

Supporting Information

Copper-catalyzed Umpolung Sonogashira-type Coupling of Arene Boronic Acids under Visible Light

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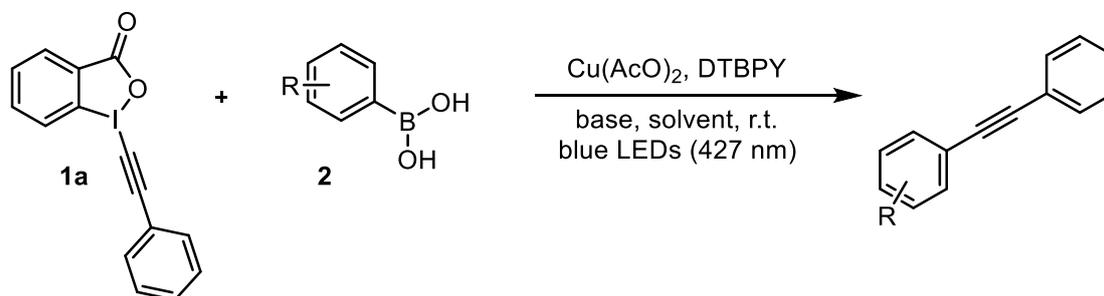
1. General Information

All reactions were carried out in oven dried glassware under an atmosphere of nitrogen, unless stated otherwise. All reactants and reagents including dry solvents were obtained from commercial suppliers and used as received. NMR spectra were obtained on the 500 MHz spectrometer using CDCl₃ as deuterated solvents, with proton and carbon resonances at 500 MHz and 125 MHz, respectively. ¹H-NMR and ¹³C-NMR chemical shifts were determined relative to internal standard TMS at δ 0.0 ppm. Chemical shifts (δ) are expressed in parts per million and are internally referenced [0.00 ppm (tetramethylsilane) for ¹H-NMR, and 77.0 ppm (CHCl₃) for ¹³C-NMR]. The following abbreviations were used to express the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, sext = sextet, sept = septet, m = multiplet, br = broad, dd = doublet of doublets, td = triplet of doublets. Unless otherwise noted, solvents were freshly dried and degassed according to the purification handbook Purification of Laboratory Chemicals before using. Flash column chromatography was carried out using 200-400 mesh silica gel.

Equipment for photocatalysis reaction: The reaction mixture was irradiated with a 34 W Kessil 427 nm blue LED lamps in a photoredox box.

2. Optimization of Conditions

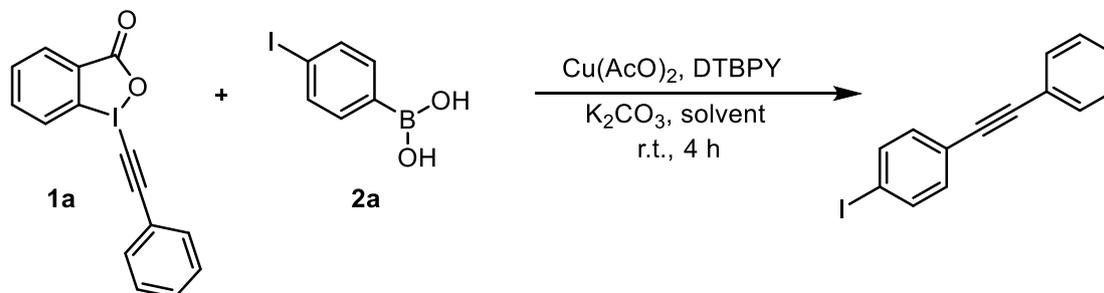
Table S1. Optimization of the reaction conditions.



entry	solvent	additive	time (h)	yield(%)
1	CF ₃ Ph	2 eq. K ₂ CO ₃	12	98 %
2	CF ₃ Ph	2 eq. K ₂ CO ₃	6	97 %
3	CF₃Ph^a	2 eq. K₂CO₃	4	98 %
4	CF ₃ Ph	2 eq. K ₂ CO ₃	2	89 %
5	CF ₃ Ph	2 eq. K ₂ CO ₃	1	77 %
6	CF ₃ Ph	0.2 eq. K ₂ CO ₃	4	92 %
7	CF ₃ Ph	-	4	87 %
8	CF ₃ Ph	2 eq. K ₂ CO ₃	4	95 %
9	CF ₃ Ph	1 eq. Et ₃ N	4	37 %
10	CF ₃ Ph ^b	2 eq. K ₂ CO ₃	4	NR
11	CF ₃ Ph ^c	2 eq. K ₂ CO ₃	4	88 %
12	CF ₃ Ph ^d	2 eq. K ₂ CO ₃	4	92 %
13	CF ₃ Ph ^e	2 eq. K ₂ CO ₃	4	84 %
14	CF ₃ Ph ^f	2 eq. K ₂ CO ₃	4	90 %
15	CF ₃ Ph ^g	-	4	82 %
16	CF ₃ Ph ^h	-	4	66 %
17	ACN ^h	-	4	44 %
18	CH ₃ OH ^h	-	4	35 %
19	H ₂ O ^h	-	4	29 %
20	CH ₂ Cl ₂ ^h	2 eq. K ₂ CO ₃	4	80 %
21	CH ₃ Ph ^h	2 eq. K ₂ CO ₃	4	78 %

Reaction conditions: (a): **1a** (1.0 mmol), **2** (2.0 mmol), Cu(AcO)₂ (0.01 mmol), DTBPY (0.01 mmol), K₂CO₃ (2.0 mmol), (trifluoromethyl)benzene (2.0 mL), N₂ atmosphere, yield related to isolation; (b): without Cu(AcO)₂; (c): without DTBPY; (d): DTBPY replaced by BPY; (e): **2** (1.0 mmol); (f): **2** (0.75 mmol); (g): achromatic light, N₂ atmosphere; (h): Air atmosphere, Isolated yield after preparative TLC.

Table S2. Optimization of the reaction conditions.



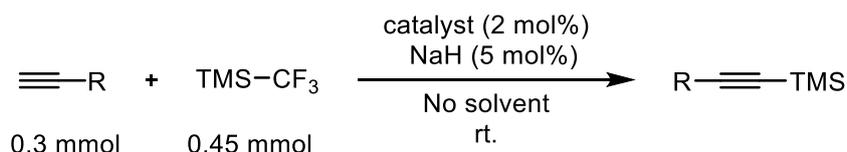
entry	solvent	2a (equiv)	photo	yield(%)
1	CF ₃ Ph	2	-	45 %
2	MeCN	1.1	-	50 %
3	CF ₃ Ph	1.1	-	50 %
4	CF ₃ Ph	1.1	<i>hν</i>	90 %

In order to further increase the yield, the conditions of different solvents, the equivalent of the reagents and the light were optimized again with 4-iodophenylboronic acid as the reagent. It was found that with (trifluoromethyl)benzene and acetonitrile as solvents, there was little difference in yield. The reaction reagents are 2 equivalent and 1.1 equivalent, and the yield is not much different. However, under UV light irradiation, the reaction yield is higher than that without UV light irradiation.

The optimal reaction was set up in the laboratory according to the general procedure, using the **1a** (1.0 eq.), **2** (2.0 eq.), Cu(AcO)₂ (0.1 eq.), DTBPY (0.1 eq.), K₂CO₃ (2.0 eq.) and (trifluoromethyl)benzene. The reaction mixture was evacuated and purged with inert gas (N₂) three times. The mixture is stirred by 427 nm blue LED lamps in the PhotoRedOx Box equipped with a fan for 4 h at room temperature under N₂ atmosphere.

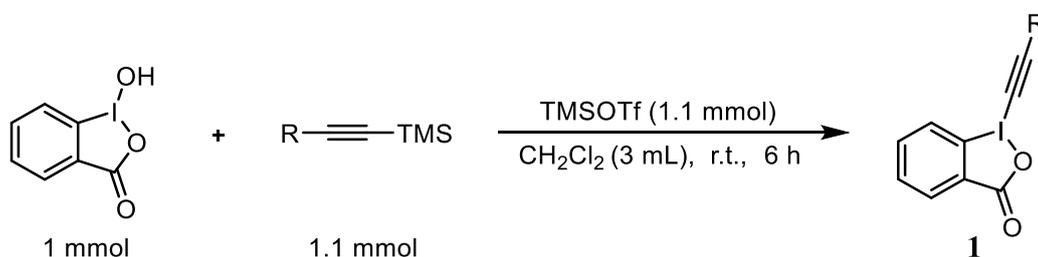
3. Preparation of Starting Materials

3.1 Preparation of the different silyl pronucleophiles. ^[1]



Trifluoromethyl trimethylsilane (0.45 mmol) was added to a mixture of catalyst (0.006 mmol), Sodium hydride (0.015 mmol) and terminal acetylene (0.3 mmol) and the resulting suspension was stirred for few minutes at room temperature until the terminal acetylene was completely consumed. The reaction mixture was diluted with hexane (2 mL) and passed through a silica gel column at ambient temperature. Removal of volatiles under vacuum furnished the pure trimethylsilyl acetylene derivative.

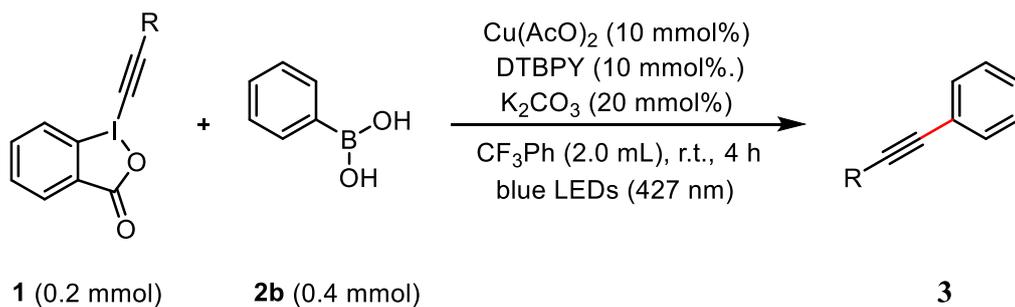
3.2 . Synthesis of the diverse EBXs. [2]



Following a reported procedure, the 1-hydroxy-1,2-phenyliodoyl-3(1H) ketone (1 mmol, 264 mg, 1.0 eq.) and trimethylsilyl trifluoromethanesulfonate (1.1 mmol, 191.7 mg, 1.1 eq.) were added to the CH₂Cl₂ (3 mL) solution and stirred for 1 hour. Then different silyl pronucleophiles (1.1 mmol, 244.5 mg, 1.1 eq.) was dissolved in CH₂Cl₂ (0.5 mL), added dropwise to the above solution and stirred at room temperature for 6 hours. After stirred for 6 hours, the reaction mixture was washed with a saturated solution of NaHCO₃ (5 mL). Then stirred vigorously for 30 minutes until delamination. The organic layer was extracted with a saturated solution of NaHCO₃ (3 * 6 mL), dried over MgSO₄, filtered and the solvent was evaporated under reduced pressure. Recrystallization from acetonitrile (5 mL) afforded **1** [3,4].

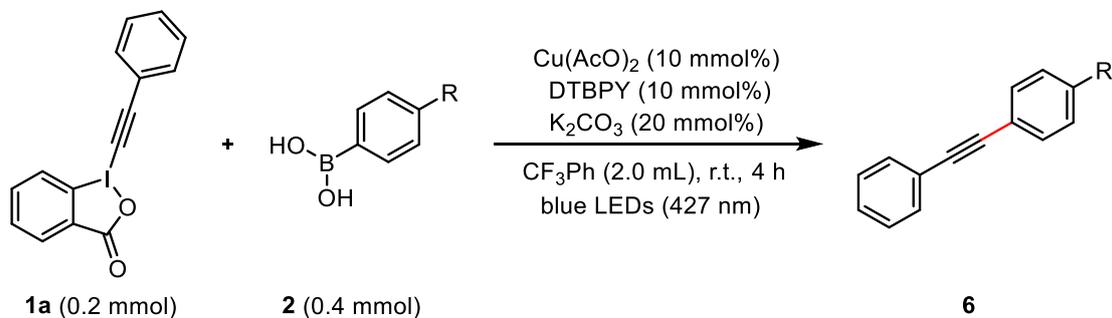
4. Study of the Diverse Phenylacetylene

4.1. Procedure A:



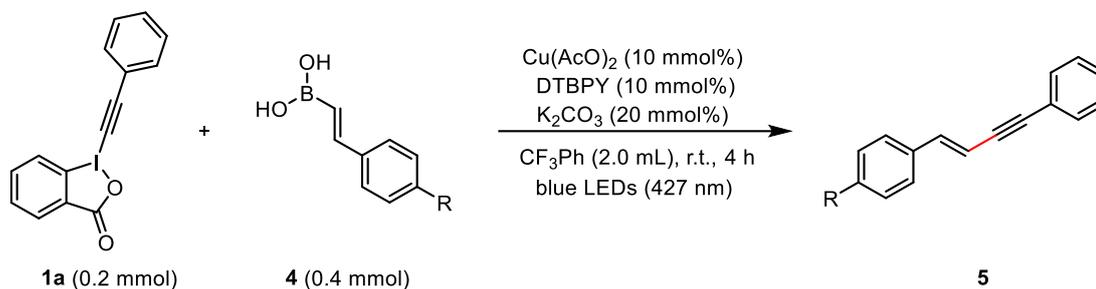
Following the **Procedure A**: The optimal reaction was set up in the laboratory according to the general procedure, using the diverse EBXs (0.2 mmol, 1.0 eq.), phenylboronic acid **2b** (0.4 mmol, 2.0 eq.), Cu(AcO)_2 (10 mmol%), DTBPY (10 mmol%), K_2CO_3 (20 mmol%) and 2.0 mL (trifluoromethyl)benzene. The reaction mixture was evacuated and purged with inert gas (N_2) three times. The mixture is stirred by 427 nm blue LED lamps in the PhotoRedOx Box equipped with a fan for 4 h at room temperature under N_2 atmosphere. After Suzuki-Miyaura cross-coupling reaction occurs 4 hours, the reaction mixture was isolated by flash chromatography (Pure petroleum ether). Then recrystallization from Methanol (2 mL) afforded **3a~3i** as white solid or pale-yellow oil.

4.2 Procedure B:



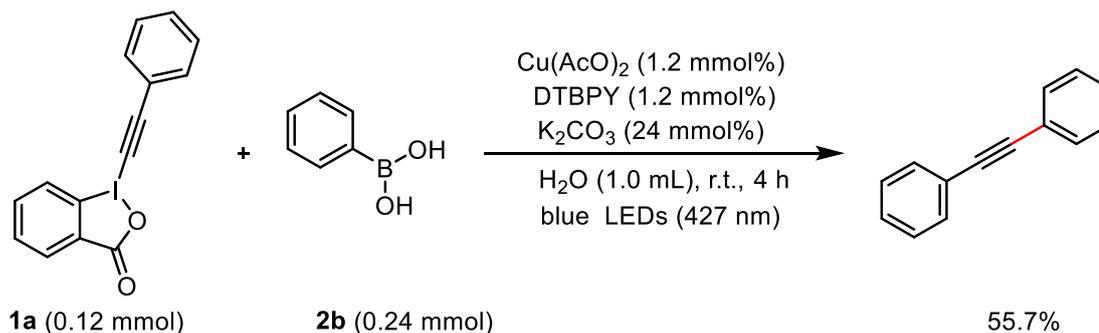
Following the **Procedure B**: The optimal reaction was set up in the laboratory according to the general procedure, using the (0.2 mmol, 1.0 eq.), **2** (0.4 mmol, 2.0 eq.), Cu(AcO)_2 (10 mmol%), DTBPY (10 mmol%), K_2CO_3 (20 mmol%) and 2.0 mL (trifluoromethyl)benzene. The reaction mixture was evacuated and purged with inert gas (N_2) three times. The mixture is stirred by 427 nm blue LED lamps in the PhotoRedOx Box equipped with a fan for 4 h at room temperature under N_2 atmosphere. After Suzuki-Miyaura cross-coupling reaction occurs 4 hours, the reaction mixture was isolated by flash chromatography (Pure petroleum ether). Then recrystallization from methanol (2 mL) afforded **6a~6h** as white solid or pale-yellow oil.

5. Research on *cis-trans* Isomerism



Following the **Procedure B**: The optimal reaction was set up in the laboratory according to the general procedure, replaced phenylboronic acid with (*E*)-styrylboronic acid, (*E*)-(4-methylstyryl)boronic acid and (*E*)-(2-([1,1'-biphenyl]-4-yl)vinyl)boronic acid. The products (**5i**~**5k**) found that the configuration were still trans.

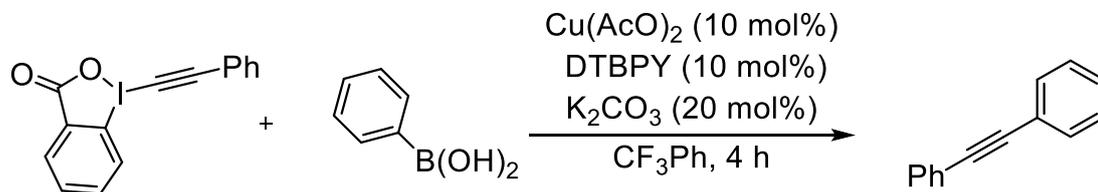
6. Using Water as Solvent



Using the EBX **1a** (0.12 mmol, 40 mg, 1.0 eq.), **2b** (0.24 mmol, 29.3 mg, 2.0 eq.), Cu(AcO)_2 (0.012 mmol, 2.39 mg, 0.1 eq.), DTBPY (0.012 mmol, 3.22 mg, 0.1 eq.), K_2CO_3 (0.24 mmol, 33.3 mg, 2.0 eq.) and 1.0 mL H_2O . The reaction mixture was evacuated and purged with inert gas (N_2) three times. The mixture is stirred by 427 nm blue LED lamps in the PhotoRedOx Box equipped with a fan for 4 h at room temperature under N_2 atmosphere. After Suzuki-Miyaura cross-coupling reaction occurs 4 hours, the reaction mixture was isolated by flash chromatography (Pure petroleum ether). Then recrystallization from methanol (2 mL) afforded the white solid. The coupling reaction between EBX and phenylboronic acid can be carried out smoothly with water as the solvent, but the yield is less 55.7%.

7. The Radical Trapping Experiment

Following the standard procedure except 2,2,6,6-tetramethylpiperidin-1-yl)oxy (TEMPO) (2 equiv.) was added before the reaction, the reaction of EBX (1 equiv.) and phenylboric acid (1 equiv.) afforded diphenylacetylene in 93% yield after 4 h.

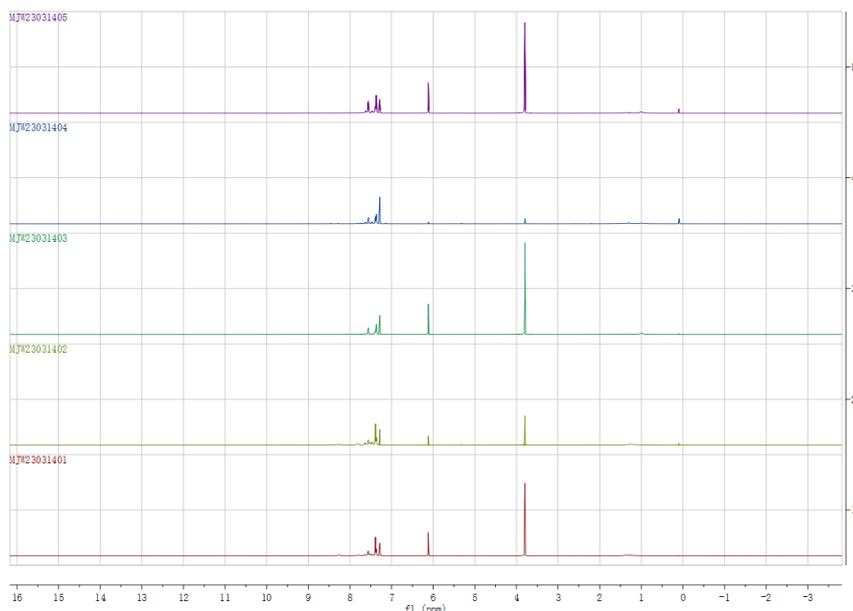


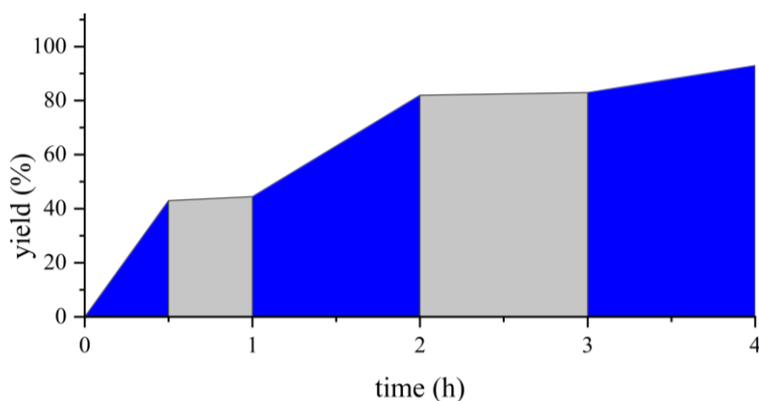
1) 2 equiv. TEMPO: 93% yield 2) In dark: 5% yield 3) 60 °C in dark: 6% yield

Scheme S7. ^aReaction conditions: Entry 6 in table, unless otherwise noted

8. The On-off-light Experiment

Following the standard procedure, the reaction between EBX (1 equiv.) and phenylboric acid (2.0 equiv.) was conducted for light-dark experiment. Aliquots of samples were taken out at various time points during the reaction. Crude NMR was taken on the concentrated crude reaction mixture and calculated using 1,3,5-trimethoxybenzene* as an internal standard.

