Ligand-Assisted Gold-Catalyzed Efficient Alkynylative Cyclization with Terminal Alkynes Using H_2O_2 as Oxidant

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Table of Contents

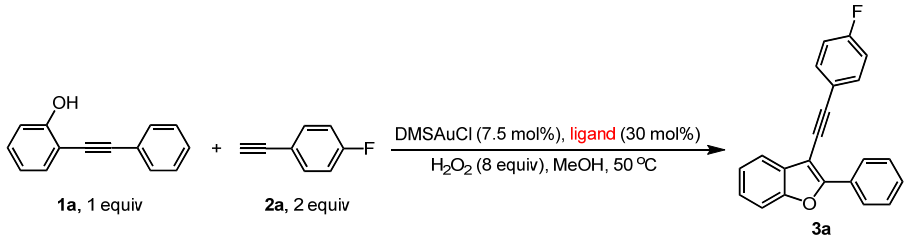
1. General Information

Chemicals were purchased from commercial suppliers and used as delivered. Dry solvents were dispensed from solvent purification system MB SPS-800. In our conditions, MeOH can be used directly without further drying and deoxygenation. Deuterated solvents were bought from Euriso-Top. Hydrogen peroxide solution (50 wt% in water, stabilized) was bought from Sigma-Aldrich. For reactions that require heating, the heat source: aluminum heating block (less than 0.5 mmol scale reactions), oil bath (more than 0.5 mmol scale reactions). Unless otherwise stated, all reactions were carried out under ambient atmosphere and monitored by thin layer chromatography (TLC). Components were visualized by fluorescence quenching under UV light (254 nm) or by treatment with aqueous potassium permanganate ($KMnO_4$) solution. ^{1}H, $^{13}C\{^{1}H\}$, ^{31}P NMR and ^{19}F NMR spectra were recorded on a Bruker Avance-III-300 (300 MHZ), Bruker Avance-III-400 (400 MHZ), Bruker Avance-III-600 (600 MHZ) NMR spectrometer. Chemical shifts are expressed as parts per million (ppm, δ) downfield of tetramethylsilane (TMS) and are referenced to $CDCl_3$ (7.26 / 77.0 ppm) and DMSO-d_6 (2.50 / 39.5 ppm) as internal standards. Data is reported as follows: s = singlet, d = doublet, t = triplet, p = pentalet, q = quartet, m = multiplet, br = broad, dd = doublet of doublets, dt = doublet of triplets, dp = doublet of pentalet, td = triplet of doublets, pd = pentalet of doublets, qd = quartet of doublets, ddd = doublet of doublet of doublets, dtd = doublet of triplets of doublets, tdd = triplet of doublet of doublets; constants are absolute values and *J* values are expressed in Hertz (Hz). Mass spectra (MS and HRMS) were determined in the chemistry department of the University Heidelberg under the direction of Dr. J. Gross. For ESI (+) spectra, a ApexQe FT-ICR-MS spectrometer was applied. Infrared Spectroscopy (IR) was processed on an FT-IR (IF528), IR (283) or FT-IR Vektor 22. Melting points (M.p.) were measured in open glass capillaries in a Büchi melting point apparatus. X-ray data was collected at a temperature of 200 K on Bruker APEX-II Quazar area detector. For computational analysis, all geometry optimizations and subsequent frequency analyses were performed in the gas phase using Orca 5.0.1[1] on the bwForCluster JUSTUS2 on a B3LYP[2-5]/def2-SVP[6] level of theory. For gold, the def2-TZVP[6] basis set was employed. Also, the RIJCOSX[7] approximation and Grimme's DFT-D3 dispersion correction[8] were used. Transition states were determined based on geometry optimizations of relaxed surface scans of initial geometries, their truthfulness was determined by a subsequent frequency analysis.

2. Experimental Procedures

2.1 Optimization of the Reaction Conditions

2.1.1 Evaluation of Different Ligands



A 4-mL vial equipped with a magnetic stir bar was charged with DMSAuCl (1.1 mg, 7.5 mol%),

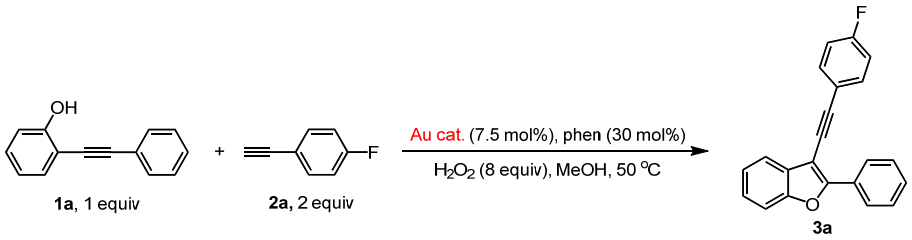
ligand (30 mol%) and 2-(phenylethynyl)phenol **1a** (9.7 mg, 0.05 mmol, 1 equiv) in 0.1 mL MeOH, then 1-ethynyl-4-fluorobenzene **2a** (11.5 μL, 0.10 mmol, 2 equiv) and H_2O_2 (22.4 μL, 0.4 mmol, 50 wt% in water) were added. The mixture was stirred at 50 °C overnight. Then the solvent was removed under reduced pressure. The yield of 3-((4-fluorophenyl)ethynyl)-2-phenylbenzofuran (**3a**) was determined by comparing the integration of the ^{19}F NMR resonance of product **3a** (-110.53 ppm) with that of trifluorotoluene (-62.75 ppm). Yields are reported in Table S1.

Table S1. Evaluation of Different Ligands.

entry	ligand (30 mol%)	yield (%)
1	-	ND
2[a]	-	ND
3	pyridin	ND
4	2,2'- bipyridin	10
5	4,4'- dimethyl- 2,2'- bipyridin	64
6	4,4'- dimethoxy- 2,2'- bipyridin	18
7	**1,10-phenanthroline**	**99**
8	4,7'- dimethoxy- 1,10-phenanthroline	90
9	4,7'- dichlor- 1,10-phenanthroline	26

[a]Ph_3PAuCl instead of DMSAuCl.

2.1.2 Evaluation of Different Gold Catalysts

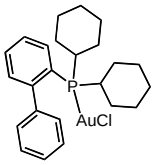


A 4-mL vial equipped with a magnetic stir bar was charged with gold catalysts (7.5 mol%), 1,10-phenanthroline (phen) (2.7 mg, 30 mol%) and 2-(phenylethynyl)phenol **1a** (9.7 mg, 0.05 mmol, 1 equiv) in 0.1 mL MeOH, then 1-ethynyl-4-fluorobenzene **2a** (11.5 μL, 0.10 mmol, 2 equiv) and H_2O_2 (22.4 μL, 0.4 mmol, 50 wt% in water) were added. The mixture was stirred at 50 °C overnight. Then the solvent was removed under reduced pressure. The yield of 3-((4-fluorophenyl)ethynyl)-2-phenylbenzofuran (**3a**) was determined by comparing the integration of the ^{19}F NMR resonance of product **3a** (-110.53 ppm) with that of trifluorotoluene (-62.75 ppm). Yields are reported in Table S2.

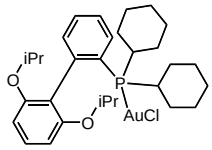
Table S2. Evaluation of Different Gold Catalysts.

entry	Au cat. (7.5 mol%)	yield (%)
1	**DMSAuCl**	**99**
2	**Ph_3PAuCl**	**99**
3	**4-MeO-Ph_3AuCl**	**98**
4	**4-CF_3-Ph_3AuCl**	**99**
5	CyJohnPhosAuCl	42
6	RuPhosAuCl	3
7	DavePhosAuCl	7
8	IPrAuCl	ND

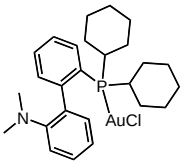
9	**DPPF(AuCl)$_2$ (3.75 mol%)**	**99**
10	**Dppm(AuCl)$_2$ (3.75 mol%)**	**99**
11	**Dfppe(AuCl)$_2$ (3.75 mol%)**	**99**
12	$AuCl_3$	88
13	$AuBr_3$	76
14	CuI	ND
15	$(Ph_3P)_2PdCl_2$	ND



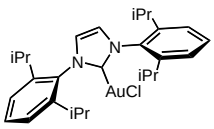
CyJohnPhosAuCl



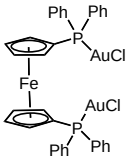
RuPhosAuCl



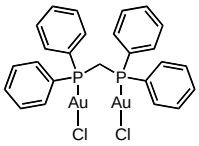
DavePhosAuCl



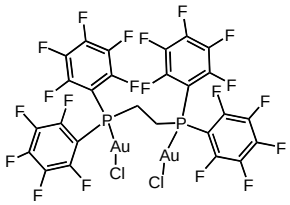
IPrAuCl



DPPF(AuCl)$_2$

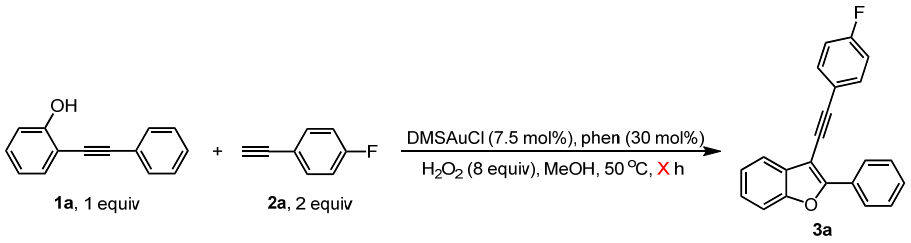


Dppm(AuCl)$_2$



Dfppe(AuCl)$_2$

2.1.3 Evaluation of Different Reaction Time



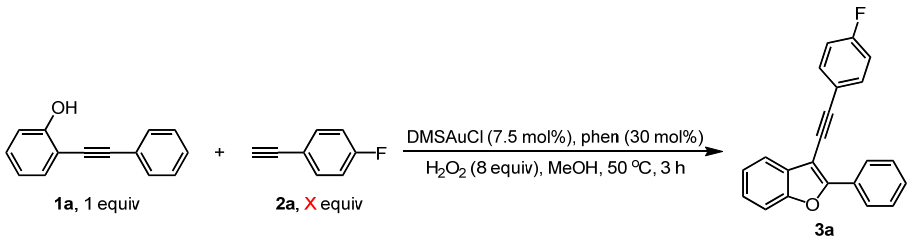
1a, 1 equiv **2a**, 2 equiv **3a**

A 4-mL vial equipped with a magnetic stir bar was charged with DMSAuCl (1.1 mg, 7.5 mol%), phen (2.7 mg, 30 mol%) and 2-(phenylethynyl)phenol **1a** (9.7 mg, 0.05 mmol, 1 equiv) in 0.1 mL MeOH, then 1-ethynyl-4-fluorobenzene **2a** (11.5 µL, 0.10 mmol, 2 equiv) and H_2O_2 (22.4 µL, 0.4 mmol, 50 wt% in water) were added. The mixture was stirred at 50 °C for X h. Then the solvent was removed under reduced pressure. The yield of 3-((4-fluorophenyl)ethynyl)-2-phenylbenzofuran (**3a**) was determined by comparing the integration of the ^{19}F NMR resonance of product **3a** (-110.53 ppm) with that of trifluorotoluene (-62.75 ppm). Yields are reported in Table S3.

Table S3. Evaluation of Different Reaction Time.

entry	time (h)	yield (%)
1	1	88
2	2	97
3	**3**	**99**
4	4	99
5	6	99
6	12	99

2.1.4 Evaluation of Different Equivalents of Alkyne 2a

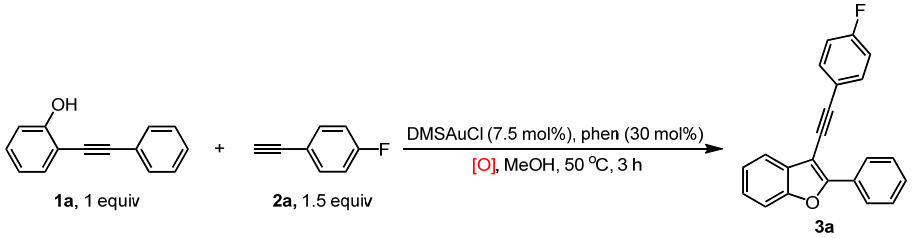


A 4-mL vial equipped with a magnetic stir bar was charged with DMSAuCl (1.1 mg, 7.5 mol%), phen (2.7 mg, 30 mol%) and 2-(phenylethynyl)phenol **1a** (9.7 mg, 0.05 mmol, 1 equiv) in 0.1 mL MeOH, then 1-ethynyl-4-fluorobenzene **2a** (X equiv) and H_2O_2 (22.4 µL, 0.4 mmol, 50 wt% in water) were added. The mixture was stirred at 50 °C for 3 h. Then the solvent was removed under reduced pressure. The yield of 3-((4-fluorophenyl)ethynyl)-2-phenylbenzofuran (**3a**) was determined by comparing the integration of the ^{19}F NMR resonance of product **3a** (-110.53 ppm) with that of trifluorotoluene (-62.75 ppm). Yields are reported in Table S4.

Table S4. Evaluation of Different Equivatents of Alkune **2a**.

entry	**2a** (X equiv)	yield (%)
1	1.0	77
2	1.2	90
3	**1.5**	**99**
4	2.0	99

2.1.5 Evaluation of Different Oxidants



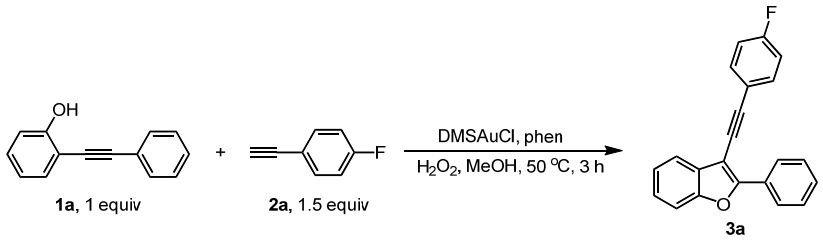
A 4-mL vial equipped with a magnetic stir bar was charged with DMSAuCl (1.1 mg, 7.5 mol%), phen (2.7 mg, 30 mol%) and 2-(phenylethynyl)phenol **1a** (9.7 mg, 0.05 mmol, 1 equiv) in 0.1 mL MeOH, then 1-ethynyl-4-fluorobenzene **2a** (8.6 µL, 0.075 mmol, 1.5 equiv) and oxidant were added. The mixture was stirred at 50 °C for 3 h. Then the solvent was removed under reduced pressure. The yield of 3-((4-fluorophenyl)ethynyl)-2-phenylbenzofuran (**3a**) was determined by comparing the integration of the ^{19}F NMR resonance of product **3a** (-110.53 ppm) with that of trifluorotoluene (-62.75 ppm). Yields are reported in Table S5.

Table S5. Evaluation of Different Oxidants.

entry	oxidant	yield (%)
1	-	ND
2	H_2O_2 (4 equiv, 50 wt% in water)	86
3	H_2O_2 (6 equiv, 50 wt% in water)	91
4	**H_2O_2 (8 equiv, 50 wt% in water)**	**99**
5	H_2O_2 (8 equiv, 35 wt% in water)	98
6	t-BuOOH (4 equiv, 5-6 M in decane)	25
7	t-BuOOH (8 equiv, 5-6 M in decane)	75

8	$PhI(OAc)_2$ (4 equiv)	ND
9	Selectfluor (4 equiv)	ND

2.1.6 Comprehensive Evaluation



A 4-mL vial equipped with a magnetic stir bar was charged with DMSAuCl, phen and 2-(phenylethynyl)phenol **1a** (9.7 mg, 0.05 mmol, 1 equiv) in 0.1 mL MeOH, then 1-ethynyl-4-fluorobenzene **2a** (8.6 μL, 0.075 mmol, 1.5 equiv) and H_2O_2 (50 wt% in water) were added. The mixture was stirred at 50 °C for 3 h. Then the solvent was removed under reduced pressure. The yield of 3-((4-fluorophenyl)ethynyl)-2-phenylbenzofuran (**3a**) was determined by comparing the integration of the ^{19}F NMR resonance of product **3a** (-110.53 ppm) with that of trifluorotoluene (-62.75 ppm). Yields are reported in Table S6.

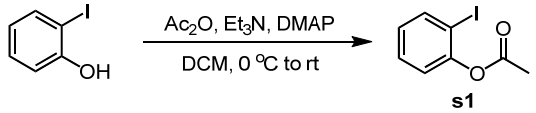
Table S6. Comprehensive Evaluation.

entry	DMSAuCl (X mol%)	phen (Y mol%)	H_2O_2 (equiv)	yield (%)
1	7.5	7.5	4	27
2	7.5	15	4	46
3	7.5	20	4	61
4	7.5	30	4	86
5	5	20	4	87
6	2.5	10	4	85
7	7.5	30	8	99
8	5	20	8	99
9	**2.5**	**10**	**8**	**99**
10	1	4	8	38
11[a]	**1**	**4**	**8**	**97**
11[b]	2.5	10	8	64
12[c]	2.5	10	8	86
13[d]	2.5	10	8	62
14[e]	2.5	10	8	60
15[f]	2.5	10	8	13
16[g]	2.5	10	8	35
17[h]	2.5	10	8	98
18[i]	2.5	10	8	91
19[j]	2.5	10	8	89

[a]The reaction time was extended to 16 h. [b]MeCN as solvent. [c]Acetone as solvent. [d]DCM as solvent. [e]1,4-Dioxane as solvent. [f]Room temperature. [g]40 °C. [h]60 °C. [i]MeOH (0.2 mL). [j]MeOH (0.05 mL).

2.2 Preparation of Substrates

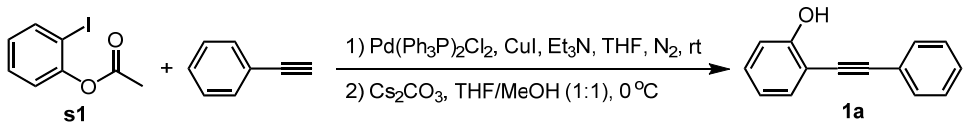
2-Iodophenyl acetate (s1)



To a solvent of 2-iodophenol (11.0 g, 50 mmol, 1 equiv), triethylamine (Et_3N) (10.4 mL, 75 mmol, 1.5 equiv) and 4-dimethylaminopyridine (DMAP) (300 mg, 2.5 mmol, 0.05 equiv) in 100 mL DCM was added dropwise acetic anhydride (Ac_2O) (5.7 mL, 60 mmol, 1.2 equiv) at 0 °C. The mixture was stirred at this temperature for 30 min and then warmed up to room temperature and stirred overnight. After completion of the reaction, 50 mL saturated NH_4Cl was added and the aqueous phase was extracted three times with 50 mL DCM, the organic phases were combined, dried over Na_2SO_4, filtered, concentrated in vacuo. The residual mixture was purified by silica gel chromatography with PE/EA (15:1) as eluting solvent to afford 2-iodophenyl acetate **s1** as light yellow oil (12.8 g, 98%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.83 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.37 (ddd, *J* = 8.0, 7.5, 1.5 Hz, 1H), 7.10 (dd, *J* = 8.1, 1.5 Hz, 1H), 6.98 (td, *J* = 7.8, 1.5 Hz, 1H), 2.37 (s, 3H). Characterization data of **s1** corresponded to the literature values.[9]

2-(Phenylethynyl)phenol (1a)

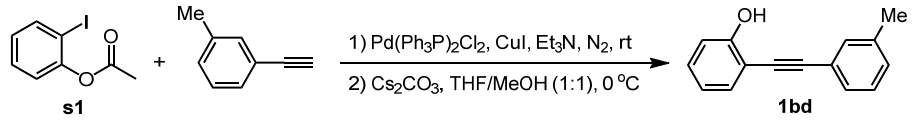


Step 1: To a suspension of 2-iodophenyl acetate **s1** (13.1 g, 50 mmol, 1 equiv), $(Ph_3P)_2PdCl_2$ (225 mg, 0.5 mol%) and CuI (190 mg, 2 mol%) in 60 mL dry THF were added phenylacetylene (6.0 mL, 55 mmol, 1.1 equiv) and Et_3N (27 mL, 200 mmol, 4 equiv). Evacuate the resulting solution and flush with N_2 several times. The mixture allowed to stir at room temperature overnight. After completion of the reaction, 50 mL saturated NH_4Cl was added and the aqueous phase was extracted three times with 50 mL DCM, the organic phases were combined, dried over Na_2SO_4, filtered, concentrated in vacuo. The residual mixture was purified by silica gel chromatography with PE/EA (15:1) as eluting solvent to afford 2-(phenylethynyl)phenyl acetate **1a-1** as light yellow oil.

Step 2: To a solvent of 2-(phenylethynyl)phenyl acetate **1a-1** in 200 mL THF/MeOH (1:1) was added Cs_2CO_3 (17.8 g, 55 mmol, 1.1 equiv) at 0 °C. The mixture was stirred at this temperature for 30 min. After completion of the reaction, 50 mL saturated NH_4Cl was added, and the aqueous phase was extracted three times with 50 mL DCM, the organic phases were combined, concentrated in vacuo. Then 50 mL ethyl acetate was added and the mixture was washed with 25 mL sat. brine for two times, the aqueous phases was combined and extracted three times with 25 mL ethyl acetate, the organic phases were combined, dried over Na_2SO_4, filtered, concentrated in vacuo. The residual mixture was free from silica gel chromatography to give 2-(phenylethynyl)phenol **1a** as light yellow solid (8.68 g, 89% over 2 steps).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.60 – 7.51 (m, 2H), 7.44 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.41 – 7.36 (m, 3H), 7.28 (ddd, *J* = 7.5, 4.9, 1.9 Hz, 1H), 7.00 (dd, *J* = 8.3, 0.8 Hz, 1H), 6.92 (td, *J* = 7.6, 1.1 Hz, 1H), 5.84 (s, 1H). Characterization data of **1a** corresponded to the literature values.[10]

2-(3-Tolylethynyl)phenol (1bd)

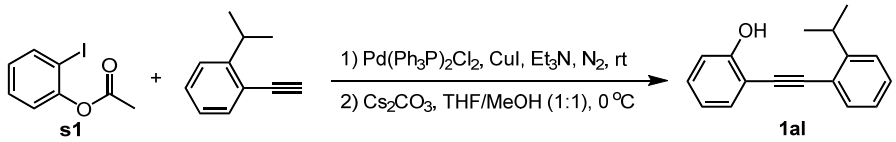


Step 1: To a suspension of 2-iodophenyl acetate **s1** (524.1 mg, 2 mmol, 1 equiv), $(Ph_3P)_2PdCl_2$ (14 mg, 1 mol%) and CuI (7.6 mg, 2 mol%) in 4 mL Et_3N was added 1-ethynyl-3-methylbenzene (278.4 mg, 2.4 mmol, 1.2 equiv). Evacuate the resulting solution and flush with N_2 several times. The mixture allowed to stir at room temperature overnight. After completion of the reaction, 20 mL saturated NH_4Cl was added and the aqueous phase was extracted three times with 20 mL DCM, the organic phases were combined, dried over Na_2SO_4, filtered, concentrated in vacuo. The residual mixture was purified by silica gel chromatography with PE/EA (10:1) as eluting solvent to afford 2-(3-tolylethynyl)phenyl acetate **1bd-1** as light yellow oil.

Step 2: To a solvent of 2-(3-tolylethynyl)phenyl acetate **1bd-1** in 20 mL THF/MeOH (1:1) was added Cs_2CO_3 (1.4 g, 4.2 mmol) at 0 °C. The mixture was stirred at this temperature for 30 min. After completion of the reaction, 20 mL saturated NH_4Cl was added, and the aqueous phase was extracted three times with 40 mL DCM, the organic phases were combined, dried over Na_2SO_4, filtered, concentrated in vacuo. The residual mixture was purified by silica gel chromatography with PE/EA (15:1) as eluting solvent to afford 2-(3-tolylethynyl)phenol **1bd** as light yellow oil (394 mg, 95% over 2 steps).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.45 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.38 (d, *J* = 8.8 Hz, 2H), 7.33 – 7.24 (m, 2H), 7.20 (d, *J* = 7.7 Hz, 1H), 7.02 (dd, *J* = 8.2, 0.5 Hz, 1H), 6.93 (td, *J* = 7.6, 1.1 Hz, 1H), 5.91 (br, 1H), 2.39 (s, 3H). Characterization data of **1bd** corresponded to the literature values.[11]

2-((2-Isopropylphenyl)ethynyl)phenol (1al)



Step 1: To a suspension of 2-iodophenyl acetate **s1** (786 mg, 3 mmol, 1 equiv), $(Ph_3P)_2PdCl_2$ (10.5 mg, 0.5 mol%) and CuI (11.4 mg, 2 mol%) in 6 mL Et_3N was added 1-ethynyl-2-isopropylbenzene (475 mg, 3.3 mmol, 1.1 equiv). Evacuate the resulting solution and flush with N_2 several times. The mixture allowed to stir at room temperature overnight. After completion of the reaction, 20 mL saturated NH_4Cl was added and the aqueous phase was extracted three times with 20 mL DCM, the organic phases were combined, dried over Na_2SO_4, filtered, concentrated in vacuo. The residual mixture was purified by silica gel chromatography with PE/EA (10:1) as eluting solvent to afford 2-((2-isopropylphenyl)ethynyl)phenyl acetate **1al-1** as light yellow oil.

Step 2: To a solvent of 2-((2-isopropylphenyl)ethynyl)phenyl acetate **1al-1** in 30 mL THF/MeOH (1:1) was added Cs_2CO_3 (1.3 g, 4.5 mmol, 1.5 equiv) at 0 °C. The mixture was stirred at this temperature for 15 min. After completion of the reaction, 20 mL saturated NH_4Cl was added, and the aqueous phase was extracted three times with 40 mL DCM, the organic phases were combined, dried over Na_2SO_4, filtered, concentrated in vacuo. The residual mixture was purified by silica gel chromatography with PE/EA (20:1) as eluting solvent to afford 2-((2-isopropylphenyl)ethynyl)phenol **1al** as light yellow oil (517 mg, 73% over 2 steps).

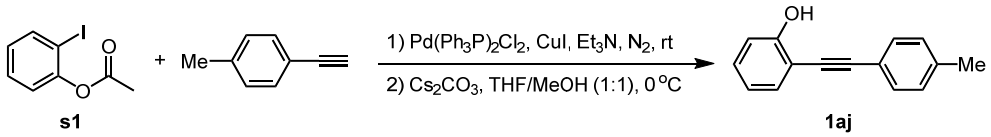
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.54 (d, *J* = 7.4 Hz, 1H), 7.45 (dd, *J* = 7.7, 1.1 Hz, 1H), 7.41 – 7.32 (m, 2H), 7.32 – 7.25 (m, 1H), 7.25 – 7.17 (m, 1H), 7.01 (d, *J* = 8.3 Hz, 1H), 6.94 (dd, *J* = 11.6, 4.1 Hz, 1H), 5.86 (s, 1H), 3.52 (dt, *J* = 13.8, 6.9 Hz, 1H), 1.34 (d, *J* = 6.9 Hz, 6H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 156.4, 150.3, 132.4, 131.5, 130.4, 129.2, 125.7, 125.1, 121.1, 120.4, 114.7, 109.9, 95.2, 86.6, 31.9, 23.1.

HRMS (EI) calcd for $C_{17}H_{16}O$ $[M]^+$: 236.11957, found: 236.11939.

IR (Reflection): $\tilde{\nu}$ = 3516, 3062, 2962, 2869, 1613, 1574, 1491, 1479, 1461, 1445, 1384, 1362, 1344, 1289, 1238, 1193, 1094, 1078, 1031, 939, 865, 807, 753.

2-(4-Tolylethynyl)phenol (1aj)



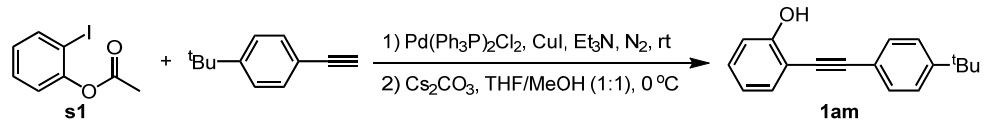
Step 1: To a suspension of 2-iodophenyl acetate **s1** (786 mg, 3 mmol, 1 equiv), $(Ph_3P)_2PdCl_2$ (10.5 mg, 0.5 mol%) and CuI (11.4 mg, 2 mol%) in 6 mL Et_3N was added 1-ethynyl-4-methylbenzene (383 mg, 3.3 mmol, 1.1 equiv). Evacuate the resulting solution and flush with N_2 several times. The mixture allowed to stir at room temperature overnight. After completion of the reaction, 20 mL saturated NH_4Cl was added and the aqueous phase was extracted three times with 20 mL DCM, the organic phases were combined, dried over Na_2SO_4, filtered, concentrated in vacuo. The residual mixture was purified by silica gel chromatography with PE/EA (20:1) as eluting solvent to afford 2-(4-tolylethynyl)phenyl acetate **1aj-1** as light yellow oil.

Step 2: To a solvent of 2-(4-tolylethynyl)phenyl acetate **1aj-1** in 30 mL THF/MeOH (1:1) was added Cs_2CO_3 (1.3 g, 4.5 mmol, 1.5 equiv) at 0 °C. The mixture was stirred at this temperature for 15 min. After completion of the reaction, 20 mL saturated NH_4Cl was added, and the aqueous phase was extracted three times with 40 mL DCM, the organic phases were combined, dried over Na_2SO_4, filtered, concentrated in vacuo. The residual mixture was purified by silica gel chromatography with PE/EA (15:1) as eluting solvent to afford 2-(4-tolylethynyl)phenol **1aj** as light yellow oil (315 mg, 50% over 2 steps).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.42 (dd, *J* = 10.6, 4.7 Hz, 3H), 7.31 – 7.23 (m, 1H), 7.19 (d, *J* = 7.9 Hz, 2H), 6.99 (d, *J* = 7.7 Hz, 1H), 6.91 (td, *J* = 7.6, 1.0 Hz, 1H), 5.85 (s, 1H), 2.39 (s, 3H).

Characterization data of **1aj** corresponded to the literature values.[12]

2-((4-(*tert*-Butyl)phenyl)ethynyl)phenol (1am)

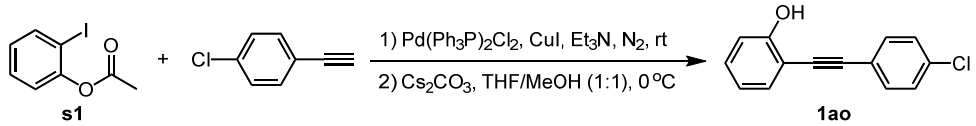


Step 1: To a suspension of 2-iodophenyl acetate **s1** (786 mg, 3 mmol, 1 equiv), $(Ph_3P)_2PdCl_2$ (10.5 mg, 0.5 mol%) and CuI (11.4 mg, 2 mol%) in 6 mL Et_3N was added 1-(*tert*-butyl)-4-ethynylbenzene (600 µL, 3.3 mmol, 1.1 equiv). Evacuate the resulting solution and flush with N_2 several times. The mixture allowed to stir at room temperature overnight. After completion of the reaction, 20 mL saturated NH_4Cl was added and the aqueous phase was extracted three times with 20 mL DCM, the organic phases were combined, dried over Na_2SO_4, filtered, concentrated in vacuo. The residual mixture was purified by silica gel chromatography with PE/EA (20:1) as eluting solvent to afford 2-((4-(*tert*-butyl)phenyl)ethynyl)phenyl acetate **1am-1** as light yellow oil.

Step 2: To a solvent of 2-((4-(*tert*-butyl)phenyl)ethynyl)phenyl acetate **1am-1** in 20 mL THF/MeOH (1:1) was added Cs_2CO_3 (1.3 g, 4.5 mmol) at 0 °C. The mixture was stirred at this temperature for 30 min. After completion of the reaction, 10 mL saturated NH_4Cl was added, and the aqueous phase was extracted three times with 20 mL DCM, the organic phases were combined, dried over Na_2SO_4, filtered, concentrated in vacuo. The residual mixture was purified by silica gel chromatography with PE/EA (20:1) as eluting solvent to afford 2-((4-(*tert*-butyl)phenyl)ethynyl)phenol **1am** as dark yellow oil (516 mg, 69% over two steps).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.37 (d, *J* = 8.4 Hz, 2H), 7.30 (dd, *J* = 12.7, 4.7 Hz, 3H), 7.15 (dd, *J* = 11.2, 4.2 Hz, 1H), 6.87 (d, *J* = 8.2 Hz, 1H), 6.79 (t, *J* = 7.5 Hz, 1H), 5.79 (s, 1H), 1.22 (s, 9H). Characterization data of **1am** corresponded to the literature values.[13]

2-((4-Chlorophenyl)ethynyl)phenol (1ao)

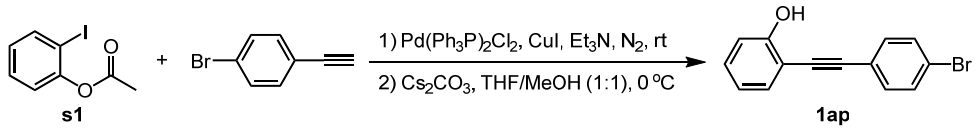


Step 1: To a suspension of 2-iodophenyl acetate **s1** (786 mg, 3 mmol, 1 equiv), $(Ph_3P)_2PdCl_2$ (10.5 mg, 0.5 mol%) and CuI (11.4 mg, 2 mol%) in 6 mL Et_3N was added 1-chloro-4-ethynylbenzene (450 mg, 3.3 mmol, 1.1 equiv). Evacuate the resulting solution and flush with N_2 several times. The mixture allowed to stir at room temperature overnight. After completion of the reaction, 20 mL saturated NH_4Cl was added and the aqueous phase was extracted three times with 20 mL DCM, the organic phases were combined, dried over Na_2SO_4, filtered, concentrated in vacuo. The residual mixture was purified by silica gel chromatography with PE/EA (20:1) as eluting solvent to afford 2-((4-chlorophenyl)ethynyl)phenyl acetate **1ao-1** as light yellow oil.

Step 2: To a solvent of 2-((4-chlorophenyl)ethynyl)phenyl acetate **1ao-1** in 20 mL THF/MeOH (1:1) was added Cs_2CO_3 (1.3 g, 4.5 mmol) at 0 °C. The mixture was stirred at this temperature for 30 min. After completion of the reaction, 10 mL saturated NH_4Cl was added, and the aqueous phase was extracted three times with 20 mL DCM, the organic phases were combined, dried over Na_2SO_4, filtered, concentrated in vacuo. The residual mixture was purified by silica gel chromatography with PE/EA (20:1) as eluting solvent to afford 2-((4-chlorophenyl)ethynyl)phenol **1ao** as light yellow solid (566 mg, 86% over two steps).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.44 (ddd, *J* = 31.7, 19.8, 7.5 Hz, 7H), 7.02 (dd, *J* = 16.6, 7.5 Hz, 2H), 5.83 (s, 1H). Characterization data of **1ao** corresponded to the literature values.[9]

2-((4-Bromophenyl)ethynyl)phenol (1ap)



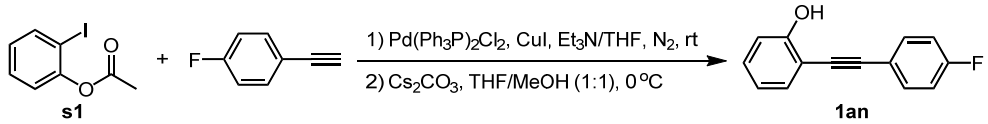
Step 1: To a suspension of 2-iodophenyl acetate **s1** (524.1 mg, 2 mmol, 1 equiv), $(Ph_3P)_2PdCl_2$ (14 mg, 1 mol%) and CuI (7.6 mg, 2 mol%) in 5 mL Et_3N was added 1-bromo-4-ethynylbenzene (434.4 mg, 2.4 mmol, 1.2 equiv). Evacuate the resulting solution and flush with N_2 several times. The mixture allowed to stir at room temperature overnight. After completion of the reaction, 20 mL saturated NH_4Cl was added and the aqueous phase was extracted three times with 20 mL DCM, the organic phases were combined, dried over Na_2SO_4, filtered, concentrated in vacuo. The residual mixture was purified by silica gel chromatography with PE/EA (15:1) as eluting solvent

to afford 2-((4-bromophenyl)ethynyl)phenyl acetate **1ap-1** as light yellow oil (412 mg, 66%).

Step 2: To a solvent of 2-((4-bromophenyl)ethynyl)phenyl acetate **1ap-1** (314 mg, 1 mmol) in 20 mL THF/MeOH (1:1) was added Cs_2CO_3 (652 mg, 2 mmol) at 0 °C. The mixture was stirred at this temperature for 30 min. After completion of the reaction, 10 mL saturated NH_4Cl was added, and the aqueous phase was extracted three times with 20 mL DCM, the organic phases were combined, dried over Na_2SO_4, filtered, concentrated in vacuo. The residual mixture was purified by silica gel chromatography with PE/EA (15:1) as eluting solvent to afford 2-((4-bromophenyl)ethynyl)phenol **1ap** as light yellow solid (267 mg, 98%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.51 (d, *J* = 8.4 Hz, 2H), 7.41 (dd, *J* = 7.0, 5.0 Hz, 3H), 7.34 – 7.20 (m, 1H), 6.98 (d, *J* = 8.2 Hz, 1H), 6.92 (t, *J* = 7.5 Hz, 1H), 5.76 (s, 1H). Characterization data of **1ap** corresponded to the literature values.[14]

2-((4-Fluorophenyl)ethynyl)phenol (1an)

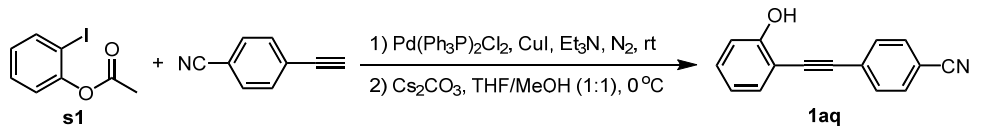


Step 1: To a suspension of 2-iodophenyl acetate **s1** (1.31 g, 5 mmol, 1 equiv), $(Ph_3P)_2PdCl_2$ (35 mg, 1 mol%) and CuI (19 mg, 2 mol%) in 25 mL Et_3N/THF (1:1) was added 1-ethynyl-4-fluorobenzene (584 μL, 6 mmol, 1.2 equiv). Evacuate the resulting solution and flush with N_2 several times. The mixture allowed to stir at room temperature overnight. After completion of the reaction, 30 mL saturated NH_4Cl was added and the aqueous phase was extracted three times with 30 mL DCM, the organic phases were combined, dried over Na_2SO_4, filtered, concentrated in vacuo. The residual mixture was purified by silica gel chromatography with PE/EA (15:1) as eluting solvent to afford 2-((4-fluorophenyl)ethynyl)phenyl acetate **1an-1** as light yellow oil.

Step 2: To a solvent of 2-((4-fluorophenyl)ethynyl)phenyl acetate **1an-1** in 40 mL THF/MeOH (1:1) was added Cs_2CO_3 (3.26 g, 10 mmol) at 0 °C. The mixture was stirred at this temperature for 30 min. After completion of the reaction, 40 mL saturated NH_4Cl was added, and the aqueous phase was extracted three times with 40 mL DCM, the organic phases were combined, dried over Na_2SO_4, filtered, concentrated in vacuo. The residual mixture was purified by silica gel chromatography with PE/EA (15:1) as eluting solvent to afford 2-((4-fluorophenyl)ethynyl)phenol **1an** as light yellow solid (784 mg, 74% over two steps).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.53 (dd, *J* = 8.0, 5.6 Hz, 2H), 7.42 (d, *J* = 7.4 Hz, 1H), 7.28 (dd, *J* = 11.2, 3.8 Hz, 1H), 7.08 (t, *J* = 8.5 Hz, 2H), 7.00 (d, *J* = 8.2 Hz, 1H), 6.92 (t, *J* = 7.4 Hz, 1H), 5.82 (s, 1H). **^{19}F NMR** (282 MHz, $CDCl_3$) δ -109.85. Characterization data of **1an** corresponded to the literature values.[15]

4-((2-Hydroxyphenyl)ethynyl)benzonitrile (1aq)



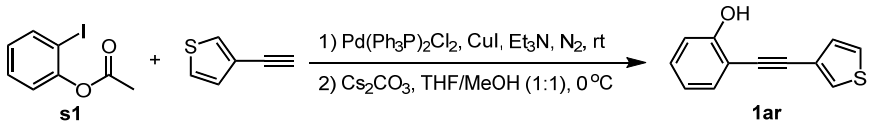
Step 1: To a suspension of 2-iodophenyl acetate **s1** (786 mg, 3 mmol, 1 equiv), $(Ph_3P)_2PdCl_2$ (21 mg, 1 mol%) and CuI (11.4 mg, 2 mol%) in 6 mL Et_3N was added 4-ethynylbenzonitrile (419.1 mg, 3.3 mmol, 1.1 equiv). Evacuate the resulting solution and flush with N_2 several times. The mixture allowed to stir at room temperature overnight. After completion of the reaction, 20 mL

saturated NH_4Cl was added and the aqueous phase was extracted three times with 20 mL DCM, the organic phases were combined, dried over Na_2SO_4, filtered, concentrated in vacuo. The residual mixture was purified by silica gel chromatography with PE/EA (8:1) as eluting solvent to afford 2-((4-cyanophenyl)ethynyl)phenyl acetate **1aq-1** as light yellow oil.

Step 2: To a solvent of 2-((4-cyanophenyl)ethynyl)phenyl acetate **1aq-1** in 40 mL THF/MeOH (1:1) was added Cs_2CO_3 (652 mg, 2 mmol) at 0 °C. The mixture was stirred at this temperature for 30 min. After completion of the reaction, 20 mL saturated NH_4Cl was added, and the aqueous phase was extracted three times with 20 mL DCM, the organic phases were combined, dried over Na_2SO_4, filtered, concentrated in vacuo. The residual mixture was purified by silica gel chromatography with PE/EA (8:1) as eluting solvent to afford 4-((2-hydroxyphenyl)ethynyl)benzonitrile **1aq** as yellow solid (495 mg, 75% over two steps).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.62 (s, 4H), 7.43 (d, *J* = 6.9 Hz, 1H), 7.30 (d, *J* = 7.0 Hz, 1H), 7.08 – 6.82 (m, 2H), 5.82 (s, 1H). Characterization data of **1aq** corresponded to the literature values.[16]

2-(Thiophen-3-ylethynyl)phenol (**1ar**)

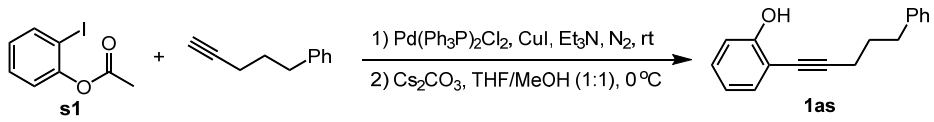


Step 1: To a suspension of 2-iodophenyl acetate **s1** (524 mg, 2 mmol, 1 equiv), $(Ph_3P)_2PdCl_2$ (7.0 mg, 0.5 mol%) and CuI (7.6 mg, 2 mol%) in 4 mL Et_3N was added 3-ethynylthiophene (217 μL, 2.2 mmol, 1.1 equiv). Evacuate the resulting solution and flush with N_2 several times. The mixture allowed to stir at room temperature overnight. After completion of the reaction, 15 mL saturated NH_4Cl was added and the aqueous phase was extracted three times with 15 mL DCM, the organic phases were combined, dried over Na_2SO_4, filtered, concentrated in vacuo. The residual mixture was purified by silica gel chromatography with PE/EA (20:1) as eluting solvent to afford 2-(thiophen-3-ylethynyl)phenyl acetate **1ar-1** as light yellow oil.

Step 2: To a solvent of 2-(thiophen-3-ylethynyl)phenyl acetate **1ar-1** in 16 mL THF/MeOH (1:1) was added Cs_2CO_3 (978 mg, 3 mmol) at 0 °C. The mixture was stirred at this temperature for 30 min. After completion of the reaction, 10 mL saturated NH_4Cl was added, and the aqueous phase was extracted three times with 20 mL DCM, the organic phases were combined, dried over Na_2SO_4, filtered, concentrated in vacuo. The residual mixture was purified by silica gel chromatography with PE/EA (20:1) as eluting solvent to afford 2-(thiophen-3-ylethynyl)phenol **1ar** as light yellow solid (357 mg, 89% over two steps).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.57 (dd, *J* = 3.0, 1.1 Hz, 1H), 7.41 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.34 (dd, *J* = 5.0, 3.0 Hz, 1H), 7.31 – 7.23 (m, 1H), 7.21 (dd, *J* = 5.0, 1.1 Hz, 1H), 6.98 (dd, *J* = 8.3, 0.7 Hz, 1H), 6.91 (td, *J* = 7.6, 1.1 Hz, 1H), 5.80 (s, 1H). Characterization data of **1ar** corresponded to the literature values.[17]

2-(5-Phenylpent-1-yn-1-yl)phenol (**1as**)



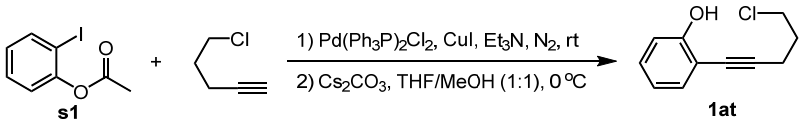
Step 1: To a suspension of 2-iodophenyl acetate **s1** (786 mg, 3 mmol, 1 equiv), $(Ph_3P)_2PdCl_2$ (10.5 mg, 0.5 mol%) and CuI (11.4 mg, 2 mol%) in 6 mL Et_3N was added pent-4-yn-1-ylbenzene

(501 μL, 3.3 mmol, 1.1 equiv). Evacuate the resulting solution and flush with N_2 several times. The mixture allowed to stir at room temperature overnight. After completion of the reaction, 20 mL saturated NH_4Cl was added and the aqueous phase was extracted three times with 20 mL DCM, the organic phases were combined, dried over Na_2SO_4, filtered, concentrated in vacuo. The residual mixture was purified by silica gel chromatography with PE/EA (20:1) as eluting solvent to afford 2-(5-phenylpent-1-yn-1-yl)phenyl acetate **1as-1** as light yellow oil.

Step 2: To a solvent of 2-(5-phenylpent-1-yn-1-yl)phenyl acetate **1as-1** in 20 mL THF/MeOH (1:1) was added Cs_2CO_3 (1.3 g, 4.5 mmol) at 0 °C. The mixture was stirred at this temperature for 30 min. After completion of the reaction, 20 mL saturated NH_4Cl was added, and the aqueous phase was extracted three times with 20 mL DCM, the organic phases were combined, dried over Na_2SO_4, filtered, concentrated in vacuo. The residual mixture was purified by silica gel chromatography with PE/EA (20:1) as eluting solvent to afford 2-(5-phenylpent-1-yn-1-yl)phenol **1as** as light yellow oil (585 mg, 83% over two steps).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.33 – 7.23 (m, 3H), 7.22 – 7.12 (m, 4H), 6.91 (dd, *J* = 8.2, 0.8 Hz, 1H), 6.82 (td, *J* = 7.5, 1.1 Hz, 1H), 5.77 (s, 1H), 2.75 (t, *J* = 7.5 Hz, 2H), 2.45 (t, *J* = 7.1 Hz, 2H), 1.98 – 1.87 (m, 2H). Characterization data of **1as** corresponded to the literature values.[18]

2-(5-Chloropent-1-yn-1-yl)phenol (1at)

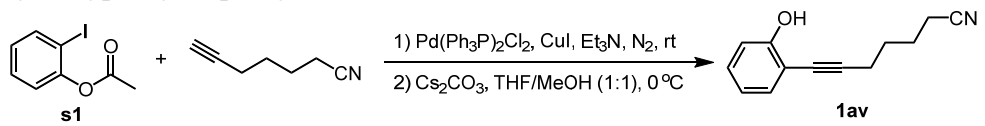


Step 1: To a suspension of 2-iodophenyl acetate **s1** (524 mg, 2 mmol, 1 equiv), $(Ph_3P)_2PdCl_2$ (14 mg, 1 mol%) and CuI (7.6 mg, 2 mol%) in 5 mL Et_3N was added 5-chloropent-1-yne (254 μL, 2.4 mmol, 1.2 equiv). Evacuate the resulting solution and flush with N_2 several times. The mixture allowed to stir at room temperature overnight. After completion of the reaction, 20 mL saturated NH_4Cl was added and the aqueous phase was extracted three times with 20 mL DCM, the organic phases were combined, dried over Na_2SO_4, filtered, concentrated in vacuo. The residual mixture was purified by silica gel chromatography with PE/EA (20:1) as eluting solvent to afford 2-(5-chloropent-1-yn-1-yl)phenyl acetate **1at-1** as light yellow oil (473 mg, 100%).

Step 2: To a solvent of 2-(5-chloropent-1-yn-1-yl)phenyl acetate **1at-1** (473 mg, 2 mmol) in 20 mL THF/MeOH (1:1) was added Cs_2CO_3 (1.4 g, 4.2 mmol) at 0 °C. The mixture was stirred at this temperature for 30 min. After completion of the reaction, 20 mL saturated NH_4Cl was added, and the aqueous phase was extracted three times with 20 mL DCM, the organic phases were combined, dried over Na_2SO_4, filtered, concentrated in vacuo. The residual mixture was purified by silica gel chromatography with PE/EA (15:1) as eluting solvent to afford 2-(5-chloropent-1-yn-1-yl)phenoll **1at** as light yellow solid (365.5 mg, 94%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.30 (dd, *J* = 7.6, 1.3 Hz, 1H), 7.26 – 7.15 (m, 1H), 6.94 (d, *J* = 8.1 Hz, 1H), 6.86 (t, *J* = 7.5 Hz, 1H), 5.78 (s, 1H), 3.72 (t, *J* = 6.2 Hz, 2H), 2.70 (t, *J* = 6.9 Hz, 2H), 2.09 (p, *J* = 6.6 Hz, 2H). Characterization data of **1at** corresponded to the literature values.[18]

7-(2-Hydroxyphenyl)hept-6-ynenitrile (**1av**)



Step 1: To a suspension of 2-iodophenyl acetate **s1** (786 mg, 3 mmol, 1 equiv), $(Ph_3P)_2PdCl_2$ (10.5 mg, 0.5 mol%) and CuI (11.4 mg, 2 mol%) in 6 mL Et_3N was added hept-6-ynenitrile (400

μL, 3.3 mmol, 1.1 equiv). Evacuate the resulting solution and flush with N_2 several times. The mixture allowed to stir at room temperature overnight. After completion of the reaction, 20 mL saturated NH_4Cl was added and the aqueous phase was extracted three times with 20 mL DCM, the organic phases were combined, dried over Na_2SO_4, filtered, concentrated in vacuo. The residual mixture was purified by silica gel chromatography with PE/EA (2:1) as eluting solvent to afford 2-(6-cyanohex-1-yn-1-yl)phenyl acetate **1av-1** as light yellow oil.

Step 2: To a solvent of 2-(6-cyanohex-1-yn-1-yl)phenyl acetate **1av-1** in 20 mL THF/MeOH (1:1) was added Cs_2CO_3 (1.3 g, 4.5 mmol) at 0 °C. The mixture was stirred at this temperature for 30 min. After completion of the reaction, 20 mL saturated NH_4Cl was added, and the aqueous phase was extracted three times with 20 mL DCM, the organic phases were combined, dried over Na_2SO_4, filtered, concentrated in vacuo. The residual mixture was purified by silica gel chromatography with PE/EA (2:1) as eluting solvent to afford 7-(2-hydroxyphenyl)hept-6-ynenitrile **1av** as light yellow solid (388 mg, 65% over two steps).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.29 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.25 – 7.18 (m, 1H), 6.93 (d, *J* = 8.2 Hz, 1H), 6.85 (t, *J* = 7.5 Hz, 1H), 5.72 (s, 1H), 2.57 (t, *J* = 6.4 Hz, 2H), 2.43 (t, *J* = 6.6 Hz, 2H), 1.93 – 1.75 (m, 4H).

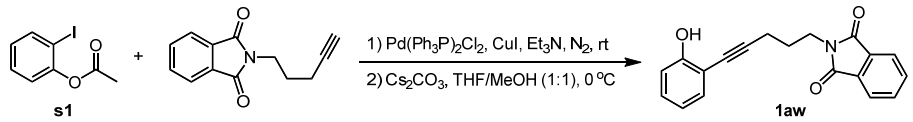
^{13}C NMR (75 MHz, $CDCl_3$) δ 156.5, 131.6, 129.9, 120.3, 119.3, 114.5, 109.7, 95.9, 75.7, 27.5, 24.5, 18.9, 16.9.

HRMS (EI) calcd for $C_{13}H_{13}NO$ $[M]^+$: 199.09917, found: 199.09890.

IR (ATR): $\tilde{\nu}$ = 3303, 2944, 2874, 2259, 1910, 1732, 1602, 1588, 1506, 1461, 1448, 1417, 1372, 1347, 1289, 1258, 1227, 1197, 1160, 1107, 1040, 1012, 977, 937, 921, 830, 759, 737, 683.

M.p. (amorphous) 67.7-69.8 °C.

2-(5-(2-Hydroxyphenyl)pent-4-yn-1-yl)isoindoline-1,3-dione (1aw)



Step 1: To a suspension of 2-iodophenyl acetate **s1** (524 mg, 2 mmol, 1 equiv), $(Ph_3P)_2PdCl_2$ (14 mg, 1 mol%) and CuI (7.6 mg, 2 mol%) in 5 mL Et_3N was added 2-(pent-4-yn-1-yl)isoindoline-1,3-dione (512 mg, 2.4 mmol, 1.2 equiv). Evacuate the resulting solution and flush with N_2 several times. The mixture allowed to stir at room temperature overnight. After completion of the reaction, 10 mL saturated NH_4Cl was added and the aqueous phase was extracted three times with 10 mL DCM, the organic phases were combined, dried over Na_2SO_4, filtered, concentrated in vacuo. The residual mixture was purified by silica gel chromatography with PE/EA (5:1) as eluting solvent to afford 2-(5-(1,3-dioxoisoindolin-2-yl)pent-1-yn-1-yl)phenyl acetate **1aw-1** as light yellow oil.

Step 2: To a solvent of 2-(5-(1,3-dioxoisoindolin-2-yl)pent-1-yn-1-yl)phenyl acetate **1aw-1** in 20 mL THF/MeOH (1:1) was added Cs_2CO_3 (1.4 g, 4.2 mmol) at 0 °C. The mixture was stirred at this temperature for 30 min. After completion of the reaction, 20 mL saturated NH_4Cl was added, and the aqueous phase was extracted three times with 20 mL DCM, the organic phases were combined, dried over Na_2SO_4, filtered, concentrated in vacuo. The residual mixture was purified by silica gel chromatography with PE/EA (15:1) as eluting solvent to afford 2-(5-(2-hydroxyphenyl)pent-4-yn-1-yl)isoindoline-1,3-dione **1aw** as colorless solid (357 mg, 58% over two steps).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (dd, *J* = 5.4, 3.1 Hz, 2H), 7.69 (dd, *J* = 5.4, 3.0 Hz, 2H), 7.20 (ddd, *J* = 13.9, 7.6, 1.5 Hz, 2H), 6.95 (dd, *J* = 8.1, 0.5 Hz, 1H), 6.86 (s, 1H), 6.80 (td, *J* = 7.5, 1.0 Hz, 1H), 3.99 – 3.91 (m, 2H), 2.50 (t, *J* = 6.5 Hz, 2H), 2.04 – 1.96 (m, 2H).

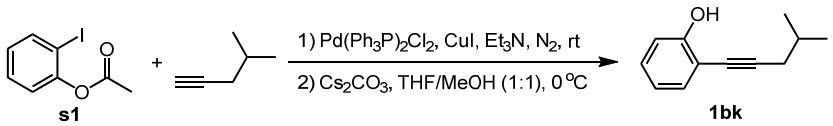
^{13}C NMR (101 MHz, $CDCl_3$) δ 168.6, 157.4, 134.1, 131.8, 131.4, 129.7, 123.4, 119.8, 114.9, 109.8, 95.3, 76.2, 36.4, 26.9, 16.8.

HRMS (EI) calcd for $C_{19}H_{15}NO_3$ $[M]^+$: 305.10464, found: 305.10460.

IR (Reflection): ṽ = 3427, 2945, 2897, 2836, 1770, 1758, 1694, 1612, 1573, 1488, 1459, 1429, 1401, 1373, 1327, 1293, 1234, 1209, 1166, 1111, 1032, 882, 829, 798, 763, 725, 715, 694, 621.

M.p. (amorphous) 125.8-127.5 °C.

2-(4-Methylpent-1-yn-1-yl)phenol (**1bk**)



Step 1: To a suspension of 2-iodophenyl acetate **s1** (786 mg, 3 mmol, 1 equiv), $(Ph_3P)_2PdCl_2$ (10.5 mg, 0.5 mol%) and CuI (11.4 mg, 2 mol%) in 6 mL Et_3N was added 4-methylpent-1-yne (388 μL, 3.3 mmol, 1.1 equiv). Evacuate the resulting solution and flush with N_2 several times. The mixture allowed to stir at room temperature overnight. After completion of the reaction, 20 mL saturated NH_4Cl was added and the aqueous phase was extracted three times with 20 mL DCM, the organic phases were combined, dried over Na_2SO_4, filtered, concentrated in vacuo. The residual mixture was purified by silica gel chromatography with PE/EA (20:1) as eluting solvent to afford 2-(4-methylpent-1-yn-1-yl)phenyl acetate **1bk-1** as light yellow oil.

Step 2: To a solvent of 2-(4-methylpent-1-yn-1-yl)phenyl acetate **1bk-1** (3 mmol) in 20 mL THF/MeOH (1:1) was added Cs_2CO_3 (1.3 g, 4.5 mmol) at 0 °C. The mixture was stirred at this temperature for 30 min. After completion of the reaction, 20 mL saturated NH_4Cl was added, and the aqueous phase was extracted three times with 20 mL DCM, the organic phases were combined, dried over Na_2SO_4, filtered, concentrated in vacuo. The residual mixture was purified by silica gel chromatography with PE/EA (15:1) as eluting solvent to afford 2-(4-methylpent-1-yn-1-yl)phenol **1bk** as light yellow oil (382 mg, 73% over two steps).

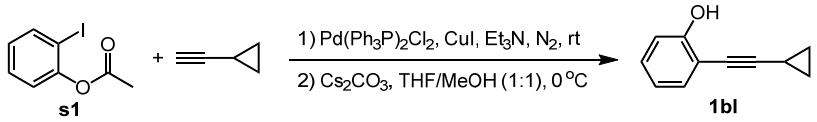
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.31 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.25 – 7.16 (m, 1H), 6.93 (d, *J* = 8.2 Hz, 1H), 6.85 (td, *J* = 7.6, 0.9 Hz, 1H), 5.80 (s, 1H), 2.38 (d, *J* = 6.5 Hz, 2H), 1.94 (dp, *J* = 13.2, 6.6 Hz, 1H), 1.06 (d, *J* = 6.7 Hz, 6H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 156.50, 131.43, 129.56, 120.14, 114.26, 110.26, 96.88, 77.00, 75.38, 28.72, 28.12, 22.03.

HRMS (EI) calcd for $C_{12}H_{14}O$ $[M]^+$: 174.10392, found: 174.10318.

IR (Reflection): ṽ = 3506, 3045, 2959, 2927, 2870, 2226, 1614, 1577, 1487, 1463, 1426, 1385, 1368, 1346, 1288, 1237, 1207, 1181, 1152, 1103, 1032, 937, 827, 752, 699.

2-(Cyclopropylethynyl)phenol (1bl)



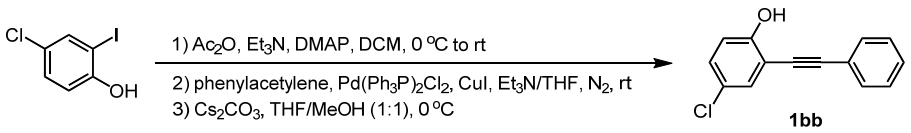
Step 1: To a suspension of 2-iodophenyl acetate **s1** (786 mg, 3 mmol, 1 equiv), $(Ph_3P)_2PdCl_2$ (10.5 mg, 0.5 mol%) and CuI (11.4 mg, 2 mol%) in 6 mL Et_3N was added ethynylcyclopropane (280 μL, 3.3 mmol, 1.1 equiv). Evacuate the resulting solution and flush with N_2 several times.

The mixture allowed to stir at room temperature overnight. After completion of the reaction, 20 mL saturated NH_4Cl was added and the aqueous phase was extracted three times with 20 mL DCM, the organic phases were combined, dried over Na_2SO_4, filtered, concentrated in vacuo. The residual mixture was purified by silica gel chromatography with PE/EA (20:1) as eluting solvent to afford 2-(cyclopropylethynyl)phenyl acetate **1bl-1** as light yellow oil.

Step 2: To a solvent of 2-(cyclopropylethynyl)phenyl acetate **1bl-1** in 20 mL THF/MeOH (1:1) was added Cs_2CO_3 (1.3 g, 4.5 mmol) at 0 °C. The mixture was stirred at this temperature for 30 min. After completion of the reaction, 20 mL saturated NH_4Cl was added, and the aqueous phase was extracted three times with 20 mL DCM, the organic phases were combined, dried over Na_2SO_4, filtered, concentrated in vacuo. The residual mixture was purified by silica gel chromatography with PE/EA (20:1) as eluting solvent to afford 2-(cyclopropylethynyl)phenol **1bl** as light yellow oil (339 mg, 71% over two steps).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.27 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.23 – 7.11 (m, 1H), 6.92 (dd, *J* = 8.2, 0.7 Hz, 1H), 6.82 (td, *J* = 7.6, 1.1 Hz, 1H), 5.80 (s, 1H), 1.51 (tt, *J* = 8.2, 5.1 Hz, 1H), 0.97 – 0.88 (m, 2H), 0.84 (ddd, *J* = 7.7, 5.4, 2.5 Hz, 2H). Characterization data of **1bl** corresponded to the literature values.[19]

4-Chloro-2-(phenylethynyl)phenol (1bb)



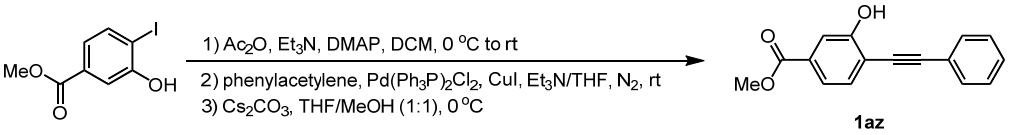
Step 1: To a solvent of 4-chloro-2-iodophenol (763 mg, 3 mmol, 1 equiv), Et_3N (0.62 mL, 4.5 mmol, 1.5 equiv) and DMAP (18.3 mg, 0.15 mmol, 0.05 equiv) in 6 mL DCM was added dropwise Ac_2O (0.34 mL, 3.6 mmol) at 0 °C. The mixture was stirred at this temperature for 30 min and then warmed up to room temperature and stirred overnight. After completion of the reaction, 10 mL saturated NH_4Cl was added and the aqueous phase was extracted three times with 10 mL DCM, the organic phases were combined, dried over Na_2SO_4, filtered, concentrated in vacuo. The residual mixture was purified by silica gel chromatography with PE/EA (15:1) as eluting solvent to afford 4-chloro-2-iodophenyl acetate **1bb-1** as light yellow oil.

Step 2: To a suspension of 4-chloro-2-iodophenyl acetate **1bb-1**, $(Ph_3P)_2PdCl_2$ (21 mg, 1 mol%) and CuI (11.4 mg, 2 mol%) in 6 mL Et_3N/THF (1:1) was added phenylacetylene (0.39 mL, 3.6 mmol, 1.2 equiv). Evacuate the resulting solution and flush with N_2 several times. The mixture allowed to stir at room temperature overnight. After completion of the reaction, 15 mL saturated NH_4Cl was added and the aqueous phase was extracted three times with 15 mL DCM, the organic phases were combined, dried over Na_2SO_4, filtered, concentrated in vacuo. The residual mixture was purified by silica gel chromatography with PE/EA (15:1) as eluting solvent to afford 4-chloro-2-(phenylethynyl)phenyl acetate **1bb-2** as light yellow oil.

Step 3: To a solvent of 4-chloro-2-(phenylethynyl)phenyl acetate **1bb-2** in 20 mL THF/MeOH (1:1) was added Cs_2CO_3 (1.0 g, 3.3 mmol) at 0 °C. The mixture was stirred at this temperature for 30 min. After completion of the reaction, 20 mL saturated NH_4Cl was added, and the aqueous phase was extracted three times with 20 mL DCM, the organic phases were combined, dried over Na_2SO_4, filtered, concentrated in vacuo. The residual mixture was purified by silica gel chromatography with PE/EA (15:1) as eluting solvent to afford 4-chloro-2-(phenylethynyl)phenol **1bb** as light yellow solid (567 mg, 83% over three steps).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.66 – 7.48 (m, 2H), 7.40 (d, *J* = 1.5 Hz, 4H), 7.22 (dd, *J* = 8.7, 2.2 Hz, 1H), 6.92 (d, *J* = 8.7 Hz, 1H), 5.81 (s, 1H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 155.1, 131.7, 130.9, 130.4, 129.2, 128.5, 125.1, 121.8, 116.0, 111.0, 97.3, 81.8. Characterization data of **1bb** corresponded to the literature values.[11]

Methyl 3-hydroxy-4-(phenylethynyl)benzoate (1az)



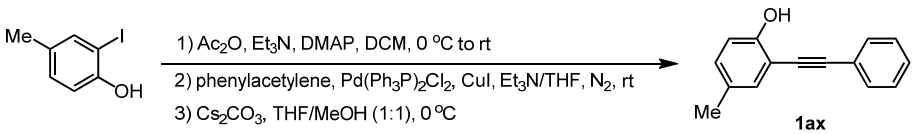
Step 1: To a solvent of methyl 3-hydroxy-4-iodobenzoate (834 mg, 3 mmol, 1 equiv), Et_3N (0.62 mL, 4.5 mmol, 1.5 equiv) and DMAP (18.3 mg, 0.15 mmol, 0.05 equiv) in 6 mL DCM was added dropwise Ac_2O (0.34 mL, 3.6 mmol) at 0 °C. The mixture was stirred at this temperature for 30 min and then warmed up to room temperature and stirred overnight. After completion of the reaction, 10 mL saturated NH_4Cl was added and the aqueous phase was extracted three times with 10 mL DCM, the organic phases were combined, dried over Na_2SO_4, filtered, concentrated in vacuo. The residual mixture was purified by silica gel chromatography with PE/EA (8:1) as eluting solvent to afford methyl 3-acetoxy-4-iodobenzoate **1az-1** as light yellow oil.

Step 2: To a suspension of methyl 3-acetoxy-4-iodobenzoate **1az-1** (3 mmol, 1 equiv), $(Ph_3P)_2PdCl_2$ (21 mg, 1 mol%) and CuI (11.4 mg, 2 mol%) in 6 mL Et_3N/THF (1:1) was added phenylacetylene (0.39 mL, 3.6 mmol, 1.2 equiv). Evacuate the resulting solution and flush with N_2 several times. The mixture allowed to stir at room temperature overnight. After completion of the reaction, 15 mL saturated NH_4Cl was added and the aqueous phase was extracted three times with 15 mL DCM, the organic phases were combined, dried over Na_2SO_4, filtered, concentrated in vacuo. The residual mixture was purified by silica gel chromatography with PE/EA (8:1) as eluting solvent to afford methyl 3-acetoxy-4-(phenylethynyl)benzoate **1az-2** as light yellow oil.

Step 3: To a solvent of methyl 3-acetoxy-4-(phenylethynyl)benzoate **1az-2** in 20 mL THF/MeOH (1:1) was added Cs_2CO_3 (1.0 g, 3.3 mmol) at 0 °C. The mixture was stirred at this temperature for 30 min. After completion of the reaction, 20 mL saturated NH_4Cl was added, and the aqueous phase was extracted three times with 20 mL DCM, the organic phases were combined, dried over Na_2SO_4, filtered, concentrated in vacuo. The residual mixture was purified by silica gel chromatography with PE/EA (15:1) as eluting solvent to afford methyl 3-hydroxy-4-(phenylethynyl)benzoate **1az** as light yellow solid (643 mg, 85% over three steps).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.65 (d, *J* = 1.4 Hz, 1H), 7.62 – 7.52 (m, 3H), 7.48 (d, *J* = 8.0 Hz, 1H), 7.39 (dd, *J* = 5.1, 1.8 Hz, 3H), 5.95 (s, 1H), 3.92 (s, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 166.3, 156.3, 131.72, 131.70, 131.6, 129.3, 128.6, 121.8, 121.5, 115.8, 114.2, 98.7, 82.5, 52.3. Characterization data of **1az** corresponded to the literature values.[20]

4-Methyl-2-(phenylethynyl)phenol (1ax)



Step 1: To a solvent of 4-chloro-2-iodophenol (702 mg, 3 mmol, 1 equiv), Et_3N (0.62 mL, 4.5 mmol, 1.5 equiv) and DMAP (18.3 mg, 0.15 mmol, 0.05 equiv) in 6 mL DCM was added dropwise Ac_2O (0.34 mL, 3.6 mmol) at 0 °C. The mixture was stirred at this temperature for 30

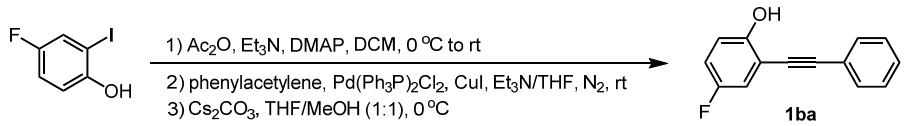
min and then warmed up to room temperature and stirred overnight. After completion of the reaction, 10 mL saturated NH_4Cl was added and the aqueous phase was extracted three times with 10 mL DCM, the organic phases were combined, dried over Na_2SO_4, filtered, concentrated in vacuo. The residual mixture was purified by silica gel chromatography with PE/EA (15:1) as eluting solvent to afford 2-iodo-4-methylphenyl acetate **1ax-1** as light yellow oil.

Step 2: To a suspension of 2-iodo-4-methylphenyl acetate **1ax-1**, $(Ph_3P)_2PdCl_2$ (10.5 mg, 0.5 mol%) and CuI (11.4 mg, 2 mol%) in 6 mL Et_3N/THF (1:1) was added phenylacetylene (0.36 mL, 3.3 mmol, 1.1 equiv). Evacuate the resulting solution and flush with N_2 several times. The mixture allowed to stir at room temperature overnight. After completion of the reaction, 15 mL saturated NH_4Cl was added and the aqueous phase was extracted three times with 15 mL DCM, the organic phases were combined, dried over Na_2SO_4, filtered, concentrated in vacuo. The residual mixture was purified by silica gel chromatography with PE/EA (20:1) as eluting solvent to afford 4-methyl-2-(phenylethynyl)phenyl acetate **1ax-2** as light yellow oil.

Step 3: To a solvent of 4-methyl-2-(phenylethynyl)phenyl acetate **1ax-2** in 20 mL THF/MeOH (1:1) was added Cs_2CO_3 (1.0 g, 3.3 mmol) at 0 °C. The mixture was stirred at this temperature for 30 min. After completion of the reaction, 20 mL saturated NH_4Cl was added, and the aqueous phase was extracted three times with 20 mL DCM, the organic phases were combined, dried over Na_2SO_4, filtered, concentrated in vacuo. The residual mixture was purified by silica gel chromatography with PE/EA (20:1) as eluting solvent to afford 4-methyl-2-(phenylethynyl)phenol **1ax** as light yellow solid (583 mg, 93% over three steps).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.42 (dd, *J* = 10.6, 4.7 Hz, 2H), 7.31 – 7.23 (m, 3H), 7.19 (d, *J* = 7.9 Hz, 1H), 6.99 (d, *J* = 7.7 Hz, 1H), 6.91 (td, *J* = 7.6, 1.0 Hz, 1H), 5.85 (s, 1H), 2.39 (s, 3H). Characterization data of **1ax** corresponded to the literature values.[14]

4-Fluoro-2-(phenylethynyl)phenol (1ba)



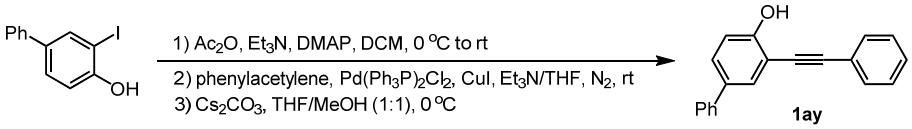
Step 1: To a solvent of 4-fluoro-2-iodophenol (476 mg, 2 mmol, 1 equiv), Et_3N (0.41 mL, 3.0 mmol, 1.5 equiv) and DMAP (12.2 mg, 0.1 mmol, 0.05 equiv) in 4 mL DCM was added dropwise Ac_2O (0.23 mL, 2.4 mmol, 1.2 equiv) at 0 °C. The mixture was stirred at this temperature for 30 min and then warmed up to room temperature and stirred overnight. After completion of the reaction, products were detected by TLC. 10 mL saturated NH_4Cl was added and the aqueous phase was extracted three times with 10 mL DCM, the organic phases were combined, dried over Na_2SO_4, filtered, concentrated in vacuo. The residual mixture was purified by silica gel chromatography with PE/EA (20:1) as eluting solvent to afford 4-fluoro-2-iodophenyl acetate **1ba-1** as light yellow oil.

Step 2: To a suspension of 4-fluoro-2-iodophenyl acetate **1ba-1**, $(Ph_3P)_2PdCl_2$ (7.0 mg, 0.5 mol%) and CuI (7.6 mg, 2 mol%) in 4 mL Et_3N/THF (1:1) was added phenylacetylene (0.24 mL, 2.2 mmol, 1.1 equiv). Evacuate the resulting solution and flush with N_2 several times. The mixture allowed to stir at room temperature overnight. After completion of the reaction, 10 mL saturated NH_4Cl was added and the aqueous phase was extracted three times with 10 mL DCM, the organic phases were combined, dried over Na_2SO_4, filtered, concentrated in vacuo. The residual mixture was purified by silica gel chromatography with PE/EA (20:1) as eluting solvent to afford 4-fluoro-2-(phenylethynyl)phenyl acetate **1ba-2** as light yellow oil.

Step 3: To a solvent of 4-fluoro-2-(phenylethynyl)phenyl acetate **1ba-2** in 20 mL THF/MeOH (1:1) was added Cs_2CO_3 (978 mg, 3 mmol) at 0 °C. The mixture was stirred at this temperature for 10 min. After completion of the reaction, 20 mL saturated NH_4Cl was added, and the aqueous phase was extracted three times with 20 mL DCM, the organic phases were combined, dried over Na_2SO_4, filtered, concentrated in vacuo. The residual mixture was purified by silica gel chromatography with PE/EA (20:1) as eluting solvent to afford 4-fluoro-2-(phenylethynyl)phenol **1ba** as light yellow solid (358 mg, 84% over three steps).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.55 (dd, *J* = 6.6, 3.0 Hz, 2H), 7.40 – 7.38 (m, 3H), 7.12 (dd, *J* = 8.5, 2.9 Hz, 1H), 7.04 – 6.85 (m, 2H), 5.68 (s, 1H). **^{19}F NMR** (282 MHz, $CDCl_3$) δ -123.83. Characterization data of **1ba** corresponded to the literature values.[14]

3-(Phenylethynyl)-[1,1'-biphenyl]-4-ol (1ay)



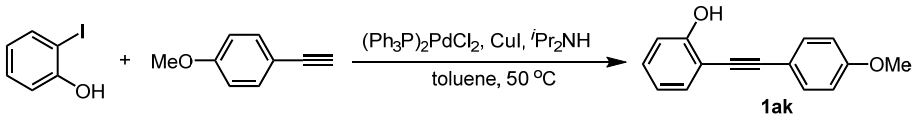
Step 1: To a solvent of 3-iodo-[1,1'-biphenyl]-4-ol (885 mg, 3 mmol, 1 equiv), triethylamine (0.62 mL, 4.5 mmol, 1.5 equiv) and DMAP (4-dimethylaminopyridine) (18.3 mg, 0.15 mmol, 0.05 equiv) in 6 mL DCM was added dropwise Ac_2O (0.34 mL, 3.6 mmol, 1.2 equiv) at 0 °C. The mixture was stirred at this temperature for 30 min and then warmed up to room temperature and stirred overnight. After completion of the reaction, products were detected by TLC. 15 mL saturated NH_4Cl was added and the aqueous phase was extracted three times with 15 mL DCM, the organic phases were combined, dried over Na_2SO_4, filtered, concentrated in vacuo. The residual mixture was purified by silica gel chromatography with PE/EA (20:1) as eluting solvent to afford 3-iodo-[1,1'-biphenyl]-4-yl acetate **1ay-1** as light yellow oil.

Step 2: To a suspension of 3-iodo-[1,1'-biphenyl]-4-yl acetate **1ay-1**, $(Ph_3P)_2PdCl_2$ (10.5 mg, 0.5 mol%) and CuI (11.4 mg, 2 mol%) in 6 mL Et_3N/THF (1:1) was added phenylacetylene (0.36 mL, 3.3 mmol, 1.1 equiv). Evacuate the resulting solution and flush with N_2 several times. The mixture allowed to stir at room temperature overnight. After completion of the reaction, 15 mL saturated NH_4Cl was added and the aqueous phase was extracted three times with 15 mL DCM, the organic phases were combined, dried over Na_2SO_4, filtered, concentrated in vacuo. The residual mixture was purified by silica gel chromatography with PE/EA (20:1) as eluting solvent to afford 3-(phenylethynyl)-[1,1'-biphenyl]-4-yl acetate **1ay-2** as light yellow oil.

Step 3: To a solvent of 3-(phenylethynyl)-[1,1'-biphenyl]-4-yl acetate **1ay-2** in 20 mL THF/MeOH (1:1) was added Cs_2CO_3 (1.0 g, 3.3 mmol) at 0 °C. The mixture was stirred at this temperature for 30 min. After completion of the reaction, 20 mL saturated NH_4Cl was added, and the aqueous phase was extracted three times with 20 mL DCM, the organic phases were combined, dried over Na_2SO_4, filtered, concentrated in vacuo. The residual mixture was purified by silica gel chromatography with PE/EA (20:1) as eluting solvent to afford 3-(phenylethynyl)-[1,1'-biphenyl]-4-ol **1ay** as light yellow solid (590 mg, 73% over three steps).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.68 (d, *J* = 2.2 Hz, 1H), 7.62 – 7.48 (m, 5H), 7.47 – 7.37 (m, 5H), 7.33 (t, *J* = 7.3 Hz, 1H), 7.06 (d, *J* = 8.5 Hz, 1H), 5.86 (s, 1H). Characterization data of **1ay** corresponded to the literature values.[13]

2-((4-Methoxyphenyl)ethynyl)phenol (1ak)

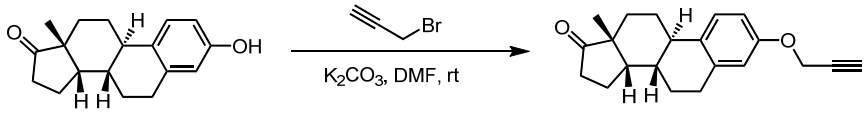


1ak

To a suspension of 2-iodophenol **s1** (3.85 g, 17.5 mmol, 1 equiv), $(Ph_3P)_2PdCl_2$ (306 mg, 2.5 mol%) and CuI (166 mg, 5 mol%) in 40 mL toluene were added 1-ethynyl-4-methoxybenzene (2.5 mL, 19.25 mmol, 1.1 equiv) and diisopropylamine (2.45 mL, 17.5 mmol, 1 equiv). Evacuate the resulting solution and flush with N_2 several times. The mixture allowed to stir at 50 °C for 2 h. After completion of the reaction, 40 mL saturated NH_4Cl was added and the aqueous phase was extracted three times with 40 mL ethyl acetate, the organic phases were combined, dried over Na_2SO_4, filtered, concentrated in vacuo. The residual mixture was purified by silica gel chromatography with PE/EA (20:1) as eluting solvent to afford 2-((4-methoxyphenyl)ethynyl)phenol **1ak** as brown solid (3.08 g, 79%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.51 – 7.45 (m, 2H), 7.40 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.30 – 7.19 (m, 1H), 6.98 (dd, *J* = 8.3, 0.8 Hz, 1H), 6.94 – 6.86 (m, 3H), 5.84 (br, 1H), 3.84 (s, 3H). Characterization data of **1ak** corresponded to the literature values.[21]

(*8S,9R,13R,14S*)-13-Methyl-3-(prop-2-yn-1-yloxy)-6,7,8,9,11,12,13,14,15,16-decahydro-*17H*-cyclopenta[*a*]phenanthren-17-one (2ae)



Oestron **2ae**

In a 25 mL flask, 3-bromopropyne (0.17 mL, 1.5 mmol, 1.5 equiv, 80 wt% in toluene) was added to a solution of Oestron (270.4 mg, 1 mmol, 1 equiv) and K_2CO_3 (552 mg, 4 mmol, 4 equiv) in DMF (10 mL) at room temperature. The mixture was stirred at room temperature overnight. Then the reaction was diluted with 30 mL ethyl acetate and washed three times with 30 mL sat. brine. The combined organic layer was dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. The residue was purified by silica gel chromatography with PE/EA (8:1) as eluting solvent to afford (*8S,9R,13R,14S*)-13-methyl-3-(prop-2-yn-1-yloxy)-6,7,8,9,11,12,13,14,15,16-decahydro-*17H*-cyclopenta[*a*]phenanthren-17-one **2ae** as colorless oil (252.0 mg, 82%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.22 (d, *J* = 8.6 Hz, 1H), 6.79 (dd, *J* = 8.6, 2.8 Hz, 1H), 6.72 (d, *J* = 2.7 Hz, 1H), 4.66 (d, *J* = 2.4 Hz, 2H), 2.91 – 2.88 (m, 2H), 2.55 – 2.38 (m, 3H), 2.33 – 2.20 (m, 1H), 2.19 – 1.89 (m, 3H), 1.70 – 1.34 (m, 6H), 0.91 (s, 3H).

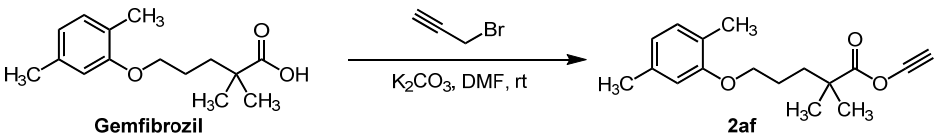
^{13}C NMR (75 MHz, $CDCl_3$) δ 220.8, 155.5, 137.8, 133.0, 126.3, 114.9, 112.3, 78.8, 75.3, 55.7, 50.4, 48.0, 44.0, 38.3, 35.8, 31.6, 29.6, 26.5, 25.9, 21.6, 13.8.

HRMS (EI) calcd for $C_{21}H_{14}O_2$ $[M]^+$: 308.17708, found: 308.17775.

IR (Reflection): ṽ =3309, 2944, 2863, 2131, 1731, 1463, 1386, 1363, 1253, 1232, 1205, 1156, 1121, 1085, 1032, 995, 815, 755, 678, 638.

M.p. (amorphous) 147.8-148.4 °C.

Prop-2-yn-1-yl 5-(2,5-dimethylphenoxy)-2,2-dimethylpentanoate (2af)



Gemfibrozil **2af**

In a 10 mL flask, 3-bromopropyne (0.17 mL, 1.5 mmol, 1.5 equiv, 80 wt% in toluene) was added to a solution of Gemfibrozil (250.3 mg, 1 mmol, 1 equiv) and K_2CO_3 (552 mg, 4 mmol, 4 equiv) in DMF (5 mL) at room temperature. The mixture was stirred at room temperature for 3 h. Then the reaction was diluted with 15 mL ethyl acetate and washed three times with 15 mL sat. brine. The combined organic layer was dried over anhydrous Na_2SO_4, filtered, concentrated in vacuo. The residue was purified by silica gel chromatography with PE/EA (20:1) as eluting solvent to afford prop-2-yn-1-yl 5-(2,5-dimethylphenoxy)-2,2-dimethylpentanoate **2af** as colorless oil (285.2 mg, 99%).

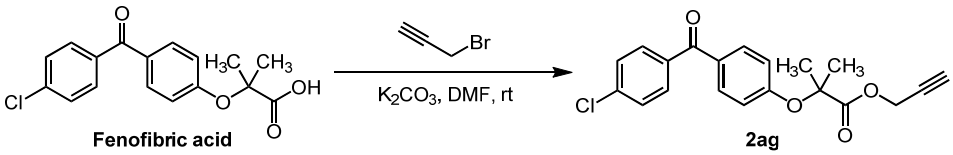
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.01 (d, *J* = 7.4 Hz, 1H), 6.67 (d, *J* = 7.5 Hz, 1H), 6.62 (s, 1H), 4.68 (d, *J* = 2.4 Hz, 2H), 3.93 (d, *J* = 3.0 Hz, 2H), 2.44 (t, *J* = 2.4 Hz, 1H), 2.32 (s, 3H), 2.19 (s, 3H), 1.77 – 1.76 (m, 4H), 1.26 (s, 6H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 176.9, 156.9, 136.4, 130.3, 123.6, 120.7, 111.9, 77.9, 74.5, 67.8, 51.9, 42.1, 37.0, 25.1, 25.0, 21.4, 15.7.

HRMS (EI) calcd for $C_{18}H_{24}O_3$ $[M]^+$: 288.17200, found: 288.17283.

IR (Reflection): ṽ = 3290, 2950, 2924, 2871, 2128, 1731, 1613, 1584, 1508, 1472, 1453, 1413, 1390, 1310, 1261, 1187, 1125, 1045, 991, 843, 802, 634.

Prop-2-yn-1-yl 2-(4-(4-chlorobenzoyl)phenoxy)-2-methylpropanoate (2ag)



In a 25 mL flask, 3-bromopropyne (0.34 mL, 3 mmol, 1.5 equiv, 80 wt% in toluene) was added to a solution of Fenofibric acid (637.5 mg, 2 mmol, 1 equiv) and K_2CO_3 (1.1 g, 8 mmol, 4 equiv) in DMF (10 mL) at room temperature. The mixture was stirred at room temperature for 3 h. Then the reaction was diluted with 30 mL ethyl acetate and washed three times with 30 mL sat. brine. The combined organic layer was dried over anhydrous Na_2SO_4, filtered, concentrated in vacuo. The residue was purified by silica gel chromatography with PE/EA (10:1) as eluting solvent to afford prop-2-yn-1-yl 2-(4-(4-chlorobenzoyl)phenoxy)-2-methylpropanoate **2ag** as light yellow oil (713.5 mg, 100%).

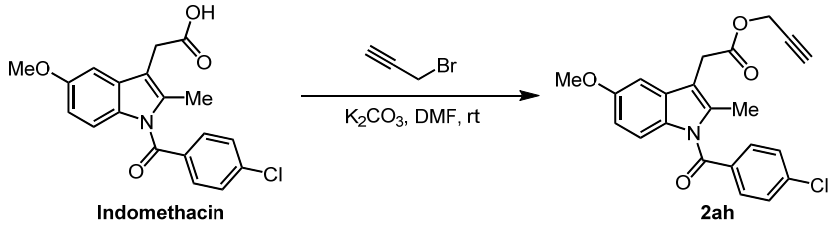
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.74 – 7.67 (m, 4H), 7.43 (d, *J* = 8.4 Hz, 2H), 6.87 (d, *J* = 8.8 Hz, 2H), 4.76 (d, *J* = 2.4 Hz, 2H), 2.48 (t, *J* = 2.4 Hz, 1H), 1.68 (s, 6H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 194.1, 172.8, 159.2, 138.3, 136.3, 131.9, 131.1, 130.6, 128.5, 117.6, 79.2, 76.7, 75.5, 52.9, 25.3.

HRMS (EI) calcd for $C_{20}H_{17}ClO_4$ $[M]^+$: 356.08099, found: 356.08069.

IR (Reflection): ṽ = 3292, 3071, 2994, 2943, 2558, 2129, 1921, 1738, 1650, 1589, 1505, 1486, 1467, 1436, 1418, 1387, 1367, 1301, 1240, 1165, 1116, 1089, 1013, 967, 924, 852, 791, 760, 740, 722, 678.

Prop-2-yn-1-yl 2-(1-(4-chlorobenzoyl)-5-methoxy-2-methyl-*1H*-indol-3-yl)acetate (2ah)



In a 25 mL flask, 3-bromopropyne (0.34 mL, 3 mmol, 1.5 equiv, 80 wt% in toluene) was added to a solution of Indomethacin (715.6 mg, 2 mmol, 1 equiv) and K_2CO_3 (1.1 g, 8 mmol, 4 equiv) in DMF (10 mL) at room temperature. The mixture was stirred at room temperature overnight. Then the reaction was diluted with 30 mL ethyl acetate and washed three times with 30 mL sat. brine. The combined organic layer was dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. The residue was purified by silica gel chromatography with PE/EA (10:1) as eluting solvent to afford prop-2-yn-1-yl 2-(1-(4-chlorobenzoyl)-5-methoxy-2-methyl-*1H*-indol-3-yl)acetate **2ah** as light yellow solid (644.2 mg, 81%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 – 7.63 (m, 2H), 7.55 – 7.40 (m, 2H), 6.97 (d, *J* = 2.5 Hz, 1H), 6.88 (d, *J* = 9.0 Hz, 1H), 6.67 (dd, *J* = 9.0, 2.5 Hz, 1H), 4.71 (d, *J* = 2.5 Hz, 2H), 3.84 (s, 3H), 3.71 (s, 2H), 2.48 (t, *J* = 2.5 Hz, 1H), 2.38 (s, 3H).

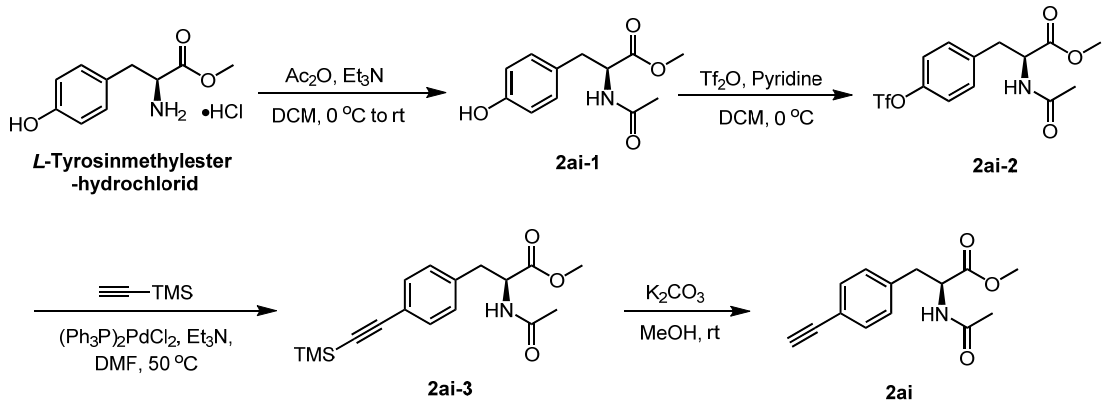
^{13}C NMR (101 MHz, $CDCl_3$) δ 169.9, 168.2, 156.0, 139.2, 136.0, 133.8, 131.1, 130.7, 130.4, 129.1, 114.9, 111.9, 111.8, 101.2, 77.4, 75.1, 55.6, 52.4, 30.0, 13.3.

HRMS (EI) calcd for $C_{22}H_{18}NO_4Cl$ $[M]^+$: 395.09189, found: 395.09170.

IR (Reflection): $\tilde{\nu}$ = 3284, 3089, 2932, 2129, 1741, 1681, 1591, 1477, 1456, 1400, 1357, 1316, 1222, 1142, 1088, 1067, 1014, 925, 833, 754, 688.

M.p. (amorphous) 86.9-88.8 °C.

Methyl (*S*)-2-acetamido-3-(4-ethynylphenyl)propanoate (2ai)



Step 1: To a suspension of *L*-Tyrosinmethylester-hydrochlorid (926.7 mg, 4 mmol) in 15 mL DCM was added Et_3N (0.59 mL, 4.2 mmol) at 0 °C and the reaction was stirred at this temperature for 10 min. Then Ac_2O (0.4 mL, 4.2 mmol) was added and the mixture was warmed up to room temperature and stirred overnight. The mixture was filtered and concentrated in vacuo. The residual mixture was purified by silica gel chromatography with PE/EA (1:1) as eluting solvent to afford methyl acetyl-*L*-Tyrosinate **2ai-1** as colorless solid (950 mg, 100%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 6.94 (d, *J* = 8.5 Hz, 2H), 6.73 (d, *J* = 8.5 Hz, 2H), 6.11 (br, 1H), 5.97 (d, *J* = 8.0 Hz, 1H), 4.87 (dt, *J* = 8.0, 5.9 Hz, 1H), 3.74 (s, 3H), 3.04 (ddd, *J* = 31.9, 14.0, 5.8 Hz, 2H), 1.99 (s, 3H).

Step 2: To a solvent of acetyl-*L*-Tyrosinate **2ai-1** (950 mg, 4 mmol) and pyridine (0.97 mL, 12 mmol) in 16 mL dry DCM was added dropwise trifluoromethanesulfonic anhydride (Tf_2O) (0.81 mL, 4.8 mmol) at 0 °C. The reaction was warmed up to room temperature and stirred for 1 h. After completion of the reaction, the mixture was washed with 15 mL sat. brine, and the aqueous phase was extracted three times with 15 mL ethyl acetate, the organic phases were combined, dried over Na_2SO_4, filtered and concentrated in vacuo. The residual mixture was purified by silica gel chromatography with DCM/MeOH (10:1) as eluting solvent to afford the methyl

(*S*)-2-acetamido-3-(4-(((trifluoromethyl)sulfonyl)oxy)phenyl)propanoate **2ai-2** as colorless solid (1.29 g, 87%).

^{1}H NMR (300MHz, $CDCl_3$) δ 7.23 – 7.06 (m, 4H), 5.95 (d, *J* = 7.4 Hz, 1H), 4.89 (dt, *J* = 7.5, 5.9 Hz, 1H), 3.72 (s, 3H), 3.16 (qd, *J* = 14.0, 5.9 Hz, 2H), 2.00 (s, 3H).

Step 3: To a suspension of $(Ph_3P)_2PdCl_2$ (84 mg, 0.12 mmol) in 7 mL DMF/Et_3N (5:2) were added compound **2ai-2** (738.6 mg, 2 mmol) and Et_3N (0.34 mL, 2.4 mmol). Evacuate the resulting solution and flush with N_2 several times. The mixture allowed to stir at 50 °C overnight. After completion of the reaction, the resulting solution was cooled to room temperature, then the solution was filtered, concentrated in vacuo. The residual mixture was purified by silica gel chromatography with PE/EA (1:1) as eluting solvent to afford methyl (*S*)-2-acetamido-3-(4-((trimethylsilyl)ethynyl)phenyl)propanoate **2ai-3** as dark yellow oil (516.9 mg, 81%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.39 (d, *J* = 8.3, 2H), 7.02 (d, *J* = 8.2, 2H), 5.87 (d, *J* = 7.6, 1H), 4.87 (dt, *J* = 7.7, 5.8, 1H), 3.71 (s, 3H), 3.21 – 3.03 (m, 2H), 1.98 (s, 3H), 0.24 (s, 9H).

Step 4: To a solvent of compound **2ai-3** (450 mg, 1.42 mmol) in 20 mL DCM/MeOH (1:1) was added K_2CO_3 (587 mg, 4.2 mmol). The mixture was stirred at room temperature. After completion of the reaction, the solution was filtered and concentrated in vacuo. The residual mixture was purified by silica gel chromatography with PE/EA (1:1) to afford methyl (*S*)-2-acetamido-3-(4-ethynylphenyl)propanoate **2ai** as dark yellow oil (235.2 mg, 68%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.41 (d, *J* = 8.1 Hz, 2H), 7.05 (d, *J* = 8.1 Hz, 2H), 5.96 (d, *J* = 6.8 Hz, 1H), 4.87 (dd, *J* = 13.5, 5.8 Hz, 1H), 3.71 (s, 3H), 3.21 – 3.02 (m, 3H), 1.98 (s, 3H).

