Electronic Supplementary Material (ESI) for Green Chemistry.

Supplementary Information for

Photo-induced direct alkynylation of methane and other light alkanes by iron catalysis

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1. General Information

1.1 Materials

Unless otherwise noted, all materials were used as received from commercial sources without further purification. $FeCl_3 \cdot 6H_2O$ and other iron salts were purchased from Tianjin Damao Chemical Reagent Factory and stored in a dryer. CH_3CN were purchased from Kermel. Other chemicals were purchased from Energy, Alfa Aesar, Innochem. The 395 nm and 365 nm LEDs were purchased from Taiwan Epileds Technologies and assembled by Shenzhen Xinxingyuan Photoelectric Technology. Methane (99.9% purity), ethane (99.5% purity), propane (99.5% purity), butane (99.5% purity) and iso-butane (99.9% purity) were purchased from Dalian Junfeng Amflo Fluid Systems Components Co., Ltd.

1.2 Methods

Reactions were performed with rigorous exclusion of air. The reaction temperature was controlled using water baths. Reactions were monitored by thin-layer chromatography (TLC) on 2.5×5 cm HSGF254 plates. Chromatographic purification of products was accomplished by column chromatography using silica gel. Most yields were determined by isolated yields. Selectivities were determined by GC and GC-MS.

1.3 Instrumentation

^1H NMR and ^{13}C NMR spectra were recorded on a Bruker Avance II 400. ^1H NMR chemical shifts were determined relative to the signal of the residual protonated solvent $CDCl_3$ δ =7.26. ^{13}C NMR chemical shifts were determined relative to $CDCl_3$ at δ 77.0. Data for ^1H NMR are represented as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, m = multiplet, br = broad), coupling constant in Hertz (Hz), integration. ^{13}C NMR spectra were reported as chemical shifts in ppm. ^{13}C NMR δ 29.6 was attributed to grease; ^1H NMR δ 1.25 ppm, 0.80 ppm, and ^{13}C NMR δ 14.08, 22.64, 31.88 were attributed to high boiling component from n-hexane (H.E. Gottlieb, *et al.*, *J. Org. Chem.* **62**, 7512-7515 (1997)); ^1H NMR δ 1.56 ppm was attributed to water from the wet air in Dalian.

Gas chromatography was carried out on an Agilent 8860 GC systems using a HP-5 (5% phenyl–95% methyl polysiloxane) column and flame ionization detector (FID).

Gas chromatography-mass spectrometry (GC-MS) was carried out on an Agilent 7000B spectrometer.

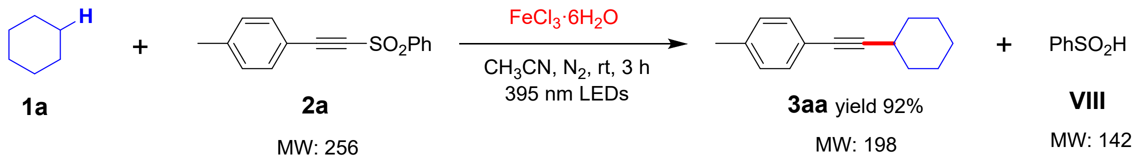
High resolution mass spectra were obtained on LCMS-IT/TOF (SHIMADZU, Japan) with electrospray ionization source and GC-TOF Mass Spectrometer (GCT, Micromass) with an electron impact ionization source.

1.4 comparison of the greenness

E-factor Calculation

$$E\,factor = \frac{mass\ of\ wastes}{mass\ of\ product}$$

The model reaction of **3aa** was chosen as an example to calculate E-factor:



$$E\,factor = \frac{mass\ of\ wastes}{mass\ of\ product}$$

$$= \frac{mass\ of\ VIII + mass\ of\ unreacted\ 2a + mass\ of\ catalyst}{mass\ of\ 3aa}$$

$$= \frac{142 \times 0.92 + 256 \times (1 - 0.92) + 270.5 \times 0.05}{198 \times 0.92} = 0.90$$

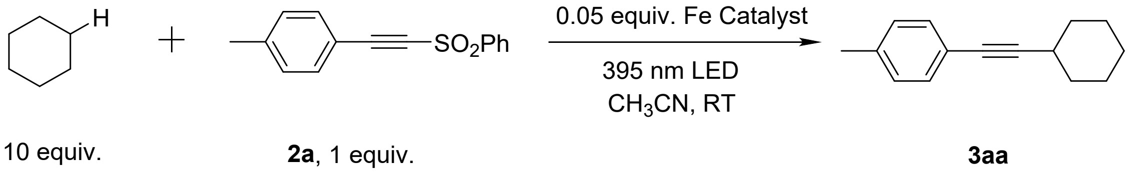
According to the formula mode, the E-factors and catalyst/oxidant costs of the reactions mentioned in Table 1 were calculated and listed in Table S1.

Table S1．Comparison of the greenness

ref	E-factor	catalyst/oxidant price (1 mol scale reaction, price from *Sigma-Aldrich*)	catalyst/oxidant total cost
Fucus 1996	1.20	AIBN (0.2 mol, 32.8 g, $ 32.8)	$ 32.8
Xu&Feng 2016	3.09	DTBP (1 mol, 146.2 g, $ 1243.2)	$ 1243.2
Lei 2016/2018	3.69	$Cu(OTf)_2$ (0.075 mol, 27.1 g, $ 893.3)+$Ni(acac)_2$ (0.075 mol, 19.3 g, $ 327.4)+ AgOAc (0.1 mol, 16.7 g, $ 535.3) and DTBP (3 mol, 438.7 g, $ 3729)	$ 5485
Tang 2021	3.90	4-Cyanopyridinium-1-olate (2 mol, 240.2 g, $ 3885.7)	$ 3885.7
Inoue 2013	2.32	Ph_2CO (1 mol, 182.2 g, $ 137)	$ 137
Guin 2017	1.37	4,4'-Cl_2Ph_2CO (0.2 mol, 50.2 g, $ 64.5)	$ 64.5
Nemoto 2020	1.24	Ph_2CO (0.2 mol, 36.4 g, $ 27.4)	$ 27.4
Hashmi 2020	1.40	4,4'-Cl_2Ph_2CO (0.15 mol, 37.7 g, $ 49.5)	$ 49.5
Capaldo 2021	1.24	TBADT (0.02 mol, 66.4 g, $ 49983.8)	$ 49983.8
This work	**0.90**	**$FeCl_3 \cdot 6H_2O$ (0.05 mol, 13.5 g, $ 4.9)**	**$ 4.9**

2. Optimization of Reaction Conditions and Control Experiments

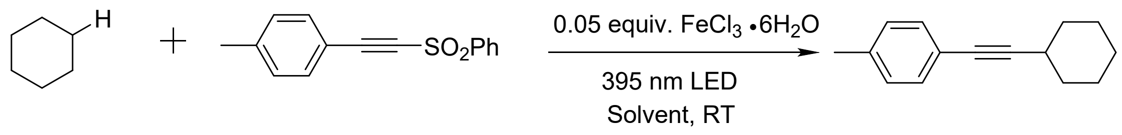
Table S2．Control experiments on catalyst



Entry	Iron catalyst	Yield%[b]
1	$FeCl_3 \cdot 6H_2O$	92%
2	anhydrous $FeCl_3$	91%
3	$Fe_2(SO_4)_3 \cdot xH_2O$	0
4	$Fe(NO_3)_3 \cdot 9H_2O$	0
5	$FeCl_2 \cdot 4H_2O$	85%
6	$FeSO_4 \cdot 7H_2O$	0
7	$Fe(NO_3)_3 \cdot 9H_2O$ + 15% TEAC	52%
8	$FeSO_4 \cdot 7H_2O$ + 15% TEAC	30%
9	TEAC	trace
10	$CuCl_2$	44%
11	$ZrCl_4$	72%
12	$FeBr_3$	0%

[a]Reaction conditions: N_2 atmosphere and irradiation with 30 W 395 nm LED, cyclohexane (**1a**) (2 mmol, 10 equiv.), (4-Methylphenyl)ethynyl phenyl sulfone (**2a**) (0.2 mmol, 1 equiv.), catalyst (10 μmol, 0.05 equiv.), additive (TEAC, 30 μmol, 0.15 equiv. if needed) CH_3CN (2 mL), temperature (rt, ~25°C), time (3 h) in a 10-mL quartz tube. [b]Isolated yield.

Table S3. Control experiments on solvents

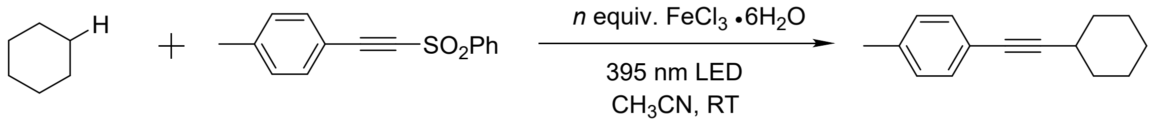


10 equiv. **2a**, 1 equiv. **3aa**

Entry	Solvent	Yield%[b]
1	CH_3CN	92%
2	DMSO	32%
3	CH_2Cl_2	25%
4	DMF	34%
5	THF	51%

[a]Reaction conditions: N_2 atmosphere and irradiation with 30 W 395 nm LED, cyclohexane (**1a**) (2 mmol, 10 equiv.), (4-Methylphenyl)ethynyl phenyl sulfone (**2a**) (0.2 mmol, 1 equiv.), $FeCl_3 \cdot 6H_2O$ (10 μmol, 0.05 equiv.), solvent (2 mL), temperature (rt, ~25°C), time (3 h) in a 10-mL quartz tube. [b]Isolated yield.

Table S4. Control experiments on catalyst loading scale

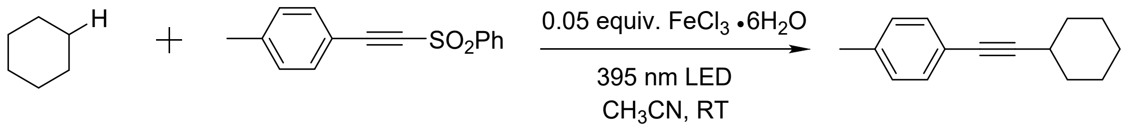


10 equiv. **2a**, 1 equiv. **3aa**

Entry	$FeCl_3 \cdot 6H_2O$ [equiv.]	Yield%[b]
1	0.01	45%
2	0.02	67%
3	0.03	78%
4	0.05	92%
5	0.1	54%

[a]Reaction conditions: N_2 atmosphere and irradiation with 30 W 395 nm LED, cyclohexane (**1a**) (2 mmol, 10 equiv.), (4-Methylphenyl)ethynyl phenyl sulfone (**2a**) (0.2 mmol, 1 equiv.), $FeCl_3 \cdot 6H_2O$ (200*n μmol, n equiv.), CH_3CN (2 mL), temperature (rt, ~25°C), time (3 h) in a 10-mL quartz tube. [b]Isolated yield.

Table S5. Control experiments on reation conditions



10 equiv. **2a**, 1 equiv. **3aa**

Entry	Variation from the standard conditions	Yield%[b]
1	none	92%
2	no $FeCl_3 \cdot 6H_2O$	0%
3	no light	0%
4	365 nm LED	75% (2 h)
5	405 nm LED	80% (24 h)
6	455 nm LED	41% (24 h)
7	White LED	28% (24 h)

[a] Reaction conditions: N_2 atmosphere and irradiation with 30 W LED, cyclohexane (**1a**) (2 mmol, 10 equiv.), (4-Methylphenyl)ethynyl phenyl sulfone (**2a**) (0.2 mmol, 1 equiv.), $FeCl_3 \cdot 6H_2O$ (10 µmol, 0.05 equiv.), CH_3CN (2 mL), temperature (rt, ~25°C), time (3-24 h) in a 10-mL quartz tube. [b] Isolated yield.

3. Experimental Procedure

3.1 General Procedure for C(sp^3)-H Alkynylation of Liquid Alkanes

A 10 mL glass reaction tube was added a magnetic stir bar, alkanes substrates (10 equiv.), iron catalyst (0.05 equiv.), radical trap (1 equiv.) and followed by CH_3CN. The reaction tube was capped with a greased two-way septum cock. The reaction mixture was degassed by nitrogen for five times, then set to stir (800 rpm) and irradiated with a 30 W 395 nm LED (2 cm away, with circulating water to keep the reaction at room temperature). After the reaction ended, the reaction solution was diluted with diethyl ether, washed with deionized water and the organic layer was concentrated in vacuo. The crude reaction mixture needed to be purified by silica gel column chromatography using the appropriate solvent system to give the desired product.

3.2 General Procedure for C(sp^3)-H Alkynylation of Ethane, Propane and Butane

A 10 mL quartz reaction tube was added a magnetic stir bar, radical trap (1 equiv.), iron catalyst (0.1 equiv.), and followed by CH_3CN. The reaction tube was sealed with a greased three-way septum cock. The reaction mixture was degassed by gaseous alkane for five times and kept at ambient pressure all the time. Then the quartz tube was set to stir (800 rpm) and irradiated with a 30 W 365 nm LED (2 cm away, with circulating water to keep the reaction at room temperature). After the reaction ended, the reaction solution was diluted with diethyl ether, washed with deionized water and the organic layer was concentrated in vacuo. The crude reaction mixture needed to be purified by silica gel column chromatography using the appropriate solvent system to give the desired product.

3.3 General Procedure for Alkynylation of methane.

A 25 ml high-pressure photoreactor with a centered sapphire window was added a magnetic stir bar, radical trap (1 equiv.), iron catalyst (0.10 equiv.), and followed by CH_3CN. The head of the high-pressure photoreactor was installed and the headspace of the reactor was flushed 5 times with methane (5 MPa). The reactor was then pressurized to 5 MPa of methane and irradiated with 70 W 365 nm LED. After the reaction ended, the reaction solution was diluted with diethyl ether, washed with deionized water and the organic layer was concentrated in vacuo. The crude reaction mixture needed to be purified by silica gel column chromatography using the appropriate solvent system to give the desired product.

3.4 Procedure for Gram Scale Synthesis of 3aa in batch reaction

A 100 ml glass reaction tube was added a magnetic stir bar, (4-Methylphenyl)ethynyl phenyl sulfone (**2a**, 1.0 g, 3.9 mmol), cyclohexane (**1a**, 4.2 ml, 39 mmol), $FeCl_3 \cdot 6H_2O$ (55 mg, 0.195 mmol) and followed by 39 mL CH_3CN. The reaction tube was capped with a greased two-way septum cock. The reaction mixture was bubbled by nitrogen for 15 min, then set to stir (800 rpm) and irradiated with three 30 W 395 nm LEDs (2 cm away, with water bath to keep the reaction at room temperature). After 24 h, the reaction solution was diluted with diethyl ether, washed with deionized water and the organic layer was concentrated in vacuo. The crude product was purified by column chromatography using petroleum ether as the eluent system to give the product **3aa** as a colorless oil (701 mg, 90.8%).

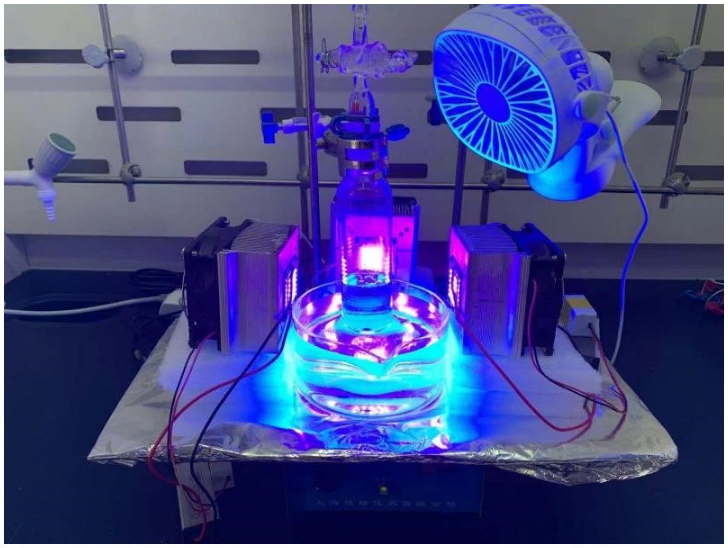


Figure S1. The detailed picture of gram scale synthesis of **3aa** under irradiation of 395 nm LEDs

3.5 Procedure for Gram Scale Synthesis of 3aa in flow

The reaction was performed with a well-designed continuous-flow photocatalytic micro-reactor (see Figure S2). A degassed solution of (4-Methylphenyl)ethynyl phenyl sulfone (**2a**, 1.0 g, 3.9 mmol), cyclohexane (**1a**, 4.2 ml, 39 mmol), $FeCl_3 \cdot 6H_2O$ (55 mg, 0.195 mmol) and CH_3CN (30 mL) was transferred into a 50 mL injector, and then equipped on a syringe pump. The micro-reactor with 3.0 mL internal volume in total was filled with degassed CH_3CN in advance. The reaction was carried out with a flow rate of 0.033 mL/min under irradiation of two 395 nm LEDs. After 19 h, the collected reaction solution was diluted with diethyl ether, washed with deionized water and the organic layer was concentrated in vacuo. The crude product was purified by column chromatography using petroleum ether as the eluent system to give the product **3aa** as a colorless oil (710 mg, 91.7%).

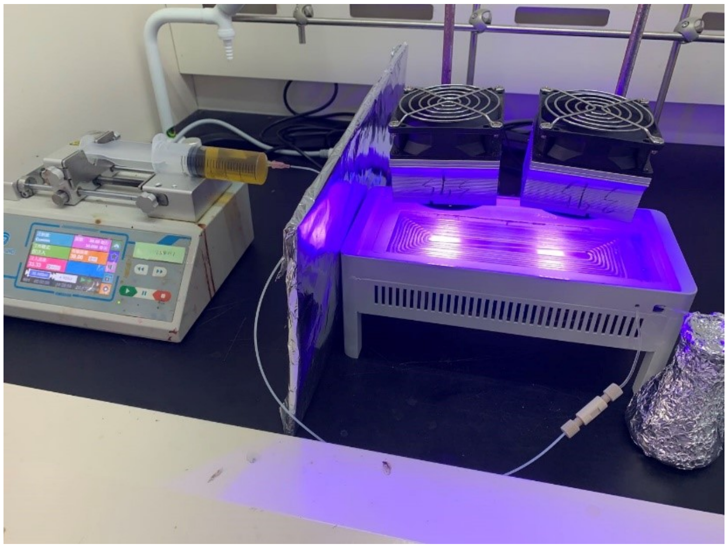
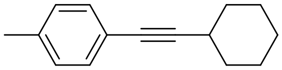


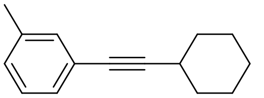
Figure S2. The detailed picture of continuous-flow synthesis of **3aa** under irradiation of 395 nm LEDs

3.6 Characterization of Products



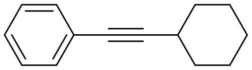
3aa

1-(Cyclohexylethynyl)-4-methylbenzene (3aa): According to the general procedure, (4-Methylphenyl)ethynyl phenyl sulfone (51.2 mg, 0.2 mmol), cyclohexane (216 μL, 2 mmol), $FeCl_3\cdot6H_2O$ (2.7 mg, 0.01 mmol) and CH_3CN (2 mL) were used. After 3 h, the crude product was purified by column chromatography using petroleum ether as the eluent system to give the product as a colorless oil (36.5 mg, 92%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.29 (d, J = 8.0 Hz, 2H), 7.08 (d, J = 7.9 Hz, 2H), 2.62-2.58 (m, 1H), 2.30 (s, 3H), 1.94-1.83 (m, 2H), 1.81-1.70 (m, 2H), 1.60-1.47 (m, 3H), 1.40-1.28 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.34, 131.45, 128.91, 121.03, 93.67, 80.50, 32.80, 29.70, 25.97, 24.96, 21.41. HRMS (EI) calculated for $C_{15}H_{18}$ $[M]^+$: 198.1403; found: 198.1401.



3ab

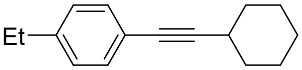
1-(Cyclohexylethynyl)-3-methylbenzene (3ab): According to the general procedure, (3-Methylphenyl)ethynyl phenyl sulfone (51.2 mg, 0.2 mmol), cyclohexane (216 μL, 2 mmol), $FeCl_3\cdot6H_2O$ (2.7 mg, 0.01 mmol) and CH_3CN (2 mL) were used. After 3 h, the crude product was purified by column chromatography using petroleum ether as the eluent system to give the product as a colorless oil (35.6 mg, 90%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.24-7.17 (m, 2H), 7.15 (t, J = 7.5 Hz, 1H), 7.08 (d, J = 7.4 Hz, 1H), 2.63-2.57 (m, 1H), 2.33 (s, 3H), 1.96-1.83 (m, 2H), 1.80-1.70 (m, 2H), 1.59-1.46 (m, 3H), 1.41-1.28 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.78, 132.23, 128.62, 128.30, 128.07, 123.93, 94.09, 80.64, 32.77, 29.68, 25.97, 24.93, 21.22. HRMS (EI) calculated for $C_{15}H_{18}$ $[M]^+$: 198.1403; found: 198.1401.



3ac

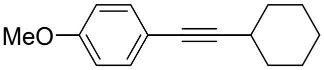
(Cyclohexylethynyl)benzene (3ac): According to the general procedure, (phenyl)ethynyl phenyl sulfone (48.4 mg, 0.2 mmol), cyclohexane (216 μL, 2 mmol), $FeCl_3\cdot6H_2O$ (2.7 mg, 0.01 mmol) and CH_3CN (2 mL) were used. After 3 h, the crude product was purified by column chromatography using petroleum ether as the eluent system to give the product as a colorless oil (33.5 mg, 91%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.43 (m, 2H), 7.32-7.26 (m, 3H), 2.62-2.56 (m, 1H), 1.97-1.86 (m, 2H), 1.85-1.74 (m, 2H), 1.66-1.49 (m, 3H), 1.47-1.32 (m, 3H). ^{13}C NMR (101

MHz, $CDCl_3$) δ 131.61, 128.18, 127.44, 124.19, 94.48, 80.58, 32.77, 29.71, 25.99, 24.96. HRMS (EI) calculated for $C_{14}H_{16}$ $[M]^+$: 182.1247; found: 182.1245.



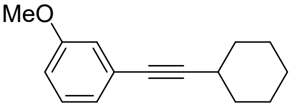
3ad

1-(Cyclohexylethynyl)-4-ethylbenzene (3ad): According to the general procedure, (4-Ethylphenyl)ethynyl phenyl sulfone (54 mg, 0.2 mmol), cyclohexane (216 µL, 2 mmol), $FeCl_3 \cdot 6H_2O$ (2.7 mg, 0.01 mmol) and CH_3CN (2 mL) were used. After 3 h, the crude product was purified by column chromatography using petroleum ether as the eluent system to give the product as a colorless oil (39.4 mg, 93%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.33 (d, J = 8.1 Hz, 2H), 7.12 (d, J = 8.1 Hz, 2H), 2.65 (q, J = 7.6 Hz, 2H), 2.63-2.57 (m, 1H), 1.95-1.82 (m, 2H), 1.85-1.71 (m, 2H), 1.60-1.44 (m, 3H), 1.36-1.32 (m, 3H), 1.22 (t, J = 7.6 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.71, 131.54, 127.72, 121.30, 93.67, 80.55, 32.81, 29.70, 28.77, 25.98, 24.95, 15.46. HRMS (EI) calculated for $C_{16}H_{20}$ $[M]^+$: 212.1560; found: 212.1562.



3ae

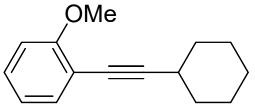
1-(Cyclohexylethynyl)-4-methoxybenzene (3ae): According to the general procedure, (4-Methoxyphenyl)ethynyl phenyl sulfone (54.4 mg, 0.2 mmol), cyclohexane (216 µL, 2 mmol), $FeCl_3 \cdot 6H_2O$ (2.7 mg, 0.01 mmol) and CH_3CN (2 mL) were used. After 3 h, the crude product was purified by column chromatography using petroleum ether as the eluent system to give the product as a colorless oil (39 mg, 91%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.36 (d, J = 8.1 Hz, 2H), 6.83 (d, J = 8.1 Hz, 2H), 3.82 (s, 3 H), 2.68-2.53 (m, 1H), 1.95-1.82 (m, 2H), 1.85-1.71 (m, 2H), 1.60-1.44 (m, 3H), 1.40-1.27 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.94, 132.90, 116.31, 113.77, 92.87, 80.16, 55.26, 32.86, 29.71, 25.97, 24.98. HRMS (EI) calculated for $C_{15}H_{18}O$ $[M]^+$: 214.1352; found: 214.1354.



3af

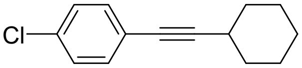
1-(Cyclohexylethynyl)-3-methoxybenzene (3af): According to the general procedure, (2-Methoxyphenyl)ethynyl phenyl sulfone (54.4 mg, 0.2 mmol), cyclohexane (216 µL, 2 mmol), $FeCl_3 \cdot 6H_2O$ (2.7 mg, 0.01 mmol) and CH_3CN (2 mL) were used. After 3 h, the crude product was purified by column chromatography using petroleum ether as the eluent system to give the product as a colorless oil (38 mg, 89%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.18 (t, J = 7.9 Hz, 1H), 7.00 (d, J = 7.6 Hz, 1H), 6.93 (s, 1H), 6.82 (d, J = 8.3 Hz, 1H), 3.79 (s, 3H), 2.62-2.58 (m, 1H), 1.96-1.81

(m, 2H), 1.81-1.69 (m, 2H), 1.61-1.46 (m, 3H), 1.41-1.28 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.26, 129.20, 125.15, 124.17, 116.37, 114.11, 94.37, 80.44, 55.25, 32.71, 29.68, 25.94, 24.94. HRMS (EI) calculated for $C_{15}H_{18}O$ $[M]^+$: 214.1352; found: 214.1352.



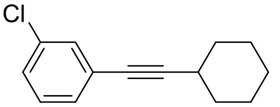
3ag

1-(Cyclohexylethynyl)-2-methoxybenzene (3ag): According to the general procedure, (2-Methoxyphenyl)ethynyl phenyl sulfone (54.4 mg, 0.2 mmol), cyclohexane (216 μL, 2 mmol), $FeCl_3·6H_2O$ (2.7 mg, 0.01 mmol) and CH_3CN (2 mL) were used. After 3 h, the crude product was purified by column chromatography using petroleum ether as the eluent system to give the product as a colorless oil (38.5 mg, 90%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (dd, J = 7.5, 1.6 Hz, 1H), 7.25-7.20 (m, 1H), 6.91-6.81 (m, 2H), 3.87 (s, 3H), 2.66-2.56 (m, 1H), 1.98-1.84 (m, 2H), 1.82-1.72 (m, 2H), 1.63-1.46 (m, 3H), 1.43-1.31 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.79, 133.70, 128.80, 120.36, 113.23, 110.61, 98.74, 76.57, 55.84, 32.78, 29.98, 26.00, 24.93. HRMS (EI) calculated for $C_{15}H_{18}O$ $[M]^+$: 214.1352; found: 214.1349.



3ah

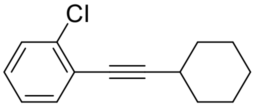
1-Chloro-4-(cyclohexylethynyl)benzene (3ah): According to the general procedure, (4-Chlorophenyl)ethynyl phenyl sulfone (55.2 mg, 0.2 mmol), cyclohexane (216 μL, 2 mmol), $FeCl_3·6H_2O$ (2.7 mg, 0.01 mmol) and CH_3CN (2 mL) were used. After 3 h, the crude product was purified by column chromatography using petroleum ether as the eluent system to give the product as a colorless oil (39.4 mg, 90%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (d, J = 8.6 Hz, 2H), 7.24 (d, J = 8.6 Hz, 2H), 2.68-2.50 (m, 1H), 1.91-1.82 (m, 2H), 1.81-1.70 (m, 2H), 1.60-1.46 (m, 3H), 1.41-1.30 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 133.31, 132.82, 128.45, 122.66, 95.53, 79.48, 32.63, 29.68, 25.91, 24.92. HRMS (EI) calculated for $C_{14}H_{15}Cl$ $[M]^+$: 218.0857; found: 218.0853.



3ai

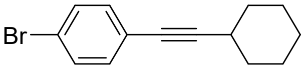
1-Chloro-3-(cyclohexylethynyl)benzene (3ai): According to the general procedure, (3-Chlorophenyl)ethynyl phenyl sulfone (55.2 mg, 0.2 mmol), cyclohexane (216 μL, 2 mmol), $FeCl_3·6H_2O$ (2.7 mg, 0.01 mmol) and CH_3CN (2 mL) were used. After 3 h, the crude product was purified by column chromatography using petroleum ether as the eluent system to give the product as a colorless oil (39.7 mg, 91%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (t, J = 1.6 Hz, 1H), 7.32-

7.17 (m, 3H), 2.65-2.57 (m, 1H), 1.92-1.85 (m, 2H), 1.81-1.68 (m, 2H), 1.55-1.51 (m, 3H), 1.43-1.29 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 133.94, 131.52, 129.70, 129.36, 127.69, 125.89, 95.88, 79.31, 32.57, 29.63, 25.90, 24.88. HRMS (EI) calculated for $C_{14}H_{15}Cl$ $[M]^+$: 218.0857; found: 218.0852.



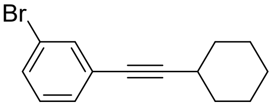
3aj

1-Chloro-2-(cyclohexylethynyl)benzene (3aj): According to the general procedure, (2-Chlorophenyl)ethynyl phenyl sulfone (55.2 mg, 0.2 mmol), cyclohexane (216 µL, 2 mmol), $FeCl_3 \cdot 6H_2O$ (2.7 mg, 0.01 mmol) and CH_3CN (2 mL) were used. After 3 h, the crude product was purified by column chromatography using petroleum ether as the eluent system to give the product as a colorless oil (39.4 mg, 90%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45-7.42 (m, 1H), 7.38-7.36 (m, 1H), 7.19-7.17 (m, 2H), 2.70-2.66 (m, 1H), 1.95-1.85 (m, 2H), 1.84-1.74 (m, 2H), 1.66-1.48 (m, 3H), 1.46-1.31 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 135.84, 133.21, 129.10, 128.42, 126.28, 123.94, 100.14, 77.61, 32.49, 29.76, 25.99, 24.70. HRMS (EI) calculated for $C_{14}H_{15}Cl$ $[M]^+$: 218.0857; found: 218.0857.



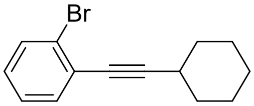
3ak

Bromo-4-(cyclohexylethynyl)benzene (3ak): According to the general procedure, (4-Bromophenyl)ethynyl phenyl sulfone (64.2 mg, 0.2 mmol), cyclohexane (216 µL, 2 mmol), $FeCl_3 \cdot 6H_2O$ (2.7 mg, 0.01 mmol) and CH_3CN (2 mL) were used. After 3 h, the crude product was purified by column chromatography using petroleum ether as the eluent system to give the product as a colorless oil (46.8 mg, 89%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, J = 8.5 Hz, 2H), 7.25 (d, J = 8.6 Hz, 2H), 2.58-2.54 (m, 1H), 1.92-1.81 (m, 2H), 1.80-1.68 (m, 2H), 1.59-1.47 (m, 3H), 1.40-1.29 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 133.07, 131.37, 123.13, 121.47, 95.75, 79.55, 32.60, 29.70, 25.90, 24.92. HRMS (EI) calculated for $C_{14}H_{15}Br$ $[M]^+$: 262.0352; found: 262.0348.



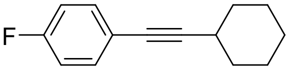
3al

Bromo-3-(cyclohexylethynyl)benzene (3al): According to the general procedure, (3-Bromophenyl)ethynyl phenyl sulfone (64.2 mg, 0.2 mmol), cyclohexane (216 µL, 2 mmol), $FeCl_3 \cdot 6H_2O$ (2.7 mg, 0.01 mmol) and CH_3CN (2 mL) were used. After 3 h, the crude product was purified by column chromatography using petroleum ether as the eluent system to give the product as a colorless oil (47.3 mg, 90%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (t, J = 1.6 Hz, 1H), 7.39 (dq, J = 8.0, 1.1 Hz, 1H), 7.32 (d, J = 6.7 Hz, 1H), 7.14 (t, J = 7.9 Hz, 1H), 2.59-2.54 (m, 1H), 1.87-1.84 (m, 2H), 1.80-1.69 (m, 2H), 1.62-1.45 (m, 3H), 1.43-1.29 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 134.40, 130.57, 130.13, 129.59, 126.20, 122.00, 96.02, 79.21, 32.58, 29.63, 25.91, 24.89. HRMS (EI) calculated for $C_{14}H_{15}Br$ $[M]^+$: 262.0352; found: 262.0348.



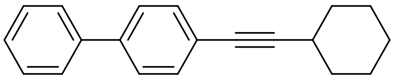
3am

Bromo-2-(cyclohexylethynyl)benzene (3am): According to the general procedure, (2-Bromophenyl)ethynyl phenyl sulfone (64.2 mg, 0.2 mmol), cyclohexane (216 μL, 2 mmol), $FeCl_3\cdot6H_2O$ (2.7 mg, 0.01 mmol) and CH_3CN (2 mL) were used. After 3 h, the crude product was purified by column chromatography using petroleum ether as the eluent system to give the product as a colorless oil (46.3 mg, 88%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (dd, J = 8.0, 0.9 Hz, 1H), 7.43 (dd, J = 7.7, 1.6 Hz, 1H), 7.22 (td, J = 7.6, 1.1 Hz, 1H), 7.10 (td, J = 7.8, 1.7 Hz, 1H), 2.68-2.65 (m, 1H), 1.96-1.72 (m, 4H), 1.69-1.47 (m, 3H), 1.47-1.30 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 133.20, 132.26, 128.58, 126.87, 126.13, 125.67, 99.54, 79.48, 32.44, 29.74, 26.00, 24.68. HRMS (EI) calculated for $C_{14}H_{15}Br$ $[M]^+$: 262.0352; found: 262.0350.



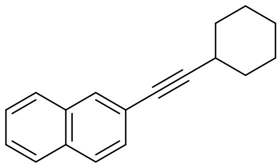
3an

1-(Cyclohexylethynyl)-4-fluorobenzene (3an): According to the general procedure, (4-Fluorophenyl)ethynyl phenyl sulfone (52.1 mg, 0.2 mmol), cyclohexane (216 μL, 2 mmol), $FeCl_3\cdot6H_2O$ (2.7 mg, 0.01 mmol) and CH_3CN (2 mL) were used. After 5 h, the crude product was purified by column chromatography using petroleum ether as the eluent system to give the product as a colorless oil (34.3 mg, 85%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39-7.33 (m, 2H), 7.01-6.92 (m, 2H), 2.60-2.54 (m, 1H), 1.96-1.82 (m, 2H), 1.75-1.73 (m, 2H), 1.62-1.45 (m, 3H), 1.43-1.28 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.01 (d, J = 249.5 Hz), 133.33 (d, J = 8.1 Hz), 120.19 (d, J = 3.0 Hz), 115.33 (d, J = 22.2 Hz), 94.07, 79.43, 32.70, 29.63, 25.92, 24.93. HRMS (EI) calculated for $C_{14}H_{15}F$ $[M]^+$: 202.1152; found: 202.1149.



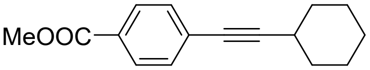
3ao

4-(Cyclohexylethynyl)-1,1'-biphenyl (3ao): According to the general procedure, 4-((phenylsulfonyl)ethynyl)-1,1'-biphenyl (63.6 mg, 0.2 mmol), cyclohexane (216 μL, 2 mmol), $FeCl_3\cdot6H_2O$ (2.7 mg, 0.01 mmol) and CH_3CN (2 mL) were used. After 3 h, the crude product was purified by column chromatography using petroleum ether as the eluent system to give the product as a colorless oil (43.2 mg, 83%). ^{1}H NMR (400 MHz, CDCl3) δ 7.61-7.57 (m, 2H), 7.55-7.49 (m, 2H), 7.49-7.41 (m, 4H), 7.37-7.29 (m, 1H), 2.66-2.57 (m, 1H), 1.96-1.83 (m, 2H), 1.82-1.70 (m, 2H), 1.62-1.48 (m, 3H), 1.40-1.29 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.57, 140.13, 131.99, 128.82, 127.45, 126.99, 126.86, 123.12, 95.23, 80.38, 32.75, 29.77, 25.96, 24.95. HRMS (EI) calculated for $C_{20}H_{20}$ $[M]^+$: 260.1560; found: 260.1555.



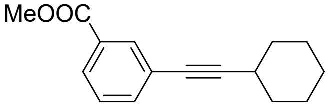
3ap

2-(Cyclohexylethynyl)naphthalene (3ap): According to the general procedure, 2-((phenylsulfonyl)ethynyl)naphthalene (58.4 mg, 0.2 mmol), cyclohexane (216 µL, 2 mmol), $FeCl_3 \cdot 6H_2O$ (2.7 mg, 0.01 mmol) and CH_3CN (2 mL) were used. After 3 h, the crude product was purified by column chromatography using petroleum ether as the eluent system to give the product as a colorless oil (39.4 mg, 84%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (s, 1H), 7.83-7.72 (m, 3H), 7.49-7.44 (m, 3H), 2.69-2.61 (m, 1H), 2.05-1.93 (m, 2H), 1.89-1.75 (m, 2H), 1.69-1.49 (m, 3H), 1.47-1.32 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 133.10, 132.45, 131.01, 128.86, 127.75, 127.70, 127.58, 126.33, 126.19, 121.50, 94.82, 80.88, 32.79, 29.81, 25.98, 24.98. HRMS (EI) calculated for $C_{20}H_{20}$ $[M]^+$: 234.1403; found: 234.1403.



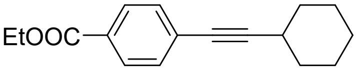
3aq

methyl 4-(cyclohexylethynyl)benzoate (3aq): According to the general procedure, methyl 4-((phenylsulfonyl)ethynyl)benzoate (60.6 mg, 0.2 mmol), cyclohexane (216 µL, 2 mmol), $FeCl_3 \cdot 6H_2O$ (2.7 mg, 0.01 mmol) and CH_3CN (2 mL) were used. After 3 h, the crude product was purified by column chromatography using petroleum ether: ethyl acetate = 10:1 as the eluent system to give the product as a colorless oil (41.2 mg, 85%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, J = 8.3 Hz, 2H), 7.44 (d, J = 8.3 Hz, 2H), 3.90 (s, 3H), 2.65-2.57 (m, 1H), 1.94-1.82 (m, 2H), 1.82-1.68 (m, 2H), 1.61-1.48 (m, 3H), 1.41-1.30 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.71, 131.50, 129.37, 129.02, 128.75, 97.94, 80.08, 52.14, 32.53, 29.76, 25.88, 24.88. HRMS (EI) calculated for $C_{16}H_{18}$ $[M]^+$: 242.1301; found: 242.1296.



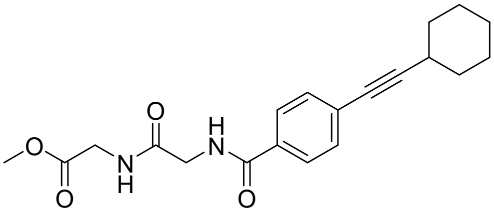
3ar

Methyl 3-(cyclohexylethynyl)benzoate (3ar): According to the general procedure, methyl 3-((phenylsulfonyl)ethynyl)benzoate (60.6 mg, 0.2 mmol), cyclohexane (216 μL, 2 mmol), $FeCl_3·6H_2O$ (2.7 mg, 0.01 mmol) and CH_3CN (2 mL) were used. After 3 h, the crude product was purified by column chromatography using petroleum ether: ethyl acetate = 10:1 as the eluent system to give the product as a colorless oil (43.1 mg, 89%). ^1H NMR (400 MHz, $CDCl_3$) δ 8.06 (t, J = 1.5 Hz, 1H), 7.93-7.88 (m, 1H), 7.59-7.52 (m, 1H), 7.34 (t, J = 7.8 Hz, 1H), 3.91 (s, 3H), 2.63-2.55 (m, 1H), 1.92-1.82 (m, 2H), 1.79-1.68 (m, 2H), 1.60-1.47 (m, 3H), 1.41-1.30 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.61, 135.76, 132.75, 130.21, 128.43, 128.28, 124.60, 95.54, 79.62, 52.21, 32.60, 29.63, 25.91, 24.88. HRMS (EI) calculated for $C_{16}H_{18}O_2$ $[M]^+$: 242.1301; found: 242.1297.



3as

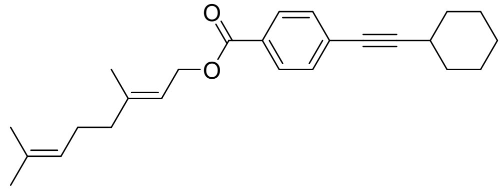
Ethyl 4-(cyclohexylethynyl)benzoate (3as): According to the general procedure, Ethyl 4-((phenylsulfonyl)ethynyl)benzoate (62.8 mg, 0.2 mmol), cyclohexane (216 μL, 2 mmol), $FeCl_3·6H_2O$ (2.7 mg, 0.01 mmol) and CH_3CN (2 mL) were used. After 3 h, the crude product was purified by column chromatography using petroleum ether: ethyl acetate = 10:1 as the eluent system to give the product as a colorless oil (43.5 mg, 85%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, J = 8.5 Hz, 2H), 7.46 (d, J = 8.5 Hz, 2H), 4.39 (q, J = 7.1 Hz, 2H), 2.67-2.58 (m, 1H), 1.91-1.81(m, 2H), 1.78-1.66 (m, 2H), 1.61-1.47 (m, 3H), 1.43-1.30 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.22, 131.45, 129.32, 129.11, 128.89, 97.81, 80.13, 61.01, 32.55, 29.77, 25.88, 24.89, 14.32. HRMS (EI) calculated for $C_{17}H_{20}O_2$ $[M]^+$: 256.1458; found: 256.1455.



3at

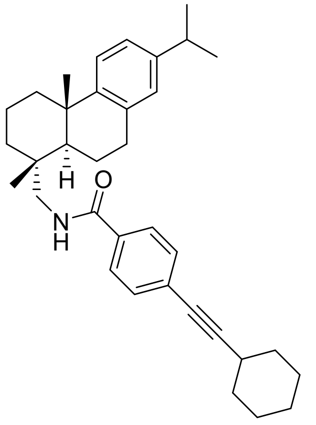
Methyl (4-(cyclohexylethynyl)benzoyl)glycylglycinate (3at): According to the general procedure, methyl (4-((phenylsulfonyl)ethynyl)benzoyl)glycylglycinate (82.9 mg, 0.2 mmol), cyclohexane (216 μL, 2 mmol), $FeCl_3·6H_2O$ (2.7 mg, 0.01 mmol) and CH_3CN (2 mL) were used. After 12 h, the crude product was purified by column chromatography using dichloromethane:

methyl alcohol = 10:1 as the eluent system to give the product as a white solid (32.1 mg, 45%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, J = 8.2 Hz, 2H), 7.44 (d, J = 8.1 Hz, 2H), 7.08 (s, 1H), 6.79 (s, 1H), 4.19 (d, J = 5.1 Hz, 2H), 4.08 (d, J = 5.3 Hz, 2H), 3.75 (s, 3H), 2.69-2.56 (m, 1H), 1.97-1.83 (m, 2H), 1.65-1.46 (m, 2H), 1.60-1.52 (m, 3H), 1.41-1.24 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.05, 169.25, 167.27, 131.88, 131.77, 128.10, 127.00, 97.59, 79.88, 52.52, 43.56, 41.25, 32.54, 29.75, 25.88, 24.90. calcd for $C_{20}H_{24}N_2O_4$ $[M+Na]^+$: 379.1628, found 379.1628.



3au

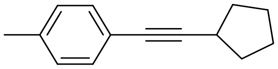
(E)-3,7-dimethylocta-2,6-dien-1-yl 4-(cyclohexylethynyl)benzoate (3au): According to the general procedure, (E)-3,7-dimethylocta-2,6-dien-1-yl 4-((phenylsulfonyl)ethynyl)benzoate (84.5 mg, 0.2 mmol), cyclohexane (216 µL, 2 mmol), $FeCl_3 \cdot 6H_2O$ (2.7 mg, 0.01 mmol) and CH_3CN (2 mL) were used. After 12 h, the crude product was purified by column chromatography using petroleum ether: ethyl acetate = 50:1 as the eluent system to give the product as a colorless oil (29.9 mg, 41%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, J = 8.4 Hz, 2H), 7.43 (d, J = 8.3 Hz, 2H), 5.46 (t, J = 6.7 Hz, 1H), 5.09 (t, J = 6.0 Hz, 1H), 4.82 (d, J = 7.0 Hz, 2H), 2.64-2.53 (m, 1H), 2.17 - 2.02 (m, 4H), 1.91-1.80 (m, 2H), 1.78-1.41 (m, 14H), 1.40-1.25 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.28, 142.42, 131.86, 131.44, 129.38, 129.13, 128.87, 123.74, 118.35, 97.81, 80.14, 61.97, 39.56, 32.54, 29.77, 26.30, 25.88, 25.68, 24.89, 17.70, 16.56. HRMS (ESI) calculated for $C_{25}H_{32}O_2$ $[M+H]^+$: 365.2481; found: 365.2476.



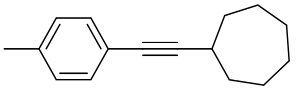
3av

4-(cyclohexylethynyl)-N-(((1R,4aS,10aR)-7-isopropyl-1,4a-dimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthren-1-yl)methyl)benzamide (3av): According to the general procedure, N-

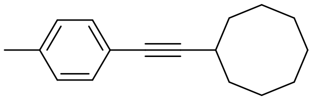
(((1R,4aS,10aR)-7-isopropyl-1,4a-dimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthren-1-yl)methyl)-4-((phenylsulfonyl)ethynyl)benzamide (110.8 mg, 0.2 mmol), cyclohexane (216 µL, 2 mmol), $FeCl_3 \cdot 6H_2O$ (2.7 mg, 0.01 mmol) and CH_3CN (2 mL) were used. After 12 h, the crude product was purified by column chromatography using petroleum ether: ethyl acetate = 10:1 as the eluent system to give the product as a white solid (42.3 mg, 43%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, J = 8.2 Hz, 2H), 7.42 (d, J = 8.1 Hz, 2H), 7.17 (d, J = 8.2 Hz, 1H), 6.99 (d, J = 8.1 Hz, 1H), 6.89 (s, 1H), 6.12 (s, 1H), 3.45-3.30 (m, 2H), 3.04-2.73 (m, 3H), 2.67-2.51 (m, 1H), 2.35-2.20 (m, 1H), 1.99-1.65 (m, 9H), 1.52-1.47 (m, 4H), 1.40-1.25 (m, 5H), 1.24-1.21 (m, 9H), 1.01 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.11, 147.03, 145.67, 134.75, 133.37, 131.73, 127.51, 126.98, 126.68, 124.24, 123.92, 97.15, 79.94, 50.41, 45.91, 38.37, 37.70, 37.59, 36.45, 33.43, 32.57, 30.44, 29.76, 25.89, 25.46, 24.91, 23.98, 23.97, 19.12, 18.80, 18.66. HRMS (ESI) calculated for $C_{35}H_{45}NO$ $[M+H]^+$: 496.3574, found 496.3585.


