Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Copper-catalyzed 1,2-Borylacylation of 1,3-Enynes: Synthesis of *β*-Alkynyl Ketones

Xin-Lian Liu,[†] Lin Li,[†] Han-Ze Lin,[†] Jing-Tong Deng,[†] Xiang-Zhi Zhang,[*,†] and Jin-Bao Peng*[,†]

[†]School of Biotechnology and Health Sciences, Wuyi University, Jiangmen, Guangdong 529020, People's Republic of China; orcid.org/0000-0002-0568-7740; E-mail: pengjb_05@126.com

Table of Contents

1. General Information

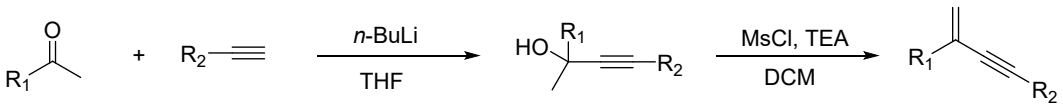
Reagents, solvents and analytical methods:

Unless otherwise noted, all reactions were carried out under a nitrogen atmosphere. All reagents were from commercial sources and used as received without further purification. All solvents were dried by standard techniques and distilled prior to use. Column chromatography was performed on silica gel (200-300 meshes) using petroleum ether (bp. 60~90 °C) and ethyl acetate as eluent. ^{1}NMR spectra were recorded on a Bruker Avance operating at for ^{1}H NMR at 500 MHz, ^{13}C NMR at 126 MHz and ^{19}F NMR at 471 MHz and spectral data were reported in ppm relative to tetramethylsilane (TMS) as internal standard and $CDCl_3$ (^{1}H NMR δ 7.27, ^{13}C NMR δ 77.0) as solvent. High-resolution mass spectra (HRMS) is produced by Thermo Fisher Scientific. Its main body is composed of two parts: Thermo Scientific's UltiMate 3000 Series liquid system and Thermo Scientific Q-Exactive combined quadrupole Orbitrap mass spectrometer. All coupling constants (*J*) are reported in Hz. The following abbreviations were used to describe peak splitting patterns when appropriate: s = singlet, d = doublet, dd = double doublet, ddd = double doublet of doublets, t = triplet, dt = double triplet, q = quatriplet, m = multiplet, br = broad.

2. Substrate Synthesis

2.1 *Synthesis of 1,3-enynes derivatives*

1,3-enynes **1** were synthesized according to the known method[S1] by using alkyne and ketone as the substrates(**1a** – **1o**).



Under nitrogen atmosphere, *n*-BuLi (2.0 M in hexane, 5 mmol, 2.5 mL) was added dropwise to a solution of alkyne (5 mmol) in anhydrous THF (20 mL) at -78 ℃. After addition, the resulting solution was stirred at room temperature for one hour. Then, cooled to -78 ℃ again, ketone (5 mmol) in THF (10 mL) was added dropwise. The reaction mixture was then allowed to warm to room temperature and was monitored by TLC. Once completion the reaction was quenched with saturated aqueous NH_4Cl and extracted with EtOAc three times. The combined organic layer was dried over Na_2SO_4 and concentrated under reduced pressure to afford the crude propargyl alcohol.

The resulting propargyl alcohol was dissolved in DCM (30 mL), and the mixture was cooled to 0 ℃. TEA (25 mmol, 5 equiv) was added to this solution and methylsulfonyl chloride (12.5 mmol, 2.5 equiv) sequentially. After one hour the reaction was monitored by TLC. Once completion the reaction was quenched with saturated aqueous NH_4Cl. The aqueous layer was extracted with DCM and the combined organic layers were washed with brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The crude material was purified by flash chromatography to yield the 1,3-enyne.

1a[S1], **1b**[S1], **1d-1f**[S1],**1h**[S1], **1i**[S2], **1j**[S3], **1k-1n**[S1] are known compounds.

2.2 Acid chloride **2a - 2l** were purchased from commercial suppliers and used without further purification.

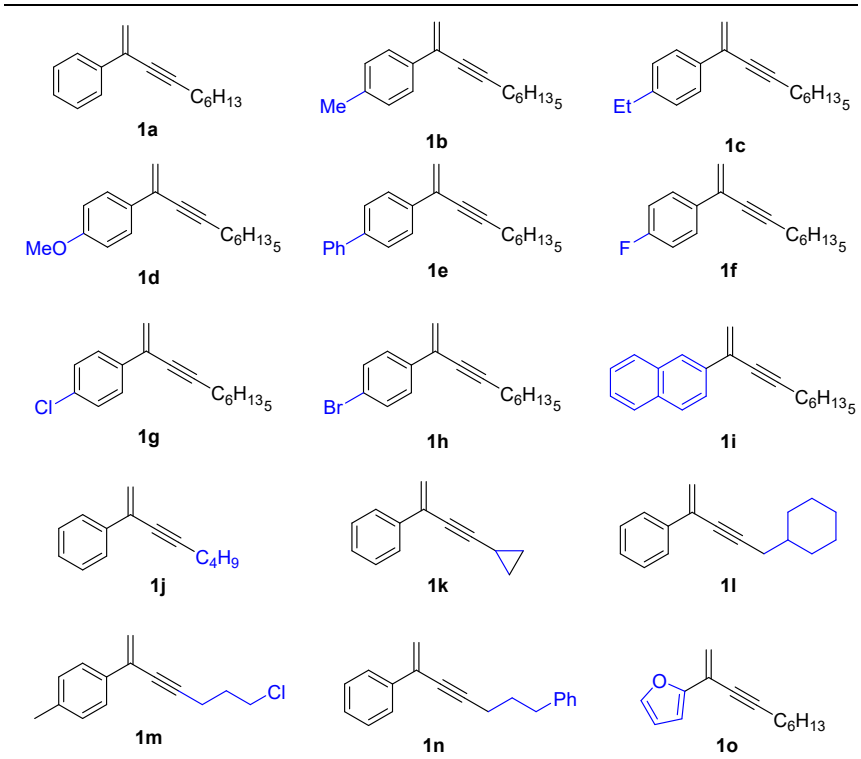


Figure S1 Substrates of 1,3-enynes derivatives

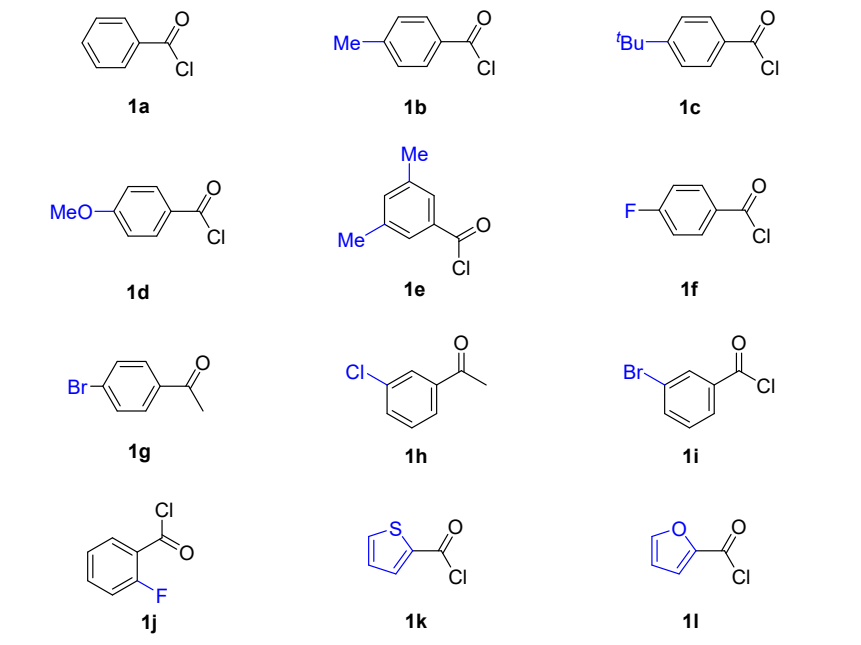
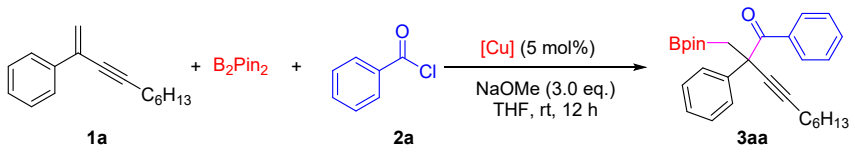


Figure S2 Substrates of acid chlorides

3. Optimization of Reaction Conditions

Table S1. Optimization of the catalyst.[a]

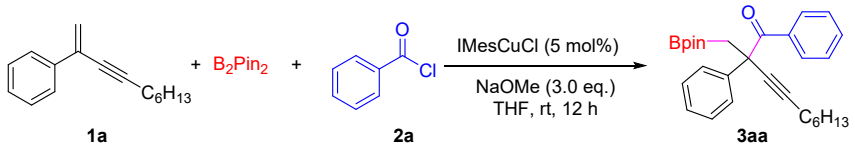


1a **2a** **3aa**

Entry	Catalyst	Yield (%)[b]
1	IPrCuCl	15
2	CuTc	trace
3	CuCl	trace
4	None	trace

[a] Reaction conditions: **1a** (0.30 mmol), B_2Pin_2 (0.45 mmol), **2a** (0.30 mmol), catalyst (5 mol%), NaOMe (3.0 equiv), THF (1 mL), N_2 atmosphere, rt for 10 h. [b] Isolated yield.

Table S2. Optimization of the ratio of B_2Pin_2 and acid chloride.[a]

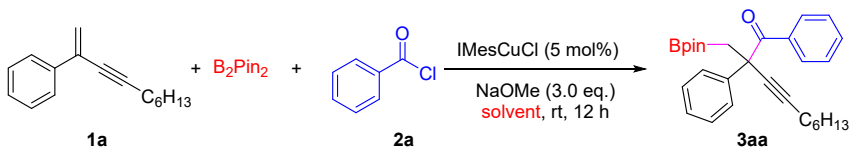


1a **2a** **3aa**

Entry	B_2Pin_2 (x mmol)	Acid chloride (x mmol)	Yield (%)[b]
1	0.24	0.30	40
2	0.30	0.40	55
3	0.30	0.24	30
4	0.40	0.30	32

[a] Reaction conditions: **1a** (0.30 mmol), B_2Pin_2 (x mmol), **2a** (x mmol), IMesCuCl (5 mol%), NaOMe (3.0 equiv), THF (1 mL), N_2 atmosphere, rt for 10 h. [b] Isolated yield.

Table S3. Optimization of the solvent.[a]

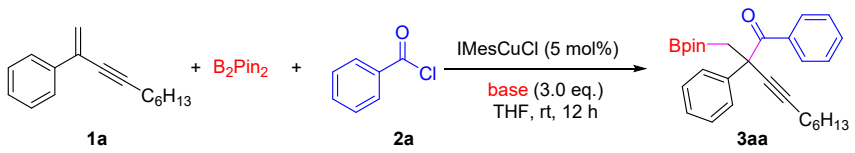


1a **2a** **3aa**

Entry	Solvent	Yield (%)[b]
1	Dioxane	23
2	Et_2O	14
3	DME	25
4	DCM	31
5	toluene	12
6	MeCN	trace

[a] Reaction conditions: **1a** (0.30 mmol), B_2Pin_2 (0.45 mmol), **2a** (0.60 mmol), IMesCuCl (5 mol%), NaOMe (3.0 equiv), solvent (1 mL), N_2 atmosphere, rt for 10 h. [b] Isolated yield.

Table S4. Optimization of the base.[a]

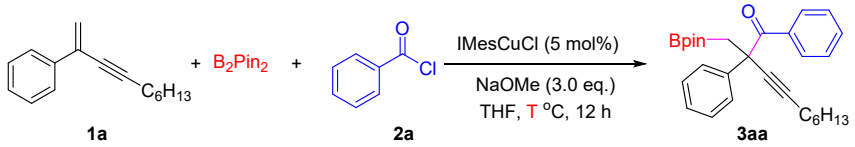


1a 2a 3aa

Entry	Base	Yield (%)[b]
1	NaO^{t}Bu	15
2	KO^{t}Bu	trace
3	Na_2CO_3	trace
4	KOMe	30
5	LiOMe	trace
6	TEA	trace
7	NaOMe	55

[a] Reaction conditions: **1a** (0.30 mmol), B_2Pin_2 (0.45 mmol), **2a** (0.60 mmol), IMesCuCl (5 mol%), base (3.0 equiv), THF (1 mL), N_2 atmosphere, rt for 10 h. [b] Isolated yield.

Table S5. Optimization of temperature.[a]

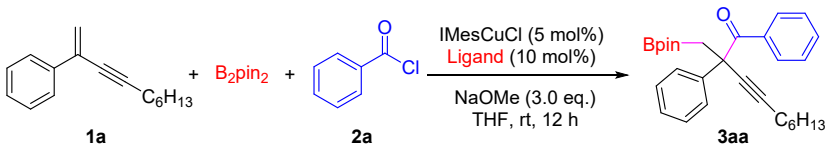


1a 2a 3aa

Entry	Temp. (°C)	Yield (%)[b]
1	0	52
2	rt	55
3	50	48
4	70	trace

[a] Reaction conditions: **1a** (0.30 mmol), B_2Pin_2 (0.45 mmol), **2a** (0.60 mmol), IMesCuCl (5 mol%), NaOMe (3.0 equiv), THF (1 mL), N_2 atmosphere, T °C for 10 h. [b] Isolated yield.

Table S6. Optimization of ligand.[a]

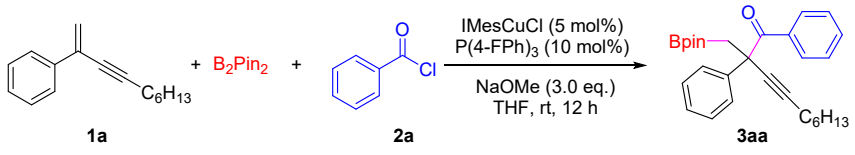


1a 2a 3aa

Entry	Ligand	Yield (%)[b]
1	PPh_3	60
2	DPEphos	68
3	Xphos	55
4	DPPF	46
5	DPPB	48
6	P(4-FPh)$_3$	78
7	dtbpy	48
8	P(pentafluorophenyl)$_3$	47
9	P(4-CF_3Ph)$_3$	73
10	P(*o*-tolyl)$_3$	45

[a] Reaction conditions: **1a** (0.30 mmol), B_2Pin_2 (0.45 mmol), **2a** (0.60 mmol), IMesCuCl (5 mol%), NaOMe (3.0 equiv), ligand (10 mol%), THF (1 mL), N_2 atmosphere, rt for 10 h. [b] Isolated yield.

Table S7. Optimization of additive.[a]

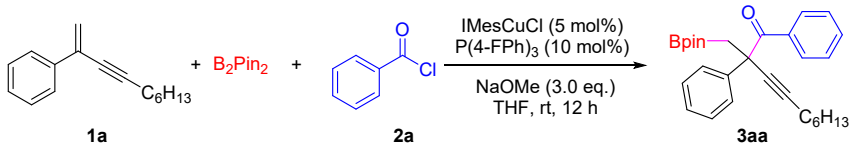


1a **2a** **3aa**

Entry	Additive	Yield (%)[b]
1	5Å MS	70
2	20% CsF	60
3	10% Ac_2O	40
4	2eq H_2O	49

[a] Reaction conditions: **1a** (0.30 mmol), B_2Pin_2 (0.45 mmol), **2a** (0.60 mmol), IMesCuCl (5 mol%), NaOMe (3.0 equiv), $P(4\text{-FPh})_3$ (10 mol%), THF (1 mL), N_2 atmosphere, rt for 10 h. [b] Isolated yield.

Table S8. Optimization of the equivalent of NaOMe.[a]

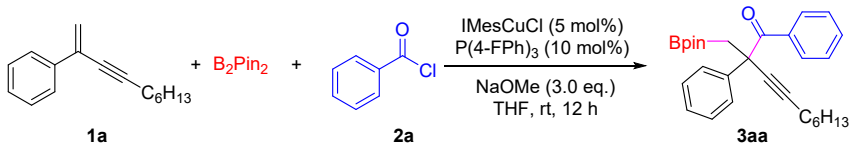


1a **2a** **3aa**

Entry	NaOMe (x eq.)	Yield (%)[b]
1	1	7
2	2	12
3	4	60

[a] Reaction conditions: **1a** (0.30 mmol), B_2Pin_2 (0.45 mmol), **2a** (0.60 mmol), IMesCuCl (5 mol %), NaOMe (3.0 equiv), $P(4\text{-FPh})_3$ (10 mol%), THF (1 mL), N_2 atmosphere, rt for 10 h. [b] Isolated yield.

Table S9. Further optimization of the reaction conditions.[a]



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

Entry	deviations from optimized conditions	Yield (%)[b]
1	CuCl instead of IMesCuCl	31
2	$CuCl_2$ instead of IMesCuCl	28
3	$Cu(OAc)_2$ instead of IMesCuCl	39
4	**2a** was added as the final component	78
5	Slow addition of **2a** with a feeding pump (2 h)	28

[a] Reaction conditions: **1a** (0.30 mmol), B_2Pin_2 (0.45 mmol), **2a** (0.60 mmol), IMesCuCl (5 mol%), NaOMe (3.0 equiv), $P(4\text{-FPh})_3$ (10 mol%), THF (1 mL), N_2 atmosphere, rt for 10 h.

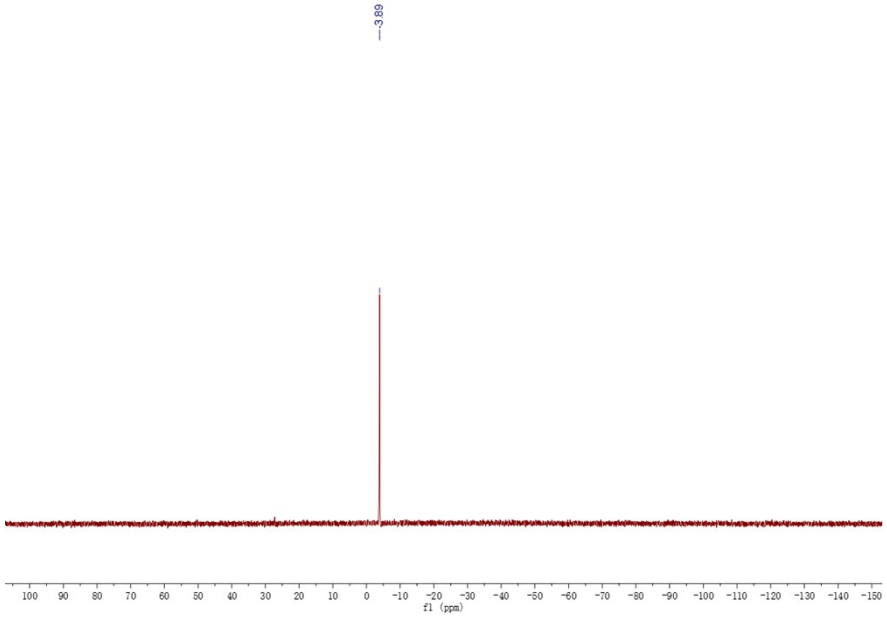


Figure S4 ^{31}P NMR of P(4-FPh)$_3$

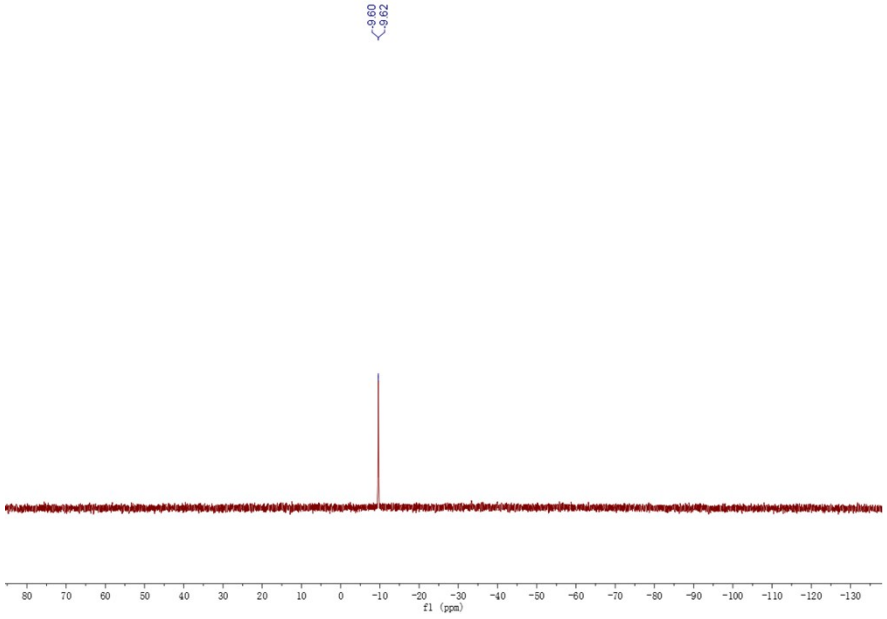
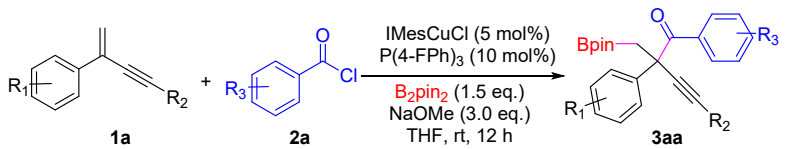


Figure S5 ^{31}P NMR of IMesCuCl + P(4-FPh)$_3$

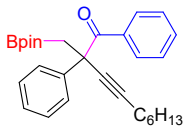
4. General Procedure



In a nitrogen-filled glove box, a 15 mL Schlenk tube equipped with magnetic stir bar was charged with B_2Pin_2 (114.3 mg, 0.45 mmol, 1.5 eq.), IMesCuCl (6.1 mg, 0.015 mmol, 0.05 eq.), P(4-FPh)$_3$ (9.5 mg, 0.03 mmol, 0.1 eq.), NaOMe (48.6 mg, 0.9 mmol, 3.0 eq.). THF (1 mL) was added to the reaction tube, and the mixture was stirred at room temperature for 10 minutes. Then **1a** (63.6 mg, 0.3 mmol, 1.0 eq.) and **2a** (84 mg, 0.6 mmol, 2.0 eq.) were sequentially added. The

Schlenk tube was sealed quickly and removed from the glove box. The reaction mixture was stirred at room temperature for 10 hours. Then the solution was extracted with EtOAc. The combined organic phase was dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel diluting with petroleum ether/EtOAc (v/v = 100:1) to afford the products **3aa**.

5. Spectroscopic Data of Products



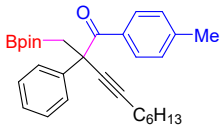
1,3-Diphenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)undec-4-yn-1-one (3aa)

The title compound was prepared from dec-1-en-3-yn-2-ylbenzene (63.6 mg, 0.3 mmol), Bis(pinacolato)diboron (114.3 mg, 0.45 mmol) and Benzoyl chloride (84 mg, 0.6 mmol). The crude residue was purified by flash chromatography (petroleum ether / ethyl acetate = 100:1, Rf = 0.75) to afford the products as a yellow liquid (general procedure: 103.8 mg, 78%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 (d, *J* = 7.5 Hz, 2H), 7.54 (d, *J* = 7.4 Hz, 2H), 7.36 (t, *J* = 7.4 Hz, 1H), 7.29 (t, *J* = 7.7 Hz, 2H), 7.25 - 7.19 (m, 3H), 2.25 (td, *J* = 6.9, 1.2 Hz, 2H), 1.75 (d, *J* = 15.2 Hz, 1H), 1.52 (d, *J* = 15.2 Hz, 1H), 1.48 - 1.43 (m, 2H), 1.29 (dd, *J* = 15.0, 7.5 Hz, 4H), 1.21 (d, *J* = 11.3 Hz, 14H), 0.86 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 197.1, 143.5, 135.2, 132.0, 130.7, 128.7, 127.6, 127.0, 126.6, 90.0, 82.9, 81.5, 53.7, 31.5, 28.6, 28.5, 25.0, 24.9, 22.7, 19.2, 14.2.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{29}H_{37}BO_3Na^+$ 467.2737; Found 467.2725.



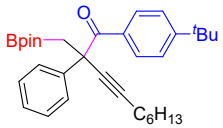
3-Phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-(p-tolyl)undec-4-yn-1-one (3ab)

The title compound was prepared from dec-1-en-3-yn-2-ylbenzene (63.6 mg, 0.3 mmol), Bis(pinacolato)diboron (114.3 mg, 0.45 mmol) and 4-methylbenzoyl chloride (92.4 mg, 0.6 mmol). The crude residue was purified by flash chromatography (petroleum ether / ethyl acetate = 100:1, Rf = 0.75) to afford the products as a yellow liquid (general procedure: 81.1 mg, 59%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.3 Hz, 2H), 7.57 - 7.49 (m, 2H), 7.28 (d, *J* = 7.5 Hz, 2H), 7.18 (t, *J* = 7.3 Hz, 1H), 7.02 (d, *J* = 8.2 Hz, 2H), 2.28 (s, 3H), 2.27 - 2.21 (m, 2H), 1.71 (d, *J* = 15.2 Hz, 1H), 1.49 (s, 1H), 1.48 - 1.41 (m, 2H), 1.31 (dt, *J* = 14.6, 7.2 Hz, 4H), 1.21 (d, *J* = 13.4 Hz, 14H), 0.86 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 196.5, 143.8, 142.7, 132.3, 130.9, 128.6, 128.3, 126.8, 126.5, 89.7, 82.8, 81.6, 53.6, 31.5, 28.6, 28.5, 25.0, 24.9, 22.7, 21.6, 19.2, 14.2.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{30}H_{39}BO_3Na^+$ 481.2895; Found 481.2886.



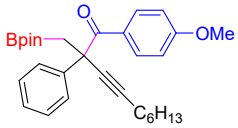
1-(4-(*tert*-Butyl)phenyl)-3-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)undec-4-yn-1-one (3ac)

The title compound was prepared from dec-1-en-3-yn-2-ylbenzene (63.6 mg, 0.3 mmol), Bis(pinacolato)diboron (114.3 mg, 0.45 mmol) and 4-(*tert*-butyl)benzoyl chloride (117.6 mg, 0.6 mmol). The crude residue was purified by flash chromatography (petroleum ether / ethyl acetate = 100:1, Rf = 0.75) to afford the products as a yellow liquid (general procedure: 88.6 mg, 59%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.6 Hz, 2H), 7.54 (d, *J* = 7.4 Hz, 2H), 7.28 (d, *J* = 7.9 Hz, 2H), 7.24 (d, *J* = 8.6 Hz, 2H), 7.19 (d, *J* = 7.3 Hz, 1H), 2.25 (td, *J* = 6.9, 1.2 Hz, 2H), 1.70 (d, *J* = 15.2 Hz, 1H), 1.48 (s, 1H), 1.46 - 1.42 (m, 2H), 1.32 - 1.29 (m, 4H), 1.25 (s, 12H), 1.21 (d, *J* = 13.5 Hz, 14H), 0.86 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 196.5, 155.6, 143.8, 132.3, 130.8, 128.7, 126.9, 126.5, 124.6, 89.8, 82.9, 81.7, 53.6, 35.0, 31.5, 31.1, 28.6, 28.5, 25.0, 24.8, 22.7, 19.3, 14.2.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{33}H_{45}BO_3Na^+$ 523.3366; Found 523.3359.



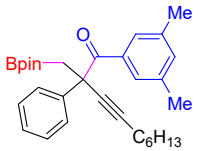
1-(4-Methoxyphenyl)-3-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)undec-4-yn-1-one (3ad)

The title compound was prepared from dec-1-en-3-yn-2-ylbenzene (63.6 mg, 0.3 mmol), Bis(pinacolato)diboron (114.3 mg, 0.45 mmol) and 4-methoxybenzoyl chloride (102.4 mg, 0.6 mmol). The crude residue was purified by flash chromatography (petroleum ether / ethyl acetate = 100:1, Rf = 0.75) to afford the products as a yellow liquid (general procedure: 91.1 mg, 64%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.9 Hz, 2H), 7.52 (d, *J* = 7.7 Hz, 2H), 7.30 - 7.26 (m, 2H), 7.18 (t, *J* = 7.3 Hz, 1H), 6.71 (d, *J* = 8.9 Hz, 2H), 3.76 (s, 3H), 2.26 (t, *J* = 6.9 Hz, 2H), 1.69 (d, *J* = 15.2 Hz, 1H), 1.52 - 1.50 (m, 1H), 1.48 (dd, *J* = 9.9, 5.7 Hz, 2H), 1.32 (dt, *J* = 14.5, 7.2 Hz, 4H), 1.21 (d, *J* = 14.7 Hz, 14H), 0.86 (t, *J* = 6.9 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 195.4, 162.6, 144.0, 133.2, 128.6, 127.6, 126.8, 126.5, 112.8, 89.7, 82.8, 81.7, 55.3, 53.5, 31.5, 28.6, 28.6, 25.0, 24.9, 22.7, 19.2, 14.2.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{30}H_{39}BO_4Na^+$ 497.2844; Found 497.2836.



1-(3,5-Dimethylphenyl)-3-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)undec-4-yn-1-one (3ae)

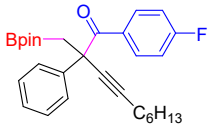
The title compound was prepared from dec-1-en-3-yn-2-ylbenzene (63.6 mg, 0.3 mmol), Bis(pinacolato)diboron (114.3 mg, 0.45 mmol) and 3,5-dimethylbenzoyl chloride (100.8 mg, 0.6

mmol). The crude residue was purified by flash chromatography (petroleum ether / ethyl acetate = 100:1, Rf = 0.75) to afford the products as a yellow liquid (general procedure: 99.2 mg, 70%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 (dd, *J* = 12.7, 5.4 Hz, 4H), 7.28 (d, *J* = 7.4 Hz, 2H), 7.18 (t, *J* = 7.3 Hz, 1H), 6.98 (s, 1H), 2.25 (q, *J* = 6.9 Hz, 2H), 2.20 (s, 6H), 1.73 (d, *J* = 15.2 Hz, 1H), 1.50 (d, *J* = 11.9 Hz, 1H), 1.45 (dd, *J* = 15.7, 9.0 Hz, 2H), 1.33 - 1.27 (m, 4H), 1.20 (d, *J* = 11.2 Hz, 14H), 0.86 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 197.3, 143.6, 137.0, 135.1, 133.7, 128.6, 128.6, 126.9, 126.5, 89.7, 82.9, 81.7, 53.7, 31.5, 28.7, 28.6, 25.0, 24.9, 22.7, 21.3, 19.3, 14.2.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{31}H_{41}BO_3Na^+$ 495.3052; Found 495.3045.



1-(4-Fluorophenyl)-3-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)undec-4-yn-1-one (3af)

The title compound was prepared from dec-1-en-3-yn-2-ylbenzene (63.6 mg, 0.3 mmol), Bis(pinacolato)diboron (114.3 mg, 0.45 mmol) and 4-fluorobenzoyl chloride (72.1 mg, 0.6 mmol). The crude residue was purified by flash chromatography (petroleum ether / ethyl acetate = 100:1, Rf = 0.75) to afford the products as a light yellow liquid (general procedure: 103.8 mg, 52%).

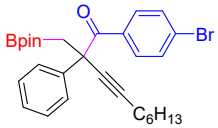
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 – 7.88 (m, 2H), 7.52 (d, *J* = 7.4 Hz, 2H), 7.30 (t, *J* = 7.7 Hz, 2H), 7.21 (t, *J* = 7.3 Hz, 1H), 6.90 (t, *J* = 8.7 Hz, 2H), 2.26 (t, *J* = 6.8 Hz, 2H), 1.73 (d, *J* = 15.3 Hz, 1H), 1.53 – 1.49 (m, 1H), 1.48 – 1.43 (m, 2H), 1.33 – 1.27 (m, 4H), 1.21 (d, *J* = 12.1 Hz, 14H), 0.86 (t, *J* = 6.9 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 195.5, 164.9 (d, *J* = 252.0 Hz), 143.3, 133.4 (d, *J* = 12.6 Hz), 131.4 (d, *J* = 2.5 Hz), 128.8, 127.1, 126.5, 114.7 (d, *J* = 21.4 Hz), 90.2, 82.9, 81.4, 53.6, 31.5, 28.6, 28.6, 25.0, 24.9, 22.7, 19.2, 14.2.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{22}H_{13}NO_2Na^+$ 346.0838; Found 346.0835.

^{19}F NMR (471 MHz, $CDCl_3$) δ -106.7.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{29}H_{36}BFO_3Na^+$ 485.2643; Found 485.2638.



1-(4-Dromophenyl)-3-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)undec-4-yn-1-one (3ag)

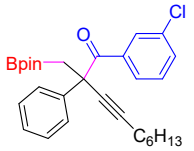
The title compound was prepared from dec-1-en-3-yn-2-ylbenzene (63.6 mg, 0.3 mmol), Bis(pinacolato)diboron (114.3 mg, 0.45 mmol) and 1-(4-bromophenyl)ethan-1-one (119.7 mg, 0.6 mmol). The crude residue was purified by flash chromatography (petroleum ether / ethyl acetate = 100:1, Rf = 0.75) to afford the products as a yellow liquid (general procedure: 98.9 mg, 63%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76 - 7.71 (m, 2H), 7.50 (dd, *J* = 8.3, 1.1 Hz, 2H), 7.37 - 7.34 (m, 2H), 7.29 (t, *J* = 7.6 Hz, 2H), 7.21 (t, *J* = 7.3 Hz, 1H), 2.24 (td, *J* = 6.9, 1.4 Hz, 2H), 1.73 (d, *J* =

15.3 Hz, 1H), 1.51 (d, *J* = 15.3 Hz, 1H), 1.46 (dd, *J* = 8.4, 5.8 Hz, 2H), 1.31 - 1.26 (m, 4H), 1.21 (dd, *J* = 12.0, 7.4 Hz, 14H), 0.86 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 196.1, 143.1, 134.0, 132.2, 131.0, 128.9, 127.2, 126.5, 90.4, 83.0, 81.2, 53.6, 31.5, 28.6, 24.9, 24.9, 22.7, 19.2, 14.2.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{29}H_{36}BBrO_3Na^+$ 545.1841; Found 545.1838.



