

Supporting information

Copper-Catalyzed Chemoselective C-H

Functionalization/Dearomatization Sequence: Direct Access to

Indole-Based Spirocyclic Scaffolds

Yuting Zhao,[†] Xin Ji,[†] Yuanjing Xiao^{†}, Xingxing Wu^{*¶} and Lu Liu^{*†‡}*

[†]School of Chemistry and Molecular Engineering, East China Normal University, 500 Dongchuan Road, Shanghai 200241, P. R. China

[¶]State Key Laboratory of Green Pesticide, Key Laboratory of Green Pesticide and Agricultural Bioengineering, Ministry of Education, Guizhou University, Huaxi District, Guiyang, 550025, P. R. China;

[‡]Shanghai Engineering Research Center of Molecular Therapeutics and New Drug Development, East China Normal University, Shanghai 200062, P. R. China

E-mail : yjxiao@chem.ecnu.edu.cn; wuxx@gzu.edu.cn; lliu@chem.ecnu.edu.cn.

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1. General Information

Unless otherwise noted, all air- and moisture-sensitive manipulations were carried out with standard Schlenk techniques under nitrogen or in a glove box under nitrogen. All reactions were carried out under a nitrogen atmosphere; materials obtained from commercial suppliers were used directly without further purification. Solvents were distilled following standard procedures before use. Reactions were monitored by thin layer chromatography (TLC) using silicycle pre-coated silica gel plates. Flash column chromatography was performed on silica gel 60 (particle size 300-400 mesh ASTM, purchased from Yantai, China) and eluted with petroleum ether/ethyl acetate.

Dichloromethane (CH_2Cl_2), Trichloromethane, dichloroethane and ethyl acetate were freshly distilled from CaH_2 ; tetrahydrofuran (THF), toluene and ether were dried with sodium benzophenone and distilled before use.

^1H NMR spectra were recorded on a BRUKER 500 (500 MHz) or BRUKER 600 (600 MHz) spectrometer in CDCl_3 . Chemical shifts are reported in ppm with tetramethylsilane (TMS: 0 ppm) with the solvent resonance as the internal standard. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz), and integration. ^{13}C NMR spectra were recorded on a BRUKER 500 (125 MHz) or BRUKER 600 (150 MHz) spectrometer in CDCl_3 with complete proton decoupling. Chemical shifts are reported in ppm with the deuterium solvent as the internal standard (e.g. CDCl_3 : 77.0 ppm)

2. Optimization of reaction conditions

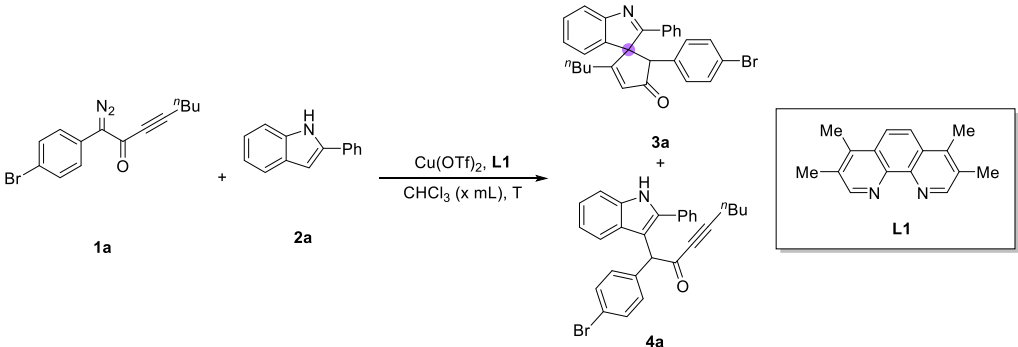
Supplementary Table 1. Optimization of reaction conditions^a

<div style="display: flex; justify-content: space-around; align-items: flex-start;"> <div style="text-align: center;"> <p>L1 R₁ = Me, R₂ = Me L2 R₁ = H, R₂ = H L3 R₁ = H, R₂ = OMe</p> </div> <div style="text-align: center;"> <p>L4 R₃ = Me, R₄ = Ph L5 R₃ = Ph, R₄ = H L6 R₃ = Me, R₄ = H</p> </div> <div style="text-align: center;"> <p>L7</p> </div> </div>					
Entry	Cat.	Solvent	L	dr ^b	Yield ^b (%)
				3a	3a/4a
1	Cu(OTf) ₂	CHCl ₃	-	2.6:1	44/0
2	Sc(OTf) ₃	CHCl ₃	-	-	-
3	AgOTf	CHCl ₃	-	1.2:1	5/5
4	Fe(OTf) ₃	CHCl ₃	-	-	-
5	CuCl	CHCl ₃	-	4.4:1	12/5
6	CuCl ₂	CHCl ₃	-	1.5:1	10/0
7	L'AuOTf	CHCl ₃	-	1.0:1	12/0
8	Rh ₂ (OAc) ₄	CHCl ₃	-	-	-
9	Cu(OTf) ₂	CHCl ₃	L2	5.5:1	40/22
10	Cu(OTf) ₂	CHCl ₃	L3	4.4:1	48/0
11	Cu(OTf) ₂	CHCl ₃	L4	1.5:1	30/0
12	Cu(OTf) ₂	CHCl ₃	L5	1.2:1	23/0
13	Cu(OTf) ₂	CHCl ₃	L6	-	-
14	Cu(OTf) ₂	CHCl ₃	L7	2.8:1	7/0
15	Cu(OTf) ₂	CHCl ₃	L1	7.3:1	75/5
16	Cu(OTf) ₂	DCE	L1	7.6:1	60/0
17	Cu(OTf) ₂	CCl ₄	L1	-	-
18	Cu(OTf)₂	DCM	L1	8.0:1	85/0
19	Cu(OTf) ₂	PhCl	L1	4.6:1	64/0
20	Cu(OTf) ₂	toluene	L1	4.0:1	50/0

^aUnless otherwise noted, all reactions were performed with **1a** (0.2 mmol), **2a** (0.1 mmol), Cat. (10 mol%), **L** (15 mol%) in solvent (2.0 mL) at 40 °C under Ar atmosphere for 2 h; The yields were determined by crude ¹H NMR using CH₂Br₂ as internal standard. L' = (2,4-^tBu₂PhO)₃P.

Initially, α -alkynyl- α -diazoketones **1a** and 2-phenylindole **2a** were selected as model substrates for reaction screening. Initially, **1a** (2.0 equiv) and **2a** were subjected to the reaction in CHCl₃ at 40 °C by using Cu(OTf)₂ as catalyst, spirocyclic product **3a** was indeed formed in 44% yield with 2.6:1 diastereoselectivity (Table 1, entry 1). Among the catalysts tested, Cu(OTf)₂ was found to be optimal (Table 1, entries 1-8) in terms of the yield of spirocyclic product **3a**. To further improve the yield and diastereoselectivity, we then explored the effect of the types of ligand on the reaction (entries 9-15). Using 4,7-dimethoxy-1,10-phenanthroline (**L3**) as a ligand, the dr value and yield of product **3a** were slightly improved (entry 10). When the ligand species was switched to 1,10-phenanthroline (**L2**), although the dr value of product **3a** was further increased to 5.5:1, however, the by-product, C-H functionalization product **4a** was obtained in 22% yield (entry 9). Continuing to screen the ligand species, we found that when the 3,4,7,8-tetramethyl-1,10-phenanthroline (**L1**) ligand was used, product **3a** achieved 75% yield and the dr value reached 7.3:1, only a little by-product **4a** was generated (entry 15). After screening the solvents, DCM gave the best results, and the yield of product **3a** was improved to 85% with 8.0:1 dr, without by-product **4a** formed (entry 18, for more details, please see Table 2 and Table 3).