3ba

1-(Cyclopentylethynyl)-4-methylbenzene (3ba): According to the general procedure, (4-Methylphenyl)ethynyl phenyl sulfone (51.2 mg, 0.2 mmol), cyclopentane (187 µL, 2 mmol), $FeCl_3 \cdot 6H_2O$ (2.7 mg, 0.01 mmol) and CH_3CN (2 mL) were used. After 3 h, the crude product was purified by column chromatography using petroleum ether as the eluent system to give the product as a colorless oil (34.2 mg, 85%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.28 (d, J = 8.1 Hz, 2H), 7.08 (d, J = 7.9 Hz, 2H), 2.86-2.76 (m, 1H), 2.33 (s, 3H), 2.08-1.93 (m, 2H), 1.85-1.67 (m, 4H), 1.63-1.51 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.32, 131.40, 128.91, 121.06, 93.76, 80.06, 33.97, 30.83, 25.06, 21.40. HRMS (EI) calculated for $C_{14}H_{16}$ $[M]^+$: 184.1247; found: 184.1244.

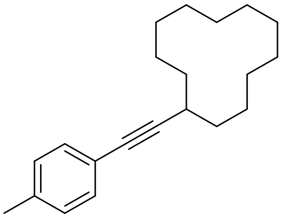

3ca

(p-Tolylethynyl)cycloheptane (3ca): According to the general procedure, (4-Methylphenyl)ethynyl phenyl sulfone (51.2 mg, 0.2 mmol), cycloheptane (242 µL, 2 mmol), $FeCl_3 \cdot 6H_2O$ (2.7 mg, 0.01 mmol) and CH_3CN (2 mL) were used. After 7 h, the crude product was purified by column chromatography using petroleum ether as the eluent system to give the product as a colorless oil (36.0 mg, 85%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.29 (d, J = 8.1 Hz, 2H), 7.08 (d, J = 7.9 Hz, 2H), 2.84-2.76 (m, 1H), 2.33 (s, 3H), 1.91-1.81 (m, 2H), 1.80-1.70 (m, 4H), 1.65-1.48 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.29, 131.39, 128.91, 121.15, 94.38, 80.79, 34.77, 31.72, 27.94, 25.66, 21.40. HRMS (EI) calculated for $C_{16}H_{20}$ $[M]^+$: 212.1560; found: 212.1559.



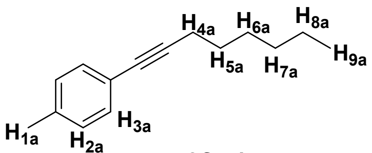
3da

(p-Tolylethynyl)cyclooctane (3da): According to the general procedure, (4-Methylphenyl)ethynyl phenyl sulfone (51.2 mg, 0.2 mmol), cyclooctane (269 μL, 2 mmol), $FeCl_3 \cdot 6H_2O$ (2.7 mg, 0.01 mmol) and CH_3CN (2 mL) were used. After 7 h, the crude product was purified by column chromatography using petroleum ether as the eluent system to give the product as a colorless oil (38.9 mg, 86%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.29 (d, J = 8.1 Hz, 2H), 7.08 (d, J = 7.9 Hz, 2H), 2.83-2.75 (m, 1H), 2.33 (s, 3H), 1.99 -1.87 (m, 2H), 1.85-1.78 (m, 4H), 1.69-1.44 (m, 8H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.27, 131.42, 128.90, 121.16, 94.62, 80.48, 31.70, 30.79, 27.46, 25.47, 24.59, 21.41. HRMS (EI) calculated for $C_{17}H_{22}$ $[M]^+$: 226.1716; found: 226.1712.

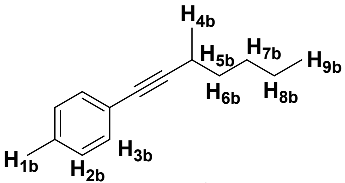


3ea

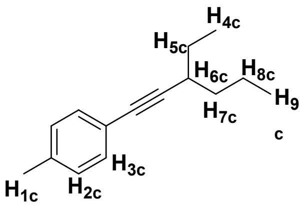
(p-Tolylethynyl)cyclododecane (3ea): According to the general procedure, (4-Methylphenyl)ethynyl phenyl sulfone (51.2 mg, 0.2 mmol), cyclododecane (336.6 mg, 2 mmol), $FeCl_3 \cdot 6H_2O$ (2.7 mg, 0.01 mmol) and CH_3CN (2 mL) were used. After 3 h, the crude product was purified by column chromatography using petroleum ether as the eluent system to give the product as a colorless oil (47.4 mg, 84%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.28 (d, J = 8.0 Hz, 2H), 7.07 (d, J = 7.9 Hz, 2H), 2.71-2.59 (m, 1H), 2.32 (s, 3H), 1.70-1.64 (m, 2H), 1.63-1.54 (m, 4H), 1.46-1.29 (m, 16H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.25, 131.45, 128.87, 121.15, 94.12, 80.22, 30.00, 27.48, 23.94, 23.87, 23.50, 23.44, 22.25, 21.38. HRMS (EI) calculated for $C_{21}H_{30}$ $[M]^+$: 282.2343; found: 282.2343.



3fa-1

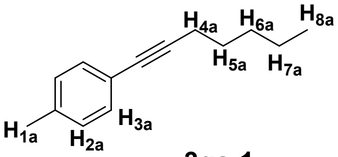


3fa-2

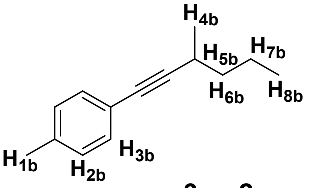


3fa-3

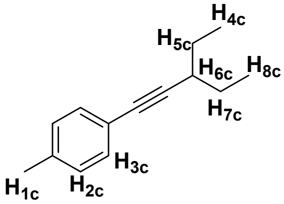
1-methyl-4-(oct-1-yn-1-yl)benzene (3fa-1), 1-methyl-4-(3-methylhept-1-yn-1-yl)benzene (3fa-2) and 1-(3-ethylhex-1-yn-1-yl)-4-methylbenzene (3fa-3): According to the general procedure, (4-Methylphenyl)ethynyl phenyl sulfone (51.2 mg, 0.2 mmol), hexane (262 µL, 2 mmol), $FeCl_3 \cdot 6H_2O$ (2.7 mg, 0.01 mmol) and CH_3CN (2 mL) were used. After 8 h, the crude product was purified by column chromatography using petroleum ether as the eluent system to give the product as a colorless oil (30 mg, 75%, **3fa-1**: **3fa-2**: **3fa-3** = 1:1.3:1.2). **3fa-1**: GC: 9.407 min. **3fa-2**: GC: 8.898 min. **3fa-3**: GC: 8.831 min (notarized by GC-MS).[1] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (d, J = 8.0 Hz, H_{3a}, H_{3b}, H_{3c}), 7.08 (d, J = 7.9 Hz, H_{2a}, H_{2b}, H_{2c}), 2.66-2.57 (m, H_{5b}), 2.50-2.44 (m, H_{6c}), 2.39 (t, J = 7.1 Hz, H_{4a}), 2.33 (s, H_{1a}, H_{1b}, H_{1c}), 1.63-1.41 (m, H_{5a}, H_{6b}, $H_{5c,}$ H_{7c}), 1.35-1.28 (m, H_{6a}, H_{7a}, $H_{8a,}$ H_{7b}, H_{8b}, H_{8c}), 1.23 (d, J = 6.9 Hz, H_{4b}), 1.06 (t, J = 7.4 Hz, H_{9b}), 0.94-0.88 (m, H_{9a}, $H_{4c,}$ H_{9c}).^{13}C NMR (101 MHz, $CDCl_3$) δ 137.40, 137.35, 137.30, 131.45, 131.44, 131.41, 128.94, 128.90, 121.16, 121.05, 94.10, 92.85, 89.66, 81.76, 80.64, 80.56, 37.08, 36.81, 33.80, 31.40, 29.68, 28.82, 28.64, 28.24, 26.52, 22.60, 21.41, 21.18, 20.70, 19.45, 14.11, 14.09, 14.06, 11.92. HRMS (EI) calculated for $C_{15}H_{20}$ $[M]^+$: 200.1560; found: 200.1556.



3ga-1



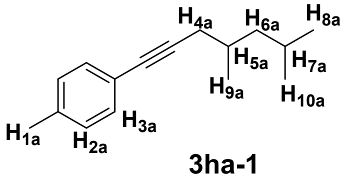
3ga-2



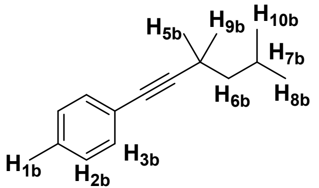
3ga-3

1-(hept-1-yn-1-yl)-4-methylbenzene (3ga-1), 1-methyl-4-(3-methylhex-1-yn-1-yl)benzene (3ga-2) and 1-(3-ethylpent-1-yn-1-yl)-4-methylbenzene (3ga-3): According to the general procedure, (4-Methylphenyl)ethynyl phenyl sulfone (51.2 mg, 0.2 mmol), pentane (231 µL, 2 mmol), $FeCl_3 \cdot 6H_2O$ (2.7 mg, 0.01 mmol) and CH_3CN (2 mL) were used. After 8 h, the crude product was purified by column chromatography using petroleum ether as the eluent system to give the product as a colorless oil (29.0 mg, 78%, **3ga-1**: (**3ga-2**+**3ga-3)** = 1:2.9). The existence of three isomers was fully proved by ^{13}C NMR with 6 obvious signals from 80 to 100 ppm. **3ga-1**: GC: 8.809 min. **3ga-2 and 3ga-3**: GC: 8.311 min (notarized by GC-MS). [1] ^{1}H NMR (400 MHz,

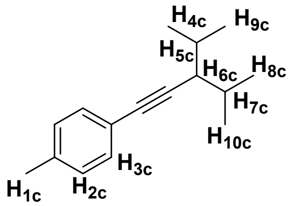
$CDCl_3$) δ 7.28 (d, J = 7.7 Hz, H_{3a}, H_{3b}, H_{3c}), 7.08 (d, J = 7.3 Hz, H_{2a}, H_{2b}, H_{2c}), 2.67-2.64 (m, H_{5b}), 2.39 (t, J = 7.1 Hz, H_{4a}), 2.33 (s, H_{1a}, H_{1b}, H_{1c}), 1.58-1.34 (m, H_{5a}, H_{6b}, H_{7c}, H_{6a}, H_{7a}, H_{7b}), 1.25 (d, J = 6.9 Hz, H_{4b}), 1.06 (t, J = 7.4 Hz, H_{8b}), 0.97-0.89 (m, H_{8a}, H_{4c}, H_{8c}). ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.41, 137.35, 137.32, 131.46, 131.44, 131.42, 128.95, 128.91, 121.16, 121.03, 121.01, 94.03, 92.68, 89.66, 81.90, 80.65, 80.55, 39.27, 35.74, 31.16, 28.56, 27.84, 26.28, 22.28, 21.41, 21.17, 20.64, 19.42, 14.04, 13.99, 11.95. HRMS (EI) calculated for $C_{14}H_{18}$ $[M]^+$: 186.1404; found: 186.1398.



3ha-1

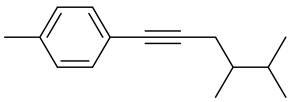


3ha-2



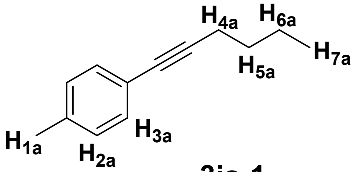
3ha-3

1-(4,6-dimethylhept-1-yn-1-yl)-4-methylbenzene (3ha-1), 1-methyl-4-(3,3,5-trimethylhex-1-yn-1-yl)benzene (3ha-2) and 1-(3-isopropyl-4-methylpent-1-yn-1-yl)-4-methylbenzene (3ha-3): According to the general procedure, (4-Methylphenyl)ethynyl phenyl sulfone (51.2 mg, 0.2 mmol), 2,4-dimethylpentane (298 μL, 2 mmol), $FeCl_3 \cdot 6H_2O$ (2.7 mg, 0.01 mmol) and CH_3CN (2 mL) were used. After 3 h, the crude product was purified by column chromatography using petroleum ether as the eluent system to give the product as a colorless oil (36.4 mg, 85%, **3ha-1**: **3ha-2**: **3ha-3** = 7.9:1:3.0). **3ha-1**: GC: 9.404 min. **3ha-2**: GC: 8.703 min. **3ha-3**: GC: 8.997 min (notarized by GC-MS). ^1H NMR (400 MHz, $CDCl_3$) δ 7.30 (d, J = 8.0 Hz, H_{3a}, H_{3b}, H_{3c}), 7.09 (d, J = 7.8 Hz, H_{2a}, H_{2b}, H_{2c}), 2.42 (dd, J = 24.9, 6.8 Hz, H_{4a}), 2.34 (s, H_{1a}, H_{1b}, H_{1c}), 2.25 (dd, J = 16.7, 7.0 Hz, H_{4a}), 2.12 (t, J = 6.8 Hz, H_{6c}), 1.88-1.82 (m, H_{5a}, H_{5c}, H_{7c}), 1.72-1.67 (m, H_{7b}), 1.36-1.30 (m, H_{6b}), 1.28 (t, J = 8.4 Hz, H_{6a}), 1.18-1.09 (m, H_{7a}), 1.03 (q, J = 14.0, 7.0 Hz, H_{5b}, H_{9b}), 0.90 (t, J = 7.1 Hz, H_{8a}, H_{9a}, H_{10a}, H_{8b}, H_{10b}, H_{4c}, H_{8c}, H_{9c}, H_{10c}). ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.37, 137.21, 131.41, 131.29, 128.93, 128.88, 121.13, 90.27, 88.45, 81.54, 47.27, 45.82, 30.51, 30.19, 29.16, 27.09, 25.71, 25.37, 24.59, 23.20, 22.42, 21.52, 21.38, 19.77, 19.46. HRMS (EI) calculated for $C_{16}H_{22}$ $[M]^+$: 214.1717; found: 214.1717.

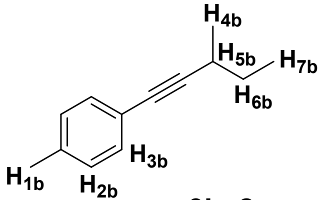


3ia

1-(3,4-dimethylpent-1-yn-1-yl)-4-methylbenzene (3ia): According to the general procedure, (4-Methylphenyl)ethynyl phenyl sulfone (51.2 mg, 0.2 mmol), 2,3-dimethylbutane (260 µL, 2 mmol), $FeCl_3{\cdot}6H_2O$ (2.7 mg, 0.01 mmol) and CH_3CN (2 mL) were used. The reaction mixture was irradiated with a 30 W 365 nm LED (2 cm away, with circulating water to keep the reaction at room temperature). After 7 h, the crude product was purified by column chromatography using petroleum ether as the eluent system to give the product as a colorless oil (24.8 mg, 62%). **3ia**: GC: 9.101 min (notarized by GC-MS). ^1H NMR (400 MHz, $CDCl_3$) δ 7.29 (d, J = 8.1 Hz, 2H), 7.08 (d, J = 7.9 Hz, 2H), 2.40 (dd, J = 16.7, 5.6 Hz, 1H), 2.33 (s, 3H), 2.27 (dd, J = 16.7, 7.8 Hz, 1H), 1.79-1.69 (m, 1H), 1.65-1.57 (m, 1H), 0.99 (d, J = 6.8 Hz, 3H), 0.93 (d, J = 6.8 Hz, 3H), 0.88 (d, J = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.37, 131.40, 128.93, 121.10, 88.90, 81.32, 38.83, 31.51, 24.58, 21.41, 20.44, 18.39, 15.90. HRMS (EI) calculated for $C_{15}H_{20}$ $[M]^+$: 200.1560; found: 200.1556.

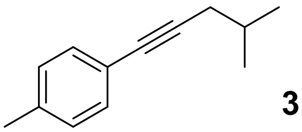


3ja-1



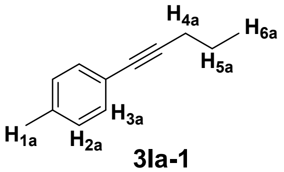
3ja-2

1-(hex-1-yn-1-yl)-4-methylbenzene (3ja-1) and 1-methyl-4-(3-methylpent-1-yn-1-yl)benzene (3ja-2): According to the general procedure, (4-Methylphenyl)ethynyl phenyl sulfone (51.2 mg, 0.2 mmol), $FeCl_3{\cdot}6H_2O$ (5.4 mg, 0.02 mmol), CH_3CN (5 mL) and butane atmosphere were used. After 3 h, the crude product was purified by column chromatography using petroleum ether as the eluent system to give the product as a colorless oil (24.1 mg, 70%, **3ja-1**: **3ja-2** = 1:1.9). **3ja-1**: GC: 8.194 min. **3ja-2**: GC: 7.739 min (notarized by GC-MS). ^1H NMR (400 MHz, $CDCl_3$) δ 7.30 (d, J = 8.1 Hz, H_{3a}, H_{3b}), 7.09 (d, J = 8.0 Hz, H_{2a}, H_{2b}), 2.63-2.58 (m, H_{5b}), 2.41 (t, J = 7.0 Hz, H_{4a}), 2.33 (s, H_{1a}, H_{1b}), 1.66-1.42 (m, H_{5a}, H_{6a}, H_{6b}), 1.25 (d, J = 6.9 Hz, H_{4b}), 1.06 (t, J = 7.4 Hz, H_{7b}), 0.95 (t, J = 7.3 Hz, H_{7a}). ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.41, 137.36, 131.45, 131.42, 128.95, 128.92, 121.04, 93.83, 89.59, 80.81, 80.56, 30.94, 30.05, 28.17, 22.05, 21.41, 20.76, 19.14, 13.69, 11.86. HRMS (EI) calculated for $C_{13}H_{16}$ $[M]^+$: 172.1247; found: 172.1246.

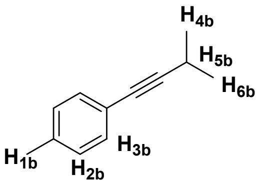


3ka

1-methyl-4-(4-methylpent-1-yn-1-yl)benzene (3ka): According to the general procedure, (4-Methylphenyl)ethynyl phenyl sulfone (51.2 mg, 0.2 mmol), $FeCl_3\cdot6H_2O$ (5.4 mg, 0.02 mmol), CH_3CN (5 mL) and iso-butane atmosphere were used. After 3 h, the crude product was purified by column chromatography using petroleum ether as the eluent system to give the product as a colorless oil (25.8 mg, 75%). **3ka**: GC: 7.895 min (notarized by GC-MS). ^1H NMR (400 MHz, $CDCl_3$) δ 7.30 (d, J = 7.6 Hz, 2H), 7.09 (d, J = 7.5 Hz, 2H), 2.33 (s, 3H), 2.29 (d, J = 6.5 Hz, 2H), 1.97-1.81 (m, 1H), 1.04 (d, J = 6.6 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.41, 131.42, 128.95, 121.05, 88.55, 81.47, 31.12, 28.61, 28.29, 22.08, 21.41. HRMS (EI) calculated for $C_{13}H_{16}$ $[M]^+$: 172.1247; found: 172.1245.

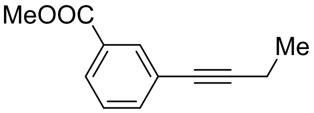


3la-1



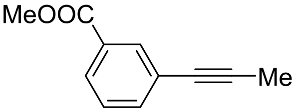
3la-2

1-methyl-4-(pent-1-yn-1-yl)benzene (3la-1) and 1-methyl-4-(3-methylbut-1-yn-1-yl)benzene (3la-2): According to the general procedure, (4-Methylphenyl)ethynyl phenyl sulfone (51.2 mg, 0.2 mmol), $FeCl_3\cdot6H_2O$ (5.4 mg, 0.02 mmol), CH_3CN (5 mL) and propane atmosphere were used. After 3 h, the crude product was purified by column chromatography using petroleum ether as the eluent system to give the product as a colorless oil (24.1 mg, 65%, **3la-1**: **3la-2** = 1.26:1). **3la-1**: GC: 7.540 min. **3la-2**: GC: 7.093 min (notarized by GC-MS). ^1H NMR (400 MHz, $CDCl_3$) δ 7.32 (d, J = 5.1 Hz, H_{3a}, H_{3b}), 7.11 (d, J = 6.5 Hz, H_{2a}, H_{2b}), 2.81-2.76 (m, H_{5b}), 2.40 (t, J = 7.0 Hz, H_{4a}), 2.36 (s, H_{1a}, H_{1b}), 1.72 -1.58 (m, H_{5a}), 1.29 (d, J = 6.9 Hz, H_{4b}, H_{6b}), 2.40 (t, J = 7.4 Hz, H_{6a}). ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.43, 131.43, 128.95, 128.92, 121.00, 120.92, 94.97, 89.44, 80.73, 79.72, 23.12, 22.30, 21.42, 21.15, 13.59. HRMS (EI) calculated for $C_{12}H_{14}$ $[M]^+$: 158.1090; found: 158.1086.



3mr

methyl 3-(but-1-yn-1-yl)benzoate (3mr): According to the general procedure, (methyl 3-((phenylsulfonyl)ethynyl)benzoate (60.6 mg, 0.2 mmol) (to improve the boiling point of final product), $FeCl_3·6H_2O$ (5.4 mg, 0.02 mmol), CH_3CN (5 mL) and ethane atmosphere were used. After 5 h, the crude product was purified by column chromatography using petroleum ether : ethyl acetate = 50:1 as the eluent system to give the product as a colorless oil (19.6 mg, 52%). ^1H NMR (400 MHz, $CDCl_3$) δ 8.07 (s, 1H), 7.93 (d, J = 7.8 Hz, 1H), 7.56 (d, J = 7.7 Hz, 1H), 7.35 (t, J = 7.8 Hz, 1H), 3.91 (s, 3H), 2.43 (q, J = 7.5 Hz, 2H), 1.24 (t, J = 7.5 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.59, 135.72, 132.73, 130.26, 128.53, 128.32, 124.48, 92.77, 78.99, 52.23, 13.83, 13.09. HRMS (EI) calculated for $C_{12}H_{12}O_2$ $[M]^+$: 188.0832; found: 188.0833.



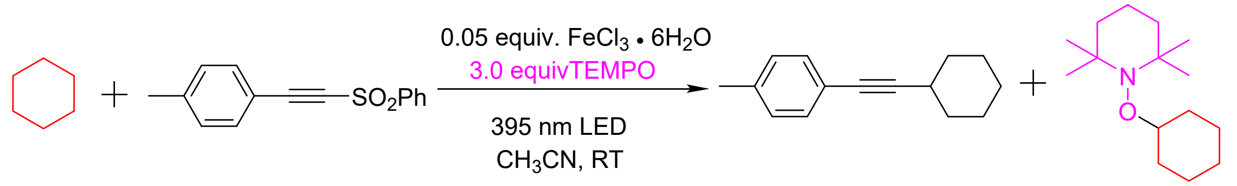
3nr

methyl 3-(prop-1-yn-1-yl)benzoate (3nr): According to the general procedure, (methyl 3-((phenylsulfonyl)ethynyl)benzoate (60.6 mg, 0.2 mmol) (to improve the boiling point of final product), $FeCl_3·6H_2O$ (5.4 mg, 0.02 mmol), CH_3CN (5 mL) and methane atmosphere were used. After 12 h, the crude product was purified by column chromatography using petroleum ether : ether = 100:1 as the eluent system to give the product as a colorless oil (17.4 mg, 50%). ^1H NMR (400 MHz, $CDCl_3$) δ 8.06 (s, 1H), 7.93 (d, J = 7.7 Hz, 1H), 7.55 (d, J = 7.6 Hz, 1H), 7.35 (t, J = 7.8 Hz, 1H), 3.91 (s, 3H), 2.06 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.56, 135.68, 132.68, 130.29, 128.55, 128.33, 124.48, 86.95, 78.83, 52.22, 4.32. HRMS (EI) calculated for $C_{11}H_{10}O_2$ $[M]^+$: 174.0675; found: 174.0673.

4. Mechanistic Experiments

4.1 Radicals Trapping Experiments

a) Radical trapping experiments with TEMPO



10 equiv. **2a**, 1.0 equiv. **3aa**, 0% m/z: 239,
detected by GC-MS

To further investigate the radicals generated inside the catalytic system, 3 equiv. radical trap 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) was added in the model reaction under standard conditions. GC-MS exhibited the disappearance of alkynylation product and the appearance of coupling product between TEMPO and cyclohexane.

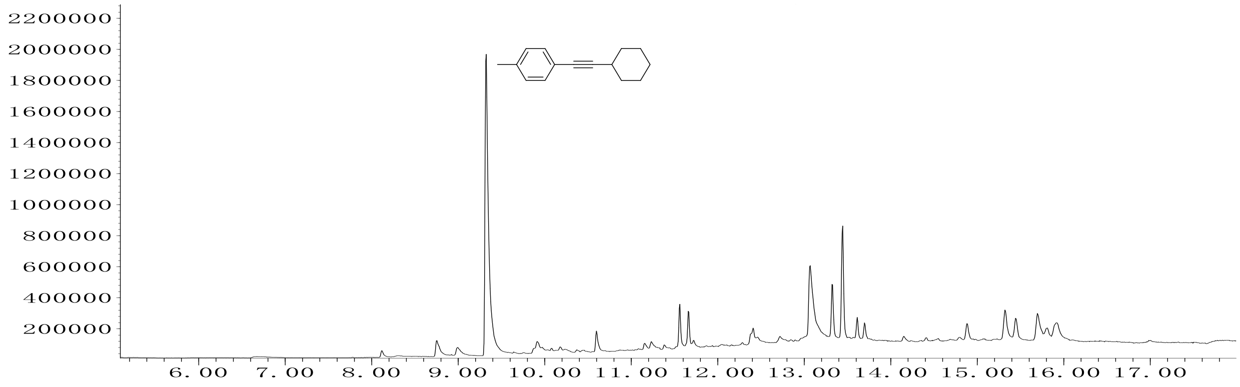


Figure S3. GC-MS date of the standard reaction (residual time of **3aa**: 9.330 min).

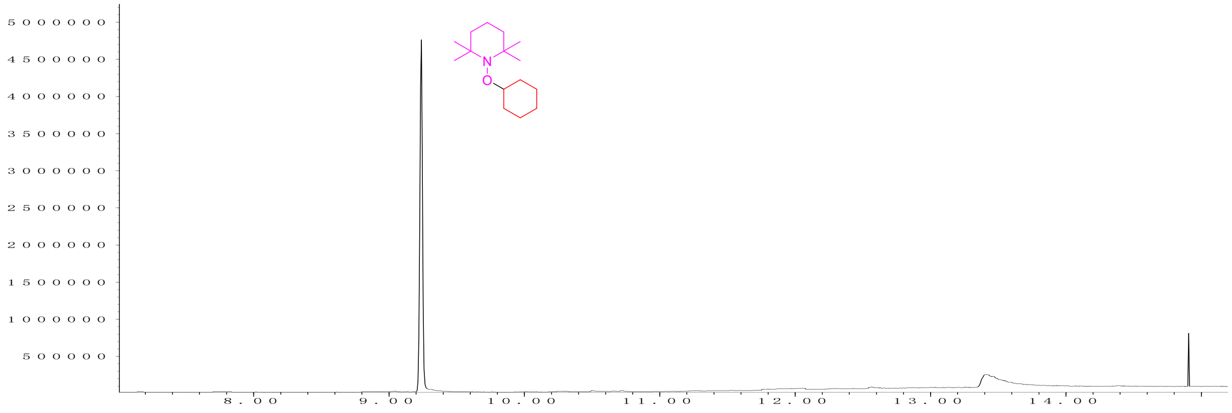
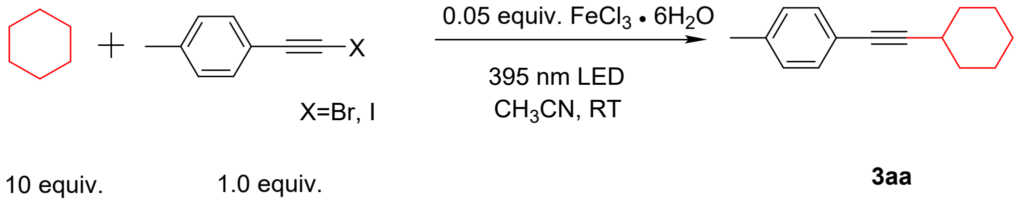


Figure S4. GC-MS date of free radical trapping results, **3aa** was not detected.

4.2 Control experiments with different radical traps

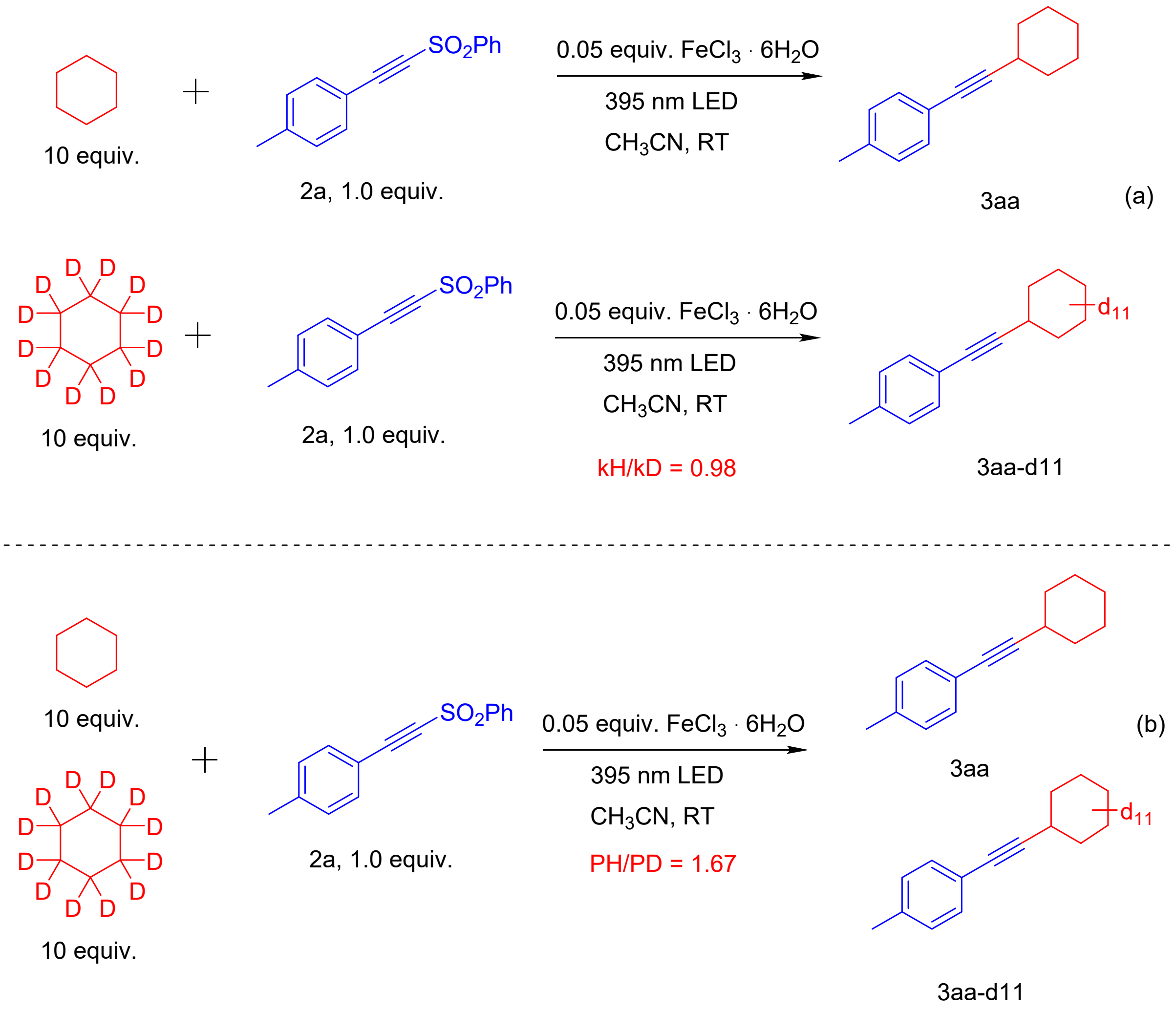


Scheme S1. Different radical traps experiments of alkynylation reaction.

According to the general procedure, 1-(bromoethynyl)-4-methylbenzene (39.0 mg, 0.2 mmol), cyclohexane (216 μL, 2 mmol), $FeCl_3 \cdot 6H_2O$ (2.7 mg, 0.01 mmol) and CH_3CN (2 mL) were used. After 7 h, the crude product was purified by column chromatography using petroleum ether as the eluent system to give the product (35.6 mg, 90%).

According to the general procedure, 1-(iodoethynyl)-4-methylbenzene (30.1 mg, 0.2 mmol), cyclohexane (216 μL, 2 mmol), $FeCl_3 \cdot 6H_2O$ (2.7 mg, 0.01 mmol) and CH_3CN (2 mL) were used. After 24 h, the crude product was purified by column chromatography using petroleum ether as the eluent system to give the product (17.8 mg, 45%).

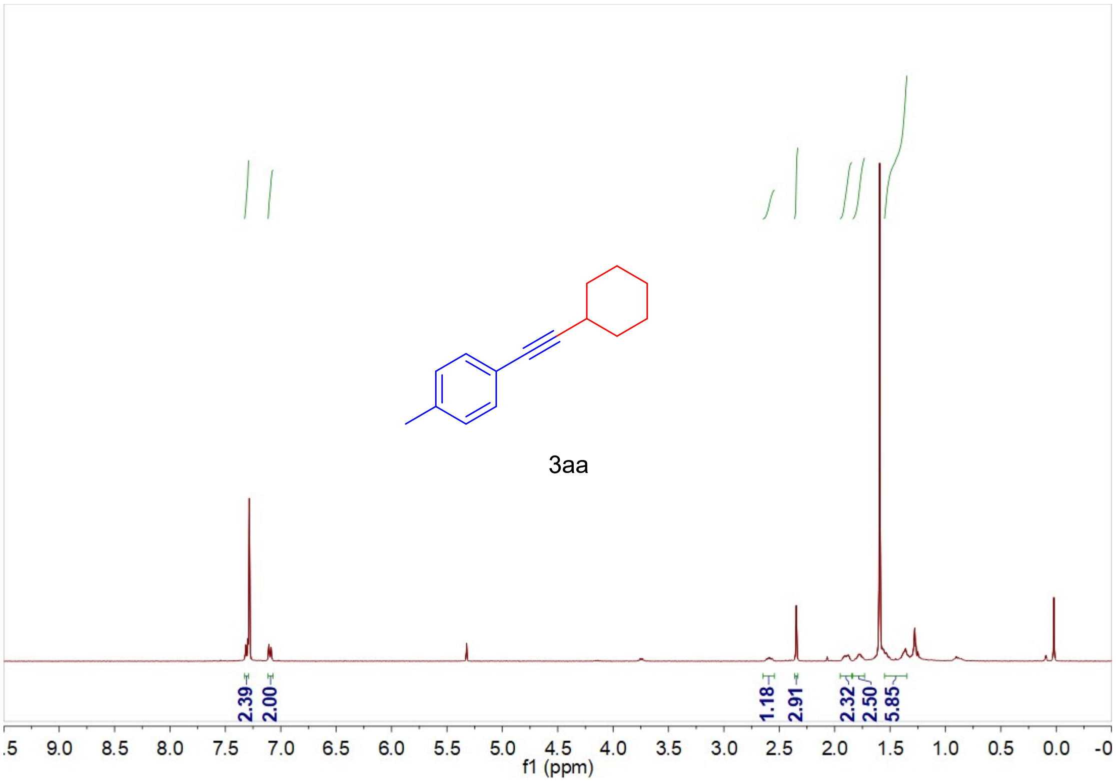
4.3 Isotope Labelling Studies

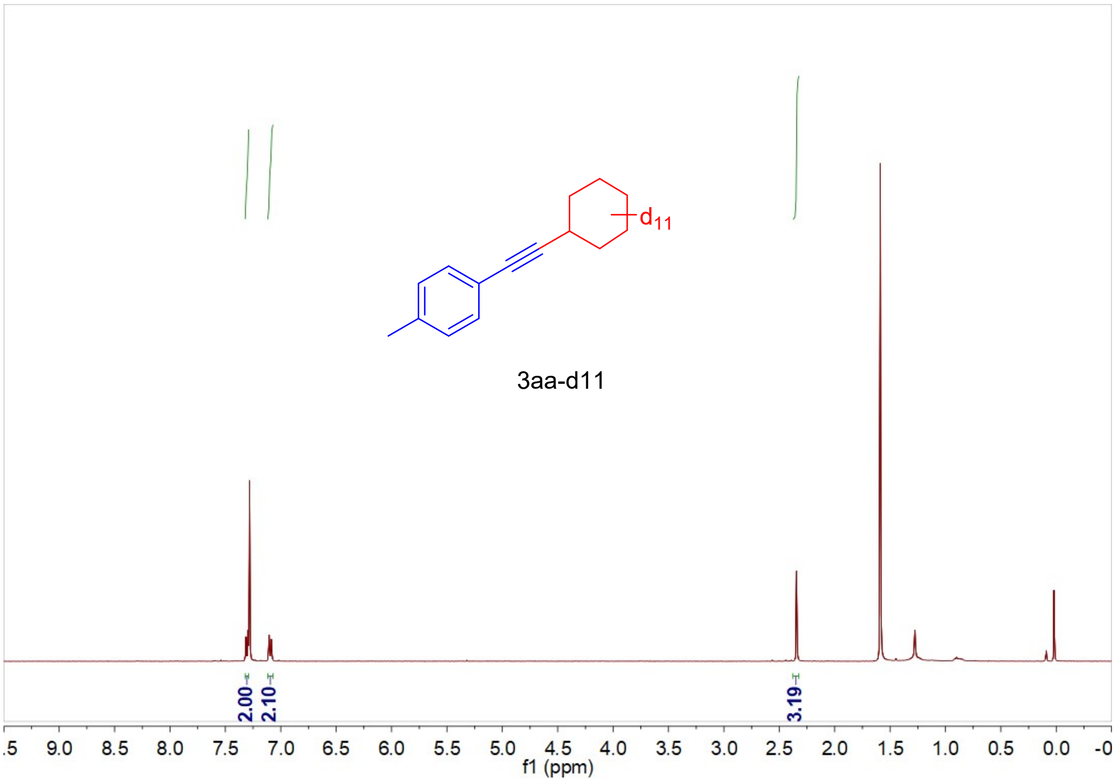


Scheme S2. Deuterium labeling experiments of alkynylation reaction.

Kinetic Isotope Effect (KIE) Competition Experiments:

We examined the KIE competition experiments (*Angew. Chem. Int. Ed.* **51**, 3066 (2012)) under standard conditions for 20 min using (a) cyclohexane/d_{12}-cyclohexane respectively as substrates and **2a** as radical trap; (b) the mixture of cyclohexane/d_{12}-cyclohexane (1:1) as substrates and **2a** as radical trap. KIE data was obtained by analyzing the ratio between deuterated and protonated products by isolated yields and ^{1}H-NMR spectrum. The product distribution yields of non-deuterium and deuterium products was (a) 40% and 41% respectively. (b) 22% and 13% respectively. The k_H/k_D and P_H/P_D value was calculated to 0.98 and 1.65 respectively.


3aa
2.39
2.00
1.18
2.91
2.32
2.50
5.85
.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
f1 (ppm)


d11
3aa-d11
2.00
2.10
3.19
.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
f1 (ppm)

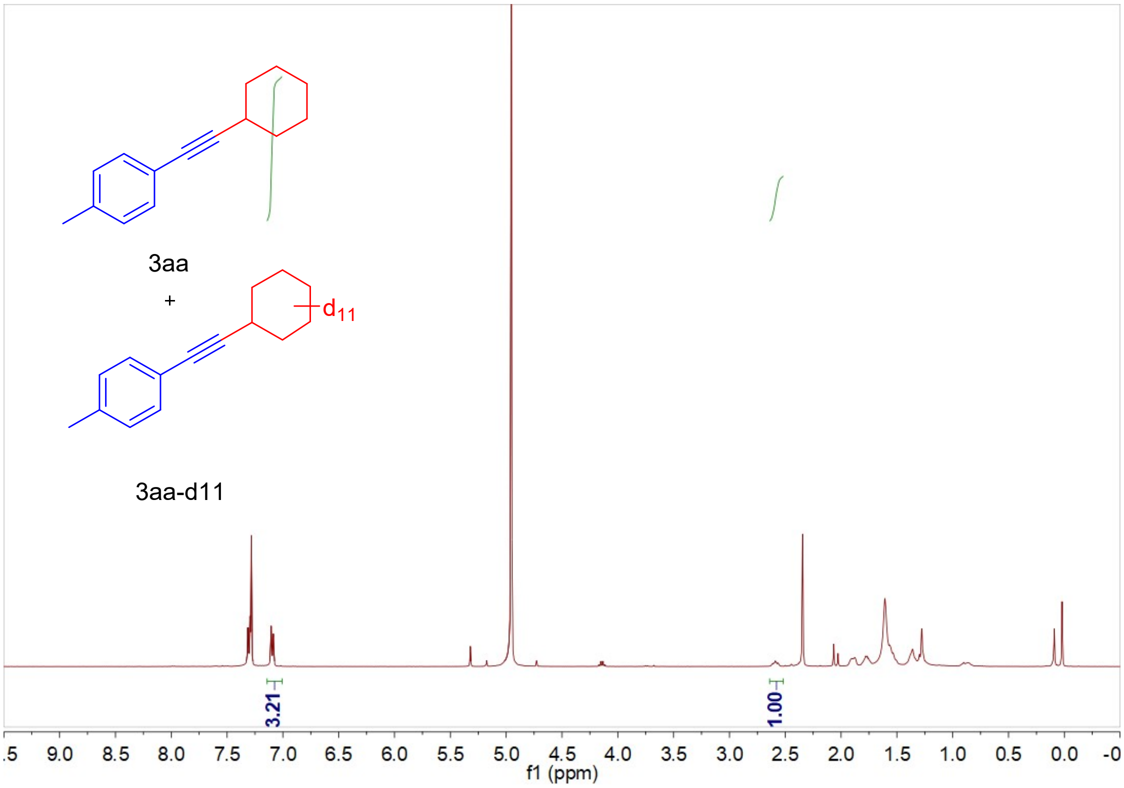
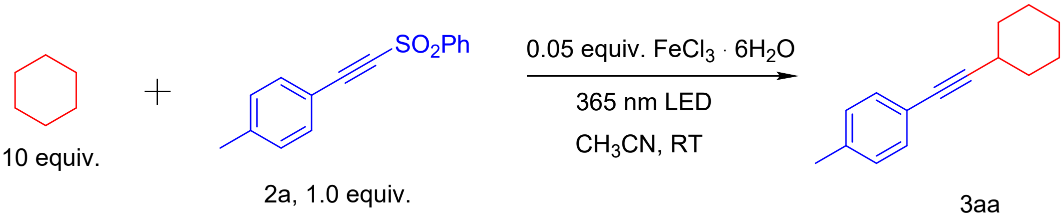


Figure S5. The ^{1}H NMR spectra of the KIE results of **3aa** and **3aa-d$_{11}$**.

4.4. Determination of quantum yield

The reaction sample was prepared following the general procedure, and sequently the sample was irradiated with a commercial 365 nm laser. The photon flux of the 365nm laser we used has been determined as 2.24 × 10^{-8} einstein s^{-1}.[2] After irradiation, the yield was determined by ^{1}H NMR based on a 1,3,5-Trimethoxybenzene standard. The quantum yield was determined using eq 1

$$\Phi = \frac{mol\,product}{flux \bullet t \bullet f} \qquad (1)$$



Scheme S3. Quantum yield determining experiment for alkynylation reaction.

Experiment: A 10 mL quartz reaction tube was added a magnetic stir bar, **2a** (25.6 mg, 0.1 mmol), cyclohexane (108 µL, 1 mmol), $FeCl_3 \cdot 6H_2O$ (1.4 mg, 0.005 mmol) and followed by 1 mL CH_3CN. The reaction tube was capped with a greased two-way septum cock. The reaction mixture was degassed by nitrogen for five times, then set to stir (800 rpm) and irradiated with the 365 nm laser for 3600 s. The yield was determined by ^{1}H NMR based on a 1,3,5-Trimethoxybenzene standard. Yield: 6 %, $\Phi = 0.074$.

$$\Phi = \frac{1 \times 10^{-4} mol \times 6\%}{2.24 \times 10^{-8} einstein\ s^{-1} \bullet 3600\ s \bullet 1.000} = 0.074$$

Determination of fraction of light absorbed at 365 nm for $FeCl_3·6H_2O$ in CH_3CN:

The absorbance of $FeCl_3·6H_2O$ in CH_3CN at a concentration of 5.0×10^{-3} M was measured and the fraction of light absorbed at 365 nm was calculated using eq 3 (f = 1.000, see Figure S6).

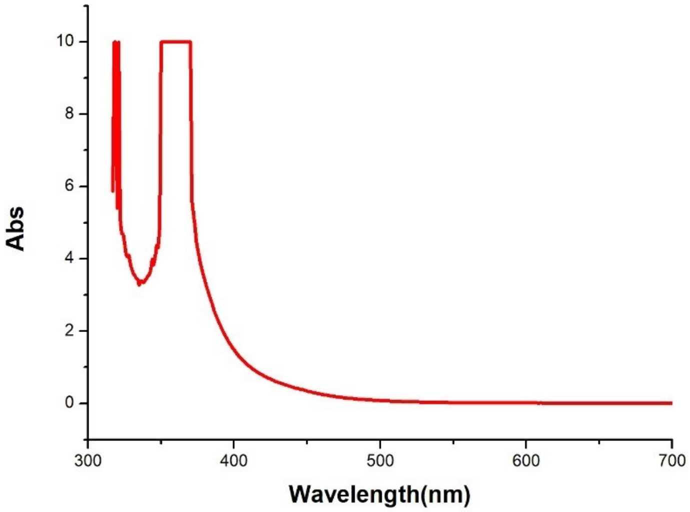
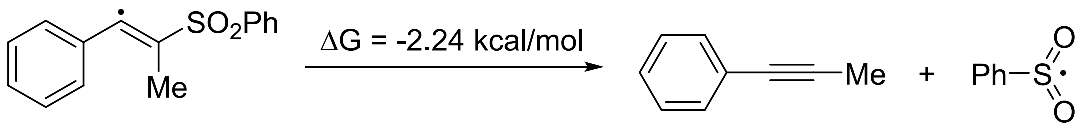


Figure S6. UV-VIS absorption spectrum of $FeCl_3·6H_2O$ (5.0×10^{-3} M) in CH_3CN.

