Supporting Information

Photoredox/Nickel dual-Catalyzed Regioselective Alkylation of Propargylic Carbonates for Trisubstituted Allenes

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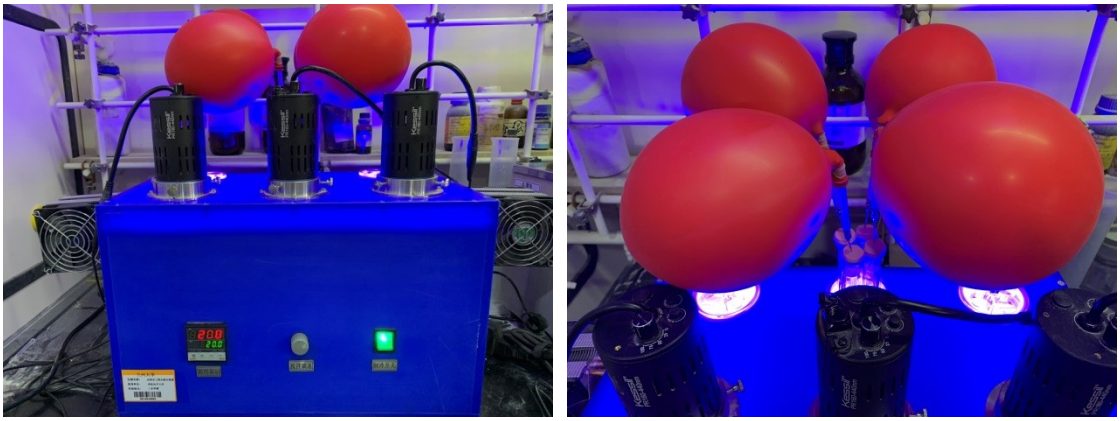
1. General Information and Materials:

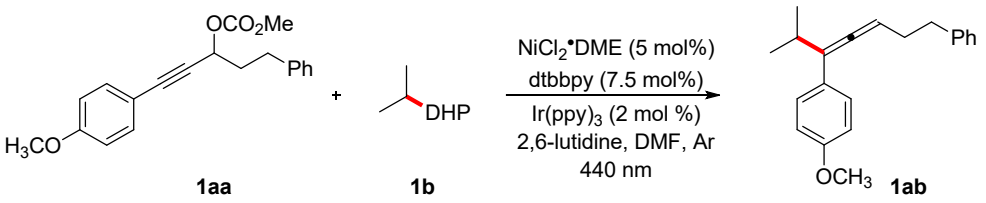
For product purification by flash column chromatography, silica gel (200~300 mesh) and *n*-pentane were used. ^{1}H NMR spectra were recorded on 400 MHz in $CDCl_3$, ^{13}C NMR spectra were recorded on 100 MHz in $CDCl_3$, ^{19}F NMR spectra were recorded on 376 MHz in $CDCl_3$ using TMS as internal 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 and ^{13}C NMR spectra were provided. The starting materials were purchased from Sigma-Aldrich, Acros, TCI, Admas or J&K Chemicals and used without further purification.

Kessil brand 440 (± 15) nm LED was used in a reaction box equipped cooling fan to keep reaction temperature between 15 °C and 25 °C.



Photoredox devices with Kessil LED lights 440 (± 15) nm

2. General Procedure for the photoredox/palladium dual-catalyzed propargylic benzylation reaction:



1aa **1b** **1ab**

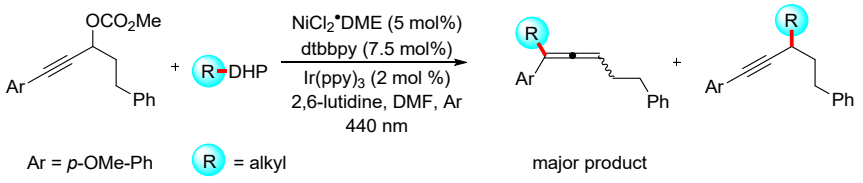
In a 5.0 mL snap vial with Teflon cover and magnetic stirring bar the internal propargylic carbonates **1aa-1ra**, **2aa-2oa** (0.2 mmol), alkyl 1,4-dihydropyridines derivatives **1b** (0.3 mmol, 1.5 equiv), $NiCl_2$·DME (0.01 mmol, 5 mol %), dtbbpy (0.015 mmol, 7.5 mol %), $Ir(ppy)_3$ (0.004 mmol, 2 mol %) were filled. After degassing with argon by syringe needle for 5 minutes and dissolving with 2.0 mL DMF, the reaction mixture was stirred for 10 minutes to become clear. Then, 2,6-lutidine (0.24 mmol, 1.2 equiv) was added and the vial was irradiated in reactor with cooling device using a 440 (± 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 saturated $CuSO_4$ solution to clean up 2,6-lutidine and final combined organic layer were dried over $MgSO_4$, filtered and concentrated in vacuum. Purification of the crude product was achieved by flash column chromatography using *n*-pentane as eluents on silica gel.

3. Preparation of Starting Materials:

All of propargylic carbonates and benzyl 1,4-dihydropyridine derivatives (DHP) 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]

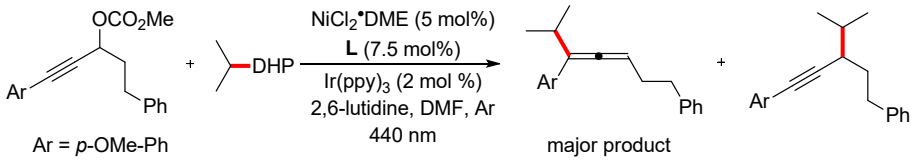
4. Optimization of Reaction Conditions:

a) Screening of alkyl 1,4-dihydropyridines derivatives:



DHP	DHP	DHP
trace	trace	yield: 86% (1:0)

b) Screening of solvents and the loading of ligand & additive:



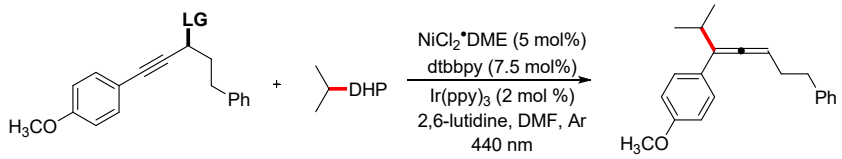
Ar = *p*-OMe-Ph

major product

entries	Catalyst (5 mol %)	Ligand (7.5 mol %)	PC (2 mol %)	additive (1.2 equiv.)	**Solvent**	yield (%)
1	$NiCl_2$·DME	dtbbpy	$Ir(ppy)_3$	2,6-lutidine	**THF**	45
2	$NiCl_2$·DME	dtbbpy	$Ir(ppy)_3$	2,6-lutidine	**Dioxane**	9
3	$NiCl_2$·DME	dtbbpy	$Ir(ppy)_3$	2,6-lutidine	**DCE**	26
4	$NiCl_2$·DME	dtbbpy	$Ir(ppy)_3$	2,6-lutidine	**Xylene**	31
5	$NiCl_2$·DME	dtbbpy	$Ir(ppy)_3$	2,6-lutidine	**CH_3CN**	8
6	$NiCl_2$·DME	dtbbpy	$Ir(ppy)_3$	2,6-lutidine	**DMF**	86
7	$NiCl_2$·DME	dtbbpy	$Ir(ppy)_3$	2,6-lutidine	**DMF**	84[a]
8	$NiCl_2$·DME	dtbbpy	$Ir(ppy)_3$	Cs_2CO_3	**DMF**	54
9	$NiCl_2$·DME	dtbbpy	$Ir(ppy)_3$	-	**DMF**	74

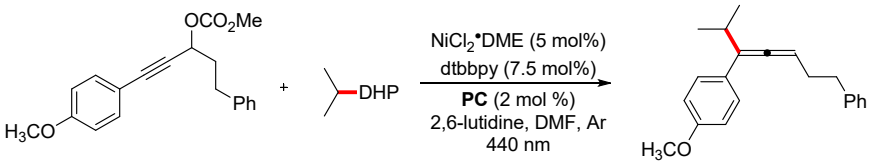
[a] With dtbbpy (10 mol %).

c) Screening of leaving group on propargylic derivatives:



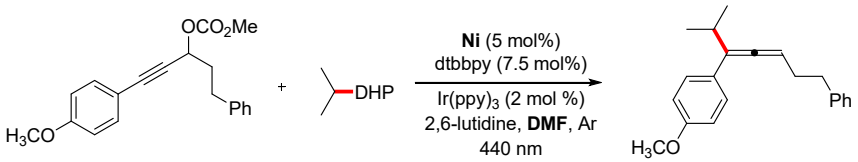
entries	Catalyst (5 mol %)	Ligand (7.5 mol %)	PC (2 mol %)	additive (1.2 equiv.)	**LG**	yield (%)
1	$NiCl_2$·DME	dtbbpy	$Ir(ppy)_3$	2,6-lutidine	**OAc**	42
2	$NiCl_2$·DME	dtbbpy	$Ir(ppy)_3$	2,6-lutidine	**Cl**	65
3	$NiCl_2$·DME	dtbbpy	$Ir(ppy)_3$	2,6-lutidine	**OCO_2Ph**	58

d) Screening of photocatalysis:



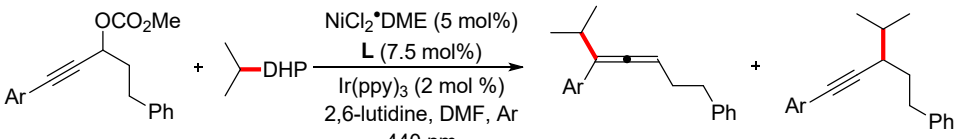
entries	Catalyst (5 mol %)	Ligand (7.5mol %)	**PC (2 mol %)**	additive (1.2 equiv.)	yield (%)
1	$NiCl_2$·DME	dtbbpy	**$Ru(bpy)_3Cl_2$**	2,6-lutidine	trace
2	$NiCl_2$·DME	dtbbpy	**4CzIPN**	2,6-lutidine	15

e) Screening of nickel catalysis:



entries	**Catalyst (5 mol %)**	Ligand (7.5 mol %)	PC (2 mol %)	additive (1.2 equiv.)	yield (%)
1	**$NiBr_2$·DME**	dtbbpy	$Ir(ppy)_3$	2,6-lutidine	69
4	**$Ni(acac)_2$**	dtbbpy	$Ir(ppy)_3$	2,6-lutidine	13
5	**$Ni(OTf)_2$**	dtbbpy	$Ir(ppy)_3$	2,6-lutidine	27

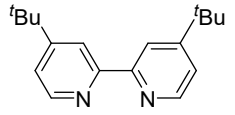
f) Screening of ligands:



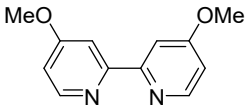
Ar = *p*-OMe-Ph

major product

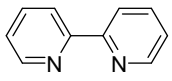
entries	Catalyst (5 mol %)	Ligand (7.5 mol %)	PC (2 mol %)	additive (1.2 equiv.)	Solvent	yield (%)
1	$NiCl_2$·DME	**L1**	$Ir(ppy)_3$	2,6-lutidine	DMF	86
2	$NiCl_2$·DME	**L2**	$Ir(ppy)_3$	2,6-lutidine	DMF	47 (9:1)
3	$NiCl_2$·DME	**L3**	$Ir(ppy)_3$	2,6-lutidine	DMF	73
4	$NiCl_2$·DME	**L4**	$Ir(ppy)_3$	2,6-lutidine	DMF	21
5	$NiCl_2$·DME	**L5**	$Ir(ppy)_3$	2,6-lutidine	DMF	26
7	$NiCl_2$·DME	**L6**	$Ir(ppy)_3$	Cs_2CO_3	DMF	44 (8:2)



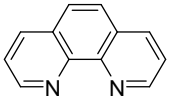
dtbbpy (**L1**)



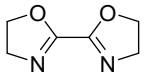
diOMe-bpy (**L2**)



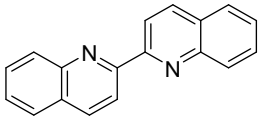
bpy (**L3**)



Phen (**L4**)



Bis(2-oxazoline) (**L5**)

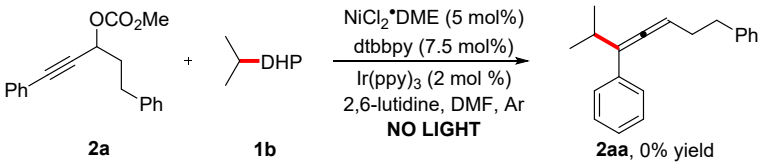


Biquinoline (**L6**)

5. Mechanism characterization:

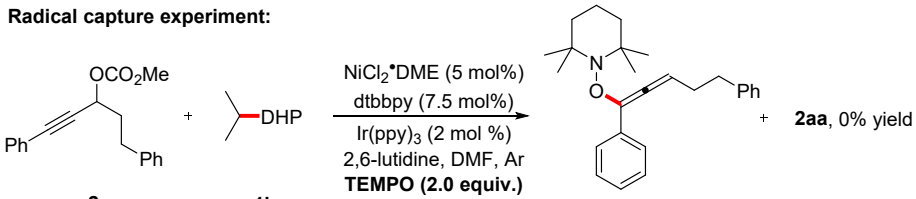
a) Control experiment and Radical capture experiment:

Control experiment:



2a **1b** **2aa**, 0% yield

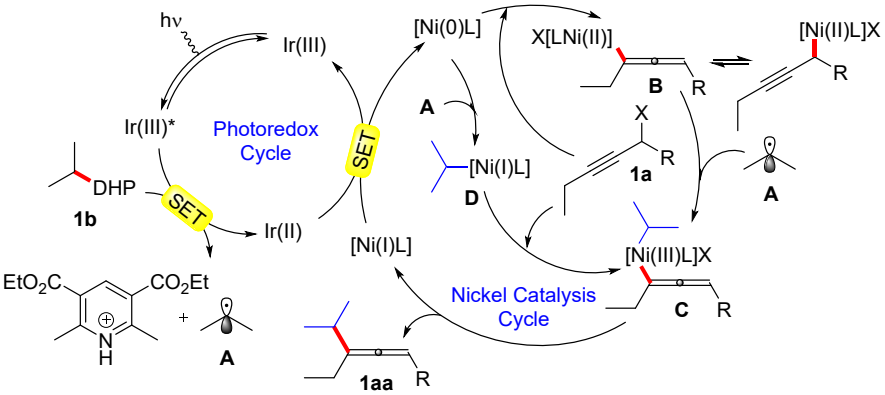
Radical capture experiment:



2a **1b** **2ab**, trace by GC-MS

Control experiment indicated that light is essential for initiation of alkyl radical. Radical capture product **2ab** was detected by GC-MS in trace yield under standard conditions through radical inhibition experiments with TEMPO, which indicated that this catalytic system with alkyl DHPs is different from nickel catalyzed allenyl substitution reaction with alkyl organometallic reagents (please see ref. 4).[4] According these results and previous work by Molander group,[5] a hypothetical mechanism was proposed as following.

b) Plausible mechanism:



A hypothetical mechanism for this regioselective allenylic alkylation is proposed here. With irradiation by visible light, the excited Ir(III)* complex induces an SET process through a reductive quenching cycle, leading to the low-valent Ir(II) complex and alkyl radical **A** from its 1,4-dihydropyridines precursor **1b**. Meanwhile, nickel(0) catalyst promotes decarboxylation of propargylic carbonate **1a** to generate a Ni(II) species regioselectively, namely allenyl nickel intermediate **B**, which then trapped by alkyl radical to generate Ni(III) intermediate **C** and obtained the desired allenylic alkylation product **1aa** after reductive elimination. Finally, complete co-catalytic system is achieved with reduction of Ni(I) complex to Ni(0) by low-valent Ir(II) complex. However, the process with intermediate **C** from alkylated Ni(I) species **D** would be an alternative pathway.

6. References:

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

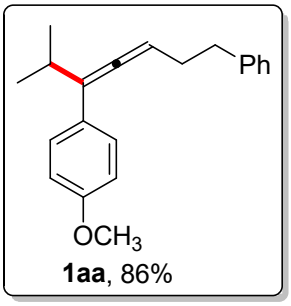
[2] (a) Á. Gutiérrez-Bonet, J. C. Tellis, J. K. Matsui, B. A. Vara and G. A. Molander, *ACS Catal.,* 2016, **6**, 8004; (b) Á Gutiérrez-Bonet, C. Remeur, J. K. Matsui and G. A. Molander, *J. Am. Chem. Soc.,* 2017, **139**, 12251.

[3] Z.-Z. Zhou, R.-Q. Jiao, K. Yang, X.-M. Chen and Y.-M. Liang, *Chem. Commun.,* 2020, **56**, 12957.

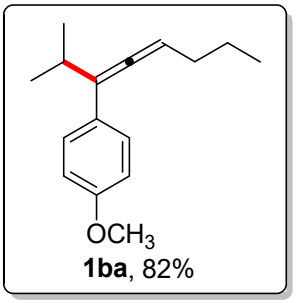
[4] (a) R. Soler-Yanes, I. Arribas-Álvarez, M. Guisán-Ceinos, E. Buñuel and D. Cárdenas, *Chem.-Eur. J.,* 2017, **23**, 1584; (b) J. Terao, F. Bando and N. Kambe, *Chem. Commun.,* 2009, 7336.

[5] (a) O. Gutierrez, J. C. Tellis, D. N. Primer, G. A. Molander and M. C. Kozlowski, J. Am. Chem. Soc., 2015, 137, 4896; (b) J. C. Tellis, C. B. Kelly, D. N. Primer, M. Jouffroy, N. R. Patel and G. A. Molander, *Acc. Chem. Res.,* 2016, **49**, 1429.

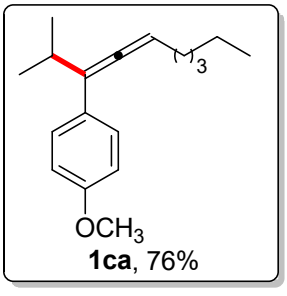
7. Characterization Data of Products 1aa-1pa:



1aa: according to **General Procedure**; colorless oil; Eluent: *n*-hexane/EtOAc = 100/1;
^{1}H NMR (400 MH_Z $CDCl_3$, δ ppm): 1.07-1.09 (d, J = 8.0 Hz, 6H), 2.39-2.45 (m, 2H), 2.75-2.79 (m, 3H), 3.78 (s, 3H), 5.52-5.55 (dt, J_1 = 4.0 Hz, J_2 = 8.0 Hz, 1H), 6.81-6.83 (d, J = 8.0 Hz, 2H), 7.16-7.28 (m, 7H);
^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 22.2, 22.5, 27.8, 31.2, 35.6, 55.2, 94.7, 112.8, 113.7, 125.8, 127.4, 128.3, 128.5, 129.3, 141.8, 158.1, 202.2;
HRMS (ESI) calcd for $C_{21}H_{24}O$ $[M+H]^+$ m/z 293.1900, found 293.1903.

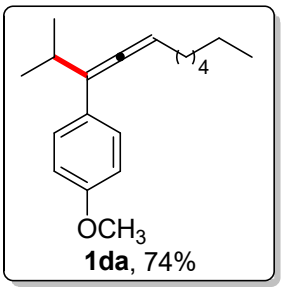


1ba: according to **General Procedure**; colorless oil; Eluent: *n*-hexane/EtOAc = 100/1;
^{1}H NMR (400 MH_Z $CDCl_3$, δ ppm): 0.93-0.97 (t, J = 8.0 Hz, 3H), 1.10-1.11 (d, J = 4.0 Hz, 6H), 1.46-1.51 (m, 2H), 2.04-2.10 (m, 2H), 2.73-2.79 (m, 2H), 3.79 (s, 3H), 5.49-5.52 (t, J = 4.0 Hz, 1H), 6.84-6.86 (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): 13.9, 22.2, 22.6, 27.9, 31.5, 55.2, 95.3, 112.3, 113.7, 127.4, 129.7, 158.1, 202.3;
HRMS (ESI) calcd for $C_{16}H_{22}O$ $[M+H]^+$ m/z 231.1743, found 231.1745.



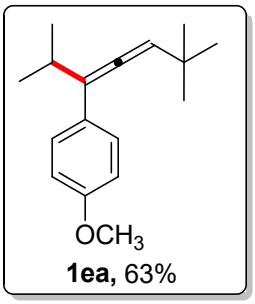
1ca: according to **General Procedure**; colorless oil; Eluent: *n*-hexane/EtOAc = 100/1;

^{1}H NMR (400 MH_Z $CDCl_3$, δ ppm): 0.86-0.89 (t, J = 4.0 Hz, 3H), 1.10-1.12 (m, 6H), 1.31-1.32 (m, 4H), 1.42-1.48 (m, 2H), 2.06-2.11 (dd, J_1 = 8.0 Hz, J_2 = 12.0 Hz, 2H), 2.72-2.79 (m, 1H), 3.78 (s, 3H), 5.48-5.52 (dt, J_1 = 4.0 Hz, J_2 = 8.0 Hz, 1H), 6.84-6.86 (d, J = 8.0 Hz, 2H), 7.30-7.32 (d, J = 8.0 Hz, 2H);
^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 14.0, 22.2, 22.5, 22.6, 27.9, 29.0, 29.3, 31.5, 55.2, 95.4, 112.3, 113.7, 127.4, 129.7, 158.1, 202.2;
HRMS (ESI) calcd for $C_{18}H_{26}O$ $[M+H]^+$ m/z 259.2056, found 259.2058.



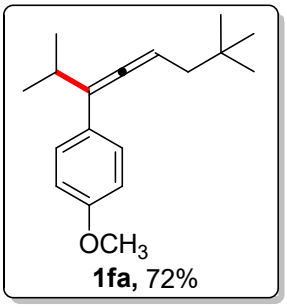
1da, 74%

1da: according to **General Procedure**; colorless oil; Eluent: *n*-hexane/EtOAc = 100/1;
^{1}H NMR (400 MH_Z $CDCl_3$, δ ppm): 0.85-0.89 (t, J = 8.0 Hz, 3H), 1.09-1.12 (m, 6H), 1.27-1.36 (m, 6H), 1.42-1.47 (m, 2H), 2.06-2.11 (dd, J_1 = 8.0 Hz, J_2 = 12.0 Hz, 2H), 2.72-2.79 (m, 1H), 3.79 (s, 3H), 5.48-5.51 (dt, J_1 = 4.0 Hz, J_2 = 8.0 Hz, 1H), 6.84-6.86 (d, J = 8.0 Hz, 2H), 7.30-7.32 (d, J = 8.0 Hz, 2H);
^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 14.1, 22.2, 22.6, 22.7, 27.9, 29.0, 29.4, 31.7, 55.2, 95.4, 112.3, 113.7, 127.4, 129.7, 158.1, 202.2;
HRMS (ESI) calcd for $C_{19}H_{28}O$ $[M+H]^+$ m/z 273.2213, found 273.2217.



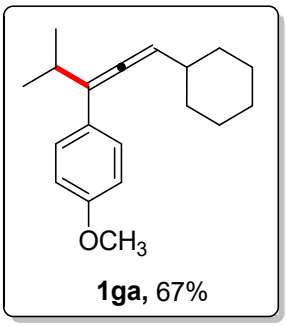
1ea, 63%

1ea: according to **General Procedure**; colorless oil; Eluent: *n*-hexane/EtOAc = 100/1;
^{1}H NMR (400 MH_Z $CDCl_3$, δ ppm): 1.10-1.12 (m, 15H), 2.75-2.81 (m, 1H), 3.79 (s, 3H), 5.51 (m, 1H), 6.84-6.87 (d, J = 12.0 Hz, 2H), 7.32-7.34 (d, J = 8.0 Hz, 2H);
^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 22.2, 22.7, 27.8, 30.3, 32.8, 55.2, 107.3, 113.7, 127.2, 129.7, 158.1, 199.1;
HRMS (ESI) calcd for $C_{17}H_{24}O$ $[M+H]^+$ m/z 245.1900, found 245.1908.



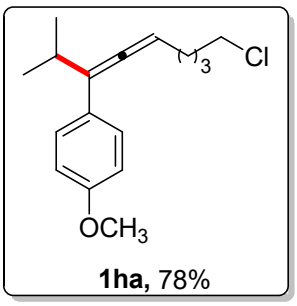
1fa, 72%

1fa: according to **General Procedure**; colorless oil; Eluent: *n*-hexane/EtOAc = 100/1;
^{1}H NMR (400 MH_Z $CDCl_3$, δ ppm): 0.96 (s, 9H), 1.10-1.13 (m, 6H), 2.00-2.03 (dd, J_1 = 4.0 Hz, J_2 = 8.0 Hz, 2H), 2.72-2.79 (m, 1H), 3.79 (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), 7.30-7.32 (d, J = 8.0 Hz, 2H);
^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 22.3, 22.6, 28.0, 29.3, 31.1, 44.4, 55.2, 92.2, 111.2, 113.7, 127.5, 129.8, 158.1, 203.3;
HRMS (ESI) calcd for $C_{18}H_{26}O$ $[M+H]^+$ m/z 259.2056, found 259.2061.



1ga, 67%

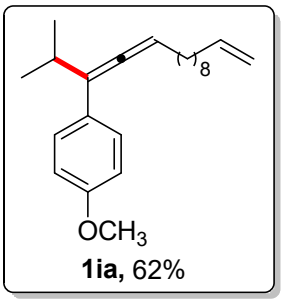
1ga: according to **General Procedure**; colorless oil; Eluent: *n*-hexane/EtOAc = 100/1;
^{1}H NMR (400 MH_Z $CDCl_3$, δ ppm): 1.10-1.12 (m, 6H), 1.19-1.30 (m, 4H), 1.63-1.74 (m, 4H), 1.82 (m, 2H),2.02-2.06 (m, 1H), 2.73-2.80 (m, 1H), 3.79 (s, 3H), 5.50-5.52 (dd, J_1 = 4.0 Hz, J_2 = 8.0 Hz, 1H), 6.84-6.86 (d, J = 12.0 Hz, 2H), 7.32-7.34 (d, J = 8.0 Hz, 2H);
^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 22.2, 22.7, 26.2, 26.2, 27.7, 33.3, 33.4, 38.1, 55.2, 101.5, 113.1, 113.7, 127.3, 129.7, 158.1, 200.9;
HRMS (ESI) calcd for $C_{19}H_{26}O$ $[M+H]^+$ m/z 271.2056, found 271.2063.



1ha, 78%

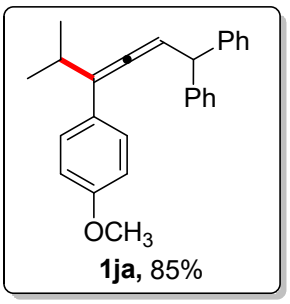
1ha: according to **General Procedure**; colorless oil; Eluent: *n*-hexane/EtOAc = 100/1;
^{1}H NMR (400 MH_Z $CDCl_3$, δ ppm): 1.09-1.12 (m, 6H), 1.54-1.66 (m, 2H), 1.79-1.86 (m, 2H), 2.09-2.15 (m, 2H), 2.73-2.80 (m, 1H), 3.50-3.53 (t, J = 8.0 Hz, 2H), 3.79 (s, 3H), 5.48-5.51 (dt, J_1 = 4.0 Hz, J_2 = 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): 22.2, 22.5, 26.4, 27.9, 28.5, 32.1, 44.8, 55.2, 94.6, 112.8, 113.7, 127.4, 129.4, 158.2, 202.3;
HRMS (ESI) calcd for $C_{17}H_{23}ClO$ $[M+H]^+$ m/z 279.1510, found 279.1515.



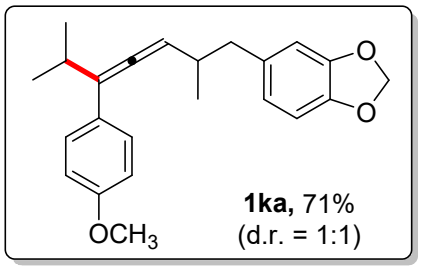
1ia, 62%

1ia: according to **General Procedure**; colorless oil; Eluent: *n*-hexane/EtOAc = 100/1;
^{1}H NMR (400 MH_Z $CDCl_3$, δ ppm): 1.09-1.12 (m, 6H), 1.27-1.36 (m, 10H), 1.42-1.47 (m, 2H), 2.00-2.11 (m, 4H), 2.72-2.79 (m, 1H), 3.79 (s, 3H), 4.91-5.01 (m, 2H), 5.48-5.51 (dt, J_1 = 4.0 Hz, J_2 = 8.0 Hz, 1H), 5.75-5.86 (m, 1H),6.84-6.86 (d, J = 8.0 Hz, 2H), 7.30-7.32 (d, J = 8.0 Hz, 2H);
^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 22.2, 22.6, 27.9, 28.9, 29.1, 29.3, 29.3, 29.4, 29.5, 33.8, 55.2, 95.4, 112.3, 113.7, 114.1, 127.4, 129.7, 139.2, 158.1, 202.2;
HRMS (ESI) calcd for $C_{23}H_{34}O$ $[M+H]^+$ m/z 327.2682, found 327.2689.



1ja, 85%

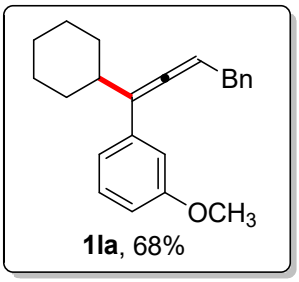
1ja: according to **General Procedure**; colorless oil; Eluent: *n*-hexane/EtOAc = 100/1;
^{1}H NMR (400 MH_Z $CDCl_3$, δ ppm): 0.82-0.84 (d, J = 8.0 Hz, 3H), 1.06-1.08 (d, J = 8.0 Hz, 3H), 2.60-2.68 (m, 1H), 3.76 (s, 3H), 4.84-4.86 (d, J = 8.0 Hz, 1H), 5.98-6.00 (dd, J_1 = 4.0 Hz, J_2 = 8.0 Hz, 1H), 6.80-6.82 (d, J = 8.0 Hz, 2H), 7.17-7.19 (m, 4H), 7.26-7.27 (m, 8H);
^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 22.1, 22.2, 28.3, 51.8, 55.2, 99.0, 113.7, 114.4, 126.3, 127.5, 128.2, 128.5, 128.6, 129.2, 143.7, 158.3, 203.2;
HRMS (ESI) calcd for $C_{26}H_{26}O$ $[M+H]^+$ m/z 355.2056, found 355.2061



1ka, 71%
(d.r. = 1:1)

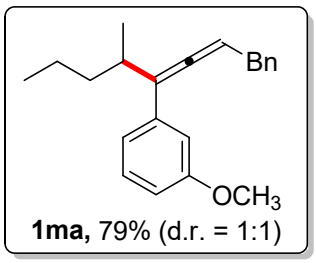
1ka: according to **General Procedure**; colorless oil; Eluent: *n*-hexane/EtOAc = 100/1;

^{1}H NMR (400 MH_Z $CDCl_3$, δ ppm): 1.03-1.10 (m, 9H), 2.44-2.77 (m, 4H), 3.77-3.78 (m, 3H), 5.43-5.53 (m, 1H), 5.88-5.90 (m, 2H), 6.60-6.74 (m, 3H), 6.78-6.84 (m, 2H), 7.10-7.12 (m, 1H), 7.23-7.25 (m, 1H);
^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 19.8, 20.3, 22.1, 22.2, 22.5, 22.6, 27.6, 27.8, 35.9, 36.7, 43.3, 43.7, 55.1, 55.2, 100.6, 100.7, 100.7, 100.8, 107.9, 108.0, 109.6, 109.6, 113.1, 113.5, 113.6, 113.7, 122.0, 122.0, 127.2, 127.3, 129.2, 129.4, 134.4, 134.7, 145.6, 145.6, 147.4, 147.4, 158.1, 158.2, 200.9, 201.0;
HRMS (ESI) calcd for $C_{23}H_{26}O_3$ $[M+H]^+$ m/z 351.1955, found 351.1958.