Supplementary Table 2. Optimization of reaction conditions^a

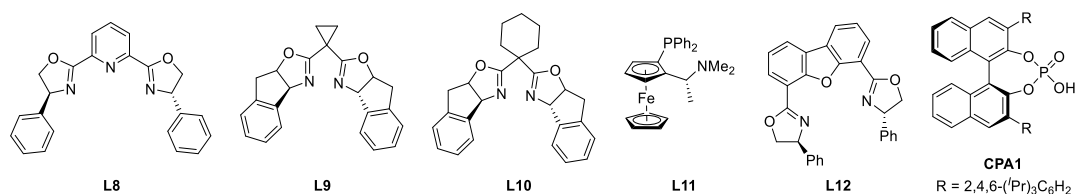
				
Entry	Cat.	Solvent (x ml)	dr ^b	
			3a	3a/4a
1	Cu(OTf) ₂ ^c	CHCl ₃ (2.0 mL)	4.5:1	22/8
2	Cu(OTf) ₂ ^d	CHCl ₃ (2.0 mL)	3.8:1	70/0
3	Cu(OTf) ₂ ^e	CHCl ₃ (2.0 mL)	-	-
4	Cu(OTf) ₂ ^f	CHCl ₃ (2.0 mL)	1.4:1	66/0
5	Cu(OTf) ₂ ^g	CHCl ₃ (2.0 mL)	3.9:1	75/0
6	Cu(OTf) ₂ ^h	CHCl ₃ (2.0 mL)	-	-
7	Cu(OTf) ₂ ⁱ	CHCl ₃ (2.0 mL)	6.2:1	60/0
8	Cu(OTf) ₂ ^j	CHCl ₃ (2.0 mL)	5.8:1	70/0
9	Cu(OTf) ₂ ^k	CHCl ₃ (2.0 mL)	7.3:1	68/0
10	Cu(OTf) ₂	CHCl ₃ (1.0 mL)	6.2:1	72/0
11	Cu(OTf) ₂	CHCl ₃ (4.0 mL)	7.2:1	66/0

^aUnless otherwise noted, all reactions were performed with **1a** (0.2 mmol), **2a** (0.1 mmol), Cat. (10 mol%), **L1** (15 mol%) in solvent (2.0 mL) at 40 °C under Ar atmosphere for 2 h; ^bYields were determined by crude ¹H NMR using CH₂Br₂ as internal standard; ^cReaction stirred at 30 °C; ^dReaction stirred at 50 °C; ^eUsing Cat. 5 mol%; ^fUsing Cat. 20 mol%; ^gUsing **L1** 10 mol%; ^hUsing **L1** 20 mol%; ⁱUsing **1a** (0.1 mmol); ^jUsing **1a** (0.25 mmol); ^kReaction stirred for 3 h.

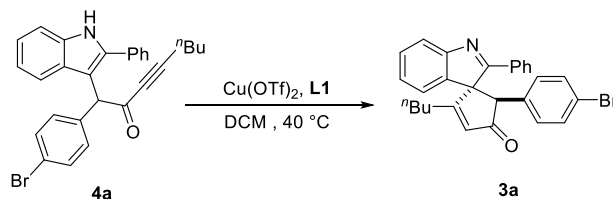
Supplementary Table 3. Optimization of reaction conditions^a

Entry	L	er ^c (%)	dr ^b	Yield ^b (%)
		3a	3a	3a/4a
1	L8	49:51	1.2:1	27/5
2	L9	55:45	1.3:1	19/3
3	L10	56:44	1.3:1	32/7
4	L11	52:48	5.5:1	27/4
5	L12	48:52	2.3:1	27/10
6	CPA1	45:55	>20:1	27/9

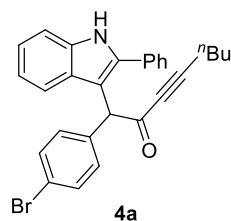
^aUnless otherwise noted, all reactions were performed with **1a** (0.2 mmol), **2a** (0.1 mmol), Cat. (10 mol%), **L** (15 mol%) in solvent (2.0 mL) at 40 °C under Ar atmosphere for 2 h; ^bYields were determined by crude ¹H NMR using CH₂Br₂ as internal standard; ^cThe er was determined by HPLC.



3. Copper catalyzed carbocyclization of 4a



1-(4-bromophenyl)-1-(2-phenyl-1*H*-indol-3-yl)oct-3-yn-2-one (4a)

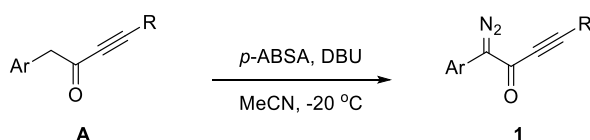


In a dried glass tube, a mixture of $\text{Cu}(\text{OTf})_2$ (7.2 mg, 10 mol%), 1,10-phenanthroline (5.4 mg, 15 mol%) in DCM (2 mL) was stirred at room temperature for 15 mins. Subsequently, indoles **2** (0.2 mmol, 1.0 equiv.) was added to the reaction mixture at room temperature, and diazo compounds **1** (0.4 mmol, 2.0 equiv.) was dissolved in 2 mL DCM and added to the reaction mixture. Then the resulting mixture was continually stirred at 40 °C for 1 h. The mixture was concentrated under reduced pressure and the residue was purified by column chromatography on silica gel (PE/EA = 30:1 to 10:1) to afford the desired product yellow oil **4a** (19.7 mg, 21%) and **3a** (34.7 mg, 37%). Subsequently, in a dried glass tube, a mixture of $\text{Cu}(\text{OTf})_2$ (1.5 mg, 10 mol%), 3,4,7,8-tetramethyl-1,10-phenanthroline (1.5 mg, 15 mol%) in DCM (0.5 mL) was stirred at room temperature for 15 mins. Subsequently, **4a** (0.04 mmol, 1.0 equiv.) was dissolved in 0.5 mL DCM and added to the reaction mixture. Then the resulting mixture was continually stirred at 40 °C for 2 h and **4a** was consumed completely determined by TLC analysis. The mixture was concentrated under reduced pressure and the residue was purified by column chromatography on silica gel (PE/EA = 30:1 to 10:1) to afford the desired product **3a**. And it was found that **4a** was almost completely converted to the cyclization product **3a** (18.2 mg, 92%). **4a** : ^1H NMR (600 MHz, CDCl_3) δ 8.35 (s, 1H), 7.49 – 7.37 (m, 9H), 7.21 (t, $J = 7.6$ Hz, 1H), 7.12 (d, $J = 8.2$ Hz, 2H), 7.07 (t, $J = 7.6$ Hz, 1H), 5.42 (s, 1H), 2.09 – 2.13 (m, 2H), 1.26 – 1.22 (m, 2H), 1.07 (h, $J = 7.3$ Hz, 2H), 0.75 (t, $J = 7.3$ Hz, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ 185.4, 138.0, 136.7, 136.0, 132.1, 131.3, 131.0, 129.0, 128.5, 128.4, 127.7, 122.6, 121.0, 121.0, 120.4, 111.0, 107.3, 96.4, 81.5, 56.7, 29.3, 21.5, 18.6, 13.4; HRMS (ESI) calculated for $[\text{C}_{28}\text{H}_{24}\text{BrNNaO}]$ $[\text{M}+\text{Na}]^+$: 492.0933, found: 492.0935.

