Supporting Information

Photoredox/Nickel Dual-Catalyzed Deaminative Cross-Electrophile for Allenylic Alkylation with Non-Activated Alkyl Katritzky Salts

Zhao-Zhao Zhou,*[a$] Xiao-Feng Zhai,[b$] Ke-Jian Xia,*[a] Xian-Rong Song,[b] Haixin Ding,[b] Wan-Fa Tian,[b] Shu-Liang Zhang,[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] *Jiangxi Province Key Laboratory of Organic Functional Molecules; Institute of Organic Chemistry, Jiangxi Science and Technology Normal University, Nanchang, 330013, 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

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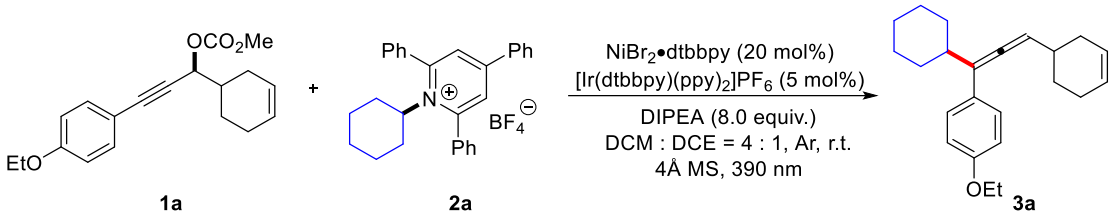
1. General Information and Materials:

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, ^{13}C NMR and ^{19}F NMR spectra were provided. The starting materials were purchased from Sigma-Aldrich, Acros, TCI, Admas, J&K Chemicals, Energy Chemical 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 Photoredox/Nickel Dual-Catalyzed Deaminative Cross-Electrophile for Allenylic Alkylation:



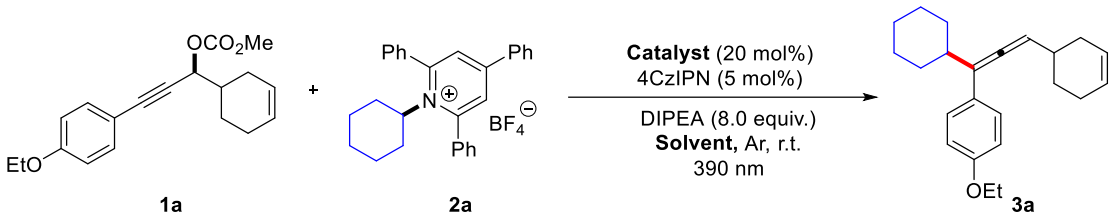
In a 10.0 mL snap vial with Teflon cover and magnetic stirring bar the internal propargylic carbonates **1a** (0.2 mmol), alkyl Katritzky salt **2a** (0.4 mmol, 2.0 equiv), $NiBr_2$·dtbbpy (0.04 mmol, 20 mol %), $[Ir(dtbbpy)(ppy)_2]PF_6$ (0.01 mmol, 5 mol %), DIPEA (1.6 mmol, 8.0 equiv.) and 4A MS (30 mg, 150 g/mol) were filled. After degassing with argon by syringe needle for 5 minutes and dissolving with 1.6 mL DCM and 0.4 ml DCE, 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 alkyl Katritzky salts 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:

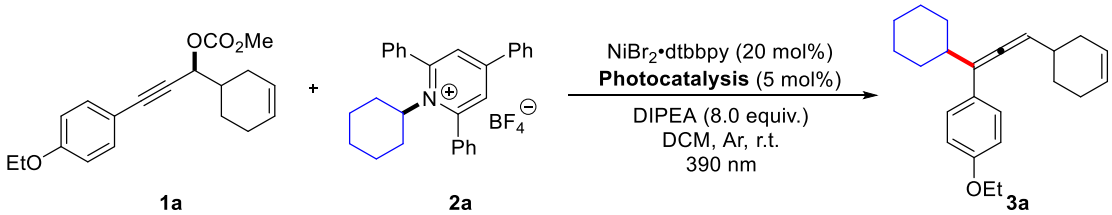


1a **2a** **3a**

Entries	Catalyst (20 mol %)	Ligand	PC (5 mol %)	Reductant (4.0 equiv)	Solvent	Yield (%)[a]
1	$NiBr_2$·dtbbpy	-	4CzIPN	DIPEA	**EA**	0
2	$NiBr_2$·dtbbpy	-	4CzIPN	DIPEA	**DMA**	0
3	$NiBr_2$·dtbbpy	-	4CzIPN	DIPEA	**DCE**	36
4	$NiBr_2$·dtbbpy	-	4CzIPN	DIPEA	**DCM**	53
5	$NiCl_2$·dtbbpy	-	4CzIPN	DIPEA	**DCM**	31
6	$NiBr_2$·dMeObpy	-	4CzIPN	DIPEA	**DCM**	29
7	$CoBr_2$	-	4CzIPN	DIPEA	**DCM**	0
8	$Co(dmgH)_2Cl_2$	-	4CzIPN	DIPEA	**DCM**	0
9	$NiBr_2$·dme	dtbbpy	4CzIPN	DIPEA	**DCM**	trace
10	$NiBr_2$·dme	dMeObpy	4CzIPN	DIPEA	**DCM**	trace

[a.] Isolated yield of **3a**.

b) Screening of PC and light:



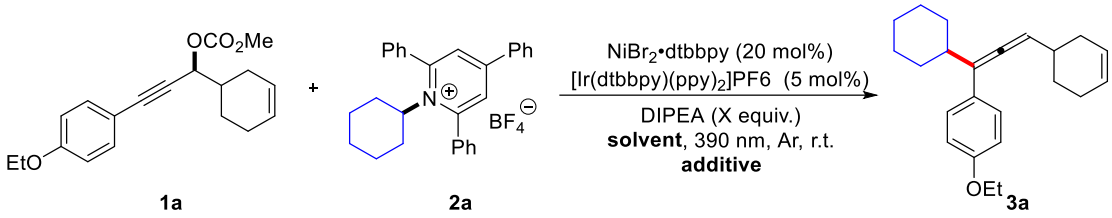
1a **2a** **3a**

Entries	Catalyst (20 mol %)	PC (5 mol %)	Reductant (4.0 equiv)	Solvent	Yield (%)[a]

1	$NiBr_2$·dtbbpy	4CzIPN	DIPEA	DCM	53
2	$NiBr_2$·dtbbpy	4CzIPN	DIPEA	DCM	48[b]
3	$NiBr_2$·dtbbpy	$[Ir(dtbbpy)(ppy)_2]PF_6$	DIPEA	DCM	59
4	$NiBr_2$·dtbbpy	$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$	DIPEA	DCM	41
5	$NiBr_2$·dtbbpy	*fac*-$Ir(ppy)_3$	DIPEA	DCM	0
6	$NiBr_2$·dtbbpy	$Ru(bpy)_3(PF_6)_2$	DIPEA	DCM	0
7	$NiBr_2$·dtbbpy	3CzClIPN	DIPEA	DCM	0

[a.] Isolated yield of **3a**. [b.] Under 440 nm Kessil LEDs.

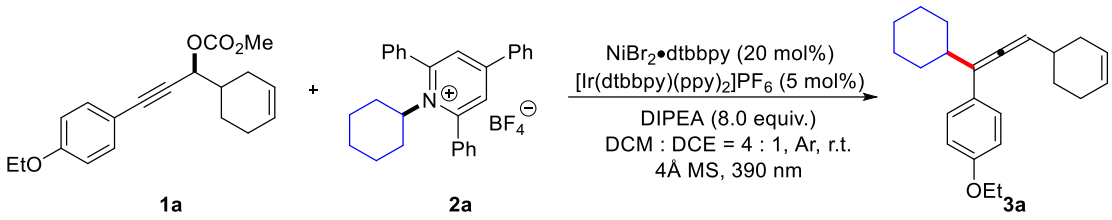
c) Screening of reductant and additive:



Entries	Catalyst (20 mol %)	PC (5 mol %)	Reductant	Solvent	Yield (%)[a]
1	$NiBr_2$·dtbbpy	$[Ir(dtbbpy)(ppy)_2]PF_6$	Et_3N (4.0 eq.)	DCM	23
2	$NiBr_2$·dtbbpy	$[Ir(dtbbpy)(ppy)_2]PF_6$	HE (4.0 eq.)	DCM	trace
3	$NiBr_2$·dtbbpy	$[Ir(dtbbpy)(ppy)_2]PF_6$	DIPEA (8.0 eq.)	DCM	63
4	$NiBr_2$·dtbbpy	$[Ir(dtbbpy)(ppy)_2]PF_6$	DIPEA (8.0 eq.)	DCM:DCE=1:1	57
5	$NiBr_2$·dtbbpy	$[Ir(dtbbpy)(ppy)_2]PF_6$	DIPEA (8.0 eq.)	DCM:DCE=2:1	61
6	$NiBr_2$·dtbbpy	$[Ir(dtbbpy)(ppy)_2]PF_6$	DIPEA (8.0 eq.)	DCM:DCE=4:1	71
7	$NiBr_2$·dtbbpy	$[Ir(dtbbpy)(ppy)_2]PF_6$	DIPEA (8.0 eq.)	DCM:DCE=4:1	79[b]
8	$NiBr_2$·dtbbpy	4CzIPN	DIPEA (8.0 eq.)	DCM:DCE=4:1	69[b]

[a.] Isolated yield of **3a**. [b.] With 4Å MS (30 mg, 150 g/mol).

d) Control experiment:

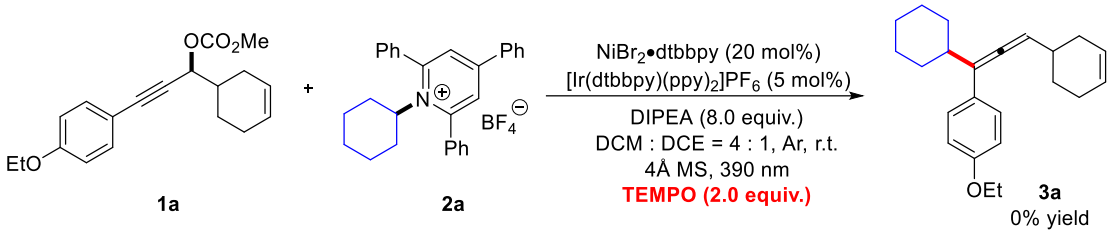


Entries	Catalyst (20 mol %)	PC (5 mol %)	Reductant	Solvent	Yield (%)[a]
1	-	$[Ir(dtbbpy)(ppy)_2]PF_6$	DIPEA (8.0 eq.)	DCM:DCE=4:1	0
2	$NiBr_2$·dtbbpy	-	DIPEA (8.0 eq.)	DCM:DCE=4:1	trace
3	$NiBr_2$·dtbbpy	$[Ir(dtbbpy)(ppy)_2]PF_6$	DIPEA (8.0 eq.)	DCM:DCE=4:1	0[b]

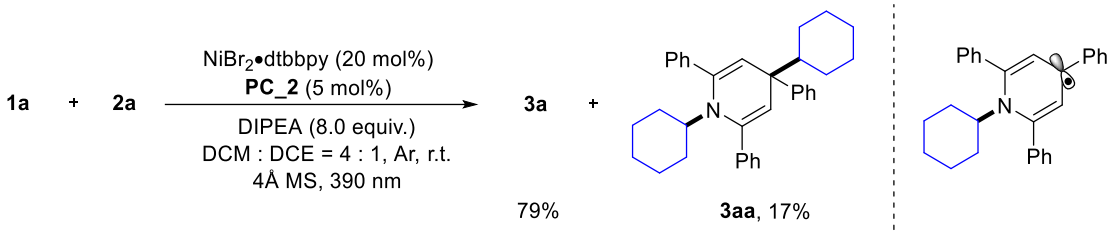
[a.] Isolated yield of **3a**. [b.] With no light

5. Mechanism Characterization:

a) Radical capture experiment:



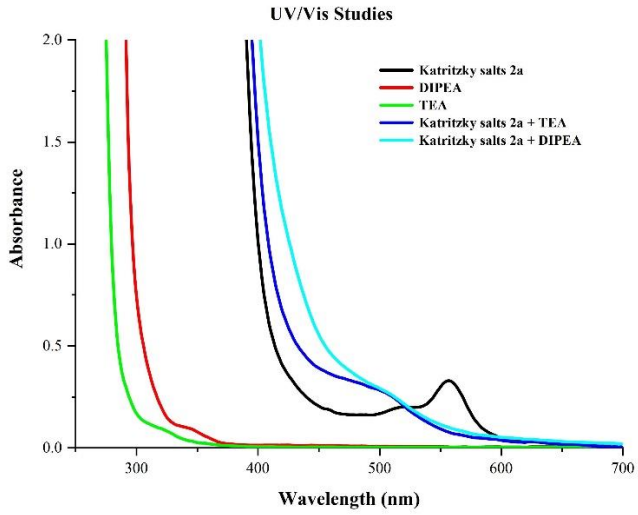
Radical capture experiment with TEMPO revealed the involvement of a radical intermediate during the reaction process with the complete suppression of the product **3a**.

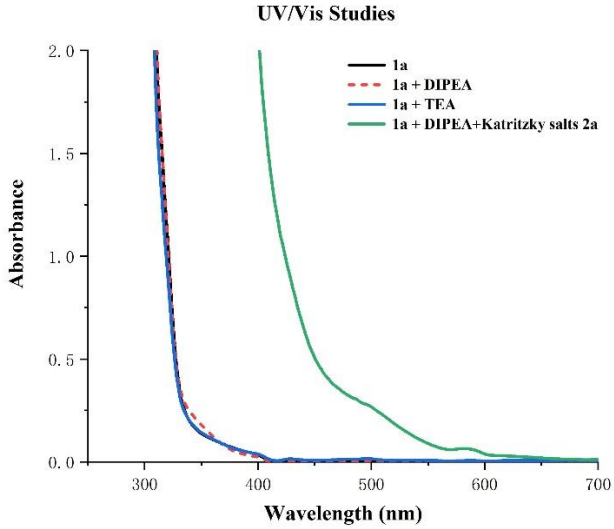


The isolated 17% yield byproduct **3aa** indicates the potential radical-radical coupling between dihydropyridine radical intermediate and alkyl radical.

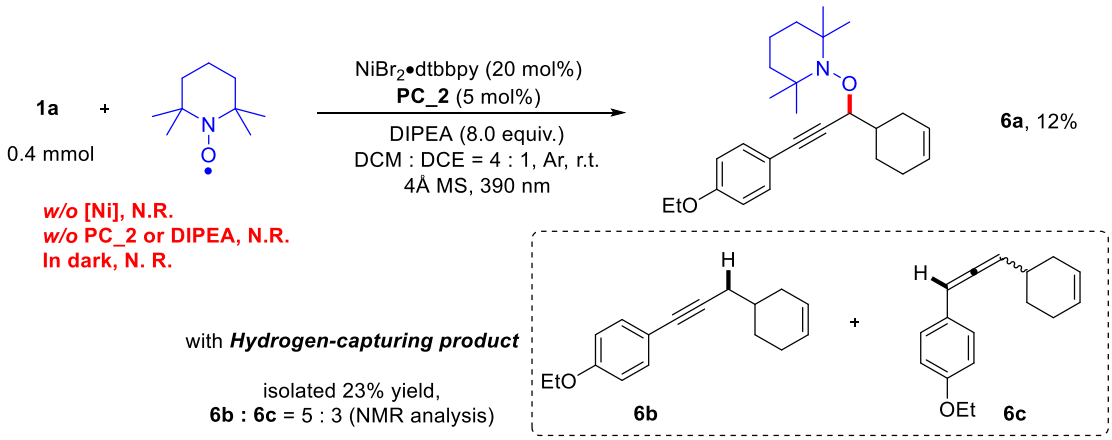
b) UV/Vis absorption spectroscopy:

According to the result of UV/Vis absorption spectroscopy, the intermolecular EDA complex was generated by the interaction of alkyl Katriitzky salt **2a** with DIPEA or TEA, which could result in the formation of alkyl radical from **2a** directly. Moreover, from the result of UV/Vis absorption spectroscopy, DIPEA or TEA exhibited no influence on propargylic carbonate **1a**.



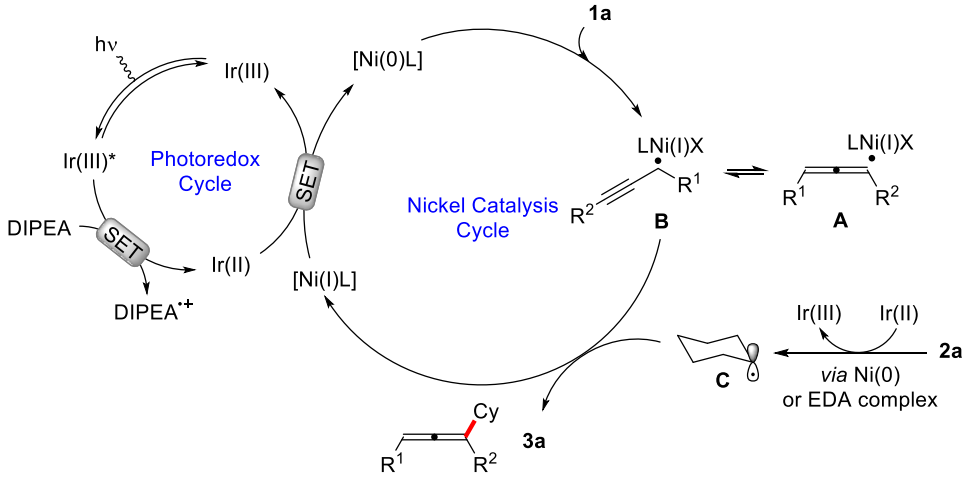


c) Confirmation experiments for radical from propargylic carbonates 1a:



Propargyl radical capture product **6a** and two kinds of hydrogen-capturing product **6b**, **6c** was isolated only in the presence of both nickel catalyst and photocatalysis with DIPEA, which confirmed the involvement of hybrid propargyl-Ni(I) or allenyl-Ni(I) species.

d) Plausible mechanism:



A hypothetical mechanism for this regioselective cross-electrophile allenylic alkylation was proposed here. With irradiation by 390 nm purple light, the excited-state Ir(III)* complex induced an SET process with DIPEA through a reductive quenching cycle, leading to the formation of reduced state Ir(II) complex. Then, low-valence nickel species Ni(0) underwent a single electron oxidation addition with **1a** to generate a hybrid allenyl-Ni(I) intermediate, namely allenyl radical **A**. Meanwhile, reduction of Katritzky salt **2a** ($E_{1/2}$ = -0.93 V vs SCE) by low-valence Ir(II) ($E_{1/2}$ = -1.51 V vs SCE) generates alkyl radical **C**, which then captured allenyl species **A** to generate the desired radical-radical coupling product **3a** and Ni(I) species. Fianlly, a complete co-catalytic system is achieved with reduction of Ni(I) complex to Ni(0) by the low-valence Ir(II) complex. Notably, despite photocatalyst play an indispensable role in reactions, the formation of alkyl radical **C** from low-valent nickel intermediate or EDA complex with DIPEA could not be ruled out. Meanwhile, though the reductive reaction atmosphere, the mechanism processing reductive elimination from Ni(III) species also could not be fully ruled out.

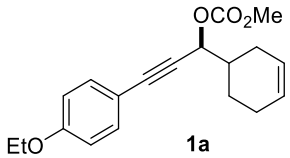
6. References:

[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,** 6918-6921. (b) Y. Miyazaki, B. Zhou, H. Tsuji and M. Kawatsura, *Org. Lett.* 2020, **22,** 2049-2053. (c) P. Wu, M. Jia, W. Lin and S. Ma, *Org. Lett.* 2018, **20,** 554-557. (d) C. R. Reddy, S. Z. Mohammed and P. Kumaraswamya, *Org. Biomol. Chem.* 2015, **13,** 8310-8321.

[2] (a) Z.-Z. Zhou, R.-Q. Jiao, K. Yang, X.-M. Chen and Y.-M. Liang, *Chem. Commun.* 2020, **56,** 12957-12960. (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,** 9390-9393. (c) Z.-Z. Zhou, X.-F. Zhai, S.-L. Zhang, K.-J. Xia, H. Ding, X.-R. Song, W.-F. Tian, Y.-M. Liang and Q. Xiao, *Org. Chem. Front.* 2023, **10,** 298-303.

[3] (a) C. H. Basch, J. Liao, J. Xu, J. J. Piane and M. P. Watson, *J. Am. Chem. Soc.* 2017, **139,** 5313-5316. (b) J. Xu, J. C. Twitty and M. P. Watson, *Org. Lett.* 2021, **23,** 6242-6245. (c) J. Liao, W. Guan, B. P. Boscoe, J. W. Tucker, J. W. Tomlin, M. R. Garnsey and M. P. Watson, *Org. Lett.* 2018, **20,** 3030-3033.

7. Characterization Data of Substrates 1a-1b, 4a-4l, 4s:



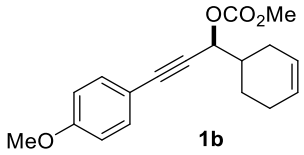
1a

1a: colorless oil; Eluent: *n*-hexane/EtOAc = 50/1;

^{1}H NMR (400 MHz $CDCl_3$, δ ppm): 1.36-1.39 (t, *J* = 8.0 Hz, 3H), 1.45-1.61 (m, 1H), 1.88-2.11 (m, 5H), 2.19-2.27 (t, *J* = 16.0 Hz, 1H), 3.80 (s, 3H), 3.95-4.00 (dd, J_1 = 8.0 Hz; J_2 = 16.0 Hz, 2H), 5.37-5.39 (d, *J* = 8.0 Hz, 1H), 5.68 (s, 2H), 6.78-6.80 (d, *J* = 8.0 Hz, 2H), 7.35-7.37 (d, *J* = 8.0 Hz, 2H);

^{13}C NMR (100 MHz, $CDCl_3$, δ ppm):14.4, 23.9, 24.3, 24.5, 24.6, 26.7, 27.0, 38.1, 38.2, 54.6, 63.2, 72.2, 72.3, 82.9, 83.0, 88.7, 86.8, 113.8, 114.1, 125.1, 125.3, 126.6, 126.8, 133.2, 155.0, 159.1;

HRMS (ESI) calcd for $C_{19}H_{22}O_4$ $[M+H]^+$ m/z 315.1591, found 315.1587.



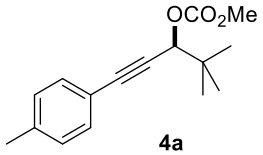
1b

1b: colorless oil; Eluent: *n*-hexane/EtOAc = 50/1;

^{1}H NMR (400 MHz $CDCl_3$, δ ppm): 1.45-1.58 (m, 1H), 1.88-2.24 (m, 6H), 3.77-3.80 (d, *J* = 12.0 Hz, 6H), 5.37-5.39 (t, *J* = 4.0 Hz, 1H), 5.69 (s, 2H), 6.30-6.32 (d, *J* = 8.0 Hz, 2H), 7.36-7.38 (d, *J* = 8.0 Hz, 2H)

^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 23.4, 24.4, 24.5, 24.6, 26.7, 27.1, 38.1, 38.3, 54.7, 55.3, 72.3, 72.4, 76.7, 77.0, 77.3, 83.0, 83.1, 86.7, 86.8, 113.7, 114.0, 125.2, 125.4, 126.7, 126.8, 133.2, 155.1, 159.8.

HRMS (ESI) calcd for $C_{18}H_{20}O_4$ $[M+H]^+$ m/z 301.1440, found 301.1439.



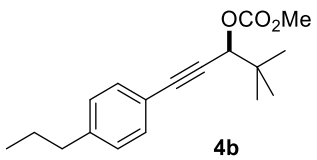
4a

4a: colorless oil; Eluent: *n*-hexane/EtOAc = 50/1;

^{1}H NMR (400 MHz $CDCl_3$, δ ppm): 1.09 (s, 9H), 2.31 (s, 3H), 3.79 (s, 3H), 5.18 (s, 1H), 7.07-7.09 (d, *J* = 8.0 Hz, 2H), 7.31-7.33 (d, *J* = 8.0 Hz, 2H);

^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 21.2, 25.4, 35.5, 54.6, 76.6, 84.0, 86.6, 119.1, 128.8, 131.6, 138.5, 155.2;

HRMS (ESI) calcd for $C_{16}H_{20}O_3$ $[M+H]^+$ m/z 261.1485, found 261.1479.



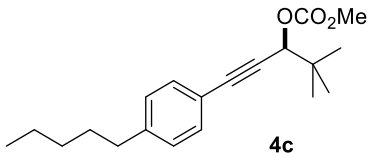
4b

4b: colorless oil; Eluent: *n*-hexane/EtOAc = 50/1;

^{1}H NMR (400 MHz $CDCl_3$, δ ppm): 0.89-0.92 (t, J = 8.0 Hz, 3H), 1.09 (s, 9H), 1.57-1.63 (dd, J_1 = 8.0 Hz; J_2 = 16.0 Hz, 2H), 2.53-2.57 (t, J = 8.0 Hz, 2H), 3.80 (s, 3H), 5.18 (s, 1H), 7.08-7.10 (d, J = 8.0 Hz, 2H), 7.34-7.36 (d, J = 8.0 Hz, 2H);

^{13}C NMR (100 MHz, $CDCl_3$, δ ppm):13.5, 24.2, 25.4, 35.5, 37.8, 54.7, 76.6, 84.0, 86.7, 119.4, 128.3, 131.6, 143.3, 155.3;

HRMS (ESI) calcd for $C_{18}H_{24}O_3$ $[M+H]^+$ m/z 289.1804, found 289.1800.



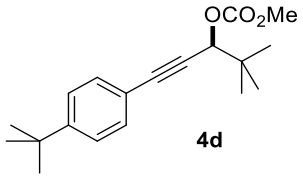
4c

4c: colorless oil; Eluent: *n*-hexane/EtOAc = 50/1;

^{1}H NMR (400 MHz $CDCl_3$, δ ppm): 0.86-0.90 (t, J = 8.0 Hz, 3H), 1.09 (s, 9H), 1.28-1.33 (m, 4H) 1.57-1.61 (t, J = 8.0 Hz, 2H), 2.56-2.60 (t, J = 8.0 Hz, 2H), 3.82 (s, 3H), 5.17 (s, 1H), 7.10-7.12 (d, J = 8.0 Hz, 2H), 7.35-7.37 (d, J = 8.0 Hz, 2H);

^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 14.0, 22.5, 25.6, 30.9, 31.4, 35.7, 35.8, 54.9, 76.7, 84.1, 86.8, 119.5, 128.3, 131.8, 143.8, 155.4;

HRMS (ESI) calcd for $C_{20}H_{28}O_3$ $[M+H]^+$ m/z 317.2117, found 317.2113.



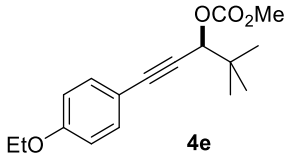
4d

4d: colorless oil; Eluent: *n*-hexane/EtOAc = 50/1;

^{1}H NMR (400 MHz $CDCl_3$, δ ppm): 1.09 (s, 9H), 1.29 (s, 9H), 3.81 (s, 3H), 5.18 (s, 1H), 7.30-7.32 (d, J = 8.0 Hz, 2H), 7.37-7.39 (d, J = 8.0 Hz, 2H);

^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 25.5, 31.0, 34.6, 35.6, 54.7, 76.7, 84.1, 86.6, 119.3, 125.1, 131.5, 151.7, 155.3;

HRMS (ESI) calcd for $C_{19}H_{26}O_3$ $[M+H]^+$ m/z 303.1960, found 303.1956.



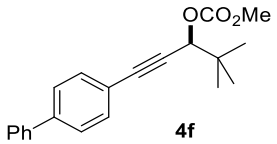
4e

4e: colorless oil; Eluent: *n*-hexane/EtOAc = 50/1;

^{1}H NMR (400 MHz $CDCl_3$, δ ppm): 1.09 (s, 9H), 1.38-1.41 (t, J = 4.0 Hz, 3H), 3.81 (s, 3H), 3.98-4.03 (dd, J_1 = 8.0 Hz; J_2 = 16.0 Hz, 2H), 5.17 (s, 1H), 6.79-6.81 (d, J = 8.0 Hz, 2H), 7.35-7.38 (d, J = 12.0 Hz, 2H);

^{13}C NMR (100 MHz, $CDCl_3$, δ ppm):14.6, 25.5, 35.6, 54.8, 63.4, 76.7, 83.2, 86.6, 114.2, 114.3, 133.3, 155.4, 159.2;

HRMS (ESI) calcd for $C_{17}H_{22}O_4$ $[M+H]^+$ m/z 291.1596, found 291.1594.



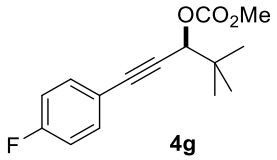
4f

4f: colorless oil; Eluent: *n*-hexane/EtOAc = 50/1;

^{1}H NMR (400 MHz $CDCl_3$, δ ppm): 1.11 (s, 9H) 3.83 (s, 3H), 5.20 (s, 1H), 7.33-7.37 (t, *J* = 8.0 Hz, 1H), 7.41-7.45 (t, *J* = 8.0 Hz, 2H), 7.50-7.58 (m, 6H);

^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 25.6, 35.7, 54.9, 76.7, 85.4, 86.5, 121.2, 126.9, 127.0, 127.7, 128.8, 132.3, 140.3, 141.3, 155.4;

HRMS (ESI) calcd for $C_{21}H_{22}O_3$ $[M+H]^+$ m/z 323.1647, found 323.1647.



4g

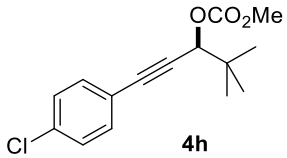
4g: colorless oil; Eluent: *n*-hexane/EtOAc = 50/1;

^{1}H NMR (400 MHz $CDCl_3$, δ ppm): 1.09 (s, 9H), 3.83 (s, 3H), 5.16 (m, 1H), 6.98-7.02 (t, *J* = 8.0 Hz, 2H), 7.41-7.44 (m, 2H);

^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 25.5, 35.6, 54.9, 76.6, 84.5, 85.5, 115.4-115.6 (d, *J* = 12.0 Hz), 118.4 (d, *J* = 4.0 Hz), 133.7-133.8 (d, *J* = 9.0 Hz), 155.4, 161.4, 163.9;

^{19}F NMR (376 MHz, $CDCl_3$, δ ppm): -110.4 (s, 1F);

HRMS (ESI) calcd for $C_{15}H_{17}FO_3$ $[M+H]^+$ m/z 265.1240, found 265.1238.



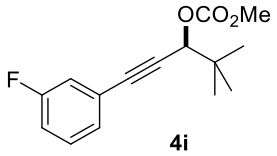
4h

4h: colorless oil; Eluent: *n*-hexane/EtOAc = 50/1;

^{1}H NMR (400 MHz $CDCl_3$, δ ppm): 1.09 (s, 9H), 3.83 (s, 3H), 5.16 (s, 1H), 7.27-7.29 (d, *J* = 8.0 Hz, 2H), 7.36-7.38 (d, *J* = 8.0 Hz, 2H);

^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 25.5, 35.6, 54.9, 76.5, 85.5, 85.8, 120.8, 128.5, 133.1, 134.6, 155.3;

HRMS (ESI) calcd for $C_{15}H_{17}ClO_3$ $[M+H]^+$ m/z 281.0944, found 281.0942.



4i

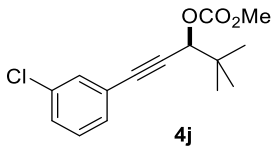
4i: colorless oil; Eluent: *n*-hexane/EtOAc = 50/1;

^{1}H NMR (400 MHz $CDCl_3$, δ ppm): 1.10 (s, 9H), 3.83 (s, 3H), 5.16 (m, 1H), 7.01-7.05 (t, *J* = 8.0 Hz, 1H), 7.13-7.15 (d, *J* = 8.0 Hz, 1H), 7.23-7.30 (m, 2H);

^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 25.5, 35.6, 55.0, 76.5, 76.7, 77.0, 77.3, 85.4 (d, *J* = 4.0 Hz), 85.4, 85.8, 115.9, 116.1, 118.6, 124.1, 124.2, 127.2, 127.8, 129.8, 129.9, 155.4, 161.0. 163.5.

^{19}F NMR (376 MHz, $CDCl_3$, δ ppm): -112.9 (s, 1F);

HRMS (ESI) calcd for $C_{15}H_{17}FO_3$ $[M+H]^+$ m/z 265.1240, found 265.1236.



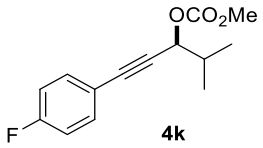
4j

4j: colorless oil; Eluent: *n*-hexane/EtOAc = 50/1;

^{1}H NMR (400 MHz $CDCl_3$, δ ppm): 1.10 (s, 9H), 3.82 (s, 3H), 5.17 (s, 1H), 7.20-7.24 (t, *J* = 8.0 Hz, 1H), 7.28-7.30 (t, *J* = 12.0 Hz, 2H), 7.42 (s, 1H);

^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 25.4, 35.5, 54.8, 76.3, 85.1, 86.0, 123.9, 128.8, 129.4, 129.8, 131.6, 134.0, 155.2;

HRMS (ESI) calcd for $C_{15}H_{17}ClO_3$ $[M+H]^+$ m/z 281.0944, found 281.0942.



4k

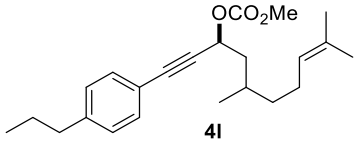
4k: colorless oil; Eluent: *n*-hexane/EtOAc = 50/1;

^{1}H NMR (400 MHz $CDCl_3$, δ ppm): 1.07-1.11 (dd, J_1 = 4.0 Hz; J_2 = 12.0 Hz, 6H), 2.10-2.18 (m, 1H), 3.82 (s, 3H), 5.28-5.29 (d, *J* = 4.0 Hz, 1H), 6.98-7.02 (t, *J* = 8.0 Hz, 2H), 7.41-7.44 (dd, J_1 = 4.0 Hz; J_2 = 8.0 Hz, 2H);

^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 17.5, 18.1, 32.7, 54.8, 73.5, 84.3, 85.6, 115.4-115.6 (d, *J* = 22.0 Hz), 118.3 (d, *J* = 3.0 Hz), 133.7-133.8 (d, *J* = 9.0 Hz), 155.1, 161.4, 163.9;

^{19}F NMR (376 MHz, $CDCl_3$, δ ppm): -110.3 (s, 1F);

HRMS (ESI) calcd for $C_{14}H_{15}FO_3$ $[M+H]^+$ m/z 251.1083, found 251.1081.



4l

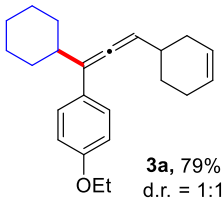
4l: colorless oil; Eluent: *n*-hexane/EtOAc = 50/1;

^{1}H NMR (400 MHz $CDCl_3$, δ ppm): 0.90-0.93 (t, *J* = 4.0 Hz, 3H), 0.97-0.99 (d, *J* = 8.0 Hz, 3H), 1.20-1.29 (m, 1H), 1.39-1.44 (m, 1H), 1.60-1.65 (m, 5H), 1.67-1.70 (m, 3H), 1.73-1.76 (m, 2H), 1.88-2.04 (m, 3H), 2.55-2.59 (t, *J* = 8.0 Hz, 2H), 3.81 (s, 3H), 5.08-5.11 (t, *J* = 8.0 Hz, 1H), 5.49-5.54 (m, 1H), 7.10-7.12 (d, *J* = 8.0 Hz, 2H), 7.34-7.36 (d, *J* = 8.0 Hz, 2H);

^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 13.7, 17.6, 19.4, 19.4, 24.3, 25.2, 25.3, 25.7, 29.0, 29.2, 36.8, 36.9, 37.9, 41.8, 42.2, 54.8, 67.4, 67.8, 85.2, 85.5, 86.2, 86.5, 119.4, 124.4, 128.4, 131.4, 131.7, 131.8, 143.5, 155.0, 155.1;

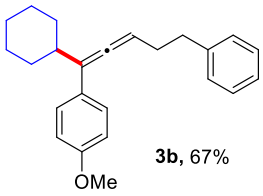
HRMS (ESI) calcd for $C_{23}H_{32}O_3$ $[M+H]^+$ m/z 357.2430, found 357.2427.

8. Characterization Data of Products 3a-3n:



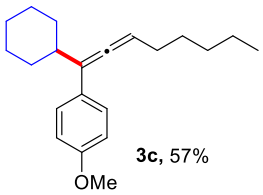
3a, 79%
d.r. = 1:1

3a: yield 79%. According to **General Procedure**; colorless oil; Eluent: *n*-hexane/EtOAc = 200/1;
^{1}H NMR (400 MHz $CDCl_3$, δ ppm): 1.13-1.21 (m, 3H), 1.25-1.34 (m, 2H), 1.38-1.42 (t, J = 8.0 Hz, 3H), 1.43-1.49 (m, 1H), 1.69-1.79 (m, 3H), 1.88-1.96 (m, 4H), 2.09-2.10 (m, 2H), 2.17-2.21 (m, 1H), 2.34-2.40 (dt, J_1 = 4.0 Hz, J_2 = 12.0 Hz, 2H), 3.99-4.04 (q, J = 8.0 Hz, 2H), 5.56 (s, 1H), 5.67 (s, 2H), 6.82-6.84 (d, J = 8.0 Hz, 2H), 7.28-7.30 (d, J = 8.0 Hz, 2H);
^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 14.9, 25.1, 25.2, 26.4, 26.7, 26.8, 29.1, 29.1, 31.3, 31.5, 32.8, 32.9, 33.3, 33.3, 34.0, 37.8, 63.4, 100.2, 100.3, 112.6, 114.4, 114.4, 126.3, 126.3, 126.8, 127.2, 129.3, 129.3, 157.6, 201.6, 201.6;
HRMS (ESI) calcd for $C_{23}H_{30}O$ $[M+H]^+$ m/z 323.2375, found 323.2379.



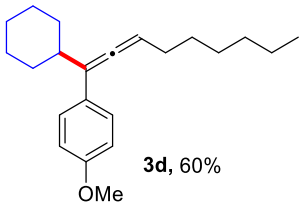
3b, 67%

3b: yield 67%. According to **General Procedure**; colorless oil; Eluent: *n*-hexane/EtOAc = 200/1;
^{1}H NMR (400 MHz $CDCl_3$, δ ppm): 1.07-1.35 (m, 5H), 1.67-1.84 (m, 5H), 2.31-2.34 (dt, J_1 = 4.0 Hz, J_2 = 12.0 Hz, 1H), 2.39-2.45 (dt, J_1 = 8.0 Hz, J_2 = 16.0 Hz, 2H), 2.76-2.79 (t, J = 8.0 Hz, 2H), 3.79 (s, 3H), 5.49-5.52 (dt, J_1 = 4.0 Hz, J_2 = 8.0 Hz, 1H), 6.81-6.83 (d, J = 8.0 Hz, 2H),7.19-7.21 (m, 5H), 7.24-7.28 (dt, J_1 = 8.0 Hz, J_2 = 12.0 Hz, 2H);
^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 26.4, 26.7, 26.7, 31.2, 32.8, 33.1, 35.6, 37.9, 55.3, 94.2, 111.8, 113.8, 125.8, 127.4, 128.3, 128.6, 129.4, 141.9, 158.2, 202.9;
HRMS (ESI) calcd for $C_{24}H_{28}O$ $[M+H]^+$ m/z 333.2218, found 333.2217.



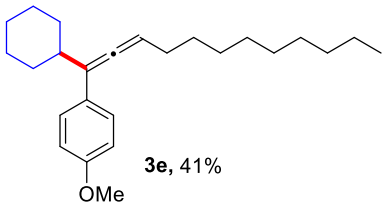
3c, 57%

3c: yield 57%. According to **General Procedure**; colorless oil; Eluent: *n*-hexane/EtOAc = 200/1;
^{1}H NMR (400 MHz $CDCl_3$, δ ppm): 0.86-0.90 (t, J = 8.0 Hz, 3H), 1.11-1.37 (m, 9H), 1.44-1.46 (m, 2H), 1.69-1.88 (m, 5H), 2.05-2.10 (dd, J_1 = 8.0 Hz, J_2 = 16.0 Hz, 2H), 2.33-2.39 (dt, J_1 = 4.0 Hz, J_2 = 12.0 Hz, 1H), 3.79 (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), 7.29-7.31 (d, J = 8.0 Hz, 2H);
^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 14.1, 22.5, 26.5, 26.7, 26.8, 29.0, 29.3, 31.5, 32.8, 33.2, 37.9, 55.3, 95.0, 111.3, 113.7, 127.4, 129.7, 158.1, 202.8;
HRMS (ESI) calcd for $C_{21}H_{30}O$ $[M+H]^+$ m/z 299.2375, found 299.2374.



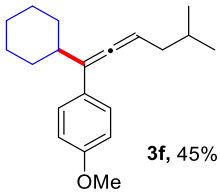
3d, 60%

3d: yield 60%. According to **General Procedure**; colorless oil; Eluent: *n*-hexane/EtOAc = 200/1;
^{1}H NMR (400 MHz $CDCl_3$, δ ppm): 0.86-0.89 (t, J = 8.0 Hz, 3H), 1.14-1.37 (m, 11H), 1.43-1.47 (m, 2H), 1.69-1.88 (m, 5H), 2.05-2.10 (dd, J_1 = 8.0 Hz, J_2 = 16.0 Hz, 2H), 2.33-2.39 (dt, J_1 = 4.0 Hz, J_2 = 12.0 Hz, 1H), 3.79 (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), 7.29-7.31 (d, J = 8.0 Hz, 2H);
^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 14.1, 22.7, 26.5, 26.7, 26.8, 29.0, 29.3, 29.4, 31.7, 32.9, 33.2, 37.9, 55.3, 95.0, 111.3, 113.7, 127.4, 129.7, 158.2, 202.8;
HRMS (ESI) calcd for $C_{22}H_{32}O$ $[M+H]^+$ m/z 313.2531, found 313.2526.



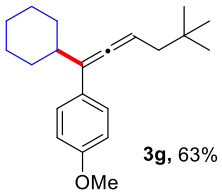
3e, 41%

3e: yield 41%. According to **General Procedure**; colorless oil; Eluent: *n*-hexane/EtOAc = 200/1;
^{1}H NMR (400 MHz $CDCl_3$, δ ppm): 0.86-0.89 (t, J = 8.0 Hz, 3H), 1.14-1.36 (m, 17H), 1.41-1.46 (m, 2H), 1.69-1.88 (m, 5H), 2.05-2.10 (dd, J_1 = 8.0 Hz, J_2 = 16.0 Hz, 2H), 2.33-2.39 (dt, J_1 = 4.0 Hz, J_2 = 12.0 Hz, 1H), 3.80 (s, 3H), 5.45-5.49 (dt, J_1 = 4.0 Hz, J_2 = 8.0 Hz, 1H), 6.84-6.86 (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): 14.1, 22.7, 26.5, 26.7, 26.8, 29.3, 29.3, 29.4, 29.5, 29.6, 31.9, 32.9, 33.2, 37.9, 55.3, 95.0, 111.3, 113.7, 127.4, 129.7, 158.2, 202.8;
HRMS (ESI) calcd for $C_{25}H_{38}O$ $[M+H]^+$ m/z 355.2995, found 355.2985.



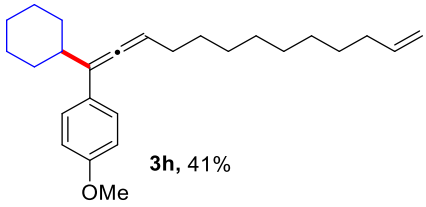
3f, 45%

3f: yield 45%. According to **General Procedure**; colorless oil; Eluent: *n*-hexane/EtOAc = 100/1;
^{1}H NMR (400 MHz $CDCl_3$, δ ppm): 0.94-0.97 (m, 6H), 1.15-1.26 (m, 3H), 1.30-1.40 (m, 2H), 1.69-1.79 (m, 4H), 1.86-1.89 (d, J = 12.0 Hz, 2H), 1.97-2.01 (dt, J_1 = 4.0 Hz, J_2 = 8.0 Hz, 2H), 2.33-2.39 (dt, J_1 = 4.0 Hz, J_2 = 12.0 Hz, 1H), 3.79 (s, 3H), 5.41-5.45 (dt, J_1 = 4.0 Hz, J_2 = 8.0 Hz, 1H), 6.84-6.86 (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): 22.5, 22.5, 26.5, 26.7, 26.8, 28.8, 32.8, 33.2, 38.0, 39.0, 55.3, 93.6, 110.7, 113.7, 127.4, 129.7, 158.1, 203.3;
HRMS (ESI) calcd for $C_{20}H_{28}O$ $[M+H]^+$ m/z 285.2218, found 285.2225.