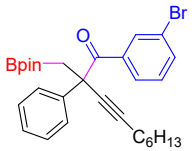
1-(3-Chlorophenyl)-3-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)undec-4-yn-1-one(3ah)

The title compound was prepared from dec-1-en-3-yn-2-ylbenzene (63.6 mg, 0.3 mmol), Bis(pinacolato)diboron (114.3 mg, 0.45 mmol) and 1-(3-chlorophenyl)ethan-1-one (92.8 mg, 0.6 mmol). The crude residue was purified by flash chromatography (petroleum ether / ethyl acetate = 100:1, Rf = 0.75) to afford the products as a yellow liquid (general procedure: 64.6 mg, 45%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 (s, 1H), 7.69 (d, *J* = 7.9 Hz, 1H), 7.52 (d, *J* = 7.7 Hz, 2H), 7.30 (dd, *J* = 12.6, 6.8 Hz, 3H), 7.21 (t, *J* = 7.3 Hz, 1H), 7.13 (td, *J* = 7.9, 1.5 Hz, 1H), 2.25 (dd, *J* = 11.1, 6.8 Hz, 2H), 1.76 (d, *J* = 15.3 Hz, 1H), 1.51 (d, *J* = 15.4 Hz, 1H), 1.46 (dd, *J* = 10.9, 6.3 Hz, 2H), 1.31–1.27 (m, 4H), 1.20 (d, *J* = 9.5 Hz, 14H), 0.86 (t, *J* = 6.9 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 196.0, 142.8, 137.0, 133.8, 131.9, 130.5, 128.9, 128.7, 127.2, 126.5, 90.5, 83.0, 81.1, 53.7, 31.5, 28.6, 24.9, 24.9, 22.7, 19.2, 14.2.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{29}H_{36}BClO_3Na^+$ 501.2342; Found 501.2338.



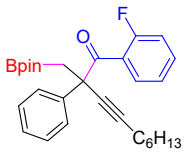
1-(3-Bromophenyl)-3-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)undec-4-yn-1-one (3ai)

The title compound was prepared from dec-1-en-3-yn-2-ylbenzene (63.6 mg, 0.3 mmol), Bis(pinacolato)diboron (114.3 mg, 0.45 mmol) and 3-bromobenzoyl chloride (131.7 mg, 0.6 mmol). The crude residue was purified by flash chromatography (petroleum ether / ethyl acetate = 100:1, Rf = 0.75) to afford the products as a yellow liquid (general procedure: 54.9 mg, 35%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05 (t, *J* = 1.8 Hz, 1H), 7.74 - 7.71 (m, 1H), 7.54 - 7.50 (m, 2H), 7.47 (ddd, *J* = 7.9, 2.0, 1.0 Hz, 1H), 7.30 (dd, *J* = 13.6, 1.7 Hz, 2H), 7.24 - 7.20 (m, 1H), 7.07 (t, *J* = 7.9 Hz, 1H), 2.25 (td, *J* = 6.9, 4.5 Hz, 2H), 1.76 (d, *J* = 15.3 Hz, 1H), 1.51 (d, *J* = 15.3 Hz, 1H), 1.48 - 1.44 (m, 2H), 1.29 (dd, *J* = 9.9, 5.2 Hz, 4H), 1.20 (d, *J* = 9.3 Hz, 14H), 0.86 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 195.9, 142.8, 137.2, 134.8, 133.4, 129.2, 129.1, 128.9, 127.2, 126.5, 121.9, 90.5, 83.0, 81.1, 53.7, 31.5, 28.6, 28.6, 24.9, 24.9, 22.7, 19.2, 14.2.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{29}H_{36}BBrO_3Na^+$ 547.1826; Found 547.1827.



1-(2-Fluorophenyl)-3-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)undec-4-yn-1-one (3aj)

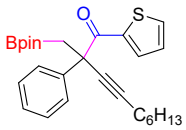
The title compound was prepared from dec-1-en-3-yn-2-ylbenzene (63.6 mg, 0.3 mmol), Bis(pinacolato)diboron (114.3 mg, 0.45 mmol) and 2-fluorobenzoyl chloride (95.1 mg, 0.6 mmol). The crude residue was purified by flash chromatography (petroleum ether / ethyl acetate = 100:1, Rf = 0.75) to afford the products as a yellow liquid (general procedure: 74.9 mg, 54%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61 (d, *J* = 7.5 Hz, 2H), 7.36 - 7.28 (m, 4H), 7.24 (d, *J* = 7.4 Hz, 1H), 7.00 - 6.91 (m, 2H), 2.19 (td, *J* = 6.9, 4.6 Hz, 2H), 1.96 (d, *J* = 15.3 Hz, 1H), 1.57 (d, *J* = 15.3 Hz, 1H), 1.41 - 1.35 (m, 2H), 1.27 - 1.23 (m, 4H), 1.20 (d, *J* = 3.2 Hz, 14H), 0.88 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 198.1 (d, *J* = 2.1 Hz), 161.1, 159.0, 141.5, 132.2 (d, *J* = 12.6 Hz), 130.5 (d, *J* = 2.5 Hz), 128.5, 127.2, 127.0, 122.9 (d, *J* = 21.4 Hz), 116.0 (d, *J* = 22.1 Hz), 89.3, 83.2, 80.7, 55.1, 31.5, 28.6, 28.5, 25.0, 24.8, 22.7, 19.1, 14.2.

^{19}F NMR (471 MHz, $CDCl_3$) δ -110.5.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{29}H_{36}BFO_3Na^+$ 485.2643; Found 485.2635.



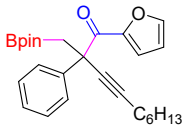
2-Phenyl-2-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)-1-(thiophen-2-yl)dec-3-yn-1-one （3ak)

The title compound was prepared from dec-1-en-3-yn-2-ylbenzene (63.6 mg, 0.3 mmol), Bis(pinacolato)diboron (114.3 mg, 0.45 mmol) and thiophene-2-carbonyl chloride (88.0 mg, 0.6 mmol). The crude residue was purified by flash chromatography (petroleum ether / ethyl acetate = 100:1, Rf = 0.75) to afford the products as a yellow liquid (general procedure: 91.9 mg, 68%)。

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.63 (dd, *J* = 3.9, 1.0 Hz, 1H), 7.57 (dd, *J* = 8.2, 1.0 Hz, 2H), 7.44 (dd, *J* = 4.9, 1.0 Hz, 1H), 7.29 (t, *J* = 7.7 Hz, 2H), 7.21 (t, *J* = 7.3 Hz, 1H), 6.88 (dd, *J* = 4.9, 3.9 Hz, 1H), 2.31 (t, *J* = 7.0 Hz, 2H), 1.74 (d, *J* = 15.3 Hz, 1H), 1.57 (d, *J* = 4.1 Hz, 1H), 1.54 (dd, *J* = 9.4, 4.3 Hz, 2H), 1.42- 1.36 (m, 2H), 1.27 (dd, *J* = 6.9, 3.3 Hz, 4H), 1.19 (d, *J* = 11.7 Hz, 12H), 0.88 (t, *J* = 6.9 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 190.0, 143.2, 141.1, 135.0, 133.0, 128.6, 127.4, 127.1, 126.8, 89.9, 82.9, 81.4, 53.8, 31.5, 28.6, 28.6, 24.9, 24.9, 22.7, 19.3, 14.2.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{27}H_{35}BO_3SNa^+$ 473.2292; Found 473.2307.



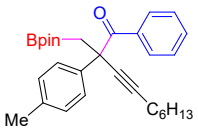
1-(Furan-2-yl)-2-phenyl-2-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)dec-3-yn-1-one （3al)

The title compound was prepared from dec-1-en-3-yn-2-ylbenzene (63.6 mg, 0.3 mmol), Bis(pinacolato)diboron (114.3 mg, 0.45 mmol) and furan-2-carbonyl chloride (78.3 mg, 0.6 mmol). The crude residue was purified by flash chromatography (petroleum ether / ethyl acetate = 100:1, Rf = 0.75) to afford the products as a yellow liquid (general procedure: 78.2 mg, 60%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56 - 7.51 (m, 2H), 7.44 (d, *J* = 1.0 Hz, 1H), 7.31 - 7.27 (m, 2H), 7.20 (t, *J* = 7.3 Hz, 1H), 6.98 (d, *J* = 3.6 Hz, 1H), 6.30 (dd, *J* = 3.6, 1.7 Hz, 1H), 2.31 (t, *J* = 7.0 Hz, 2H), 1.74 (d, *J* = 15.3 Hz, 1H), 1.55 (dt, *J* = 7.0, 3.0 Hz, 3H), 1.44 - 1.37 (m, 2H), 1.30 - 1.25 (m, 4H), 1.18 (d, *J* = 10.3 Hz, 12H), 0.88 (t, *J* = 5.0 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 185.6, 149.9, 146.0, 143.1, 128.5, 127.1, 126.6, 120.7, 111.6, 89.2, 83.0, 81.0, 52.7, 31.5, 28.7, 28.6, 24.9, 24.9, 22.7, 19.2, 14.2.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{27}H_{35}BO_4Na^+$ 457.2521; Found 457.2529.



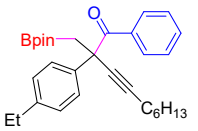
1-Phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-(p-tolyl)undec-4-yn-1-one (3ba)

The title compound was prepared from 1-(dec-1-en-3-yn-2-yl)-4-methylbenzene (67.9 mg, 0.3 mmol), Bis(pinacolato)diboron (114.3 mg, 0.45 mmol) and benzoyl chloride (84 mg, 0.6 mmol). The crude residue was purified by flash chromatography (petroleum ether / ethyl acetate = 100:1, Rf = 0.75) to afford the products as a yellow liquid (general procedure: 75.6 mg, 55%)..

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.4 Hz, 2H), 7.42 (d, *J* = 8.2 Hz, 2H), 7.35 (t, *J* = 7.4 Hz, 1H), 7.22 (t, *J* = 7.7 Hz, 2H), 7.09 (d, *J* = 8.0 Hz, 2H), 2.29 (s, 3H), 2.23 (td, *J* = 6.9, 1.7 Hz, 2H), 1.73 (d, *J* = 15.2 Hz, 1H), 1.48 (d, *J* = 15.3 Hz, 1H), 1.45 - 1.41 (m, 2H), 1.30 - 1.25 (m, 4H), 1.22 (d, *J* = 11.7 Hz, 14H), 0.85 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 197.3, 140.5, 136.5, 135.3, 131.9, 130.7, 129.4, 127.6, 126.4, 89.7, 82.9, 81.7, 53.4, 31.5, 28.6, 28.5, 25.0, 24.9, 22.7, 21.1, 19.2, 14.2.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{30}H_{39}BO_3Na^+$ 481.2895; Found 481.2888.



3-(4-Ethylphenyl)-1-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)undec-4-yn-1-one (3ca)

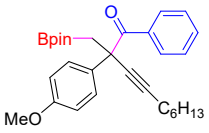
The title compound was prepared from 1-(dec-1-en-3-yn-2-yl)-4-ethylbenzene (72.1 mg, 0.3 mmol), Bis(pinacolato)diboron (114.3 mg, 0.45 mmol) and benzoyl chloride (84 mg, 0.6 mmol). The crude residue was purified by flash chromatography (petroleum ether / ethyl acetate = 100:1, Rf = 0.75) to afford the products as a yellow liquid (general procedure: 76.5 mg, 54%)..

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.87 (dd, *J* = 8.4, 1.2 Hz, 2H), 7.46 - 7.41 (m, 2H), 7.35 (t, *J* = 7.4 Hz, 1H), 7.22 (t, *J* = 7.8 Hz, 2H), 7.11 (d, *J* = 8.3 Hz, 2H), 2.60 (q, *J* = 7.6 Hz, 2H), 2.23 (td, *J* =

6.9, 1.9 Hz, 2H), 1.73 (d, *J* = 15.2 Hz, 1H), 1.50 (d, *J* = 15.2 Hz, 1H), 1.46 - 1.42 (m, 2H), 1.28 (dd, *J* = 13.7, 6.4 Hz, 3H), 1.20 (dd, *J* = 13.9, 4.7 Hz, 18H), 0.85 (t, *J* = 7.0 Hz, 3H).

^{1}C NMR (500 MHz, $CDCl_3$) δ 197.3, 142.9, 140.6, 135.4, 131.9, 130.7, 128.2, 127.6, 126.5, 89.7, 82.9, 81.8, 53.4, 31.5, 28.6, 28.5, 28.5, 25.0, 24.9, 22.7, 19.2, 15.5, 14.2.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{31}H_{41}BO_3Na^+$ 495.3052; Found 495.3045.



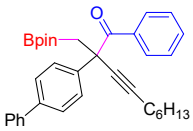
3-(4-Methoxyphenyl)-1-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)undec-4-yn-1-one (3da)

The title compound was prepared from 1-(dec-1-en-3-yn-2-yl)-4-methoxybenzene (72.7 mg, 0.3 mmol), Bis(pinacolato)diboron (114.3 mg, 0.45 mmol) and benzoyl chloride (84 mg, 0.6 mmol). The crude residue was purified by flash chromatography (petroleum ether / ethyl acetate = 100:1, Rf = 0.75) to afford the products as a yellow liquid (general procedure: 85.4 mg, 60%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.08 - 7.65 (m, 2H), 7.53 - 7.41 (m, 2H), 7.40 - 7.32 (m, 1H), 7.23 (t, *J* = 7.8 Hz, 2H), 6.89 - 6.76 (m, 2H), 3.77 (s, 3H), 2.23 (td, *J* = 6.9, 1.7 Hz, 2H), 1.73 (d, *J* = 15.2 Hz, 1H), 1.50 (d, *J* = 15.2 Hz, 1H), 1.47 - 1.41 (m, 2H), 1.32 - 1.25 (m, 4H), 1.22 (d, *J* = 10.0 Hz, 14H), 0.86 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 197.2, 158.4, 135.4, 135.3, 131.8, 130.5, 127.6, 127.5, 113.9, 89.6, 82.8, 81.7, 55.2, 52.9, 52.9, 31.4, 28.5, 28.4, 24.9, 24.8, 22.6, 19.1, 14.1.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{30}H_{39}BO_4Na^+$ 497.2833; Found 497.2835.



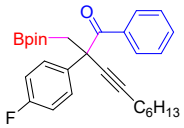
3-([1,1'-Biphenyl]-4-yl)-1-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)undec-4-yn-1-one (3ea)

The title compound was prepared from 4-(dec-1-en-3-yn-2-yl)-1,1'-biphenyl (86.5 mg, 0.3 mmol), Bis(pinacolato)diboron (114.3 mg, 0.45 mmol) and benzoyl chloride (84 mg, 0.6 mmol). The crude residue was purified by flash chromatography (petroleum ether / ethyl acetate = 100:1, Rf = 0.75) to afford the products as a yellow liquid (general procedure: 107.7 mg, 69%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.3 Hz, 2H), 7.62 (d, *J* = 8.1 Hz, 2H), 7.57 (d, *J* = 8.0 Hz, 2H), 7.54 (d, *J* = 8.2 Hz, 2H), 7.42 (d, *J* = 6.5 Hz, 2H), 7.37 (t, *J* = 7.4 Hz, 1H), 7.31 (d, *J* = 7.4 Hz, 1H), 7.26 - 7.21 (m, 2H), 2.26 (t, *J* = 6.9 Hz, 2H), 1.79 (d, *J* = 15.3 Hz, 1H), 1.57 (d, *J* = 15.2 Hz, 1H), 1.50 - 1.45 (m, 2H), 1.34 - 1.28 (m, 4H), 1.22 (d, *J* = 11.3 Hz, 14H), 0.87 (t, *J* = 6.6 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 197.1, 142.5, 140.7, 139.7, 135.2, 132.1, 130.7, 128.8, 127.6, 127.4, 127.1, 127.0, 90.0, 82.9, 81.5, 60.5, 53.4, 31.5, 28.6, 28.5, 25.0, 24.9, 22.7, 19.2, 14.2.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{35}H_{41}BO_3Na^+$ 543.3054; Found 543.3046.



3-(4-Fluorophenyl)-1-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)undec-4-yn-1-one (3fa)

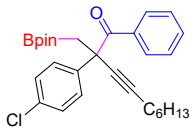
The title compound was prepared from 1-(dec-1-en-3-yn-2-yl)-4-fluorobenzene (69.1mg, 0.3 mmol), Bis(pinacolato)diboron (114.3 mg, 0.45 mmol) and benzoyl chloride (84 mg, 0.6 mmol). The crude residue was purified by flash chromatography (petroleum ether / ethyl acetate = 100:1, Rf = 0.75) to afford the products as a yellow liquid (general procedure: 81.8 mg, 59%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85 (d, *J* = 7.4 Hz, 2H), 7.50 (dd, *J* = 8.8, 5.3 Hz, 2H), 7.37 (t, *J* = 7.4 Hz, 1H), 7.23 (t, *J* = 7.8 Hz, 2H), 6.97 (t, *J* = 8.7 Hz, 2H), 2.23 (t, *J* = 6.7 Hz, 2H), 1.70 (d, *J* = 15.3 Hz, 1H), 1.51 (d, *J* = 15.3 Hz, 1H), 1.47 - 1.41 (m, 2H), 1.28 - 1.24 (m, 5H), 1.20 (d, *J* = 8.3 Hz, 13H), 0.85 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 196.9, 161.9 (d, *J* = 245.7 Hz), 139.1 (d, *J* = 2.8 Hz), 135.1, 132.2, 130.7, 128.4 (d, *J* = 8.1 Hz), 127.7, 115.5 (d, *J* = 21.2 Hz), 90.2, 83.0, 81.4, 53.1, 31.5, 28.6, 25.0, 24.9, 22.7, 19.2, 14.2.

^{19}F NMR (471 MHz, $CDCl_3$) δ -116.2.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{29}H_{36}BFO_3Na^+$ 485.2643; Found 485.2635.



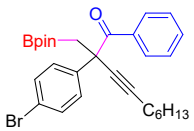
3-(4-Chlorophenyl)-1-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)undec-4-yn-1-one(3ga)

The title compound was prepared from 1-chloro-4-(dec-1-en-3-yn-2-yl)benzene (74.0 mg, 0.3 mmol), Bis(pinacolato)diboron (114.3 mg, 0.45 mmol) and benzoyl chloride (84 mg, 0.6 mmol). The crude residue was purified by flash chromatography (petroleum ether / ethyl acetate = 100:1, Rf = 0.75) to afford the products as a yellow liquid (general procedure: 74.7 mg, 52%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.2 Hz, 2H), 7.48 (d, *J* = 8.4 Hz, 2H), 7.37 (t, *J* = 6.9 Hz, 2H), 7.23 (dd, *J* = 14.0, 6.1 Hz, 3H), 2.23 (t, *J* = 6.9 Hz, 2H), 1.70 (d, *J* = 15.3 Hz, 1H), 1.48 (s, 1H), 1.46 - 1.41 (m, 2H), 1.29 (d, *J* = 7.6 Hz, 4H), 1.21 (d, *J* = 8.5 Hz, 14H), 0.86 (d, *J* = 6.6 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 196.7, 142.1, 134.9, 132.9, 132.2, 130.6, 128.8, 128.1, 127.7, 90.3, 83.0, 81.2, 60.5, 53.2, 31.4, 28.5, 24.9, 24.9, 22.7, 19.2, 14.2.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{29}H_{36}BClO_3Na^+$ 501.2342; Found 501.2340.



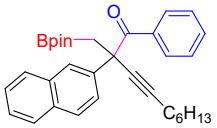
3-(4-Bromophenyl)-1-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)undec-4-yn-1-one (3ha)

The title compound was prepared from 1-bromo-4-(dec-1-en-3-yn-2-yl)benzene (87.4 mg, 0.3 mmol), Bis(pinacolato)diboron (114.3 mg, 0.45 mmol) and benzoyl chloride (84 mg, 0.6 mmol). The crude residue was purified by flash chromatography (petroleum ether / ethyl acetate = 100:1, Rf = 0.75) to afford the products as a yellow liquid (general procedure: 78.5 mg, 50%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71 (dd, *J* = 8.4, 1.1 Hz, 2H), 7.26 - 7.20 (m, 4H), 7.12 - 7.07 (m, 3H), 2.08 (td, *J* = 6.9, 1.0 Hz, 2H), 1.55 (d, *J* = 15.3 Hz, 1H), 1.34 (d, *J* = 15.3 Hz, 1H), 1.29 (ddd, *J* = 8.2, 7.0, 2.0 Hz, 2H), 1.14 - 1.10 (m, 4H), 1.06 (d, *J* = 8.4 Hz, 14H), 0.70 (t, *J* = 7.0 Hz, 3H).

^{1}C NMR (126 MHz, $CDCl_3$) δ 196.6, 142.6, 134.9, 132.3, 131.8, 130.7, 128.5, 127.7, 121.0, 90.4, 83.0, 81.1, 53.3, 31.4, 28.5, 25.0, 24.9, 22.7, 19.2, 14.2.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{29}H_{36}BBrO_3Na^+$ 545.1833; Found 545.1835.



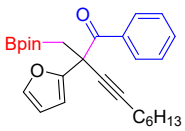
3-(Naphthalen-2-yl)-1-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)undec-4-yn-1-one (3ia)

The title compound was prepared from 2-(dec-1-en-3-yn-2-yl)naphthalene (78.7 mg, 0.3 mmol), Bis(pinacolato)diboron (114.3 mg, 0.45 mmol) and benzoyl chloride (84 mg, 0.6 mmol). The crude residue was purified by flash chromatography (petroleum ether / ethyl acetate = 100:1, Rf = 0.75) to afford the products as a yellow liquid (general procedure: 59.3 mg, 40%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.12 (s, 1H), 7.92 (d, *J* = 8.2 Hz, 2H), 7.83 - 7.75 (m, 3H), 7.58 (d, *J* = 8.6 Hz, 1H), 7.44 (dd, *J* = 14.2, 6.9 Hz, 2H), 7.32 (t, *J* = 6.9 Hz, 1H), 7.19 (t, *J* = 7.4 Hz, 2H), 2.30 (t, *J* = 6.8 Hz, 2H), 1.84 (d, *J* = 15.3 Hz, 1H), 1.59 (d, *J* = 15.3 Hz, 1H), 1.52 - 1.47 (m, 2H), 1.38 - 1.31 (m, 4H), 1.21 (d, *J* = 14.5 Hz, 14H), 0.87 (t, *J* = 6.6 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 197.1, 141.1, 135.2, 133.6, 132.5, 132.1, 130.7, 128.5, 128.2, 127.7, 127.6, 126.2, 125.9, 125.4, 124.7, 90.2, 82.9, 81.6, 53.9, 31.5, 28.6, 25.0, 24.9, 22.7, 19.3, 14.2.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{33}H_{39}BO_3Na^+$ 517.2896; Found 517.2892.

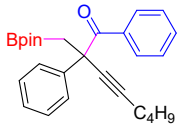


3-(Furan-2-yl)-1-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)undec-4-yn-1-one (3ja)

The title compound was prepared from 2-(dec-1-en-3-yn-2-yl)furan (60.7 mg, 0.3 mmol), Bis(pinacolato)diboron (114.3 mg, 0.45 mmol) and benzoyl chloride (84 mg, 0.6 mmol). The crude residue was purified by flash chromatography (petroleum ether / ethyl acetate = 100:1, Rf = 0.75) to afford the products as a yellow liquid (general procedure: 49.5 mg, 38%).

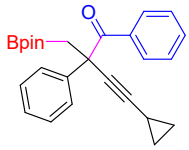
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02 (d, *J* = 7.7 Hz, 2H), 7.42 (t, *J* = 7.5 Hz, 1H), 7.30 (t, *J* = 7.7 Hz, 3H), 6.43 (d, *J* = 3.2 Hz, 1H), 6.32 - 6.28 (m, 1H), 2.22 (t, *J* = 6.9 Hz, 2H), 1.86 (d, *J* = 15.2 Hz, 1H), 1.54 (d, *J* = 15.2 Hz, 1H), 1.45 (dd, *J* = 14.1, 7.1 Hz, 2H), 1.33 - 1.28 (m, 4H), 1.23 (d, *J* = 6.9 Hz, 12H), 0.88 - 0.83 (m, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 194.9, 155.6, 142.2, 135.6, 132.2, 130.0, 127.7, 110.7, 106.9, 87.8, 83.1, 79.9, 49.0, 31.5, 28.5, 28.5, 24.9, 24.9, 22.7, 19.1, 14.2.
HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{27}H_{35}BO_3SNa^+$ 473.2292; Found 473.2285.



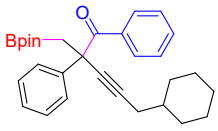
1,3-Diphenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)non-4-yn-1-one (3ka)

The title compound was prepared from oct-1-en-3-yn-2-ylbenzene (55.3 mg, 0.3 mmol), Bis(pinacolato)diboron (114.3 mg, 0.45 mmol) and benzoyl chloride (84 mg, 0.6 mmol). The crude residue was purified by flash chromatography (petroleum ether / ethyl acetate = 100:1, Rf = 0.75) to afford the products as a yellow liquid (general procedure: 78.7 mg, 63%).
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 (d, *J* = 7.5 Hz, 2H), 7.53 (d, *J* = 7.5 Hz, 2H), 7.35 (t, *J* = 7.4 Hz, 1H), 7.28 (t, *J* = 7.7 Hz, 2H), 7.21 (dd, *J* = 13.9, 6.4 Hz, 3H), 2.24 (t, *J* = 6.9 Hz, 2H), 1.73 (d, *J* = 15.2 Hz, 1H), 1.51 (d, *J* = 15.2 Hz, 1H), 1.46 - 1.40 (m, 2H), 1.34 - 1.30 (m, 2H), 1.20 (d, *J* = 11.8 Hz, 12H), 0.82 (t, *J* = 7.3 Hz, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 197.2, 143.5, 135.3, 132.0, 130.7, 128.7, 127.6, 127.0, 126.6, 90.0, 82.9, 81.5, 53.7, 30.7, 25.0, 24.9, 21.9, 18.9, 13.7.
HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{27}H_{33}BO_3Na^+$ 439.2423; Found 439.2413.



5-Cyclopropyl-1,3-diphenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-4-yn-1-one (3la)

The title compound was prepared from (4-cyclopropylbut-1-en-3-yn-2-yl)benzene (50.5 mg, 0.3 mmol), Bis(pinacolato)diboron (114.3 mg, 0.45 mmol) and benzoyl chloride (84 mg, 0.6 mmol). The crude residue was purified by flash chromatography (petroleum ether / ethyl acetate = 100:1, Rf = 0.75) to afford the products as a yellow liquid (general procedure: 60.0 mg, 50%).
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85 (d, *J* = 7.5 Hz, 2H), 7.50 (d, *J* = 7.6 Hz, 2H), 7.35 (t, *J* = 7.3 Hz, 1H), 7.28 (d, *J* = 7.5 Hz, 2H), 7.24 - 7.17 (m, 3H), 1.72 (d, *J* = 15.2 Hz, 1H), 1.48 (d, *J* = 15.2 Hz, 1H), 1.29 - 1.18 (m, 13H), 0.71 (dt, *J* = 6.1, 3.7 Hz, 2H), 0.61 (dt, *J* = 6.7, 3.9 Hz, 2H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 197.0, 143.4, 135.2, 132.0, 130.6, 128.7, 127.6, 127.0, 126.5, 93.0, 82.9, 76.3, 53.6, 25.0, 24.9, 8.1, 0.1.
HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{26}H_{29}BO_3Na^+$ 423.2109; Found 423.2104.



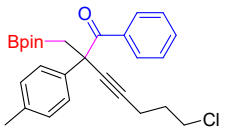
6-Cyclohexyl-1,3-diphenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hex-4-yn-1-one (3ma)

The title compound was prepared from (4-cyclohexylbut-1-en-3-yn-2-yl)benzene (63.0 mg, 0.3 mmol), Bis(pinacolato)diboron (114.3 mg, 0.45 mmol) and benzoyl chloride (84 mg, 0.6 mmol). The crude residue was purified by flash chromatography (petroleum ether / ethyl acetate = 100:1, Rf = 0.75) to afford the products as a yellow liquid (general procedure: 60.2 mg, 44%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84 (d, *J* = 7.6 Hz, 2H), 7.54 (d, *J* = 7.5 Hz, 2H), 7.34 (t, *J* = 7.4 Hz, 1H), 7.29 (t, *J* = 7.7 Hz, 2H), 7.22 (t, *J* = 7.8 Hz, 3H), 2.13 (d, *J* = 6.5 Hz, 2H), 1.73 (d, *J* = 15.3 Hz, 1H), 1.69 - 1.56 (m, 6H), 1.53 (d, *J* = 15.3 Hz, 1H), 1.20 (d, *J* = 12.3 Hz, 12H), 0.96 - 0.82 (m, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 197.3, 143.5, 135.4, 132.0, 130.6, 128.7, 127.6, 127.0, 126.6, 126.3, 88.9, 82.9, 82.2, 78.0, 53.9, 53.8, 37.5, 32.6, 27.1, 26.3, 25.0, 24.9.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{30}H_{37}BO_3Na^+$ 479.2738; Found 479.2730.



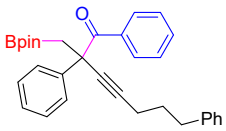
8-Chloro-1-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-(p-tolyl)oct-4-yn-1-one (3na)

The title compound was prepared from 1-(7-chlorohept-1-en-3-yn-2-yl)-4-methylbenzene (65.6 mg, 0.3 mmol), Bis(pinacolato)diboron (114.3 mg, 0.45 mmol) and benzoyl chloride (84 mg, 0.6 mmol). The crude residue was purified by flash chromatography (petroleum ether / ethyl acetate = 100:1, Rf = 0.75) to afford the products as a yellow liquid (general procedure: 67.6 mg, 50%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.87 - 7.79 (m, 2H), 7.39 (d, *J* = 8.2 Hz, 2H), 7.36 (d, *J* = 7.4 Hz, 1H), 7.23 (d, *J* = 7.5 Hz, 2H), 7.10 (d, *J* = 8.0 Hz, 2H), 3.58 - 3.46 (m, 2H), 2.43 (dd, *J* = 13.0, 6.7 Hz, 2H), 2.30 (s, 3H), 1.9 - 1.83 (m, 2H), 1.70 (d, *J* = 15.3 Hz, 1H), 1.48 (d, *J* = 15.3 Hz, 1H), 1.22 (d, *J* = 17.4 Hz, 12H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 197.2, 140.2, 136.7, 135.3, 132.1, 130.5, 129.6, 127.7, 126.3, 87.5, 83.0, 82.9, 53.5, 43.7, 31.4, 25.0, 24.8, 21.1, 16.6.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{27}H_{32}BClO_3Na^+$ 473.2037; Found 473.2028.



1,3,8-Triphenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)oct-4-yn-1-one (3oa)

The title compound was prepared from hept-6-en-4-yne-1,6-diyldibenzene (49.3 mg, 0.3 mmol), Bis(pinacolato)diboron (114.3 mg, 0.45 mmol) and benzoyl chloride (84 mg, 0.6 mmol). The crude residue was purified by flash chromatography (petroleum ether / ethyl acetate = 100:1, Rf = 0.75) to afford the products as a yellow liquid (general procedure: 74.6 mg, 52%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89 (dd, *J* = 8.4, 1.2 Hz, 2H), 7.56 (dd, *J* = 8.3, 1.1 Hz, 2H), 7.37-7.34 (m, 1H), 7.31 (t, *J* = 7.7 Hz, 2H), 7.25 - 7.20 (m, 5H), 7.17 (d, *J* = 7.3 Hz, 1H), 7.07 - 7.03 (m,

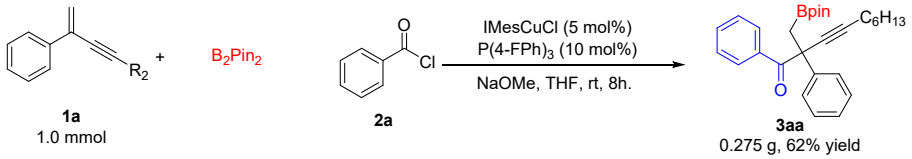
2H), 2.63 (dd, *J* = 13.6, 7.1 Hz, 2H), 2.26 (td, *J* = 6.9, 1.4 Hz, 2H), 1.78 (dd, *J* = 8.7, 5.0 Hz, 2H), 1.75 (d, *J* = 4.1 Hz, 1H), 1.56 (d, *J* = 15.3 Hz, 1H), 1.20 (d, *J* = 11.2 Hz, 12H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 197.1, 143.5, 141.9, 135.2, 132.1, 130.7, 128.8, 128.7, 128.4, 127.7, 127.0, 126.5, 125.9, 89.5, 83.0, 82.1, 53.8, 34.6, 30.3, 25.0, 24.8, 18.5, 18.2.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{32}H_{35}BO_3Na^+$ 501.2583; Found 501.2075.

6. Scale-up syntheses and further transformations

6.1 Scale-up reaction



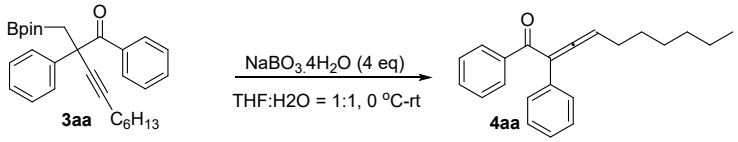
1a 1.0 mmol

2a

3aa 0.275 g, 62% yield

In a nitrogen-filled glove box, a 15 mL Schlenk tube equipped with magnetic stir bar was charged with **1a** (212.0 mg, 1.0 mmol, 1.0 eq.), B_2Pin_2 (381 mg, 1.5 mmol, 1.5 eq.), **2a** (281 mg, 2.0 mmol, 2.0 eq.), IMesCuCl (20 mg, 0.05 mmol, 0.05 eq.), $P(4\text{-}FPh)_3$ (32 mg, 0.1 mmol, 0.1 eq.), NaOMe (162 mg, 3 mmol, 3.0 eq.). THF (2 mL) was added to the reaction tube. and the Schlenk tube was sealed quickly, removed from the glove box. The reaction mixture was stirred at room temperature for 10 hours. Then the solution was extracted with EtOAc. The combined organic phase was dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel diluting with petroleum ether/EtOAc (v/v = 100:1) to afford the products **3aa**(0.275 g, 62% yield).

5.2 Further transformations



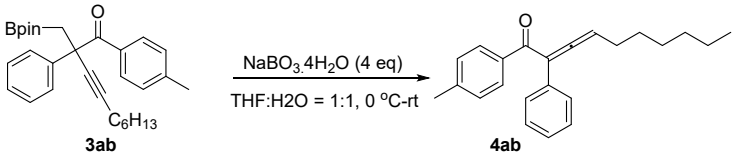
3aa **4aa**

3aa (0.3 mmol), $NaBO_3{\cdot}4H_2O$ (4.0 eq.) were transferred into an 15 mL tube under N_2 atmosphere. THF/H_2O = 1:1 (2 mL) was added to the reaction tube. The reaction mixture was stirred at room temperature for 10 hours. Then the solution was extracted with EtOAc. The combined organic phase was dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel diluting with petroleum ether/EtOAc (v/v = 100:1, Rf = 0.65) to afford the products **4aa** as a dark yellow oily liquid (63.8 mg, 70%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92 (d, J = 7.2 Hz, 2H), 7.55 (t, J = 7.4 Hz, 1H), 7.48 (d, J = 7.5 Hz, 2H), 7.44 (t, J = 7.7 Hz, 2H), 7.37 (t, J = 7.6 Hz, 2H), 7.30 (d, J = 7.4 Hz, 1H), 5.70 (t, J = 7.2 Hz, 1H), 2.18 (dt, J = 14.8, 7.4 Hz, 2H), 1.29 - 1.19 (m, 8H), 0.85 (t, J = 6.7 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 211.2, 194.3, 138.7, 133.8, 132.7, 129.5, 128.6, 128.2, 128.2, 127.6, 109.0, 97.5, 31.7, 29.1, 28.8, 28.6, 22.7, 14.2.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{22}H_{24}ONa^+$ 327.1719; Found 327.1729.