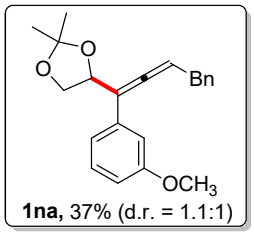
1la, 68%

1la: according to **General Procedure**; colorless oil; Eluent: *n*-hexane/EtOAc = 100/1;
^{1}H NMR (400 MH_Z $CDCl_3$, δ ppm): 1.02-1.36 (m, 6H), 1.67-1.89 (m, 4H), 2.34-2.40 (dt, J_1 = 4.0 Hz, J_2 = 8.0 Hz, 1H), 3.42-3.44 (d, J = 8.0 Hz, 2H), 3.75 (s, 3H), 5.64-5.67 (dt, J_1 = 4.0 Hz, J_2 = 8.0 Hz, 1H), 6.71-6.74 (dd, J_1 = 4.0 Hz, J_2 = 8.0 Hz, 1H), 6.90-6.96 (m, 2H), 7.18-7.30 (m, 6H);
^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 26.4, 26.6, 26.6, 32.7, 33.0, 36.0, 37.9, 55.1, 94.5, 111.8, 112.3, 112.5, 118.8, 126.1, 128.3, 128.6, 129.1, 138.6, 140.4, 159.6, 203.9;
HRMS (ESI) calcd for $C_{23}H_{26}O$ $[M+H]^+$ m/z 319.2056, found 319.2059.



1ma, 79% (d.r. = 1:1)

1ma: according to **General Procedure**; colorless oil; Eluent: *n*-hexane/EtOAc = 100/1;
^{1}H NMR (400 MH_Z $CDCl_3$, δ ppm): 0.84-0.89 (dd, J_1 = 8.0 Hz, J_2 = 16.0 Hz, 3H), 1.03-1.10 (dd, J_1 = 8.0 Hz, J_2 = 24.0 Hz, 3H), 1.26-1.56 (m, 4H), 2.59-2.64 (m, 1H), 3.43-3.46 (dd, J_1 = 4.0 Hz, J_2 = 8.0 Hz, 2H), 3.77 (s, 3H), 5.66-5.68 (m, 1H), 6.73-6.75 (d, J = 8.0 Hz, 1H), 6.92-6.98 (m, 2H), 7.20-7.29 (m, 6H);
^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 14.2, 14.3, 20.1, 20.4, 20.4, 20.5, 33.1, 33.1, 35.9, 36.0, 38.4, 38.7, 55.1, 94.8, 94.8, 111.9, 112.0, 112.2, 112.6, 112.7, 118.9, 126.1, 126.1, 128.3, 128.4, 128.6, 128.6, 129.2, 139.0, 139.0, 140.4, 140.4, 159.6, 203.7, 203.8;
HRMS (ESI) calcd for $C_{22}H_{26}O$ $[M+H]^+$ m/z 307.2056, found 307.2058.



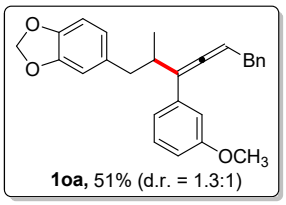
1na, 37% (d.r. = 1.1:1)

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

^{1}H NMR (400 MHz $CDCl_3$, δ ppm): 1.42-1.45 (m, 6H), 3.47-3.51 (t, J = 8.0 Hz, 2H),3.77 (s, 3H), 3.91-4.19 (m, 2H), 4.95-5.03 (m, 1H), 5.77-5.91 (dt, J_1 = 4.0 Hz, J_2 = 40.0 Hz, 1H), 6.77-6.79 (d, J = 8.0 Hz, 1H), 6.95-7.04 (m, 2H), 7.22-7.29 (m, 6H);

^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 25.9, 26.6, 26.6, 35.3, 35.4, 55.2, 68.5, 68.9, 4.0, 74.2, 76.7, 77.0, 96.1, 96.3, 106.0, 106.2, 109.6, 109.7, 112.2, 112.4, 112.7, 118.9, 119.1, 126.4, 126.4, 128.5, 128.5, 128.6, 129.4, 136.6, 136.6, 139.5, 139.7, 159.6, 203.7, 203.8;

HRMS (ESI) calcd for $C_{22}H_{24}O_3$ $[M+H]^+$ m/z 337.1798, found 337.1802.



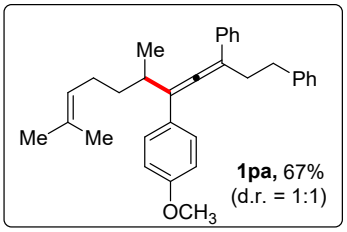
1oa, 51% (d.r. = 1.3:1)

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

^{1}H NMR (400 MHz $CDCl_3$, δ ppm): 0.97-1.04 (m, 3H), 2.30-2.41 (m, 1H), 2.77-2.88 (m, 2H), 3.36-3.46 (m, 2H), 3.78 (s, 3H), 5.66-5.73 (m, 1H), 5.87-5.90 (m, 2H), 6.57-6.77 (m, 4H), 6.91-7.01 (m, 2H), 7,20-7.31 (m, 6H);

^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 19.0, 19.7, 34.9, 35.4, 35.7, 35.9, 41.9, 55.2, 95.2, 95.3, 100.7, 107.9, 107.9, 109.5, 109.6, 112.1, 112.2, 118.8, 122.0, 122.1, 126.2, 128.4, 128.6, 129.3, 129.3, 134.4, 134.7, 138.5, 140.2, 140.3, 145.6, 145.6, 147.3, 147.3, 159.7, 159.7, 204.0;

HRMS (ESI) calcd for $C_{27}H_{26}O_3$ $[M+H]^+$ m/z 399.1955, found 399.1959.



1pa, 67%
(d.r. = 1:1)

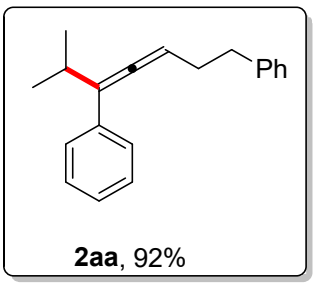
1pa: according to **General Procedure**; colorless oil; Eluent: *n*-hexane/EtOAc = 100/1;

^{1}H NMR (400 MHz $CDCl_3$, δ ppm): 1.07-1.08 (d, J = 4.0 Hz, 3H), 1.26-1.34 (m, 2H), 1.56 (s, 3H), 1.68 (s, 3H), 2.00-2.05 (m, 2H), 2.39-2.45 (m, 2H), 2.56-2.60 (m, 1H), 2.75-2.80 (m, 2H), 3.77 (s, 3H)， 5.09-5.11 (d, J = 8.0 Hz, 1H), 5.51-5.54 (dd, J_1 = 4.0 Hz, J_2 = 8.0 Hz, 1H), 6.80-6.82 (d, J = 8.0 Hz, 2H), 7.20-7.26 (m, 7H);

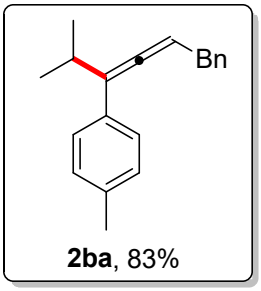
^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 17.6, 17.7, 20.0, 20.6, 25.7, 25.7, 25.8, 25.9, 31.2, 31.3, 32.7, 32.8, 35.6, 35.8, 36.1, 36.4, 55.2, 94.6, 94.7, 111.5, 111.7, 113.7, 124.7, 124.7, 125.8, 125.8, 127.4, 128.3, 128.3, 128.5, 128.5, 129.6, 131.3, 131.4, 141.8, 141.8, 158.2, 202.6;

HRMS (ESI) calcd for $C_{32}H_{36}O$ $[M+H]^+$ m/z 437.2839, found 437.2845.

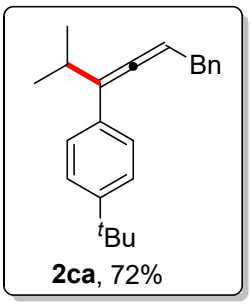
8. Characterization Data of Products 2aa-2oa:



2aa: according to **General Procedure**; colorless oil; Eluent: *n*-hexane;
^{1}H NMR (400 MH_Z $CDCl_3$, δ ppm): 1.08 (s, 3H), 1.10 (s, 3H), 2.40-2.45 (m, 2H), 2.75-2.82 (m, 3H), 5.53-5.57 (dt, J_1 = 4.0 Hz, J_2 = 8.0 Hz, 1H), 7.13-7.19 (m, 4H), 7.24-7.31 (m, 6H);
^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 22.2,22.5, 27.7, 31.1, 35.6, 94.8, 113.3, 125.8, 126.3, 126.4, 128.3, 128.3, 128.5, 137.1, 141.7, 202.8;
HRMS (ESI) calcd for $C_{20}H_{22}$ $[M+H]^+$ m/z 263.1794, found 263.1797.

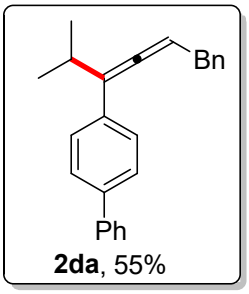


2ba: according to **General Procedure**; colorless oil; Eluent: *n*-hexane;
^{1}H NMR (400 MH_Z $CDCl_3$, δ ppm): 1.03-1.05 (d, J = 8.0 Hz, 3H), 1.08-1.10 (d, J = 8.0 Hz, 3H), 2.32 (s, 3H), 2.72-2.79 (m, 1H), 3.43-3.45 (d, J = 8.0 Hz, 2H), 5.64-5.67 (dt, J_1 = 4.0 Hz, J_2 = 8.0 Hz, 1H), 7.10-7.12 (m, 2H), 7.17-7.30 (m, 7H);
^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 21.0, 22.2, 22.5, 28.0, 36.1, 94.7, 113.4, 126.1, 126.4, 128.3, 128.7, 129.0, 134.1, 136.1, 140.5, 203.1;
HRMS (ESI) calcd for $C_{20}H_{22}$ $[M+H]^+$ m/z 263.1794, found 263.1797.



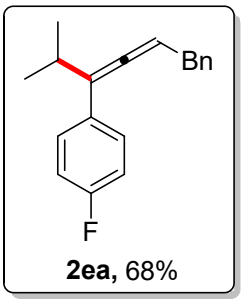
2ca: according to **General Procedure**; colorless oil; Eluent: *n*-hexane;
^{1}H NMR (400 MH_Z $CDCl_3$, δ ppm): 1.05-1.07 (d, J = 8.0 Hz, 3H), 1.10-1.12 (d, J = 8.0 Hz, 3H), 1.31 (s, 9H), 2.72-2.83 (m, 1H), 3.43-3.44 (d, J = 4.0 Hz, 2H), 5.66-5.69 (dt, J_1 = 4.0 Hz, J_2 = 8.0

Hz, 1H), 7.19-7.34 (m, 9H);
^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 22.3, 22.6, 28.0, 31.3, 34.4, 36.1, 94.8, 113.3, 125.2, 126.1, 128.3, 128.6, 134.0, 140.5, 149.3, 203.3;
HRMS (ESI) calcd for $C_{23}H_{28}$ $[M+H]^+$ m/z 305.2264, found 305.2269.



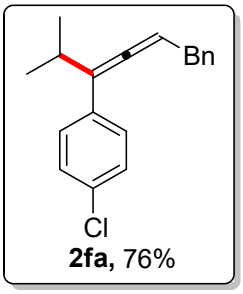
2da, 55%

2da: according to **General Procedure**; colorless oil; Eluent: *n*-hexane;
^{1}H NMR (400 MH_Z $CDCl_3$, δ ppm): 1.07-1.09 (d, *J* = 8.0 Hz, 3H), 1.12-1.14 (d, *J* = 8.0 Hz, 3H), 2.78-2.85 (m, 1H), 3.46-3.47 (d, *J* = 4.0 Hz, 2H), 5.71-5.74 (t, *J* = 8.0 Hz, 1H), 7.19-7.21 (m, 1H), 7.26-7.33 (m, 5H), 7.40-7.44 (m, 4H), 7.53-7.55 (d, *J* = 4.0 Hz, 2H), 7.58-7.60 (d, *J* = 4.0 Hz, 2H);
^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 22.2, 22.5, 27.9, 36.0, 95.1, 113.4, 126.1, 126.8, 126.9, 127.0, 127.1, 128.4, 128.7, 128.7, 136.1, 139.2, 140.3, 140.8, 203.5;
HRMS (ESI) calcd for $C_{25}H_{24}$ $[M+H]^+$ m/z 329.1951, found 329.1955.



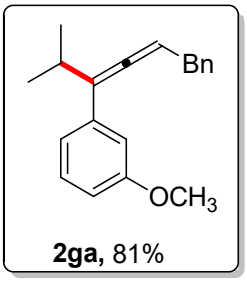
2ea, 68%

2ea: according to **General Procedure**; colorless oil; Eluent: *n*-hexane;
^{1}H NMR (400 MH_Z $CDCl_3$, δ ppm): 1.02-1.04 (d, *J* = 8.0 Hz, 3H), 1.08-1.10 (d, *J* = 8.0 Hz, 3H), 2.68-2.75 (m, 1H), 3.43-3.44 (d, *J* = 4.0 Hz, 2H), 5.66-5.70 (dt, J_1 = 4.0 Hz, J_2 = 8.0 Hz, 1H), 6.95-7.00 (t, *J* = 8.0 Hz, 2H), 7.18-7.30 (m, 7H);
^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 22.1, 22.3, 28.2, 36.0, 95.1, 112.9, 115.0, 115.2, 126.2, 127.9-128.0 (d, *J* = 7.0 Hz), 128.4-128.6 (d, *J* = 29.0 Hz), 133.0, 133.0, 140.2, 160.4-162.8 (d, *J* = 244.0 Hz), 203.3;
^{19}F NMR (376 MHz, $CDCl_3$, δ ppm): -116.5 (s, 1F);
HRMS (ESI) calcd for $C_{19}H_{19}F$ $[M+H]^+$ m/z 267.1544, found 267.1547.



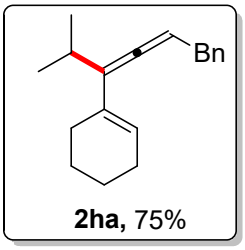
2fa, 76%

2fa: according to **General Procedure**; colorless oil; Eluent: *n*-hexane/EtOAc = 100/1;
^{1}H NMR (400 MH_Z $CDCl_3$, δ ppm): 1.01-1.03 (d, J = 8.0 Hz, 3H), 1.07-1.09 (d, J = 8.0 Hz, 3H), 2.67-2.74 (m, 1H), 3.42-3.44 (d, J = 8.0 Hz, 2H), 5.68-5.72 (dt, J_1 = 4.0 Hz, J_2 = 8.0 Hz, 1H), 7.17-7.30 (m, 9H);
^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 22.0, 22.3, 28.0, 35.9, 95.4, 112.9, 126.2, 127.7, 128.4, 128.6, 132.0, 135.6, 140.1, 203.4;
HRMS (ESI) calcd for $C_{19}H_{19}Cl$ $[M+H]^+$ m/z 283.1248, found 283.1252.



2ga, 81%

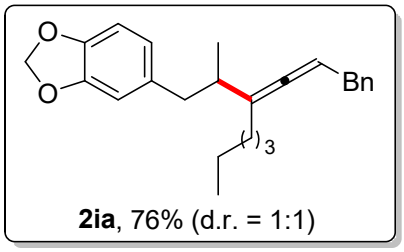
2ga: according to **General Procedure**; colorless oil; Eluent: *n*-hexane/EtOAc = 100/1;
^{1}H NMR (400 MH_Z $CDCl_3$, δ ppm): 1.04-1.06 (d, J = 8.0 Hz, 3H), 1.09-1.11 (d, J = 8.0 Hz, 3H), 2.72-2.79 (m, 1H), 3.43-3.45 (d, J = 8.0 Hz, 2H), 3.76 (s, 3H), 5.67-5.71 (dt, J_1 = 4.0 Hz, J_2 = 8.0 Hz, 1H), 6.73-6.75 (d, J = 8.0 Hz, 1H), 6.91-6.97 (m, 2H), 7.19-7.30 (m, 6H);
^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 22.2, 22.5, 28.0, 36.0, 55.1, 95.0, 112.0, 112.2, 113.6, 118.9, 126.1, 128.3, 128.6, 129.1, 138.7, 140.4, 159.6, 203.4;
HRMS (ESI) calcd for $C_{20}H_{22}O$ $[M+H]^+$ m/z 279.1743, found 279.1749.



2ha, 75%

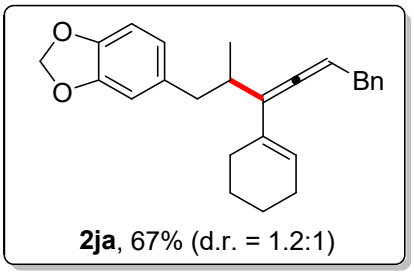
2ha: according to **General Procedure**; colorless oil; Eluent: *n*-hexane;
^{1}H NMR (400 MH_Z $CDCl_3$, δ ppm): 0.98-1.03 (m, 6H), 1.57-1.64 (m, 4H), 2.00-2.03 (m, 4H), 2.50-2.58 (m, 1H), 3.36-3.37 (d, J = 4.0 Hz, 2H), 5.49-5.53 (t, J = 8.0 Hz, 1H), 5.73 (m, 1H), 7.17-7.36 (m, 5H);
^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 22.5, 22.9, 23.1, 26.0, 26.4, 27.8, 36.5, 94.6, 115.4, 122.0, 126.0, 128.3, 128.6, 132.0, 140.7, 202.9;

HRMS (ESI) calcd for $C_{19}H_{24}$ $[M+H]^+$ m/z 253.1951, found 253.1954.



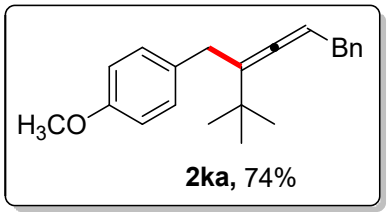
2ia, 76% (d.r. = 1:1)

2ia: according to **General Procedure**; colorless oil; Eluent: *n*-hexane/EtOAc = 100/1;
^{1}H NMR (400 MH_Z $CDCl_3$, δ ppm): 0.86-0.92 (m, 6H), 1.27-1.28 (m, 4H), 1.35-1.41 (m, 2H), 1.88-1.94 (m, 2H), 2.12-2.14 (m, 1H), 2.25-2.36 (m, 1H), 2.66-2.72 (m, 1H), 3.26-3.28 (m, 2H), 5.27-5.29 (m, 1H), 5.88 (s, 2H), 6.55-6.71 (m, 3H), 7.18-7.30 (m, 5H);
^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 14.1, 19.0, 19.4, 22.6, 27.5, 27.5, 30.9, 31.3, 31.6, 36.3, 36.4, 38.4, 39.0, 41.9, 42.0, 92.7, 92.8, 100.6, 100.6, 107.8, 109.5, 109.5, 109.7, 109.9, 121.9, 122.0, 125.9, 128.2, 128.2, 128.6, 135.0, 135.2, 141.0, 141.0, 145.5, 147.3, 201.0, 201.1;
HRMS (ESI) calcd for $C_{25}H_{30}O_2$ $[M+H]^+$ m/z 363.2319, found 363.2323.



2ja, 67% (d.r. = 1.2:1)

2ja: according to **General Procedure**; colorless oil; Eluent: *n*-hexane;
^{1}H NMR (400 MH_Z $CDCl_3$, δ ppm): 0.90-0.95 (m, 3H), 1.57-1.65 (m, 4H), 2.05-2.14 (m, 4H), 2.25-2.34 (m, 1H), 2.60-2.66 (m, 1H), 2.71-2.81 (m, 1H), 3.27-3.38 (m, 2H), 5.48-5.54 (m, 1H), 5.77-5.79 (m, 1H), 5.87-5.90 (m, 2H), 6.55-6.63 (m, 2H), 6.69-6.72 (m, 1H), 7.17-7.22 (m, 3H), 7.27-7.32 (m, 2H);
^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 19.2, 19.9, 22.5, 23.1 26.0, 26.0, 27.8, 27.9, 33.1, 33.5, 36.2, 36.3, 42.3, 42.4, 94.8, 95.0, 100.6, 107.8, 107.8, 109.5, 109.6, 113.7, 113.9, 121.9, 122.0, 122.0, 122.1, 126.0, 128.3, 128.6, 128.6, 132.0, 135.0, 135.2, 140.6, 145.4, 145.5, 147.2, 203.5;
HRMS (ESI) calcd for $C_{26}H_{28}O_2$ $[M+H]^+$ m/z 373.2162, found 373.2166.



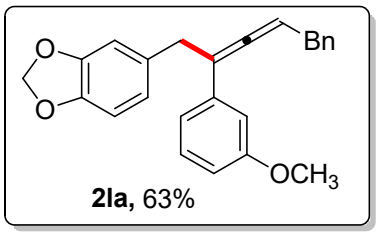
2ka, 74%

2ka: according to **General Procedure**; colorless oil; Eluent: *n*-hexane/EtOAc = 100/1;
^{1}H NMR (400 MH_Z $CDCl_3$, δ ppm): 1.04 (s, 9H), 3.12-3.20 (m, 4H), 3.75 (s, 3H), 5.06-5.10 (m, 1H), 6.77-6.79 (d, J = 8.0 Hz, 2H), 6.90-6.92 (d, J = 8.0 Hz, 2H),7.02-7.04 (d, J = 8.0 Hz, 2H), 7.11-

7.20 (m, 3H);

^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 29.5, 33.7, 33.9, 36.0, 55.1, 92.7, 113.3, 114.7, 125.8, 128.0, 128.7, 130.1, 132.8, 140.5, 157.7, 202.0;

HRMS (ESI) calcd for $C_{22}H_{26}O$ $[M+H]^+$ m/z 307.2056, found 307.2061.



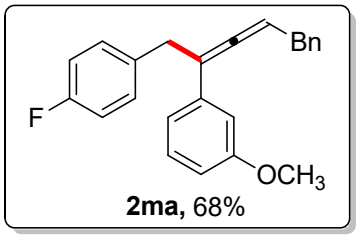
2la, 63%

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

^{1}H NMR (400 MH_Z $CDCl_3$, δ ppm): 3.37-3.39 (d, J = 8.0 Hz, 2H), 3.66 (s, 2H), 3.73 (s, 3H), 5.58-5.62 (t, J = 8.0 Hz, 1H), 5.85 (s, 2H), 6.63-6.73 (m, 4H), 6.94-6.99 (m, 2H), 7.09-7.11 (d, J = 8.0 Hz, 2H), 7.16-7.20 (t, J = 8.0 Hz, 2H), 7.23-7.27 (t, J = 8.0 Hz, 2H);

^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 35.6, 36.8, 55.1, 94.1, 100.7, 105.7, 108.0, 108.0, 108.8, 109.3, 111.8, 112.2, 118.6, 121.1, 121.7, 126.2, 128.3, 128.5, 129.2, 133.1, 135.4, 138.0, 139.9, 145.8, 147.4, 159.5, 205.6;

HRMS (ESI) calcd for $C_{25}H_{22}O_3$ $[M+H]^+$ m/z 371.1642, found 371.1647.



2ma, 68%

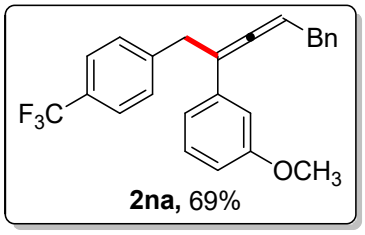
2ma: according to **General Procedure**; colorless oil; Eluent: *n*-hexane/EtOAc = 100/1;

^{1}H NMR (400 MH_Z $CDCl_3$, δ ppm): 3.34-3.35 (d, J = 4.0 Hz, 2H), 3.68 (s, 2H), 3.72 (s, 3H), 5.57-5.60 (m, 1H), 6.71-6.74 (dd, J_1 = 4.0 Hz, J_2 = 8.0 Hz, 1H), 6.88-6.98 (m, 4H), 7.05-7.10 (m, 4H), 7.16-7.26 (m, 4H);

^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 35.5, 36.3, 55.1, 94.3, 105.8, 111.8, 112.2, 114.9, 115.1, 118.5, 126.2, 128.3-128.5 (d, J = 18.0 Hz), 129.2, 130.2-130.3 (d, J = 8.0 Hz), 134.9, 135.0, 137.9, 139.8, 159.6, 160.2-162.6 (d, J = 42.0 Hz), 205.6;

^{19}F NMR (376 MHz, $CDCl_3$, δ ppm): -117.1 (s, 1F);

HRMS (ESI) calcd for $C_{24}H_{21}FO$ $[M+H]^+$ m/z 345.1649, found 345.1652.



2na, 69%

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

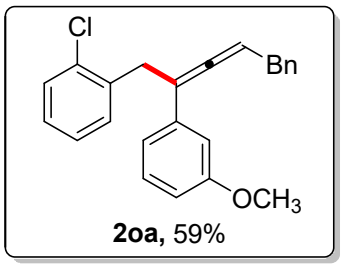
^{1}H NMR (400 MH_Z $CDCl_3$, δ ppm): 3.35-3.37 (d, J = 8.0 Hz, 2H), 3.75 (s, 3H), 3.78 (s, 2H), 5.60-

5.63 (m, 1H), 6.73-6.76 (dd, J_1 = 4.0 Hz, J_2 = 8.0 Hz, 1H), 6.92-6.97 (m, 2H), 7.05-7.07 (d, J = 8.0 Hz, 2H), 7.19-7.25 (m, 6H), 7.47-7.49 (d, J = 8.0 Hz, 2H);

^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 35.4, 36.9, 55.1, 94.7, 105.1, 111.9, 112.3, 118.5, 123.0, 125.1-125.2 (q, J = 4.0 Hz), 125.7, 126.3, 128.3-128.6 (q, J = 10.0 Hz), 129.2, 129.3, 137.7, 139.7, 143.5, 159.7, 205.7;

^{19}F NMR (376 MHz, $CDCl_3$, δ ppm): -62.2 (s, 3F);

HRMS (ESI) calcd for $C_{25}H_{21}F_3O$ $[M+H]^+$ m/z 395.1617, found 395.1621.



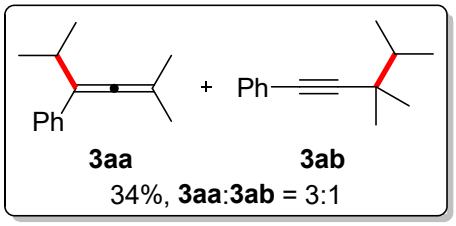
2oa, 59%

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

^{1}H NMR (400 MH_Z $CDCl_3$, δ ppm): 3.29-3.33 (t, J = 8.0 Hz, 2H), 3.75 (s, 3H), 3.79-3.91 (m, 2H), 5.52-5.56 (m, 1H), 6.72-6.74 (d, J = 8.0 Hz, 1H), 6.96-7.03 (m, 4H), 7.12-7.35 (m, 8H);

^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 34.5, 35.3, 55.1, 94.7, 104.5, 111.6, 112.4, 118.4, 126.1, 126.7, 127.6, 128.3, 128.5, 129.2, 129.3, 130.8, 134.3, 137.1, 138.0, 139.9, 159.6, 205.3;

HRMS (ESI) calcd for $C_{24}H_{21}ClO$ $[M+H]^+$ m/z 361.1354, found 361.1359.