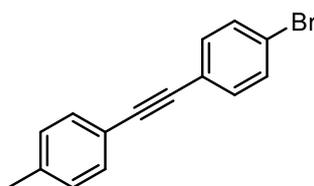




Scheme S8. The blue area indicates the blue LED irradiation, while grey area indicates the dark treatment. The x axis is the reaction time, and the y axis is the reaction yield.

9. Characterizations

1-bromo-4-(*p*-tolylethynyl)benzene **3a** ^[5]



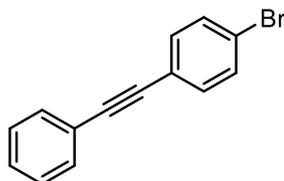
3a

Following the **Procedure A:** using the 1-((4-bromophenyl)ethynyl)-1-benzo[*d*][1,2]iodaoxol-3(*1H*)-one (0.1 mmol, 42.8 mg, 1.0 eq.), *p*-tolylboronic acid (0.2 mmol, 27.2 mg, 2.0 eq.), Cu(AcO)₂ (0.01 mmol, 2.0 mg, 0.1 eq.), DTBPY (0.01 mmol, 2.68 mg, 0.1 eq.), K₂CO₃ (0.2 mmol, 27.6 mg, 2.0 eq.) and 2.0 mL (trifluoromethyl)benzene. The reaction mixture was evacuated and purged with inert gas (N₂) three times. The mixture is stirred by 427 nm blue LED lamps in the PhotoRedOx Box equipped with a fan for 4 h at room temperature under N₂ atmosphere. After Suzuki-Miyaura cross-coupling reaction occurs 4 hours, the reaction mixture was isolated by flash chromatography (Pure petroleum ether). Then recrystallization from methanol (1 mL) afforded **3a** as white solid (23.1 mg, 85.2%).

¹H-NMR (500 MHz, CDCl₃): δ_H 7.47 (d, *J* = 8.4 Hz, 2H), 7.41 (d, *J* = 8.0 Hz, 2H), 7.37 (d, *J* = 8.4 Hz, 2H), 7.16 (d, *J* = 7.9 Hz, 2H), 2.36 (s, 3H).

¹³C-NMR (125 MHz, CDCl₃): δ_C 138.7, 133.0, 131.6, 131.5, 129.2, 122.5, 122.3, 119.8, 90.7, 87.7, 21.5.

1-bromo-4-(phenylethynyl)benzene 3b^[6]



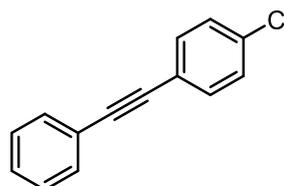
3b

Following the **Procedure A**: using the 1-((4-bromophenyl)ethynyl)-1-benzo[*d*][1,2]iodaoxol-3(*1H*)-one (0.4 mmol, 171.2 mg, 1.0 eq.), phenylboronic acid (0.8 mmol, 97.54 mg, 2.0 eq.), Cu(AcO)₂ (0.04 mmol, 7.96 mg, 0.1eq.), DTBPY (0.04 mmol, 10.72 mg, 0.1 eq.), K₂CO₃ (0.8 mmol, 110.4 mg, 2.0 eq.) and 4.0 mL (trifluoromethyl)benzene. The reaction mixture was evacuated and purged with inert gas (N₂) three times. The mixture is stirred by 427 nm blue LED lamps in the PhotoRedOx Box equipped with a fan for 4 h at room temperature under N₂ atmosphere. After Suzuki-Miyaura cross-coupling reaction occurs 4 hours, the reaction mixture was isolated by flash chromatography (Pure petroleum ether). Then recrystallization from methanol (4 mL) afforded **3b** as white solid (91.1 mg, 88.7%).

¹H-NMR (500 MHz, CDCl₃): δ_H 7.52 (dd, *J* = 6.6, 3.0 Hz, 2H), 7.50-7.46 (m, 2H), 7.39 (d, *J* = 8.4 Hz, 2H), 7.35 (dd, *J* = 4.9, 1.8 Hz, 3H).

¹³C-NMR (125 MHz, CDCl₃): δ_C 133.0, 131.6, 131.6, 128.5, 128.4, 122.9, 122.5, 122.3, 90.5, 88.3.

1-chloro-4-(phenylethynyl)benzene 3c^[10]



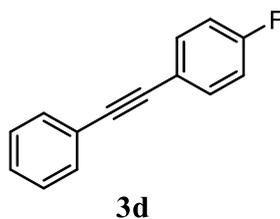
3c

Following the **Procedure A**: using the 1-((4-chlorophenyl)ethynyl)-1-benzo[*d*][1,2]iodaoxol-3(1H)-one (0.212 mmol, 78.4 mg, 1.0 eq.), phenylboronic acid (0.42 mmol, 51.3 mg, 2.0 eq.), Cu(AcO)₂ (0.0212 mmol, 4.3 mg, 0.1 eq.) , DTBPY (0.0212 mmol, 5.7 mg, 0.1 eq.), K₂CO₃ (0.42 mmol, 58 mg, 2.0 eq.) and 1.5 mL (trifluoromethyl)benzene. The reaction mixture was evacuated and purged with inert gas (N₂) three times. The mixture is stirred by 427 nm blue LED lamps in the PhotoRedOx Box equipped with a fan for 4 h at room temperature under N₂ atmosphere. After Suzuki-Miyaura cross-coupling reaction occurs 4 hours, the reaction mixture was isolated by flash chromatography (Pure petroleum ether). Then recrystallization from methanol (2 mL) afforded **3c** as white solid (38.9 mg, 86.3%).

¹H-NMR (500 MHz, CDCl₃): δ_H 7.54-7.51 (m, 2H), 7.47-7.45 (m, 2H), 7.37-7.31 (m, 5H).

¹³C-NMR (125 MHz, CDCl₃): δ_C 134.3, 132.8, 131.6, 128.7, 128.5, 128.4, 122.9, 121.8, 90.3, 88.2.

1-fluoro-4-(phenylethynyl)benzene **3d** ^[9]



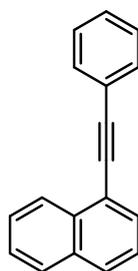
Following the **Procedure A**: using the 1-((4-fluorophenyl)ethynyl)-1-benzo[*d*][1,2]iodaoxol-3(1H)-one (0.19 mmol, 70.0 mg, 1.0 eq.), phenylboronic acid (0.38 mmol, 46.3 mg, 2.0 eq.), Cu(AcO)₂ (0.019 mmol, 3.8 mg, 0.1 eq.) , DTBPY (0.019 mmol, 4.3 mg, 0.1 eq.), K₂CO₃ (0.38 mmol, 52.4 mg, 2.0 eq.) and 1.5 mL (trifluoromethyl)benzene. The reaction mixture was evacuated and purged with inert gas (N₂) three times. The mixture is stirred by 427 nm blue LED lamps in the PhotoRedOx Box equipped with a fan for 4 h at room temperature under N₂ atmosphere. After Suzuki-Miyaura cross-coupling reaction occurs 4 hours, the reaction mixture was

isolated by flash chromatography (Pure petroleum ether). Then recrystallization from methanol (2 mL) afforded **3d** as white solid (28.9 mg, 77.8%).

¹H-NMR (500 MHz, CDCl₃): δ_H 7.56-7.48 (m, 4H), 7.35 (dd, $J = 5.1, 1.9$ Hz, 3H), 7.05 (t, $J = 8.7$ Hz, 2H).

¹³C-NMR (125 MHz, CDCl₃): δ_C 162.0 (d, $J = 250$ Hz), 161.5, 133.5, 133.5, 131.6, 128.4, 128.3, 123.1, 119.4, 119.4, 115.7, 115.6, 89.0, 88.3.

1-(phenylethynyl)naphthalene **3e** ^[7]



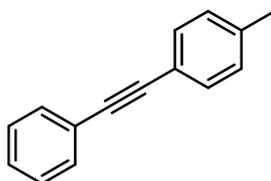
3e

Following the **Procedure A**: using the 1-(naphthalen-1-ylethynyl)-1-benzo[*d*] [1,2] iodoaxol-3(1H)-one (0.1153 mmol, 45.9 mg, 1.0 eq.), phenylboronic acid (0.23 mmol, 28 mg, 2.0 eq.), Cu(AcO)₂ (0.0153 mmol, 3.1 mg, 0.1 eq.), DTBPY (0.0153 mmol, 4.1 mg, 0.1 eq.), K₂CO₃ (0.23 mmol, 31.5 mg, 2.0 eq.) and 1.5 mL (trifluoromethyl)benzene. The reaction mixture was evacuated and purged with inert gas (N₂) three times. The mixture is stirred by 427 nm blue LED lamps in the PhotoRedOx Box equipped with a fan for 4 h at room temperature under N₂ atmosphere. After Suzuki-Miyaura cross-coupling reaction occurs 4 hours, the reaction mixture was isolated by flash chromatography (Pure petroleum ether). Then recrystallization from methanol (2 mL) afforded **3e** as white solid (21.9 mg, 83.7%).

¹H-NMR (500 MHz, CDCl₃): δ_H 8.47 (d, $J = 8.4$ Hz, 1H), 7.87 (dd, $J = 12.3, 8.2$ Hz, 2H), 7.79 (dd, $J = 7.1, 1.0$ Hz, 1H), 7.69-7.66 (m, 2H), 7.62 (ddd, $J = 8.2, 6.9, 1.2$ Hz, 1H), 7.55 (dd, $J = 10.9, 4.0$ Hz, 1H), 7.48 (dd, $J = 8.1, 7.3$ Hz, 1H), 7.44-7.37 (m, 3H).

¹³C-NMR (125 MHz, CDCl₃): δ_C 133.3, 133.3, 131.7, 130.4, 128.8, 128.5, 128.4, 128.3, 126.8, 126.5, 126.3, 125.3, 123.5, 121.0, 94.4, 87.6.

1-methyl-4-(phenylethynyl)benzene 3f^[9]



3f

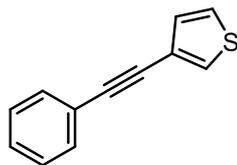
Following the **Procedure A**: using the 1-(p-tolyethynyl)-1-benzo[*d*][1,2]iodaoxol-3(1H)-one (0.23 mmol, 80 mg, 1.0 eq.), phenylboronic acid (0.46 mmol, 56.1 mg, 2.0 eq.), Cu(AcO)₂ (0.023 mmol, 4.5 mg, 0.1 eq.), DTBPY (0.023 mmol, 6.2 mg, 0.1 eq.), K₂CO₃ (0.46 mmol, 63.5 mg, 2.0 eq.) and 1.5 mL (trifluoromethyl)benzene. The reaction mixture was evacuated and purged with inert gas (N₂) three times. The mixture is stirred by 427 nm blue LED lamps in the PhotoRedOx Box equipped with a fan for 4 h at room temperature under N₂ atmosphere. After Suzuki-Miyaura cross-coupling reaction occurs 4 hours, the reaction mixture was isolated by flash chromatography (Pure petroleum ether). Then recrystallization from methanol (2 mL) afforded **3f** as white solid (42.7 mg, 96.7%).

¹H-NMR (500 MHz, CDCl₃): δ_H 7.55-7.52 (m, 2H), 7.44 (d, *J* = 8.1 Hz, 2H), 7.38-7.31 (m, 3H), 7.17 (d, *J* = 7.9 Hz, 2H), 2.38 (s, 3H).

¹³C-NMR (125 MHz, CDCl₃): δ_C 138.4, 131.5, 131.5, 129.1, 128.3, 128.1, 123.5, 120.2, 89.6, 88.7, 21.5.

3-(phenylethynyl)thiophene 3g^[8]

Following the **Procedure A**: using the 1-(thiophen-3-ylethynyl)-1-benzo[*d*][1,2]



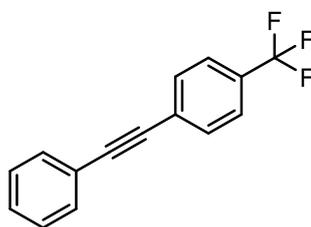
3g

iiodaoxol-3(1H)-one (0.1 mmol, 35.4 mg, 1.0 eq.), phenylboronic acid (0.2 mmol, 24.4 mg, 2.0 eq.), Cu(AcO)₂ (0.01 mmol, 2 mg, 0.1 eq.), DTBPY (0.01 mmol, 2.7 mg, 0.1 eq.), K₂CO₃ (0.2 mmol, 27.6 mg, 2.0 eq.) and 1.0 mL (trifluoromethyl)benzene. The reaction mixture was evacuated and purged with inert gas (N₂) three times. The mixture is stirred by 427 nm blue LED lamps in the PhotoRedOx Box equipped with a fan for 4 h at room temperature under N₂ atmosphere. After Suzuki-Miyaura cross-coupling reaction occurs 4 hours, the reaction mixture was isolated by flash chromatography (Pure petroleum ether). Then recrystallization from Methanol (2 mL) afforded **3g** as pale-yellow oil (12.3 mg, 66.5%).

¹H-NMR (500 MHz, CDCl₃): δ_H 7.54-7.50 (m, 3H), 7.36-7.33 (m, 3H), 7.31 (dd, *J* = 5.0, 3.0 Hz, 1H), 7.21 (m, 1H).

¹³C-NMR (125 MHz, CDCl₃): δ_C 131.5, 129.9, 128.6, 128.3, 128.2, 125.3, 123.2, 122.3, 88.9, 84.5.

1-(phenylethynyl)-4-(trifluoromethyl)benzene **3h** ^[10]



3h

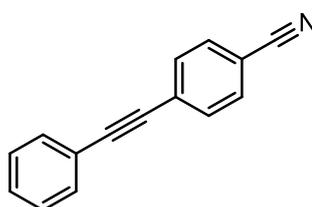
Following the **Procedure A**: using the 1-((4-(trifluoromethyl)phenyl)ethynyl)-1-benzo[*d*][1,2]iodaoxol-3(1H)-one (0.2 mmol, 78.4 mg, 1.0 eq.), phenylboronic acid (0.4 mmol, 48.8 mg, 2.0 eq.), Cu(AcO)₂ (0.02 mmol, 4 mg, 0.1 eq.), DTBPY (0.02

mmol, 5.4 mg, 0.1 eq.), K₂CO₃ (0.4 mmol, 55.4 mg, 2.0 eq.) and 1.0 mL (trifluoromethyl)benzene. The reaction mixture was evacuated and purged with inert gas (N₂) three times. The mixture is stirred by 427 nm blue LED lamps in the PhotoRedOx Box equipped with a fan for 4 h at room temperature under N₂ atmosphere. After Suzuki-Miyaura cross-coupling reaction occurs 4 hours, the reaction mixture was isolated by flash chromatography (Pure petroleum ether). Then recrystallization from methanol (1.5 mL) afforded **3h** as white solid (32.9 mg, 66.9%).

¹H-NMR (500 MHz, CDCl₃): δ_H 7.62 (q, *J* = 8.5 Hz, 4H), 7.57-7.53 (m, 2H), 7.40-7.36 (m, 3H).

¹³C-NMR (125 MHz, CDCl₃): δ_C 131.8, 130.1, 129.8, 128.8, 128.5, 127.1, 125.3, 124.0 (q, *J* = 271.2 Hz), 122.6, 91.8, 88.0.

4-(phenylethynyl)benzonitrile **3i** ^[11]



3i

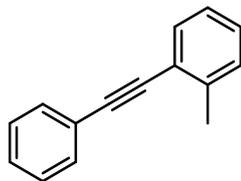
Following the **Procedure A**: using the 4-((3-oxo-1-benzo[*d*][1,2] iodoaxol-1(3H)-yl)ethynyl)benzonitrile (0.2 mmol, 78.4 mg, 1.0 eq.), phenylboronic acid (0.4 mmol, 48.8 mg, 2.0 eq.), Cu(AcO)₂ (0.02 mmol, 4.0 mg, 0.1 eq.) , DTBPY (0.02 mmol, 5.4 mg, 0.1 eq.), K₂CO₃ (0.4 mmol, 55.2 mg, 2.0 eq.) and 1.5 mL (trifluoromethyl)benzene. The reaction mixture was evacuated and purged with inert gas (N₂) three times. The mixture is stirred by 427 nm blue LED lamps in the PhotoRedOx Box equipped with a fan for 4 h at room temperature under N₂ atmosphere. After Suzuki-Miyaura cross-coupling reaction occurs 4 hours, the reaction mixture was isolated by flash

chromatography (1:50 ethyl acetate: n-hexane). Then recrystallization from methanol (1.5 mL) afforded **3i** as white solid (26.5 mg, 79.3%).

¹H-NMR (500 MHz, CDCl₃): δ_H 7.62 (td, $J = 8.6, 6.5$ Hz, 4H), 7.55 (dd, $J = 6.5, 3.2$ Hz, 2H), 7.38 (dd, $J = 5.1, 1.8$ Hz, 3H).

¹³C-NMR (125 MHz, CDCl₃): δ_C 132.1, 131.8, 129.1, 128.5, 128.3, 122.2, 118.5, 111.5, 93.8, 87.7.

1-methyl-2-(phenylethynyl)benzene **6a** ^[9]



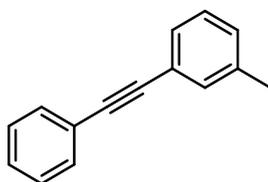
6a

Following the **Procedure B**: using the 1-(phenylethynyl)-1-benzo[*d*][1,2] iodaaxol-3(1H)-one (0.1 mmol, 34.7 mg, 1.0 eq.), *o*-tolylboronic acid (0.2 mmol, 27.2 mg, 2.0 eq.), Cu(AcO)₂ (0.01 mmol, 2.0 mg, 0.1 eq.) , DTBPY (0.01 mmol, 3.0 mg, 0.1 eq.), K₂CO₃ (0.2 mmol, 27.6 mg, 2.0 eq.) and 1.0 mL (trifluoromethyl)benzene. The reaction mixture was evacuated and purged with inert gas (N₂) three times. The mixture is stirred by 427 nm blue LED lamps in the PhotoRedOx Box equipped with a fan for 4 h at room temperature under N₂ atmosphere. After Suzuki-Miyaura cross-coupling reaction occurs 4 hours, the reaction mixture was isolated by flash chromatography (Pure petroleum ether). Then recrystallization from methanol (1.5 mL) afforded **6a** as pale yellow oil (17.7 mg, 92.11%).

¹H-NMR (500 MHz, CDCl₃): δ_H 7.61-7.52 (m, 3H), 7.42-7.35 (m, 3H), 7.29-7.25 (m, 2H), 7.23-7.18 (m, 1H), 2.56 (s, 3H).

¹³C-NMR (125 MHz, CDCl₃): δ_C 140.2, 131.9, 131.5, 129.5, 128.4, 128.3, 128.2, 125.6, 123.6, 123.0, 93.4, 88.4, 20.8.

1-methyl-3-(phenylethynyl)benzene 6b ^[9]



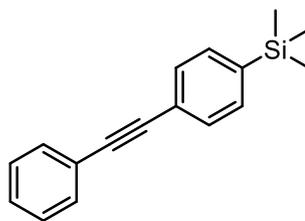
6b

Following the **Procedure B**: using the 1-(phenylethynyl)-1-benzo[*d*][1,2]iodaoxol-3(1H)-one (0.1 mmol, 34.7 mg, 1.0 eq.), *m*-tolylboronic acid (0.2 mmol, 27.2 mg, 2.0 eq.), Cu(AcO)₂ (0.01 mmol, 2.0 mg, 0.1 eq.), DTBPY (0.01 mmol, 3.0 mg, 0.1 eq.), K₂CO₃ (0.2 mmol, 27.6 mg, 2.0 eq.) and 1.0 mL (trifluoromethyl)benzene. The reaction mixture was evacuated and purged with inert gas (N₂) three times. The mixture is stirred by 427 nm blue LED lamps in the PhotoRedOx Box equipped with a fan for 4 h at room temperature under N₂ atmosphere. After Suzuki-Miyaura cross-coupling reaction occurs 4 hours, the reaction mixture was isolated by flash chromatography (Pure petroleum ether). Then recrystallization from methanol (1.5 mL) afforded **6b** as yellow oil (18.4mg, 96.12%).

¹H-NMR (500 MHz, CDCl₃): δ_H 7.60-7.52 (m, 2H), 7.43-7.34 (m, 5H), 7.28 (dd, *J* = 10.2, 5.0 Hz, 1H), 7.18 (d, *J* = 7.6 Hz, 1H), 2.39 (s, 3H).

¹³C-NMR (125 MHz, CDCl₃): δ_C 138.0, 132.2, 131.6, 129.2, 128.7, 128.3, 128.2, 128.2, 123.4, 123.1, 89.6, 89.0, 21.2.

trimethyl(4-(phenylethynyl)phenyl)silane 6c ^[9]



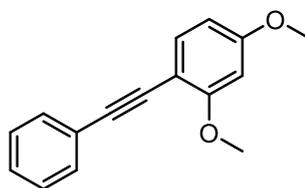
6c

Following the **Procedure B**: using the 1-(phenylethynyl)-1-benzo[*d*][1,2] iodaaxol-3(1H)-one (0.1 mmol, 34.7 mg, 1.0 eq.), (4-(trimethylsilyl)phenyl)boronic acid (0.2 mmol, 38.8 mg, 2.0 eq.), Cu(AcO)₂ (0.01 mmol, 2.0 mg, 0.1 eq.), DTBPY (0.01 mmol, 3.0 mg, 0.1 eq.), K₂CO₃ (0.2 mmol, 27.6 mg, 2.0 eq.) and 1.0 mL (trifluoromethyl)benzene. The reaction mixture was evacuated and purged with inert gas (N₂) three times. The mixture is stirred by 427 nm blue LED lamps in the PhotoRedOx Box equipped with a fan for 4 h at room temperature under N₂ atmosphere. After Suzuki-Miyaura cross-coupling reaction occurs 4 hours, the reaction mixture was isolated by flash chromatography (Pure petroleum ether). Then recrystallization from methanol (1.5 mL) afforded **6c** as white solid (19.5 mg, 78%).