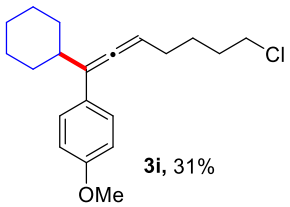
3g, 63%

3g: yield 63%. According to **General Procedure**; colorless oil; Eluent: *n*-hexane/EtOAc = 200/1;
^{1}H NMR (400 MHz $CDCl_3$, δ ppm): 0.96 (s, 9H), 1.16-1.24 (m, 3H), 1.30-1.40 (m, 2H), 1.68-1.89 (m, 5H), 2.00-2.02 (d, J = 8.0 Hz, 2H), 2.33-2.39 (dt, J_1 = 4.0 Hz, J_2 = 12.0 Hz, 1H), 3.79 (s, 3H), 5.43-5.46 (t, J = 8.0 Hz, 1H), 6.84-6.86 (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): 26.5, 26.7, 26.8, 29.4, 31.1, 32.9, 33.2, 38.0, 44.5, 55.3, 91.8, 110.1, 113.7, 127.4, 129.7, 158.1, 203.9;
HRMS (ESI) calcd for $C_{21}H_{30}O$ $[M+H]^+$ m/z 299.2375, found 299.2377.



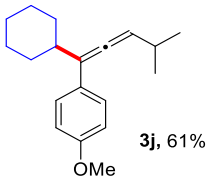
3h, 41%

3h: yield 41%. According to **General Procedure**; colorless oil; Eluent: *n*-hexane/EtOAc = 200/1;
^{1}H NMR (400 MHz $CDCl_3$, δ ppm): 1.11-1.36 (m, 15H), 1.41-1.46 (m, 2H), 1.69-1.87 (m, 5H), 2.00-2.10 (m, 4H), 2.33-2.39 (dt, J_1 = 4.0 Hz, J_2 = 12.0 Hz, 1H), 3.79 (s, 3H), 4.91-5.01 (m, 2H), 5.43-5.46 (dt, J_1 = 4.0 Hz, J_2 = 8.0 Hz, 1H), 5.76-5.86 (m, 1H), 6.84-6.86 (d, J = 8.0 Hz, 2H), 7.28-7.30 (d, J = 8.0 Hz, 2H);
^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 26.5, 26.7, 26.8, 29.0, 29.1, 29.3, 29.3, 29.4, 29.4, 29.5, 32.9, 33.2, 33.8, 37.9, 55.3, 95.0, 111.3, 113.7, 114.1, 127.4, 129.7, 139.2, 158.2, 202.8;
HRMS (ESI) calcd for $C_{26}H_{38}O$ $[M+H]^+$ m/z 367.2995, found 367.2990.

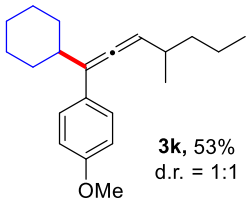


3i, 31%

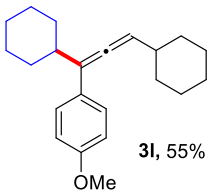
3i: yield 31%. According to **General Procedure**; colorless oil; Eluent: *n*-hexane/EtOAc = 200/1;
^{1}H NMR (400 MHz $CDCl_3$, δ ppm): 1.09-1.25 (m, 3H), 1.31-1.41 (m, 2H), 1.58-1.63 (m, 2H), 1.69-1.87 (m, 7H), 2.09-2.14 (dd, J_1 = 8.0 Hz, J_2 = 16.0 Hz, 2H), 2.34-2.40 (dt, J_1 = 4.0 Hz, J_2 = 12.0 Hz, 1H), 3.51-3.54 (t, J = 8.0 Hz, 2H), 3.80 (s, 3H), 5.45-5.48 (d, J = 8.0 Hz, 1H), 6.84-6.86 (d, J = 8.0 Hz, 2H), 7.27-7.30 (d, J = 12.0 Hz, 2H);
^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 26.4, 26.5, 26.7, 26.7, 28.6, 32.2, 32.9, 33.2, 38.0, 44.9, 55.3, 94.2, 111.8, 113.8, 127.4, 129.4, 158.3, 202.9;
HRMS (ESI) calcd for $C_{20}H_{27}ClO$ $[M+H]^+$ m/z 319.1823, found 319.1816.



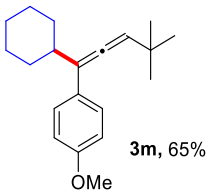
3j: yield 61%. According to **General Procedure**; colorless oil; Eluent: *n*-hexane/EtOAc = 200/1;
^{1}H NMR (400 MHz $CDCl_3$, δ ppm): 1.06-1.07 (d, *J* = 4.0 Hz, 6H), 1.13-1.26 (m, 3H), 1.31-1.41 (m, 2H), 1.69-1.79 (m, 3H), 1.85-1.91 (t, *J* = 12.0 Hz, 2H), 2.35-2.43 (m, 2H), 3.79 (s, 3H), 5.50-5.52 (dd, 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): 22.6, 22.7, 26.5, 26.7, 26.8, 28.7, 32.9, 33.3, 37.9, 55.3, 102.4, 112.5, 113.8, 127.2, 129.7, 158.2, 201.0;
HRMS (ESI) calcd for $C_{19}H_{26}O$ $[M+K]^+$ m/z 309.1621, found 309.1619.



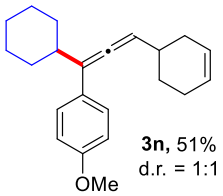
3k: yield 53%. According to **General Procedure**; colorless oil; Eluent: *n*-hexane/EtOAc = 200/1;
^{1}H NMR (400 MHz $CDCl_3$, δ ppm): 0.88-0.92 (t, *J* = 8.0 Hz, 3H), 1.03-1.05 (m, 3H), 1.11-1.25 (m, 3H), 1.31-1.40 (m, 6H), 1.69-1.79 (m, 3H), 1.85-1.91 (t, *J* = 12.0 Hz, 2H), 2.21-2.25 (m, 1H), 2.34-2.40 (dt, J_1 = 4.0 Hz, J_2 = 8.0 Hz, 1H), 3.79 (s, 3H), 5.44-5.48 (dd, 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): 14.2, 20.4, 20.5, 20.6, 26.5, 26.8, 26.8, 32.9, 32.9, 33.3, 33.3, 33.7, 33.8, 37.9, 37.9, 39.6, 39.7, 55.3, 101.2, 101.3, 112.0, 112.0, 113.7, 113.7, 127.3, 127.3, 129.7, 158.1, 201.5, 201.5;
HRMS (ESI) calcd for $C_{21}H_{30}O$ $[M+K]^+$ m/z 337.1934, found 337.1934.



3l: yield 55%. According to **General Procedure**; colorless oil; Eluent: *n*-hexane/EtOAc = 200/1;
^{1}H NMR (400 MHz $CDCl_3$, δ ppm): 1.11-1.37 (m, 10H), 1.63-1.91 (m, 10H), 2.01-2.08 (m, 1H), 2.33-2.39 (m, 1H), 3.79 (s, 3H), 5.47-5.48 (d, *J* = 4.0 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): 26.2, 26.2, 26.5, 26.7, 26.8, 32.9, 33.3, 33.4, 33.4, 37.8, 38.1, 55.3, 101.0, 112.1, 113.8, 127.2, 129.7, 158.1, 201.5;
HRMS (ESI) calcd for $C_{22}H_{30}O$ $[M+H]^+$ m/z 311.2375, found 311.2377.

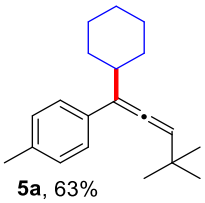


3m: yield 65%. According to **General Procedure**; colorless oil; Eluent: *n*-hexane/EtOAc = 200/1;
^{1}H NMR (400 MH_Z $CDCl_3$, δ ppm): 1.10 (s, 9H), 1.14-1.25 (m, 3H), 1.31-1.41 (m, 2H), 1.70-1.79 (m, 3H), 1.85-1.93 (t, *J* = 16.0 Hz, 2H), 2.34-2.41 (dt, J_1 = 4.0 Hz, J_2 = 12.0 Hz, 1H), 3.79 (s, 3H), 5.48 (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): 26.5, 26.8, 26.8, 29.1, 30.4, 32.8, 32.9, 33.4, 37.9, 55.3, 106.9, 112.8, 113.8, 127.1, 129.7, 132.8, 158.2, 199.7;
HRMS (ESI) calcd for $C_{20}H_{28}O$ $[M+H]^+$ m/z 285.2218, found 285.2214.



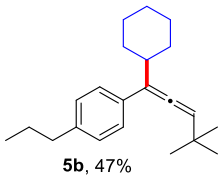
3n: yield 51%. According to **General Procedure**; colorless oil; Eluent: *n*-hexane/EtOAc = 200/1;
^{1}H NMR (400 MH_Z $CDCl_3$, δ ppm): 1.14-1.21 (m, 3H), 1.31-1.41 (m, 3H), 1.69-1.79 (m, 3H), 1.86-1.97 (m, 4H), 2.09-2.21 (m, 3H), 2.34-2.40 (dt, J_1 = 4.0 Hz, J_2 = 12.0 Hz, 2H), 3.79 (s, 3H), 5.56 (s, 1H), 5.67 (s, 2H), 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): 25.1, 25.2, 26.4, 26.7, 26.8, 29.1, 29.1, 31.3, 31.5, 32.8, 32.9, 33.3, 34.0, 37.8, 55.3, 100.3, 100.3, 112.6, 112.6, 113.8, 113.8, 126.3, 126.3, 126.8, 127.3, 129.5, 129.5, 158.2, 201.6, 201.7;
HRMS (ESI) calcd for $C_{22}H_{28}O$ $[M+K]^+$ m/z 347.1772, found 347.1761.

9. Characterization Data of Products 5a-5s, 3aa, 5ba, 6a-6c:



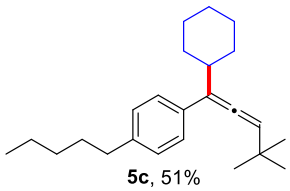
5a, 63%

5a: yield 63%. According to **General Procedure**; colorless oil; Eluent: *n*-hexane/EtOAc = 300/1;
^{1}H NMR (400 MHz $CDCl_3$, δ ppm): 1.10 (s, 9H), 1.15-1.25 (m, 3H), 1.32-1.41 (m, 2H), 1.69-1.80 (m, 3H), 1.85-1.93 (t, J = 16.0 Hz, 2H), 2.32(s, 3H), 2.37-2.43 (dt, J_1 = 4.0 Hz, J_2 = 12.0 Hz, 1H), 5.48 (m, 1H), 7.09-7.11 (d, J = 8.0 Hz, 2H), 7.27-7.29 (d, J = 8.0 Hz, 2H);
^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 26.5, 26.8, 26.8, 29.1, 30.4, 32.8, 32.9, 33.4, 37.9, 55.3, 106.9, 112.8, 113.8, 127.1, 129.7, 132.8, 158.2, 199.7;
HRMS (ESI) calcd for $C_{20}H_{28}$ $[M+H]^+$ m/z 269.2269, found 269.2269.



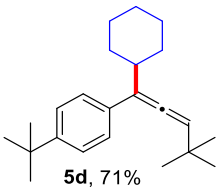
5b, 47%

5b: yield 47%. According to **General Procedure**; colorless oil; Eluent: *n*-hexane/EtOAc = 300/1;
^{1}H NMR (400 MHz $CDCl_3$, δ ppm): 0.92-0.96 (t, J = 8.0 Hz, 3H), 1.11 (s, 9H), 1.15-1.25 (m, 3H), 1.31-1.41 (m, 2H), 1.60-1.65 (m, 2H), 1.70-1.79 (m, 3H), 1.86-1.94 (t, J = 16.0 Hz, 2H), 2.37-2.43 (dt, J_1 = 4.0 Hz, J_2 = 12.0 Hz, 1H), 2.53-2.57 (t, J = 8.0 Hz, 2H), 5.49 (m, 1H), 7.10-7.12 (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): 13.9, 24.5, 26.5, 26.8, 26.9, 30.4, 32.8, 32.9, 33.4, 37.7, 37.8, 106.9, 113.2, 125.9, 128.4, 134.6, 140.7, 200.0;
HRMS (ESI) calcd for $C_{22}H_{32}$ $[M+H]^+$ m/z 297.2577, found 297.2571.



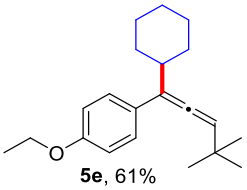
5c, 51%

5c: yield 51%. According to **General Procedure**; colorless oil; Eluent: *n*-hexane/EtOAc = 300/1;
^{1}H NMR (400 MHz $CDCl_3$, δ ppm): 0.87-0.91 (t, J = 8.0 Hz, 3H), 1.11 (s, 9H), 1.15-1.21 (m, 3H), 1.32-1.38 (m, 6H), 1.58-1.61 (m, 2H), 1.69-1.79 (m, 3H), 1.86-1.94 (t, J = 16.0 Hz, 2H), 2.37-2.44 (dt, J_1 = 4.0 Hz, J_2 = 12.0 Hz, 1H), 2.55-2.58 (t, J = 8.0 Hz, 2H), 5.49 (m, 1H), 7.09-7.11 (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): 14.0, 22.6, 26.5, 26.8, 26.9, 30.3, 30.4, 31.1, 31.5, 32.8, 32.9, 33.4, 35.5, 37.8, 106.9, 113.2, 125.9, 126.3, 128.3, 128.6, 134.6, 140.9, 200.0;
HRMS (ESI) calcd for $C_{24}H_{36}$ $[M+K]^+$ m/z 363.2449, found 363.2441.



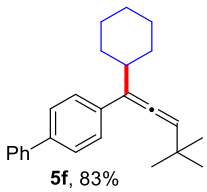
5d, 71%

5d: yield 71%. According to **General Procedure**; colorless oil; Eluent: *n*-hexane/EtOAc = 100/1;
^{1}H NMR (400 MH_Z $CDCl_3$, δ ppm): 1.11 (s, 9H), 1.15-1.22 (m, 3H), 1.26-1.40 (m, 11H), 1.70-1.77 (m, 3H), 1.87-1.95 (t, J = 16.0 Hz, 2H), 2.38-2.44 (dt, J_1 = 4.0 Hz, J_2 = 12.0 Hz, 1H), 5.48-5.49 (t, J = 4.0 Hz, 1H), 7.33 (s, 4H);
^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 14.0, 22.6, 26.5, 26.8, 26.9, 30.3, 30.4, 31.1, 31.5, 32.8, 32.9, 33.4, 35.5, 37.8, 106.9, 113.2, 125.9, 126.3, 128.3, 128.6, 134.6, 140.9, 200.0;
HRMS (ESI) calcd for $C_{23}H_{34}$ $[M+K]^+$ m/z 349.2298, found 349.2292.



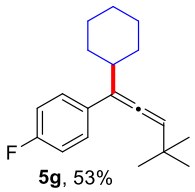
5e, 61%

5e: yield 61%. According to **General Procedure**; colorless oil; Eluent: *n*-hexane/EtOAc = 200/1;
^{1}H NMR (400 MH_Z $CDCl_3$, δ ppm): 1.10 (s, 9H), 1.14-1.25 (m, 3H), 1.30-1.42 (m, 5H), 1.69-1.79 (m, 3H), 1.85-1.93 (t, J = 16.0 Hz, 2H), 2.34-2.40 (dt, J_1 = 4.0 Hz, J_2 = 12.0 Hz, 1H), 3.99-4.04 (dd, J_1 = 8.0 Hz, J_2 = 12.0 Hz, 2H), 5.48 (m, 1H), 6.82-6.84 (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): 14.9, 26.5, 26.8, 26.9, 30.4, 32.8, 32.9, 33.4, 37.9, 63.4, 106.8, 112.8, 114.4, 127.1, 129.5, 157.5, 199.6;
HRMS (ESI) calcd for $C_{21}H_{30}O$ $[M+H]^+$ m/z 299.2375, found 299.2373.



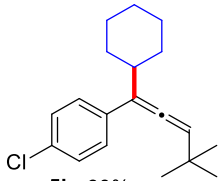
5f, 83%

5f: yield 83%. According to **General Procedure**; colorless oil; Eluent: *n*-hexane/EtOAc = 300/1;
^{1}H NMR (400 MH_Z $CDCl_3$, δ ppm): 1.13 (s, 9H), 1.17-1.28 (m, 3H), 1.34-1.44 (m, 2H), 1.71-1.82 (m, 3H), 1.90-1.98 (t, J = 16.0 Hz, 2H), 2.43-2.49 (dt, J_1 = 4.0 Hz, J_2 = 12.0 Hz, 1H), 5.54 (m, 1H), 7.29-7.33 (t, J = 8.0 Hz, 1H), 7.40-7.43 (t, J = 8.0 Hz, 2H), 7.46-7.48 (d, J = 8.0 Hz, 2H), 7.52-7.55 (d, J = 12.0 Hz, 2H), 7.57-7.59 (d, J = 12.0 Hz, 2H);
^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 26.5, 26.8, 26.9, 30.4, 32.9, 32.9, 33.4, 37.7, 107.1, 113.1, 126.5, 126.9, 127.0, 127.0, 128.7, 136.4, 139.0, 140.9, 200.5;
HRMS (ESI) calcd for $C_{25}H_{30}$ $[M+H]^+$ m/z 331.2426, found 331.2425.



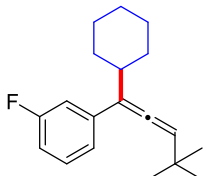
5g, 53%

5g: yield 53%. According to **General Procedure**; colorless oil; Eluent: *n*-hexane/EtOAc = 200/1;
^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 1.10 (s, 9H), 1.15-1.25 (m, 3H), 1.31-1.40 (m, 2H), 1.70-1.91 (m, 5H), 2.34-2.40 (dt, J_1 = 8.0 Hz, J_2 = 12.0 Hz, 1H), 5.50 (m, 1H), 6.96-6.70 (dt, J_1 = 4.0 Hz, J_2 = 8.0 Hz, 2H), 7.32-7.36 (dt, J_1 = 4.0 Hz, J_2 = 8.0 Hz, 2H);
^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 26.4, 26.7, 26.8, 30.4, 32.8, 32.8, 33.3, 38.0, 107.1, 112.5, 115.0-115.2 (d, *J* = 21.0 Hz), 127.5-127.6 (d, *J* = 8.0 Hz), 133.3 (d, *J* = 3.0 Hz), 160.3, 162.7, 200.0-200.1 (d, *J* = 2.0 Hz);
^{19}F NMR (376 MHz, $CDCl_3$, δ ppm): -117.0 (s, 1F);
HRMS (ESI) calcd for $C_{19}H_{25}F$ $[M+K]^+$ m/z 311.1577, found 311.1576.



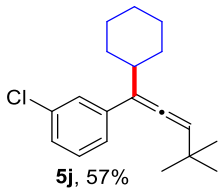
5h, 60%

5h: yield 60%. According to **General Procedure**; colorless oil; Eluent: *n*-hexane/EtOAc = 200/1;
^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 1.10 (s, 9H), 1.16-1.25 (m, 3H), 1.31-1.38 (m, 2H), 1.70-1.91 (m, 5H), 2.33-2.40 (dt, J_1 = 4.0 Hz, J_2 = 12.0 Hz, 1H), 5.51 (d, 1H), 7.24-7.26 (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): 26.4, 26.7, 26.8, 30.4, 32.8, 32.8, 33.3, 37.7, 107.3, 112.6, 127.4, 128.4, 131.8, 135.9, 200.3;
HRMS (ESI) calcd for $C_{19}H_{25}Cl$ $[M+H]^+$ m/z 289.1723, found 289.1718.



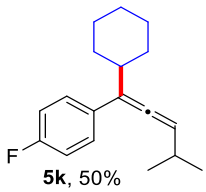
5i, 55%

5i: yield 55%. According to **General Procedure**; colorless oil; Eluent: *n*-hexane/EtOAc = 100/1;
^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 1.10 (s, 9H), 1.15-1.25 (m, 3H), 1.31-1.40 (m, 2H), 1.70-1.91 (m, 5H), 2.34-2.40 (dt, J_1 = 8.0 Hz, J_2 = 12.0 Hz, 1H), 5.50 (m, 1H), 6.96-6.70 (dt, J_1 = 4.0 Hz, J_2 = 8.0 Hz, 2H), 7.32-7.36 (dt, J_1 = 4.0 Hz, J_2 = 8.0 Hz, 2H);
^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 26.4, 26.7, 26.8, 30.3, 32.8, 33.3, 37.7, 107.4, 112.7 (d, *J* = 2.0 Hz), 112.8-113.0 (d, *J* = 2.0 Hz), 121.6 (d, *J* = 3.0 Hz), 129.5-129.6 (d, *J* = 8.0 Hz), 140.0-140.1 (d, *J* = 7.0 Hz), 161.9, 164.3, 200.5;
^{19}F NMR (376 MHz, $CDCl_3$, δ ppm): -113.9 (s, 1F);
HRMS (ESI) calcd for $C_{19}H_{25}F$ $[M+H]^+$ m/z 273.2019, found 273.2019.



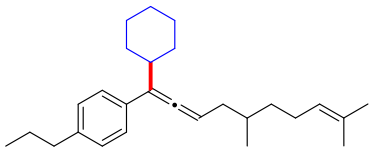
5j, 57%

5j: yield 57%. According to **General Procedure**; colorless oil; Eluent: *n*-hexane/EtOAc = 200/1;
^{1}H NMR (400 MH_Z $CDCl_3$, δ ppm): 1.11 (s, 9H), 1.13-1.25 (m, 3H), 1.32-1.42 (m, 2H), 1.70-1.91 (m, 5H), 2.33-2.40 (dt, J_1 = 4.0 Hz, J_2 = 12.0 Hz, 1H), 5.53 (m, 1H), 7.12-7.14 (d, J = 8.0 Hz, 1H), 7.19-7.23 (t, J = 8.0 Hz, 1H), 7.25-7.27 (d, J = 8.0 Hz, 1H), 7.35 (s, 1H);
^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 26.4, 26.7, 26.7, 30.4, 32.8, 32.9, 33.3, 37.7, 107.4, 112.6, 124.3, 126.2, 129.4, 134.3, 139.6, 200.6;
HRMS (ESI) calcd for $C_{19}H_{25}Cl$ $[M+H]^+$ m/z 289.1723, found 289.1718.



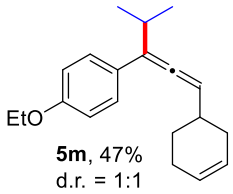
5k, 50%

5k: yield 50%. According to **General Procedure**; colorless oil; Eluent: *n*-hexane/EtOAc = 200/1;
^{1}H NMR (400 MH_Z $CDCl_3$, δ ppm): 1.06-1.08 (d, J = 8.0 Hz, 6H), 1.13-1.25 (m, 3H), 1.30-1.41 (m, 2H), 1.70-1.90 (m, 5H), 2.33-2.44 (m, 2H), 5.52-5.53 (d, J = 4.0 Hz, 1H), 6.96-6.70 (t, J = 8.0 Hz, 2H), 7.31-7.35 (dt, J_1 = 4.0 Hz, J_2 = 8.0 Hz, 2H);
^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 22.6, 22.7, 26.4, 26.7, 26.8, 28.6, 32.8, 33.2, 37.9, 102.6, 112.2, 115.0-115.2 (d, J = 11.0 Hz), 127.6-127.7 (d, J = 8.0 Hz), 133.3-133.4 (d, J = 3.0 Hz), 160.3, 162.7, 201.4 (d, J = 1.0 Hz);
^{19}F NMR (376 MHz, $CDCl_3$, δ ppm): -117.0 (s, 1F);
HRMS (ESI) calcd for $C_{18}H_{23}F$ $[M+H]^+$ m/z 259.1857, found 259.1844.



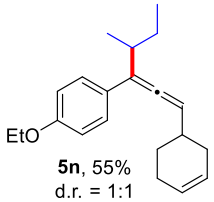
5l, 35%
d.r. = 1:1 ***Citronellal derivative***

5l: yield 35%. According to **General Procedure**; colorless oil; Eluent: *n*-hexane/EtOAc = 200/1;
^{1}H NMR (400 MH_Z $CDCl_3$, δ ppm): 0.92-0.97 (m, 6H), 1.16-1.25 (m, 4H), 1.31-1.37 (m, 3H), 1.53-1.67 (m, 10H), 1.75-1.79 (d, J = 16.0 Hz, 2H), 1.87-2.02 (m, 5H), 2.08-2.17 (m, 1H), 2.36-2.42 (dt, J_1 = 4.0 Hz, J_2 = 12.0 Hz, 1H), 2.53-2.57 (t, J = 8.0 Hz, 2H), 5.05-5.11 (m, 1H), 5.41-5.45 (t, J = 8.0 Hz, 1H), 7.09-7.11 (d, J = 8.0 Hz, 2H), 7.27-7.29 (d, J = 8.0 Hz, 2H);
^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 13.9, 17.6, 17.6, 19.7, 24.5, 25.6, 25.7, 26.5, 26.8, 26.8, 32.9, 33.1, 33.1, 33.2, 33.3, 36.7, 36.7, 36.9, 37.7, 37.9, 93.4, 111.1, 124.8, 126.2, 128.4, 131.1, 131.1, 134.6, 140.6, 203.7, 203.7;
HRMS (ESI) calcd for $C_{27}H_{40}$ $[M+H]^+$ m/z 365.3203, found 365.3195.



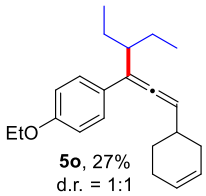
5m, 47%
d.r. = 1:1

5m: yield 47%. According to **General Procedure**; colorless oil; Eluent: *n*-hexane/EtOAc = 200/1;
^{1}H NMR (400 MHz $CDCl_3$, δ ppm): 1.10-1.12 (d, *J* = 8.0 Hz, 6H), 1.39-1.42 (t, *J* = 8.0 Hz, 3H), 1.44-1.50 (m, 1H), 1.87-1.99 (m, 2H), 2.09-2.10 (m, 2H), 2.17-2.21 (m, 1H), 2.34-2.40 (m, 1H), 2.73-2.80 (m, 1H), 4.00-4.05 (q, *J* = 8.0 Hz, 2H), 5.59 (s, 1H), 5.67 (s, 2H), 6.83-6.85 (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): 14.9, 22.2, 22.2, 22.7, 25.0, 25.2, 27.8, 29.1, 29.1, 31.3, 31.5, 34.0, 34.0, 63.4, 100.6, 100.7, 113.6, 114.4, 126.3, 126.3, 126.8, 127.3, 129.4, 129.4, 157.6, 201.1, 201.1;
HRMS (ESI) calcd for $C_{20}H_{26}O$ $[M+H]^+$ m/z 283.2062, found 283.2063.



5n, 55%
d.r. = 1:1

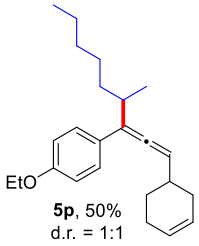
5n: yield 55%. according to **General Procedure**; colorless oil; Eluent: *n*-hexane/EtOAc = 200/1;
^{1}H NMR (400 MHz $CDCl_3$, δ ppm): 0.89-0.92 (dt, J_1 = 4.0 Hz, J_2 = 8.0 Hz, 3H), 1.08-1.12 (dt, J_1 = 4.0 Hz, J_2 = 8.0 Hz, 3H), 1.32-1.49 (m, 5H), 1.57-1.64 (m, 1H), 1.87-2.00 (m, 2H), 2.09-2.10 (m, 2H), 2.17-2.22 (m, 1H), 2.36-2.38 (m, 1H), 2.50-2.56 (m, 1H), 3.99-4.04 (q, *J* = 8.0 Hz, 2H), 5.57 (s, 1H), 5.67 (s, 2H), 6.83-6.85 (d, *J* = 8.0 Hz, 2H), 7.29-7.32 (dd, J_1 = 4.0 Hz, J_2 = 8.0 Hz, 2H);
^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 11.8, 11.8, 14.9, 19.2, 19.2, 20.2, 20.2, 25.0, 25.1, 25.2, 28.8, 28.8, 29.1, 29.1, 29.2, 29.2, 29.2, 31.4, 31.5, 31.7, 33.9, 34.0, 34.1, 34.1, 34.6, 34.8, 63.4, 100.4, 100.5, 100.5, 100.5, 112.3, 112.3, 112.5, 112.5, 114.3, 114.4, 126.2, 126.3, 126.8, 126.8, 127.0, 127.0, 127.3, 127.3, 129.7, 129.7, 129.8, 129.8, 157.6, 157.6, 201.5, 201.5, 201.5, 201.6;
HRMS (ESI) calcd for $C_{21}H_{28}O$ $[M+K]^+$ m/z 335.1772, found 335.1764.



5o, 27%
d.r. = 1:1

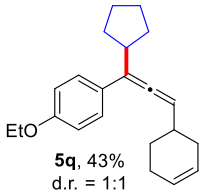
5o: yield 27%. According to **General Procedure**; colorless oil; Eluent: *n*-hexane/EtOAc = 200/1;
^{1}H NMR (400 MHz $CDCl_3$, δ ppm): 0.86-0.91 (m, 6H), 1.38-1.42 (t, *J* = 8.0 Hz, 3H), 1.45-1.53 (m, 5H), 1.87-2.00 (m, 2H), 2.10 (m, 2H), 2.18-2.22 (m, 1H), 2.33-2.38 (m, 2H), 3.99-4.05 (q, *J* = 8.0 Hz, 2H), 5.53-5.56 (t, *J* = 8.0 Hz, 1H), 5.68 (s, 2H), 6.82-6.84 (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): 11.7, 11.7, 14.9, 25.0, 25.1, 26.2, 26.2, 27.2, 29.2, 29.3, 31.6, 31.7, 34.2, 34.2, 42.2, 63.4, 100.2, 100.3, 110.5, 110.5, 114.3, 114.3, 126.3, 126.3, 126.9,

127.4, 130.5, 130.5, 157.6, 201.9, 201.9;
HRMS (ESI) calcd for $C_{22}H_{30}O$ $[M+K]^+$ m/z 349.1928, found 349.1926.



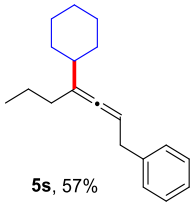
5p, 50%
d.r. = 1:1

5p: yield 50%. According to **General Procedure**; colorless oil; Eluent: *n*-hexane/EtOAc = 200/1;
^{1}H NMR (400 MH_Z $CDCl_3$, δ ppm): 0.85-0.87 (t, *J* = 4.0 Hz, 3H), 1.09-1.10 (t, *J* = 4.0 Hz, 3H), 1.26-1.31 (m, 8H), 1.38-1.42 (t, *J* = 8.0 Hz, 3H), 1.44-1.49 (m, 1H), 1.87-1.99 (m, 2H), 2.10 (m, 2H), 2.17-2.22 (m, 1H), 2.36-2.38 (d, *J* = 8.0 Hz, 1H), 2.57-2.59 (t, *J* = 4.0 Hz, 1H), 4.00-4.05 (q, *J* = 8.0 Hz, 2H), 5.57 (s, 1H), 5.67 (s, 2H), 6.83-6.85 (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): 14.1, 14.9, 19.8, 19.9, 20.8, 20.8, 22.7, 22.7, 25.0, 25.1, 25.2, 27.1, 27.2, 27.2, 29.1, 29.1, 29.2, 29.2, 31.3, 31.4, 31.5, 31.7, 32.1, 32.1, 33.1, 33.2, 33.2, 34.0, 34.0, 34.1, 34.2, 36.1, 36.1, 36.7, 36.7, 63.4, 76.7, 77.0, 77.3, 100.5, 100.6, 100.6, 112.7, 112.8, 114.4, 126.2, 126.3, 126.3, 126.8, 127.3, 129.7, 129.8, 129.8, 158.6, 201.4, 201.5, 201.5.
HRMS (ESI) calcd for $C_{24}H_{34}O$ $[M+K]^+$ m/z 377.2247, found 377.2248.



5q, 43%
d.r. = 1:1

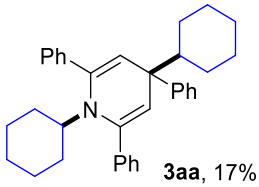
5q: yield 43%. According to **General Procedure**; colorless oil; Eluent: *n*-hexane/EtOAc = 200/1;
^{1}H NMR (400 MH_Z $CDCl_3$, δ ppm): 1.38-1.42 (t, *J* = 8.0 Hz, 3H), 1.44-1.52 (m, 3H), 1.58-1.68 (m, 4H), 1.87-1.95 (m, 4H), 2.09-2.10 (t, *J* = 4.0 Hz, 2H), 2.17-2.21 (d, *J* = 16.0 Hz, 1H), 2.35-2.41 (m, 1H), 2.88-2.92 (m, 1H), 4.00-4.05 (q, *J* = 8.0 Hz, 2H), 5.55-5.58 (t, *J* = 8.0 Hz, 1H), 5.67 (s, 2H), 6.83-6.84 (d, *J* = 4.0 Hz, 2H), 7.33-7.35 (d, *J* = 8.0 Hz, 2H);
^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 14.9, 25.1, 25.1, 25.2, 29.1, 31.2, 31.5, 32.3, 32.4, 32.9, 34.1, 39.3, 63.4, 100.5, 100.6, 111.5, 114.3, 126.2, 126.3, 126.9, 127.4, 157.6, 200.8, 200.8.
HRMS (ESI) calcd for $C_{22}H_{28}O$ $[M+K]^+$ m/z 347.1777, found 347.1775.


5s, 57%

5s: yield 57%. According to **General Procedure**; colorless oil; Eluent: *n*-hexane/EtOAc = 200/1;
^{1}H NMR (400 MH_Z $CDCl_3$, δ ppm): 0.88-0.91 (t, *J* = 6.0 Hz, 3H) 1.01-1.07 (t, *J* = 12.0 Hz, 2H), 1.10-1.26 (m, 4H), 1.38-1.43 (m, 2H), 1.62-1.73 (m, 6H), 1.88-1.93 (m, 2H), 3.31-3.32 (d, *J* = 4.0 Hz, 2H), 5.25-5.26 (d, *J* = 4.0 Hz 1H), 6.17-6.21 (m, 2H), 7.23-7.30 (m, 3H);

^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 14.0, 21.1, 26.4, 26.6, 32.3, 32.4, 33.1, 36.6, 40.8, 76.7, 77.0, 77.3, 92.1, 110.3, 125.9, 128.2, 128.5, 128.6, 141.2, 201.0.

HRMS (ESI) calcd for $C_{19}H_{26}$ $[M+Na]^+$ m/z 277.1932, found 277.1930.



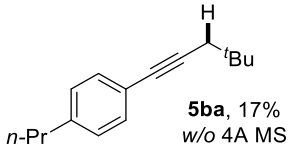
3aa, 17%

3aa: yield 17%. According to **General Procedure**; colorless oil; Eluent: *n*-hexane/EtOAc = 200/1;

^{1}H NMR (400 MH_Z $CDCl_3$, δ ppm): 0.50-0.56 (m, 1H), 0.60-0.75 (m, 4H), 0.90-1.28 (m, 10H), 1.43-1.46 (d, *J* = 12.0 Hz, 2H), 1.52-1.55 (d, *J* = 12.0 Hz, 2H), 1.61-1.64 (d, *J* = 12.0 Hz, 2H), 2.76-2.81 (t, *J* = 12.0 Hz, 1H), 5.27 (s, 2H), 7.12-7.16 (t, *J* = 8.0 Hz, 1H), 7.30-7.43 (m, 10H), 7.60-7.62 (d, *J* = 8.0 Hz, 4H);

^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 25.4, 26.6, 26.6, 26.9, 28.6, 33.2, 46.9, 50.2, 62.7, 115.8, 125.0, 126.9, 127.6, 127.8, 127.9, 128.0, 141.0, 145.2, 151.2;

HRMS (ESI) calcd for $C_{35}H_{39}N$ $[M+H]^+$ m/z 474.3161, found 474.3156.



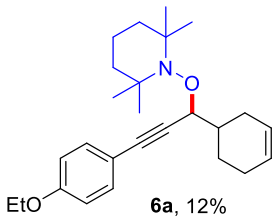
5ba, 17%
w/o 4A MS

5ba: yield 17%. According to **General Procedure**; colorless oil; Eluent: *n*-hexane/EtOAc = 200/1;

^{1}H NMR (400 MH_Z $CDCl_3$, δ ppm): 0.90-0.94 (t, *J* = 8.0 Hz, 3H), 1.05 (s, 9H), 1.59-1.66 (m, 2H), 2.26 (s, 2H), 2.54-2.58 (t, *J* = 8.0 Hz, 2H), 7.08-7.10 (d, *J* = 8.0 Hz, 2H), 7.31-7.33 (d, *J* = 8.0 Hz, 2H);

^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 13.7, 24.4, 29.1, 31.4, 34.5, 37.9, 82.1, 88.0, 121.4, 128.3, 131.4, 142.2;

HRMS (ESI) calcd for $C_{16}H_{22}$ $[M+H]^+$ m/z 215.1800, found 215.1798.



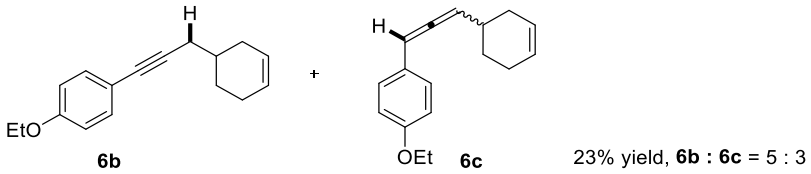
6a, 12%

6a: yield 12%. According to **General Procedure**; colorless oil; Eluent: *n*-hexane/EtOAc = 200/1;

^{1}H NMR (400 MH_Z $CDCl_3$, δ ppm): 1.11-1.21 (m, 9H), 1.26-1.54 (m, 12H), 1.76-2.04 (m, 2H), 2.12-2.24 (m, 5H), 3.99-4.04 (q, *J* = 8.0 Hz, 2H), 4.62-4.64 (t, *J* = 4.0 Hz, 1H), 5.66-5.75 (m, 2H), 6.79-6.81 (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): 14.7, 17.2, 20.4, 24.0, 25.1, 25.3, 25.5, 26.8, 28.1, 33.9, 34.6, 38.7, 38.9, 40.2, 59.5, 60.5, 63.4, 78.7, 79.4, 86.6, 86.8, 88.0, 88.1, 114.3, 115.7, 126.3, 126.5, 126.7, 127.0, 132.7, 158.6;

HRMS (ESI) calcd for $C_{26}H_{37}NO_2$ $[M+H]^+$ m/z 396.2903, found 396.2899.



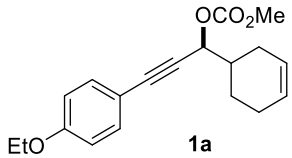
6b+6c: yield 23%. According to **General Procedure**; colorless oil; Eluent: *n*-hexane/EtOAc = 200/1;

^{1}H NMR (400 MHz $CDCl_3$, δ ppm): 1.38-1.42 (t, *J* = 8.0 Hz, 3H), 1.86-2.38 (m, 8H), 3.99-4.04 (q, *J* = 8.0 Hz, 2H), 5.59-5.67 (m, 2.4H), 6.05-6.16 (m, 0.38H), 6.78-6.84 (m, 2H), 7.19-7.21 (d, *J* = 8.0 Hz, 0.76H), 7.30-7.33 (d, *J* = 12.0 Hz, 1.26H);

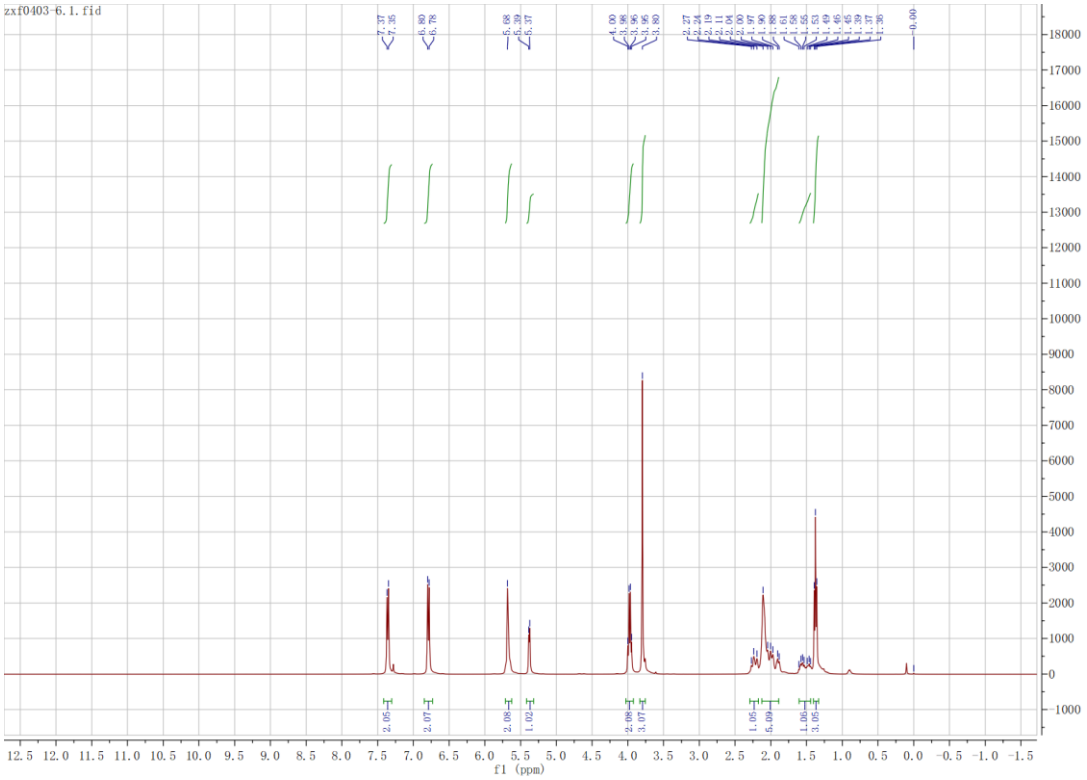
^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 14.8, 14.8, 24.9, 25.0, 26.3, 28.2, 28.8, 28.9, 31.2, 31.3, 31.4, 33.4, 33.6, 33.7, 63.5, 63.5, 81.3, 87.1, 95.2, 95.2, 100.2, 100.2, 114.4, 114.7, 114.7, 116.1, 126.0, 126.1, 126.2, 126.6, 126.7, 126.8, 126.9, 127.2, 127.2, 127.5, 127.6, 132.8, 158.0, 158.4, 203.5, 203.6;

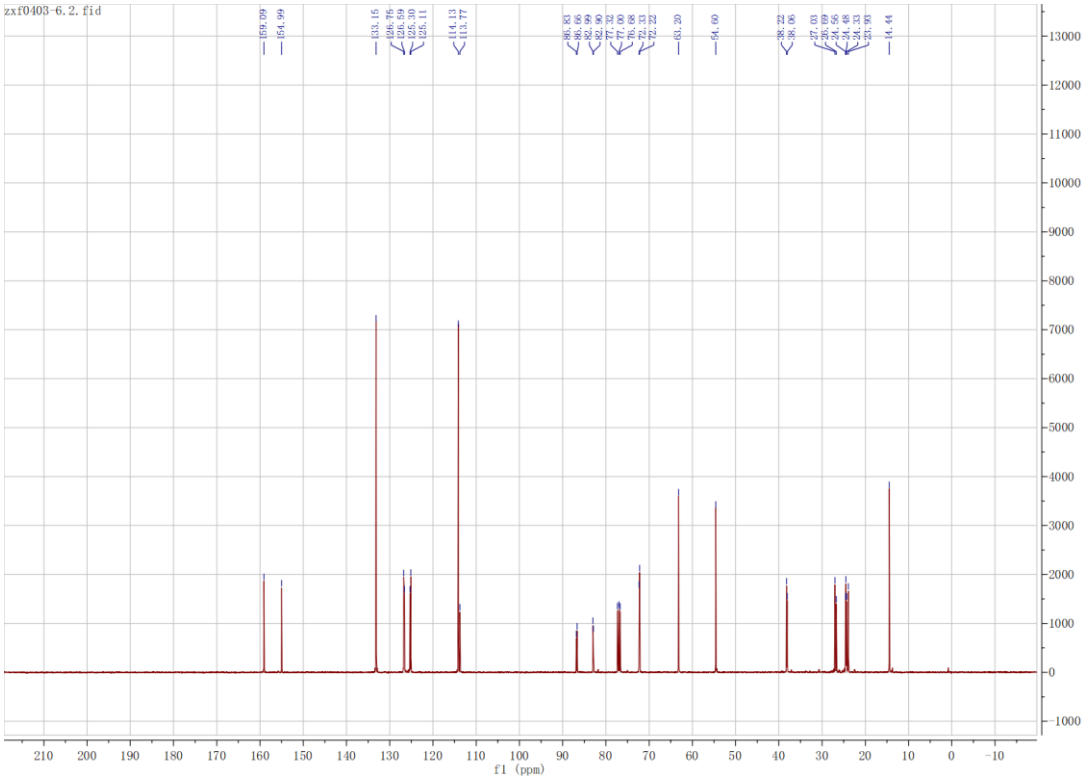
HRMS (ESI) calcd for $C_{17}H_{20}O$ $[M+H]^+$ m/z 241.1592, found 241.1589.