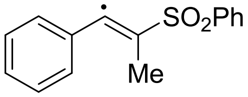
4.5. DFT optimized geometries in the gas phase

All the calculations were carried out using Gaussian16, Revision A.03[3]. Structures reported below have been optimized at the (U)ωB97XD/def2tzvp level of theory in the gas phase. Radical **V** and **VII** were reported in literature.[4] 1-Phenyl-1-propyne was optimized with the same method at the same level and was verified that there were no imaginary frequencies. The Gibbs free energy change for the conversion of **V** to **3** was calculated to -2.24 kcal/mol < 0, which proved the reaction could take place spontaneously according to the thermodynamic law.



V **3** **VII**

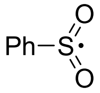
V[4]:



C	-0.26505000	1.65413400	-0.29739700
C	-1.54767800	1.49496700	-0.26708800
C	1.09193700	1.41036000	-0.20060700
C	1.82382200	0.91045100	-1.30375500
C	1.78341400	1.65725200	1.01025200
C	3.17131300	0.65215200	-1.18391000
H	1.30490200	0.71844300	-2.23332700
C	3.13152900	1.39529700	1.10705800
H	1.23280200	2.04326800	1.85802500
C	3.83453900	0.88986300	0.01650100
H	3.71604800	0.25791100	-2.03238600
H	3.64593200	1.58252100	2.04112400
H	4.89381100	0.68546100	0.10104300
S	-2.22922200	-0.11603800	0.20243800
O	-2.68190300	-0.01620500	1.56084500
O	-3.14907400	-0.49901700	-0.83162500

C	-2.61880000	2.51047500	-0.55691100
H	-3.26958900	2.62827300	0.31140400
H	-2.16506100	3.47035300	-0.79422600
H	-3.23315200	2.18120300	-1.39544800
C	-0.83185000	-1.20032900	0.14526200
C	-0.04640100	-1.35886000	1.27588700
C	-0.51732200	-1.83173400	-1.04849700
C	1.08766800	-2.15022400	1.20164400
H	-0.32347700	-0.86093400	2.19530900
C	0.61422500	-2.62736100	-1.11031200
H	-1.15847100	-1.69941000	-1.90976200
C	1.41852800	-2.77848500	0.01022800
H	1.71495500	-2.27405300	2.07450000
H	0.86983800	-3.12864900	-2.03474800
H	2.30758700	-3.39375400	-0.04440300

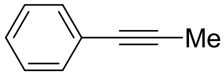
VII[4]:



S	0.24202003	-1.69087915	0.00000000
O	-0.25284789	-2.19003722	1.26419305
O	-0.25284789	-2.19003722	-1.26419305
C	0.08036394	0.09040684	0.00000000
C	0.05148297	0.76123879	1.21322015
C	0.05148297	0.76123879	-1.21322015
C	-0.03150810	2.14418479	1.20446821
H	0.07450604	0.20620176	2.14103913
C	-0.03150810	2.14418479	-1.20446821
H	0.07450604	0.20620176	-2.14103913
C	-0.07089019	2.83195783	0.00000000
H	-0.06768908	2.68428675	2.14143223

H	-0.06768908	2.68428675	-2.14143223
H	-0.13484825	3.91253983	0.00000000

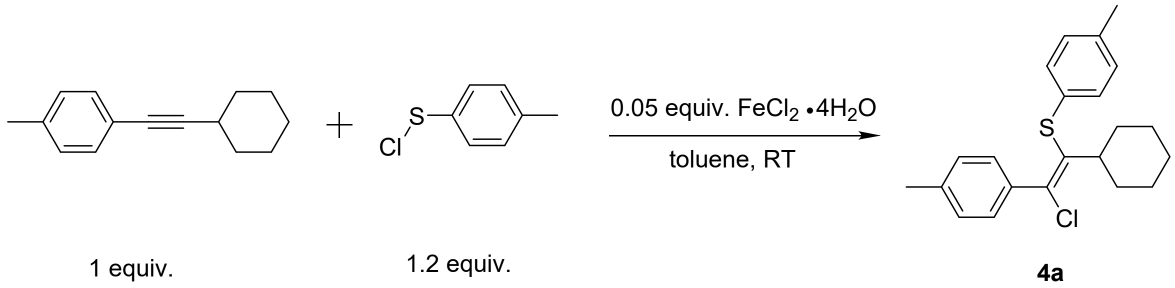
3:



C	0.04049200	0.00182000	0.00227500
C	0.74741900	-1.20208400	0.00138100
C	2.13168400	-1.20084100	-0.00086000
C	2.82974900	-0.00229400	-0.00212800
C	2.13517400	1.19827000	-0.00088700
C	0.75088800	1.20365300	0.00136700
H	0.20056800	-2.13593000	0.00226000
H	2.66780000	-2.14147200	-0.00175100
H	3.91240000	-0.00389600	-0.00412000
H	2.67405400	2.13732400	-0.00179700
H	0.20684400	2.13913200	0.00224000
C	-1.39062400	0.00315500	0.00277900
C	-2.59121500	0.00229200	0.00148600
C	-4.04650100	-0.00157000	-0.00273100
H	-4.42905100	-0.81760700	-0.61802400
H	-4.43882700	-0.12771900	1.00800500
H	-4.43618300	0.93576800	-0.40289900

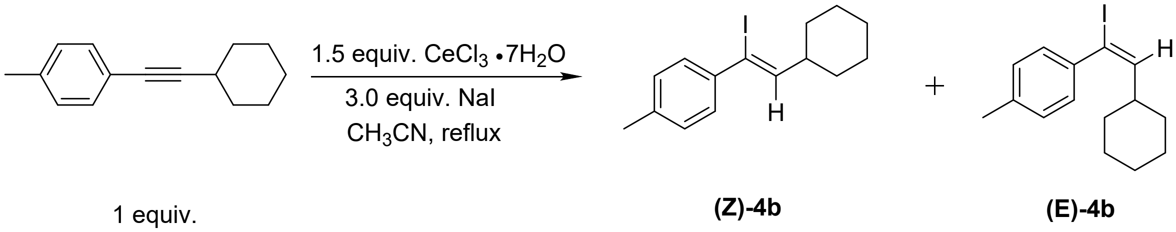
5. Further application of the synthesized products

4a:



(E)-(2-chloro-1-cyclohexyl-2-(p-tolyl)vinyl)(p-tolyl)sulfane (4a): To a mixture of 1-(cyclohexylethynyl)-4-methylbenzene (39.6 mg, 0.2 mmol), p-tolyl hypochlorothioite (37.9 mg, 0.24 mmol), $FeCl_2 \cdot 4H_2O$ (1.9 mg, 0.01 mmol) in toluene (2 mL) and the reaction was stirred at room temperature under N_2 atmosphere. After 12 h, the crude product was purified by column chromatography using petroleum ether as the eluent system to give the product as a yellow oil (43.4 mg, 61%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.29-7.25 (m, 2H), 7.23-7.19 (m, 4H), 7.10 (d, J = 8.2 Hz, 2H), 2.64-2.60 (m, 1H), 2.40 (s, 3H), 2.31 (s, 3H), 1.74-1.50 (m, 7H), 1.09-1.07 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.48, 138.75, 137.97, 136.07, 135.04, 133.03, 129.68, 129.16, 128.15, 126.92, 44.57, 31.26, 25.78, 25.51, 21.38, 21.01. HRMS (EI) calculated for $C_{22}H_{25}ClS$ $[M]^+$: 356.1360; found: 356.1360.

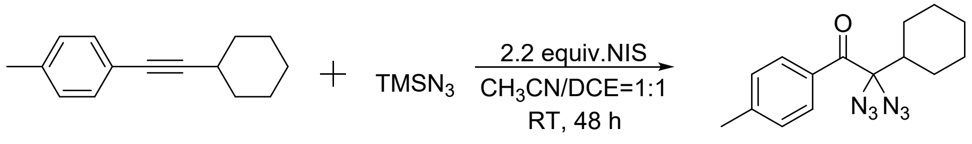
4b:



(Z)-1-(2-cyclohexyl-1-iodovinyl)-4-methylbenzene ((Z)-4b) and (E)-1-(2-cyclohexyl-1-iodovinyl)-4-methylbenzene ((E)-4b): To a mixture of 1-(cyclohexylethynyl)-4-methylbenzene (39.6 mg, 0.2 mmol), $CeCl_3 \cdot 7H_2O$ (111.8 mg, 0.3 mmol), sodium iodide (89.9 mg, 0.6 mmol) in CH_3CN (2 mL) and the reaction was stirred at reflux. After 24 h, the crude product was purified by column chromatography using petroleum ether as the eluent system to give the product as a colorless oil (55.4 mg, 85%, **(Z)-4b: (E)-4b=2.65:1**). ^1H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, J =

8.2 Hz, 0.7H), 7.19 (d, J = 8.1 Hz, 2H), 7.15-7.06 (m, 2.7H), 6.31 (d, J = 10.2 Hz, 1H), 5.68 (d, J = 8.4 Hz, 0.35H), 2.46-2.30 (m, 4.4H), 2.08-2.05 (m, 1H), 1.90-1.53 (m, 7.4H), 1.45-1.32 (m, 0.7H), 1.30-1.09 (m, 5.4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.84, 143.12, 140.55, 139.42, 137.95, 137.78, 128.88, 128.79, 128.52, 128.39, 102.52, 94.07, 46.61, 41.20, 32.72, 31.64, 25.99, 25.77, 25.68, 25.46, 21.32, 21.10. HRMS (EI) calculated for $C_{15}H_{19}I$ $[M]^+$: 326.0526; found: 326.0526.

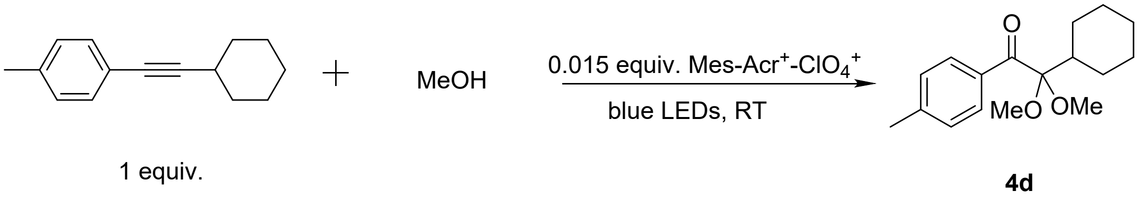
4c:



4c

2,2-diazido-2-cyclohexyl-1-(p-tolyl)ethan-1-one (4c): To a mixture of 1-(cyclohexylethynyl)-4-methylbenzene (39.6 mg, 0.2 mmol), three methyl azide silane (58 μL, 0.44 mmol), N-Iodosuccinimide (49.5 mg, 0.22 mmol) in CH_3CN:DCE=1:1 (1 mL:1 mL) and the reaction was stirred at room temperature under an argon atmosphere. After 48 h, the crude product was purified by column chromatography using petroleum ether as the eluent system to give the product as a colorless oil (22.6 mg, 38%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, J = 8.4 Hz, 2H), 7.28 (d, J = 8.1 Hz, 2H), 2.43 (s, 3H), 2.15-2.13 (m, 1H), 1.76-1.75 (m, 2H), 1.68-1.65 (m, 3H), 1.29-1.25 (m, 2H), 1.18-1.07 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.55, 144.85, 131.15, 130.28, 129.38, 88.76, 46.33, 26.73, 25.86, 25.85, 21.75. HRMS (EI) calculated for $C_{15}H_{18}N_6O$ $[M]^+$: 298.1537; found: 298.1537.

4d:

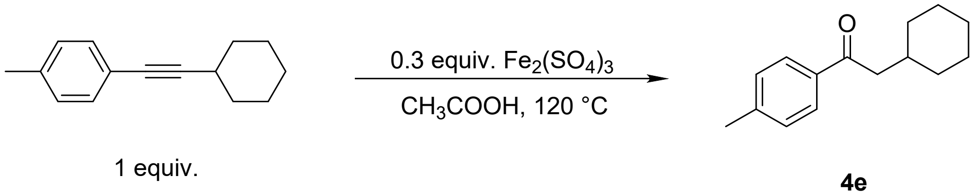


4d

2-cyclohexyl-2,2-dimethoxy-1-(p-tolyl)ethan-1-one (4d): A 10 mL glass reaction tube was added a magnetic stir bar, 1-(cyclohexylethynyl)-4-methylbenzene (39.6 mg, 0.2 mmol), 9-Mesityl-10-methylacridinium Perchlorate (1.2 mg, 0.003 mmol) in MeOH:CH_3CN=6:1 (2.4 mL:

0.4 mL) under an oxygen atmosphere. Then the reaction tube was set to stir (800 rpm) and irradiated with a blue LED (2 cm away, with circulating water to keep the reaction at room temperature). After 12 h, the crude product was purified by column chromatography using petroleum ether : ether = 30:1 as the eluent system to give the product as a colorless oil (37.0 mg, 67%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, J = 8.3 Hz, 2H), 7.20 (d, J = 8.2 Hz, 2H), 3.30 (s, 6H), 2.39 (s, 3H), 1.97-1.91 (m, 1H), 1.90-1.88 (m, 2H), 1.72-1.70 (m, 2H), 1.58-1.56 (m, 1H), 1.18-1.14 (m, 2H), 1.02- 0.82 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.07, 143.48, 134.72, 130.85, 128.78, 107.86, 49.85, 42.82, 27.85, 26.63, 26.16, 21.63. HRMS (EI) calculated for $C_{17}H_{24}O_3$ $[M]^+$: 276.1720; found: 276.1720.

4e:

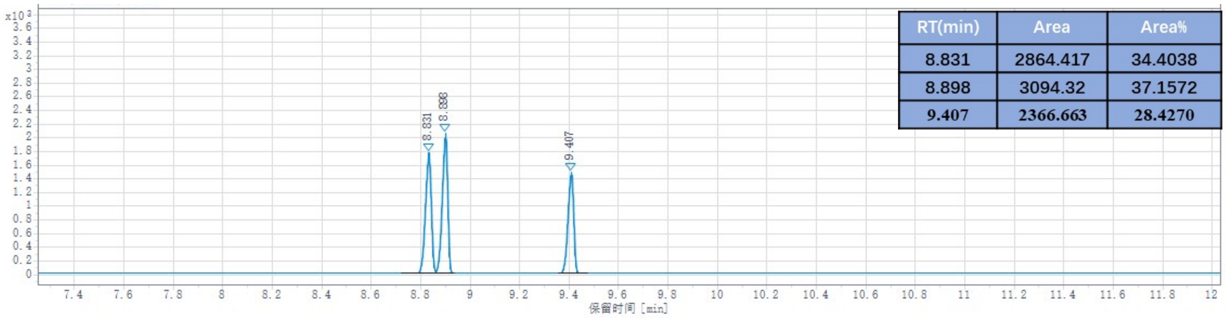


2-cyclohexyl-1-(p-tolyl)ethan-1-one (4e): To a mixture of 1-(cyclohexylethynyl)-4-methylbenzene (39.6 mg, 0.2 mmol), $Fe_2(SO_4)_3$ (24.0 mg, 0.06 mmol) in CH_3COOH (1 mL) and the reaction was stirred at 120 °C. After 16 h, the crude product was purified by column chromatography using petroleum ether : ether = 50:1 as the eluent system to give the product as a colorless oil (41.1 mg, 95%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, J = 8.2 Hz, 2H), 7.24 (d, J = 7.9 Hz, 2H), 2.78 (d, J = 6.8 Hz, 2H), 2.40 (s, 3H), 2.01-1.90 (m, 1H), 1.81-1.55 (m, 5H), 1.35-0.94 (m, 5H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 200.03, 143.60, 135.02, 129.23, 128.31, 46.14, 34.71, 33.47, 26.29, 26.19, 21.62. HRMS (EI) calculated for $C_{15}H_{20}O$ $[M]^+$: 216.1509; found: 216.1509.

6. GC Chromatogram, GC-MS Chromatogram and NMR Spectra

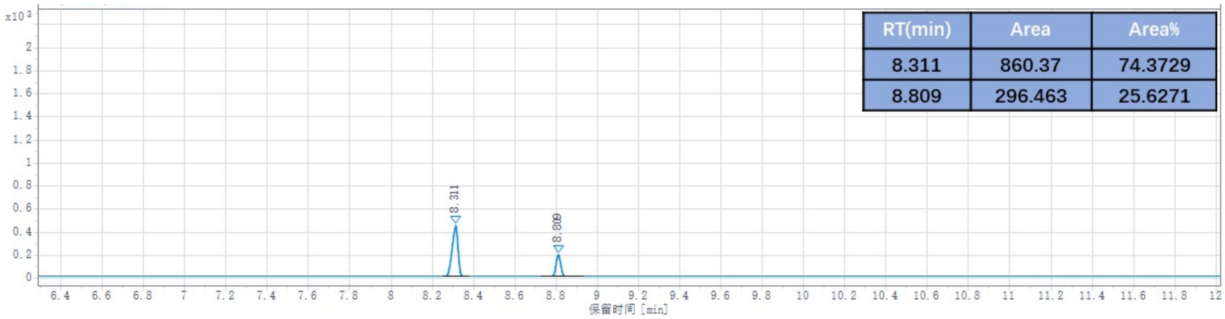
6.1 GC Chromatogram

3fa:



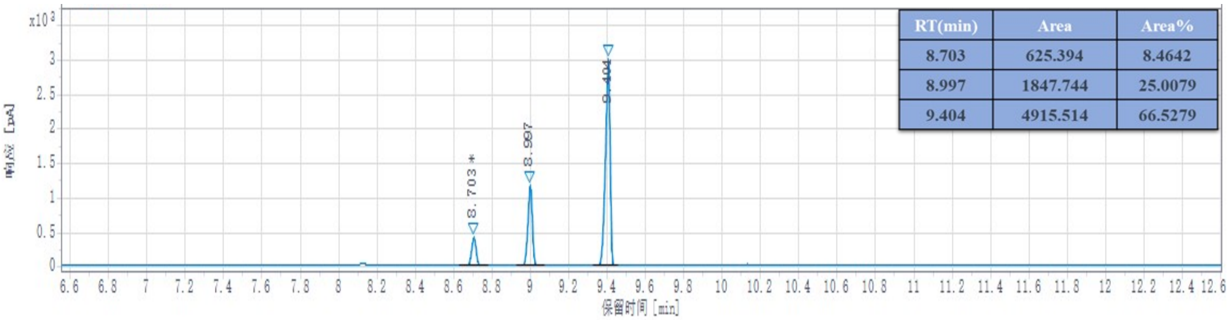
RT(min)	Area	Area%
8.831	2864.417	34.4038
8.898	3094.32	37.1572
9.407	2366.663	28.4270

3ga:



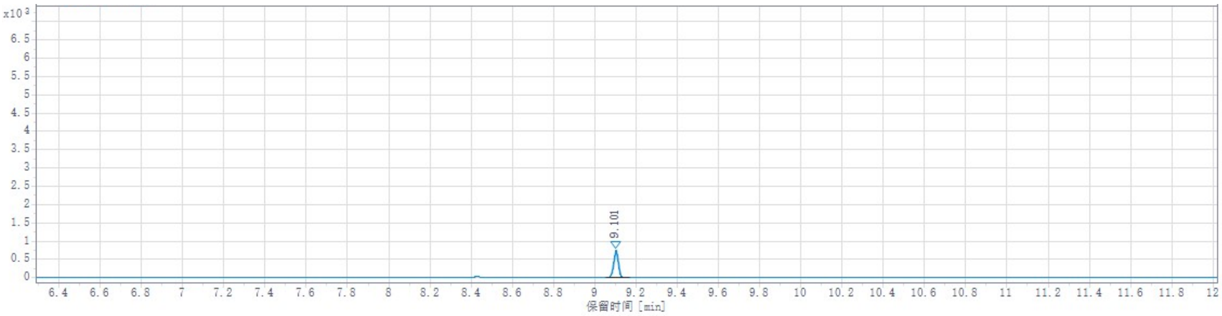
RT(min)	Area	Area%
8.311	860.37	74.3729
8.809	296.463	25.6271

3ha:

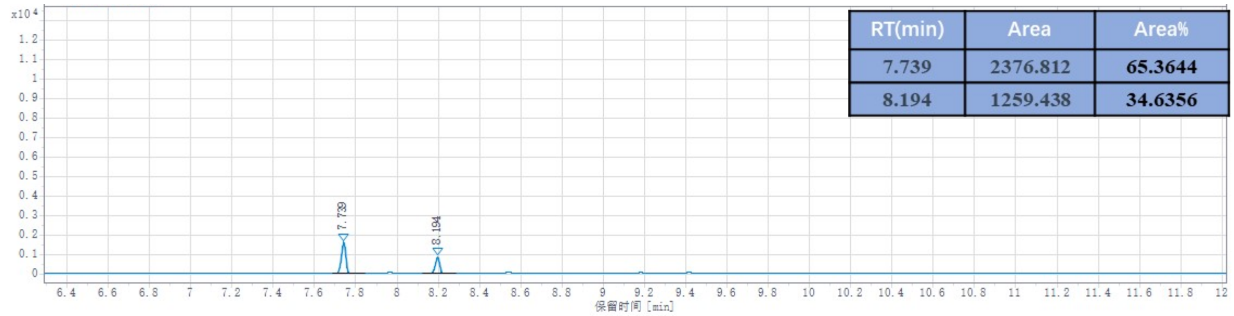


RT(min)	Area	Area%
8.703	625.394	8.4642
8.997	1847.744	25.0079
9.404	4915.514	66.5279

3ia:

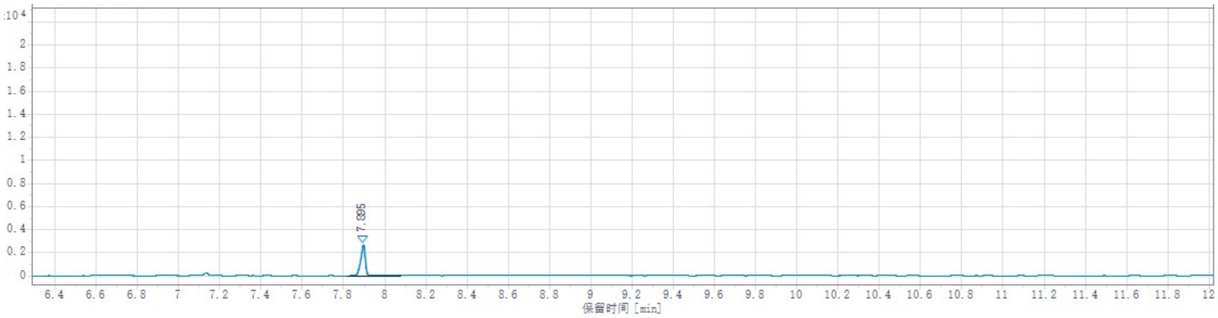


3ja:

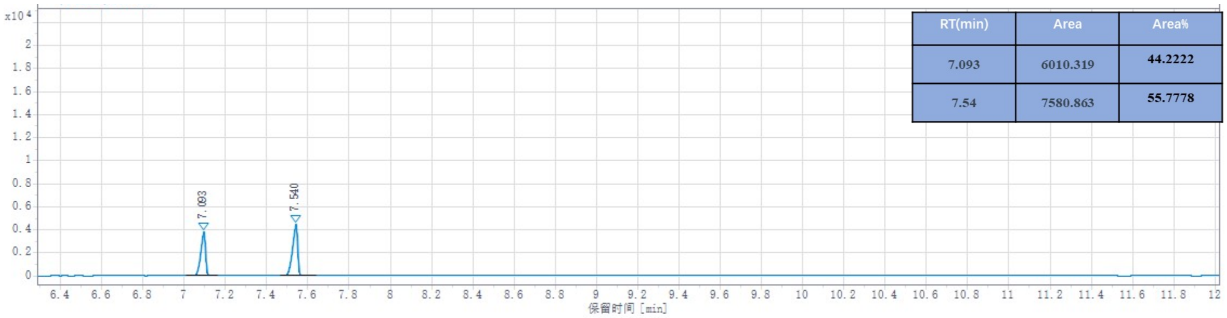


RT(min)	Area	Area%
7.739	2376.812	**65.3644**
8.194	1259.438	**34.6356**

3ka:



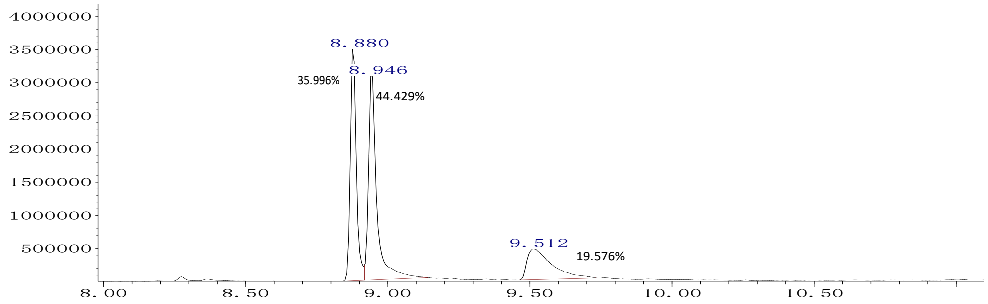
3la:



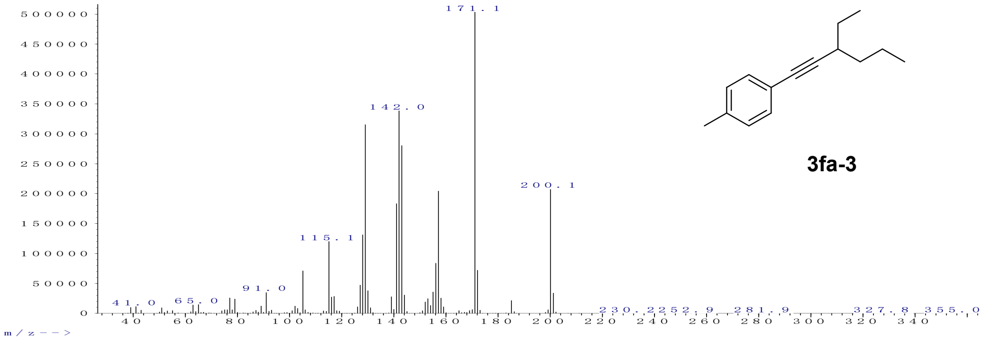
RT(min)	Area	Area%
7.093	6010.319	**44.2222**
7.54	7580.863	**55.7778**

6.2 GC-MS spectrum

3fa:

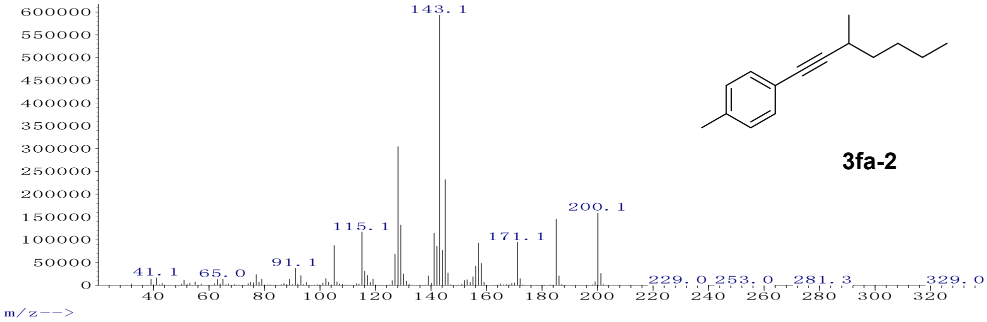


8.880 min:



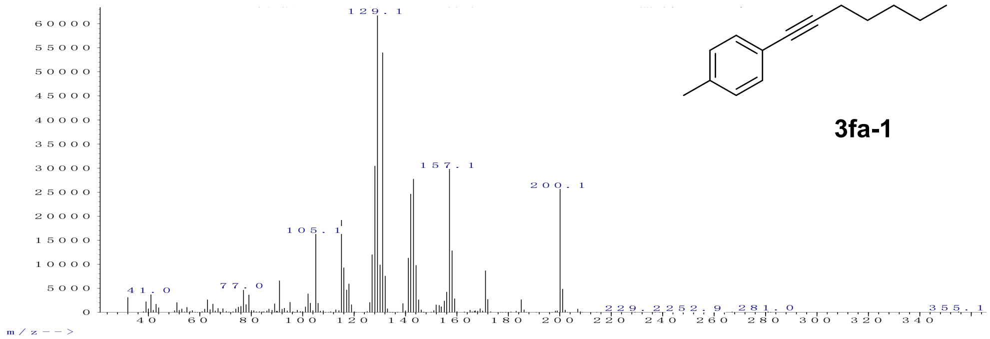
3fa-3

8.946 min:



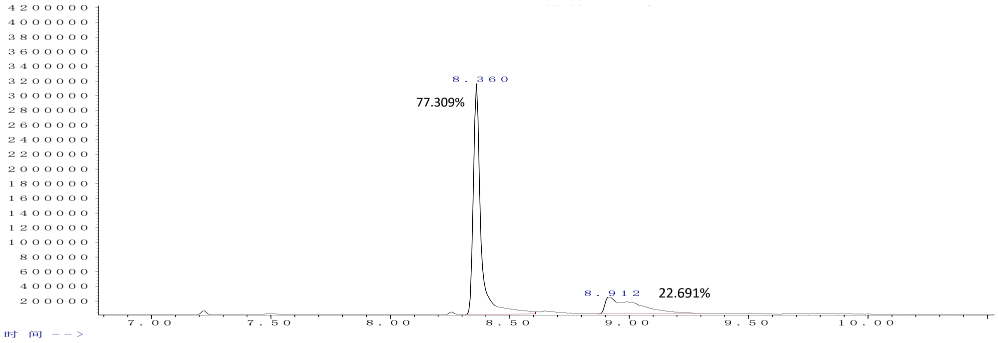
3fa-2

9.512 min:

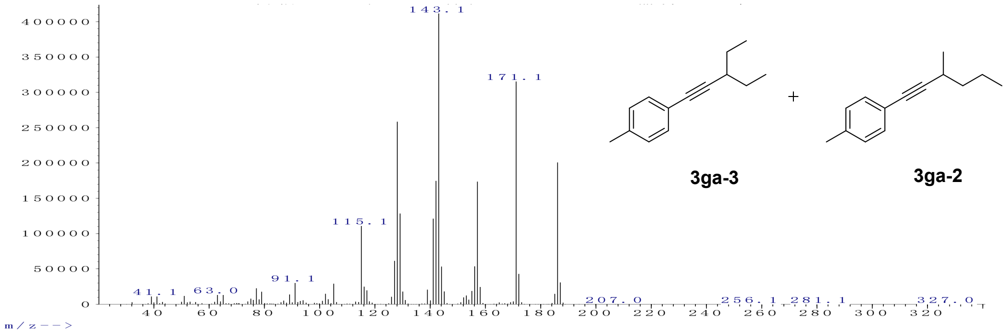


3fa-1

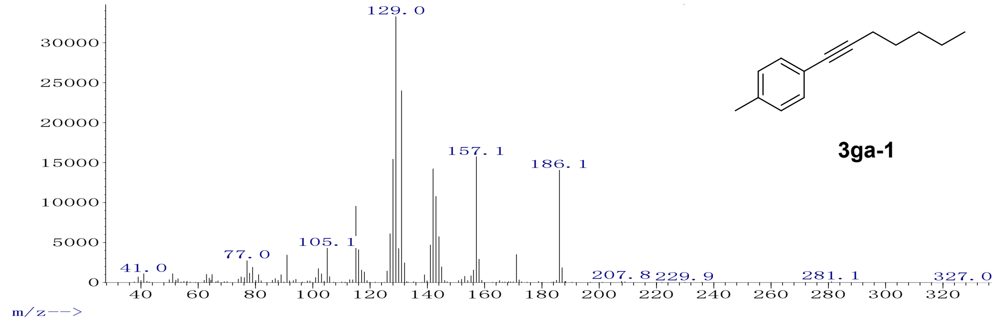
3ga:



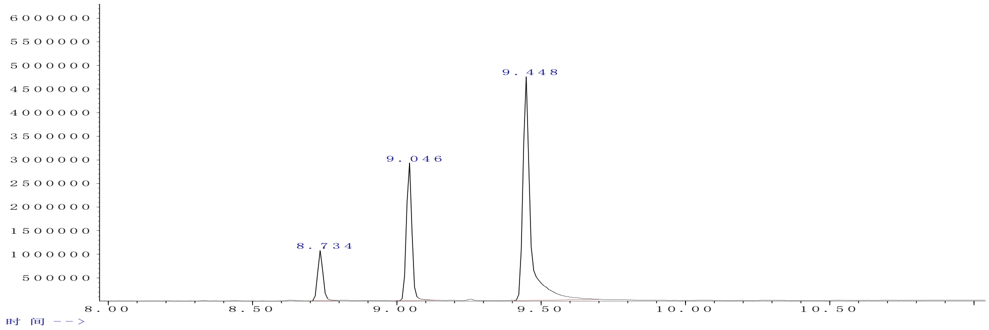
8.360 min:



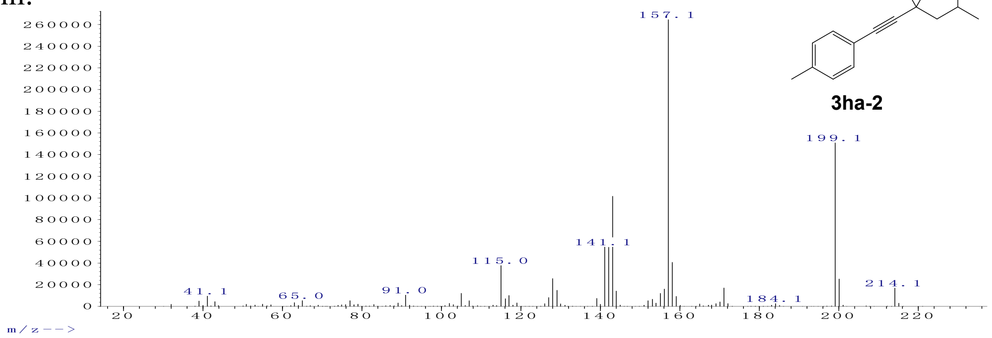
8.912 min:



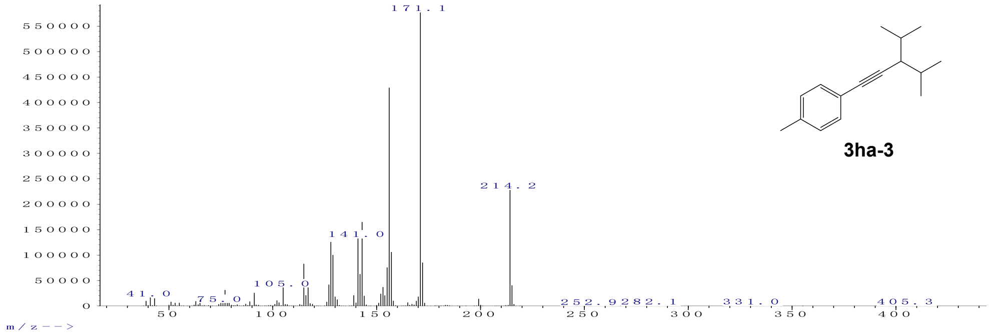
3ha:



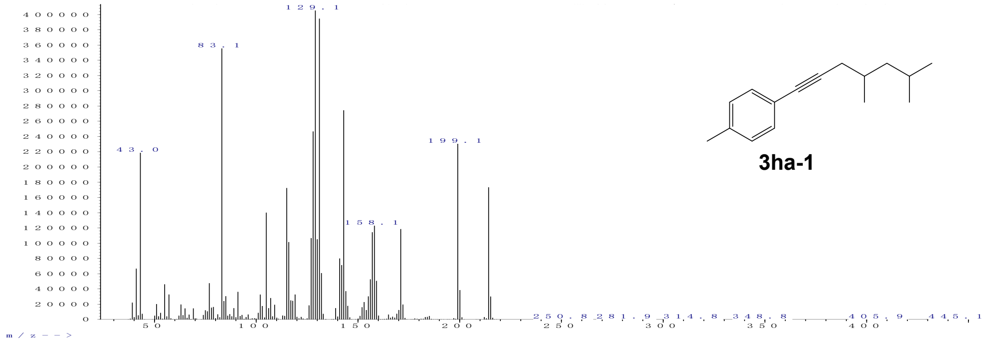
8.734 min:



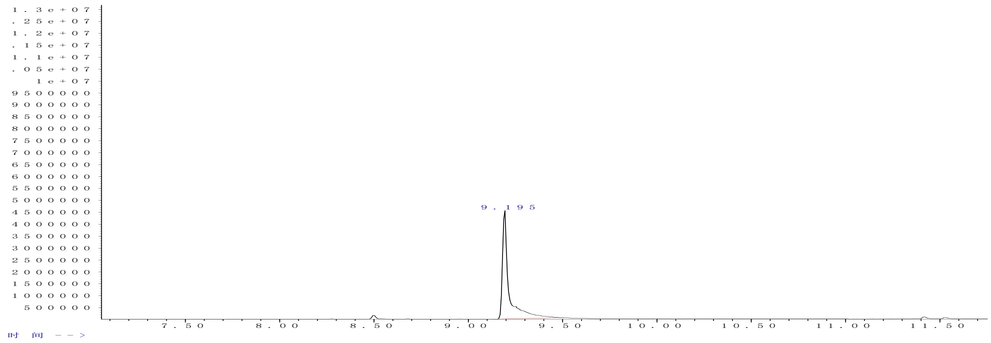
9.046 min:



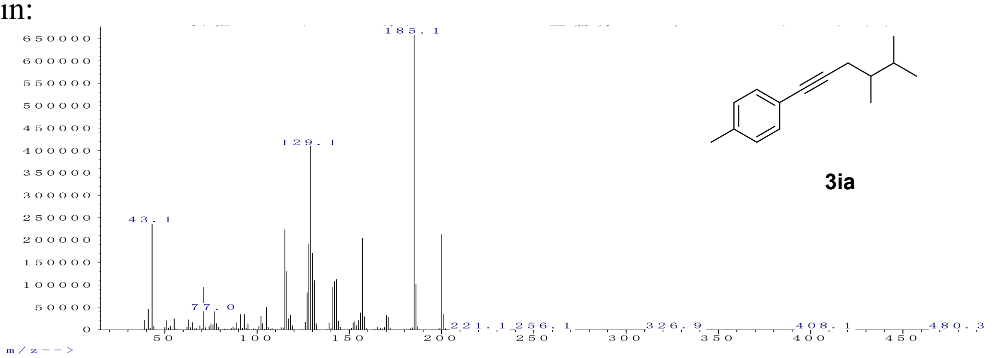
9.448 min:



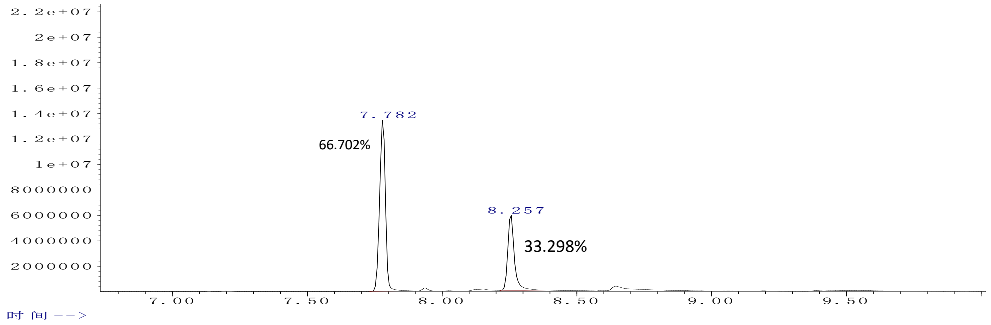
3ia:


1.3e+07
.25e+07
1.2e+07
.15e+07
1.1e+07
.05e+07
1e+07
9500000
9000000
8500000
8000000
7500000
7000000
6500000
6000000
5500000
5000000
4500000
4000000
3500000
3000000
2500000
2000000
1500000
1000000
500000
9.195
7.50
8.00
8.50
9.00
9.50
10.00
10.50
11.00
11.50
时间 -->

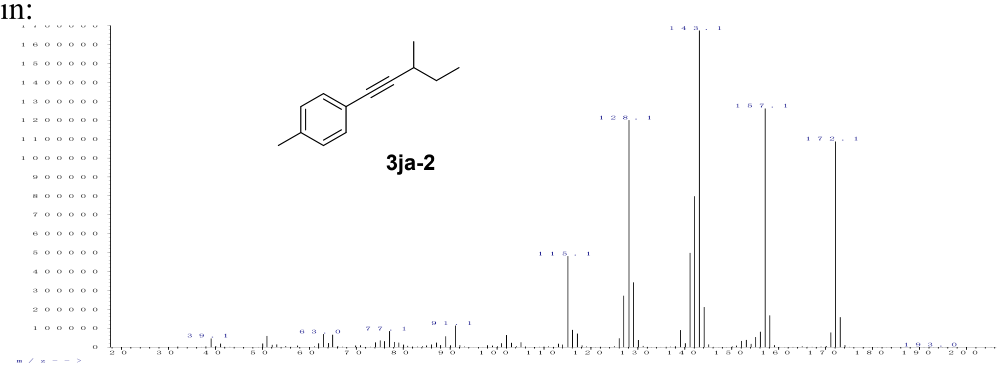
9.195 min:


650000
600000
550000
500000
450000
400000
350000
300000
250000
200000
150000
100000
50000
0
185.1
129.1
43.1
77.0
221.1
256.1
326.9
408.1
480.3
50
100
150
200
250
300
350
400
450
m/z-->
3ia

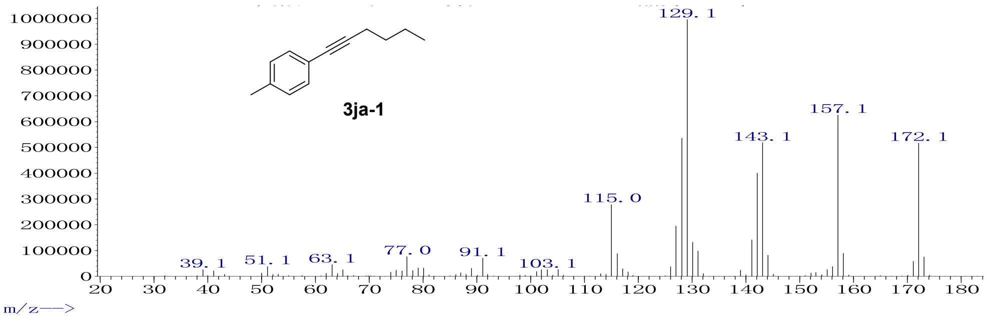
3ja:



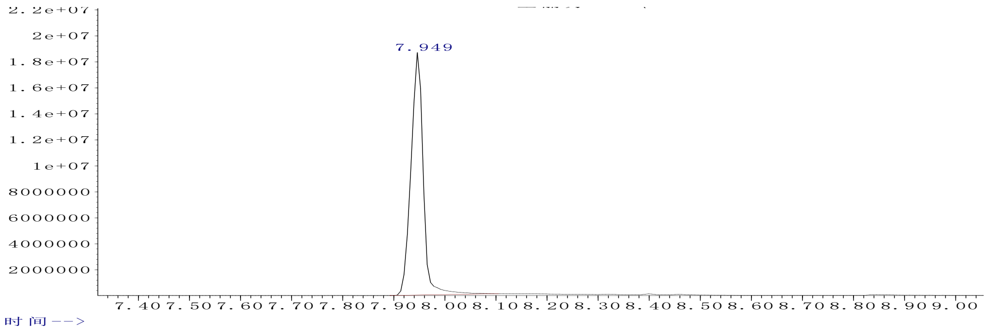
7.782 min:



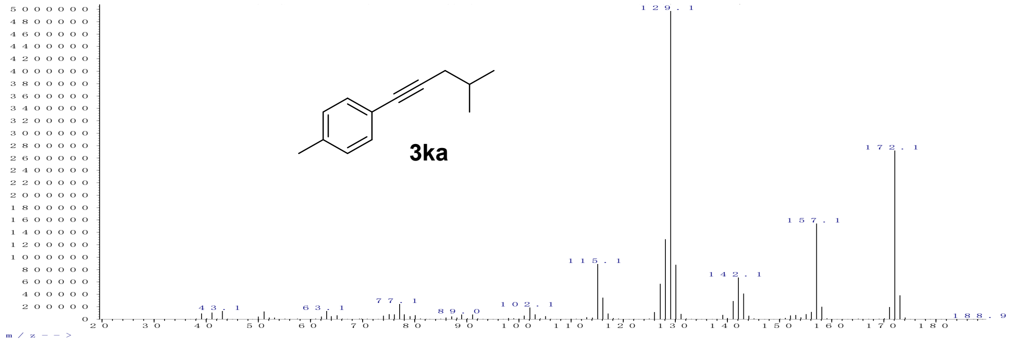
8.257 min:



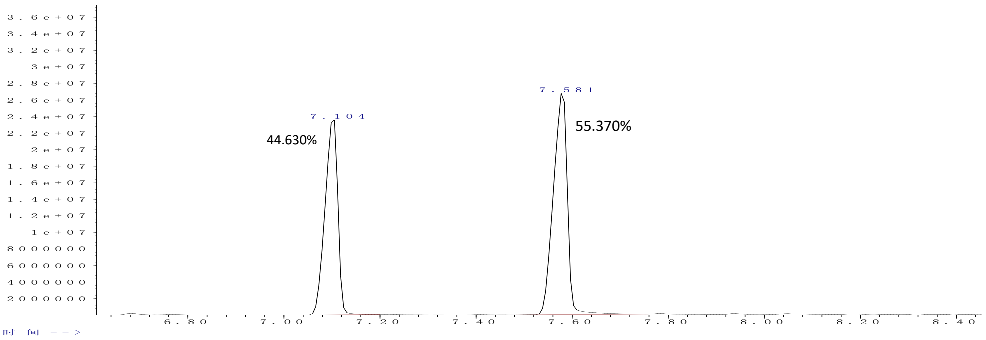
3ka:


2.2e+07
2e+07
1.8e+07
1.6e+07
1.4e+07
1.2e+07
1e+07
8000000
6000000
4000000
2000000
7.949
7.40
7.50
7.60
7.70
7.80
7.90
8.00
8.10
8.20
8.30
8.40
8.50
8.60
8.70
8.80
8.90
9.00
时间-->