3aa **3ab**

34%, **3aa**:**3ab** = 3:1

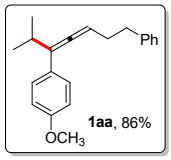
3aa+3ab: according to **General Procedure**; colorless oil; Eluent: *n*-hexane;

^{1}H NMR (400 MH_Z $CDCl_3$, δ ppm): 0.90-1.03 (m, 3H), 1.09-1.12 (m, 4.5H), 1.76-1.79 (m, 4.5H), 1.97-1.98 (m, 0.25H), 2.76-2.84 (m, 0.75H), 7.10-7.38 (m, 5H);

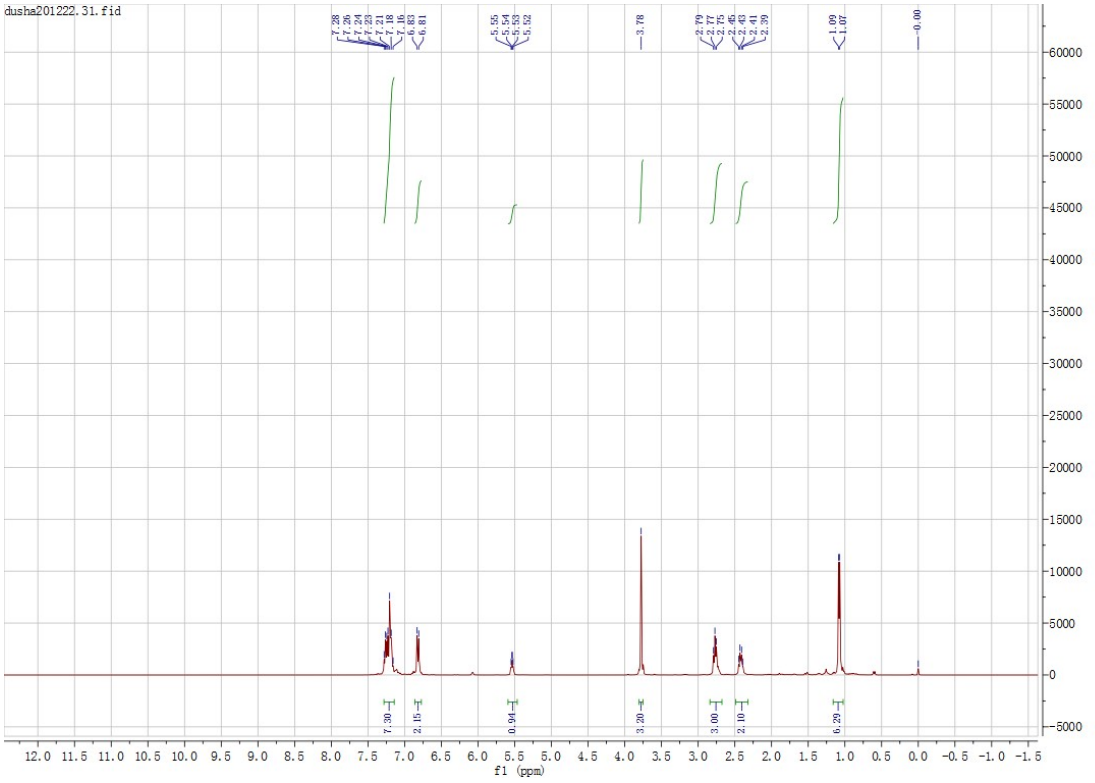
^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 19.0, 20.5, 21.7, 22.5, 22.5, 22.6, 22.8, 22.9, 26.5, 28.3, 28.3, 44.1, 99.2, 102.8, 110.9, 111.2, 116.4, 125.9, 126.0, 126.4, 126.5, 126.8, 127.4, 128.2, 128.2, 128.5, 129.2, 138.3, 200.8;

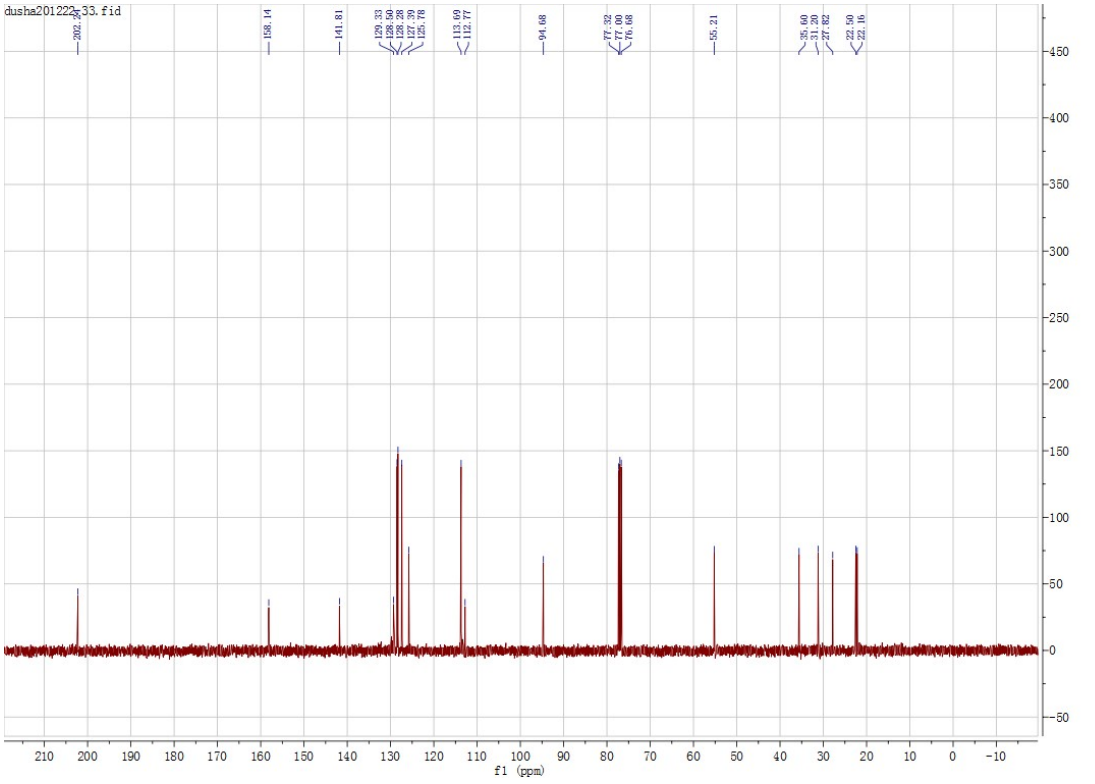
HRMS (ESI) calcd for $C_{14}H_{18}$ $[M+H]^+$ m/z 187.1481, found 187.1483.

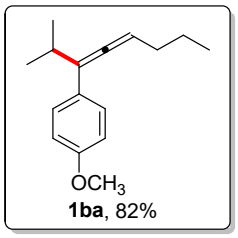
9. ^{1}H NMR and ^{13}C NMR Spectra of the Products 1aa-1pa:



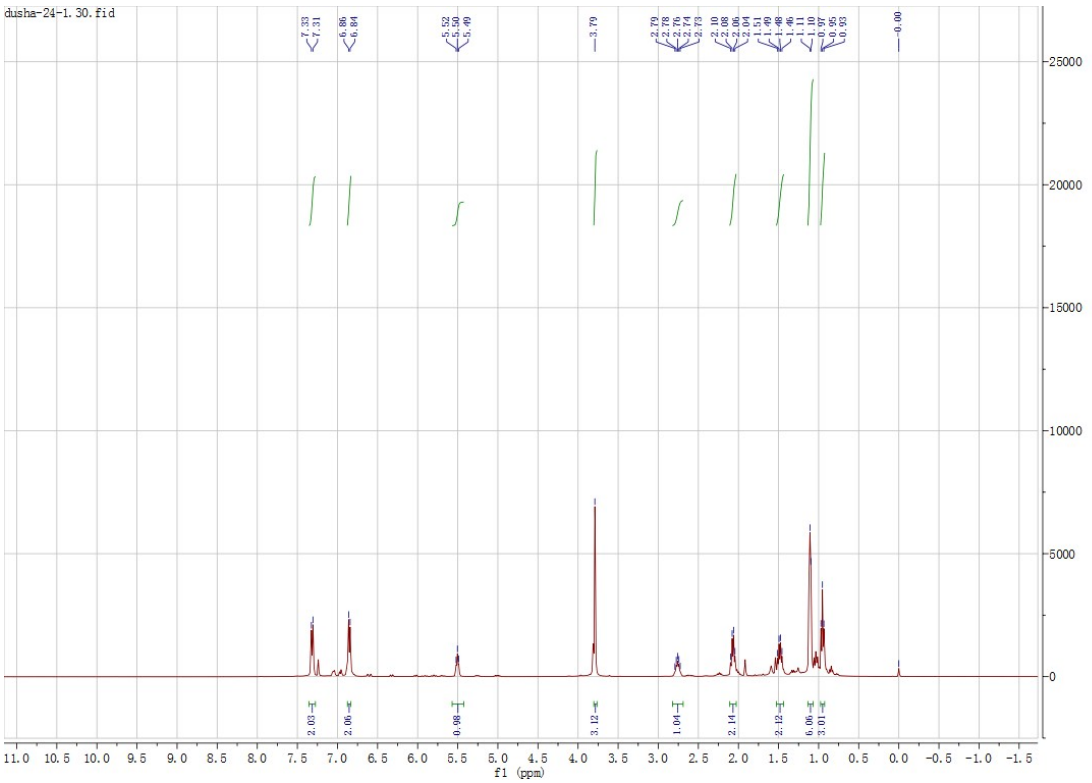
1aa, 86%

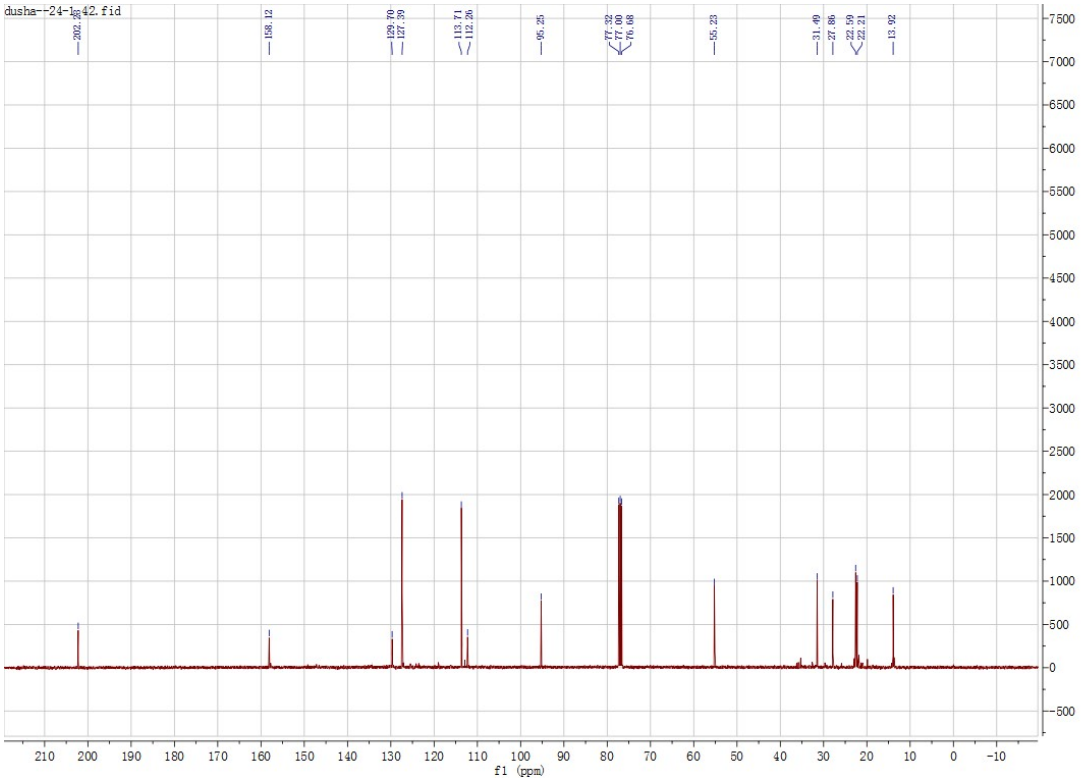


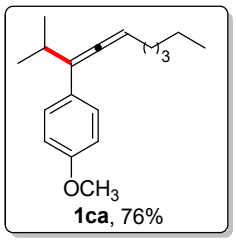




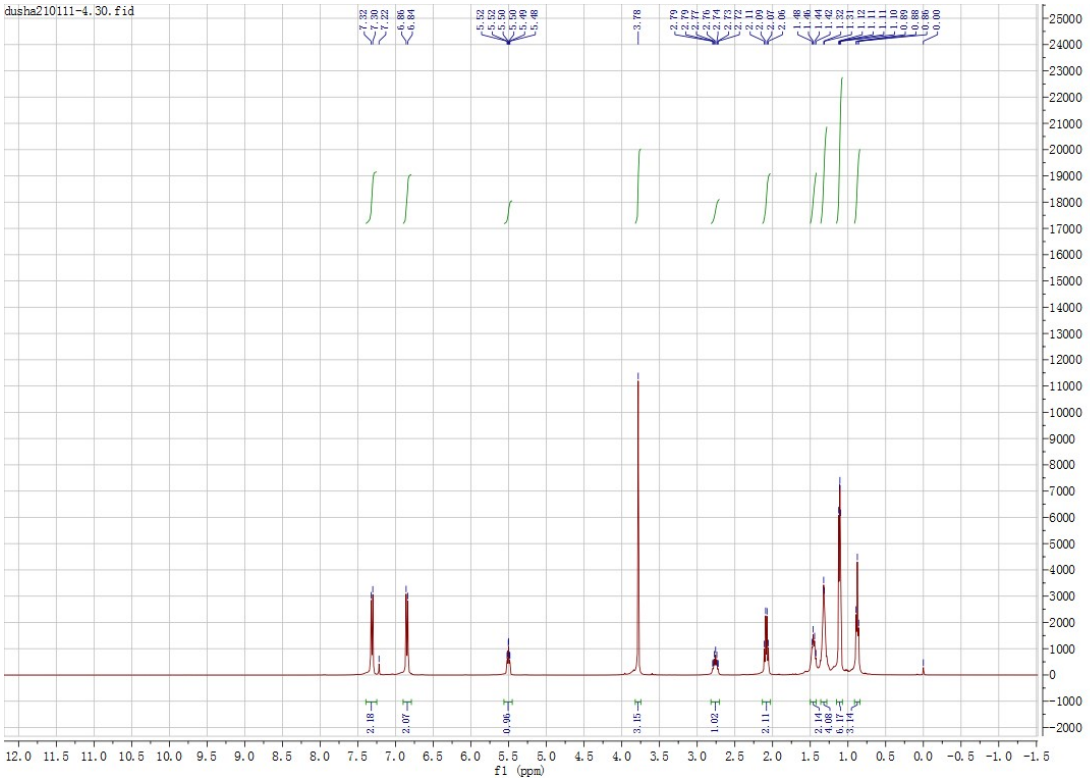
1ba, 82%

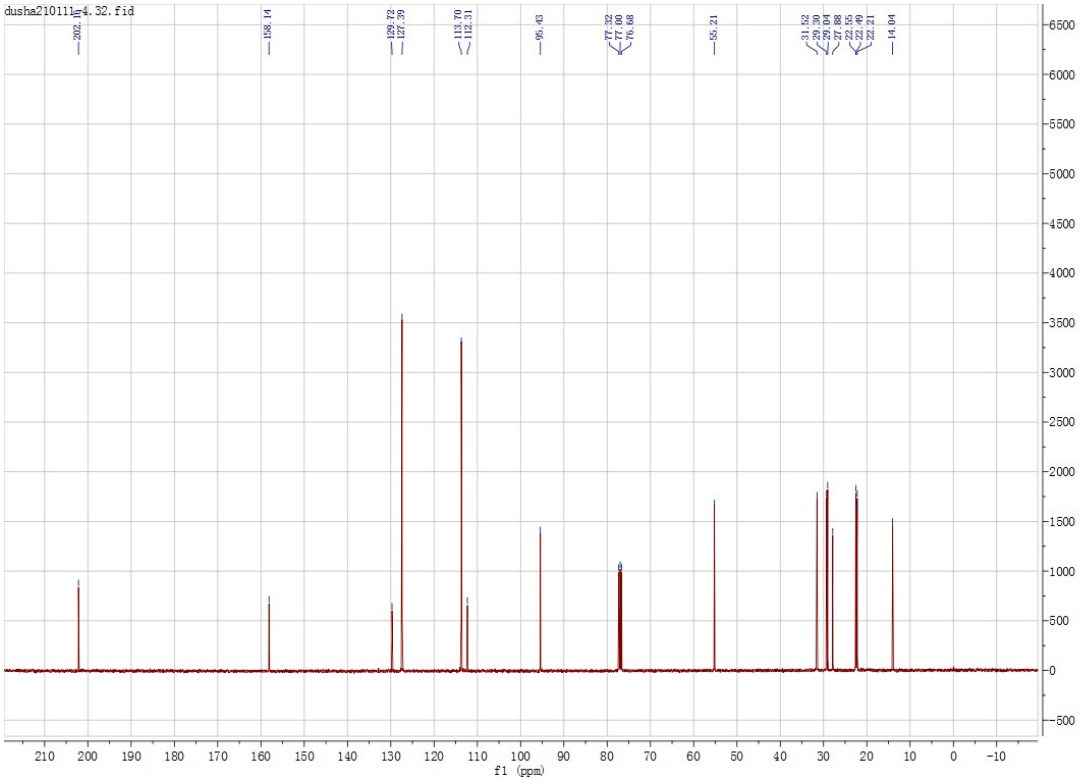


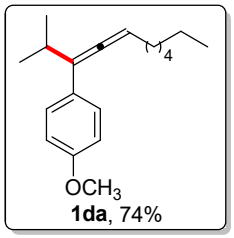




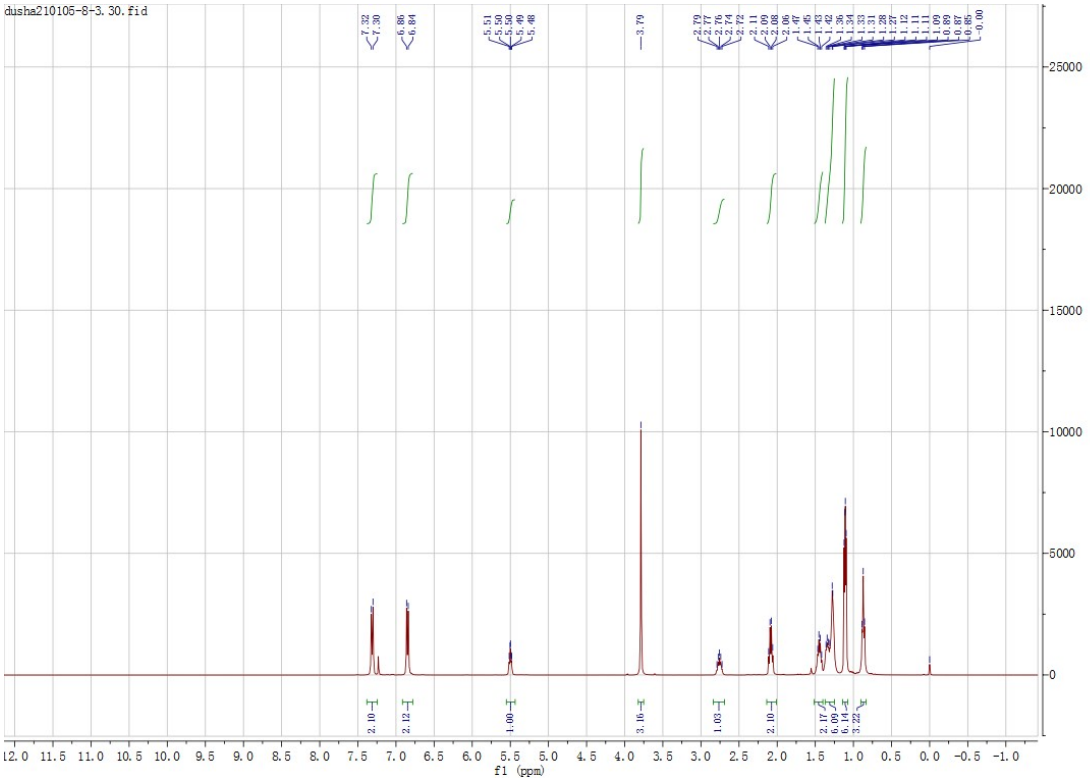
1ca, 76%

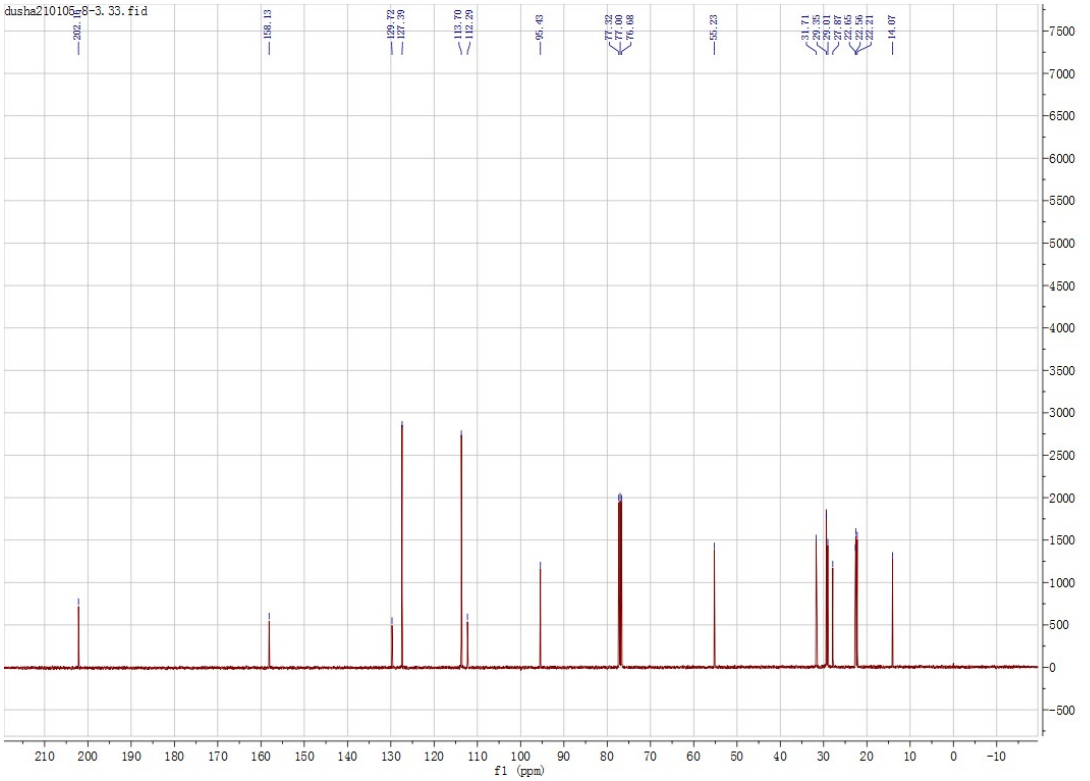


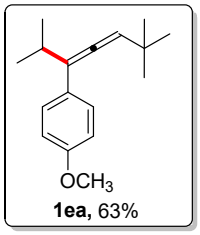



4
OCH3

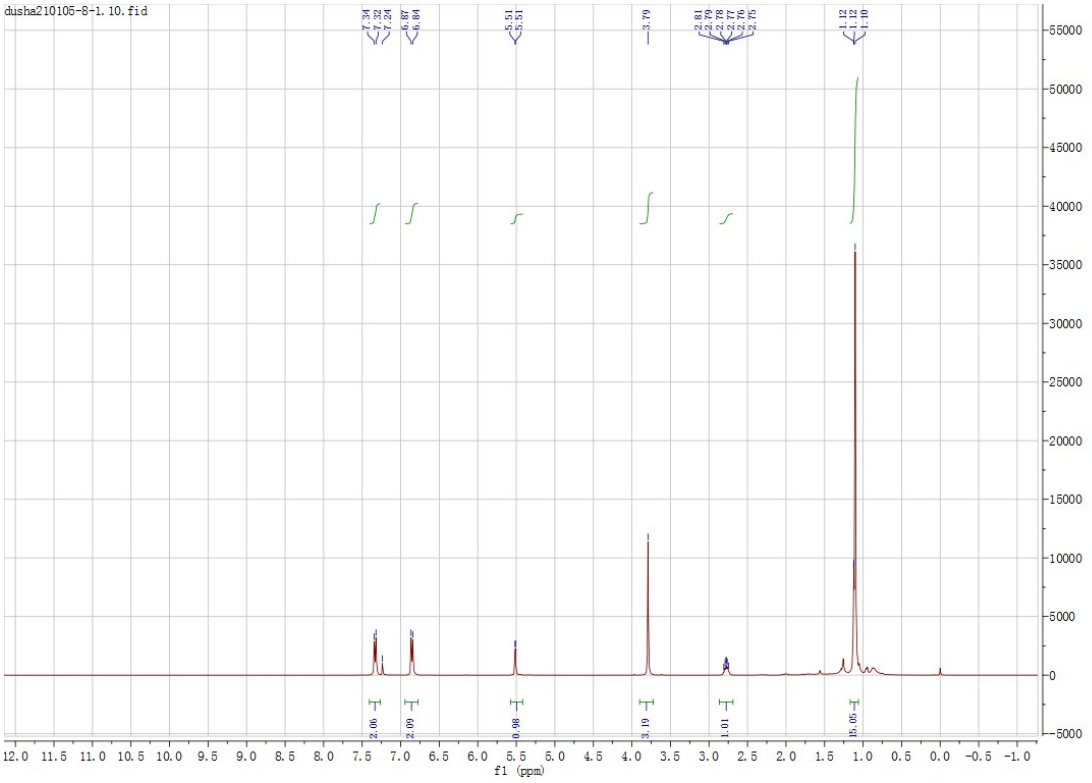
1da, 74%


dusha210105-8-3.30.fid
f1 (ppm)


dusha210105-8-3.33.fid
f1 (ppm)


OCH3

1ea, 63%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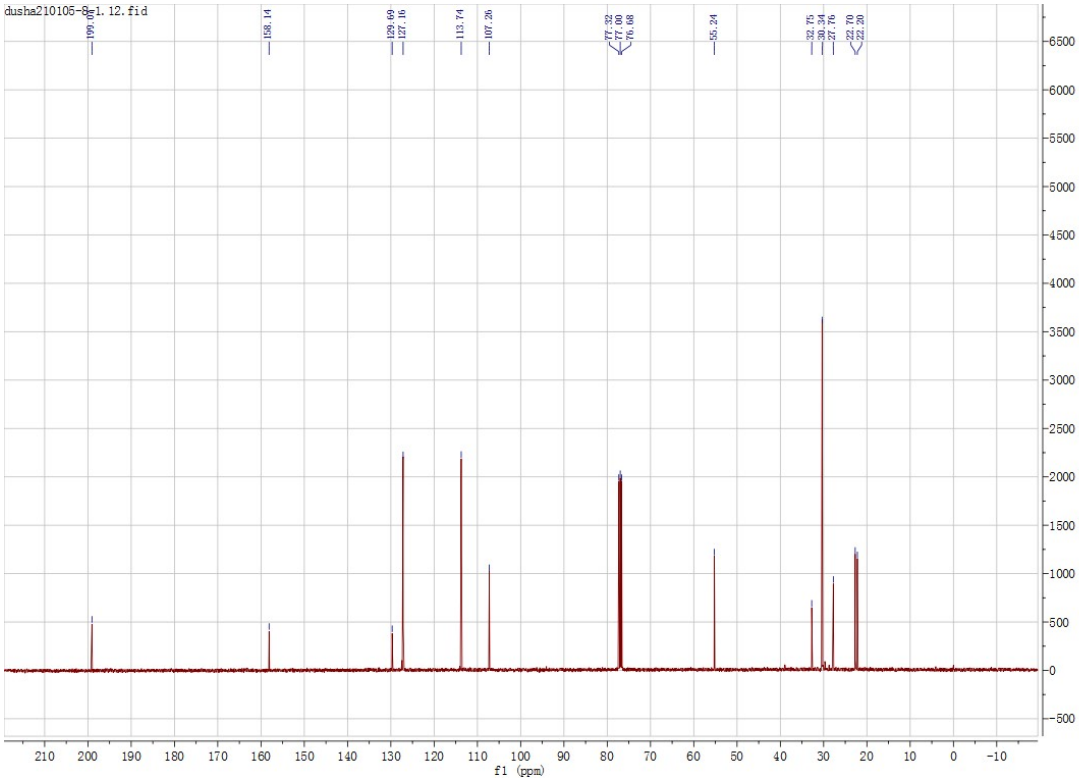
f1 (ppm)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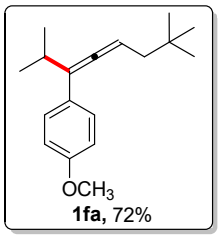
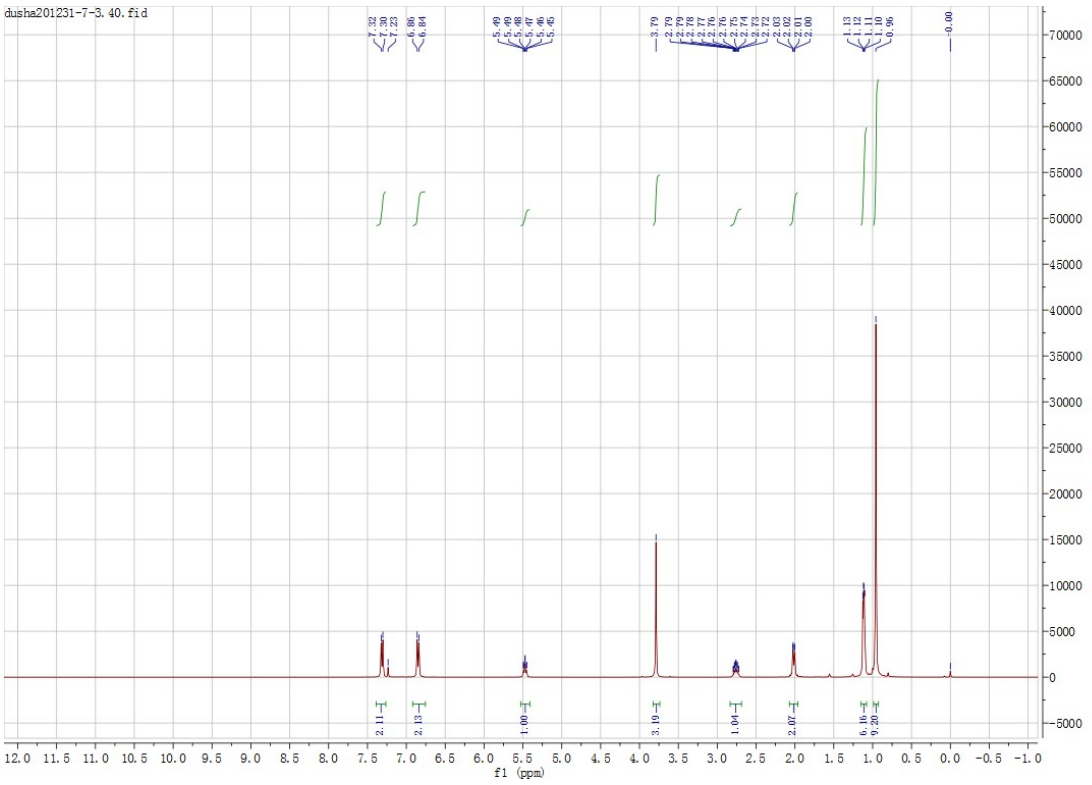
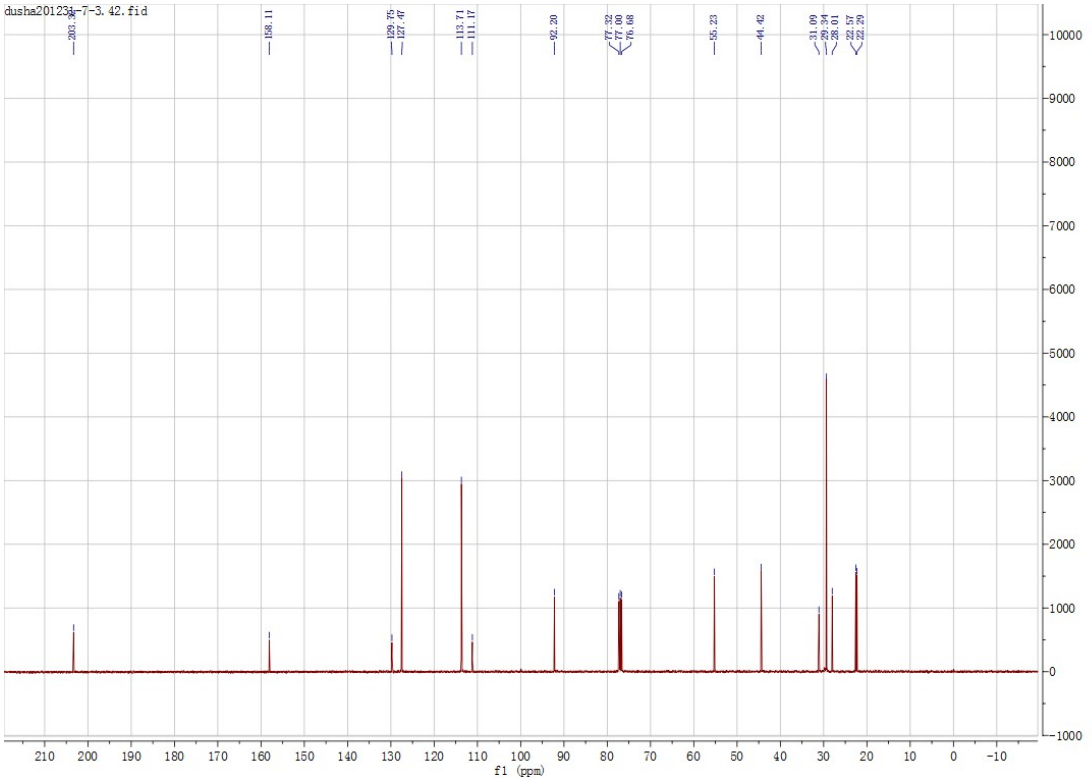
f1 (ppm)