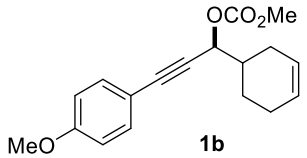
10. ^{1}H NMR and ^{13}C NMR Spectra of the Substrates 1a-1b, 4a-4l, 4s:



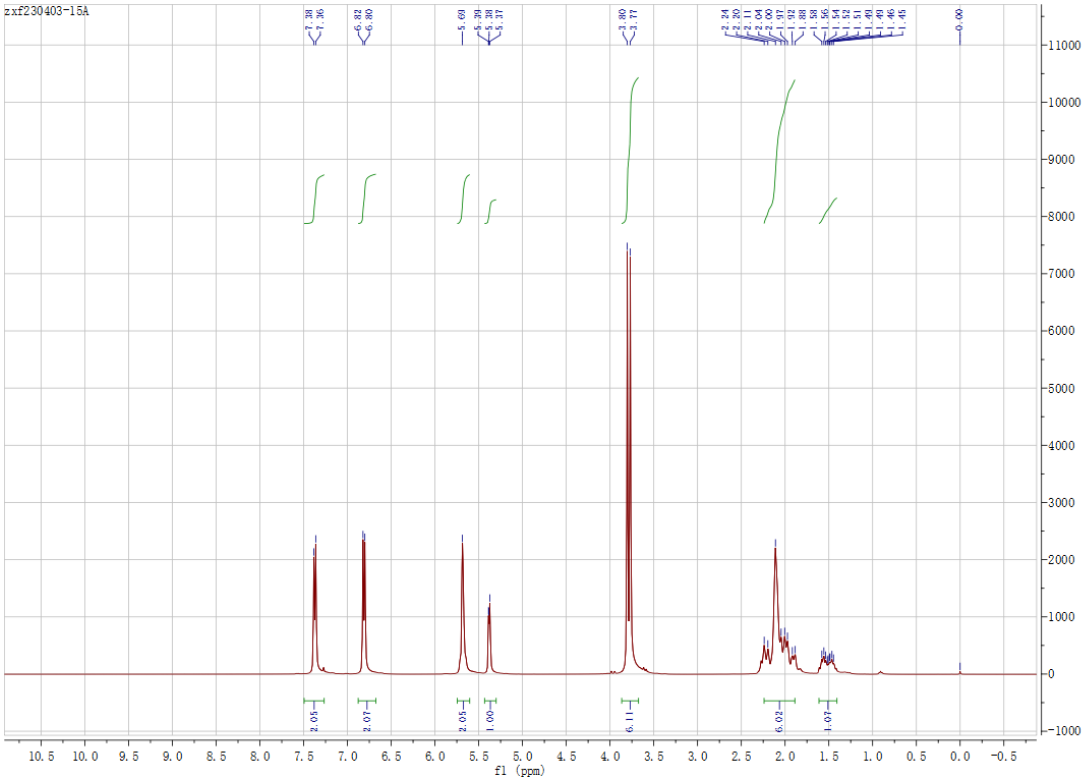
1a

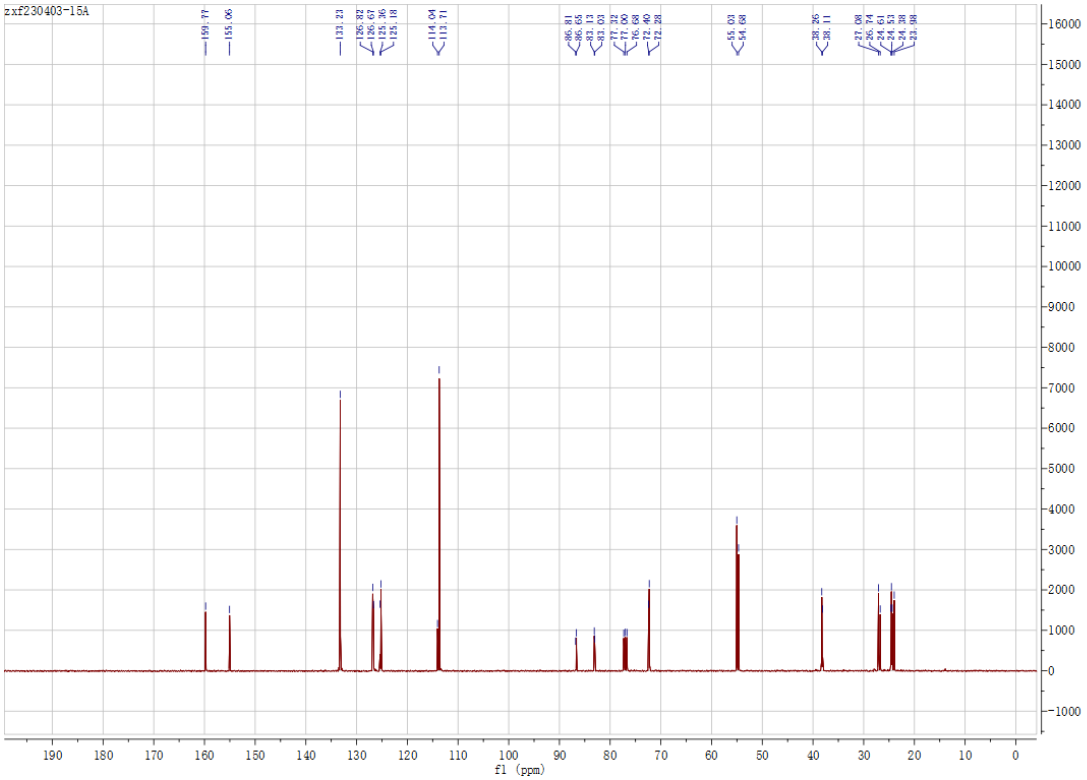


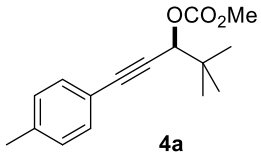




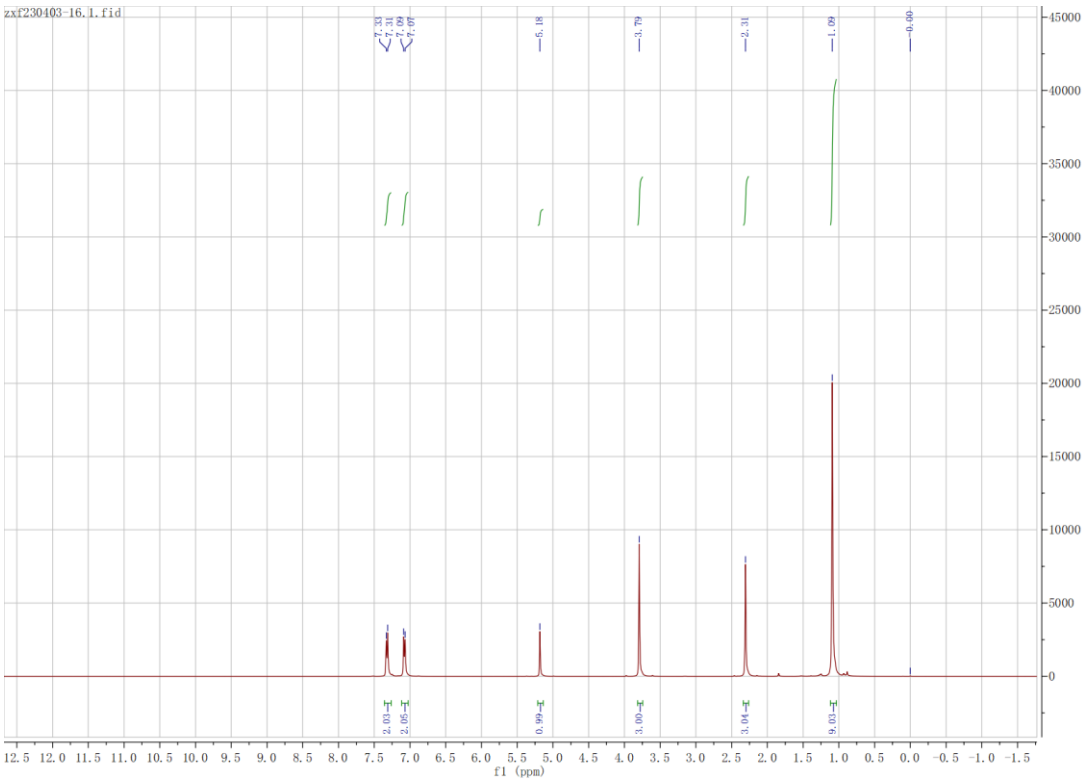
1b






OCO2Me

4a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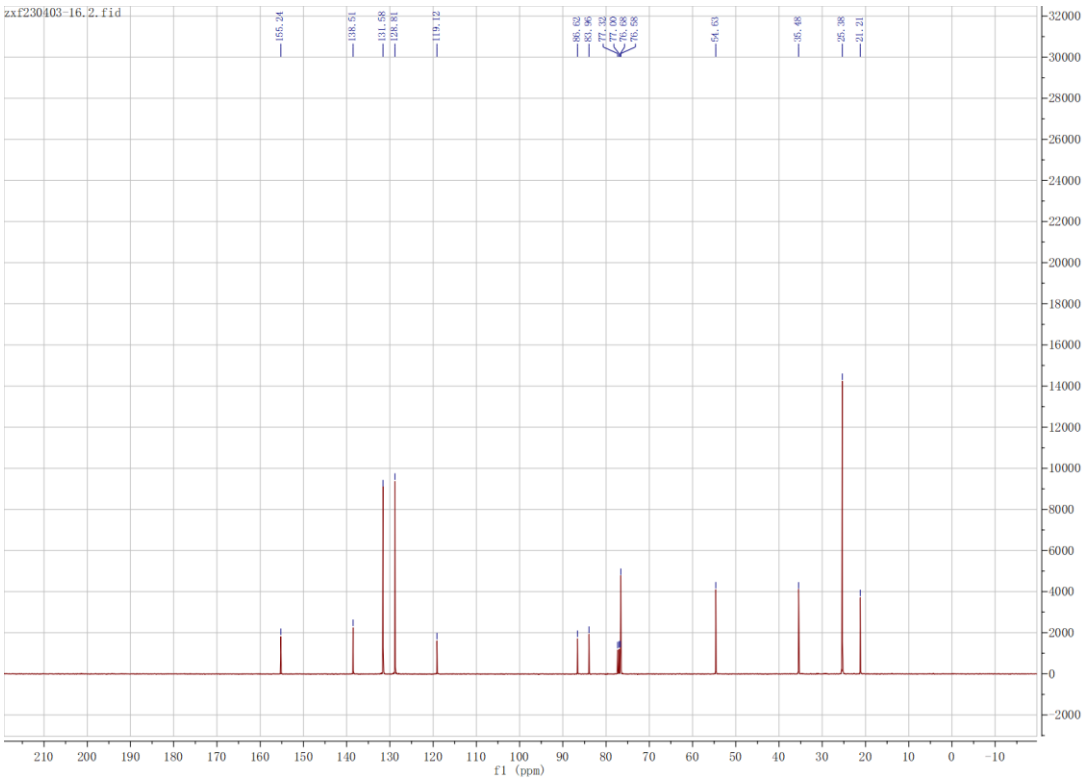
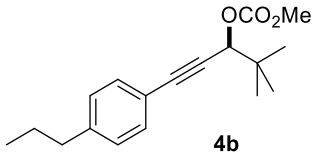
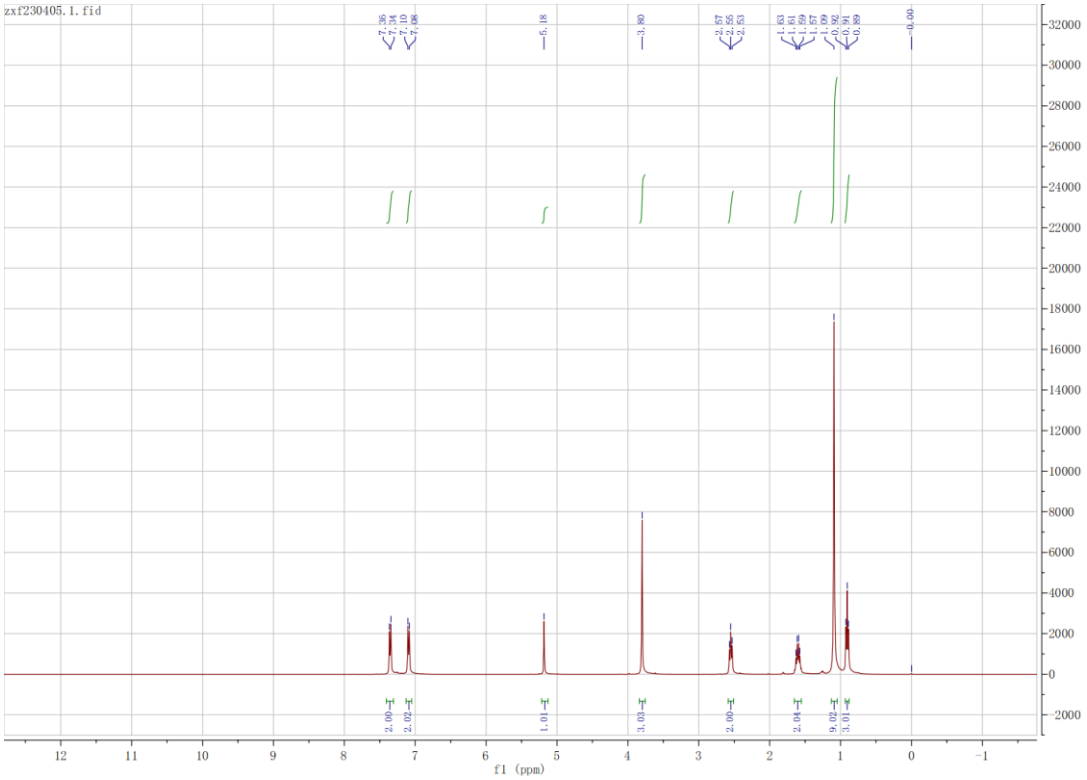
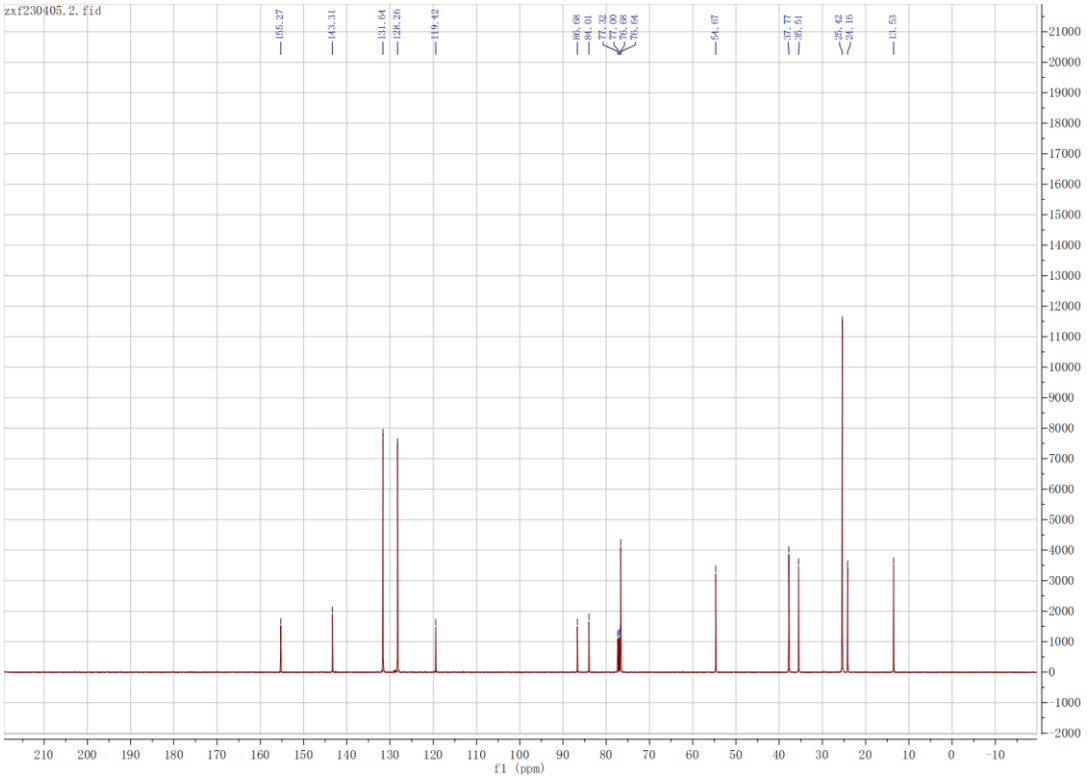
7.33
7.31
7.09
7.07
5.18
3.79
2.31
1.09
0.00
2.03
2.05
0.99
3.00
3.04
9.03
f1 (ppm)

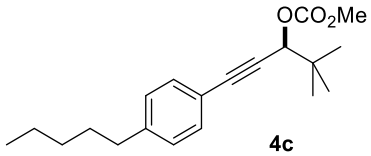

zxf230403-16.2.fid
155.24
138.51
131.58
128.84
119.72
86.62
85.96
77.32
77.00
76.68
76.38
64.63
36.48
25.38
21.21
f1 (ppm)



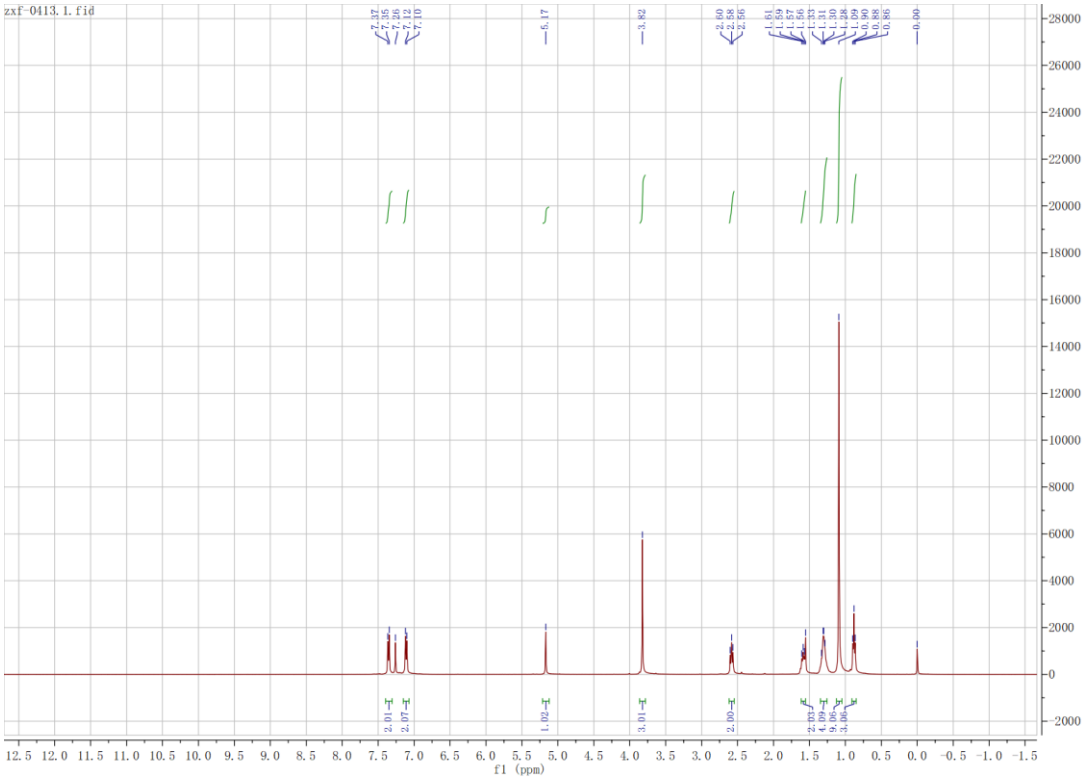
4b

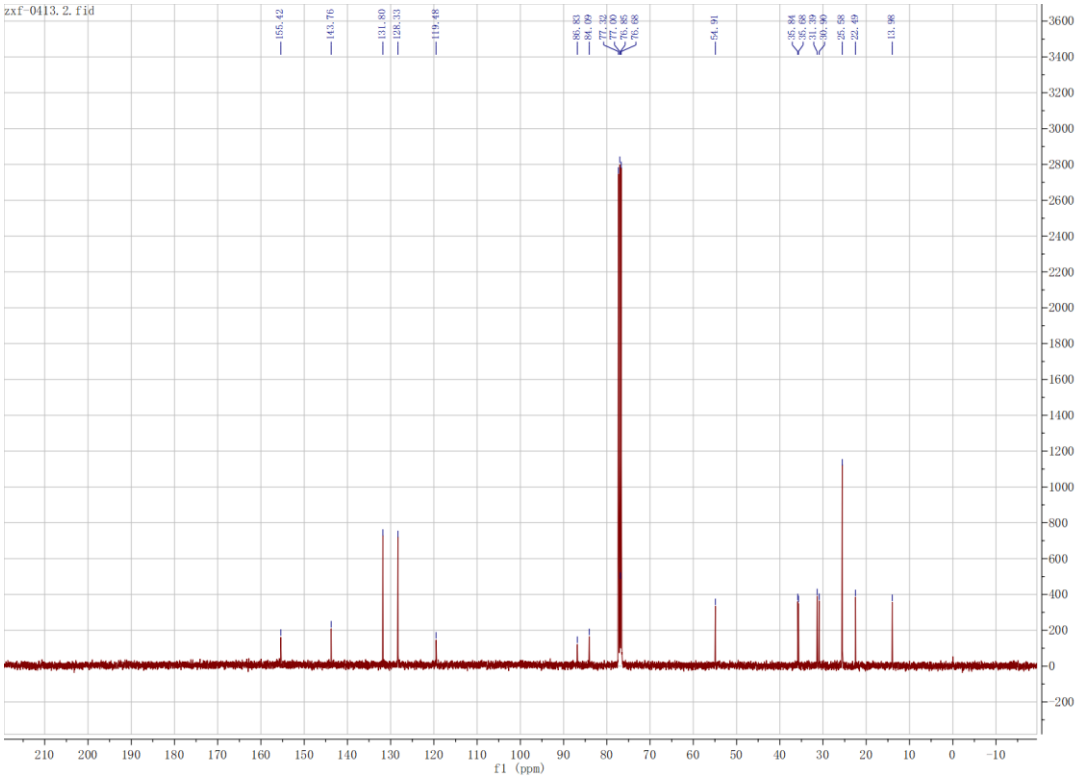


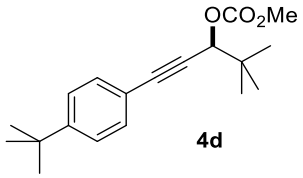




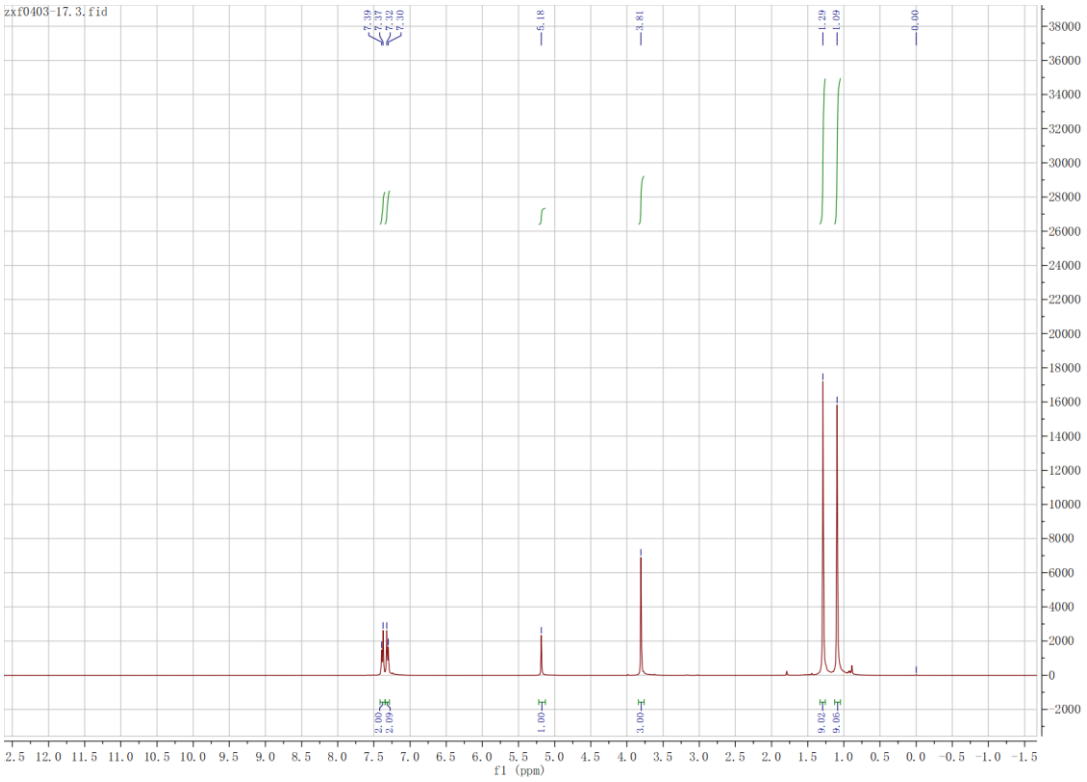
4c






OCO2Me

4d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7.39
7.37
7.32
7.30
6.18
3.81
1.29
1.09
0.00
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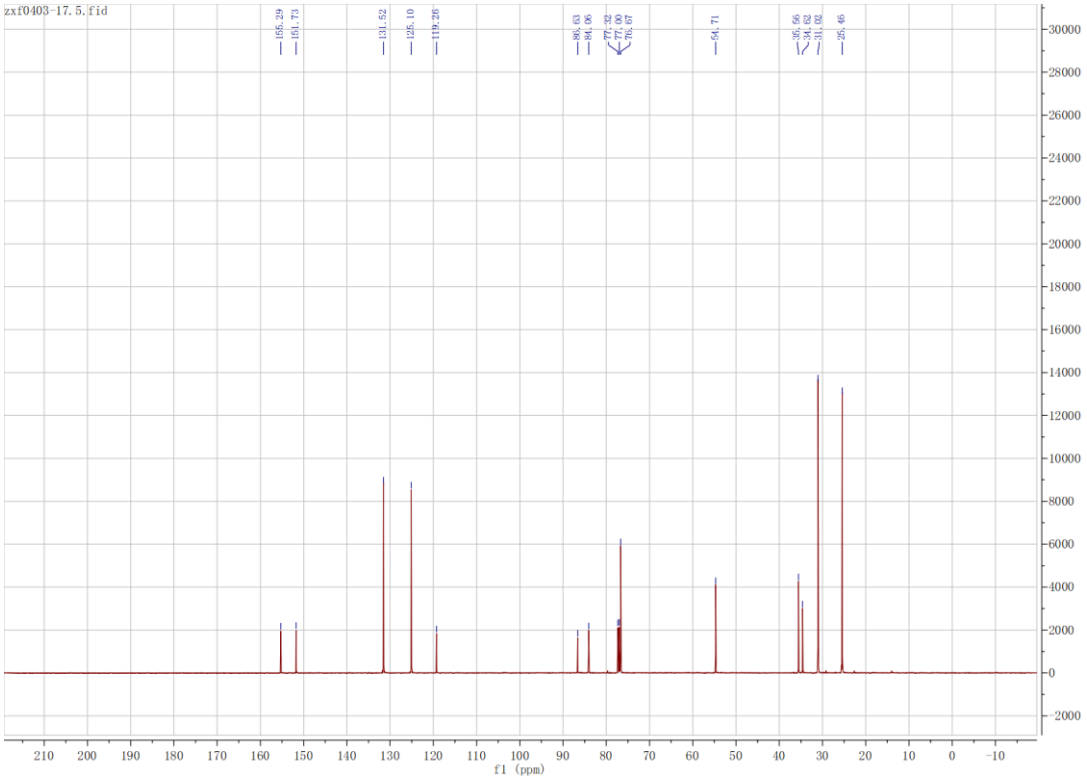
2.09
1.00
3.00
9.02
9.06
f1 (ppm)


zxf0403-17.5.fid
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151.73
131.52
125.10
119.26
86.63
84.56
77.32
77.00
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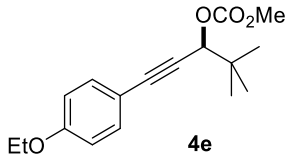
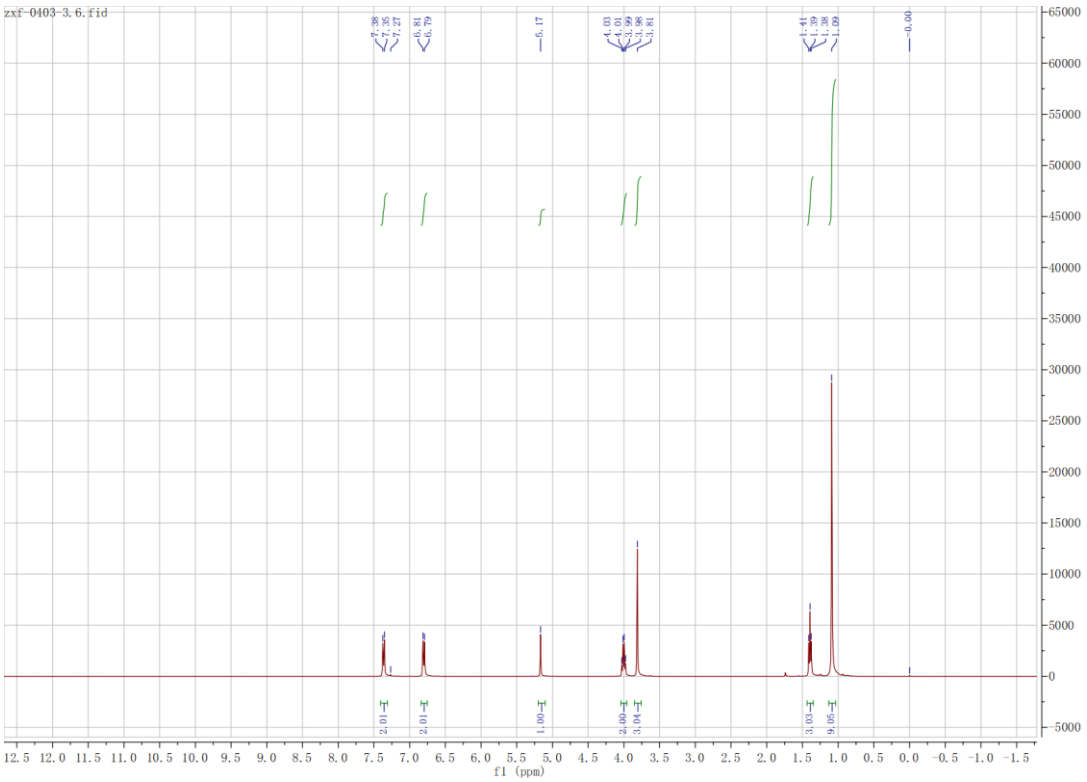
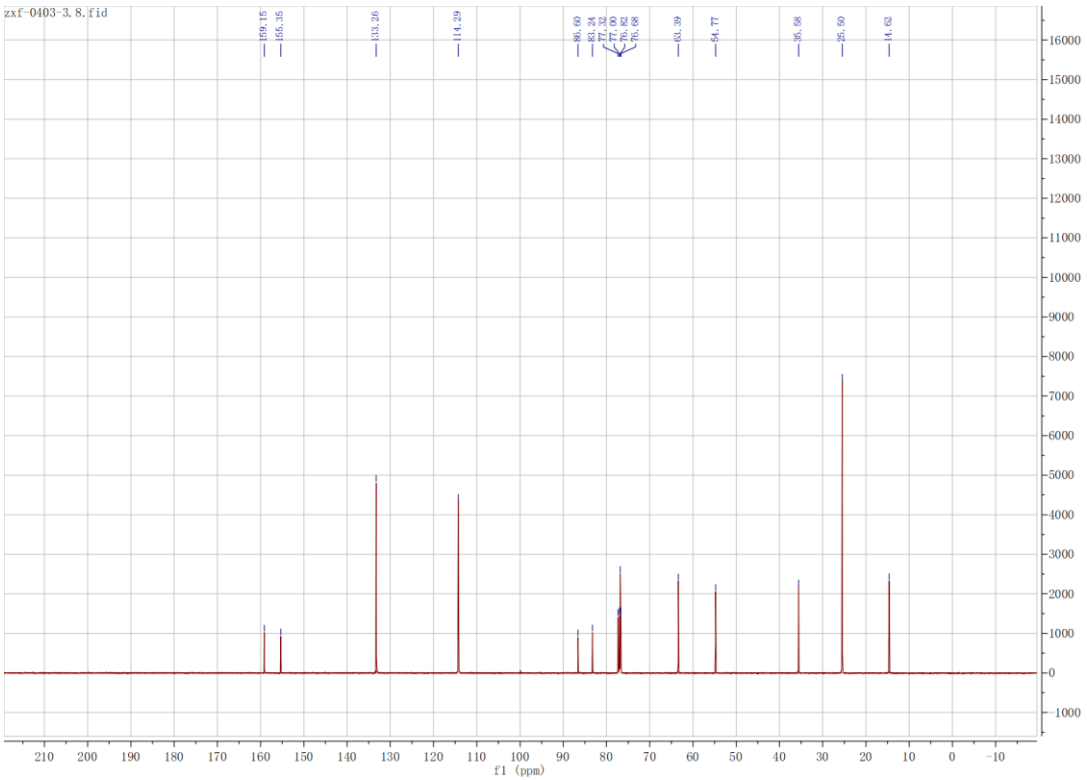
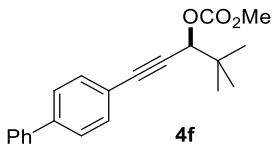
35.56
34.62
31.02
25.46
f1 (ppm)