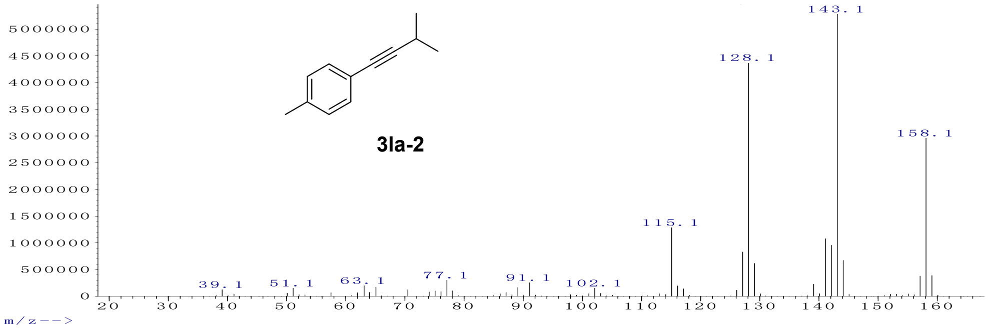
7.949 min:


5000000
4800000
4600000
4400000
4200000
4000000
3800000
3600000
3400000
3200000
3000000
2800000
2600000
2400000
2200000
2000000
1800000
1600000
1400000
1200000
1000000
800000
600000
400000
200000
0
3ka
43.1
63.1
77.1
89.0
102.1
115.1
129.1
142.1
157.1
172.1
188.9
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
m/z-->

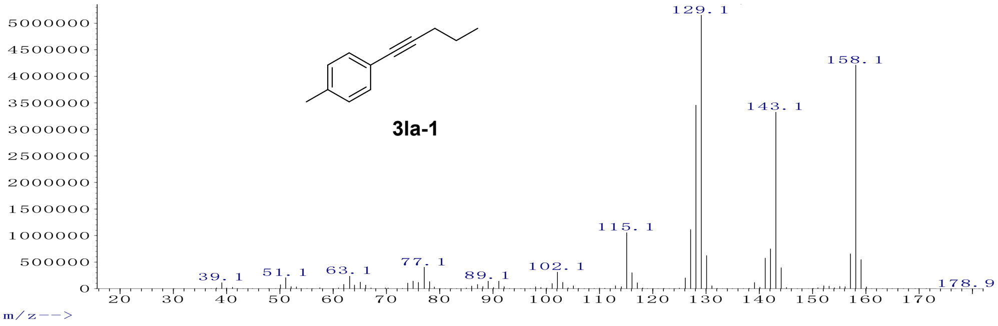
3la:



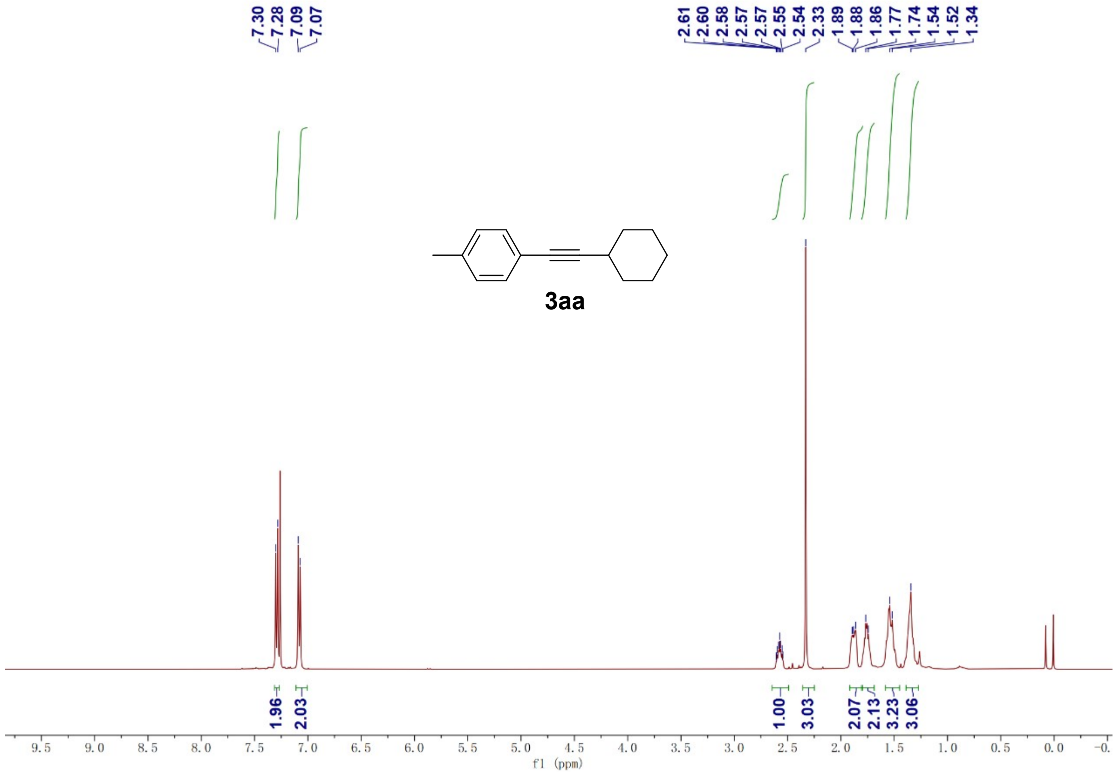
7.104 min:

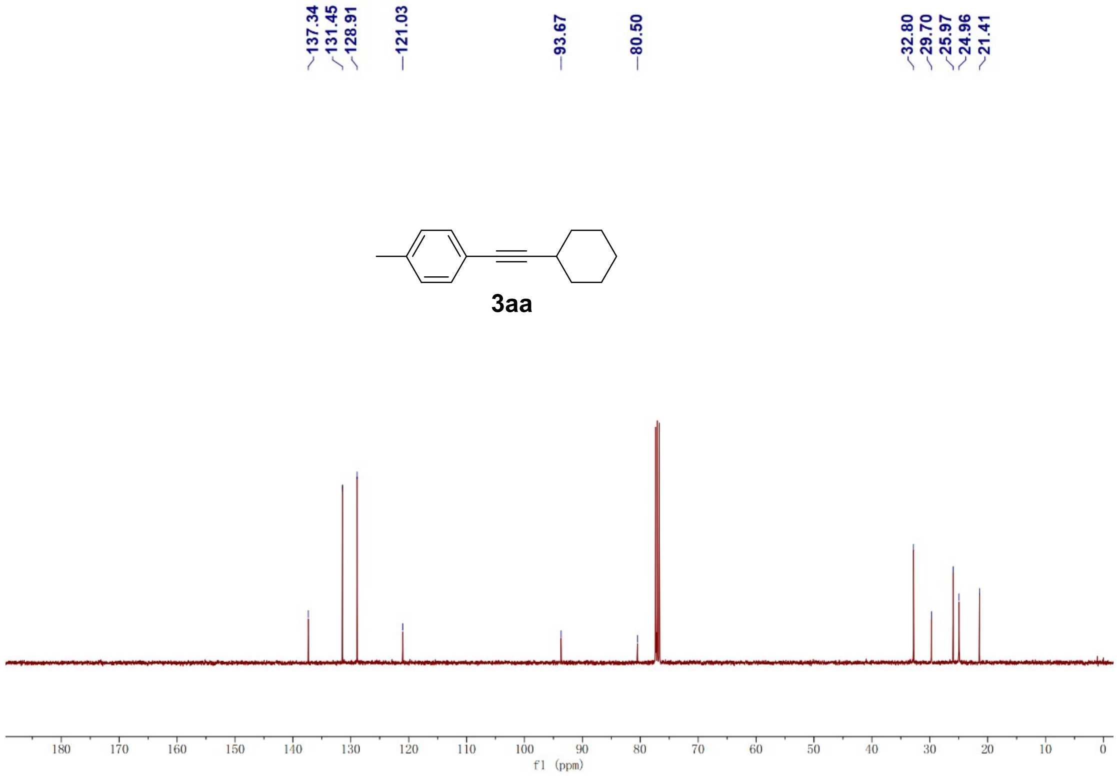


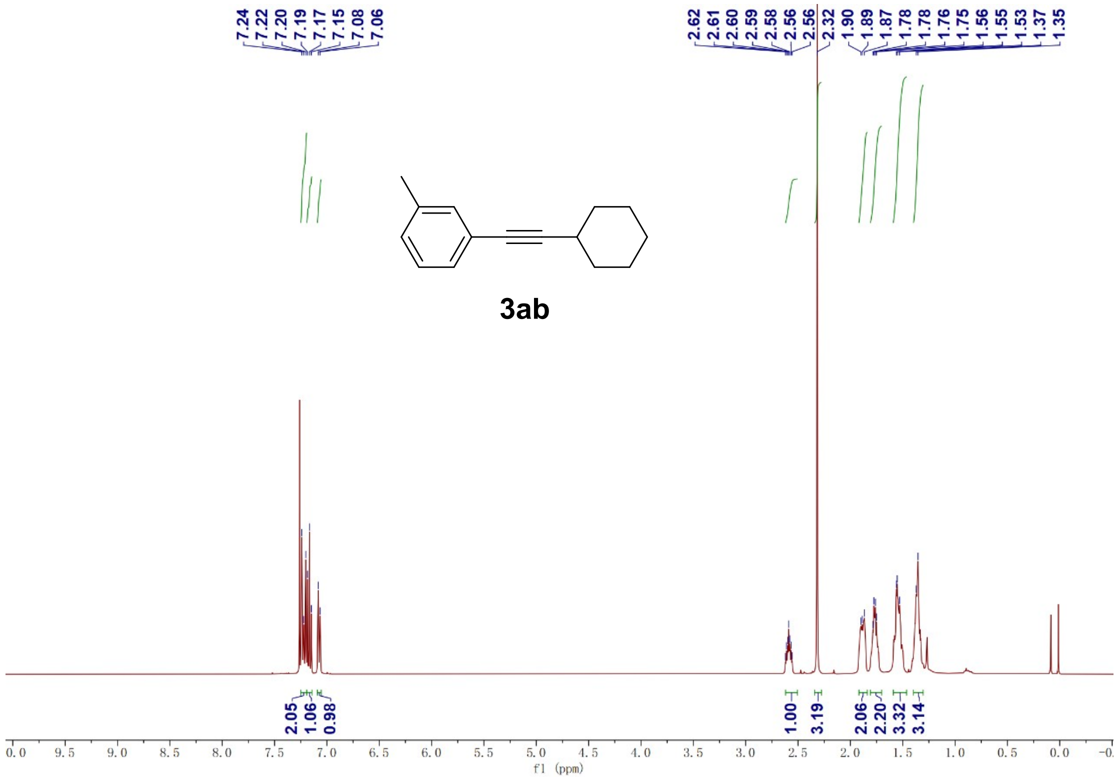
7.581 min:

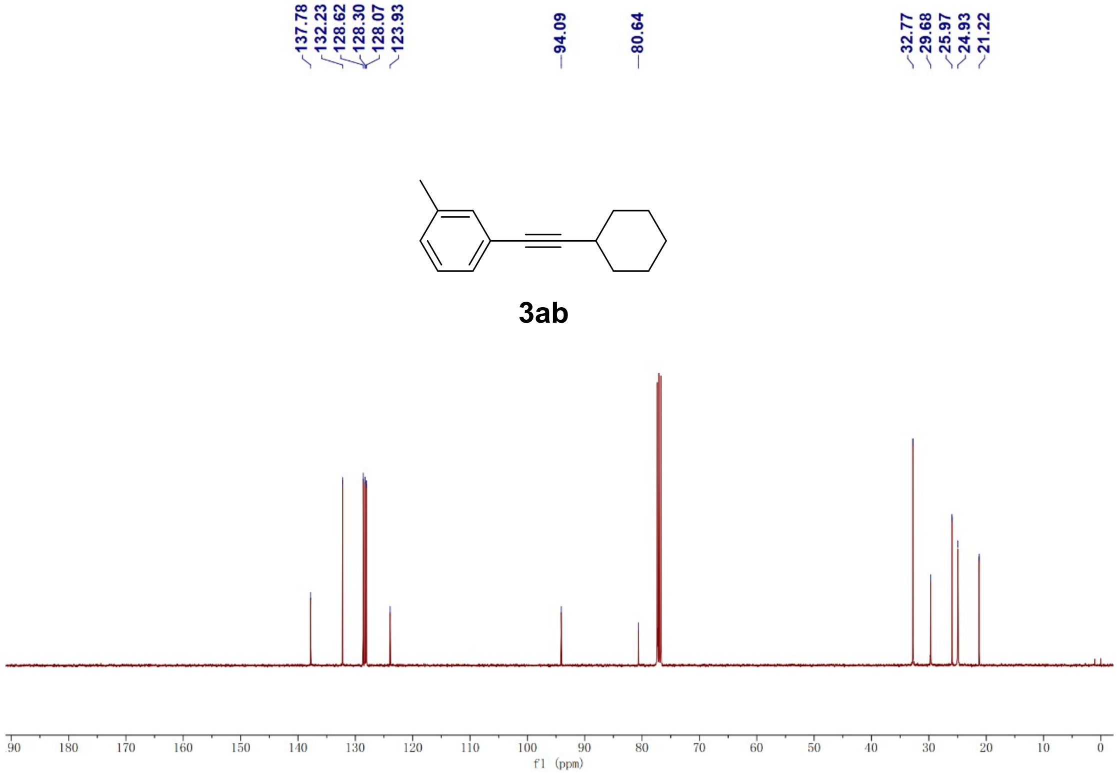


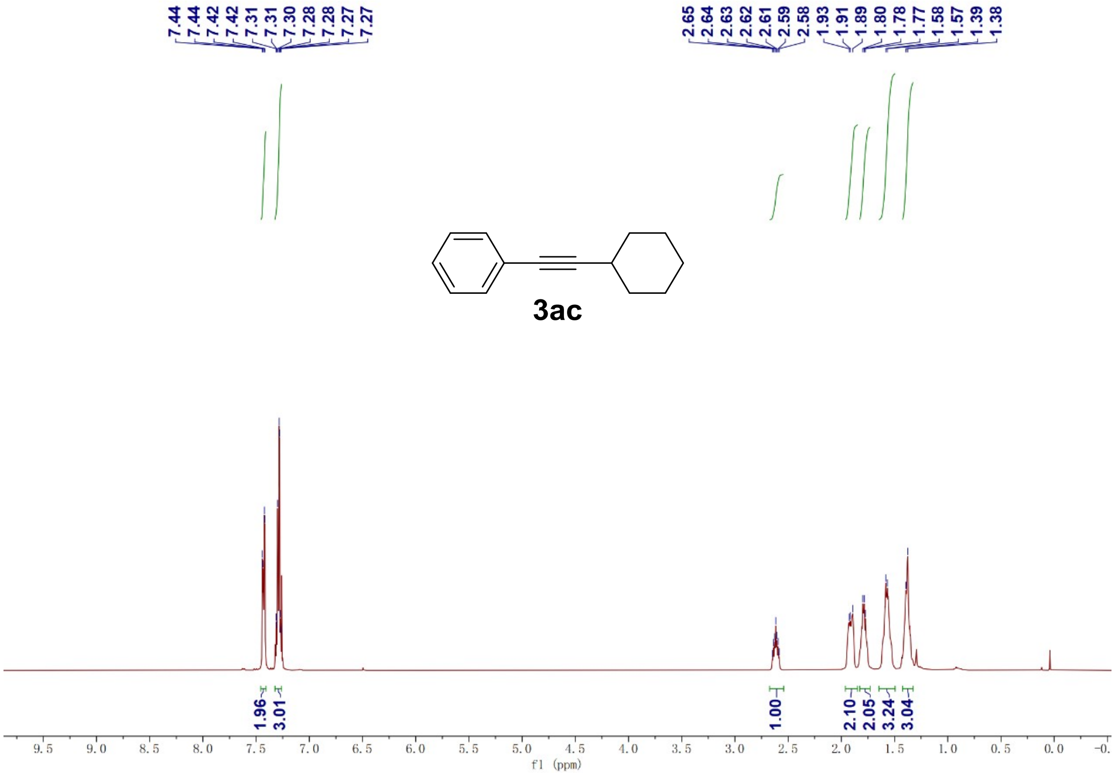
6.3 NMR Spectra of the Products

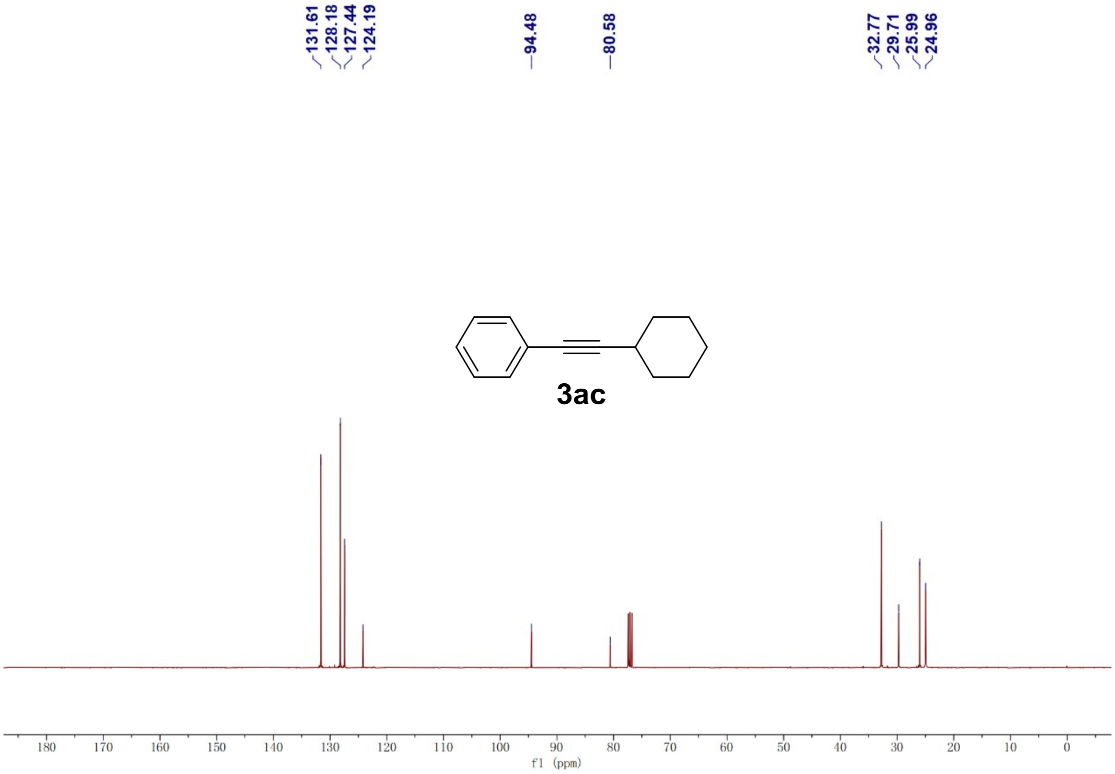


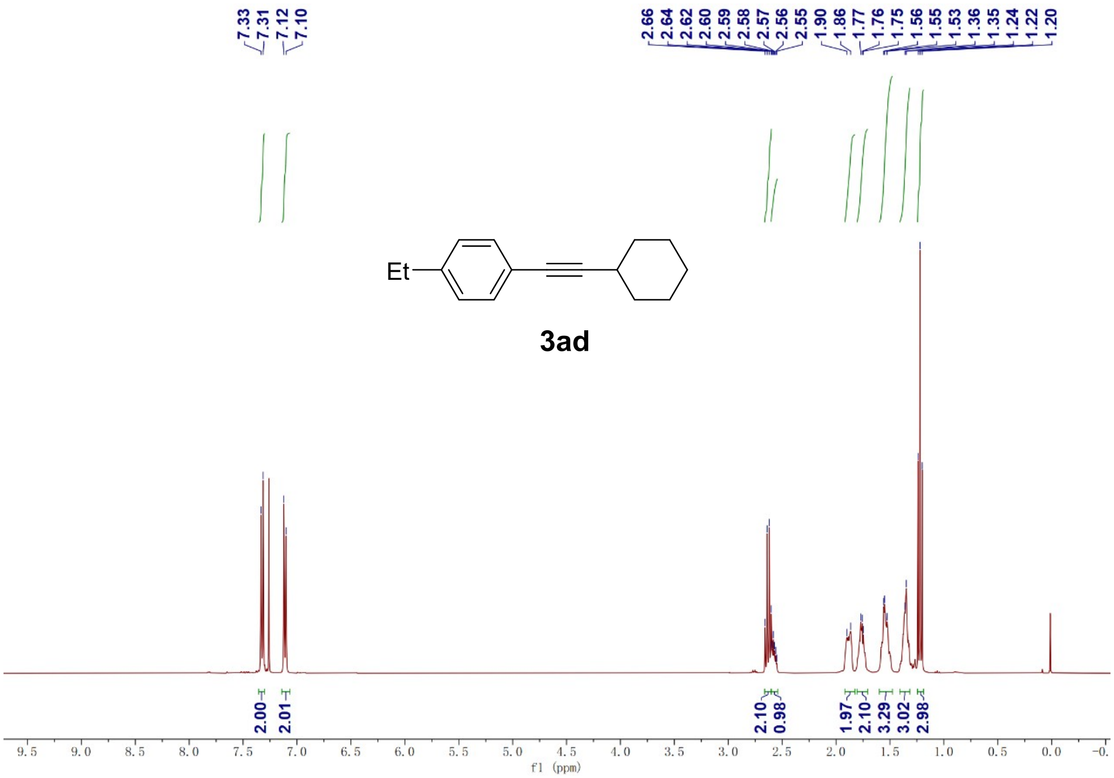



7.24
7.22
7.20
7.19
7.17
7.15
7.08
7.06
2.62
2.61
2.60
2.59
2.58
2.56
2.56
2.32
1.90
1.89
1.87
1.78
1.78
1.76
1.75
1.56
1.55
1.53
1.37
1.35
3ab
2.05
1.06
0.98
1.00
3.19
2.06
2.20
3.32
3.14
0.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.
f1 (ppm)

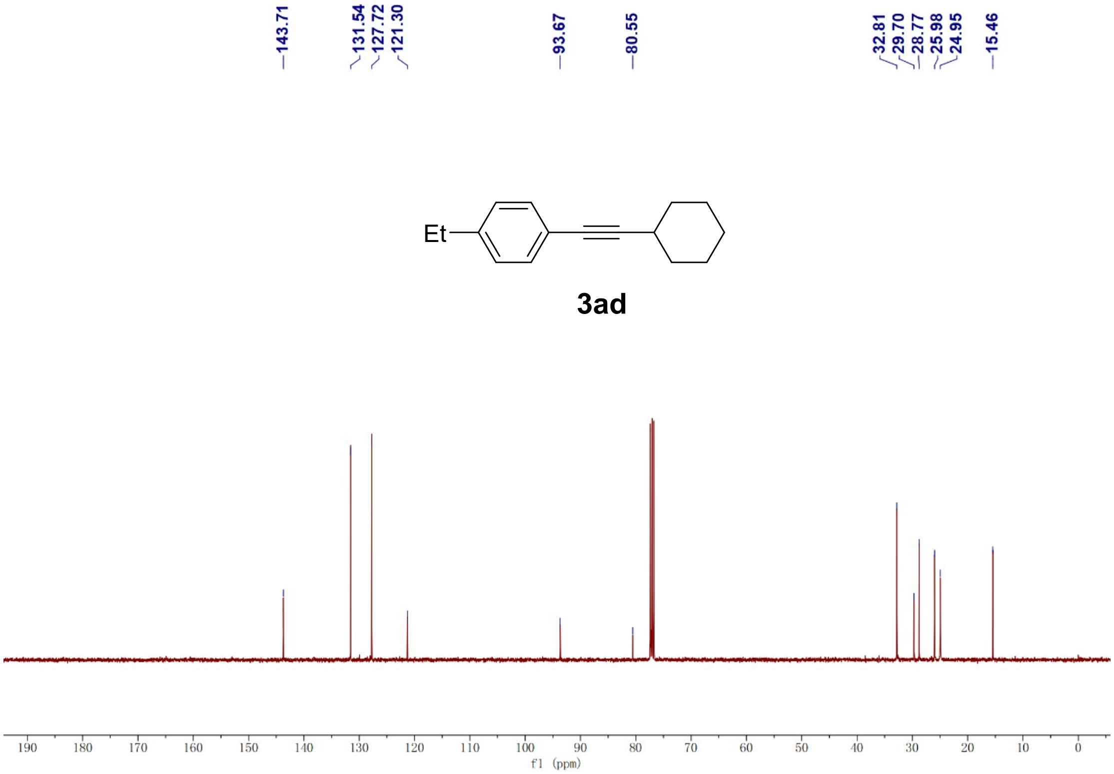

137.78
132.23
128.62
128.30
128.07
123.93
94.09
80.64
32.77
29.68
25.97
24.93
21.22
3ab
90
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


3ac
7.44
7.44
7.42
7.42
7.31
7.31
7.30
7.28
7.28
7.27
7.27
2.65
2.64
2.63
2.62
2.61
2.59
2.58
1.93
1.91
1.89
1.80
1.78
1.77
1.58
1.57
1.39
1.38
1.96
3.01
1.00
2.10
2.05
3.24
3.04
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.
f1 (ppm)

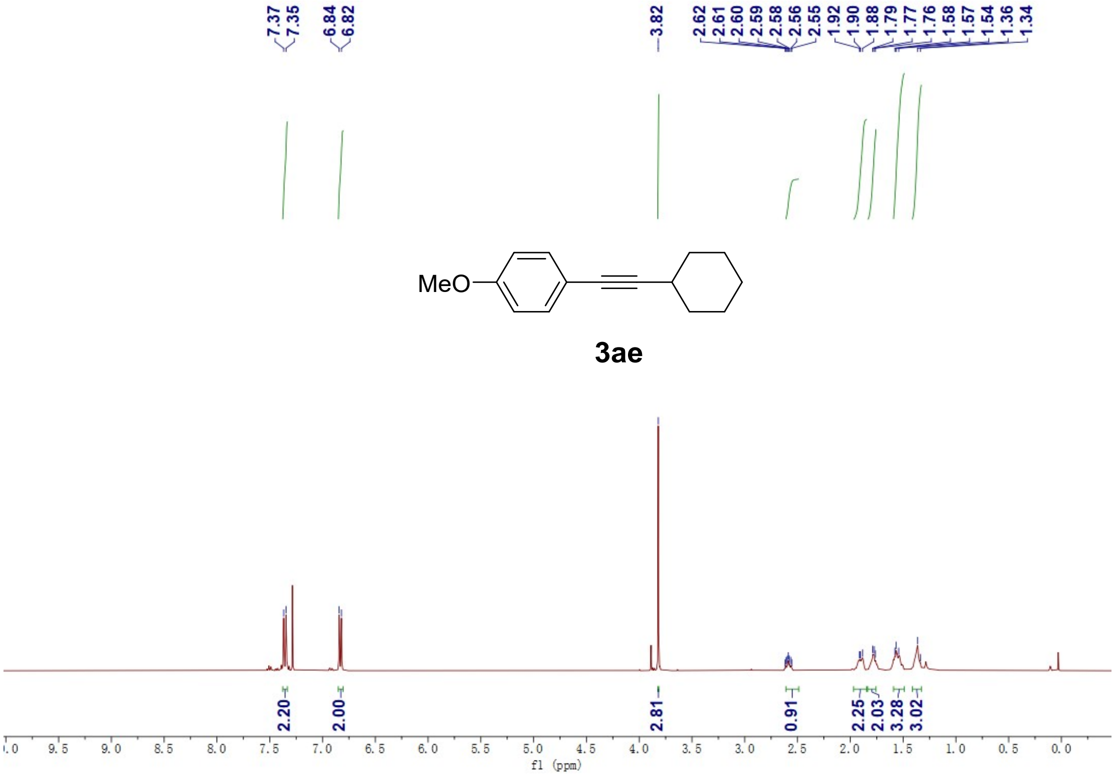

3ac
131.61
128.18
127.44
124.19
94.48
80.58
32.77
29.71
25.99
24.96
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

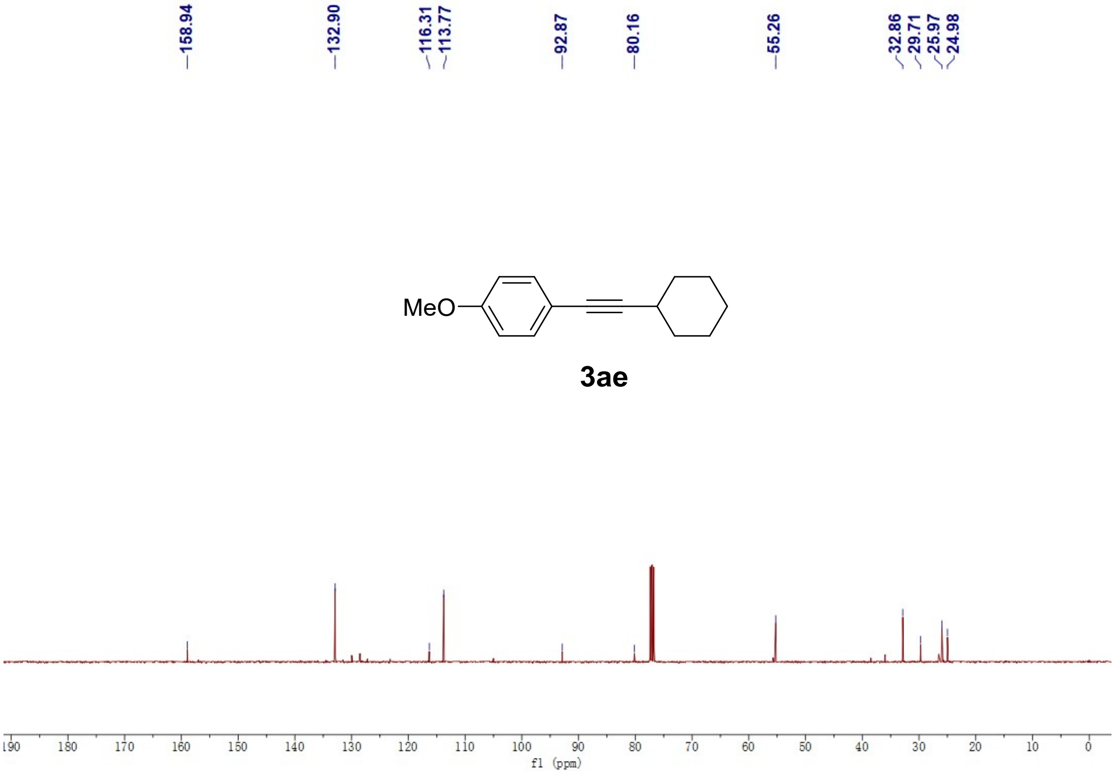

7.33
7.31
7.12
7.10
2.66
2.64
2.62
2.60
2.59
2.58
2.57
2.56
2.55
1.90
1.86
1.77
1.76
1.75
1.56
1.55
1.53
1.36
1.35
1.24
1.22
1.20
Et
2.00
2.01
2.10
0.98
1.97
2.10
3.29
3.02
2.98
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.
f1 (ppm)

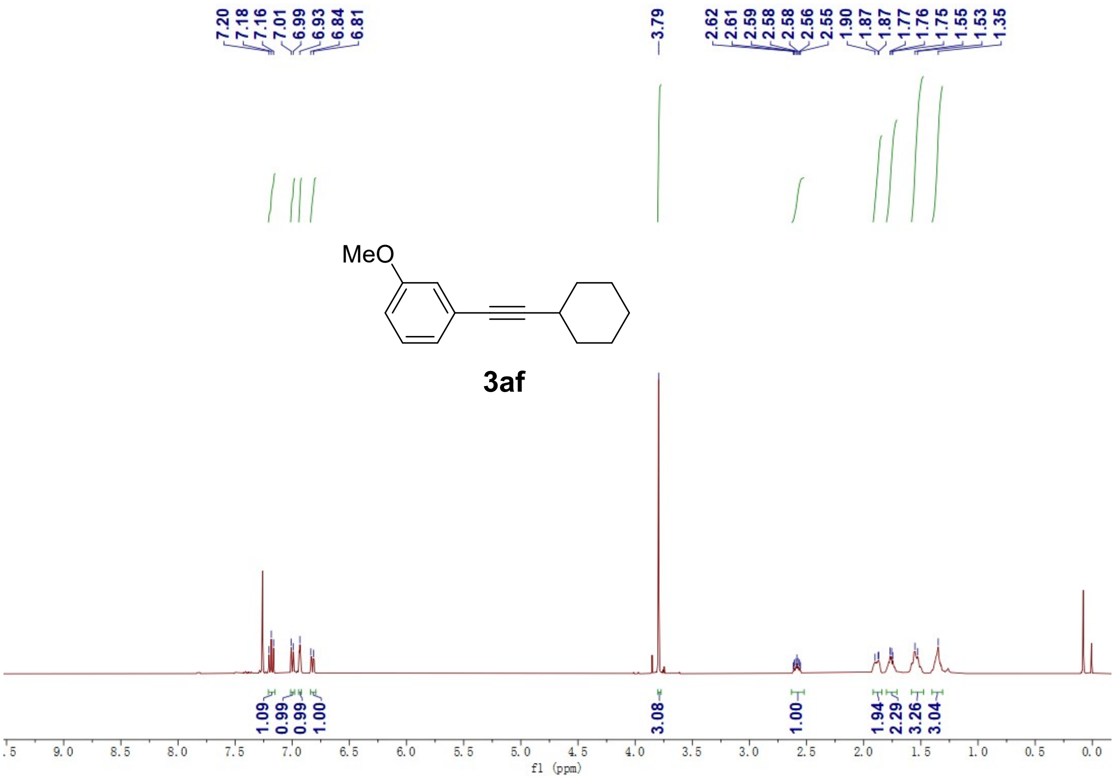
3ad

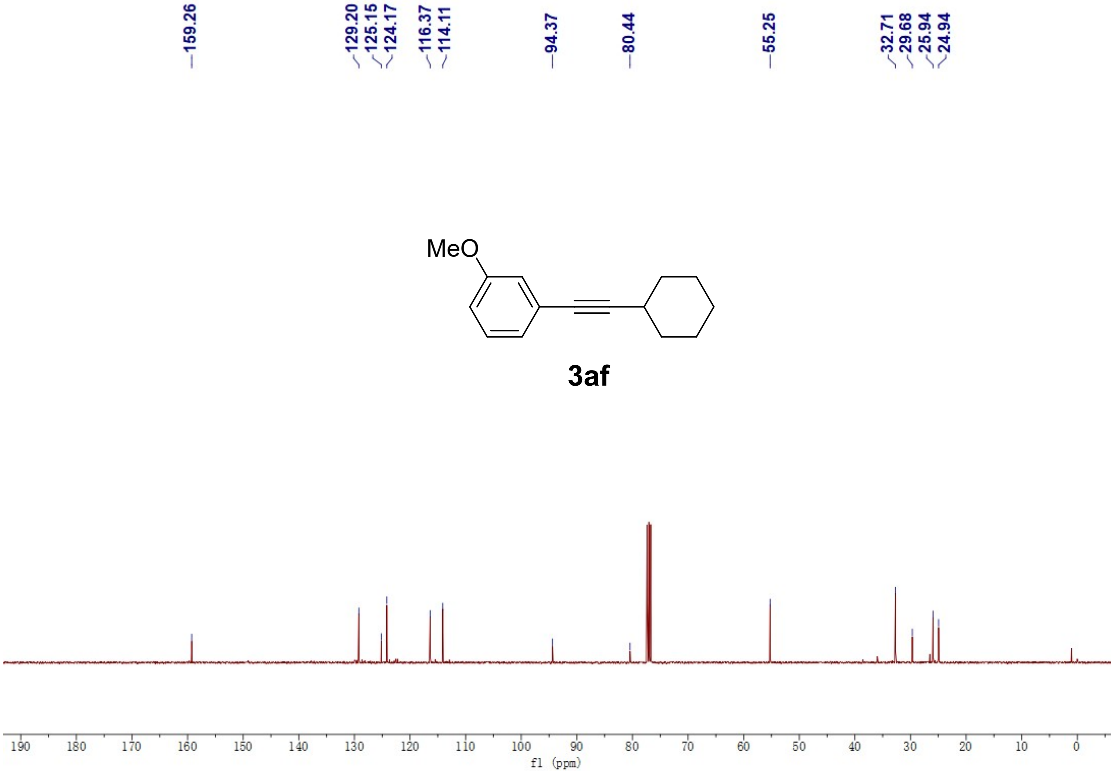

143.71
131.54
127.72
121.30
93.67
80.55
32.81
29.70
28.77
25.98
24.95
15.46
Et
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

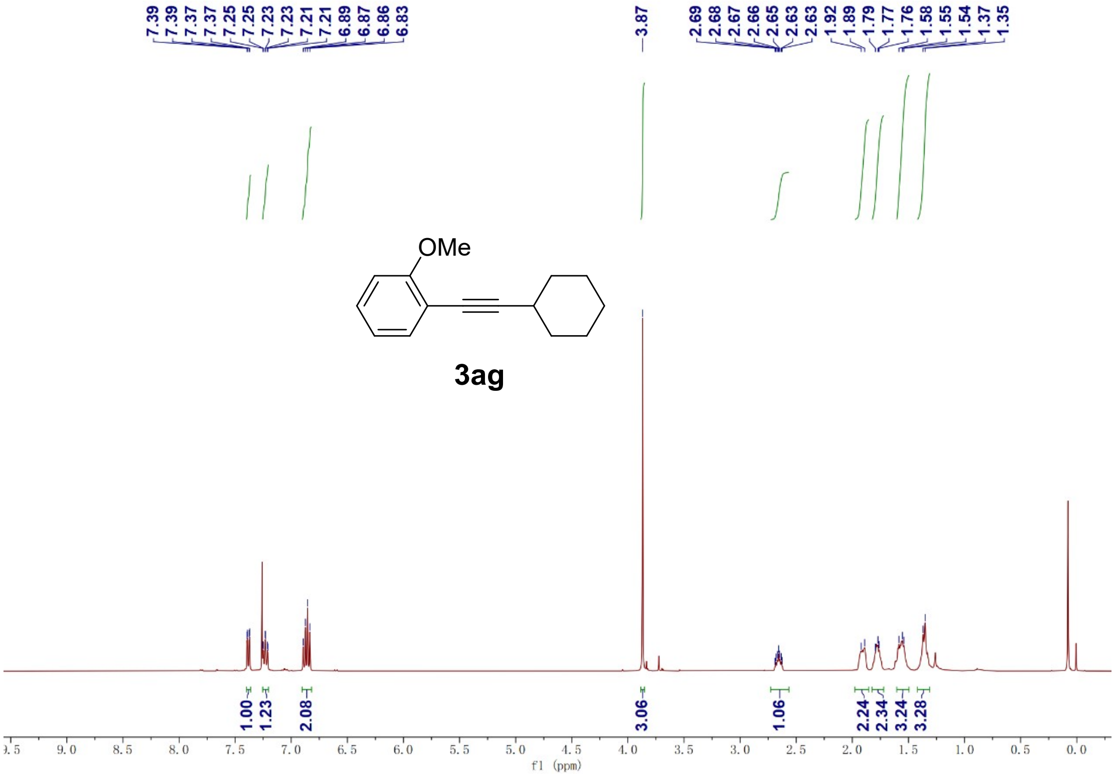
3ad

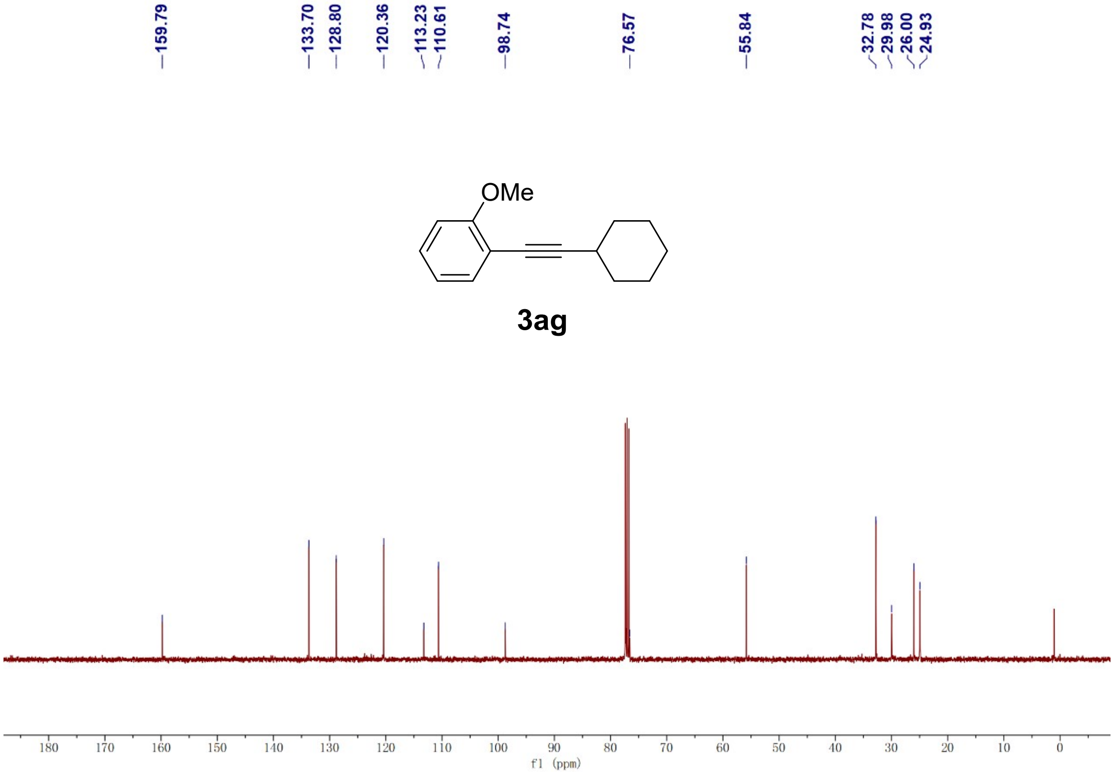

7.37
7.35
6.84
6.82
3.82
2.62
2.61
2.60
2.59
2.58
2.56
2.55
1.92
1.90
1.88
1.79
1.77
1.76
1.58
1.57
1.54
1.36
1.34
MeO
3ae
2.20
2.00
2.81
0.91
2.25
2.03
3.28
3.02
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


158.94
132.90
116.31
113.77
92.87
80.16
55.26
32.86
29.71
25.97
24.98
MeO
3ae
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.20
7.18
7.16
7.01
6.99
6.93
6.84
6.81
3.79
2.62
2.61
2.59
2.58
2.58
2.56
2.55
1.90
1.87
1.87
1.77
1.76
1.75
1.55
1.53
1.35
MeO
3af
1.09
0.99
0.99
1.00
3.08
1.00
1.94
2.29
3.26
3.04
.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


