Supporting Information

# Photo-induced nickel-mediated cross-electrophile coupling for alkylated allenes via electron donor-acceptor complexes

Zhao-Zhao Zhou,*[a$] Xiao-Feng Zhai,[b$] Shu-Liang Zhang,[b] Ke-Jian Xia,[a] Haixin Ding,*[b] Xian-Rong Song,[b] Wan-Fa Tian,[b] Yong-Min Liang[c] and Qiang Xiao*[b]

[a] *College of Chemistry and Food Science, Nanchang Normal University, Nanchang, 330000, P.R. China.*
[b] *Institute of Organic Chemistry, Jiangxi Science & Technology Normal University, Key Laboratory of Organic Chemistry, Nanchang, 330000, Jiangxi Province, P.R. China.*
[c] *State Key Laboratory of Applied Organic Chemistry, Lanzhou University, Lanzhou 730000, P.R. China*

E-mail: zhouzz@lzu.edu.cn, xiaoqiang@tsinghua.org.cn

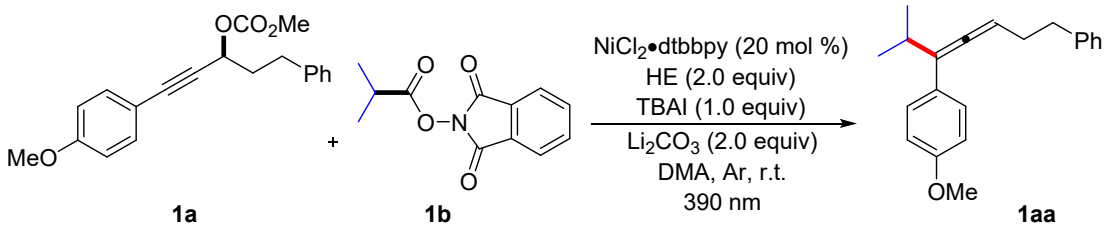
**Table of Contents**

S1. General Information and Materials
S2. General Procedure for the photo-induced nickel-mediated cross-electrophile coupling for alkylated allenes
S3. Preparation of Starting Materials
S4. Optimization of Reaction Conditions
S5. Mechanism Characterization
S6. References
S7. Characterization Data of Products **1aa-1oa**
S8. Characterization Data of Products **2aa-2oa, 3aa, 3ba-3bb**
S9. $^{1}$H NMR and $^{13}$C NMR Spectra of the Products **1aa-1oa**
S10. $^{1}$H NMR and $^{13}$C NMR Spectra of the Products **2aa-2oa, 3aa, 3ba-3bb**

## 1. General Information and Materials:

For product purification by flash column chromatography, silica gel (200~300 mesh) and *n*-pentane were used. $^{1}$H NMR spectra were recorded on 400 MHz in $CDCl_3$, $^{13}$C NMR spectra were recorded on 100 MHz in $CDCl_3$, $^{19}$F NMR spectra were recorded on 376 MHz in $CDCl_3$ using TMS as internal standard. Melting points were determined on a microscopic apparatus and were uncorrected. All products were further characterized by HRMS (high-resolution mass spectra). Copies of their $^{1}$H NMR and $^{13}$C NMR spectra were provided. The starting materials were purchased from Sigma-Aldrich, Acros, TCI, Admas or J&K Chemicals and used without further purification. Kessil brand 390 (± 15) nm LED was used in a reaction box equipped cooling fan to keep reaction temperature between 15 °C and 25 °C.

## 2. General Procedure for photo-induced nickel-mediated cross-electrophile coupling for alkylated allenes:




**1a** **1b** **1aa**

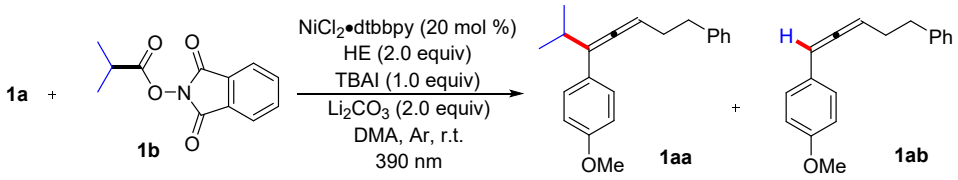
In a 10.0 mL snap vial with Teflon cover and magnetic stirring bar the internal propargylic carbonates **1a** (0.2 mmol), alkyl NHP ester **1b** (0.5 mmol, 2.5 equiv), $NiCl_2$·dtbbpy (0.04 mmol, 20 mol %), HE (0.4 mmol, 2.0 equiv), TBAI (0.2 mmol, 1.0 equiv), $Li_2CO_3$ (0.4 mmol, 2.0 equiv) were filled. After degassing with argon by syringe needle for 5 minutes and dissolving with 2.0 mL DMA, the reaction mixture was stirred for 10 minutes to become clear. Then, the vial was irradiated in reactor with cooling device using a Kessil brand 390 (± 15) nm LED (50 W). The reaction progress was monitored by TLC and GC-MS analysis. After full conversion (generally 24 hours), the reaction mixture was transferred into a separating funnel and 10 mL of distilled water and 2 mL of brine were added. Then the resulting mixture was extracted with EtOAc (10 mL*2) and final combined organic layer were dried over $MgSO_4$, filtered and concentrated in vacuum. Purification of the crude product was achieved by flash column chromatography using *n*-pentane as eluents on silica gel.

## 3. Preparation of Starting Materials:

All of propargylic carbonates and benzyl alkyl NHP ester were synthesized according to the previous literatures, and the NMR spectroscopy and GC-MS data were in full accordance with the data in the reported literatures.[1,2,3]

## 4. Optimization of Reaction Conditions:

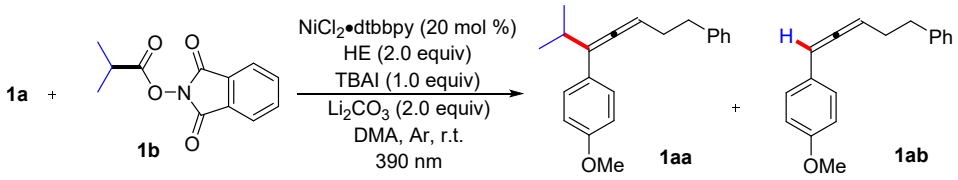
**a) Screening of nickel catalysis and solvents:**




| entries | Catalyst (20 mol %) | Reductant (2.0 equiv) | Base (2.0 equiv) | Light | **Solvent** | yield (%)[a] |
|---|---|---|---|---|---|---|
| 1 | $NiBr_2$·dtbbpy | HE | - | 440 nm | **DMA** | 25 |
| 2 | $NiBr_2$·bpy | HE | - | 440 nm | **DMA** | 16 |
| 3 | $NiBr_2$·dMeObpy | HE | - | 440 nm | **DMA** | 20 |
| 4 | $NiCl_2$·dtbbpy | HE | - | 440 nm | **DMA** | 36 |
| 5 | $NiCl_2$·dtbbpy | HE | - | 390 nm | **DMA** | 45 |
| 6 | $NiCl_2$·dtbbpy | HE | - | 390 nm | **DMF** | 23 |
| 7 | $NiCl_2$·dtbbpy | HE | - | 390 nm | **MeCN** | trace |
| 8 | $NiCl_2$·dtbbpy | HE | - | 390 nm | **THF** | trace |
| 9 | $NiCl_2$·dtbbpy | HE | - | 390 nm | **Acetone** | trace |

[a.] yield of **1aa**.

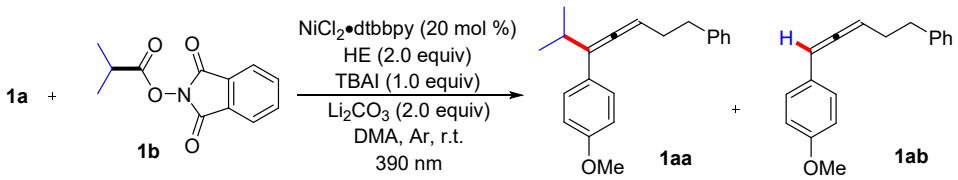
**b) Screening of base:**




| entries | Catalyst (20 mol %) | Reductant (2.0 equiv) | **Base (2.0 equiv)** | Light | Solvent | yield (%)[a] |
|---|---|---|---|---|---|---|
| 1 | $NiCl_2$·dtbbpy | HE | **$Na_2CO_3$** | 390 nm | DMA | 61 (30:70) |
| 2 | $NiCl_2$·dtbbpy | HE | **$NaHCO_3$** | 390 nm | DMA | 52 (65:35) |
| 3 | $NiCl_2$·dtbbpy | HE | **$K_2CO_3$** | 390 nm | DMA | mixture |
| 4 | $NiCl_2$·dtbbpy | HE | **$Li_2CO_3$** | 390 nm | DMA | 56 (100:0) |

[a.] ratio of **1aa**:**1ab**

**c) Screening of additive and loading:**

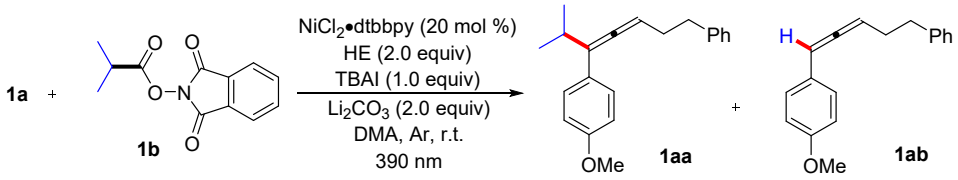



| entries | Catalyst (20 mol %) | Reductant (2.0 equiv) | Base (2.0 equiv) | Light | additive (1.0 equiv) | yield (%)[a] |
|---|---|---|---|---|---|---|

| | | | | | | |
|---|---|---|---|---|---|---|
| 1 | $NiCl_2$·dtbbpy | HE | $Li_2CO_3$ | 390 nm | NaI | 72 |
| 2 | $NiCl_2$·dtbbpy | HE | $Li_2CO_3$ | 390 nm | TBAI | 75 |
| 3 | $NiCl_2$·dtbbpy | HE | $Li_2CO_3$ | 390 nm | DIPEA | 58 |
| 4 | $NiCl_2$·dtbbpy | HE | $Li_2CO_3$ | 390 nm | TBAI[b] | 61 |
| 5 | $NiCl_2$·dtbbpy | HE | $Li_2CO_3$ | 390 nm | TBAI | 88[c] |
| 6 | $NiCl_2$·dtbbpy | HE | $Li_2CO_3$ | 390 nm | TBAI | 69[d] |

[a.] yield of **1aa**. [b.] TBAI (0.5 equiv) [c.] With NHP ester **1b** (2.5 equiv). [d.] With NHP ester **1b** (2.5 equiv) and $NiCl_2$·dtbbpy (15 mol %).

### d) Control experiment:

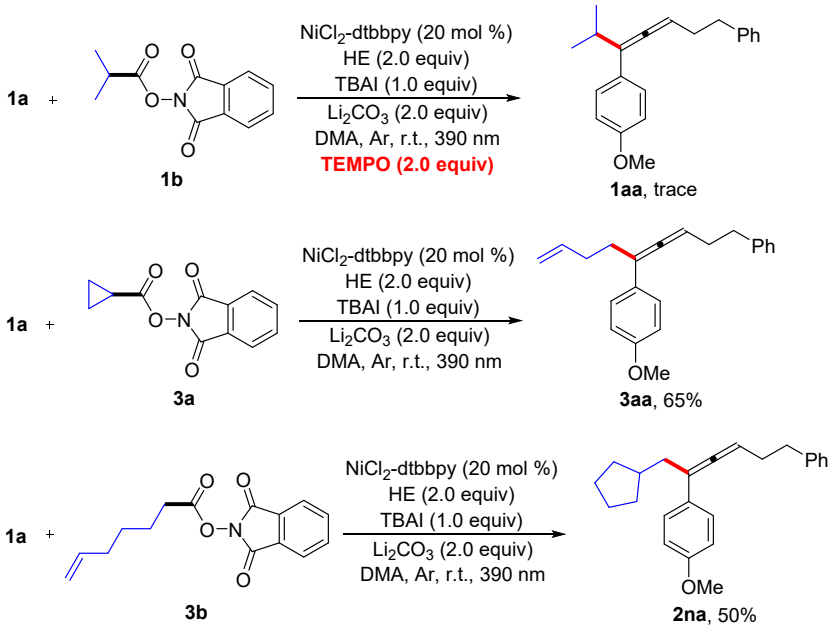



| entries | Catalyst (20 mol %) | Reductant (2.0 equiv) | Base (2.0 equiv) | Light | additive (1.0 equiv) | yield (%)[a] |
|---|---|---|---|---|---|---|
| 1 | - | HE | $Li_2CO_3$ | 390 nm | TBAI | N.D. |
| 2 | $NiCl_2$·dtbbpy | - | $Li_2CO_3$ | 390 nm | TBAI | trace |
| 3 | $NiCl_2$·dtbbpy | HE | $Li_2CO_3$ | 390 nm | TBAI | N.D.[b] |

[a.] yield of **1aa**. [b.] no light

## 5. Mechanism characterization:

### a) Clock experiment and radical capture experiment:




Radical capture experiment with TEMPO revealed the involvement of a radical

intermediate during the reaction process. Furthermore, radical clock experiment indicated the formation of alkyl radicals intermediate from NHP esters.

**b) UV/Vis absorption spectroscopy:**

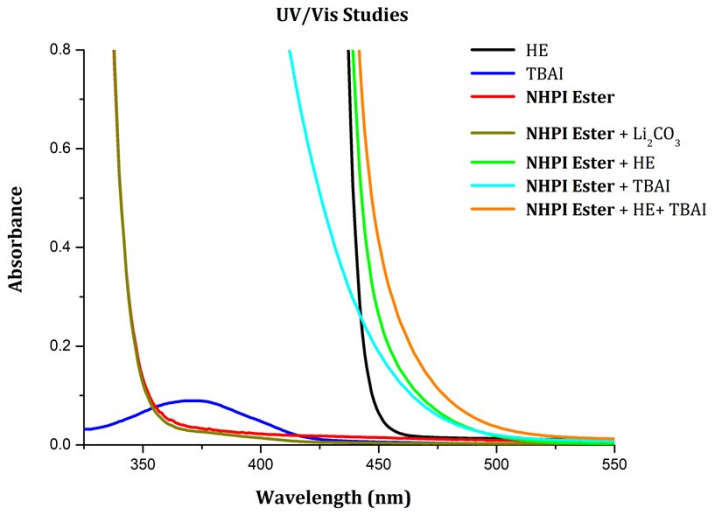



**Figure A:** UV/vis absorption spectra measured in DMA (0.05 M) unless otherwise noted. NHPI Ester = **1b**.

According to the result of UV/Vis absorption spectroscopy, the intermolecular EDA complex was generated by the interaction of NHP ester **1b** with HE and TBAI. Moreover, $Li_2CO_3$ exhibited no influence on NHP ester **1b**.

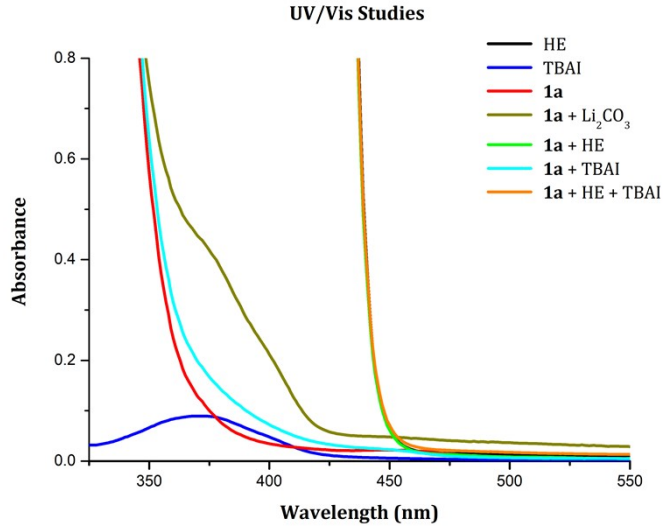
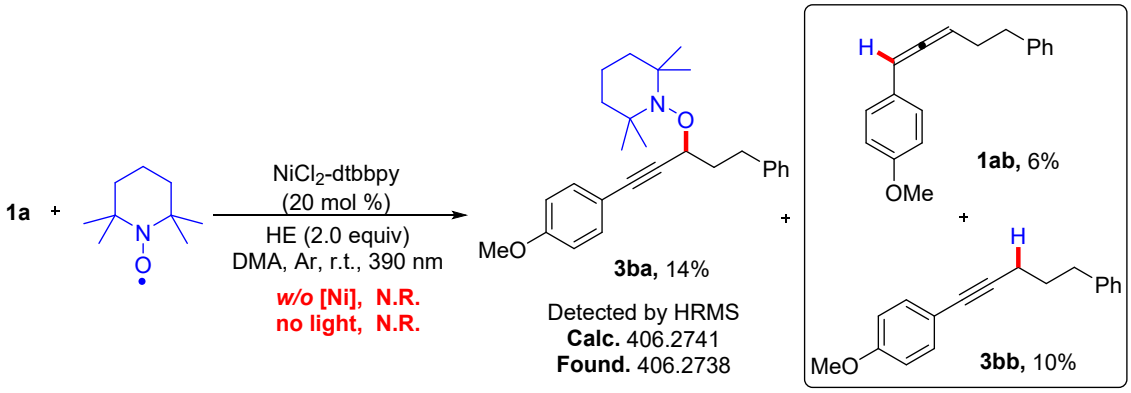
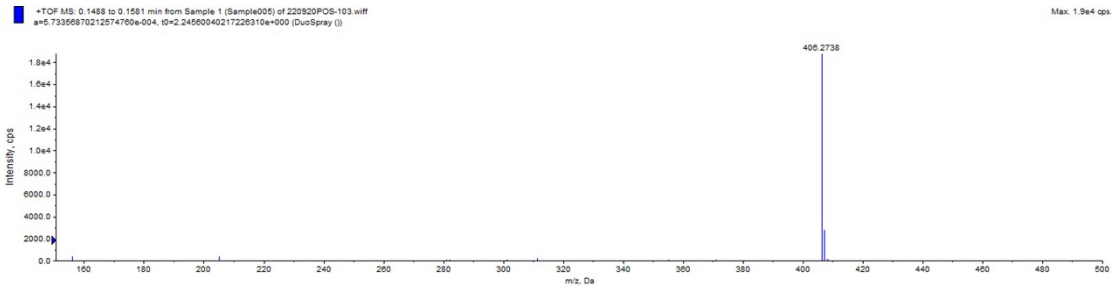



**Figure B:** UV/vis absorption spectra measured in DMA (0.05 M) unless otherwise noted.

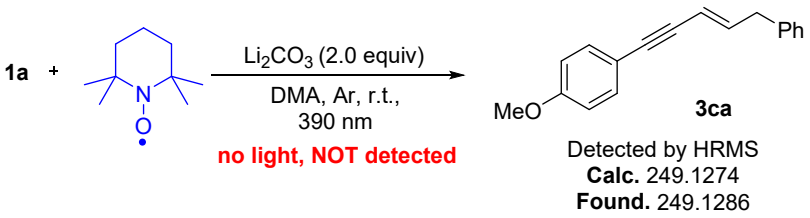
For propargylic carbonate **1a**, the result of UV/Vis absorption spectroscopy revealed the interaction of **1a** with $Li_2CO_3$. A distinctive bathochromic displacement with a small absorption in the visible-light region (brown line) revealed the possible role of $Li_2CO_3$ in the establishment of a EDA complex with **1a**. Moreover, HE and TBAI exhibited no influence on propargylic carbonate **1a**.

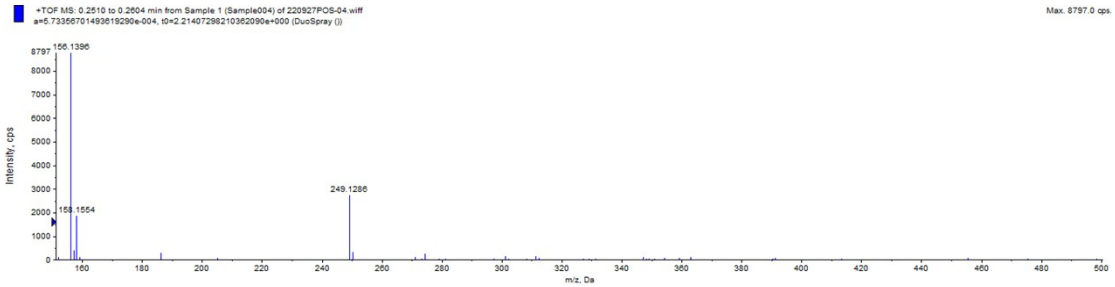
**c) Confirmation experiments for radical from propargylic carbonates 1a:**



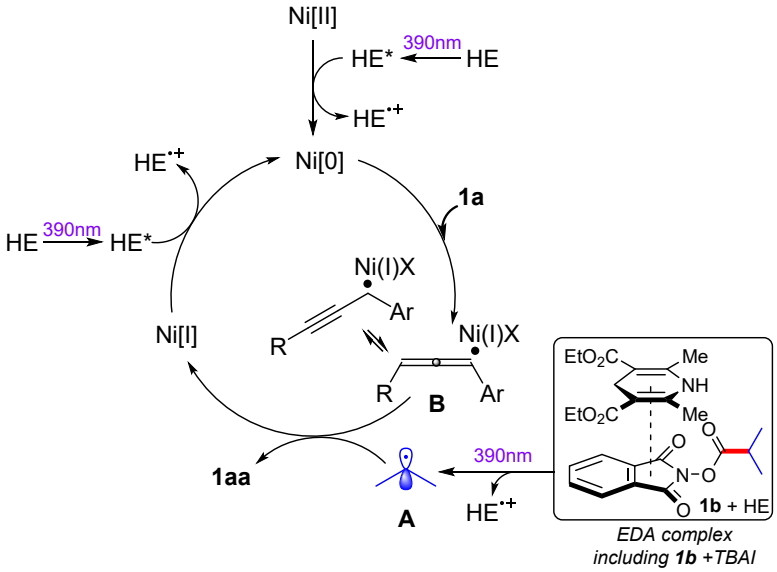

Propargylic radical capture product **3ba** was detected by NMR analysis only in the presence of both nickel and light, which indicated that excited-state HE* would reduce Ni(II) and then oxidative addition between **1a** and Ni(0) proceeded *via* SET generated a hybrid propargylic Ni(I) intermediate and allenyl Ni(I) intermediate.




The EDA complex or interaction between **1a** and $Li_2CO_3$ was also preliminarily confirmed by HRMS. With 390nm purple light, detection of propargyl radical elimination product **3ca** stated this EDA complex photoactivation process, which revealed the addition of $Li_2CO_3$ promoted the one electron reduction process of **1a**.

**d) Plausible mechanism:**




A hypothetical mechanism for this cross-electrophile coupling was proposed. Initially, the EDA complex generated by the interaction of NHP ester with HE and TBAI produced the alkyl radical **A** via a photo-induced SET process. Next, low-valent nickel species, reduced from Ni(II) by excited-state HE*, proceeded a single electron oxidation addition with **1a** to generate a hybrid allenyl-Ni(I) intermediate, namely allenyl radical **B**[4], which then captured alkyl radical **A** to generate the desired radical-radical coupling product **1aa**. Notably, the addition of $Li_2CO_3$ promoted this one electron reduction process of **1a**. Finally, the complete catalytic system was achieved with the reduction of Ni(I) complex to Ni(0) by extra excited-state HE*. However, despite with reductive reaction atmosphere and an allenyl radical process revealed by radical capture experiment, the mechanism processing reductive elimination of Ni(III) species, which generated from alkyl radical with allenyl Ni(II) species, could not be fully ruled out

## 6. References:

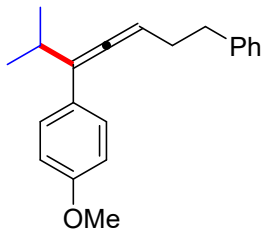
[1] (a) Z.-S. Chen, X.-H. Duan, L.-Y. Wu, S. Ali, K.-G. Ji, P.-X. Zhou, X.-Y. Liu and Y.-M. Liang, *Chem. Eur. J.,* 2011, **17**, 6918; (b) Y. Miyazaki, B. Zhou, H. Tsuji and M. Kawatsura, *Org. Lett.,* 2020, **22**, 2049; (c) P. Wu, M. Jia, W. Lin and S. Ma, *Org. Lett.,* 2018, **20**, 554; (d) C. R. Reddy, S. Z. Mohammed and P. Kumaraswamya, *Org. Biomol. Chem.,* 2015, **13**, 8310.

[2] (a) Z.-Z. Zhou, R.-Q. Jiao, K. Yang, X.-M. Chen and Y.-M. Liang, *Chem. Commun.,* 2020, **56**, 12957; (b) Z.-Z. Zhou, X.-R. Song, S. Du, K.-J. Xia, W.-F. Tian, Q. Xiao and Y.-M. Liang, *Chem. Commun.,* 2021, **57**, 9390.

[3] X. Zhu and H. Fu, *Chem. Commun.,* 2021, **57**, 9656–9671.

[4] (a) B. J. Shields and A. G. Doyle, *J. Am. Chem. Soc.,* 2016, **138**, 12719; (b) T. T. Tsou, J. K. Kochi, *J. Am. Chem. Soc.,* 1979, **101**, 6319; (c) A. J. Oelke, J. Sun and G. C. Fu, *J. Am. Chem. Soc.,* 2012, **134**, 6, 2966.

## 7. Characterization Data of Products 1aa-1oa:



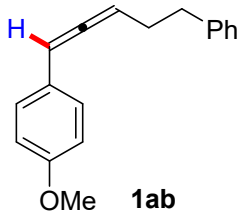

**1aa**, 88%

**1aa**: according to **General Procedure**; colorless oil; Eluent: *n*-hexane/EtOAc = 100/1;

**$^1$H NMR** (400 $MH_Z$ $CDCl_3$, δ ppm): 1.07-1.09 (d, $J$ = 8.0 Hz, 6H), 2.39-2.45 (m, 2H), 2.64-2.80 (m, 3H), 3.80 (s, 3H), 5.52-5.56 (dt, $J_1$ = 4.0 Hz, $J_2$ = 8.0 Hz, 1H), 6.82-6.84 (d, $J$ = 8.0 Hz, 2H), 7.19-7.29 (m, 7H);

**$^{13}$C NMR** (100 MHz, $CDCl_3$, δ ppm): 22.2, 22.5, 27.9, 31.2, 35.6, 55.3, 94.7, 112.8, 113.7, 125.8, 127.4, 128.3, 128.5, 129.4, 141.9, 158.2, 202.3;

**HRMS** (ESI) calcd for $C_{21}H_{24}O$ $[M+H]^+$ m/z 293.1900, found 293.1903.



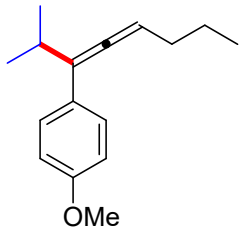

**1ab**

**1ab**: according to **General Procedure**; colorless oil; Eluent: *n*-hexane/EtOAc = 100/1;

**$^1$H NMR** (400 $MH_Z$ $CDCl_3$, δ ppm): 2.40-2.50 (m, 2H), 2.75-2.84 (m, 2H), 3.79 (s, 3H), 5.53-5.58 (dd, $J_1$ = 4.0 Hz, $J_2$ = 12.0 Hz, 1H), 6.07-6.09 (m, 1H), 6.79-6.81 (d, $J$ = 8.0 Hz, 2H), 7.06-7.09 (d, $J$ = 12.0 Hz, 2H), 7.20-7.24 (m, 3H), 7.26-7.30 (m, 2H);

**$^{13}$C NMR** (100 MHz, $CDCl_3$, δ ppm): 30.7, 35.4, 55.3, 94.3, 94.4, 114.0, 125.9, 127.1, 127.7, 128.3, 128.6, 141.6, 158.5, 204.6;

**HRMS** (ESI) calcd for $C_{18}H_{18}O$ $[M+H]^+$ m/z 251.1430, found 251.1433.



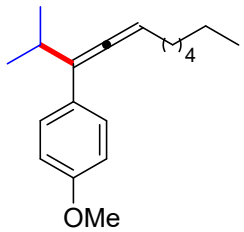

**1ba**, 68%

**1ba**: according to **General Procedure**; colorless oil; Eluent: *n*-hexane/EtOAc = 100/1;

**$^1$H NMR** (400 $MH_Z$ $CDCl_3$, δ ppm): 0.94-0.97 (t, $J$ = 8.0 Hz, 3H), 1.10-1.12 (dd, $J_1$ = 4.0 Hz, $J_2$ = 8.0 Hz, 6H), 1.46-1.53 (m, 2H), 2.04-2.10 (m, 2H), 2.71-2.81 (m, 2H), 3.80 (s, 3H), 5.49-5.52 (m, 1H), 6.84-6.87 (d, $J$ = 12.0 Hz, 2H), 7.30-7.33 (d, $J$ = 12.0 Hz, 2H);

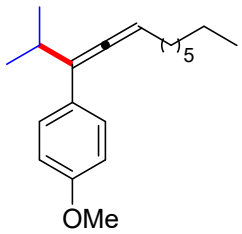
**$^{13}$C NMR** (100 MHz, $CDCl_3$, δ ppm): 13.9, 22.2, 22.6, 27.9, 31.5, 55.3, 95.3, 112.3, 113.7, 127.4, 129.8, 158.1, 202.3;

**HRMS** (ESI) calcd for $C_{16}H_{22}O$ $[M+H]^+$ m/z 231.1743, found 231.1745.



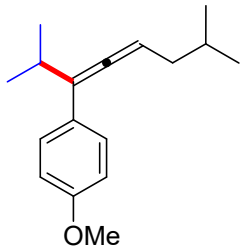

**1ca**, 78%

**1ca**: according to **General Procedure**; colorless oil; Eluent: *n*-hexane/EtOAc = 100/1;
**$^1$H NMR** (400 $MH_Z$ $CDCl_3$, δ ppm): 0.86-0.89 (t, $J$ = 8.0 Hz, 3H), 1.09-1.12 (m, 6H), 1.27-1.36 (m, 6H), 1.42-1.49 (m, 2H), 2.06-2.11 (dd, $J_1$ = 8.0 Hz, $J_2$ = 12.0 Hz, 2H), 2.73-2.80 (m, 1H), 3.80 (s, 3H), 5.49-5.54 (dt, $J_1$ = 4.0 Hz, $J_2$ = 8.0 Hz, 1H), 6.85-6.87 (d, $J$ = 8.0 Hz, 2H), 7.30-7.32 (d, $J$ = 8.0 Hz, 2H);
**$^{13}$C NMR** (100 MHz, $CDCl_3$, δ ppm): 14.1, 22.2, 22.6, 22.7, 27.9, 29.0, 29.4, 31.7, 55.3, 95.5, 112.3, 113.7, 127.4, 129.8, 158.1, 202.2;
**HRMS** (ESI) calcd for $C_{19}H_{28}O$ $[M+H]^+$ m/z 273.2213, found 273.2217.