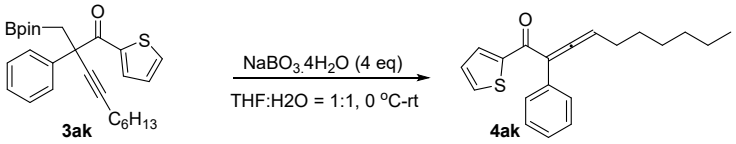


Compound **4ab** was prepared **3ab** (137.5 mg, 0.3 mmol). The crude residue was purified by flash chromatography (petroleum ether / ethyl acetate = 100:1, Rf = 0.65) to afford the products as a dark yellow oily liquid (51.2 mg, 55%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.87 (d, J = 8.1 Hz, 2H), 7.48 (d, J = 7.6 Hz, 2H), 7.38 (t, J = 7.7 Hz, 2H), 7.32 - 7.28 (m, 1H), 7.26 (d, J = 8.0 Hz, 2H), 5.71 (t, J = 7.2 Hz, 1H), 2.44 (s, 3H), 2.21 (dt, J = 14.6, 7.3 Hz, 2H), 1.44 (dd, J = 14.3, 7.1 Hz, 2H), 1.31 - 1.21 (m, 6H), 0.88 (t, J = 6.6 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 209.8, 184.9, 144.1, 134.0, 133.9, 133.6, 128.6, 128.1, 127.8, 127.7, 109.2, 98.2, 31.6, 29.0, 28.9, 28.9, 22.7, 14.2.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{23}H_{26}ONa^+$ 341.1876; Found 341.1877.

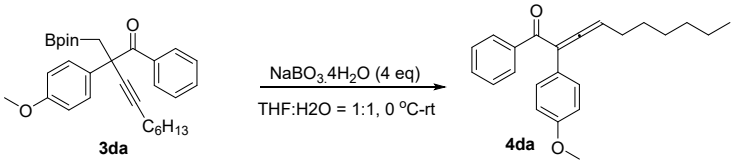


Compound **4ak** was prepared **3ak** (135.0 mg, 0.3 mmol). The crude residue was purified by flash chromatography (petroleum ether / ethyl acetate = 100:1, Rf = 0.65) to afford the products as a dark yellow oily liquid (51.2 mg, 55%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.87 (d, *J* = 3.0 Hz, 1H), 7.67 (d, *J* = 4.9 Hz, 1H), 7.49 (d, *J* = 7.4 Hz, 2H), 7.38 (t, *J* = 7.6 Hz, 2H), 7.33 - 7.27 (m, 1H), 7.16 - 7.12 (m, 1H), 5.87 (t, *J* = 7.2 Hz, 1H), 2.30 (ddd, *J* = 14.5, 7.3, 4.1 Hz, 2H), 1.56 - 1.50 (m, 2H), 1.35 (dd, *J* = 13.6, 7.9 Hz, 2H), 1.30 - 1.26 (m, 4H), 0.88 (t, *J* = 6.8 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 209.8, 184.9, 144.1, 134.0, 133.9, 133.6, 128.6, 128.1, 127.8, 127.7, 109.2, 98.2, 31.6, 29.0, 28.9, 28.9, 22.7, 14.2.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{20}H_{22}OSNa^+$ 333.1284; Found 333.1284.

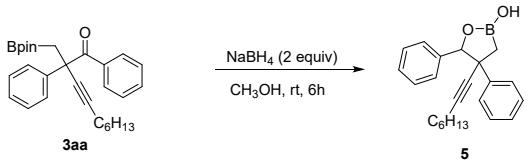


Compound **4da** was prepared **3da** (137.5 mg, 0.3 mmol). The crude residue was purified by flash chromatography (petroleum ether / ethyl acetate = 100:1, Rf = 0.65) to afford the products as a dark yellow oily liquid (64.0 mg, 45%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.1 Hz, 2H), 7.48 - 7.45 (m, 2H), 7.36 (dd, *J* = 10.4, 4.8 Hz, 2H), 7.28 (d, *J* = 7.4 Hz, 1H), 7.24 (d, *J* = 8.0 Hz, 2H), 5.69 (t, *J* = 7.2 Hz, 1H), 2.42 (s, 3H), 2.19 (dt, *J* = 14.6, 7.3 Hz, 2H), 1.27 (dd, *J* = 14.9, 11.0 Hz, 8H), 0.86 (t, *J* = 6.8 Hz, 4H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 210.4, 193.8, 143.6, 136.0, 134.0, 129.8, 129.0, 128.6, 128.1, 127.6, 108.9, 97.4, 31.7, 29.1, 28.9, 28.7, 22.7, 21.8, 14.2.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{23}H_{26}O_2Na^+$ 357.1825; Found 357.1832.

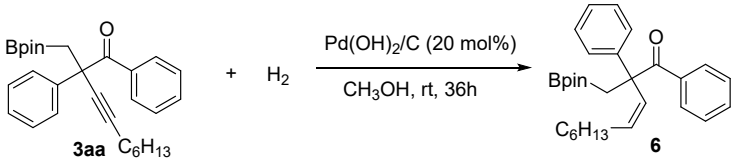


3aa (0.3 mmol), $NaBH_4$ (2 eq.) were transferred into an 15 mL tube under N_2 atmosphere. CH_3OH (2 mL) was added to the reaction tube. The reaction mixture was stirred at room temperature for 6 hours. Then the solution was extracted with EtOAc. The combined organic phase was dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel diluting with petroleum ether/EtOAc (v/v = 100:1, Rf = 0.2) to afford the products **5** as a yellow oily liquid (72.7 mg, 70%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.13 - 6.99 (m, 8H), 6.93 (d, *J* = 7.3 Hz, 2H), 5.54 (s, 1H), 4.95 (s, 1H), 2.33 (t, *J* = 7.0 Hz, 2H), 1.90 (q, *J* = 16.7 Hz, 2H), 1.65 - 1.56 (m, 2H), 1.48 (dt, *J* = 14.4, 7.1 Hz, 2H), 1.35 (dd, *J* = 7.1, 3.6 Hz, 4H), 0.92 (t, *J* = 6.9 Hz, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 140.6, 138.0, 127.5, 127.5, 127.4, 127.4, 126.6, 126.0, 90.3, 85.0, 84.4, 60.6, 51.0, 31.5, 29.1, 28.8, 22.8, 19.0, 14.2.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{23}H_{27}BO_2Na^+$ 369.1996; Found 369.2006.

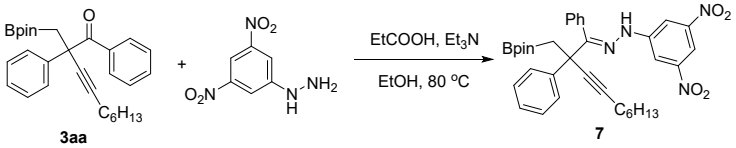


3aa (0.3 mmol), $Pd(OH)_2/C$ (0.06 mmol) were transferred into an 15 mL tube under H_2 atmosphere. CH_3OH (2 mL) was added to the reaction tube. The reaction mixture was stirred at room temperature for 36 hours. Then the solution was extracted with EtOAc. The combined organic phase was dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel diluting with petroleum ether/EtOAc (v/v = 100:1, Rf = 0.5) to afford the products **6** as a yellow oily liquid (79.6 mg, 60%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.67 - 7.62 (m, 2H), 7.44 (d, *J* = 7.4 Hz, 2H), 7.34 (t, *J* = 7.4 Hz, 1H), 7.29 (d, *J* = 7.5 Hz, 2H), 7.21 (dd, *J* = 14.8, 7.2 Hz, 3H), 6.53 (dt, *J* = 11.7, 1.6 Hz, 1H), 5.44 (dt, *J* = 11.7, 7.5 Hz, 1H), 1.77 (dd, *J* = 34.8, 15.5 Hz, 3H), 1.32 (d, *J* = 24.4 Hz, 1H), 1.28 - 1.23 (m, 2H), 1.20 - 1.15 (m, 2H), 1.11 (d, *J* = 1.2 Hz, 14H), 0.82 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 202.3, 144.1, 136.4, 133.1, 132.6, 131.3, 130.2, 128.3, 127.5, 127.5, 126.4, 82.8, 57.8, 31.7, 29.0, 28.8, 28.5, 24.8, 24.6, 22.5, 14.1.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{29}H_{39}BO_3Na^+$ 469.2884; Found 469.2890.



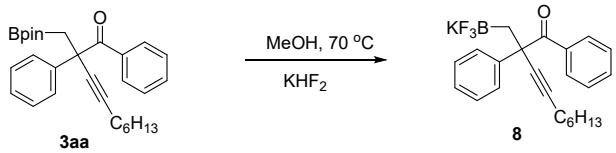
3aa (0.3 mmol), (3,5-dinitrophenyl)hydrazine (0.4 mmol), Et_3N (0.2 mL) and EtCOOH (0.2 mL) were transferred into an 15 mL tube under N_2 atmosphere. EtOH (2 mL) was added to the reaction tube. The reaction mixture was stirred at 80 °C for 12 hours. Then the solution was extracted with EtOAc. The combined organic phase was dried over Na_2SO_4 and concentrated

under reduced pressure. The residue was purified by flash chromatography on silica gel diluting with petroleum ether/EtOAc (v/v = 100:1, Rf = 0.5) to afford the products **7** as a yellow oily liquid (84.3 mg, 45%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 10.74 (s, 1H), 9.05 (d, *J* = 2.5 Hz, 1H), 8.35 (dd, *J* = 9.6, 2.5 Hz, 1H), 8.26 (d, *J* = 9.6 Hz, 1H), 7.62 - 7.57 (m, 2H), 7.42 (t, *J* = 7.4 Hz, 1H), 7.39 - 7.29 (m, 5H), 7.26 (dd, *J* = 9.6, 4.9 Hz, 2H), 2.21 (dd, *J* = 14.5, 7.4 Hz, 3H), 1.80 (d, *J* = 15.3 Hz, 1H), 1.45 (dd, *J* = 14.1, 7.1 Hz, 2H), 1.36 - 1.26 (m, 6H), 1.18 (d, *J* = 16.0 Hz, 12H), 0.90 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 161.5, 145.1, 142.3, 137.9, 132.5, 130.0, 129.7, 128.9, 128.3, 127.4, 127.2, 123.5, 117.1, 88.8, 83.1, 80.8, 50.0, 31.5, 28.7, 28.6, 25.3, 24.6, 22.7, 19.0, 14.3.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{35}H_{41}BN_4O_6Na^+$ 647.3011; Found 647.3020.



3aa (0.3 mmol), KHF_2 (7 eq.) were transferred into an 15 mL tube under N_2 atmosphere. MeOH (2 mL) was added to the reaction tube. The reaction mixture was stirred at 70 °C for 14 hours. After the reaction was completed, it was cooled to room temperature, concentrated, and the remaining solid was washed with hexane : ether for 15 minutes. After filtration, the solid was washed with ether to afford the products **8** as a whits solid (70.0 mg, 55%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.82 (d, *J* = 7.7 Hz, 2H), 7.51 (d, *J* = 7.5 Hz, 2H), 7.26 - 7.02 (m, 6H), 2.27 - 1.99 (m, 2H), 1.19 (dd, *J* = 66.8, 30.0 Hz, 10H), 0.80 (t, *J* = 6.9 Hz, 3H).

^{13}C NMR (126 MHz, CDCl3) δ 200.2, 144.9, 136.1, 131.7, 130.7, 128.5, 127.4, 126.8, 126.4, 88.4, 83.6, 54.4, 32.9, 31.6, 28.8, 28.7, 22.7, 19.1, 14.2.

^{19}F NMR (471 MHz, $CDCl_3$) δ -134.3.

7. References

S1. Zeng, Y.; Chiou, M.; Bao, H. *J. Am. Chem. Soc.* **2020**, *142*, 18014–18021.

S2. Zhu, X.; Deng, W.; Chiou, M. F.; Ye, C.; Jian, W.; Zeng, Y.; Jiao, Y.; Ge, L.; Li, Y.; Zhang, X.; Bao, H. *J. Am. Chem. Soc.* **2019**, *141*, 548–559.

S3. Yan, W.; Ye, X. h. Novruz, G. and Shi, X. D. *Org. Lett.* **2012**, *14*, 2358–2361.

