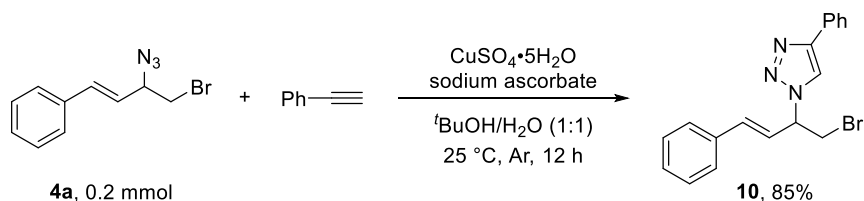
To an oven dried 25-mL Schlenk tube equipped with a magnetic stir bar, were added **4a** (0.2520 g, 1.0 mmol), morpholine (0.2610 g, 3.0 mmol), MeOH (2.5 mL) under argon atmosphere. The reaction mixture was stirred at 25 °C for 24 h. After solvent was removed under reduced pressure, the residue was purified by column chromatography on silica gel and eluted with ethyl acetate/petroleum ether (1:5) to afford compound **8** (187.7 mg, 73%) as a pale yellow oil. Besides, the byproduct **12** was obtained in 18% isolated yield.



To an oven dried 10-mL Schlenk tube equipped with a magnetic stir bar, were added Zn (0.0396 g, 0.6 mmol), NH<sub>4</sub>Cl (0.0535 g, 1.0 mmol), **8** (0.0517 g, 0.2 mmol), EtOH (0.75 mL), H<sub>2</sub>O (0.25 mL) under argon atmosphere. The reaction mixture was stirred at 25 °C for 3 h. Then, the reaction was quenched with *Sat.* Na<sub>2</sub>CO<sub>3</sub> (aq.), extracted with ethyl acetate, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated under vacuum. The

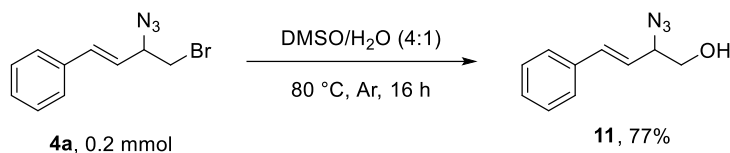
residue was purified by column chromatography on silica gel and eluted with DCM/MeOH (10:1 to 5:1) to afford **9** (41.0 mg, 88%) as a pale yellow solid.

#### (5) Synthesis of (*E*)-1-(1-bromo-4-phenylbut-3-en-2-yl)-4-phenyl-1H-1,2,3-triazole



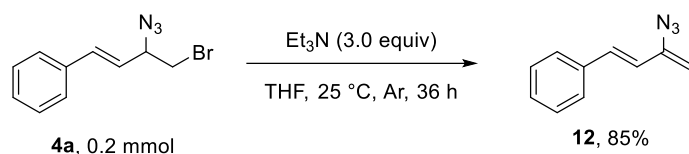
To a 10-mL Schlenk tube equipped with a magnetic stir bar, were added  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  (0.0050g, 10 mol%), sodium ascorbate (0.0079 g, 20 mol%), **4a** (0.0504 g, 0.2 mmol), phenylacetylene (0.0306 g, 0.3 mmol),  $t\text{BuOH}$  (0.5 mL),  $\text{H}_2\text{O}$  (0.5 mL) under argon atmosphere. The reaction mixture was stirred at  $25\text{ }^\circ\text{C}$  for 12 h. Then, the reaction was quenched with  $\text{H}_2\text{O}$ , extracted with  $\text{CH}_2\text{Cl}_2$ , dried over anhydrous  $\text{Na}_2\text{SO}_4$  and concentrated under vacuum. The residue was purified by column chromatography on silica gel and eluted with ethyl acetate/petroleum ether (1:5) to afford compound **10** (60.2 mg, 85%) as a white solid.

#### (6) Synthesis of (*E*)-2-azido-4-phenylbut-3-en-1-ol



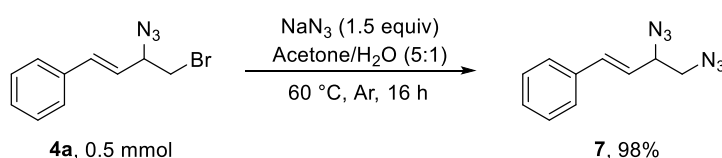
To a 10-mL Schlenk tube equipped with a magnetic stir bar, were added **4a** (0.0504 g, 0.2 mmol), DMSO (0.8 mL),  $\text{H}_2\text{O}$  (0.2 mL) under argon atmosphere. The reaction mixture was stirred at  $80\text{ }^\circ\text{C}$  for 16 h. Then, the reaction was extracted with ethyl acetate, washed with  $\text{H}_2\text{O}$  and brine, dried over anhydrous  $\text{Na}_2\text{SO}_4$  and concentrated under vacuum. The residue was purified by column chromatography on silica gel and eluted with ethyl acetate/petroleum ether (1:5) to afford **11** (29.0 mg, 77%) as a brownish yellow oil.

#### (7) Synthesis of (*E*)-(3-azidobuta-1,3-dien-1-yl)benzene



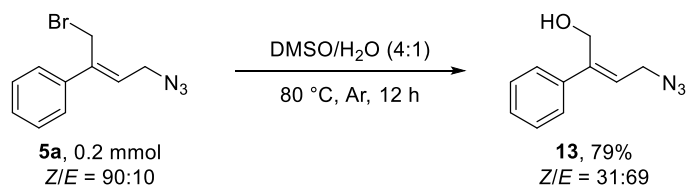
To an oven dried 10-mL Schlenk tube equipped with a magnetic stir bar, were added **4a** (0.0504 g, 0.2 mmol), Et<sub>3</sub>N (3.0 equiv, 0.6 mmol), THF (1.0 mL) under argon atmosphere. The reaction mixture was stirred at 25 °C for 36 h. Then, the reaction was quenched with *Sat.* NH<sub>4</sub>Cl (aq.), extracted with CH<sub>2</sub>Cl<sub>2</sub>, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated under vacuum. The residue was purified by column chromatography on silica gel and eluted with petroleum ether to afford **12** (27.3 mg, 85%) as a pale yellow oil.

### (8) Synthesis of (*E*)-(3,4-diazidobut-1-en-1-yl)benzene



To a 25-mL Schlenk tube equipped with a magnetic stir bar, were added NaN<sub>3</sub> (0.0488 g, 0.75 mmol), **4a** (0.1261 g, 0.5 mmol), acetone (2 mL), H<sub>2</sub>O (0.4 mL) under argon atmosphere. The reaction mixture was stirred at 60 °C for 16 h. Then, the reaction was quenched with H<sub>2</sub>O, extracted with ethyl acetate, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated under vacuum. The residue was purified by column chromatography on silica gel and eluted with ethyl acetate/petroleum ether (1:20) to afford **7** (105.1 mg, 98%) as a brownish yellow oil.

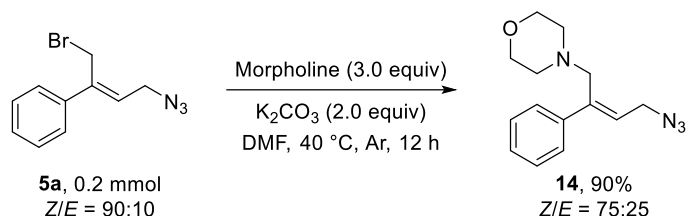
### (9) Synthesis of (*Z*)-4-azido-2-phenylbut-2-en-1-ol



To a 10-mL Schlenk tube equipped with a magnetic stir bar, were added **5a** (0.0504 g, 0.2 mmol), DMSO (0.8 mL), H<sub>2</sub>O (0.2 mL) under argon atmosphere. The reaction mixture was stirred at 80 °C for 12 h. Then, the reaction was extracted with ethyl acetate, washed with H<sub>2</sub>O and brine, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated under

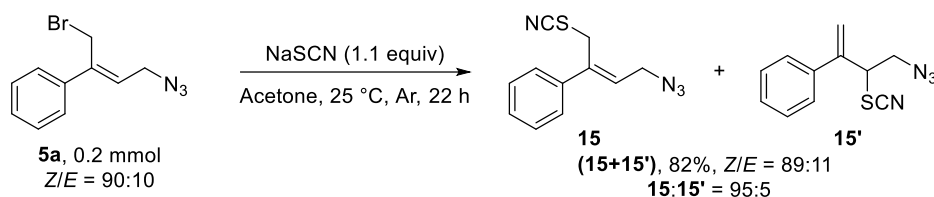
vacuum. The residue was purified by column chromatography on silica gel and eluted with ethyl acetate/petroleum ether (1:5) to afford **13** (30.0 mg, 79%, *Z/E* = 31:69) as a pale yellow oil.

### (10) Synthesis of (*Z*)-4-(4-azido-2-phenylbut-2-en-1-yl)morpholine



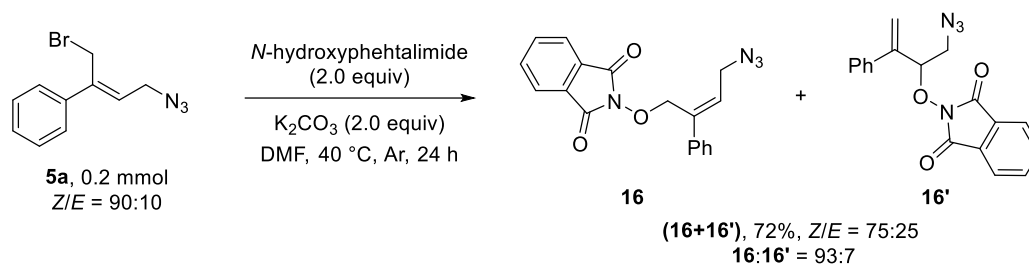
To an oven dried 10-mL Schlenk tube equipped with a magnetic stir bar, were added  $\text{K}_2\text{CO}_3$  (0.0553 g, 0.4 mmol), **5a** (0.0504 g, 0.2 mmol), morpholine (0.2610 g, 0.6 mmol), DMF (1.0 mL) under argon atmosphere. The reaction mixture was stirred at 40 °C for 12 h. Then, the reaction was extracted with ethyl acetate, washed with  $\text{H}_2\text{O}$  and brine, dried over anhydrous  $\text{Na}_2\text{SO}_4$  and concentrated under vacuum. The residue was purified by column chromatography on silica gel and eluted with ethyl acetate/petroleum ether (1:5) to afford **14** (46.4 mg, 90%, *Z/E* = 75:25) as a pale yellow oil.

### (11) Synthesis of (*Z*)-4-(4-azido-1-thiocyanatobut-2-en-2-yl)benzene



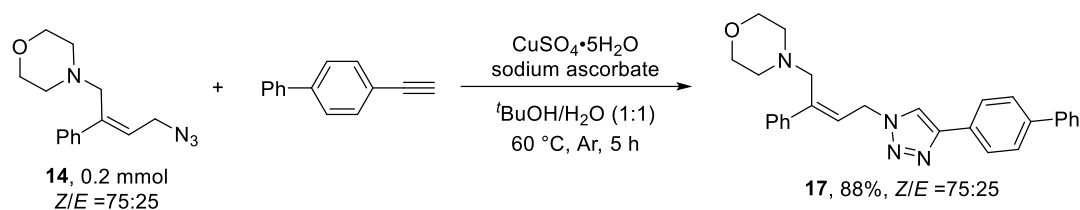
To an oven dried 10-mL Schlenk tube equipped with a magnetic stir bar, were added  $\text{NaSCN}$  (0.0178 g, 0.22 mmol), **2a** (0.0504 g, 0.2 mmol), acetone (1.0 mL) under argon atmosphere. The reaction mixture was stirred at 25 °C for 22 h. Then, the reaction was quenched with  $\text{H}_2\text{O}$ , extracted with ethyl acetate, dried over anhydrous  $\text{Na}_2\text{SO}_4$  and concentrated under vacuum. The residue was purified by column chromatography on silica gel and eluted with ethyl acetate/petroleum ether (1:5) to afford **15** (37.5 mg, 82%, *Z/E* = 89:11, **15:15'** = 95:5) as a pale yellow oil.

## (12) Synthesis of (*Z*)-2-((4-azido-2-phenylbut-2-en-1-yl)oxy)isoindoline-1,3-dione



To an oven dried 10-mL Schlenk tube equipped with a magnetic stir bar, were added  $K_2CO_3$  (0.0553 g, 0.4 mmol), *N*-hydroxyphthalimide (0.0652 g, 0.4 mmol), **5a** (0.0504 g, 0.2 mmol), DMF (1.0 mL) under argon atmosphere. The reaction mixture was stirred at 40 °C for 24 h. Then, the reaction was extracted with ethyl acetate, washed with  $H_2O$  and brine, dried over anhydrous  $Na_2SO_4$  and concentrated under vacuum. The residue was purified by column chromatography on silica gel and eluted with ethyl acetate/petroleum ether (1:5) to afford **16** (48.1 mg, 72%, *Z/E* = 75:25, **16:16'** = 93:7) as a white solid.

## (13) Synthesis of (*Z*)-4-(4-(4-([1,1'-biphenyl]-4-yl)-1*H*-1,2,3-triazol-1-yl)-2-phenylbut-2-en-1-yl)morpholine



To a 10-mL Schlenk tube equipped with a magnetic stir bar, were added  $CuSO_4 \cdot 5H_2O$  (0.0050 g, 10 mol%), sodium ascorbate (0.0079 g, 20 mol%), **14** (0.0517 g, 0.2 mmol), 4-biphenylacetylene (0.0535 g, 0.3 mmol),  $tBuOH$  (0.5 mL),  $H_2O$  (0.5 mL) under argon atmosphere. The reaction mixture was stirred at 60 °C for 5 h. Then, the reaction was quenched with  $H_2O$ , extracted with  $CH_2Cl_2$ , dried over anhydrous  $Na_2SO_4$  and concentrated under vacuum. The residue was purified by column chromatography on silica gel and eluted with ethyl acetate/petroleum ether (1:5) to afford **17** (76.4 mg, 88%) as a white solid.

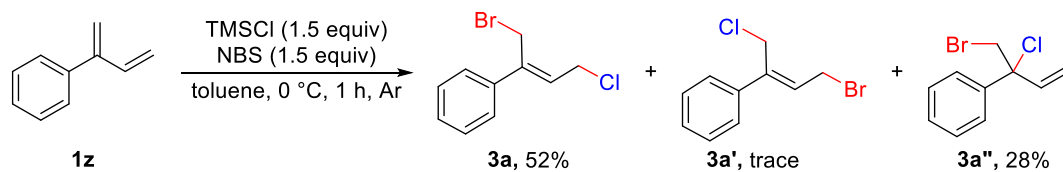
### 3.4 Control Experiments Study for the Transformation between Relevant Vicinal and Allyl Chlorobromides.

According to the results of control experiments, we were pleased to find that **3a''** could be smoothly converted to **3a** and **3a'** in the NMR tube at 25 °C after 8 h. Besides, the results indicated that the higher the reaction temperature, the faster the conversion rate, but solvent and light had no obvious effect on the transformation. Subsequently, it is noteworthy that **2g'** was completely transformed into **2g** in CDCl<sub>3</sub> at 25 °C after 12 h. Likewise, solvent and light did not evidently affect the transformation. Frustratingly, there was no mutual transformation between **2w** and **2w'**.

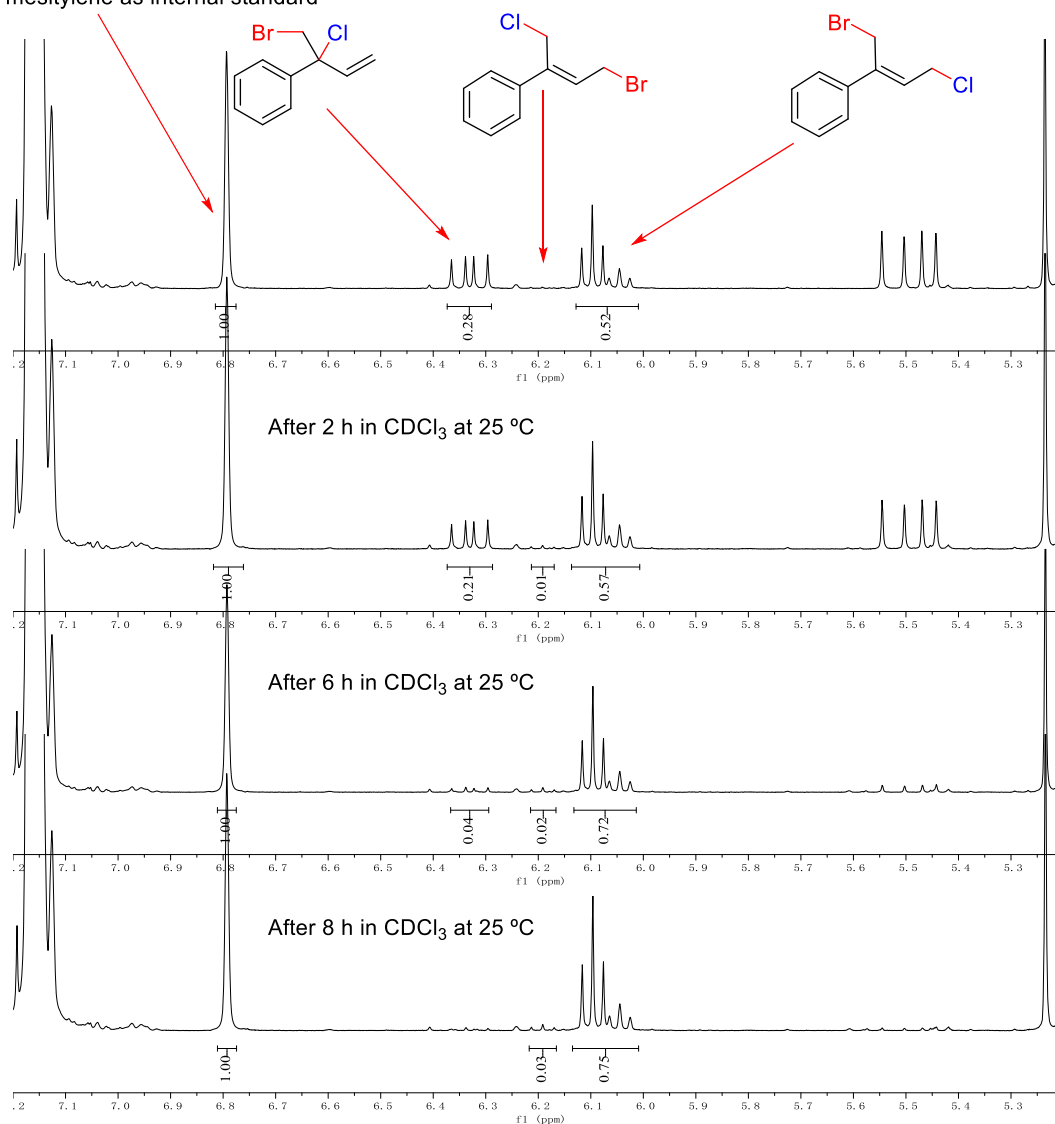
Thus, taking into account the results of the above control experiments, we found that heating had an obvious effect on the conversion and the higher the temperature, the faster the conversion rate. It is worth noting that the products generated from the transformations, always contain a conjugated structure. Therefore, we proposed that the driving force of the transformation may be due to the thermodynamic stability of the conjugated structure and the possible mechanism of neighboring group participation was proposed.

## Control Experiments for the Transformation of 3a'' into 3a and 3a'

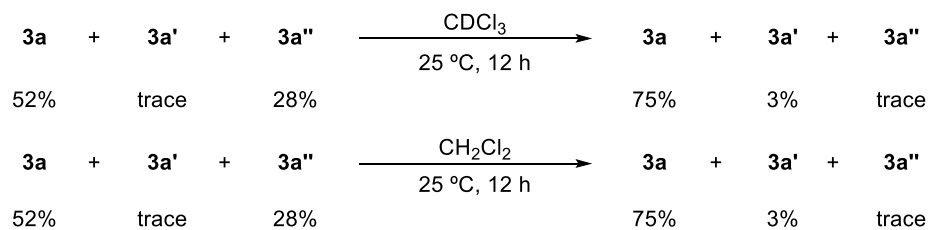
A) Time effect on the transformation of 3a'' into 3a and 3a'



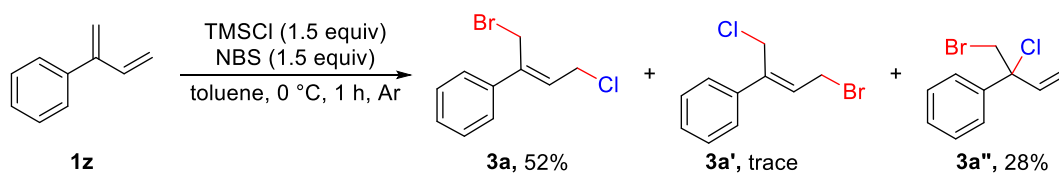
mesitylene as internal standard



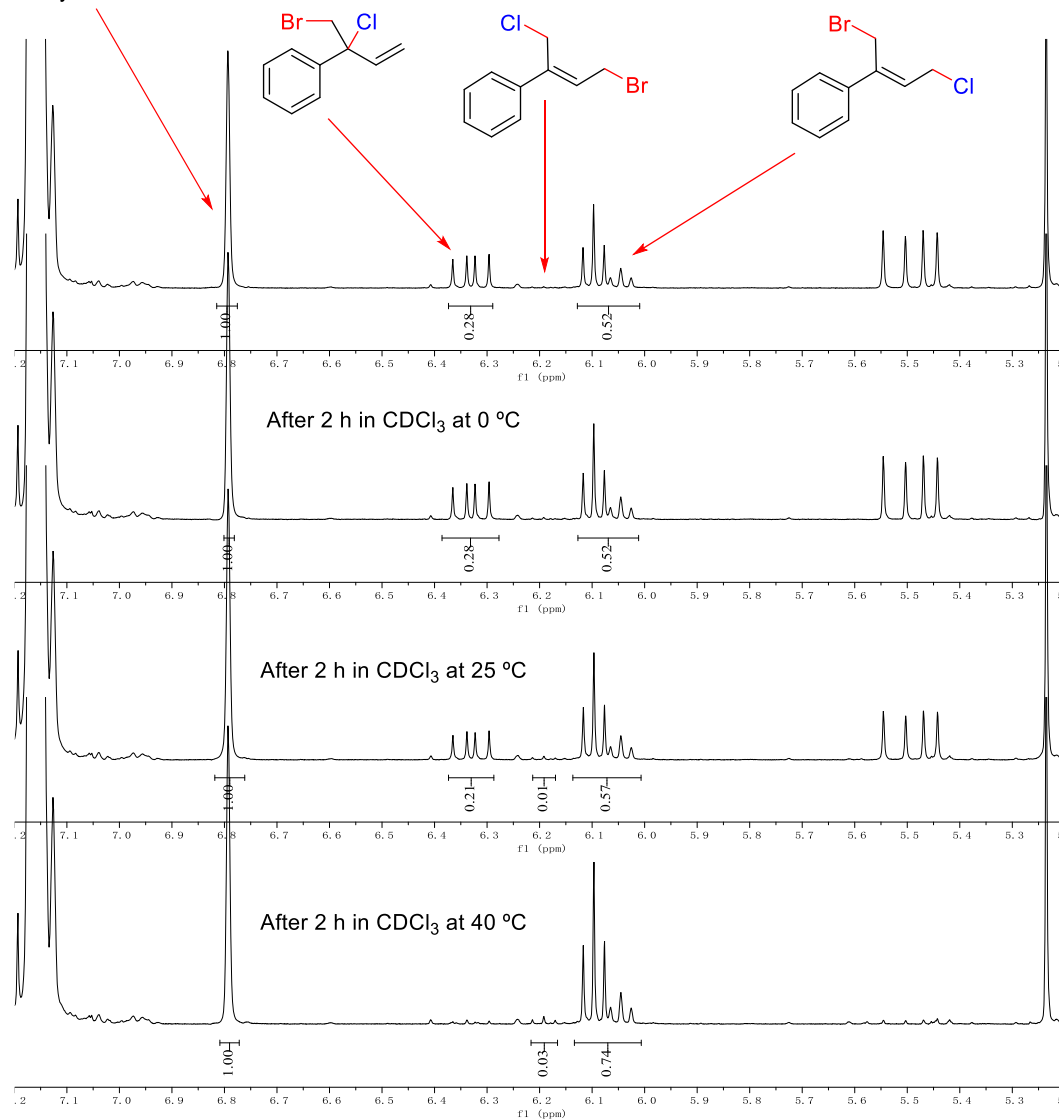
B) Solvent effect on the transformation of 3a'' into 3a and 3a' (mesitylene as internal standard)



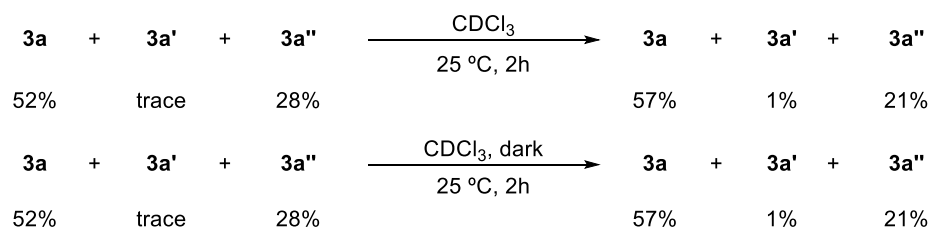
B) Temperature effect on the transformation of **3a''** into **3a** and **3a'**



mesitylene as internal standard



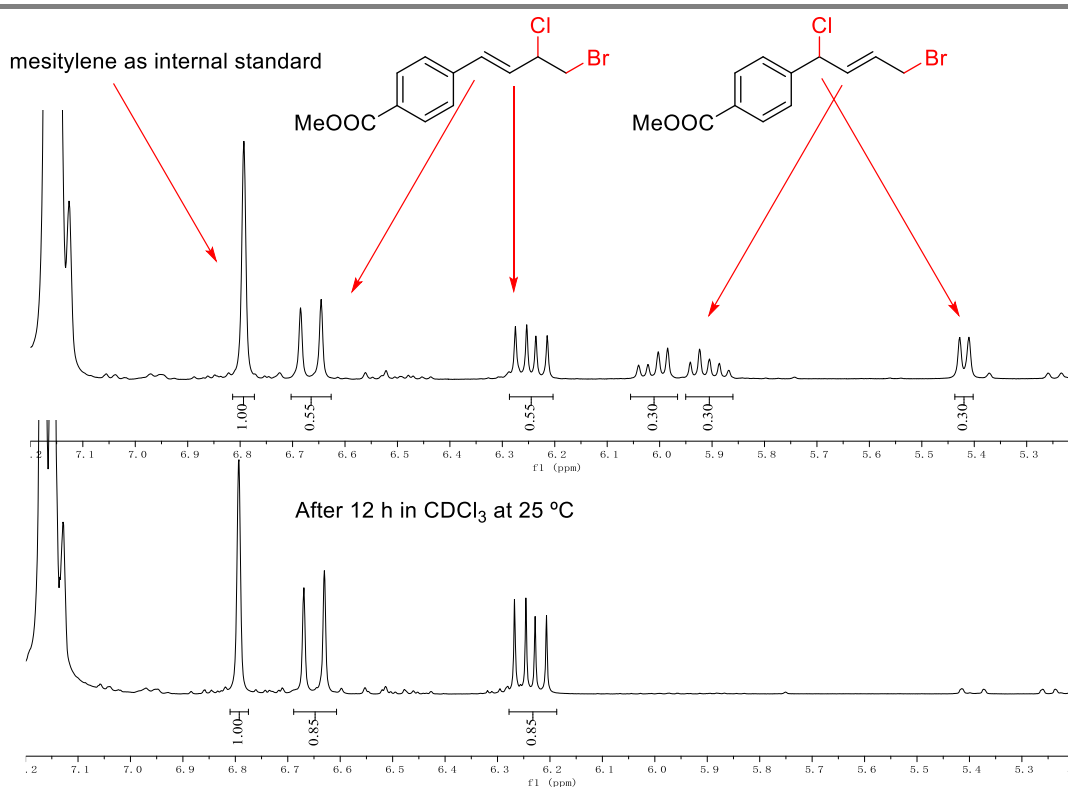
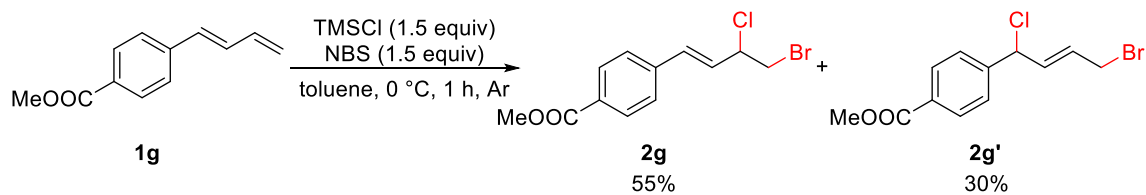
D) Light effect on the transformation of **3a''** into **3a** and **3a'** (mesitylene as internal standard)



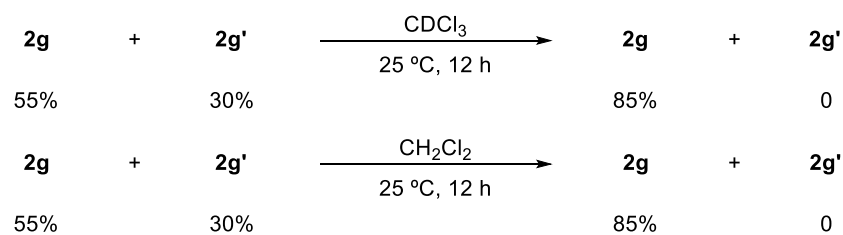


## (2) Control Experiments for the Transformation of 2g' to 2g and No Mutual Transformation between 2w and 2w'.

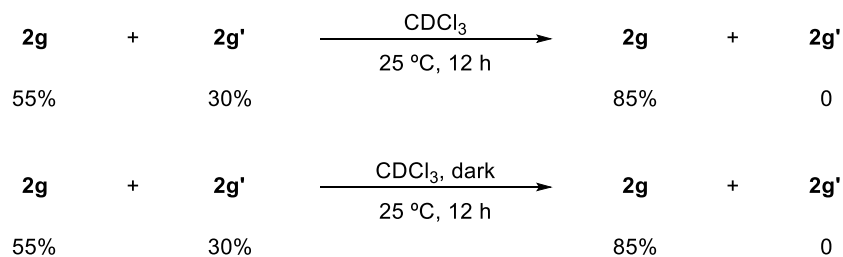
A) Transformation of 2g' to 2g



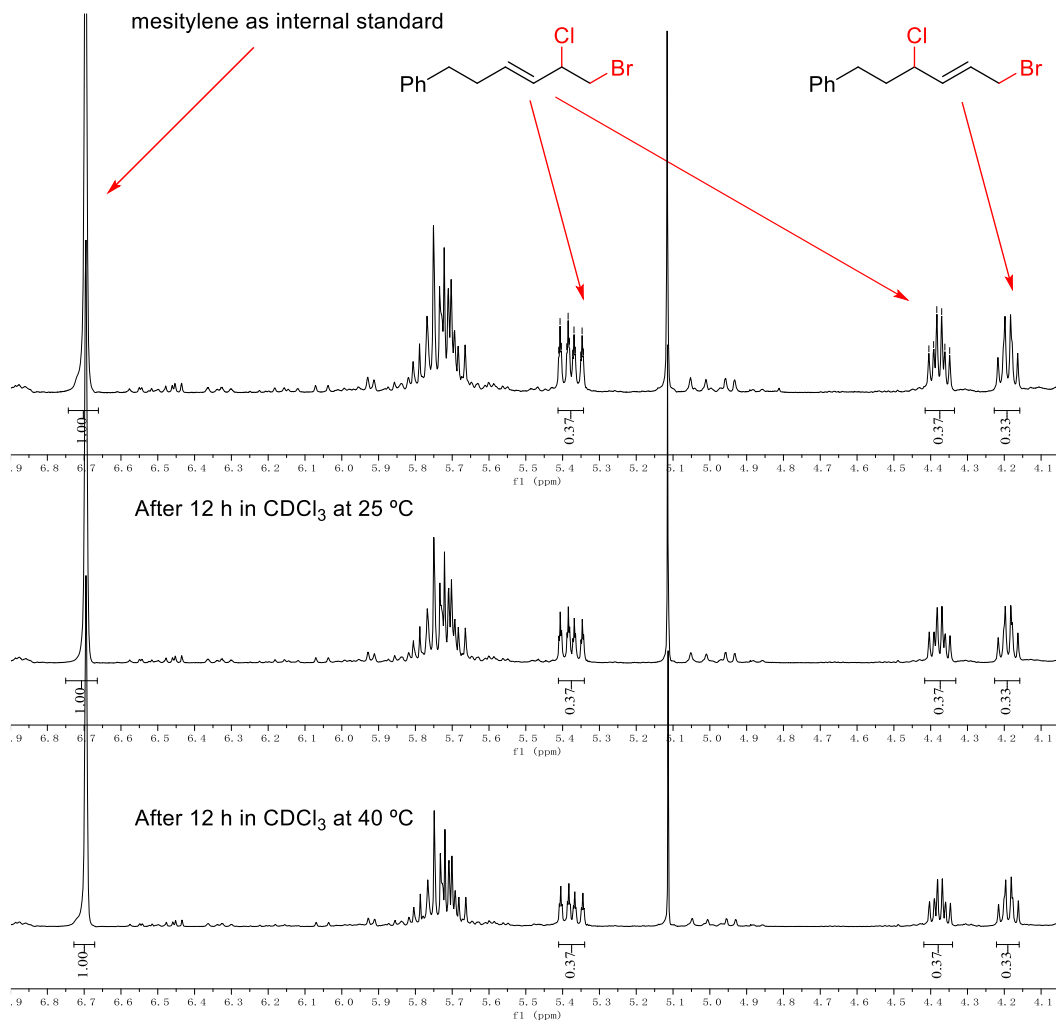
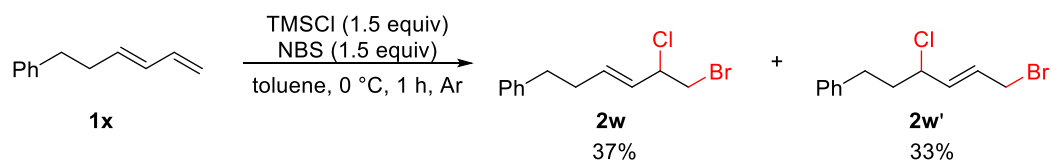
Sovent effect on the transformation of 2g' into 2g (mesitylene as internal standard)



Light effect on the transformation of 2g' into 2g (mesitylene as internal standard)



B) No mutual transformation between **2w** and **2w'**



### 3.5 X-Ray Crystallographic Data of 17.

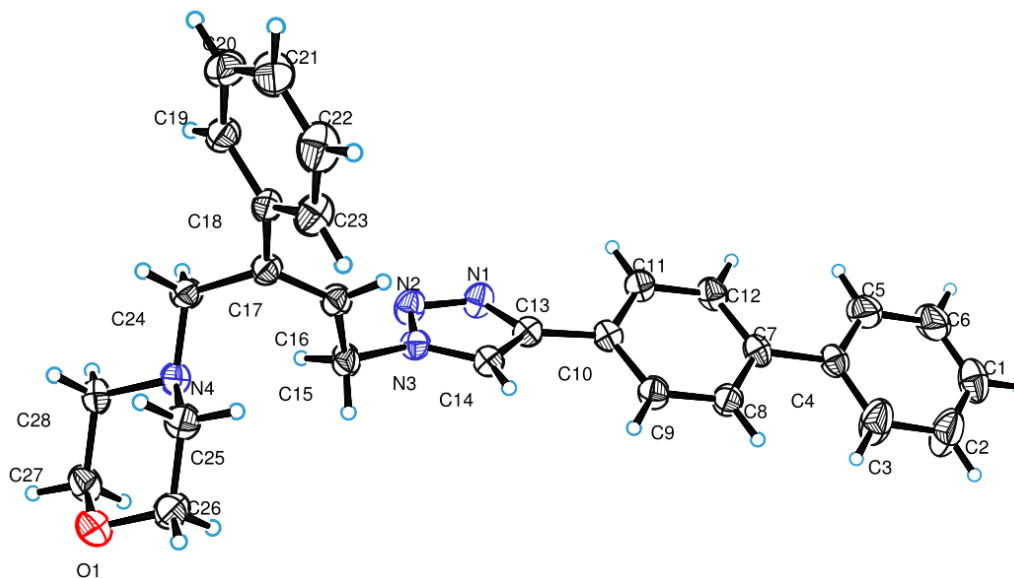


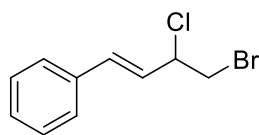
Table S1. Crystal data and structure refinement for **17**

|                                  |                    |
|----------------------------------|--------------------|
| Identification code              | <b>17</b>          |
| Empirical formula                | $C_{28}H_{28}N_4O$ |
| Formula weight                   | 436.54             |
| Temperature/K                    | 293(2)             |
| Crystal system                   | monoclinic         |
| Space group                      | $P2_1$             |
| a/Å                              | 10.8599(9)         |
| b/Å                              | 5.6056(3)          |
| c/Å                              | 19.3263(14)        |
| $\alpha/^\circ$                  | 90                 |
| $\beta/^\circ$                   | 95.592(7)          |
| $\gamma/^\circ$                  | 90                 |
| Volume/Å <sup>3</sup>            | 1170.91(14)        |
| Z                                | 2                  |
| $\rho_{\text{calc}}/\text{cm}^3$ | 1.238              |
| $\mu/\text{mm}^{-1}$             | 0.603              |
| F(000)                           | 464.0              |

|   |   |
|---|---|
| Crystal size/mm <sup>3</sup>                | 0.18 × 0.15 × 0.14  |
| Radiation                                   | Cu Kα (λ = 1.54184)   |
| 2θ range for data collection/°              | 8.18 to 145.646   |
| Index ranges                                | -13 ≤ h ≤ 13, -6 ≤ k ≤ 4, -23 ≤ l ≤ 21                        |
| Reflections collected                       | 4469  |
| Independent reflections                     | 3078 [R <sub>int</sub> = 0.0388, R <sub>sigma</sub> = 0.0558] |
| Data/restraints/parameters                  | 3078/1/299  |
| Goodness-of-fit on F <sup>2</sup>           | 1.064   |
| Final R indexes [I ≥ 2σ (I)]                | R <sub>1</sub> = 0.0564, wR <sub>2</sub> = 0.1271             |
| Final R indexes [all data]                  | R <sub>1</sub> = 0.0806, wR <sub>2</sub> = 0.1500             |
| Largest diff. peak/hole / e Å <sup>-3</sup> | 0.19/-0.18  |

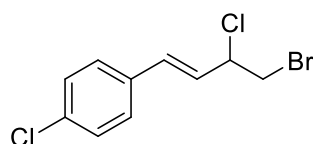
## 4. Characterization Data and Spectrum of Products

### (*E*)-(4-bromo-3-chlorobut-1-en-1-yl)benzene (**2a**)



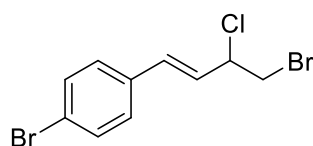
Following the general procedure A, **2a** was obtained in 81% yield (38.3 mg) as colorless oil.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.44 – 7.39 (m, 2H), 7.37 – 7.32 (m, 2H), 7.32 – 7.27 (m, 1H), 6.71 (d,  $J = 15.6$  Hz, 1H), 6.18 (dd,  $J = 15.6, 8.8$  Hz, 1H), 4.74 (tdd,  $J = 8.8, 5.2, 0.8$  Hz, 1H), 3.77 (dd,  $J = 10.3, 5.2$  Hz, 1H), 3.64 (dd,  $J = 10.3, 8.8$  Hz, 1H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  135.5, 135.1, 128.8, 128.8, 127.1, 126.5, 60.8, 35.7. **HRMS (ESI)**:  $m/z$  calculated for  $[\text{C}_{10}\text{H}_{10}\text{BrCl}^+ - \text{Cl}]$ : 208.9965, found: 208.9978.

### (*E*)-1-(4-bromo-3-chlorobut-1-en-1-yl)-4-chlorobenzene (**2b**)



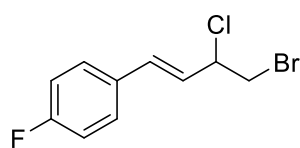
Following the general procedure A, **2b** was obtained in 76% yield (42.6 mg) as colorless oil.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.36 – 7.30 (m, 4H), 6.66 (d,  $J = 15.6$  Hz, 1H), 6.16 (dd,  $J = 15.6, 8.8$  Hz, 1H), 4.72 (tdd,  $J = 8.8, 5.0, 0.8$  Hz, 1H), 3.77 (dd,  $J = 10.3, 5.0$  Hz, 1H), 3.63 (dd,  $J = 10.3, 8.8$  Hz, 1H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  134.5, 134.0, 133.9, 129.0, 128.3, 127.1, 60.5, 35.5. **HRMS (ESI)**:  $m/z$  calculated for  $[\text{C}_{10}\text{H}_9\text{BrCl}_2^+ - \text{Cl}]$ : 242.9576, found: 242.9591.

### (*E*)-1-bromo-4-(4-bromo-3-chlorobut-1-en-1-yl)benzene (**2c**)



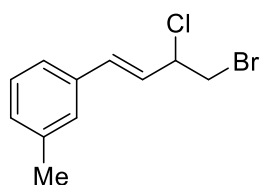
Following the general procedure A, **2c** was obtained in 76% yield (49.3 mg) as colorless oil.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.49 – 7.45 (m, 2H), 7.30 – 7.26 (m, 2H), 6.65 (d,  $J = 15.6$  Hz, 1H), 6.18 (ddd,  $J = 15.6, 8.8, 0.6$  Hz, 1H), 4.79 – 4.67 (m, 1H), 3.77 (ddd,  $J = 10.3, 5.0, 0.6$  Hz, 1H), 3.66 – 3.59 (m, 1H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  134.4, 133.9, 132.0, 128.5, 127.2, 122.7, 60.4, 35.4. **HRMS (ESI)**:  $m/z$  calculated for  $[\text{C}_{10}\text{H}_9\text{Br}_2\text{Cl}^+ - \text{Cl}]$ : 286.9071, found: 286.9069.

### (*E*)-1-(4-bromo-3-chlorobut-1-en-1-yl)-4-fluorobenzene (**2d**)



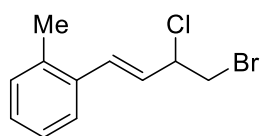
Following the general procedure A, **2d** was obtained in 82% yield (43.2 mg) as colorless oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.42 – 7.36 (m, 2H), 7.08 – 7.00 (m, 2H), 6.67 (d, *J* = 15.6 Hz, 1H), 6.10 (dd, *J* = 15.6, 8.9 Hz, 1H), 4.73 (tdd, *J* = 8.9, 5.1, 0.8 Hz, 1H), 3.77 (dd, *J* = 10.3, 5.1 Hz, 1H), 3.63 (dd, *J* = 10.3, 8.9 Hz, 1H). <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ -112.65 (tt, *J* = 8.8, 5.4 Hz). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 163.1 (d, *J* = 248.4 Hz), 134.0, 131.7 (d, *J* = 3.3 Hz), 128.7 (d, *J* = 8.2 Hz), 126.3 (d, *J* = 2.3 Hz), 115.9 (d, *J* = 21.8 Hz), 60.7, 35.6. HRMS (ESI): *m/z* calculated for [C<sub>10</sub>H<sub>9</sub>BrClF<sup>+</sup>-Cl]: 226.9871, found: 226.9880.

(*E*)-1-(4-bromo-3-chlorobut-1-en-1-yl)-3-methylbenzene (**2e**)



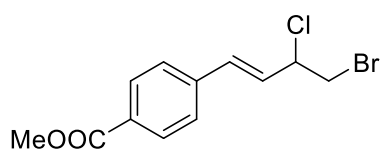
Following the general procedure A, **2e** was obtained in 86% yield (51.9 mg) as colorless oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.25 – 7.18 (m, 3H), 7.15 – 7.09 (m, 1H), 6.67 (d, *J* = 15.6 Hz, 1H), 6.16 (dd, *J* = 15.6, 8.9 Hz, 1H), 4.73 (td, *J* = 8.9, 5.1 Hz, 1H), 3.76 (dd, *J* = 10.3, 5.1 Hz, 1H), 3.63 (dd, *J* = 10.3, 8.9 Hz, 1H), 2.35 (s, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 138.5, 135.4, 135.3, 129.6, 128.7, 127.7, 126.2, 124.3, 61.0, 35.7, 21.5. HRMS (ESI): *m/z* calculated for [C<sub>11</sub>H<sub>12</sub>BrCl<sup>+</sup>-Cl]: 223.0122, found: 223.0126.

(*E*)-1-(4-bromo-3-chlorobut-1-en-1-yl)-2-methylbenzene (**2f**)



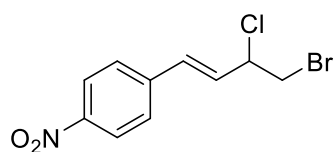
Following the general procedure A, **2f** was obtained in 77% yield (39.9 mg) as colorless oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.47 – 7.43 (m, 1H), 7.21 – 7.14 (m, 3H), 6.92 (d, *J* = 15.5 Hz, 1H), 6.05 (dd, *J* = 15.5, 8.9 Hz, 1H), 4.75 (tdd, *J* = 8.9, 5.1, 0.8 Hz, 1H), 3.78 (dd, *J* = 10.3, 5.1 Hz, 1H), 3.63 (dd, *J* = 10.3, 8.9 Hz, 1H), 2.37 (s, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 136.1, 134.7, 133.1, 130.6, 128.6, 127.9, 126.3, 126.2, 60.9, 35.7, 19.9. HRMS (ESI): *m/z* calculated for [C<sub>11</sub>H<sub>12</sub>BrCl<sup>+</sup>-Cl]: 223.0122, found: 223.0125.

methyl (*E*)-4-(4-bromo-3-chlorobut-1-en-1-yl)benzoate (**2g**)



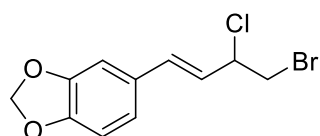
Following the general procedure A, **2g** was obtained in 80% yield (48.9 mg) as colorless oil (4,3-adduct:4,1-adduct = 65:35, the regioisomeric ratio was determined by  $^1\text{H}$  NMR analysis of crude reaction mixture and 4,1-adduct was completely transformed into 4,3-adduct at 25 °C after 12 h).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.04 – 8.00 (m, 2H), 7.50 – 7.45 (m, 2H), 6.75 (d,  $J$  = 15.6 Hz, 1H), 6.30 (dd,  $J$  = 15.6, 8.8 Hz, 1H), 4.75 (tdd,  $J$  = 8.8, 5.0, 0.8 Hz, 1H), 3.92 (s, 3H), 3.78 (dd,  $J$  = 10.3, 5.0 Hz, 1H), 3.64 (dd,  $J$  = 10.3, 8.8 Hz, 1H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  166.8, 139.9, 134.1, 130.1, 130.1, 129.0, 126.9, 60.2, 52.3, 35.3. **HRMS (ESI)**:  $m/z$  calculated for  $\text{C}_{12}\text{H}_{13}\text{BrClO}_2$   $[\text{M}+\text{H}]^+$ : 302.9787, found: 302.9795.

*(E)*-1-(4-bromo-3-chlorobut-1-en-1-yl)-4-nitrobenzene (**2h**)



Following the general procedure A, **2h** was obtained in 82% yield (47.4 mg) as colorless oil (4,3-adduct:4,1-adduct = 60:40, the regioisomeric ratio was determined by  $^1\text{H}$  NMR analysis of crude reaction mixture and 4,1-adduct was transformed into 4,3-adduct very slowly at 25 °C).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.23 – 8.19 (m, 2H), 7.58 – 7.54 (m, 2H), 6.79 (d,  $J$  = 15.7 Hz, 1H), 6.37 (dd,  $J$  = 15.7, 8.6 Hz, 1H), 4.81 – 4.72 (m, 1H), 3.80 (dd,  $J$  = 10.3, 4.9 Hz, 1H), 3.64 (dd,  $J$  = 10.3, 9.1 Hz, 1H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  147.7, 141.8, 132.8, 131.0, 127.7, 124.2, 59.5, 35.0. **HRMS (ESI)**:  $m/z$  calculated for  $[\text{C}_{10}\text{H}_9\text{BrClNO}_2^+\text{-Cl}]$ : 253.9816, found: 253.9834.

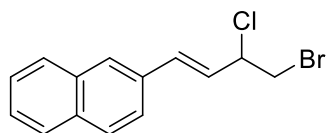
*(E)*-5-(4-bromo-3-chlorobut-1-en-1-yl)benzo[*d*][1,3]dioxole (**2i**)



Following the general procedure A, **2i** was obtained in 73% yield (43.2 mg) as colorless oil.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  6.95 (d,  $J$  = 1.7 Hz, 1H), 6.85 (m, 1H), 6.77 (d,  $J$  = 7.9 Hz, 1H), 6.61 (d,  $J$  = 15.6 Hz, 1H), 6.00 (dd,  $J$  = 15.6, 8.9 Hz 1H), 5.97 (s, 2H), 4.72 (tdd,  $J$  = 8.9, 5.1, 0.8 Hz, 1H), 3.76 (dd,  $J$  = 10.3, 5.1 Hz, 1H), 3.63 (dd,  $J$  = 10.3, 8.9 Hz, 1H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  148.3,

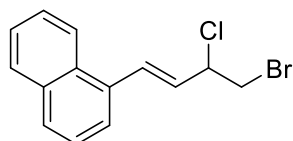
148.2, 134.8, 129.9, 124.7, 122.2, 108.5, 106.1, 101.4, 61.1, 35.8. **HRMS (ESI):**  $m/z$  calculated for  $[C_{11}H_{10}BrClO_2^+-Cl]$ : 288.9631, found: 288.9636.

**(E)-2-(4-bromo-3-chlorobut-1-en-1-yl)naphthalene (2j)**



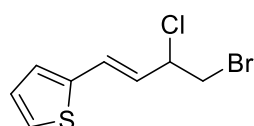
Following the general procedure A, **2j** was obtained in 95% yield (56.1 mg) as colorless oil.  **$^1H$  NMR** (400 MHz,  $CDCl_3$ )  $\delta$  7.84 – 7.76 (m, 4H), 7.61 – 7.57 (m, 1H), 7.51 – 7.43 (m, 2H), 6.86 (d,  $J = 15.6$  Hz, 1H), 6.30 (dd,  $J = 15.6, 8.8$  Hz, 1H), 4.79 (td,  $J = 8.8, 5.2$  Hz, 1H), 3.79 (dd,  $J = 10.3, 5.2$  Hz, 1H), 3.67 (dd,  $J = 10.3, 8.8$  Hz, 1H).  **$^{13}C$  NMR** (101 MHz,  $CDCl_3$ )  $\delta$  135.2, 133.6, 133.6, 133.0, 128.6, 128.3, 127.8, 127.6, 126.7, 126.6, 126.6, 123.6, 61.0, 35.7. **HRMS (ESI):**  $m/z$  calculated for  $[C_{14}H_{12}BrCl^+-Cl]$ : 259.0122, found: 259.0134.

**(E)-1-(4-bromo-3-chlorobut-1-en-1-yl)naphthalene (2k)**



Following the general procedure A, **2k** was obtained in 92% yield (54.3 mg) as colorless oil.  **$^1H$  NMR** (400 MHz,  $CDCl_3$ )  $\delta$  8.13 – 8.02 (m, 1H), 7.90 – 7.77 (m, 2H), 7.67 – 7.58 (m, 1H), 7.57 – 7.44 (m, 4H), 6.21 (dd,  $J = 15.4, 8.8$  Hz, 1H), 4.87 (tdd,  $J = 8.8, 5.1, 0.9$  Hz, 1H), 3.83 (dd,  $J = 10.3, 5.0$  Hz, 1H), 3.69 (dd,  $J = 10.3, 9.0$  Hz, 1H).  **$^{13}C$  NMR** (101 MHz,  $CDCl_3$ )  $\delta$  133.7, 133.3, 132.5, 131.3, 129.7, 129.0, 128.8, 126.5, 126.1, 125.7, 124.6, 123.8, 60.6, 35.6. **HRMS (ESI):**  $m/z$  calculated for  $[C_{14}H_{12}BrCl^+-Cl]$ : 259.0122, found: 259.0115.

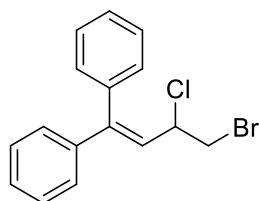
**(E)-2-(4-bromo-3-chlorobut-1-en-1-yl)thiophene (2l)**



Following the general procedure A, **2l** was obtained in 74% yield (37.2 mg) as pale yellow oil.  **$^1H$  NMR** (400 MHz,  $CDCl_3$ )  $\delta$  7.25 – 7.22 (m, 1H), 7.06 – 7.03 (m, 1H), 6.99 (dd,  $J = 5.1, 3.6$  Hz, 1H), 6.83 (dd,  $J = 15.5, 0.7$  Hz, 1H), 6.01 (dd,  $J = 15.5, 8.8$  Hz, 1H), 4.70 (tdd,  $J = 8.8, 5.2, 0.8$  Hz, 1H), 3.75 (dd,  $J = 10.3, 5.2$  Hz, 1H), 3.62 (dd,  $J = 10.3, 8.8$  Hz, 1H).  **$^{13}C$  NMR** (101 MHz,  $CDCl_3$ )  $\delta$  140.3, 128.2, 127.7, 127.6, 125.9, 125.6, 60.7, 35.5. **HRMS (ESI):**  $m/z$  calculated for  $[C_8H_8BrClS^+-Cl]$ : 214.9530, found: 214.9529.

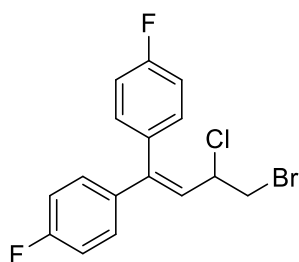


(4-bromo-3-chlorobut-1-ene-1,1-diyl)dibenzene (**2m**)



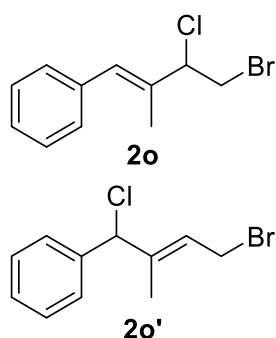
Following the general procedure A, **2m** was obtained in 77% yield (49.8 mg) as colorless oil.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.46 – 7.35 (m, 3H), 7.32 – 7.26 (m, 7H), 6.06 (d,  $J = 10.5$  Hz, 1H), 4.68 (ddd,  $J = 10.5, 9.1, 5.1$  Hz, 1H), 3.69 (dd,  $J = 10.1, 5.1$  Hz, 1H), 3.63 (dd,  $J = 10.1, 9.1$  Hz, 1H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  147.2, 140.9, 138.4, 129.6, 128.7, 128.5, 128.4, 128.1, 127.9, 125.7, 57.5, 35.8. **HRMS (ESI)**:  $m/z$  calculated for  $[\text{C}_{16}\text{H}_{14}\text{BrCl}^+ - \text{Cl}]$ : 285.0278, found: 285.0290.

4,4'-(4-bromo-3-chlorobut-1-ene-1,1-diyl)bis(fluorobenzene) (**2n**)



Following the general procedure A, **2n** was obtained in 90% yield (64.4 mg) as colorless oil.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.29 – 7.19 (m, 4H), 7.16 – 7.08 (m, 2H), 7.04 – 6.96 (m, 2H),  $\delta$  5.99 (d,  $J = 10.5$  Hz, 1H), 4.63 (ddd,  $J = 10.5, 9.6, 4.8$  Hz, 1H), 3.69 (dd,  $J = 10.1, 4.8$  Hz, 1H), 3.61 (dd,  $J = 10.1, 9.6$  Hz, 1H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  163.1 (d,  $J = 249.9$  Hz), 162.7 (d,  $J = 249.0$  Hz), 145.3, 136.9 (d,  $J = 3.3$  Hz), 134.1 (d,  $J = 3.6$  Hz), 131.4 (d,  $J = 8.1$  Hz), 129.6 (d,  $J = 8.1$  Hz), 126.0, 115.9 (d,  $J = 21.5$  Hz), 115.5 (d,  $J = 21.6$  Hz), 57.1, 35.5.  $^{19}\text{F NMR}$  (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -113.08 – -113.18 (m), -113.19 – -113.28 (m). **HRMS (ESI)**:  $m/z$  calculated for  $[\text{C}_{16}\text{H}_{12}\text{BrClF}_2^+ - \text{Cl}]$ : 321.0090, found: 321.0089.

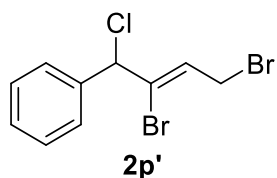
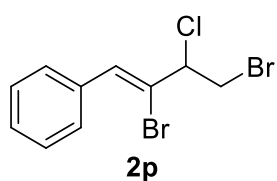
(*E*)-(4-bromo-3-chloro-2-methylbut-1-en-1-yl)benzene (**2o**)



Following the general procedure A, **2o** was obtained in 93% yield (48.3 mg) as colorless oil. (4,3-adduct:4,1-adduct = 69:31, the regioisomeric ratio was determined by  $^1\text{H NMR}$  analysis of crude reaction mixture).  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.39 – 7.33 (m, 3H), 7.33 – 7.28 (m, 2H), 7.28 – 7.23 (m, 1.2H), 6.64 (s, 1H) (**2o**), 6.05 – 5.96 (m, 0.24H) (**2o'**),

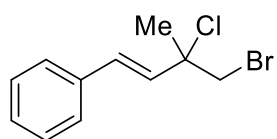
5.50 (s, 0.24H) (**2o'**), 4.74 (dd,  $J = 10.1, 5.8$  Hz, 1H) (**2o**), 4.01 (d,  $J = 8.3$  Hz, 0.48H) (**2o'**), 3.78 – 3.64 (m, 2H) (**2o**), 1.93 (d,  $J = 1.7$  Hz, 3H) (**2o**), 1.72 (d,  $J = 1.6$  Hz, 0.72H) (**2o'**).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ) **2o**:  $\delta$  136.5, 133.6, 132.1, 129.2, 128.4, 127.5, 66.9, 33.0, 12.0. **2o'**:  $\delta$  141.0, 138.7, 128.6, 128.3, 127.5, 124.9, 67.9, 27.6, 13.1. **HRMS (ESI)**:  $m/z$  calculated for  $[\text{C}_{11}\text{H}_{12}\text{BrCl}^+ - \text{Cl}]$ : 223.0122, found: 223.0124.

(*Z*)-(2,4-dibromo-3-chlorobut-1-en-1-yl)benzene (**2p**)



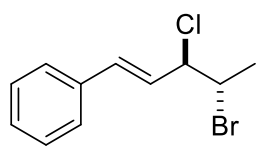
Following the general procedure A, (**2p+2p'**) was obtained in 95% yield (61.6 mg) as colorless oil. (4,3-adduct:4,1-adduct = 58:42, the regioisomeric ratio was determined by  $^1\text{H}$  NMR analysis of crude reaction mixture).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.69 – 7.63 (m, 2H), 7.43 – 7.38 (m, 3H), 7.38 – 7.33 (m, 3.25H), 7.16 (s, 1H) (**2p**), 6.64 (td,  $J = 7.9, 1.2$  Hz, 0.65H) (**2p'**), 5.64 (s, 0.65H) (**2p'**), 4.82 (dd,  $J = 9.8, 5.0$  Hz, 1H) (**2p**), 4.10 (d,  $J = 7.9$  Hz, 1.3H) (**2p'**), 3.89 (dd,  $J = 10.4, 9.8$  Hz, 1H) (**2p**), 3.71 (dd,  $J = 10.4, 5.0$  Hz, 1H) (**2p**).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ) **2p**:  $\delta$  134.1, 129.5, 129.1, 128.9, 128.4, 127.9, 65.4, 33.6. **2p'**:  $\delta$  137.7, 134.3, 130.9, 129.1, 128.2, 123.0, 65.7, 28.9. **HRMS (ESI)**:  $m/z$  calculated for  $[\text{C}_{10}\text{H}_9\text{Br}_2\text{Cl}^+ - \text{Cl}]$ : 286.9071, found: 286.9075.

(*E*)-(4-bromo-3-chloro-3-methylbut-1-en-1-yl)benzene (**2q**)



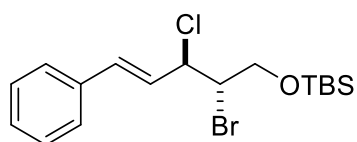
Following the general procedure A, **2q** was obtained in 50% yield (26.0 mg) as colorless oil. The stability of the product **2q** is relatively poor.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.44 – 7.41 (m, 2H), 7.38 – 7.32 (m, 2H), 7.31 – 7.26 (m, 1H), 6.70 (d,  $J = 16.0$  Hz, 1H), 6.35 (d,  $J = 16.0$  Hz, 1H), 3.84 – 3.76 (m, 2H), 1.94 (s, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  135.8, 131.4, 131.1, 128.8, 128.5, 127.0, 69.0, 42.6, 27.7. **HRMS (ESI)**:  $m/z$  calculated for  $[\text{C}_{11}\text{H}_{12}\text{BrCl}^+ - \text{Cl}]$ : 223.0122, found: 223.0119.

(*E*)-(4-bromo-3-chloropent-1-en-1-yl)benzene (**2r**)



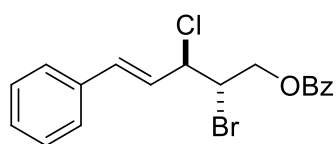
Following the general procedure A, **2r** was obtained in 70% yield (36.3 mg, dr = 50:50) as colorless oil.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.44 – 7.40 (m, 2H), 7.37 – 7.32 (m, 2H), 7.31 – 7.26 (m, 1H), 6.74 – 6.64 (m, 1H), 6.36 – 6.22 (m, 1H), 4.82 – 4.75 (m, 0.5H), 4.62 (dd,  $J = 9.1, 6.7$  Hz, 0.5H), 4.40 (qd,  $J = 6.8, 3.9$  Hz, 0.5H), 4.34 – 4.25 (m, 0.5H), 1.85 (d,  $J = 6.7$  Hz, 1.5H), 1.81 (d,  $J = 6.8$  Hz, 1.5H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  135.7, 135.7, 135.3, 134.7, 128.8, 128.7, 127.1, 127.0, 126.8, 124.7, 67.2, 66.2, 52.2, 51.6, 23.4, 21.3. **HRMS (ESI)**:  $m/z$  calculated for  $[\text{C}_{11}\text{H}_{12}\text{BrCl}^+ - \text{Cl}]$ : 223.0122, found: 223.0114. Since the product is mixtures of diastereomers, not all  $^{13}\text{C}$  NMR signals are resolved.

*(E)*-((2-bromo-3-chloro-5-phenylpent-4-en-1-yl)oxy)(tert-butyl)dimethylsilane (**2s**)



Following the general procedure A, **2s** was obtained in 90% yield (70.2 mg, dr = 60:40) as colorless oil.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.743 – 7.38 (m, 2H), 7.37 – 7.31 (m, 2H), 7.30 – 7.25 (m, 1H), 6.72 – 6.63 (m, 1H), 6.39 (dd,  $J = 15.7, 8.5$  Hz, 0.4H), 6.30 (dd,  $J = 15.7, 9.3$  Hz, 0.6H), 5.06 – 4.87 (m, 1H), 4.27 (ddd,  $J = 6.9, 5.8, 4.5$  Hz, 0.6H), 4.21 (ddd,  $J = 8.1, 5.3, 2.9$  Hz, 0.4H), 4.05 (dd,  $J = 10.9, 4.5$  Hz, 0.6H), 3.99 (dd,  $J = 10.4, 8.1$  Hz, 0.4H), 3.92 (dd,  $J = 10.4, 5.3$  Hz, 0.4H), 3.85 (dd,  $J = 10.9, 6.9$  Hz, 0.6H). 0.97 – 0.88 (m, 9H), 0.15 – 0.05 (m, 6H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  135.8, 135.8, 134.9, 133.8, 128.8, 128.6, 128.6, 127.2, 127.0, 126.1, 64.9, 64.6, 62.1, 61.8, 58.2, 57.7, 26.0, 18.4, 18.4, -5.2, -5.2, -5.3. **HRMS (ESI)**:  $m/z$  calculated for  $[\text{C}_{17}\text{H}_{26}\text{BrClOSi}^+ - \text{Cl}]$ : 353.0936, found: 353.0953. Since the product is mixtures of diastereomers, not all  $^{13}\text{C}$  NMR signals are resolved.

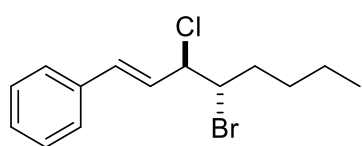
*(E)*-2-bromo-3-chloro-5-phenylpent-4-en-1-yl benzoate (**2t**)



Following the general procedure A, **2t** was obtained in 79% yield (60.0 mg, dr = 55:45) as colorless oil.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.10 – 8.04 (m, 2H), 7.62 – 7.56 (m, 1H), 7.49 – 7.38 (m, 4H), 7.36 – 7.26 (m, 3H), 6.75 (d,  $J = 4.6$  Hz, 0.45H), 6.71 (d,  $J = 4.6$  Hz, 0.55H), 6.45 – 6.26 (m, 1H), 5.03 –

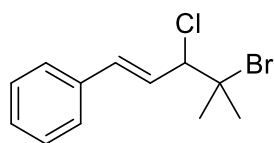
4.86 (m, 1H), 4.84 – 4.69 (m, 2H), 4.60 – 4.54 (m, 0.55H), 4.54 – 4.49 (m, 0.45H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 165.9, 165.9, 135.4, 135.4, 135.3, 134.9, 133.6, 129.9, 129.9, 129.5, 129.5, 128.8, 128.8, 128.7, 127.1, 125.9, 125.4, 65.7, 65.3, 62.6, 62.3, 53.5, 53.3. **HRMS (ESI)**: m/z calculated for [C<sub>18</sub>H<sub>16</sub>BrClO<sub>2</sub><sup>+</sup>-Cl]: 343.0333, found: 343.0314. Since the product is mixtures of diastereomers, not all <sup>13</sup>C NMR signals are resolved.

*(E)*-(4-bromo-3-chlorooct-1-en-1-yl)benzene (**2u**)



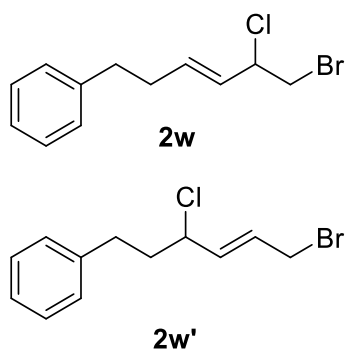
Following the general procedure A, **2u** was obtained in 74% yield (44.4 mg, dr = 52:48) as colorless oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.44 – 7.39 (m, 2H), 7.37 – 7.31 (m, 2H), 7.31 – 7.26 (m, 1H), 6.73 – 6.63 (m, 1H), 6.35 (d, *J* = 15.6, 8.6 Hz, 0.48H), 6.29 (dd, *J* = 15.6, 9.1 Hz, 0.52H), 4.82 (ddd, *J* = 8.6, 3.7, 0.9 Hz, 0.48H), 4.68 (ddd, *J* = 9.1, 6.6, 0.7 Hz, 0.52H), 4.28 – 4.16 (m, 1H), 2.18 – 2.01 (m, 1H), 1.95 – 1.80 (m, 1H), 1.69 – 1.56 (m, 1H), 1.50 – 1.27 (m, 3H), 0.97 – 0.90 (m, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 135.8, 135.7, 134.7, 134.6, 128.8, 128.6, 128.6, 127.0, 127.0, 127.0, 125.6, 65.8, 65.7, 59.6, 59.1, 35.5, 34.1, 29.9, 29.4, 22.2, 22.1, 14.1. **HRMS (ESI)**: m/z calculated for [C<sub>14</sub>H<sub>18</sub>BrCl<sup>+</sup>-Cl]: 265.0591, found: 265.0600. Since the product is mixtures of diastereomers, not all <sup>13</sup>C NMR signals are resolved.

*(E)*-(4-bromo-3-chloro-4-methylpent-1-en-1-yl)benzene (**2v**)



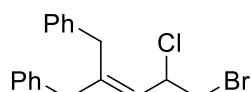
Following the general procedure A, **2v** was obtained in 60% yield (32.8 mg) as colorless oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.45 – 7.40 (m, 2H), 7.37 – 7.31 (m, 2H), 7.31 – 7.27 (m, 1H), 6.68 (d, *J* = 15.6 Hz, 1H), 6.40 (ddd, *J* = 15.6, 9.0, 1.0 Hz, 1H), 4.64 (d, *J* = 9.0 Hz, 1H), 1.90 (s, 3H), 1.88 (s, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 135.8, 134.9, 128.8, 128.6, 127.0, 126.2, 72.0, 66.8, 32.6, 30.1. **HRMS (ESI)**: m/z calculated for [C<sub>12</sub>H<sub>14</sub>BrCl<sup>+</sup>-Cl]: 237.0278, found: 237.0303.

*(E)*-(6-bromo-5-chlorohex-3-en-1-yl)benzene (**2w**)



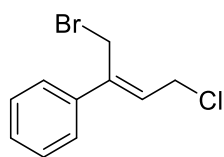
Following the general procedure A, (**2w+2w'**) was obtained in 58% yield (31.7 mg) as colorless oil (**2w:2w'** = 52:48, the regioisomeric ratio was determined by <sup>1</sup>H NMR analysis of crude reaction mixture). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.31 – 7.26 (m, 3.38H) (**2w+2w'**), 7.22 – 7.16 (m, 5.15H) (**2w+2w'**), 5.95 – 5.80 (m, 2.42H) (**2w+2w'**), 5.50 (ddt, *J* = 15.2, 8.8, 1.5 Hz, 1H) (**2w**), 4.51 (td, *J* = 8.8, 5.2 Hz, 1H) (**2w**), 4.31 (td, *J* = 7.7, 6.0 Hz, 0.68H) (**2w'**), 3.93 (dd, *J* = 6.8, 1.2 Hz, 1.36H) (**2w'**), 3.64 (dd, *J* = 10.3, 5.2 Hz, 1H) (**2w**), 3.49 (dd, *J* = 10.3, 8.8 Hz, 1H) (**2w**), 2.80 – 2.70 (m, 3.4H) (**2w+2w'**), 2.45 – 2.38 (m, 2H) (**2w**), 2.19 – 2.06 (m, 1.38H) (**2w'**). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) **2w**: δ 141.3, 136.2, 128.7, 128.6, 128.5, 126.1, 60.7, 35.8, 35.3, 33.9. **2w'**: δ 140.6, 135.1, 128.8, 128.7, 128.4, 126.4, 60.5, 39.8, 32.6, 31.2. **HRMS (ESI)**: *m/z* calculated for [C<sub>12</sub>H<sub>14</sub>BrCl<sup>+</sup>-Cl]: 237.0278, found: 237.0301.

(2-(3-bromo-2-chloropropylidene)propane-1,3-diyl)dibenzene (**2x**)



Following the general procedure A, **2x** was obtained in 52% yield (36.4 mg) as colorless oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.34 – 7.27 (m, 5H), 7.23 – 7.11 (m, 5H), 5.48 (d, *J* = 9.9 Hz, 1H), 5.01 (td, *J* = 9.9, 4.8 Hz, 1H), 3.74 (dd, *J* = 9.9, 4.8 Hz, 1H), 3.58 (dd, *J* = 9.9, 9.6 Hz, 1H), 3.49 (d, *J* = 15.1 Hz, 1H), 3.33 (d, *J* = 15.1 Hz, 1H), 3.28 (s, 2H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 145.0, 138.6, 138.3, 129.3, 129.0, 128.7, 128.6, 126.7, 126.6, 126.6, 55.8, 42.8, 36.1, 35.9. **HRMS (ESI)**: *m/z* calculated for [C<sub>18</sub>H<sub>18</sub>BrCl<sup>+</sup>-Cl]: 313.0591, found: 313.0598.

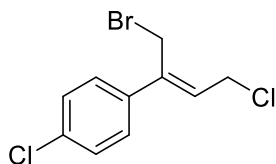
(*Z*)-(1-bromo-4-chlorobut-2-en-2-yl)benzene (**3a**)



Following the general procedure B, **3a** was obtained in 77% yield (37.8 mg, *Z/E* = 77:23, **3a:3a'** > 98:2) as colorless oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.49 – 7.45 (m, 2H), 7.42 – 7.37 (m, 2H), 7.36 (m, 1H), 6.12 (t, *J* = 8.1 Hz, 1H), 4.38 (s, 2H), 4.32 (d, *J* = 8.1 Hz, 2H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 141.0, 139.0, 128.8, 128.7, 128.1, 126.4,

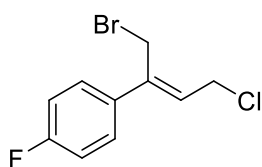
39.6, 27.1. **HRMS (ESI)**:  $m/z$  calculated for  $[C_{10}H_{10}BrCl^+-Cl]$ : 208.9965, found: 208.9973.

(*Z*)-1-(1-bromo-4-chlorobut-2-en-2-yl)-4-chlorobenzene (**3b**)



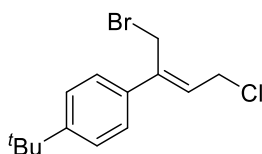
Following the general procedure B, **3b** was obtained in 76% yield (42.6 mg,  $Z/E = 78:22$ , **3b:3b'** = 98:2) as colorless oil.<sup>[9]</sup> **<sup>1</sup>H NMR** (400 MHz,  $CDCl_3$ )  $\delta$  7.41 – 7.38 (m, 2H), 7.36 – 7.33 (m, 2H), 6.10 (t,  $J = 8.0$  Hz, 1H), 4.33 (s, 2H), 4.29 (d,  $J = 8.0$  Hz, 2H). **<sup>13</sup>C NMR** (101 MHz,  $CDCl_3$ )  $\delta$  139.9, 137.4, 134.6, 129.0, 128.4, 127.7, 39.4, 26.7. **HRMS (ESI)**:  $m/z$  calculated for  $[C_{10}H_9BrCl_2^+-Cl]$ : 242.9576, found: 242.9576.

(*Z*)-1-(1-bromo-4-chlorobut-2-en-2-yl)-4-fluorobenzene (**3c**)



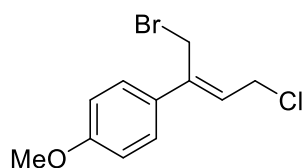
Following the general procedure B, **3c** was obtained in 80% yield (40.5 mg,  $Z/E = 79:21$ , **3c:3c'** = 97:3) as colorless oil. **<sup>1</sup>H NMR** (400 MHz,  $CDCl_3$ )  $\delta$  7.47 – 7.42 (m, 2H), 7.09 – 7.04 (m, 2H), 6.07 (t,  $J = 8.1$  Hz, 1H), 4.34 (s, 2H), 4.30 (d,  $J = 8.1$  Hz, 2H). **<sup>13</sup>C NMR** (101 MHz,  $CDCl_3$ )  $\delta$  163.0 (d,  $J = 248.4$  Hz), 140.0, 135.1 (d,  $J = 3.4$  Hz), 130.3 (d,  $J = 8.1$  Hz), 128.2 (d,  $J = 8.1$  Hz), 128.0 (d,  $J = 1.4$  Hz), 115.8 (d,  $J = 21.6$  Hz), 39.5, 27.0. **<sup>19</sup>F NMR** (376 MHz,  $CDCl_3$ )  $\delta$  -113.16 (ddd,  $J = 13.9, 8.7, 5.3$  Hz). **HRMS (ESI)**:  $m/z$  calculated for  $[C_{10}H_9BrClF^+-Cl]$ : 226.9871, found: 226.9878.

(*Z*)-1-(1-bromo-4-chlorobut-2-en-2-yl)-4-(tert-butyl)benzene (**3d**)



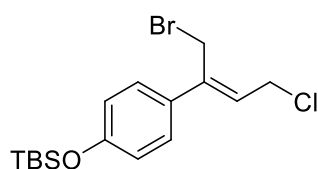
Following the general procedure B, **3d** was obtained in 74% yield (44.6 mg,  $Z/E = 78:22$ , **3d:3d'** = 96:4) as colorless oil. **<sup>1</sup>H NMR** (400 MHz,  $CDCl_3$ )  $\delta$  7.42 – 7.40 (m, 4H), 6.13 (t,  $J = 8.1$  Hz, 1H), 4.38 (s, 2H), 4.32 (d,  $J = 8.1$  Hz, 2H), 1.33 (s, 9H). **<sup>13</sup>C NMR** (101 MHz,  $CDCl_3$ )  $\delta$  151.8, 140.7, 135.9, 127.3, 125.9, 125.7, 39.8, 34.8, 31.4, 27.0. **HRMS (ESI)**:  $m/z$  calculated for  $[C_{14}H_{18}BrCl^+-Cl]$ : 265.0591, found: 265.0592.

(Z)-1-(1-bromo-4-chlorobut-2-en-2-yl)-4-methoxybenzene (**3e**)



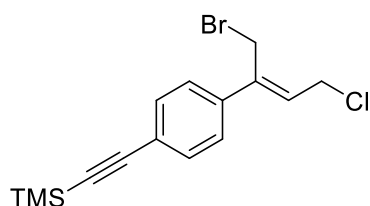
Following the general procedure B, **3e** was obtained in 83% yield (45.9mg, *Z/E* = 84:16, **3e:3e'** = 97:3) as colorless oil. **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.44 – 7.39 (m, 2H), 6.92 – 6.88 (m, 2H), 6.06 (t, *J* = 8.1 Hz, 1H), 4.36 (s, 2H), 4.31 (d, *J* = 8.1 Hz, 2H), 3.83 (s, 3H). **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 160.0, 140.5, 129.7, 127.6, 126.3, 114.2, 55.5, 39.9, 27.2. **HRMS (ESI)**: *m/z* calculated for [C<sub>11</sub>H<sub>12</sub>BrClO<sup>+</sup>-Cl]: 239.0071, found: 239.0075.

(Z)-4-(1-bromo-4-chlorobut-2-en-2-yl)phenoxy(*tert*-butyl)dimethylsilane (**3f**)



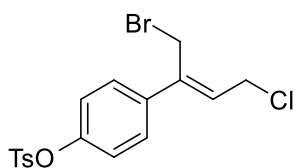
Following the general procedure B, **3f** was obtained in 81% yield (60.9 mg, *Z/E* = 88:12, **3f:3f'** = 97:3) as colorless oil. **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.37 – 7.33 (m, 2H), 6.85 – 6.81 (m, 2H), 6.07 (t, *J* = 8.1 Hz, 1H), 4.35 (s, 2H), 4.31 (d, *J* = 8.1 Hz, 2H), 0.99 (s, 9H), 0.21 (s, 6H). **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 156.3, 140.6, 129.7, 127.5, 126.4, 120.3, 39.9, 27.2, 25.8, 18.4, -4.2. **HRMS (ESI)**: *m/z* calculated for [C<sub>16</sub>H<sub>24</sub>BrClOSi<sup>+</sup>-Cl]: 339.0779, found: 339.0784.

(Z)-((4-(1-bromo-4-chlorobut-2-en-2-yl)phenyl)ethynyl)trimethylsilane (**3g**)



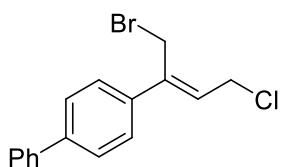
Following the general procedure B, **3g** was obtained in 70% yield (47.7 mg, *Z/E* = 81:19, **3g:3g'** = 93:7) as colorless oil. **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.48 – 7.45 (m, 2H), 7.43 – 7.38 (m, 2H), 6.15 (t, *J* = 8.1 Hz, 1H), 4.34 (s, 2H), 4.31 (d, *J* = 8.1 Hz, 2H), 0.26 (s, 9H). **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 140.3, 138.9, 132.4, 128.6, 128.4, 126.1, 104.7, 95.8, 39.5, 26.6, 0.1. **HRMS (ESI)**: *m/z* calculated for [C<sub>15</sub>H<sub>18</sub>BrClSi<sup>+</sup>-Cl]: 305.0361, found: 305.0360.

(Z)-4-(1-bromo-4-chlorobut-2-en-2-yl)phenyl 4-methylbenzenesulfonate (**3h**)



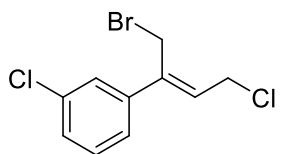
Following the general procedure B, **3h** was obtained in 78% yield (64.8 mg, *Z/E* = 78:22, **3h:3h'** = 97:3) as pale yellow oil.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.74 – 7.70 (m, 2H), 7.41 – 7.38 (m, 2H), 7.35 – 7.30 (m, 2H), 7.02 – 6.97 (m, 2H), 6.08 (t,  $J$  = 8.0 Hz, 1H), 4.30 (s, 2H), 4.28 (d,  $J$  = 8.0 Hz, 2H), 2.46 (s, 3H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  149.7, 145.6, 139.7, 138.0, 132.4, 130.0, 128.9, 128.6, 127.6, 122.7, 39.4, 26.7, 21.9. **HRMS (ESI)**:  $m/z$  calculated for  $[\text{C}_{17}\text{H}_{16}\text{BrClO}_3\text{S}^+ - \text{Cl}]$ : 379.0003, found: 378.9999.

(*Z*)-4-(1-bromo-4-chlorobut-2-en-2-yl)-1,1'-biphenyl (**3i**)



Following the general procedure B, **3i** was obtained in 75% yield (48.3 mg, *Z/E* = 82:18, **3i:3i'** = 93:7) as colorless oil.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.60 (m, 4H), 7.56 – 7.53 (m, 2H), 7.47 – 7.42 (m, 2H), 7.38 – 7.34 (m, 1H), 6.19 (t,  $J$  = 8.1 Hz, 1H), 4.40 (s, 2H), 4.33 (d,  $J$  = 8.1 Hz, 2H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  141.5, 140.5, 140.4, 137.7, 129.0, 127.9, 127.7, 127.5, 127.2, 126.7, 39.7, 26.9. **HRMS (ESI)**:  $m/z$  calculated for  $[\text{C}_{16}\text{H}_{14}\text{BrCl}^+ - \text{Cl}]$ : 285.0278, found: 285.0283.

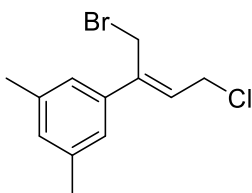
(*Z*)-1-(1-bromo-4-chlorobut-2-en-2-yl)-3-chlorobenzene (**3j**)



Following the general procedure B, **3j** was obtained in 70% yield (39.0 mg, *Z/E* = 65:35, **3j:3j'** = 97:3) as colorless oil.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.46 – 7.44 (m, 1H), 7.37 – 7.34 (m, 2H), 7.32 (m, 1H), 6.12 (t,  $J$  = 8.0 Hz, 1H), 4.33 (s, 2H), 4.30 (d,  $J$  = 8.0 Hz, 2H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  140.9, 139.8, 134.8, 130.1, 129.2, 128.7, 126.6, 124.6, 39.3, 26.6. **HRMS (ESI)**:  $m/z$  calculated for  $[\text{C}_{10}\text{H}_9\text{BrCl}_2^+ - \text{Cl}]$ : 242.9576, found: 242.9588.

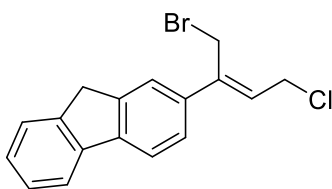
(*Z*)-1-(1-bromo-4-chlorobut-2-en-2-yl)-3,5-dimethylbenzene (**3k**)





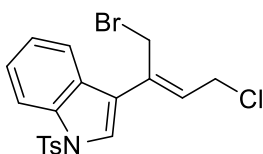
Following the general procedure B, **3k** was obtained in 78% yield (42.6 mg, *Z/E* = 76:24, **3k**:**3k'** = 94:6) as colorless oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.08 – 7.06 (m, 2H), 7.00 – 6.98 (m, 1H), 6.09 (t, *J* = 8.1 Hz, 1H), 4.36 (s, 2H), 4.30 (d, *J* = 8.1 Hz, 2H), 2.34 (s, 6H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 141.2, 139.0, 138.3, 130.4, 127.7, 124.2, 39.8, 27.3, 21.5. HRMS (ESI): *m/z* calculated for [C<sub>12</sub>H<sub>14</sub>BrCl<sup>+</sup>-Cl]: 237.0278, found: 237.0281.

(*Z*)-2-(1-bromo-4-chlorobut-2-en-2-yl)-9H-fluorene (**3l**)



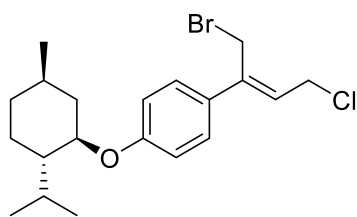
Following the general procedure B, **3l** was obtained in 43% yield (28.7 mg, *Z/E* = 77:23, **3l**:**3l'** = 94:6) as colorless oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.80 – 7.77 (m, 2H), 7.66 (s, 1H), 7.57 – 7.54 (m, 1H), 7.51 – 7.47 (m, 1H), 7.41 – 7.36 (m, 1H), 7.32 (m, 1H), 6.19 (td, *J* = 8.1, 1.3 Hz, 1H), 4.44 (d, *J* = 1.3 Hz, 2H), 4.35 (dd, *J* = 8.1, 1.3 Hz, 2H), 3.92 (s, 2H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 143.8, 143.7, 142.3, 141.3, 141.2, 137.5, 127.6, 127.2, 127.0, 125.2, 125.2, 123.0, 120.2, 120.1, 39.8, 37.1, 27.4. HRMS (ESI): *m/z* calculated for [C<sub>17</sub>H<sub>14</sub>BrCl<sup>+</sup>-Cl]: 297.0278, found: 297.0275.

(*Z*)-3-(1-bromo-4-chlorobut-2-en-2-yl)-1-tosyl-1*H*-indole (**3m**)



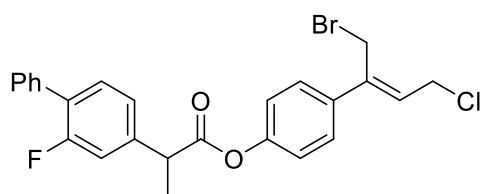
Following the general procedure B, **3m** was obtained in 57% yield (50.0 mg, *Z/E* = 67:33, **3m**:**3m'** = 94:6) as pale yellow oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.03 – 7.99 (m, 1H), 7.82 – 7.77 (m, 3H), 7.73 – 7.67 (m, 1H), 7.38 – 7.33 (m, 1H), 7.32 – 7.27 (m, 1H), 7.25 – 7.23 (m, 2H), 6.31 (t, *J* = 8.1 Hz, 1H), 4.37 – 4.34 (m, 4H), 2.35 (s, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 145.4, 135.4, 134.9, 133.8, 130.1, 128.7, 128.5, 127.1, 125.3, 124.5, 123.9, 121.2, 120.7, 114.0, 39.3, 27.4, 21.8. HRMS (ESI): *m/z* calculated for [C<sub>19</sub>H<sub>17</sub>BrClNO<sub>2</sub><sup>+</sup>-Cl]: 402.0163, found: 402.0160.

1-((*Z*)-1-bromo-4-chlorobut-2-en-2-yl)-4-(((1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl)oxy)benzene (**3n**)



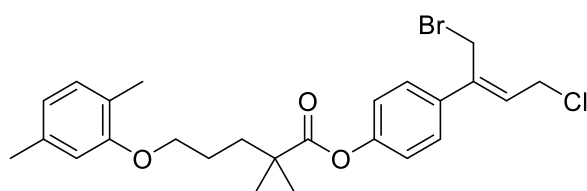
Following the general procedure B, **3n** was obtained in 50% yield (40.0 mg, *Z/E* = 90:10, **3n:3n'** = 97:3) as colorless oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.42 – 7.37 (m, 2H), 6.91 – 6.86 (m, 2H), 6.07 (t, *J* = 8.1 Hz, 1H), 4.65 (m, 1H) 4.37 (s, 2H), 4.31 (d, *J* = 8.1 Hz, 2H), 2.15 – 2.04 (m, 1H), 1.82 – 1.61 (m, 6H), 1.11 – 0.98 (m, 2H), 0.93 (d, *J* = 6.7 Hz, 3H), 0.85 (d, *J* = 6.6 Hz, 3H), 0.82 (d, *J* = 6.6 Hz, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 158.8, 140.6, 129.7, 127.5, 126.0, 115.7, 73.4, 47.9, 40.0, 37.7, 35.1, 29.4, 27.2, 26.3, 25.0, 22.4, 21.2, 21.0. HRMS (ESI): *m/z* calculated for [C<sub>20</sub>H<sub>28</sub>BrClO<sup>+</sup>-Cl]: 363.1323, found: 363.1317.

(*Z*)-4-(1-bromo-4-chlorobut-2-en-2-yl)phenyl  
yl)propanoate (**3o**)



Following the general procedure B, **3o** was obtained in 76% yield (74.1 mg, *Z/E* = 83:17, **3o:3o'** = 98:2) as colorless oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.57 – 7.54 (m, 2H), 7.47 – 7.42 (m, 5H), 7.41 – 7.35 (m, 1H), 7.27 – 7.23 (m, 2H), 7.08 – 7.03 (m, 2H), 6.08 (t, *J* = 8.1 Hz, 1H), 4.32 (s, 2H), 4.28 (d, *J* = 8.1 Hz, 2H), 4.00 (q, *J* = 7.1 Hz, 1H), 1.66 (d, *J* = 7.2 Hz, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 172.4, 159.9 (d, *J* = 248.7 Hz), 151.0, 141.2 (d, *J* = 7.7 Hz), 140.1, 136.8, 135.5, 131.2 (d, *J* = 4.0 Hz), 129.6, 129.1 (d, *J* = 3.0 Hz), 128.6, 128.3, 127.9, 127.5, 123.7 (d, *J* = 3.4 Hz), 121.7, 115.5 (d, *J* = 23.8 Hz), 45.3, 39.5, 26.9, 18.5. HRMS (ESI): *m/z* calculated for [C<sub>25</sub>H<sub>21</sub>BrClFO<sub>2</sub><sup>+</sup>-Cl]: 451.0708, found: 451.0707.

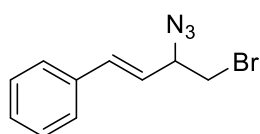
(*Z*)-4-(1-bromo-4-chlorobut-2-en-2-yl)phenyl  
dimethylpentanoate (**3p**)



Following the general procedure B, **3p** was obtained in 80% yield (79.0 mg, *Z/E* = 82:18, **3p:3p'** = 98:2) as colorless oil. <sup>1</sup>H NMR (400 MHz,

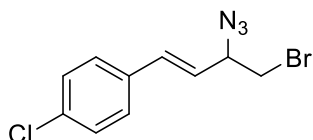
CDCl<sub>3</sub>)  $\delta$  7.49 – 7.43 (m, 2H), 7.07 – 7.02 (m, 2H), 7.00 (d,  $J$  = 7.4 Hz, 1H), 6.67 (d,  $J$  = 7.4 Hz, 1H), 6.63 (s, 1H), 6.10 (t,  $J$  = 8.1 Hz, 1H), 4.35 (s, 2H), 4.30 (d,  $J$  = 8.1 Hz, 2H), 3.98 (m, 2H), 2.30 (s, 3H), 2.18 (s, 3H), 1.88 (m, 4H), 1.37 (s, 6H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  176.3, 157.0, 151.3, 140.2, 136.6, 136.6, 130.5, 128.2, 127.5, 123.8, 121.9, 120.9, 112.1, 67.9, 42.6, 39.5, 37.3, 27.0, 25.4, 25.3, 21.6, 15.9. **HRMS (ESI):**  $m/z$  calculated for [C<sub>25</sub>H<sub>30</sub>BrClO<sub>3</sub><sup>+</sup>-Cl]: 457.1378, found: 457.1384.