¹H-NMR (500 MHz, CDCl₃): δ_H 7.54 (ddd, *J* = 8.4, 3.6, 2.5 Hz, 2H), 7.50 (s, 4H), 7.38-7.31 (m, 3H), 0.27 (m, 9H).

¹³C-NMR (125 MHz, CDCl₃): δ_C 141.0, 133.2, 131.6, 130.7, 128.3, 128.2, 123.5, 123.3, 89.7, 89.6, -1.2.

2,4-dimethoxy-1-(phenylethynyl)benzene **6d**^[12]



6d

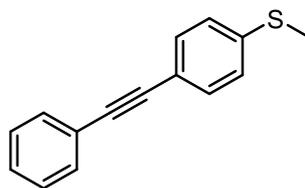
Following the **Procedure B**: using the 1-(phenylethynyl)-1-benzo[*d*][1,2] iodaaxol-3(1H)-one (0.1 mmol, 34.7 mg, 1.0 eq.), (2,4-dimethoxyphenyl)boronic acid (0.2 mmol, 36.4 mg, 2.0 eq.), Cu(AcO)₂ (0.01 mmol, 2.0 mg, 0.1 eq.), DTBPY (0.01 mmol, 3.0

mg, 0.1 eq.), K₂CO₃ (0.2 mmol, 27.6 mg, 2.0 eq.) and 1.0 mL (trifluoromethyl)benzene. The reaction mixture was evacuated and purged with inert gas (N₂) three times. The mixture is stirred by 427 nm blue LED lamps in the PhotoRedOx Box equipped with a fan for 4 h at room temperature under N₂ atmosphere. After Suzuki-Miyaura cross-coupling reaction occurs 4 hours, the reaction mixture was isolated by flash chromatography (Pure petroleum ether). Then recrystallization from methanol (1.5 mL) afforded **6d** as pale-yellow oil (13.6 mg, 57%).

¹H-NMR (500 MHz, CDCl₃): δ_H 7.57-7.52 (m, 2H), 7.42 (d, $J = 8.3$ Hz, 1H), 7.35-7.26 (m, 3H), 6.48 (dt, $J = 5.8, 2.3$ Hz, 2H), 3.90 (s, 3H), 3.83 (s, 3H).

¹³C-NMR (125 MHz, CDCl₃): δ_C 161.2, 161.2, 134.3, 131.5, 128.2, 127.8, 123.9, 105.0, 104.9, 98.5, 92.0, 85.8, 55.9, 55.4.

methyl(4-(phenylethynyl)phenyl)sulfane **6e** ^[13]



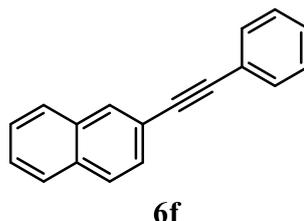
6e

Following the **Procedure B**: using the 1-(phenylethynyl)-1-benzo[*d*][1,2]iodaoxol-3(1H)-one (0.1 mmol, 34.7 mg, 1.0 eq.), (4-(methylthio)phenyl)boronic acid (0.2 mmol, 33.6 mg, 2.0 eq.), Cu(AcO)₂ (0.01 mmol, 2.0 mg, 0.1 eq.), DTBPY (0.01 mmol, 3.0 mg, 0.1 eq.), K₂CO₃ (0.2 mmol, 27.6 mg, 2.0 eq.) and 1.0 mL (trifluoromethyl)benzene. The reaction mixture was evacuated and purged with inert gas (N₂) three times. The mixture is stirred by 427 nm blue LED lamps in the PhotoRedOx Box equipped with a fan for 4 h at room temperature under N₂ atmosphere. After Suzuki-Miyaura cross-coupling reaction occurs 4 hours, the reaction mixture was isolated by flash chromatography (Pure petroleum ether). Then recrystallization from methanol (1.5 mL) afforded **6e** as white solid (39 mg, 87.1%).

¹H-NMR (500 MHz, CDCl₃): δ_H 7.54-7.50 (m, 2H), 7.46-7.42 (m, 2H), 7.37-7.31 (m, 3H), 7.23-7.19 (m, 2H), 2.50 (s, 3H).

¹³C-NMR (125 MHz, CDCl₃): δ_C 139.3, 131.9, 131.6, 128.4, 128.2, 125.9, 123.3, 119.6, 89.5, 89.2, 15.4.

2-(phenylethynyl)naphthalene 6f ^[14]

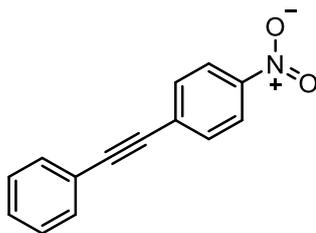


Following the **Procedure B**: using the 1-(phenylethynyl)-1-benzo[*d*][1,2]iodaoxol-3(1H)-one (0.1 mmol, 34.7 mg, 1.0 eq.), naphthalen-2-ylboronic acid (0.2 mmol, 34.4 mg, 2.0 eq.), Cu(AcO)₂ (0.01 mmol, 2.0 mg, 0.1 eq.), DTBPY (0.01 mmol, 3.0 mg, 0.1 eq.), K₂CO₃ (0.2 mmol, 27.6 mg, 2.0 eq.) and 1.0 mL (trifluoromethyl)benzene. The reaction mixture was evacuated and purged with inert gas (N₂) three times. The mixture is stirred by 427 nm blue LED lamps in the PhotoRedOx Box equipped with a fan for 4 h at room temperature under N₂ atmosphere. After Suzuki-Miyaura cross-coupling reaction occurs 4 hours, the reaction mixture was isolated by flash chromatography (Pure petroleum ether). Then recrystallization from methanol (1.5 mL) afforded **6f** as white solid (21.9 mg, 89.77%).

¹H-NMR (500 MHz, CDCl₃): δ_H 8.07 (s, 1H), 7.86-7.80 (m, 3H), 7.60 (dt, *J* = 5.6, 1.4 Hz, 3H), 7.53-7.47 (m, 2H), 7.41-7.33 (m, 3H).

¹³C-NMR (125 MHz, CDCl₃): δ_C 133.1, 132.8, 131.7, 131.5, 128.4, 128.4, 128.3, 128.0, 127.8, 127.8, 126.7, 126.6, 123.3, 120.6, 89.8, 89.8.

1-nitro-4-(phenylethynyl)benzene 6h ^[10]



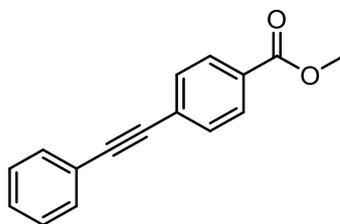
6h

Following the **Procedure B**: using the 1-(phenylethynyl)-1-benzo[*d*][1,2] iodoxol-3(1H)-one (0.3 mmol, 104.1 mg, 1.0 eq.), (4-nitrophenyl)boronic acid (0.6 mmol, 100.2 mg, 2.0 eq.), Cu(AcO)₂ (0.03 mmol, 6.0 mg, 0.1 eq.), DTBPY (0.03 mmol, 9.0 mg, 0.1 eq.), K₂CO₃ (0.6 mmol, 82.8 mg, 2.0 eq.) and 3.0 mL (trifluoromethyl)benzene. The reaction mixture was evacuated and purged with inert gas (N₂) three times. The mixture is stirred by 427 nm blue LED lamps in the PhotoRedOx Box equipped with a fan for 4 h at room temperature under N₂ atmosphere. After Suzuki-Miyaura cross-coupling reaction occurs 4 hours, the reaction mixture was isolated by flash chromatography (Pure petroleum ether). Then recrystallization from methanol (3 mL) afforded **6h** as pale-yellow oil (31 mg, 46.4%).

¹H-NMR (500 MHz, CDCl₃): δ_H 8.25-8.20 (m, 2H), 7.69-7.64 (m, 2H), 7.59-7.54 (m, 2H), 7.42-7.36 (m, 3H).

¹³C-NMR (125 MHz, CDCl₃): δ_C 147.0, 132.3, 131.9, 130.3, 129.3, 128.6, 123.7, 122.1, 94.7, 87.6.

methyl 4-(phenylethynyl)benzoate 6g ^[15]



6g

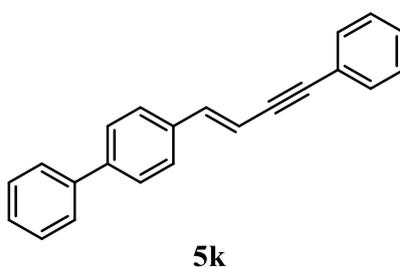
Following the **Procedure B**: using the 1-(phenylethynyl)-1-benzo[*d*][1,2] iodoxol-3(1H)-one (0.1 mmol, 34.7 mg, 1.0 eq.), (4-(methoxycarbonyl)phenyl)boronic acid (0.2

mmol, 36 mg, 2.0 eq.), Cu(AcO)₂ (0.01 mmol, 2.0 mg, 0.1 eq.) , DTBPY (0.01 mmol, 3.0 mg, 0.1 eq.), K₂CO₃ (0.2 mmol, 27.6 mg, 2.0 eq.) and 1.0 mL (trifluoromethyl)benzene. The reaction mixture was evacuated and purged with inert gas (N₂) three times. The mixture is stirred by 427 nm blue LED lamps in the PhotoRedOx Box equipped with a fan for 4 h at room temperature under N₂ atmosphere. After Suzuki-Miyaura cross-coupling reaction occurs 4 hours, the reaction mixture was isolated by flash chromatography (Pure petroleum ether). Then recrystallization from methanol (1.5 mL) afforded **6g** as pale-yellow oil (37 mg, 82.7%).

¹H-NMR (500 MHz, CDCl₃): δ_H 8.02 (d, $J = 8.4$ Hz, 2H), 7.59 (d, $J = 8.4$ Hz, 2H), 7.57-7.53 (m, 2H), 7.40-7.34 (m, 3H), 3.93 (s, 3H).

¹³C-NMR (125 MHz, CDCl₃): δ_C 166.6, 131.7, 131.5, 129.5, 129.5, 128.8, 128.4, 128.0, 122.7, 92.4, 88.6, 52.2.

(E)-4-(4-phenylbut-1-en-3-yn-1-yl)-1,1'-biphenyl 5k



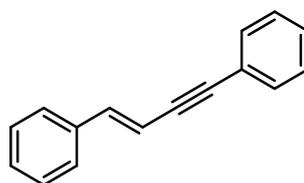
Following the **Procedure B**: using the 1-(phenylethynyl)-1-benzo[*d*][1,2]iodaoxol-3(1H)-one (0.1 mmol, 34.7 mg, 1.0 eq.), (*E*)-(2-([1,1'-biphenyl]-4-yl)vinyl)boronic acid (0.2 mmol, 44.8 mg, 2.0 eq.), Cu(AcO)₂ (0.01 mmol, 2.0 mg, 0.1 eq.) , DTBPY (0.01 mmol, 3.0 mg, 0.1 eq.), K₂CO₃ (0.2 mmol, 27.6 mg, 2.0 eq.) and 1.0 mL (trifluoromethyl)benzene. The reaction mixture was evacuated and purged with inert gas (N₂) three times. The mixture is stirred by 427 nm blue LED lamps in the PhotoRedOx Box equipped with a fan for 4 h at room temperature under N₂ atmosphere. After Suzuki-Miyaura cross-coupling reaction occurs 4 hours, the reaction mixture was

isolated by flash chromatography (Pure petroleum ether). Then recrystallization from methanol (1.5 mL) afforded **5k** as pale-yellow solid (13.3 mg, 47.5%).

¹H-NMR (500 MHz, CDCl₃): δ_H 7.61 (dd, $J = 12.9, 4.8$ Hz, 4H), 7.53-7.42 (m, 6H), 7.35 (tt, $J = 5.7, 5.0$ Hz, 4H), 7.09 (d, $J = 16.2$ Hz, 1H), 6.43 (d, $J = 16.2$ Hz, 1H).

¹³C-NMR (125 MHz, CDCl₃): δ_C 141.4, 140.8, 140.4, 135.4, 131.5, 128.9, 128.4, 128.2, 127.5, 127.4, 127.0, 126.8, 123.4, 108.1, 92.0, 89.0.

(*E*)-but-1-en-3-yne-1,4-diyldibenzene **5i** ^[14]



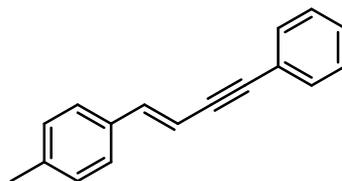
5i

Following the **Procedure B**: using the 1-(phenylethynyl)-1-benzo[*d*][1,2]iodaoxol-3(1H)-one (0.3 mmol, 104.4 mg, 1.0 eq.), (*E*)-styrylboronic acid (0.6 mmol, 88.8 mg, 2.0 eq.), Cu(AcO)₂ (0.03 mmol, 6.0 mg, 0.1 eq.), DTBPY (0.03 mmol, 9.0 mg, 0.1 eq.), K₂CO₃ (0.6 mmol, 62.8 mg, 2.0 eq.) and 3.0 mL (trifluoromethyl)benzene. The reaction mixture was evacuated and purged with inert gas (N₂) three times. The mixture is stirred by 427 nm blue LED lamps in the PhotoRedOx Box equipped with a fan for 4 h at room temperature under N₂ atmosphere. After Suzuki-Miyaura cross-coupling reaction occurs 4 hours, the reaction mixture was isolated by flash chromatography (Pure petroleum ether). Then recrystallization from methanol (2 mL) afforded **5i** as pale-yellow solid (56.4 mg, 86.2%).

¹H-NMR (500 MHz, CDCl₃): δ_H 7.51-7.47 (m, 2H), 7.44 (d, $J = 7.4$ Hz, 2H), 7.38-7.27 (m, 6H), 7.06 (d, $J = 16.2$ Hz, 1H), 6.40 (d, $J = 16.2$ Hz, 1H).

¹³C-NMR (125 MHz, CDCl₃): δ_C 141.3, 136.4, 131.6, 128.8, 128.7, 128.4, 128.2, 126.3, 123.5, 108.2, 91.8, 88.9.

(E)-1-methyl-4-(4-phenylbut-1-en-3-yn-1-yl)benzene 5j ^[16]



5j

Following the **Procedure B**: using the 1-(phenylethynyl)-1-benzo[*d*][1,2]iodaoxol-3(1H)-one (0.1 mmol, 34.7 mg, 1.0 eq.), (*E*)-(4-methylstyryl)boronic acid (0.2 mmol, 32.4 mg, 2.0 eq.), Cu(AcO)₂ (0.01 mmol, 2.0 mg, 0.1 eq.), DTBPY (0.01 mmol, 3.0 mg, 0.1 eq.), K₂CO₃ (0.2 mmol, 27.6 mg, 2.0 eq.) and 1.0 mL (trifluoromethyl)benzene. The reaction mixture was evacuated and purged with inert gas (N₂) three times. The mixture is stirred by 427 nm blue LED lamps in the PhotoRedOx Box equipped with a fan for 4 h at room temperature under N₂ atmosphere. After Suzuki-Miyaura cross-coupling reaction occurs 4 hours, the reaction mixture was isolated by flash chromatography (Pure petroleum ether). Then recrystallization from methanol (1.5 mL) afforded **5j** as pale-yellow oil (17.7 mg, 81.2%).

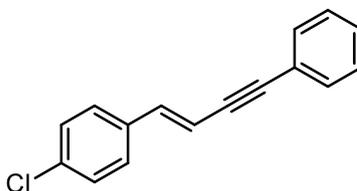
¹H-NMR (500 MHz, CDCl₃): δ_H 7.49 (dd, *J* = 7.6, 1.8 Hz, 2H), 7.36-7.31 (m, 5H), 7.17 (d, *J* = 8.0 Hz, 2H), 7.04 (d, *J* = 16.2 Hz, 1H), 6.35 (d, *J* = 16.2 Hz, 1H), 2.37 (s, 3H).

¹³C-NMR (125 MHz, CDCl₃): δ_C 141.3, 138.7, 133.6, 131.5, 129.5, 128.3, 128.1, 126.3, 123.5, 107.0, 91.4, 89.1, 21.3.

(E)-1-chloro-4-(4-phenylbut-1-en-3-yn-1-yl)benzene 5l

Following the **Procedure B**: using the 1-(phenylethynyl)-1-benzo[*d*][1,2]iodaoxol-3(1H)-one (0.1 mmol, 34.7 mg, 1.0 eq.), (*E*)-(4-chlorostyryl)boronic acid (0.2 mmol, 36.4 mg, 2.0 eq.), Cu(AcO)₂ (0.01 mmol, 2.0 mg, 0.1 eq.), DTBPY (0.01 mmol, 3.0 mg, 0.1 eq.), K₂CO₃ (0.2 mmol, 27.6 mg, 2.0 eq.) and 1.0 mL (trifluoromethyl)benzene. The reaction mixture was evacuated and purged with inert gas (N₂) three times. The mixture is stirred by 427 nm blue LED lamps in the PhotoRedOx Box equipped with a

fan for 4 h at room temperature under N₂ atmosphere. After Suzuki-Miyaura cross-coupling reaction occurs 4 hours, the reaction mixture was isolated by flash chromatography (Pure petroleum ether). Then recrystallization from methanol (1.5 mL) afforded **5l** as white solid (18.9 mg, 79.5%).



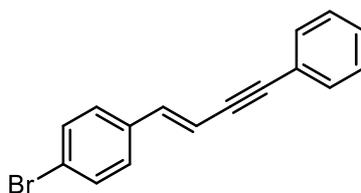
5l

¹H-NMR (500 MHz, CDCl₃): δ_H 7.57-7.55 (m, 2H), 7.51-7.47 (m, 2H), 7.38 (dd, $J = 5.4, 3.8$ Hz, 4H), 7.32 (m, 1H), 7.01 (d, $J = 16.2$ Hz, 1H), 6.38 (d, $J = 16.2$ Hz, 1H).

¹³C-NMR (125 MHz, CDCl₃): δ_C 139.8, 132.5, 131.5, 129.0, 128.9, 128.4, 128.3, 127.5, 127.4, 108.9, 92.3, 88.5.

(E)-1-bromo-4-(4-phenylbut-1-en-3-yn-1-yl)benzene 5m

Following the **Procedure B**: using the 1-(phenylethynyl)-1-benzo[*d*][1,2]iodaoxol-3(1H)-one (0.1 mmol, 34.7 mg, 1.0 eq.), (*E*)-(4-bromostyryl)boronic acid (0.2 mmol, 45.1 mg, 2.0 eq.), Cu(AcO)₂ (0.01 mmol, 2.0 mg, 0.1 eq.), DTBPY (0.01 mmol, 3.0 mg, 0.1 eq.), K₂CO₃ (0.2 mmol, 27.6 mg, 2.0 eq.) and 1.0 mL (trifluoromethyl)benzene. The reaction mixture was evacuated and purged with inert gas (N₂) three times. The mixture is stirred by 427 nm blue LED lamps in the PhotoRedOx Box equipped with a fan for 4 h at room temperature under N₂ atmosphere. After Suzuki-Miyaura cross-coupling reaction occurs 4 hours, the reaction mixture was isolated by flash chromatography (Pure petroleum ether). Then recrystallization from methanol (1.5 mL) afforded **5m** as white solid (21.5 mg, 75.9%).



5m

¹H-NMR (500 MHz, CDCl₃): δ_H 7.57-7.55 (m, 2H), 7.49 (dd, $J = 6.3, 2.1$ Hz, 2H), 7.36 (dd, $J = 10.4, 4.9$ Hz, 4H), 7.32-7.31 (m, 1H), 6.99 (d, $J = 16.2$ Hz, 1H), 6.39 (d, $J = 16.2$ Hz, 1H).

¹³C-NMR (125 MHz, CDCl₃): δ_C 139.9, 132.5, 131.9, 131.5, 129.2, 128.5, 128.4, 127.9, 127.7, 109.0, 92.4, 88.6.

