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Photoredox catalytic phosphine-mediated deoxygenative alkynylation of carboxylic acids with alkynyl sulfones for alkynone synthesis

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Table of Contents

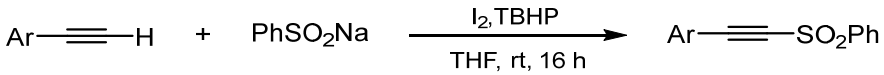
1. General Experimental Information.

Alkynyl sulfones **2** were synthesized following literature process.[1] All other chemicals and solvents used in the experiments were obtained from commercial sources and used directly without further purification. The organic solvents were treated following standard procedures before use. The NMR spectra were recorded on a Bruker AV 400 and 600 NMR spectrometer with $CDCl_3$ as solvent. The chemical shifts were reported as ppm with TMS or solvent residue peaks as standard (1 H NMR: TMS at 0.00 ppm; 13C NMR: CDCl3 at 77.0 ppm).

The setup of photochemical reaction is illustrated as in Figure S1. The 24 W blue LEDs (440–450 nm) employed in this work were bought from Wuhan Geao Chemical Technology Co. LTD The distance from the light source to the irradiation vessel is about 0.9 cm. The reaction vessels are 15 mL Schlenk glass tubes. The temperature is controlled by a fan.

Figure S1. Setup of the photochemical reaction.

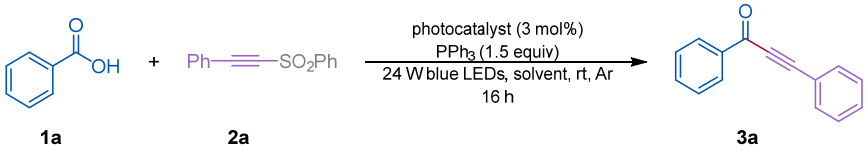
2. General Procedures for the Synthesis of Alkynyl Sulfones. [1]



A round bottom flask charged with arylacetylene (5.0 mmol), $PhSO_2Na$ (10.0 mmol). I_2 (2.5 mmol), and THF (20 mL) was added TBHP (70 wt% in water) dropwise. The resulting mixture was stirred at room temperature for 16 h. The reaction mixture was quenched by saturated $Na_2S_2O_3$ solution, diluted with water (20 mL), and extracted with EtOAc (3x20 mL). The organic layer was washed with brine, dried over anhydrous Na_2SO_4, and concentrated to dryness in vacuo. The residue was purified by column chromatography (eluting with PE / EtOAc = 50 / 1 to 30 / 1) to afford the corresponding product.

3. Reaction Optimization.

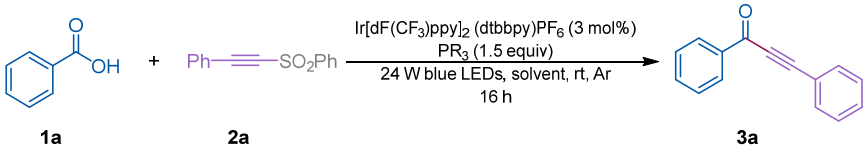
Table S1. Screening of optimal photocatalyst[a]



Entry	Photocatalyst (3 mol%)	Yield[b]
1	$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$	51%
2	None	N.R.
3	$4CzIPN$	19%
4	$Ir(ppy)_3$	N.R.
5	$Ru(bpy)_3(PF_6)_2$	N.R.
6	9-Mesityl-10-methylacridin-10-ium Perchlorate	N.R.

[a]Reaction conditions: 1a (0.3 mmol 1.5 equiv), 2a (0.2 mmol), photocatalyst (0.006 mmol, 3 mol%), PPh_3 (0.3 mmol, 1.5 equiv), DCE (4.0 mL), rt, under Ar, 16 h. [b]Isolated yield. N.R. = No reaction occurred.

Table S2. Screening of optimal phosphine[a]

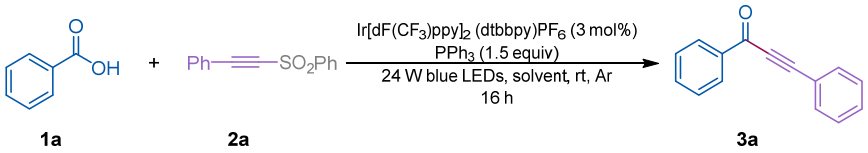


Entry	phosphine	Yield[b]

1	PPh_3	51%
2	None	N.R.
3	(pF-Ph)$_3$P	38%
4	(Ph)$_2$POEt	N.R.
5	(p-OMe-Ph)$_2$PPh	44%

[a]Reaction conditions: 1a (0.3 mmol 1.5 equiv), 2a (0.2 mmol), Ir[dF(CF_3)ppy]$_2$ (dtbbpy)PF_6 (0.006 mmol, 3 mol%), PR_3 (0.3 mmol, 1.5 equiv), DCE (4.0 mL), rt, under Ar, 16 h. [b]Isolated yield. N.R. = No reaction occurred.

Table S3. Screening of optimal solvent[a]

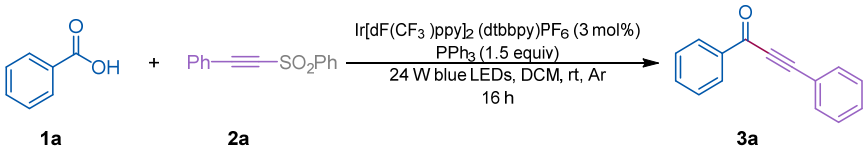


1a 2a 3a

Entry	Solvent	Yield[b]
1	DCE	51%
2	THF	Trace
3	DCM	55%
4	Acetone	35 %
5	$CHCl_3$	37%.
6	1.4-dioxane	Trace

[a]Reaction conditions: 1a (0.3 mmol 1.5 equiv), 2a (0.2 mmol), Ir[dF(CF_3)ppy]$_2$ (dtbbpy)PF_6 (0.006 mmol, 3 mol%), PPh_3 (0.3 mmol, 1.5 equiv), solvent (4.0 mL), rt, under Ar, 16 h. [b]Isolated yield. N.R. = No reaction occurred.

Table S4. Screening of optimal amount of **2a**[a]



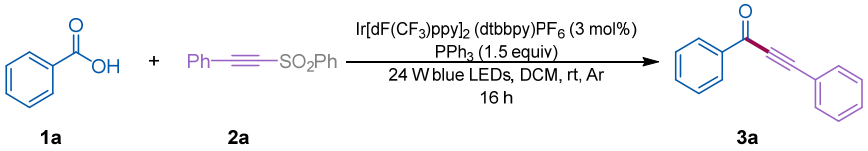
1a 2a 3a

Entry	**2a** (x molar)	Yield[b]
1	0.1 mmol	52%
2	0.15 mmol	62%
3	0.2 mmol	55%
4	0.25 mmol	50 %

[a]Reaction conditions: 1a (0.3 mmol), 2a (x mmol 1.0 equiv), Ir[dF(CF_3)ppy]$_2$ (dtbbpy)PF_6 (3 mol%), PPh_3 (0.3 mmol), DCM (4.0 mL), rt, under Ar, 16 h. [b]Isolated yield. N.R. = No reaction

occurred.

Table S5. Screening of optimal amount of **1a**[a]

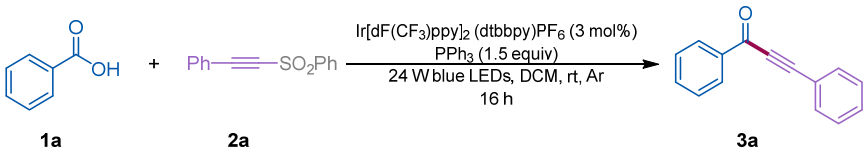


1a **2a** **3a**

Entry	**1a** (x equiv relative of **2a**)	**Yield**[b]
1	1.6	61%
2	1.8	74%
3	2.0	62%
4	2.2	53%

[a]Reaction conditions: 1a (x equiv), 2a (0.15 mmol 1.0 equiv), Ir[dF(CF_3)ppy]$_2$ (dtbbpy)PF_6 (0.0045 mmol 3 mol%), PPh_3 (0.3 mmol 2.0 equiv), DCM (4.0 mL), rt, under Ar, 16 h. [b]Isolated yield. N.R. = No reaction occurred.

Table S6. Screening of optimal amount of PPh_3[a]

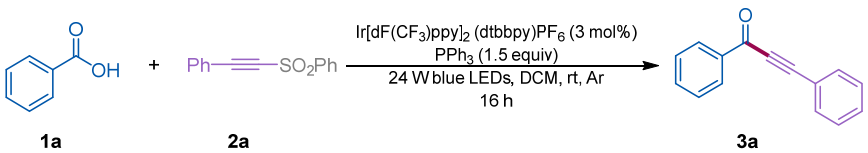


1a **2a** **3a**

Entry	PPh_3 (x equiv relative of **2a**)	**Yield**[b]
1	1.6	55%
2	1.8	61%
3	2.0	74%
4	2.2	63 %

[a]Reaction conditions: 1a (0.27 mmol 1.8 equiv), 2a (0.15 mmol 1.0 equiv), Ir[dF(CF_3)ppy]$_2$ (dtbbpy)PF_6 (0.0045 mmol 3 mol%), PPh_3 (x equiv), DCM (4.0 mL), rt, under Ar, 16 h. [b]Isolated yield. N.R. = No reaction occurred.

Table S7. Screening of optimal volume of DCM[a]



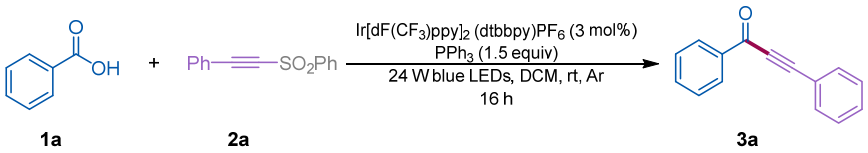
1a **2a** **3a**

Entry	DCM (x mL)	**Yield**[b]

1	2	57%
2	3	62%
3	4	74%
4	5	60%

[a]Reaction conditions: 1a (0.27 mmol 1.8 equiv), 2a (0.15 mmol 1.0 equiv), Ir[dF(CF_3)ppy]$_2$ (dtbbpy)PF_6 (0.0045 mmol 3 mol%), PPh_3 (0.3 mmol 2.0 equiv), DCM (x mL), rt, under Ar, 16 h. [b]Isolated yield. N.R. = No reaction occurred.

Table S8. Screening of optimal loading of [Ir][a]

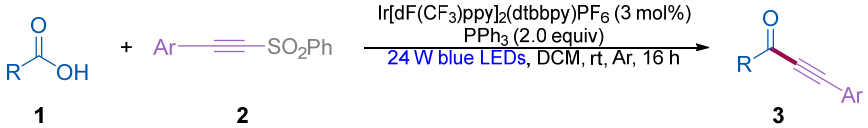


1a 2a 3a

Entry	[Ir] (x mol%)	**Yield[b]**
1	1	56%
2	3	74%
3	5	75%

[a]Reaction conditions: 1a (0.27 mmol 1.8 equiv), 2a (0.15 mmol 1.0 equiv), Ir[dF(CF_3)ppy]$_2$ (dtbbpy)PF_6 (x mol%), PPh_3 (0.3 mmol 2.0 equiv), DCM (4 mL), rt, under Ar, 16 h. [b]Isolated yield. N.R. = No reaction occurred.

4. General Procedure for Synthesis of Ynones.

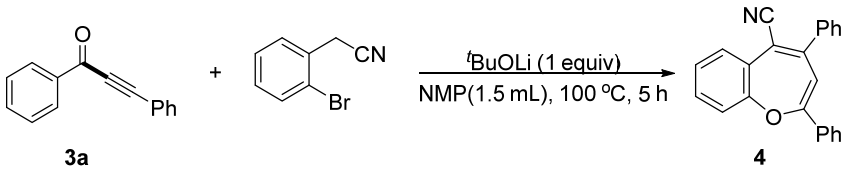


1 2 3

Under an argon atmosphere, (phenylethynyl)sulfones (0.15 mmol, 1.0 equiv), carboxylic acid (0.27 mmol, 1.8 equiv), Ir[dF(CF_3)ppy)]$_2$(dtbbpy)PF_6 (5.0 mg, 0.0045 mmol, 3 mol%), triphenylphosphine (78.6 mg, 0.3 mmol, 2.0 equiv), and anhydrous DCM (4 mL) were sequentially added to a 15 mL Schlenk flask. After stirring under irradiation of blue LEDs (440-450 nm) at room temperature for 16 h. After the completion of reaction (monitored by TLC), The organic phase was concentrated under vacuum. the reaction mixture was purified by column chromatography (eluting with PE / EtOAc = 50 / 1 to 30 / 1) to afford the desired product.

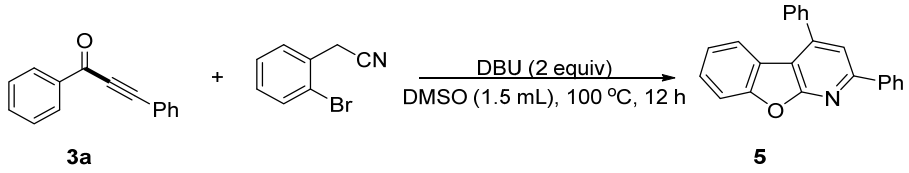
5. Experimental Procedure for the Functionalization of Ynones.

5.1 Synthesis of 4.



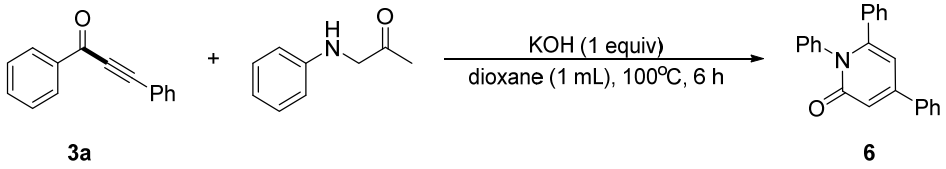
An oven dried 25 mL Schlenk tube was charged with 2-bromobenzyl cyanide (0.3 mmol, 1.0 equiv), 1,3-diphenylprop-2-yn-1-one **3a** (0.3 mmol, 1.0 equiv), ^{t}BuOLi (0.3 mmol, 1.0 equiv), and NMP (1.5 mL), then the tube was sealed and the reaction mixture was stirred at 100 ℃ for 5 h. Then the mixture was cooled to room temperature, added by water (5 mL), extracted with EtOAc (3 mL×3). The combined organic phases were dried over anhydrous Na_2SO_4, filtered and concentrated under vacuum. Further purification by flash column chromatography on silica gel (eluting with PE / EtOAc = 50 / 1) provided the product **4** in 85% yield.[2]

5.2 Synthesis of 5.



An oven dried 25 mL Schlenk tube was charged with 2-bromobenzyl cyanide (0.3 mmol, 1.0 equiv), 1,3-diphenylprop-2-yn-1-one **3a** (0.45 mmol, 1.5 equiv), DBU (0.6 mmol, 2.0 equiv), and DMSO (1.5 mL), then the tube was sealed and the reaction mixture was stirred at 100 ℃ for 12 h. Then the mixture was cooled to room temperature, added by water (5 mL), extracted with EtOAc (3 mL×3). The combined organic phases were dried over anhydrous Na_2SO_4, filtered and concentrated under vacuum. Further purification by flash column chromatography on silica gel (eluting with PE / EtOAc = 100 / 1) provided the product **5** in 71% yield. [2]

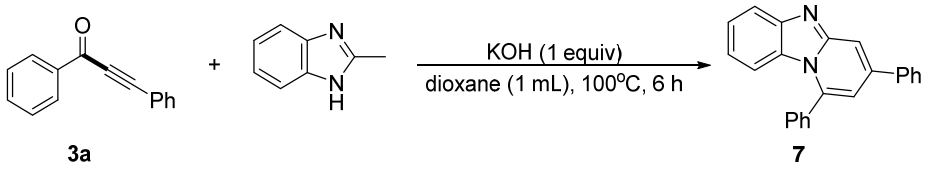
5.3 Synthesis of 6.



An oven dried 25 mL Schlenk tube was charged with N-phenylacetamide (0.5 mmol, 1.0 equiv), 1,3-diphenylprop-2-yn-1-one **3a** (0.6 mmol, 1.2 equiv), KOH (0.25 mmol, 1.0 equiv) and 1,4-

dioxane (1.5 mL), then the tube was sealed and the reaction mixture was stirred at 100 ℃ for 6 h. Then the mixture was cooled to room temperature, added by water (5 mL), extracted with EtOAc (5 mL×3). The combined organic phases were dried over anhydrous Na_2SO_4, filtered and concentrated under vacuum. Further purification by flash column chromatography on silica gel (eluting with PE / EtOAc = 10 / 1, 100 mL (petroleum ether and ethyl mixture)+1 mL (Et_3N)) provided the product **6** in 82% yield. [3]

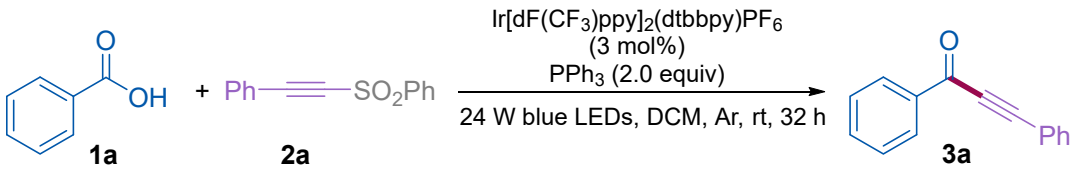
5.4 Synthesis of 7.



3a **7**

An oven dried 25 mL Schlenk tube was charged with 2-methylbenzimidazole (0.5 mmol, 1.0 equiv), 1,3-diphenylprop-2-yn-1-one **3a** (0.6 mmol, 1.2 equiv), KOH (0.5 mmol, 1.0 equiv) and 1,4-dioxane (1.5 mL), then the tube was sealed and the reaction mixture was stirred at 100 ℃ for 6 h. Then the mixture was cooled to room temperature, added by water (5 mL), extracted with EtOAc (5 mL×3). The combined organic phases were dried over anhydrous Na_2SO_4, filtered and concentrated under vacuum. Further purification by flash column chromatography on silica gel (eluting with PE / EtOAc = 5 / 1, 100 mL (petroleum ether and ethyl mixture)+1 mL (Et_3N)) provided the product **7** in 72% yield. [3]

5.5 Gram-scale reaction.



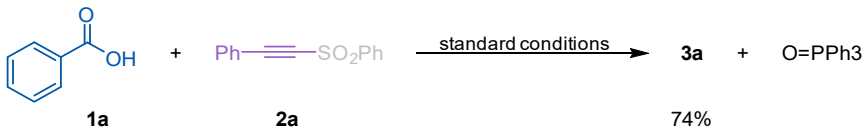
1a **2a** **3a**

7.2 mmol, 0.88 g 4 mmol, 0.97 g 461.4 mg, 56%

Under an argon atmosphere, (phenylethynyl)sulfones (0.97 g, 4 mmol, 1.0 equiv), benzoic acid (0.88 g 7.2 mmol, 1.8 equiv), $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (134.6 mg, 0.12 mmol, 3 mol%), triphenylphosphine (2.1 g, 8 mmol, 2.0 equiv), and anhydrous DCM (60 mL) were sequentially added to a 100 mL round-bottom flask and seal it**.** After stirring under irradiation of blue LEDs (440-450 nm) at room temperature for 32 h. After the completion of reaction (monitored by TLC), The organic phase was concentrated under vacuum. the reaction mixture was purified by column chromatography (eluting with PE / EtOAc = 50 / 1) to afford the desired product **3a** (461.4 mg, 56%).

6. Control Experiments.

6.1 Synthesis of 3a.



Under an argon atmosphere, (phenylethynyl)sulfones (0.15 mmol, 1.0 equiv), carboxylic acid (0.27 mmol, 1.8 equiv), $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (5.0 mg, 0.0045 mmol, 3 mol%), triphenylphosphine (78.6 mg, 0.3 mmol, 2.0 equiv), and anhydrous DCM (4 mL) were sequentially added to a 10 mL Schlenk flask. After stirring under irradiation of blue LEDs (440-450 nm) at room temperature for 16 h. After the completion of reaction (monitored by TLC), the reaction solution was concentrated under reduced pressure and the residue was analyzed by TLC and GC-MS, O=PPh3 was observed. **(Figure S2)**

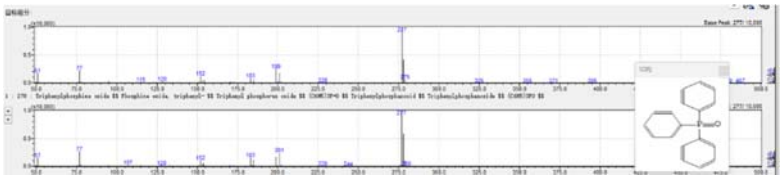
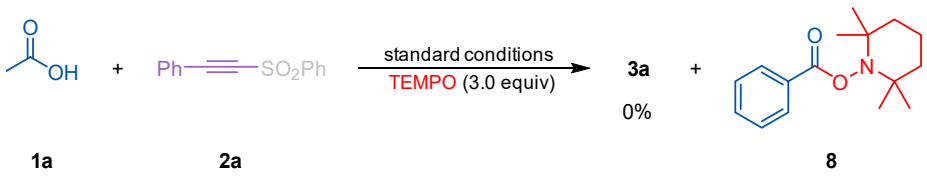


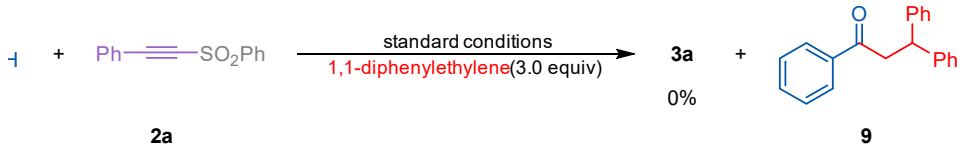
Figure S2. $O=PPh_3$ was detected by GC-Ms.

6.2 Radical-inhibiting experiment with TEMPO.



Under an argon atmosphere, (phenylethynyl)sulfones (0.15 mmol, 1.0 equiv), benzoic acid (0.27 mmol, 1.8 equiv), $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (5.0 mg, 0.0045 mmol, 3 mol%), triphenylphosphine (78.6 mg, 0.3 mmol, 2.0 equiv), TEMPO (70.3 mg, 3.0 equiv) and anhydrous DCM (4 mL) were sequentially added to a 15 mL Schlenk flask. After stirring under irradiation of blue LEDs (440-450 nm) at room temperature for 5 h. After the completion of reaction (monitored by TLC), the reaction solution was concentrated under reduced pressure and the residue was analyzed by TLC and GC-MS, product **8** was observed.

6.3 Radical-inhibiting experiment with DPE.



Under an argon atmosphere, (phenylethynyl)sulfones (0.15 mmol, 1.0 equiv), benzoic acid (0.27 mmol, 1.8 equiv), $Ir[dF(CF_3)ppy)]_2(dtbbpy)PF_6$ (5.0 mg, 0.0045 mmol, 3 mol%), triphenylphosphine (78.6 mg, 0.3 mmol, 2.0 equiv), DPE (81.0 mg, 3.0 equiv) and anhydrous DCM (4 mL) were sequentially added to a 15 mL Schlenk flask. After stirring under irradiation of blue LEDs (440-450 nm) at room temperature for 5 h. After the completion of reaction (monitored by TLC), the reaction solution was concentrated under reduced pressure and the residue was analyzed by TLC and GC-MS, product 9 was observed. **(Figure S3)**

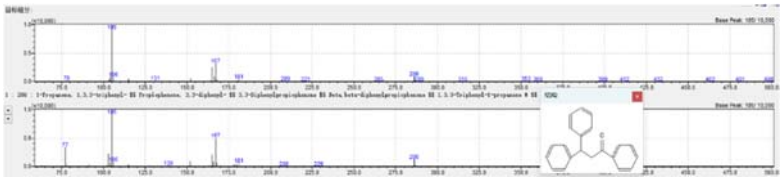
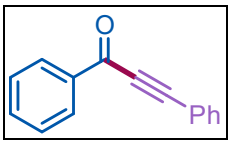


Figure S3. The acyl radical trapping product **9** was detected by GC-Ms.

7. Characterization Data of Products.

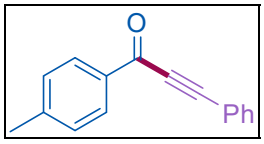
1,3-diphenylprop-2-yn-1-one 3a[4]



According to the general procedure, the product **3a** was obtained by a flash column chromatography on silica gel (eluent: PE / EtOAc = 50 / 1) in 74% yield (22.9 mg) as a yellow oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.25 – 8.19 (m, 2H), 7.70 – 7.64 (m, 2H), 7.61 (t, *J* = 7.4 Hz, 1H), 7.50 (t, *J* = 7.7 Hz, 2H), 7.46 (t, *J* = 7.5 Hz, 1H), 7.40 (t, *J* = 7.5 Hz, 2H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 178.0, 136.9, 134.1, 133.0, 130.8, 129.5, 128.7, 128.6, 120.1, 93.1, 86.9.

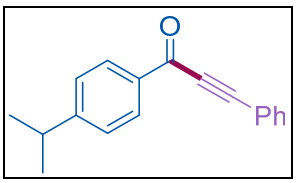
3-phenyl-1-(p-tolyl)prop-2-yn-1-one 3b[5]



According to the general procedure, the product **3b** was obtained by a flash column chromatography on silica gel (eluent: PE / EtOAc = 50 / 1) in 64% yield (21.1 mg) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, *J* = 8.0 Hz, 2H), 7.66 (d, *J* = 6.8 Hz, 2H), 7.49 – 7.43 (m, 1H), 7.40 (t, *J* = 7.2 Hz, 2H), 7.29 (d, *J* = 7.8 Hz, 2H), 2.43 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 177.7, 145.2, 134.6, 133.0, 130.6, 129.7, 129.3, 128.6, 120.2, 92.6, 87.0, 21.8.

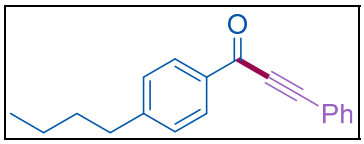
1-(4-isopropylphenyl)-3-phenylprop-2-yn-1-one 3c[6]



According to the general procedure, the product **3c** was obtained by a flash column chromatography on silica gel (eluent: PE / EtOAc = 50 / 1) in 74% yield (27.5 mg) as a white oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, *J* = 7.9 Hz, 2H), 7.68 (d, *J* = 7.4 Hz, 2H), 7.49 – 7.34 (m, *J* = 21.2, 15.4, 7.6 Hz, 5H), 3.07 – 2.92 (m, *J* = 6.9 Hz, 1H), 1.30 (d, *J* = 6.9 Hz, 6H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 177.7, 155.9, 135.0, 133.0, 130.6, 129.8, 128.6, 126.7, 120.3, 92.6, 87.0, 34.4, 23.6.

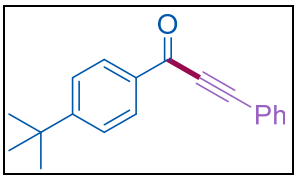
1-(4-butylphenyl)-3-phenylprop-2-yn-1-one 3d[7]



According to the general procedure, the product **3d** was obtained by a flash column chromatography on silica gel (eluent: PE / EtOAc= 50 / 1) in 68% yield (26.7 mg) as a white oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, *J* = 8.1 Hz, 2H), 7.67 (d, *J* = 6.9 Hz, 2H), 7.49 – 7.44 (m, 1H), 7.41 (t, *J* = 7.2 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 2.69 (t, *J* = 7.6 Hz, 2H), 1.67 – 1.60 (m, 2H), 1.37 (m, *J* = 14.7, 7.2 Hz, 2H), 0.94 (t, *J* = 7.3 Hz, 3H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 177.7, 150.1, 134.8, 133.0, 130.6, 129.7, 128.7, 128.6, 120.3, 92.6, 87.0, 35.8, 33.1, 22.3, 13.8.

1-(4-(tert-butyl)phenyl)-3-phenylprop-2-yn-1-one 3e[8]

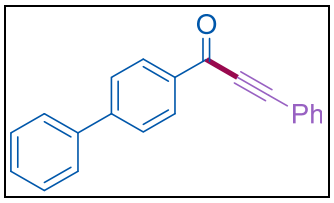


According to the general procedure, the product **3e** was obtained by a flash column chromatography on silica gel (eluent: PE / EtOAc= 50 / 1) in 65% yield (25.5 mg) as a white oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, *J* = 8.4 Hz), 7.67 (d, *J* = 6.8 Hz), 7.53 (d, *J* = 8.4 Hz), 7.46 (d, *J* = 7.3 Hz), 7.41 (t, *J* = 7.2 Hz), 1.36 (s, 9H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 177.7, 158.1, 134.5, 133.0, 130.7, 129.6, 128.7, 125.6, 120.3, 92.6, 87.0, 35.3, 31.0.

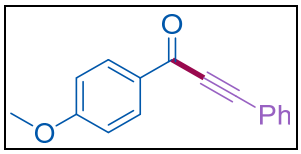
1-([1,1'-biphenyl]-4-yl)-3-phenylprop-2-yn-1-one 3f[7]



According to the general procedure, the product **3f** was obtained by a flash column chromatography on silica gel (eluent: PE / EtOAc= 50 / 1) in 67% yield (28.3 mg) as a white solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.30 (d, *J* = 8.3 Hz, 2H), 7.76 – 7.73 (m, 2H), 7.73 – 7.70 (m, 2H), 7.67 – 7.64 (m, 2H), 7.52 – 7.47 (m, 3H), 7.46 – 7.41 (m, 3H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 177.6, 146.8, 139.8, 135.8, 133.1, 130.8, 130.2, 129.0, 128.7, 128.4, 127.34, 127.28, 120.2, 93.1, 87.0.

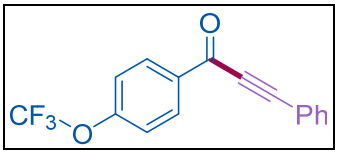
1-(4-methoxyphenyl)-3-phenylprop-2-yn-1-one 3g[5]



According to the general procedure, the product **3g** was obtained by a flash column chromatography on silica gel (eluent: PE / EtOAc= 50 / 1) in 49% yield (17.3 mg) as a white oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, *J* = 8.8 Hz, 2H), 7.68 (d, *J* = 6.8 Hz, 2H), 7.53 – 7.38 (m, 3H), 6.99 (d, *J* = 8.8 Hz, 2H), 3.90 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 176.7, 164.5, 133.0, 132.0, 130.5, 130.4, 128.6, 120.4, 113.9, 92.3, 87.0, 55.6.