8. Copies of NMR Spectra for Compounds

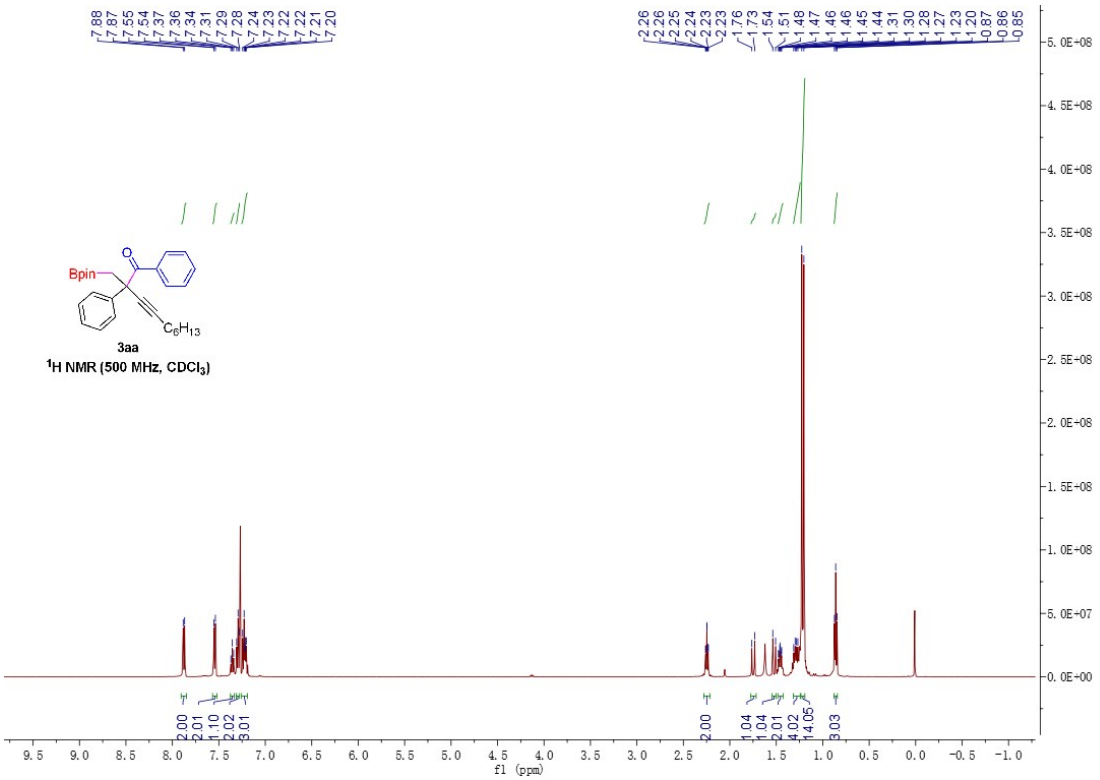


Figure S1. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 3aa

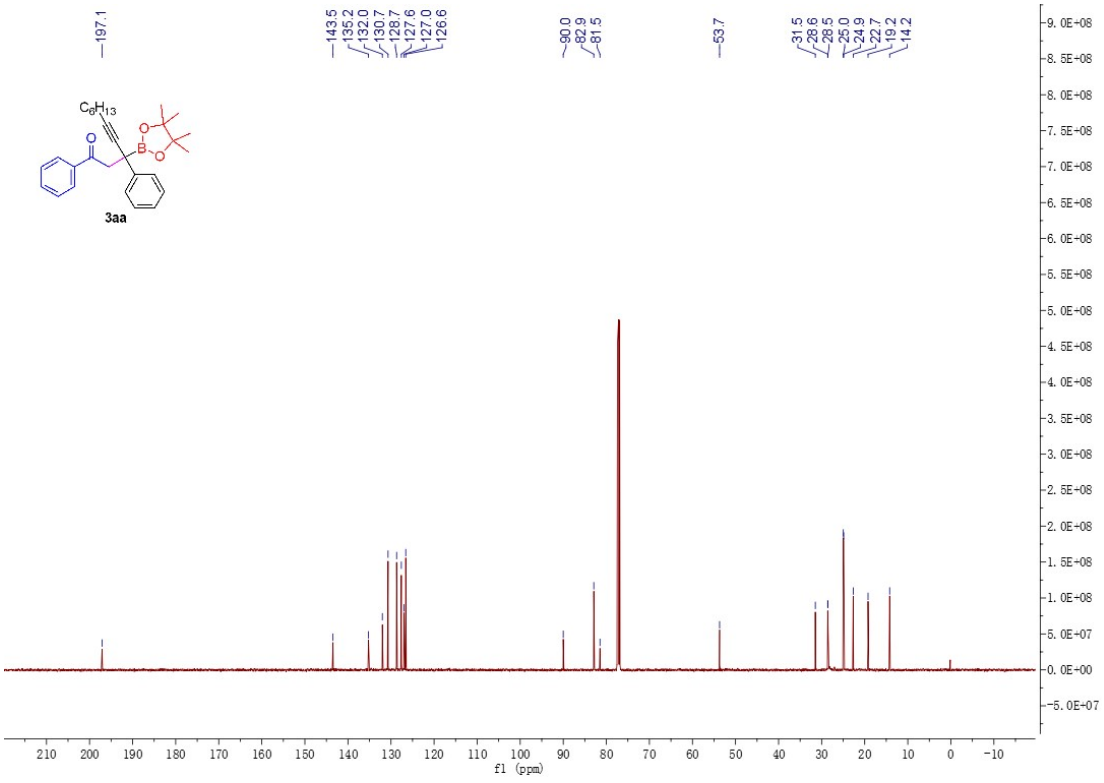


Figure S2. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of 3aa

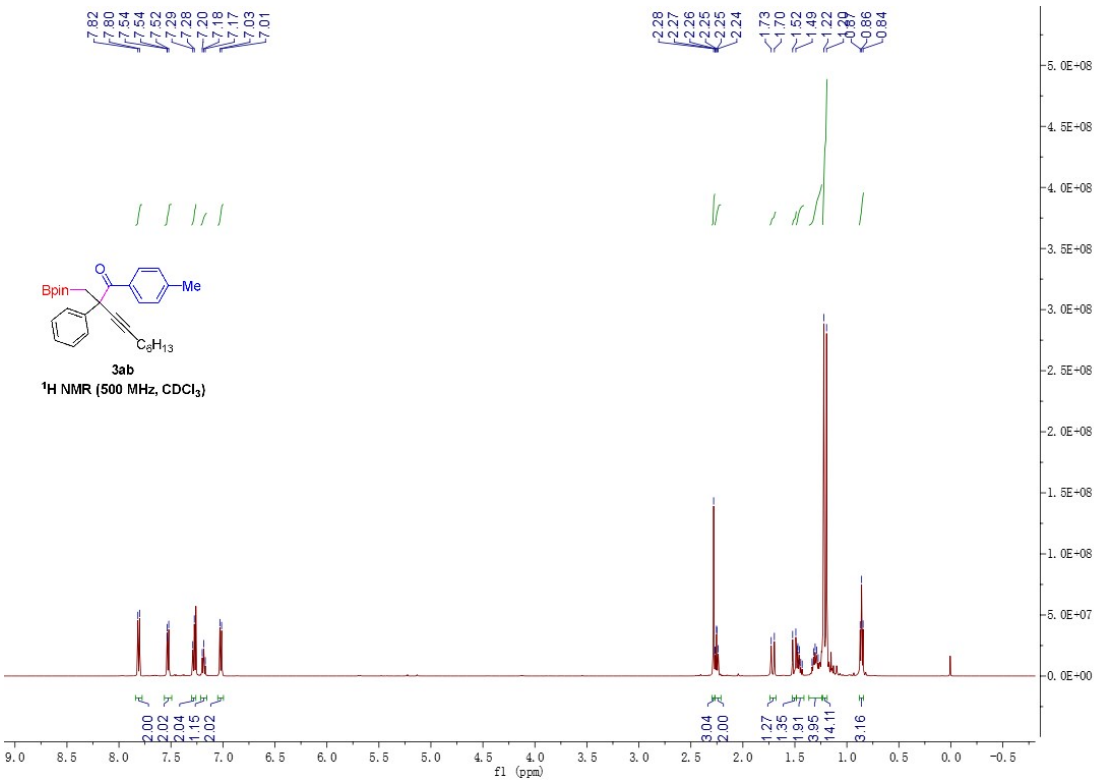


Figure S3. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 3ab

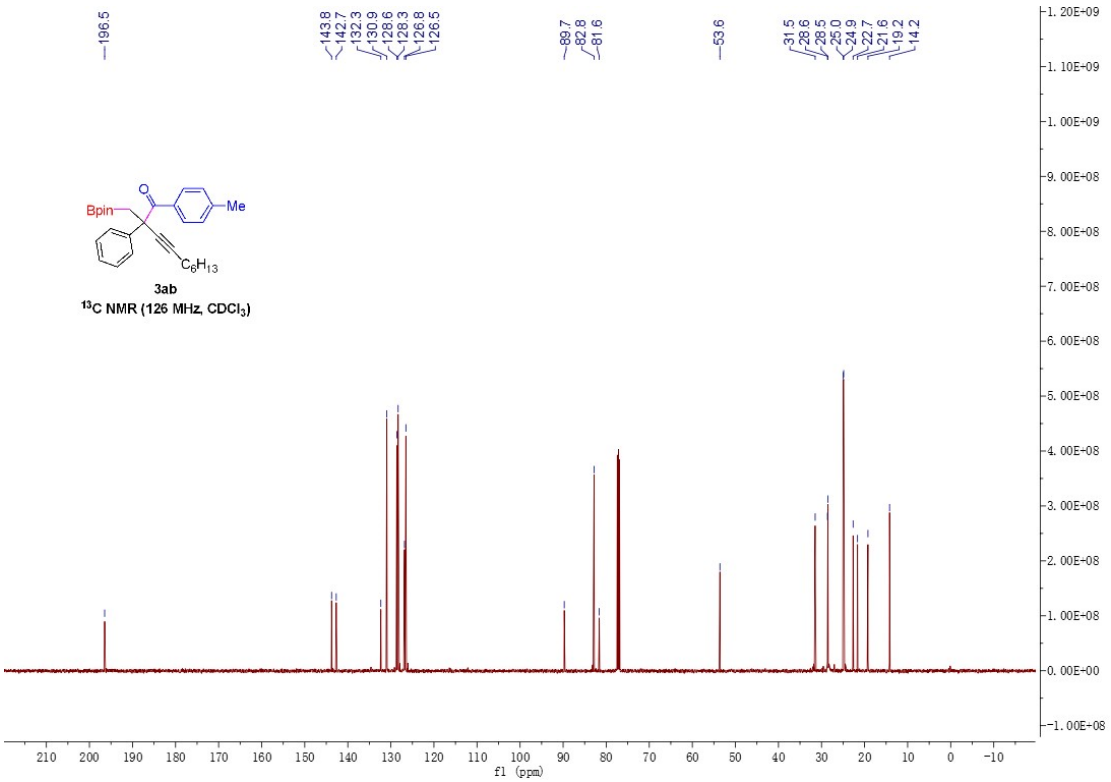


Figure S4. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of 3ab

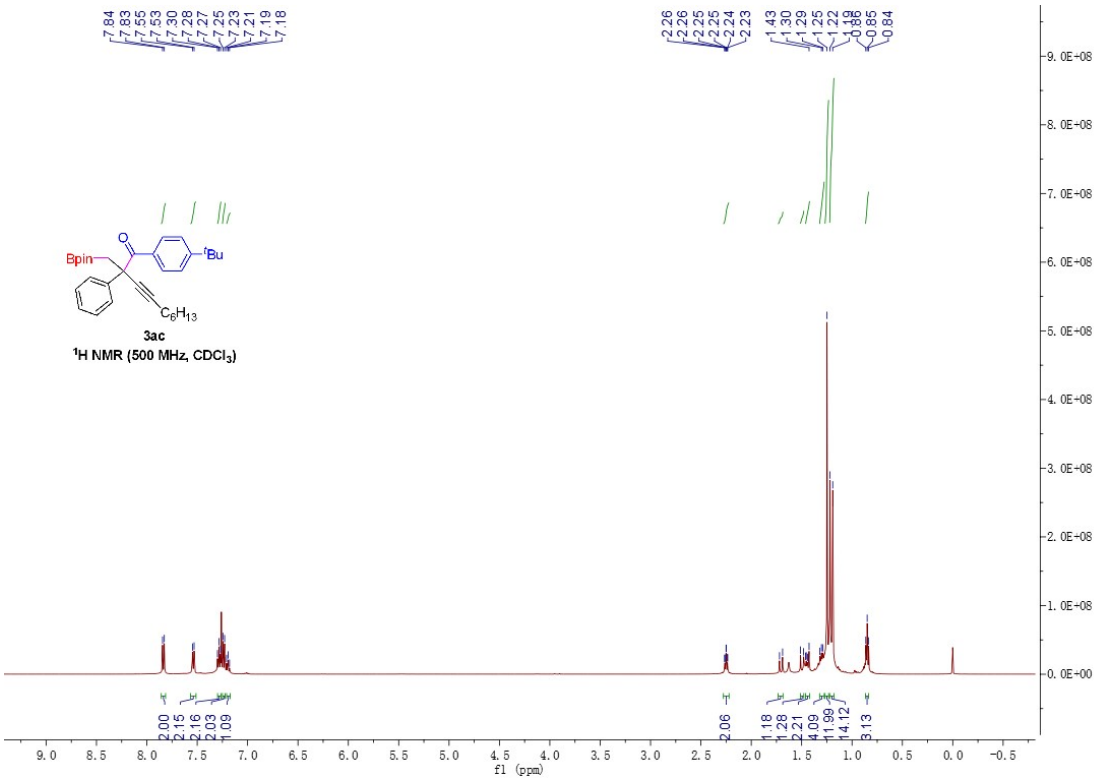


Figure S5. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 3ac

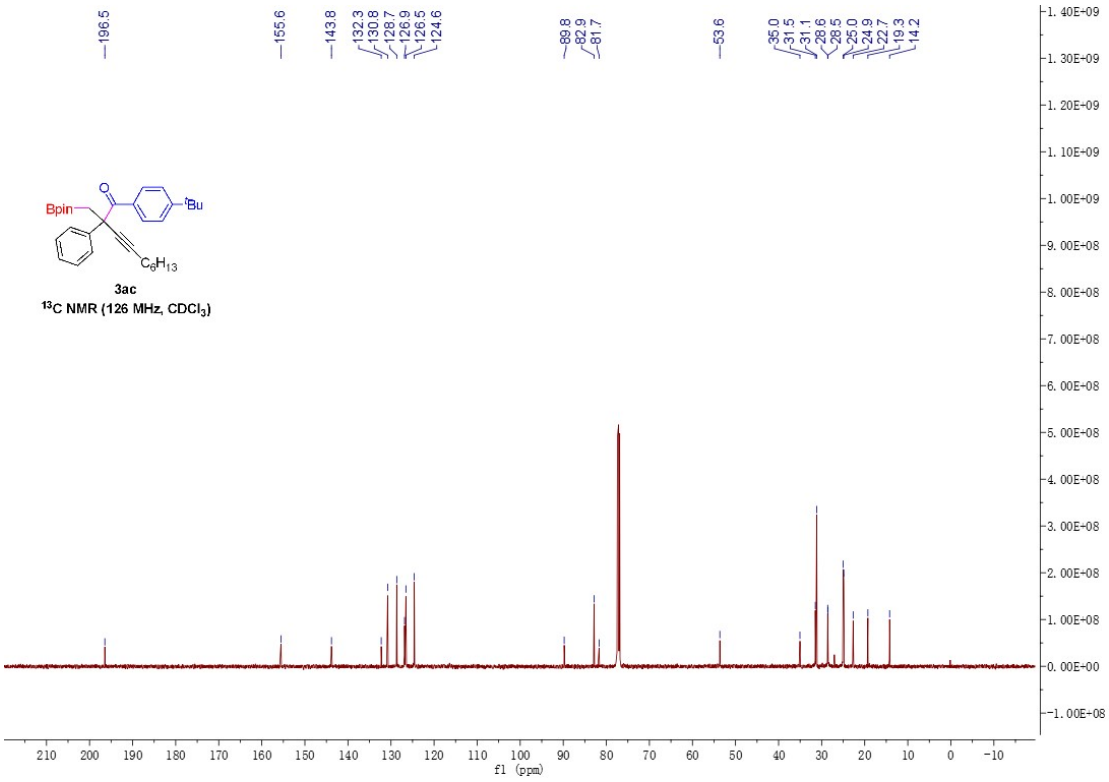


Figure S6. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of 3ac

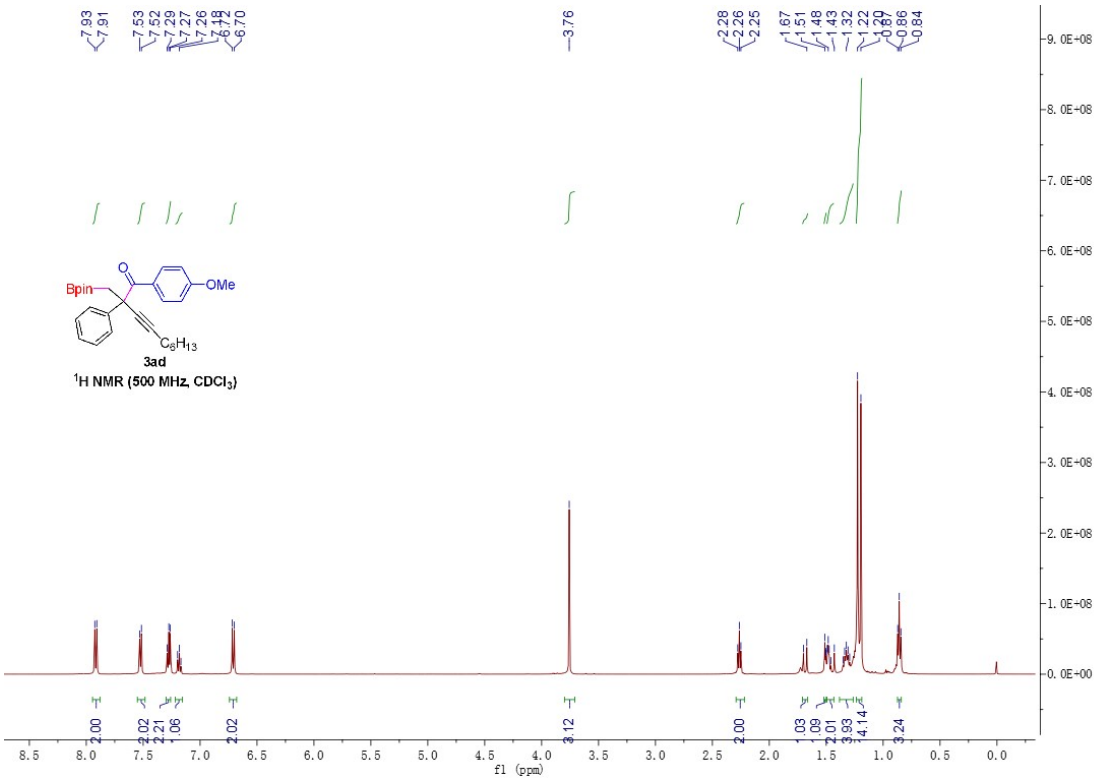


Figure S7. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 3ad

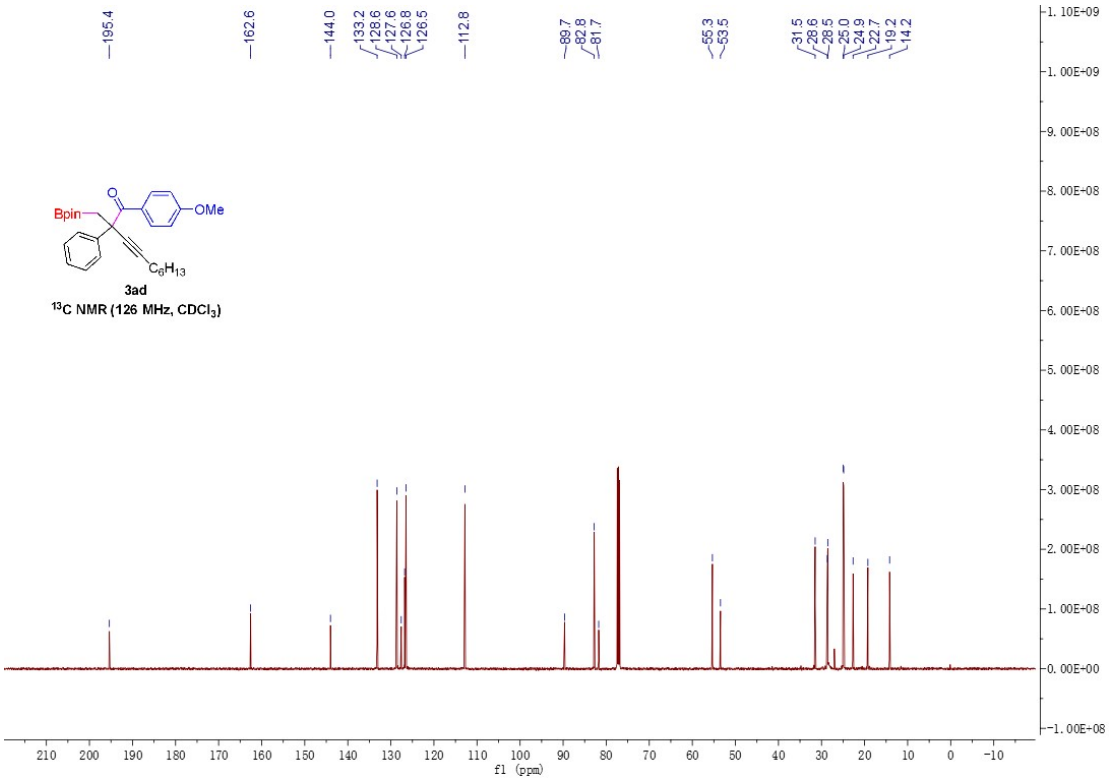


Figure S8. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of 3ad

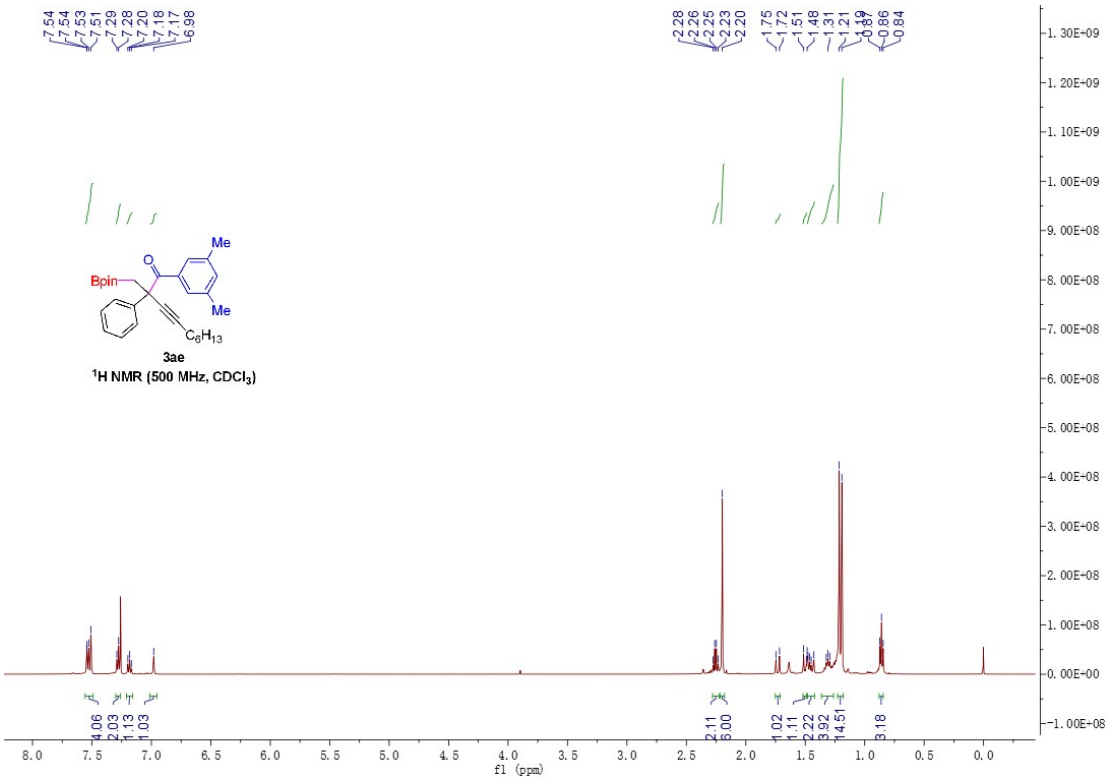


Figure S9. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 3ae

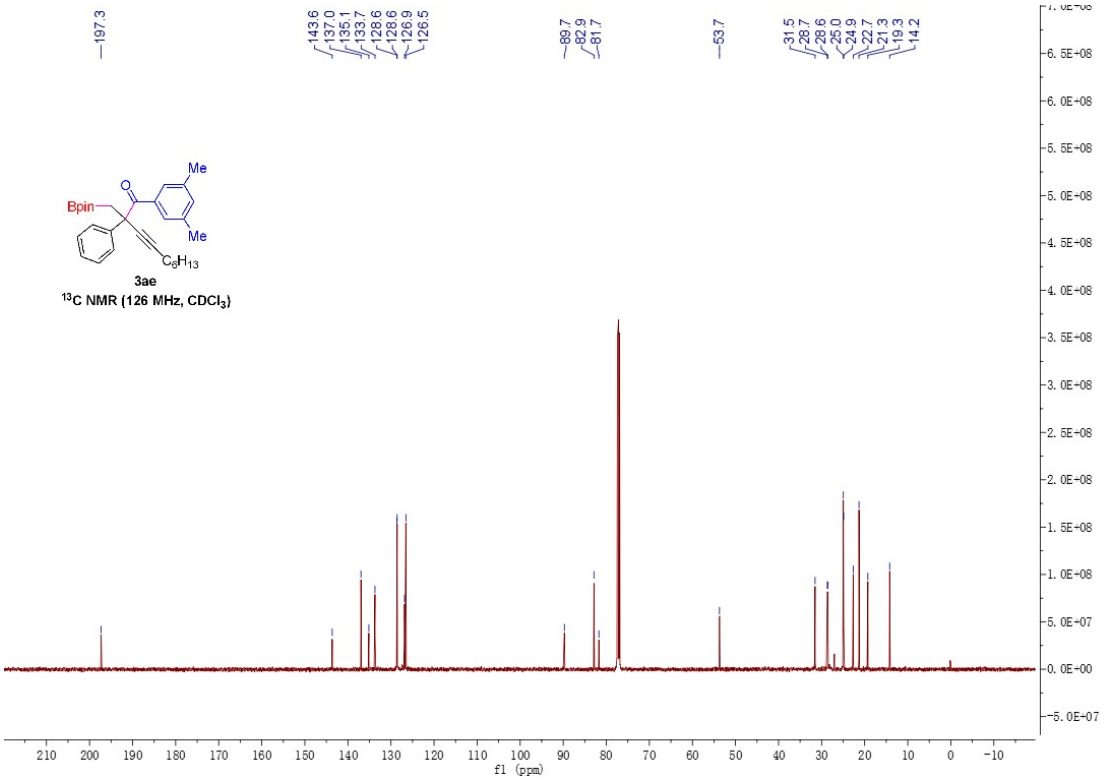


Figure S10. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of 3ae

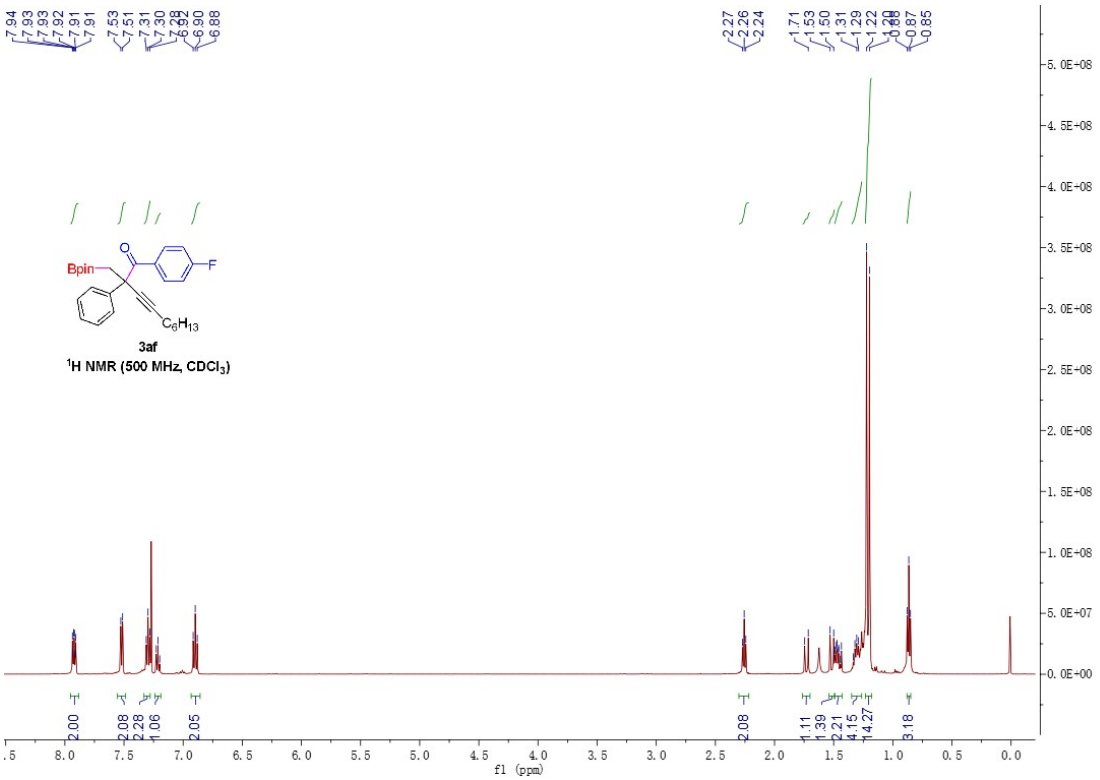


Figure S11. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 3af

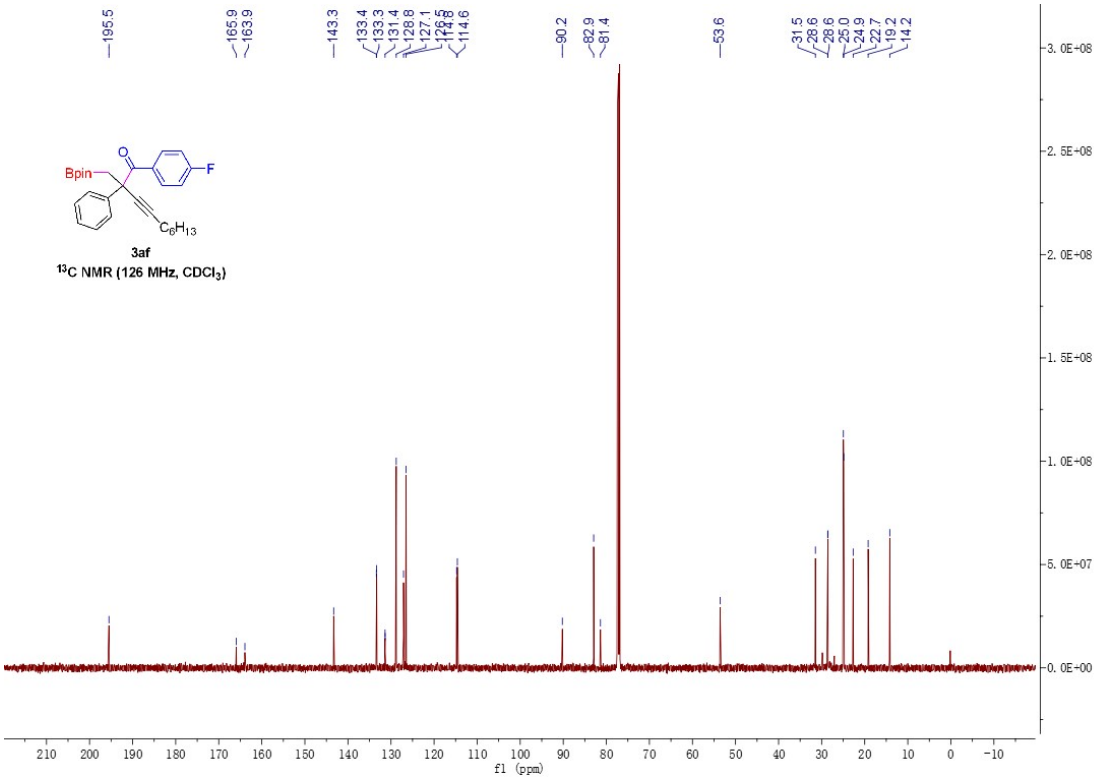


Figure S12. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of 3af

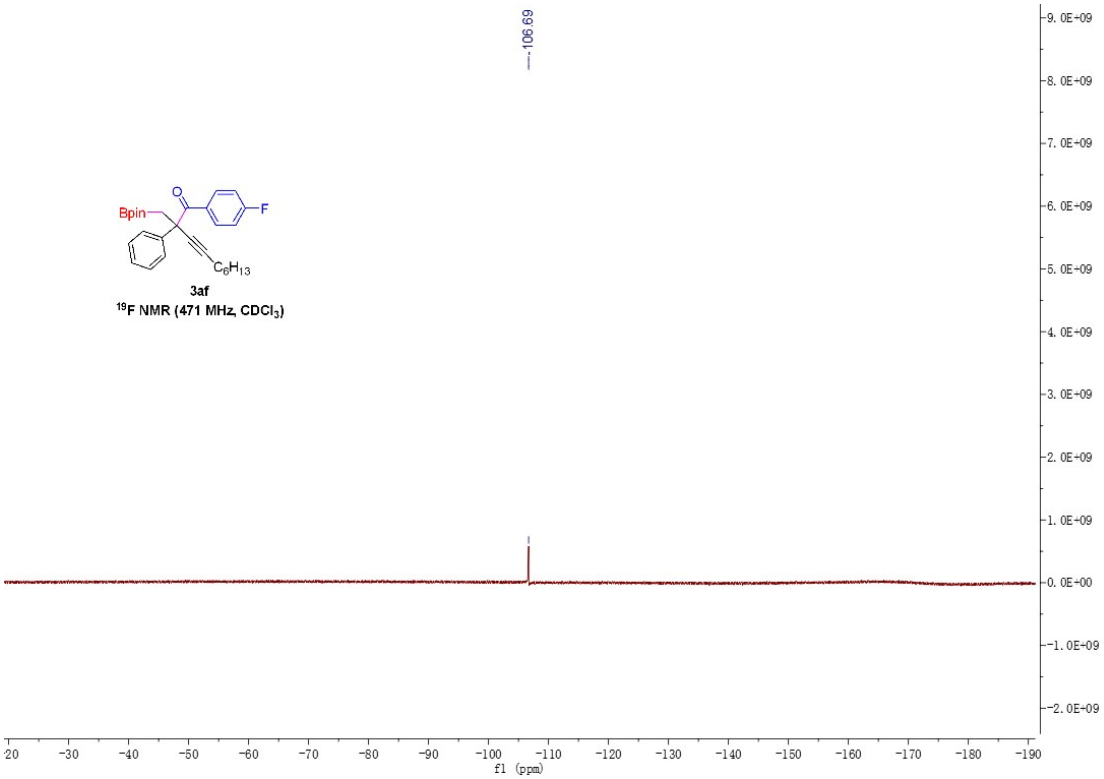


Figure S13. ^{19}F NMR (471 MHz, $CDCl_3$) spectrum of 3af

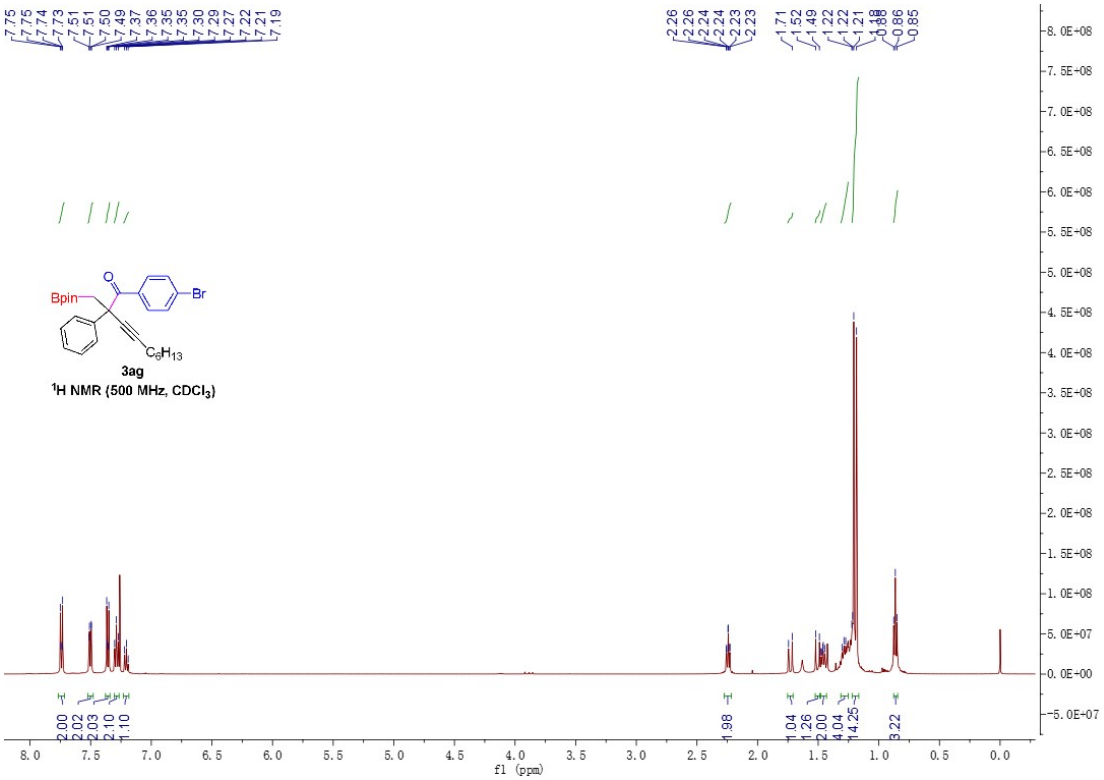


Figure S14. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 3ag