**1da**, 80%

**1ca**: according to **General Procedure**; colorless oil; Eluent: *n*-hexane/EtOAc = 100/1;
**$^1$H NMR** (400 $MH_Z$ $CDCl_3$, δ ppm): 0.85-0.89 (t, $J$ = 8.0 Hz, 3H), 1.09-1.12 (dd, $J_1$ = 4.0 Hz, $J_2$ = 8.0 Hz, 6H), 1.26-1.33 (m, 8H), 1.42-1.47 (m, 2H), 2.06-2.11 (dd, $J_1$ = 8.0 Hz, $J_2$ = 12.0 Hz, 2H), 2.73-2.80 (m, 1H), 3.80 (s, 3H), 5.48-5.52 (dt, $J_1$ = 4.0 Hz, $J_2$ = 8.0 Hz, 1H), 6.84-6.87 (d, $J$ = 12.0 Hz, 2H), 7.30-7.33 (d, $J$ = 12.0 Hz, 2H);
**$^{13}$C NMR** (100 MHz, $CDCl_3$, δ ppm): 14.1, 22.2, 22.6, 22.6, 27.9, 29.2, 29.3, 29.4, 31.9, 55.3, 95.4, 112.3, 113.7, 127.4, 129.8, 158.1, 202.2;
**HRMS** (ESI) calcd for $C_{20}H_{30}O$ $[M+H]^+$ m/z 287.2369, found 287.2371.



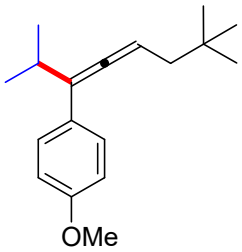

**1ea,** 77%

**1ea**: according to **General Procedure**; colorless oil; Eluent: *n*-hexane/EtOAc = 100/1;
**$^1$H NMR** (400 $MH_Z$ $CDCl_3$, δ ppm): 0.94-0.97 (m, 3H), 1.10-1.12 (m, 6H), 1.67-1.11 (m, 1H), 1.98-

2.02 (m, 2H), 2.72-2.79 (m, 2H), 3.80 (s, 3H), 5.43-5.48 (dt, $J_1$ = 4.0 Hz, $J_2$ = 8.0 Hz, 1H), 6.84-6.86 (d, $J$ = 8.0 Hz, 2H), 7.30-7.32 (d, $J$ = 8.0 Hz, 2H);

**$^{13}$C NMR** (100 MHz, $CDCl_3$, δ ppm):22.2, 22.5, 22.5, 22.6, 28.0, 28.8, 39.0, 55.3, 94.1, 111.7, 113.7, 127.4, 129.7, 158.1, 202.7;

**HRMS** (ESI) calcd for $C_{17}H_{24}O$ $[M+H]^+$ m/z 245.1900, found 245.1901.



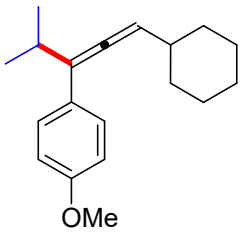

**1fa,** 79%

**1fa**: according to **General Procedure**; colorless oil; Eluent: *n*-hexane/EtOAc = 100/1;

**$^{1}$H NMR** (400 $MH_Z$ $CDCl_3$, δ ppm): 0.96 (s, 9H), 1.10-1.13 (d, $J_1$ = 4.0 Hz, $J_2$ = 8.0 Hz, 6H), 2.00-2.03 (dd, $J_1$ = 4.0 Hz, $J_2$ = 8.0 Hz, 2H), 2.72-2.80 (m, 1H), 3.80 (s, 3H), 5.45-5.50 (dt, $J_1$ = 4.0 Hz, $J_2$ = 8.0 Hz, 1H), 6.84-6.86 (d, $J$ = 8.0 Hz, 2H), 7.30-7.32 (d, $J$ = 8.0 Hz, 2H);

**$^{13}$C NMR** (100 MHz, $CDCl_3$, δ ppm): 22.3, 22.6, 28.0, 29.3, 31.1, 44.4, 55.3, 92.2, 111.2, 113.7, 127.5, 129.8, 158.1, 203.3;

**HRMS** (ESI) calcd for $C_{18}H_{26}O$ $[M+H]^+$ m/z 259.2056, found 259.2061.



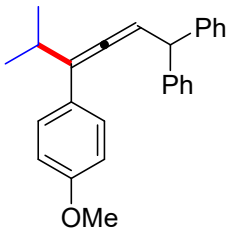

**1ga,** 83%

**1ga**: according to **General Procedure**; colorless oil; Eluent: *n*-hexane/EtOAc = 100/1;

**$^{1}$H NMR** (400 $MH_Z$ $CDCl_3$, δ ppm): 1.10-1.12 (dd, $J_1$ = 4.0 Hz, $J_2$ = 8.0 Hz, 6H), 1.17-1.33 (m, 4H), 1.63-1.74 (m, 4H), 1.82 (m, 2H),2.02-2.10 (m, 1H), 2.73-2.80 (m, 1H), 3.80 (s, 3H), 5.50-5.52 (dd, $J_1$ = 4.0 Hz, $J_2$ = 8.0 Hz, 1H), 6.85-6.87 (d, $J$ = 8.0 Hz, 2H), 7.32-7.34 (d, $J$ = 8.0 Hz, 2H);

**$^{13}$C NMR** (100 MHz, $CDCl_3$, δ ppm): 22.2, 22.7, 26.2, 26.2, 27.7, 33.3, 33.4, 38.1, 55.3, 101.5, 113.1, 113.7, 127.3, 129.7, 158.1, 200.9;

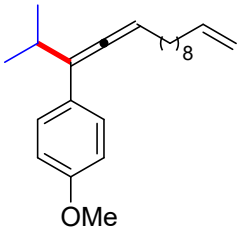
**HRMS** (ESI) calcd for $C_{19}H_{26}O$ $[M+H]^+$ m/z 271.2056, found 271.2063.




**1ha,** 58%

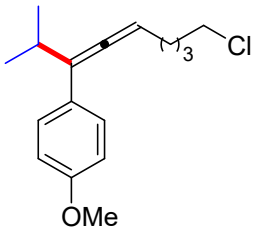
**1ha**: according to **General Procedure**; colorless oil; Eluent: *n*-hexane/EtOAc = 100/1;

**$^1$H NMR** (400 $MH_Z$ $CDCl_3$, δ ppm): 0.82-0.84 (d, $J$ = 8.0 Hz, 3H), 1.06-1.08 (d, $J$ = 8.0 Hz, 3H), 2.61-2.68 (m, 1H), 3.79 (s, 3H), 4.85-4.86 (d, $J$ = 4.0 Hz, 1H), 5.99-6.01 (dd, $J_1$ = 4.0 Hz, $J_2$ = 8.0 Hz, 1H), 6.81-6.83 (d, $J$ = 8.0 Hz, 2H), 7.17-7.19 (m, 4H), 7.25-7.28 (m, 8H);
**$^{13}$C NMR** (100 MHz, $CDCl_3$, δ ppm): 22.0, 22.2, 28.4, 51.8, 55.2, 99.0, 113.7, 114.4, 126.3, 127.5, 128.2, 128.6, 128.6, 143.7, 158.3, 203.2;
**HRMS** (ESI) calcd for $C_{26}H_{26}O$ $[M+H]^+$ m/z 355.2056, found 355.2061



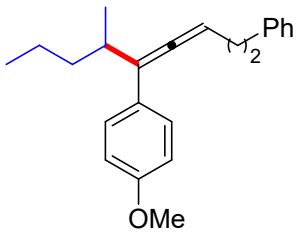

**1ia,** 68%

**1ia**: according to **General Procedure**; colorless oil; Eluent: *n*-hexane/EtOAc = 100/1;
**$^1$H NMR** (400 $MH_Z$ $CDCl_3$, δ ppm): 1.09-1.12 (dd, $J_1$ = 4.0 Hz, $J_2$ = 8.0 Hz, 6H), 1.27-1.36 (m, 10H), 1.41-1.46 (m, 2H), 2.00-2.11 (m, 4H), 2.72-2.80 (m, 1H), 3.79 (s, 3H), 4.91-5.01 (m, 2H), 5.48-5.52 (dt, $J_1$ = 4.0 Hz, $J_2$ = 8.0 Hz, 1H), 5.75-5.86 (m, 1H), 6.84-6.86 (d, $J$ = 8.0 Hz, 2H), 7.30-7.32 (d, $J$ = 8.0 Hz, 2H);
**$^{13}$C NMR** (100 MHz, $CDCl_3$, δ ppm): 22.2, 22.6, 27.9, 28.9, 29.1, 29.3, 29.3, 29.4, 29.5, 33.8, 55.2, 95.4, 112.3, 113.7, 114.1, 127.4, 129.7, 139.2, 158.1, 202.2;
**HRMS** (ESI) calcd for $C_{23}H_{34}O$ $[M+H]^+$ m/z 327.2682, found 327.2689.



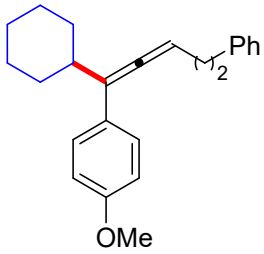

**1ja,** 85%

**1ja**: according to **General Procedure**; colorless oil; Eluent: *n*-hexane/EtOAc = 100/1;
**$^1$H NMR** (400 $MH_Z$ $CDCl_3$, δ ppm): 1.09-1.12 (m, 6H), 1.59-1.65 (m, 2H), 1.80-1.87 (m, 2H), 2.10-2.16 (m, 2H), 2.73-2.80 (m, 1H), 3.51-3.55 (t, $J$ = 8.0 Hz, 2H), 3.80 (s, 3H), 5.48-5.52 (dt, $J_1$ = 4.0 Hz, $J_2$ = 8.0 Hz, 1H), 6.85-6.87 (d, $J$ = 8.0 Hz, 2H), 7.29-7.31 (d, $J$ = 8.0 Hz, 2H);
**$^{13}$C NMR** (100 MHz, $CDCl_3$, δ ppm): 22.2, 22.5, 26.5, 27.9, 28.6, 32.2, 44.9, 55.3, 94.7, 112.8, 113.8, 127.4, 129.4, 158.2, 202.3;
**HRMS** (ESI) calcd for $C_{17}H_{23}ClO$ $[M+H]^+$ m/z 279.1510, found 279.1515.



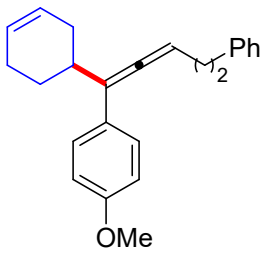

**1ma,** 62%
(dr = 1:1 )

**1ma**: according to **General Procedure**; colorless oil; Eluent: *n*-hexane/EtOAc = 100/1;
**$^1$H NMR** (400 $MH_Z$ $CDCl_3$, δ ppm): 0.86-0.90 (dt, $J_1$ = 4.0 Hz, $J_2$ = 8.0 Hz, 3H), 1.06-1.07 (d, $J$ = 4.0 Hz, 3H), 1.25-1.52 (m, 4H), 2.39-2.44 (m, 2H), 2.58-2.59 (m, 1H), 2.75-2.80 (dd, $J_1$ = 4.0 Hz, $J_2$ = 12.0 Hz, 2H), 3.79 (m, 3H), 5.51-5.54 (t, $J$ = 4.0 Hz, 1H), 6.81-6.83 (d, $J$ = 8.0 Hz, 2H), 7.20-7.30 (m, 7H);
**$^{13}$C NMR** (100 MHz, $CDCl_3$, δ ppm): 14.3, 14.3, 20.1, 20.5, 20.5, 31.2, 31.3, 33.0, 33.0, 35.7, 35.8, 38.4, 38.7, 55.3, 94.5, 94.6, 111.7, 111.8, 113.7, 125.8, 125.8, 127.4, 128.3, 128.3, 128.5, 129.7, 129.8, 141.8, 158.2, 202.6, 202.7;
**HRMS** (ESI) calcd for $C_{23}H_{28}O$ $[M+H]^+$ m/z 321.2213, found 321.2215.




**1na,** 64%

**1na**: according to **General Procedure**; colorless oil; Eluent: *n*-hexane/EtOAc = 100/1;
**$^1$H NMR** (400 $MH_Z$ $CDCl_3$, δ ppm): 1.04-1.38 (m, 6H), 1.67-1.85 (m, 4H), 2.31-2.34 (dt, $J_1$ = 4.0 Hz, $J_2$ = 8.0 Hz, 1H), 2.39-2.45 (dd, $J_1$ = 8.0 Hz, $J_2$ = 16.0 Hz, 2H), 2.76-2.80 (t, $J$ = 4.0 Hz, 2H), 3.79 (s, 3H), 5.49-5.53 (dt, $J_1$ = 4.0 Hz, $J_2$ = 8.0 Hz, 1H), 6.81-6.83 (d, $J$ = 8.0 Hz, 2H), 7.20-7.29 (m, 7H);
**$^{13}$C NMR** (100 MHz, $CDCl_3$, δ ppm): 26.4, 26.7, 26.7, 31.2, 32.8, 33.1, 35.6, 37.8, 55.3, 94.3, 111.8, 113.7, 125.8, 127.4, 128.3, 128.6, 129.3, 141.9, 158.2, 202.8;
**HRMS** (ESI) calcd for $C_{24}H_{28}O$ $[M+H]^+$ m/z 333.2213, found 333.2214.




**1oa,** 59%
(dr = 2:1)

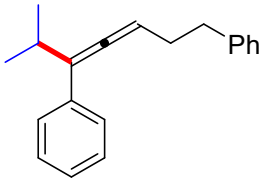
**1oa**: according to **General Procedure**; colorless oil; Eluent: *n*-hexane/EtOAc = 100/1;

**$^{1}$H NMR** (400 $MH_Z$ $CDCl_3$, δ ppm): 1.85-2.16 (m, 6H), 2.39-2.45 (m, 2H), 2.66-2.68 (m, 1H), 2.77-2.82 (m, 2H), 3.78-3.79 (m, 3H), 5.52-5.58 (m, 1H), 5.69 (m, 2H), 6.79-6.84 (m, 2H), 7.19-7.27 (m, 7H);

**$^{13}$C NMR** (100 MHz, $CDCl_3$, δ ppm): 25.6, 25.8, 28.5, 28.6, 30.7, 31.2, 31.3, 31.7, 33.6, 33.7, 35.4, 35.6, 55.3, 94.4, 94.7, 111.0, 111.2, 113.8, 114.0, 126.5, 126.6, 126.8, 127.4, 127.4, 127.7, 128.3, 128.3, 128.5, 141.6, 141.8, 158.3, 158.5, 202.8, 204.6;

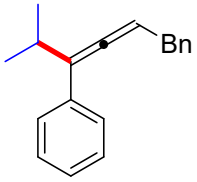
**HRMS** (ESI) calcd for $C_{24}H_{26}O$ $[M+H]^+$ m/z 331.2056, found 331.2058.

## 8. Characterization Data of Products 2aa-2oa, 3aa, 3ba-3bb:



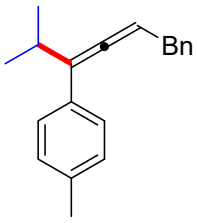

**2aa**, 89%

**2aa**: according to **General Procedure**; colorless oil; Eluent: *n*-hexane;
**$^1$H NMR** (400 $MH_Z$ $CDCl_3$, δ ppm): 1.08-1.10 (d, $J$ = 8.0 Hz, 6H), 2.41-2.47 (m, 2H), 2.77-2.81 (m, 3H), 5.55-5.59 (dt, $J_1$ = 4.0 Hz, $J_2$ = 8.0 Hz, 1H), 7.15-7.22 (m, 4H), 7.26-7.32 (m, 6H);
**$^{13}$C NMR** (100 MHz, $CDCl_3$, δ ppm): 22.2, 22.5, 27.7, 31.1, 35.6, 94.8, 113.3, 125.8, 126.3, 126.4, 128.3, 128.3, 128.5, 137.1, 141.8, 202.8;
**HRMS** (ESI) calcd for $C_{20}H_{22}$ $[M+H]^+$ m/z 263.1794, found 263.1797.



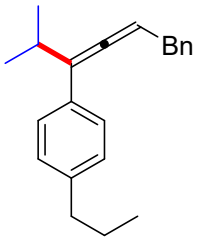

**2ba**, 73%

**2ba**: according to **General Procedure**; colorless oil; Eluent: *n*-hexane;
**$^1$H NMR** (400 $MH_Z$ $CDCl_3$, δ ppm): 1.04-1.06 (d, $J$ = 8.0 Hz, 3H), 1.10-1.12 (d, $J$ = 8.0 Hz, 3H), 2.73-2.84 (m, 1H), 3.45-3.46 (d, $J$ = 4.0 Hz, 2H), 5.67-5.71 (dt, $J_1$ = 4.0 Hz, $J_2$ = 8.0 Hz, 1H), 7.17-7.22 (m, 2H), 7.25-7.32 (m, 6H), 7.35-7.37 (m, 2H);
**$^{13}$C NMR** (100 MHz, $CDCl_3$, δ ppm): 22.2, 22.5, 36.0, 94.9, 113.6, 126.1, 126.4, 126.5, 128.3, 128.3, 128.7, 137.1, 140.4, 203.4;
**HRMS** (ESI) calcd for $C_{19}H_{20}$ $[M+H]^+$ m/z 249.1638, found 249.1641.



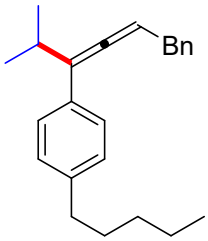

**2ca**, 68%

**2ca**: according to **General Procedure**; colorless oil; Eluent: *n*-hexane;
**$^1$H NMR** (400 $MH_Z$ $CDCl_3$, δ ppm): 1.03-1.05 (d, $J$ = 8.0 Hz, 3H), 1.08-1.10 (d, $J$ = 8.0 Hz, 3H), 2.32 (s, 3H), 2.71-2.80 (m, 1H), 3.43-3.45 (d, $J$ = 8.0 Hz, 2H), 5.64-5.68 (dt, $J_1$ = 4.0 Hz, $J_2$ = 8.0 Hz, 1H), 7.10-7.12 (m, 2H), 7.18-7.31 (m, 7H);
**$^{13}$C NMR** (100 MHz, $CDCl_3$, δ ppm): 21.0, 22.2, 22.5, 28.0, 36.1, 94.7, 113.4, 126.1, 126.4, 128.3, 128.7, 129.0, 134.1, 136.1, 140.5, 203.1;
**HRMS** (ESI) calcd for $C_{20}H_{22}$ $[M+H]^+$ m/z 263.1794, found 263.1797.



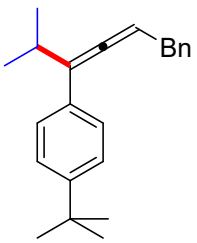

**2da**, 78%

**2da**: according to **General Procedure**; colorless oil; Eluent: *n*-hexane;
**$^1$H NMR** (400 $MH_Z$ $CDCl_3$, δ ppm): 0.92-0.96 (t, $J$ = 8.0 Hz, 3H), 1.04-1.06 (d, $J$ = 8.0 Hz, 3H), 1.09-1.11 (d, $J$ = 8.0 Hz, 3H), 1.59-1.68 (m, 2H), 2.54-2.58 (t, $J$ = 8.0 Hz, 2H), 2.72-2.81 (m, 1H), 3.44-3.46 (d, $J$ = 8.0 Hz, 2H), 5.65-5.69 (dt, $J_1$ = 4.0 Hz, $J_2$ = 8.0 Hz, 1H), 7.11-7.13 (m, 2H), 7.19-7.32 (m, 7H);
**$^{13}$C NMR** (100 MHz, $CDCl_3$, δ ppm): 13.9, 22.2, 22.5, 24.5, 28.0, 36.1, 37.7, 94.8, 113.4, 126.1, 126.3, 128.3, 128.4, 128.7, 134.3, 140.5, 141.0, 203.2;
**HRMS** (ESI) calcd for $C_{22}H_{26}$ $[M+H]^+$ m/z 291.2107, found 291.2108.




**2ea,** 87%

**2da**: according to **General Procedure**; colorless oil; Eluent: *n*-hexane;
**$^1$H NMR** (400 $MH_Z$ $CDCl_3$, δ ppm): 0.87-0.91 (t, $J$ = 8.0 Hz, 3H), 1.04-1.06 (d, $J$ = 8.0 Hz, 3H), 1.09-1.11 (d, $J$ = 8.0 Hz, 3H), 1.32-1.33 (m, 4H), 1.59-1.64 (m, 2H), 2.55-2.59 (t, $J$ = 8.0 Hz, 2H), 2.73-2.81 (m, 1H), 3.44-3.45 (d, $J$ = 4.0 Hz, 2H), 5.65-5.69 (dt, $J_1$ = 4.0 Hz, $J_2$ = 8.0 Hz, 1H), 7.11-7.13 (m, 2H), 7.18-7.31 (m, 7H);
**$^{13}$C NMR** (100 MHz, $CDCl_3$, δ ppm): 14.0, 22.2, 22.5, 22.6, 28.0, 31.2, 31.5, 35.5, 36.1, 94.8, 113.5, 126.1, 126.3, 128.3, 128.4, 128.7, 134.2, 140.5, 141.2, 203.2;
**HRMS** (ESI) calcd for $C_{24}H_{30}$ $[M+H]^+$ m/z 319.2420, found 319.2421.



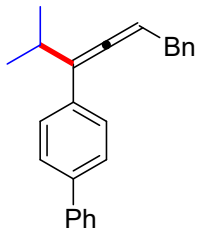

**2fa,** 83%

**2fa**: according to **General Procedure**; colorless oil; Eluent: *n*-hexane;
**$^1$H NMR** (400 $MH_Z$ $CDCl_3$, δ ppm): 1.05-1.07 (d, $J$ = 8.0 Hz, 3H), 1.10-1.12 (d, $J$ = 8.0 Hz, 3H),

1.32 (s, 9H), 2.75-2.82 (m, 1H), 3.44-3.46 (d, $J$ = 8.0 Hz, 2H), 5.65-5.69 (dt, $J_1$ = 4.0 Hz, $J_2$ = 8.0 Hz, 1H), 7.21-7.35 (m, 9H);

**$^{13}$C NMR** (100 MHz, $CDCl_3$, δ ppm): 22.3, 22.6, 28.0, 31.3, 34.4, 36.1, 94.8, 113.3, 125.2, 126.1, 128.3, 128.6, 134.0, 140.5, 149.3, 203.3;

**HRMS** (ESI) calcd for $C_{23}H_{28}$ $[M+H]^+$ m/z 305.2264, found 305.2269.



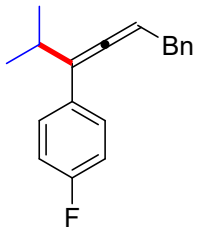

**2ga,** 45%

**2ga**: according to **General Procedure**; colorless oil; Eluent: *n*-hexane;

**$^{1}$H NMR** (400 $MH_Z$ $CDCl_3$, δ ppm): 1.07-1.09 (d, $J$ = 8.0 Hz, 3H), 1.12-1.14 (d, $J$ = 8.0 Hz, 3H), 2.77-2.87 (m, 1H), 3.46-3.48 (d, $J$ = 8.0 Hz, 2H), 5.71-5.75 (dt, $J_1$ = 4.0 Hz, $J_2$ = 8.0 Hz, 1H), 7.21-7.23 (m, 1H), 7.27-7.34 (m, 5H), 7.41-7.44 (m, 4H), 7.53-7.55 (d, $J$ = 4.0 Hz, 2H), 7.59-7.61 (d, $J$ = 4.0 Hz, 2H);

**$^{13}$C NMR** (100 MHz, $CDCl_3$, δ ppm): 22.2, 22.5, 27.9, 36.0, 95.1, 113.4, 126.1, 126.8, 126.9, 127.0, 127.1, 128.4, 128.7, 128.7, 136.1, 139.2, 140.4, 140.8, 203.6;

**HRMS** (ESI) calcd for $C_{25}H_{24}$ $[M+H]^+$ m/z 329.1951, found 329.1955.




**2ha,** 79%

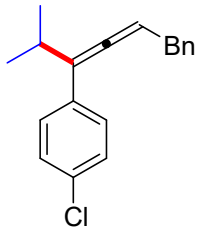
**2ha**: according to **General Procedure**; colorless oil; Eluent: *n*-hexane;

**$^{1}$H NMR** (400 $MH_Z$ $CDCl_3$, δ ppm): 1.02-1.04 (d, $J$ = 8.0 Hz, 3H), 1.08-1.10 (d, $J$ = 8.0 Hz, 3H), 2.68-2.75 (m, 1H), 3.44-3.45 (d, $J$ = 4.0 Hz, 2H), 5.66-5.70 (dt, $J_1$ = 4.0 Hz, $J_2$ = 8.0 Hz, 1H), 6.96-7.01 (t, $J$ = 8.0 Hz, 2H), 7.19-7.31 (m, 7H);

**$^{13}$C NMR** (100 MHz, $CDCl_3$, δ ppm): 22.1, 22.3, 28.2, 36.0, 95.1, 112.8, 115.0, 115.2, 126.2, 127.9-128.0 (d, $J$ = 7.0 Hz), 128.4-128.6 (d, $J$ = 29.0 Hz), 133.0, 140.3, 160.4-162.8 (d, $J$ = 244.0 Hz), 203.2;

**$^{19}$F NMR** (376 MHz, $CDCl_3$, δ ppm): -116.6 (s, 1F);

**HRMS** (ESI) calcd for $C_{19}H_{19}F$ $[M+H]^+$ m/z 267.1544, found 267.1547.



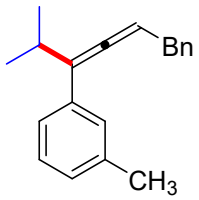

**2ia**, 80%

**2ia**: according to **General Procedure**; colorless oil; Eluent: *n*-hexane/EtOAc = 100/1;

**$^1$H NMR** (400 MHz CDCl$_3$, δ ppm): 1.01-1.03 (d, $J$ = 8.0 Hz, 3H), 1.07-1.09 (d, $J$ = 8.0 Hz, 3H), 2.68-2.75 (m, 1H), 3.43-3.45 (d, $J$ = 8.0 Hz, 2H), 5.68-5.72 (dt, $J_1$ = 4.0 Hz, $J_2$ = 8.0 Hz, 1H), 7.19-7.31 (m, 9H);

**$^{13}$C NMR** (100 MHz, CDCl$_3$, δ ppm): 22.0, 22.3, 28.0, 35.9, 95.4, 112.9, 126.2, 127.7, 128.4, 128.6, 132.0, 135.6, 140.1, 203.4;

**HRMS** (ESI) calcd for $C_{19}H_{19}Cl$ $[M+H]^+$ m/z 283.1248, found 283.1252.



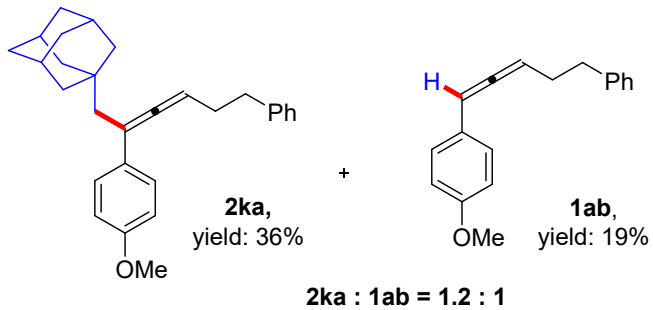

**2ja**, 90%

**2ja**: according to **General Procedure**; colorless oil; Eluent: *n*-hexane/EtOAc = 100/1;

**$^1$H NMR** (400 MHz CDCl$_3$, δ ppm): 1.04-1.06 (d, $J$ = 8.0 Hz, 3H), 1.09-1.11 (d, $J$ = 8.0 Hz, 3H), 2.33 (s, 3H), 2.74-2.81 (m, 1H), 3.44-3.46 (d, $J$ = 8.0 Hz, 2H), 5.65-5.69 (dt, $J_1$ = 4.0 Hz, $J_2$ = 8.0 Hz, 1H), 7.00-7.01 (d, $J$ = 4.0 Hz, 1H), 7.19-7.30 (m, 8H);

**$^{13}$C NMR** (100 MHz, CDCl$_3$, δ ppm):21.5, 22.2, 22.5, 28.0, 36.1, 94.7, 113.7, 123.5, 126.1, 127.2, 127.3, 128.2, 128.3, 128.7, 137.1, 137.8, 140.5, 203.4;

**HRMS** (ESI) calcd for $C_{20}H_{22}O$ $[M+H]^+$ m/z 279.1743, found 279.1749.




**2ka,** yield: 36%

**1ab**, yield: 19%

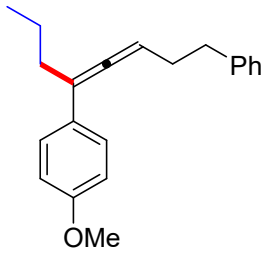
**2ka : 1ab = 1.2 : 1**

**2ka**: according to **General Procedure**; colorless oil; Eluent: *n*-hexane/EtOAc = 100/1;

**$^1$H NMR** (400 MHz CDCl$_3$, δ ppm): 1.47-1.55 (m, 4H), 1.63-1.66 (m, 2H), 1.84-1.89 (m, 2H), 2.16 (m, 1H), 2.39-2.47 (m, 2H), 2.77-2.81 (m, 2H), 3.79 (s, 3H), 5.34-5.37 (t, $J$ = 8.0 Hz, 0.55H), 5.53-5.58 (dd, $J_1$ = 8.0 Hz, $J_2$ = 12.0 Hz, 0.45H), 6.07-6.09 (m, 0.45H), 6.78-6.81 (m, 2H), 7.20-7.30 (m, 7H);

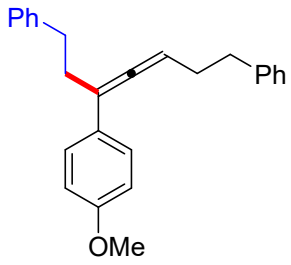
**$^{13}$C NMR** (100 MHz, CDCl$_3$, δ ppm): 28.8, 30.7, 31.4, 34.3, 35.4, 35.8, 37.0, 42.9, 44.6, 55.2, 55.3,

91.0, 94.3, 94.4, 101.5, 113.5, 114.0, 125.8, 125.9, 127.4, 127.7, 128.3, 128.6, 131.1, 141.6, 141.8, 158.0, 158.6, 204.6, 205.9;
**HRMS** (ESI) calcd for $C_{29}H_{34}O$ $[M+H]^+$ m/z 399.2682, found 399.2685.