OCH3

1fa, 72%


dusha201231-7-3.40.fid
f1 (ppm)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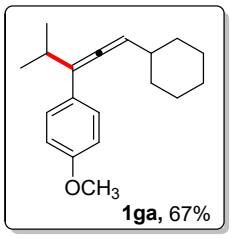
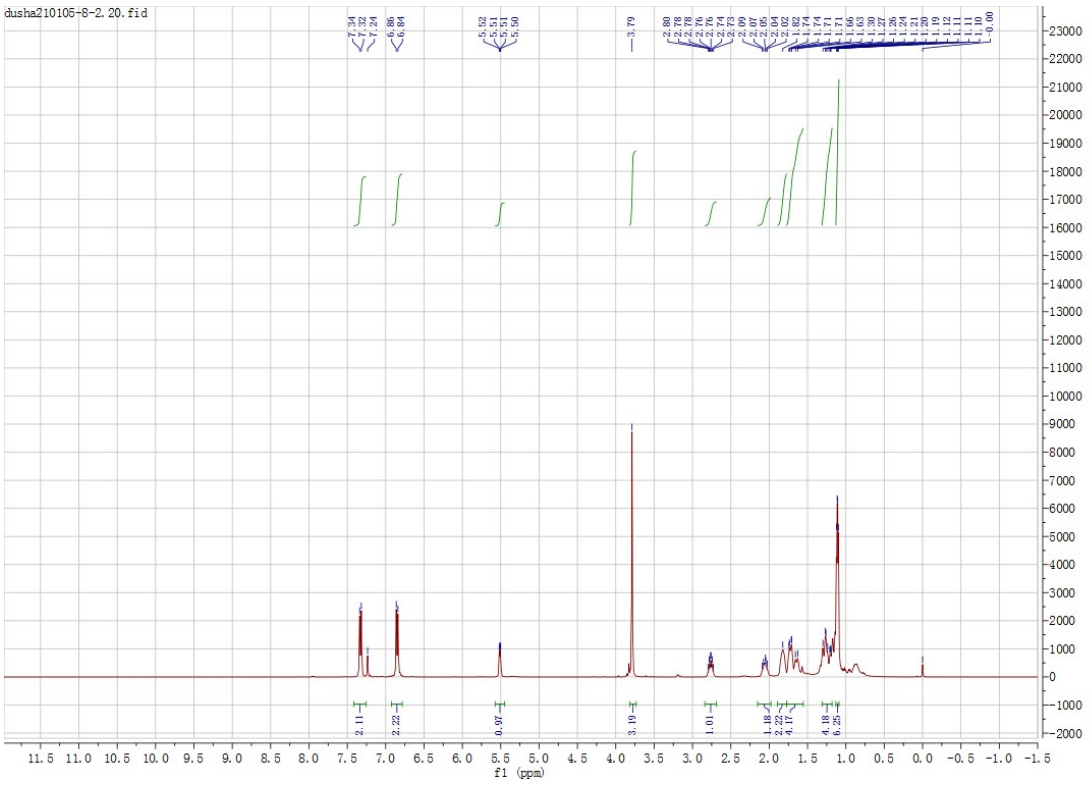
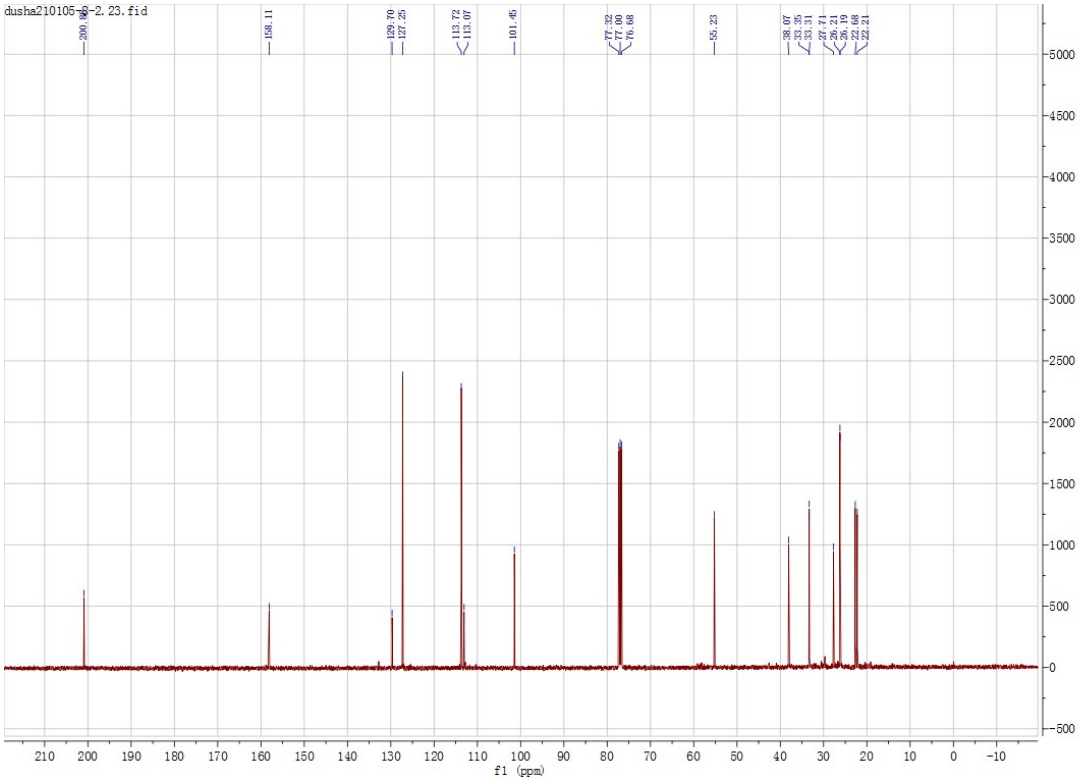
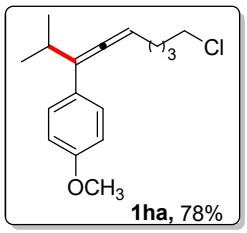
f1 (ppm)


OCH3

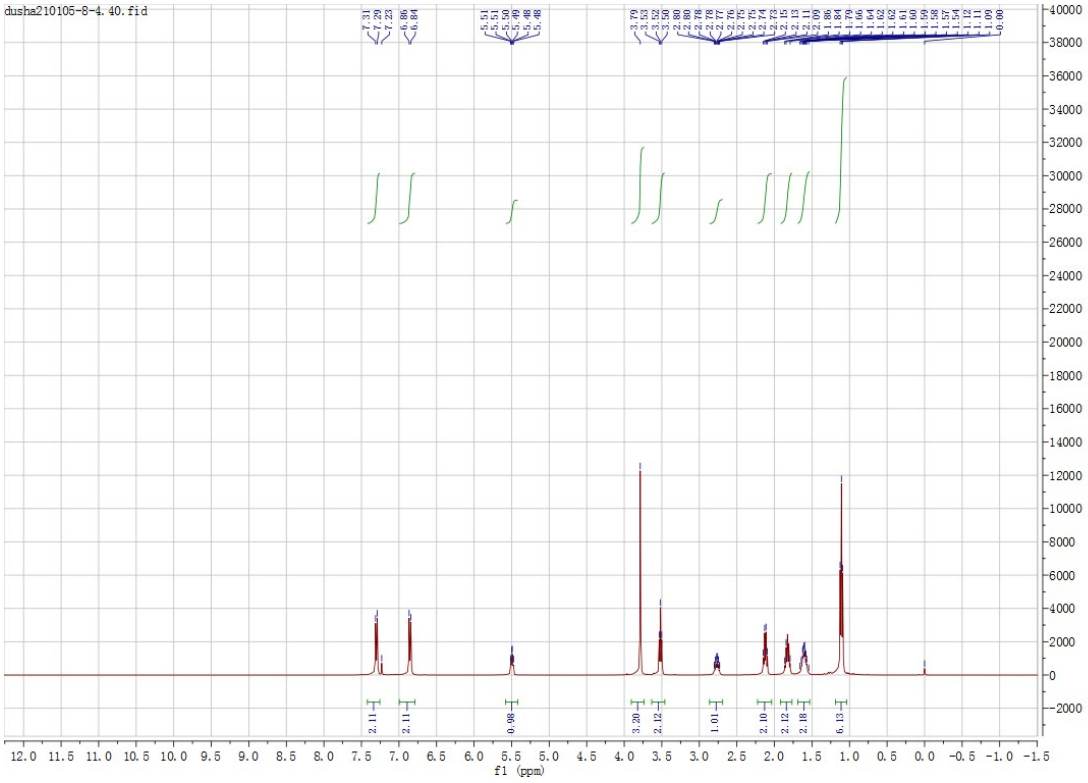
1ga, 67%

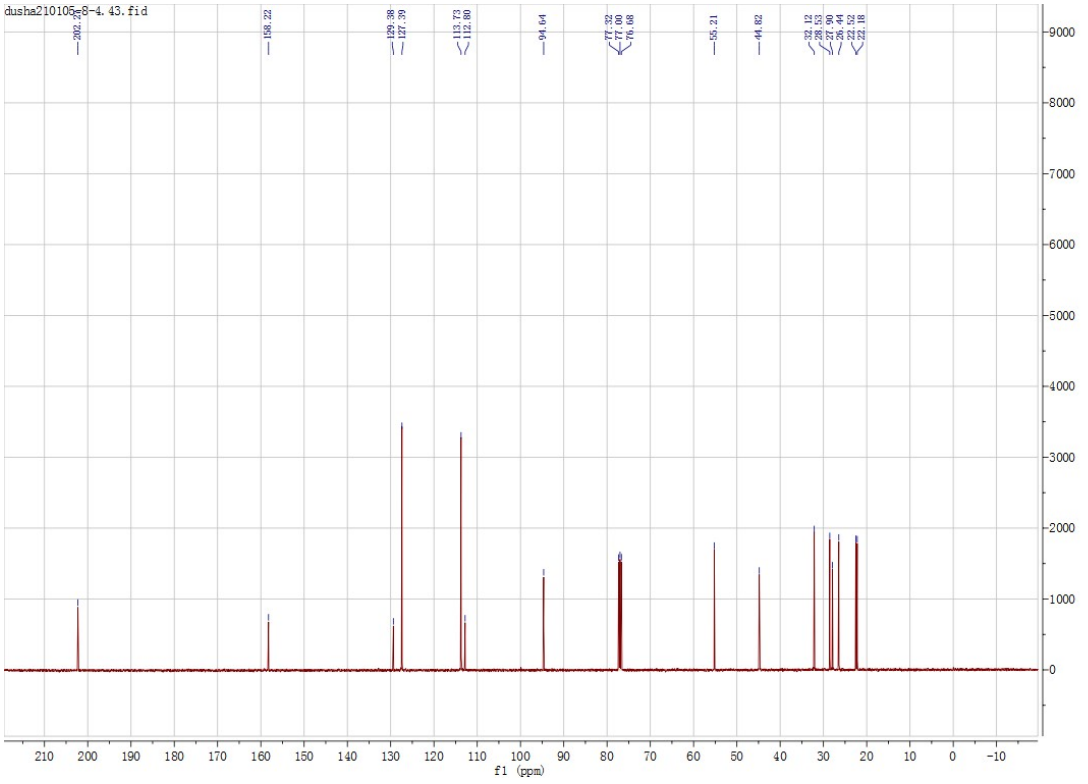

dusha210105-8-2.20.fid
f1 (ppm)

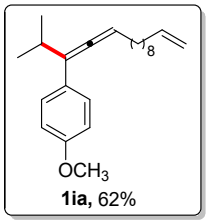

dusha210105-8-2.23.fid
f1 (ppm)


3
Cl
OCH3

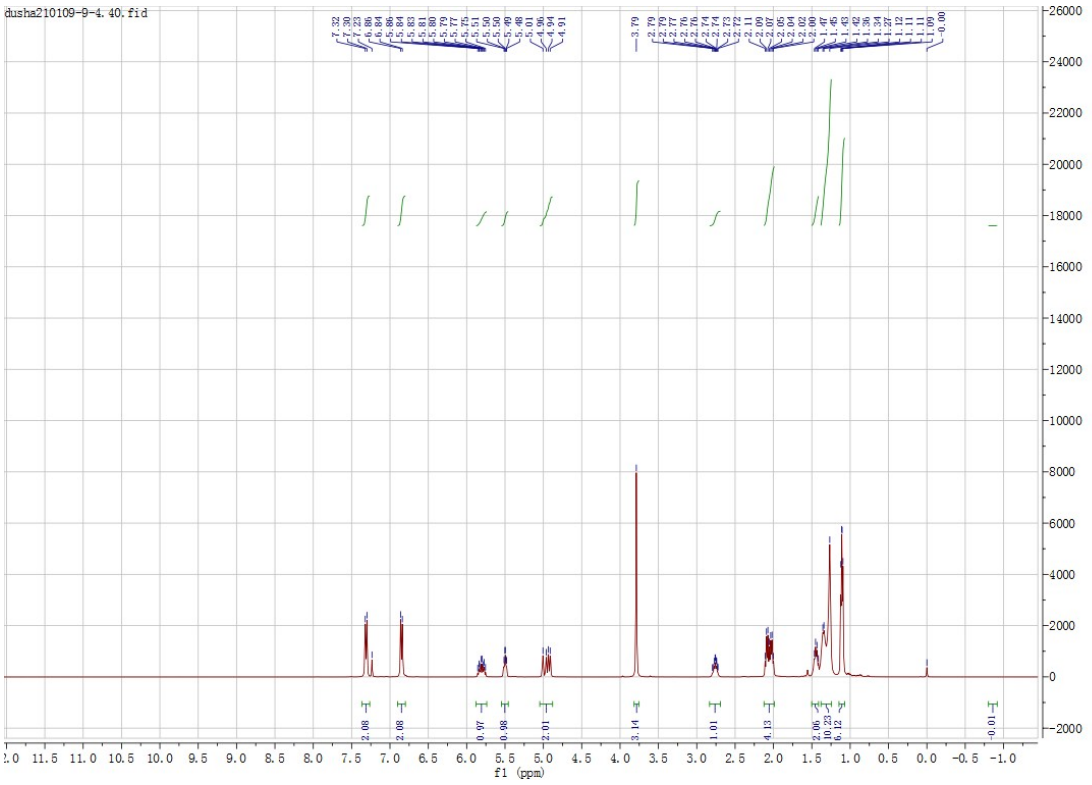
1ha, 78%

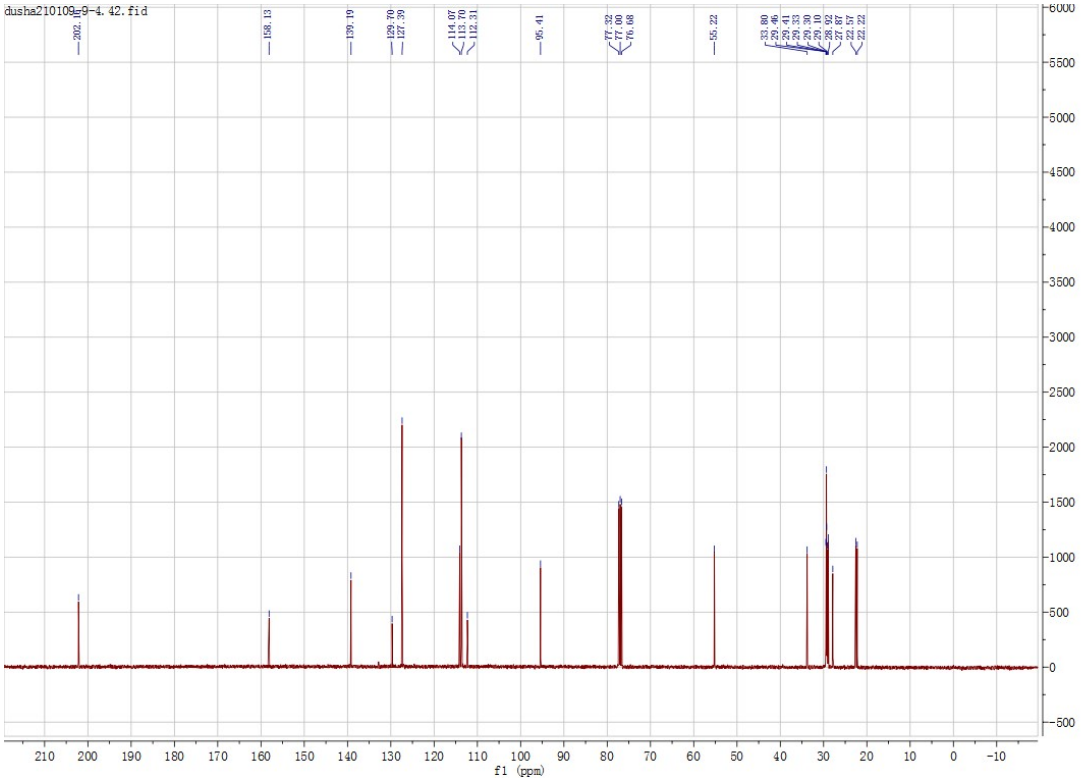

dusha210105-8-4.40.fid
f1 (ppm)

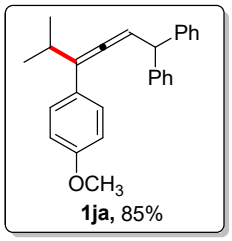

dusha210105-8-4.43.fid
f1 (ppm)


8
OCH3

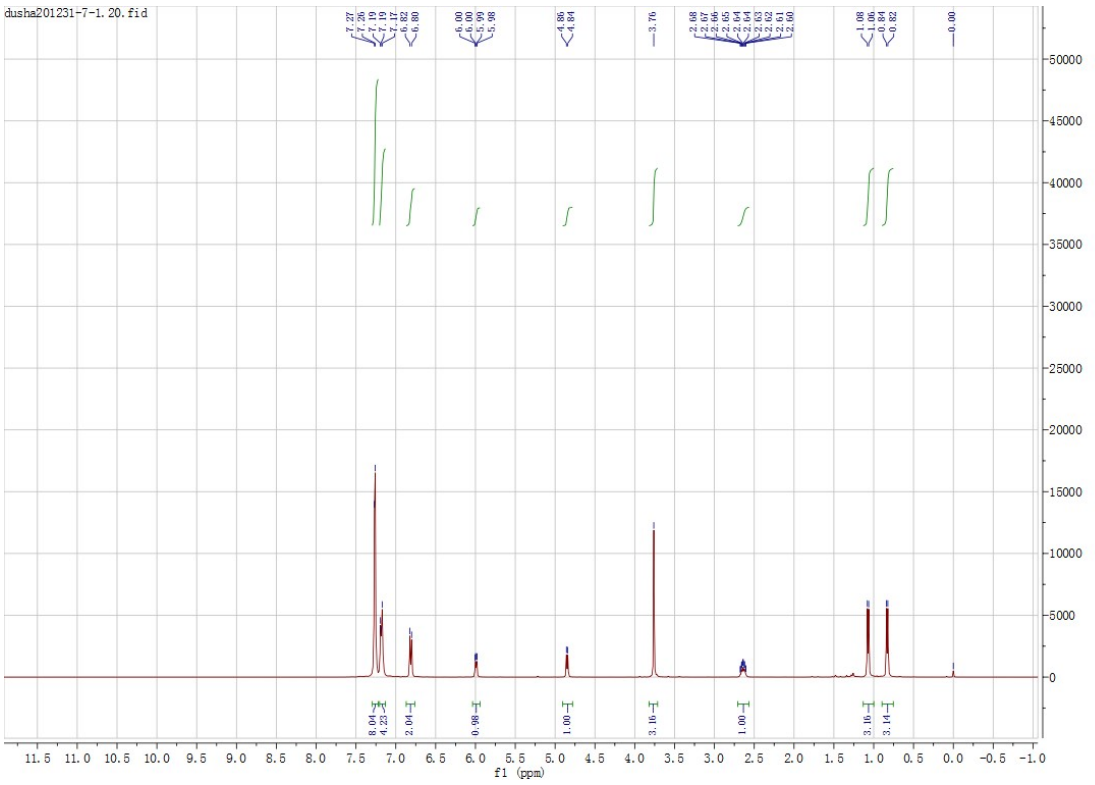
1ia, 62%

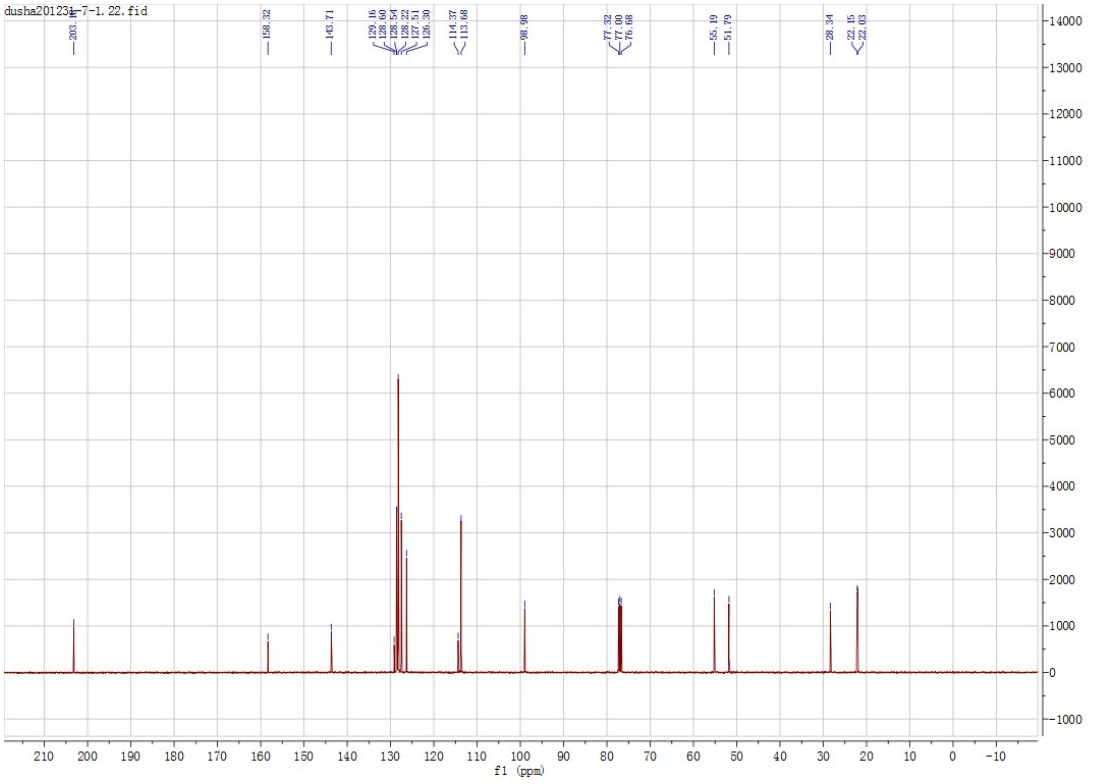

dusha210109-9-4.40.fid
f1 (ppm)

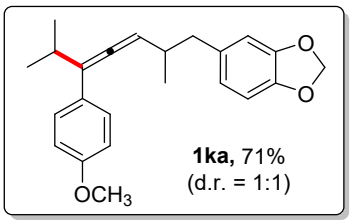

dusha210109-9-4.42.fid
f1 (ppm)


Ph
Ph
OCH3

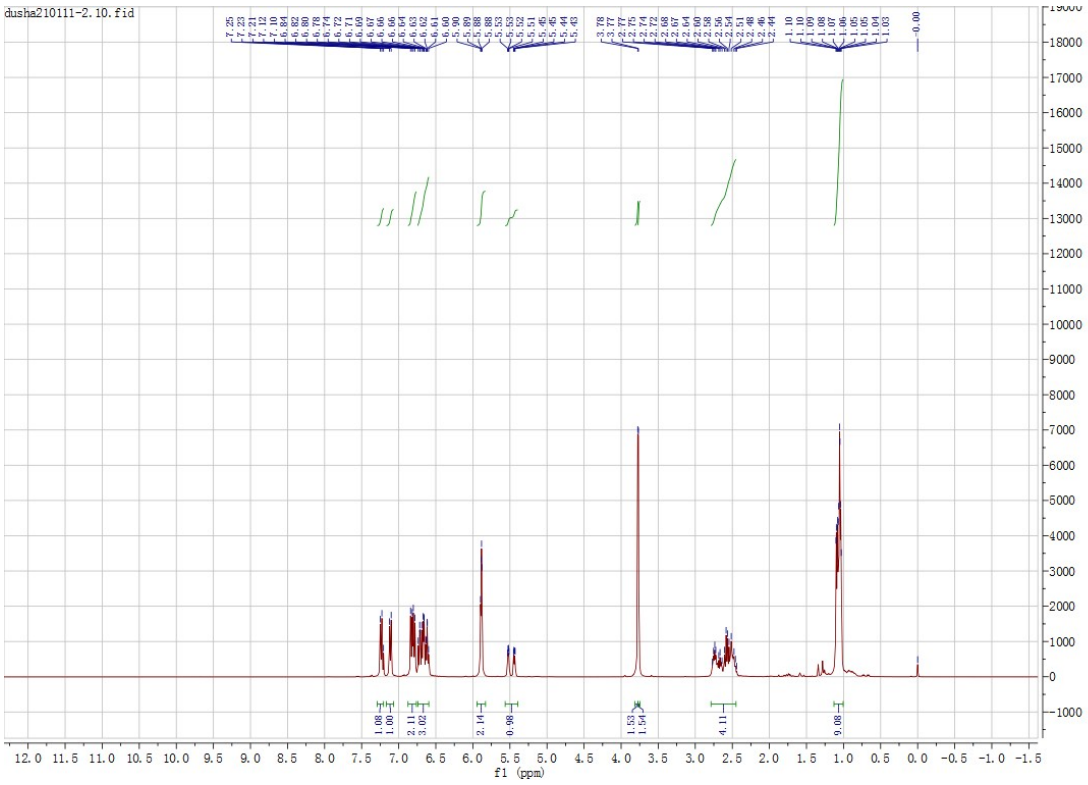
1ja, 85%

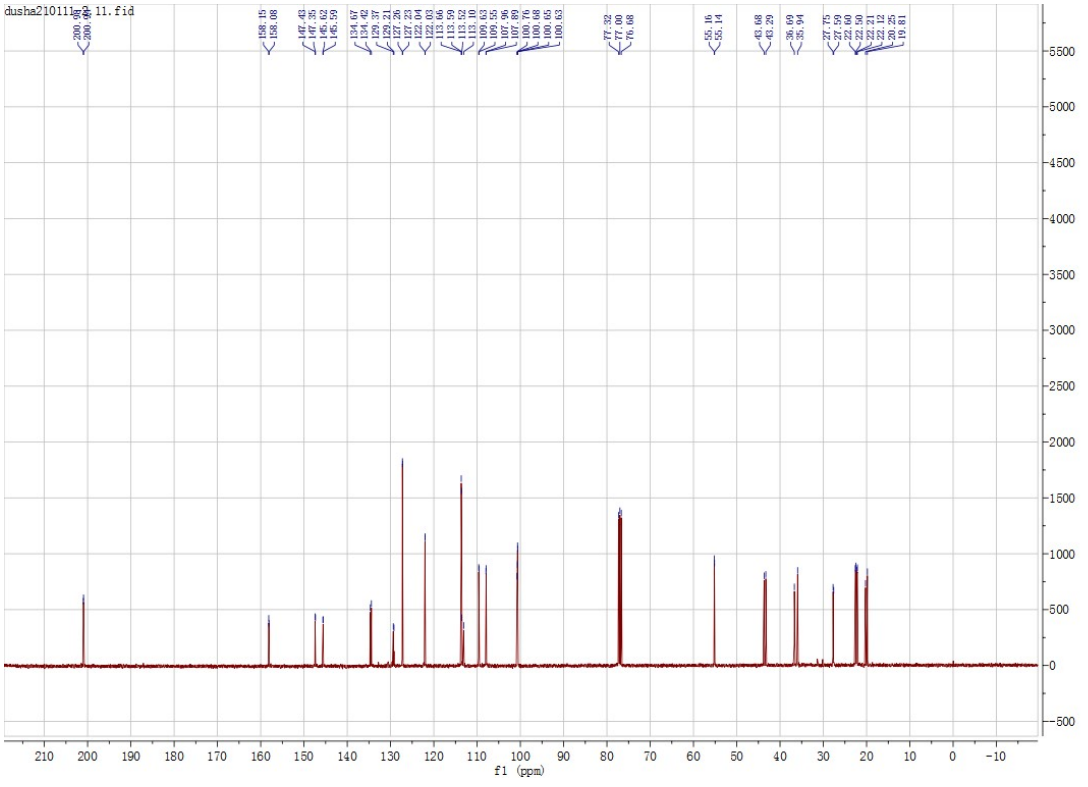

dusha201231-7-1.20.fid
f1 (ppm)

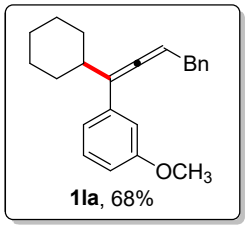

dusha201231-7-1.22.fid
f1 (ppm)


O
O
OCH3

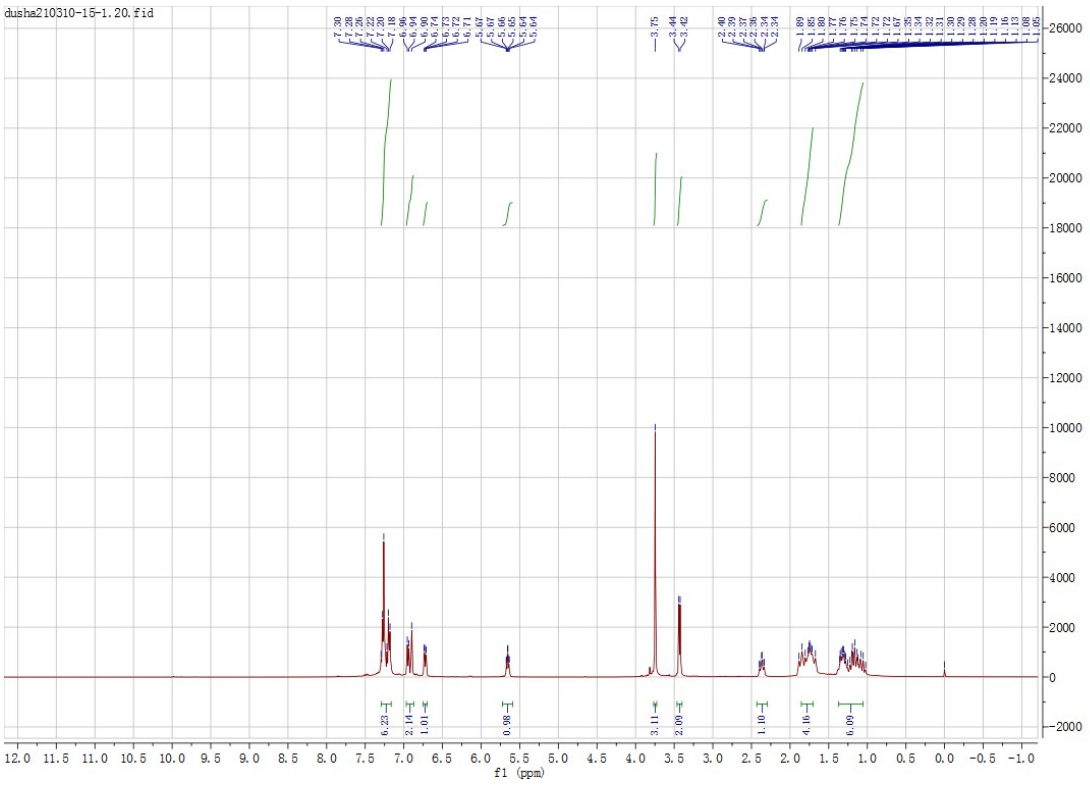
1ka, 71%
(d.r. = 1:1)