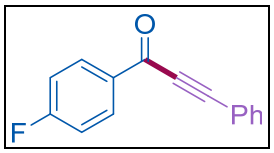
3-phenyl-1-(4-(trifluoromethoxy)phenyl)prop-2-yn-1-one 3h[9]



According to the general procedure, the product **3h** was obtained by a flash column chromatography on silica gel (eluent: PE / EtOAc= 50 / 1) in 52% yield (22.6 mg) as a yellow solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.29 – 8.22 (m, 2H), 7.69 – 7.64 (m, 2H), 7.51 – 7.46 (m, 1H), 7.41 (t, *J* = 7.6 Hz, 2H), 7.33 (d, *J* = 8.1 Hz, 2H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 176.2, 153.3, 135.0, 133.0, 131.5, 131.0, 128.7, 120.23, 120.22 (q, *J* = 259.2 Hz), 119.7, 93.7, 86.5.
^{19}F NMR (565 MHz, $CDCl_3$) δ -57.6 .

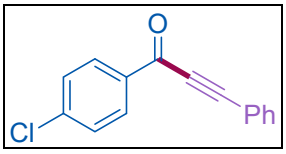
1-(4-fluorophenyl)-3-phenylprop-2-yn-1-one 3i[5]



According to the general procedure, the product **3i** was obtained by a flash column chromatography on silica gel (eluent: PE / EtOAc= 50 / 1) in 42% yield (14.1 mg) as a yellow solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.28 – 8.20 (m, 2H), 7.68 (d, *J* = 7.7 Hz, 2H), 7.50 (t, *J* = 7.4 Hz, 1H), 7.43 (t, *J* = 7.6 Hz, 2H), 7.19 (t, *J* = 8.5 Hz, 2H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 176.4, 166.5 (d, *J* = 257.1 Hz), 133.5 (d, *J* = 2.1 Hz), 133.1, 132.3 (d, *J* = 8.9 Hz), 130.9, 128.8, 120.0, 115.9 (d, *J* = 22.7 Hz), 93.4, 86.6.
^{19}F NMR (376 MHz, $CDCl_3$) δ -103.2.

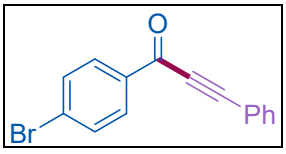
1-(4-chlorophenyl)-3-phenylprop-2-yn-1-one 3j[5]



According to the general procedure, the product **3j** was obtained by a flash column chromatography on silica gel (eluent: PE / EtOAc= 50 / 1) in 51% yield (18.4 mg) as a yellow oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.16 (d, *J* = 7.4 Hz, 2H), 7.69 (d, *J* = 7.4 Hz, 2H), 7.50 (d, *J* = 7.5 Hz, 3H), 7.43 (t, *J* = 7.4 Hz, 2H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 176.7, 140.7, 135.1, 133.1, 131.0, 130.9, 129.0, 128.7, 119.9, 93.6, 86.6.

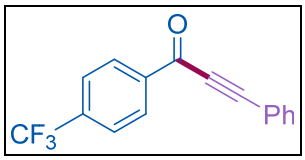
1-(4-bromophenyl)-3-phenylprop-2-yn-1-one 3k[10]



According to the general procedure, the product **3k** was obtained by a flash column chromatography on silica gel (eluent: PE / EtOAc= 50 / 1) in 57% yield (24.4 mg) as a yellow oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.08 (d, *J* = 7.9 Hz, 2H), 7.71 – 7.61 (m, 4H), 7.50 (t, *J* = 7.4 Hz, 1H), 7.43 (t, *J* = 7.6 Hz, 2H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 176.8, 135.7, 133.1, 132.0, 130.98, 130.92, 130.0, 128.7, 119.9, 93.7, 86.6.

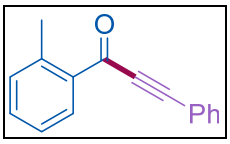
3-phenyl-1-(4-(trifluoromethyl)phenyl)prop-2-yn-1-one 3l[11]



According to the general procedure, the product **3l** was obtained by a flash column chromatography on silica gel (eluent: PE / EtOAc= 50 / 1) in 43% yield (17.7 mg) as a yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (d, *J* = 7.7 Hz, 2H), 7.79 (d, *J* = 7.7 Hz, 2H), 7.70 (d, *J* = 7.0 Hz, 2H), 7.55 – 7.48 (m, 1H), 7.44 (t, *J* = 7.0 Hz, 2H).
^{13}C NMR (150MHz, $CDCl_3$) δ 176.7, 139.4, 135.2 (q, *J* = 32.7 Hz), 133.2, 131.2, 129.8, 128.8, 125.7 (q, *J* = 4.0 Hz), 123.6 (d, *J* = 272.6 Hz), 119.7, 94.5, 86.6.
^{19}F NMR (565 MHz, $CDCl_3$) δ -63.1 .

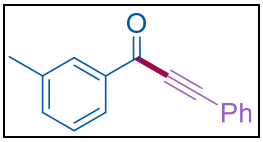
3-phenyl-1-(o-tolyl)prop-2-yn-1-one 3m[5]



According to the general procedure, the product **3m** was obtained by a flash column chromatography on silica gel (eluent: PE / EtOAc= 50 / 1) in 55% yield (18.2 mg) as a white oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.28 (d, *J* = 7.7 Hz, 1H), 7.58 (d, *J* = 8.4 Hz, 2H), 7.42 – 7.36 (m, 2H), 7.32 (q, *J* = 7.4 Hz, 3H), 7.20 (d, *J* = 7.6 Hz, 1H), 2.65 (s, 3H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 179.2, 140.0, 135.3, 132.9, 132.6, 132.5, 131.9, 130.3, 128.3, 125.6, 119.9, 91.4, 88.1, 21.6.

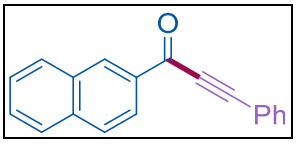
3-phenyl-1-(m-tolyl)prop-2-yn-1-one 3n[5]



According to the general procedure, the product **3n** was obtained by a flash column chromatography on silica gel (eluent: PE / EtOAc= 50 / 1) in 61% yield (20.1 mg) as a white solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.06 – 7.99 (m, 2H), 7.69 (d, *J* = 7.9 Hz, 2H), 7.48 (t, *J* = 7.3 Hz, 1H), 7.42 (p, *J* = 7.6 Hz, 4H), 2.45 (s, 3H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 178.2, 138.5, 136.9, 135.0, 133.0, 130.7, 129.7, 128.6, 128.5, 127.1, 120.2, 92.8, 87.0, 21.3.

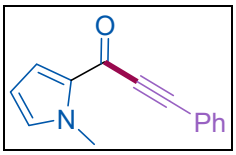
1-(naphthalen-2-yl)-3-phenylprop-2-yn-1-one 3o[7]



According to the general procedure, the product **3o** was obtained by a flash column chromatography on silica gel (eluent: PE / EtOAc= 50 / 1) in 61% yield (23.4 mg) as a yellow solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.78 (s, 1H), 8.20 (d, *J* = 8.6 Hz, 1H), 8.01 (d, *J* = 8.1 Hz, 1H), 7.94 – 7.86 (m, 2H), 7.73 (d, *J* = 7.7 Hz, 2H), 7.62 (t, *J* = 7.5 Hz, 1H), 7.56 (t, *J* = 7.5 Hz, 1H), 7.49 (t, *J* = 7.3 Hz, 1H), 7.43 (t, *J* = 7.5 Hz, 2H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 177.9, 136.1, 134.4, 133.0, 132.6, 132.4, 130.7, 129.9, 129.0, 128.7, 128.5, 127.9, 126.9, 123.9, 120.2, 93.0, 87.1.

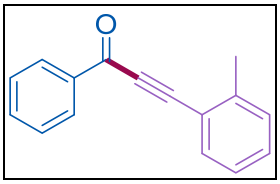
1-(1-methyl-1H-pyrrol-2-yl)-3-phenylprop-2-yn-1-one 3p[14]



According to the general procedure, the product **3p** was obtained by a flash column chromatography on silica gel (eluent: PE / EtOAc= 20 / 1) in 42% yield (13.2 mg) as a yellow solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.63 (d, *J* = 7.21 Hz, 2H), 7.44 (t, *J* = 7.37 Hz, 1H), 7.39 (t, *J* = 7.46 Hz, 2H), 7.31 – 7.28 (m, 1H), 6.89 (s, 1H), 6.20 (m, *J* = 3.68, 2.45 Hz, 1H), 3.99 (s, 3H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 166.7, 132.6, 132.5, 132.1, 130.1, 128.5, 123.7, 120.6, 109.0, 88.4, 87.5, 37.3.

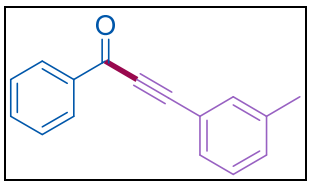
1-phenyl-3-(o-tolyl)prop-2-yn-1-one 3q[4]



According to the general procedure, the product **3q** was obtained by a flash column chromatography on silica gel (eluent: PE / EtOAc= 50 / 1) in 56% yield (18.5 mg) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (d, *J* = 7.2 Hz, 2H), 7.66 – 7.58 (m, 2H), 7.50 (t, *J* = 7.5 Hz, 2H), 7.35 (t, *J* = 7.3 Hz, 1H), 7.31 – 7.19 (m, 2H), 2.57 (s, 3H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 178.0, 142.1, 137.0, 134.0, 133.6, 130.8, 129.8, 129.5, 128.6, 125.9, 119.9, 92.1, 90.7, 20.8.

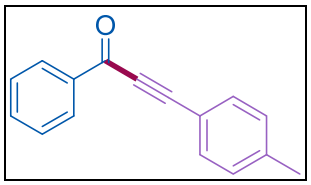
1-phenyl-3-(m-tolyl)prop-2-yn-1-one 3r[4]



According to the general procedure, the product **3r** was obtained by a flash column chromatography on silica gel (eluent: PE / EtOAc= 50 / 1) in 63% yield (20.8 mg) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (d, *J* = 7.2 Hz, 2H), 7.62 (t, *J* = 7.3 Hz, 1H), 7.56 – 7.46 (m, 4H), 7.30 (d, *J* = 5.4 Hz, 2H), 2.38 (s, 3H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 178.0, 138.5, 137.0, 134.0, 133.5, 131.7, 130.2, 129.6, 128.59, 128.57, 119.9, 93.5, 86.7, 21.1.

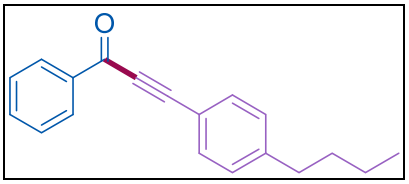
1-phenyl-3-(p-tolyl)prop-2-yn-1-one 3s[4]



According to the general procedure, the product **3s** was obtained by a flash column chromatography on silica gel (eluent: PE / EtOAc= 50 / 1) in 67% yield (22.1 mg) as a yellow oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.24 – 8.20 (m, 2H), 7.62 – 7.59 (m, 1H), 7.57 (d, *J* = 8.1 Hz, 2H), 7.52 – 7.48 (m, 2H), 7.20 (d, *J* = 7.9 Hz, 2H), 2.38 (s, 3H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 177.9, 141.5 136.9, 133.9, 133.0, 129.41, 129.39, 128.5, 116.9, 93.7, 86.7, 21.6.

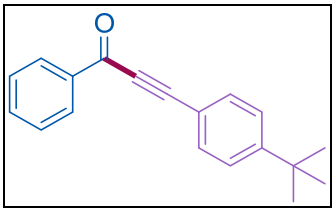
3-(4-butylphenyl)-1-phenylprop-2-yn-1-one 3t[5]



According to the general procedure, the product **3t** was obtained by a flash column chromatography on silica gel (eluent: PE / EtOAc= 50 / 1) in 72% yield (28.3 mg) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (d, *J* = 7.2 Hz, 2H), 7.60 (d, *J* = 8.0 Hz, 3H), 7.51 (t, *J* = 7.5 Hz, 2H), 7.23 (d, *J* = 7.9 Hz, 2H), 2.65 (t, *J* = 7.6 Hz, 2H), 1.65 – 1.57 (m, 2H), 1.41 – 1.31 (m, 2H), 0.93 (t, *J* = 7.3 Hz, 3H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 178.1, 146.5, 137.0, 134.0, 133.1, 129.5, 128.8, 128.6, 117.2, 93.9, 86.8, 35.8, 33.2, 22.3, 13.8.

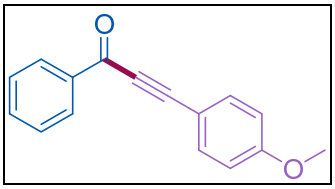
3-(4-(tert-butyl)phenyl)-1-phenylprop-2-yn-1-one 3u[12]



According to the general procedure, the product **3u** was obtained by a flash column chromatography on silica gel (eluent: PE / EtOAc= 50 / 1) in 67% yield (26.3 mg) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (d, *J* = 7.2 Hz, 2H), 7.61 (t, *J* = 8.2 Hz, 3H), 7.50 (t, *J* = 7.5 Hz, 2H), 7.44 (d, *J* = 8.2 Hz, 2H), 1.33 (s, 9H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 178.1, 154.6, 137.0, 134.0, 133.0, 129.5, 128.6, 125.7, 117.0, 93.8, 86.7, 35.1, 31.0.

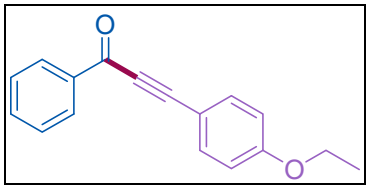
3-(4-methoxyphenyl)-1-phenylprop-2-yn-1-one 3v[4]



According to the general procedure, the product **3v** was obtained by a flash column chromatography on silica gel (eluent: PE / EtOAc= 50 / 1) in 44% yield (15.6 mg) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (d, *J* = 7.2 Hz, 2H), 7.62 (t, *J* = 10.6 Hz, 3H), 7.51 (t, *J* = 7.1 Hz, 2H), 6.93 (d, *J* = 7.9 Hz, 2H), 3.85 (s, 3H)..
^{13}C NMR (150 MHz, $CDCl_3$) δ 178.1, 161.8, 137.1, 135.2, 133.9, 129.5, 128.6, 114.5, 111.9, 94.4, 86.9, 55.5.

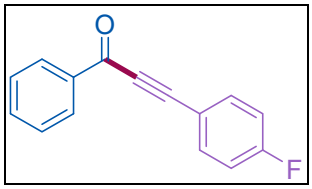
3-(4-ethoxyphenyl)-1-phenylprop-2-yn-1-one 3w[13]



According to the general procedure, the product **3w** was obtained by a flash column chromatography on silica gel (eluent: PE / EtOAc= 50 / 1) in 47% yield (17.6 mg) as a white solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.22 (d, *J* = 7.5 Hz, 2H), 7.65 – 7.59 (m, 3H), 7.51 (t, *J* = 7.7 Hz, 2H), 6.91 (d, *J* = 8.7 Hz, 2H), 4.09 – 4.05 (m, 2H), 1.43 (t, *J* = 7.0 Hz, 3H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 178.0, 161.2, 137.0, 135.1, 133.8, 129.4, 128.5, 114.8, 111.6, 94.5, 86.8, 63.7, 14.6.

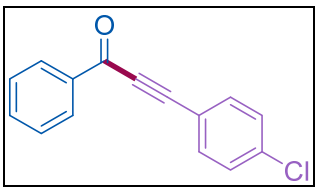
3-(4-fluorophenyl)-1-phenylprop-2-yn-1-one 3x[4]



According to the general procedure, the product **3x** was obtained by a flash column chromatography on silica gel (eluent: PE / EtOAc= 50 / 1) in 58% yield (19.5 mg) as a yellow solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.21 (d, *J* = 7.8 Hz, 2H), 7.72 – 7.67 (m, 2H), 7.64 (t, *J* = 7.3 Hz, 1H), 7.52 (t, *J* = 7.6 Hz, 2H), 7.13 (t, *J* = 8.4 Hz, 2H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 177.9, 164.9 (d, *J* = 253.9 Hz), 136.8, 135.4 (d, *J* = 8.8 Hz), 134.2, 129.5, 128.6, 116.3 (d, *J* = 3.7 Hz), 116.3 (d, *J* = 21.9 Hz), 92.0, 86.8.
^{19}F NMR (565 MHz, $CDCl_3$) δ -106.1 .

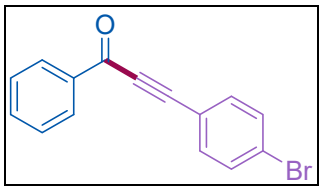
3-(4-chlorophenyl)-1-phenylprop-2-yn-1-one 3y[4]



According to the general procedure, the product **3y** was obtained by a flash column chromatography on silica gel (eluent: PE / EtOAc= 50 / 1) in 55% yield (19.8 mg) as a yellow solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.20 (d, *J* = 7.8 Hz, 2H), 7.66 – 7.58 (m, 3H), 7.51 (t, *J* = 7.5 Hz, 2H), 7.39 (d, *J* = 8.0 Hz, 2H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 177.7, 137.1, 136.7, 134.2, 129.5, 129.1, 128.6, 118.5, 91.5, 87.5.

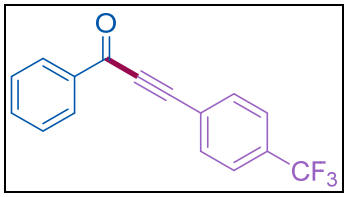
3-(4-bromophenyl)-1-phenylprop-2-yn-1-one 3z[4]



According to the general procedure, the product **3z** was obtained by a flash column chromatography on silica gel (eluent: PE / EtOAc= 50 / 1) in 47% yield (20.1 mg) as a white solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.23 – 8.17 (m, 2H), 7.67 – 7.63 (m, 1H), 7.59 – 7.51 (m, 6H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 177.8, 136.7, 134.3, 134.3, 132.1, 129.6, 128.7, 125.6, 119.1, 91.6, 87.7.

1-phenyl-3-(4-(trifluoromethyl)phenyl)prop-2-yn-1-one 3aa[4]

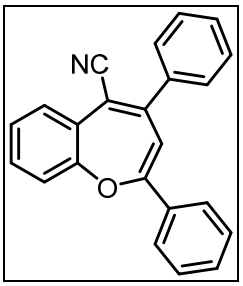


According to the general procedure, the product **3aa** was obtained by a flash column chromatography on silica gel (eluent: PE / EtOAc= 50 / 1) in 41% yield (16.9 mg) as a yellow solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.20 (d, *J* = 7.9 Hz, 2H), 7.76 (d, *J* = 8.2 Hz, 2H), 7.68 – 7.61 (m, 3H), 7.51 (t, *J* = 7.7 Hz, 2H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 177.5, 136.5, 134.5, 133.1, 132.2 (q, *J* = 32.7 Hz), 129.5, 128.6, 125.5 (q, *J* = 3.4 Hz), 124.4, 123.8 (q, *J* = 272.6 Hz), 90.3, 88.0.
^{19}F NMR (565 MHz, $CDCl_3$) δ -63.1.

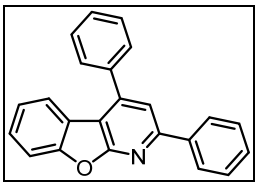
2,4-diphenylbenzo[b]oxepine-5-carbonitrile 4[2]



The representative general procedure mentioned above was followed. the product **4** was obtained by a flash column chromatography on silica gel (eluent: PE / EtOAc= 50 / 1) in 85% (0.3 mmol scale, 81.9 mg) as a yellow solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.88 – 7.84 (m, 2H), 7.74 – 7.71 (m, 1H), 7.61 – 7.57 (m, 2H), 7.50 – 7.40 (m, 7H), 7.31 – 7.27 (m, 1H), 7.16 – 7.13 (m, 1H), 6.41 (s, 1H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 159.9, 156.1, 152.9, 139.3, 133.5, 131.7, 130.3, 129.6, 128.8, 128.7, 128.7, 128.4, 126.2, 125.7, 121.4, 118.6, 112.3, 111.0.

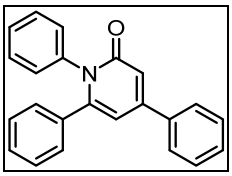
2,4-diphenylbenzofuro[2,3-b]pyridine 5[2]



The representative general procedure mentioned above was followed. the product **5** was obtained by a flash column chromatography on silica gel (eluent: PE / EtOAc= 50 / 1) in 71% (0.3 mmol scale, 68.4 mg) as a yellow solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.21 – 8.16 (m, 2H), 7.78 – 7.71 (m, 3H), 7.67 – 7.54 (m, 5H), 7.54 – 7.42 (m, 4H), 7.23 – 7.18 (m, 1H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 163.8, 154.9, 154.7, 147.0, 138.6, 137.9, 129.3, 129.2, 129.0, 128.8, 128.5, 128.0, 127.2, 123.0, 122.5, 122.3, 116.9, 112.9, 112.0.

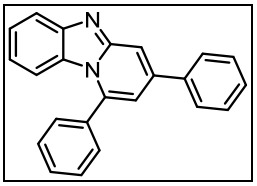
1,4,6-triphenylpyridin-2(1H)-one 6[3]



The representative general procedure mentioned above was followed. the product **6** was obtained by a flash column chromatography on silica gel (eluent: PE / EtOAc= 50 / 1) in 82% (0.5 mmol scale, 132.4 mg) as a white solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.69 – 7.65 (m, 2H), 7.52 – 7.41 (m, 3H), 7.30 – 7.24 (m, 2H), 7.23 – 7.10 (m, 8H), 6.93 (t, *J* = 1.8 Hz, 1H), 6.55 (d, *J* = 1.9 Hz, 1H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 163.6, 151.3, 149.4, 138.4, 137.5, 135.7, 129.5, 129.01, 129.00, 128.97, 128.7, 128.4, 128.0, 127.9, 116.2, 107.5.

1,3-diphenylbenzo[4,5]imidazo[1,2-a]pyridine 7[3]



The representative general procedure mentioned above was followed. the product **7** was obtained by a flash column chromatography on silica gel (eluent: PE / EtOAc= 50 / 1) in 72% (0.5 mmol scale, 115.2 mg) as a white solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.93 – 7.89 (m, 2H), 7.74 (d, *J* = 7.6 Hz, 2H), 7.68 – 7.58 (m, 5H), 7.49 (t, *J* = 7.5 Hz, 2H), 7.45 – 7.39 (m, 2H), 6.99 – 6.94 (m, 2H), 6.59 (d, *J* = 8.5 Hz, 1H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 150.1, 145.7, 141.7, 141.1, 138.1, 134.4, 130.1, 129.10, 129.07, 129.0, 128.8, 126.9, 125.1, 120.3, 119.5, 114.5, 113.1, 112.0.

8. NMR Spectrum.

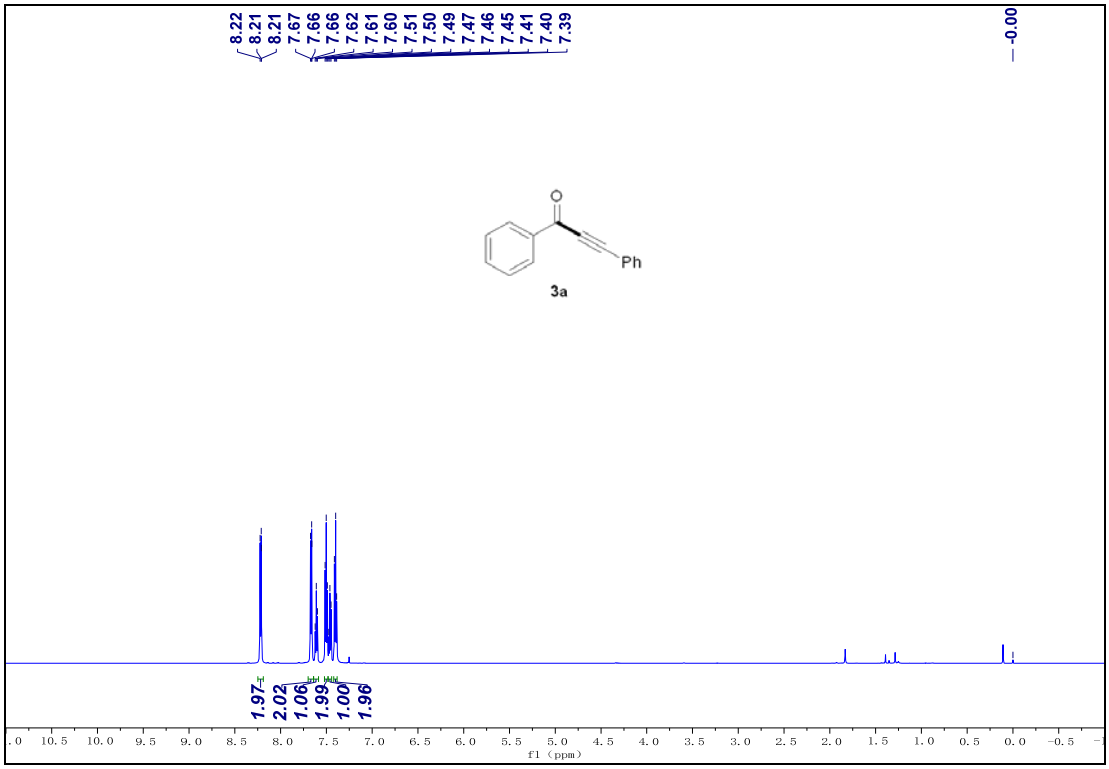


Figure S4. ^{1}H NMR spectrum of **3a** (600 MHz, $CDCl_3$, 298 K).

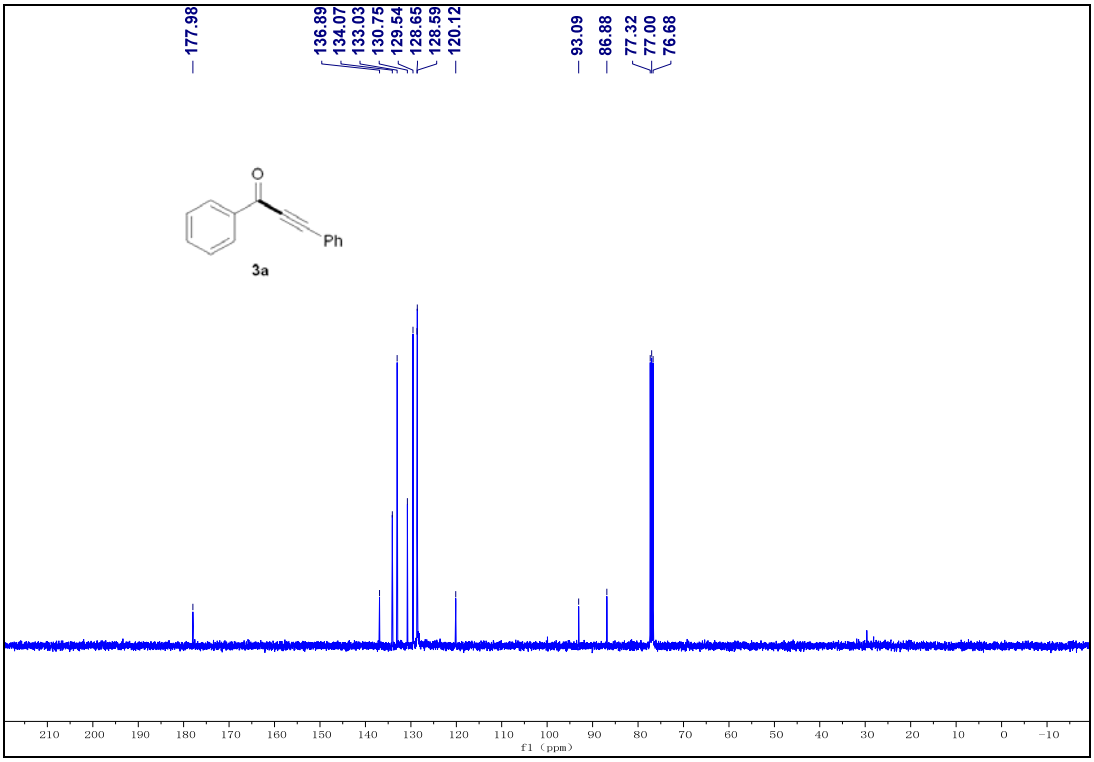


Figure S5. ^{13}C NMR spectrum of **3a** (100 MHz, $CDCl_3$, 298 K).

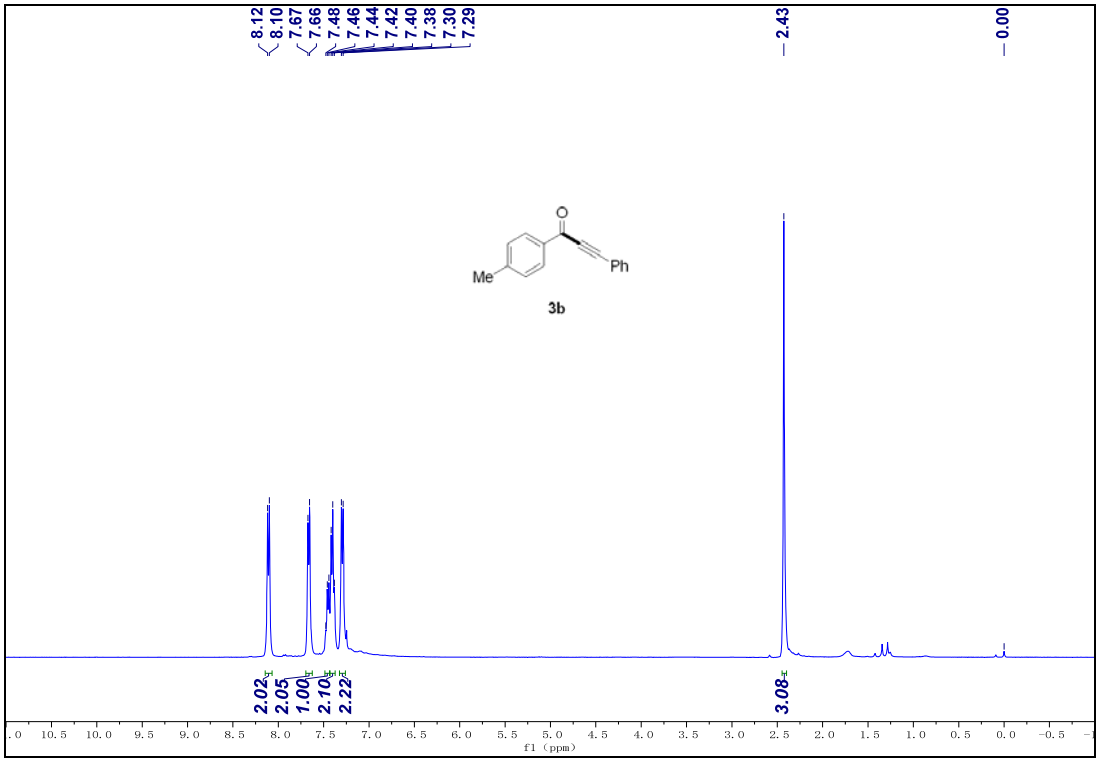


Figure S6. ^{1}H NMR spectrum of **3b** (400 MHz, $CDCl_3$, 298 K).