159.26
129.20
125.15
124.17
116.37
114.11
94.37
80.44
55.25
32.71
29.68
25.94
24.94
MeO
3af
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.39
7.39
7.37
7.37
7.25
7.25
7.23
7.23
7.21
7.21
6.89
6.87
6.86
6.83
3.87
2.69
2.68
2.67
2.66
2.65
2.65
2.63
2.63
1.92
1.89
1.79
1.77
1.76
1.58
1.55
1.54
1.37
1.35
OMe
3ag
1.00
1.23
2.08
3.06
1.06
2.24
2.34
3.24
3.28
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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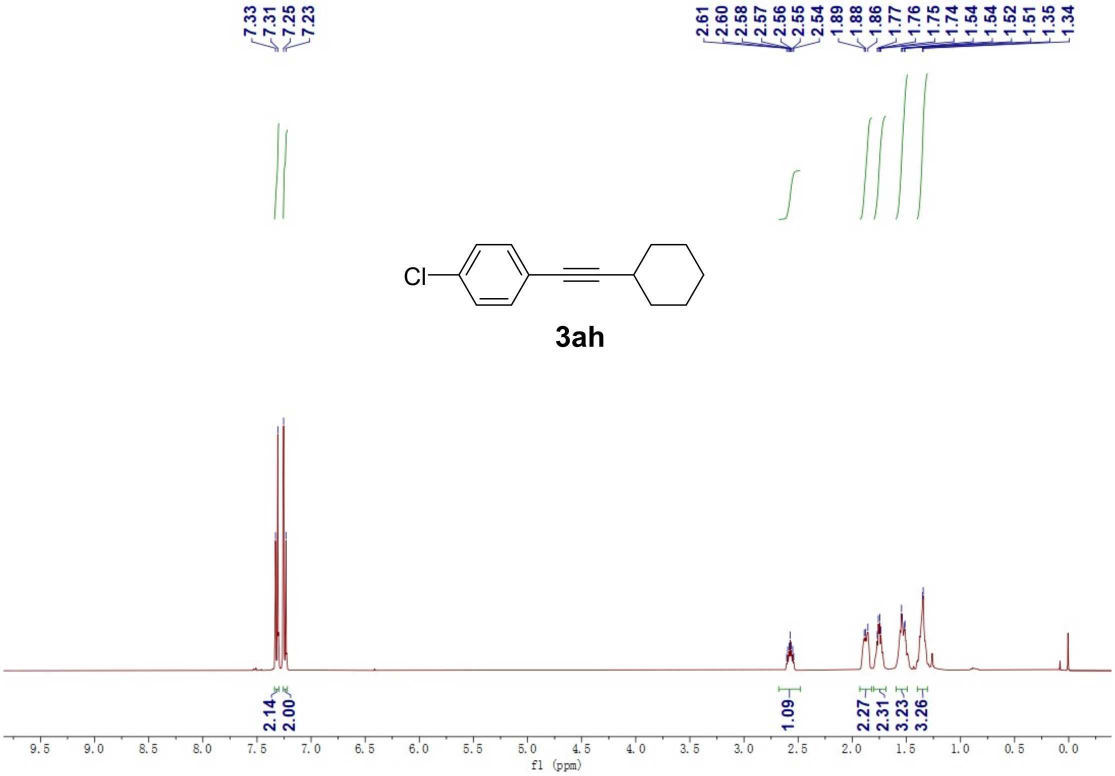
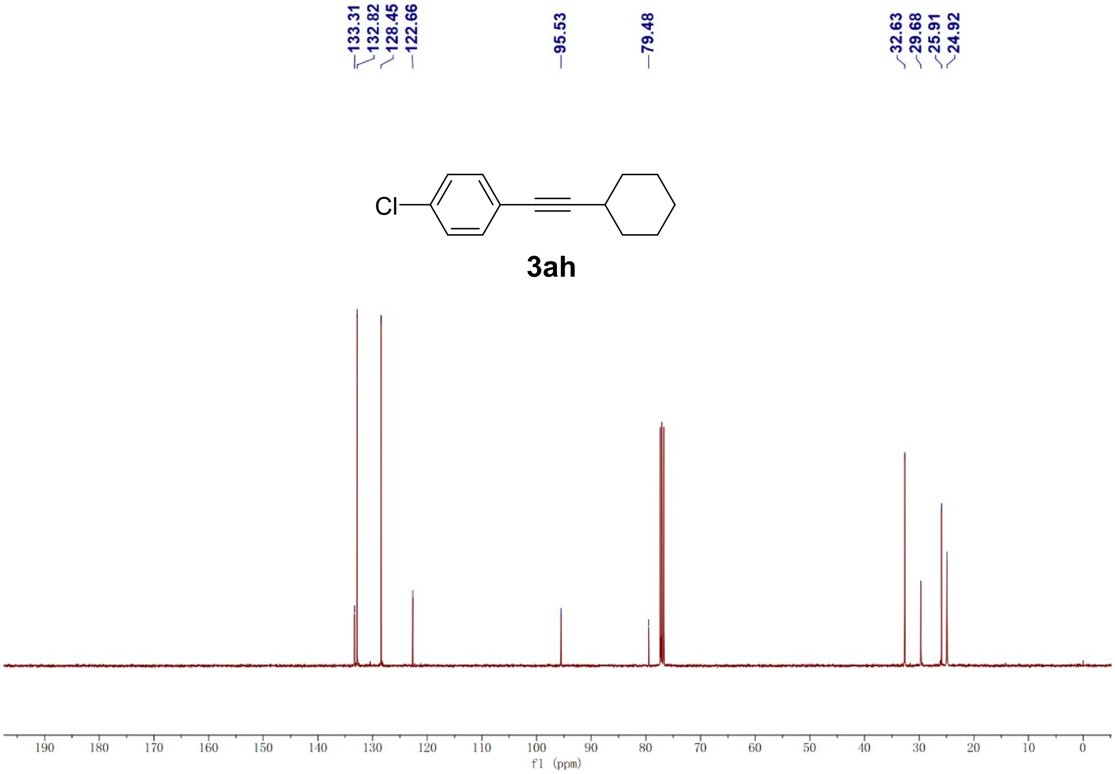
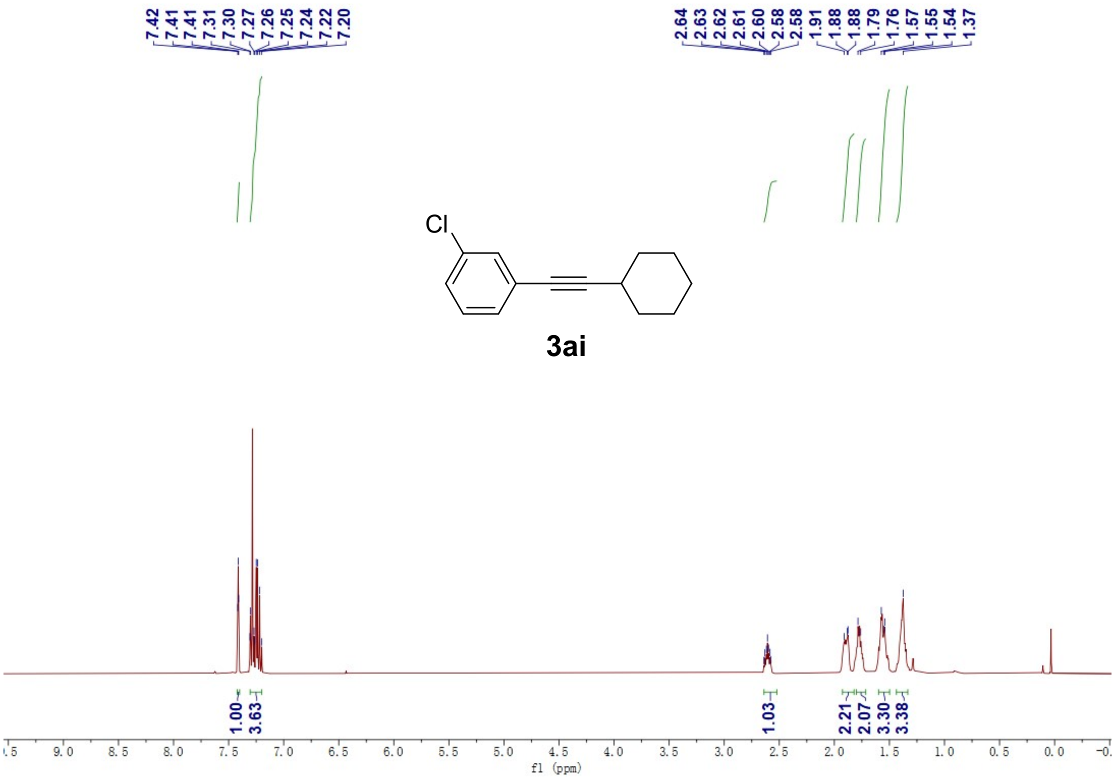
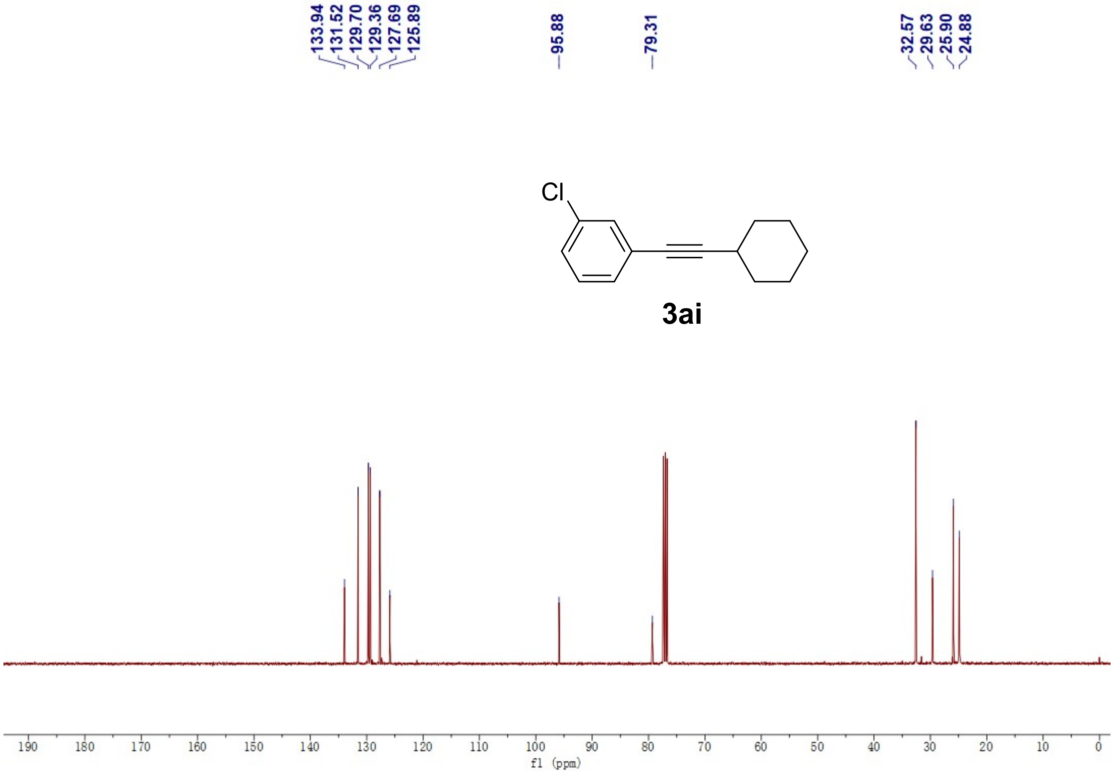
128.80
120.36
113.23
110.61
98.74
76.57
55.84
32.78
29.98
26.00
24.93
OMe
3ag
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.33
7.31
7.25
7.23
2.61
2.60
2.58
2.57
2.56
2.55
2.54
1.89
1.88
1.86
1.77
1.76
1.75
1.74
1.54
1.54
1.52
1.51
1.35
1.34
Cl
3ah
2.14
2.00
1.09
2.27
2.31
3.23
3.26
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

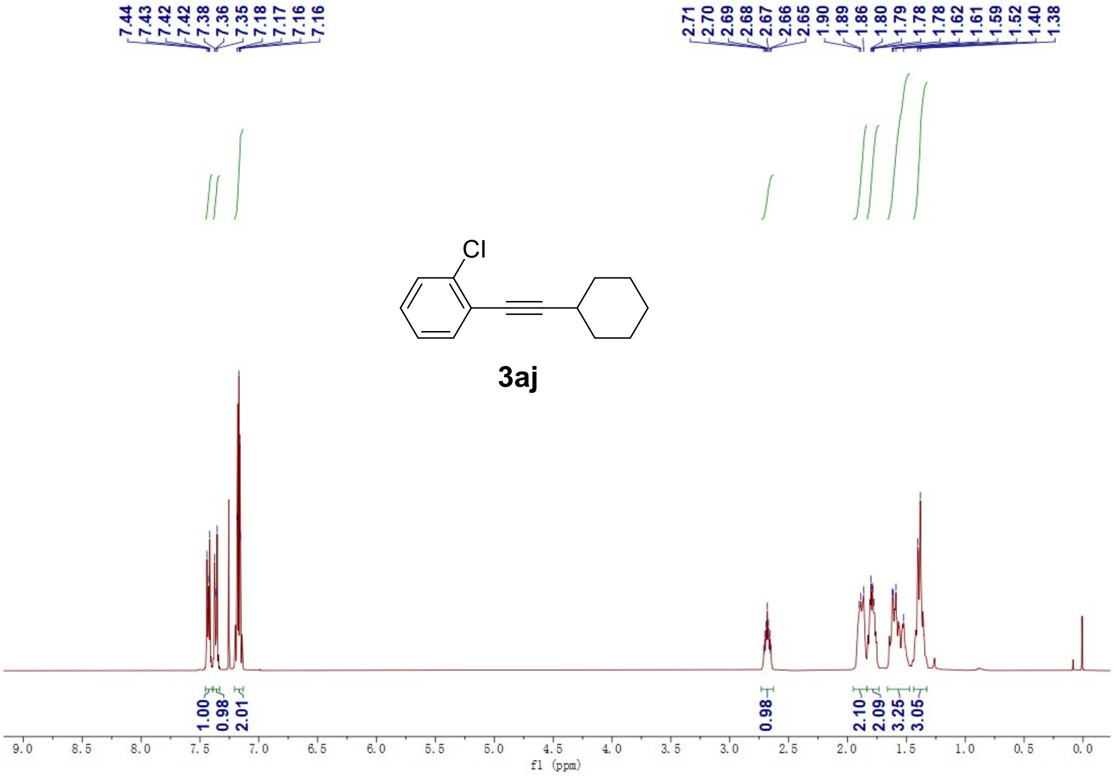

133.31
132.82
128.45
122.66
95.53
79.48
32.63
29.68
25.91
24.92
Cl
3ah
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.42
7.41
7.41
7.31
7.30
7.27
7.26
7.25
7.24
7.22
7.20
2.64
2.63
2.62
2.61
2.60
2.58
2.58
1.91
1.88
1.88
1.79
1.76
1.57
1.55
1.54
1.37
Cl
1.00
3.63
1.03
2.21
2.07
3.30
3.38
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.
f1 (ppm)

3ai


133.94
131.52
129.70
129.36
127.69
125.89
95.88
79.31
32.57
29.63
25.90
24.88
Cl
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

3ai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7.43
7.42
7.42
7.38
7.36
7.35
7.18
7.17
7.16
7.16
2.71
2.70
2.69
2.68
2.67
2.66
2.65
1.90
1.89
1.86
1.80
1.79
1.78
1.62
1.61
1.59
1.52
1.40
1.38
Cl
3aj
1.00
0.98
2.01
0.98
2.10
2.09
3.25
3.05
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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2.5
2.0
1.5
1.0
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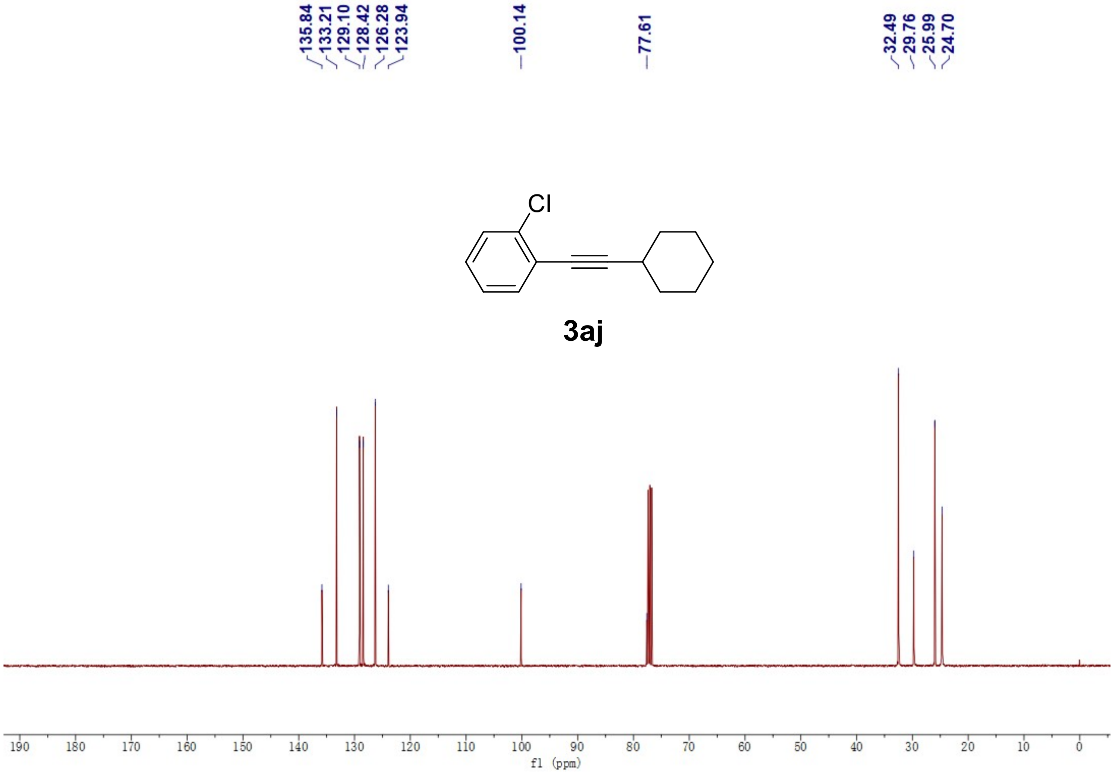
0.0
f1 (ppm)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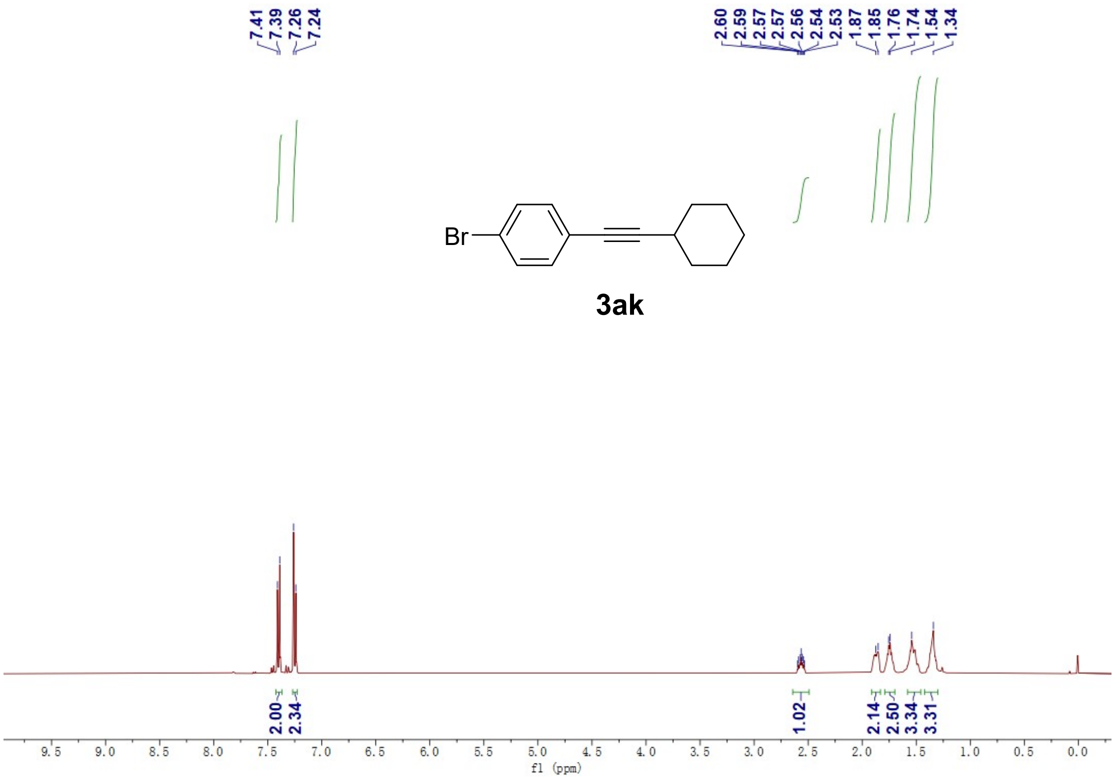
126.28
123.94
100.14
77.61
32.49
29.76
25.99
24.70
Cl
3aj
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.26
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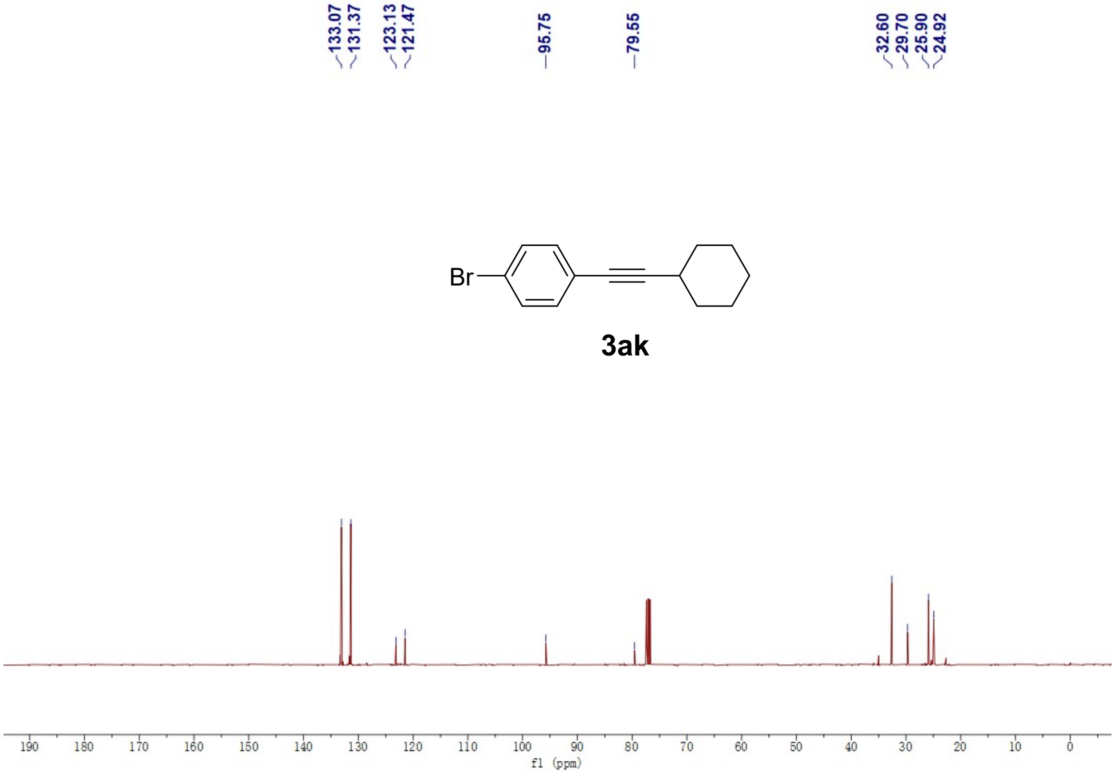
2.59
2.57
2.57
2.56
2.54
2.53
1.87
1.85
1.76
1.74
1.54
1.34
Br
3ak
2.00
2.34
1.02
2.14
2.50
3.34
3.31
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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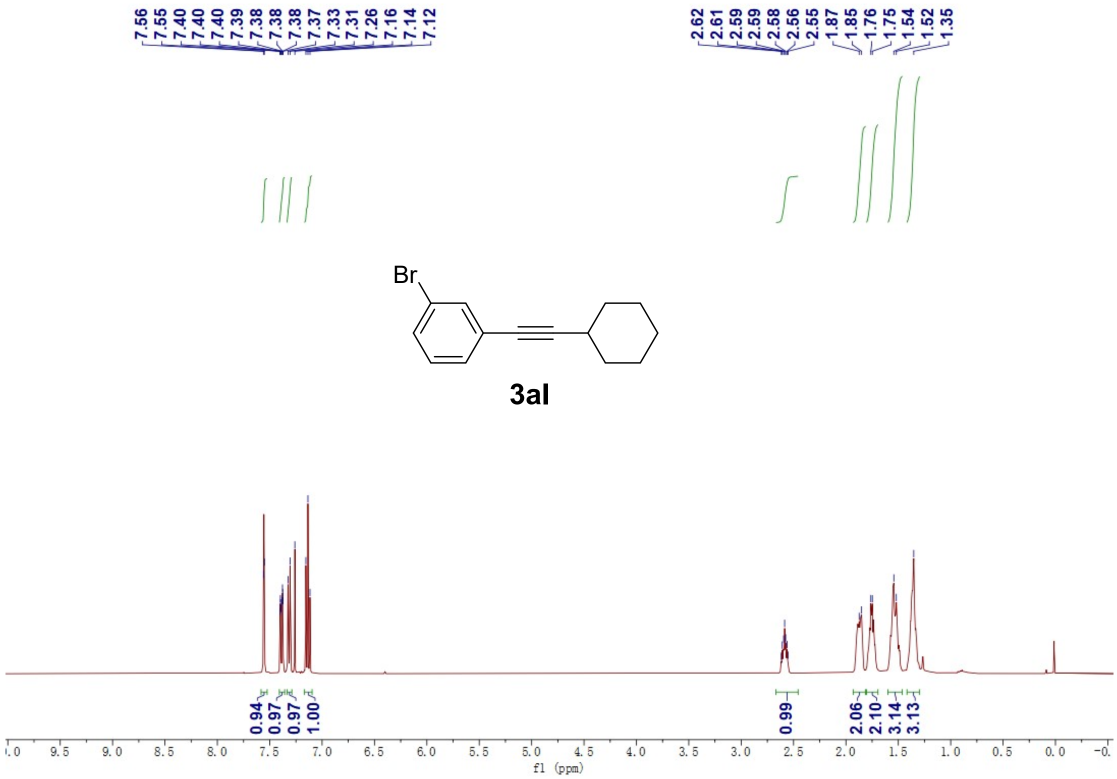
123.13
121.47
95.75
79.55
32.60
29.70
25.90
24.92
Br
3ak
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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7.55
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7.40
7.40
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7.38
7.38
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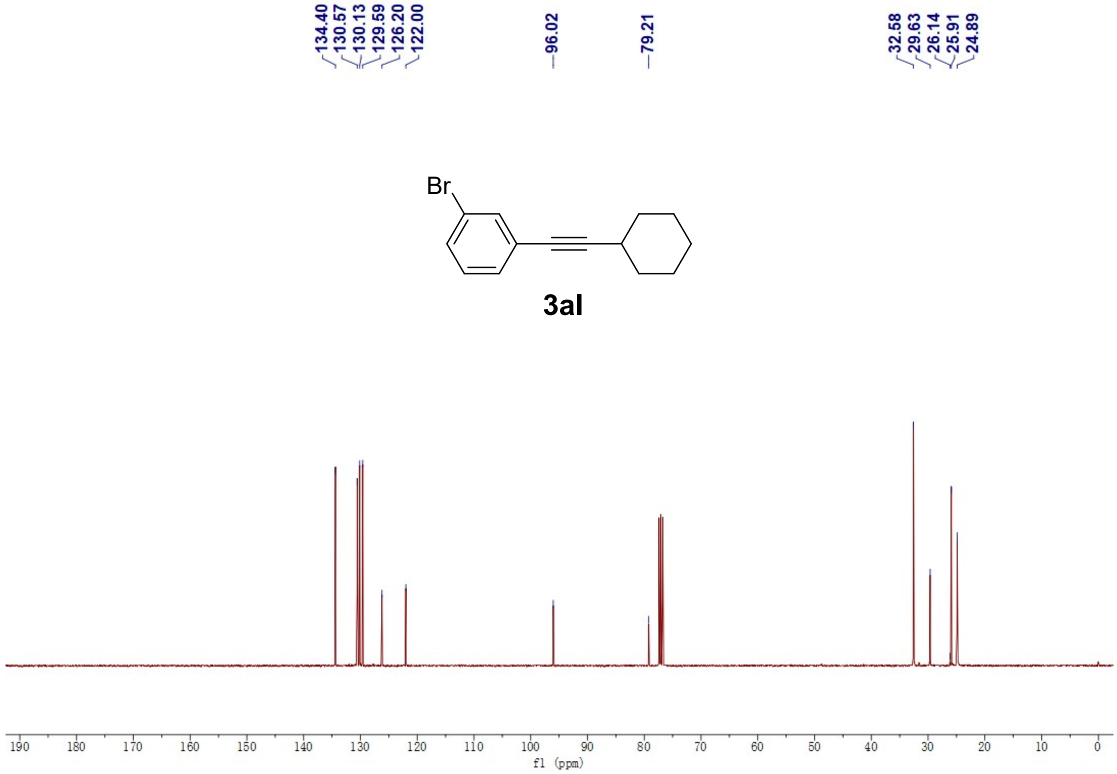
7.37
7.33
7.31
7.26
7.16
7.14
7.12
2.62
2.61
2.59
2.59
2.58
2.56
2.55
1.87
1.85
1.76
1.75
1.54
1.52
1.35
Br
0.94
0.97
0.97
1.00
0.99
2.06
2.10
3.14
3.13
f1 (ppm)

3al


134.40
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96.02
79.21
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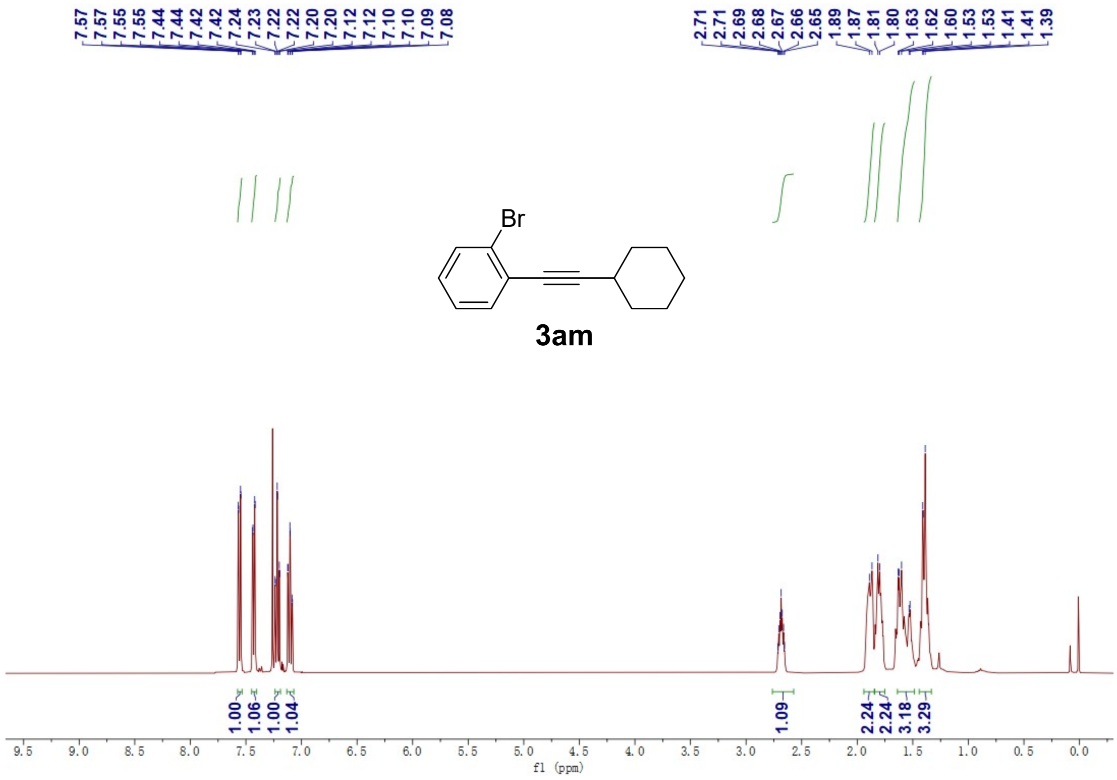
26.14
25.91
24.89
Br
f1 (ppm)

3al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7.44
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7.42
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7.20
7.12
7.12
7.10
7.09
7.08
2.71
2.71
2.69
2.68
2.67
2.66
2.65
1.89
1.87
1.81
1.80
1.63
1.62
1.60
1.53
1.53
1.41
1.41
1.39
Br
3am
1.00
1.06
1.00
1.04
1.09
2.24
2.24
3.18
3.29
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
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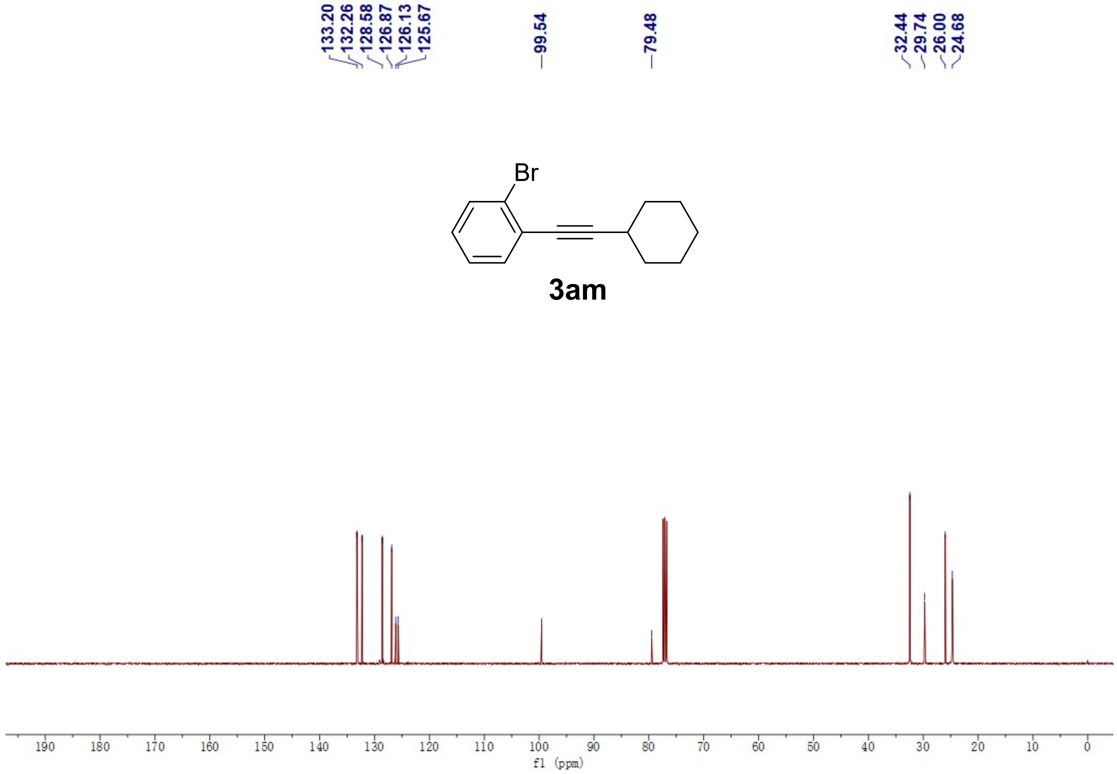
0.0
f1 (ppm)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132.26
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126.87
126.13
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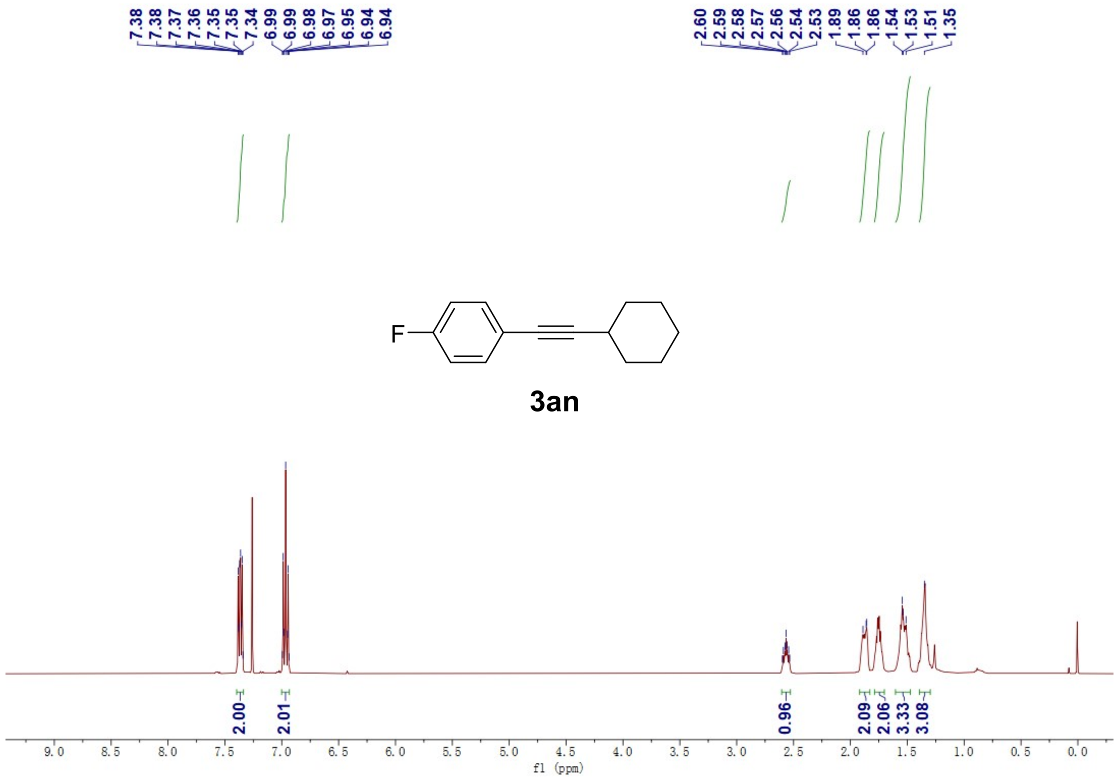
99.54
79.48
32.44
29.74
26.00
24.68
Br
3am
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.35
7.34
6.99
6.99
6.98
6.97
6.95
6.94
6.94
2.60
2.59
2.58
2.57
2.56
2.54
2.53
1.89
1.86
1.86
1.54
1.53
1.51
1.35
F
2.00
2.01
0.96
2.09
2.06
3.33
3.08
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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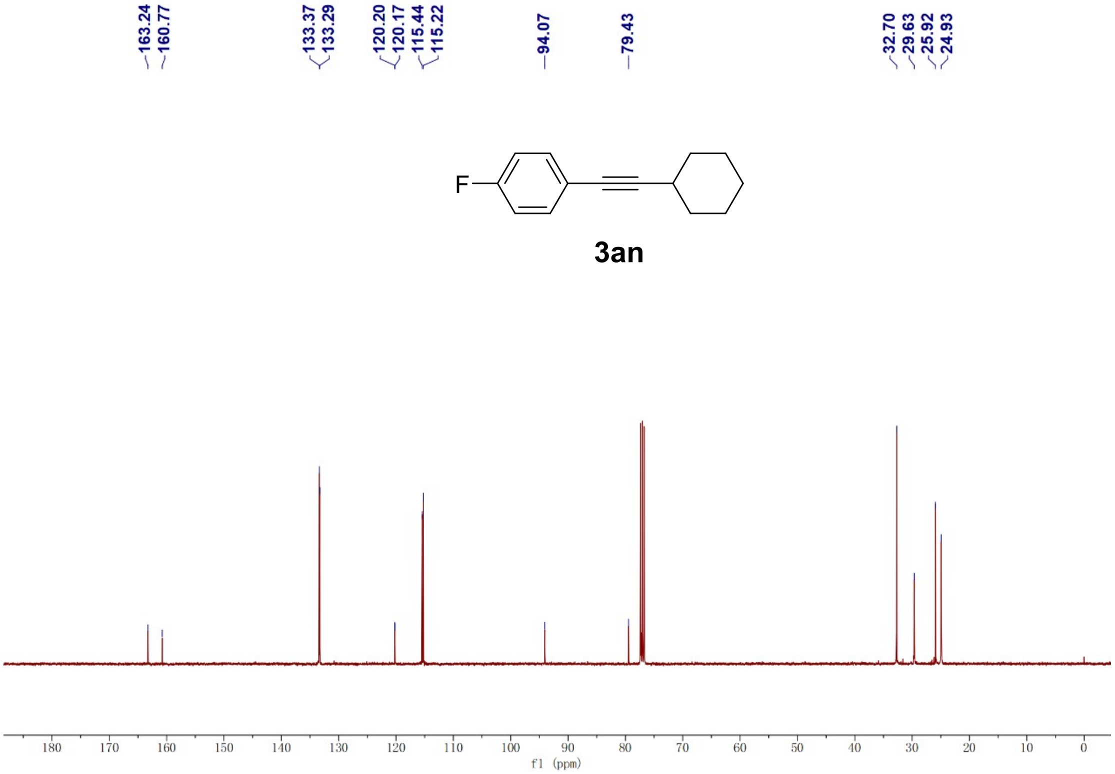
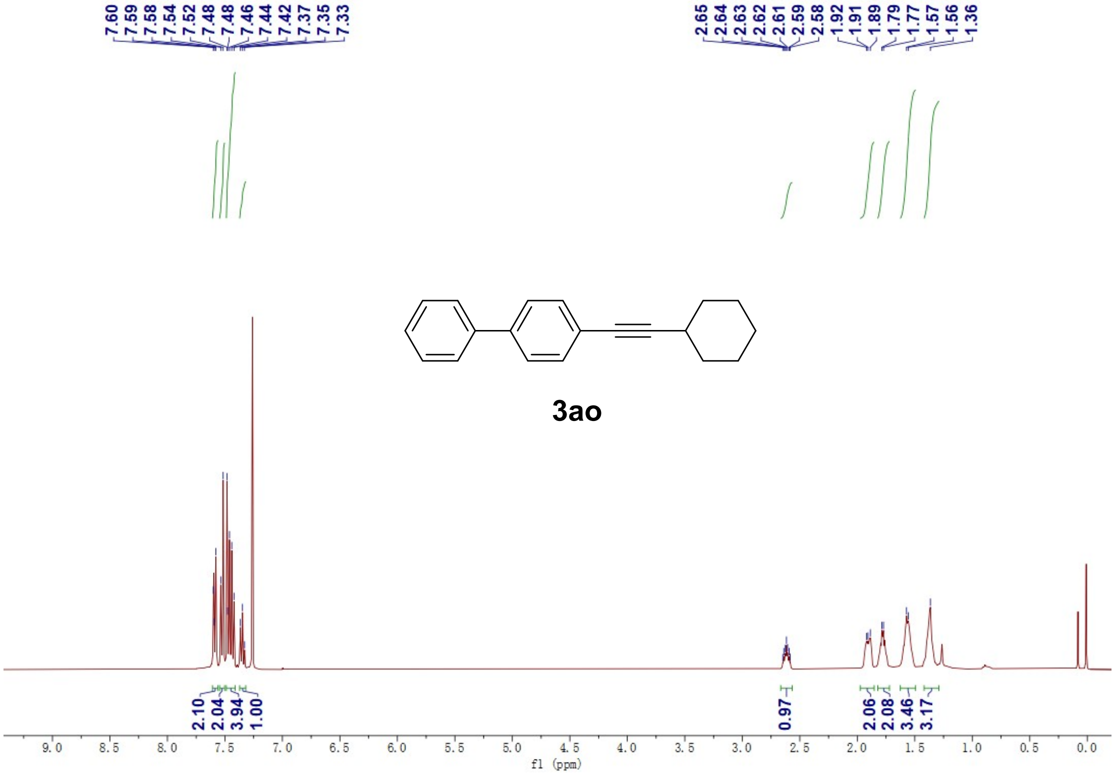
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

3an


163.24
160.77
133.37
133.29
120.20
120.17
115.44
115.22
94.07
79.43
32.70
29.63
25.92
24.93
F
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

3an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7.59
7.58
7.54
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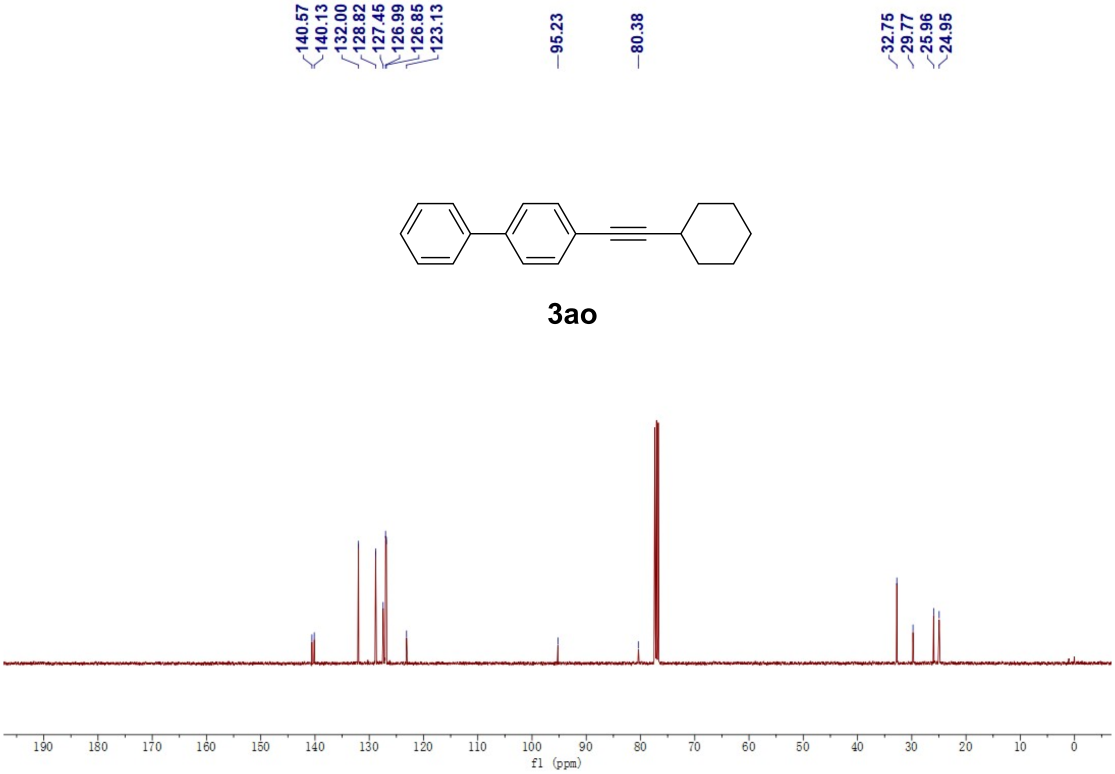
7.48
7.48
7.46
7.44
7.42
7.37
7.35
7.33
2.65
2.64
2.63
2.62
2.61
2.59
2.58
1.92
1.91
1.89
1.79
1.77
1.57
1.56
1.36
3ao
2.10
2.04
3.94
1.00
0.97
2.06
2.08
3.46
3.17
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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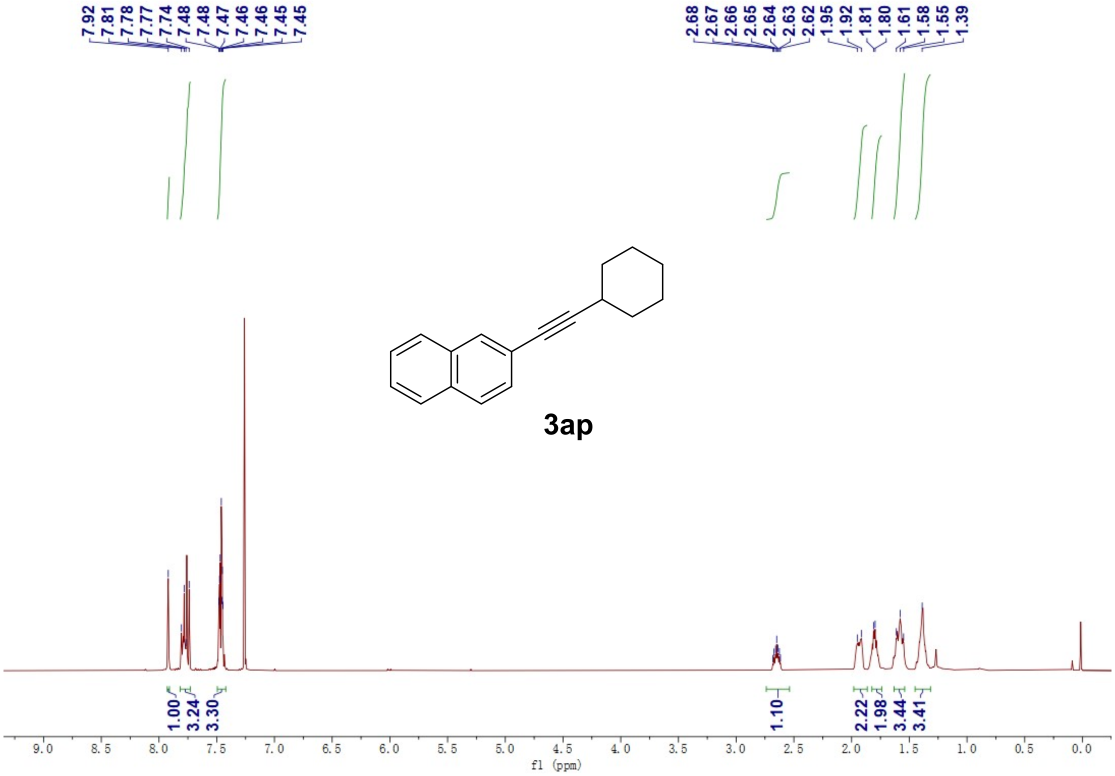
140.13
132.00
128.82
127.45
126.99
126.85
123.13
95.23
80.38
32.75
29.77
25.96
24.95
3ao
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.77
7.74
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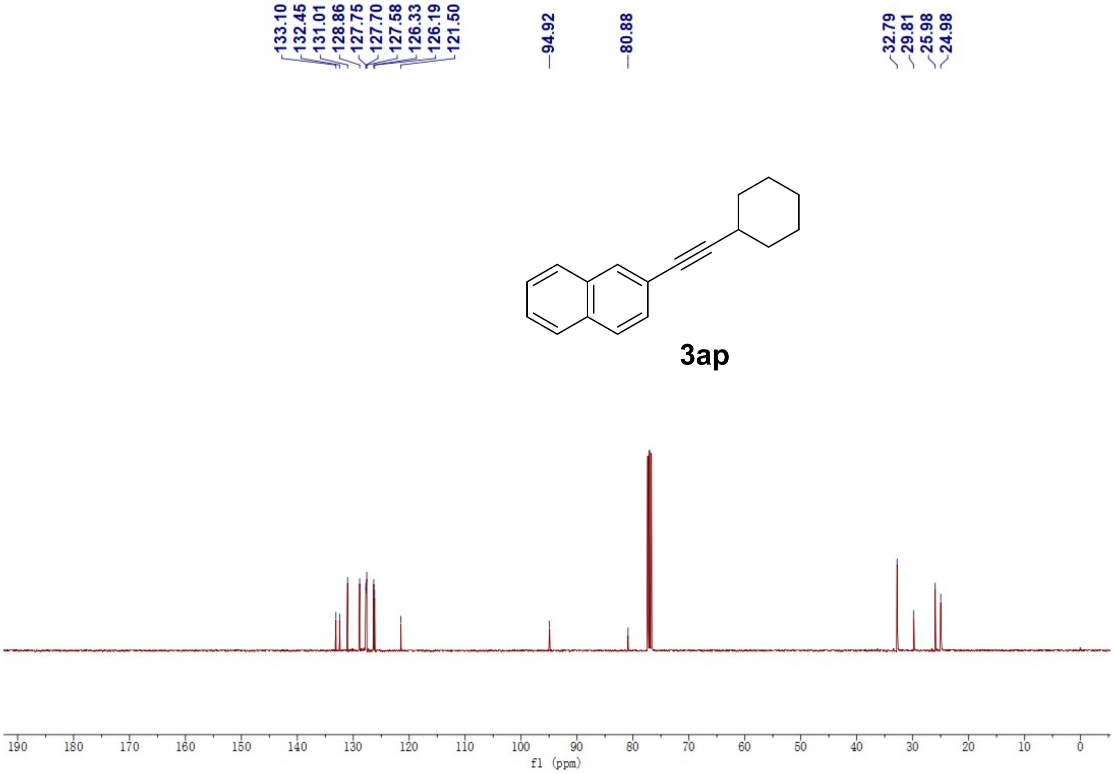
7.48
7.47
7.46
7.46
7.45
7.45
2.68
2.67
2.66
2.65
2.64
2.63
2.62
1.95
1.92
1.81
1.80
1.61
1.58
1.55
1.39
3ap
1.00
3.24
3.30
1.10
2.22
1.98
3.44
3.41
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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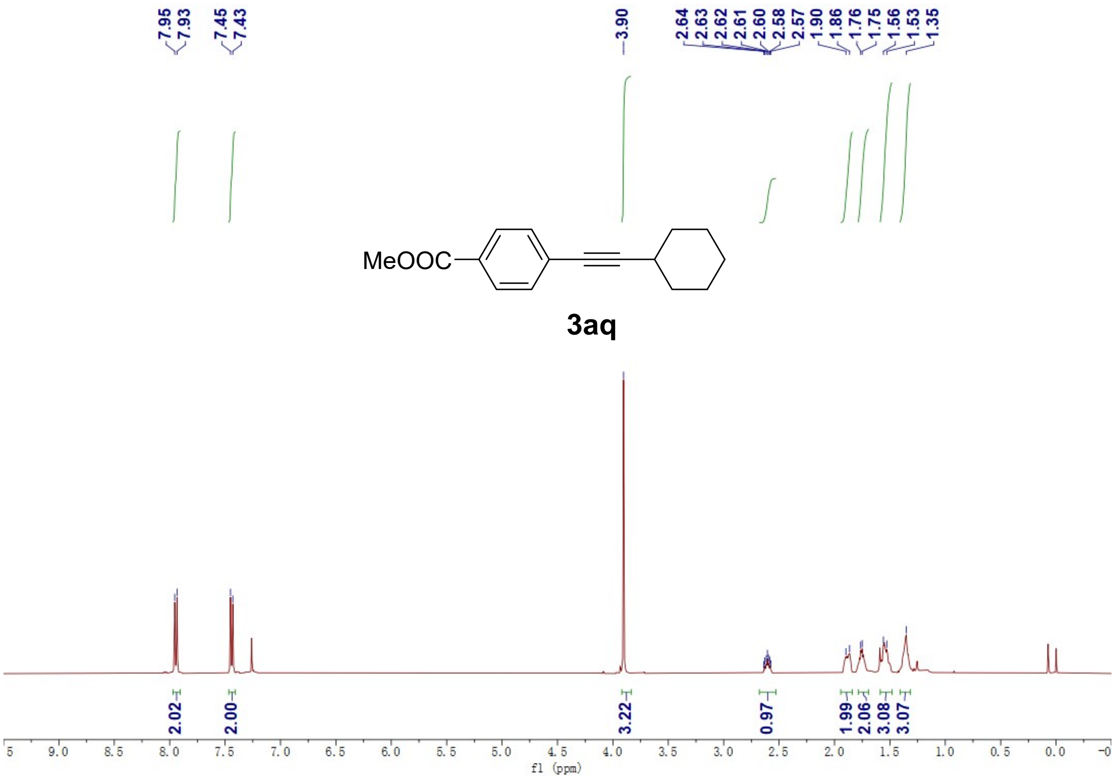
127.75
127.70
127.58
126.33
126.19
121.50
94.92
80.88
32.79
29.81
25.98
24.98
3ap
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