*(E)*-(3-azido-4-bromobut-1-en-1-yl)benzene (**4a**)



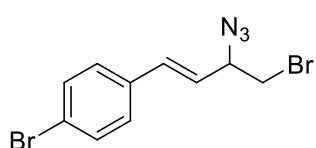
Following the general procedure C, **4a** was obtained in 90% yield (45.4 mg) as colorless oil, using ethyl acetate/petroleum ether (1:20) as eluent. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.45 – 7.39 (m, 2H), 7.38 – 7.27 (m, 3H), 6.73 (d,  $J$  = 15.8 Hz, 1H), 6.14 (dd,  $J$  = 15.8, 7.9 Hz, 1H), 4.35 (dddd,  $J$  = 7.9, 6.6, 5.4, 1.0 Hz, 1H), 3.50 – 3.41 (m, 2H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  135.7, 135.5, 128.9, 128.8, 127.0, 124.0, 64.8, 34.4. **HRMS (ESI):**  $m/z$  calculated for [C<sub>10</sub>H<sub>10</sub>BrN<sub>3</sub><sup>+</sup>-N<sub>3</sub>]: 208.9966, found: 208.9967.

*(E)*-1-(3-azido-4-bromobut-1-en-1-yl)-4-chlorobenzene (**4b**)



Following the general procedure C, **4b** was obtained in 91% yield (52.2 mg) as colorless oil, using ethyl acetate/petroleum ether 1:20 as eluent. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.37 – 7.30 (m, 4H), 6.68 (d,  $J$  = 15.8 Hz, 1H), 6.11 (dd,  $J$  = 15.8, 7.8 Hz, 1H), 4.34 (dddd,  $J$  = 7.8, 6.6, 5.5, 1.0 Hz, 1H), 3.53 – 3.38 (m, 2H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  134.6, 134.4, 134.0, 129.1, 128.2, 124.7, 64.6, 34.2. **HRMS (ESI):**  $m/z$  calculated for [C<sub>10</sub>H<sub>9</sub>BrClN<sub>3</sub><sup>+</sup>-N<sub>3</sub>]: 242.9576, found: 242.9578.

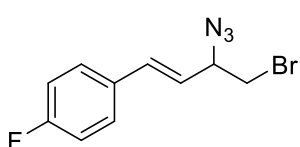
*(E)*-1-(3-azido-4-bromobut-1-en-1-yl)-4-bromobenzene (**4c**)



Following the general procedure C, **4c** was obtained in 82% yield (54.6 mg) as pale yellow oil, using ethyl acetate/petroleum ether (1:20) as eluent. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.51 – 7.44 (m, 2H), 7.28 (dq,  $J$  = 8.2, 1.6 Hz, 2H), 6.67 (d,  $J$  = 15.8 Hz, 1H), 6.13 (ddd,  $J$  = 15.8, 7.8, 1.4 Hz, 1H), 4.40 – 4.27 (m, 1H),

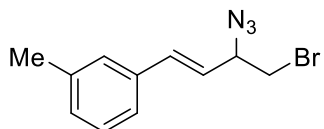
3.52 – 3.39 (m, 2H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  134.4, 132.0, 128.5, 124.8, 122.7, 64.6, 34.2. **HRMS (ESI)**:  $m/z$  calculated for  $[\text{C}_{10}\text{H}_9\text{Br}_2\text{N}_3^+-\text{N}_3]$ : 286.9071, found: 286.9075.

*(E)*-1-(3-azido-4-bromobut-1-en-1-yl)-4-fluorobenzene (**4d**)



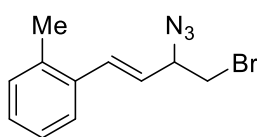
Following the general procedure C, **4d** was obtained in 92% yield (49.8 mg) as colorless oil, using ethyl acetate/petroleum ether (1:20) as eluent.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.42 – 7.36 (m, 2H), 7.07 – 7.01 (m, 2H), 6.69 (d,  $J = 15.8$  Hz, 1H), 6.06 (dd,  $J = 15.8, 7.9$  Hz, 1H), 4.34 (dddd,  $J = 7.9, 6.6, 5.5, 1.0$  Hz, 1H), 3.50 – 3.40 (m, 2H).  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -112.58 (ddd,  $J = 13.8, 8.7, 5.4$  Hz).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  163.1 (d,  $J = 248.6$  Hz), 134.5, 131.7 (d,  $J = 3.3$  Hz), 128.6 (d,  $J = 8.1$  Hz), 123.8 (d,  $J = 2.3$  Hz), 115.9 (d,  $J = 21.7$  Hz), 64.7, 34.3. **HRMS (ESI)**:  $m/z$  calculated for  $[\text{C}_{10}\text{H}_9\text{BrFN}_3^+-\text{N}_3]$ : 226.9872, found: 226.9873.

*(E)*-1-(3-azido-4-bromobut-1-en-1-yl)-3-methylbenzene (**4e**)



Following the general procedure C, **4e** was obtained in 89% yield (47.4 mg) as colorless oil, using ethyl acetate/petroleum ether (1:20) as eluent.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.28 – 7.18 (m, 3H), 7.14 – 7.07 (m, 1H), 6.70 (d,  $J = 15.8$  Hz, 1H), 6.12 (dd,  $J = 15.8, 7.9$  Hz, 1H), 4.33 (dddd,  $J = 7.9, 6.6, 5.5, 1.0$  Hz, 1H), 3.53 – 3.37 (m, 2H) 2.36 (s, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  138.5, 135.9, 135.4, 129.6, 128.8, 127.6, 124.2, 123.7, 64.9, 34.4, 21.5. **HRMS (ESI)**:  $m/z$  calculated for  $[\text{C}_{11}\text{H}_{12}\text{BrN}_3^+-\text{N}_3]$ : 223.0123, found: 223.0126.

*(E)*-1-(3-azido-4-bromobut-1-en-1-yl)-2-methylbenzene (**4f**)

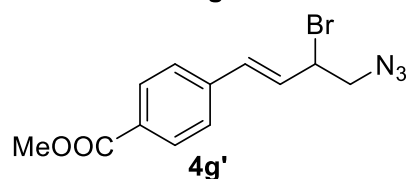
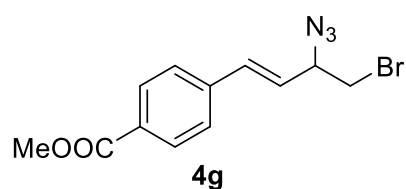


Following the general procedure, **4f** was obtained in 85% yield (45.0 mg) as colorless oil, using ethyl acetate/petroleum ether (1:20) as eluent.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.28 – 7.18 (m, 3H), 7.14 – 7.07 (m, 1H), 6.70 (d,  $J = 15.8$  Hz, 1H), 6.12 (dd,  $J = 15.8, 7.9$  Hz, 1H), 4.33 (dddd,  $J = 7.9, 6.6, 5.5, 1.0$  Hz, 1H), 3.53 – 3.37 (m, 2H).  $^{13}\text{C}$  NMR (101 MHz,

CDCl<sub>3</sub>)  $\delta$  136.0, 134.8, 133.9, 130.6, 128.6, 126.4, 126.2, 125.3, 64.9, 34.3, 20.0.

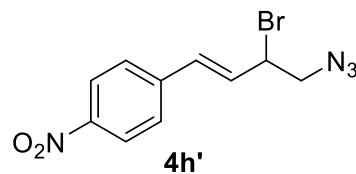
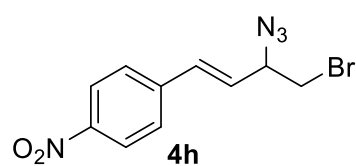
**HRMS (ESI):**  $m/z$  calculated for [C<sub>11</sub>H<sub>12</sub>BrN<sub>3</sub><sup>+</sup>-N<sub>3</sub>]: 223.0123, found: 223.0121.

(*E*)-1-(3-azido-4-bromobut-1-en-1-yl)-2-methylbenzene (**4g**)



Following the general procedure C, (**4g+4g'**) was obtained in 82% yield (49.6 mg, **4g:4g'** = 79:21) as colorless oil, using ethyl acetate/petroleum ether (1:10) as eluent. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.05 – 7.99 (m, 2.56H) (**4g+4g'**), 7.50 – 7.44 (m, 2.56H) (**4g+4g'**), 6.77 (d,  $J$  = 15.9 Hz, 1H) (**4g**), 6.71 (d,  $J$  = 15.7 Hz, 0.28H) (**4g'**), 6.41 (dd,  $J$  = 15.7, 9.5 Hz, 0.28H) (**4g'**), 6.25 (dd,  $J$  = 15.9, 7.6 Hz, 1H) (**4g**), 4.77 (dddd,  $J$  = 9.5, 6.8, 6.0, 0.7 Hz, 0.28H) (**4g'**), 4.38 (dddd,  $J$  = 7.6, 6.6, 5.6, 1.1 Hz, 1H) (**4g**), 3.92 (s, 3H) (**4g**), 3.92 (s, 0.84H) (**4g'**), 3.81 – 3.69 (m, 0.56H) (**4g'**), 3.54 – 3.42 (m, 2H) (**4g**). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) **4g**:  $\delta$  166.8, 139.8, 134.5, 130.2, 130.2, 126.9, 126.7, 64.5, 52.3, 34.0. **4g'**: 166.8, 139.8, 133.5, 130.1, 129.2, 127.0, 126.9, 57.0, 50.8, 34.8. **HRMS (ESI):**  $m/z$  calculated for [C<sub>12</sub>H<sub>12</sub>BrN<sub>3</sub>O<sub>2</sub><sup>+</sup>-N<sub>3</sub>]: 267.0021, found: 267.0021.

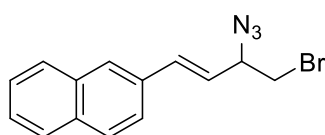
(*E*)-1-(3-azido-4-bromobut-1-en-1-yl)-4-nitrobenzene (**4h**)



Following the general procedure C, (**4h+4h'**) was obtained in 78% yield (46.2 mg, **4h:4h'** = 38:62) as pale yellow oil, using ethyl acetate/petroleum ether (1:10) as eluent. **4h** and **4h'** were determined by analysis of <sup>1</sup>H-<sup>13</sup>C HSQC spectroscopy. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.25 – 8.18 (m, 3.28H) (**4h+4h'**), 7.59 – 7.52 (m, 3.29H) (**4h+4h'**), 6.81 (d,  $J$  = 15.9 Hz, 0.64H) (**4h**), 6.76 (d,  $J$  = 15.7 Hz, 1H) (**4h'**), 6.47 (dd,  $J$  = 15.7, 9.4 Hz, 1H) (**4h'**), 6.32 (dd,  $J$  = 15.9, 7.4 Hz, 0.64H) (**4h**), 4.76 (m, 1H) (**4h'**), 4.45 – 4.38 (m, 0.64H) (**4h**), 3.84 – 3.71 (m, 2H) (**4h'**), 3.53 – 3.47 (m, 1.29H) (**4h**). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) **4h**:  $\delta$  147.7, 141.8, 133.2, 128.9, 127.6, 124.3, 64.1, 33.7. <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) **4h'**:  $\delta$  147.8, 141.8, 132.2, 131.2, 127.7, 124.2, 56.9, 49.9. **HRMS (ESI):**  $m/z$  calculated for [C<sub>10</sub>H<sub>9</sub>BrN<sub>4</sub>O<sub>2</sub><sup>+</sup>-N<sub>3</sub>]:

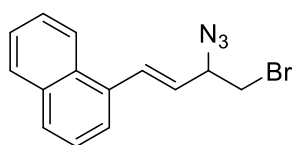
253.9817, found: 253.9812.

*(E)*-2-(3-azido-4-bromobut-1-en-1-yl)naphthalene (**4i**)



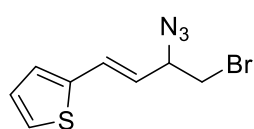
Following the general procedure C, **4i** was obtained in 85% yield (51.4 mg) as colorless oil, using ethyl acetate/petroleum ether (1:20) as eluent.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.86 – 7.77 (m, 4H), 7.60 (dd,  $J = 8.6, 1.8$  Hz, 1H), 7.53 – 7.44 (m, 2H), 6.88 (d,  $J = 15.8$  Hz, 1H), 6.25 (dd,  $J = 15.8, 7.9$  Hz, 1H), 4.40 (dddd,  $J = 7.9, 6.6, 5.4, 1.0$  Hz, 1H), 3.54 – 3.43 (m, 2H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  135.7, 133.6, 132.9, 128.6, 128.3, 127.9, 127.6, 126.7, 126.6, 124.2, 123.5, 64.9, 34.4. **HRMS (ESI)**:  $m/z$  calculated for  $[\text{C}_{14}\text{H}_{12}\text{BrN}_3^+ - \text{N}_3]$ : 259.0123, found: 259.0127.

*(E)*-1-(3-azido-4-bromobut-1-en-1-yl)naphthalene (**4j**)



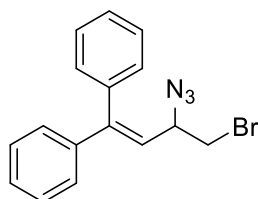
Following the general procedure C, **4j** was obtained in 95% yield (57.3 mg) as colorless oil, using ethyl acetate/petroleum ether (1:20) as eluent.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.08 (dd,  $J = 8.2, 1.4$  Hz, 1H), 7.92 – 7.78 (m, 2H), 7.61 (d,  $J = 7.2$  Hz, 1H), 7.57 – 7.43 (m, 4H), 6.16 (dd,  $J = 15.5, 7.8$  Hz, 1H), 4.47 (dddd,  $J = 7.8, 6.6, 5.8, 1.0$  Hz, 1H), 3.59 – 3.47 (m, 2H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  133.7, 133.4, 133.2, 131.2, 129.1, 128.8, 127.2, 126.6, 126.2, 125.7, 124.6, 123.7, 64.8, 34.3. **HRMS (ESI)**:  $m/z$  calculated for  $[\text{C}_{14}\text{H}_{12}\text{BrN}_3^+ - \text{N}_3]$ : 259.0123, found: 259.0134.

*(E)*-2-(3-azido-4-bromobut-1-en-1-yl)thiophene (**4k**)



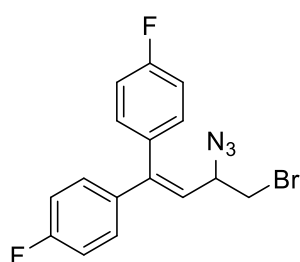
Following the general procedure C, **4k** was obtained in 62% yield (32.0 mg) as brownish yellow oil, using ethyl acetate/petroleum ether (1:20) as eluent.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.24 (dt,  $J = 5.1, 0.9$  Hz, 1H), 7.06 (dt,  $J = 3.6, 0.9$  Hz, 1H), 6.99 (dd,  $J = 5.1, 3.6$  Hz, 1H), 6.86 (dq,  $J = 15.6, 0.8$  Hz, 1H), 5.96 (dd,  $J = 15.6, 7.8$  Hz, 1H), 4.31 (dddd,  $J = 7.8, 6.6, 5.4, 1.0$  Hz, 1H), 3.50 – 3.38 (m, 2H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  140.3, 128.5, 127.7, 127.6, 125.8, 123.2, 64.7, 34.2. **HRMS (ESI)**:  $m/z$  calculated for  $[\text{C}_8\text{H}_8\text{BrN}_3\text{S}^+ - \text{N}_3]$ : 214.9530, found: 214.9533.

(3-azido-4-bromobut-1-ene-1,1-diyl)dibenzene (**4l**)



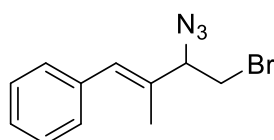
Following the general procedure C, **4l** was obtained in 72% yield (47.1 mg) as colorless oil, using ethyl acetate/petroleum ether (1:20) as eluent.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.46 – 7.37 (m, 3H), 7.33 – 7.26 (m, 5H), 7.24 – 7.19 (m, 2H), 6.05 (d,  $J = 9.8$  Hz, 1H), 4.30 (dt,  $J = 9.8, 6.1$  Hz, 1H), 3.45 – 3.37 (m, 2H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  148.9, 140.6, 138.4, 129.7, 128.8, 128.6, 128.5, 128.2, 127.7, 122.9, 60.7, 34.7. **HRMS (ESI)**:  $m/z$  calculated for  $[\text{C}_{16}\text{H}_{14}\text{BrN}_3^+ - \text{N}_3]$ : 285.0279, found: 285.0280.

4,4'-(3-azido-4-bromobut-1-ene-1,1-diyl)bis(fluorobenzene) (**4m**)



Following the general procedure C, **4m** was obtained in 78% yield (56.7 mg) as colorless oil, using ethyl acetate/petroleum ether (1:20) as eluent.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.26 – 7.21 (m, 2H), 7.21 – 7.10 (m, 4H), 7.05 – 6.97 (m, 2H), 5.99 (d,  $J = 9.8$  Hz, 1H), 4.25 (dt,  $J = 9.8, 6.2$  Hz, 1H), 3.41 (d,  $J = 6.2$  Hz, 2H).  $^{19}\text{F NMR}$  (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -112.94 – -113.04 (m), -113.06 – -113.15 (m).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  163.1 (d,  $J = 249.0$  Hz), 162.7 (d,  $J = 249.0$  Hz), 146.9, 136.7 (d,  $J = 3.3$  Hz), 134.1 (d,  $J = 3.5$  Hz), 131.5 (d,  $J = 8.1$  Hz), 129.5 (d,  $J = 8.2$  Hz), 123.2, 116.0 (d,  $J = 21.5$  Hz), 115.5 (d,  $J = 21.6$  Hz), 60.6, 34.3. **HRMS (ESI)**:  $m/z$  calculated for  $[\text{C}_{16}\text{H}_{12}\text{BrF}_2\text{N}_3^+ - \text{N}_3]$ : 321.0091, found: 321.0095.

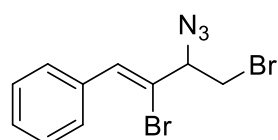
(*E*)-(3-azido-4-bromo-2-methylbut-1-en-1-yl)benzene (**4n**)



Following the general procedure C, **4n** was obtained in 86% yield (48.3 mg, 4,3-adduct:4,1-adduct = 67:33) as colorless oil, using ethyl acetate/petroleum ether (1:20) as eluent.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.40 – 7.33 (m, 3.2H) (**4n+4n'**), 7.31 – 7.26 (m, 3.8H) (**4n+4n'**), 6.61 (s, 1H) (**4n**), 6.09 – 6.00 (m, 0.4H) (**4n'**), 5.04 (s, 0.4H) (**4n'**), 4.32 (t,  $J = 7.1$  Hz, 1H) (**4n**), 4.04 (d,  $J = 8.4$  Hz, 0.8H) (**4n'**), 3.51 – 3.43 (m, 2H)

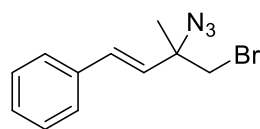
(**4n**), 1.89 (d,  $J = 1.5$  Hz, 3H) (**4n**), 1.59 (d,  $J = 1.3$  Hz, 1.2H) (**4n'**).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ) **4n**:  $\delta$  139.5, 136.3, 131.4, 129.2, 128.4, 127.4, 71.1, 32.6, 13.6. **4n'**:  $\delta$  137.2, 133.0, 128.9, 128.4, 127.2, 124.6, 71.2, 27.4, 13.1. **HRMS (ESI)**:  $m/z$  calculated for  $[\text{C}_{11}\text{H}_{12}\text{BrN}_3^+ - \text{N}_3]$ : 223.0123, found: 223.0126.

(*Z*)-(3-azido-2,4-dibromobut-1-en-1-yl)benzene (**4o**)



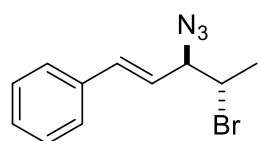
Following the general procedure C, **4o** was obtained in 81% yield (53.4 mg, 4,3-adduct:4,1-adduct = 55:45) as colorless oil, using ethyl acetate/petroleum ether (1:20) as eluent.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.67 – 7.62 (m, 2H), 7.44 – 7.31 (m, 6.4H), 7.16 (s, 1H) (**4o**), 6.53 (td,  $J = 7.9, 1.1$  Hz, 0.68H) (**4o'**), 5.28 (s, 0.68H) (**4o'**), 4.48 (t,  $J = 6.7$  Hz, 1H) (**4o**), 4.11 (d,  $J = 7.9$  Hz, 1.36H) (**4o'**), 3.65 (dd,  $J = 10.7, 6.4$  Hz, 1H) (**4o**), 3.53 (dd,  $J = 10.6, 7.1$  Hz, 1H) (**4o**).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ) **4o**:  $\delta$  134.2, 133.4, 129.4, 129.0, 128.5, 127.6, 70.3, 32.4. **4o'**:  $\delta$  135.8, 133.5, 129.2, 129.1, 128.0, 121.0, 70.8, 28.6. **HRMS (ESI)**:  $m/z$  calculated for  $[\text{C}_{10}\text{H}_9\text{Br}_2\text{N}_3^+ - \text{N}_3]$ : 286.9071, found: 286.9073.

(*E*)-(3-azido-4-bromo-3-methylbut-1-en-1-yl)benzene (**4p**)



Following the general procedure C, **4p** was obtained in 72% yield (38.3 mg) as colorless oil, using ethyl acetate/petroleum ether (1:20) as eluent.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.44 – 7.39 (m, 2H), 7.37 – 7.27 (m, 3H), 6.71 (d,  $J = 16.1$  Hz, 1H), 6.21 (d,  $J = 16.1$  Hz, 1H), 3.51 – 3.44 (m, 2H), 1.65 (s, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  135.8, 132.3, 128.9, 128.6, 126.9, 63.9, 40.8, 22.8. **HRMS (ESI)**:  $m/z$  calculated for  $[\text{C}_{11}\text{H}_{12}\text{BrN}_3^+ - \text{N}_3]$ : 223.0123, found: 223.0118.

(*E*)-(3-azido-4-bromopent-1-en-1-yl)benzene (**4q**)

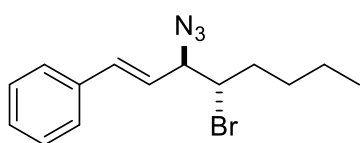


Following the general procedure C, **4q** was obtained in 88% yield (46.8 mg, dr = 54:46) as colorless oil, using ethyl acetate/petroleum ether (1:20) as eluent.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.47 – 7.41 (m, 2H), 7.39 – 7.28 (m, 3H), 6.72 (d,  $J = 15.8$  Hz, 1H), 6.24 (dd,  $J = 8.0, 4.9$  Hz, 0.54H), 6.20 (dd,  $J = 8.0, 4.9$  Hz, 0.46H), 4.24



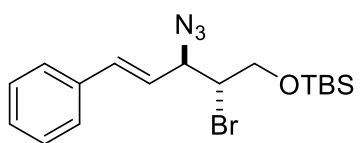
– 4.15 (m, 1.46H), 4.14 – 4.07 (m, 0.54H), 1.73 (d,  $J = 6.7$  Hz, 1.38H), 1.71 (d,  $J = 6.6$  Hz, 1.62H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  136.5, 136.0, 135.6, 128.9, 128.8, 127.0, 127.0, 123.7, 123.4, 70.0, 69.7, 51.0, 50.8, 22.6, 22.0. **HRMS (ESI)**:  $m/z$  calculated for  $[\text{C}_{11}\text{H}_{12}\text{BrN}_3^+ - \text{N}_3]$ : 223.0123, found: 223.0131. Since the product is mixtures of diastereomers, not all  $^{13}\text{C}$  NMR signals are resolved.

*(E)*-(3-azido-4-bromooct-1-en-1-yl)benzene (**4r**)



Following the general procedure C, **4r** was obtained in 92% yield (56.5 mg, dr = 58:42) as colorless oil, using ethyl acetate/petroleum ether (1:20) as eluent.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.47 – 7.40 (m, 2H), 7.40 – 7.27 (m, 3H), 6.72 (d,  $J = 15.8$  Hz, 1H), 6.33 – 6.19 (m, 1H), 4.28 – 4.21 (m, 1H), 4.05 (dt,  $J = 9.2, 4.5$  Hz, 0.58H), 3.99 (dt,  $J = 9.3, 4.7$  Hz, 0.42H), 1.96 – 1.74 (m, 2H), 1.65 – 1.56 (m, 1H), 1.46 – 1.26 (m, 3H), 0.95 – 0.87 (m, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  136.4, 135.7, 135.7, 128.9, 128.7, 128.7, 127.0, 127.0, 124.2, 123.6, 68.8, 68.6, 58.2, 58.1, 35.1, 34.7, 29.8, 29.8, 22.2, 22.2, 14.0. **HRMS (ESI)**:  $m/z$  calculated for  $[\text{C}_{14}\text{H}_{18}\text{BrN}_3^+ - \text{N}_3]$ : 265.0592, found: 265.0598. Since the product is mixtures of diastereomers, not all  $^{13}\text{C}$  NMR signals are resolved.

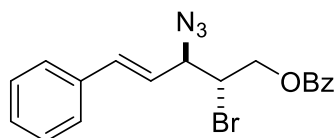
*(E)*-((3-azido-2-bromo-5-phenylpent-4-en-1-yl)oxy)(tert-butyl)dimethylsilane (**4s**)



Following the general procedure C, **4s** was obtained in 76% yield (60.3 mg, dr = 63:37) as colorless oil, using ethyl acetate/petroleum ether (1:20) as eluent.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.46 – 7.41 (m, 2H), 7.39 – 7.27 (m, 3H), 6.78 – 6.66 (m, 1H), 6.36 – 6.23 (m, 1H), 4.58 – 4.46 (m, 1H), 4.09 (dt,  $J = 8.1, 4.7$  Hz, 0.37H), 4.04 – 3.97 (m, 0.63H), 3.95 – 3.86 (m, 1.63H), 3.77 (dd,  $J = 10.7, 8.2$  Hz, 0.37H), 0.95 – 0.90 (m, 9H), 0.11 (d,  $J = 7.0$  Hz, 3.78H), 0.07 (d,  $J = 3.6$  Hz, 2.22H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  136.8, 135.8, 135.4, 128.9, 128.7, 128.7, 127.0, 127.0, 124.6, 122.9, 64.8, 64.4, 64.4, 64.0, 56.3, 55.9, 26.0, 26.0, 18.4, 18.4, -5.2, -5.2, -5.3, -5.3. **HRMS (ESI)**:  $m/z$  calculated for  $[\text{C}_{17}\text{H}_{26}\text{BrN}_3\text{OSi}^+ - \text{N}_3]$ : 353.0937, found: 353.0978. Since the product is mixtures of diastereomers, not all  $^{13}\text{C}$  NMR signals are

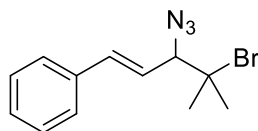
resolved.

*(E)*-3-azido-2-bromo-5-phenylpent-4-en-1-yl benzoate (**4t**)



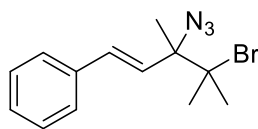
Following the general procedure C, **4t** was obtained in 81% yield (62.4 mg, dr = 64:36) as colorless oil, using ethyl acetate/petroleum ether (1:10) as eluent. **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 8.08 – 8.01 (m, 2H), 7.62 – 7.54 (m, 1H), 7.48 – 7.38 (m, 4H), 7.37 – 7.28 (m, 3H), 6.83 – 6.71 (m, 1H), 6.38 – 6.23 (m, 1H), 4.72 – 4.55 (m, 2H), 4.52 – 4.42 (m, 1H), 4.38 – 4.33 (m, 0.36H), 4.33 – 4.27 (m, 0.64H). **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 165.8, 165.8, 137.1, 136.4, 135.3, 133.6, 133.5, 129.9, 129.9, 129.4, 128.9, 128.9, 128.7, 128.6, 127.1, 127.0, 123.3, 122.6, 65.9, 65.3, 65.3, 65.0, 52.0, 51.7. **HRMS (ESI)**: *m/z* calculated for [C<sub>18</sub>H<sub>16</sub>BrN<sub>3</sub>O<sub>2</sub><sup>+</sup>-N<sub>3</sub>]: 343.0334, found: 343.0333. Since the product is mixtures of diastereomers, not all <sup>13</sup>C NMR signals are resolved.

*(E)*-(3-azido-4-bromo-4-methylpent-1-en-1-yl)benzene (**4u**)



Following the general procedure C, **4u** was obtained in 60% yield (33.6 mg) as colorless oil, using ethyl acetate/petroleum ether (1:20) as eluent. **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.47 – 7.43 (m, 2H), 7.38 – 7.34 (m, 2H), 7.33 – 7.28 (m, 1H), 6.73 (d, *J* = 15.8 Hz, 1H), 6.31 (dd, *J* = 15.8, 8.5 Hz, 1H), 4.01 (dd, *J* = 8.5, 0.8 Hz, 1H), 1.80 (s, 3H), 1.75 (s, 3H). **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 136.7, 135.7, 128.9, 128.7, 127.0, 123.6, 74.6, 66.3, 31.4, 31.0. **HRMS (ESI)**: *m/z* calculated for [C<sub>12</sub>H<sub>14</sub>BrN<sub>3</sub><sup>+</sup>-N<sub>3</sub>]: 237.0279, found: 237.0293.

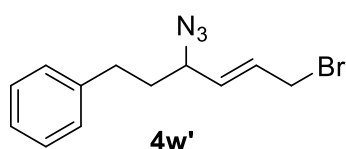
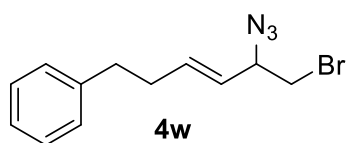
*(E)*-(3-azido-4-bromo-3,4-dimethylpent-1-en-1-yl)benzene (**4v**)



Following the general procedure C, **4v** was obtained as colorless oil. Yield = 54%, using ethyl acetate/petroleum ether (1:20) as eluent. **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.45 – 7.40 (m, 2H), 7.38 – 7.32 (m, 2H), 7.31 – 7.26 (m, 1H), 6.71 (d, *J* = 16.0 Hz, 1H), 6.44 (d, *J* = 16.0 Hz, 1H), 1.83 (s, 3H), 1.81 (s, 3H), 1.74 (s, 3H). **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 136.2,

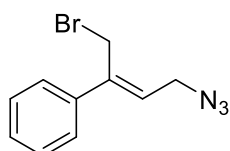
132.5, 128.8, 128.7, 128.3, 126.9, 72.1, 70.9, 30.3, 30.2, 20.9. **HRMS (ESI):** m/z calculated for [C<sub>13</sub>H<sub>16</sub>BrN<sub>3</sub><sup>+</sup>-N<sub>3</sub>]: 251.0436, found: 251.0470.

(*E*)-(5-azido-6-bromohex-3-en-1-yl)benzene (**4w**)



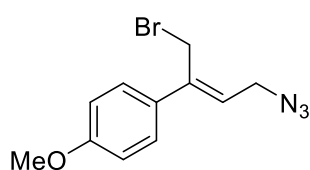
Following the general procedure C, (**4w+4w'**) was obtained in 71% yield (39.8 mg, **4w:4w'** = 82:18) as colorless oil, using ethyl acetate/petroleum ether (1:20) as eluent. **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.33 – 7.26 (m, 2.6H), 7.23 – 7.16 (m, 3.8H), 5.99 – 5.90 (m, 1H) (**4w'**), 5.90 – 5.83 (m, 0.28H) (**4w**), 5.71 (ddt, *J* = 15.2, 7.7, 1.1 Hz, 1H) (**4w'**), 5.42 (ddt, *J* = 15.3, 8.0, 1.5 Hz, 0.28H) (**4w**), 4.15 – 4.07 (m, 0.28H) (**4w**), 4.01 – 3.91 (m, 2H) (**4w'**), 3.88 – 3.81 (m, 1H) (**4w'**), 3.36 – 3.26 (m, 0.56H) (**4w**), 2.77 – 2.66 (m, 2.56H), 2.48 – 2.40 (m, 0.56H) (**4w**), 1.95 – 1.77 (m, 2H) (**4w'**). **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) **4w**: δ 141.2, 137.1, 128.6, 128.5, 126.2, 125.6, 64.6, 35.5, 34.4, 34.1. **4w'**: δ 140.8, 132.5, 130.4, 128.7, 128.6, 126.3, 62.5, 36.0, 31.9, 31.2. **HRMS (ESI):** m/z calculated for [C<sub>12</sub>H<sub>14</sub>BrN<sub>3</sub><sup>+</sup>-N<sub>3</sub>]: 237.0279, found: 237.0277.

(*Z*)-(4-azido-1-bromobut-2-en-2-yl)benzene (**5a**)



Following the general procedure D, **5a** was obtained in 87% yield (43.9 mg, *Z/E* = 95:5, **5a:5a'** > 98:2) as colorless oil, using ethyl acetate/petroleum ether (1:20) as eluent. **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.50 – 7.44 (m, 2H), 7.41 – 7.33 (m, 3H), 6.01 (t, *J* = 7.2 Hz, 1H), 4.33 (s, 2H), 4.09 (d, *J* = 7.2 Hz, 2H). **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 141.4, 139.3, 128.8, 128.6, 126.4, 126.2, 48.4, 27.5. **HRMS (ESI):** m/z calculated for [C<sub>10</sub>H<sub>10</sub>BrN<sub>3</sub><sup>+</sup>-N<sub>3</sub>]: 208.9966, found: 208.9952.

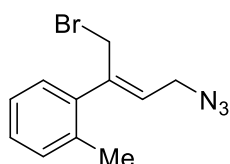
(*Z*)-1-(4-azido-1-bromobut-2-en-2-yl)-4-methoxybenzene (**5b**)



Following the general procedure D, **5b** was obtained in 82% yield (46.3 mg, *Z/E* = 84:16, **5b:5b'** > 98:2) as pale yellow oil, using ethyl acetate/petroleum ether (1:20) as eluent. **<sup>1</sup>H**

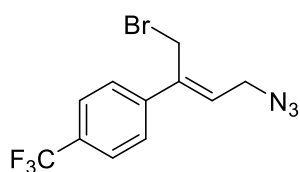
**NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.50 – 7.44 (m, 2H), 7.41 – 7.33 (m, 3H), 6.01 (t, *J* = 7.2 Hz, 1H), 4.33 (s, 2H), 4.09 (d, *J* = 7.2 Hz, 2H). **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 160.0, 140.9, 129.9, 127.5, 124.4, 114.2, 55.5, 48.4, 27.6. **HRMS (ESI)**: *m/z* calculated for [C<sub>10</sub>H<sub>10</sub>BrN<sub>3</sub><sup>+</sup>-N<sub>3</sub>]: 208.9966, found: 208.9952.

(*Z*)-1-(4-azido-1-bromobut-2-en-2-yl)-2-methylbenzene (**5c**)



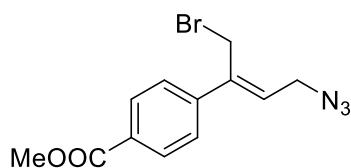
Following the general procedure D, **5c** was obtained in 92% yield (49.0 mg, *Z/E* = 98:2, **5c:5c'** > 98:2) as colorless oil, using ethyl acetate/petroleum ether (1:20) as eluent. **<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 7.27 – 7.22 (m, 2H), 7.21 – 7.16 (m, 2H), 5.65 (t, *J* = 7.3 Hz, 1H), 4.22 (s, 2H), 4.06 (d, *J* = 7.3 Hz, 2H), 2.32 (s, 3H). **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 142.0, 140.2, 135.2, 130.6, 129.2, 128.2, 128.0, 125.9, 48.0, 29.6, 20.0. **(ESI)**: *m/z* calculated for [C<sub>11</sub>H<sub>12</sub>BrN<sub>3</sub><sup>+</sup>-N<sub>3</sub>]: 223.0123, found: 223.0124.

(*Z*)-1-(4-azido-1-bromobut-2-en-2-yl)-4-(trifluoromethyl)benzene (**5d**)



Following the general procedure D, **5d** was obtained in 81% yield (51.9 mg, *Z/E* = 98:2, **5d:5d'** = 78:22) as pale yellow oil, using ethyl acetate/petroleum ether (1:20) as eluent. **5d** and **5d'** were determined by analysis of <sup>1</sup>H-<sup>13</sup>C HSQC spectroscopy. **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.66 – 7.63 (m, 2H), 7.60 – 7.56 (m, 2H), 6.06 (t, *J* = 7.1 Hz, 1H), 4.32 (s, 2H), 4.12 (d, *J* = 7.1 Hz, 2H). **<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>) δ -62.67. **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 142.8 (q, *J* = 1.5 Hz), 140.1, 128.2, 126.9, 126.7, 125.8 (q, *J* = 3.8 Hz), 124.1 (q, *J* = 272.0 Hz), 48.3, 26.9. **HRMS (ESI)**: *m/z* calculated for [C<sub>11</sub>H<sub>9</sub>BrF<sub>3</sub>N<sub>3</sub><sup>+</sup>-N<sub>3</sub>]: 276.9840, found: 276.9836.

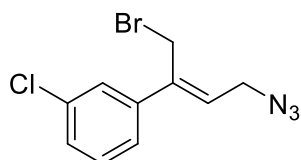
methyl (*Z*)-4-(4-azido-1-bromobut-2-en-2-yl)benzoate (**5e**)



Following the general procedure D, **5e** was obtained in 79% yield (50.6 mg, *Z/E* = 98:2, **5e:5e'** = 75:25) as colorless oil, using ethyl acetate/petroleum ether (1:10) as eluent. **<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 8.06 – 8.03 (m, 2H), 7.55 – 7.52 (m, 2H), 6.09 (t, *J* = 7.2 Hz, 1H), 4.33 (s, 2H), 4.12 (d, *J* = 7.2 Hz, 2H),

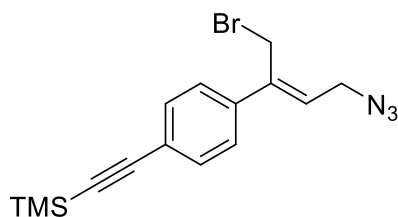
3.93 (s, 3H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  166.7, 143.6, 140.4, 130.1, 130.1, 128.0, 126.3, 52.3, 48.4, 26.9. **HRMS (ESI)**:  $m/z$  calculated for  $[\text{C}_{12}\text{H}_{12}\text{BrN}_3\text{O}_2^+-\text{N}_3]$ : 267.0021, found: 267.0031.

(Z)-1-(4-azido-1-bromobut-2-en-2-yl)-3-chlorobenzene (**5f**)



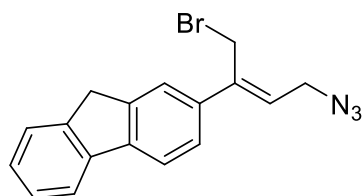
Following the general procedure D, **5f** was obtained in 69% yield (39.5 mg,  $Z/E = 98:2$ , **5f:5f'** = 90:10) as colorless oil, using ethyl acetate/petroleum ether (1:20) as eluent.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.45 – 7.43 (m, 1H), 7.36 – 7.30 (m, 3H), 6.00 (t,  $J = 7.2$  Hz, 1H), 4.29 (s, 2H), 4.09 (d,  $J = 7.2$  Hz, 2H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  141.1, 140.2, 134.8, 130.1, 128.6, 127.4, 126.6, 124.6, 48.3, 27.1. **HRMS (ESI)**:  $m/z$  calculated for  $[\text{C}_{10}\text{H}_9\text{BrClN}_3^+-\text{N}_3]$ : 242.9576, found: 242.9584.

(Z)-((4-(4-azido-1-bromobut-2-en-2-yl)phenyl)ethynyl)trimethylsilane (**5g**)



Following the general procedure D, **5g** was obtained in 80% yield (55.7 mg,  $Z/E = 97:3$ , **5g:5g'** = 92:8) as colorless oil, using ethyl acetate/petroleum ether (1:20) as eluent.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.49 – 7.45 (m, 2H), 7.43 – 7.37 (m, 2H), 6.02 (t,  $J = 7.2$  Hz, 1H), 4.30 (s, 2H), 4.09 (d,  $J = 7.2$  Hz, 2H), 0.26 (s, 9H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  140.6, 139.1, 132.4, 126.8, 126.1, 123.4, 104.7, 95.7, 48.4, 27.0, 0.1. **HRMS (ESI)**:  $m/z$  calculated for  $[\text{C}_{15}\text{H}_{18}\text{BrN}_3\text{Si}^+-\text{N}_3]$ : 305.0361, found: 305.0362.

(Z)-2-(4-azido-1-bromobut-2-en-2-yl)-9H-fluorene (**5h**)

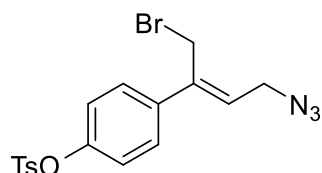


Following the general procedure D, **5h** was obtained in 53% yield (36.1 mg,  $Z/E = 87:13$ , **5h:5h'** > 98:2) as colorless oil, using ethyl acetate/petroleum ether (1:20) as eluent.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.81 – 7.77 (m, 2H), 7.66 – 7.64 (m, 1H), 7.57 – 7.53 (m, 1H), 7.48 (dd,  $J = 8.0, 1.7$  Hz, 1H), 7.41 – 7.36 (m, 1H), 7.34 – 7.29 (m, 1H), 6.07 (t,  $J = 7.2$  Hz, 1H), 4.39 (s, 2H), 4.12 (d,  $J = 7.2$  Hz, 2H), 3.93 (s, 2H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  143.8, 143.7, 142.3, 141.7,

141.2, 137.7, 127.2, 127.0, 125.8, 125.2, 125.2, 123.0, 120.2, 120.1, 48.5, 37.1, 27.8.

**HRMS (ESI):**  $m/z$  calculated for  $[C_{17}H_{14}BrN_3^+-N_3]$ : 297.0279, found: 297.0283.

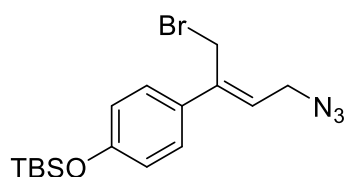
(*Z*)-4-(4-azido-1-bromobut-2-en-2-yl)phenyl 4-methylbenzenesulfonate (**5i**)



Following the general procedure D, **5i** was obtained in 76% yield (64.2 mg,  $Z/E = 97:3$ , **5i:5i'** = 95:5) as colorless oil, using ethyl acetate/petroleum ether (1:10) as eluent.  $^1H$

**NMR** (400 MHz,  $CDCl_3$ )  $\delta$  7.75 – 7.70 (m, 2H), 7.42 – 7.36 (m, 2H), 7.35 – 7.31 (m, 2H), 7.01 – 6.97 (m, 2H), 5.96 (t,  $J = 7.2$  Hz, 1H), 4.26 (s, 2H), 4.08 (d,  $J = 7.2$  Hz, 2H), 2.46 (s, 3H).  $^{13}C$  **NMR** (101 MHz,  $CDCl_3$ )  $\delta$  149.7, 145.6, 140.0, 138.2, 132.4, 130.0, 128.6, 127.6, 127.2, 122.7, 48.3, 27.2, 21.9. **HRMS (ESI):**  $m/z$  calculated for  $[C_{17}H_{16}BrN_3O_3S^+-N_3]$ : 379.0004, found: 379.0001.

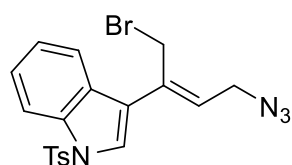
(*Z*)-4-(4-azido-1-bromobut-2-en-2-yl)phenoxy(*tert*-butyl)dimethylsilane (**5j**)



Following the general procedure D, **5j** was obtained in 77% yield (58.9 mg,  $Z/E = 86:14$ , **5j:5j'** > 98:2) as colorless oil, using ethyl acetate/petroleum ether (1:20) as eluent.  $^1H$

**NMR** (400 MHz,  $CDCl_3$ )  $\delta$  7.37 – 7.33 (m, 2H), 6.85 – 6.81 (m, 2H), 5.95 (t,  $J = 7.3$  Hz, 1H), 4.31 (s, 2H), 4.07 (d,  $J = 7.3$  Hz, 2H), 0.99 (s, 9H), 0.21 (s, 6H).  $^{13}C$  **NMR** (101 MHz,  $CDCl_3$ )  $\delta$  156.2, 140.9, 132.1, 127.4, 124.5, 120.3, 48.4, 27.6, 25.8, 18.4, -4.2. **HRMS (ESI):**  $m/z$  calculated for  $[C_{16}H_{24}BrN_3OSi^+-N_3]$ : 339.0780, found: 339.0785.

(*Z*)-3-(4-azido-1-bromobut-2-en-2-yl)-1-tosyl-1*H*-indole (**5k**)

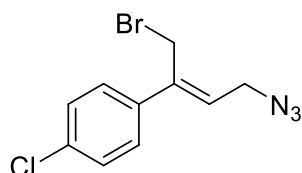


Following the general procedure D, **5k** was obtained in 62% yield (55.2 mg,  $Z/E = 79:21$ , **5k:5k'** > 98:2) as pale yellow oil, using ethyl acetate/petroleum ether (1:10) as eluent.  $^1H$

**NMR** (400 MHz,  $CDCl_3$ )  $\delta$  8.01 (dt,  $J = 8.2, 1.0$  Hz, 1H), 7.81 – 7.76 (m, 3H), 7.69 – 7.66 (m, 1H), 7.38 – 7.26 (m, 2H), 7.25 – 7.21 (m, 2H), 6.16 (t,  $J = 7.3$  Hz, 1H), 4.30 (s, 2H), 4.13 (d,  $J = 7.3$  Hz, 2H), 2.34 (s, 3H).  $^{13}C$  **NMR** (101 MHz,  $CDCl_3$ )  $\delta$  145.4, 135.4, 135.0, 134.0, 130.1, 128.7, 127.0, 126.7, 125.3, 124.3,

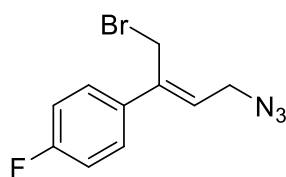
123.9, 121.3, 120.6, 114.0, 48.1, 27.8, 21.7. **HRMS (ESI)**:  $m/z$  calculated for  $[C_{19}H_{17}BrN_4O_2S^+-N_3]$ : 402.0164, found: 402.0162.

(*Z*)-1-(4-azido-1-bromobut-2-en-2-yl)-4-chlorobenzene (**5l**)



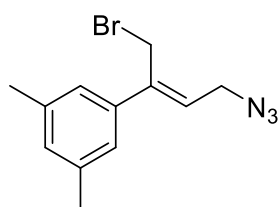
Following the general procedure D, **5l** was obtained in 68% yield (39.0 mg,  $Z/E = 96:4$ , **5l:5l'** = 90:10) as colorless oil, using ethyl acetate/petroleum ether (1:20) as eluent.  **$^1H$  NMR** (400 MHz,  $CDCl_3$ )  $\delta$  7.42 – 7.38 (m, 2H), 7.37 – 7.33 (m, 2H), 5.99 (t,  $J = 7.2$  Hz, 1H), 4.29 (s, 2H), 4.09 (d,  $J = 7.2$  Hz, 2H).  **$^{13}C$  NMR** (101 MHz,  $CDCl_3$ )  $\delta$  140.3, 137.6, 134.6, 129.0, 127.7, 126.7, 48.3, 27.2. **HRMS (ESI)**:  $m/z$  calculated for  $[C_{10}H_9BrClN_3^+-N_3]$ : 242.9576, found: 242.9577.

(*Z*)-1-(4-azido-1-bromobut-2-en-2-yl)-4-fluorobenzene (**5m**)



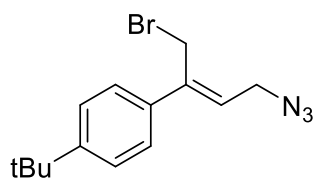
Following the general procedure D, **5m** was obtained in 78% yield (42.1 mg,  $Z/E = 96:4$ , **5m:5m'** = 96:4) as colorless oil, using ethyl acetate/petroleum ether (1:20) as eluent.  **$^1H$  NMR** (400 MHz,  $CDCl_3$ )  $\delta$  7.47 – 7.41 (m, 2H), 7.10 – 7.04 (m, 2H), 5.95 (t,  $J = 7.2$  Hz, 1H), 4.30 (s, 2H), 4.08 (d,  $J = 7.2$  Hz, 2H).  **$^{13}C$  NMR** (101 MHz,  $CDCl_3$ )  $\delta$  163.0 (d,  $J = 248.1$  Hz), 140.4, 135.3 (d,  $J = 3.3$  Hz), 128.2 (d,  $J = 8.1$  Hz), 126.2 (d,  $J = 1.0$  Hz), 115.8 (d,  $J = 21.6$  Hz), 48.3, 27.5.  **$^{19}F$  NMR** (376 MHz,  $CDCl_3$ )  $\delta$  -113.30 (ddd,  $J = 14.0, 8.7, 5.3$  Hz). **HRMS (ESI)**:  $m/z$  calculated for  $[C_{10}H_9BrFN_3^+-N_3]$ : 226.9872, found: 226.9873.

(*Z*)-1-(4-azido-1-bromobut-2-en-2-yl)-3,5-dimethylbenzene (**5n**)



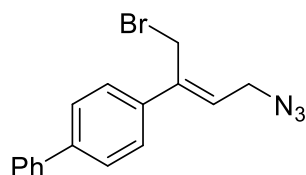
Following the general procedure D, **5n** was obtained in 82% yield (45.9 mg,  $Z/E = 94:6$ , **5n:5n'** = 94:6) as colorless oil, using ethyl acetate/petroleum ether (1:20) as eluent.  **$^1H$  NMR** (400 MHz,  $CDCl_3$ )  $\delta$  7.08 – 7.06 (m, 2H), 7.01 – 6.97 (m, 1H), 5.97 (t,  $J = 7.3$  Hz, 1H), 4.32 (s, 2H), 4.07 (d,  $J = 7.3$  Hz, 2H), 2.34 (s, 6H).  **$^{13}C$  NMR** (101 MHz,  $CDCl_3$ )  $\delta$  141.6, 139.2, 138.3, 130.3, 125.8, 124.2, 48.4, 27.7, 21.5. **HRMS (ESI)**:  $m/z$  calculated for  $[C_{12}H_{14}BrN_3^+-N_3]$ : 237.0278, found: 237.0280.

(Z)-1-(4-azido-1-bromobut-2-en-2-yl)-4-(tert-butyl)benzene (**5o**)



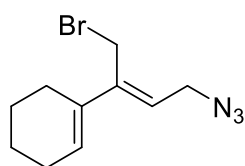
Following the general procedure D, **5o** was obtained in 85% yield (52.4 mg, *Z/E* = 93:7, **5o:5o'** = 96:4) as colorless oil, using ethyl acetate/petroleum ether (1:20) as eluent.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.44 – 7.38 (m, 4H), 6.01 (t, *J* = 7.3 Hz, 1H), 4.33 (s, 2H), 4.08 (d, *J* = 7.3 Hz, 2H), 1.33 (s, 9H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  151.7, 141.0, 136.1, 125.9, 125.7, 125.4, 48.4, 34.7, 31.4, 27.5. HRMS (ESI): *m/z* calculated for  $[\text{C}_{14}\text{H}_{18}\text{BrN}_3^+ - \text{N}_3]$ : 265.0591, found: 265.0592.

(Z)-4-(4-azido-1-bromobut-2-en-2-yl)-1,1'-biphenyl (**5p**)



Following the general procedure D, **5p** was obtained in 74% yield (48.6 mg, *Z/E* = 91:9, **5p:5p'** = 96:4) as colorless oil, using ethyl acetate/petroleum ether (1:20) as eluent.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.63 – 7.59 (m, 4H), 7.57 – 7.53 (m, 2H), 7.47 – 7.43 (m, 2H), 7.39 – 7.34 (m, 1H), 6.07 (t, *J* = 7.2 Hz, 1H), 4.37 (s, 2H), 4.11 (d, *J* = 7.2 Hz, 2H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  141.5, 140.9, 140.5, 137.9, 129.0, 127.7, 127.5, 127.2, 126.7, 126.1, 48.4, 27.4. HRMS (ESI): *m/z* calculated for  $[\text{C}_{16}\text{H}_{14}\text{BrN}_3^+ - \text{N}_3]$ : 285.0279, found: 285.0280.

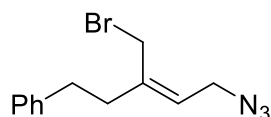
(Z)-1-(4-azido-1-bromobut-2-en-2-yl)cyclohex-1-ene (**5q**)



Following the general procedure D, **5q** was obtained in 44% yield (22.5 mg, *Z/E* = 86:14, **5q:5q'** > 98:2) as colorless oil, using ethyl acetate/petroleum ether (1:20) as eluent.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  6.10 (t, *J* = 4.0 Hz, 1H), 5.71 (t, *J* = 7.3 Hz, 1H), 4.12 (s, 2H), 4.00 (d, *J* = 7.3 Hz, 2H), 2.25 – 2.15 (m, 4H), 1.75 – 1.67 (m, 2H), 1.65 – 1.57 (m, 2H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  141.6, 133.7, 127.2, 121.6, 77.5, 77.2, 76.8, 48.4, 26.1, 26.0, 25.3, 22.8, 22.0. HRMS (ESI): *m/z* calculated for  $[\text{C}_{10}\text{H}_{14}\text{BrN}_3 - \text{N}_3]^+$ : 213.0278, found: 213.0274.

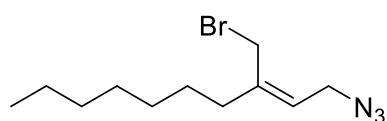
(Z)-(5-azido-3-(bromomethyl)pent-3-en-1-yl)benzene (**5r**)





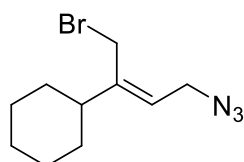
Following the general procedure D, **5r** was obtained in 73% yield (40.9 mg, *Z/E* > 98:2, **5r:5r'** > 98:2) as colorless oil, using ethyl acetate/petroleum ether (1:20) as eluent. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.32 – 7.27 (m, 2H), 7.22 – 7.18 (m, 3H), 5.52 (tt, *J* = 7.4, 1.3 Hz, 1H), 3.96 (s, 2H), 3.87 (d, *J* = 7.4 Hz, 2H), 2.84 – 2.79 (m, 2H), 2.60 – 2.54 (m, 2H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 141.5, 141.0, 128.6, 128.5, 126.3, 123.8, 47.6, 37.2, 34.4, 28.7. HRMS (ESI): *m/z* calculated for [C<sub>12</sub>H<sub>14</sub>BrN<sub>3</sub>-N<sub>3</sub>]<sup>+</sup>: 237.0279, found: 237.0328.

(*Z*)-1-azido-3-(bromomethyl)dec-2-ene (**5s**)



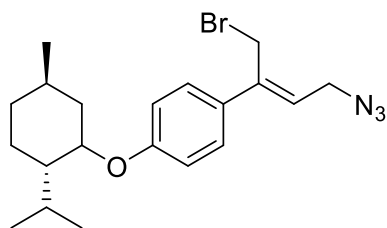
Following the general procedure D, **5s** was obtained in 85% yield (46.6 mg, *Z/E* > 98:2, **5s:5s'** > 98:2) as colorless oil, using ethyl acetate/petroleum ether (1:20) as eluent. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 5.51 (t, *J* = 7.3 Hz, 1H), 3.96 (s, 2H), 3.87 (d, *J* = 7.3 Hz, 2H), 2.24 (t, *J* = 7.6 Hz, 2H), 1.52 – 1.40 (m, 2H), 1.34 – 1.26 (m, 8H), 0.89 (t, *J* = 6.5 Hz, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 142.5, 123.0, 47.7, 35.6, 31.9, 29.2, 29.2, 28.6, 27.8, 22.8, 14.2. HRMS (ESI): *m/z* calculated for [C<sub>11</sub>H<sub>20</sub>BrN<sub>3</sub>-N<sub>3</sub>]<sup>+</sup>: 245.0779, found: 245.0758.

(*Z*)-(4-azido-1-bromobut-2-en-2-yl)cyclohexane (**5t**)



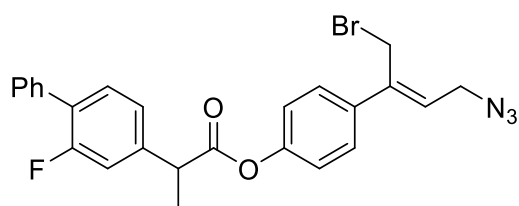
Following the general procedure D, **5t** was obtained in 78% yield (40.3 mg, *Z/E* > 98:2, **5t:5t'** > 98:2) as colorless oil, using ethyl acetate/petroleum ether (1:20) as eluent. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 5.51 (t, *J* = 7.3 Hz, 1H), 3.97 (s, 2H), 3.91 (d, *J* = 7.3 Hz, 2H), 2.18 – 2.08 (m, 1H), 1.88 – 1.74 (m, 5H), 1.34 – 1.15 (m, 5H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 147.5, 122.0, 47.7, 44.1, 32.7, 28.1, 26.7, 26.2. HRMS (ESI): *m/z* calculated for [C<sub>10</sub>H<sub>16</sub>BrN<sub>3</sub>-N<sub>3</sub>]<sup>+</sup>: 257.0528, found: 257.0536.

1-((*Z*)-4-azido-1-bromobut-2-en-2-yl)-4-(((2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl)oxy)benzene (**5u**)



Following the general procedure D, **5u** was obtained in 76% yield (61.8 mg, *Z/E* = 87:13, **5u:5u'** > 98:2) as colorless oil, using ethyl acetate/petroleum ether (1:20) as eluent.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.42 – 7.36 (m, 1.15H), 7.13 – 7.07 (m, 0.85H), 6.93 – 6.87 (m, 2H), 5.95 (t,  $J = 7.3$  Hz, 1H), 4.65 (s, 1H), 4.32 (s, 1.15H), 4.24 (s, 0.86H), 4.07 (d,  $J = 7.3$  Hz, 1.14H), 3.78 (d,  $J = 7.2$  Hz, 0.88H), 2.15 – 2.05 (m, 1H), 1.87 – 1.48 (m, 5H), 1.12 – 0.94 (m, 3H), 0.95 – 0.91 (m, 3H), 0.88 – 0.80 (m, 6H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  158.8, 140.9, 130.8, 127.5, 124.1, 115.7, 73.5, 48.4, 47.9, 37.8, 35.1, 29.4, 26.3, 25.0, 22.4, 21.2, 21.0. **HRMS (ESI)**:  $m/z$  calculated for  $[\text{C}_{20}\text{H}_{28}\text{BrN}_3\text{O}-\text{N}_3]^+$ : 363.1323, found: 363.1327.

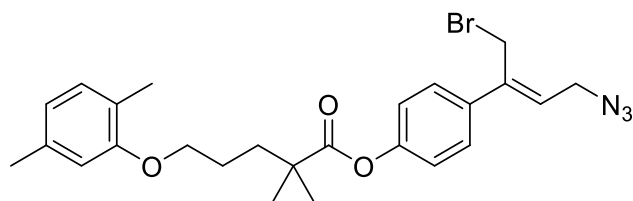
(*Z*)-4-(4-azido-1-bromobut-2-en-2-yl)phenyl  
yl)propanoate (**5v**)



Following the general procedure D, **5v** was obtained in 82% yield (81.1 mg, *Z/E* = 93:7, **5v:5v'** > 98:2) as colorless oil, using ethyl acetate/petroleum ether (1:10) as eluent.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.58 – 7.53 (m, 2.97H), 7.49 – 7.41 (m, 7.28H), 7.40 – 7.35 (m, 1.5H), 7.28 – 7.21 (m, 3.02H), 7.12 – 7.04 (m, 2.94H), 5.97 (t,  $J = 7.3$  Hz, 1.45H), 4.29 (s, 2H), 4.20 (s, 0.91H), 4.07 (d,  $J = 7.3$  Hz, 2H), 4.01 (q,  $J = 7.2$  Hz, 1.46H), 3.71 (d,  $J = 7.2$  Hz, 0.9H), 1.66 (d,  $J = 7.1$  Hz, 4.38H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  172.4, 159.9 (d,  $J = 248.6$  Hz), 150.9, 141.2 (d,  $J = 7.7$  Hz), 140.4, 137.0, 135.5, 131.2 (d,  $J = 3.9$  Hz), 129.8, 129.1 (d,  $J = 3.0$  Hz), 128.6, 127.9, 127.5, 126.5, 123.7 (d,  $J = 3.4$  Hz), 121.7, 115.5 (d,  $J = 23.9$  Hz), 48.3, 45.3, 27.3, 18.52. **HRMS (ESI)**:  $m/z$  calculated for  $[\text{C}_{25}\text{H}_{21}\text{BrFN}_3\text{O}_2-\text{N}_3]^+$ : 451.0708, found: 451.0706.

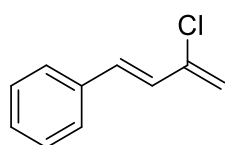
(*Z*)-4-(4-azido-1-bromobut-2-en-2-yl)phenyl  
dimethylpentanoate (**5w**)

5-(2,5-dimethylphenoxy)-2,2-



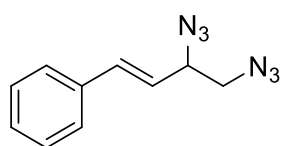
Following the general procedure D, **5w** was obtained in 84% yield (84.1 mg, *Z/E* = 94:6, **5w**:**5w'** > 98:2) as colorless oil, using ethyl acetate/petroleum ether (1:10) as eluent.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.49 – 7.43 (m, 2H), 7.07 – 7.03 (m, 2H), 7.00 (d,  $J = 7.5$  Hz, 1H), 6.67 (d,  $J = 7.5$  Hz, 1H), 6.63 (s, 1H), 5.98 (t,  $J = 7.3$  Hz, 1H), 4.30 (s, 2H), 4.08 (d,  $J = 7.3$  Hz, 2H), 4.02 – 3.96 (m, 2H), 2.30 (s, 3H), 2.18 (s, 3H), 1.90 – 1.85 (m, 2H), 1.38 (s, 6H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  176.3, 157.0, 151.3, 140.6, 136.7, 136.6, 130.5, 127.4, 126.4, 123.7, 121.9, 120.9, 112.1, 67.9, 48.3, 42.6, 37.3, 27.4, 25.4, 25.3, 21.5, 15.9. **HRMS (ESI)**:  $m/z$  calculated for  $[\text{C}_{25}\text{H}_{28}\text{BrN}_3\text{O}_3\text{-N}_3]^+$ : 457.1378, found: 457.1379.

*(E)*-(3-chlorobuta-1,3-dien-1-yl)benzene (**6**)



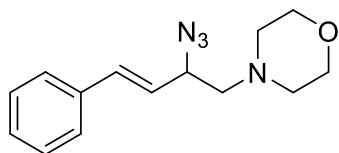
Derivatization product **6** was obtained in 62% yield (20.4 mg) as colorless oil, using petroleum ether as eluent. Product **6** is a known compound.<sup>[10]</sup>  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.48 – 7.43 (m, 2H), 7.38 – 7.32 (m, 2H), 7.31 – 7.27 (m, 1H), 6.99 (d,  $J = 15.4$  Hz, 1H), 6.82 (d,  $J = 15.4$  Hz, 1H), 5.48 (s, 1H), 5.45 (s, 1H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  138.8, 136.0, 133.5, 128.9, 128.6, 127.2, 125.5, 116.1.

*(E)*-(3,4-diazidobut-1-en-1-yl)benzene (**7**)



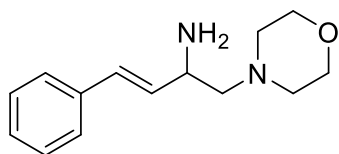
Derivatization product **7** was obtained in 65% (27.9 mg) as pale yellow oil, using ethyl acetate/petroleum ether (1:20) as eluent. Product **7** is a known compound.<sup>[11]</sup>  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.43 – 7.39 (m, 2H), 7.38 – 7.32 (m, 2H), 7.32 – 7.27 (m, 1H), 6.73 (d,  $J = 15.8$  Hz, 1H), 6.12 (dd,  $J = 15.8, 8.0$  Hz, 1H), 4.31 – 4.19 (m, 1H), 3.44 – 3.33 (m, 2H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  135.7, 135.5, 128.9, 128.8, 126.9, 123.1, 64.0, 54.7.

*(E)*-4-(2-azido-4-phenylbut-3-en-1-yl)morpholine (**8**)



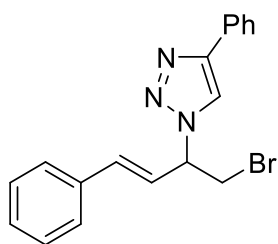
Derivatization product **8** was obtained in 73% yield (187.7 mg) as pale yellow oil, using ethyl acetate/petroleum ether (1:5) as eluent.. **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.41 – 7.37 (m, 2H), 7.36 – 7.31 (m, 2H), 7.29 – 7.24 (m, 1H), 6.65 (d, *J* = 15.8 Hz, 1H), 6.08 (dd, *J* = 15.8, 7.5 Hz, 1H), 4.29 – 4.20 (m, 1H), 3.73 (m, 4H), 2.65 – 2.56 (m, 3H), 2.50 (m, 3H). **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 136.0, 133.6, 128.8, 128.3, 126.7, 125.4, 77.5, 77.2, 76.8, 67.0, 63.0, 61.5, 54.0. **HRMS (ESI)**: *m/z* calculated for C<sub>14</sub>H<sub>19</sub>N<sub>4</sub>O [M+H]<sup>+</sup>: 259.1559, found: 259.1557.

*(E)*-1-morpholino-4-phenylbut-3-en-2-amine (**9**)



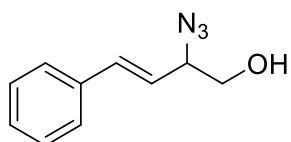
Derivatization product **9** was obtained in 88% yield (41.0 mg) as pale yellow oil, using MeOH/CH<sub>2</sub>Cl<sub>2</sub> (1:5) as eluent. **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.39 – 7.34 (m, 2H), 7.33 – 7.28 (m, 2H), 7.26 – 7.20 (m, 1H), 6.61 (d, *J* = 15.9 Hz, 1H), 6.17 (dd, *J* = 15.9, 6.9 Hz, 1H), 3.82 – 3.63 (m, 5H), 3.39 (s, 2H), 2.66 – 2.54 (m, 2H), 2.50 – 2.35 (m, 4H). **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 136.7, 131.5, 130.0, 128.7, 127.8, 126.5, 67.1, 64.2, 53.9, 50.5. **HRMS (ESI)**: *m/z* calculated for C<sub>14</sub>H<sub>21</sub>N<sub>2</sub>O [M+H]<sup>+</sup>: 233.1654, found: 233.1652.

*(E)*-1-(1-bromo-4-phenylbut-3-en-2-yl)-4-phenyl-1H-1,2,3-triazole (**10**)



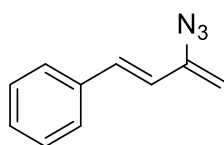
Derivatization product **10** was obtained in 85% yield (60.2 mg) as white solid, using ethyl acetate/petroleum ether (1:5) as eluent. **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.90 (s, 1H), 7.88 – 7.82 (m, 2H), 7.46 – 7.38 (m, 4H), 7.38 – 7.29 (m, 4H), 6.71 (d, *J* = 15.9 Hz, 1H), 6.50 (dd, *J* = 15.9, 7.7 Hz, 1H), 5.50 (td, *J* = 7.2, 5.2 Hz, 1H), 4.06 (dd, *J* = 10.8, 7.2 Hz, 1H), 3.94 (dd, *J* = 10.8, 5.2 Hz, 1H). **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 147.6, 136.3, 135.1, 130.5, 129.1, 129.0, 128.9, 128.4, 127.0, 125.9, 123.4, 119.4, 64.0, 33.9. **HRMS (ESI)**: *m/z* calculated for C<sub>18</sub>H<sub>17</sub>BrN<sub>3</sub> [M+H]<sup>+</sup>: 354.0606, found: 354.0607.

*(E)*-2-azido-4-phenylbut-3-en-1-ol (**11**)



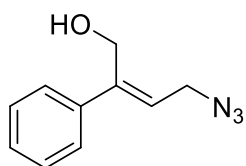
Derivatization product **11** was obtained in 77% yield (29.0 mg) as brownish yellow oil, using ethyl acetate/petroleum ether (1:5) as eluent.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.43 – 7.39 (m, 2H), 7.37 – 7.32 (m, 2H), 7.31 – 7.26 (m, 1H), 6.73 (d,  $J = 15.9$  Hz, 1H), 6.14 (dd,  $J = 15.9, 8.1$  Hz, 1H), 4.25 (dddd,  $J = 8.1, 7.2, 4.4, 0.7$  Hz, 1H), 3.73 (dd,  $J = 11.4, 4.4$  Hz, 1H), 3.64 (dd,  $J = 11.4, 7.2$  Hz, 1H), 1.99 (s, 1H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  135.7, 135.5, 128.8, 128.6, 126.9, 123.0, 66.5, 65.1. **HRMS (ESI)**:  $m/z$  calculated for  $\text{C}_{10}\text{H}_{12}\text{N}_3\text{O}$   $[\text{M}+\text{H}]^+$ : 190.0980, found: 190.0976.

*(E)*-(3-azidobuta-1,3-dien-1-yl)benzene (**12**)



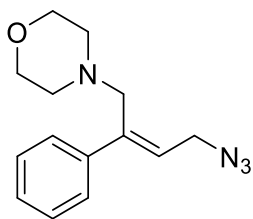
Derivatization product **12** was obtained in 85% yield (27.3 mg) as pale yellow oil, using petroleum ether as eluent. Product **12** is a known compound.<sup>[12]</sup>  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.43 – 7.38 (m, 2H), 7.35 – 7.29 (m, 2H), 7.28 – 7.23 (m, 1H), 6.86 (d,  $J = 15.7$  Hz, 1H), 6.55 (d,  $J = 15.7$  Hz, 1H), 5.07 (d,  $J = 1.9$  Hz, 1H), 4.91 (d,  $J = 1.9$  Hz, 1H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  144.0, 136.2, 131.0, 128.8, 128.4, 127.0, 123.3, 101.5.

*(Z)*-4-azido-2-phenylbut-2-en-1-ol (**13**)



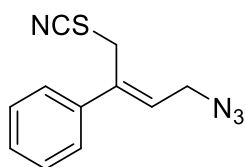
Derivatization product **13** was obtained in 79% yield (30.0 mg,  $Z/E = 31:69$ ) as pale yellow oil, using ethyl acetate/petroleum ether (1:5) as eluent.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ) 7.47 – 7.43 (m, 0.8H) (**Z-13**), 7.42 – 7.31 (m, 4.2H), 7.20 – 7.14 (m, 2H) (**E-13**), 5.94 (t,  $J = 7.4$  Hz, 0.4H) (**Z-13**), 5.87 (tt,  $J = 7.4, 1.6$  Hz, 1H) (**E-13**), 4.58 (s, 0.8H) (**Z-13**), 4.36 (s, 2H) (**E-13**), 4.08 (d,  $J = 7.4$  Hz, 0.8H) (**Z-13**), 3.74 (d,  $J = 7.4$  Hz, 2H) (**E-13**), 1.97 (s, 1.4H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ ) **Z-13**:  $\delta$  144.6, 139.7, 128.8, 128.2, 126.7, 123.9, 59.9, 48.2. **E-13**: 146.6, 136.7, 128.7, 128.6, 128.1, 119.8, 66.9, 48.8. **HRMS (ESI)**:  $m/z$  calculated for  $\text{C}_{10}\text{H}_{12}\text{N}_3\text{O}$   $[\text{M}+\text{H}]^+$ : 190.0980, found: 190.0977.

*(Z)*-4-(4-azido-2-phenylbut-2-en-1-yl)morpholine (**14**)



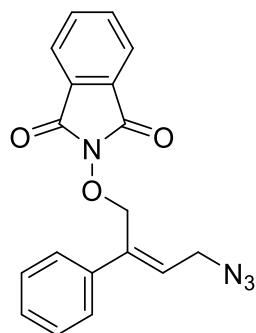
Derivatization product **14** was obtained in 90% yield (46.4 mg,  $Z/E = 75:25$ ) as pale yellow oil, using ethyl acetate/petroleum ether (1:5) as eluent.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.51 – 7.43 (m, 2H), 7.36 – 7.30 (m, 3H), 5.98 (t,  $J = 7.3$  Hz, 1H), 4.12 (d,  $J = 7.3$  Hz, 2H), 3.64 (t,  $J = 4.6$  Hz, 4H), 3.39 (s, 2H), 2.45 (t,  $J = 4.6$  Hz, 4H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  141.9, 141.3, 128.3, 127.7, 126.7, 125.6, 67.0, 57.8, 53.5, 48.6. **HRMS (ESI)**:  $m/z$  calculated for  $\text{C}_{14}\text{H}_{19}\text{N}_4\text{O}$   $[\text{M}+\text{H}]^+$ : 259.1559, found: 259.1558.

(*Z*)-4-(4-azido-1-thiocyanatobut-2-en-2-yl)benzene (**15**)



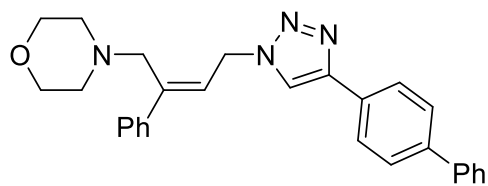
Derivatization product **15** was obtained in 82% yield (37.5 mg,  $Z/E = 89:11$ , **15:15'** = 95:5) as pale yellow oil, using ethyl acetate/petroleum ether (1:5) as eluent.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.39 (m, 5H), 6.10 (t,  $J = 7.3$  Hz, 1H), 4.11 (d,  $J = 7.3$  Hz, 2H), 4.10 (s, 2H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  138.4, 138.1, 129.0, 129.0, 127.8, 126.7, 111.4, 48.3, 33.3. **HRMS (ESI)**:  $m/z$  calculated for  $[\text{C}_{11}\text{H}_{10}\text{N}_4\text{S}^+-\text{N}_3]$ : 188.0534, found: 188.0531.

(*Z*)-2-((4-azido-2-phenylbut-2-en-1-yl)oxy)isoindoline-1,3-dione (**16**)

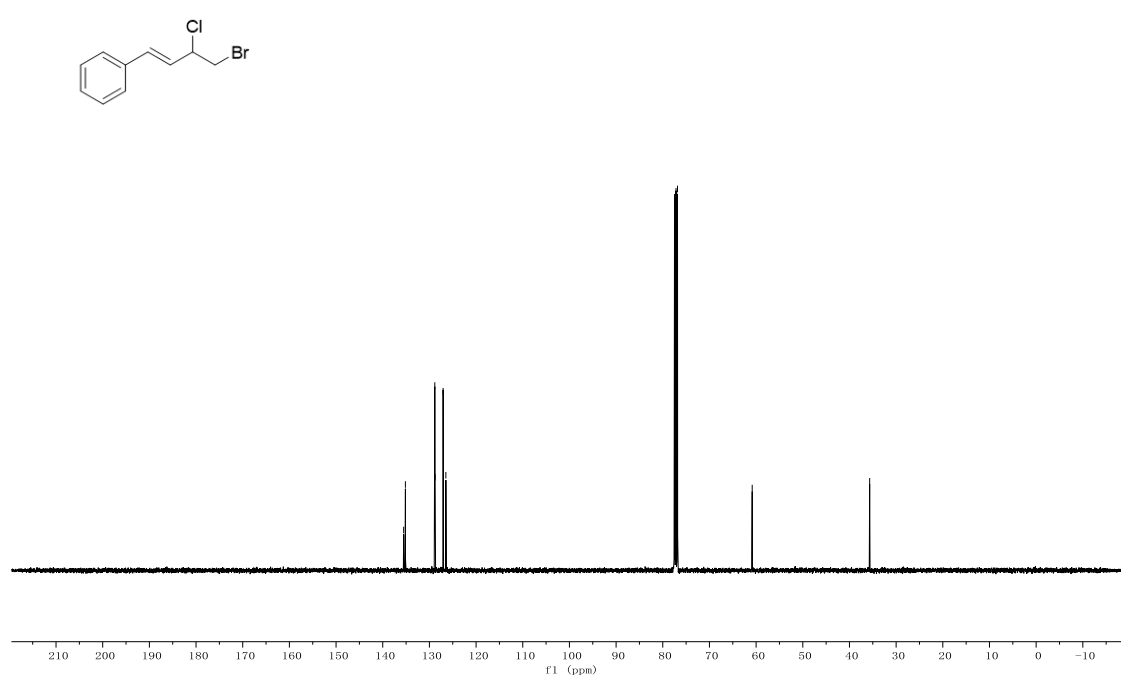
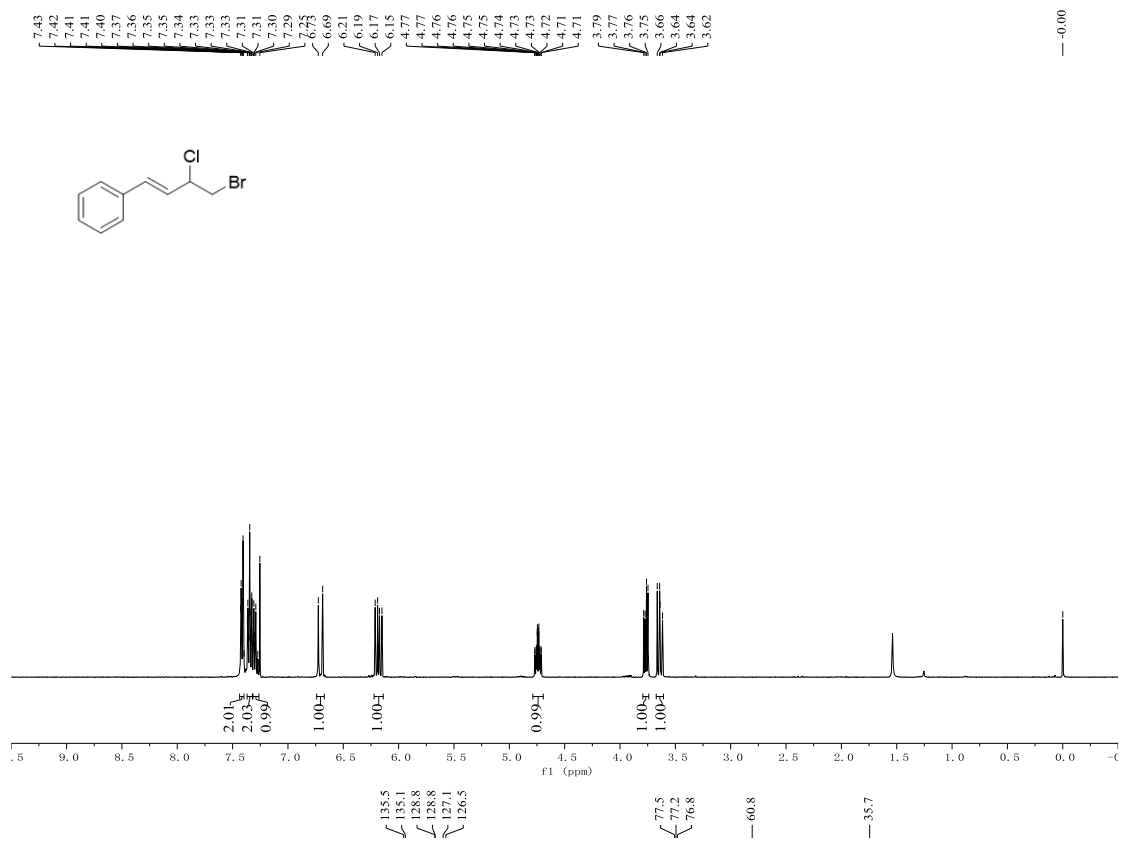


Derivatization product **16** was obtained in 72% yield (48.1 mg,  $Z/E = 75:25$ , **16:16'** = 93:7) as white solid, using ethyl acetate/petroleum ether (1:5) as eluent.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.85 – 7.81 (m, 2H), 7.77 – 7.73 (m, 2H), 7.66 – 7.61 (m, 2H), 7.41 – 7.34 (m, 3H), 6.25 (t,  $J = 7.4$  Hz, 1H), 5.08 (s, 2H), 4.31 (d,  $J = 7.4$  Hz, 2H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  163.5, 139.6, 137.3, 134.7, 130.2, 128.9, 128.8, 128.6, 128.3, 126.4, 123.7, 74.4, 48.6. **HRMS (ESI)**:  $m/z$  calculated for  $\text{C}_{18}\text{H}_{14}\text{N}_4\text{NaO}_3$   $[\text{M}+\text{Na}]^+$ : 357.0964, found: 357.0965.

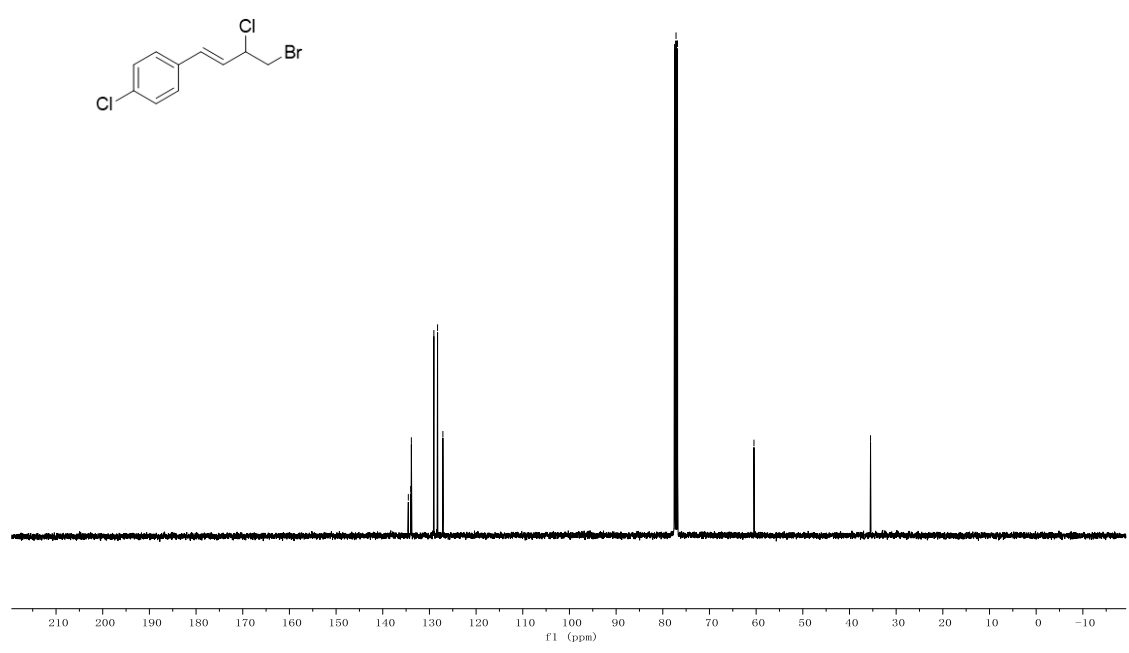
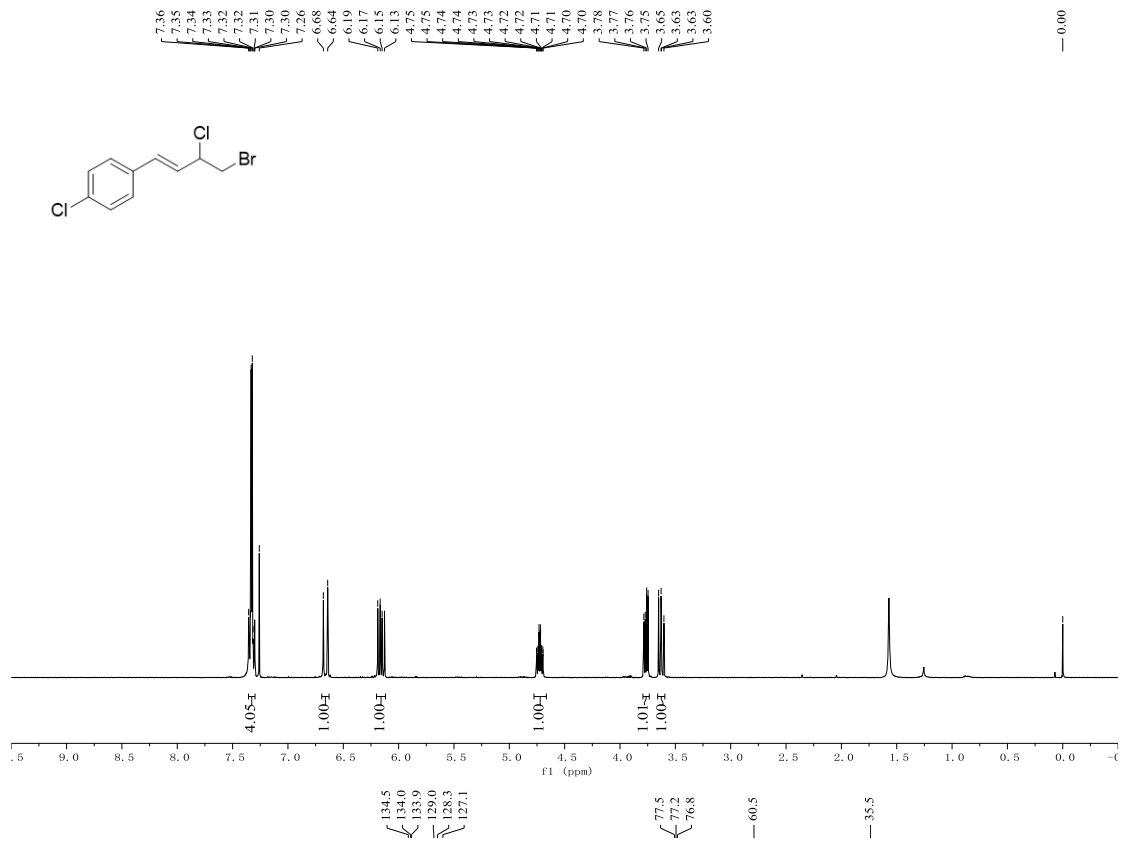
(*Z*)-4-(4-(4-([1,1'-biphenyl]-4-yl)-1H-1,2,3-triazol-1-yl)-2-phenylbut-2-en-1-yl)morpholine (**17**)

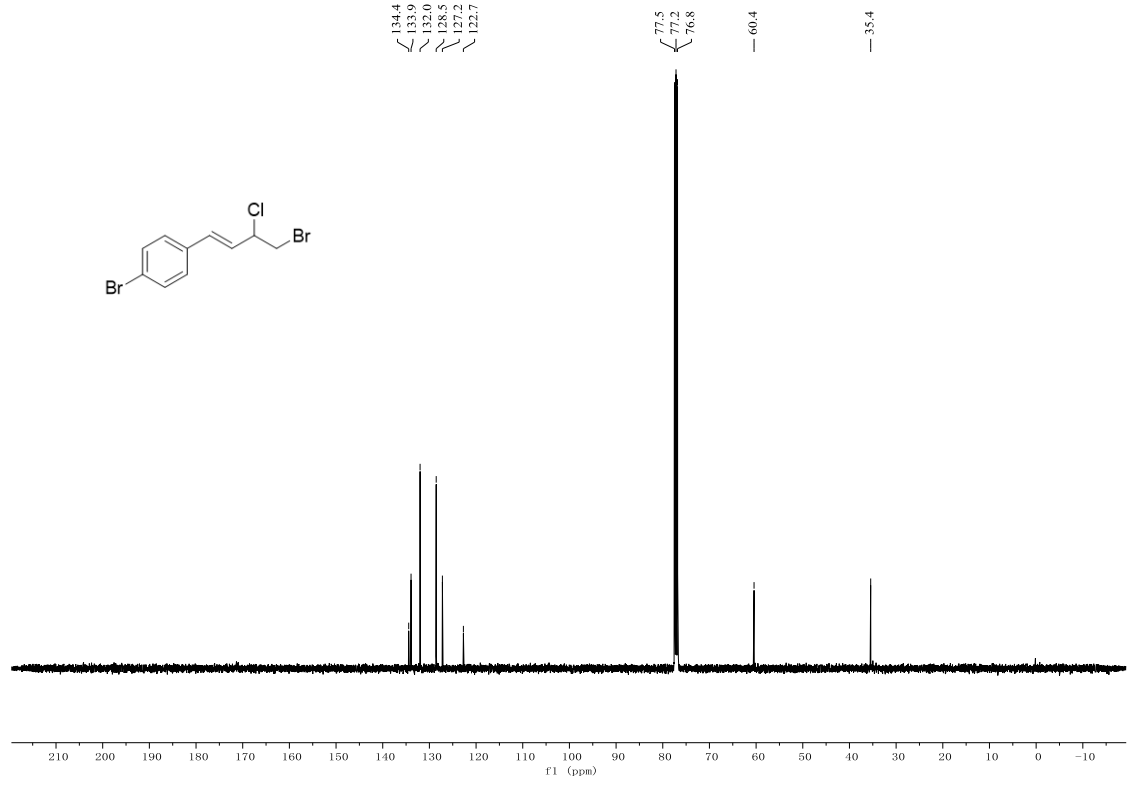
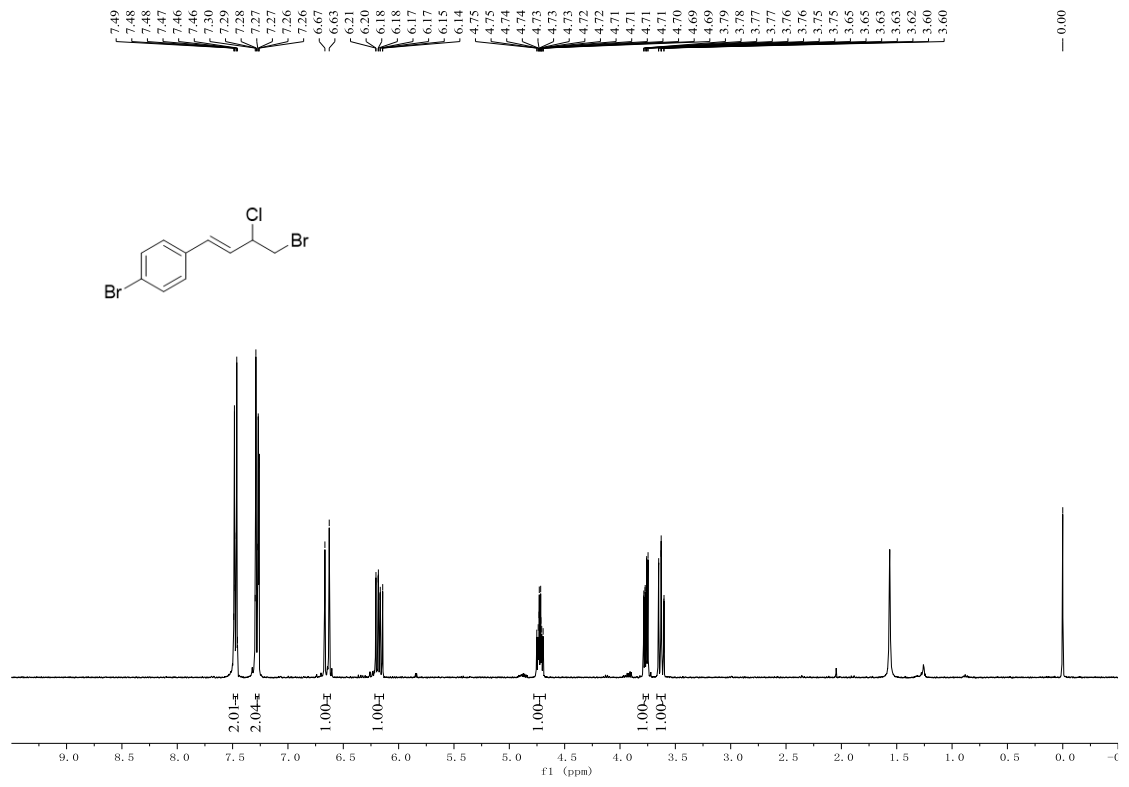


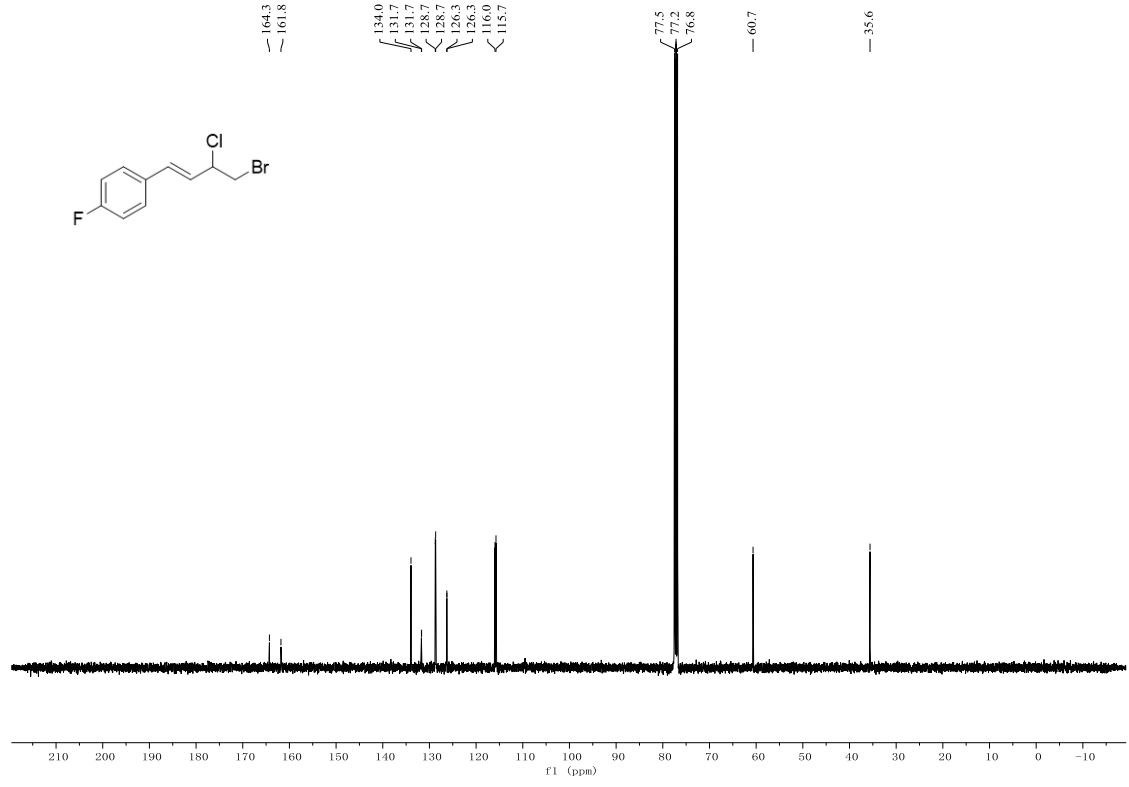
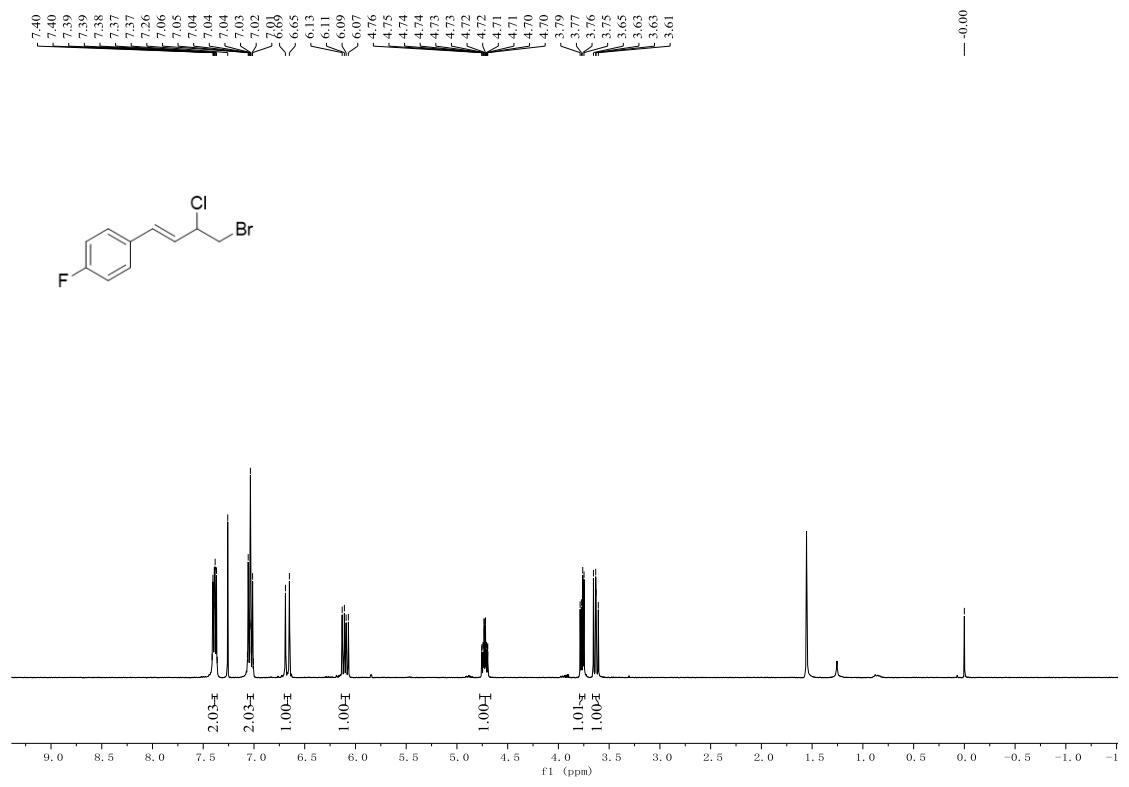
Derivatization product **17** was obtained in 88% yield (76.4 mg. *Z/E* = 75:25) as white solid, using ethyl acetate/petroleum ether (1:5) as eluent. **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.91 – 7.85 (m, 2H), 7.67 – 7.58 (m, 4H), 7.46 – 7.39 (m, 4H), 7.37 – 7.25 (m, 4H), 7.24 (s, 1H), 6.09 (t, *J* = 7.0 Hz, 1H), 5.35 (d, *J* = 7.0 Hz, 2H), 3.70 – 3.63 (m, 4H), 3.50 (s, 2H), 2.58 – 2.43 (m, 4H). **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 147.7, 141.6, 141.5, 140.9, 140.5, 129.7, 128.9, 128.4, 128.0, 127.5, 127.5, 127.0, 126.6, 126.1, 125.1, 119.5, 67.0, 58.2, 53.5, 48.6. **HRMS (ESI)**: *m/z* calculated for C<sub>28</sub>H<sub>29</sub>N<sub>4</sub>O [M+H]<sup>+</sup>: 437.2341, found: 437.2346.