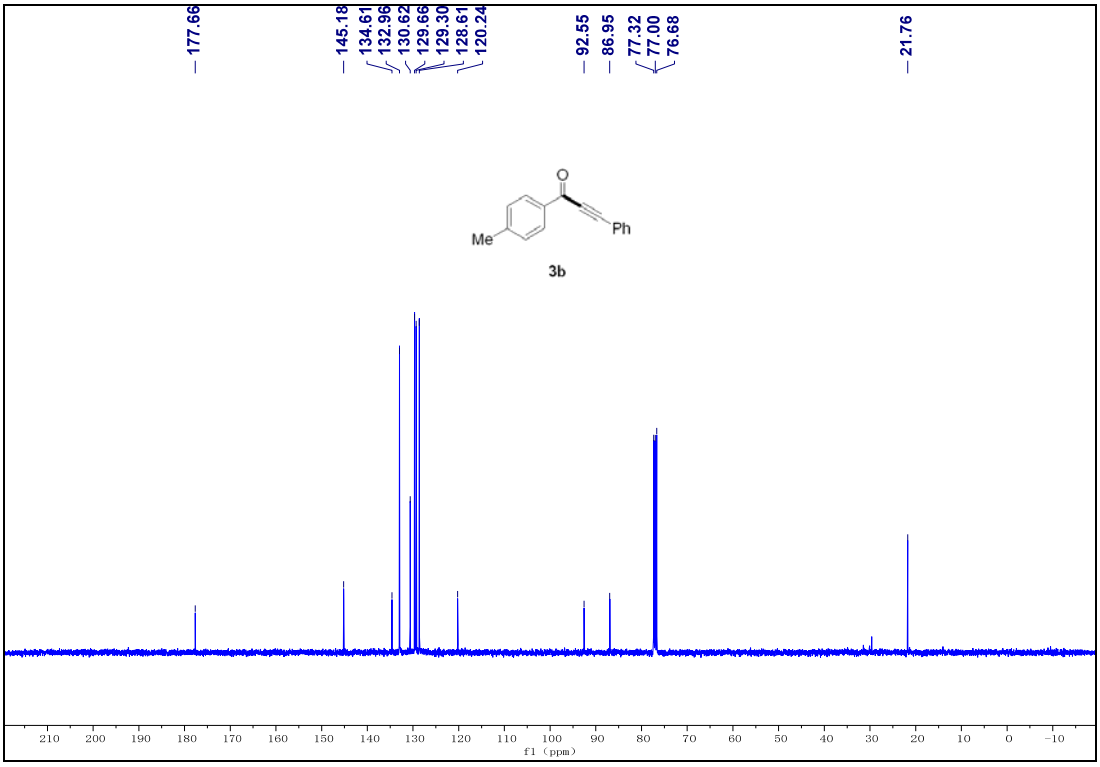


Figure S7. ^{13}C NMR spectrum of **3b** (100 MHz, $CDCl_3$, 298 K).

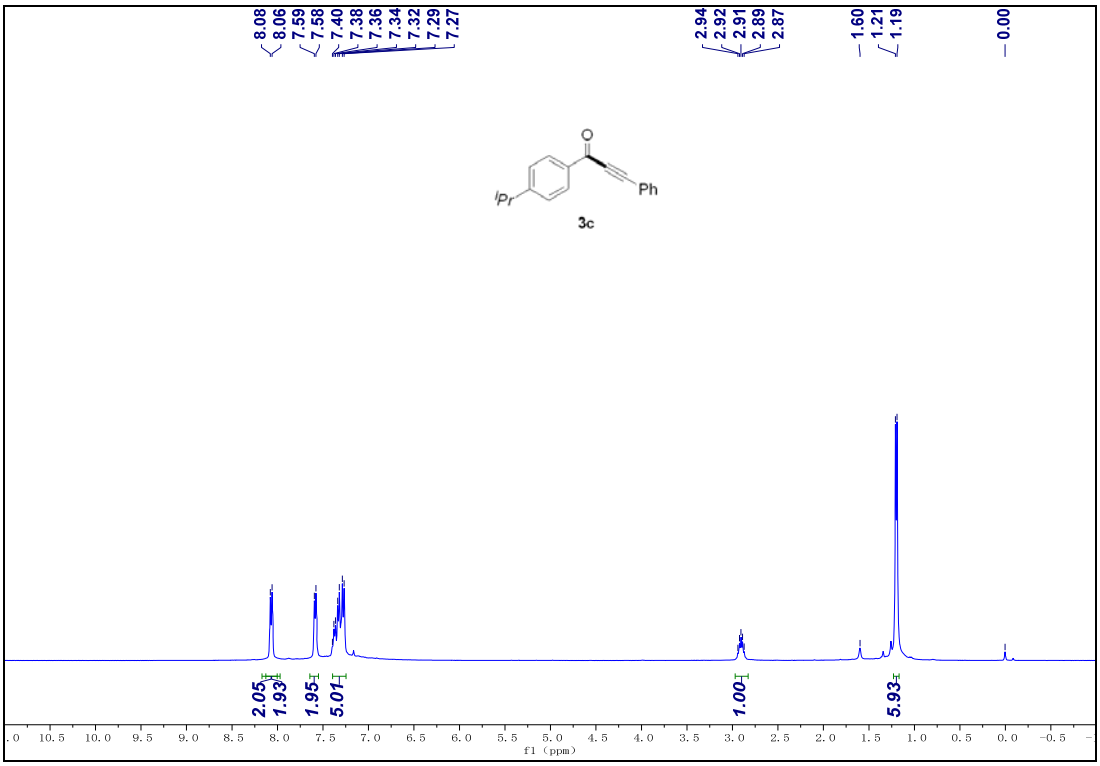


Figure S8. ^{1}H NMR spectrum of **3c** (400 MHz, $CDCl_3$, 298 K).

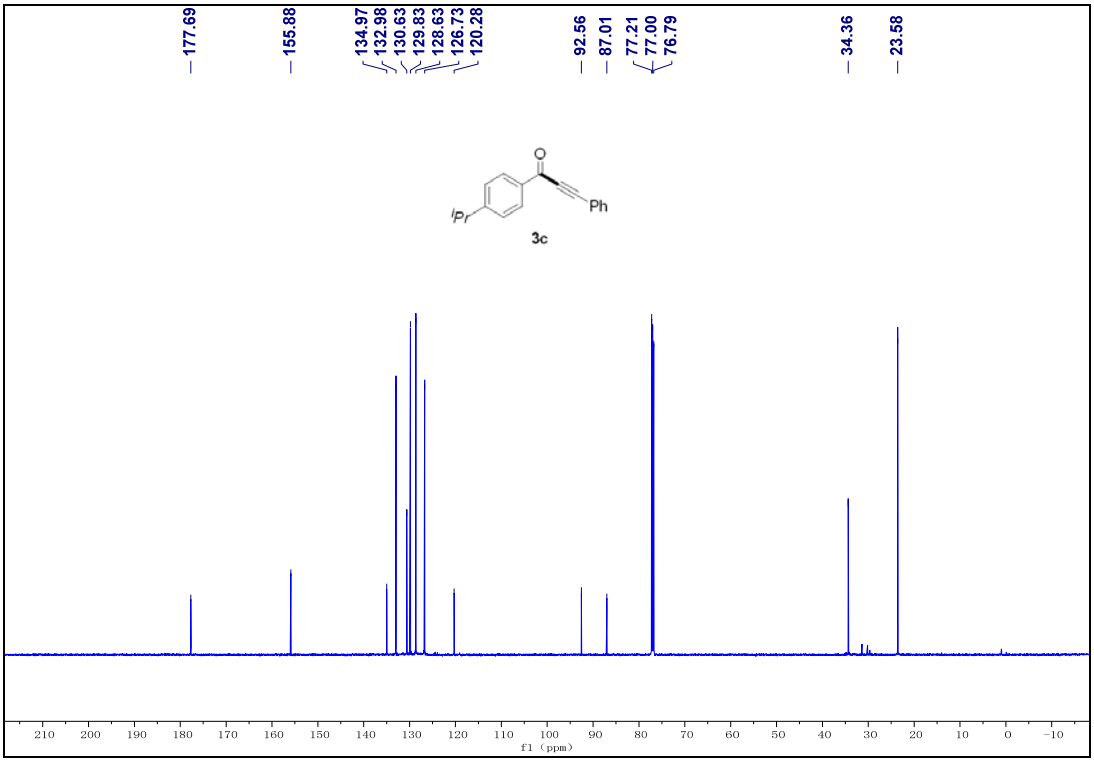


Figure S9. ^{13}C NMR spectrum of **3c** (150 MHz, $CDCl_3$, 298 K).

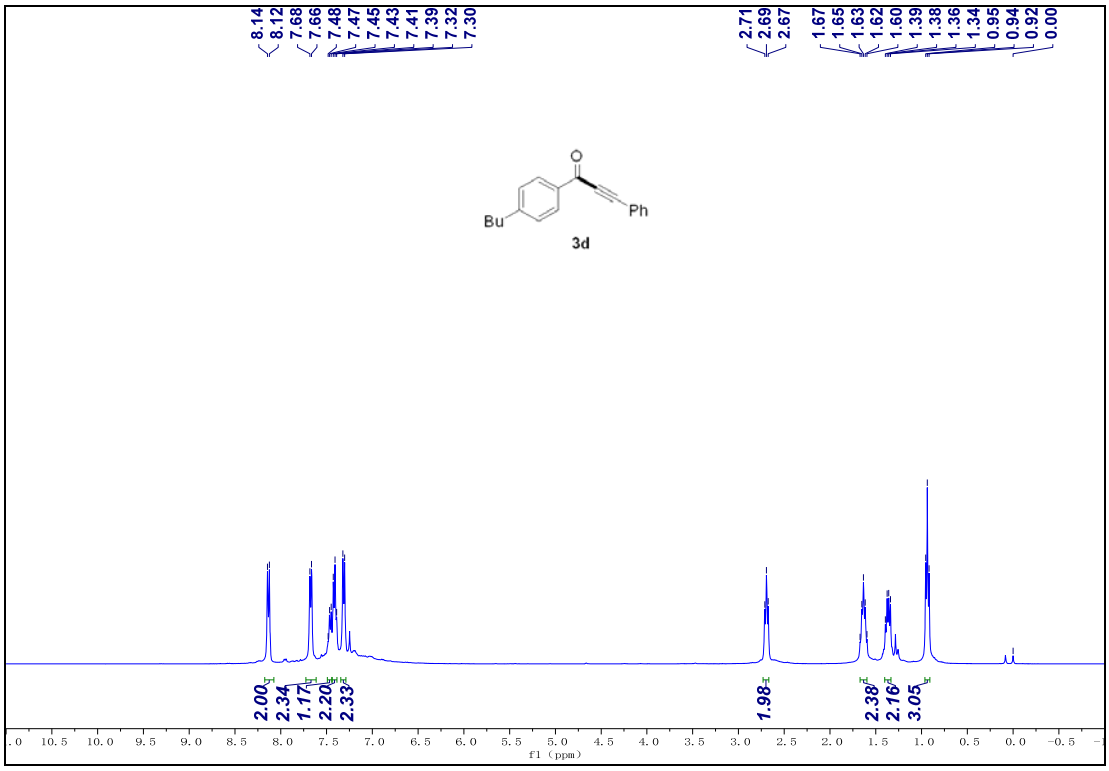


Figure S10. ^{1}H NMR spectrum of **3d** (400 MHz, $CDCl_3$, 298 K).

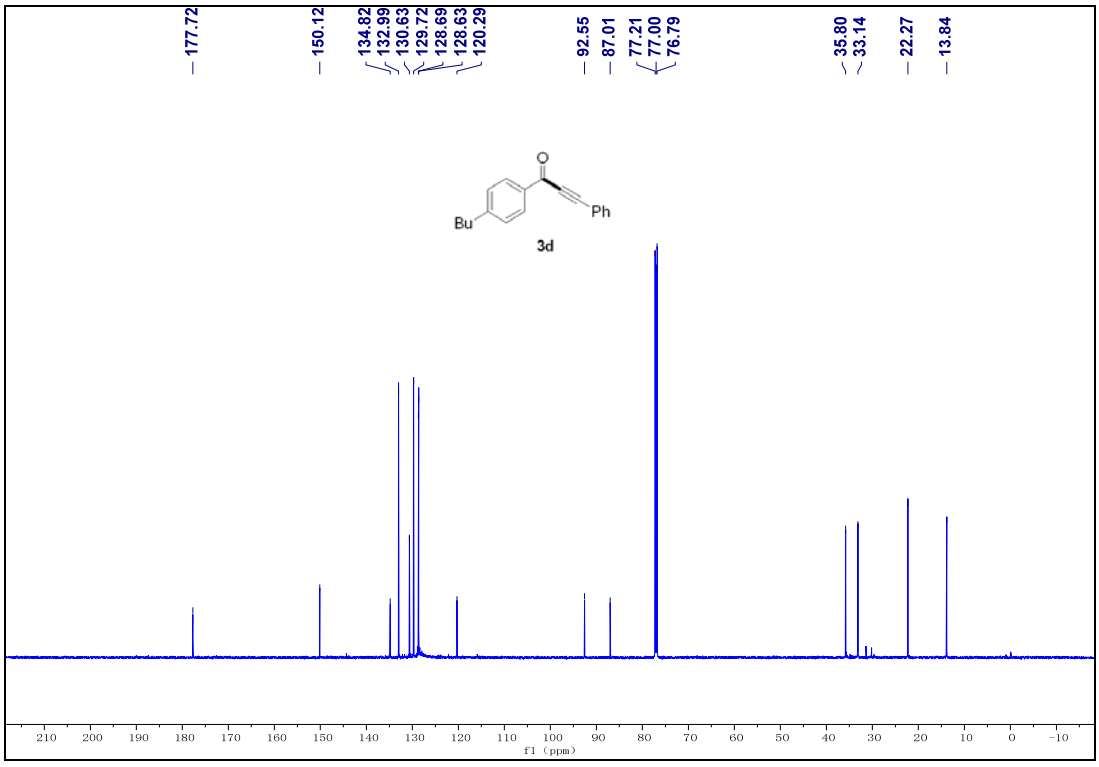


Figure S11. ^{13}C NMR spectrum of **3d** (150 MHz, $CDCl_3$, 298 K).

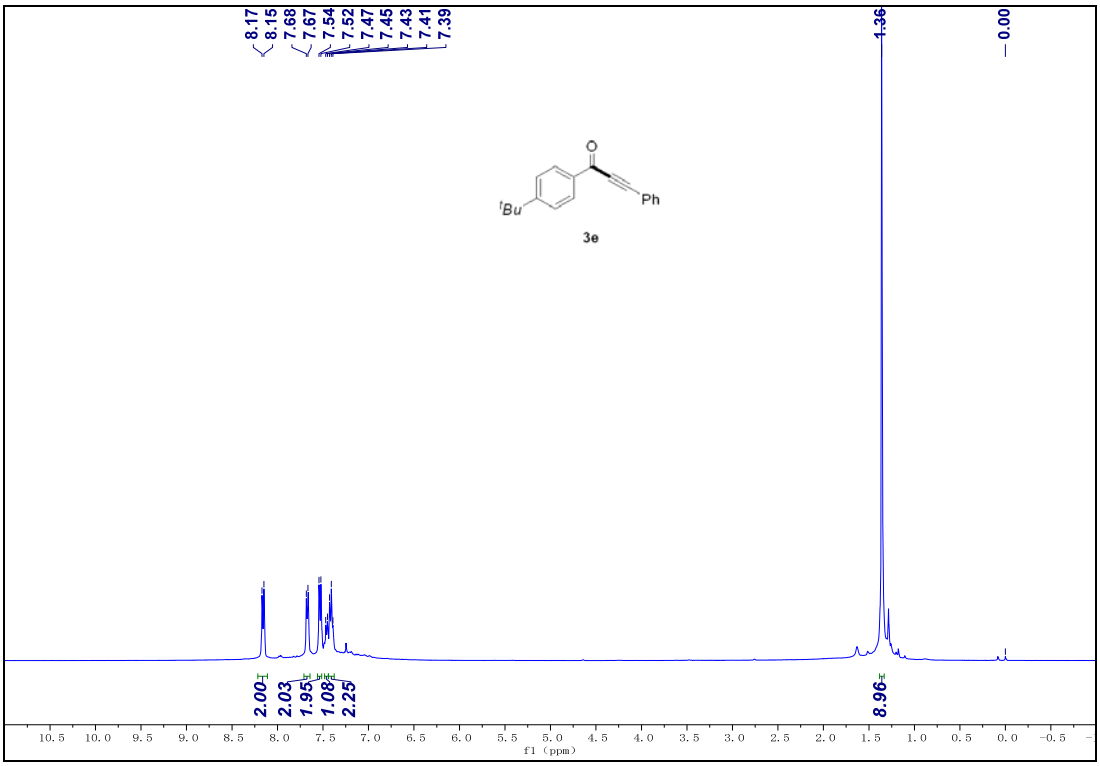


Figure S12. ^{1}H NMR spectrum of **3e** (400 MHz, $CDCl_3$, 298 K).

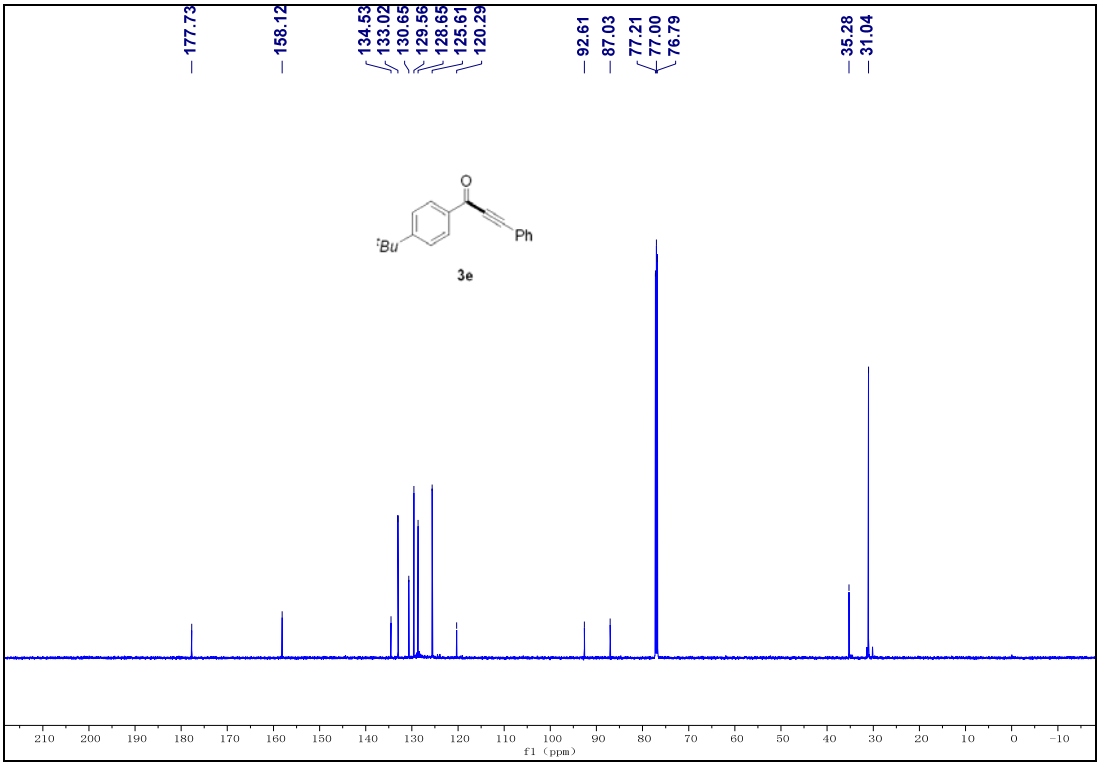


Figure S13. ^{13}C NMR spectrum of **3e** (150 MHz, $CDCl_3$, 298 K).

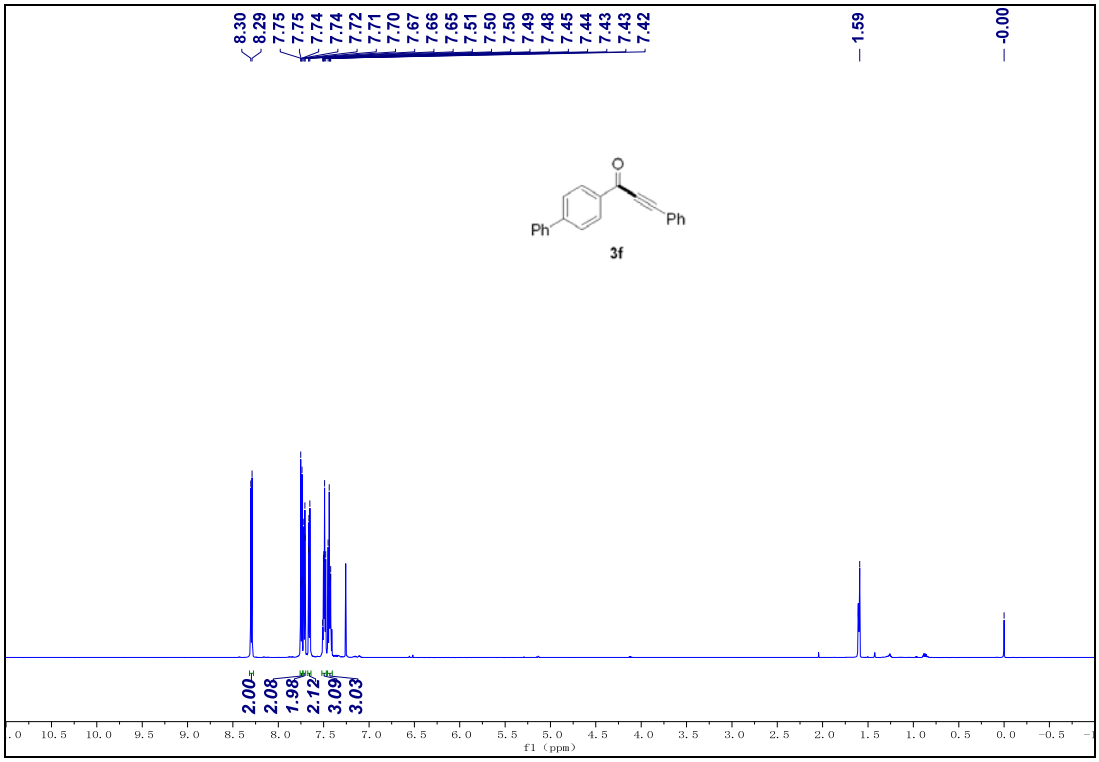


Figure S14. ^{1}H NMR spectrum of **3f** (600 MHz, $CDCl_3$, 298 K).

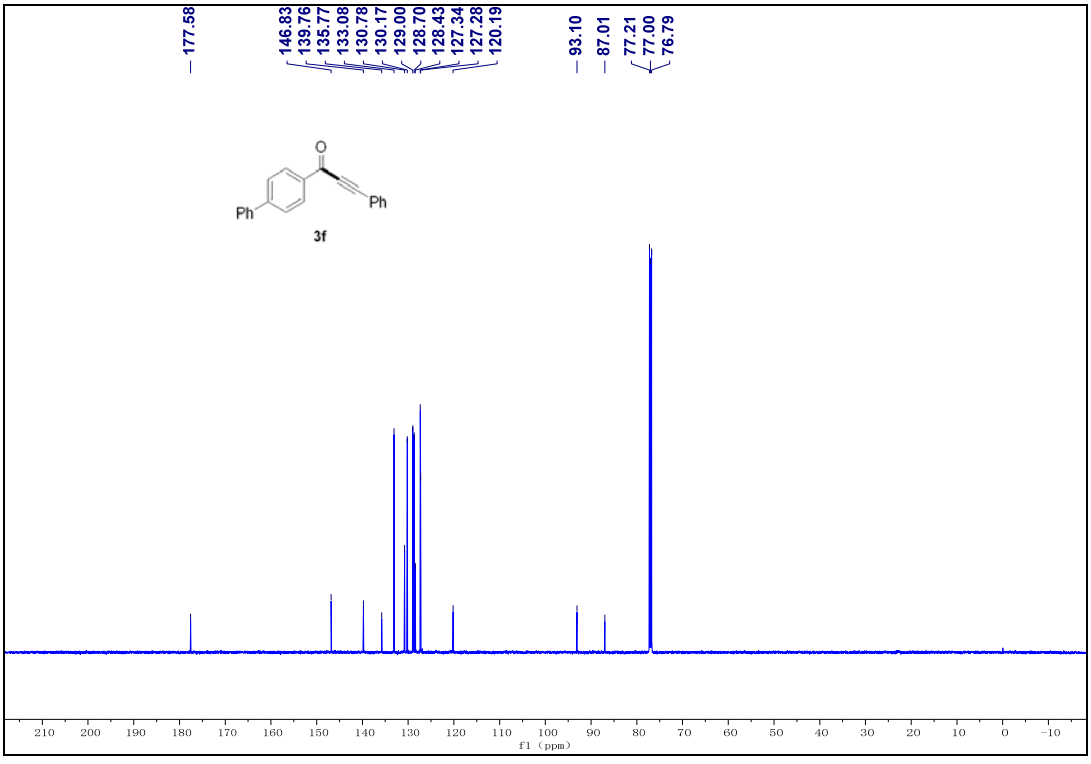


Figure S15. ^{13}C NMR spectrum of **3f** (150 MHz, $CDCl_3$, 298 K).

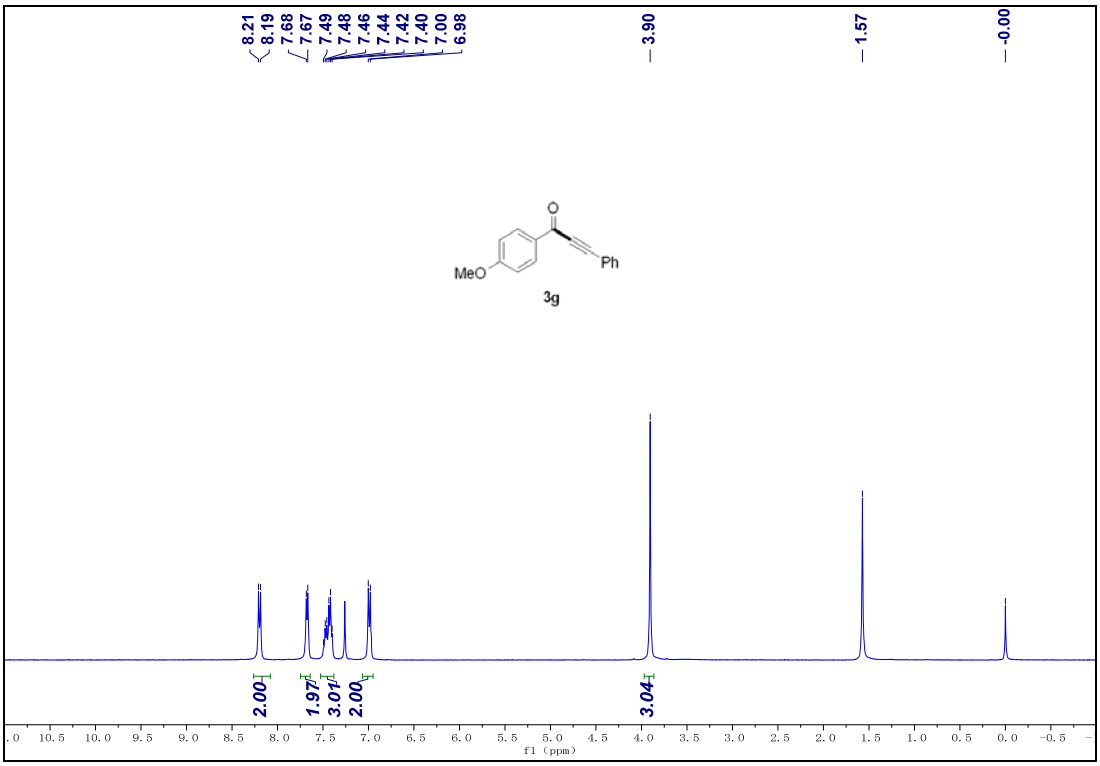


Figure S16. ^{1}H NMR spectrum of **3g** (400 MHz, $CDCl_3$, 298 K).