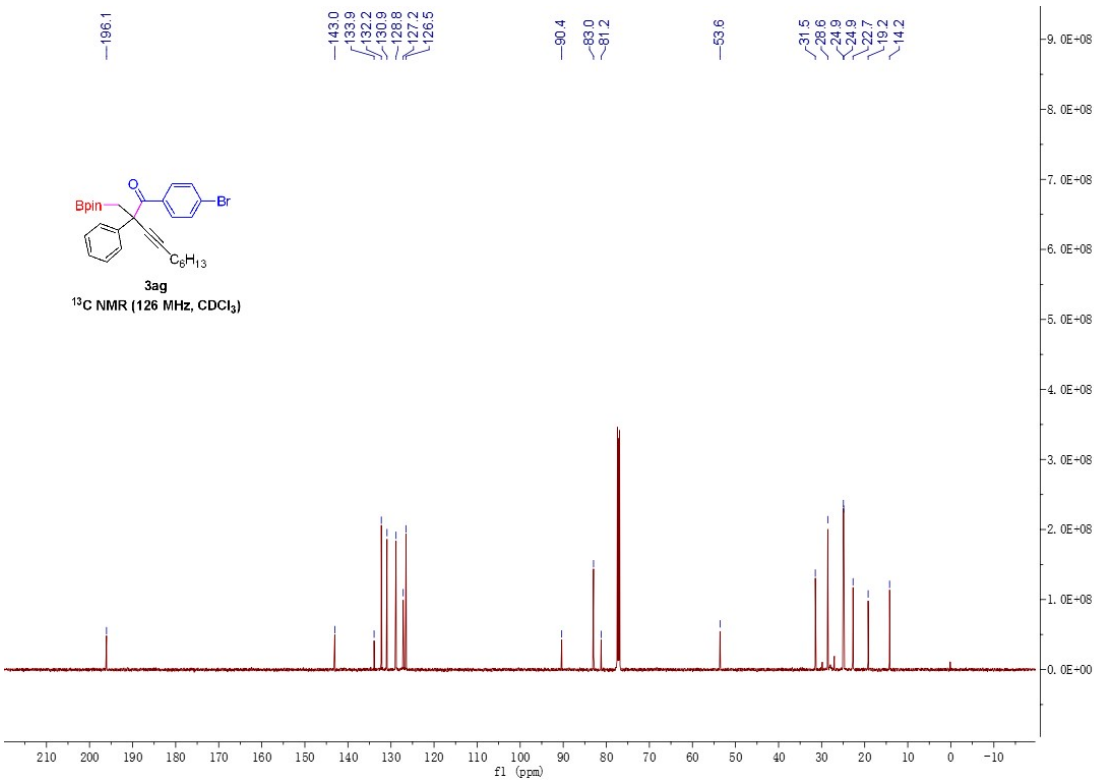


Figure S15. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of 3ag

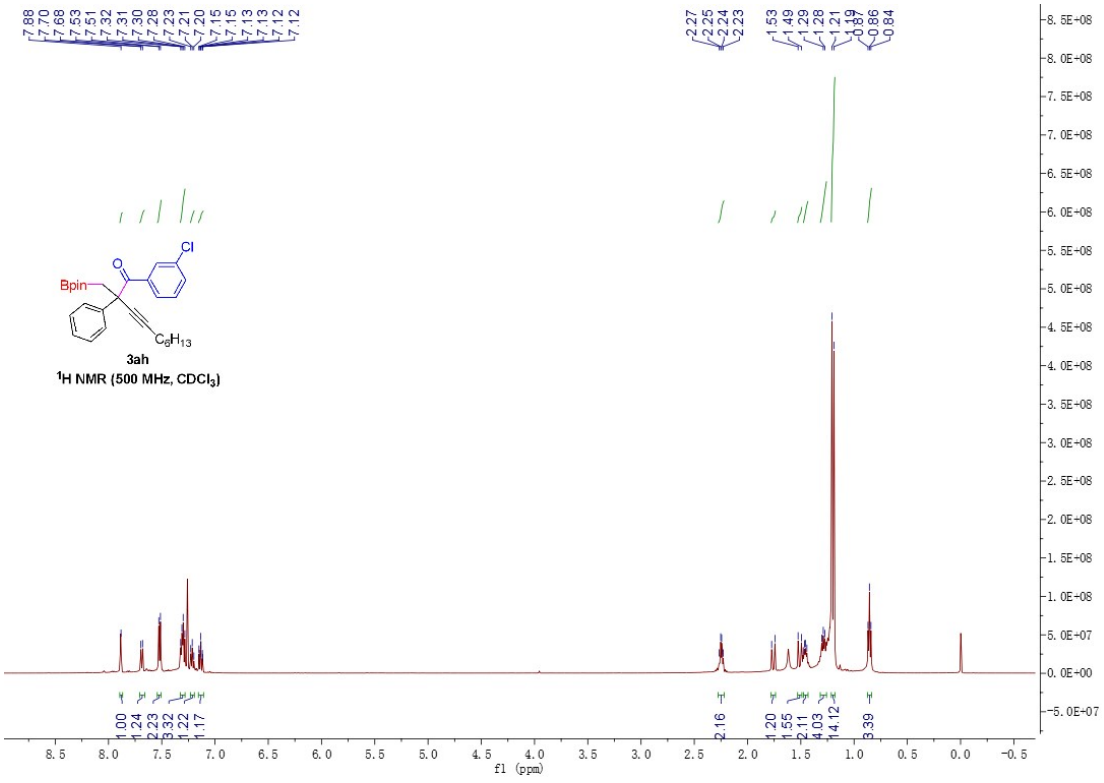


Figure S16. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 3ah

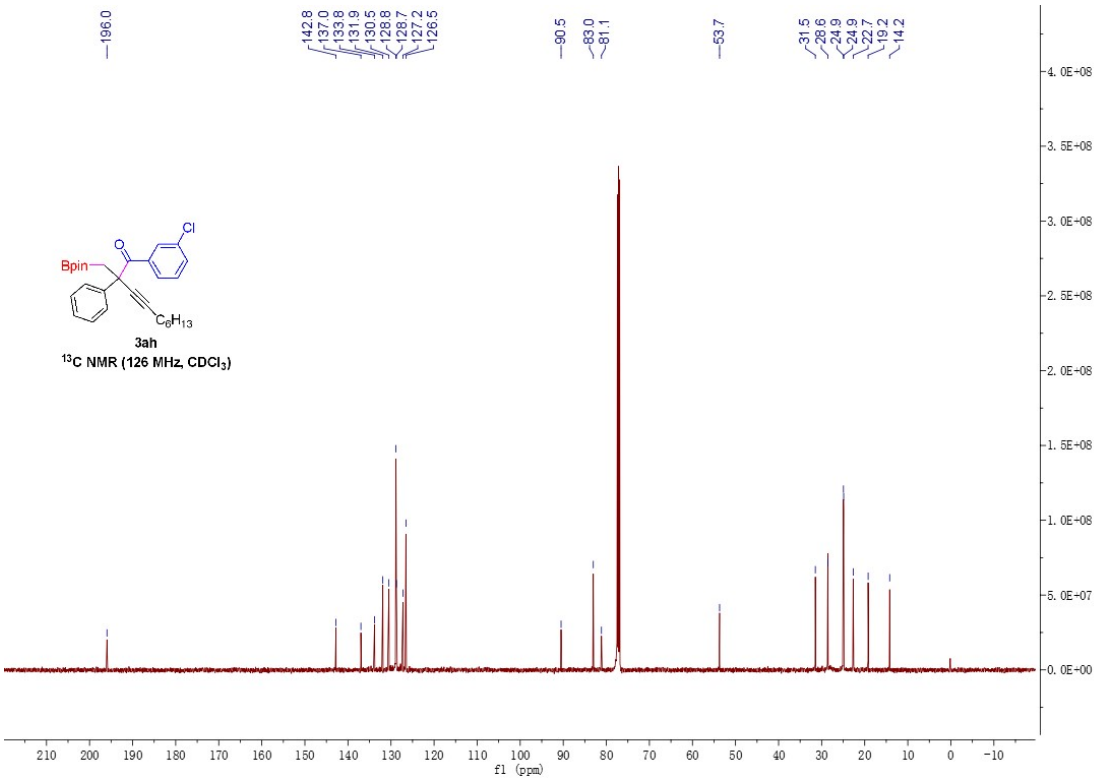


Figure S17. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of 3ah

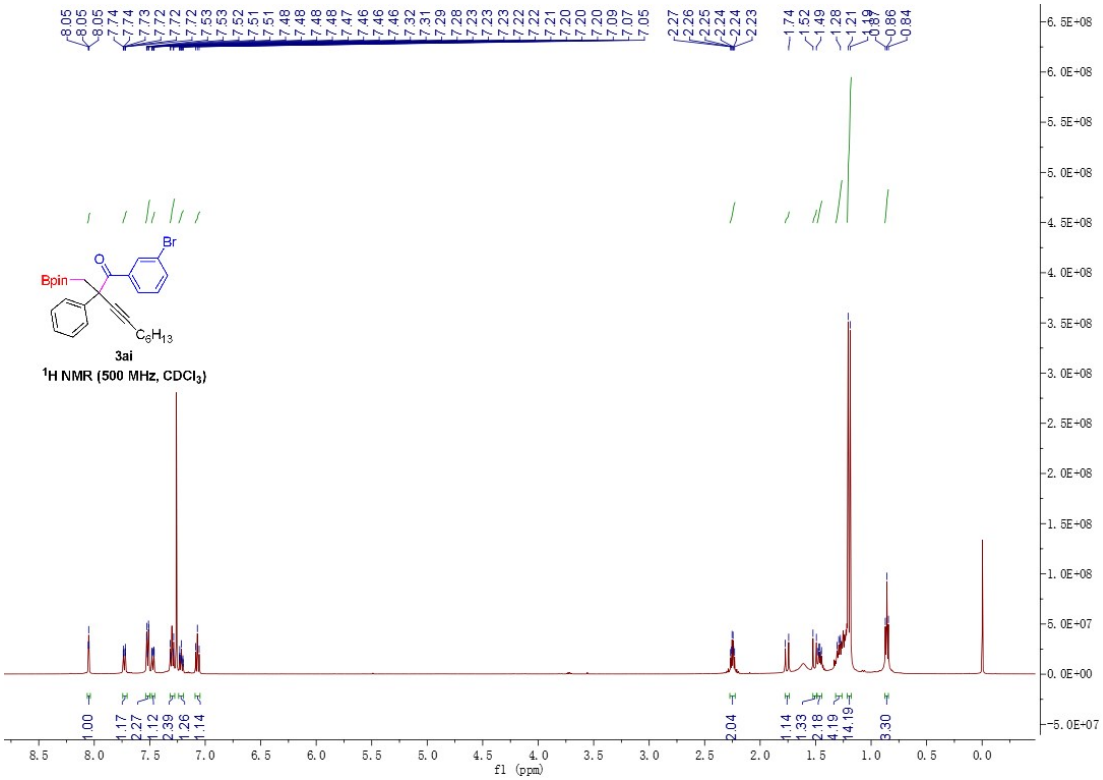


Figure S18. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 3ai

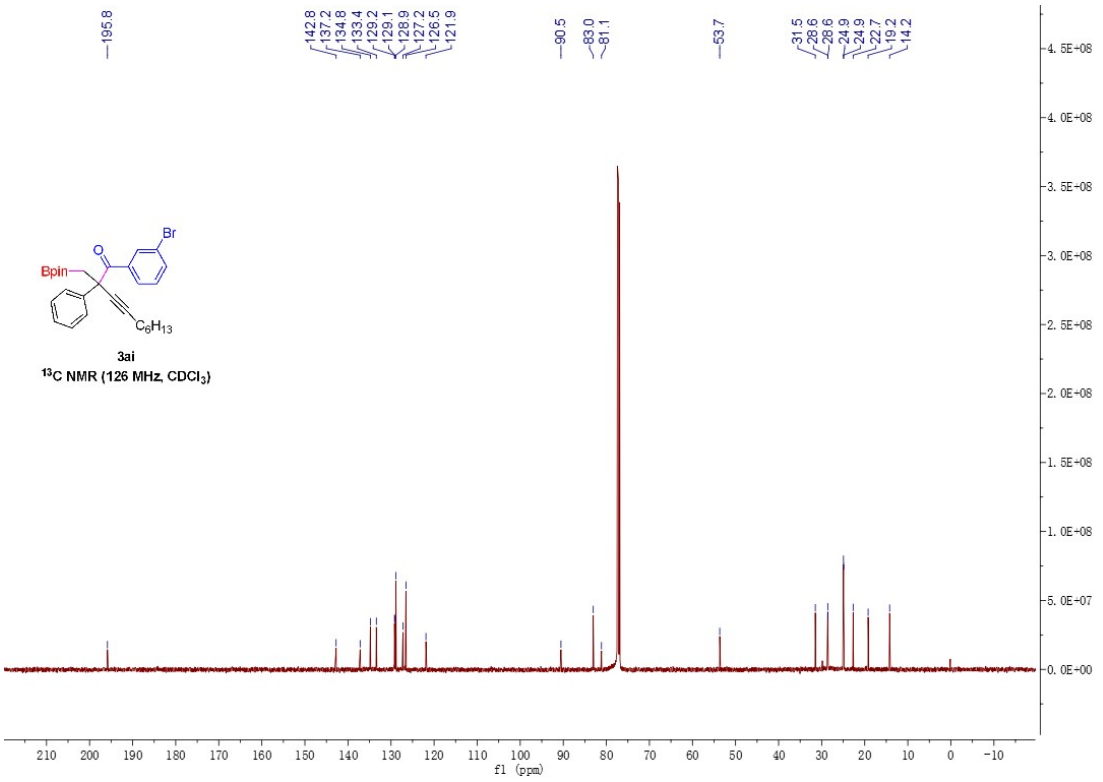


Figure S19. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of 3ai

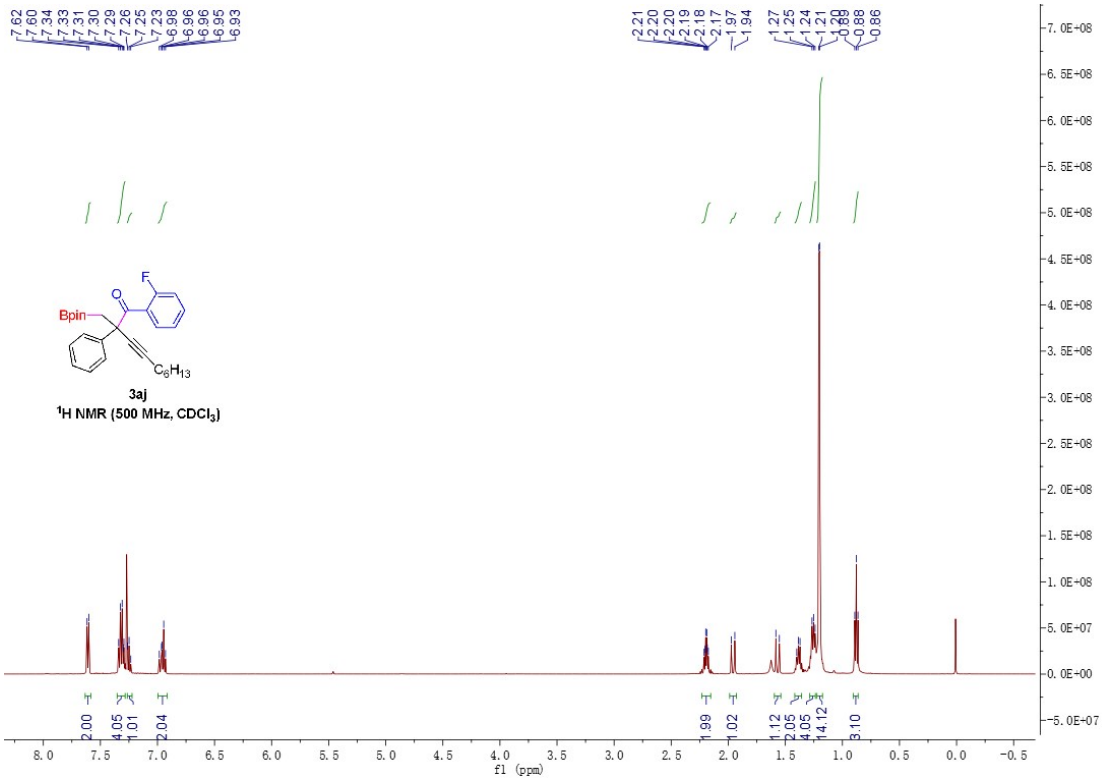


Figure S20. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 3aj

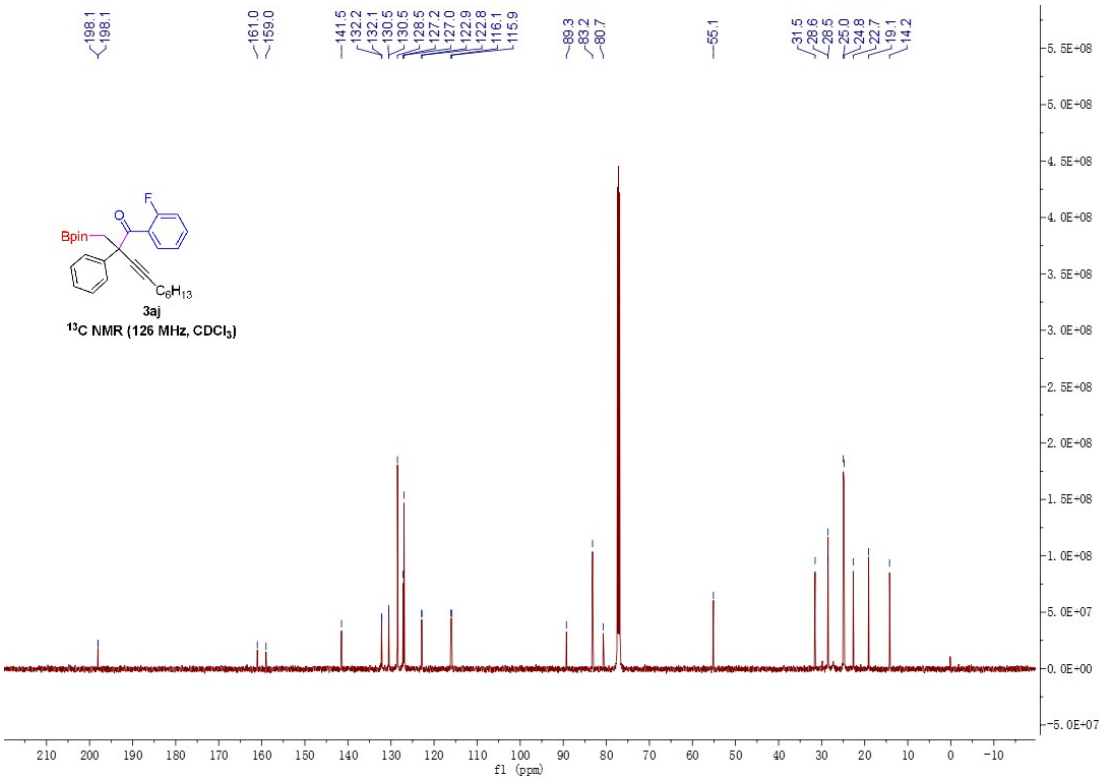


Figure S21. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of 3aj

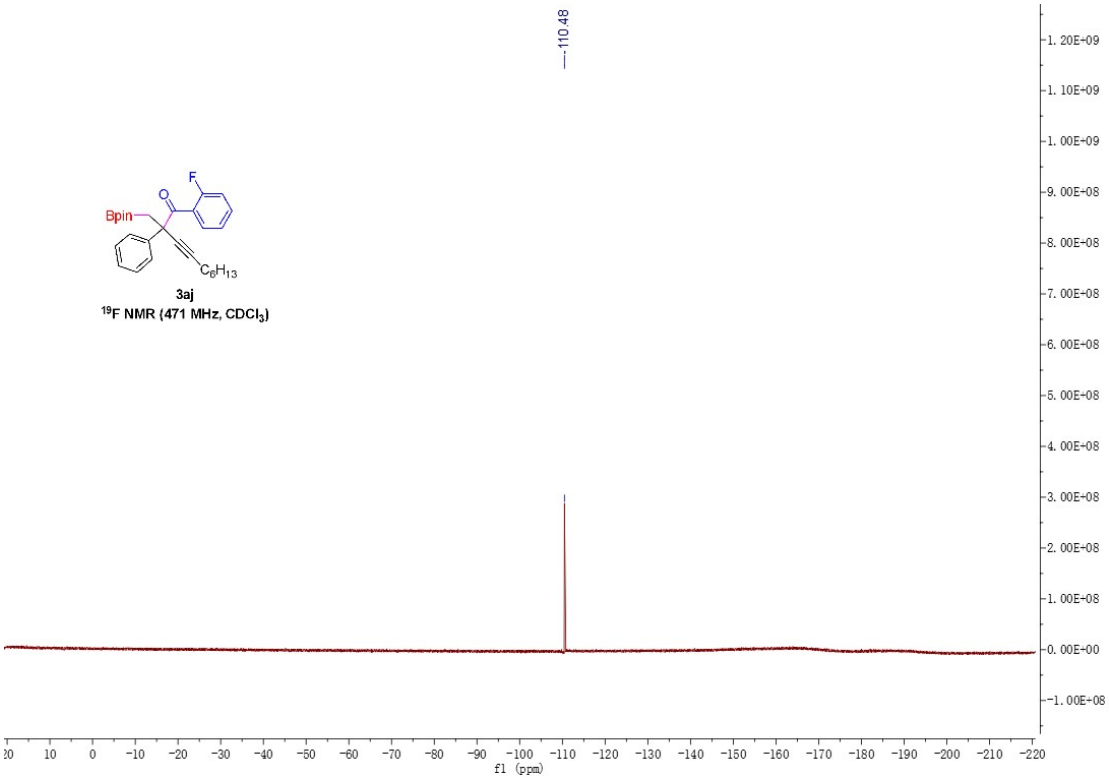


Figure S22. ^{19}F NMR (471 MHz, $CDCl_3$) spectrum of 3aj

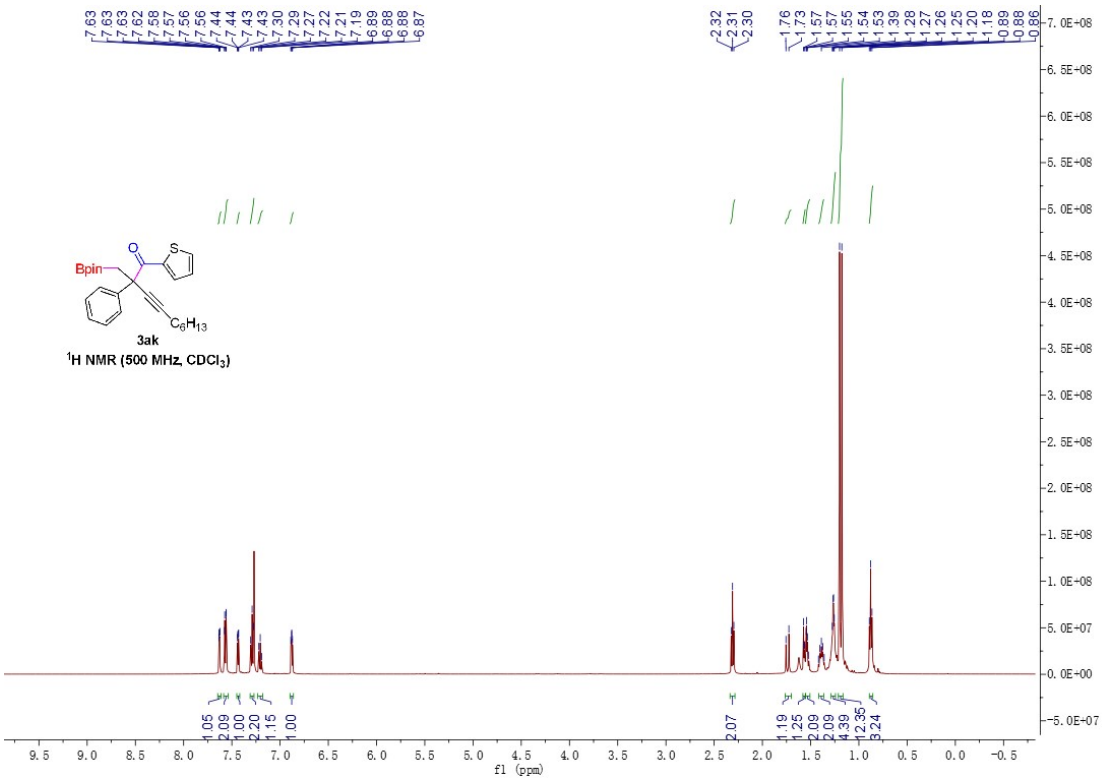


Figure S23. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 3ak

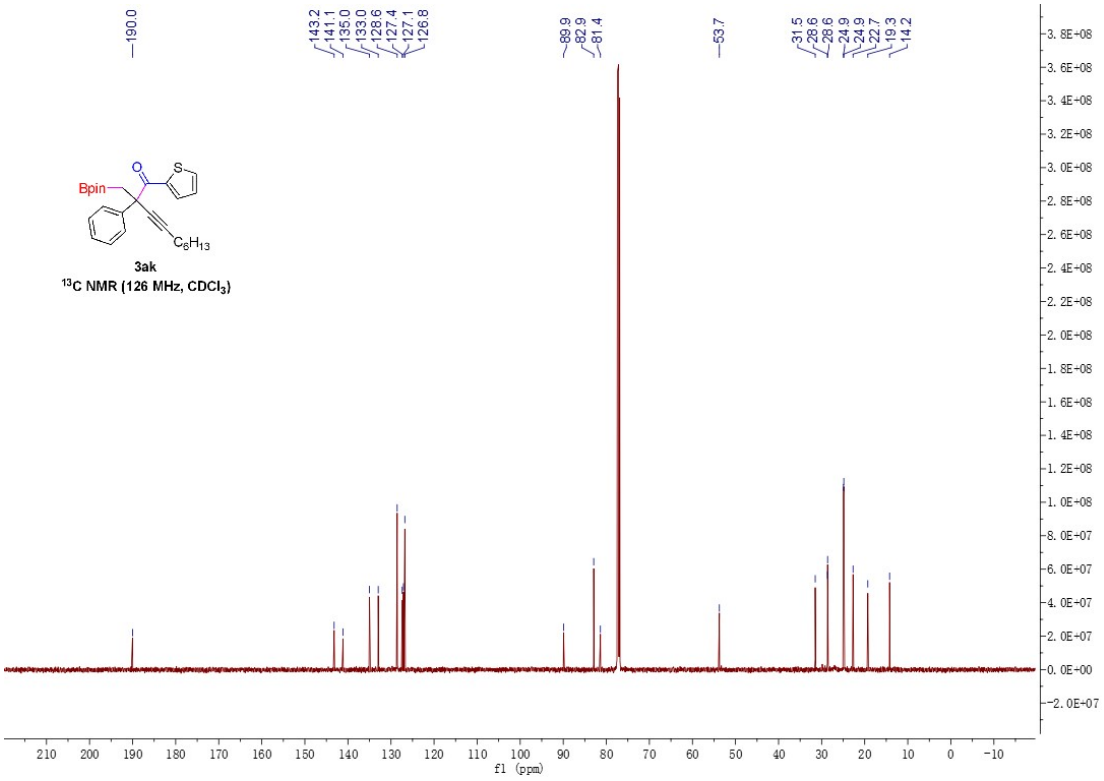


Figure S24. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of 3ak

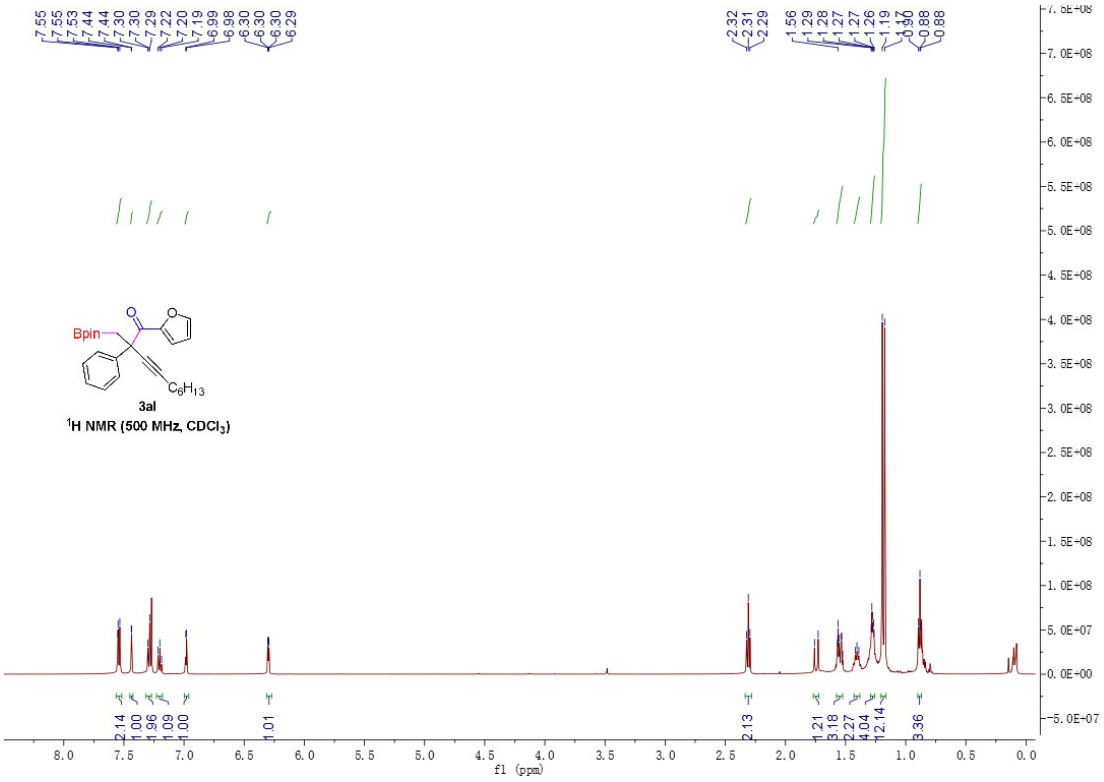


Figure S25. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 3al

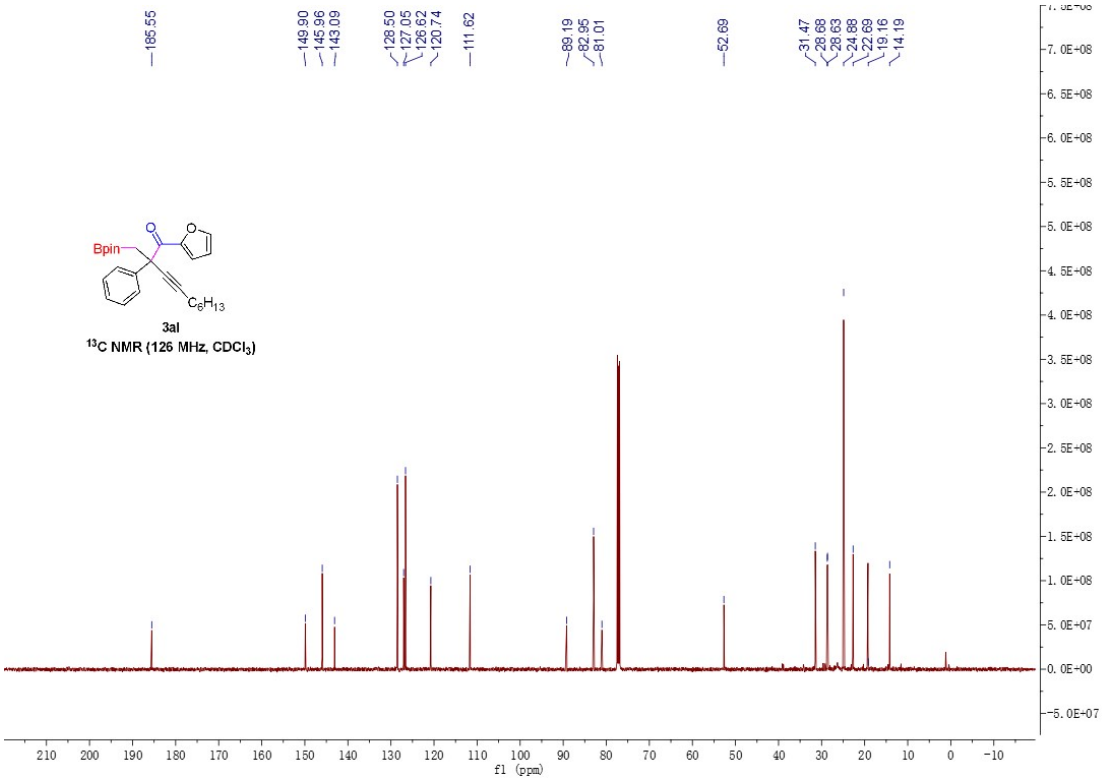


Figure S26. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of 3al

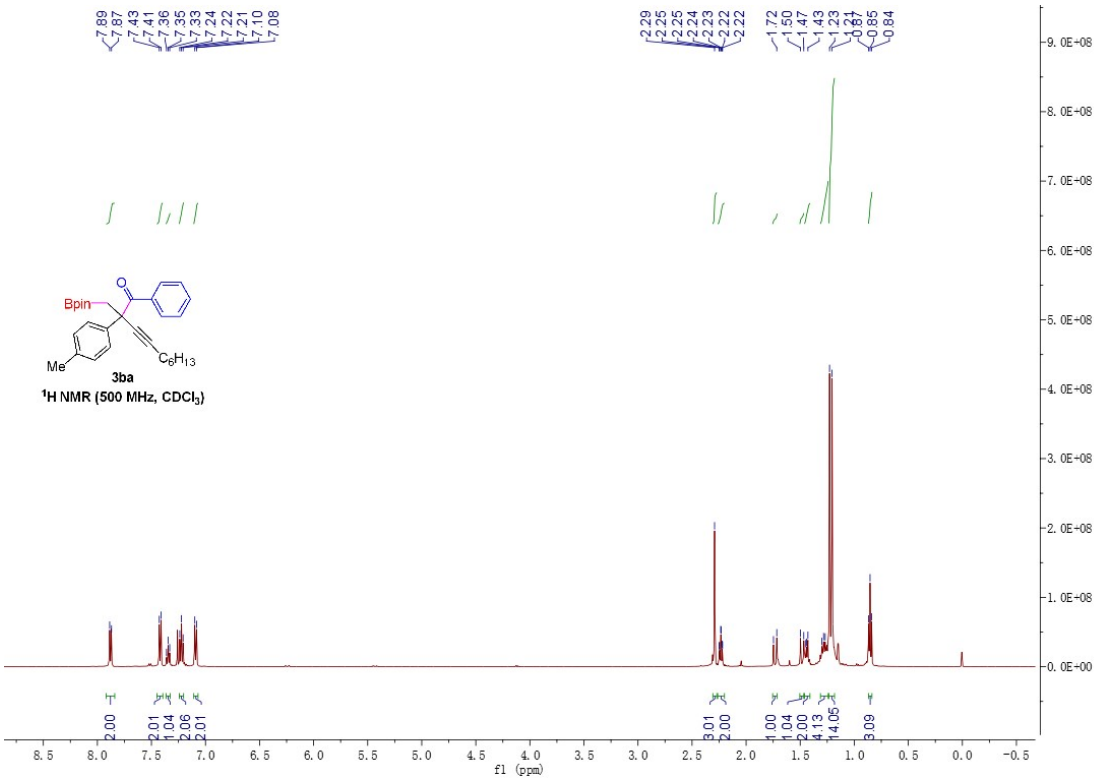


Figure S27. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 3ba

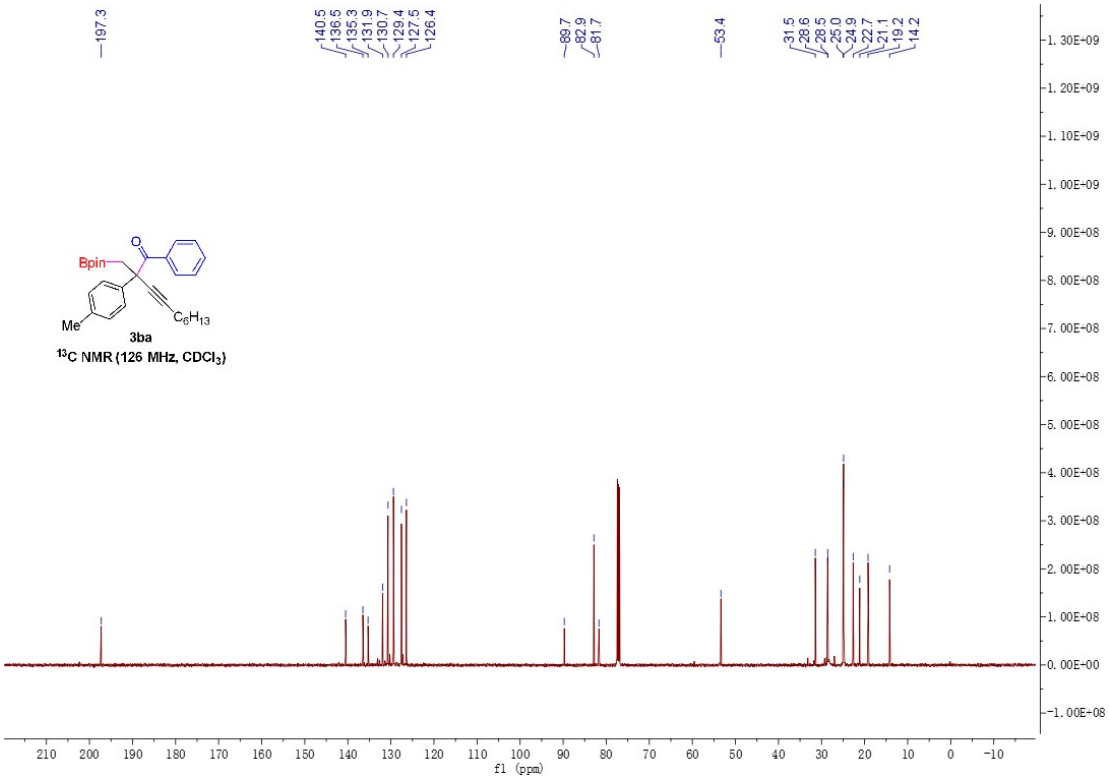


Figure S28. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of 3ba

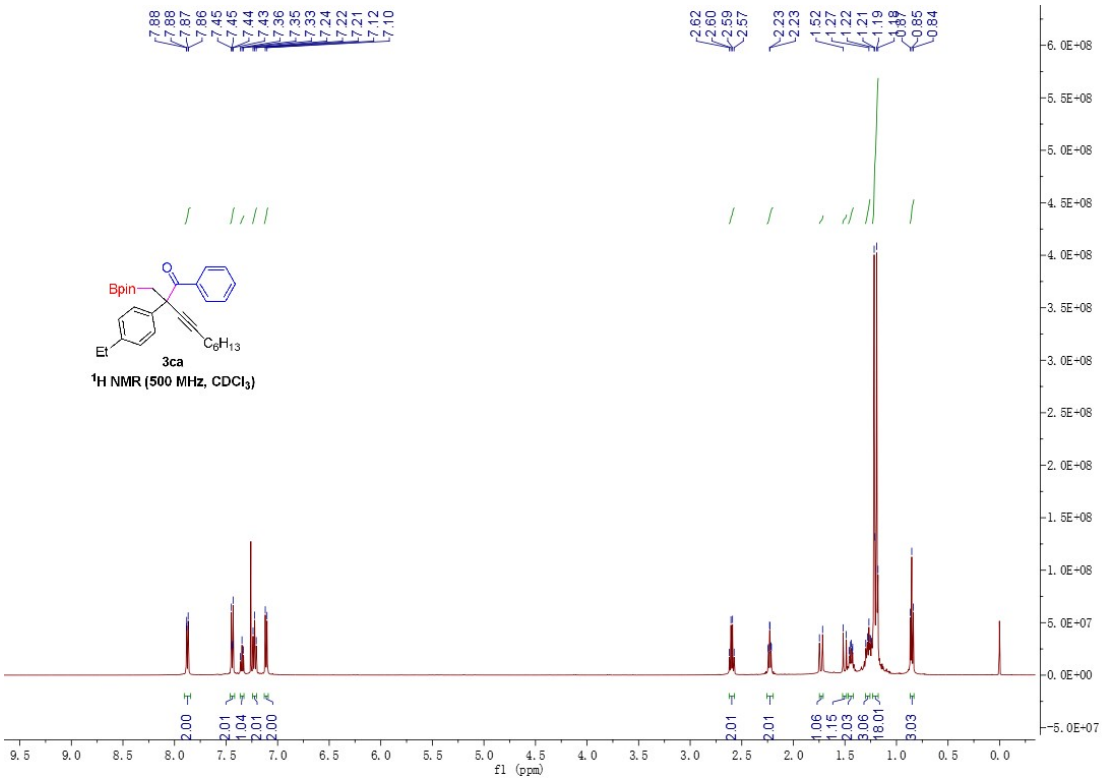