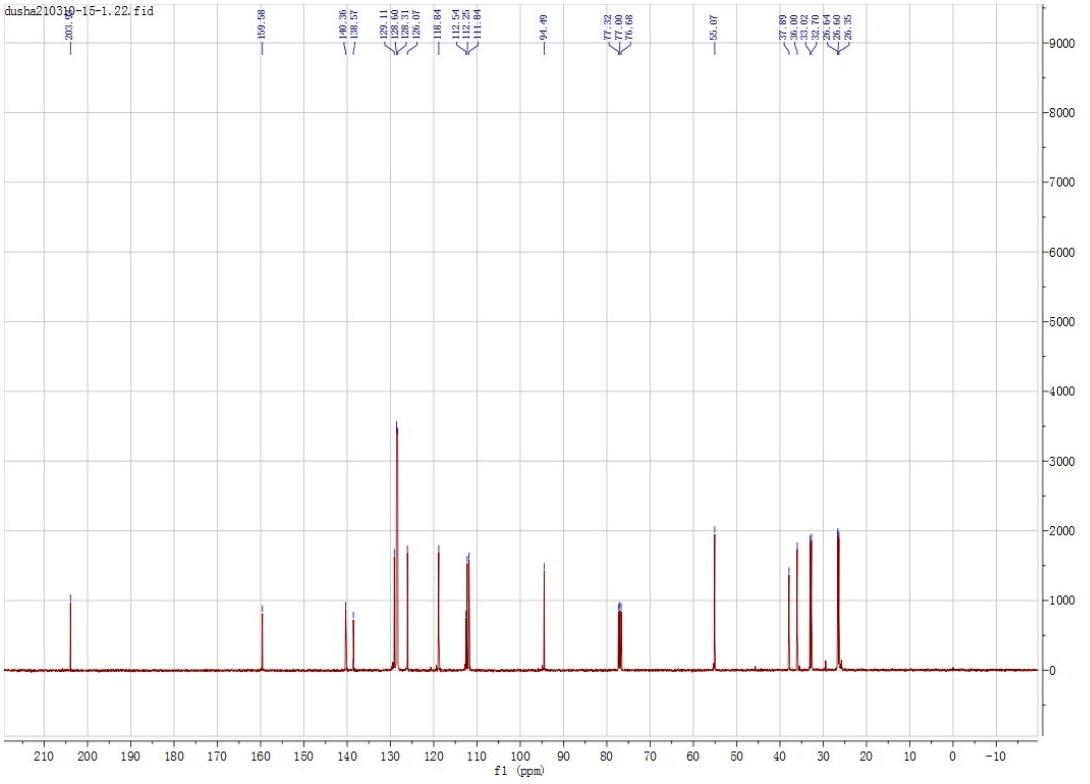

dusha210111-2.10.fid
f1 (ppm)

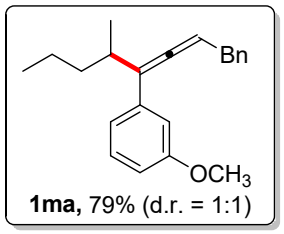

dusha210111-2.11.fid
f1 (ppm)


Bn
OCH3

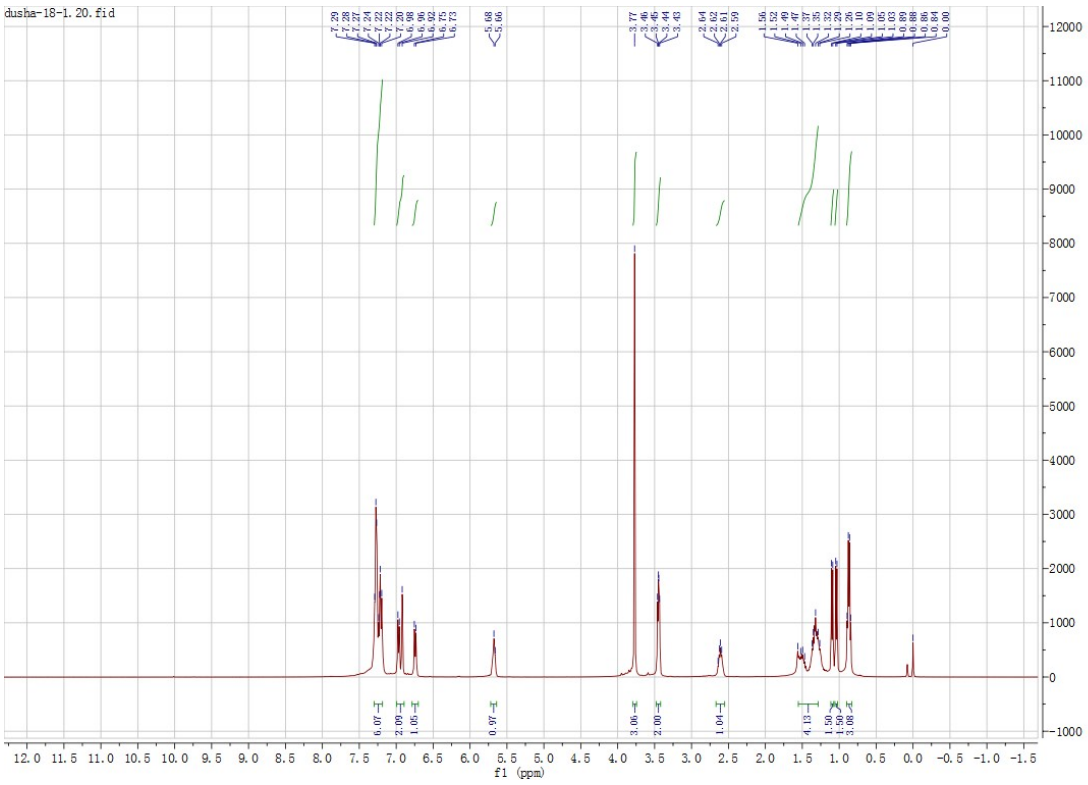
1la, 68%

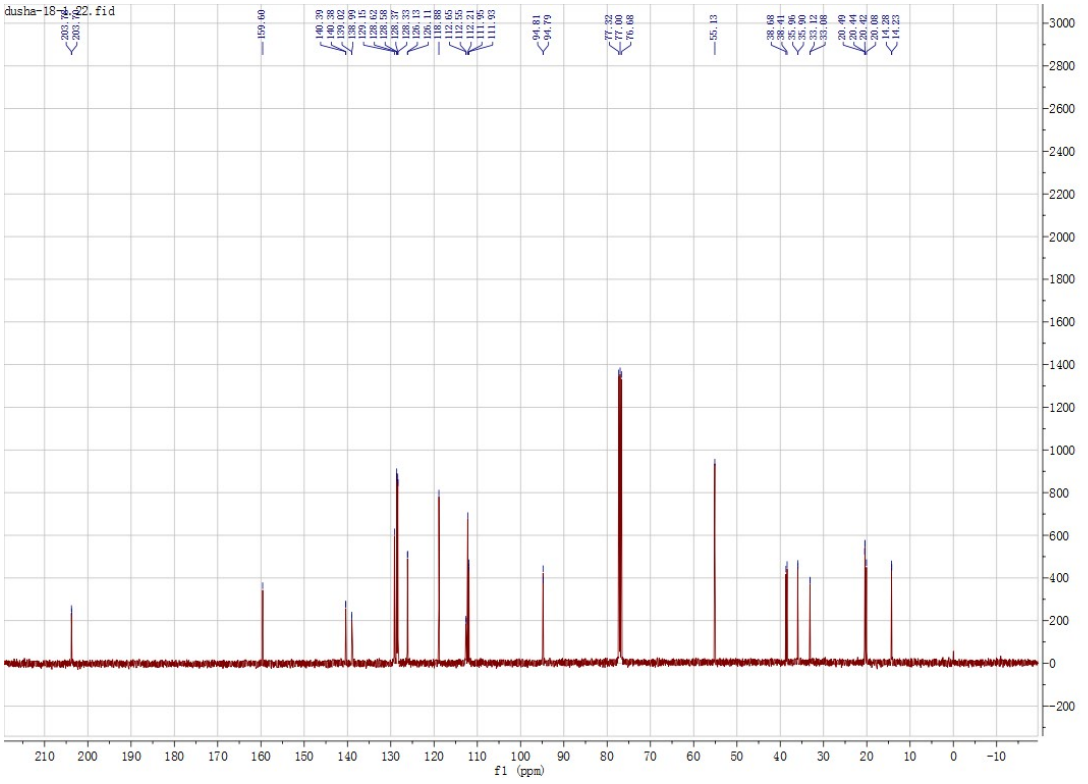

dusha210310-15-1.20.fid
f1 (ppm)

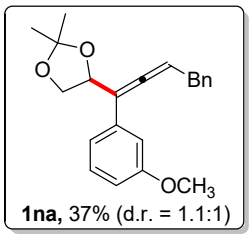

dusha210310-15-1.22.fid
f1 (ppm)



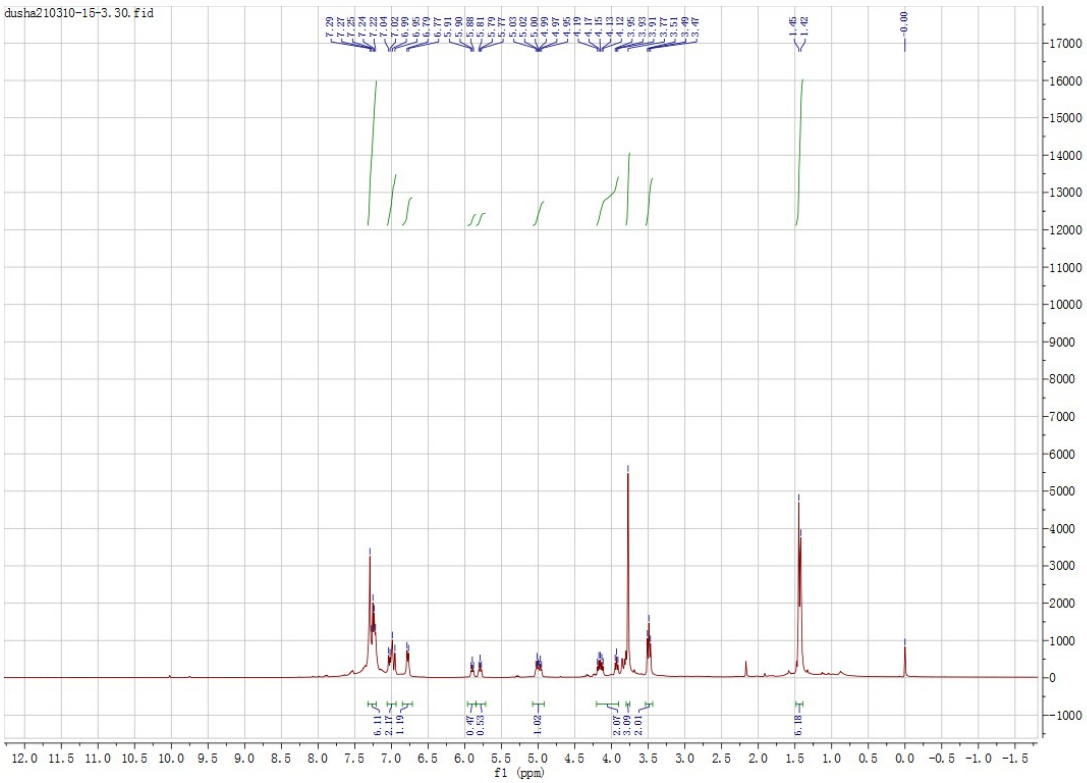
1ma, 79% (d.r. = 1:1)

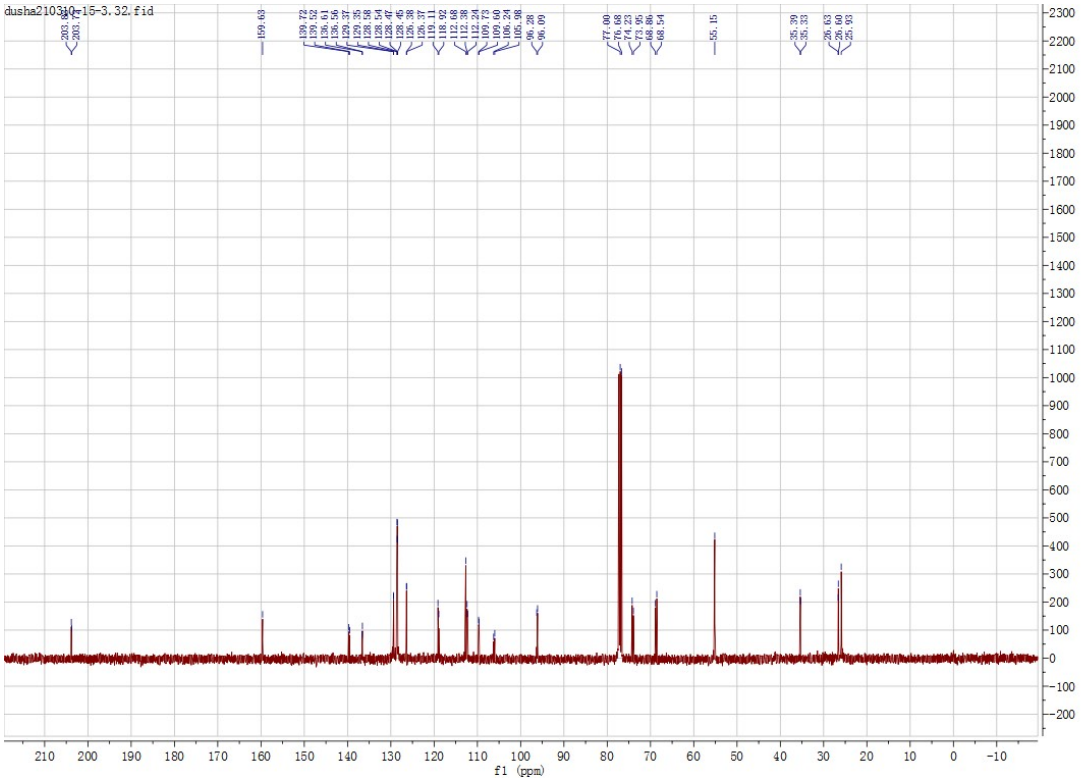


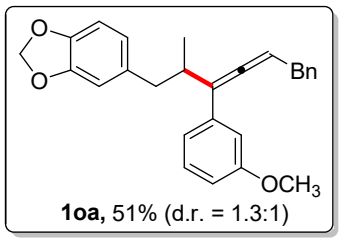



O
O
Bn
OCH3

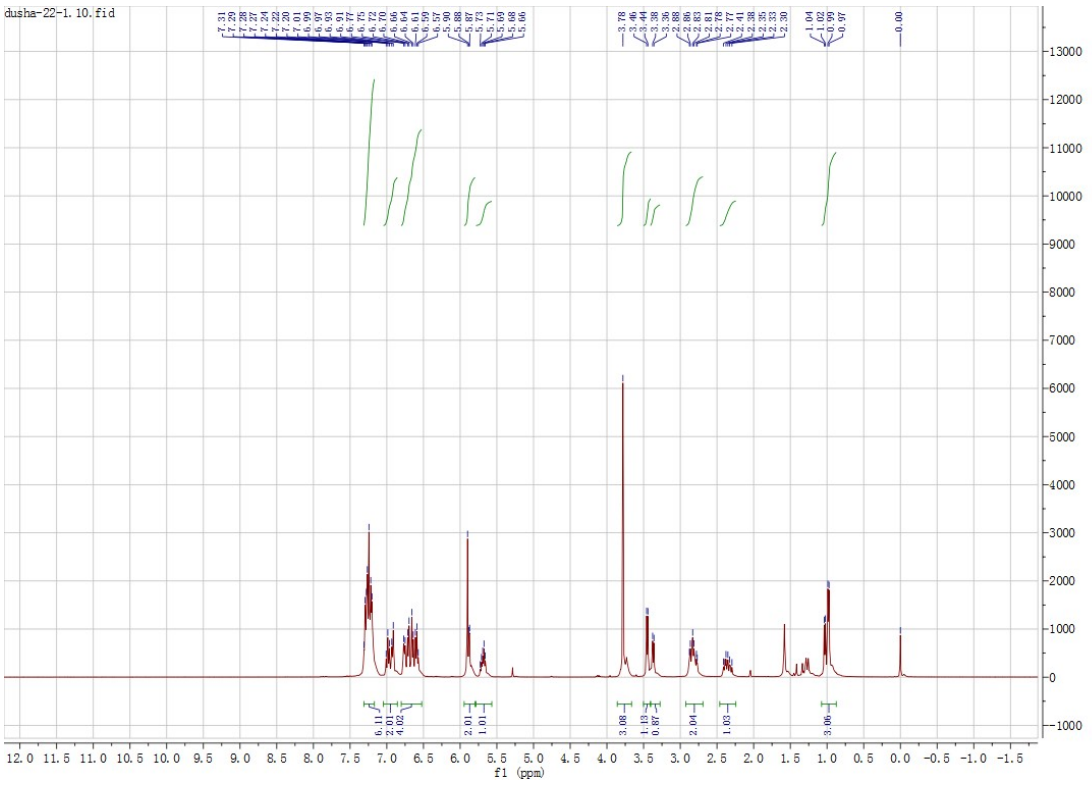
1na, 37% (d.r. = 1.1:1)

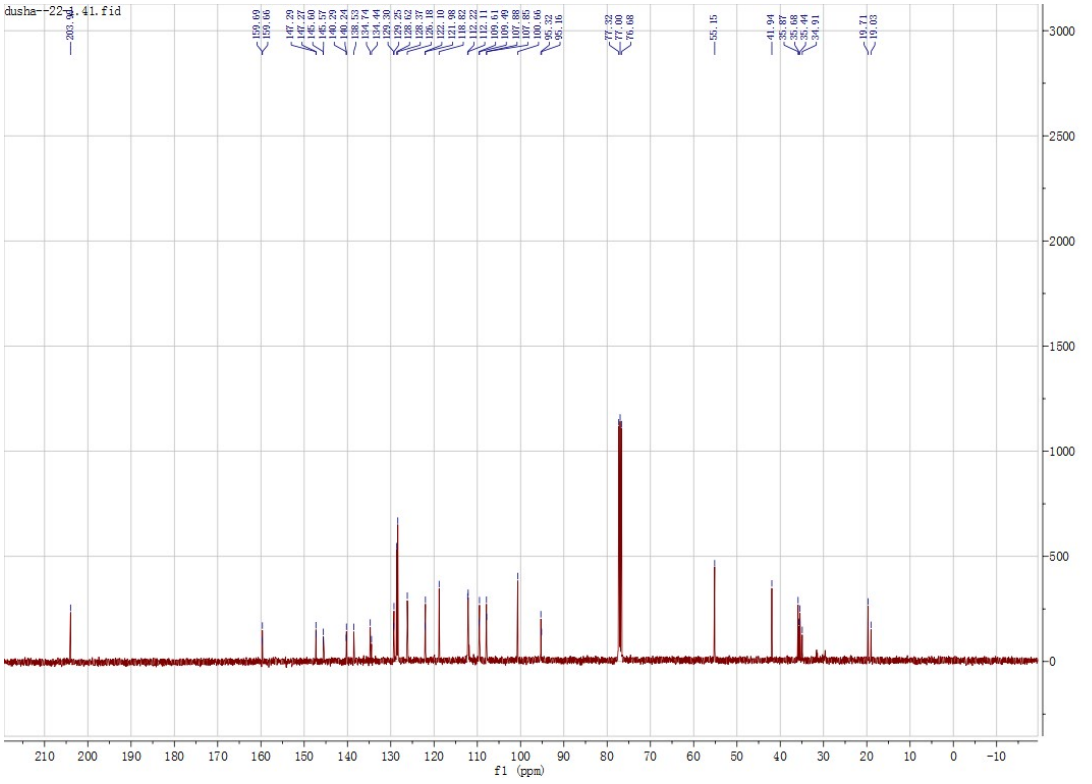

dusha210310-15-3.30.fid
f1 (ppm)

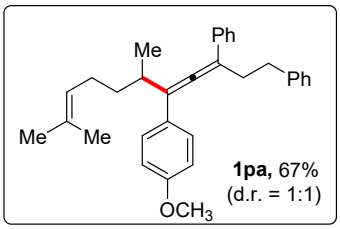

dusha210310-15-3.32.fid
f1 (ppm)



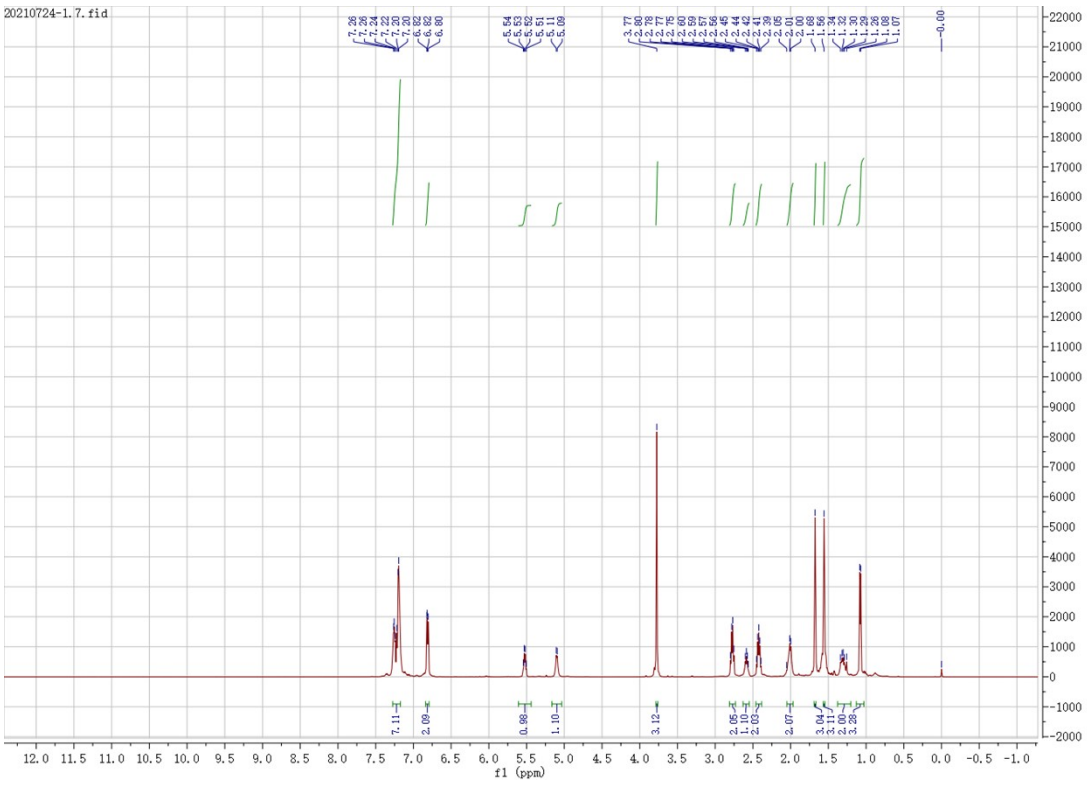
1oa, 51% (d.r. = 1.3:1)

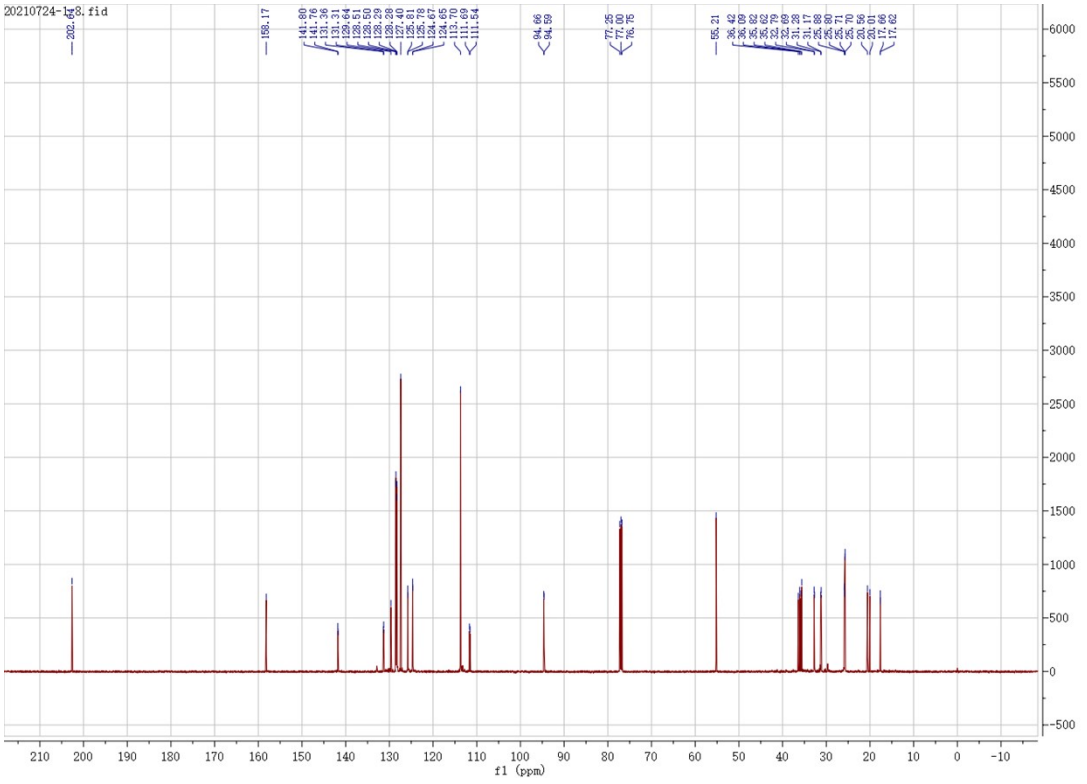




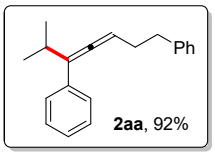

Me
Ph
Ph
Me
Me
OCH3

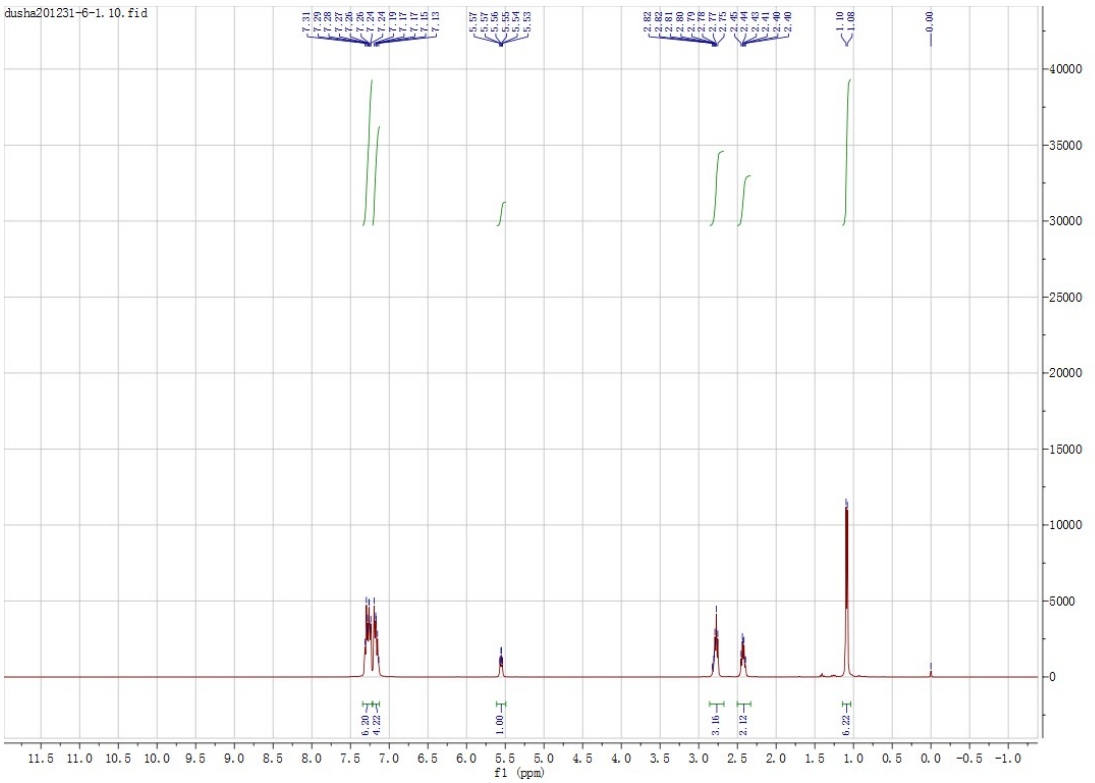
1pa, 67%
(d.r. = 1:1)