10. References

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11. Copy of ^1H -NMR and ^{13}C -NMR

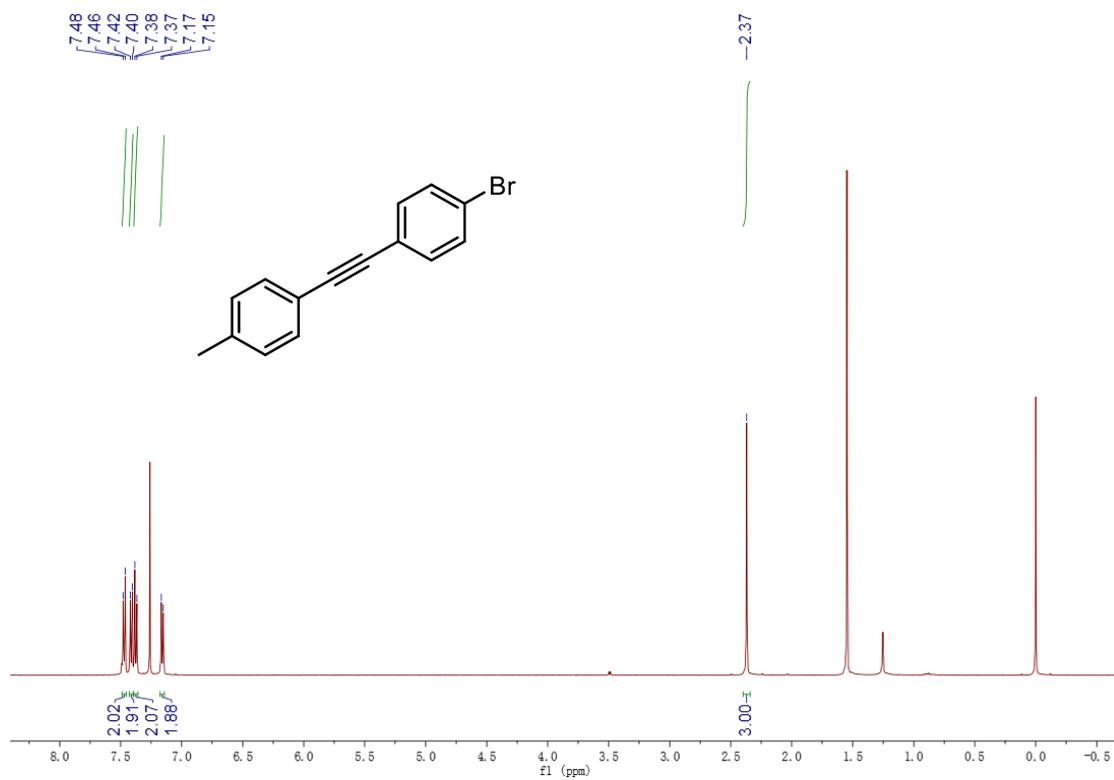


Figure S1. ^1H NMR of **3a** (500 MHz, CDCl_3)

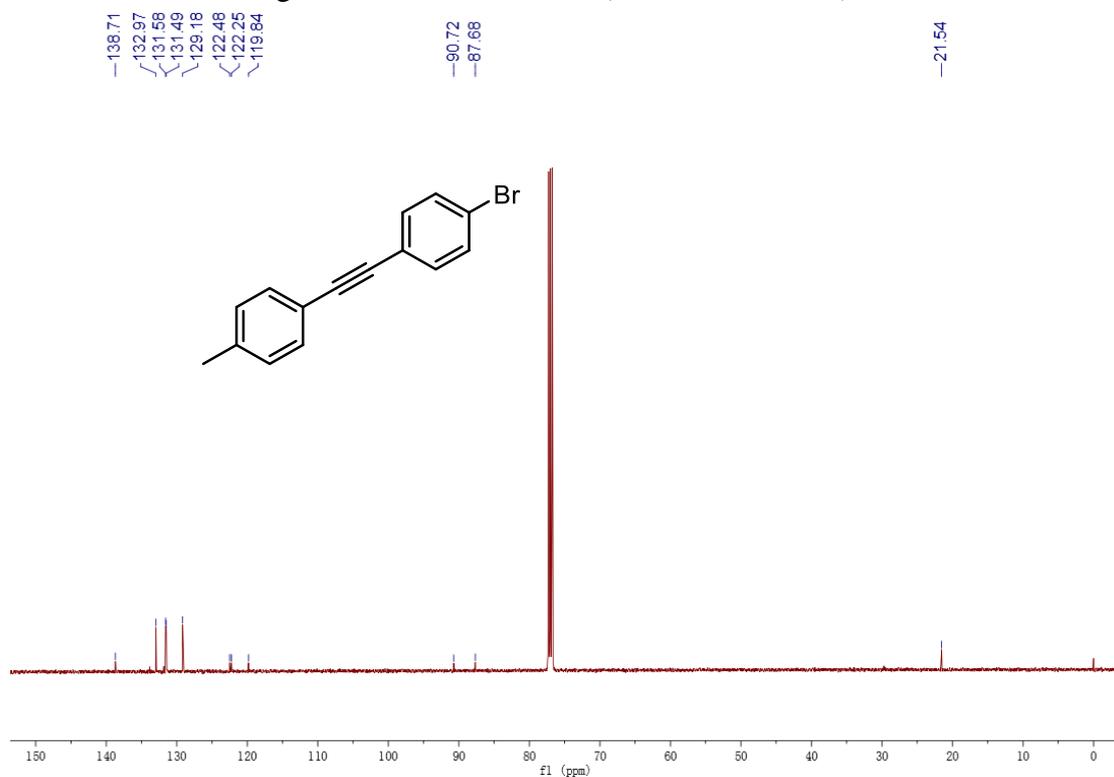


Figure S2. ^{13}C NMR of **3a** (125 MHz, CDCl_3)

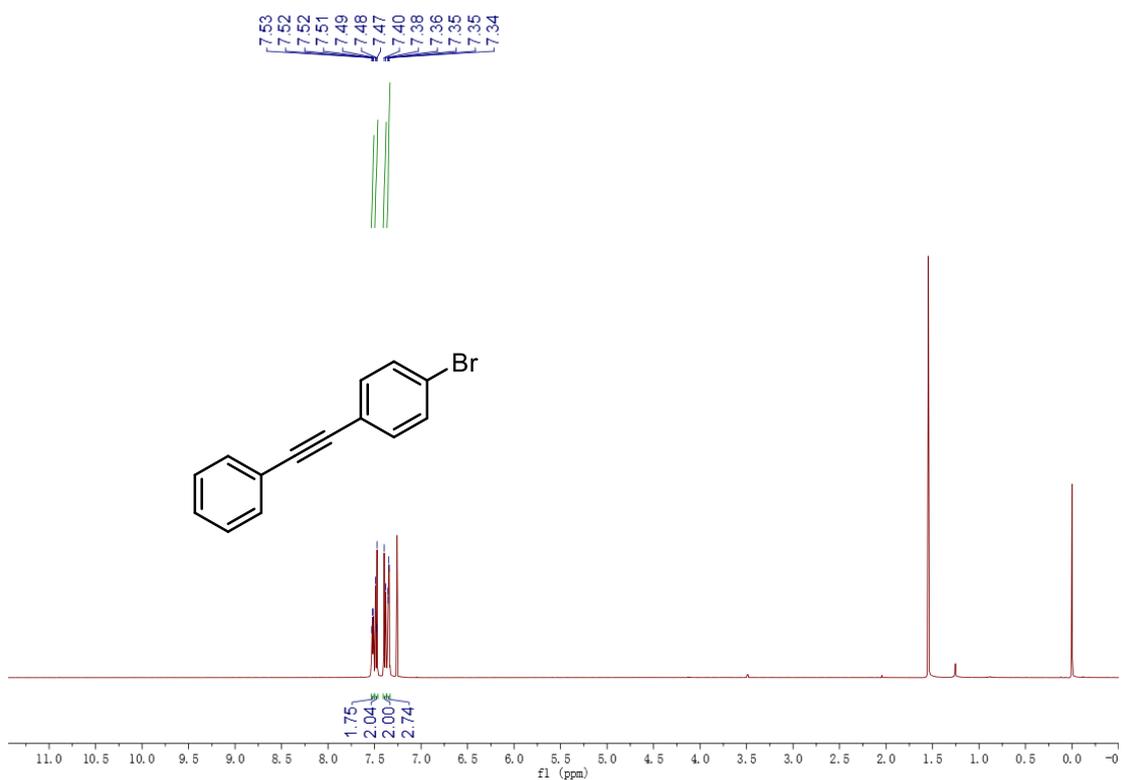


Figure S3. ¹H NMR of **3b** (500 MHz, CDCl₃)

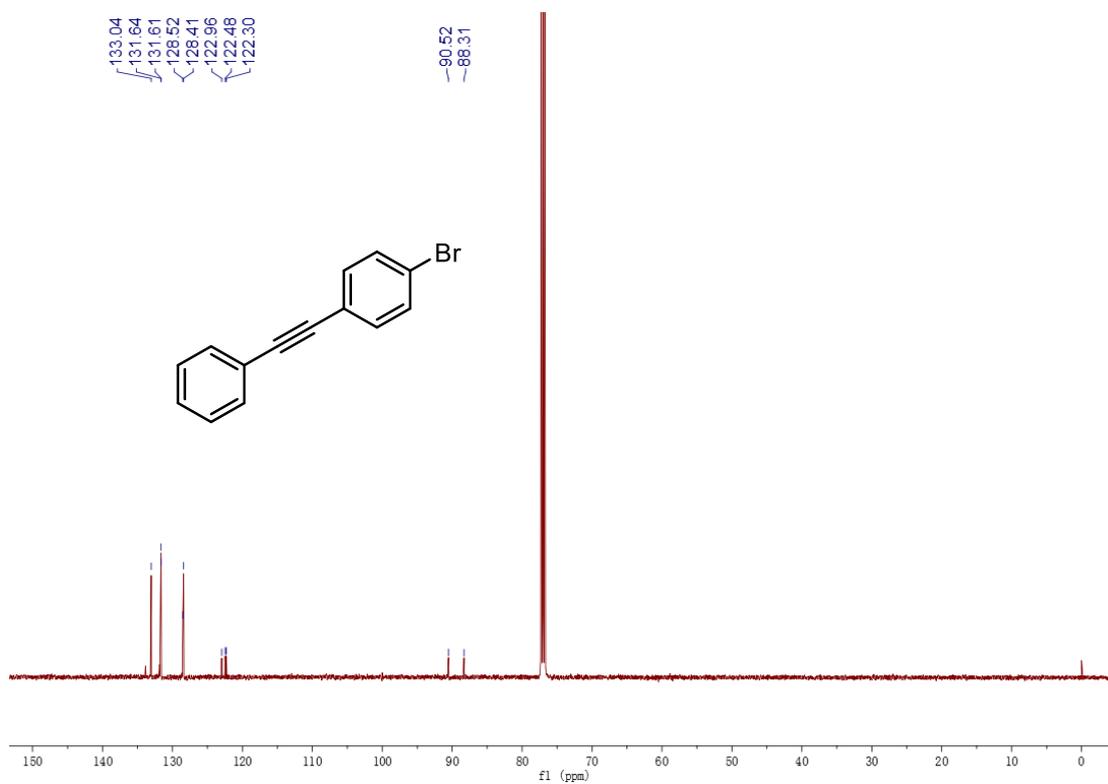


Figure S4. ¹³C NMR of **3b** (125 MHz, CDCl₃)

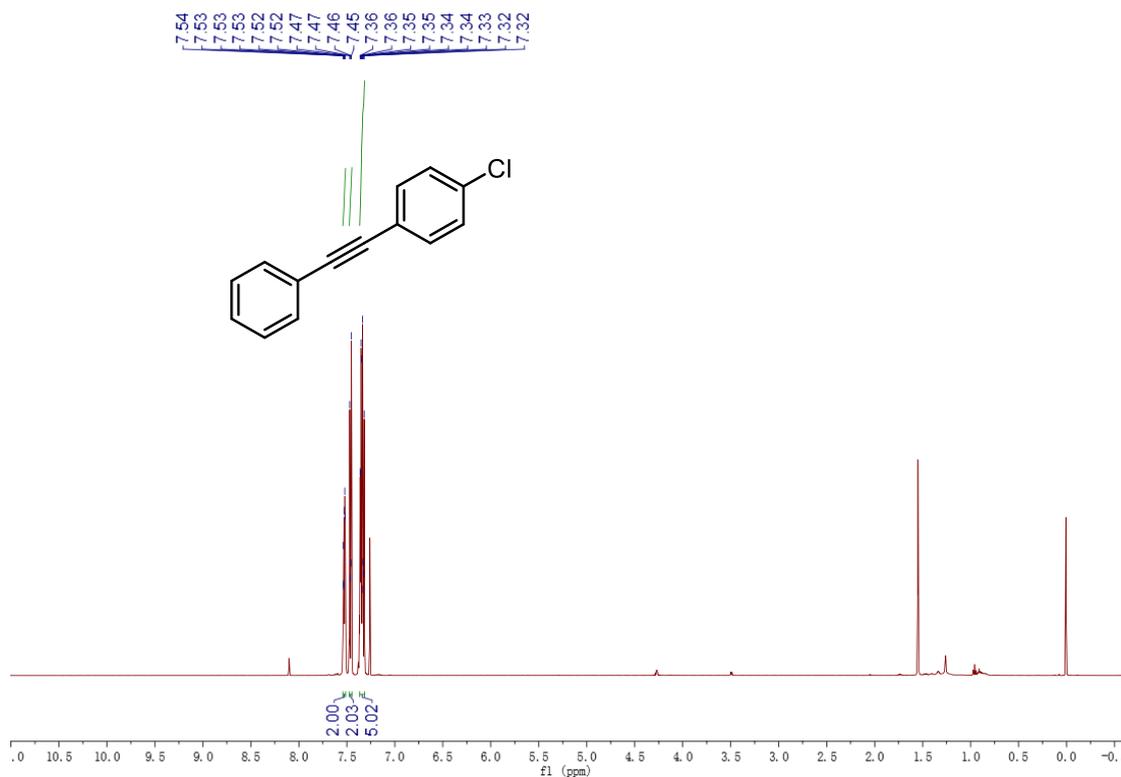


Figure S5. ¹H NMR of **3c** (500 MHz, CDCl₃)

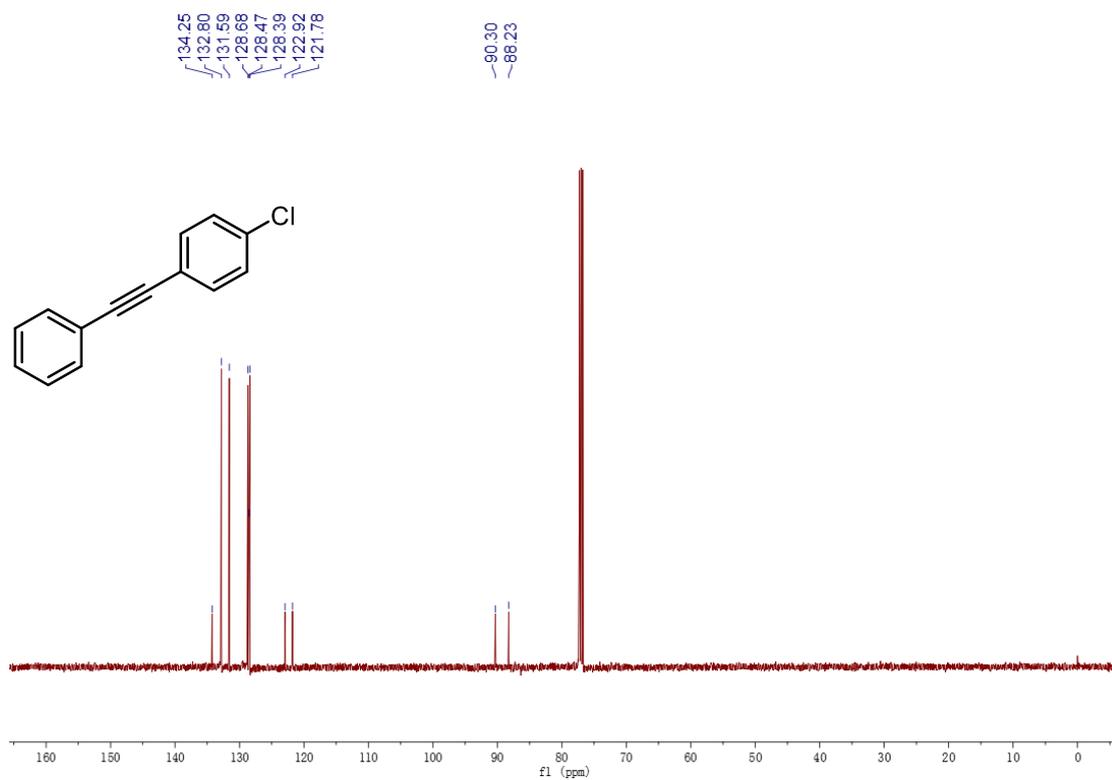


Figure S6. ¹³C NMR of **3c** (125 MHz, CDCl₃)

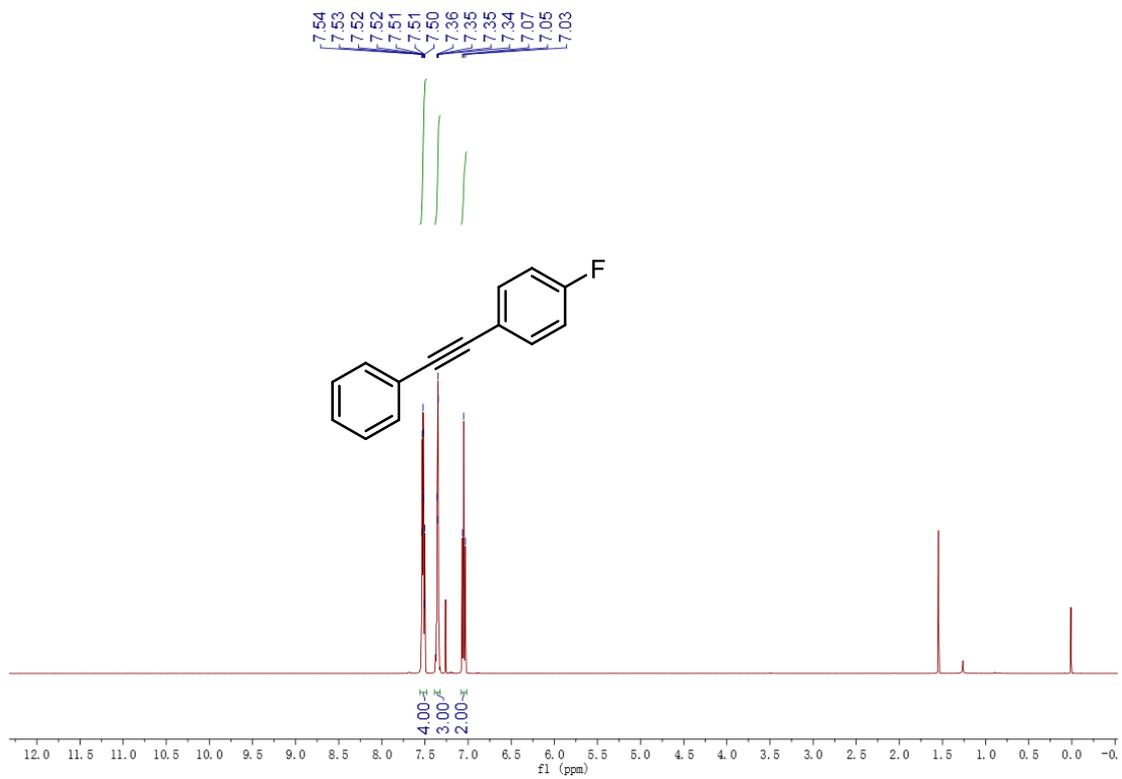


Figure S7. ¹H NMR of **3d** (500 MHz, CDCl₃)

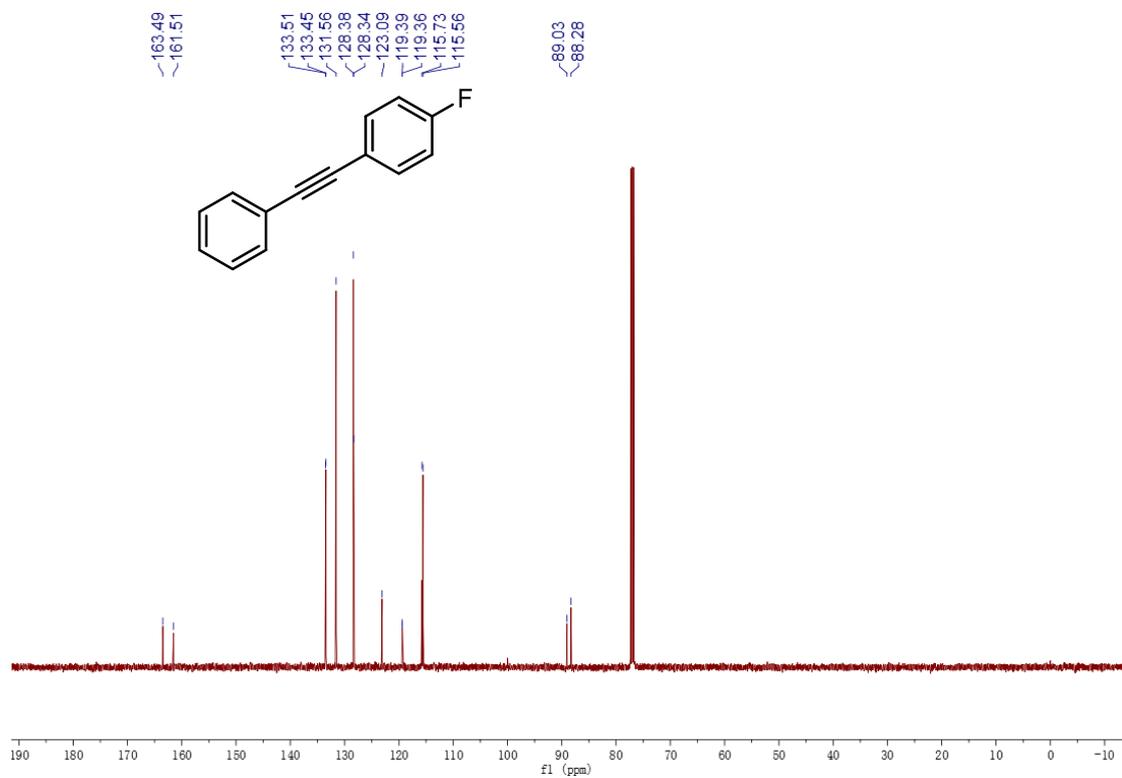


Figure S8. ¹³C NMR of **3d** (125 MHz, CDCl₃)