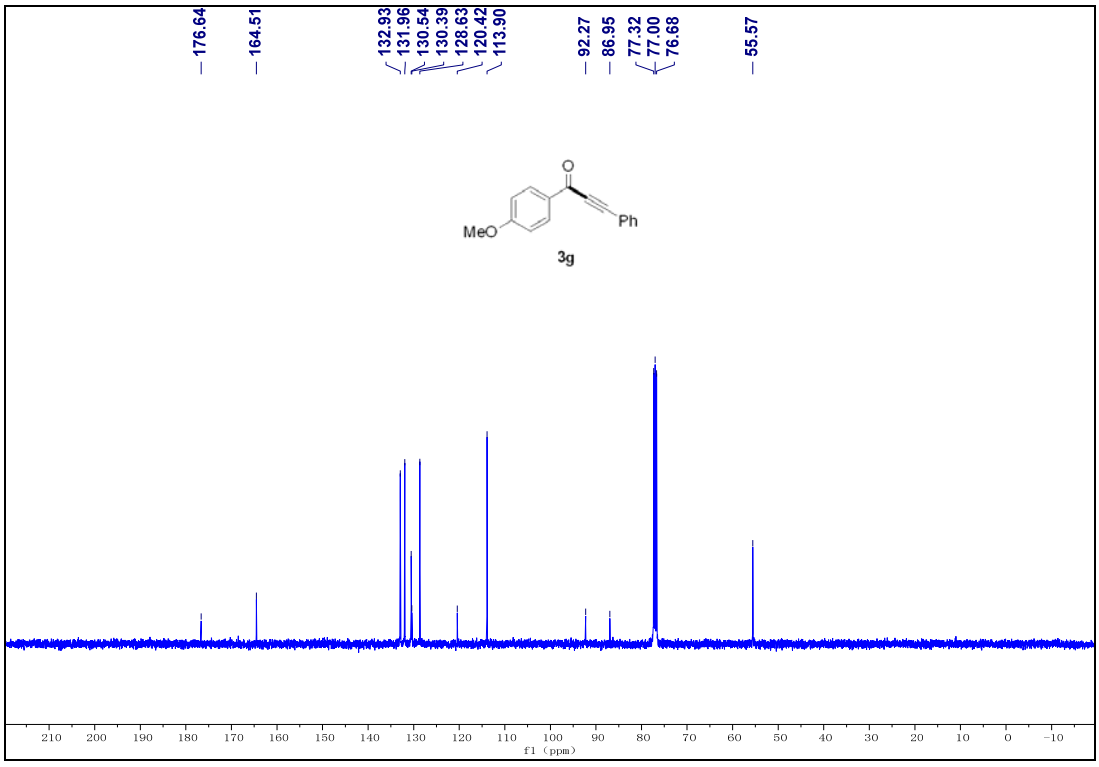


Figure S17. ^{13}C NMR spectrum of **3g** (100 MHz, $CDCl_3$, 298 K).

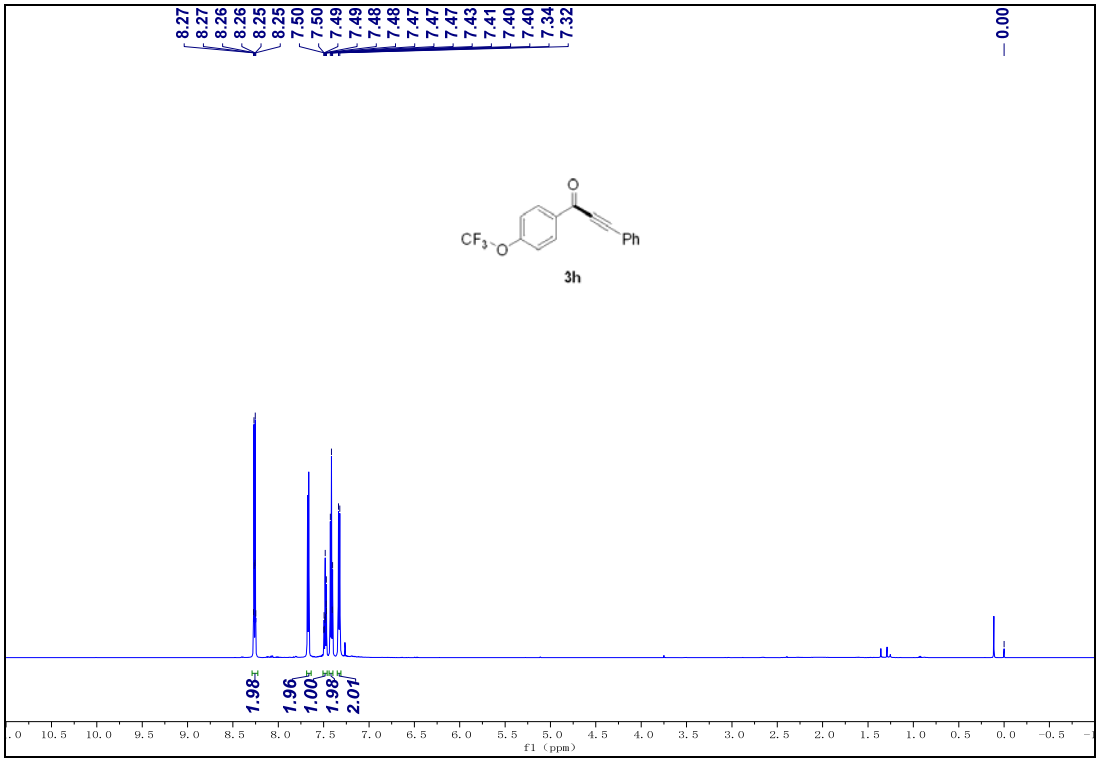


Figure S18. ^{1}H NMR spectrum of **3h** (600 MHz, $CDCl_3$, 298 K).

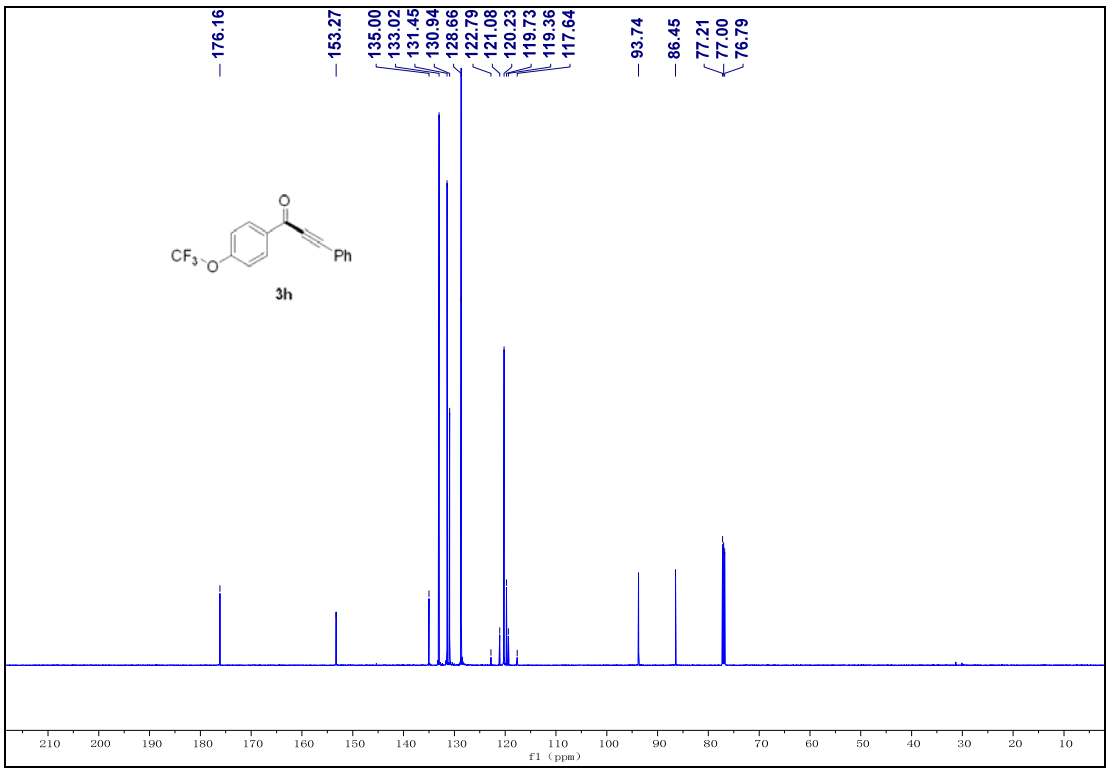


Figure S19. ^{13}C NMR spectrum of **3h** (150 MHz, $CDCl_3$, 298 K).

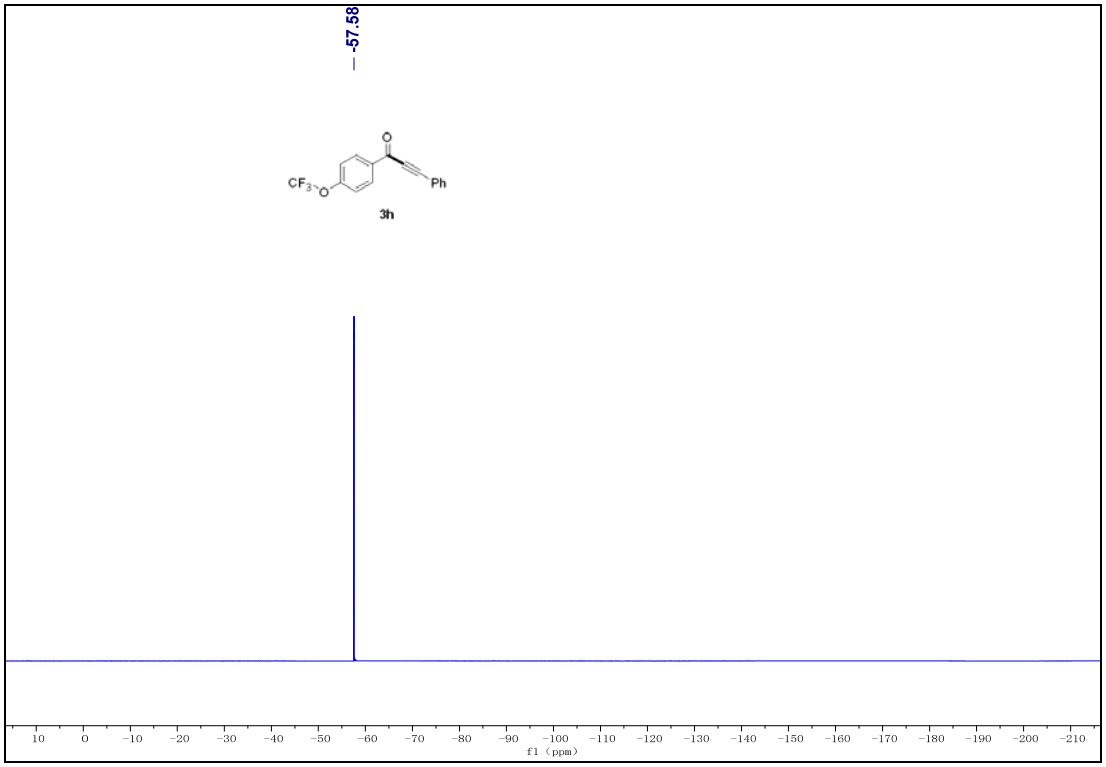


Figure S20. ^{19}F NMR spectrum of **3h** (565 MHz, $CDCl_3$, 298 K).

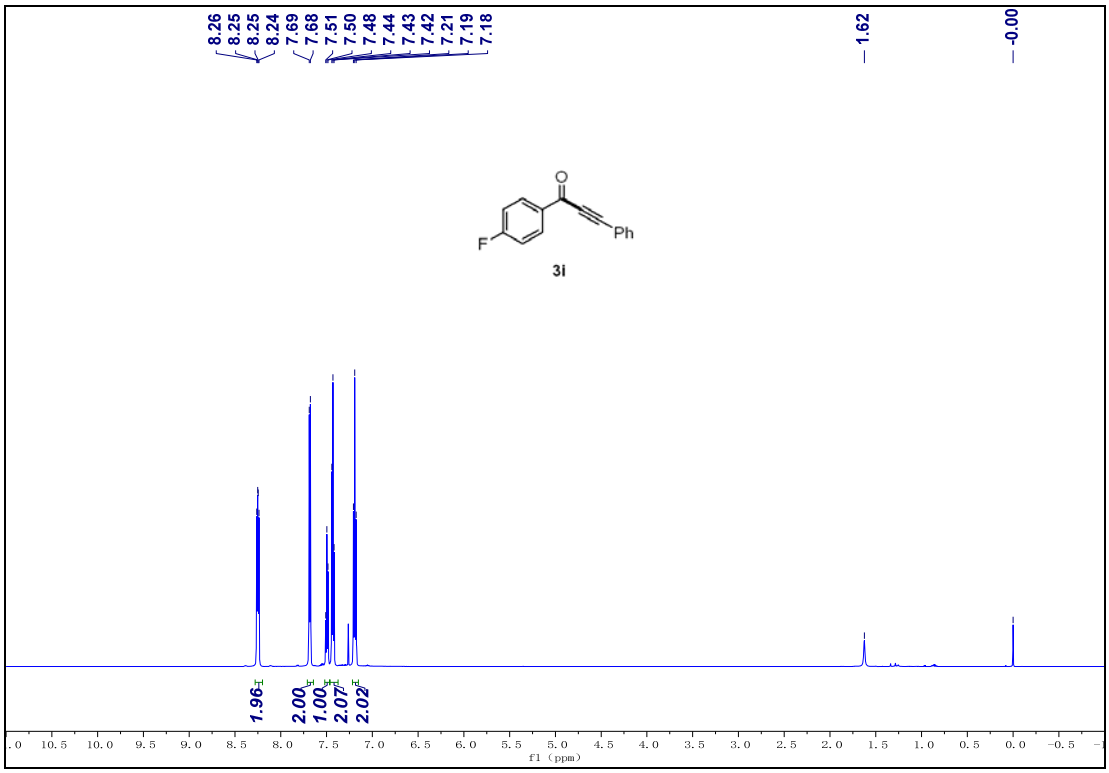


Figure S21. ^{1}H NMR spectrum of **3i** (600 MHz, $CDCl_3$, 298 K).

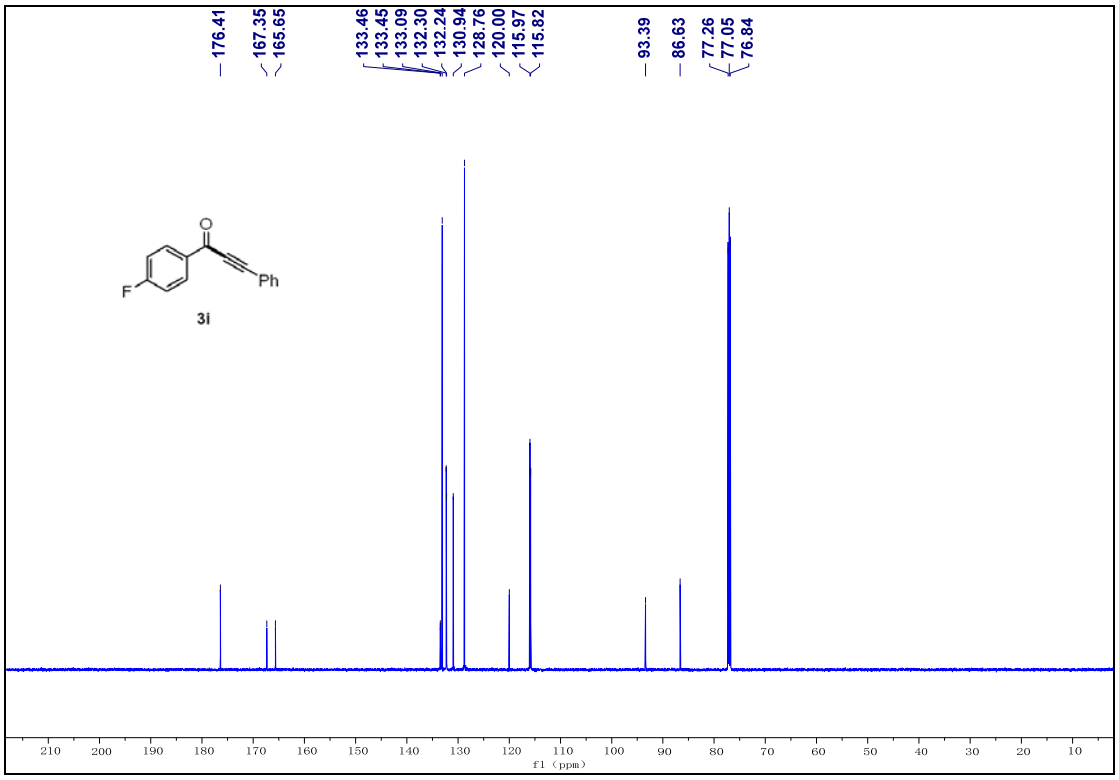


Figure S22. ^{13}C NMR spectrum of **3i** (150 MHz, $CDCl_3$, 298 K).

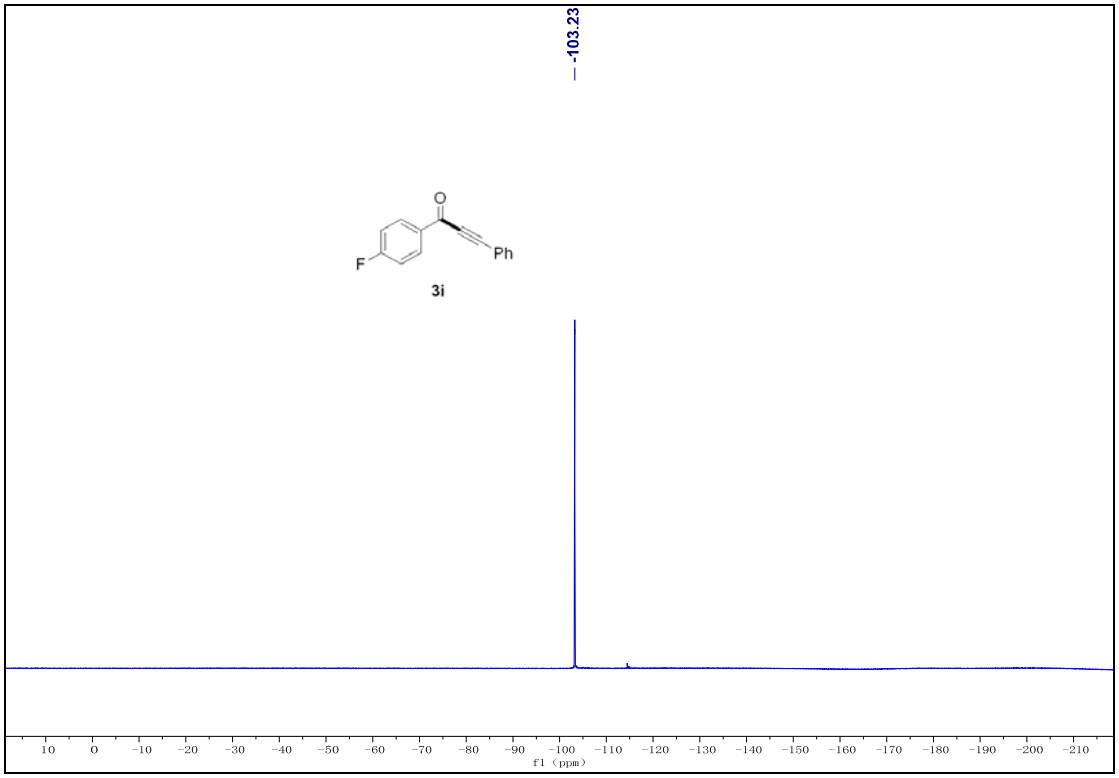


Figure S23. ^{19}F NMR spectrum of **3i** (376 MHz, $CDCl_3$, 298 K).

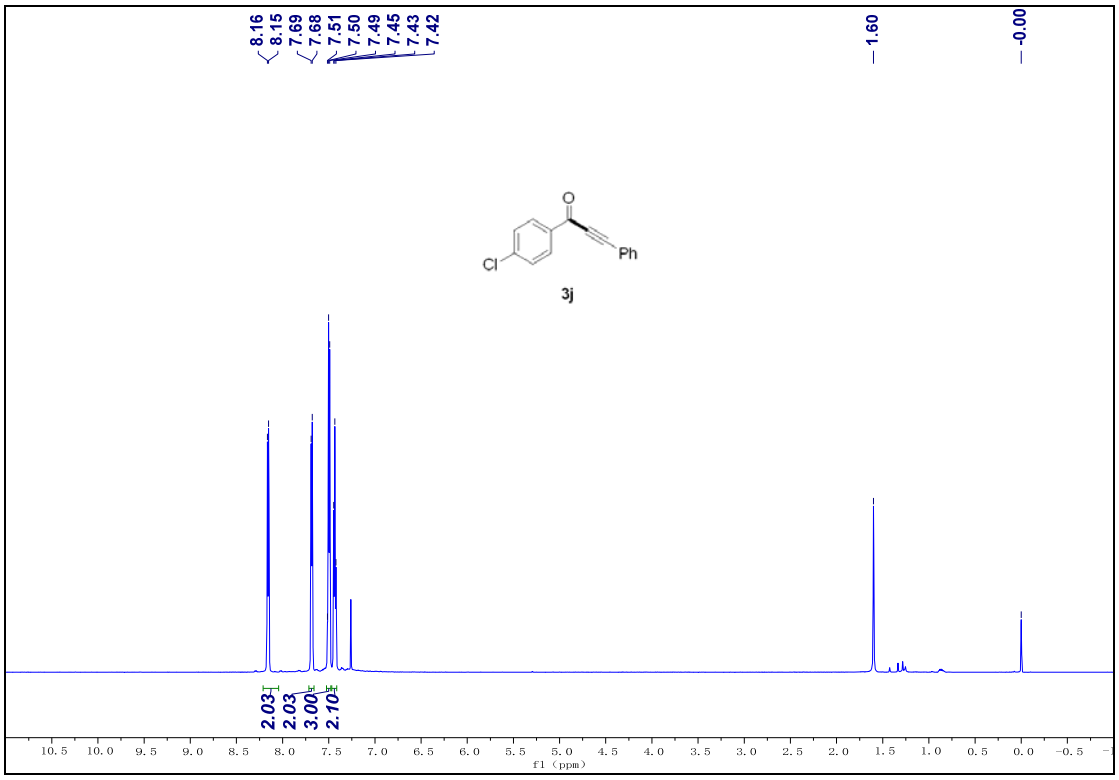


Figure S24. ^{1}H NMR spectrum of **3j** (600 MHz, $CDCl_3$, 298 K).

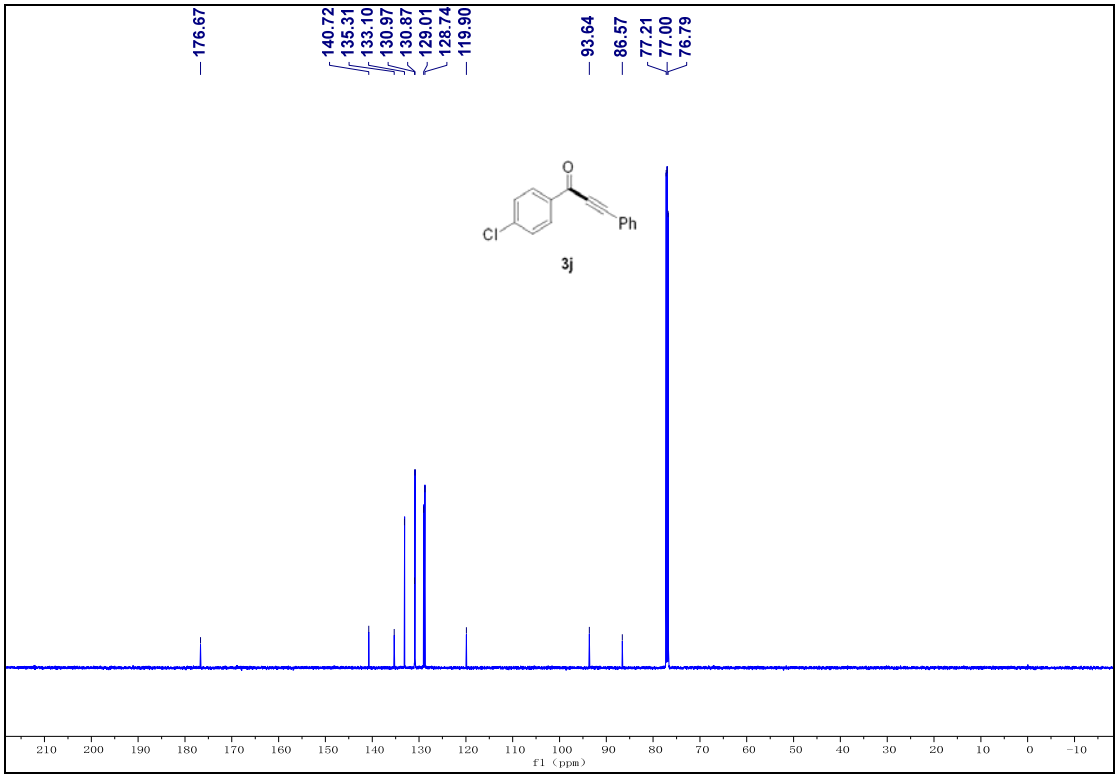


Figure S25. ^{13}C NMR spectrum of **3j** (150 MHz, $CDCl_3$, 298 K).

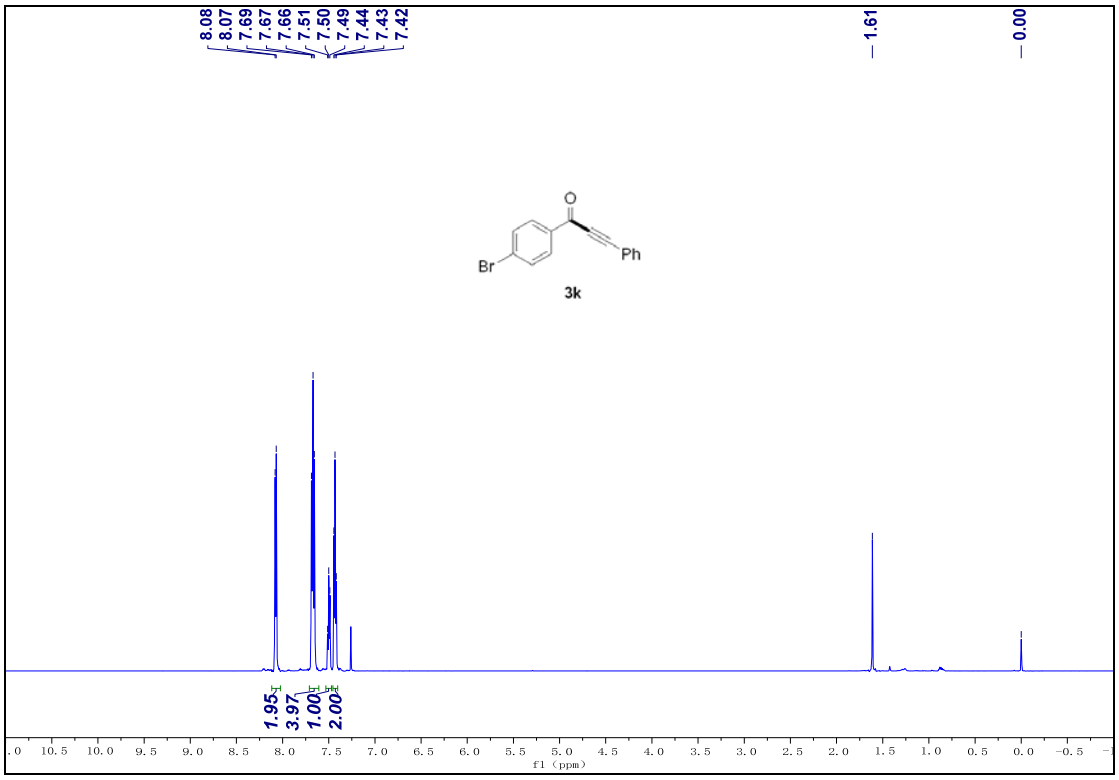


Figure S26. ^{1}H NMR spectrum of **3k** (600 MHz, $CDCl_3$, 298 K).

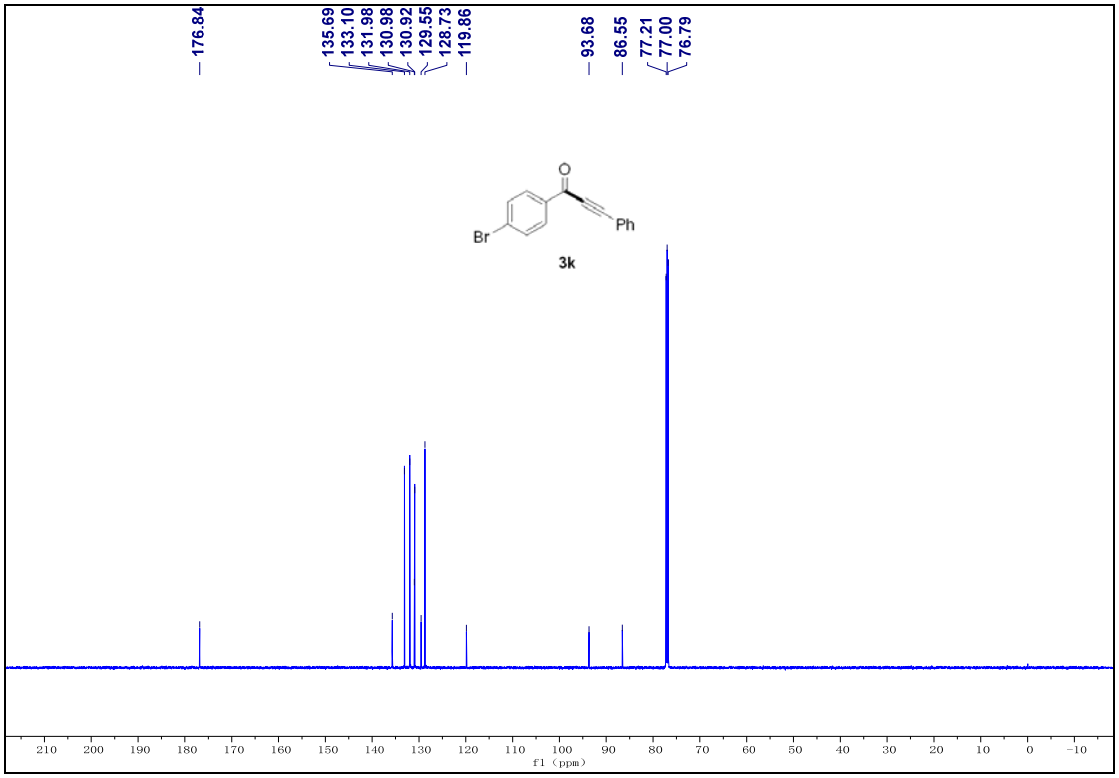


Figure S27. ^{13}C NMR spectrum of **3k** (150 MHz, $CDCl_3$, 298 K).