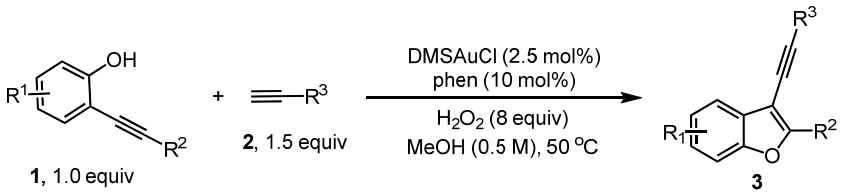
^{13}C NMR (75 MHz, $CDCl_3$) δ 171.9, 169.6, 136.8, 132.3, 129.2, 120.9, 83.2, 77.4, 52.9, 52.4, 37.7, 23.1.

HRMS (EI) calcd for $C_{14}H_{15}NO_3$ $[M]^+$: 245.10464, found: 245.10497.

IR (Reflection): ṽ = 3282, 3065, 3001, 2953, 2848, 2107, 1917, 1744, 1655, 1540, 1508, 1436, 1373, 1273, 1217, 1130, 1019, 844, 826, 666.

2.3 General Procedure for the Gold-Catalyzed Alkynylative Cyclization

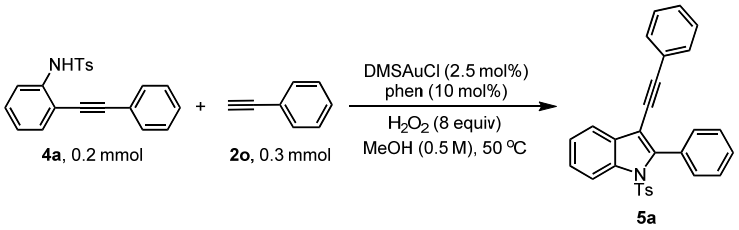
2.3.1 General Procedure for the Synthesis of 3-Alkynylbenzofurans



A 4-mL vial equipped with a magnetic stir bar was charged with DMSAuCl (1.5 mg, 2.5 mol%), phen (3.6 mg, 10 mol%), 2-(alkynyl)phenol **1** (0.2 mmol, if as solid), terminal alkynes **2** (0.3 mmol, 1.5 equiv, if as solid) in MeOH (0.4 mL), then 2-(alkynyl)phenol **1** (0.2 mmol, if as oil), terminal alkynes **2** (0.3 mmol, 1.5 equiv, if as oil) and H_2O_2 (89.6 μL, 1.6 mmol, 50 wt% in water) were added. The mixture was stirred at 50 °C. After completion of the reaction (monitored by TLC), the resulting solution was cooled to room temperature. 2.0 mL DCM was added, the solution was dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. The residual mixture was purified by column chromatography on silica gel, to afford the crude products.

2.3.2 General Procedure for the Synthesis of Other Alkynylative Cyclization Products.

2-Phenyl-3-(phenylethynyl)-1-tosyl-*1H*-indole (5a)



A solution of the 4-methyl-*N*-(2-(phenylethynyl)phenyl)benzenesulfonamide **4a** (69.5 mg, 0.2 mmol), ethynylbenzene **2o** (32.9 µL, 0.3 mmol, 1.5 equiv), DMSAuCl (1.5 mg, 2.5 mol%), phen (3.6 mg, 10 mol%) and H_2O_2 (89.6 µL, 1.6 mmol, 50 wt% in water) in MeOH (0.4 mL) was stirred at 50 °C. After completion of the reaction, the solvent was removed under reduced pressure by an aspirator, the residual mixture was purified by silica gel chromatography with PE/EA (5:1) as eluting solvent to afford 2-phenyl-3-(phenylethynyl)-1-tosyl-*1H*-indole **5a** as colorless solid (84.4 mg, 94%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.37 (d, *J* = 8.1 Hz, 1H), 7.75 – 7.63 (m, 3H), 7.56 – 7.49 (m, 3H), 7.49 – 7.35 (m, 4H), 7.31 (dd, *J* = 7.2, 4.0 Hz, 5H), 7.06 (d, *J* = 8.2 Hz, 2H), 2.29 (s, 3H).

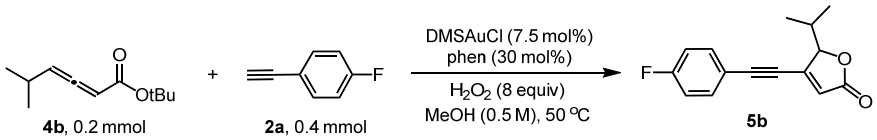
^{13}C NMR (75 MHz, $CDCl_3$) δ 144.9 143.5, 137.1, 134.4, 131.4, 131.2, 130.7, 130.7, 129.3, 129.1, 128.3, 127.2, 126.8, 125.7, 124.7, 123.0, 120.1, 116.6, 108.2, 94.7, 81.4, 21.5.

HRMS (EI) calcd for $C_{29}H_{21}NO_2S$ $[M]^+$: 447.12875, found: 447.12725.

IR (Reflection): ṽ = 3063, 2924, 2853, 2249, 2205, 1733, 1597, 1493, 1474, 1450, 1374, 1305, 1253, 1213, 1188, 1178, 1122, 1091, 1071, 1026, 957, 912, 838, 812, 756, 733, 695, 665.

M.p. (amorphous) 59.7-63.9 °C.

4-((4-Fluorophenyl)ethynyl)-5-isopropylfuran-2(*5H*)-one (5b)



A solution of the *tert*-butyl 5-methylhexa-2,3-dienoate **4b** (36.5 mg, 0.2 mmol), 1-ethynyl-4-fluorobenzene **2a** (46 µL, 0.4 mmol, 2 equiv), DMSAuCl (4.4 mg, 7.5 mol%), phen (10.8 mg, 30 mol%) and H_2O_2 (89.6 µL, 1.6 mmol, 50 wt% in water) in MeOH (0.4 mL) was stirred at 50 °C. After completion of the reaction, the solvent was removed under reduced pressure by an aspirator, the residual mixture was purified by silica gel chromatography with PE/DCM (1:1) as eluting solvent to afford 4-((4-fluorophenyl)ethynyl)-5-isopropylfuran-2(*5H*)-one **5b** as colorless solid (37.8 mg, 77%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.58 – 7.44 (m, 2H), 7.16 – 7.04 (m, 2H), 6.23 (d, *J* = 1.7 Hz, 1H), 4.94 (dd, *J* = 2.9, 1.8 Hz, 1H), 2.30 (dtd, *J* = 13.8, 6.9, 3.0 Hz, 1H), 1.17 (d, *J* = 7.0 Hz, 3H), 0.89 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 172.7, 163.6 (d, *J* = 253.2 Hz), 149.6, 134.2 (d, *J* = 8.8 Hz), 122.9, 117.1 (d, *J* = 3.6 Hz), 116.1 (d, *J* = 22.3 Hz), 104.6, 88.2, 79.7 (d, *J* = 1.4 Hz), 30.8, 19.0, 14.7.

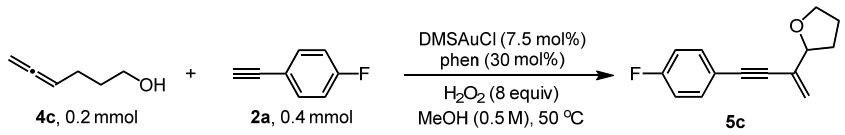
^{19}F NMR (282 MHz, $CDCl_3$) δ -107.11.

HRMS (EI) calcd for $C_{15}H_{13}O_2F$ $[M]^+$: 244.08941, found: 244.08897.

IR (ATR): ṽ = 3105, 2965, 2930, 2203, 1786, 1742, 1610, 1587, 1504, 1461, 1370, 1353, 1319, 1296, 1274, 1255, 1228, 1218, 1164, 1154, 1092, 1024, 973, 911, 893, 876, 834, 820, 746, 730, 707.

M.p. (amorphous) 87.2-89.1 °C.

2-(4-(4-Fluorophenyl)but-1-en-3-yn-2-yl)tetrahydrofuran (5c)



A solution of the hexa-4,5-dien-1-ol **4c** (19.7 mg, 0.2 mmol), 1-ethynyl-4-fluorobenzene **2a** (46 μL, 0.4 mmol, 2 equiv), DMSAuCl (4.4 mg, 7.5 mol%), phen (10.8 mg, 30 mol%) and H_2O_2 (89.6 μL, 1.6 mmol, 50 wt% in water) in MeOH (0.4 mL) was stirred at 50 °C. After completion of the reaction, products were monitored by TLC. The solvent was removed under reduced pressure by an aspirator, the residual mixture was purified by silica gel chromatography with PE/DCM (1:1) as eluting solvent to afford 2-(4-(4-fluorophenyl)but-1-en-3-yn-2-yl)tetrahydrofuran **5c** as colorless oil (20.4 mg, 47%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.46 – 7.36 (m, 2H), 7.09 – 6.87 (m, 2H), 5.58 (t, *J* = 1.5 Hz, 1H), 5.51 (s, 1H), 4.48 (dd, *J* = 6.8, 5.8 Hz, 1H), 4.06 – 3.96 (m, 1H), 3.92 – 3.83 (m, 1H), 2.23 – 2.09 (m, 1H), 2.08 – 1.85 (m, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 162.5 (d, *J* = 249.6 Hz), 133.5 (d, *J* = 8.3 Hz), 133.1, 120.7, 119.2 (d, *J* = 3.5 Hz), 115.6 (d, *J* = 22.1 Hz), 89.4, 87.1 (d, *J* = 1.4 Hz), 80.6, 68.9, 31.5, 25.6.

^{19}F NMR (282 MHz, $CDCl_3$) δ -110.88.

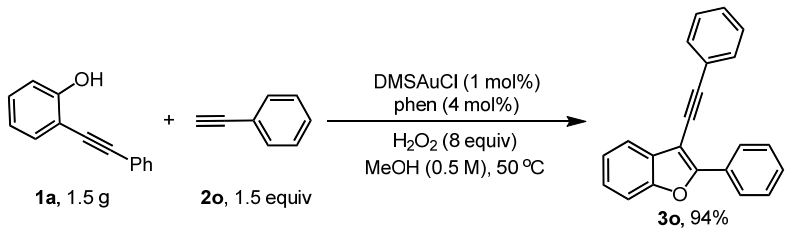
HRMS (EI) calcd for $C_{14}H_{13}OF$ $[M]^+$: 216.09449, found: 216.09326.

IR (Reflection): $\tilde{\nu}$ = 3436, 3073, 2955, 2927, 2875, 2204, 1729, 1674, 1600, 1508, 1460, 1411, 1233, 1157, 1070, 930, 838.

2.4 Comprehensive Application

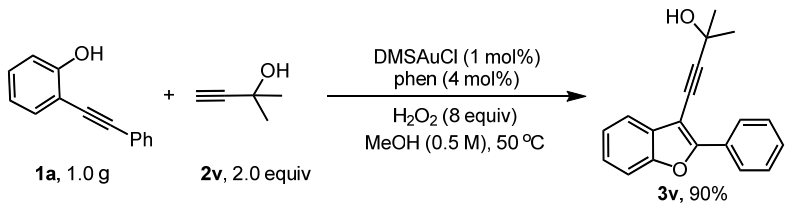
2.4.1 General Procedure for Gram Scale Synthesis

A. Gram scale synthesis of 2-phenyl-3-(phenylethynyl)benzofuran (3o)



A round-bottomed of 50 mL equipped with a magnetic stir bar was charged with DMSAuCl (22.7 mg, 1 mol%), phen (55.4 mg, 4 mol%), 2-(phenylethynyl)phenol **1a** (1.5 g, 7.7 mmol) in MeOH (15 mL), then ethynylbenzene **2o** (1.27 mL, 11.55 mmol, 1.5 equiv) and H_2O_2 (3.45 mL, 61.6 mmol, 50 wt% in water) were added. The mixture was stirred at 50 °C for 16 h. After completion of the reaction, the solvent was removed under reduced pressure, then diluted with 5 mL ethyl acetate. The residual aqueous phase was extracted three times with 5 mL ethyl acetate, the organic phases were combined, dried over Na_2SO_4, filtered and concentrated in vacuo. The residual mixture was purified by silica gel chromatography with petroleum ether as eluting solvent to afford 2-phenyl-3-(phenylethynyl)benzofuran **3o** as light yellow solid (2.13 g, 94%).

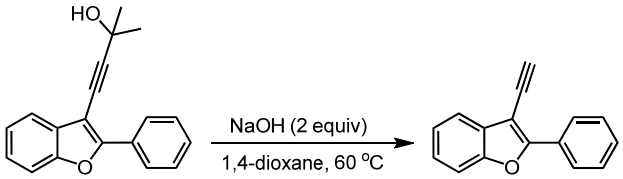
B. Gram scale synthesis of 2-methyl-4-(2-phenylbenzofuran-3-yl)but-3-yn-2-ol (3v)



1a, 1.0 g **2v**, 2.0 equiv **3v**, 90%

A round-bottomed of 25 mL equipped with a magnetic stir bar was charged with DMSAuCl (15.2 mg, 1 mol%), phen (37.1 mg, 4 mol%), 2-(phenylethynyl)phenol **1a** (1.0 g, 5.15 mmol) in MeOH (10 mL), then 2-methylbut-3-yn-2-ol **2v** (0.75 mL, 7.72 mmol, 1.5 equiv) and H_2O_2 (2.3 mL, 41.2 mmol, 50 wt% in water) were added. The mixture was stirred at 50 °C. After 12 h, 2-(phenylethynyl)phenol **1a** was not complected (monitored by TLC), 2-methylbut-3-yn-2-ol **2v** (0.25 mL, 2.57 mmol, 0.5 equiv) was added, then the mixture was stirred at 50 °C for an additional 12 h. After completion of the reaction, the solvent was removed under reduced pressure, then diluted with 5 mL ethyl acetate. And the residual aqueous phase was extracted three times with 5 mL ethyl acetate, the organic phases were combined, dried over Na_2SO_4, filtered and concentrated in vacuo. The residual mixture was purified by silica gel chromatography with PE:DCM (1:1) as eluting solvent to afford 2-methyl-4-(2-phenylbenzofuran-3-yl)but-3-yn-2-ol **3v** as light yellow solid (1.28 g, 90%).

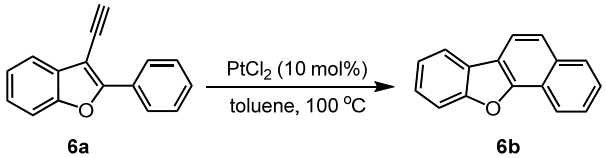
2.4.2 Post-functionalization of Ethynylbenzofuran



3v **6a**

3-Ethynyl-2-phenylbenzofuran (6a)

In a 50-mL flask, 2-methyl-4-(2-phenylbenzofuran-3-yl)but-3-yn-2-ol **3v** (552 mg, 2 mmol) was added to a solution of well-ground anhydrous NaOH (160 mg, 4 mmol, 2 equiv) in 1,4-dioxane (20 mL) at room temperature. Evacuate the resulting solution and flush with N_2 several times. The mixture allowed to stir at 60 °C overnight. After completion of the reaction, the resulting solution was cooled to room temperature. Then 20 mL saturated NH_4Cl was added, and the aqueous phase was extracted three times with 20 mL ethyl acetate, the organic phases were combined, dried over Na_2SO_4, filtered, concentrated in vacuo. The residue was purified by silica gel chromatography with PE as eluting solvent to afford 3-ethynyl-2-phenylbenzofuran **6a** as dark yellow oil (432 mg, 99 %). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.46 – 8.23 (m, 2H), 7.77 – 7.66 (m, 1H), 7.55 – 7.49 (m, 3H), 7.46 – 7.40 (m, 1H), 7.40 – 7.29 (m, 2H), 3.63 (s, 1H). Characterization data of **6a** corresponded to the literature values.[22]

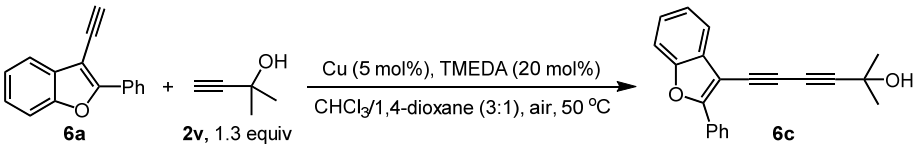


6a **6b**

Naphtho[1,2-*b*]benzofuran (6b)

A solution of the 3-ethynyl-2-phenylbenzofuran **6a** (43.6 mg, 0.2 mmol) and $PtCl_2$ (5.3 mg, 10 mol%) in toluene (1.5 mL) was stirred at 100 °C overnight. After completion of the reaction, the solvent was removed under reduced pressure by an aspirator, the residual mixture was purified by

silica gel chromatography with PE as eluting solvent to afford naphtho[1,2-*b*]benzofuran **6b** as colorless solid (34.1 mg, 78%). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.47 (d, *J* = 8.2 Hz, 1H), 8.09 – 7.97 (m, 3H), 7.79 (d, *J* = 8.5 Hz, 1H), 7.73 (d, *J* = 8.1 Hz, 1H), 7.70 – 7.62 (m, 1H), 7.58 (ddd, *J* = 8.2, 7.0, 1.3 Hz, 1H), 7.53 – 7.45 (m, 1H), 7.41 (td, *J* = 7.5, 1.0 Hz, 1H). Characterization data of **6b** corresponded to the literature values.[22]



6a **2v**, 1.3 equiv **6c**

2-Methyl-6-(2-phenylbenzofuran-3-yl)hexa-3,5-diyn-2-ol (6c)

A solution of the 3-ethynyl-2-phenylbenzofuran **6a** (43.6 mg, 0.2 mmol), 2-methylbut-3-yn-2-ol **2v** (25.3 μL, 0.26 mmol), copper powder (0.6 mg, 5 mol%), TMEDA (5.9 μL, 20 mol%) in 0.4 mL $CHCl_3$/1,4-dioxane (3:1) was stirred at 50 °C overnight. After completion of the reaction, the resulting solution was cooled to room temperature. The solvent was removed under reduced pressure by an aspirator, then the residual mixture was purified by silica gel chromatography with PE/DCM (1:1) as eluting solvent to afford 2-methyl-6-(2-phenylbenzofuran-3-yl)hexa-3,5-diyn-2-ol **6c** as colorless solid (35.3 mg, 59%).

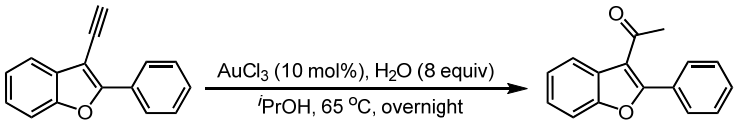
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.27 – 8.22 (m, 2H), 7.73 – 7.63 (m, 1H), 7.56 – 7.47 (m, 3H), 7.46 – 7.40 (m, 1H), 7.39 – 7.27 (m, 2H), 2.18 (br, 1H), 1.65 (s, 6H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 159.0, 153.3, 129.9, 129.7, 129.6, 128.8, 125.9, 125.6, 123.6, 120.3, 111.3, 97.7, 88.3, 80.4, 70.7, 67.4, 65.9, 31.1.

HRMS (EI) calcd for $C_{21}H_{16}O_2$ $[M]^+$: 300.11448, found: 300.11359.

IR (Reflection): $\tilde{\nu}$ = 3061, 2151, 1957, 1888, 1737, 1593, 1559, 1497, 1455, 1443, 1400, 1337, 1293, 1272, 1257, 1202, 1180, 1151, 1100, 1069, 1028, 962, 897, 847, 827, 771, 744, 685, 644, 624.

M.p. (amorphous) 128.9-130.2 °C.



6a **6d**

1-(2-Phenylbenzofuran-3-yl)ethan-1-one (6d)

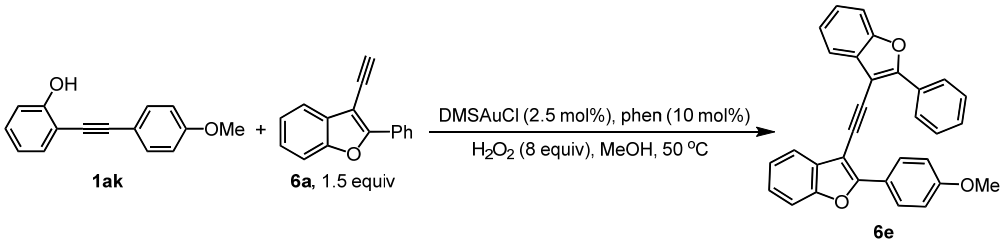
A solution of the 3-ethynyl-2-phenylbenzofuran **6a** (21.8 mg, 0.1 mmol), $AuCl_3$ (3.0 mg, 10 mol%) and H_2O (14.4 μL, 8 equiv) in ^{i}PrOH (0.5 mL) was stirred at 65 °C overnight. After completion of the reaction, the solvent was removed under reduced pressure by an aspirator. The residual mixture was purified by silica gel chromatography with PE as eluting solvent to afford 1-(2-phenylbenzofuran-3-yl)ethan-1-one **6d** as light yellow oil (23.6 mg, 100%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 – 8.09 (m, 1H), 7.81 – 7.72 (m, 2H), 7.56 – 7.48 (m, 4H), 7.42 – 7.32 (m, 2H), 2.39 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 195.4, 160.3, 153.9, 130.5, 130.2, 129.7, 128.6, 126.8, 125.4, 124.2, 122.4, 118.4, 111.1, 30.5.

HRMS (EI) calcd for $C_{16}H_{12}O_2$ $[M]^+$: 236.08318, found: 236.08278.

IR (Reflection): $\tilde{\nu}$ = 3059, 2925, 1904, 1736, 1664, 1607, 1561, 1490, 1475, 1451, 1381, 1287, 1255, 1202, 1185, 1110, 1089, 1072, 1025, 956, 893, 825, 772, 750, 700, 665, 631.



1ak **6a**, 1.5 equiv **6e**

2-(4-Methoxyphenyl)-3-((2-phenylbenzofuran-3-yl)ethynyl)benzofuran (6e)

A 4-mL vial equipped with a magnetic stir bar was charged with DMSAuCl (0.7 mg, 2.5 mol%), phen (1.8 mg, 10 mol%) and 2-((4-methoxyphenyl)ethynyl)phenol **1ak** (22.4 mg, 0.1 mmol) in MeOH (0.2 mL), then 3-ethynyl-2-phenylbenzofuran **6a** (32.7 mg, 0.15 mmol, 1.5 equiv) and H_2O_2 (44.8 μL, 0.8 mmol, 50 wt% in water) were added. The mixture was stirred at 50 °C. After completion of the reaction, the resulting solution was cooled to room temperature. 1 mL DCM was added, the solution was dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. The residual mixture was purified by flash column chromatography on silica gel with PE/DCM (5:1) as eluting solvent to afford 2-(4-methoxyphenyl)-3-((2-phenylbenzofuran-3-yl)ethynyl)benzofuran **6e** as yellow solid (34.8 mg, 79%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (dd, *J* = 5.3, 3.3 Hz, 2H), 8.41 – 8.36 (m, 2H), 7.87 – 7.78 (m, 2H), 7.58 – 7.49 (m, 4H), 7.44 (dt, *J* = 4.5, 1.8 Hz, 1H), 7.42 – 7.34 (m, 4H), 7.05 – 6.97 (m, 2H), 3.88 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 160.5, 156.6, 156.1, 153.6, 153.4, 130.2, 130.1, 130.0, 129.3, 128.7, 127.7, 126.0, 125.5, 125.0, 123.6, 123.5, 123.0, 120.2, 119.9, 114.2, 111.3, 111.1, 99.6, 97.7, 89.0, 88.1, 55.4.

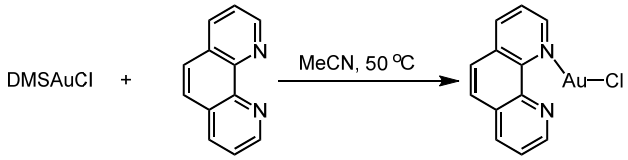
HRMS (EI) calcd for $C_{31}H_{20}O_3$ $[M]^+$: 440.14070, found: 440.14065.

IR (ATR): ṽ = 3056, 2925, 2837, 2184, 1733, 1606, 1509, 1454, 1422, 1302, 1249, 1202, 1176, 1104, 1068, 1029, 897, 828, 785, 740, 686, 607.

M.p. (amorphous) 125.9-127.6 °C.

2.5 Mechanistic Study

A. The general synthesis of (1,10-phenanthroline-N^1,N^{10})-gold(I) chloride (9a)



A round-bottomed of 25 mL equipped with a magnetic stir bar was charged with DMSAuCl (147.2 mg, 0.5 mmol), 1,10-phenanthroline (90 mg, 0.5 mmol) and MeCN (10 mL), the mixture was stirred at 50 °C under nitrogen. After 1 h, the solvent was removed under reduced pressure, and washed sequentially with MeCN (10 mL), to obtain the product **9a** as colorless solid (167 mg, 81%).

^{1}H NMR (400 MHz, DMSO) δ 9.29 (dd, *J* = 4.8, 1.5 Hz, 2H), 9.02 (dd, *J* = 8.2, 1.5 Hz, 2H), 8.33 (s, 2H), 8.18 (dd, *J* = 8.2, 4.8 Hz, 2H).

^{13}C NMR (101 MHz, DMSO) δ 147.9, 141.2, 138.5, 129.4, 127.4, 125.4.

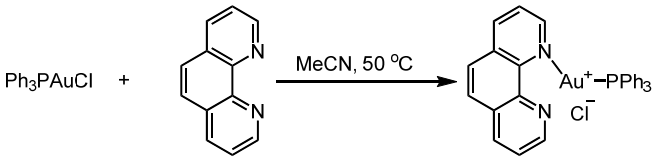
HRMS (ESI) calcd for $C_{12}H_8AuN_2$ $[M]^+$: 377.0348, found: 377.0355.

IR (ATR): ṽ = 3110, 3055, 1981, 1931, 1807, 1616, 1596, 1546, 1504, 1475, 1455, 1419, 1378, 1337, 1318, 1289, 1249, 1218, 1192, 1153, 1136, 1096, 1036, 992, 935, 884, 842, 772, 734, 716,

619.

M.p. (amorphous) 211.5-213.8 °C.

B. The general synthesis of (1,10-phenanthroline-N^1,N^{10})(triphenylphosphine)-gold(I) (9b)



A round-bottomed of 25 mL equipped with a magnetic stir bar was charged with Ph_3PAuCl (247.2 mg, 0.5 mmol), 1,10-phenanthroline (90 mg, 0.5 mmol) and MeCN (10 mL), the mixture was stirred at 50 °C under nitrogen. After 1 h, the solvent was removed under reduced pressure by an aspirator, without purification to give the product **9b** as dark solid (337 mg, 99%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 9.20 (dd, *J* = 4.3, 1.7 Hz, 2H), 8.27 (dd, *J* = 8.1, 1.7 Hz, 2H), 7.81 (s, 2H), 7.65 (dd, *J* = 8.1, 4.4 Hz, 2H), 7.59 – 7.38 (m, 15H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 150.2, 146.0, 136.1, 134.1 (d, *J* = 13.7 Hz), 132.0 (d, *J* = 2.6 Hz), 129.2 (d, *J* = 11.9 Hz), 129.1, 128.4 (d, *J* = 28.4 Hz), 126.5, 123.1.

^{31}P NMR (122 MHz, $CDCl_3$) δ 33.17.

HRMS (ESI) calcd for $C_{30}H_{23}AuN_2P$ $[M]^+$: 639.1264, found: 639.1284.

IR (ATR): $\tilde{\nu}$ = 3374, 3059, 2685, 2202, 1651, 1587, 1561, 1505, 1479, 1434, 1312, 1179, 1102, 1027, 999, 853, 740, 712, 691, 624.

M.p. (amorphous) 119.7-121.6 °C.

C. Exploring the possibility of H_2O_2 oxidation of Au^I

As shown in Figure S1, the chemical shift of Ph_3P, Ph_3PO and Ph_3PAuCl was performed (entries a-c), no changes of the chemical shift were observed by ^{31}P NMR (entry d). Even after stirring the reaction mixture at 50 °C for 12 h, Ph_3PO was undetectable. However traces of $[(Ph_3P)_2Au]^+$ were formed, (^{31}P NMR: δ 43.7 ppm, *m/z*: 721.1501) and a gold mirror was observed (entry e). Ph_3PO was detected by ^{31}P NMR from a mixture of Ph_3PAuCl, phen and H_2O_2 which was stirred at 50 °C for 2 h. It is worth mentioning that a large amount of gold mirror was observed after a reaction time of 12 h, which indicates that the Au^{III} complex may not be stable in H_2O_2 solution. Furthermore, Ph_3PO was also detectable by ^{31}P NMR from a mixture of $[PhenAu^+PPh_3]Cl^-$ (**9b**) and H_2O_2 which was stirred at 50 °C for 3 h (entry g). This indicates that $[PhenAu^+PPh_3]Cl^-$ (**9b**) is stable and at this stage, Ph_3P is unlikely to dissociate from the metal center of Au^I. In contrast, the dissociated Ph_3P was rapidly oxidized in the presence of H_2O_2 after dissociation from the metal center Au^{III}, which confirms that phen can effectively promote the oxidation of Au^I to Au^{III}.

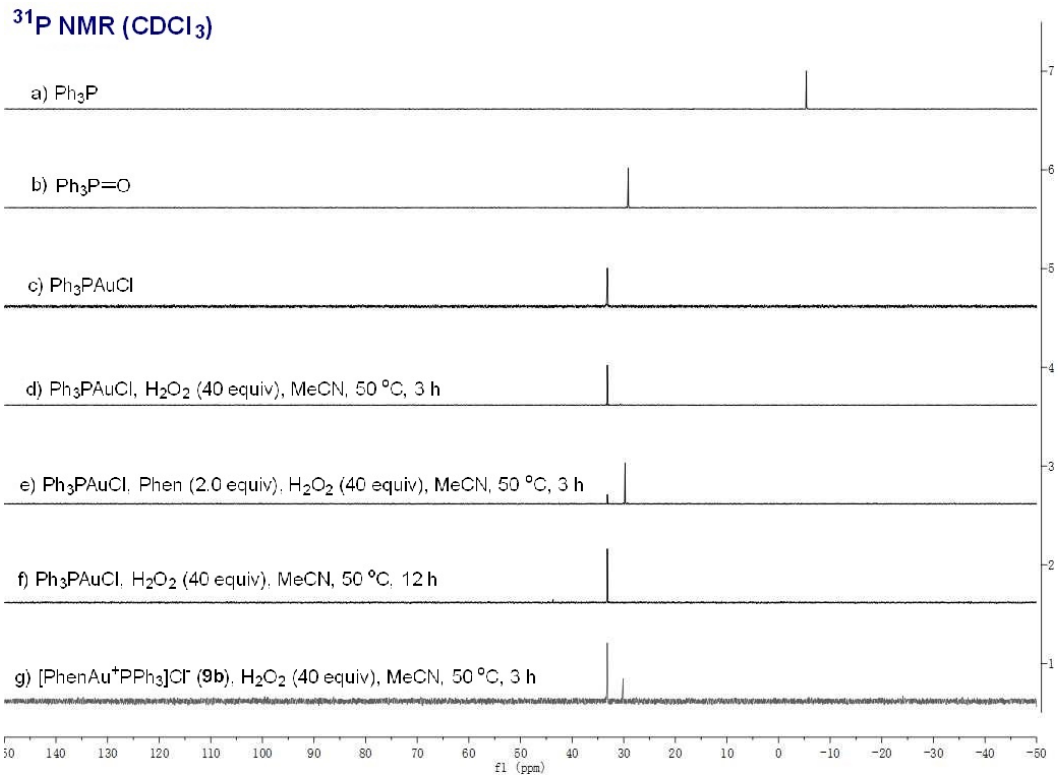
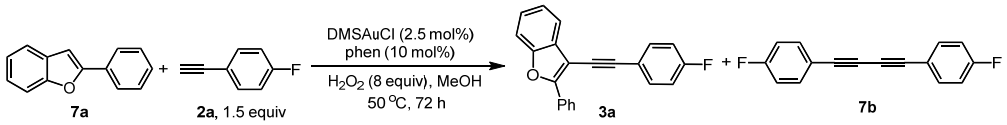


Figure S1. Exploring the possibility of H_2O_2 oxidation of Au^I using ^{31}P NMR (122 MHz, $CDCl_3$) spectroscopy.

D. The experiment of gold-catalyzed cascade cyclization-alkynylation



A 4-mL vial equipped with a magnetic stir bar was charged with DMSAuCl (0.7 mg, 2.5 mol%), phen (1.8 mg, 10 mol%), 2-phenylbenzofuran **7a** (19.4 mg, 0.1 mmol) in MeOH (0.2 mL), then 1-ethynyl-4-fluorobenzene **2a** (16.6 μL, 0.15 mmol) and H_2O_2 (44.8 μL, 1.6 mmol, 50 wt% in water) were added. The mixture was stirred at 50 °C for 72 h, then the solvent was removed under reduced pressure. 0.5 mL $CDCl_3$ was added and removed the mixture into a NMR tube. As shown in Figure S2, no alkynyl cyclization product **3a** (-110.53 ppm, ^{19}F NMR) was observed. Then recovery of the mixture, the residual mixture was purified by flash column chromatography on silica gel with PE as eluting solvent to afford homocoupling product **7b** as light yellow solid (32.8 mg, 92%). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.71 – 7.38 (m, 4H), 7.10 – 6.91 (m, 4H); **^{19}F NMR** (282 MHz, $CDCl_3$) δ -108.49. Characterization data of **7b** corresponded to the literature values.[23]

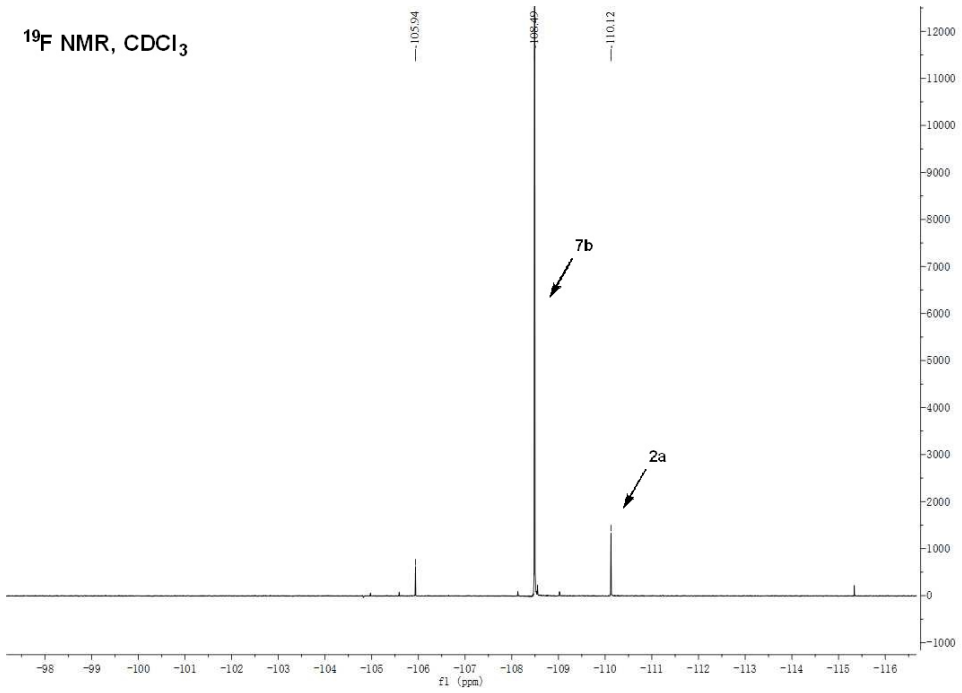
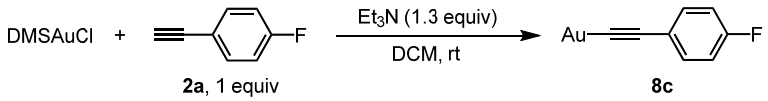


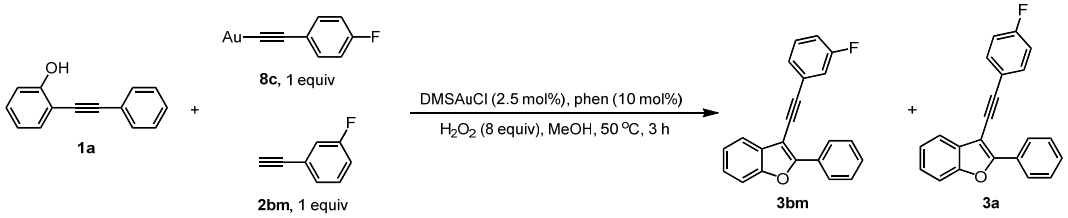
Figure S2. ^{19}F NMR (282 MHz, $CDCl_3$) spectra of gold-catalyzed cascade cyclization-alkynylation.

E. The General synthesis of ((4-fluorophenyl)ethynyl)gold (8c)



((4-Fluorophenyl)ethynyl)gold **8c** was prepared according to a published procedure.[24] A round-bottomed of 50 mL equipped with a magnetic stir bar was charged with DMSAuCl (147 mg, 0.5 mmol) in 15 mL DCM, 1-ethynyl-4-fluorobenzene **2a** (57.2 µL, 0.5 mmol, 1 equiv) was added. While stirring, Et_3N (90 µL, 0.65 mmol, 1.3 equiv) was added. The mixture was stirred at room temperature in the dark. After 12 h, the solvent was removed under reduced pressure, the precipitate was filtered, washed with DCM and dried under vacuum to obtain the product **8c** as yellow solid (121 mg, 77%). **Note:** the gold complex **8c** is insoluble in solvents such as DCM, acetone, MeCN, EtOH, MeOH, THF, Et_2O, water and DMSO. The IR data was in agreement with literature values.[24] **IR** (ATR): $\tilde{\nu}$ = 2963, 2008, 1651, 1596, 1501, 1260, 1226, 1095, 835, 800, 740.

F. The stoichiometric reaction of gold(I)-acetylide (8c) with 2-(phenylethynyl)phenol (1a) and 1-ethynyl-3-fluorobenzene (2bm)



A 4-mL vial equipped with a magnetic stir bar was charged with DMSAuCl (0.7 mg, 2.5 mol%), phen (1.8 mg, 10 mol%), 2-(phenylethynyl)phenol **1a** (19.4 mg, 0.1 mmol), ((4-fluorophenyl)ethynyl)gold **8c** (31.6 mg, 0.1 mmol, 1 equiv) in MeOH (0.2 mL), then 3-ethynyl-4-fluorobenzene **2bm** (11.6 µL, 0.1 mmol, 1 equiv) and H_2O_2 (44.8 µL, 1.6 mmol, 50

wt% in water, 8 equiv) were added. The mixture was stirred at 50 °C for 3 h, then the solvent was removed under reduced pressure. The yields of 3-((3-fluorophenyl)ethynyl)-2-phenylbenzofuran **3bm** (78%) and 3-((4-fluorophenyl)ethynyl)-2-phenylbenzofuran **3a** (6%) were determined by comparing the integration of the ^{19}F NMR resonance of products **3am** (-112.62 ppm) and **3a** (-110.53 ppm) with that of trifluorotoluene (-62.75 ppm).

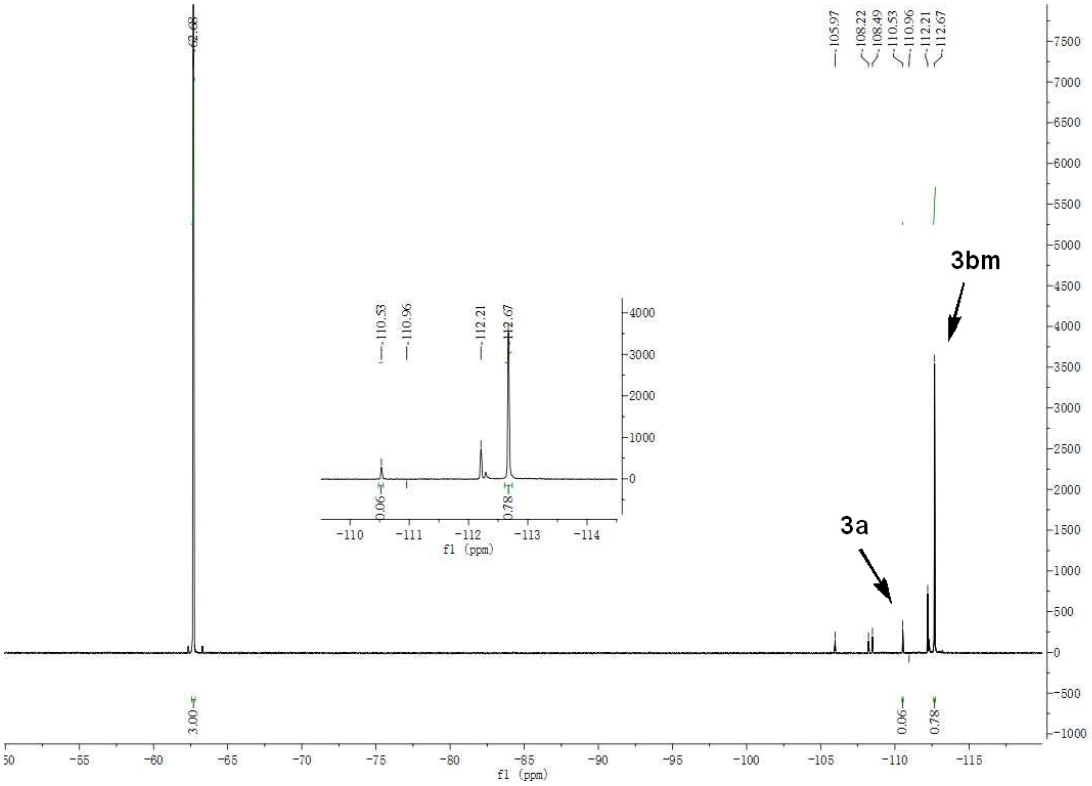
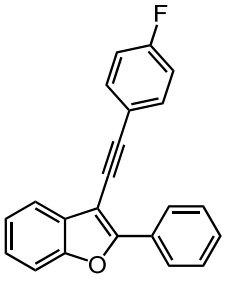


Figure S3. ^{19}F NMR (282 MHz, $CDCl_3$) spectra of the stoichiometric reaction of gold(I)-acetylide (**8c**) with 2-(phenylethynyl)phenol (**1a**) and 1-ethynyl-3-fluorobenzene (**2bm**)

3. Characterization of Products



3-((4-Fluorophenyl)ethynyl)-2-phenylbenzofuran

3a, light yellow solid, 62.2 mg, 99% yield.

R_f = 0.4 (*n*-Hexane), chromatography eluent: *n*-Hexane.

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.37 – 8.29 (m, 2H), 7.74 (dd, *J* = 6.4, 2.3 Hz, 1H), 7.66 – 7.56 (m, 2H), 7.56 – 7.48 (m, 3H), 7.46 – 7.39 (m, 1H), 7.35 (tt, *J* = 7.3, 5.8 Hz, 2H), 7.16 – 7.06 (m, 2H).

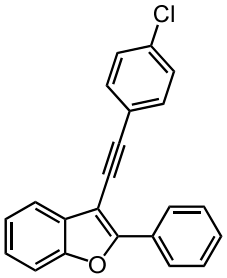
^{13}C NMR (75 MHz, $CDCl_3$) δ 162.6(d, *J* = 250.0 Hz), 156.4, 153.5, 133.4 (d, *J* = 8.4 Hz), 130.1, 129.9, 129.2, 128.7, 126.0, 125.4, 123.4, 120.3, 119.5 (d, *J* = 3.5 Hz), 115.8 (d, *J* = 22.1 Hz), 111.2, 99.0, 95.6, 80.9 (d, *J* = 1.4 Hz).

^{19}F NMR (282 MHz, $CDCl_3$) δ -110.53.

HRMS (EI) calcd for $C_{22}H_{13}OF$ $[M]^+$: 312.09449, found: 312.09432.

IR (ATR): $\tilde{\nu}$ = 3063, 3046, 1891, 1600, 1507, 1492, 1456, 1443, 1293, 1256, 1232, 1201, 1110, 1090, 1027, 832, 767, 742, 682, 624.

M.p. (amorphous) 89.3-91.6 °C.



3-((4-Chlorophenyl)ethynyl)-2-phenylbenzofuran

3b, light yellow solid, 62.8 mg, 96% yield.

R_f = 0.7 (PE:EA = 10:1), chromatography eluent: Petroleum ether.

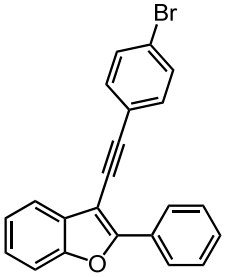
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44 – 8.25 (m, 2H), 7.81 – 7.71 (m, 1H), 7.58 – 7.50 (m, 5H), 7.46 – 7.41 (m, 1H), 7.41 – 7.31 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 156.5, 153.5, 134.4, 132.6, 129.2, 128.8, 128.7, 126.0, 125.4, 123.4, 121.8, 120.3, 111.2, 98.9, 95.6, 82.2.

HRMS (EI) calcd for $C_{22}H_{13}OCl$ $[M]^+$: 328.06494, found: 328.06451.

IR (ATR): $\tilde{\nu}$ = 3049, 2219, 1897, 1732, 1597, 1561, 1486, 1475, 1457, 1444, 1396, 1294, 1258, 1240, 1204, 1114, 1086, 1070, 1027, 1013, 957, 930, 909, 898, 824, 766, 751, 740, 681, 628.

M.p. (amorphous) 112.6-114.5 °C.



3-((4-Bromophenyl)ethynyl)-2-phenylbenzofuran

3c, light yellow solid, 57.1 mg, 77% yield.

R_f = 0.5 (PE:DCM = 20:1), chromatography eluent: 5% Dichloromethane in petroleum ether.

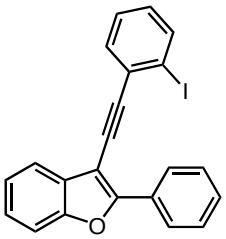
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.39 – 8.26 (m, 2H), 7.78 – 7.70 (m, 1H), 7.58 – 7.41 (m, 8H), 7.41 – 7.30 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 156.5, 153.5, 132.9, 131.7, 130.0, 129.7, 129.3, 128.7, 126.0, 125.4, 123.4, 122.6, 122.3, 120.3, 111.2, 98.9, 95.6, 82.4.

HRMS (EI) calcd for $C_{22}H_{13}OBr$ $[M]^+$: 372.01443, found: 372.01347.

IR (ATR): $\tilde{\nu}$ = 3049, 2216, 1897, 1737, 1595, 1558, 1483, 1474, 1457, 1443, 1391, 1342, 1294, 1258, 1239, 1203, 1113, 1093, 1067, 1027, 1009. 957, 930, 895, 818, 766, 740, 681, 626.

M.p. (amorphous) 125.8-127.1 °C.



3-((2-Iodophenyl)ethynyl)-2-phenylbenzofuran

3d, light yellow solid, 76.8 mg, 91% yield.

R_f = 0.5 (PE:DCM = 20:1), chromatography eluent: 5% Dichloromethane in petroleum ether.

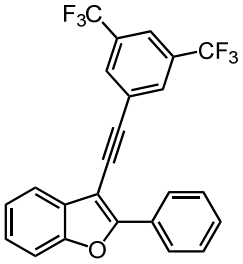
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.45 (d, *J* = 8.1 Hz, 2H), 7.93 (d, *J* = 8.0 Hz, 1H), 7.90 (d, *J* = 7.4 Hz, 1H), 7.64 (d, *J* = 7.7 Hz, 1H), 7.55 (d, *J* = 8.2 Hz, 1H), 7.52 (t, *J* = 7.7 Hz, 2H), 7.43 (t, *J* = 7.3 Hz, 1H), 7.37 (dq, *J* = 14.6, 7.5 Hz, 3H), 7.06 (t, *J* = 7.7 Hz, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 156.6, 153.5, 138.8, 132.8, 130.02, 130.00, 129.9, 129.4, 129.3, 128.7, 127.9, 126.2, 125.4, 123.5, 120.7, 111.2, 100.0, 98.9, 98.5, 85.0.

HRMS (EI) calcd for $C_{22}H_{13}OI$ $[M]^+$: 420.00056, found: 420.00282.

IR (ATR): ṽ = 3058, 2207, 2191, 1551, 1456, 1442, 1426, 1383, 1291, 1254, 1230, 1202, 1121, 1093, 1068, 1016, 930, 897, 829, 769, 744, 705, 682, 643, 626.

M.p. (amorphous) 99.7-102.0 ºC.



3-((3,5-Bis(trifluoromethyl)phenyl)ethynyl)-2-phenylbenzofuran

3e, light yellow solid, 81.9 mg, 95% yield.

R_f = 0.8 (PE:DCM = 10:1), chromatography eluent: 1% Dichloromethane in petroleum ether.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.28 (d, *J* = 7.5 Hz, 2H), 8.01 (s, 2H), 7.87 (s, 1H), 7.73 (d, *J* = 7.4 Hz, 1H), 7.54 (t, *J* = 7.3 Hz, 3H), 7.46 (t, *J* = 7.4 Hz, 1H), 7.41 – 7.34 (m, 2H).

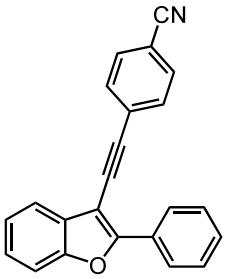
^{13}C NMR (151 MHz, $CDCl_3$) δ 157.6, 153.5, 132.1 (q, *J* = 33.8 Hz), 131.2 (d, *J* = 3.0 Hz), 129.7 (d, *J* = 6.4 Hz), 129.4, 128.8, 126.2, 125.7, 123.9, 123.7, 122.1, 121.6 (dt, *J* = 7.4, 3.6 Hz), 120.2, 97.9, 93.4, 85.0.

^{19}F NMR (282 MHz, $CDCl_3$) δ -63.07.

HRMS (EI) calcd for $C_{24}H_{12}OF_6$ $[M]^+$: 430.07869, found: 430.07935.

IR (ATR): ṽ = 3067, 2212, 1613, 1559, 1458, 1443, 1402, 1358, 1280, 1201, 1172, 1130, 1097, 1071, 1028, 905, 890, 847, 828, 769, 742, 683, 628.

M.p. (amorphous) 137.4-138.6 ºC.



4-((2-Phenylbenzofuran-3-yl)ethynyl)benzonitrile

3f, light yellow solid, 50.3 mg, 79% yield.

R_f = 0.3 (PE:DCM = 2:1), chromatography eluent: 50% Petroleum ether in dichlormethan.

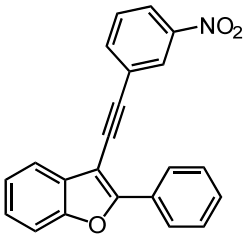
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (dd, *J* = 5.3, 3.3 Hz, 2H), 7.75 – 7.69 (m, 1H), 7.65 (s, 4H), 7.56 – 7.49 (m, 3H), 7.48 – 7.42 (m, 1H), 7.41 – 7.31 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 157.3, 153.5, 132.1, 131.8, 129.8, 129.5, 129.4, 128.7, 128.1, 126.1, 125.6, 123.6, 120.1, 118.4, 111.5, 111.3, 98.3, 95.0, 85.9.

HRMS (EI) calcd for $C_{23}H_{13}NO$ $[M]^+$: 319.09917, found: 319.09856.

IR (ATR): ṽ = 3063, 2223, 2204, 1922, 1782, 1681, 1604, 1583, 1561, 1508, 1489, 1475, 1456, 1444, 1407, 1393, 1342, 1293, 1258, 1241, 1203, 1176, 1114, 1092, 1070, 1026, 1007, 967, 929, 912, 898, 837, 767, 750, 737, 682, 634, 623.

M.p. (amorphous) 166.4-167.2 °C.



3-((3-Nitrophenyl)ethynyl)-2-phenylbenzofuran

3g, yellow solid, 55.4 mg, 82% yield.

R_f = 0.4 (PE:DCM = 2:1), chromatography eluent: 30% Dichloromethane in petroleum ether.

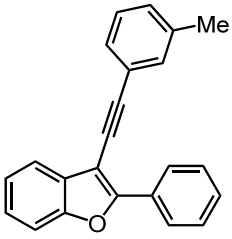
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.47 – 8.40 (m, 1H), 8.35 – 8.27 (m, 2H), 8.26 – 8.17 (m, 1H), 7.89 (d, *J* = 7.7 Hz, 1H), 7.79 – 7.70 (m, 1H), 7.60-7.51 (m, 4H), 7.45 (dd, *J* = 8.4, 6.2 Hz, 1H), 7.42 – 7.30 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 157.2, 153.5, 148.2, 137.0, 129.8, 129.6, 129.50, 129.45, 128.8, 126.1, 125.6, 125.1, 123.6, 122.9, 120.2, 111.3, 98.2, 94.1, 84.0.

HRMS (EI) calcd for $C_{22}H_{13}NO_3$ $[M]^+$: 339.08899, found: 339.08792.

IR (ATR): ṽ = 3083, 2924, 2863, 2214, 1731, 1585, 1524, 1498, 1472, 1455, 1443, 1349, 1302, 1277, 1256, 1235, 1200, 1127, 1111, 1090, 1071, 1028, 999, 910, 896, 827, 811, 802, 766, 739, 700, 673, 655, 626.

M.p. (amorphous) 136.4-137.1 °C.



2-Phenyl-3-(*m*-tolylethynyl)benzofuran

3h, light yellow oil, 59.9 mg, 97% yield.

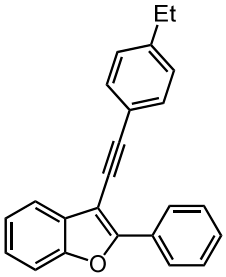
R_f = 0.4 (PE:DCM = 20:1), chromatography eluent: 5% Dichloromethane in petroleum ether.

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.40 (d, *J* = 7.5 Hz, 2H), 7.80 (dd, *J* = 5.9, 3.0 Hz, 1H), 7.59 – 7.43 (m, 6H), 7.43 – 7.29 (m, 3H), 7.23 (d, *J* = 7.5 Hz, 1H), 2.44 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 156.2, 153.5, 138.1, 132.0, 130.2, 129.9, 129.3, 129.1, 128.63, 128.61, 128.35, 126.0, 125.3, 123.3, 123.2, 120.3, 111.2, 99.3, 97.0, 80.8, 21.3.

HRMS (EI) calcd for $C_{23}H_{16}O$ $[M]^+$: 308.11957, found: 308.12046.

IR (Reflection): $\tilde{\nu}$ = 3057, 2920, 2859, 2210, 1734, 1682, 1602, 1561, 1482, 1455, 1443, 1382, 1340, 1291, 1256, 1203, 1181, 1112, 1096, 1070, 1028, 1006, 896, 826, 782, 769, 745, 689, 664, 625.



3-((4-Ethylphenyl)ethynyl)-2-phenylbenzofuran

3i, light yellow solid, 56.2 mg, 87% yield.

R_f = 0.5 (PE:DCM = 20:1), chromatography eluent: 5% Dichloromethane in petroleum ether.

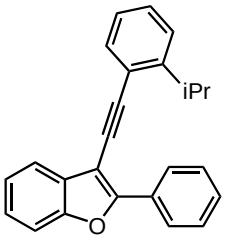
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.39 (d, *J* = 8.0 Hz, 2H), 7.79 (dd, *J* = 6.0, 2.3 Hz, 1H), 7.61 – 7.49 (m, 5H), 7.48 – 7.31 (m, 3H), 7.27 (d, *J* = 7.9 Hz, 2H), 2.73 (q, *J* = 7.6 Hz, 2H), 1.31 (t, *J* = 7.6 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 156.1, 153.5, 144.9, 131.5, 130.2, 130.0, 129.0, 128.6, 128.0, 126.0, 125.3, 123.3, 120.5, 120.4, 111.1, 99.4, 97.0, 80.4, 28.9, 15.4.

HRMS (EI) calcd for $C_{24}H_{18}O$ $[M]^+$: 322.13522, found: 322.13391.

IR (ATR): $\tilde{\nu}$ = 2964, 2930, 2871, 2205, 1886, 1735, 1601, 1509, 1488, 1474, 1455, 1442, 1386, 1290, 1257, 1232, 1202, 1113, 1096, 1069, 1028, 919, 897, 829, 771, 741, 688, 624.

M.p. (amorphous) 73.6-75.5 °C.



3-((2-Isopropylphenyl)ethynyl)-2-phenylbenzofuran

3j, light yellow oil, 63.4 mg, 94% yield.

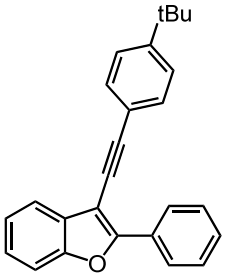
R_f = 0.6 (PE:DCM = 20:1), chromatography eluent: 5% Dichloromethane in petroleum ether.

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.41 (d, *J* = 7.8 Hz, 2H), 7.86 – 7.74 (m, 1H), 7.67 (d, *J* = 7.6 Hz, 1H), 7.60 – 7.49 (m, 3H), 7.46 (d, *J* = 7.3 Hz, 1H), 7.41 – 7.37 (m, 4H), 7.31 – 7.24 (m, 1H), 3.76 (dt, *J* = 13.8, 6.9 Hz, 1H), 1.43 (d, *J* = 6.9 Hz, 6H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 155.9, 153.5, 150.2, 132.5, 130.2, 130.1, 129.1, 128.9, 128.6, 126.0, 125.7, 125.3, 125.0, 123.4, 122.1, 120.3, 111.2, 99.5, 95.7, 84.6, 31.8, 23.3.

HRMS (EI) calcd for $C_{25}H_{20}O$ $[M]^+$: 336.15087, found: 336.15184.

IR (Reflection): ṽ = 3062, 2961, 2928, 2867, 1591, 1482, 1456, 1444, 1384, 1362, 1340, 1291, 1257, 1234, 1203, 1119, 1095, 1069, 1028, 1006, 895, 828, 744, 689, 660, 625.



3-((4-(*tert*-Butyl)phenyl)ethynyl)-2-phenylbenzofuran

3k, light yellow solid, 68.1 mg, 97% yield.

R_f = 0.6 (PE:DCM = 20:1), chromatography eluent: 5% Dichloromethane in petroleum ether.

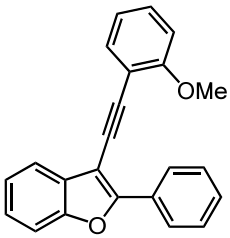
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.51 – 8.18 (m, 2H), 7.85 – 7.75 (m, 1H), 7.65 – 7.59 (m, 2H), 7.59 – 7.50 (m, 3H), 7.50 – 7.41 (m, 3H), 7.41 – 7.30 (m, 2H), 1.40 (s, 9H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 156.1, 153.5, 151.8, 131.3, 130.2, 130.0, 129.1, 128.6, 126.0, 125.5, 125.3, 123.3, 120.4, 111.1, 99.4, 96.9, 80.5, 34.8, 31.2.

HRMS (EI) calcd for $C_{26}H_{22}O$ $[M]^+$: 350.16652, found: 350.16545.

IR (Reflection): ṽ = 2963, 2864, 2360, 1592, 1492, 1456, 1443, 1392, 1257, 1239, 1203, 1103, 1091, 1067, 1013, 897, 833, 769, 745, 701, 685, 623.

M.p. (amorphous) 113.8-115.0 °C.



3-((2-Methoxyphenyl)ethynyl)-2-phenylbenzofuran

3l, light yellow solid, 59.9 mg, 97% yield.

R_f = 0.5 (PE:EA = 10:1), chromatography eluent: 5% Ethyl acetate in petroleum ether.

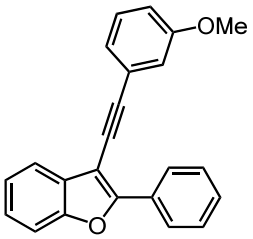
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62 – 8.40 (m, 2H), 7.89 – 7.78 (m, 1H), 7.62 (d, *J* = 7.5 Hz, 1H), 7.58 – 7.48 (m, 3H), 7.43 (t, *J* = 7.4 Hz, 1H), 7.40 – 7.32 (m, 3H), 7.02 (t, *J* = 7.5 Hz, 1H), 6.97 (d, *J* = 8.4 Hz, 1H), 4.01 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 160.1, 156.0, 153.5, 133.0, 130.2, 130.0, 129.8, 129.0, 128.5, 126.0, 125.2, 123.3, 120.5, 120.5, 112.8, 111.1, 110.7, 99.6, 93.7, 85.2, 55.8.

HRMS (EI) calcd for $C_{23}H_{16}O_2$ $[M]^+$: 324.11448, found: 324.11289.

IR (Reflection): ṽ = 3062, 2960, 2937, 2834, 2204, 1895, 1715, 1598, 1573, 1488, 1456, 1442, 1434, 1386, 1339, 1289, 1278, 1256, 1228, 1203, 1180, 1162, 1126, 1106, 1093, 1070, 1044, 1025, 931, 896, 832, 768, 745, 690, 660, 625.

M.p. (amorphous) 96.2-97.8 °C.



3-((3-Methoxyphenyl)ethynyl)-2-phenylbenzofuran

3m, light yellow oil, 56.4 mg, 87% yield.

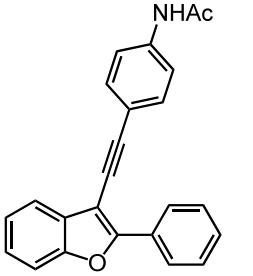
R_f = 0.3 (PE:DCM = 10:1), chromatography eluent: 10% Dichloromethane in petroleum ether.

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.38 (d, *J* = 7.4 Hz, 2H), 7.79 (dd, *J* = 6.0, 2.7 Hz, 1H), 7.60 – 7.49 (m, 3H), 7.46 – 7.41 (m, 1H), 7.40 – 7.31 (m, 3H), 7.30 – 7.23 (m, 1H), 7.19 (s, 1H), 7.01 – 6.92 (m, 1H), 3.88 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 159.4, 156.4, 153.5, 130.1, 129.9, 129.5, 129.2, 128.6, 126.0, 125.3, 124.3, 124.1, 123.4, 120.3, 116.5, 114.8, 111.2, 99.1, 96.6, 81.0, 55.3.

HRMS (EI) calcd for $C_{23}H_{16}O_2$ $[M]^+$: 324.11448, found: 324.11515.

IR (Reflection): ṽ = 3064, 3001, 2937, 2833, 2210, 1734, 1574, 1485, 1474, 1455, 1442, 1426, 1384, 1316, 1284, 1257, 1203, 1176, 1166, 1111, 1095, 1069, 1045, 1006, 993, 917, 896, 869, 850, 826, 770, 744, 686, 625.



***N*-(4-((2-Phenylbenzofuran-3-yl)ethynyl)phenyl)acetamide**

3n, light yellow solid, 60.6 mg, 86% yield.

R_f = 0.3 (PE:EA = 1:1), chromatography eluent: 50% Ethyl acetate in petroleum ether.

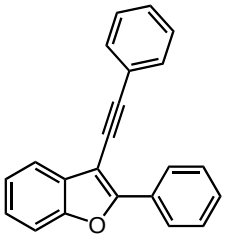
^{1}H NMR (400 MHz, DMSO) δ 10.17 (s, 1H), 8.37 – 8.12 (m, 2H), 7.80 – 7.75 (m, 1H), 7.73 – 7.69 (m, 3H), 7.67 – 7.57 (m, 4H), 7.50 (t, *J* = 7.4 Hz, 1H), 7.47 – 7.36 (m, 2H), 2.09 (s, 3H).

^{13}C NMR (101 MHz, DMSO) δ 168.6, 155.3, 152.9, 140.0, 132.1, 129.7, 129.2, 129.2, 128.9, 126.0, 125.4, 123.9, 120.1, 118.9, 116.2, 111.5, 98.7, 97.3, 79.5, 24.1.

HRMS (EI) calcd for $C_{24}H_{17}NO_2$ $[M]^+$: 351.12538, found: 351.12666.

IR (ATR): ṽ = 3293, 3064, 2208, 1662, 1586, 1524, 1493, 1456, 1442, 1403, 1370, 1312, 1292, 1257, 1237, 1202, 1111, 1093, 1069, 1028, 970, 896, 828, 797, 768, 741, 685, 626.

M.p. (amorphous) 212.6-213.2 °C.



2-Phenyl-3-(phenylethynyl)benzofuran

3o, colorless solid, 58.3 mg, 99% yield.

R_f = 0.4 (PE:DCM = 20:1), chromatography eluent: 5% Dichloromethane in petroleum ether.

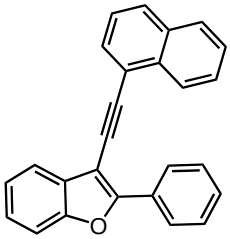
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.48 – 8.33 (m, 2H), 7.85 – 7.76 (m, 1H), 7.68 (dd, *J* = 7.3, 2.1 Hz, 2H), 7.60 – 7.50 (m, 3H), 7.49 – 7.41 (m, 4H), 7.37 (ddd, *J* = 8.8, 5.1, 1.7 Hz, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 156.3, 153.5, 131.5, 130.1, 129.9, 129.1, 128.6, 128.5, 128.4, 126.0, 125.3, 123.4, 120.3, 111.2, 99.2, 96.8, 81.2.

HRMS (EI) calcd for $C_{22}H_{14}O$ $[M]^+$: 294.10392, found: 294.10420.

IR (ATR): ṽ = 3060, 2215, 1733, 1592, 1561, 1485, 1474, 1456, 1443, 1385, 1291, 1256, 1232, 1203, 1114, 1093, 1069, 1026, 1008, 915, 897, 827, 769, 742, 687, 665, 627.

M.p. (amorphous) 81.3-82.6 °C.



3-(Naphthalen-1-ylethynyl)-2-phenylbenzofuran

3p, light yellow solid, 66.9 mg, 97% yield.

R_f = 0.7 (PE:EA = 10:1), chromatography eluent: Petroleum ether.

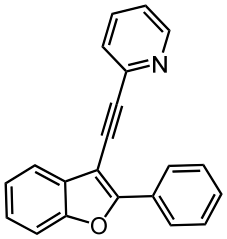
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.60 (d, *J* = 8.2 Hz, 1H), 8.47 (d, *J* = 7.4 Hz, 2H), 8.00 – 7.84 (m, 4H), 7.71 – 7.50 (m, 6H), 7.49 – 7.35 (m, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 156.4, 153.6, 133.3, 133.1, 130.5, 130.2, 130.0, 129.2, 128.9, 128.7, 128.4, 126.9, 126.5, 126.2, 126.1, 125.4, 125.3, 123.5, 121.0, 120.4, 111.3, 99.4, 95.0, 85.9.

HRMS (EI) calcd for $C_{26}H_{16}O$ $[M]^+$: 344.11957, found: 344.11860.

IR (ATR): ṽ = 3054, 2927, 2852, 2203, 1738, 1587, 1556, 1507, 1456, 1441, 1406, 1375, 1291, 1258, 1234, 1203, 1180, 1129, 1109, 1068, 1027, 1008, 897, 827, 793, 765, 744, 683, 657, 626.

M.p. (amorphous)113.5-115.6 °C.



2-((2-Phenylbenzofuran-3-yl)ethynyl)pyridine

3q, light yellow oil, 59.9 mg, 97% yield.

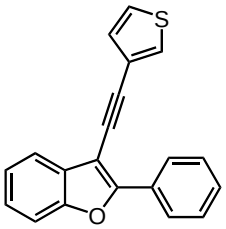
R_f = 0.6 (PE:EA = 1:1), chromatography eluent: 50% Ethyl acetate in petroleum ether.

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.71 (d, *J* = 4.5 Hz, 1H), 8.47 – 8.26 (m, 2H), 7.88 – 7.81 (m, 1H), 7.73 (td, *J* = 7.7, 1.6 Hz, 1H), 7.62 (d, *J* = 7.8 Hz, 1H), 7.57-7.52 (m, 3H), 7.48 – 7.33 (m, 3H), 7.31 – 7.24 (m, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 157.4, 153.4, 150.1, 143.4, 136.1, 129.8, 129.6, 129.4, 128.7, 127.2, 126.1, 125.4, 123.5, 122.8, 120.5, 111.1, 98.3, 95.9, 81.3.

HRMS (EI) calcd for $C_{21}H_{13}NO$ $[M]^+$: 295.09917, found: 295.09945.

IR (Reflection): ṽ = 3058, 2220, 1733, 1579, 1560, 1496, 1460, 1443, 1427, 1386, 1339, 1292, 1249, 1202, 1150, 1123, 1090, 1070, 1045, 1027, 1006, 988, 917, 896, 829, 776, 746, 690, 624.



2-Phenyl-3-(thiophen-3-ylethynyl)benzofuran

3r, light yellow solid, 59.6 mg, 99% yield.

R_f = 0.4 (PE), chromatography eluent: Petroleum ether.

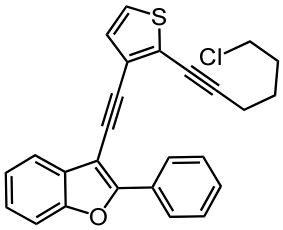
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.44 – 8.24 (m, 2H), 7.83 – 7.72 (m, 1H), 7.63 (dd, *J* = 2.9, 1.0 Hz, 1H), 7.58 – 7.48 (m, 3H), 7.46 – 7.40 (m, 1H), 7.39 – 7.30 (m, 4H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 156.2, 153.5, 130.1, 129.9, 129.8, 129.1, 128.7, 128.6, 125.9, 125.5, 125.3, 123.4 122.4, 120.3, 111.2, 99.1, 91.8, 80.6.

HRMS (EI) calcd for $C_{20}H_{12}OS$ $[M]^+$: 300.06034, found: 300.05967.

IR (Reflection): ṽ = 3108, 1731, 1590, 1487, 1455, 1441, 1352, 1290, 1256, 1226, 1202, 1184, 1109, 1093, 1068, 1027, 1007, 929, 914, 896, 870, 827, 777, 742, 720, 684, 621.

M.p. (amorphous) 86.5-88.1 ºC.



3-((2-(6-Chlorohex-1-yn-1-yl)thiophen-3-yl)ethynyl)-2-phenylbenzofuran

3s, yellow solid, 55.8 mg, 67% yield.

R_f = 0.4 (PE:DCM = 20:1), chromatography eluent: 5% Dichloromethane in petroleum ether.

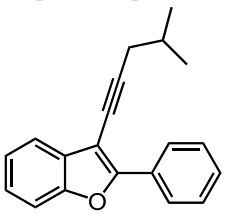
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.45 – 8.37 (m, 2H), 7.82 – 7.73 (m, 1H), 7.58 – 7.47 (m, 3H), 7.46 – 7.29 (m, 3H), 7.16 (dd, *J* = 12.2, 5.3 Hz, 2H), 3.44 (t, *J* = 6.4 Hz, 2H), 2.55 (t, *J* = 6.9 Hz, 2H), 1.95 – 1.84 (m, 2H), 1.73 (tt, *J* = 7.0, 3.8 Hz, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 156.2, 153.5, 130.1, 129.9, 129.1, 128.6, 127.1, 126.0, 125.9, 125.4, 125.1, 123.3, 120.3, 111.2, 99.1, 98.2, 91.5, 84.3, 73.8, 44.4, 31.5, 25.6, 19.3.

HRMS (EI) calcd for $C_{26}H_{19}OSCl$ $[M]^+$: 414.08397, found: 414.07951.

IR (ATR): ṽ = 3059, 2952, 2867, 2226, 2204, 1734, 1565, 1492, 1457, 1443, 1404, 1332, 1255, 1200, 1129, 1093, 1065, 1029, 910, 898, 831, 765, 733, 715, 682, 635.

M.p. (amorphous) 80.1-82.2 ºC.



3-(4-Methylpent-1-yn-1-yl)-2-phenylbenzofuran

3t, light yellow oil, 35.4 mg, 65% yield.

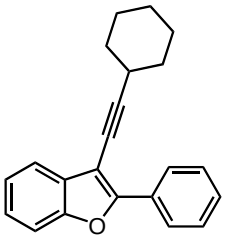
R_f = 0.4 (PE:DCM = 20:1), chromatography eluent: 5% Dichloromethane in petroleum ether.

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.37 – 8.22 (m, 2H), 7.75 – 7.64 (m, 1H), 7.48 (t, *J* = 7.9 Hz, 3H), 7.43 – 7.35 (m, 1H), 7.36 – 7.27 (m, 2H), 2.52 (d, *J* = 6.4 Hz, 2H), 2.04 (dp, *J* = 13.2, 6.6 Hz, 1H), 1.15 (d, *J* = 6.7 Hz, 6H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 155.5, 153.4, 130.5, 130.4, 128.8, 128.5, 125.8, 125.1, 123.1, 120.3, 111.0, 99.8, 97.2, 72.8, 29.2, 28.3, 22.1.

HRMS (EI) calcd for $C_{20}H_{18}O$ $[M]^+$: 274.13522, found: 274.13543.

IR (Reflection): ṽ = 3063, 2926, 2869, 2227, 1946, 1892, 1736, 1682, 1592, 1562, 1495, 1456, 1443, 1426, 1383, 1368, 1339, 1291, 1276, 1257, 1205, 1164, 1107, 1089, 1067, 1028, 1006, 968, 916, 896, 826, 768, 747, 690, 625.



3-(Cyclohexylethynyl)-2-phenylbenzofuran

3u, light yellow oil, 45.9 mg, 76% yield.

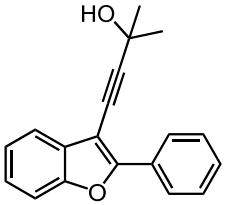
R_f = 0.4 (PE), chromatography eluent: Petroleum ether.

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.42 – 8.17 (m, 2H), 7.73 – 7.60 (m, 1H), 7.52 – 7.47 (m, 3H), 7.43 – 7.36 (m, 1H), 7.37 – 7.27 (m, 2H), 2.93 – 2.73 (m, 1H), 2.09 – 1.95 (m, 2H), 1.87 (dt, *J* = 9.9, 6.2 Hz, 2H), 1.78 – 1.56 (m, 3H), 1.54 – 1.41 (m, 3H).

^{13}C NMR (75MHz, $CDCl_3$) δ 155.4, 153.4, 130.4, 130.4, 128.7, 128.5, 125.7, 125.1, 123.1, 120.3, 111.0, 102.3, 99.9, 72.0, 32.7, 30.1, 25.9, 24.8.

HRMS (EI) calcd for $C_{22}H_{20}O$ $[M]^+$: 300.15087, found: 300.15252.

IR (Reflection): ṽ = 3063, 2936, 2853, 2662, 2223, 1947, 1892, 1735, 1681, 1593, 1562, 1494, 1475, 1444, 1383, 1349, 1314, 1290, 1256, 1233, 1205, 1166, 1132, 1109, 1066, 1028, 1006, 936, 915, 895, 860, 827, 769, 751, 689, 624.



2-Methyl-4-(2-phenylbenzofuran-3-yl)but-3-yn-2-ol

3v, colorless solid, 53.5 mg, 97% yield.

R_f = 0.2 (PE:DCM = 1:1), chromatography eluent: 50% Dichloromethane in petroleum ether.

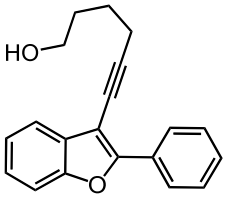
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.33-8.18 (m, 2H), 7.71-7.61 (m, 1H), 7.51-7.46 (m, 3H), 7.44-7.37 (m, 1H), 7.37-7.27 (m, 2H), 2.32 (br, 1H), 1.75 (s, 6H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 156.3, 153.4, 130.0, 129.8, 129.1, 128.6, 125.8, 125.3, 123.3, 120.1, 111.1, 101.3, 98.5, 74.1, 66.0, 31.5.

HRMS (EI) calcd for $C_{19}H_{16}O_2$ $[M]^+$: 276.11448, found: 276.11453.

IR (ATR): ṽ = 3198, 2982, 2931, 2226, 1738, 1494, 1455, 1442, 1407, 1378, 1361, 1292, 1256, 1227, 1202, 1159, 1138, 1095, 1066, 1030, 1008, 961, 911, 897, 826, 776, 766, 737, 683, 625.

M.p. (crystal) 87.5-89.3 ºC.



6-(2-Phenylbenzofuran-3-yl)hex-5-yn-1-ol

3w, light yellow oil, 47.0 mg, 81% yield.

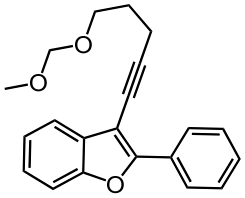
R_f = 0.2 (PE:EA = 5:1), chromatography eluent: 20% Ethyl acetate in petroleum ether.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 – 8.21 (m, 2H), 7.73 – 7.57 (m, 1H), 7.53 – 7.45 (m, 3H), 7.43 – 7.36 (m, 1H), 7.31 (pd, *J* = 7.2, 1.4 Hz, 2H), 3.76 (t, *J* = 5.8 Hz, 2H), 2.66 (t, *J* = 6.5 Hz, 2H), 1.93 – 1.75 (m, 4H), 1.62 (br, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 155.6, 153.4, 130.4, 130.3, 128.8, 128.5, 125.7, 125.1, 123.1, 120.2, 111.0, 99.6, 97.6, 72.4, 62.4, 31.9, 25.1, 19.8.

HRMS (EI) calcd for $C_{20}H_{18}O_2$ $[M]^+$: 290.13013, found: 290.13023.

IR (Reflection): ṽ = 3353, 3062, 2935, 2864, 2226, 1894, 1733, 1592, 1562, 1494, 1475, 1455, 1443, 1381, 1339, 1290, 1257, 1204, 1165, 1108, 1067, 1029, 1007, 983, 917, 895, 826, 769, 745, 690, 624.



3-(4-(Methoxymethoxy)but-1-yn-1-yl)-2-phenylbenzofuran

3x, light yellow oil, 39.8 mg, 65% yield.

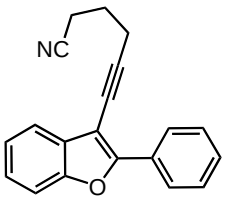
R_f = 0.4 (PE:DCM = 2:1), chromatography eluent: 50% Dichloromethane in petroleum ether.

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.31 (d, *J* = 7.5 Hz, 2H), 7.72 – 7.62 (m, 1H), 7.51 – 7.46 (m, 3H), 7.43 – 7.36 (m, 1H), 7.38 – 7.26 (m, 2H), 4.75 (s, 2H), 3.87 (t, *J* = 6.8 Hz, 2H), 3.42 (s, 3H), 2.92 (t, *J* = 6.8 Hz, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 155.9, 153.3, 130.3, 130.2, 128.9, 128.5, 125.8, 125.1, 123.2, 120.2, 111.1, 99.3, 96.6, 94.6, 73.1, 66.2, 55.4, 21.6.

HRMS (EI) calcd for $C_{20}H_{18}O_3$ $[M]^+$: 306.12505, found: 306.12633.

IR (Reflection): ṽ = 3062, 2931, 2883, 2822, 2768, 2231, 1947, 1895, 1733, 1683, 1592, 1562, 1495, 1475, 1456, 1443, 1381, 1335, 1291, 1257, 1205, 1150, 1112, 1071, 1030, 1006, 989, 968, 918, 895, 876, 826, 770, 749, 691, 624.



6-(2-Phenylbenzofuran-3-yl)hex-5-ynenitrile

3y, light yellow oil, 47.4 mg, 83% yield.

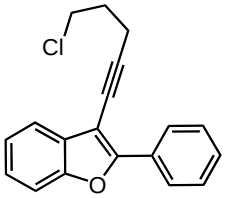
R_f = 0.3 (DCM), chromatography eluent: Dichloromethane.

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.31 – 8.17 (m, 2H), 7.68 – 7.60 (m, 1H), 7.57 – 7.47 (m, 3H), 7.45 – 7.38 (m, 1H), 7.38 – 7.27 (m, 2H), 2.81 (t, *J* = 6.8 Hz, 2H), 2.63 (t, *J* = 7.1 Hz, 2H), 2.06 (p, *J* = 7.0 Hz, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 156.1, 153.3, 130.1, 129.1, 128.6, 125.7, 125.3, 123.3, 120.0, 119.0, 111.1, 98.9, 94.5, 74.1, 24.6, 19.0, 16.2.

HRMS (EI) calcd for $C_{20}H_{15}NO$ $[M]^+$: 285.11482, found: 285.11462.

IR (Reflection): ṽ = 3062, 2940, 2836, 2248, 1732, 1683, 1592, 1562, 1493, 1475, 1455, 1443, 1429, 1381, 1341, 1290, 1257, 1204, 1165, 1108, 1068, 1028, 1006, 917, 895, 826, 770, 746, 690, 624.



3-(5-Chloropent-1-yn-1-yl)-2-phenylbenzofuran

3z, light yellow oil, 46.1 mg, 78% yield.

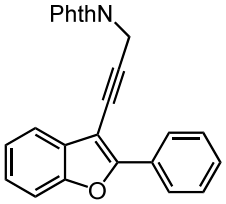
R_f = 0.6 (PE:EA = 10:1), chromatography eluent: Petroleum ether.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 – 8.22 (m, 2H), 7.68 – 7.59 (m, 1H), 7.52 – 7.46 (m, 3H), 7.40 (ddd, *J* = 7.4, 3.8, 1.1 Hz, 1H), 7.36 – 7.27 (m, 2H), 3.81 (t, *J* = 6.3 Hz, 2H), 2.82 (t, *J* = 6.8 Hz, 2H), 2.17 (p, *J* = 6.6 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 156.0, 153.4, 130.3, 130.2, 129.0, 128.6, 125.8, 125.2, 123.2, 120.2, 111.1, 99.3, 95.7, 73.2, 43.7, 31.4, 17.4.

HRMS (EI) calcd for $C_{19}H_{15}OCl$ $[M]^+$: 294.08059, found: 294.08058.

IR (Reflection): ṽ = 3062, 2958, 2840, 2231, 1755, 1592, 1562, 1495, 1475, 1455, 1442, 1382, 1341, 1289, 1257, 1204, 1166, 1108, 1067, 1028, 1006, 949, 914, 895, 850, 826, 769, 746, 690, 666, 624.



2-(3-(2-Phenylbenzofuran-3-yl)prop-2-yn-1-yl)isoindoline-1,3-dione

3aa, colorless solid, 70.6 mg, 94% yield.

R_f = 0.2 (PE:DCM = 1:1), chromatography eluent: 50% Dichloromethane in petroleum ether.

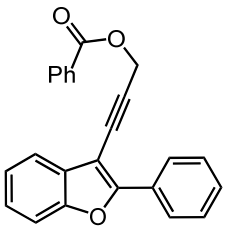
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (dd, *J* = 5.3, 3.3 Hz, 2H), 7.89 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.74 – 7.68 (m, 2H), 7.68 – 7.64 (m, 1H), 7.50 – 7.44 (m, 3H), 7.41 – 7.35 (m, 1H), 7.29 (tdd, *J* = 12.1, 7.1, 1.3 Hz, 2H), 4.85 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.0, 157.1, 153.3, 134.1, 132.0, 129.8, 129.7, 129.2, 128.6, 125.9, 125.2, 123.5, 123.4, 120.3, 111.0, 98.1, 90.4, 75.2, 28.3.

HRMS (EI) calcd for $C_{25}H_{15}NO_3$ $[M]^+$: 377.10464, found: 377.10430.

IR (ATR): ṽ = 2227, 1770, 1703, 1612, 1457, 1444, 1418, 1396, 1380, 1336, 1307, 1257, 1205, 1168, 1113, 1089, 1069, 1028, 938, 826, 797, 770, 745, 723, 708, 685, 625.

M.p. (amorphous) 149.4-150.9 ºC.



3-(2-Phenylbenzofuran-3-yl)prop-2-yn-1-yl benzoate

3ab, light yellow solid, 55.4 mg, 79% yield.

R_f = 0.4 (PE:EA = 10:1), chromatography eluent: 10% Ethyl acetate in petroleum ether.

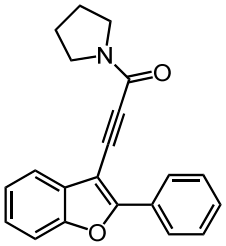
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.37 – 8.24 (m, 2H), 8.24 – 8.11 (m, 2H), 7.75 – 7.68 (m, 1H), 7.61 (t, *J* = 7.4 Hz, 1H), 7.55 – 7.45 (m, 5H), 7.44 – 7.38 (m, 1H), 7.38 – 7.28 (m, 2H), 5.34 (s, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 165.9, 157.3, 153.3, 133.3, 129.8, 129.6, 129.3, 128.6, 128.4, 126.0, 125.3, 123.4, 120.3, 111.2, 98.1, 90.7, 78.7, 53.6.

HRMS (EI) calcd for $C_{24}H_{16}O_3$ $[M]^+$: 352.10940, found: 352.10974.

IR (ATR): $\tilde{\nu}$ = 3059, 2928, 2236, 1720, 1601, 1492, 1454, 1389, 1359, 1315, 1266, 1204, 1171, 1109, 1068, 1026, 963, 936, 920, 895, 854, 826, 769, 748, 706, 689, 659, 627.

M.p. (amorphous) 61.7-63.0 ºC.



3-(2-Phenylbenzofuran-3-yl)-1-(pyrrolidin-1-yl)prop-2-yn-1-one

3ac, light yellow solid, 62.5 mg, 99% yield.

R_f = 0.4 (PE:EA = 1:1), chromatography eluent: 50% Ethyl acetate in petroleum ether.

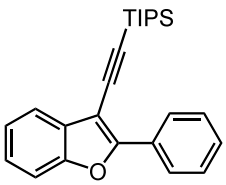
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.25 (d, *J* = 7.1 Hz, 2H), 7.72 – 7.63 (m, 1H), 7.57 – 7.39 (m, 4H), 7.38 – 7.29 (m, 2H), 3.80 (t, *J* = 6.4 Hz, 2H), 3.58 (t, *J* = 6.4 Hz, 2H), 2.13 – 1.84 (m, 4H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 158.9, 153.4, 152.5, 129.9, 129.3, 129.3, 128.7, 126.3, 125.6, 123.7, 120.2, 111.3, 96.7, 90.1, 81.0, 48.1, 45.4, 25.4, 24.6.

IR (ATR): $\tilde{\nu}$ = 2966, 2879, 2203, 1625, 1603, 1558, 1443, 1413, 1370, 1335, 1290, 1256, 1199, 1157, 1068, 1029, 1006, 910, 826, 756, 741, 719, 706, 680, 620.

HRMS (EI) calcd for $C_{21}H_{17}NO_2$ $[M]^+$: 315.12538, found: 315.12457.

M.p. (amorphous) 158.1-159.8 ºC.



Triisopropyl((2-phenylbenzofuran-3-yl)ethynyl)silane

3ad, light yellow solid, 46.8 mg, 63% yield.

R_f = 0.6 (PE), chromatography eluent: Petroleum ether.

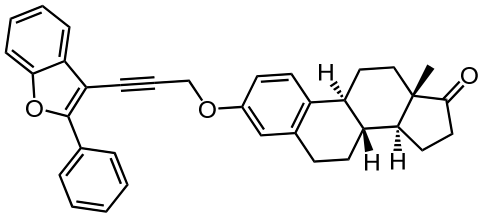
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.41 (d, *J* = 8.3 Hz, 2H), 7.73 – 7.64 (m, 1H), 7.53 – 7.40 (m, 4H), 7.39 – 7.28 (m, 2H), 1.24 (s, 21H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 156.8, 153.3, 130.3, 130.1, 129.1, 128.5, 126.0, 125.3, 123.4, 120.3, 111.1, 99.6, 99.6, 98.3, 18.7, 11.4.

HRMS (EI) calcd for $C_{25}H_{30}OSi$ $[M]^+$: 374.20604, found: 374.20685.

IR (ATR): ṽ = 3066, 2941, 2889, 2863, 2158, 1458, 1442, 1366, 1291, 1257, 1203, 1135, 1096, 1072, 1018, 995, 914, 883, 828, 767, 741, 681, 633.

M.p. (amorphous) 59.2-60.4 °C.



***(8R,9S,13S,14S)*-13-Methyl-3-((3-(2-phenylbenzofuran-3-yl)prop-2-yn-1-yl)oxy)-6,7,8,9,11,12,13,14,15,16-decahydro-17*H*-cyclopenta[*a*]phenanthren-17-one**

3ae, colorless solid, 51.5 mg, 53% yield.

R_f = 0.2 (PE:DCM = 1:2), chromatography eluent: 50% Petroleum ether in dichlormethan.

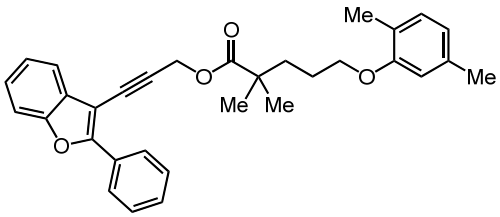
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.22 – 8.04 (m, 2H), 7.66 – 7.55 (m, 1H), 7.47 (d, *J* = 7.6 Hz, 1H), 7.42 – 7.33 (m, 3H), 7.32 – 7.22 (m, 3H), 6.91 (dd, *J* = 8.6, 2.7 Hz, 1H), 6.84 (d, *J* = 2.5 Hz, 1H), 5.05 (s, 2H), 3.04 – 2.78 (m, 2H), 2.49 (dd, *J* = 18.4, 8.2 Hz, 1H), 2.43 – 2.35 (m, 1H), 2.28 (dd, *J* = 18.8, 9.5 Hz, 1H), 2.14 (dd, *J* = 18.0, 9.2 Hz, 1H), 2.09 – 1.92 (m, 3H), 1.71 – 1.32 (m, 6H), 0.90 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 220.8, 156.9, 155.7, 153.4, 137.8, 132.9, 129.9, 129.8, 129.2, 128.6, 126.4, 126.0, 125.3, 123.4, 120.2, 115.2, 112.8, 111.2, 98.2, 91.9, 79.0, 56.7, 50.4, 48.0, 44.0, 38.3, 35.8, 31.6, 29.7, 26.5, 25.9, 21.6, 13.8.

HRMS (EI) calcd for $C_{35}H_{32}O_3$ $[M]^+$: 500.23460, found: 500.23406.

IR (Reflection): ṽ = 3453, 3286, 3060, 2929, 2862, 2249, 2225, 2120, 1737, 1608, 1576, 1498, 1455, 1405, 1374, 1340, 1307, 1281, 1256, 1231, 1187, 1163, 1101, 1084, 1055, 1030, 1008, 965, 912, 871, 844, 818, 771, 732, 691, 648.

M.p. (amorphous) 74.1-75.3 °C.



3-(2-Phenylbenzofuran-3-yl)prop-2-yn-1-yl 5-(2,5-dimethylphenoxy)-2,2-dimethylpentanoate

3af, light yellow oil, 87.3 mg, 91% yield.

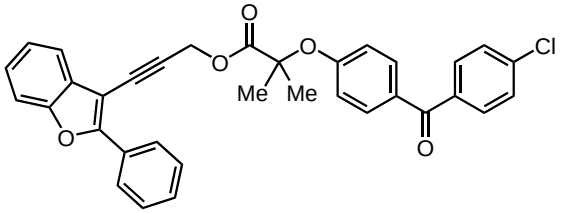
R_f = 0.2 (PE:DCM = 5:1), chromatography eluent: 25% Dichlormethan in petroleum ether.

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.29 (d, *J* = 7.5 Hz, 2H), 7.75 – 7.62 (m, 1H), 7.51 (t, *J* = 7.5 Hz, 3H), 7.45 – 7.38 (m, 1H), 7.33 (dq, *J* = 7.3, 6.3 Hz, 2H), 7.00 (d, *J* = 7.5 Hz, 1H), 6.66 (d, *J* = 7.5 Hz, 1H), 6.56 (s, 1H), 5.10 (s, 2H), 3.90 (t, *J* = 2.9 Hz, 2H), 2.30 (s, 3H), 2.16 (s, 3H), 1.83 (s, 4H), 1.34 (s, 6H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 177.1, 157.1, 156.8, 153.3, 136.3, 130.2, 129.8, 129.3, 128.6, 126.0, 125.3, 123.5, 123.4, 120.6, 120.2, 111.8, 111.1, 98.1, 91.0, 78.2, 67.7, 60.3, 53.0, 42.2, 37.1, 25.12, 25.10, 21.3, 15.7.

HRMS (EI) calcd for $C_{32}H_{32}O_4$ $[M]^+$: 480.22951, found: 480.23130.

IR (Reflection): ṽ = 3057, 2950, 2924, 2870, 2229, 1735, 1614, 1585, 1509, 1473, 1456, 1443, 1388, 1311, 1263, 1203, 1186, 1157, 1129, 1068, 1047, 983, 934, 895, 845, 826, 803, 770, 745, 689, 625.



3-(2-Phenylbenzofuran-3-yl)prop-2-yn-1-yl
2-(4-(4-chlorobenzoyl)phenoxy)-2-methylpropanoate

3ag, light yellow oil, 65.4 mg, 60% yield.

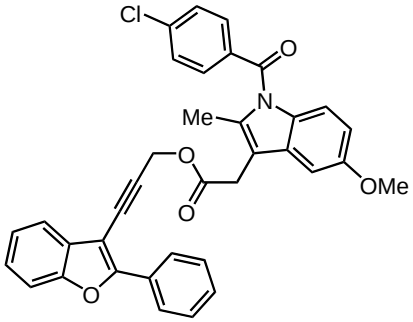
R_f = 0.4 (PE:DCM = 1:2), chromatography eluent: 5% Petroleum ether in dichlormethan.

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.26 – 8.15 (m, 2H), 7.64 – 7.59 (m, 1H), 7.59 – 7.50 (m, 5H), 7.47 (t, *J* = 7.3 Hz, 2H), 7.39 (dd, *J* = 8.8, 4.2 Hz, 1H), 7.37 – 7.24 (m, 4H), 6.92 (d, *J* = 8.8 Hz, 2H), 5.20 (s, 2H), 1.77 (s, 6H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 193.9, 173.1, 159.2, 157.4, 153.3, 138.1, 136.1, 132.0, 130.9, 130.4, 129.6, 129.5, 128.7, 128.3, 125.9, 125.5, 123.5, 120.0, 117.4, 111.3, 97.7, 89.9, 79.3, 79.0, 54.0, 25.4.

HRMS (EI) calcd for $C_{34}H_{25}O_5Cl$ $[M]^+$: 548.13850, found: 548.14040.

IR (Reflection): ṽ = 3064, 2994, 2940, 2229, 1741, 1654, 1598, 1504, 1487, 1456, 1443, 1386, 1363, 1303, 1276, 1249, 1202, 1170, 1130, 1090, 1069, 1014, 965, 927, 852, 837, 791, 746, 689, 664, 625.



3-(2-Phenylbenzofuran-3-yl)prop-2-yn-1-yl
2-(1-(4-chlorobenzoyl)-5-methoxy-2-methyl-*1H*-indol-3-yl)acetate

3ah, light yellow solid, 79.6 mg, 68% yield.

R_f = 0.6 (PE:DCM = 1:1), chromatography eluent: 50% Dichloromethane in petroleum ether.

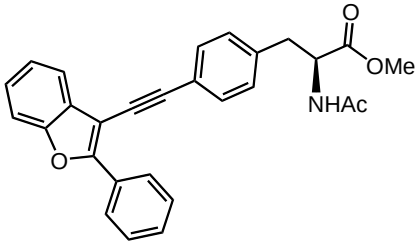
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (dd, *J* = 5.3, 3.3 Hz, 2H), 7.65 – 7.57 (m, 3H), 7.51 (d, *J* = 8.1 Hz, 1H), 7.47 – 7.37 (m, 5H), 7.36 – 7.31 (m, 1H), 7.31 – 7.25 (m, 1H), 7.02 (d, *J* = 2.5 Hz, 1H), 6.88 (d, *J* = 9.0 Hz, 1H), 6.66 (dd, *J* = 9.0, 2.5 Hz, 1H), 5.11 (s, 2H), 3.79 (s, 2H), 3.75 (s, 3H), 2.41 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.1, 168.2, 157.2, 156.1, 153.3, 139.2, 136.0, 133.8, 131.1, 130.8, 130.5, 129.8, 129.7, 129.4, 129.0, 128.6, 125.9, 125.4, 123.5, 120.1, 114.9, 112.1, 111.7, 111.2, 101.2, 97.9, 90.5, 78.7, 55.6, 53.6, 30.2, 13.4.

HRMS (EI) calcd for $C_{36}H_{26}NO_5Cl$ $[M]^+$: 587.14940, found: 587.14793.

IR (ATR): ṽ = 2925, 2230, 1733, 1668, 1610, 1477, 1457, 1444, 1398, 1374, 1354, 1320, 1289, 1235, 1215, 1166, 1152, 1089, 1072, 1036, 1025, 1014, 992, 954, 913, 868, 847, 826, 806, 774, 753, 692, 662, 627.