Figure S29. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 3ca

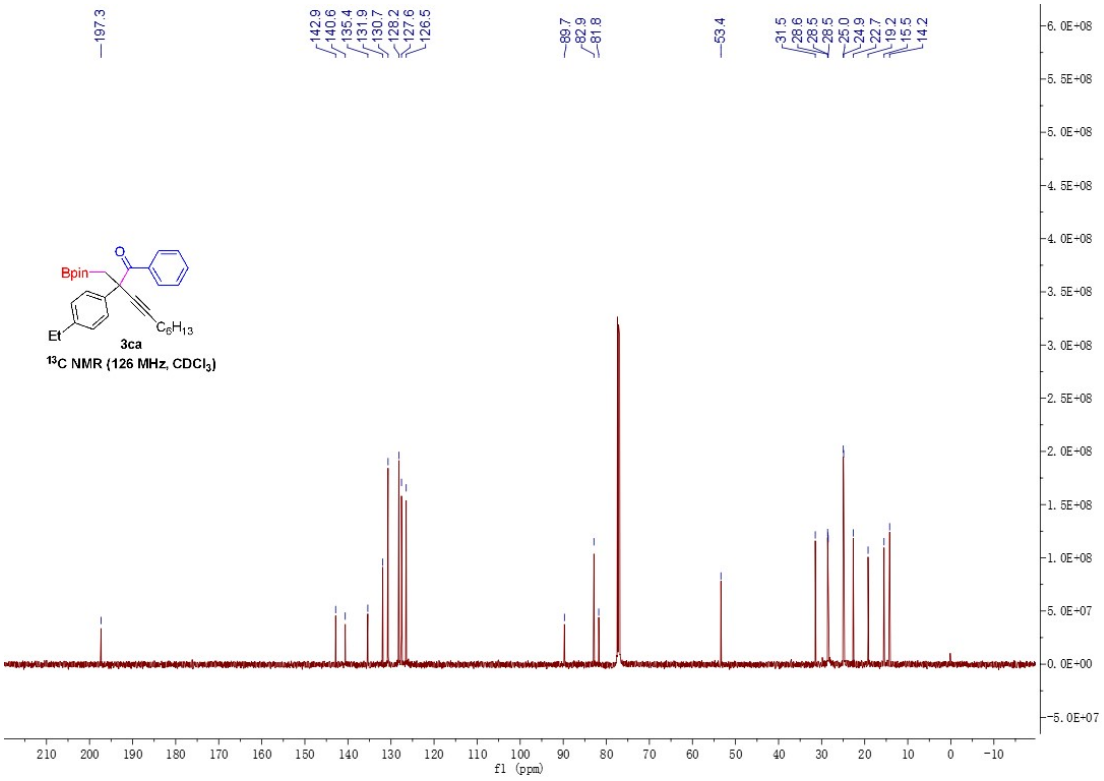


Figure S30. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of 3ca

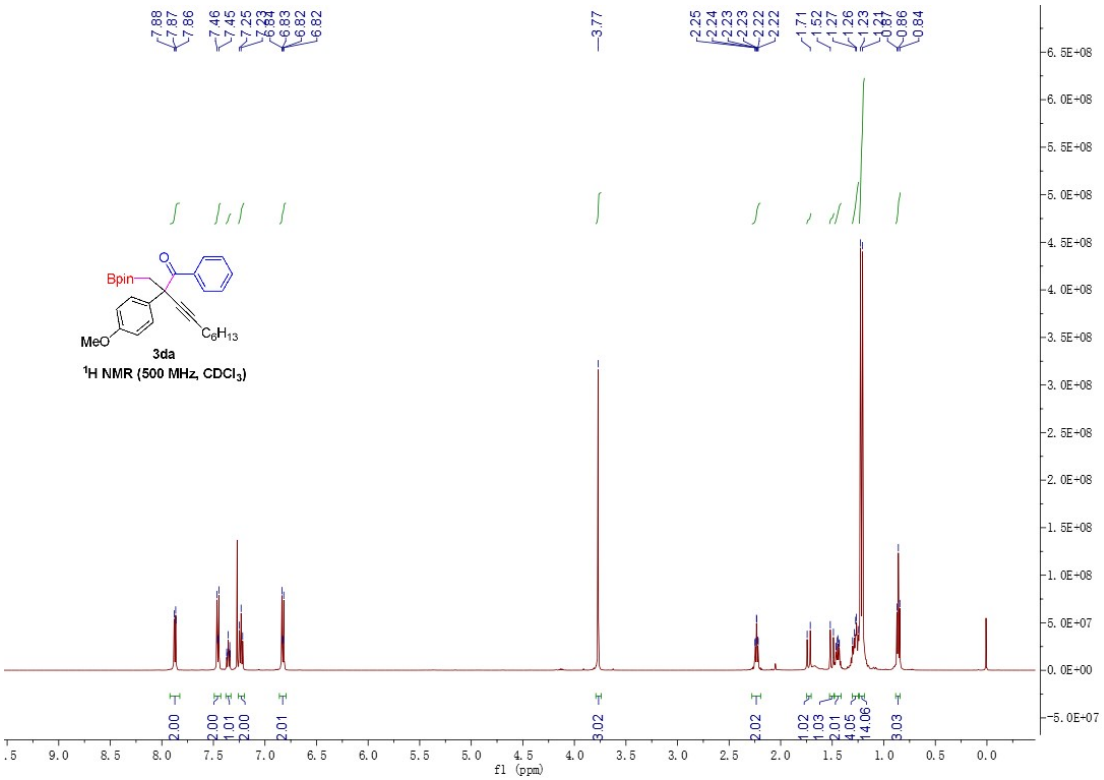


Figure S31. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 3da

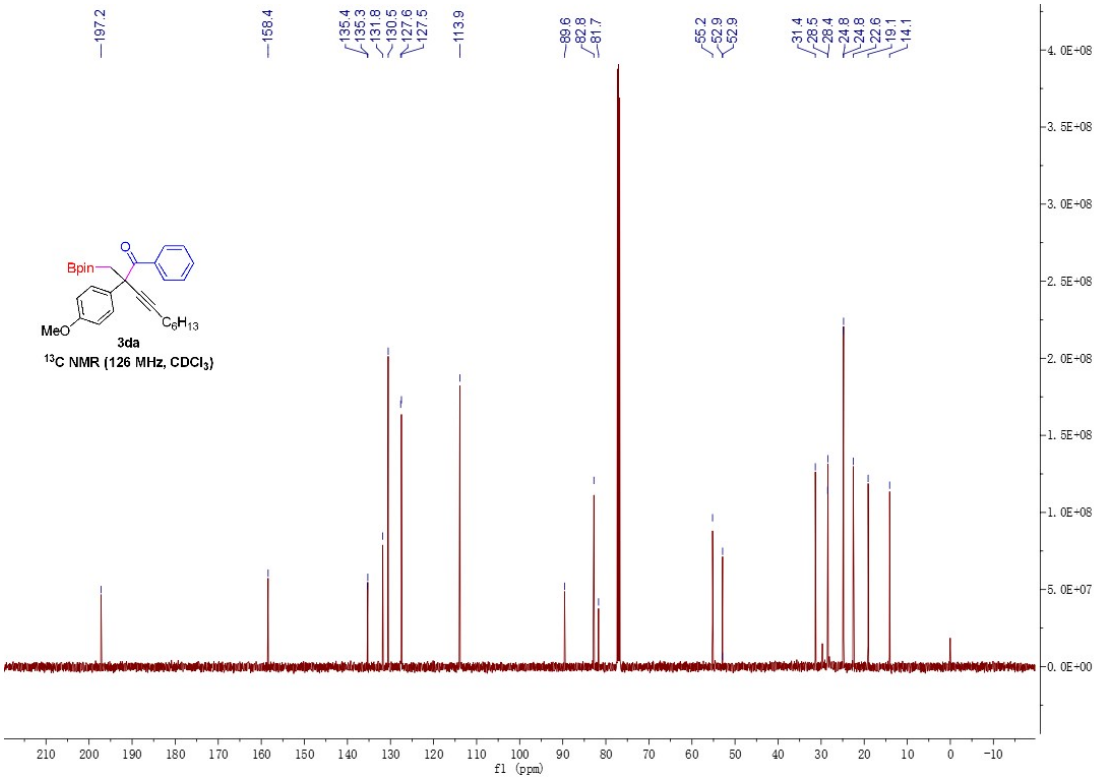


Figure S32. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of 3da

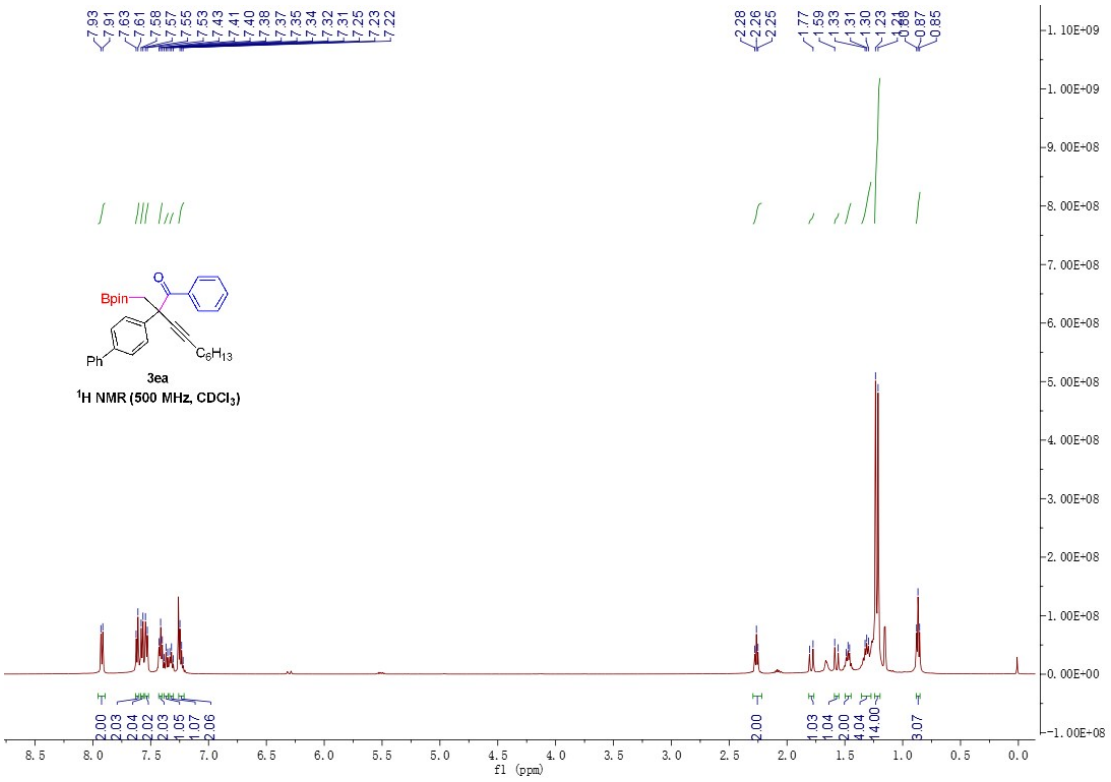


Figure S33. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 3ea

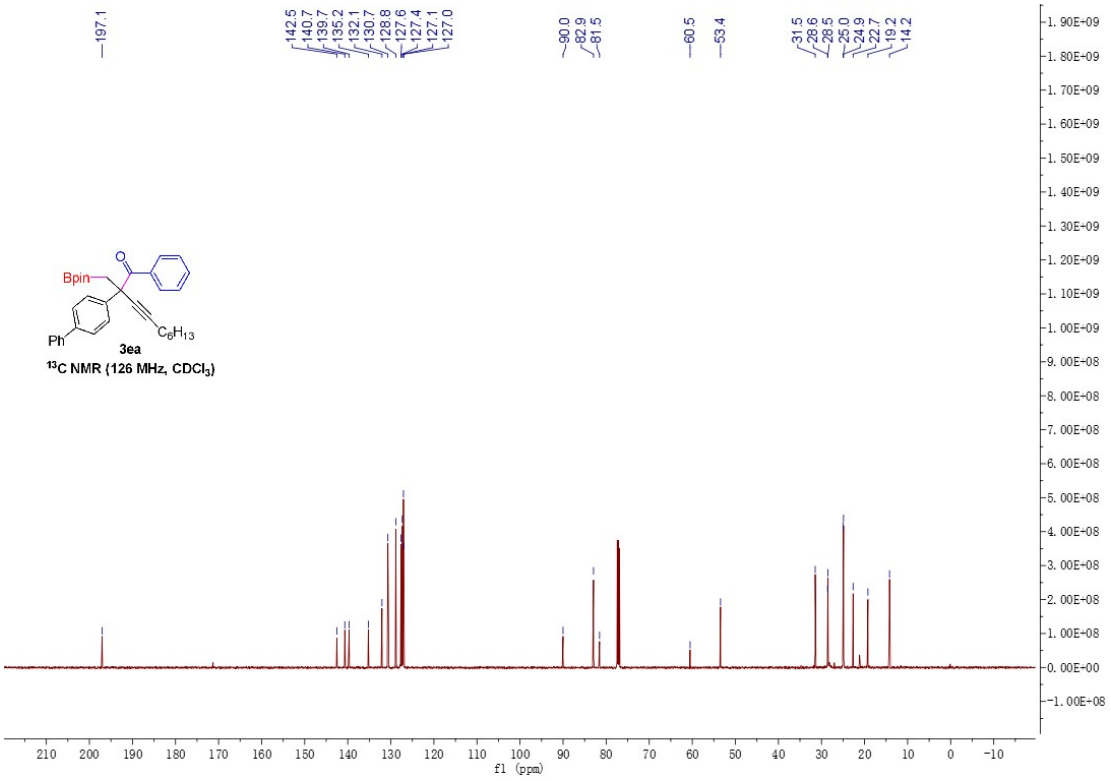


Figure S34. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of 3ea

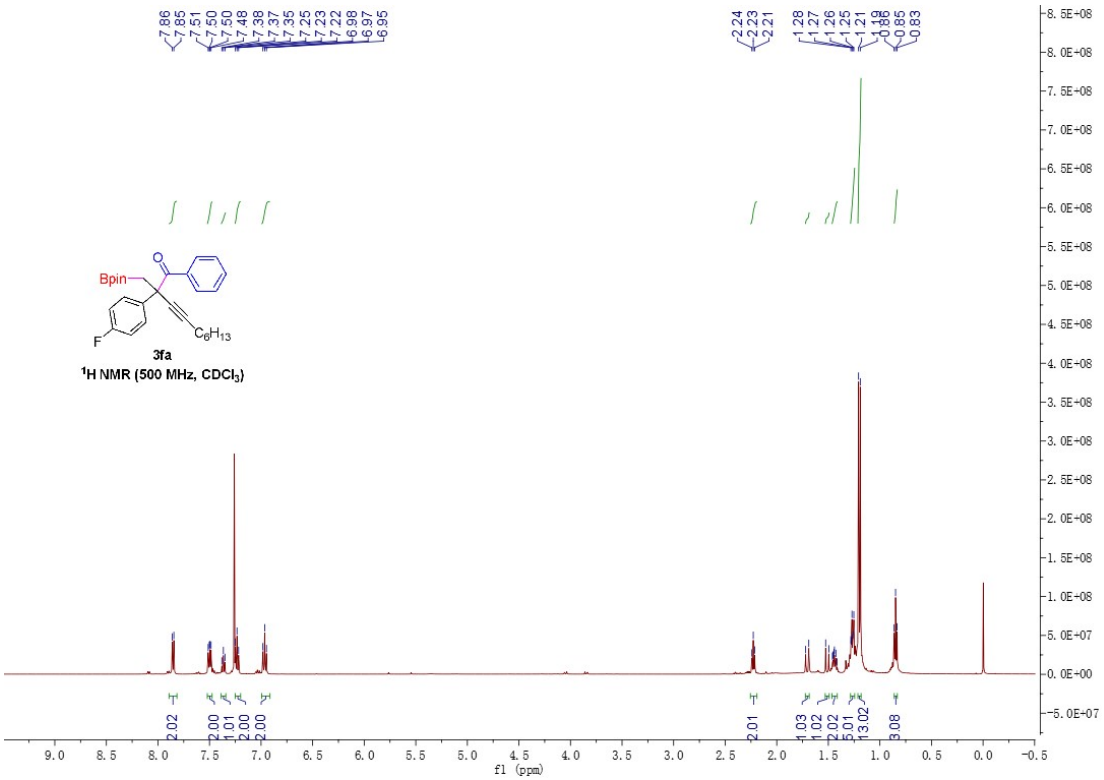


Figure S35. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 3fa

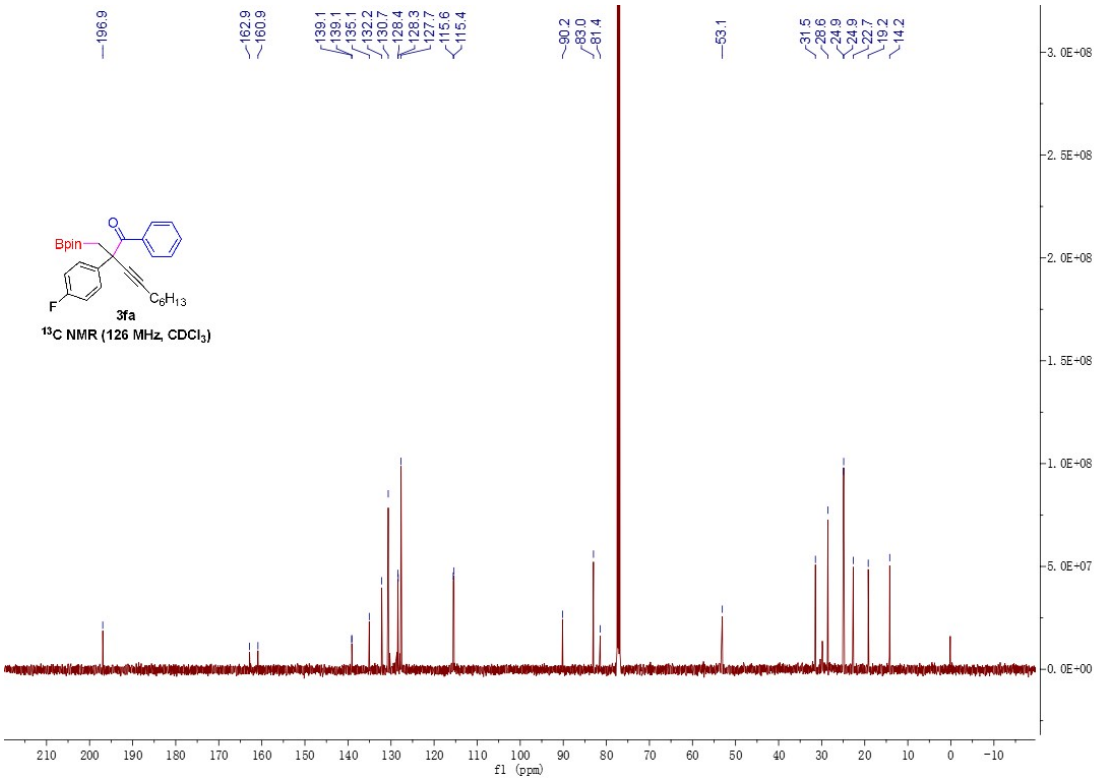


Figure S36. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of 3fa

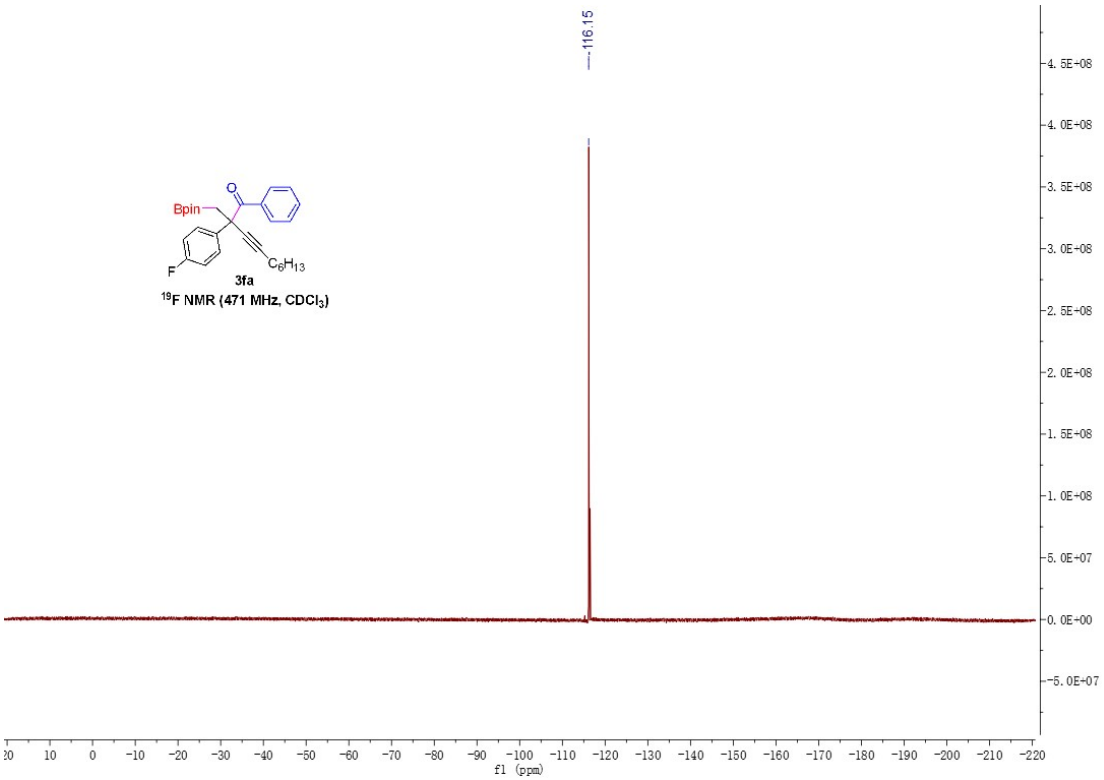


Figure S37. ^{19}F NMR (471 MHz, $CDCl_3$) spectrum of 3fa

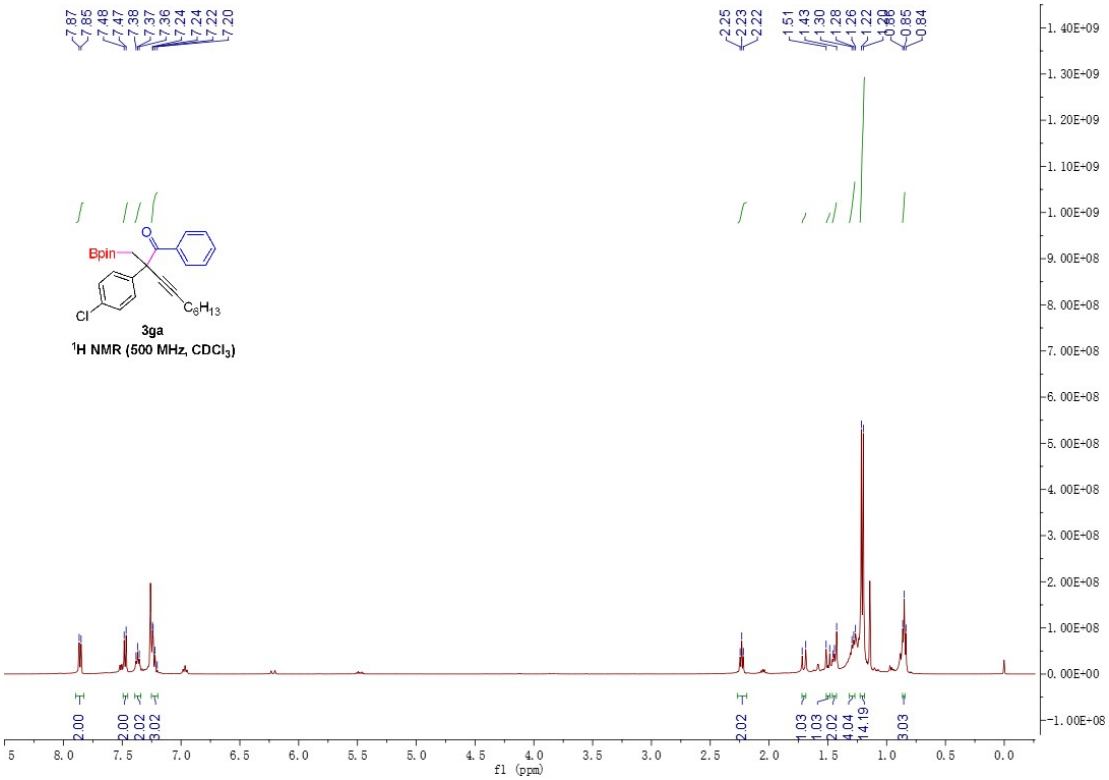


Figure S38. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 3ga

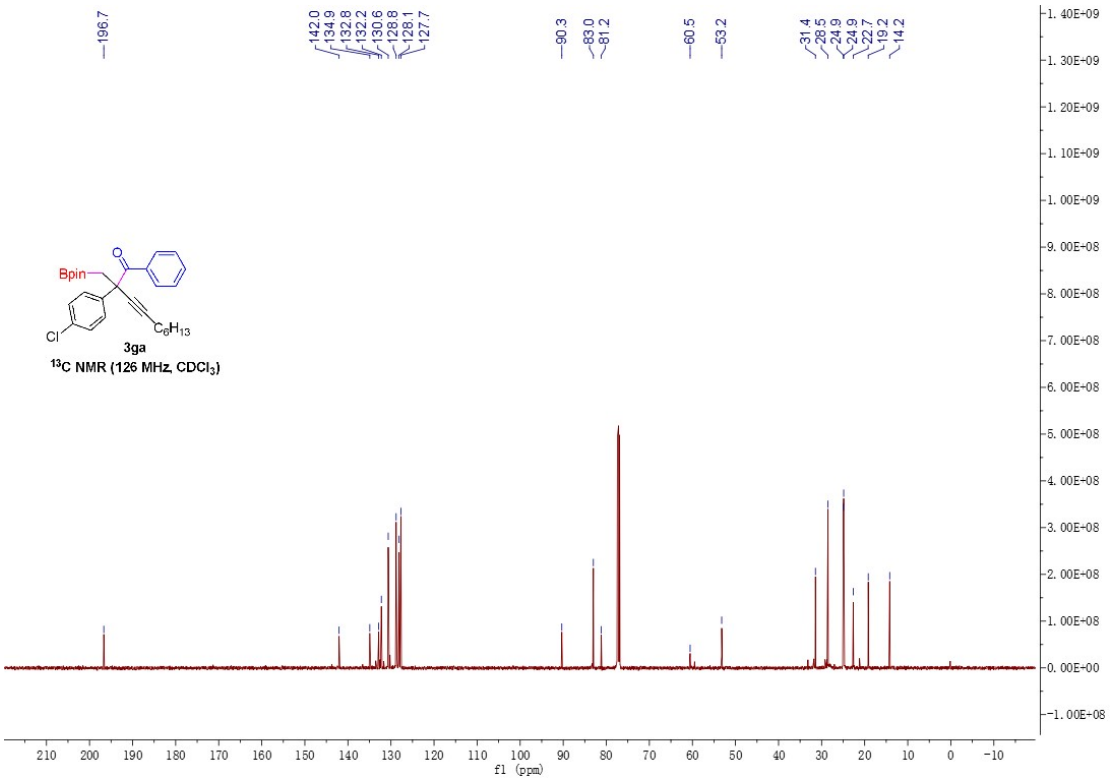


Figure S39. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of 3ga

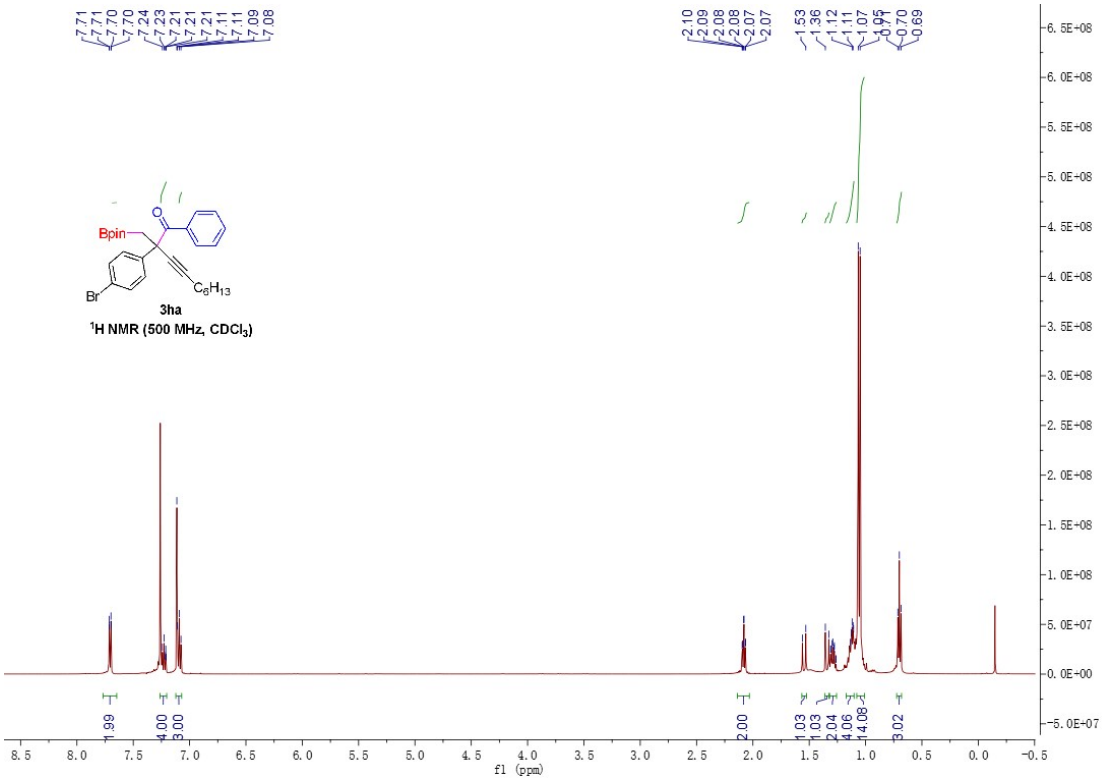


Figure S40. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 3ha

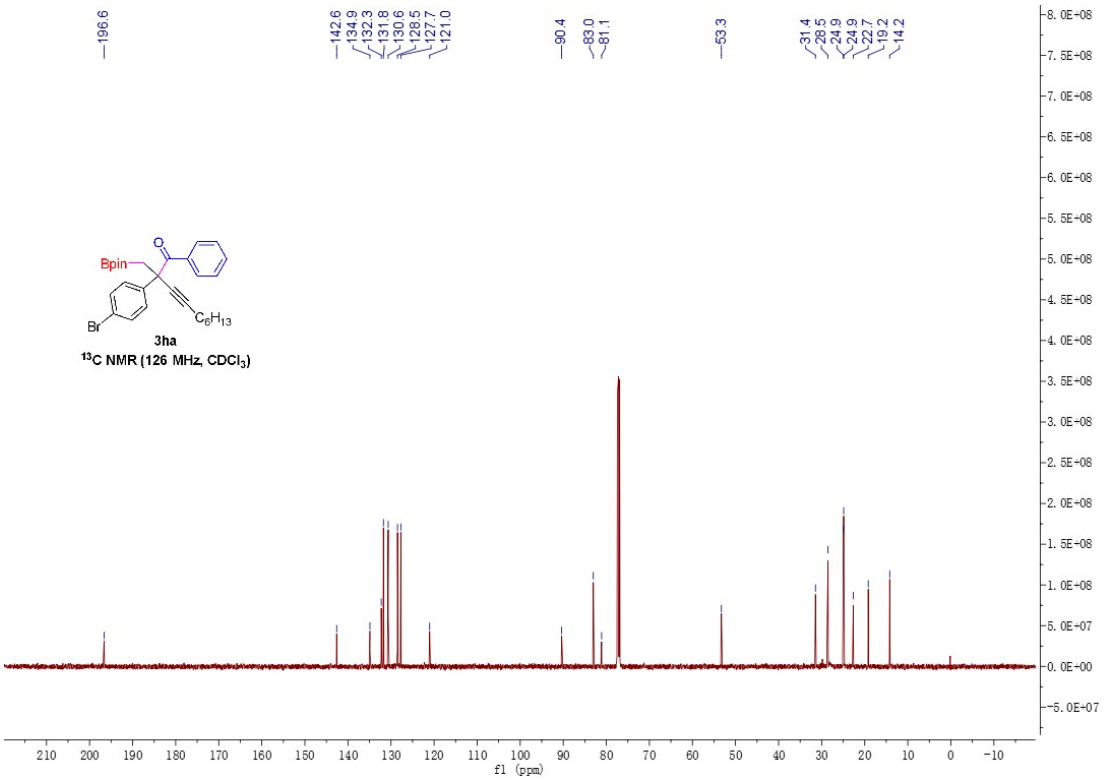


Figure S41. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of 3ha

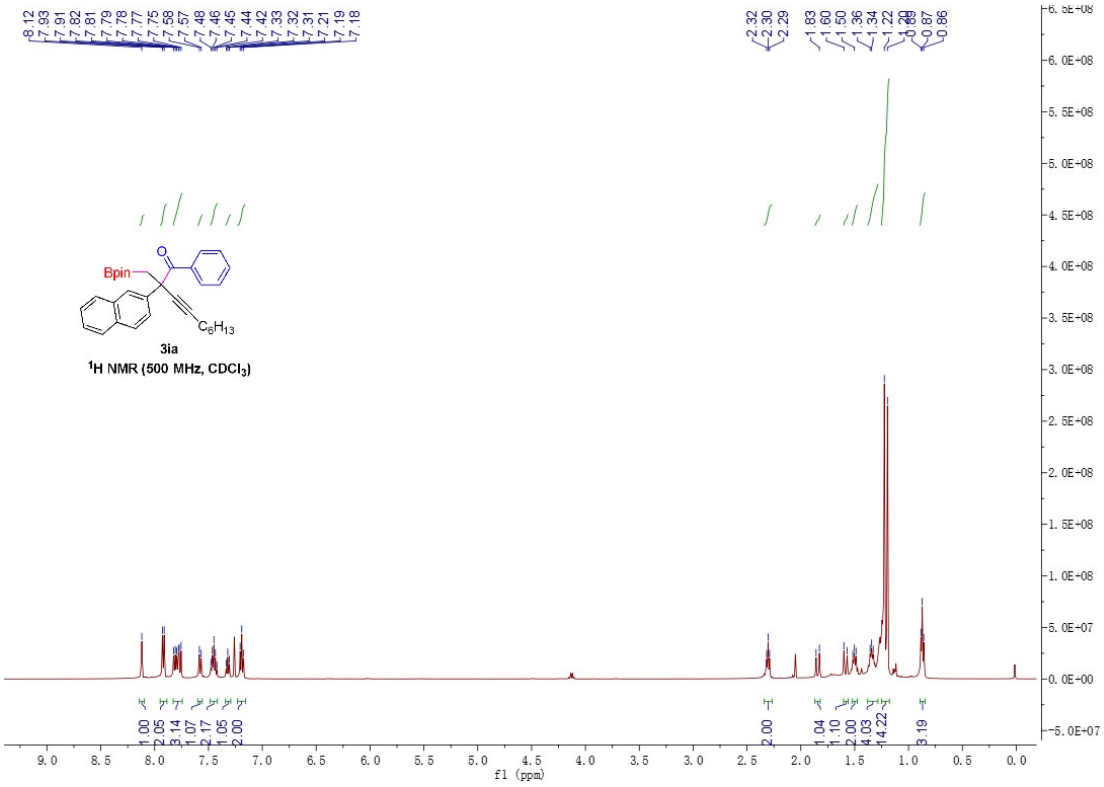


Figure S42. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 3ia

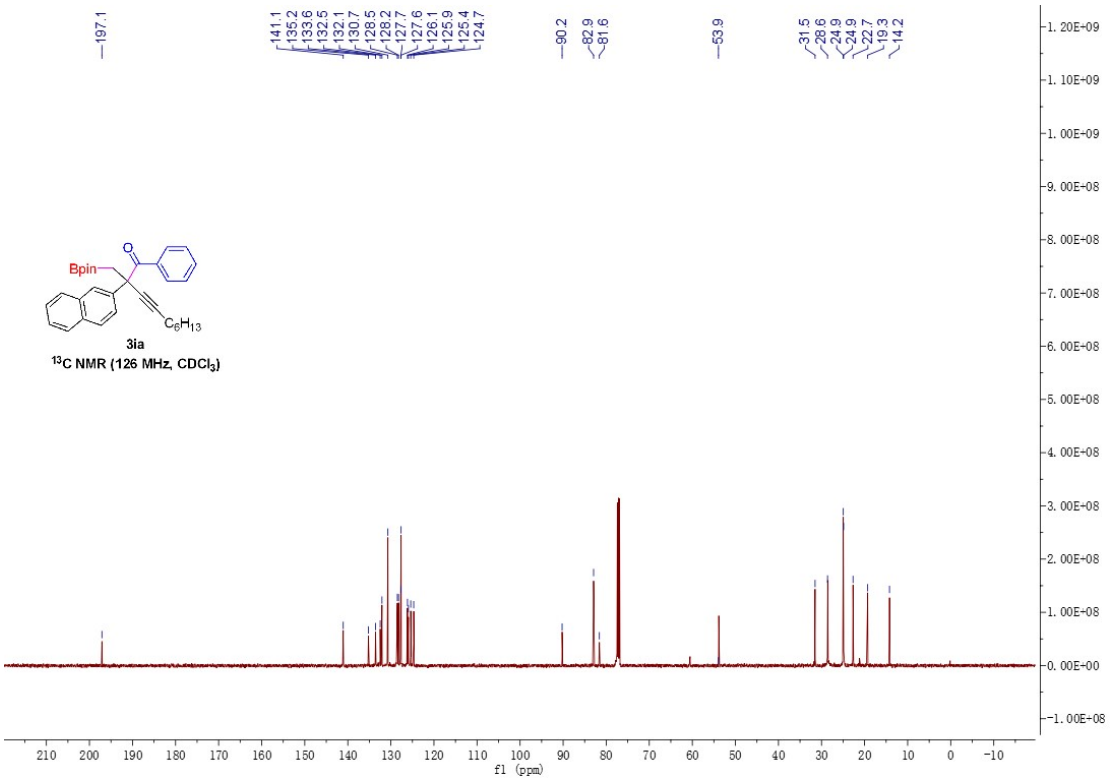


Figure S43. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of 3ia