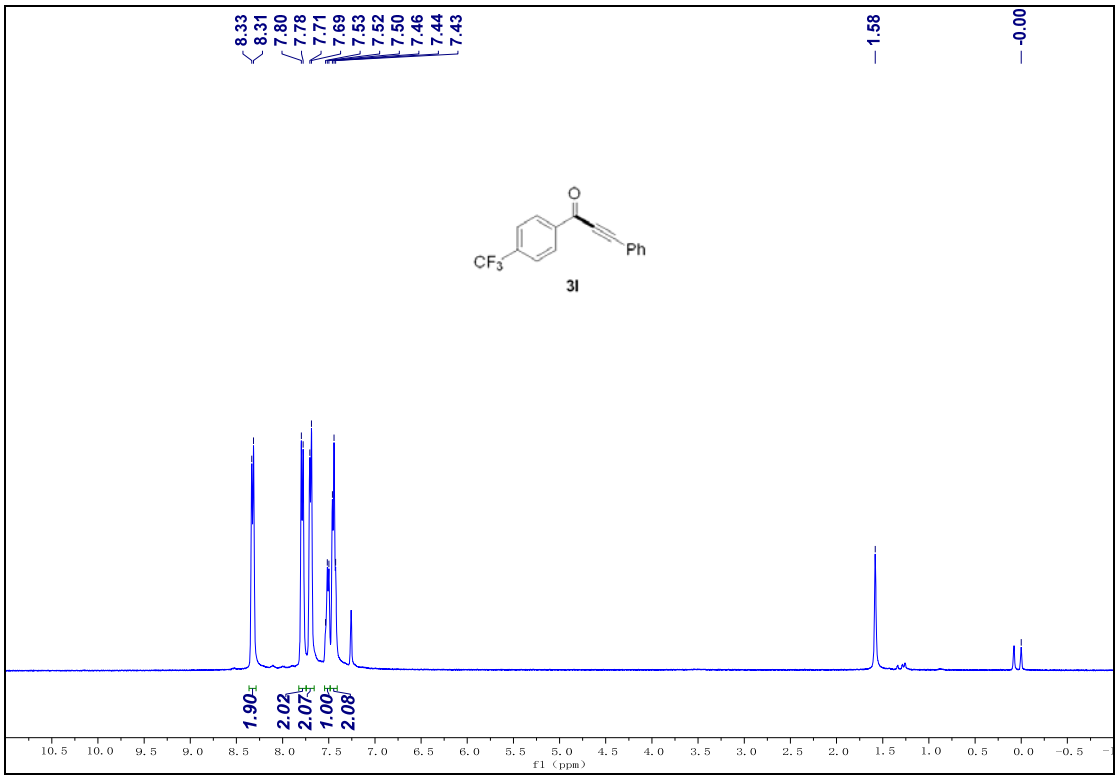


Figure S28. ^{1}H NMR spectrum of **3l** (400 MHz, $CDCl_3$, 298 K).

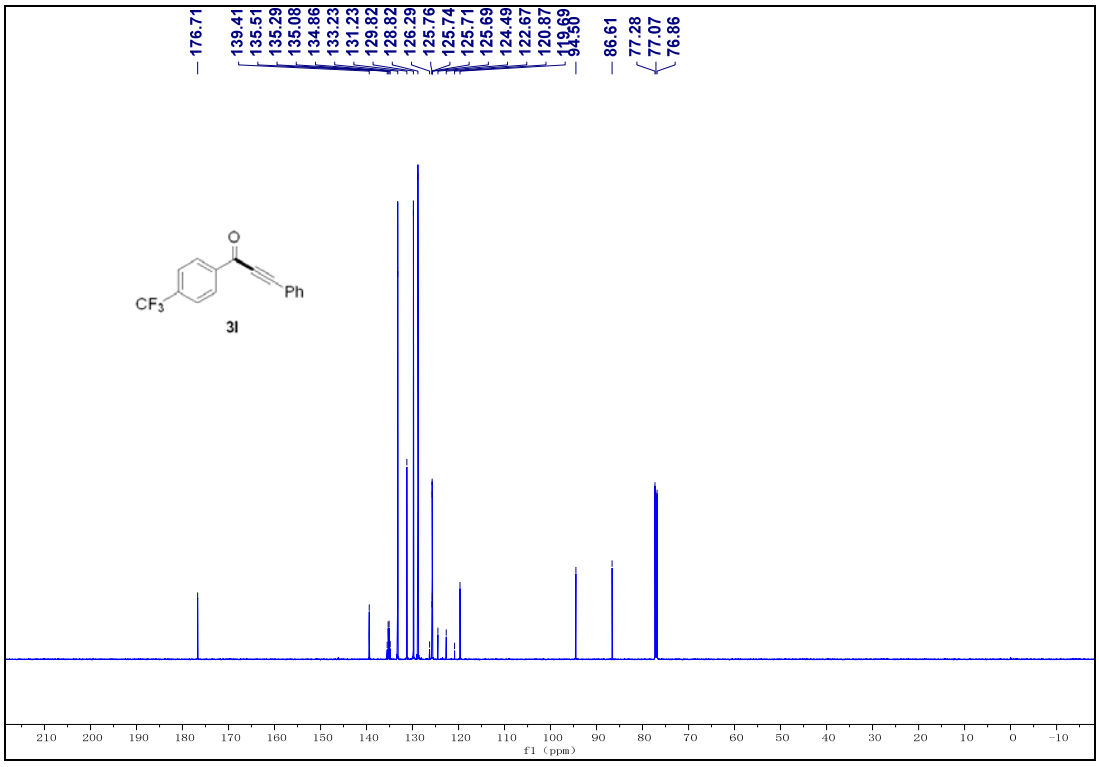


Figure S29. ^{13}C NMR spectrum of **3l** (150 MHz, $CDCl_3$, 298 K).

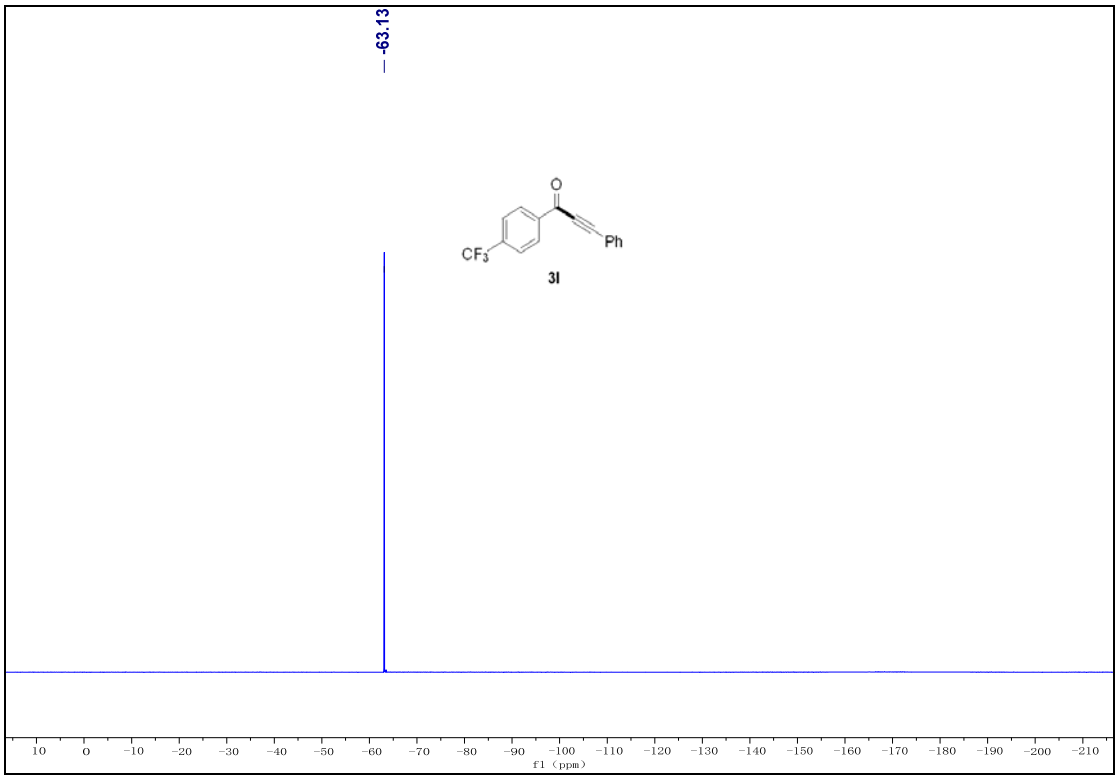


Figure S30. ^{19}F NMR spectrum of **3l** (565 MHz, $CDCl_3$, 298 K).

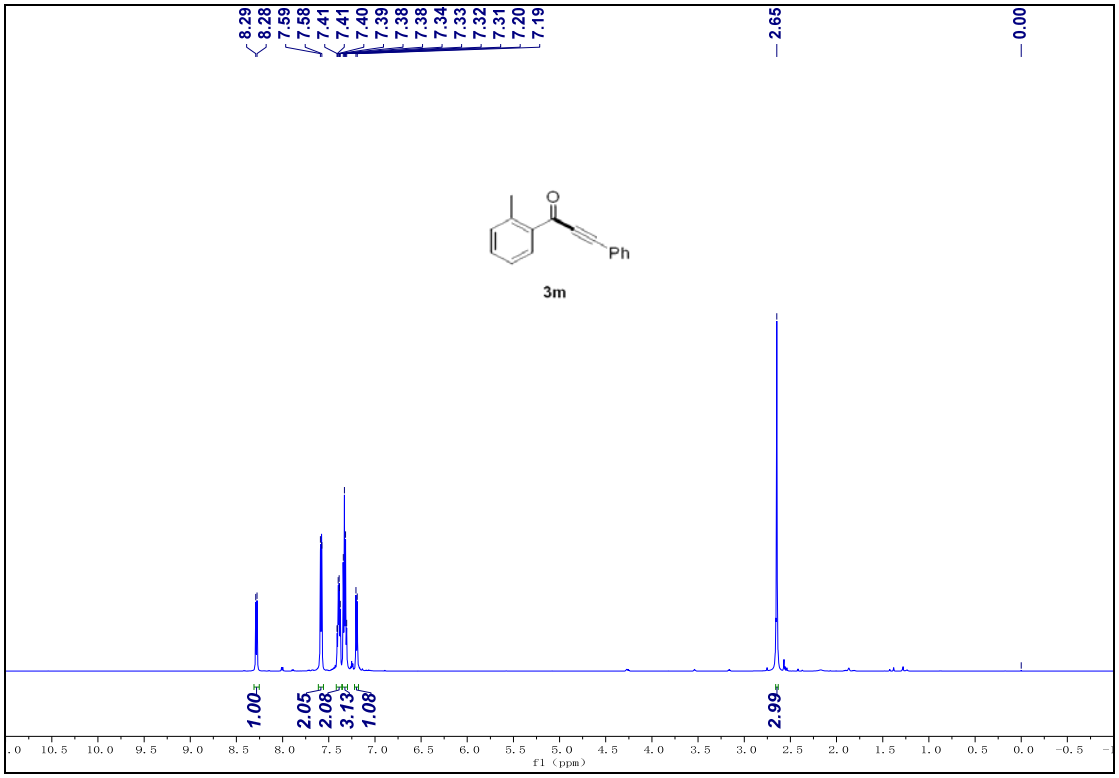


Figure S31. ^{1}H NMR spectrum of **3m** (600 MHz, $CDCl_3$, 298 K).

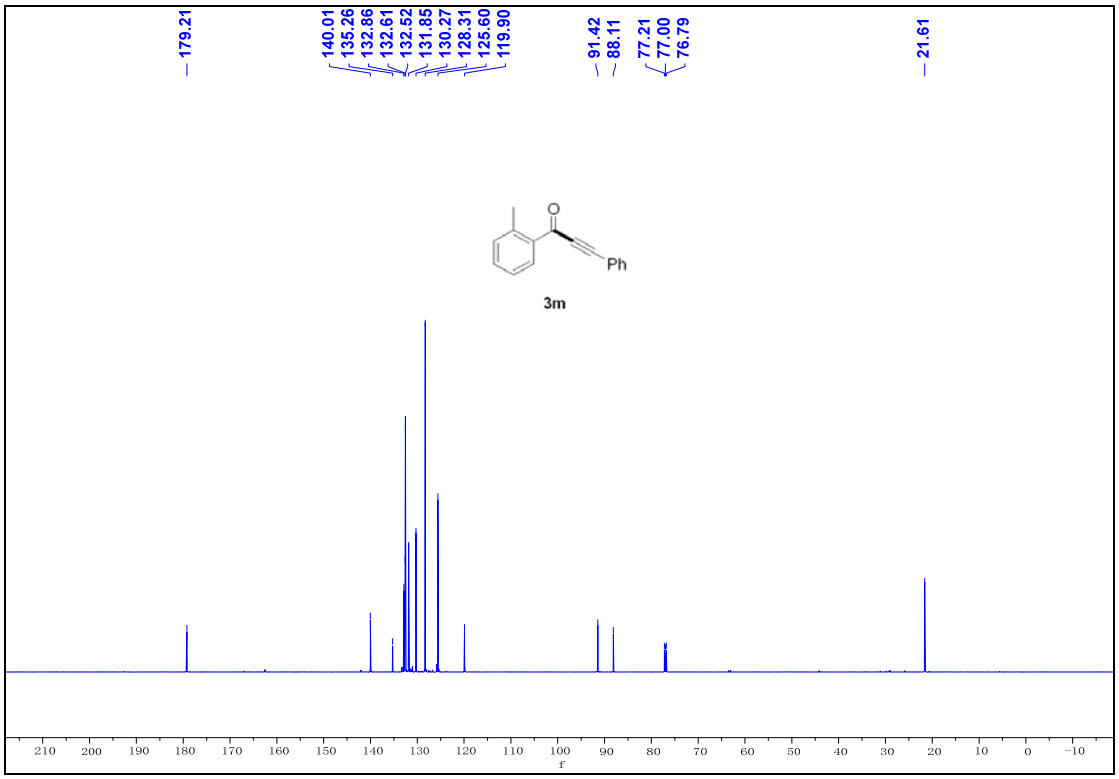


Figure S32. ^{13}C NMR spectrum of **3m** (150 MHz, $CDCl_3$, 298 K).

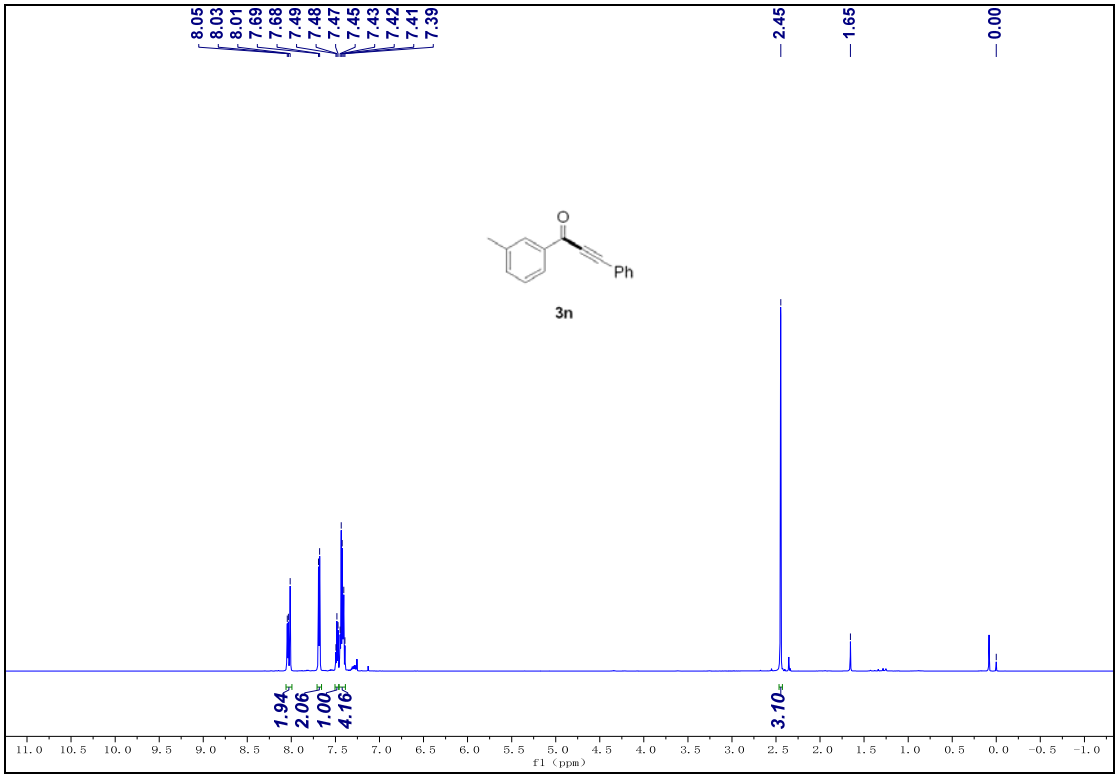


Figure S33. ^{1}H NMR spectrum of **3n** (600 MHz, $CDCl_3$, 298 K).

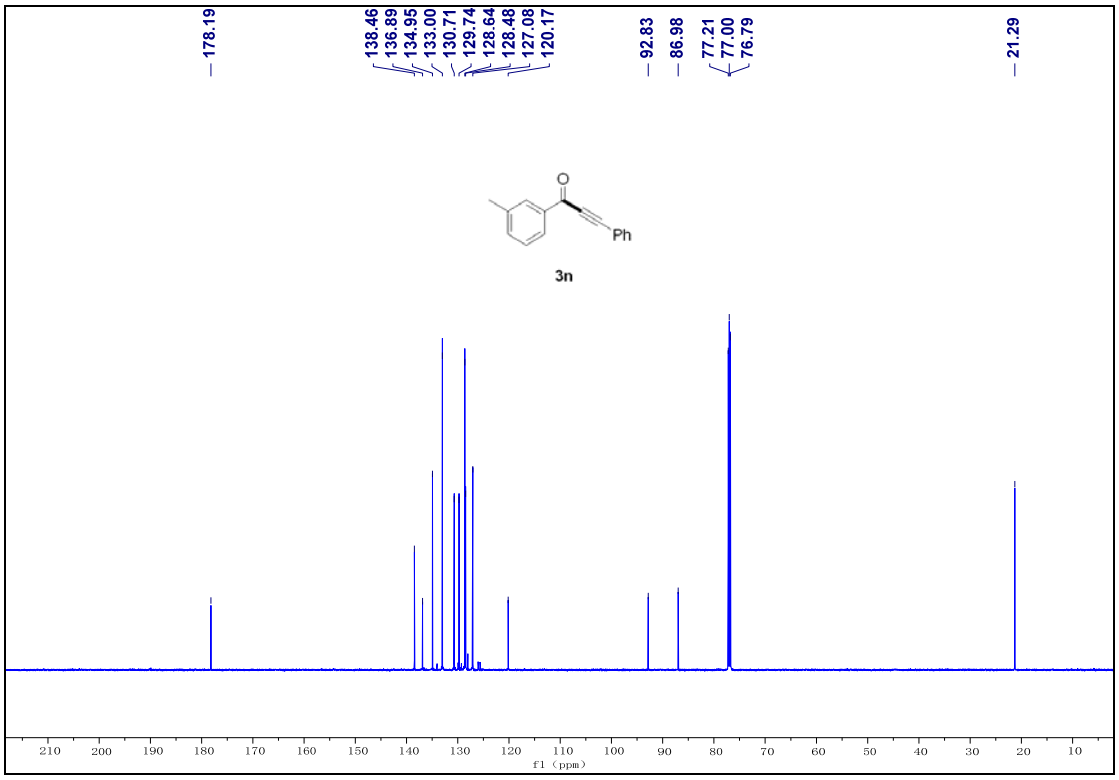


Figure S34. ^{13}C NMR spectrum of **3n** (150 MHz, $CDCl_3$, 298 K).

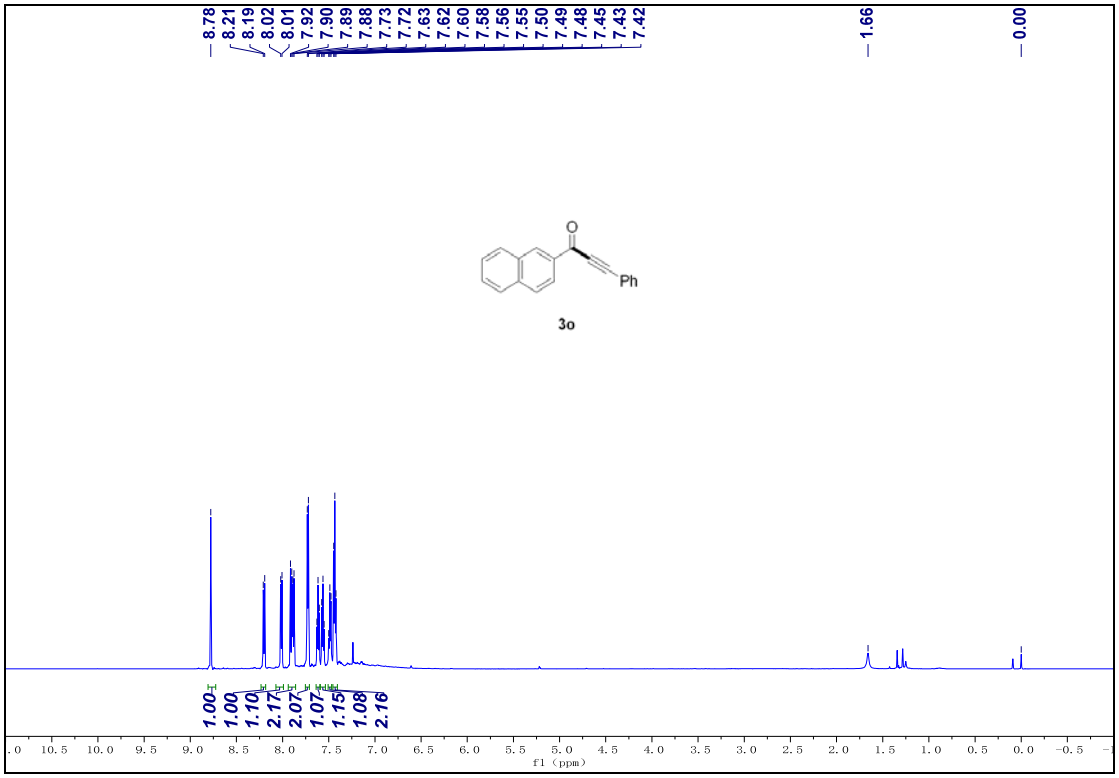


Figure S35. ^{1}H NMR spectrum of **3o** (600 MHz, $CDCl_3$, 298 K).

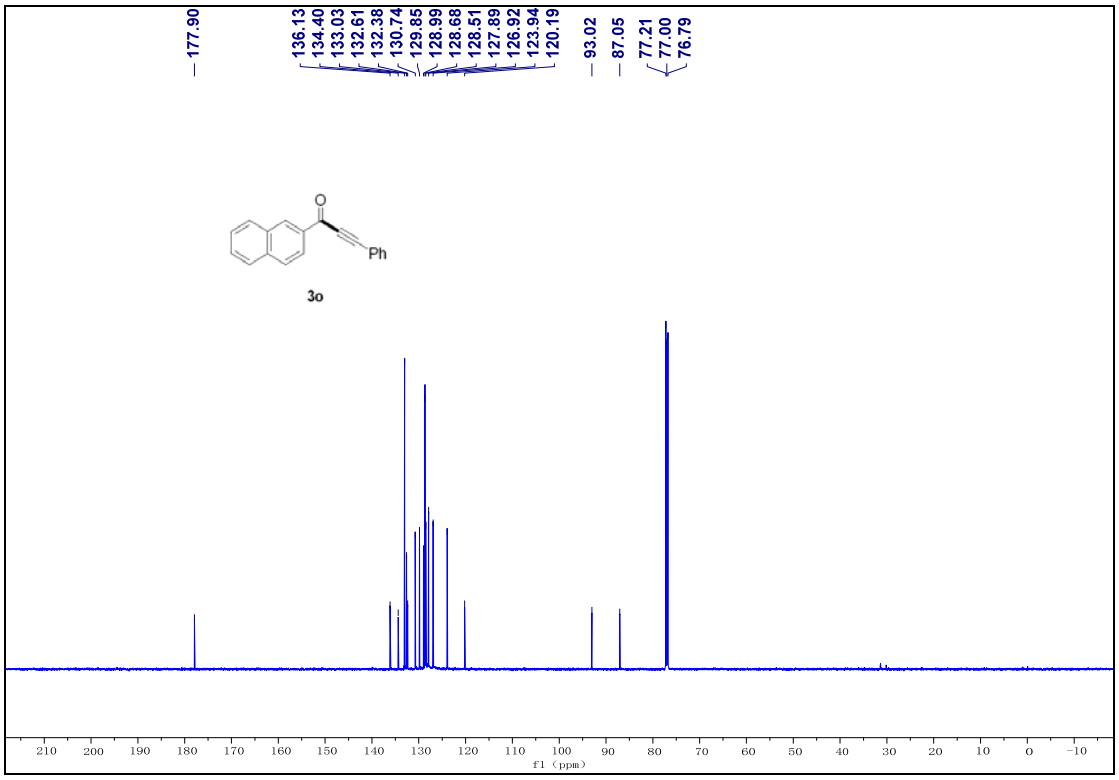


Figure S36. ^{13}C NMR spectrum of **3o** (150 MHz, $CDCl_3$, 298 K).

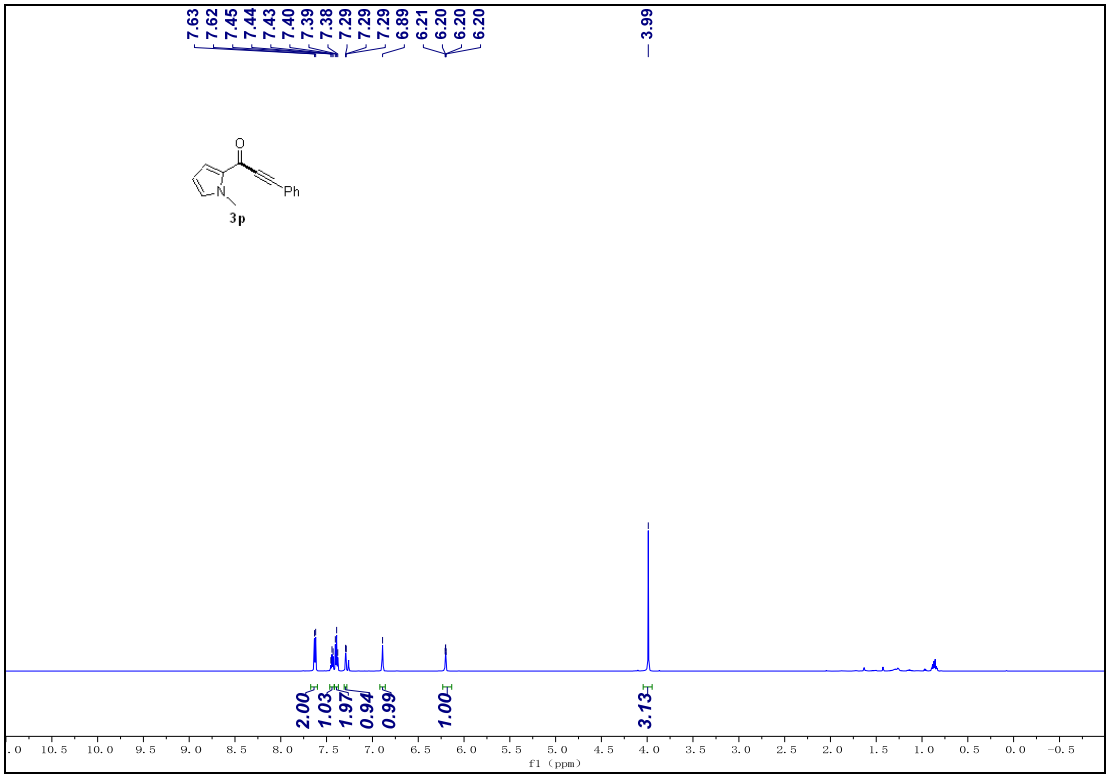


Figure S37. ^{1}H NMR spectrum of **3p** (600 MHz, $CDCl_3$, 298 K).

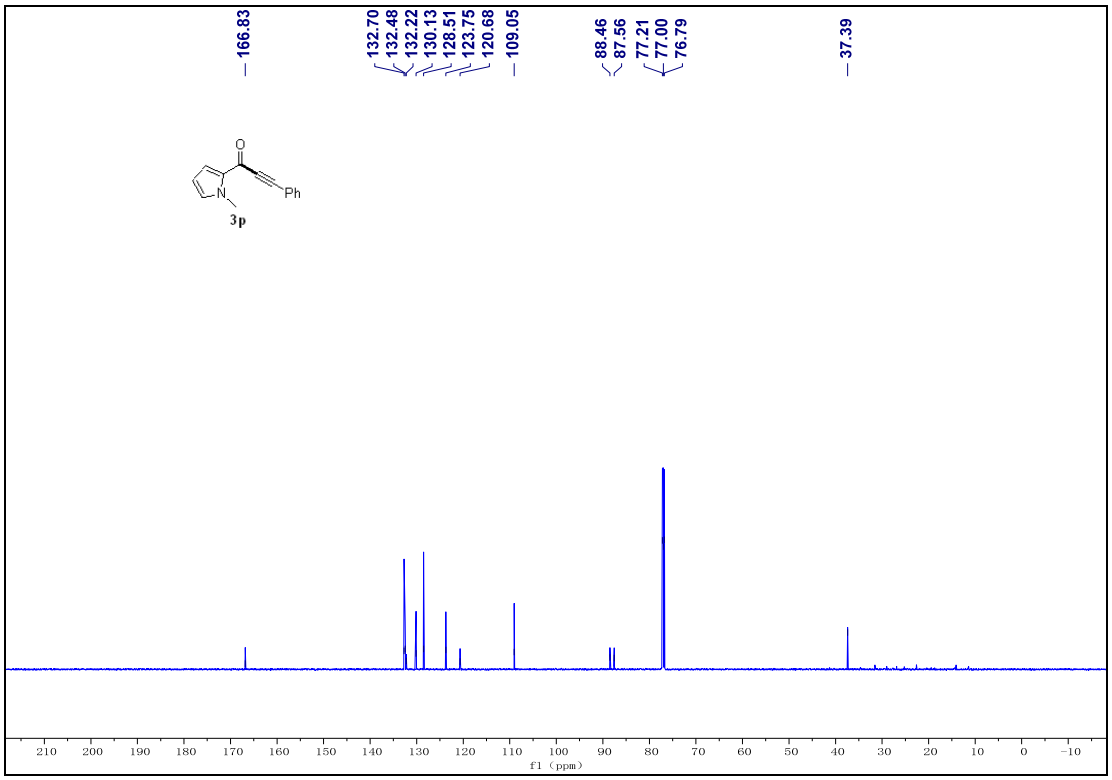


Figure S38. ^{13}C NMR spectrum of **3p** (150 MHz, $CDCl_3$, 298 K).