M.p. (amorphous) 153.5-154.4 ºC.



Methyl (*S*)-2-acetamido-3-(4-((2-phenylbenzofuran-3-yl)ethynyl)phenyl)propanoate

3ai, light yellow solid, 65.2 mg, 75% yield.

R_f = 0.3 (DCM:EA = 2:1), chromatography eluent: 50% Ethyl acetate in dichloromethane.

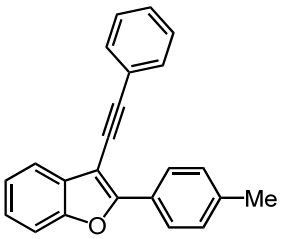
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 (dd, *J* = 5.3, 3.3 Hz, 2H), 7.82 – 7.68 (m, 1H), 7.58 – 7.47 (m, 5H), 7.45 – 7.39 (m, 1H), 7.38 – 7.29 (m, 2H), 7.15 (d, *J* = 8.1 Hz, 2H), 6.08 (s, 1H), 4.93 (dd, *J* = 13.5, 5.8 Hz, 1H), 3.76 (s, 3H), 3.21 (dd, *J* = 13.8, 5.9 Hz, 1H), 3.13 (dd, *J* = 13.8, 5.7 Hz, 1H), 2.02 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.9, 169.6, 156.3, 153.5, 136.4, 131.6, 130.1, 129.8, 129.4, 129.1, 128.6, 126.0, 125.3, 123.3, 122.2, 120.3, 111.2, 99.1, 96.4, 81.4, 53.0, 52.4, 37.8, 23.1.

HRMS (EI) calcd for $C_{28}H_{23}NO_4$ $[M]^+$: 437.16216, found: 437.16488.

IR (ATR): ṽ = 3289, 2953, 2207, 1741, 1649, 1540, 1512, 1490, 1455, 1433, 1373, 1351, 1297, 1255, 1216, 1168, 1111, 1069, 1052, 1028, 1007, 959, 913, 828, 771, 744, 686, 625, 615.

M.p. (amorphous) 155.4-158.8 ºC.



3-(Phenylethynyl)-2-(*p*-tolyl)benzofuran

3aj, colorless solid, 55.9 mg, 91% yield.

R_f = 0.6 (PE:EA = 20:1), chromatography eluent: Petroleum ether.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (d, *J* = 7.8 Hz, 2H), 7.78 (dd, *J* = 7.1, 0.5 Hz, 1H), 7.66 (d, *J* = 6.7 Hz, 2H), 7.55 (dd, *J* = 4.5, 4.0 Hz, 1H), 7.47 – 7.40 (m, 3H), 7.39 – 7.33 (m, 4H), 2.45 (s, 3H).

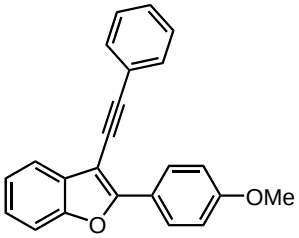
^{13}C NMR (101 MHz, $CDCl_3$) δ 156.7, 153.4, 139.3, 131.5, 130.0, 129.4, 128.4, 128.3, 127.4, 126.0, 125.1, 123.5, 123.3, 120.2, 111.1, 98.4, 96.5, 81.4, 21.5.

HRMS (EI) calcd for $C_{23}H_{16}O$ $[M]^+$: 308.11957, found: 308.11975.

IR (ATR): ṽ = 3061, 3031, 2920, 2859, 2215, 1609, 1587, 1510, 1487, 1474, 1453, 1388, 1341, 1291, 1255, 1231, 1202, 1188, 1098, 1068, 1018, 909, 896, 835, 818, 785, 751, 737, 687, 667, 654,

608.

M.p. (amorphous) 118.7-119.9 ºC.



2-(4-Methoxyphenyl)-3-(phenylethynyl)benzofuran

3ak, light yellow solid, 45.7 mg, 70% yield.

R_f = 0.4 (PE:DCM = 10:1), chromatography eluent: 10% Dichloromethane in petroleum ether.

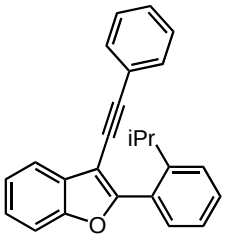
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.31 (d, *J* = 8.9 Hz, 2H), 7.74 (dd, *J* = 6.0, 3.0 Hz, 1H), 7.64 (dd, *J* = 7.4, 2.0 Hz, 2H), 7.55 – 7.48 (m, 1H), 7.47 – 7.37 (m, 3H), 7.37 – 7.28 (m, 2H), 7.04 (d, *J* = 9.0 Hz, 2H), 3.89 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 160.4, 156.6, 153.3, 131.5, 130.1, 128.4, 128.3, 127.6, 124.8, 123.5, 123.3, 123.0, 120.0, 114.1, 111.0, 97.4, 96.2, 81.5, 55.3.

HRMS (EI) calcd for $C_{23}H_{16}O_2$ $[M]^+$: 324.11448, found: 324.11613.

IR (ATR): ṽ = 2213, 1456, 1403, 1357, 1279, 1249, 1201, 1171, 1129, 1119, 1095, 1023, 905, 889, 847, 829, 783, 740, 682, 629, 607.

M.p. (amorphous) 103.6-105.7 ºC.



2-(2-Isopropylphenyl)-3-(phenylethynyl)benzofuran

3al, colorless oil, 62.9 mg, 94% yield.

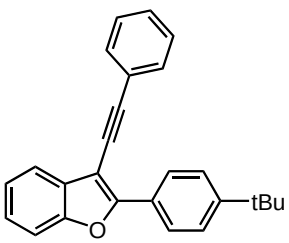
R_f = 0.7 (PE:EA = 10:1), chromatography eluent: Petroleum ether.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 – 7.82 (m, 1H), 7.78 (d, *J* = 7.7 Hz, 1H), 7.59 – 7.55 (m, 1H), 7.54 – 7.47 (m, 4H), 7.42 – 7.39 (m, 2H), 7.38 – 7.32 (m, 4H), 3.46 (dt, *J* = 13.6, 6.8 Hz, 1H), 1.33 (d, *J* = 6.8 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.0, 153.9, 148.8, 131.5, 130.8, 130.1, 129.2, 128.4, 128.3, 128.2, 126.0, 125.5, 125.0, 123.4, 123.3, 120.4, 111.3, 101.9, 94.8, 80.5, 30.4, 24.2.

HRMS (EI) calcd for $C_{25}H_{20}O$ $[M]^+$: 336.15087, found: 336.15175.

IR (Reflection): ṽ = 3061, 2964, 2928, 2868, 2219, 1755, 1587, 1493, 1452, 1384, 1363, 1293, 1273, 1253, 1231, 1196, 1160, 1099, 1069, 1050, 1028, 1007, 903, 828, 811, 747, 689, 660, 626.



2-(4-(*tert*-Butyl)phenyl)-3-(phenylethynyl)benzofuran

3am, light yellow oil, 53.6 mg, 77% yield.

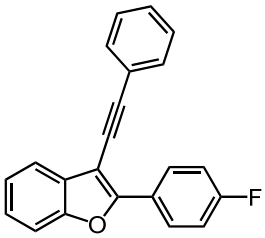
R_f = 0.4 (PE), chromatography eluent: Petroleum ether.

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.32 (d, *J* = 8.4 Hz, 2H), 7.78 (dd, *J* = 4.8, 3.0 Hz, 1H), 7.71 – 7.64 (m, 2H), 7.58 – 7.53 (m, 3H), 7.48 – 7.38 (m, 3H), 7.38 – 7.30 (m, 2H), 1.41 (s, 9H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 156.6, 153.4, 152.5, 131.5, 130.0, 128.4, 128.3, 127.4, 125.8, 125.6, 125.1, 123.5, 123.3, 120.2, 111.1, 98.5, 96.5, 81.4, 34.9, 31.2.

HRMS (EI) calcd for $C_{26}H_{22}O$ $[M]^+$: 350.16652, found: 350.16500.

IR (Reflection): $\tilde{\nu}$ = 3062, 2961, 2903, 2867, 2216, 1755, 1579, 1513, 1487, 1474, 1453, 1409, 1387, 1363, 1293, 1268, 1256, 1231, 1204, 1108, 1095, 1069, 1014, 897, 836, 746, 688.



2-(4-Fluorophenyl)-3-(phenylethynyl)benzofuran

3an, colorless solid, 60.9 mg, 98% yield.

R_f = 0.6 (PE:DCM = 10:1), chromatography eluent: 5% Dichlormethan in petroleum ether.

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.41 – 8.27 (m, 2H), 7.83 – 7.73 (m, 1H), 7.69 – 7.60 (m, 2H), 7.57 – 7.49 (m, 1H), 7.49 – 7.40 (m, 3H), 7.40 – 7.32 (m, 2H), 7.25 – 7.16 (m, 2H).

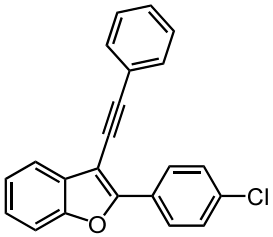
^{13}C NMR (75 MHz, $CDCl_3$) δ 163.0 (d, *J* = 250.3 Hz), 155.4 (d, *J* = 1.0 Hz), 153.4, 131.5, 129.8, 128.5, 129.0 (d, *J* = 8.3 Hz), 126.5(d, *J* = 3.3 Hz), 125.3, 123.4, 123.2, 120.3, 115.9, 115.6, 111.1, 98.9 (d, *J* = 1.6 Hz), 96.7, 81.0.

^{19}F NMR (282 MHz, $CDCl_3$) δ -110.67.

HRMS (EI) calcd for $C_{22}H_{13}OF$ $[M]^+$: 312.09449, found: 312.09563.

IR (ATR): $\tilde{\nu}$ = 3064, 2925, 2853, 2216, 1893, 1595, 1570, 1507, 1488, 1475, 1453, 1411, 1388, 1342, 1290, 1255, 1229, 1201, 1161, 1116, 1093, 1012, 896, 836, 798, 755, 741, 689, 668, 629, 606.

M.p. (amorphous) 99.8-101.5 °C.



2-(4-Chlorophenyl)-3-(phenylethynyl)benzofuran

3ao, light yellow solid, 53.6 mg, 82% yield.

R_f = 0.4 (PE), chromatography eluent: Petroleum ether.

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.38 – 8.21 (m, 2H), 7.79 – 7.72 (m, 1H), 7.63 (dd, *J* = 6.5, 3.2 Hz, 2H), 7.55 – 7.39 (m, 6H), 7.38 – 7.30 (m, 2H).

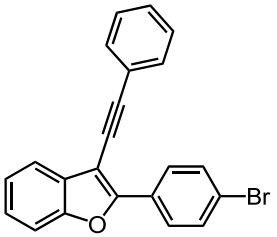
^{13}C NMR (75 MHz, $CDCl_3$) δ 155.1, 153.5, 134.9, 131.5, 129.7, 128.9, 128.6, 128.6, 128.5, 127.2, 125.6, 123.5, 123.1, 120.4, 111.2, 99.7, 97.2, 80.9.

HRMS (EI) calcd for $C_{22}H_{13}OCl$ $[M]^+$: 336.15087, found: 336.15175.

IR (ATR): $\tilde{\nu}$ = 3056, 3035, 2219, 1925, 1898, 1734, 1645, 1577, 1496, 1483, 1453, 1405, 1387,

1343, 1308, 1293, 1256, 1234, 1202, 1182, 1124, 1114, 1092, 1071, 1012, 925, 895, 825, 738, 726, 684, 669, 642, 625.

M.p. (amorphous) 132.1-133.7 °C.



2-(4-Bromophenyl)-3-(phenylethynyl)benzofuran

3ap, colorless solid, 65.2 mg, 88% yield.

R_f = 0.6 (PE:DCM = 10:1), chromatography eluent: 5% Dichlormethan in petroleum ether.

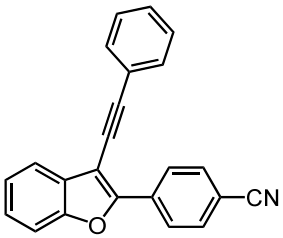
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.20 (d, *J* = 8.6 Hz, 2H), 7.75 (dd, *J* = 6.5, 2.3 Hz, 1H), 7.67 – 7.58 (m, 4H), 7.51 (dd, *J* = 6.9, 1.7 Hz, 1H), 7.46 – 7.39 (m, 3H), 7.38 – 7.31 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 155.1, 153.5, 131.8, 131.5, 129.7, 129.0, 128.6, 128.5, 127.3, 125.6, 123.5, 123.2, 123.1, 120.4, 111.2, 99.8, 97.3, 80.9.

HRMS (EI) calcd for $C_{22}H_{13}OBr$ $[M]^+$: 372.01443, found: 372.01255.

IR (ATR): $\tilde{\nu}$ = 3054, 3036, 2925, 2854, 2219, 1898, 1737, 1574, 1553, 1494, 1483, 1452, 1401, 1386, 1342, 1293, 1256, 1234, 1201, 1182, 1156, 1124, 1094, 1071, 1009, 925, 894, 848, 822, 751, 738, 709, 685, 667, 638.

M.p. (amorphous) 139.6-141.1°C.



4-(3-(Phenylethynyl)benzofuran-2-yl)benzonitrile

3aq, light yellow solid, 46.7 mg, 73% yield.

R_f = 0.3 (PE:DCM = 2:1), chromatography eluent: 50% Petroleum ether in dichlormethan.

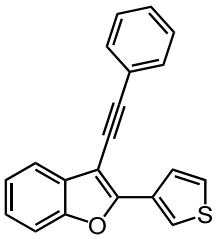
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.41 (d, *J* = 8.6 Hz, 2H), 7.79 – 7.73 (m, 3H), 7.67 – 7.59 (m, 2H), 7.53 (d, *J* = 7.7 Hz, 1H), 7.47 – 7.42 (m, 3H), 7.40 (dd, *J* = 8.1, 1.5 Hz, 1H), 7.35 (td, *J* = 7.4, 1.1 Hz, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 153.8, 153.5, 134.0, 132.4, 131.6, 129.5, 128.9, 128.6, 126.5, 125.9, 123.8, 122.7, 120.8, 118.7, 111.8, 111.4, 102.3, 98.5, 80.3.

HRMS (EI) calcd for $C_{23}H_{13}NO$ $[M]^+$: 319.09917, found: 319.09744.

IR (ATR): $\tilde{\nu}$ = 3047, 2925, 2224, 1730, 1604, 1573, 1546, 1487, 1474, 1450, 1412, 1342, 1293, 1256, 1234, 1203, 1172, 1095, 1073, 1033, 1016, 910, 897, 840, 813, 756, 738, 684, 647, 614.

M.p. (amorphous) 175.2-176.7 °C.



3-(Phenylethynyl)-2-(thiophen-3-yl)benzofuran

3ar, light yellow solid, 52.5 mg, 87% yield.

R_f = 0.4 (PE), chromatography eluent: Petroleum ether.

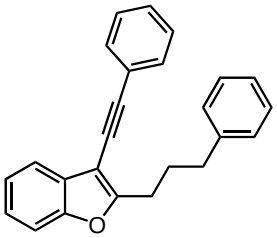
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.24 – 8.13 (m, 1H), 8.00 (d, *J* = 5.1 Hz, 1H), 7.82 – 7.73 (m, 1H), 7.66 (dd, *J* = 7.6, 1.6 Hz, 2H), 7.52 (dd, *J* = 5.7, 3.3 Hz, 1H), 7.48 – 7.40 (m, 4H), 7.39 – 7.30 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 153.8, 153.3, 131.6, 131.5, 129.5, 128.5, 128.4, 126.2, 125.6, 125.1, 123.7, 123.4, 123.3, 120.2, 111.1, 98.2, 96.6, 81.0.

HRMS (EI) calcd for $C_{20}H_{12}OS$ $[M]^+$: 300.06034, found: 300.06066.

IR (ATR): ṽ = 3104, 2208, 1588, 1487, 1474, 1454, 1351, 1285, 1263, 1239, 1203, 1190, 1097, 1008, 925, 906, 868, 832, 784, 767, 742, 685, 661, 643.

M.p. (amorphous) 111.5-112.4 ºC.



3-(Phenylethynyl)-2-(3-phenylpropyl)benzofuran

3as, light yellow oil, 50.6 mg, 75% yield.

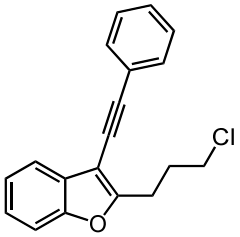
R_f = 0.3 (PE), chromatography eluent: Petroleum ether.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.76 – 7.65 (m, 1H), 7.63 – 7.53 (m, 2H), 7.51 – 7.45 (m, 1H), 7.44 – 7.36 (m, 3H), 7.36 – 7.18 (m, 7H), 3.03 (t, *J* = 7.3 Hz, 2H), 2.78 (t, *J* = 7.6 Hz, 2H), 2.22 (p, *J* = 7.5 Hz, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 162.3, 153.8, 141.6, 131.4, 128.7, 128.6, 128.3, 128.1, 125.9, 124.2, 123.5, 123.1, 119.8, 111.0, 100.4, 94.8, 79.9, 35.1, 29.2, 27.1.

HRMS (EI) calcd for $C_{25}H_{20}O$ $[M]^+$: 336.15087, found: 336.15110.

IR (Reflection): ṽ = 3061, 3027, 2932, 2860, 2219, 1945, 1891, 1732, 1588, 1491, 1475, 1454, 1387, 1324, 1277, 1235, 1177, 1108, 1090, 1071, 1028, 1008, 928, 867, 846, 811, 746, 690, 652.



2-(3-Chloropropyl)-3-(phenylethynyl)benzofuran

3at, light yellow oil, 48.8 mg, 83% yield.

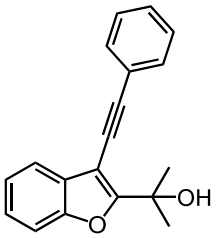
R_f = 0.4 (PE:DCM = 20:1), chromatography eluent: 5% Dichloromethane in petroleum ether.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 – 7.65 (m, 1H), 7.63 – 7.56 (m, 2H), 7.49 – 7.43 (m, 1H), 7.42 – 7.35 (m, 3H), 7.35 – 7.28 (m, 2H), 3.67 (t, *J* = 6.5 Hz, 2H), 3.18 (t, *J* = 7.2 Hz, 2H), 2.33 (p, *J* = 6.8 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 160.7, 153.8, 131.5, 128.6, 128.4, 128.2, 124.5, 123.3, 123.2, 120.0, 111.0, 101.0, 95.1, 79.4, 44.0, 30.6, 25.0.

HRMS (EI) calcd for $C_{19}H_{15}OCl$ $[M]^+$: 294.08059, found: 294.08011.

IR (Reflection): ṽ = 3060, 2959, 2923, 2869, 2220, 1946, 1895, 1733, 1589, 1491, 1475, 1454, 1443, 1387, 1276, 1235, 1177, 1108, 1087, 1069, 1028, 1008, 971, 929, 916, 867, 842, 810, 747, 690, 652.



2-(3-(Phenylethynyl)benzofuran-2-yl)propan-2-ol

3au, light yellow oil, 25.6 mg, 46% yield (unstable).

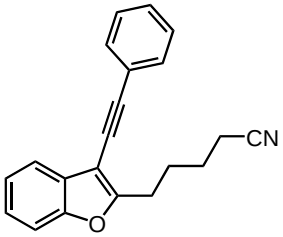
R_f = 0.5 (PE:EA = 5:1), chromatography eluent: 10% Ethyl acetate in petroleum ether.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.76 – 7.67 (m, 1H), 7.56 (dd, *J* = 6.5, 3.2 Hz, 2H), 7.51 – 7.44 (m, 1H), 7.41 – 7.35 (m, 3H), 7.35 – 7.29 (m, 2H), 2.54 (br, 1H), 1.82 (s, 6H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 164.2, 153.1, 131.4, 129.1, 128.44, 128.43, 125.0, 123.3, 123.1, 120.3, 111.2, 98.0, 96.3, 79.5, 71.1, 29.0.

HRMS (EI) calcd for $C_{19}H_{16}O_2$ $[M]^+$: 276.11448, found: 276.11475.

IR (Reflection): ṽ = 3450, 3061, 2981, 2929, 2218, 1805, 1730, 1597, 1490, 1475, 1454, 1382, 1334, 1259, 1236, 1132, 1109, 1081, 1007, 960, 912, 865, 806, 748, 690.



5-(3-(Phenylethynyl)benzofuran-2-yl)pentanenitrile

3av, light yellow oil, 43.6 mg, 73% yield.

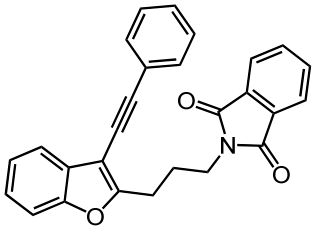
R_f = 0.5 (PE:EA = 5:1), chromatography eluent: 10% Ethyl acetate in petroleum ether.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.70 – 7.64 (m, 1H), 7.61 – 7.54 (m, 2H), 7.48 – 7.42 (m, 1H), 7.42 – 7.35 (m, 3H), 7.34 – 7.27 (m, 2H), 3.04 (t, *J* = 7.1 Hz, 2H), 2.42 (t, *J* = 7.1 Hz, 2H), 2.02 (ddd, *J* = 19.5, 9.8, 5.1 Hz, 2H), 1.85 – 1.71 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 160.9, 153.8, 131.4, 128.5, 128.4, 128.3, 124.5, 123.2, 123.2, 119.9, 119.3, 111.0, 100.8, 95.0, 79.4, 26.6, 26.5, 24.5, 16.8.

HRMS (EI) calcd for $C_{21}H_{17}NO$ $[M]^+$: 299.13047, found: 299.13030.

IR (Reflection): ṽ = 3059, 2949, 2868, 2246, 2219, 1731, 1588, 1491, 1475, 1454, 1427, 1328, 1270, 1235, 1178, 1110, 1093, 1069, 1045, 1008, 930, 848, 750, 691, 651.



2-(3-(3-(Phenylethynyl)benzofuran-2-yl)propyl)isoindoline-1,3-dione

3aw, light yellow oil, 48.1 mg, 59% yield.

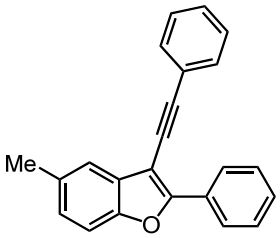
R_f = 0.3 (PE:EA = 5:1), chromatography eluent: 20% Ethyl acetate in petroleum ether.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (dd, *J* = 5.5, 3.0 Hz, 2H), 7.67 (dd, *J* = 5.4, 3.1 Hz, 2H), 7.63 – 7.58 (m, 1H), 7.56 – 7.51 (m, 2H), 7.41 – 7.32 (m, 4H), 7.29 – 7.22 (m, 2H), 3.87 (t, *J* = 7.1 Hz, 2H), 3.07 (t, *J* = 7.6 Hz, 2H), 2.34 – 2.24 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.2, 160.9, 153.7, 133.8, 132.0, 131.4, 128.5, 128.3, 128.1, 124.3, 123.3, 123.1, 123.1, 119.8, 111.0, 100.6, 95.1, 79.5, 37.6, 26.4, 25.3.

HRMS (EI) calcd for $C_{27}H_{19}NO_3$ $[M]^+$: 405.13594, found: 405.13705.

IR (Reflection): $\tilde{\nu}$ = 3466, 3060, 2934, 2849, 2253, 2220, 1773, 1717, 1588, 1491, 1467, 1454, 1397, 1370, 1236, 1173, 1105, 1078, 1021, 910, 885, 793, 752, 719, 691, 651.



5-Methyl-2-phenyl-3-(phenylethynyl)benzofuran

3ax, colorless solid, 55.6 mg, 90% yield.

R_f = 0.5 (PE:DCM = 10:1), chromatography eluent: 5% Petroleum ether in dichlormethan.

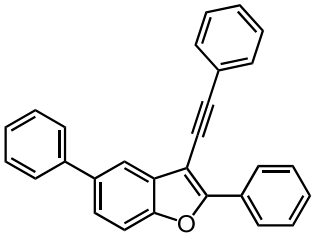
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.48 – 8.25 (m, 2H), 7.68 (d, *J* = 6.6 Hz, 2H), 7.56 – 7.51 (m, 3H), 7.48 – 7.38 (m, 5H), 7.18 (d, *J* = 8.3 Hz, 1H), 2.52 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 156.4, 152.0, 133.0, 131.5, 130.3, 129.9, 129.0, 128.6, 128.45, 128.36, 126.6, 126.0, 123.5, 120.1, 110.7, 98.9, 96.6, 81.4, 21.3.

HRMS (EI) calcd for $C_{23}H_{16}O$ $[M]^+$: 308.11957, found: 308.11779.

IR (ATR): $\tilde{\nu}$ = 3055, 3027, 2921, 2214, 1944, 1736, 1599, 1561, 1474, 1443, 1383, 1321, 1262, 1243, 1204, 1178, 1163, 1113, 1096, 1069, 1027, 998, 940, 913, 871, 832, 821, 794, 765, 750, 686, 655, 619.

M.p. (amorphous) 126.5-128.2 °C.



2,5-Diphenyl-3-(phenylethynyl)benzofuran

3ay, light yellow solid, 57.7 mg, 78% yield.

R_f = 0.4 (PE:DCM = 30:1), chromatography eluent: 2% Dichloromethane in petroleum ether.

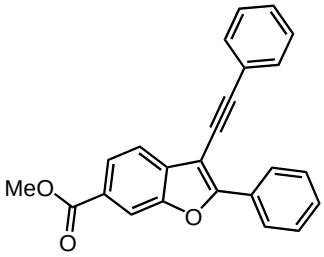
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.49 – 8.32 (m, 2H), 7.95 (s, 1H), 7.76 – 7.64 (m, 4H), 7.60 (d, *J* = 1.0 Hz, 2H), 7.58 – 7.36 (m, 9H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 156.9, 153.1, 141.4, 137.2, 131.6, 130.4, 130.1, 129.2, 128.7, 128.7, 128.5, 127.5, 127.0, 126.0, 125.0, 123.3, 118.8, 111.3, 99.4, 97.0, 81.1.

HRMS (EI) calcd for $C_{28}H_{18}O$ $[M]^+$: 370.13522, found: 370.13275.

IR (ATR): ṽ = 3055, 3032, 2211, 1954, 1877, 1739, 1600, 1555, 1485, 1463, 1442, 1385, 1272, 1253, 1222, 1199, 1133, 1113, 1072, 1024, 913, 880, 817, 759, 747, 688, 665, 629.

M.p. (amorphous) 101.1-101.8 °C.



Methyl 2-phenyl-3-(phenylethynyl)benzofuran-6-carboxylate

3az, light yellow solid, 7.8 mg, 11% yield, 67% recovered yield of methyl 3-hydroxy-4-(phenylethynyl)benzoate **1az.**

R_f = 0.5 (PE:DCM = 1:1), chromatography eluent: 30% Dichlormethan in petroleum ether.

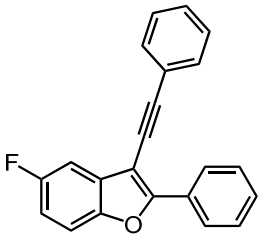
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.34 (d, *J* = 7.3 Hz, 2H), 8.19 (s, 1H), 8.02 (dd, *J* = 8.2, 1.1 Hz, 1H), 7.75 (d, *J* = 8.2 Hz, 1H), 7.63 (dd, *J* = 6.5, 3.1 Hz, 2H), 7.52 (t, *J* = 7.3 Hz, 2H), 7.47 – 7.38 (m, 4H), 3.96 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 166.9, 158.8, 152.8, 134.1, 131.5, 129.8, 129.6, 128.7, 128.6, 128.5, 127.2, 126.3, 124.7, 123.0, 119.9, 112.8, 99.3, 97.2, 80.4, 52.2.

HRMS (EI) calcd for $C_{24}H_{16}O_3$ $[M]^+$: 352.10940, found: 352.11079.

IR (Reflection): ṽ = 3063, 2950, 2926, 2850, 2217, 1717, 1619, 1584, 1485, 1434, 1389, 1292, 1221, 1198, 1114, 1082, 984, 762, 688.

M.p. (amorphous) 133.4-135.1 °C.



5-Fluoro-2-phenyl-3-(phenylethynyl)benzofuran

3ba, colorless solid, 57.5 mg, 92% yield.

R_f = 0.3 (*n*-Hexane), chromatography eluent: *n*-Hexane.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.43 – 8.23 (m, 2H), 7.64 (dt, *J* = 4.3, 2.5 Hz, 2H), 7.52 (dd, *J* = 10.4, 4.7 Hz, 2H), 7.48 – 7.37 (m, 6H), 7.07 (td, *J* = 9.0, 2.6 Hz, 1H).

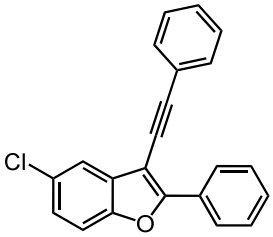
^{13}C NMR (101 MHz, $CDCl_3$) δ 159.7 (d, *J* = 239.9 Hz), 157.8, 149.7, 131.5, 130.9 (d, *J* = 10.6 Hz), 129.9, 129.4, 128.7, 128.6, 128.5, 126.1, 123.1, 113.0 (d, *J* = 26.5 Hz), 111.9 (d, *J* = 9.5 Hz), 106.0 (d, *J* = 25.5 Hz), 99.4 (d, *J* = 3.9 Hz), 97.1, 80.5.

^{19}F NMR (282 MHz, $CDCl_3$) δ -119.69.

HRMS (EI) calcd for $C_{22}H_{13}OF$ $[M]^+$: 312.09449, found: 312.09405.

IR (ATR): ṽ = 3058, 2219, 1956, 1887, 1854, 1732, 1697, 1598, 1561, 1488, 1470, 1444, 1385, 1334, 1277, 1247, 1198, 1179, 1159, 1116, 1096, 1070, 1026, 999, 952, 916, 848, 835, 823, 801, 777, 759, 739, 686, 660, 616.

M.p. (amorphous) 101.3-102.9 °C.



5-Chloro-2-phenyl-3-(phenylethynyl)benzofuran

3bb, colorless solid, 49.7 mg, 76% yield.

R_f = 0.6 (PE:DCM = 10:1), chromatography eluent: 5% Dichlormethan in petroleum ether.

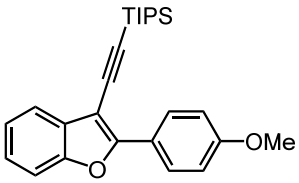
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.46 – 8.28 (m, 2H), 7.71 (d, *J* = 2.1 Hz, 1H), 7.64 (dd, *J* = 6.5, 3.2 Hz, 2H), 7.56 – 7.47 (m, 2H), 7.48 – 7.39 (m, 5H), 7.30 (dd, *J* = 8.7, 2.1 Hz, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 157.5, 151.8, 131.5, 131.3, 129.7, 129.5, 129.1, 128.7, 128.6, 128.5, 126.1, 125.5, 123.1, 120.0, 112.2, 98.8, 97.2, 80.3.

HRMS (EI) calcd for $C_{22}H_{13}OCl$ $[M]^+$: 328.06494, found: 328.06435.

IR (ATR): ṽ = 3059, 2925, 1945, 1860, 1728, 1603, 1585, 1573, 1559, 1500, 1485, 1441, 1385, 1322, 1258, 1232, 1201, 1111, 1092, 1068, 1048, 1027, 998, 919, 862, 831, 818, 802, 763, 750, 715, 680, 646, 611.

M.p. (amorphous) 108.6-109.9 °C.



Triisopropyl((2-(4-methoxyphenyl)benzofuran-3-yl)ethynyl)silane

3bc, light yellow solid, 49.5 mg, 61% yield.

R_f = 0.4 (PE:DCM = 10:1), chromatography eluent: 5% Petroleum ether in dichlormethan.

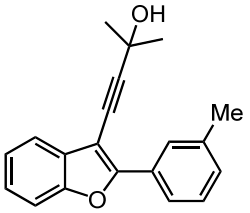
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.35 (d, *J* = 8.9 Hz, 2H), 7.65 (dd, *J* = 6.2, 2.8 Hz, 1H), 7.48 (dd, *J* = 6.2, 2.9 Hz, 1H), 7.35 – 7.28 (m, 2H), 6.99 (d, *J* = 8.9 Hz, 2H), 3.89 (s, 3H), 1.23 (s, 21H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 160.4, 157.1, 153.1, 130.4, 127.7, 124.8, 123.3, 123.0, 120.0, 113.9, 110.9, 98.8, 98.7, 97.8, 55.3, 18.7, 11.4.

HRMS (EI) calcd for $C_{26}H_{32}O_2Si$ $[M]^+$: 404.21661, found: 404.21954.

IR (Reflection): ṽ = 3066, 2942, 2891, 2864, 2152, 1735, 1609, 1565, 1508, 1454, 1422, 1370, 1305, 1255, 1203, 1178, 1136, 1105, 1071, 1033, 996, 920, 883, 833, 807, 786, 772, 745, 677, 660, 635, 624, 606.

M.p. (amorphous) 57.6-58.7 °C.



2-Methyl-4-(2-(m-tolyl)benzofuran-3-yl)but-3-yn-2-ol

3bd, light yellow solid, 44.6 mg, 77% yield.

R_f = 0.3 (PE:DCM = 1:2), chromatography eluent: 50% Dichloromethane in petroleum ether.

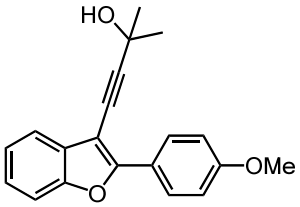
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.13 (s, 1H), 8.06 (d, *J* = 7.9 Hz, 1H), 7.65 (dd, *J* = 6.6, 2.2 Hz, 1H), 7.50 (dd, *J* = 6.9, 1.7 Hz, 1H), 7.43 – 7.27 (m, 3H), 7.22 (d, *J* = 7.6 Hz, 1H), 2.45 (s, 3H), 2.29 (br, 1H), 1.75 (s, 6H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 156.6, 153.4, 138.2, 130.0, 129.9, 129.8, 128.5, 126.5, 125.2, 123.3, 123.0, 120.1, 111.1, 101.2, 98.3, 74.2, 66.0, 31.5, 21.5.

HRMS (EI) calcd for $C_{20}H_{18}O_2$ $[M]^+$: 290.13013, found: 290.13042.

IR (ATR): ṽ = 3308, 3040, 2980, 2926, 2222, 1933, 1889, 1850, 1609, 1565, 1452, 1371, 1293, 1259, 1228, 1185, 1161, 1141, 1109, 1092, 1068, 1042, 1006, 955, 909, 872, 787, 772, 743, 697, 678, 646, 628.

M.p. (amorphous) 71.0-72.1 °C.



4-(2-(4-Methoxyphenyl)benzofuran-3-yl)-2-methylbut-3-yn-2-ol

3be, light yellow oil, 35.9 mg, 59% yield.

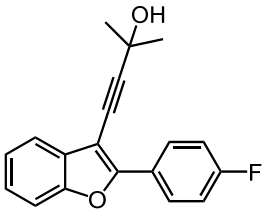
R_f = 0.2 (PE:DCM = 1:2), chromatography eluent: 30% Petroleum ether in dichloromethane.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 – 8.14 (m, 2H), 7.67 – 7.57 (m, 1H), 7.51 – 7.40 (m, 1H), 7.34 – 7.24 (m, 2H), 7.06 – 6.95 (m, 2H), 3.87 (s, 3H), 2.15 (br, 1H), 1.74 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 160.4, 156.7, 153.2, 130.0, 127.5, 124.8, 123.2, 122.9, 119.8, 114.1, 110.9, 100.8, 96.7, 74.4, 66.0, 55.3, 31.6.

HRMS (EI) calcd for $C_{20}H_{18}O_3$ $[M]^+$: 306.12505, found: 306.12563.

IR (Reflection): ṽ = 3390, 2979, 2933, 2837, 2223, 1731, 1608, 1509, 1455, 1422, 1379, 1304, 1253, 1223, 1203, 1178, 1105, 1067, 1030, 957, 896, 833, 785, 772, 745.



4-(2-(4-Fluorophenyl)benzofuran-3-yl)-2-methylbut-3-yn-2-ol

3bf, colorless solid, 52.7 mg, 90% yield.

R_f = 0.3 (PE:DCM = 1:2), chromatography eluent: 50% Dichloromethane in petroleum ether.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.23 (dd, *J* = 8.7, 5.4 Hz, 2H), 7.63 (d, *J* = 7.4 Hz, 1H), 7.47 (d, *J* = 8.1 Hz, 1H), 7.31 (ddd, *J* = 21.3, 11.0, 4.1 Hz, 2H), 7.16 (t, *J* = 8.6 Hz, 2H), 2.34 (br, 1H), 1.74 (s, 6H).

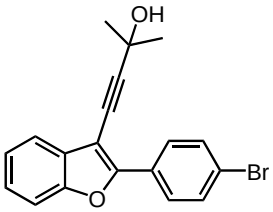
^{13}C NMR (151 MHz, $CDCl_3$) δ 163.0 (d, *J* = 250.4 Hz), 155.4, 153.3, 129.7, (d, *J* = 8.2 Hz), 126.31 (d, *J* = 3.3 Hz), 125.3, 123.4, 120.1, 115.8, 115.6, 111.1, 101.3, 98.11 (d, *J* = 1.3 Hz), 73.9, 66.0, 31.5.

^{19}F NMR (282 MHz, $CDCl_3$) δ -63.07.

HRMS (EI) calcd for $C_{19}H_{15}O_2F$ $[M]^+$: 294.10506, found: 294.10474.

IR (ATR): $\tilde{\nu}$ = 3284, 3064, 2977, 2929, 2861, 2232, 1731, 1601, 1574, 1505, 1477, 1454, 1377, 1361, 1303, 1257, 1228, 1203, 1156, 1110, 1098, 1064, 1013, 953, 897, 834, 798, 773, 738, 659, 627, 606.

M.p. (amorphous) 84.6-86.9 ºC.



4-(2-(4-Bromophenyl)benzofuran-3-yl)-2-methylbut-3-yn-2-ol

3bg, light yellow solid, 63.8 mg, 90% yield.

R_f = 0.3 (PE:DCM = 1:1), chromatography eluent: 50% Dichloromethane in petroleum ether.

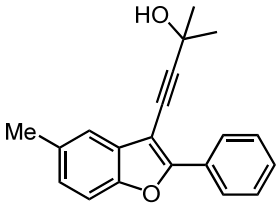
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 – 7.99 (m, 2H), 7.62 (dd, *J* = 7.5, 0.9 Hz, 1H), 7.60 – 7.55 (m, 2H), 7.46 (d, *J* = 7.7 Hz, 1H), 7.37 – 7.23 (m, 2H), 2.41 (br, 1H), 1.73 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 155.2, 153.4, 131.8, 129.7, 128.9, 127.2, 125.6, 123.5, 123.2, 120.2, 111.2, 102.0, 99.1, 73.8, 66.0, 31.5.

HRMS (EI) calcd for $C_{19}H_{15}O_2Br$ $[M]^+$: 354.02499, found: 354.02361.

IR (ATR): $\tilde{\nu}$ = 3295, 2979, 2928, 2221, 1579, 1489, 1450, 1399, 1375, 1340, 1253, 1225, 1200, 1142, 1103, 1075, 1061, 1007, 959, 893, 828, 775, 743, 707, 651, 632.

M.p. (amorphous) 105.4-107.2 ºC.



2-Methyl-4-(5-methyl-2-phenylbenzofuran-3-yl)but-3-yn-2-ol

3bh, colorless solid, 41.9 mg, 72% yield.

R_f = 0.3 (PE:DCM = 1:2), chromatography eluent: 30% Petroleum ether in dichloromethane.

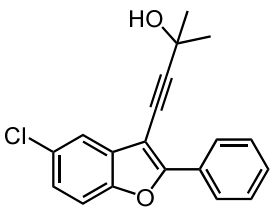
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 – 8.16 (m, 2H), 7.52 – 7.45 (m, 2H), 7.44 – 7.34 (m, 3H), 7.13 (dd, *J* = 8.4, 1.3 Hz, 1H), 2.48 (s, 3H), 2.17 (br, 1H), 1.75 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 156.5, 151.9, 132.9, 130.2, 129.9, 129.0, 128.5, 126.6, 125.8, 119.9, 110.6, 101.2, 98.2, 74.3, 66.0, 31.5, 21.3.

HRMS (EI) calcd for $C_{20}H_{18}O_2$ $[M]^+$: 290.13013, found: 290.13149.

IR (ATR): $\tilde{\nu}$ = 3453, 2980, 2922, 2863, 2227, 1600, 1562, 1475, 1443, 1371, 1314, 1282, 1260, 1230, 1205, 1159, 1121, 1098, 1065, 1026, 957, 940, 915, 891, 873, 831, 792, 769, 748, 680, 645, 620.

M.p. (amorphous) 116.0-118.2 ºC.



4-(5-Chloro-2-phenylbenzofuran-3-yl)-2-methylbut-3-yn-2-ol

3bi, light yellow solid, 38.6 mg, 62% yield.

R_f = 0.3 (PE:DCM = 1:2), chromatography eluent: 30% Petroleum ether in dichloromethane.

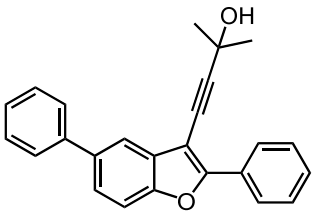
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (dd, *J* = 5.3, 3.3 Hz, 2H), 7.58 (d, *J* = 2.1 Hz, 1H), 7.51 – 7.45 (m, 2H), 7.42 (dt, *J* = 4.7, 1.9 Hz, 1H), 7.38 (d, *J* = 8.7 Hz, 1H), 7.26 (dd, *J* = 8.7, 2.1 Hz, 1H), 2.25 (br, 1H), 1.74 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 157.6, 151.7, 131.2, 129.57, 129.55, 129.1, 128.6, 126.0, 125.5, 119.8, 112.1, 101.8, 98.1, 73.4, 66.0, 31.5.

HRMS (EI) calcd for $C_{19}H_{15}O_2Cl$ $[M]^+$: 310.07551, found: 310.07484.

IR (ATR): ṽ = 3464, 2980, 2359, 2251, 1583, 1452, 1441, 1375, 1318, 1259, 1223, 1204, 1165, 1079, 1052, 1027, 958, 908, 872, 831, 800, 782, 770, 735, 703, 683, 650.

M.p. (amorphous) 93.9-95.7 ºC.



4-(2,5-Diphenylbenzofuran-3-yl)-2-methylbut-3-yn-2-ol

3bj, light yellow oil, 48.9 mg, 69% yield.

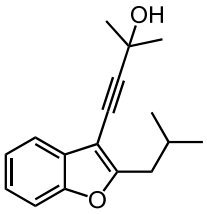
R_f = 0.4 (PE:EA = 5:1), chromatography eluent: 20% Ethyl acetate in petroleum ether.

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.35 – 8.23 (m, 2H), 7.81 (s, 1H), 7.71 – 7.63 (m, 2H), 7.57 – 7.45 (m, 6H), 7.40 (ddd, *J* = 10.7, 8.4, 6.2 Hz, 2H), 2.23 (br, 1H), 1.76 (s, 6H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 157.0, 153.0, 141.3, 137.1, 130.3, 130.0, 129.2, 128.7, 128.6, 127.5, 127.0, 125.9, 125.0, 118.5, 111.2, 101.5, 98.7, 74.0, 66.0, 31.5.

HRMS (EI) calcd for $C_{25}H_{20}O_2$ $[M]^+$: 352.14578, found: 352.14501.

IR (ATR): ṽ = 3338, 3061, 2980, 2931, 2224, 1951, 1879, 1737, 1601, 1495, 1465, 1445, 1375, 1243, 1217, 1162, 1065, 1028, 958, 915, 881, 814, 785, 762, 749, 690, 625.



4-(2-Isobutylbenzofuran-3-yl)-2-methylbut-3-yn-2-ol

3bk, light yellow oil, 37.9 mg, 74% yield.

R_f = 0.3 (PE:DCM = 1:1), chromatography eluent: 50% Petroleum ether in dichloromethane.

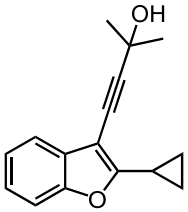
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 – 7.53 (m, 1H), 7.44 – 7.37 (m, 1H), 7.29 – 7.22 (m, 2H), 2.76 (d, *J* = 7.1 Hz, 2H), 2.20 (dp, *J* = 13.6, 6.8 Hz, 1H), 2.08 (br, 1H), 1.68 (s, 6H), 1.01 (d, *J* = 6.7 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 162.3, 153.7, 128.7, 124.1, 122.9, 119.6, 110.9, 100.2, 99.2, 73.0, 65.9, 36.5, 31.7, 28.2, 22.4.

HRMS (EI) calcd for $C_{17}H_{20}O_2$ $[M]^+$: 256.14578, found: 256.14706.

IR (Reflection): ṽ = 3346, 3064, 2958, 2931, 2870, 2228, 1731, 1596, 1455, 1368, 1275, 1231,

1167, 1103, 1070, 1007, 958, 926, 897, 870, 774, 746, 658, 638.



4-(2-Cyclopropylbenzofuran-3-yl)-2-methylbut-3-yn-2-ol

3bl, colorless oil, 14.9 mg, 31% yield.

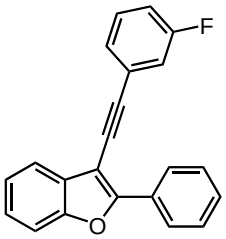
R_f = 0.2 (PE:DCM = 1:1), chromatography eluent: 50% Petroleum ether in dichloromethane.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 – 7.47 (m, 1H), 7.35 – 7.29 (m, 1H), 7.25 – 7.16 (m, 2H), 2.24 (tt, *J* = 8.4, 5.1 Hz, 1H), 2.04 (br, 1H), 1.68 (s, 6H), 1.24 – 1.18 (m, 2H), 1.08 (ddd, *J* = 11.2, 6.9, 4.3 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 163.0, 152.9, 129.2, 123.8, 123.0, 119.1, 110.7, 99.4, 98.1, 72.8, 65.9, 31.7, 9.4, 7.9.

HRMS (EI) calcd for $C_{16}H_{16}O_2$ $[M]^+$: 240.11448, found: 240.11643.

IR (ATR): $\tilde{\nu}$ = 3349, 3091, 2980, 2931, 2866, 2227, 1893, 1731, 1594, 1475, 1457, 1401, 1362, 1326, 1282, 1265, 1223, 1199, 1163, 1096, 1048, 1026, 1007, 958, 943, 894, 868, 830, 811, 786, 773, 744, 687, 640, 625.



3-((3-fluorophenyl)ethynyl)-2-phenylbenzofuran

3bm, light yellow solid, 53.8 mg, 86% yield.

R_f = 0.4 (*n*-Hexane), chromatography eluent: *n*-Hexane.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 (dd, *J* = 5.3, 3.4 Hz, 1H), 7.79 – 7.72 (m, 1H), 7.57 – 7.50 (m, 2H), 7.48 – 7.30 (m, 3H), 7.11 (tdd, *J* = 8.5, 2.6, 1.4 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 162.5 (d, *J* = 246.8 Hz), 156.7, 153.5, 130.1, 130.0 (d, *J* = 2.9 Hz), 129.7, 129.3, 128.7, 127.4 (d, *J* = 3.0 Hz), 126.1, 125.4, 125.2 (d, *J* = 9.5 Hz), 123.5, 120.3, 118.2 (d, *J* = 22.7 Hz), 115.7 (d, *J* = 21.2 Hz), 111.2, 98.8, 95.4 (d, *J* = 3.4 Hz), 82.2.

^{19}F NMR (282 MHz, $CDCl_3$) δ -112.62.

HRMS (EI) calcd for $C_{22}H_{13}OF$ $[M]^+$: 312.09449, found: 312.09613.

IR (ATR): $\tilde{\nu}$ = 3069, 2211, 1935, 1781, 1739, 1609, 1578, 1483, 1456, 1432, 1384, 1342, 1293, 1262, 1203, 1176, 1155, 1109, 1094, 1070, 1027, 1008, 931, 897, 873, 828, 785, 745, 686, 661, 627.

M.p. (amorphous) 92.5-93.8 °C.

4. NMR Spectra

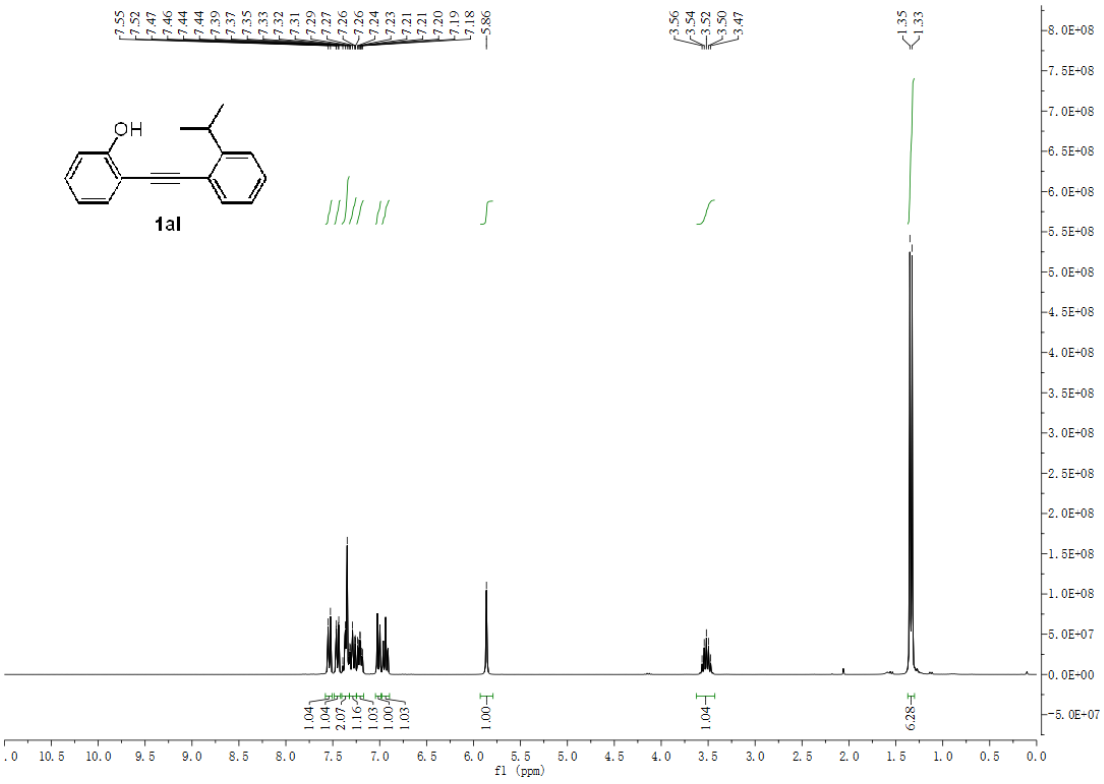


Figure S4. ^{1}H NMR (300 MHz, $CDCl_3$) spectra of **1al** in MestReNova.

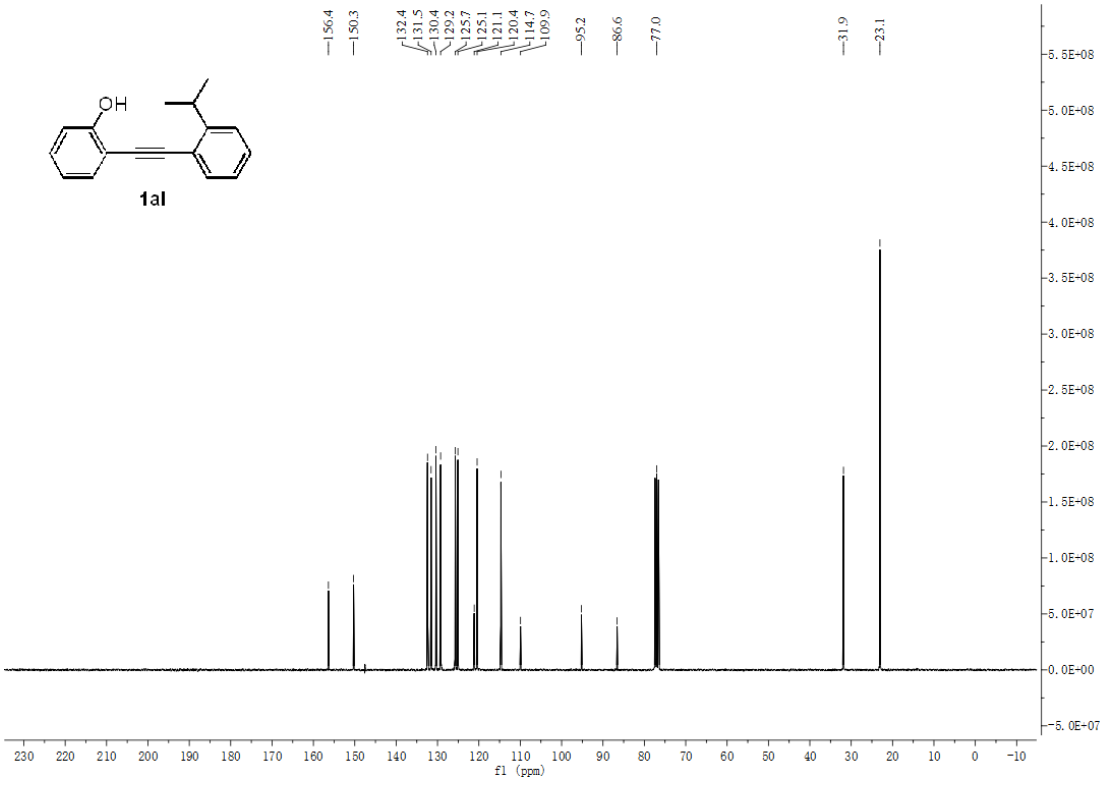


Figure S5. ^{13}C NMR (75 MHz, $CDCl_3$) spectra of **1al** in MestReNova.

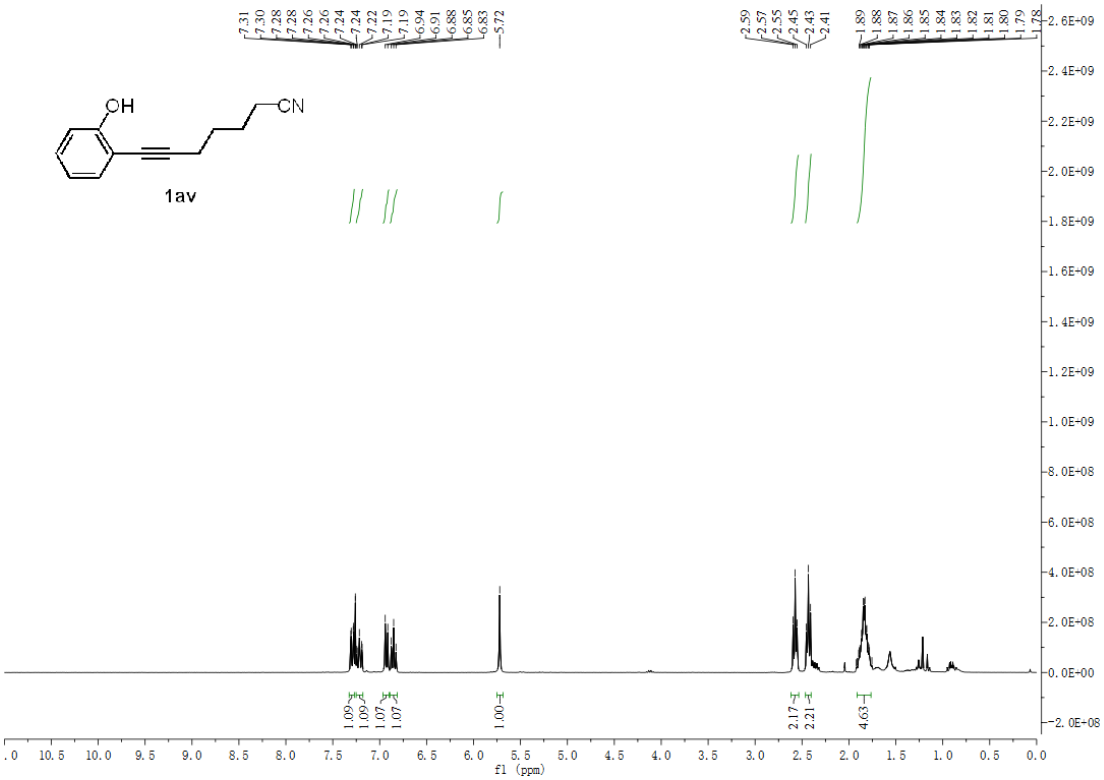


Figure S6. ^{1}H NMR (300 MHz, $CDCl_3$) spectra of **1av** in MestReNova.

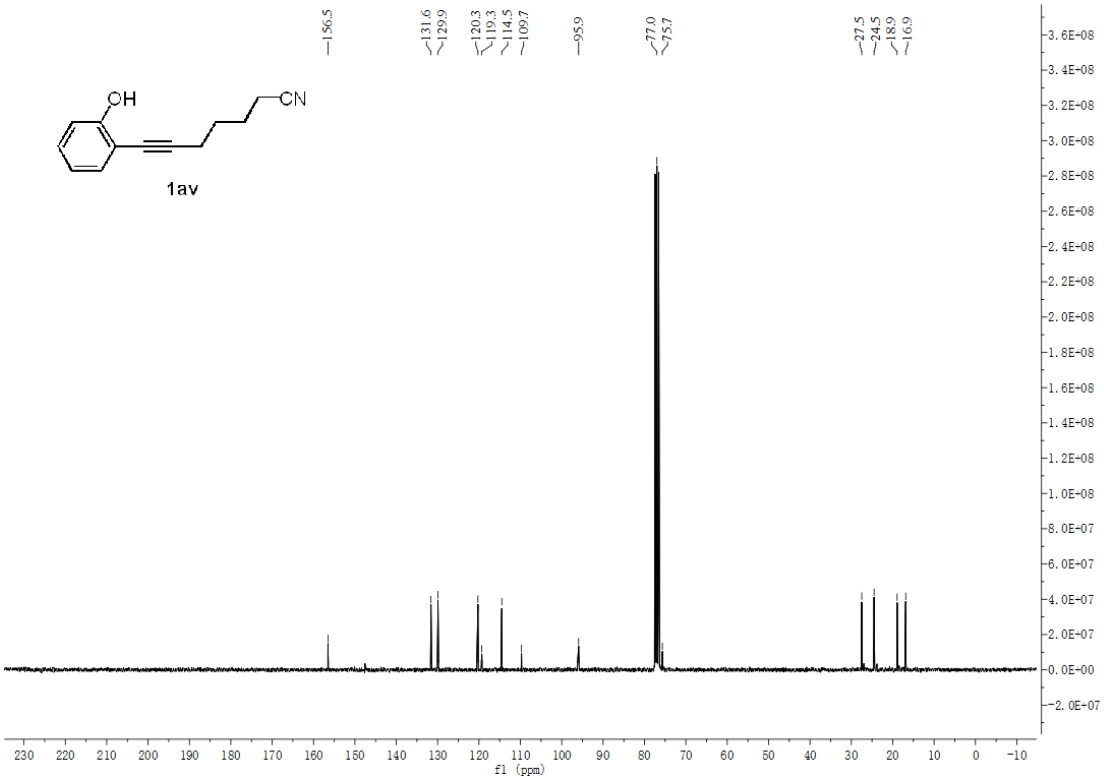


Figure S7. ^{13}C NMR (75 MHz, $CDCl_3$) spectra of **1aw** in MestReNova.

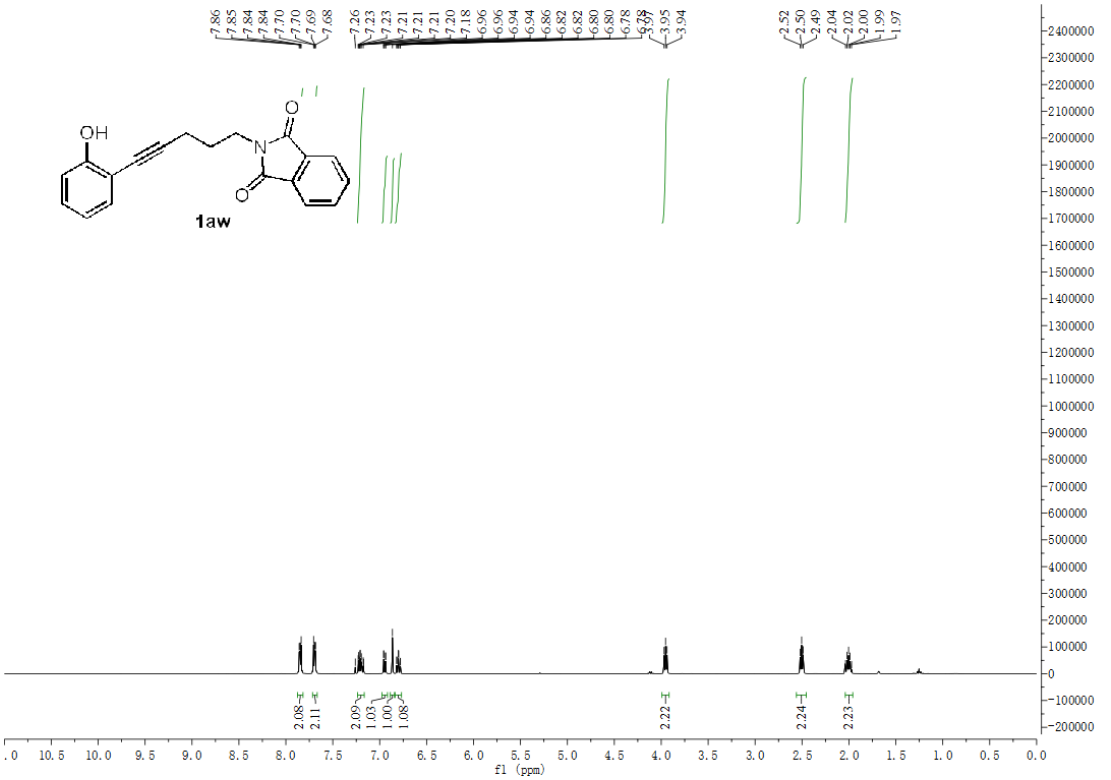


Figure S8. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of **1aw** in MestReNova.

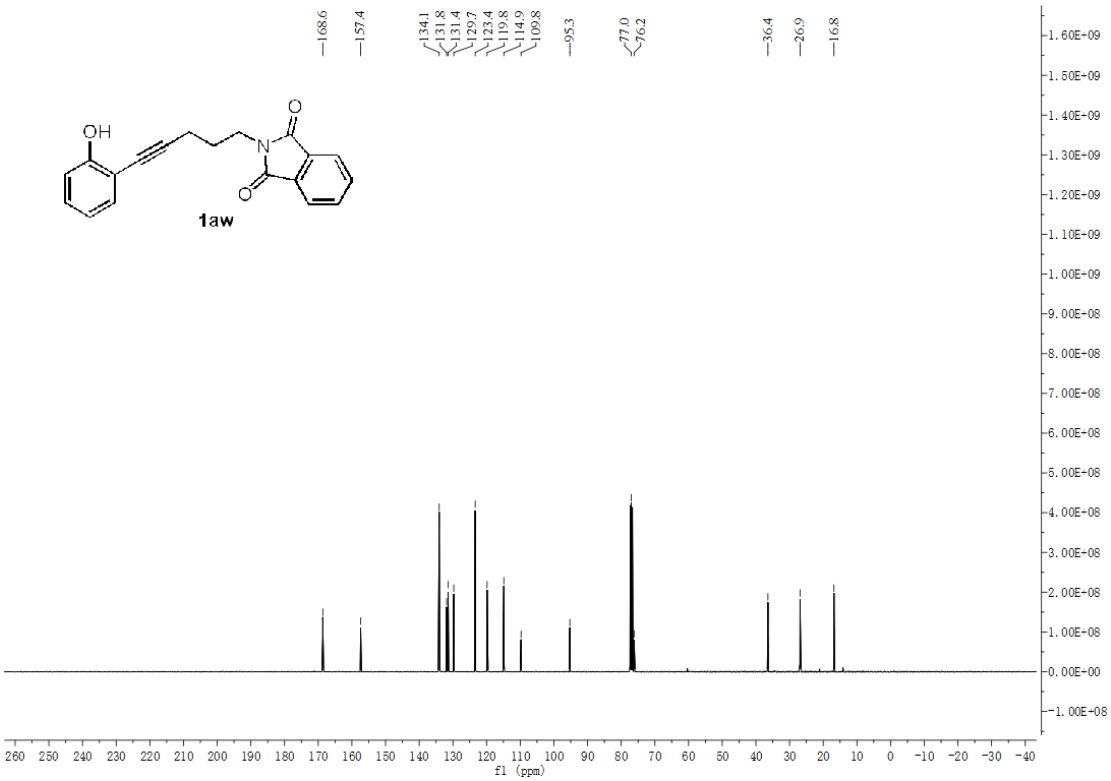


Figure S9. ^{13}C NMR (101 MHz, $CDCl_3$) spectra of **1aw** in MestReNova.

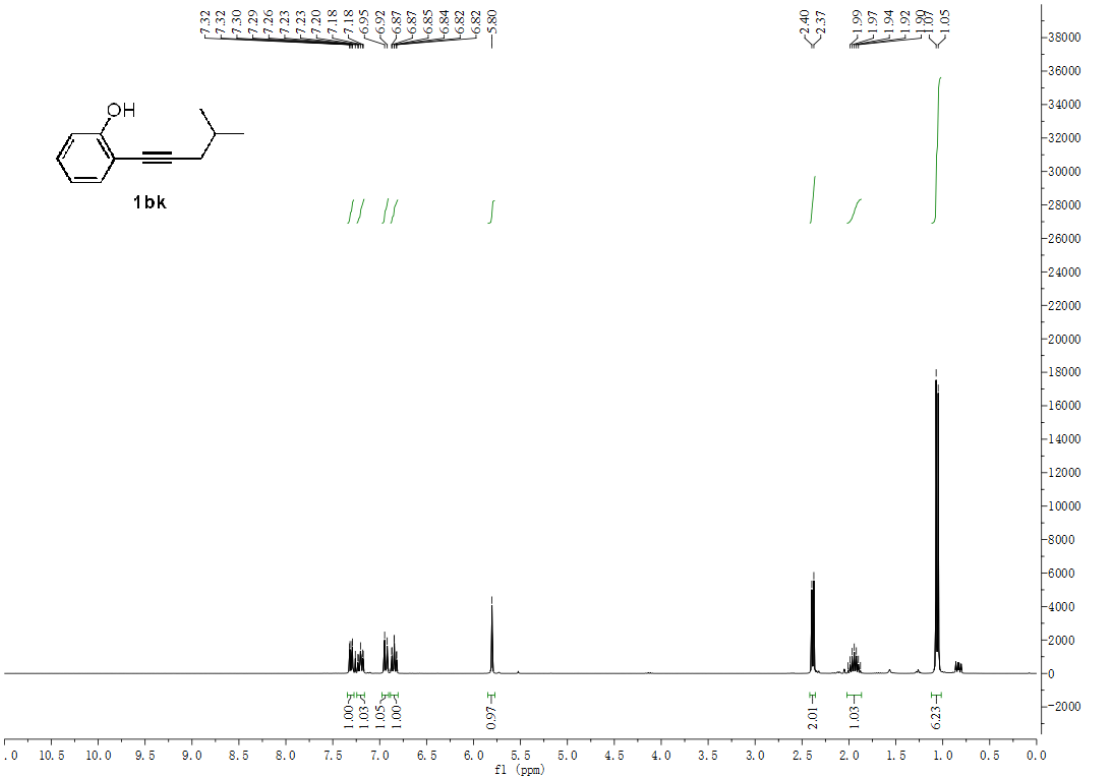


Figure S10. ^{1}H NMR (300 MHz, $CDCl_3$) spectra of **1bk** in MestReNova.

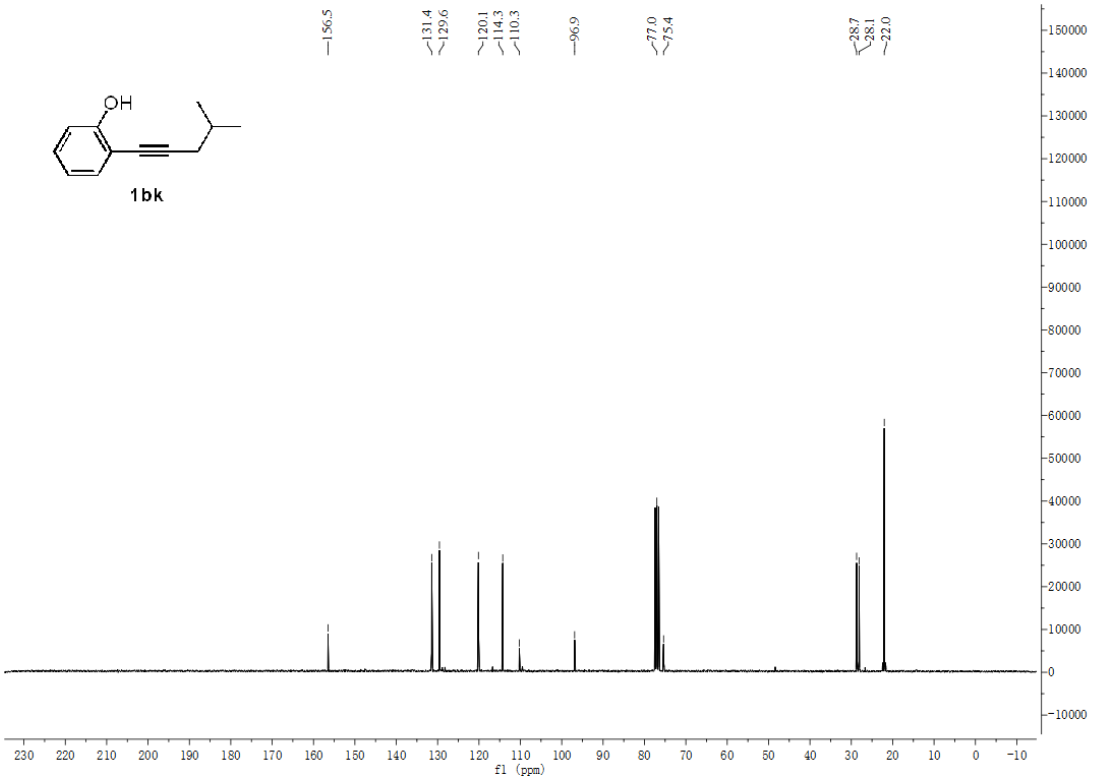


Figure S11. ^{13}C NMR (75 MHz, $CDCl_3$) spectra of **1bk** in MestReNova.

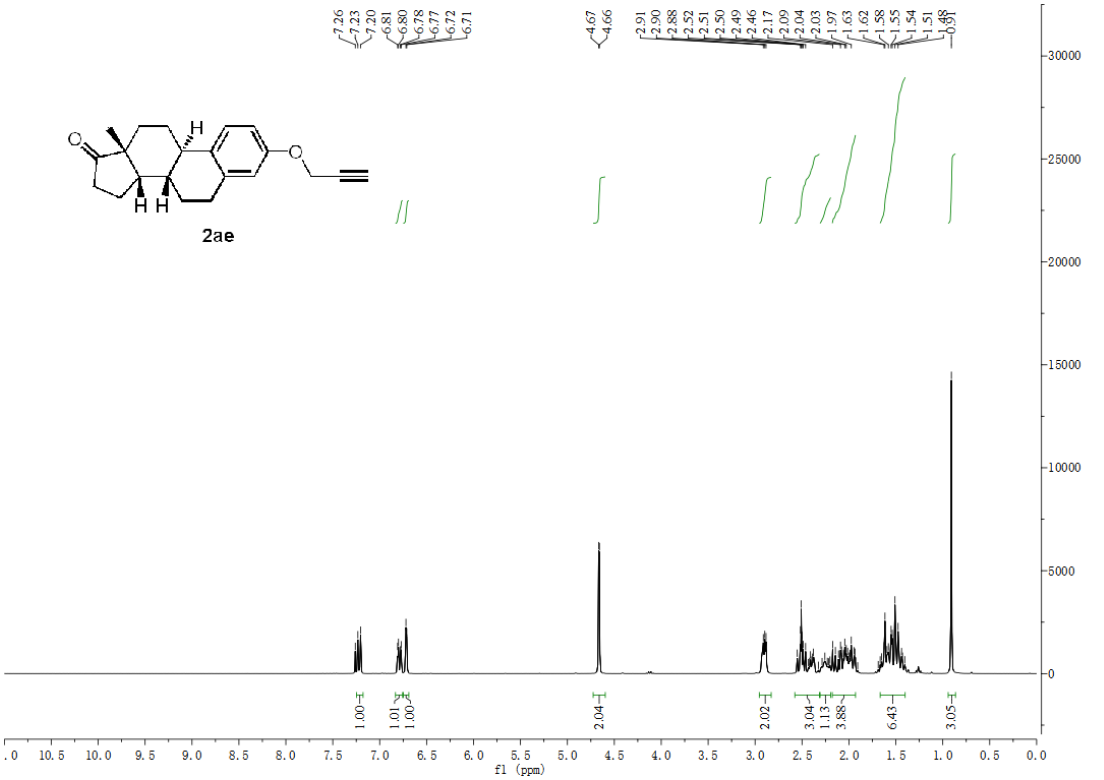


Figure S12. ^{1}H NMR (300 MHz, $CDCl_3$) spectra of **2ae** in MestReNova.

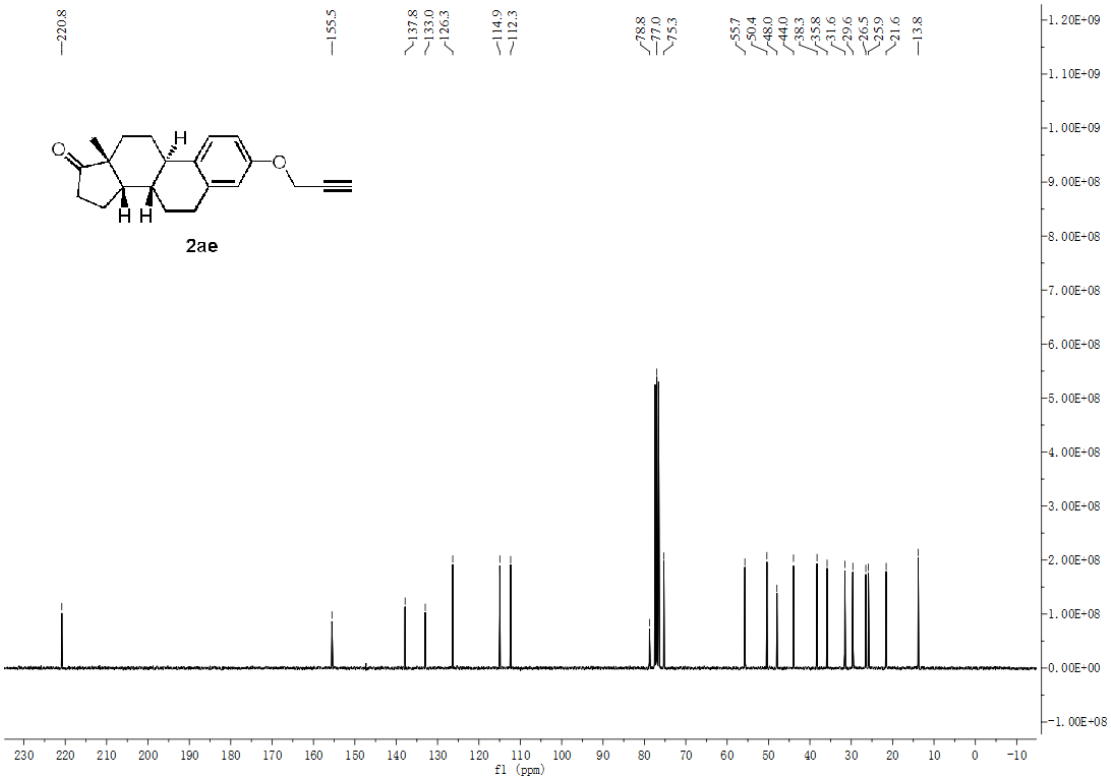


Figure S13. ^{13}C NMR (75 MHz, $CDCl_3$) spectra of **2ae** in MestReNova.

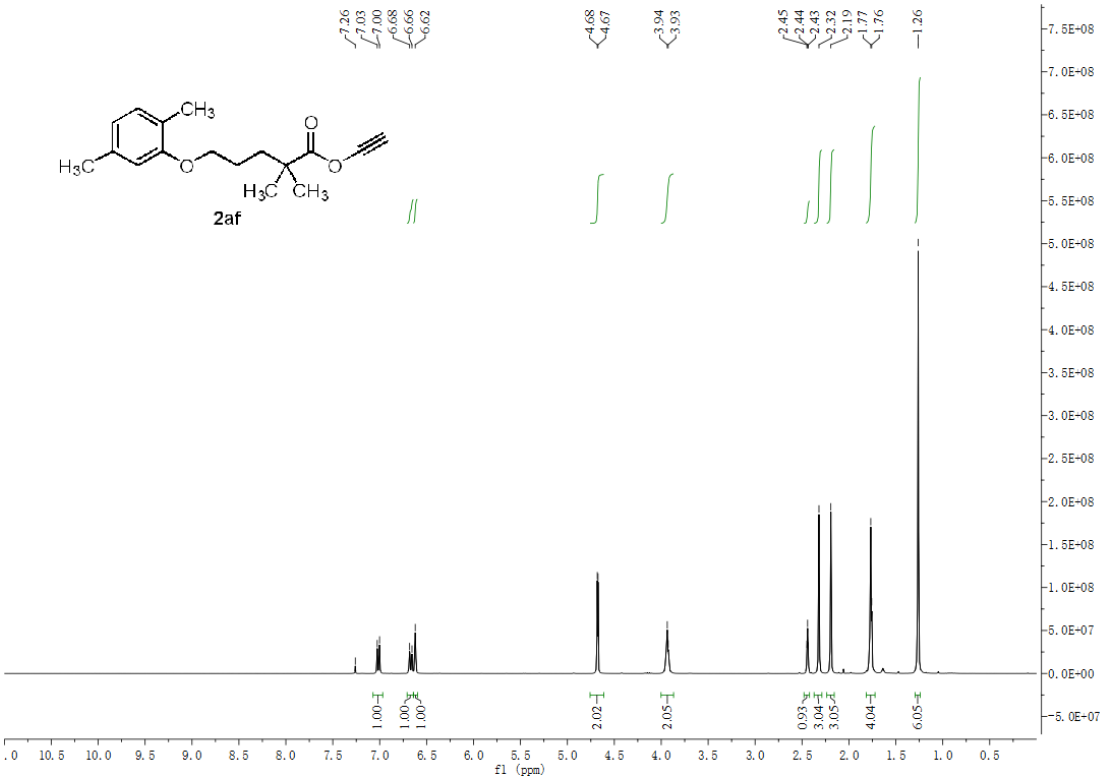


Figure S14. ^{1}H NMR (300 MHz, $CDCl_3$) spectra of **2af** in MestReNova.

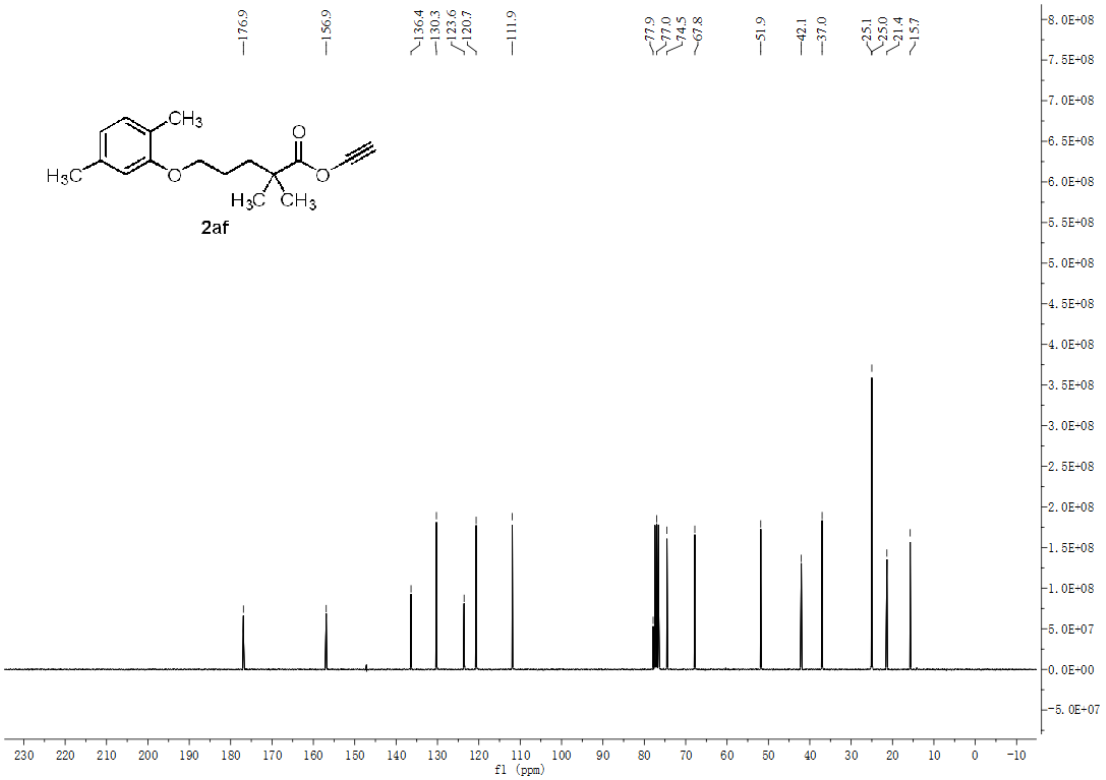


Figure S15. ^{13}C NMR (75 MHz, $CDCl_3$) spectra of **2af** in MestReNova.

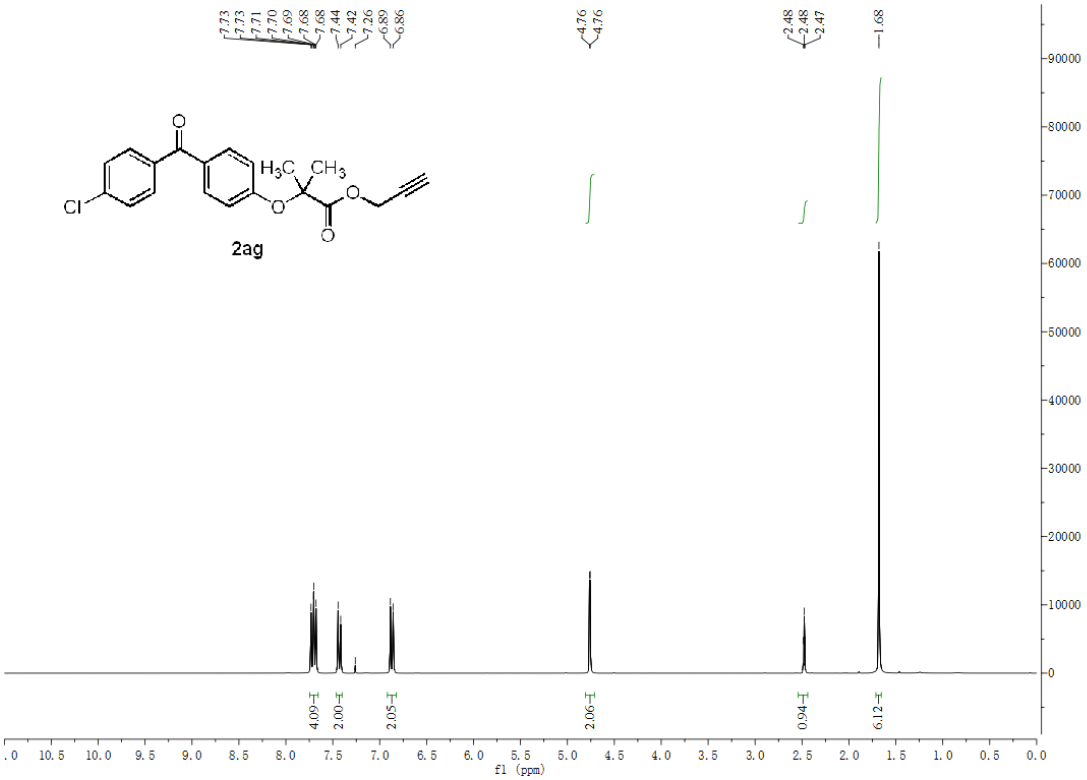


Figure S16. ^{1}H NMR (300 MHz, $CDCl_3$) spectra of **2ag** in MestReNova.

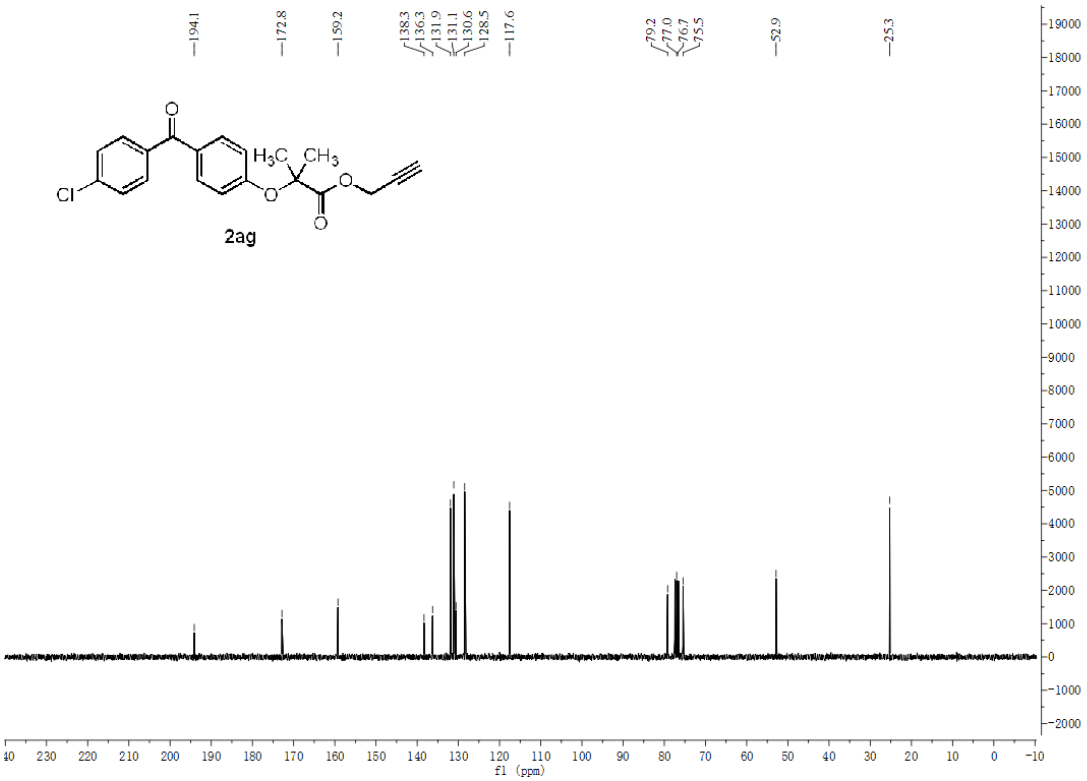


Figure S17. ^{13}C NMR (75 MHz, $CDCl_3$) spectra of **2ag** in MestReNova.

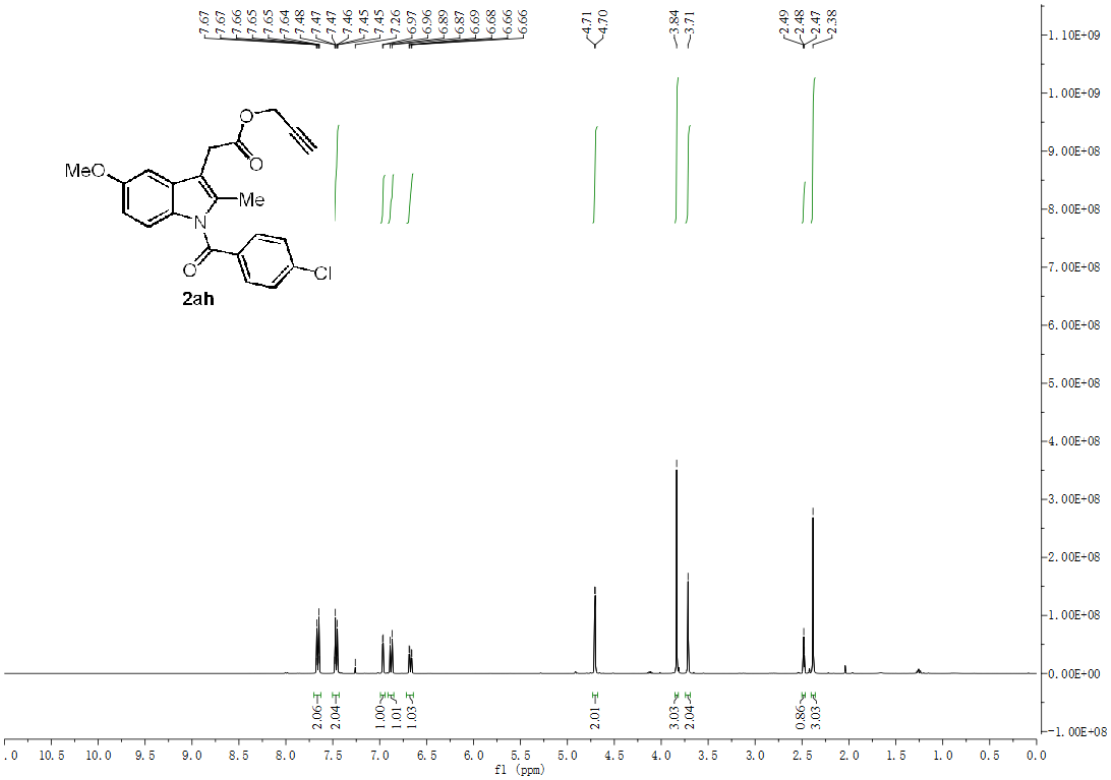


Figure S18. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of **2ah** in MestReNova.

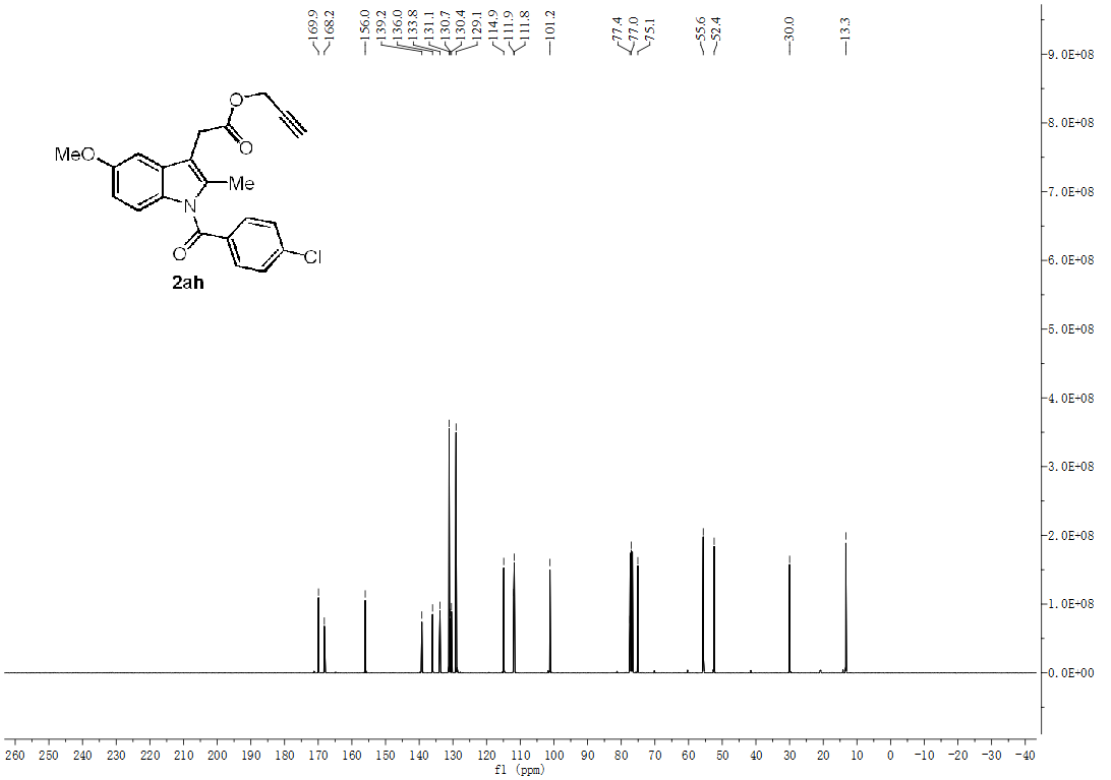


Figure S19. ^{13}C NMR (101 MHz, $CDCl_3$) spectra of **2ah** in MestReNova.

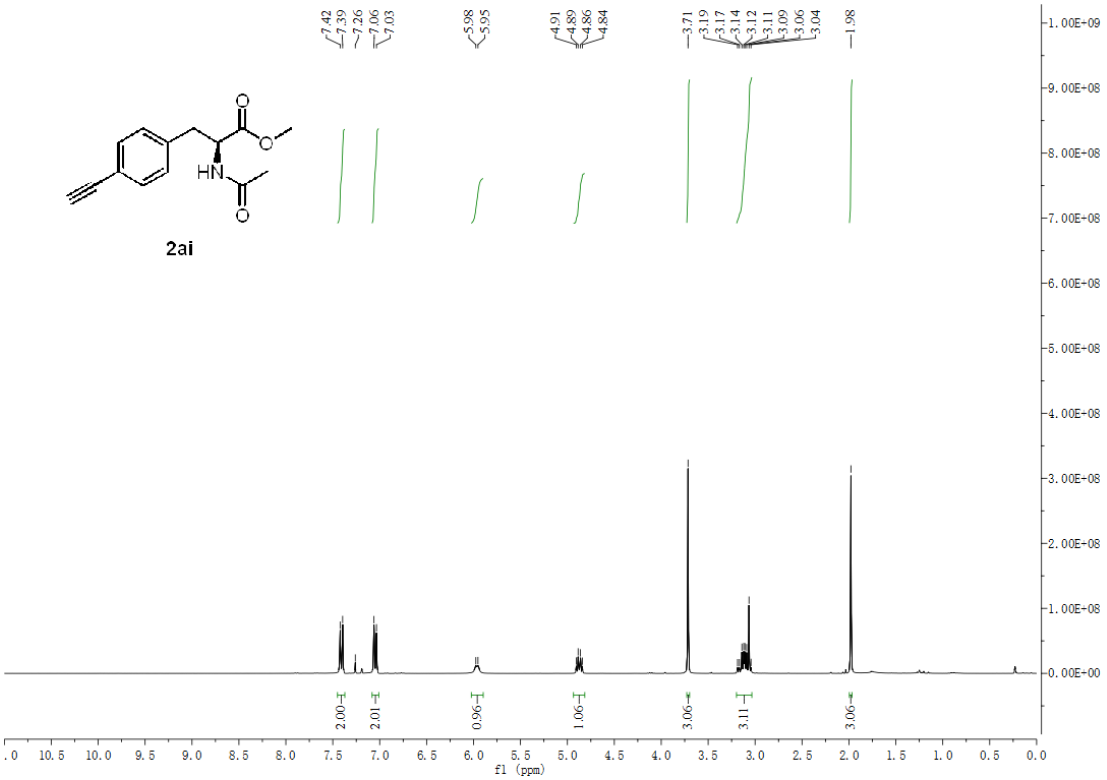


Figure S20. ^{1}H NMR (300 MHz, $CDCl_3$) spectra of **2ai** in MestReNova.