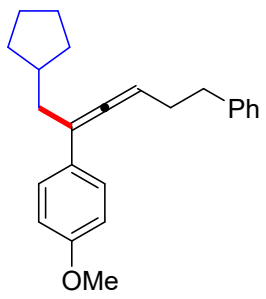

**2la,** 72%

**2la**: according to **General Procedure**; colorless oil; Eluent: *n*-hexane/EtOAc = 100/1;
**$^1$H NMR** (400 $MH_Z$ $CDCl_3$, δ ppm): 0.93-0.97 (t, *J* = 8.0 Hz, 3H), 1.44-1.53 (m, 2H), 2.29-2.33 (t, *J* = 8.0 Hz, 2H), 2.40-2.46 (m, 2H), 2.76-2.80 (t, *J* = 8.0 Hz, 2H), 3.79 (s, 3H), 5.47-5.50 (m, 1H), 6.80-6.83 (d, *J* = 12.0 Hz, 2H), 7.19-7.23 (m, 5H), 7.26-7.29 (m, 2H);
**$^{13}$C NMR** (100 MHz, $CDCl_3$, δ ppm): 14.0, 21.1, 31.1, 32.2, 35.6, 55.3, 93.5, 105.3, 113.7, 125.8, 126.9, 128.3, 128.6, 129.6, 141.8, 158.2, 203.4;
**HRMS** (ESI) calcd for $C_{21}H_{24}O$ $[M+H]^+$ m/z 293.1900, found 293.1903.



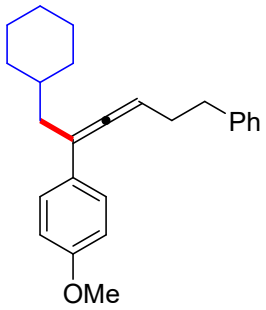

**2ma,** 77%

**2ma**: according to **General Procedure**; colorless oil; Eluent: *n*-hexane/EtOAc = 100/1;
**$^1$H NMR** (400 $MH_Z$ $CDCl_3$, δ ppm): 2.35-2.41 (m, 2H), 2.62-2.78 (m, 6H), 3.80 (s, 3H), 5.49-5.52 (m, 1H), 6.81-6.84 (d, *J* = 12.0 Hz, 2H), 7.19-7.31 (m, 12H);
**$^{13}$C NMR** (100 MHz, $CDCl_3$, δ ppm): 30.9, 31.9, 34.2, 35.5, 55.3, 94.2, 105.0, 113.8, 125.8, 125.8, 126.9, 128.3, 128.3, 128.5, 128.6, 129.3, 141.7, 142.2, 158.3, 203.4;
**HRMS** (ESI) calcd for $C_{26}H_{26}O$ $[M+H]^+$ m/z 355.2056, found 355.2056.



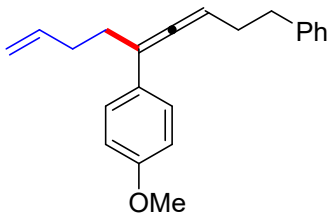

**2na,** 68%

**2na**: according to **General Procedure**; colorless oil; Eluent: *n*-hexane/EtOAc = 100/1;
**$^1$H NMR** (400 MHz $CDCl_3$, δ ppm): 0.87-0.97 (m, 2H), 1.12-1.20 (m, 2H), 1.42-1.50 (m, 1H), 1.64-1.79 (m, 4H), 2.21-2.24 (m, 2H), 2.40-2.45 (dd, $J_1$ = 4.0 Hz, $J_2$ = 8.0 Hz, 2H), 2.76-2.80 (dt, $J_1$ = 4.0 Hz, $J_2$ = 8.0 Hz, 2H), 3.79 (s, 3H), 5.41-5.45 (m, 1H), 6.80-6.82 (d, $J$ = 8.0 Hz, 2H), 7.09-7.21 (m, 5H), 7.24-7.30 (m, 2H);
**$^{13}$C NMR** (100 MHz, $CDCl_3$, δ ppm): 26.3, 26.6, 31.2, 33.4, 33.5, 35.8, 36.1, 38.4, 55.3, 92.5, 103.5, 113.7, 125.8, 127.1, 128.3, 128.6, 129.7, 141.8, 158.2, 204.0;
**HRMS** (ESI) calcd for $C_{24}H_{28}O$ $[M+H]^+$ m/z 333.2213, found 333.2214.



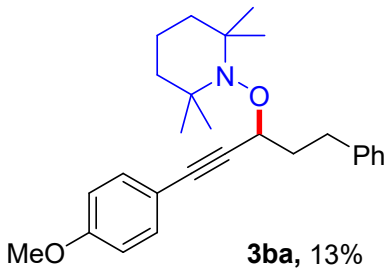
**2oa,** 73%

**2oa**: according to **General Procedure**; colorless oil; Eluent: *n*-hexane/EtOAc = 100/1;
**$^1$H NMR** (400 MHz $CDCl_3$, δ ppm): 1.12-1.23 (m, 2H), 1.48-1.77 (m, 8H), 1.98-2.05 (m, 1H), 2.32-2.36 (dt, $J_1$ = 4.0 Hz, $J_2$ = 8.0 Hz, 2H), 2.41-2.46 (dd, $J_1$ = 4.0 Hz, $J_2$ = 8.0 Hz, 2H), 2.77-2.81 (t, $J$ = 8.0 Hz, 2H), 3.78 (s, 3H), 5.44-5.47 (m, 1H), 6.80-6.82 (d, $J$ = 8.0 Hz, 2H), 7.09-7.21 (m, 5H), 7.24-7.30 (m, 2H);
**$^{13}$C NMR** (100 MHz, $CDCl_3$, δ ppm): 25.3, 31.2, 32.8, 35.7, 37.1, 38.2, 55.3, 93.0, 104.9, 113.7, 125.8, 127.0, 128.3, 128.6, 129.7, 141.8, 158.2, 203.9;
**HRMS** (ESI) calcd for $C_{25}H_{30}O$ $[M+H]^+$ m/z 347.2369, found 347.2370.



**3aa**, 65%

**3aa**: according to **General Procedure**; colorless oil; Eluent: *n*-hexane/EtOAc = 100/1;
**$^1$H NMR** (400 MHz $CDCl_3$, δ ppm): 2.15-2.25 (m, 2H), 2.40-2.46 (m, 4H), 2.77-2.80 (t, $J$ = 8.0 Hz, 2H), 3.79 (s, 3H), 4.97-5.06 (m, 2H), 5.50-5.57 (m, 1H), 5.83-5.93 (m, 1H), 6.81-6.83 (d, $J$ = 8.0 Hz, 2H), 7.19-7.29 (m, 7H);
**$^{13}$C NMR** (100 MHz, $CDCl_3$, δ ppm): 29.4, 31.1, 32.1, 35.6, 55.3, 94.1, 105.0, 113.8, 114.6, 125.8, 126.9, 128.3, 128.6, 129.5, 138.5, 141.8, 158.3, 203.4;
**HRMS** (ESI) calcd for $C_{22}H_{24}O$ $[M+H]^+$ m/z 305.1900, found 305.1901.



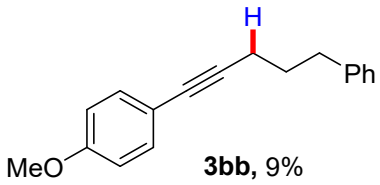

**3ba,** 13%

**3ba**: according to **General Procedure**; colorless oil; Eluent: *n*-hexane/EtOAc = 50/1;

**$^1$H NMR** (400 $MH_Z$ $CDCl_3$, δ ppm): 1.11-1.57 (m, 18H), 2.12-2.18 (m, 2H), 2.80-2.96 (m, 2H), 3.81 (s, 3H), 4.61-4.64 (t, *J* = 8.0 Hz, 1H), 6.82-6.85 (d, *J* = 12.0 Hz, 2H), 7.16-7.30 (m, 5H), 7.36-7.38 (d, *J* = 8.0 Hz, 2H);

**$^{13}$C NMR** (100 MHz, $CDCl_3$, δ ppm): 17.2, 20.3, 20.5, 31.7, 33.7, 34.7, 36.9, 40.1, 40.2, 55.3, 59.4, 60.4, 75.2, 86.5, 89.1, 113.8, 115.8, 125.8, 128.3, 128.5, 132.8, 142.0, 159.4;

**HRMS** (ESI) calcd for $C_{27}H_{35}NO_2$ $[M+H]^+$ m/z 406.2741, found 406.2738.




**3bb,** 9%

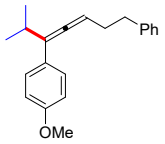
**3bb**: according to **General Procedure**; colorless oil; Eluent: *n*-hexane/EtOAc = 100/1;

**$^1$H NMR** (400 $MH_Z$ $CDCl_3$, δ ppm): 1.88-1.95 (m, 2H), 2.39-2.42 (t, *J* = 8.0 Hz, 2H), 2.77-2.80 (t, *J* = 4.0 Hz, 2H), 3.80 (s, 3H), 6.81-6.83 (d, *J* = 8.0 Hz, 2H), 7.19-7.35 (m, 7H);

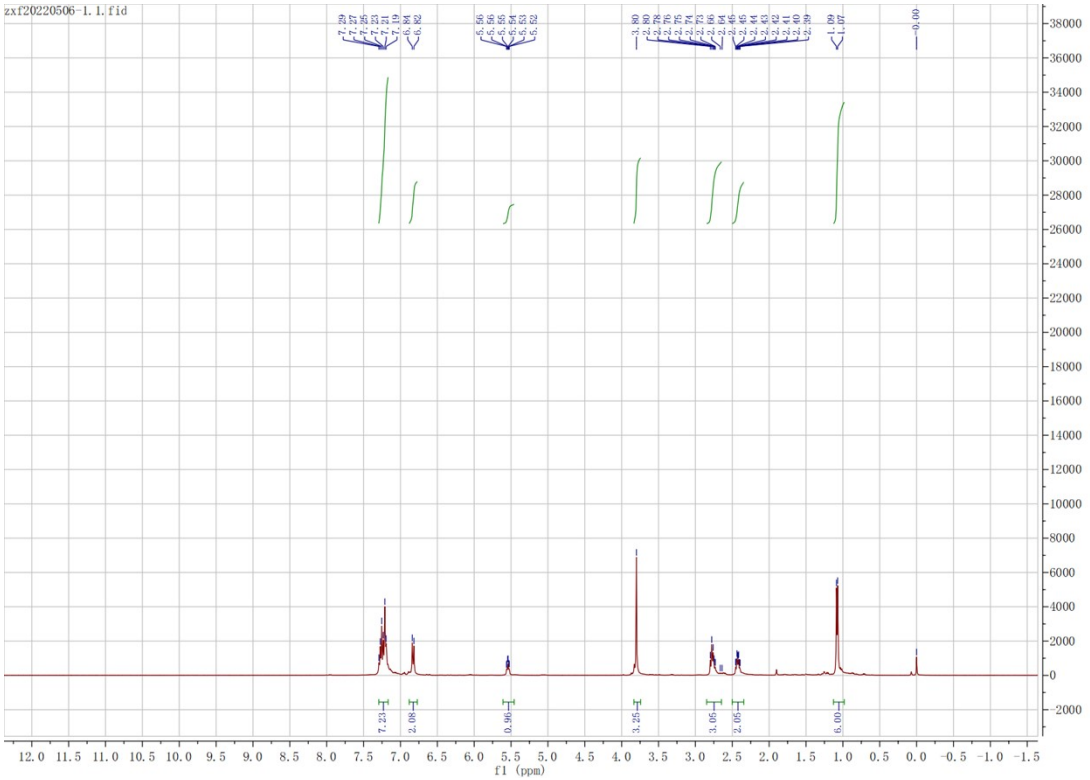
**$^{13}$C NMR** (100 MHz, $CDCl_3$, δ ppm): 18.9, 30.4, 34.9, 55.3, 88.2, 113.8, 116.2, 125.9, 128.3, 128.6, 132.9, 141.7, 159.1;

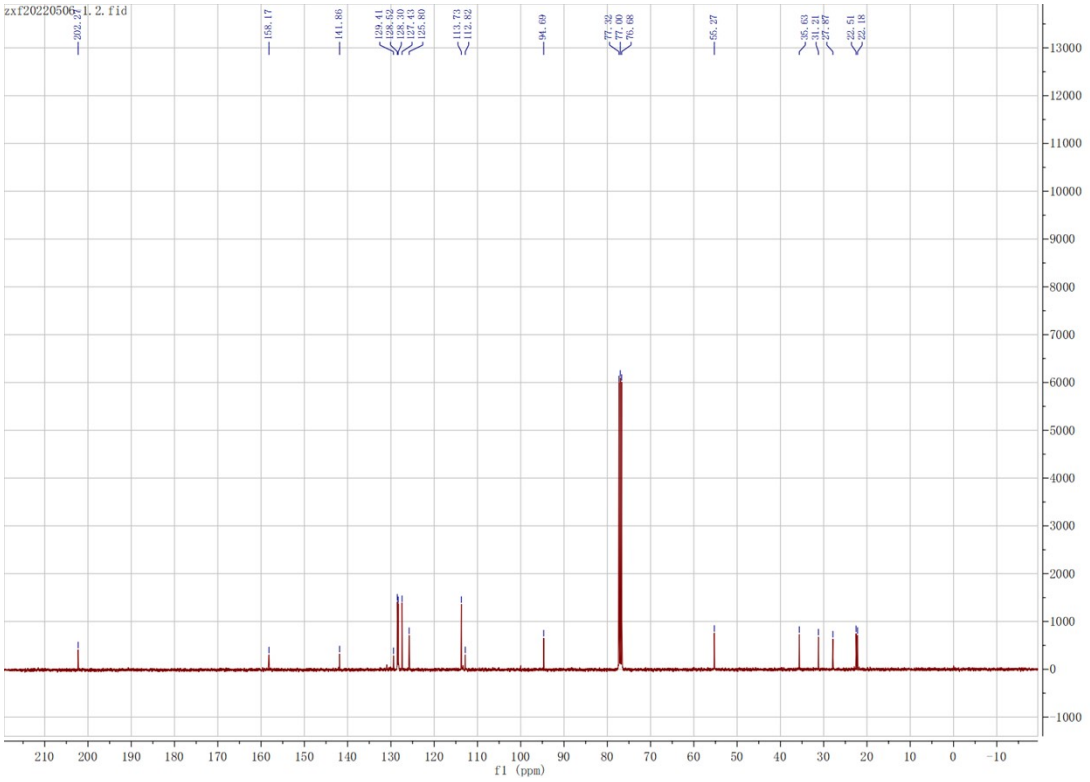
**HRMS** (ESI) calcd for $C_{18}H_{18}O$ $[M+H]^+$ m/z 251.1430, found 251.1432.

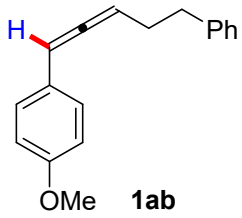
# 9. $^{1}$H NMR and $^{13}$C NMR Spectra of the Products 1aa-1oa:



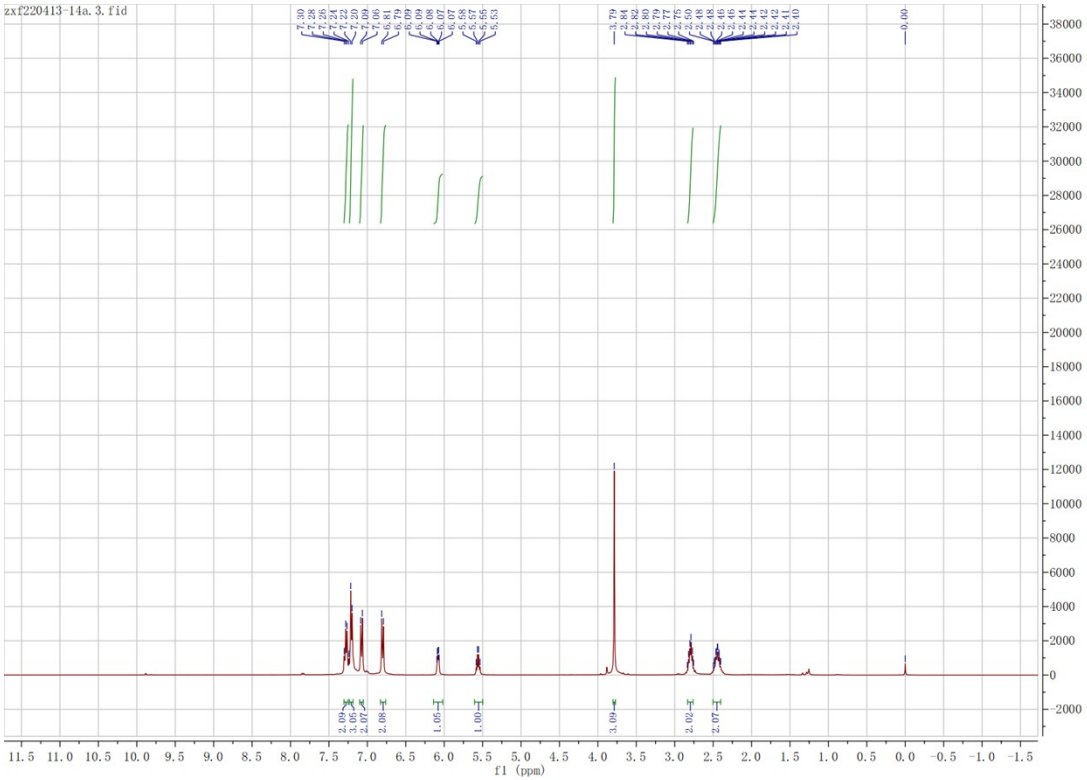

**1aa**, 88%

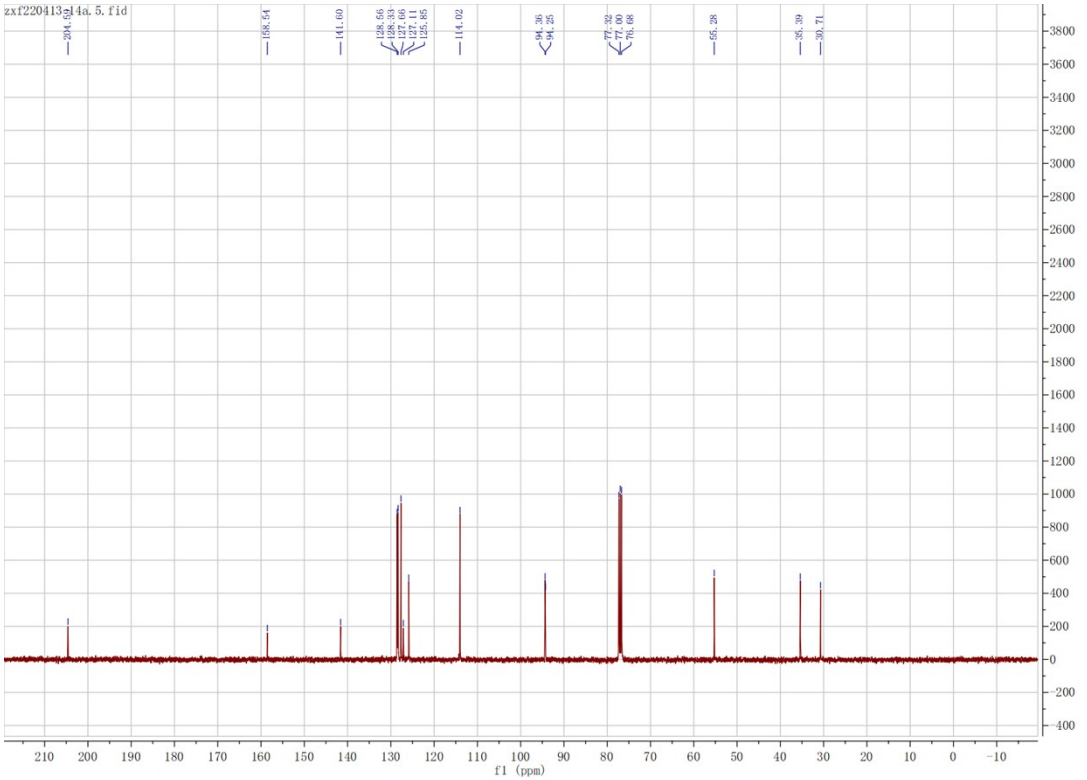


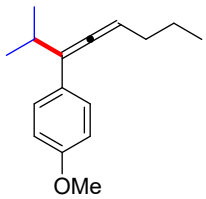





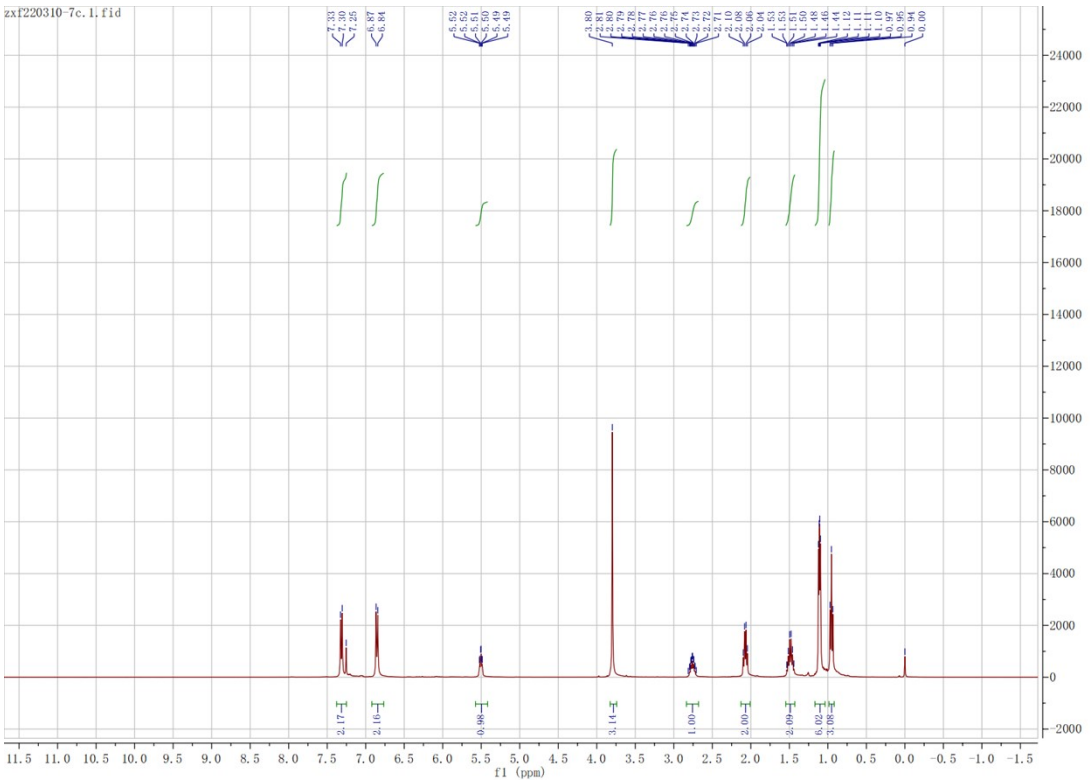

**1ab**

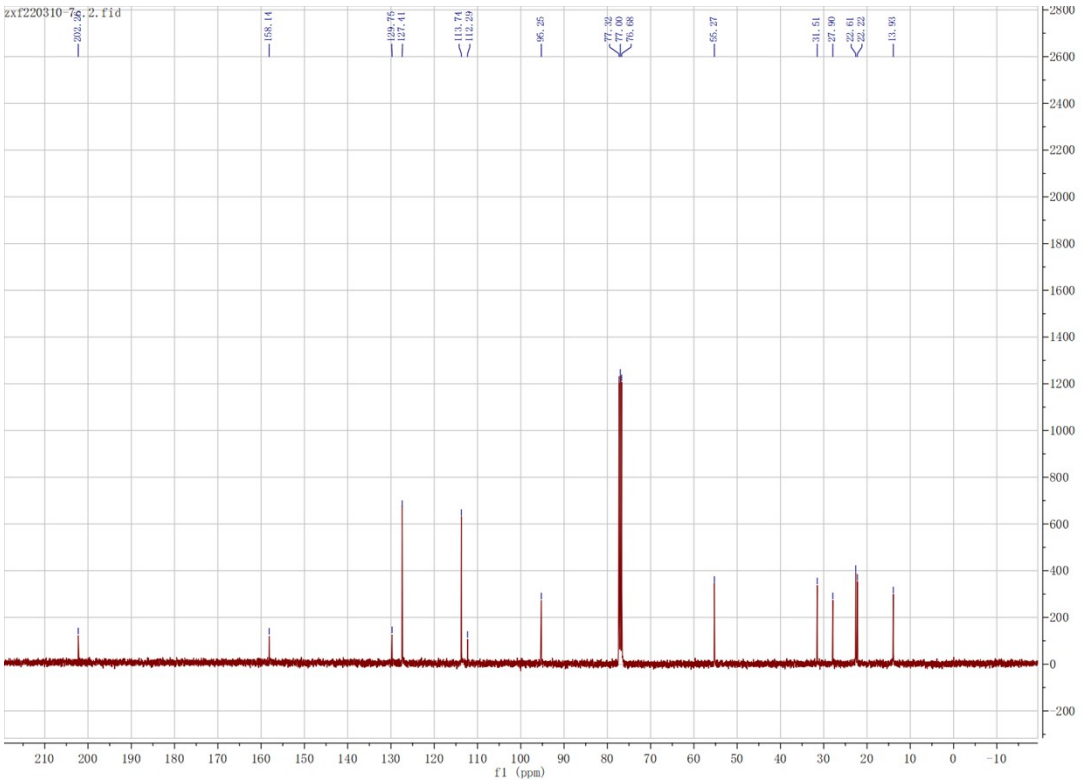


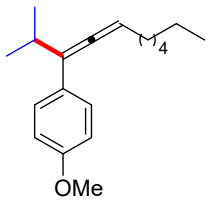





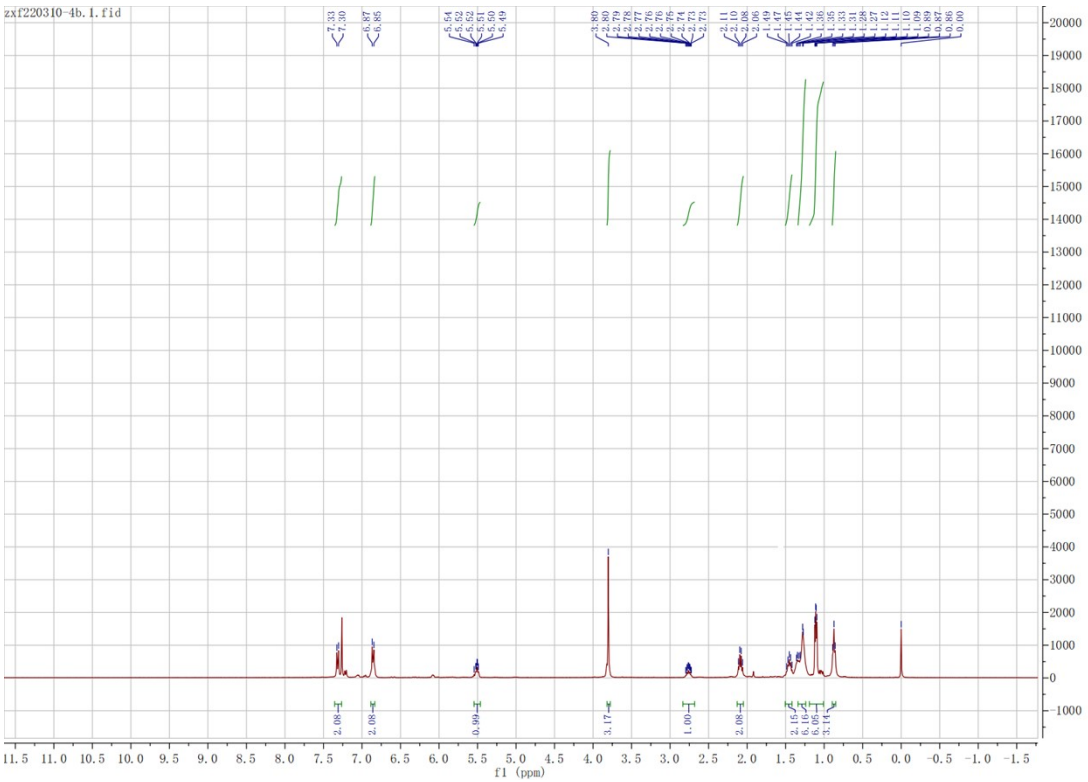

**1ba**, 68%

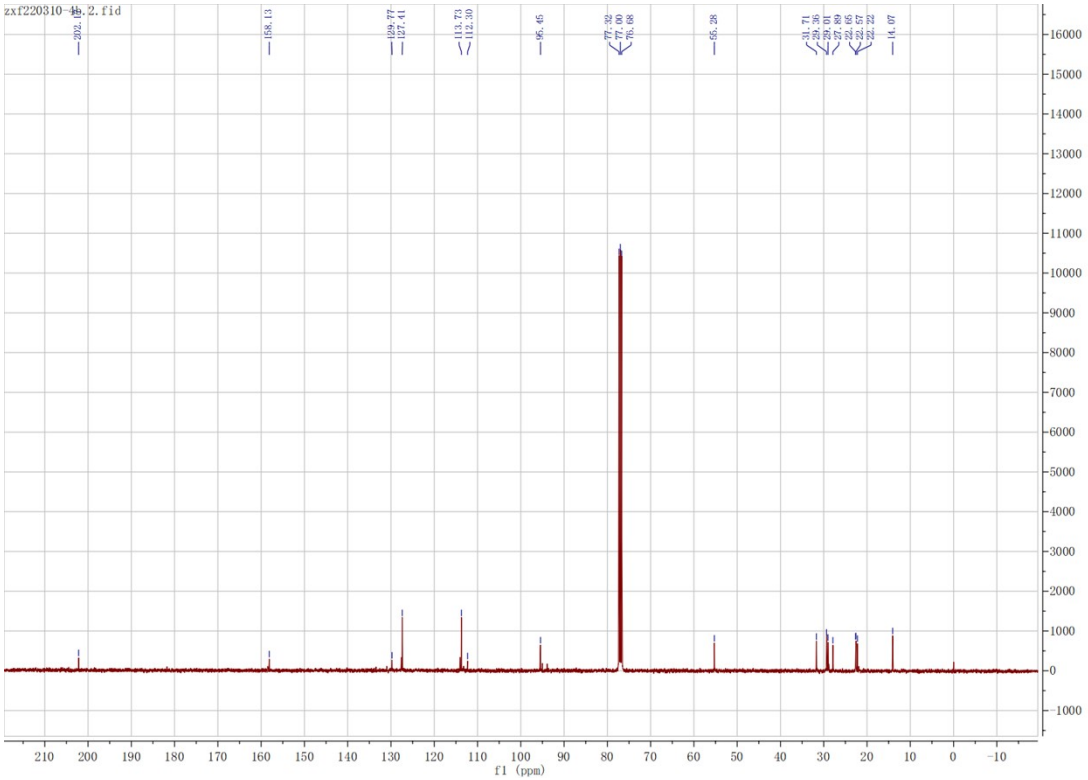


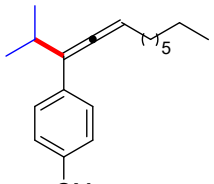





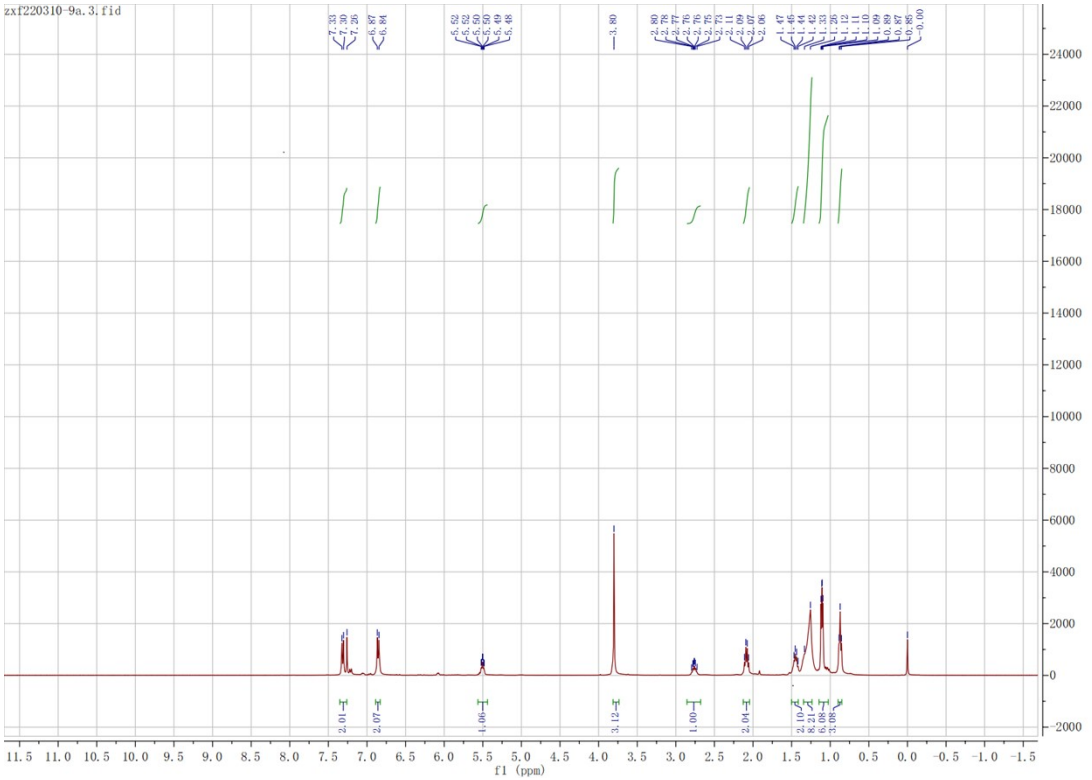

**1ca**, 78%

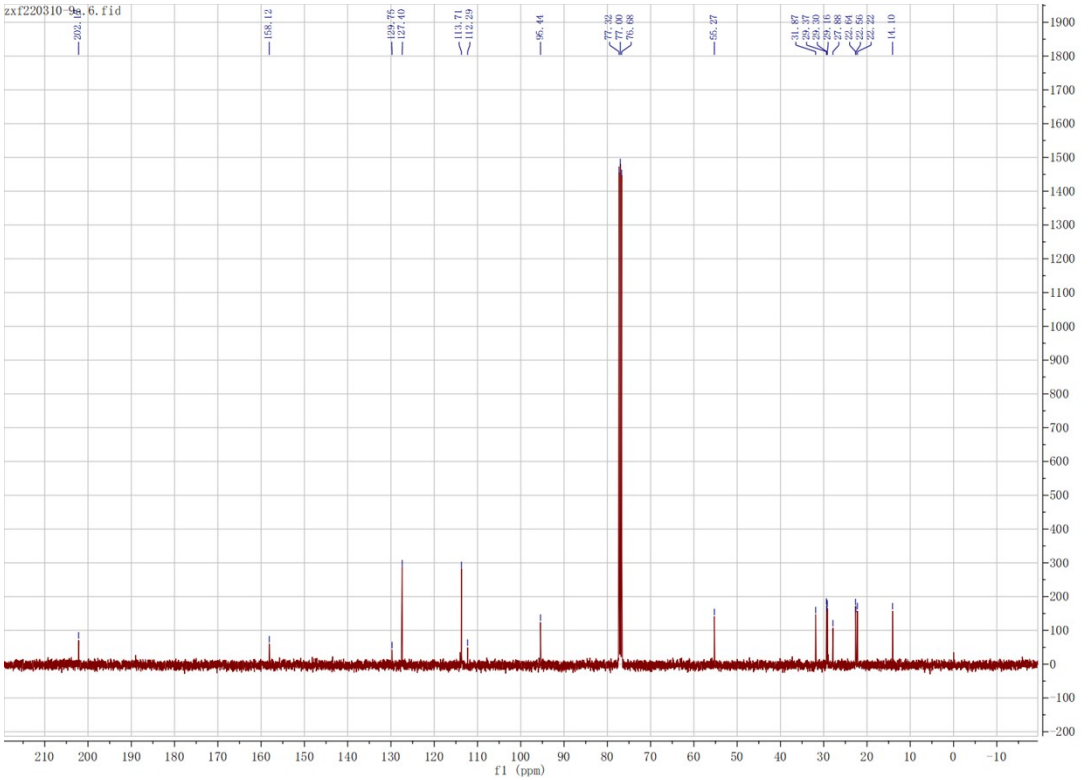


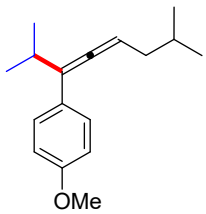





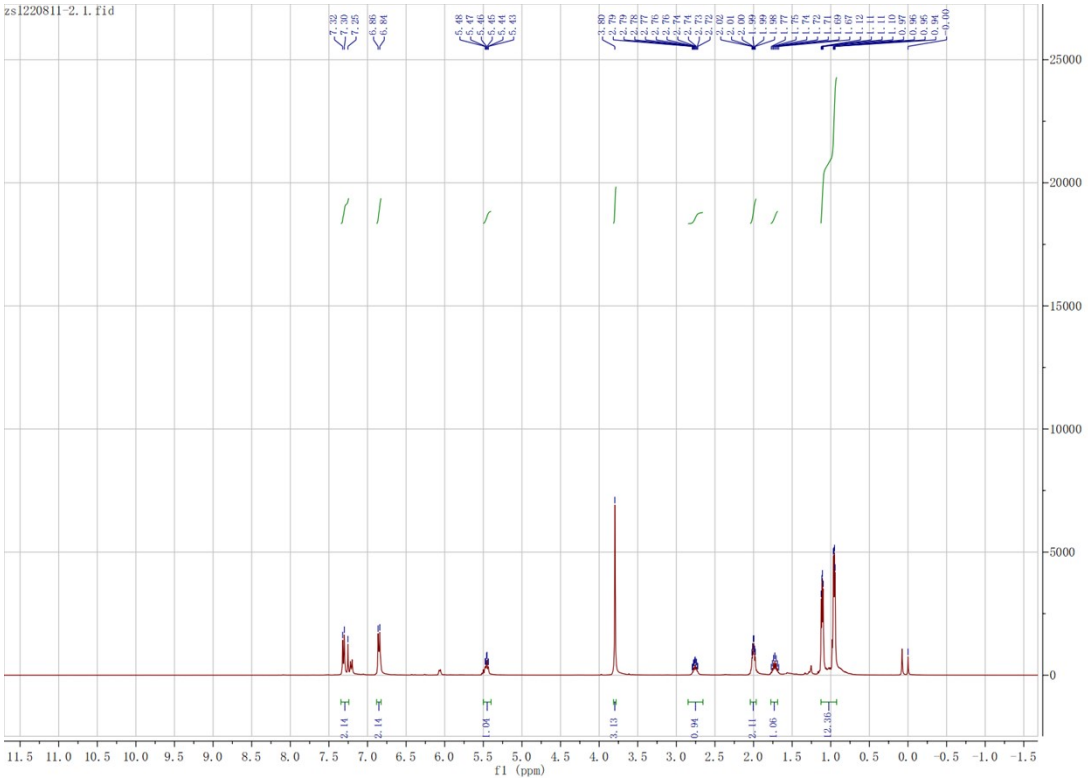

**1da**, 80%

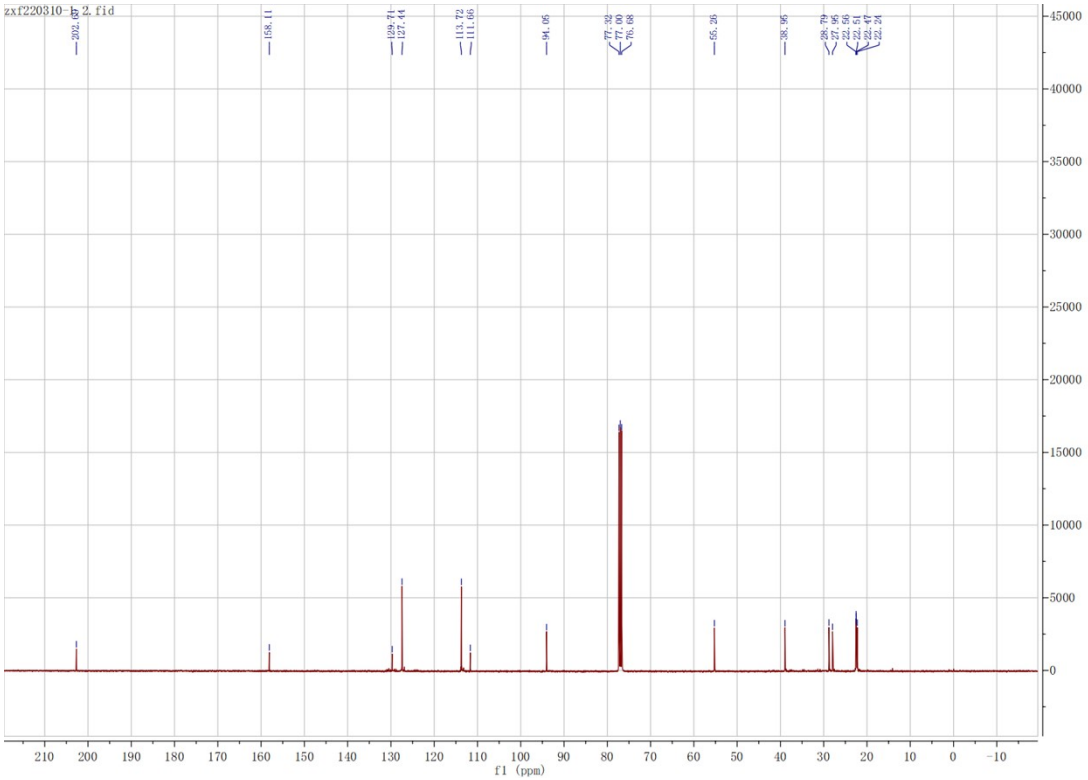


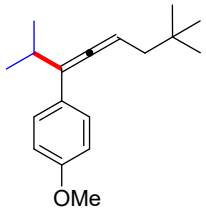





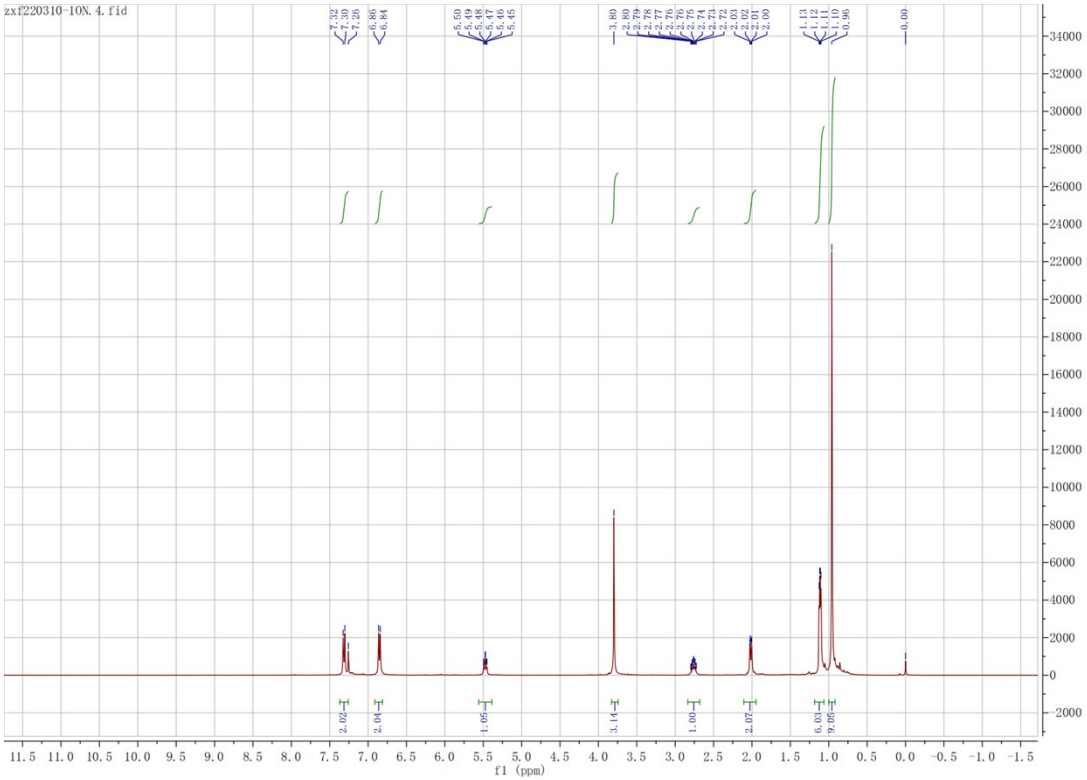

**1ea,** 77%

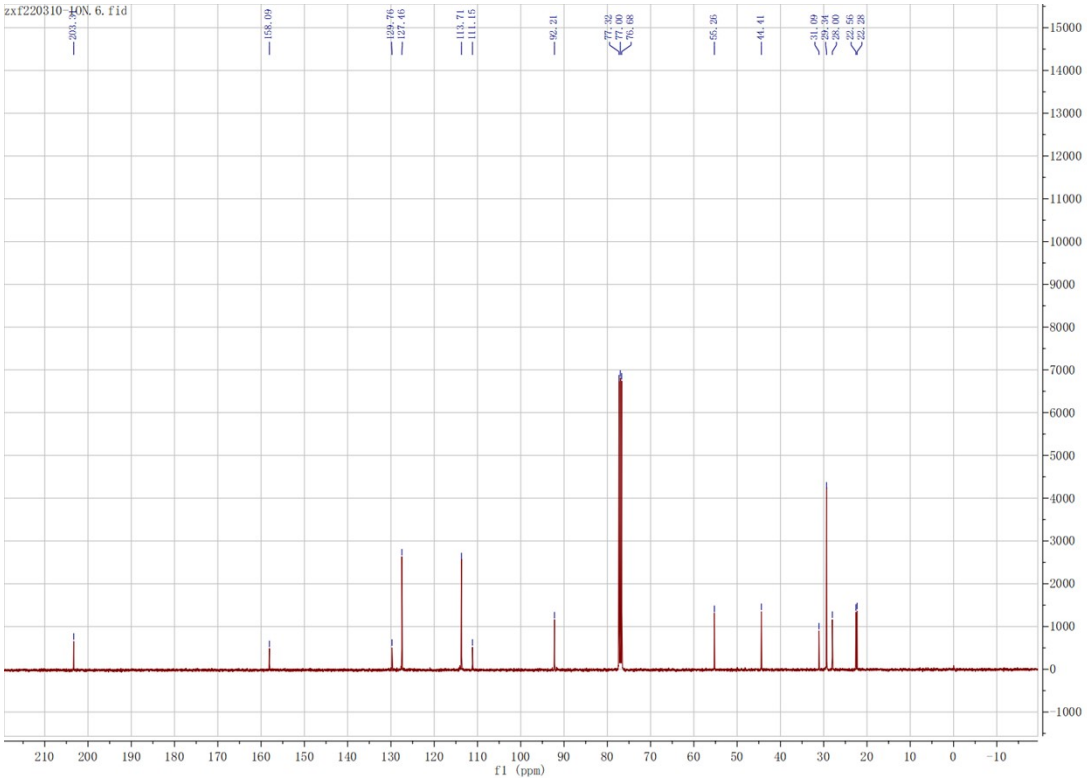


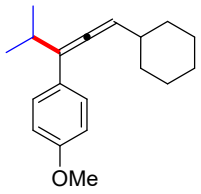





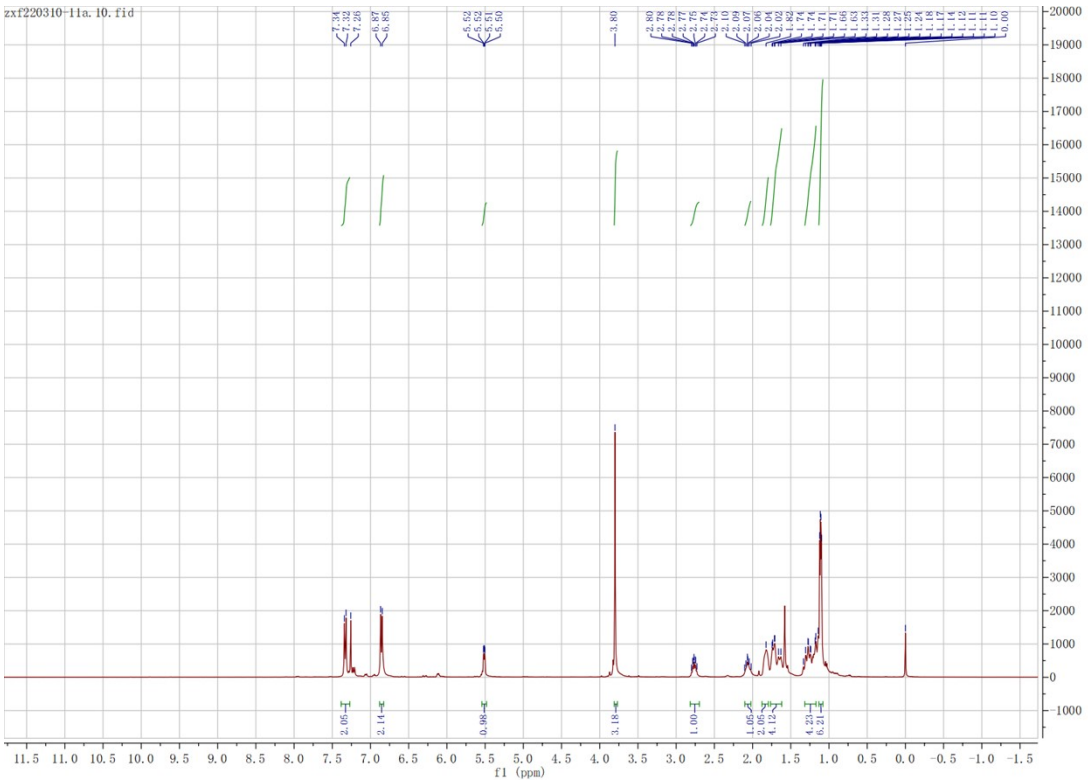

**1fa,** 79%

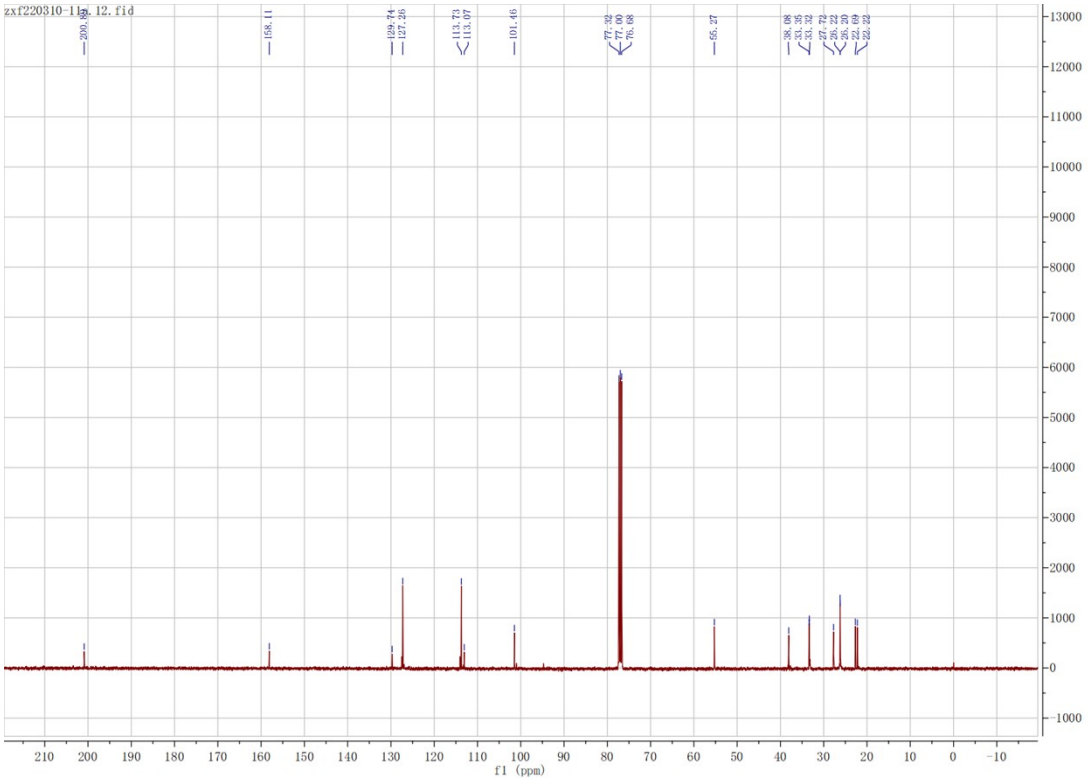


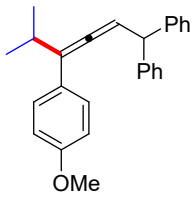





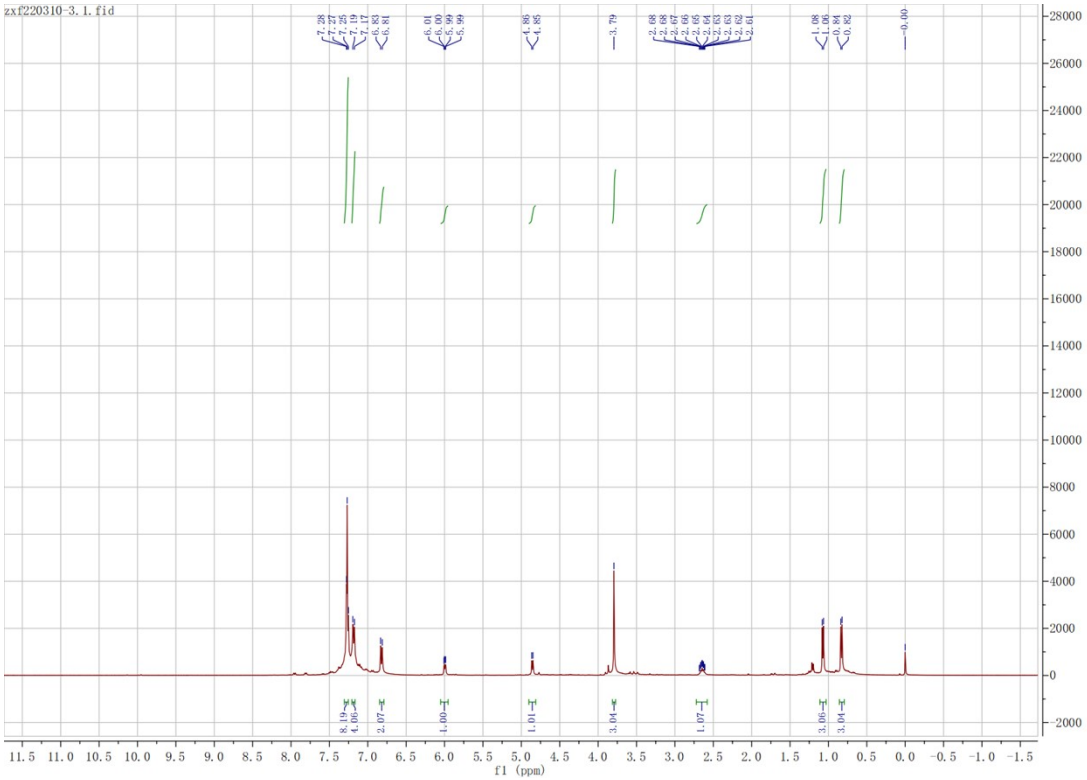