4. General procedure for the synthesis of 1 and 2

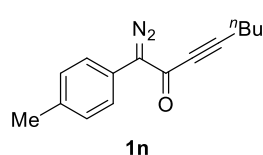
4.1 Synthesis of diazo compound 1

Under argon atmosphere, an oven dried round-bottom flask was charged with diazo precursor (5 mmol, 1 equiv.) and *p*-acetamidobenzenesulfonyl azide (*p*-ABSA, 6 mmol, 1.2 equiv.) in acetonitrile (20 mL). To this solution at 0 °C was added 1,8-diazaobicyclo [5.4.0]undec-7-ene (7.5 mmol, 1.5 equiv.) in one portion. After stirring at 0 °C for 5 minutes, the reaction was quenched with saturated sodium bicarbonate solution. Diethyl ether was added and layers were separated. The aqueous layer was extracted with diethyl ether for two more times. The combined organic layers were washed with brine, dried over magnesium sulfate, filtered through a plug of silica gel and concentrated in vacuo. The crude residue was purified by flash chromatography.



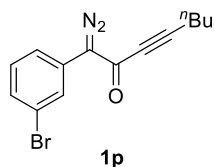
All of the known diazo **1** were prepared according to the literature procedures.^[1] Characterization of new diazo **1n**, **1p**, **1q**, **1r** and **1s** are listed below.

1. 1-diazo-1-(*p*-tolyl)oct-3-yn-2-one (**1n**)



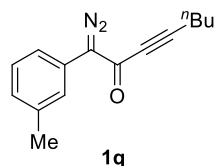
Following the general procedure. 897.2 mg, 61% yield; yellow solid; R_f = 0.5 (PE/EA = 10:1). ¹H NMR (500 MHz, CDCl₃) δ 7.50 (d, J = 8.8 Hz, 2H), 7.37 (d, J = 8.8 Hz, 2H), 2.41 (t, J = 7.1 Hz, 2H), 1.61 – 1.55 (m, 2H), 1.44 (q, J = 7.5 Hz, 2H), 0.94 (t, J = 7.3 Hz, 3H).

2. 1-(3-bromophenyl)-1-diazo-oct-3-yn-2-one (**1p**)



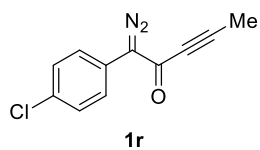
Following the general procedure. 768.8 mg, 45% yield; yellow oil; R_f = 0.5 (PE/EA = 10:1). ¹H NMR (600 MHz, CDCl₃) δ 7.75 (t, J = 1.7 Hz, 1H), 7.47 (d, J = 8.0 Hz, 1H), 7.36 (d, J = 7.9 Hz, 1H), 7.29 – 7.25 (m, 1H), 2.41 (t, J = 7.1 Hz, 2H), 1.60 – 1.55 (m, 2H), 1.48 – 1.40 (m, 2H), 0.94 (t, J = 7.4 Hz, 3H); HRMS (ESI) calculated for [C₁₄H₁₃BrN₂NaO] [M+Na]⁺: 327.0103, found: 327.0092.

3. 1-diazo-1-(*m*-tolyl)oct-3-yn-2-one (1q)



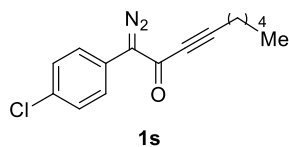
Following the general procedure. 340.2mg, 40% yield; yellow oil; $R_f = 0.45$ (PE/EA = 10:1). $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.37 – 7.32 (m, 2H), 7.28 (t, $J = 7.7$ Hz, 1H), 7.05 (d, $J = 7.5$ Hz, 1H), 2.40 (t, $J = 7.1$ Hz, 2H), 2.36 (s, 3H), 1.60 – 1.54 (m, 2H), 1.47 – 1.40 (m, 2H), 0.93 (t, $J = 7.2$ Hz, 3H); **HRMS** (ESI) calculated for $[\text{C}_{15}\text{H}_{16}\text{N}_2\text{NaO}]$ $[\text{M}+\text{Na}]^+$: 263.1155, found: 263.1149.

4. 1-(4-chlorophenyl)-1-diazopent-3-yn-2-one (1r)



Following the general procedure. 340.2mg, 40% yield; yellow solid; $R_f = 0.45$ (PE/EA = 10:1). $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.51 – 7.47 (m, 2H), 7.36 (d, $J = 8.8$ Hz, 2H), 2.06 (s, 3H).

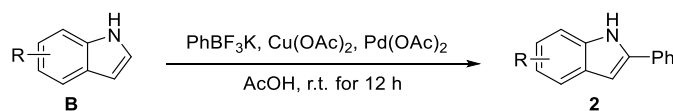
5. 1-(4-chlorophenyl)-1-diazonon-3-yn-2-one (1s)



Following the general procedure. 1.0076g, 52% yield; yellow solid; $R_f = 0.5$ (PE/EA = 10:1). $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.50 (d, $J = 8.8$ Hz, 2H), 7.37 (d, $J = 8.7$ Hz, 2H), 2.40 (t, $J = 7.1$ Hz, 2H), 1.63 – 1.58 (m, 2H), 1.44 – 1.30 (m, 4H), 0.92 (t, $J = 7.1$ Hz, 3H). **HRMS** (ESI) calculated for $[\text{C}_{15}\text{H}_{15}\text{ClN}_2\text{NaO}]$ $[\text{M}+\text{Na}]^+$: 297.0765, found: 297.0757.

4.2 Synthesis of indoles 2

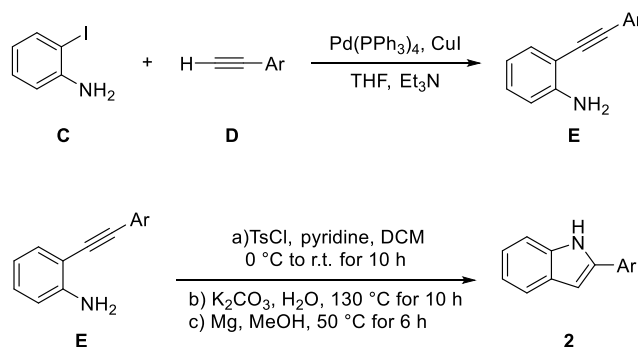
Method A:



Synthesis compound **2** with reference to Chen's report^[2]. A mixture of indole (2 mmol), $\text{Pd}(\text{OAc})_2$ (22.4 mg, 5 mol%), $\text{Cu}(\text{OAc})_2$ (36.4 mg, 10 mol%), potassium phenylfluoroborate (3 mmol), acetic acid (10 mL) was stirred at room temperature under air for 12 h. Afterward, the reaction mixture was filtered through a plug of Celite and the filtrate was evaporated. The resulting oil was dissolved in ether (25 mL) and washed with aqueous NaHCO_3 (2×15 mL). The organic layer was dried with Na_2SO_4

and concentrated. The residue was purified by flash column chromatography to afford the corresponding product **2**. Compound **2k** synthesised according to **method A**.