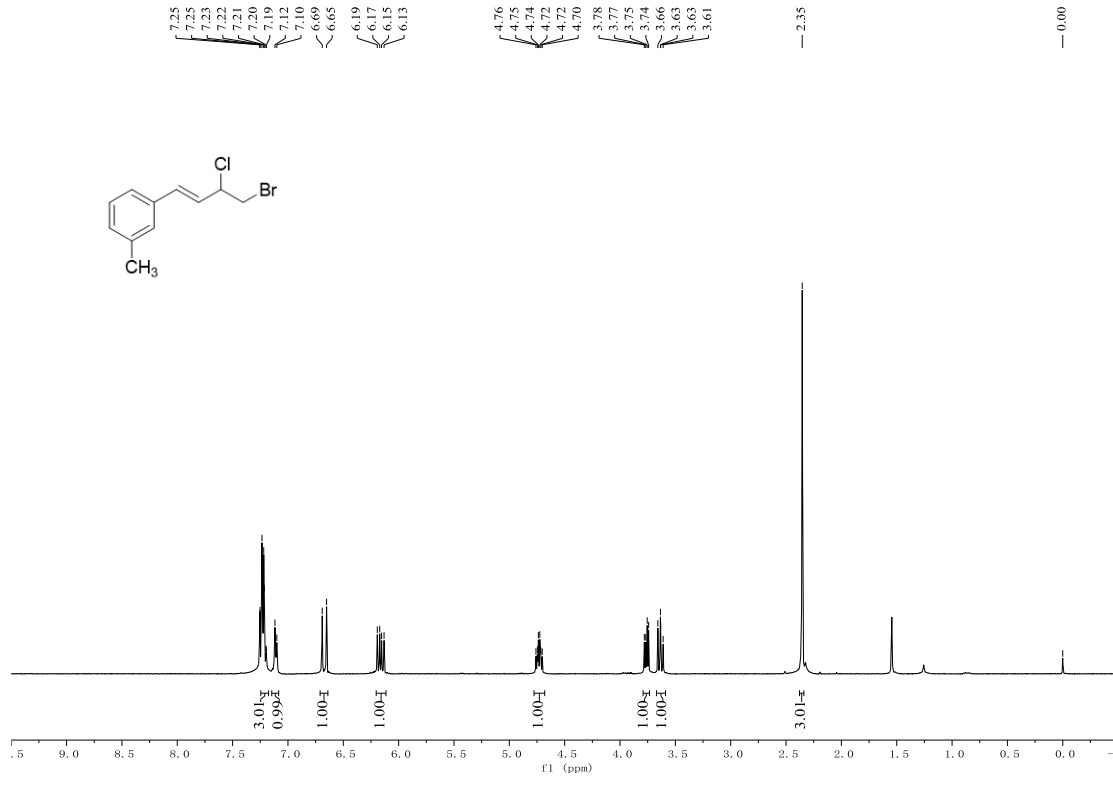
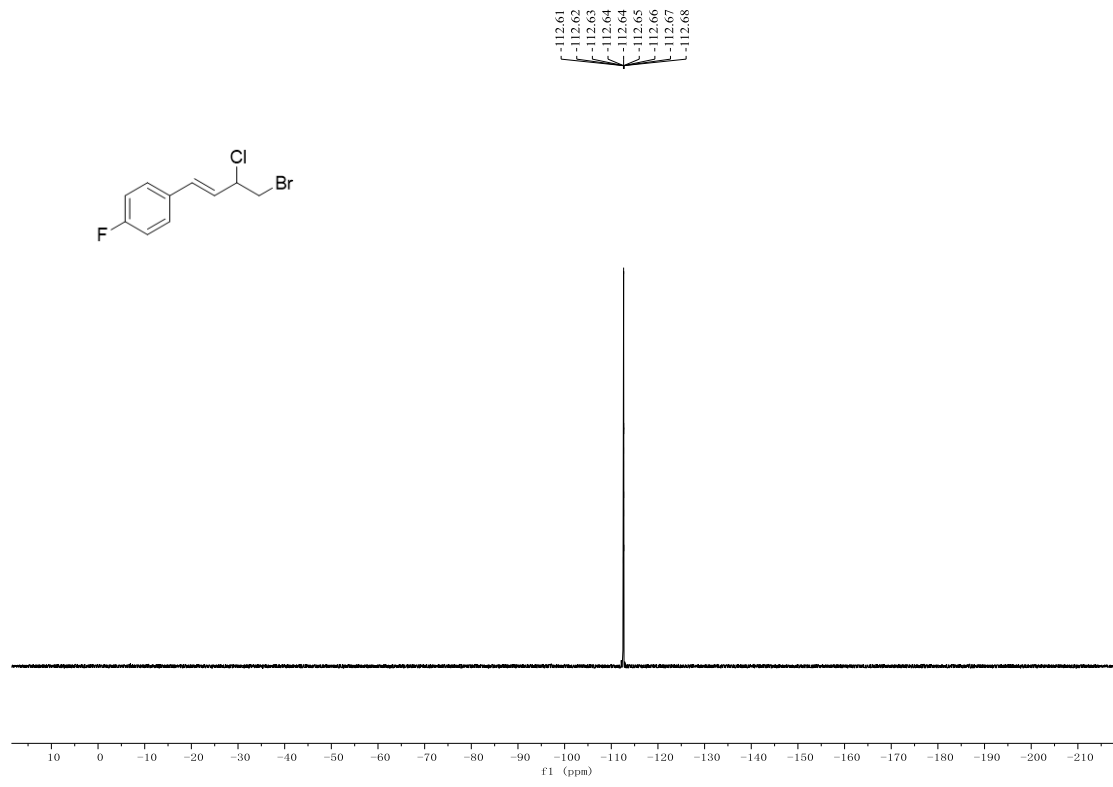


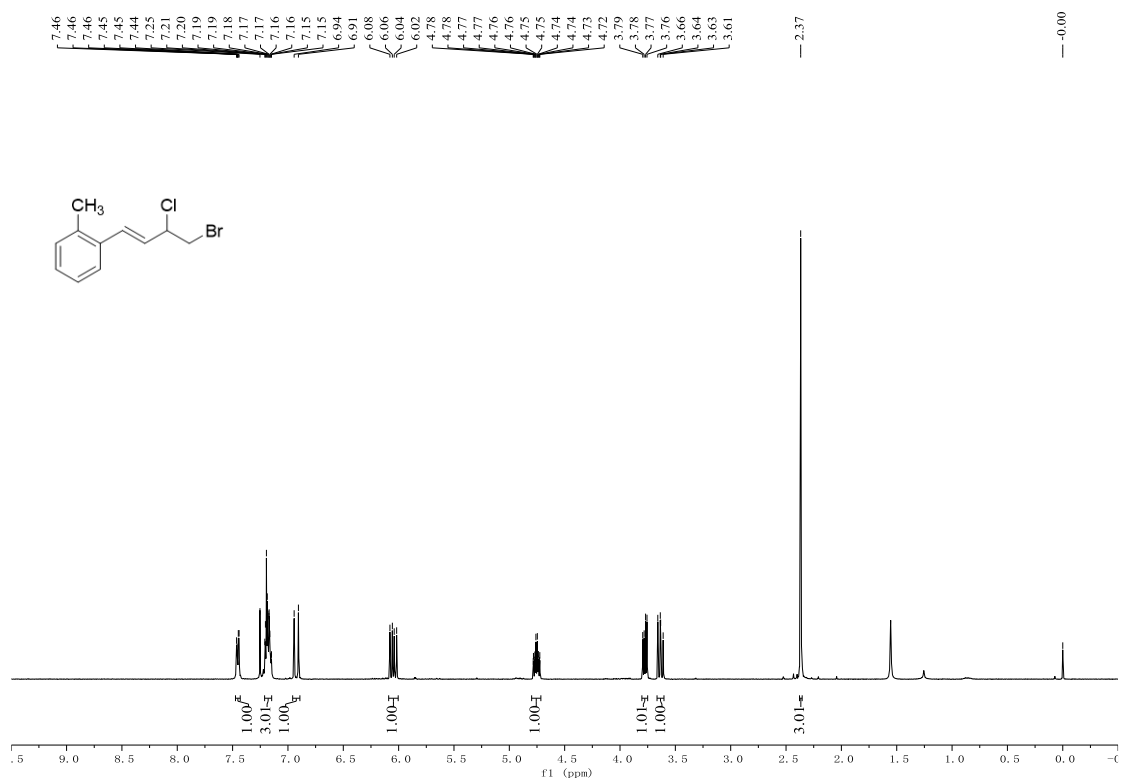
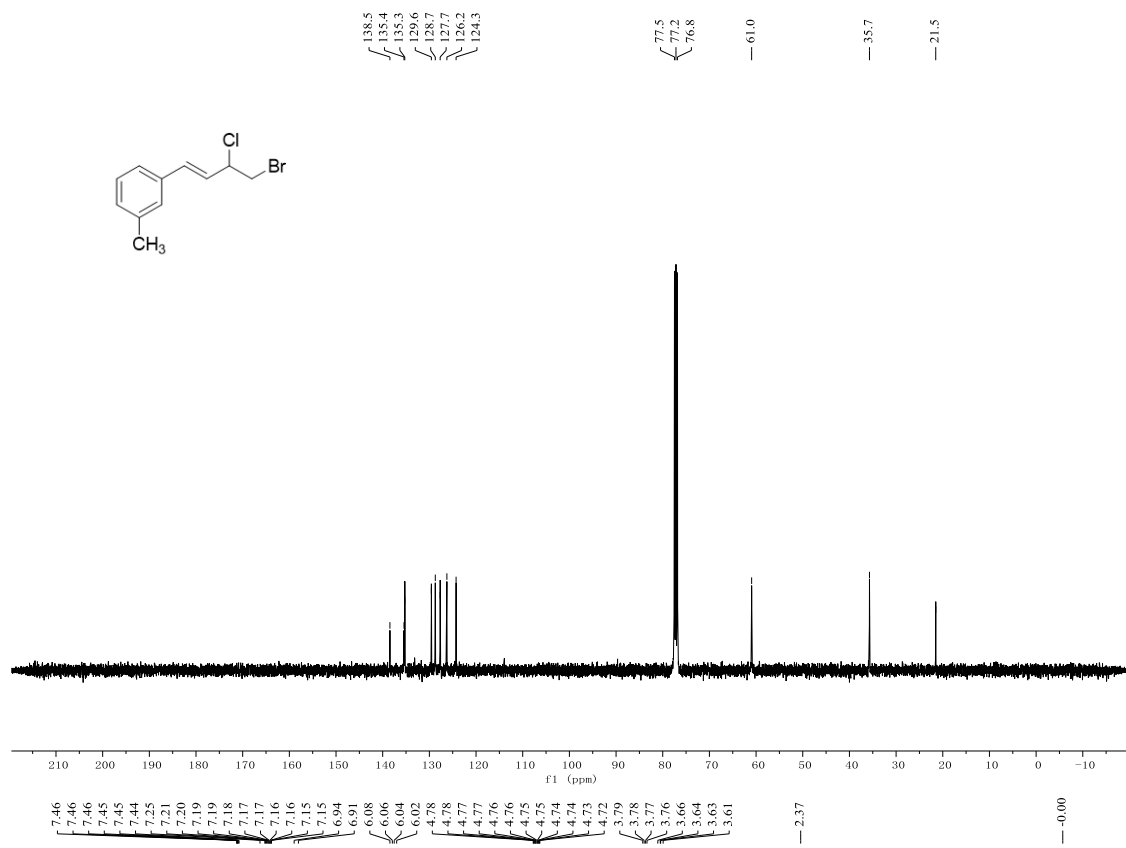


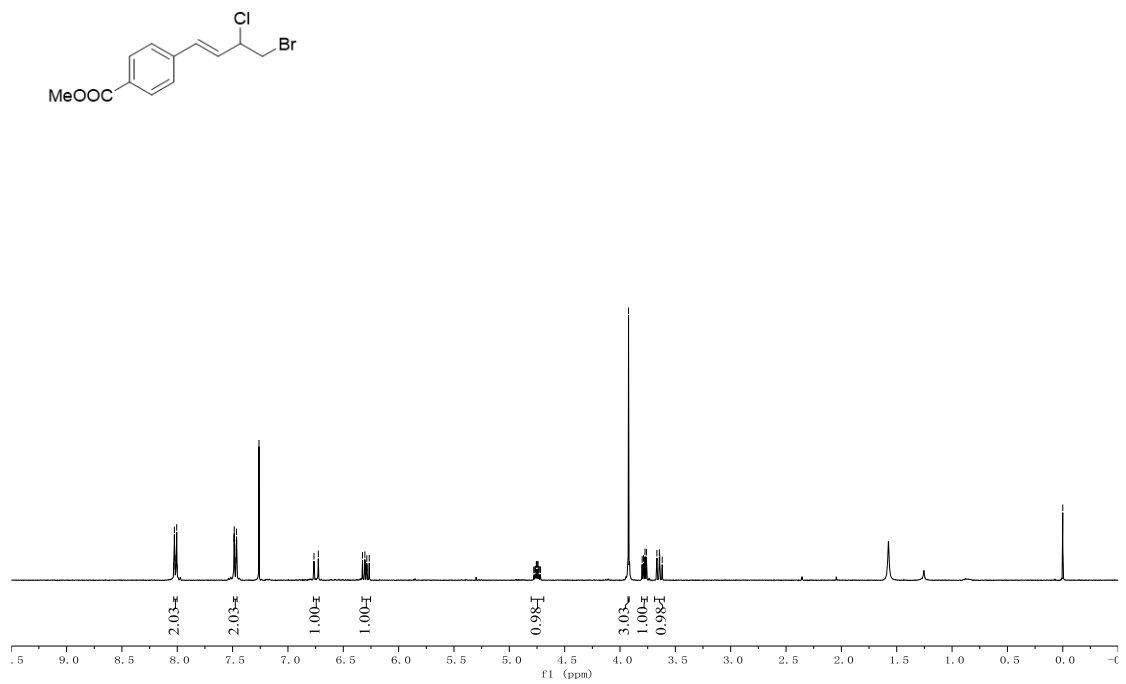
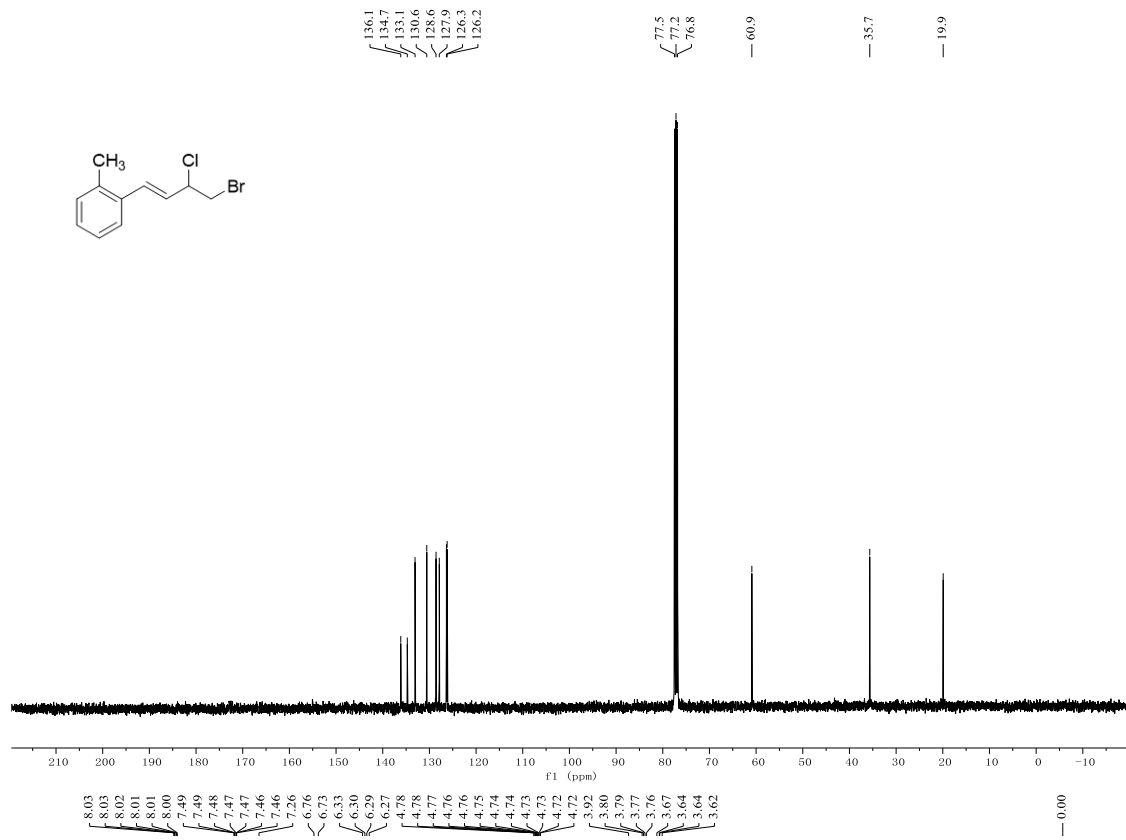


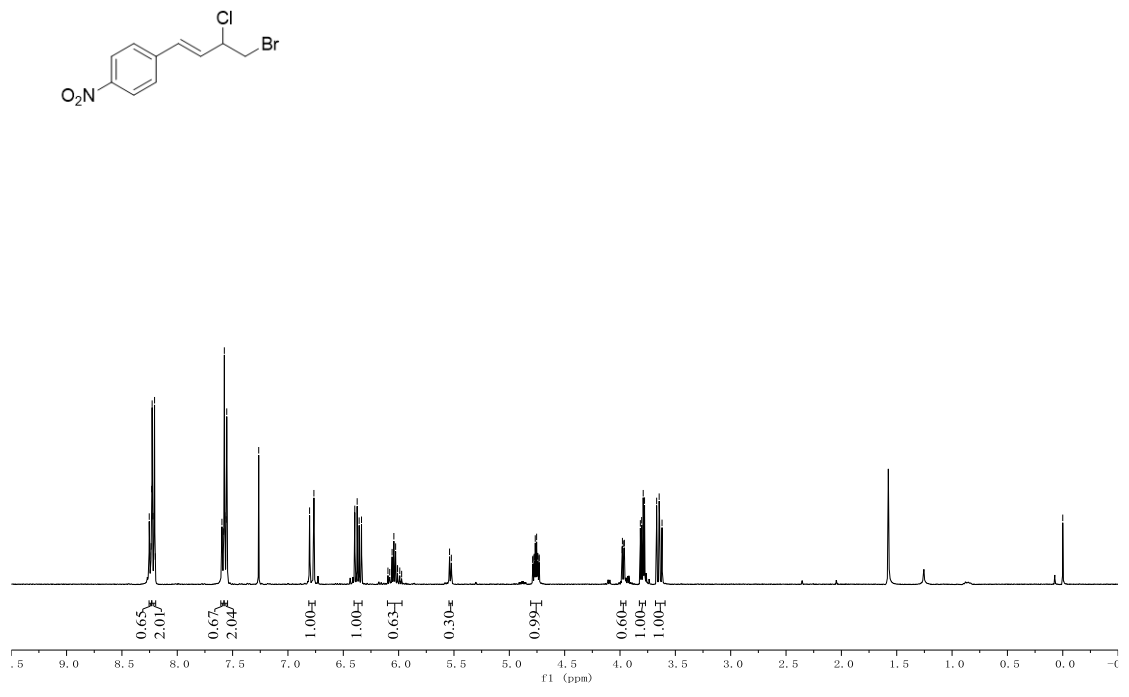
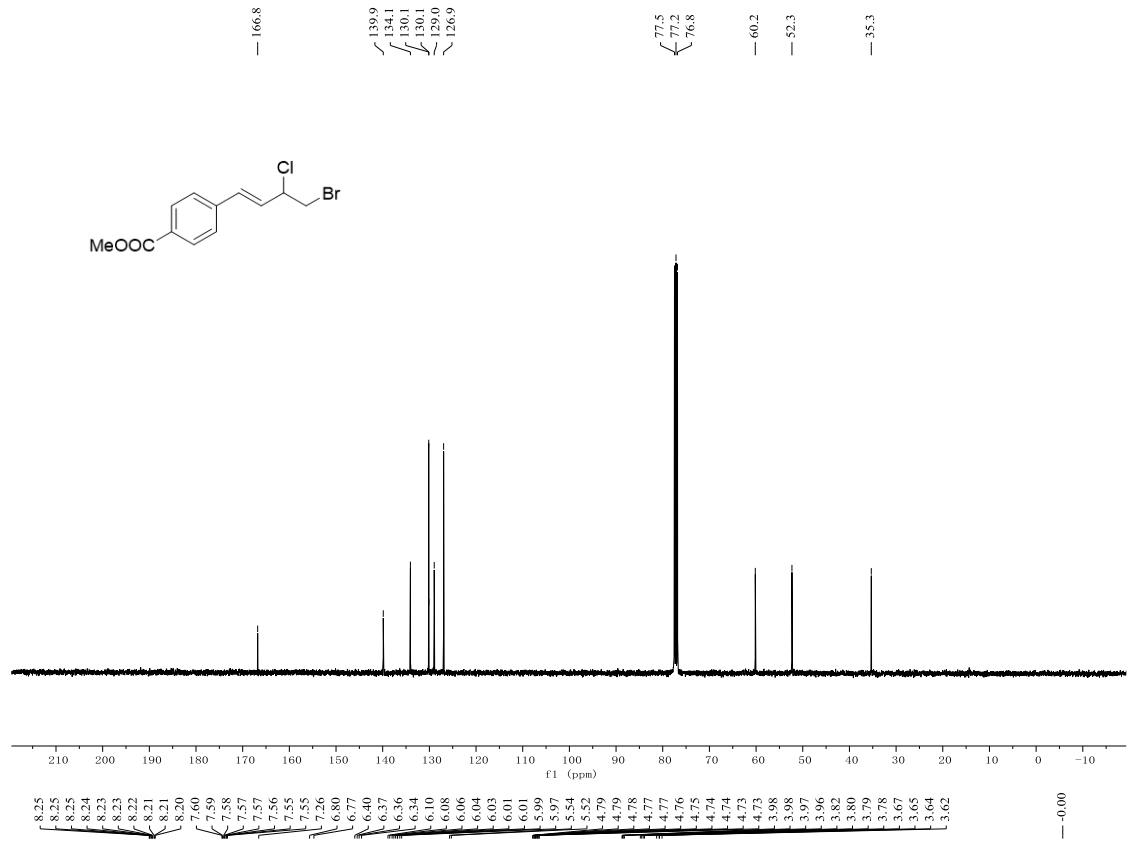


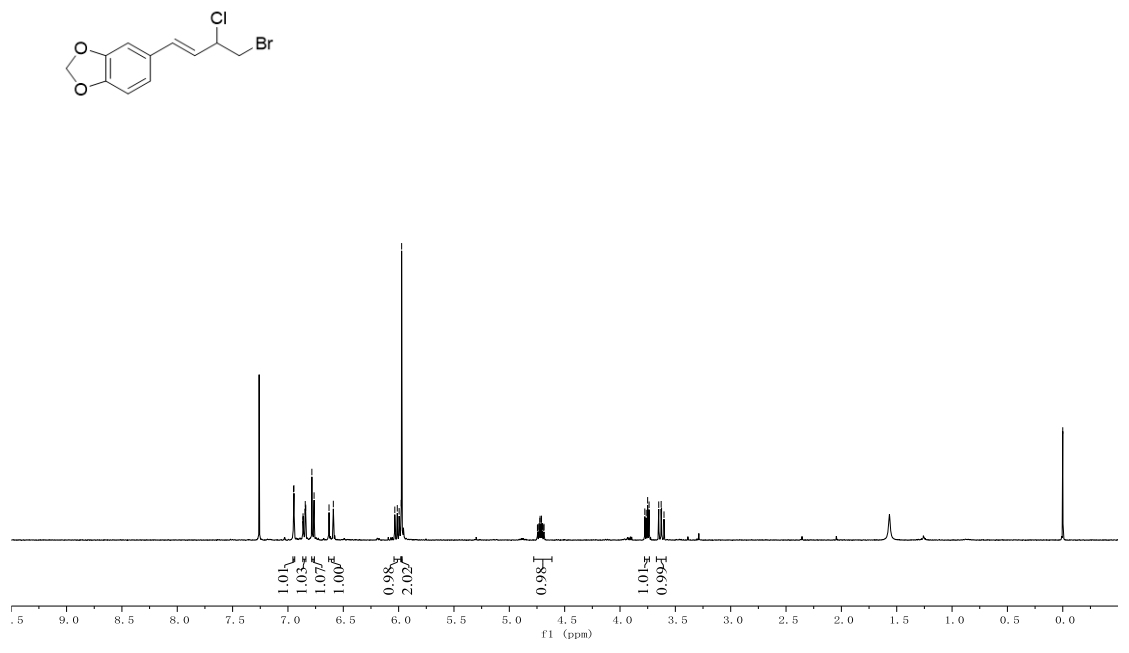
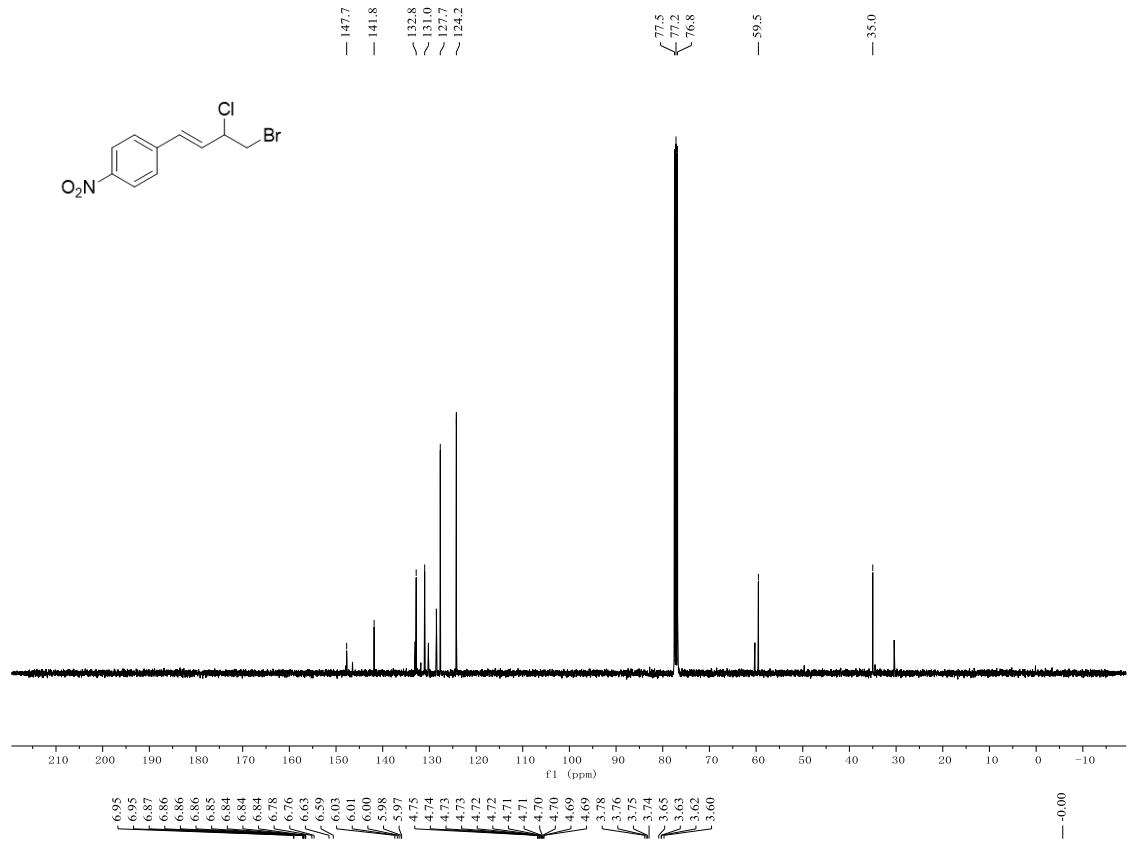




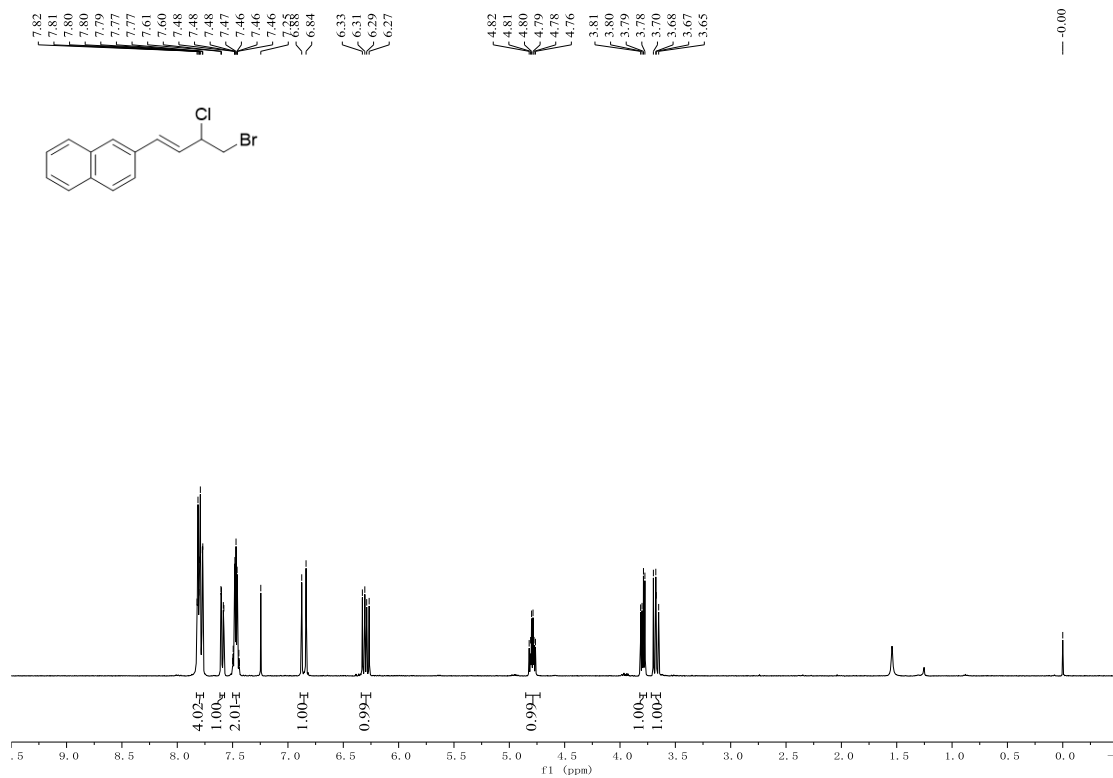
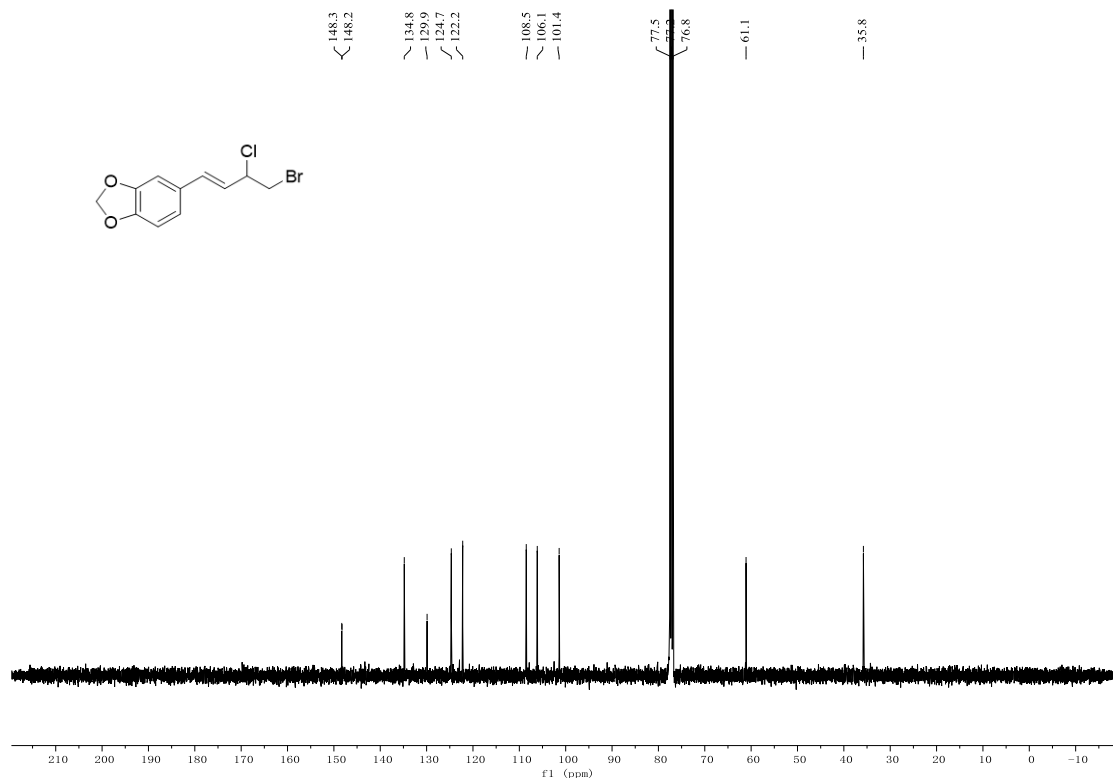


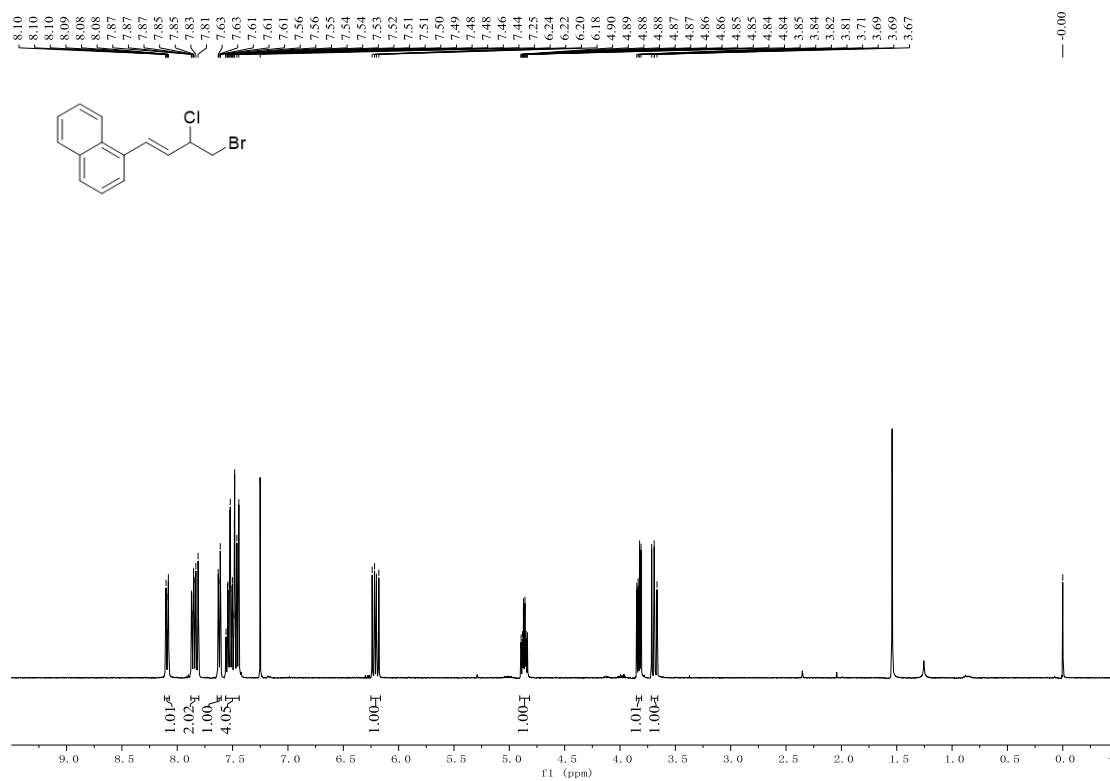
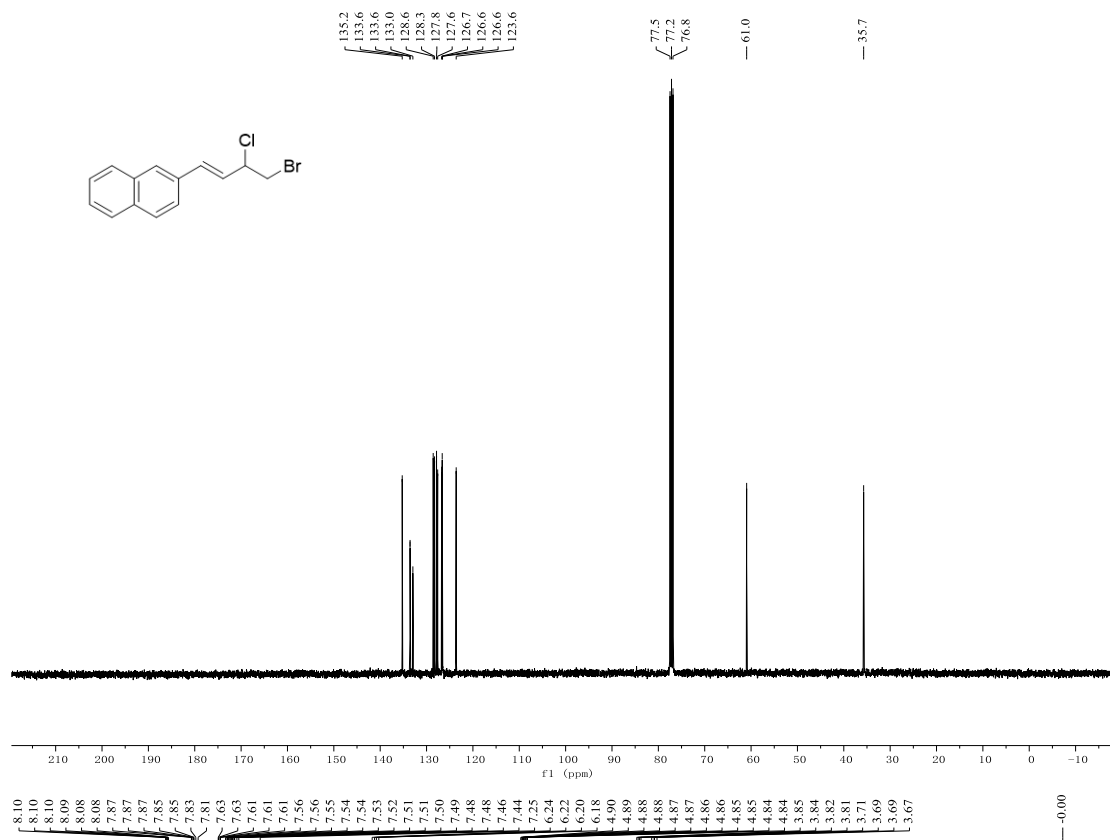




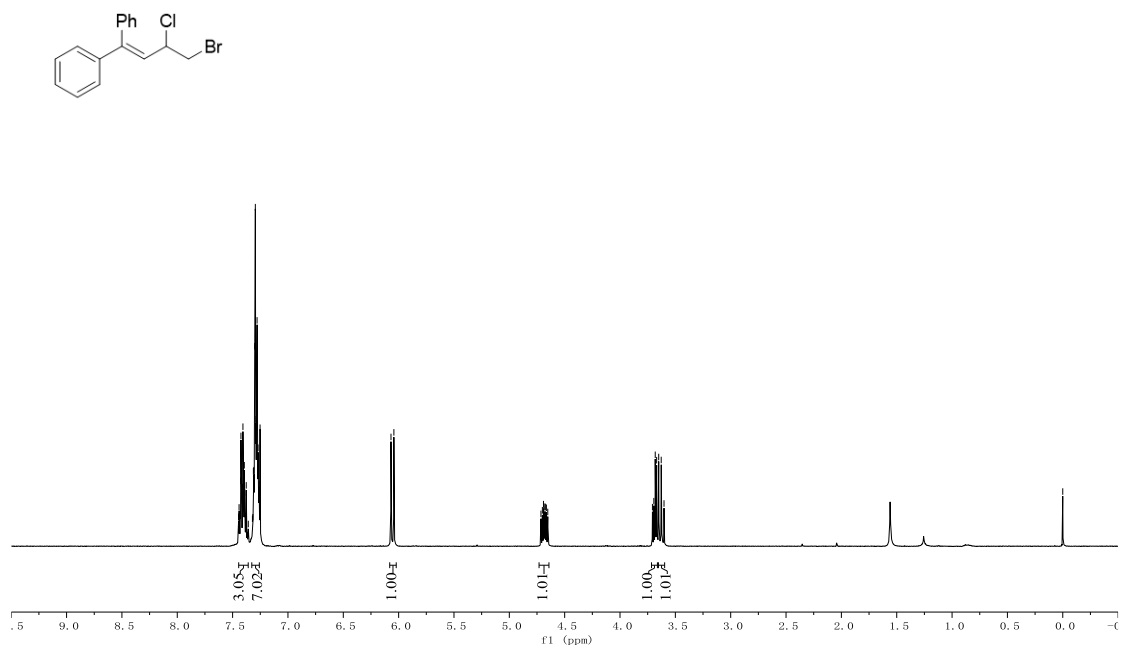
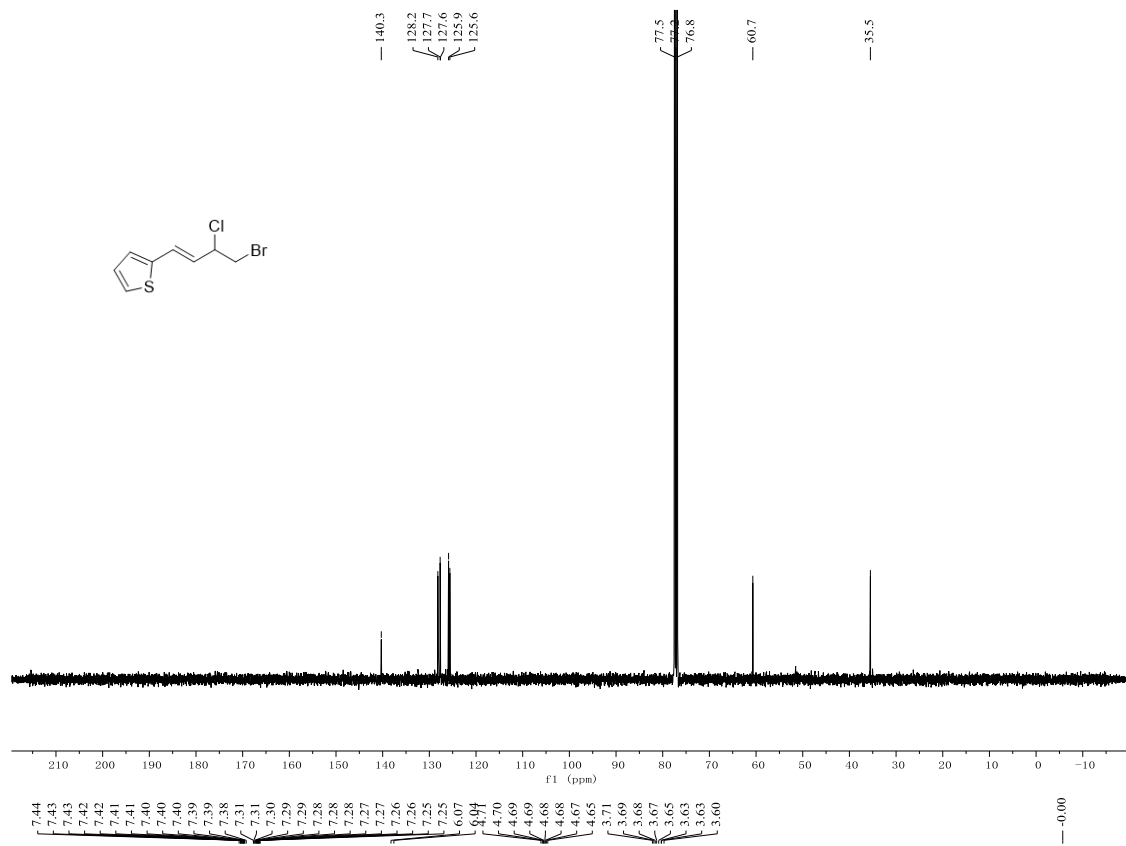


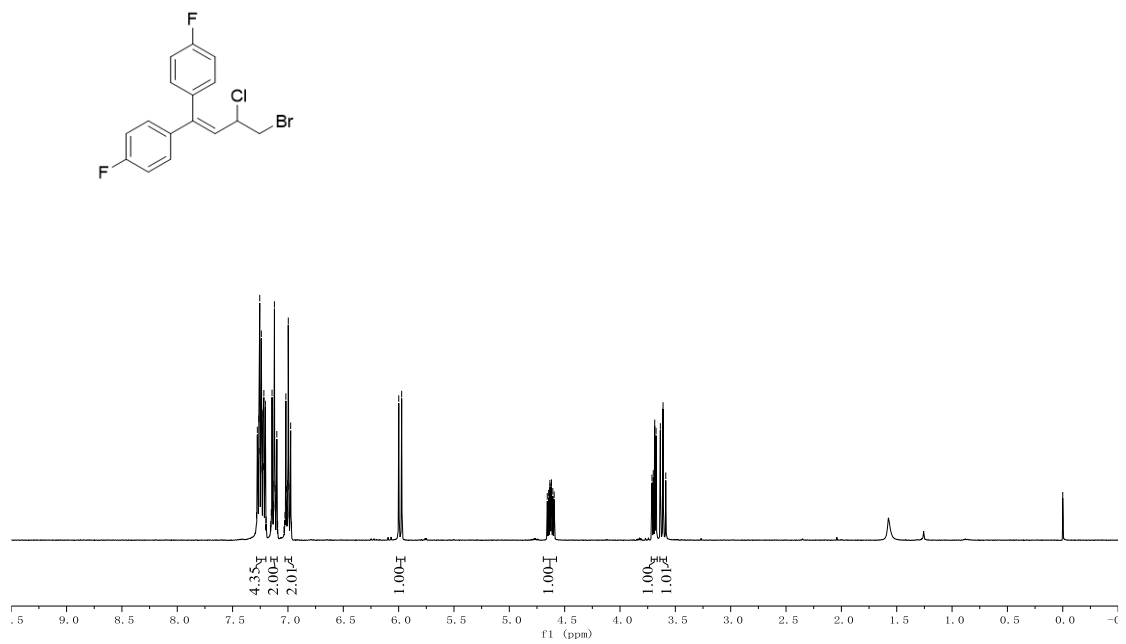
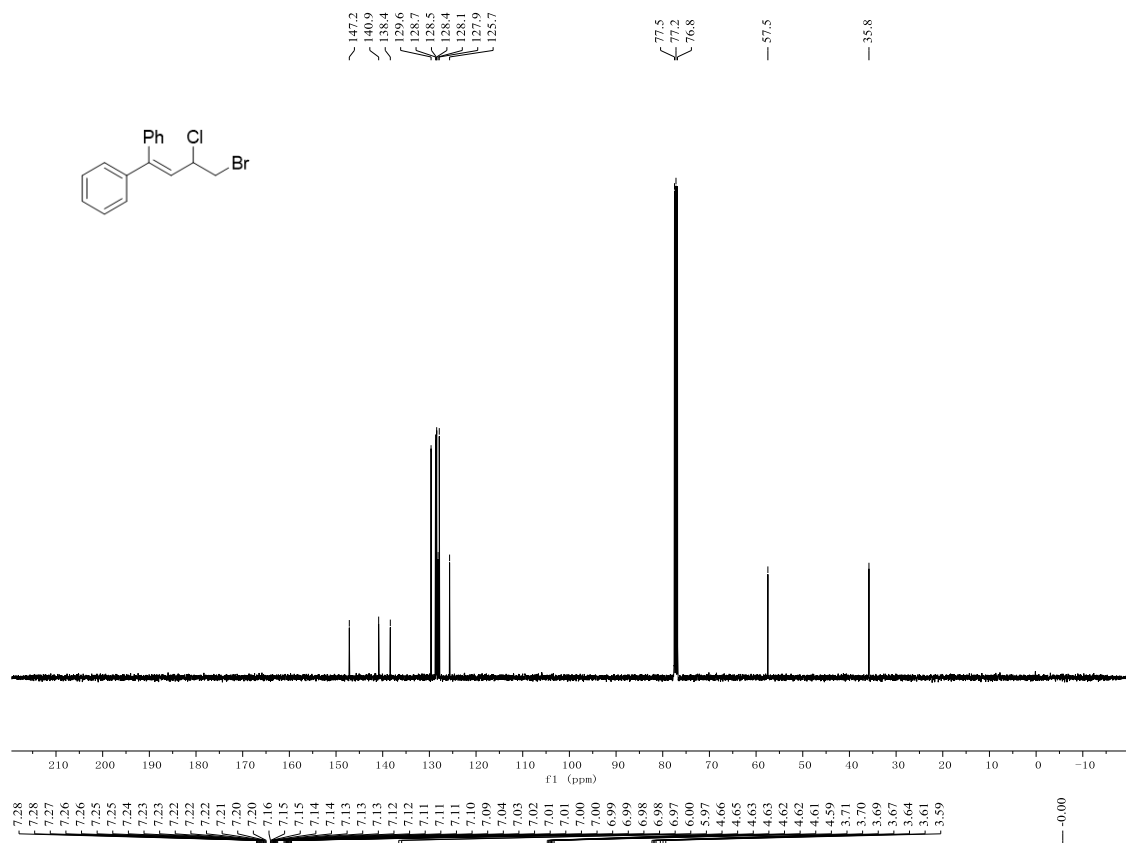


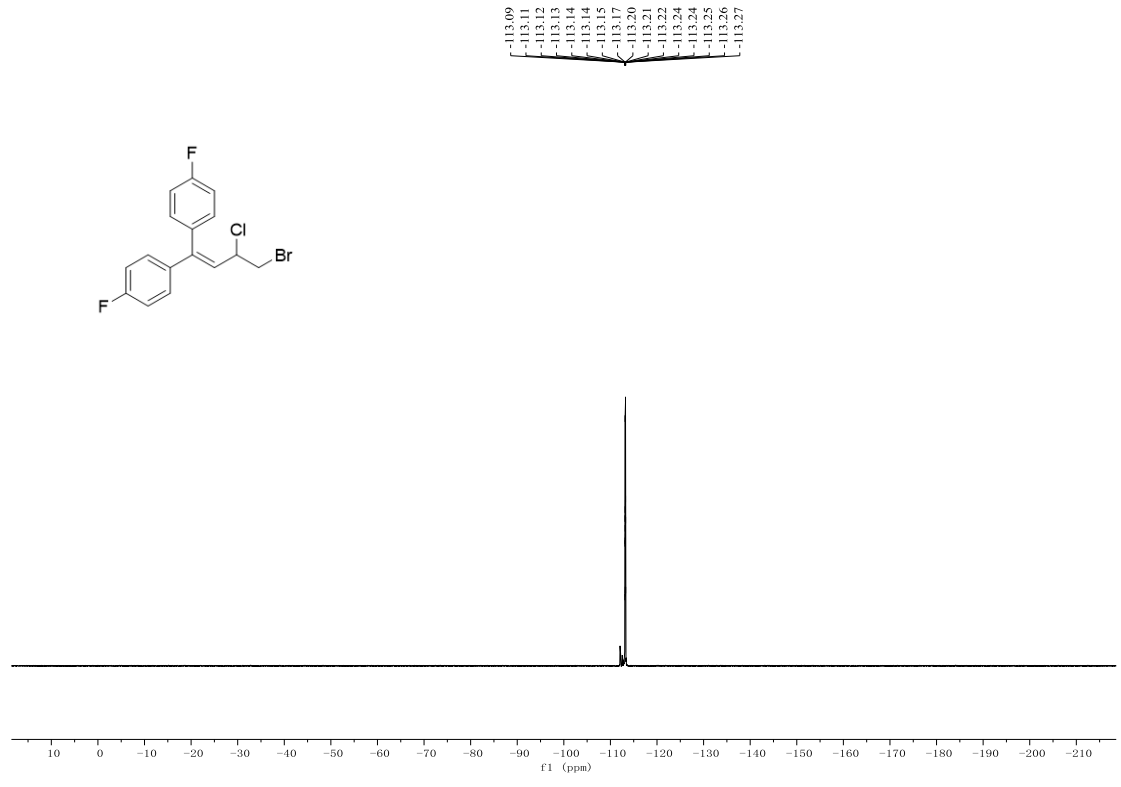
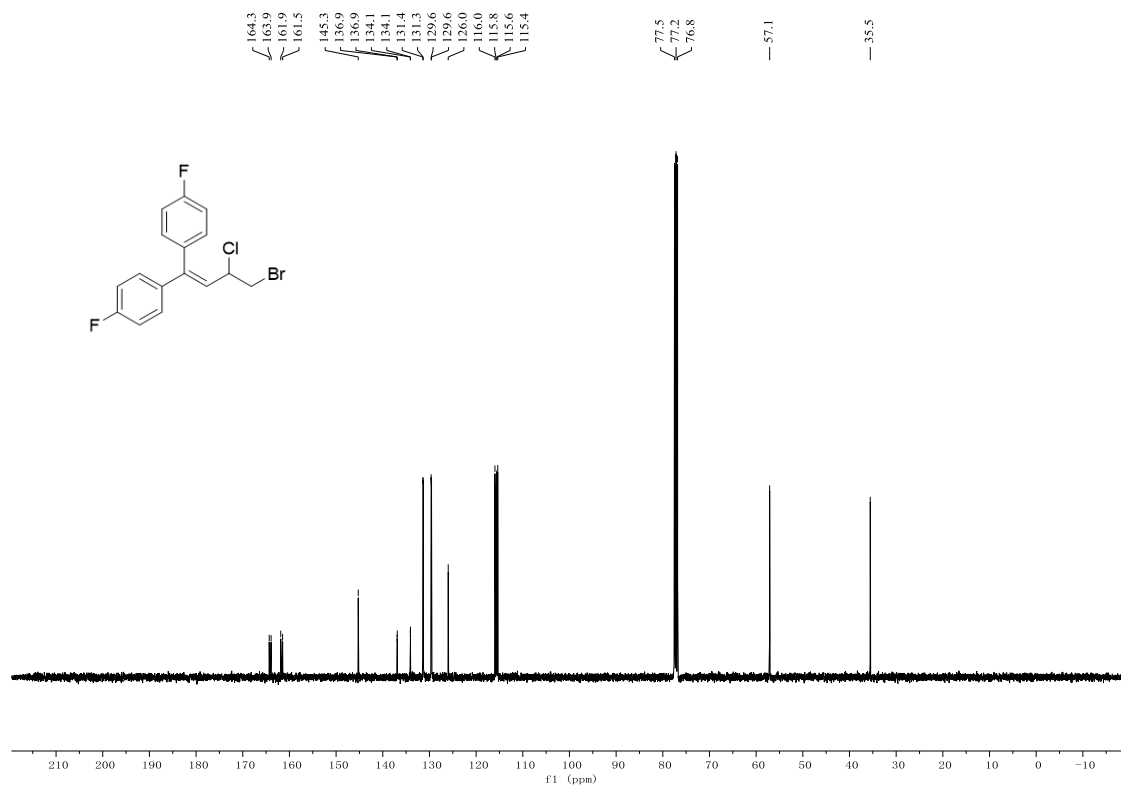


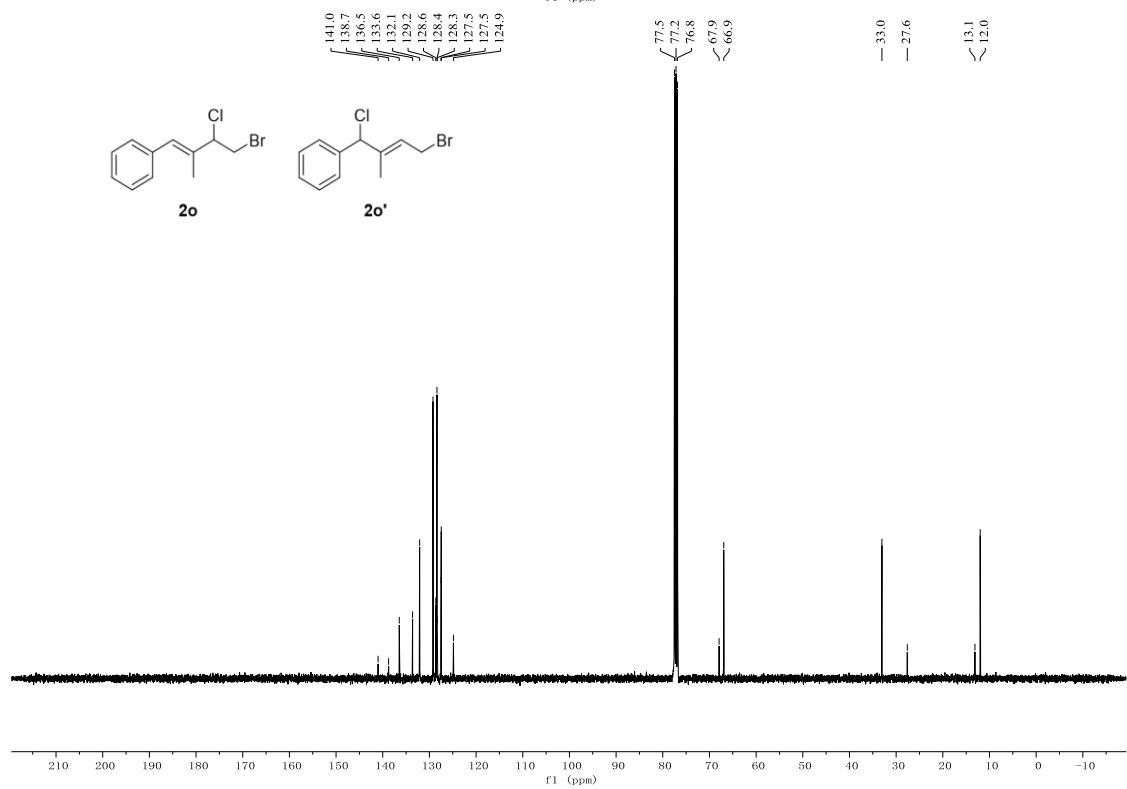
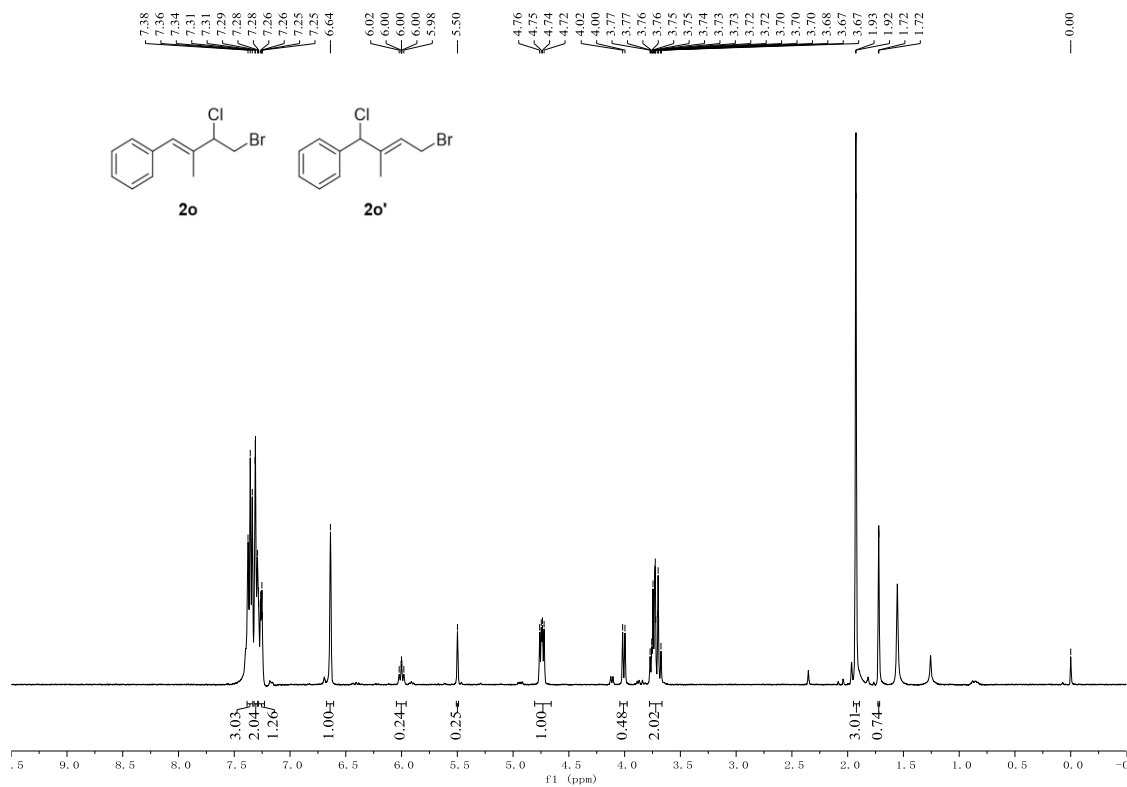


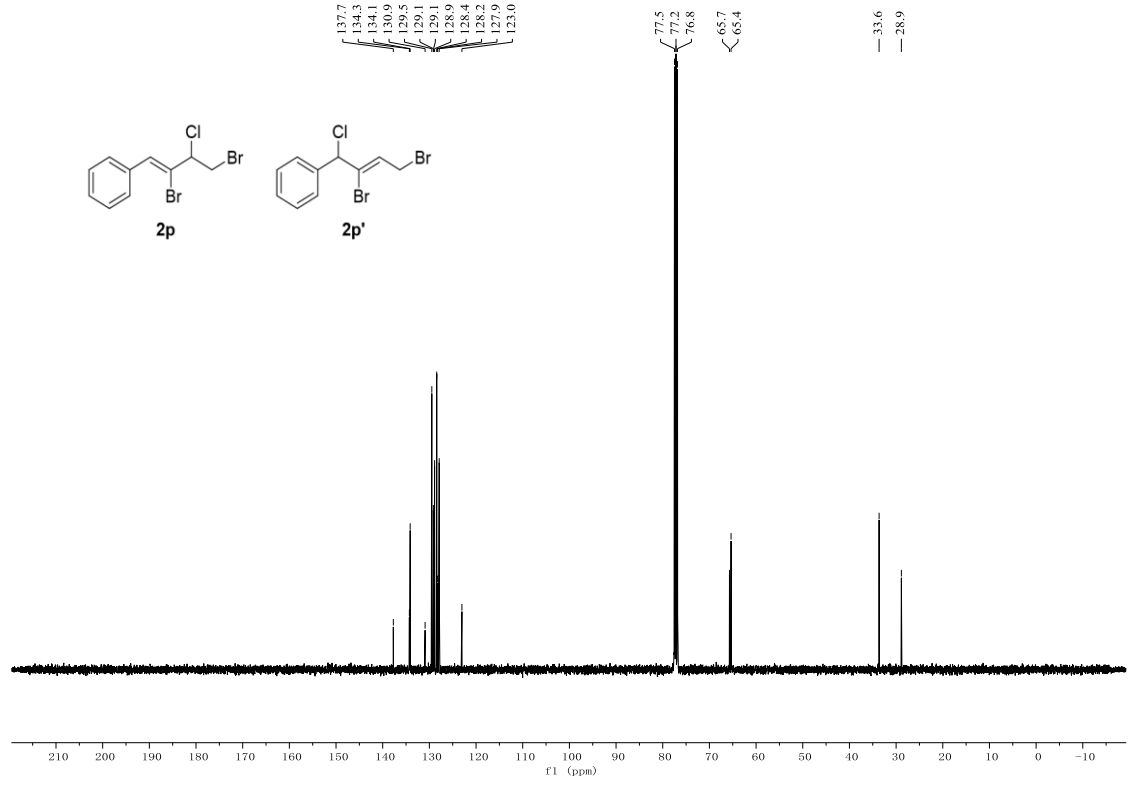
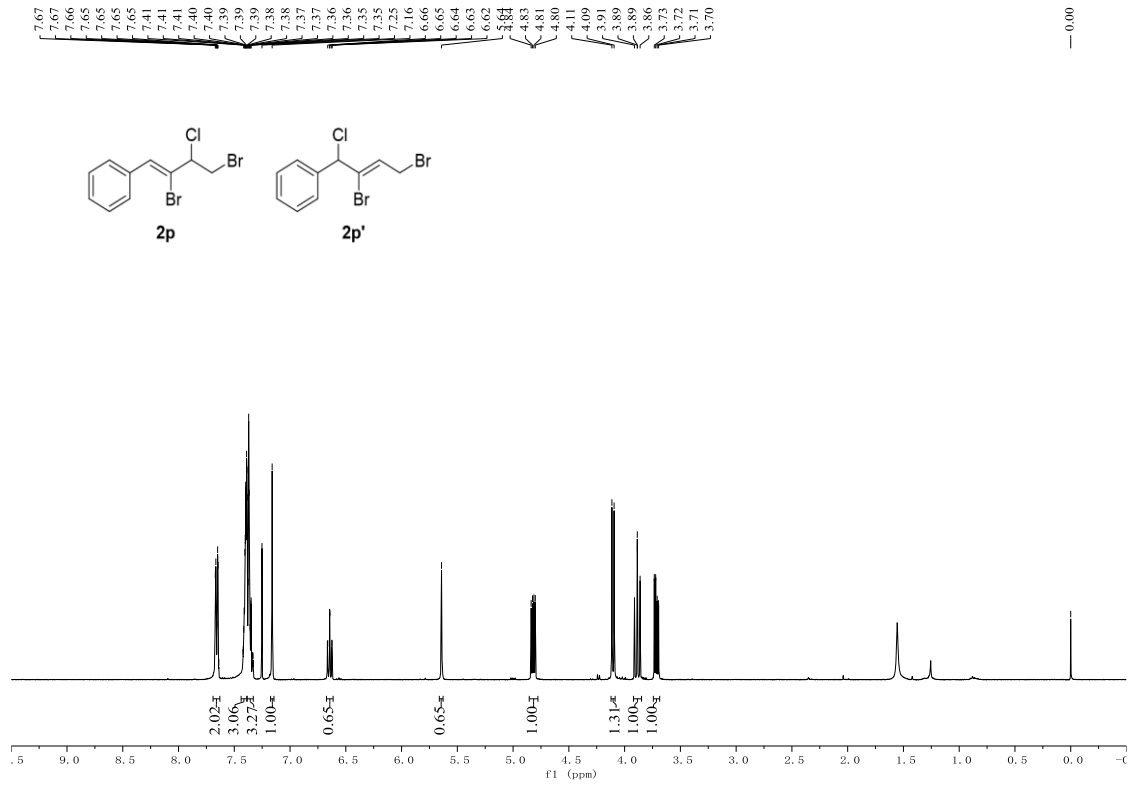




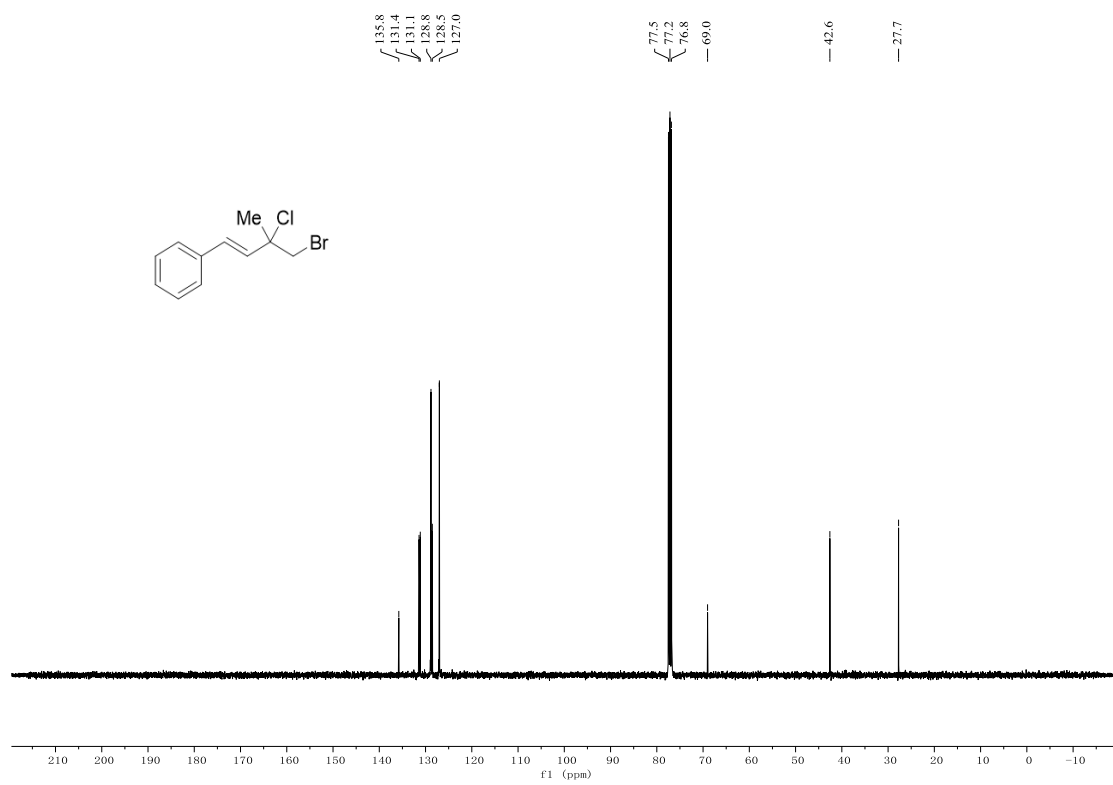
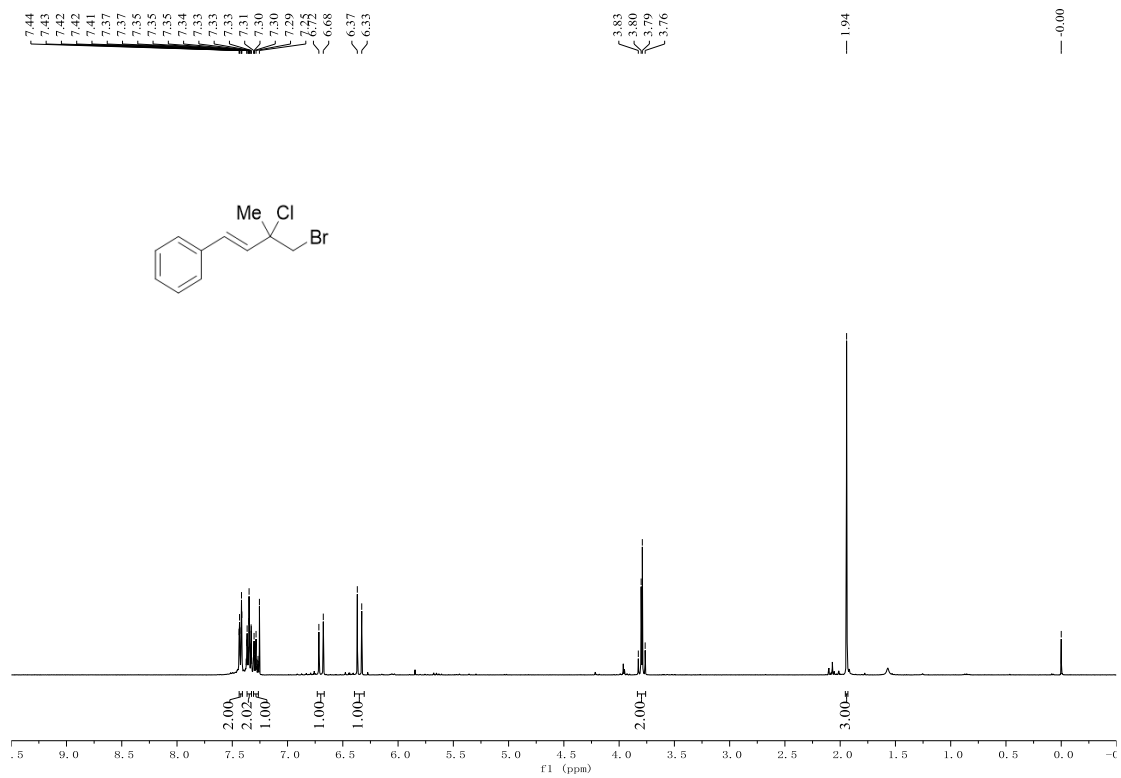


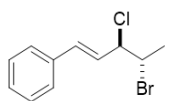
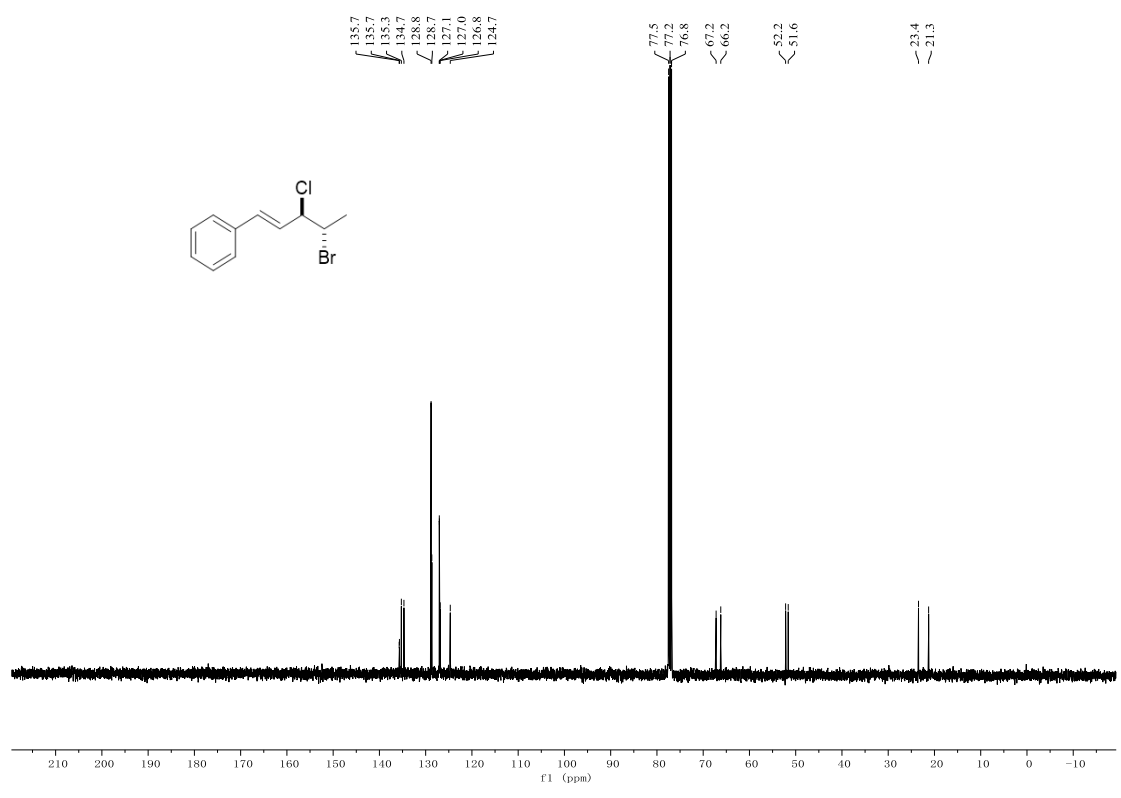
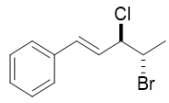
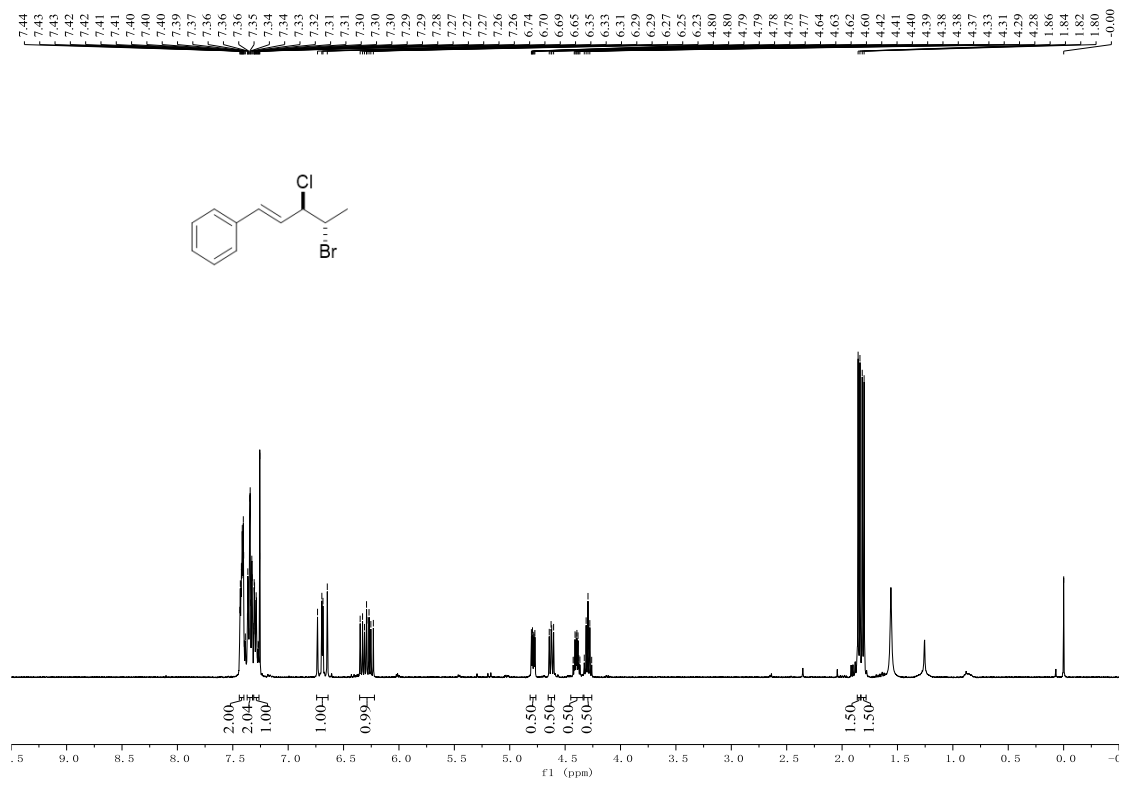


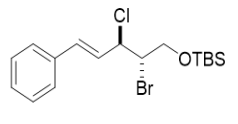
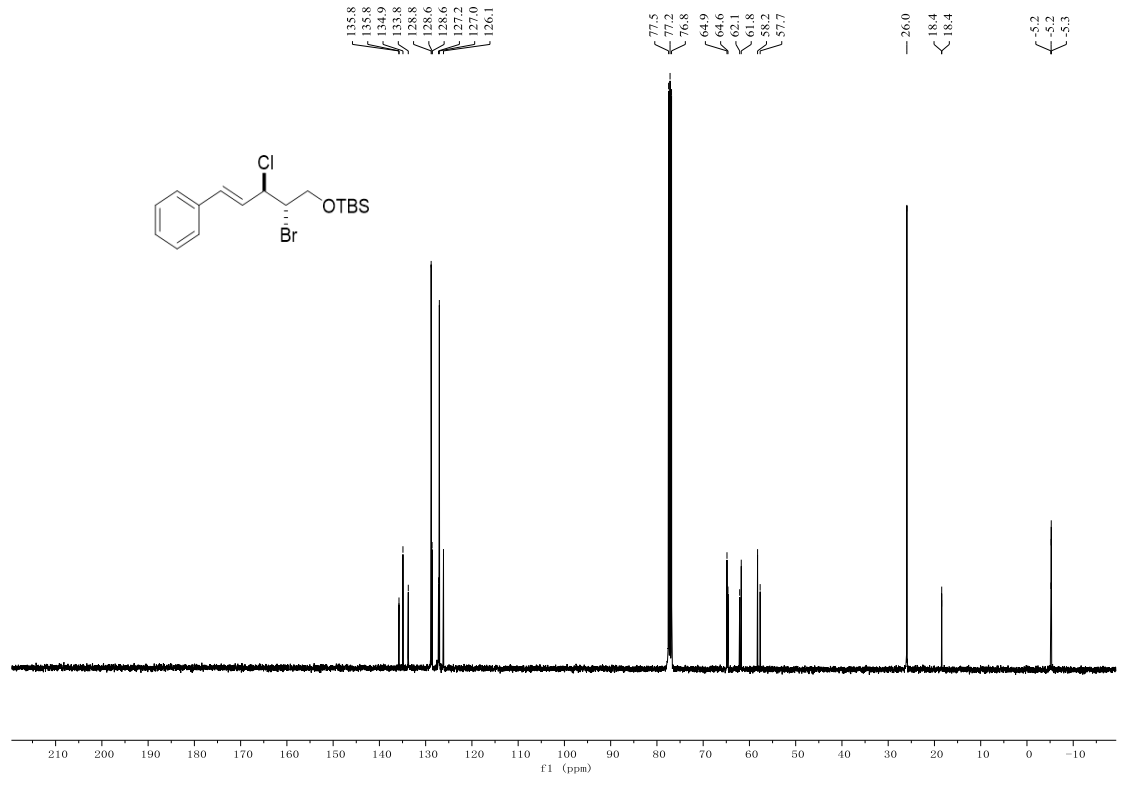
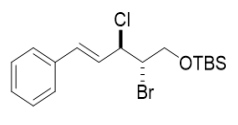
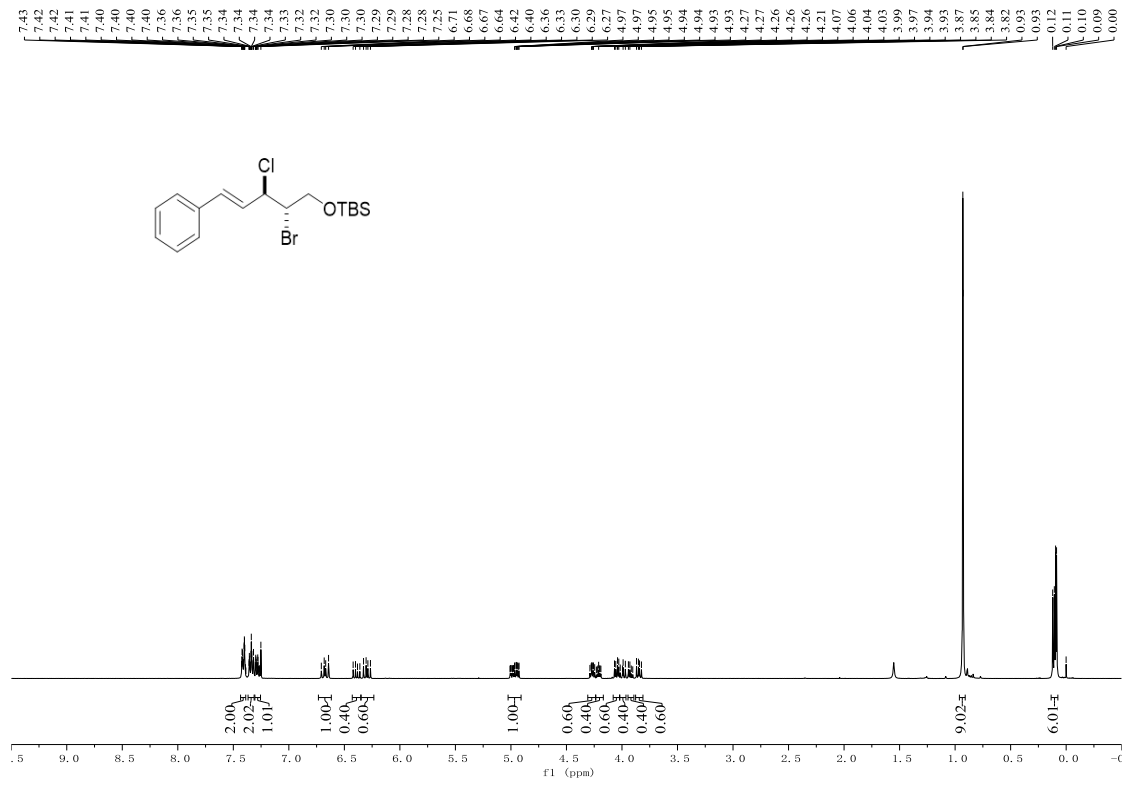