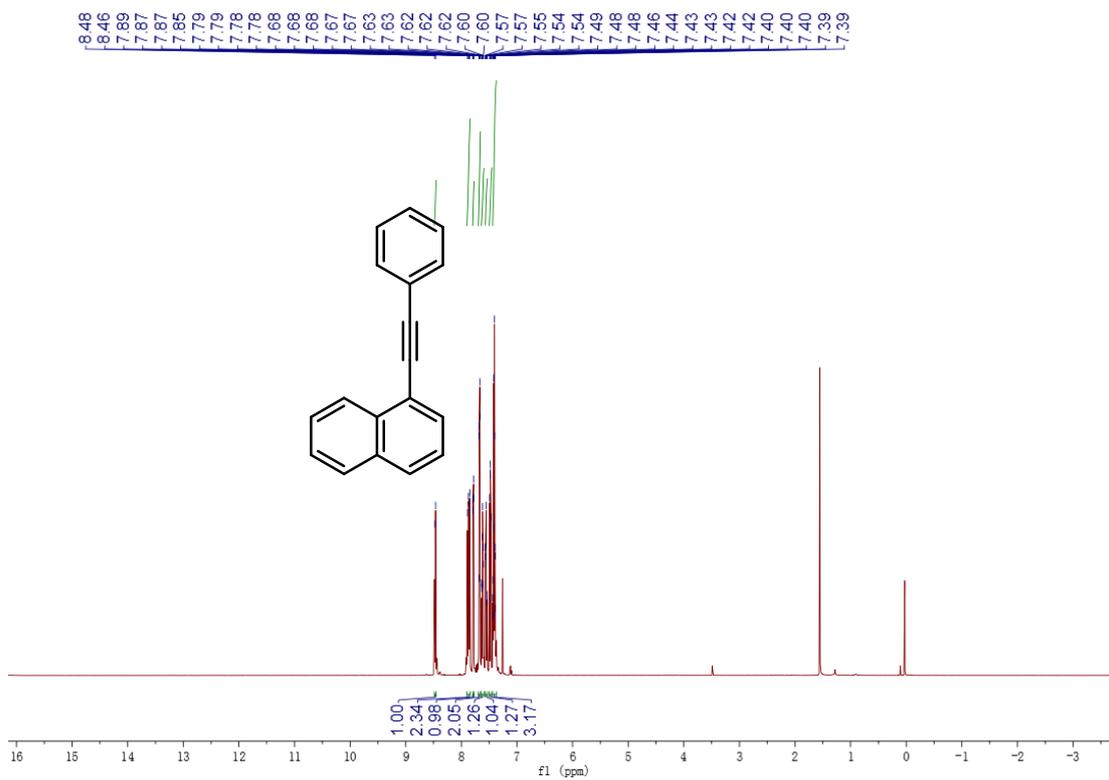


Figure S9. ^1H NMR of **3e** (500 MHz, CDCl_3)

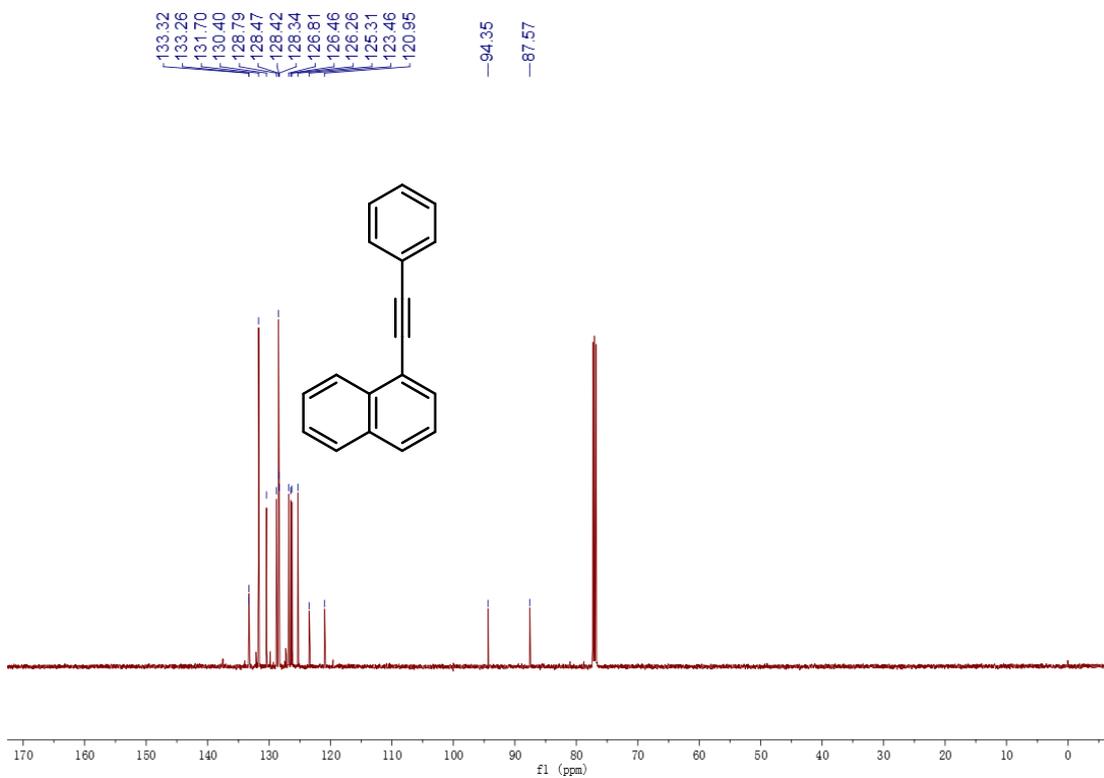


Figure S10. ^{13}C NMR of **3e** (125 MHz, CDCl_3)

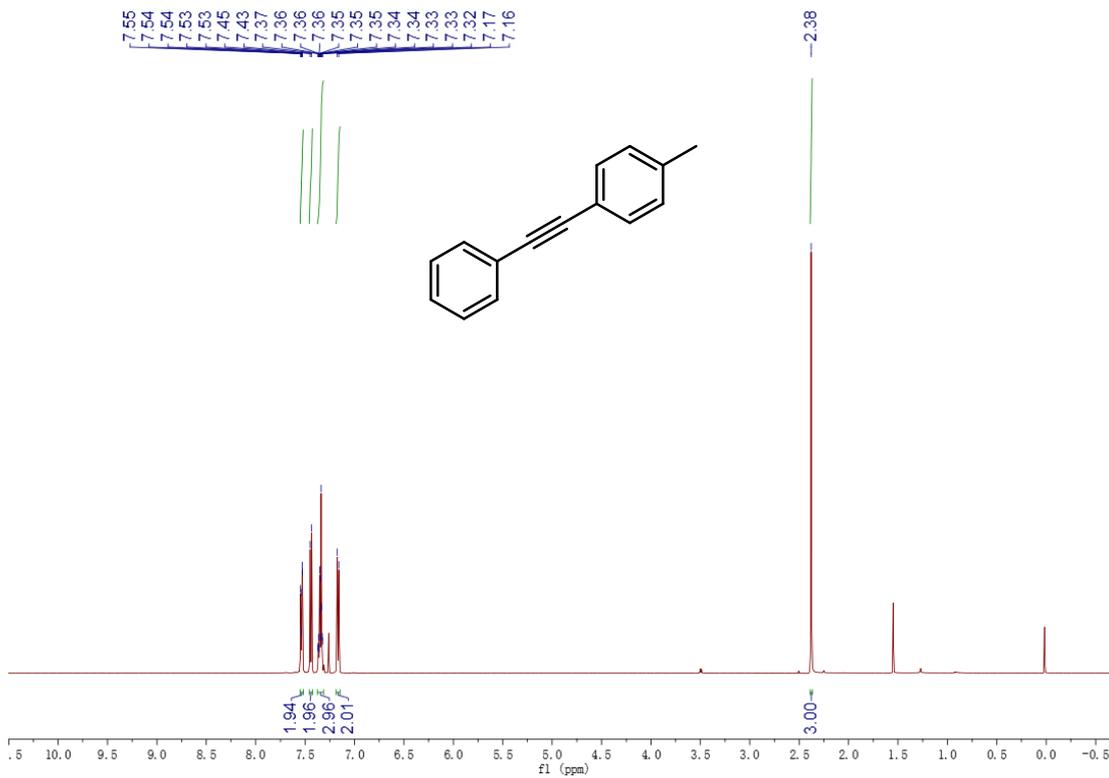


Figure S11. ¹H NMR of **3f** (500 MHz, CDCl₃)

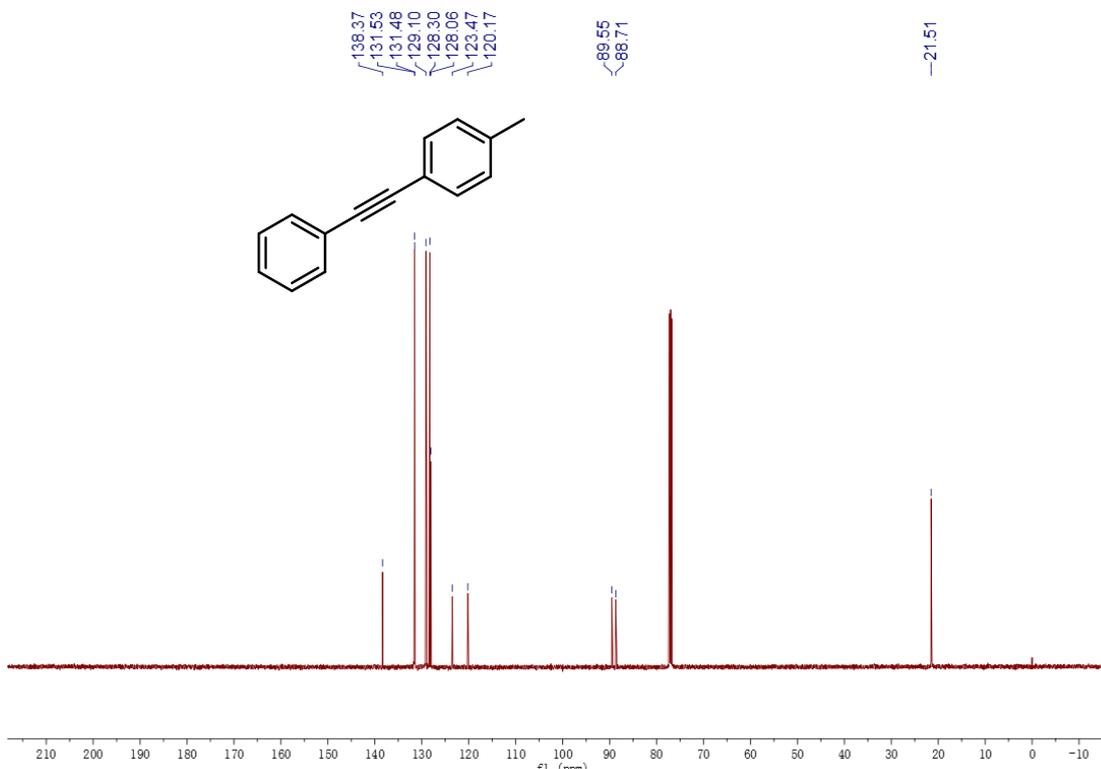


Figure S12. ¹³C NMR of **3f** (125 MHz, CDCl₃)

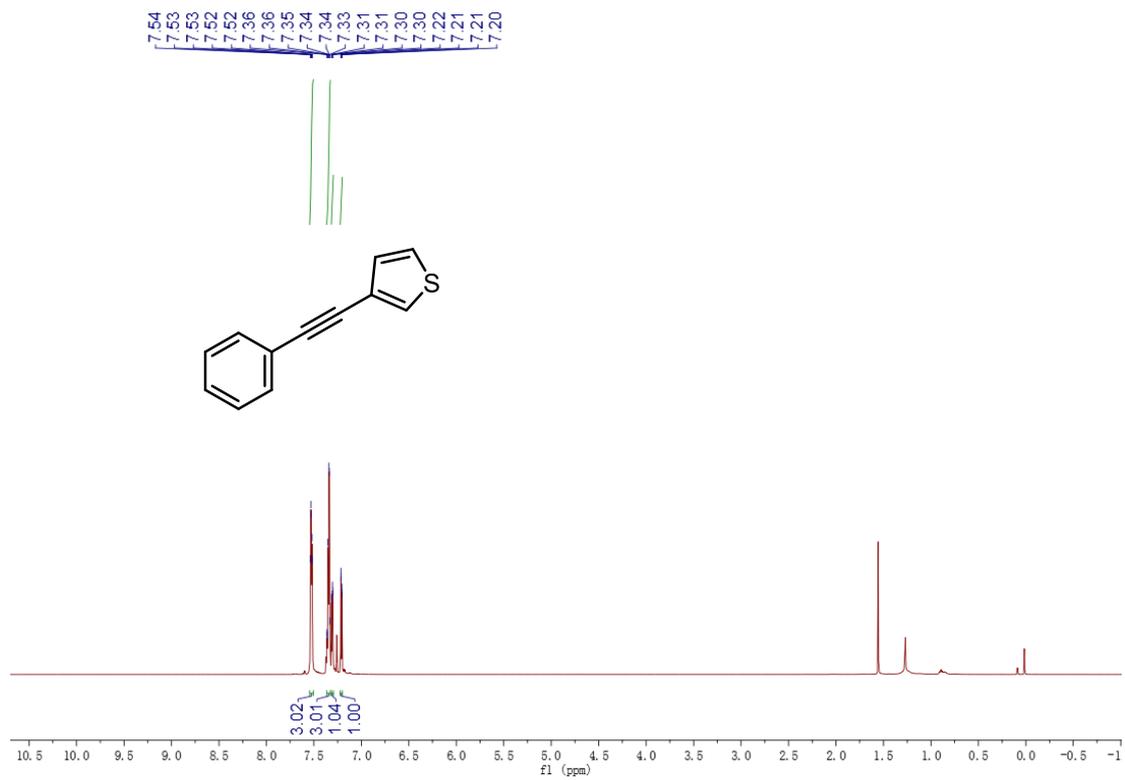


Figure S13. ¹H NMR of **3g** (500 MHz, CDCl₃)

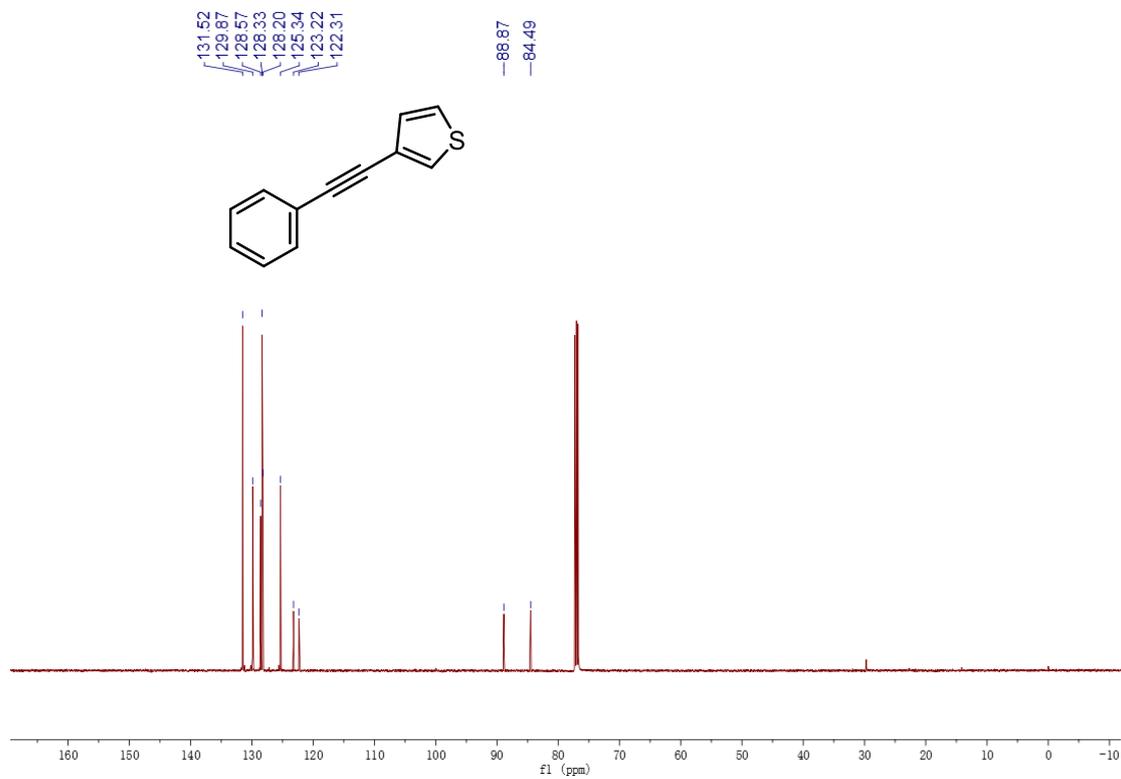


Figure S14. ¹³C NMR of **3g** (125 MHz, CDCl₃)



Figure S15. ¹H NMR of **3h** (500 MHz, CDCl₃)

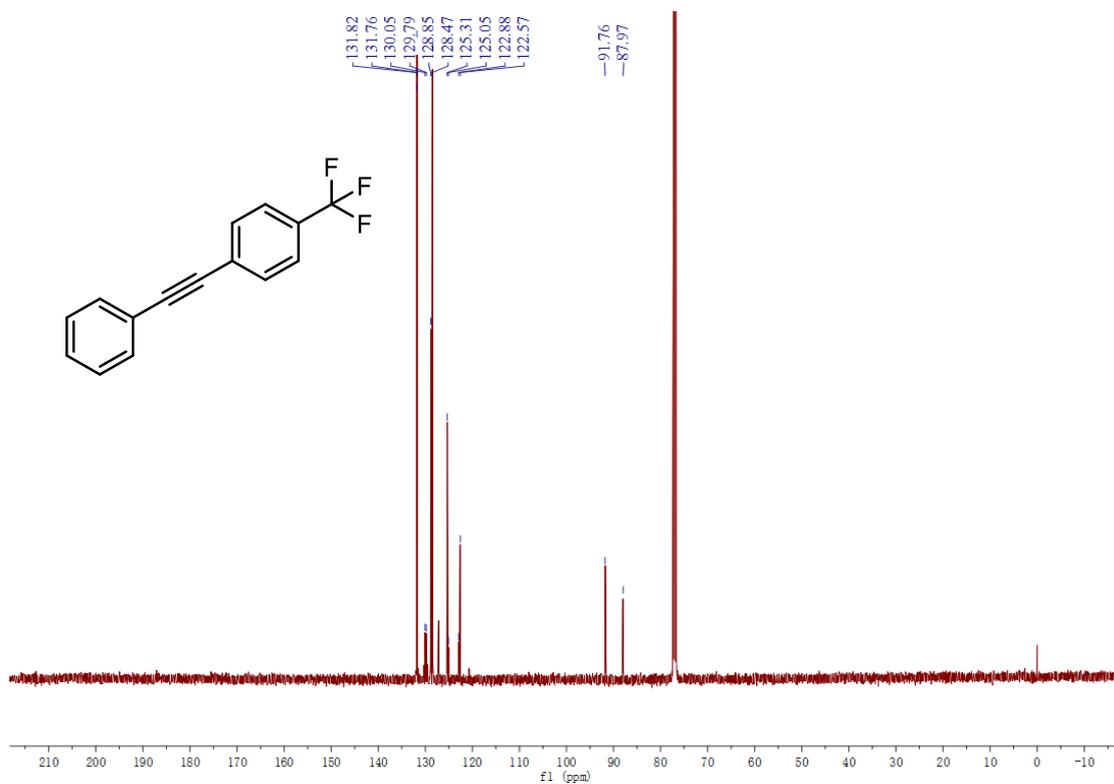


Figure S16. ¹³C NMR of **3h** (125 MHz, CDCl₃)

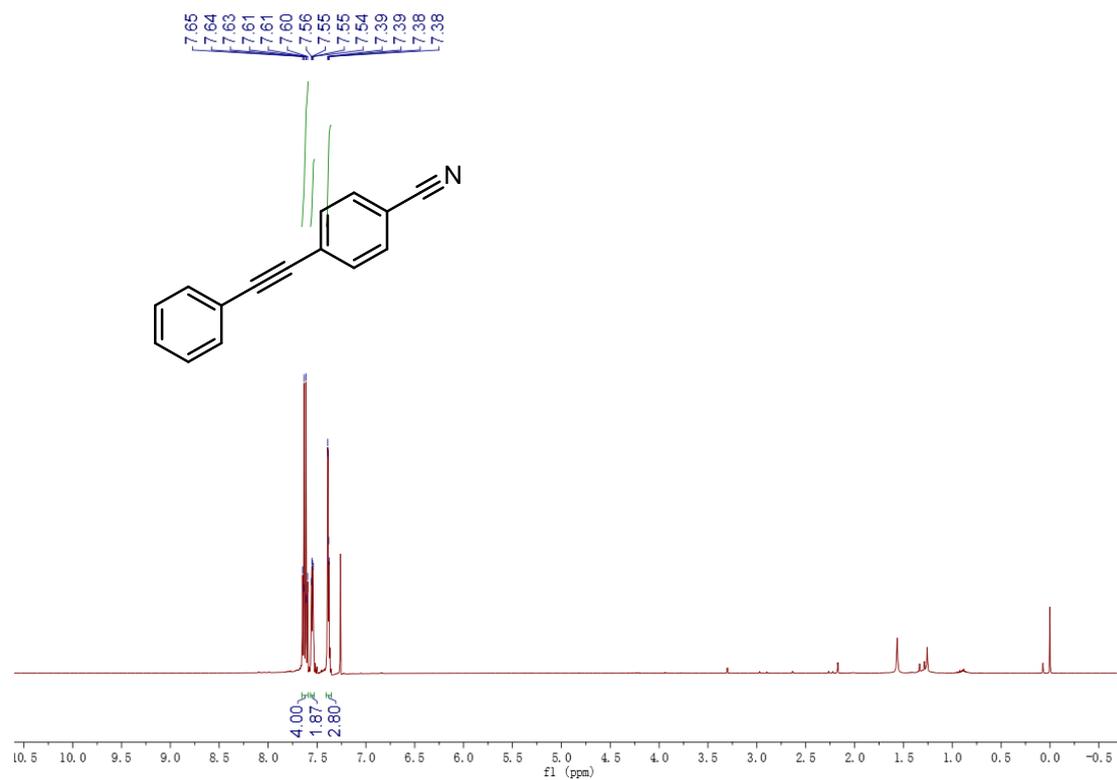


Figure S17. ¹H NMR of **3i** (500 MHz, CDCl₃)