7.95
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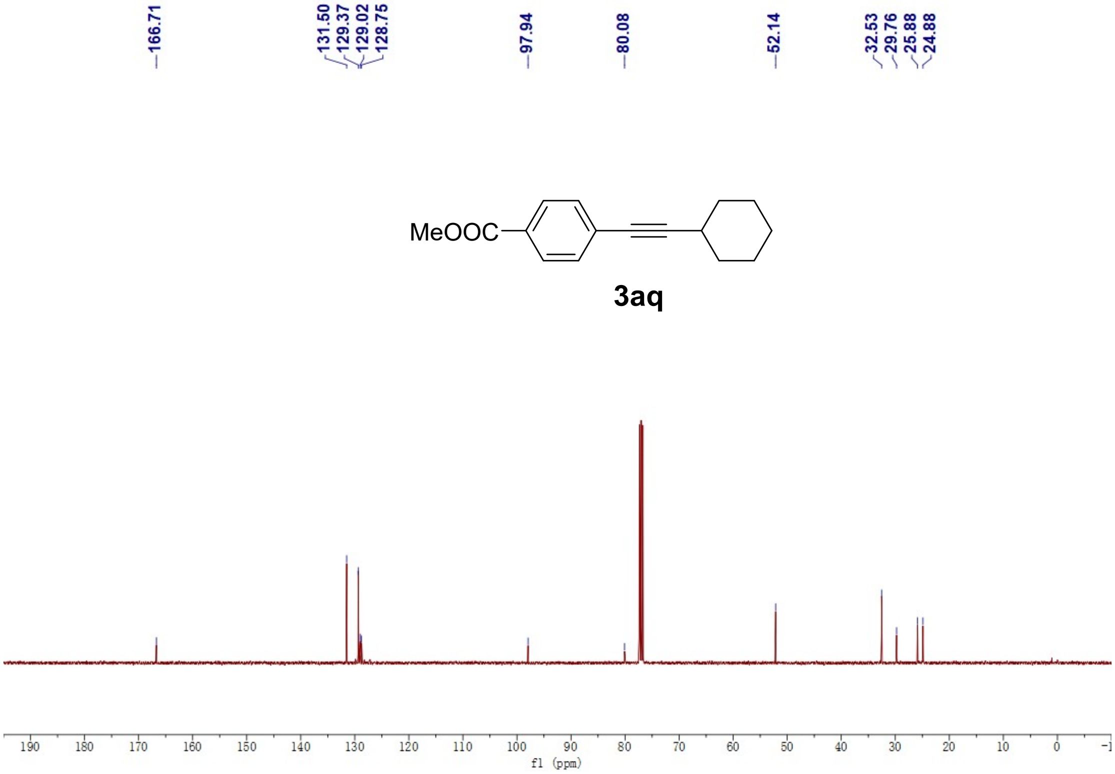
2.60
2.58
2.57
1.90
1.86
1.76
1.75
1.56
1.53
1.35
MeOOC
2.02
2.00
3.22
0.97
1.99
2.06
3.08
3.07
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

3aq

166.71
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129.02
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32.53
29.76
25.88
24.88
MeOOC
190
180
170
160
150
140
130
120
110
100
90
80
70
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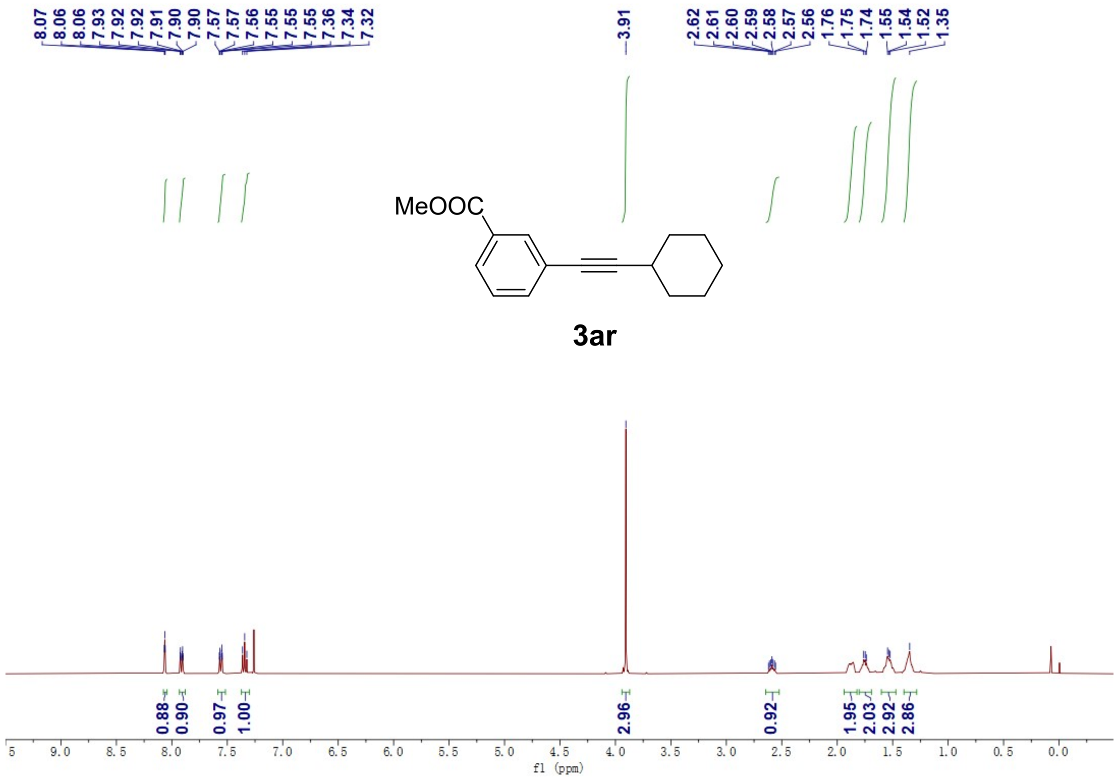
50
40
30
20
10
0
f1 (ppm)

3aq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8.06
8.06
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7.92
7.91
7.90
7.90
7.57
7.57
7.56
7.55
7.55
7.55
7.36
7.34
7.32
3.91
2.62
2.61
2.60
2.59
2.58
2.57
2.56
1.76
1.75
1.74
1.55
1.54
1.52
1.35
MeOOC
0.88
0.90
0.97
1.00
2.96
0.92
1.95
2.03
2.92
2.86
5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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3.0
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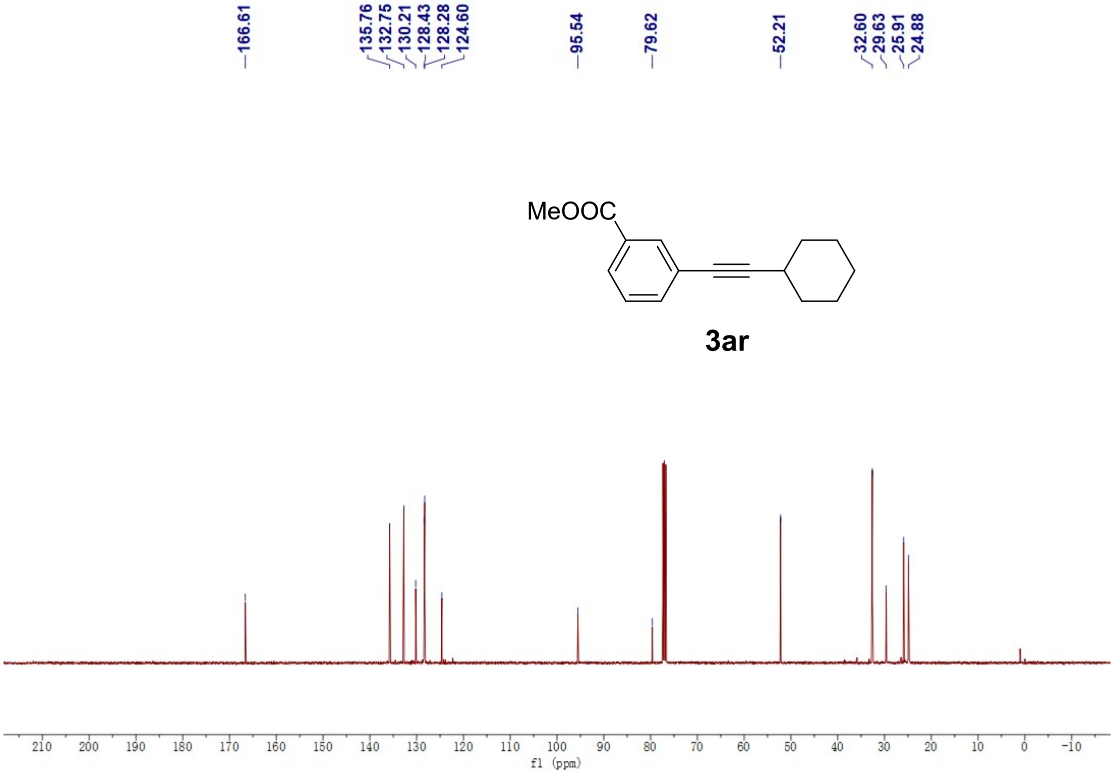
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

3ar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124.60
95.54
79.62
52.21
32.60
29.63
25.91
24.88
MeOOC
210
200
190
180
170
160
150
140
130
120
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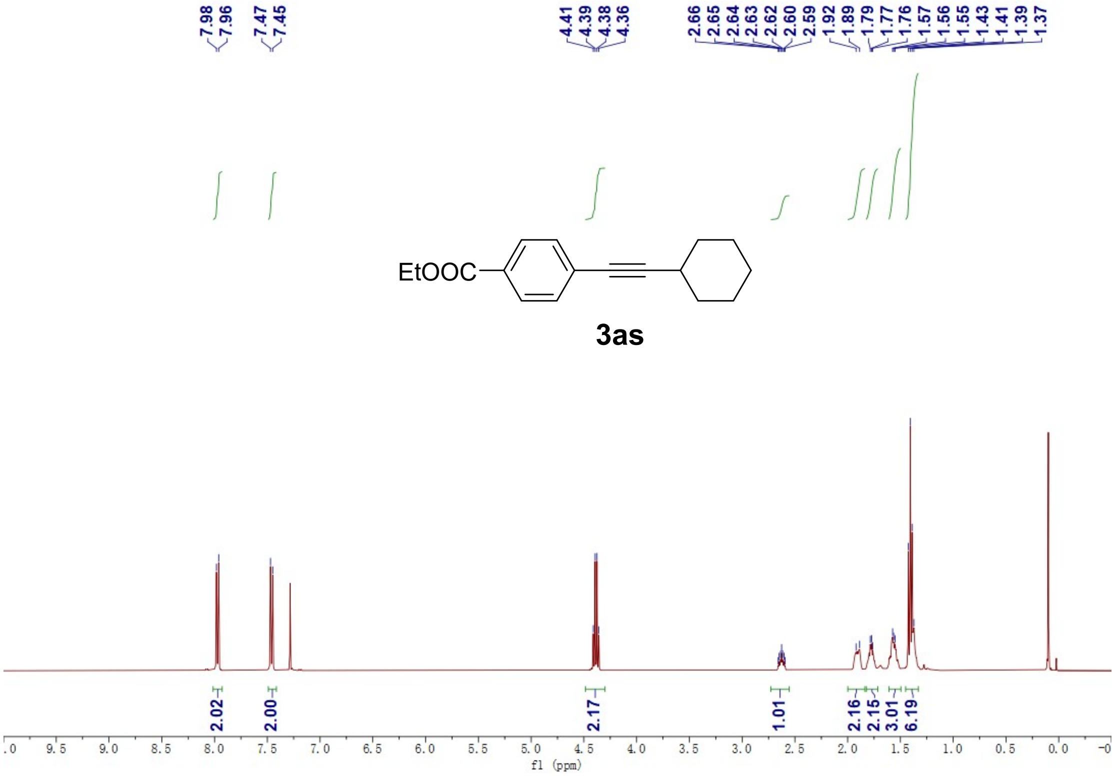
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

3ar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4.39
4.38
4.36
2.66
2.65
2.64
2.63
2.62
2.60
2.59
1.92
1.89
1.79
1.77
1.76
1.57
1.56
1.55
1.43
1.41
1.39
1.37
EtOOC
3as
2.02
2.00
2.17
1.01
2.16
2.15
3.01
6.19
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)


166.22
131.45
129.32
129.11
128.89
97.81
80.13
61.01
32.55
29.77
25.88
24.89
14.32
EtOOC
3as
190
180
170
160
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140
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120
110
100
90
80
70
60
50
40
30
20
10
0
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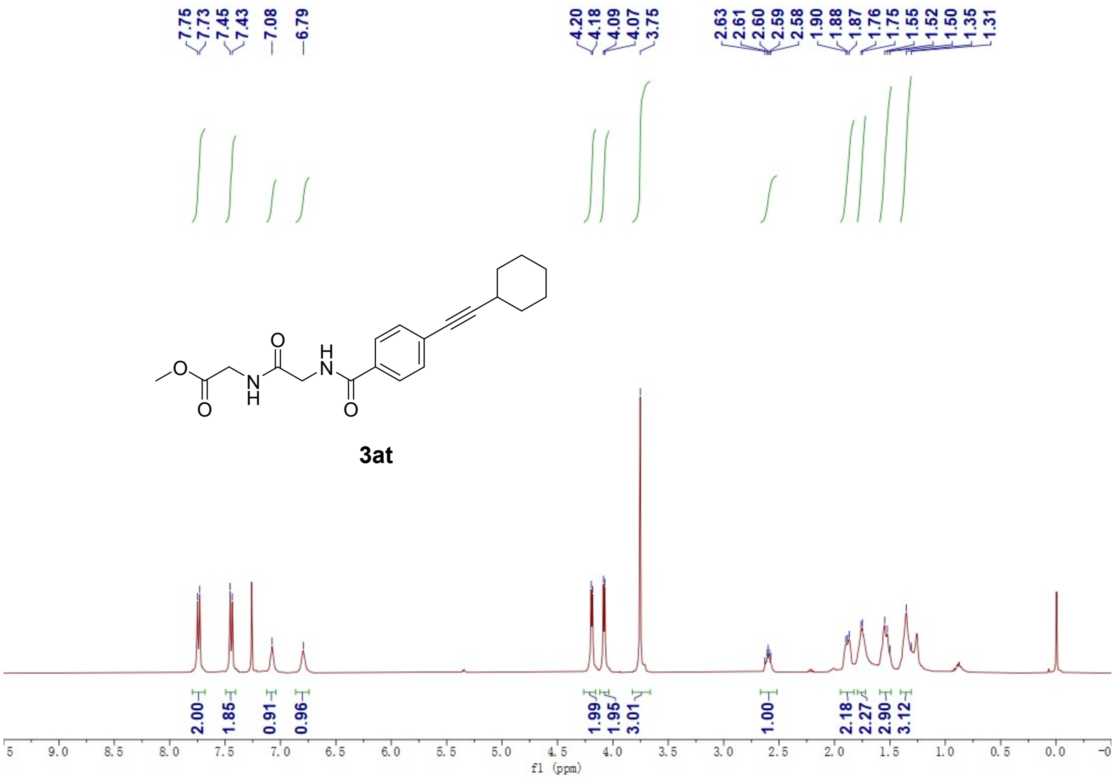
f1 (ppm)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4.07
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2.63
2.61
2.60
2.59
2.58
1.90
1.88
1.87
1.76
1.75
1.55
1.52
1.50
1.35
1.31
O
N
H
O
H
N
O
O
2.00
1.85
0.91
0.96
1.99
1.95
3.01
1.00
2.18
2.27
2.90
3.12
5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
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3.5
3.0
2.5
2.0
1.5
1.0
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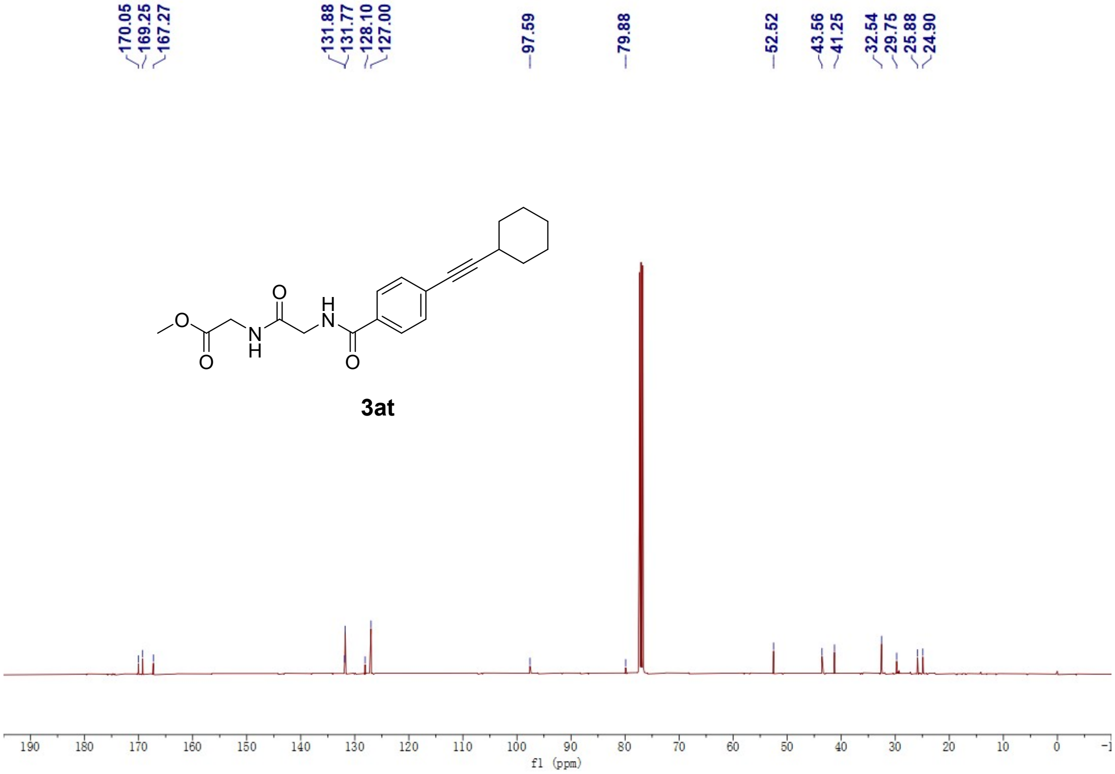
0.0
-0
f1 (ppm)

3at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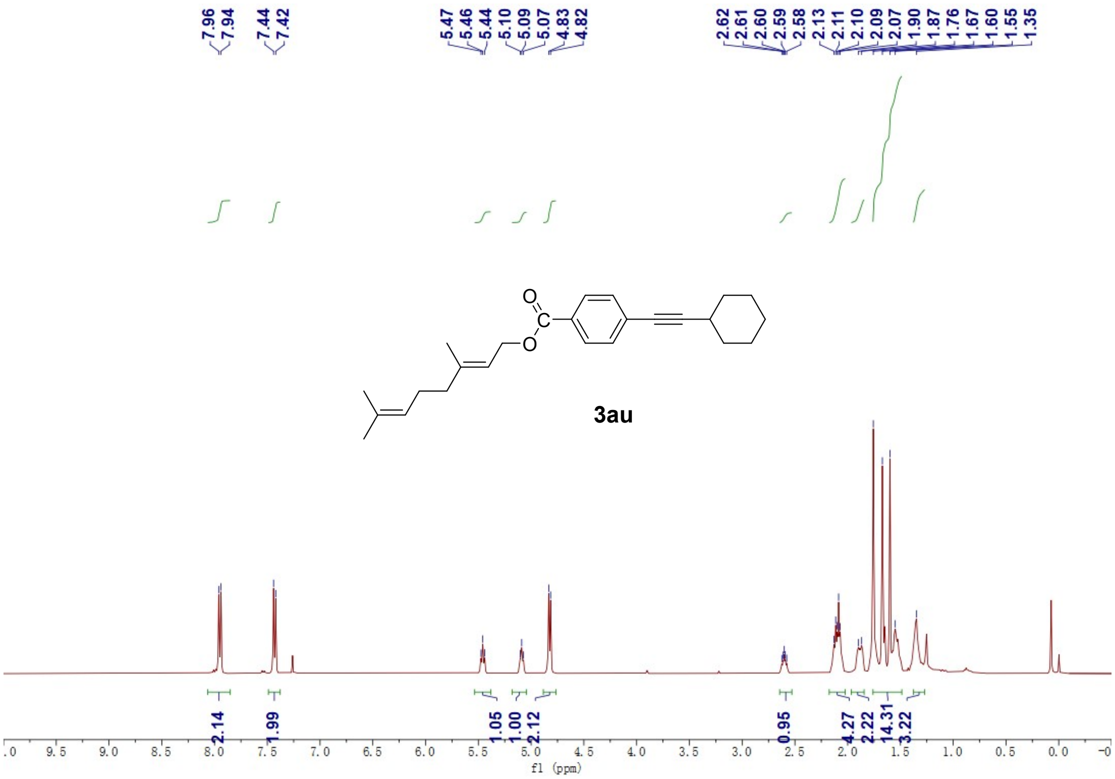
131.77
128.10
127.00
97.59
79.88
52.52
43.56
41.25
32.54
29.75
25.88
24.90
O
N
H
O
H
N
O
O
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)

3at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5.44
5.10
5.09
5.07
4.83
4.82
2.62
2.61
2.60
2.59
2.58
2.13
2.11
2.10
2.09
2.07
1.90
1.87
1.76
1.67
1.60
1.55
1.35
O
C
O
3au
2.14
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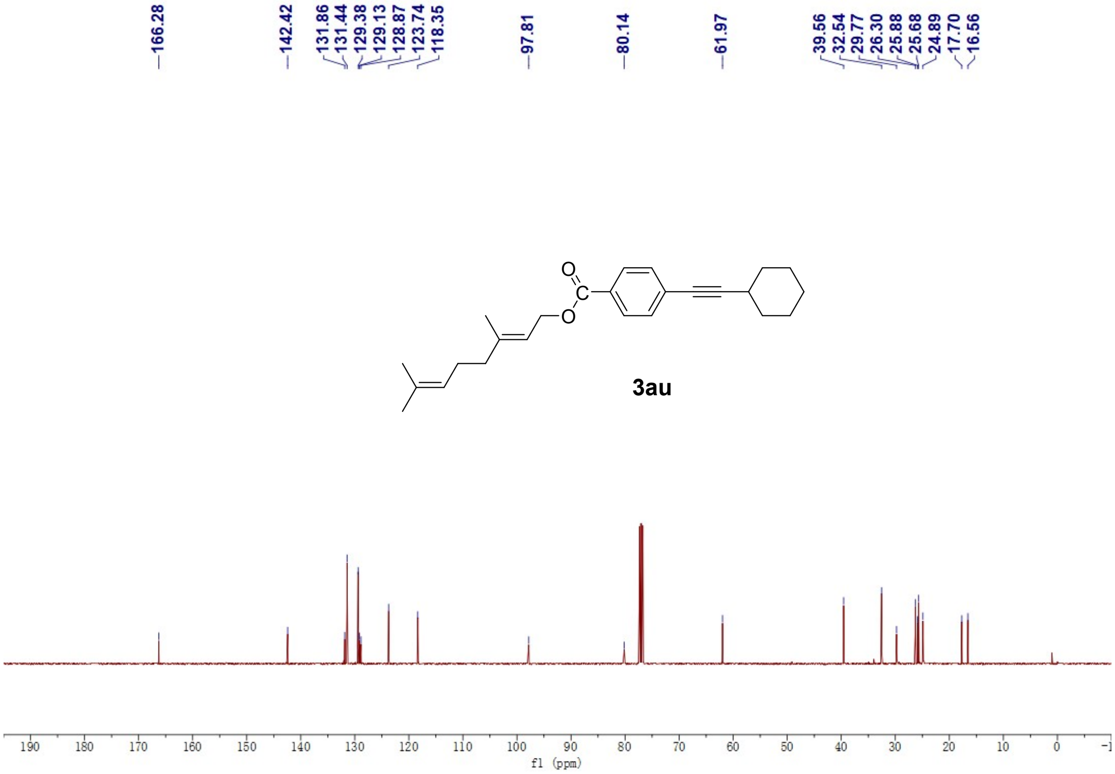
1.05
1.00
2.12
0.95
4.27
2.22
14.31
3.22
f1 (ppm)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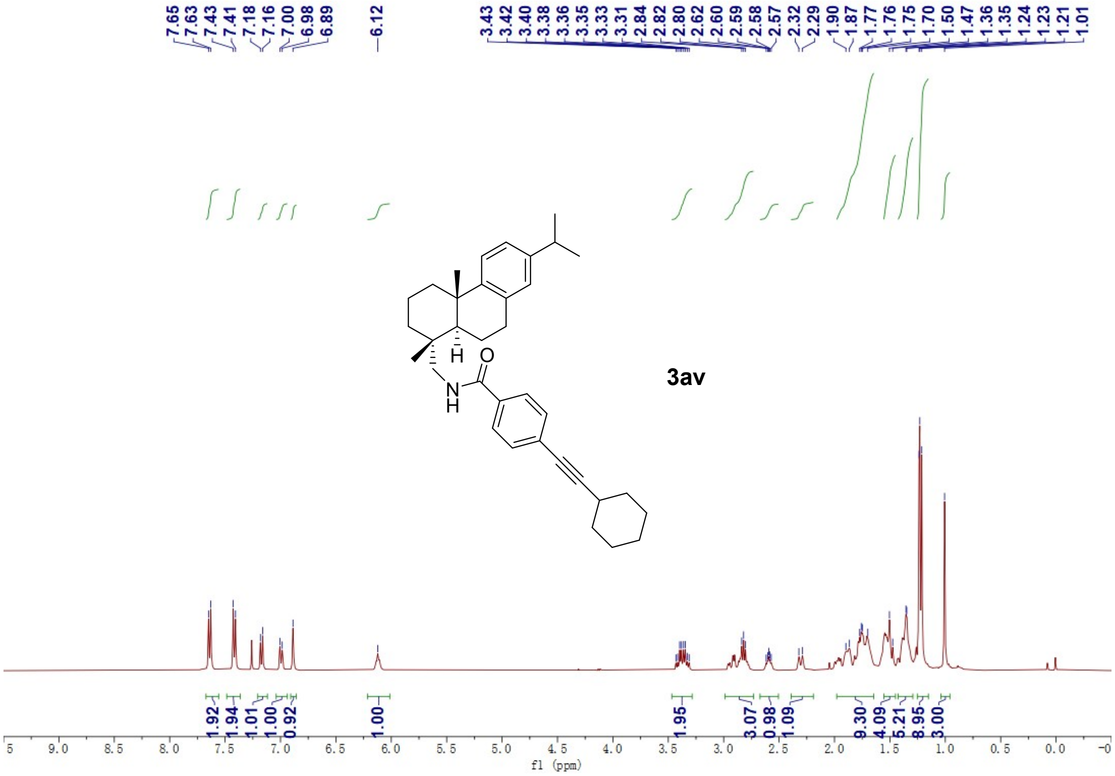
128.87
123.74
118.35
97.81
80.14
61.97
39.56
32.54
29.77
26.30
25.88
25.68
24.89
17.70
16.56
O
C
O
3au
f1 (ppm)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6.12
3.43
3.42
3.40
3.38
3.36
3.35
3.33
3.31
2.84
2.82
2.80
2.62
2.60
2.59
2.58
2.57
2.32
2.29
1.90
1.87
1.77
1.76
1.75
1.70
1.50
1.47
1.36
1.35
1.24
1.23
1.21
1.01
H
O
N
H
3av
1.92
1.94
1.01
1.00
0.92
1.00
1.95
3.07
0.98
1.09
9.30
4.09
5.21
8.95
3.00
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8.5
8.0
7.5
7.0
6.5
6.0
5.5
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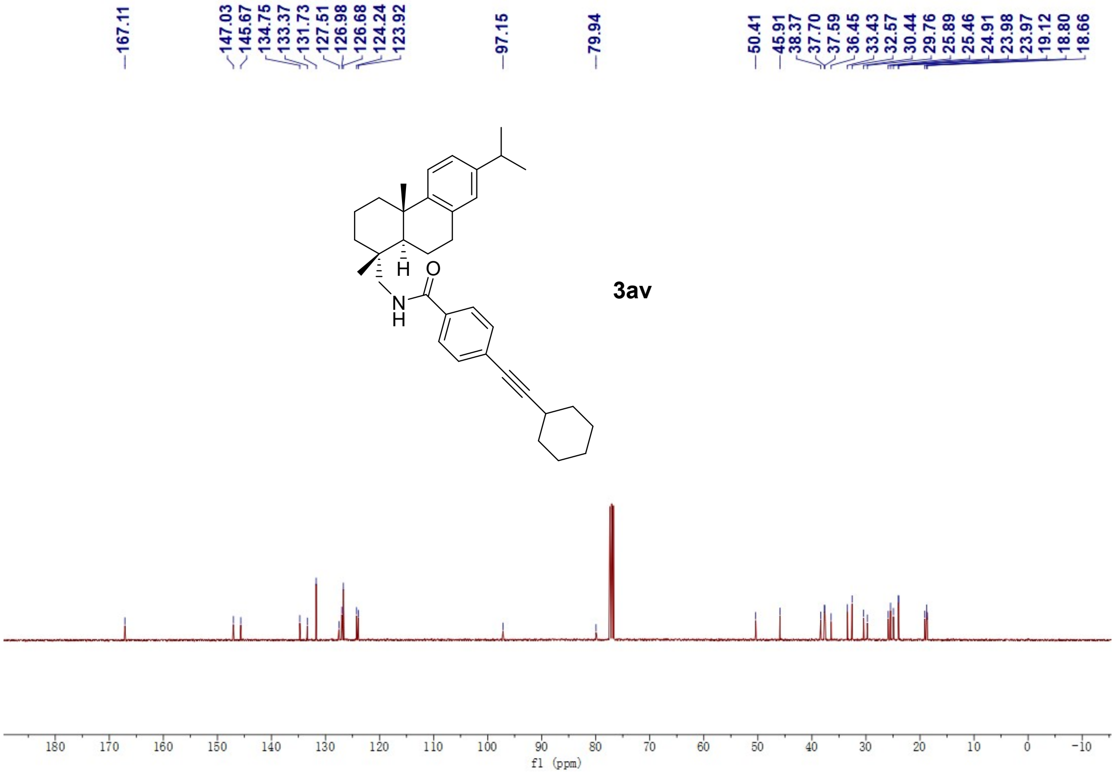
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