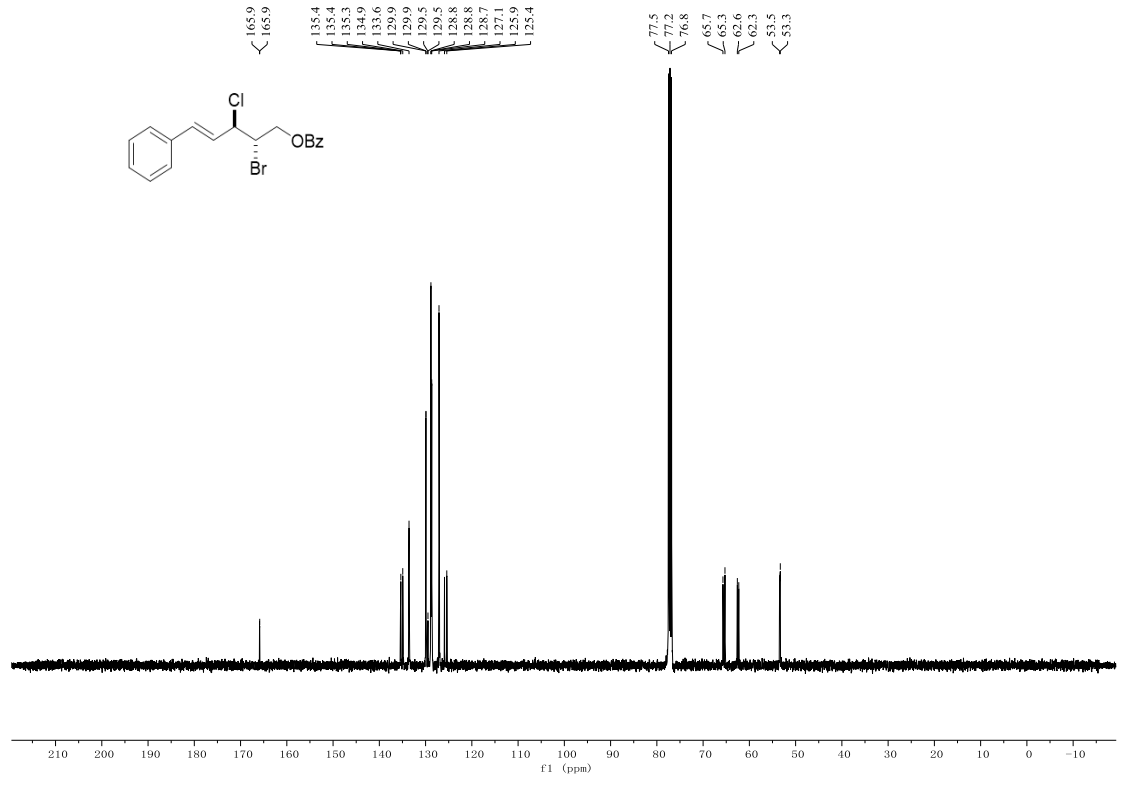
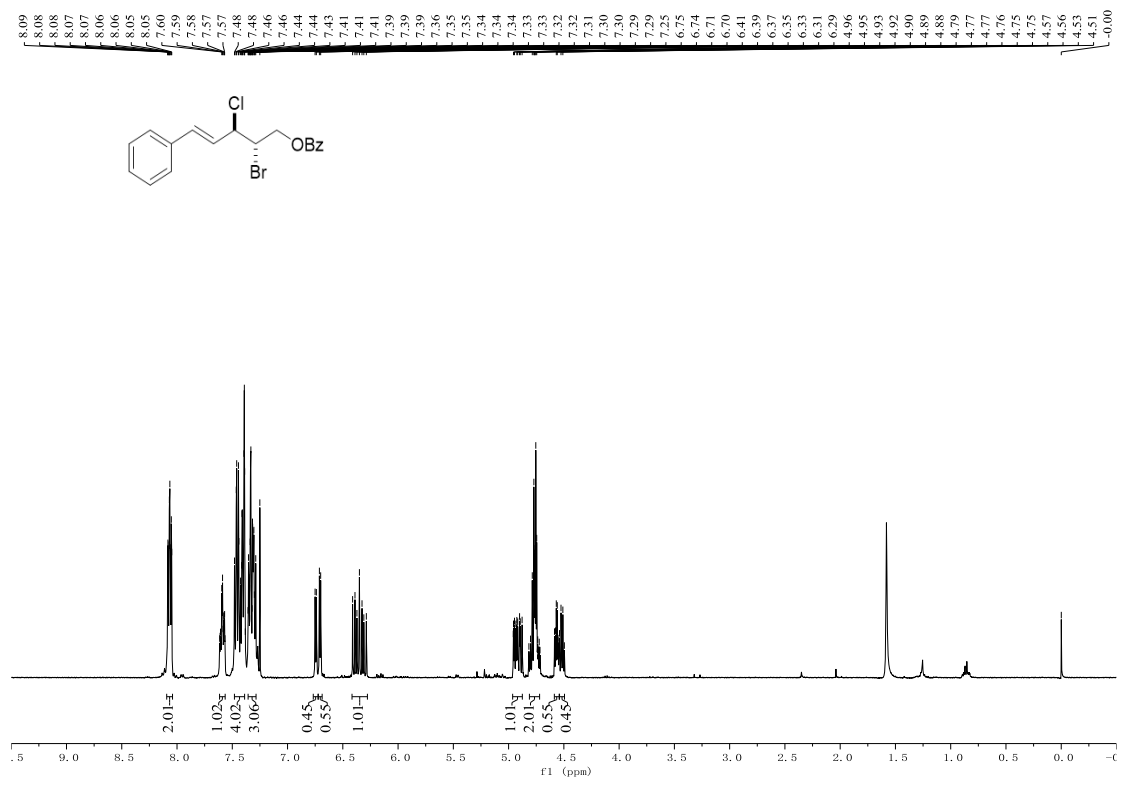


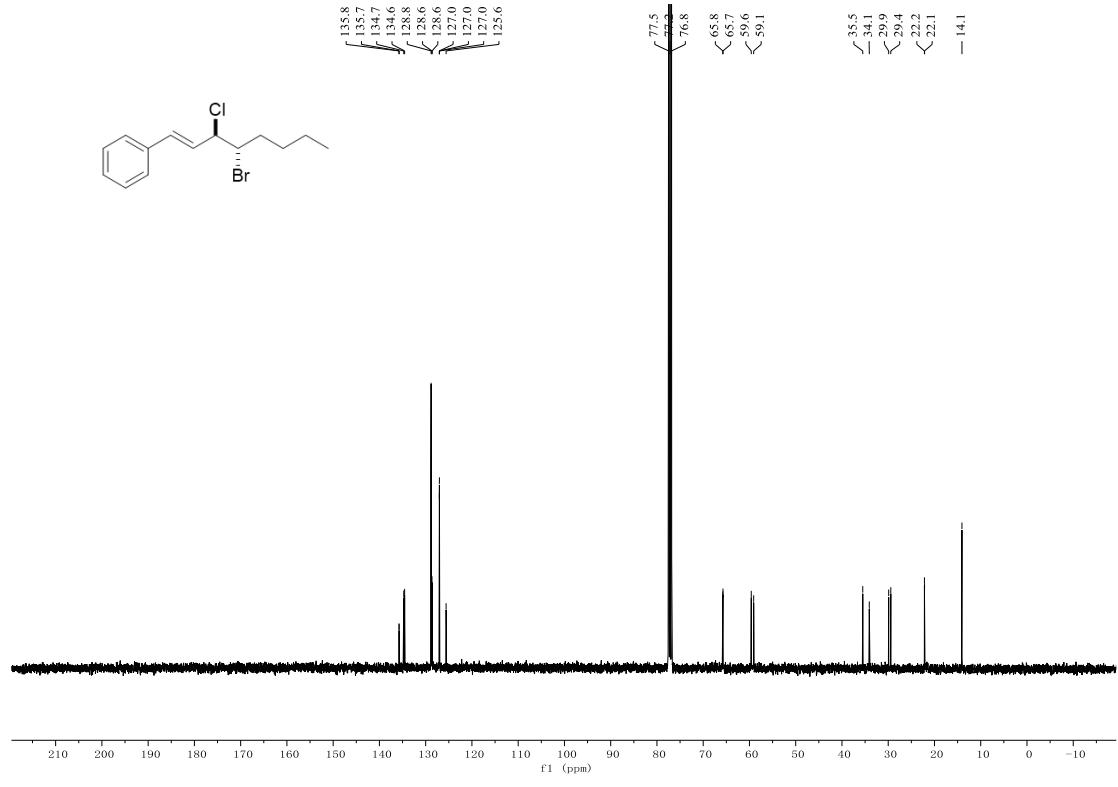
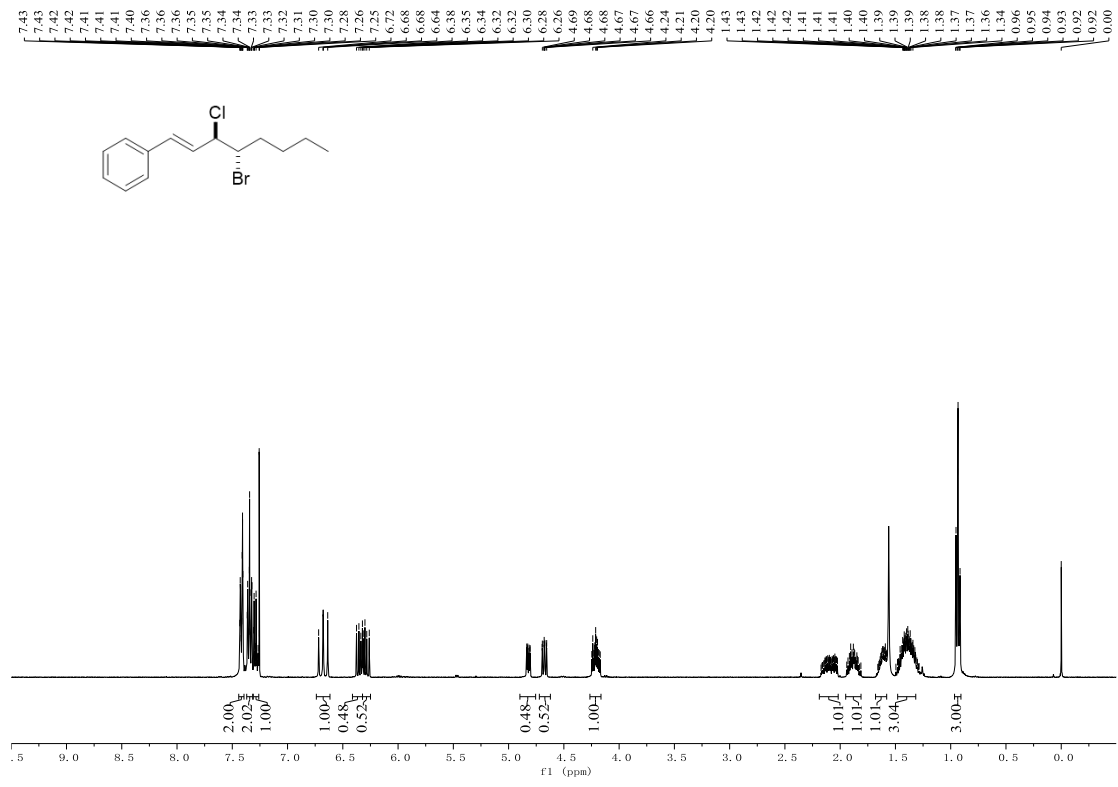


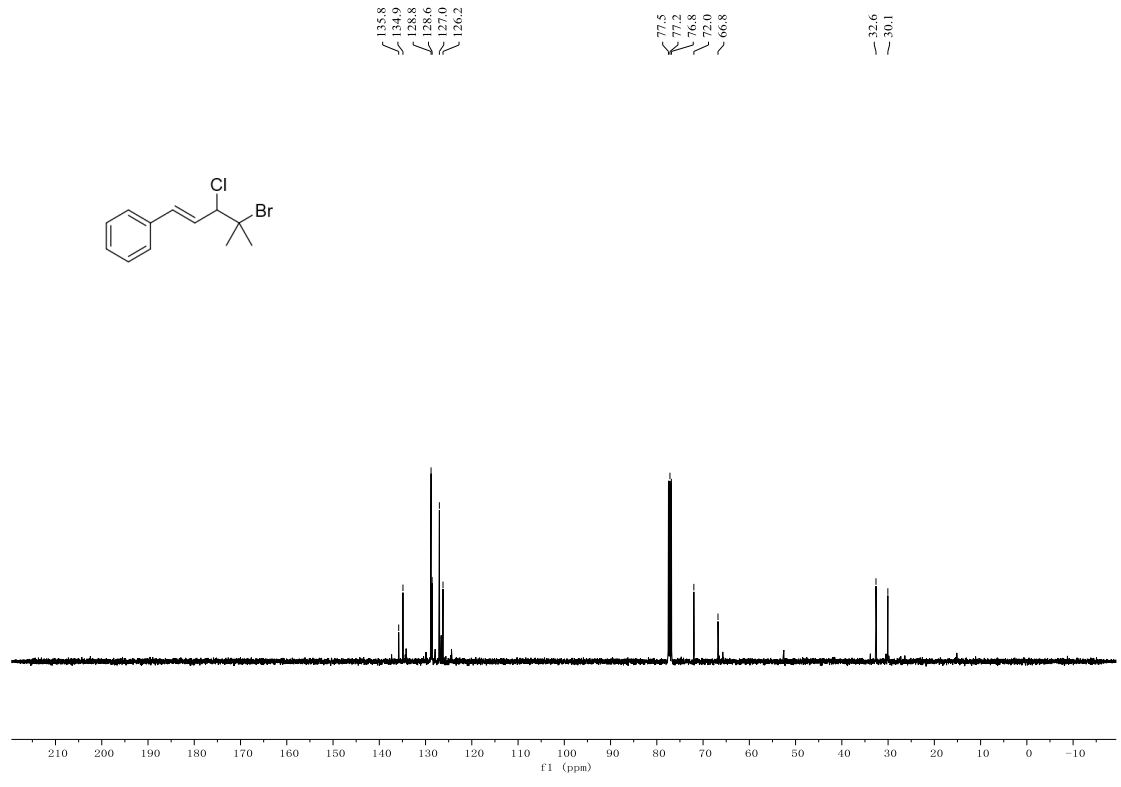
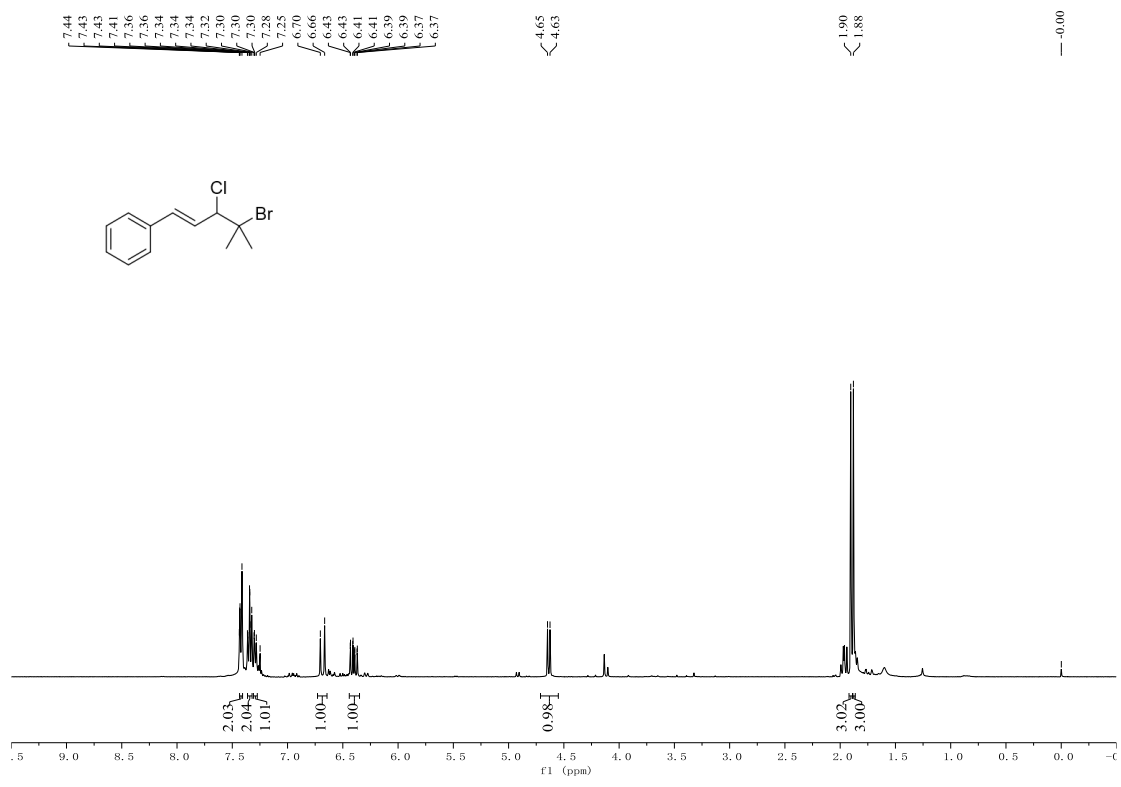




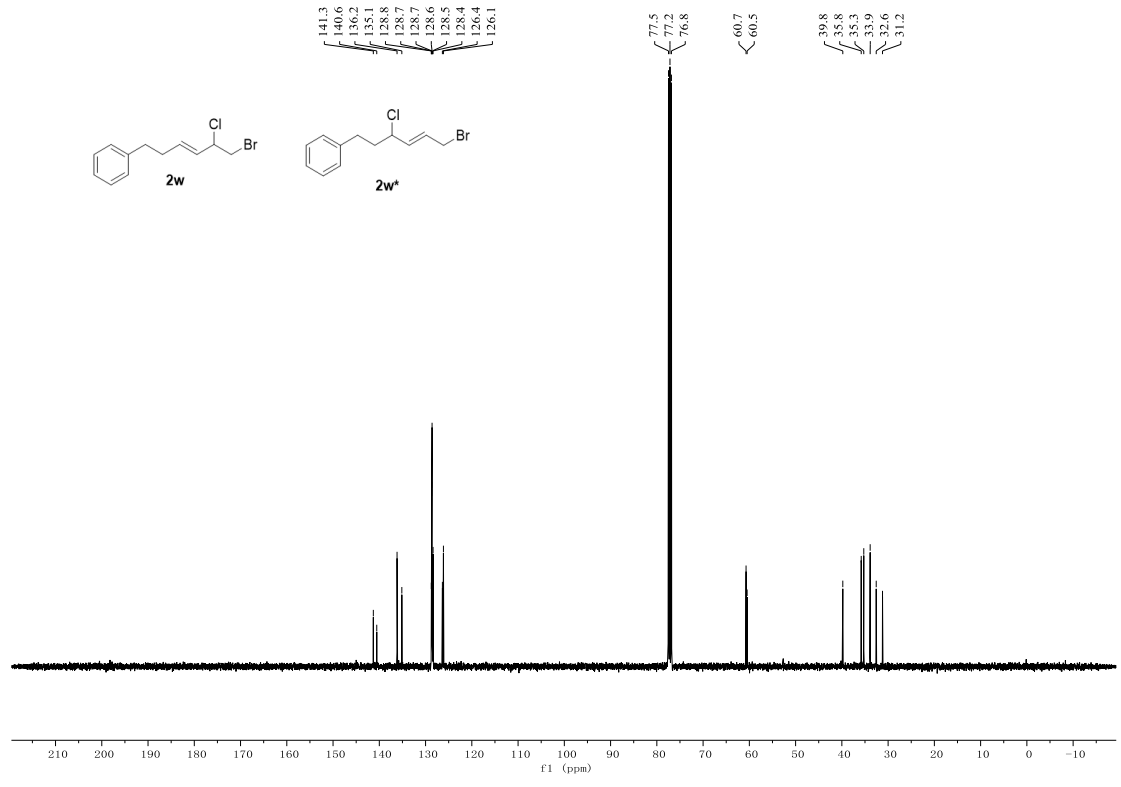
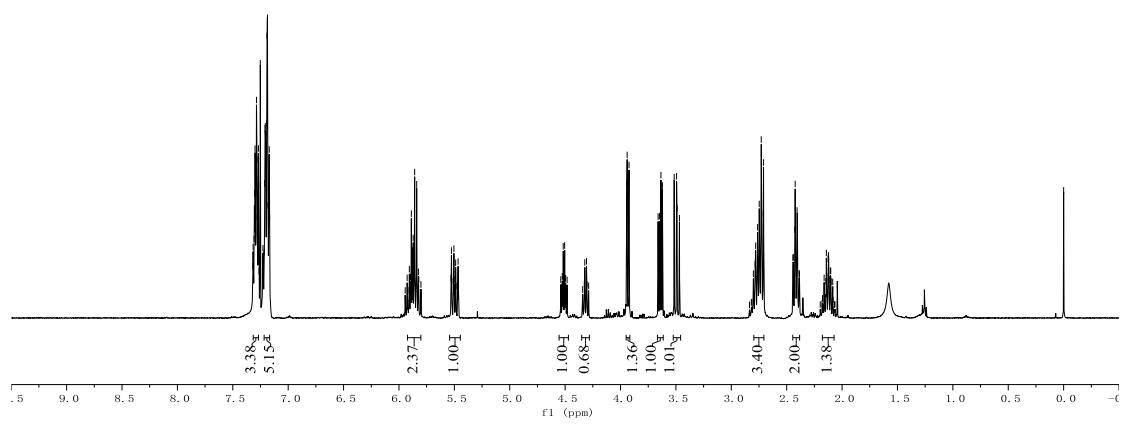
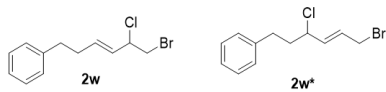


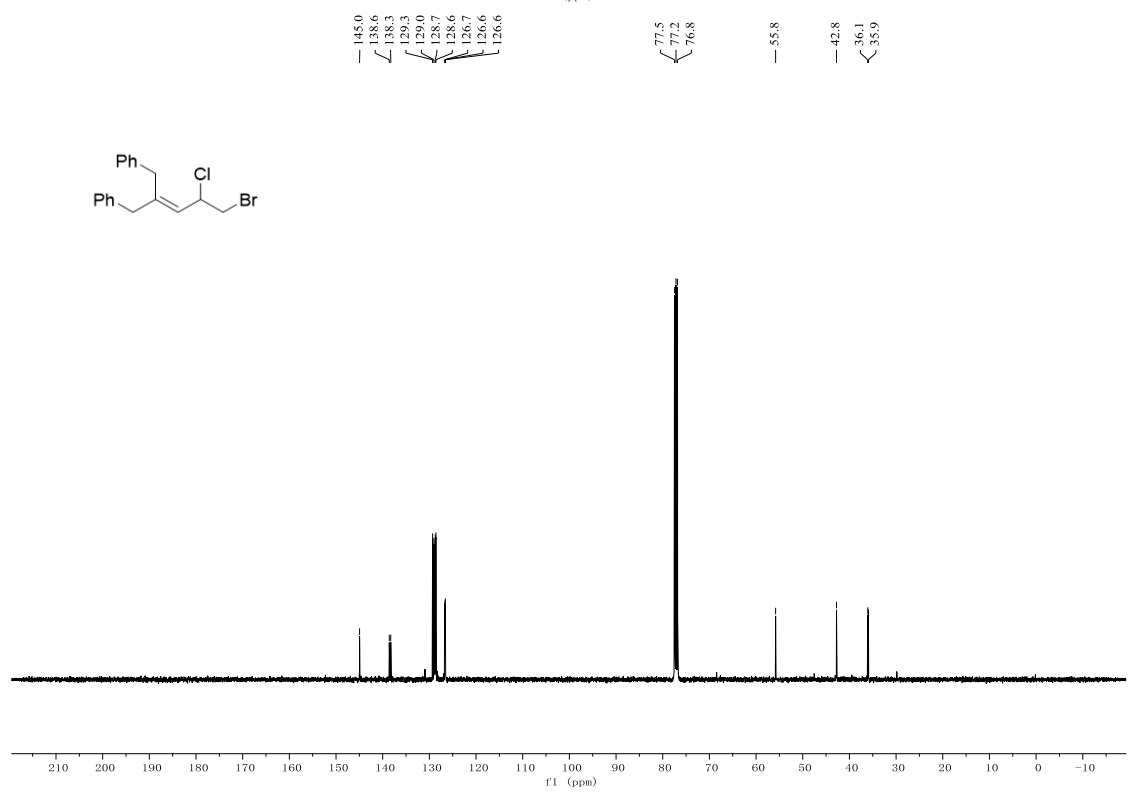
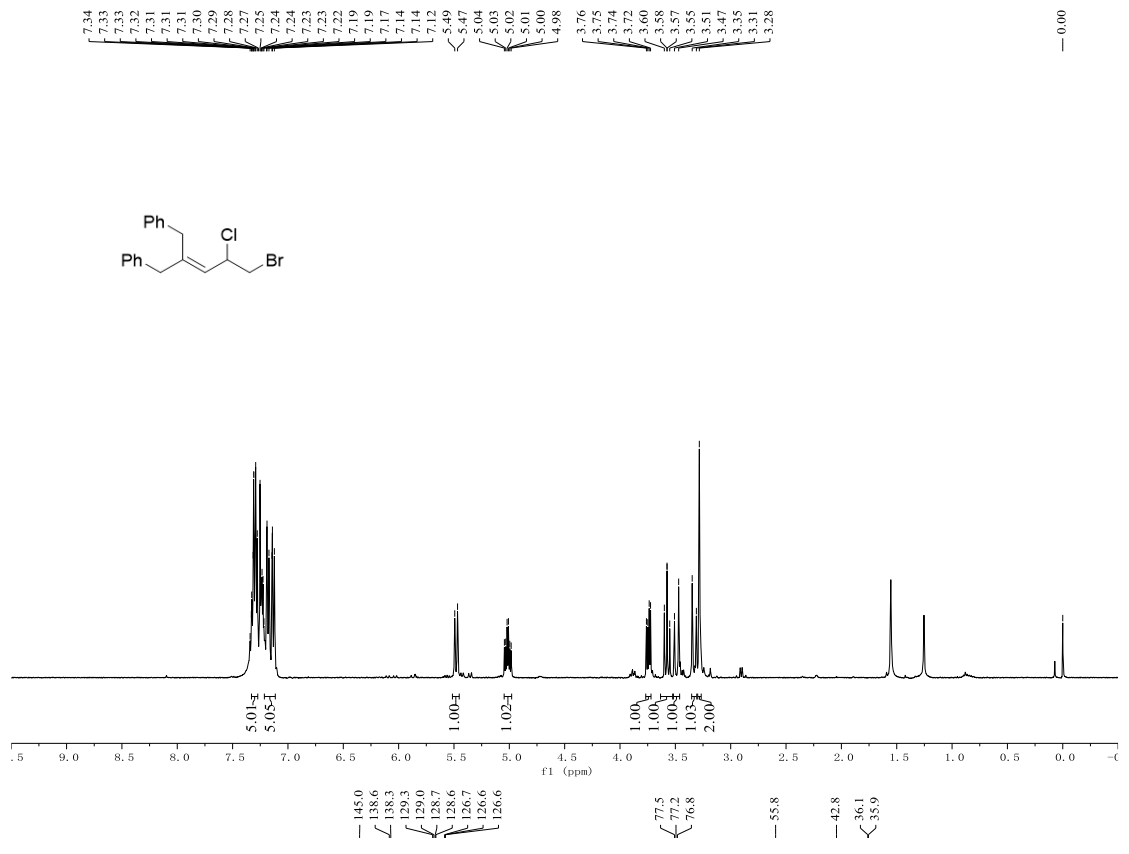




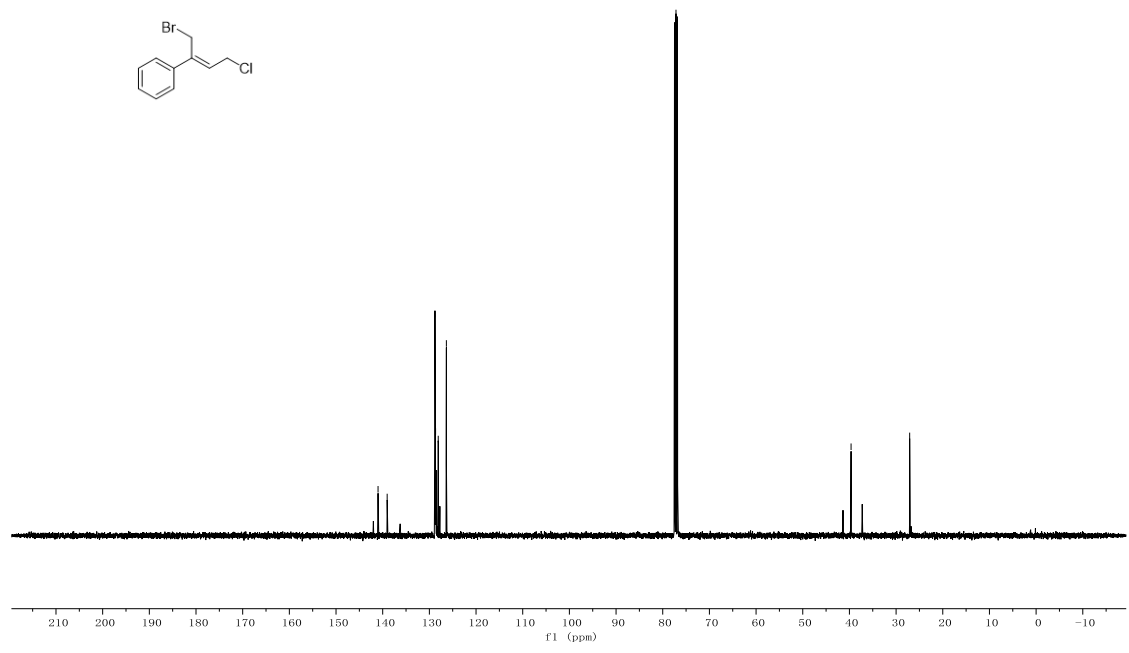
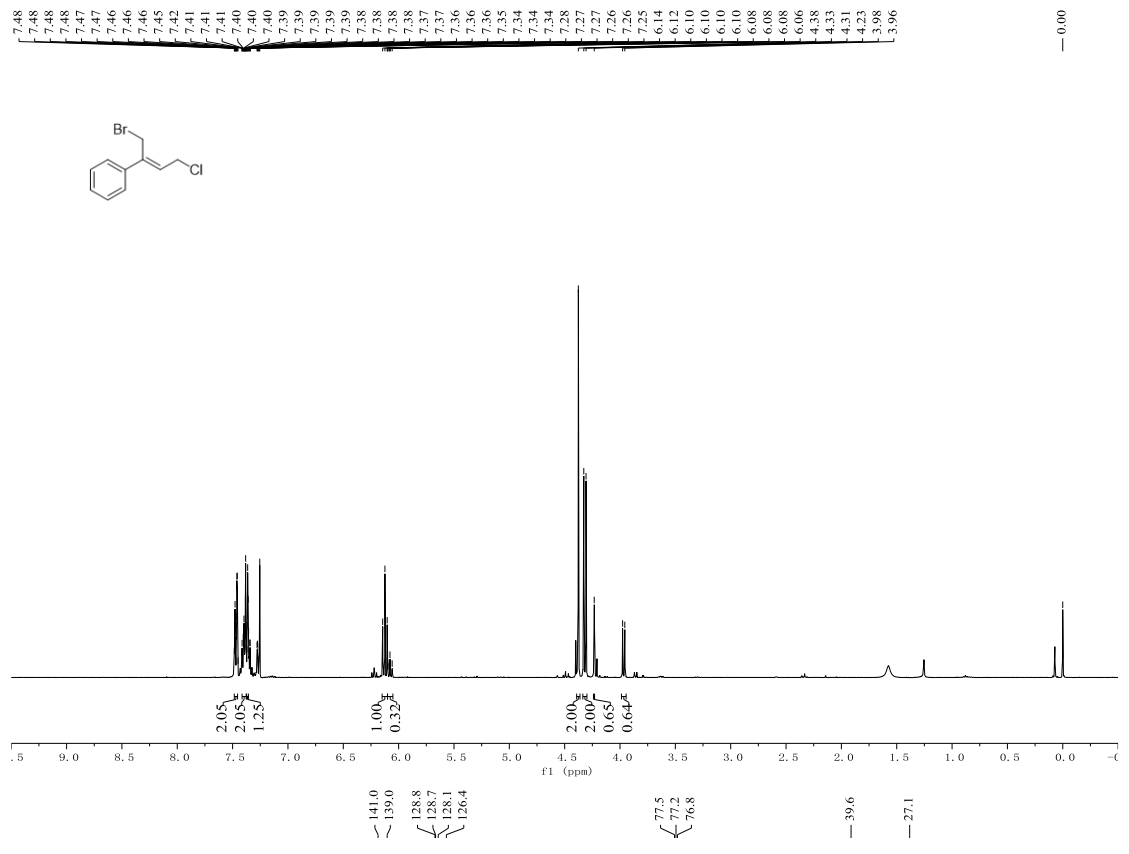


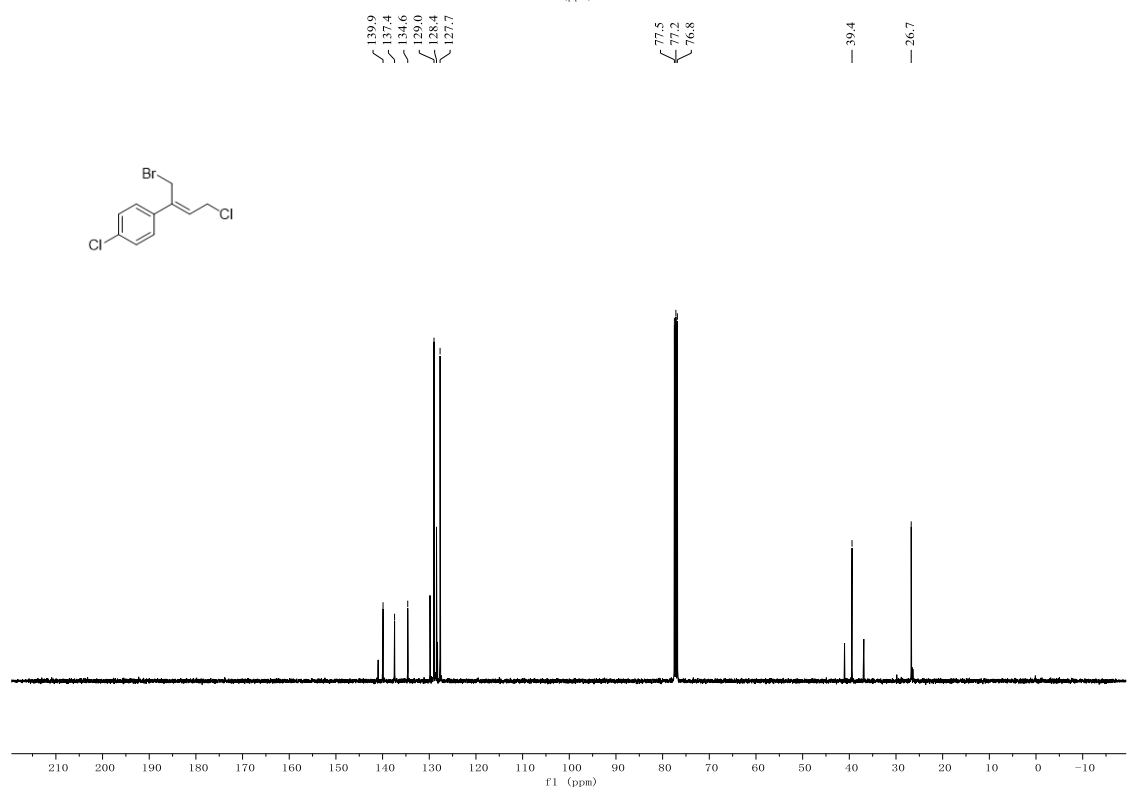
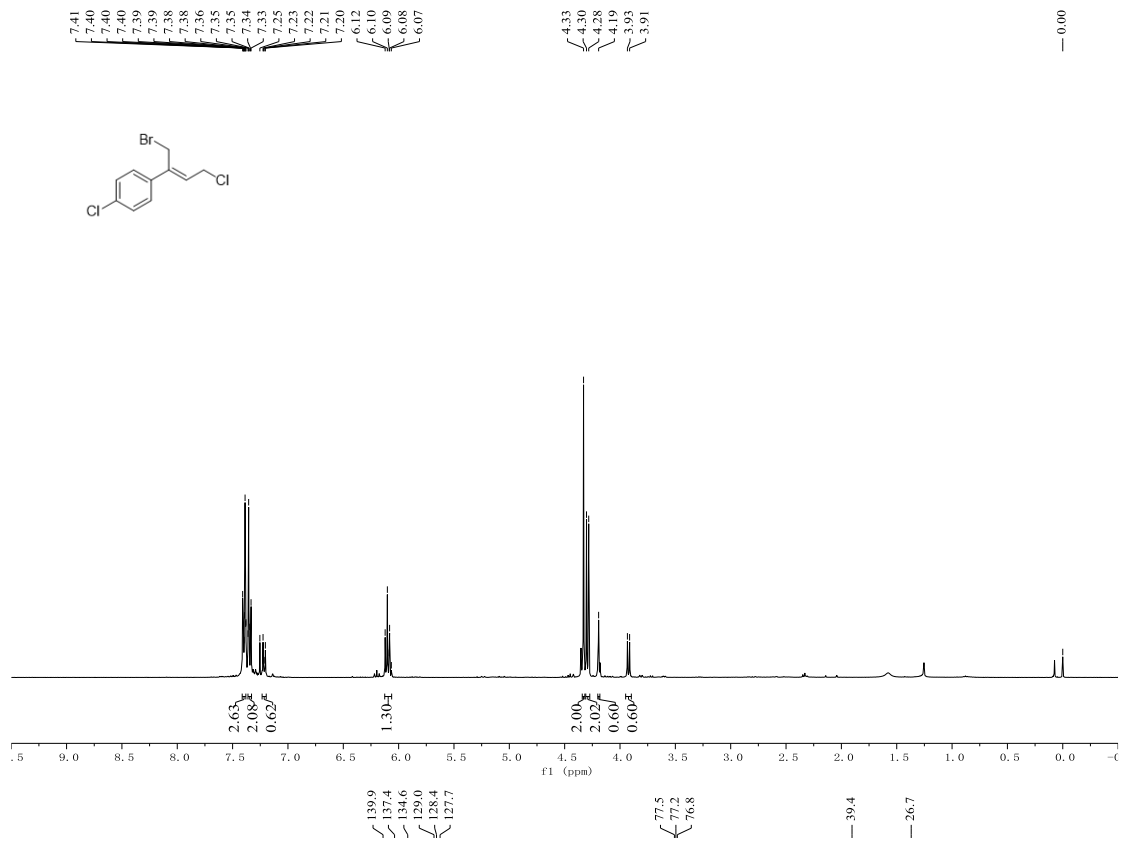
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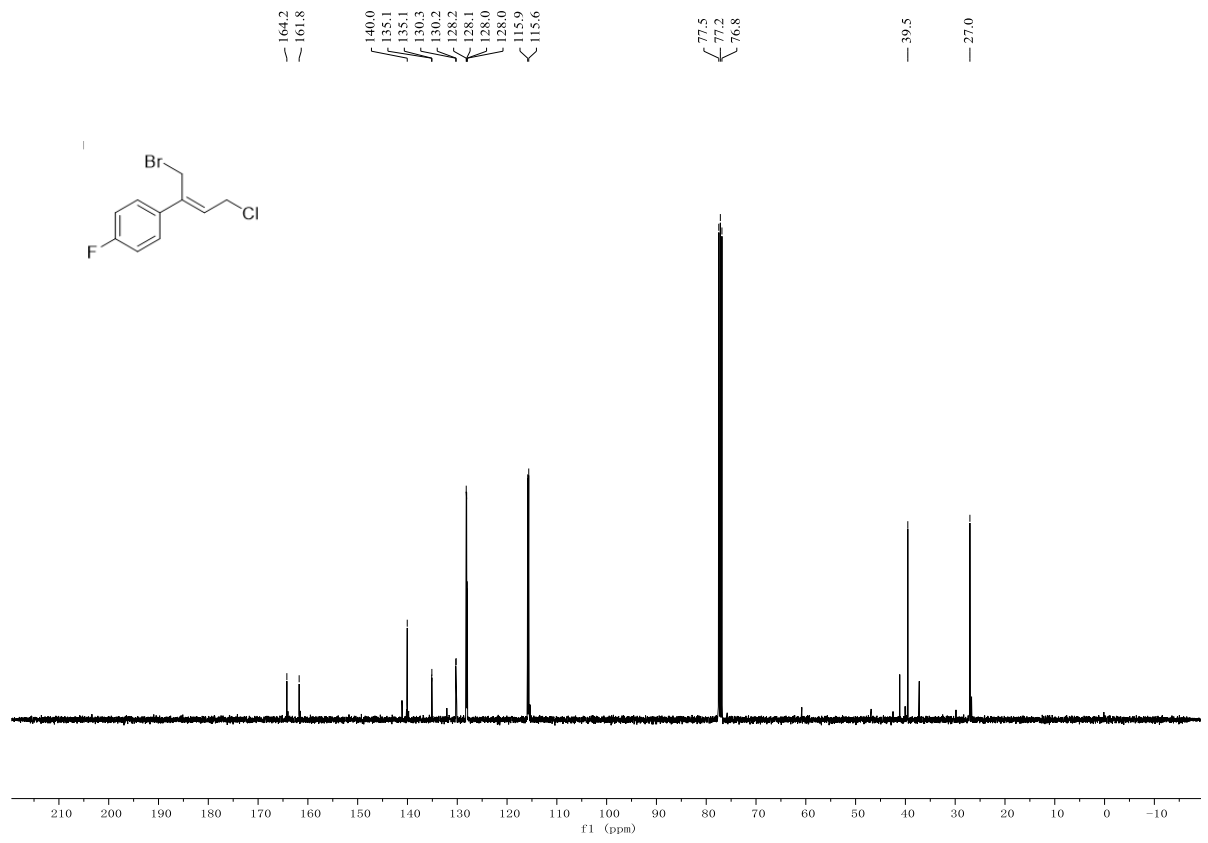
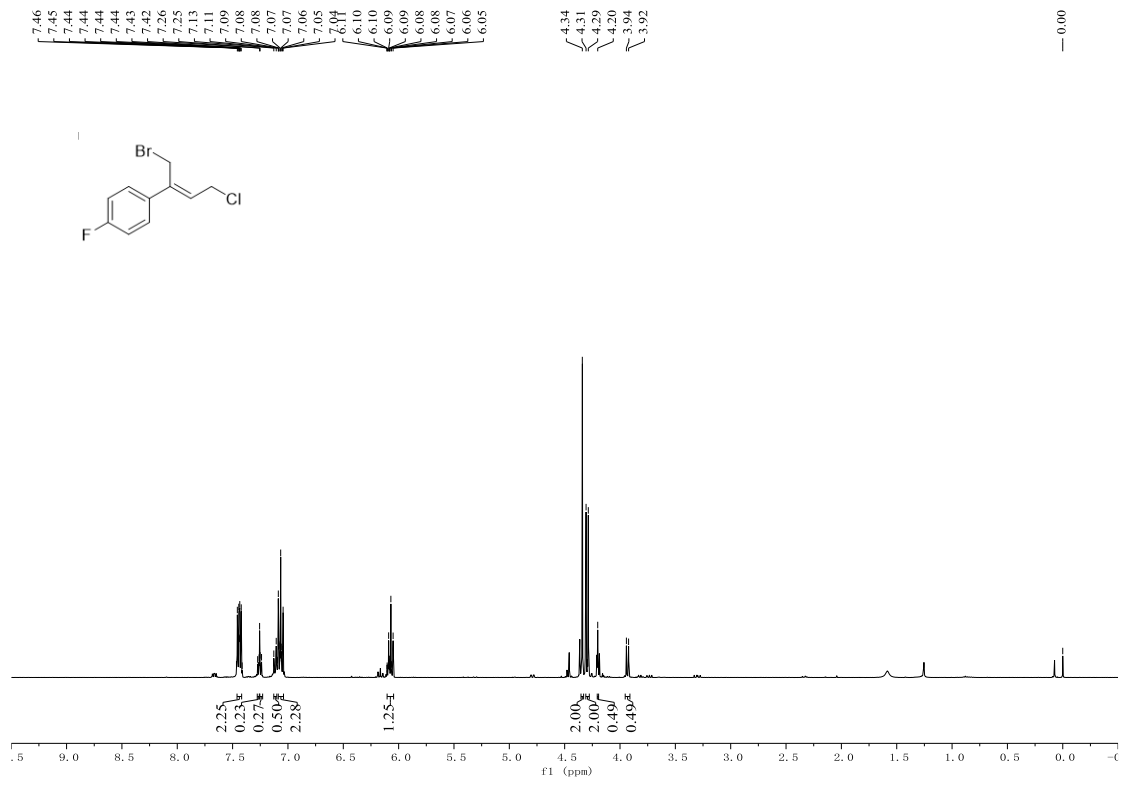


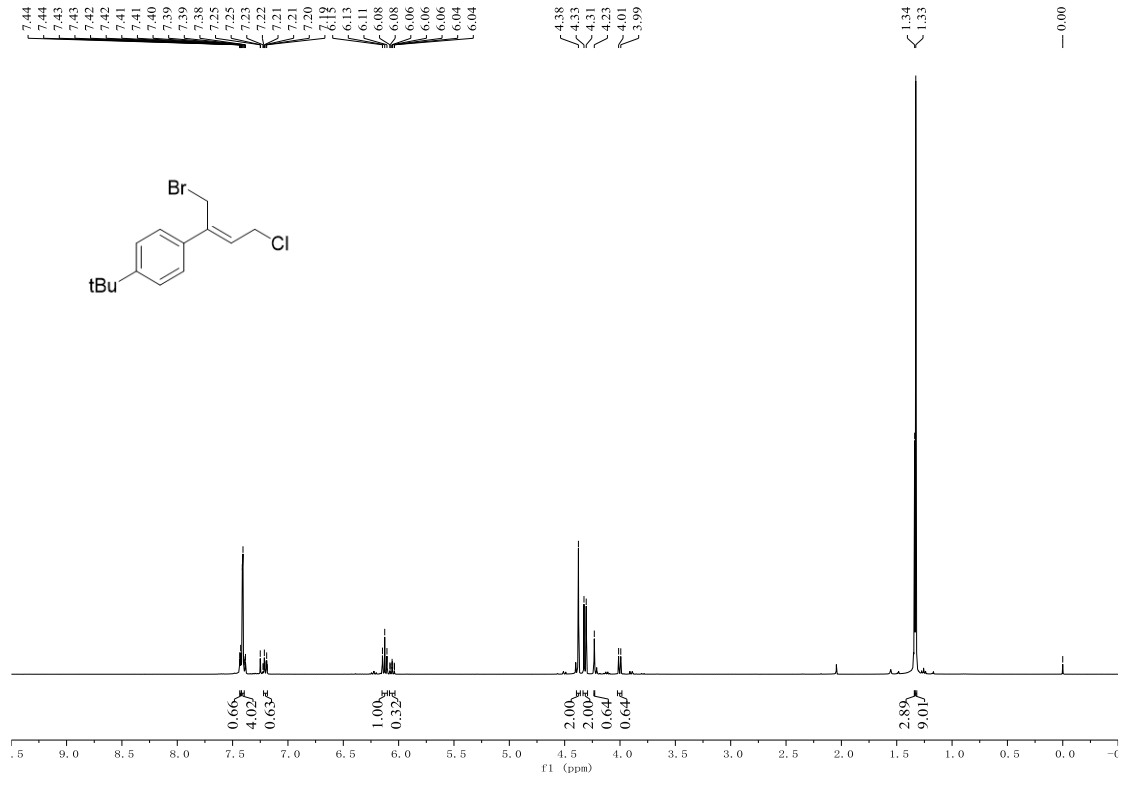
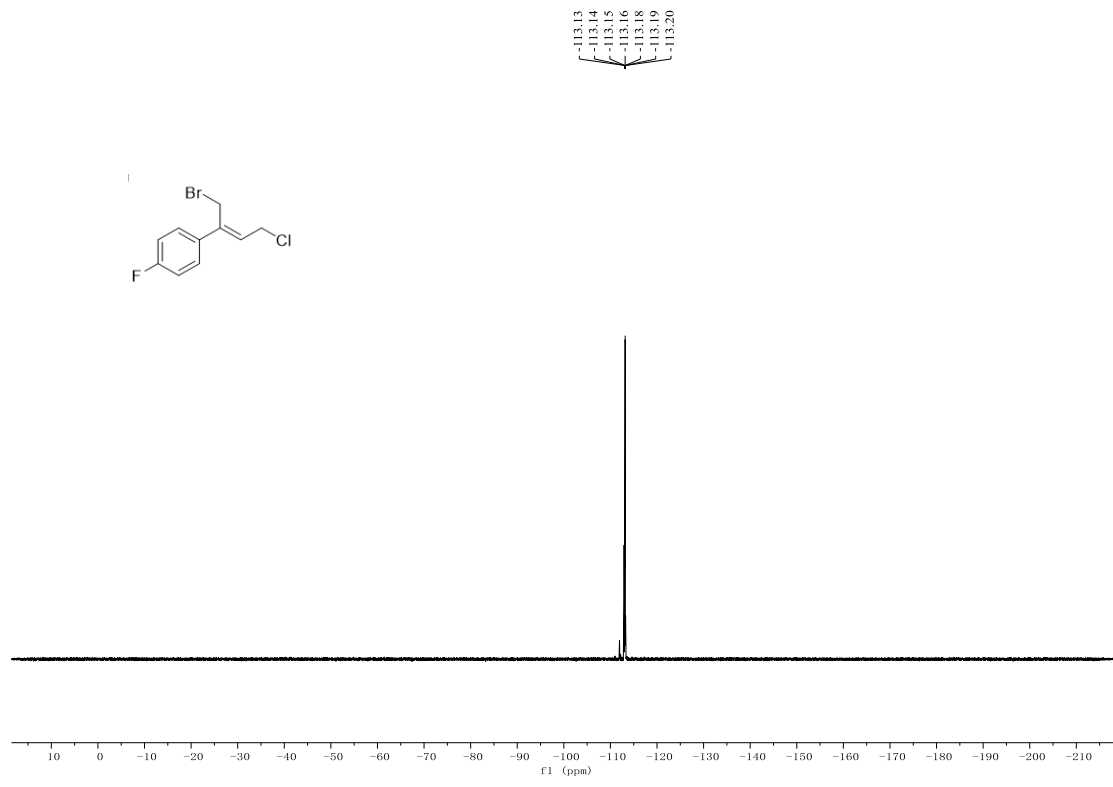


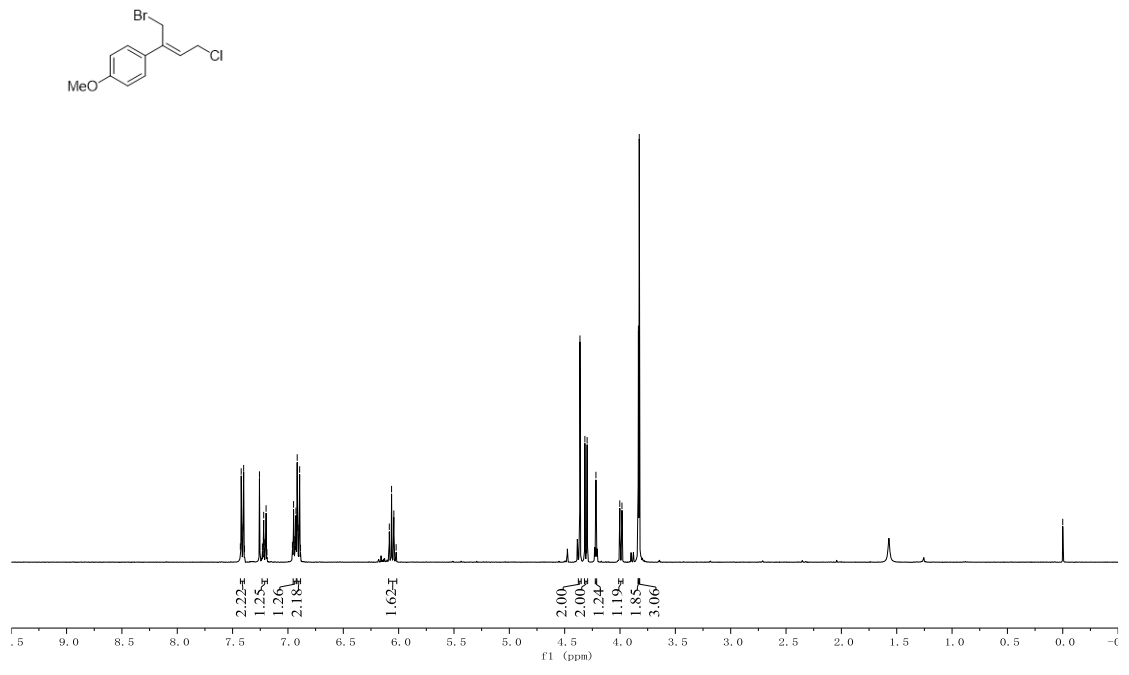
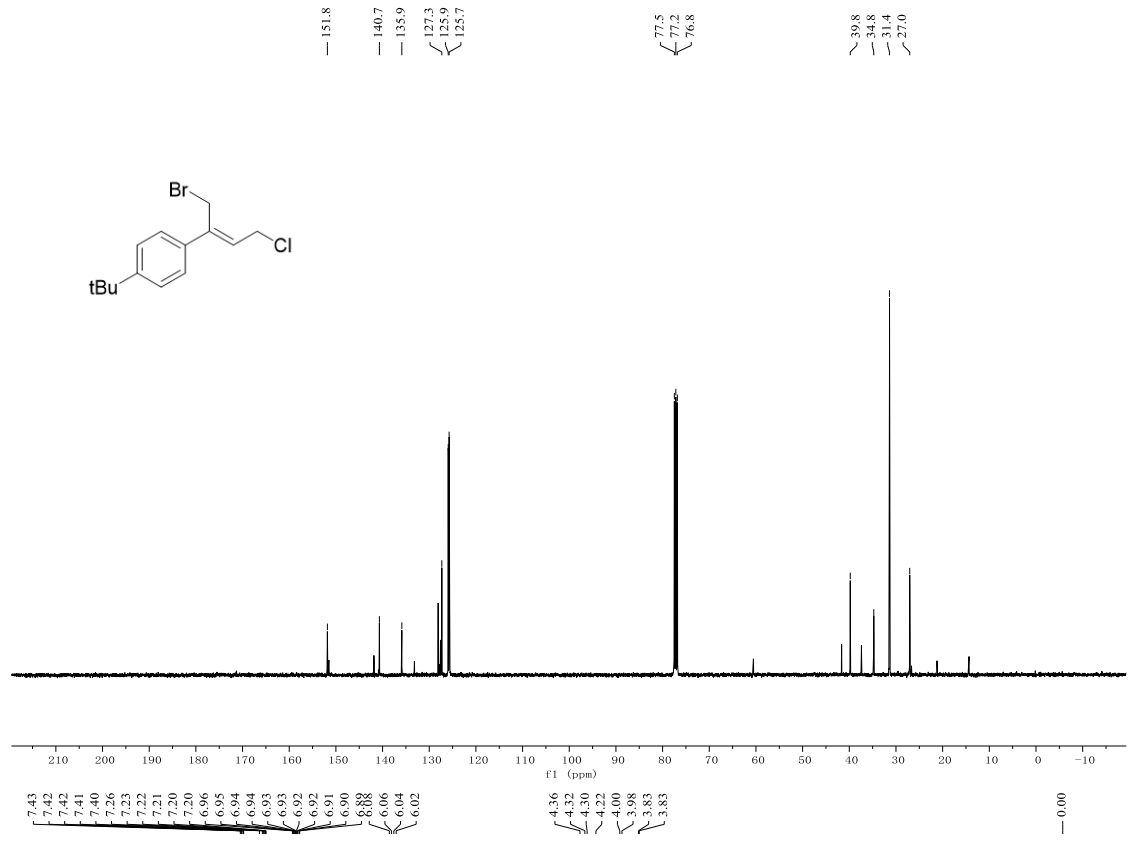


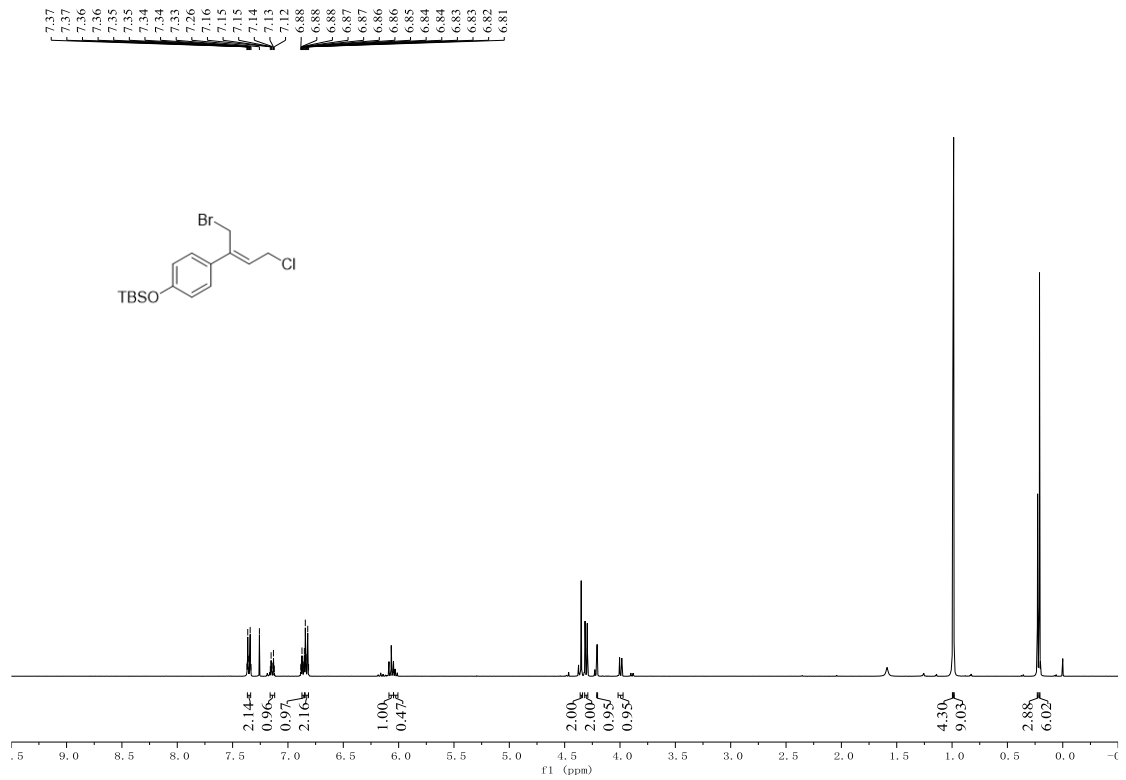
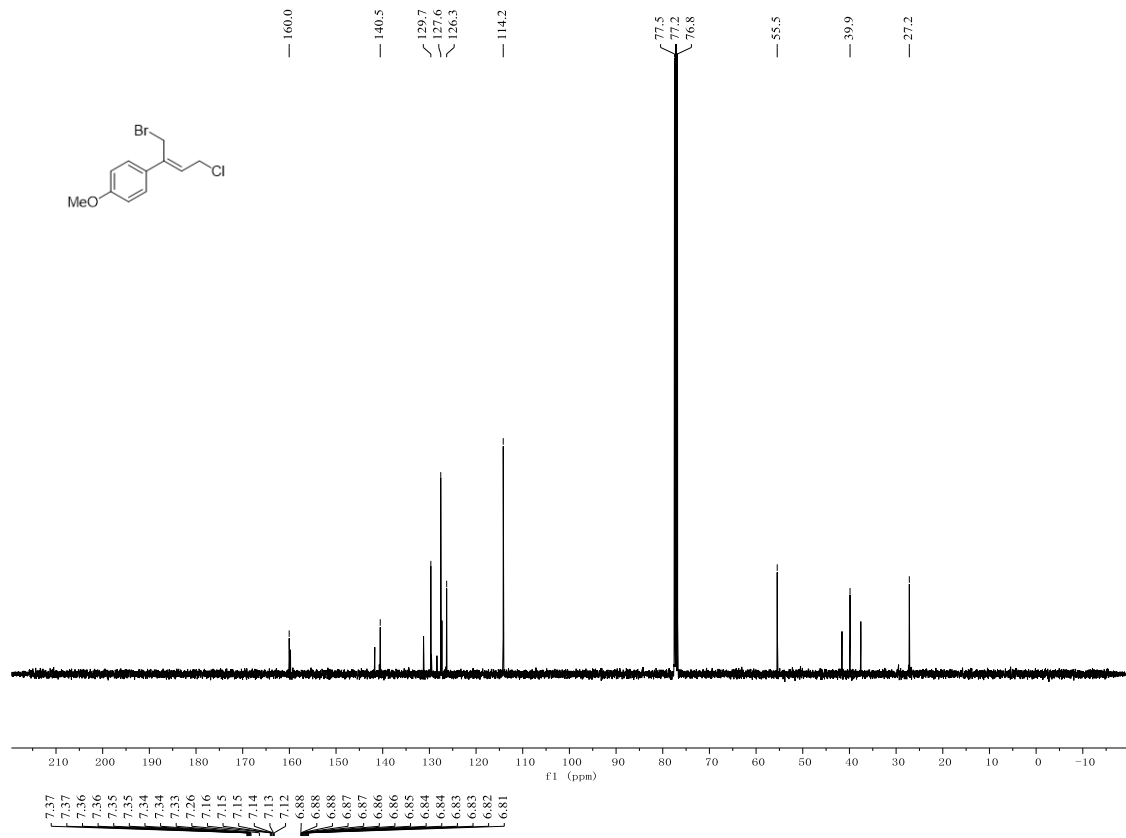


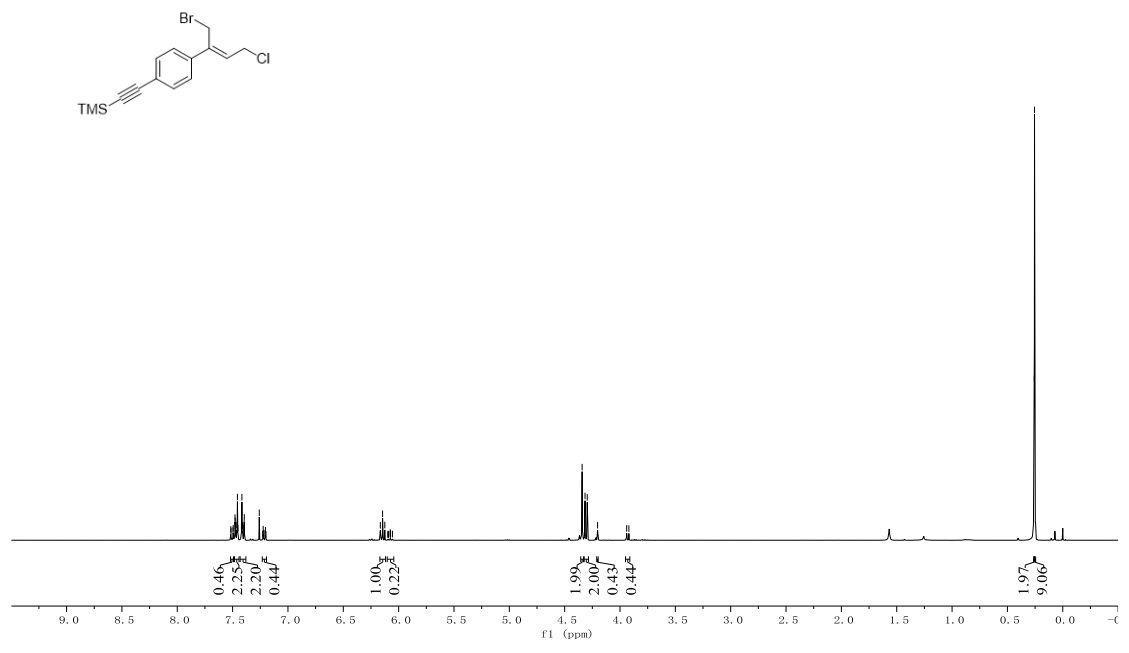
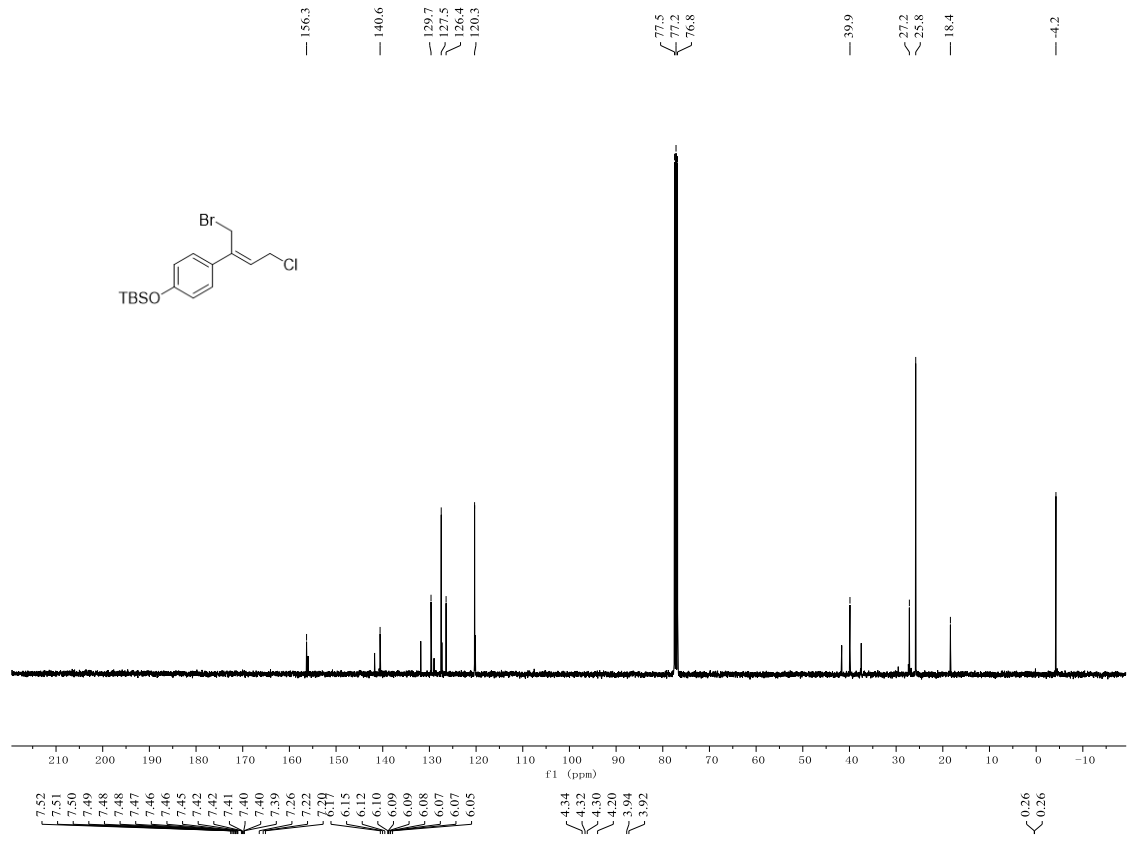


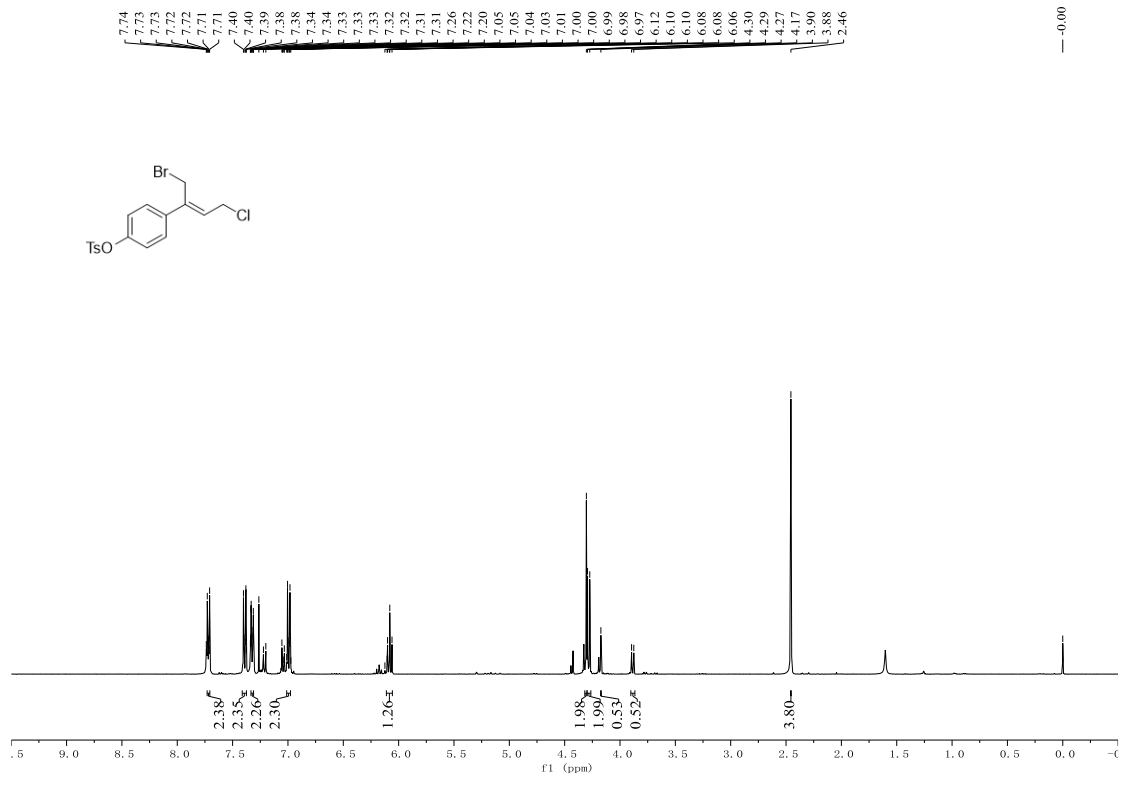
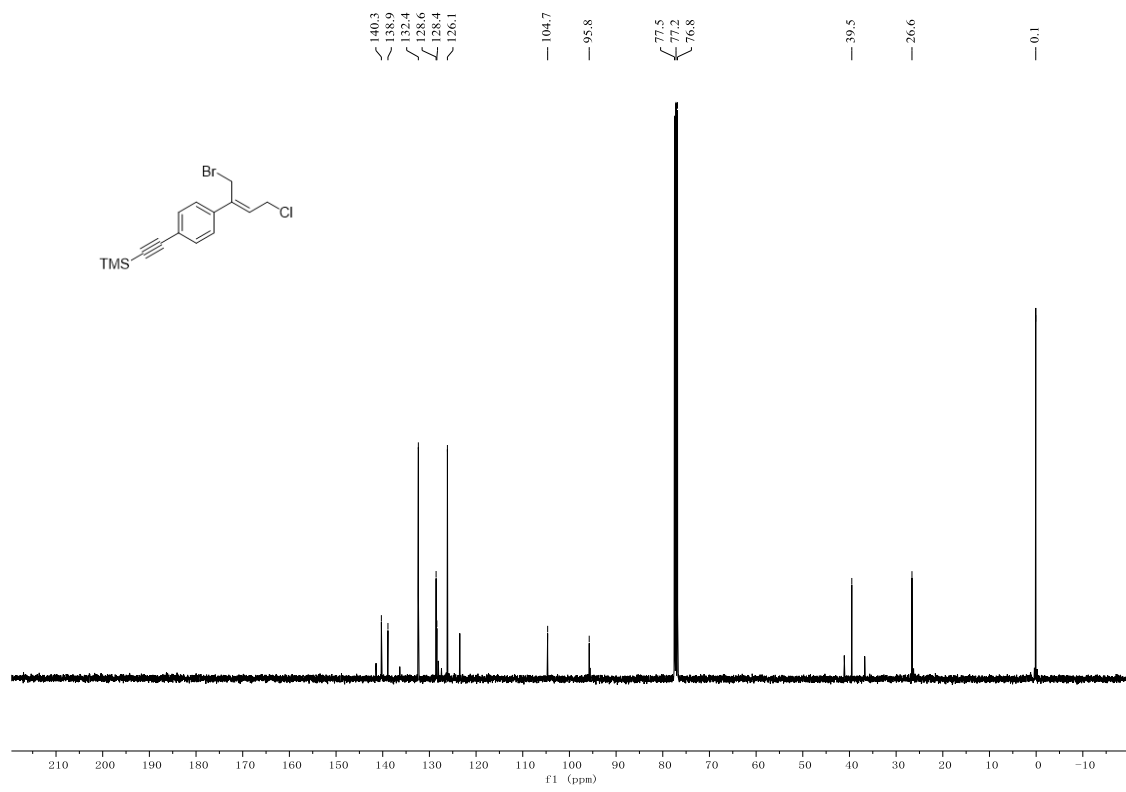




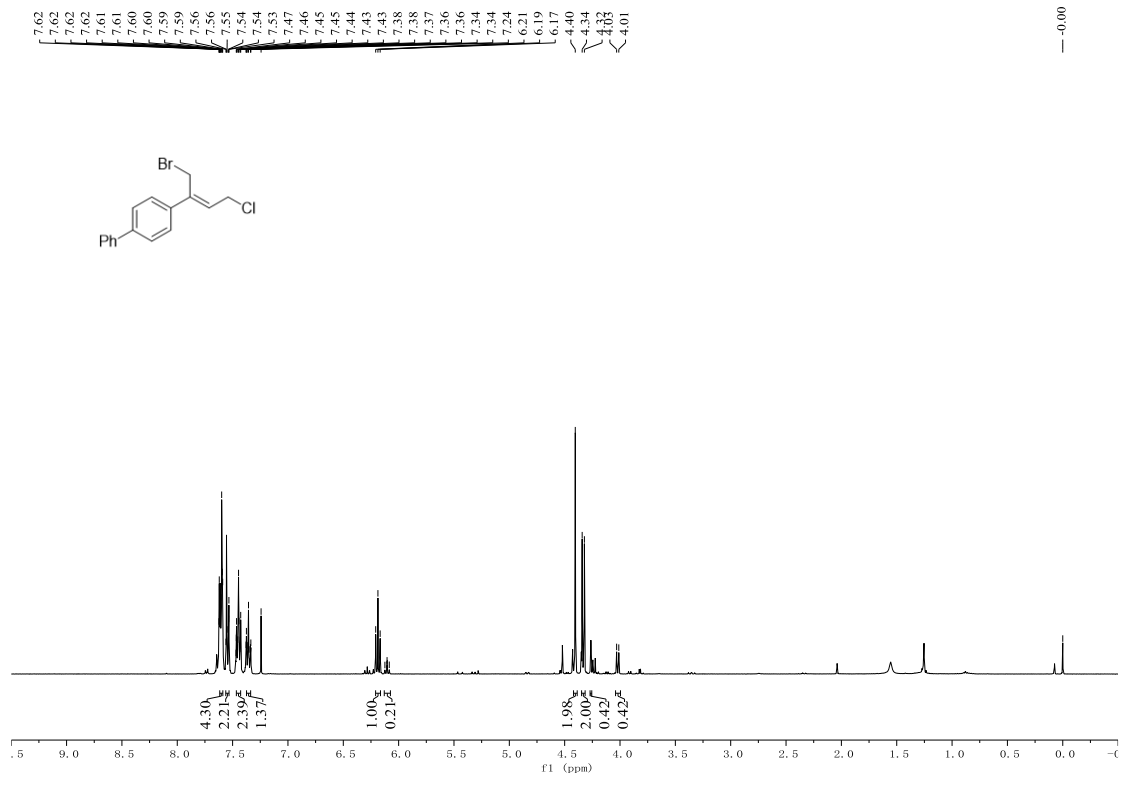
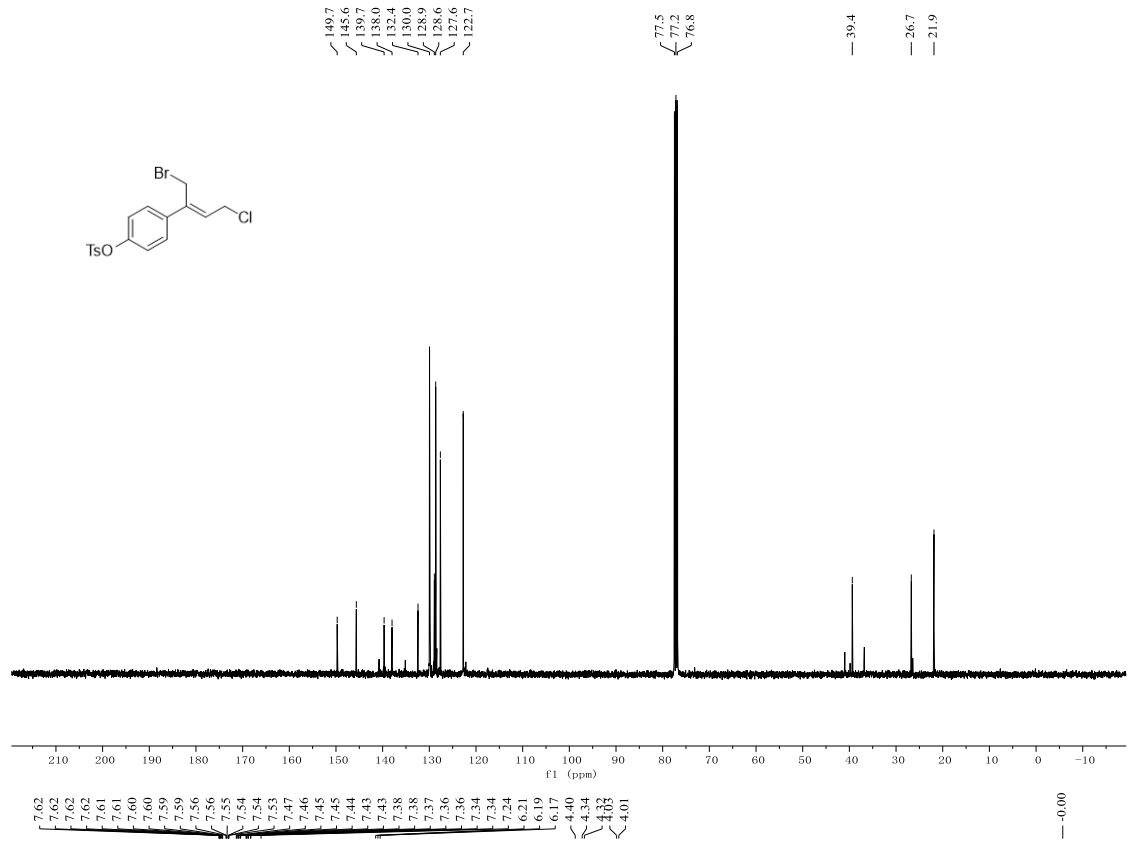


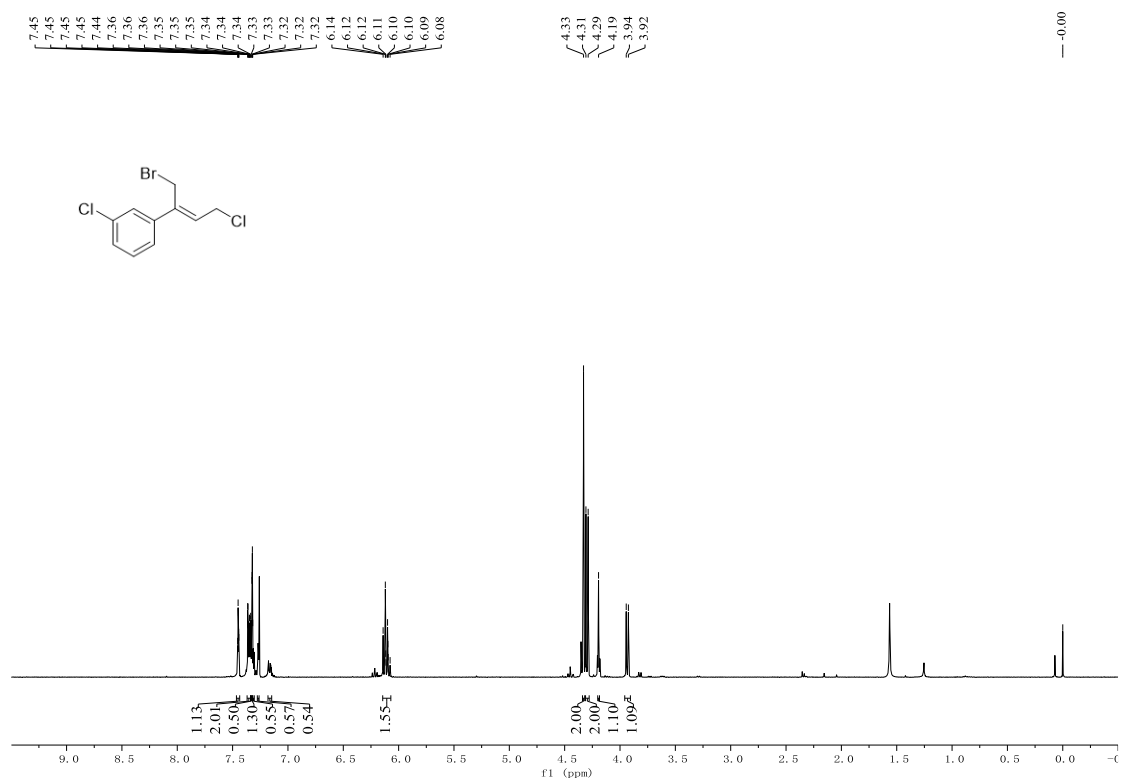
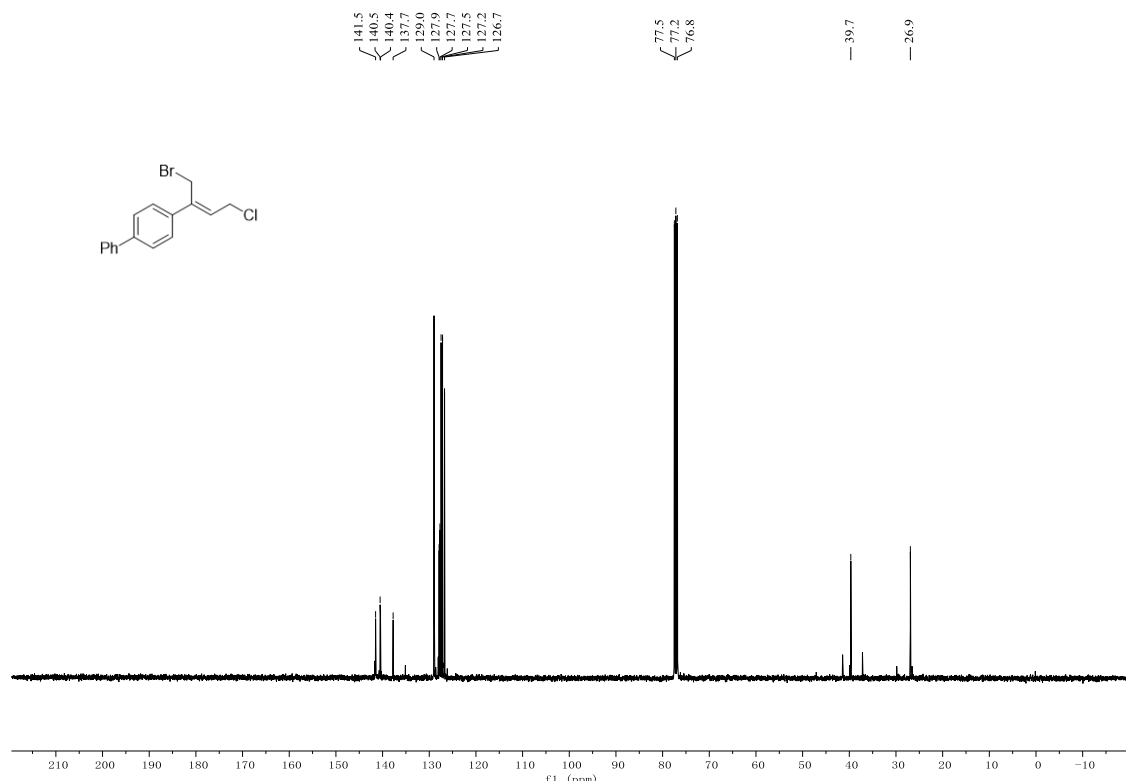


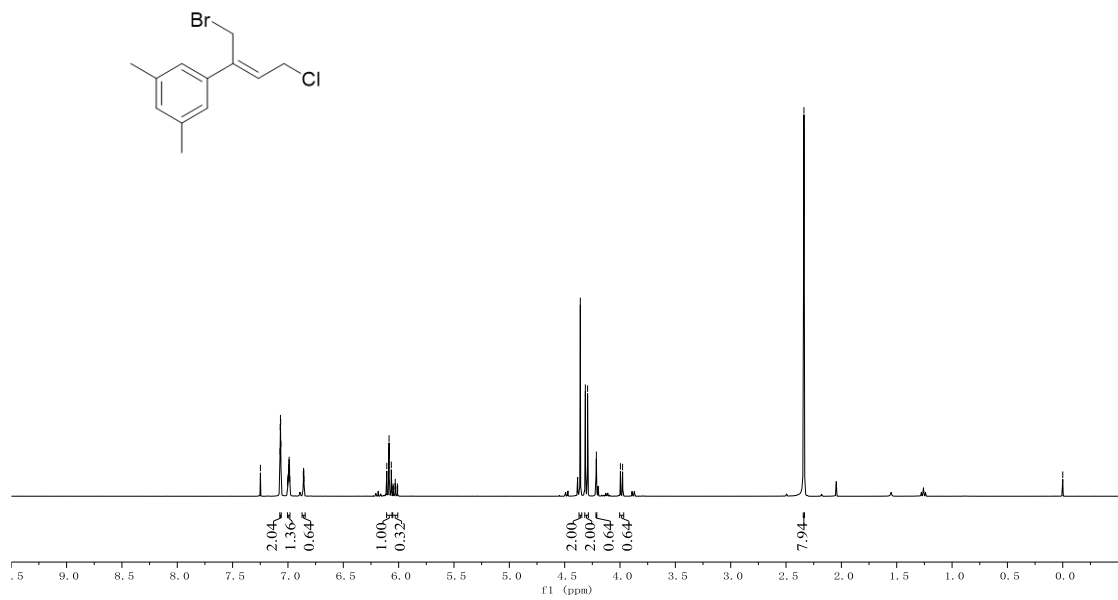
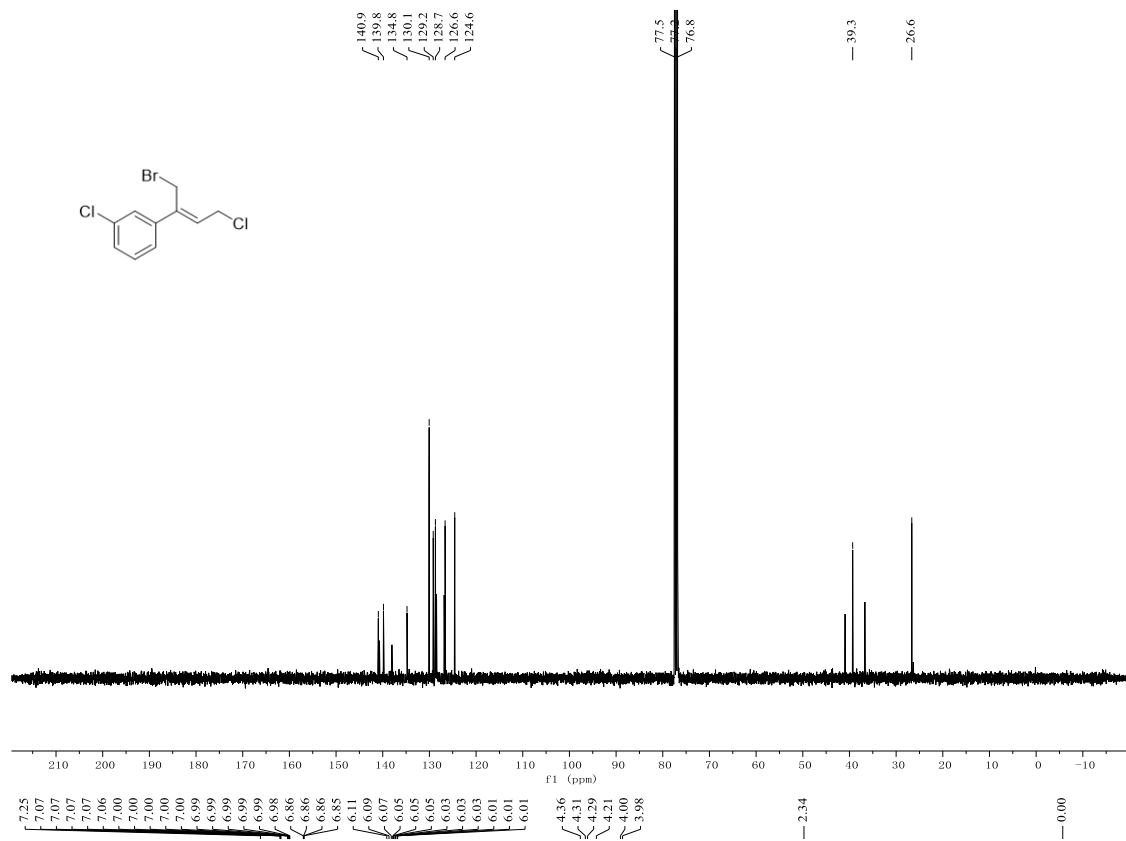


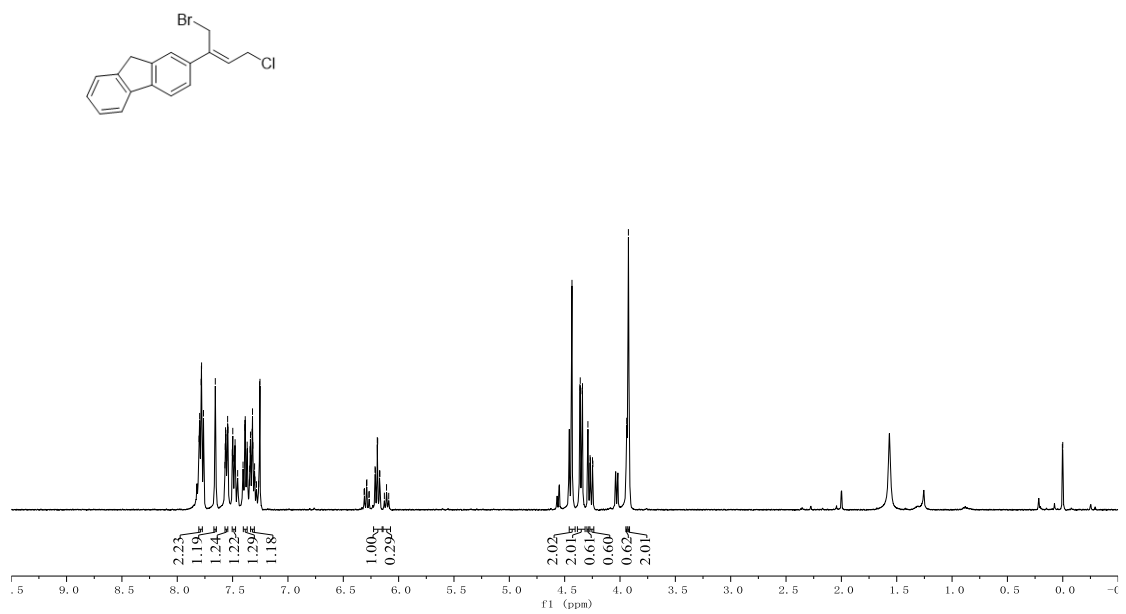
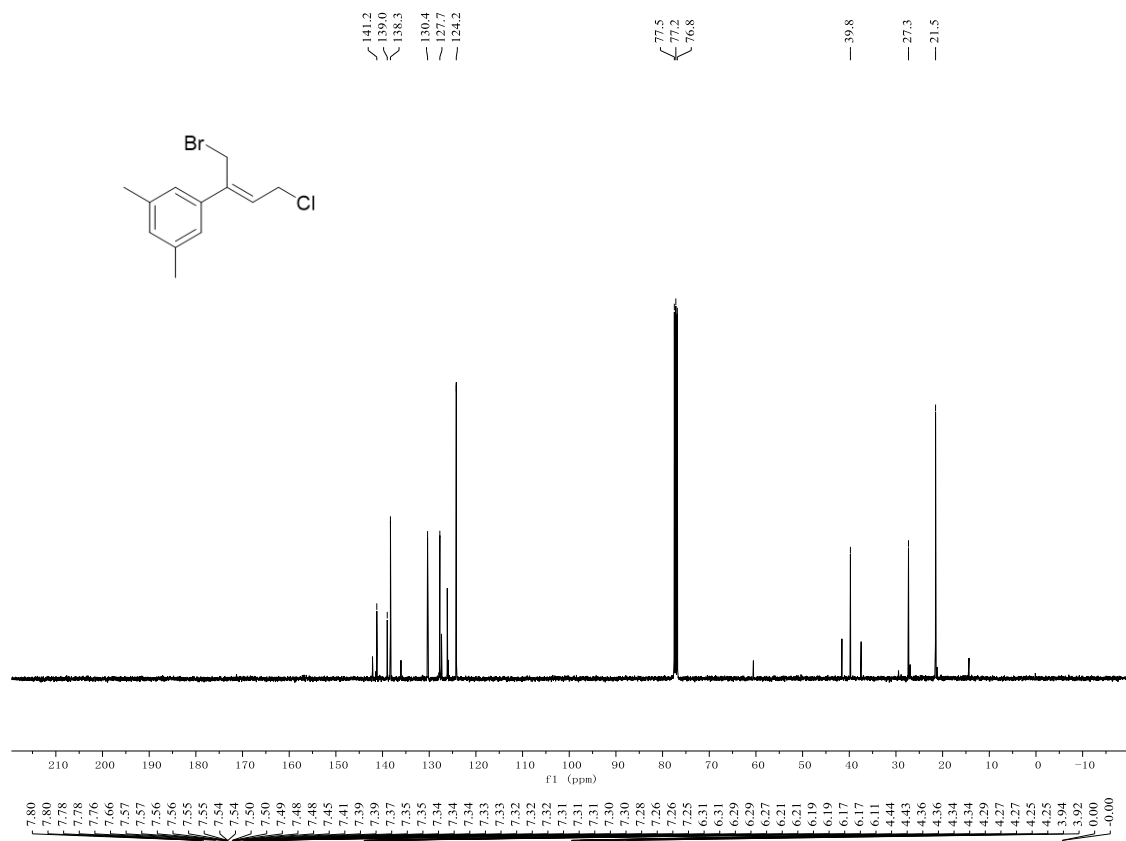