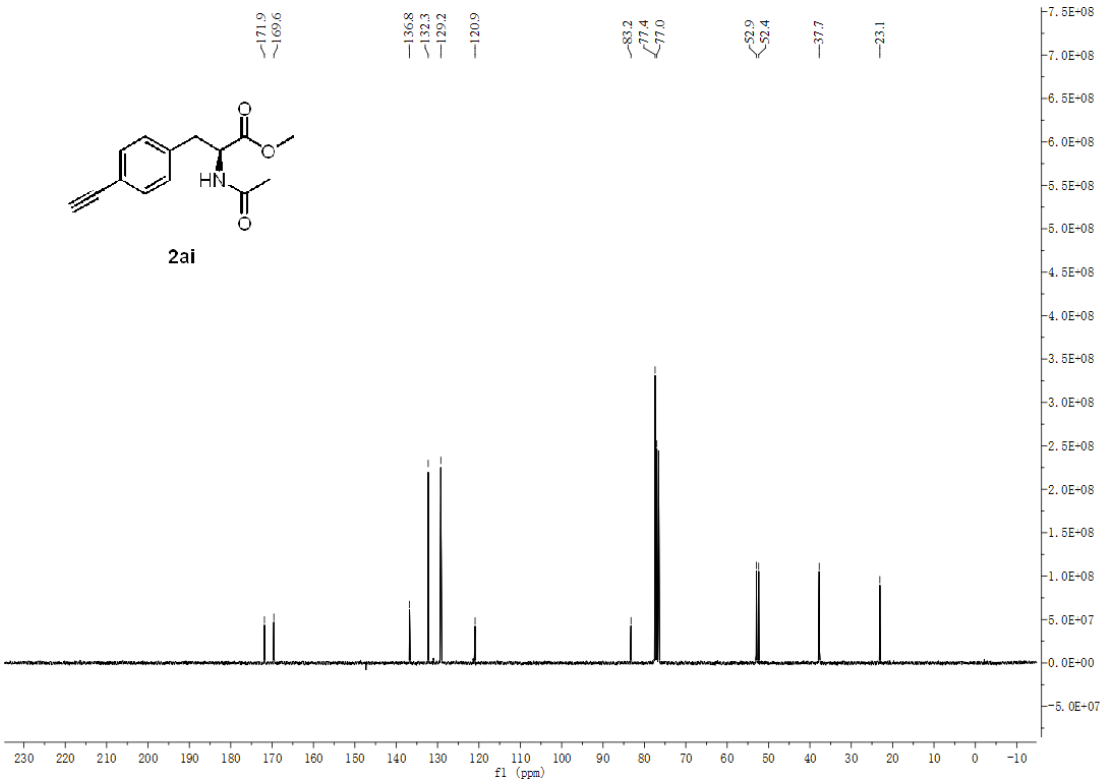


Figure S21. ^{13}C NMR (75 MHz, $CDCl_3$) spectra of **2ai** in MestReNova.

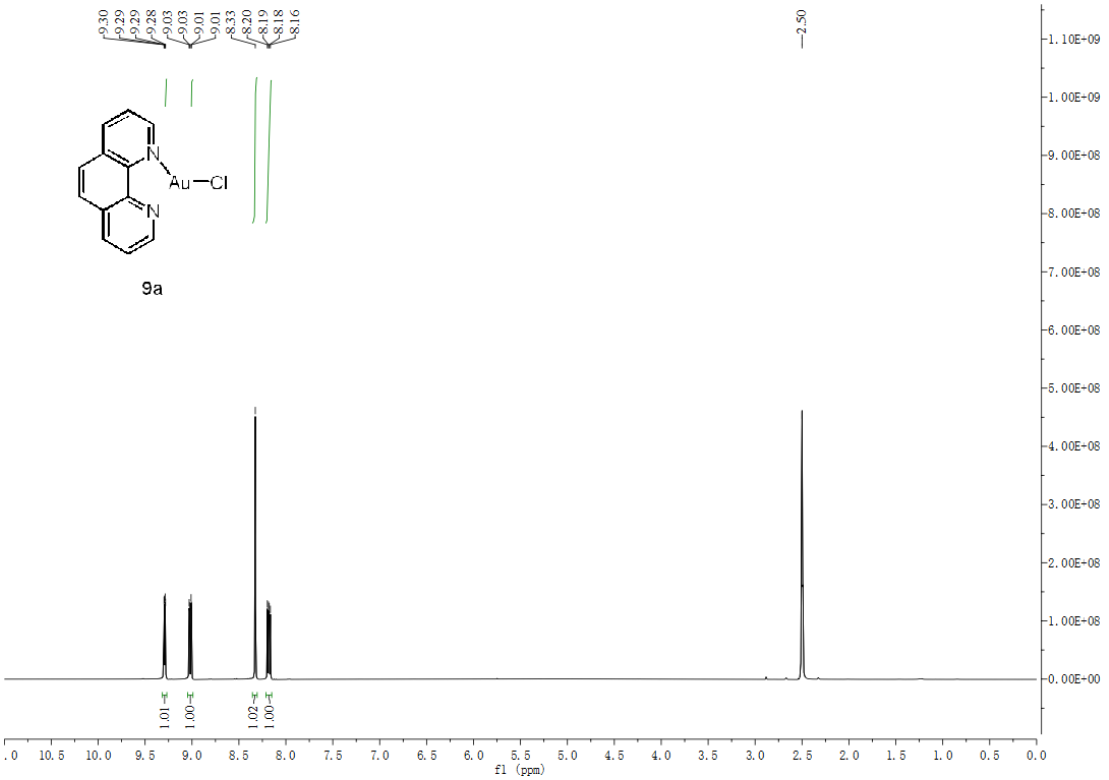


Figure S22. [1]H NMR (400 MHz, DMSO) spectra of **9a** in MestReNova.

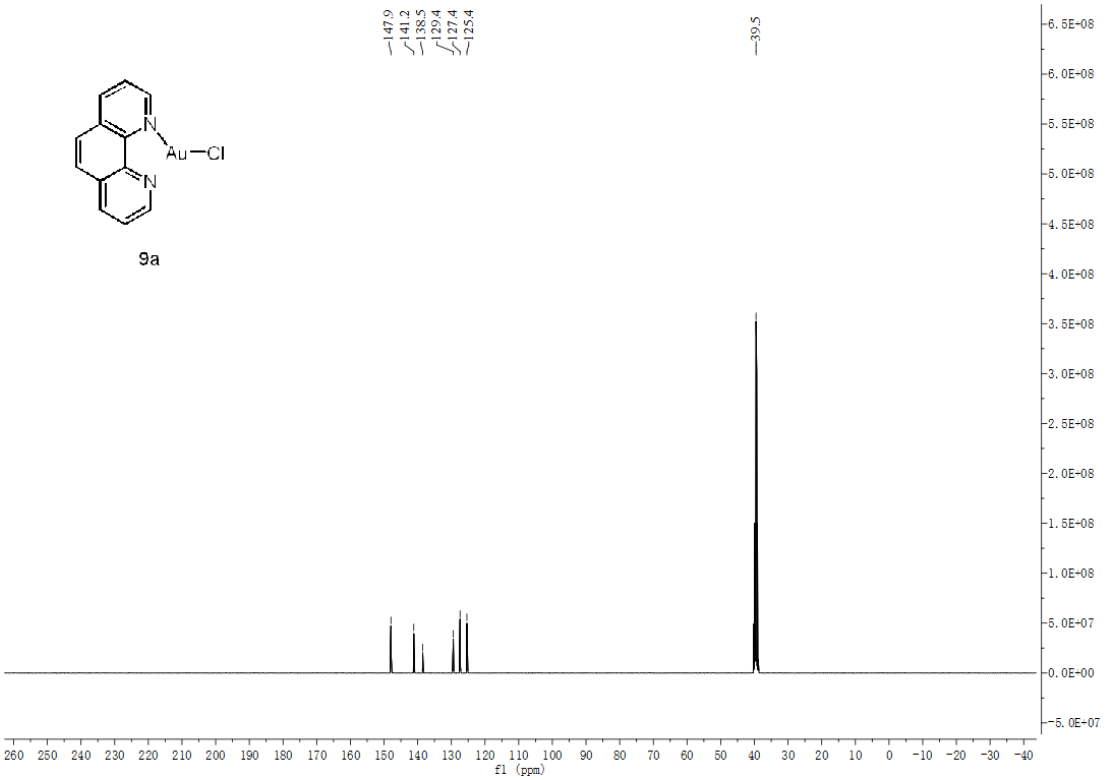


Figure S23. [13]C NMR (101 MHz, DMSO) spectra of **9a** in MestReNova.

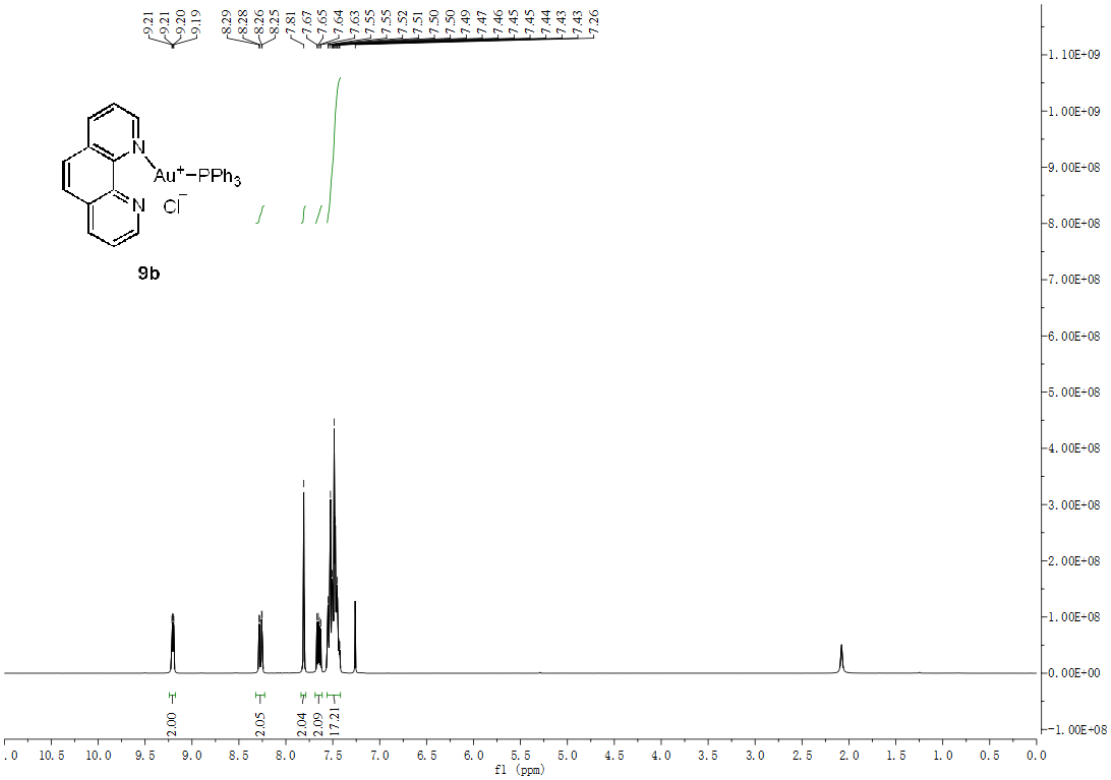


Figure S24. ^{1}H NMR (300 MHz, $CDCl_3$) spectra of **9b** in MestReNova.

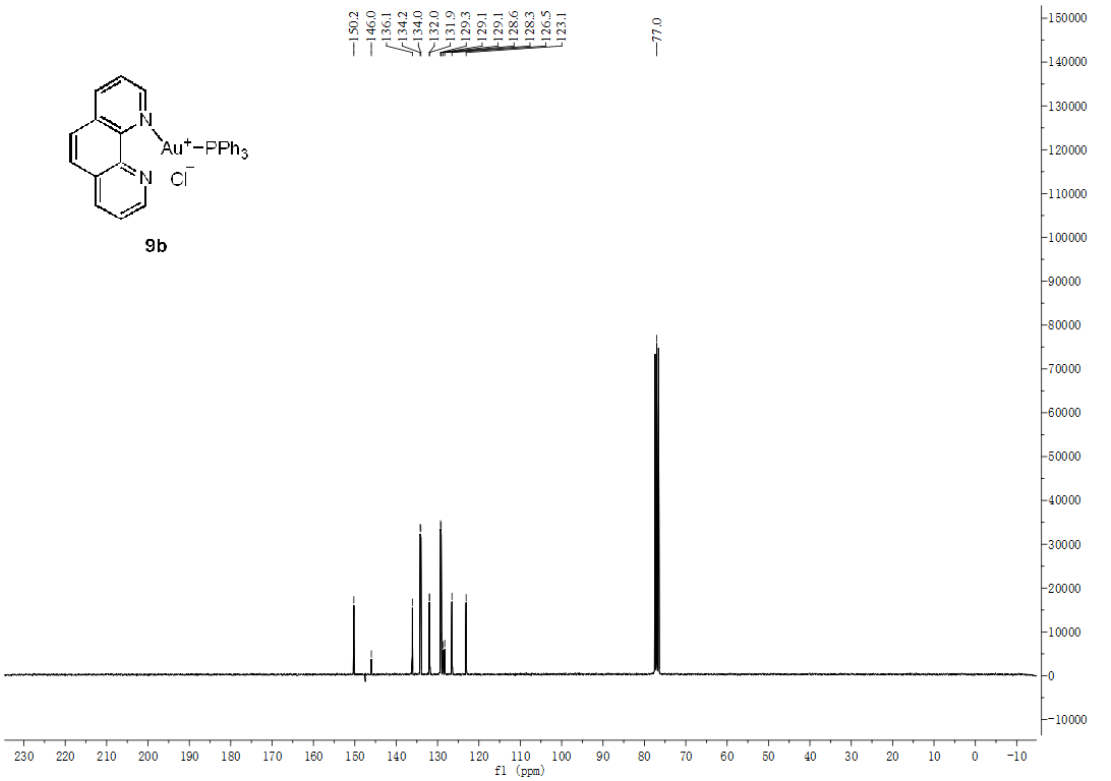


Figure S25. ^{13}C NMR (75 MHz, $CDCl_3$) spectra of **9b** in MestReNova.

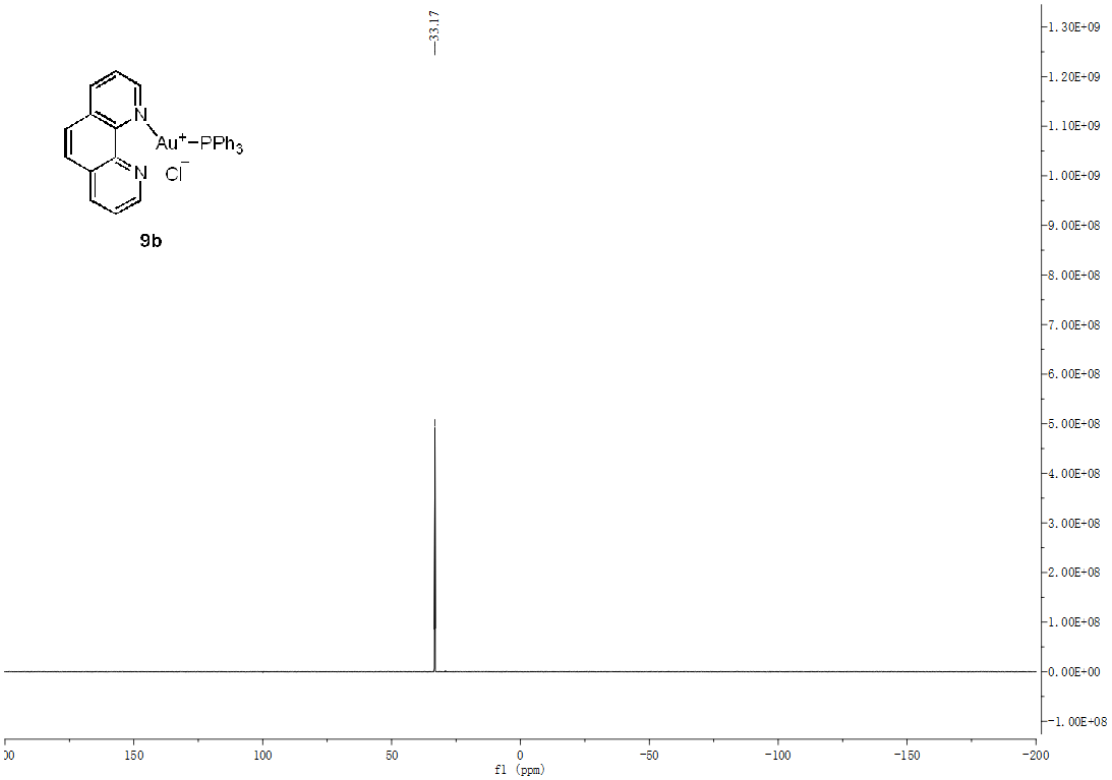


Figure S26. ^{31}P NMR (122 MHz, $CDCl_3$) spectra of **9b** in MestReNova.

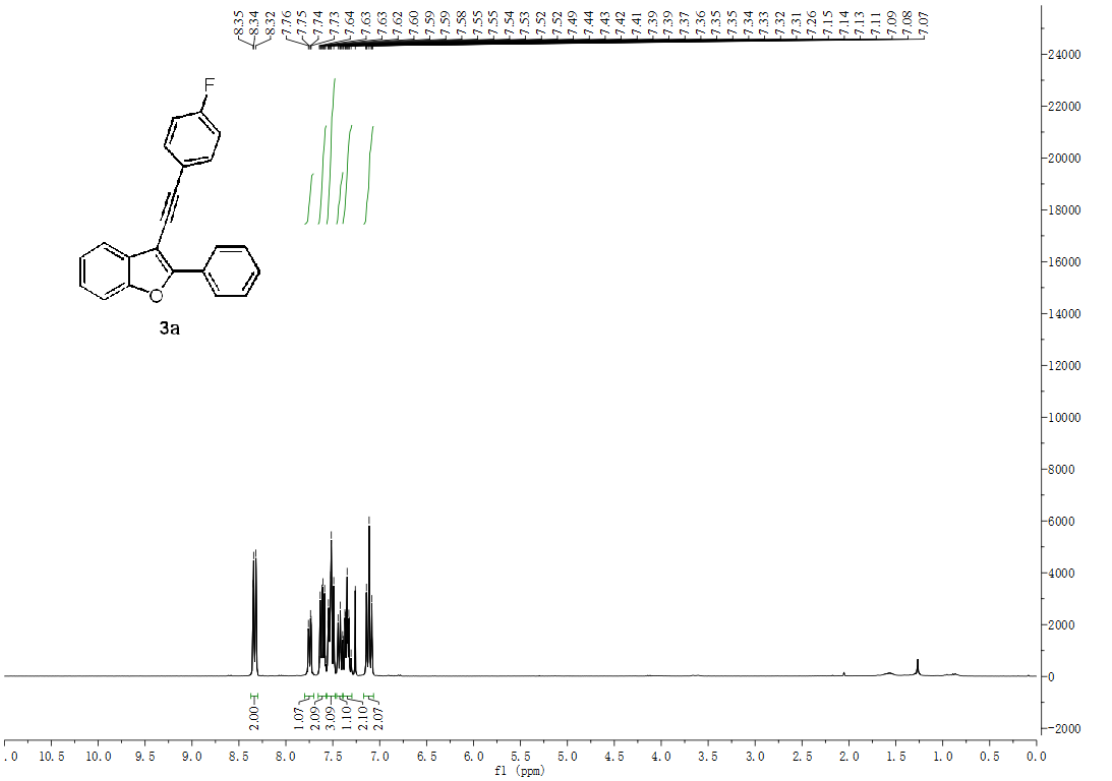


Figure S27. ^{1}H NMR (300 MHz, $CDCl_3$) spectra of **3a** in MestReNova.

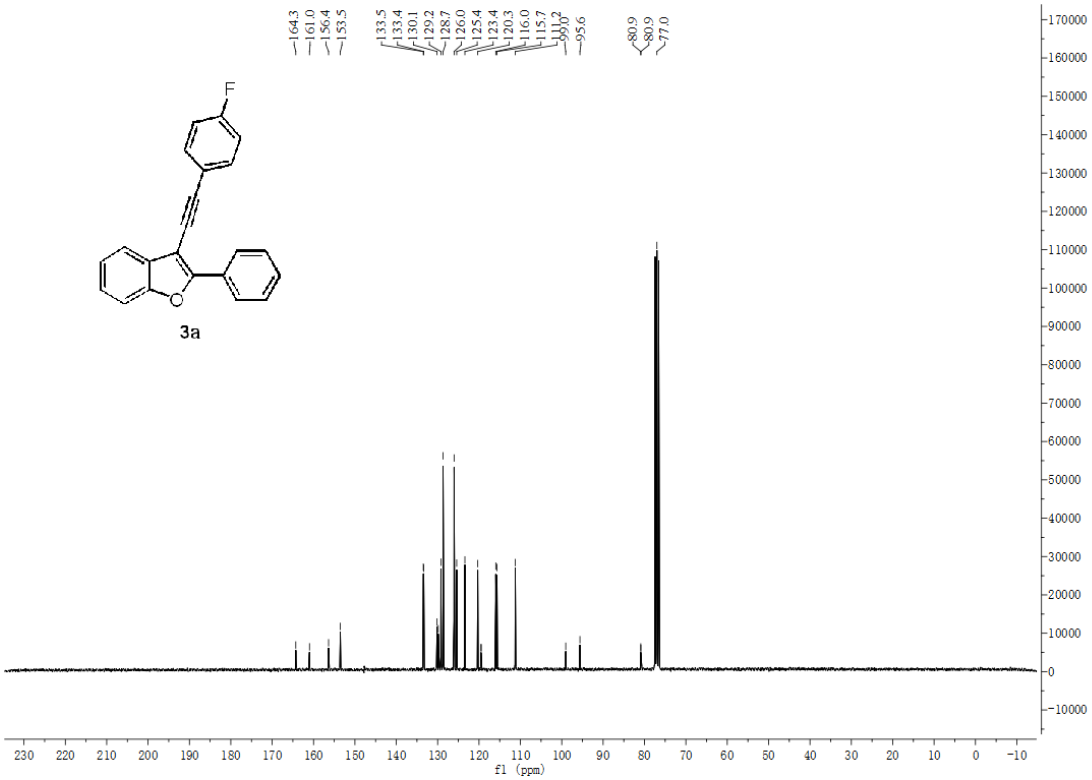


Figure S28. ^{13}C NMR (75 MHz, $CDCl_3$) spectra of **3a** in MestReNova.

Figure S29. ^{19}F NMR (282 MHz, $CDCl_3$) spectra of **3a** in MestReNova.

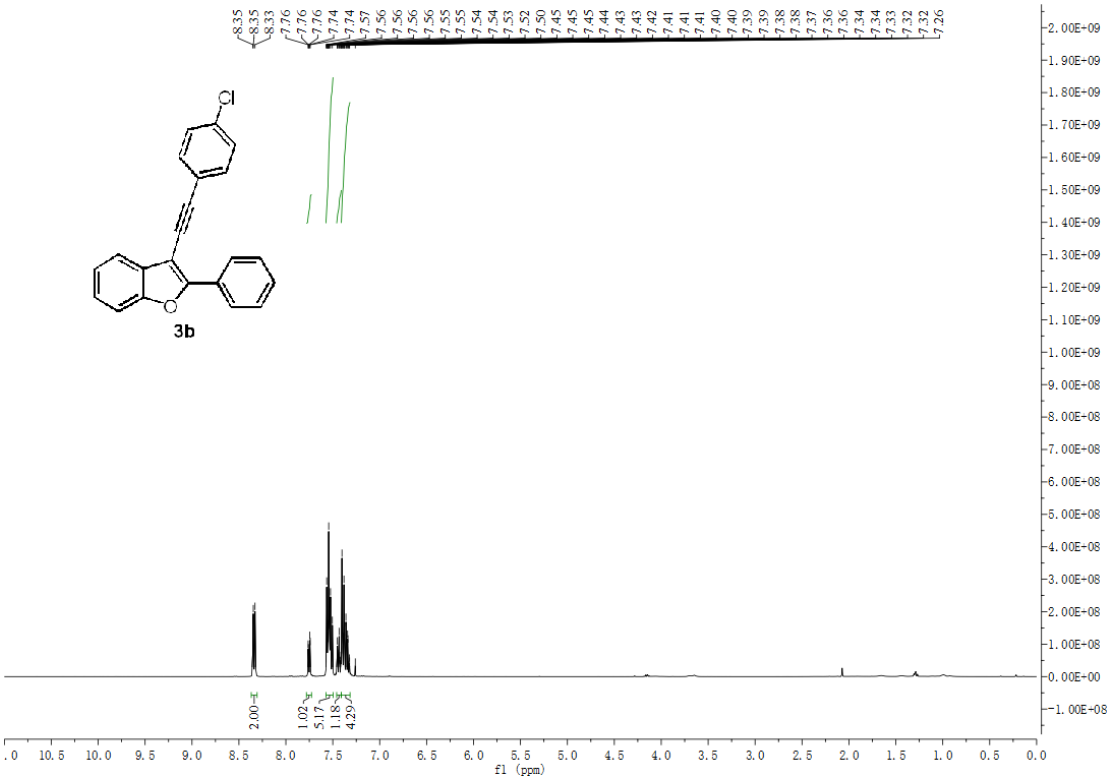


Figure S30. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3b** in MestReNova.

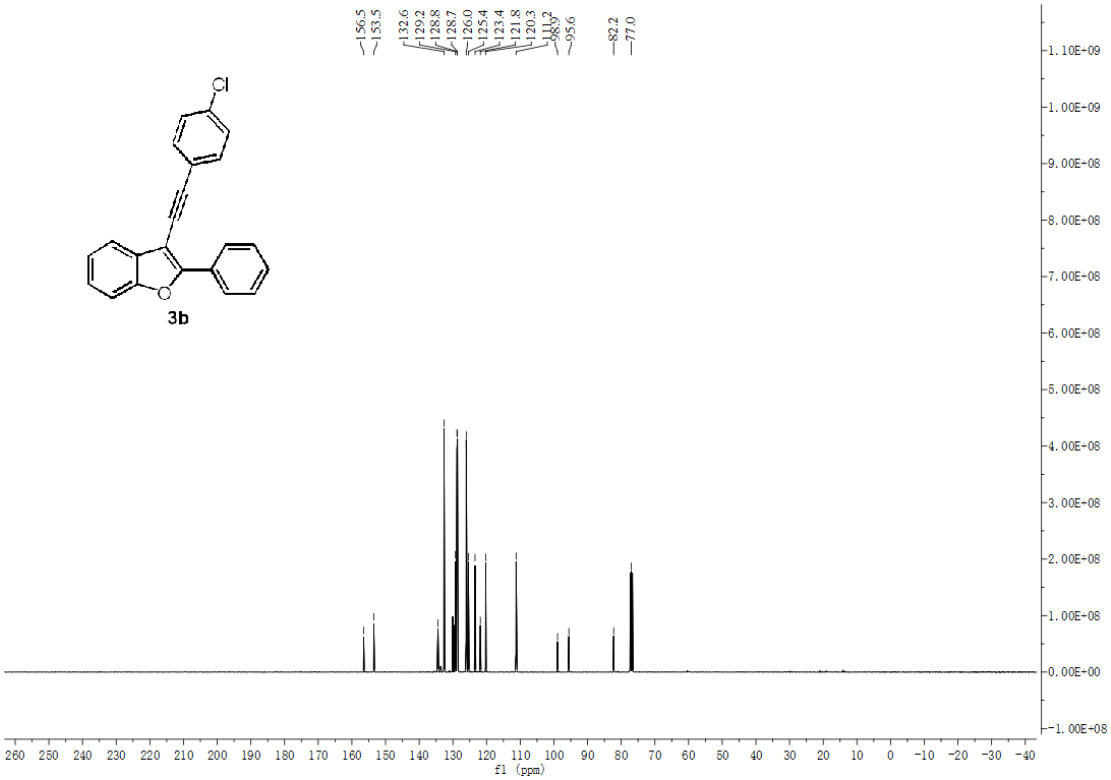


Figure S31. ^{13}C NMR (101 MHz, $CDCl_3$) spectra of **3b** in MestReNova.

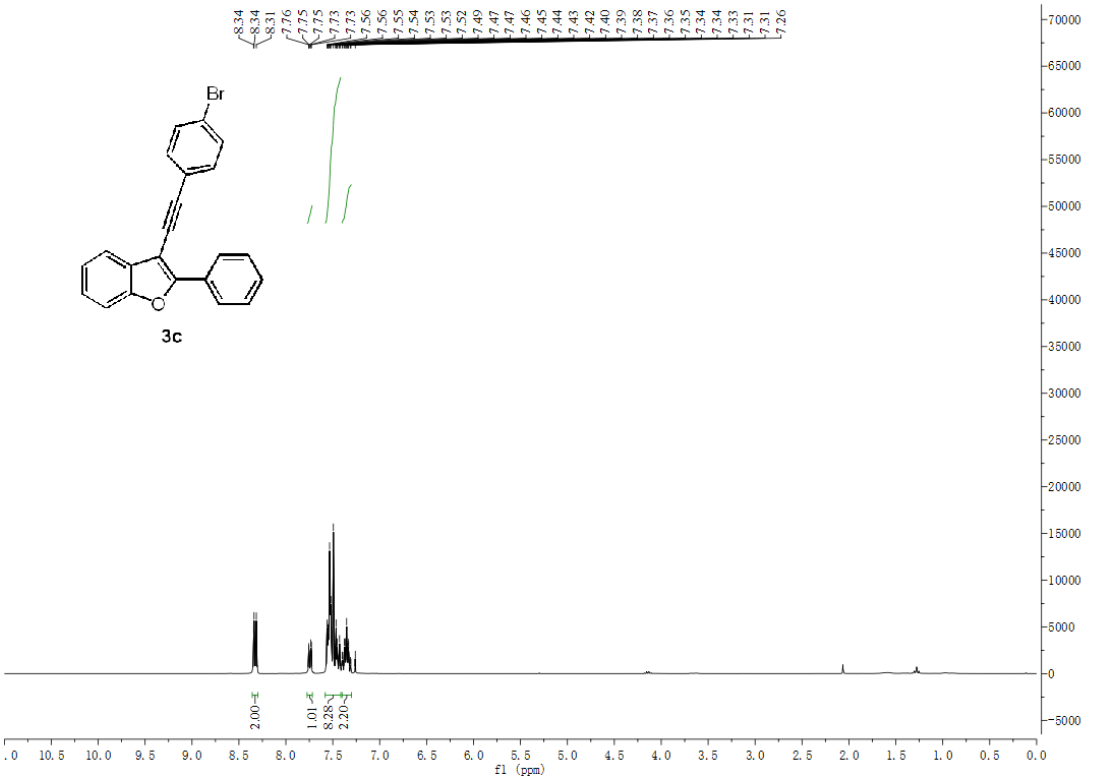


Figure S32. ^{1}H NMR (300 MHz, $CDCl_3$) spectra of **3c** in MestReNova.

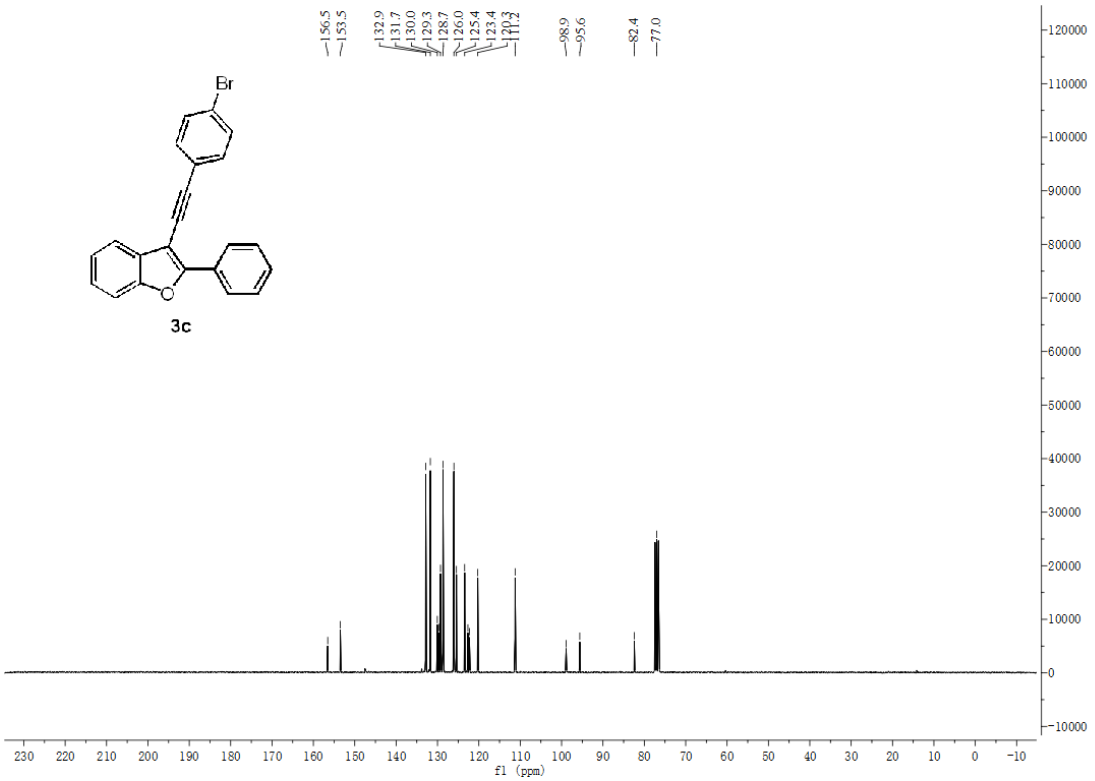


Figure S33. ^{13}C NMR (75 MHz, $CDCl_3$) spectra of **3c** in MestReNova.

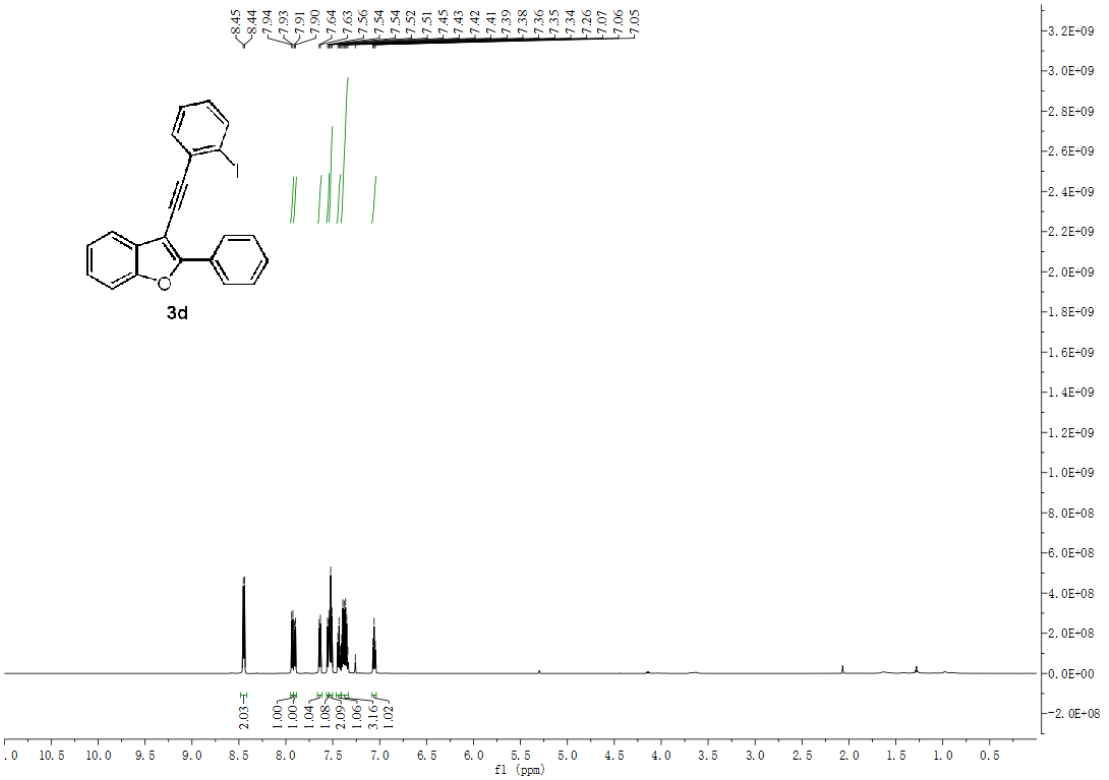


Figure S34. ^{1}H NMR (600 MHz, $CDCl_3$) spectra of **3d** in MestReNova.

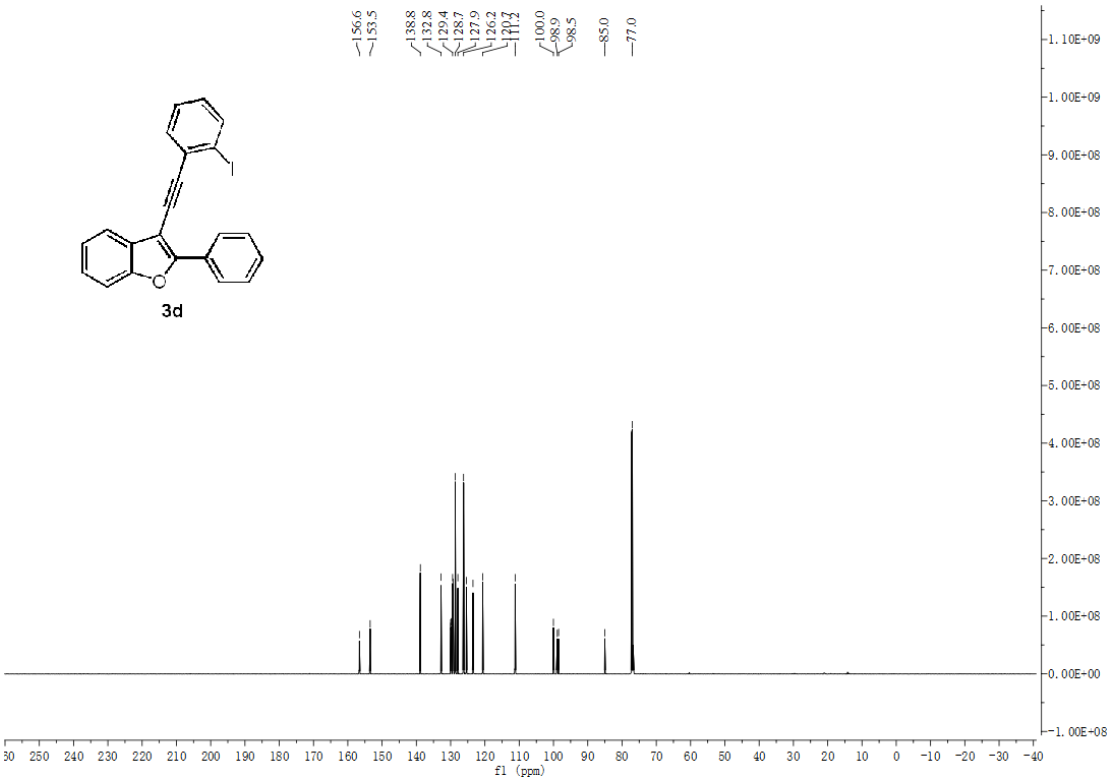


Figure S35. ^{13}C NMR (151 MHz, $CDCl_3$) spectra of **3d** in MestReNova.

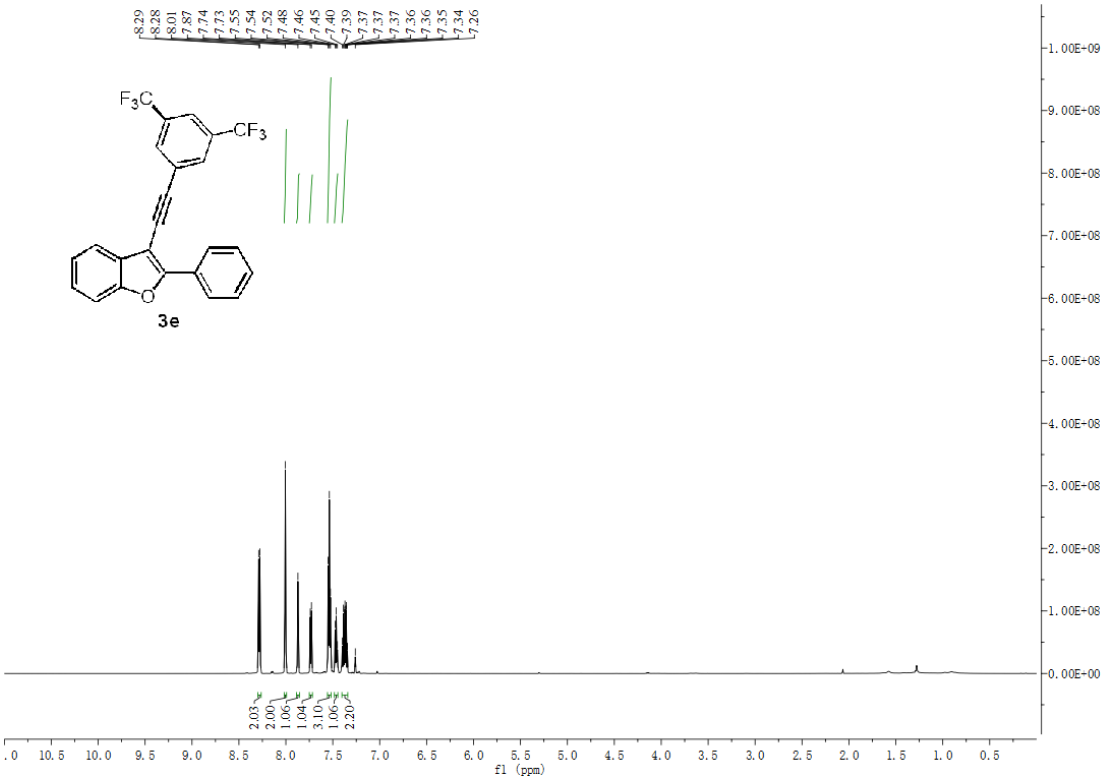


Figure S36. ^{1}H NMR (600 MHz, $CDCl_3$) spectra of **3e** in MestReNova.

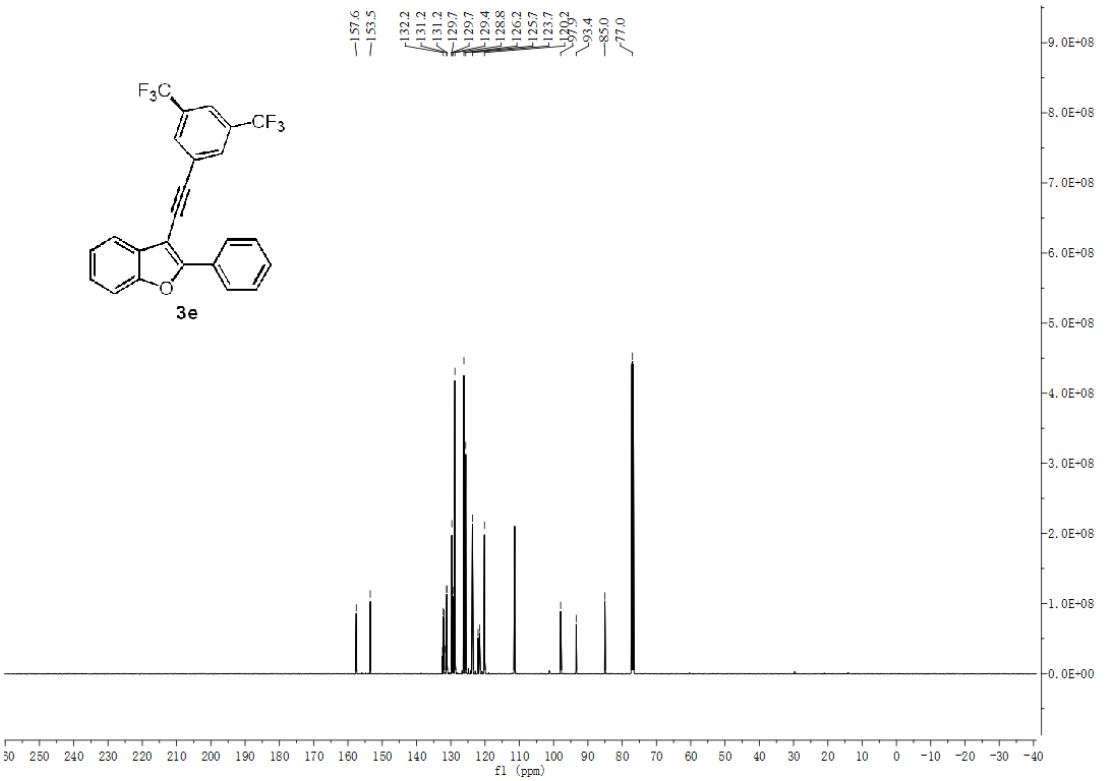


Figure S37. ^{13}C NMR (151 MHz, $CDCl_3$) spectra of **3e** in MestReNova.

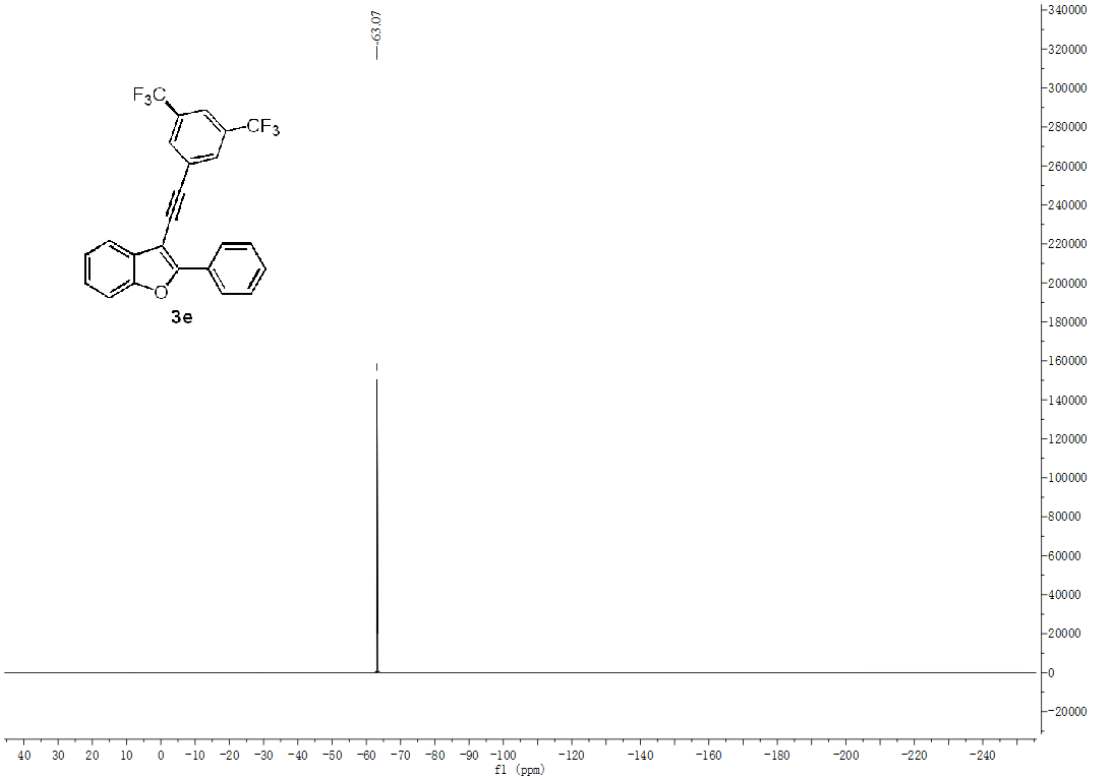


Figure S38. ^{19}F NMR (282 MHz, $CDCl_3$) spectra of **3e** in MestReNova.

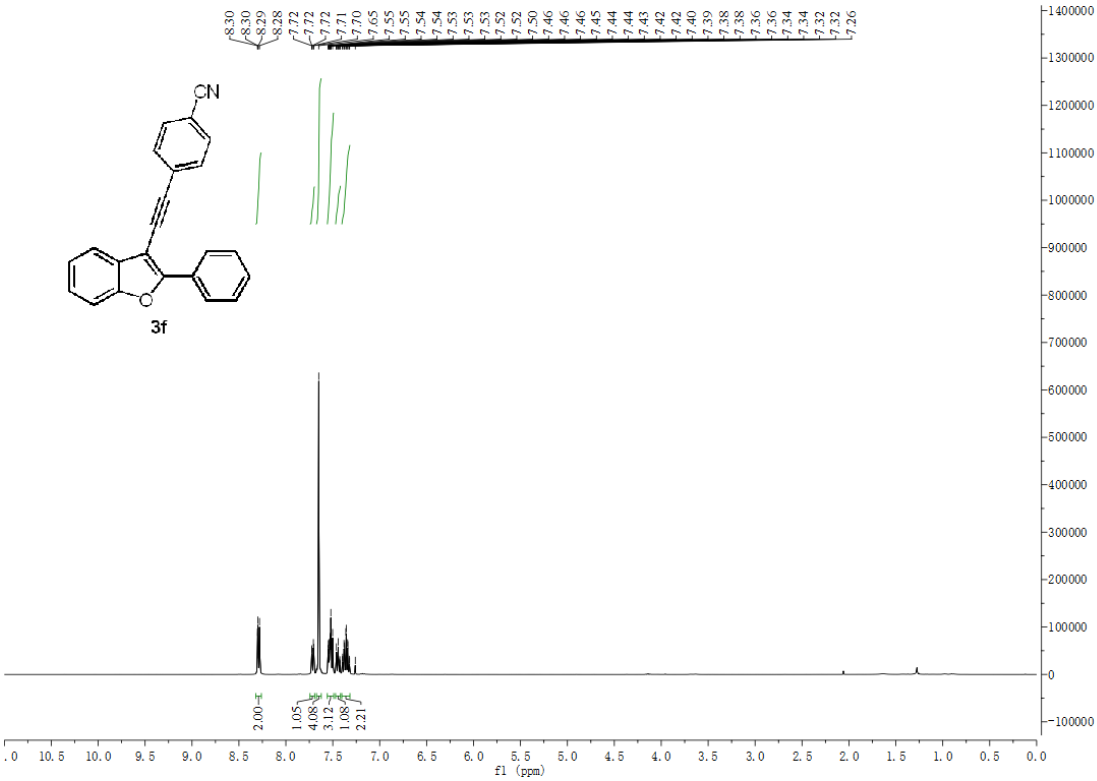


Figure S39. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3f** in MestReNova.

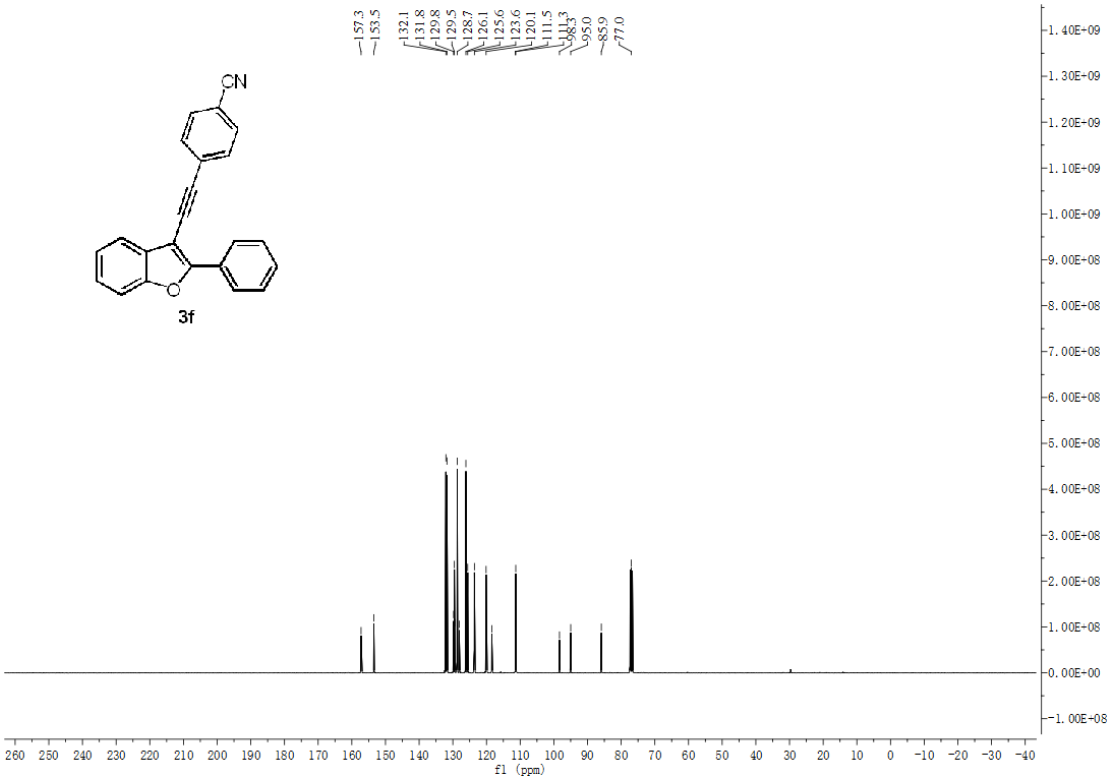


Figure S40. ^{13}C NMR (101 MHz, $CDCl_3$) spectra of **3f** in MestReNova.

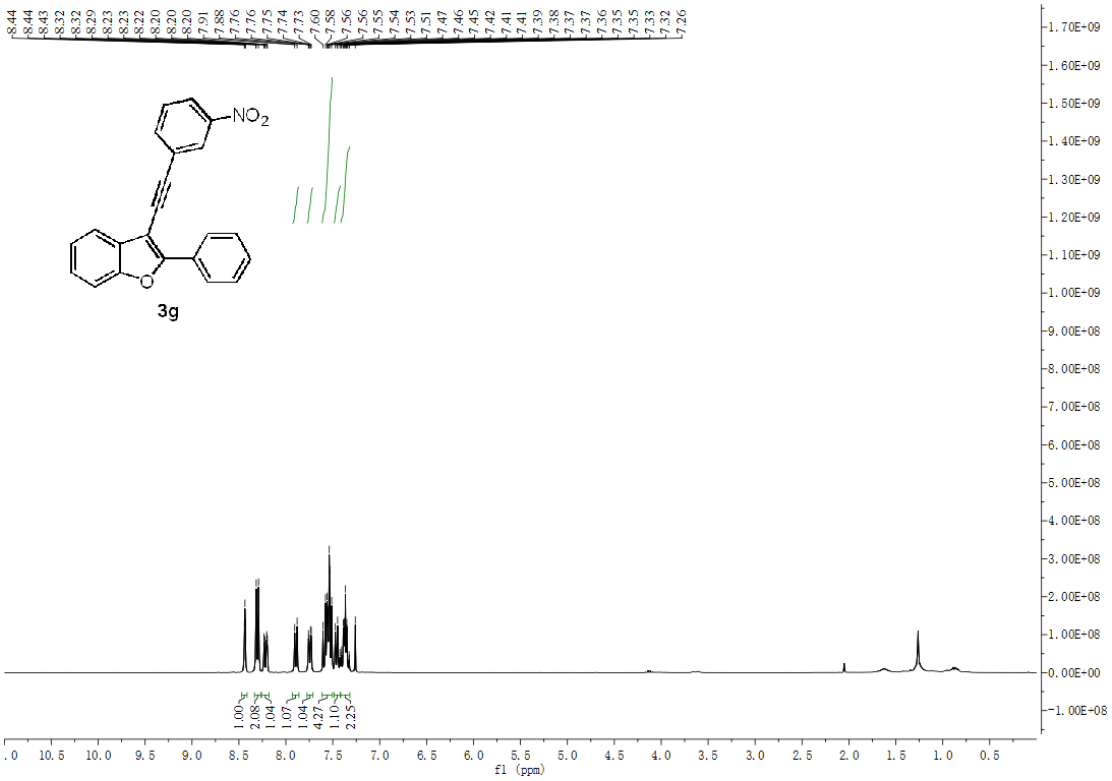


Figure S41. ^{1}H NMR (300 MHz, $CDCl_3$) spectra of **3g** in MestReNova.

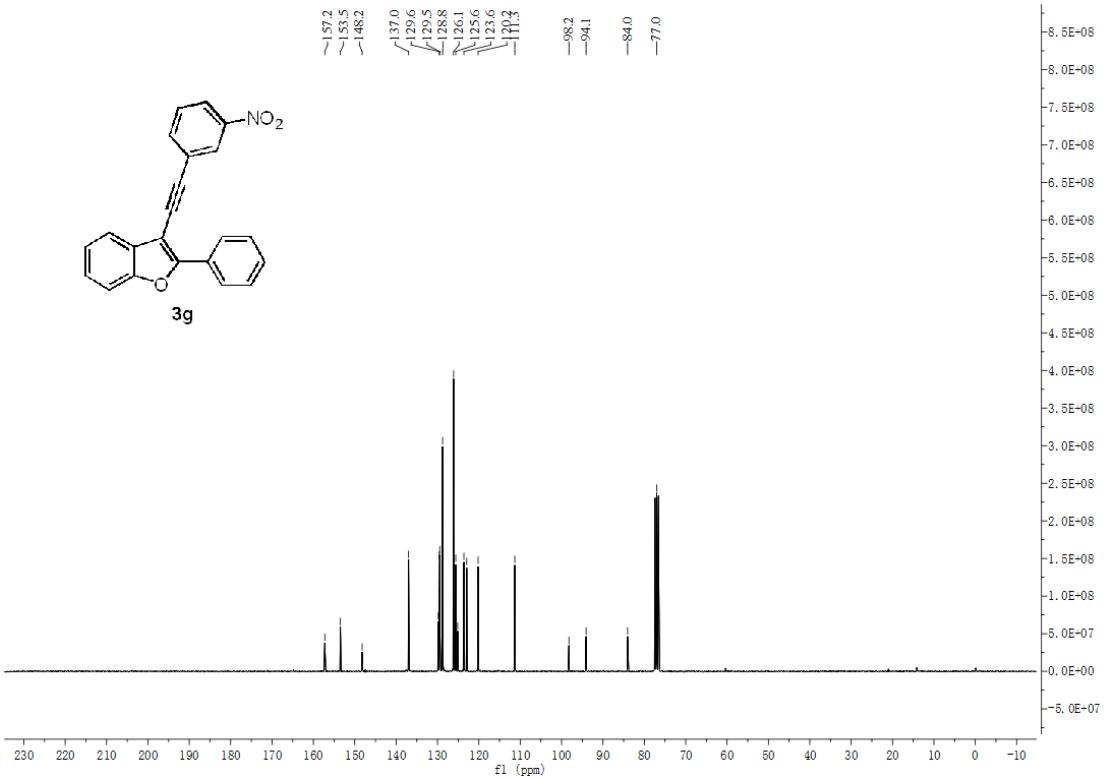


Figure S42. ^{13}C NMR (75 MHz, $CDCl_3$) spectra of **3g** in MestReNova.

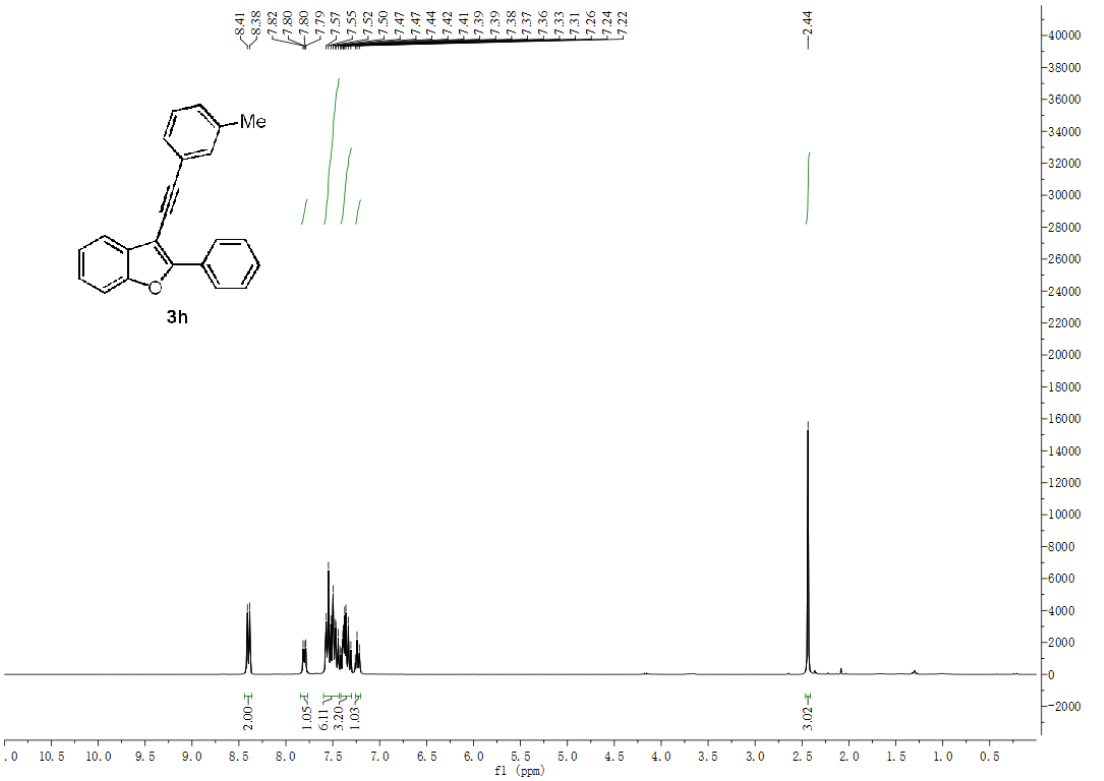


Figure S43. ^{1}H NMR (300 MHz, $CDCl_3$) spectra of **3h** in MestReNova.

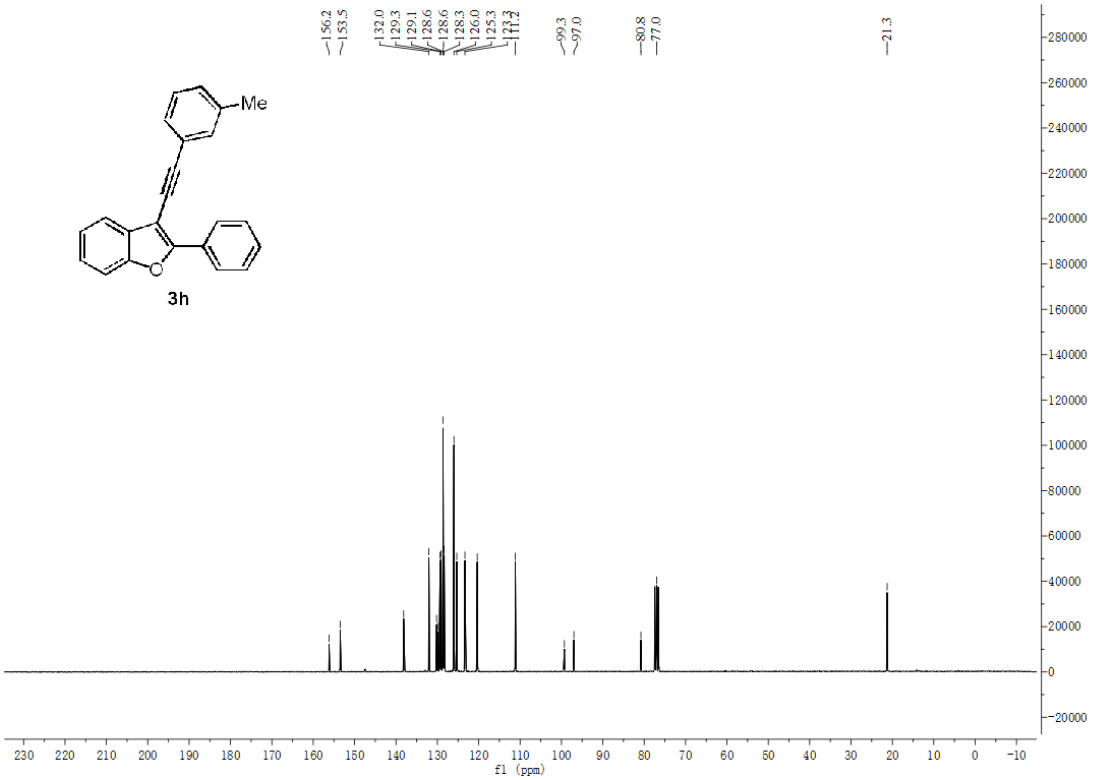


Figure S44. ^{13}C NMR (75 MHz, $CDCl_3$) spectra of **3h** in MestReNova.

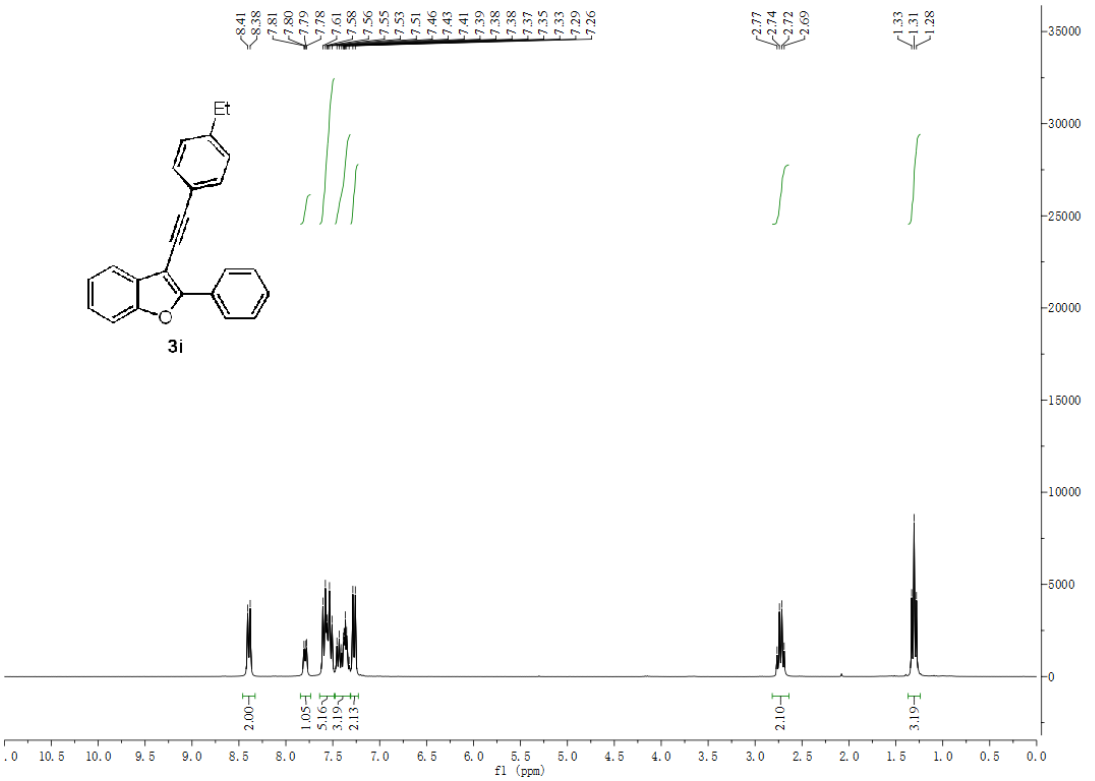


Figure S45. ^{1}H NMR (300 MHz, $CDCl_3$) spectra of **3i** in MestReNova.

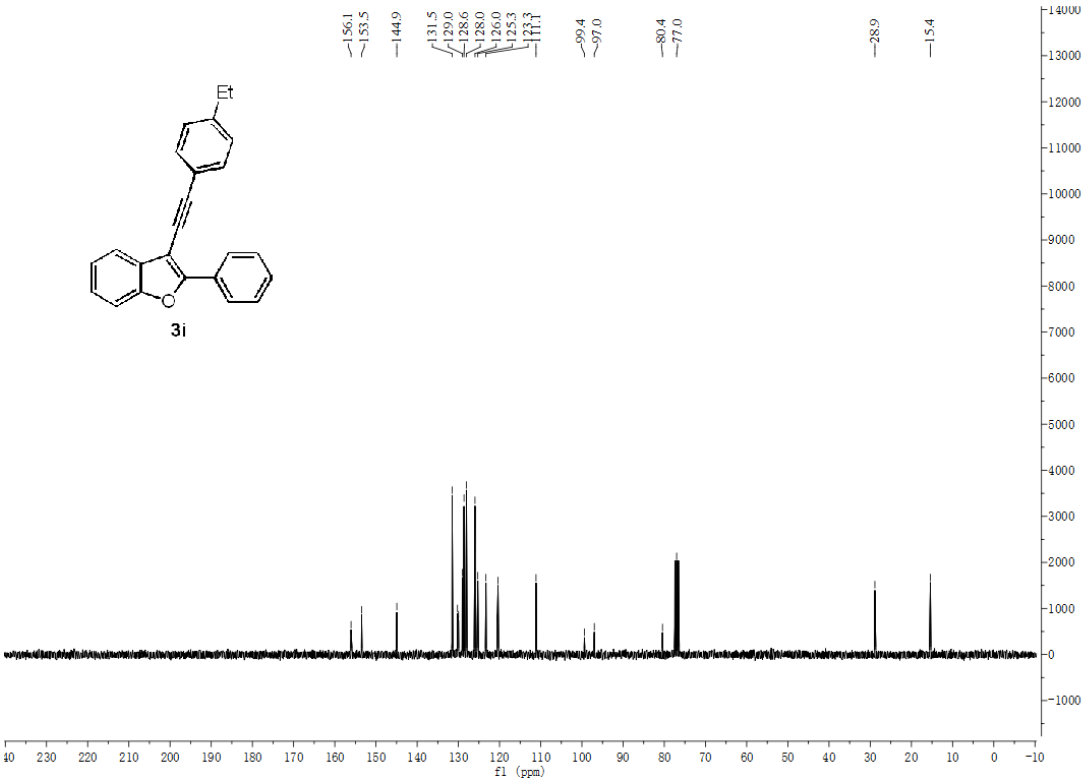


Figure S46. ^{13}C NMR (75 MHz, $CDCl_3$) spectra of **3i** in MestReNova.

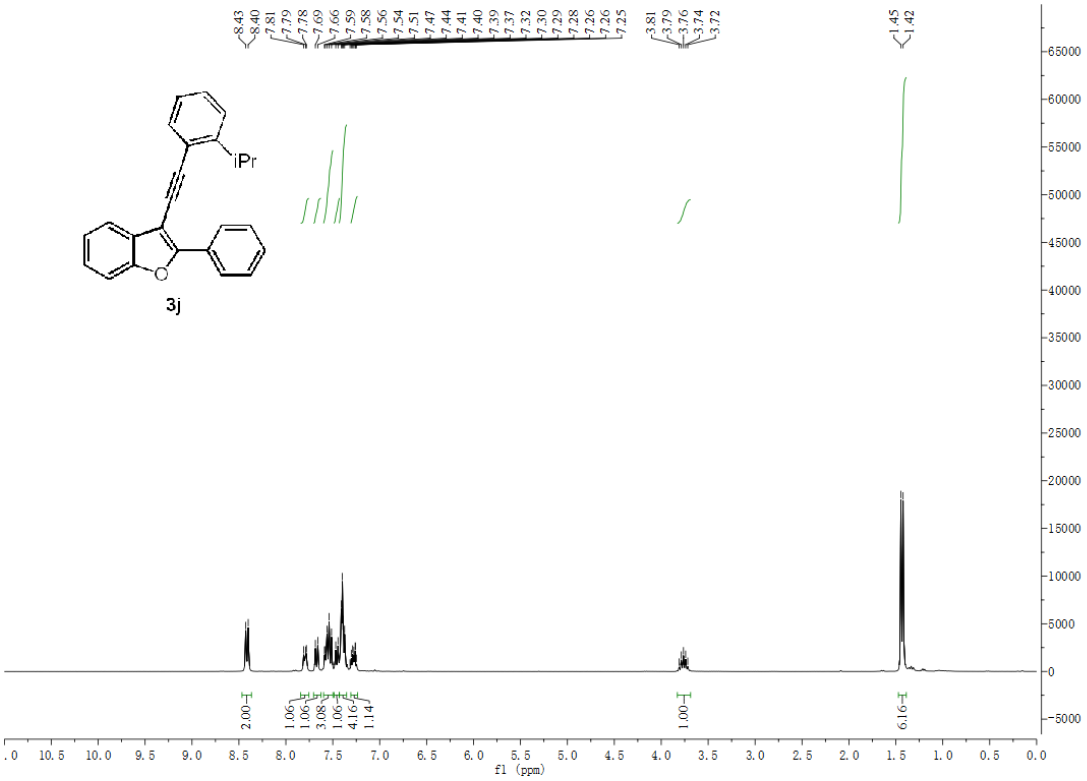


Figure S47. ^{1}H NMR (300 MHz, $CDCl_3$) spectra of **3j** in MestReNova.

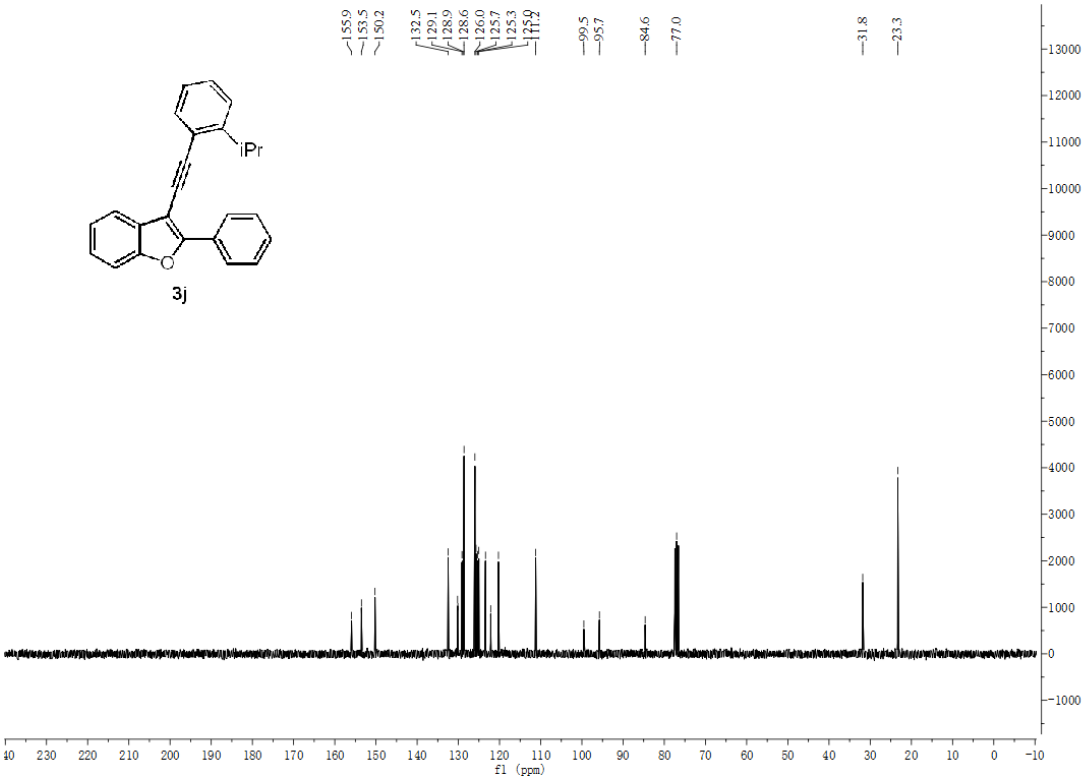


Figure S48. ^{13}C NMR (75 MHz, $CDCl_3$) spectra of **3j** in MestReNova.

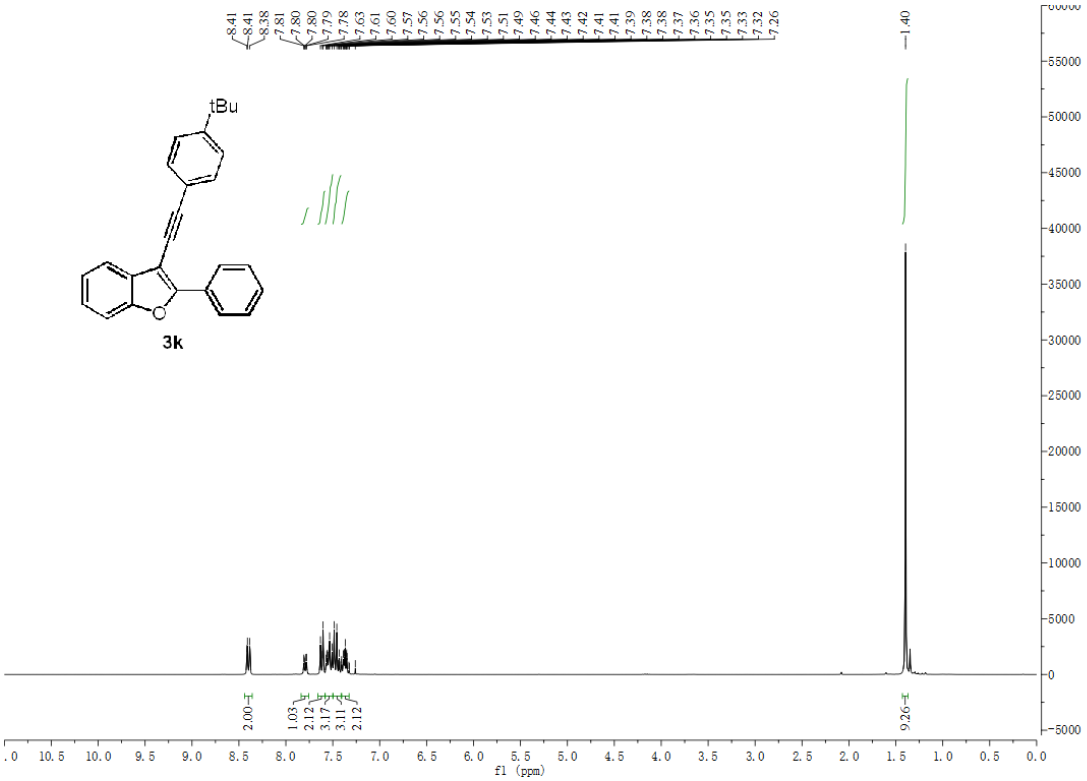


Figure S49. ^{1}H NMR (300 MHz, $CDCl_3$) spectra of **3k** in MestReNova.

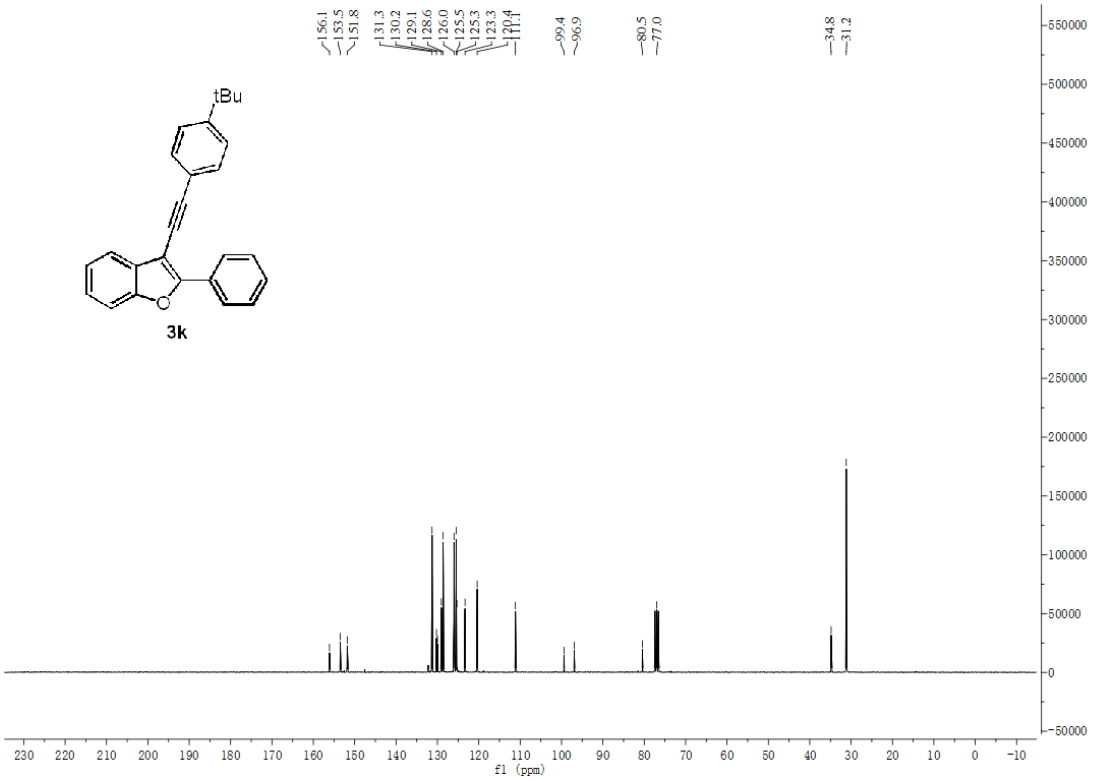


Figure S50. ^{13}C NMR (75 MHz, $CDCl_3$) spectra of **3k** in MestReNova.

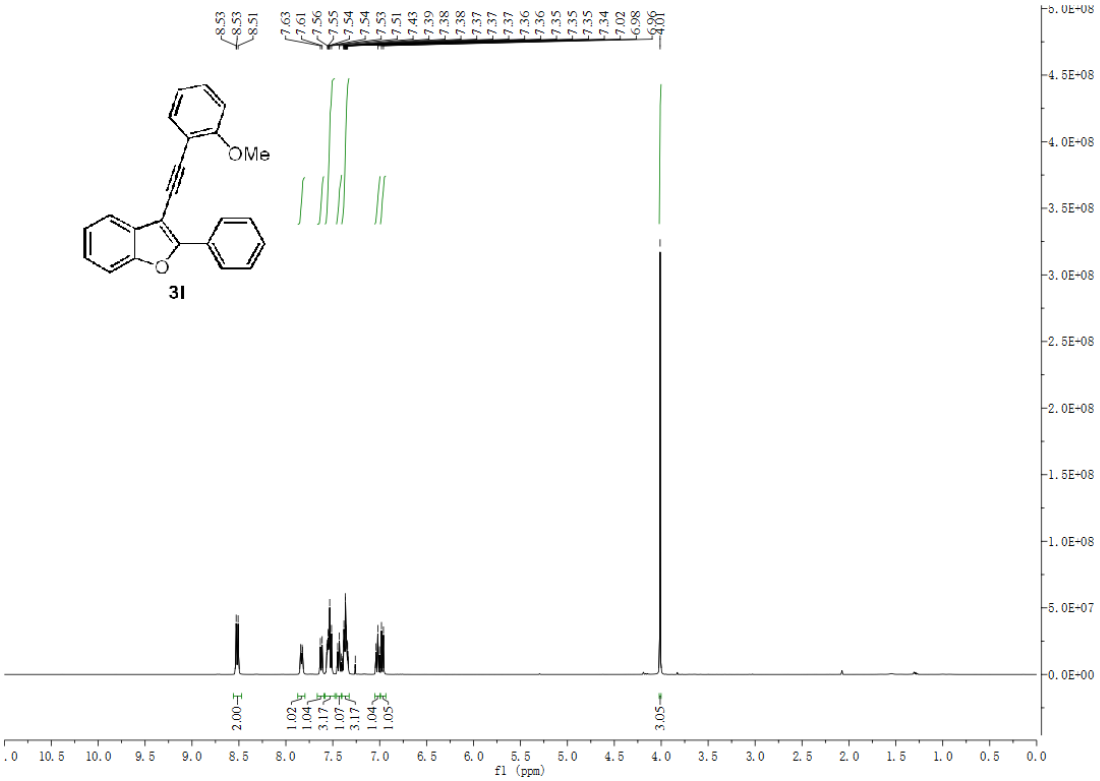


Figure S51. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3l** in MestReNova.

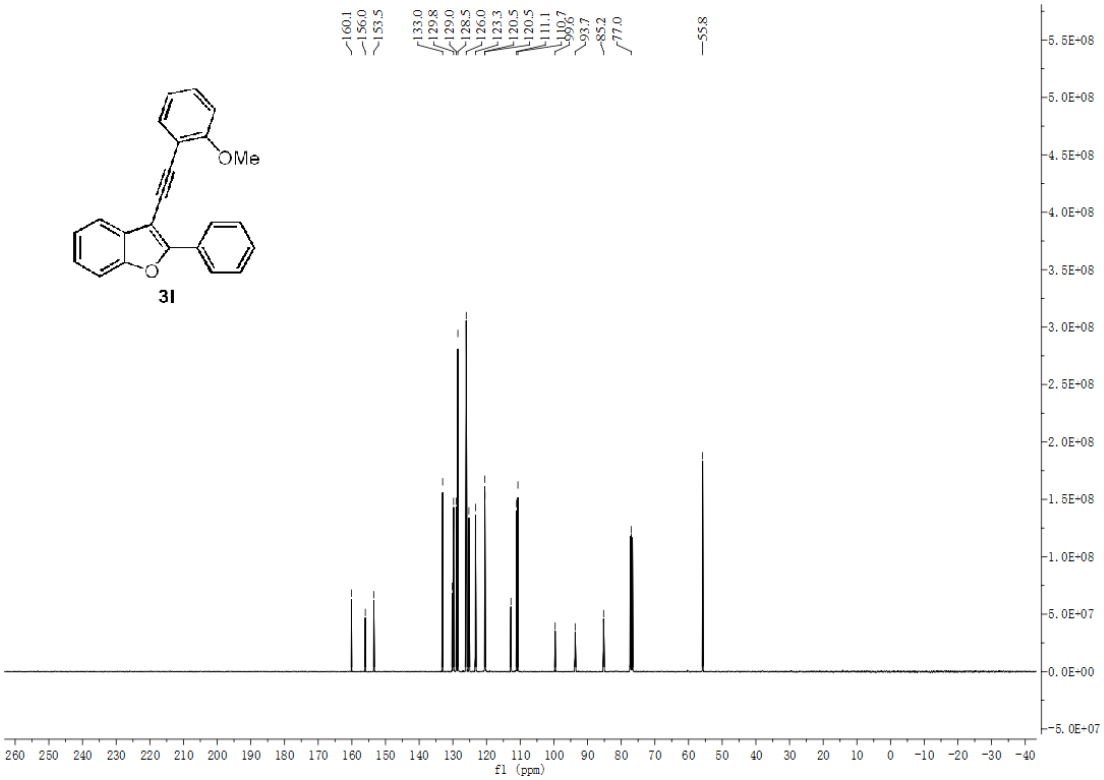


Figure S52. ^{13}C NMR (101 MHz, $CDCl_3$) spectra of **3l** in MestReNova.

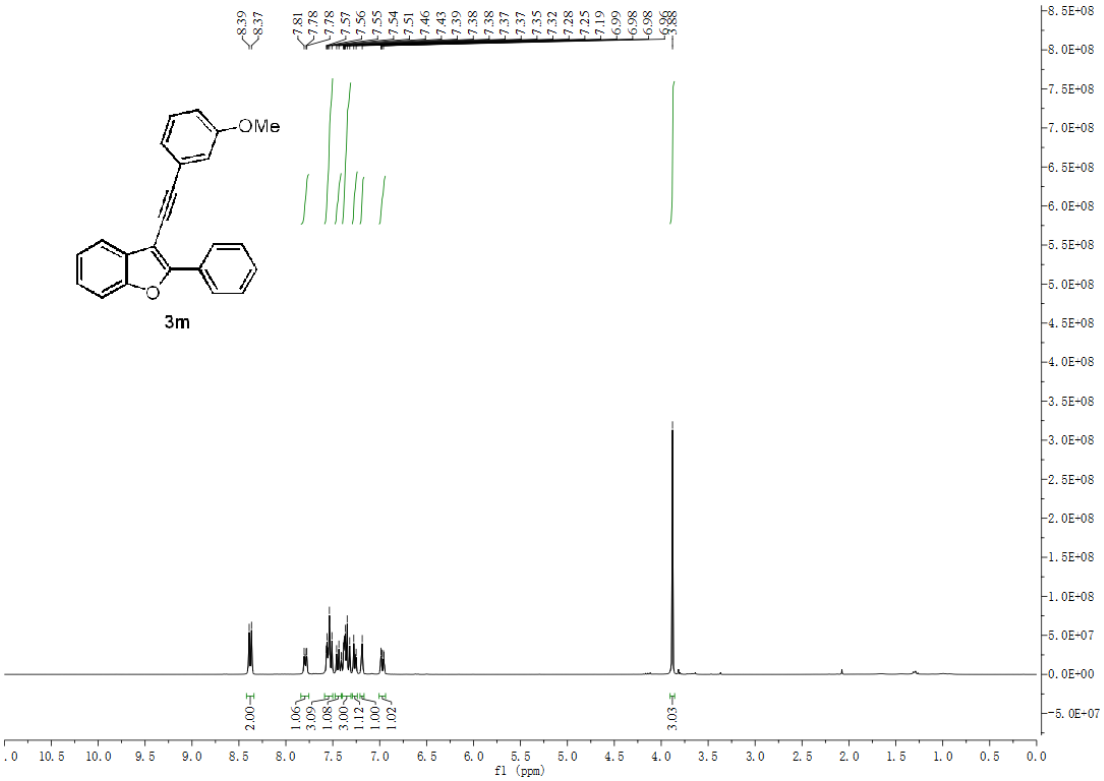


Figure S53. ^{1}H NMR (300 MHz, $CDCl_3$) spectra of **3m** in MestReNova.

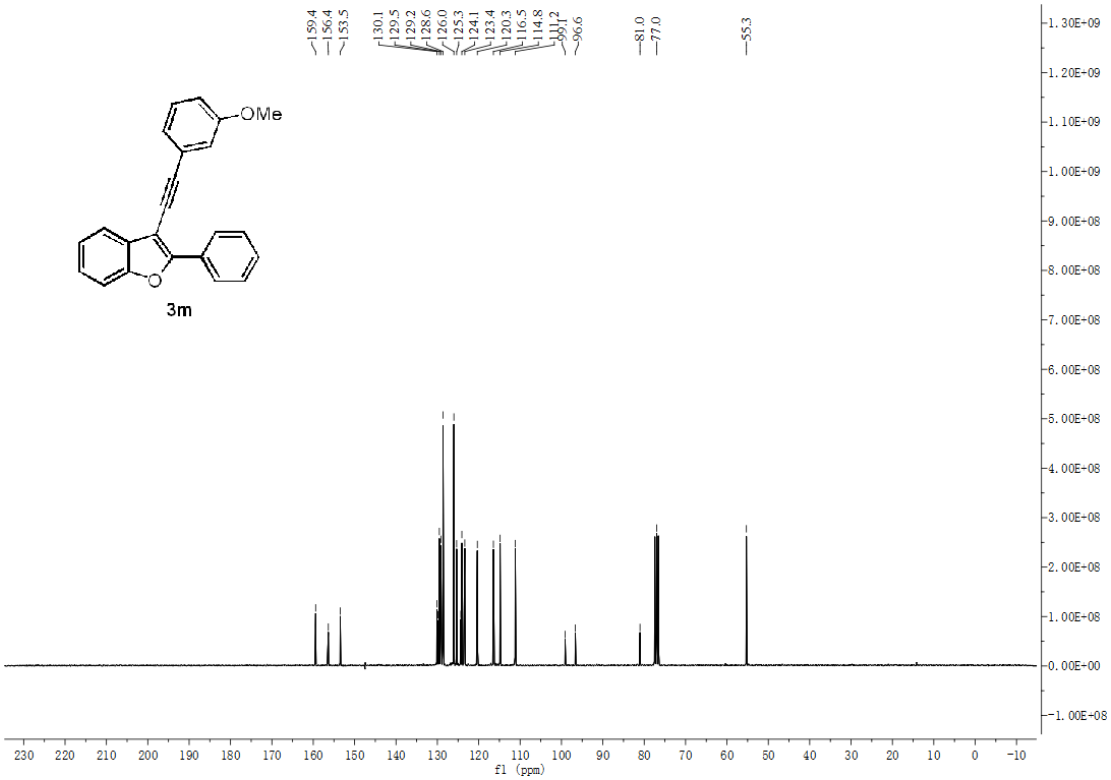


Figure S54. ^{13}C NMR (75 MHz, $CDCl_3$) spectra of **3m** in MestReNova.

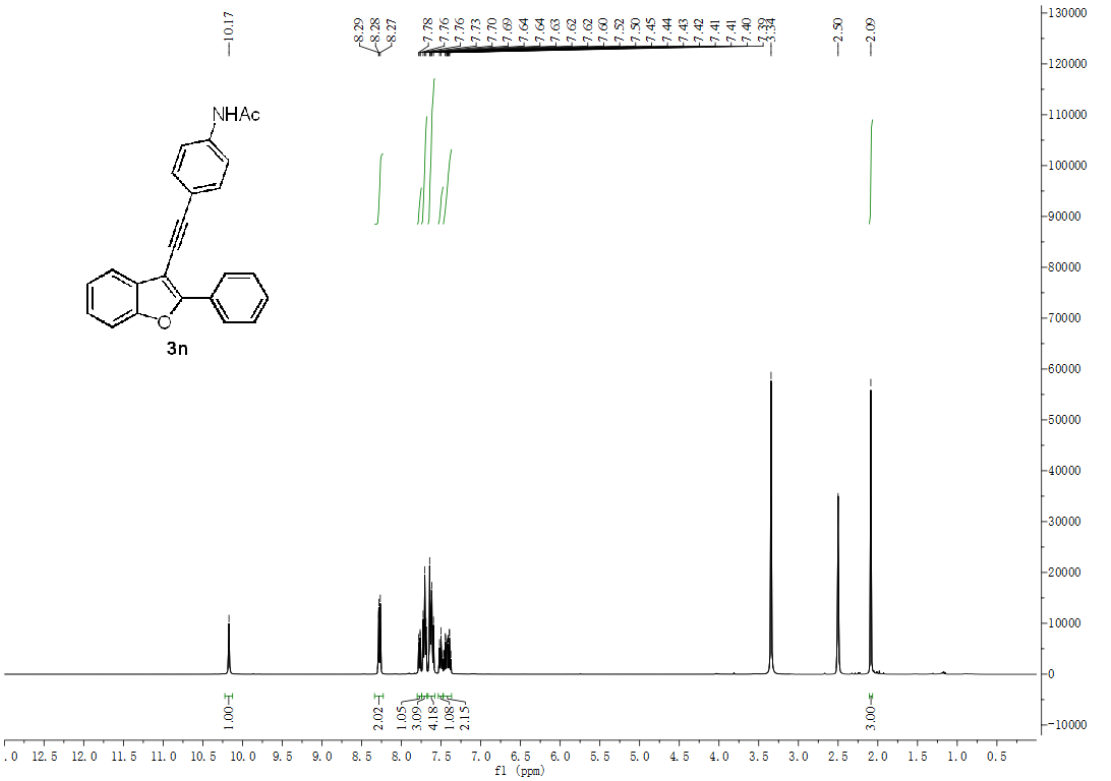


Figure S55. ^{1}H NMR (400 MHz, DMSO) spectra of **3n** in MestReNova.

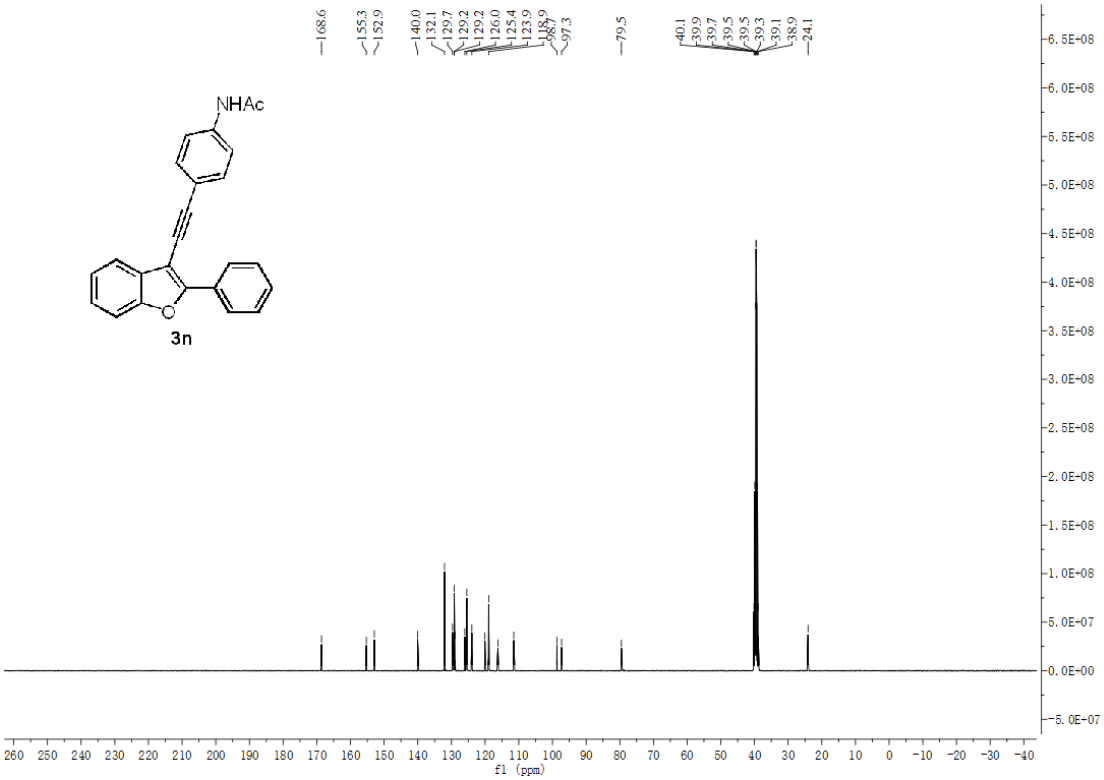


Figure S56. ^{13}C NMR (101 MHz, DMSO) spectra of **3n** in MestReNova.