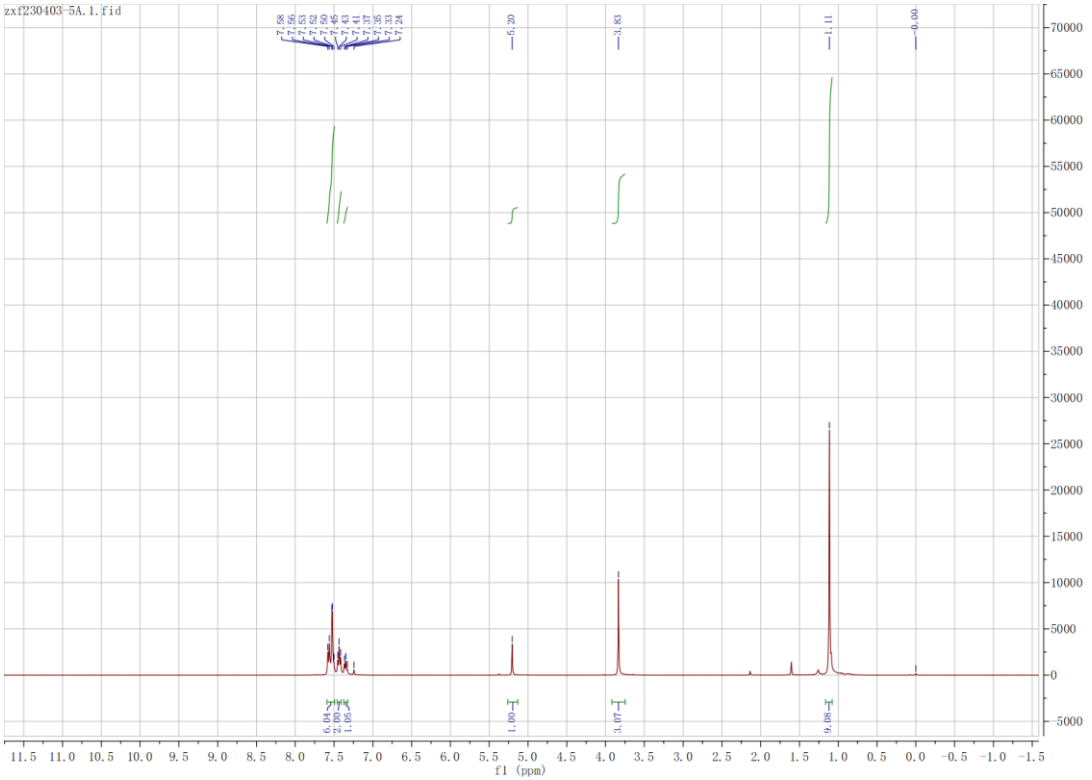
4e

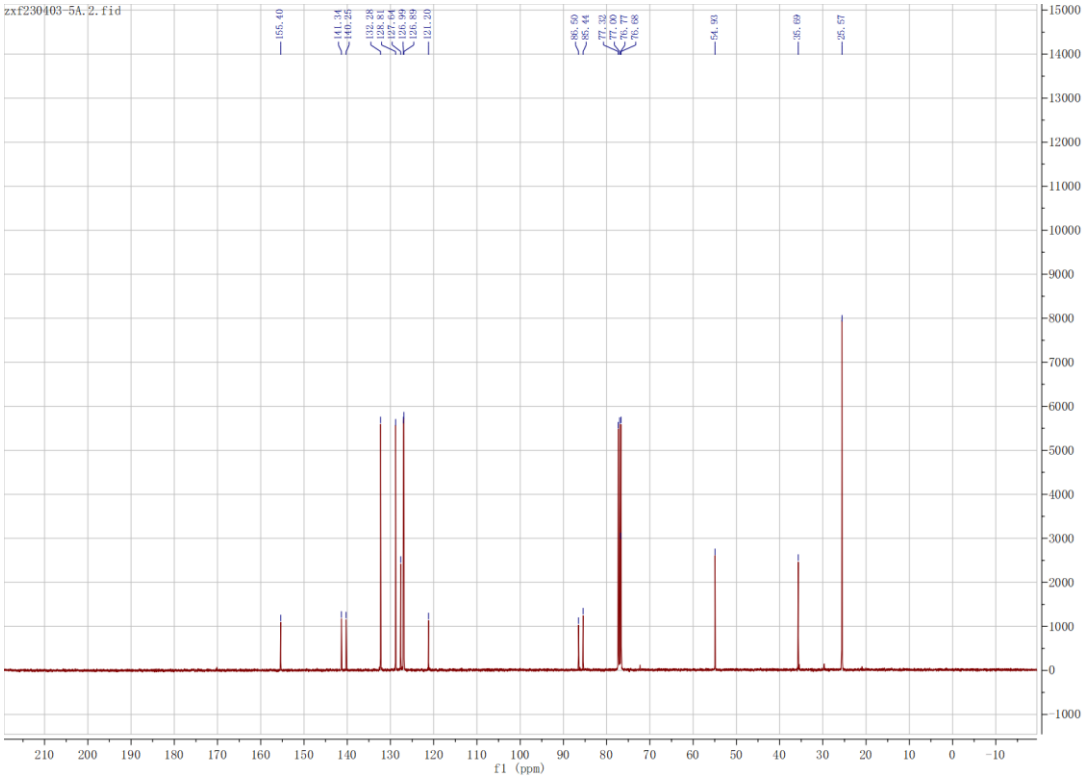


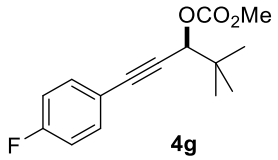




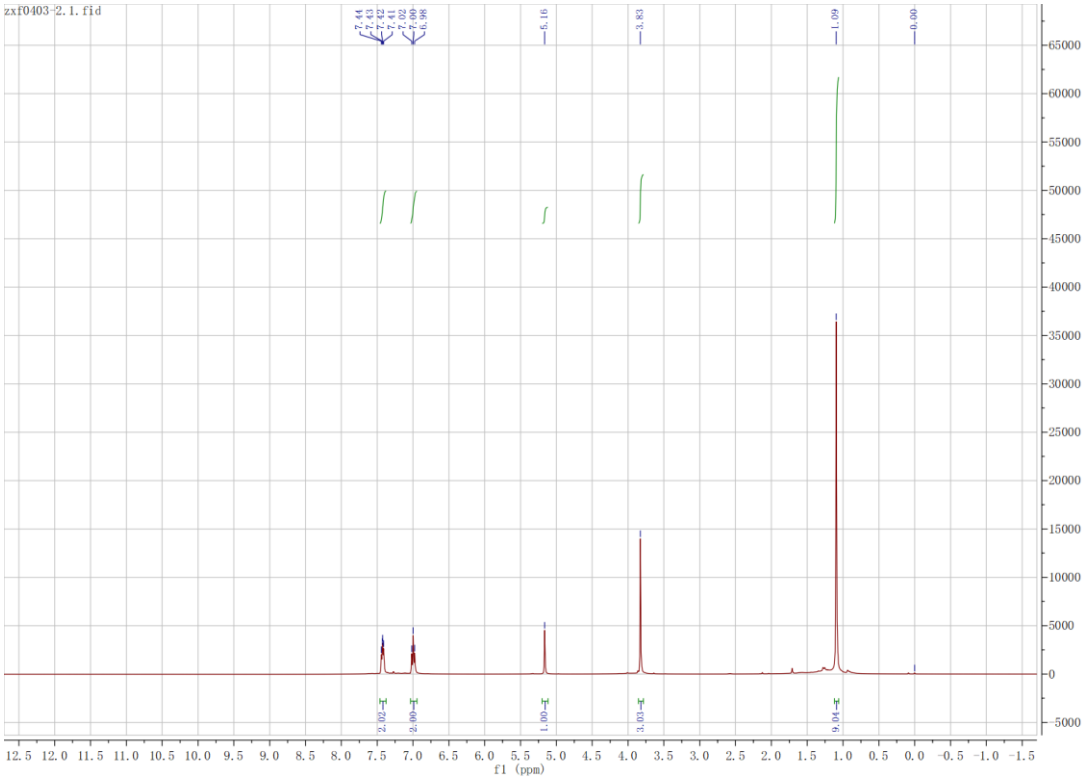
4f






OCO2Me
F

4g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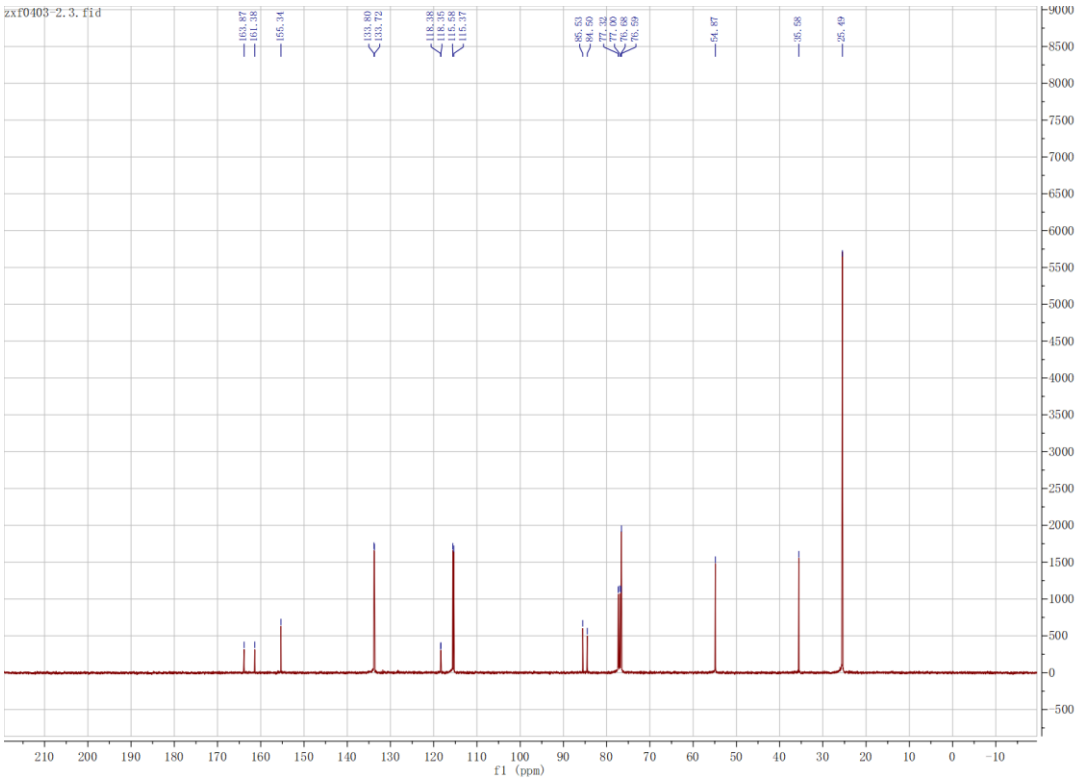
7.43
7.42
7.41
7.02
7.00
6.98
5.16
3.83
1.09
0.00
2.02
2.00
1.00
3.03
9.04
f1 (ppm)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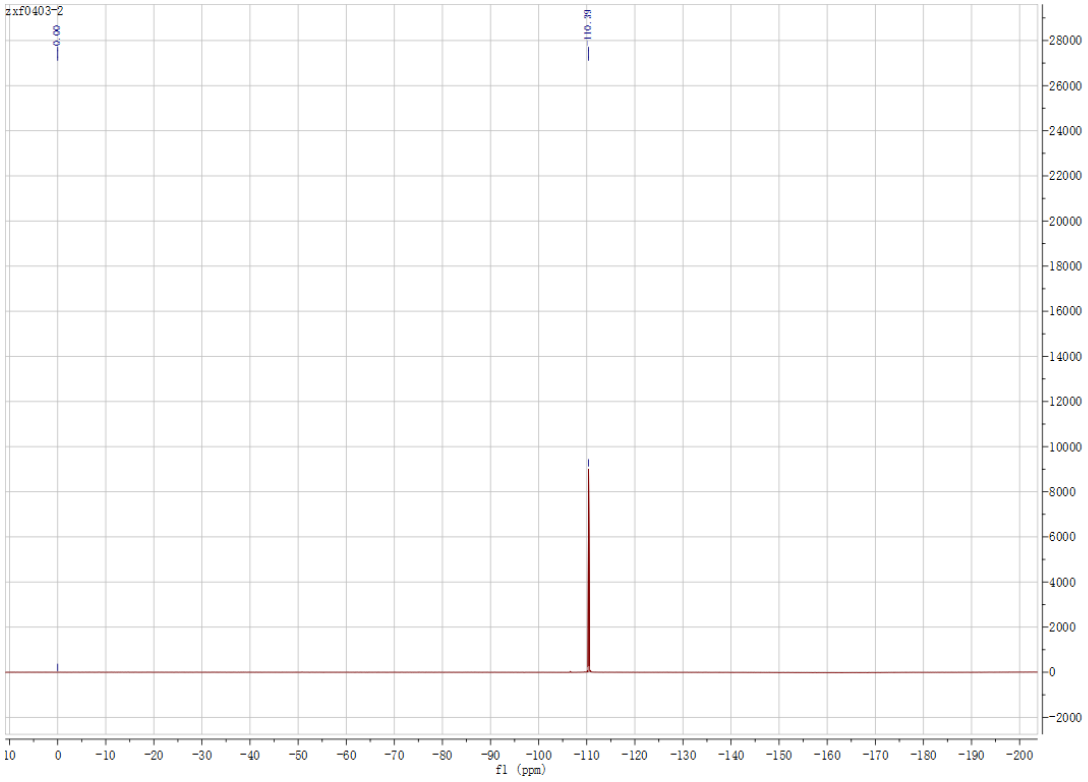
161.36
155.34
133.80
133.72
118.38
118.35
116.58
116.37
86.53
84.59
77.32
77.00
76.68
76.59
54.87
35.58
25.49
f1 (ppm)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-110.79
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26000
24000
22000
20000
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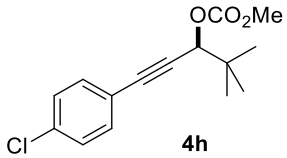
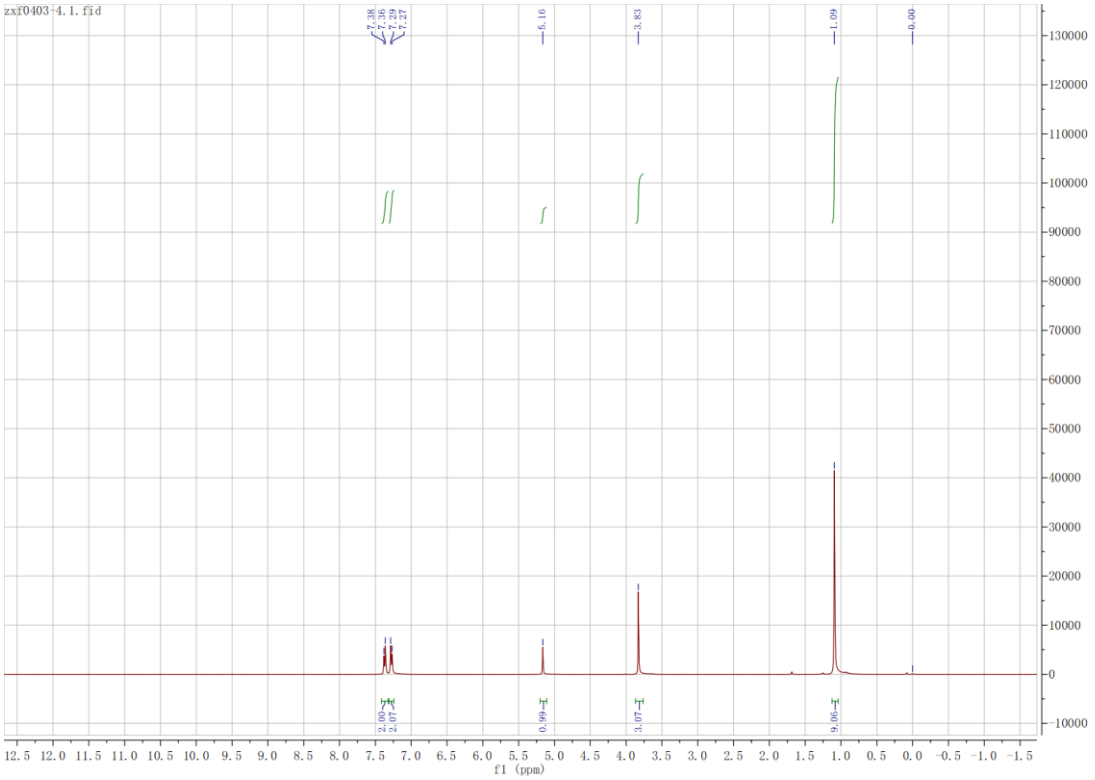
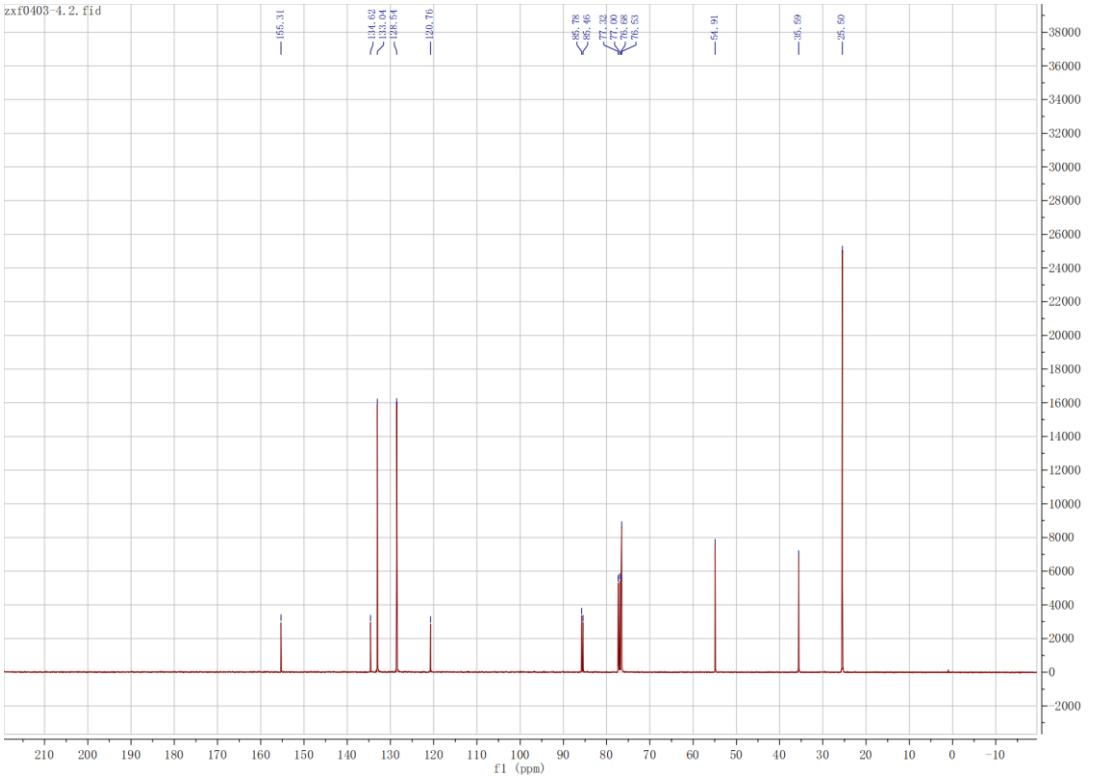
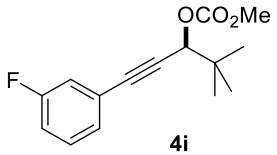
14000
12000
10000
8000
6000
4000
2000
0
-2000
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)



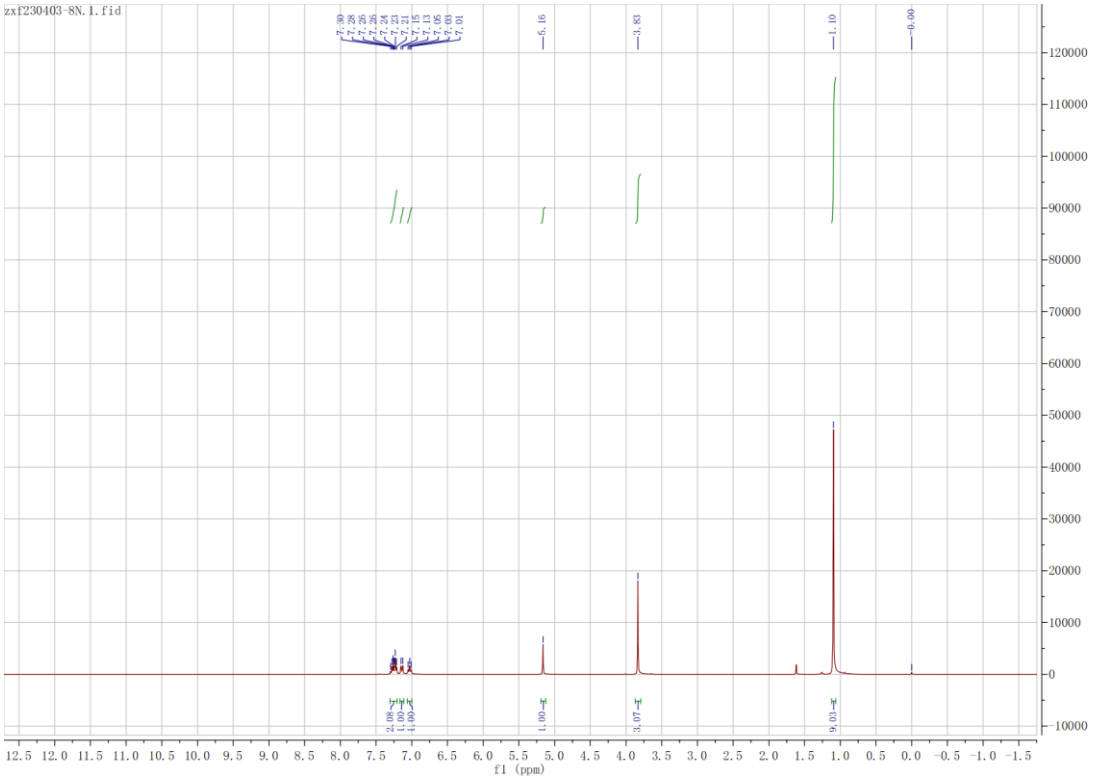
4h

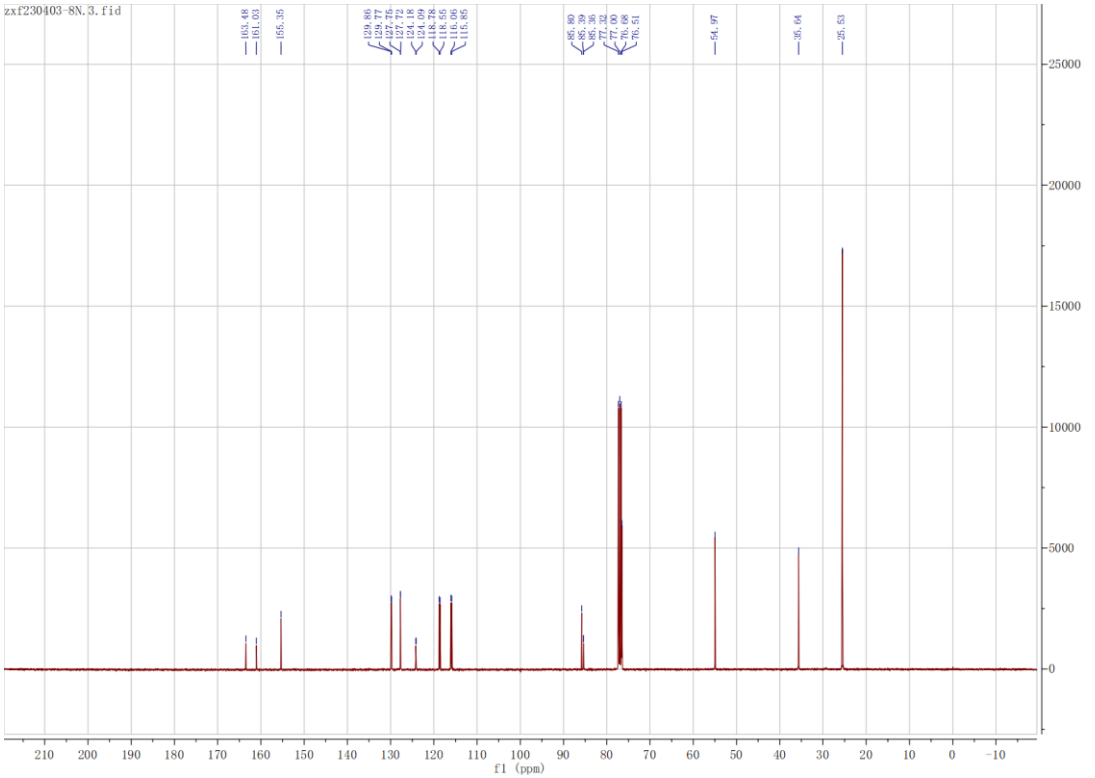


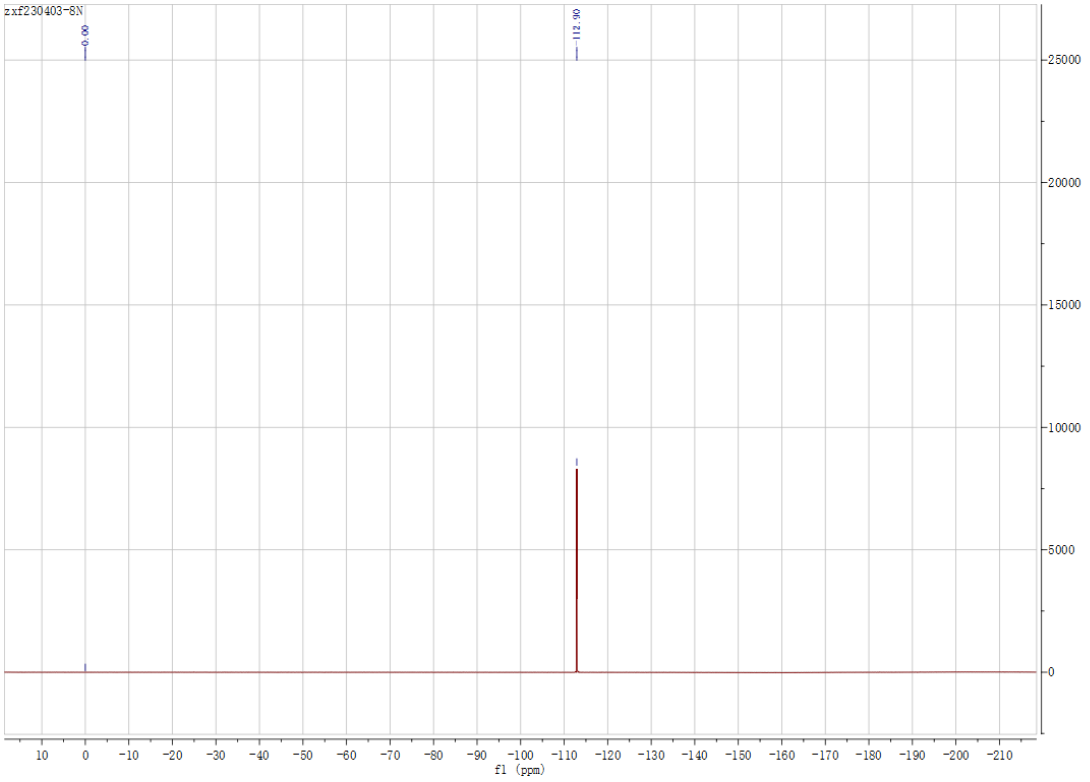


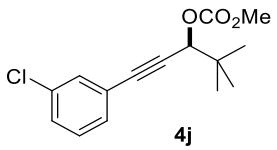


4i

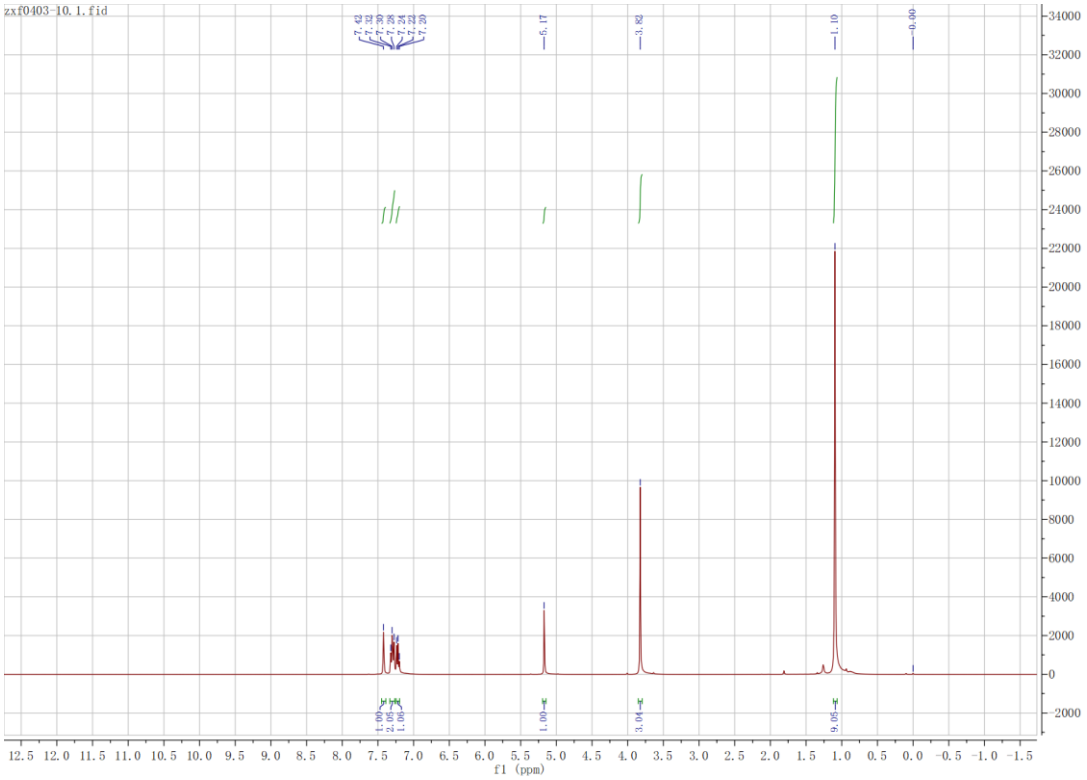


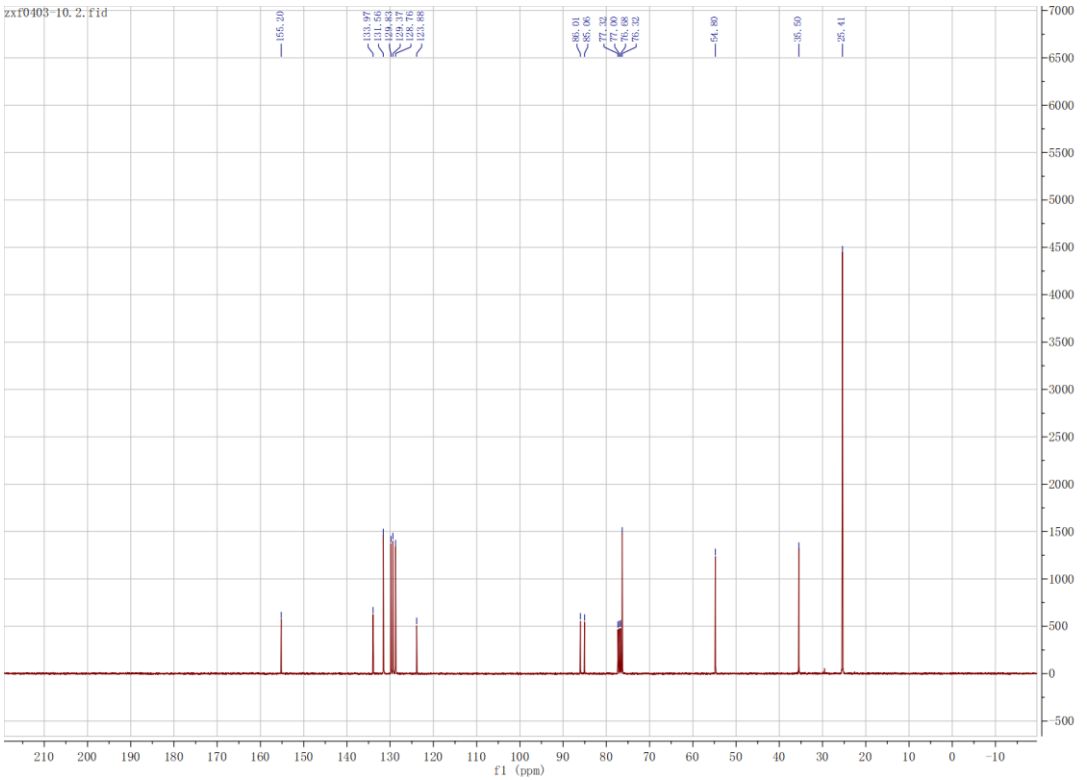


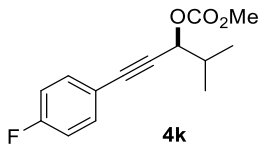

zxf230403-8N
0.00
-112.90
25000
20000
15000
10000
5000
0
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)



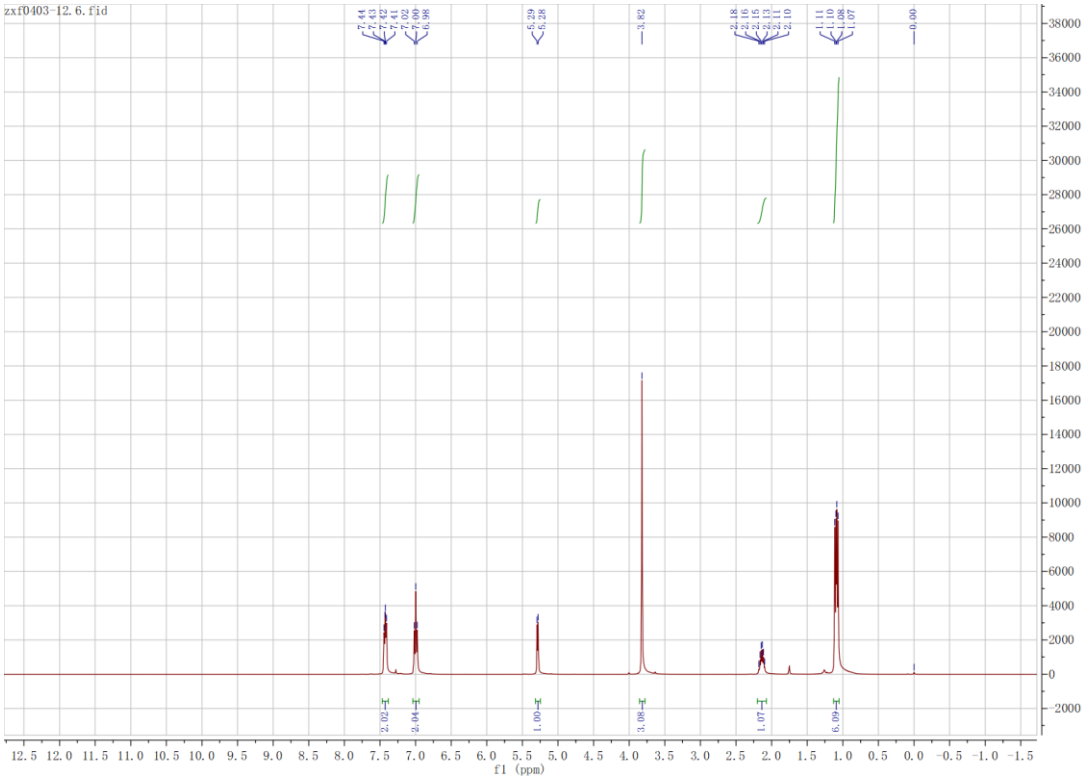
4j

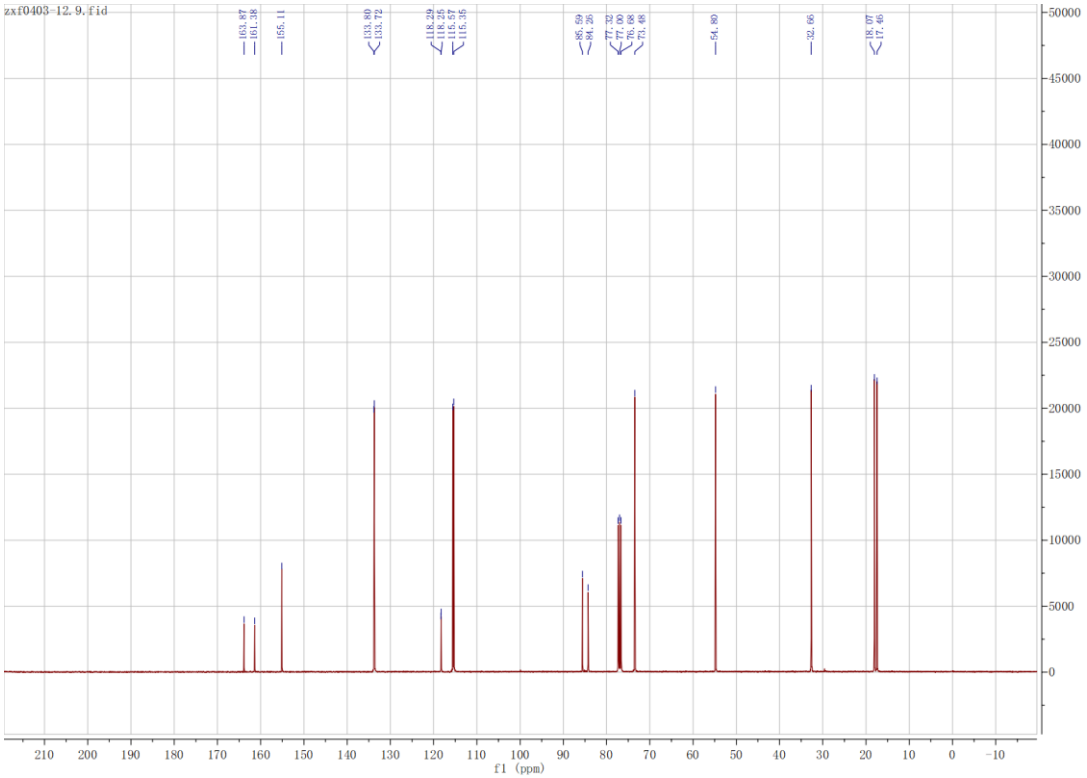


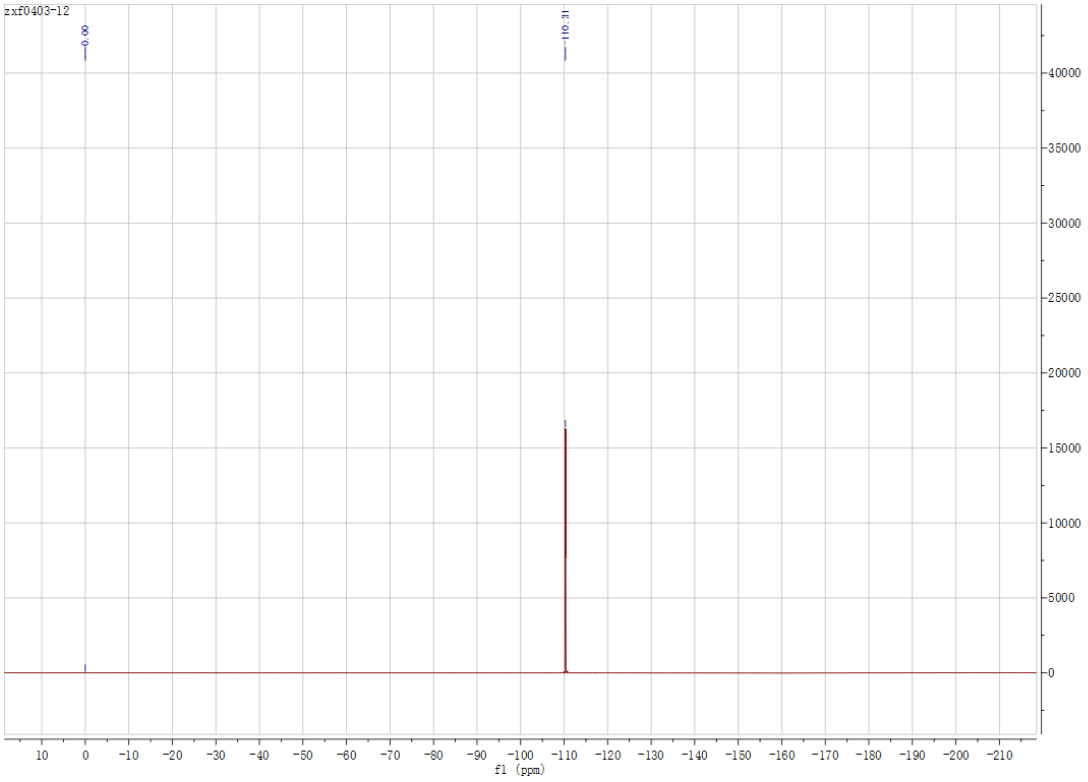


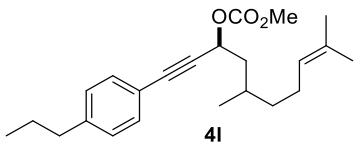


4k

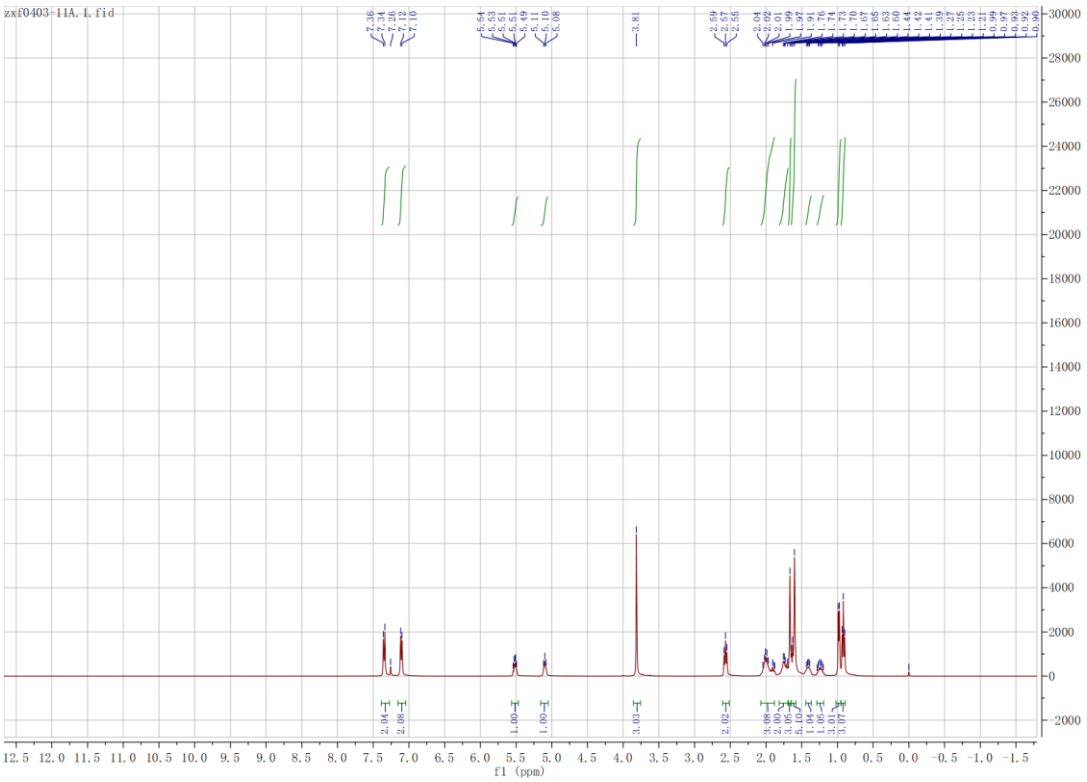


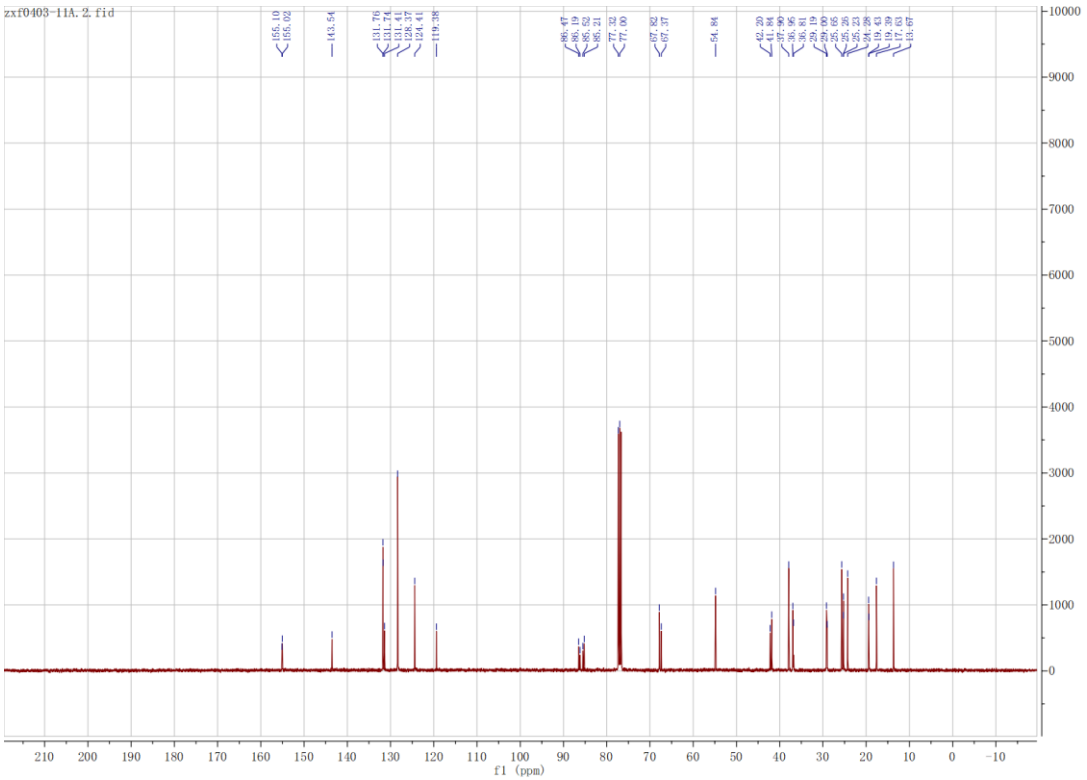



zxf0403-12
0.00
-110.31
40000
35000
30000
25000
20000
15000
10000
5000
0
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

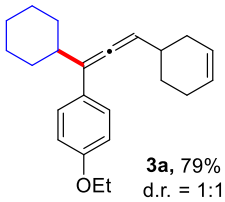


4l

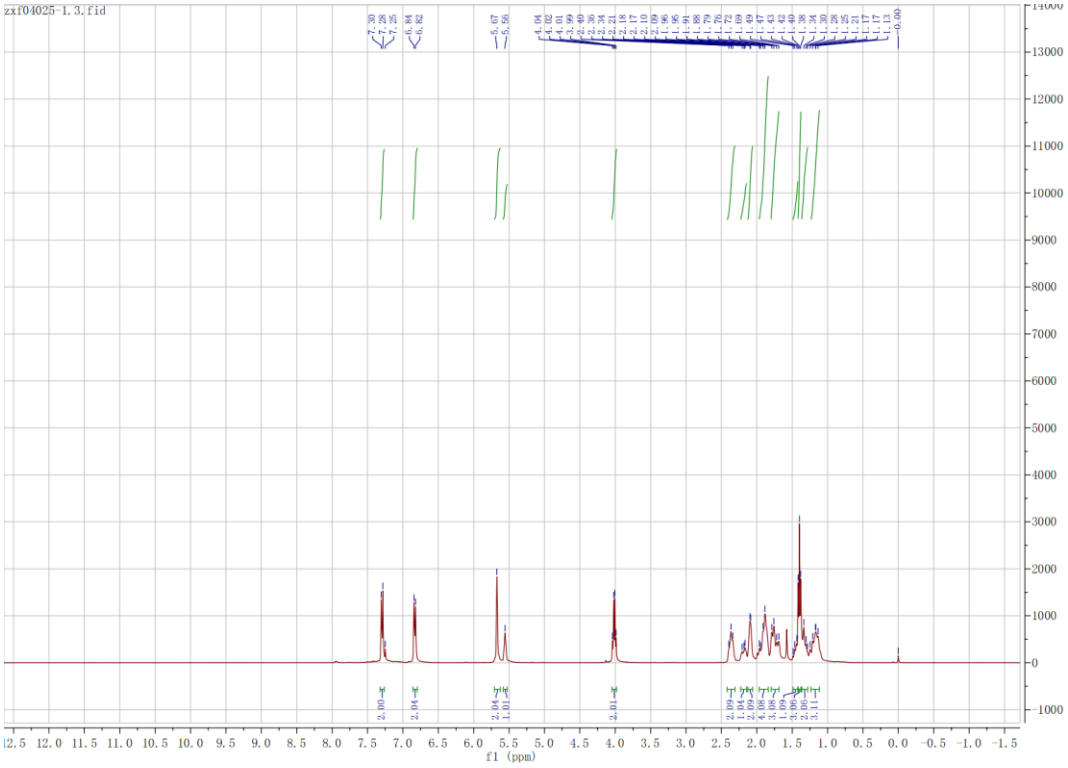


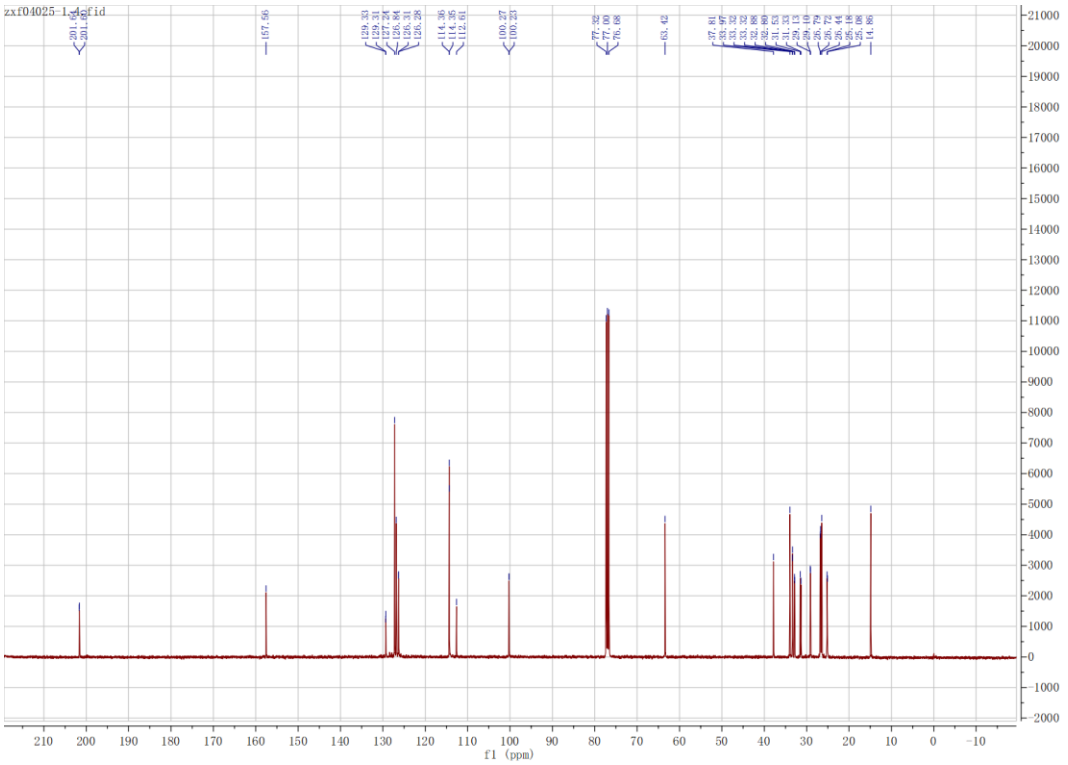


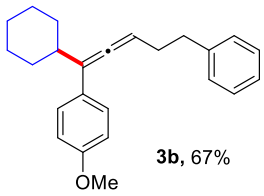
11. ^{1}H NMR and ^{13}C NMR Spectra of the Products 3a-3n:



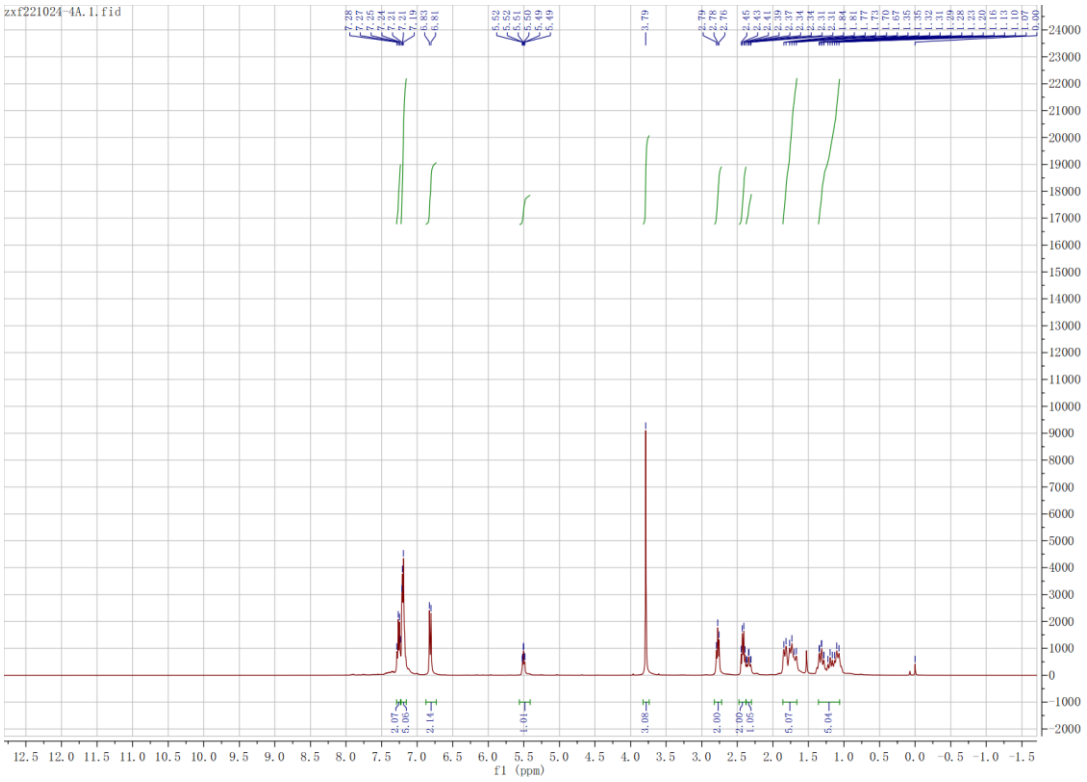
3a, 79%
d.r. = 1:1

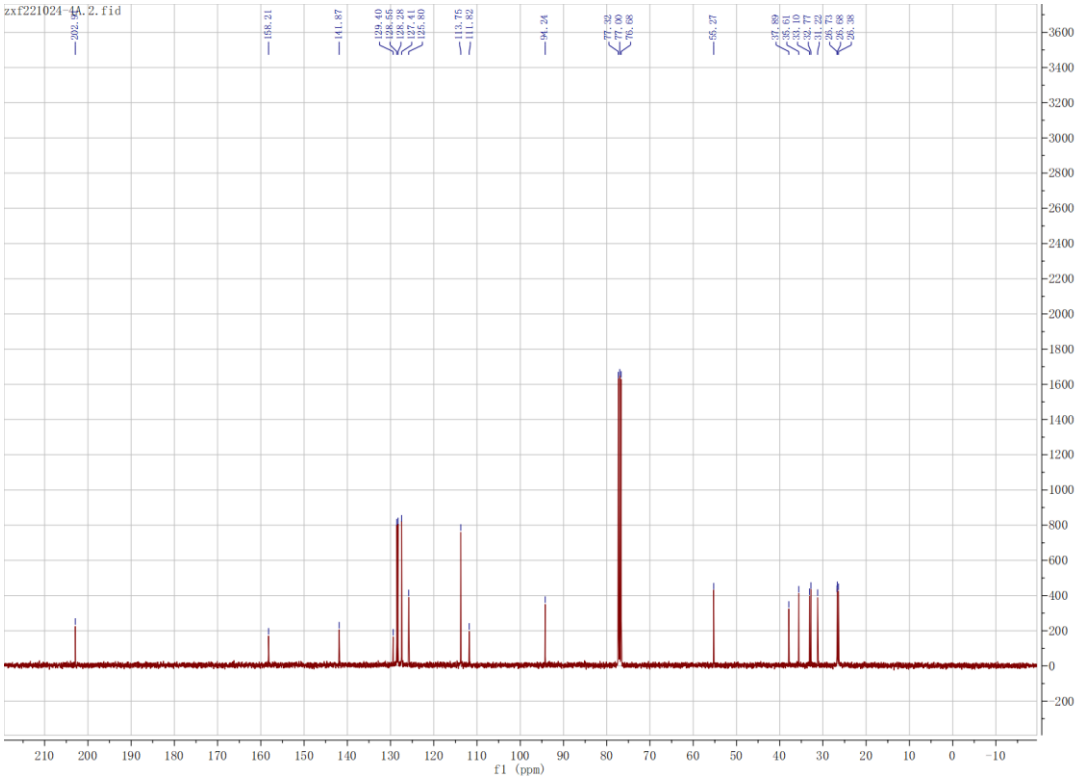


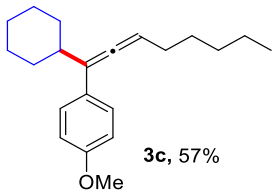




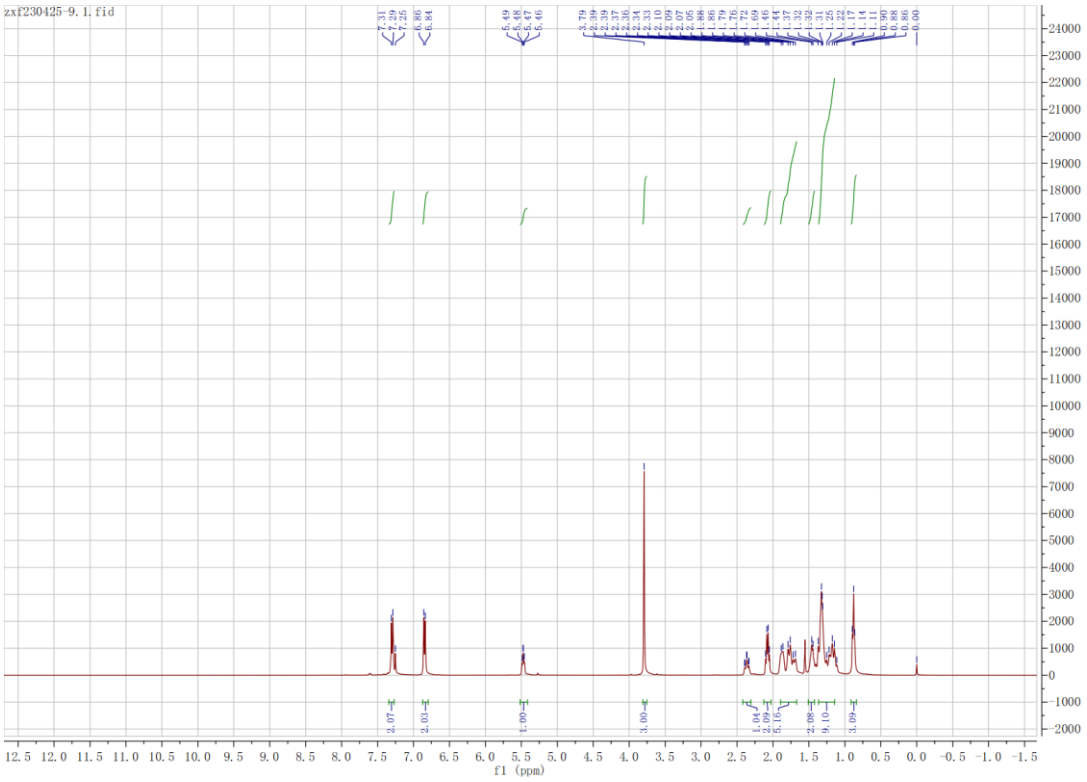
3b, 67%

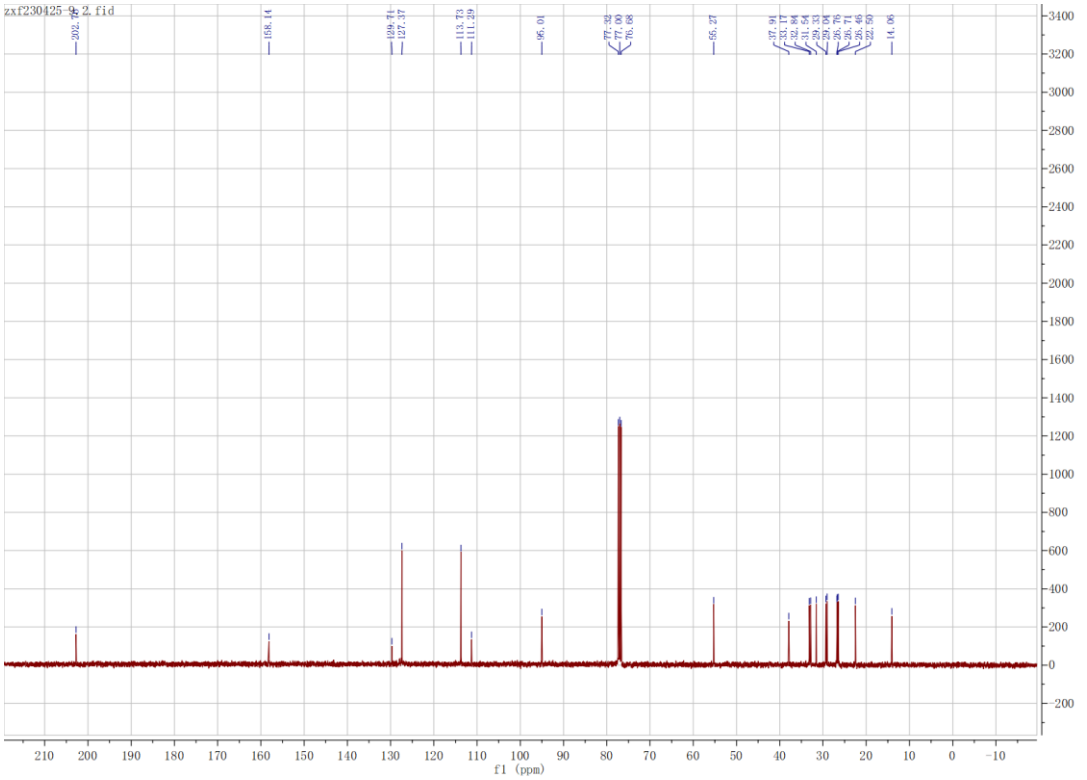


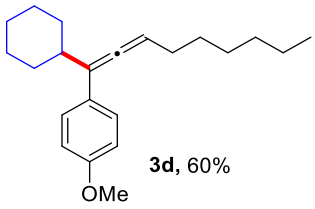




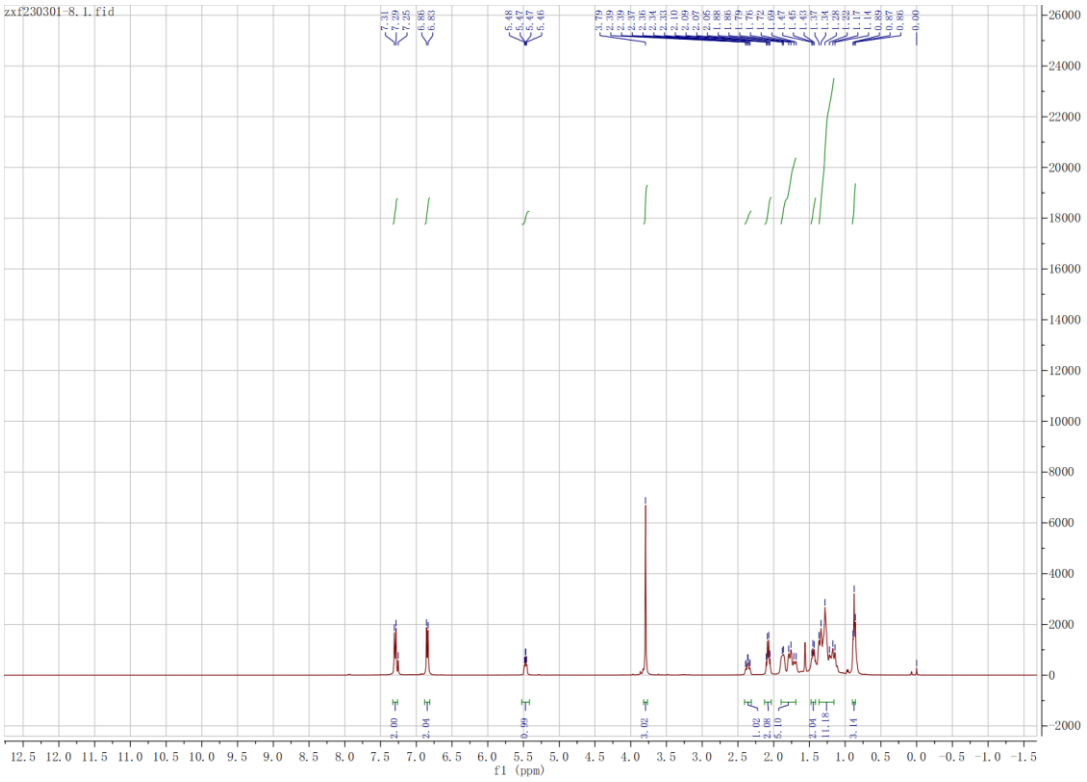
3c, 57%

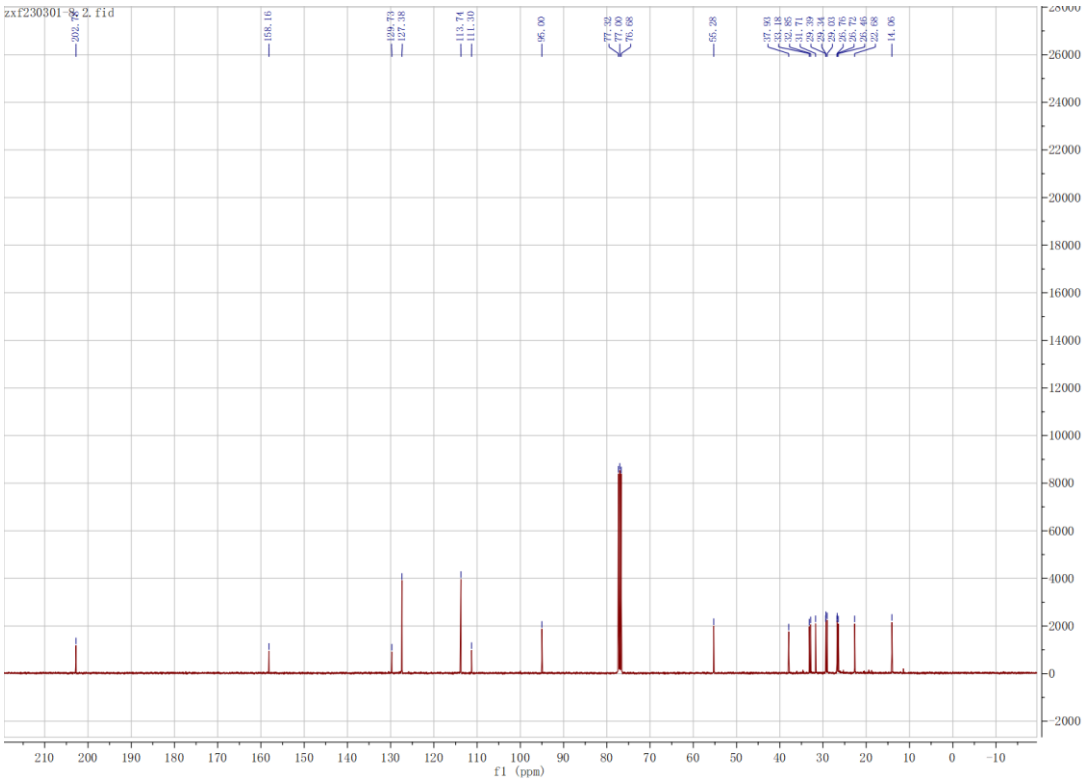


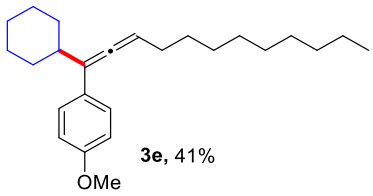




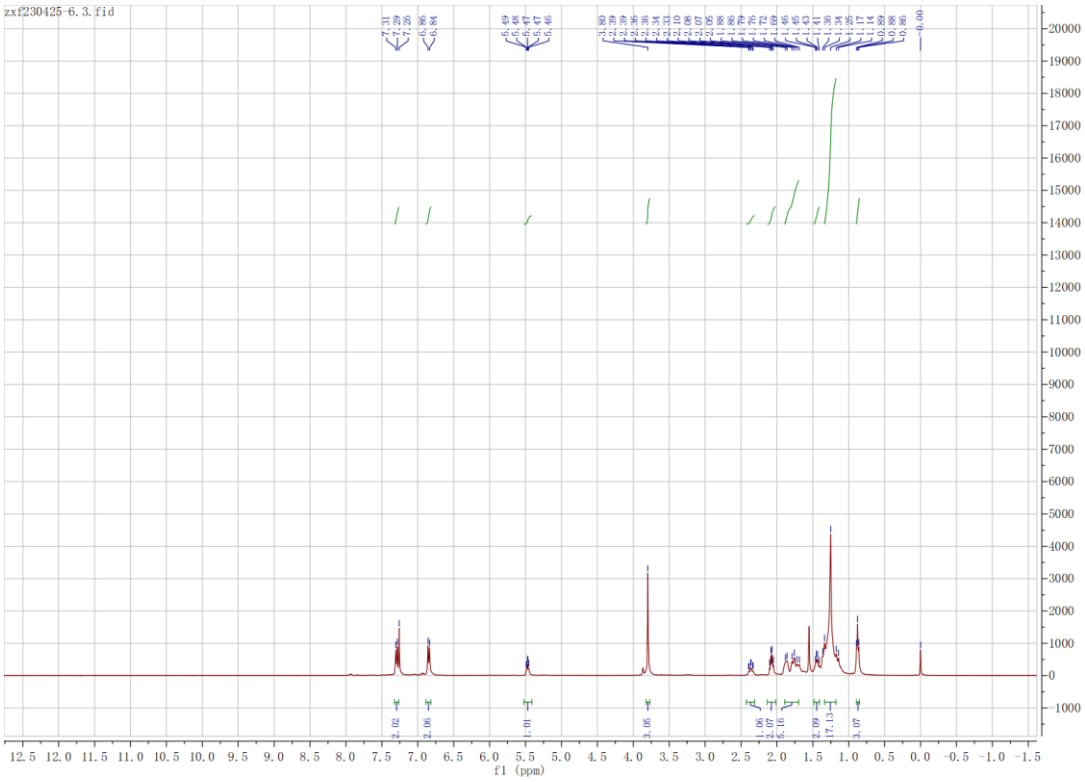
3d, 60%

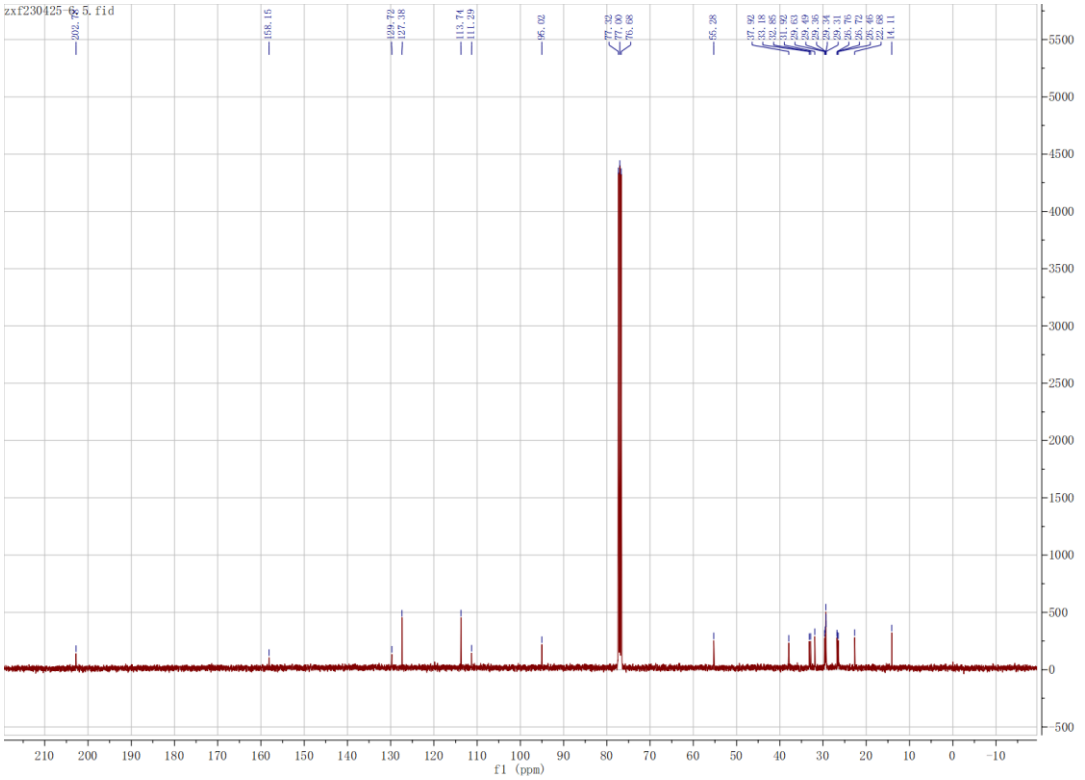


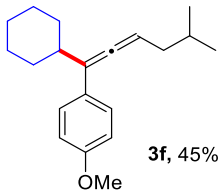




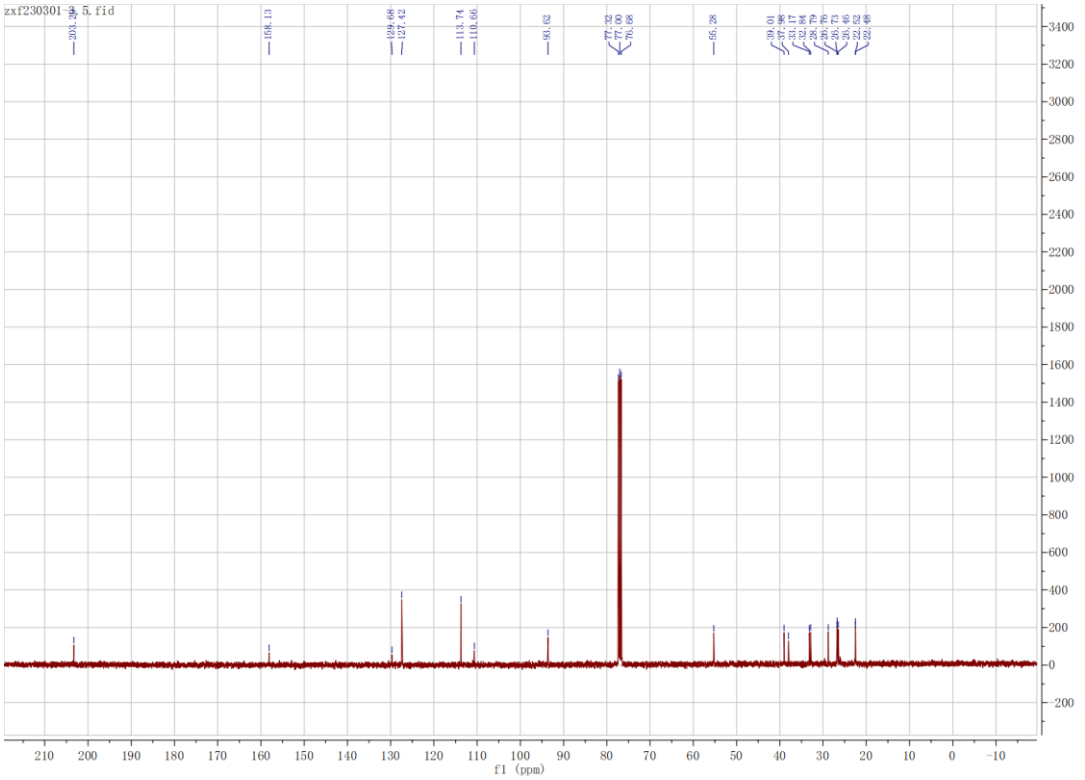
3e, 41%

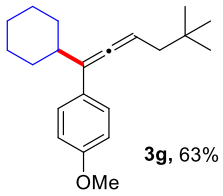




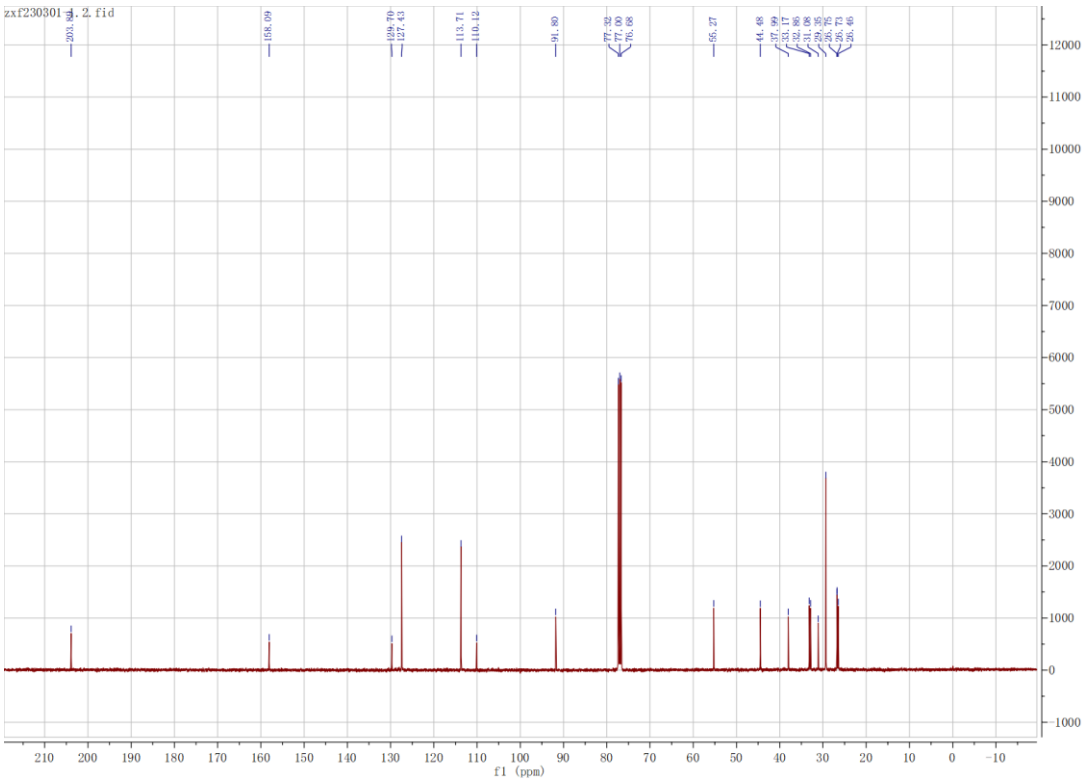


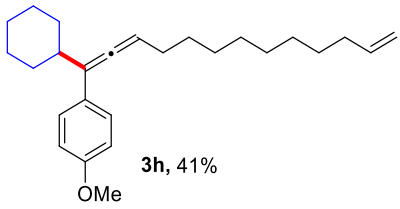
3f, 45%



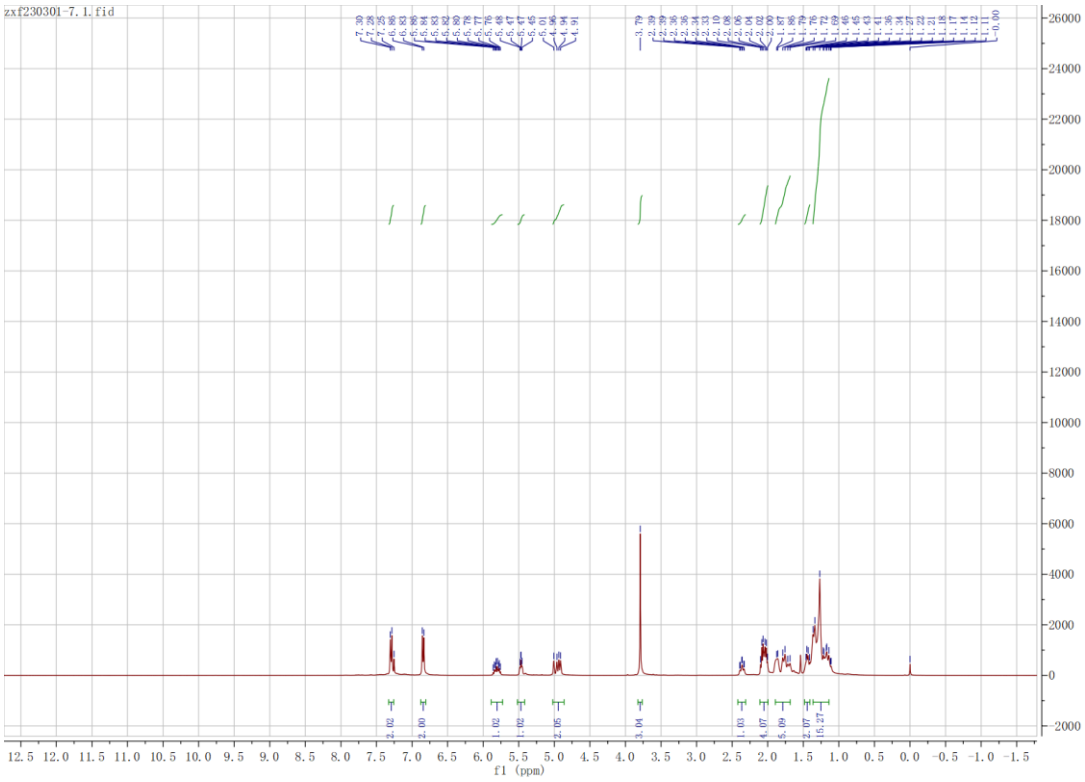


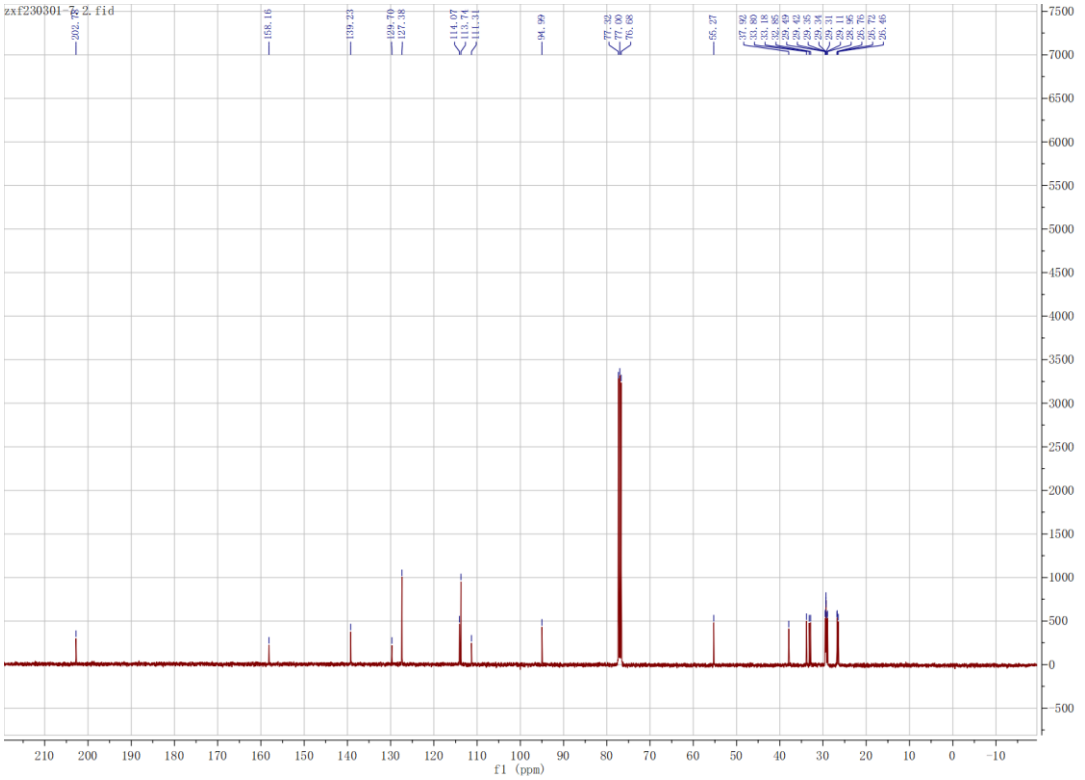
3g, 63%

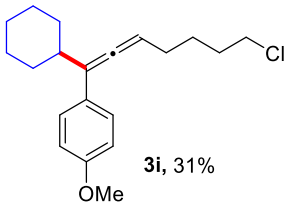




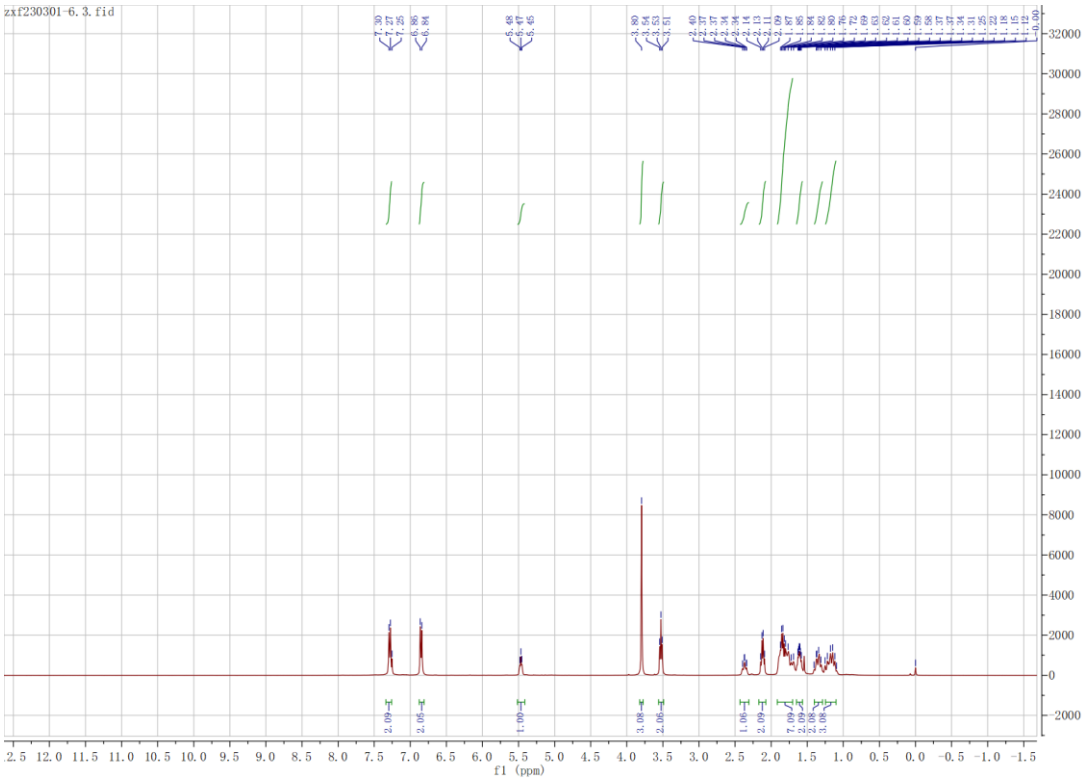
3h, 41%

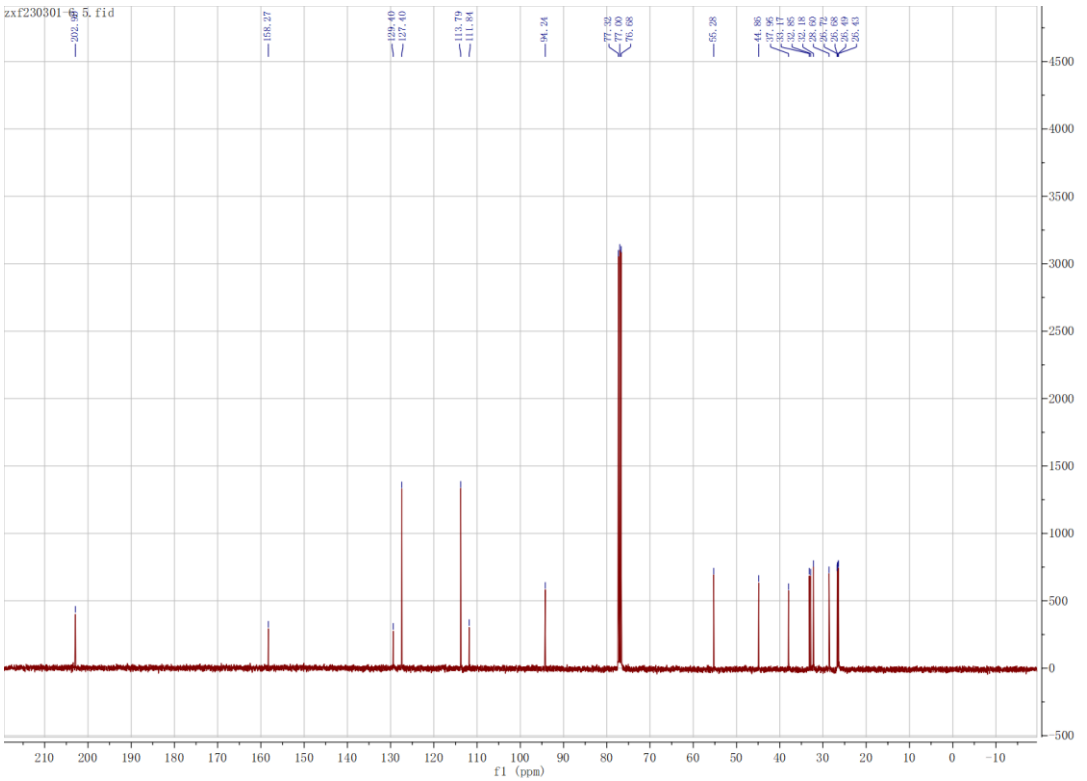