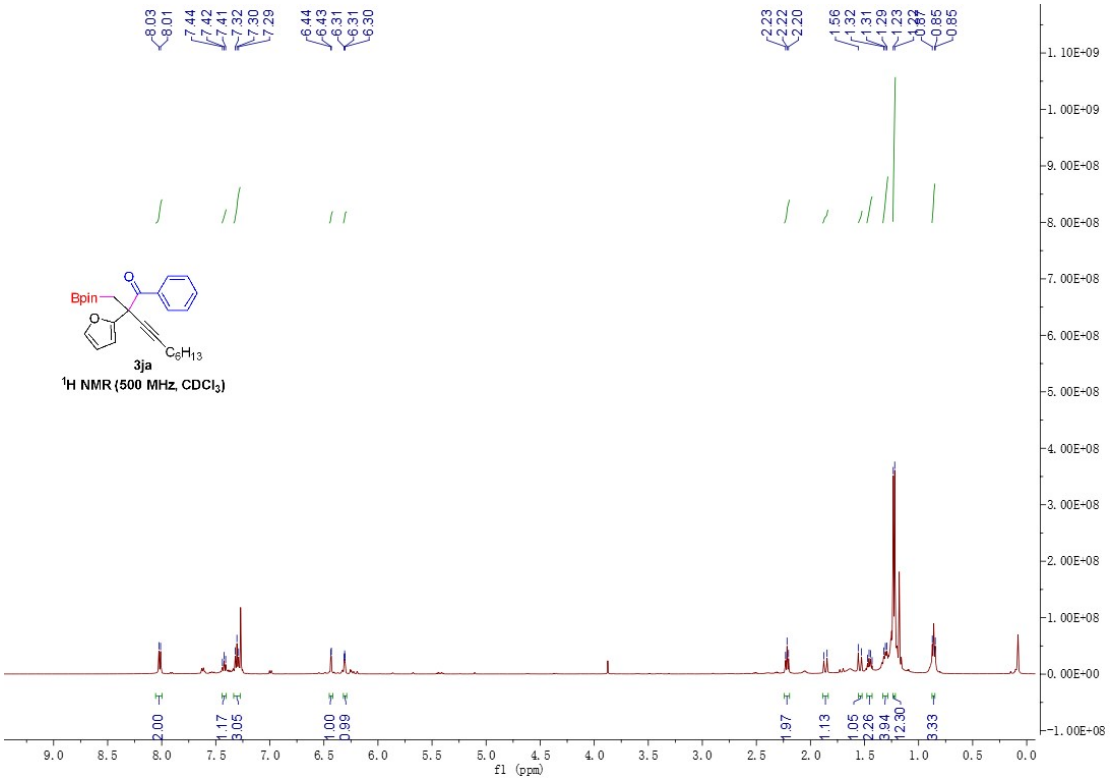


Figure S44. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 3ja

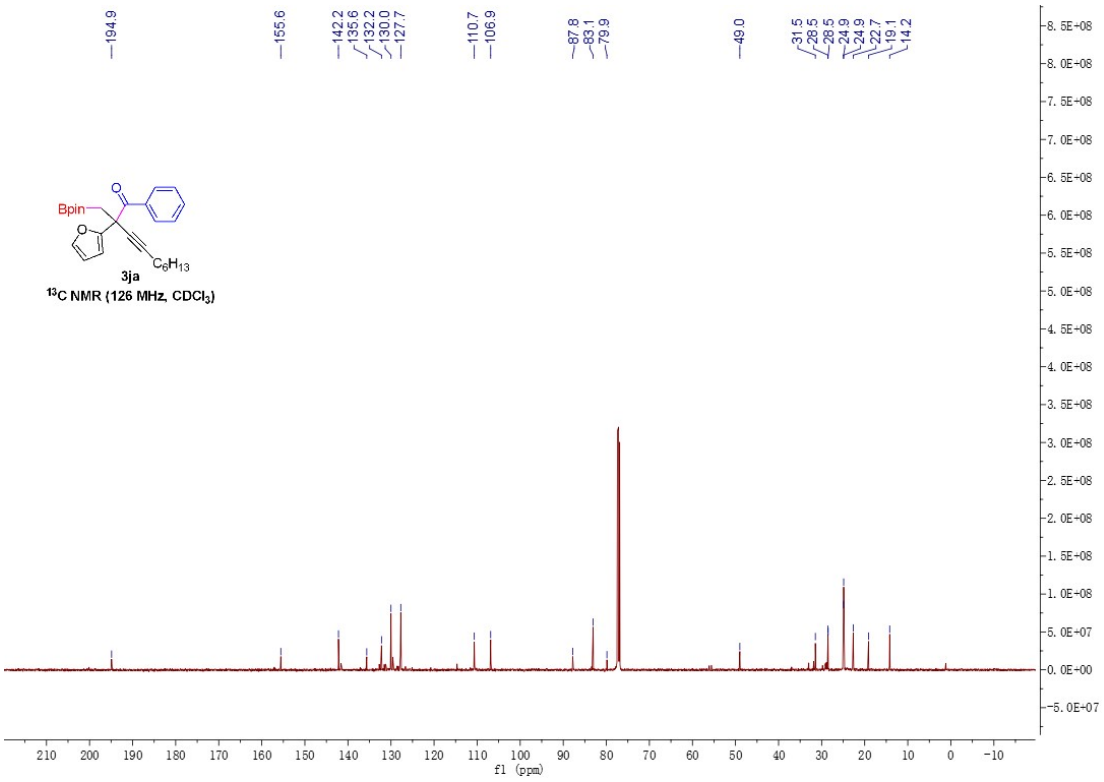


Figure S45. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of 3ja

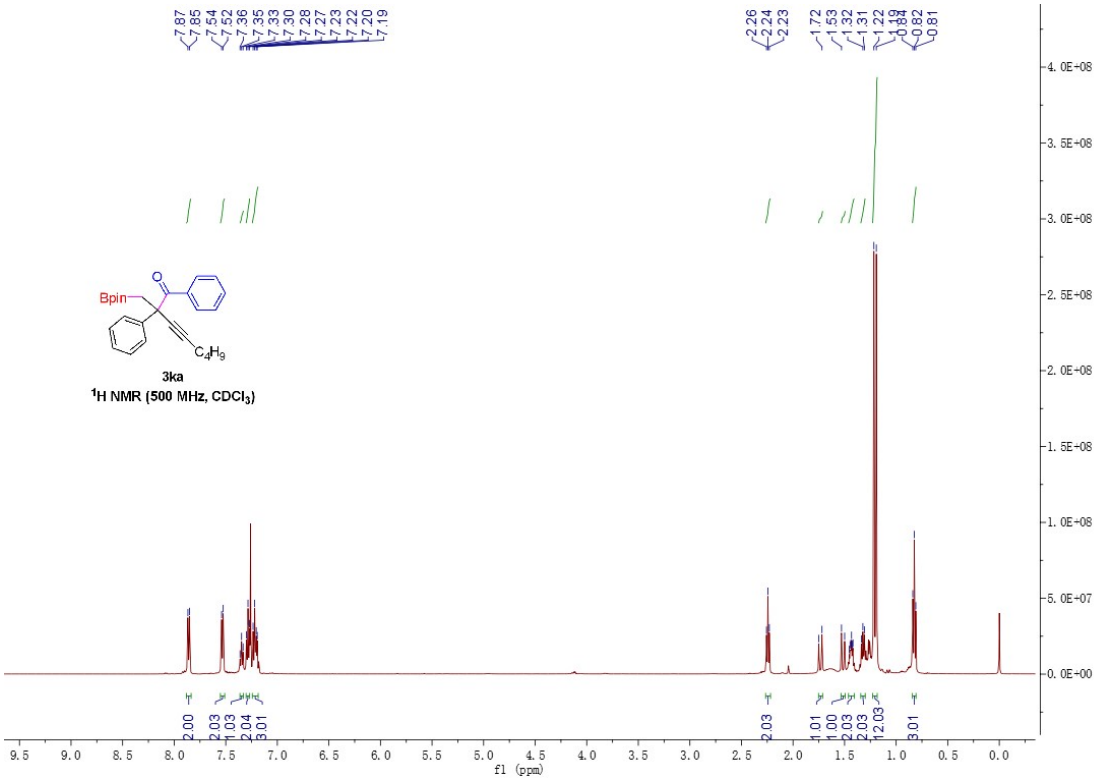


Figure S46. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 3ka

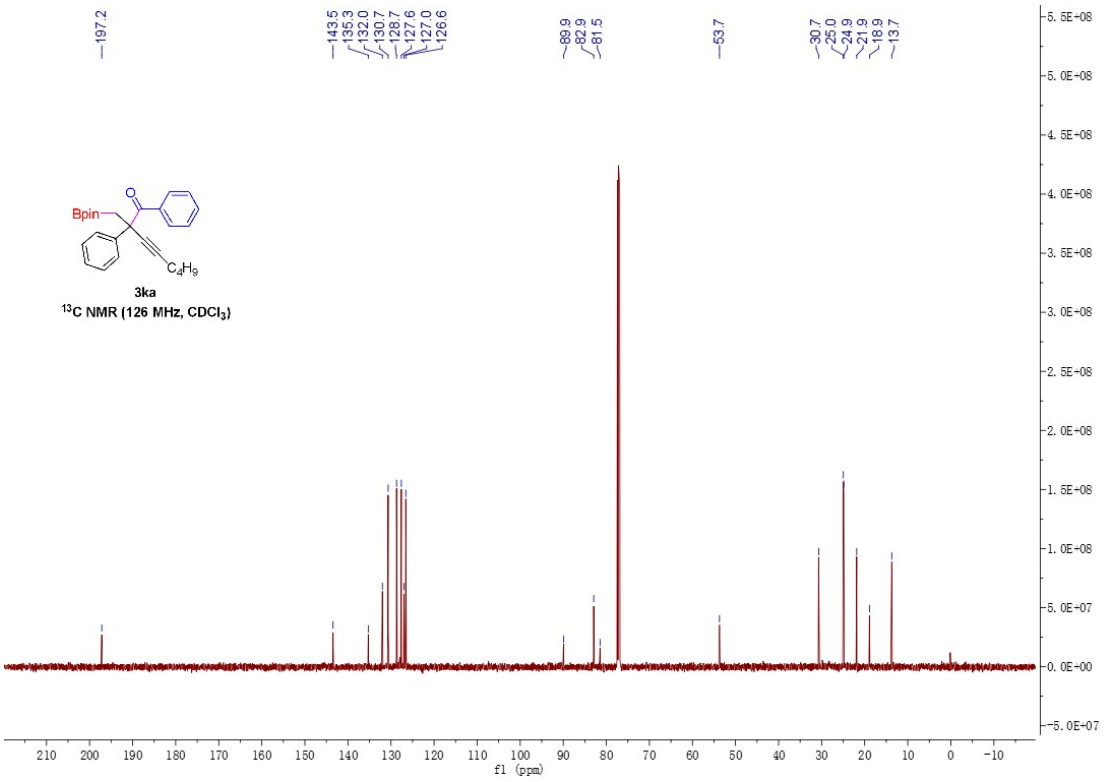


Figure S47. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of 3ka

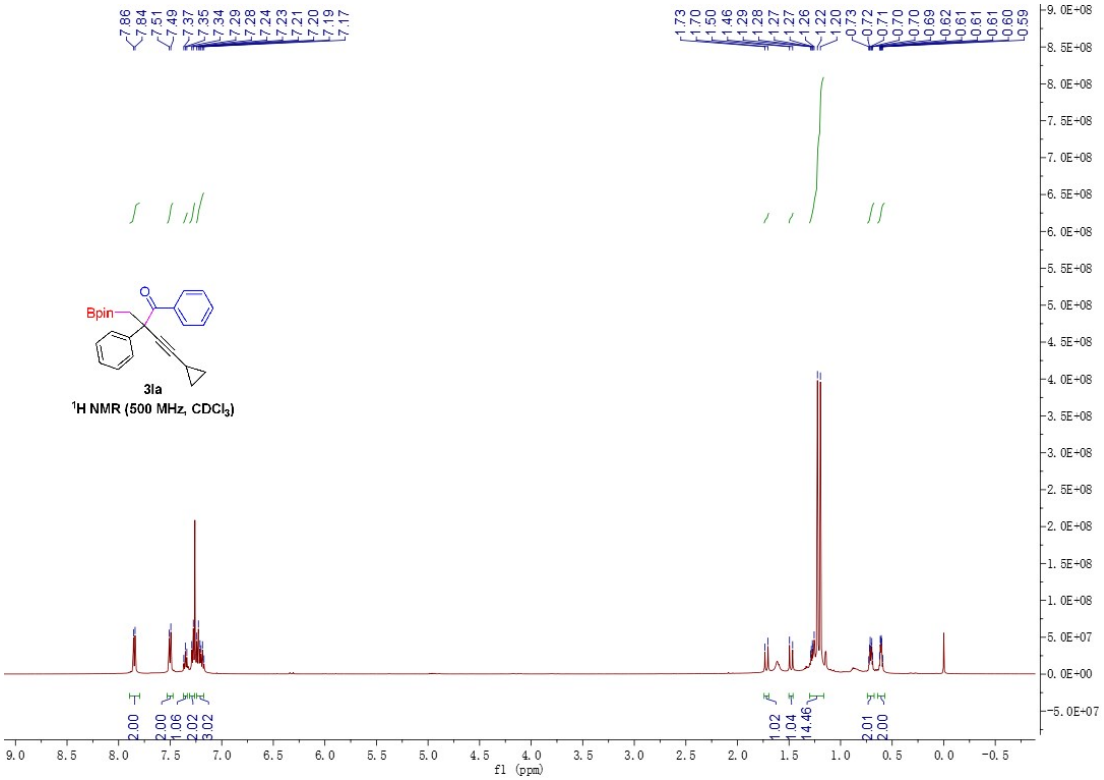


Figure S48. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 3la

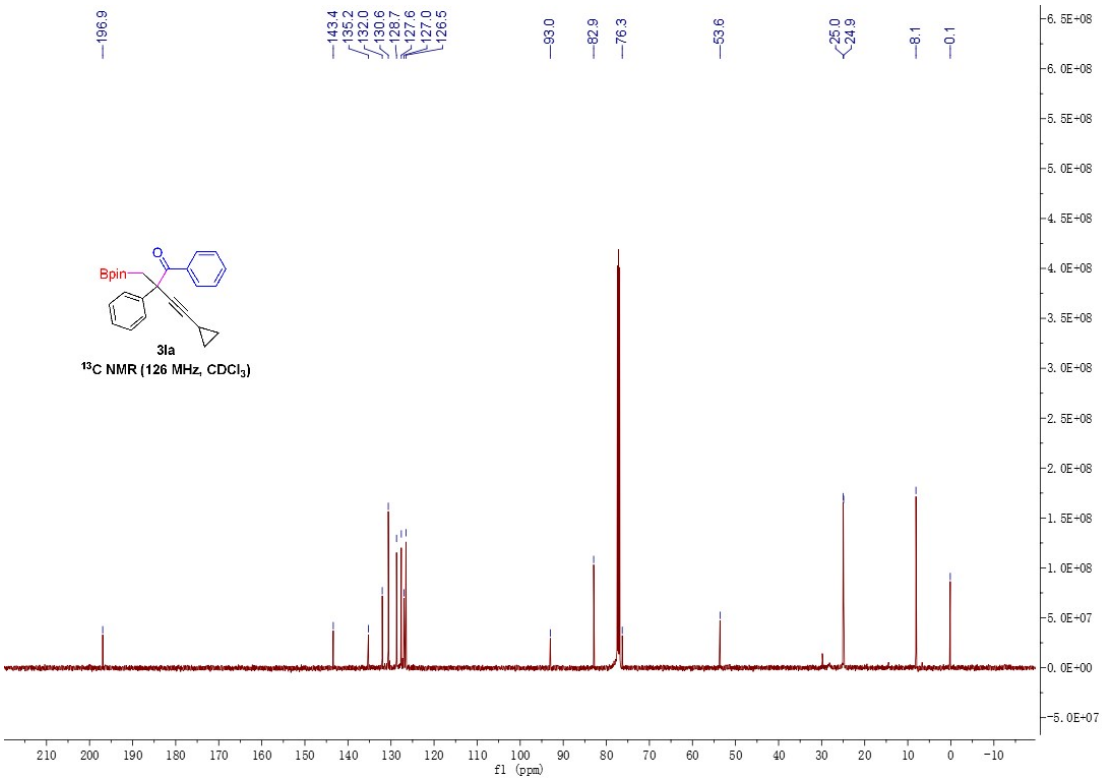


Figure S49. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of 3la

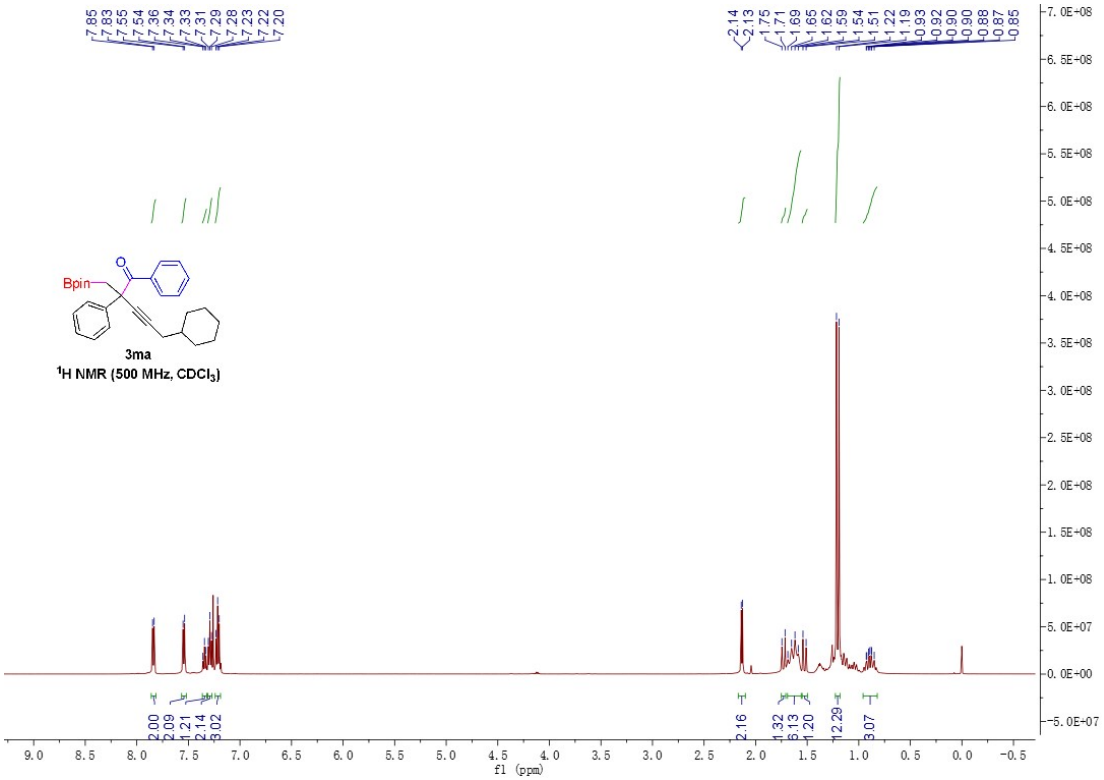


Figure S50. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 3ma

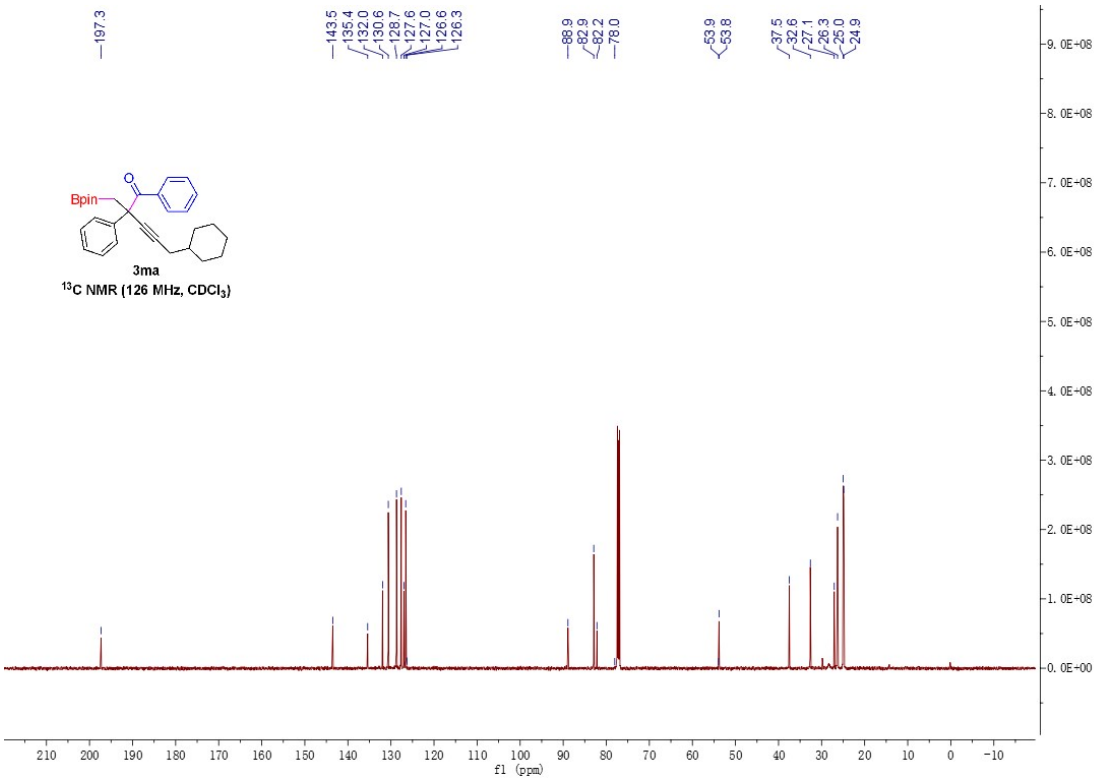


Figure S51. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of 3ma

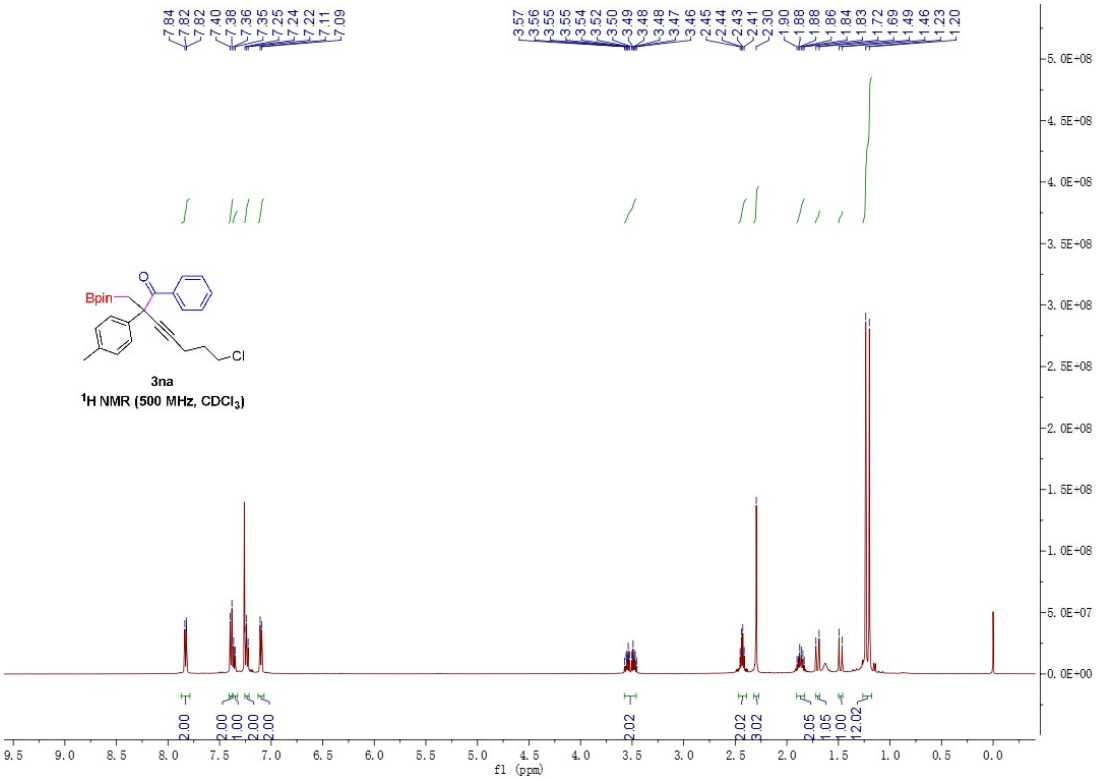


Figure S52. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 3na

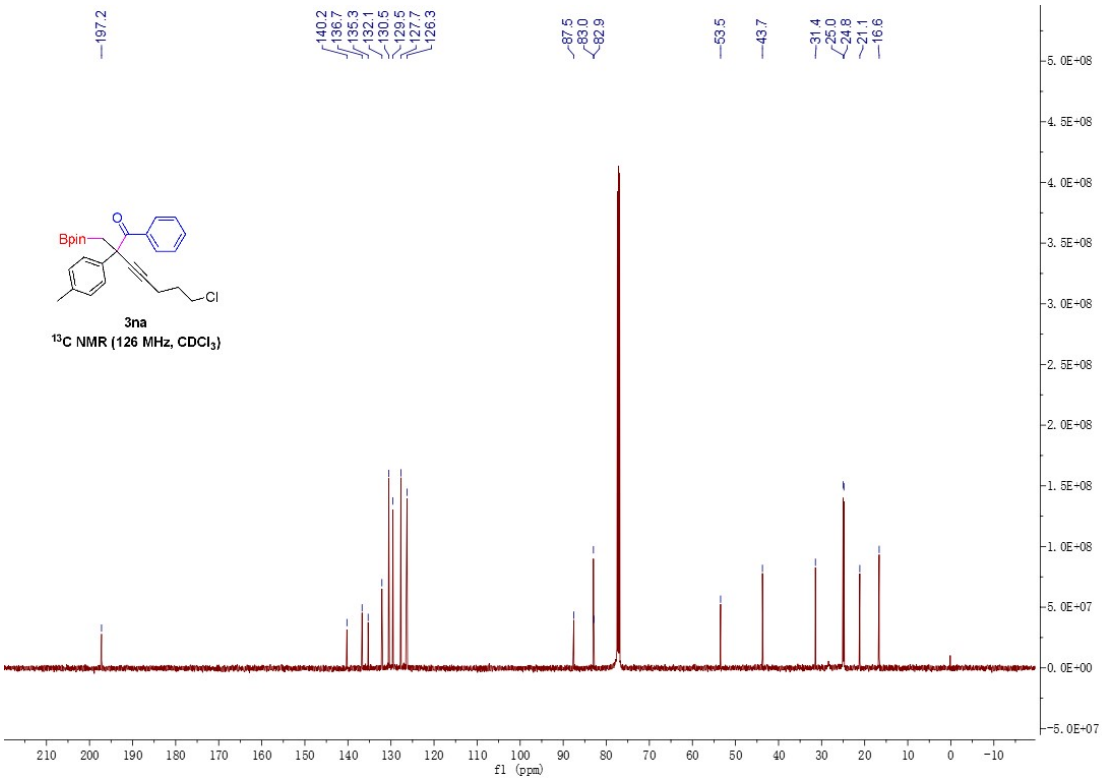


Figure S53. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of 3na

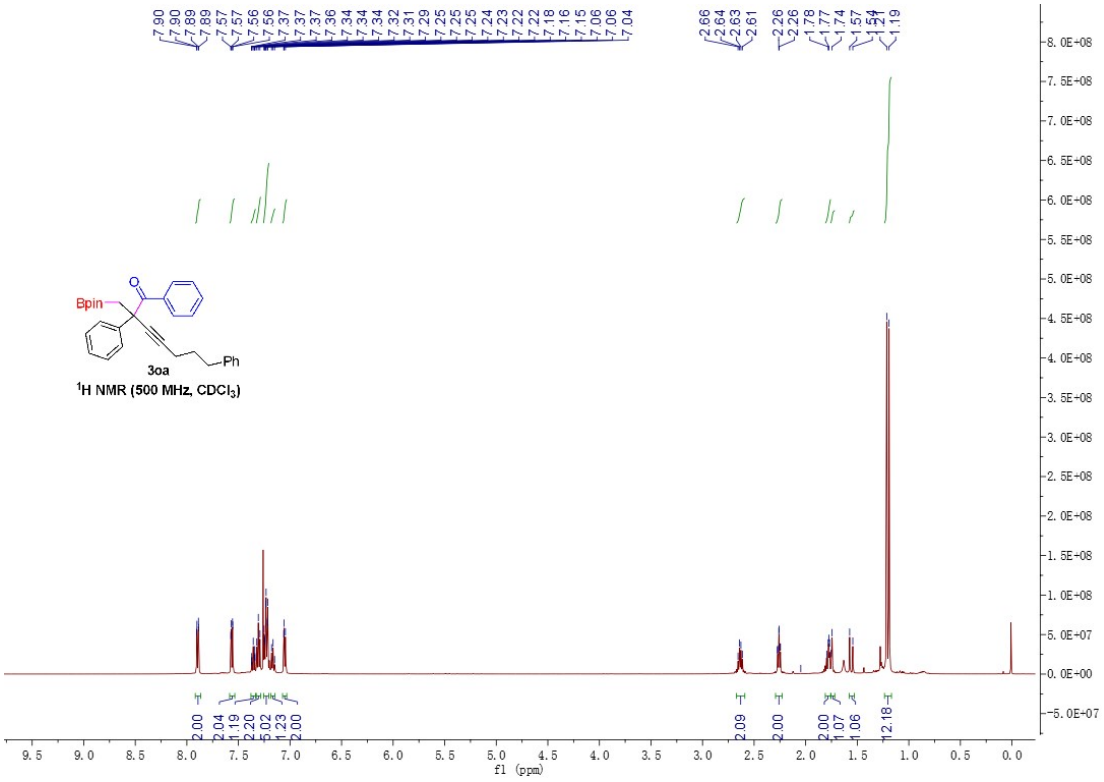


Figure S54. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 3oa

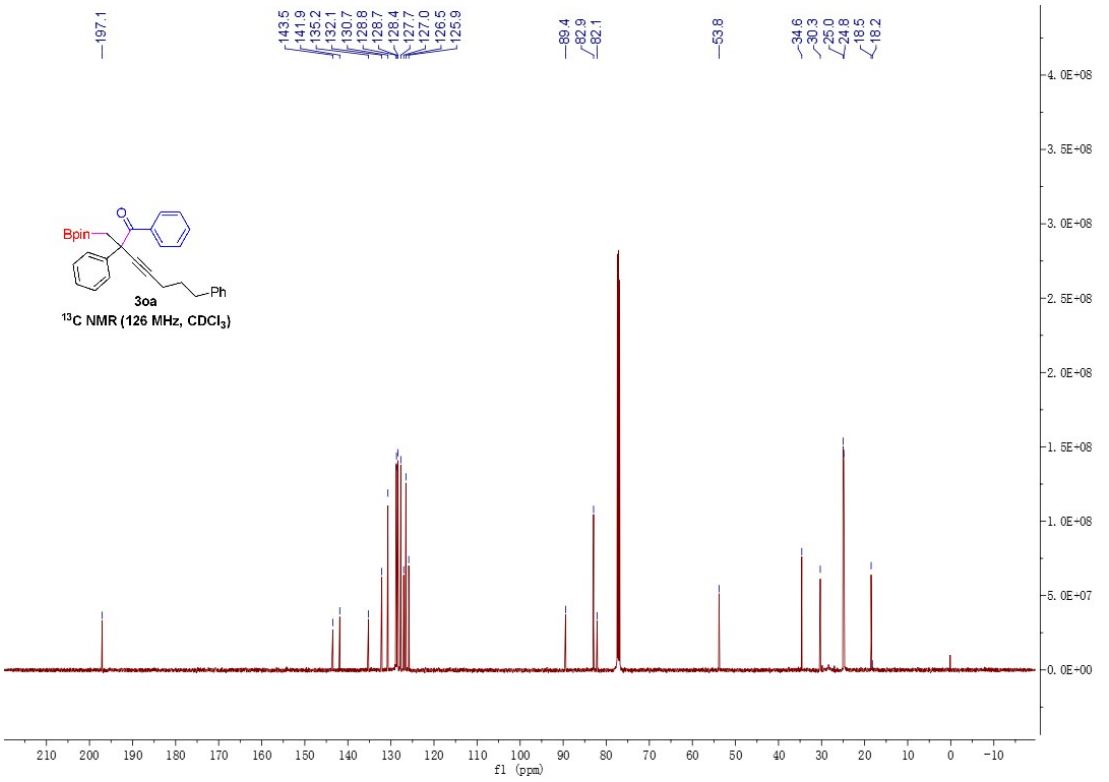


Figure S55. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of 3oa

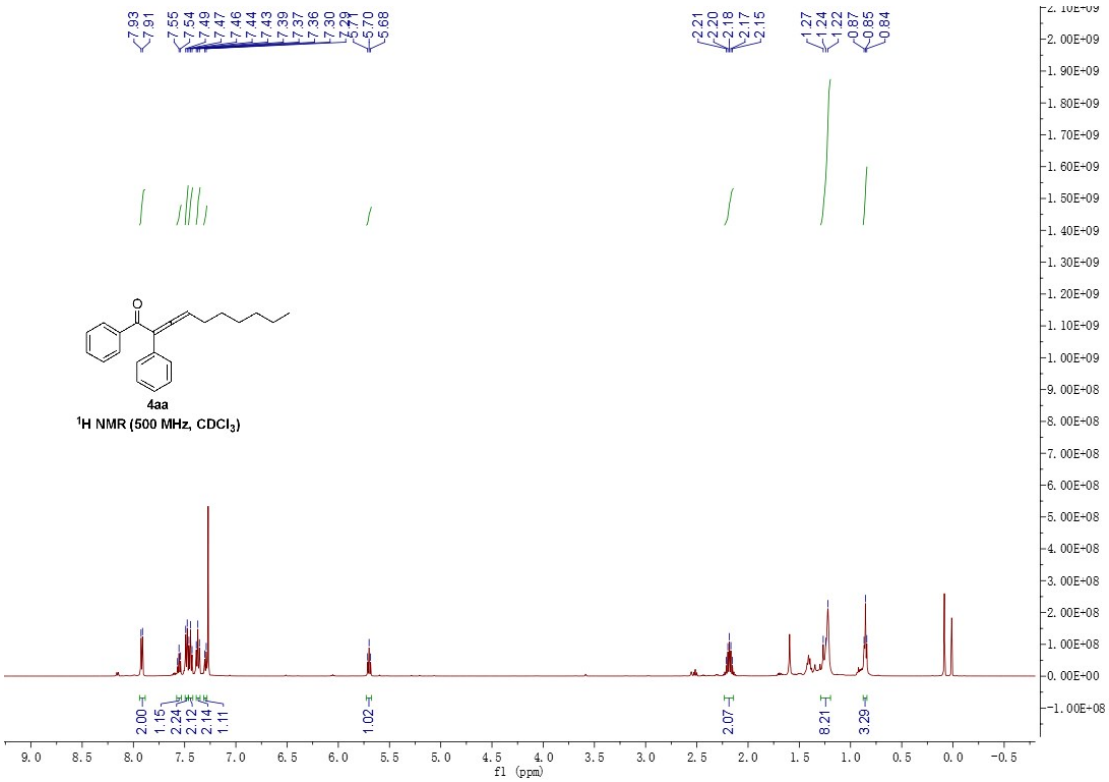


Figure S56. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 4aa

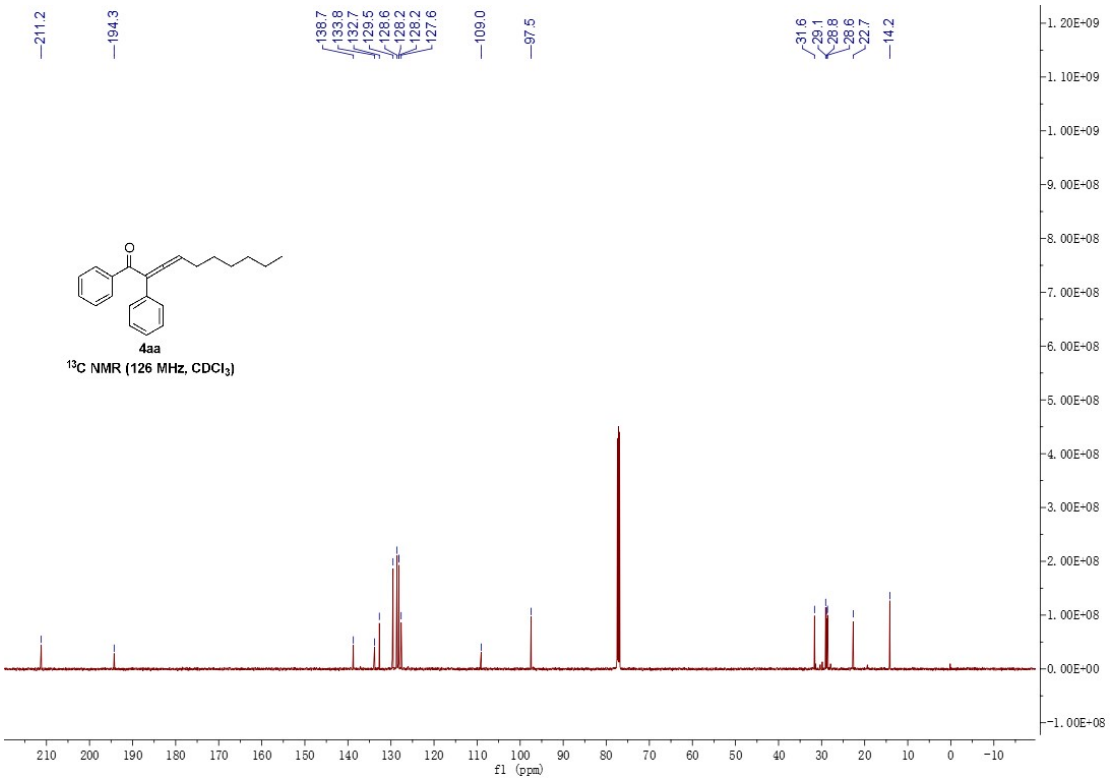


Figure S57. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of 4aa

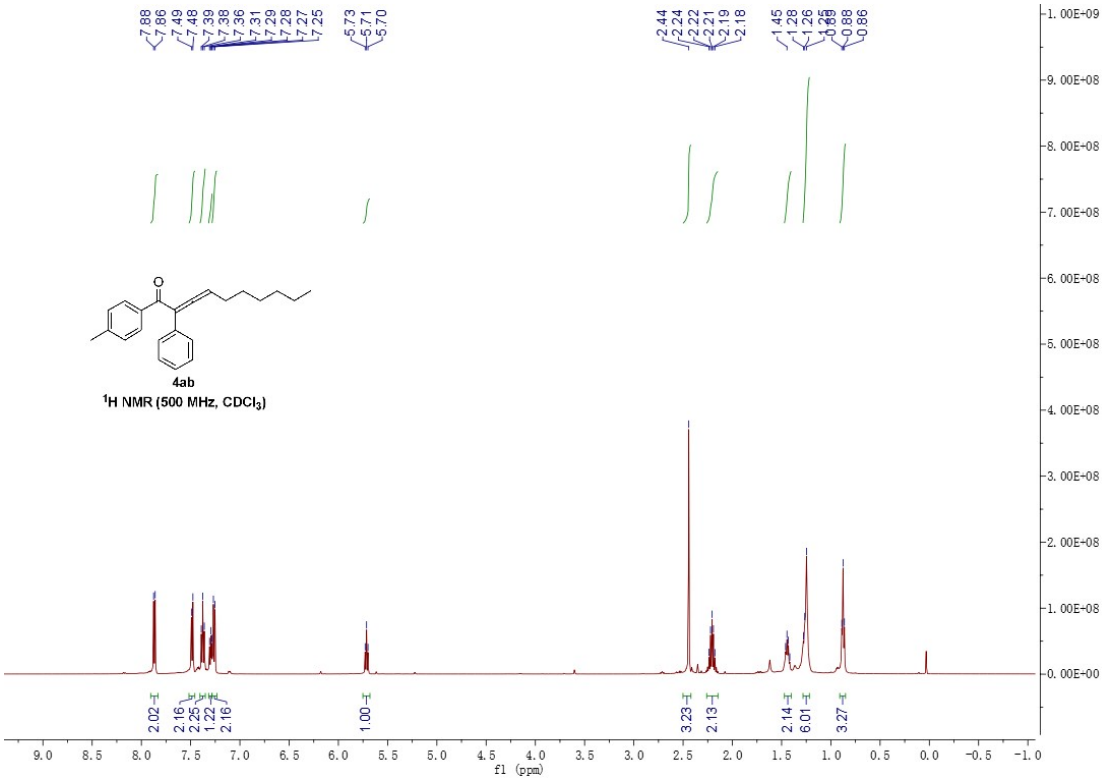