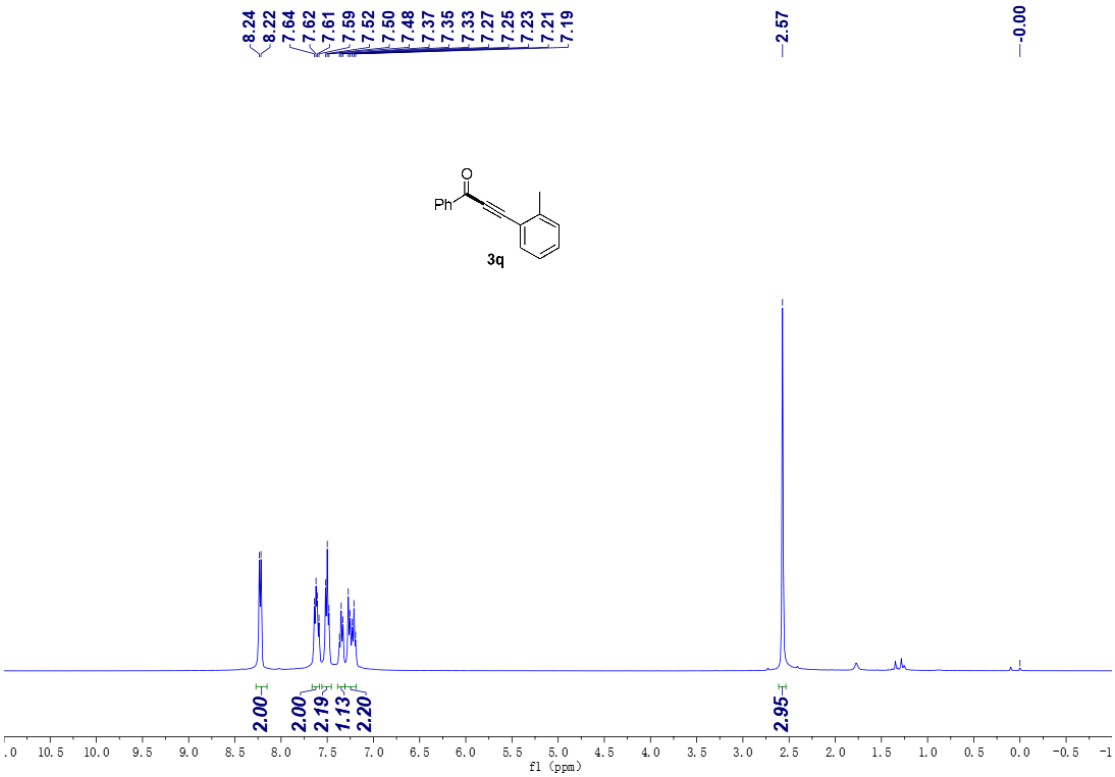


Figure S39. ^{1}H NMR spectrum of **3q** (400 MHz, $CDCl_3$, 298 K).

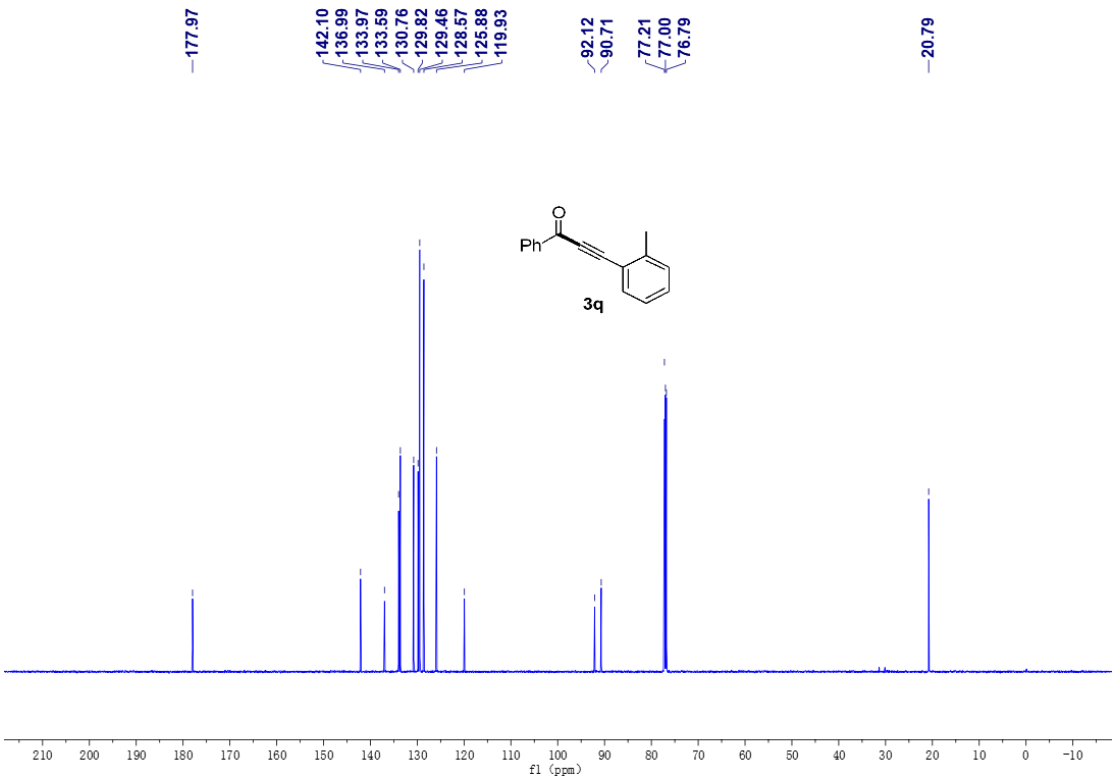


Figure S40. ^{13}C NMR spectrum of **3q** (150 MHz, $CDCl_3$, 298 K).

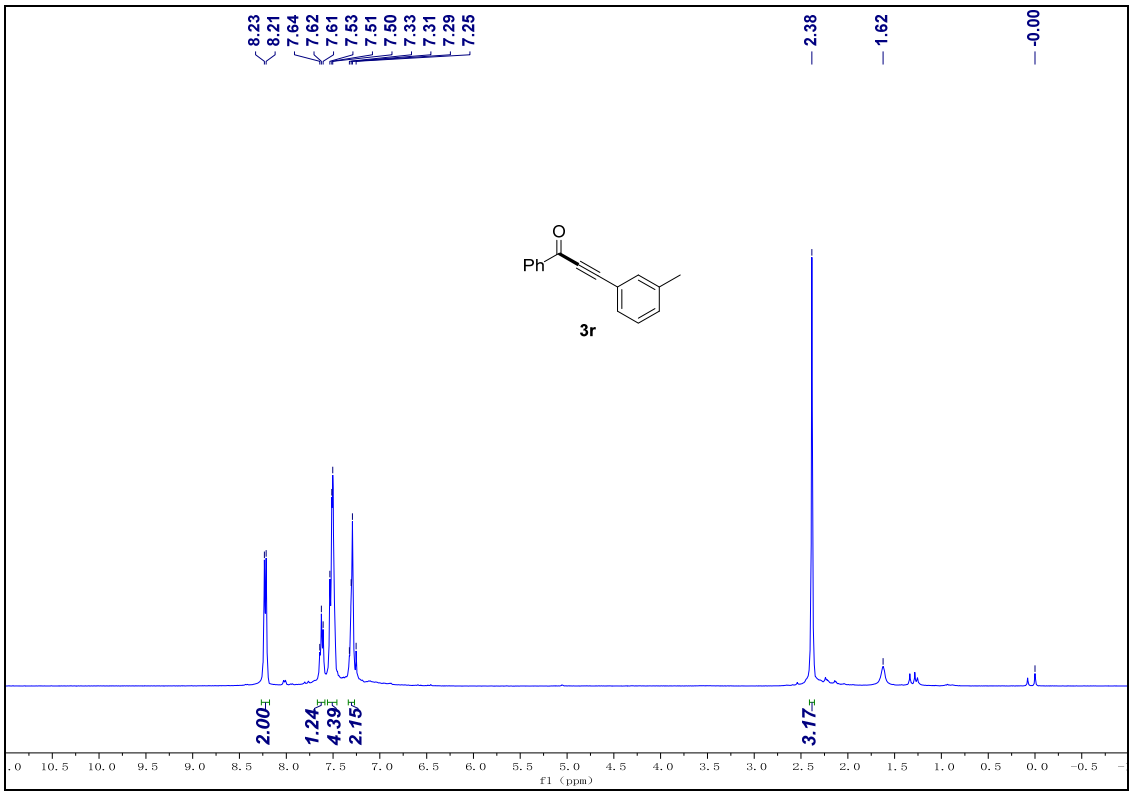


Figure S41. ^{1}H NMR spectrum of **3r** (400 MHz, $CDCl_3$, 298 K).

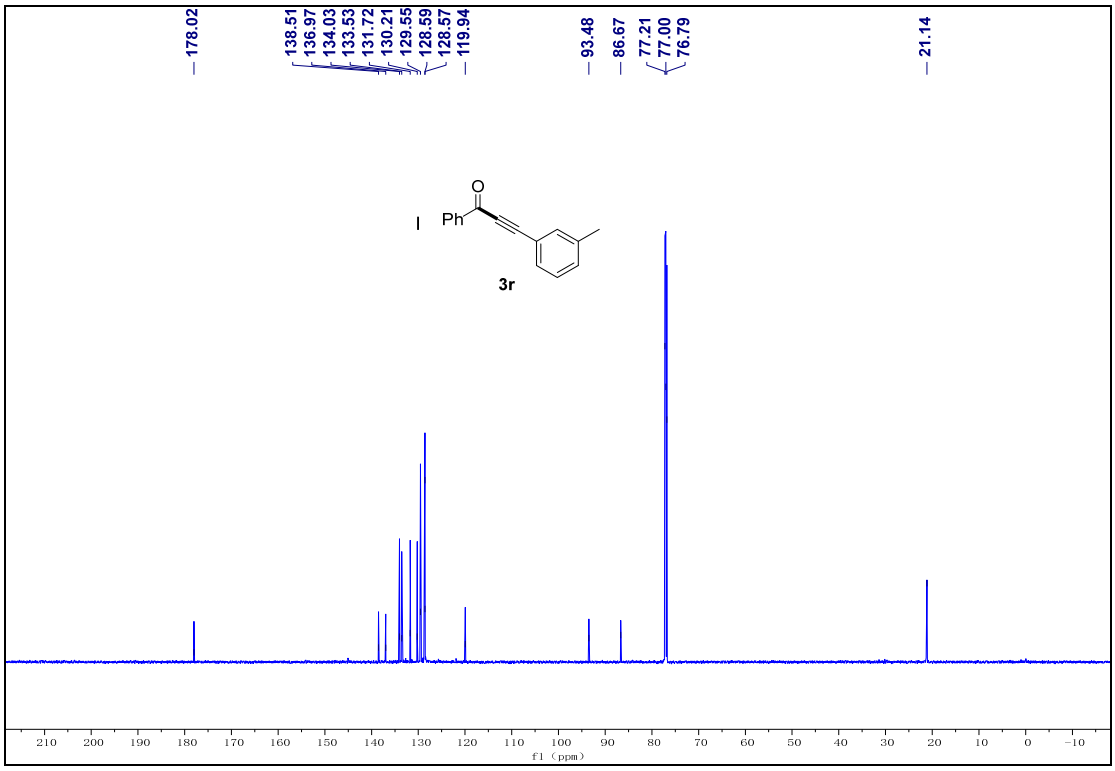


Figure S42. ^{13}C NMR spectrum of **3r** (150 MHz, $CDCl_3$, 298 K).

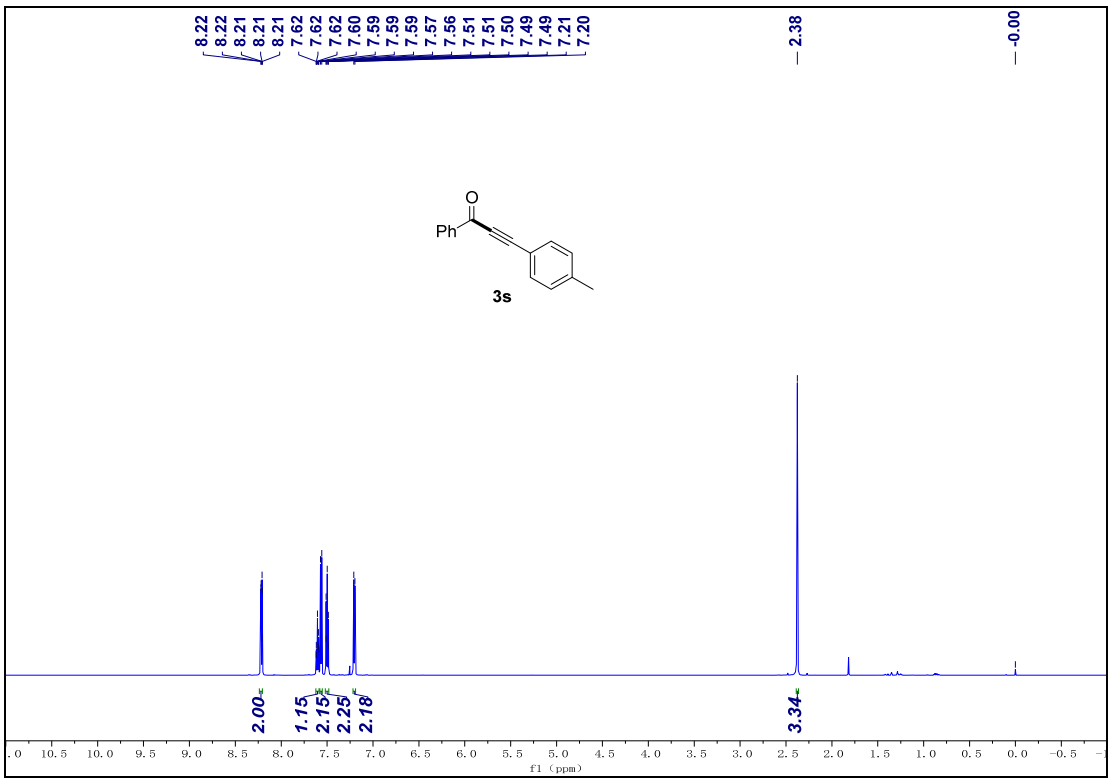


Figure S43. ^{1}H NMR spectrum of **3s** (600 MHz, $CDCl_3$, 298 K).

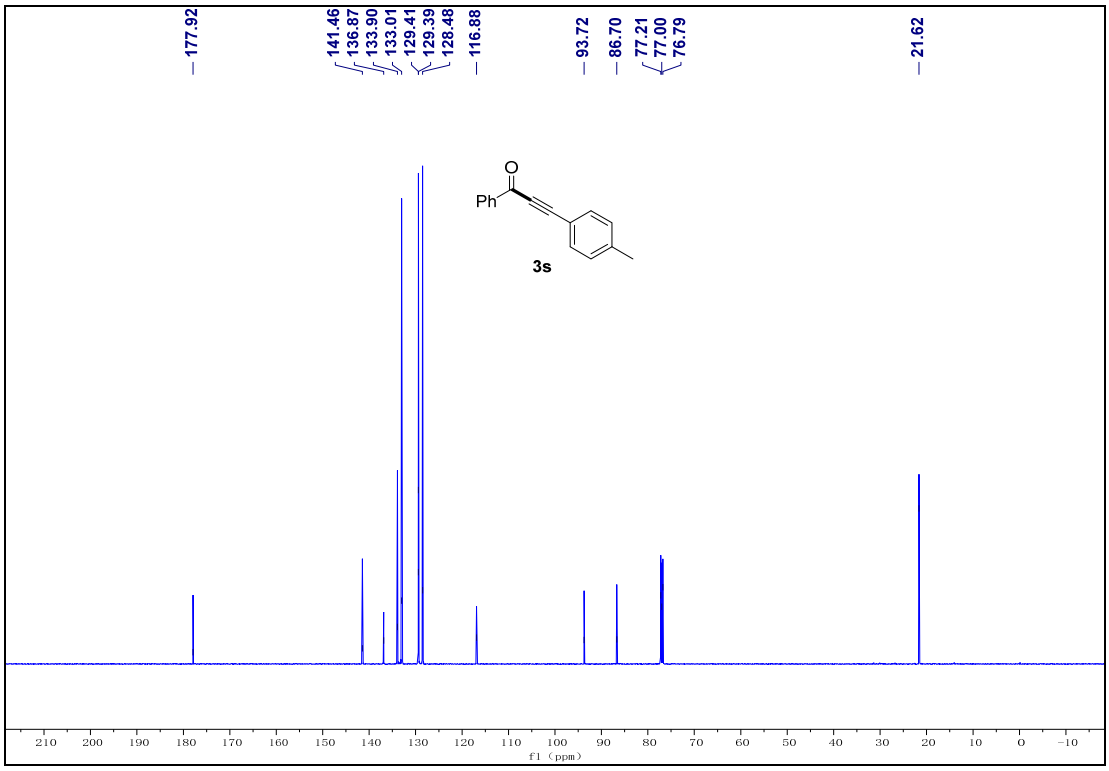


Figure S44. ^{13}C NMR spectrum of **3s** (150 MHz, $CDCl_3$, 298 K).

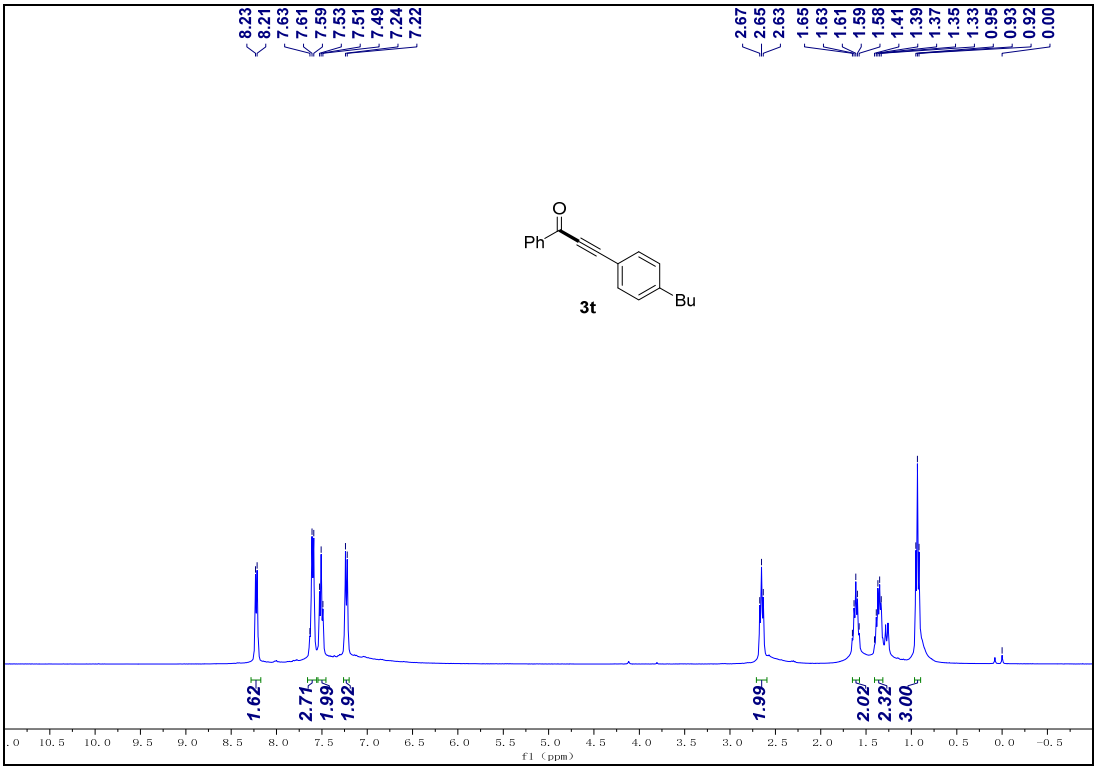


Figure S45. ^{1}H NMR spectrum of **3t** (400 MHz, $CDCl_3$, 298 K).

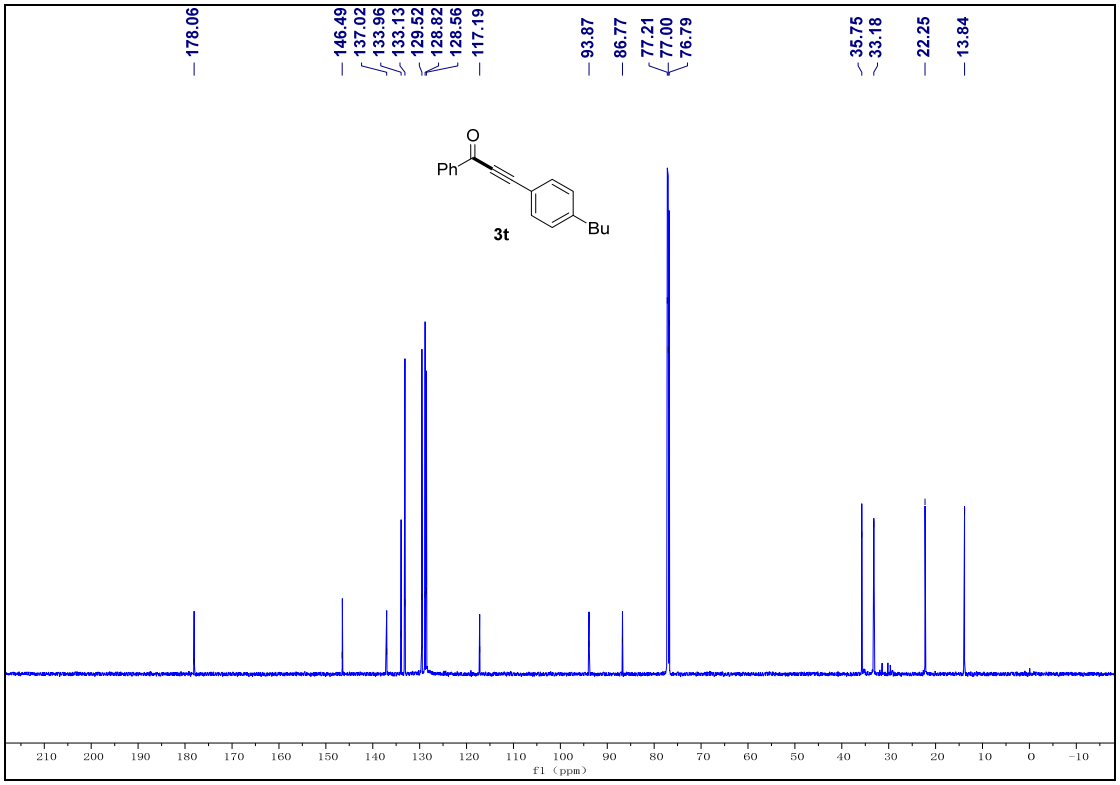


Figure S46. ^{13}C NMR spectrum of **3t** (150 MHz, $CDCl_3$, 298 K).

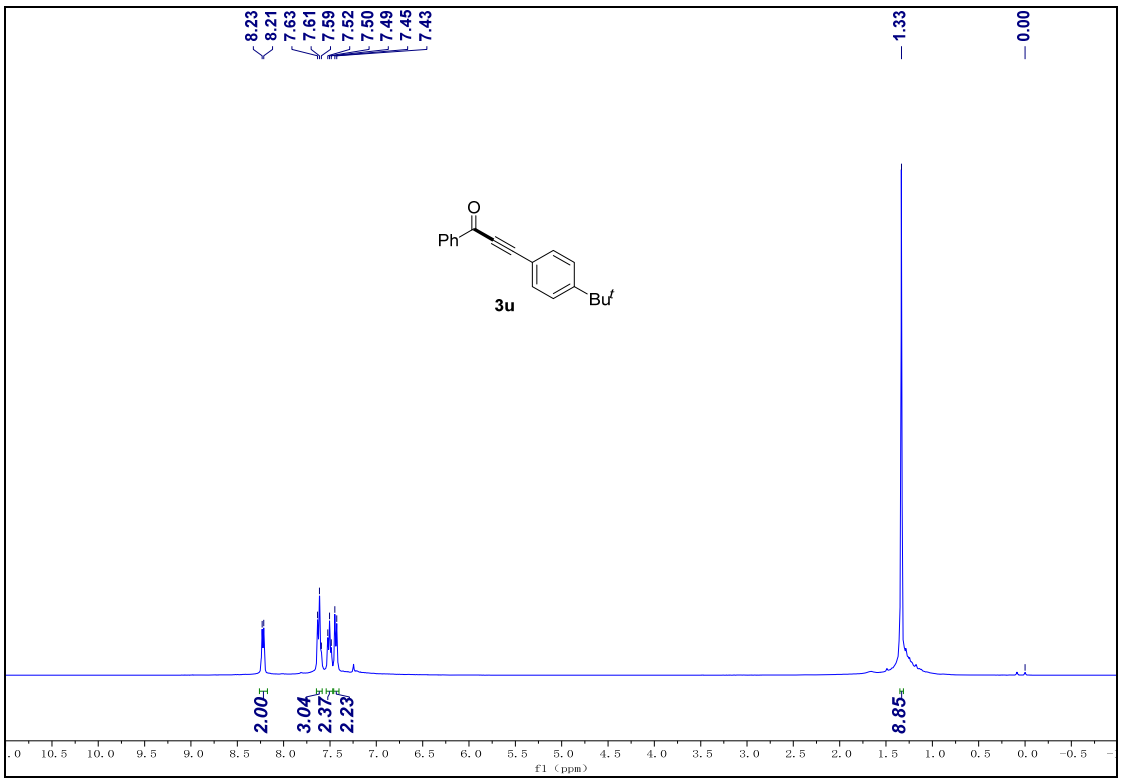


Figure S47. ^{1}H NMR spectrum of **3u** (400 MHz, $CDCl_3$, 298 K).

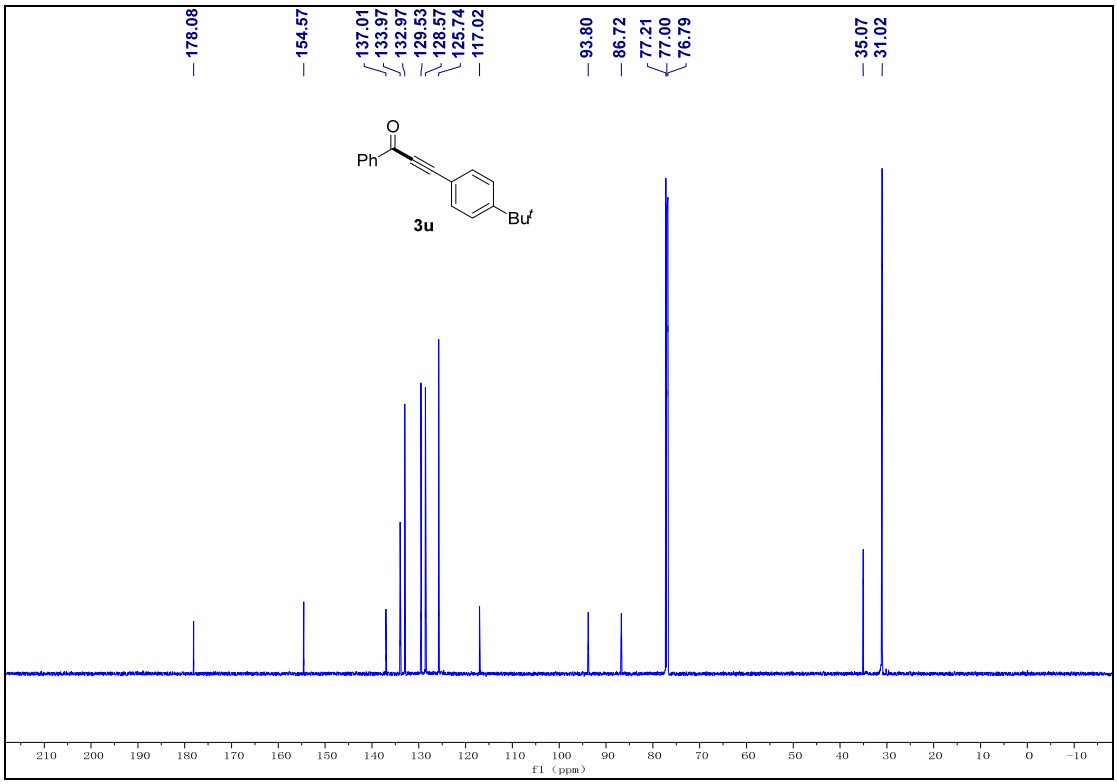


Figure S48. ^{13}C NMR spectrum of **3u** (150 MHz, $CDCl_3$, 298 K).