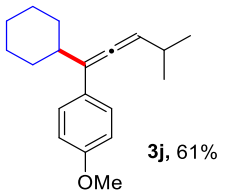




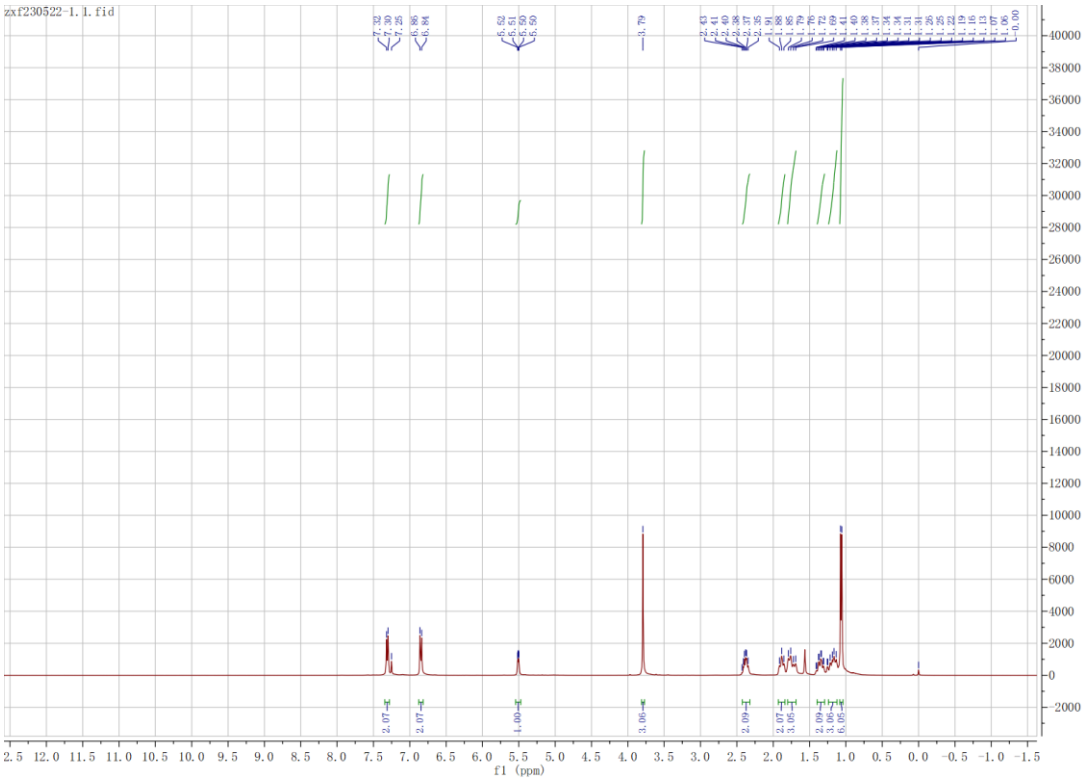
3i, 31%

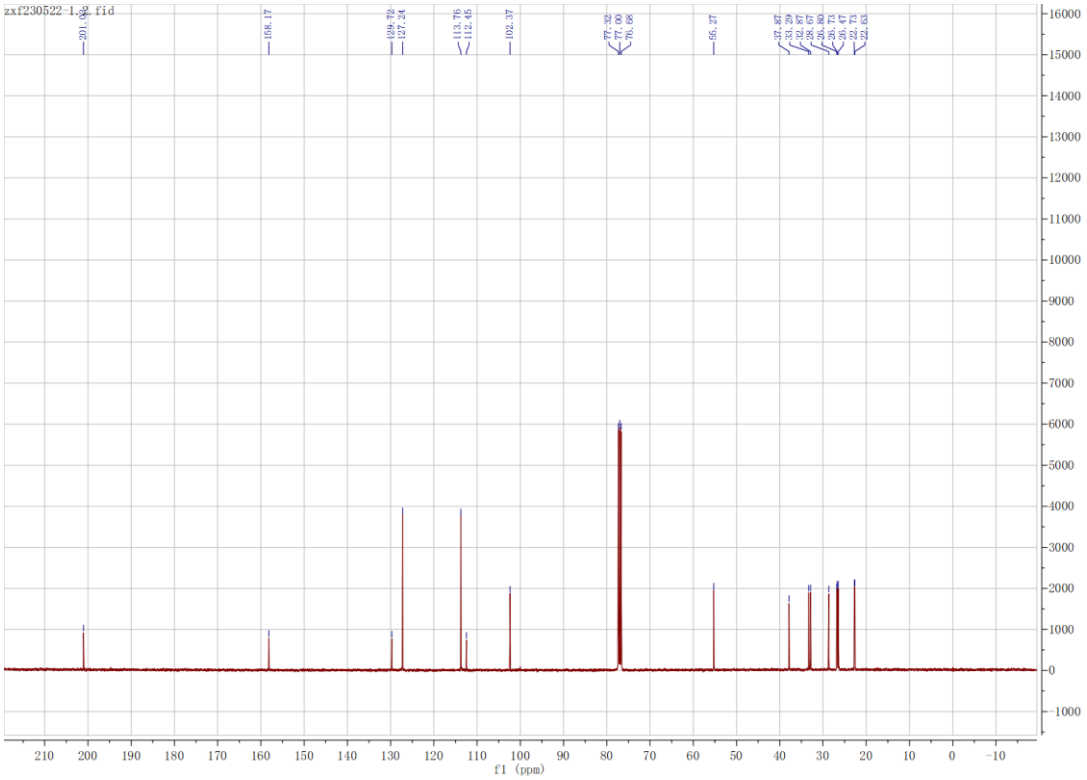


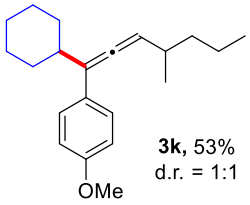




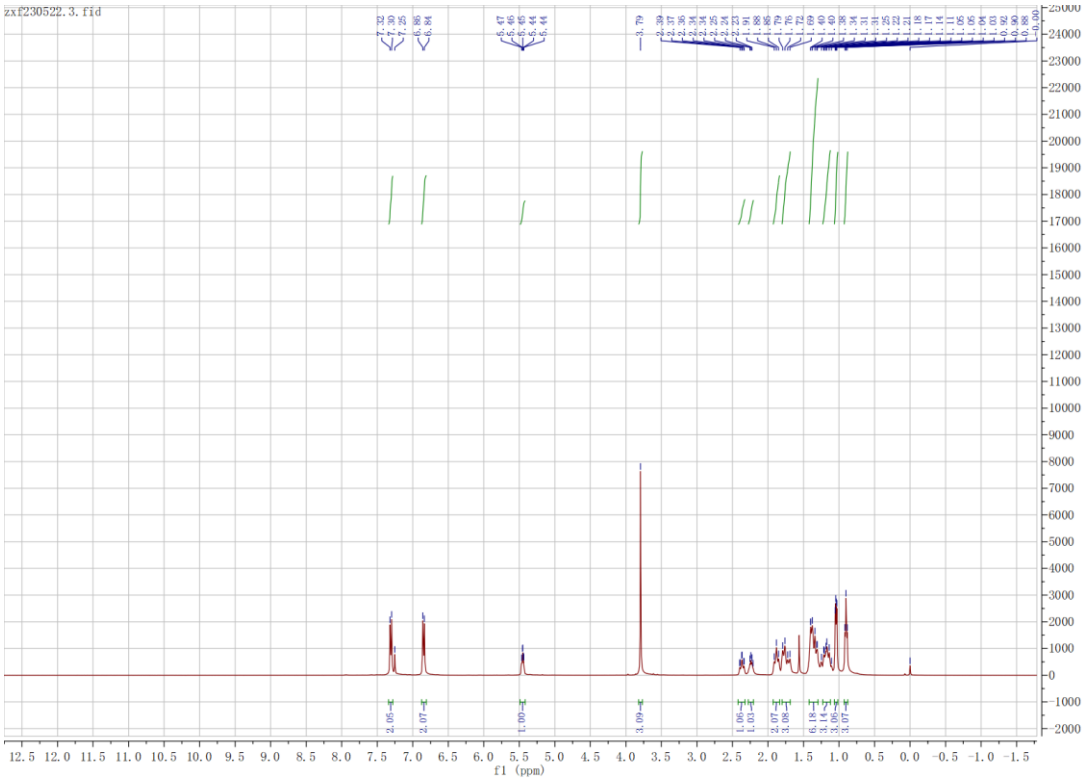
3j, 61%

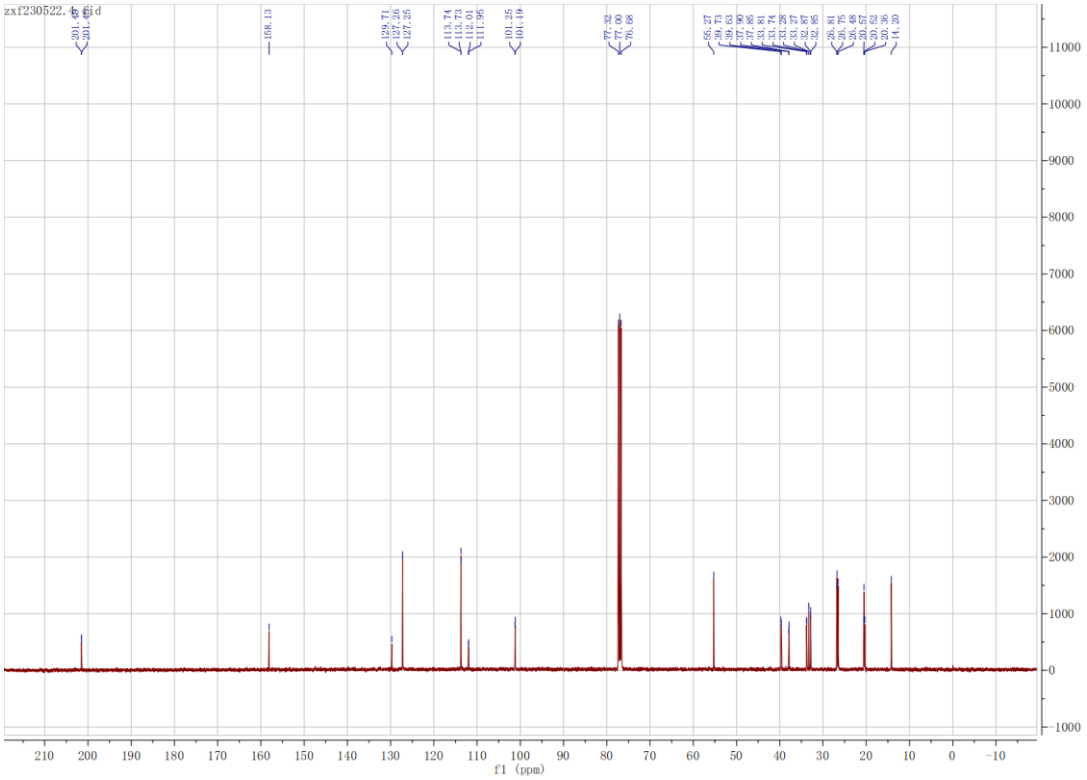


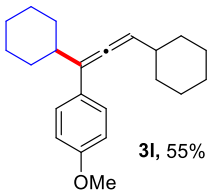




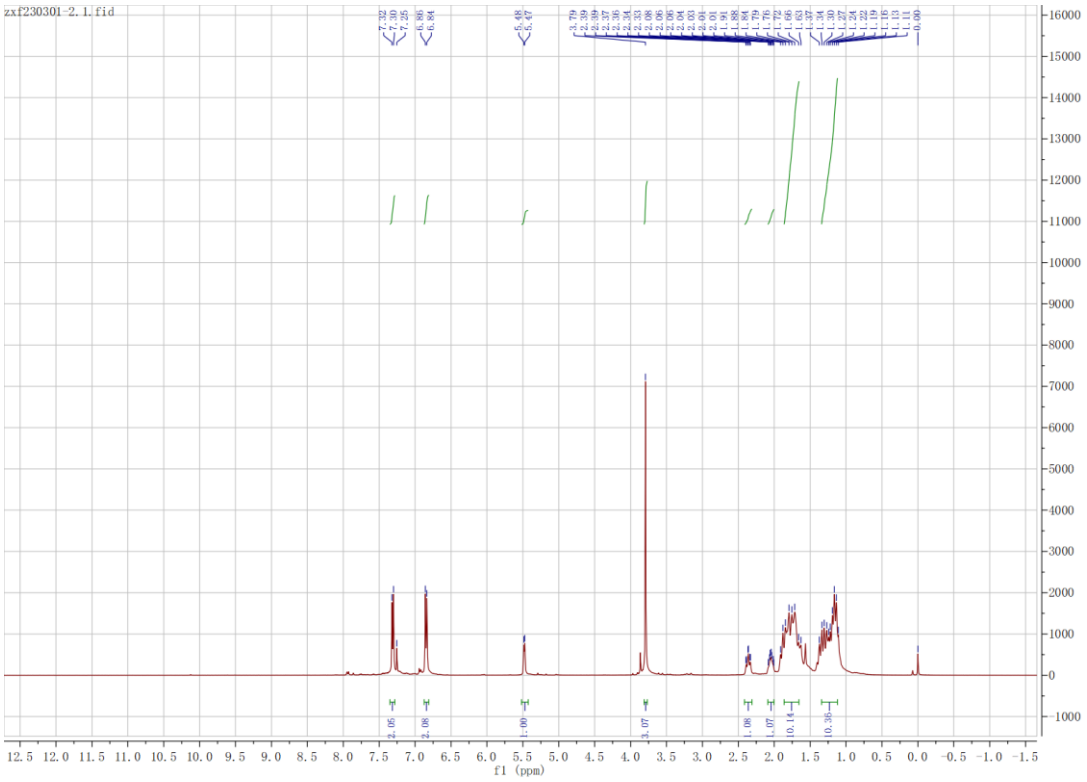
3k, 53%
d.r. = 1:1

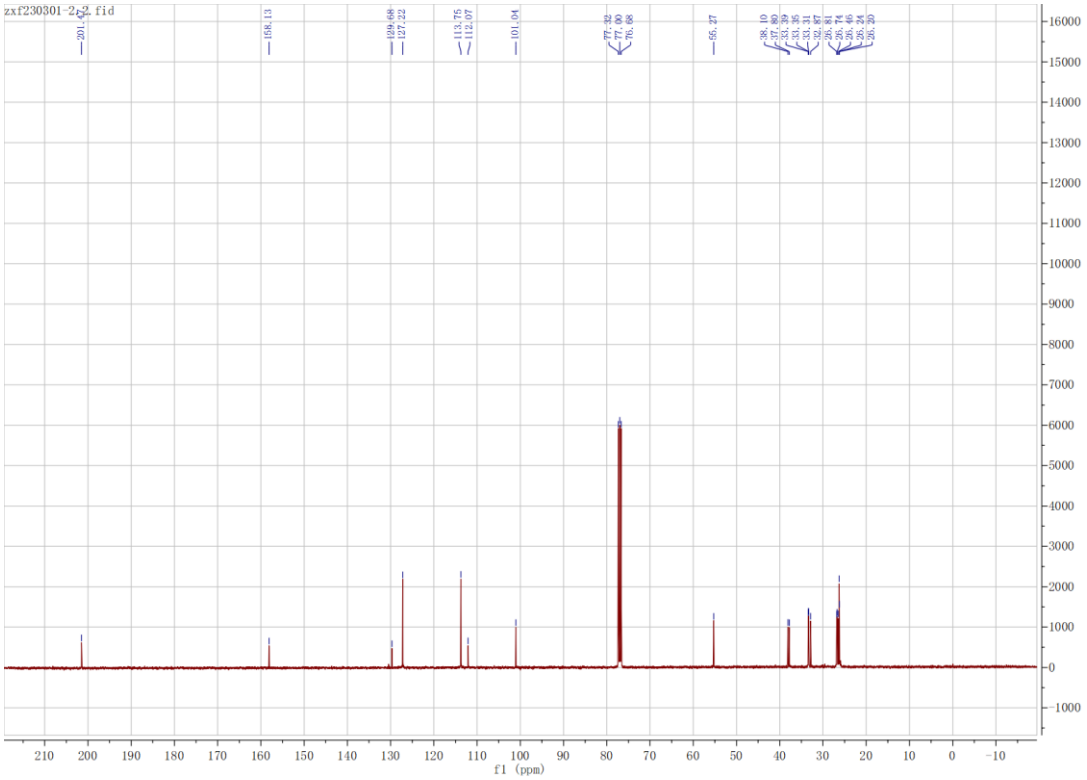


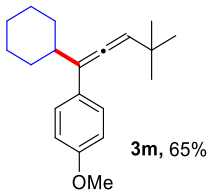




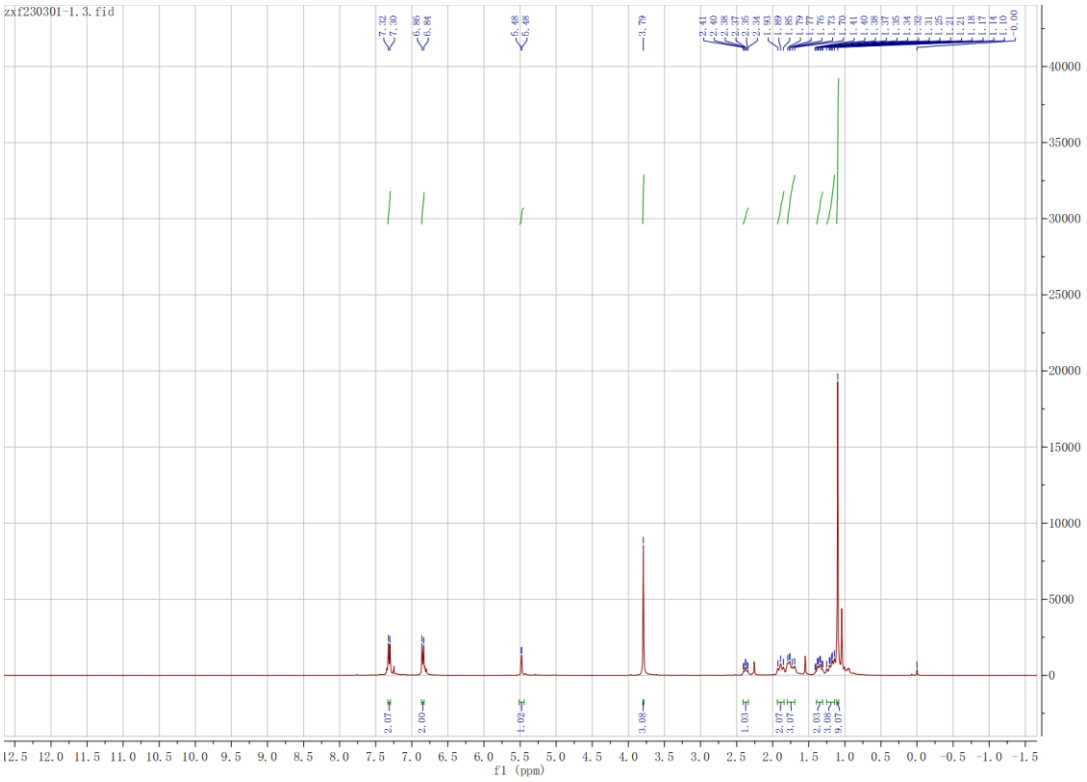
3l, 55%

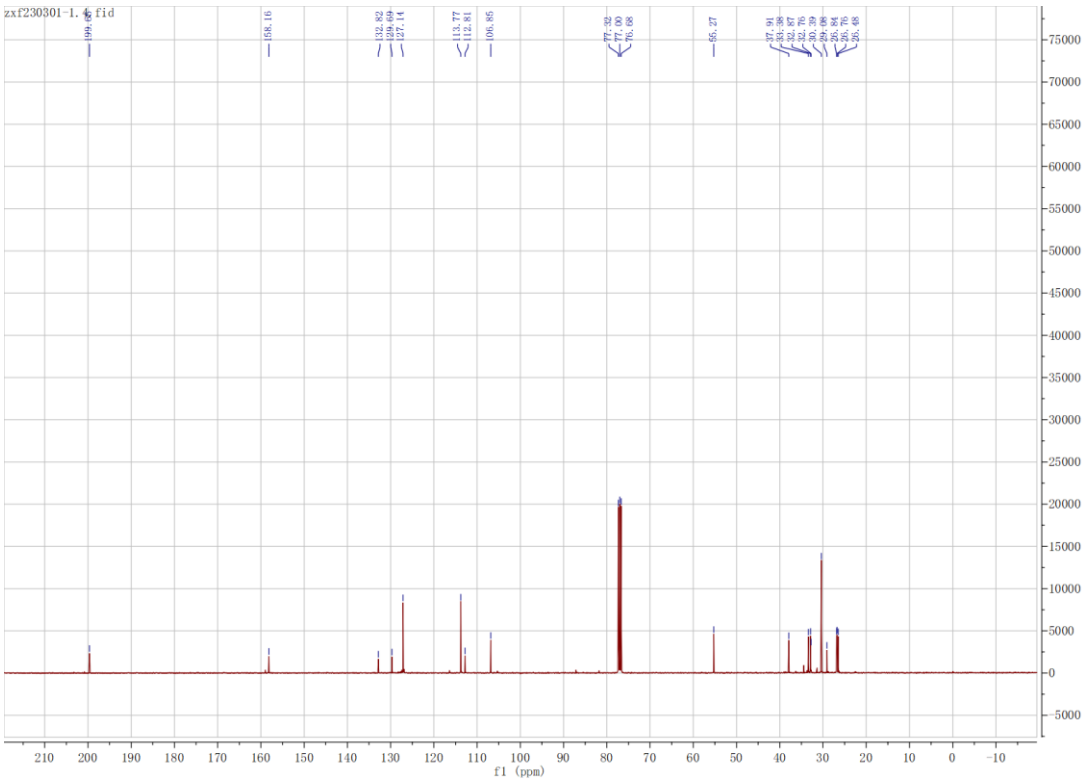


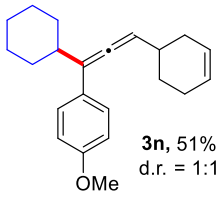




3m, 65%







3n, 51%
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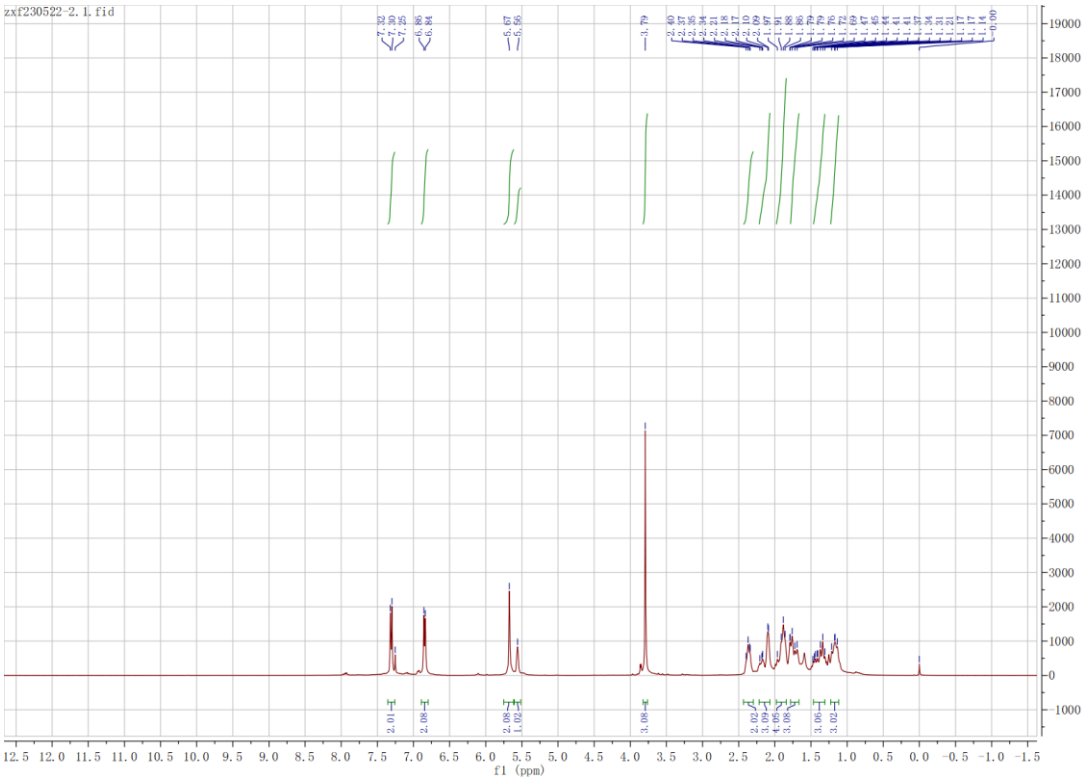
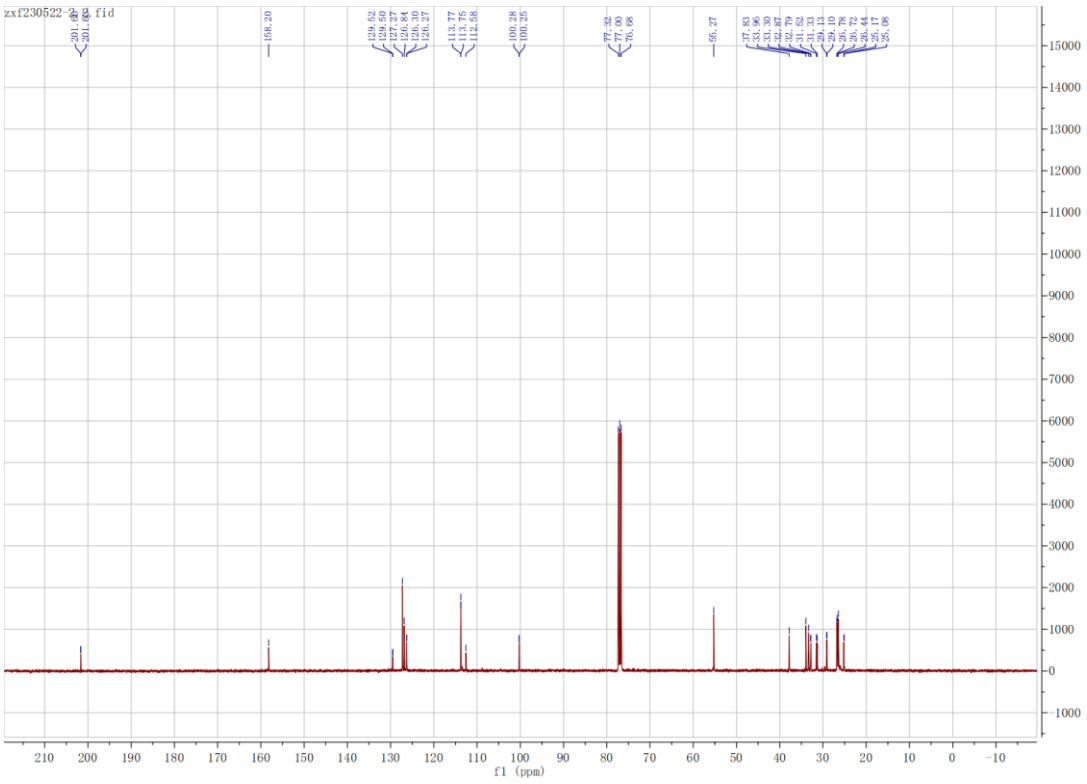
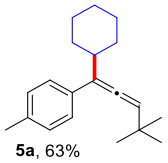
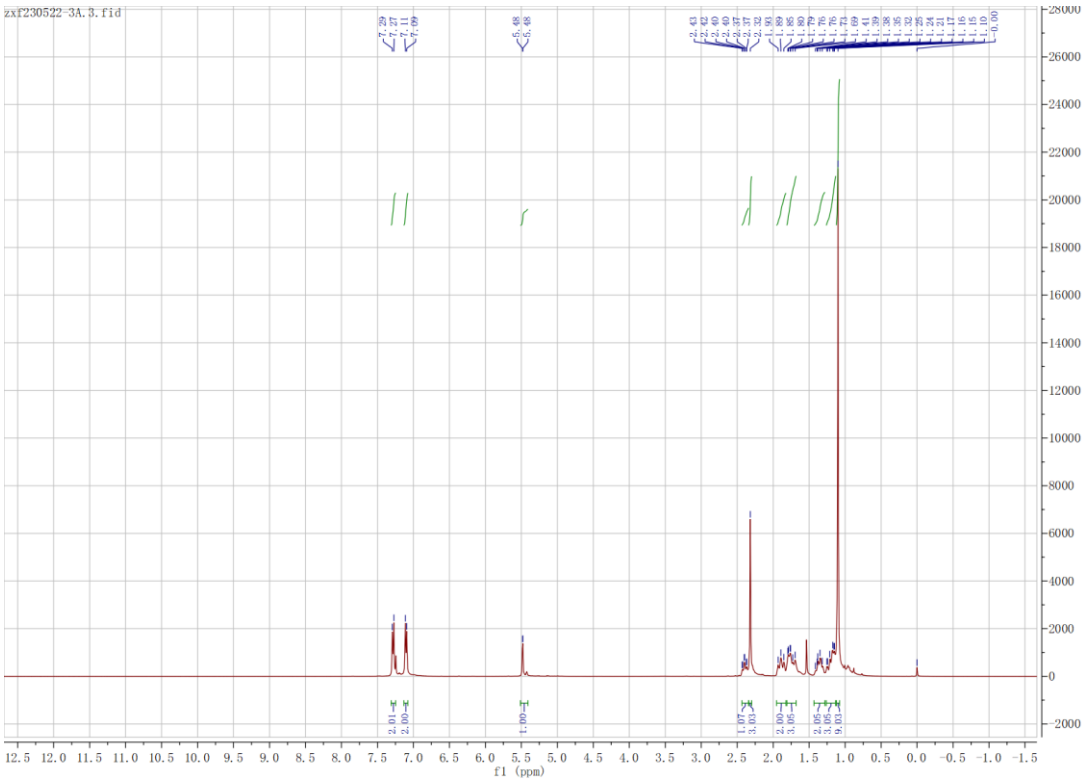


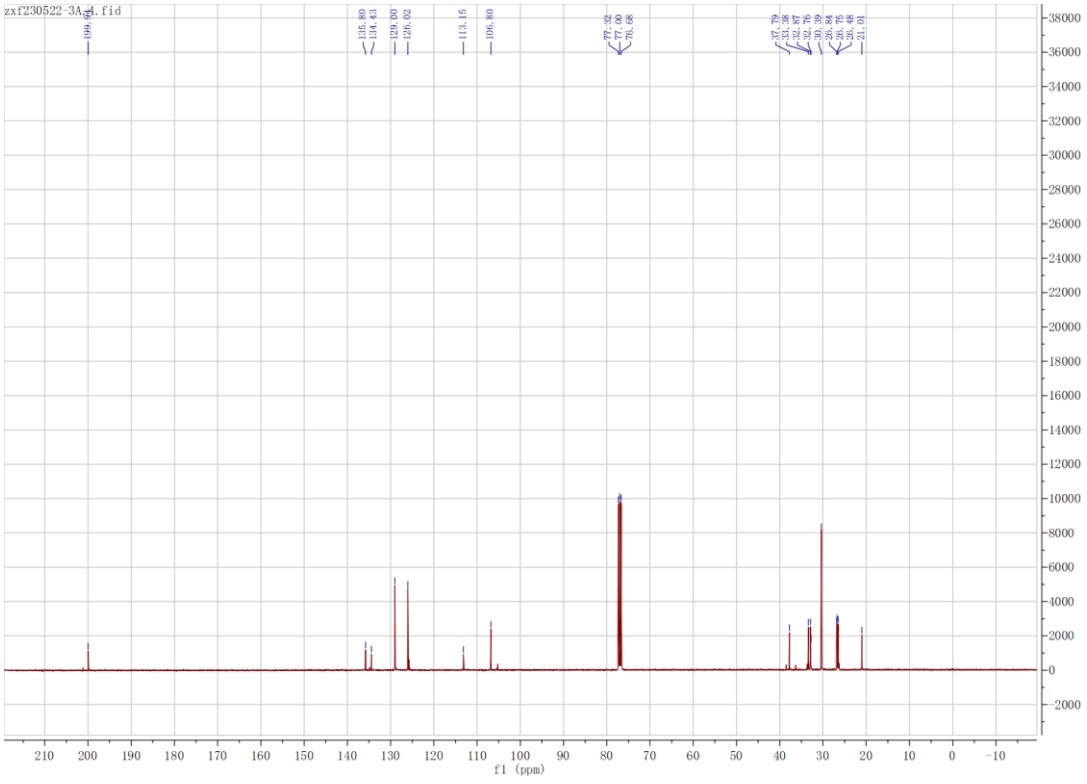


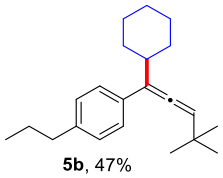
12. ^{1}H NMR and ^{13}C NMR Spectra of Products 5a-5s, 3aa, 5ba, 6a-6c:



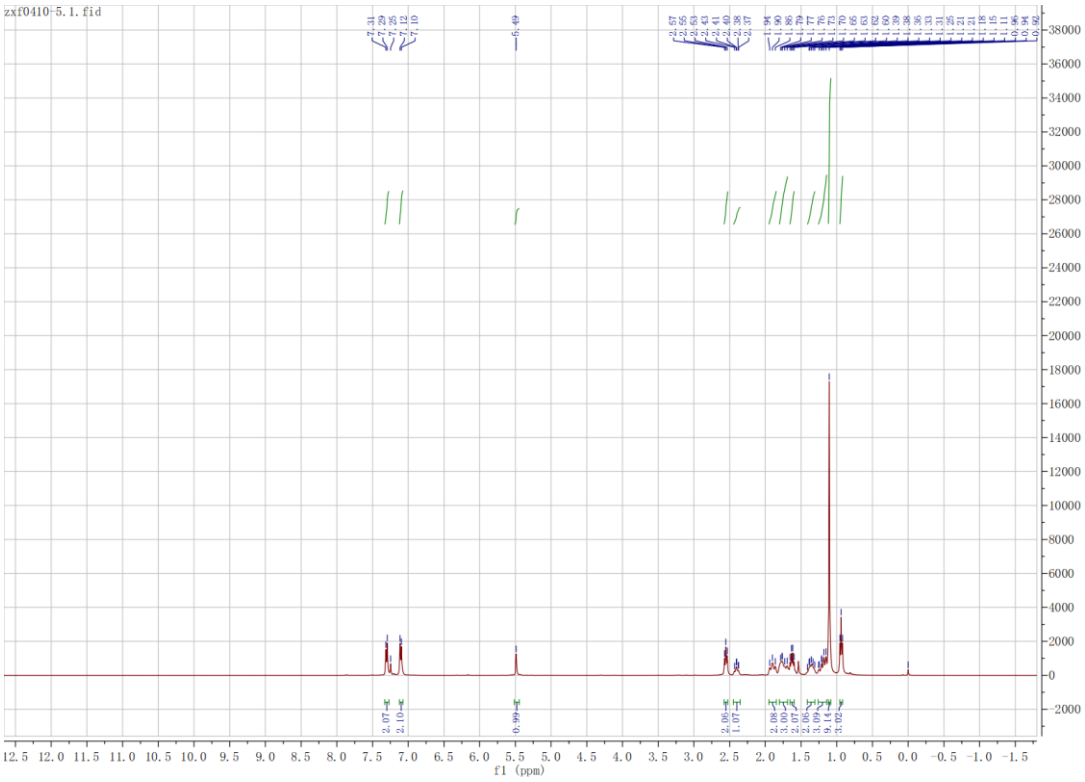
5a, 63%

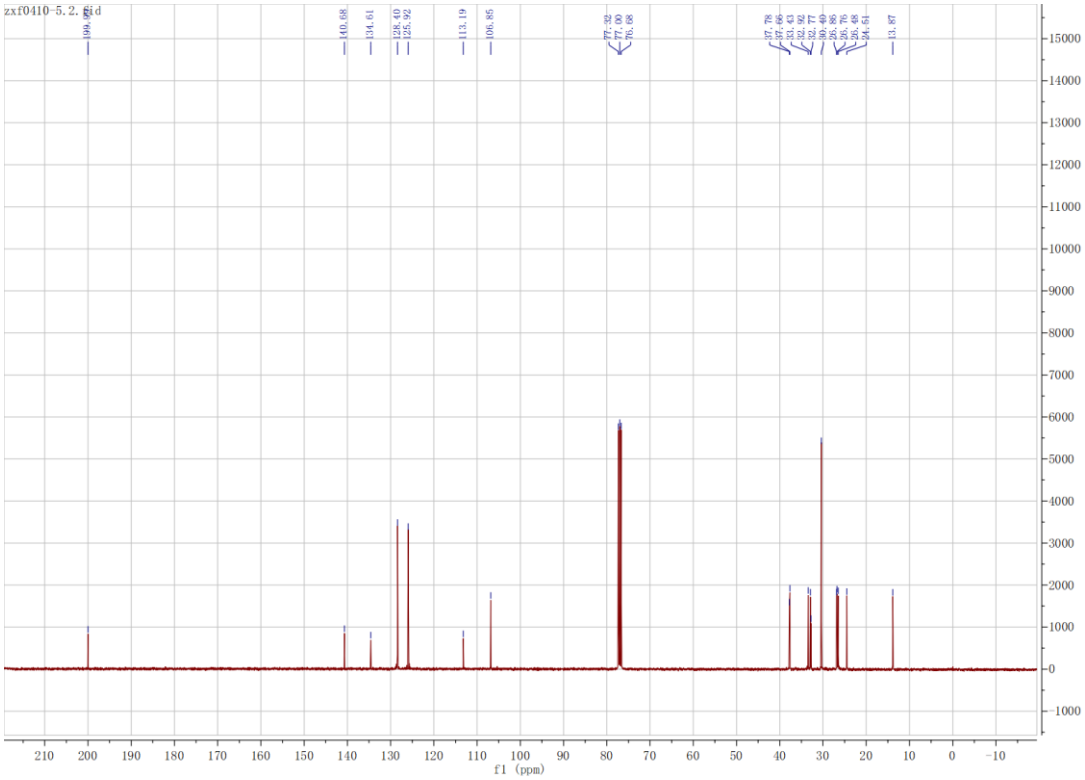


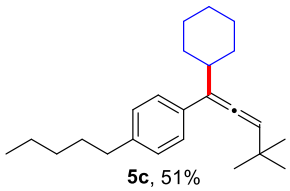




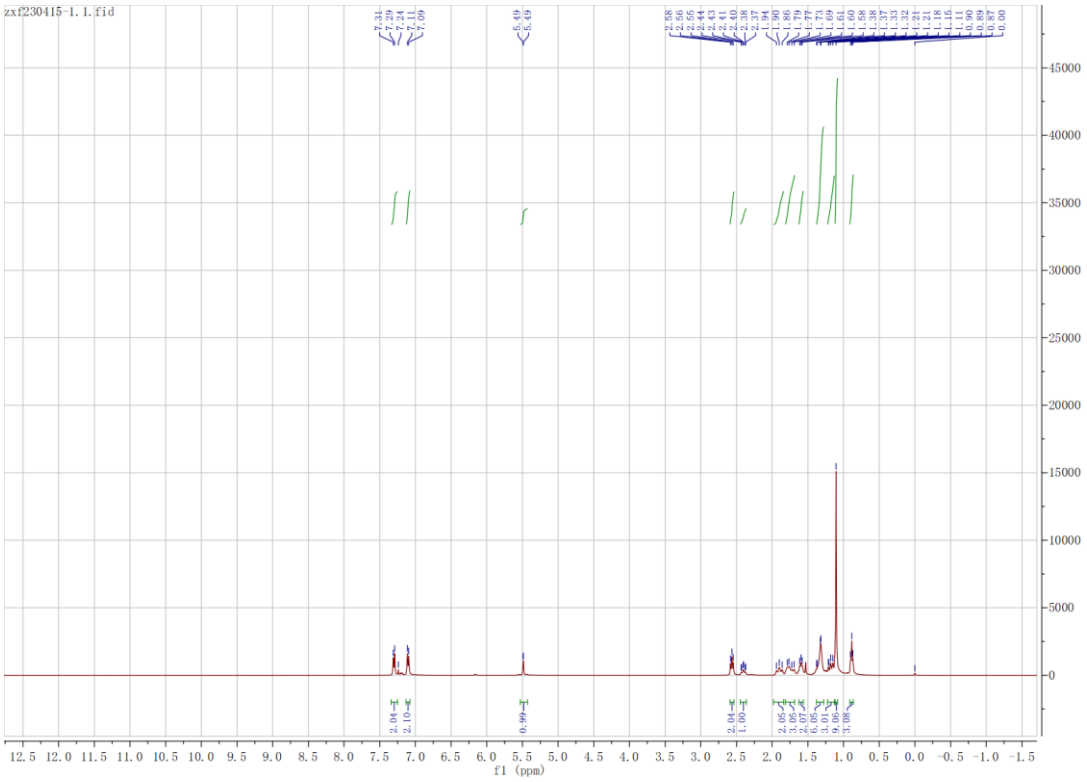
5b, 47%

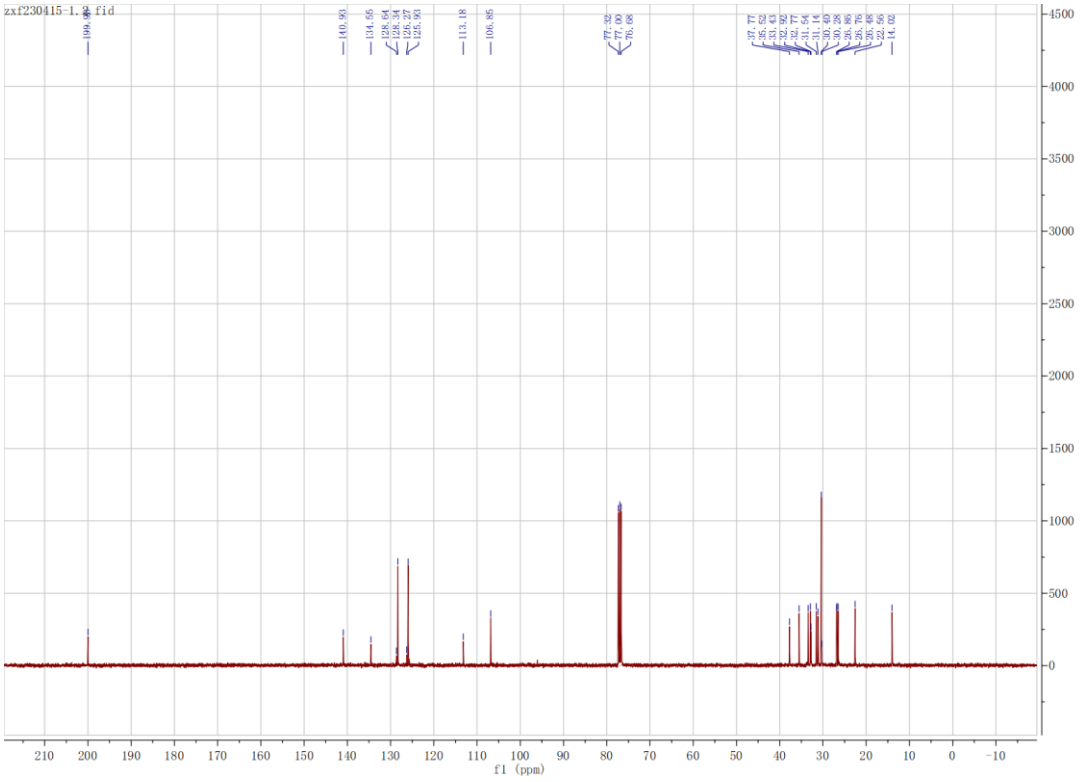


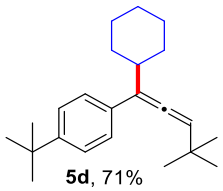




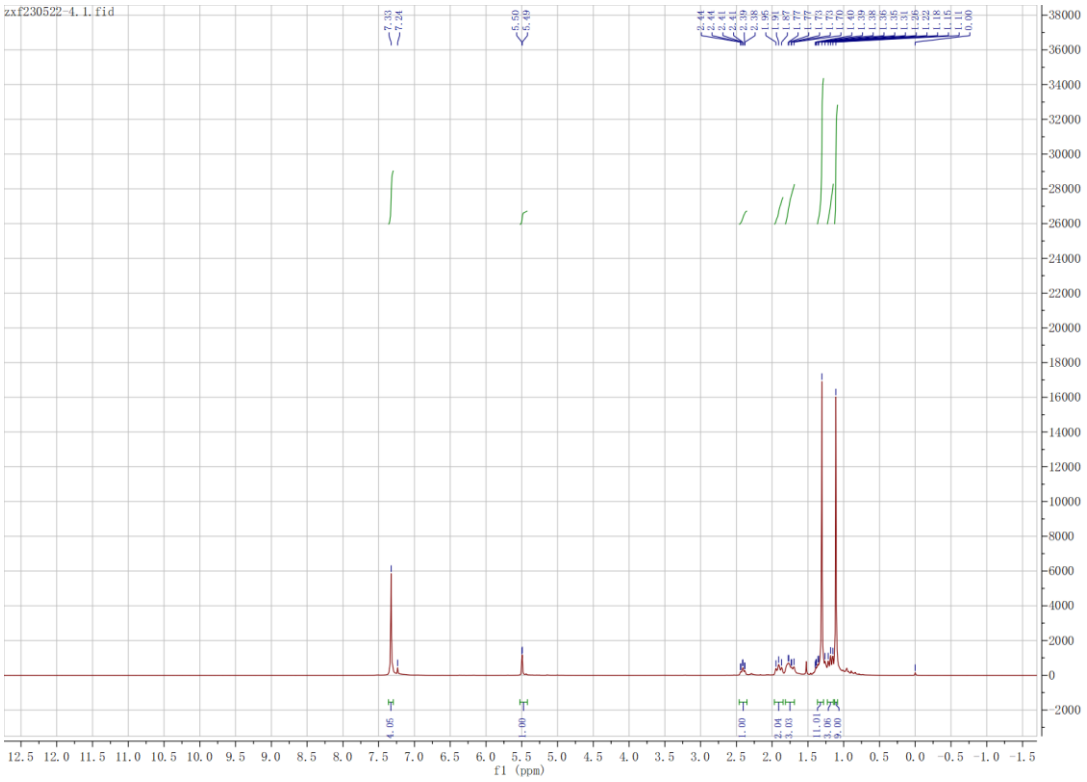
5c, 51%

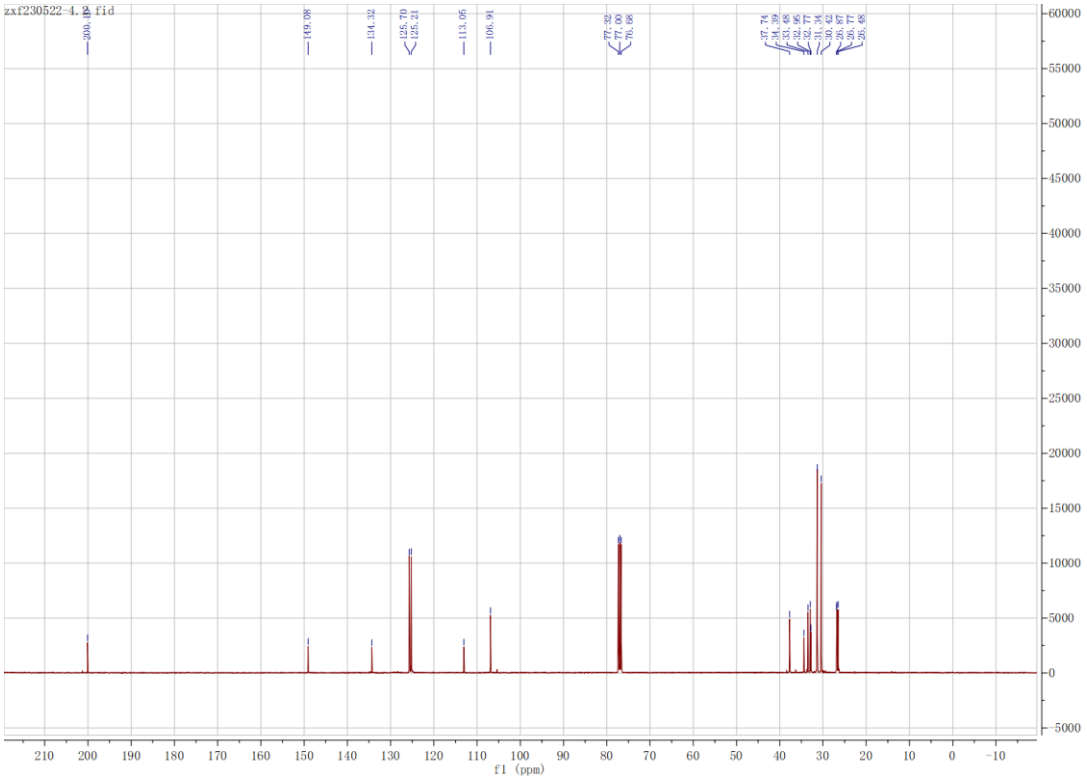


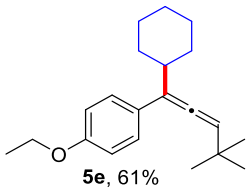




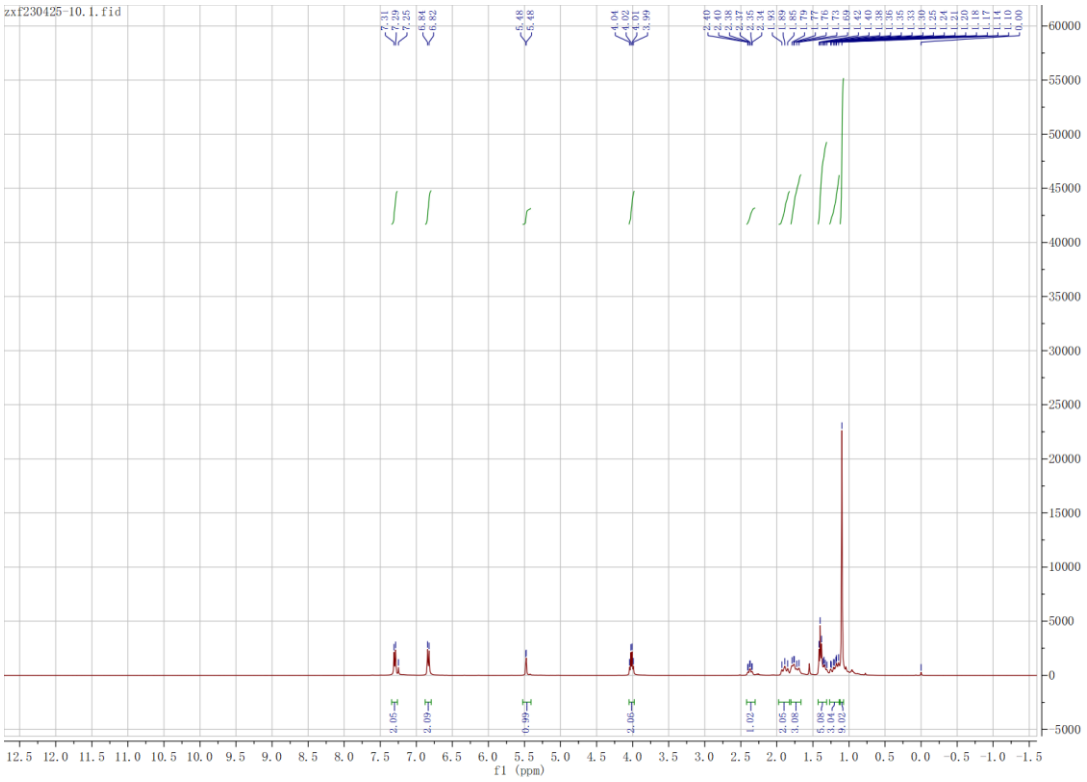
5d, 71%

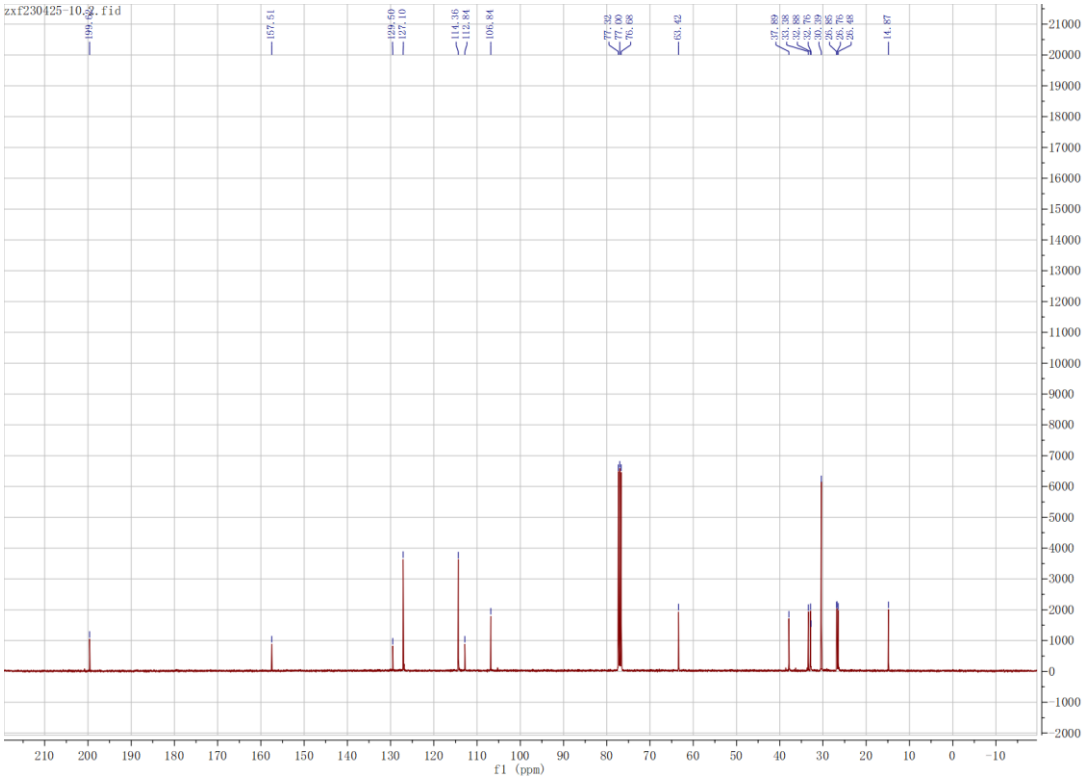


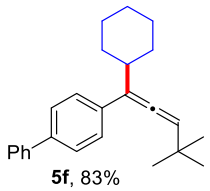




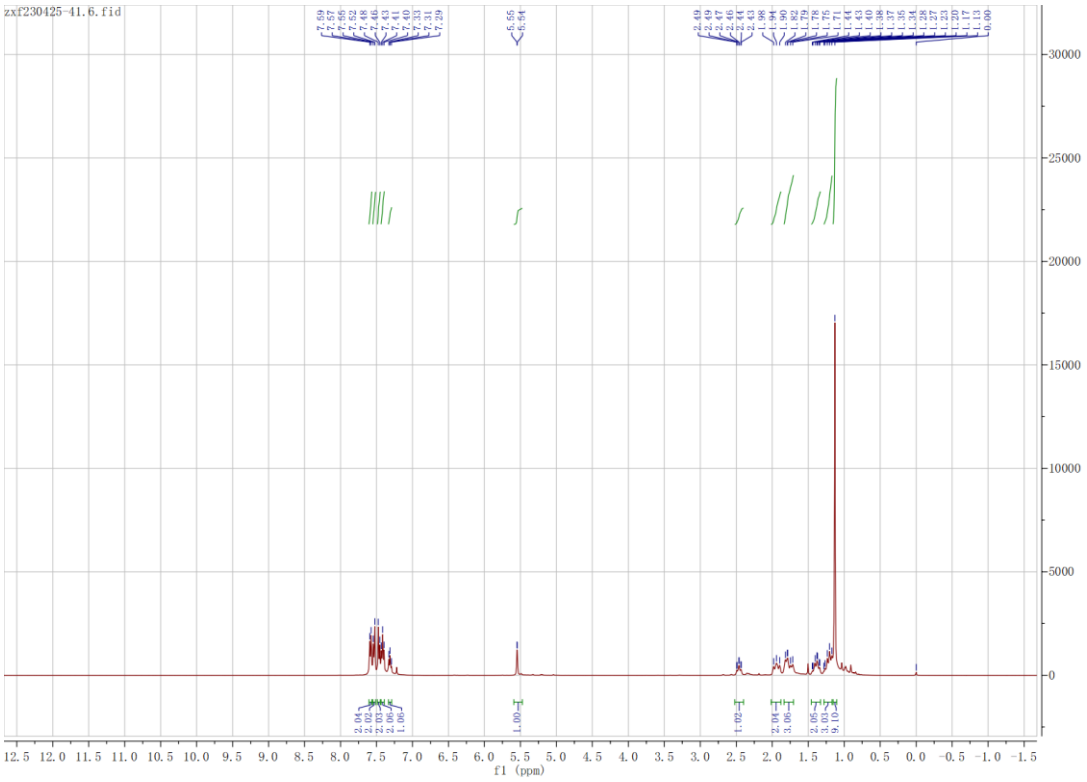
5e, 61%

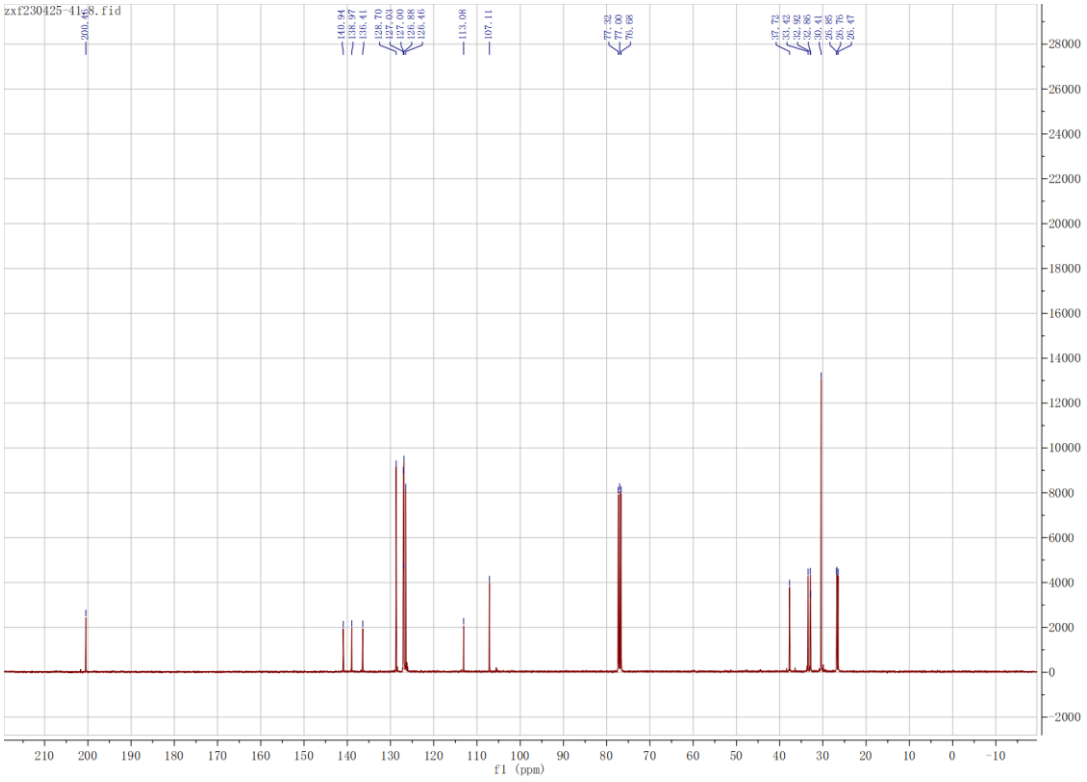


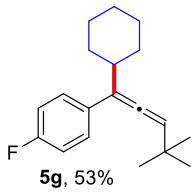




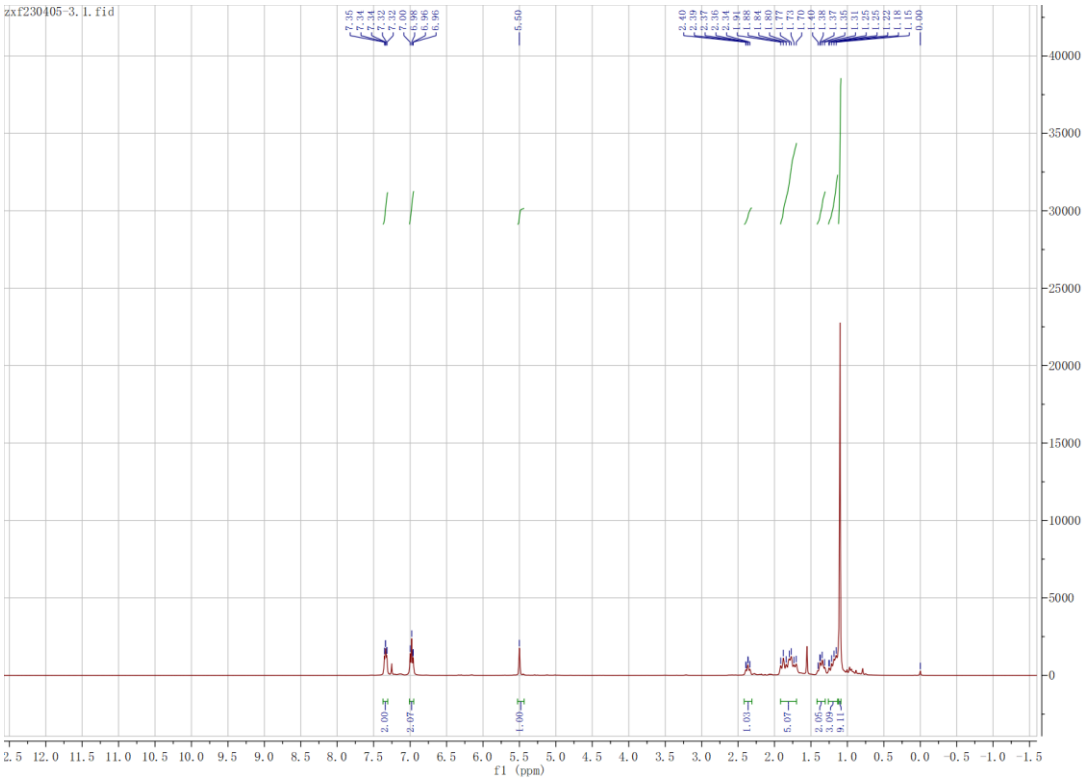
5f, 83%

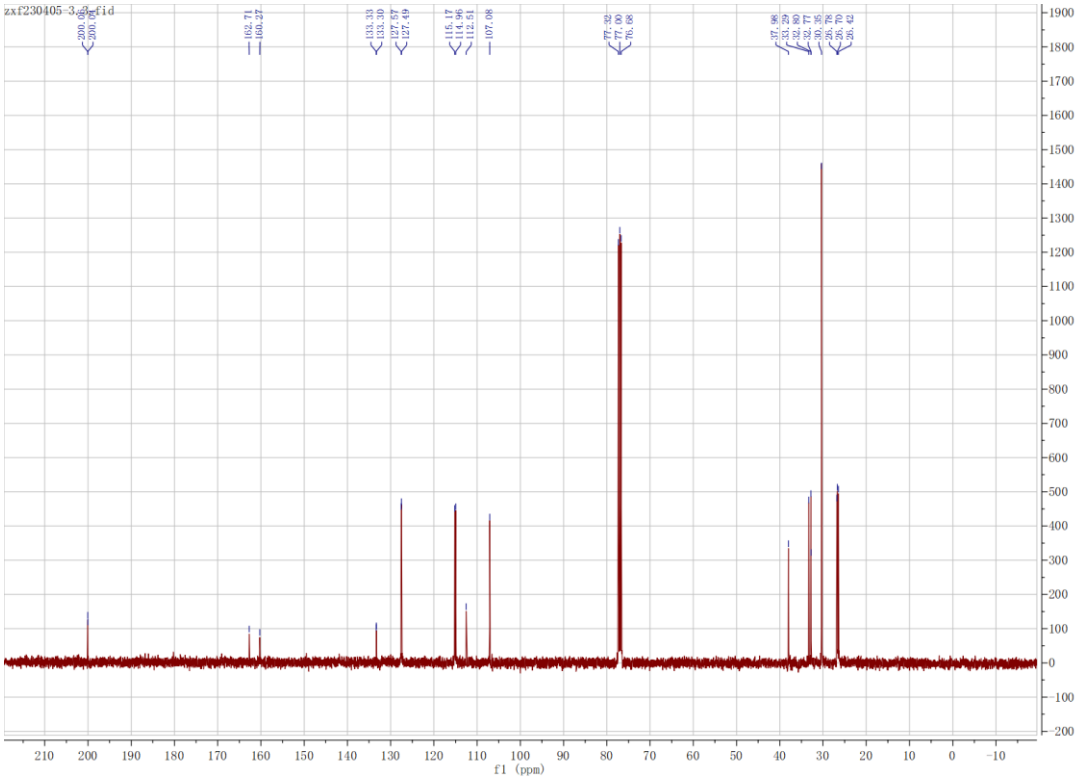


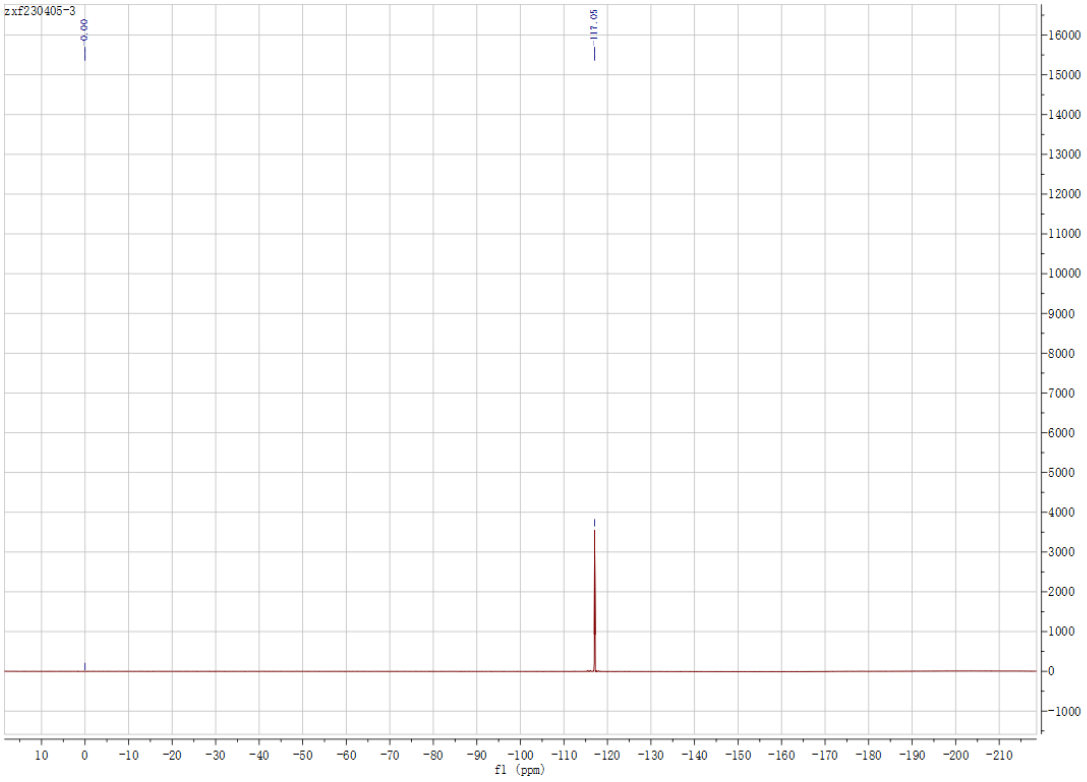




5g, 53%



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3000
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-1000
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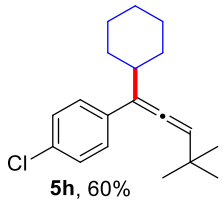
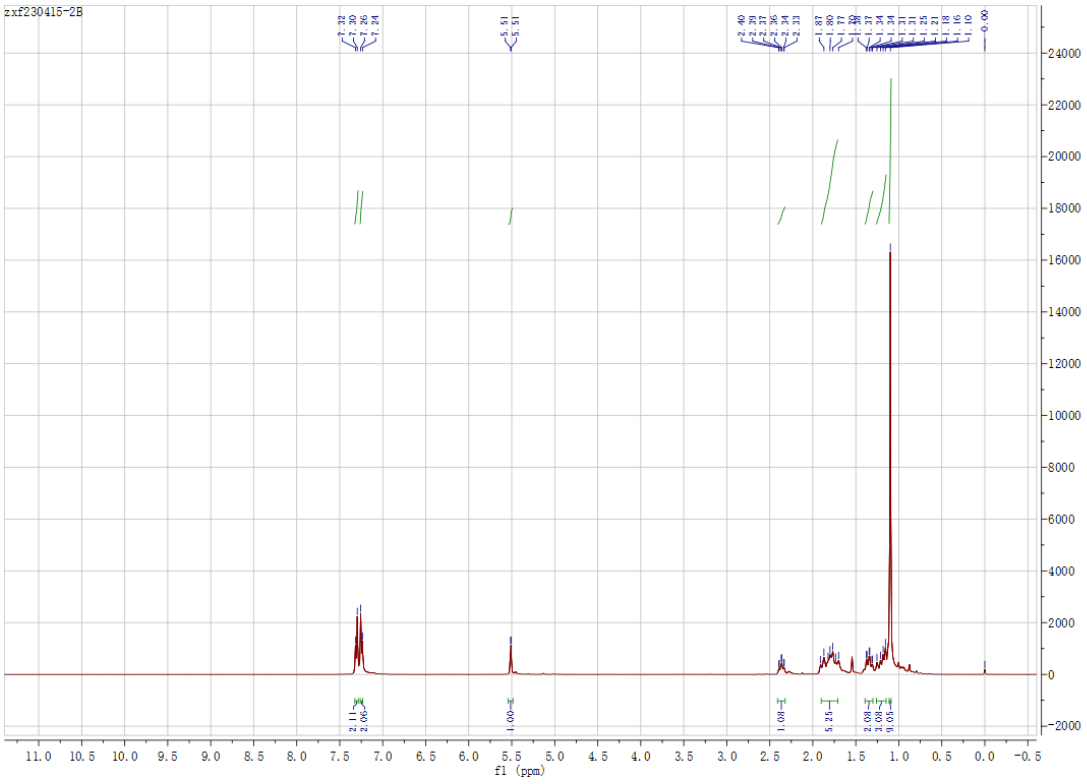
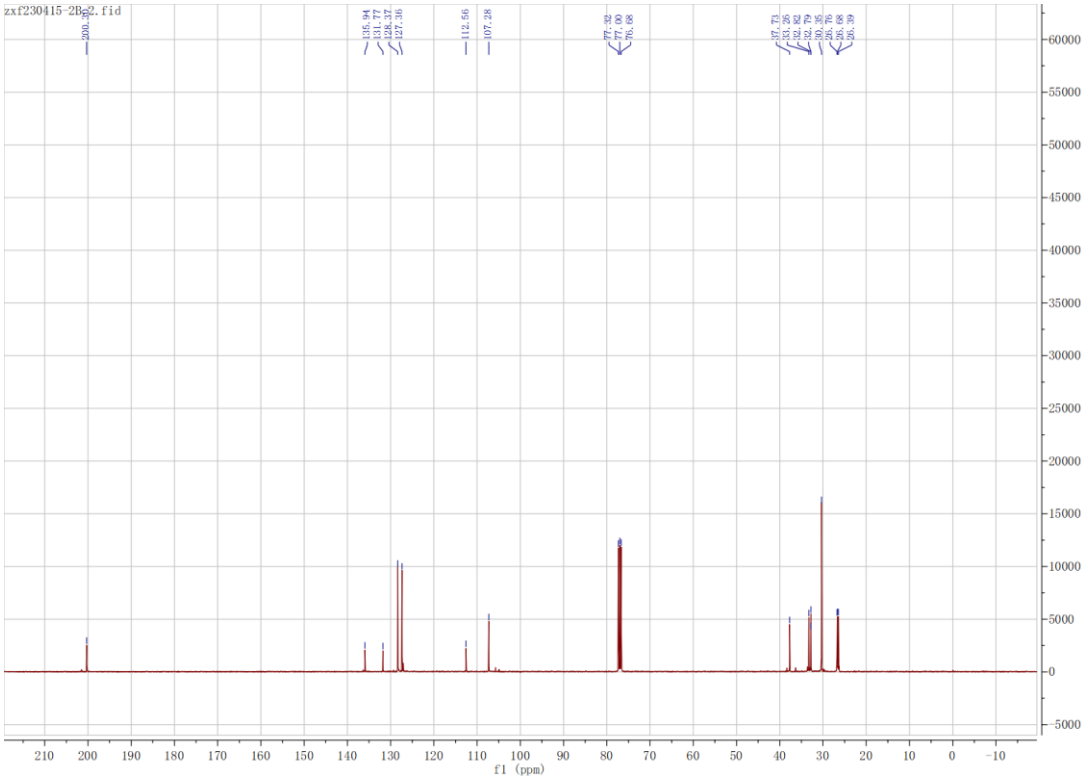
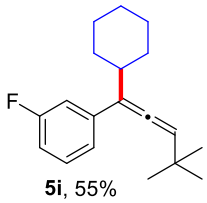
f1 (ppm)



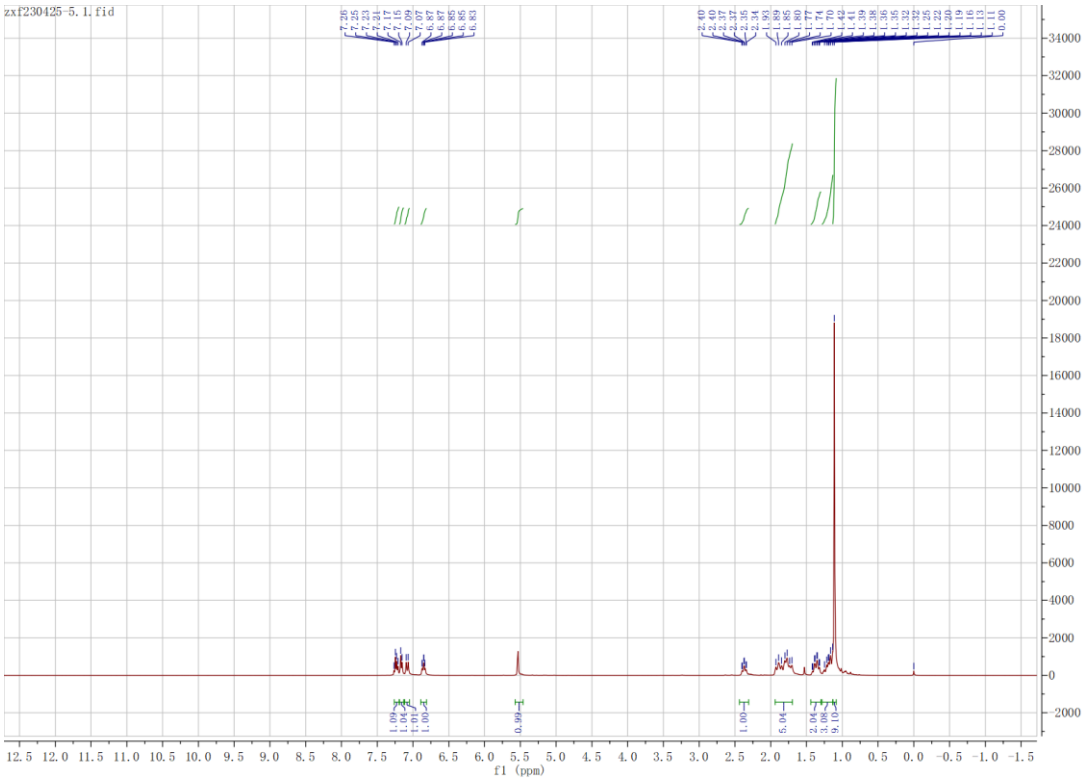
5h, 60%

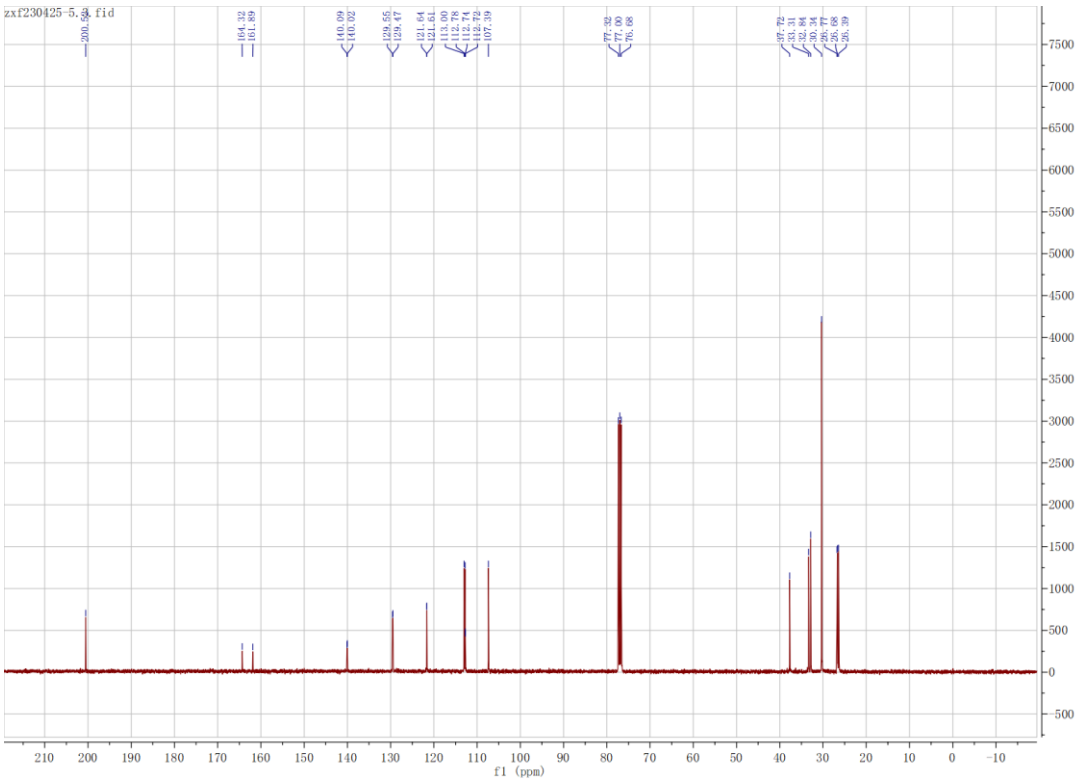


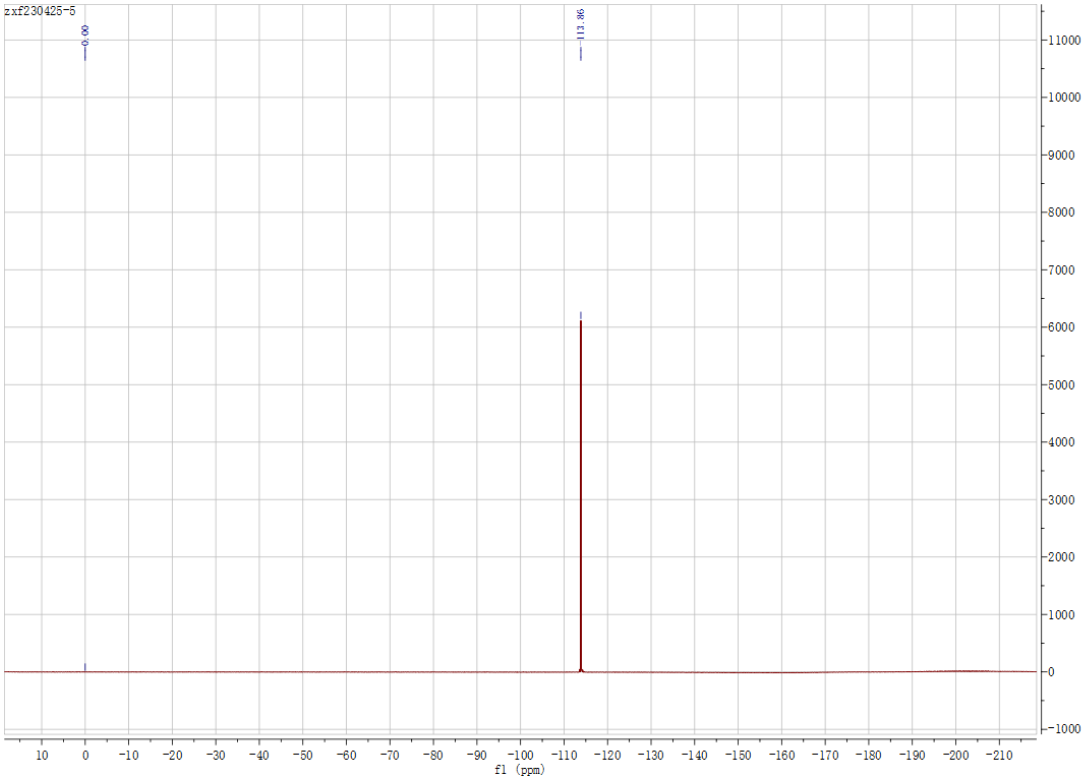




5i, 55%



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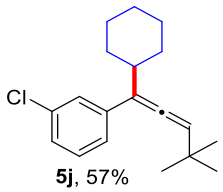
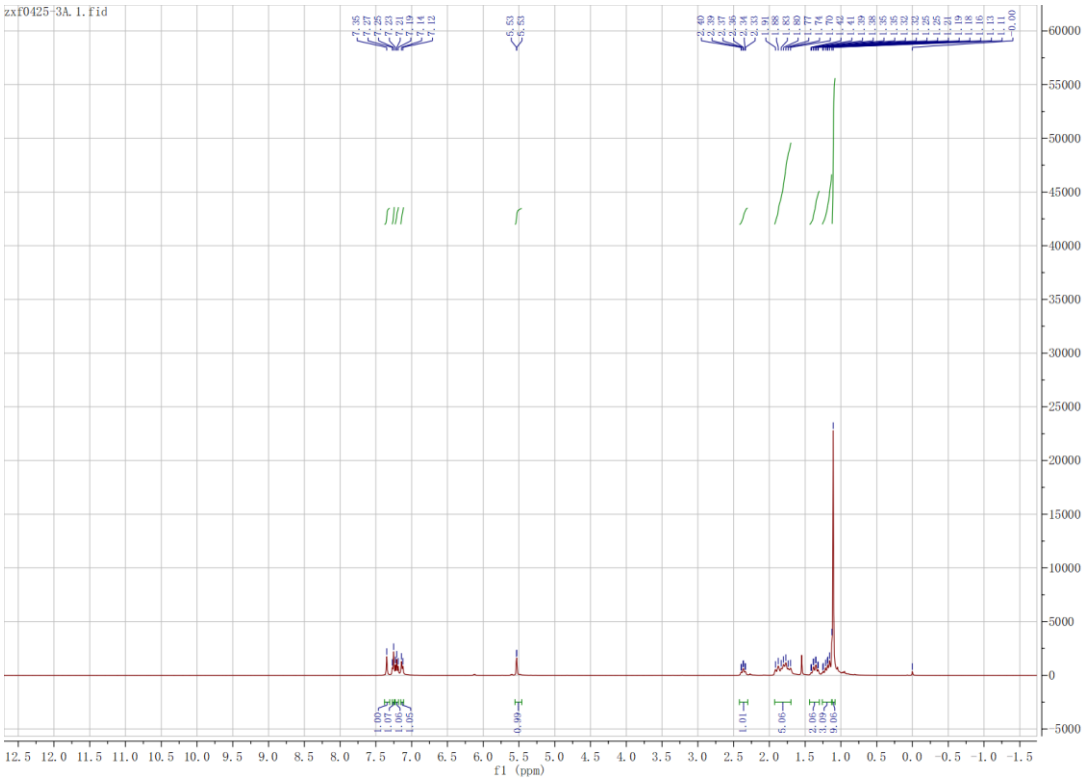
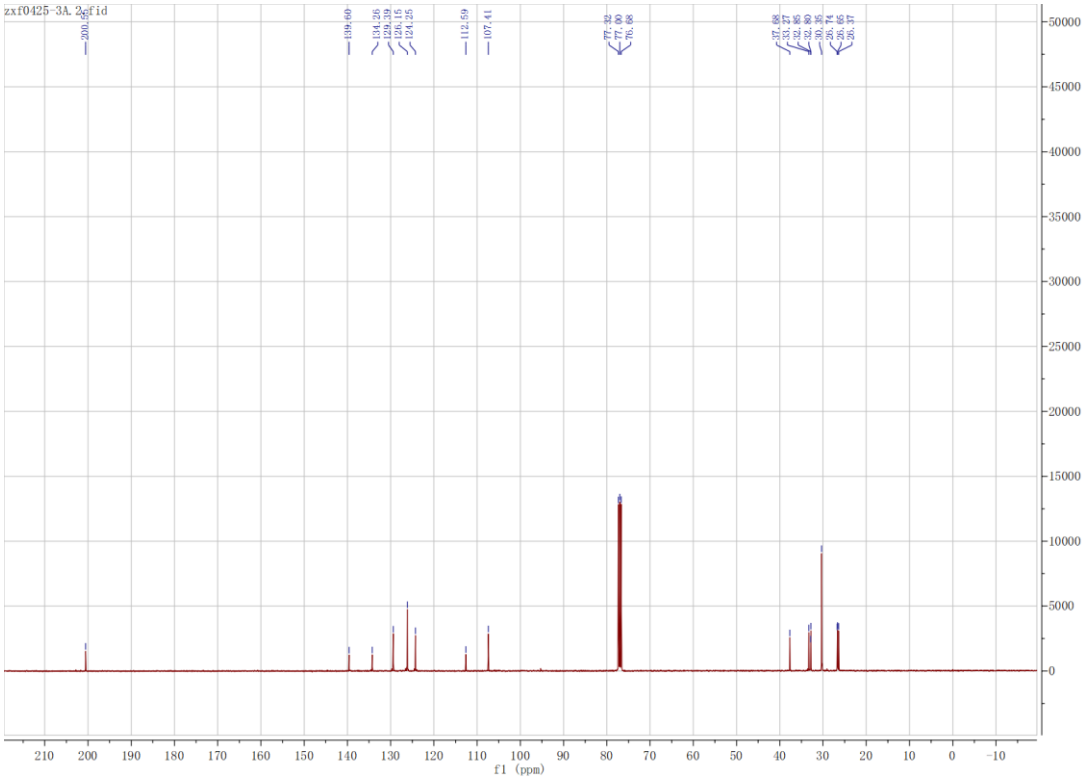
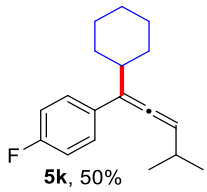
f1 (ppm)



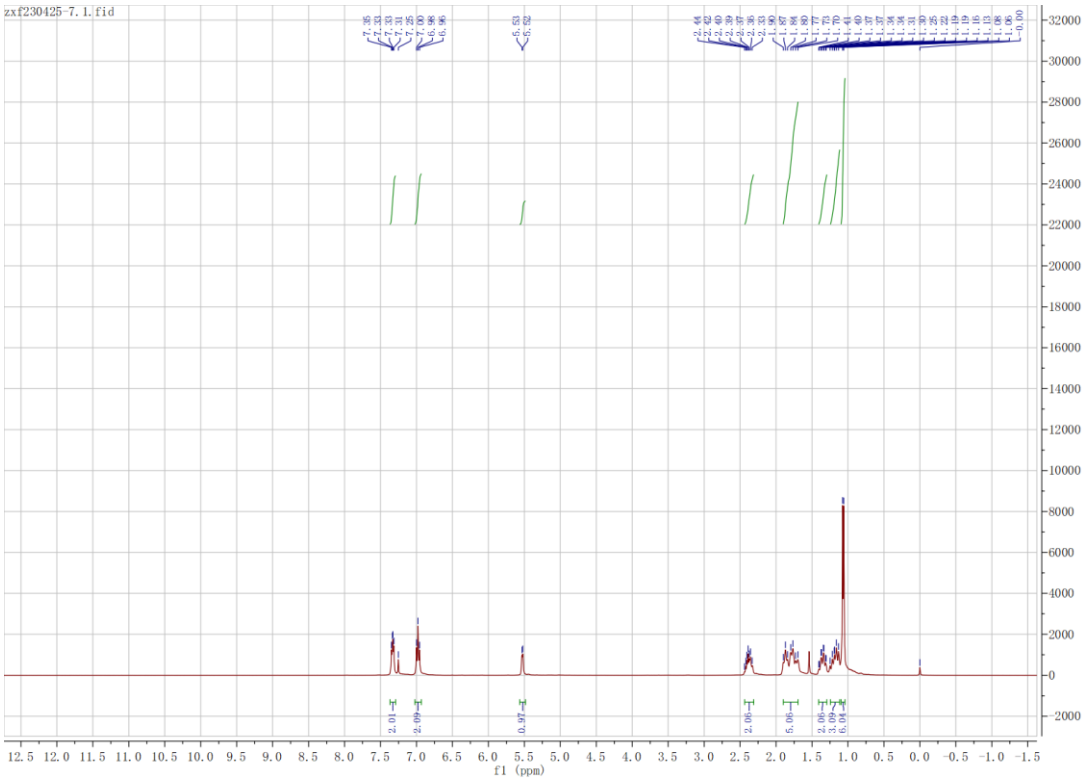
5j, 57%

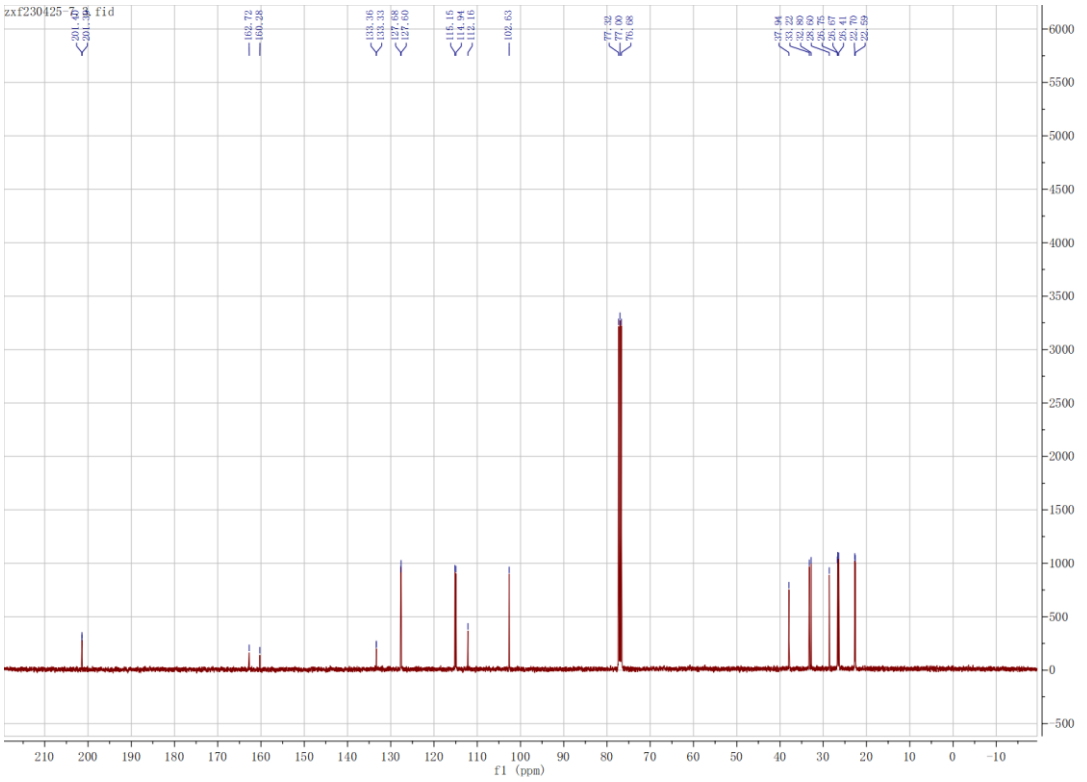


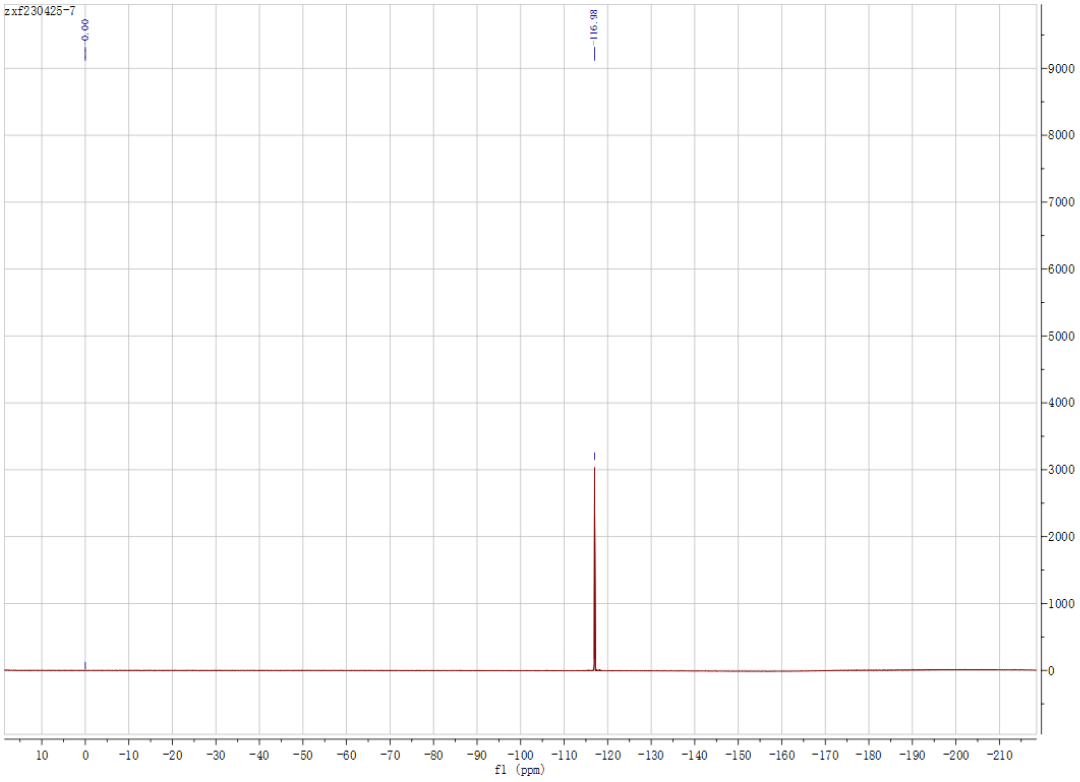




5k, 50%



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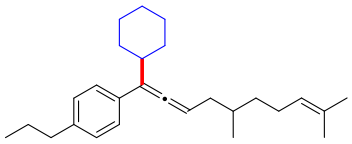
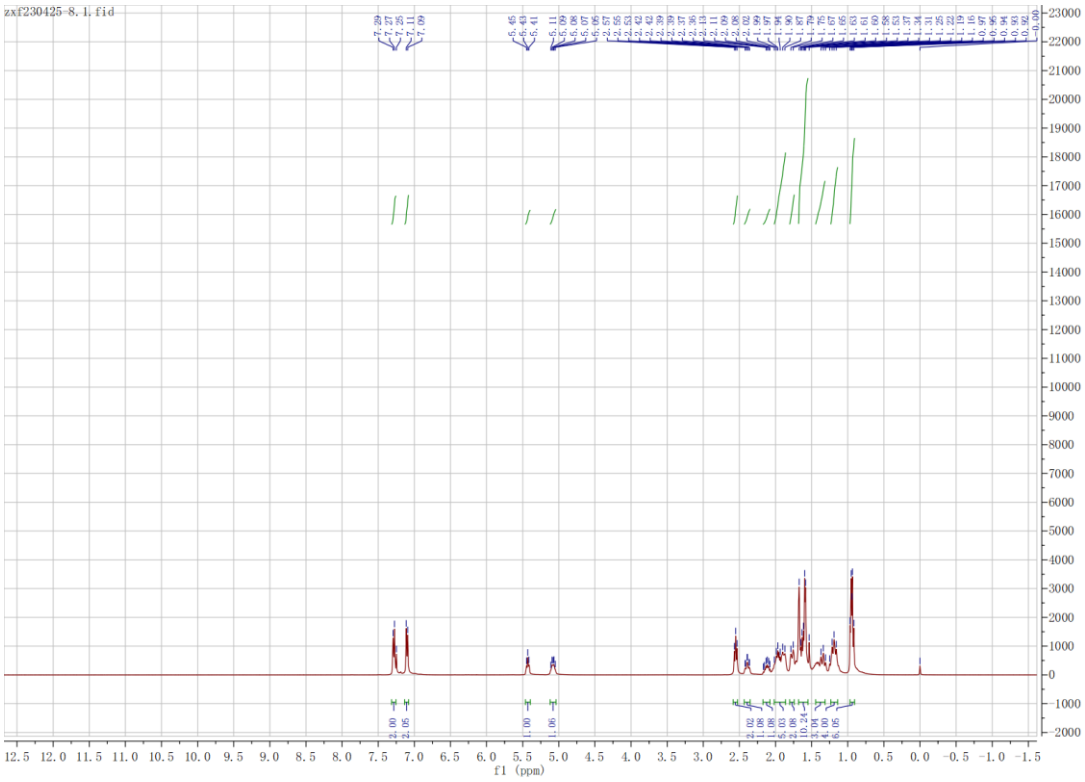
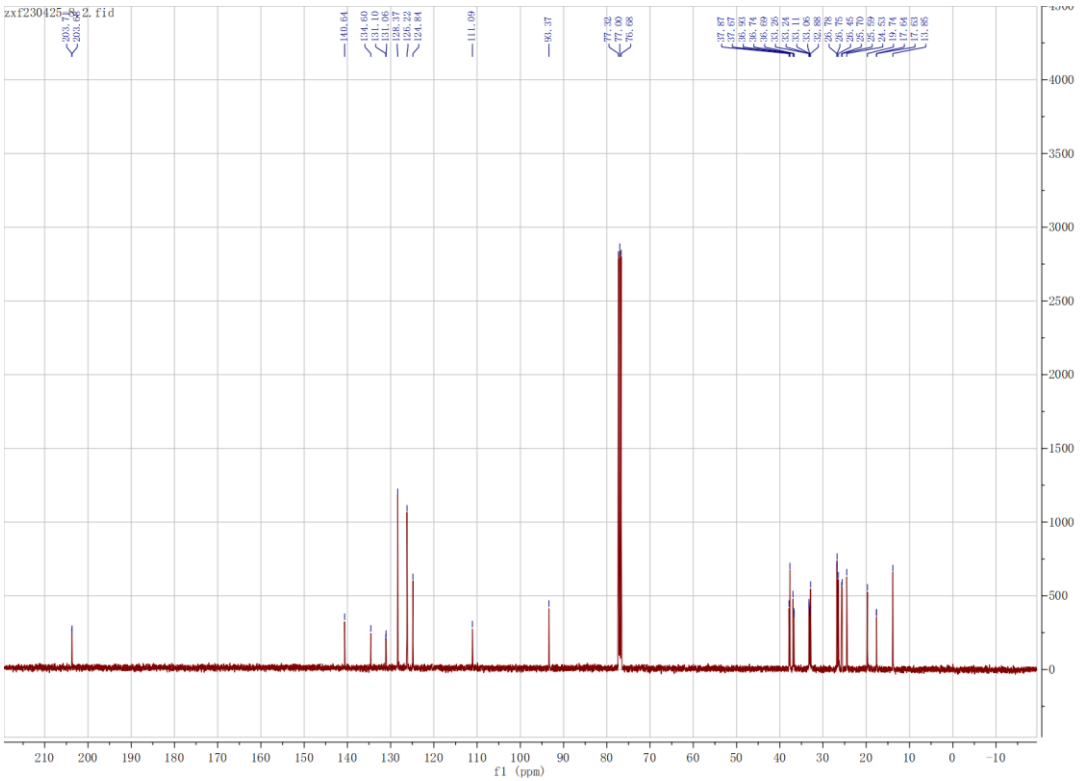
-200
-210
f1 (ppm)