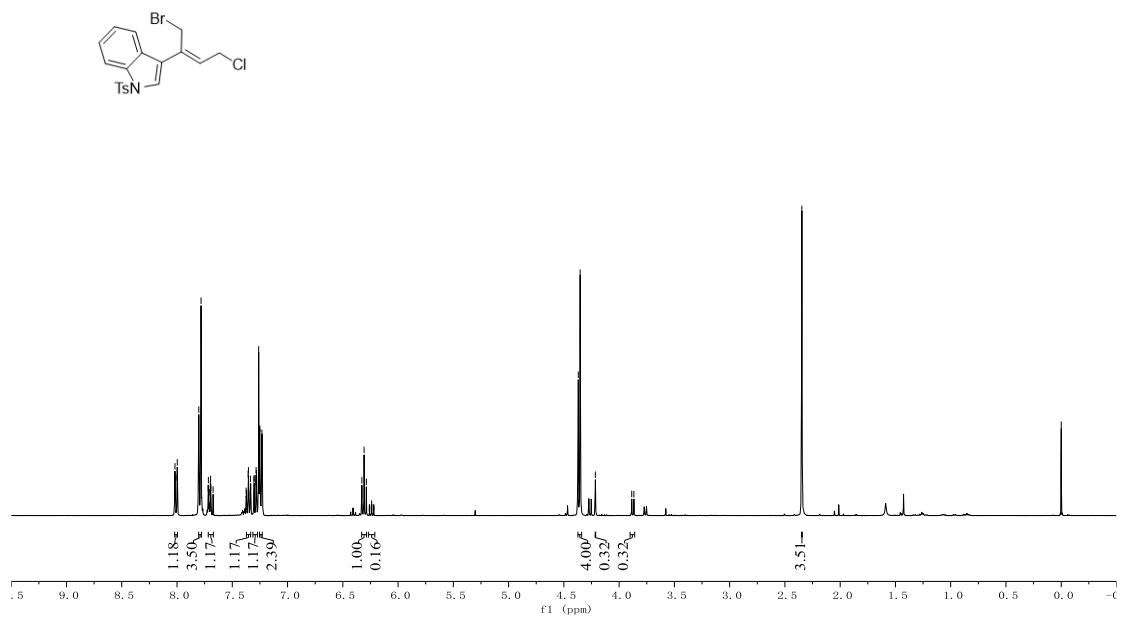
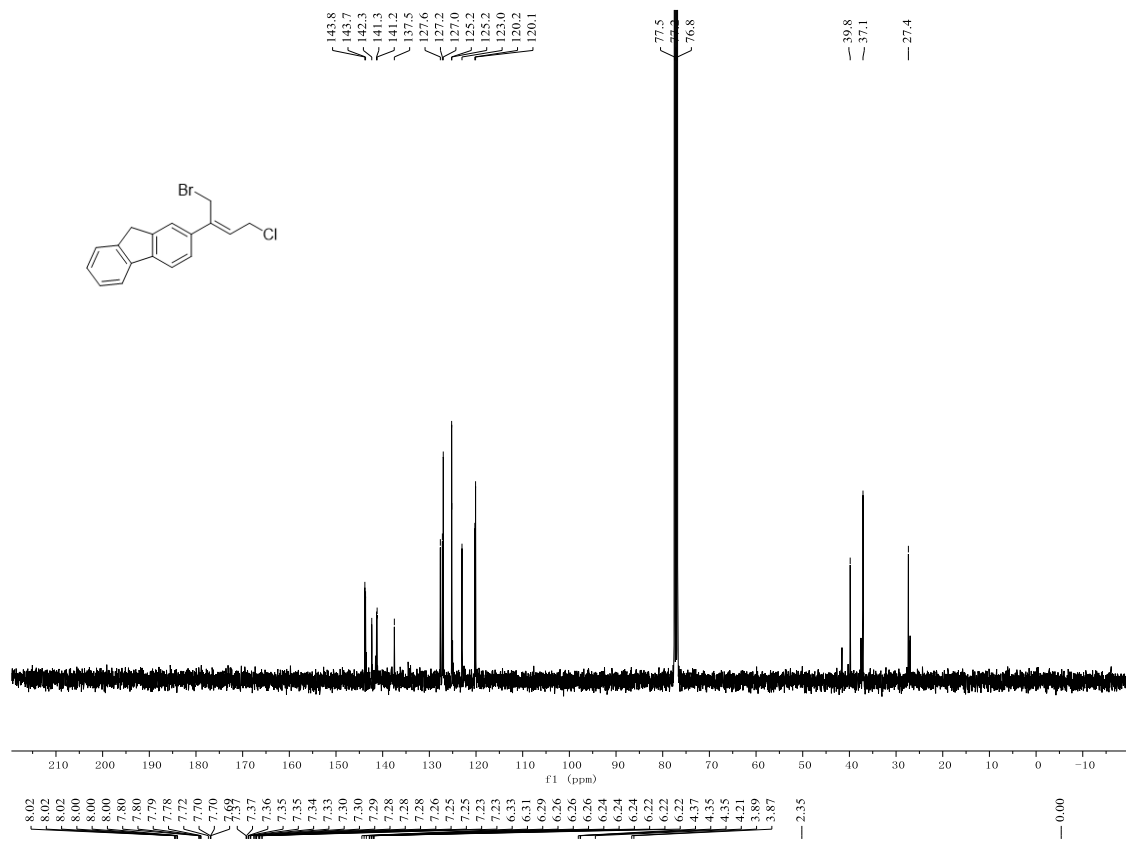


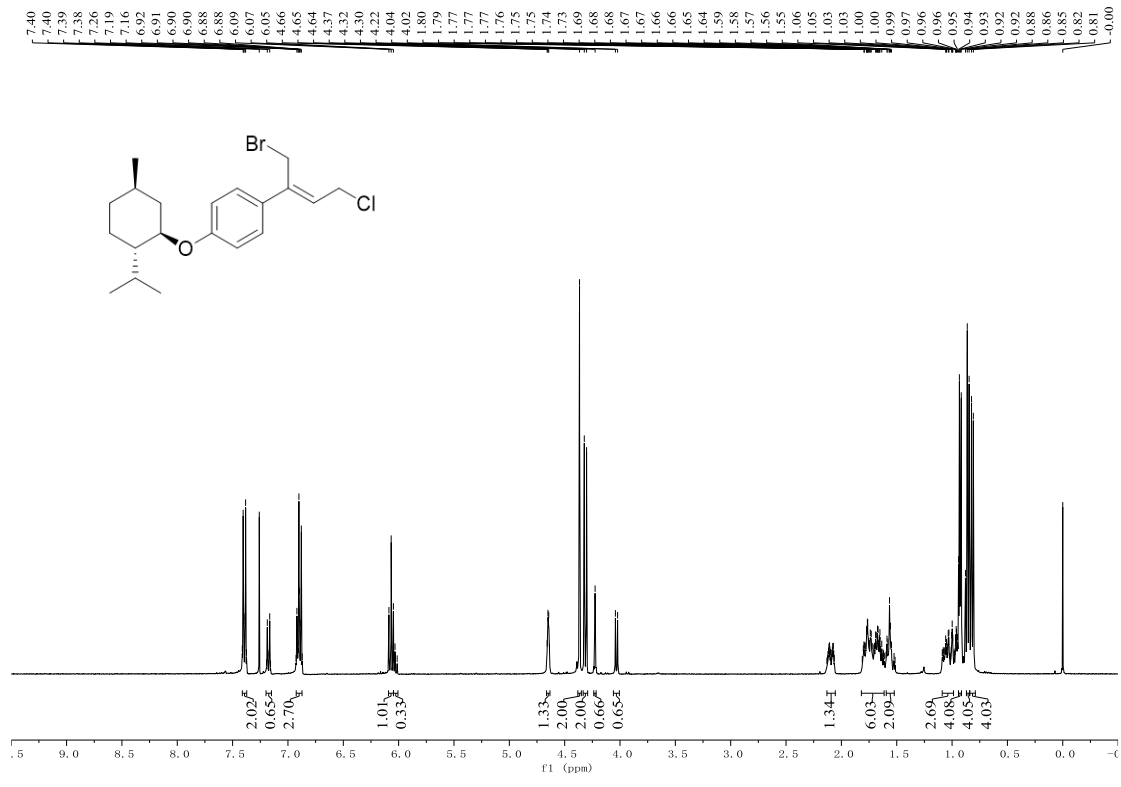
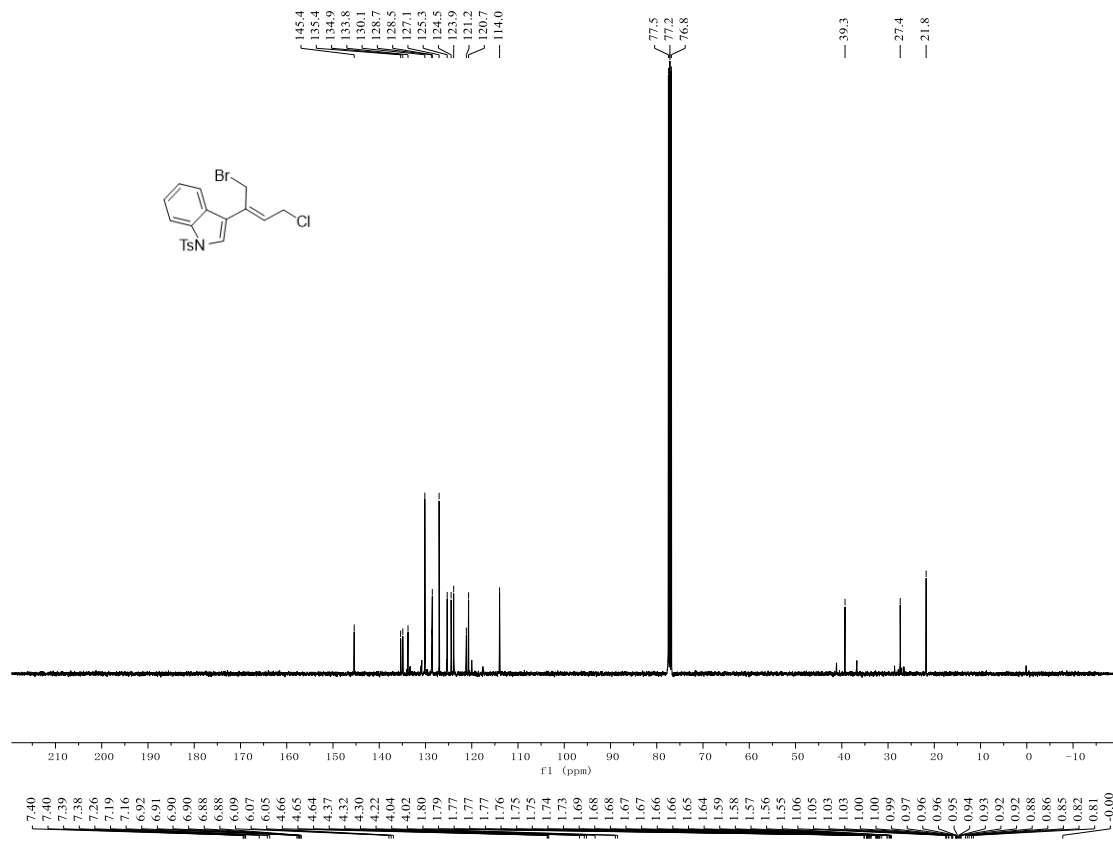


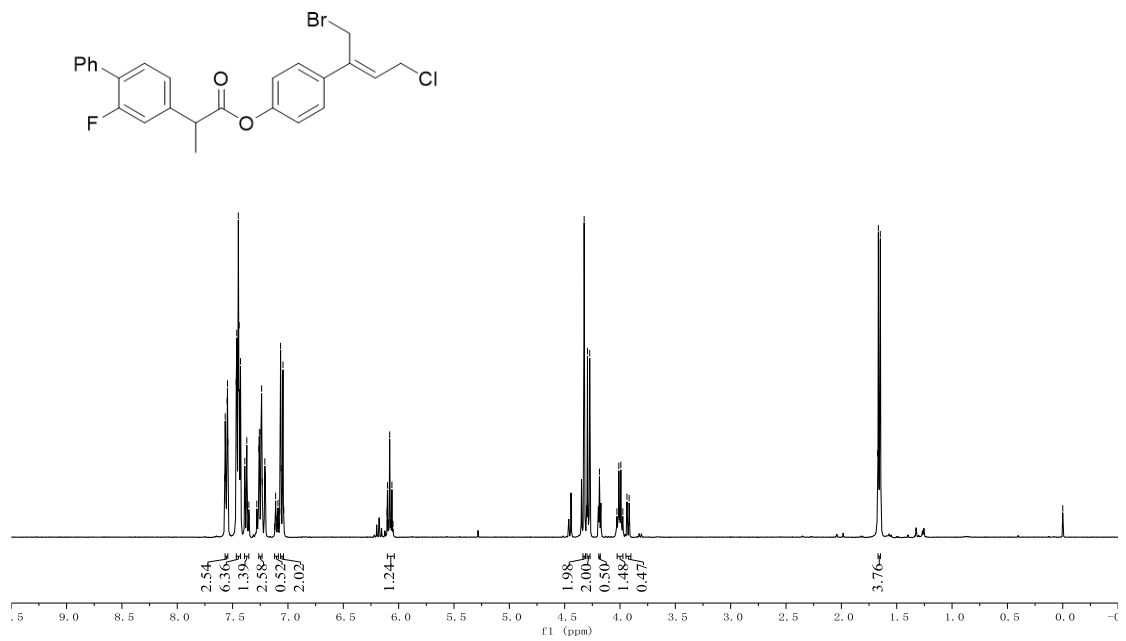
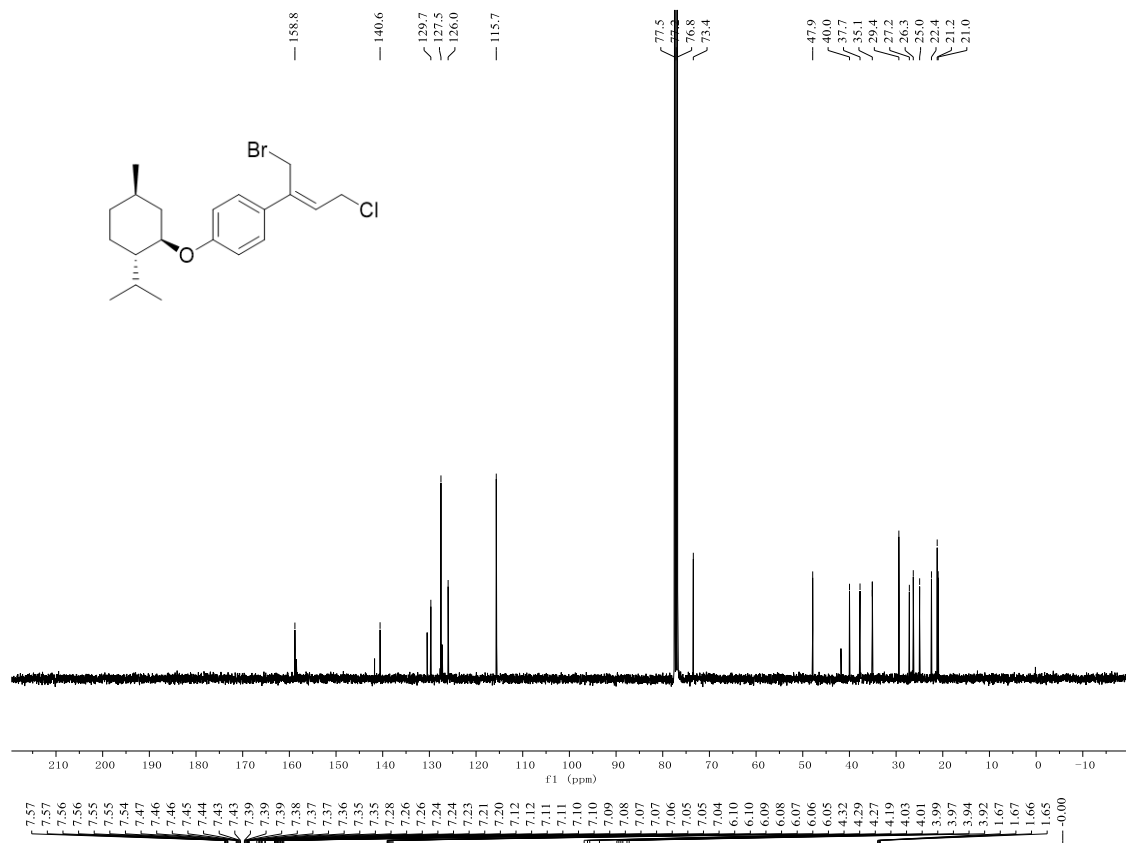


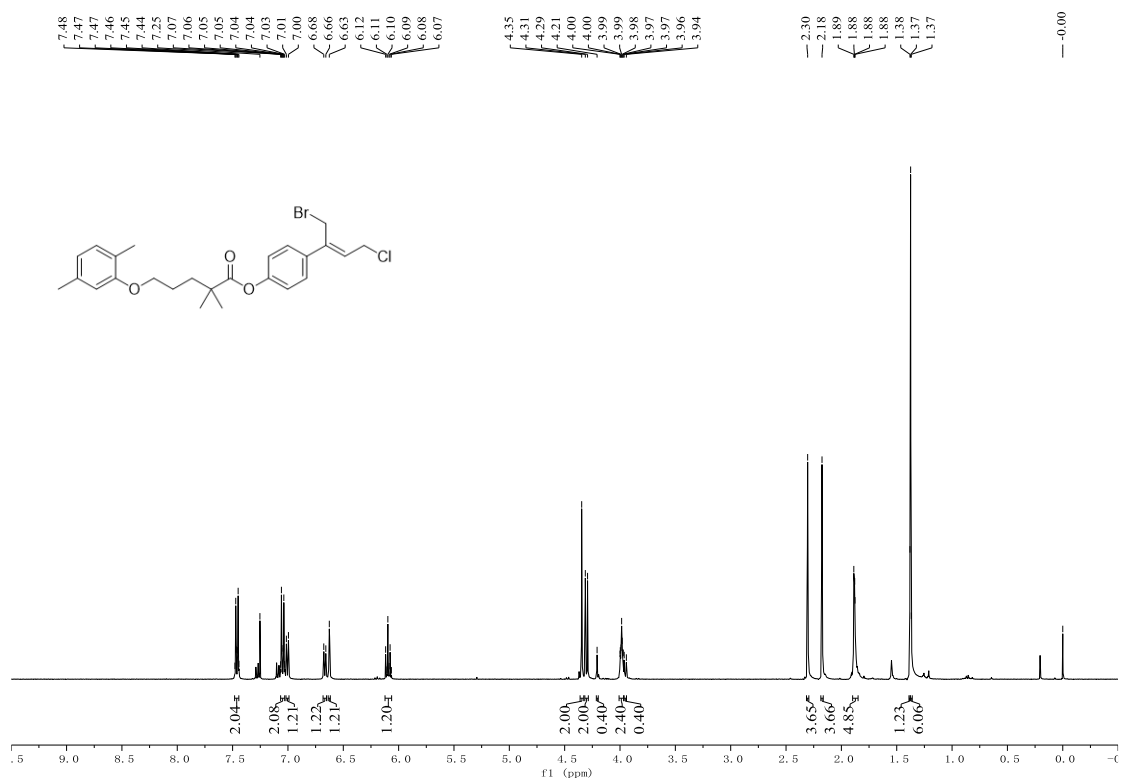
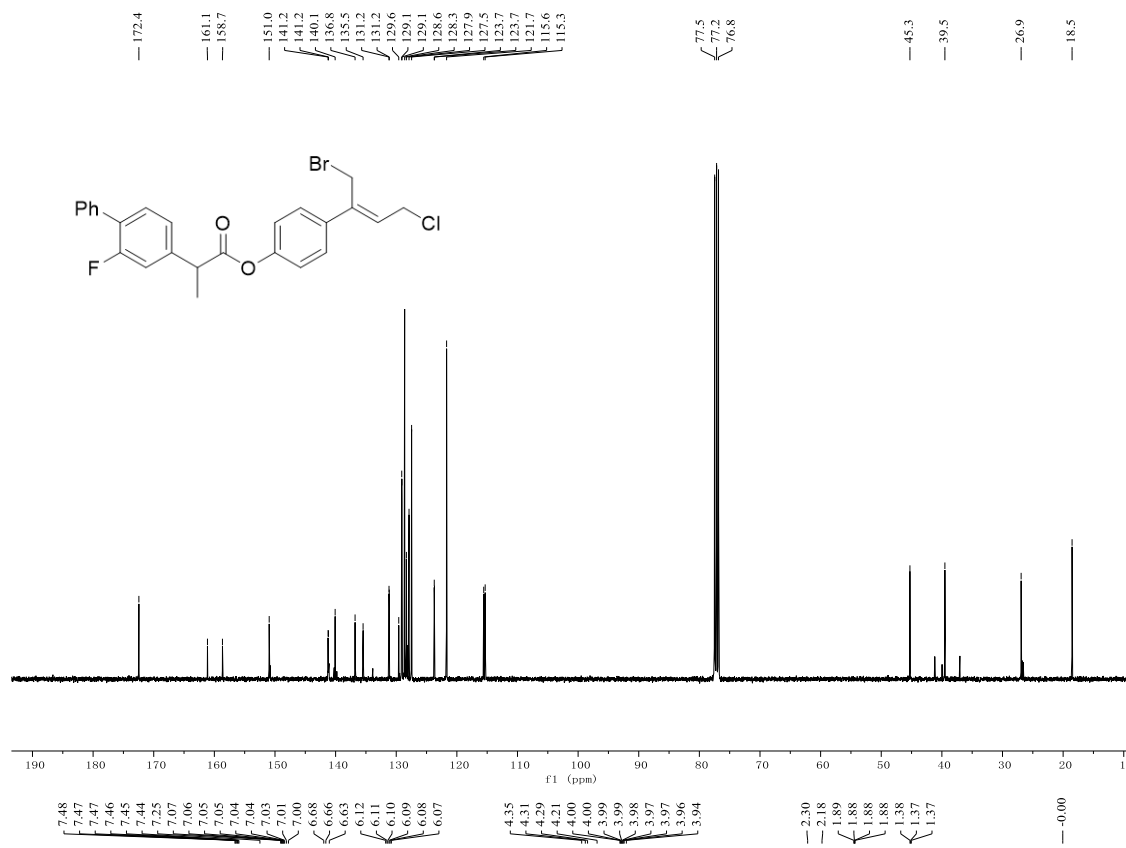




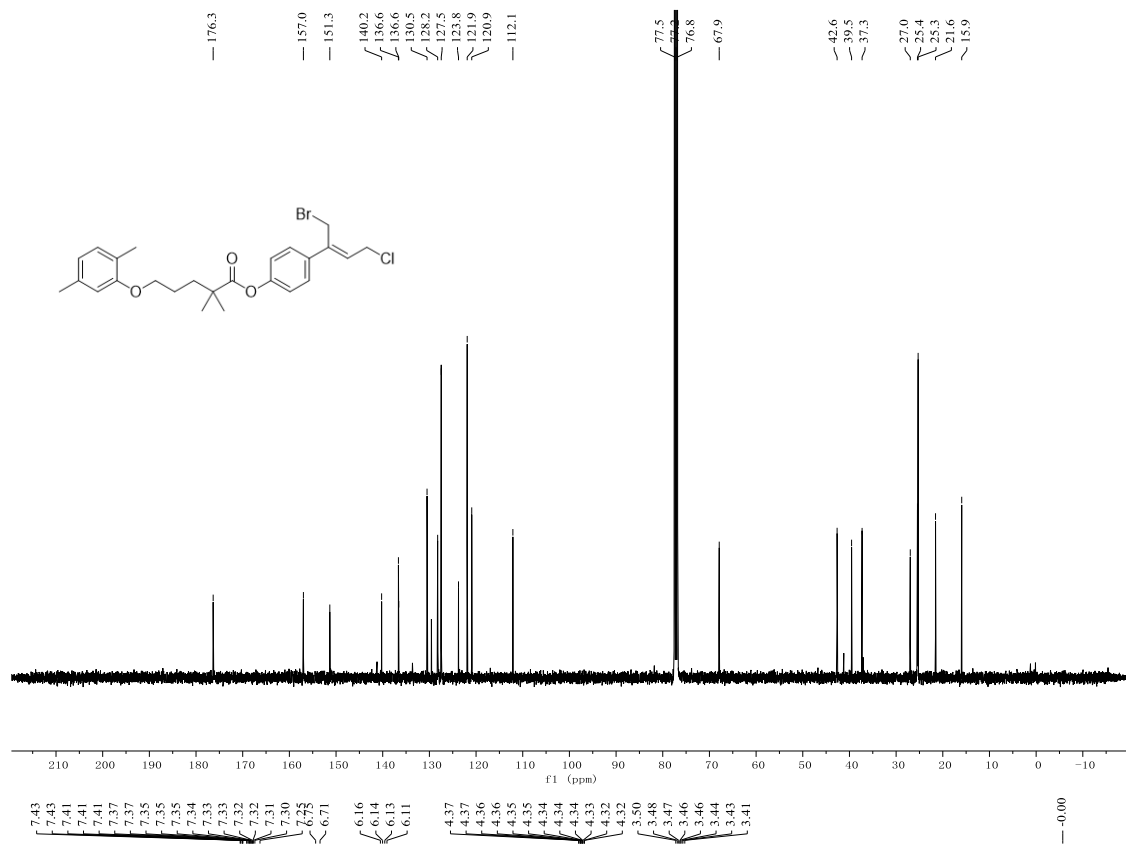


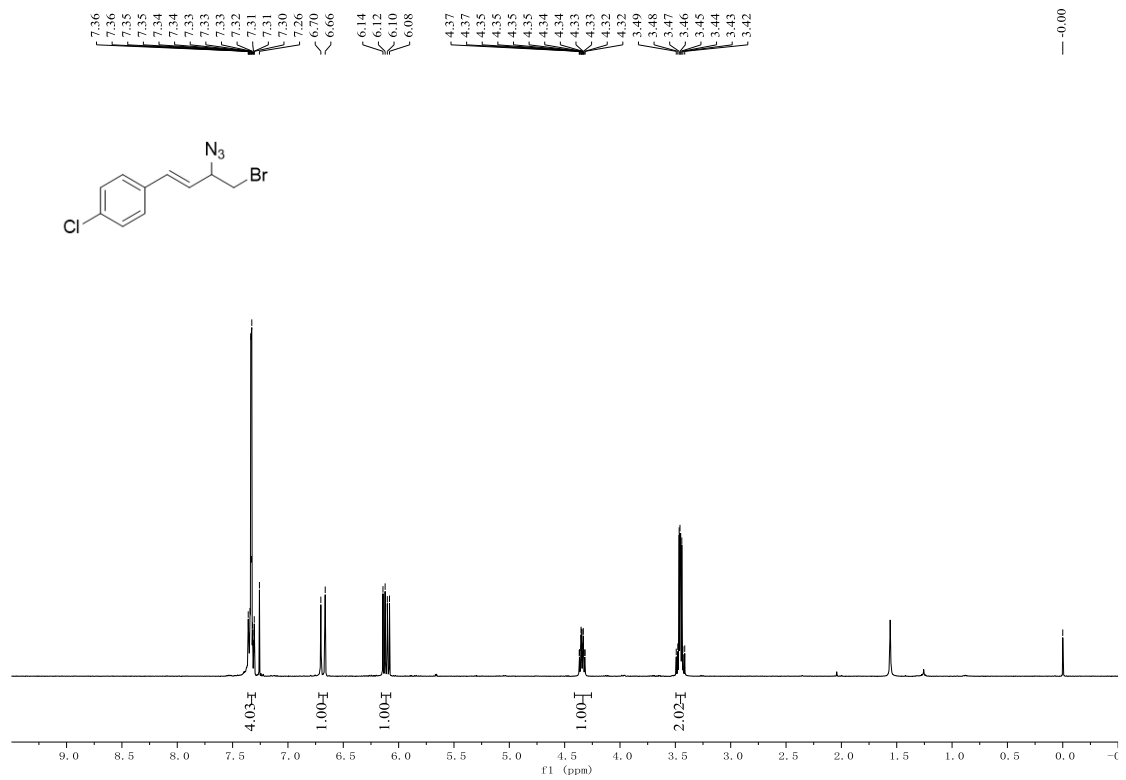
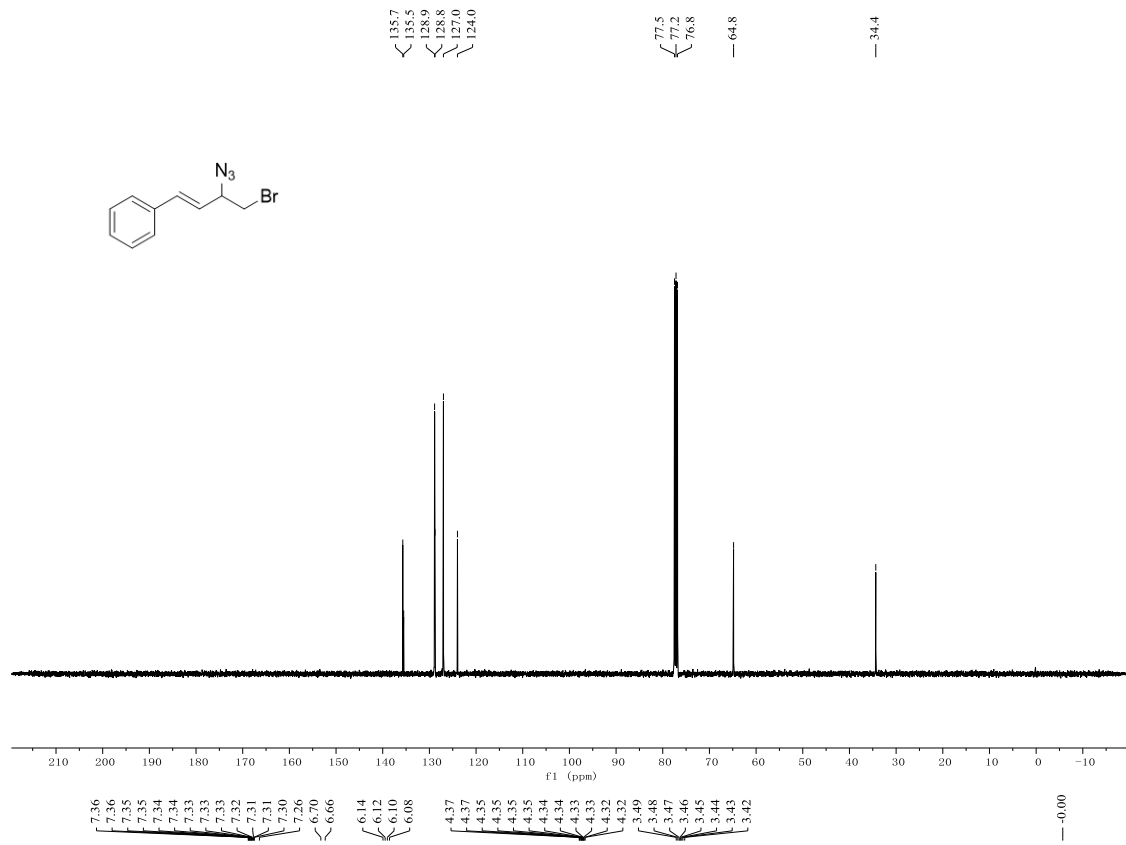


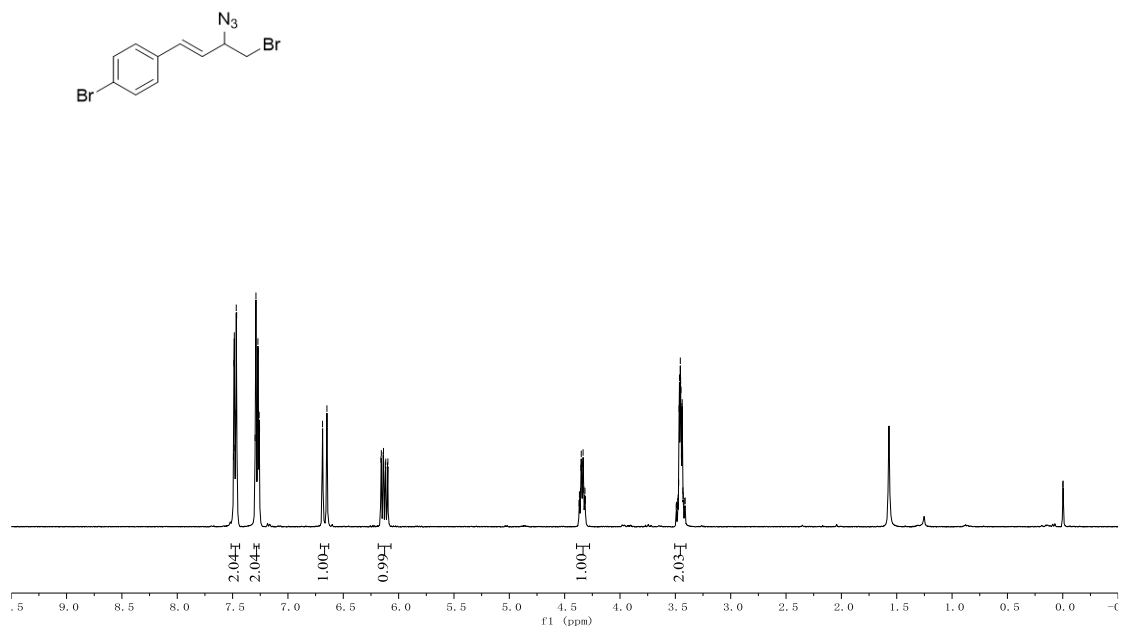
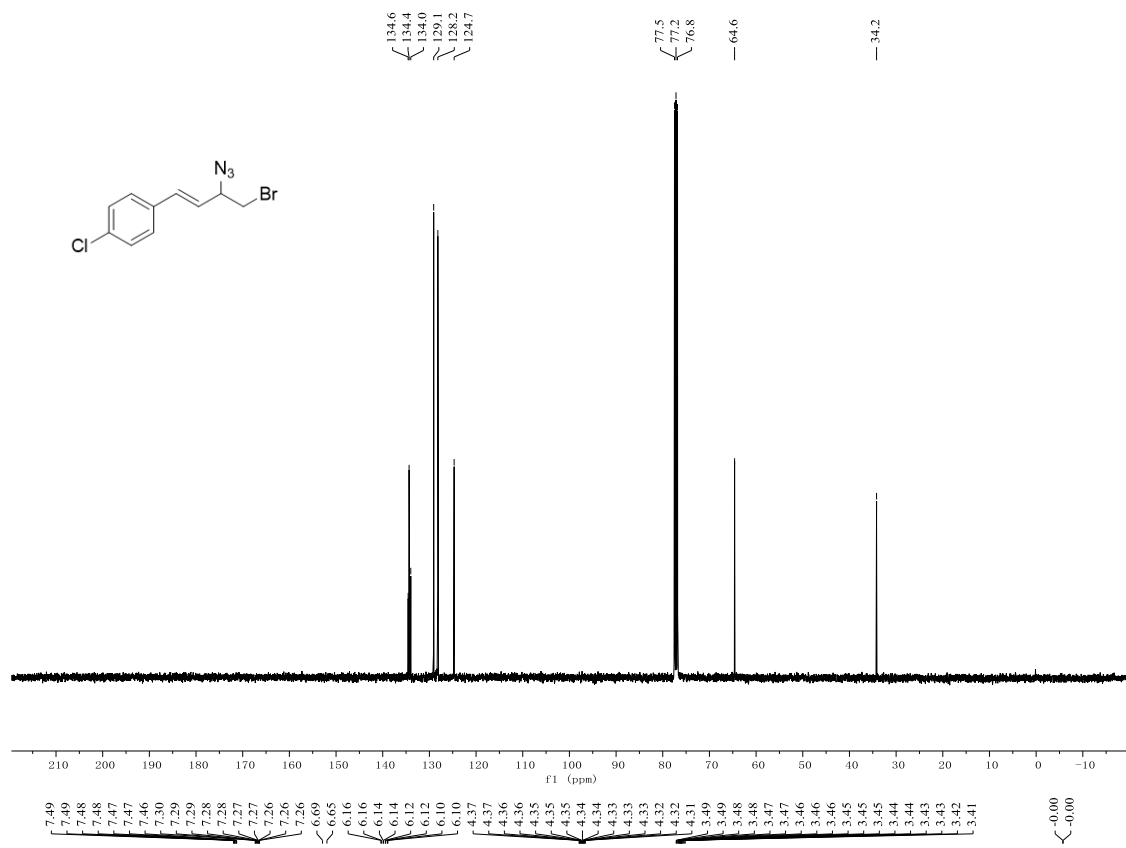


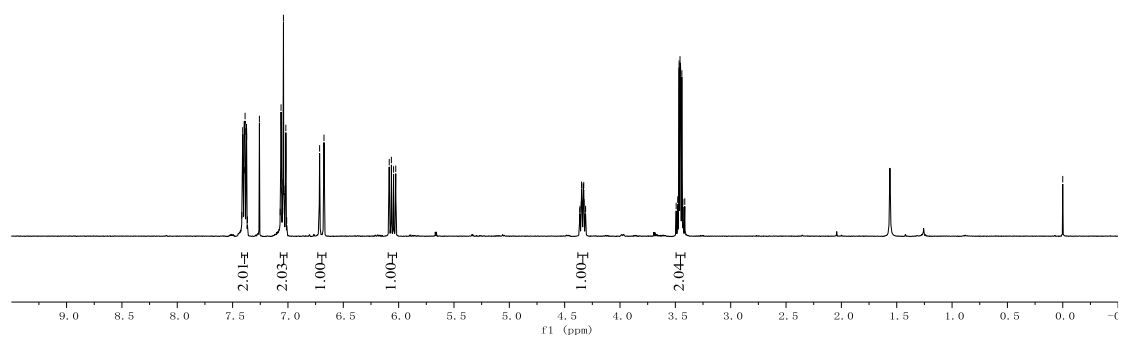
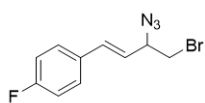
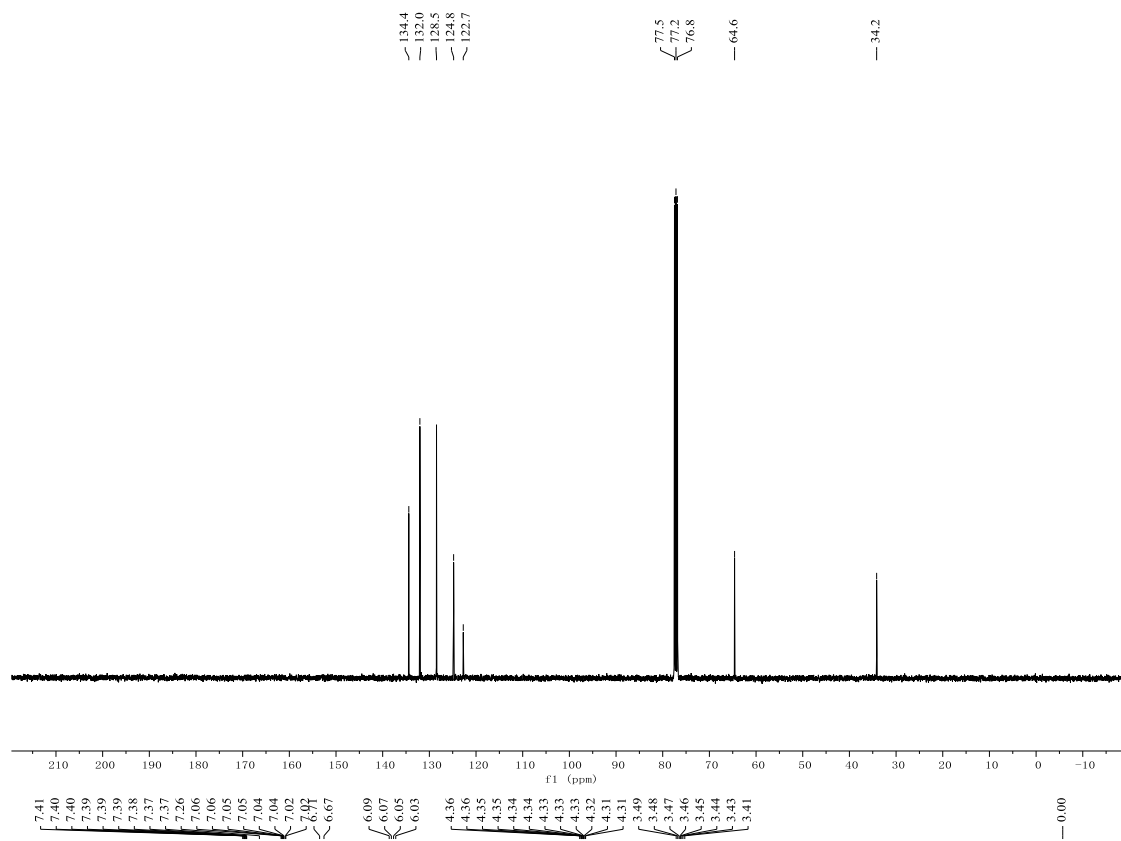


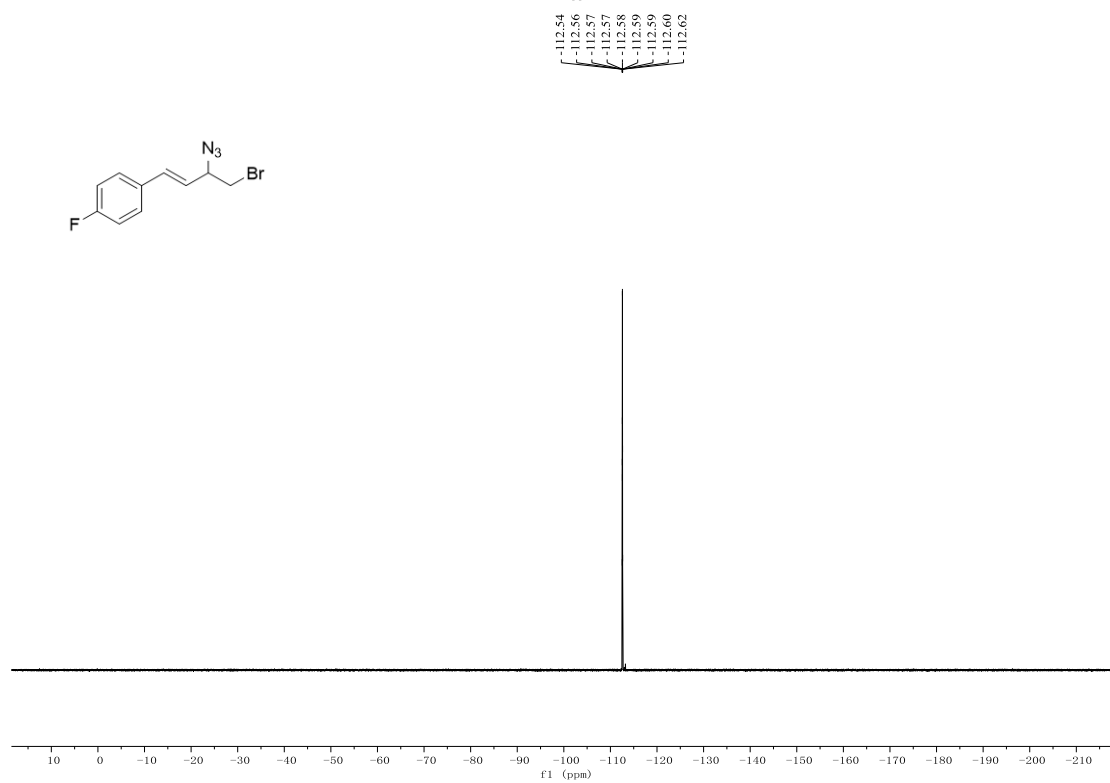
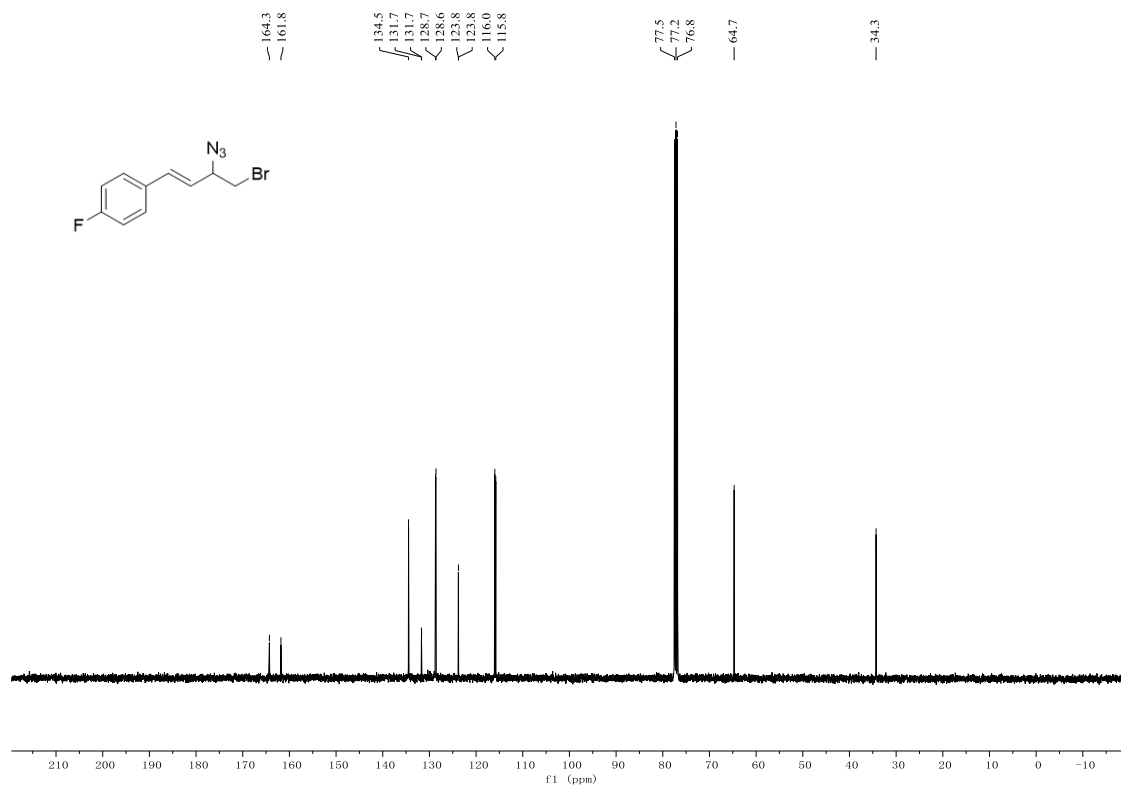


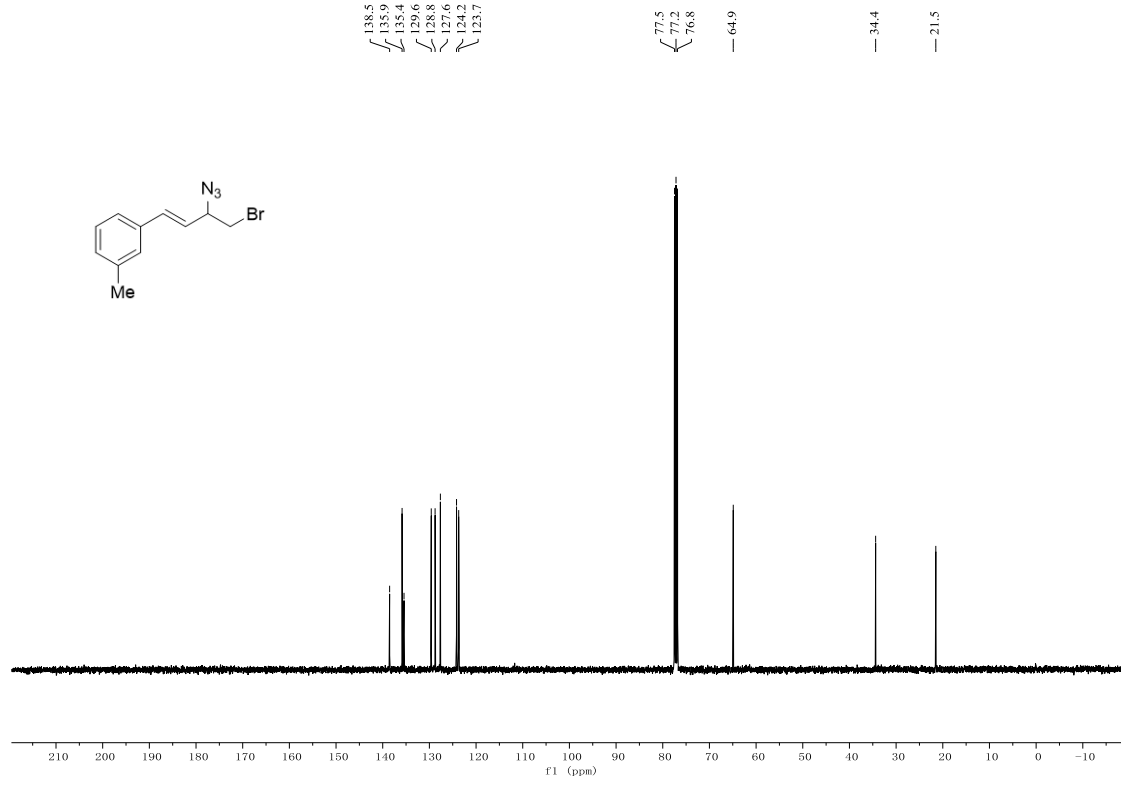
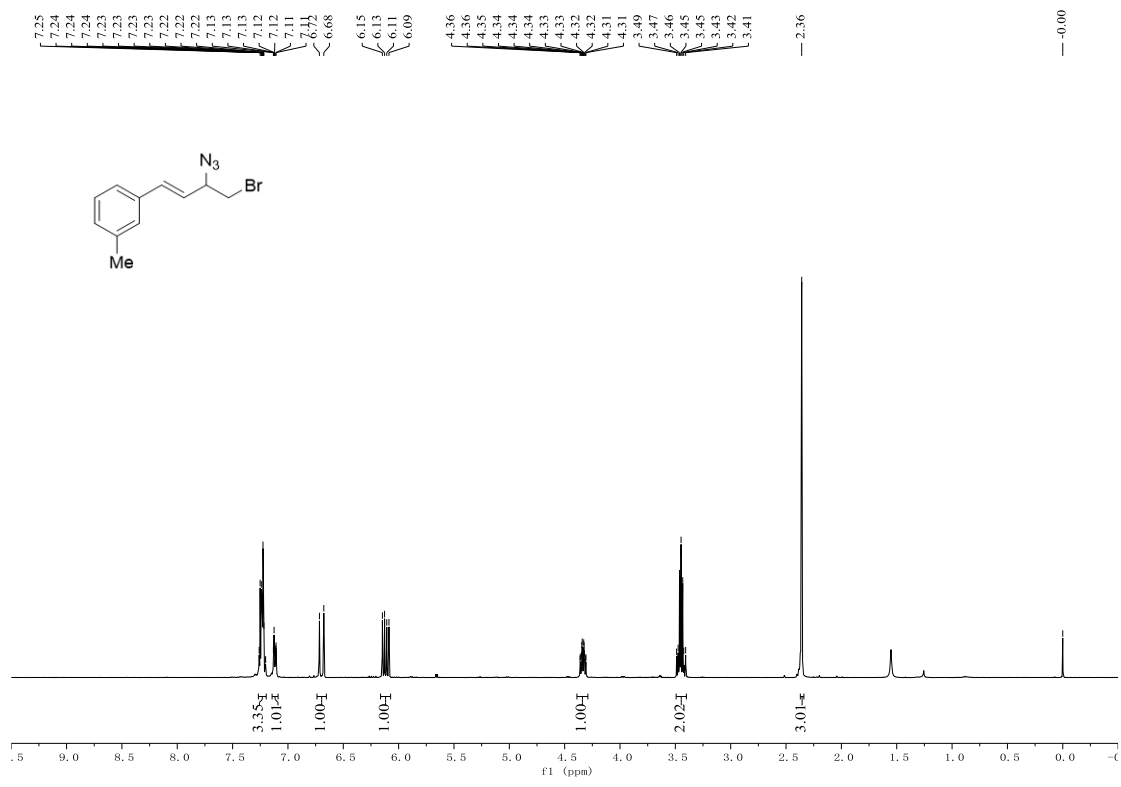


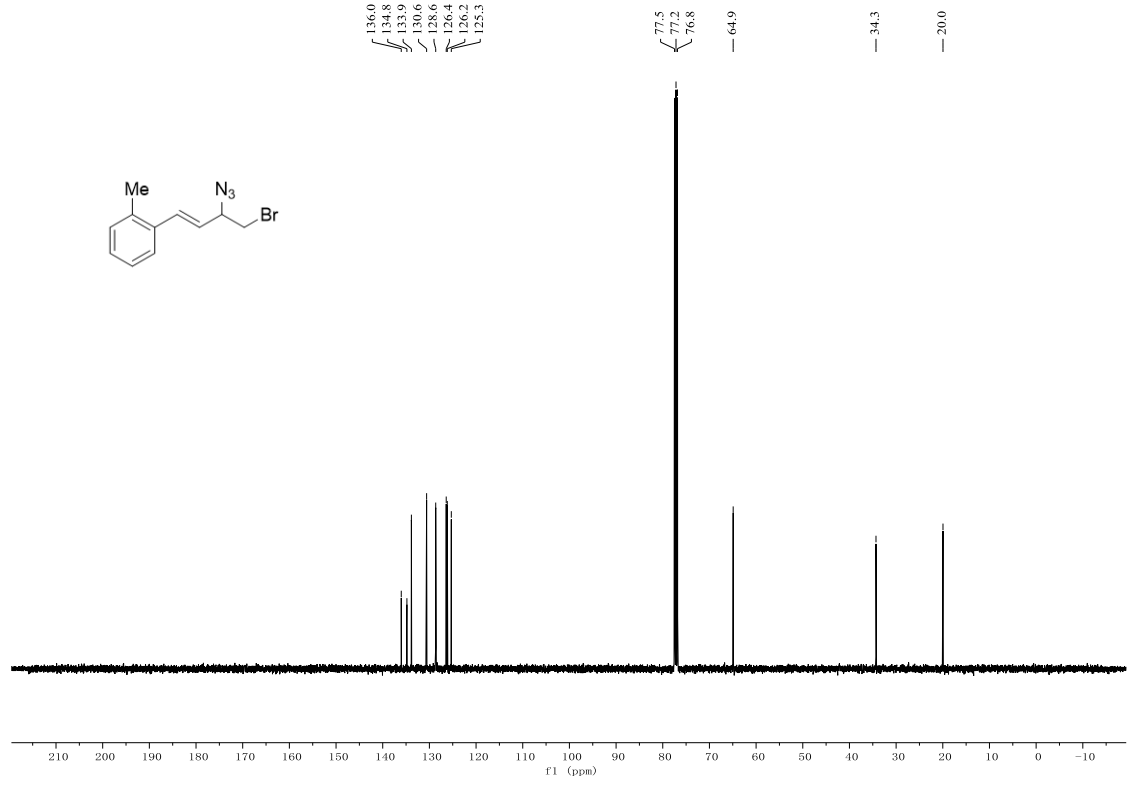
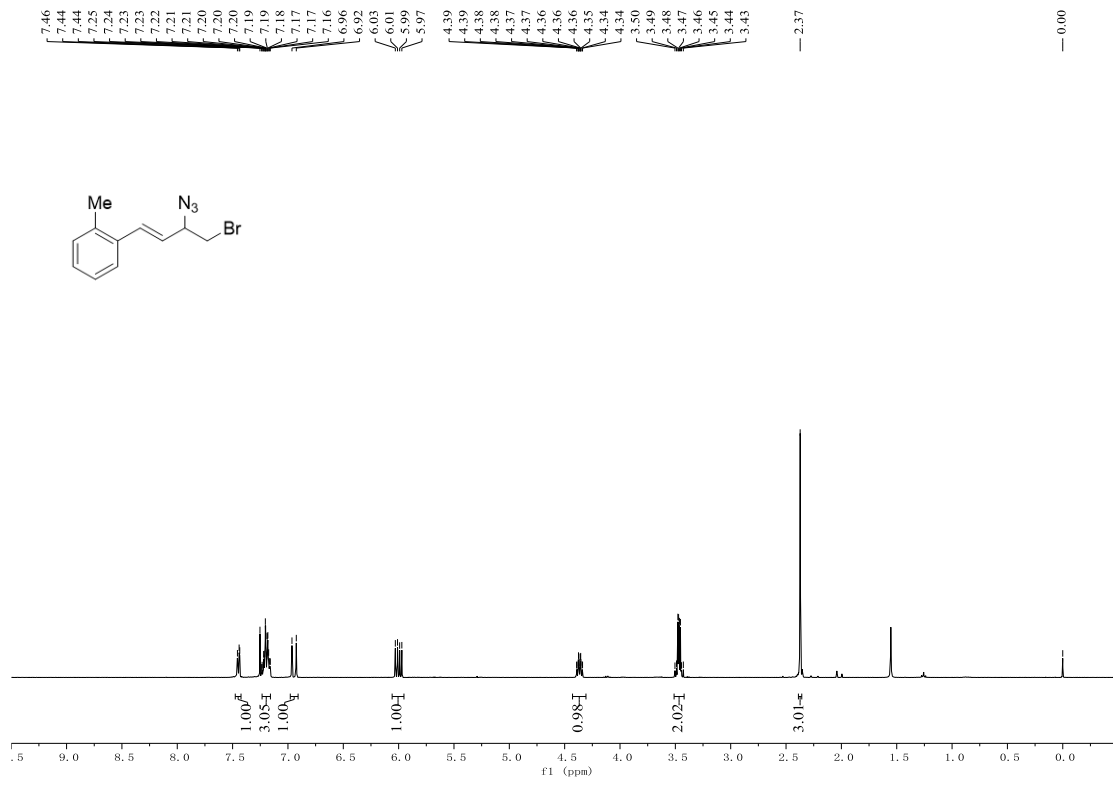


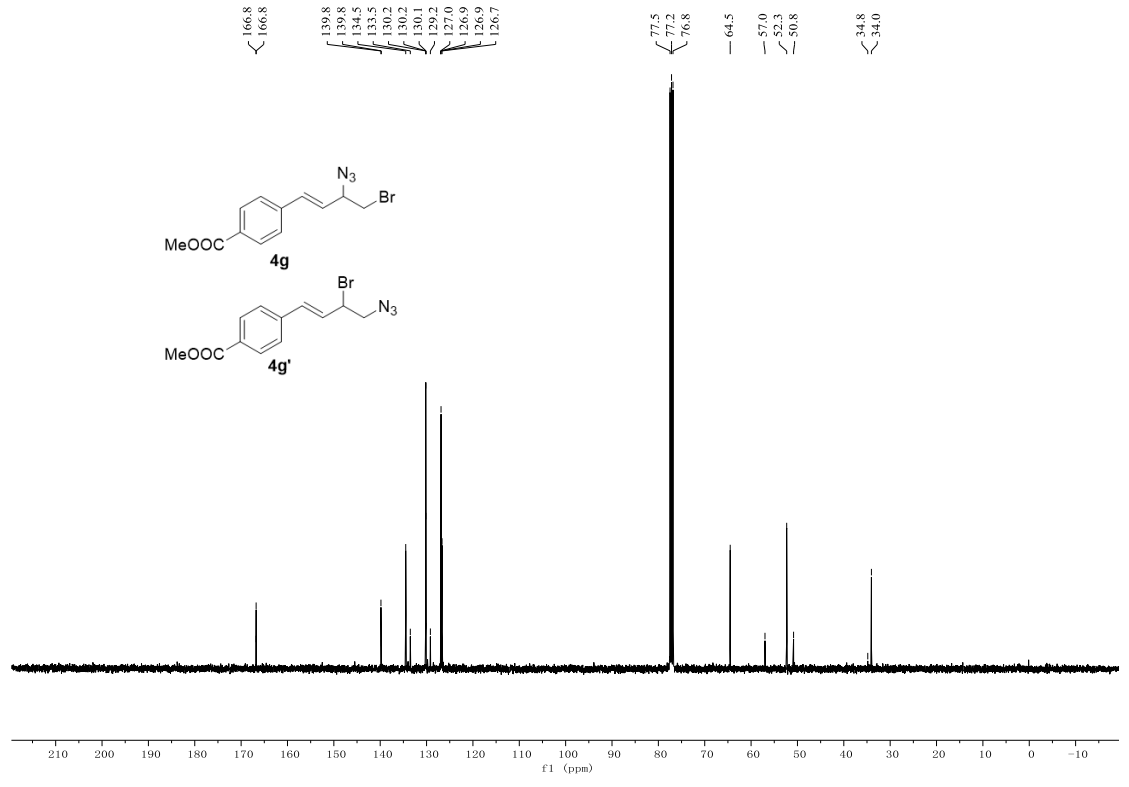
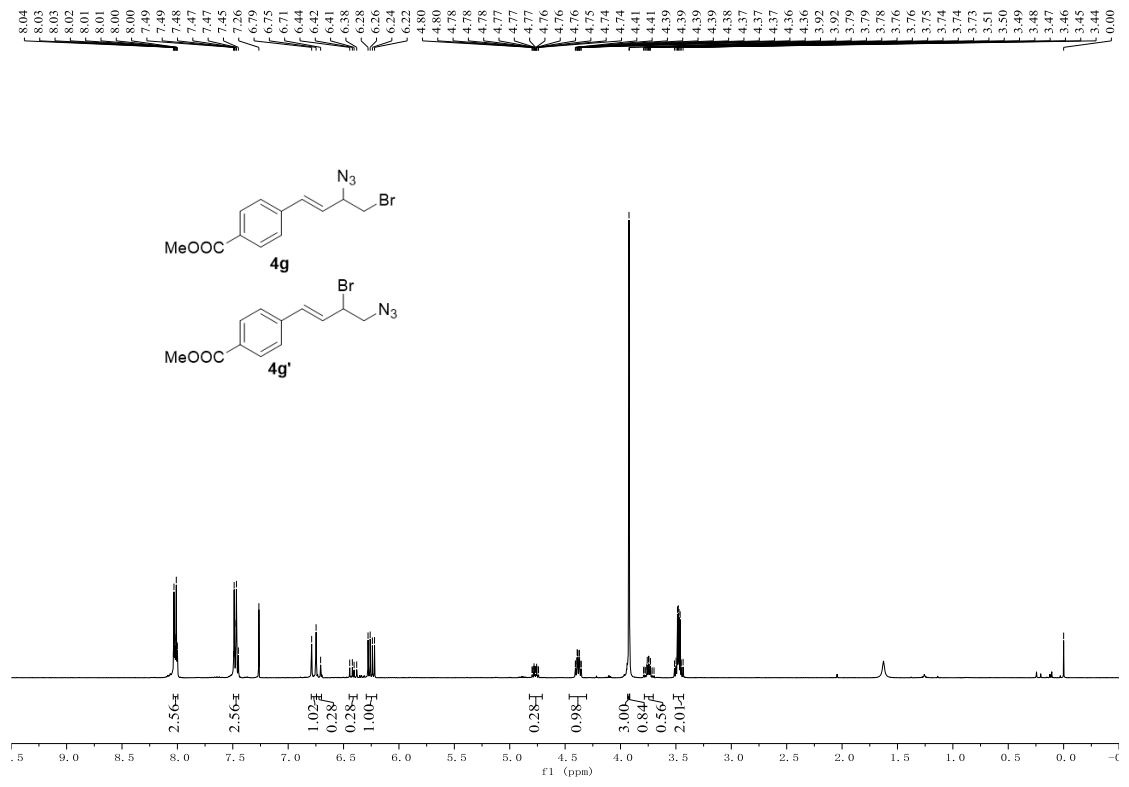




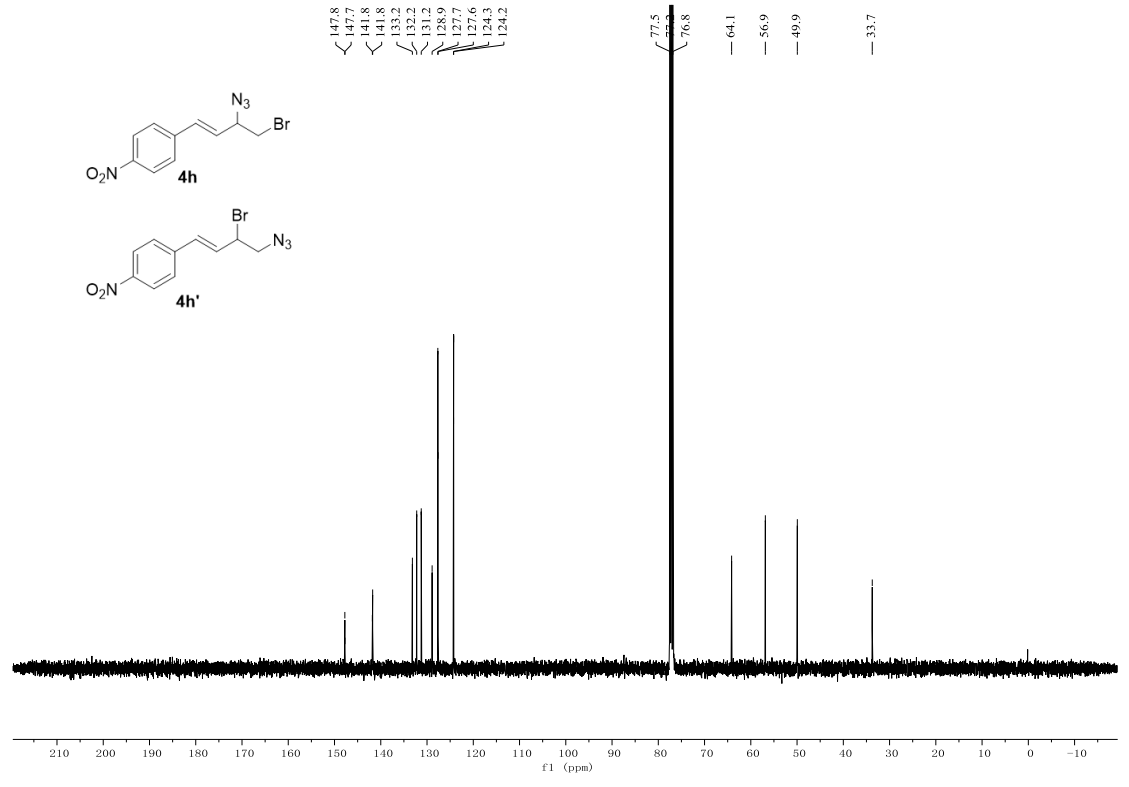
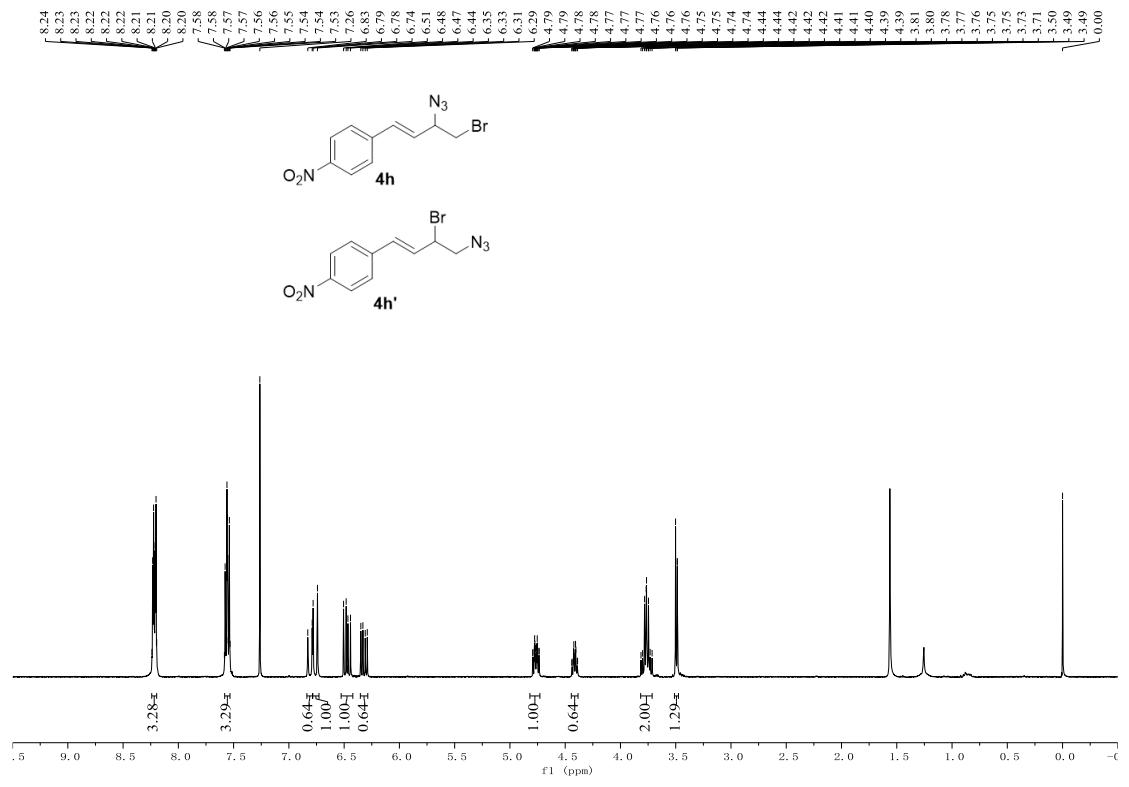


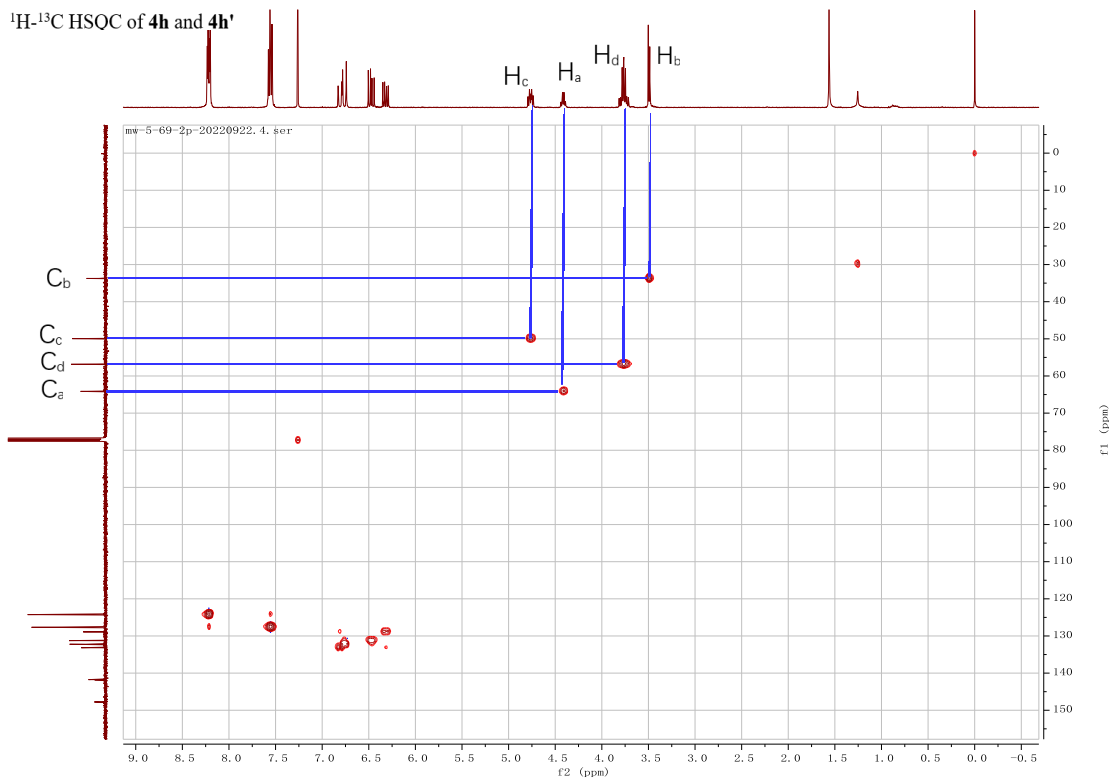
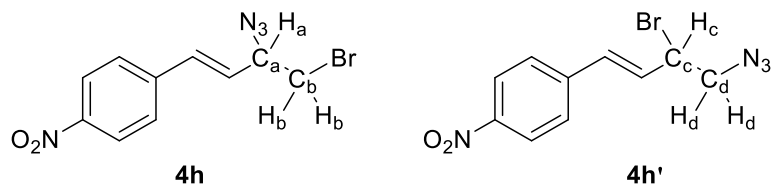




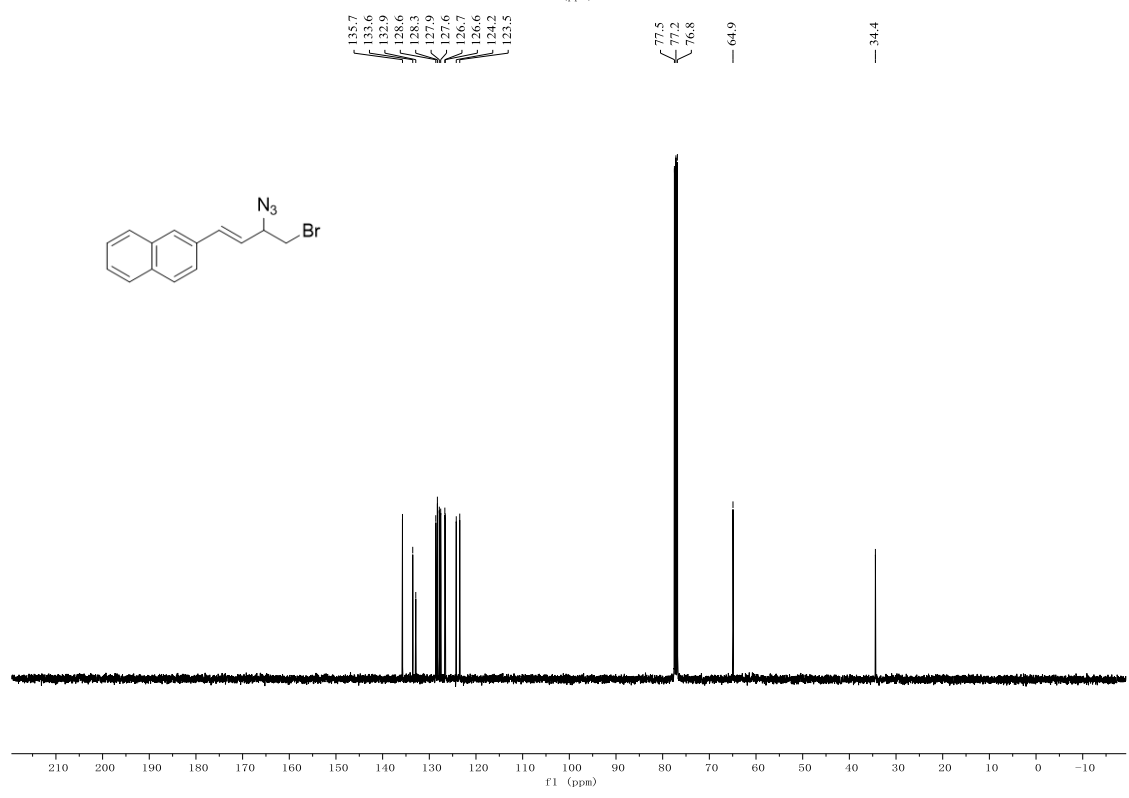
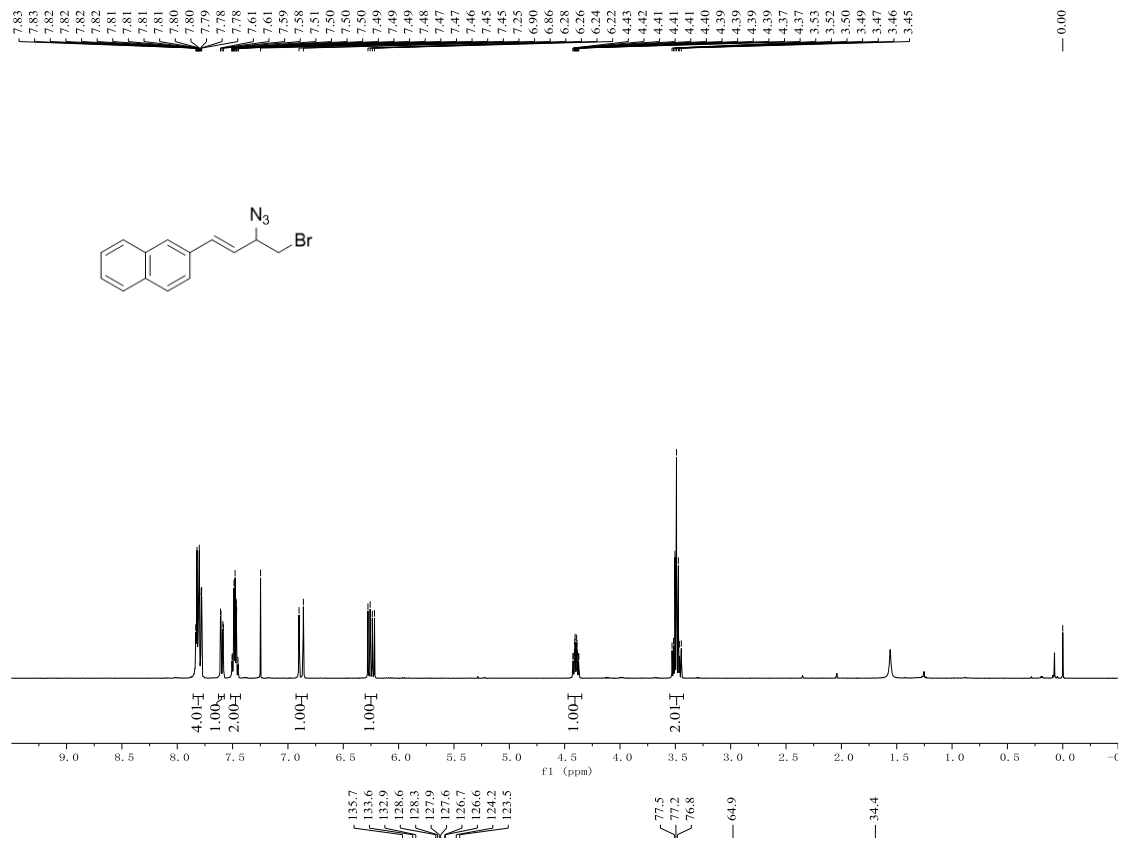


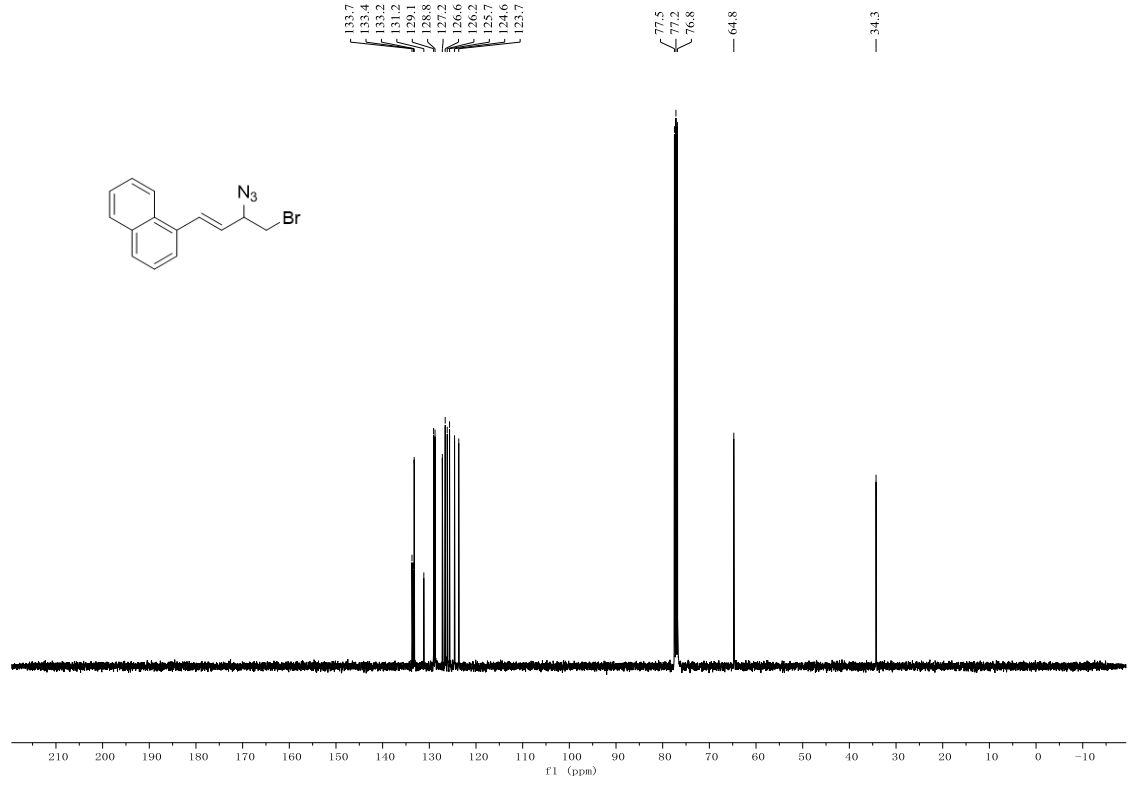
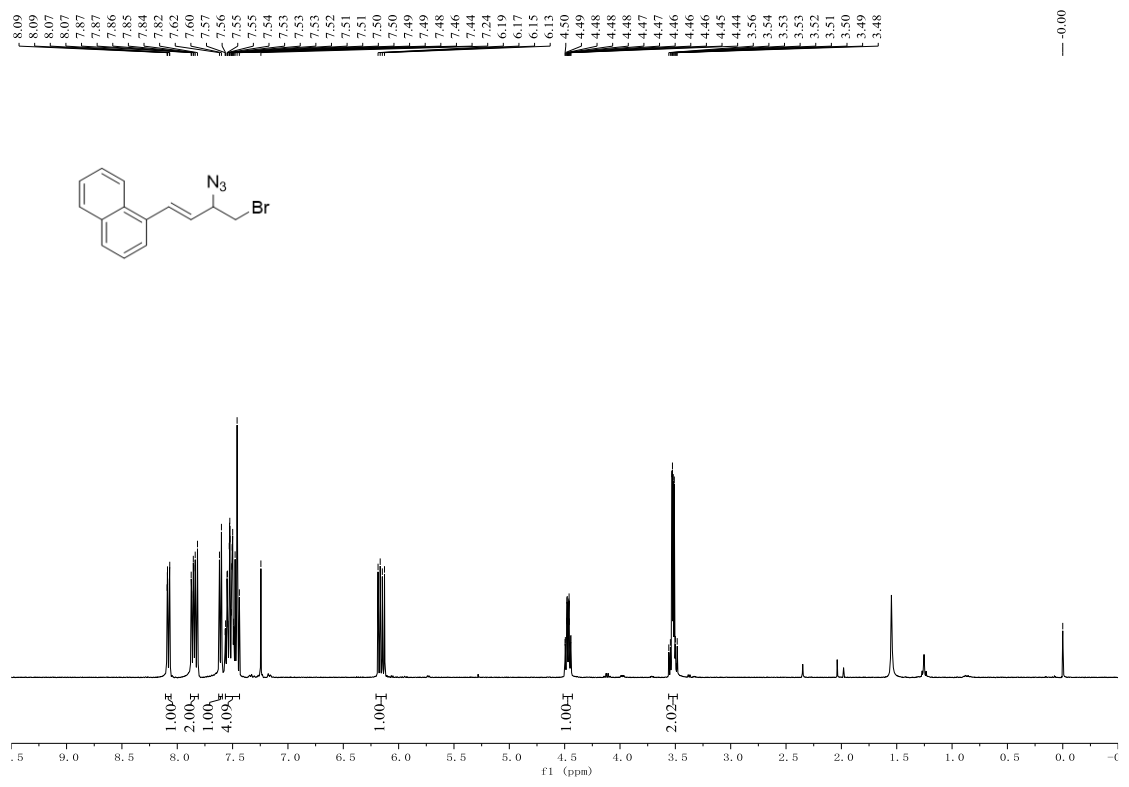


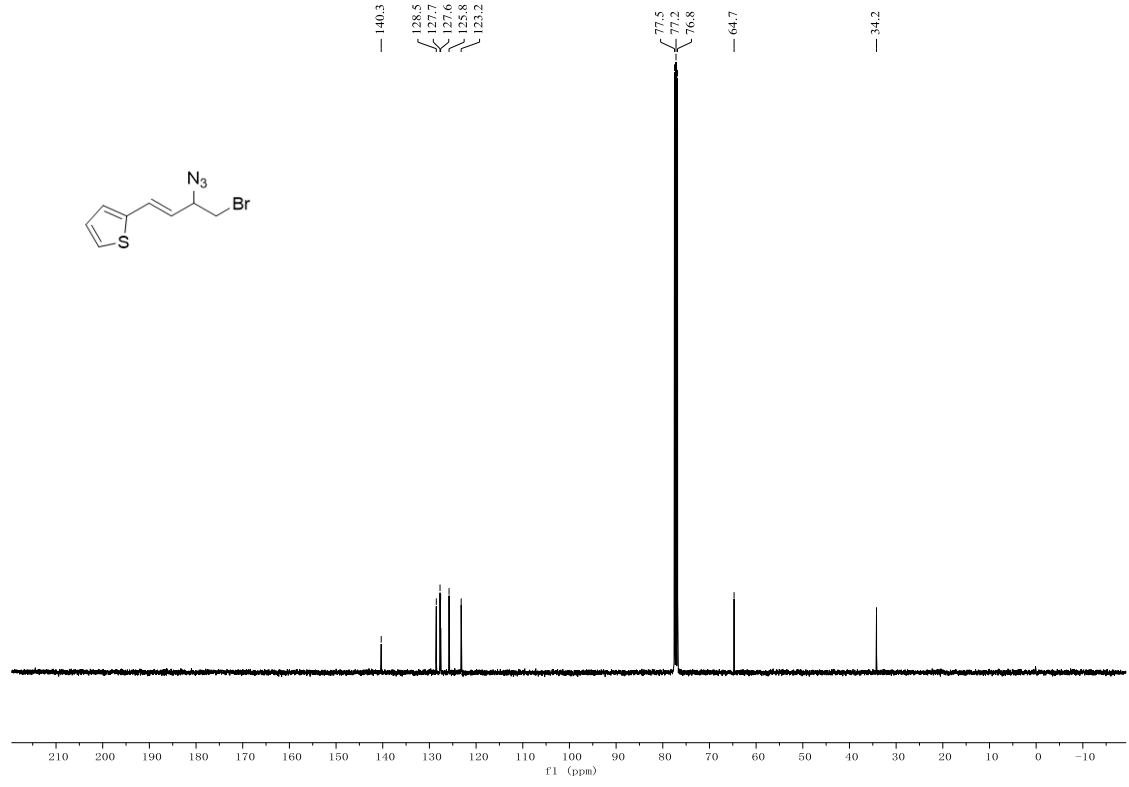
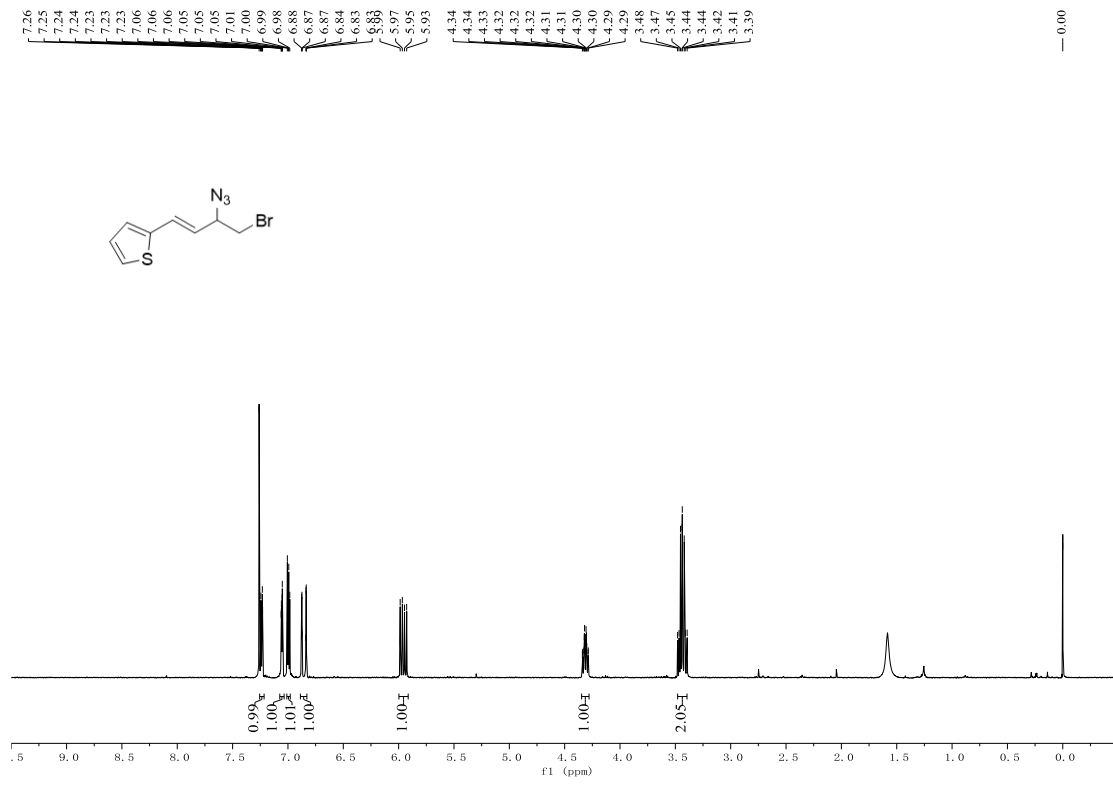


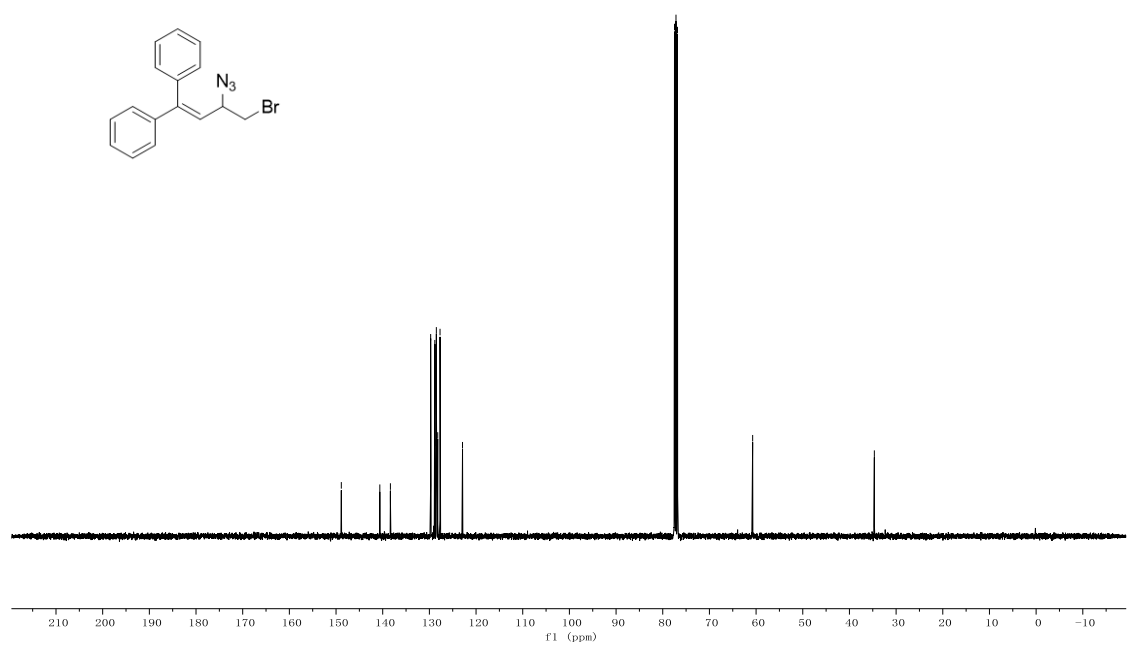
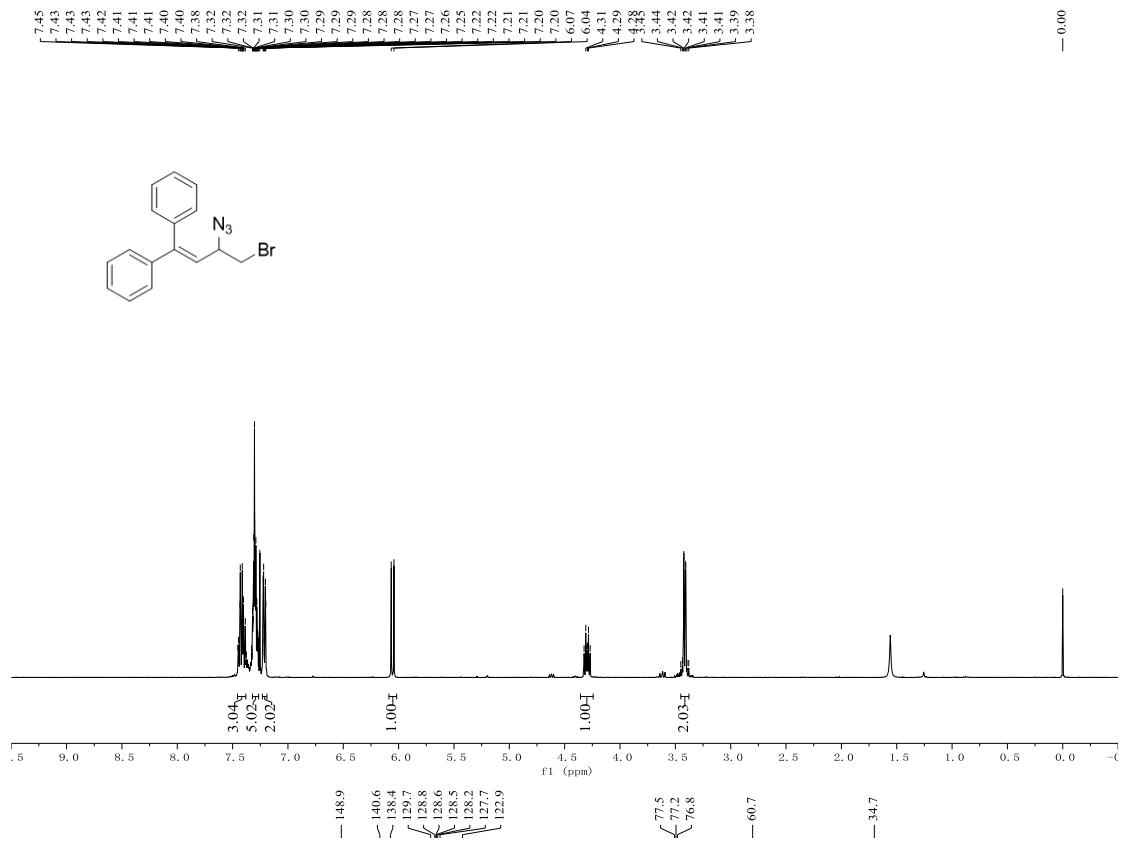


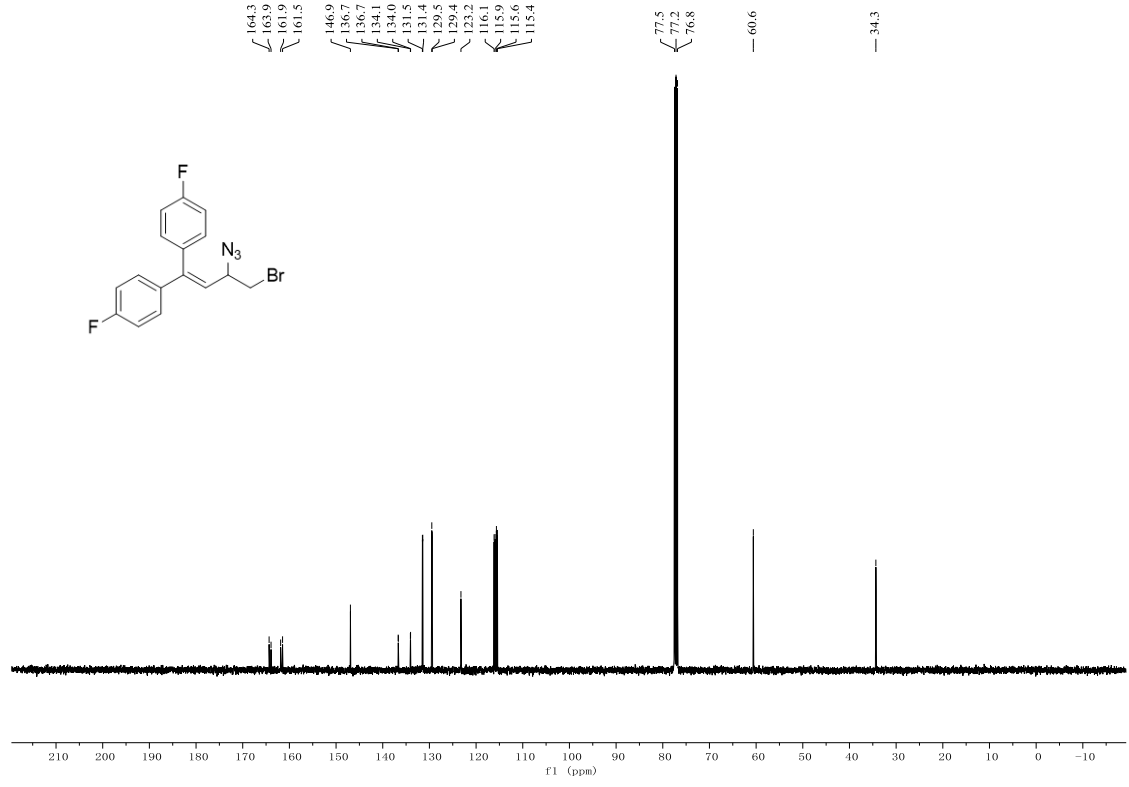
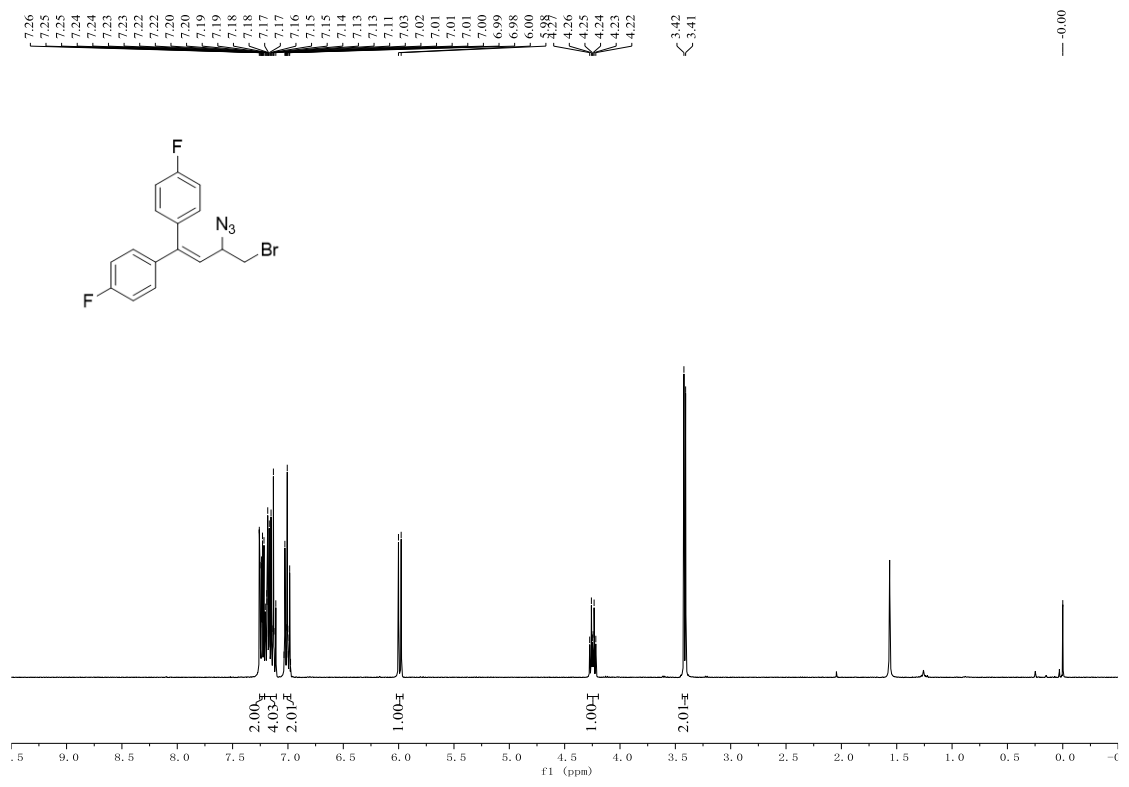
The compounds **4h** and **4h'** were determined by analysis of <sup>1</sup>H-<sup>13</sup>C HSQC spectroscopy. Due to the presence of azide group, the chemical shift of C<sub>a</sub> is obviously larger than that of C<sub>b</sub> and the chemical shift of C<sub>d</sub> is larger than that of C<sub>c</sub>. The chemical shifts of compounds (1-azido-2-bromoethyl)benzene<sup>[13]</sup> and (2-azido-1-bromoethyl)benzene<sup>[14]</sup> can be used as reference values.