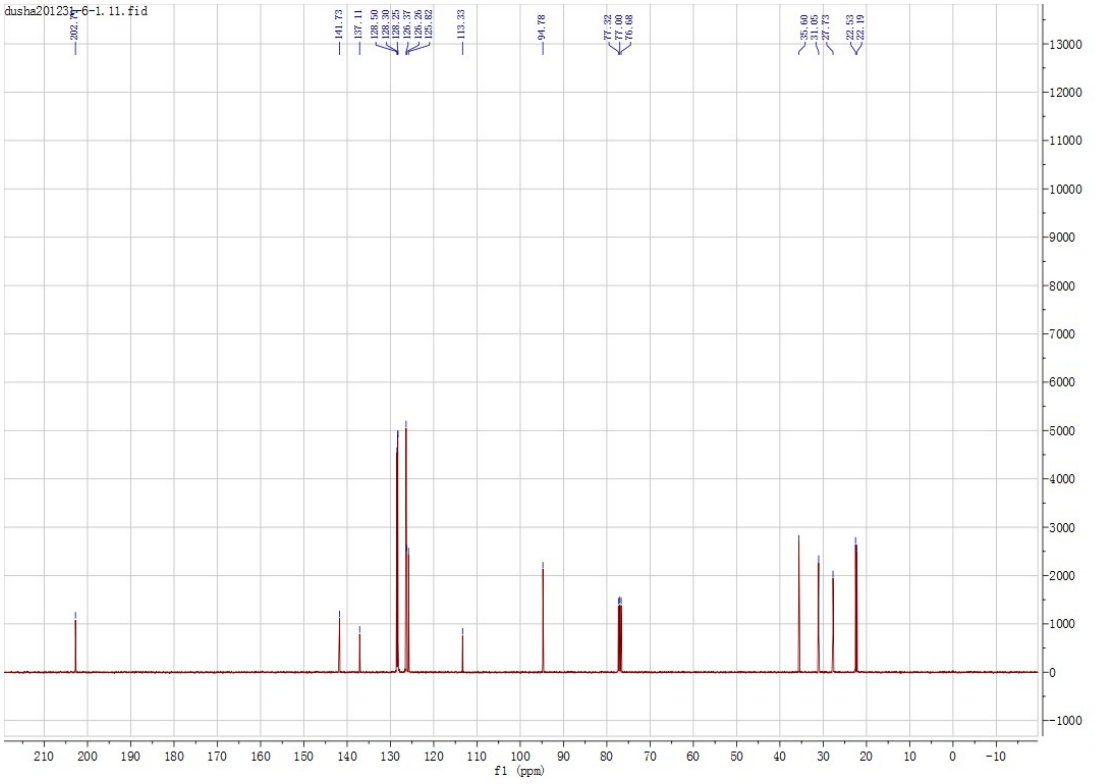

20210724-1.7.fid
f1 (ppm)

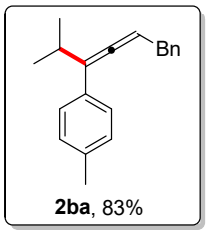

20210724-1.8.fid
f1 (ppm)

10. ^{1}H NMR and ^{13}C NMR Spectra of the Products 2aa-2oa, 3aa/3ab:

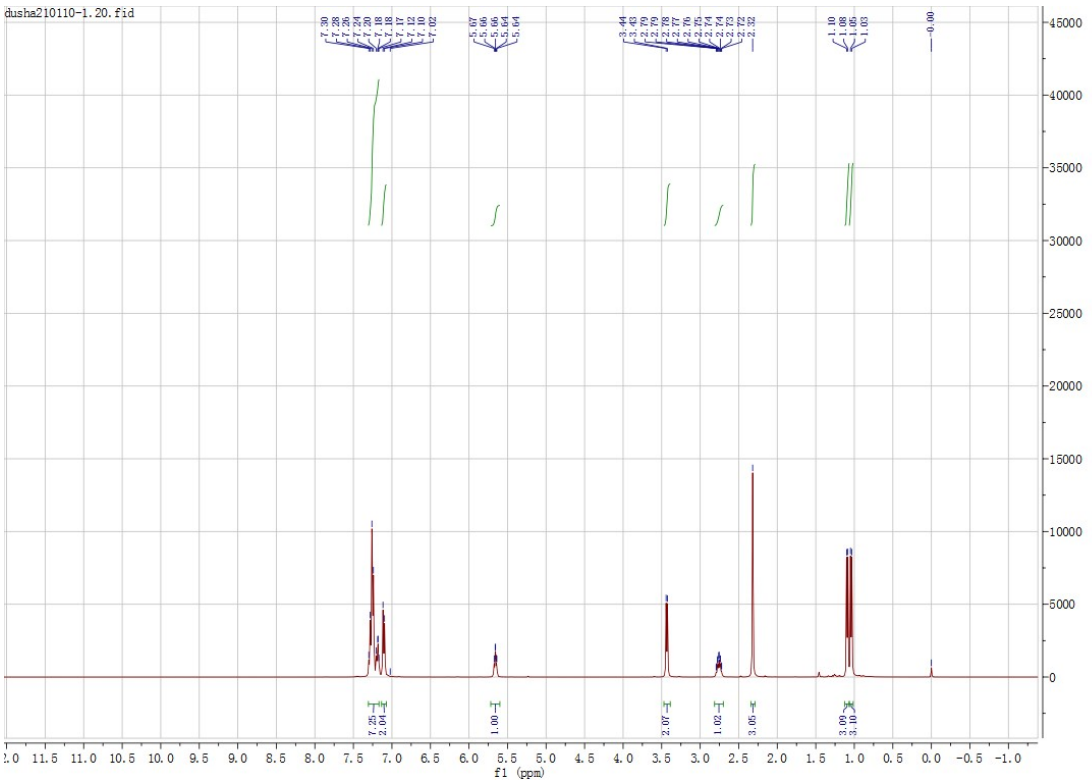


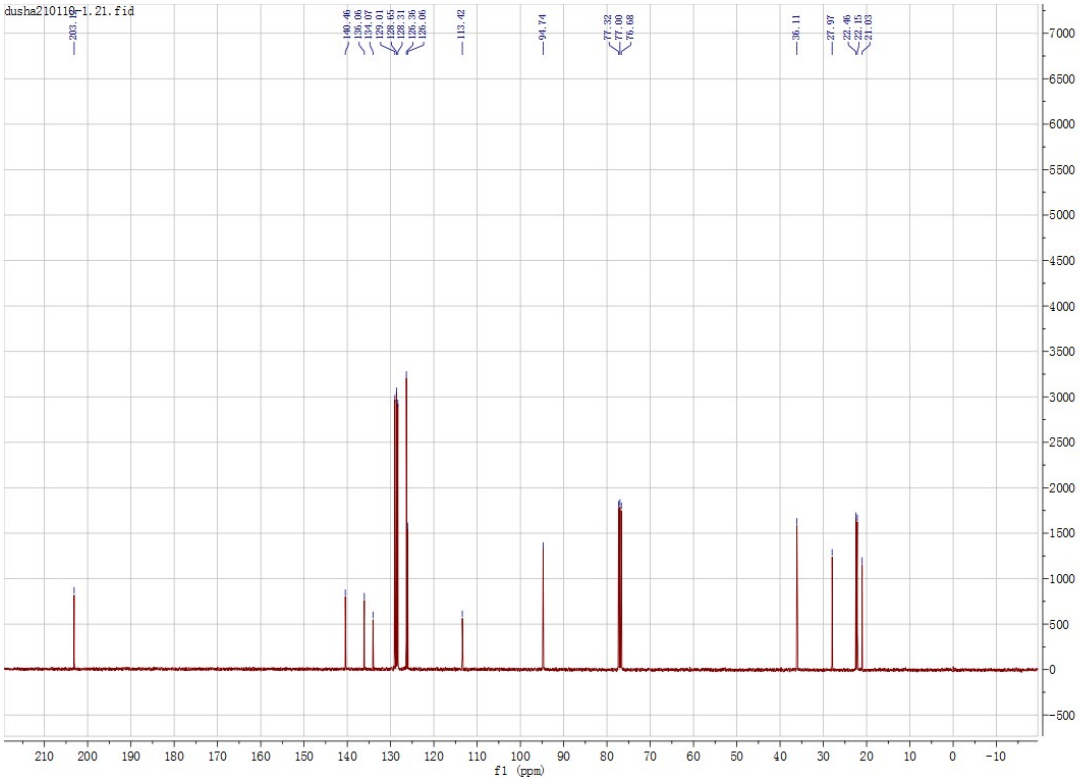


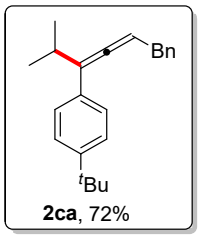




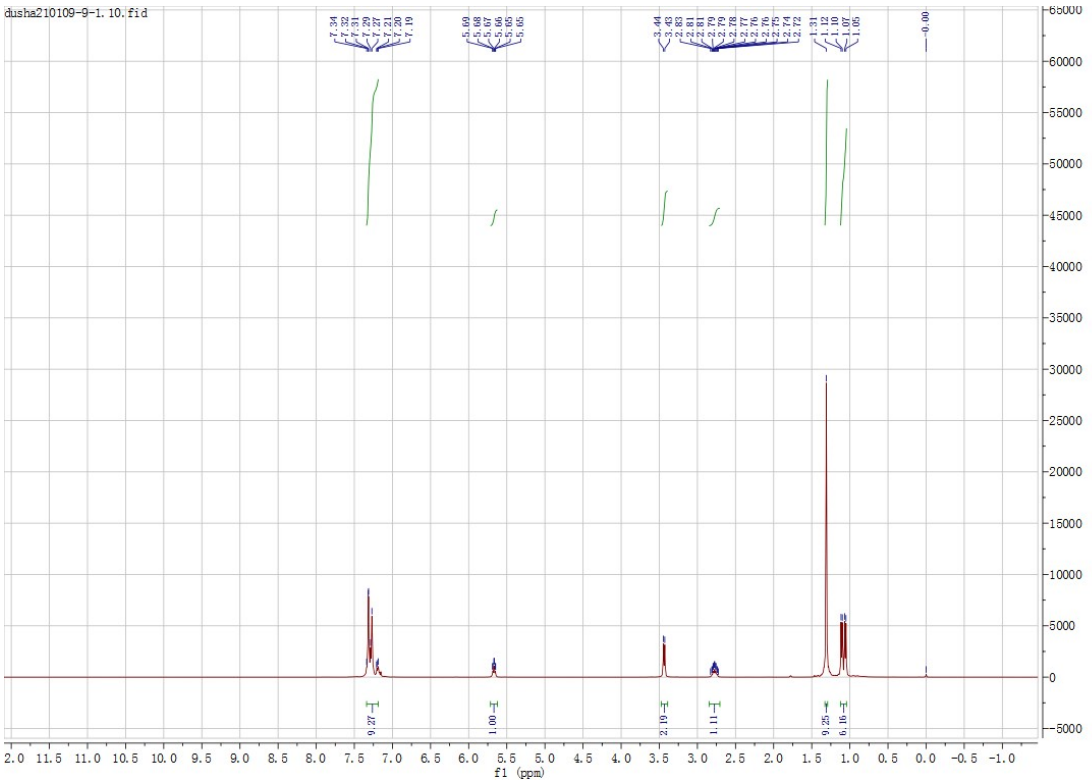
2ba, 83%

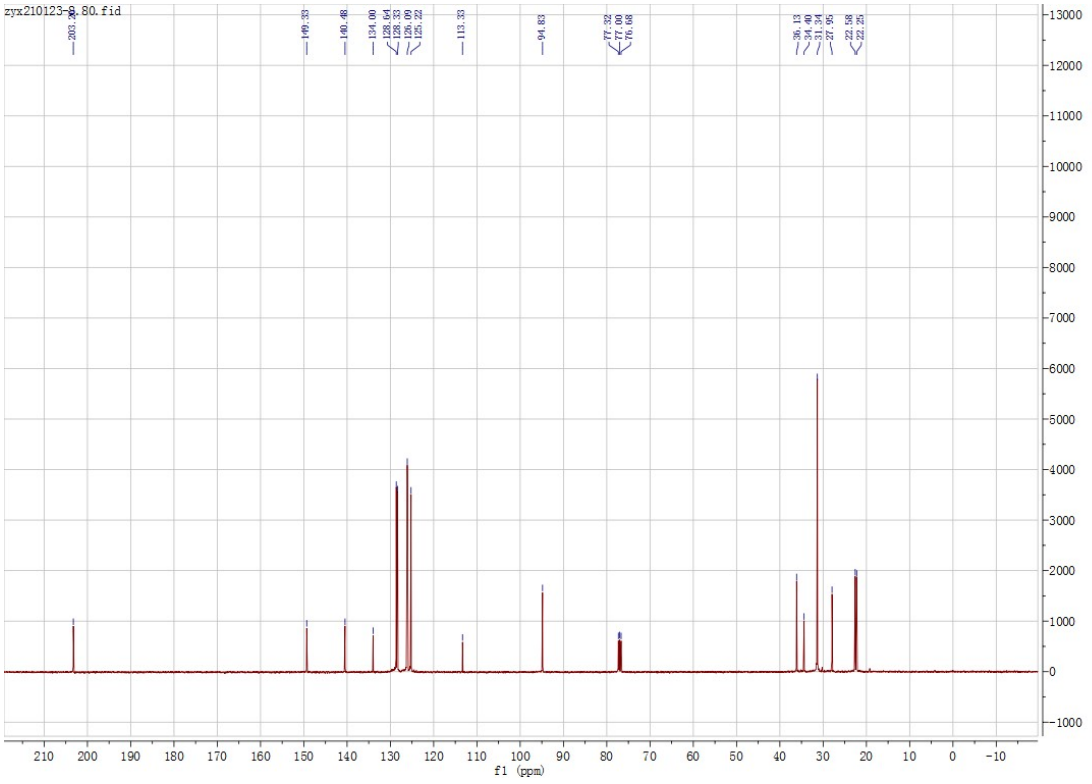


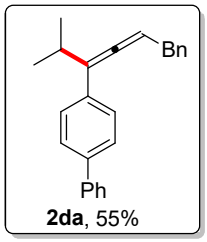




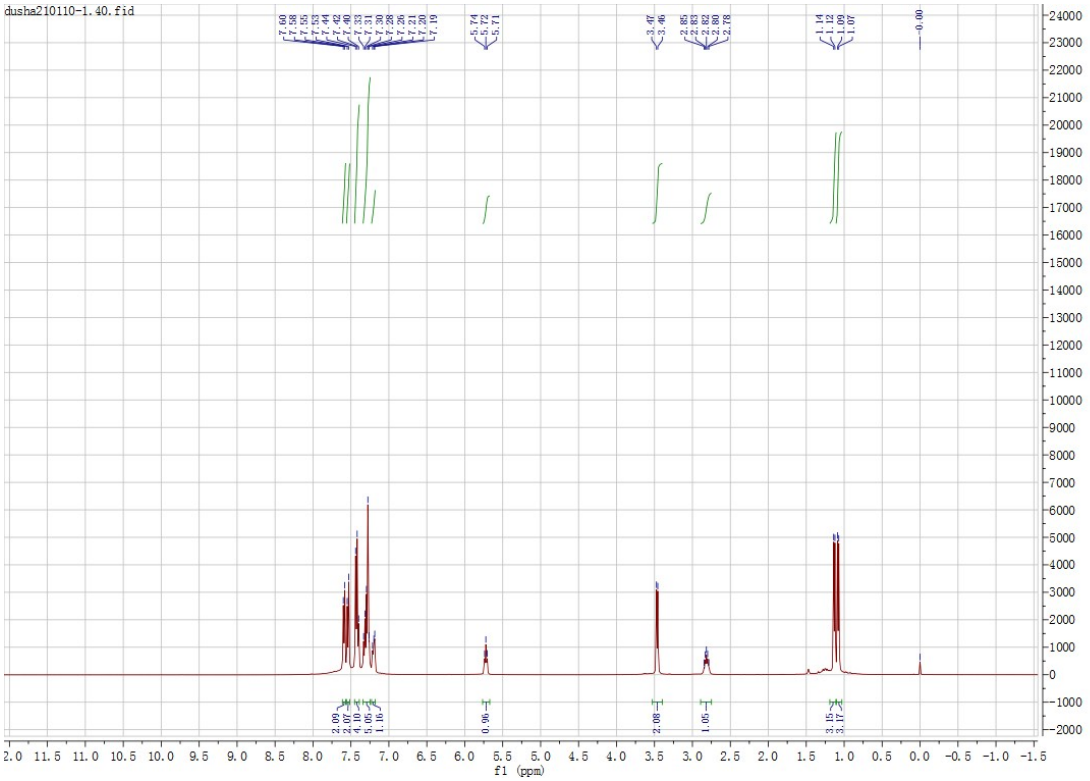
2ca, 72%

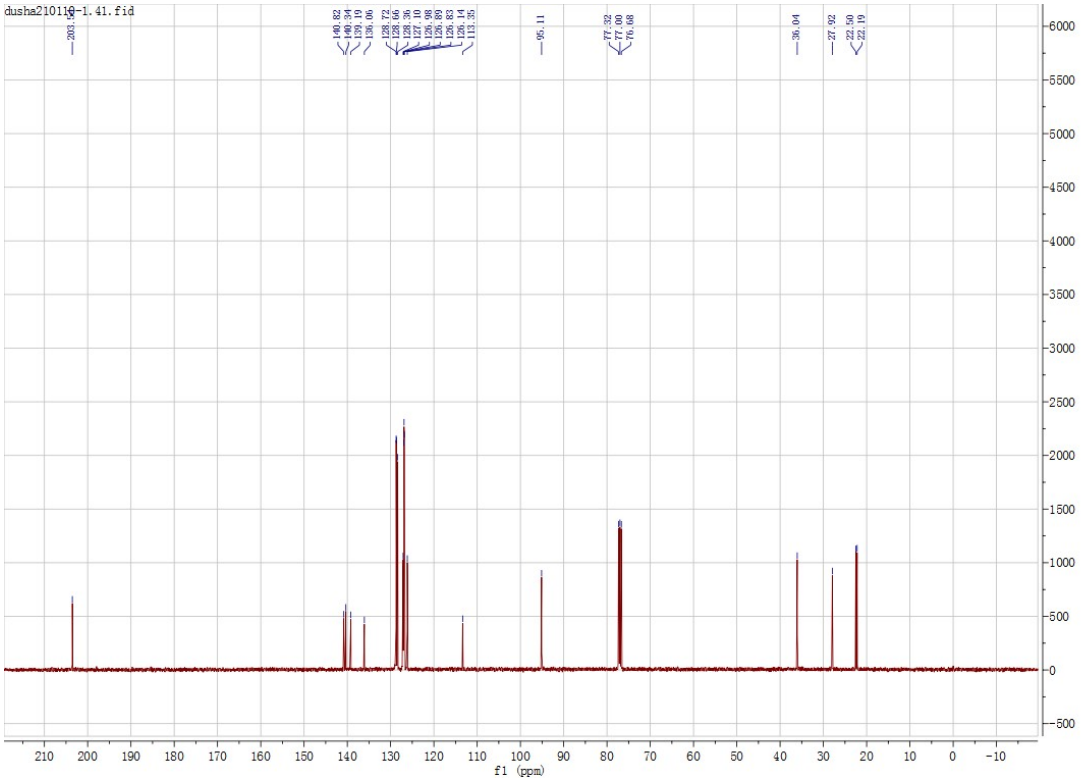


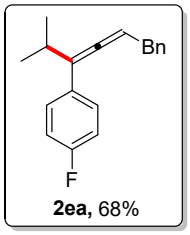




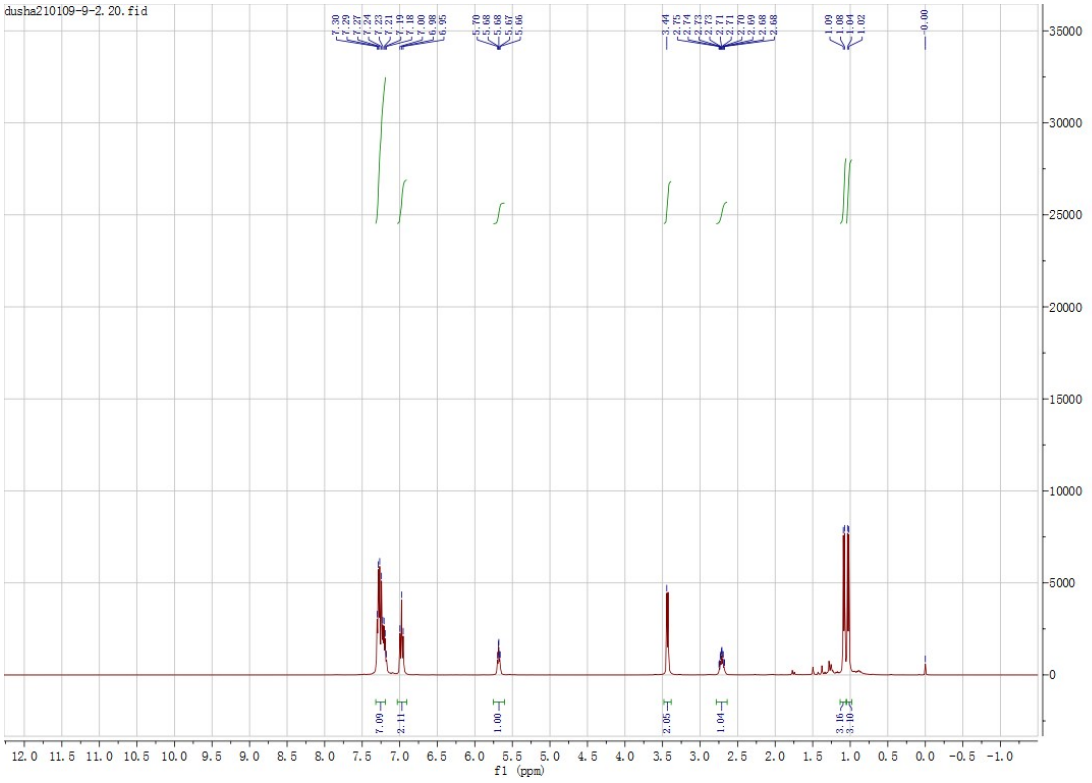
2da, 55%

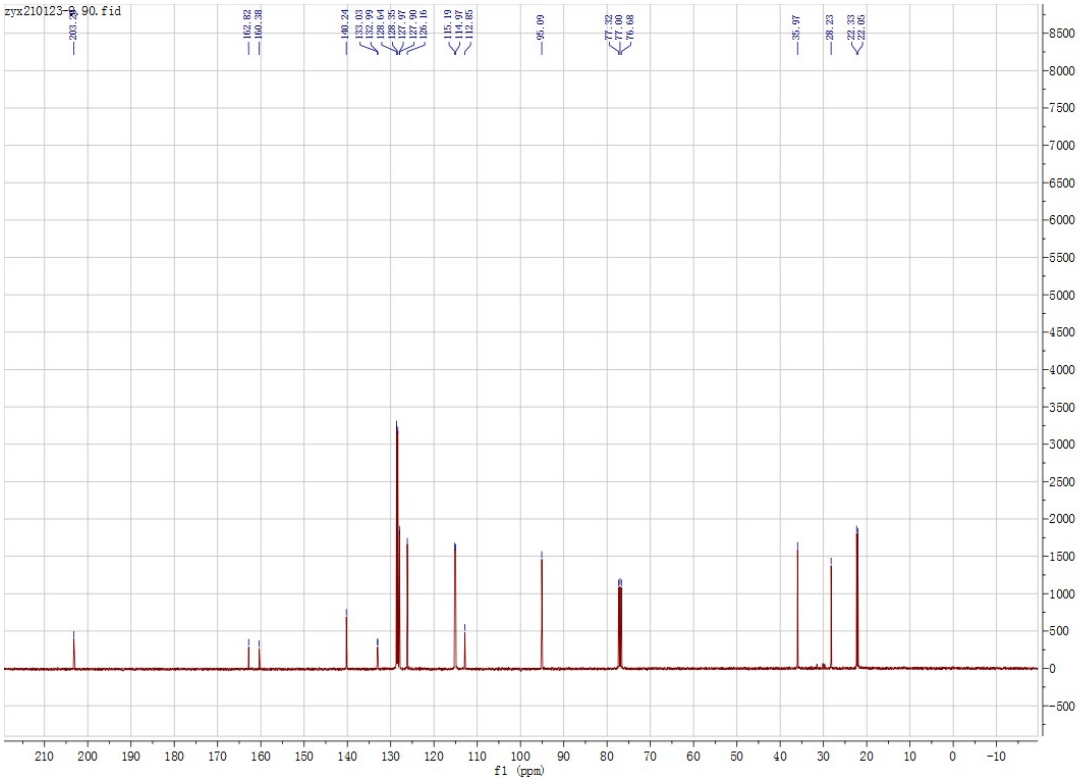


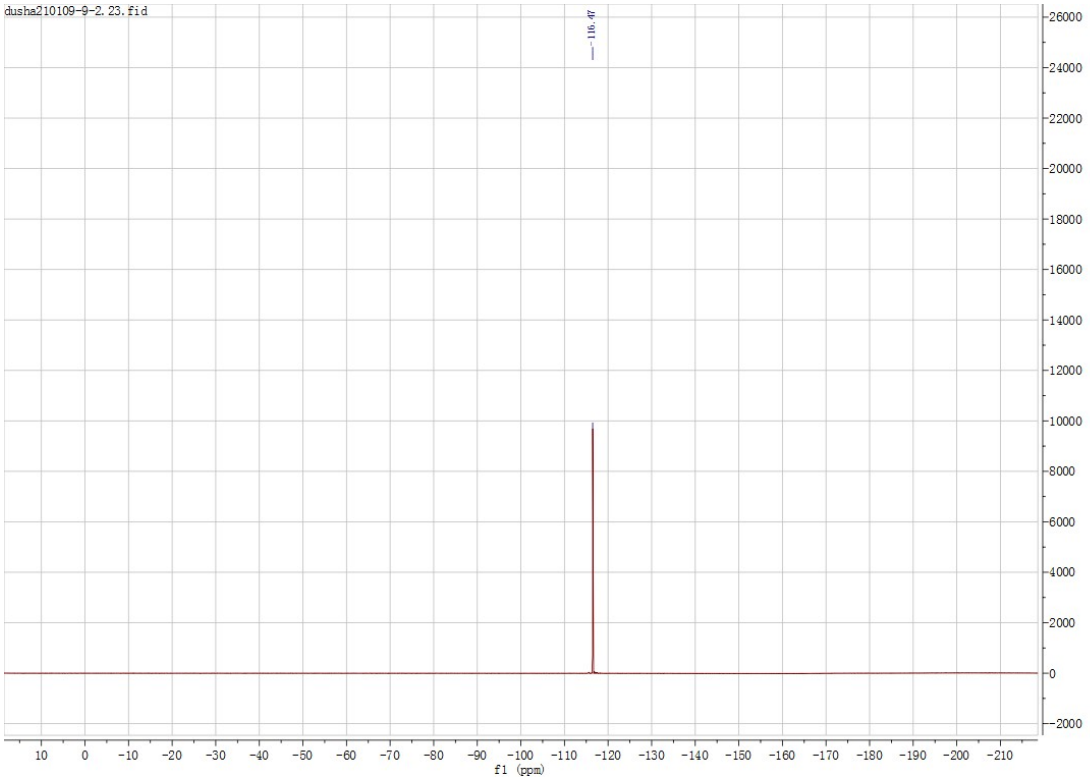


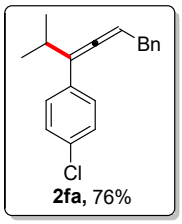


2ea, 68%

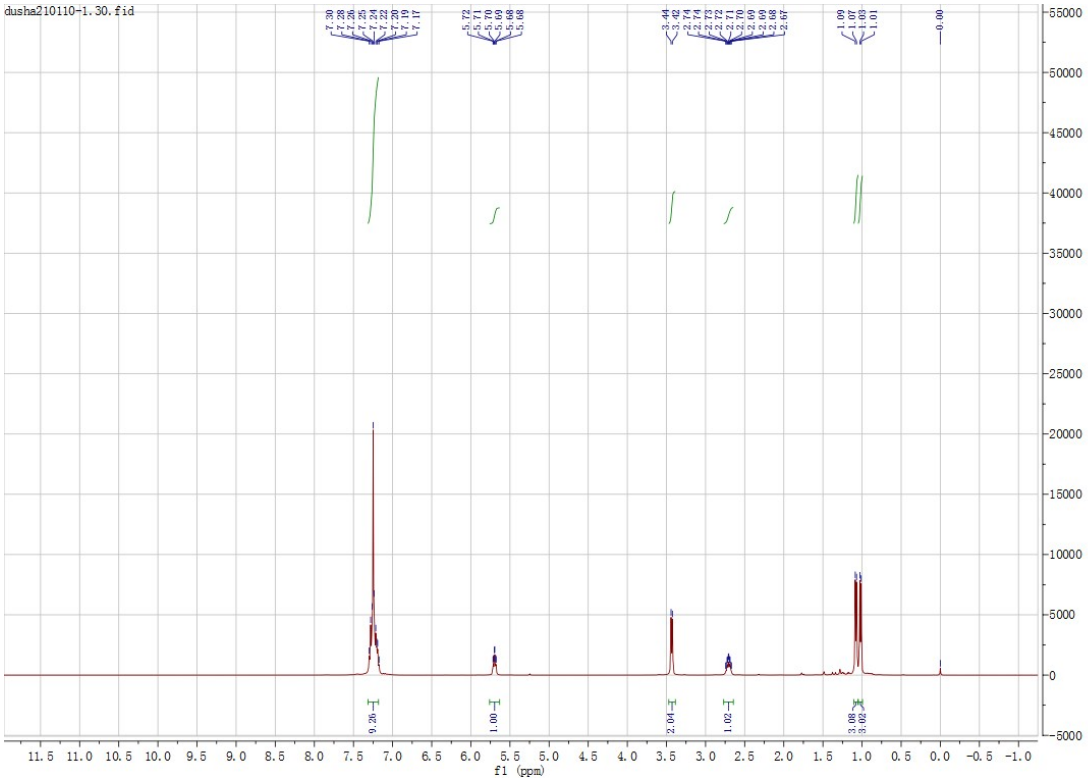


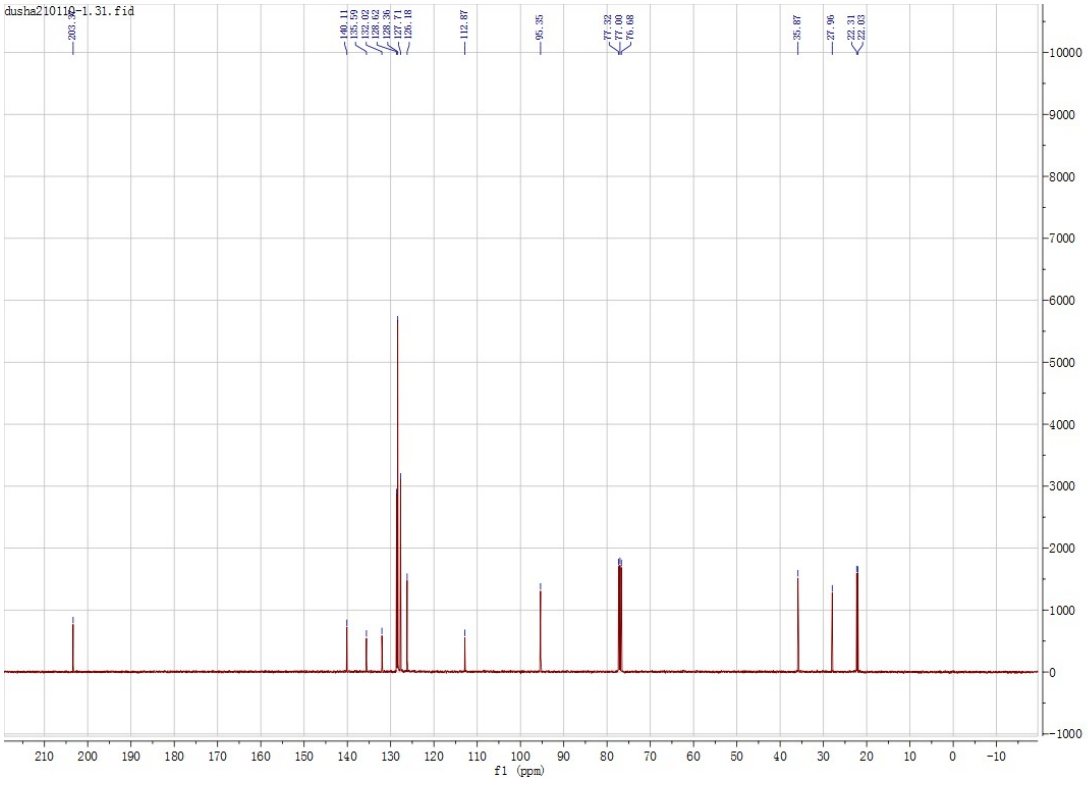


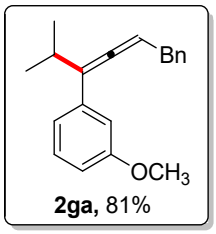

dusha210109-9-2.23.fid
-116.47
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)