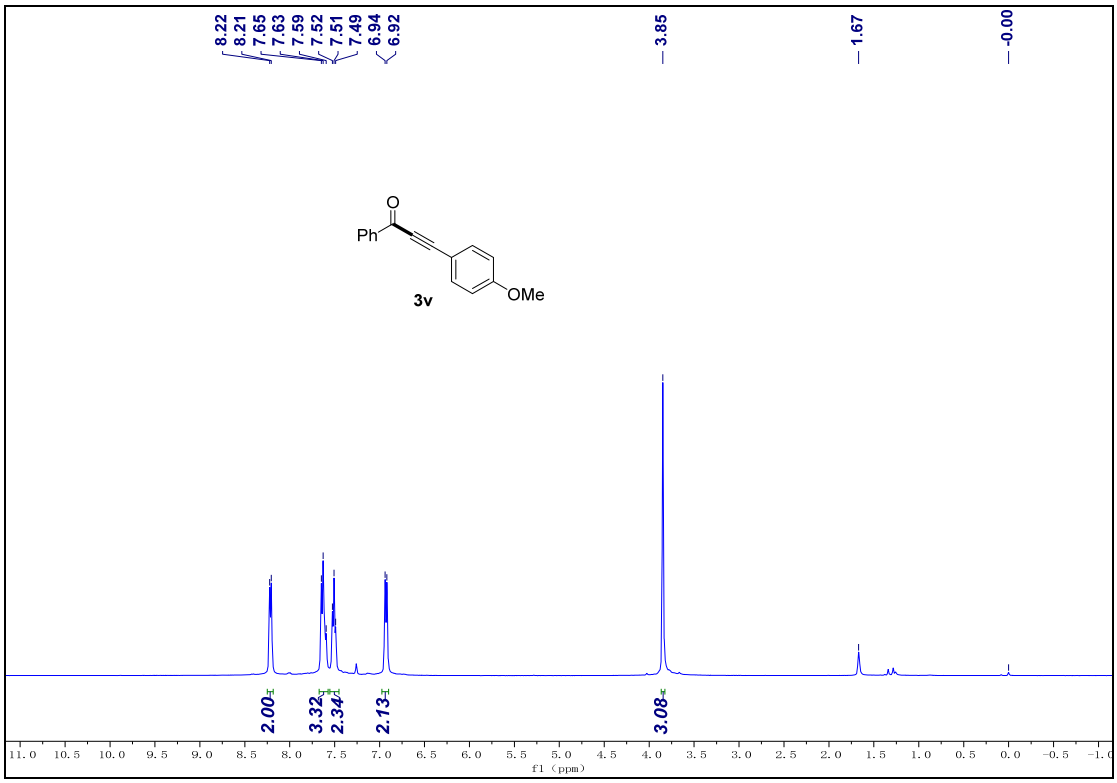


Figure S49. ^{1}H NMR spectrum of **3v** (400 MHz, $CDCl_3$, 298 K).

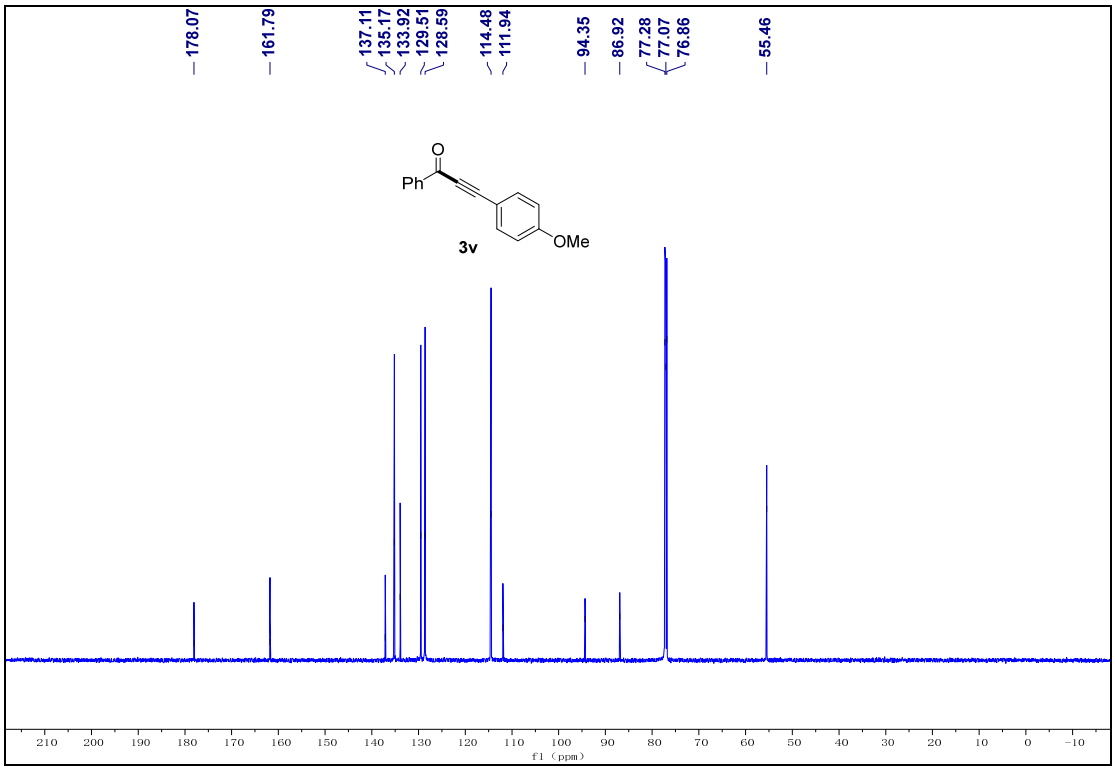


Figure S50. ^{13}C NMR spectrum of **3v** (150 MHz, $CDCl_3$, 298 K).

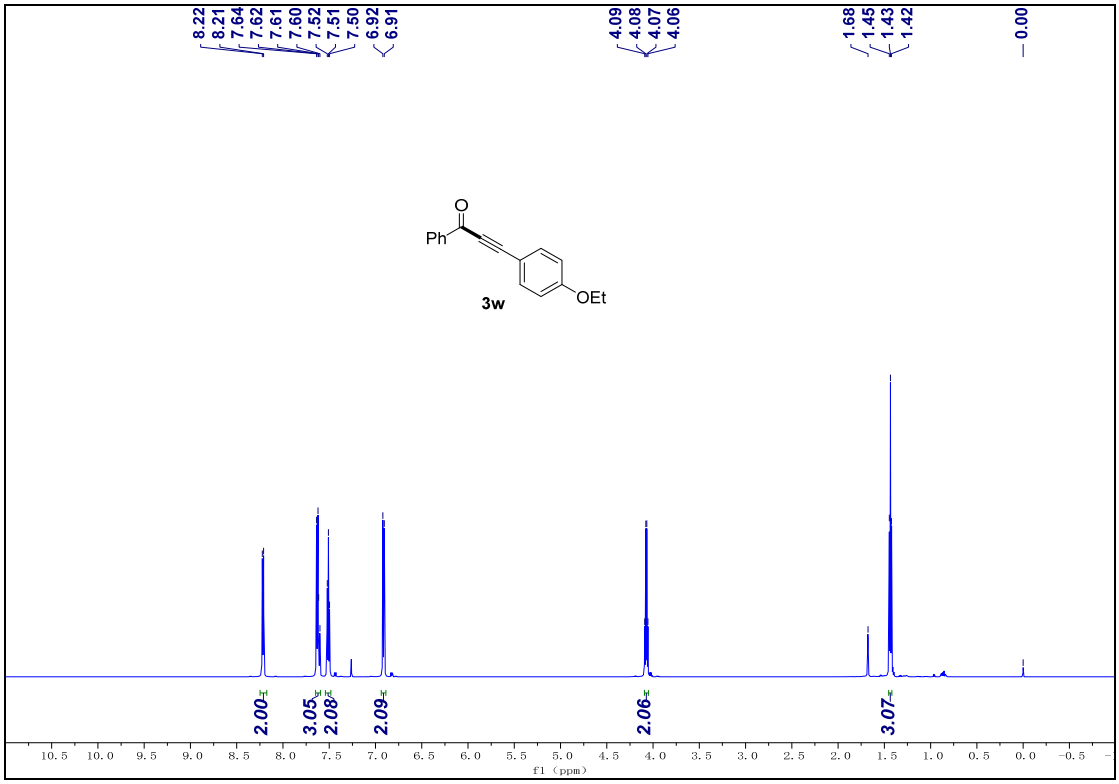


Figure S51. ^{1}H NMR spectrum of **3w** (600 MHz, $CDCl_3$, 298 K).

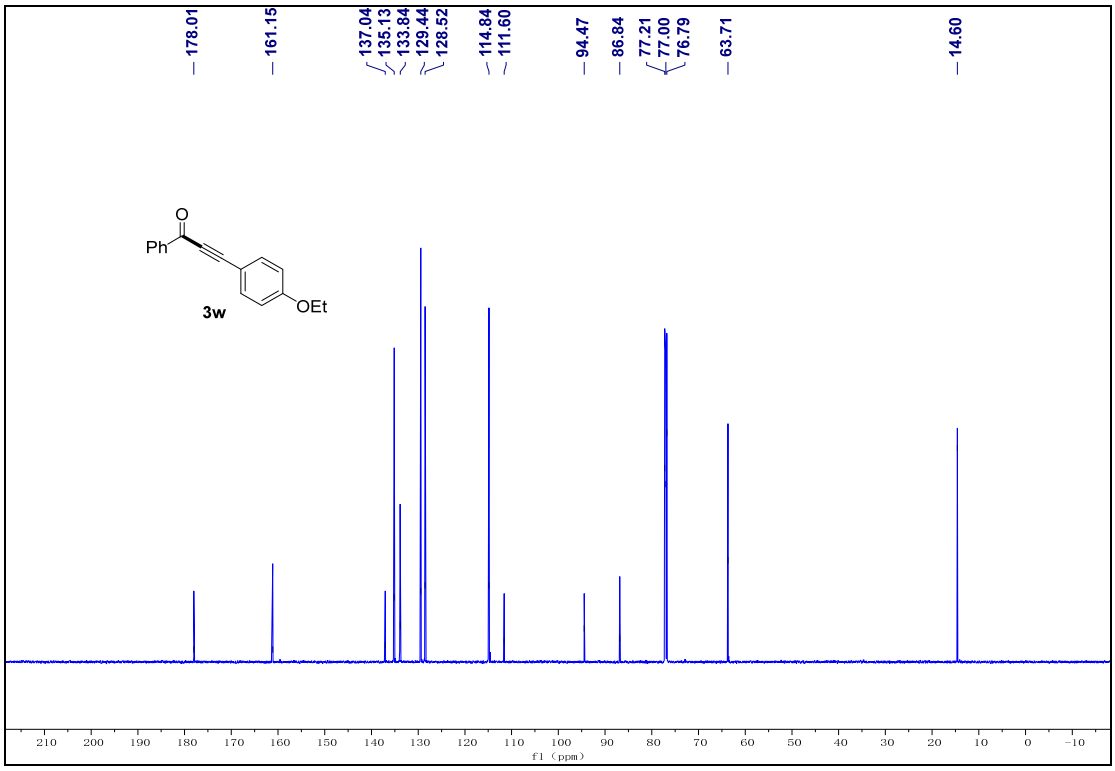


Figure S52. ^{13}C NMR spectrum of **3w** (150 MHz, $CDCl_3$, 298 K).

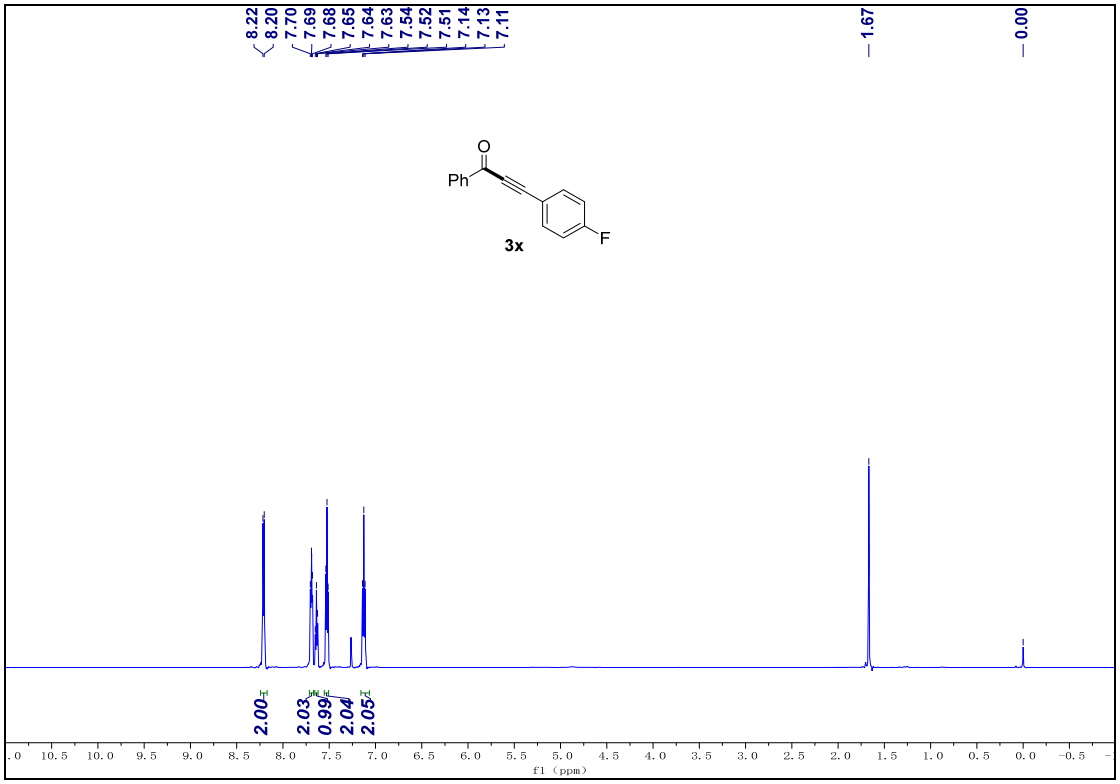


Figure S53. ^{1}H NMR spectrum of **3x** (600 MHz, $CDCl_3$, 298 K).

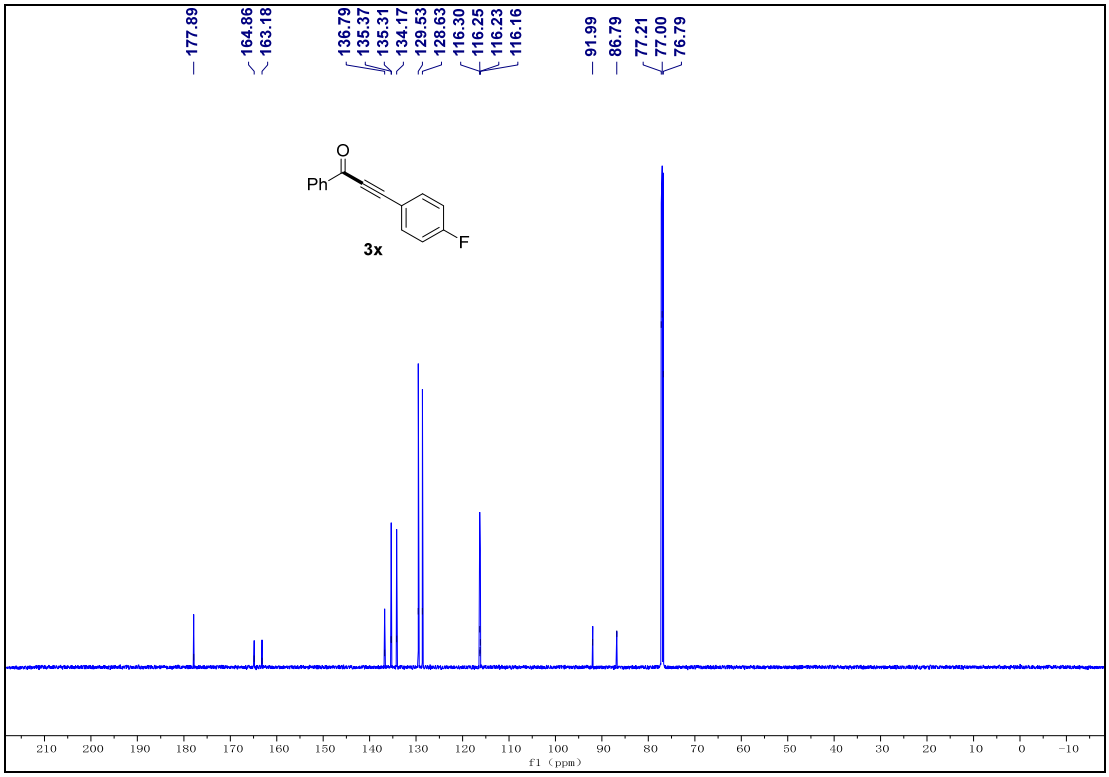


Figure S54. ^{13}C NMR spectrum of **3x** (150 MHz, $CDCl_3$, 298 K).

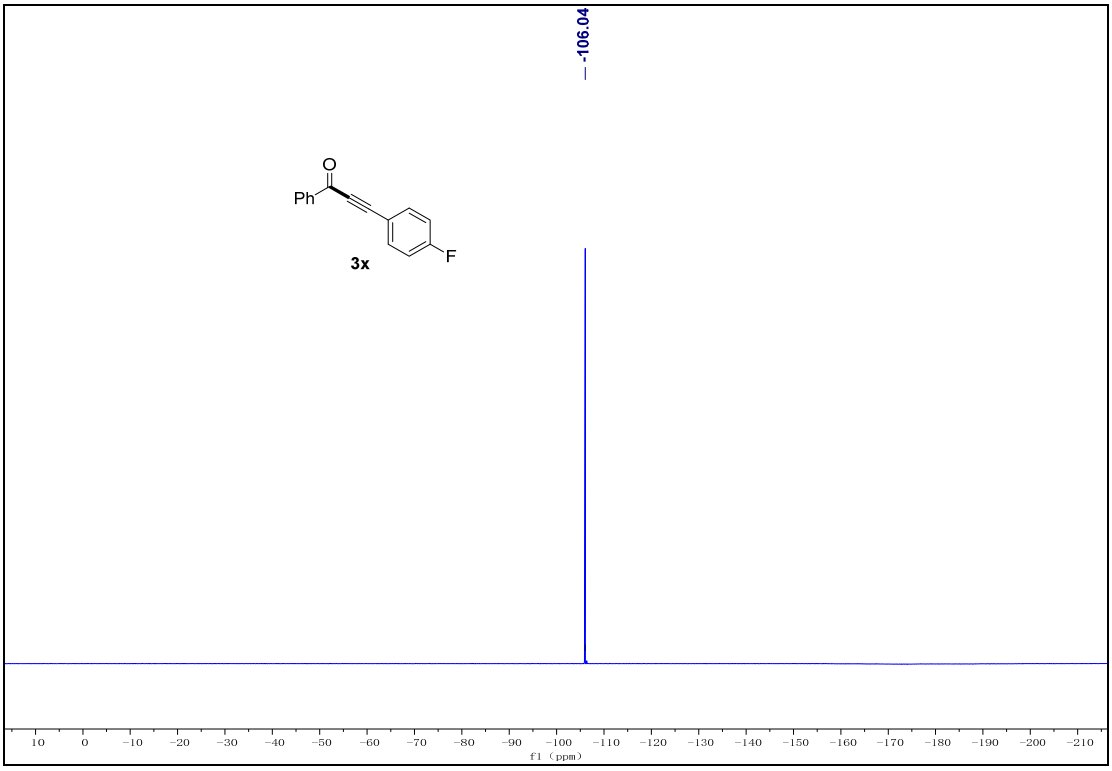


Figure S55. ^{19}F NMR spectrum of **3x** (565 MHz, $CDCl_3$, 298 K).

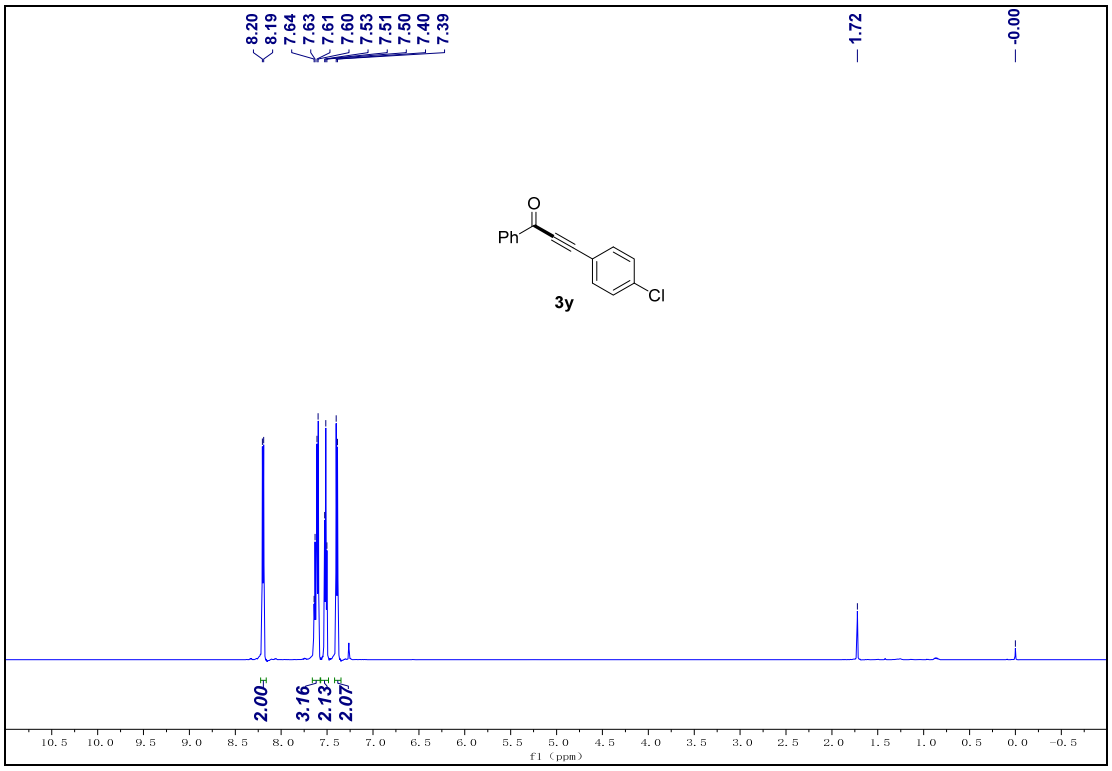


Figure S56. ^{1}H NMR spectrum of **3y** (600 MHz, $CDCl_3$, 298 K).

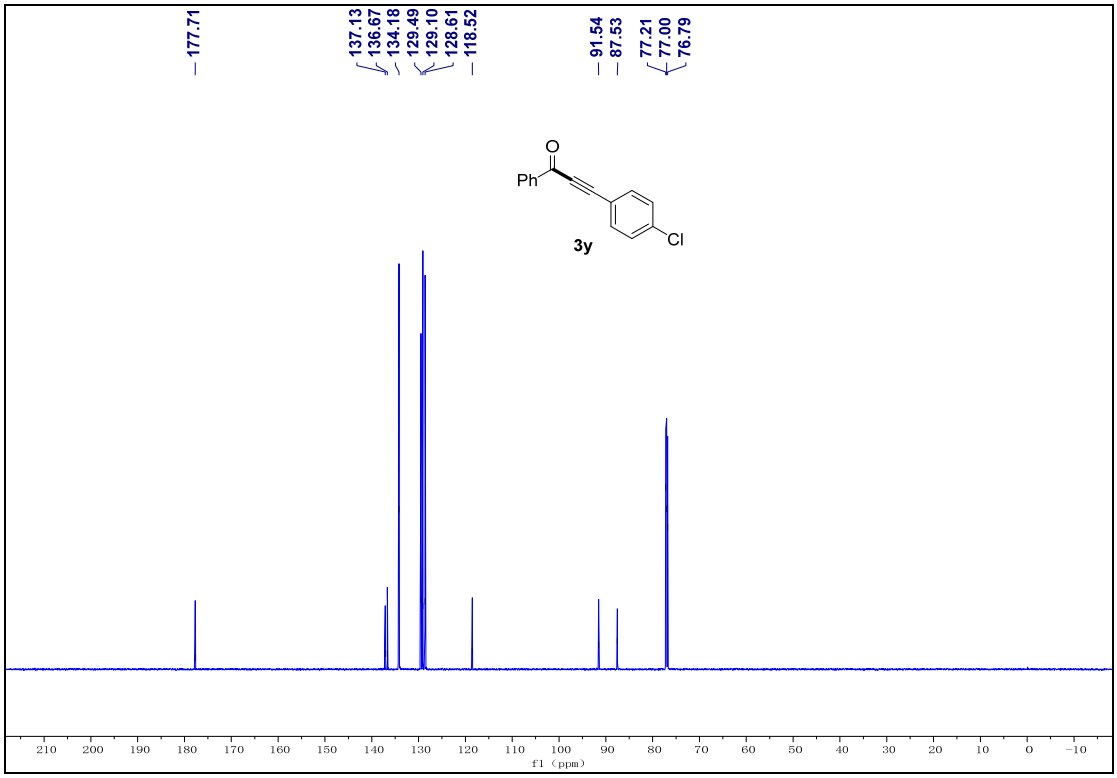


Figure S57. ^{13}C NMR spectrum of **3y** (150 MHz, $CDCl_3$, 298 K).

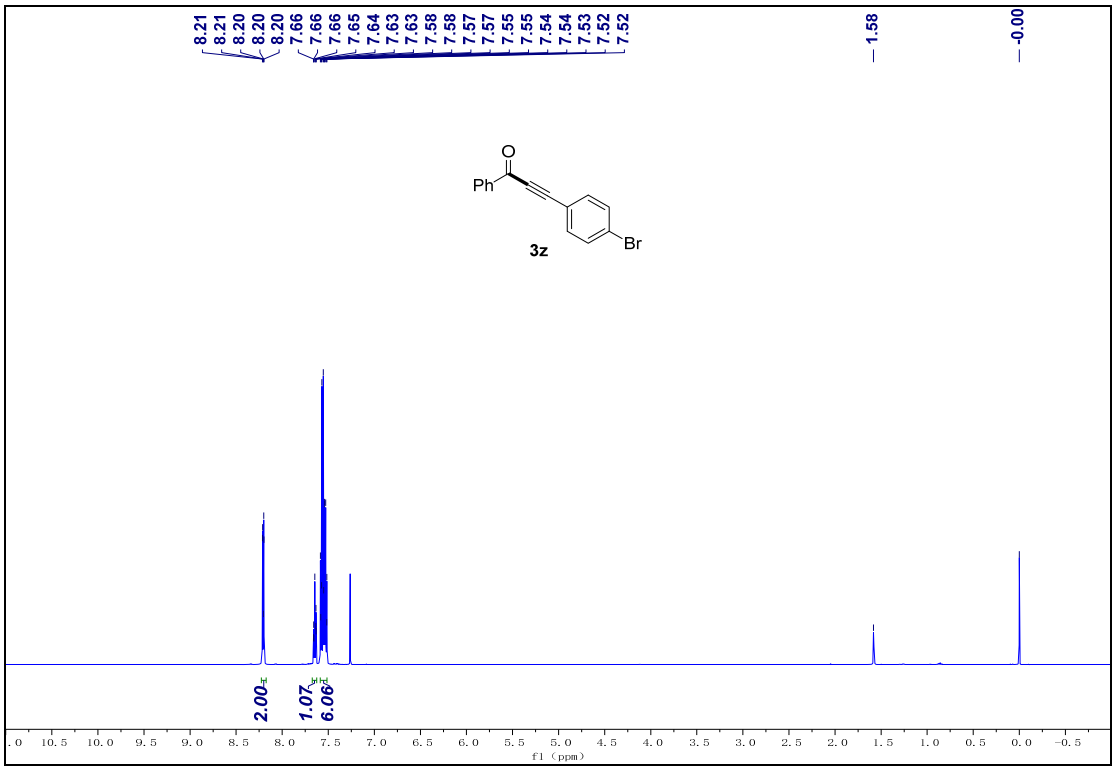


Figure S58. ^{1}H NMR spectrum of **3z** (600 MHz, $CDCl_3$, 298 K).

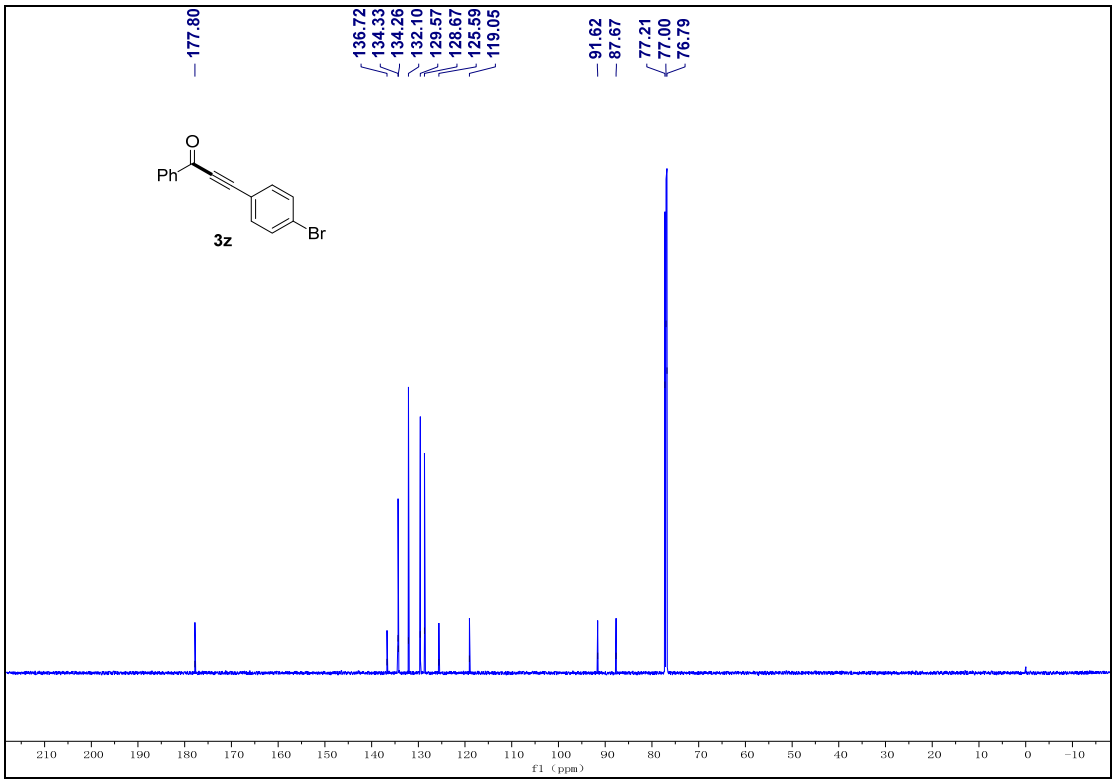


Figure S59. ^{13}C NMR spectrum of **3z** (150 MHz, $CDCl_3$, 298 K).