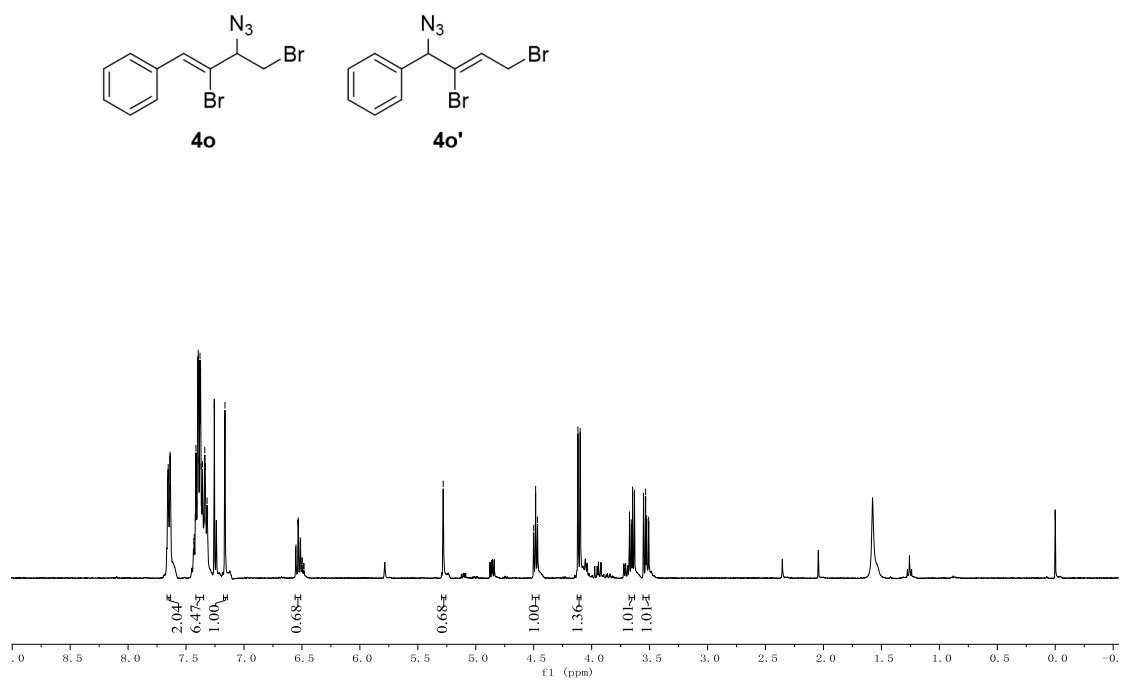
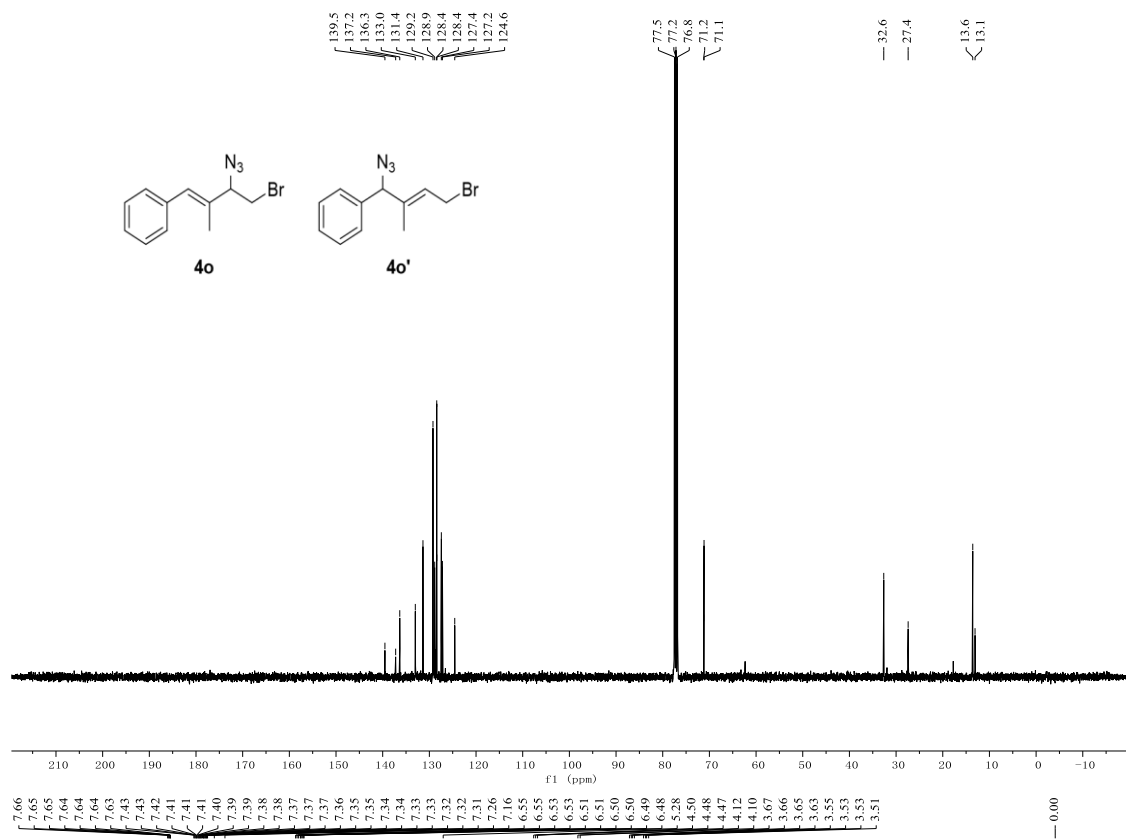


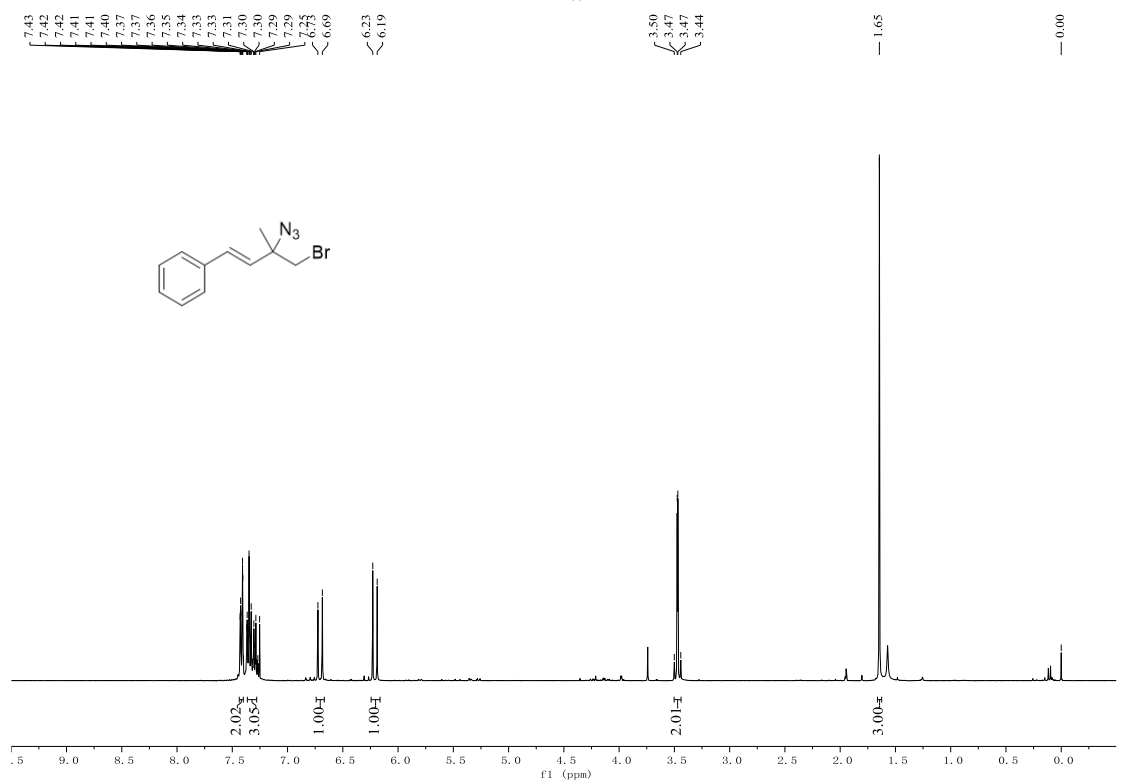
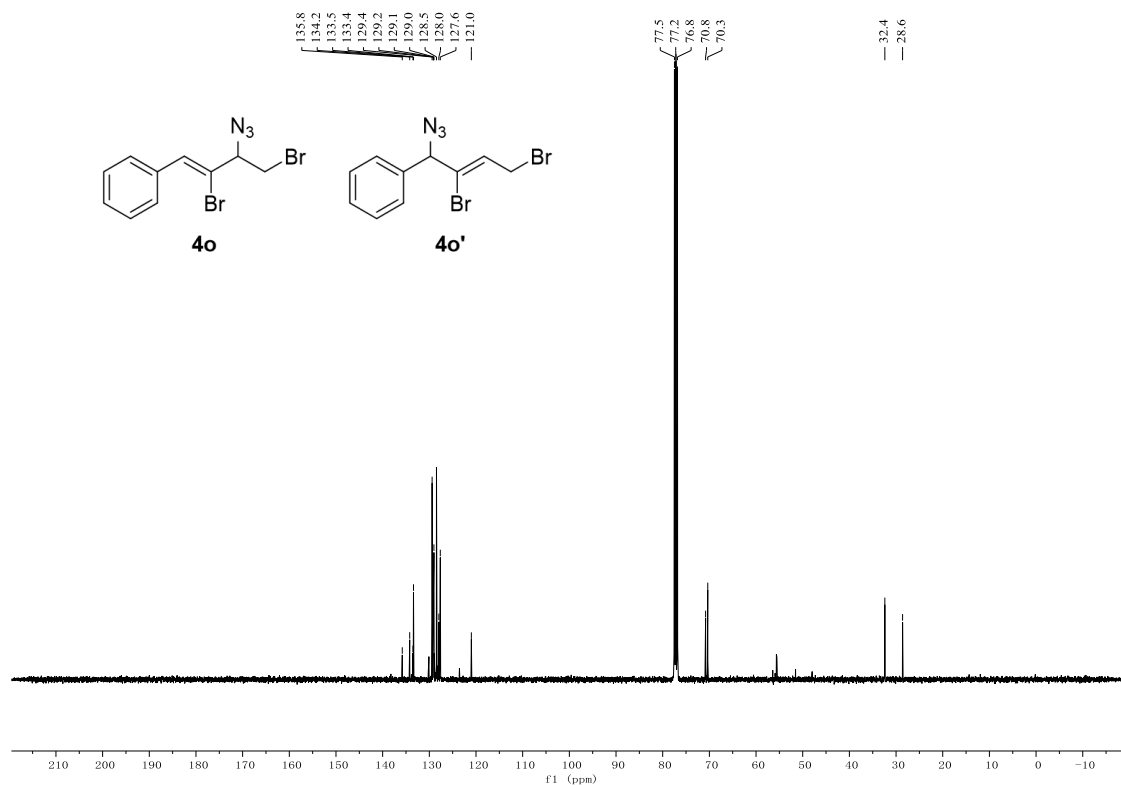


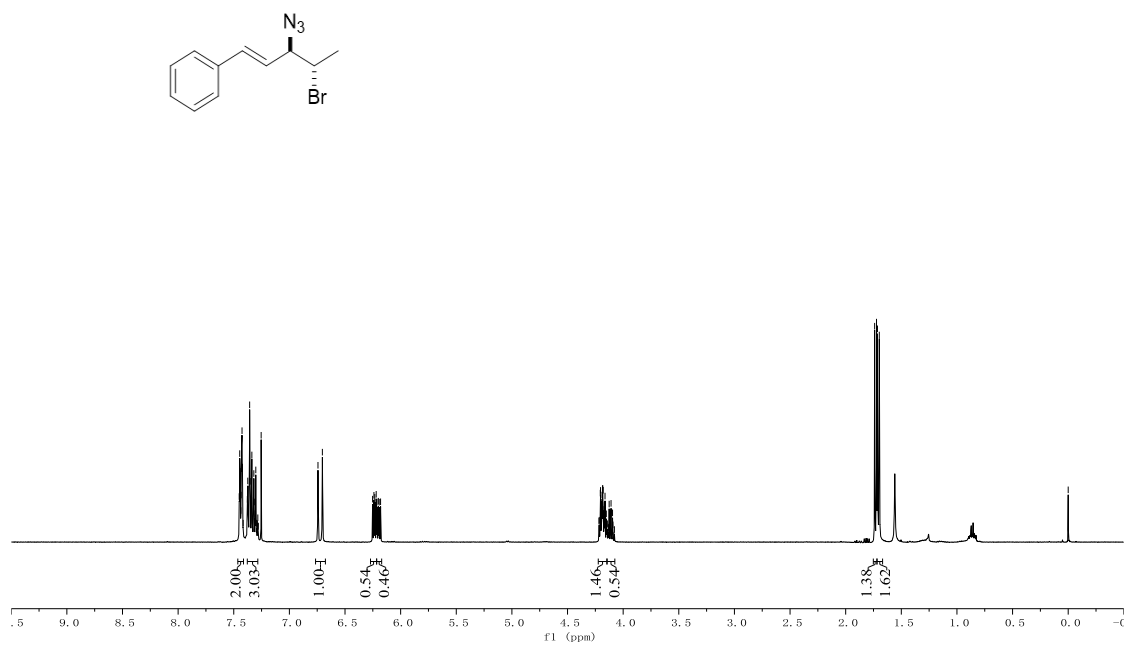
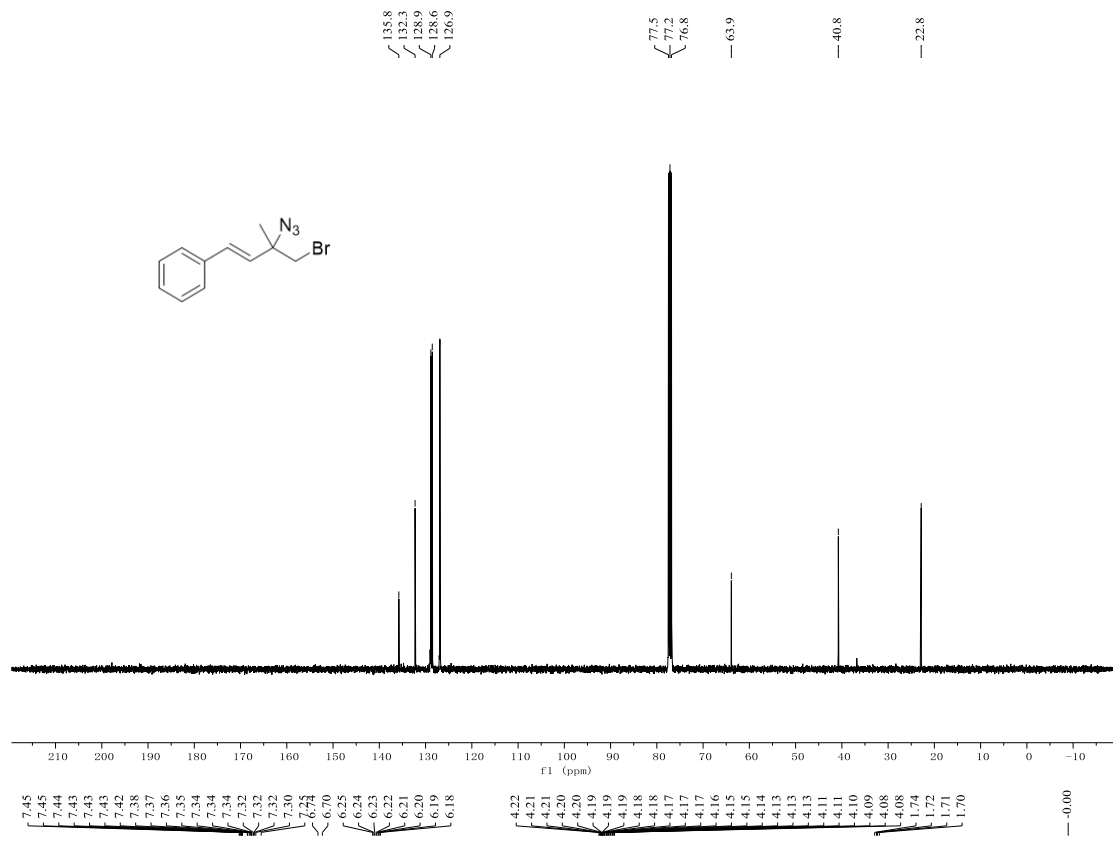


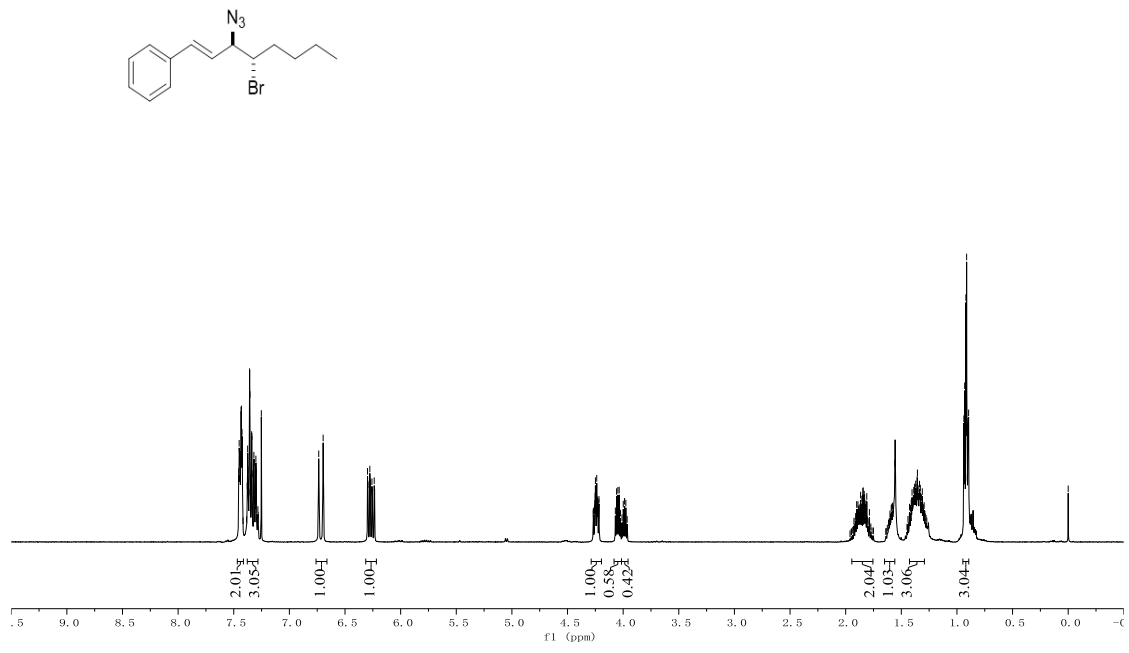
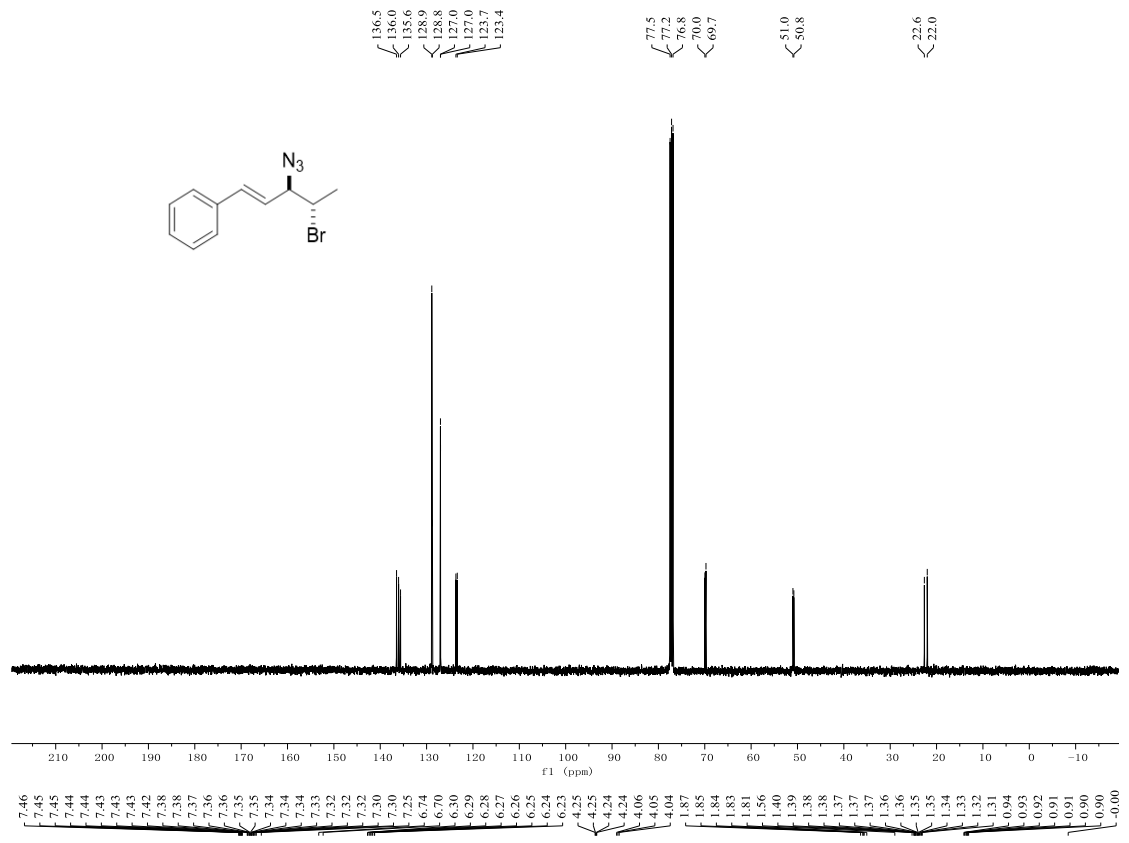


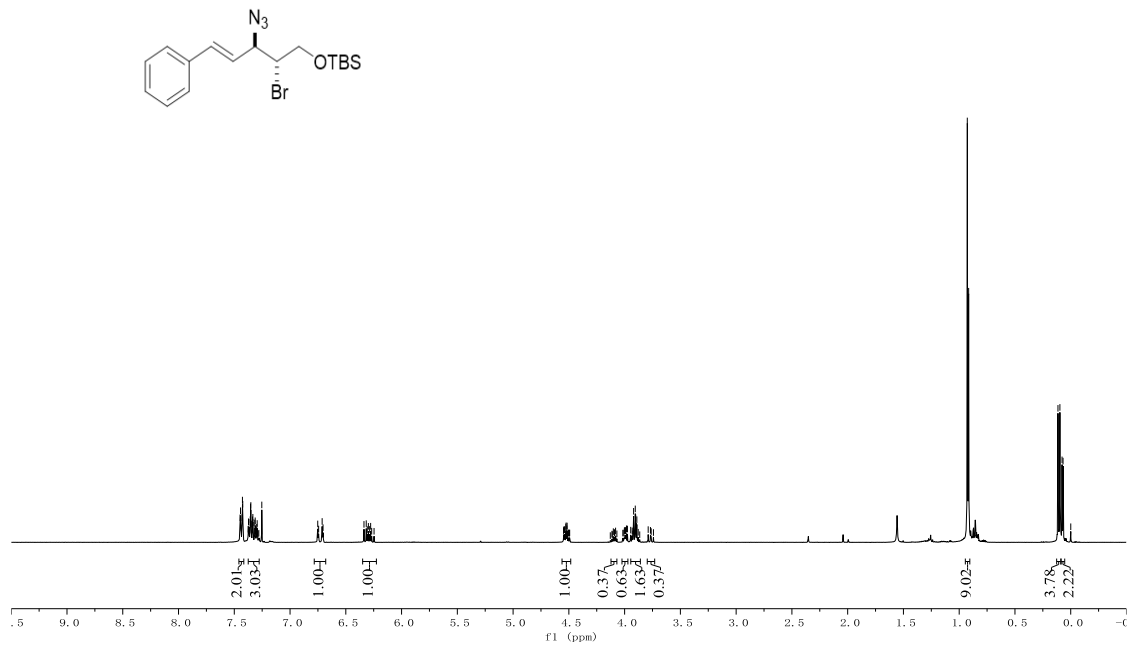
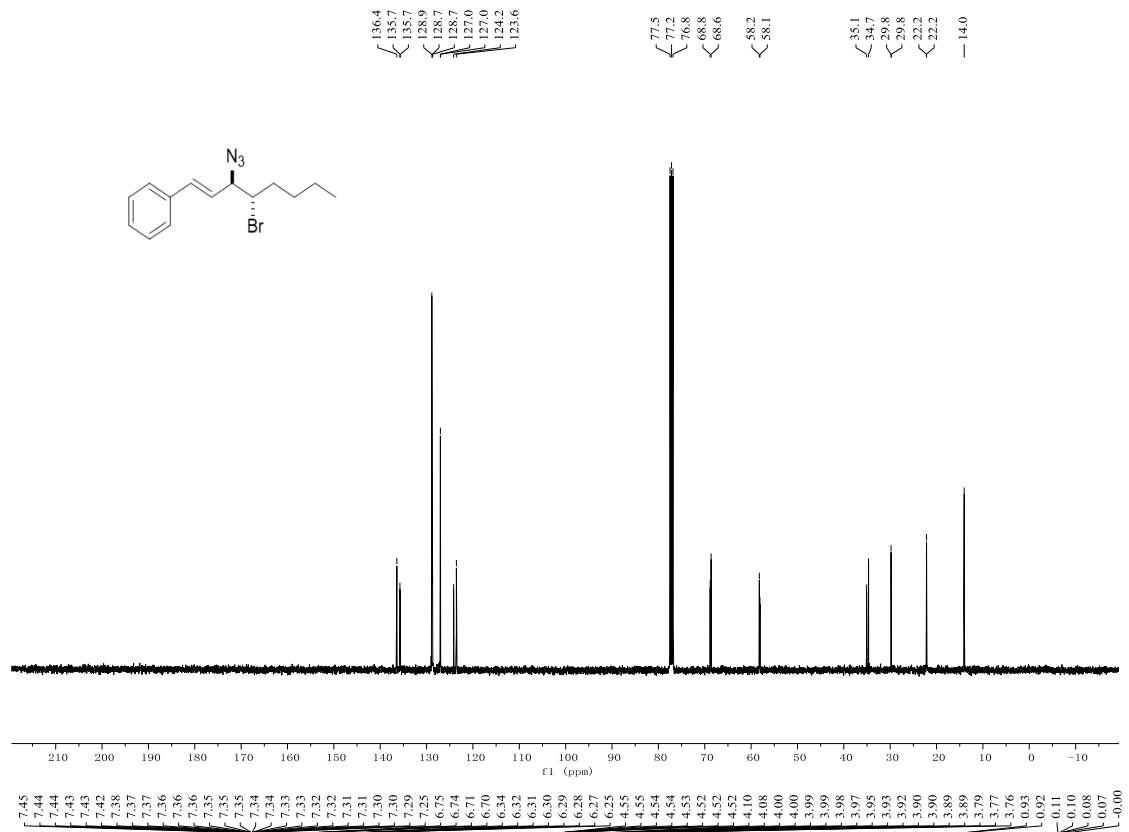


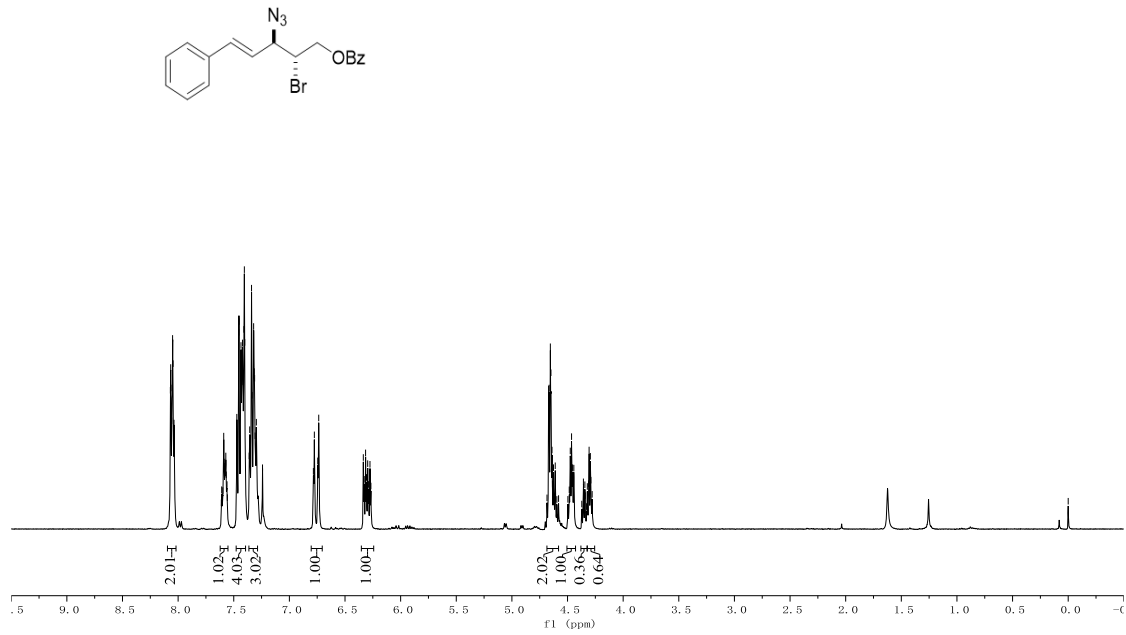
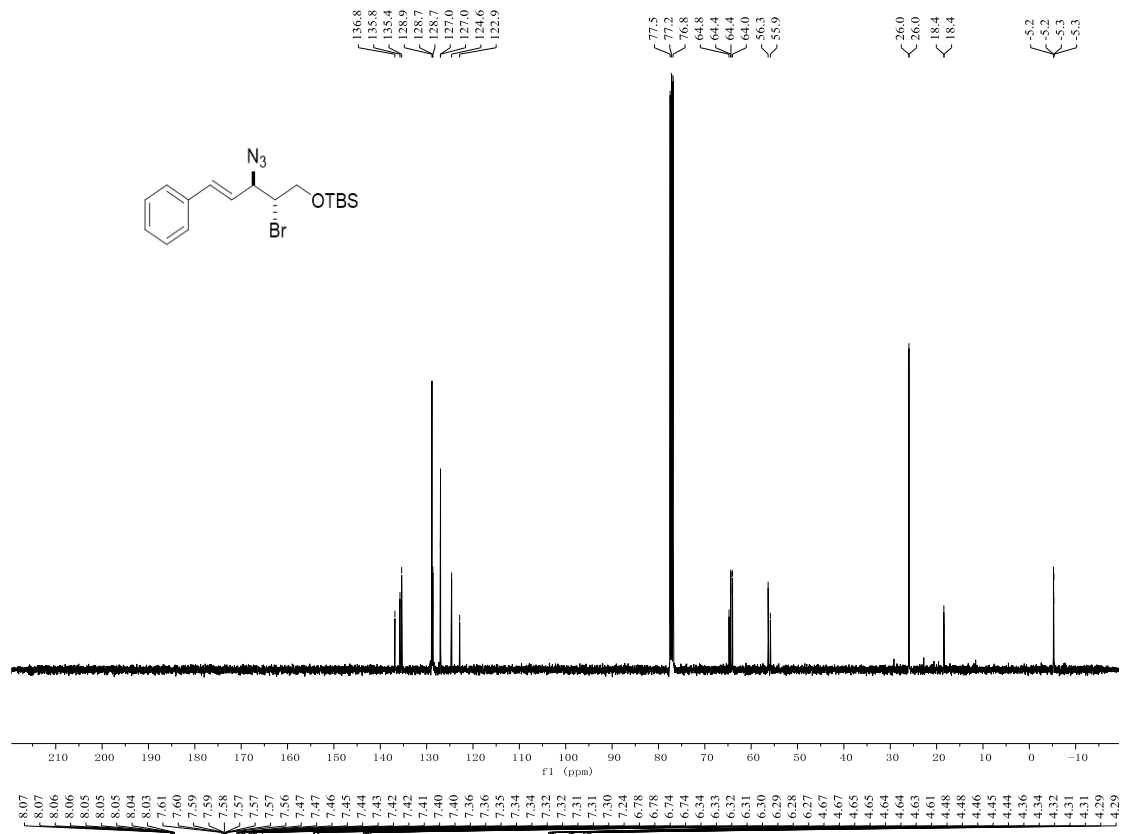


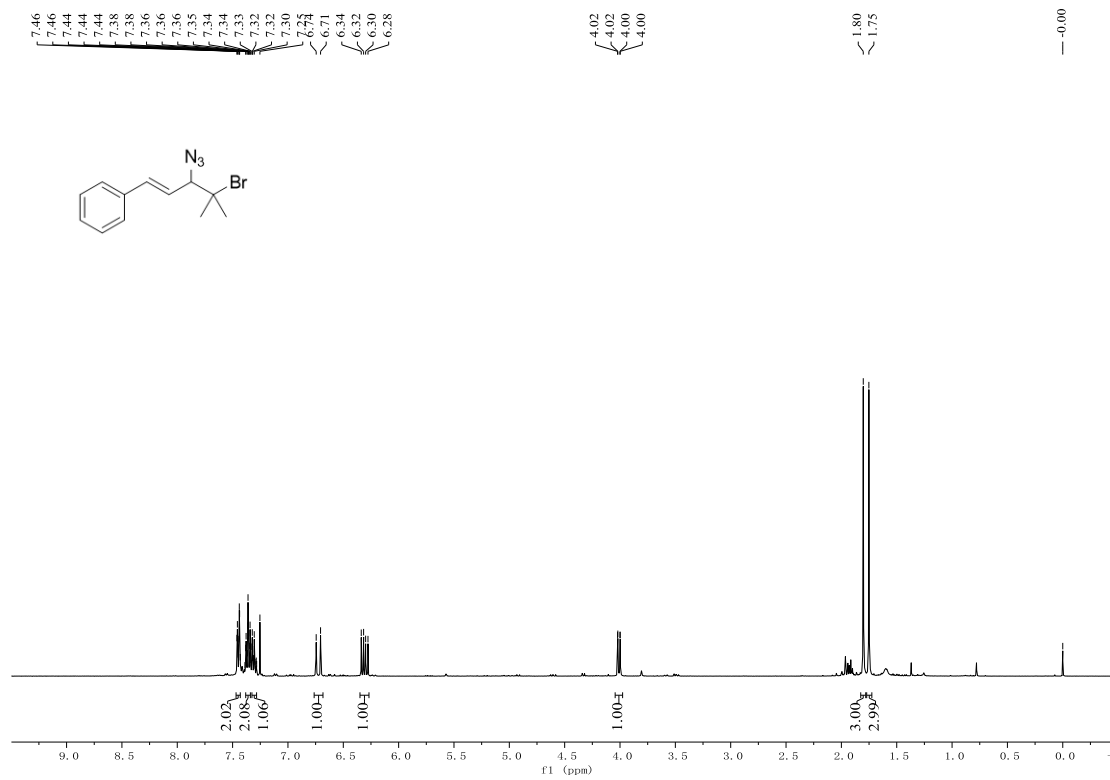
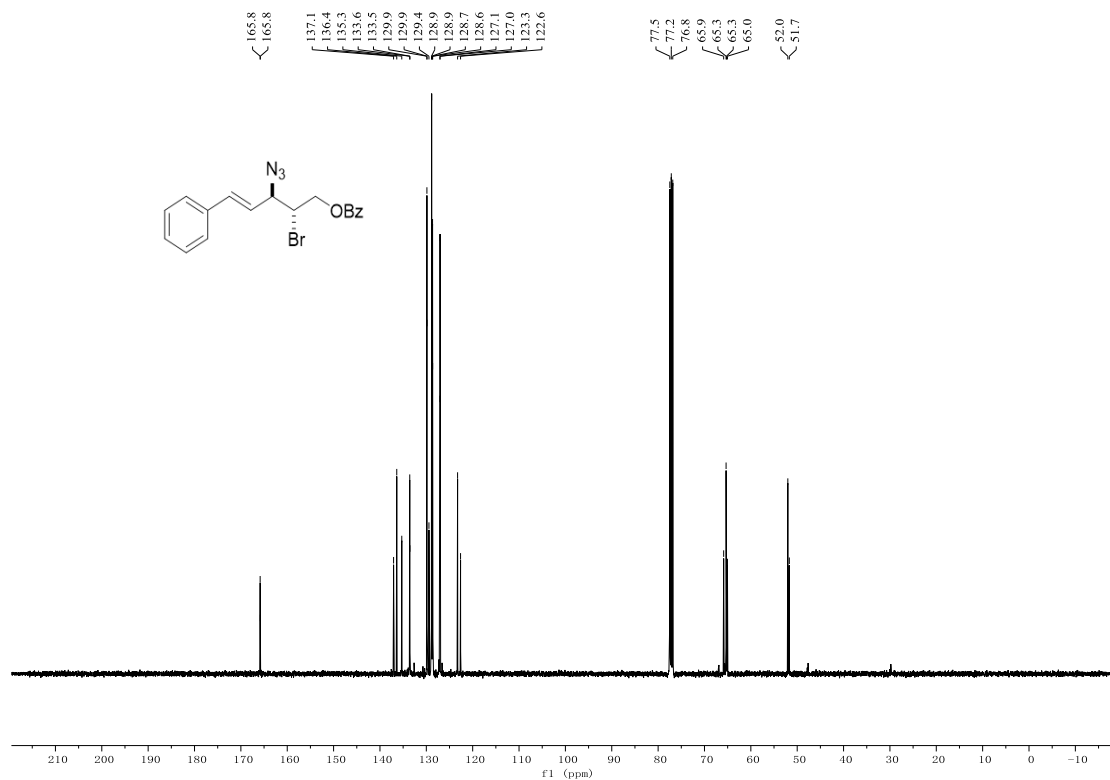


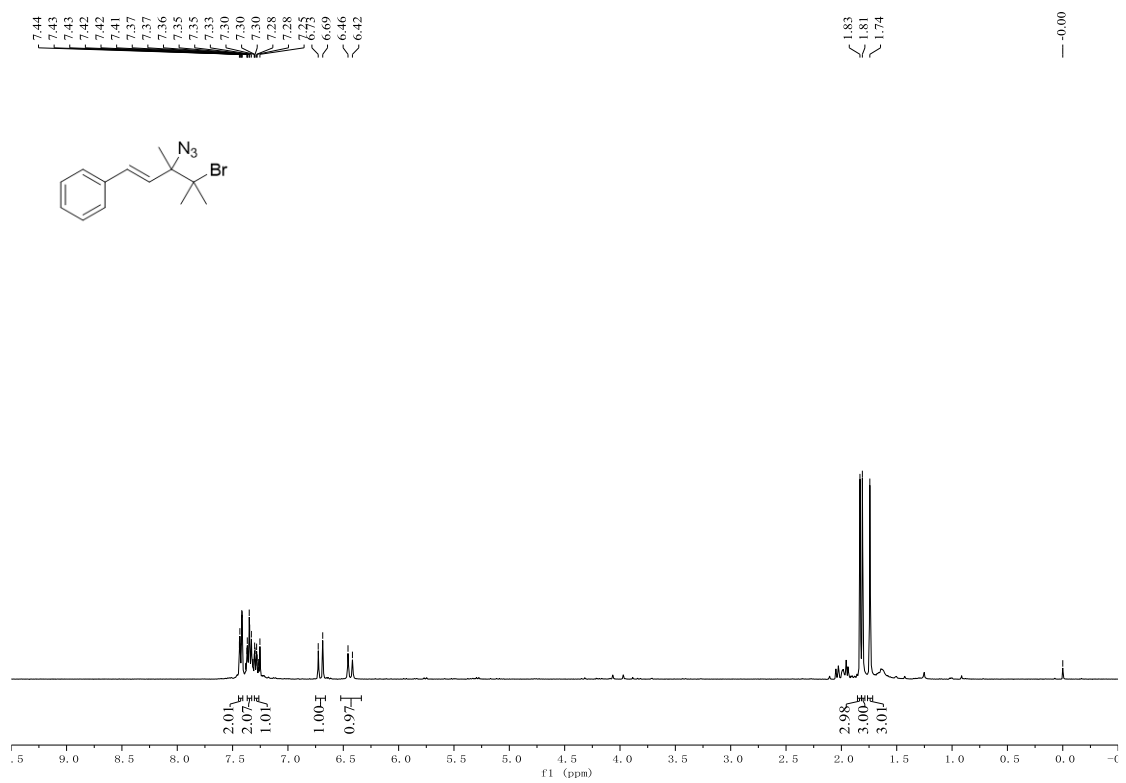
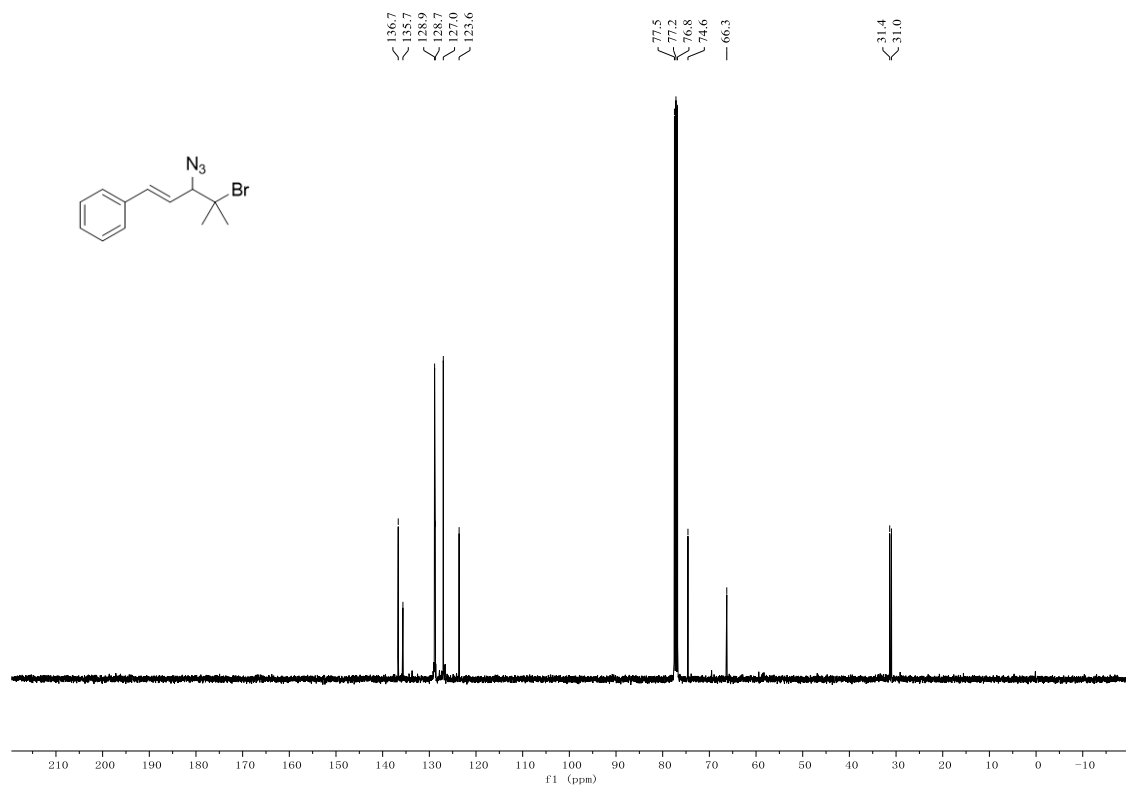




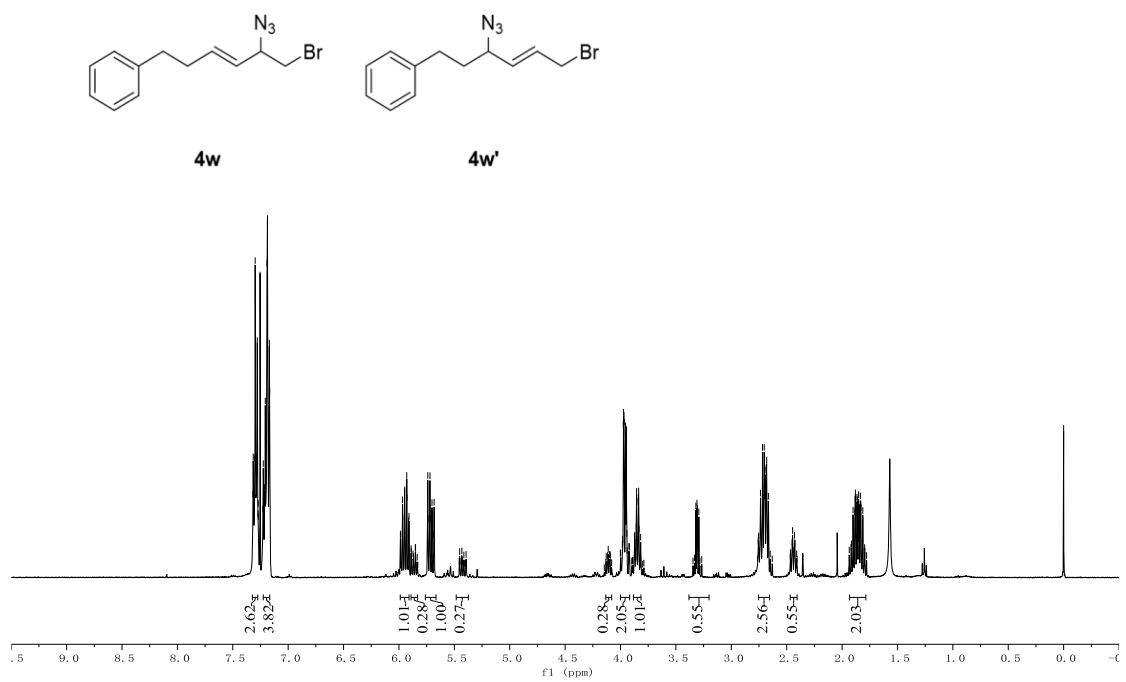
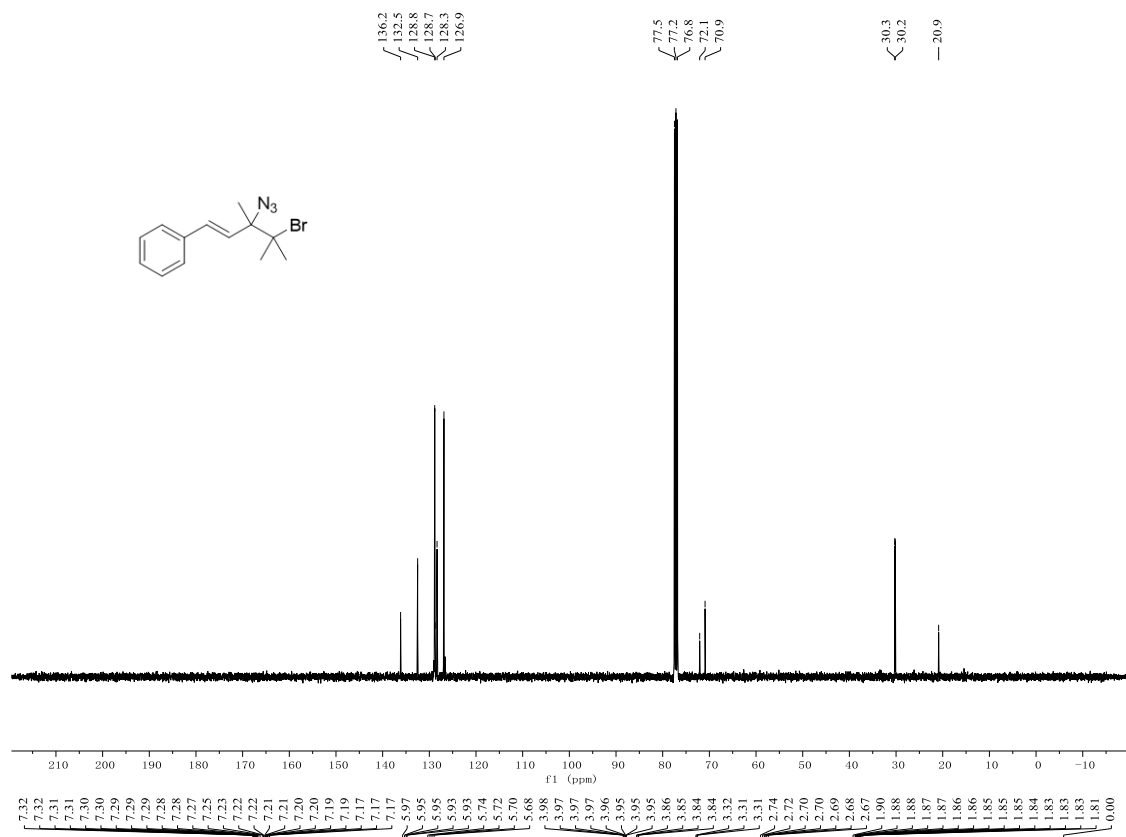


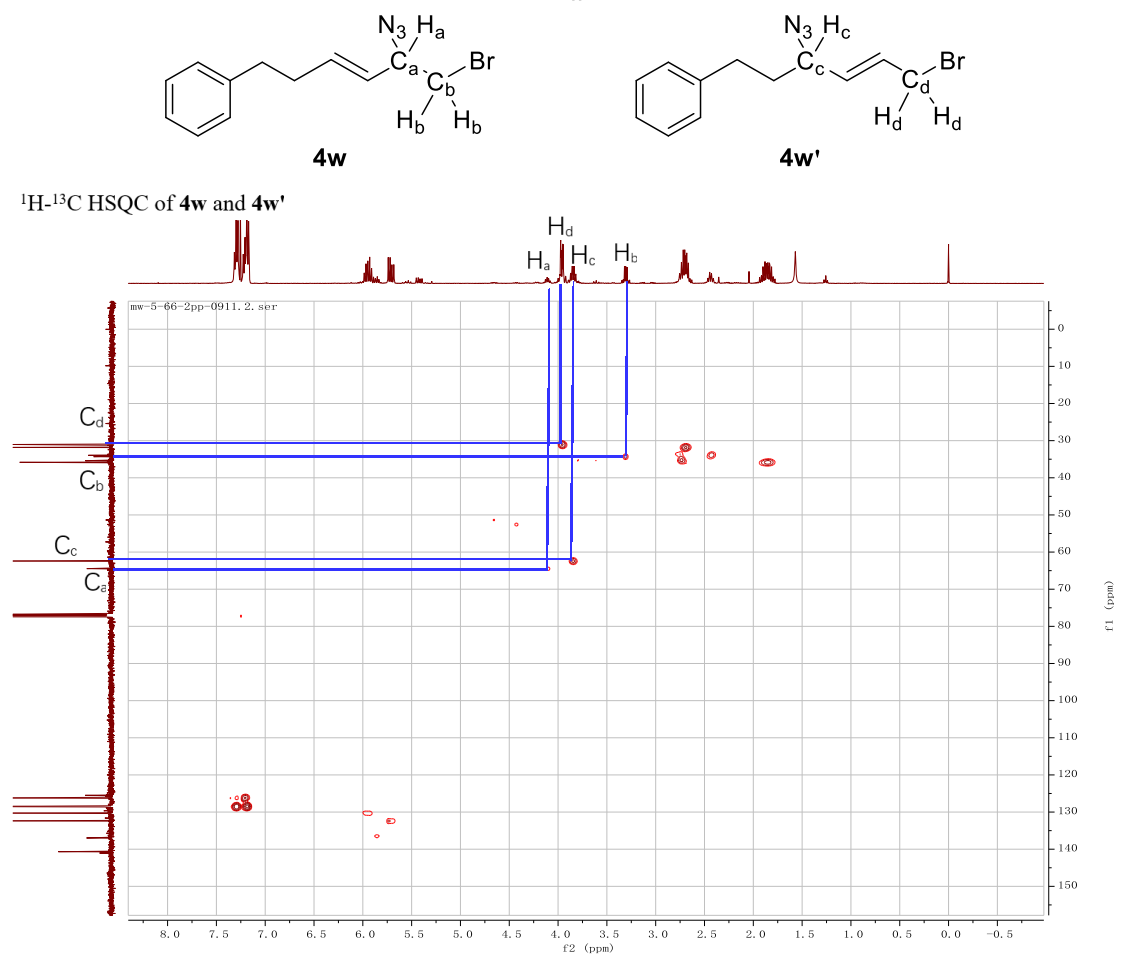
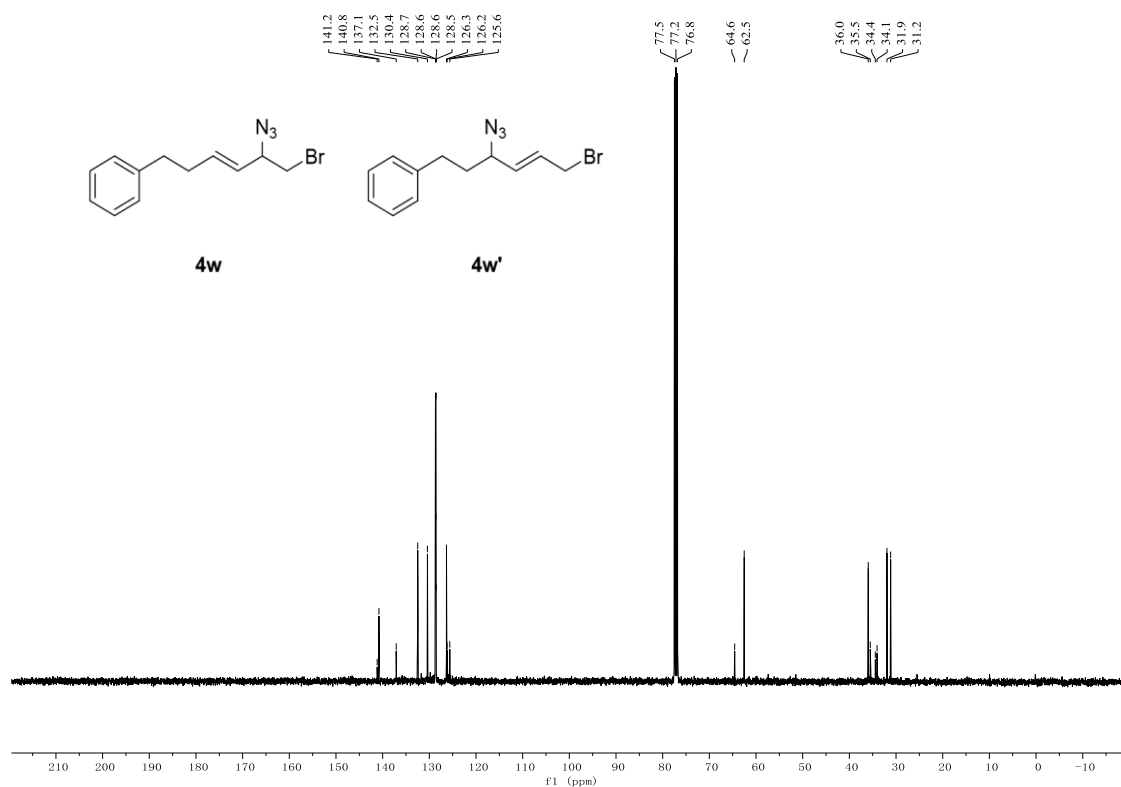




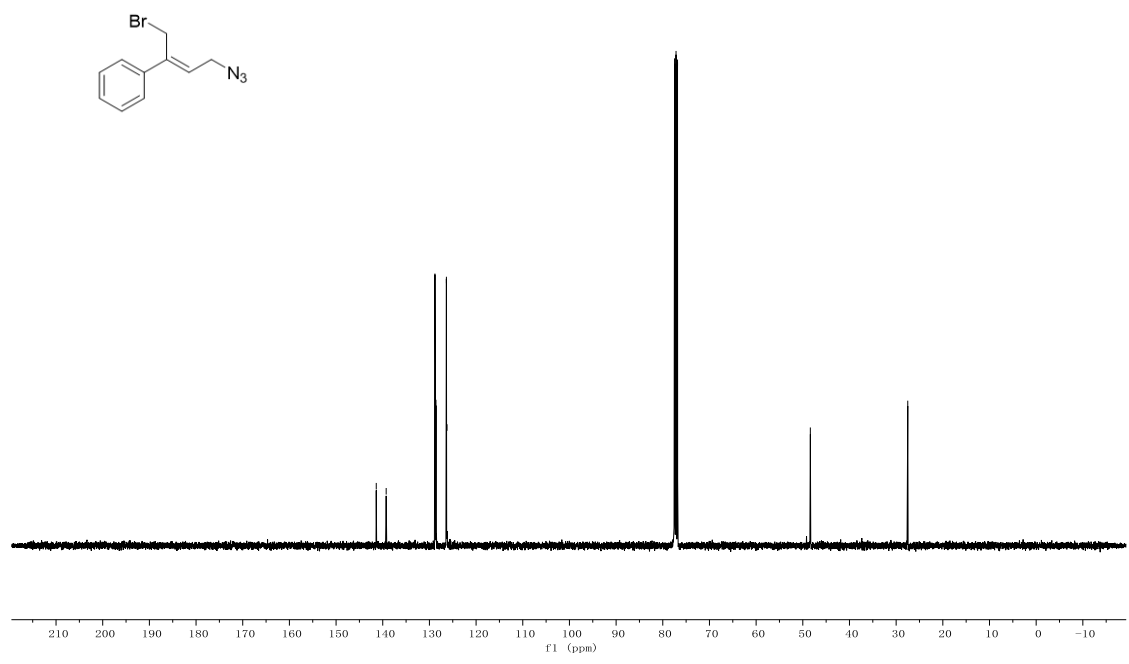
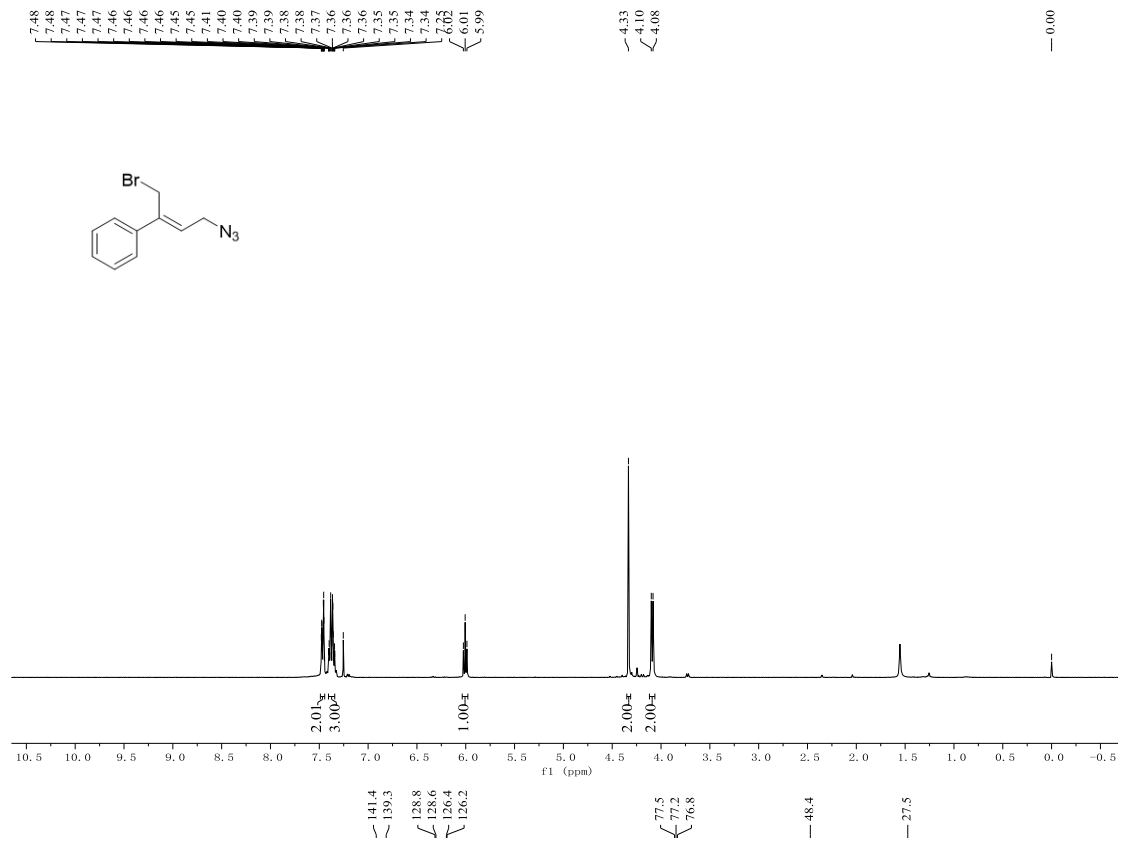




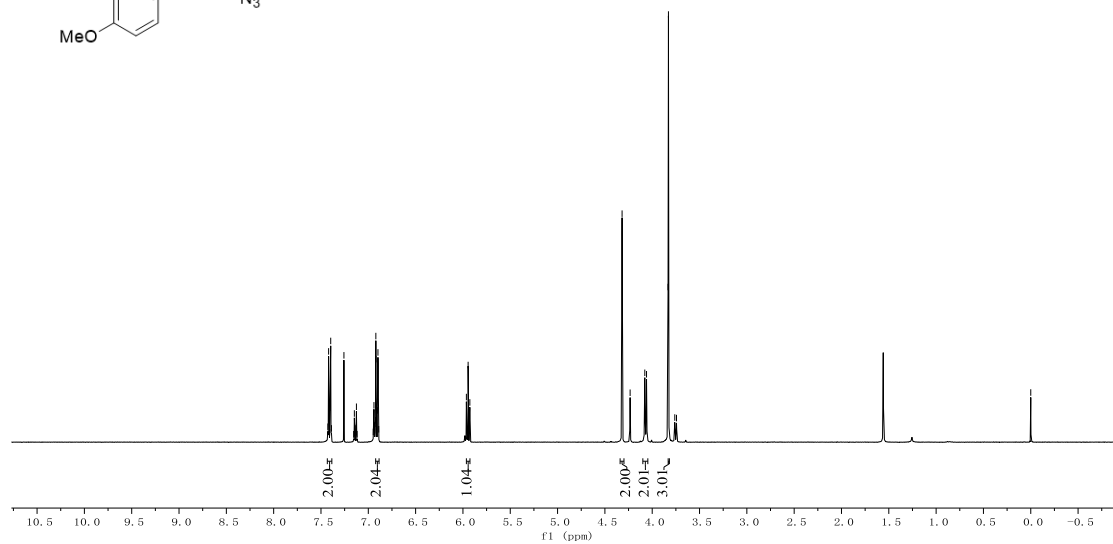
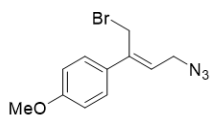
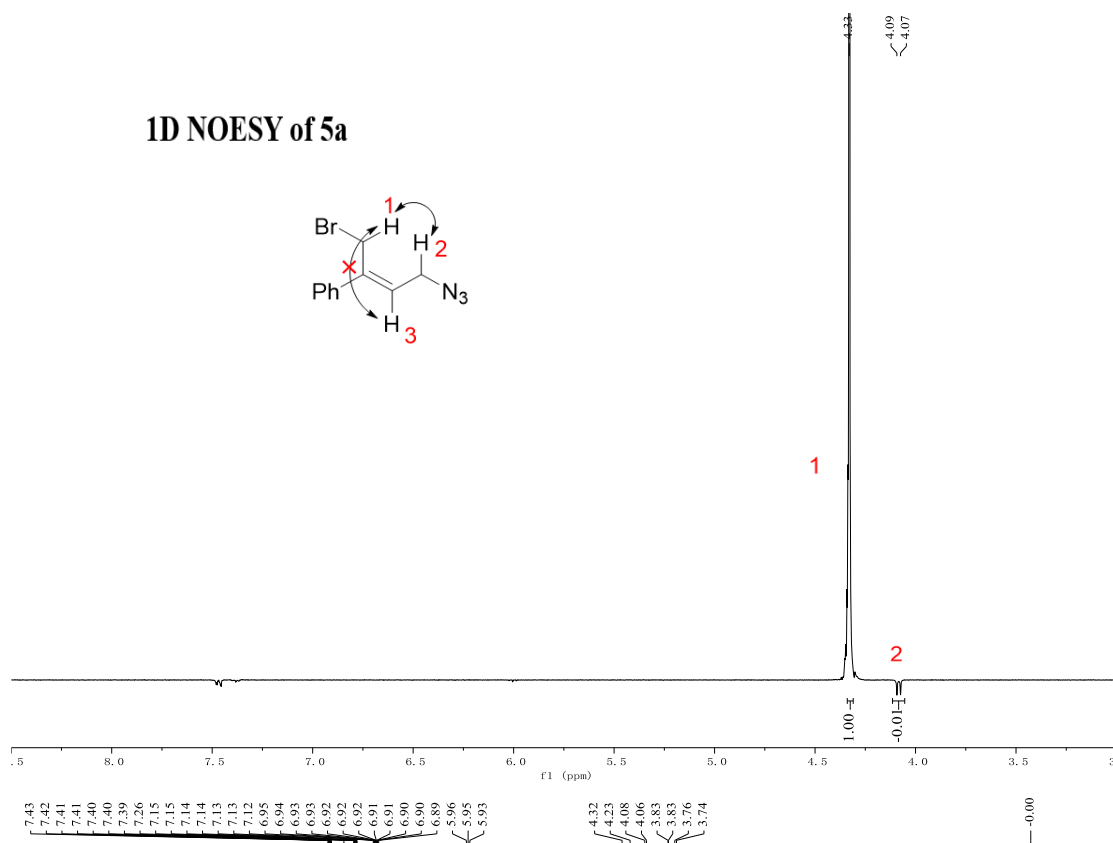
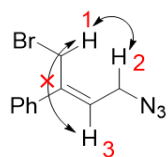


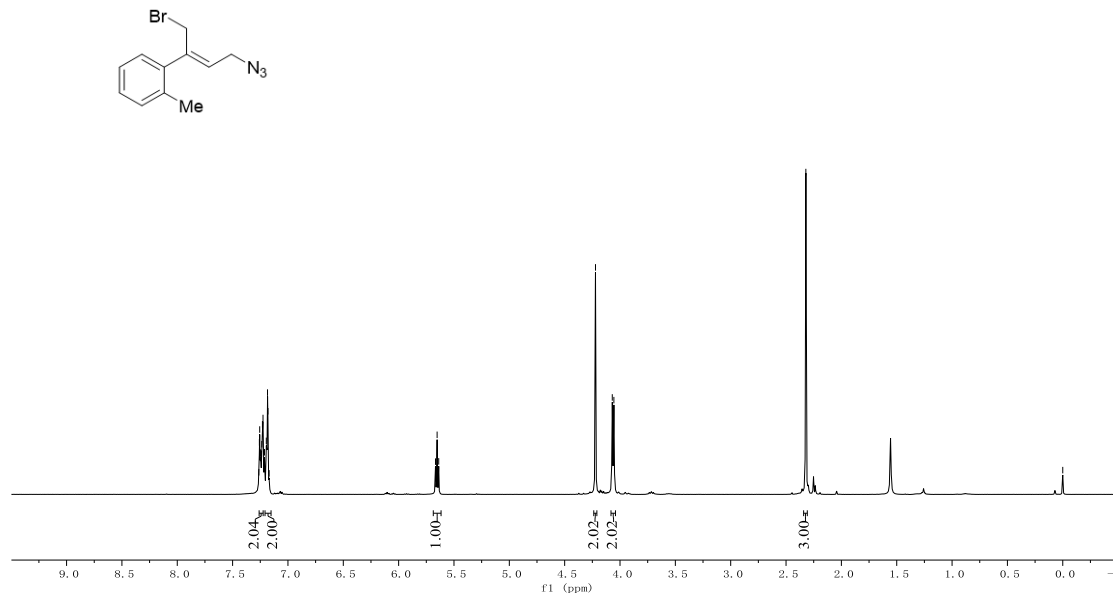
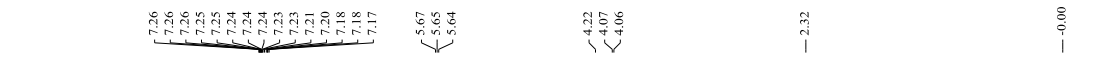
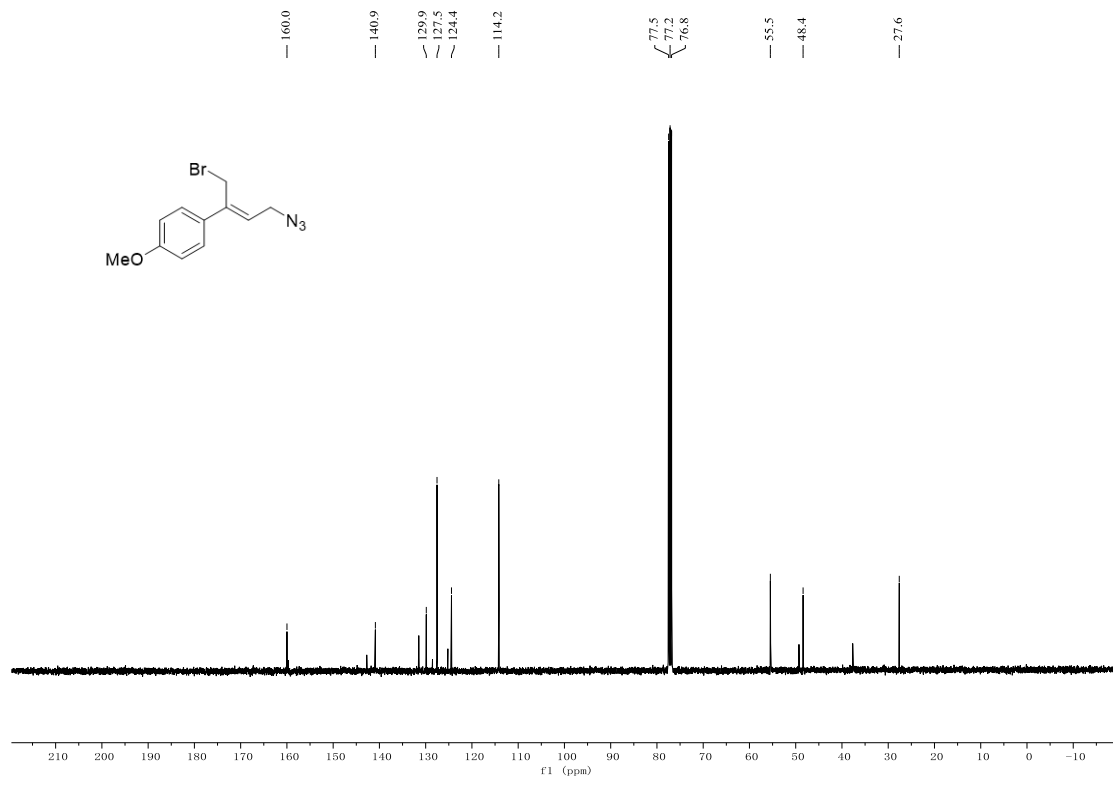


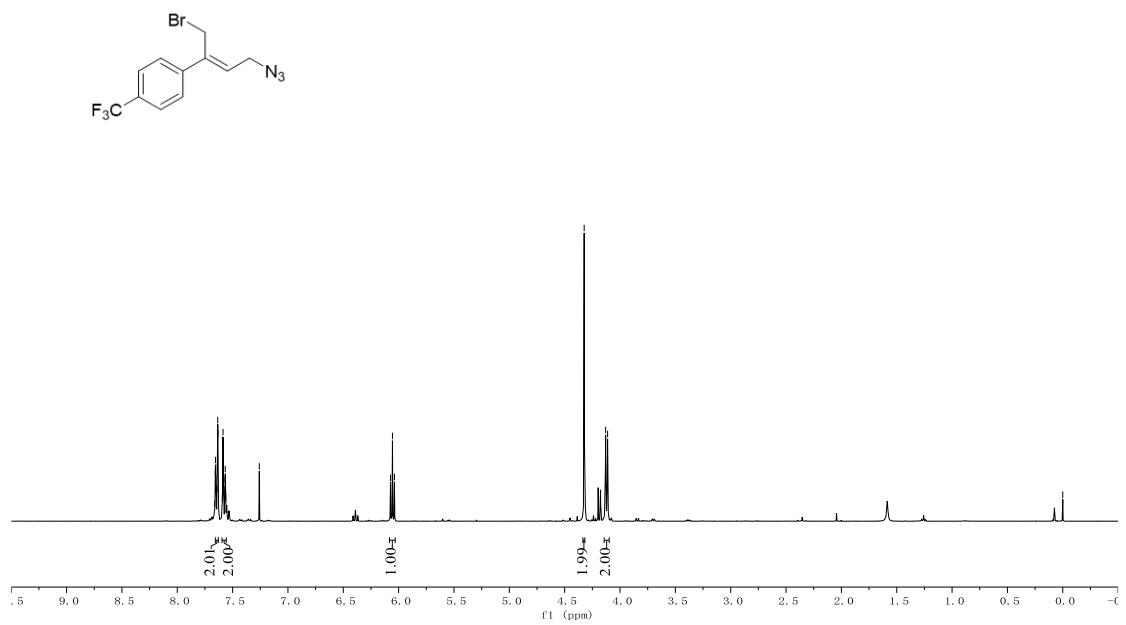
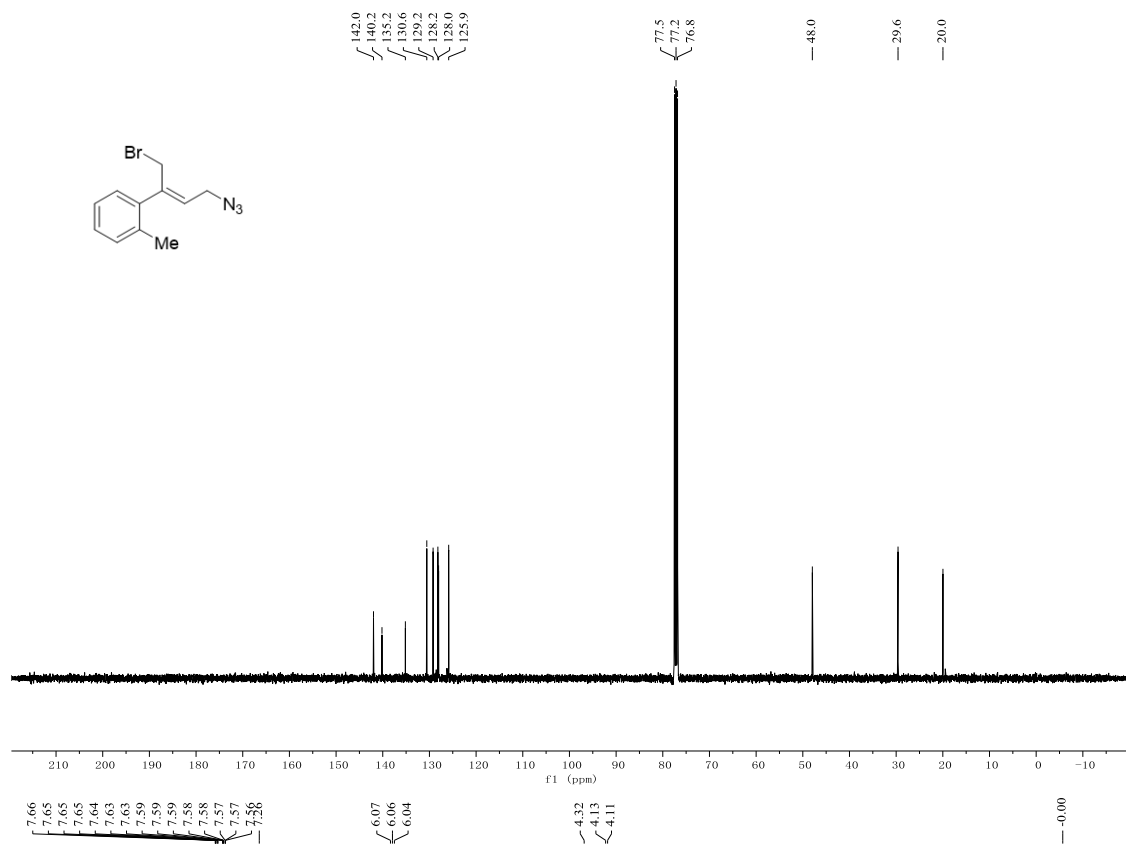
The compounds **4w** and **4w'** were determined by analysis of  $^1\text{H}$ - $^{13}\text{C}$  HSQC spectroscopy. The determination method is similar to that of **4h** and **4h'**.