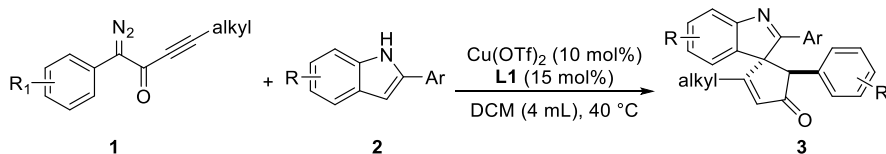
Method B:



To a solution of 2-Iodoaniline (2.0 mmol) in dry Et₃N and THF (v/v = 1:1, 3 mL) **D** (2.0 mmol), Pd(PPh₃)₄ (115.6 mg, 5 mol%) and CuI (4.0 mg, 2 mol%) was added. The mixture was heated at reflux for 4 h. The solvent was removed under reduced pressure and the residue was filtered through Celite using toluene as solvent. The solvent was removed and the crude residue was purified by flash chromatography on silica gel. Then the obtained **E** taken in DCM (20 mL) was added with pyridine (3 equiv.) followed by tosyl chloride (1.3 equiv.) at 0 °C over a period of 15 mins. After addition completes, reaction stirred at RT for 12 h. After reaction completed (monitored by TLC), reaction mass quenched with ice-cold water and extracted into DCM. The obtained crude material passed through flash column chromatography to give pure product. To a solution of K₂CO₃ (0.15 equiv.) in water (1.5 mL) was added to the product obtained in one step up. The resulting mixture was stirred vigorously at 130 °C in a sealed tube under an argon atmosphere for 10 h. The reaction solution was cooled to room temperature and extracted by DCM (three times), and the organic phase was collected. Pure product was obtained by flash chromatography on silica gel. To a solution of the product obtained in one step up in MeOH (0.05 M) was added Mg (15 equiv.). After being stirred at 50 °C for 6 h, the reaction mixture was poured into aq. NH₄Cl and then the product was extracted with DCM (three times). The combined organic layer was washed with brine, dried over MgSO₄, and concentrated in vacuo. The residue was

purified by column chromatography on silica gel to afford **2**. Compound **2a**, **2b**, **2c**, **2d**, **2e**, **2f**, **2g**, **2h**, **2i** and **2j** synthesised according to **method B**^[3].

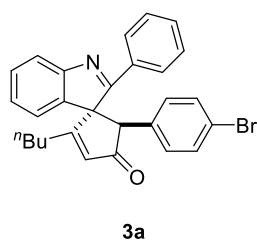
5. General procedure for the synthesis of spirocyclic **3**



General procedure 1 (GP-1): In a dried glass tube, a mixture of $\text{Cu}(\text{OTf})_2$ (7.2 mg, 10 mol%), 3,4,7,8-tetramethyl-1,10-phenanthroline (7.1 mg, 15 mol%) in DCM (2 mL) was stirred at room temperature for 15 mins. Subsequently, indoles **2** (0.2 mmol, 1.0 equiv.) was added to the reaction mixture at room temperature, and diazo compounds **1** (0.4 mmol, 2.0 equiv.) was dissolved in 2 mL DCM and added to the reaction mixture. Then the resulting mixture was continually stirred at 40 °C for 2 h and **2** was consumed completely determined by TLC analysis. The dr of the product was calculated by crude ^1H NMR. The mixture was concentrated under reduced pressure and the residue was purified by column chromatography on silica gel (PE/EA = 60:1 to 30:1 or PE/EA = 50:1 to 20:1) to afford the desired product **3**.

1. (1*R*,5*R*)-5-(4-bromophenyl)-2-butyl-2'-phenylspiro[cyclopentane-1,3'-indol]-2-en-4-one

(**3a**)

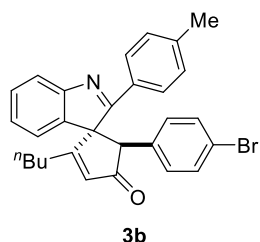


The general procedure was followed using **1a** (121.3 mg, 0.4 mmol, 2.0 equiv.) and **2a** (37.5 mg, 0.2 mmol, 1.0 equiv.), $\text{Cu}(\text{OTf})_2$ (7.2 mg, 10 mol%), 3,4,7,8-tetramethyl-1,10-phenanthroline (7.1 mg, 15 mol%) and 4 mL DCM by **GP-1**, TLC (R_f = 0.3, PE/EA = 10:1). After purification by column chromatography (PE/EA = 60:1 to 30:1), **3a** (dr = 9.0:1, 62.4 mg,

83%) was obtained as yellow oil: Two diastereoisomers are hard to be separated by column chromatography on silica gel. ^1H NMR (500 MHz, CDCl_3) δ [8.07 – 8.03 (m, 1.8H), 7.76 – 7.73 (m, 0.1H), 7.51 – 7.50 (m, 0.1H)], [7.57 – 7.51 (m, 3.6H), 7.38 – 7.35 (m, 0.4H)], 7.25 – 7.21 (m, 1H), [7.10 (d, J = 8.4 Hz, 1.8H), 6.94 (d, J = 8.4 Hz, 0.2H)], 7.05 (t, J = 7.5 Hz, 1H), [7.19 – 7.17 (m, 0.1H), 6.85 (d, J = 7.4 Hz, 0.9H)], [6.60 (d, J = 8.2 Hz, 1.8H), 6.34 (d, J = 8.2 Hz, 0.2H)], 6.58 (s, 1H), [4.47 (s, 0.9H), 4.36 (s, 0.1H)], 2.11 – 2.02 (m, 1H), 1.71 – 1.64 (m, 1H), 1.50 – 1.39 (m,

2H), 1.19 – 1.13 (m, 2H), [0.79 – 0.77 (m, 0.3H), 0.74 (t, $J = 7.3$ Hz, 2.7H)]; ^{13}C NMR (125 MHz, CDCl_3) δ 204.2, 181.1, 176.4, 154.7, 137.9, 132.7, 132.3, 131.8, 131.0, 130.4, 129.4, 129.4, 129.2, 127.4, 125.8, 123.0, 121.2, 121.1, 73.5, 59.9, 29.5, 28.7, 22.0, 13.6; HRMS (ESI) calculated for $[\text{C}_{28}\text{H}_{24}\text{BrNNaO}]$ $[\text{M}+\text{Na}]^+$: 492.0933, found: 492.0936.

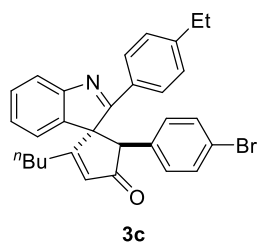
2. **(1*R*,5*R*)-5-(4-bromophenyl)-2-butyl-2'-(*p*-tolyl)spiro[cyclopentane-1,3'-indol]-2-en-4-one (3b)**



The general procedure was followed using **1a** (121.0 mg, 0.4 mmol, 2.0 equiv.) and **2b** (37.8 mg, 0.2 mmol, 1.0 equiv.), $\text{Cu}(\text{OTf})_2$ (7.2 mg, 10 mol%), 3,4,7,8-tetramethyl-1,10-phenanthroline (7.1 mg, 15 mol%) and 4 mL DCM by **GP-1**, TLC ($R_f = 0.3$, PE/EA = 10:1). After purification by column chromatography (PE/EA = 60:1 to 30:1), **3b** (dr = 5:1, 83.9 mg, 95%) was obtained as yellow solid: Two diastereoisomers are hard to be separated by column chromatography on silica gel. ^1H NMR (500 MHz, CDCl_3) δ [7.95 (d, $J = 8.0$ Hz, 1.8H), 7.72 (d, $J = 8.0$ Hz, 0.1H), 7.95 (m, 0.1H)], [7.50 (d, $J = 7.7$ Hz, 0.9H), 7.30 – 7.28 (m, 0.1H)], [7.34 (d, $J = 7.9$ Hz, 1.8H), 7.31 (d, $J = 7.9$ Hz, 0.2H)], 7.22 (t, $J = 7.7$ Hz, 1H), [7.09 (d, $J = 8.3$ Hz, 1.8H), 7.00 – 6.98 (m, 0.2H)], 7.02 (t, $J = 7.4$ Hz, 1H), [6.95 (d, $J = 7.4$ Hz, 0.1H), 6.83 (d, $J = 7.4$ Hz, 0.9H)], [6.60 (d, $J = 8.1$ Hz, 1.8H), 6.37 (d, $J = 8.1$ Hz, 0.2H)] 6.57 (s, 1H), [4.47 (s, 0.9H), 4.36 (s, 0.1H)], [2.45 (s, 2.7H), 1.69 (s, 0.3H)], 2.10 – 2.02 (m, 1H), 1.69 – 1.63 (m, 1H), 1.49 – 1.39 (m, 2H), 1.16 (q, $J = 6.6, 5.9$ Hz, 2H), [0.78 – 0.76 (m, 0.3H), 0.73 (d, $J = 7.3$ Hz, 2.7H)]; ^{13}C NMR (125 MHz, CDCl_3) δ 204.3, 181.2, 176.3, 154.8, 142.4, 137.8, 132.7, 131.0, 130.4, 130.2, 129.6, 129.3, 129.2, 127.4, 125.6, 123.0, 121.1, 120.9, 73.4, 60.2, 29.5, 28.7, 22.0, 21.6, 13.6; m.p. = 119.7 – 129.1 °C; HRMS (ESI) calculated for $[\text{C}_{29}\text{H}_{26}\text{BrNNaO}]$ $[\text{M}+\text{Na}]^+$: 506.1090, found: 506.1090.