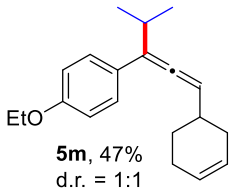


5l, 35%
d.r. = 1:1

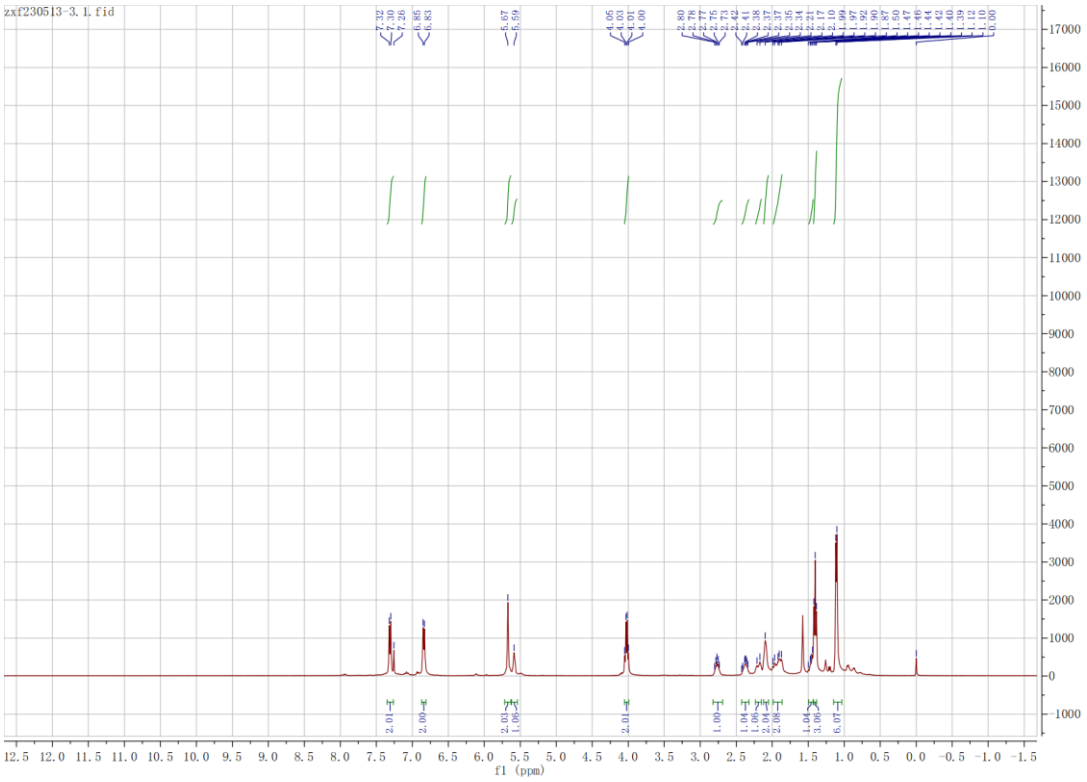
Citronellal derivative

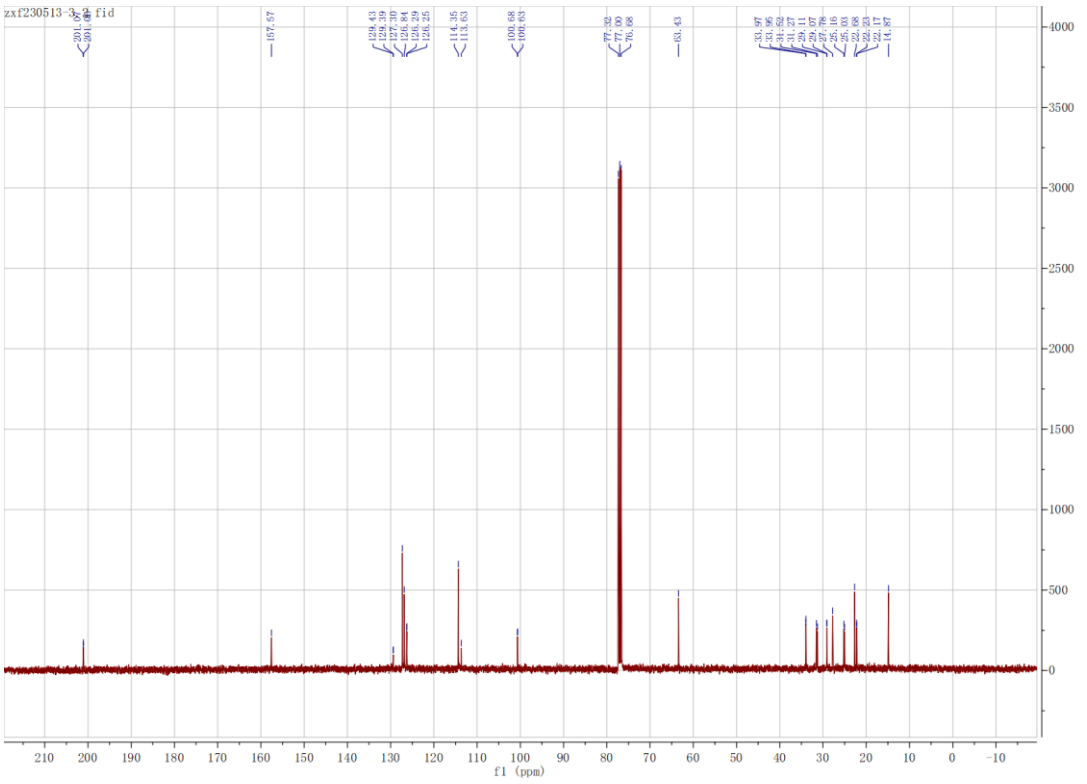


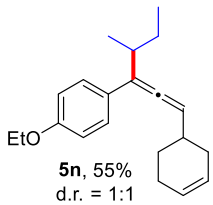




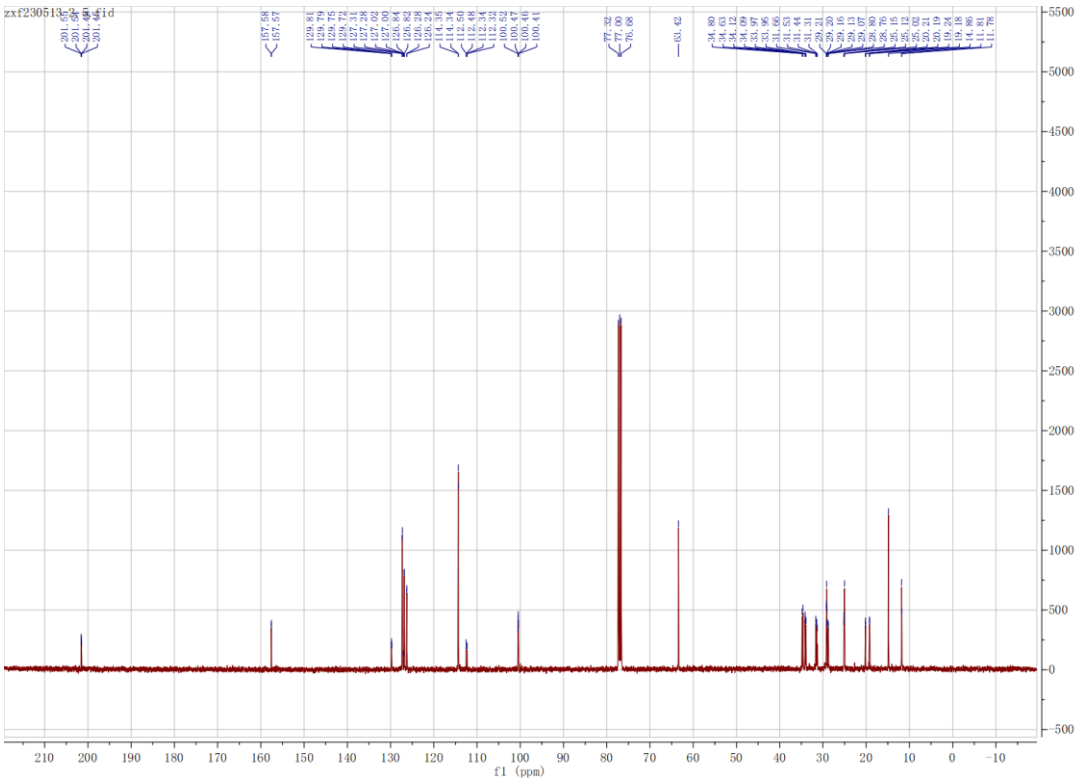
5m, 47%
d.r. = 1:1

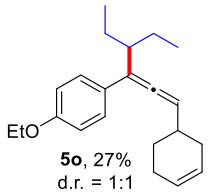




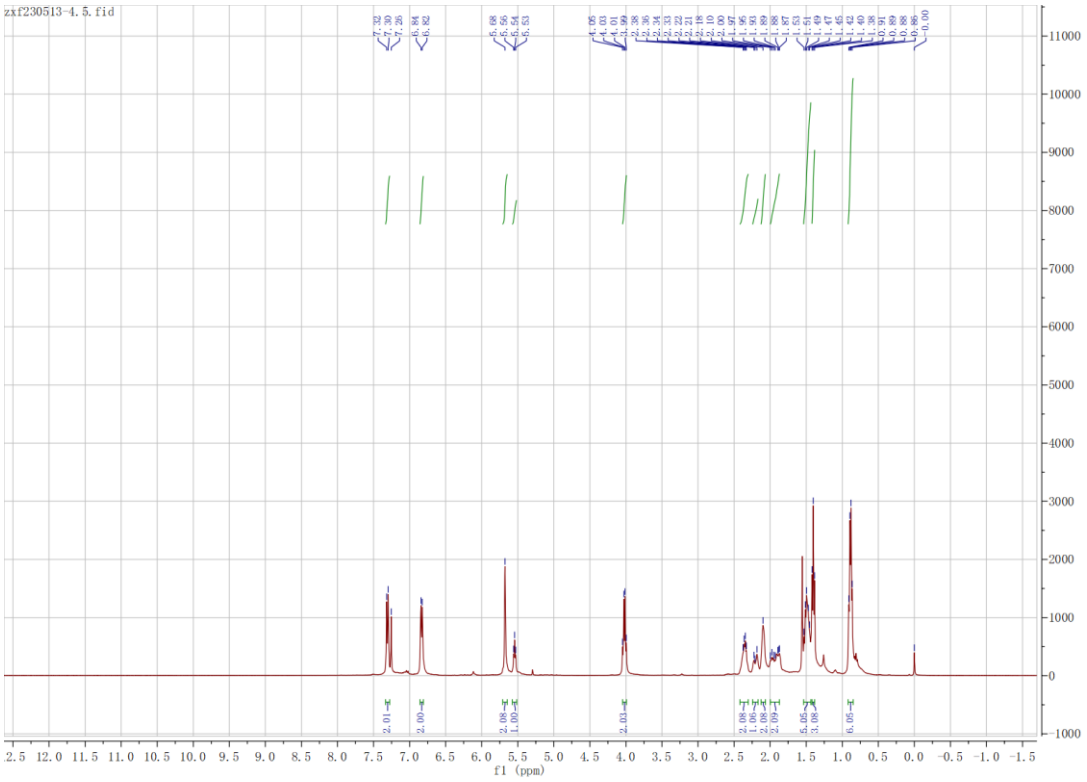


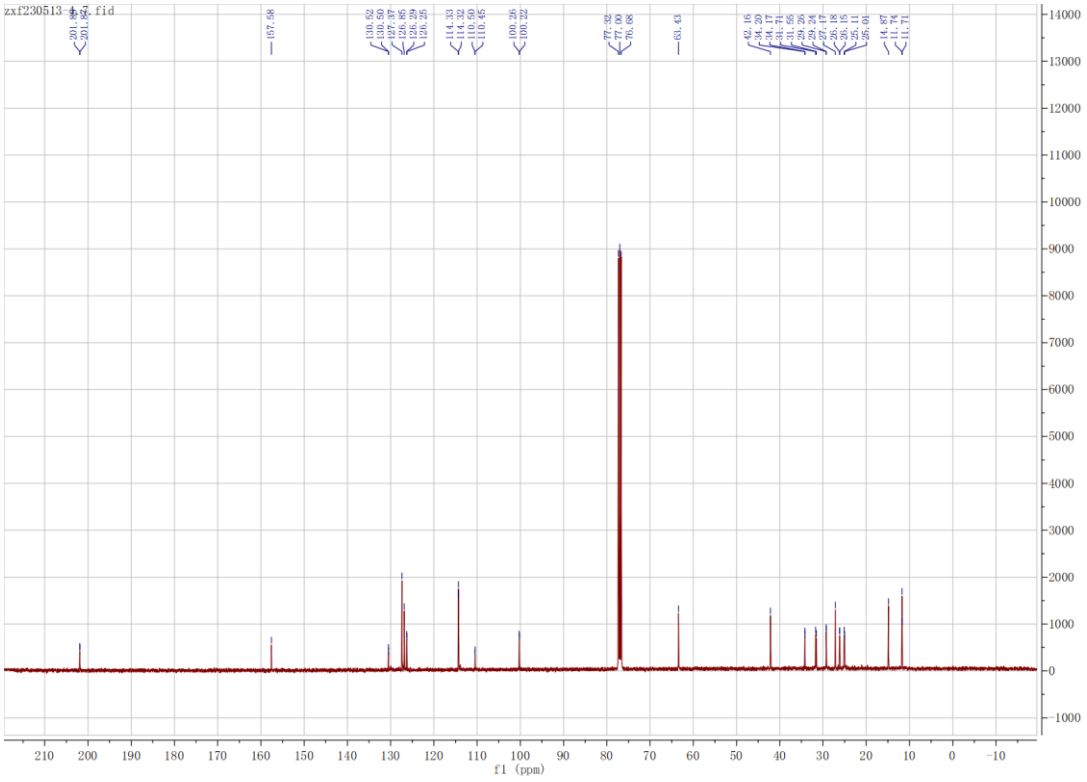
5n, 55%
d.r. = 1:1

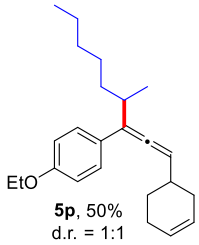




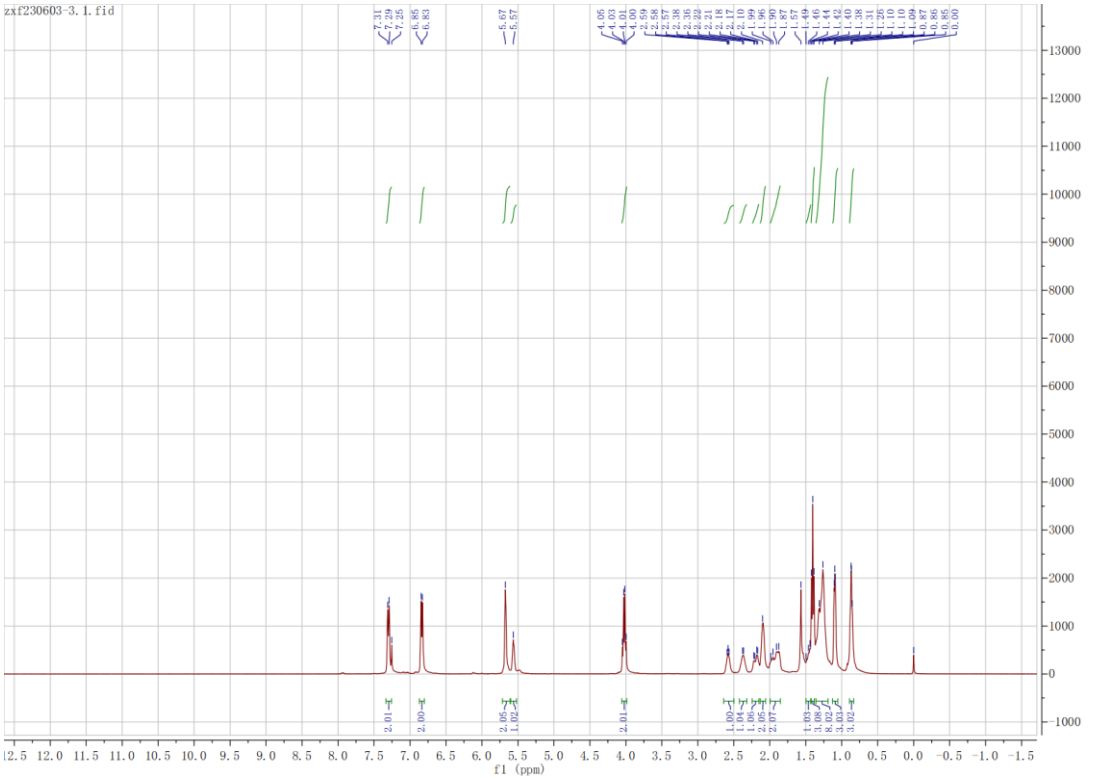
5o, 27%
d.r. = 1:1

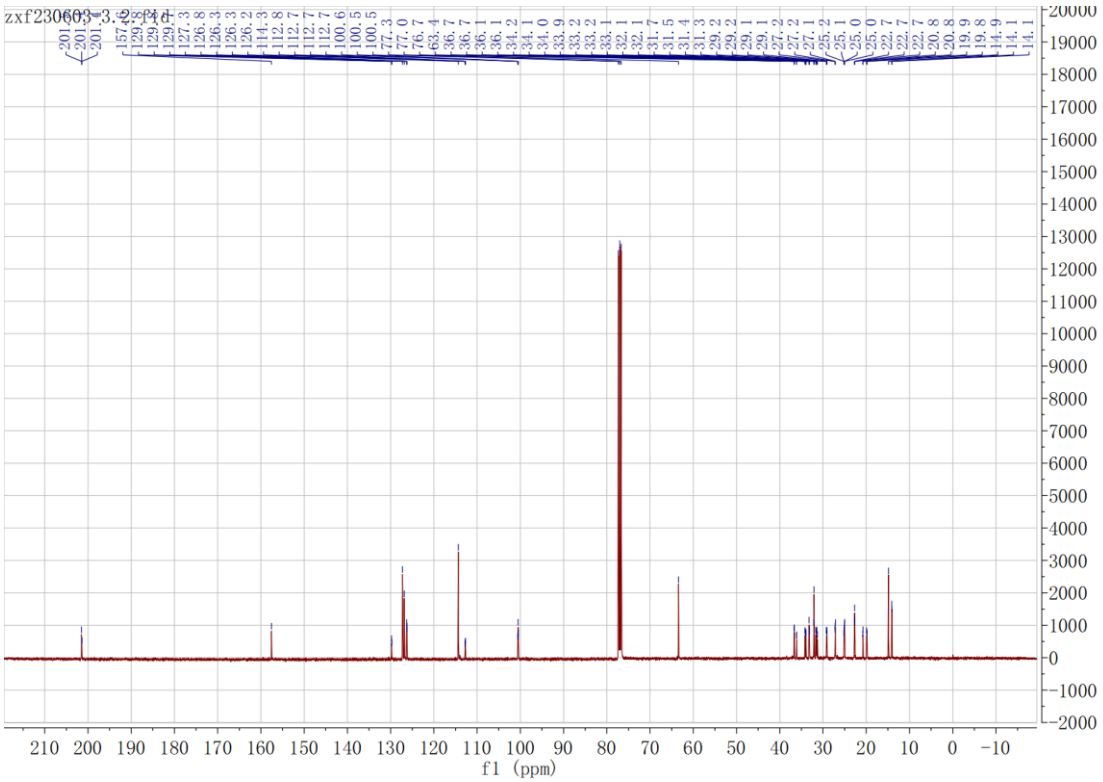


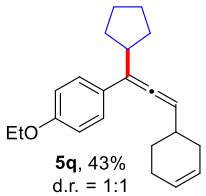




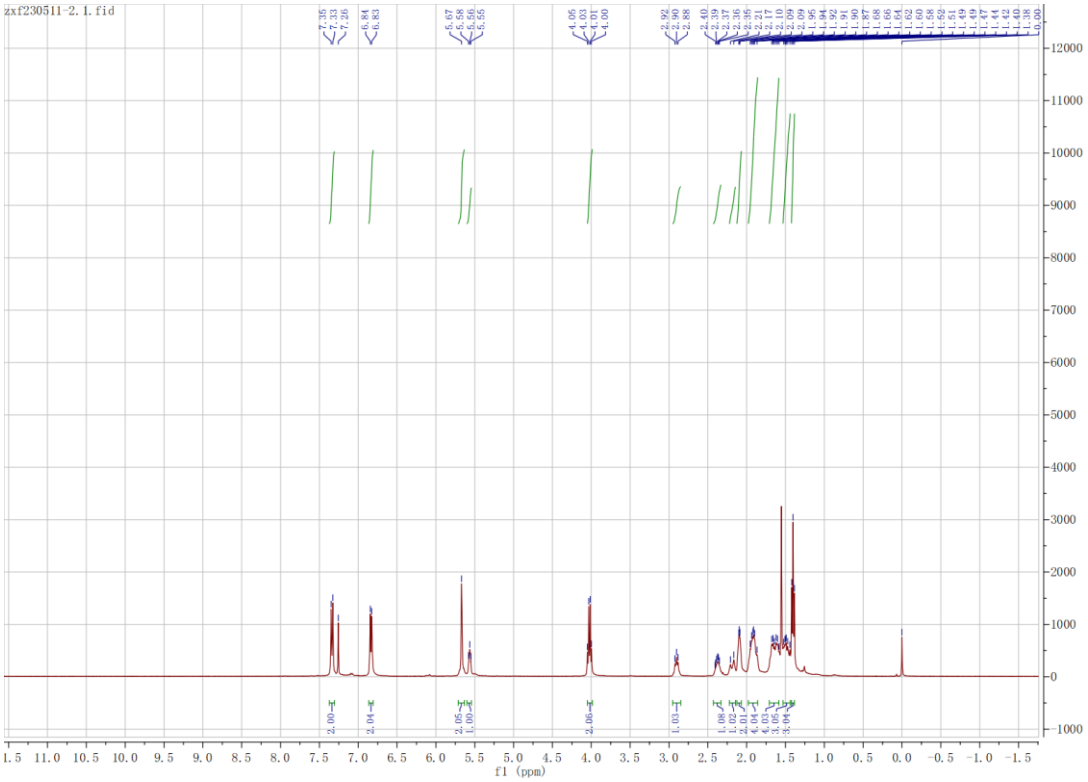
5p, 50%
d.r. = 1:1

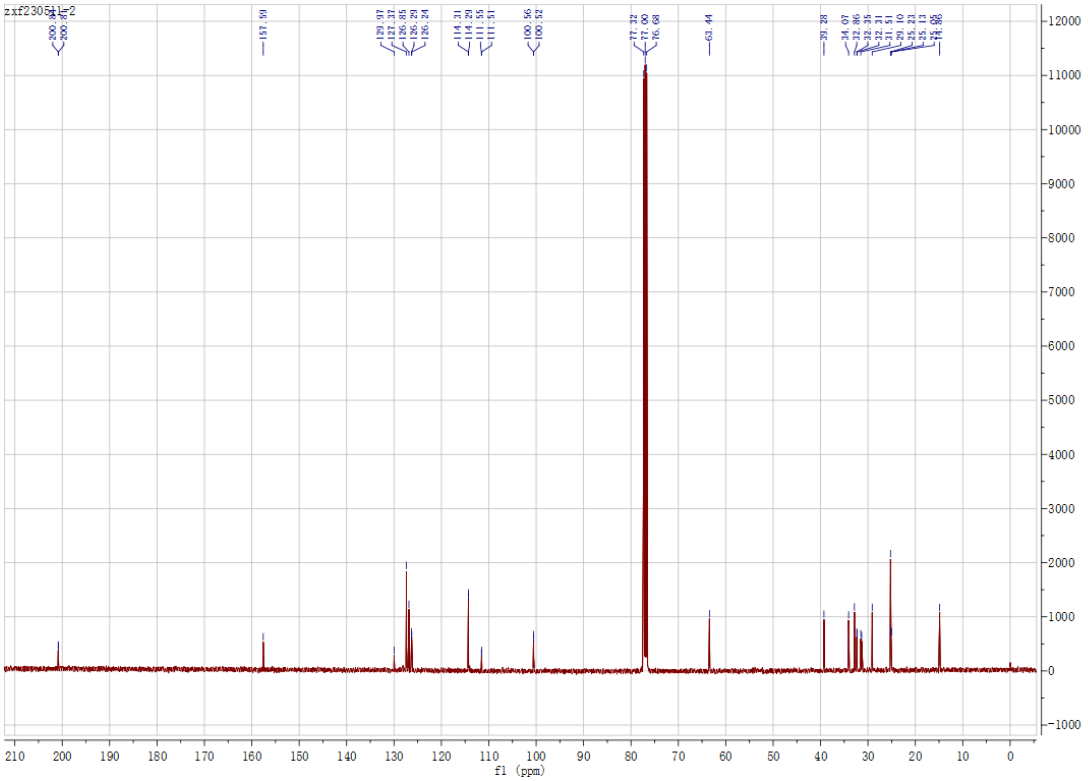


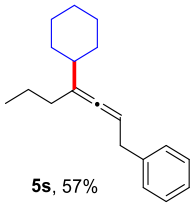




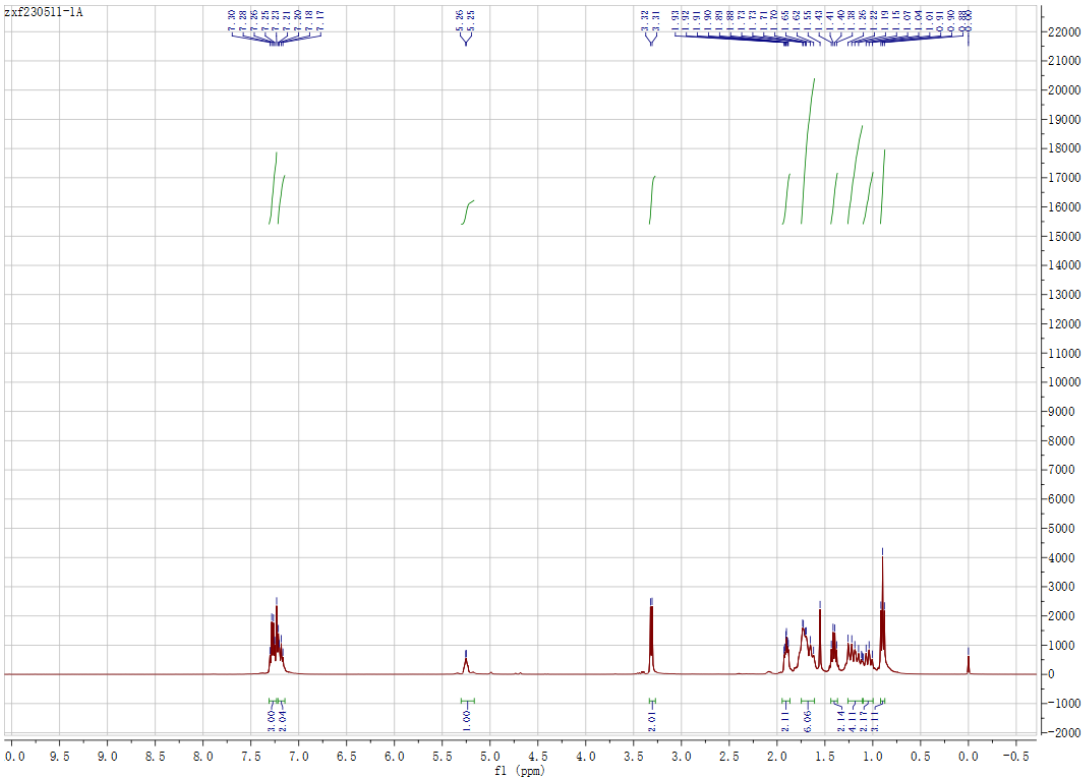
5q, 43%
d.r. = 1:1

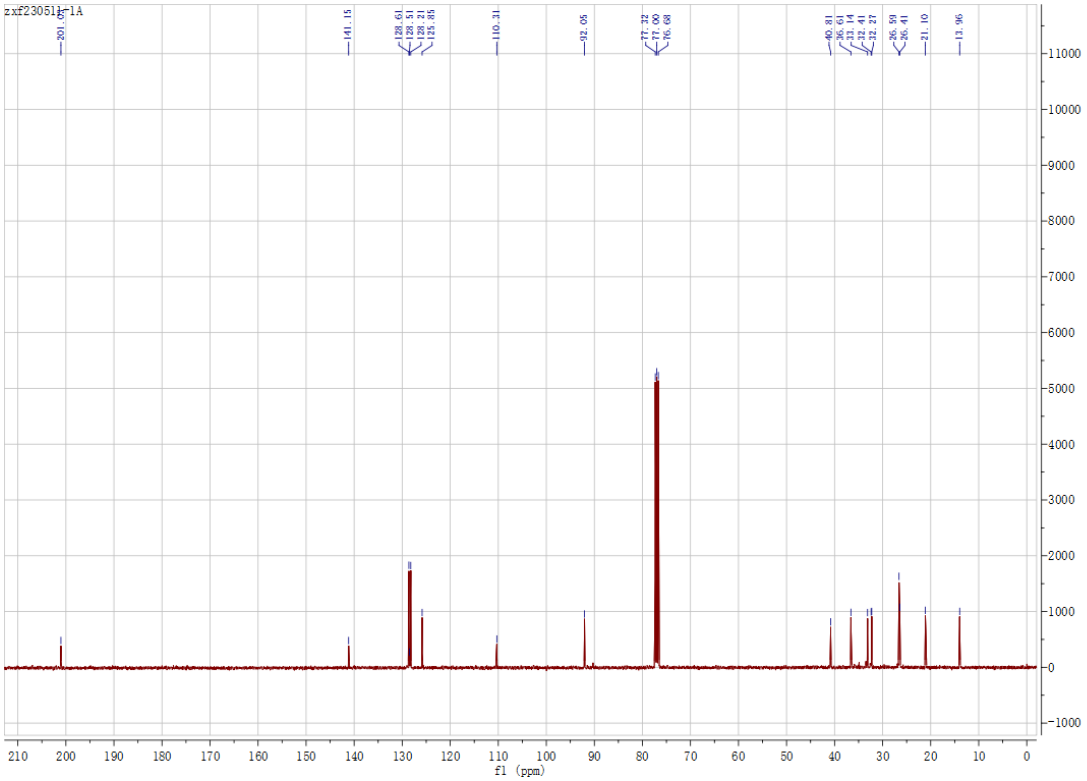


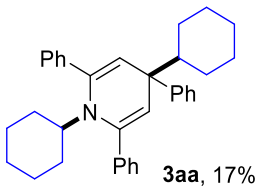




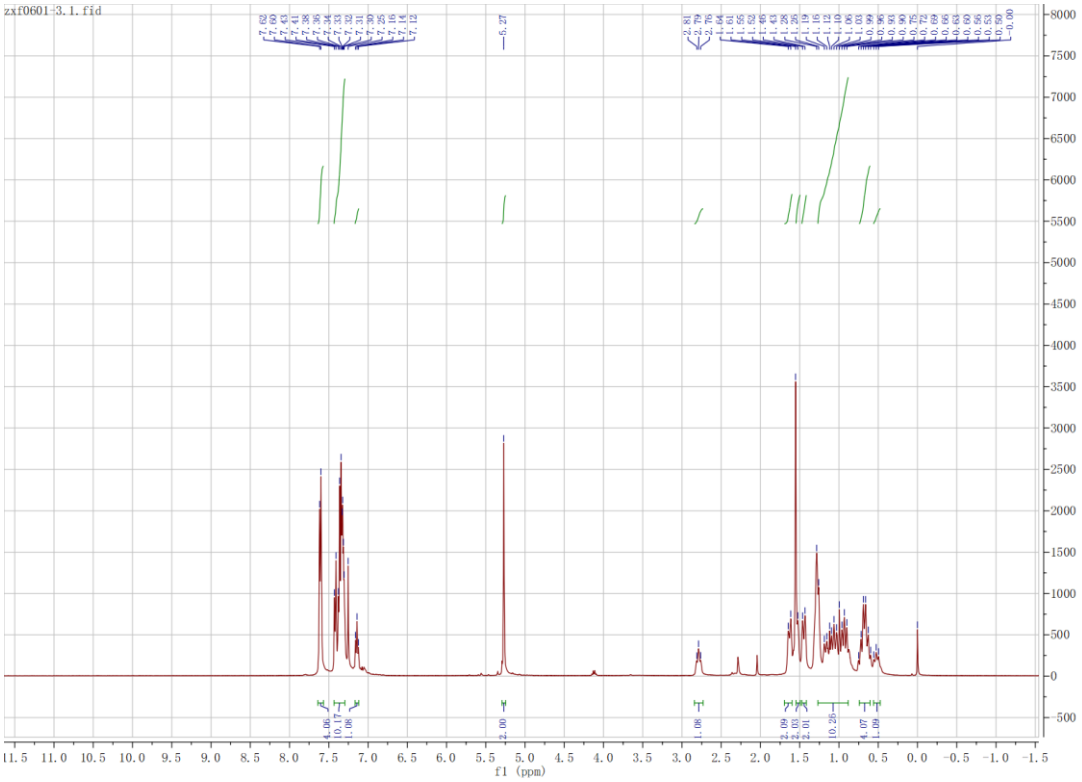
5s, 57%

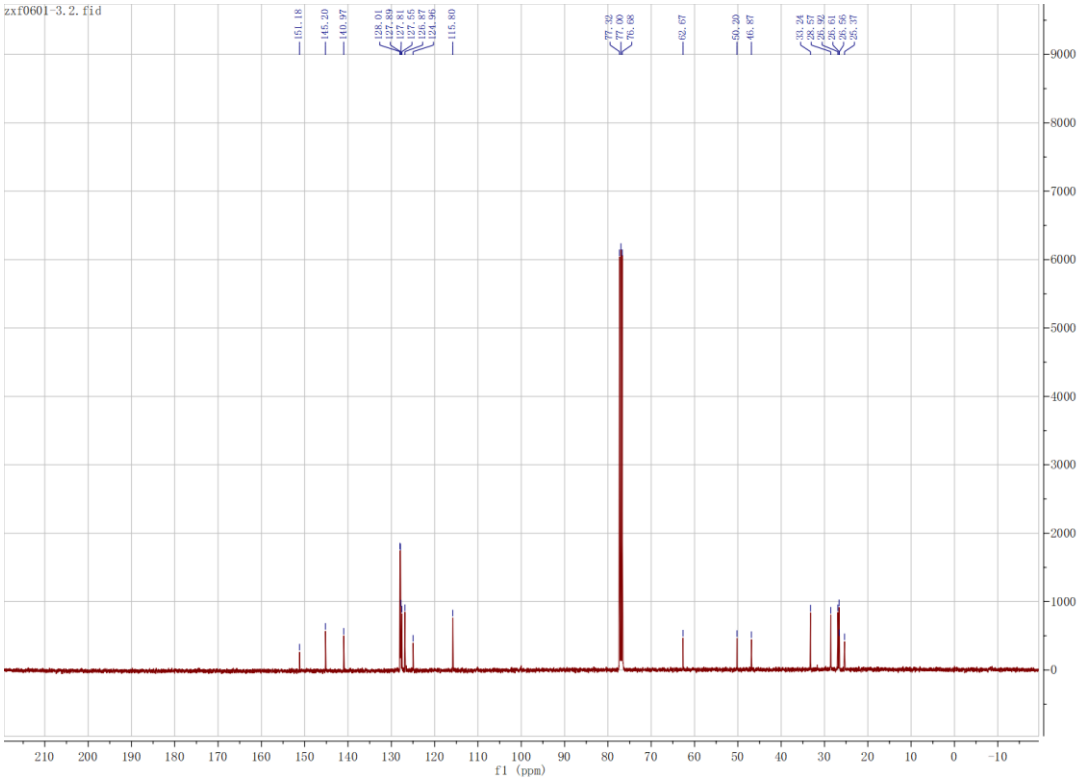


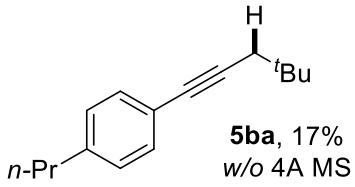




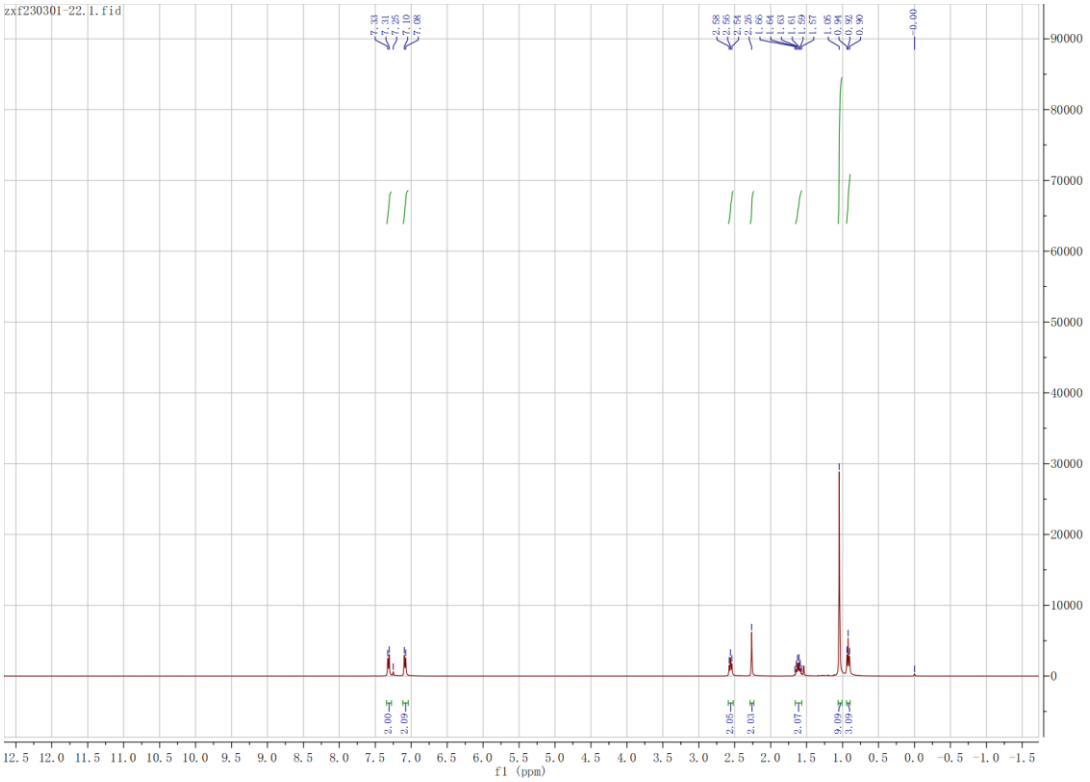
3aa, 17%

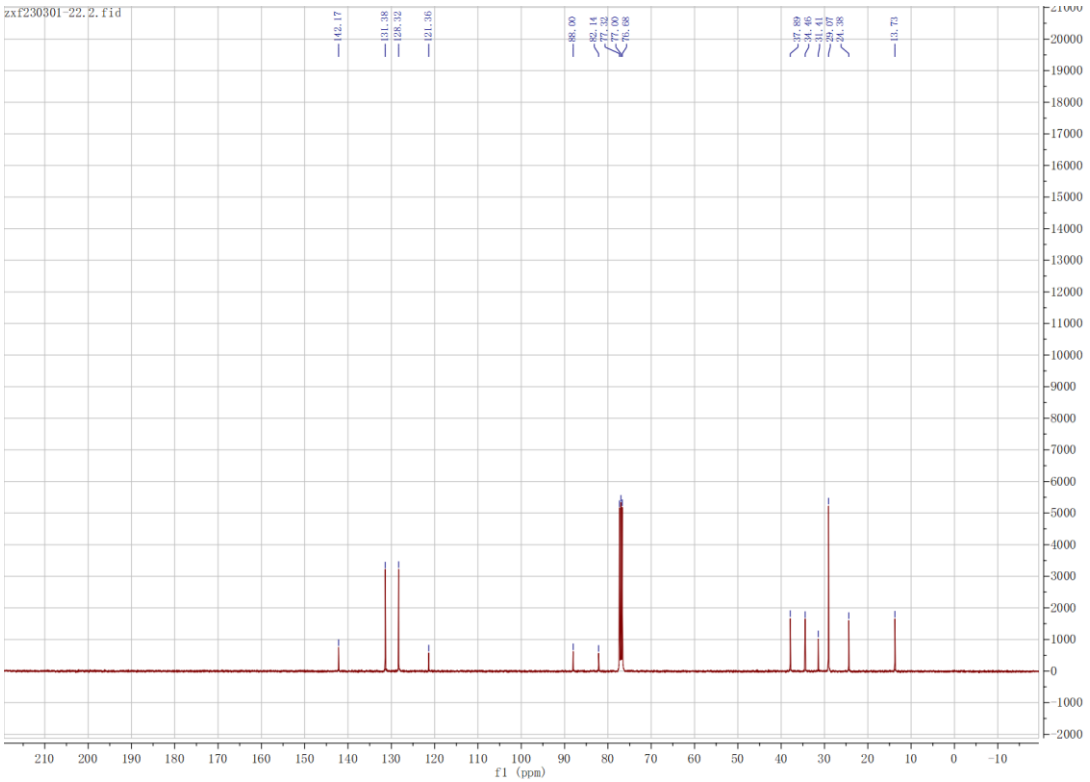


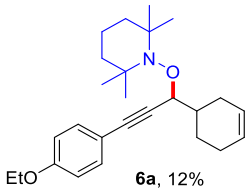




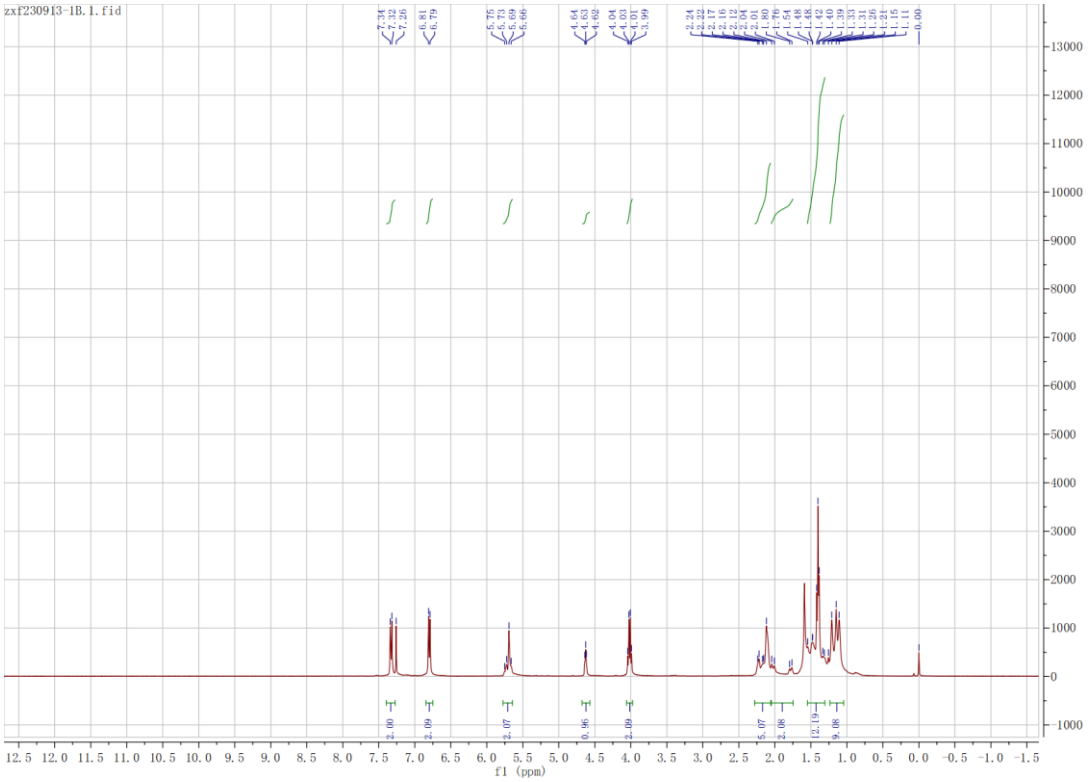
5ba, 17%
w/o 4A MS

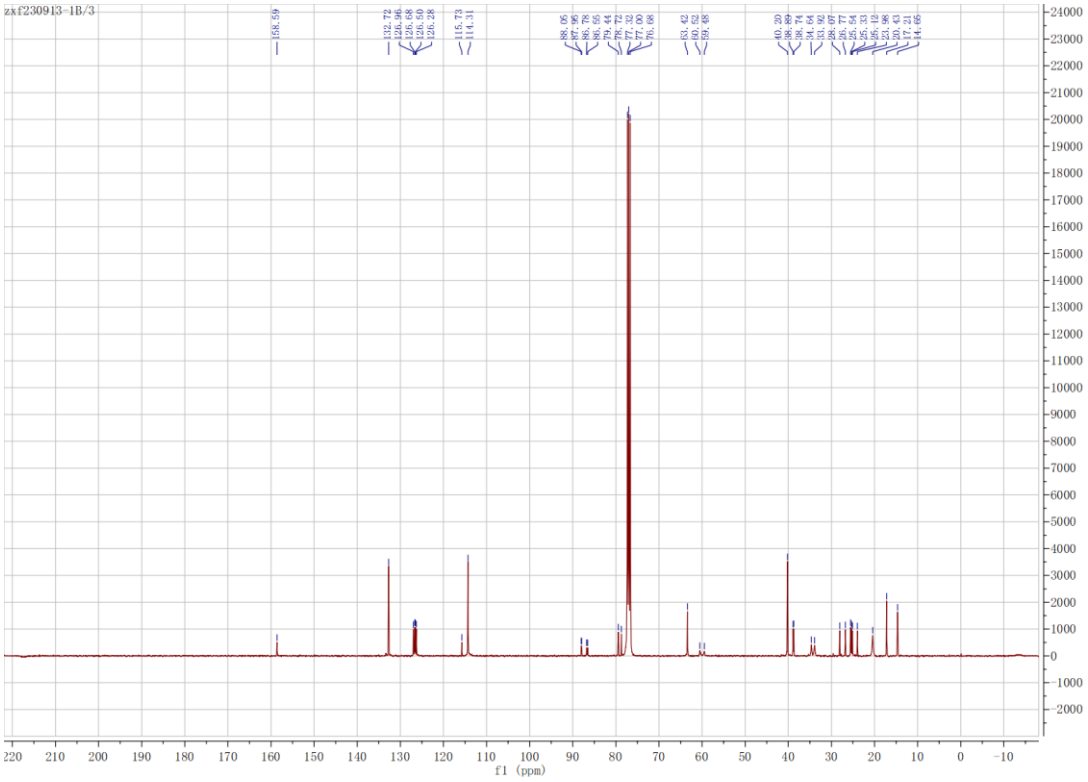


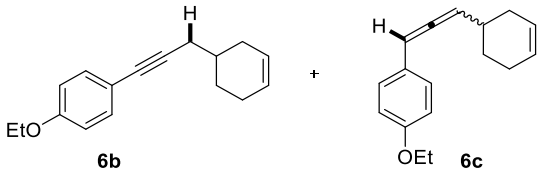




6a, 12%







6b +

6c

23% yield, **6b : 6c** = 5 : 3