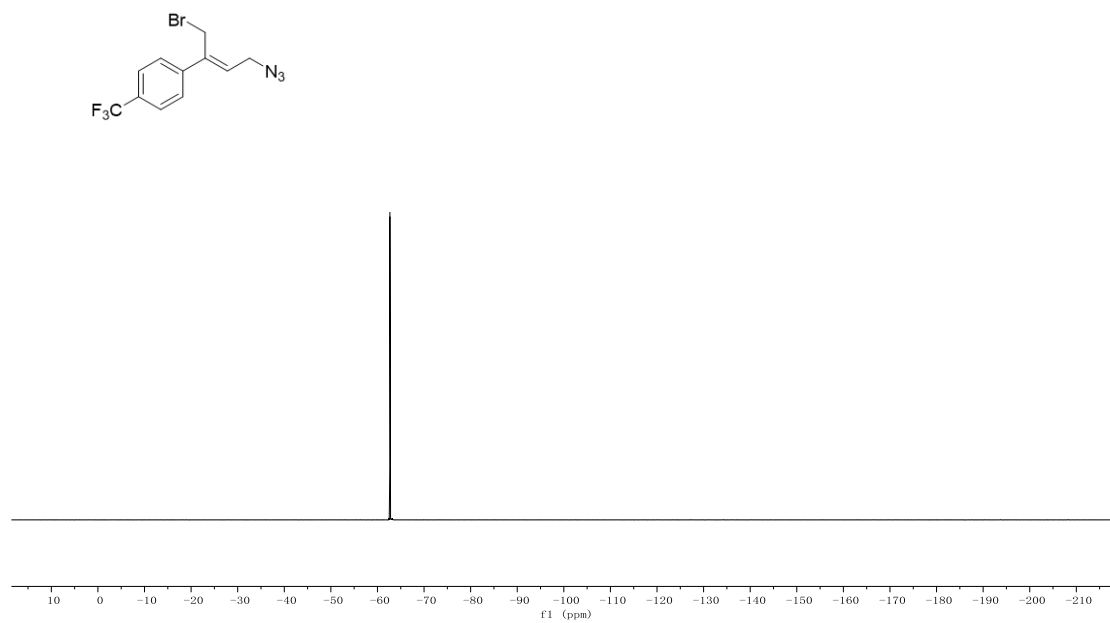
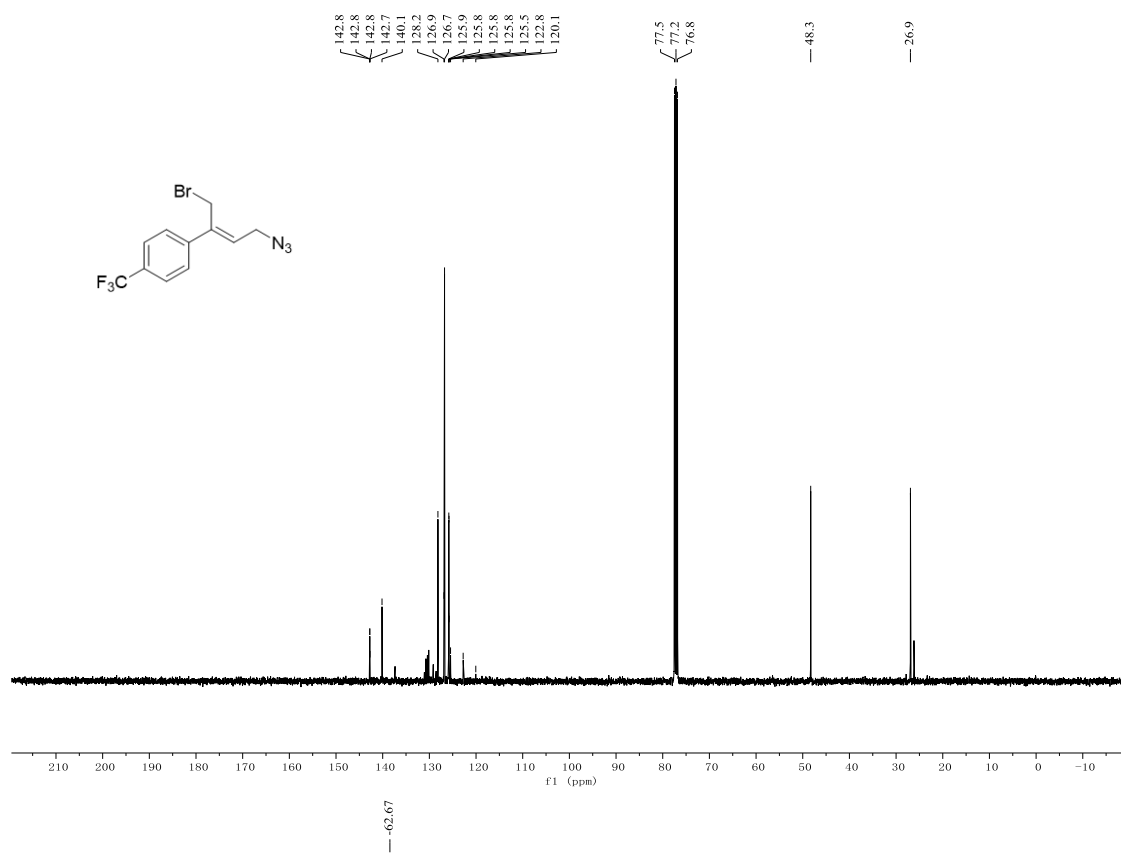


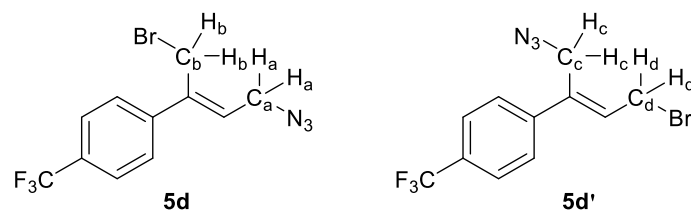
# 1D NOESY of 5a



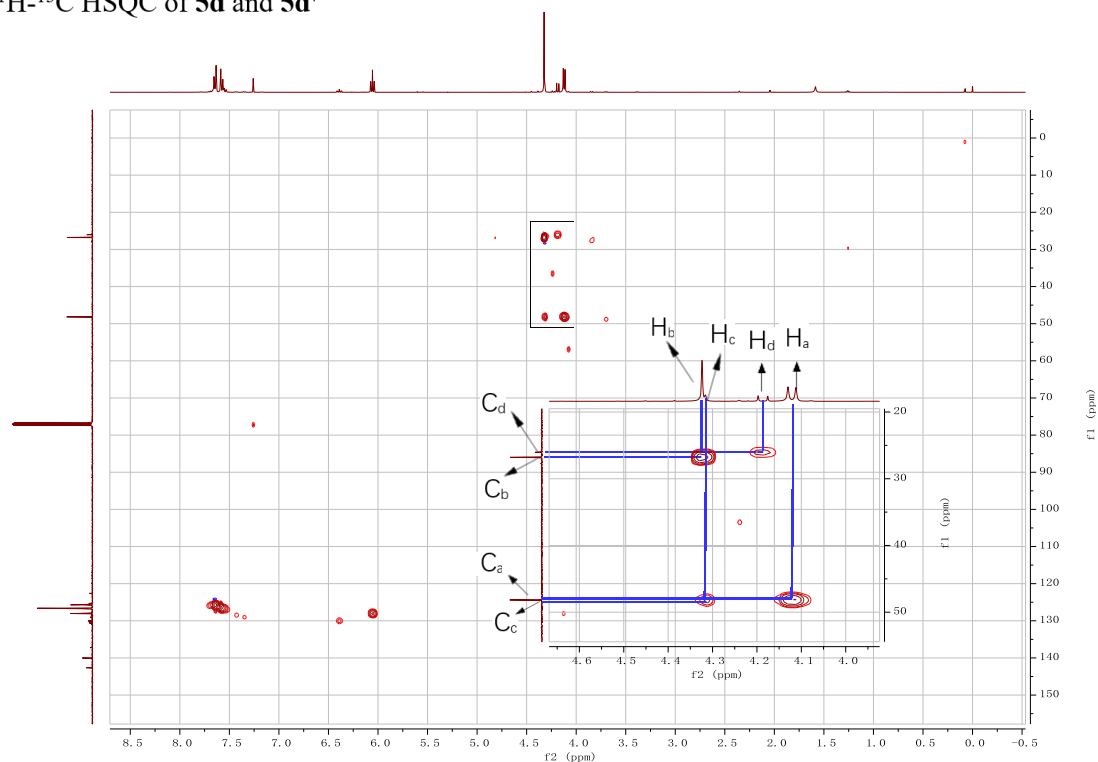






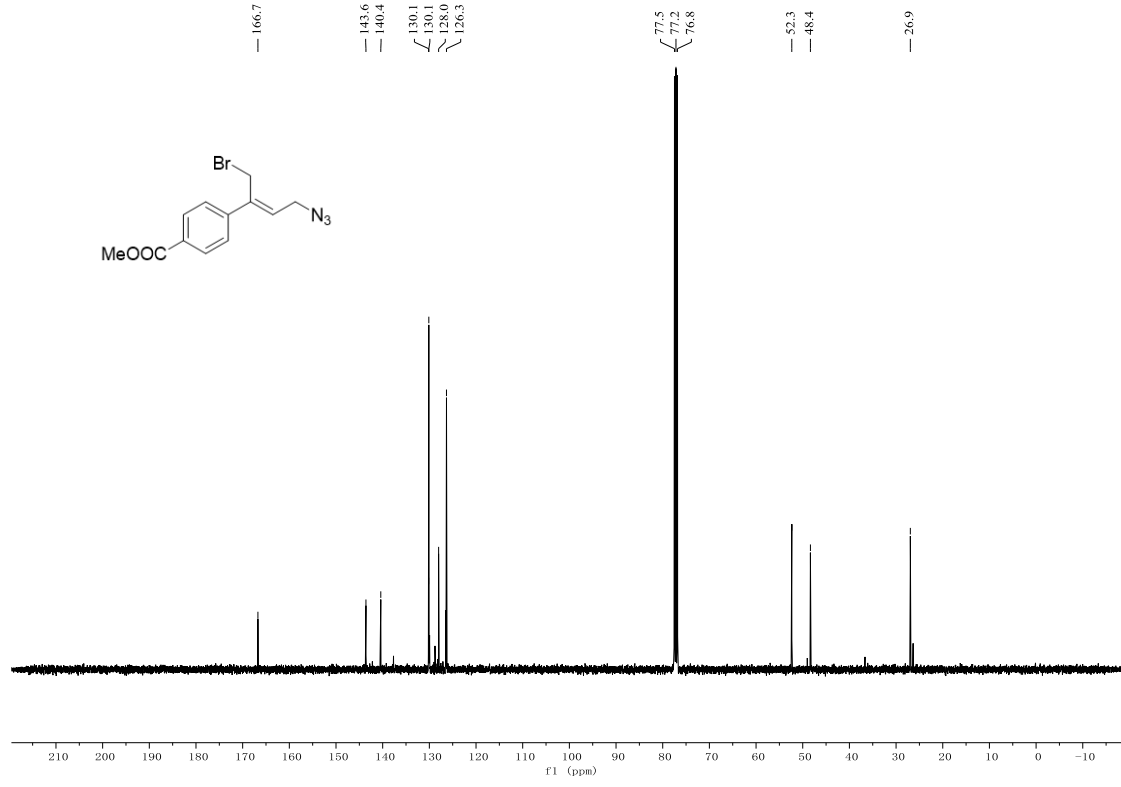
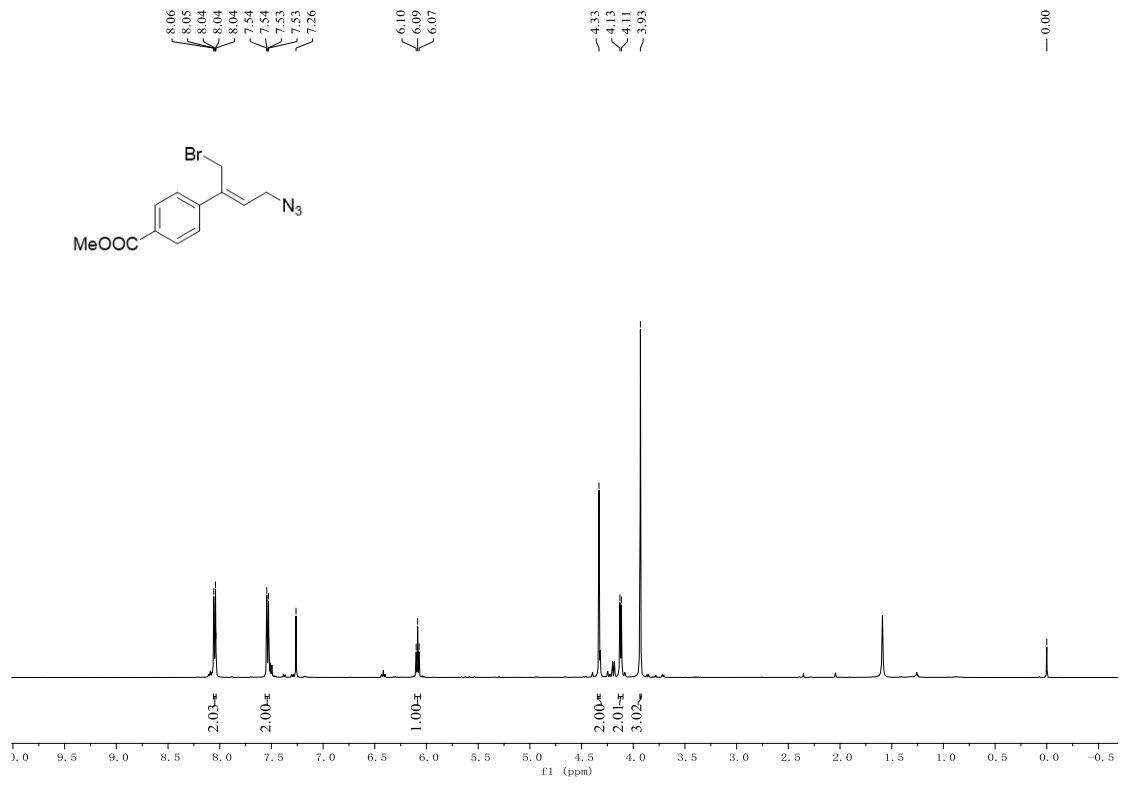


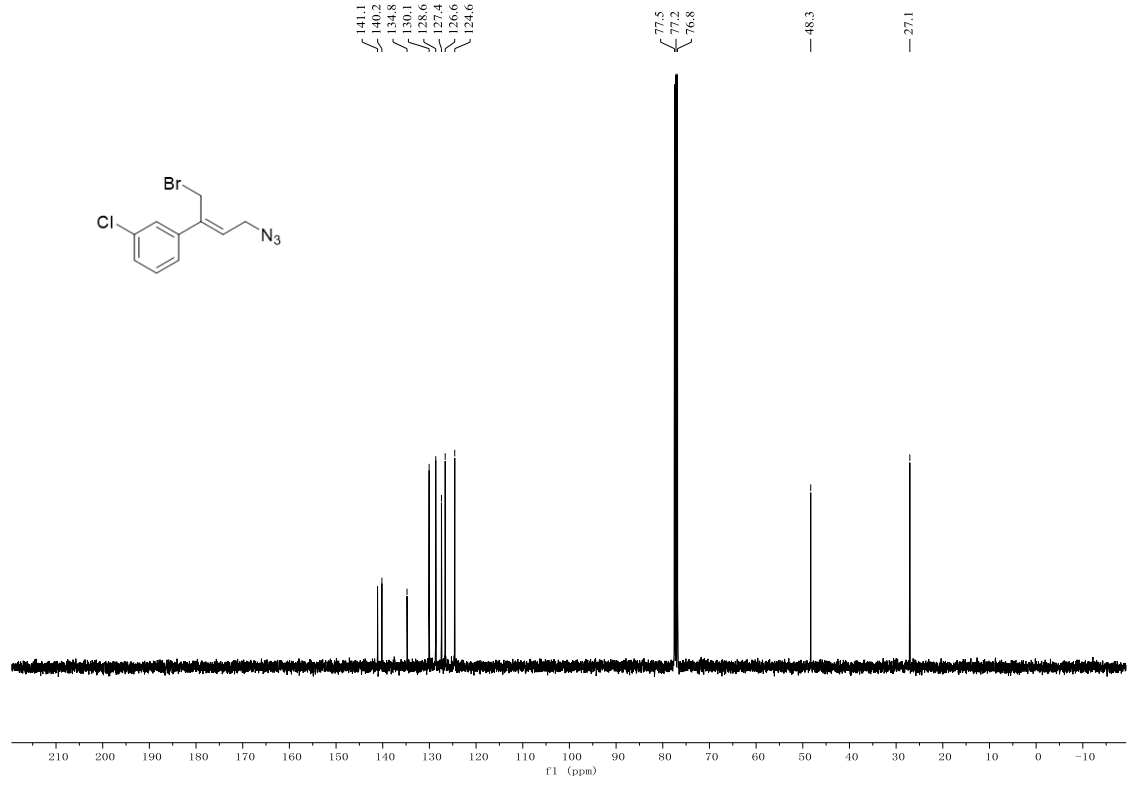
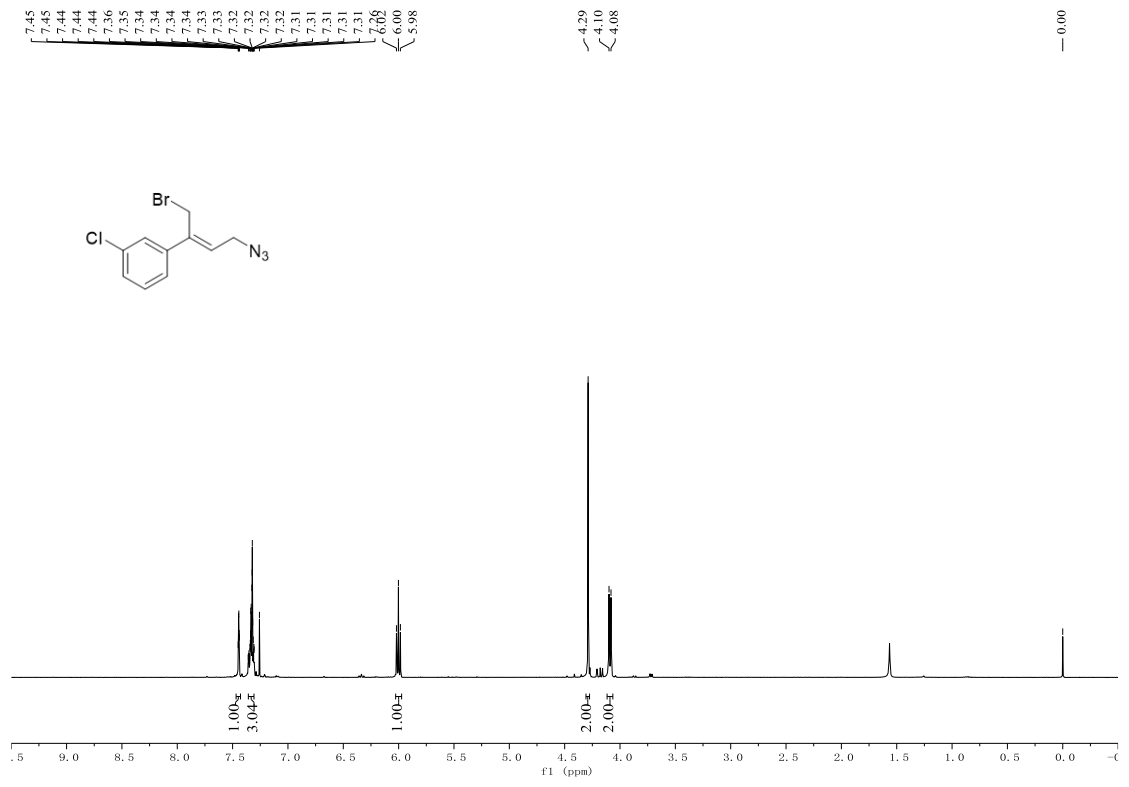
$^1\text{H}$ - $^{13}\text{C}$  HSQC of **5d** and **5d'**

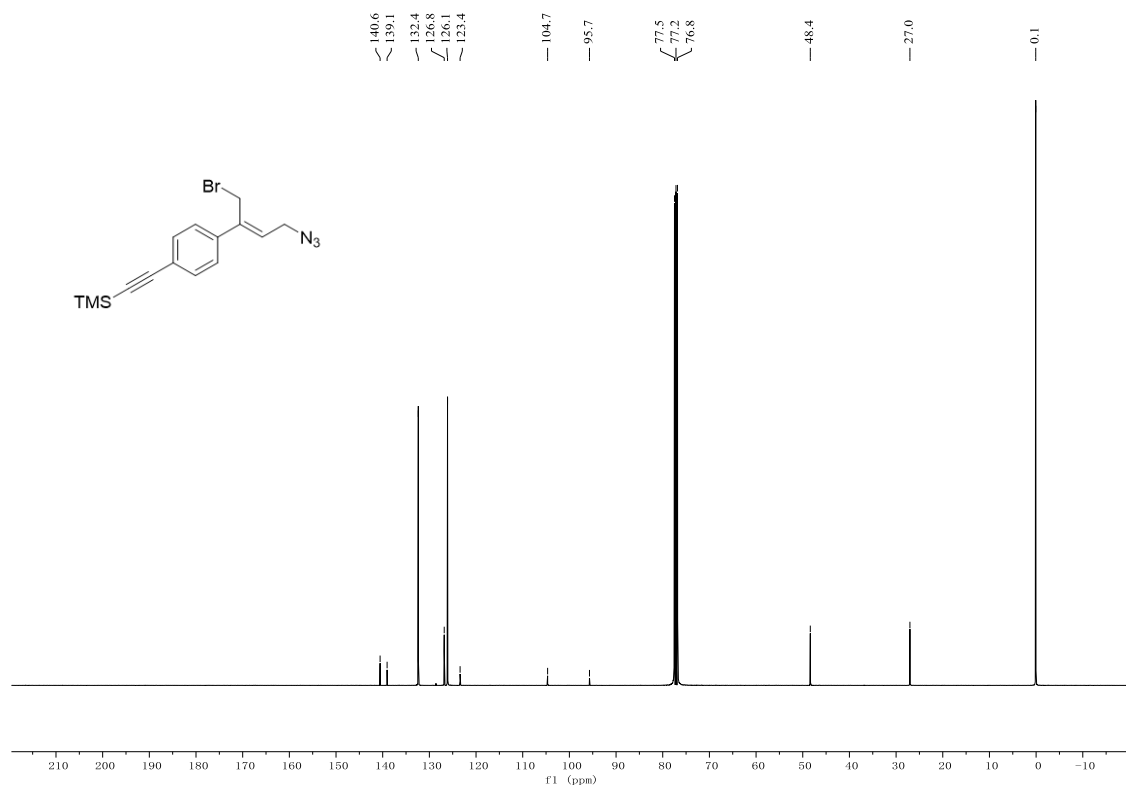
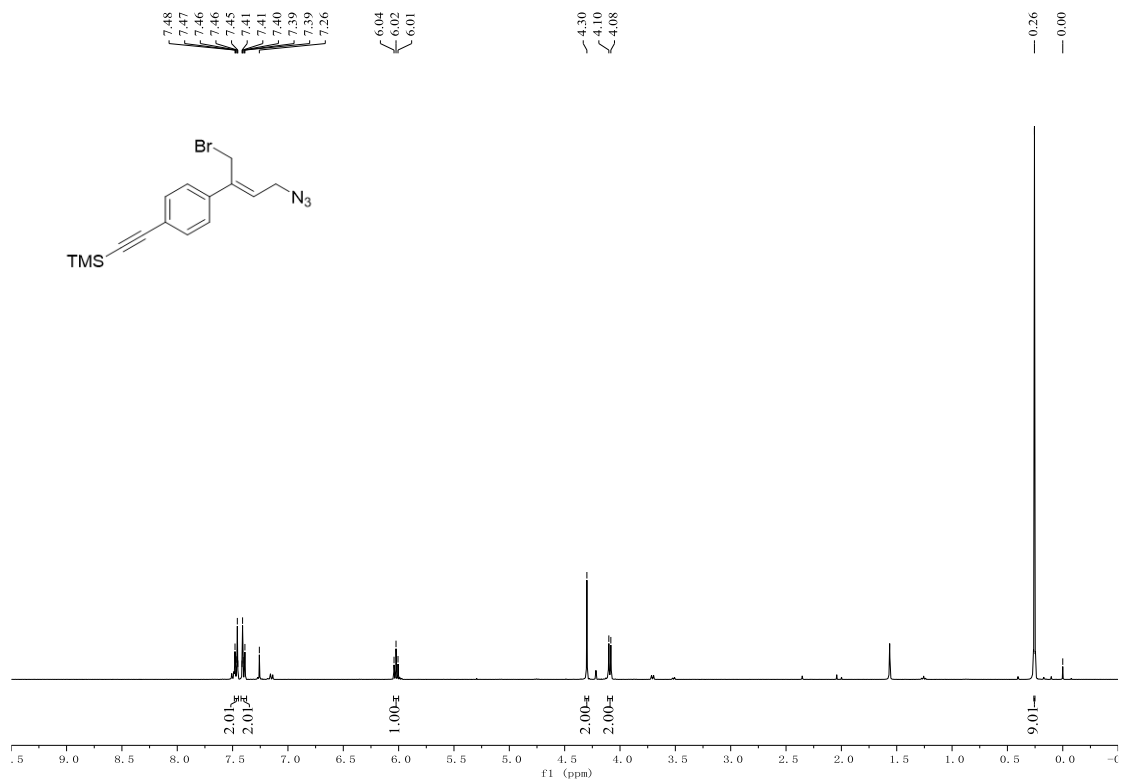


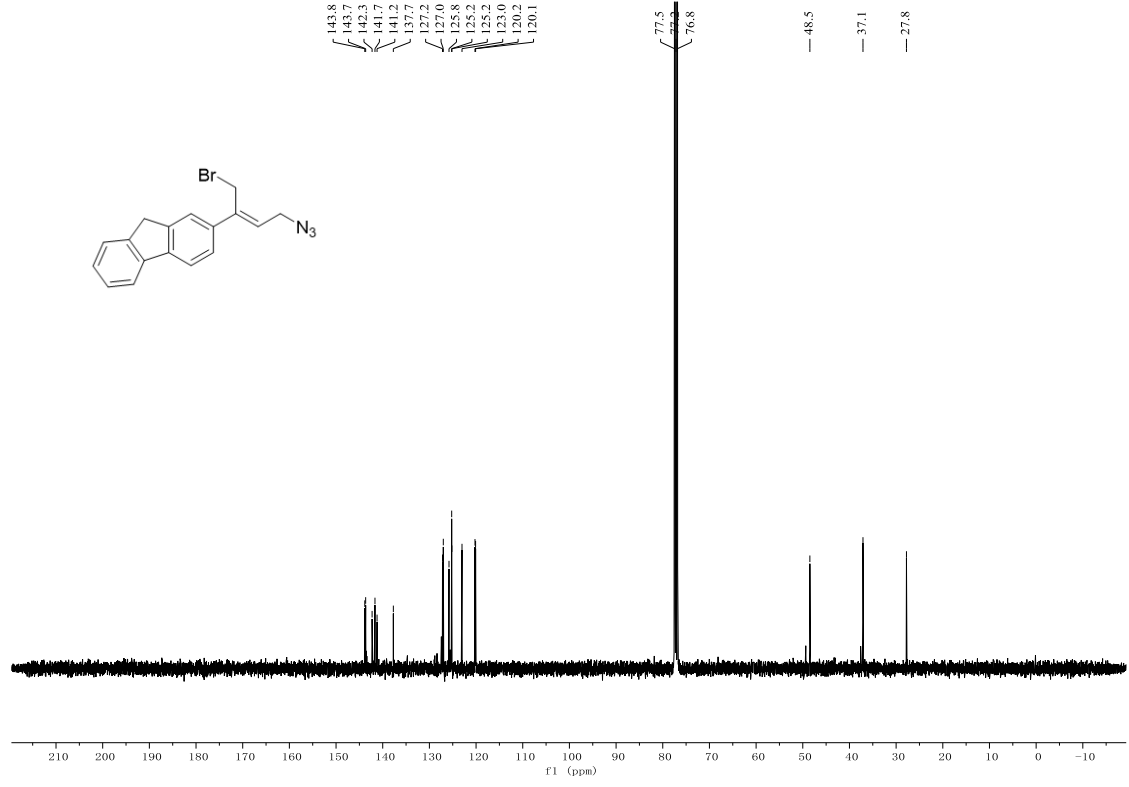
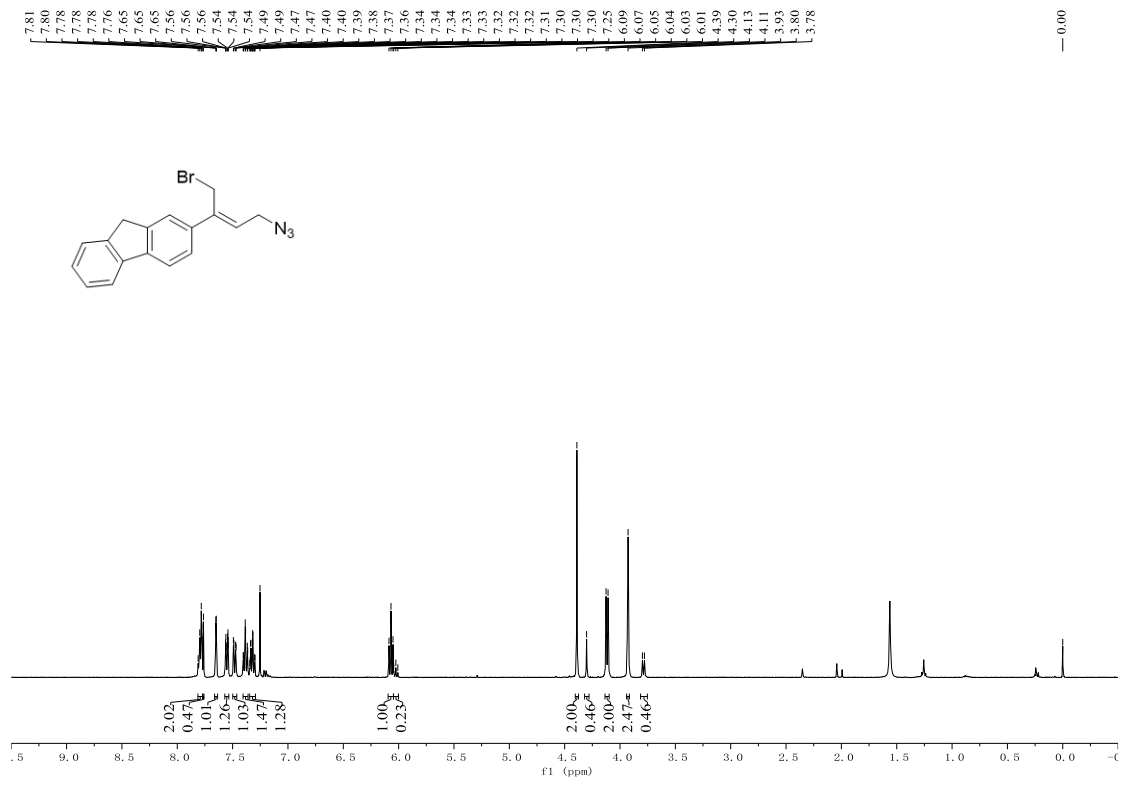
The compounds **5d** and **5d'** were determined by analysis of  $^1\text{H}$ - $^{13}\text{C}$  HSQC spectroscopy. Due to the presence of azide group, the chemical shift of  $\text{C}_a$  is obviously larger than that of  $\text{C}_b$  and the chemical shift of  $\text{C}_c$  is larger than that of  $\text{C}_d$ . The chemical shifts of compounds (*E*)-(3-azidoprop-1-en-1-yl)benzene<sup>[15]</sup> and (*E*)-(3-bromoprop-1-en-1-yl)benzene<sup>[16]</sup> can be used as reference values.

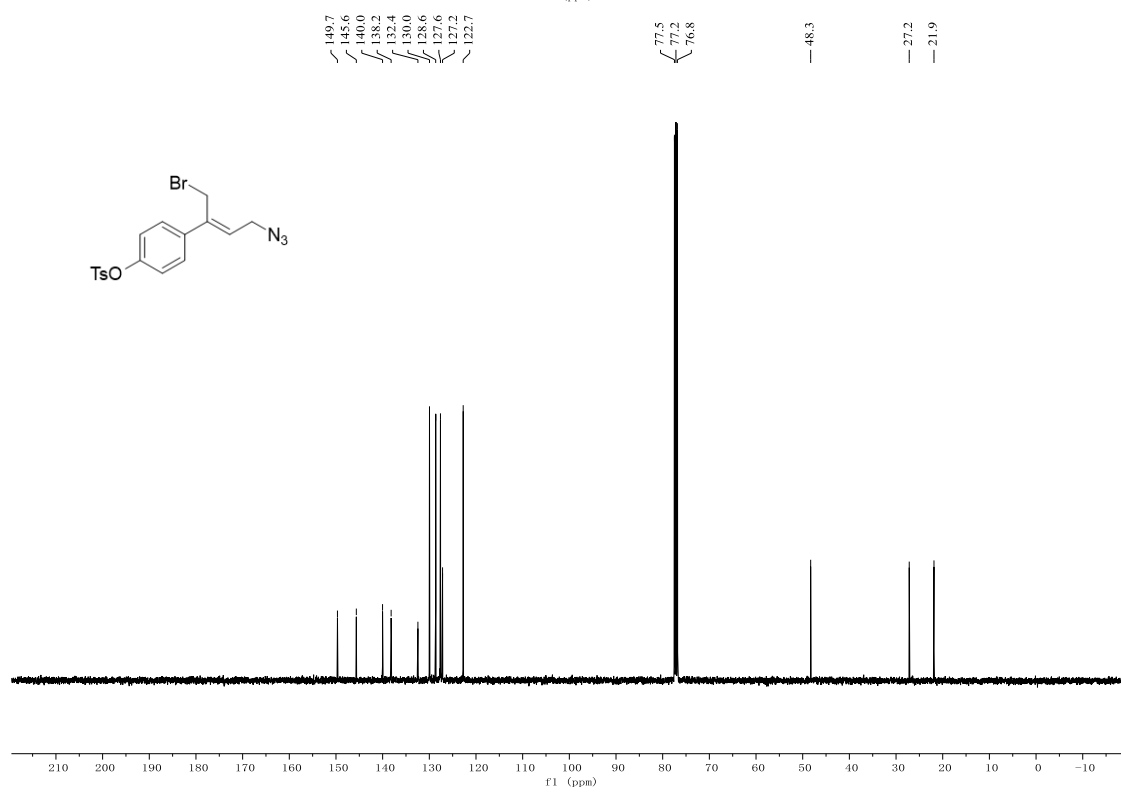
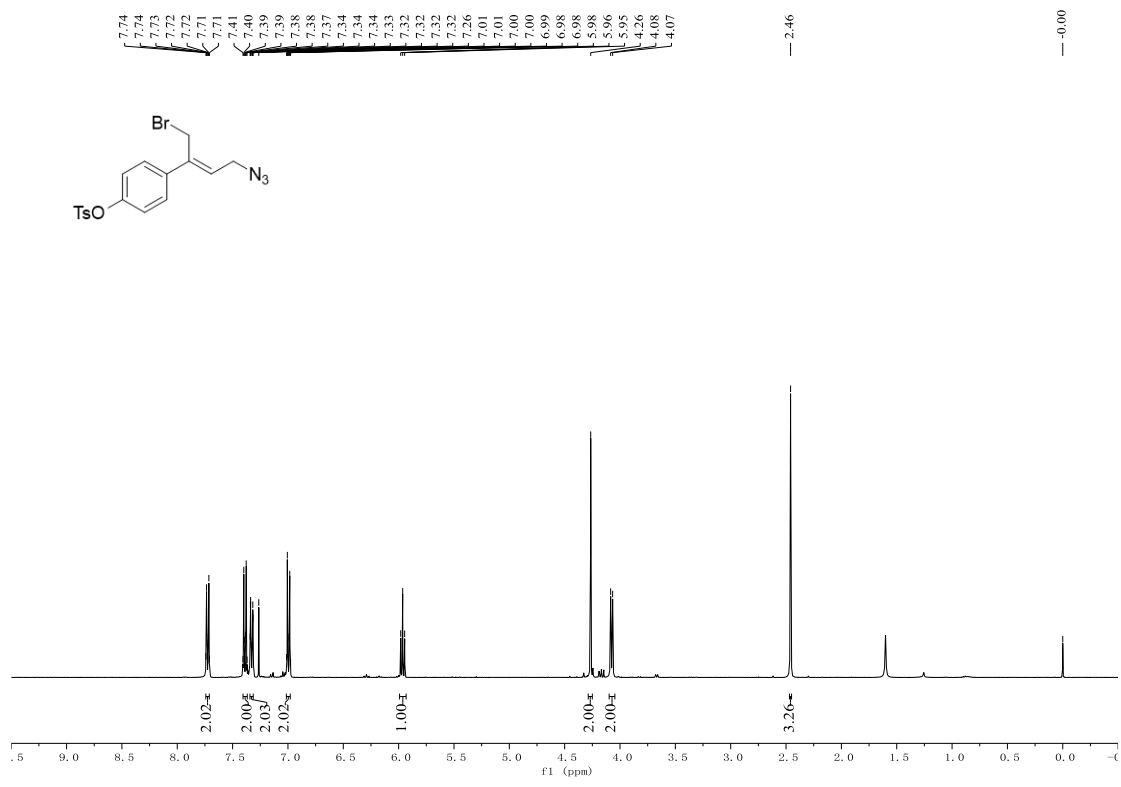


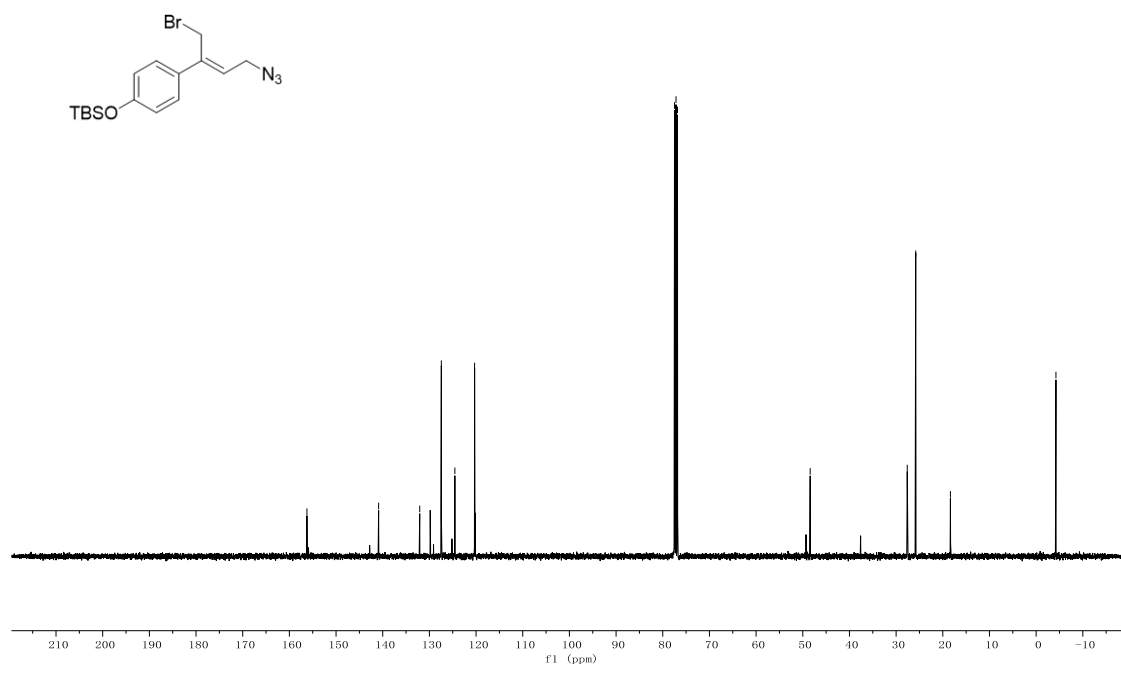
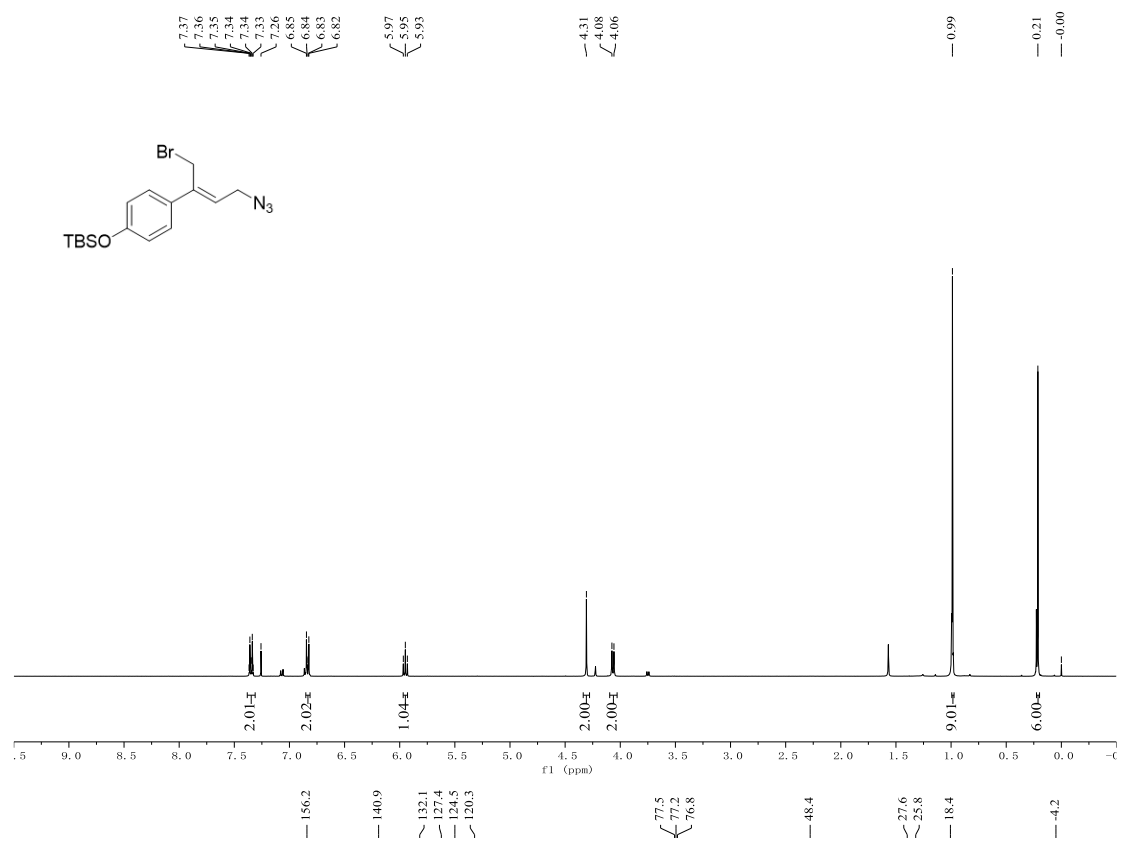








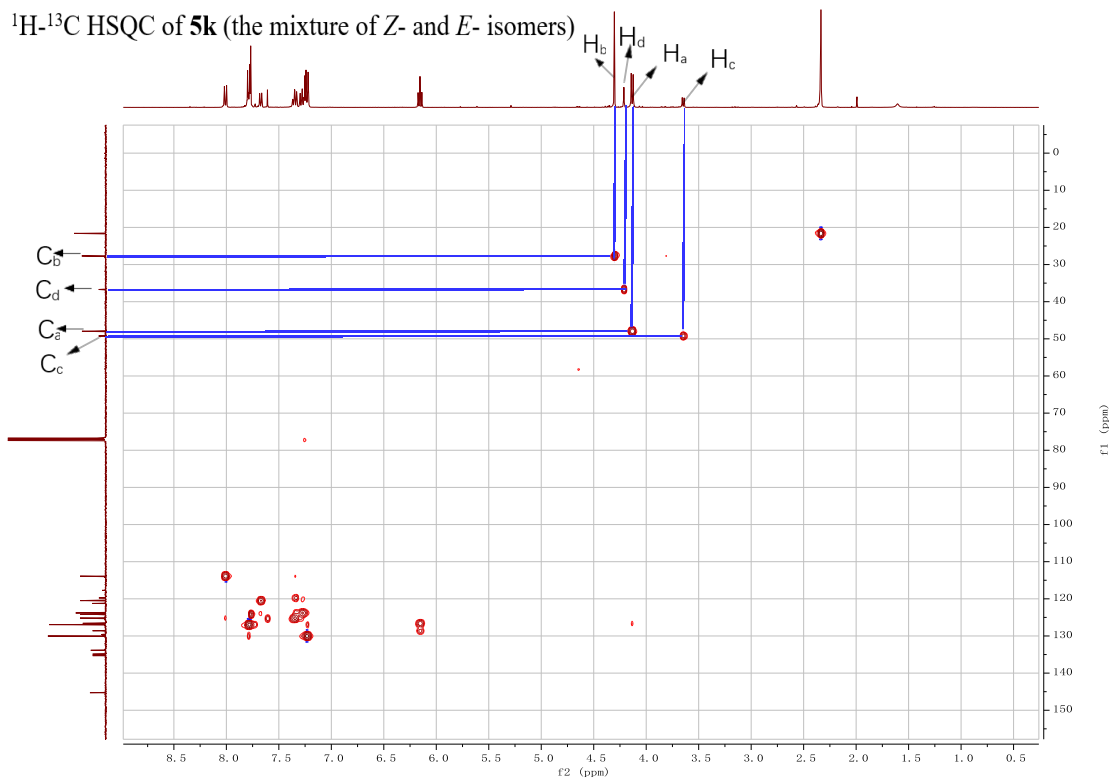
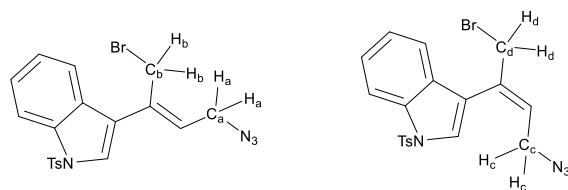




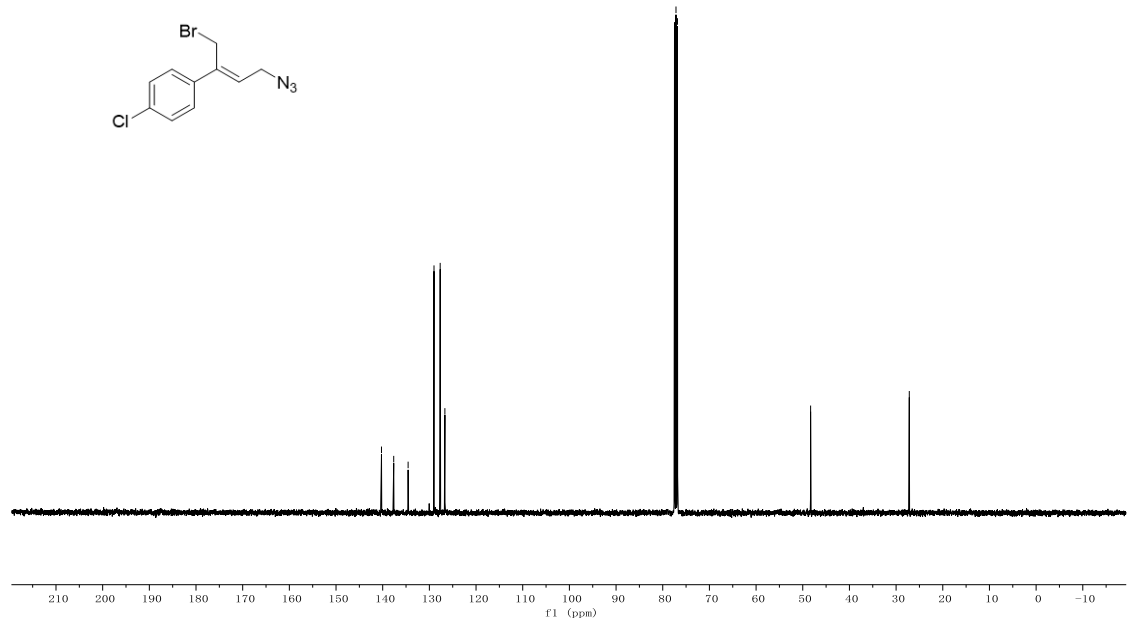
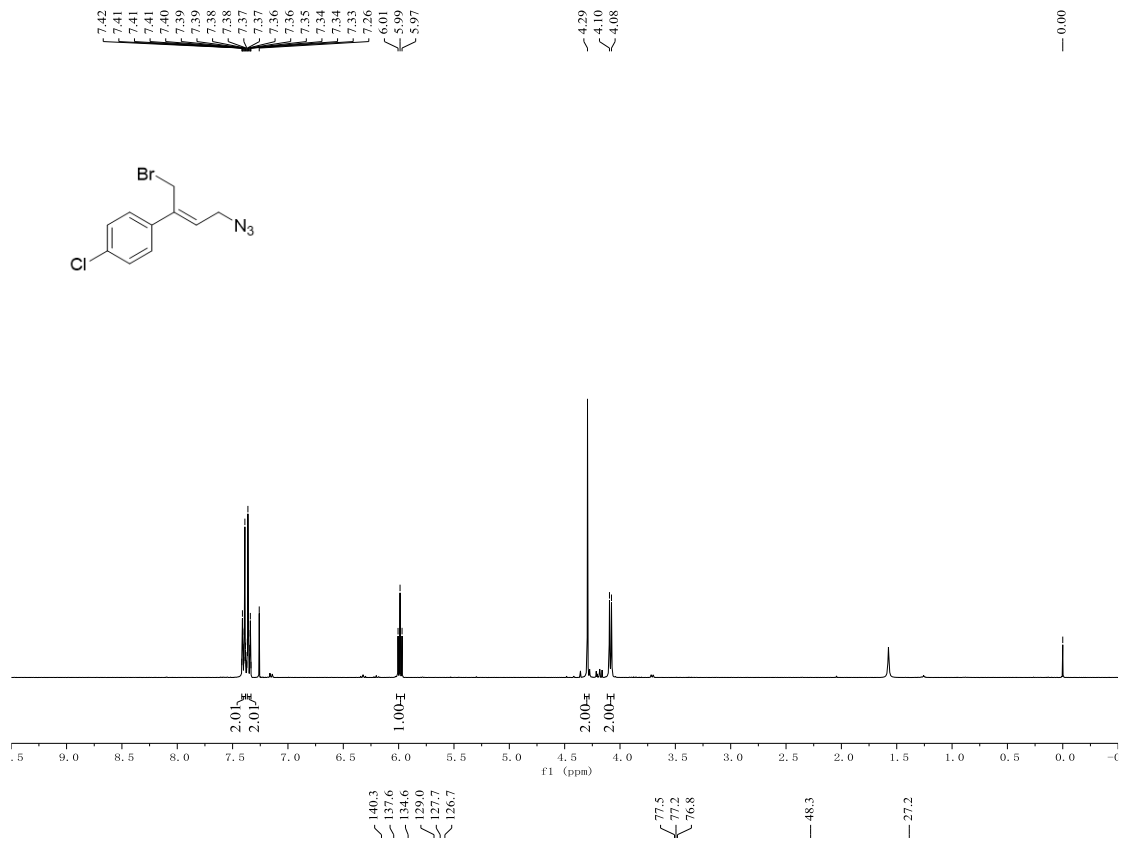


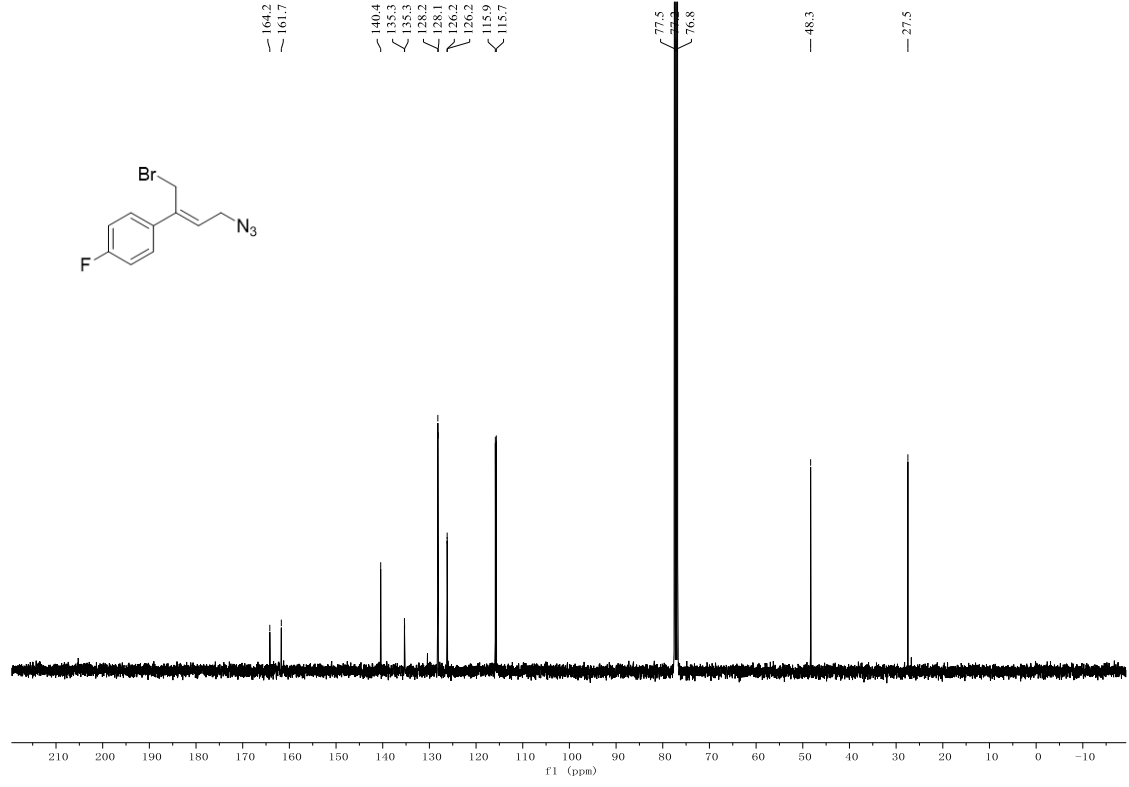
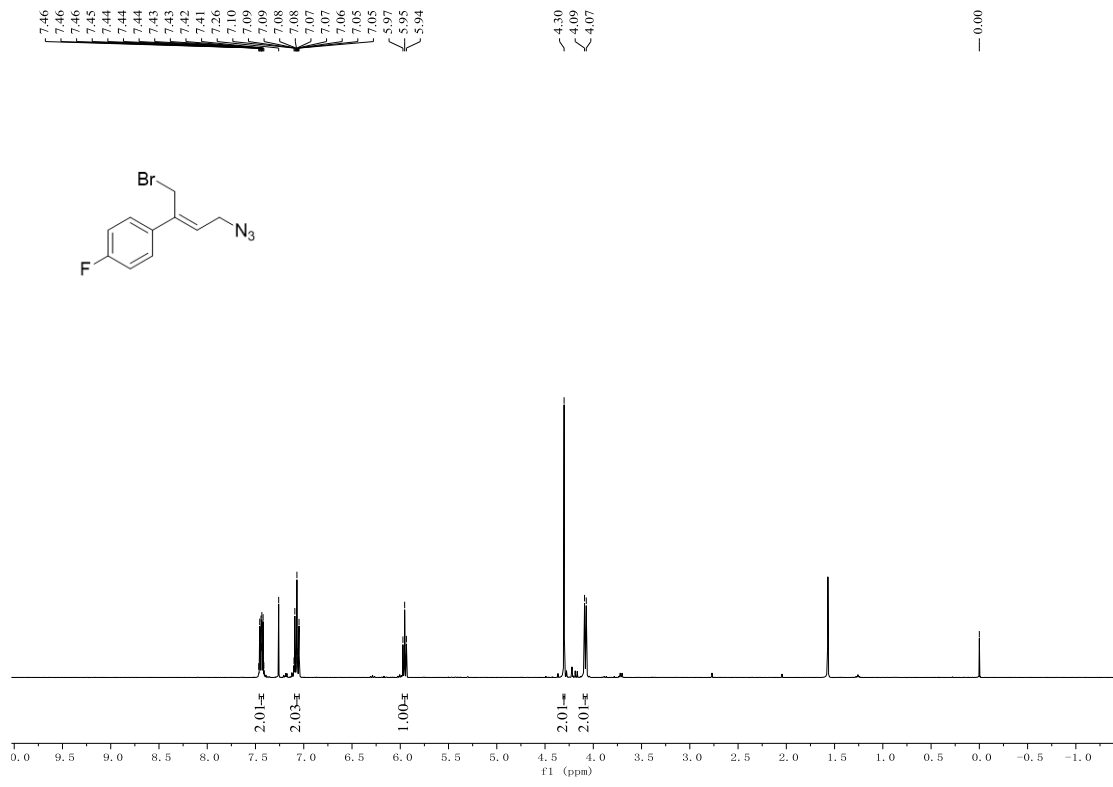


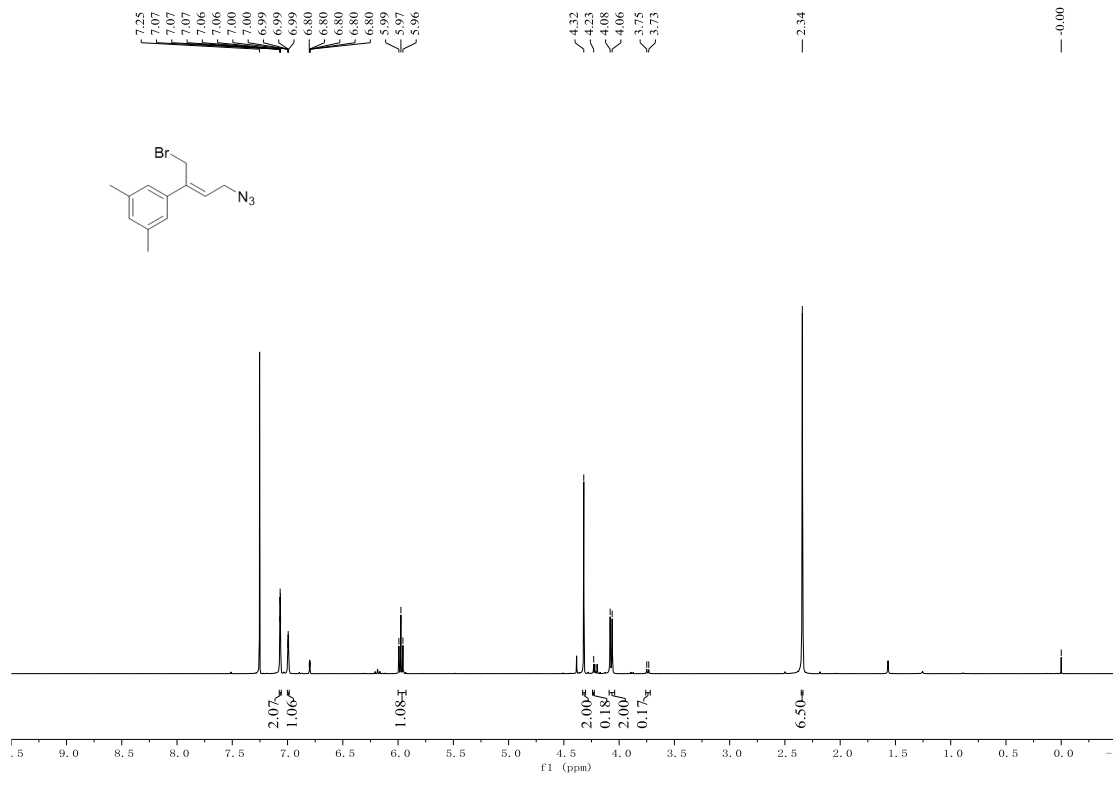
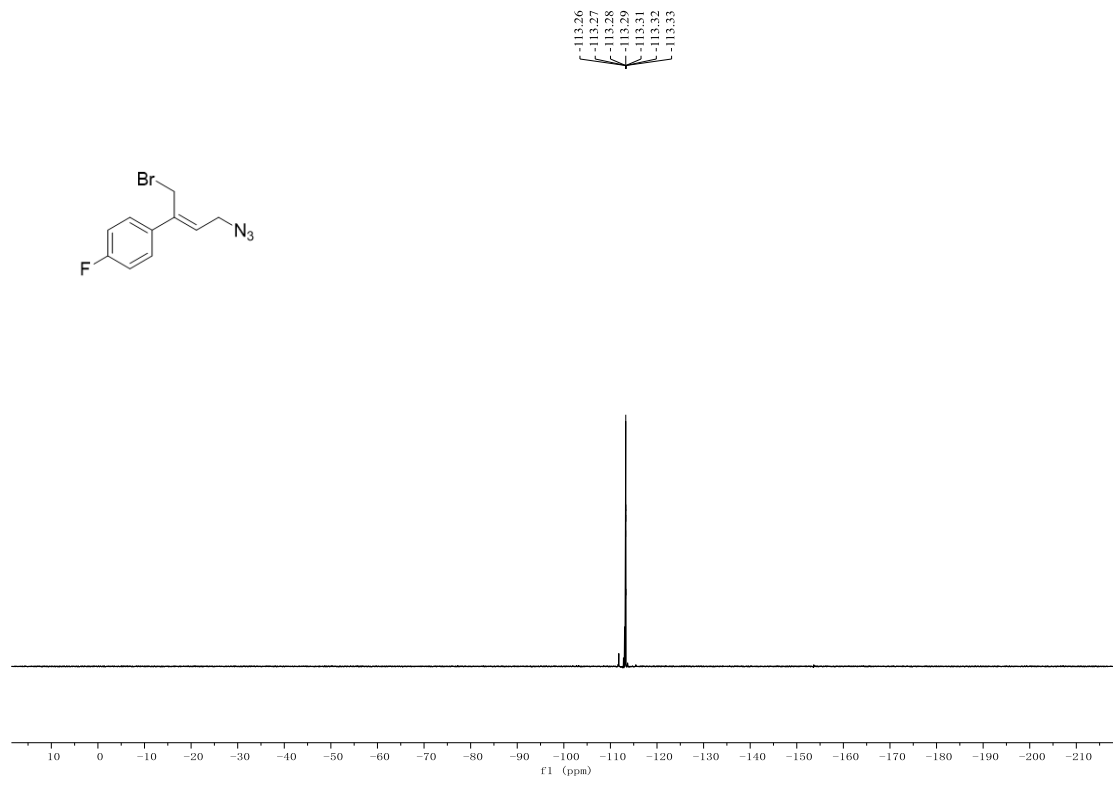


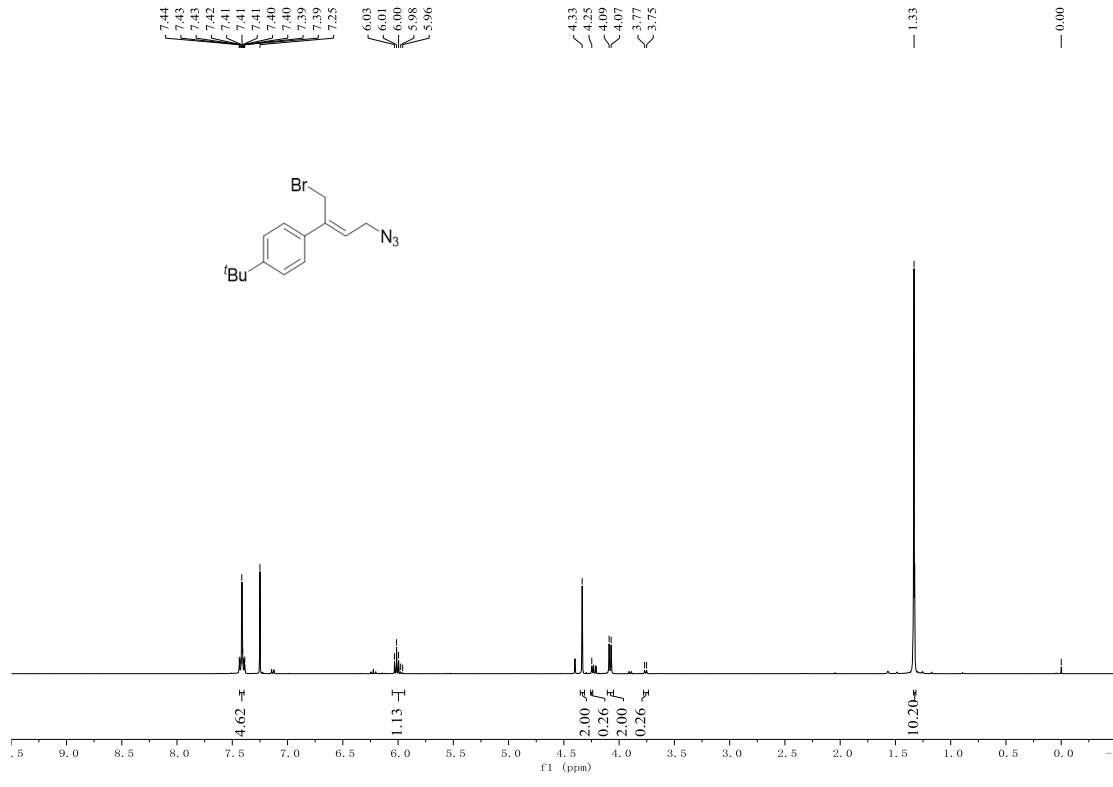
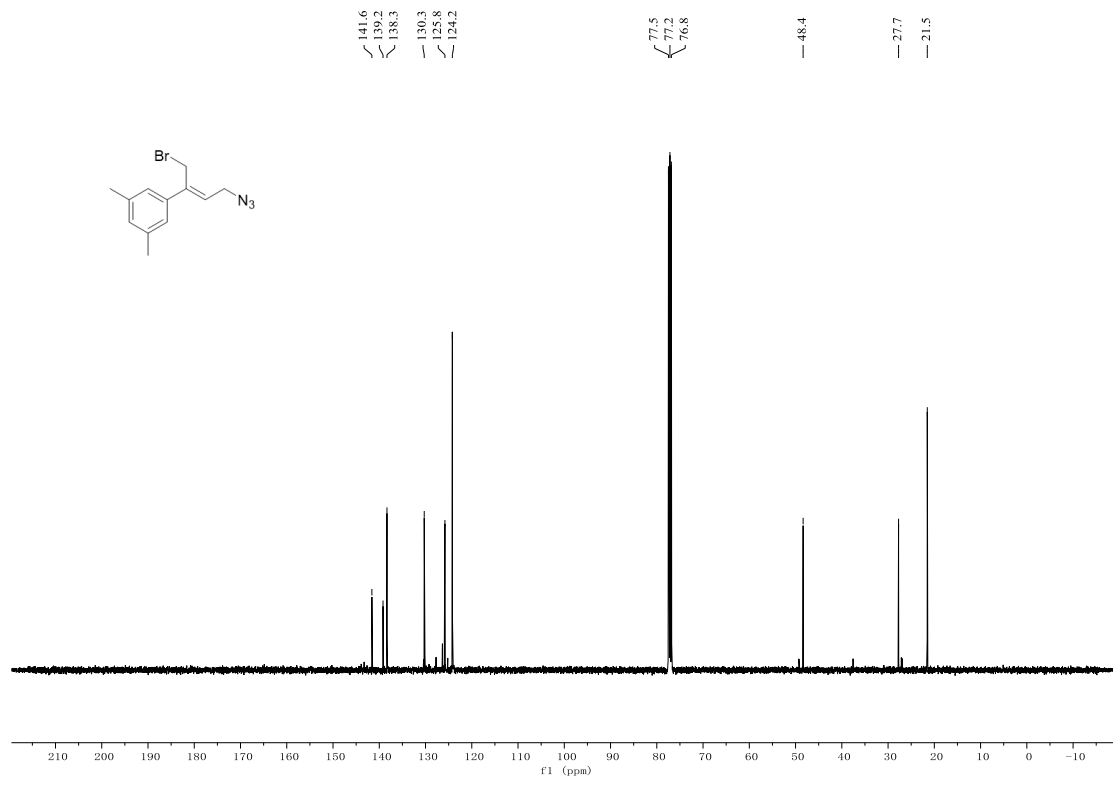


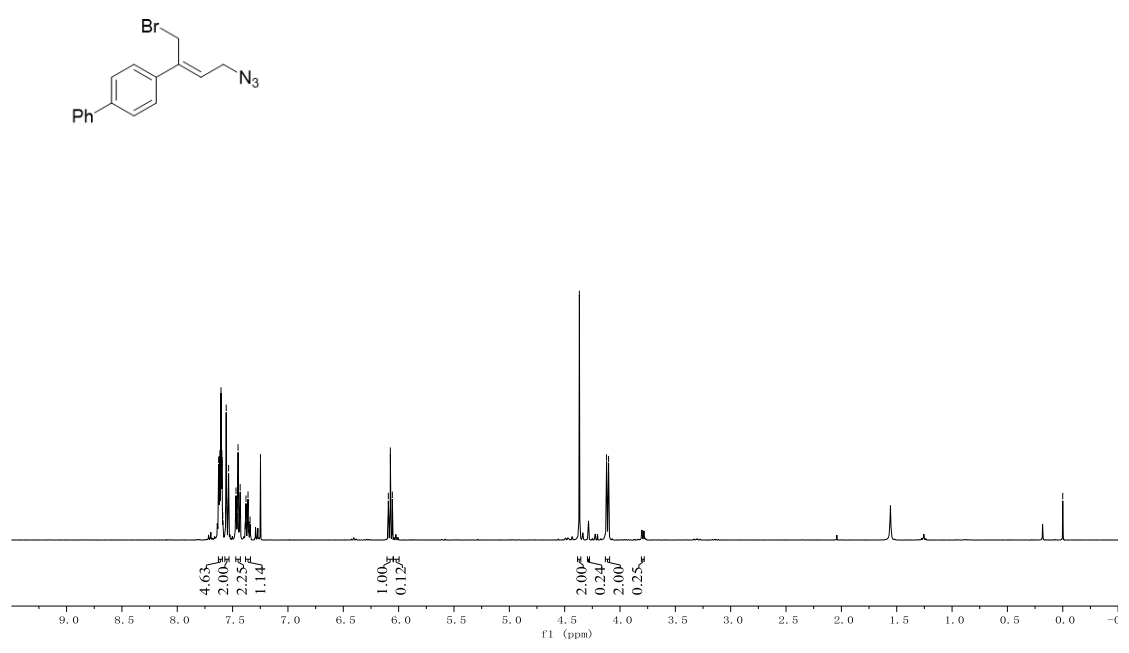
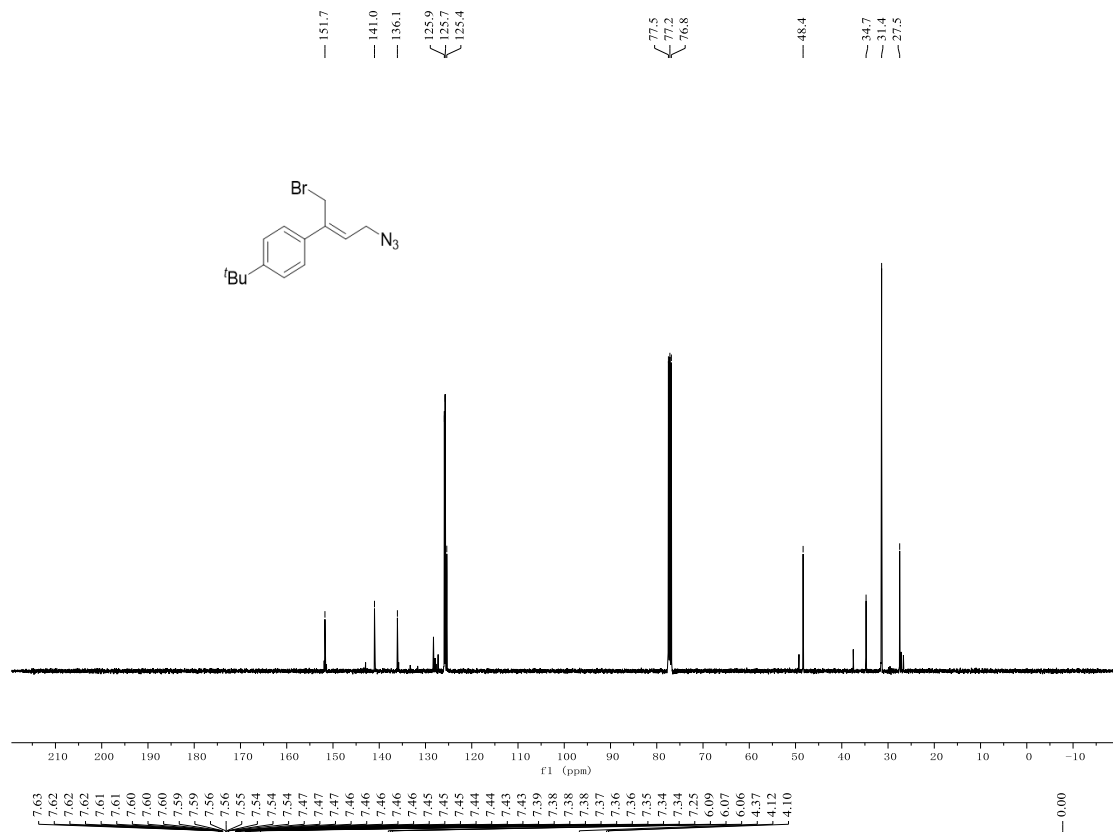
The product **5k** was produced as a mixture of *Z*- and *E*-isomers, which was determined by analysis of  $^1\text{H}$ - $^{13}\text{C}$  HSQC spectroscopy, because the chemical shift of  $\text{C}_a$  is obviously larger than that of  $\text{C}_b$  and the chemical shift of  $\text{C}_c$  is obviously larger than that of  $\text{C}_d$ .

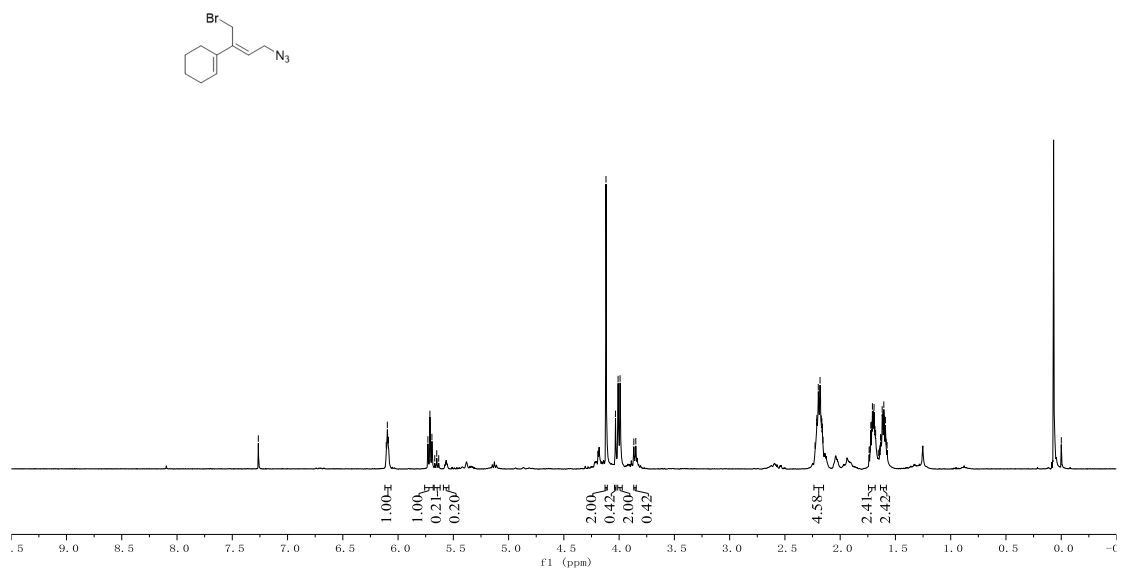
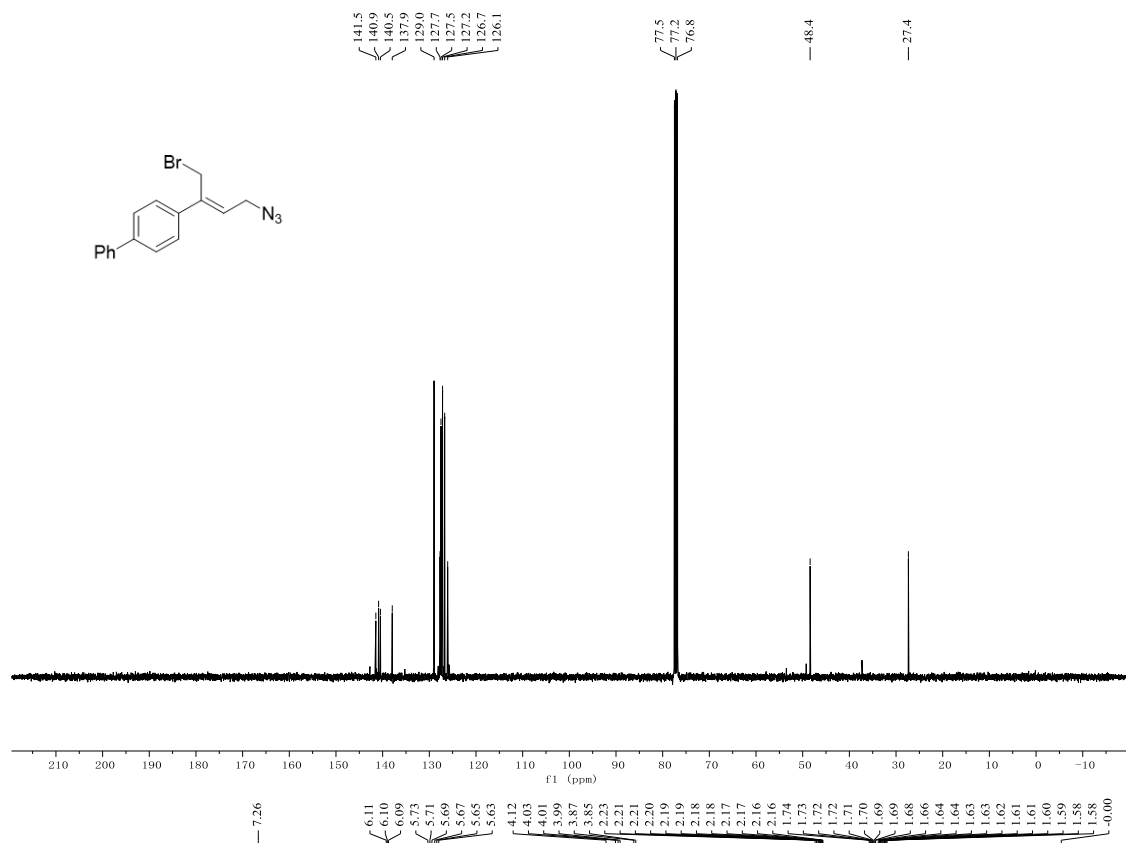


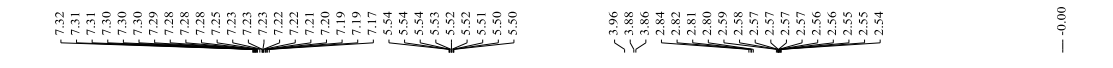
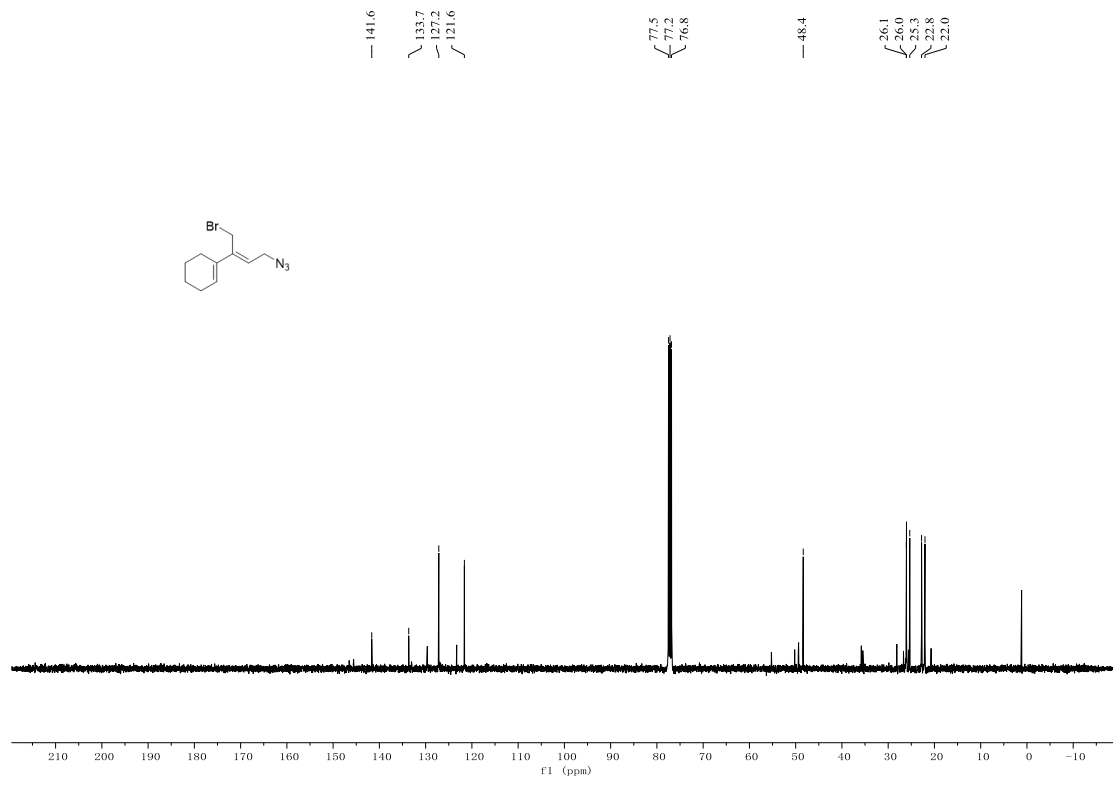




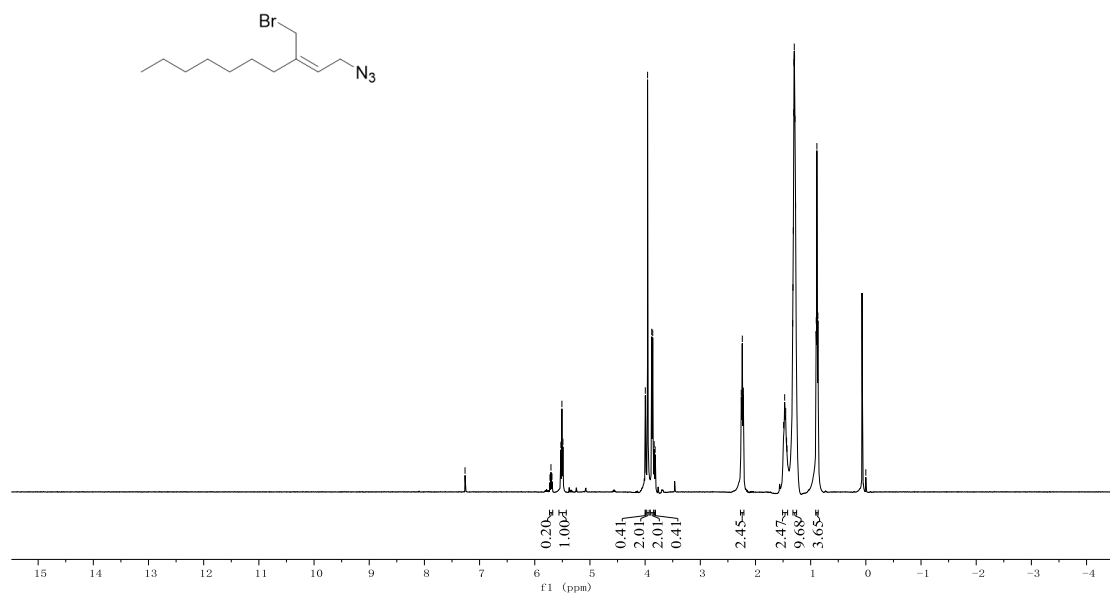
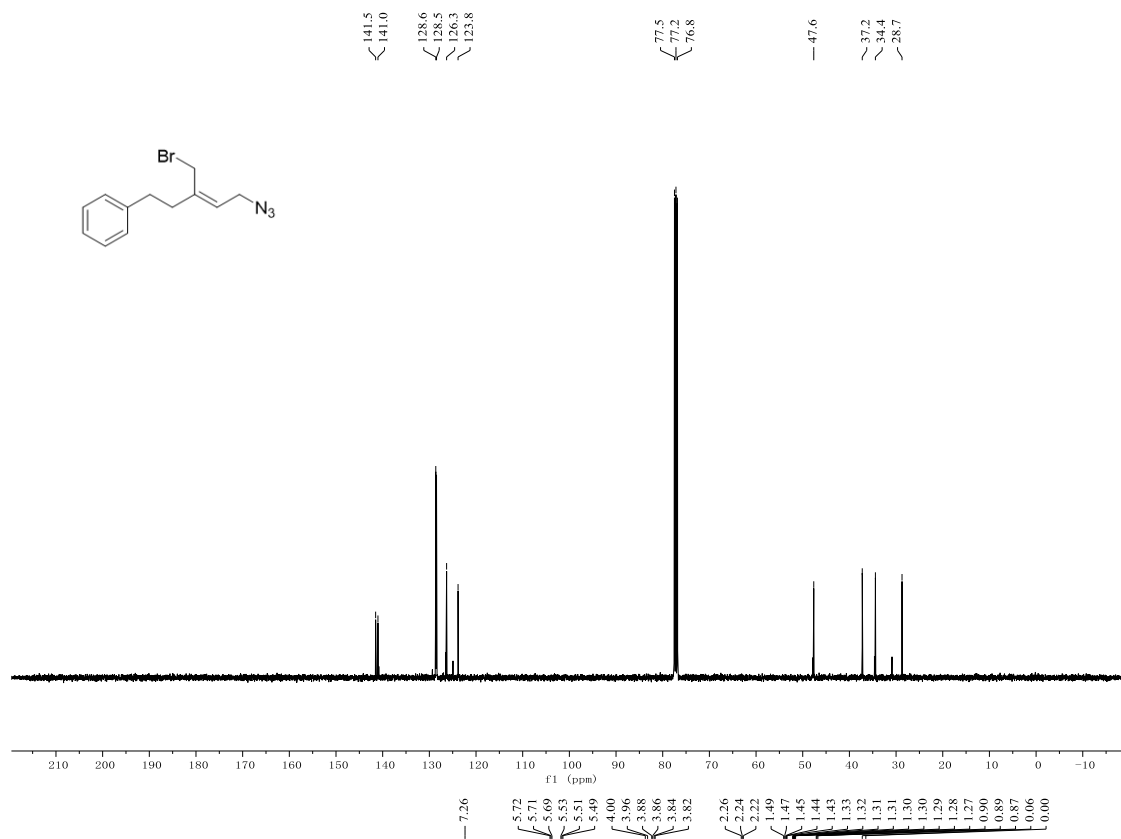


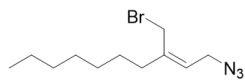
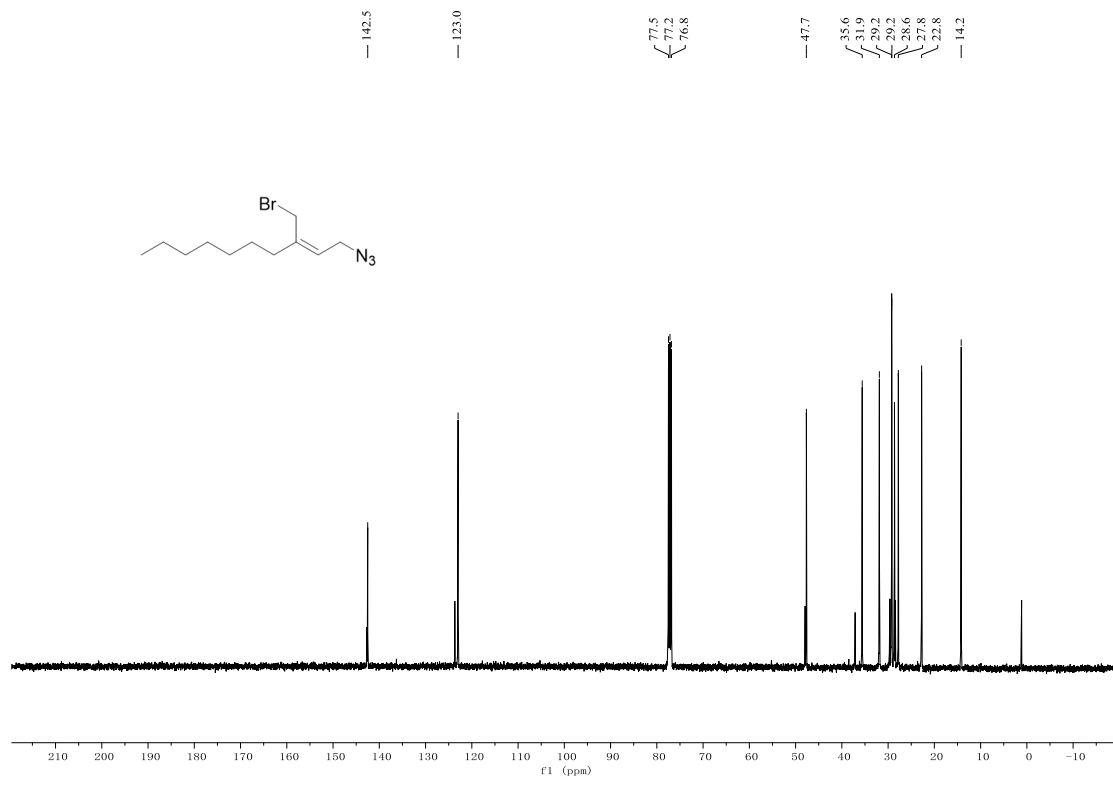




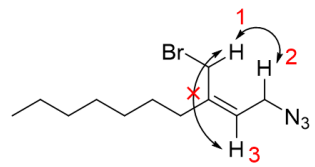
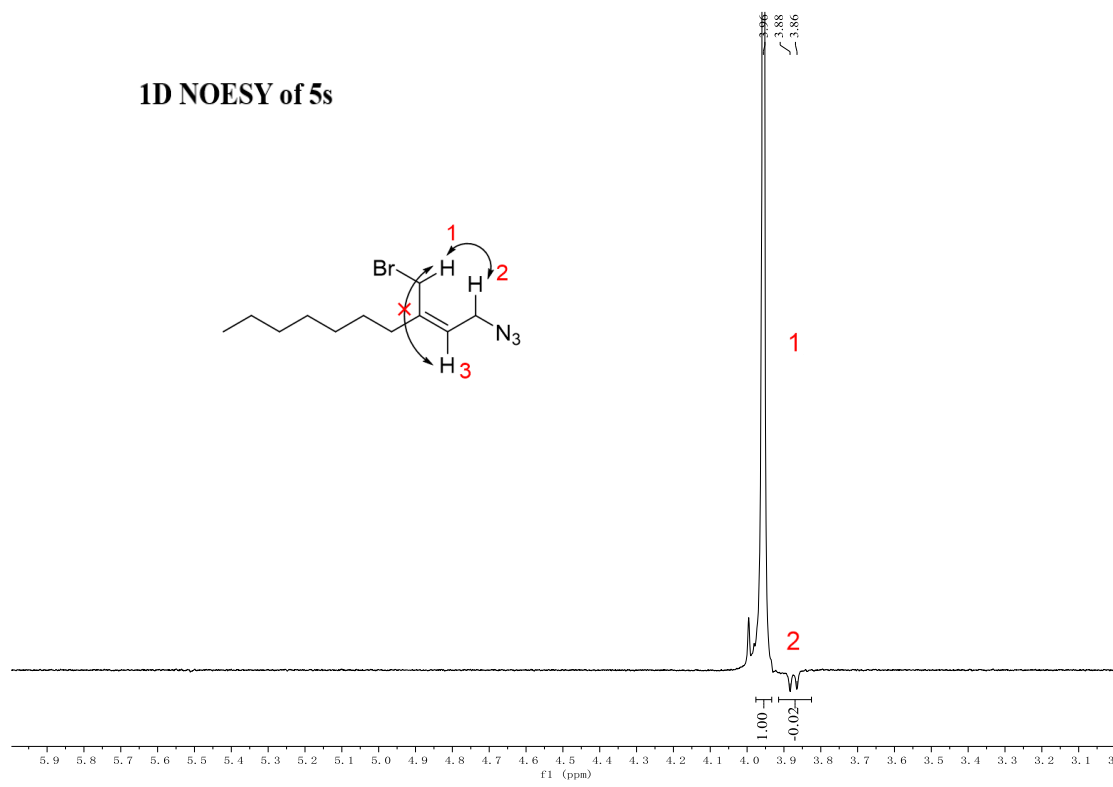


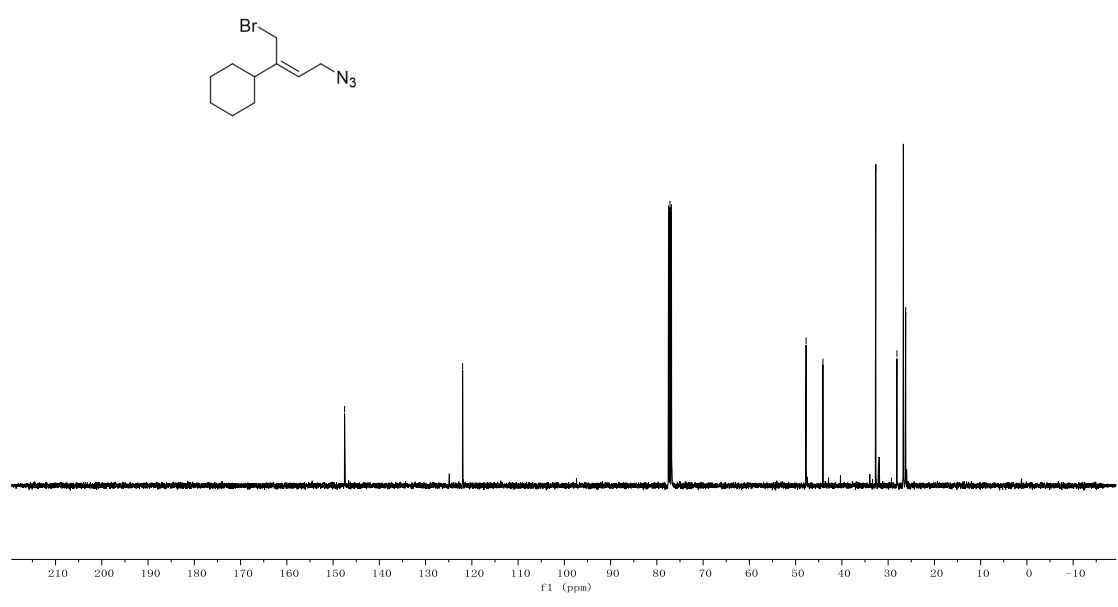
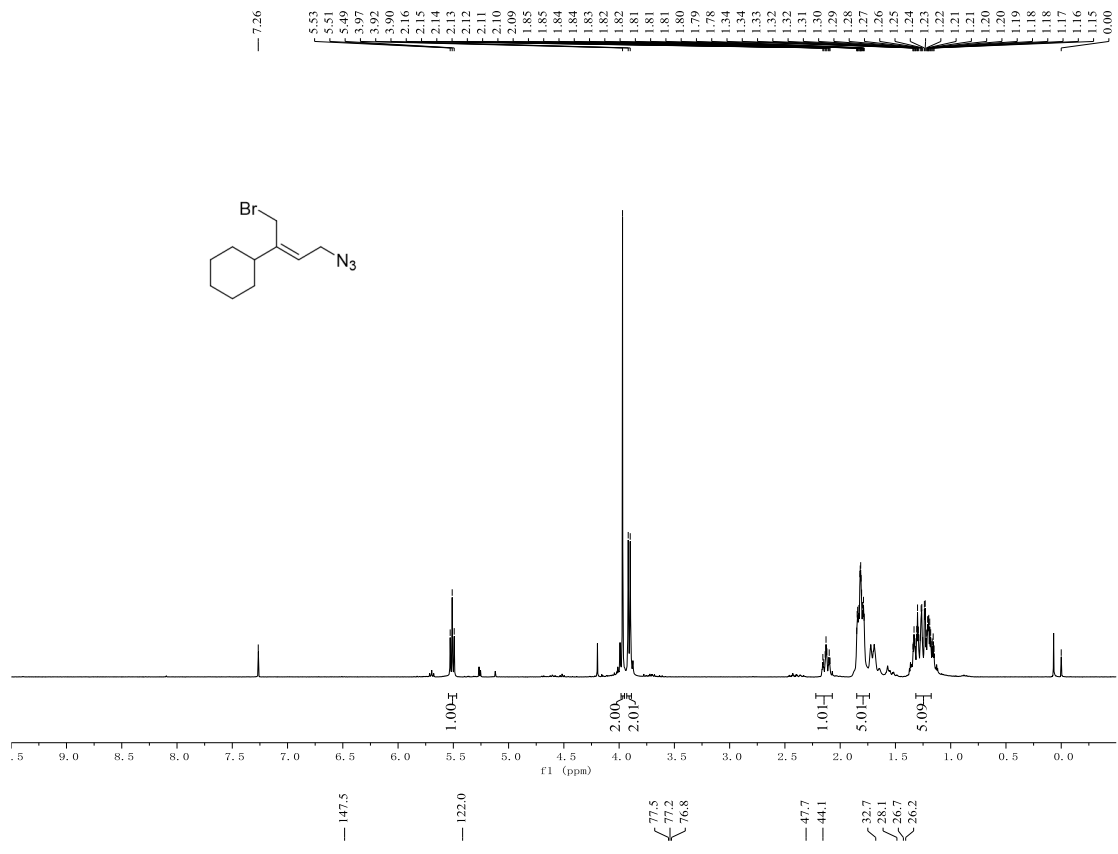