3. **(1*R*,5*R*)-5-(4-bromophenyl)-2-butyl-2'-(4-ethylphenyl)spiro[cyclopentane-1,3'-indol]-2-en-4-one (3c)**

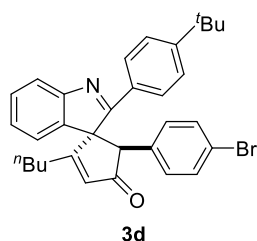
The general procedure was followed using **1a** (121.1 mg, 0.4 mmol, 2.0 equiv.) and **2c** (41.5 mg, 0.2 mmol, 1.0 equiv.), $\text{Cu}(\text{OTf})_2$ (7.3 mg, 10 mol%), 3,4,7,8-tetramethyl-1,10-phenanthroline (7.1 mg, 15 mol%) and 4 mL DCM by **GP-1**, TLC ($R_f = 0.3$, PE/EA = 10:1). After purification by column chromatography (PE/EA = 50:1 to 20:1), **3c** (dr = 5.4:1, 52.3 mg, 56%) was obtained as



yellow oil: Two diastereoisomers are hard to be separated by column chromatography on silica gel. **¹H NMR (600 MHz, CDCl₃)** δ 8.02 – 7.92 (m, 2H), 7.50 (d, *J* = 5.3 Hz, 1H), 7.37 (d, *J* = 5.7 Hz, 2H), 7.22 (t, *J* = 7.4 Hz, 1H), [7.12 – 7.08 (m, 1.8H), 6.94 – 6.91 (m, 0.2H)], 7.02 (d, *J* = 6.2 Hz, 1H), 6.83 (d, *J* = 7.1 Hz, 1H), [6.61 (d, *J* = 5.7 Hz, 1.8H), 6.36 – 6.34

(m, 0.2H)], 6.57 (s, 1H), [4.47 (s, 0.9H), 4.35 (s, 0.1H)], [2.76 – 2.74 (m, 1.8H), 2.64 – 2.60 (m, 0.2H)], 2.10 – 2.04 (m, 1H), 1.69 – 1.64 (m, 1H), 1.48 – 1.39 (m, 2H), 1.33 – 1.27 (m, 3H), 1.20 – 1.14 (m, 2H), 0.76 – 0.72 (m, 3H); **¹³C NMR (150 MHz, CDCl₃)** δ 204.4, 176.4, 148.6, 137.8, 132.7, 131.0, 130.4, 129.8, 129.3, 129.1, 129.0, 127.5, 125.6, 123.0, 121.1, 120.9, 73.4, 60.1, 29.5, 28.9, 28.7, 22.0, 15.1, 13.6; **HRMS** (ESI) calculated for [C₃₀H₂₈BrNNaO] [M+Na]⁺: 520.1246, found: 520.1240.

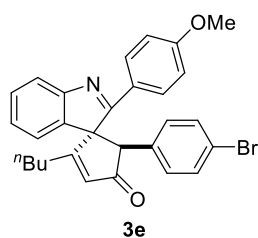
4. **(1R,5R)-5-(4-bromophenyl)-2-butyl-2'-(4-*tert*-butylphenyl)spiro[cyclopentane-1,3'-indol]-2-en-4-one (3d)**



The general procedure was followed using **1a** (122.0 mg, 0.4 mmol, 2.0 equiv.) and **2d** (50.0 mg, 0.2 mmol, 1.0 equiv.), Cu(OTf)₂ (7.2 mg, 10 mol%), 3,4,7,8-tetramethyl-1,10-phenanthroline (7.1 mg, 15 mol%) and 4 mL DCM by **GP-1**, TLC (*R_f* = 0.4, PE/EA = 10:1). After purification by column chromatography (PE/EA = 50:1 to 20:1), **3d** (dr = 3.3:1, 31.7 mg, 30%) was obtained as yellow oil: Two diastereoisomers are hard to be separated by column

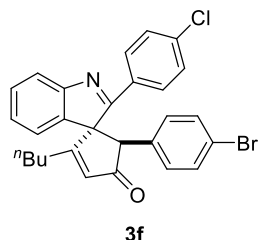
chromatography on silica gel, following column chromatography separation, the second diastereomer is scarcely discernible in the NMR spectrum. **¹H NMR (500 MHz, CDCl₃)** δ 7.97 (d, *J* = 8.5 Hz, 2H), 7.55 (d, *J* = 8.5 Hz, 2H), 7.51 (d, *J* = 7.8 Hz, 1H), 7.22 (t, *J* = 7.6 Hz, 1H), 7.10 (d, *J* = 8.4 Hz, 2H), 7.02 (t, *J* = 7.5 Hz, 1H), 6.83 (d, *J* = 7.5 Hz, 1H), 6.61 (d, *J* = 8.0 Hz, 2H), 6.57 (s, 1H), 4.47 (s, 1H), 2.11 – 2.05 (m, 1H), 1.70 – 1.66 (m, 1H), 1.64 (d, *J* = 3.2 Hz, 1H), 1.51 – 1.44 (m, 2H), 1.38 (s, 9H), 1.19 – 1.15 (m, 2H), 0.75 (t, *J* = 7.3 Hz, 3H); **¹³C NMR (125 MHz, CDCl₃)** δ 204.4, 181.4, 177.7, 156.0, 138.0, 134.8, 132.8, 131.8, 131.7, 131.0, 130.4, 129.4, 129.2, 127.3, 126.5, 125.6, 123.0, 121.0, 73.1, 61.0, 34.4, 31.1, 29.7, 27.4, 22.1, 14.5; **HRMS** (ESI) calculated for [C₃₂H₃₂BrNNaO] [M+Na]⁺: 548.1559, found: 548.1547.

5. **(1*R*,5*R*)-5-(4-bromophenyl)-2-butyl-2'-(4-methoxyphenyl)spiro[cyclopentane-1,3'-indol]-2-en-4-one (3e)**