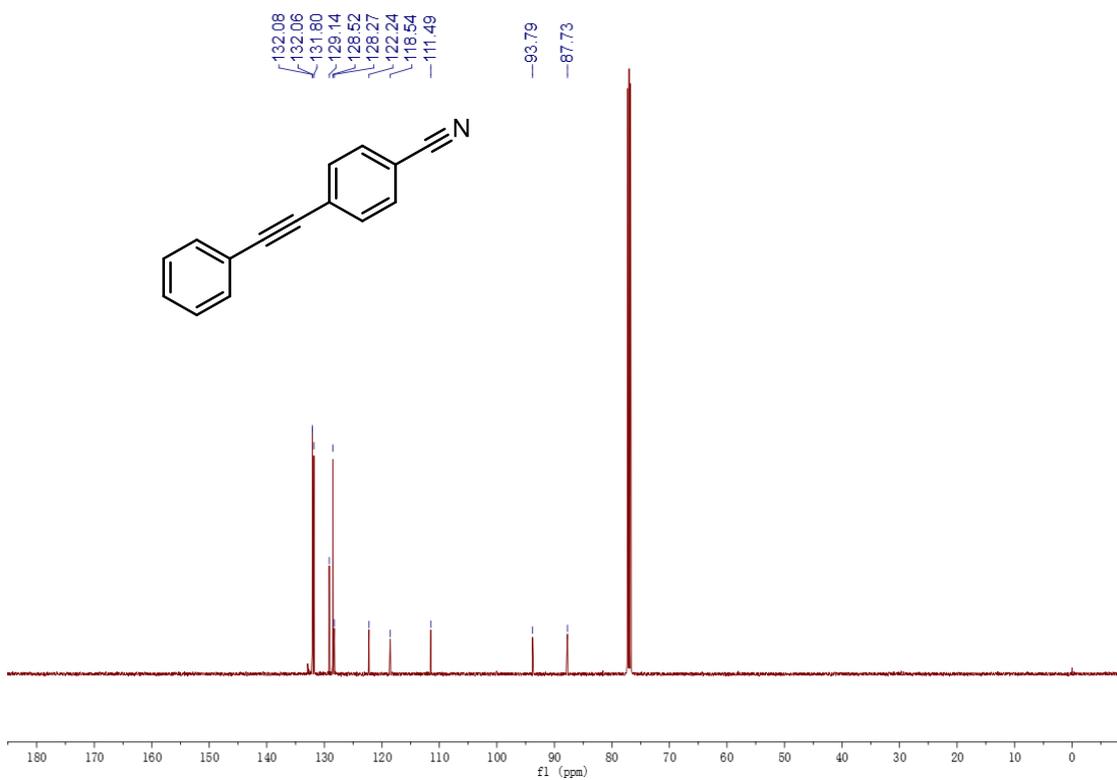


Figure S18. ¹³C NMR of **3i** (126 MHz, CDCl₃)

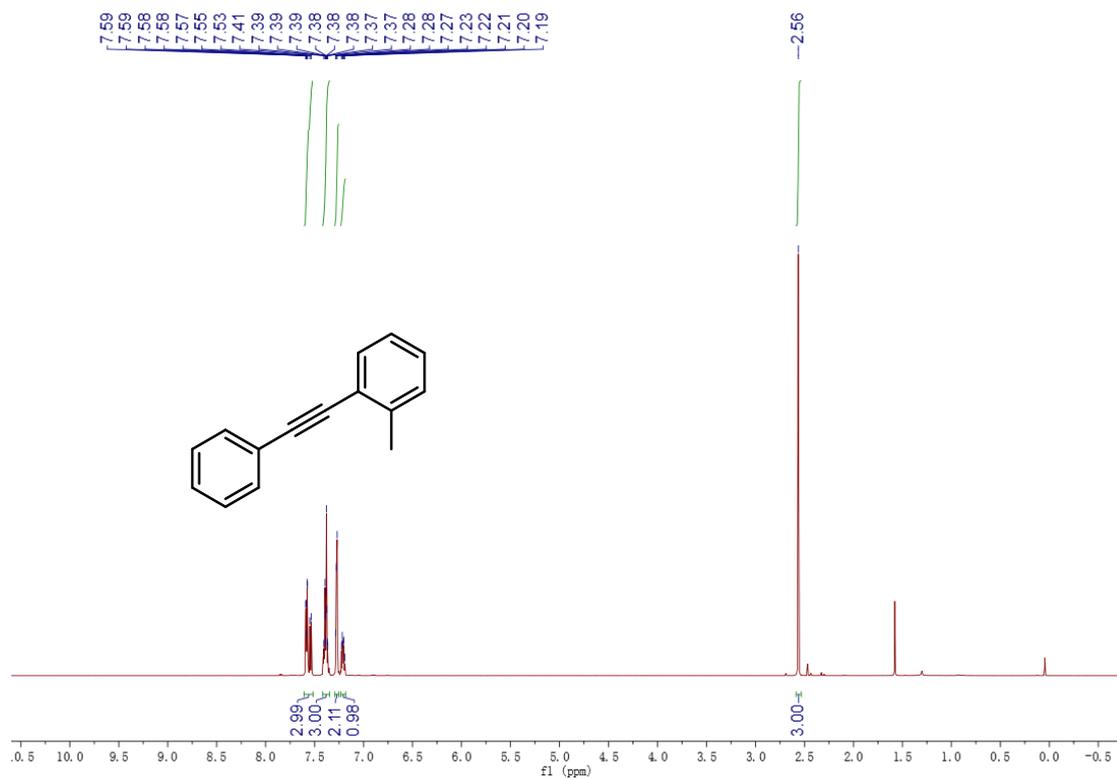


Figure S19. ¹H NMR of **6a** (500 MHz, CDCl₃)

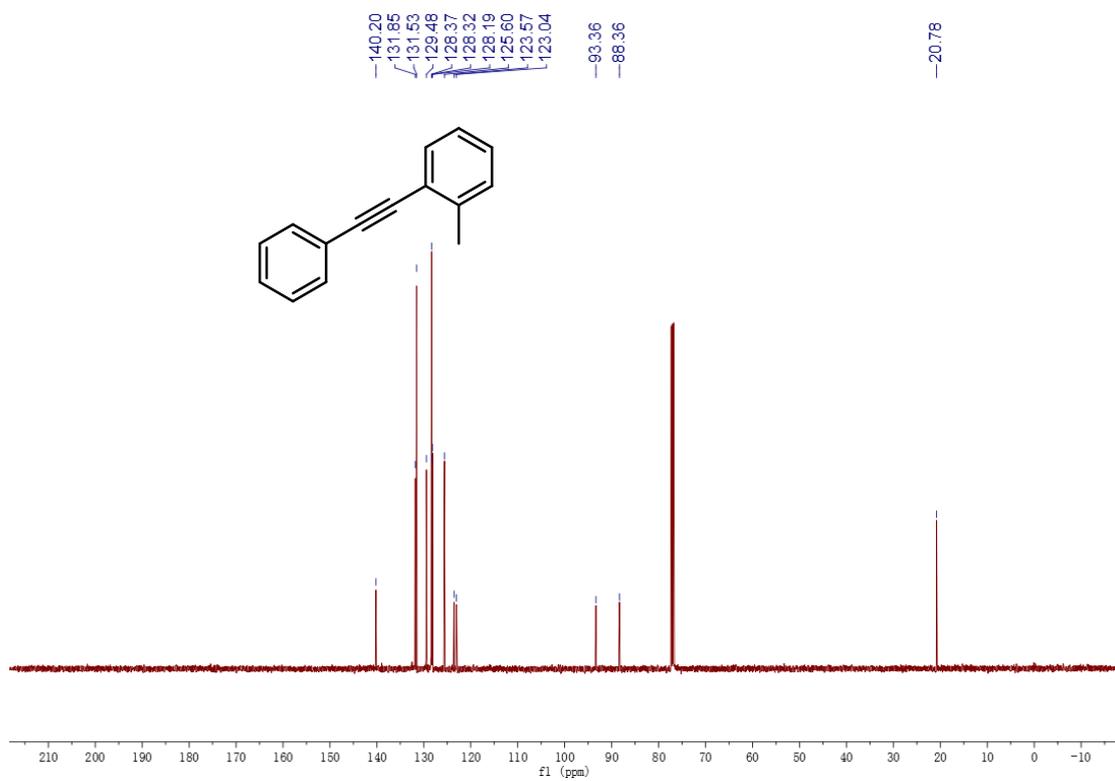


Figure S20. ¹³C NMR of **6a** (125 MHz, CDCl₃)

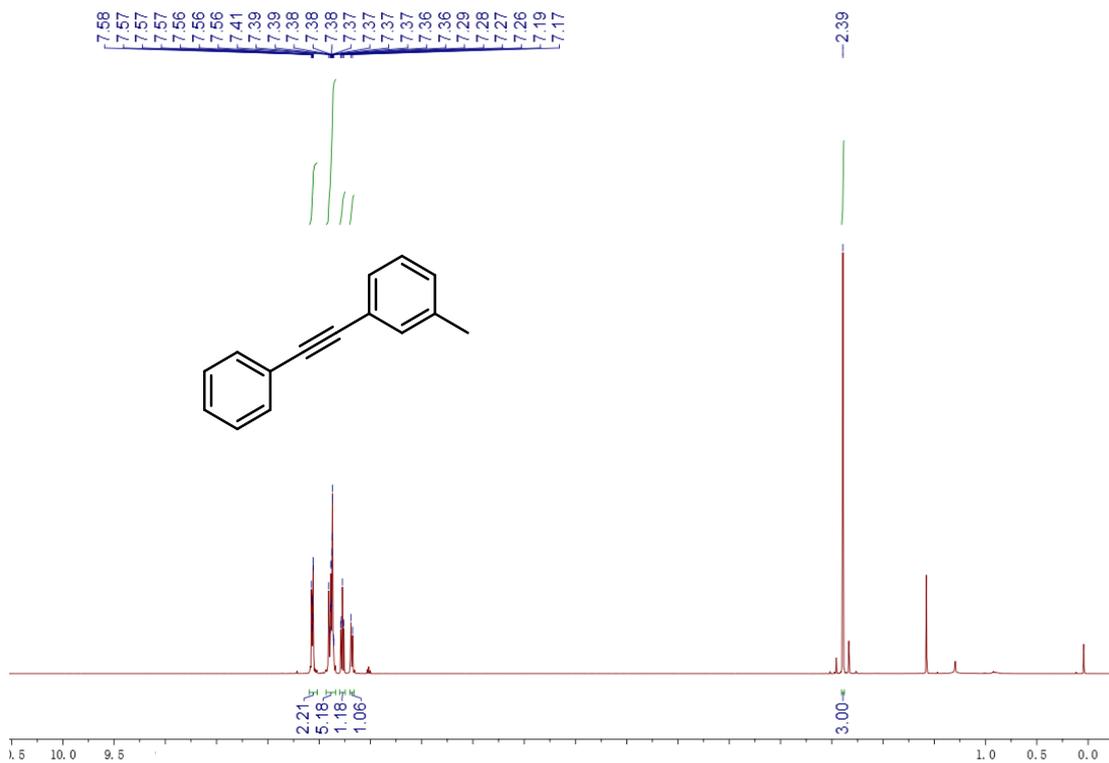


Figure S21. ¹H NMR of **6b** (500 MHz, CDCl₃)

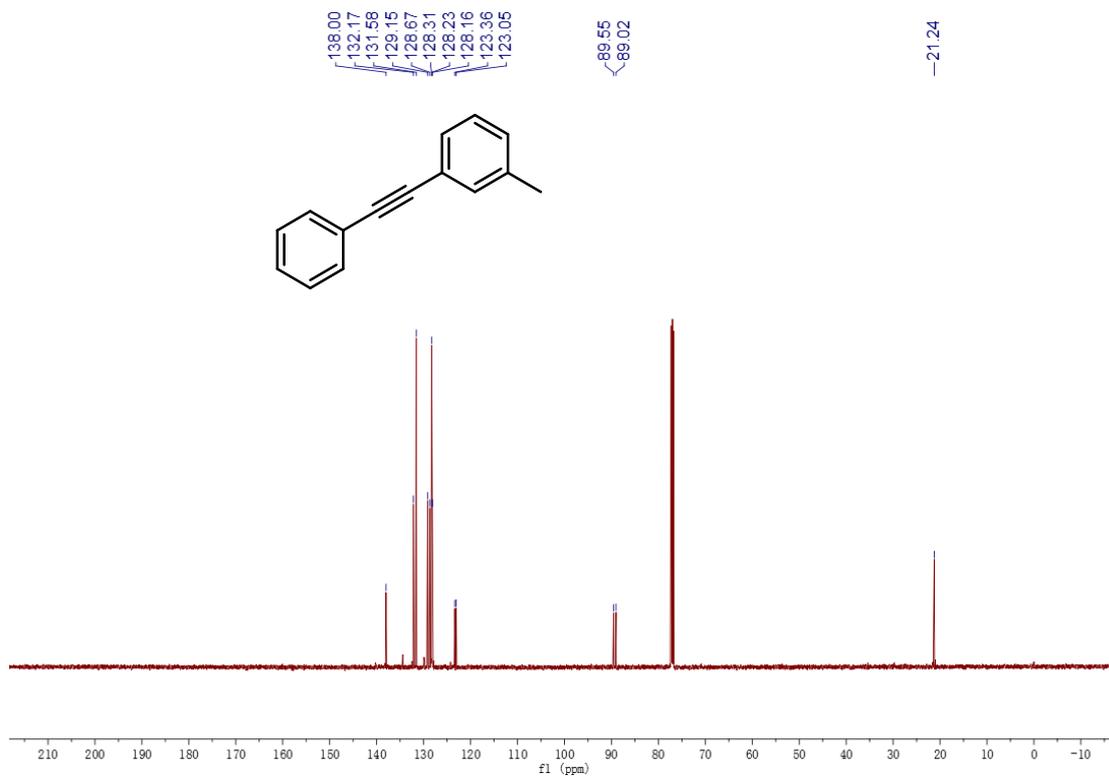


Figure S22. ¹³C NMR of **6b** (125 MHz, CDCl₃)

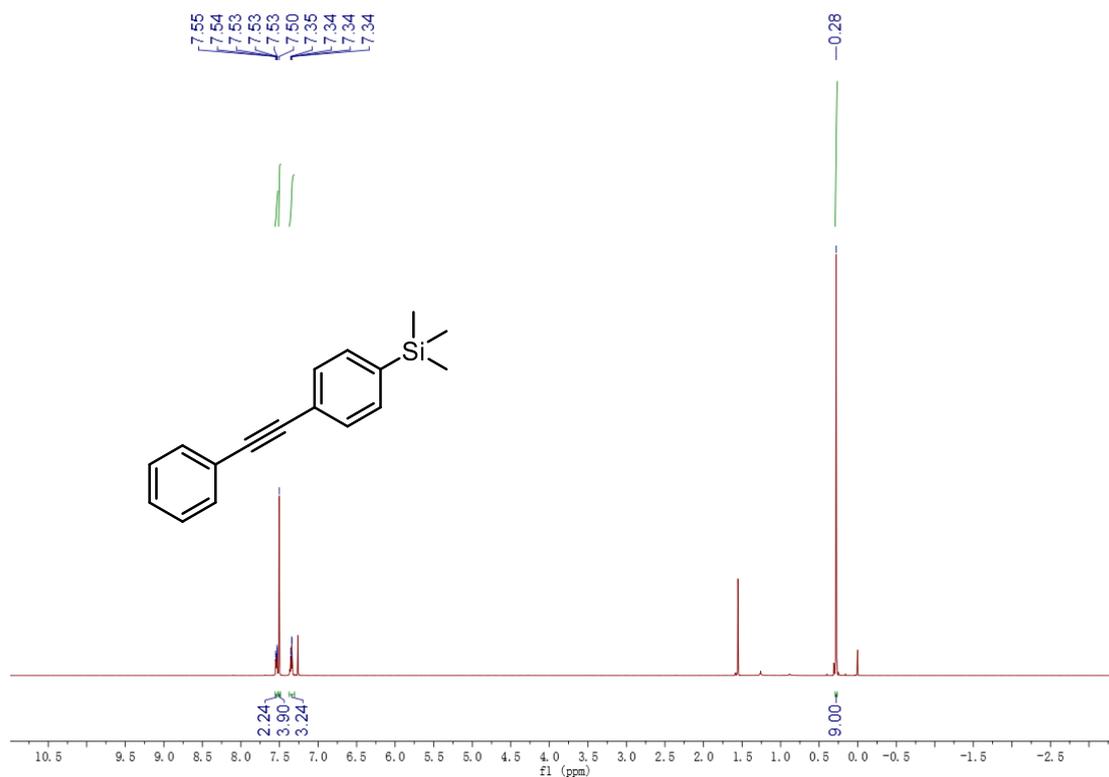


Figure S23. ¹H NMR of 6c (500 MHz, CDCl₃)

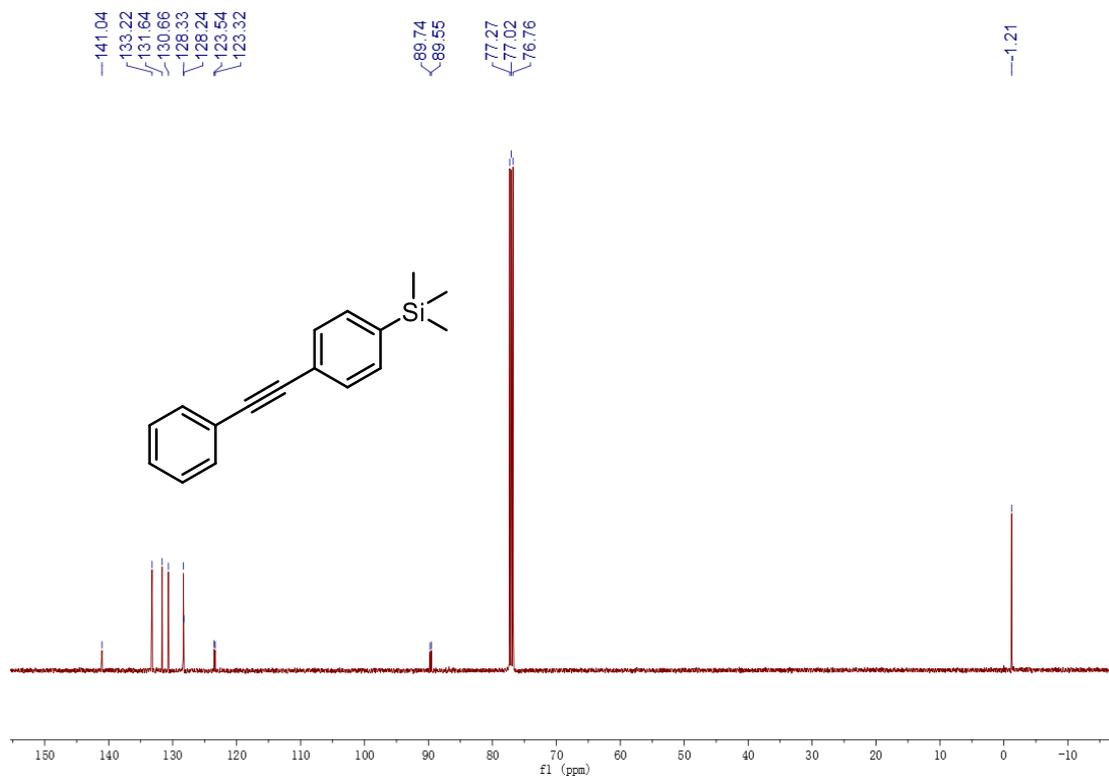


Figure S24. ¹³C NMR of 6c (125 MHz, CDCl₃)



Figure S25. ¹H NMR of 6d (500 MHz, CDCl₃)

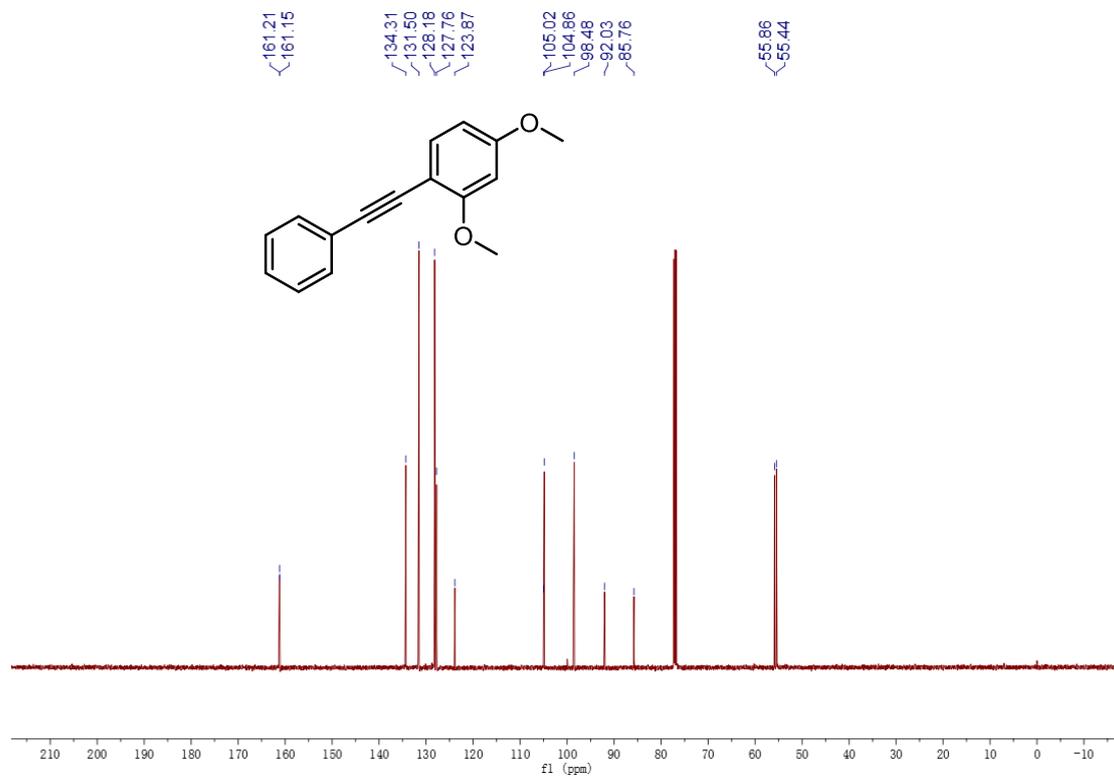


Figure S26. ¹³C NMR of 6d (125 MHz, CDCl₃)