**1ga,** 83%

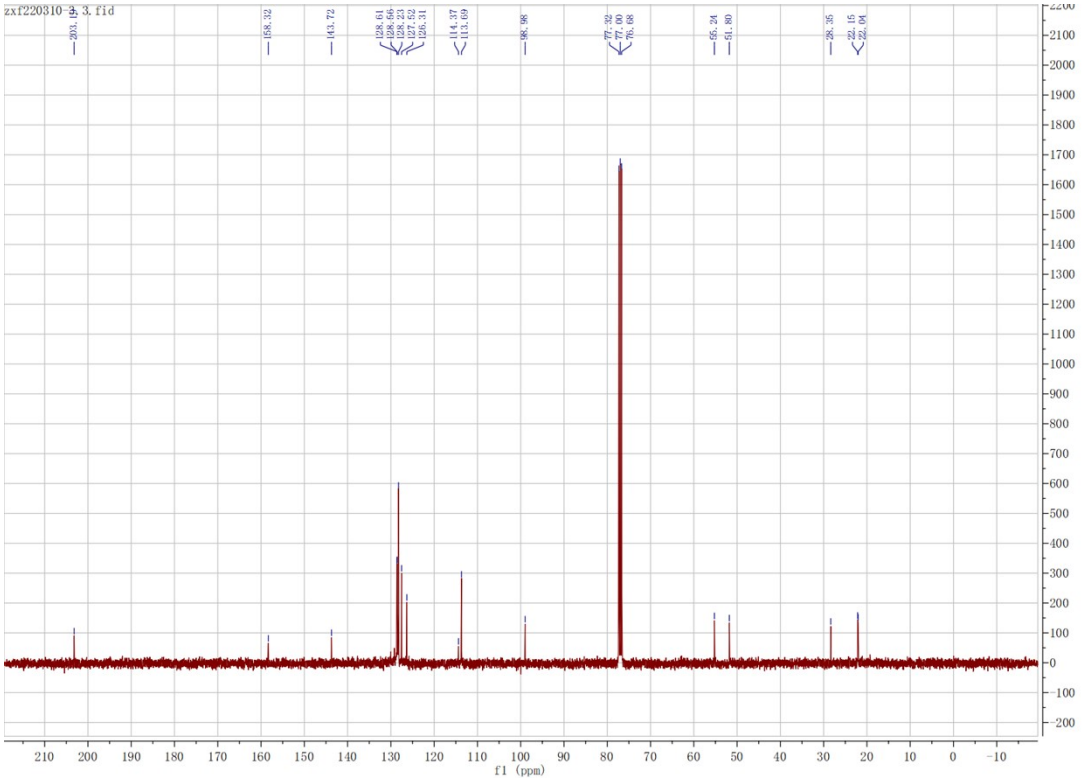


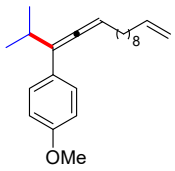





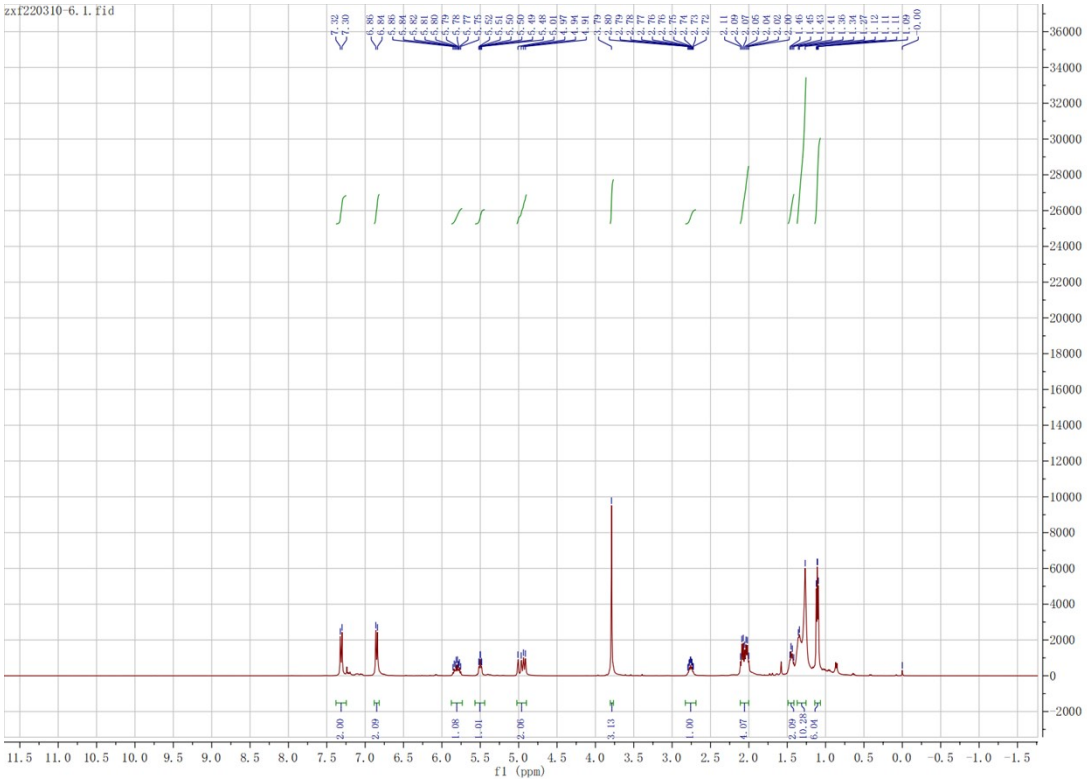

**1ha,** 58%

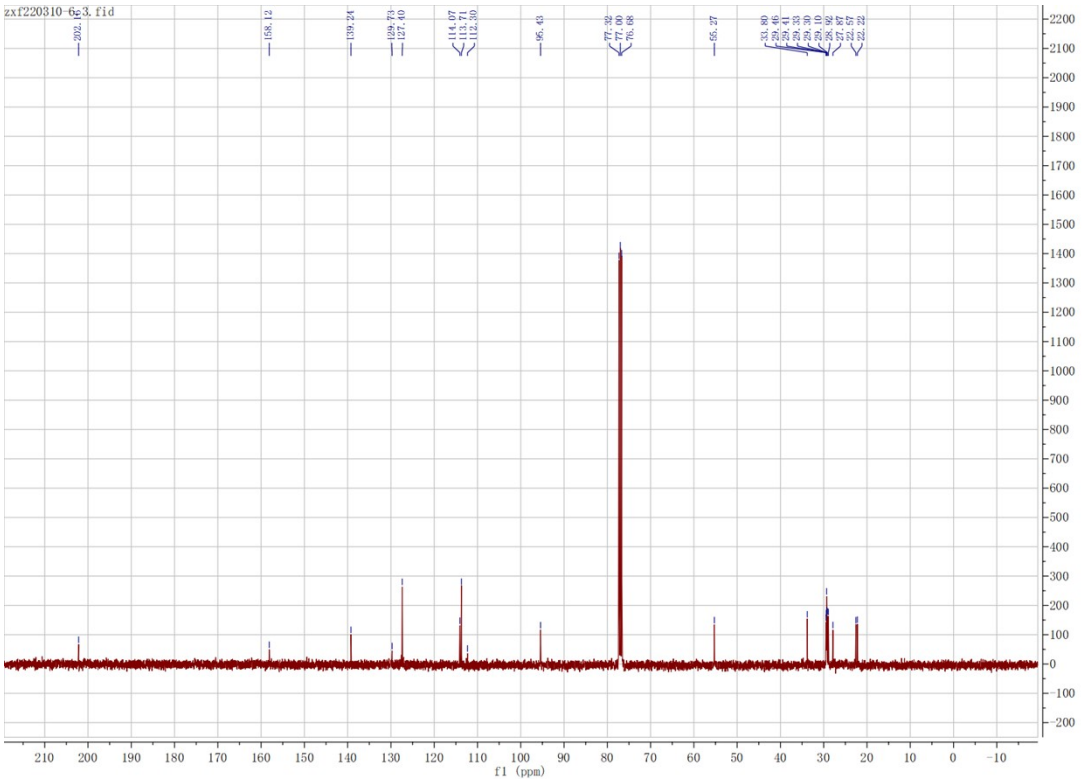


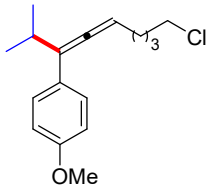





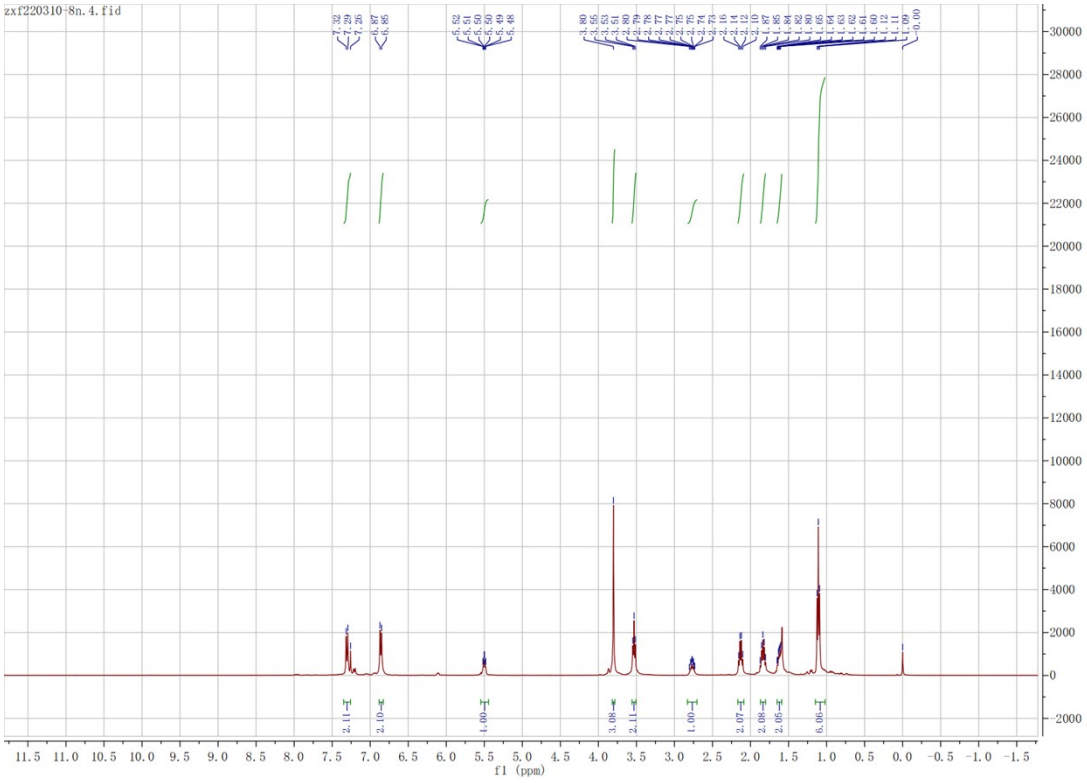

**1ia,** 68%

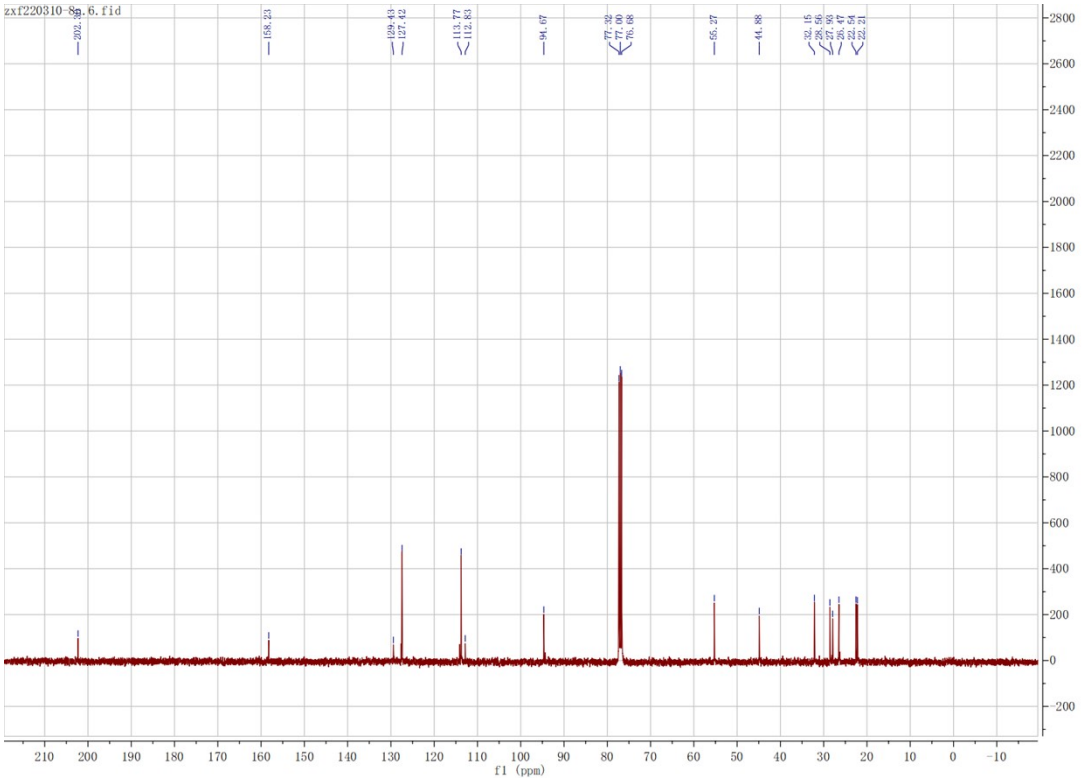


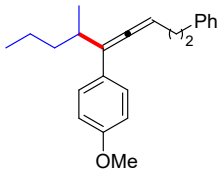





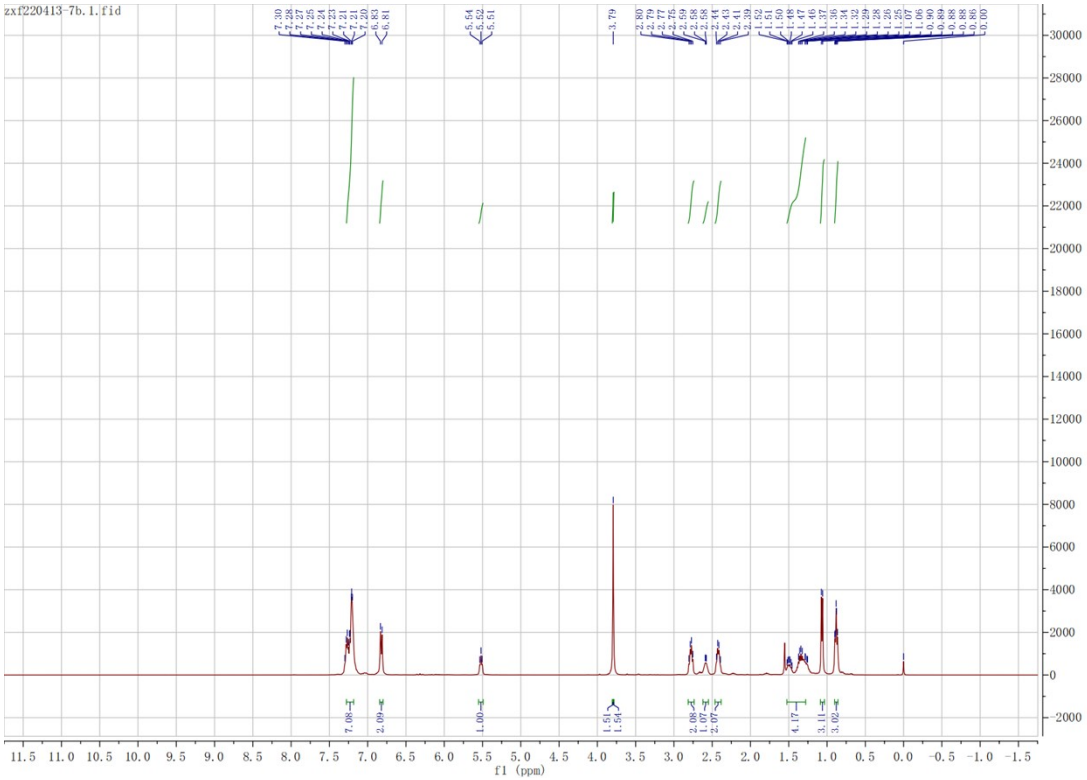

**1ja,** 85%

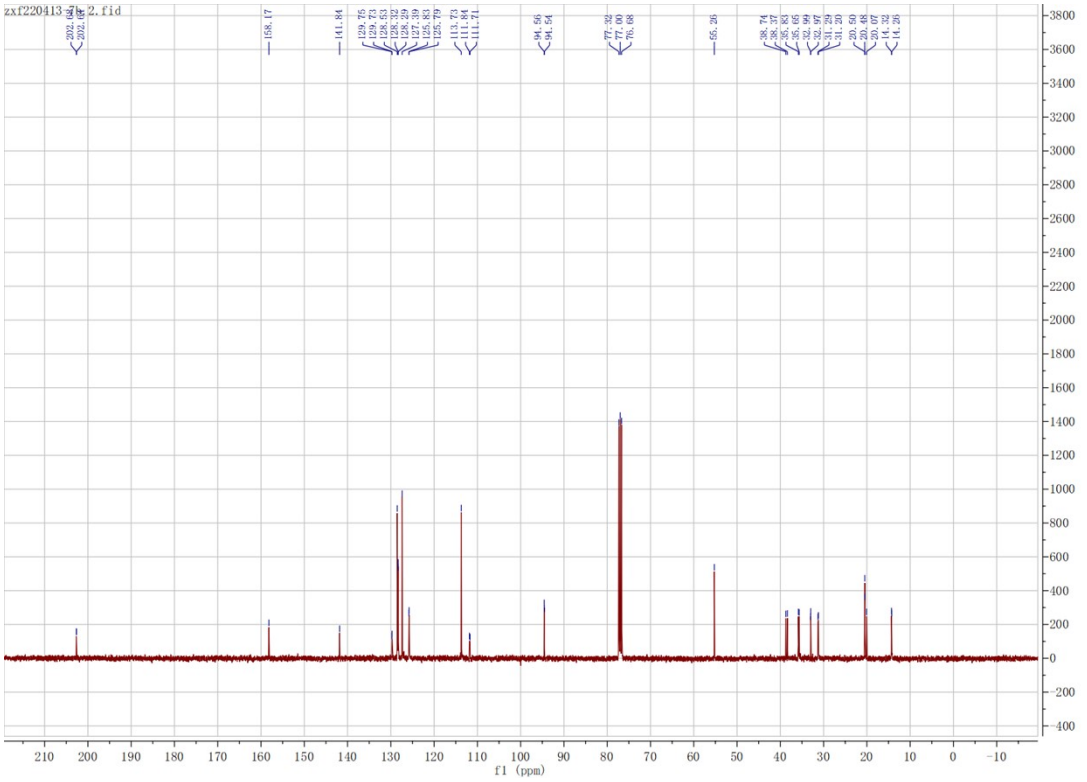


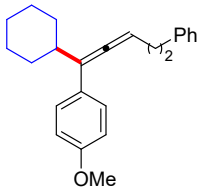





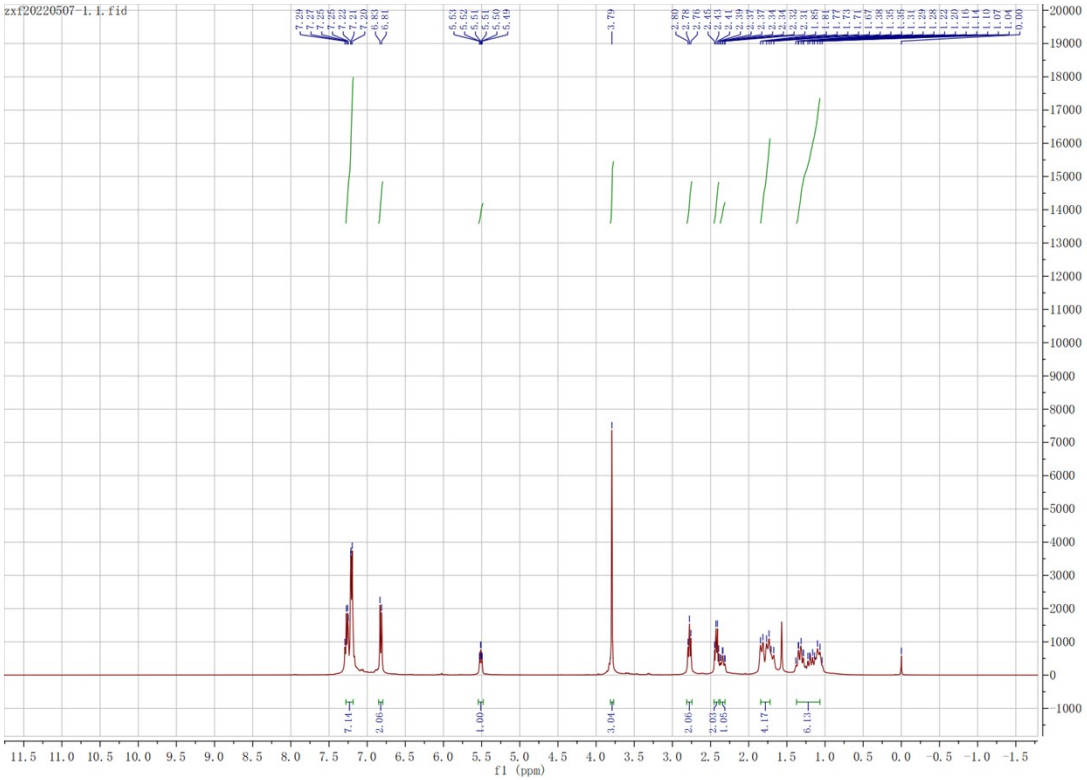

**1ma,** 62%
(dr = 1:1 )

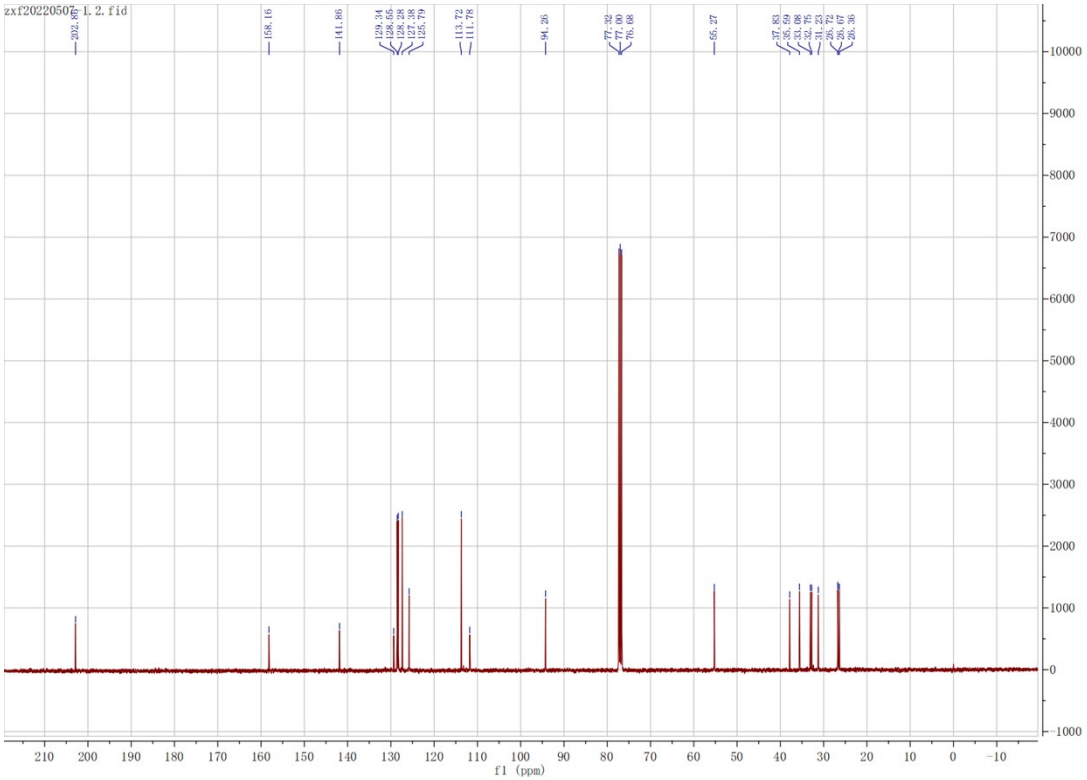


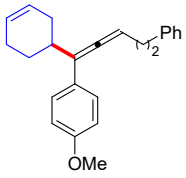





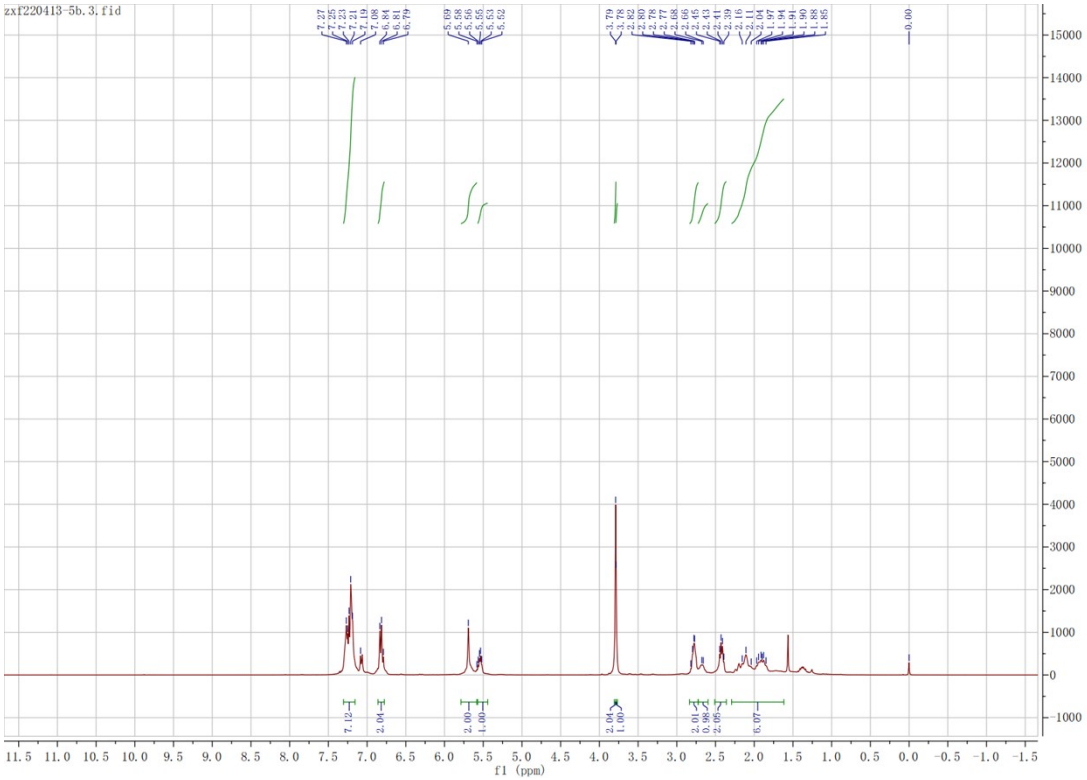

**1na**, 64%

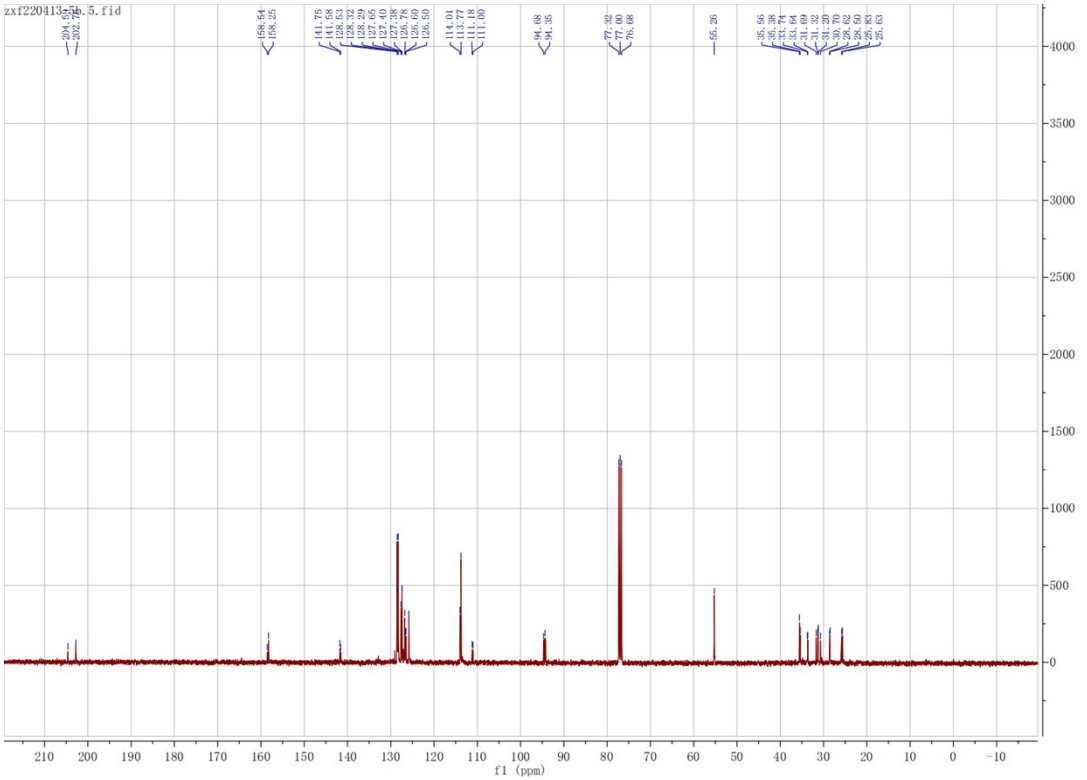


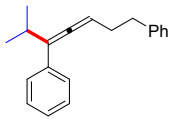



**1oa,** 59%
(dr = 2:1)

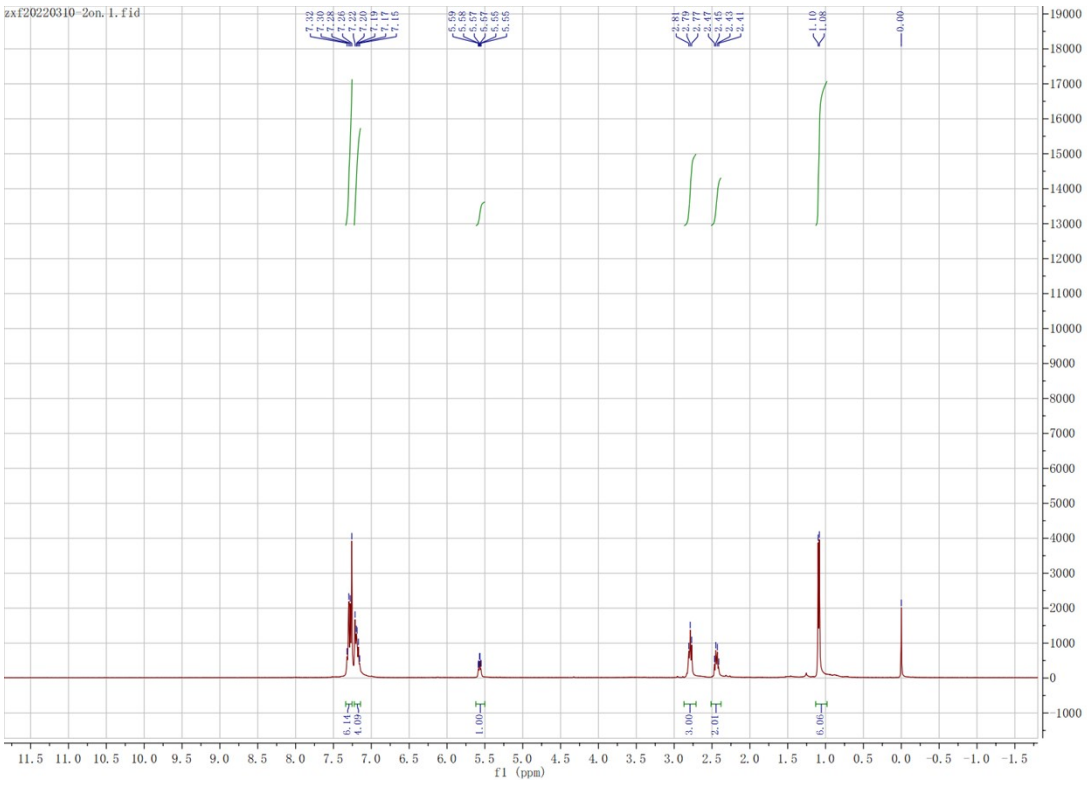


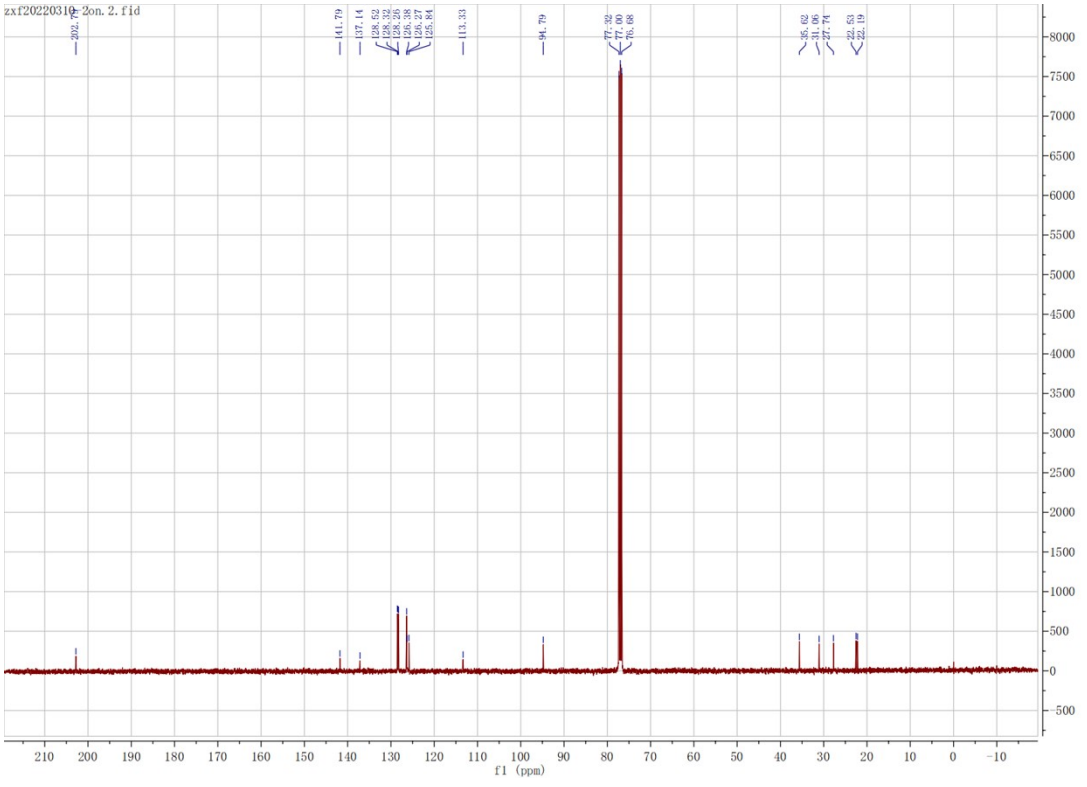



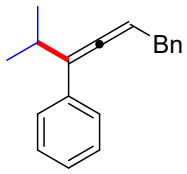
# 10. $^{1}$H NMR and $^{13}$C NMR Spectra of Products 2aa-2oa, 3aa, 3ba-3bb:



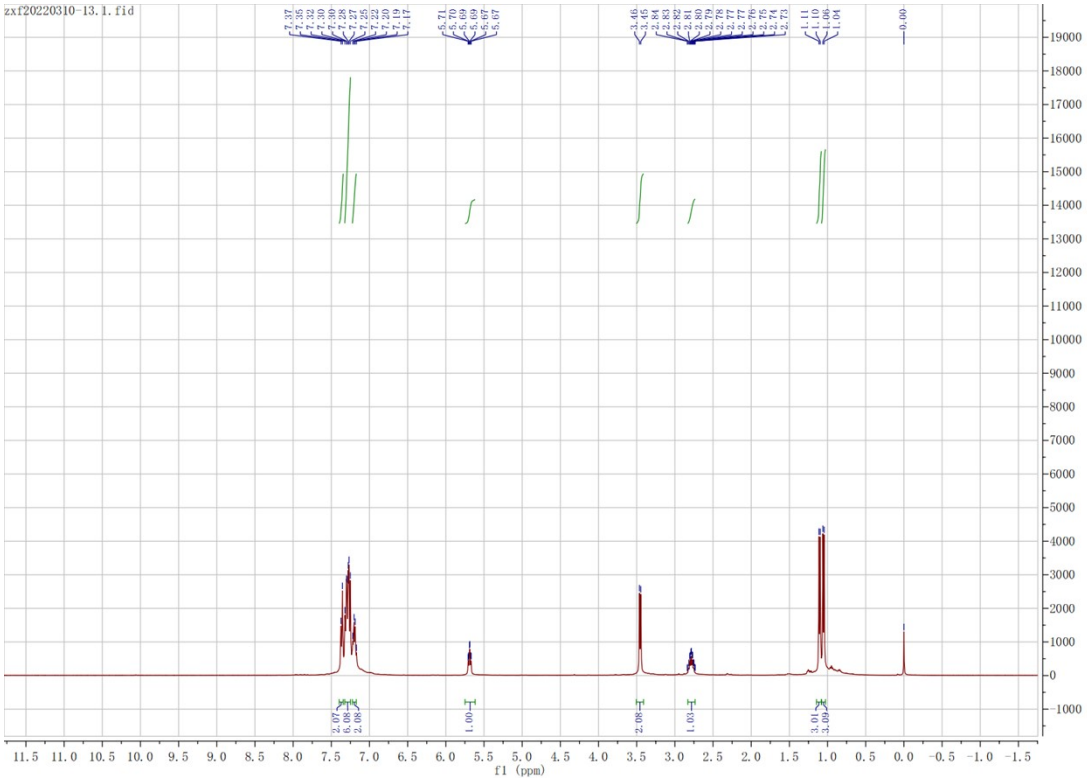

**2aa**, 89%

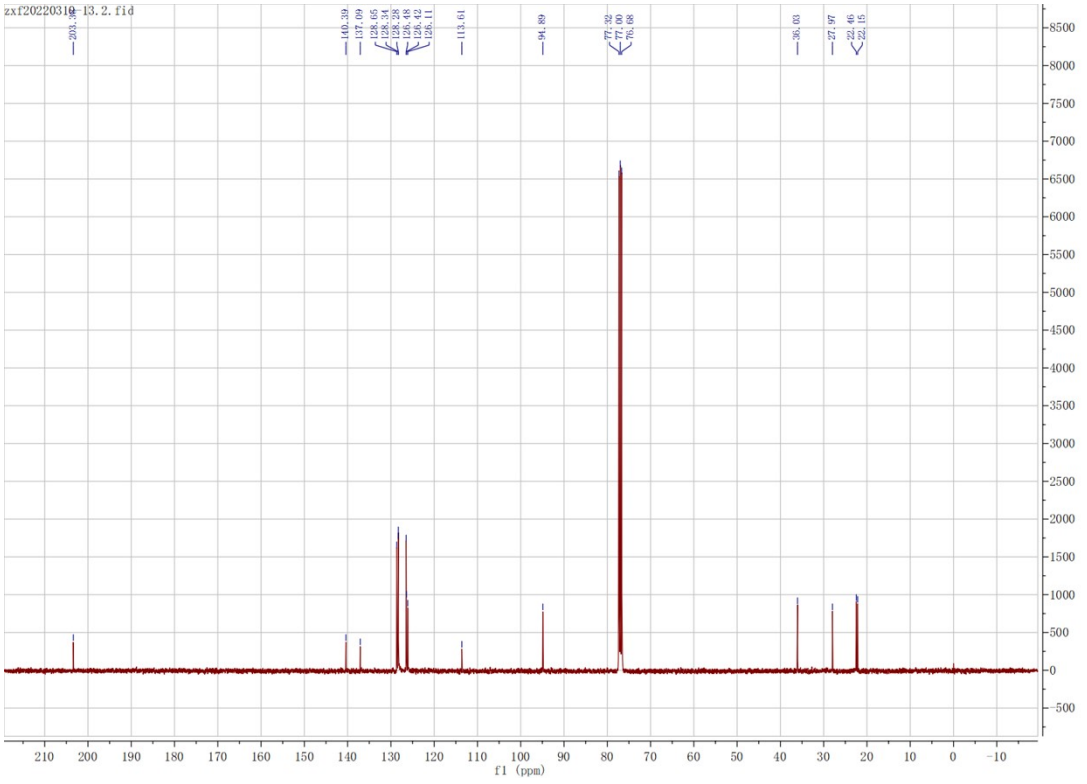


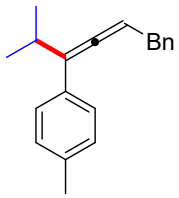





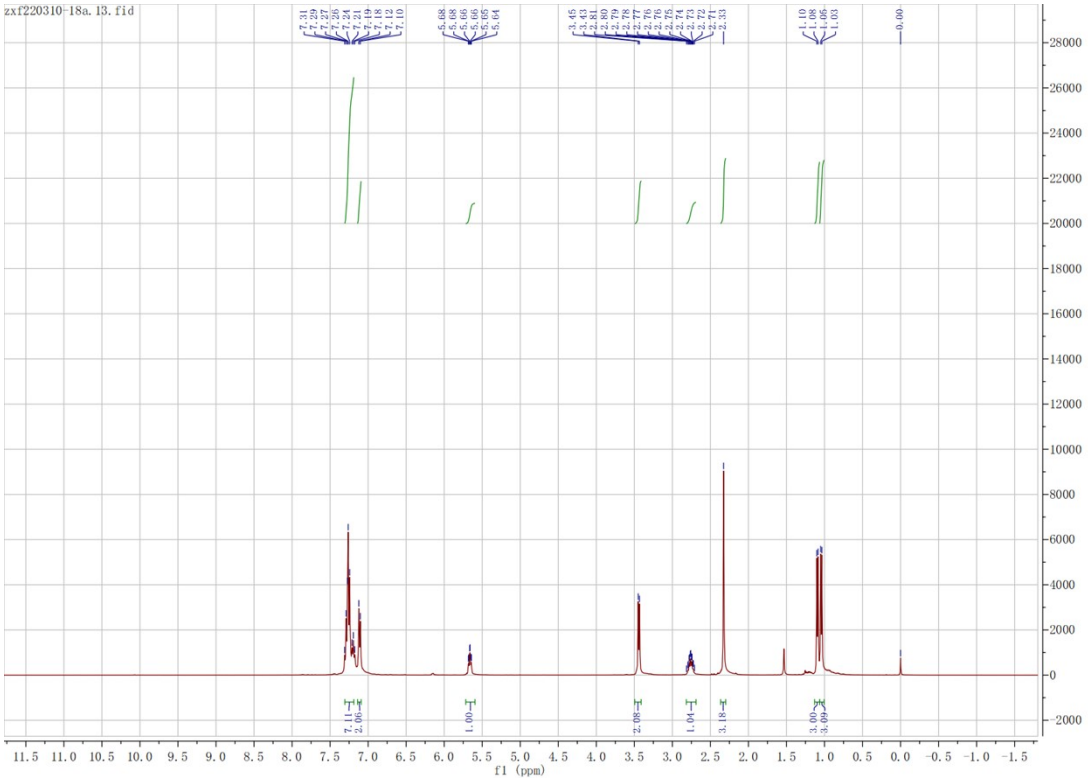

**2ba**, 73%

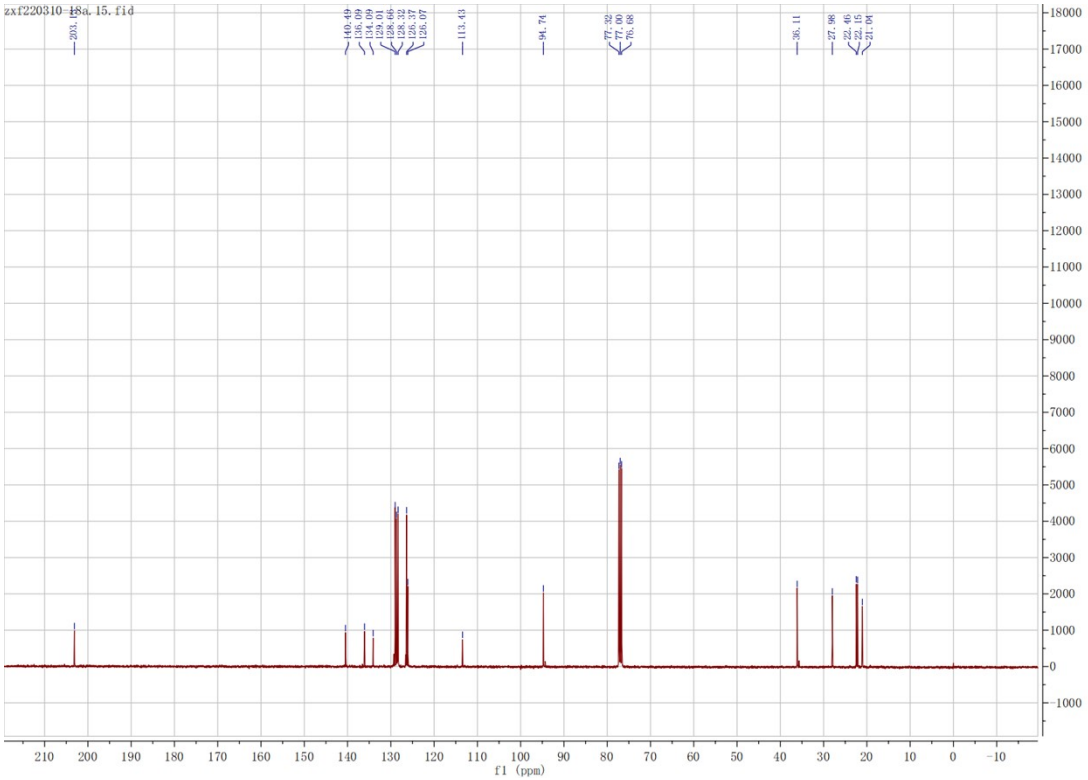


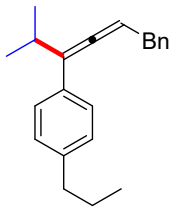





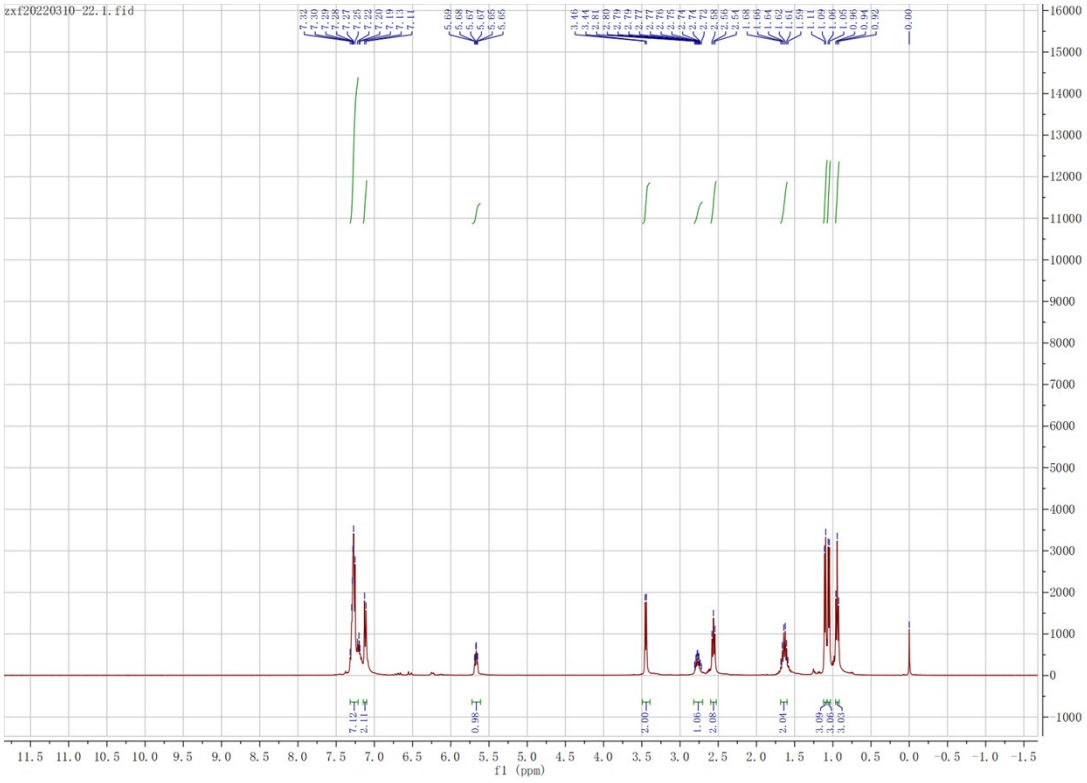

**2ca**, 68%

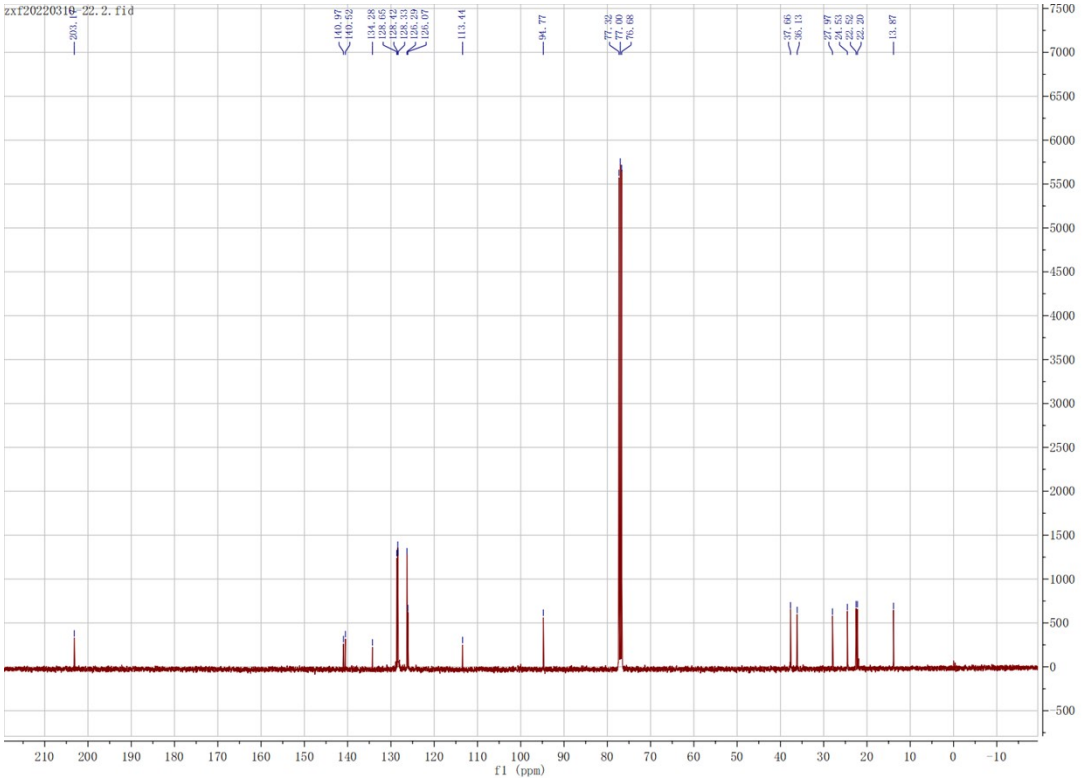


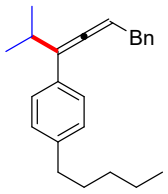





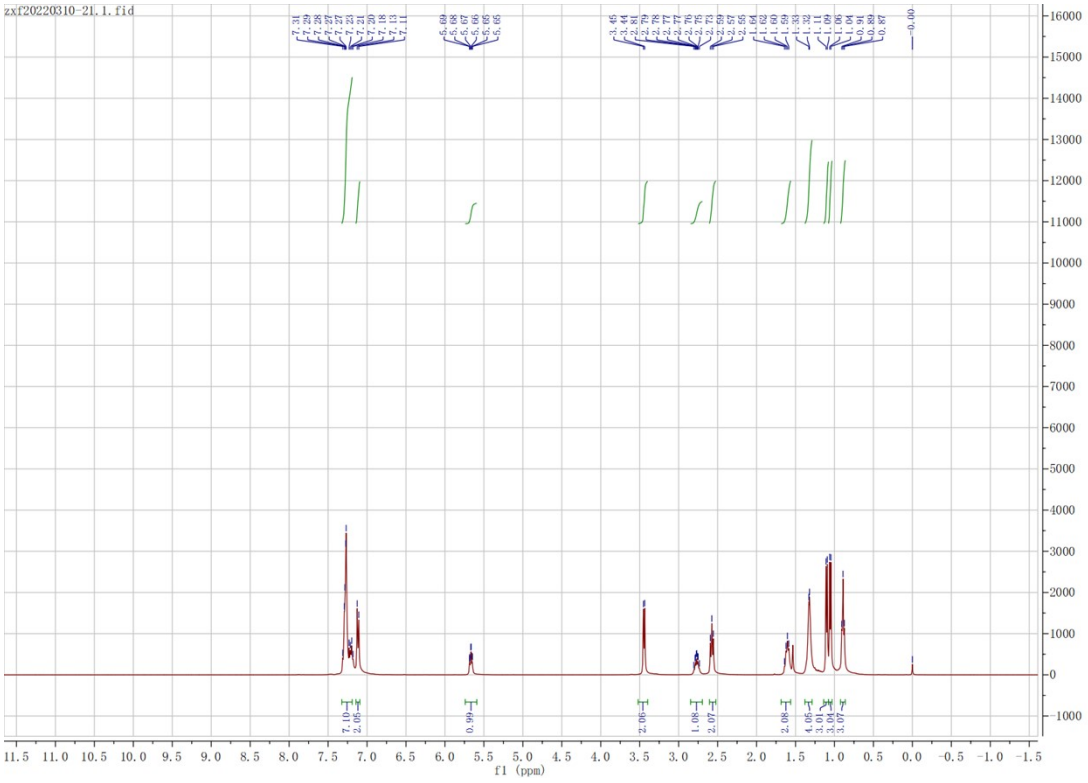

**2da**, 78%

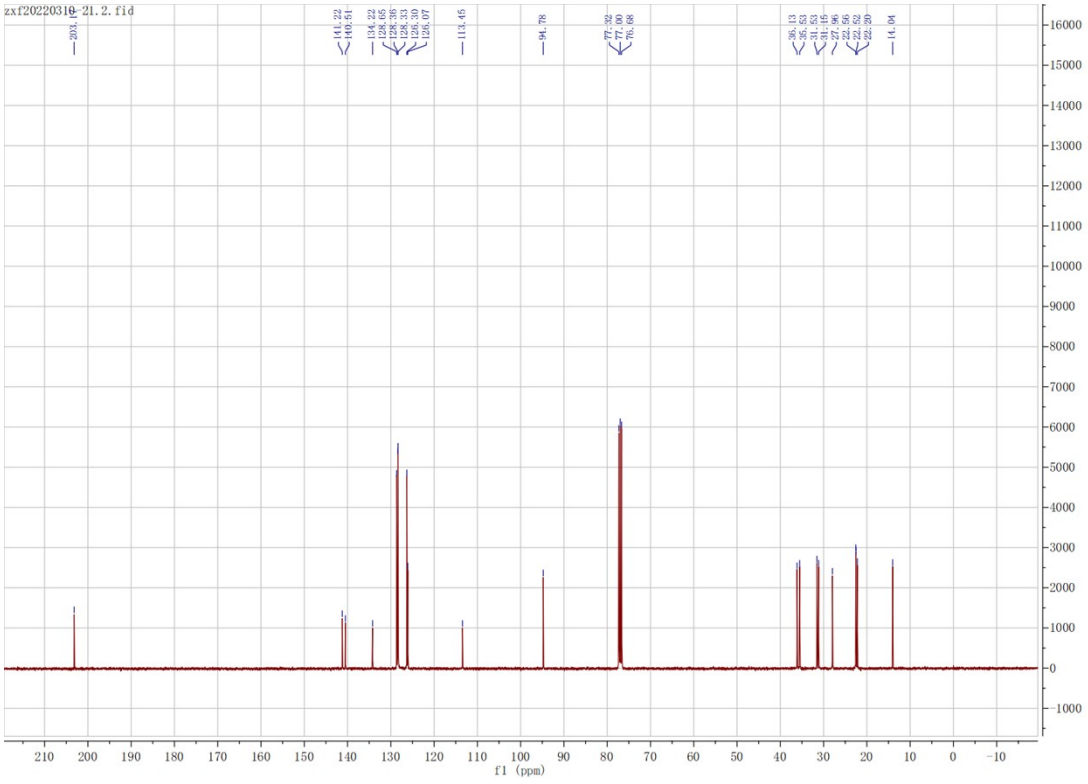


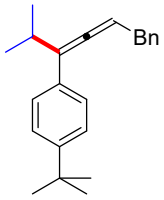





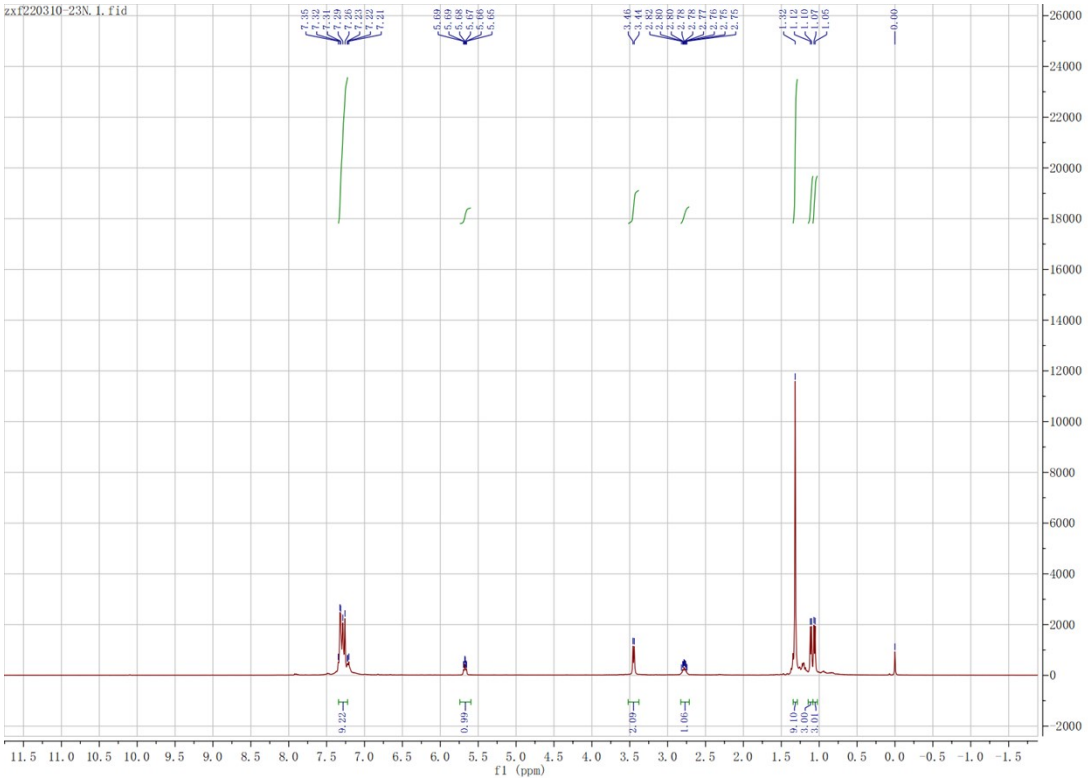

**2ea**, 87%

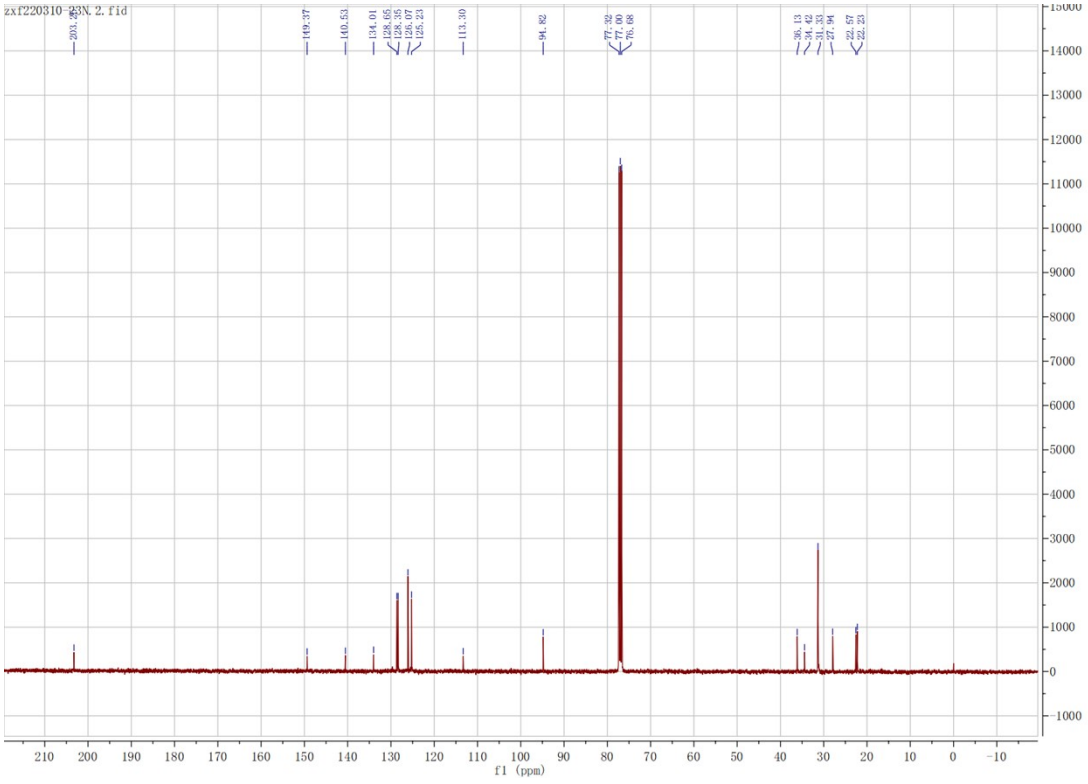


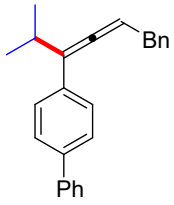





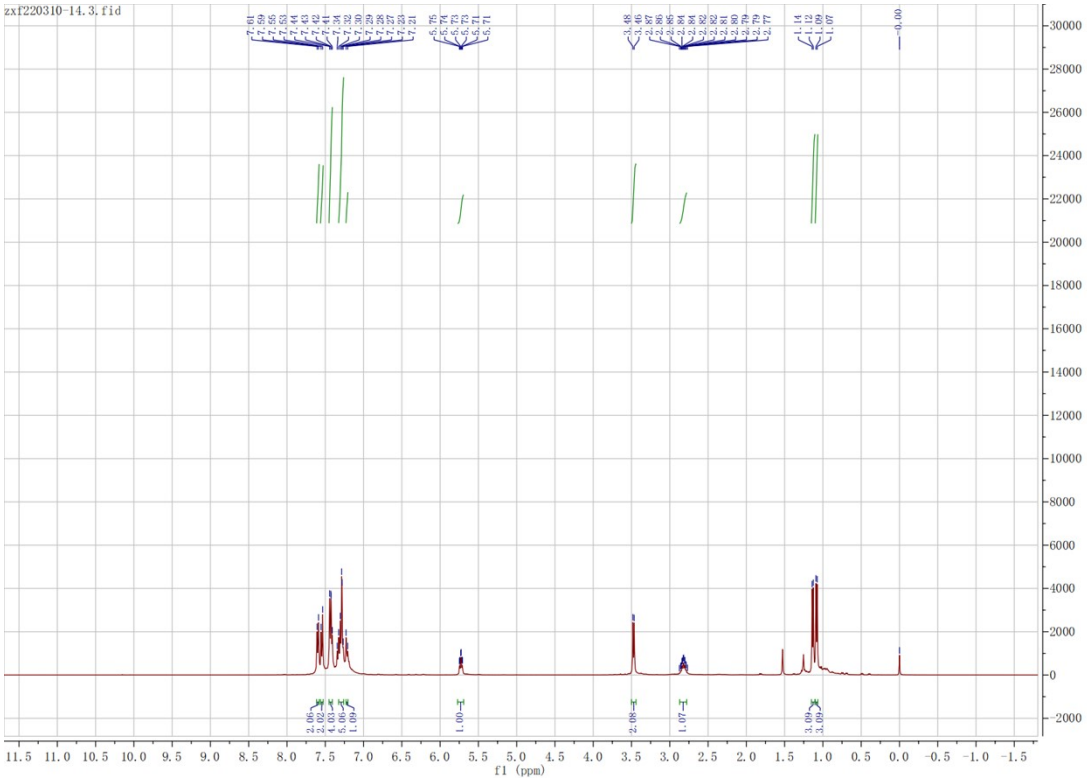

**2fa,** 83%

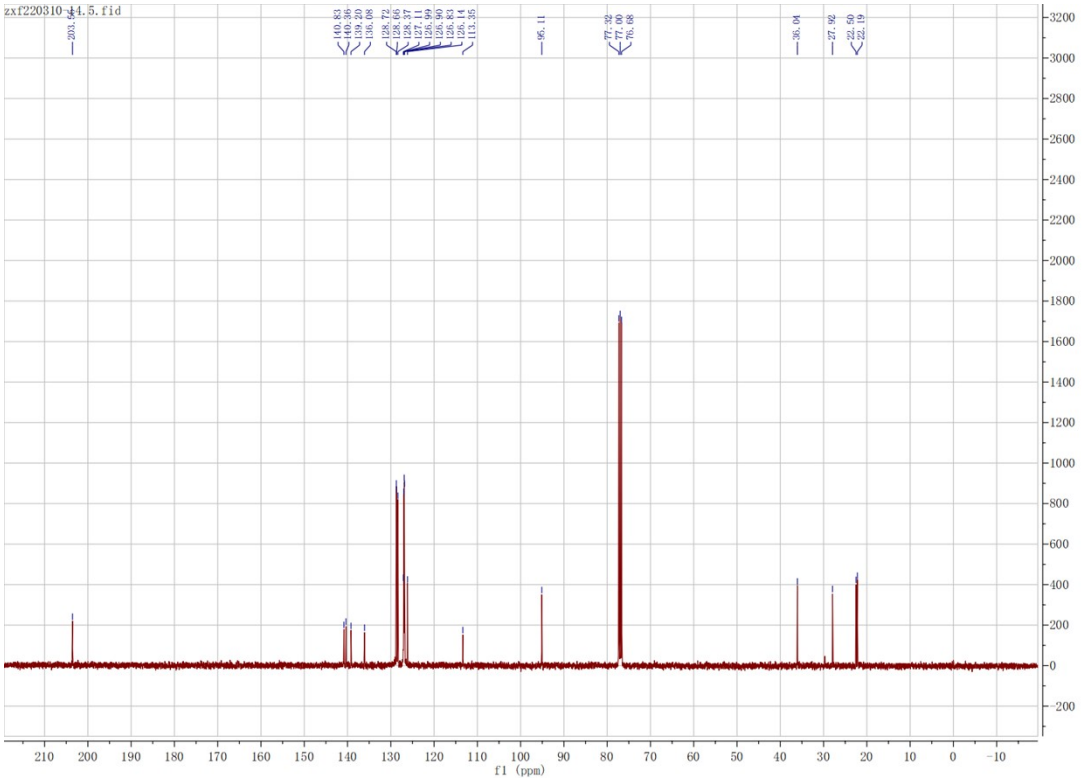