The general procedure was followed using **1a** (119.9 mg, 0.4 mmol, 2.0 equiv.) and **2e** (45.1 mg, 0.2 mmol, 1.0 equiv.), Cu(OTf)₂ (7.2 mg, 10 mol%), 3,4,7,8-tetramethyl-1,10-phenanthroline (7.1 mg, 15 mol%) and 4 mL DCM by **GP-1**, TLC (*R_f* = 0.3, PE/EA = 10:1). After purification by column chromatography (PE/EA = 60:1 to 30:1), **3e** (dr = 7.0:1, 85.6 mg, 85%) was obtained as yellow oil: Two diastereoisomers are hard to be separated by column chromatography on silica gel. ¹H NMR (500 MHz, CDCl₃) δ [7.75 (d, *J* = 7.6 Hz, 0.1H), 7.52 (d, *J* = 7.6 Hz, 1.8H), 7.50 – 7.48 (m, 0.1H)], [7.71 – 7.69 (m, 0.9H), 7.34 – 7.31 (m, 0.1H)], [7.43 (t, *J* = 7.9 Hz, 0.9H), 7.39 (t, *J* = 7.9 Hz, 0.1H)], [7.25 – 7.21 (m, 0.9H), 6.98 – 6.96 (m, 0.1H)], 7.15 – 7.07 (m, 3H), [7.07 – 7.03 (m, 0.9H), 6.90 – 6.87 (m, 0.1H)], [6.97 (d, *J* = 7.6 Hz, 0.1H), 6.85 (d, *J* = 7.6 Hz, 0.9H)], [6.79 (s, 0.1H), 6.57 (s, 0.9H)], [6.61 (d, *J* = 8.5 Hz, 1.8H), 6.34 (d, *J* = 8.5 Hz, 2H)], [4.50 (s, 0.9H), 4.34 (s, 0.1H)], [3.92 (s, 2.7H), 3.72 (s, 0.3H)], 2.13 – 2.01 (m, 1H), 1.70 – 1.63 (m, 1H), 1.53 – 1.37 (m, 2H), 1.21 – 1.13 (m, 2H), [0.78 (t, *J* = 7.3 Hz, 0.3H), 0.74 (t, *J* = 7.3 Hz, 2.7H)]; ¹³C NMR (125 MHz, CDCl₃) δ 204.2, 181.1, 176.3, 160.4, 154.6, 138.0, 133.6, [132.6, 131.5], [131.0, 130.7], [130.4, 129.8], [129.5, 129.4], [129.2, 129.1], [127.2, 125.9], [123.0, 121.6], [121.2, 121.1], [119.8, 119.6], [118.1, 117.6], [112.2, 111.9], 73.6, [60.0, 59.5], [55.5, 55.2], [29.5, 29.2], [28.9, 28.7], [22.2, 22.0], 13.6; HRMS (ESI) calculated for [C₂₉H₂₆BrNNaO₂] [M+Na]⁺: 522.1039, found: 522.1037.

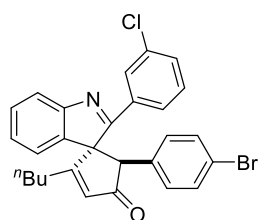
6. **(1*R*,5*R*)-5-(4-bromophenyl)-2-butyl-2'-(4-chlorophenyl)spiro[cyclopentane-1,3'-indol]-2-en-4-one (3f)**



The general procedure was followed using **1a** (127.1 mg, 0.4 mmol, 2.0 equiv.) and **2f** (45.0 mg, 0.2 mmol, 1.0 equiv.), Cu(OTf)₂ (7.2 mg, 10 mol%), 3,4,7,8-tetramethyl-1,10-phenanthroline (7.1 mg, 15 mol%) and 4 mL DCM by **GP-1**, TLC (*R_f* = 0.4, PE/EA = 10:1). After purification by column chromatography (PE/EA = 50:1 to 20:1), **3f** (dr = 4.8:1, 39.8 mg, 40%) was obtained as yellow oil: Two diastereoisomers are hard to be separated by column chromatography on silica gel. ¹H NMR (500 MHz, CDCl₃) δ [8.06 – 8.03 (m, 1.8H), 7.72 – 7.69

(m, 0.2H)], [7.57 – 7.52 (m, 3.6H), 7.40 – 7.34 (m, 0.4H)], 7.25 – 7.21 (m, 1H), [7.10 (d, $J = 8.5$ Hz, 1.8H), 6.94 (d, $J = 8.5$ Hz, 0.2H)], 7.07 – 7.02 (m, 1H), [7.19 – 7.17 (m, 0.1H), 6.85 (d, $J = 7.0$ Hz, 0.9H)], [6.60 (d, $J = 8.4$ Hz, 1.8H), 6.34 (d, $J = 8.4$ Hz, 0.2H)], 6.58 (s, 1H), [4.47 (s, 0.9H), 4.36 (s, 0.1H)], 2.11 – 2.03 (m, 1H), 1.70 – 1.64 (m, 1H), 1.49 – 1.41 (m, 2H), 1.21 – 1.14 (m, 2H), [0.79 – 0.77 (m, 0.3H), 0.74 (t, $J = 7.3$ Hz, 2.7H)]; ^{13}C NMR (125 MHz, CDCl_3) δ 204.3, 181.1, 176.4, 154.7, 137.9, 132.6, 132.3, 131.8, 131.0, 130.4, 129.5, 129.4, 129.2, 127.4, 125.8, 123.0, 121.2, 121.1, 73.5, 59.9, 29.5, 28.7, 22.0, 13.6; MALDI-MS calculated for $[\text{C}_{28}\text{H}_{24}\text{BrClNO}]$ $[\text{M}+\text{H}]^+$: 504.0730, found: 503.9740.

7. **(1*R*,5*R*)-5-(4-bromophenyl)-2-butyl-2'-(3-chlorophenyl)spiro[cyclopentane-1,3'-indol]-2-en-4-one (3g)**

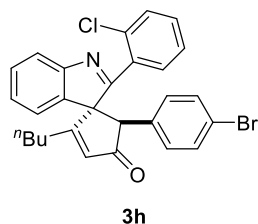


3g

The general procedure was followed using **1a** (125.1 mg, 0.4 mmol, 2.0 equiv.) and **2g** (45.8 mg, 0.2 mmol, 1.0 equiv.), $\text{Cu}(\text{OTf})_2$ (7.2 mg, 10 mol%), 3,4,7,8-tetramethyl-1,10-phenanthroline (7.1 mg, 15 mol%) and 4 mL DCM by **GP-1**, TLC ($R_f = 0.3$, PE/EA = 10:1). After purification by column chromatography (PE/EA = 50:1 to 20:1), **3g** (dr = 4.8:1, 70.2 mg,

68%) was obtained as yellow oil: Two diastereoisomers are hard to be separated by column chromatography on silica gel. ^1H NMR (500 MHz, CDCl_3) δ [8.17 (s, 0.9H), 8.06 – 8.04 (m, 0.1H)], [7.82 (d, $J = 7.8$ Hz, 0.9H), 7.77 – 7.74 (m, 0.1H)], 7.54 (t, $J = 6.6$ Hz, 2H), 7.47 (t, $J = 7.9$ Hz, 1H), 7.24 (d, $J = 8.9$ Hz, 1H), [7.11 (d, $J = 8.4$ Hz, 1.8H), 7.01 (d, $J = 8.4$ Hz, 0.2H)], 7.07 (t, $J = 7.5$ Hz, 1H), [7.41 – 7.31 (m, 0.1H), 6.85 (d, $J = 7.5$ Hz, 0.9H)], [6.60 (d, $J = 4.0$ Hz, 1.8H), 6.37 – 6.35 (m, 0.2H)], [6.63 (s, 0.1H), 6.59 (s, 0.9H)], [4.43 (s, 0.9H), 4.36 (s, 0.1H)], 2.07 – 1.99 (m, 1H), 1.70 – 1.63 (m, 1H), 1.50 – 1.39 (m, 2H), 1.20 – 1.15 (m, 2H), [0.80 – 0.78 (m, 0.3H), 0.75 (t, $J = 7.4$ Hz, 2.7H)]; ^{13}C NMR (125 MHz, CDCl_3) δ 203.9, 180.6, 175.0, 154.4, 138.0, 135.8, 134.0, 132.5, 131.8, 131.1, 130.7, 130.4, 129.8, 129.4, 127.6, 126.3, 125.1, 123.1, 121.5, 121.3, 73.5, 59.6, 29.7, 28.7, 22.0, 13.6; HRMS (ESI) calculated for $[\text{C}_{28}\text{H}_{23}\text{BrClNNaO}]$ $[\text{M}+\text{Na}]^+$: 526.0544, found: 526.0557.