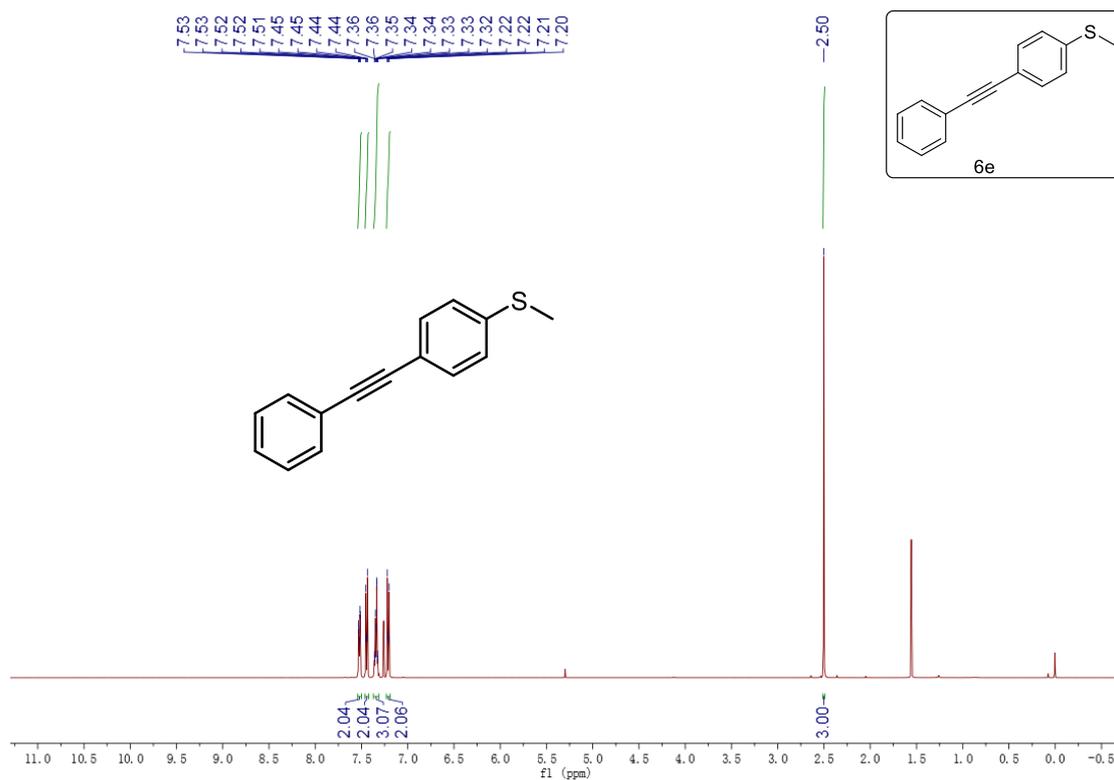


Figure S27. ¹H NMR of 6e (500 MHz, CDCl₃)

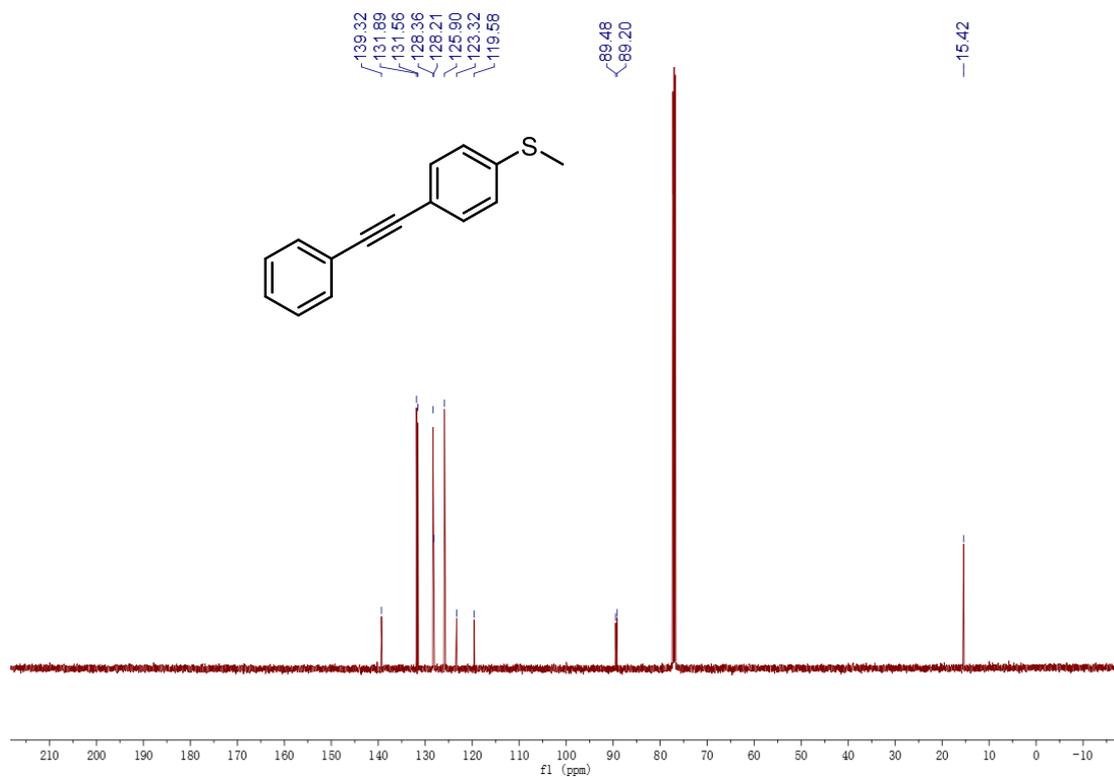


Figure S28. ¹³C NMR of 6e (125 MHz, CDCl₃)

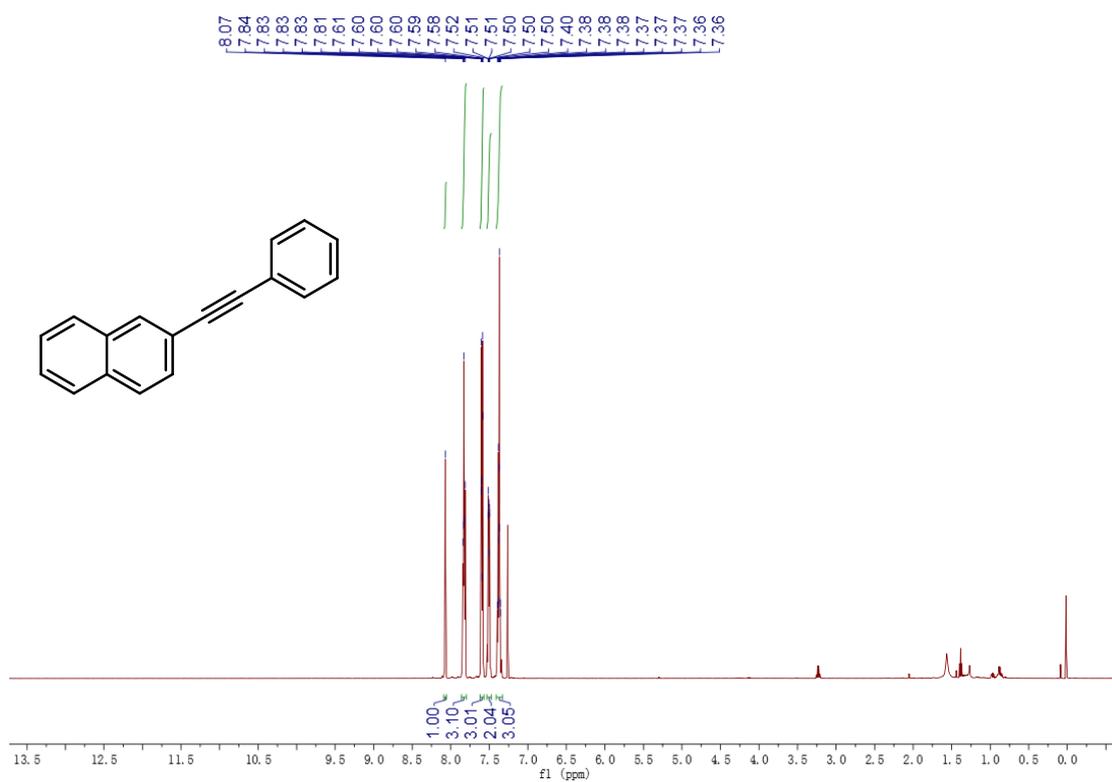


Figure S29. ¹H NMR of 6f (500 MHz, CDCl₃)

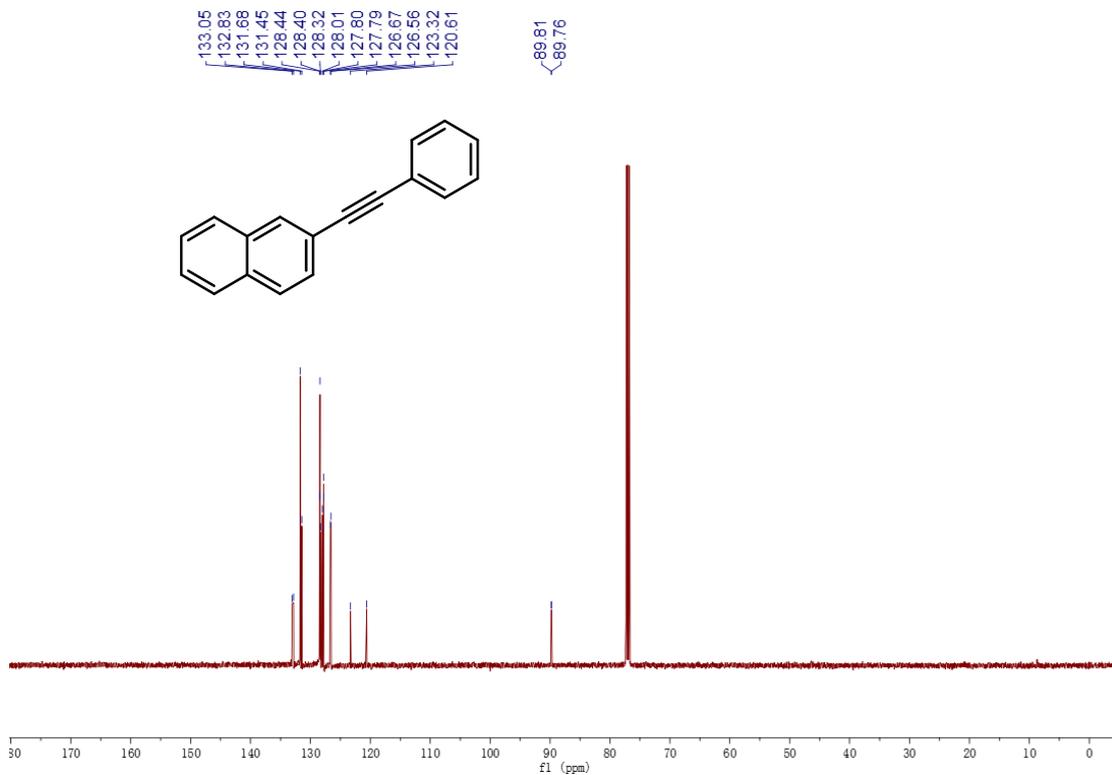


Figure S30. ¹³C NMR of 6f (125 MHz, CDCl₃)



Figure S31. ¹H NMR of **6g** (500 MHz, CDCl₃)

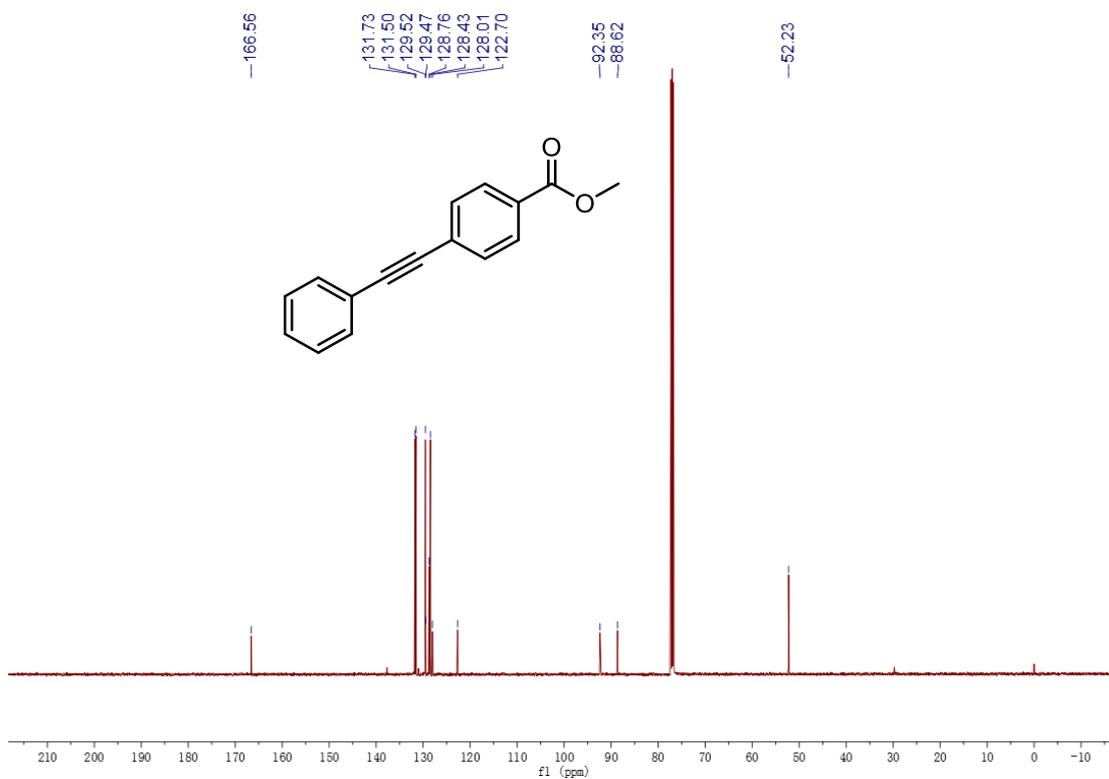


Figure S32. ¹³C NMR of **6g** (125 MHz, CDCl₃)

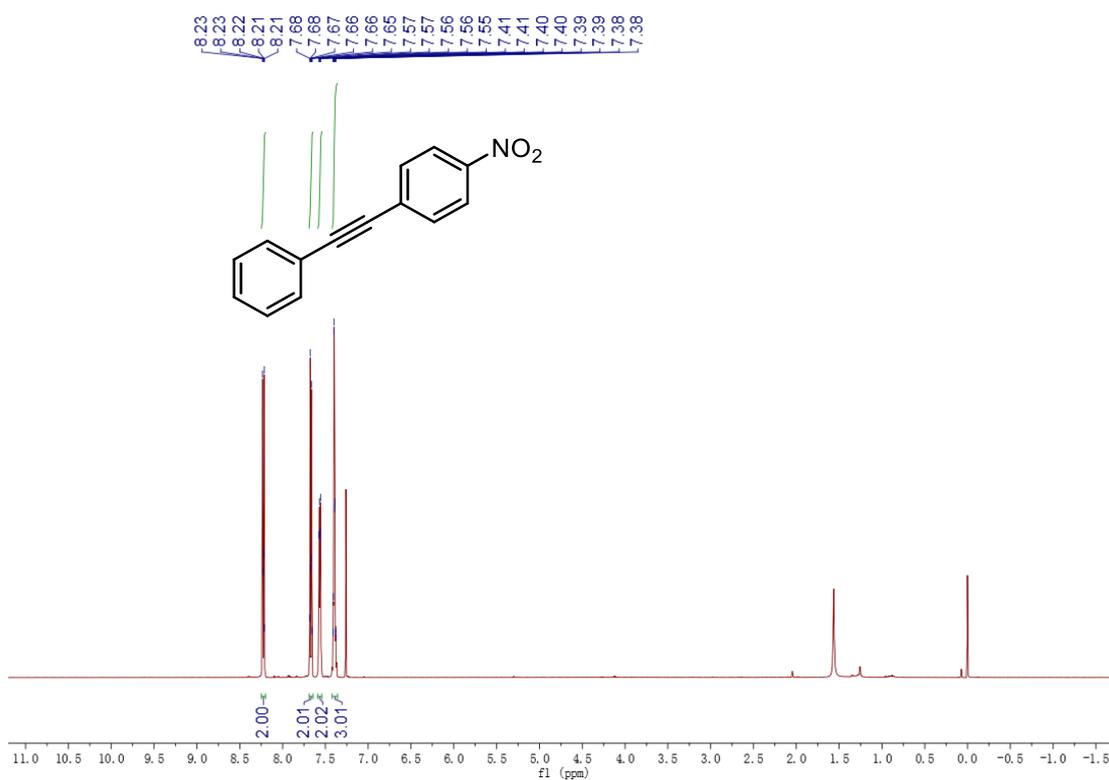


Figure S33. ¹H NMR of 6h (500 MHz, CDCl₃)

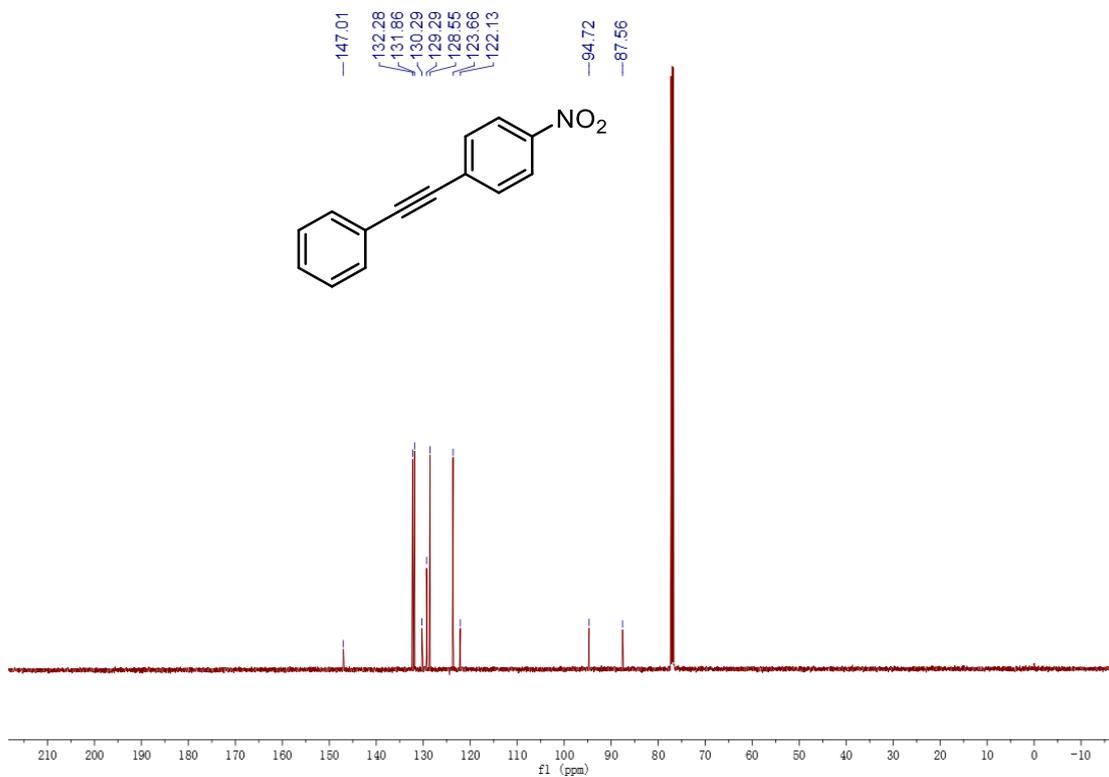


Figure S34. ¹³C NMR of 6h (125 MHz, CDCl₃)