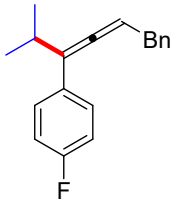





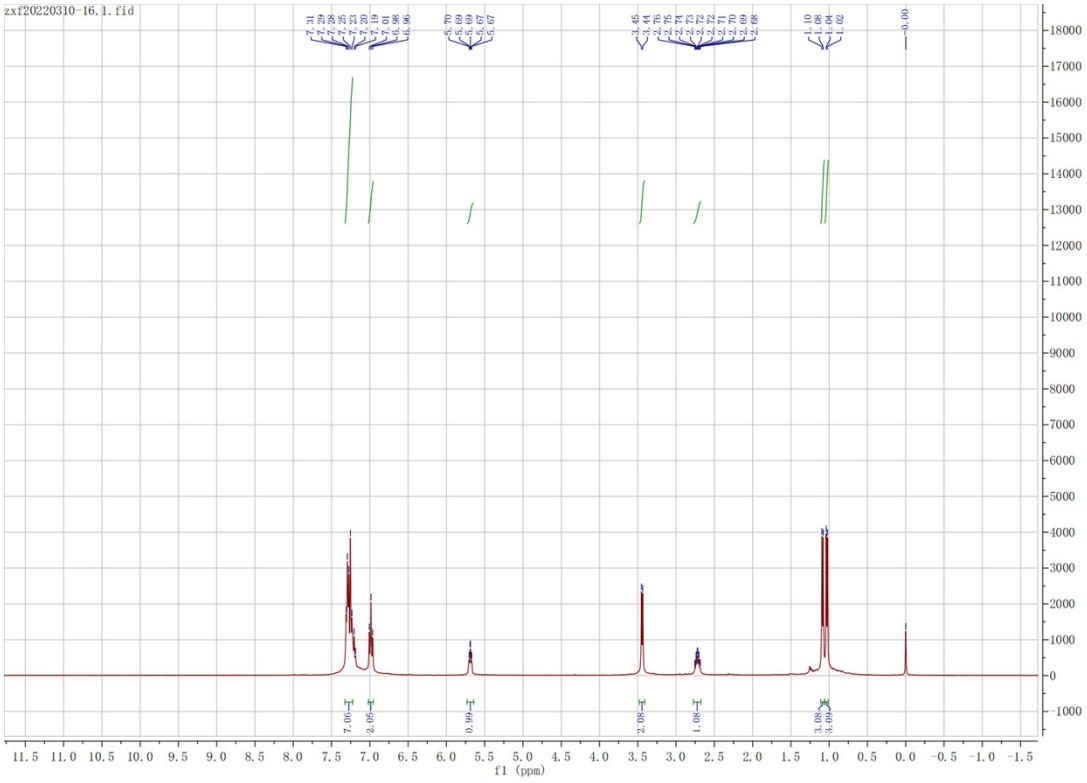

**2ga**, 45%

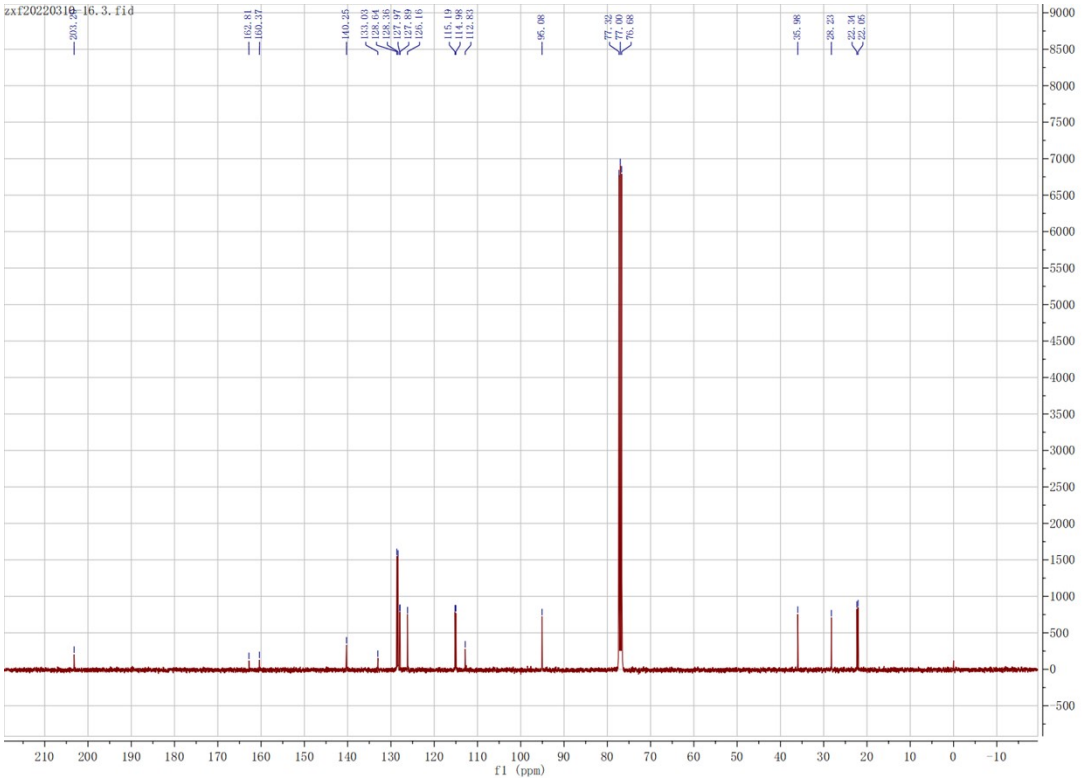


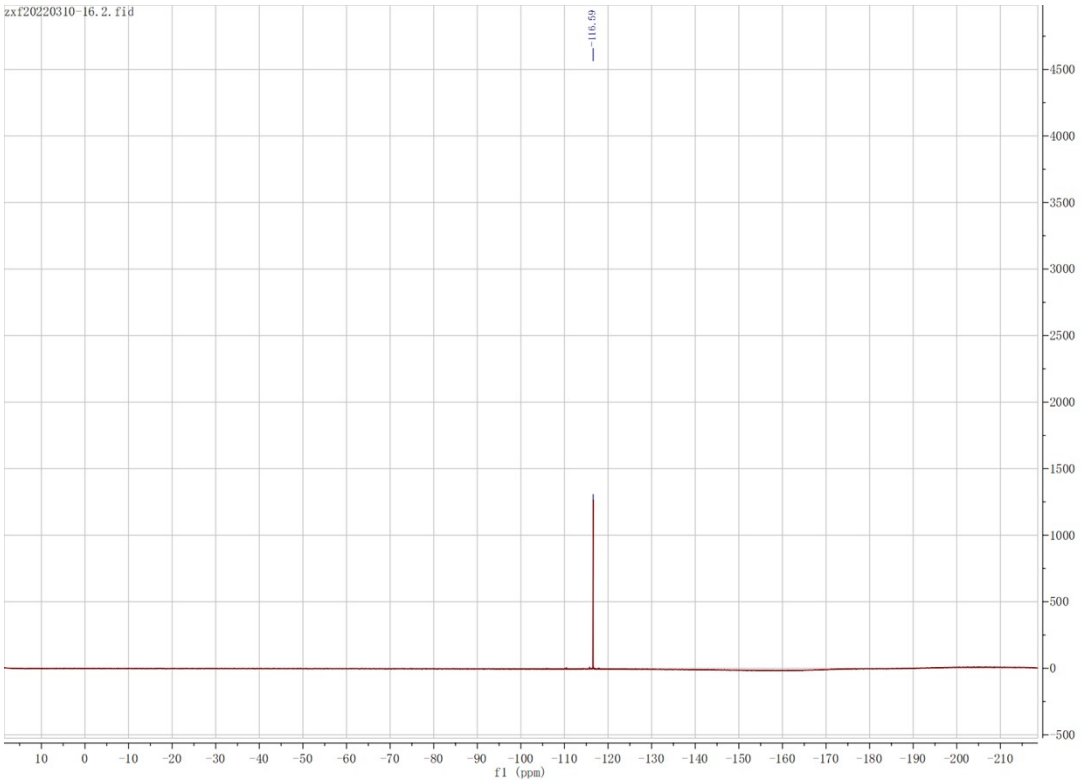



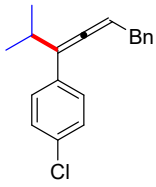



**2ha,** 79%

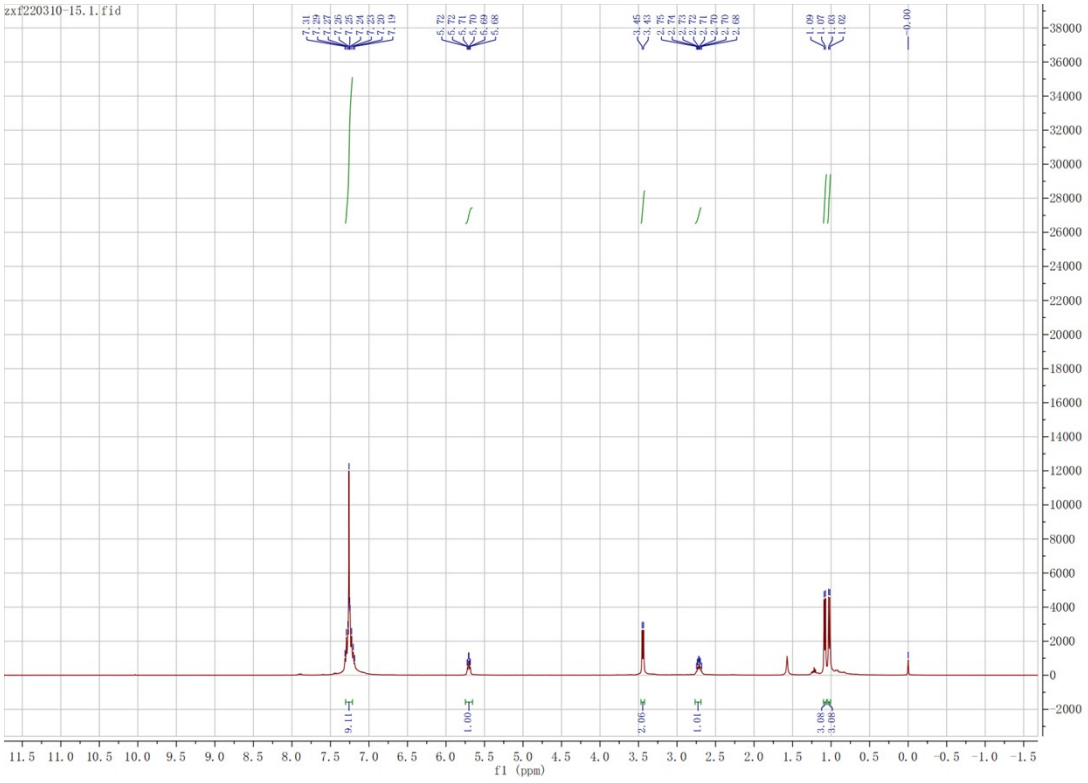


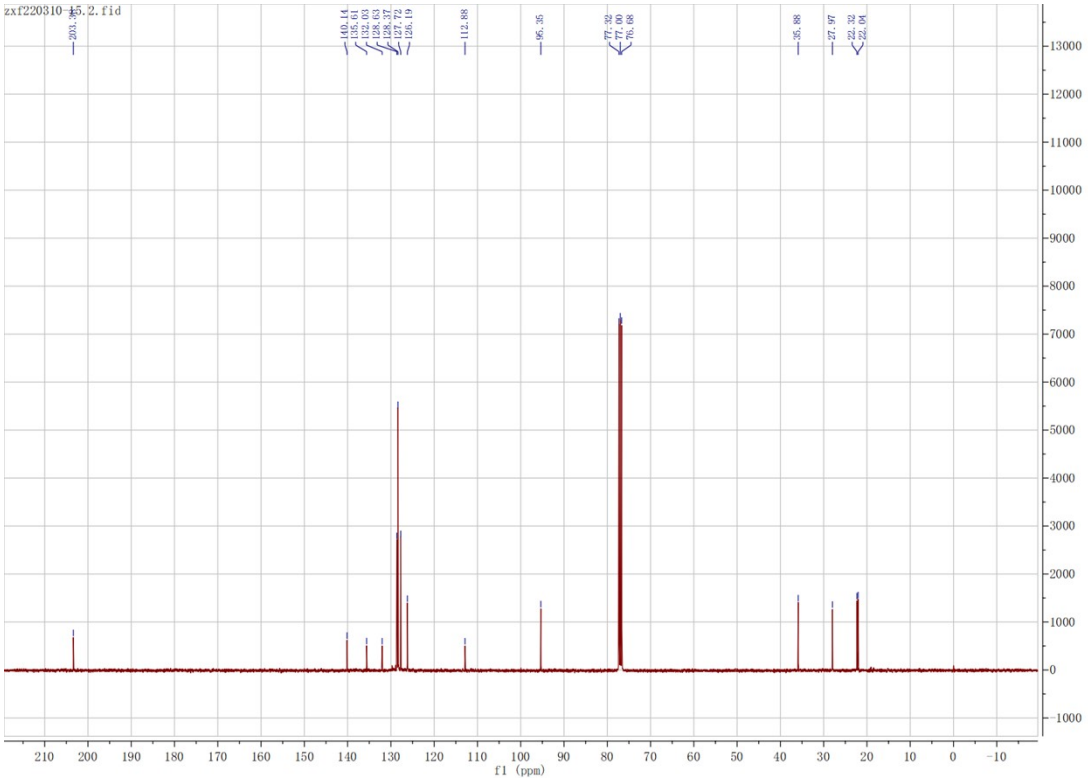



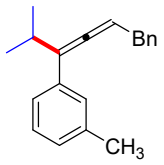

zxf20220310-16.2.fid
-116.59
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)



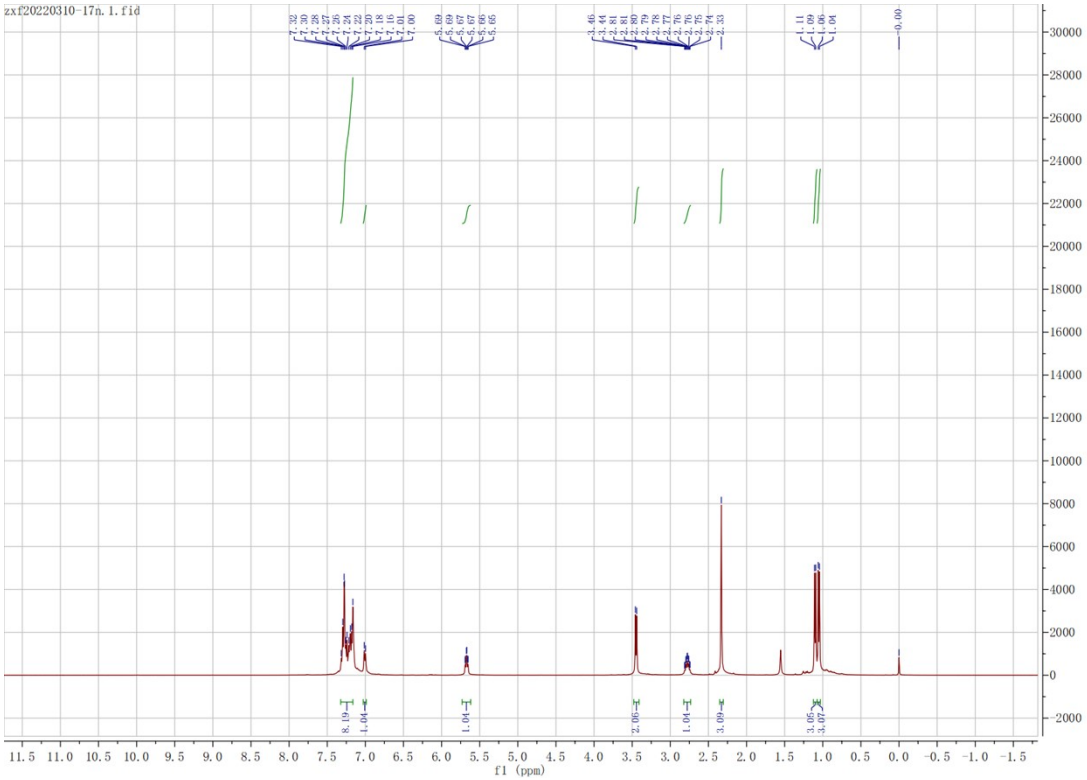

**2ia**, 80%

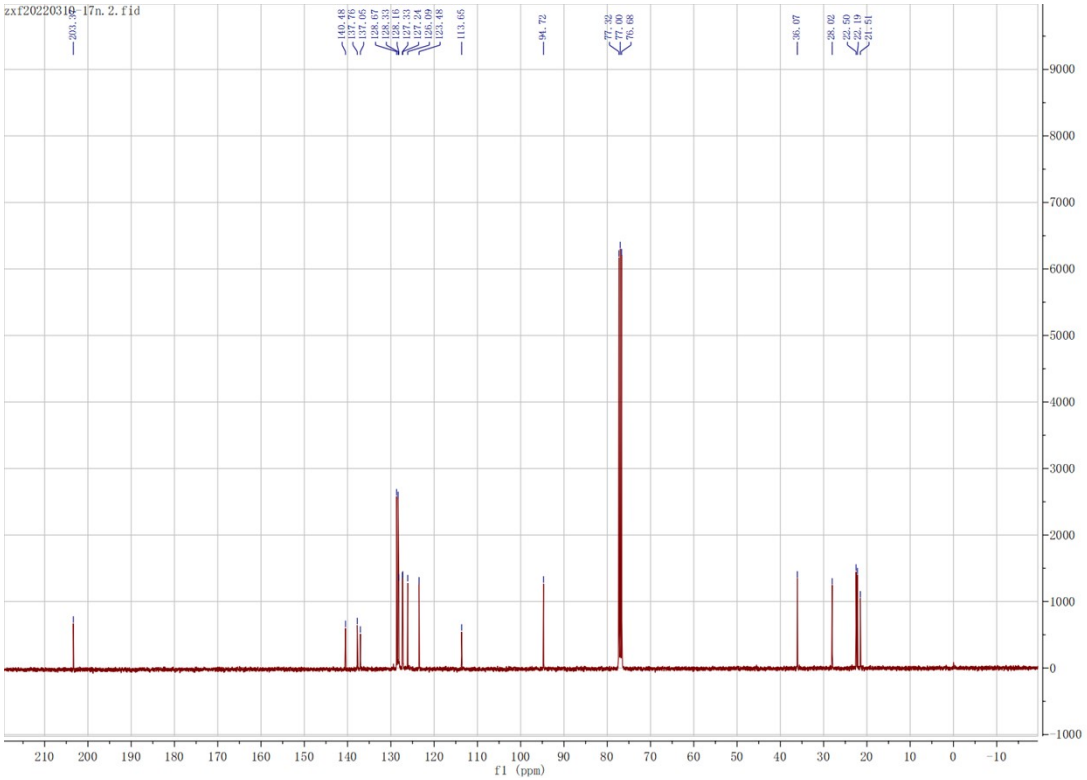


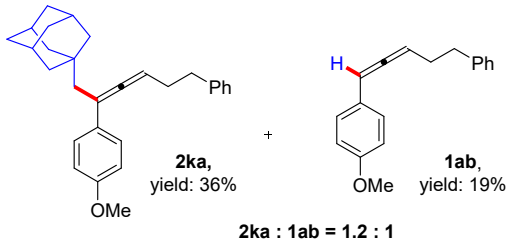




Bn
CH3

**2ja**, 90%

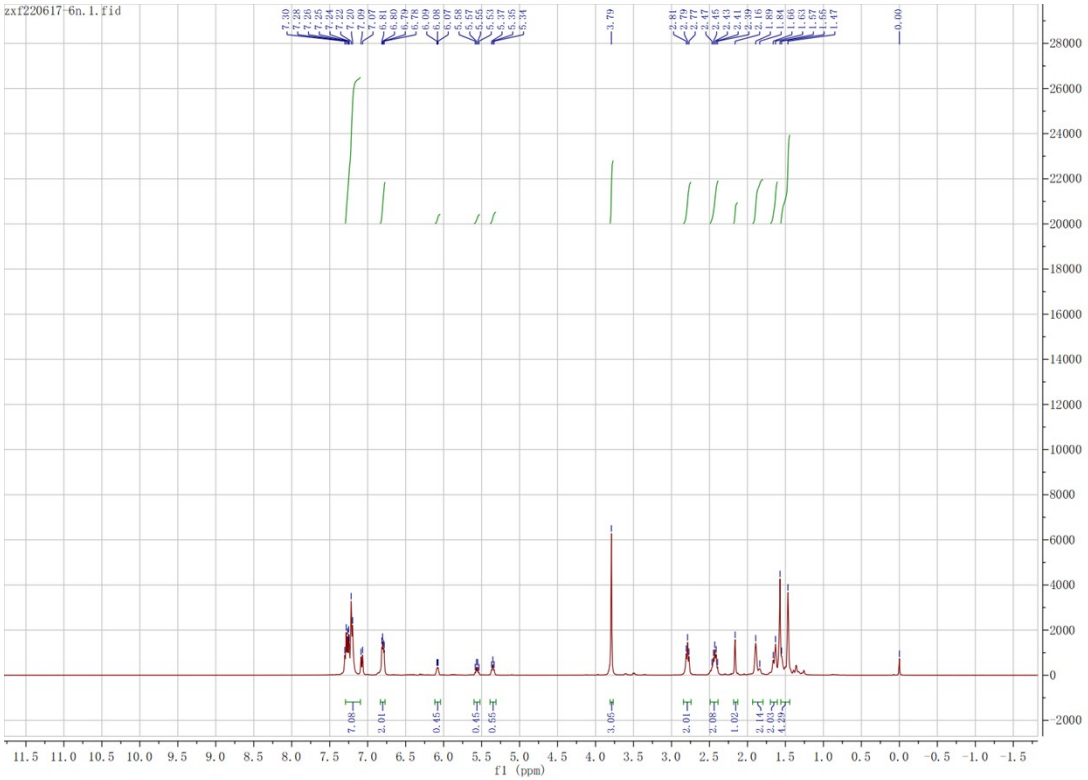

zxf20220310-17n.1.fid
f1 (ppm)

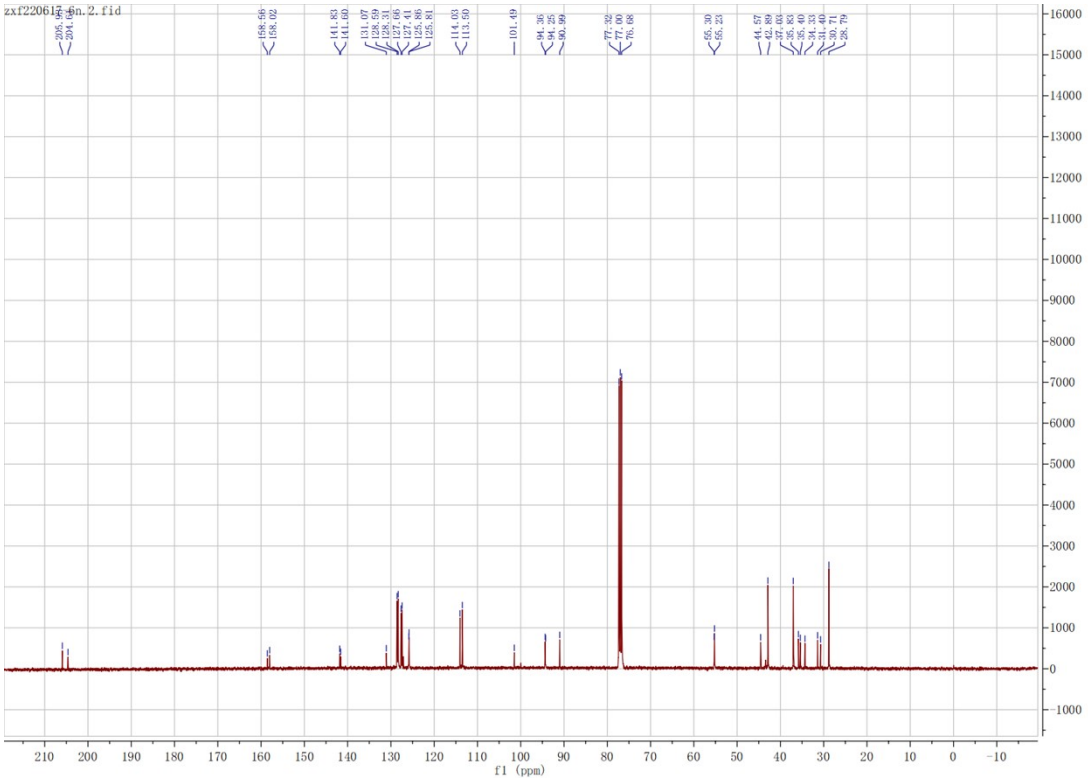

zxf20220310-17n.2.fid
f1 (ppm)