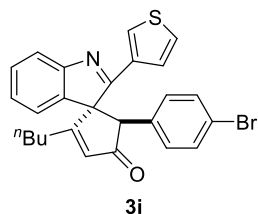
8. **(1*R*,5*R*)-5-(4-bromophenyl)-2-butyl-2'-(2-chlorophenyl)spiro[cyclopentane-1,3'-indol]-2-en-4-one (3h)**



The general procedure was followed using **1a** (118.5 mg, 0.4 mmol, 2.0 equiv.) and **2h** (43.9 mg, 0.2 mmol, 1.0 equiv.), Cu(OTf)₂ (7.3 mg, 10 mol%), 3,4,7,8-tetramethyl-1,10-phenanthroline (7.1 mg, 15 mol%) and 4 mL DCM by **GP-1**, TLC (*R_f* = 0.3, PE/EA = 10:1). After purification by column chromatography (PE/EA = 60:1 to 30:1), **3h** (dr = 5.4:1, 93 mg,

96%) was obtained as yellow oil: Two diastereoisomers are hard to be separated by column chromatography on silica gel. **¹H NMR (500 MHz, CDCl₃)** δ [8.06 – 8.04 (m, 1.8H), 7.76 – 7.73 (m, 0.1H), 7.51 – 7.48 (m, 0.1H)], [7.57 – 7.51 (m, 3.6H), 7.39 – 7.33 (m, 0.4H)], [7.32 – 7.30 (m, 0.1H), 7.25 – 7.21 (m, 0.9H)], [7.10 (d, *J* = 8.5 Hz, 1.8H), 6.94 (d, *J* = 8.5 Hz, 0.2H)], 7.04 (t, *J* = 7.5 Hz, 1H), [7.18 (d, *J* = 7.1 Hz, 0.1H), 6.85 (d, *J* = 7.1 Hz, 0.9H)], 6.61 (s, 1H), [6.59 (d, *J* = 7.9 Hz, 1.8H), 6.34 (d, *J* = 7.9 Hz, 0.2H)], [4.47 (s, 0.9H), 4.37 (s, 0.1H)], 2.11 – 2.03 (m, 1H), 1.71 – 1.64 (m, 1H), 1.52 – 1.39 (m, 2H), 1.21 – 1.12 (m, 2H), [0.79 – 0.77 (m, 0.3H), 0.74 (t, *J* = 7.3 Hz, 2.7H)]; **¹³C NMR (125 MHz, CDCl₃)** δ 204.2, 181.1, 176.4, 154.7, 137.9, 132.6, 132.3, 131.8, 131.0, 130.4, 129.4, 129.4, 129.2, 127.4, 125.8, 123.0, 121.2, 121.1, 73.5, 59.9, 29.5, 28.7, 22.0, 13.6; **MALDI-MS** calculated for [C₂₈H₂₄BrClNO] [M+H]⁺: 504.0730, found: 504.0050.

9. **(1R,5R)-5-(4-bromophenyl)-2-butyl-2'-(thiophen-3-yl)spiro[cyclopentane-1,3'-indol]-2-en-4-one (3i)**

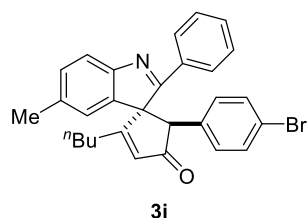


The general procedure was followed using **1a** (113.0 mg, 0.4 mmol, 2.0 equiv.) and **2i** (36.2 mg, 0.2 mmol, 1.0 equiv.), Cu(OTf)₂ (7.2 mg, 10 mol%), 3,4,7,8-tetramethyl-1,10-phenanthroline (7.1 mg, 15 mol%) and 4 mL DCM by **GP-1**, TLC (*R_f* = 0.3, PE/EA = 10:1). After purification by

column chromatography (PE/EA = 60:1 to 30:1), **3i** (dr = 4.7:1, 70.4 mg, 81%) was obtained as yellow oil: Two diastereoisomers are hard to be separated by column chromatography on silica gel. **¹H NMR (500 MHz, CDCl₃)** δ [7.91 – 7.90 (m, 0.9H), 7.72 – 7.68 (m, 0.1H)], [7.84 – 7.81 (m, 0.9H), 7.48 – 7.46 (m, 0.1H)], [7.52 – 7.48 (m, 1.8H), 7.40 – 7.32 (m, 0.2H)], 7.24 – 7.19 (m, 1H), [7.18 – 7.15 (m, 0.2H), 7.11 (d, *J* = 8.5 Hz, 1.8H)], 7.02 – 6.98 (m, 1H), [7.04 – 7.02 (m, 0.1H), 6.79 (d, *J* = 7.5 Hz, 0.9H)], [6.63 (d, *J* = 8.5 Hz, 1.8H), 6.37 (d, *J* = 8.5 Hz, 0.2H)], 6.58 (s, 1H), [4.49 (s, 0.9H), 4.36 (s, 0.1H)], 2.04 – 1.95 (m, 1H), 1.68 – 1.62 (m, 1H), 1.48 – 1.37 (m, 2H), 1.19 – 1.12 (m, 2H), [0.79 – 0.76 (m, 0.3H), 0.74 (t, *J* = 7.4 Hz, 2.7H)]; **¹³C NMR (125 MHz, CDCl₃)** δ

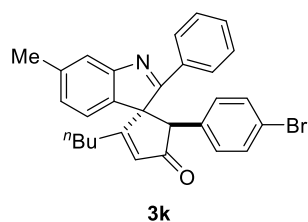
204.4, [181.0, 179.4], 172.6, 155.1, 137.4, 134.9, 132.9, [131.0, 130.8], 130.3, [130.0, 129.6], 129.2, 127.3, 127.0, 126.9, [125.8, 125.6], 123.1, 121.1, 121.0, 73.6, 60.1, 29.5, 28.7, 22.0, 13.6; **HRMS** (ESI) calculated for $[C_{26}H_{22}BrNNaOS]$ $[M+Na]^+$: 498.0498, found: 498.0497.

10. **(1*R*,5*R*)-5-(4-bromophenyl)-2-butyl-5'-methyl-2'-phenylspiro[cyclopentane-1,3'-indol]-2-en-4-one (3j)**



The general procedure was followed using **1a** (122.0 mg, 0.4 mmol, 2.0 equiv.) and **2j** (40.7 mg, 0.2 mmol, 1.0 equiv.), $Cu(OTf)_2$ (7.2 mg, 10 mol%), 3,4,7,8-tetramethyl-1,10-phenanthroline (7.1 mg, 15 mol%) and 4 mL DCM by **GP-1**, TLC (R_f = 0.3, PE/EA = 10:1). After purification by column chromatography (PE/EA = 50:1 to 20:1), **3j** (dr = 3.0:1, 55.6 mg, 58%) was obtained as yellow oil : Two diastereoisomers are hard to be separated by column chromatography on silica gel, following column chromatography separation, the second diastereomer is scarcely discernible in the NMR spectrum. **1H NMR (600 MHz, $CDCl_3$)** δ [8.03 (d, J = 5.4 Hz, 1.8H), 7.61 – 7.63 (m, 0.2H), 7.29 – 7.31 (m, 0.2H)], [7.51 – 7.55 (m, 2.4H), 7.15 – 7.19 (m, 0.6H)], [7.39 (d, J = 7.8 Hz, 0.8H), 7.34 (d, J = 7.7 Hz, 0.2H)], 7.10 (d, J = 8.3 Hz, 2H), [7.28 – 7.30 (m, 0.2H), 7.02 (d, J = 7.8 Hz, 0.8H)], [6.93 (d, J = 8.3 Hz, 0.4H), 6.63 (s, 0.8H), 6.57 (s, 1H)], 6.60 (d, J = 8.1 Hz, 2H), [4.46 (s, 0.8H), 4.34 (s, 0.2H)], [2.47 (s, 0.6H), 2.25 (s, 2.4H)], 2.10 – 2.04 (m, 1H), 1.76 – 1.64 (m, 1H), 1.53 – 1.42 (m, 2H), 1.14 – 1.22 (m, 2H), 0.73 – 0.78 (m, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ [205.1, 204.3], [181.2, 180.1], [175.9, 175.3], [152.6, 142.0], [138.0, 137.2], [135.8, 134.7], [132.9, 132.7], 132.4, [131.5, 131.2], [130.9, 130.7], [130.4, 130.1], [129.8, 129.7], [129.4, 129.2], 128.1, [127.4, 127.3], [123.6, 121.8], [121.1, 121.1], [120.9, 120.7], [73.7, 73.3], [60.3, 59.9], [29.5, 29.2], [28.8, 28.6], [22.1, 22.0], [21.6, 21.4], [14.2, 13.5]; **HRMS** (ESI) calculated for $[C_{29}H_{26}BrNNaO]$ $[M+Na]^+$: 506.1090, found: 506.1093.