167.11
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126.98
126.68
124.24
123.92
97.15
79.94
50.41
45.91
38.37
37.70
37.59
36.45
33.43
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30.44
29.76
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25.46
24.91
23.98
23.97
19.12
18.80
18.66
H
O
N
H
3av
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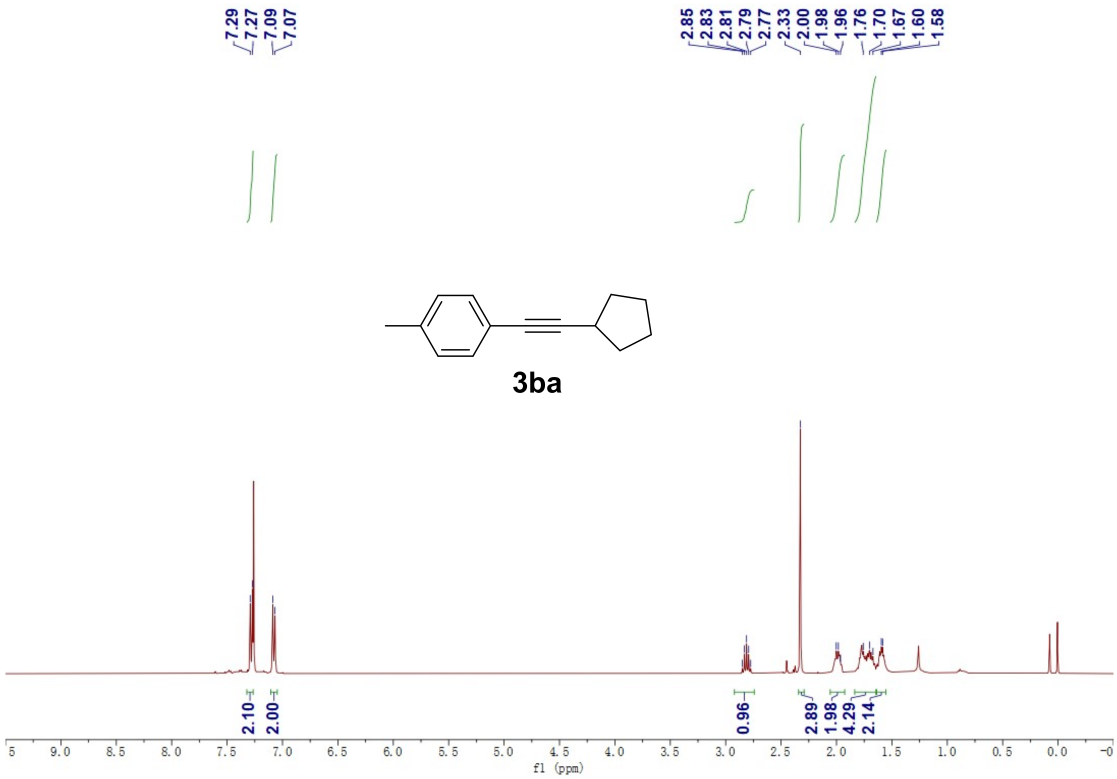
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2.00
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1.98
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2.14
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8.0
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7.0
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6.0
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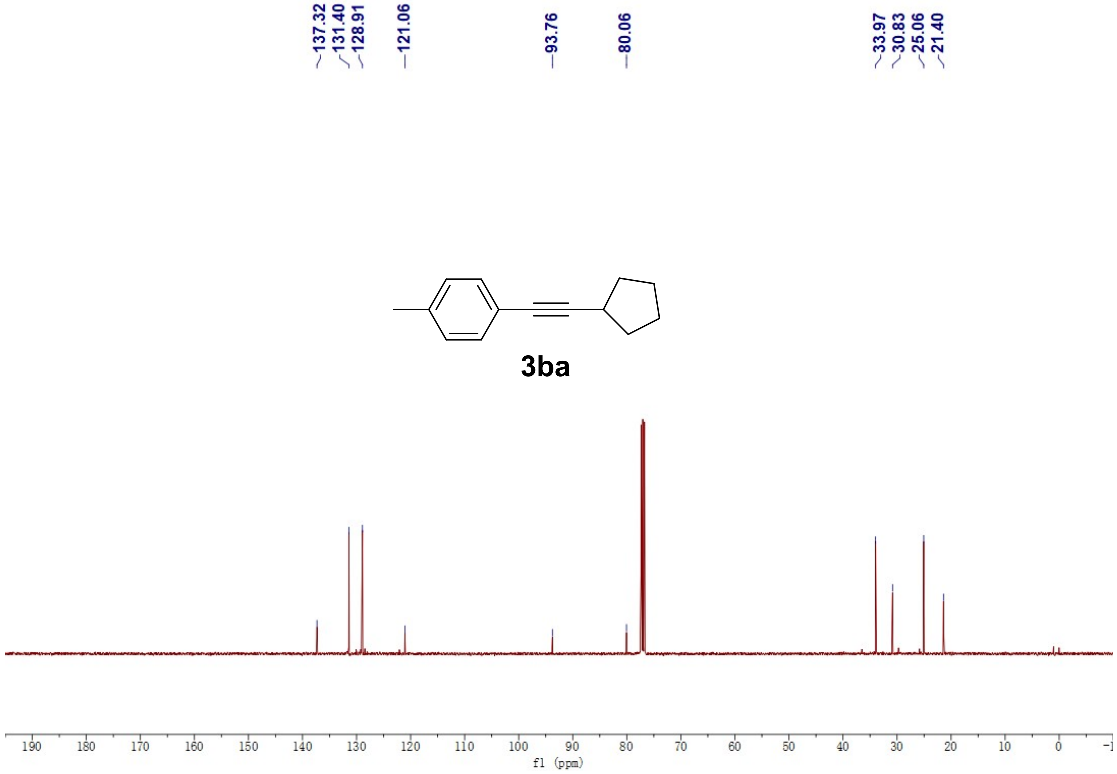
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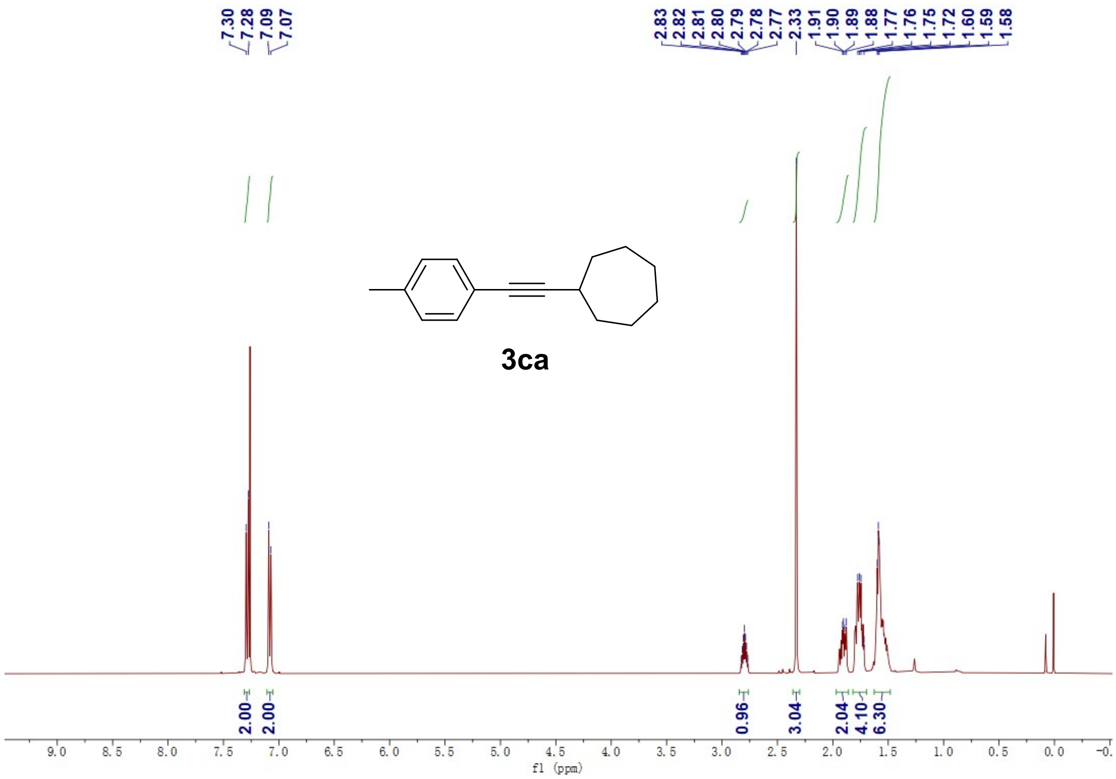
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1.90
1.89
1.88
1.77
1.76
1.75
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1.60
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1.58
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2.00
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3.04
2.04
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6.30
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8.5
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7.0
6.5
6.0
5.5
5.0
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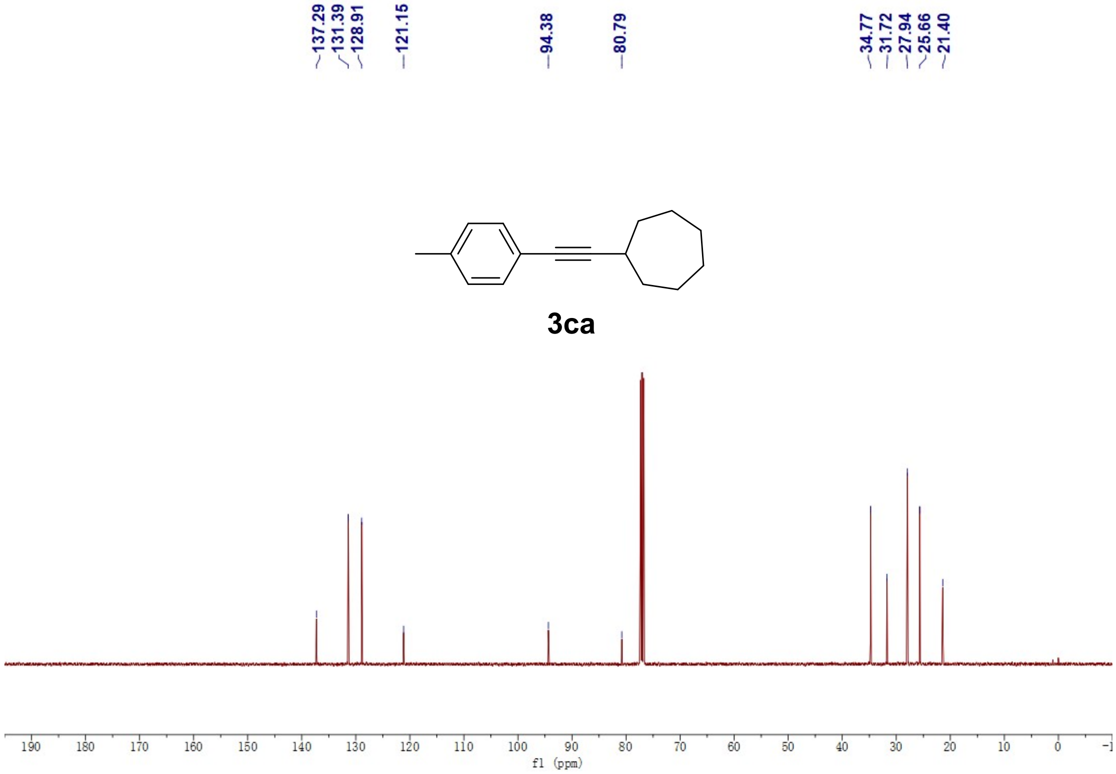
f1 (ppm)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180
170
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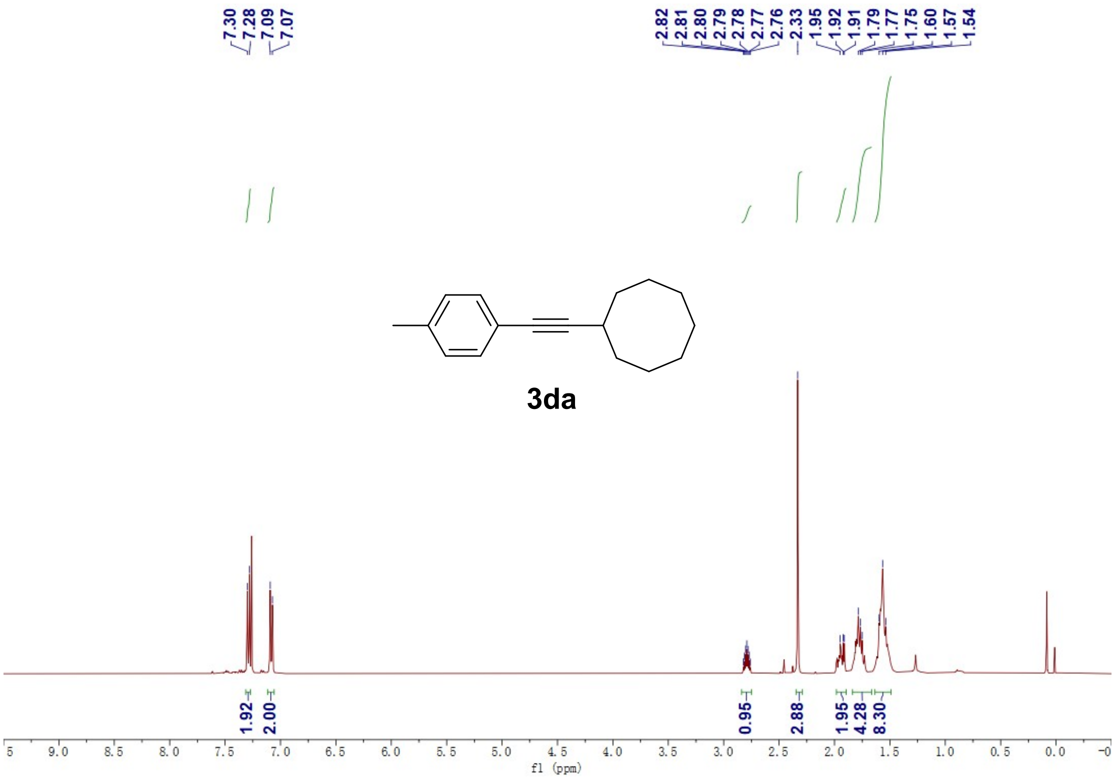
-1
f1 (ppm)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5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
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5.0
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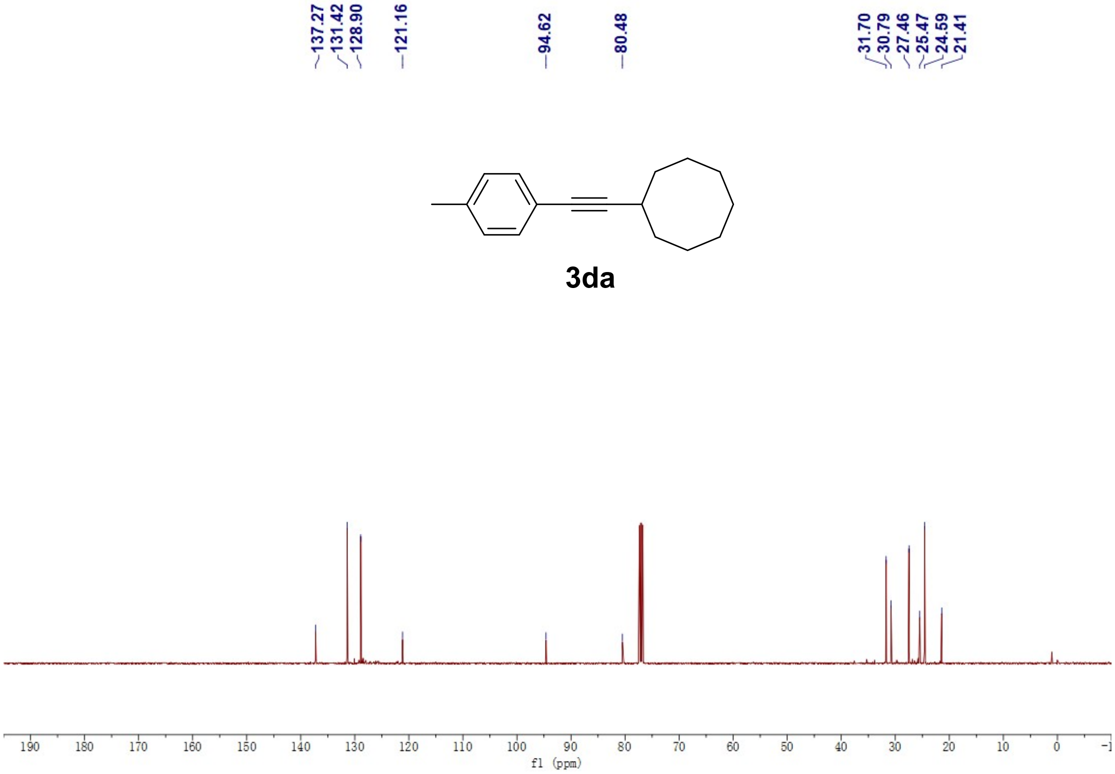
f1 (ppm)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180
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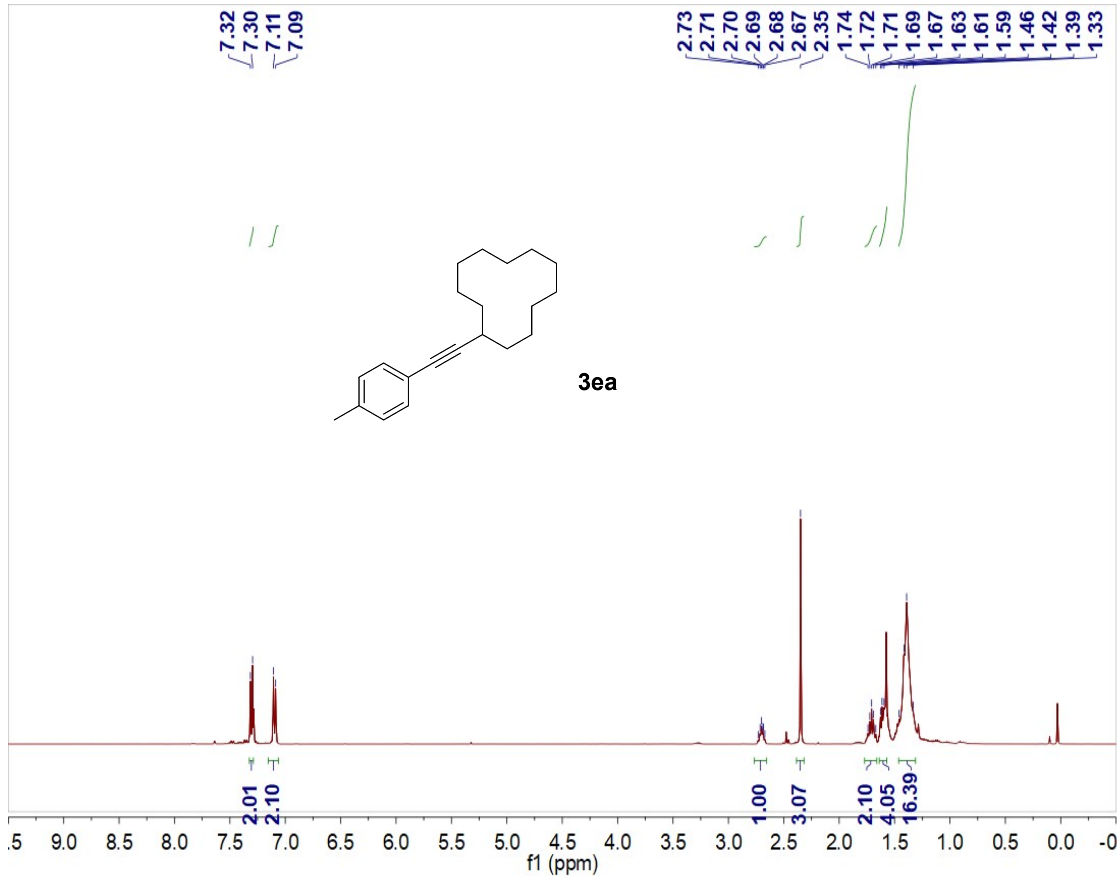
f1 (ppm)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1.71
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1.67
1.63
1.61
1.59
1.46
1.42
1.39
1.33
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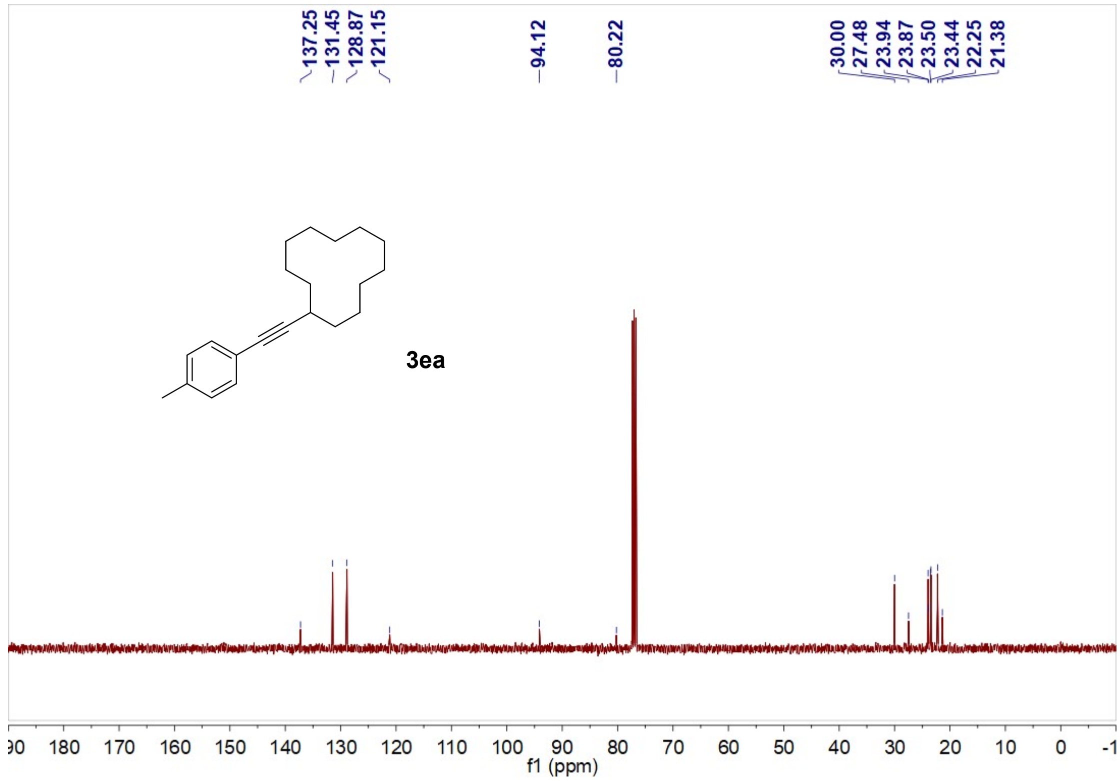
2.01
2.10
1.00
3.07
2.10
4.05
16.39
.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
f1 (ppm)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22.25
21.38
3ea
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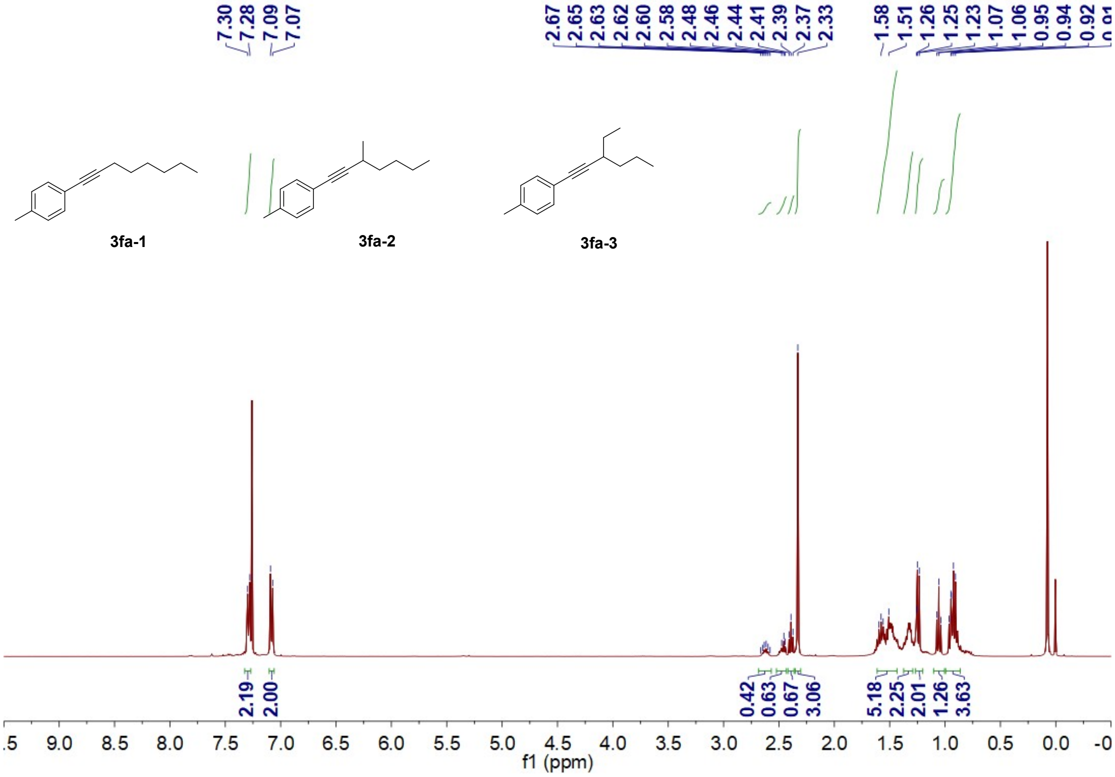
f1 (ppm)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2.39
2.37
2.33
1.58
1.51
1.26
1.25
1.23
1.07
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0.92
3fa-1
3fa-2
3fa-3
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0.63
0.67
3.06
5.18
2.25
2.01
1.26
3.63
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8.5
8.0
7.5
7.0
6.5
6.0
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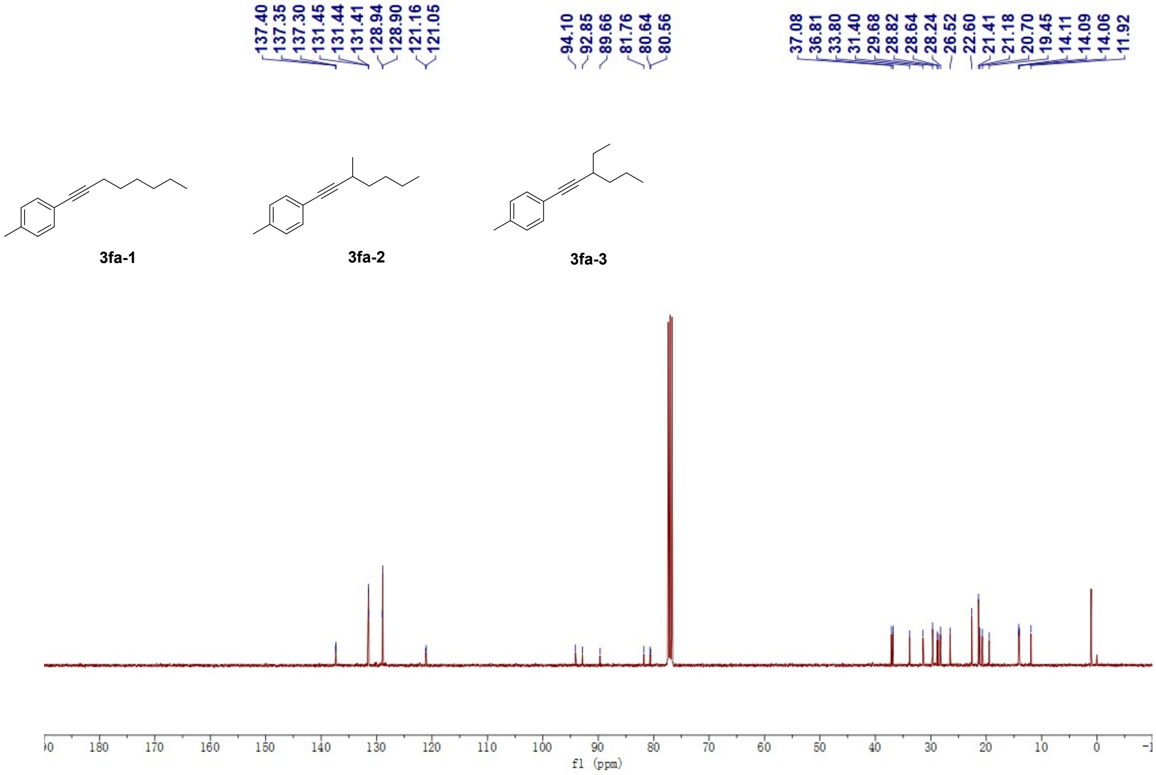
f1 (ppm)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80.56
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33.80
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28.64
28.24
26.52
22.60
21.41
21.18
20.70
19.45
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14.09
14.06
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3fa-2
3fa-3
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110
100
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10
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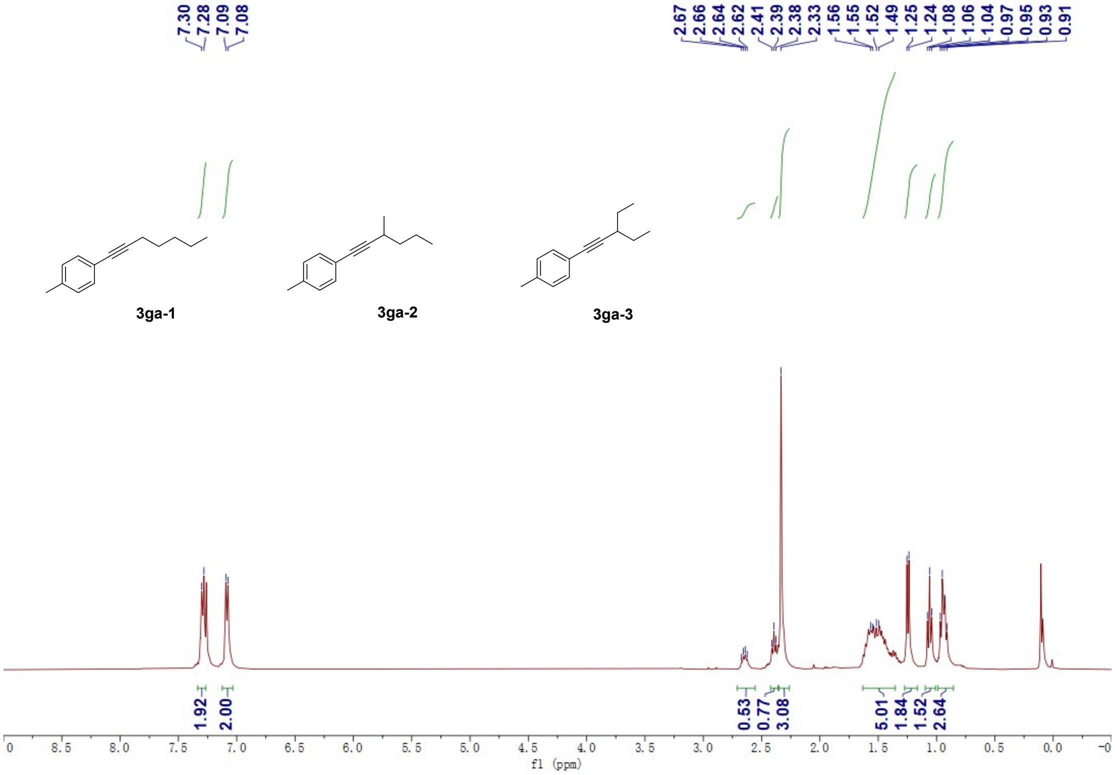
f1 (ppm)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1.25
1.24
1.08
1.06
1.04
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0.95
0.93
0.91
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3ga-3
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6.0
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1.0
0.5
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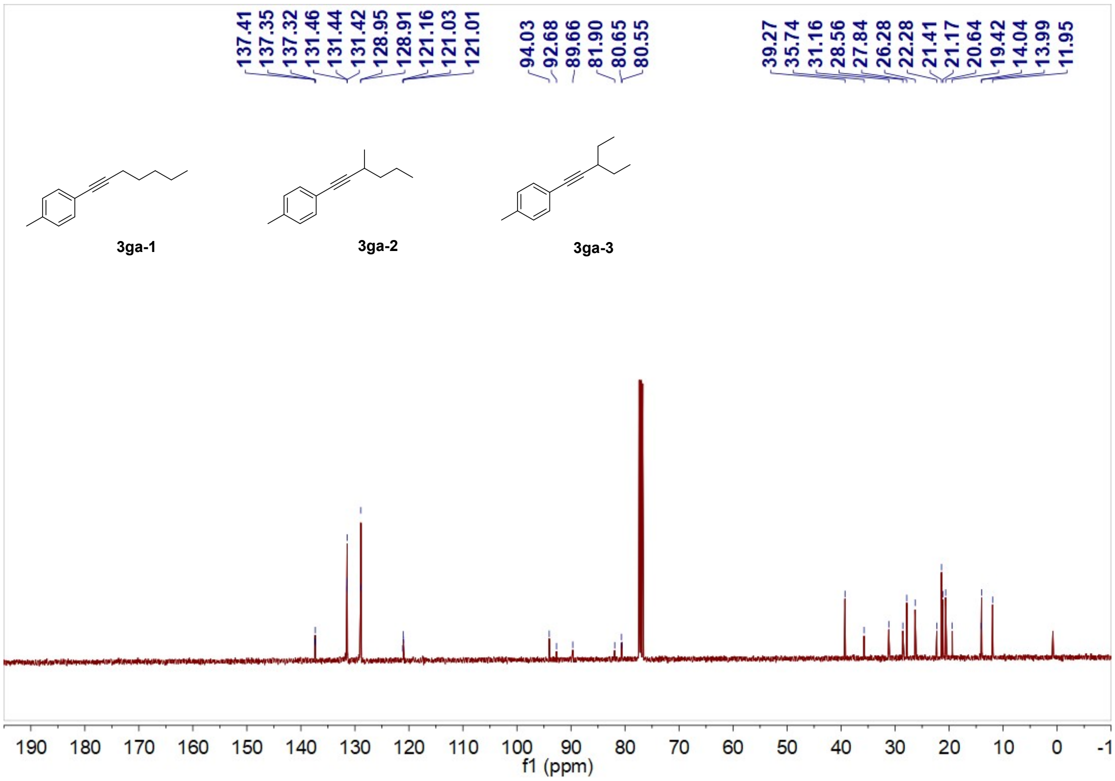
f1 (ppm)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21.17
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19.42
14.04
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3ga-2
3ga-3
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170
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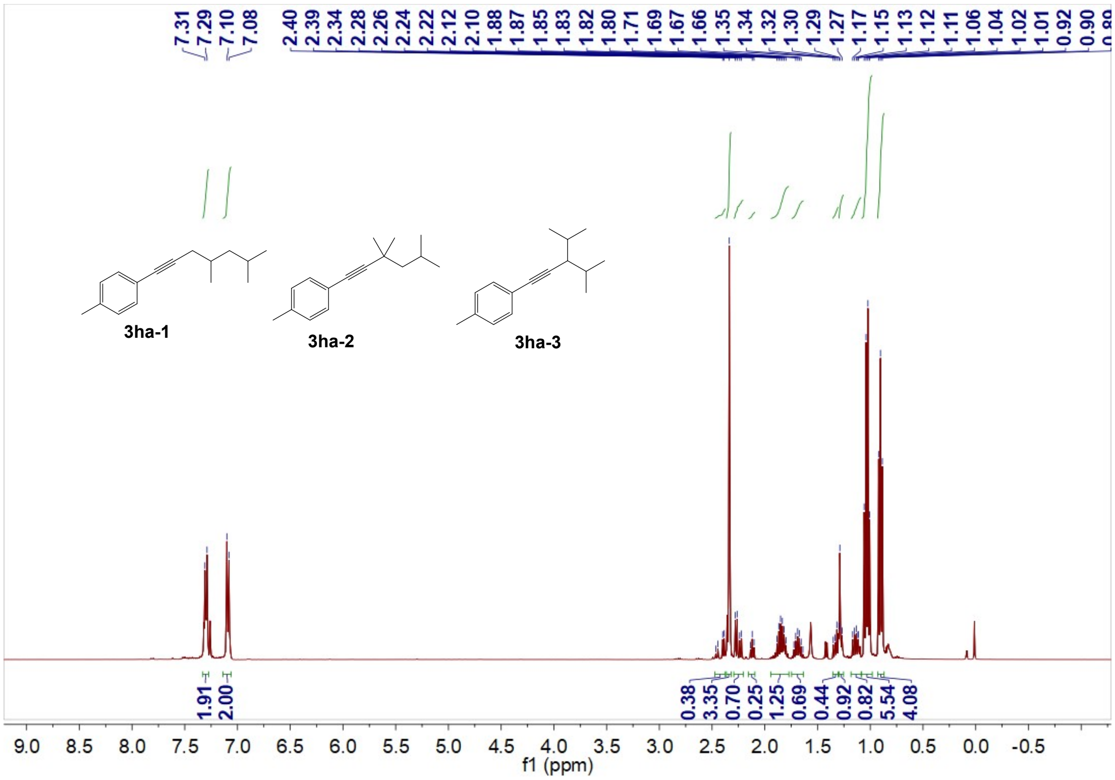
f1 (ppm)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1.29
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5.0
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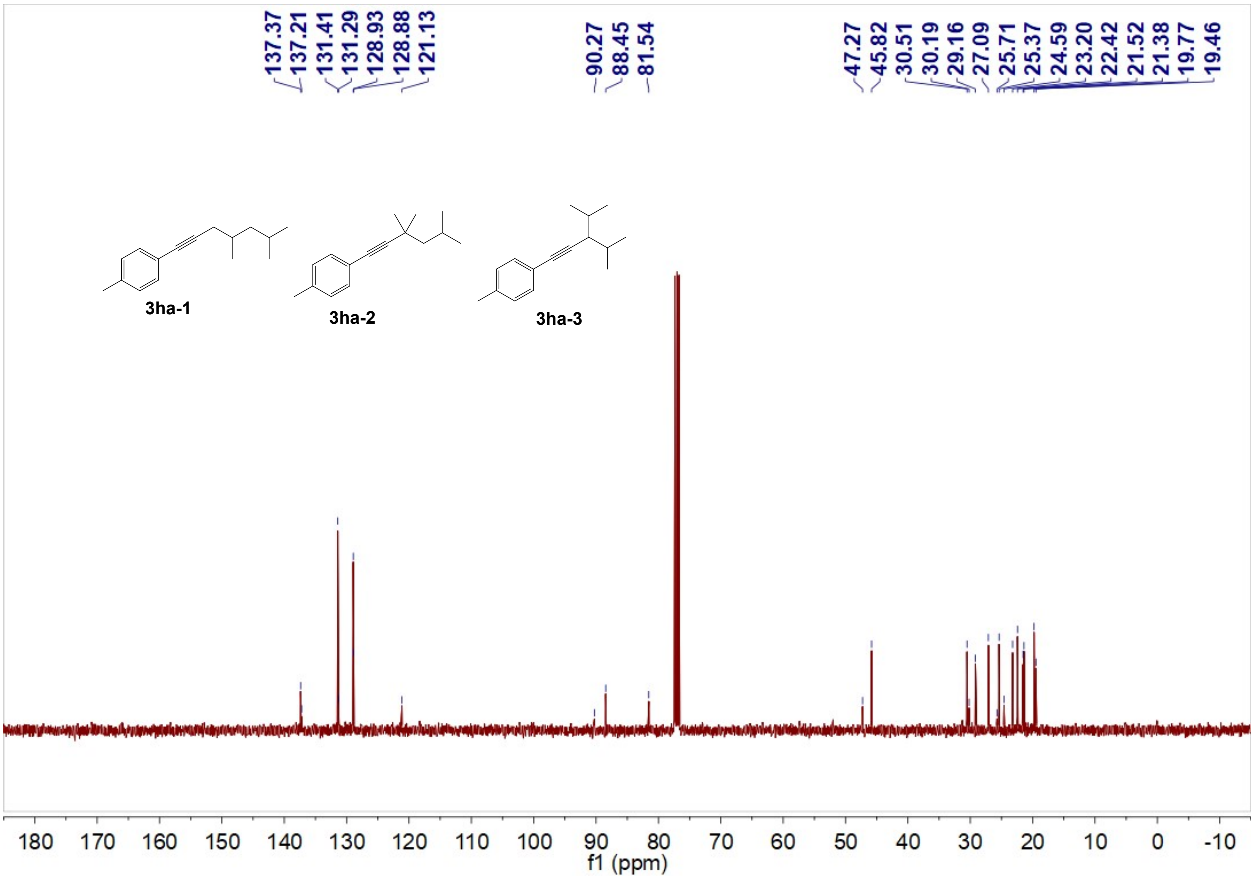
f1 (ppm)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29.16
27.09
25.71
25.37
24.59
23.20
22.42
21.52
21.38
19.77
19.46
3ha-1
3ha-2
3ha-3
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170
160
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140
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120
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100
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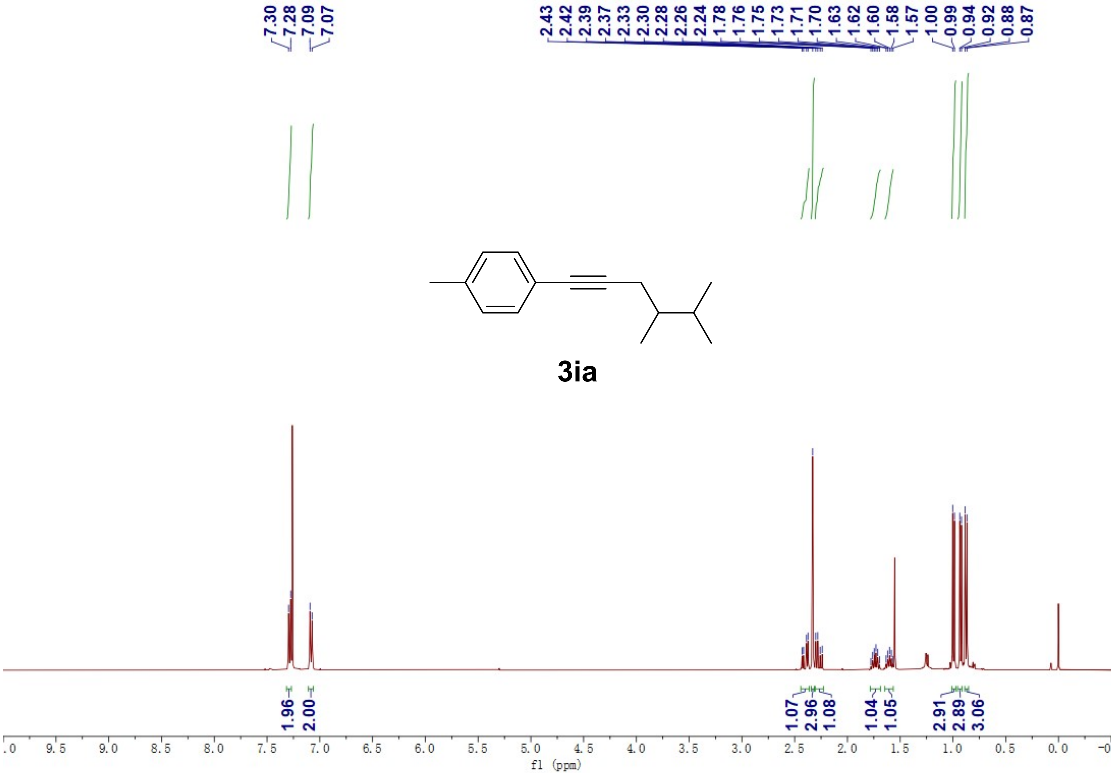
f1 (ppm)



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0.88
0.87
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1.04
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3.06
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6.0
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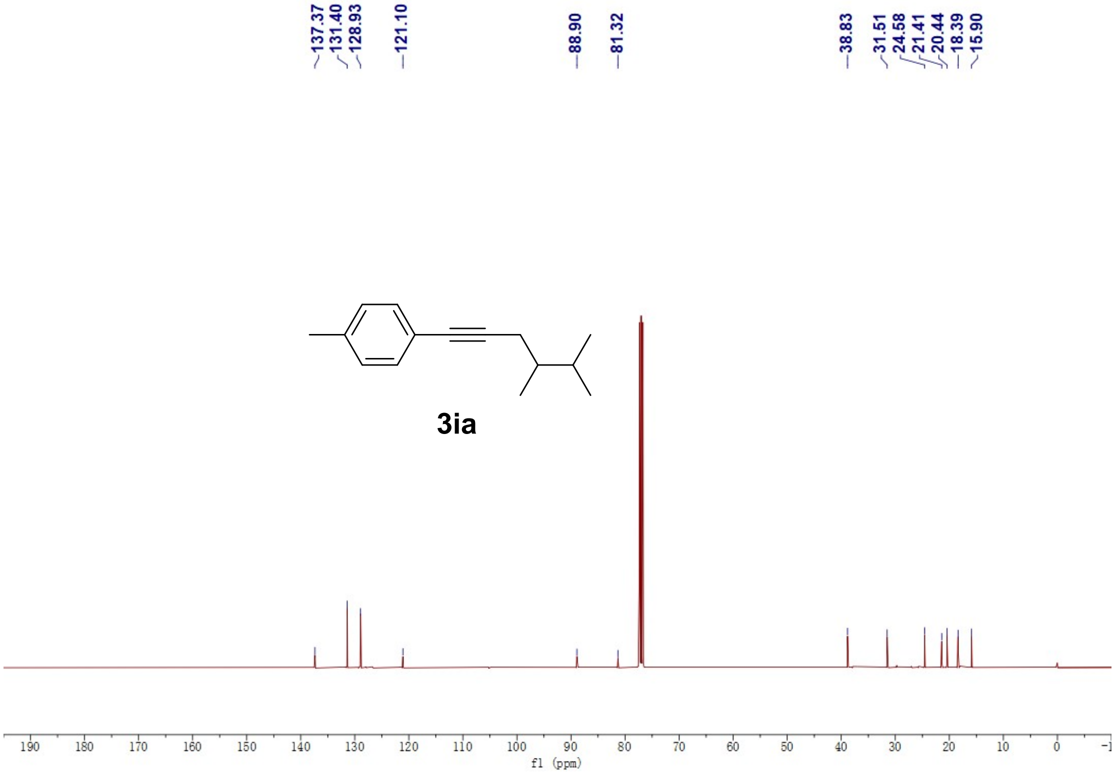
f1 (ppm)