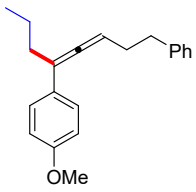



**2ka,** yield: 36% + **1ab**, yield: 19%

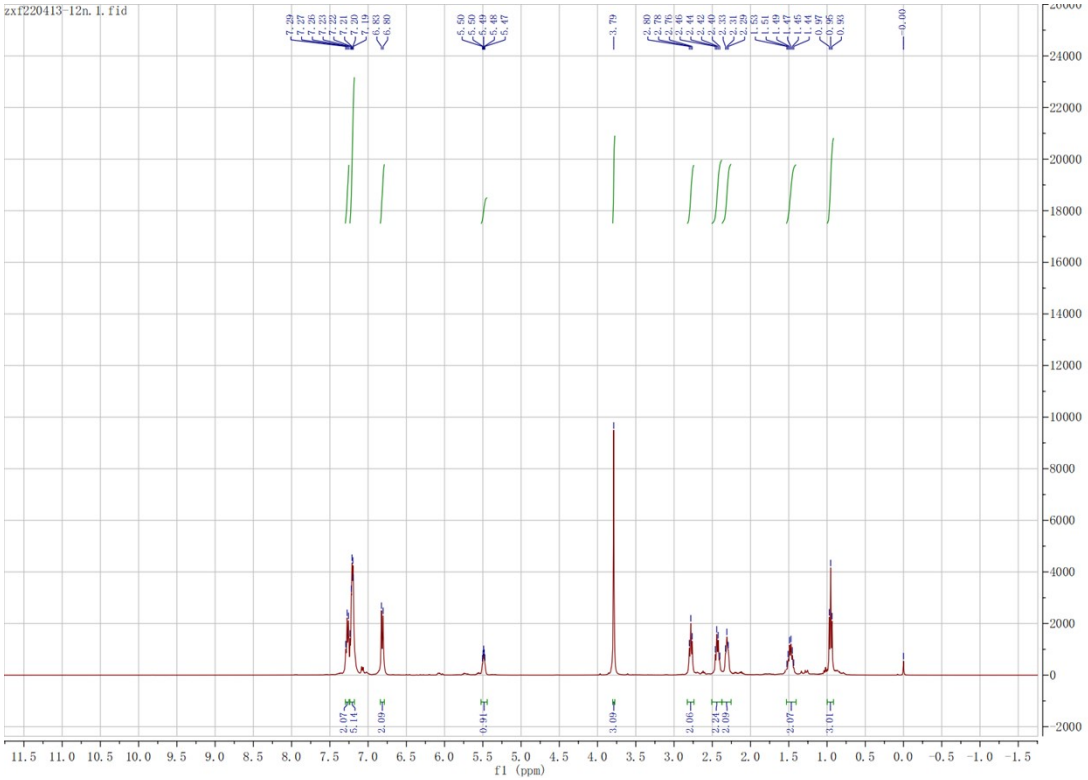
**2ka : 1ab = 1.2 : 1**

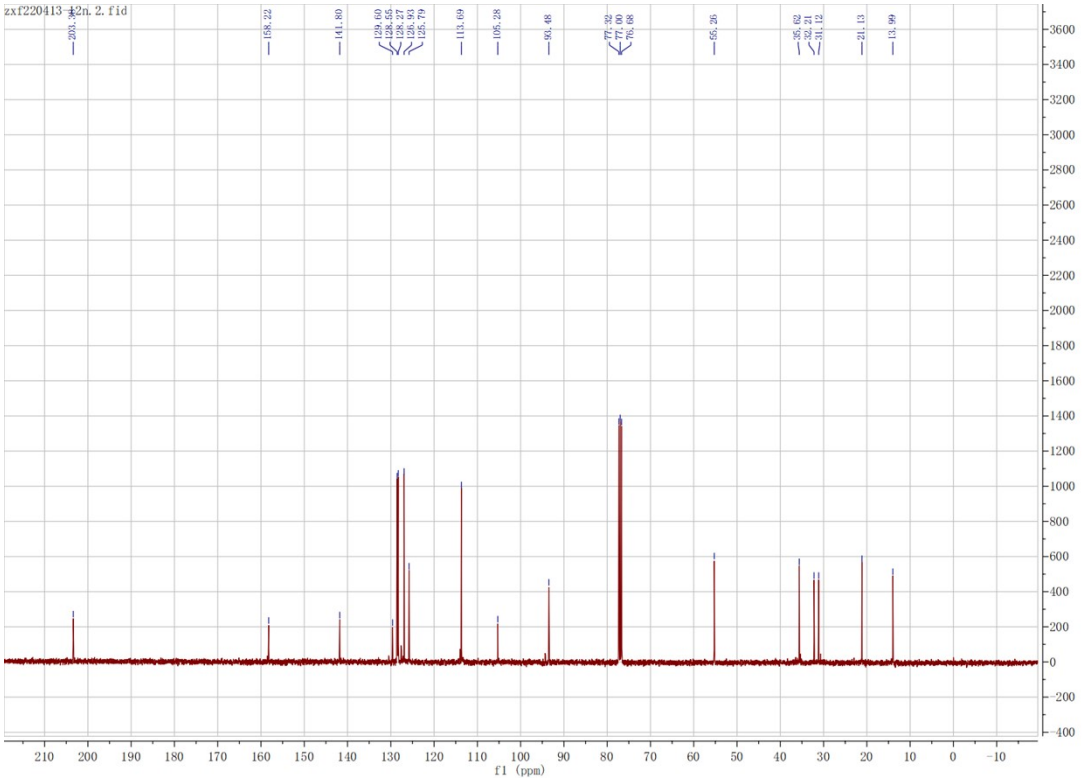


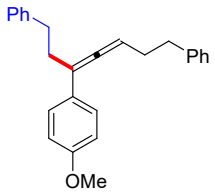





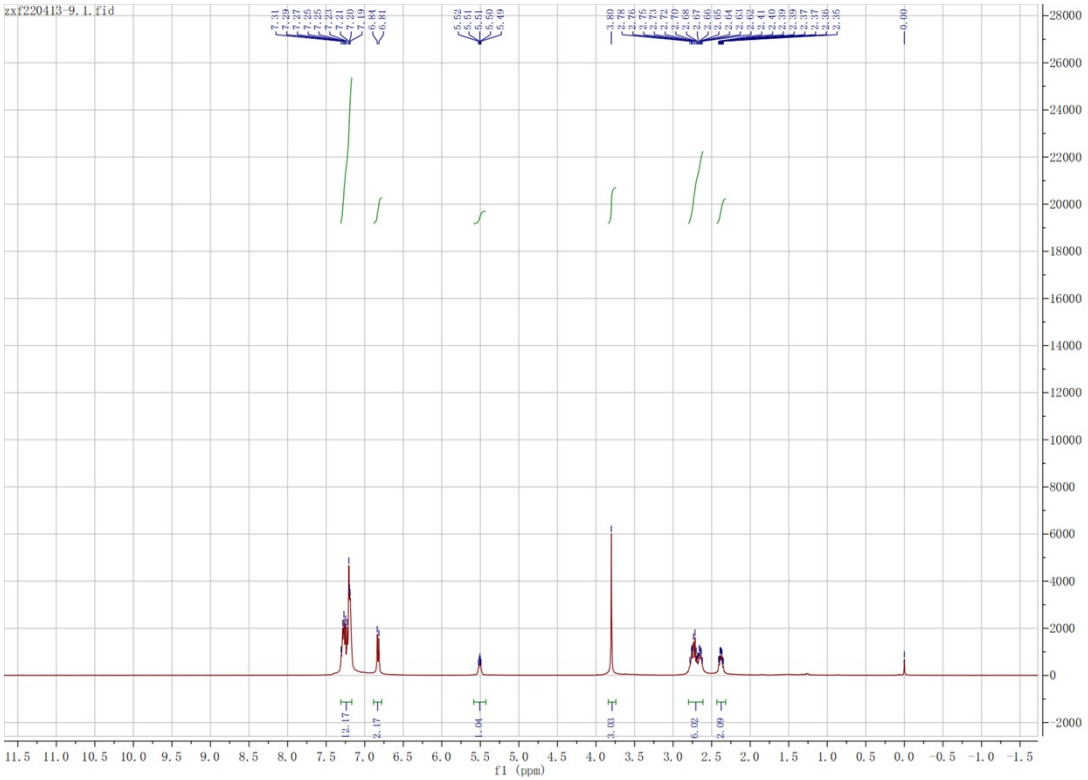

**2la,** 72%

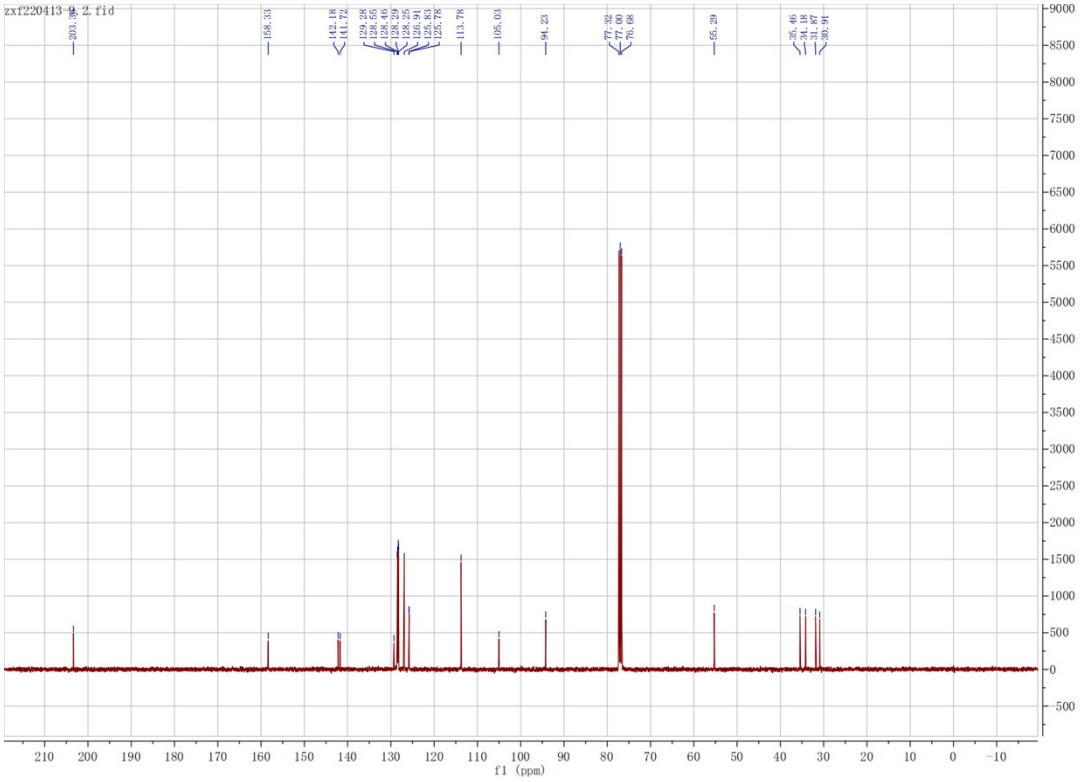


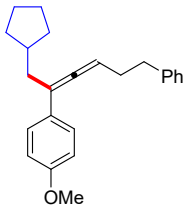





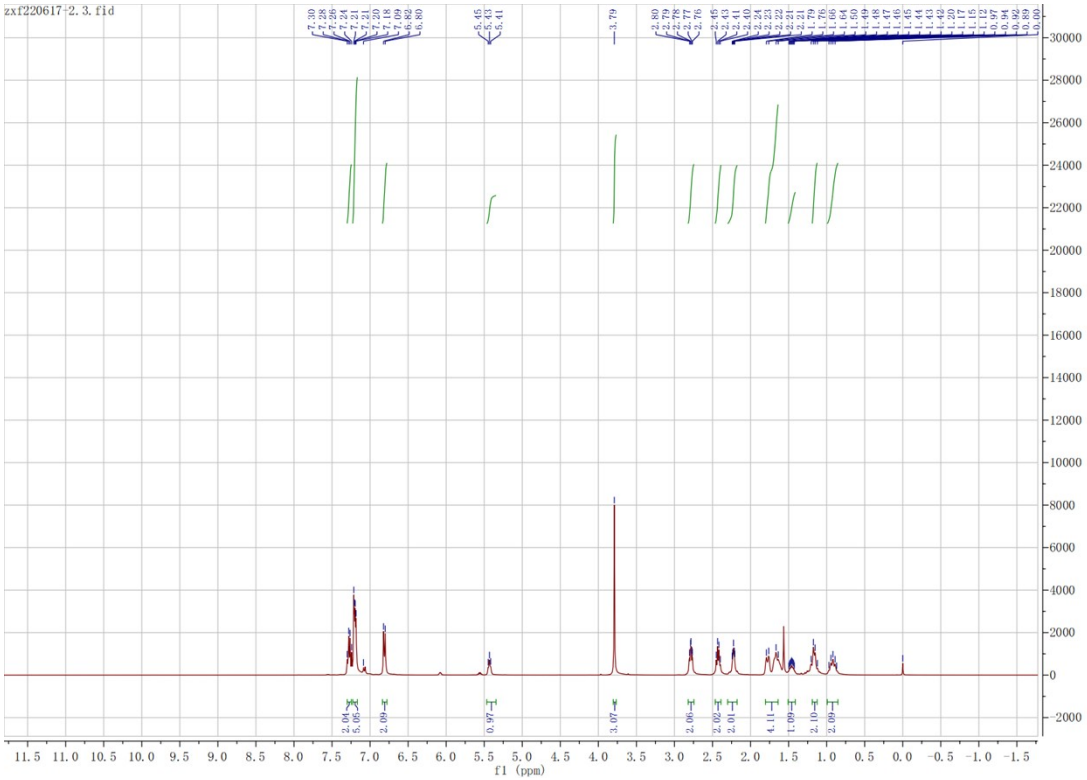

**2ma,** 77%

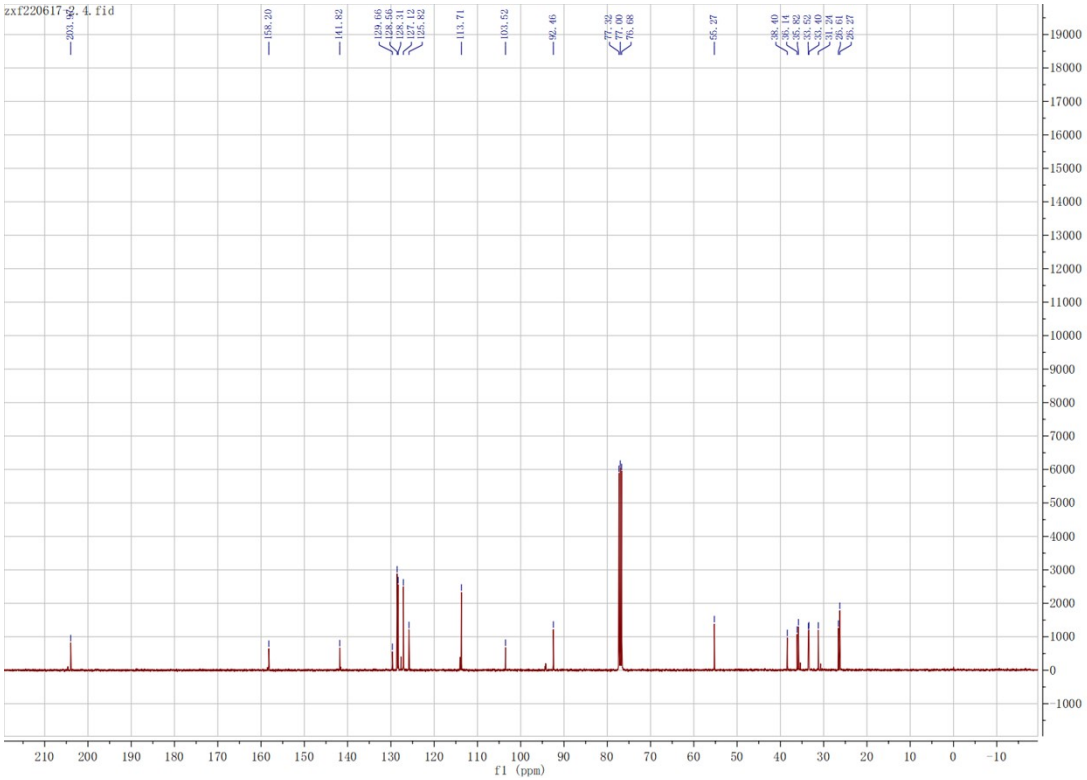


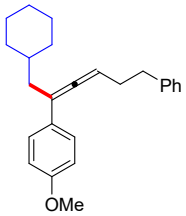





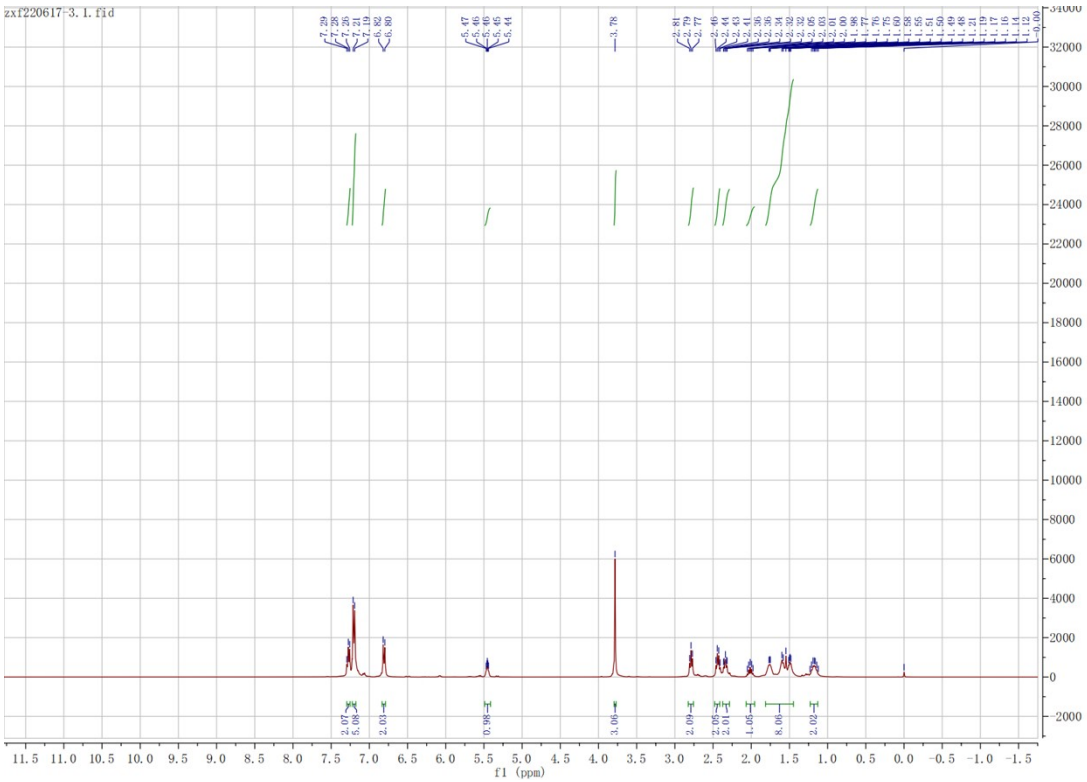

**2na,** 68%

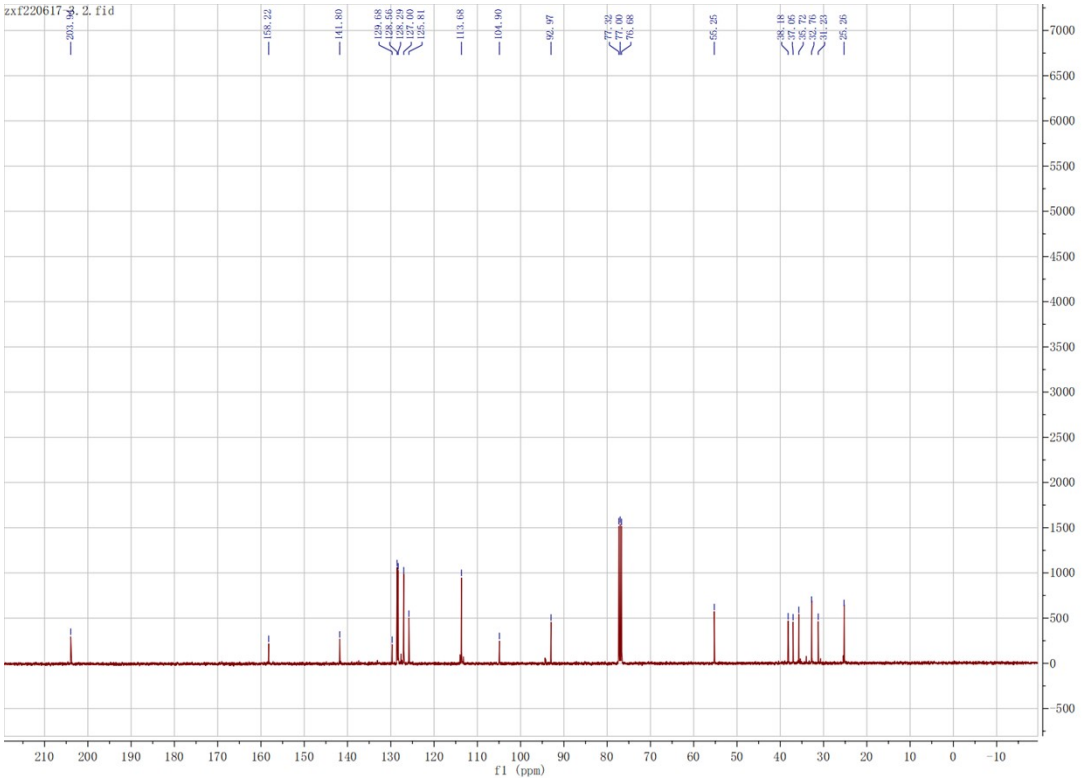


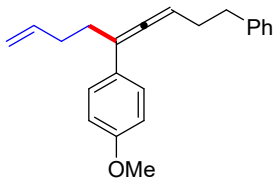





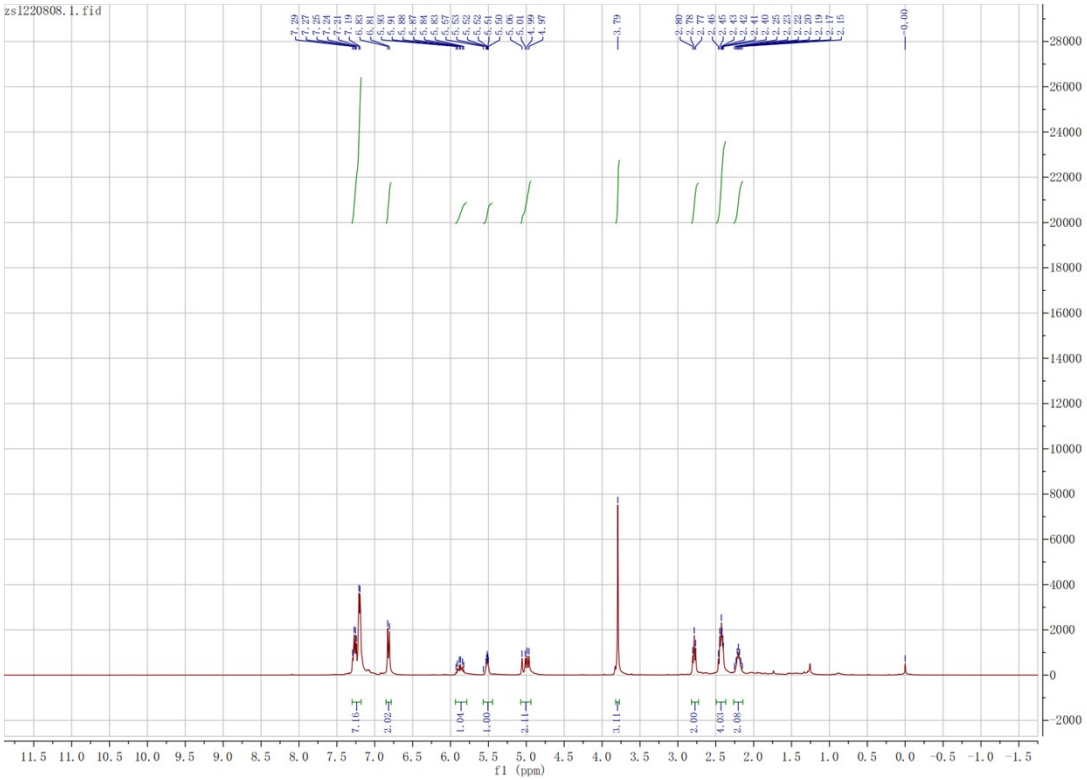

**2oa,** 73%

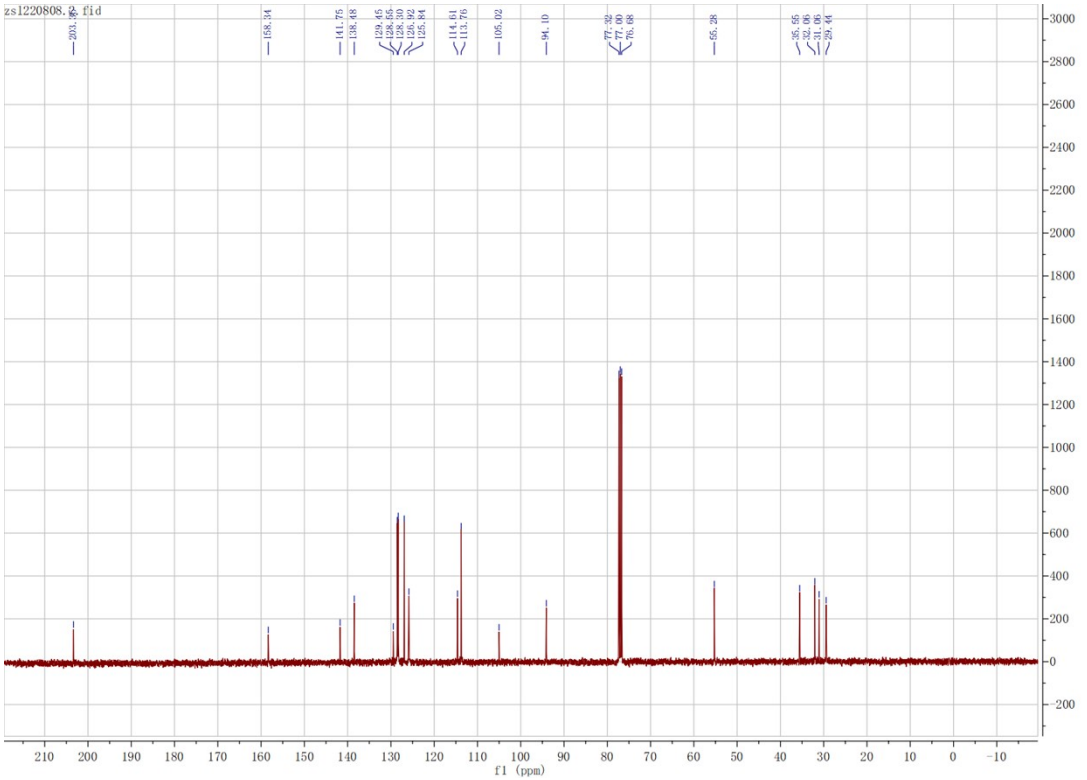


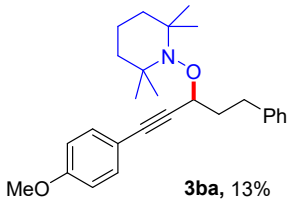





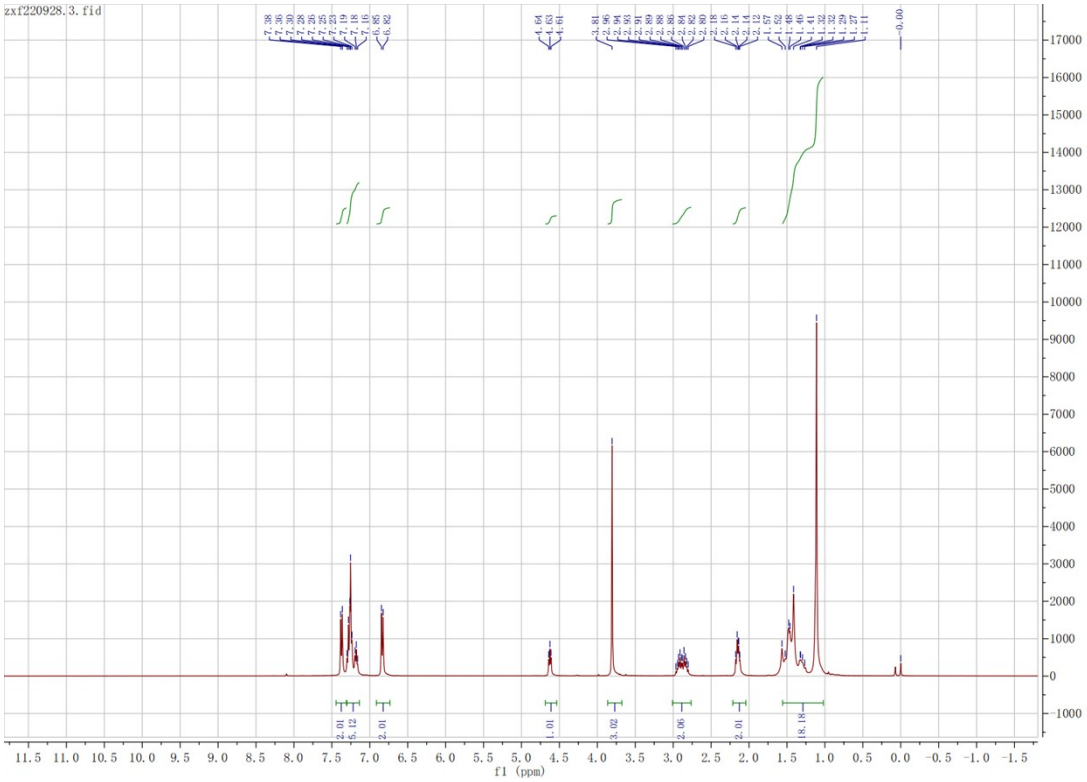

**3aa**, 65%

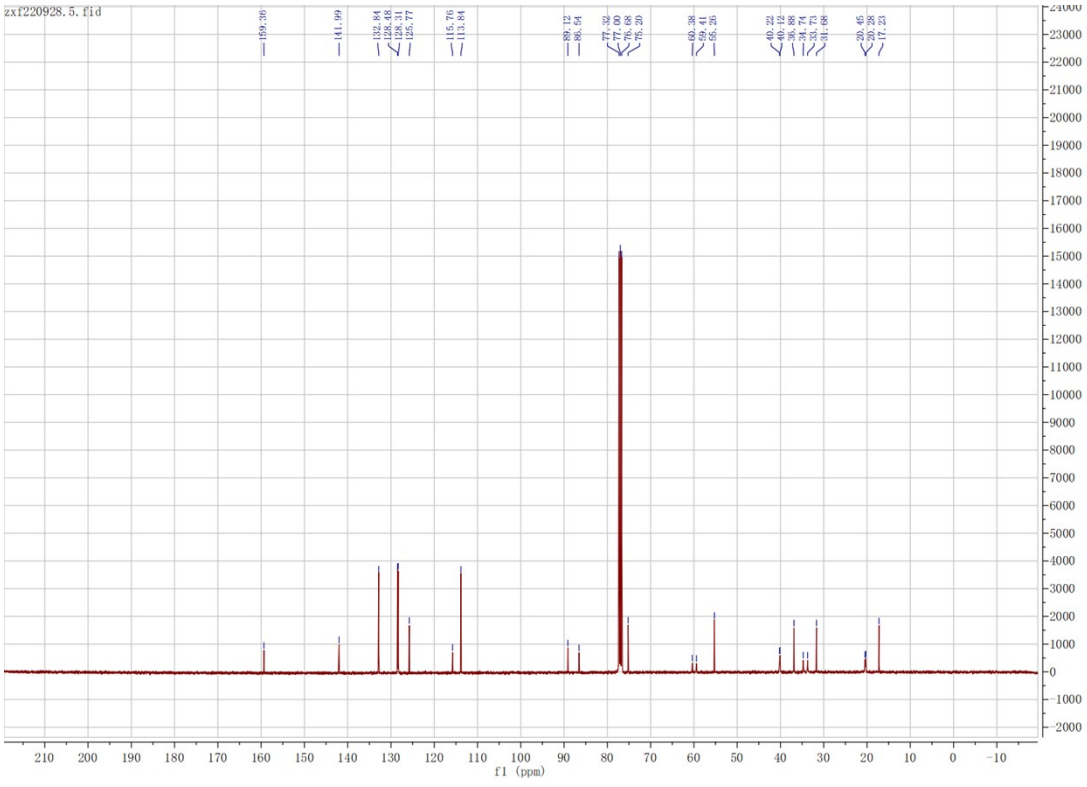


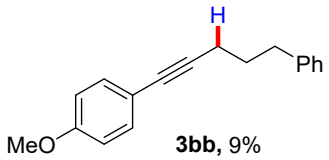






**3ba,** 13%






**3bb,** 9%