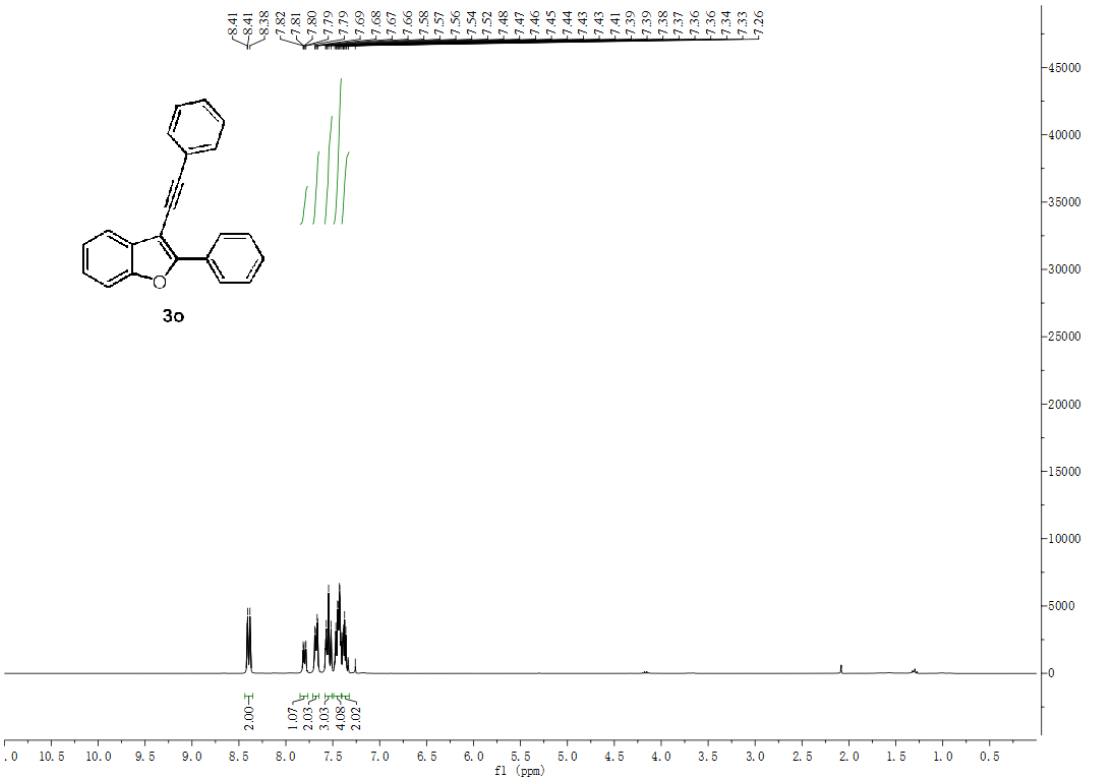


Figure S57. ^{1}H NMR (300 MHz, $CDCl_3$) spectra of **3o** in MestReNova.

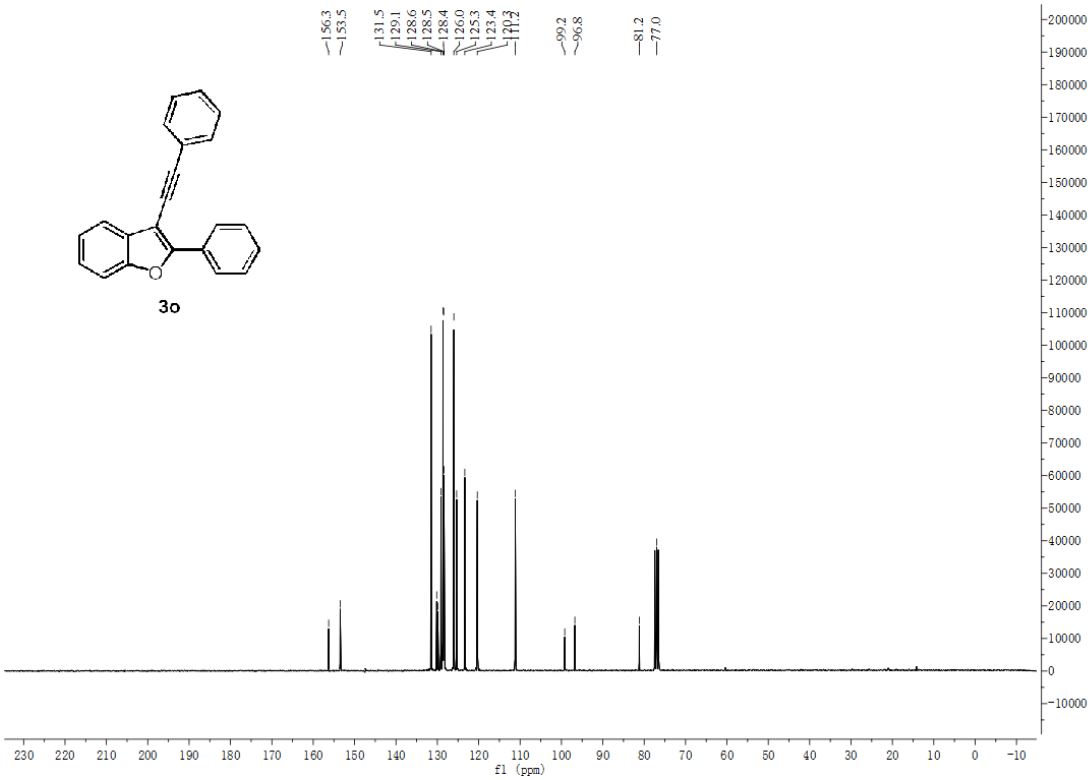


Figure S58. ^{13}C NMR (75 MHz, $CDCl_3$) spectra of **3o** in MestReNova.

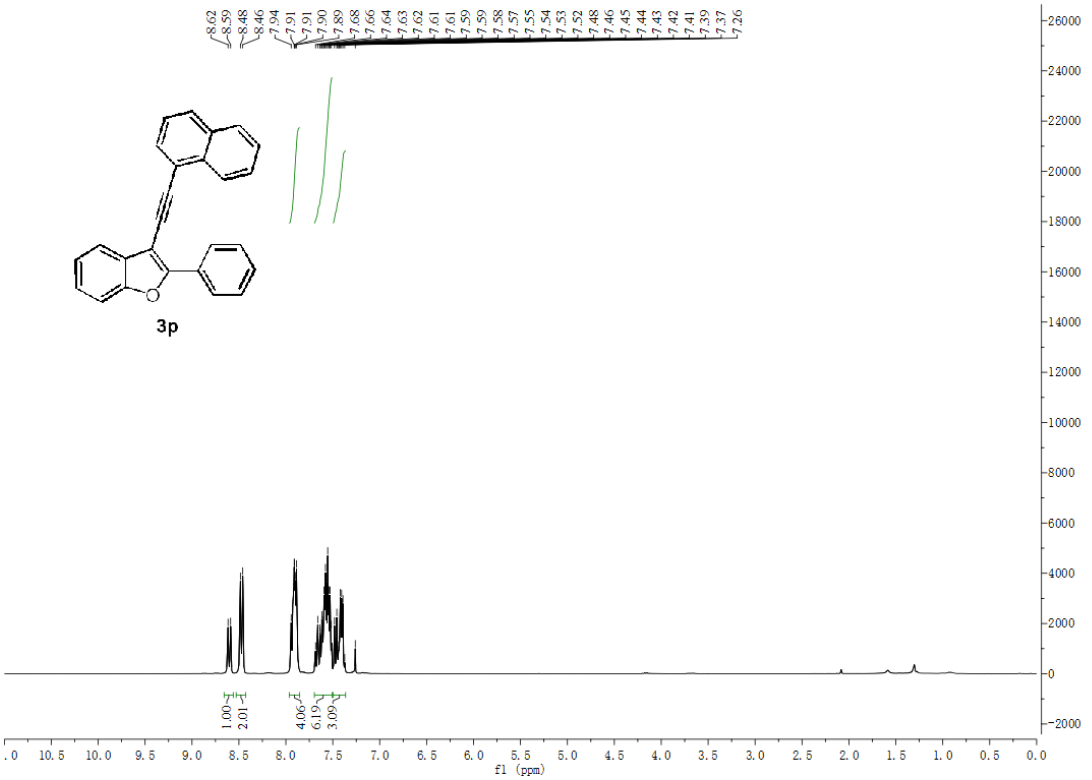


Figure S59. ^{1}H NMR (300 MHz, $CDCl_3$) spectra of **3p** in MestReNova.

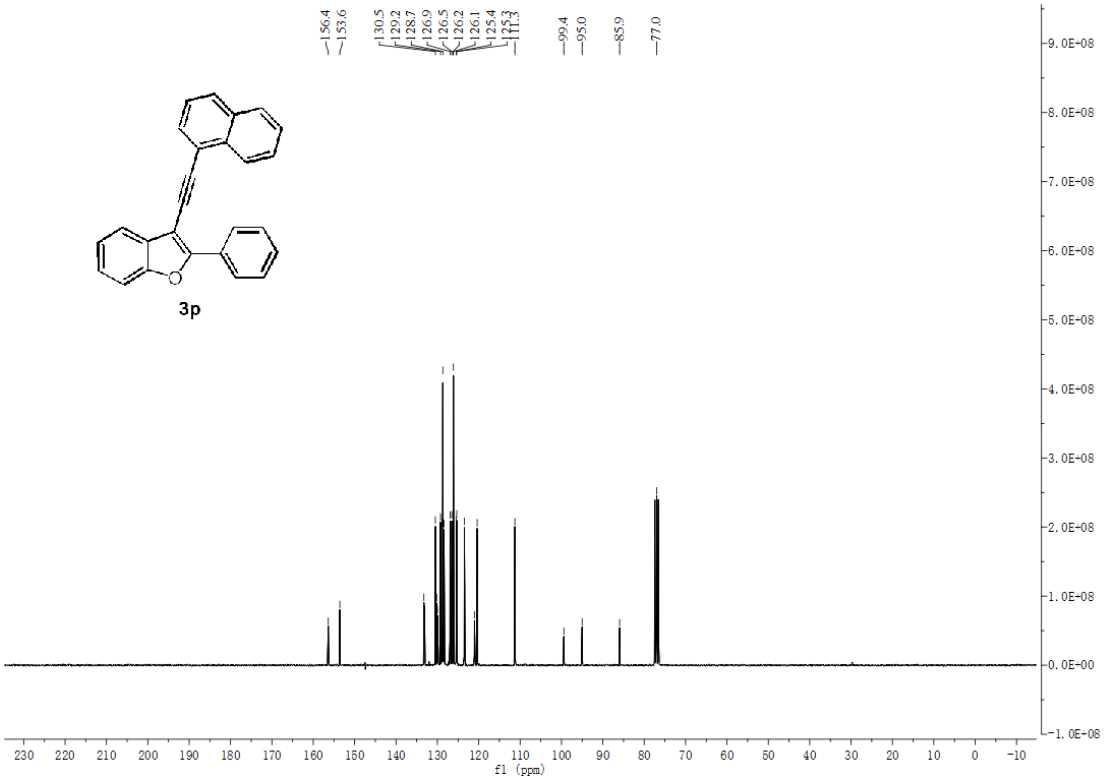


Figure S60. ^{13}C NMR (75 MHz, $CDCl_3$) spectra of **3p** in MestReNova.

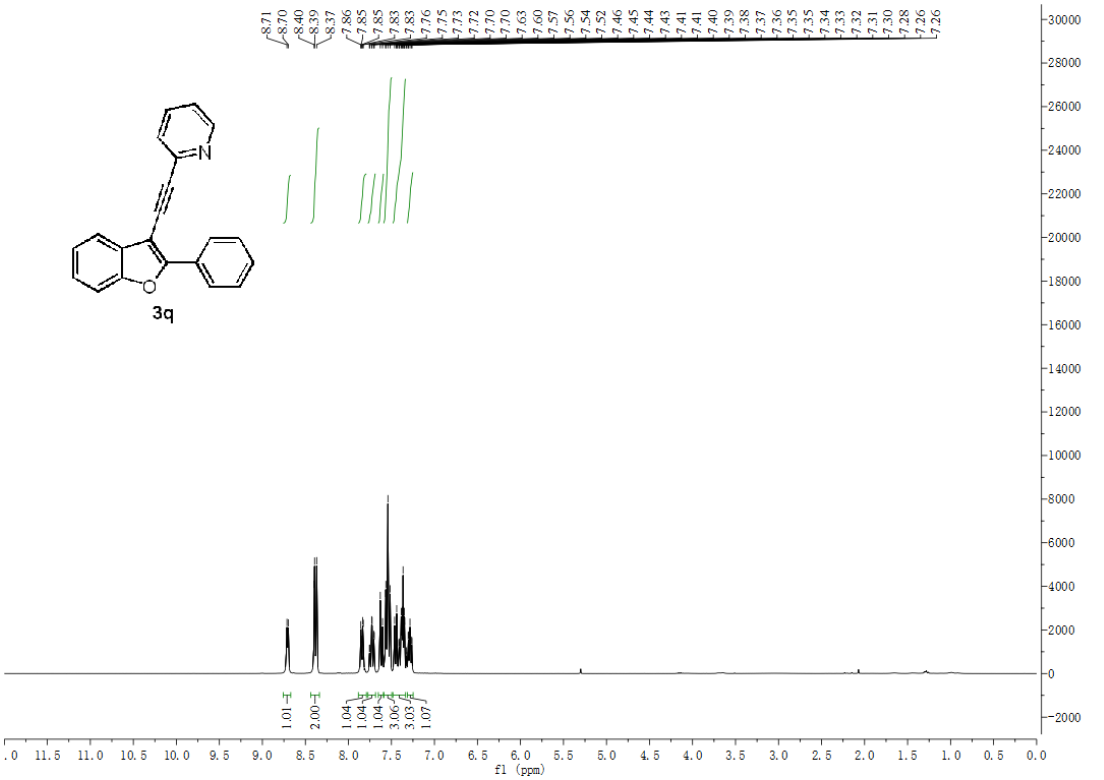


Figure S61. ^{1}H NMR (300 MHz, $CDCl_3$) spectra of **3q** in MestReNova.

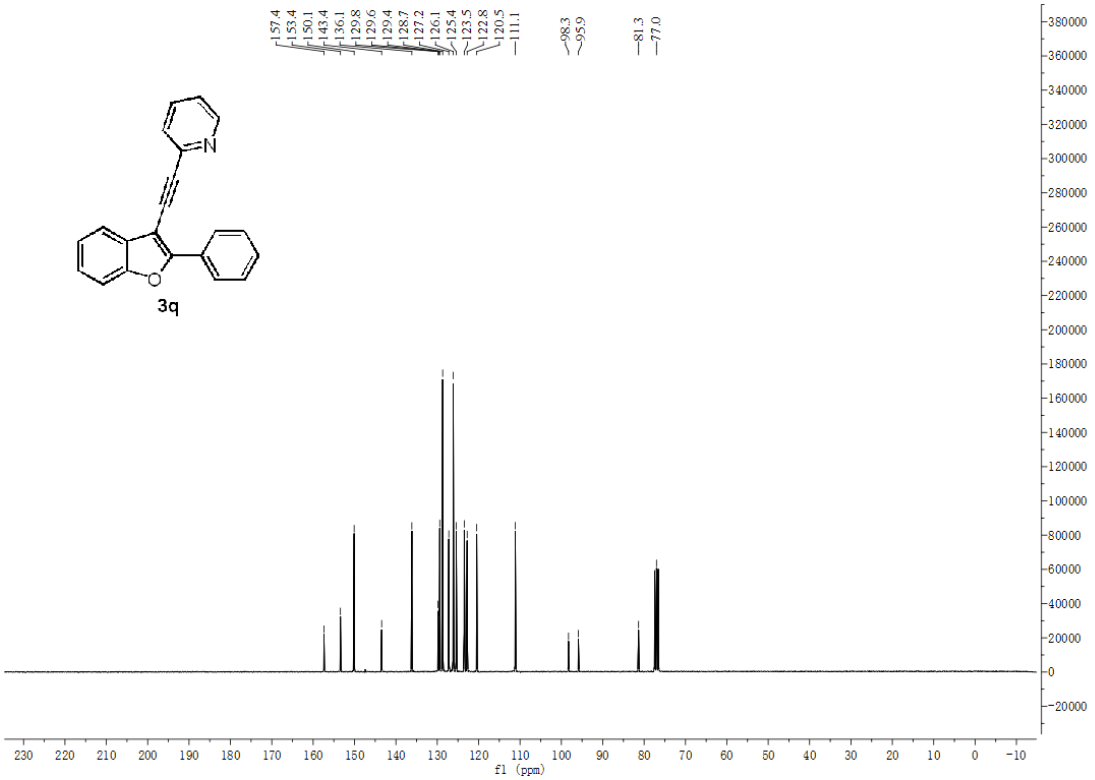


Figure S62. ^{13}C NMR (75 MHz, $CDCl_3$) spectra of **3q** in MestReNova.

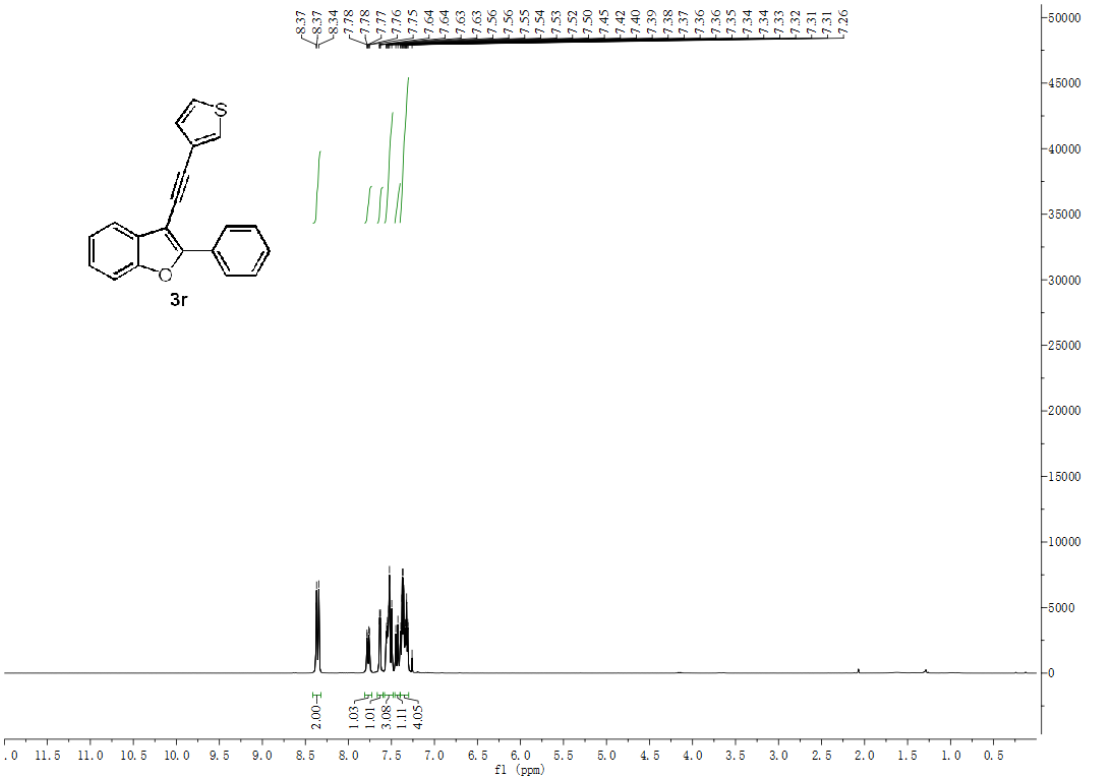


Figure S63. ^{1}H NMR (300 MHz, $CDCl_3$) spectra of **3r** in MestReNova.

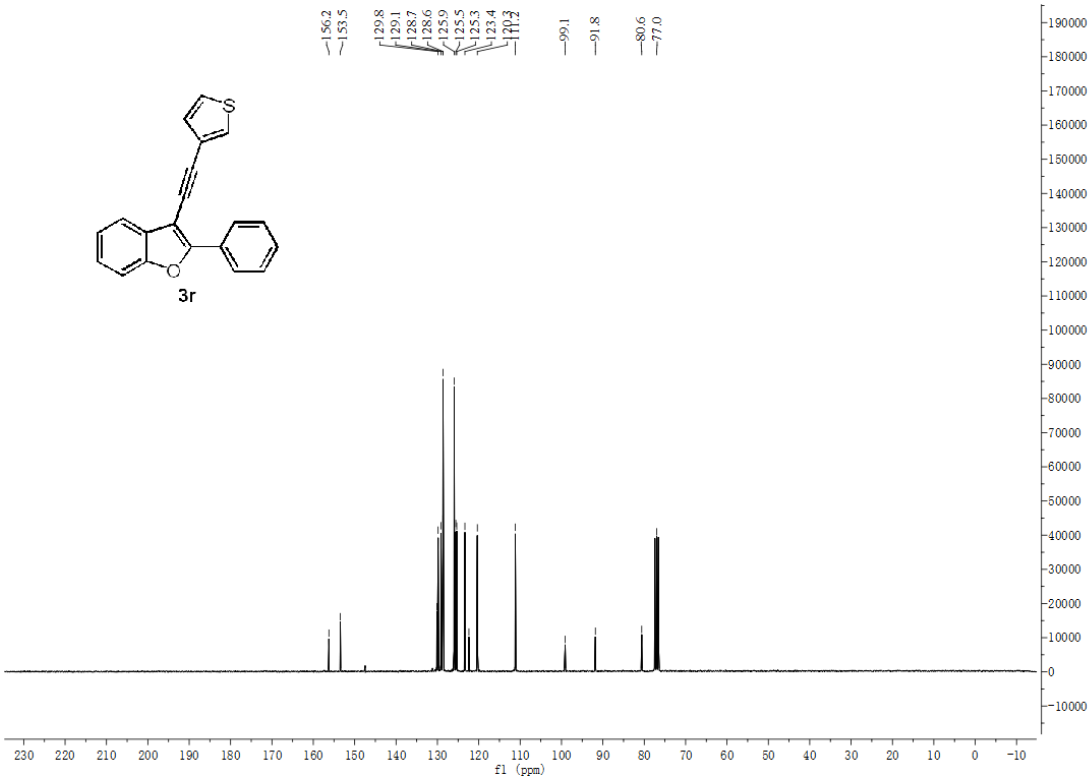


Figure S64. ^{13}C NMR (75 MHz, $CDCl_3$) spectra of **3r** in MestReNova.

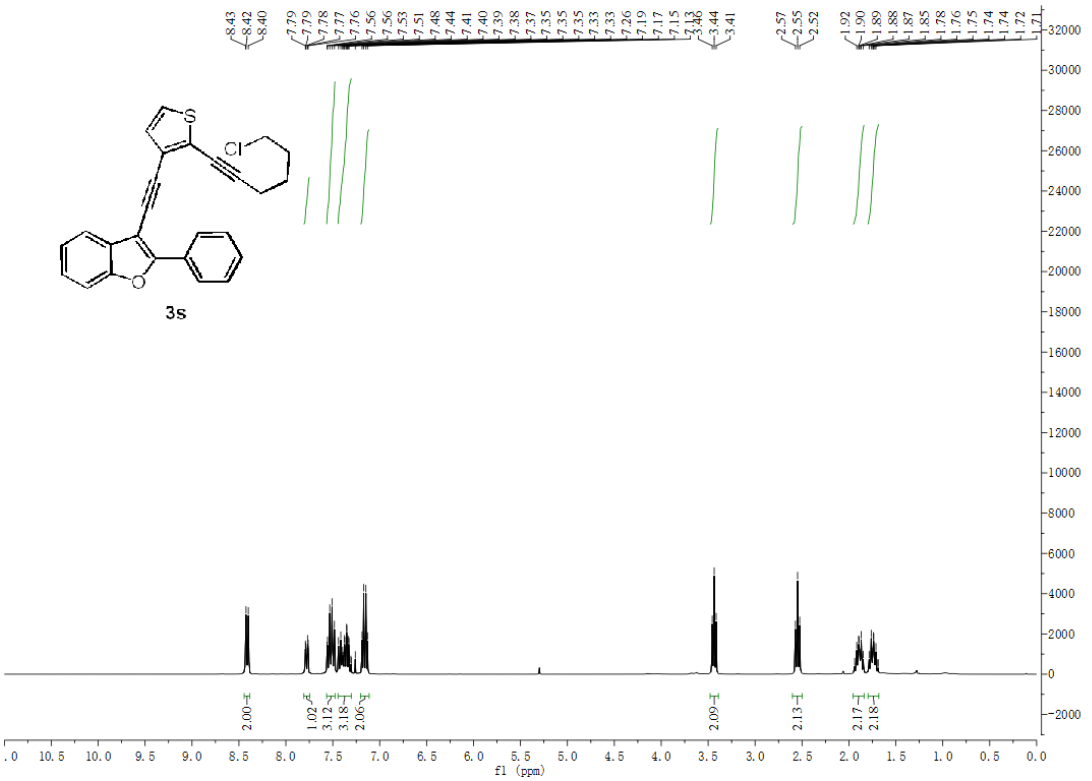


Figure S65. ^{1}H NMR (300 MHz, $CDCl_3$) spectra of **3s** in MestReNova.

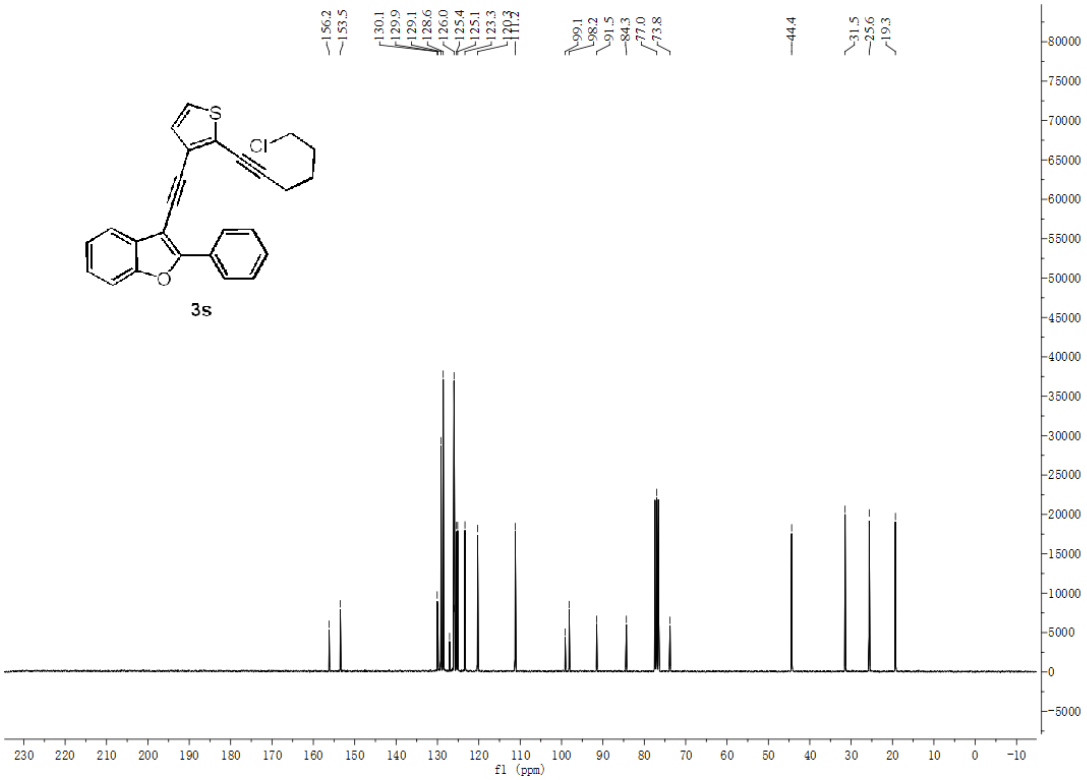


Figure S66. ^{13}C NMR (75 MHz, $CDCl_3$) spectra of **3s** in MestReNova.

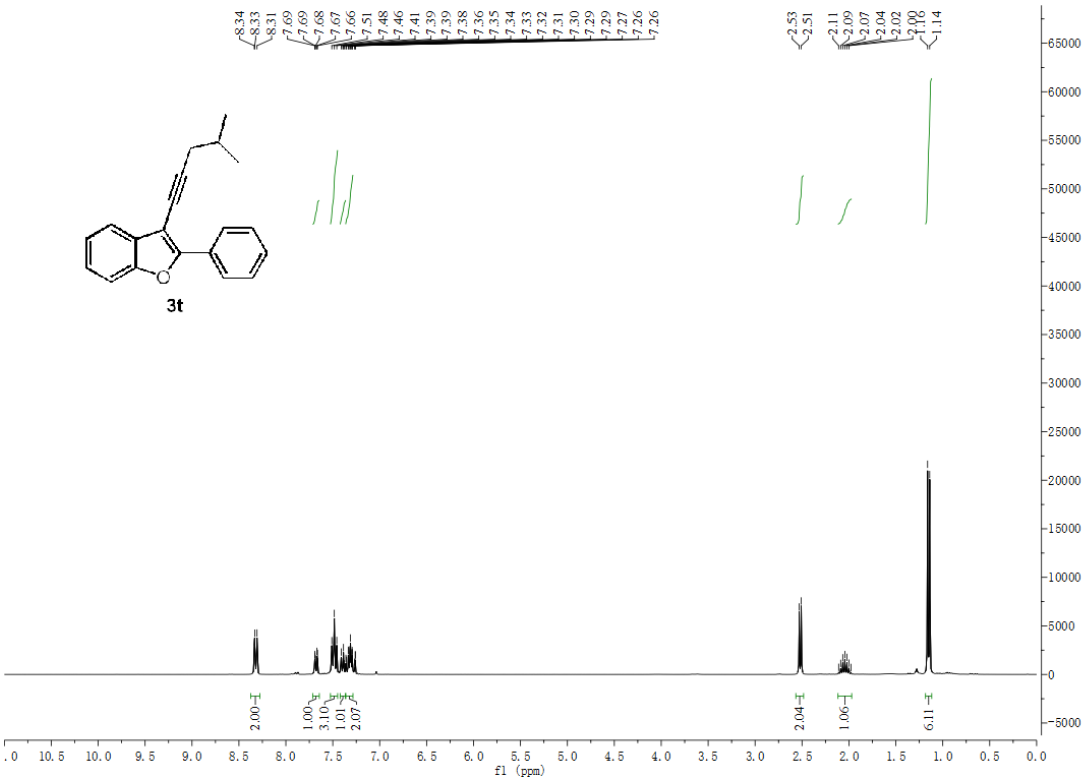


Figure S67. ^{1}H NMR (300 MHz, $CDCl_3$) spectra of **3t** in MestReNova.

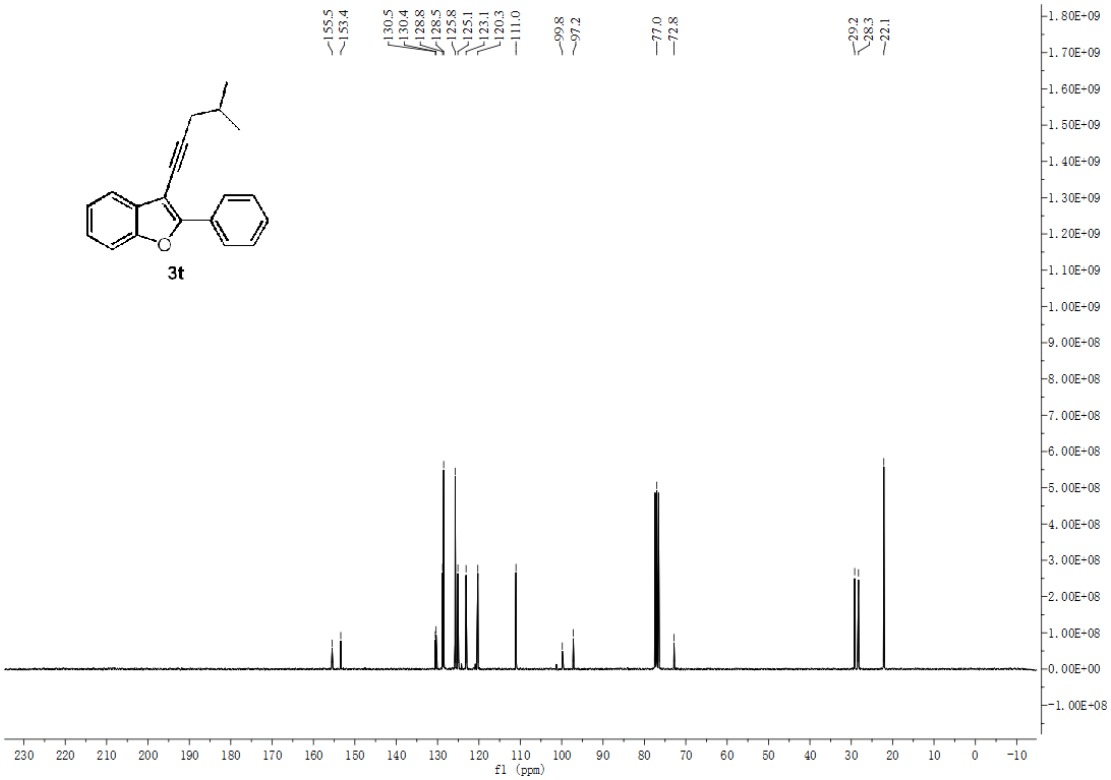


Figure S68. ^{13}C NMR (75 MHz, $CDCl_3$) spectra of **3t** in MestReNova.

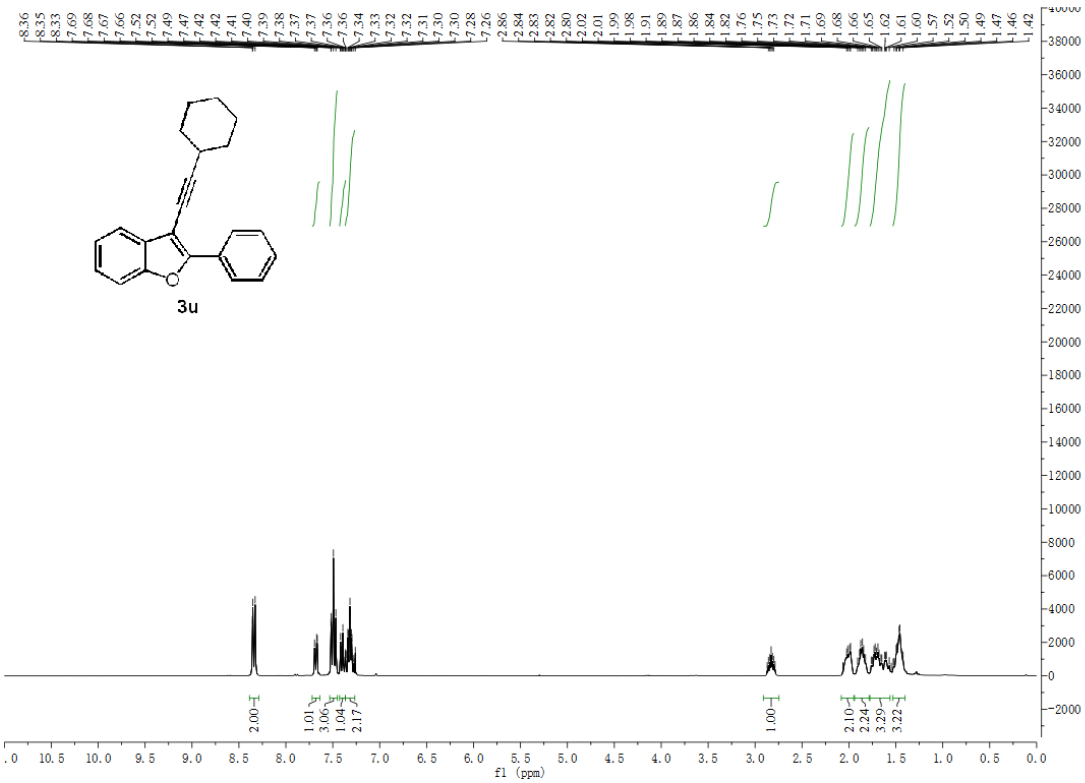


Figure S69. ^{1}H NMR (300 MHz, $CDCl_3$) spectra of **3u** in MestReNova.

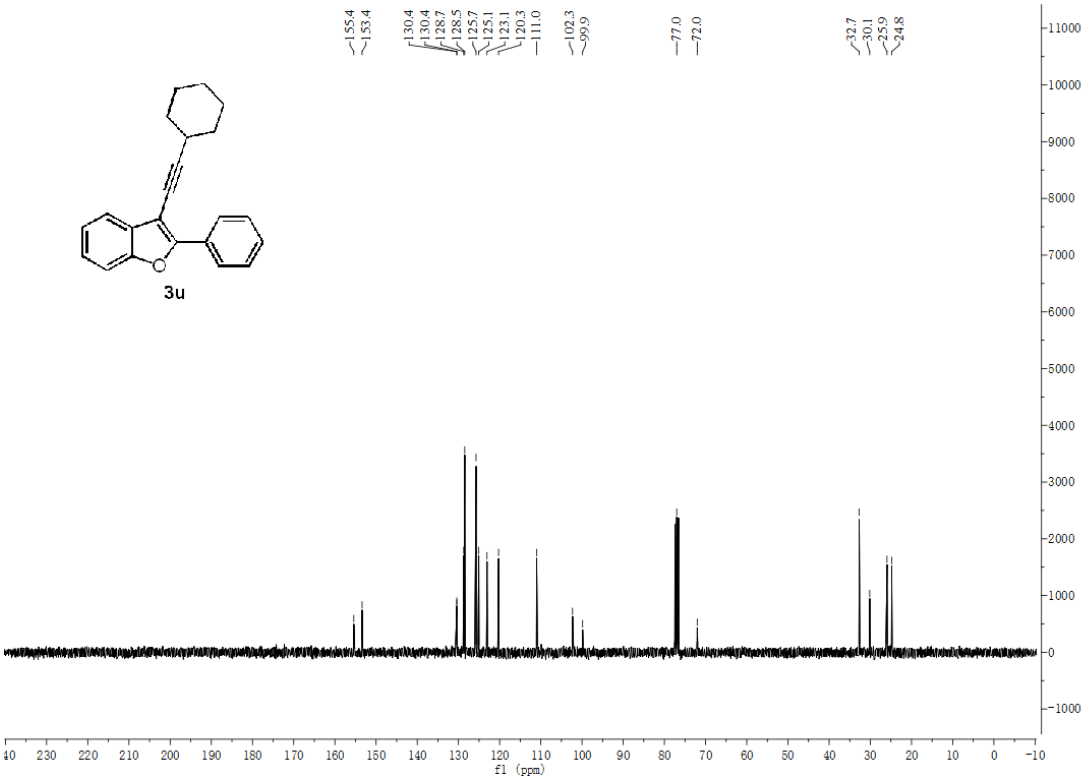


Figure S70. ^{13}C NMR (75MHz, $CDCl_3$) spectra of **3u** in MestReNova.

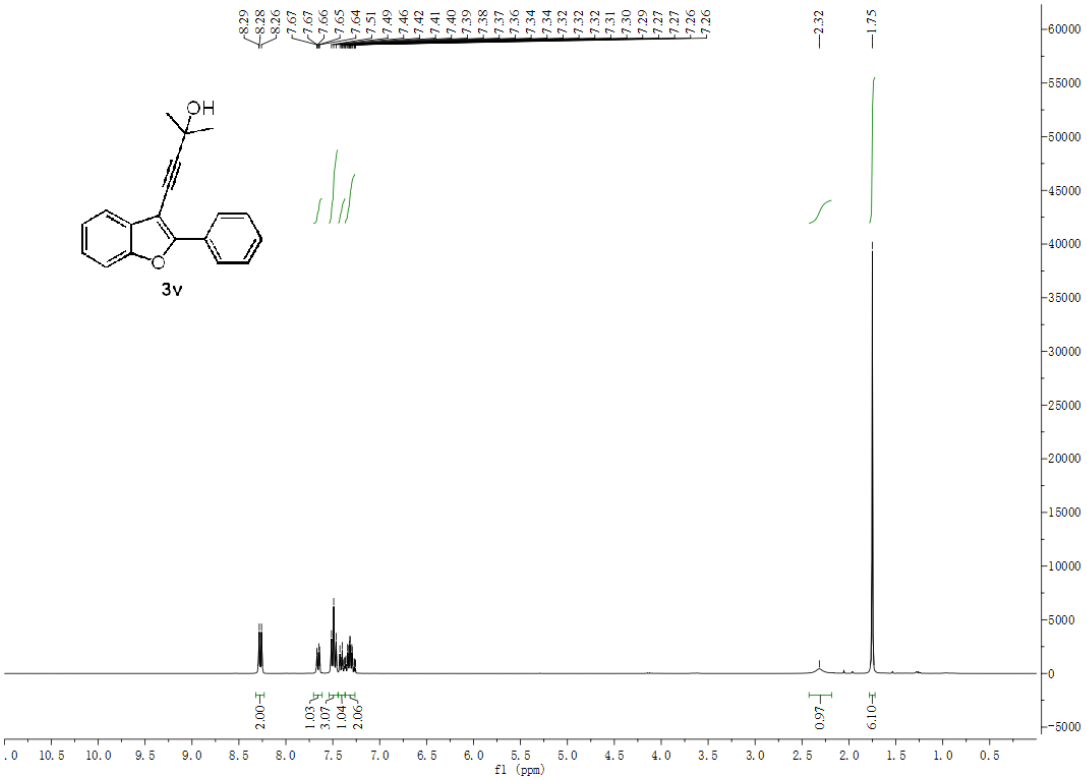


Figure S71. ^{1}H NMR (300 MHz, $CDCl_3$) spectra of **3v** in MestReNova.

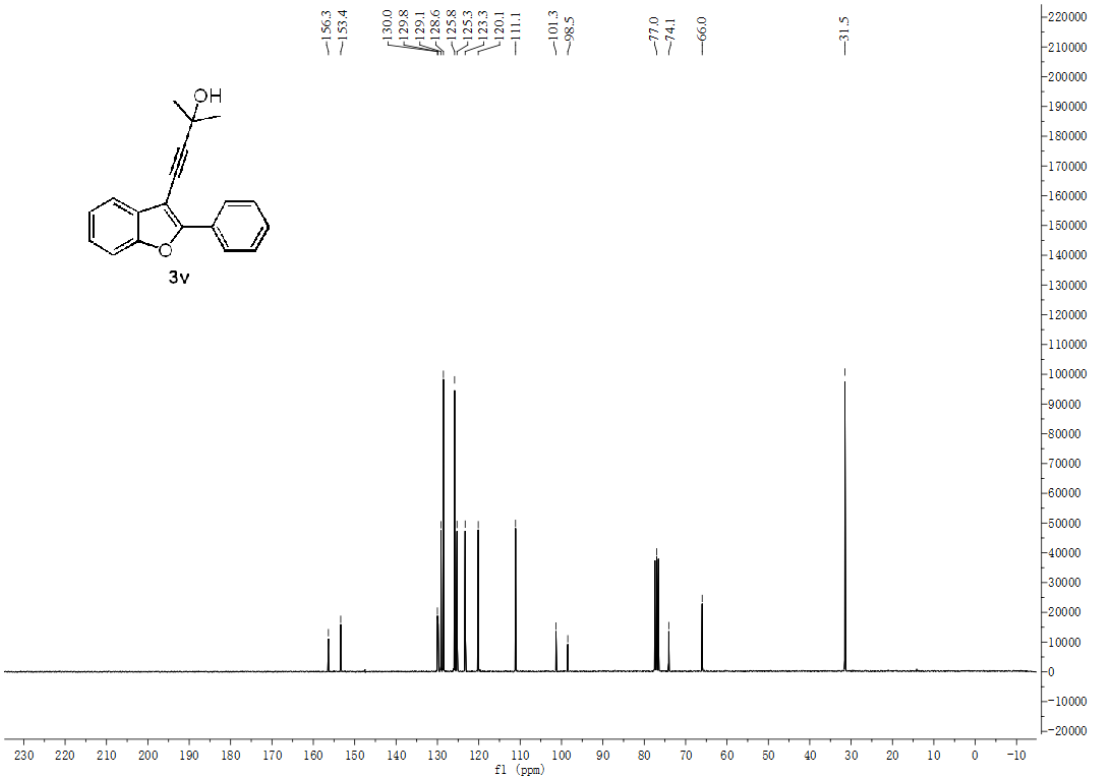


Figure S72. ^{13}C NMR (75 MHz, $CDCl_3$) spectra of **3v** in MestReNova.

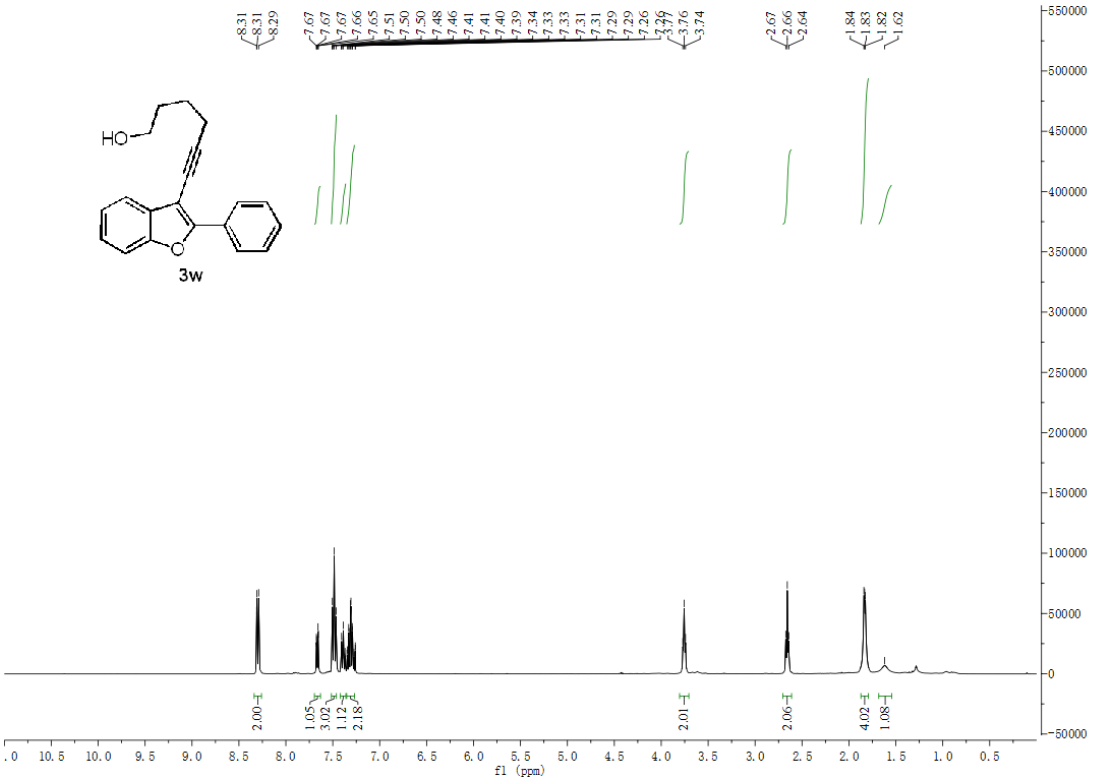


Figure S73. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3w** in MestReNova.

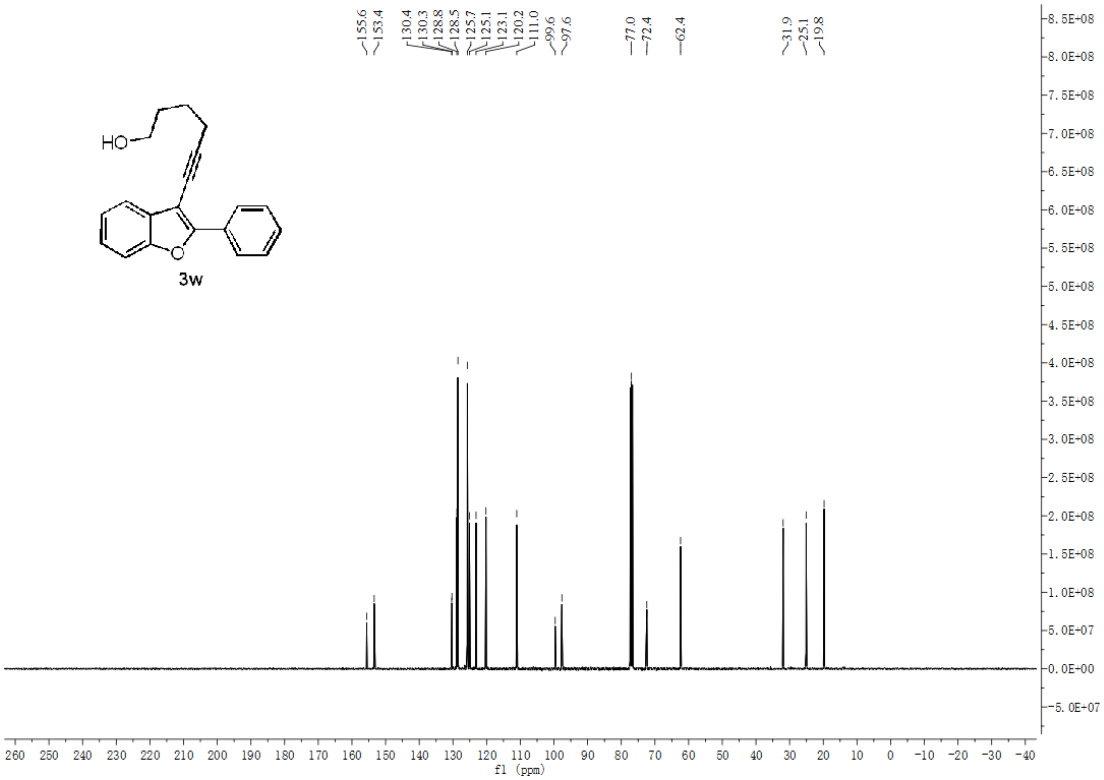


Figure S74. ^{13}C NMR (101 MHz, $CDCl_3$) spectra of **3w** in MestReNova.

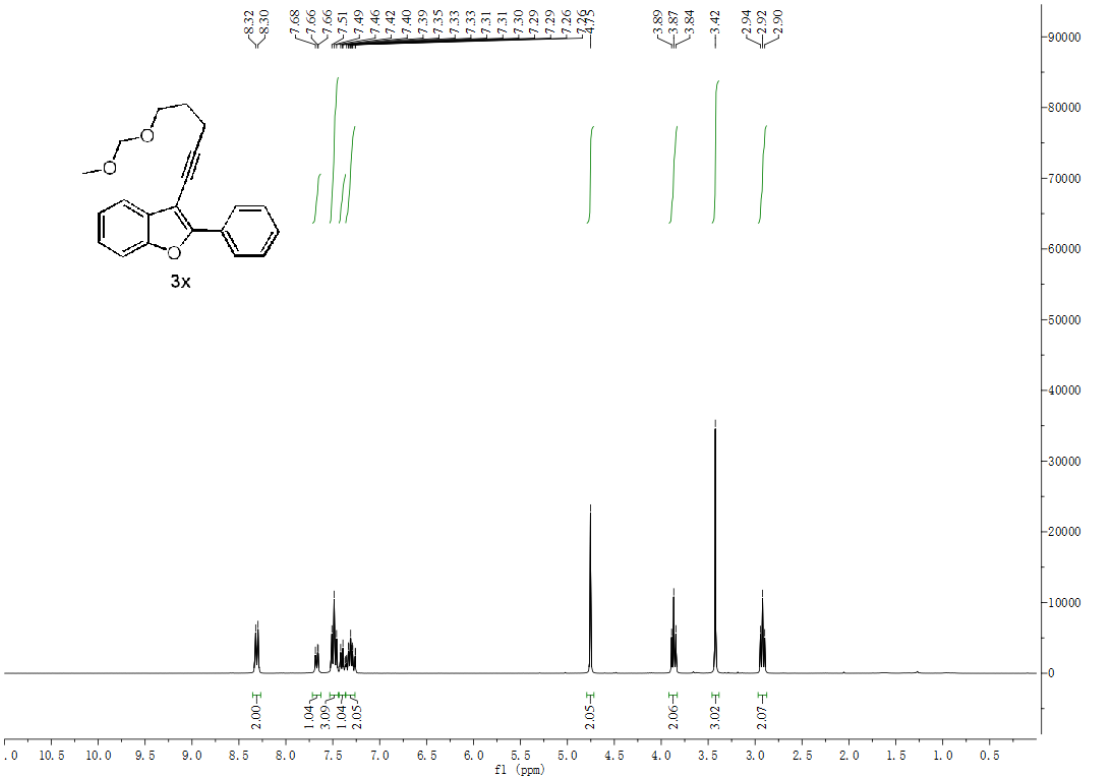


Figure S75. ^{1}H NMR (300 MHz, $CDCl_3$) spectra of **3x** in MestReNova.

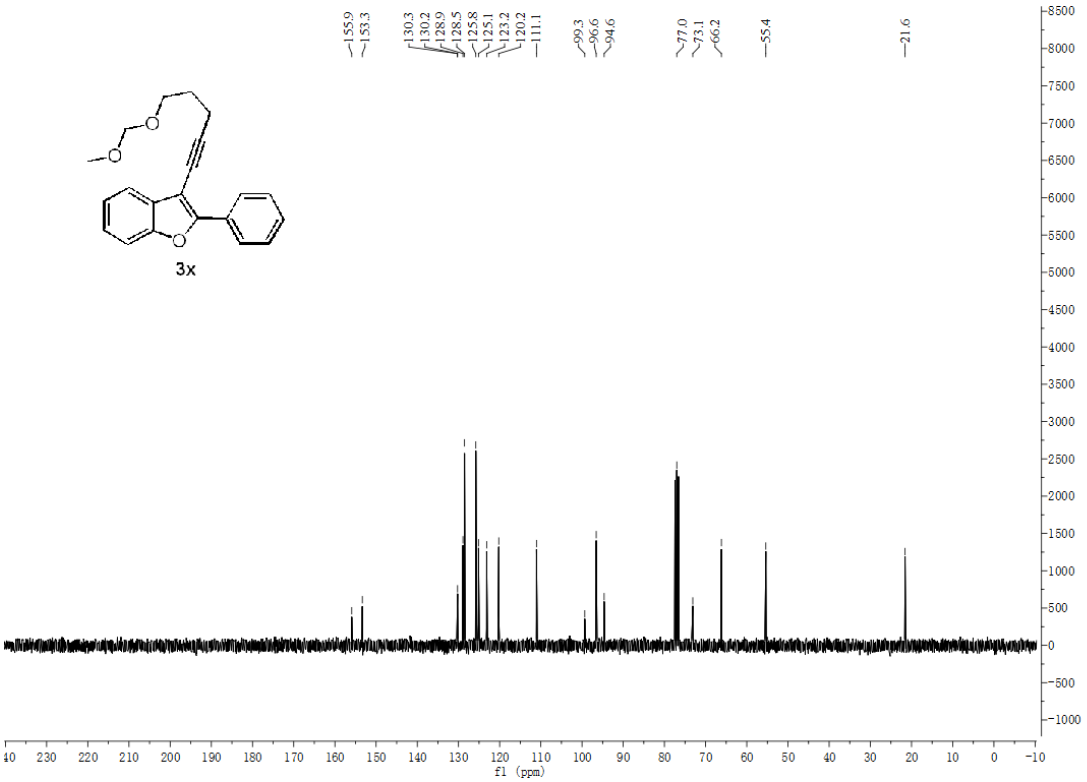


Figure S76. ^{13}C NMR (75 MHz, $CDCl_3$) spectra of **3x** in MestReNova.

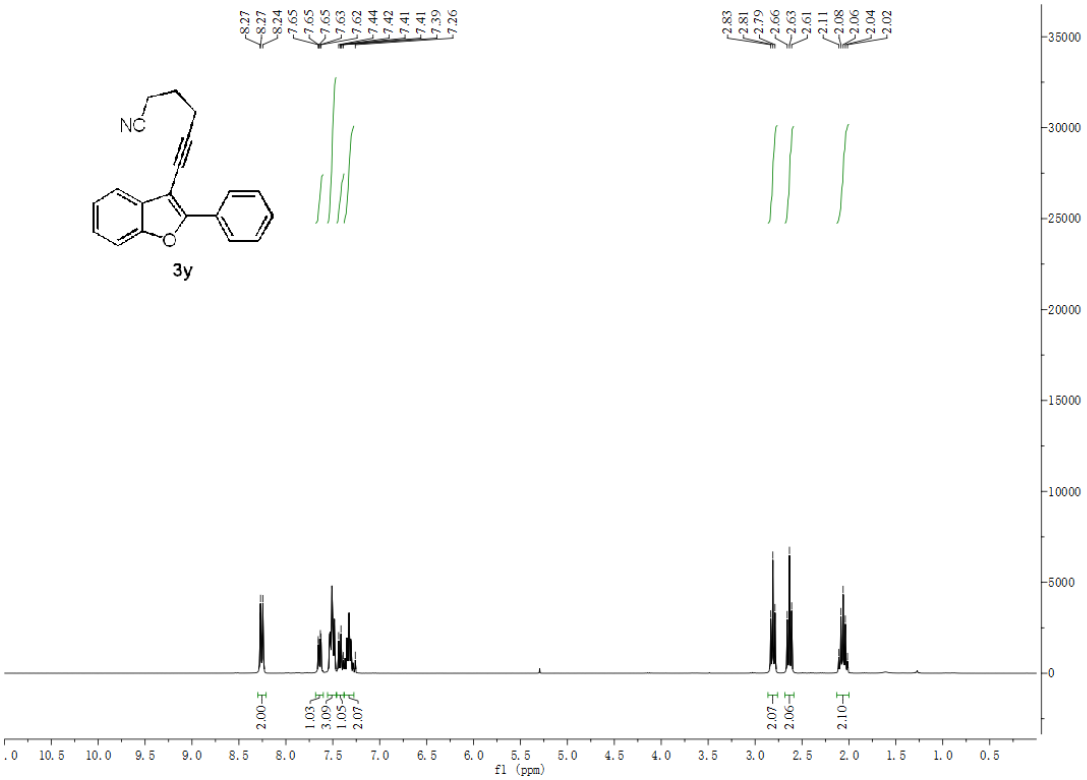


Figure S77. ^{1}H NMR (300 MHz, $CDCl_3$) spectra of **3y** in MestReNova.

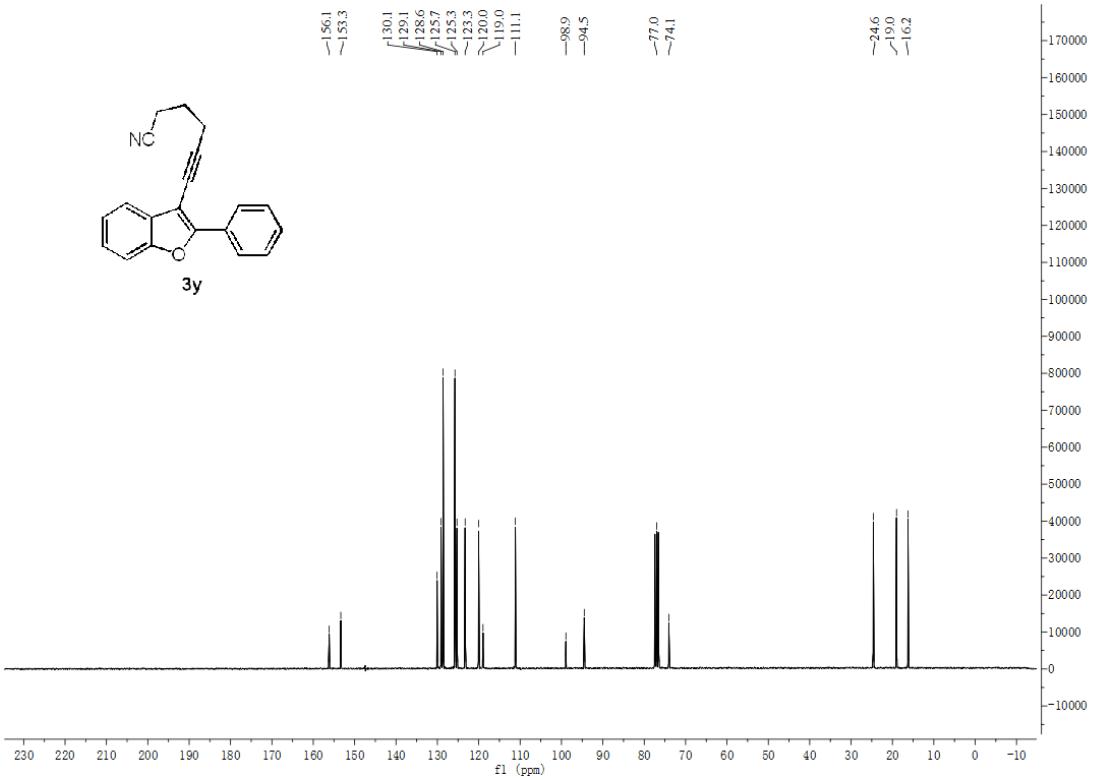


Figure S78. ^{13}C NMR (75 MHz, $CDCl_3$) spectra of **3y** in MestReNova.

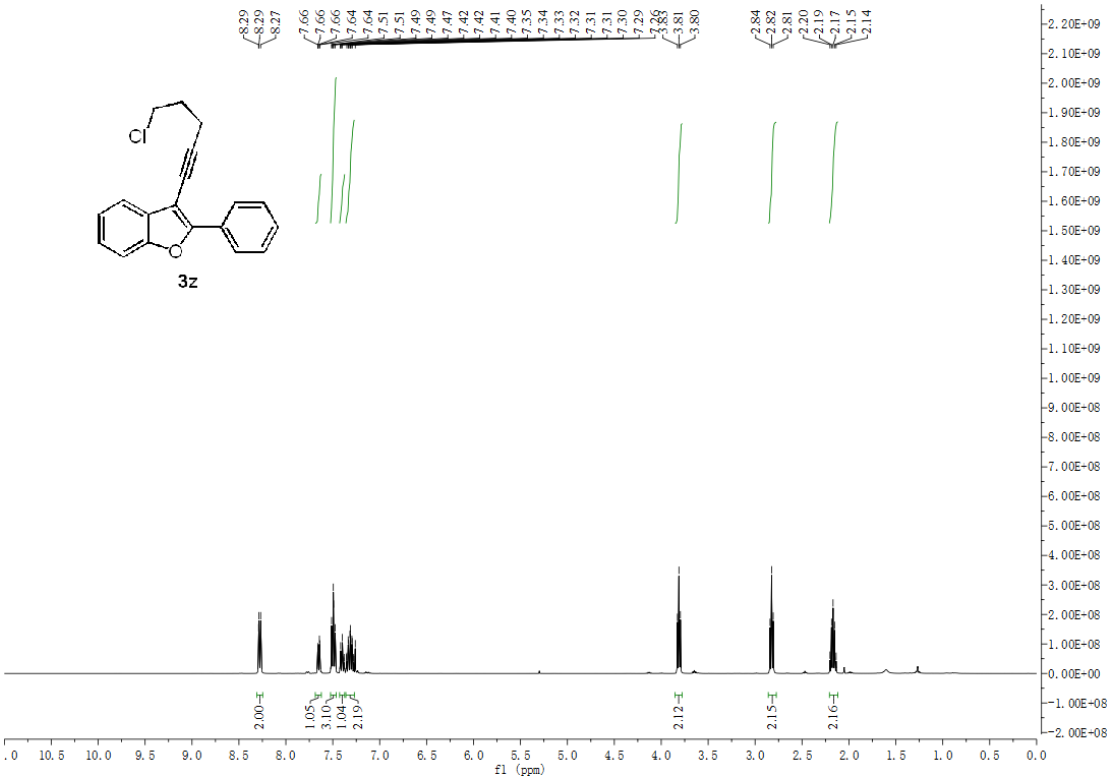


Figure S79. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3z** in MestReNova.

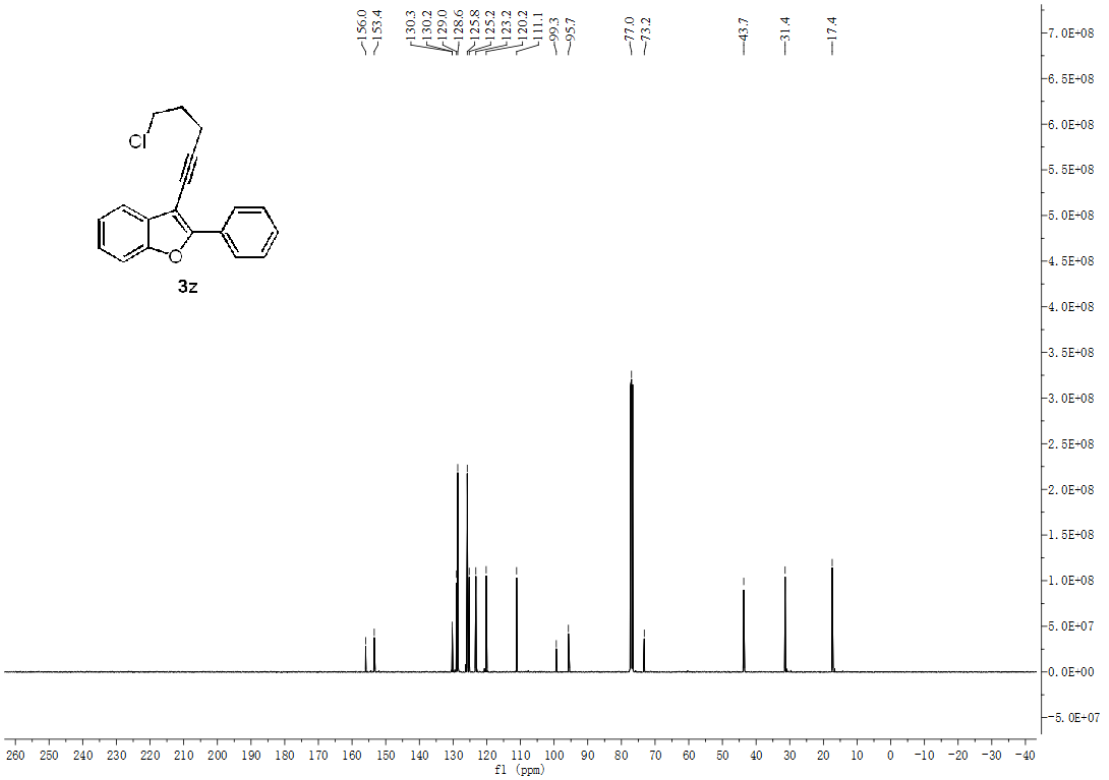


Figure S80. ^{13}C NMR (101 MHz, $CDCl_3$) spectra of **3z** in MestReNova.

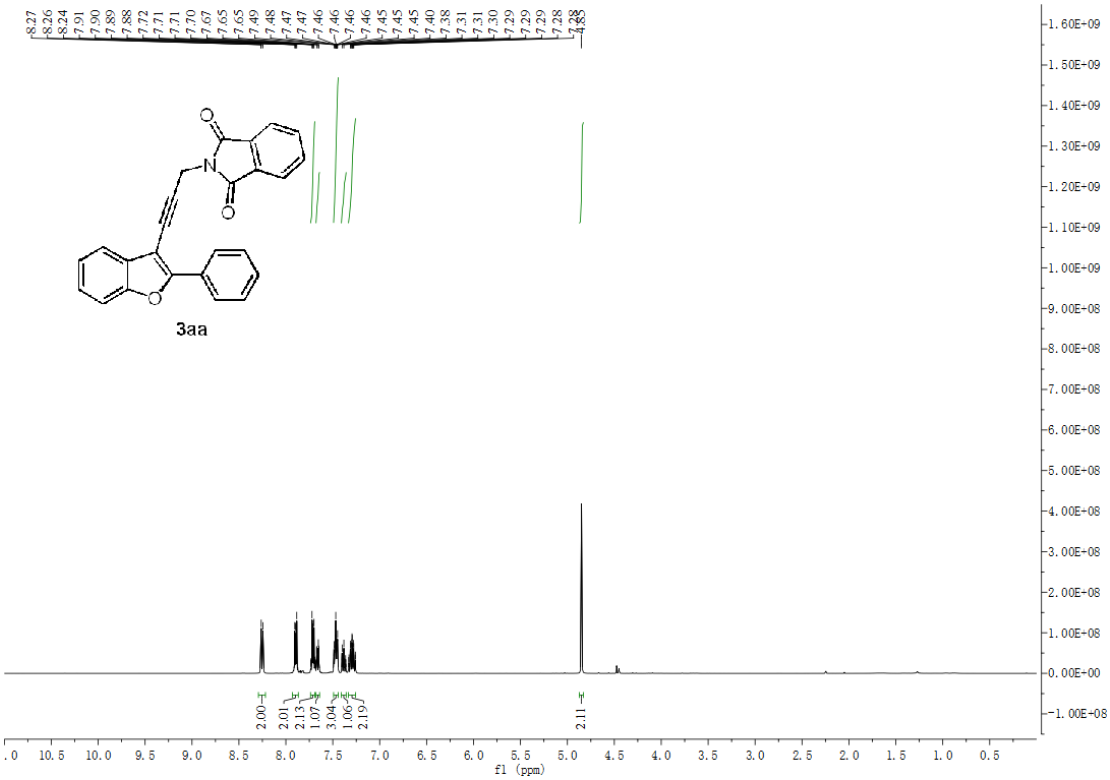


Figure S81. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3aa** in MestReNova.

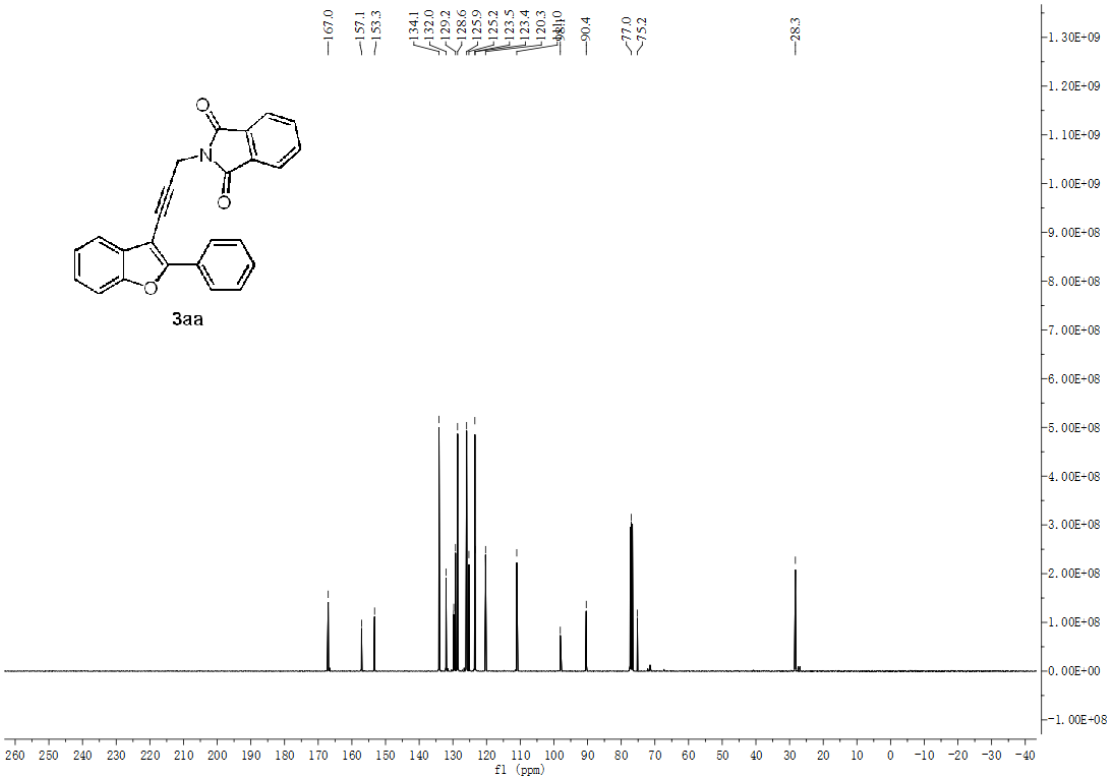


Figure S82. ^{13}C NMR (101 MHz, $CDCl_3$) spectra of **3aa** in MestReNova.

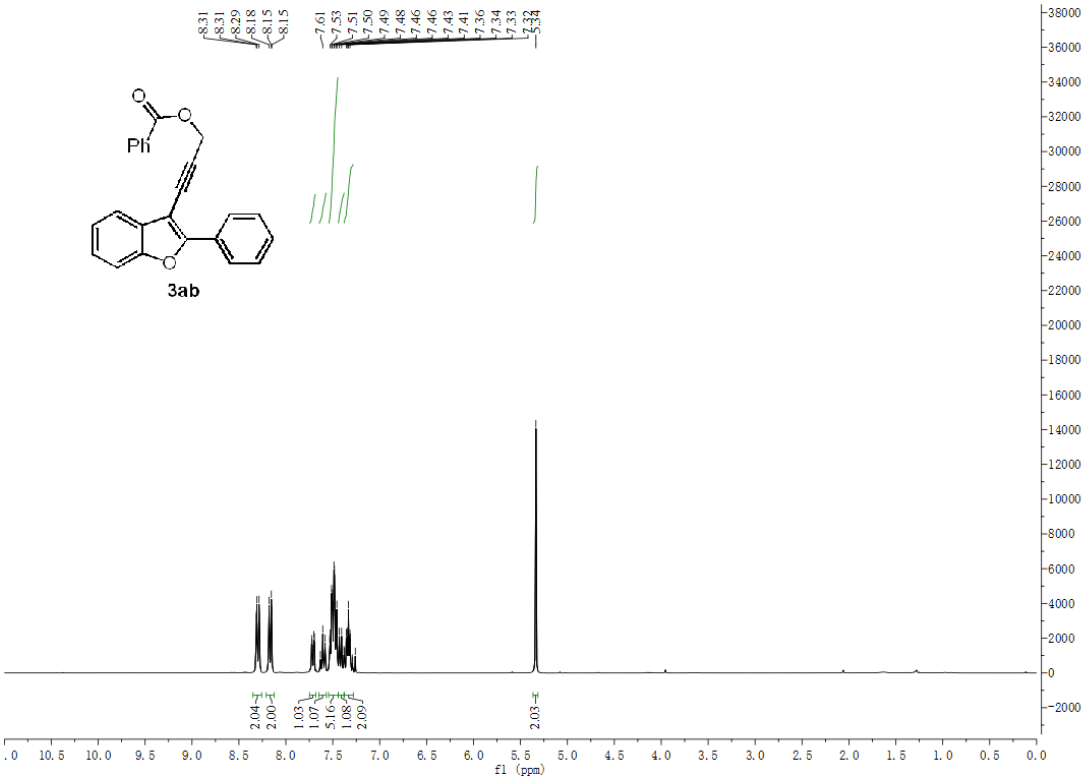


Figure S83. ^{1}H NMR (300 MHz, $CDCl_3$) spectra of **3ab** in MestReNova.

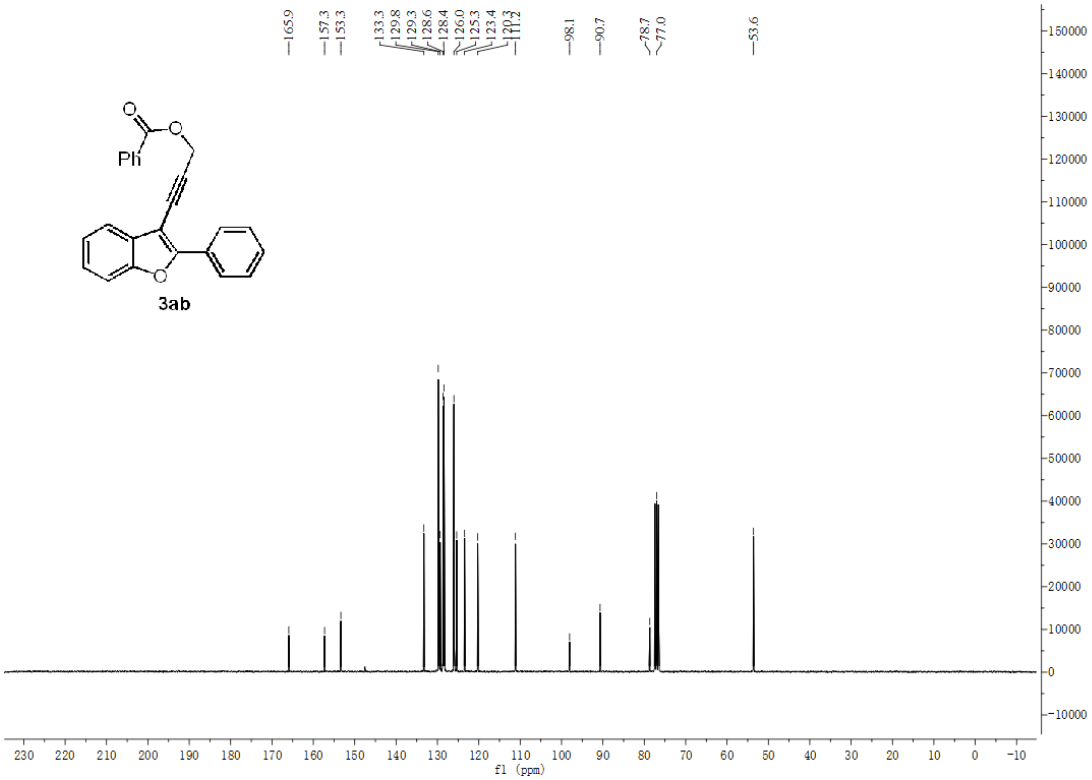


Figure S84. ^{13}C NMR (75 MHz, $CDCl_3$) spectra of **3ab** in MestReNova.

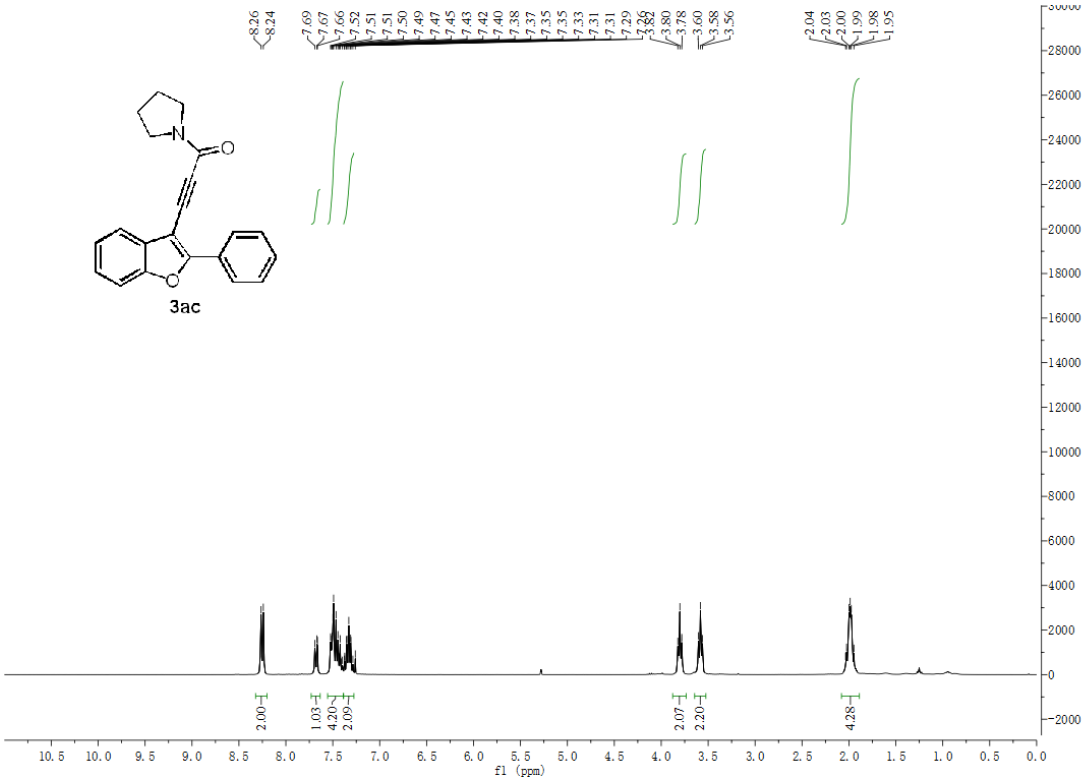


Figure S85. ^{1}H NMR (300 MHz, $CDCl_3$) spectra of **3ac** in MestReNova.

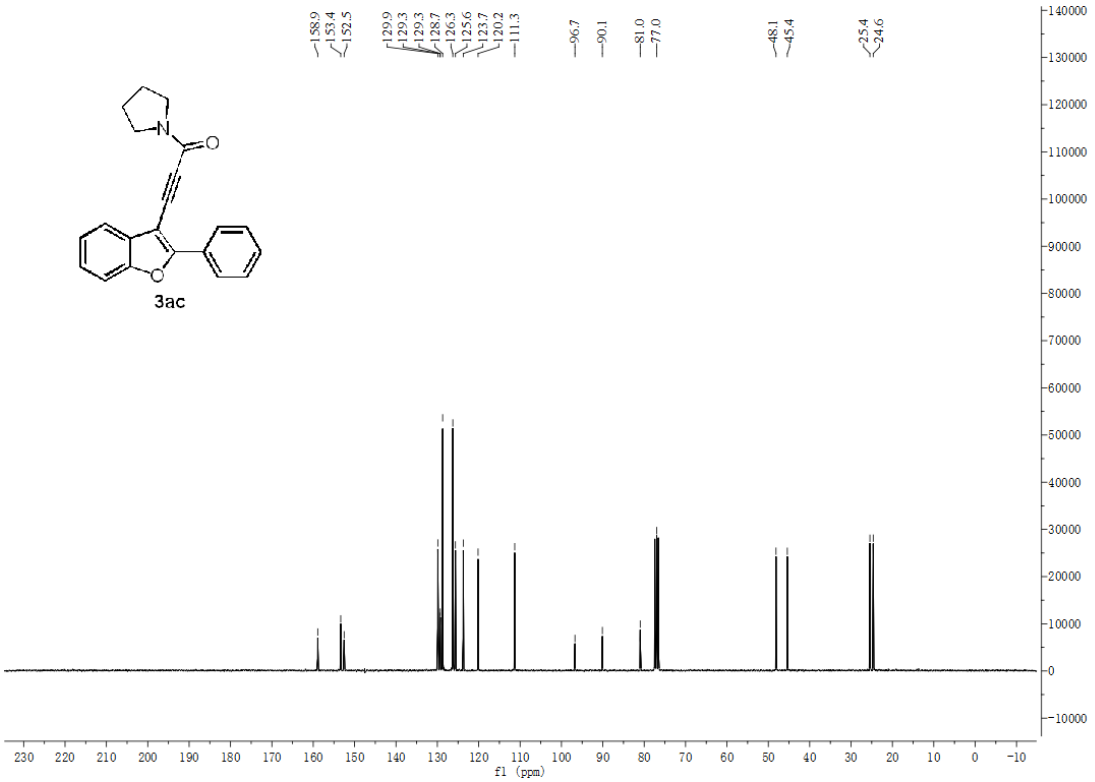


Figure S86. ^{13}C NMR (75 MHz, $CDCl_3$) spectra of **3ac** in MestReNova.

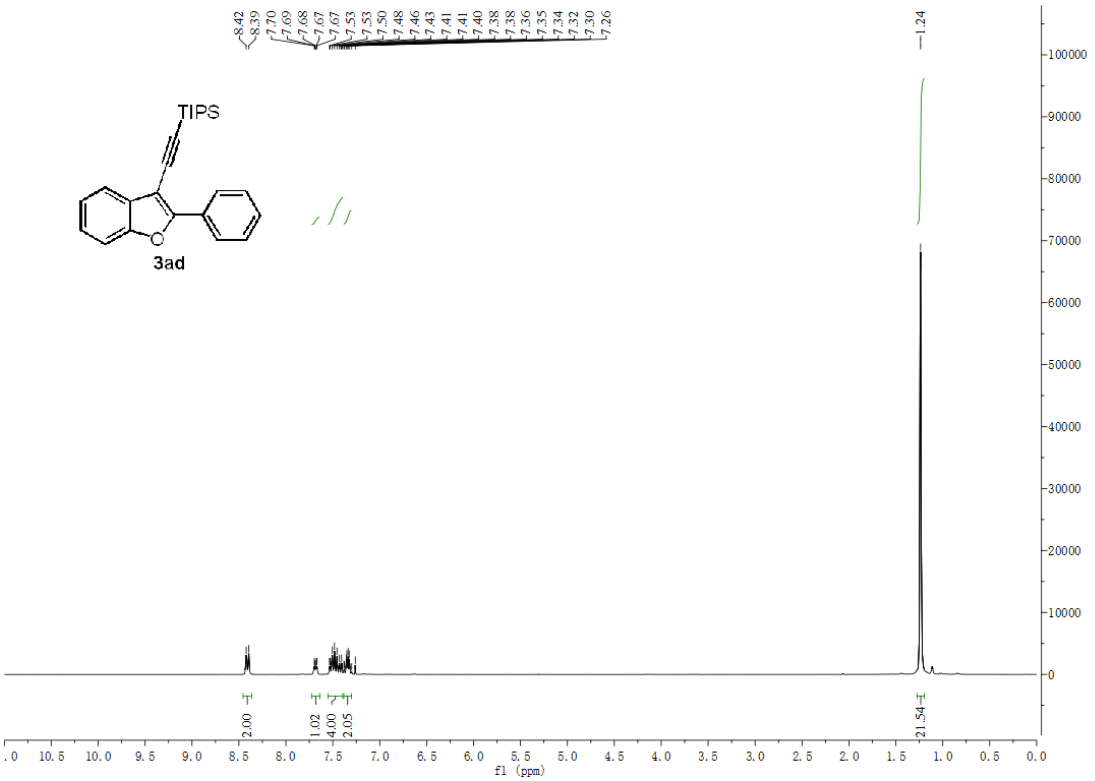


Figure S87. ^{1}H NMR (300 MHz, $CDCl_3$) spectra of **3ad** in MestReNova.

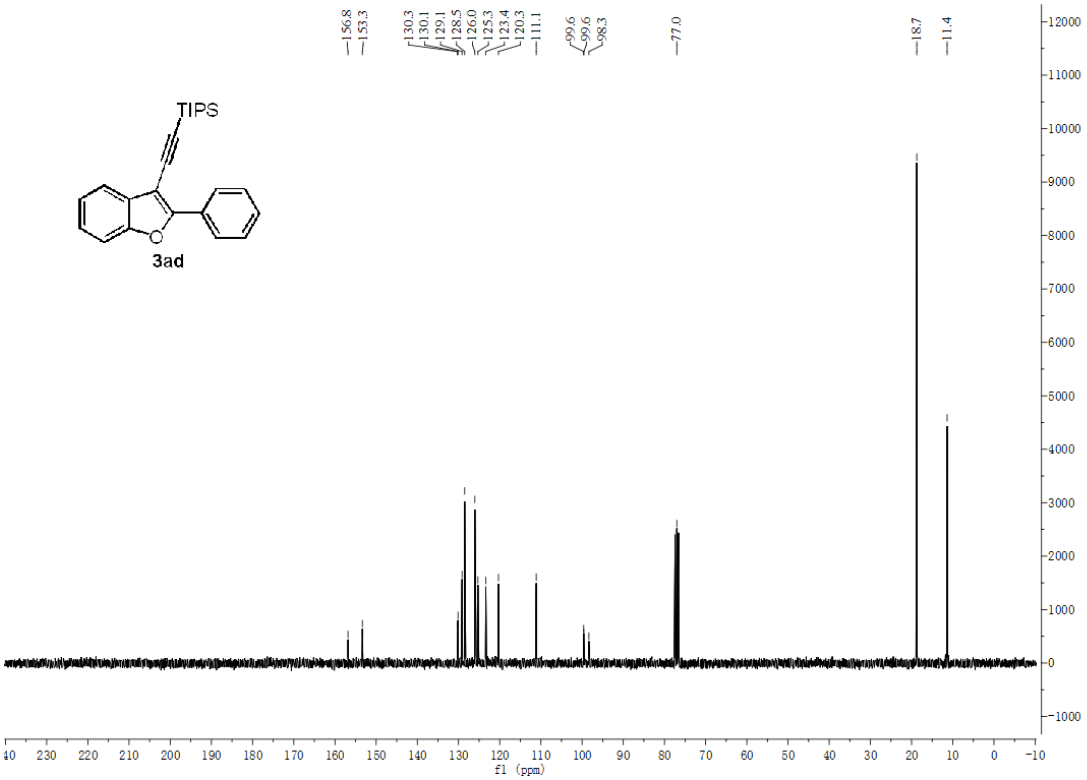


Figure S88. ^{13}C NMR (75 MHz, $CDCl_3$) spectra of **3ad** in MestReNova.

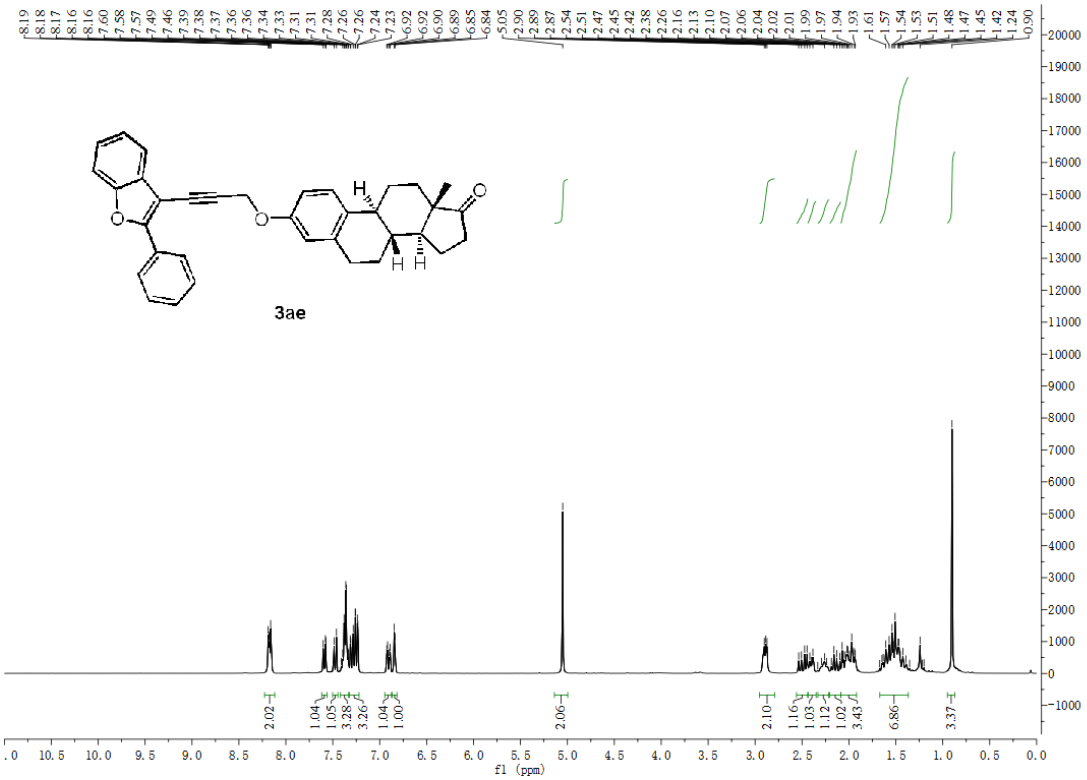


Figure S89. ^{1}H NMR (300 MHz, $CDCl_3$) spectra of **3ae** in MestReNova.

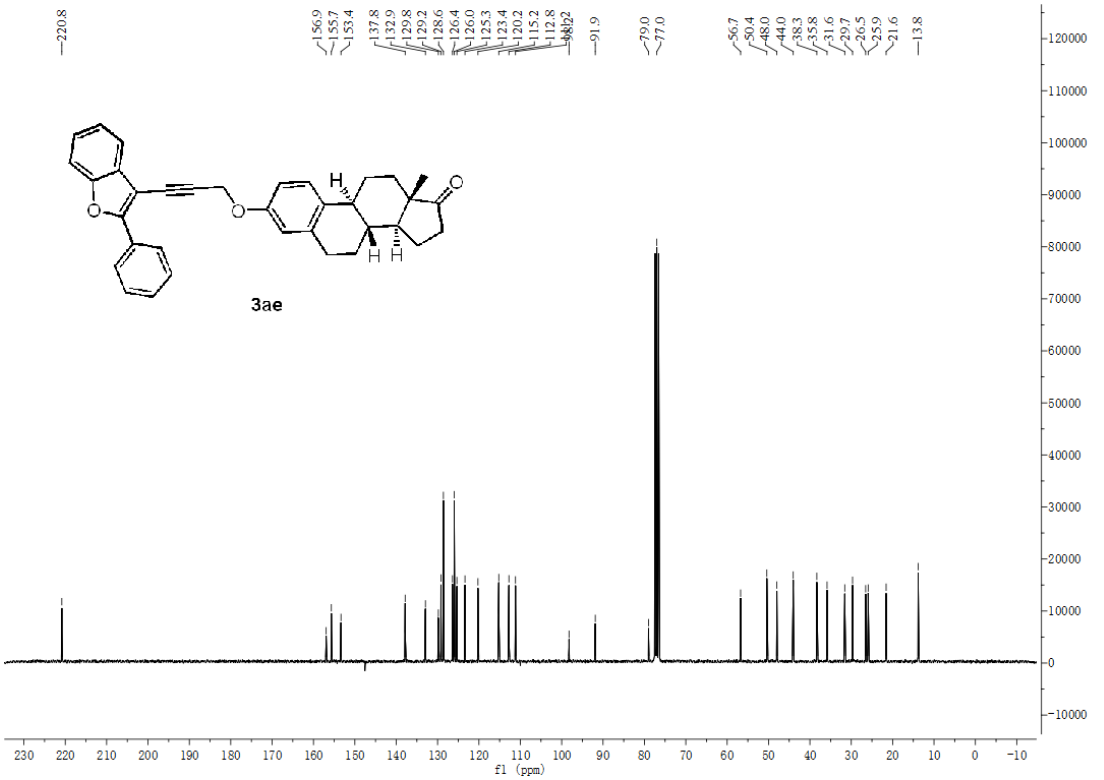


Figure S90. ^{13}C NMR (75 MHz, $CDCl_3$) spectra of **3ae** in MestReNova.

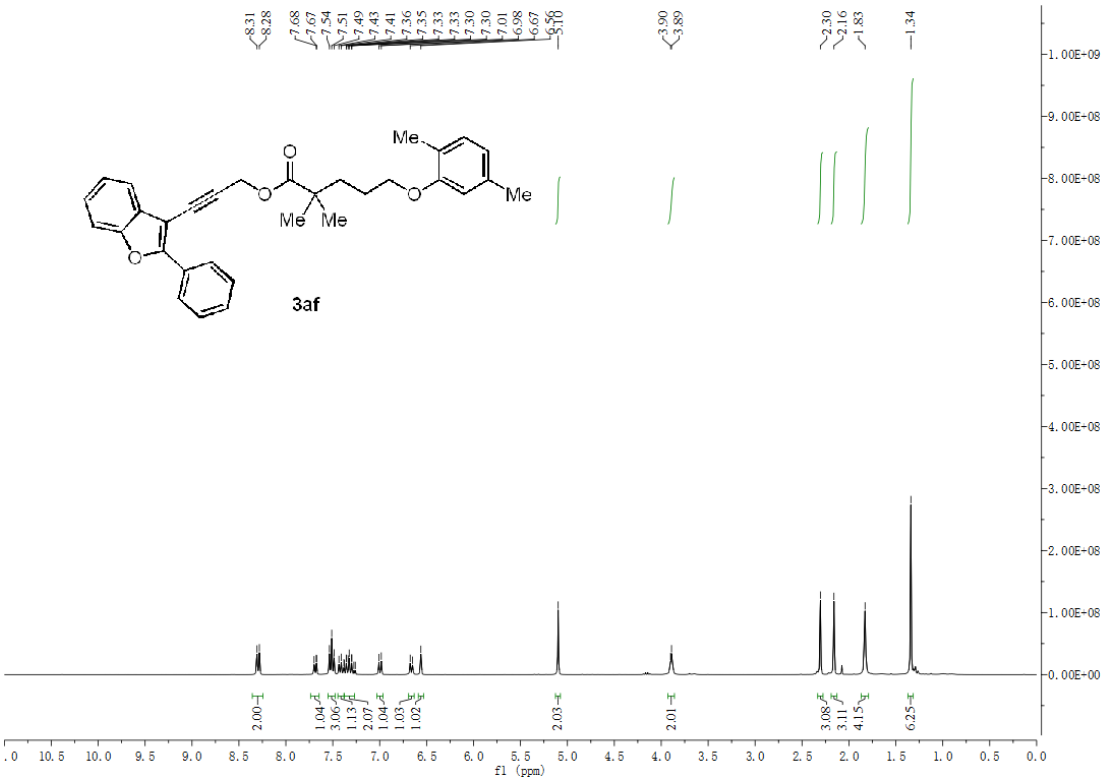


Figure S91. ^{1}H NMR (300 MHz, $CDCl_3$) spectra of **3af** in MestReNova.