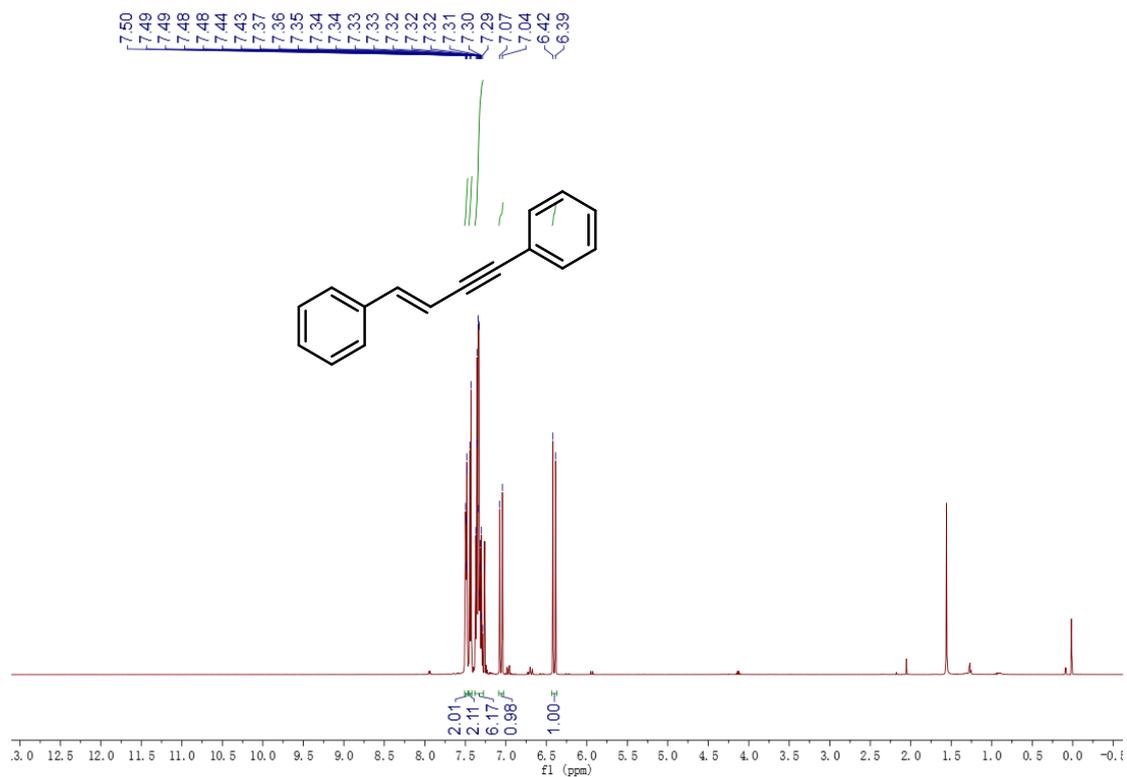


Figure S35. ¹H NMR of 5i (500 MHz, CDCl₃)

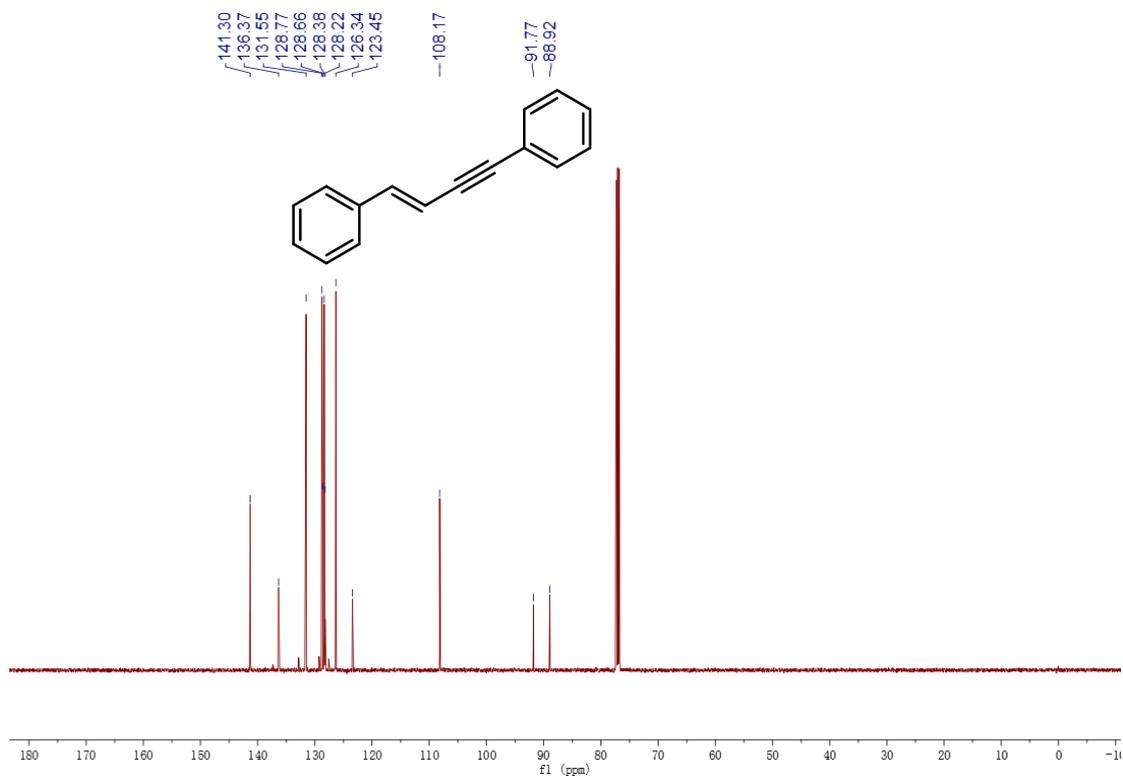


Figure S36. ¹³C NMR of 5i (125 MHz, CDCl₃)

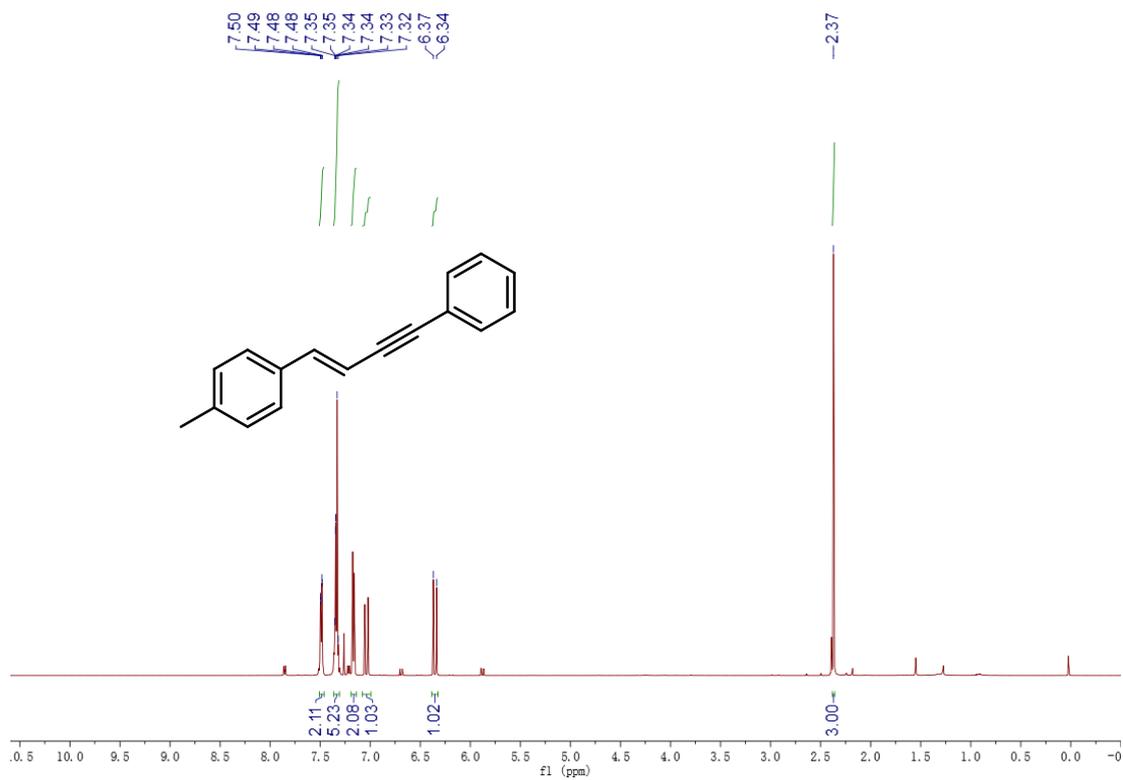


Figure S37. ¹H NMR of 5j (500 MHz, CDCl₃)

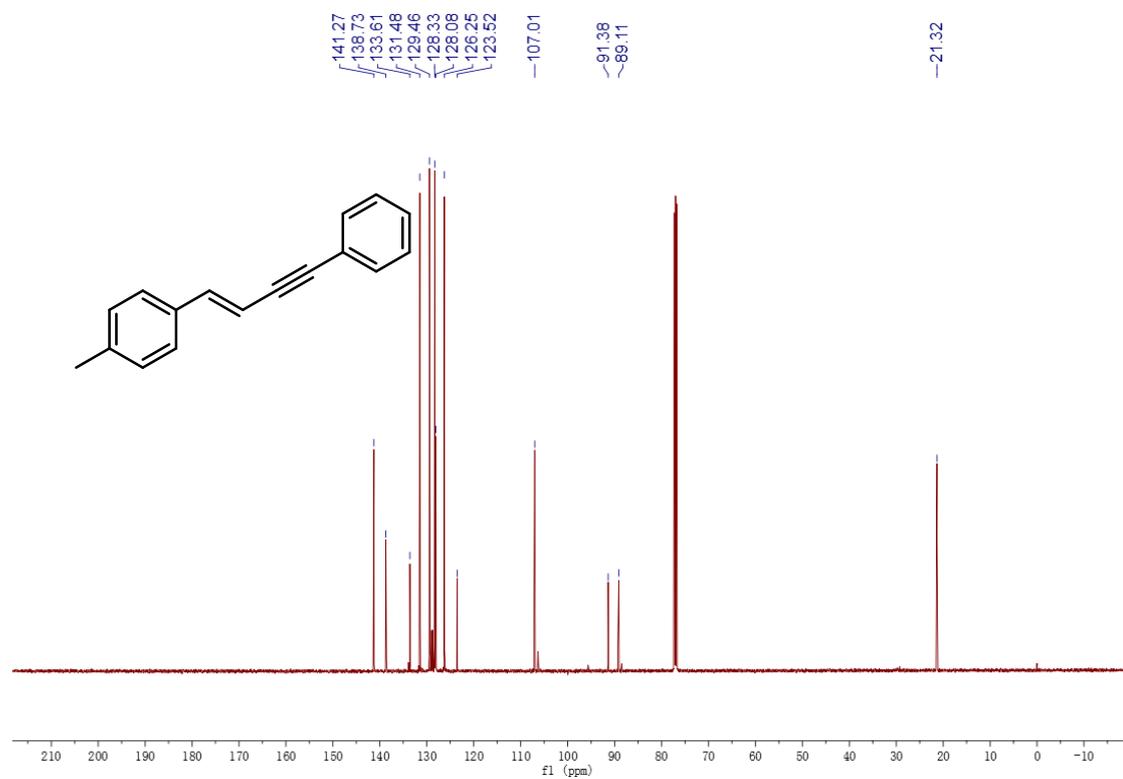


Figure S38. ¹³C NMR of 5j (125 MHz, CDCl₃)

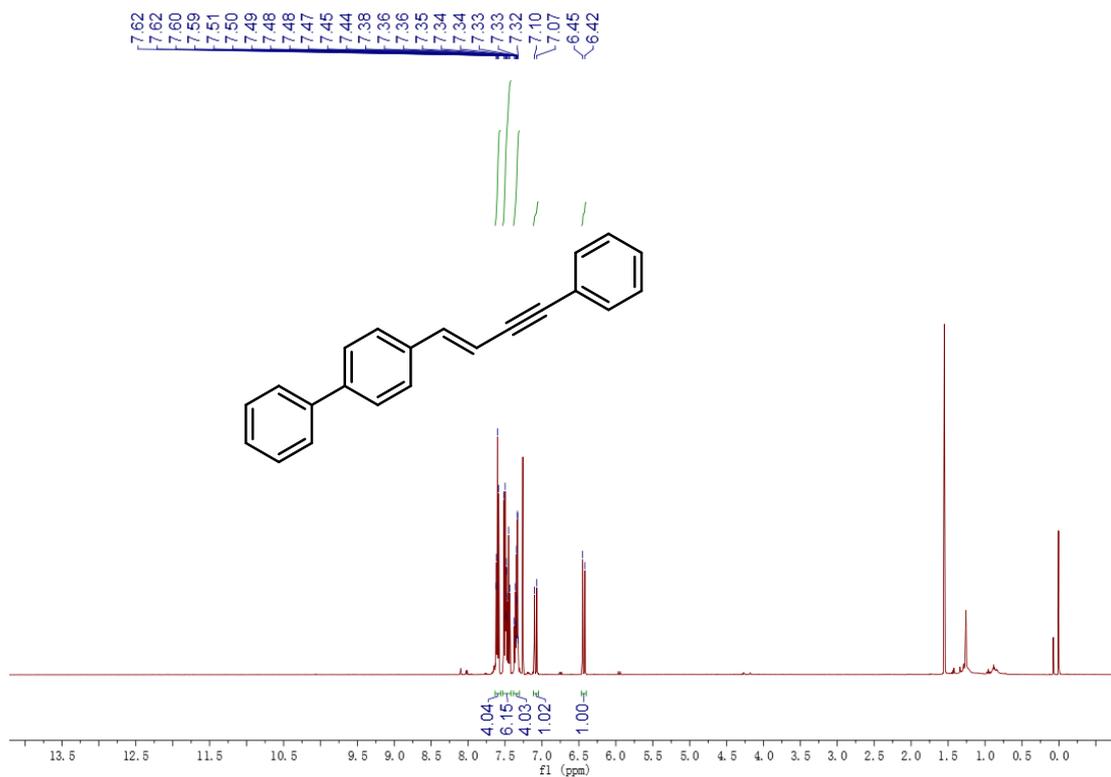


Figure S39. ¹H NMR of 5k (500 MHz, CDCl₃)

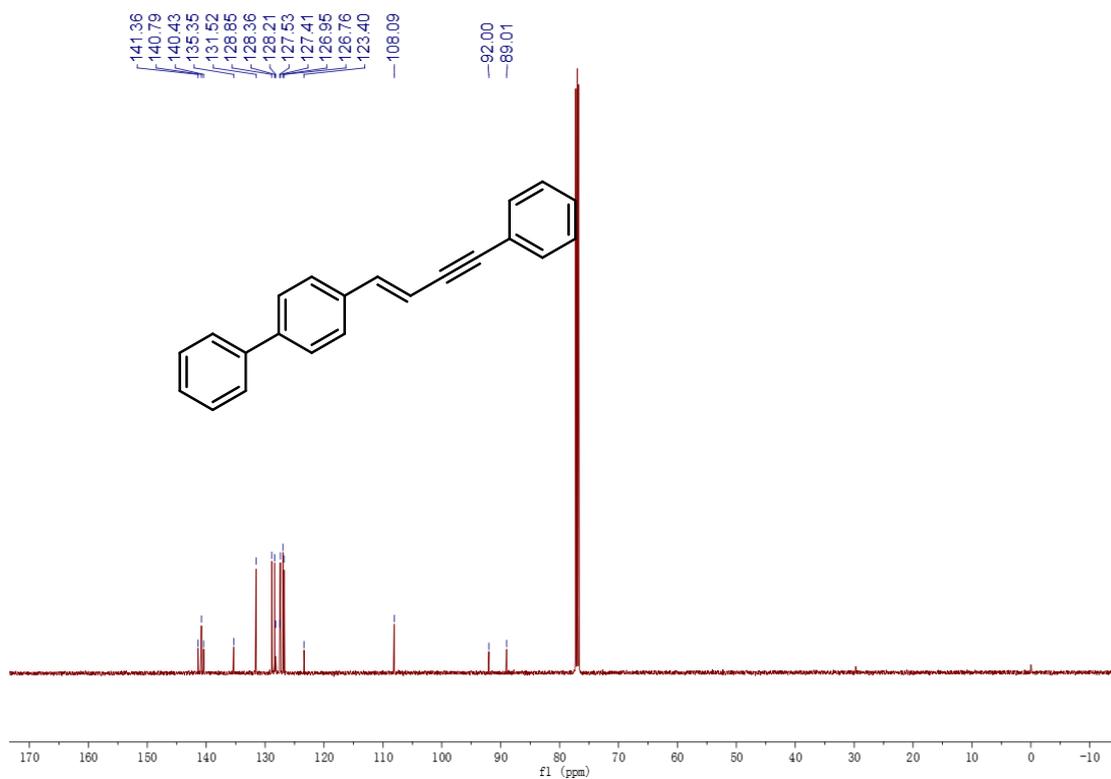


Figure S40. ¹³C NMR of 5k (125 MHz, CDCl₃)

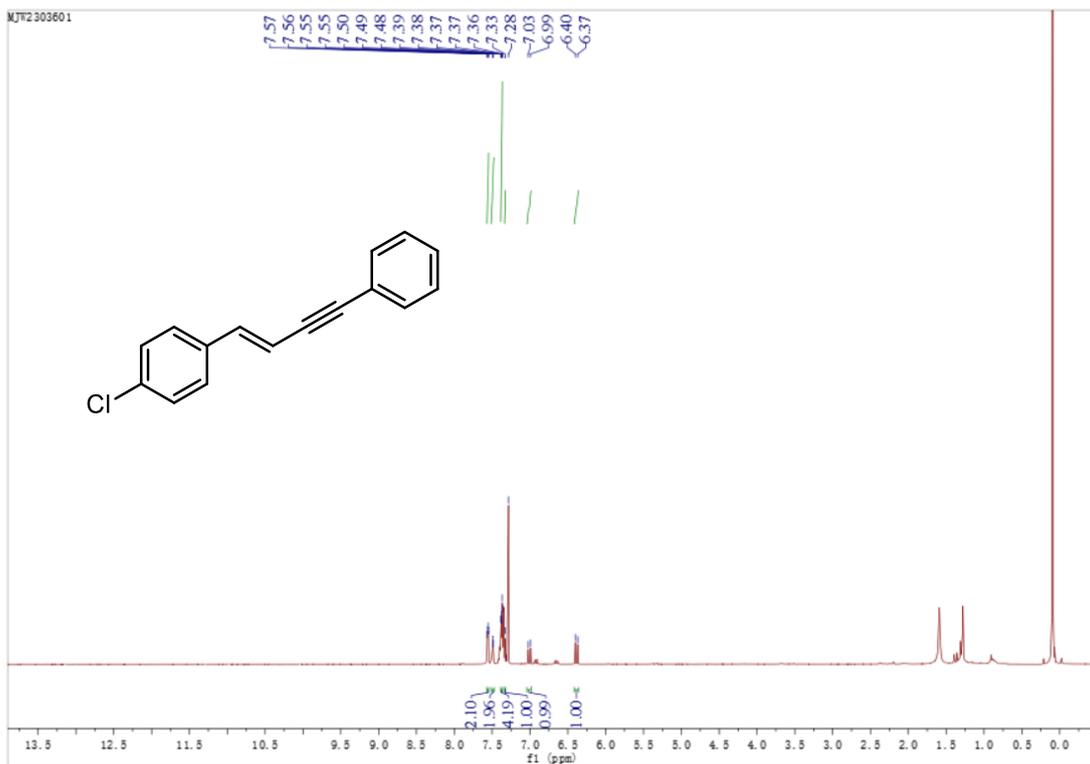


Figure S39. ¹H NMR of 5l (500 MHz, CDCl₃)

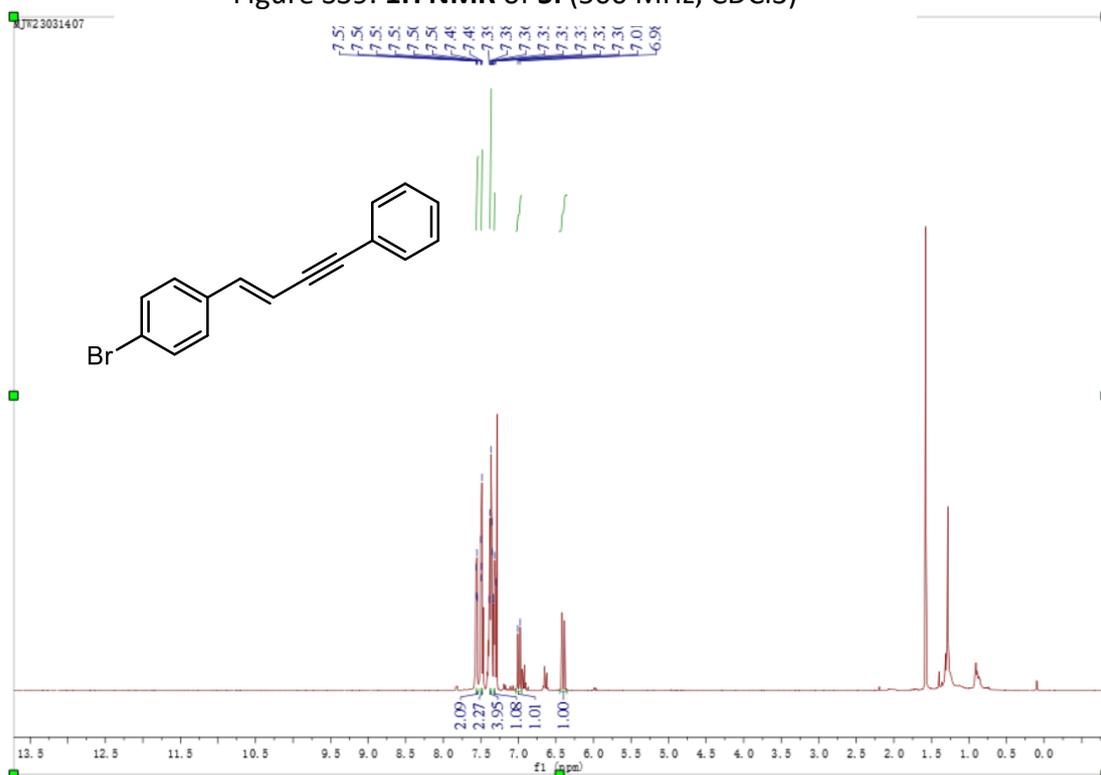


Figure S39. ¹H NMR of 5m (500 MHz, CDCl₃)