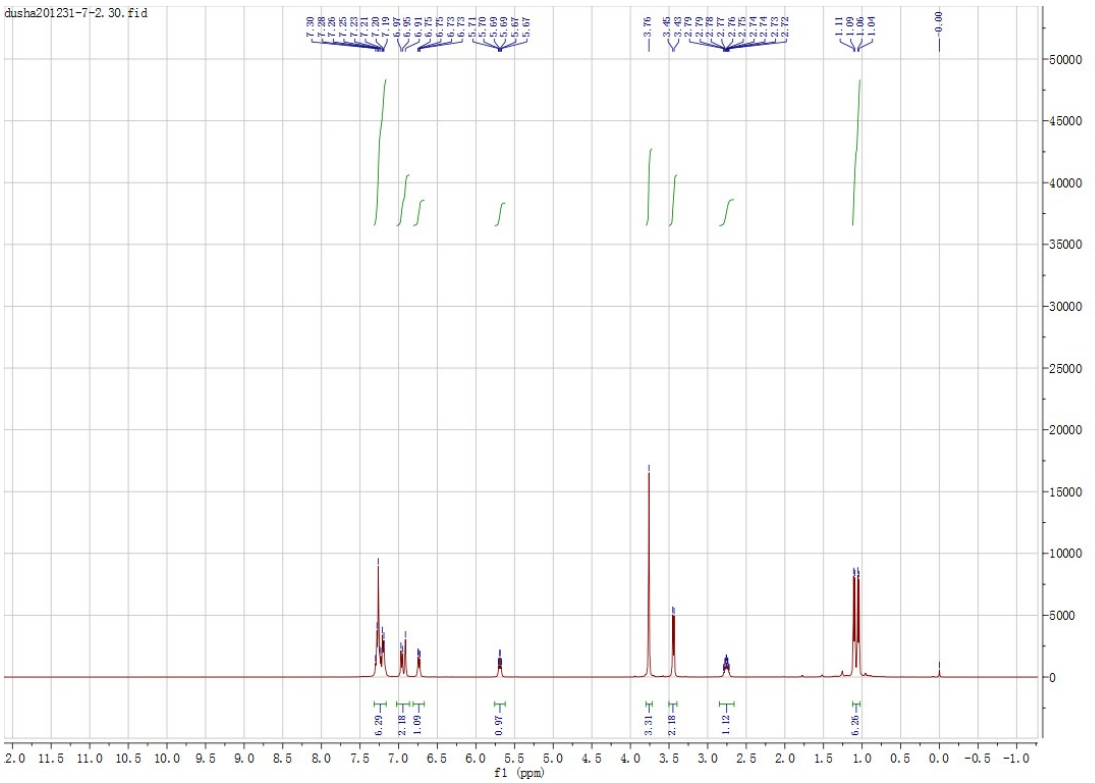
2fa, 76%

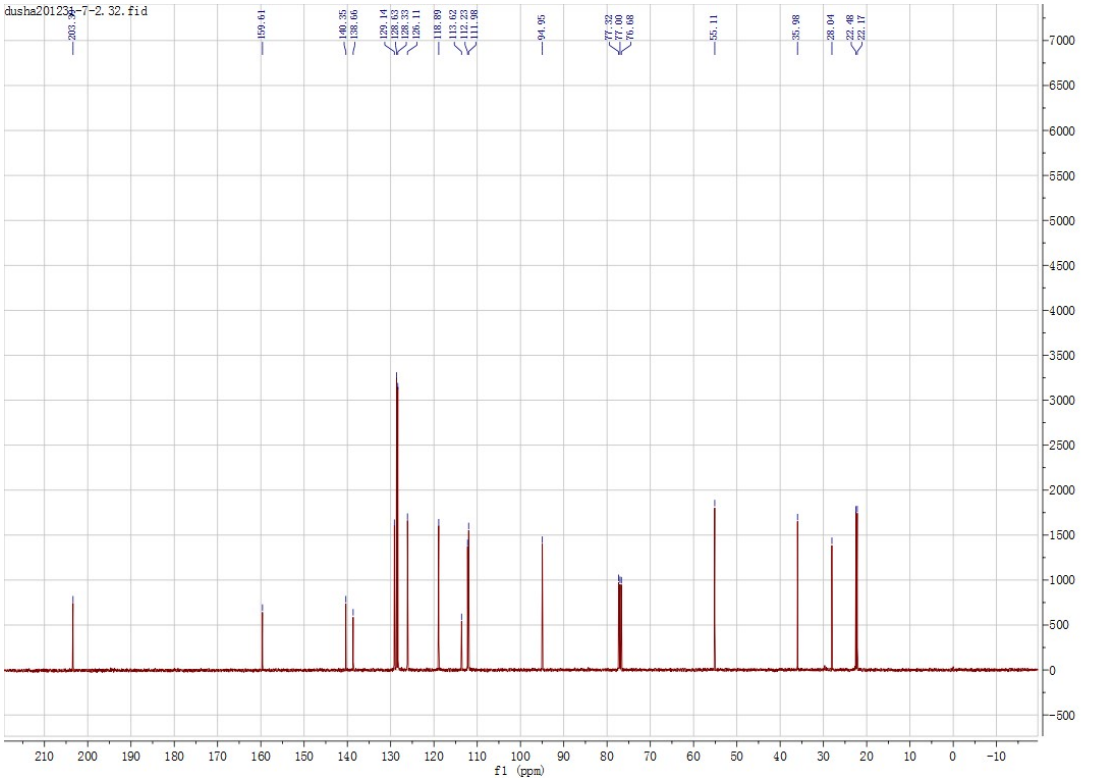


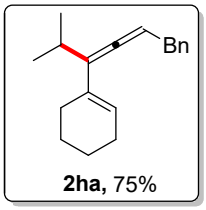



Bn
OCH3

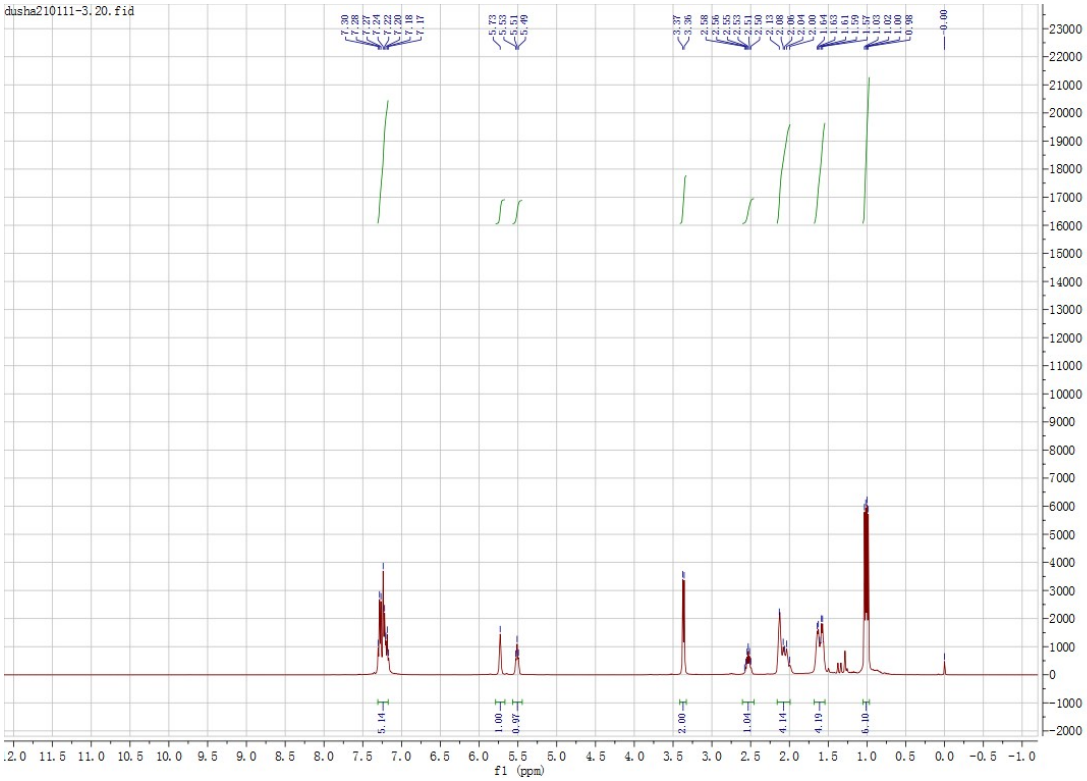
2ga, 81%

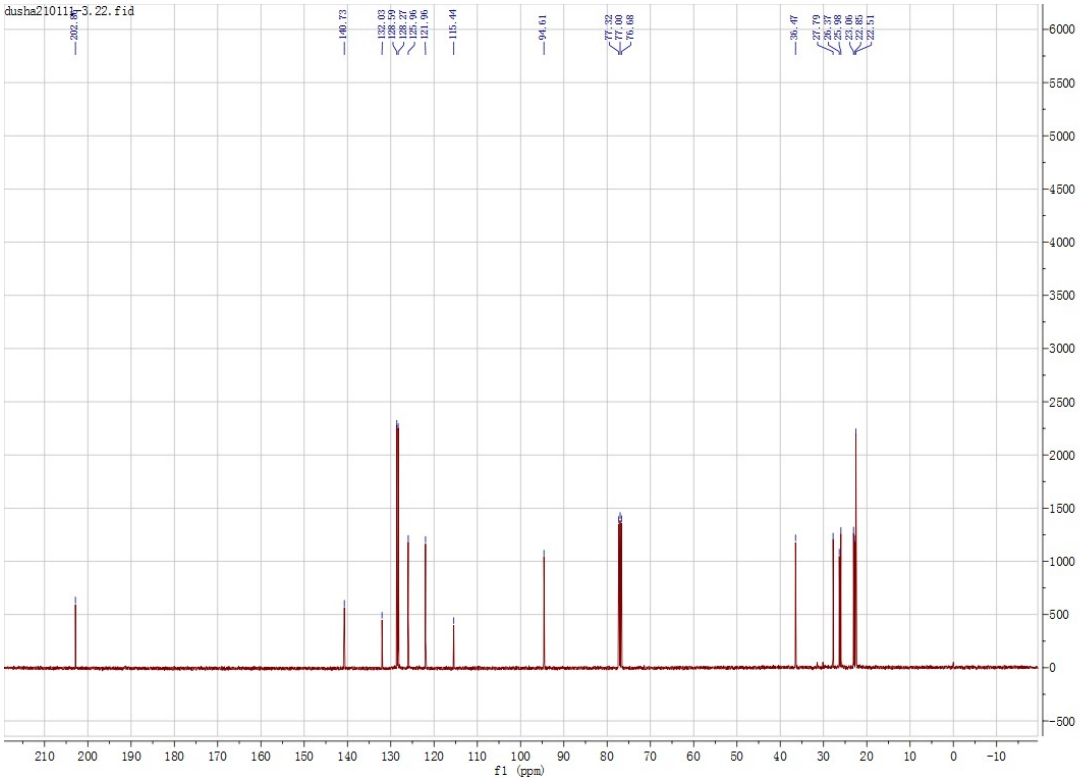

dusha201231-7-2.30.fid
f1 (ppm)

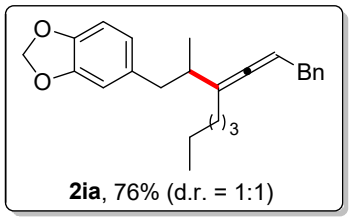

dusha201231-7-2.32.fid
f1 (ppm)



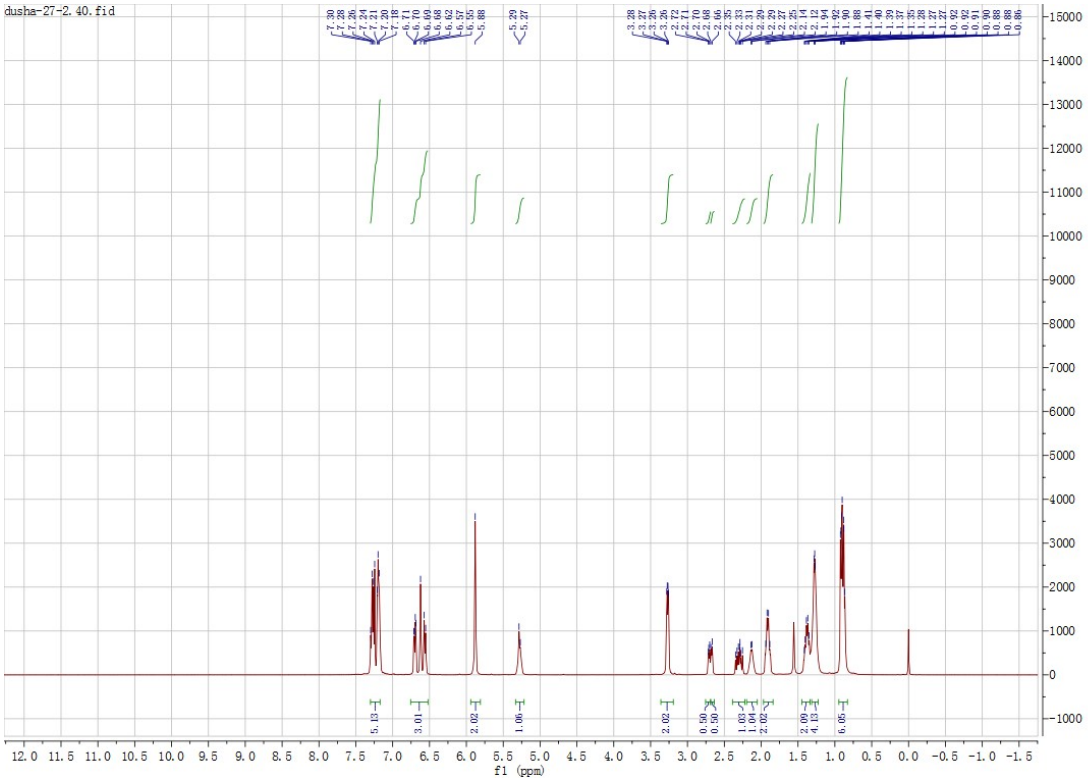
2ha, 75%

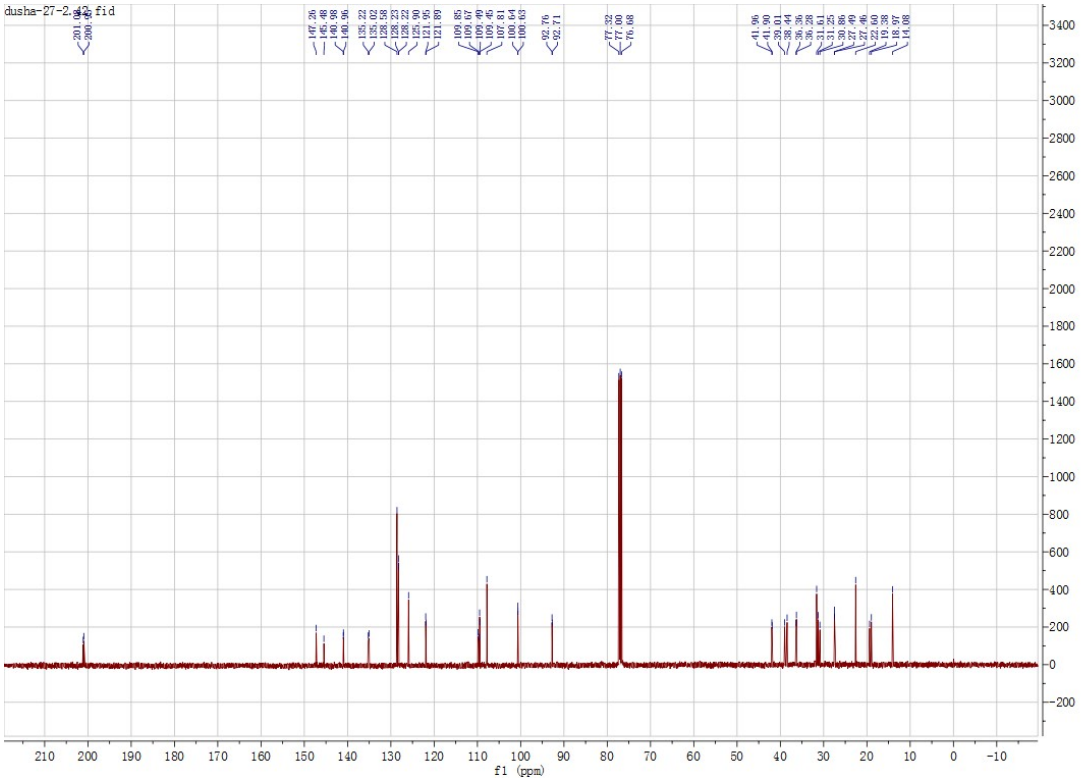


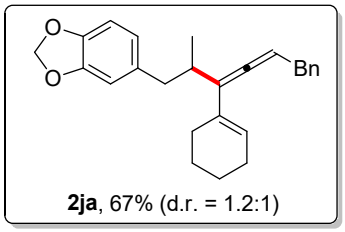




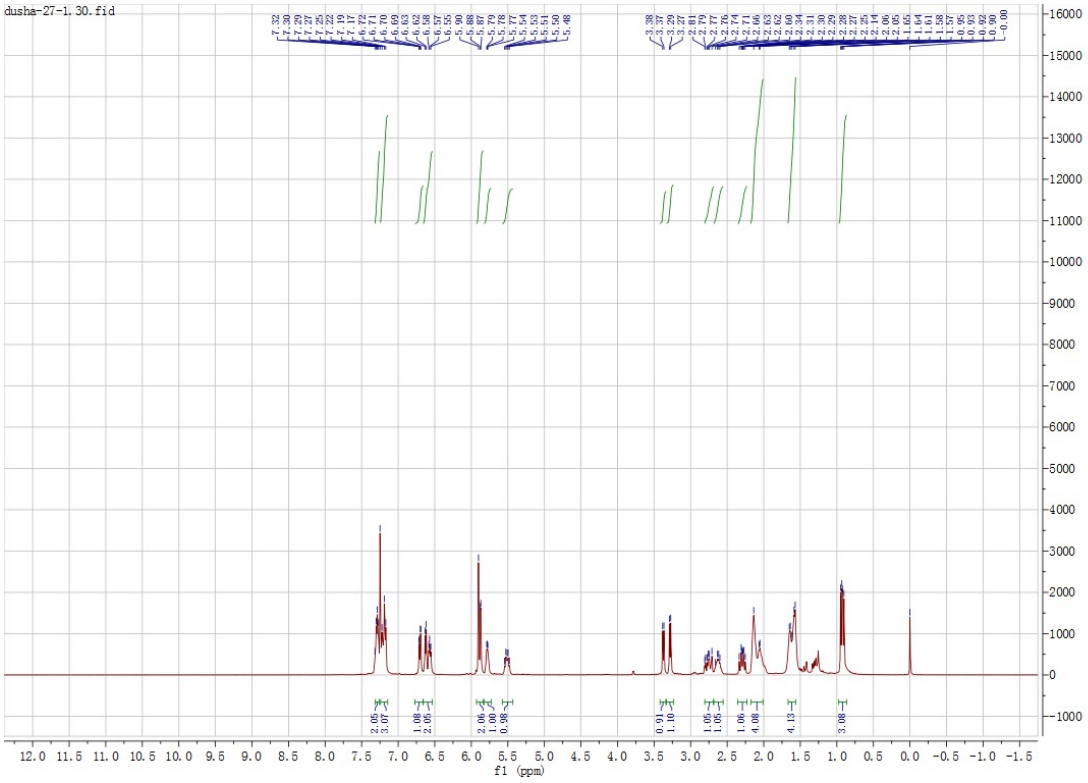
2ia, 76% (d.r. = 1:1)

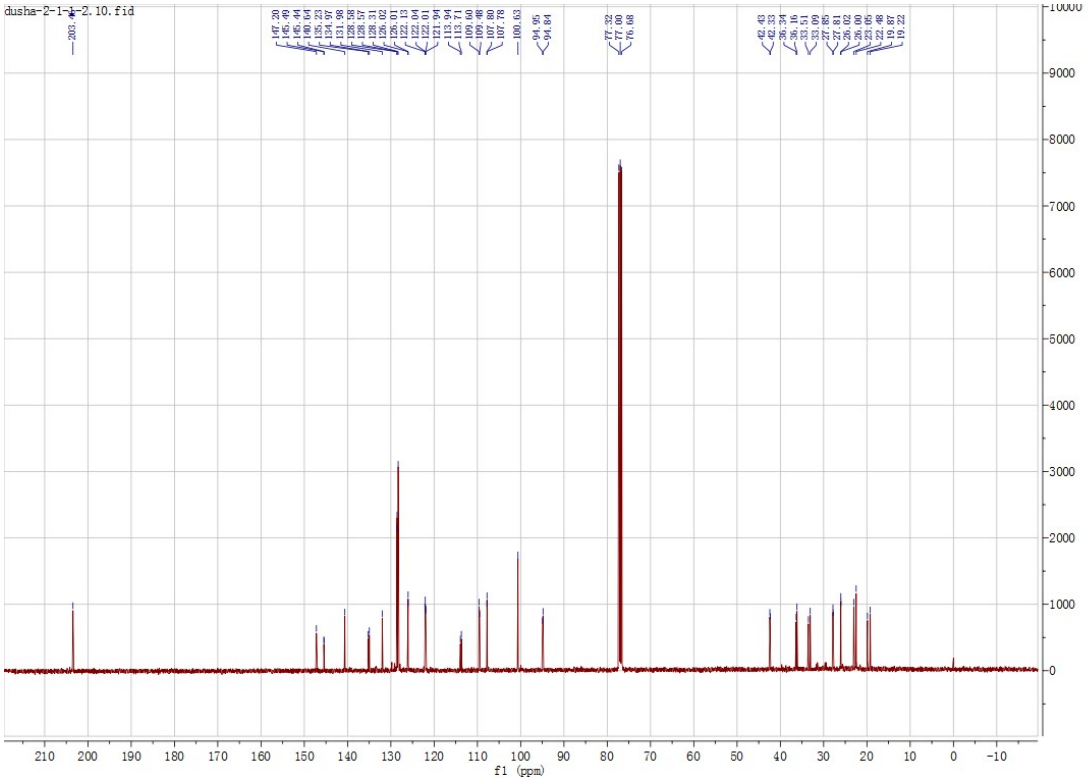


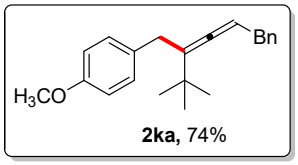




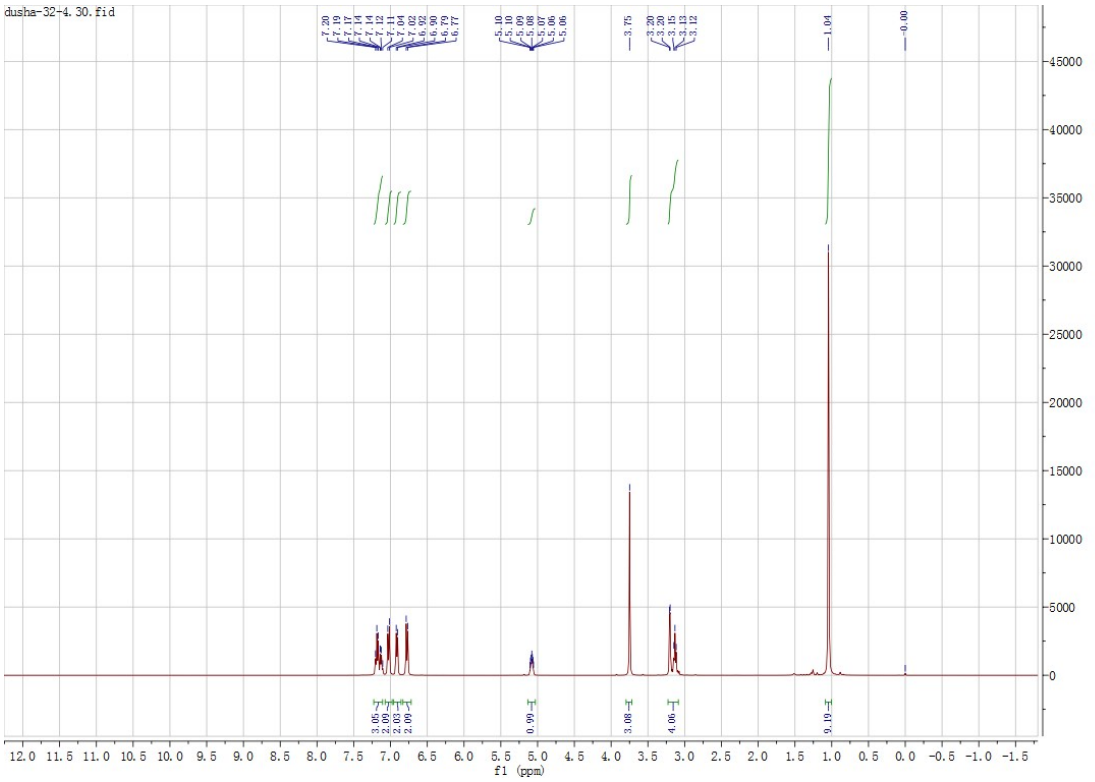
2ja, 67% (d.r. = 1.2:1)