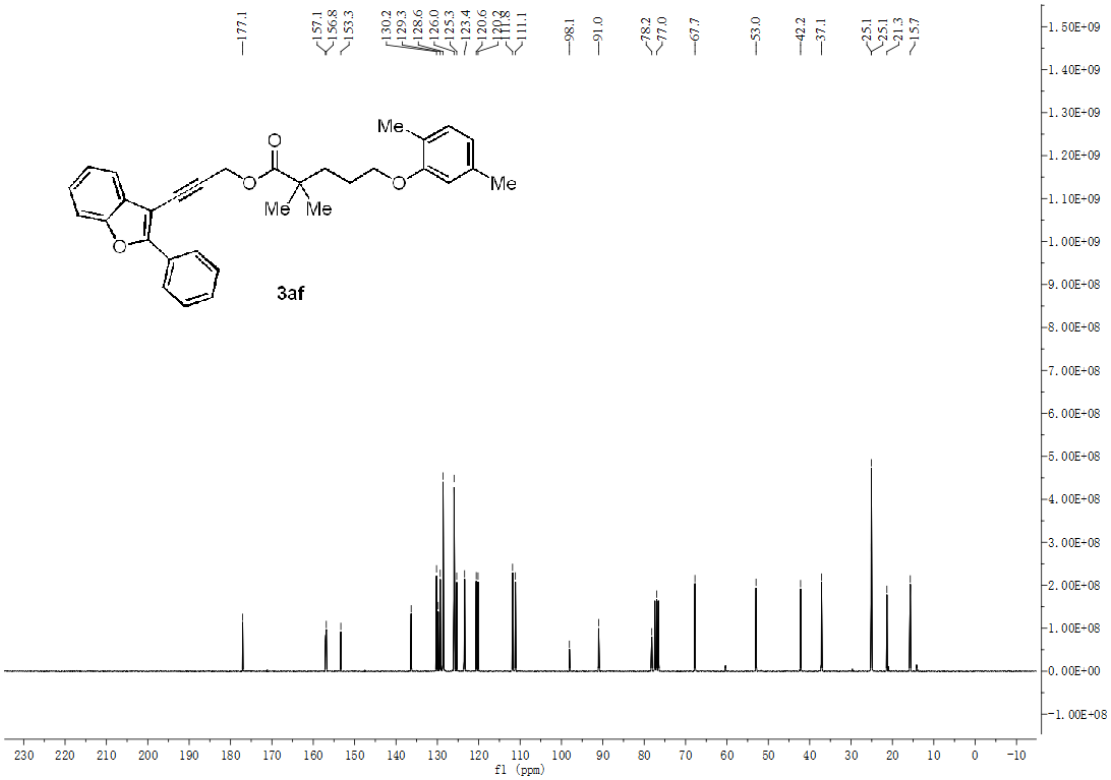


Figure S92. ^{13}C NMR (75 MHz, $CDCl_3$) spectra of **3af** in MestReNova.

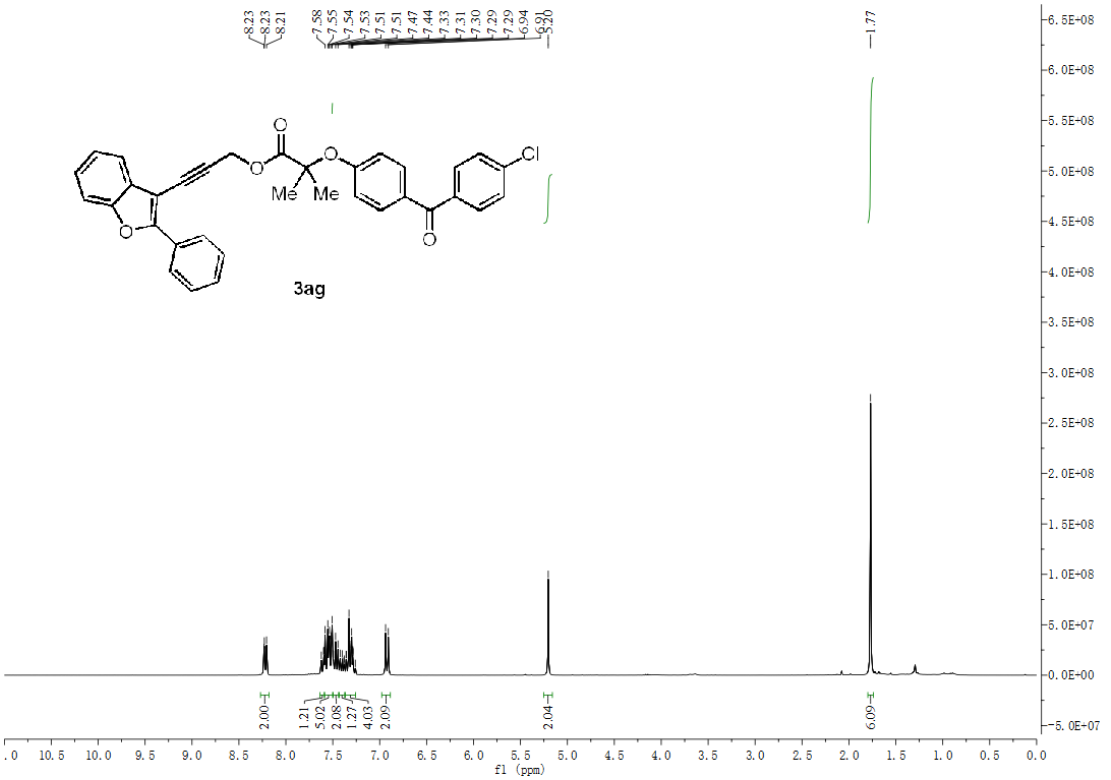


Figure S93. ^{1}H NMR (300 MHz, $CDCl_3$) spectra of **3ag** in MestReNova.

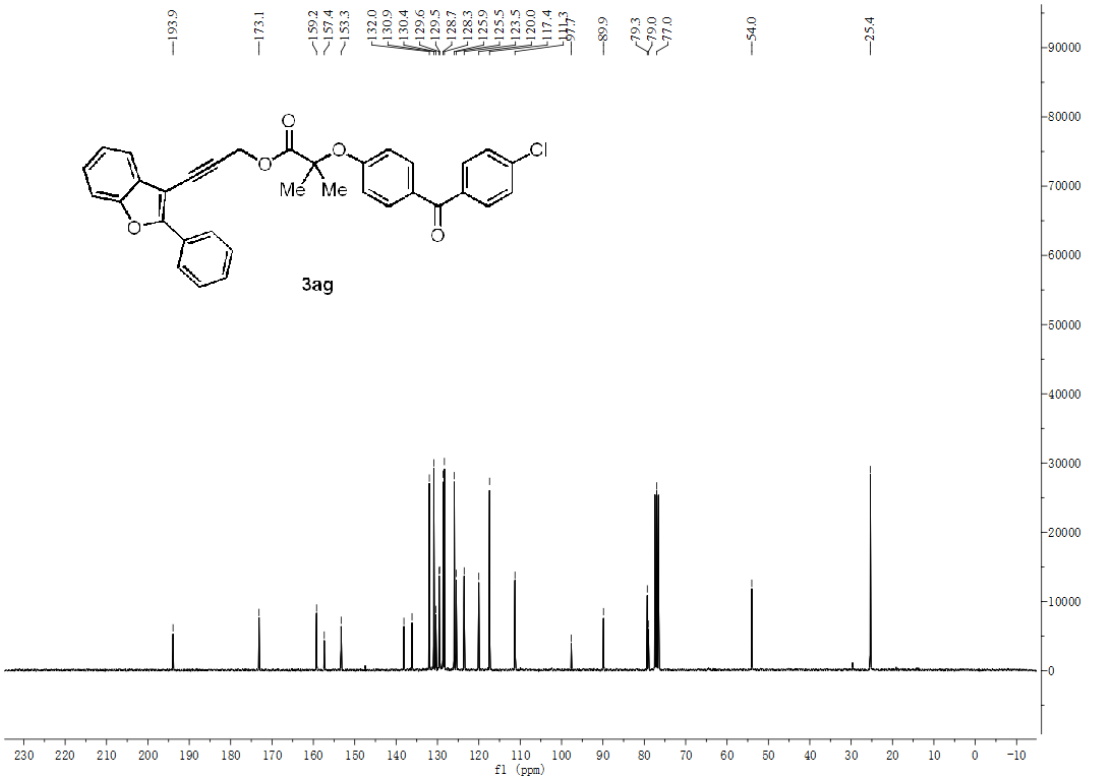


Figure S94. ^{13}C NMR (75 MHz, $CDCl_3$) spectra of **3ag** in MestReNova.

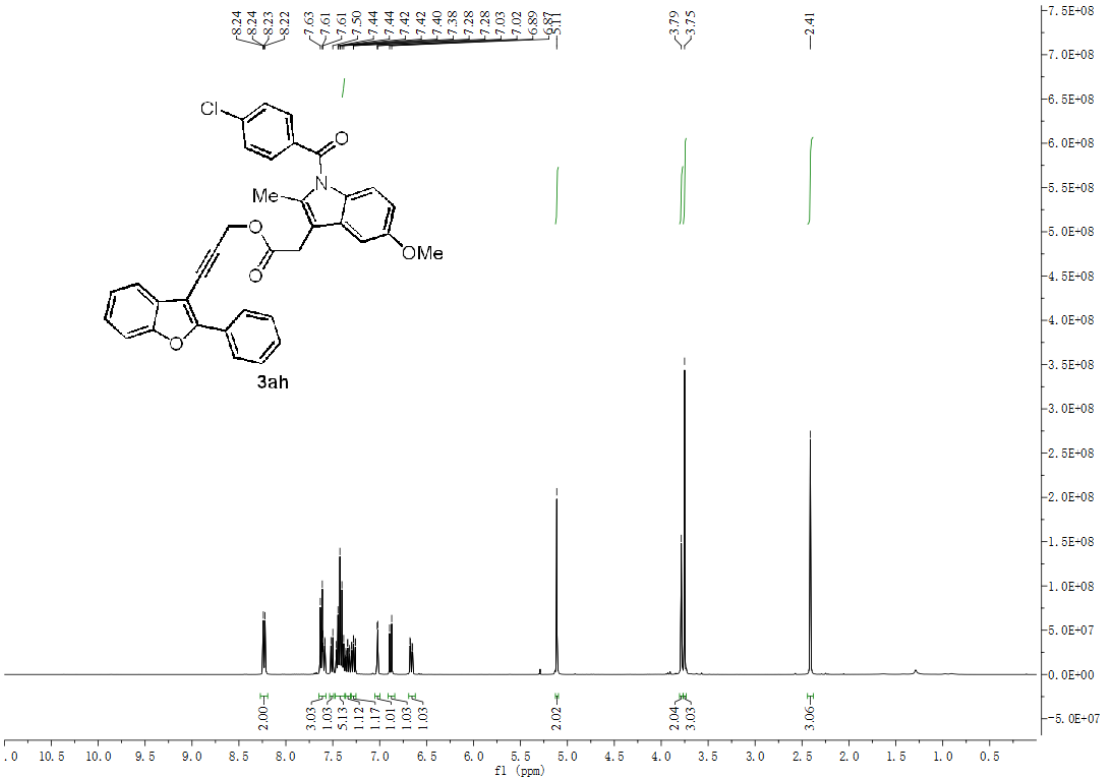


Figure S95. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3ah** in MestReNova.

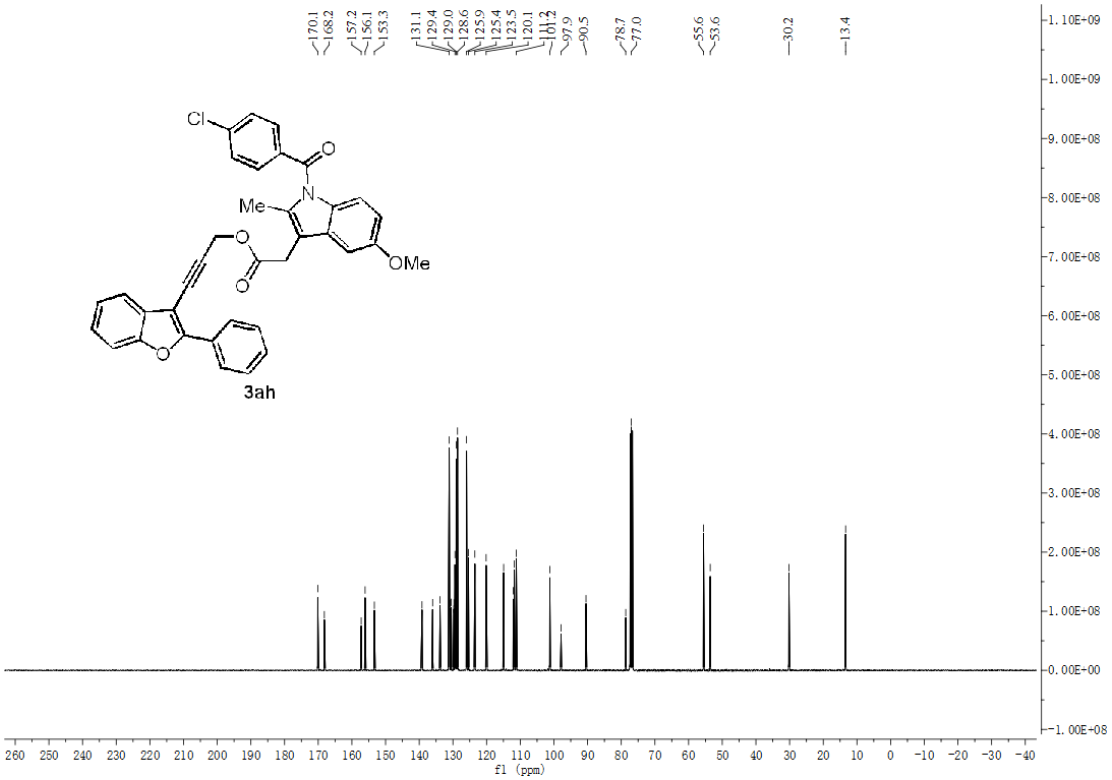


Figure S96. ^{13}C NMR (101 MHz, $CDCl_3$) spectra of **3ah** in MestReNova.

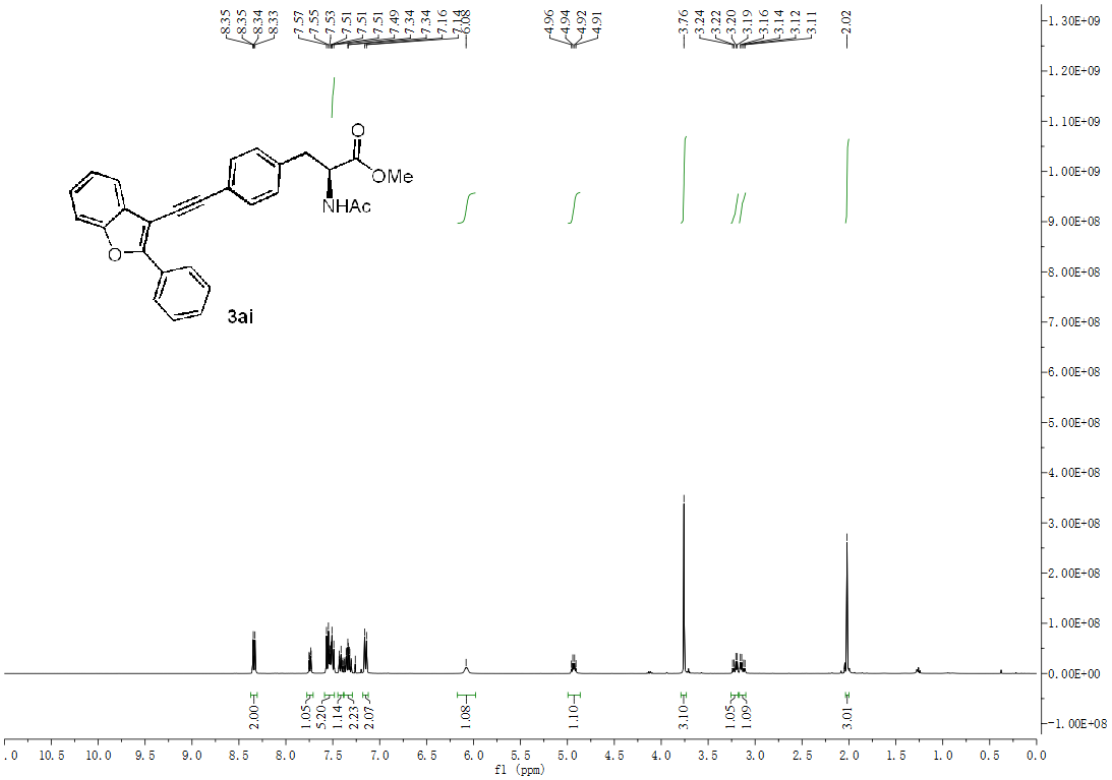


Figure S97. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3ai** in MestReNova.

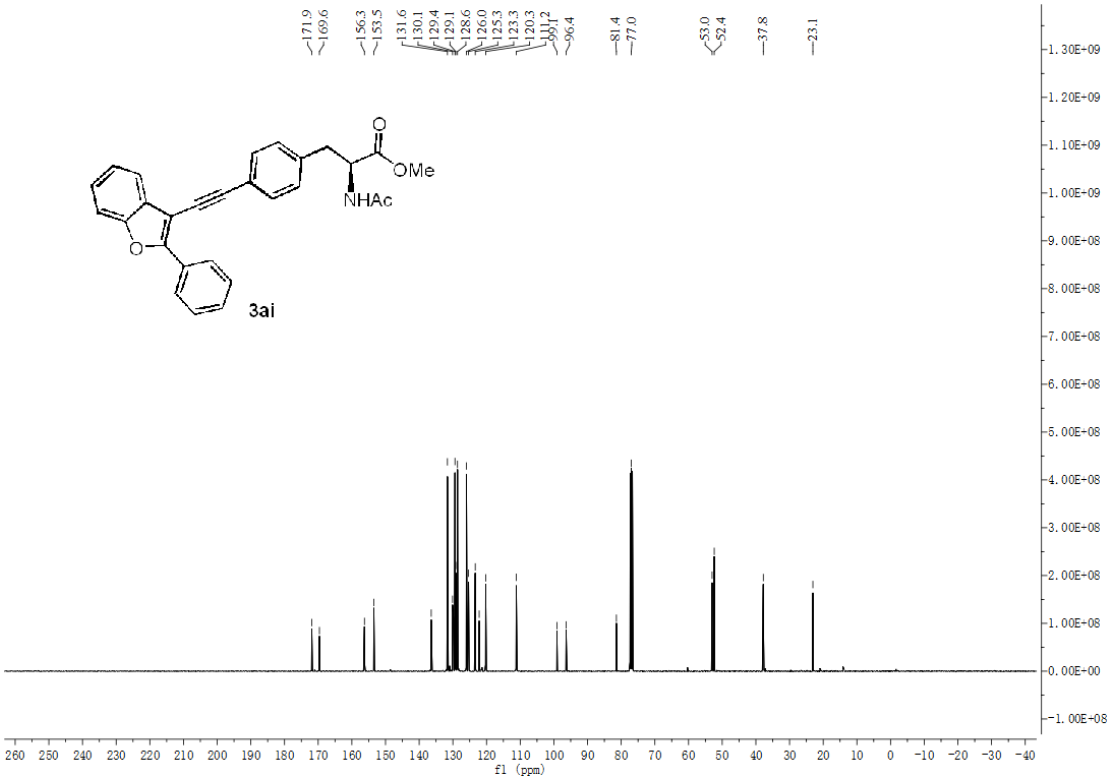


Figure S98. ^{13}C NMR (101 MHz, $CDCl_3$) spectra of **3ai** in MestReNova.

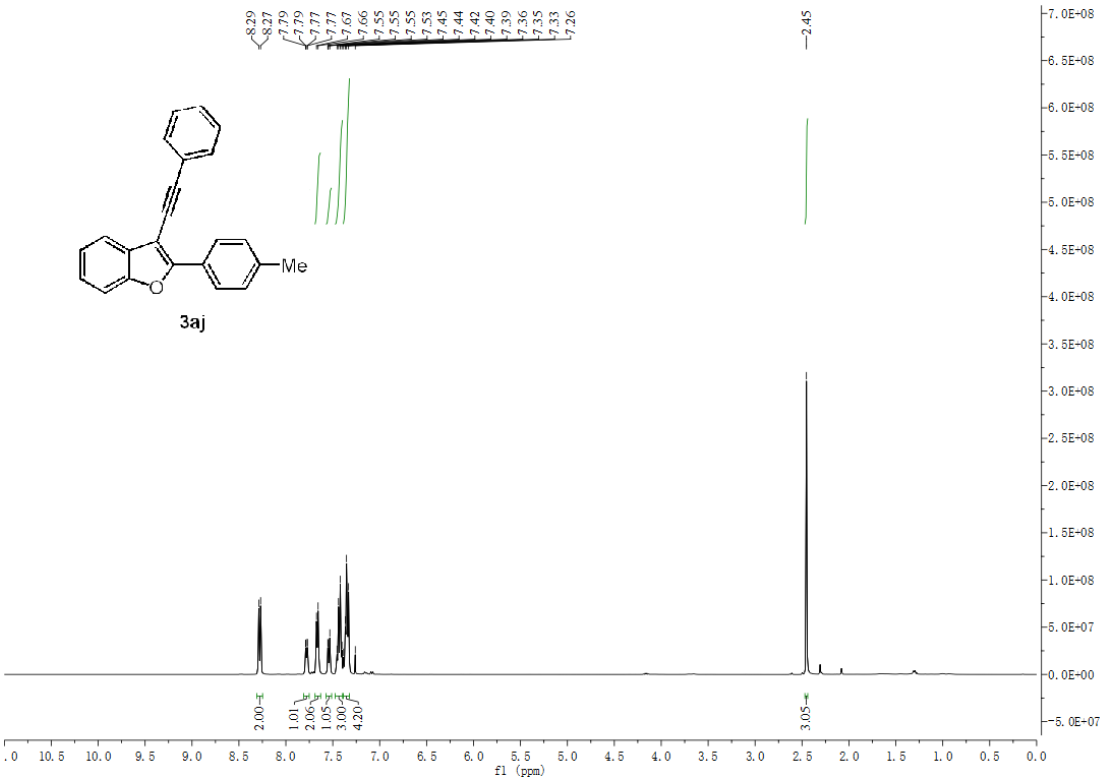


Figure S99. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3aj** in MestReNova.

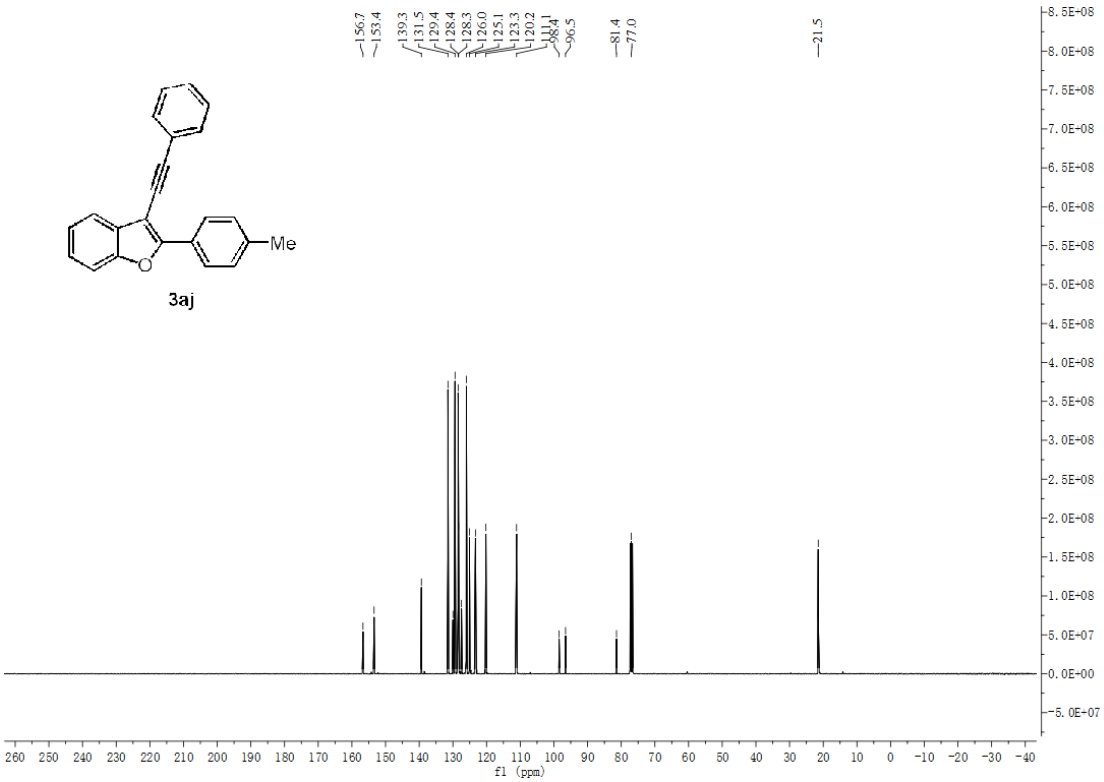


Figure S100. ^{13}C NMR (101 MHz, $CDCl_3$) spectra of **3aj** in MestReNova.

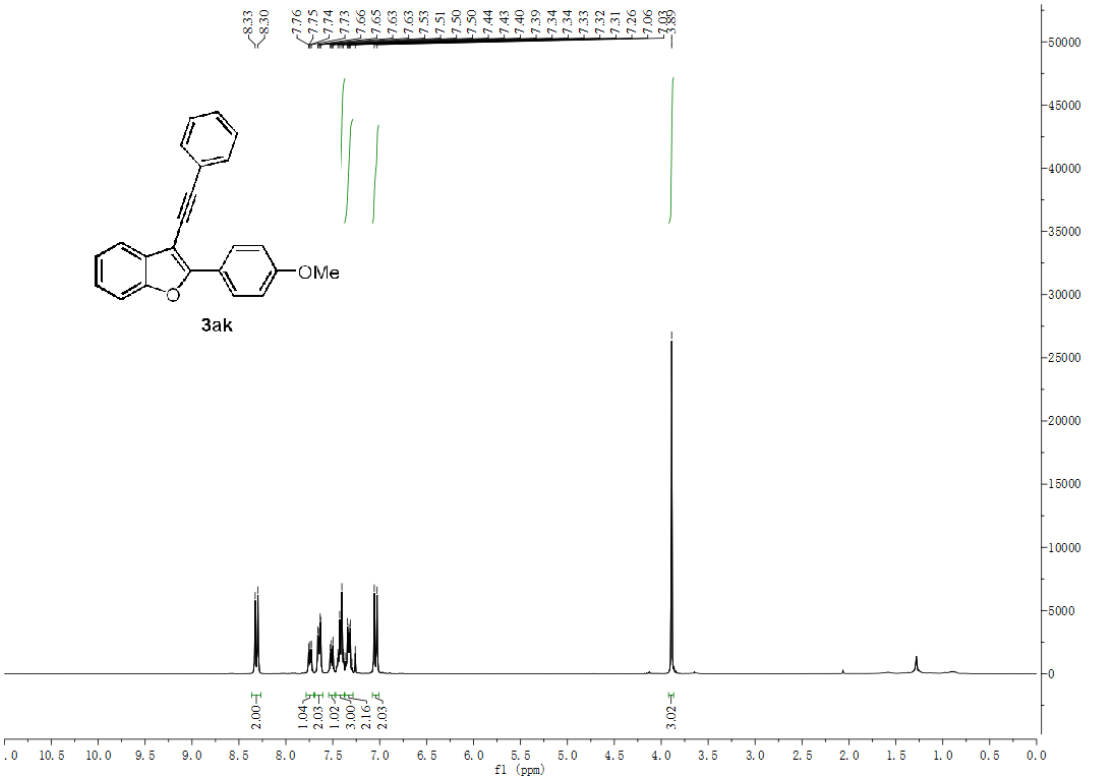


Figure S101. ^{1}H NMR (300 MHz, $CDCl_3$) spectra of **3ak** in MestReNova.

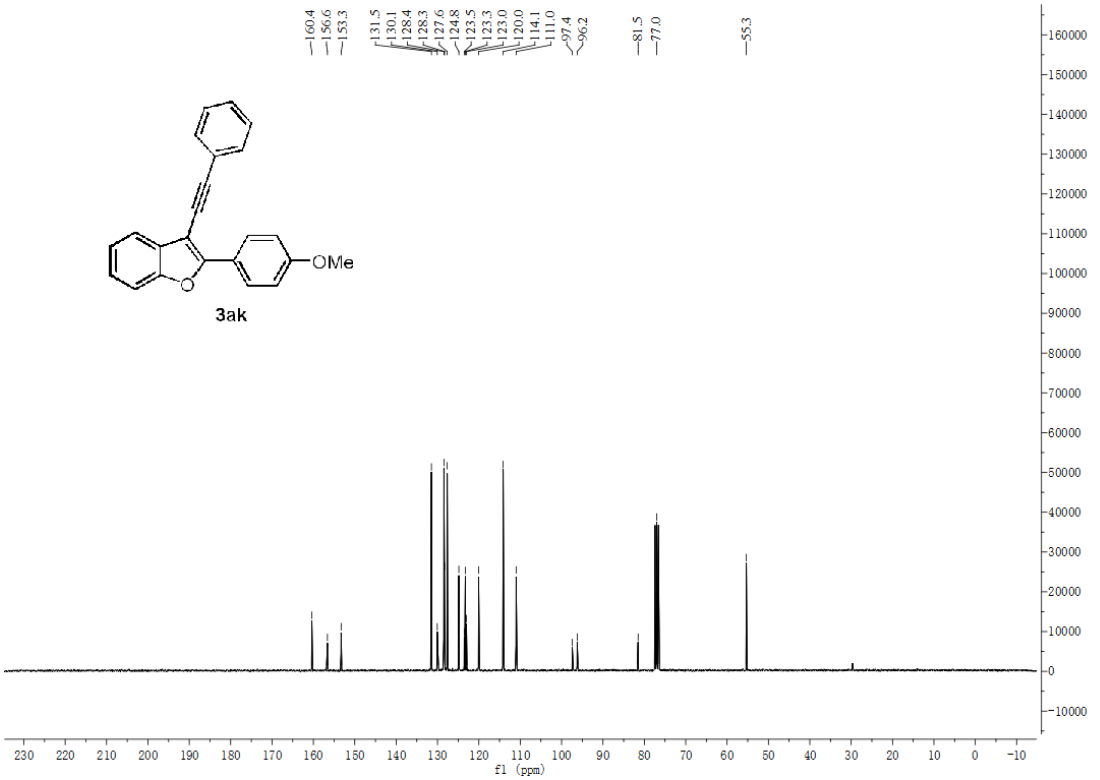


Figure S102. ^{13}C NMR (75 MHz, $CDCl_3$) spectra of **3ak** in MestReNova.

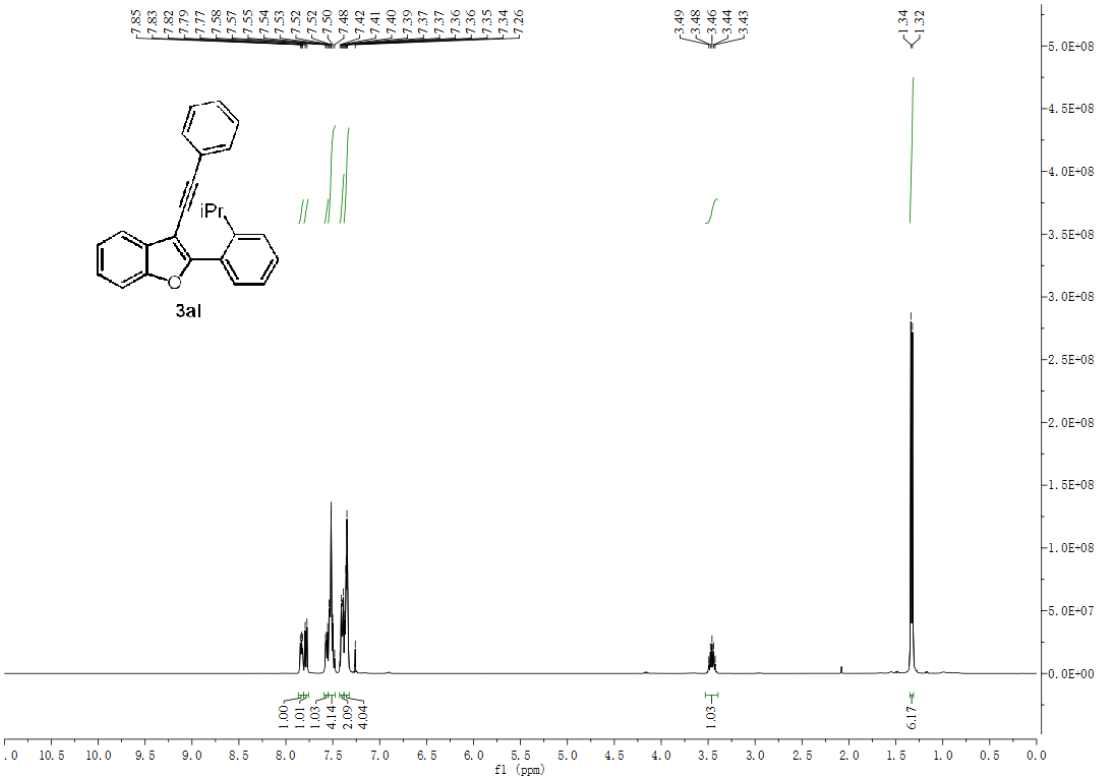


Figure S103. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3al** in MestReNova.

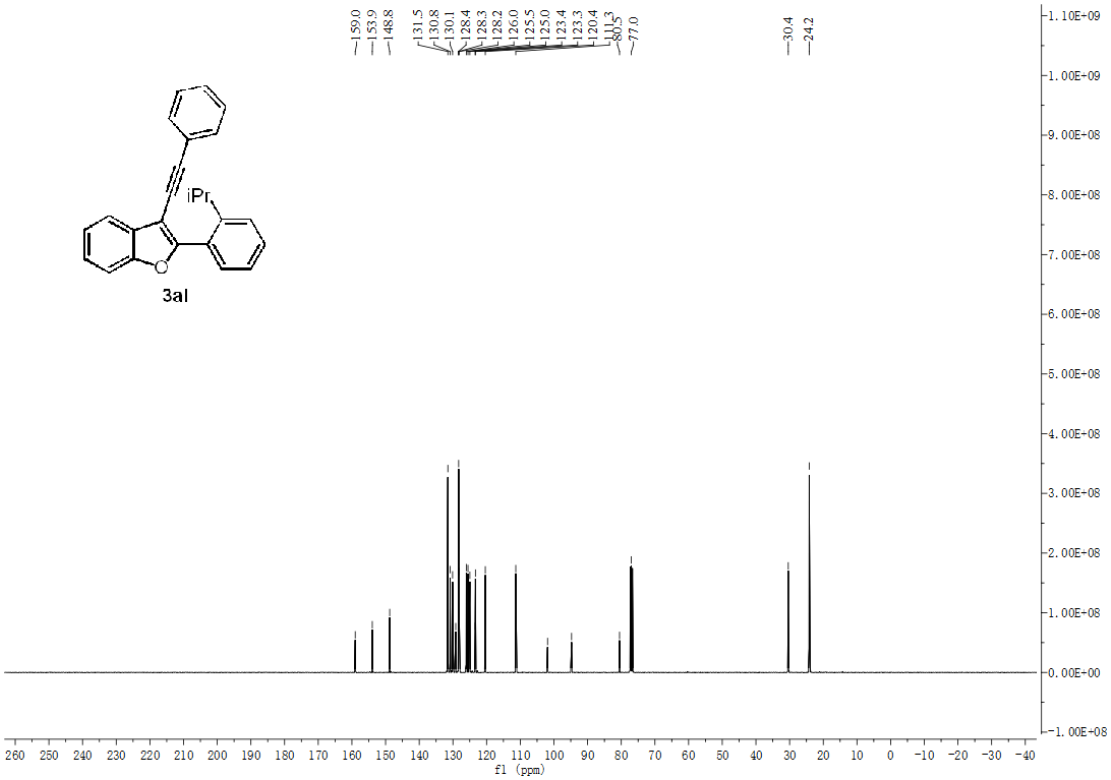


Figure S104. ^{13}C NMR (101 MHz, $CDCl_3$) spectra of **3al** in MestReNova.

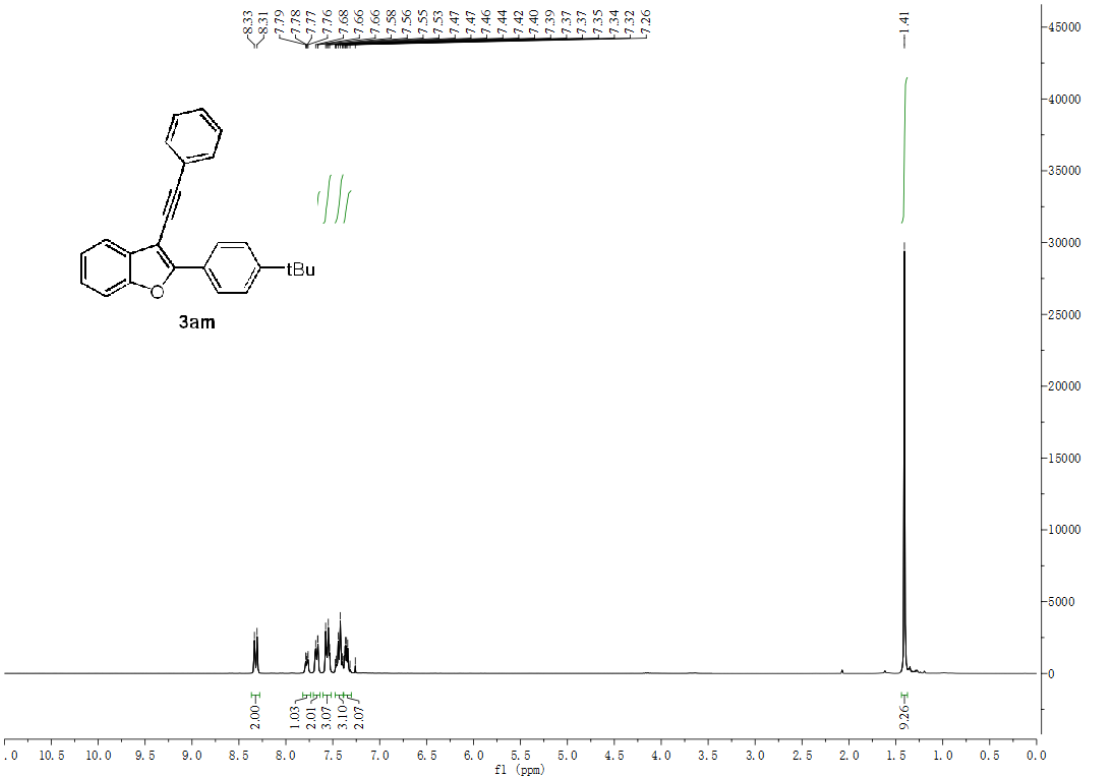


Figure S105. ^{1}H NMR (300 MHz, $CDCl_3$) spectra of **3am** in MestReNova.

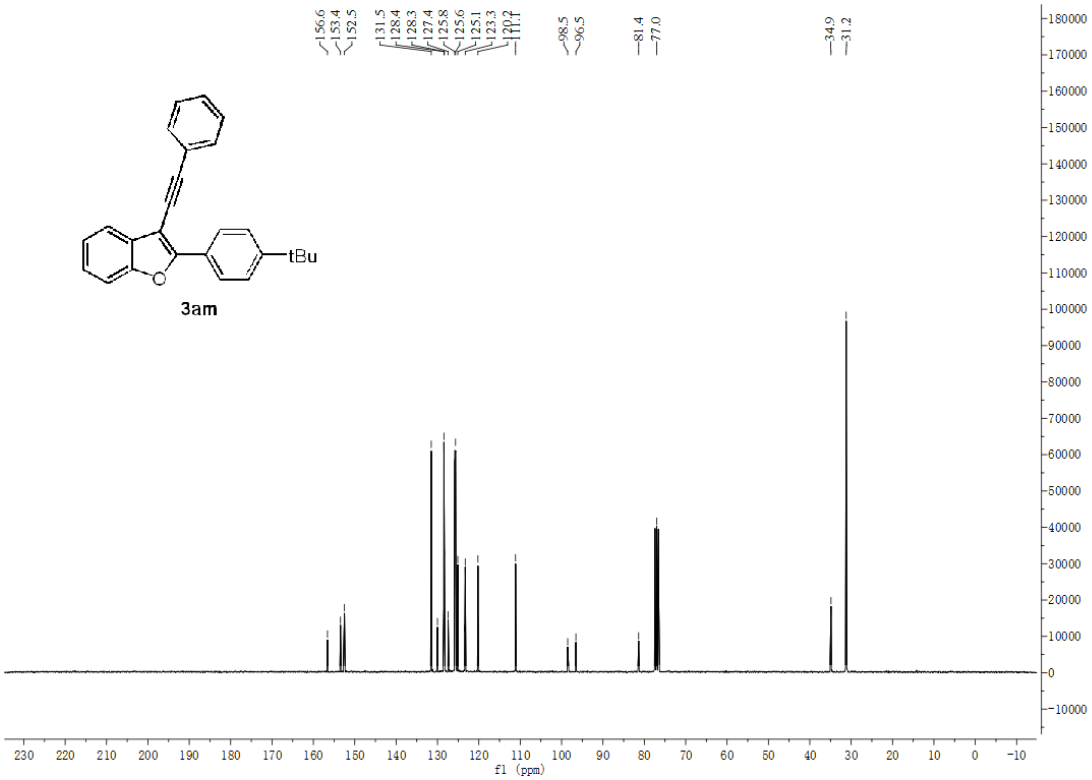


Figure S106. ^{13}C NMR (75 MHz, $CDCl_3$) spectra of **3am** in MestReNova.

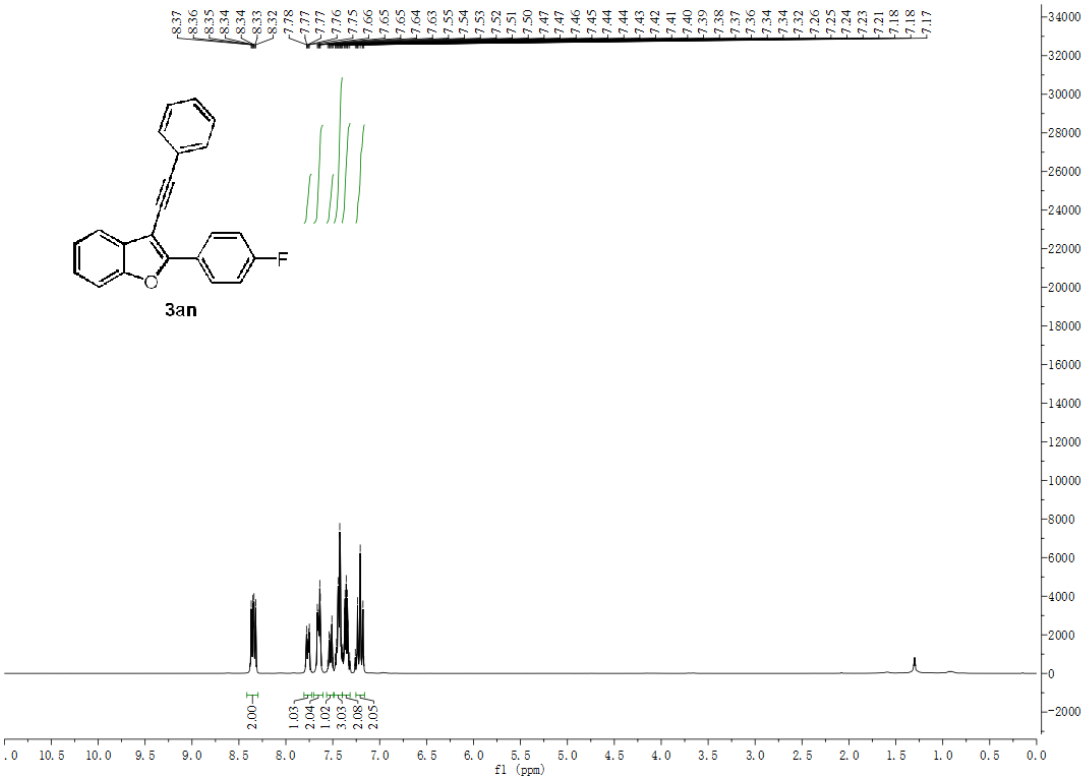


Figure S107. ^{1}H NMR (300 MHz, $CDCl_3$) spectra of **3an** in MestReNova.

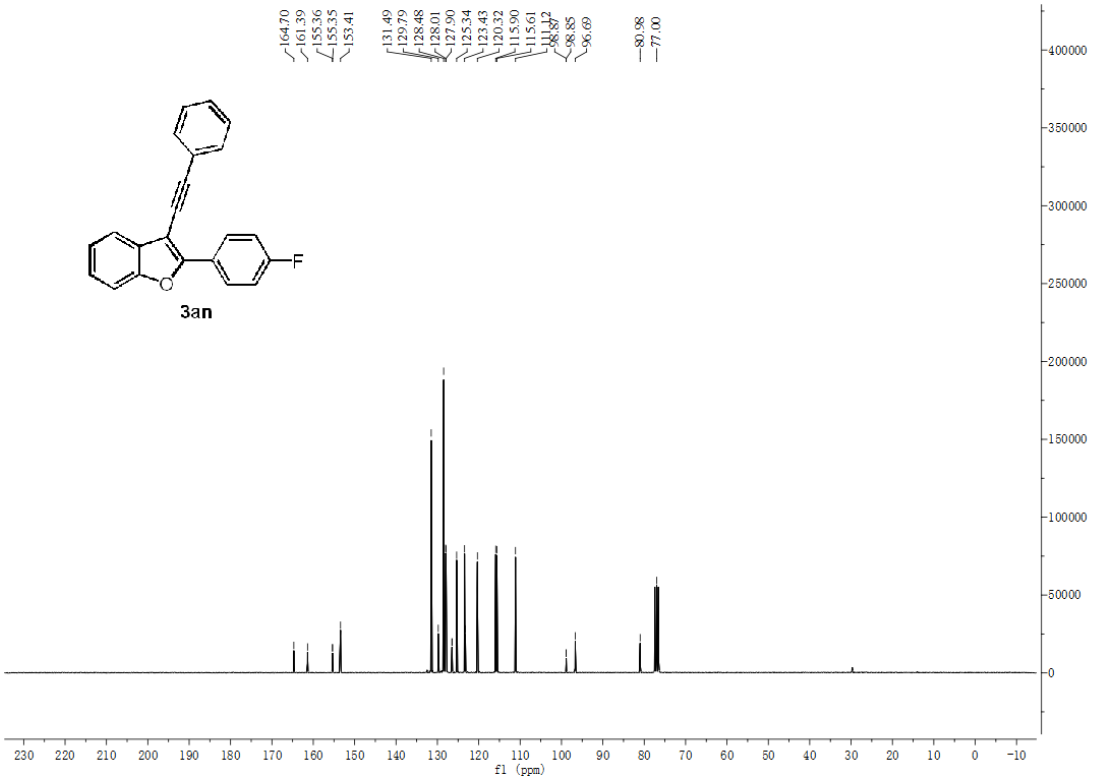


Figure S108. ^{13}C NMR (75 MHz, $CDCl_3$) spectra of **3an** in MestReNova.

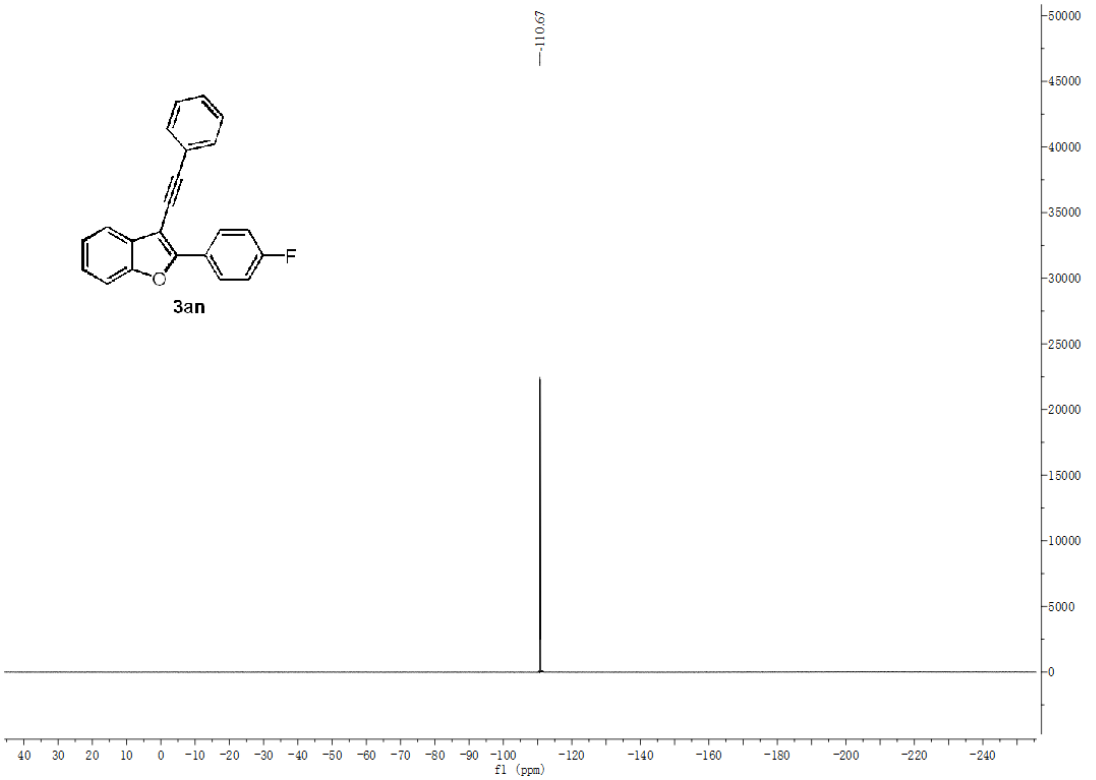


Figure S109. ^{19}F NMR (282 MHz, $CDCl_3$) spectra of **3an** in MestReNova.

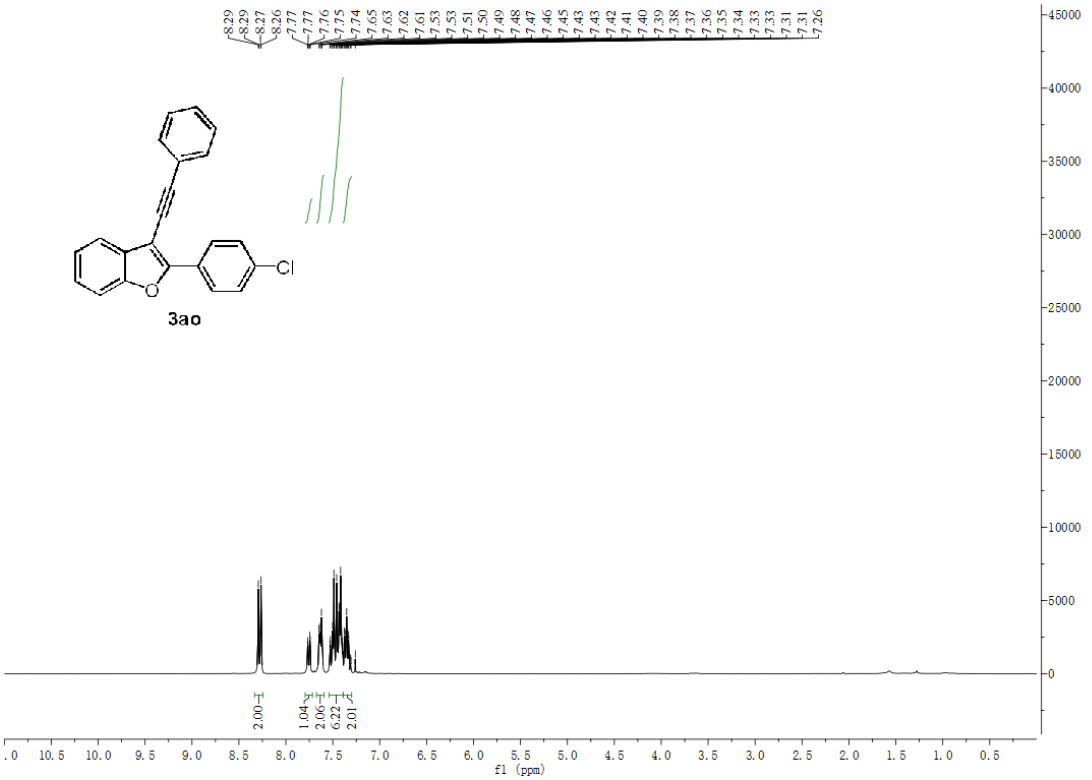


Figure S110. ^{1}H NMR (300 MHz, $CDCl_3$) spectra of **3ao** in MestReNova.

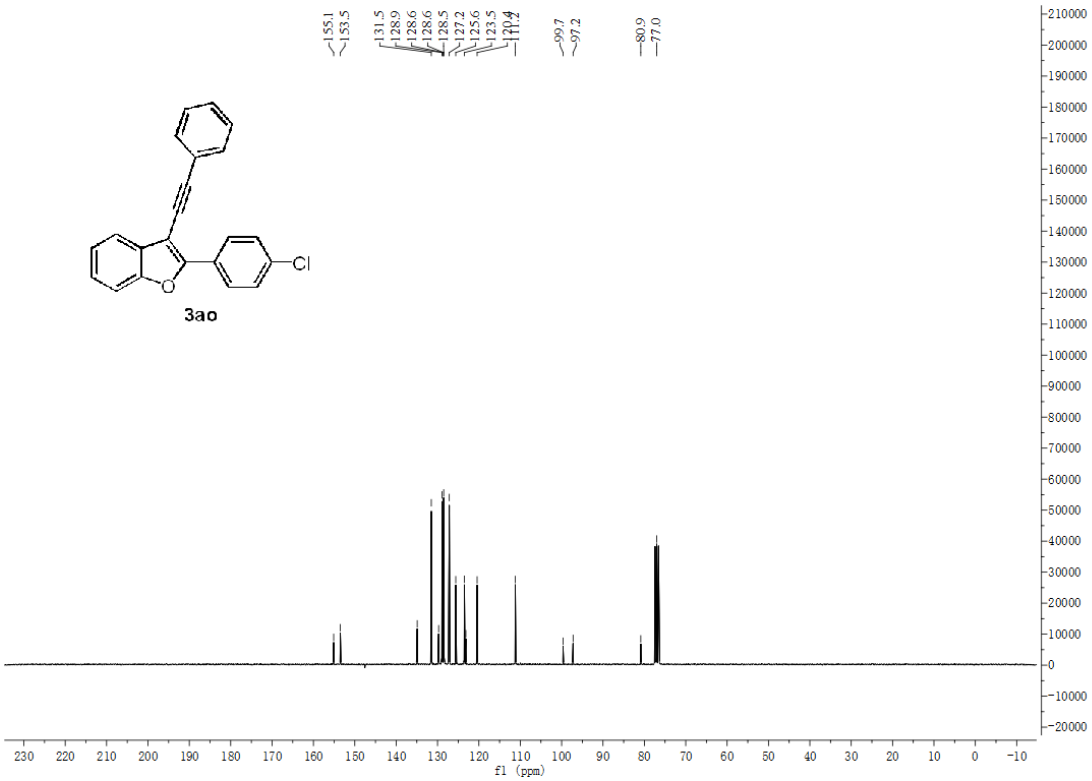


Figure S111. ^{13}C NMR (75 MHz, $CDCl_3$) spectra of **3ao** in MestReNova.

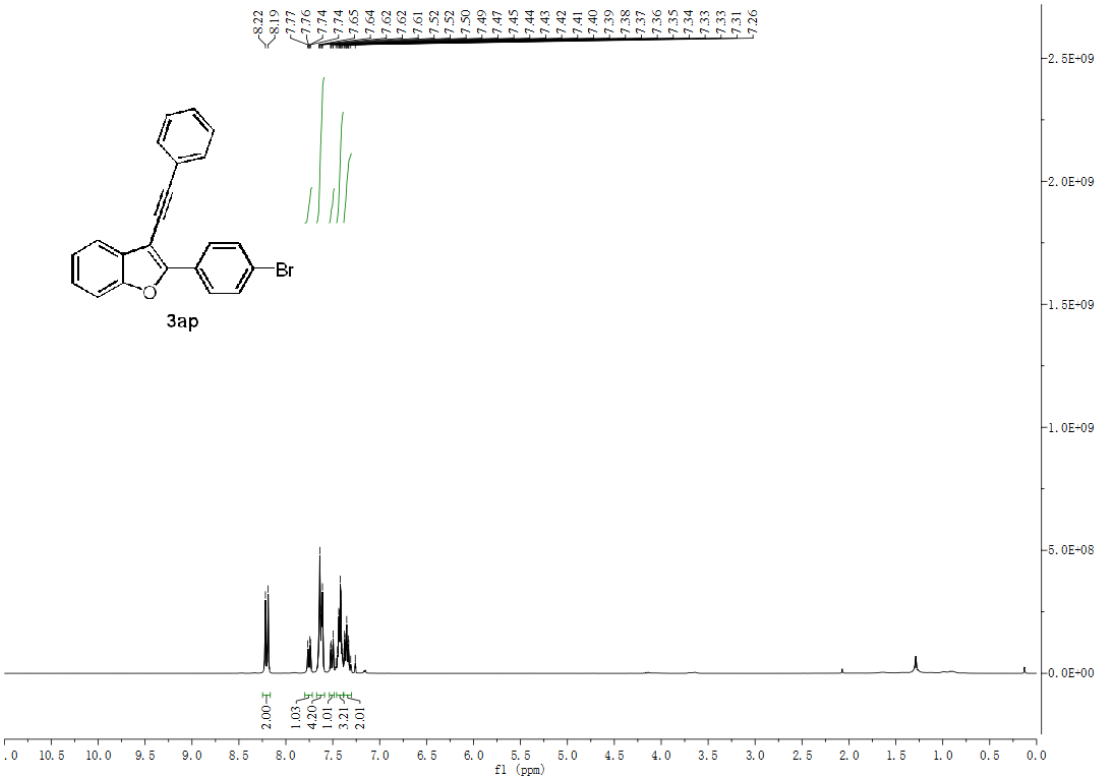


Figure S112. ^{1}H NMR (300 MHz, $CDCl_3$) spectra of **3ap** in MestReNova.

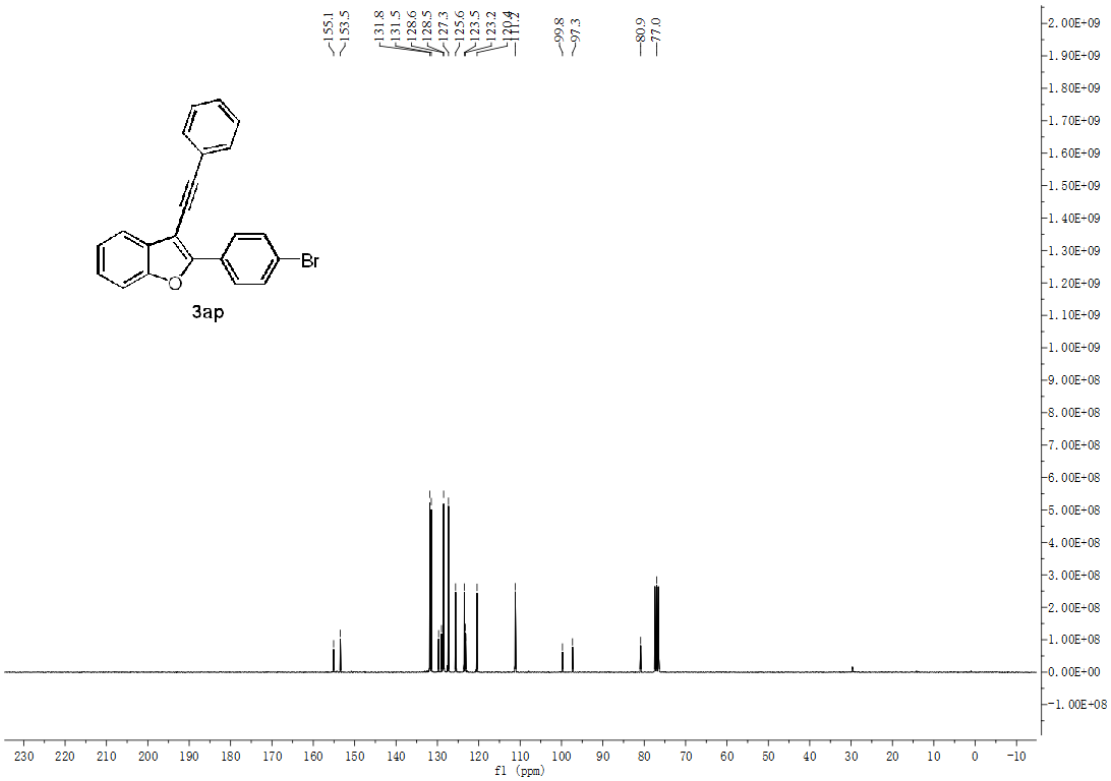


Figure S113. ^{13}C NMR (75 MHz, $CDCl_3$) spectra of **3ap** in MestReNova.

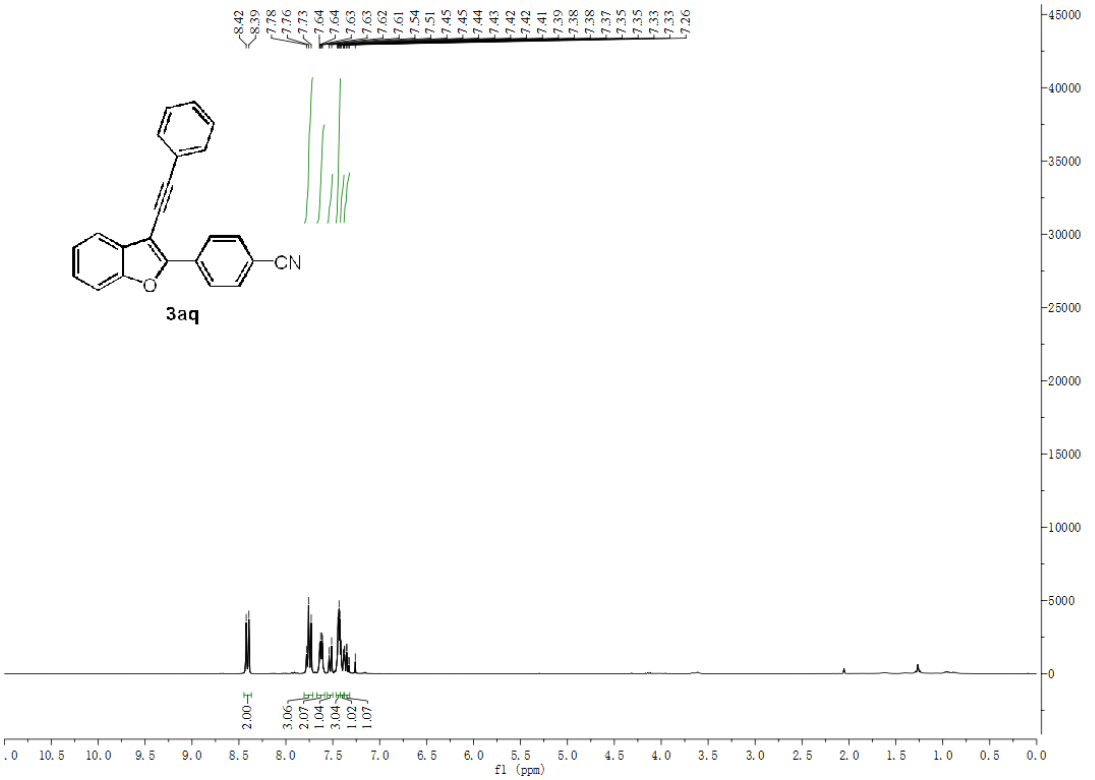


Figure S114. ^{1}H NMR (300 MHz, $CDCl_3$) spectra of **3aq** in MestReNova.

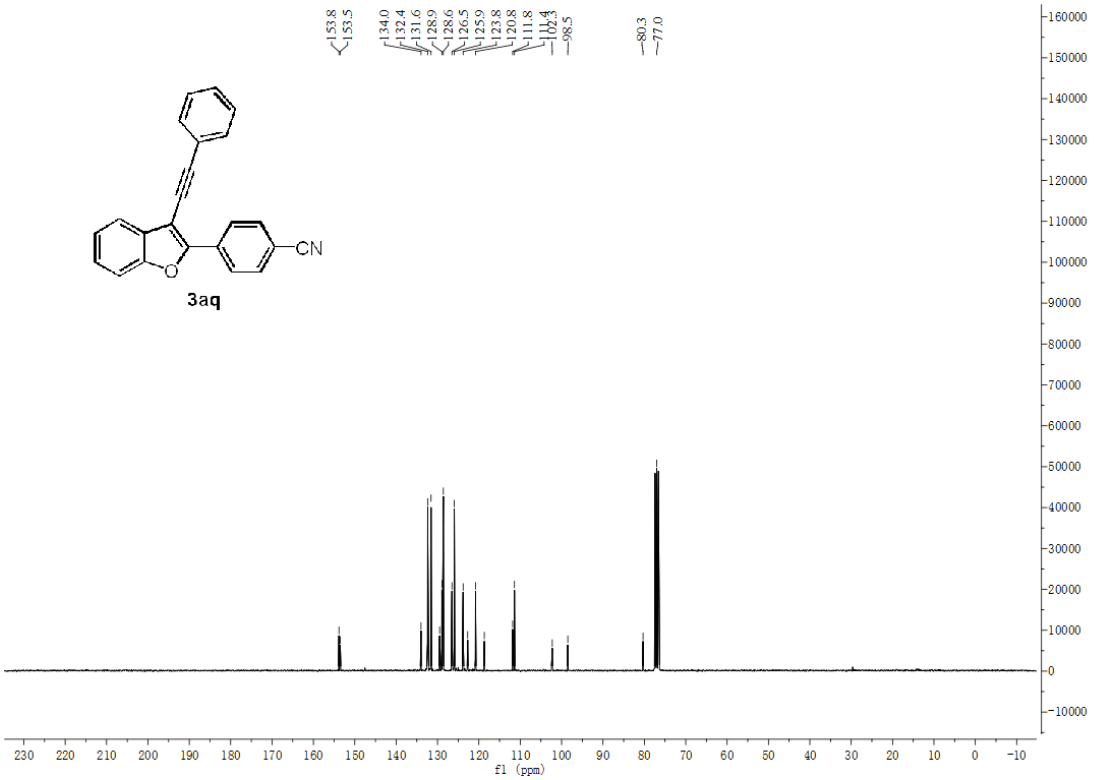


Figure S115. ^{13}C NMR (75 MHz, $CDCl_3$) spectra of **3aq** in MestReNova.

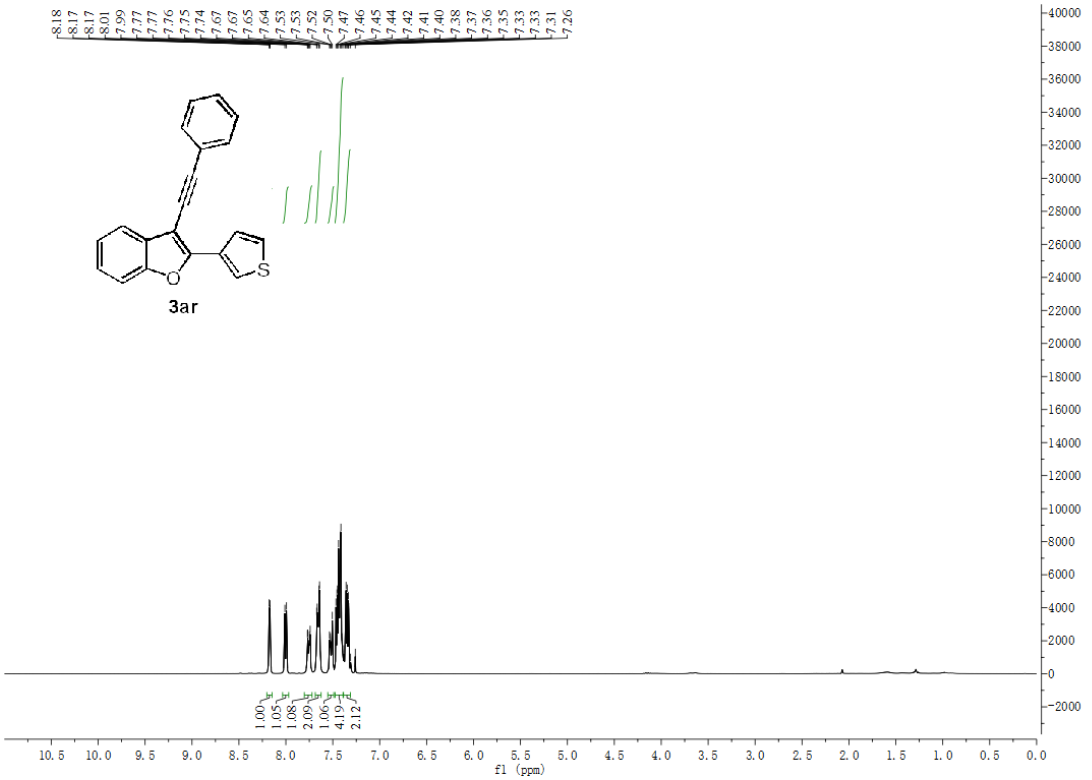


Figure S116. ^{1}H NMR (300 MHz, $CDCl_3$) spectra of **3ar** in MestReNova.

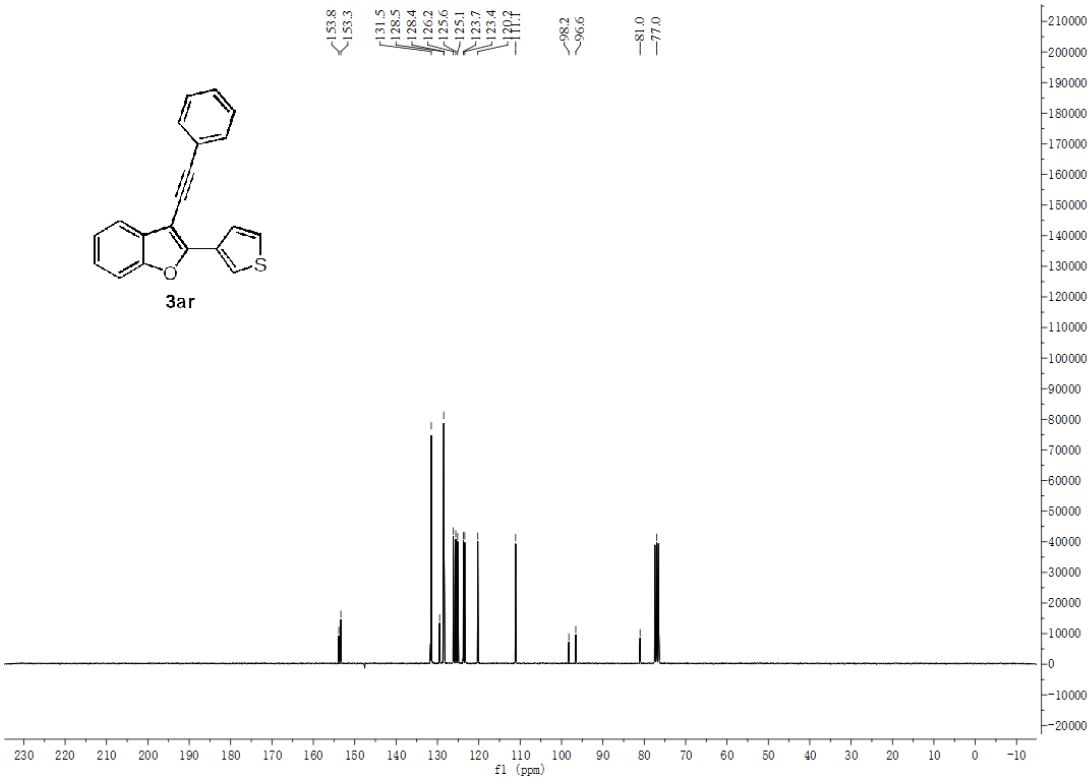


Figure S117. ^{13}C NMR (75 MHz, $CDCl_3$) spectra of **3ar** in MestReNova.

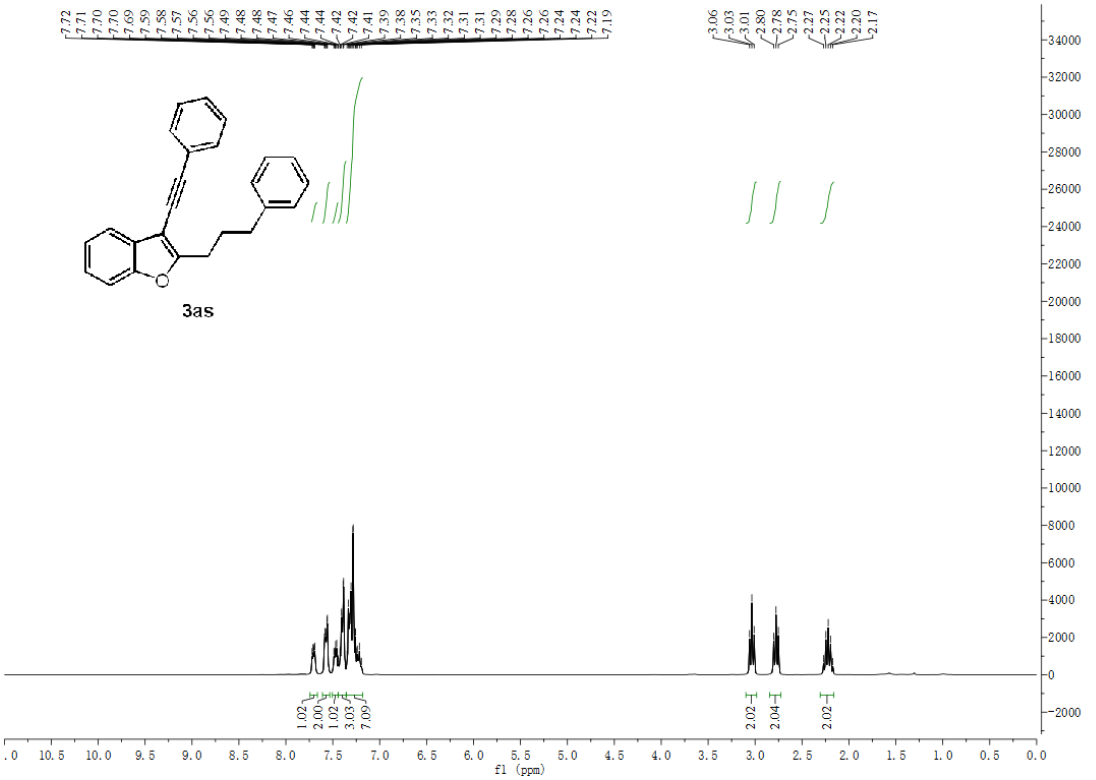


Figure S118. ^{1}H NMR (300 MHz, $CDCl_3$) spectra of **3as** in MestReNova.

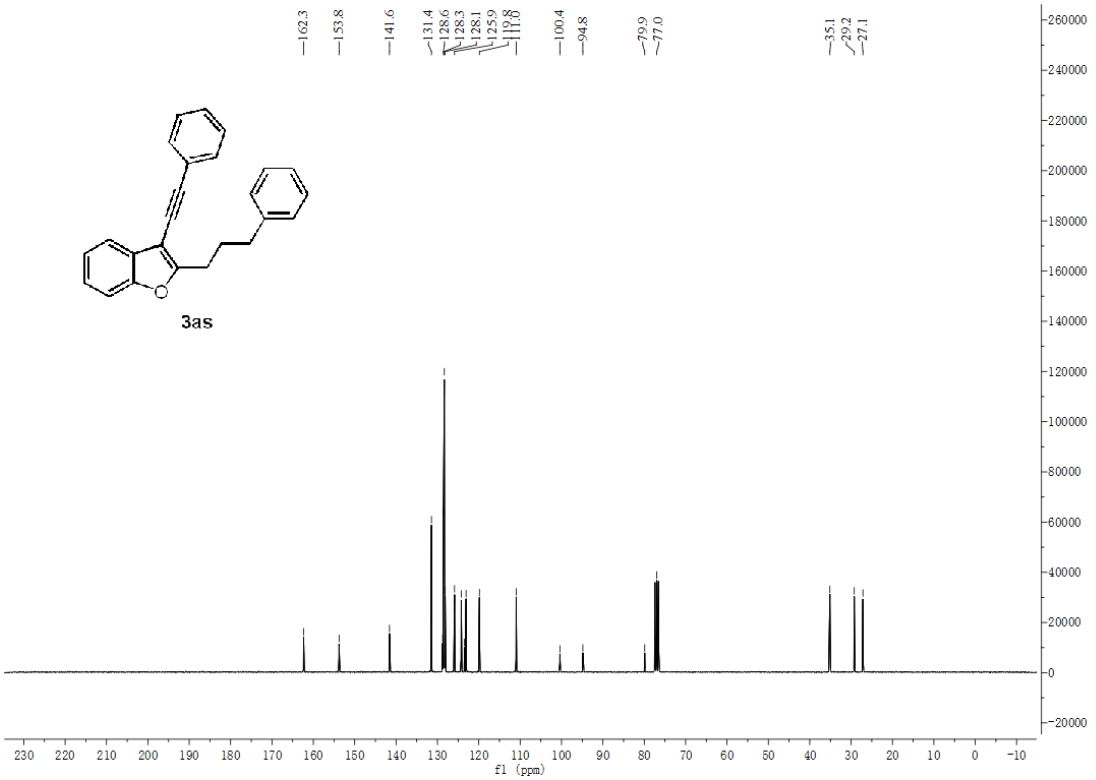


Figure S119. ^{13}C NMR (75 MHz, $CDCl_3$) spectra of **3as** in MestReNova.

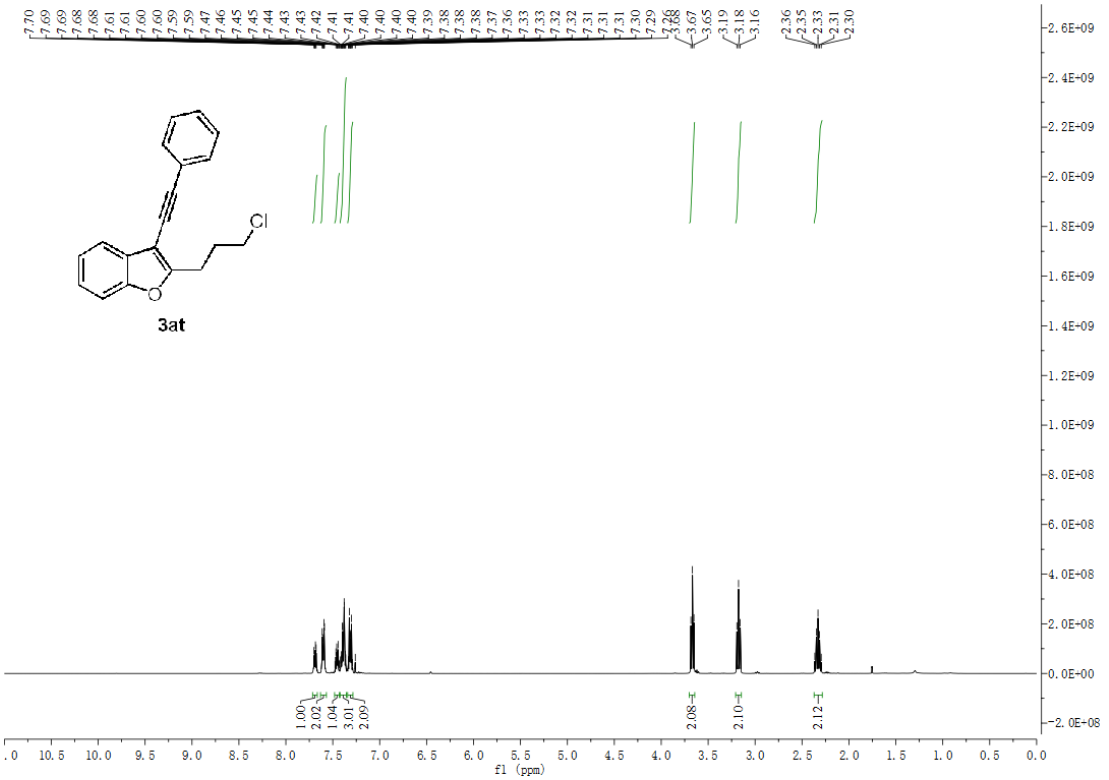


Figure S120. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3at** in MestReNova.

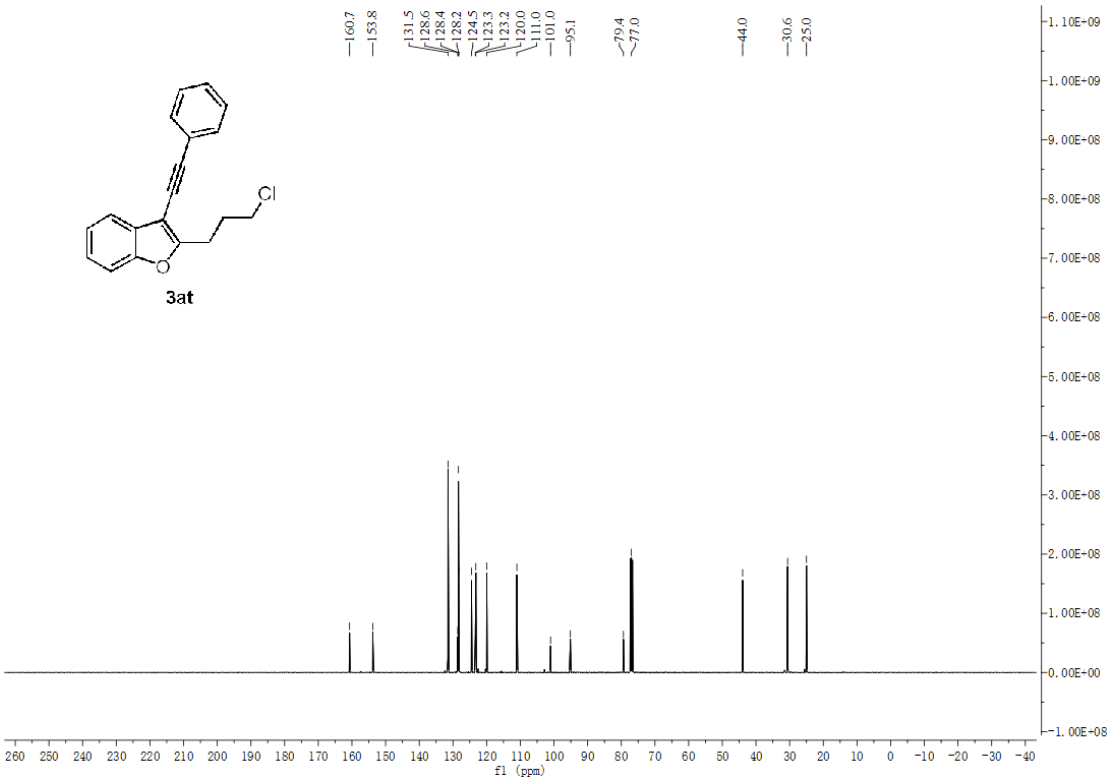


Figure S121. ^{13}C NMR (101 MHz, $CDCl_3$) spectra of **3at** in MestReNova.

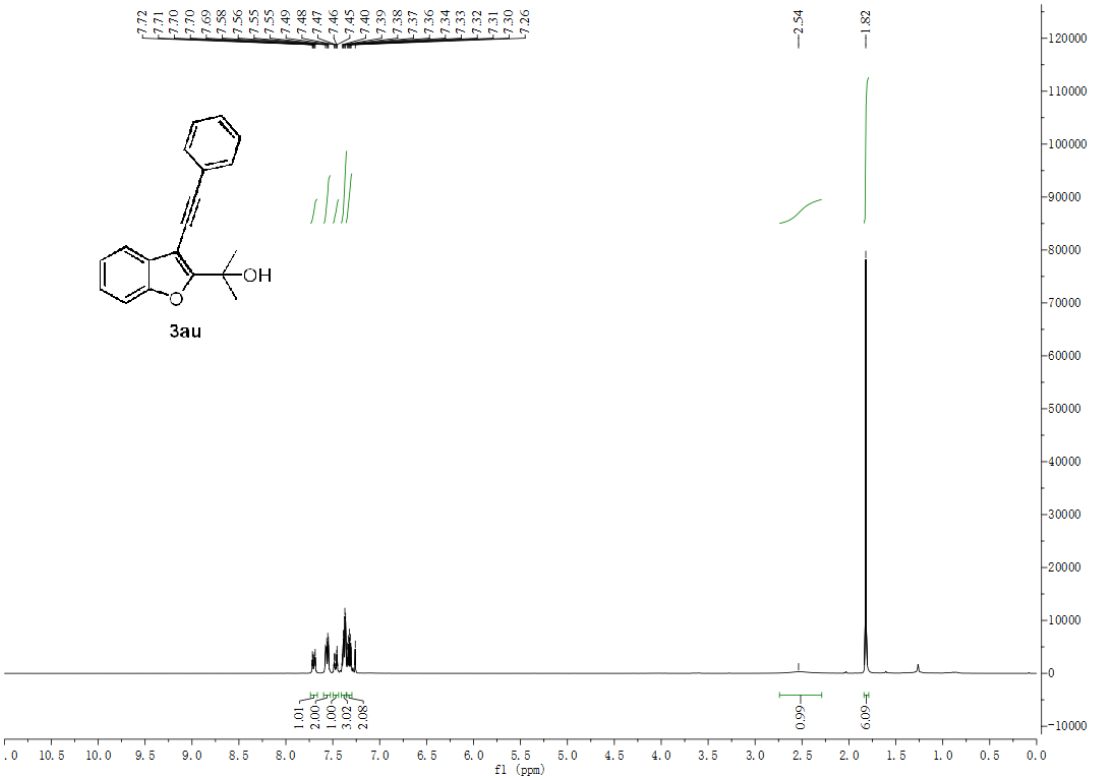


Figure S122. ^{1}H NMR (300 MHz, $CDCl_3$) spectra of **3au** in MestReNova.

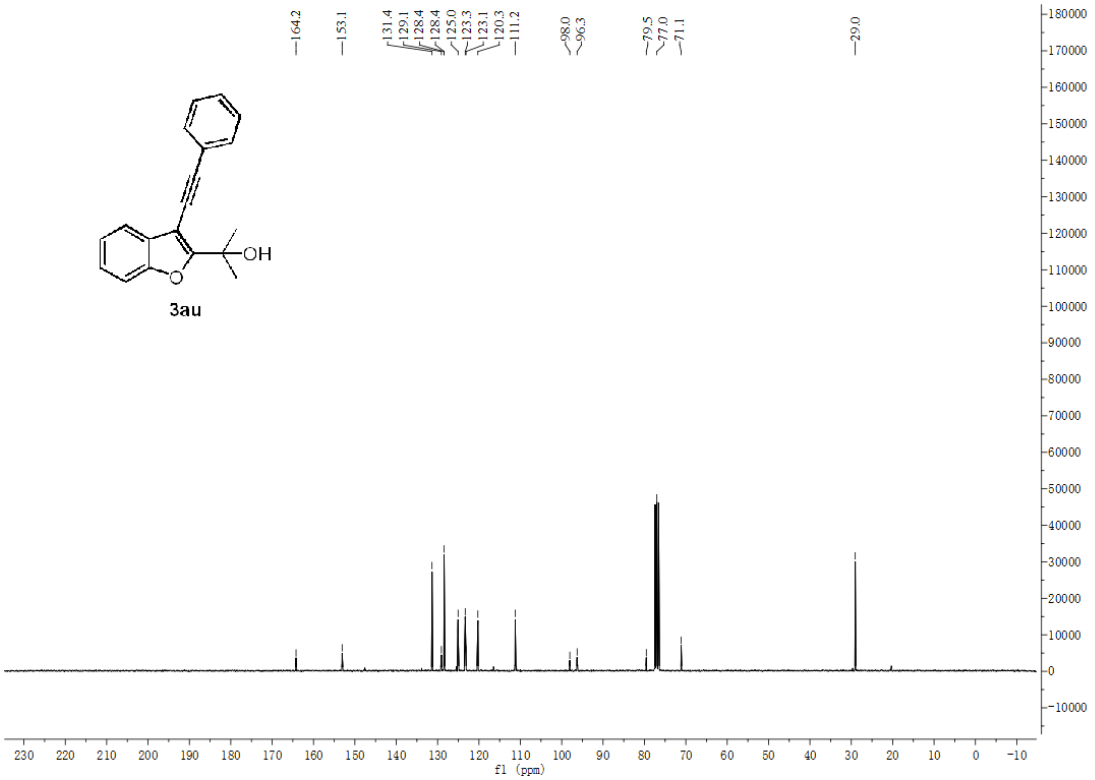


Figure S123. ^{13}C NMR (75 MHz, $CDCl_3$) spectra of **3au** in MestReNova.

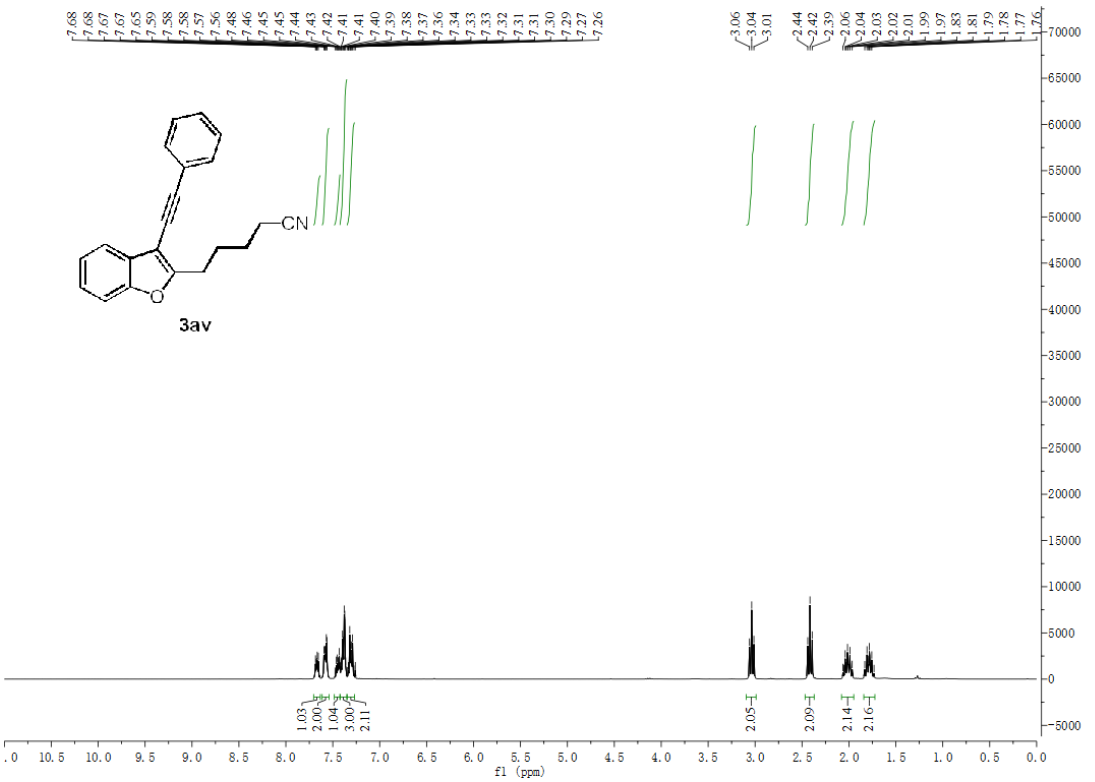


Figure S124. ^{1}H NMR (300 MHz, $CDCl_3$) spectra of **3av** in MestReNova.

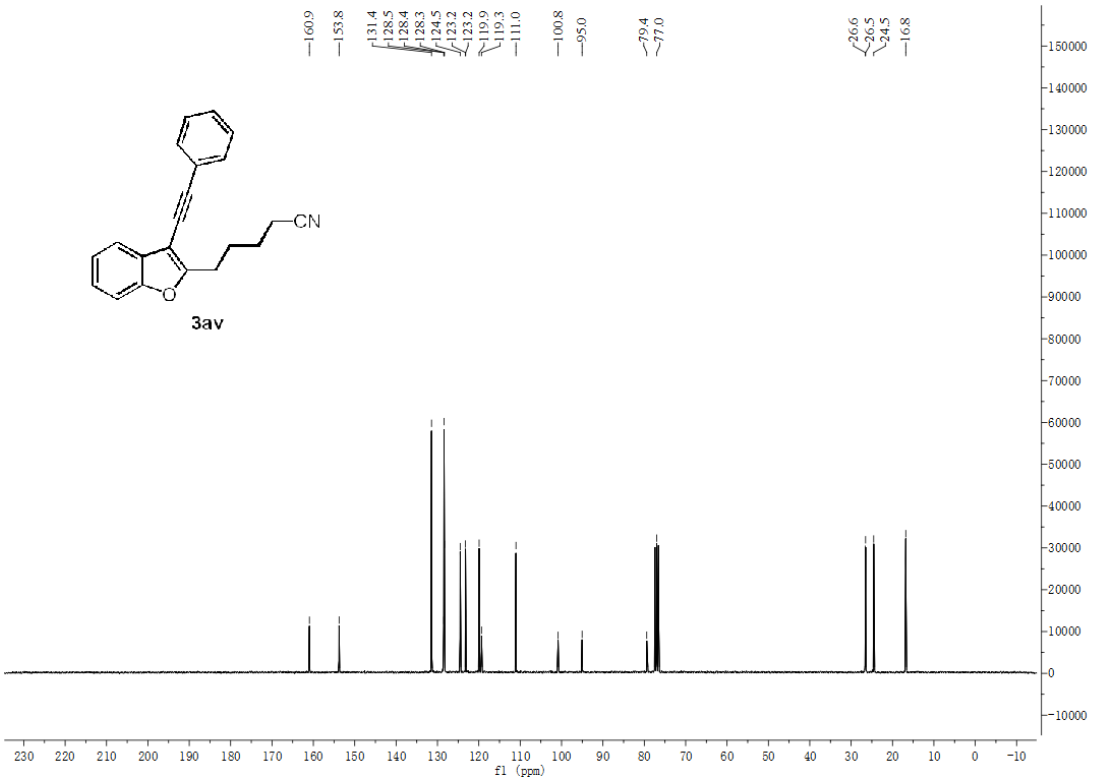


Figure S125. ^{13}C NMR (75 MHz, $CDCl_3$) spectra of **3av** in MestReNova.