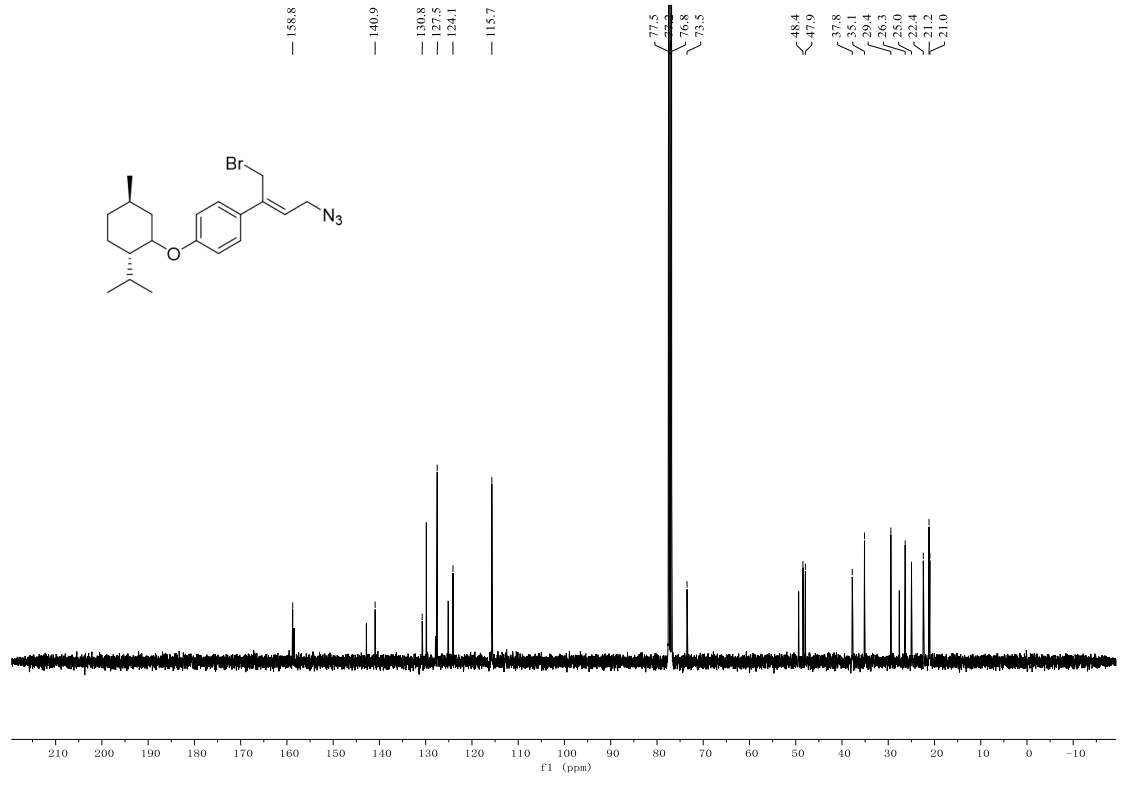
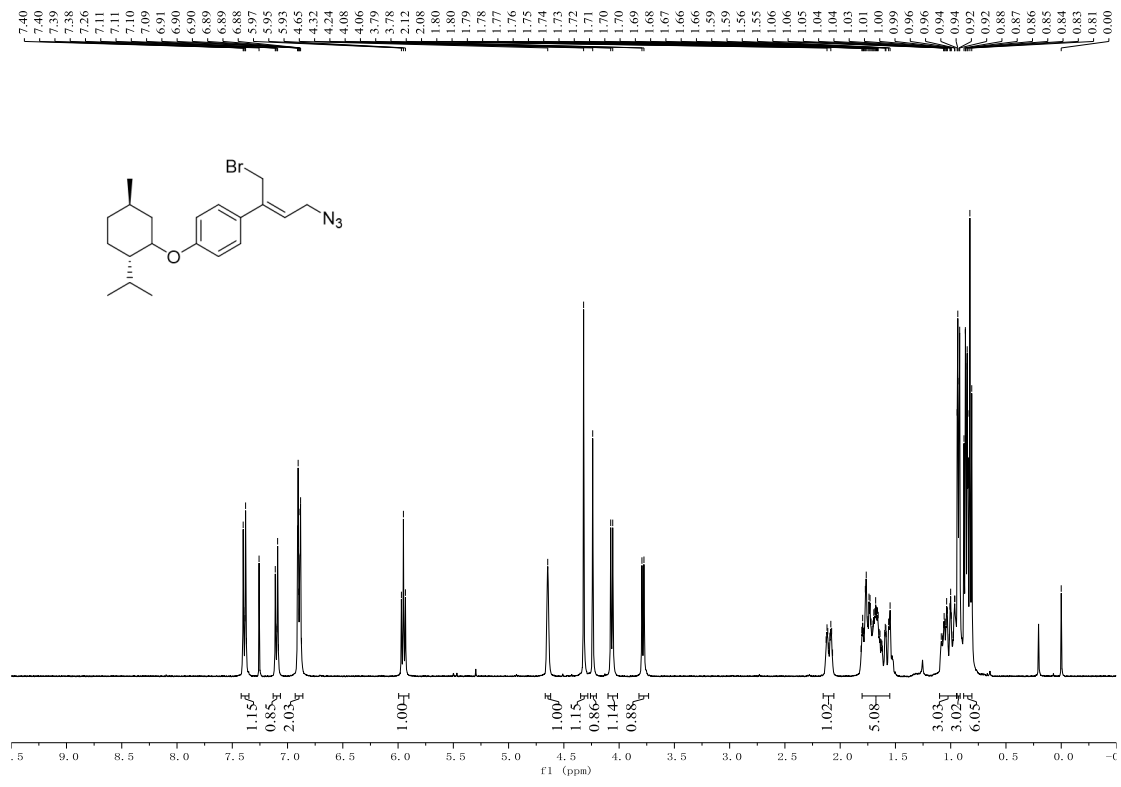


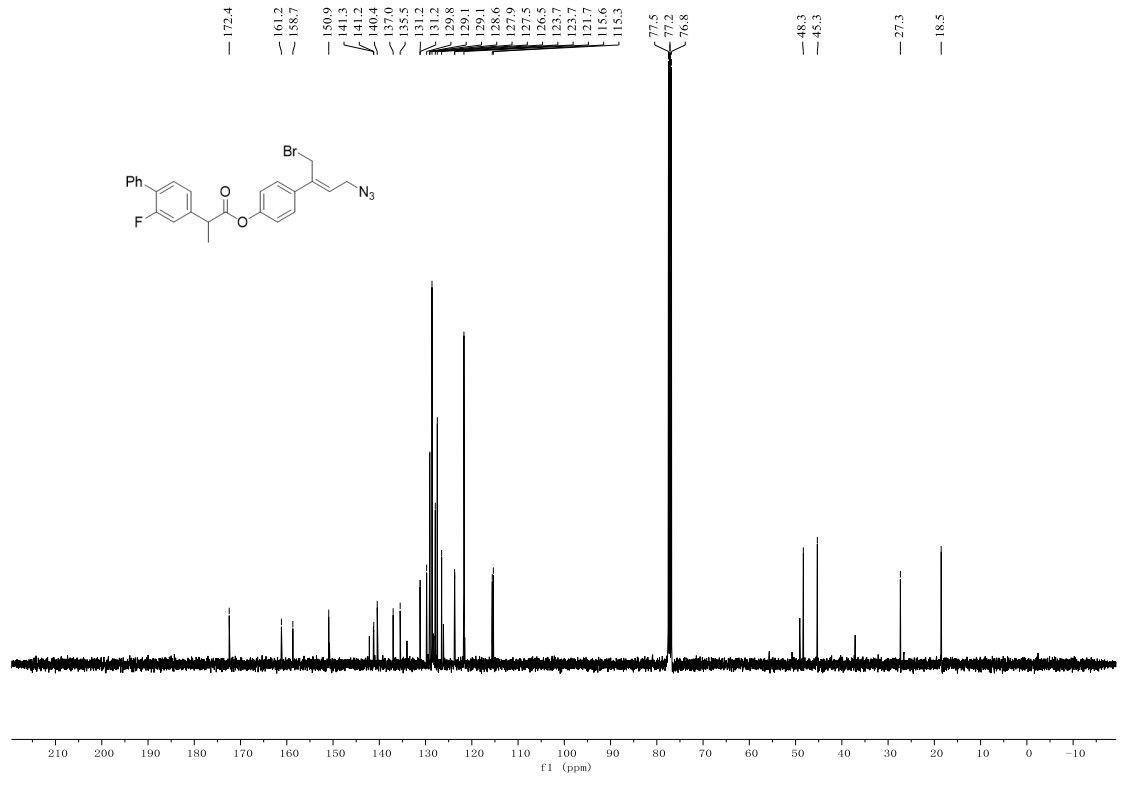
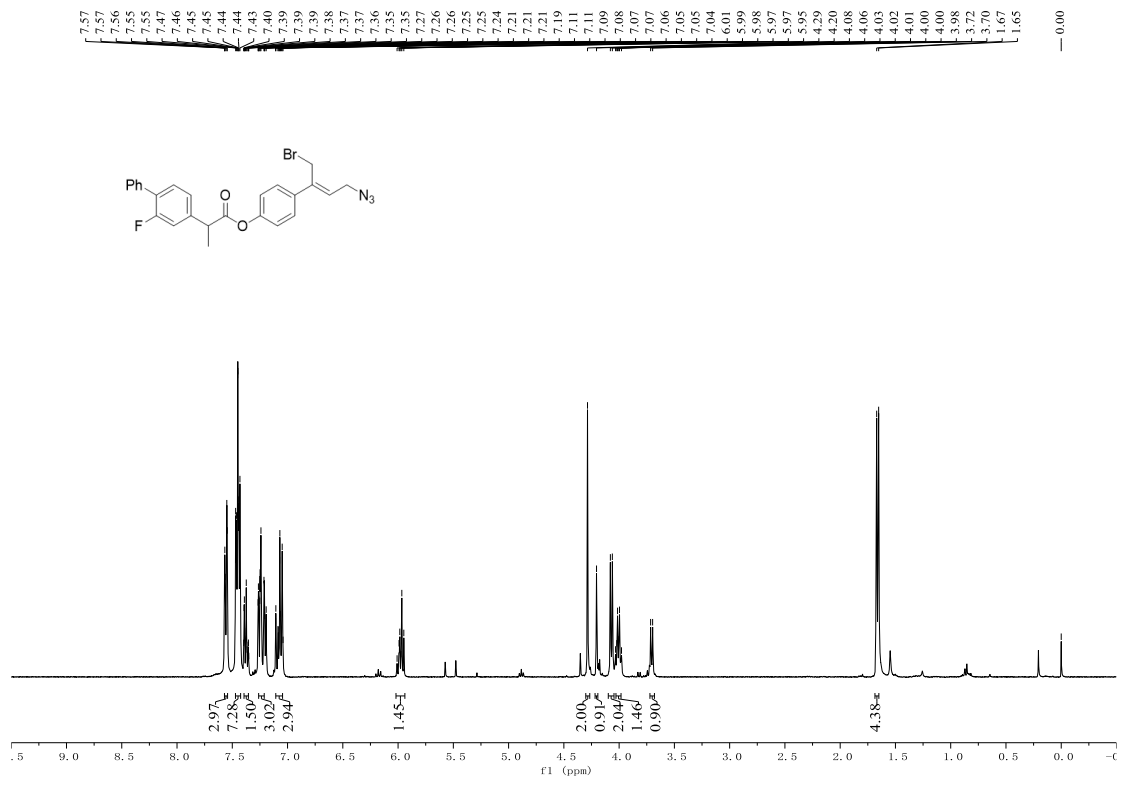


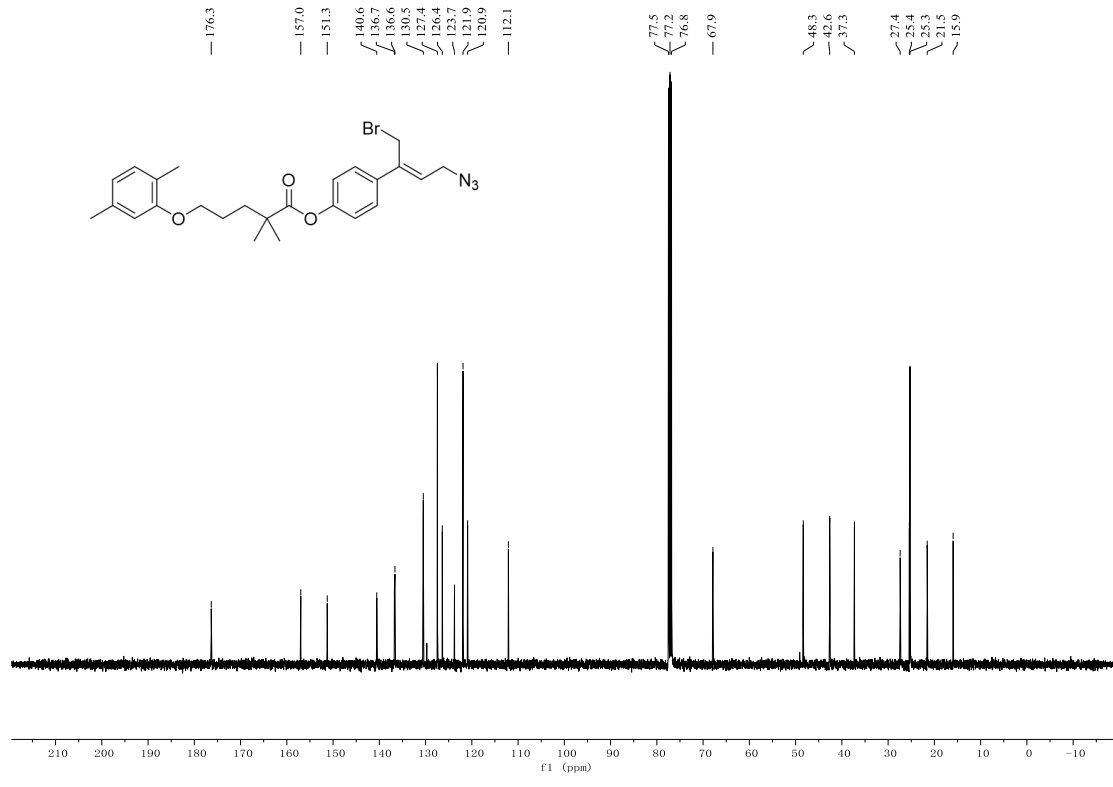
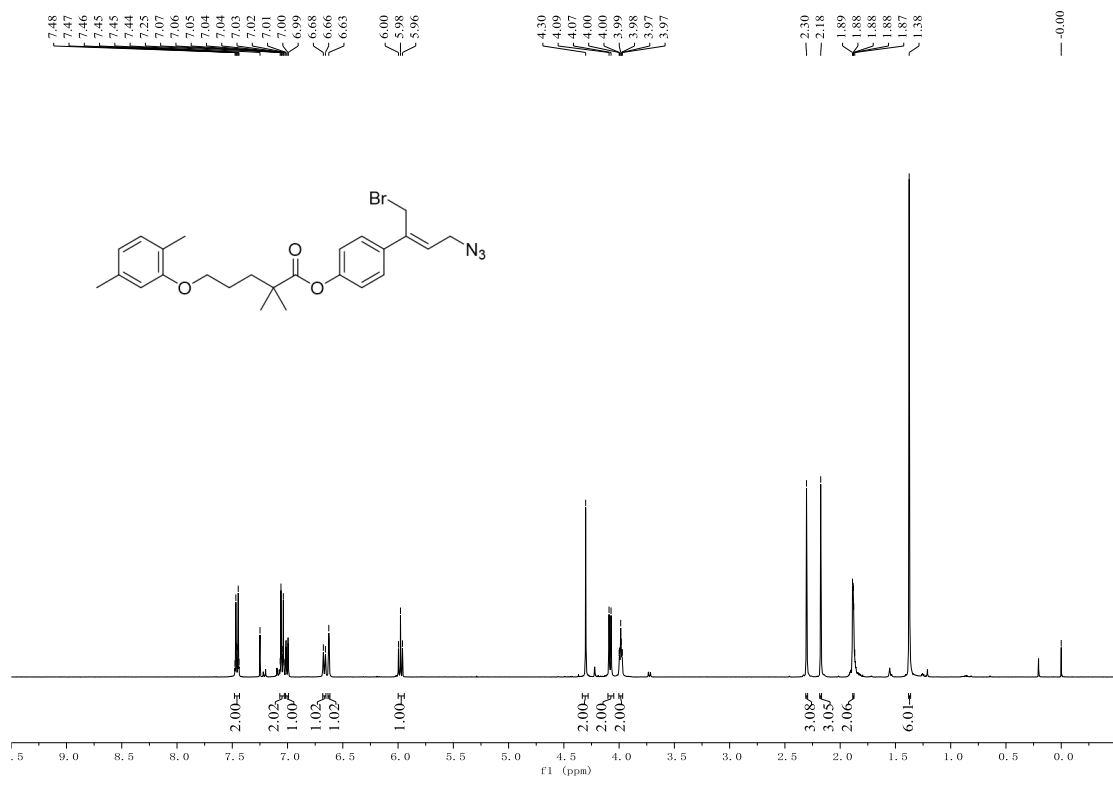
**1D NOESY of 5s**

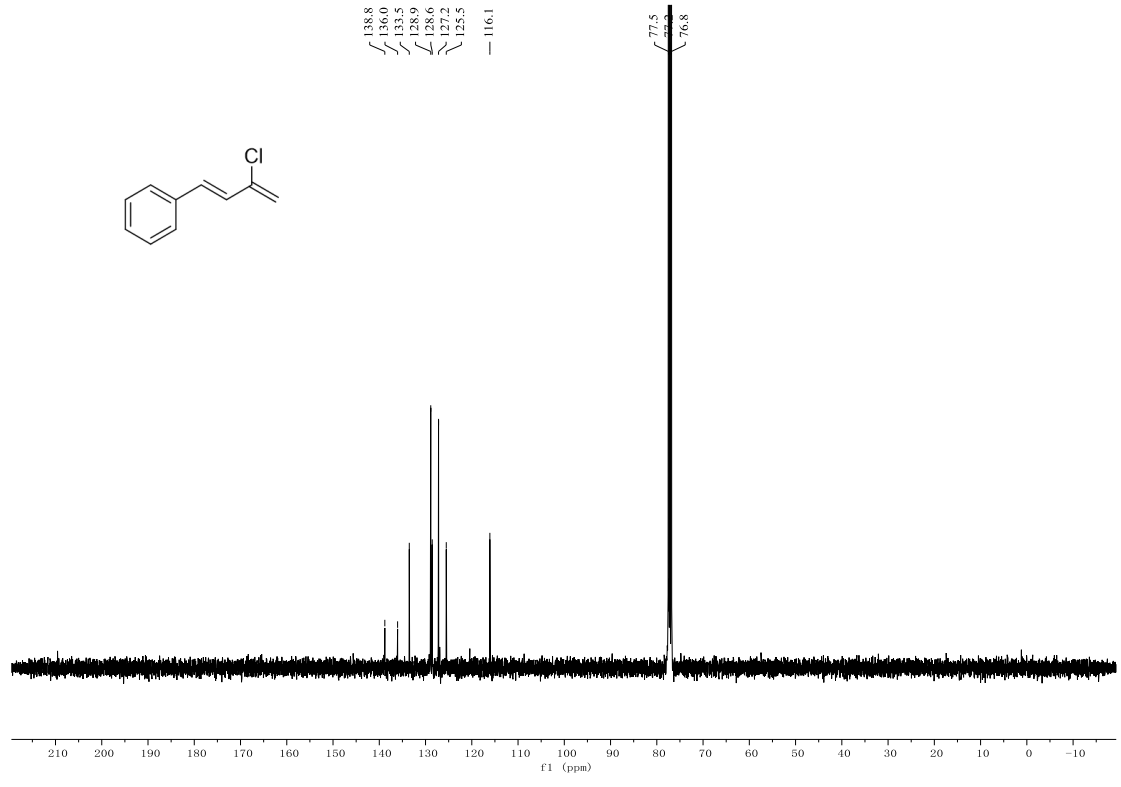
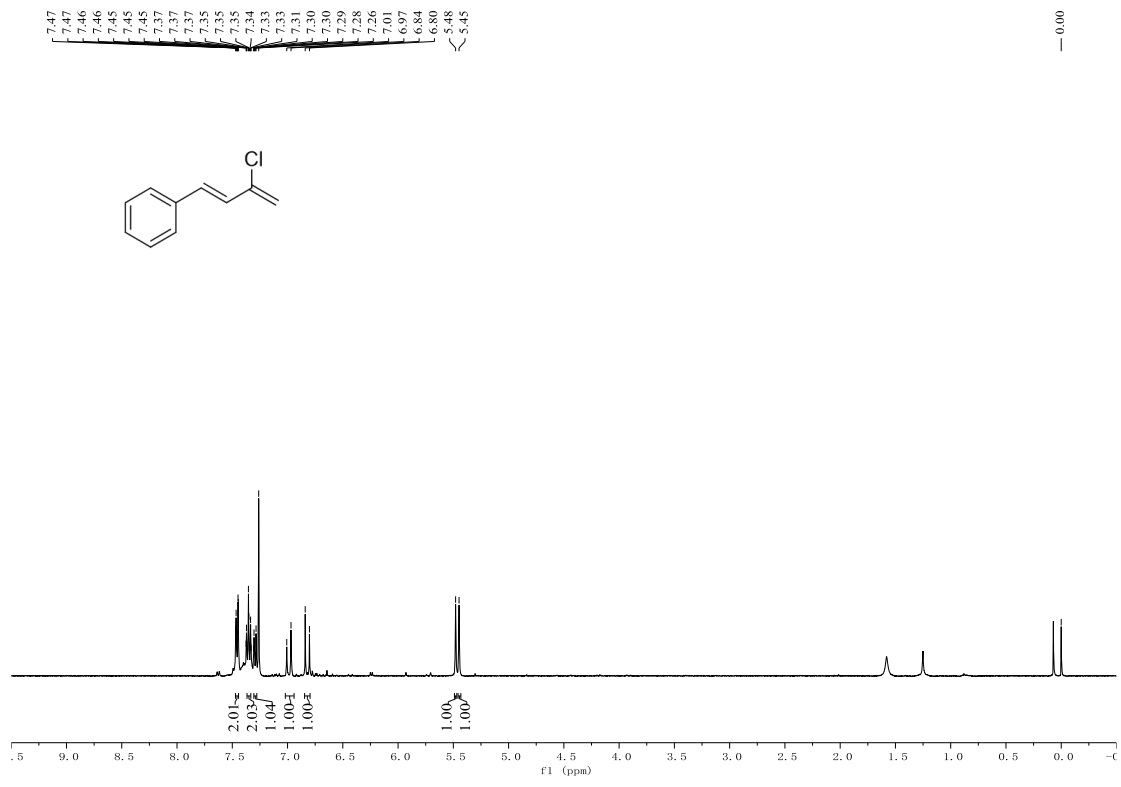


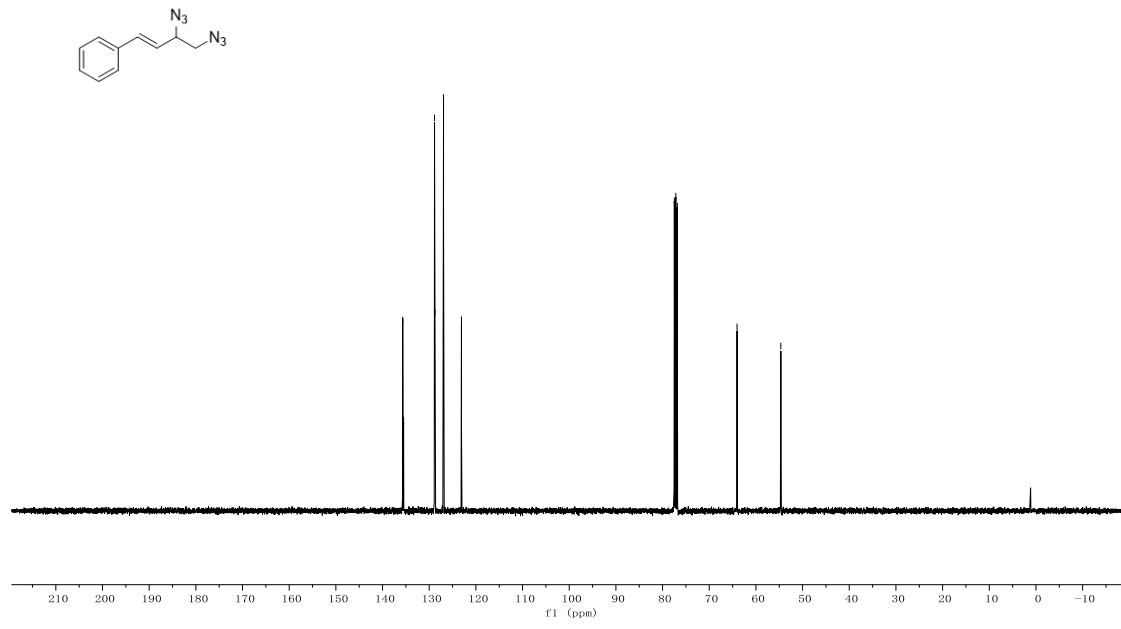
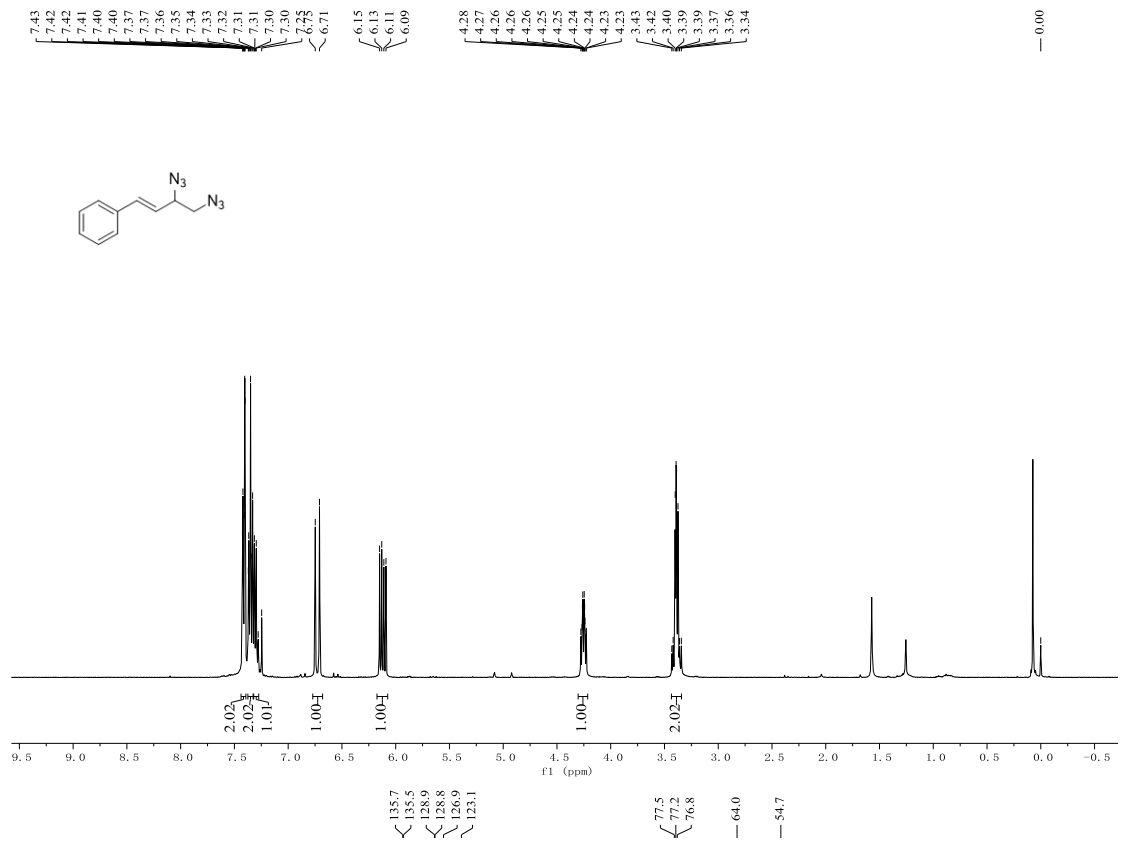




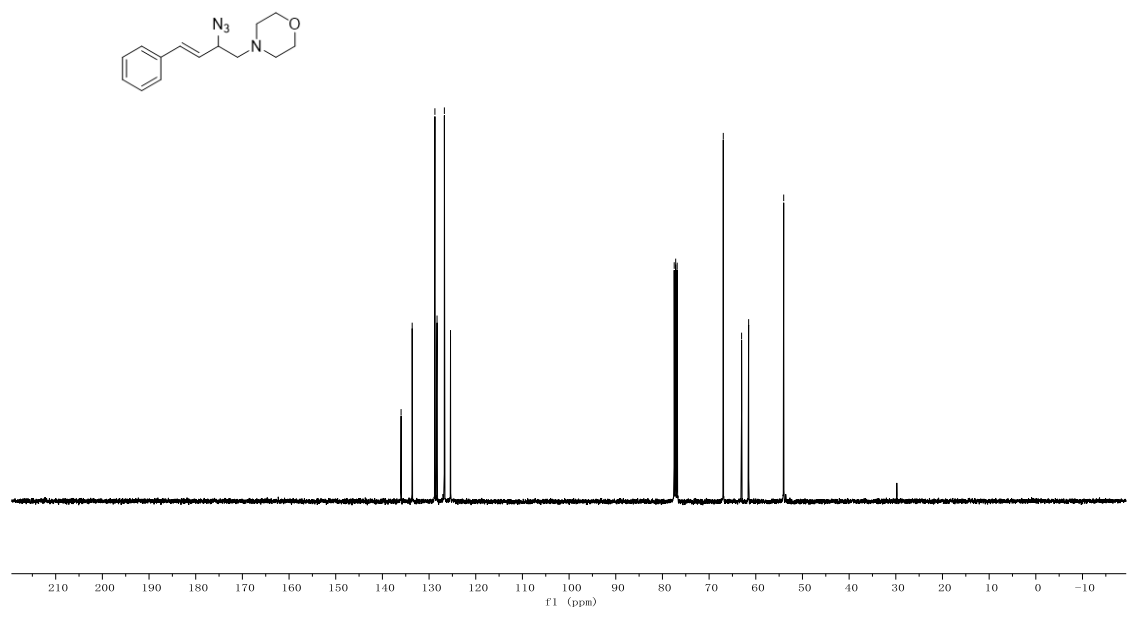
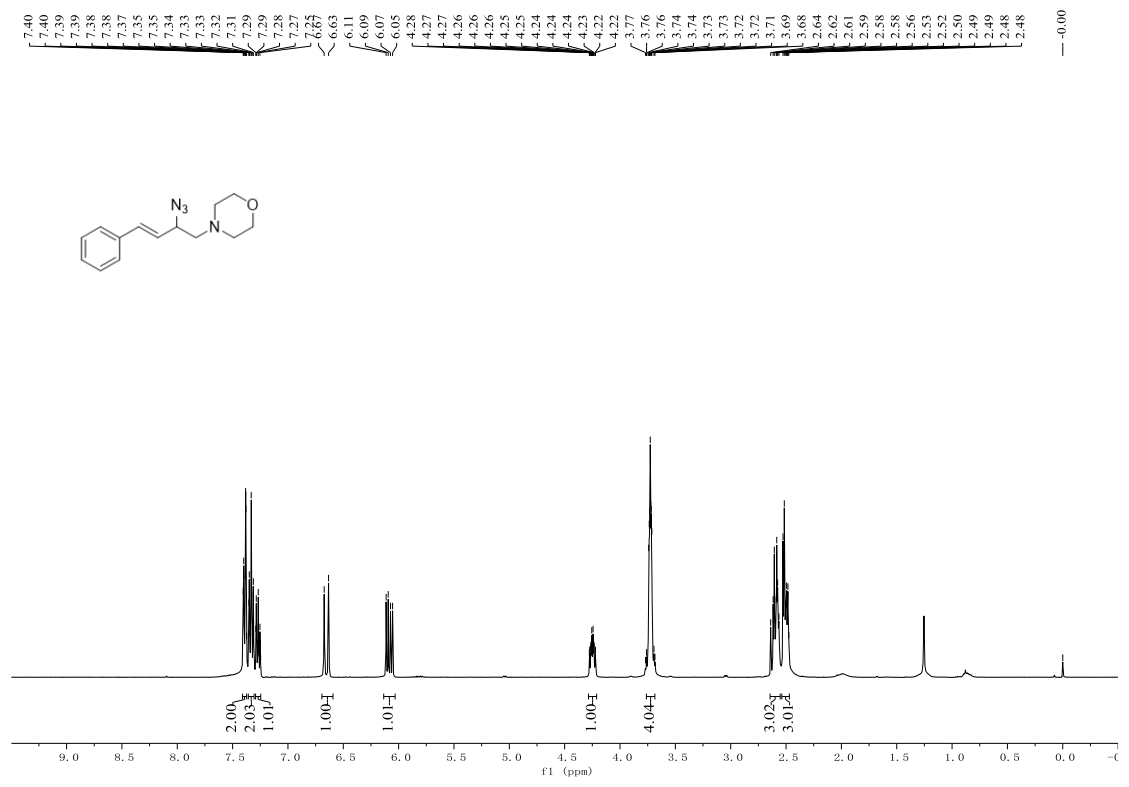


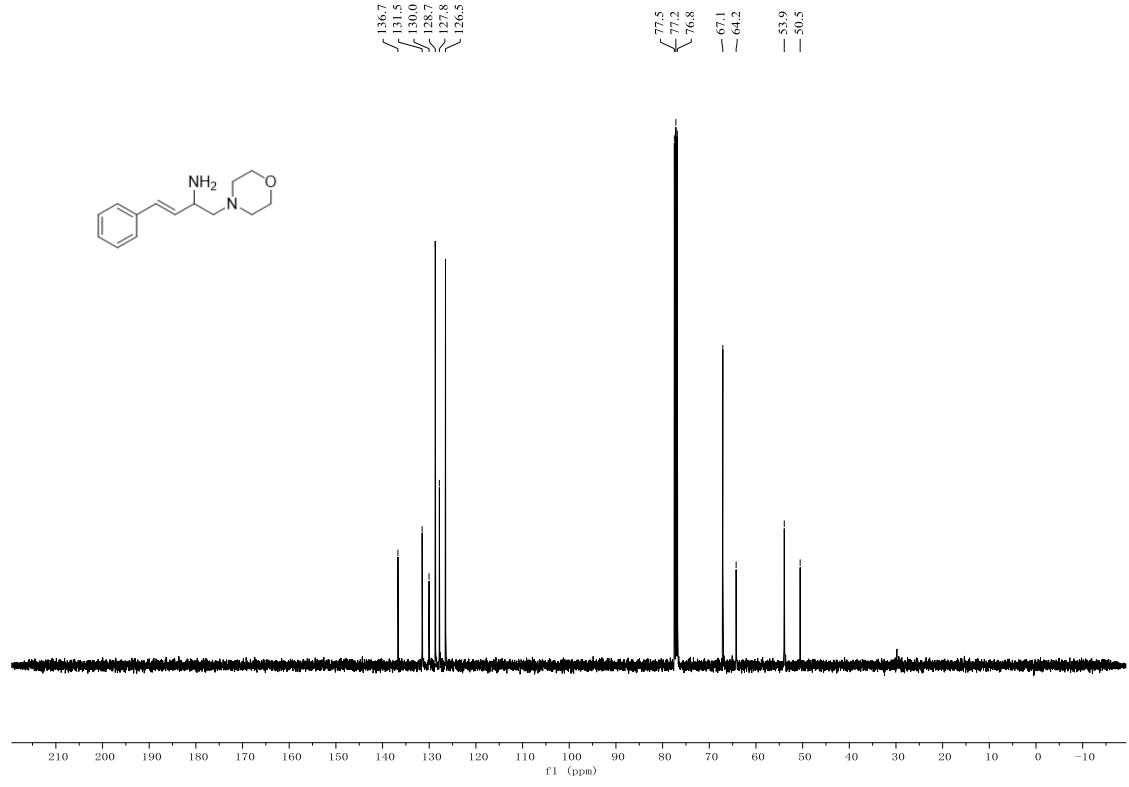
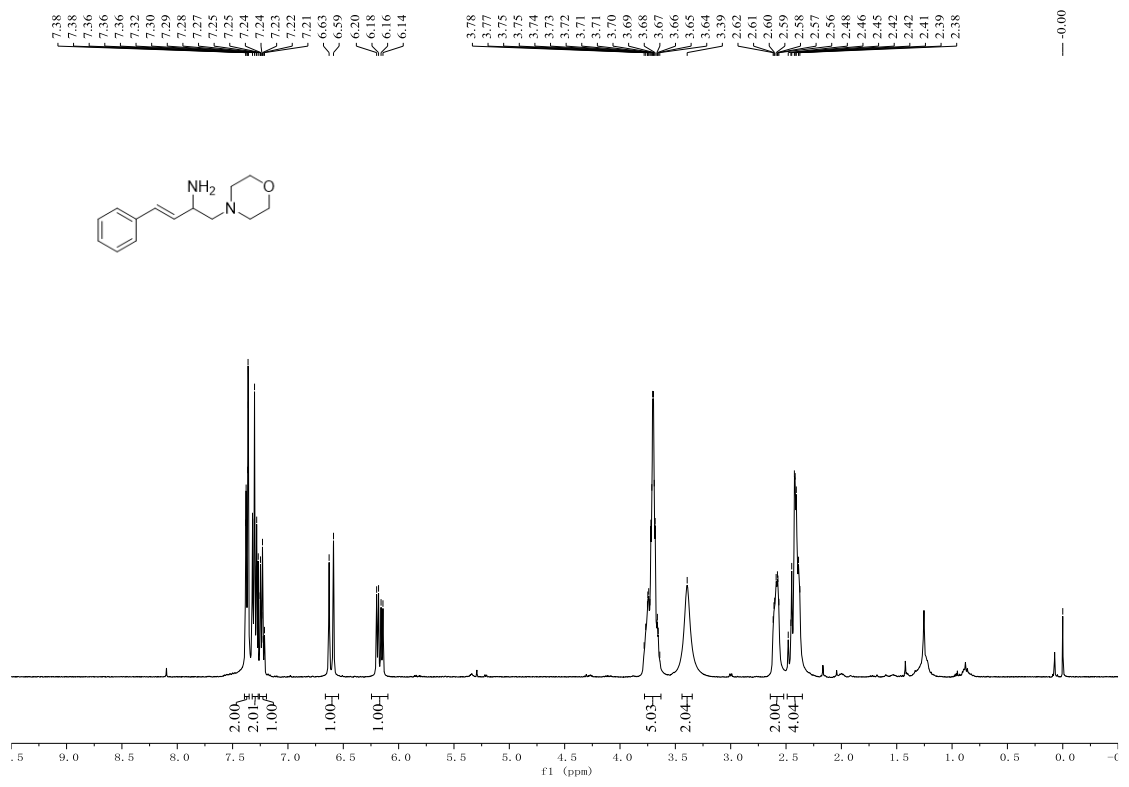


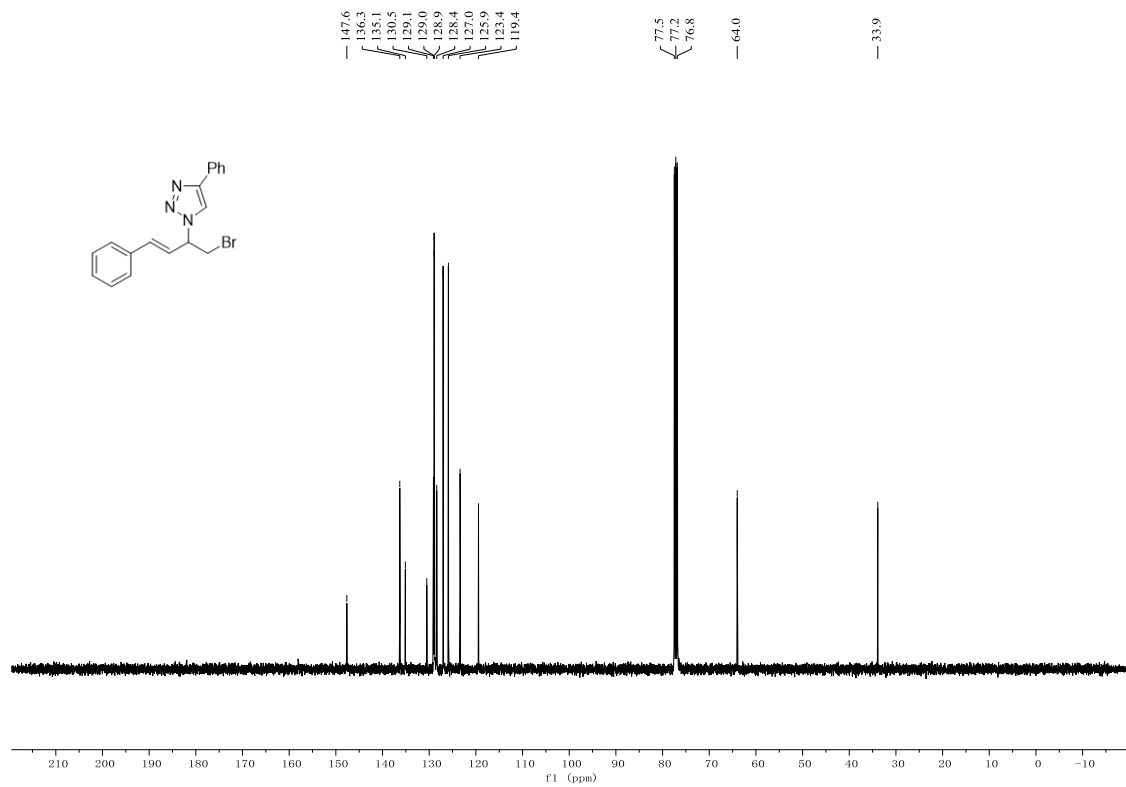
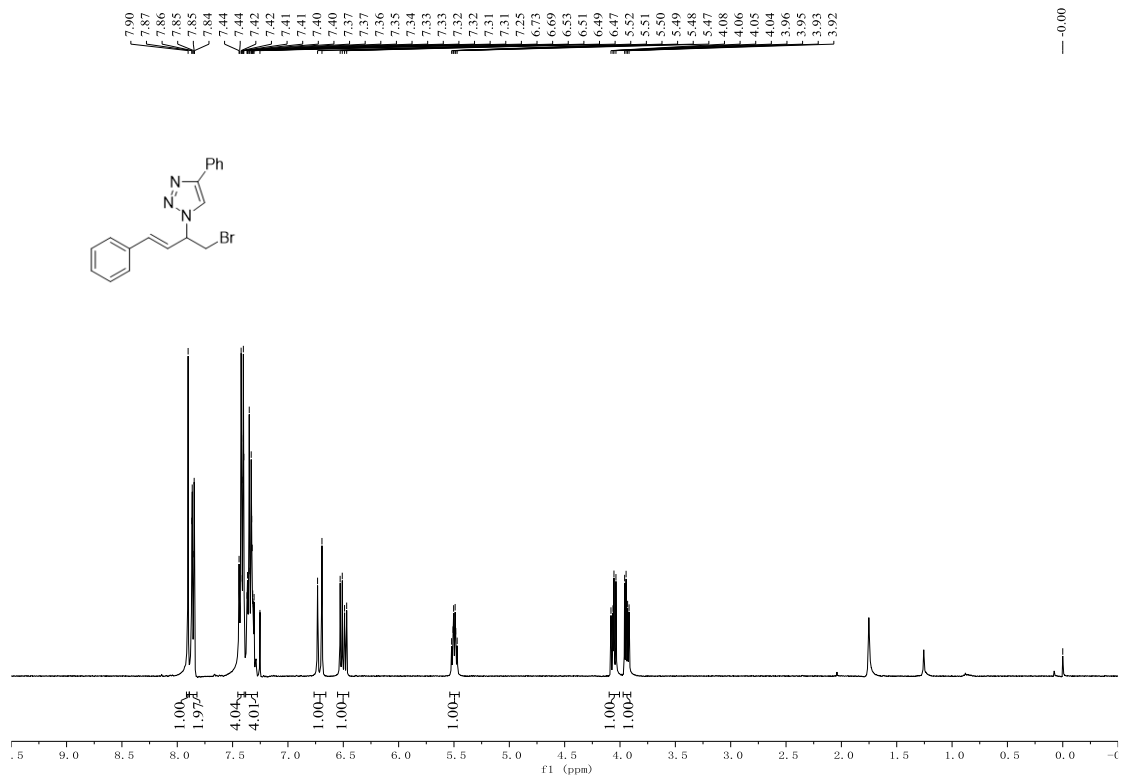


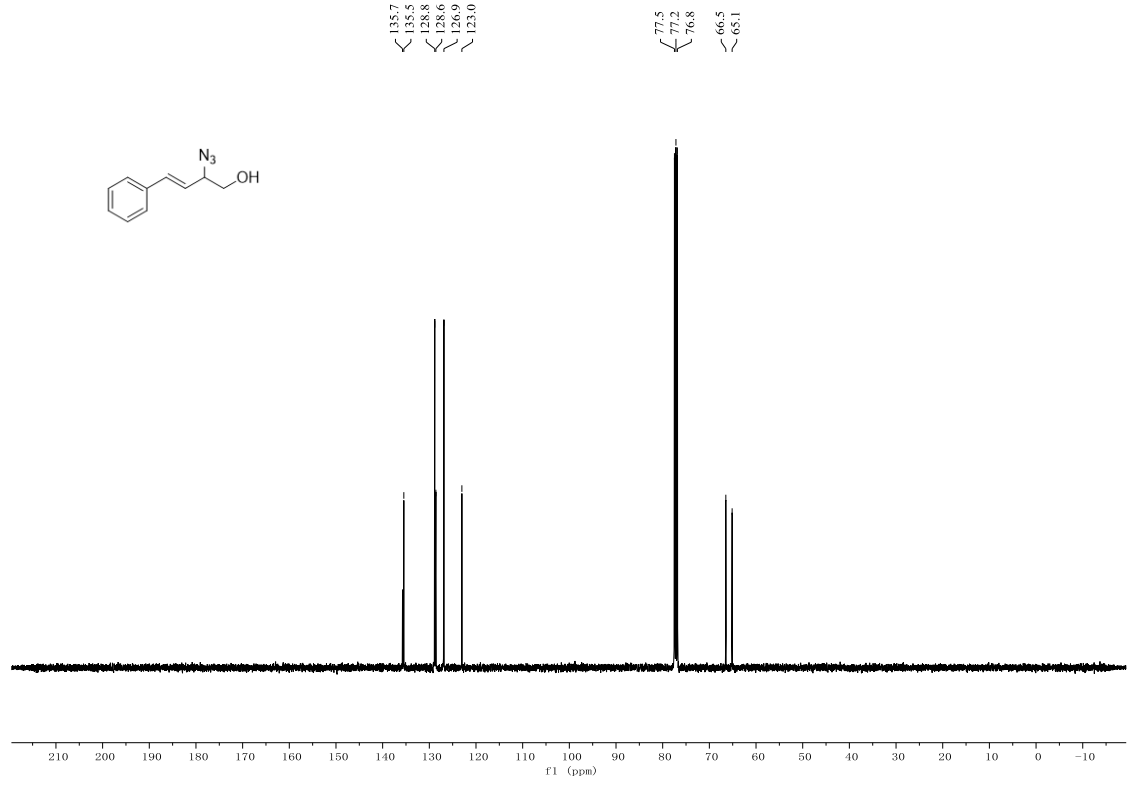
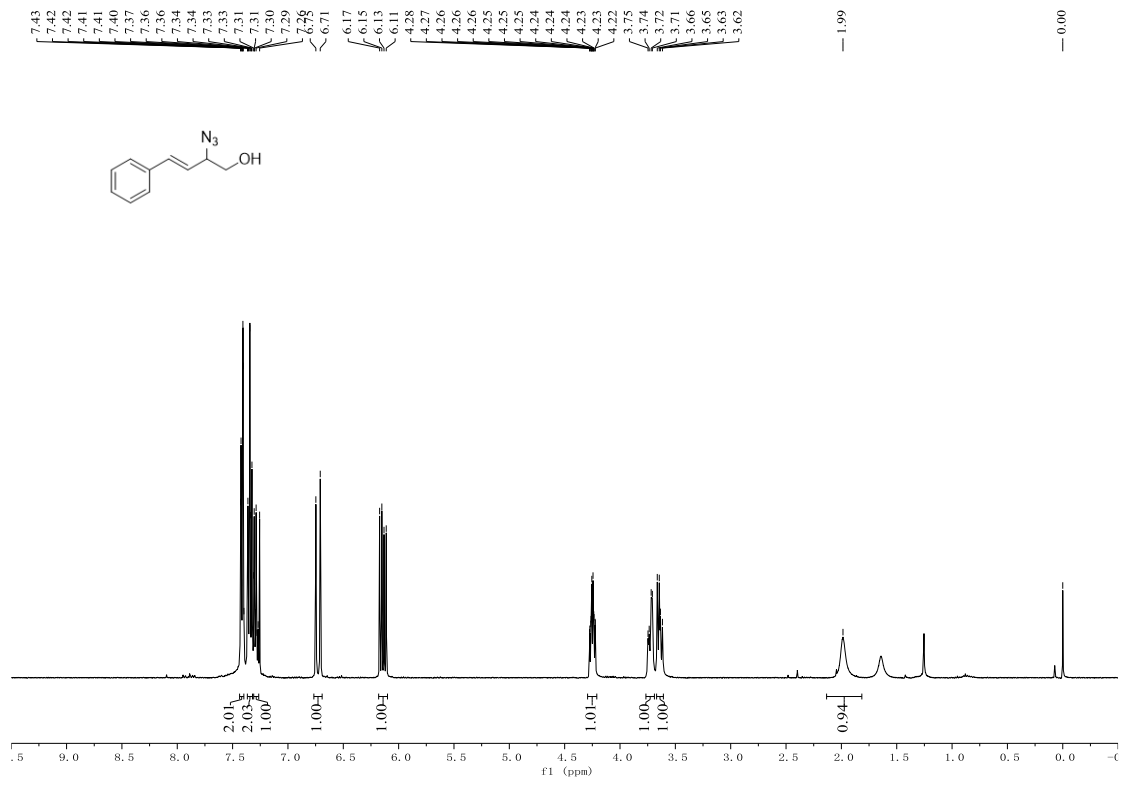


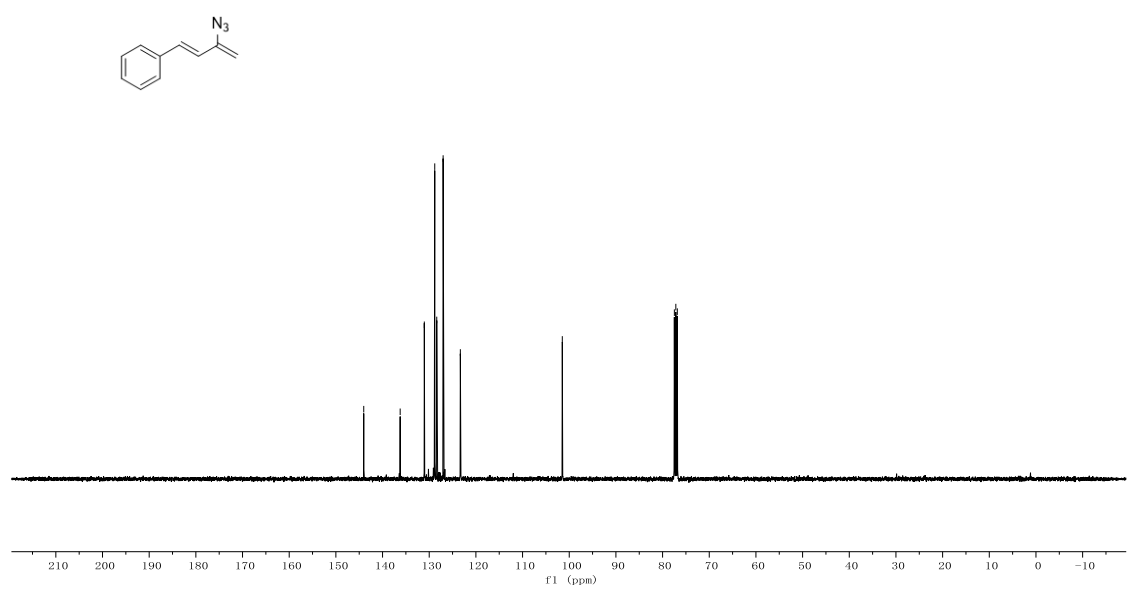
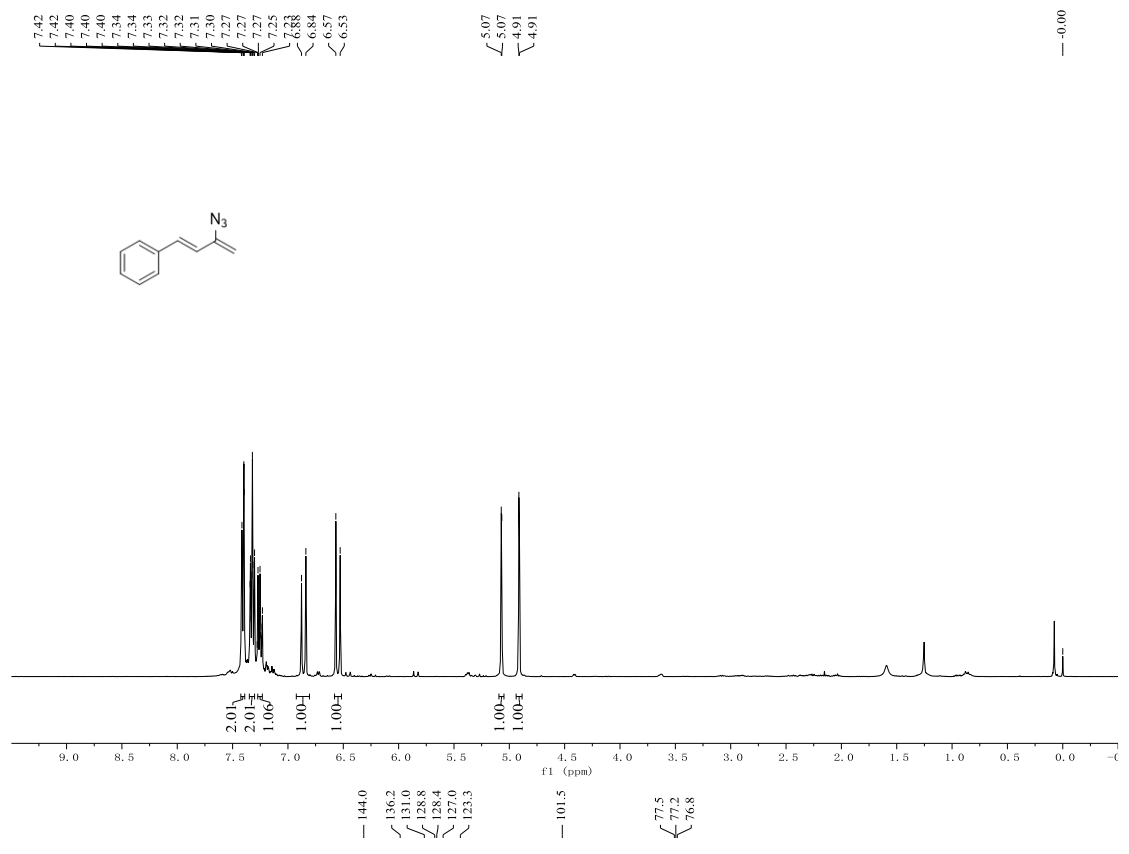


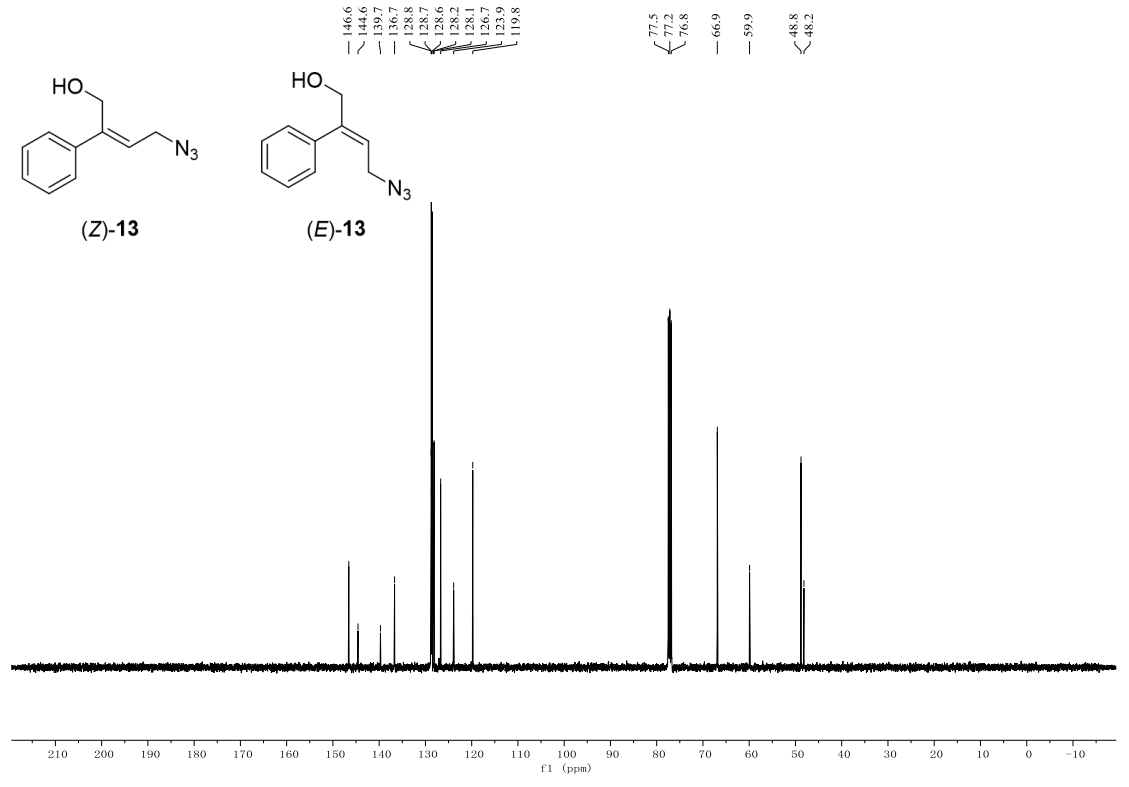
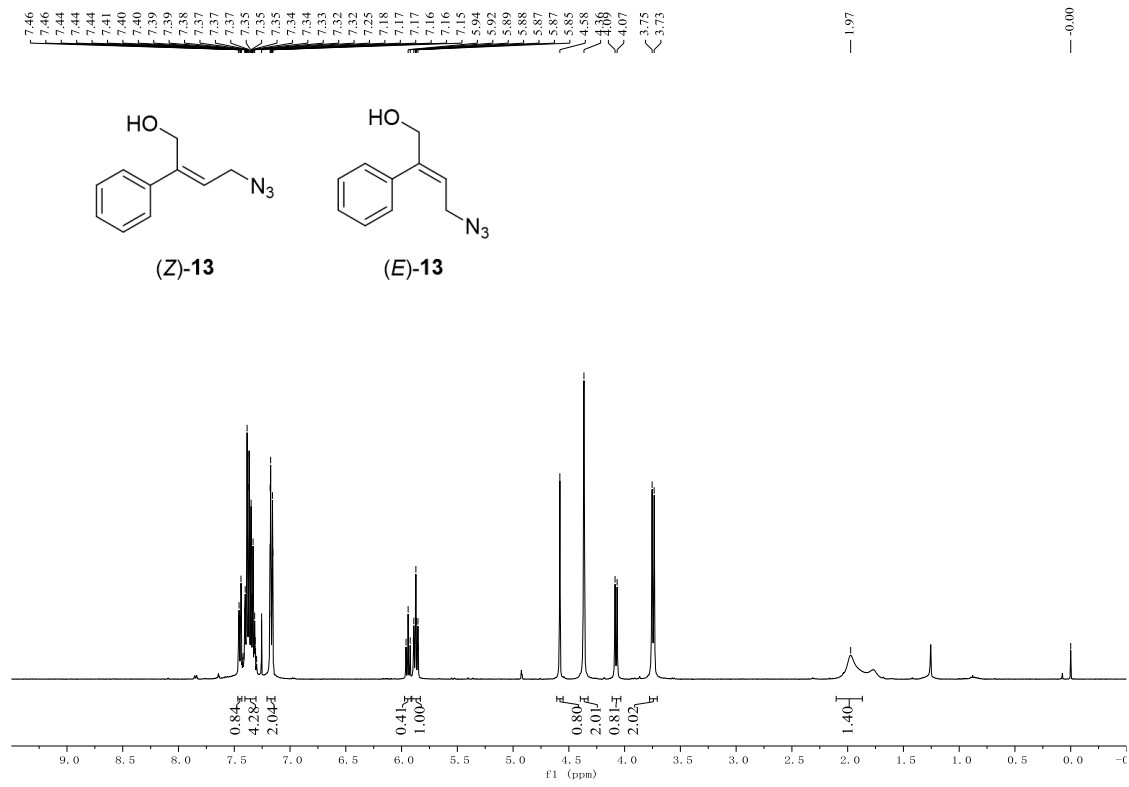




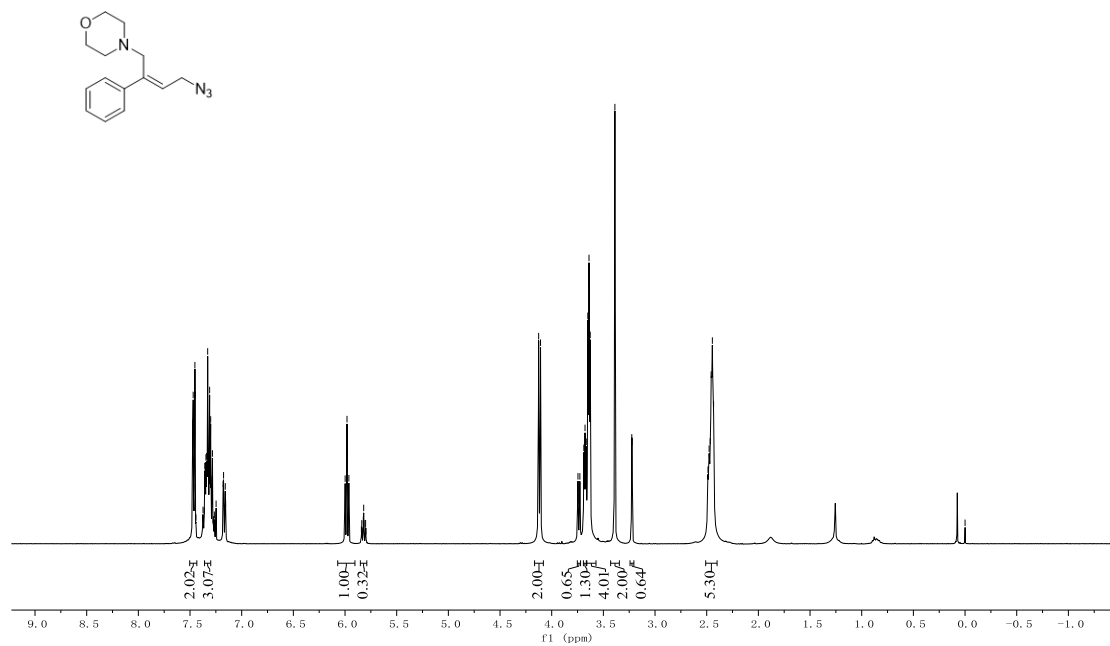
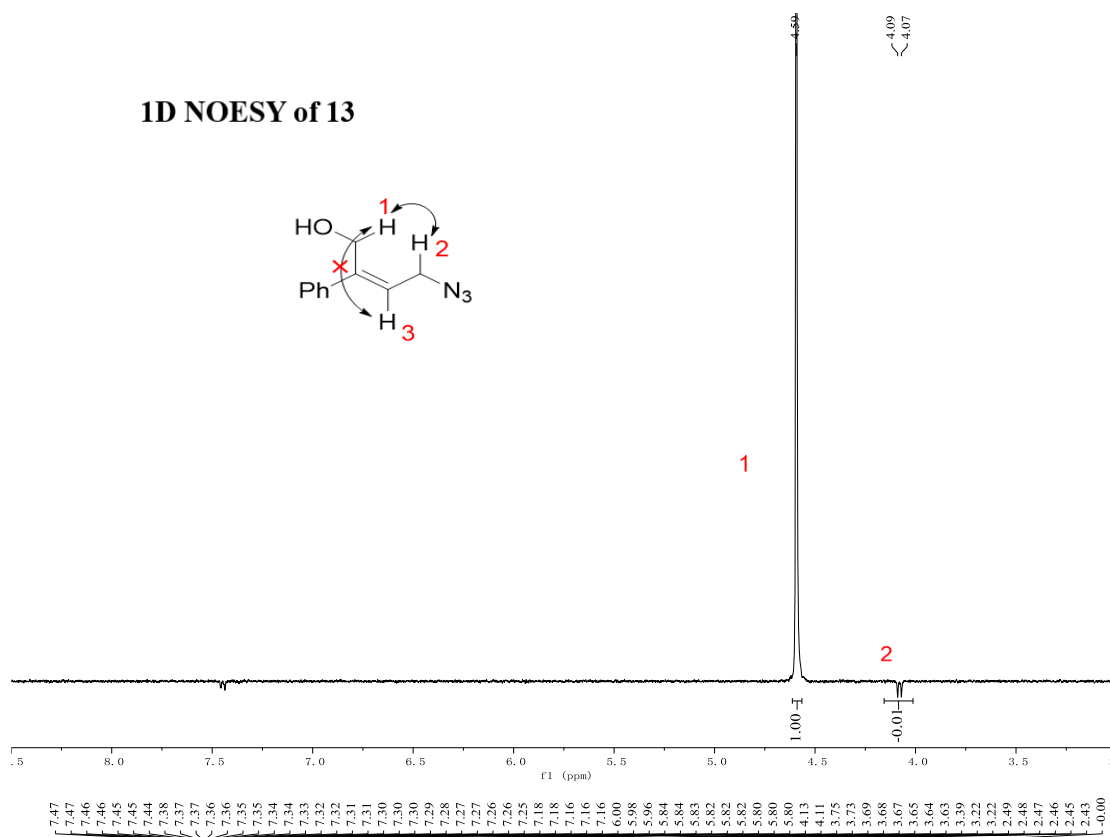
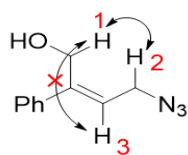


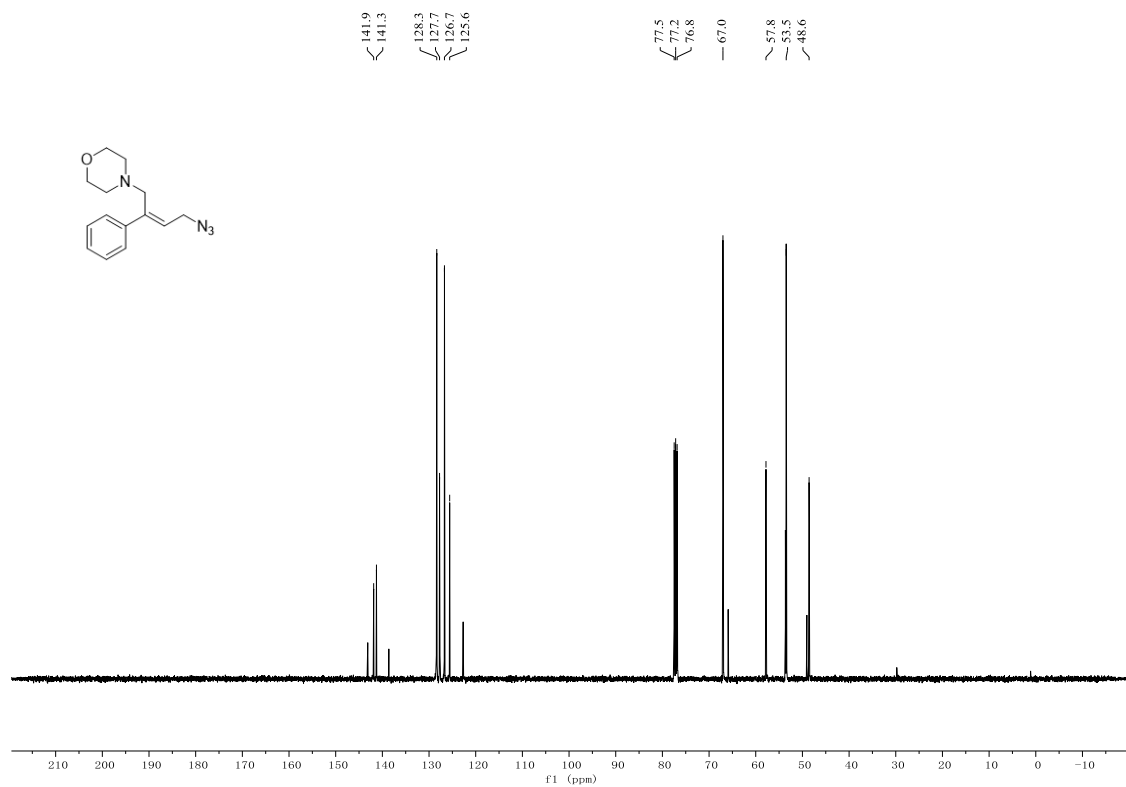




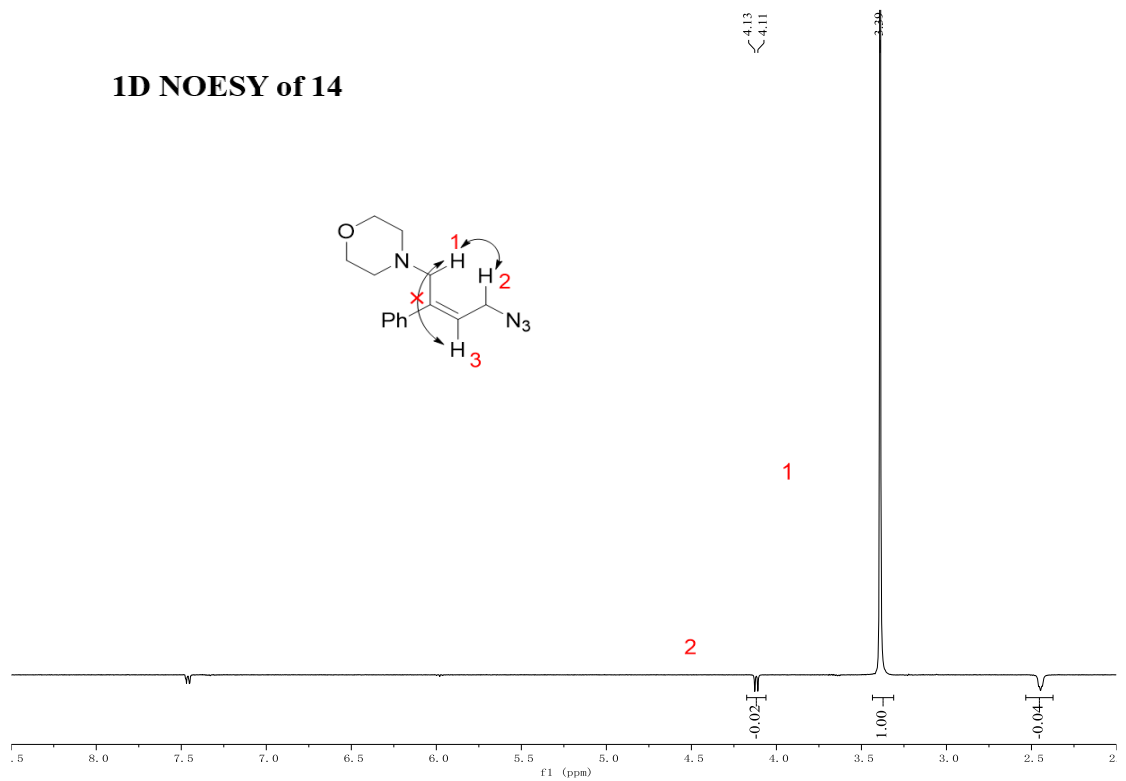


# 1D NOESY of 13

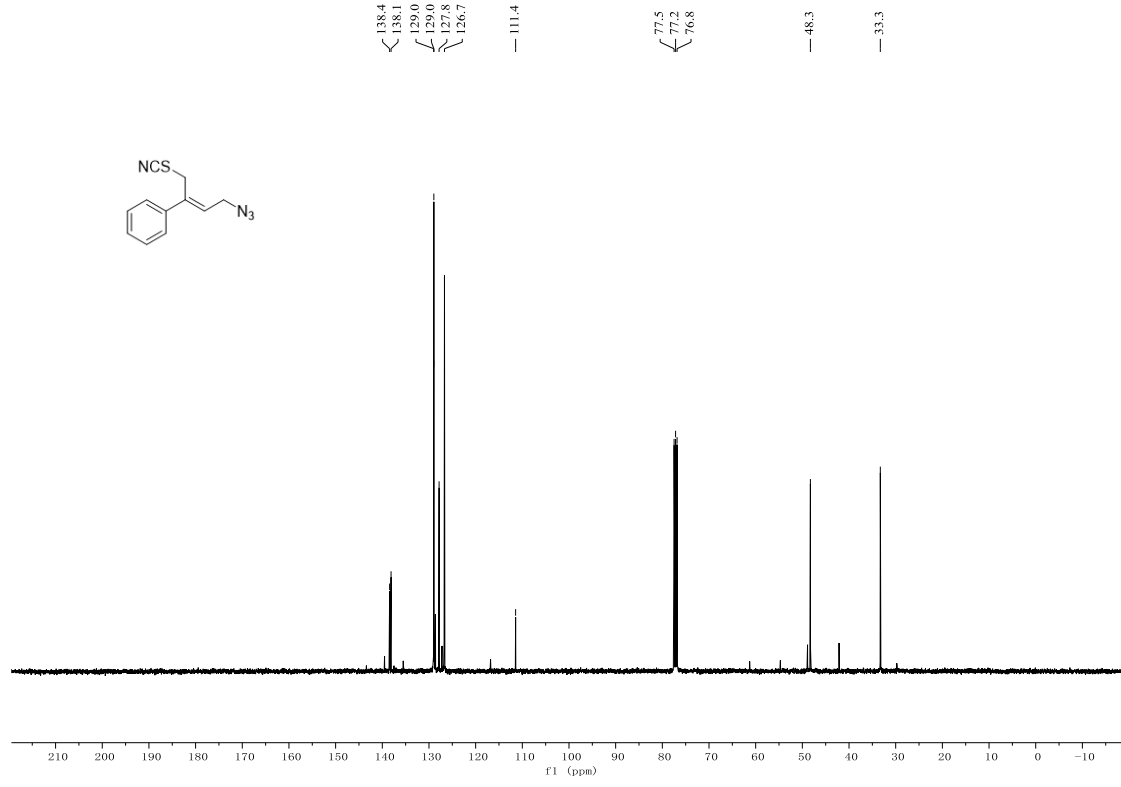
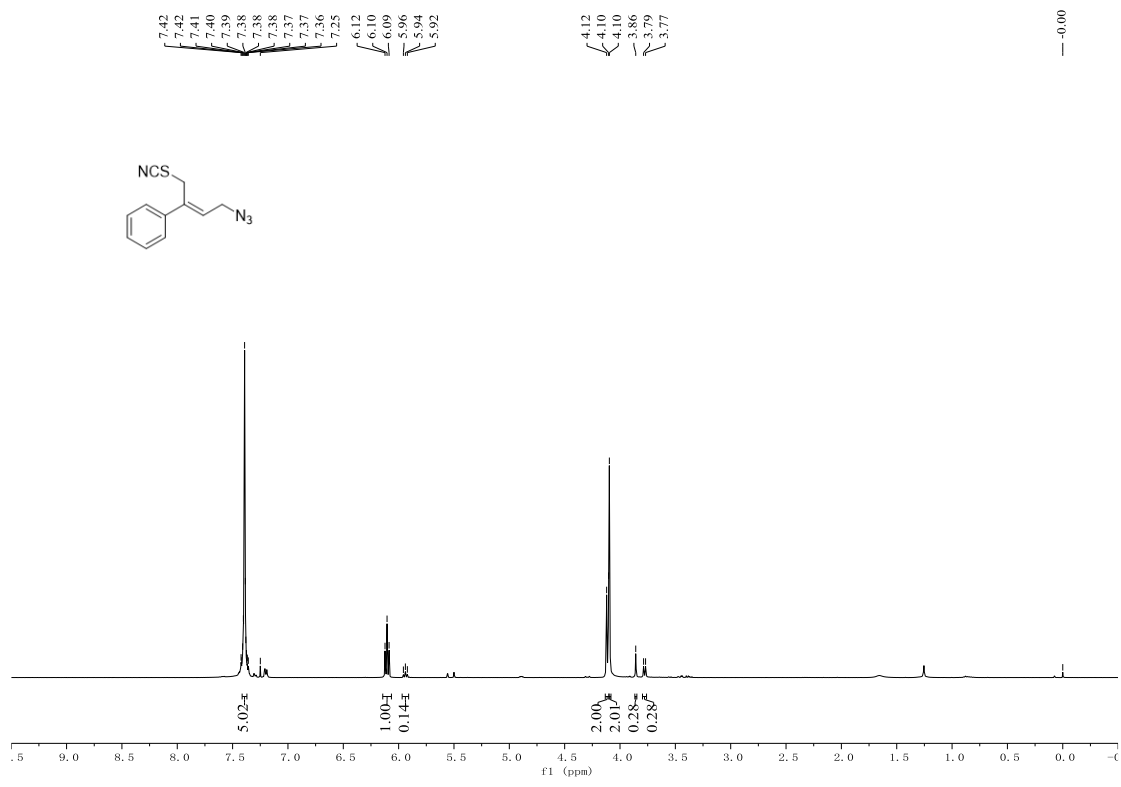


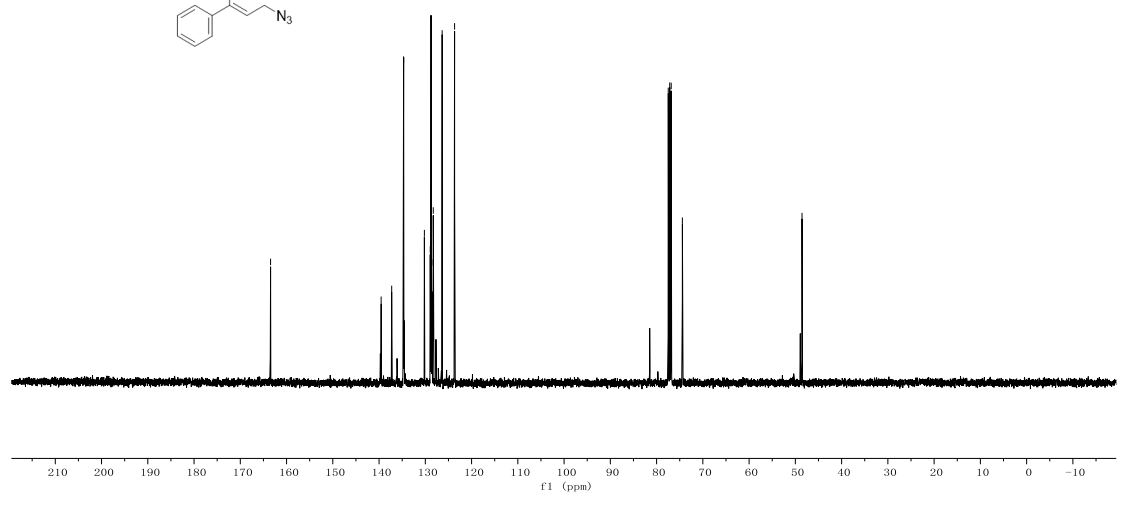
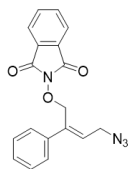
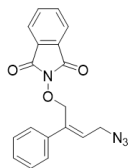
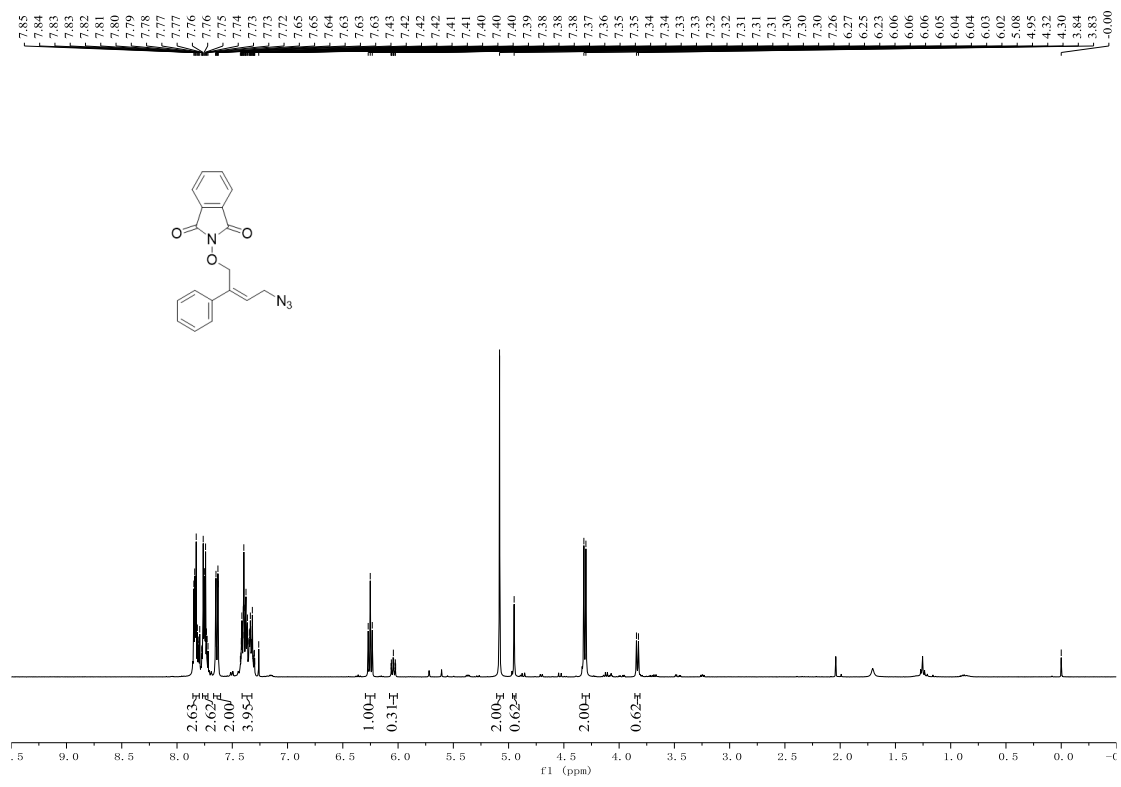


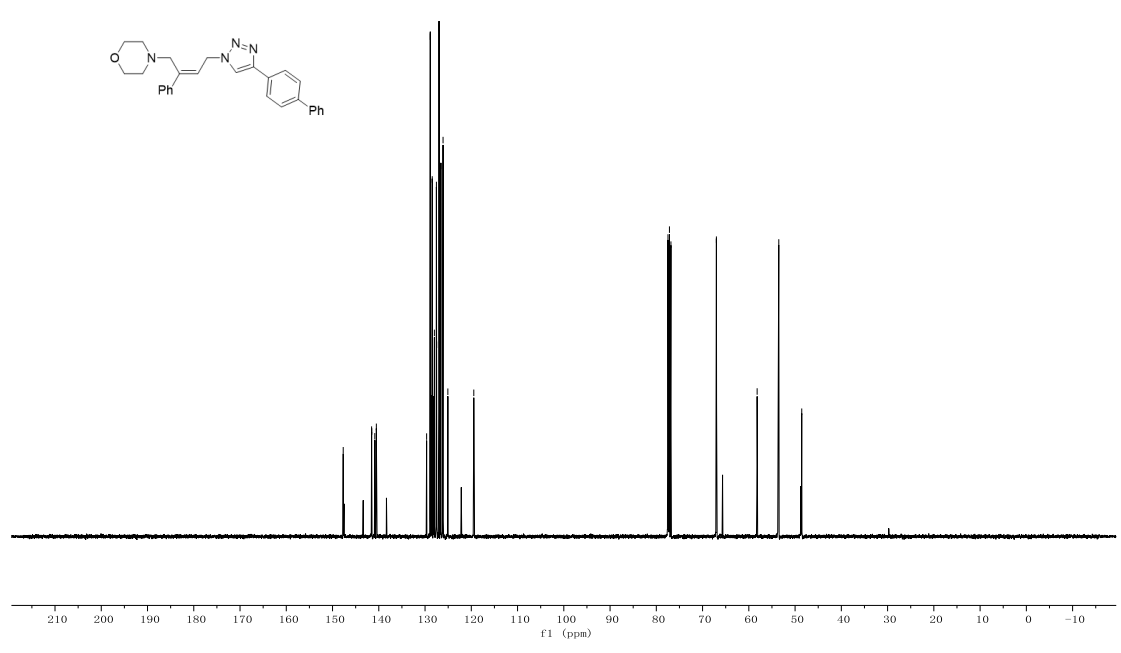
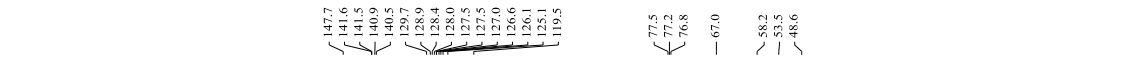
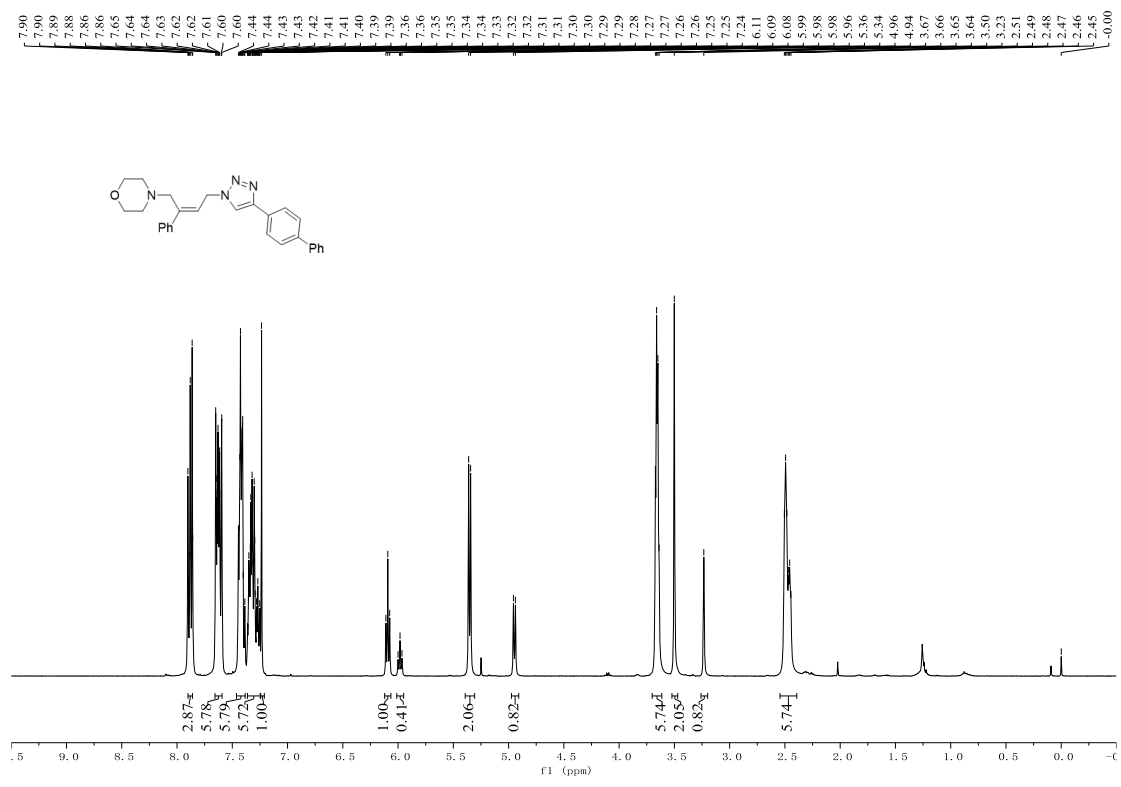
### 1D NOESY of 14











## 5. References

- [1] (a) Takaya, J.; Sasano, K.; Iwasawa, N. *Org. Lett.* **2011**, *13*, 1698–1701. (b) Ji, D.-W.; He, G.-C.; Zhang, W.-S.; Zhao, C.-Y.; Hu, Y.-C.; Chen, Q.-A. *Chem. Commun.* **2020**, *56*, 7431–7464.
- [2] Liao, L.; Sigman, M. S. *J. Am. Chem. Soc.* **2010**, *132*, 10209–10211.
- [3] Marcum, J. S.; Roberts, C. C.; Manan, R. S.; Cervarich, T. N.; Meek, S. J. *J. Am. Chem. Soc.* **2017**, *139*, 15580–15583.
- [4] Ely, R. J.; Morken, J. P. *J. Am. Chem. Soc.* **2010**, *132*, 2534–2535.
- [5] Jiang, X.; Hartwig, J. F. *Angew. Chem. Int. Ed.* **2017**, *56*, 8887–8891.
- [6] Krijnen, E. S.; Zuilhof, H.; Lodder, G. *J. Org. Chem.* **1994**, *59*, 8139–8150.
- [7] Chen, C.-N.; Cheng, W.-M.; Wang, J.-K.; Chao, T.-H.; Cheng, M.-J.; Liu, R.-S. *Angew. Chem. Int. Ed.* **2021**, *60*, 4479–4484.
- [8] (a) Fiorito, D.; Folliet, S.; Liu, Y.; Mazet, C. *ACS Catal.* **2018**, *8*, 1392–1398. (b) Wang, Z.-L.; Wang, Y.; Xu, J.-L.; Zhao, M.; Dai, K.-Y.; Shan, C.-C.; Xu, Y.-H. *Org. Lett.* **2021**, *23*, 4736–4742. (c) Wang, Y.; Wang, Z.-L.; Ma, W.-W.; Xu, Y.-H. *Org. Lett.* **2022**, *24*, 4081–4086.
- [9] Lim, B.; Oh, E.-T.; Im, J. O.; Lee, K. S.; Jung, H.; Kim, M.; Kim, D.; Oh, J. T.; Bae, S.-H.; Chung, W.-J.; Ahn, K.-H.; Koo, S. *Eur. J. Org. Chem.* **2017**, *2017*, 6390–6400.
- [10] Jose, B.; Patricia, M.; Fernando, A.; Carlos, V. *Adv. Synth. Catal.* **2006**, *348*, 347–353.
- [11] Shen, S.-J.; Zhu, C.-L.; Lu, D.-Fu; Xu, H. *ACS Catal.* **2018**, *8*, 4473–4482.
- [12] Liu, Z.-H.; Liao, P.-Q.; Bi, X.-H. *Org. Lett.* **2014**, *16*, 3668–3671.
- [13] Qi, Z.; Li, W.; Niu, Y.; Benassi, E.; Qian, B. *Org. Lett.* **2021**, *23*, 2399–2404.
- [14] Fumagalli, G.; Rabet, P. T. G.; Boyd, S.; Greaney, M. F. *Angew. Chem., Int. Ed.* **2015**, *54*, 11481–11484.
- [15] Rueping, M.; Vila, C.; Uria, U. *Org. Lett.* **2012**, *14*, 768–771.
- [16] Kroesen, U.; Knauer, L.; Strohmam, C. *Angew. Chem., Int. Ed.* **2017**, *56*, 6232–6235.