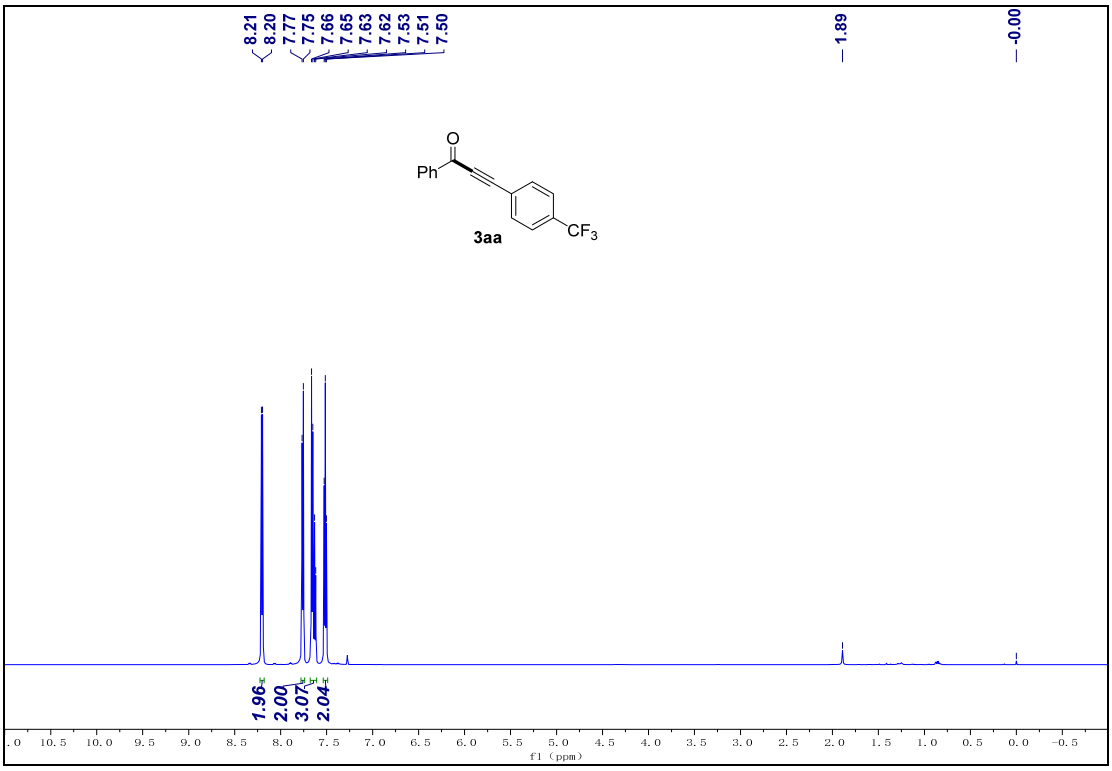


Figure S60. ^{1}H NMR spectrum of **3aa** (600 MHz, $CDCl_3$, 298 K).

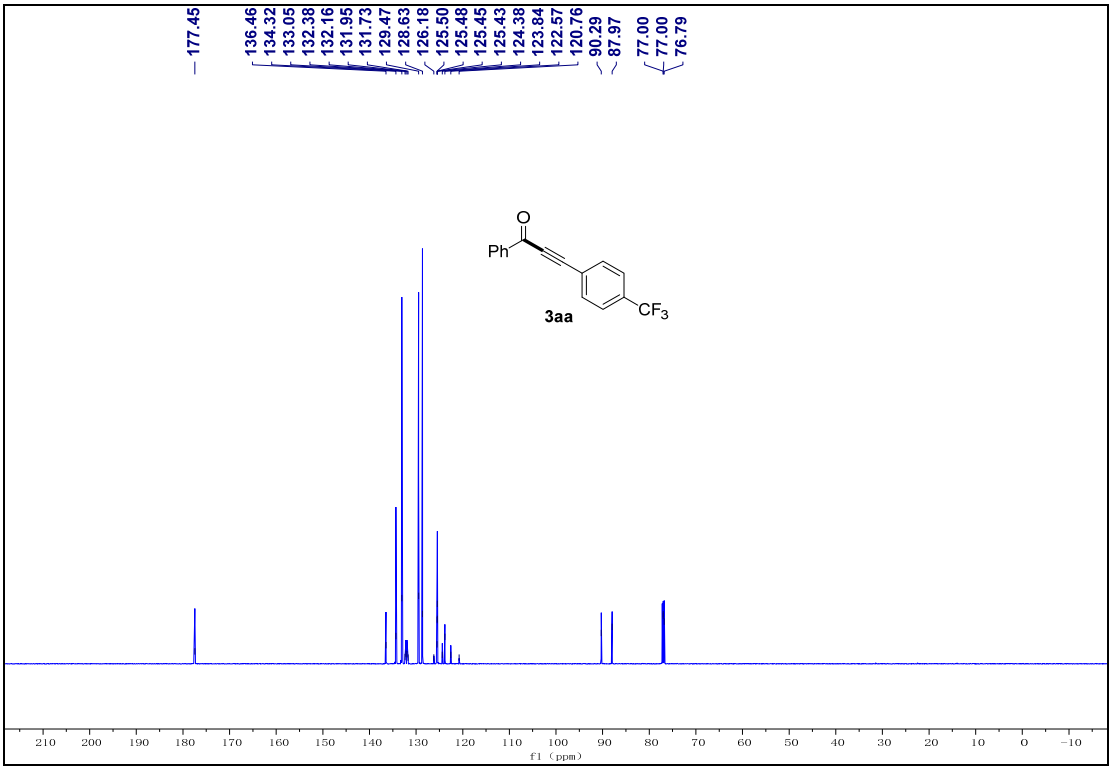


Figure S61. ^{13}C NMR spectrum of **3aa** (150 MHz, $CDCl_3$, 298 K).

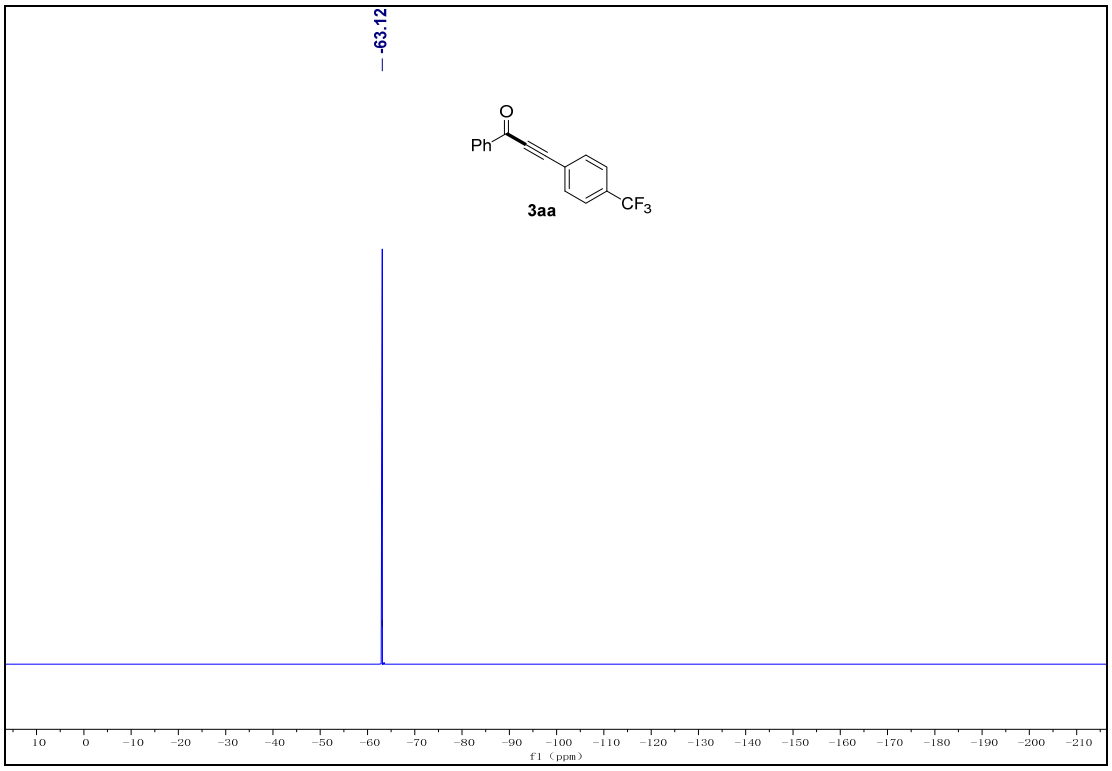


Figure S62. ^{19}F NMR spectrum of **3aa** (565 MHz, $CDCl_3$, 298 K).

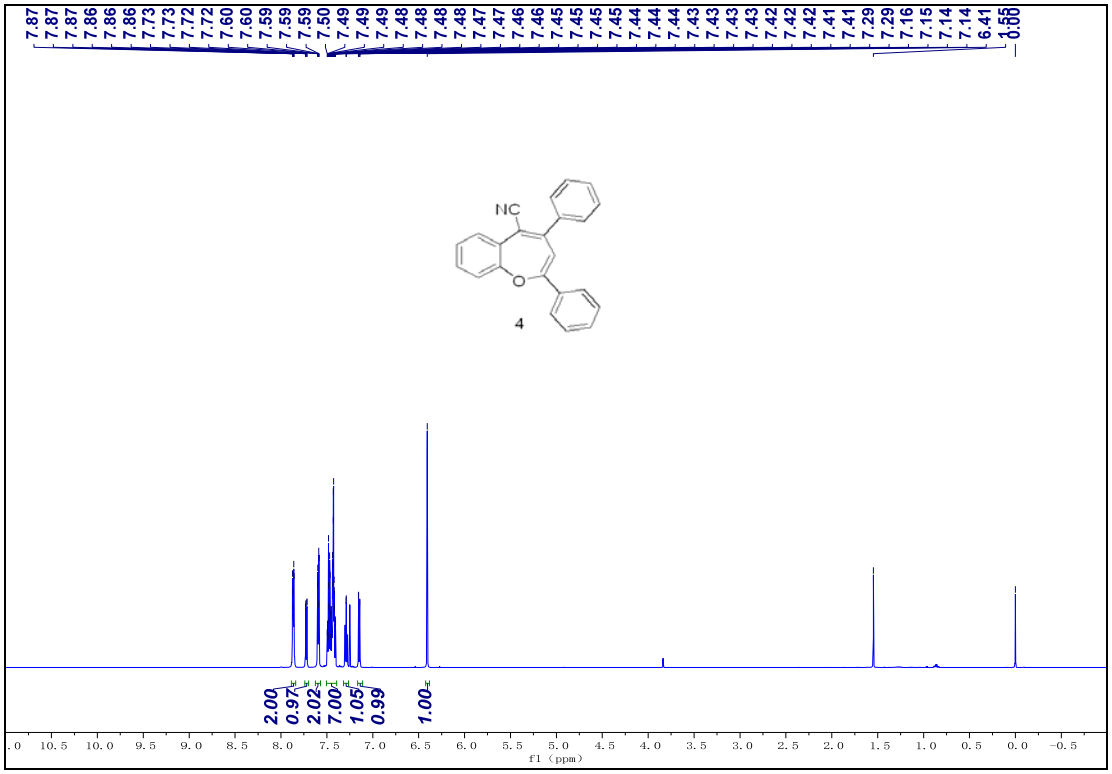


Figure S63. ^{1}H NMR spectrum of **4** (600 MHz, $CDCl_3$, 298 K).

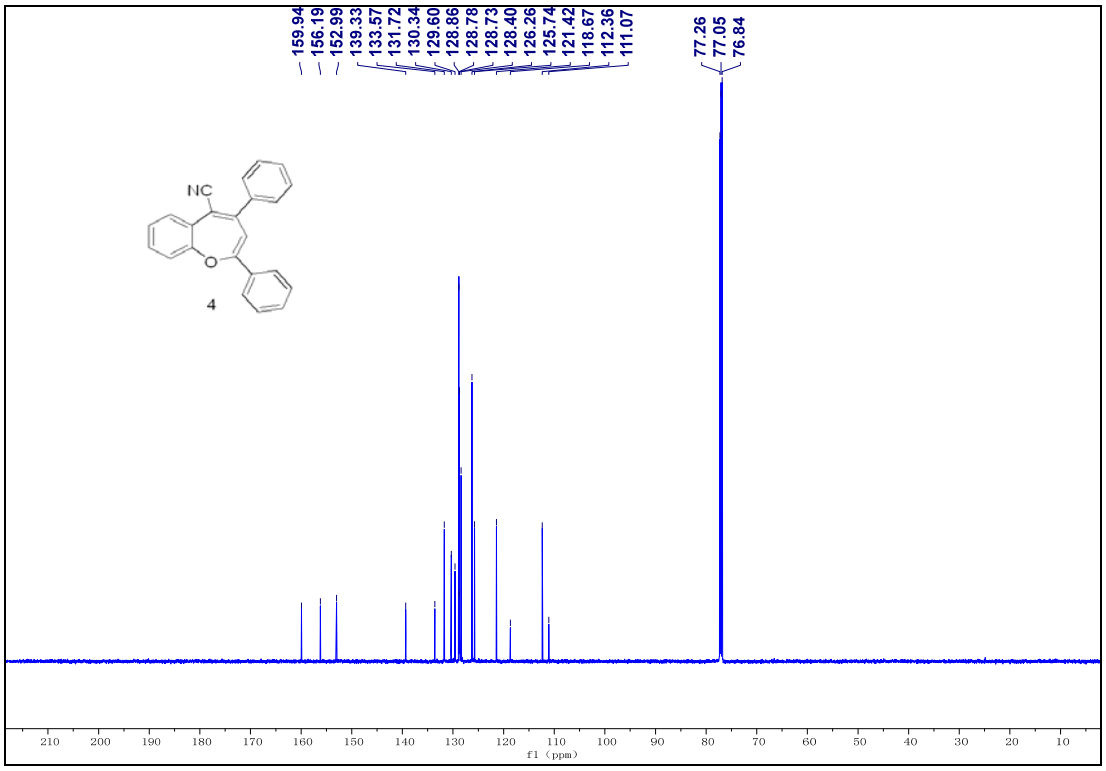


Figure S64. ^{13}C NMR spectrum of **4** (150 MHz, $CDCl_3$, 298 K).

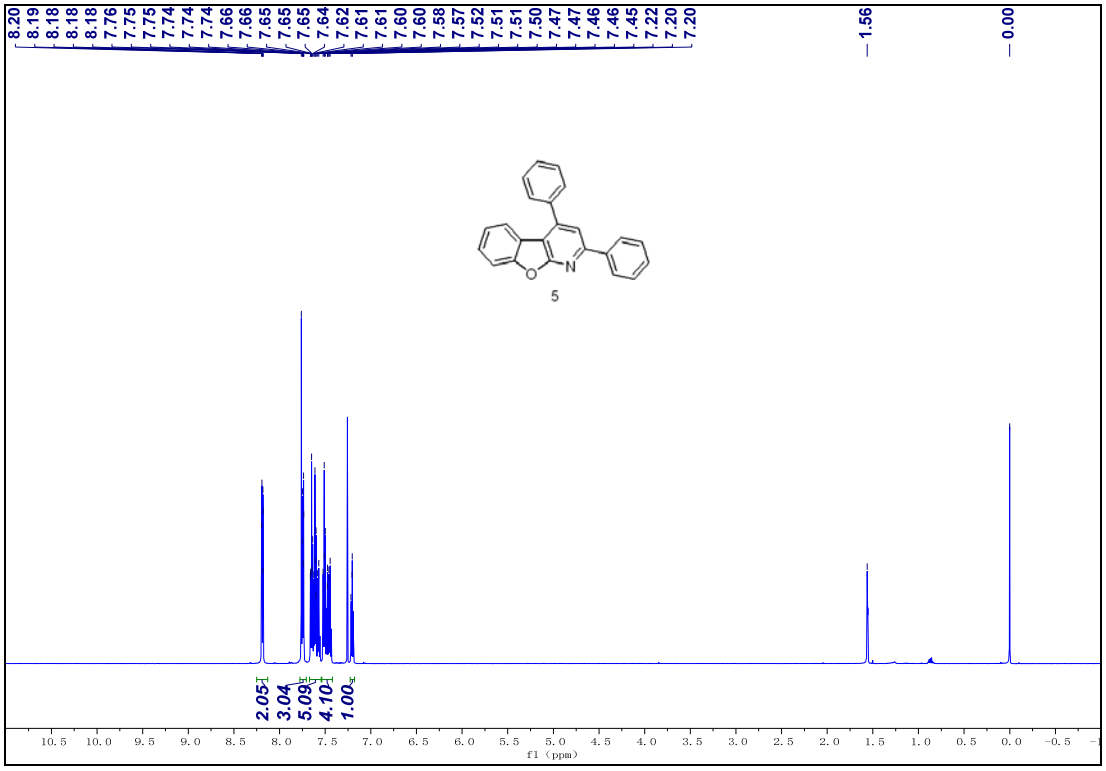


Figure S65. ^{1}H NMR spectrum of **5** (600 MHz, $CDCl_3$, 298 K).

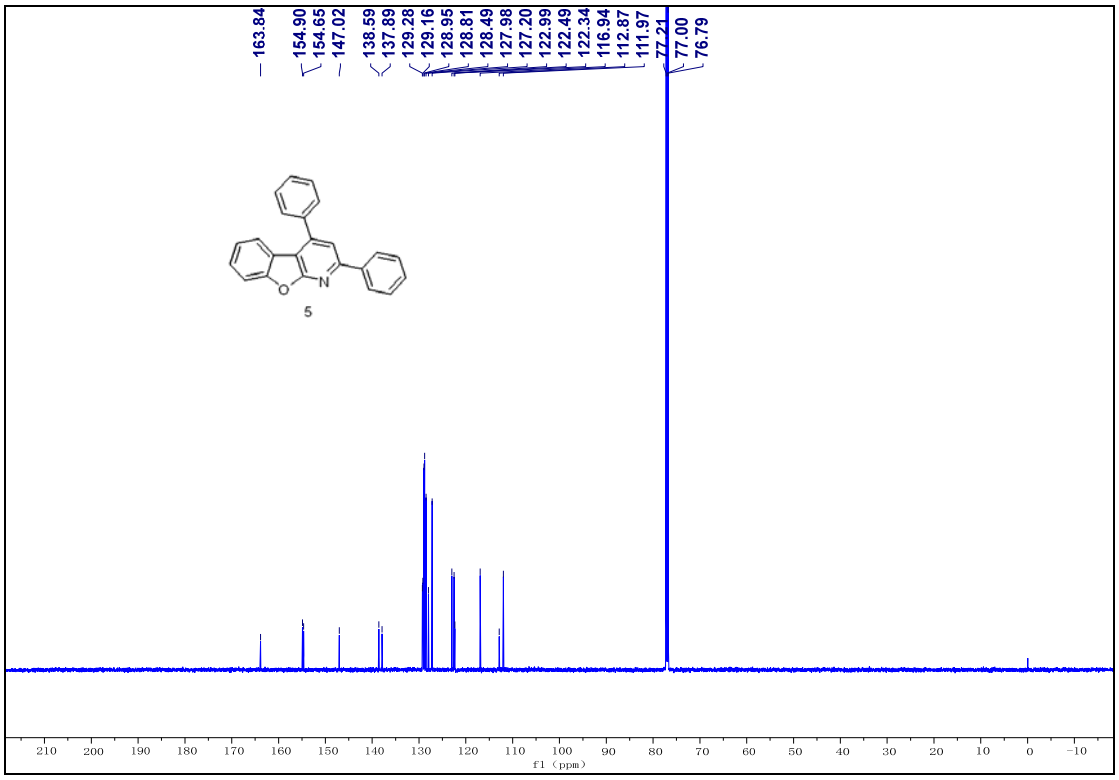


Figure S66. ^{13}C NMR spectrum of **5** (150 MHz, $CDCl_3$, 298 K).

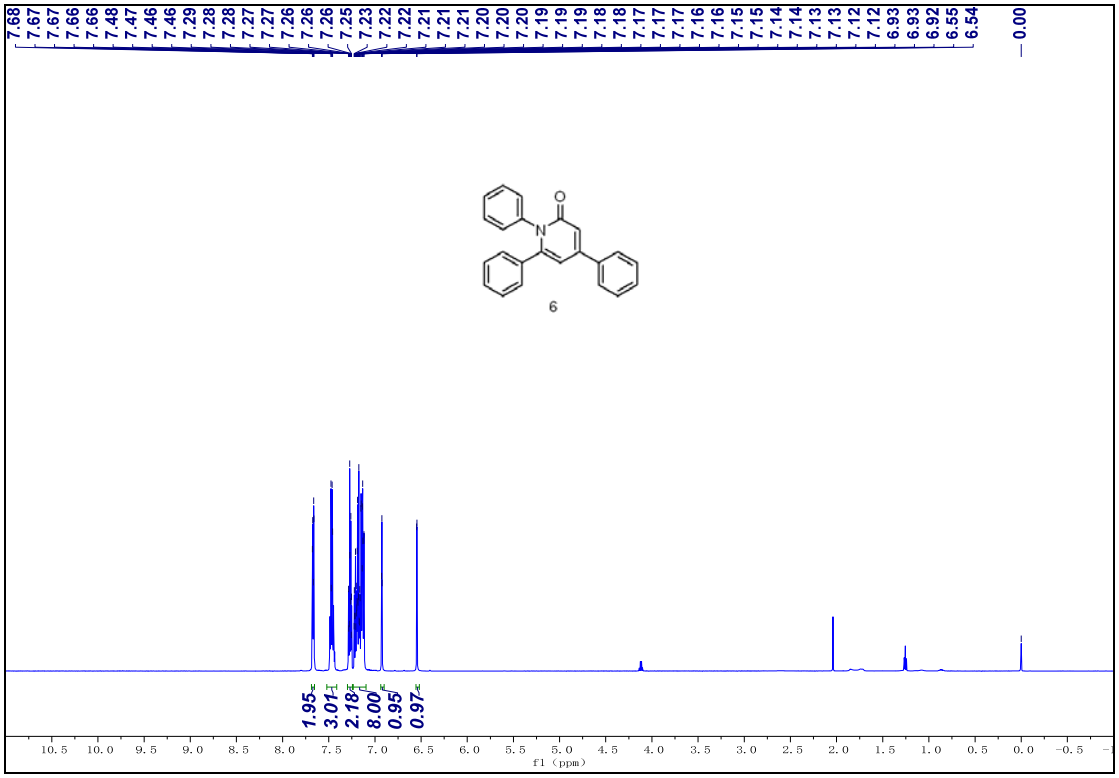


Figure S67. ^{1}H NMR spectrum of **6** (600 MHz, $CDCl_3$, 298 K).

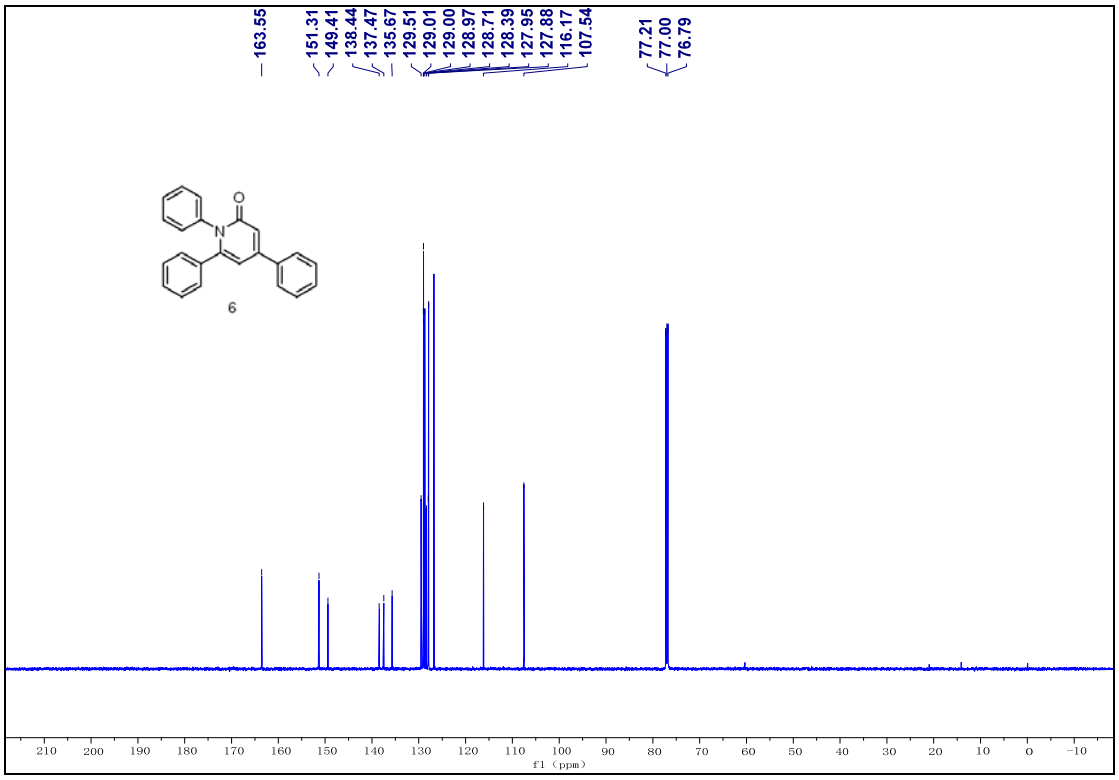


Figure S68. ^{13}C NMR spectrum of **6** (150 MHz, $CDCl_3$, 298 K).

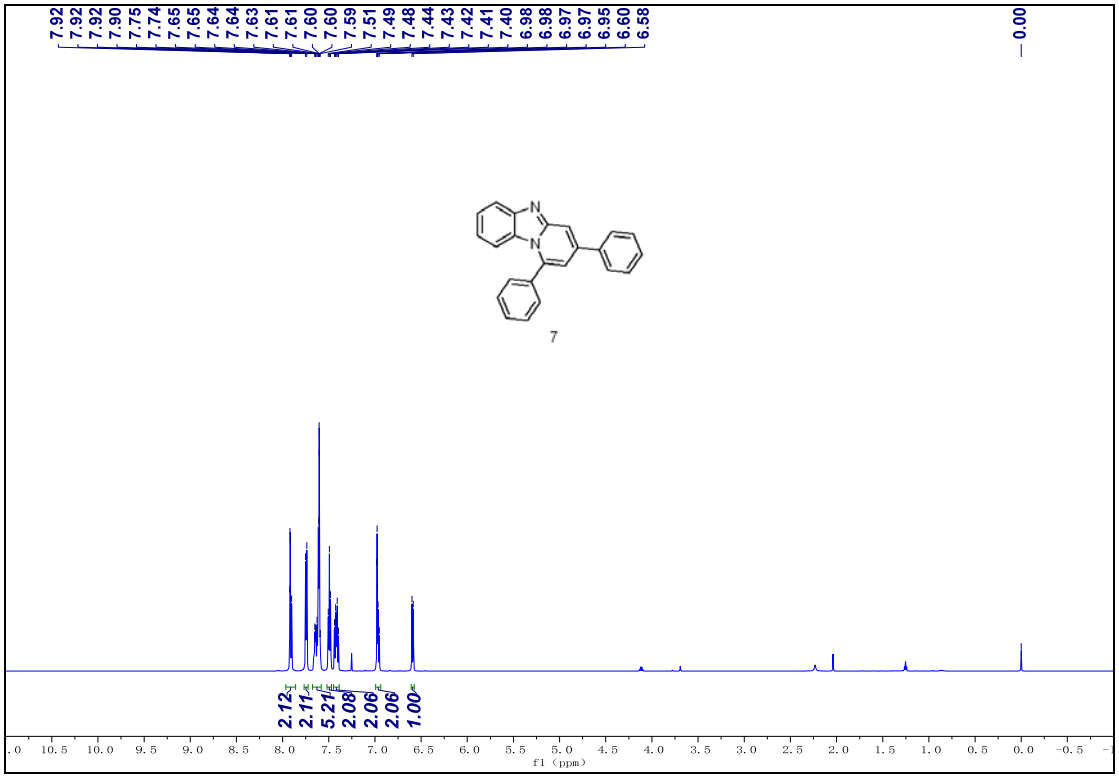


Figure S69. ^{1}H NMR spectrum of **7** (600 MHz, $CDCl_3$, 298 K).

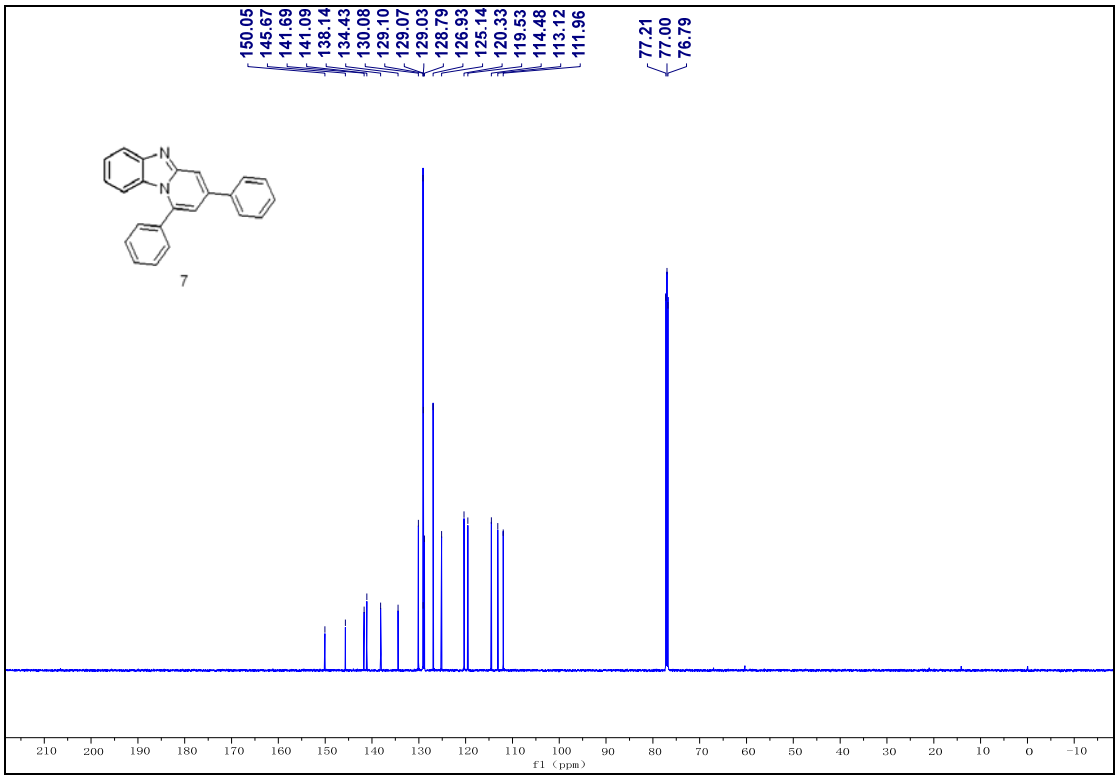


Figure S70. ^{13}C NMR spectrum of **7** (150 MHz, $CDCl_3$, 298 K).

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