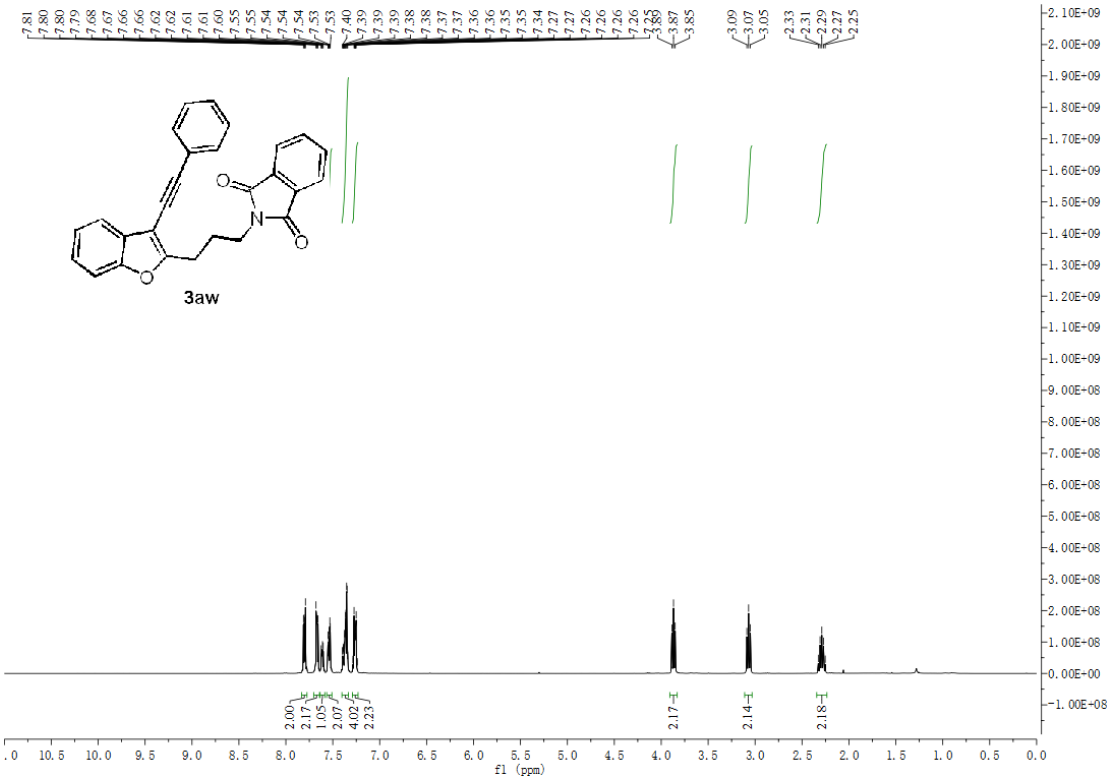


Figure S126. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3aw** in MestReNova.

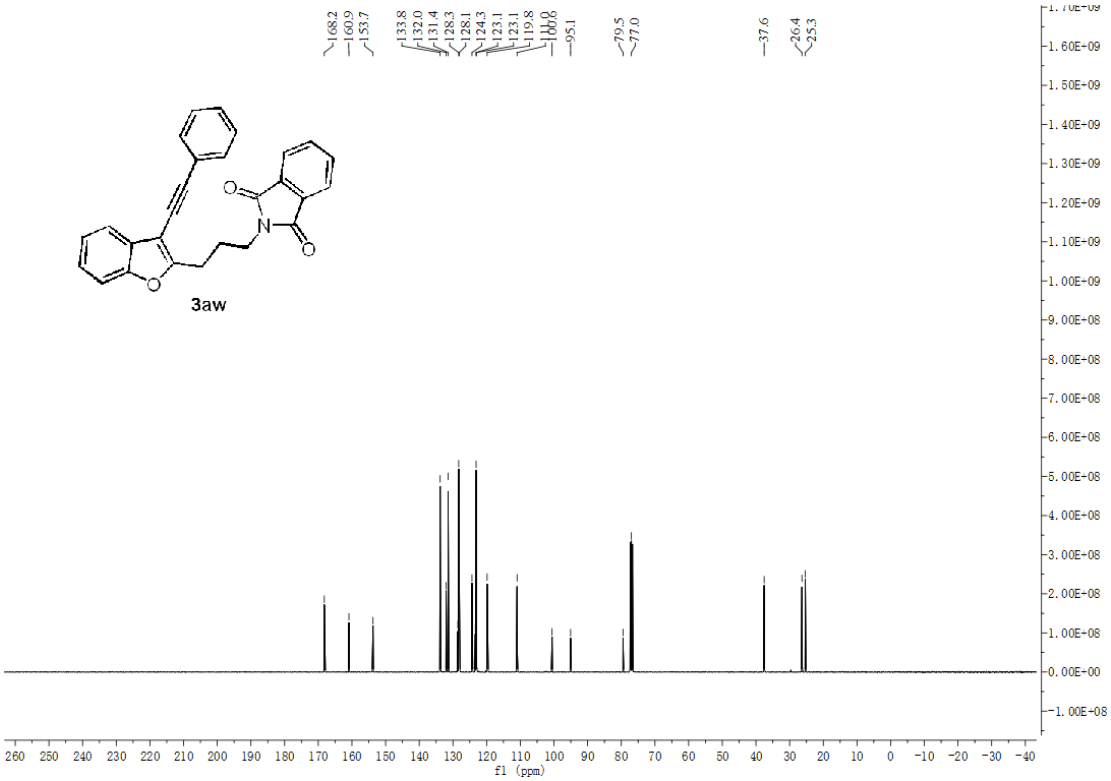


Figure S127. ^{13}C NMR (101 MHz, $CDCl_3$) spectra of **3aw** in MestReNova.

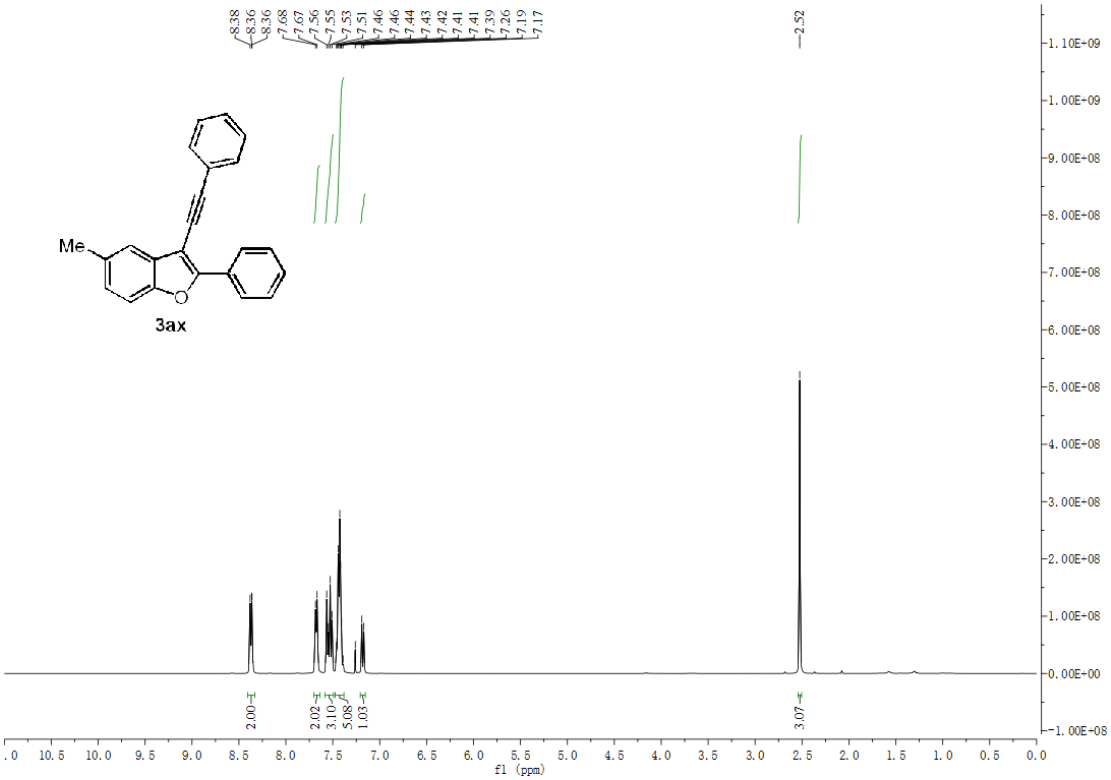


Figure S128. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3ax** in MestReNova.

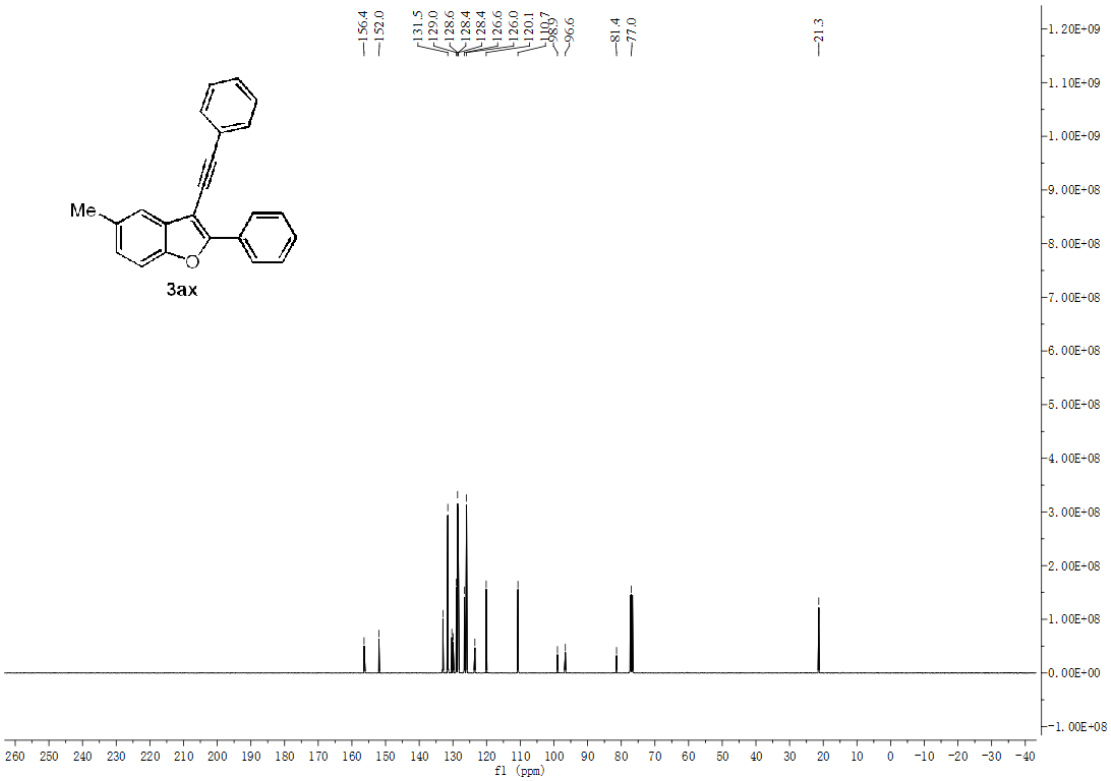


Figure S129. ^{13}C NMR (101 MHz, $CDCl_3$) spectra of **3ax** in MestReNova.

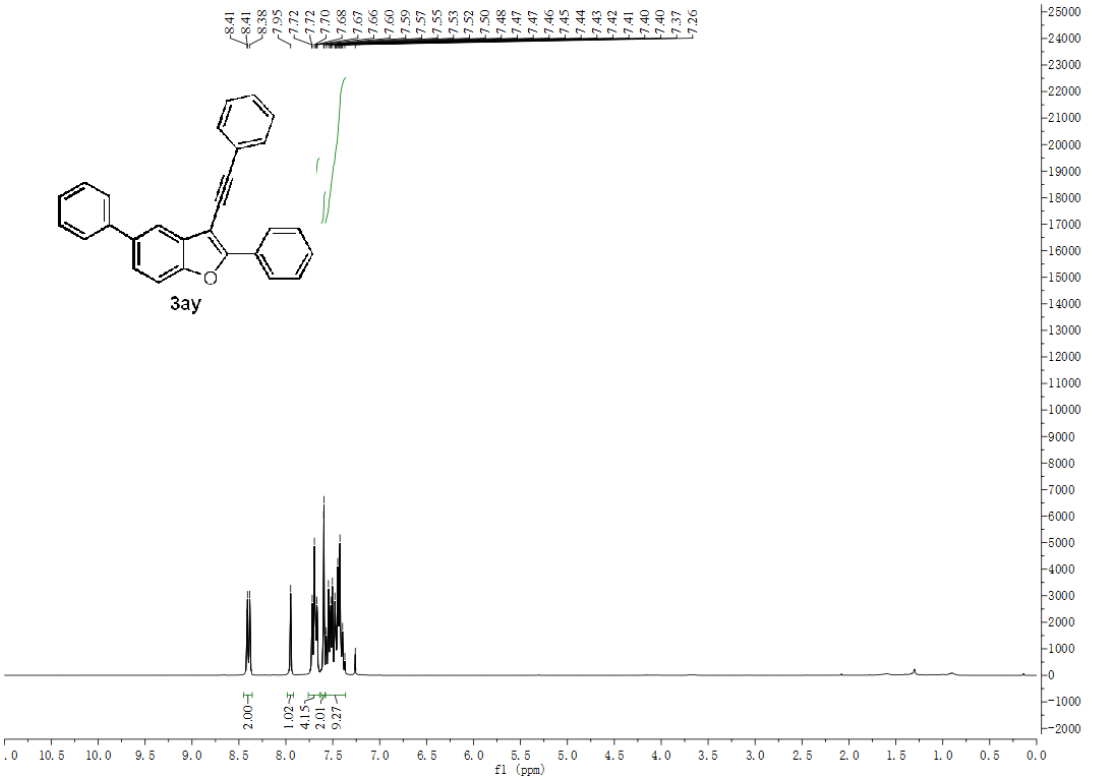


Figure S130. ^{1}H NMR (300 MHz, $CDCl_3$) spectra of **3ay** in MestReNova.

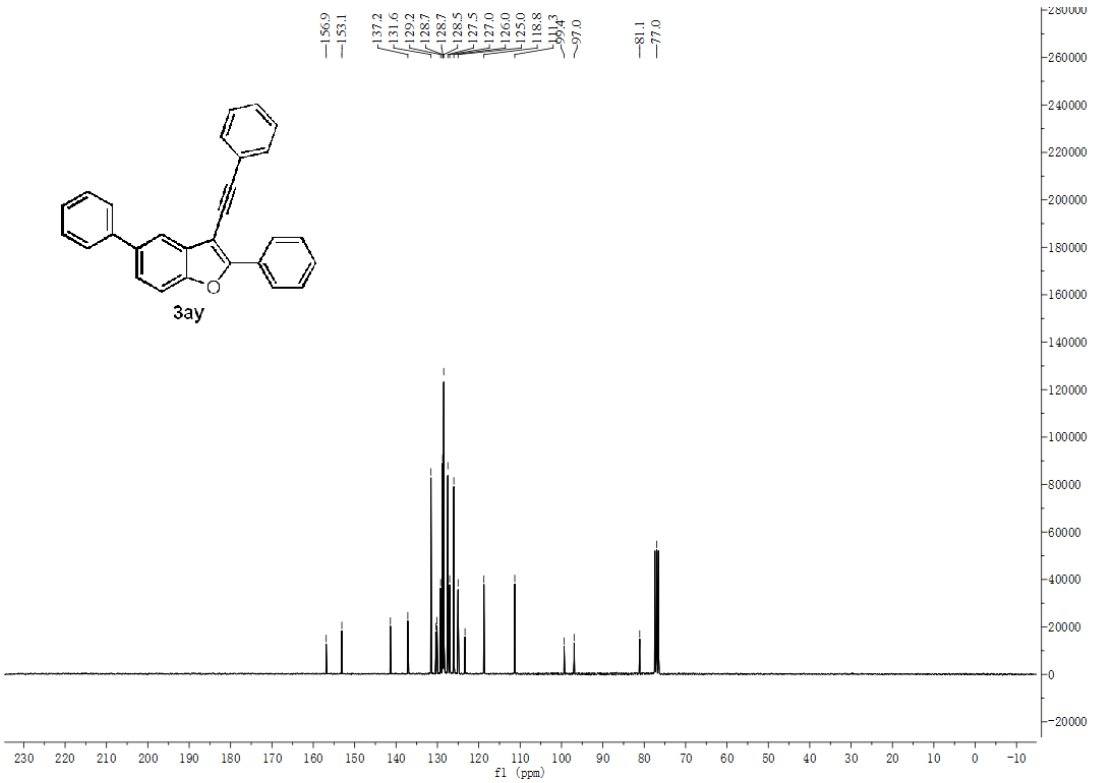


Figure S131. ^{13}C NMR (75 MHz, $CDCl_3$) spectra of **3ay** in MestReNova.

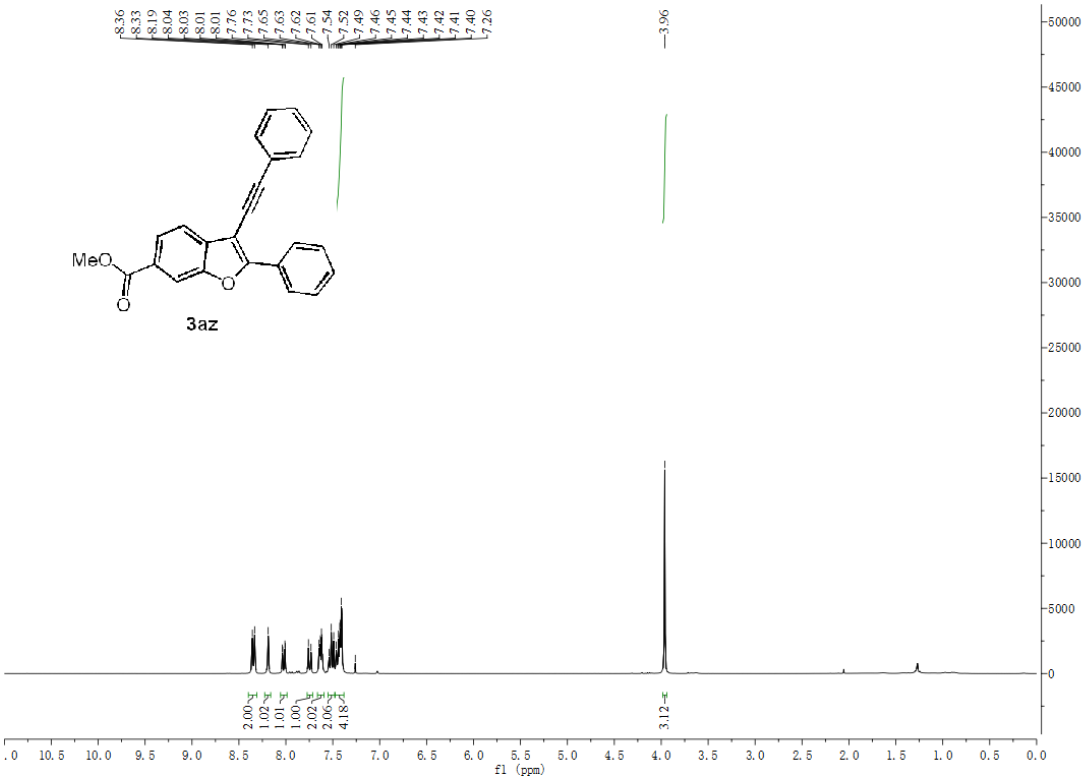


Figure S132. ^{1}H NMR (300 MHz, $CDCl_3$) spectra of **3az** in MestReNova.

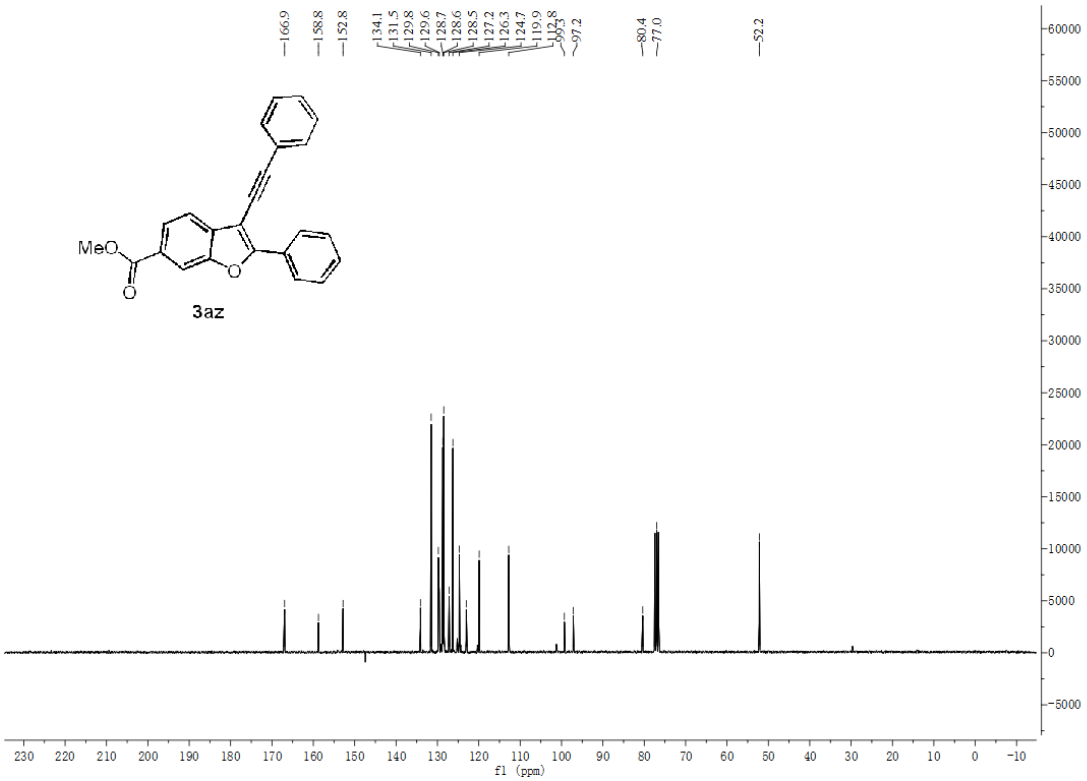


Figure S133. ^{13}C NMR (75 MHz, $CDCl_3$) spectra of **3az** in MestReNova.

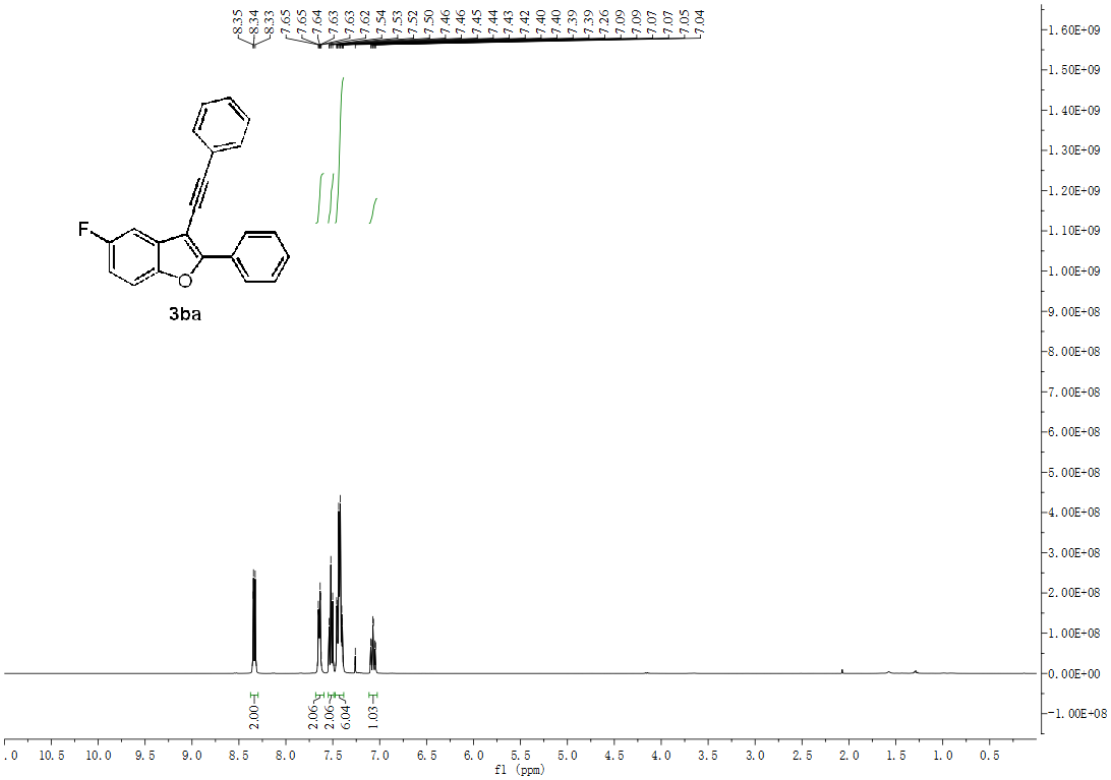


Figure S134. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3ba** in MestReNova.

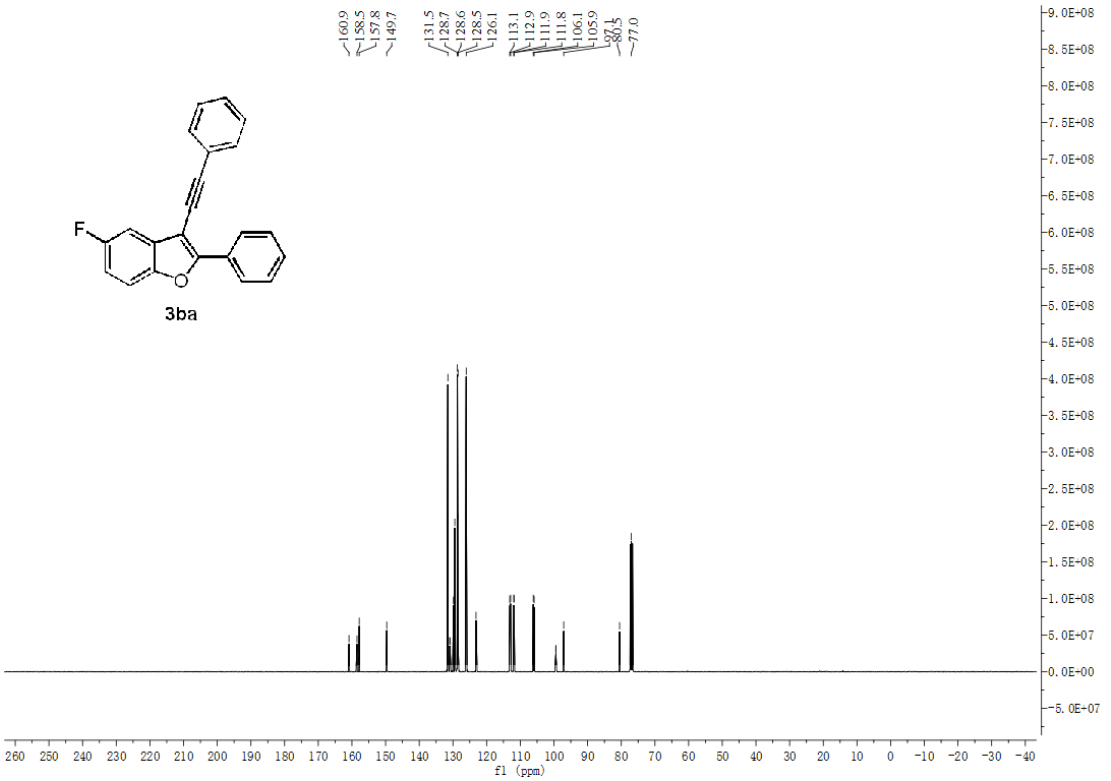


Figure S135. ^{13}C NMR (101 MHz, $CDCl_3$) spectra of **3ba** in MestReNova.

Figure S136. ^{19}F NMR (282 MHz, $CDCl_3$) spectra of **3ba** in MestReNova.

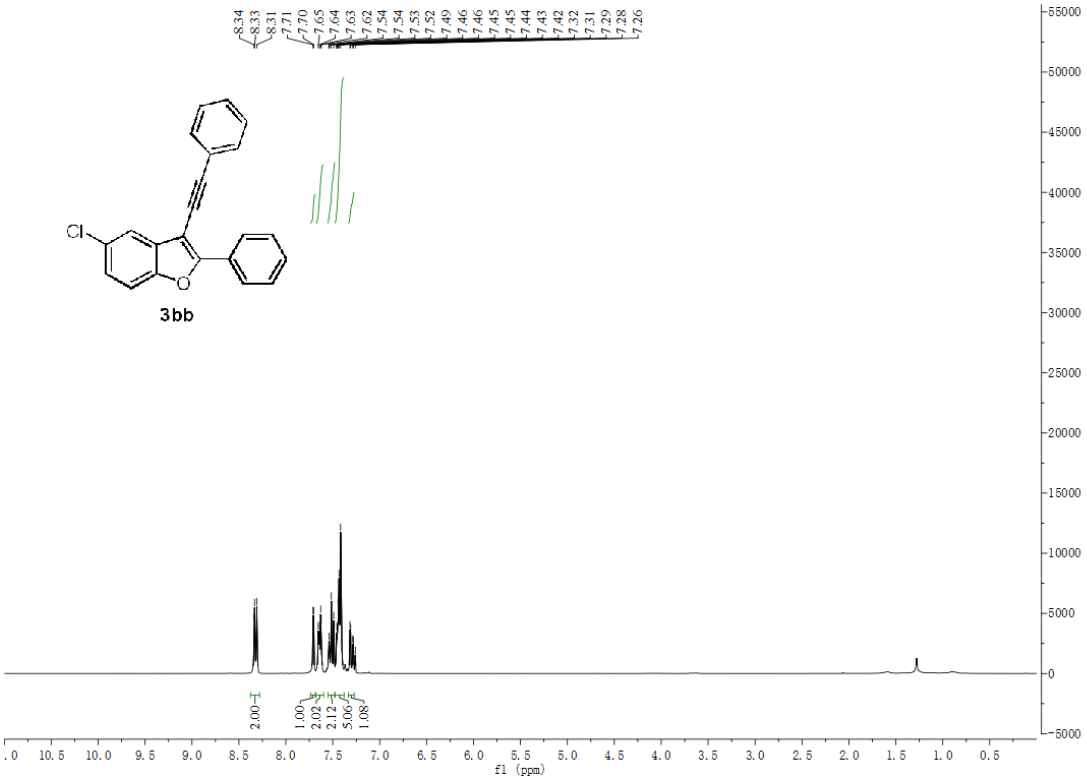


Figure S137. ^{1}H NMR (300 MHz, $CDCl_3$) spectra of **3bb** in MestReNova.

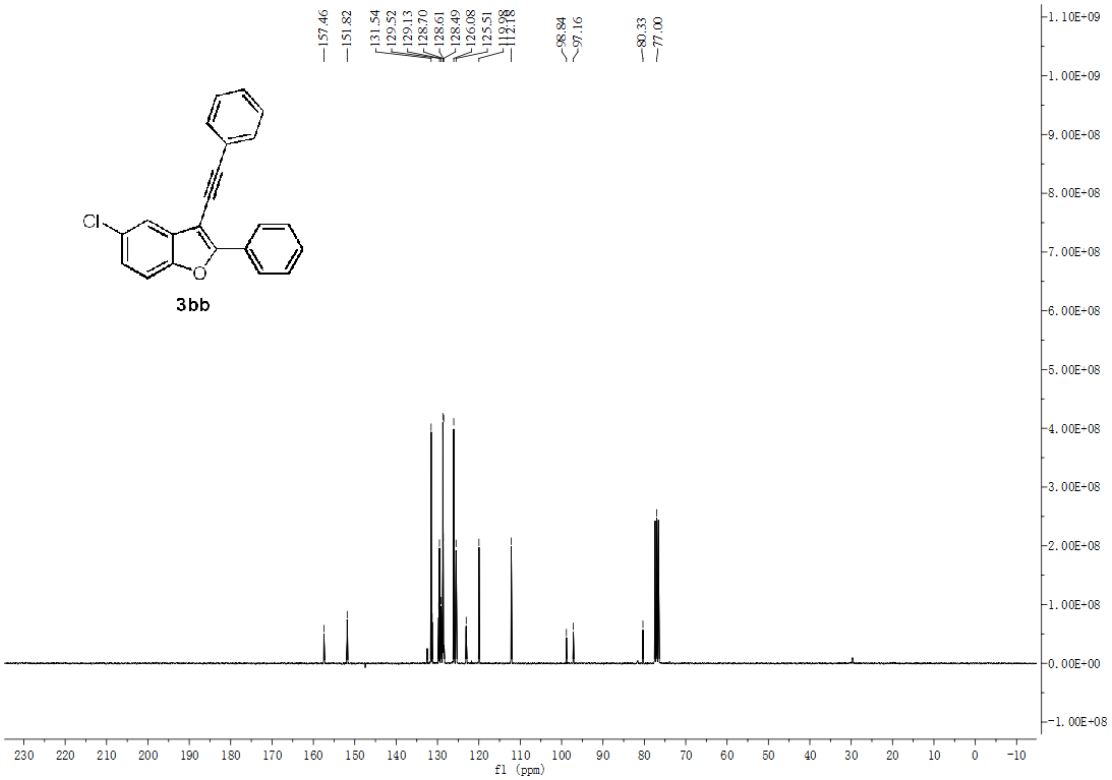


Figure S138. ^{13}C NMR (75 MHz, $CDCl_3$) spectra of **3bb** in MestReNova.

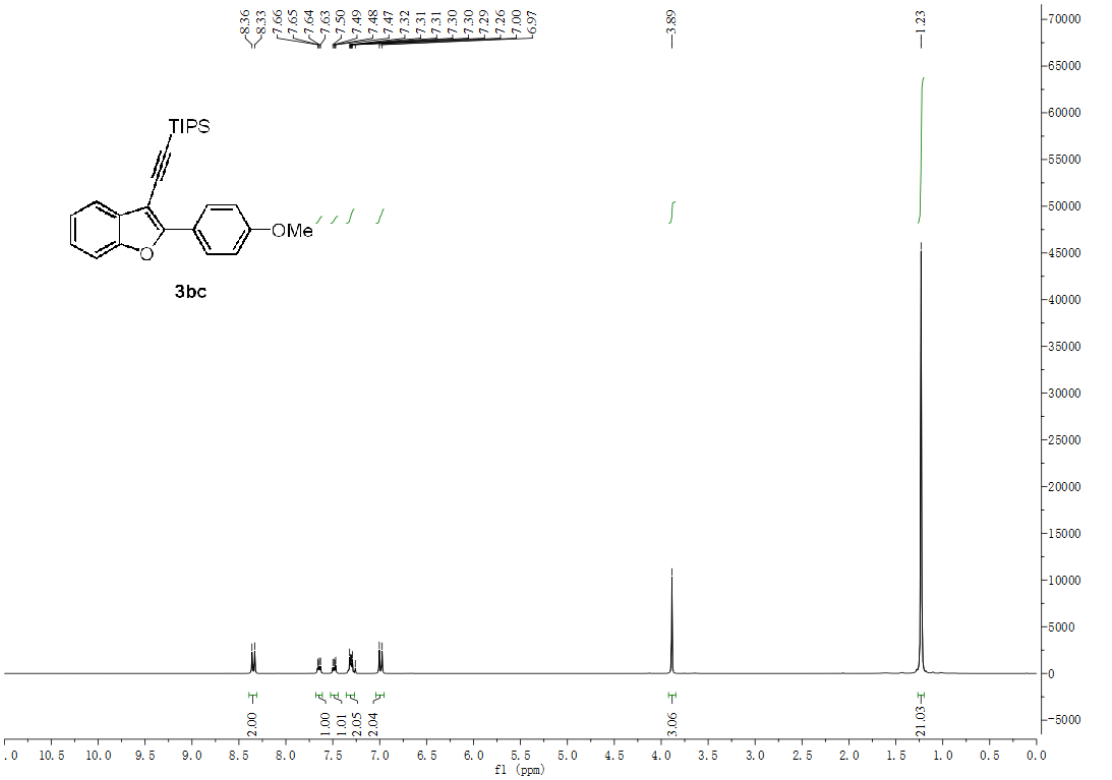


Figure S139. ^{1}H NMR (300 MHz, $CDCl_3$) spectra of **3bc** in MestReNova.

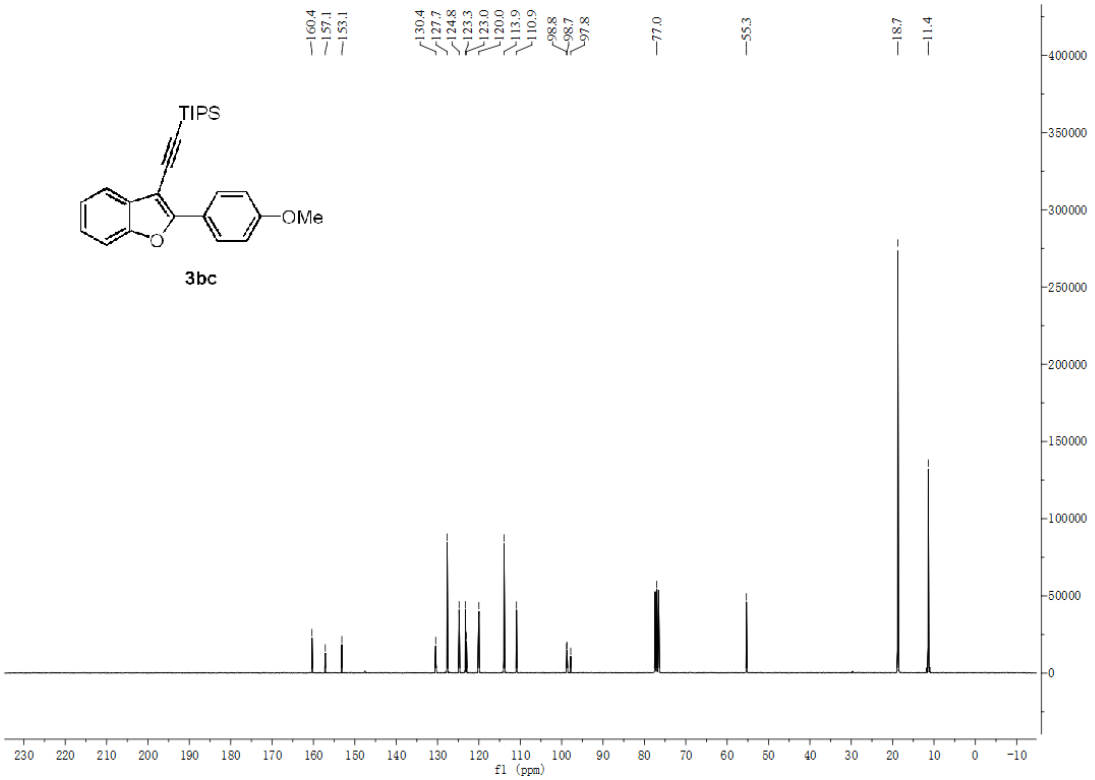


Figure S140. ^{13}C NMR (75 MHz, $CDCl_3$) spectra of **3bc** in MestReNova.

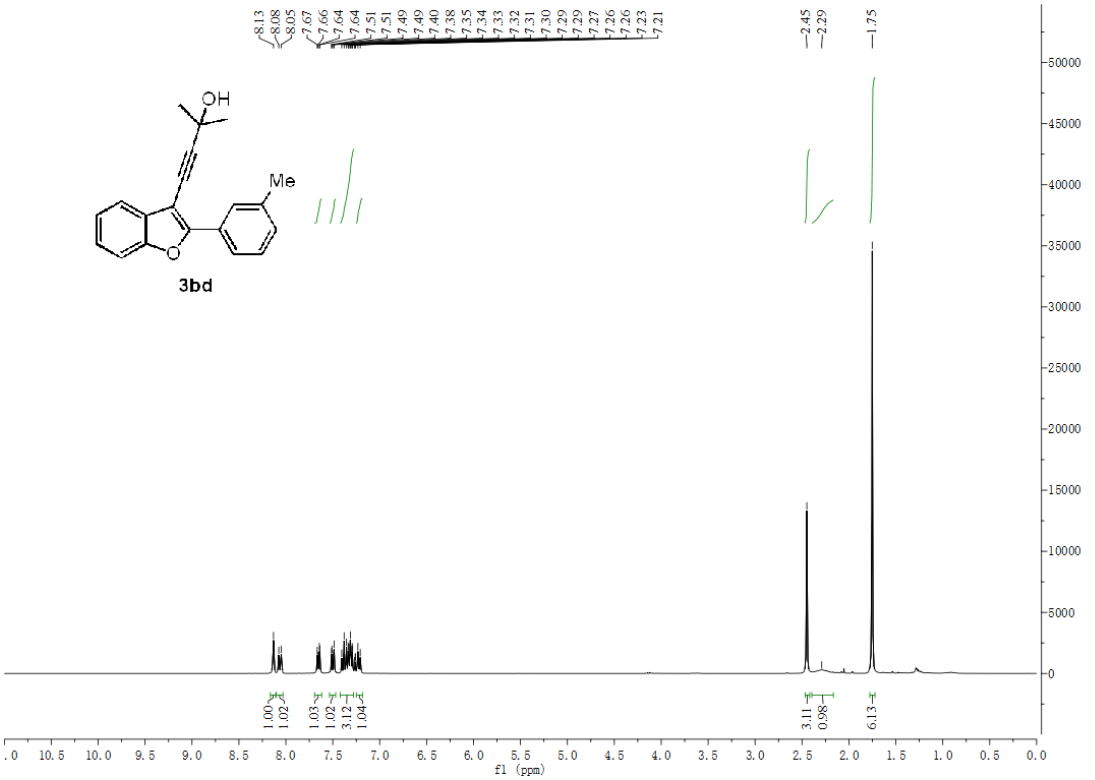


Figure S141. ^{1}H NMR (300 MHz, $CDCl_3$) spectra of **3bd** in MestReNova.

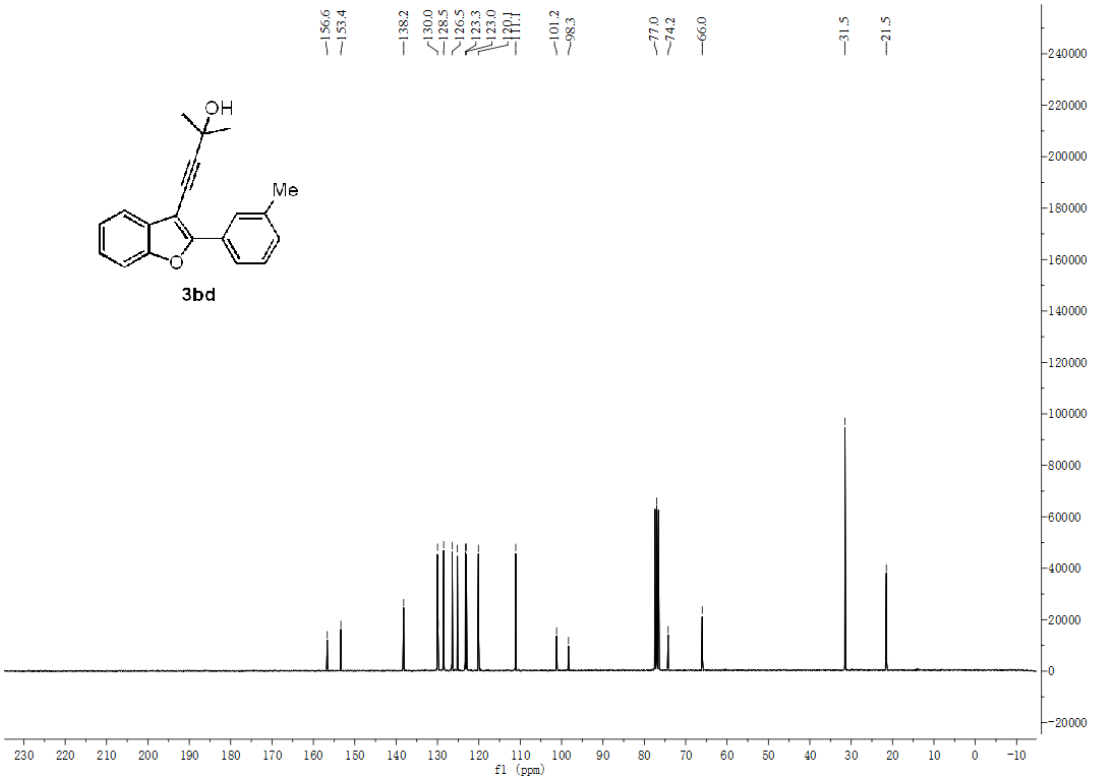


Figure S142. ^{13}C NMR (75 MHz, $CDCl_3$) spectra of **3bd** in MestReNova.

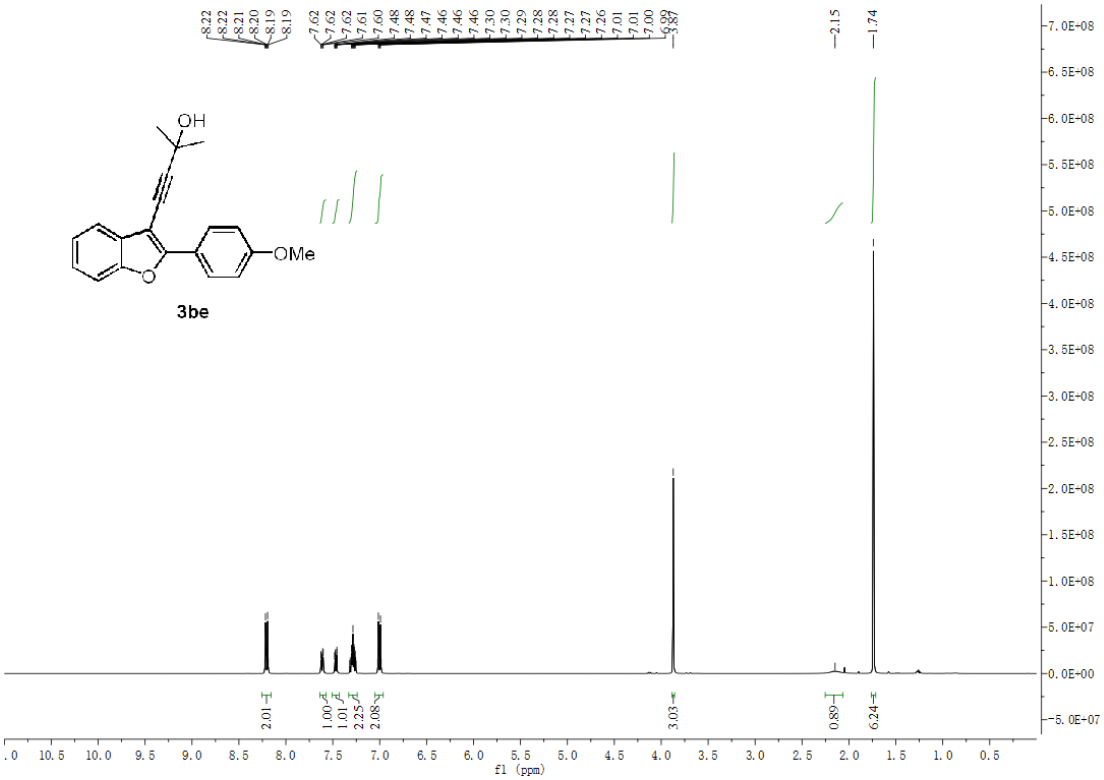


Figure S143. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3be** in MestReNova.

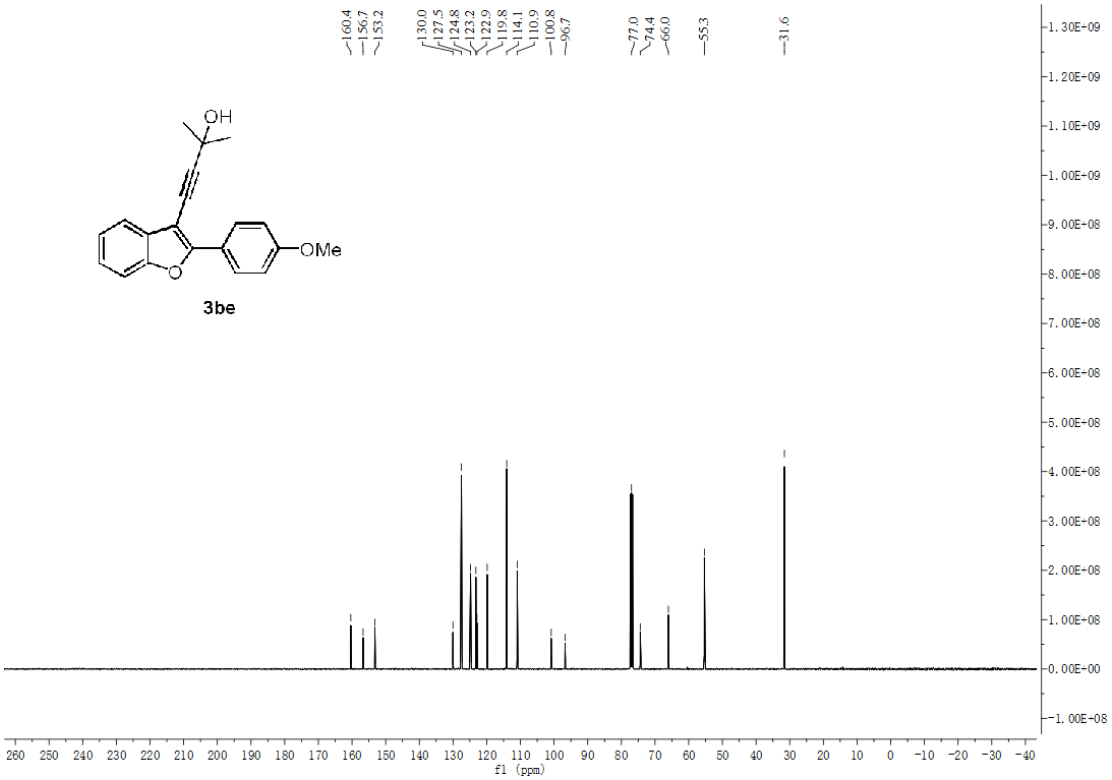


Figure S144. ^{13}C NMR (101 MHz, $CDCl_3$) spectra of **3be** in MestReNova.

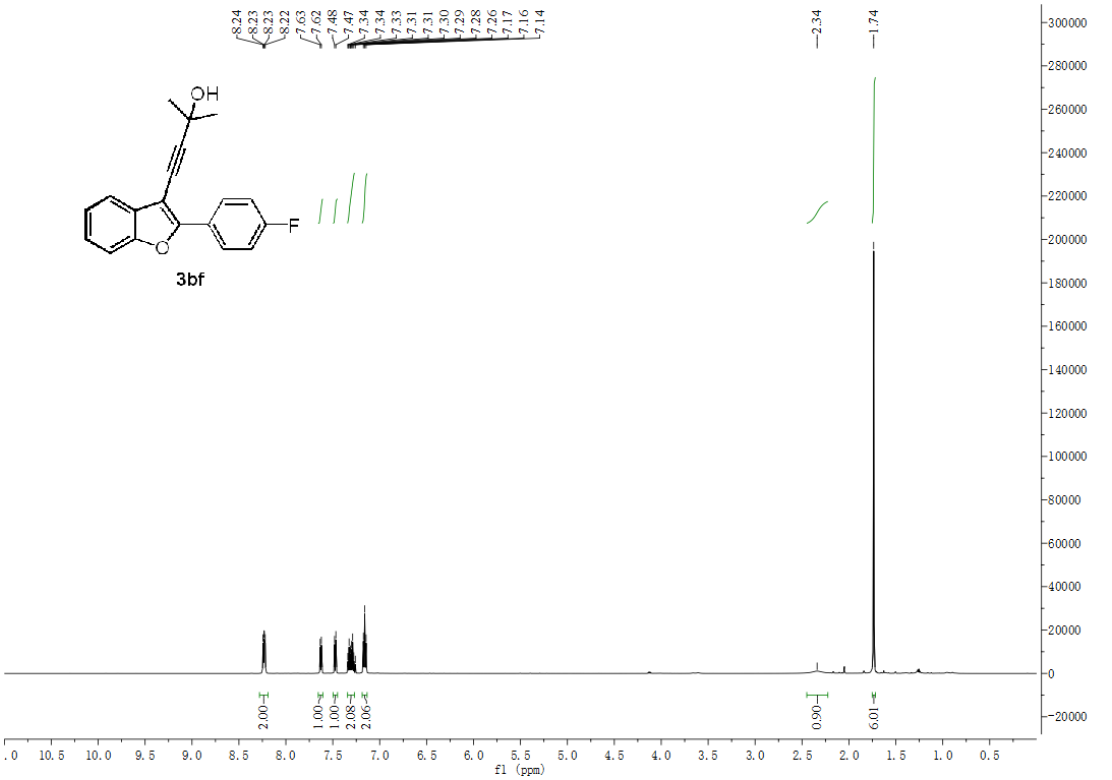


Figure S145. ^{1}H NMR (600 MHz, $CDCl_3$) spectra of **3bf** in MestReNova.

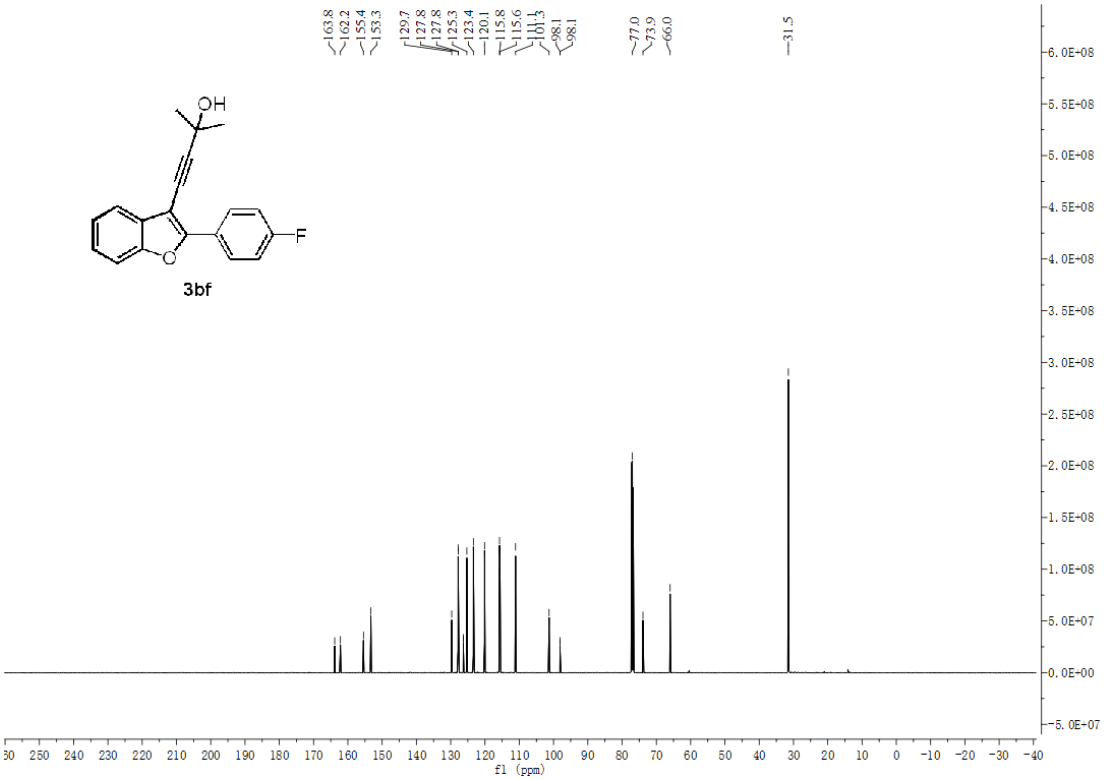


Figure S146. ^{13}C NMR (151 MHz, $CDCl_3$) spectra of **3bf** in MestReNova.

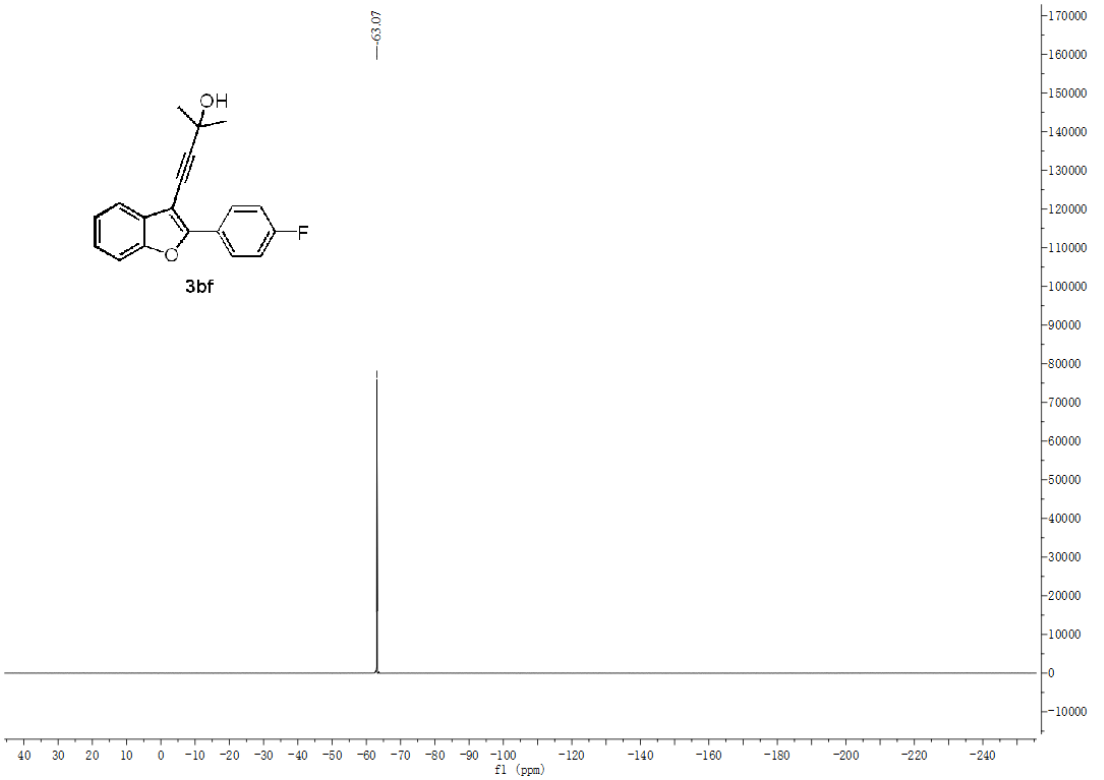


Figure S147. ^{19}F NMR (282 MHz, $CDCl_3$) spectra of **3bf** in MestReNova.

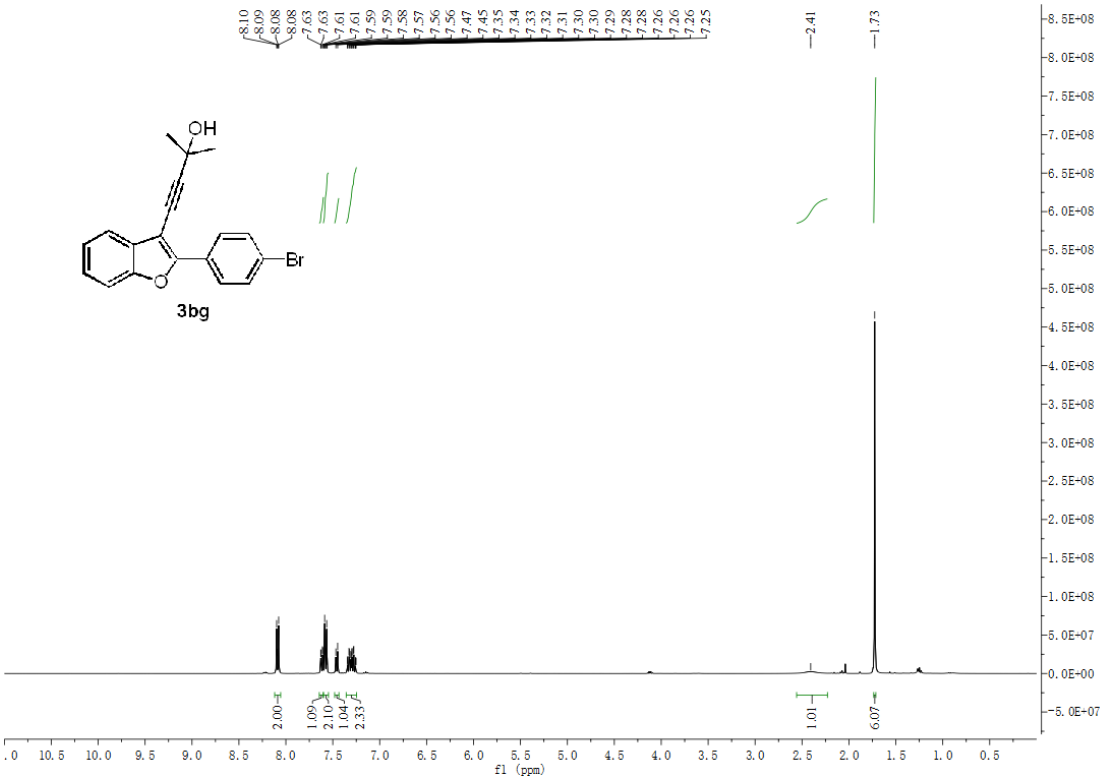


Figure S148. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3bg** in MestReNova.

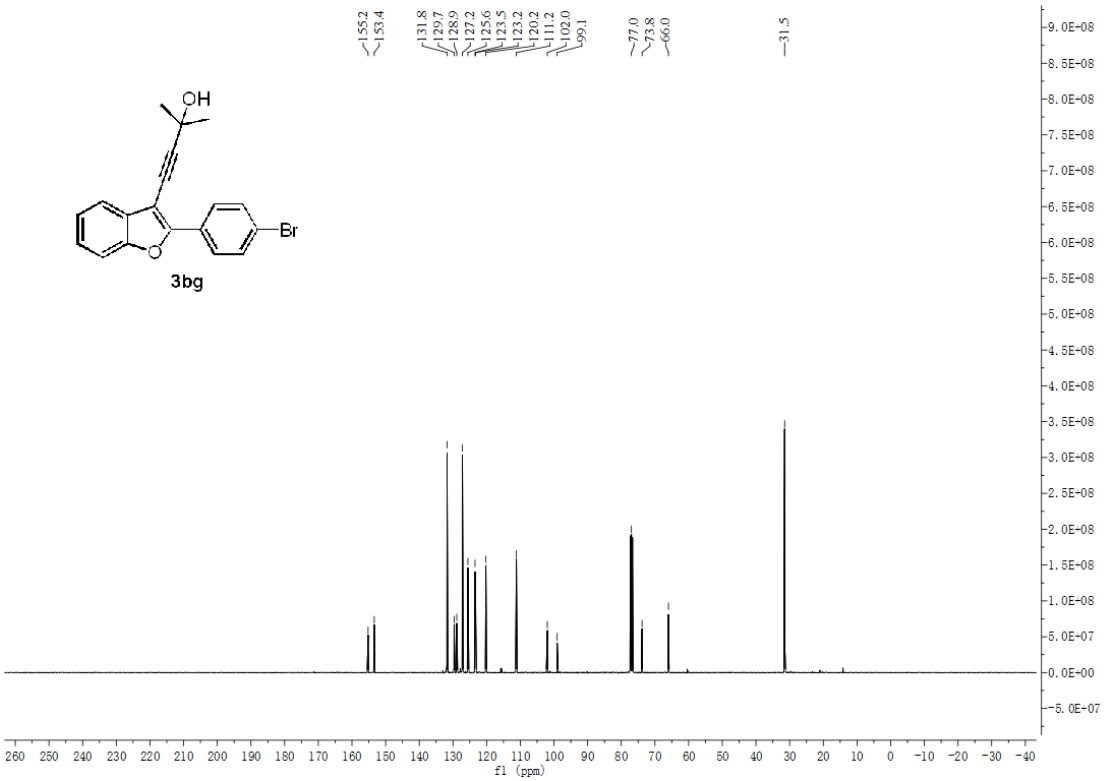


Figure S149. ^{13}C NMR (101 MHz, $CDCl_3$) spectra of **3bg** in MestReNova.

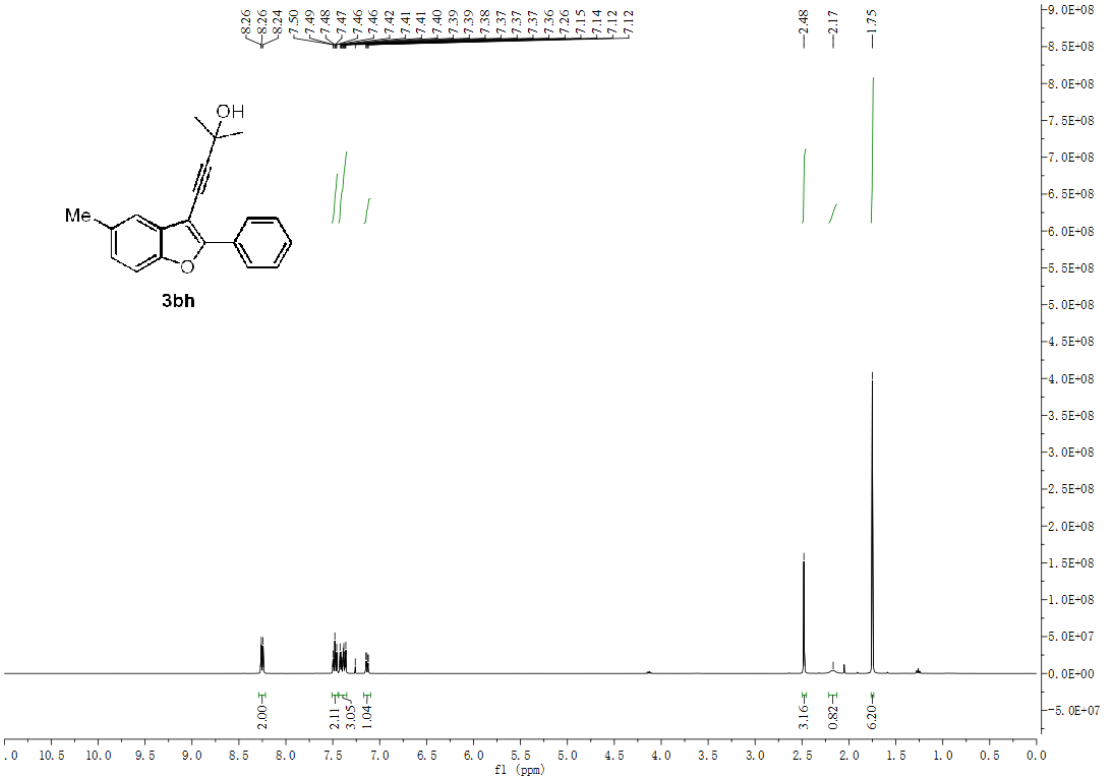


Figure S150. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3bh** in MestReNova.

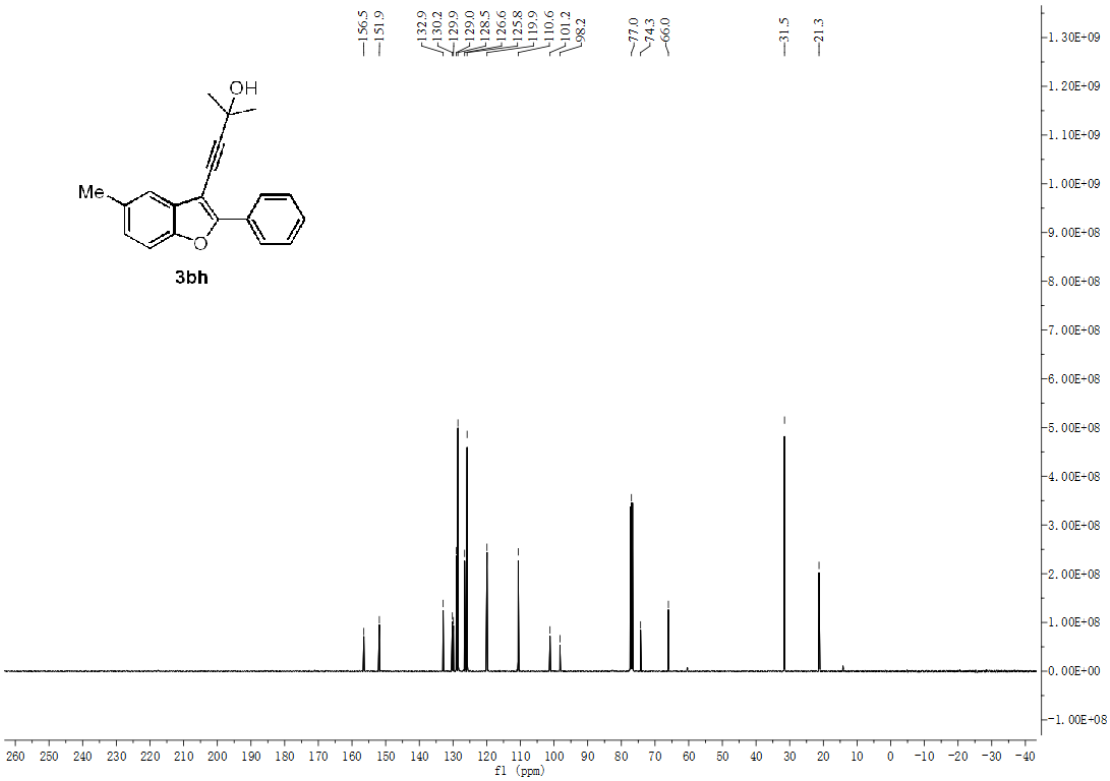


Figure S151. ^{13}C NMR (101 MHz, $CDCl_3$) spectra of **3bh** in MestReNova.

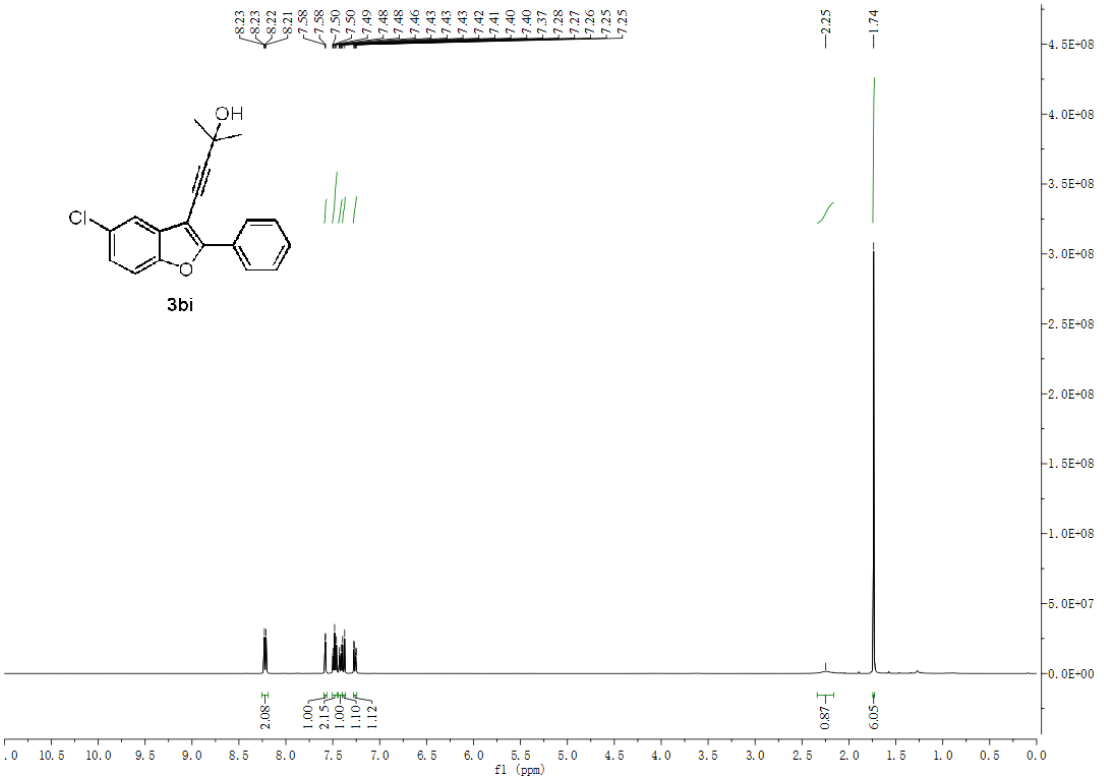


Figure S152. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3bi** in MestReNova.

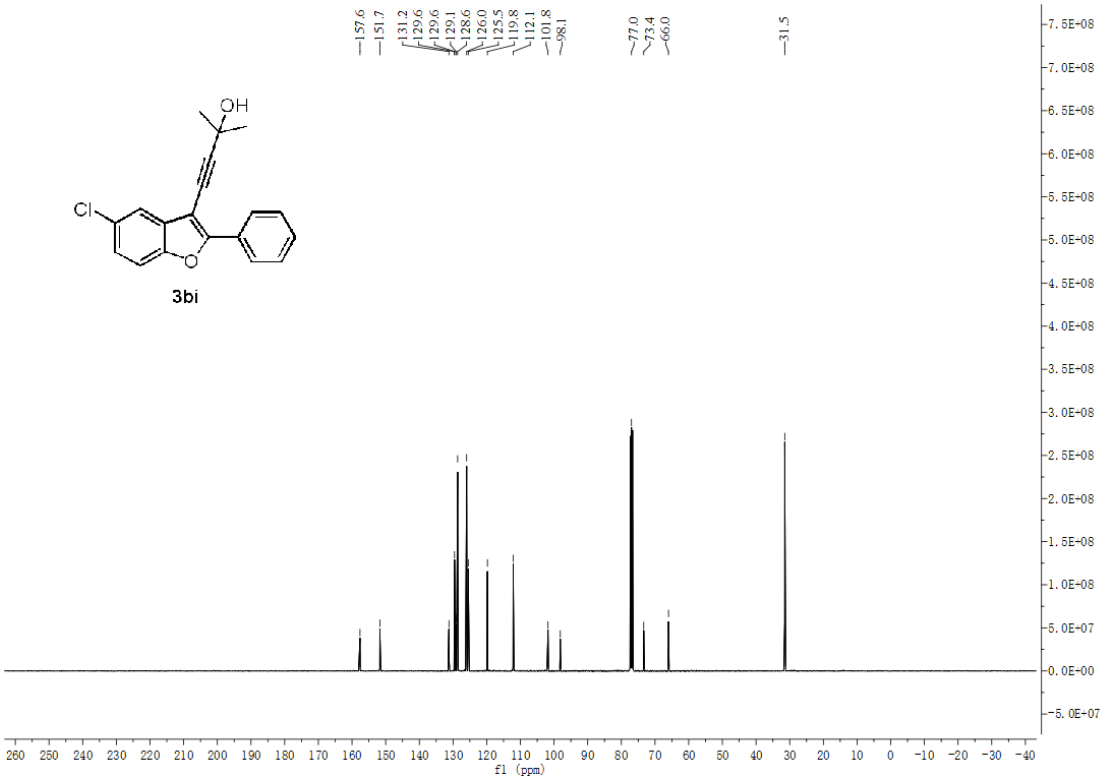


Figure S153. ^{13}C NMR (101 MHz, $CDCl_3$) spectra of **3bi** in MestReNova.

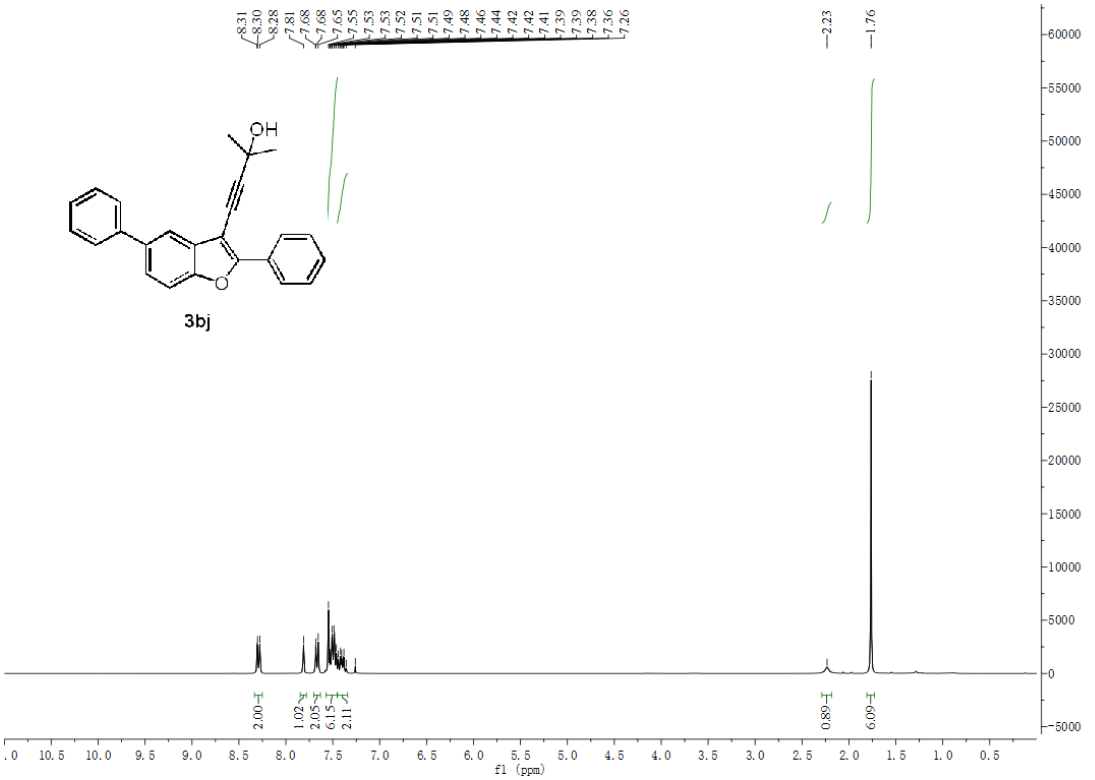


Figure S154. ^{1}H NMR (300 MHz, $CDCl_3$) spectra of **3bj** in MestReNova.

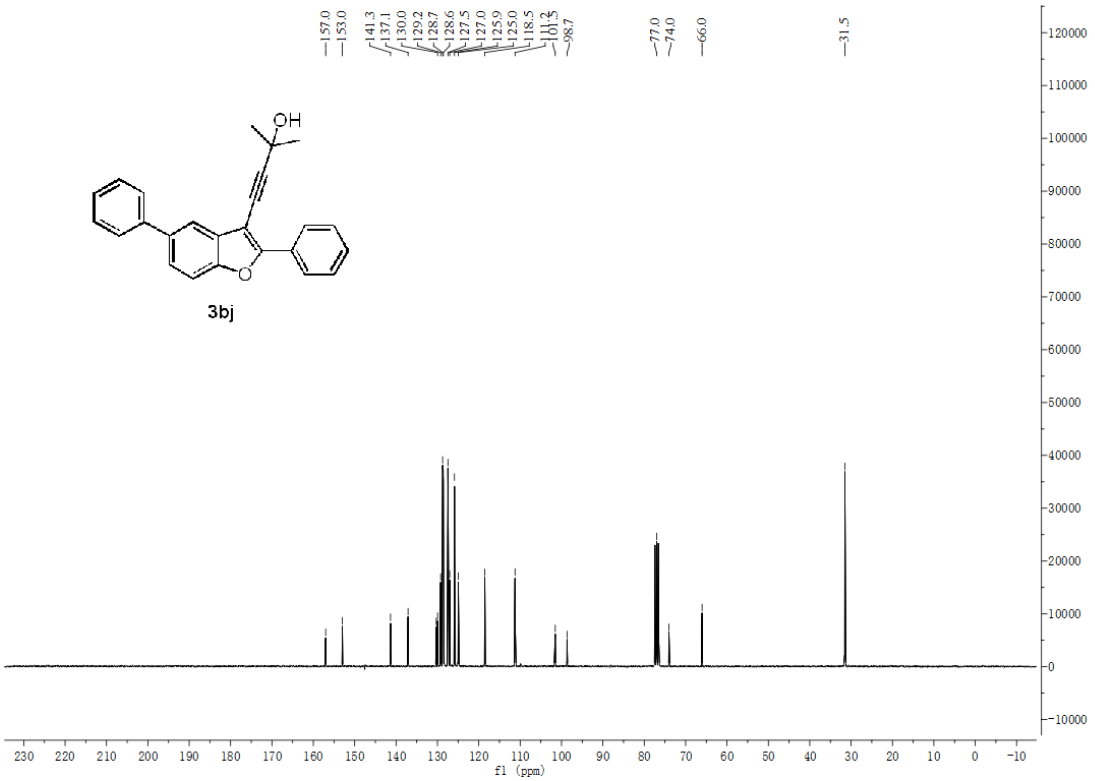


Figure S155. ^{13}C NMR (75 MHz, $CDCl_3$) spectra of **3bj** in MestReNova.

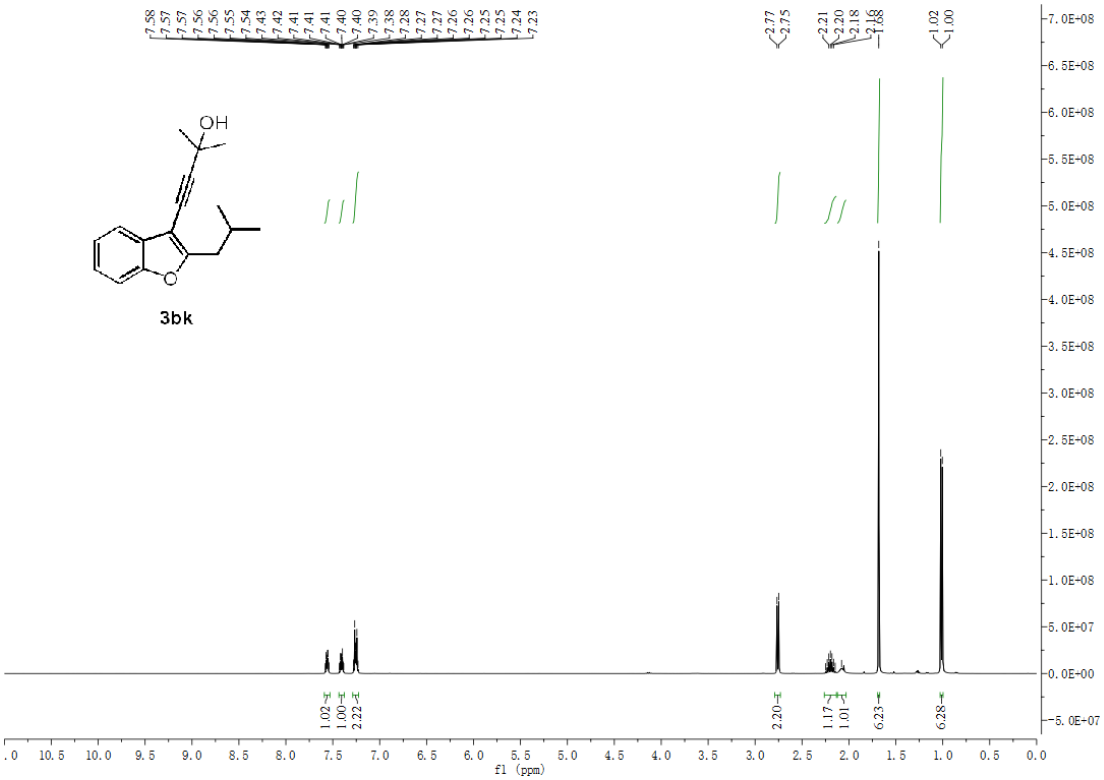


Figure S156. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3bk** in MestReNova.

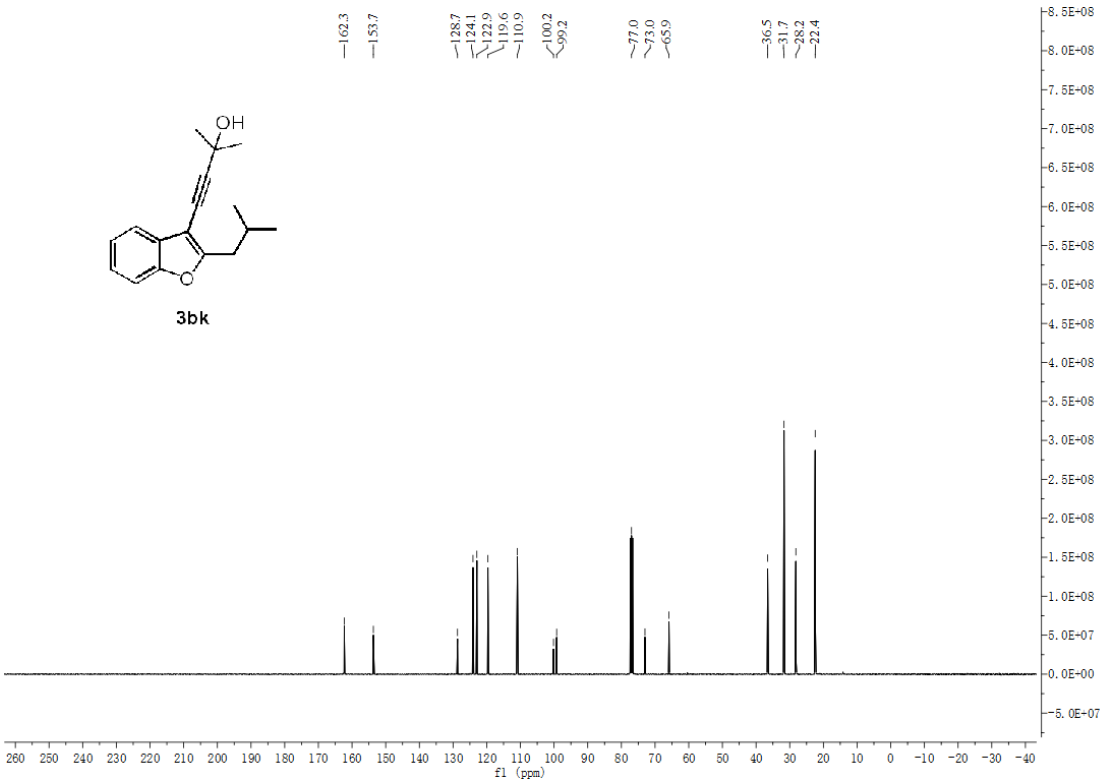


Figure S157. ^{13}C NMR (101 MHz, $CDCl_3$) spectra of **3bk** in MestReNova.

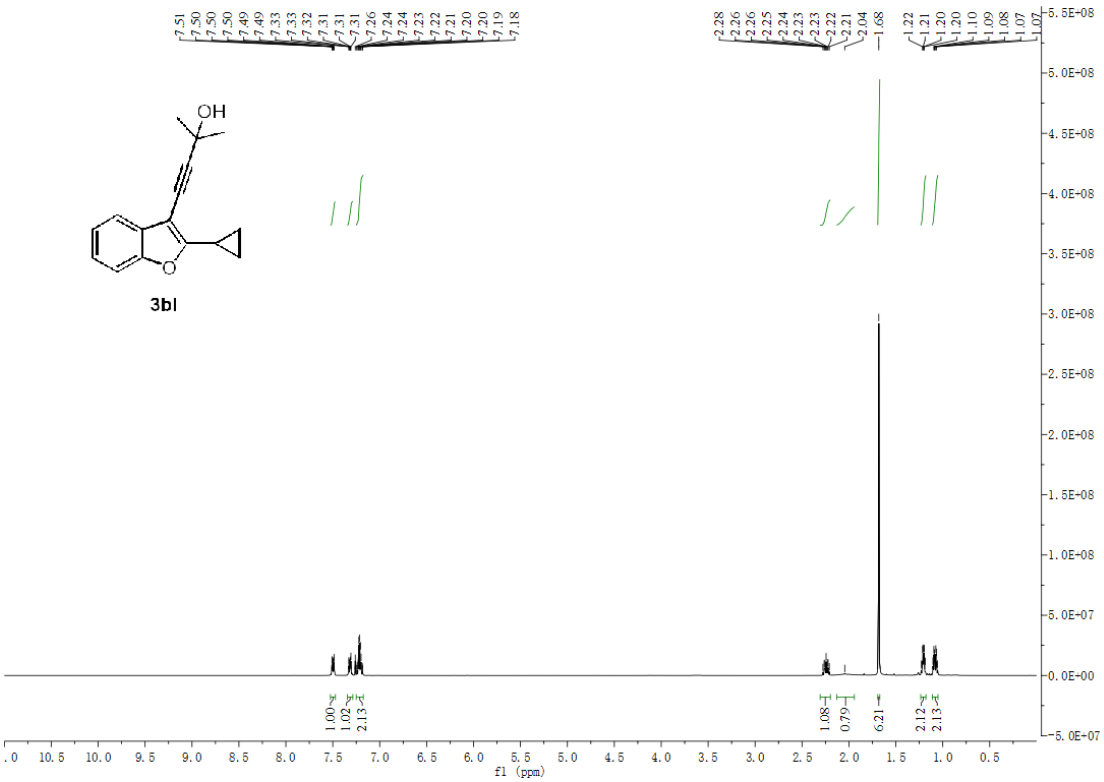


Figure S158. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3bl** in MestReNova.

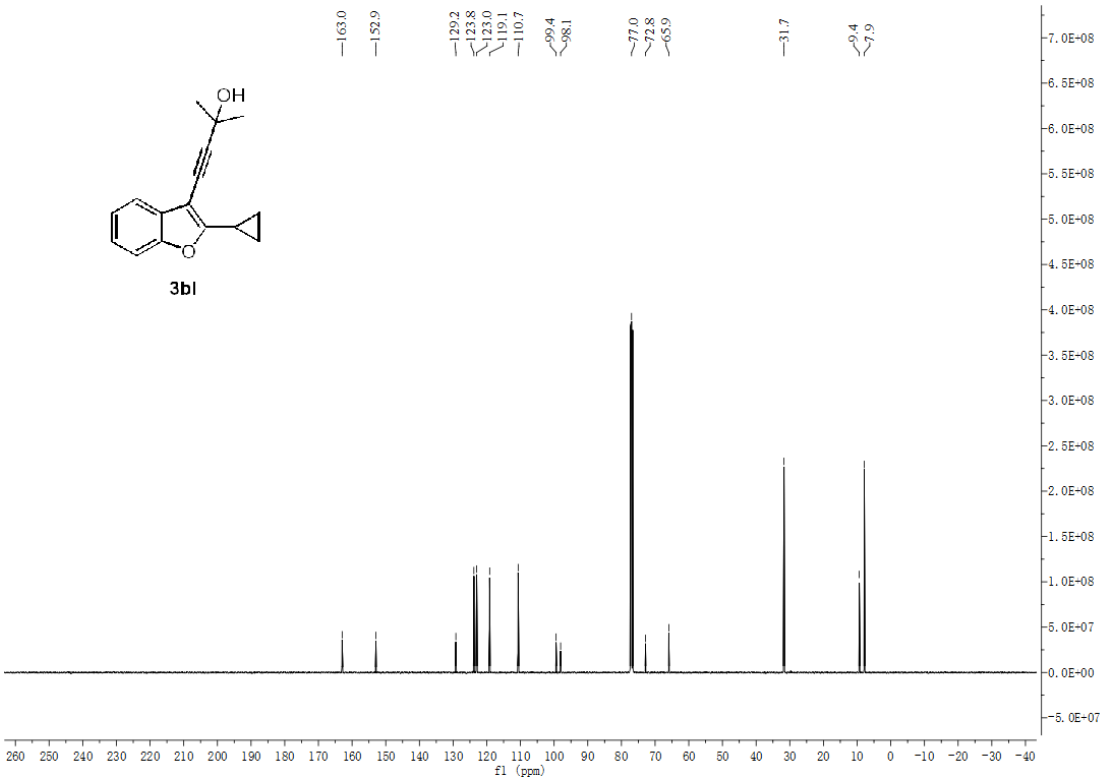


Figure S159. ^{13}C NMR (101 MHz, $CDCl_3$) spectra of **3bl** in MestReNova.

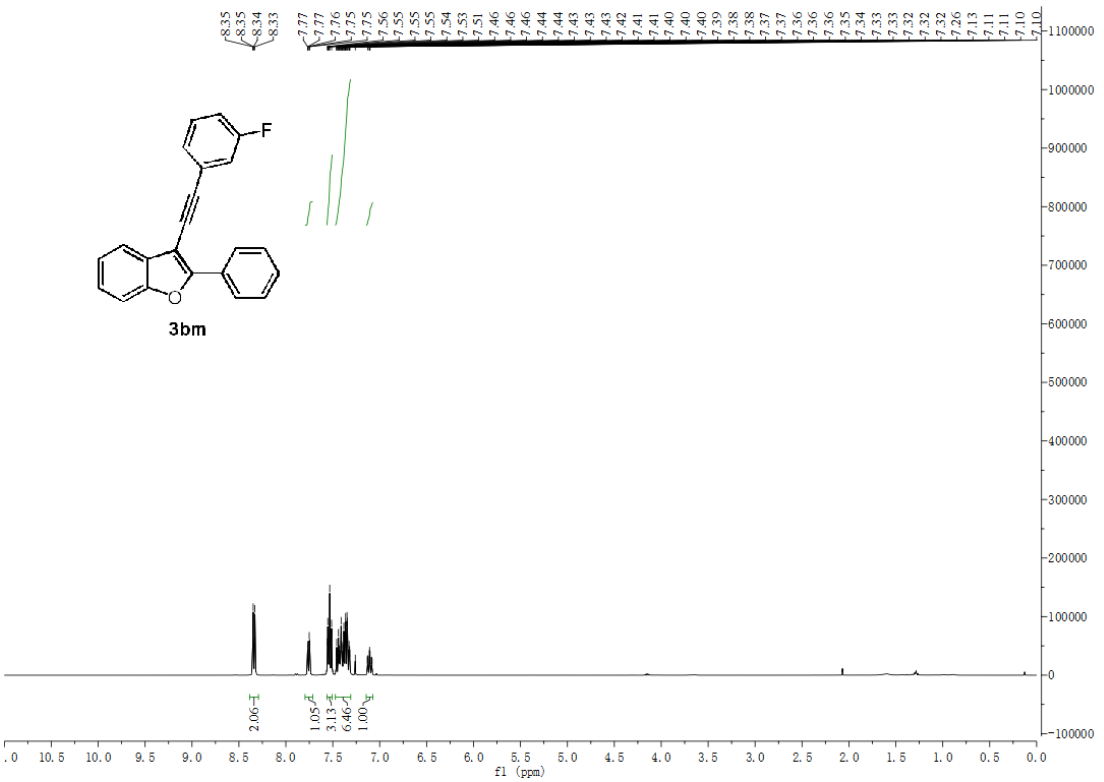


Figure S160. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3bm** in MestReNova.

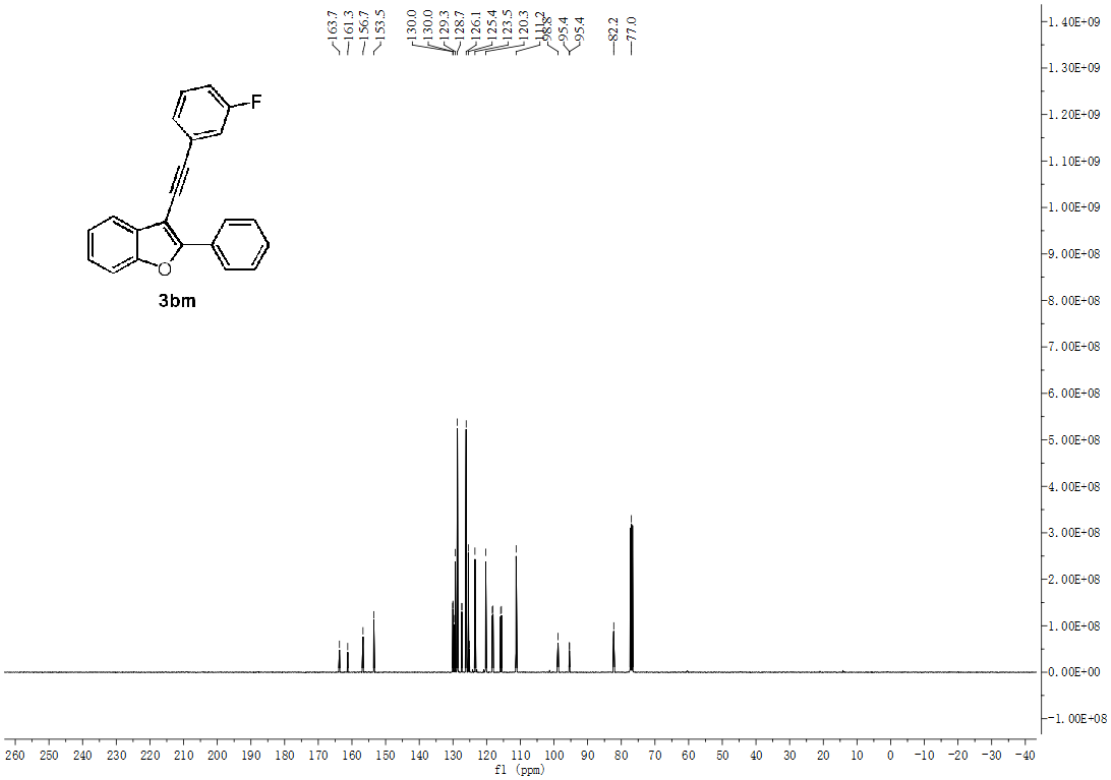


Figure S161. ^{13}C NMR (101 MHz, $CDCl_3$) spectra of **3bm** in MestReNova.