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180
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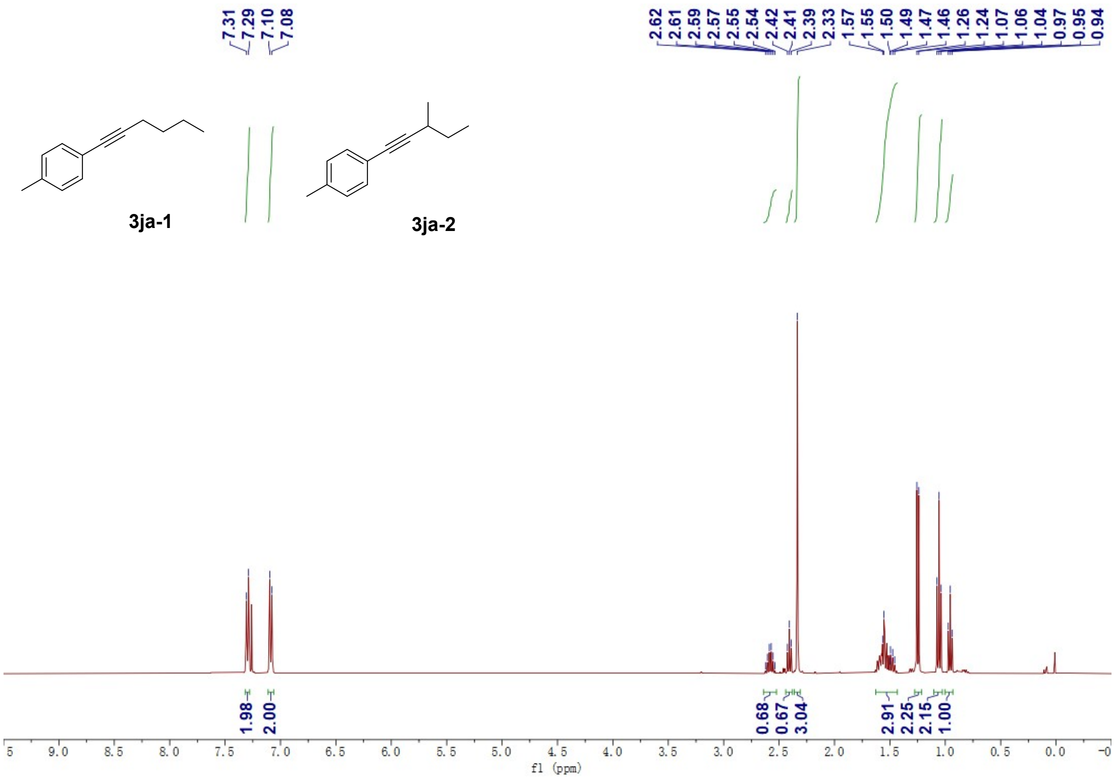
f1 (ppm)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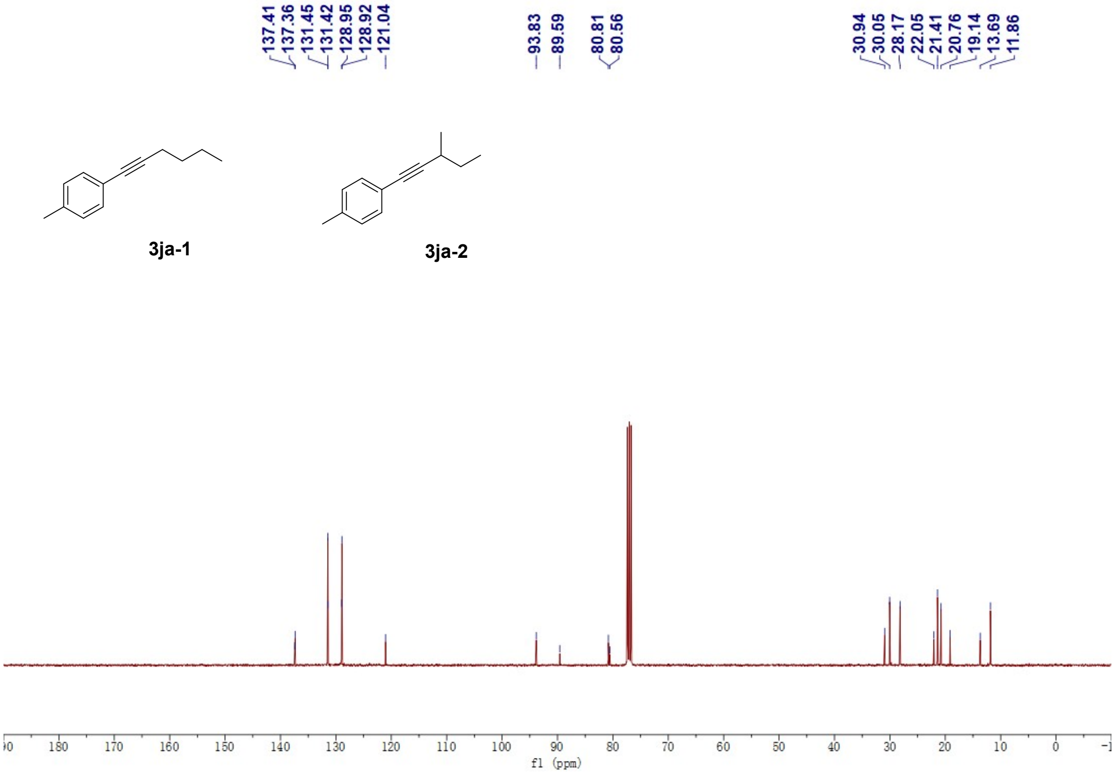
3ja-2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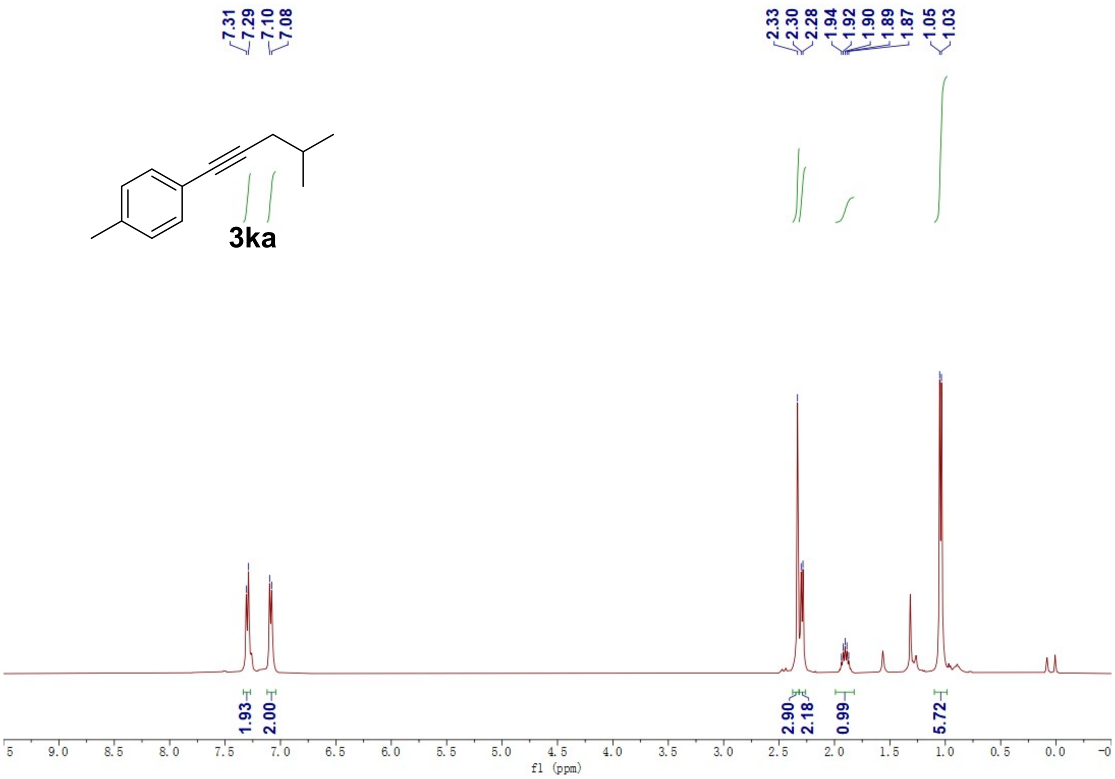
3ja-2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2.90
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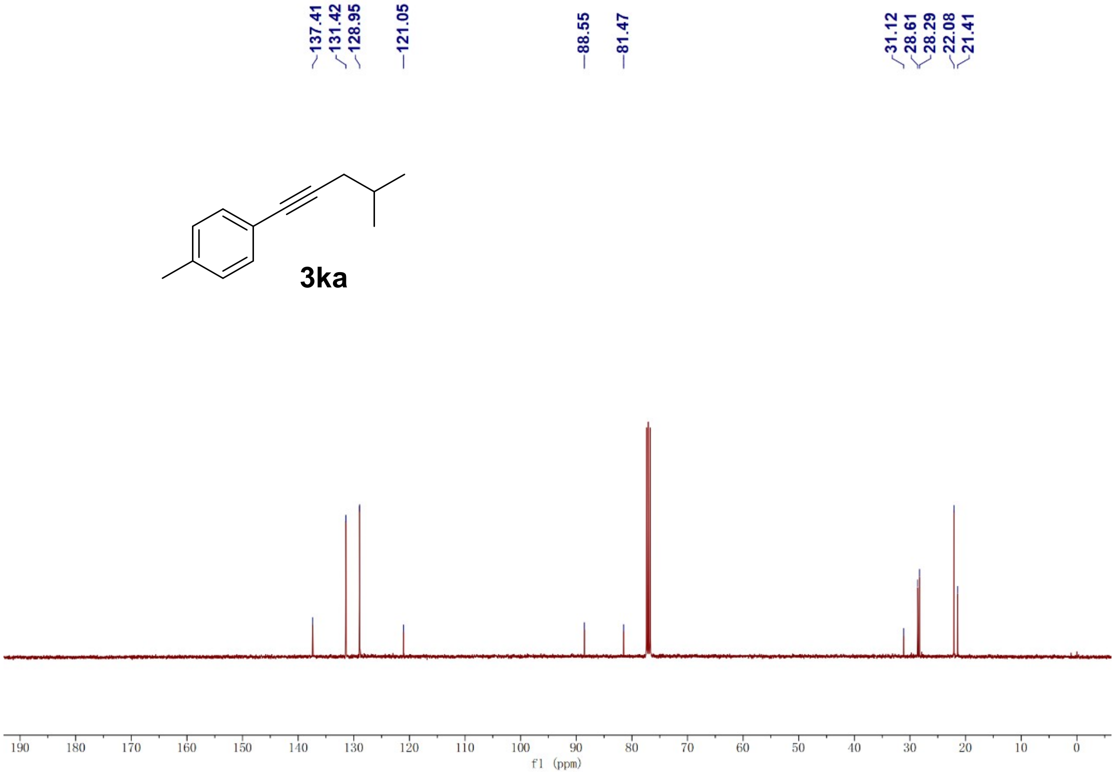
0.0
f1 (ppm)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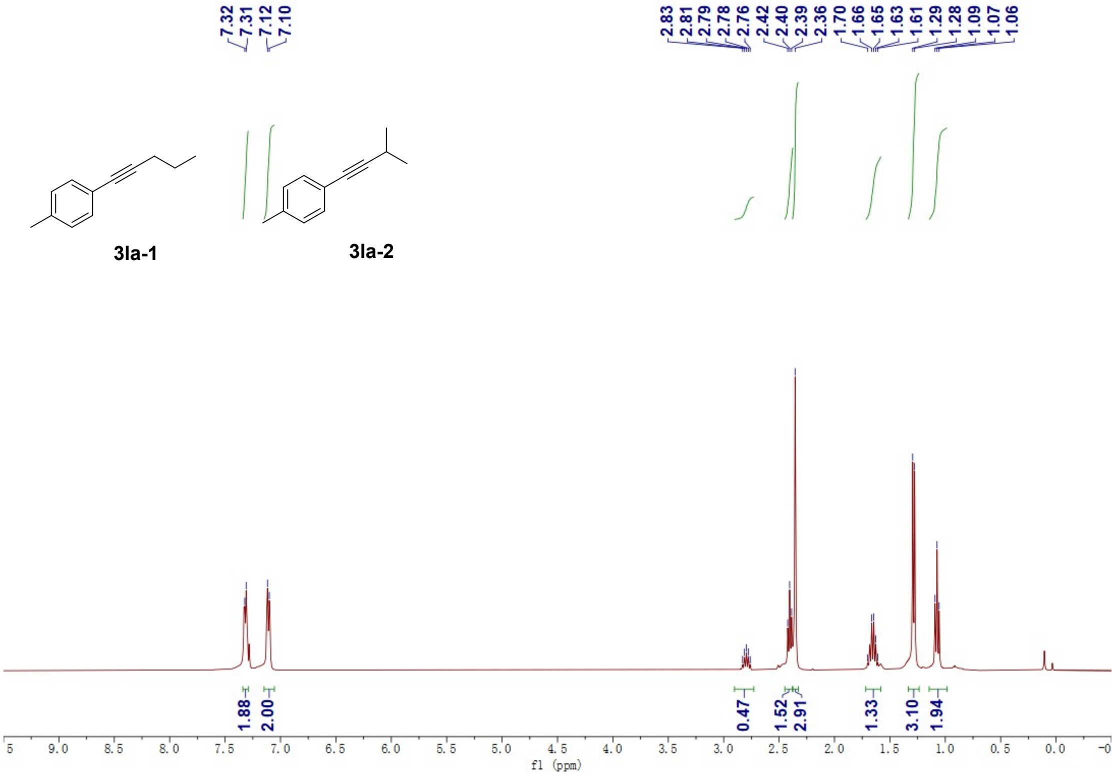
f1 (ppm)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1.63
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1.07
1.06
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3la-2
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1.94
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8.0
7.5
7.0
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6.0
5.5
5.0
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1.5
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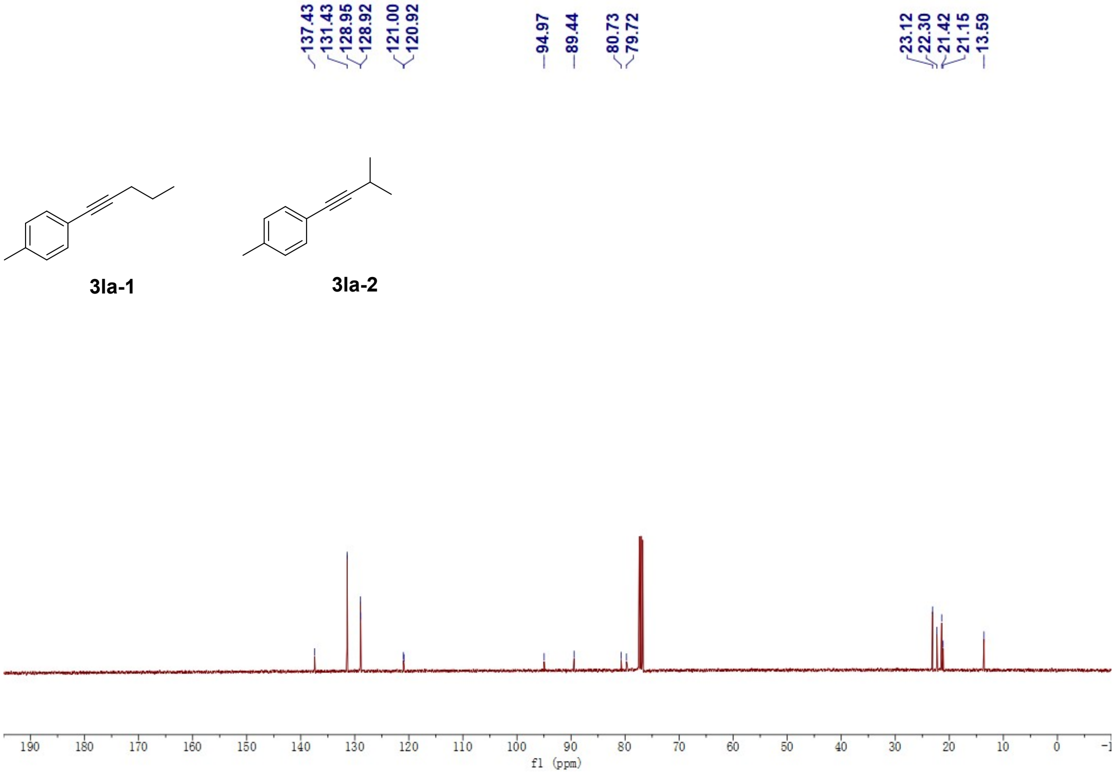
f1 (ppm)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22.30
21.42
21.15
13.59
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3la-2
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180
170
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100
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80
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60
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30
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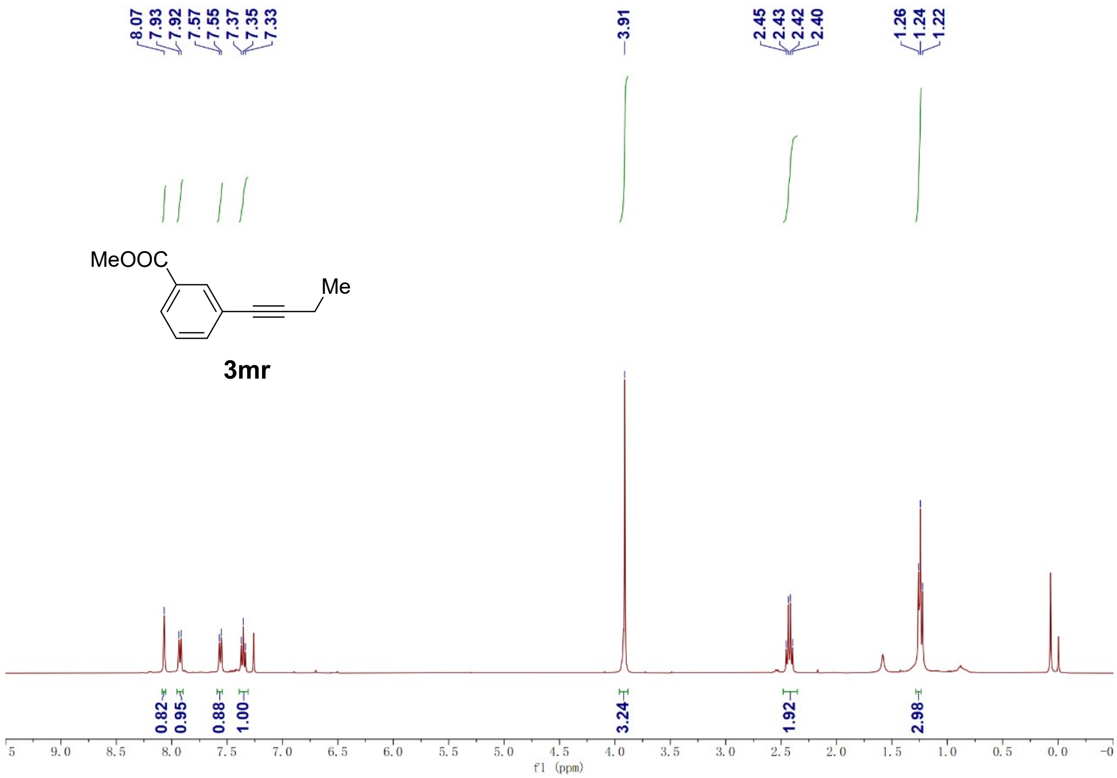
-1
f1 (ppm)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2.40
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1.24
1.22
MeOOC
Me
3mr
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0.95
0.88
1.00
3.24
1.92
2.98
5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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3.0
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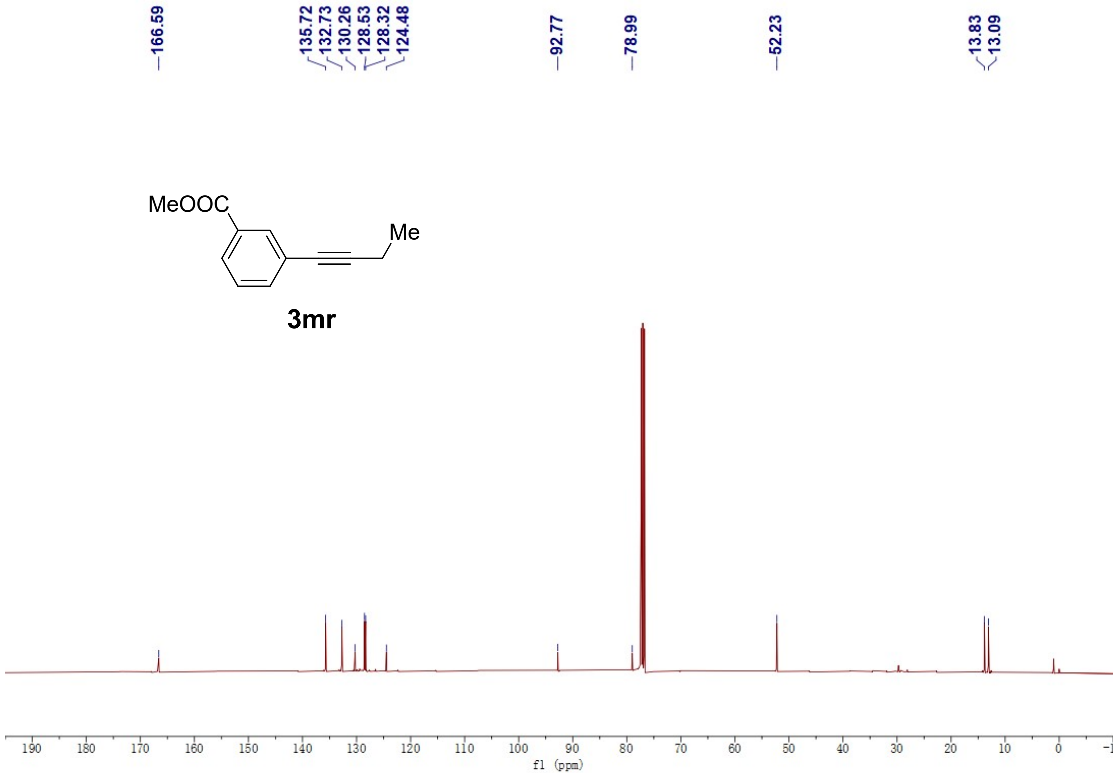
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)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13.09
MeOOC
Me
3mr
190
180
170
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100
90
80
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60
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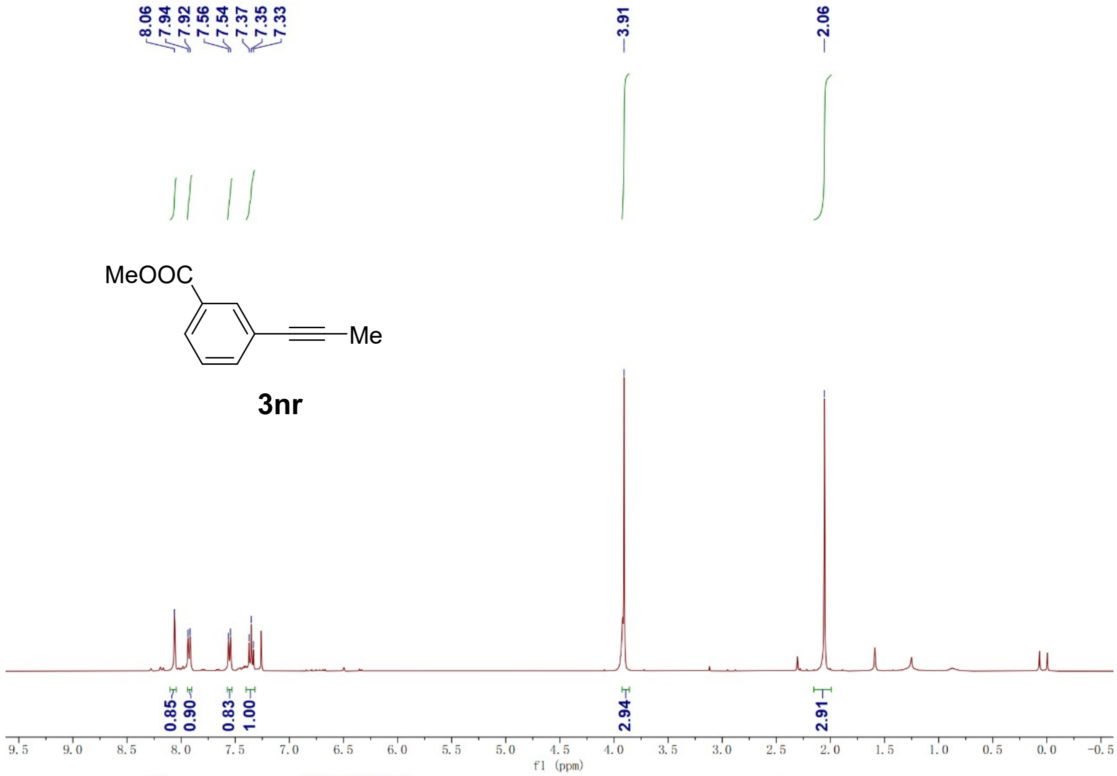
40
30
20
10
0
-1
f1 (ppm)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Me
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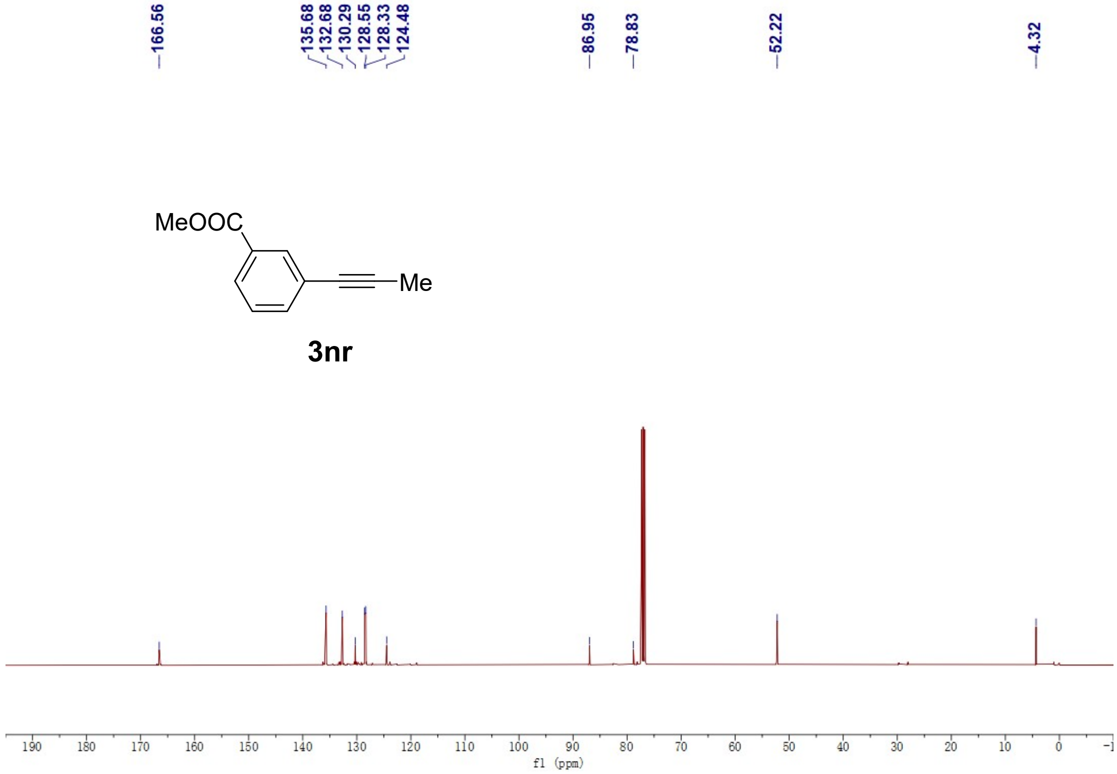
0.83
1.00
2.94
2.91
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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4.32
MeOOC
Me
3nr
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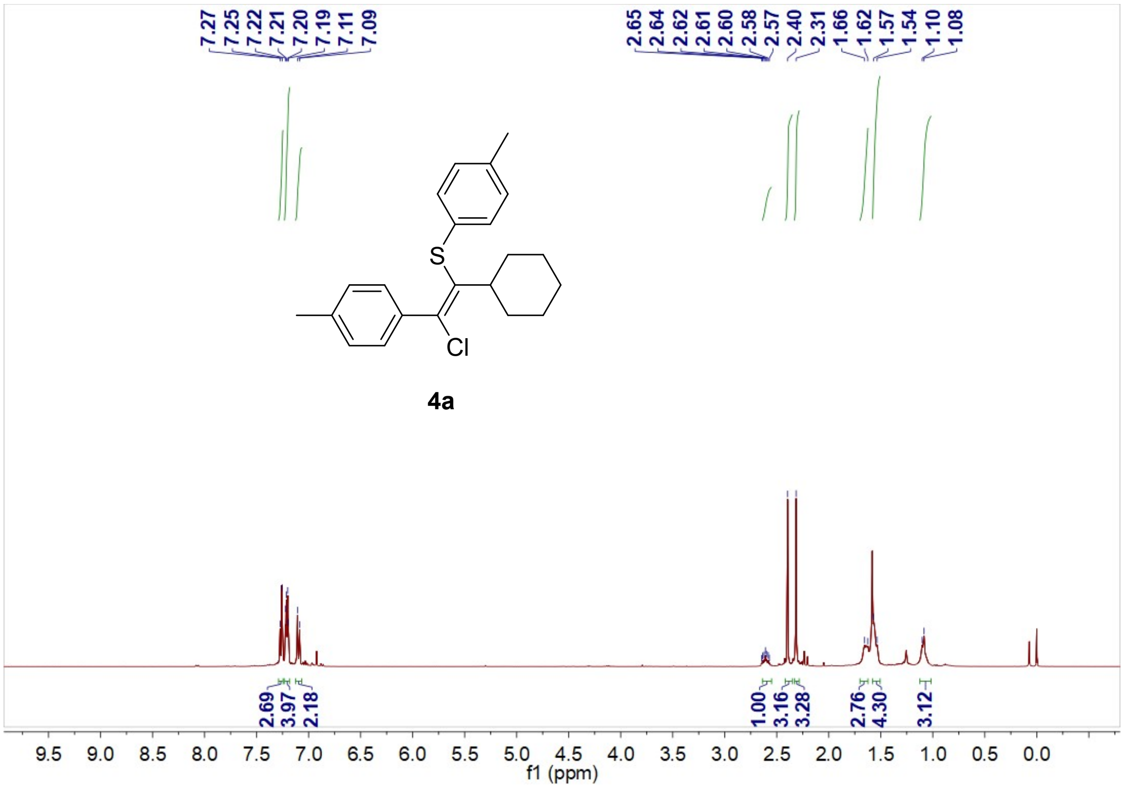
f1 (ppm)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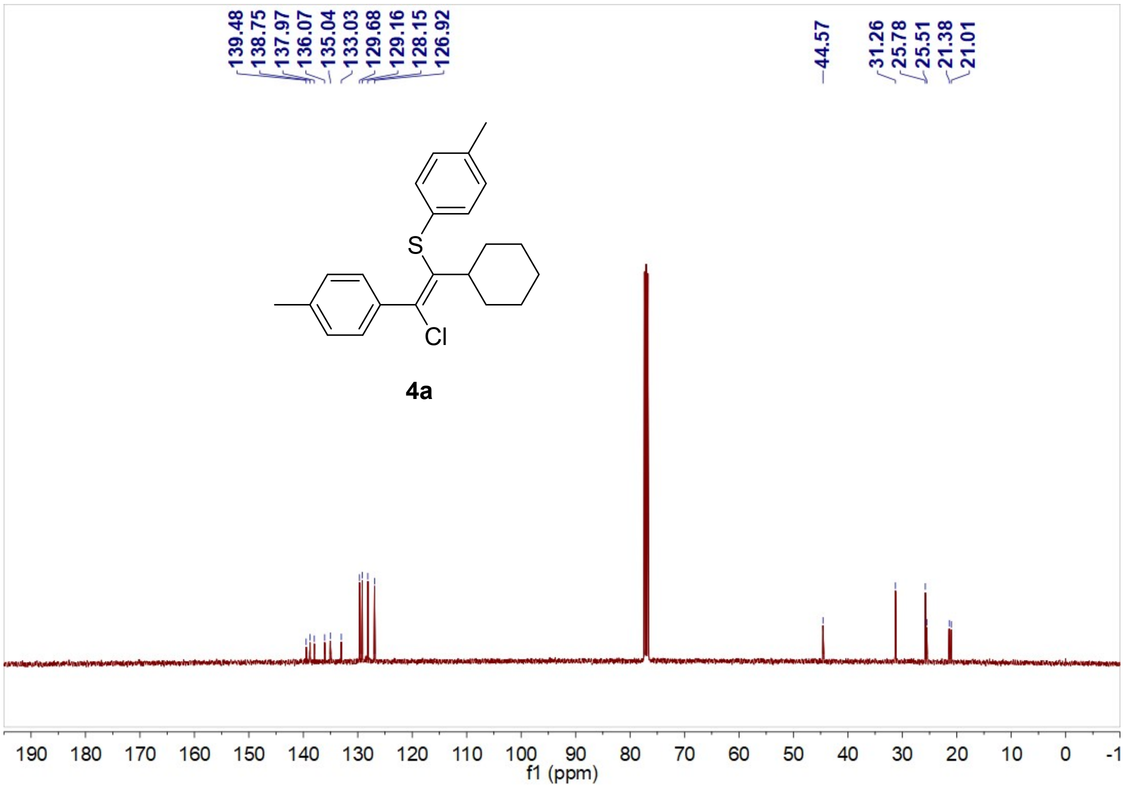
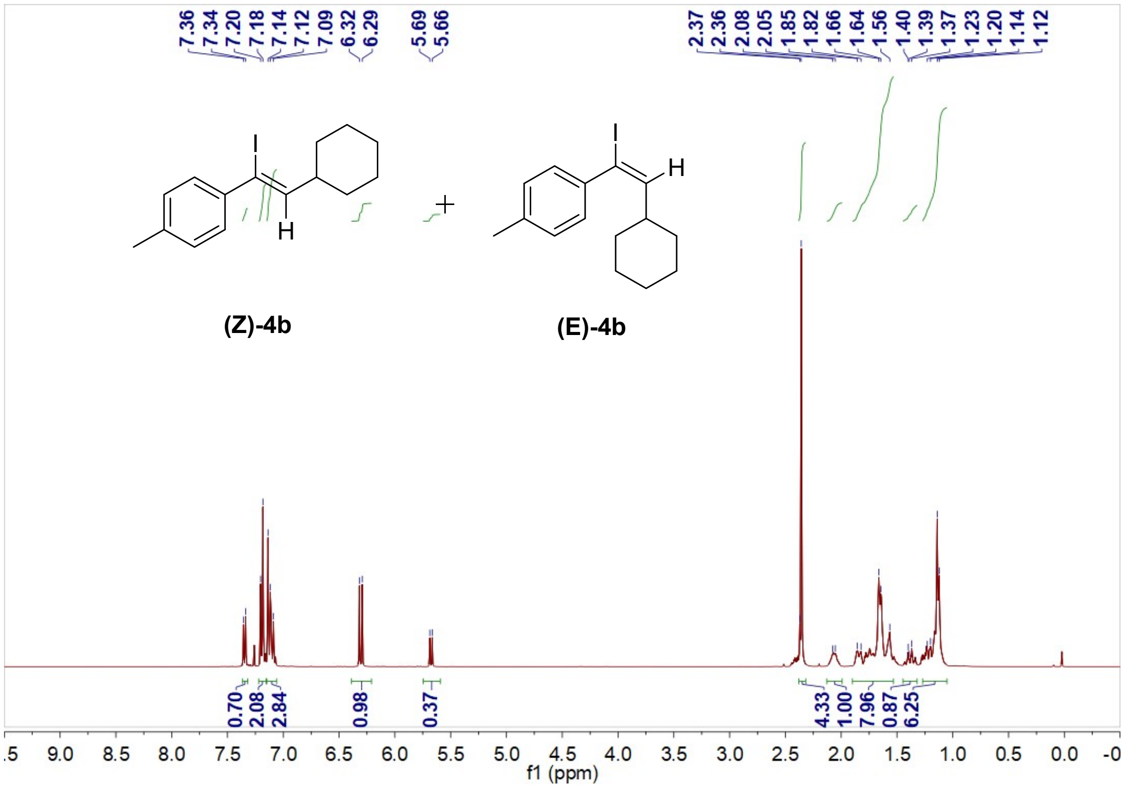
1.62
1.57
1.54
1.10
1.08
S
Cl
4a
2.69
3.97
2.18
1.00
3.16
3.28
2.76
4.30
3.12
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


139.48
138.75
137.97
136.07
135.04
133.03
129.68
129.16
128.15
126.92
44.57
31.26
25.78
25.51
21.38
21.01
S
Cl
4a
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)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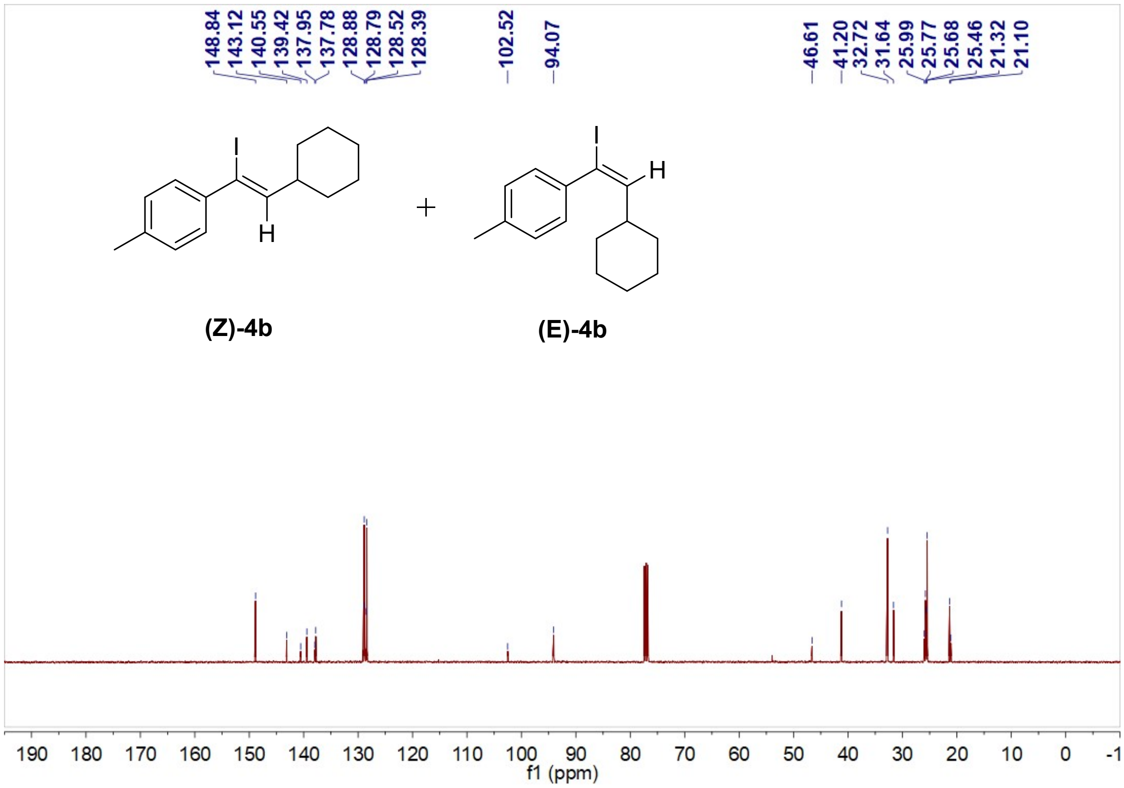
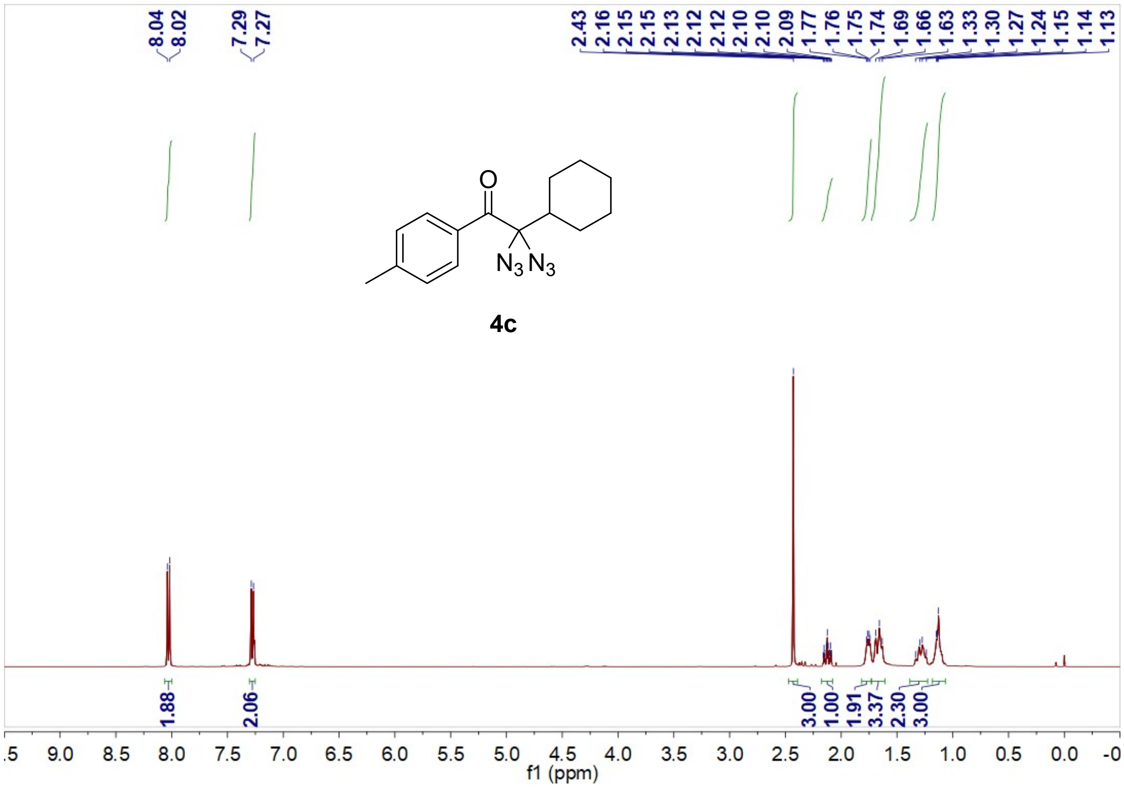
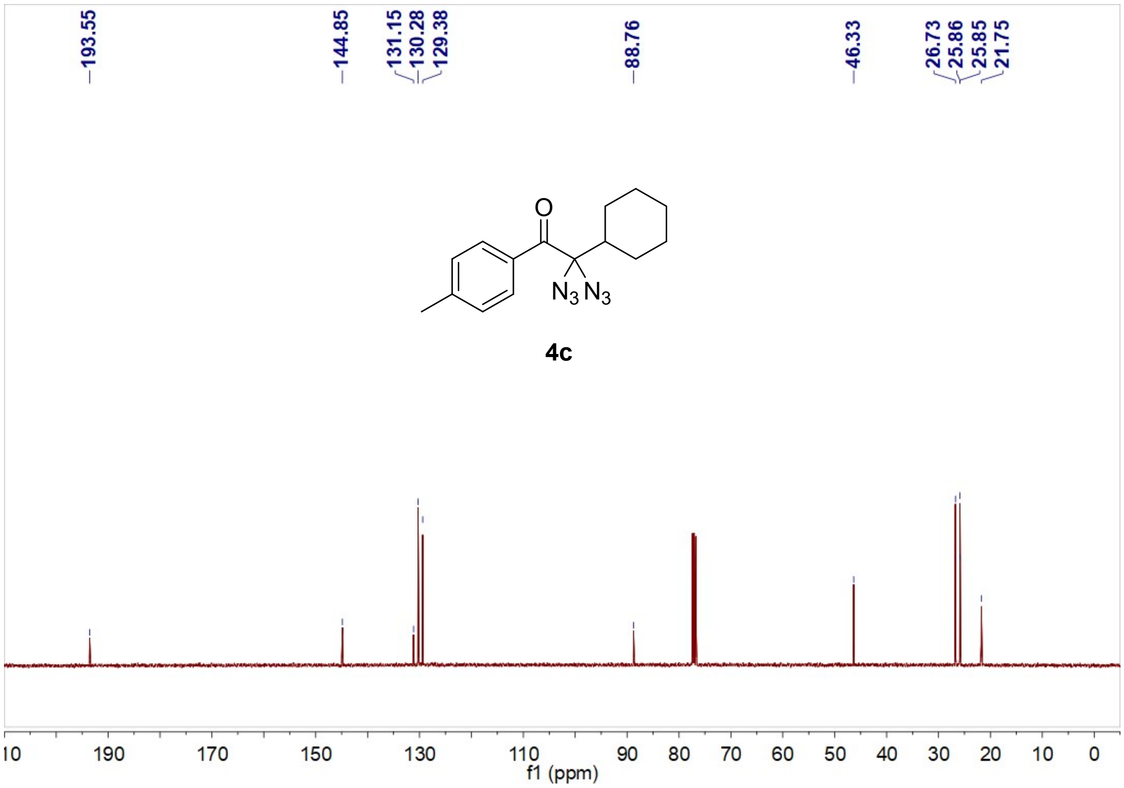
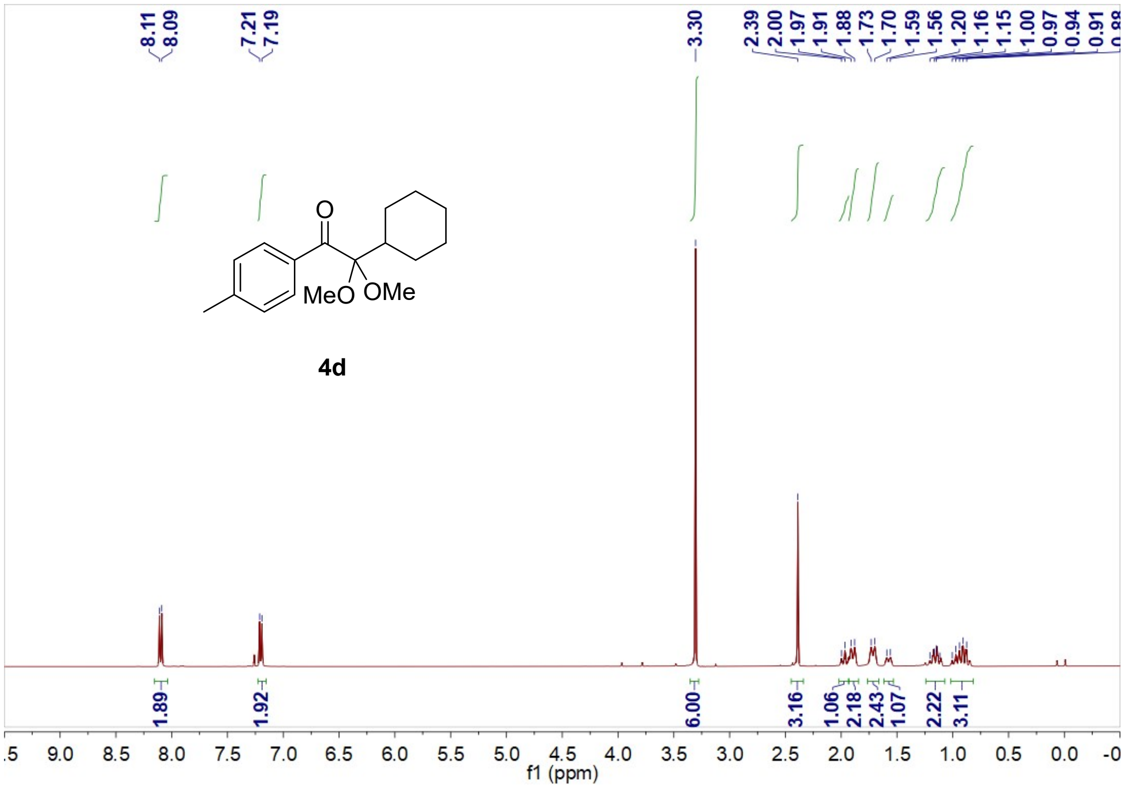
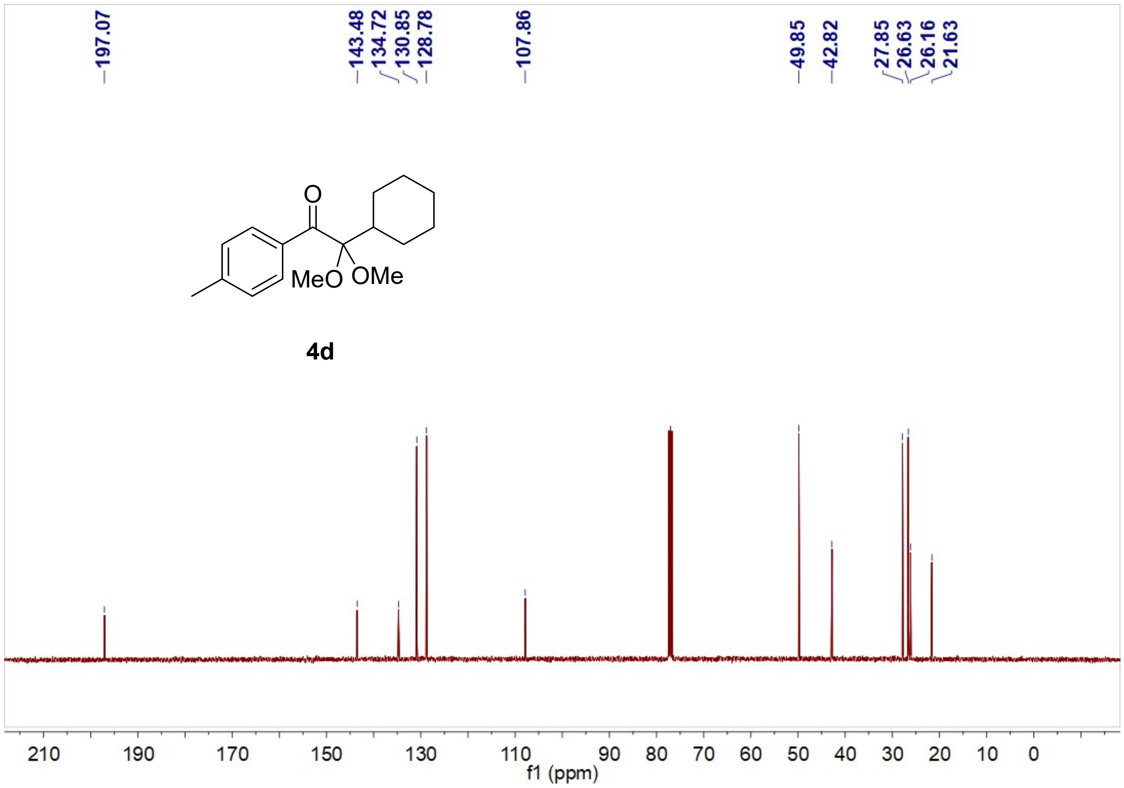
7.34
7.20
7.18
7.14
7.12
7.09
6.32
6.29
5.69
5.66
2.37
2.36
2.08
2.05
1.85
1.82
1.66
1.64
1.56
1.40
1.39
1.37
1.23
1.20
1.14
1.12
I
H
+
I
H
(Z)-4b
(E)-4b
0.70
2.08
2.84
0.98
0.37
4.33
1.00
7.96
0.87
6.25
.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
f1 (ppm)

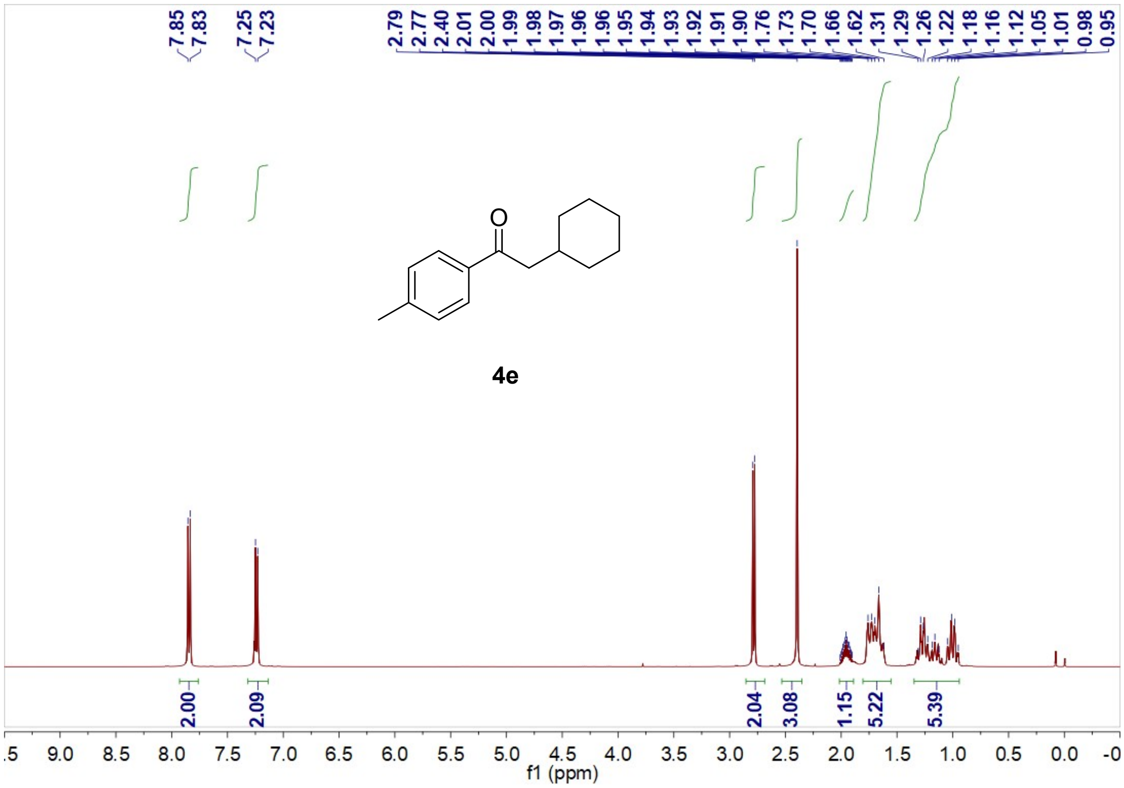

148.84
143.12
140.55
139.42
137.95
137.78
128.88
128.79
128.52
128.39
102.52
94.07
46.61
41.20
32.72
31.64
25.99
25.77
25.68
25.46
21.32
21.10
I
H
+
I
H
(Z)-4b
(E)-4b
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)

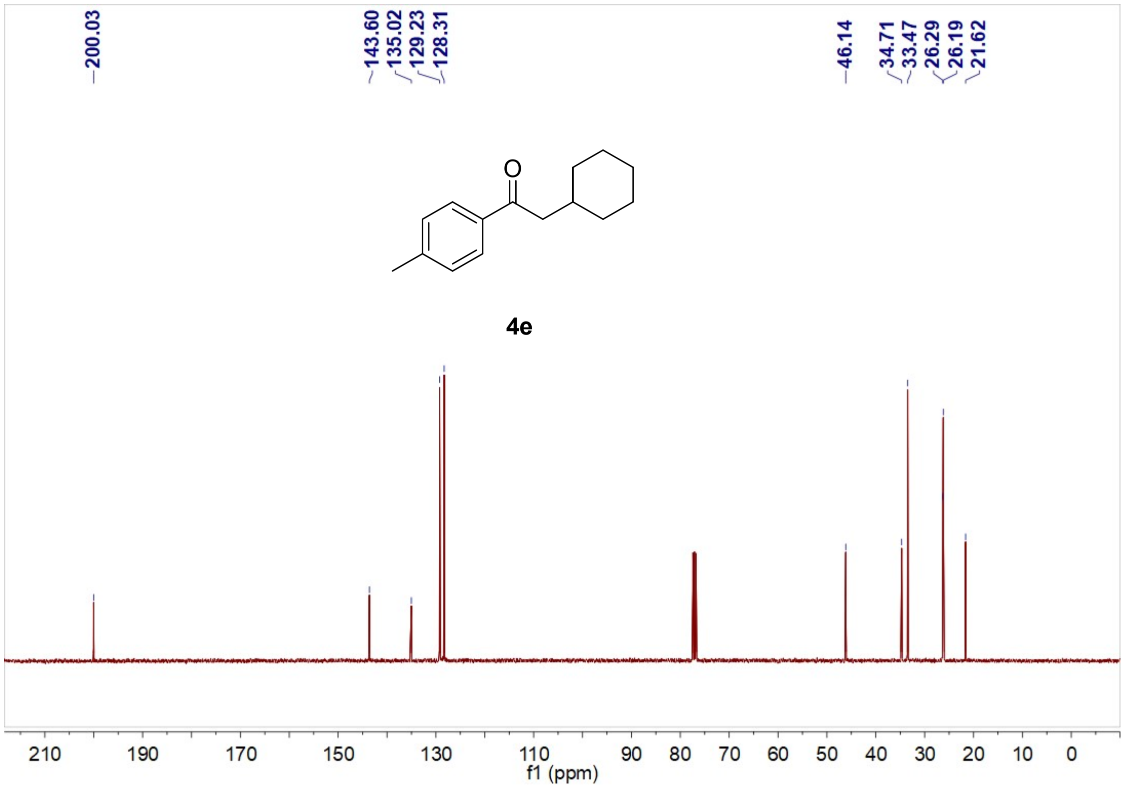

8.04
8.02
7.29
7.27
2.43
2.16
2.15
2.15
2.13
2.12
2.12
2.10
2.10
2.09
1.77
1.76
1.75
1.74
1.69
1.66
1.63
1.33
1.30
1.27
1.24
1.15
1.14
1.13
O
N3 N3
4c
1.88
2.06
3.00
1.00
1.91
3.37
2.30
3.00
.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)


193.55
144.85
131.15
130.28
129.38
88.76
46.33
26.73
25.86
25.85
21.75
O
N3 N3
4c
10
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.11
8.09
7.21
7.19
3.30
2.39
2.00
1.97
1.91
1.88
1.73
1.70
1.59
1.56
1.20
1.16
1.15
1.00
0.97
0.94
0.91
O
MeO
OMe
4d
1.89
1.92
6.00
3.16
1.06
2.18
2.43
1.07
2.22
3.11
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


197.07
143.48
134.72
130.85
128.78
107.86
49.85
42.82
27.85
26.63
26.16
21.63
O
MeO
OMe
4d
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.85
7.83
7.25
7.23
2.79
2.77
2.40
2.01
2.00
1.99
1.98
1.97
1.96
1.96
1.95
1.94
1.93
1.92
1.91
1.90
1.76
1.73
1.70
1.66
1.62
1.31
1.29
1.26
1.22
1.18
1.16
1.12
1.05
1.01
0.98
0.95
O
4e
2.00
2.09
2.04
3.08
1.15
5.22
5.39
.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
f1 (ppm)


200.03
143.60
135.02
129.23
128.31
46.14
34.71
33.47
26.29
26.19
21.62
O
4e
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

7. Reference

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[4] Luca Capaldo. Davide Ravelli, *Org. Lett.* 2021, 23, 6, 2243–224710.