Figure S58. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 4ab

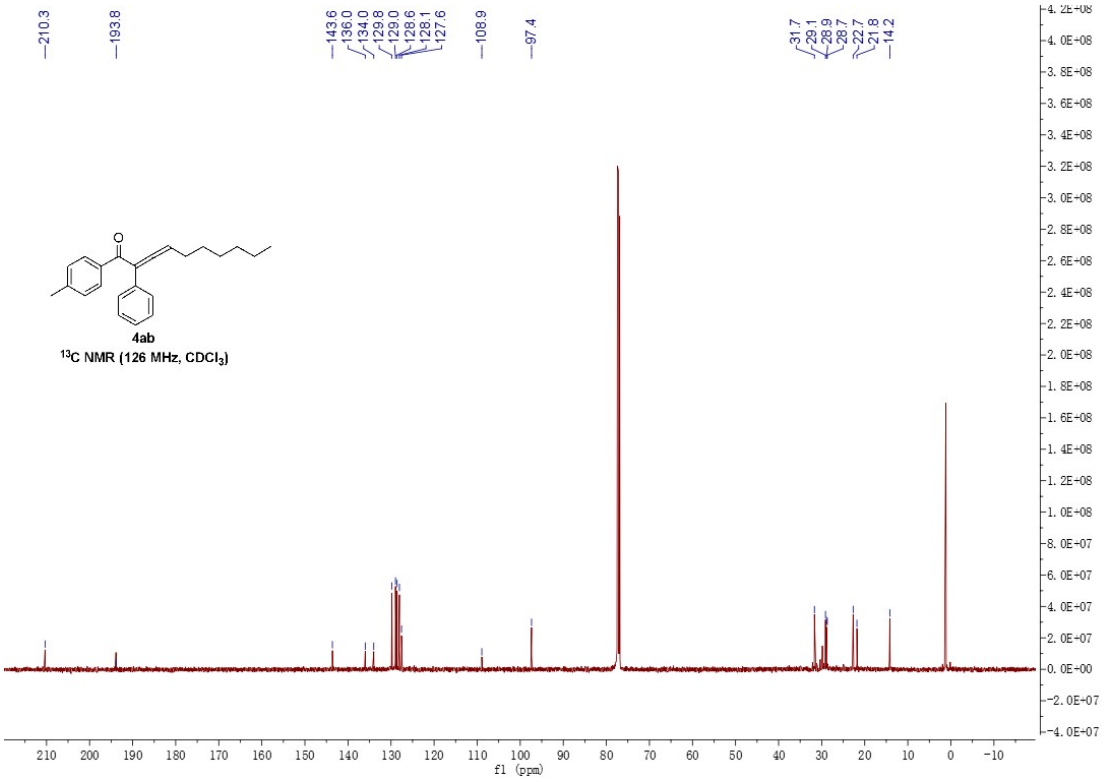


Figure S59. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of 4ab

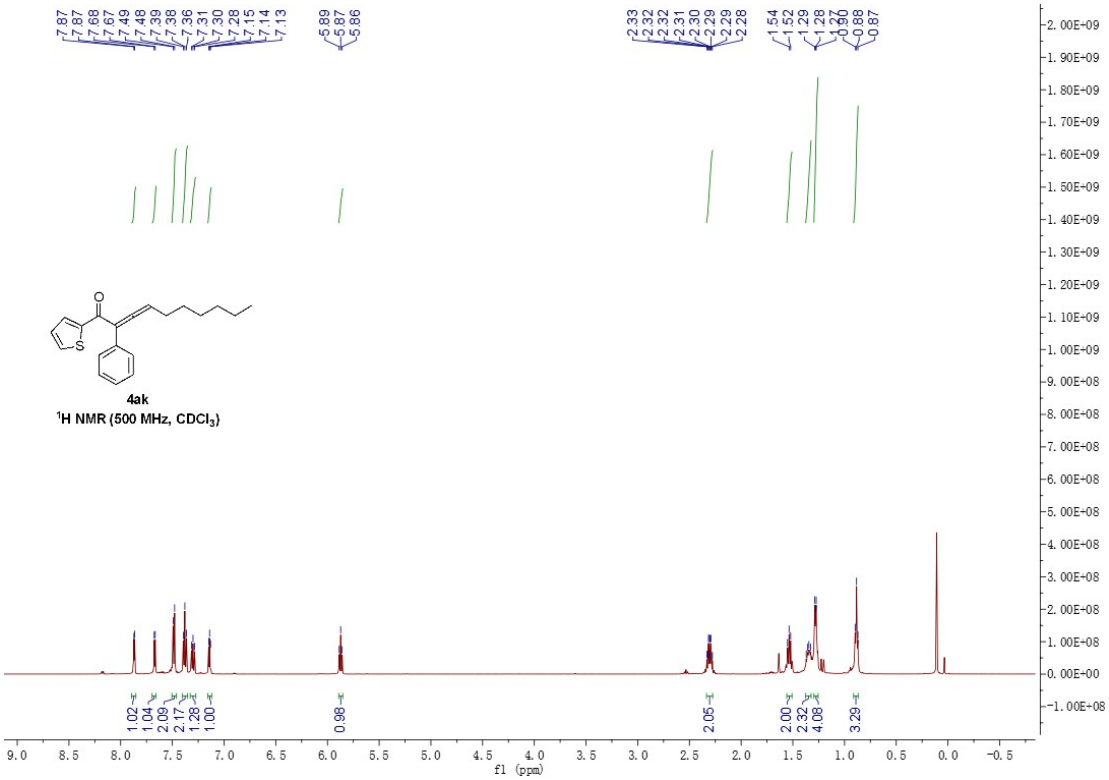


Figure S60. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 4ak

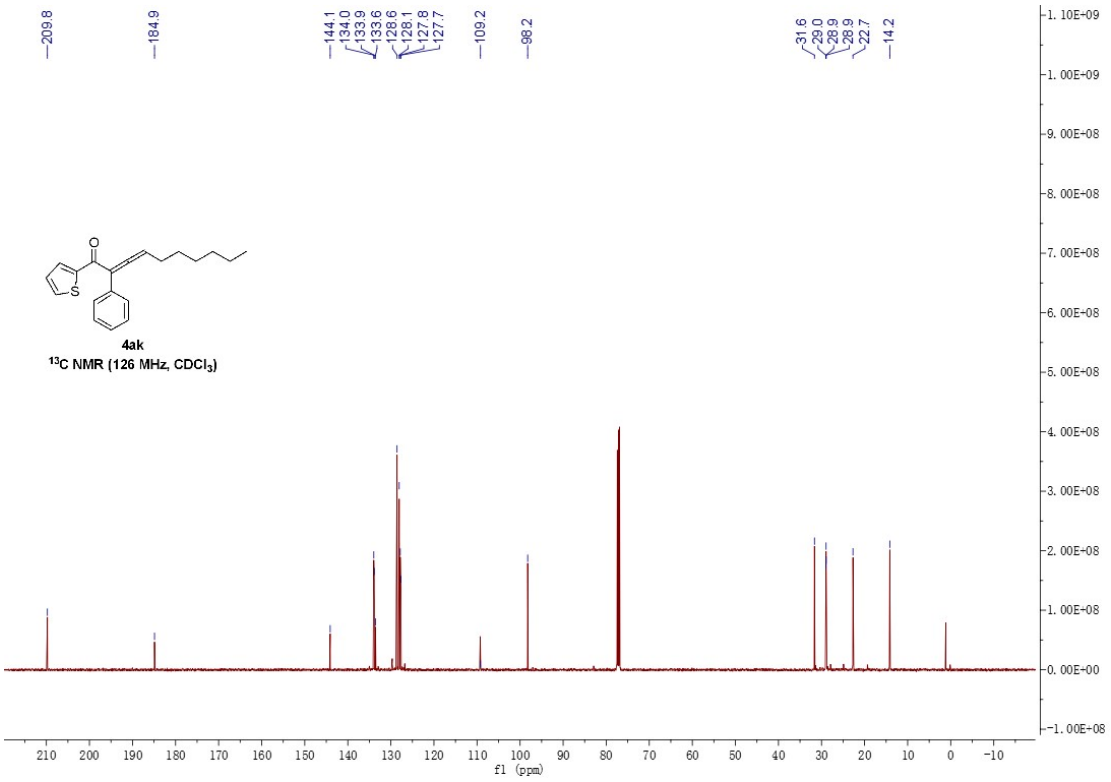


Figure S61. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of 4ak

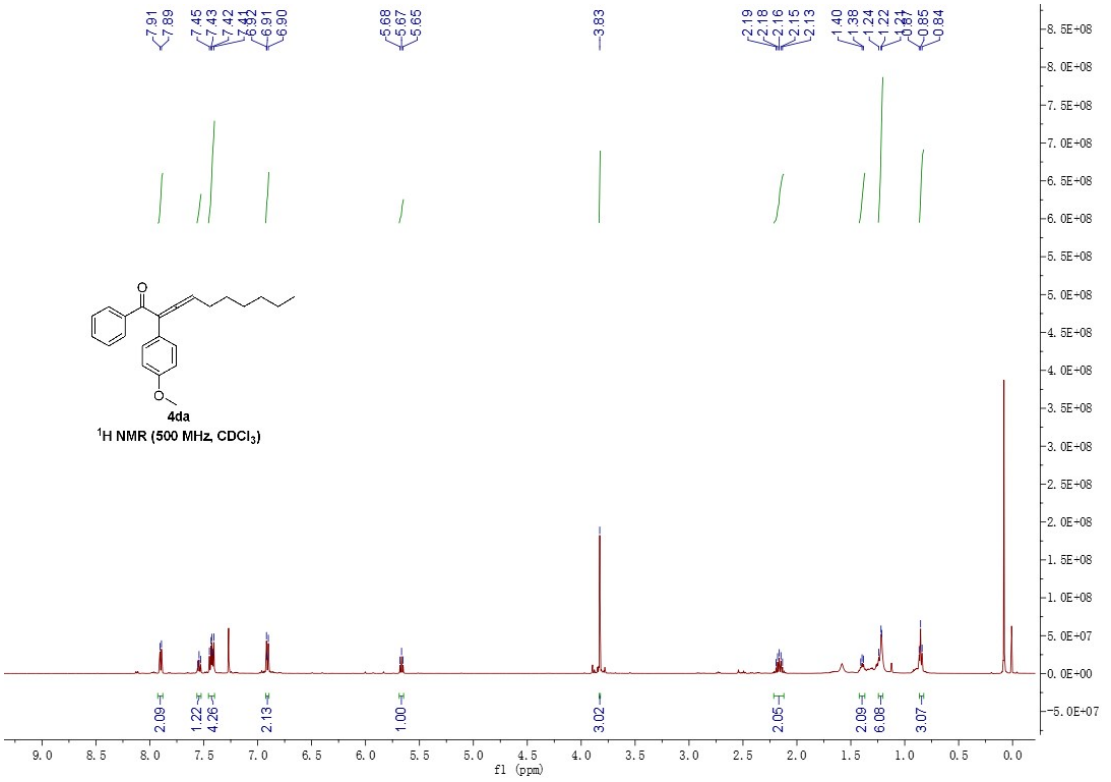


Figure S62. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 4da

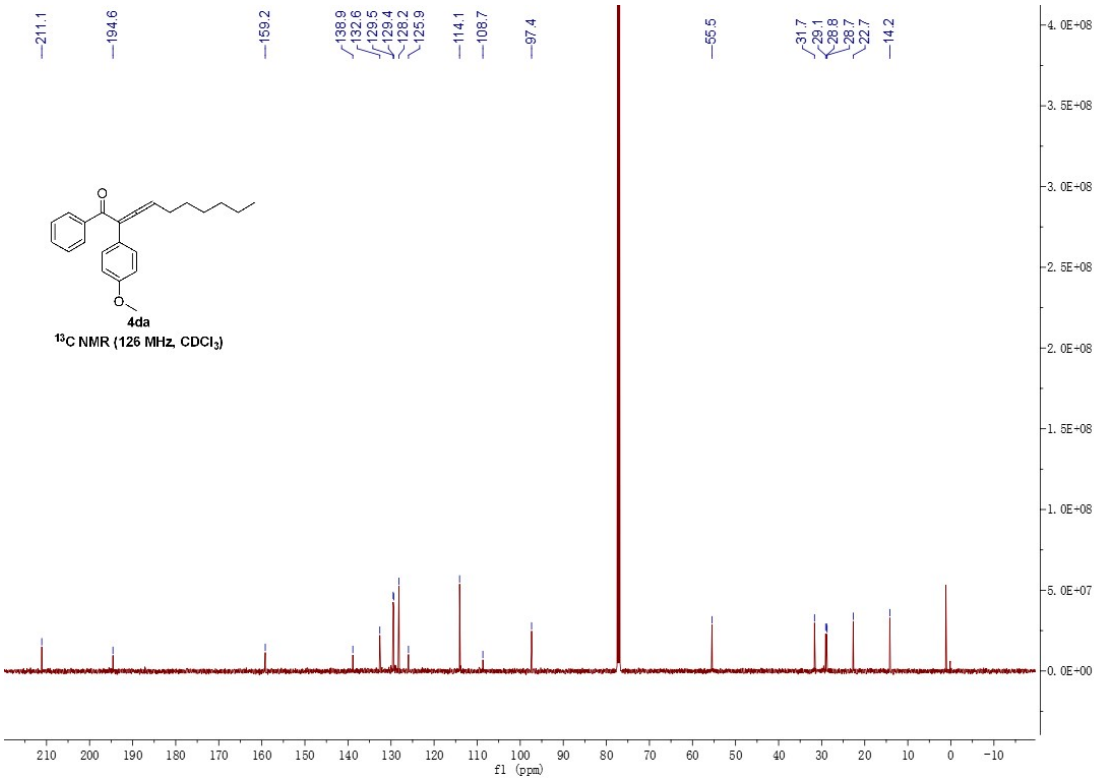


Figure S63. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of 4da

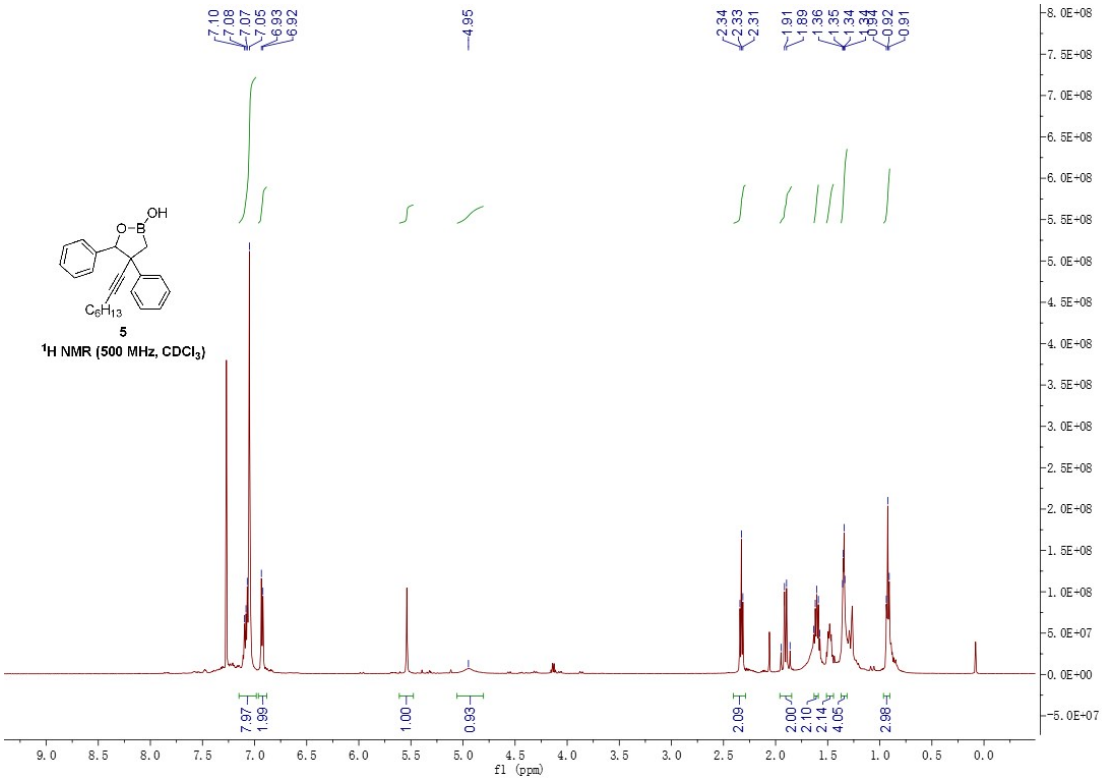


Figure S64. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 5

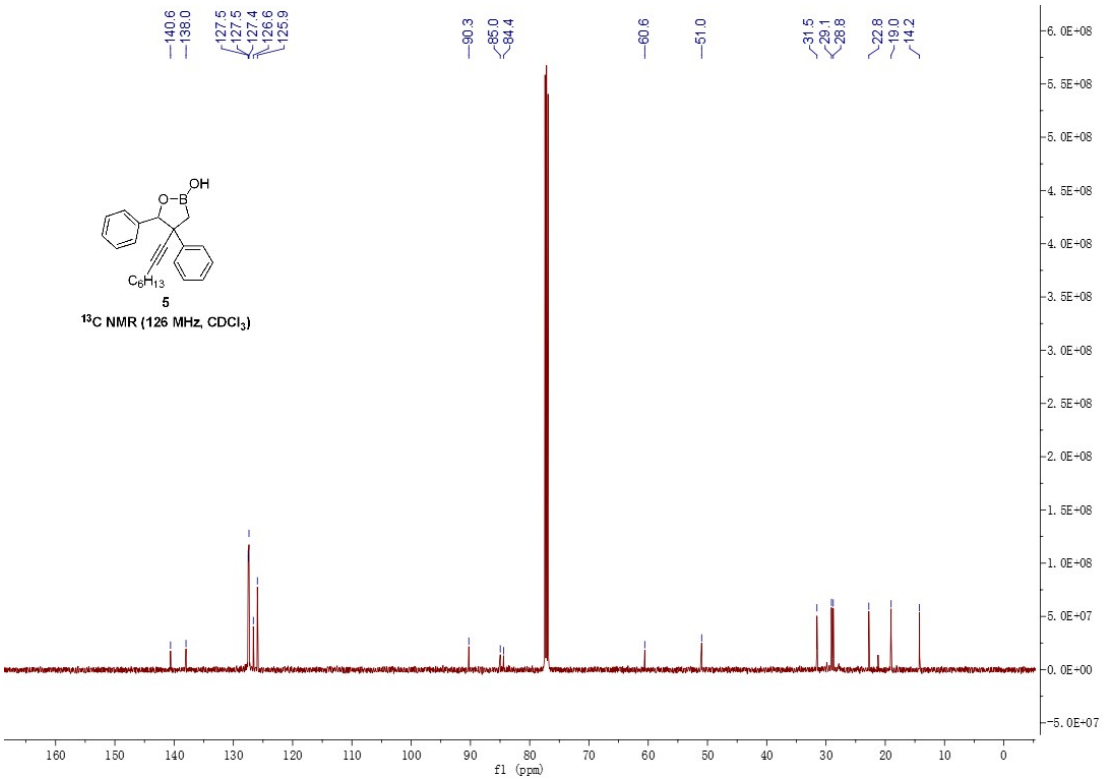


Figure S65. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of 5

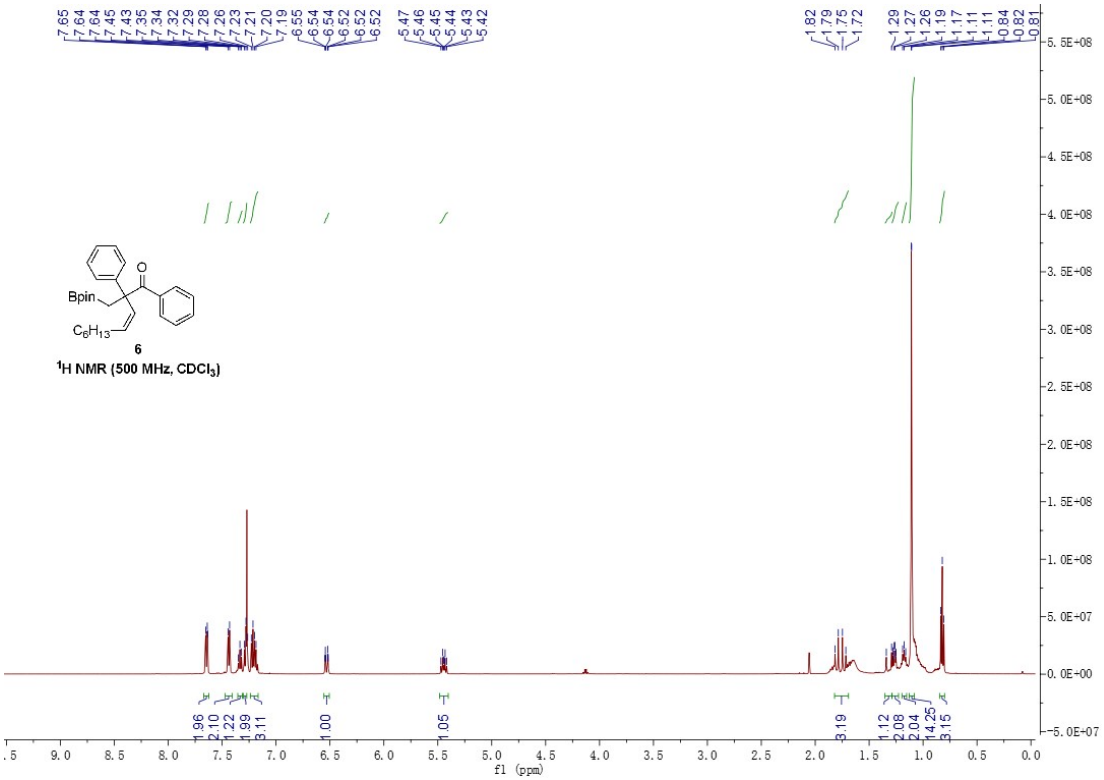


Figure S66. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 6

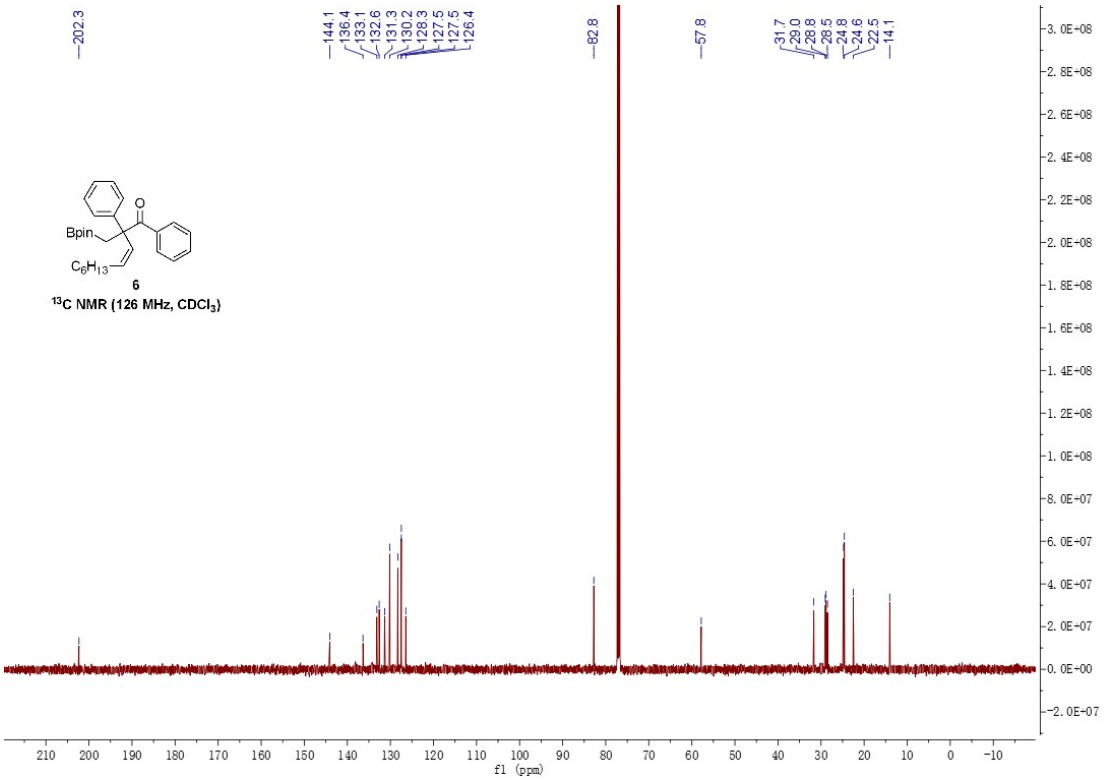


Figure S67. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of 6

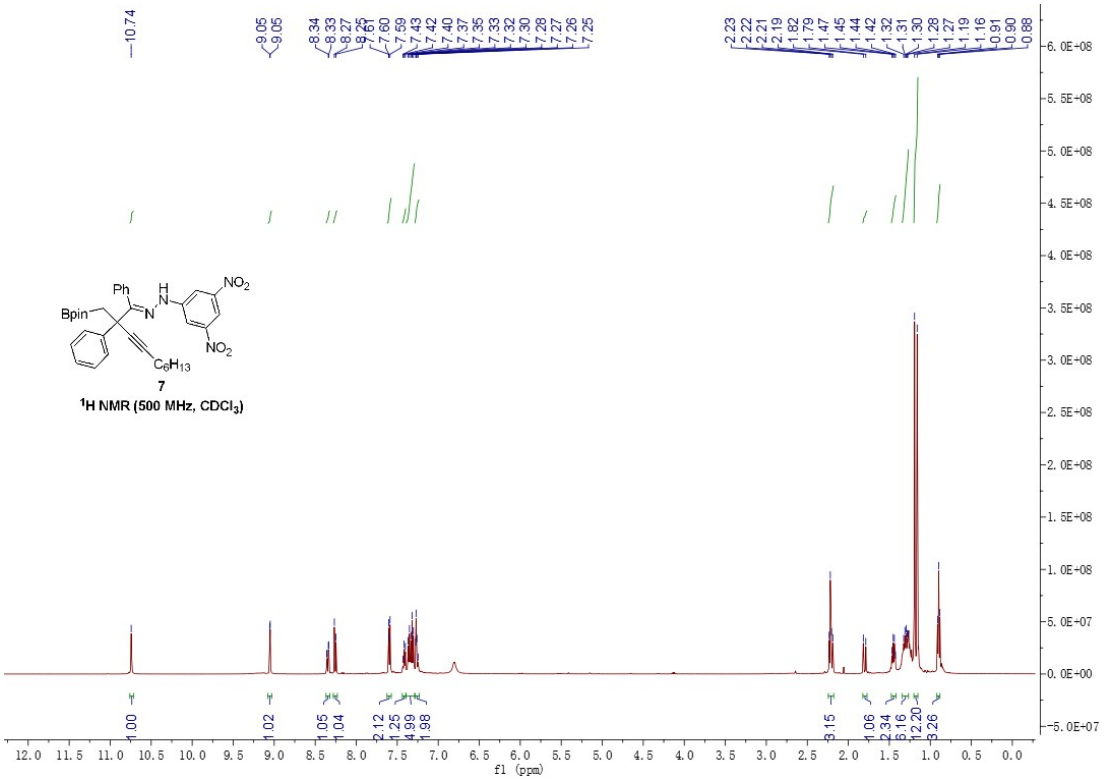


Figure S68. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 7

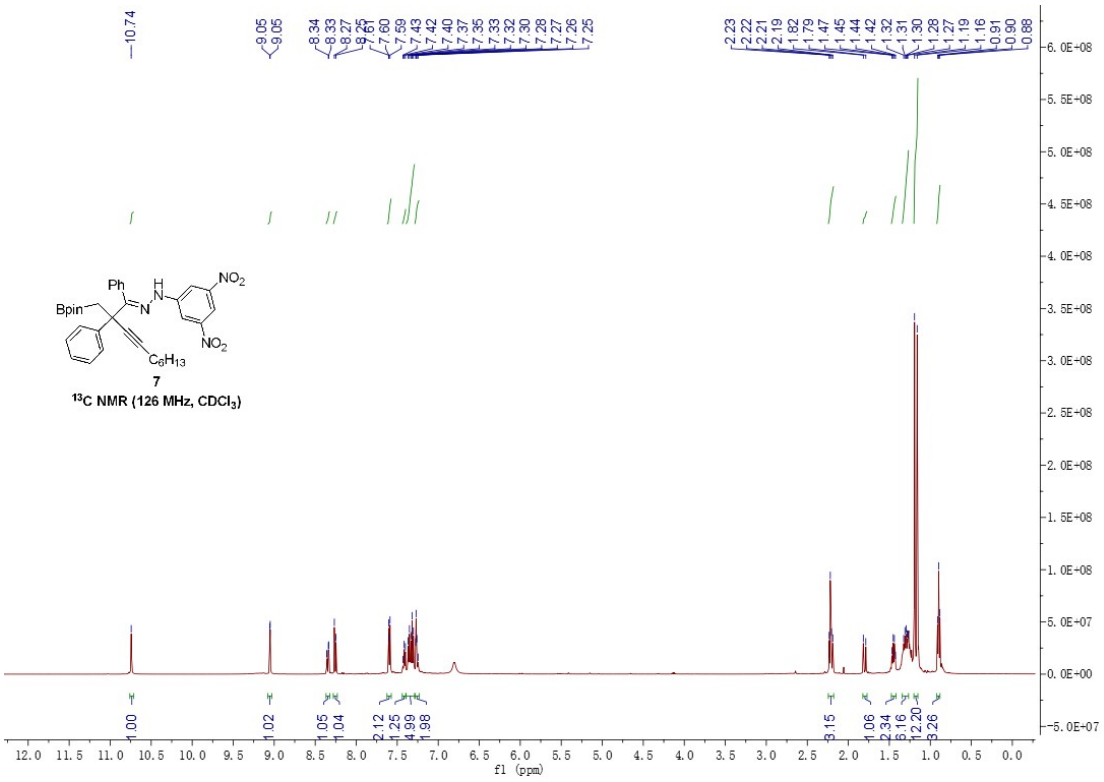


Figure S69. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of 7

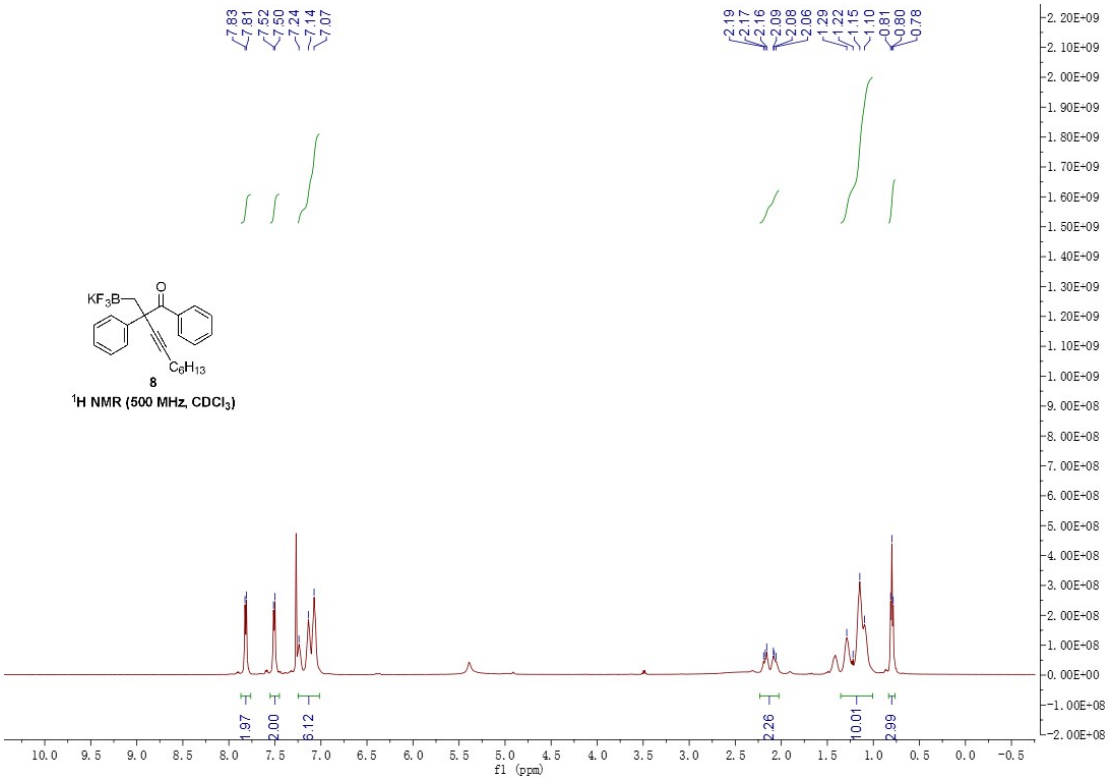


Figure S70. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 8

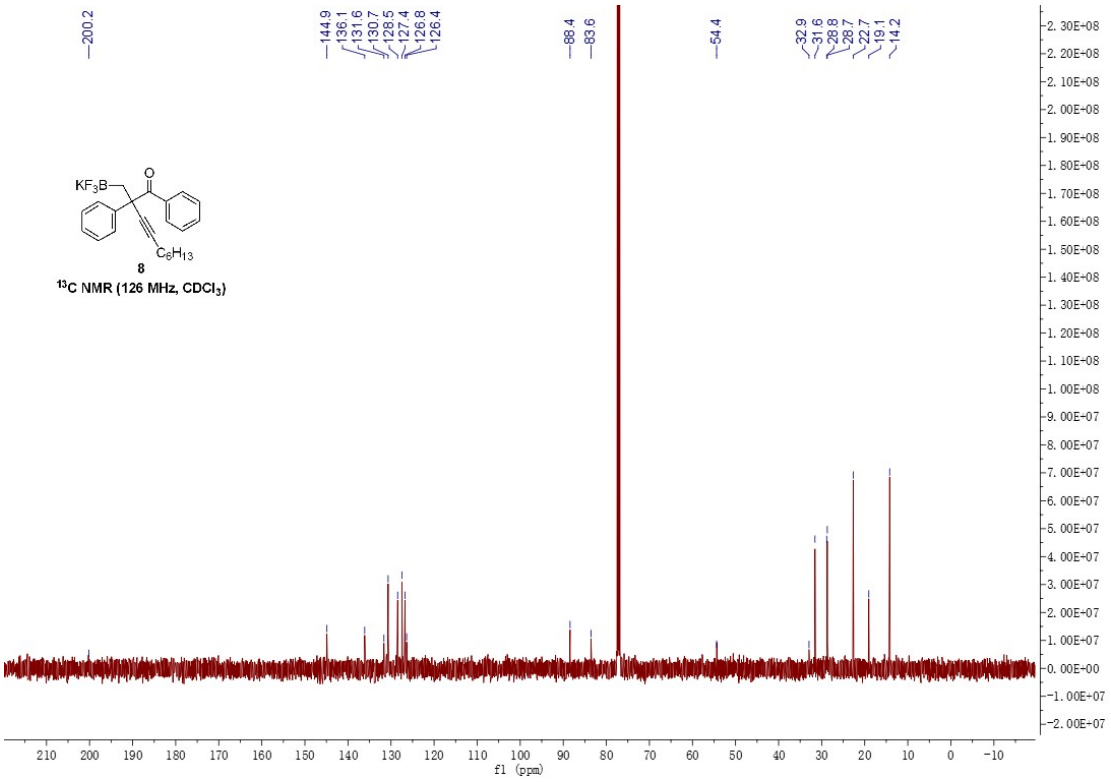


Figure S71. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of 8

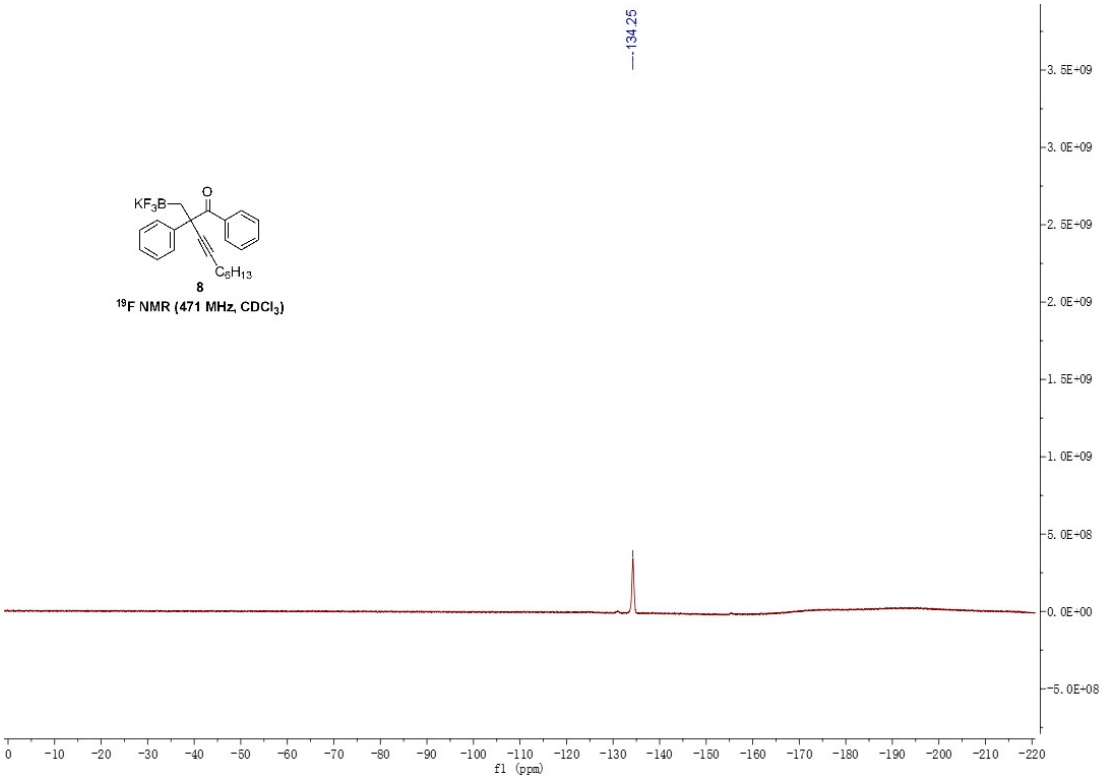


Figure S72. ^{19}F NMR (471 MHz, $CDCl_3$) spectrum of 8