Figure S162. ^{19}F NMR (282 MHz, $CDCl_3$) spectra of **3bm** in MestReNova.

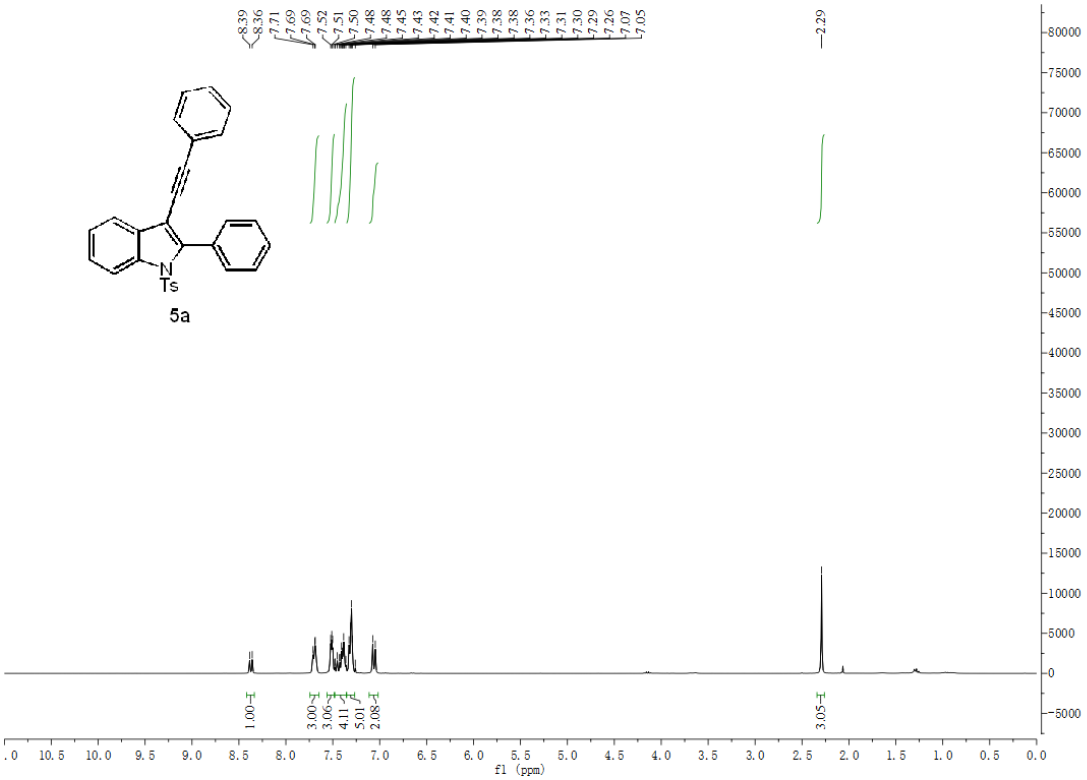


Figure S163. ^{1}H NMR (300 MHz, $CDCl_3$) spectra of **5a** in MestReNova.

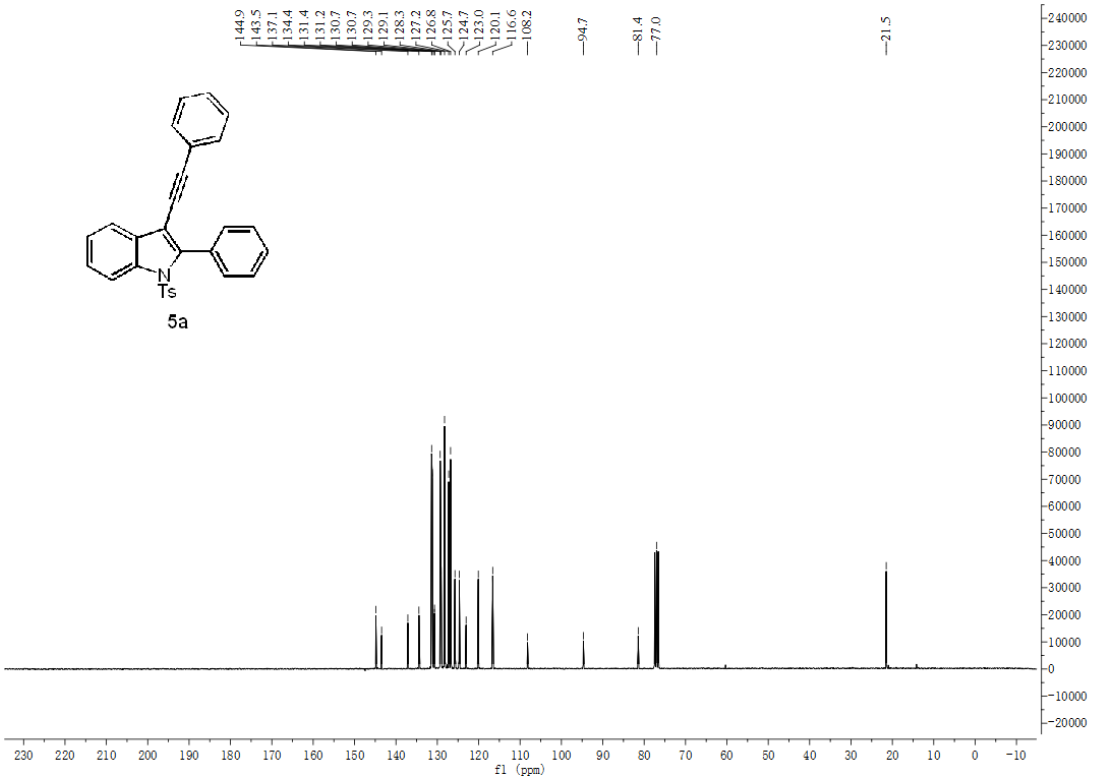


Figure S164. ^{13}C NMR (75 MHz, $CDCl_3$) spectra of **5a** in MestReNova.

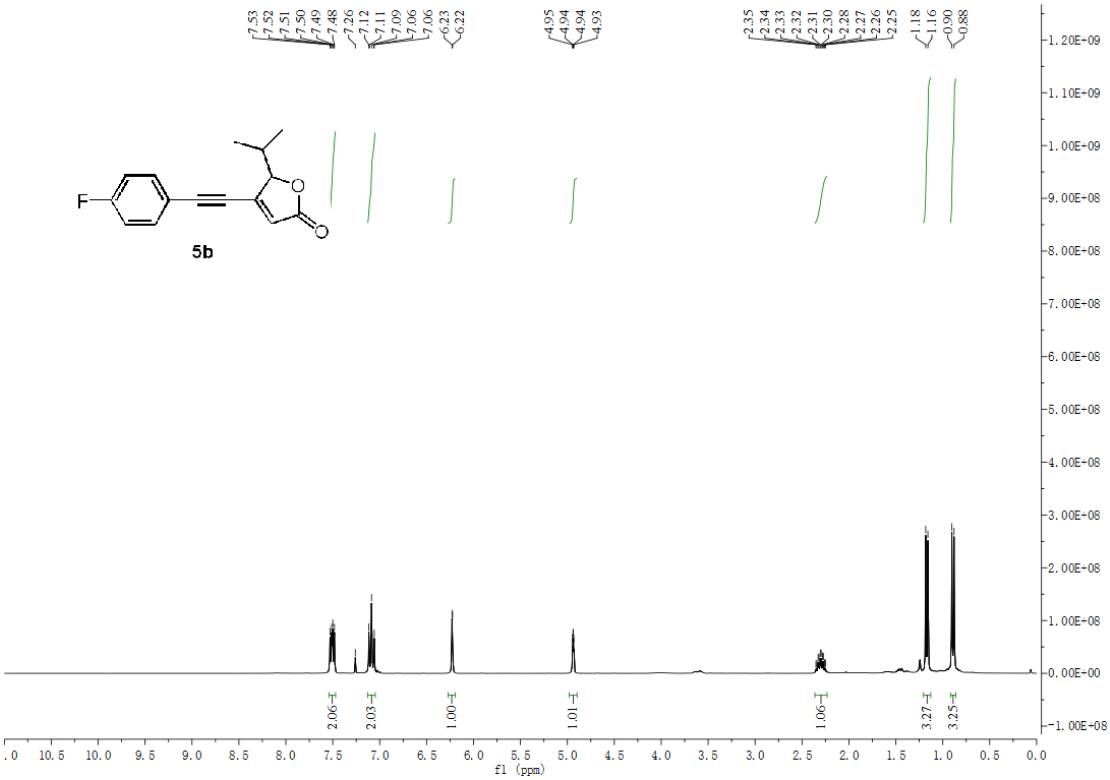


Figure S165. ^{1}H NMR (300 MHz, $CDCl_3$) spectra of **5b** in MestReNova.

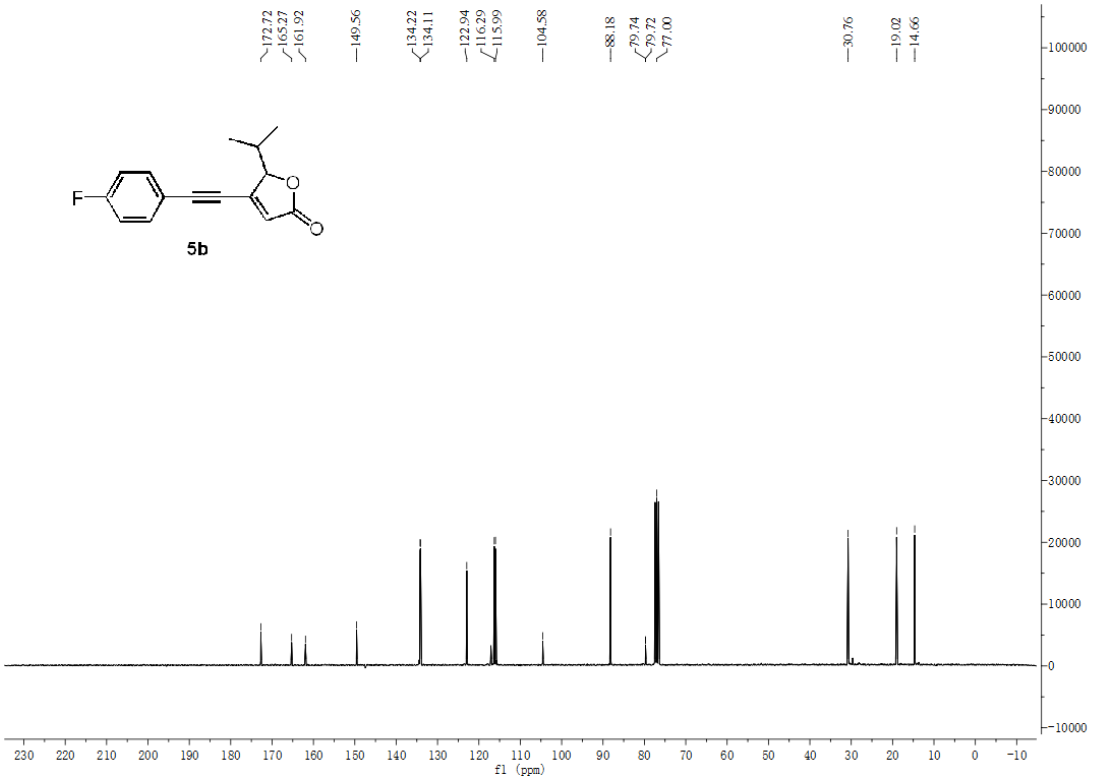


Figure S166. ^{13}C NMR (75 MHz, $CDCl_3$) spectra of **5b** in MestReNova.

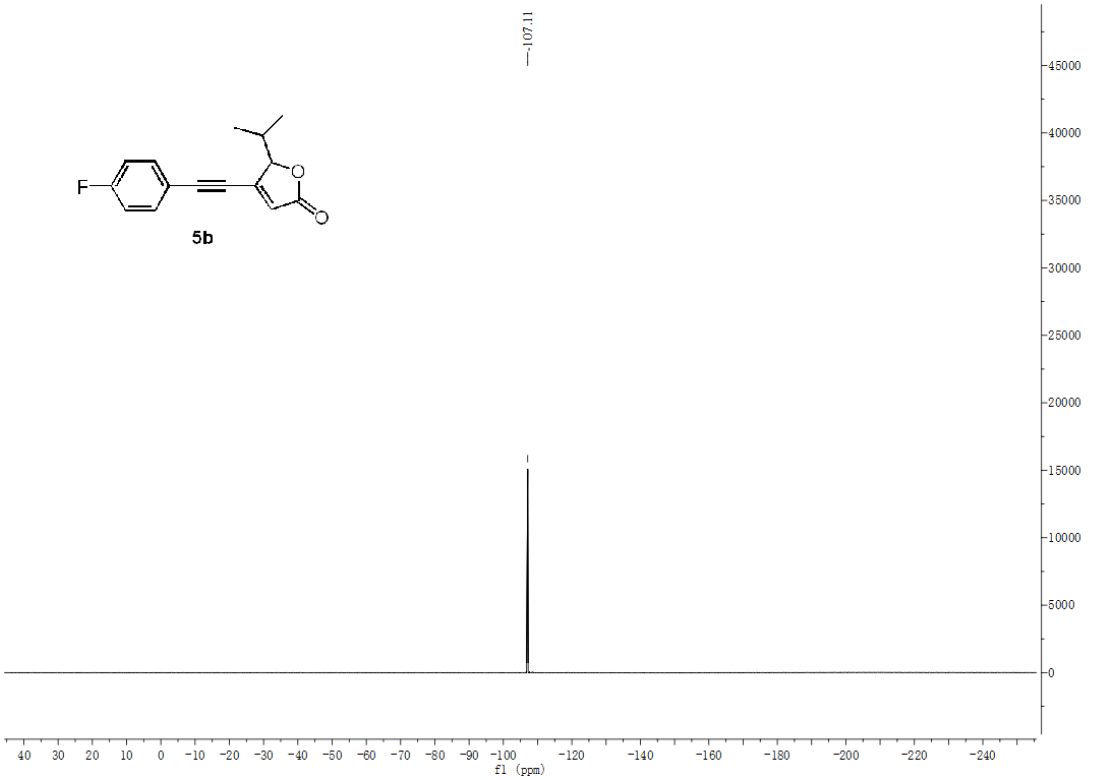


Figure S167. ^{19}F NMR (282 MHz, $CDCl_3$) spectra of **5b** in MestReNova.

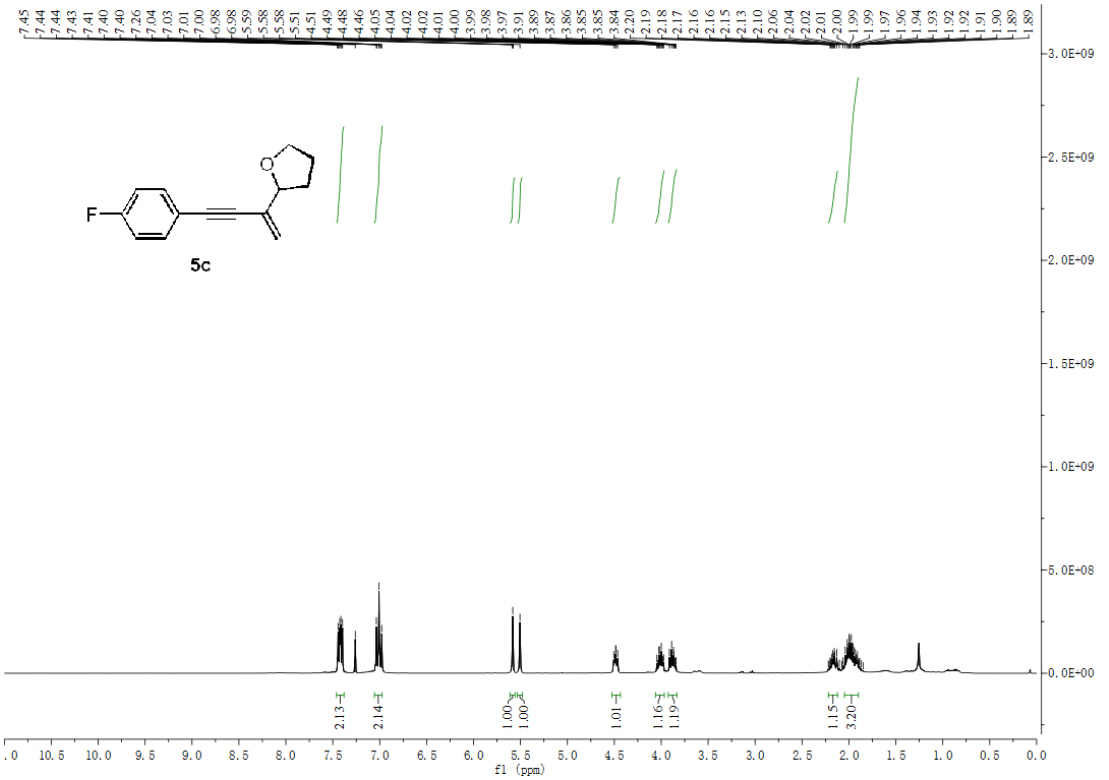


Figure S168. ^{1}H NMR (300 MHz, $CDCl_3$) spectra of **5c** in MestReNova.

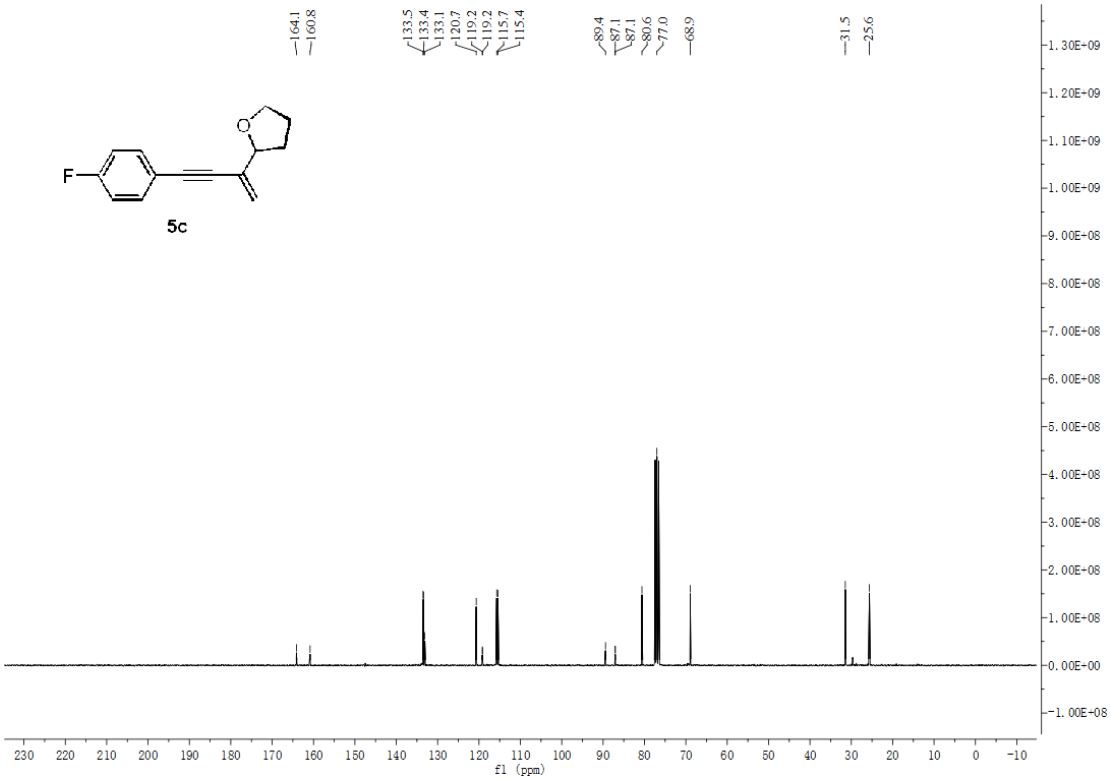


Figure S169. ^{13}C NMR (75 MHz, $CDCl_3$) spectra of **5c** in MestReNova.

Figure S170. ^{19}F NMR (282 MHz, $CDCl_3$) spectra of **5c** in MestReNova.

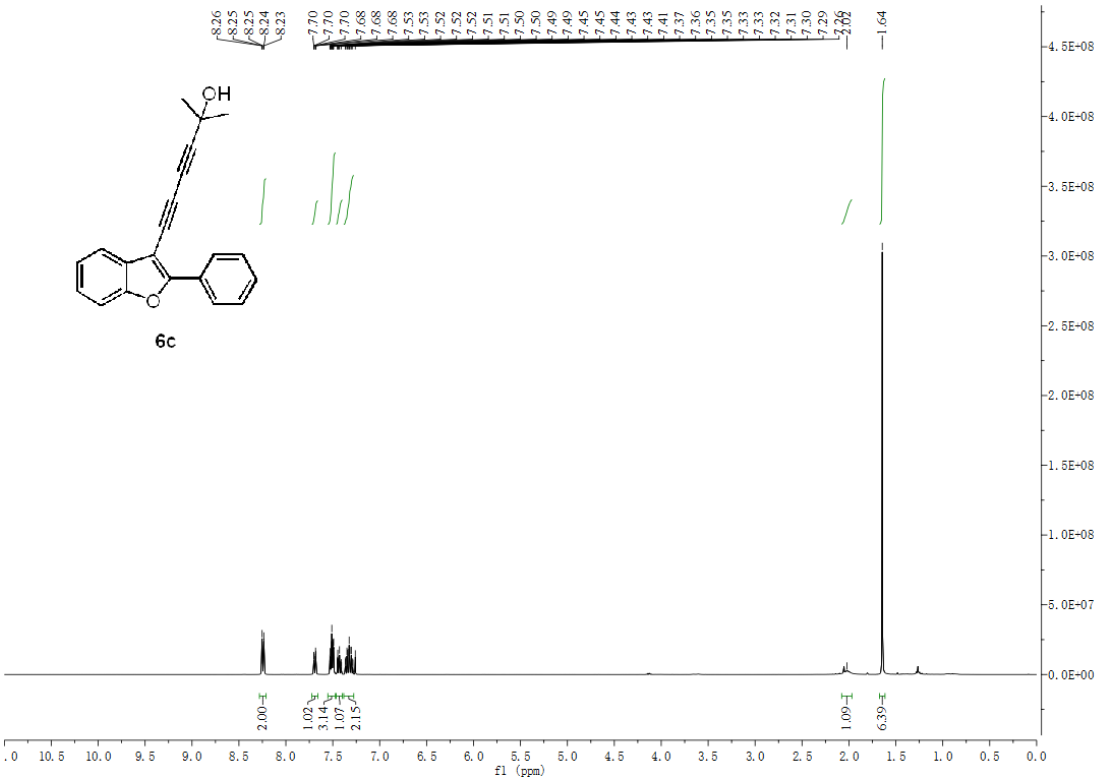


Figure S171. ^{1}H NMR (300 MHz, $CDCl_3$) spectra of **6c** in MestReNova.

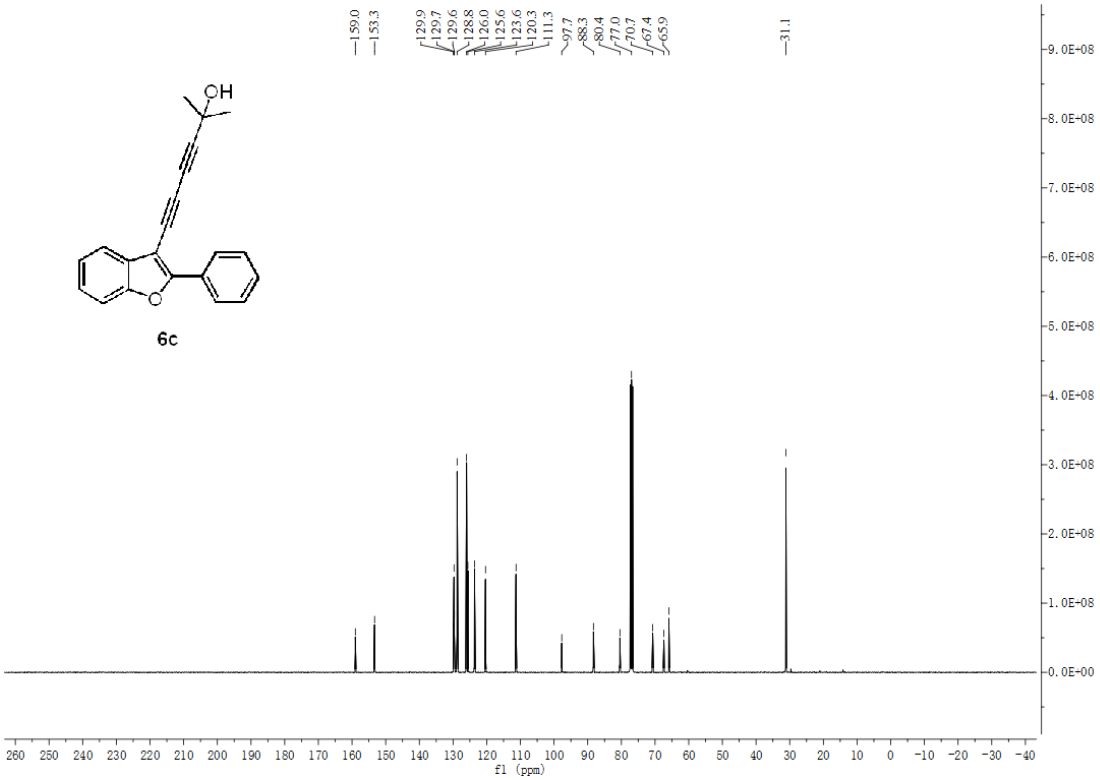


Figure S172. ^{13}C NMR (75 MHz, $CDCl_3$) spectra of **6c** in MestReNova.

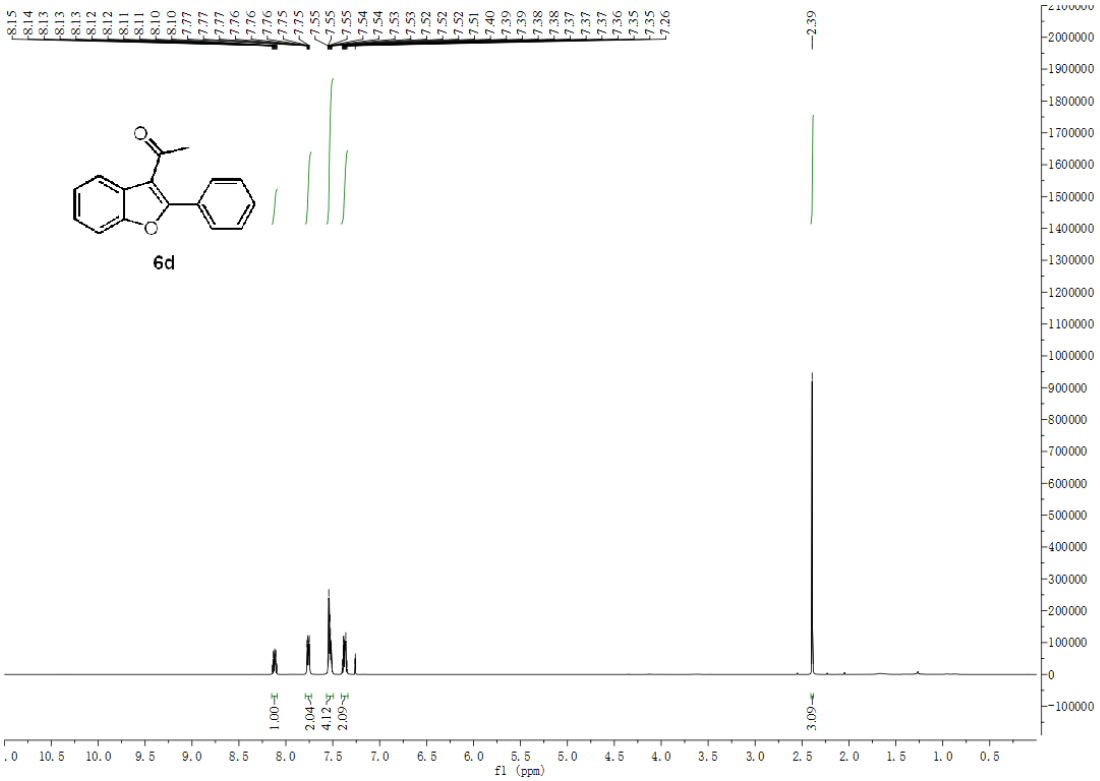


Figure S173. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of **6d** in MestReNova.

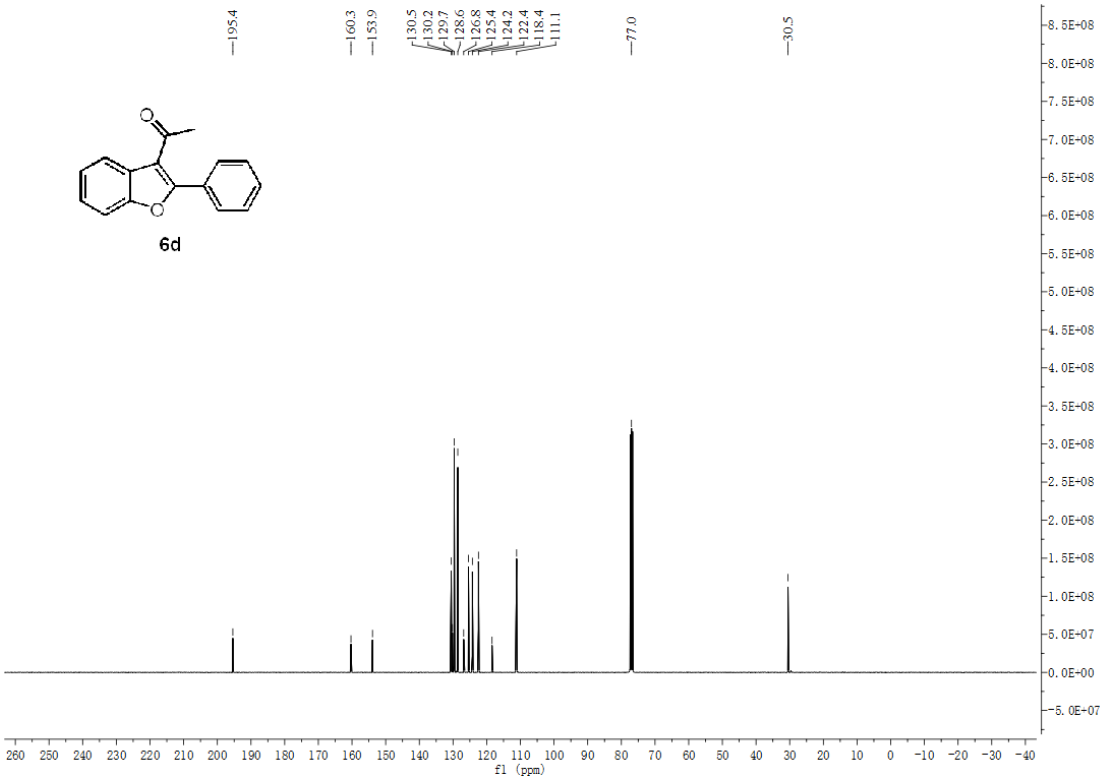


Figure S174. ^{13}C NMR (101 MHz, $CDCl_3$) spectra of **6d** in MestReNova.

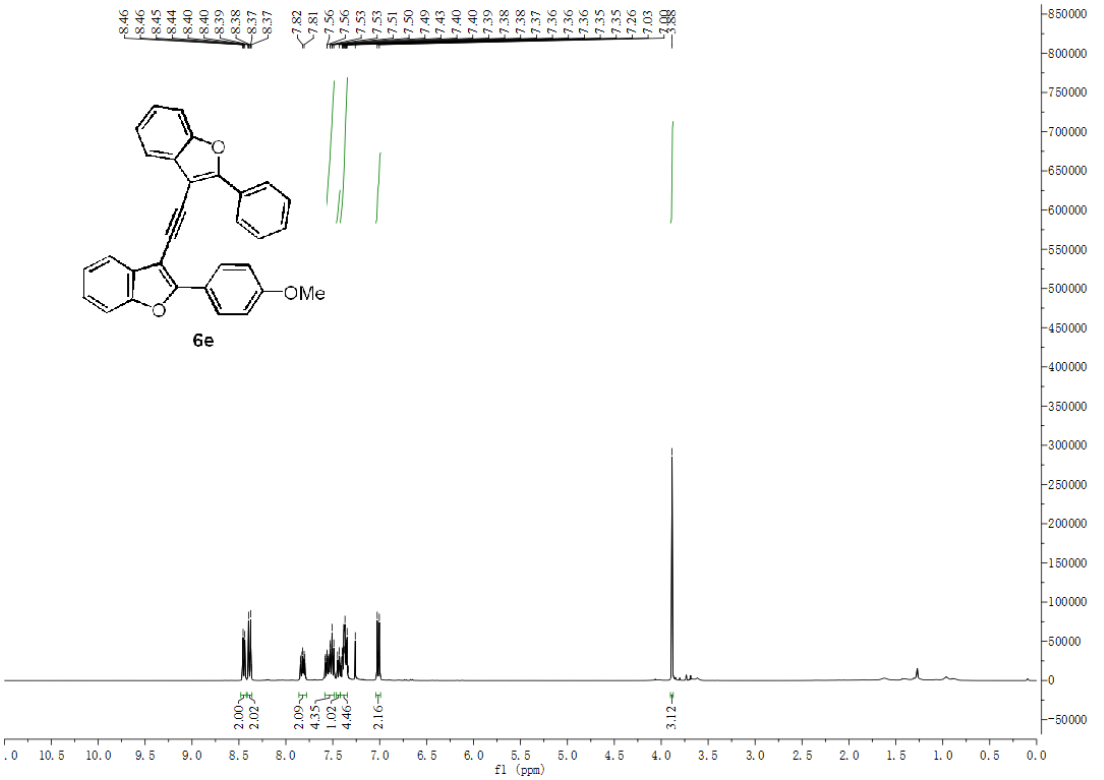


Figure S175. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of **6e** in MestReNova.

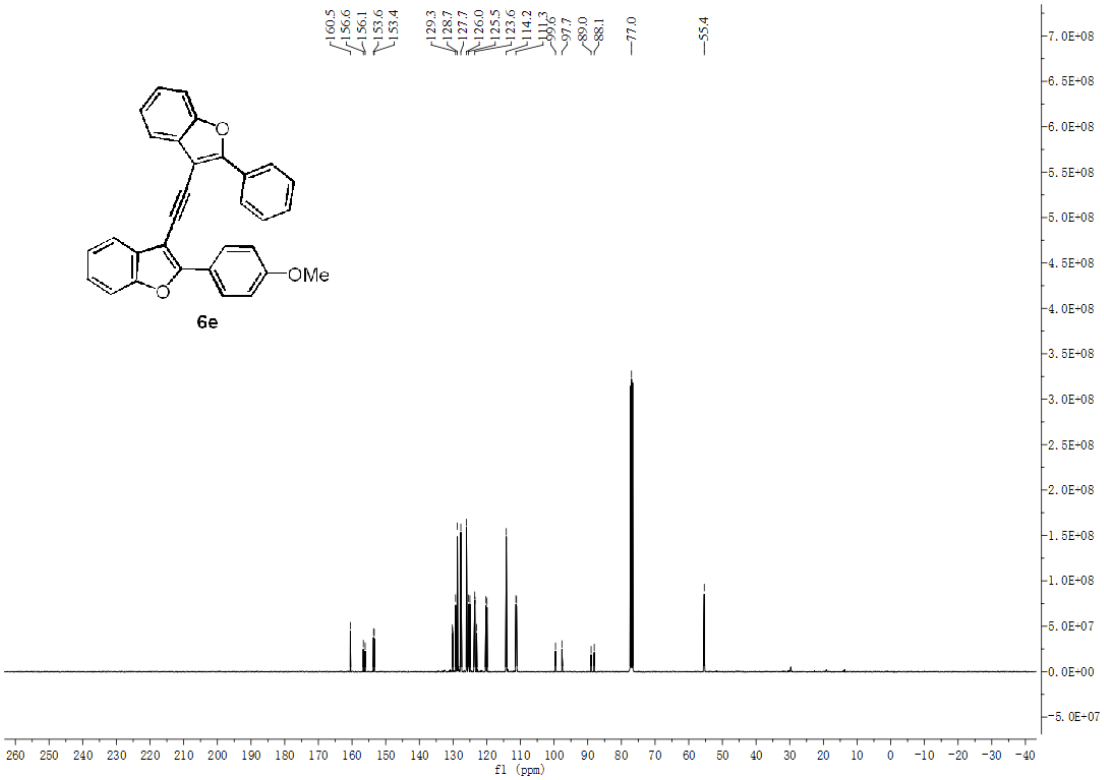
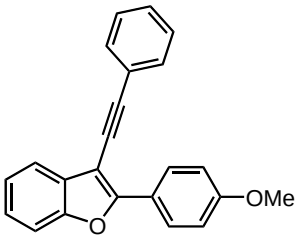


Figure S176. ^{13}C NMR (101 MHz, $CDCl_3$) spectra of **6e** in MestReNova.

5. X-Ray Crystallographic Data of 3ak



2-(4-methoxyphenyl)-3-(phenylethynyl)benzofuran (**3ak**)
CCDC 2180908

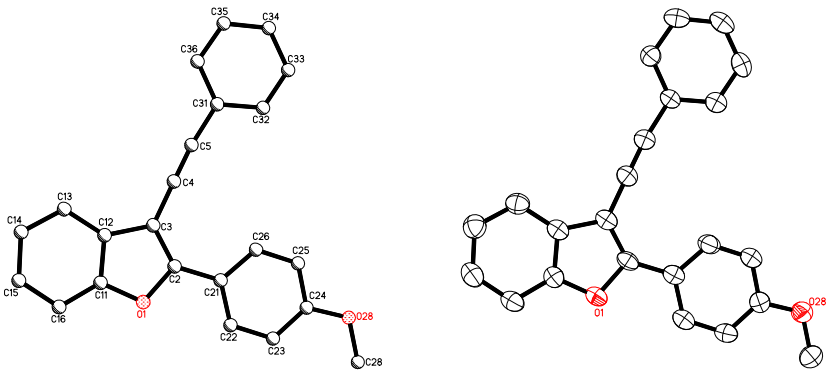


Figure S177. The ORTEP projection of crystal structure of **3ak**.

Table S7. Crystal Data and Structure Refinement for **3ak.**

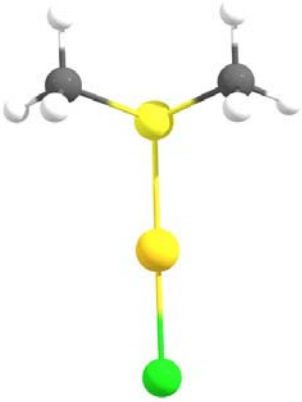
Identification code	hws12 (**3ak**)	
Empirical formula	$C_{23}H_{16}O_2$	
Formula weight	324.36	
Temperature	200(2) K	
Wavelength	0.71073 Å	
Crystal system	monoclinic	
Space group	$P2_1/c$	
Z	4	
Unit cell dimensions	a = 16.084(2) Å	□ α = 90 deg.
	b = 5.0200(7) Å	□ β = 104.717(4) deg.
	c = 21.009(3) Å	□ γ = 90 deg.
Volume	1640.6(4) $Å^3$	
Density (calculated)	1.31 g/cm^3	
Absorption coefficient	0.08 mm^{-1}	
Crystal shape	plank	
Crystal size	0.321 x 0.040 x 0.035 mm^3	
Crystal colour	colourless	
Theta range for data collection	1.3 to 25.0 deg.	
Index ranges	$-19 \leq h \leq 19$, $-5 \leq k \leq 5$, $-25 \leq l \leq 25$	
Reflections collected	14479	
Independent reflections	2873 (R(int) = 0.0827)	
Observed reflections	1770 ($I > 2\sigma(I)$)	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.96 and 0.90	
Refinement method	Full-matrix least-squares on F^2	
Data/restraints/parameters	2873 / 0 / 227	
Goodness-of-fit on F^2	1.04	
Final R indices (I > 2sigma(I))	R1 = 0.048, wR2 = 0.100	
Largest diff. peak and hole	0.16 and -0.25 $eÅ^{-3}$	

Crystal structure determinations and refinements

hws12: colourless crystal (plank), dimensions 0.321 x 0.040 x 0.035 mm^3, crystal system monoclinic, space group $P2_1/c$, Z = 4, a = 16.084(2) Å, b = 5.0200(7) Å, c = 21.009(3) Å, alpha = 90 deg, beta = 104.717(4) deg, gamma = 90 deg, V= 1640.6(4) $Å^3$, rho = 1.313 g/cm^3, T = 200(2) K, $Theta_{max}$ = 25.024 deg, radiation MoKα, lambda = 0.71073 Å, 0.5 deg omega-scans with CCD area detector, covering the asymmetric unit in reciprocal space with a mean redundancy of 0.84and a completeness of 99.9% to a resolution of 4.81 Å, 14479 reflections measured, 2873 unique (R(int) = 0.0827), 1770 observed ($I > 2\sigma(I)$), intensities were corrected for Lorentz and polarization effects, an empirical scaling and absorption correction was applied using SADABS[25] based on the Laue symmetry of the reciprocal space, mu = 0.08mm^{-1}, T_{min} = 0.90, T_{max} = 0.96, structure solved with SHELXT-2018/2 (Sheldrick 2015)[26] and refined against F^2 with a Full-matrix least-squares algorithm using the SHELXL-2018/3 (Sheldrick, 2018) software[27], 227 parameters refined, hydrogen atoms were treated using appropriate riding models, goodness of fit 1.04 for observed reflections, final residual values R1(F) = 0.048, $wR(F^2)$ = 0.100 for observed

reflections, residual electron density -0.25 to 0.16 eÅ^{-3}. CCDC 2180908 contains the supplementary crystallographic data for this paper. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures.

6. Cartesian Coordinates and energies of calculated structures

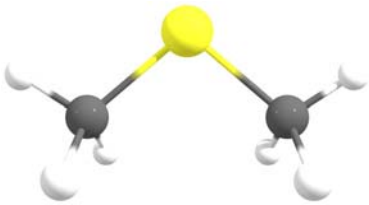


DMSAuCl

Energy: -1073,49280266 Eh

Charge 0; Multiplicity 1

16	-0.250106000	-7.065738000	-3.294350000
6	1.397415000	-7.781348000	-2.959851000
6	-0.594241000	-6.305352000	-1.669401000
1	-1.616830000	-5.906993000	-1.712612000
1	0.117361000	-5.484094000	-1.505309000
1	-0.521398000	-7.055099000	-0.870653000
79	-1.674120000	-8.899005000	-3.447315000
17	-3.051056000	-10.706231000	-3.598719000
1	2.099298000	-6.964166000	-2.741851000
1	1.704868000	-8.308320000	-3.873104000
1	1.347058000	-8.492125000	-2.124574000



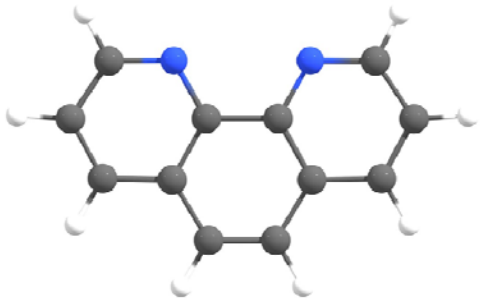
Dimethylsulfane (DMS)

Energy : -477.67982653 Eh

Charge 0; Multiplicity 1

16	-0.462427000	-7.025031000	-2.551266000
6	1.347639000	-6.889869000	-2.452293000
6	-0.907918000	-5.716995000	-1.370241000
1	-2.005746000	-5.660866000	-1.343526000
1	-0.510643000	-4.740328000	-1.691747000
1	-0.537046000	-5.946994000	-0.358157000
1	1.772388000	-7.623676000	-3.151116000

1	1.713954000	-7.116572000	-1.437903000
1	1.691130000	-5.885058000	-2.747851000

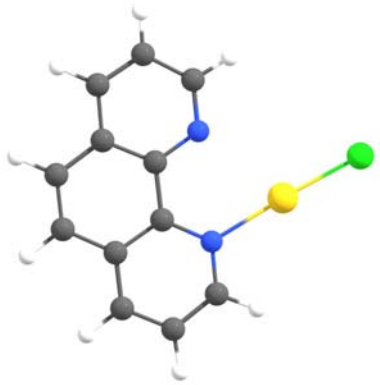


1 10-Phenanthroline (phen)

Energy: -570,76412435 Eh

Charge 0; Multiplicity 1

6	0.239886000	-6.564887000	-2.194397000
6	1.307415000	-5.767009000	-1.725628000
7	2.555753000	-6.186271000	-1.639292000
6	2.843482000	-7.448972000	-2.017005000
6	1.841713000	-8.343307000	-2.503450000
6	0.514980000	-7.860989000	-2.584051000
6	4.222626000	-7.919597000	-1.923603000
6	4.520719000	-9.258125000	-2.321460000
6	3.479717000	-10.118108000	-2.808436000
6	2.192103000	-9.679054000	-2.895409000
6	5.863124000	-9.690289000	-2.217040000
6	6.821342000	-8.816711000	-1.742756000
6	6.416534000	-7.512078000	-1.379783000
7	5.173141000	-7.078401000	-1.465978000
1	1.110766000	-4.736500000	-1.403827000
1	-0.771879000	-6.155277000	-2.243936000
1	-0.273710000	-8.520544000	-2.955662000
1	3.744395000	-11.133535000	-3.114990000
1	1.403134000	-10.337486000	-3.268005000
1	6.124880000	-10.707927000	-2.519525000
1	7.866681000	-9.118744000	-1.644439000
1	7.160380000	-6.799149000	-1.002779000

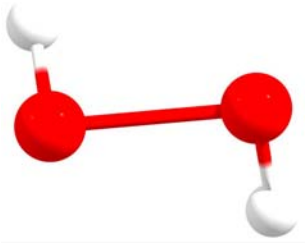


PhenAuCl

Energy: -1166,58075736 Eh

Charge 0; Multiplicity 1

6	-0.563086000	0.343816000	-0.000865000
6	-0.537898000	-1.068016000	-0.002163000
6	0.641431000	1.021303000	-0.000024000
6	1.855110000	0.294907000	-0.000205000
7	0.584011000	-1.759699000	-0.002365000
6	1.767588000	-1.128178000	-0.001061000
1	0.675350000	2.114409000	0.000765000
1	-1.515344000	0.878029000	-0.000528000
1	-1.467372000	-1.648622000	-0.003255000
6	2.994162000	-1.915917000	-0.000623000
6	4.243994000	-1.230026000	-0.000006000
6	4.281142000	0.205932000	0.000466000
6	3.134331000	0.940457000	0.000499000
6	5.431649000	-1.993078000	0.000269000
6	5.353915000	-3.371757000	-0.000166000
6	4.088396000	-3.976121000	-0.000569000
7	2.946731000	-3.280778000	-0.000641000
1	6.396811000	-1.480397000	0.000829000
1	6.247097000	-3.998070000	0.000027000
1	3.988185000	-5.062671000	-0.000786000
1	5.258241000	0.694817000	0.000896000
1	3.169733000	2.033196000	0.000877000
79	1.166737000	-4.432498000	0.002333000
17	-0.677355000	-5.768679000	0.006284000



Hydrogen peroxide (H_2O_2)

Energy: -151.35327557 Eh

Charge 0; Multiplicity 1

8	0.282298000	-6.470865000	-3.981471000
1	1.110009000	-6.375043000	-4.478997000
8	-0.319924000	-7.568480000	-4.695731000
1	-1.153309000	-7.155036000	-4.975133000

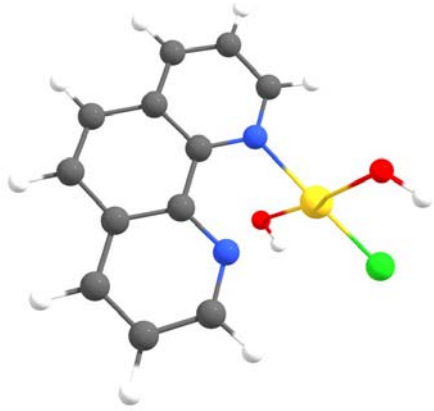
II-cis

Energy: -1317.96538932 Eh

Charge 0; Multiplicity 1

6	-5.008367000	1.096148000	0.482040000
6	-5.041066000	-0.301735000	0.588998000
6	-3.809313000	1.707352000	0.171797000
7	-3.955915000	-1.055015000	0.415775000
6	-2.743301000	-0.483589000	0.174403000
6	-2.643176000	0.927462000	0.011512000
1	-3.745117000	2.791616000	0.048956000
1	-5.925057000	1.668249000	0.630349000
1	-5.964554000	-0.834562000	0.820036000
6	-1.535949000	-1.289984000	0.086087000
6	-1.378725000	1.525043000	-0.314497000
6	-0.309839000	-0.656597000	-0.268624000
6	-0.259866000	0.762873000	-0.466341000
1	0.695187000	1.221322000	-0.734758000
1	-1.342235000	2.607989000	-0.454956000
6	0.832586000	-1.481856000	-0.395713000
6	0.725574000	-2.837670000	-0.153960000

6	-0.528308000	-3.353149000	0.244482000
7	-1.603203000	-2.602203000	0.364138000
1	1.785191000	-1.032248000	-0.687767000
1	1.586286000	-3.501860000	-0.253877000
1	-0.648599000	-4.416715000	0.480155000
79	-4.343083000	-3.112048000	0.305463000
8	-4.813921000	-5.011531000	0.297583000
8	-4.910628000	-3.037372000	2.205281000
1	-5.225925000	-3.941687000	2.365287000
17	-3.805403000	-3.150070000	-1.976425000
1	-4.766510000	-5.263018000	-0.638969000



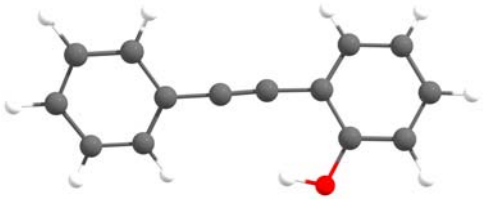
II-trans

Energy: -1317.96119237 Eh

Charge 0; Multiplicity 1

6	-4.999146000	1.222822000	-0.017179000
6	-5.054963000	-0.167013000	-0.195093000
6	-3.768691000	1.811389000	0.200953000
7	-3.964277000	-0.929045000	-0.166333000
6	-2.731021000	-0.382779000	0.000564000
6	-2.599615000	1.019468000	0.208510000
1	-3.682789000	2.887142000	0.374198000
1	-5.921393000	1.804628000	-0.035404000
1	-6.003303000	-0.682971000	-0.351425000
6	-1.532135000	-1.207171000	-0.038186000
6	-1.301973000	1.593664000	0.426983000
6	-0.267294000	-0.592549000	0.189821000
6	-0.181527000	0.819055000	0.428037000
1	0.801272000	1.261204000	0.609667000
1	-1.239175000	2.669244000	0.608092000
6	0.874754000	-1.427552000	0.159077000
6	0.727531000	-2.776840000	-0.096322000
6	-0.572140000	-3.278082000	-0.335513000
7	-1.645952000	-2.516643000	-0.310698000

1	1.859911000	-0.989917000	0.340405000
1	1.588907000	-3.446890000	-0.125419000
1	-0.731896000	-4.338450000	-0.562791000
79	-4.326466000	-2.989450000	-0.008254000
17	-4.860628000	-5.198095000	0.299179000
8	-4.802172000	-3.038446000	-1.937758000
1	-5.082894000	-3.949332000	-2.113253000
8	-3.856017000	-2.725318000	1.911376000
1	-4.062938000	-3.567443000	2.343895000

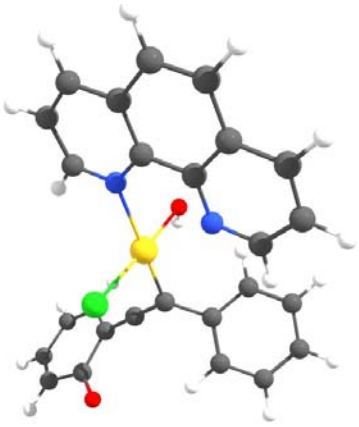


2-(Phenylethynyl)phenol (1a)

Energy: -613.76496304 Eh

Charge 0; Multiplicity 1

6	-2.076132000	-1.401918000	0.136908000
6	-1.047359000	-1.121269000	-0.774221000
6	0.066370000	-1.955035000	-0.831887000
6	0.167370000	-3.082821000	0.010683000
6	-0.887608000	-3.360083000	0.921565000
6	-1.998678000	-2.509219000	0.981108000
8	-0.849560000	-4.437409000	1.732909000
1	-2.792463000	-2.741164000	1.693984000
1	0.882855000	-1.744933000	-1.526277000
1	-2.951153000	-0.748611000	0.188519000
1	-1.114814000	-0.249656000	-1.428779000
6	1.289185000	-3.962883000	-0.003147000
6	2.212852000	-4.762305000	0.042309000
6	3.298976000	-5.690246000	0.056819000
6	3.499779000	-6.554396000	1.155763000
6	4.186759000	-5.768216000	-1.039124000
6	4.553456000	-7.468376000	1.152685000
6	5.235558000	-6.687161000	-1.034035000
6	5.423119000	-7.541036000	0.058834000
1	6.247780000	-8.258387000	0.059858000
1	5.909262000	-6.743859000	-1.893277000
1	2.825459000	-6.495266000	2.013371000
1	4.702308000	-8.126085000	2.013138000
1	4.035624000	-5.105236000	-1.893644000
1	-0.017696000	-4.913649000	1.572262000



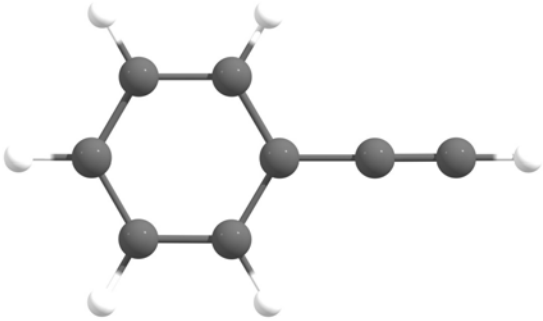
IIIa

Energy: -1855.40882693 Eh

Charge 0; Multiplicity 1

C	-7.44868501331905	-0.00393110644612	-4.60649629338595
C	-7.81717649551782	-1.07712452220604	-3.76014011831297
C	-6.39885060306186	0.82114035599078	-4.24860443302791
C	-7.06631989749797	-1.24760559560933	-2.56074644070988
N	-6.05022688085835	-0.43082690945764	-2.23546476575873
C	-5.71953324405609	0.56270301342355	-3.03691532826308
C	-8.89385949512716	-1.97457316675334	-4.07079199929270
C	-9.22319904449961	-2.98901566586333	-3.22167992449589
C	-8.49908481554700	-3.19515942101027	-1.99794395835461
C	-7.41479954553580	-2.33487990352486	-1.65818349249450
N	-6.71931768247241	-2.52436609252617	-0.50844295196595
C	-7.04911638392775	-3.50630924465499	0.32324366166823
C	-8.83119801481642	-4.23591807439253	-1.10086761245183
C	-8.10654106602997	-4.39412481656794	0.06477572238846
H	-6.45297823787652	-3.59461415596738	1.23352044911132
H	-8.33867988334733	-5.18157650774841	0.78337278055107
H	-9.66188812261240	-4.90436922049321	-1.34044779467978
H	-9.44778340798944	-1.82579306397501	-5.00081014283894
H	-10.04452518987267	-3.67036087773687	-3.45664668563892
H	-8.00124453551423	0.15951982148773	-5.53553810096280
H	-6.08944133255043	1.65416980743847	-4.88305693635271
H	-4.87615807156227	1.18642955835124	-2.72000533564212
Au	-4.97490488684403	-1.32071999074589	0.10579864375013
O	-3.83837549616945	-2.55709996170892	-1.00141288074488
H	-2.98784260552450	-2.64133853153255	-0.54603433750915
C	-2.58472579988203	0.53339568045102	-0.22619463873884
C	-2.10729063474773	1.77068802445563	0.24597458187273
C	-2.33449457075115	0.15558321092475	-1.55776044574608
C	-1.57317386483358	0.98367390327902	-2.38507142162033
C	-1.07177800970701	2.19790343629355	-1.90328996647953

C	-1.34930928969094	2.59246467466210	-0.58997215454662
C	-3.29658717396702	-0.35415302360450	0.71925040560832
C	-2.94750386384195	-0.56697730987765	1.94893876964194
H	-2.35223553261764	2.07244660117651	1.26727934382459
H	-0.47199562998589	2.84029711962436	-2.55365019431806
H	-0.97185246991670	3.54648067910976	-0.21315061157780
H	-2.72492220635423	-0.79970285756686	-1.91427838132706
H	-1.35530227857216	0.66796637932575	-3.40921421470337
Cl	-6.34740797253213	0.03779974477048	1.39928047306586
C	-2.62602217469045	-0.76068544320422	3.23393375540583
C	-3.05296591823076	0.27297787334536	4.25086742523241
C	-1.90306793153554	-1.94345443395350	3.66955154551815
C	-2.83539947753103	-0.11188743033048	5.65263248856984
C	-2.18285565009322	-1.25589469811047	5.98814796503435
C	-1.69025281378216	-2.18129427495704	4.99007733584945
H	-1.15768489089653	-3.07748609643890	5.31618725348860
H	-1.55501470030323	-2.64119652419662	2.90472515946392
H	-3.19750648131816	0.59570096057330	6.40175668997766
H	-2.00901846340372	-1.49459845802176	7.04236693678480
O	-3.51374224868292	1.36061653449965	3.93279017513497



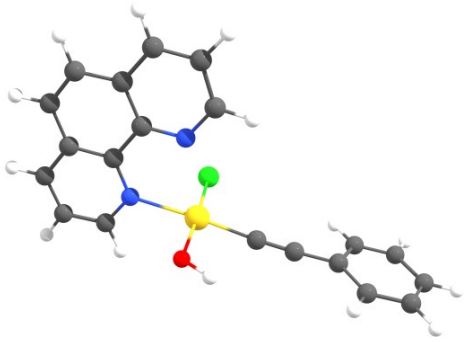
Phenylacetylene (2o)

Energy: -307.92227915 Eh

Charge 0; Multiplicity 1

6	-0.370706000	-7.305034000	-0.312326000
6	-0.777858000	-8.445328000	-0.398846000
6	-1.263811000	-9.788403000	-0.490537000
6	-2.649348000	-10.044439000	-0.534571000
6	-0.367349000	-10.875011000	-0.534988000
6	-3.121716000	-11.353762000	-0.617059000
6	-2.224735000	-12.425675000	-0.657724000
6	-0.848167000	-12.181466000	-0.617547000
1	-0.143816000	-13.016008000	-0.652501000
1	-2.600433000	-13.449837000	-0.724127000
1	-3.344899000	-9.203575000	-0.500502000
1	-4.198128000	-11.541420000	-0.650170000
1	0.706747000	-10.678852000	-0.503223000

1	-0.009211000	-6.297581000	-0.230469000



IIIb

Energy: -1549.57829051 Eh

Charge 0; Multiplicity 1

6	-5.241547000	0.336325000	0.194970000
6	-5.158131000	-1.064241000	0.169709000
6	-4.073351000	1.069006000	0.124182000
7	-3.999289000	-1.711874000	0.081430000
6	-2.829033000	-1.021581000	0.025108000
6	-2.831854000	0.402425000	0.038227000
1	-4.092153000	2.162215000	0.135830000
1	-6.217506000	0.818170000	0.267689000
1	-6.057715000	-1.680429000	0.218759000
6	-1.555571000	-1.720292000	-0.047911000
6	-1.593990000	1.126154000	-0.034535000
6	-0.352270000	-0.960642000	-0.123782000
6	-0.401271000	0.472629000	-0.114763000
1	0.537504000	1.028937000	-0.173334000
1	-1.635483000	2.218241000	-0.025442000
6	0.863863000	-1.679680000	-0.202908000
6	0.842897000	-3.061185000	-0.202505000
6	-0.406455000	-3.715263000	-0.115006000
7	-1.548141000	-3.062700000	-0.036971000
1	1.806375000	-1.129360000	-0.267545000
1	1.763790000	-3.643882000	-0.268546000
1	-0.469576000	-4.809685000	-0.109262000
79	-4.173224000	-3.858754000	-0.053866000
8	-4.297260000	-3.884070000	1.931847000
1	-4.445526000	-4.808863000	2.180575000
17	-4.123398000	-3.691339000	-2.381728000
6	-4.454515000	-5.779948000	-0.149103000
6	-4.593459000	-6.984777000	-0.281927000
6	-4.743651000	-8.382747000	-0.538215000
6	-4.856488000	-8.838485000	-1.869641000
6	-4.770139000	-9.329376000	0.505662000

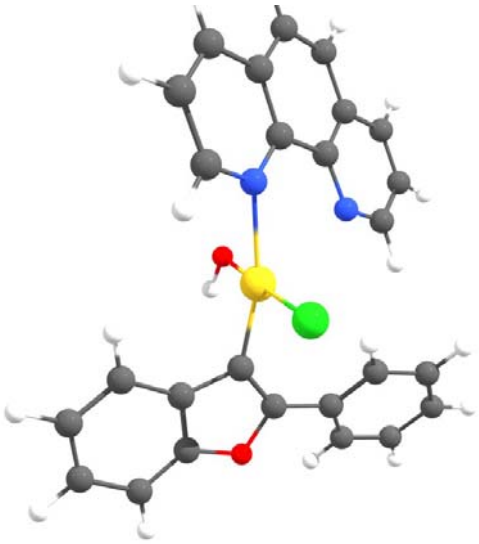
6	-4.984798000	-10.198737000	-2.144078000
6	-5.004508000	-11.129843000	-1.100300000
6	-4.898647000	-10.689191000	0.223017000
1	-5.072206000	-10.538632000	-3.179688000
1	-5.106465000	-12.195973000	-1.319904000
1	-4.837158000	-8.103919000	-2.677264000
1	-4.684738000	-8.983304000	1.538291000
1	-4.916305000	-11.412039000	1.042819000

Water (H_2O)

Energy: -76.3189149 Eh

Charge 0; Multiplicity 1

8	-1.630132000	0.606606000	-0.019422000
1	-0.664806000	0.631000000	0.027171000
1	-1.902352000	1.036894000	0.802451000



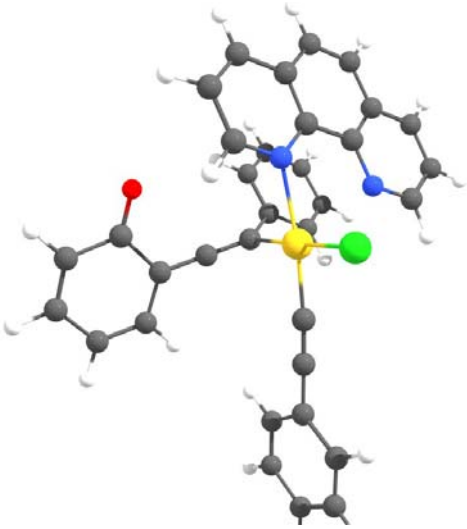
IVa

Energy: -1855.47532352 Eh

Charge 0; Multiplicity 1

6	-6.463998000	-1.043871000	-4.759743000
6	-7.122155000	-1.602020000	-3.638980000
6	-5.371254000	-0.220864000	-4.565777000
6	-6.592279000	-1.295372000	-2.353173000
7	-5.534954000	-0.481729000	-2.184761000
6	-4.943770000	0.037502000	-3.243777000
6	-8.295882000	-2.419997000	-3.759136000

6	-8.940498000	-2.884805000	-2.651893000
6	-8.441637000	-2.601880000	-1.335785000
6	-7.242535000	-1.850890000	-1.179537000
7	-6.720560000	-1.631984000	0.050790000
6	-7.372546000	-2.031774000	1.138203000
6	-9.104880000	-3.043528000	-0.169777000
6	-8.586390000	-2.734426000	1.073419000
1	-6.909621000	-1.785985000	2.096643000
1	-9.085103000	-3.040930000	1.993875000
1	-10.031861000	-3.614180000	-0.266600000
1	-8.678962000	-2.644922000	-4.757839000
1	-9.853231000	-3.477744000	-2.742328000
1	-6.836298000	-1.269103000	-5.762776000
1	-4.842035000	0.232559000	-5.405906000
1	-4.082276000	0.686146000	-3.055088000
79	-4.626566000	-1.061504000	0.445220000
8	-4.076901000	-2.711886000	-0.524935000
1	-3.145157000	-2.861886000	-0.306693000
6	-1.454141000	0.835324000	-0.300772000
6	-2.523152000	1.517730000	-0.914183000
6	-0.138091000	1.130513000	-0.709017000
6	0.100576000	2.071162000	-1.711894000
6	-0.966076000	2.735933000	-2.324538000
6	-2.275237000	2.456264000	-1.916589000
6	-1.689188000	-0.134807000	0.765299000
6	-2.776122000	-0.872219000	1.165763000
1	-3.542449000	1.343301000	-0.568137000
1	-0.774612000	3.474951000	-3.106995000
1	-3.113528000	2.991384000	-2.369324000
1	0.692268000	0.610467000	-0.229178000
1	1.126137000	2.290366000	-2.021481000
17	-5.340292000	0.844438000	1.578911000
6	-2.364151000	-1.611118000	2.336780000
6	-1.016238000	-1.256249000	2.555658000
6	-2.989956000	-2.506946000	3.219751000
6	-0.266379000	-1.743142000	3.623465000
6	-0.909169000	-2.631214000	4.491068000
6	-2.253111000	-3.009133000	4.290593000
1	-2.723586000	-3.700834000	4.993926000
1	-4.032842000	-2.791773000	3.065441000
1	0.767656000	-1.429675000	3.778156000
1	-0.359529000	-3.038571000	5.342976000
8	-0.607400000	-0.376687000	1.602258000



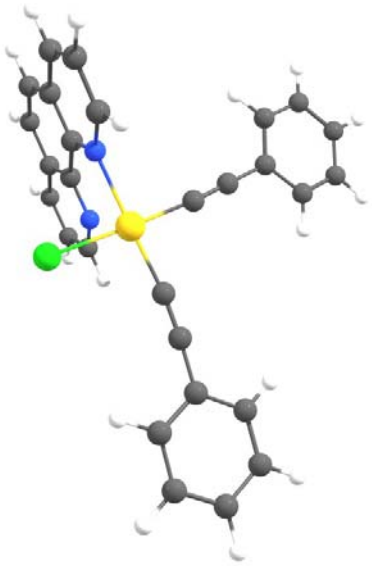
IVb

Energy: -2087.034911 Eh

Charge 0; Multiplicity 1

6	-5.087265000	-0.698811000	-0.403915000
6	-4.838337000	-1.993919000	0.079144000
6	-4.019873000	0.155072000	-0.580977000
7	-3.615007000	-2.418731000	0.384444000
6	-2.542654000	-1.588220000	0.255028000
6	-2.711941000	-0.272151000	-0.252106000
1	-4.164724000	1.157429000	-0.991415000
1	-6.104909000	-0.421864000	-0.678953000
1	-5.651855000	-2.709612000	0.183352000
6	-1.212161000	-2.037616000	0.624903000
6	-1.566764000	0.570615000	-0.445219000
6	-0.104593000	-1.166667000	0.420576000
6	-0.311659000	0.138380000	-0.134272000
1	0.555342000	0.782679000	-0.298631000
1	-1.726368000	1.567605000	-0.862154000
6	1.172572000	-1.644210000	0.798674000
6	1.296667000	-2.902363000	1.356588000
6	0.131891000	-3.683668000	1.516546000
7	-1.063520000	-3.262652000	1.156024000
1	2.047373000	-1.006501000	0.645682000
1	2.265328000	-3.295633000	1.671928000
1	0.185495000	-4.688853000	1.948551000
79	-3.416550000	-4.551616000	0.640420000
17	-3.994258000	-4.435747000	2.938014000
6	-3.151996000	-4.573337000	-1.436053000
6	-4.246114000	-4.926077000	-2.013985000
6	-5.460043000	-5.258748000	-2.487199000
6	-6.501513000	-4.179053000	-2.570670000

6	-5.787755000	-6.623386000	-2.847520000
6	-7.039571000	-6.946079000	-3.272192000
6	-8.051663000	-5.923152000	-3.375007000
6	-7.808493000	-4.621785000	-3.052548000
1	-8.581181000	-3.853634000	-3.132079000
8	-6.275458000	-3.011850000	-2.239395000
1	-7.292490000	-7.974774000	-3.537815000
1	-9.045554000	-6.214424000	-3.728870000
1	-5.006481000	-7.379598000	-2.746635000
6	-1.914524000	-3.984155000	-1.970952000
6	-1.981478000	-2.810732000	-2.742356000
6	-0.809795000	-2.189184000	-3.178956000
6	0.436706000	-2.732842000	-2.853905000
6	0.507048000	-3.905327000	-2.093046000
6	-0.659764000	-4.525540000	-1.647241000
1	-2.960467000	-2.384300000	-2.972431000
1	-0.871279000	-1.269988000	-3.766436000
1	1.352028000	-2.240906000	-3.192435000
1	1.477664000	-4.332375000	-1.829152000
1	-0.615907000	-5.423314000	-1.027125000
6	-3.293042000	-6.501156000	0.633102000
6	-3.220243000	-7.712639000	0.503921000
6	-3.153165000	-9.131354000	0.343959000
6	-3.150087000	-9.989830000	1.463022000
6	-3.097808000	-9.702045000	-0.945795000
6	-3.099666000	-11.372921000	1.292723000
6	-3.052020000	-11.926528000	0.009005000
6	-3.050482000	-11.085784000	-1.108773000
1	-3.010118000	-11.514694000	-2.113741000
1	-3.091201000	-9.039953000	-1.814414000
1	-3.192896000	-9.552862000	2.462712000
1	-3.099739000	-12.025145000	2.169684000
1	-3.014643000	-13.011285000	-0.122483000



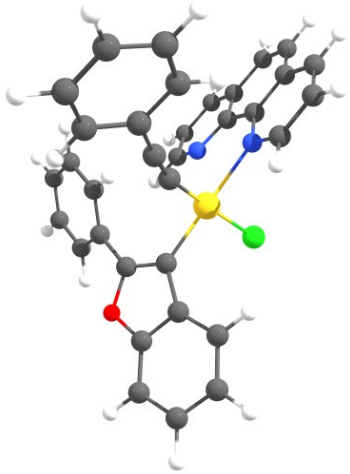
IVc

Energy: -1781.19196931 Eh

Charge 0; Multiplicity 1

6	-5.292806000	0.265534000	0.294976000
6	-5.190246000	-1.133427000	0.283892000
6	-4.132129000	1.013965000	0.277165000
7	-4.019243000	-1.764670000	0.253589000
6	-2.857651000	-1.059468000	0.235609000
6	-2.879331000	0.364319000	0.247669000
1	-4.166943000	2.106769000	0.285555000
1	-6.277682000	0.734050000	0.318300000
1	-6.083024000	-1.761229000	0.298925000
6	-1.575202000	-1.742887000	0.202216000
6	-1.647872000	1.102267000	0.229433000
6	-0.378675000	-0.970073000	0.185139000
6	-0.445277000	0.462505000	0.200400000
1	0.488612000	1.029586000	0.186393000
1	-1.702836000	2.193675000	0.238997000
6	0.847005000	-1.676259000	0.151525000
6	0.840556000	-3.057903000	0.135569000
6	-0.403818000	-3.726323000	0.154098000
7	-1.554052000	-3.084802000	0.186838000
1	1.785820000	-1.116287000	0.136545000
1	1.769408000	-3.630765000	0.107222000
1	-0.456116000	-4.821032000	0.139713000
79	-4.141420000	-3.924025000	0.188231000
6	-4.125544000	-3.975071000	2.165271000
17	-4.188436000	-3.789823000	-2.162806000
6	-4.424158000	-5.849109000	0.107963000
6	-4.604807000	-7.038962000	-0.082647000

6	-4.812117000	-8.414391000	-0.410866000
6	-4.967058000	-8.792943000	-1.762062000
6	-4.858871000	-9.413819000	0.581675000
6	-5.153383000	-10.130678000	-2.106120000
6	-5.190365000	-11.115270000	-1.113203000
6	-5.044785000	-10.750707000	0.229249000
1	-5.273313000	-10.410352000	-3.156489000
1	-5.338712000	-12.163182000	-1.387285000
1	-4.933540000	-8.016518000	-2.529271000
1	-4.743585000	-9.124781000	1.628804000
1	-5.078017000	-11.515642000	1.009402000
6	-4.063197000	-3.914722000	3.383292000
6	-3.974559000	-3.849621000	4.808766000
6	-3.926319000	-2.606312000	5.474528000
6	-3.932539000	-5.030142000	5.580615000
6	-3.850217000	-4.964762000	6.970872000
6	-3.808542000	-3.725964000	7.619066000
6	-3.844933000	-2.548444000	6.865284000
1	-3.809504000	-1.578077000	7.367999000
1	-3.956669000	-1.688922000	4.882741000
1	-3.818702000	-5.888057000	7.554922000
1	-3.743805000	-3.676996000	8.709315000
1	-3.967782000	-5.994253000	5.069527000



Va

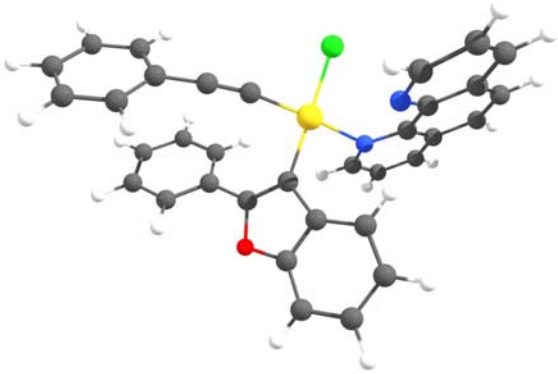
Energy: -2087.0875888 Ea

Charge 0; Multiplicity 1

6	-4.854978000	1.858826000	-1.387475000
6	-5.216588000	0.558606000	-1.003729000
7	-4.472840000	-0.180055000	-0.184713000
6	-3.309356000	0.310724000	0.314641000
6	-2.892028000	1.637955000	0.005490000
6	-3.691597000	2.400295000	-0.874877000

6	-2.472969000	-0.508695000	1.176642000
6	-1.329588000	0.079993000	1.789249000
6	-0.959302000	1.430309000	1.474986000
6	-1.695079000	2.168794000	0.596331000
6	-0.585604000	-0.729607000	2.680526000
6	-0.977228000	-2.035805000	2.903526000
6	-2.096893000	-2.536903000	2.202535000
7	-2.800355000	-1.797304000	1.367539000
1	-5.499142000	2.417697000	-2.068293000
1	-6.129457000	0.095596000	-1.381457000
1	-3.377750000	3.412073000	-1.143086000
1	-0.067655000	1.850753000	1.946728000
1	-1.394880000	3.184405000	0.327755000
1	0.289883000	-0.308986000	3.181989000
1	-0.429700000	-2.684738000	3.589654000
1	-2.421351000	-3.574263000	2.330943000
79	-5.275605000	-2.185144000	0.256233000
17	-5.801171000	-1.571519000	2.471922000
6	-6.073282000	-3.994612000	0.573089000
6	-7.479403000	-4.269599000	0.727741000
6	-3.994985000	-5.542312000	0.851521000
6	-3.537008000	-6.502997000	1.775816000
6	-3.073587000	-4.970252000	-0.046104000
6	-2.188927000	-6.862122000	1.816421000
6	-1.277535000	-6.276313000	0.930916000
6	-1.727239000	-5.335186000	-0.001484000
1	-3.419495000	-4.252188000	-0.789397000
1	-1.026064000	-4.886687000	-0.709412000
1	-4.251969000	-6.960486000	2.461351000
1	-1.846416000	-7.606103000	2.540751000
1	-0.223841000	-6.566570000	0.958516000
6	-7.555465000	-5.634679000	1.080535000
6	-8.664720000	-3.525821000	0.617504000
6	-8.758429000	-6.302434000	1.288964000
6	-9.926547000	-5.548420000	1.154393000
6	-9.878733000	-4.177110000	0.828175000
1	-10.813230000	-3.618304000	0.736902000
1	-8.625164000	-2.464927000	0.363008000
1	-8.775674000	-7.360826000	1.554772000
1	-10.893961000	-6.031462000	1.312557000
8	-6.307635000	-6.169413000	1.160999000
6	-5.408496000	-5.166149000	0.828258000
6	-5.063700000	-2.556106000	-1.674885000
6	-4.979098000	-2.477747000	-2.892697000

6	-4.894082000	-2.278169000	-4.306505000
6	-4.883392000	-3.356523000	-5.214207000
6	-4.833124000	-0.964138000	-4.821211000
6	-4.820616000	-3.122980000	-6.588277000
6	-4.769702000	-1.816541000	-7.085086000
6	-4.775266000	-0.737873000	-6.194871000
1	-4.733605000	0.285869000	-6.577150000
1	-4.834388000	-0.124418000	-4.123117000
1	-4.814495000	-3.969747000	-7.279081000
1	-4.724740000	-1.636694000	-8.162539000
1	-4.929864000	-4.376076000	-4.826195000



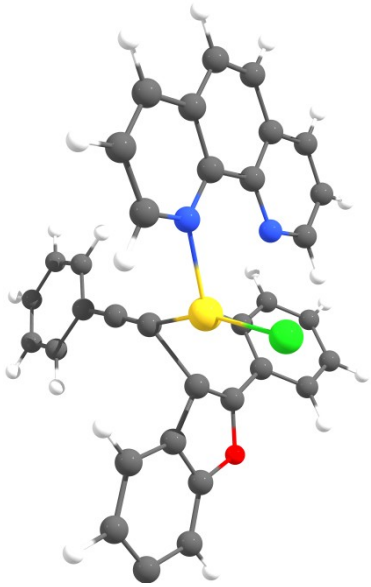
Vb

Energy: -2087.08750787 Eh

Charge 0; Multiplicity 1

6	-4.349391000	0.492278000	1.004776000
6	-3.859363000	-0.781590000	0.678477000
6	-3.750747000	1.185509000	2.039689000
7	-2.821937000	-1.331329000	1.306127000
6	-2.150138000	-0.632156000	2.260498000
6	-2.625673000	0.636151000	2.693948000
1	-4.133118000	2.156927000	2.362152000
1	-5.204066000	0.896138000	0.460634000
1	-4.326756000	-1.385819000	-0.101322000
6	-0.936601000	-1.170867000	2.846739000
6	-1.964974000	1.315492000	3.774075000
6	-0.323024000	-0.473114000	3.924396000
6	-0.871470000	0.771808000	4.380029000
1	-0.380647000	1.285806000	5.209920000
1	-2.371084000	2.273309000	4.106609000
6	0.835176000	-1.053360000	4.493933000
6	1.332233000	-2.233313000	3.976036000
6	0.675172000	-2.814016000	2.867780000
7	-0.409441000	-2.294333000	2.328095000
1	1.325690000	-0.555396000	5.334107000

1	2.217630000	-2.710784000	4.399551000
1	1.057796000	-3.732120000	2.409661000
79	-2.597697000	-3.466663000	1.033272000
17	-3.196173000	-3.731844000	3.331140000
6	-2.932861000	-3.762492000	-2.020765000
6	-2.283585000	-3.191466000	-0.949585000
6	-1.286155000	-2.300919000	-1.506377000
6	-1.421515000	-2.409637000	-2.908292000
6	-0.308668000	-1.432574000	-0.987993000
6	0.470629000	-0.694545000	-1.878292000
6	0.298846000	-0.811757000	-3.272939000
6	-0.654998000	-1.680251000	-3.811792000
1	-0.803397000	-1.788423000	-4.888355000
8	-2.403005000	-3.298441000	-3.215294000
1	1.233340000	-0.015488000	-1.487504000
1	0.923184000	-0.217837000	-3.944448000
1	-0.157858000	-1.356578000	0.088897000
6	-4.015931000	-4.739857000	-2.157880000
6	-4.000329000	-5.662854000	-3.220478000
6	-5.000715000	-6.629313000	-3.337248000
6	-6.037341000	-6.686222000	-2.402388000
6	-6.073225000	-5.760142000	-1.353752000
6	-5.076692000	-4.793223000	-1.234088000
1	-3.178449000	-5.633456000	-3.938367000
1	-4.958481000	-7.355688000	-4.152967000
1	-6.809562000	-7.455443000	-2.485163000
1	-6.881377000	-5.795400000	-0.618308000
1	-5.109700000	-4.084618000	-0.404982000
6	-2.588618000	-5.384891000	0.687046000
6	-2.816029000	-6.517325000	0.296113000
6	-3.214811000	-7.780749000	-0.232833000
6	-4.338544000	-8.444562000	0.301847000
6	-2.566165000	-8.340687000	-1.352317000
6	-4.808345000	-9.620956000	-0.278688000
6	-4.164563000	-10.161028000	-1.397505000
6	-3.038880000	-9.520036000	-1.926150000
1	-2.530070000	-9.940055000	-2.797620000
1	-1.705796000	-7.821364000	-1.778214000
1	-4.845426000	-8.004994000	1.162616000
1	-5.684654000	-10.120217000	0.142715000
1	-4.541820000	-11.077667000	-1.857683000



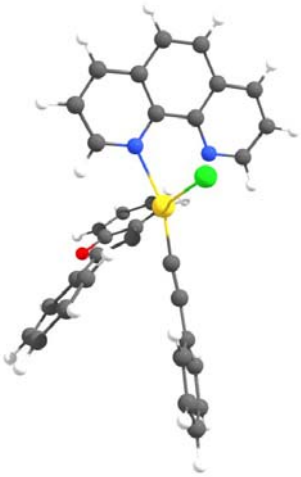
TS-a

Energy: -2087.06325103 Eh

Charge 0; Multiplicity 1

6	-5.481585000	2.583982000	0.505696000
6	-5.745929000	1.208607000	0.623787000
7	-4.785152000	0.304558000	0.760672000
6	-3.488879000	0.695097000	0.817502000
6	-3.127575000	2.064315000	0.663738000
6	-4.166748000	3.008409000	0.509250000
6	-2.446147000	-0.285120000	1.072980000
6	-1.087292000	0.140900000	1.090290000
6	-0.762176000	1.520130000	0.866527000
6	-1.743448000	2.447194000	0.679479000
6	-0.105773000	-0.840594000	1.364676000
6	-0.495708000	-2.135903000	1.643846000
6	-1.873943000	-2.445459000	1.633691000
7	-2.800194000	-1.555521000	1.334910000
1	-6.310292000	3.285694000	0.401468000
1	-6.770705000	0.829788000	0.606426000
1	-3.915717000	4.066664000	0.398546000
1	0.289738000	1.817770000	0.874542000
1	-1.495266000	3.501575000	0.535618000
1	0.949550000	-0.554199000	1.371241000
1	0.232620000	-2.914795000	1.875514000
1	-2.219492000	-3.451666000	1.881008000
79	-5.439685000	-1.868582000	0.771074000
17	-6.016043000	-1.644324000	3.088703000
6	-6.072638000	-3.733875000	0.166486000
6	-7.485700000	-4.061205000	0.155251000

6	-3.994362000	-5.295421000	0.478597000
6	-3.574648000	-6.297400000	1.378411000
6	-3.041343000	-4.706888000	-0.375753000
6	-2.235333000	-6.682085000	1.436507000
6	-1.294896000	-6.091022000	0.584038000
6	-1.706199000	-5.110838000	-0.324767000
1	-3.356301000	-3.939597000	-1.081417000
1	-0.981506000	-4.651387000	-1.001190000
1	-4.311852000	-6.763105000	2.034076000
1	-1.921973000	-7.452164000	2.146400000
1	-0.248605000	-6.405335000	0.622679000
6	-7.556522000	-5.440707000	0.423320000
6	-8.668749000	-3.334702000	-0.032628000
6	-8.756459000	-6.141226000	0.498546000
6	-9.925864000	-5.401888000	0.304046000
6	-9.882075000	-4.017172000	0.042512000
1	-10.817277000	-3.471721000	-0.103537000
1	-8.626579000	-2.263315000	-0.238894000
1	-8.772462000	-7.211288000	0.712531000
1	-10.892483000	-5.908558000	0.360086000
8	-6.304554000	-5.954617000	0.583657000
6	-5.403363000	-4.922244000	0.412392000
6	-5.408545000	-2.520215000	-1.114133000
6	-5.217273000	-2.570734000	-2.330119000
6	-4.954871000	-2.767371000	-3.716172000
6	-5.817084000	-3.565555000	-4.501543000
6	-3.807223000	-2.210787000	-4.323863000
6	-5.522908000	-3.815475000	-5.840673000
6	-4.374905000	-3.270534000	-6.427333000
6	-3.523961000	-2.462086000	-5.665468000
1	-2.630949000	-2.026756000	-6.121456000
1	-3.140590000	-1.588429000	-3.722792000
1	-6.193650000	-4.444430000	-6.431970000
1	-4.138400000	-3.483494000	-7.472940000
1	-6.706244000	-3.997054000	-4.037475000



TS-b

Energy: -2087.05967447 Eh

Charge 0; Multiplicity 1

6	-4.558720000	0.439195000	1.091946000
6	-4.024907000	-0.820380000	0.769305000
6	-3.949731000	1.176107000	2.090402000
7	-2.940721000	-1.310619000	1.357991000
6	-2.274994000	-0.574754000	2.281441000
6	-2.783938000	0.680961000	2.716892000
1	-4.356595000	2.139304000	2.408105000
1	-5.448499000	0.800250000	0.573998000
1	-4.501285000	-1.458570000	0.019365000
6	-1.030459000	-1.069744000	2.845288000
6	-2.116409000	1.398230000	3.767643000
6	-0.420812000	-0.342685000	3.907258000
6	-0.994146000	0.894430000	4.354990000
1	-0.500004000	1.433756000	5.166767000
1	-2.541003000	2.349232000	4.097358000
6	0.755170000	-0.886271000	4.475083000
6	1.272752000	-2.064483000	3.973195000
6	0.618405000	-2.675046000	2.880588000
7	-0.480337000	-2.188100000	2.337523000
1	1.240762000	-0.364052000	5.303546000
1	2.169314000	-2.518552000	4.398959000
1	1.015460000	-3.595957000	2.439099000
79	-2.563239000	-3.516921000	1.036355000
17	-3.140630000	-3.884997000	3.343741000
6	-3.258426000	-3.643544000	-2.019278000
6	-2.303758000	-3.591429000	-1.009688000
6	-1.173975000	-2.866002000	-1.562959000
6	-1.549428000	-2.518897000	-2.874593000
6	0.056237000	-2.419483000	-1.057817000

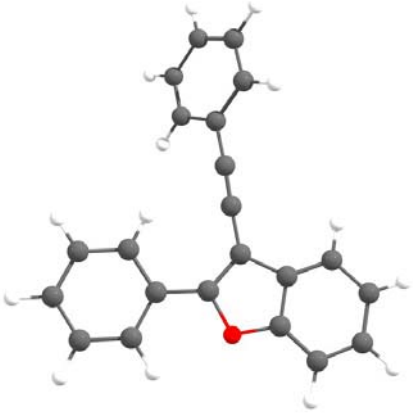
6	0.866700000	-1.643486000	-1.884581000
6	0.465767000	-1.306422000	-3.193568000
6	-0.757339000	-1.739235000	-3.713169000
1	-1.089686000	-1.470026000	-4.717071000
8	-2.792844000	-3.003688000	-3.151248000
1	1.824729000	-1.276347000	-1.508100000
1	1.123145000	-0.692699000	-3.814509000
1	0.347301000	-2.658859000	-0.035689000
6	-4.502708000	-4.385713000	-2.159236000
6	-4.964157000	-4.740258000	-3.444085000
6	-6.078204000	-5.565823000	-3.593493000
6	-6.755087000	-6.048682000	-2.469232000
6	-6.324309000	-5.676520000	-1.191411000
6	-5.216526000	-4.846722000	-1.033900000
1	-4.418396000	-4.383595000	-4.318367000
1	-6.413638000	-5.852263000	-4.593836000
1	-7.618627000	-6.707329000	-2.590326000
1	-6.854040000	-6.041424000	-0.308311000
1	-4.890548000	-4.564290000	-0.033134000
6	-2.243523000	-5.200063000	0.033423000
6	-2.356245000	-6.398699000	-0.214697000
6	-2.650527000	-7.761773000	-0.494191000
6	-3.830817000	-8.329743000	0.039969000
6	-1.827913000	-8.560443000	-1.316649000
6	-4.179889000	-9.645537000	-0.253657000
6	-3.363280000	-10.423734000	-1.082643000
6	-2.187719000	-9.876036000	-1.607619000
1	-1.544153000	-10.481242000	-2.251571000
1	-0.914477000	-8.130961000	-1.732335000
1	-4.466073000	-7.714391000	0.679838000
1	-5.095283000	-10.068867000	0.168105000
1	-3.647888000	-11.450550000	-1.325924000

TS-c

Energy: -1781.17017145 Eh

6	-4.911210000	0.377504000	-0.106487000
6	-4.752985000	-0.920815000	-0.623152000
6	-3.961384000	0.859791000	0.773761000
7	-3.708200000	-1.682127000	-0.317022000
6	-2.702775000	-1.193954000	0.453696000
6	-2.816951000	0.082486000	1.070394000
1	-4.075308000	1.841868000	1.239610000
1	-5.787790000	0.965104000	-0.383174000
1	-5.487241000	-1.373594000	-1.295518000
6	-1.489851000	-1.972805000	0.647912000
6	-1.787378000	0.537551000	1.964049000
6	-0.493651000	-1.480834000	1.539552000
6	-0.681151000	-0.223135000	2.205532000
1	0.094612000	0.122966000	2.893218000
1	-1.913726000	1.507669000	2.449733000
6	0.671475000	-2.266498000	1.708464000
6	0.806994000	-3.443455000	0.997895000
6	-0.231744000	-3.825417000	0.119356000
7	-1.330717000	-3.115178000	-0.046047000
1	1.453307000	-1.928104000	2.393138000
1	1.694556000	-4.071016000	1.100043000
1	-0.151875000	-4.749417000	-0.463738000
79	-4.055009000	-3.872860000	-0.502745000
6	-3.818795000	-4.406678000	1.388597000
17	-4.632684000	-3.546207000	-2.784258000
6	-4.444936000	-5.714460000	0.050947000
6	-4.795723000	-6.888697000	0.056549000
6	-5.210516000	-8.248421000	-0.034650000
6	-4.627156000	-9.097368000	-1.001043000
6	-6.232697000	-8.760288000	0.793890000
6	-5.068190000	-10.411359000	-1.143509000

6	-6.092317000	-10.904295000	-0.327038000
6	-6.666536000	-10.077324000	0.644619000
1	-4.616157000	-11.054737000	-1.902648000
1	-6.448616000	-11.929653000	-0.454328000
1	-3.840204000	-8.700514000	-1.645490000
1	-6.686715000	-8.106476000	1.541187000
1	-7.464638000	-10.460606000	1.286020000
6	-3.589339000	-4.200690000	2.575178000
6	-3.311542000	-3.807258000	3.919572000
6	-3.052263000	-2.445891000	4.194307000
6	-3.302160000	-4.724853000	4.989263000
6	-3.052027000	-4.288623000	6.291219000
6	-2.804505000	-2.937198000	6.552086000
6	-2.803087000	-2.018585000	5.496966000
1	-2.604489000	-0.960949000	5.691917000
1	-3.055830000	-1.731595000	3.370356000
1	-3.054603000	-5.010120000	7.112047000
1	-2.609667000	-2.598220000	7.572839000
1	-3.505038000	-5.778426000	4.785223000



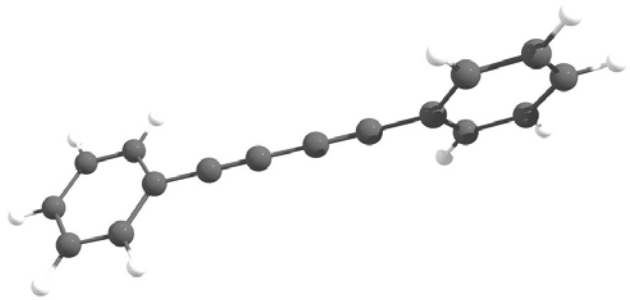
VI

Energy: -920.56600028 Eh

Charge 0; Multiplicity 1

6	-1.756720000	-2.300091000	-0.275665000
6	-2.644357000	-3.394412000	-0.309945000
6	-2.177223000	-4.707704000	-0.266617000
6	-0.792711000	-4.912855000	-0.183833000
6	0.071510000	-3.804116000	-0.149152000
6	-0.374068000	-2.486626000	-0.194767000
8	1.366065000	-4.226093000	-0.075005000
1	0.325705000	-1.649927000	-0.169656000
1	-2.861631000	-5.558115000	-0.300064000
1	-2.159664000	-1.285120000	-0.316348000
1	-3.718532000	-3.204047000	-0.377377000

6	0.067396000	-6.082488000	-0.133562000
6	1.368678000	-5.599394000	-0.065467000
6	2.670898000	-6.244985000	0.009070000
6	2.792759000	-7.648772000	0.063877000
6	3.844217000	-5.462451000	0.027843000
6	4.050806000	-8.244425000	0.128551000
6	5.098170000	-6.067115000	0.091897000
6	5.208774000	-7.460449000	0.140998000
1	6.191757000	-7.935359000	0.193206000
1	5.996949000	-5.445870000	0.104237000
1	1.898294000	-8.269740000	0.059056000
1	4.128787000	-9.333943000	0.173954000
1	3.755570000	-4.375850000	-0.010930000
6	-0.381468000	-7.421579000	-0.179874000
6	-0.813039000	-8.561403000	-0.243261000
6	-1.257383000	-9.912436000	-0.365279000
6	-2.361205000	-10.387753000	0.374034000
6	-0.591240000	-10.796108000	-1.242024000
6	-2.788967000	-11.707280000	0.230485000
6	-2.128655000	-12.571185000	-0.649704000
6	-1.027867000	-12.112400000	-1.381152000
1	-0.507672000	-12.785801000	-2.066909000
1	-2.476264000	-13.600296000	-0.770492000
1	-2.875981000	-9.708491000	1.056645000
1	-3.645802000	-12.065225000	0.806945000
1	0.264565000	-10.431040000	-1.813706000



Vc

Energy: -614.67866378 Eh

Charge 0; Multiplicity 1

6	-6.739717000	-9.781177000	-2.505638000
6	-7.305899000	-10.598454000	-3.221390000
6	-7.946242000	-11.569454000	-4.044785000
6	-9.342746000	-11.725945000	-4.027677000
6	-7.176913000	-12.392796000	-4.890662000
6	-9.952804000	-12.688591000	-4.836592000
6	-9.181799000	-13.498037000	-5.670785000

6	-7.796978000	-13.349586000	-5.698266000
1	-7.172573000	-13.968677000	-6.341812000
1	-6.095247000	-12.283404000	-4.919464000
1	-11.035876000	-12.791086000	-4.800047000
1	-9.668900000	-14.247751000	-6.300741000
1	-9.957694000	-11.100352000	-3.383013000
6	-6.102810000	-8.886892000	-1.695296000
6	-5.516304000	-8.091347000	-0.971453000
6	-4.795250000	-7.190394000	-0.135488000
6	-4.165439000	-7.654615000	1.035637000
6	-4.680242000	-5.831826000	-0.479776000
6	-3.427260000	-6.777742000	1.833668000
6	-3.310895000	-5.435538000	1.475877000
6	-3.937462000	-4.963869000	0.323719000
1	-3.857262000	-3.919298000	0.024460000
1	-5.163668000	-5.450194000	-1.376274000
1	-2.948411000	-7.168375000	2.730329000
1	-2.729043000	-4.751026000	2.099012000
1	-4.251964000	-8.699754000	1.326319000

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