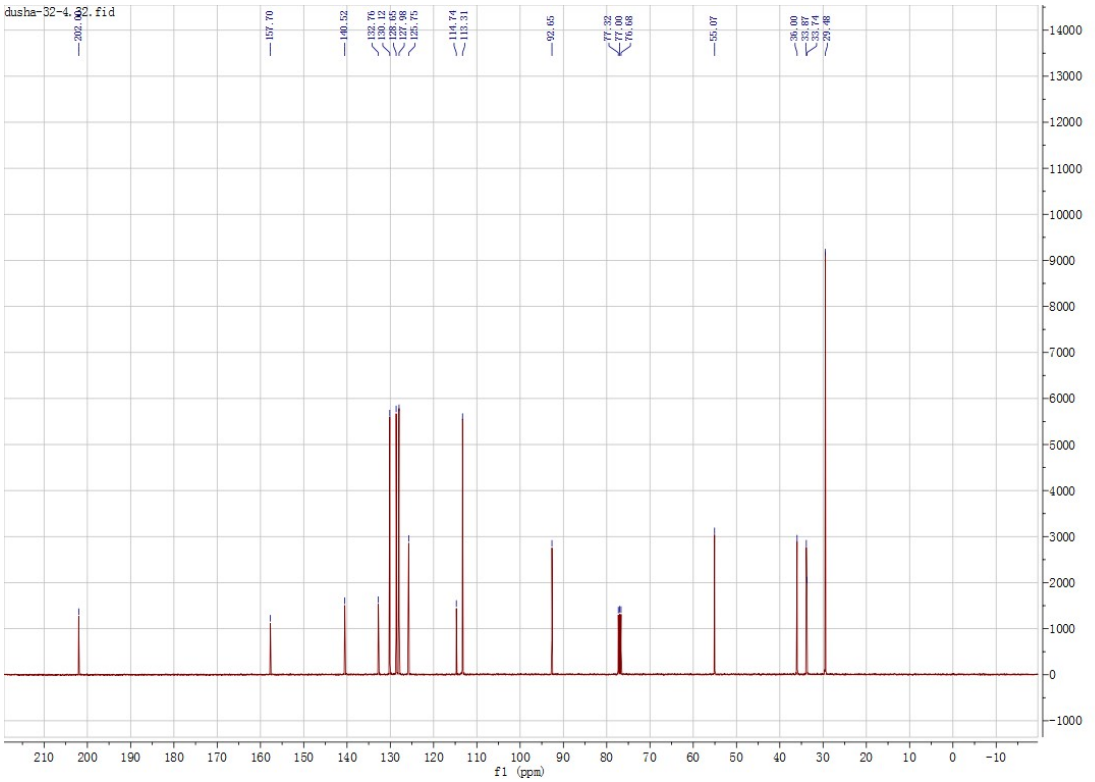


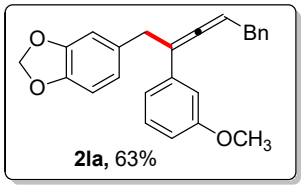




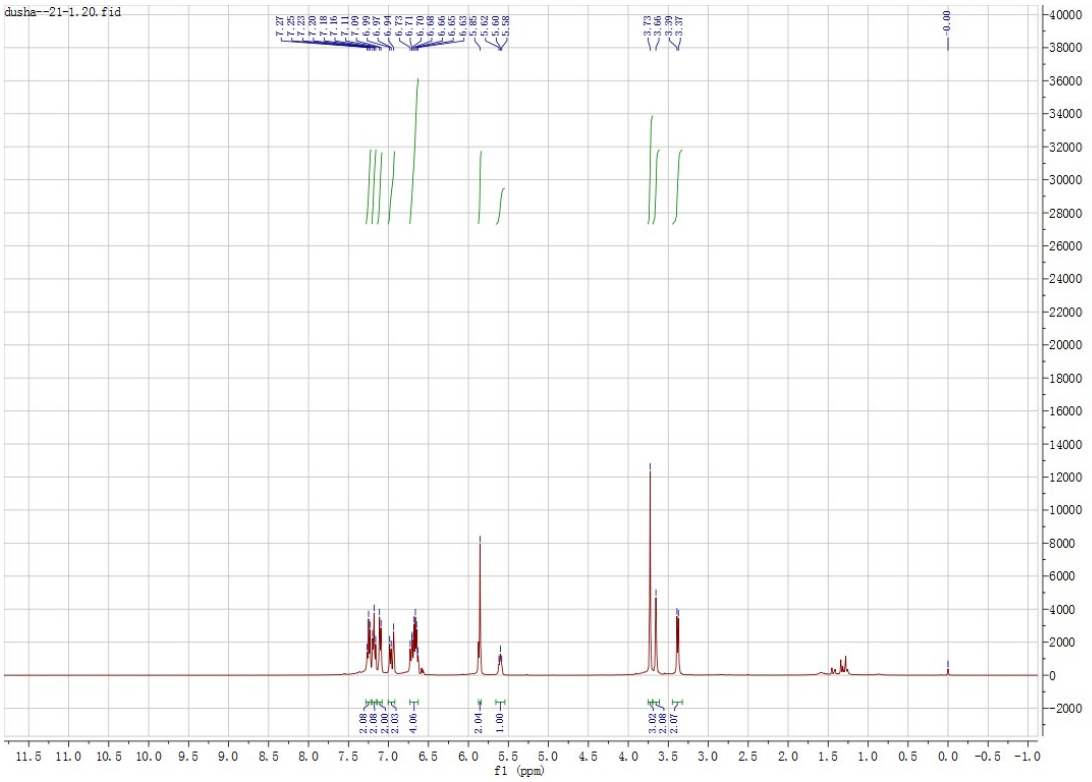
2ka, 74%

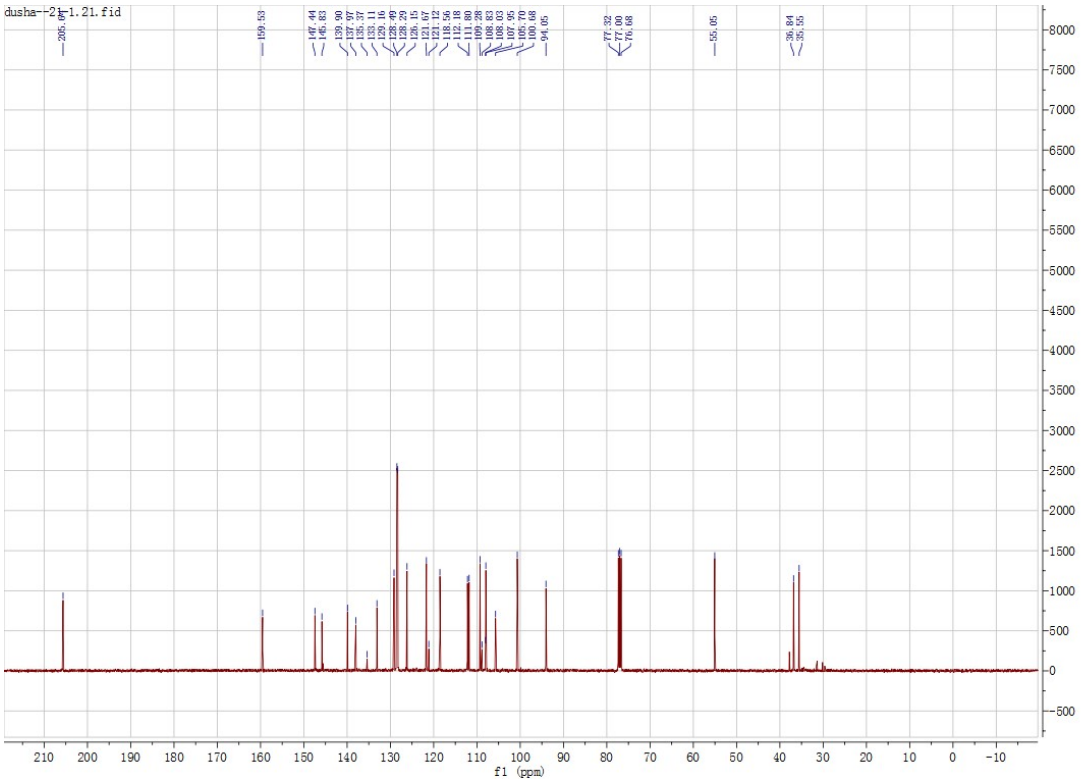


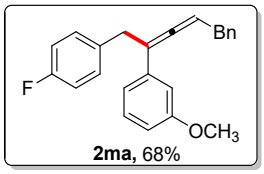




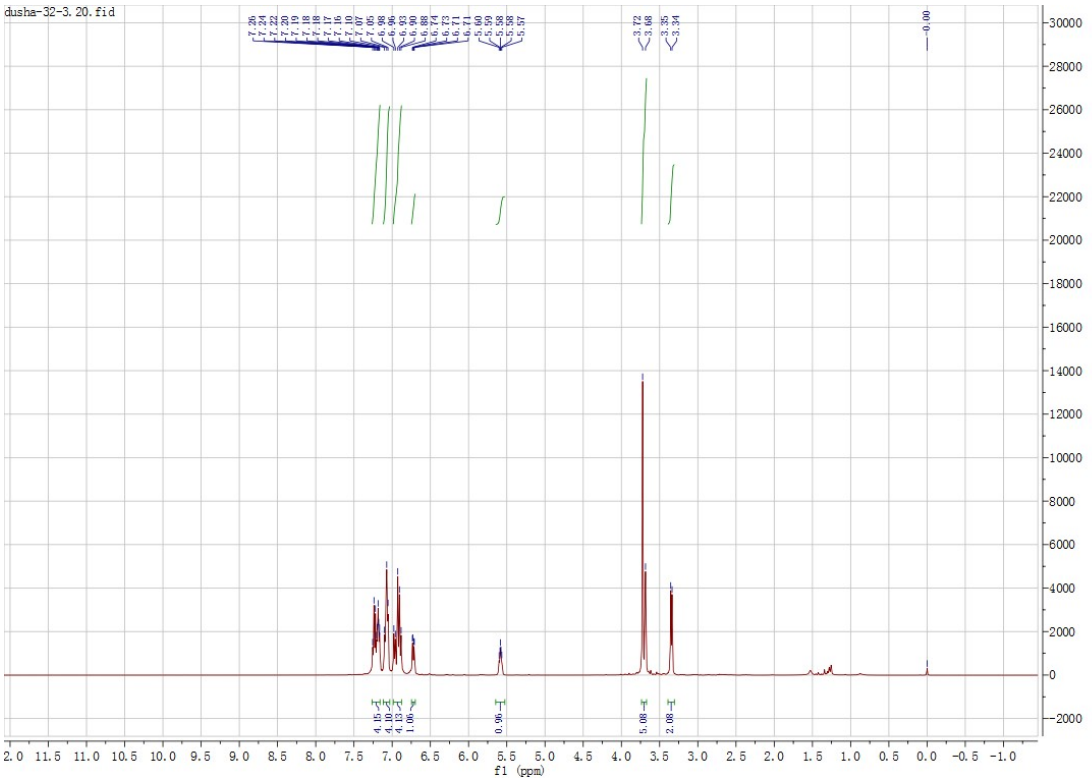
2la, 63%

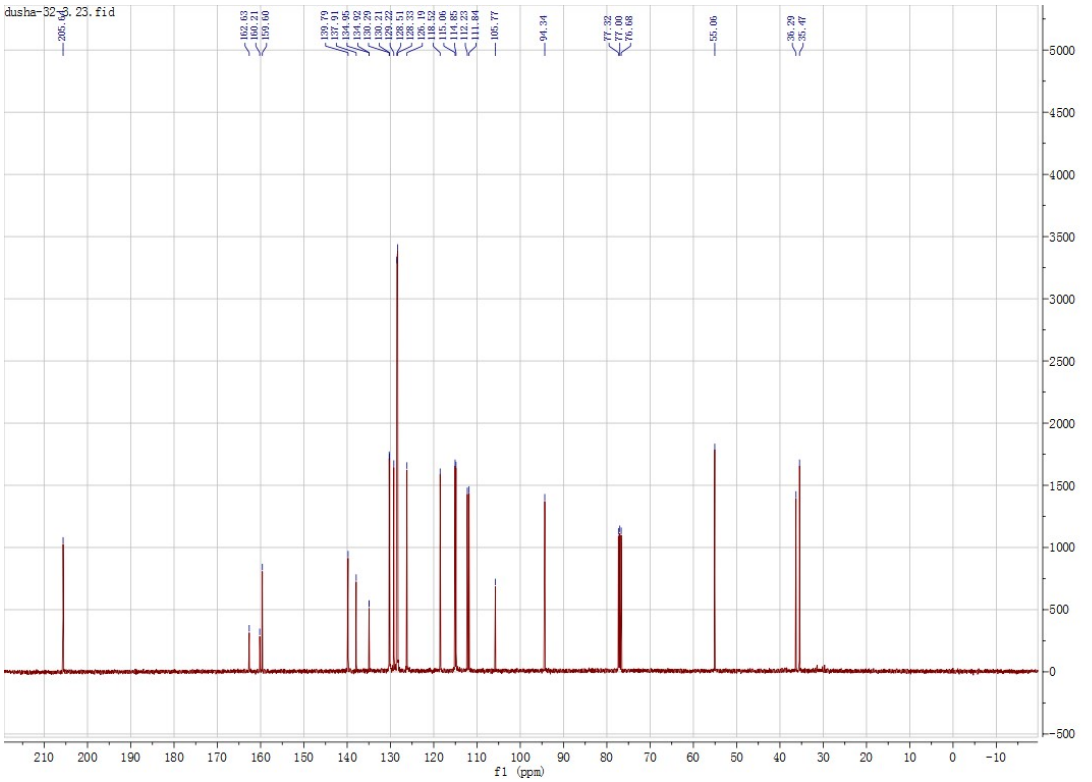


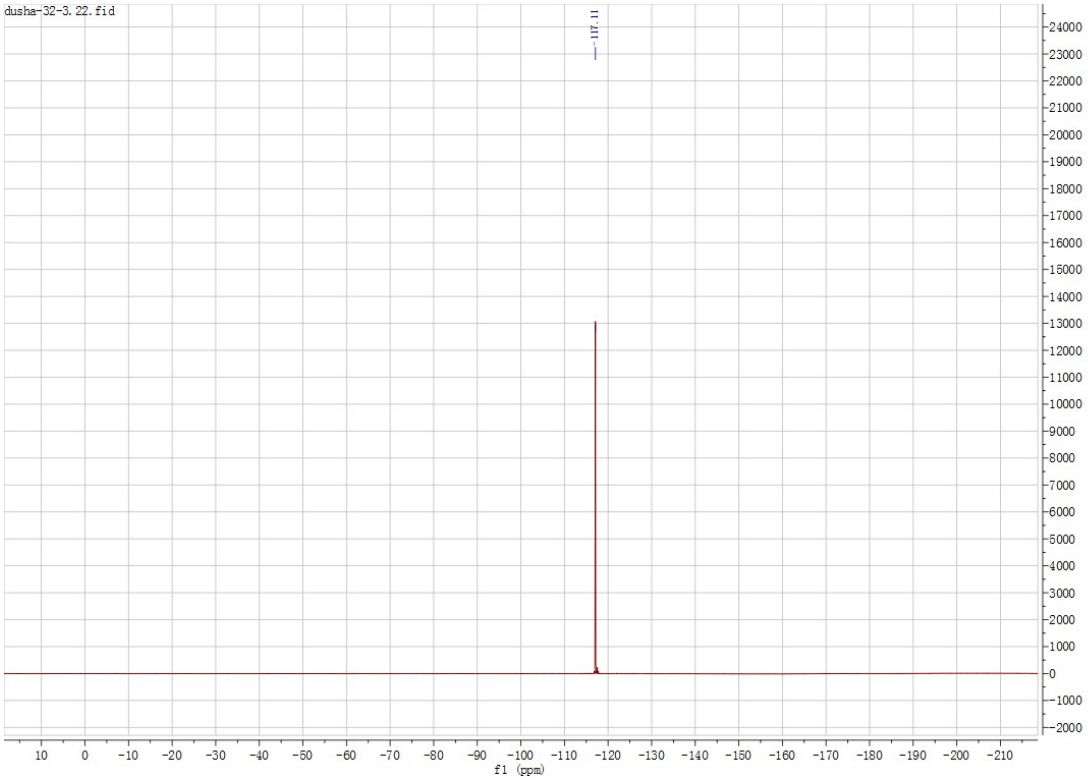




2ma, 68%



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23000
22000
21000
20000
19000
18000
17000
16000
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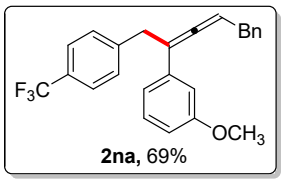
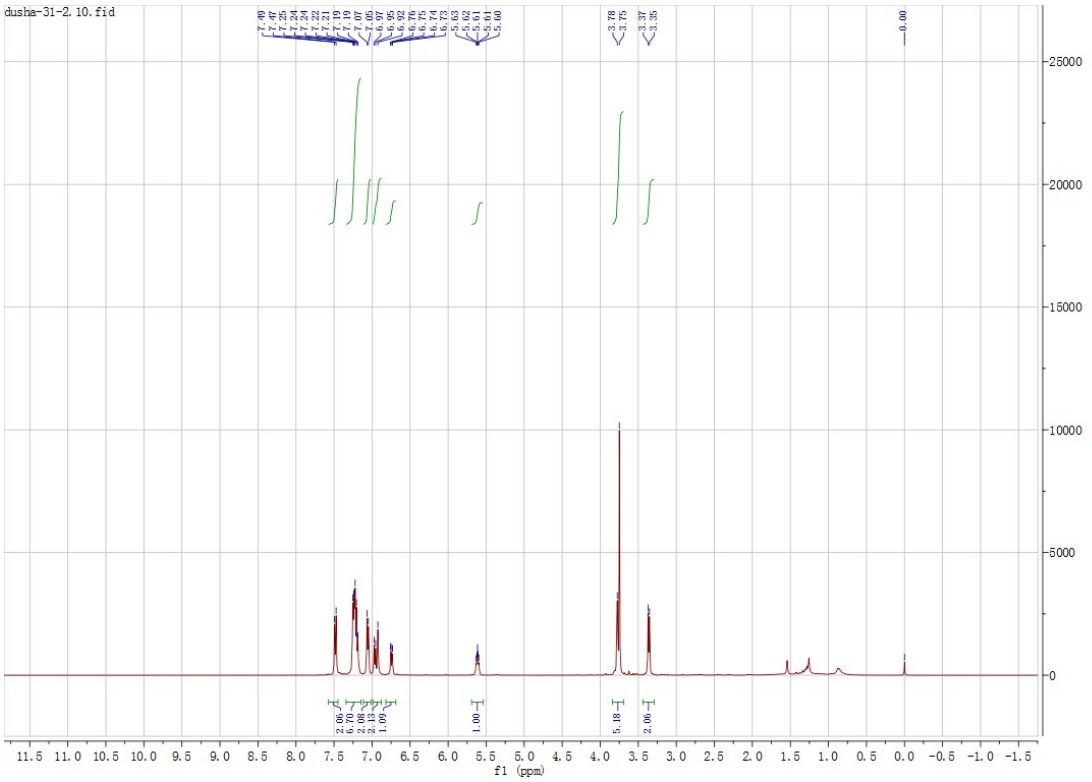
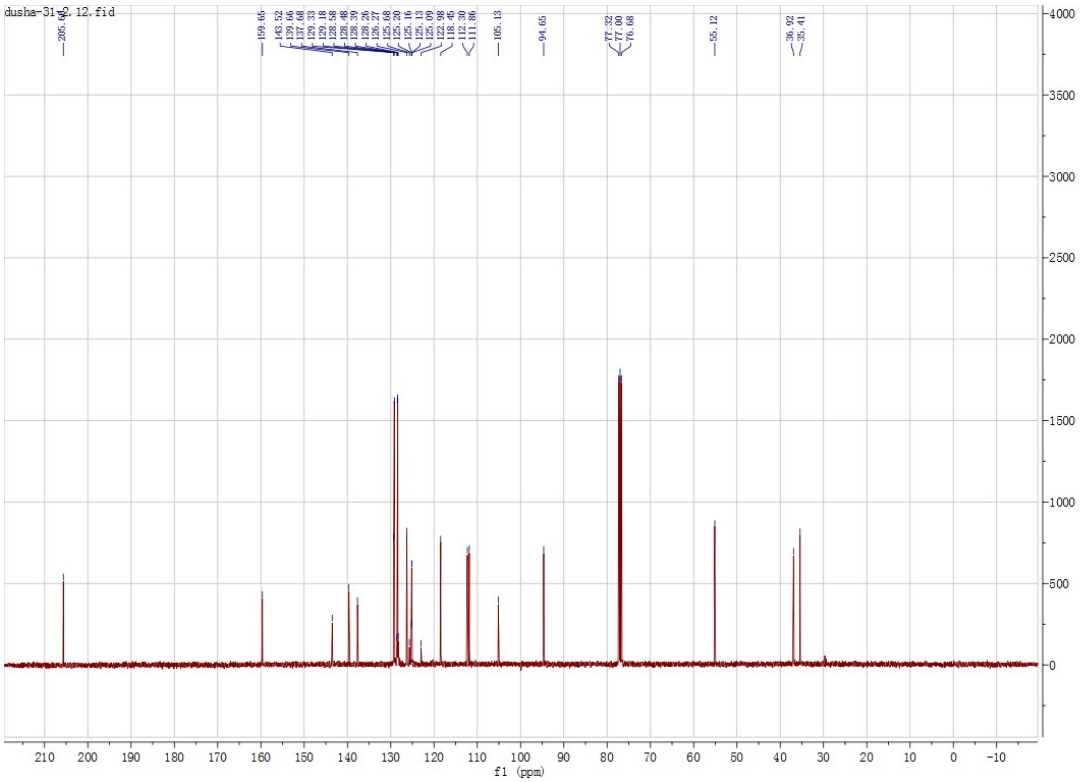
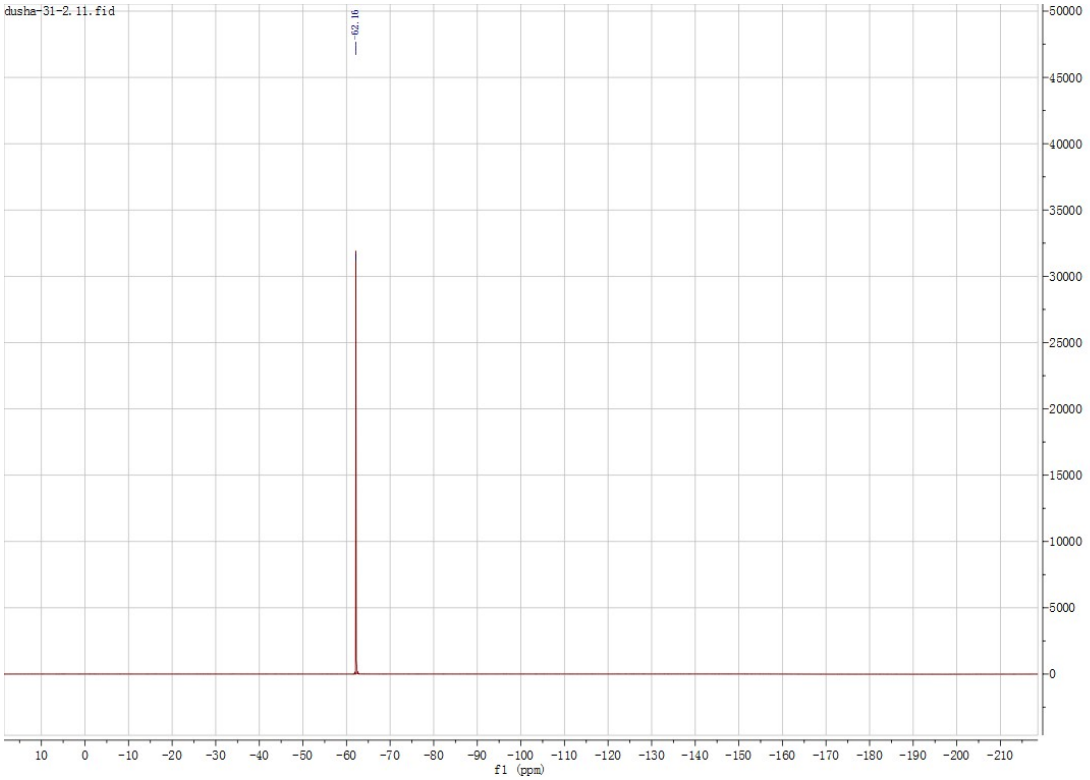
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
-2000
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)



2na, 69%



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-62.16
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0
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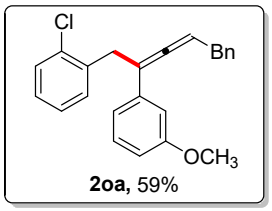
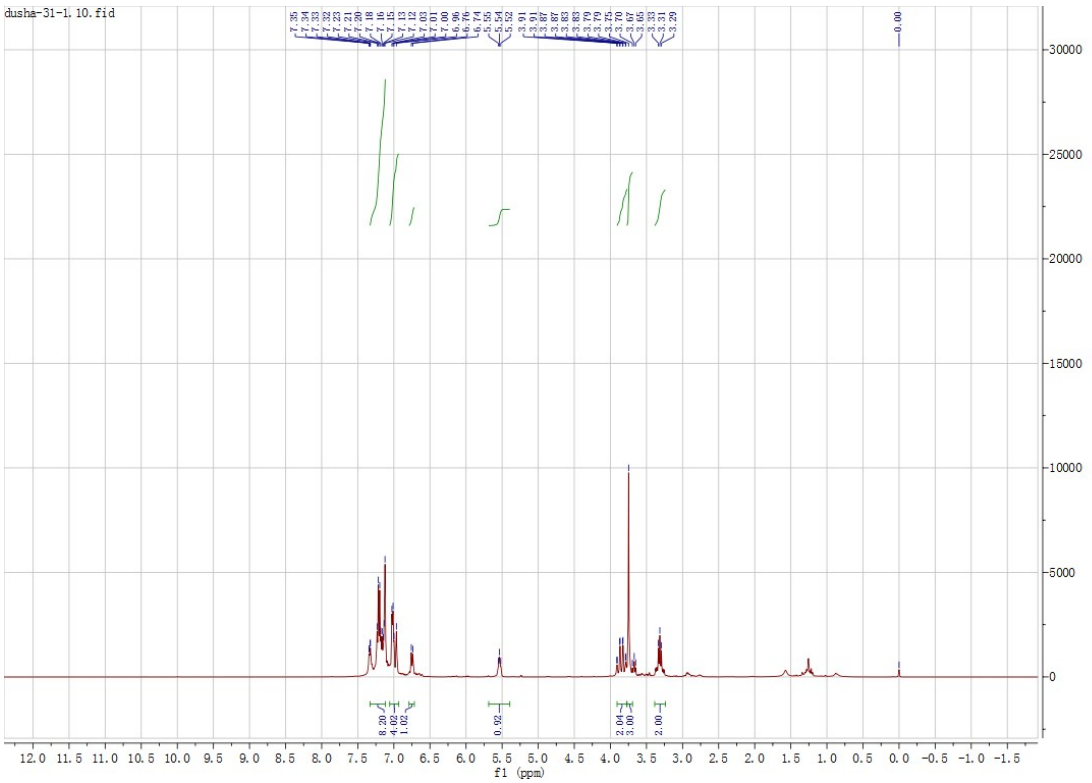
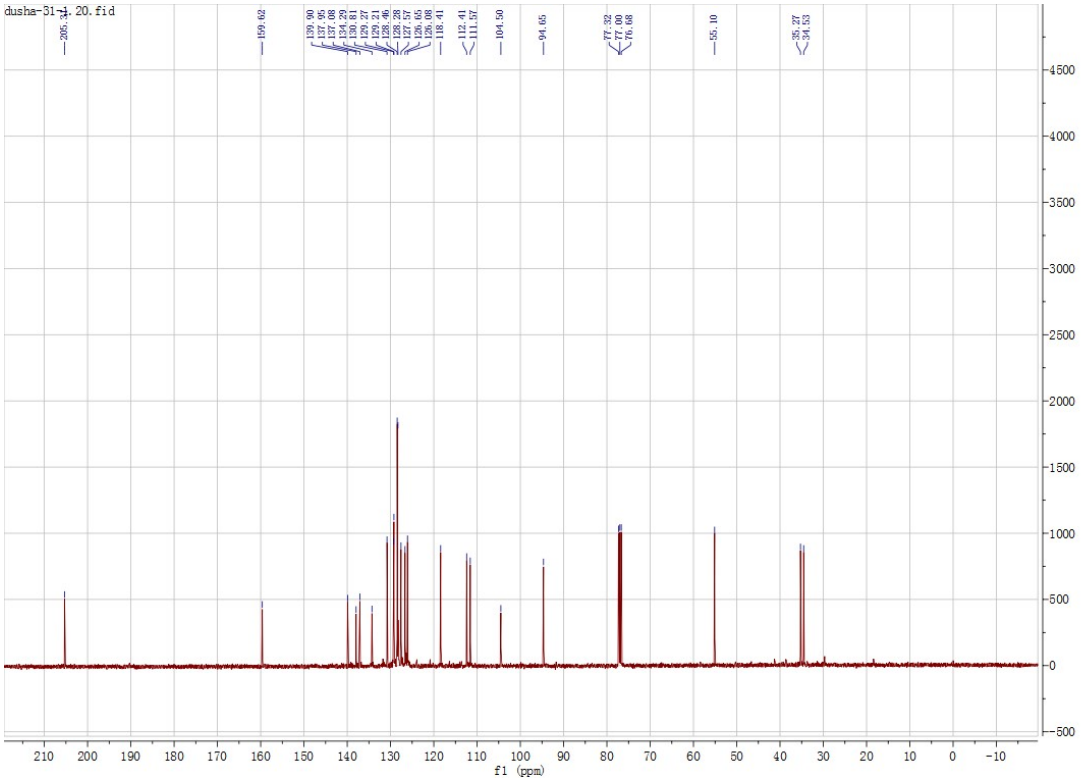
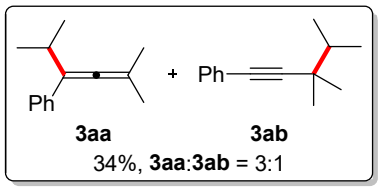
f1 (ppm)

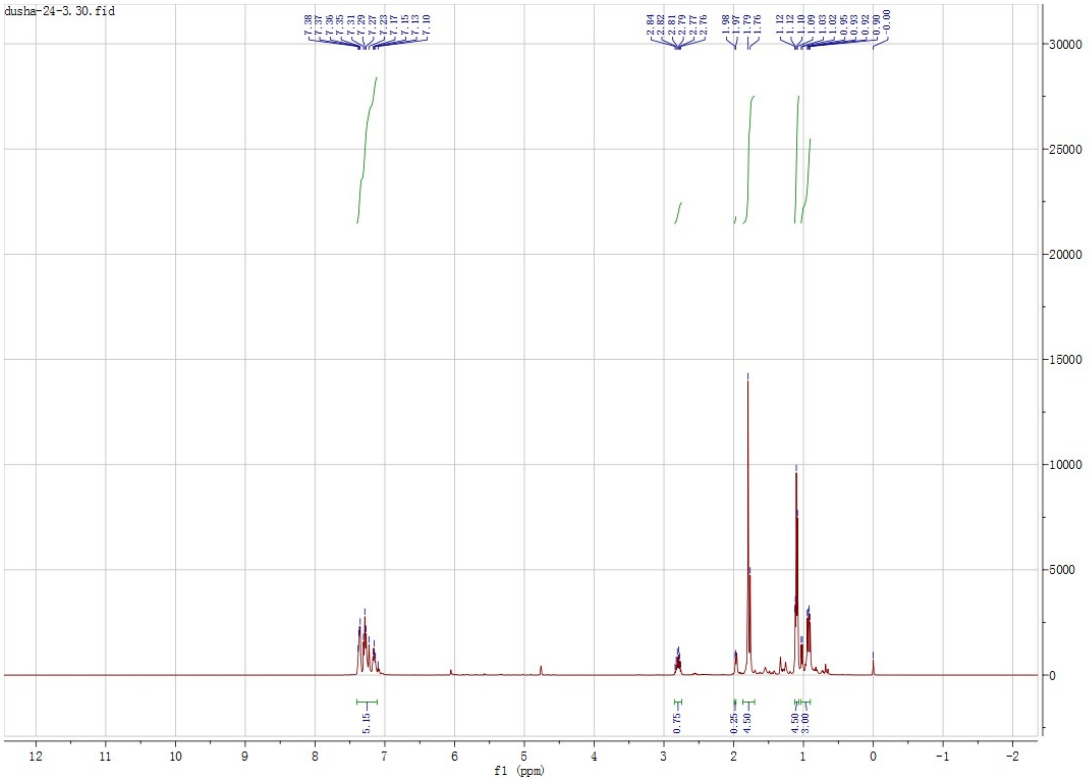


2oa, 59%






Ph
+
Ph
3aa
3ab
34%, 3aa:3ab = 3:1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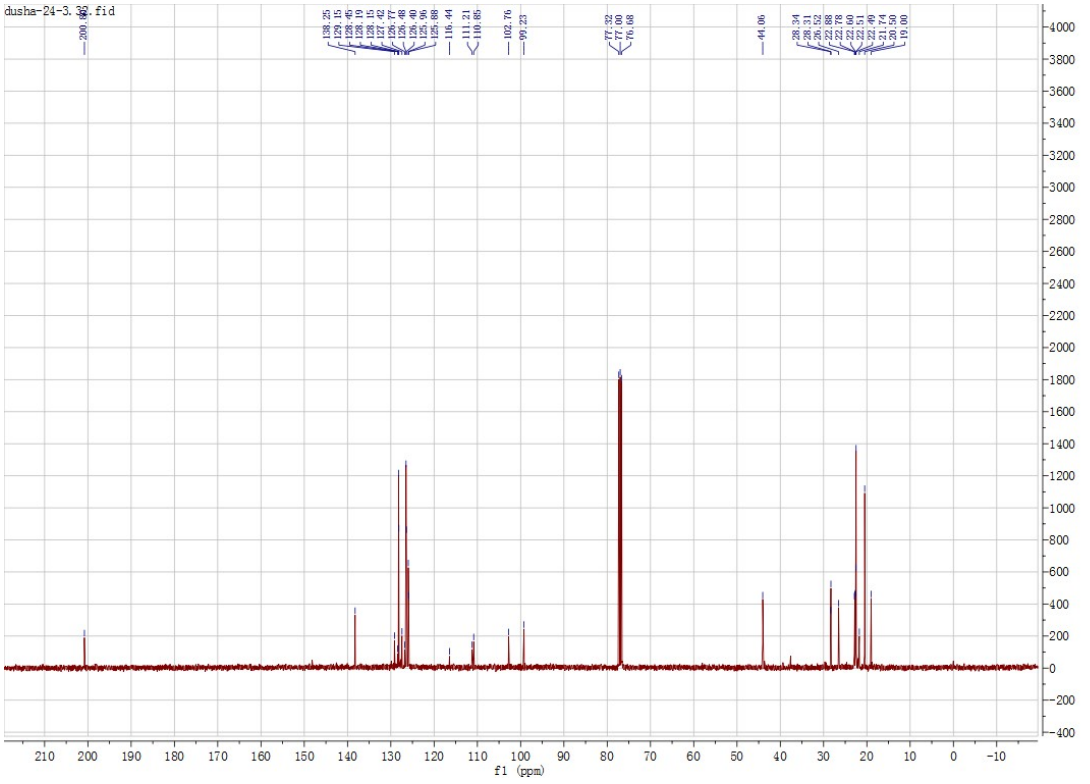
f1 (ppm)


dusha-24-3.32.fid
f1 (ppm)