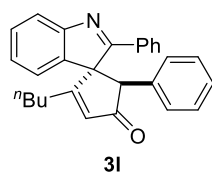
11. **(1*R*,5*R*)-5-(4-bromophenyl)-2-butyl-6'-methyl-2'-phenylspiro[cyclopentane-1,3'-indol]-2-en-4-one (3k)**



The general procedure was followed using **1a** (118.4 mg, 0.4 mmol, 2.0 equiv.) and **2k** (37.0 mg, 0.2 mmol, 1.0 equiv.), $Cu(OTf)_2$ (7.2 mg, 10 mol%), 3,4,7,8-tetramethyl-1,10-phenanthroline (7.0 mg, 15 mol%) and 4 mL DCM by **GP-1**, TLC (R_f = 0.3, PE/EA = 10:1). After

purification by column chromatography (PE/EA = 60:1 to 30:1), **3k** (dr = 5.0:1, 72.1 mg, 83%) was obtained as yellow solid: Two diastereoisomers are hard to be separated by column chromatography on silica gel. **¹H NMR (500 MHz, CDCl₃)** δ [8.04 – 8.00 (m, 1.84H), 7.49 – 7.46 (m, 0.16H)], 7.54 (q, *J* = 7.1, 6.3 Hz, 3H), 7.33 (s, 1H), [7.11 (d, *J* = 8.4 Hz, 1.84H), 6.93 (d, *J* = 8.4 Hz, 0.16H)], 6.85 (d, *J* = 7.0 Hz, 1H), 6.72 (d, *J* = 7.6 Hz, 1H), [6.60 (d, *J* = 8.4 Hz, 1.84H), 6.35 (d, *J* = 8.4 Hz, 0.16H)], 6.55 (s, 1H), [4.45 (s, 0.92H), 4.34 (s, 0.08H)], [2.50 (s, 0.24H), 2.32 (s, 2.76H)], 2.08 – 2.01 (m, 1H), 1.70 – 1.63 (m, 1H), 1.51 – 1.39 (m, 2H), 1.13 – 1.20 (m, 2H), [0.80 – 0.77 (m, 0.24H), 0.75 (t, *J* = 7.4 Hz, 2.76H)]; **¹³C NMR (125 MHz, CDCl₃)** δ 204.4, 181.4, 176.5, 155.0, 139.2, 134.8, 132.8, 132.5, 131.6, 131.0, 130.4, 129.4, 129.1, 127.4, 126.7, 122.7, 121.9, 121.1, 73.2, 59.8, 29.4, 28.7, 22.0, 21.5, 13.6; m.p. = 119.5 – 129.9 °C; **HRMS** (ESI) calculated for [C₂₉H₂₆BrNNaO] [M+Na]⁺: 506.1090, found: 506.1082.

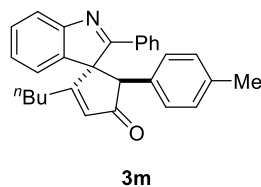
12. (1*R*,5*R*)-2-butyl-2',5-diphenylspiro[cyclopentane-1,3'-indol]-2-en-4-one (**3l**)



The general procedure was followed using **1l** (90.5 mg, 0.4 mmol, 2.0 equiv.) and **2a** (37.5 mg, 0.2 mmol, 1.0 equiv.), Cu(OTf)₂ (7.3 mg, 10 mol%), 3,4,7,8-tetramethyl-1,10-phenanthroline (7.1 mg, 15 mol%) and 4 mL DCM by **GP-1**, TLC (*R_f* = 0.3, PE/EA = 10:1). After purification by column chromatography

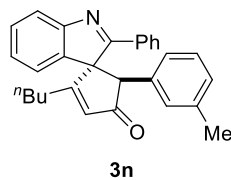
(PE/EA = 30:1), **3l** (dr = 6.0:1, 63 mg, 83%) was obtained as yellow oil: Two diastereoisomers are hard to be separated by column chromatography on silica gel, following column chromatography separation, the second diastereomer is scarcely discernible in the NMR spectrum. **¹H NMR (500 MHz, CDCl₃)** δ 8.09 – 8.03 (m, 2H), 7.58 – 7.51 (m, 4H), 7.22 (t, *J* = 7.5 Hz, 1H), 7.07 (q, *J* = 7.7 Hz, 2H), 6.94 (s, 1H), 6.87 – 6.80 (m, 2H), 6.60 (d, *J* = 11.9 Hz, 2H), 4.47 (s, 1H), 2.11 – 2.03 (m, 1H), 1.72 – 1.65 (m, 1H), 1.50 – 1.39 (m, 2H), 1.20 – 1.13 (m, 2H), 0.74 (t, *J* = 7.3 Hz, 3H); **¹³C NMR (125 MHz, CDCl₃)** δ 204.0, 181.2, 176.3, 154.7, 137.8, 135.9, 132.3, 131.8, 131.6, 130.2, 129.5, 129.5, 129.4, 129.2, 127.4, 127.3, 125.7, 123.1, 121.9, 121.1, 73.6, 59.7, 29.5, 28.7, 22.0, 13.6; **MALDI-MS** calculated for [C₂₈H₂₆NO] [M+H]⁺: 414.1834, found: 414.1710.

13. (1*R*,5*R*)-2-butyl-2'-phenyl-5-(*p*-tolyl)spiro[cyclopentane-1,3'-indol]-2-en-4-one (**3m**)



The general procedure was followed using **1m** (99.0 mg, 0.4 mmol, 2.0 equiv.) and **2a** (37.5 mg, 0.2 mmol, 1.0 equiv.), Cu(OTf)₂ (7.2 mg, 10 mol%), 3,4,7,8-tetramethyl-1,10-phenanthroline (7.1 mg, 15 mol%) and 4 mL DCM by **GP-1**, TLC (*R_f* = 0.3, PE/EA = 10:1). After purification by column chromatography (PE/EA = 50:1 to 20:1), **3m** (dr = 10:1, 62.4 mg, 79%) was obtained as yellow oil: Two diastereoisomers are hard to be separated by column chromatography on silica gel, nevertheless, following column chromatography separation, the second diastereomer is scarcely discernible in the NMR spectrum. ¹H NMR (500 MHz, CDCl₃) δ 8.06 (d, *J* = 6.2 Hz, 2H), 7.56 – 7.49 (m, 4H), 7.20 (t, *J* = 7.6 Hz, 1H), 7.03 (t, *J* = 7.5 Hz, 1H), 6.89 (d, *J* = 7.5 Hz, 1H), 6.77 (d, *J* = 7.7 Hz, 2H), 6.60 (d, *J* = 7.7 Hz, 2H), 6.58 (s, 1H), 4.50 (s, 1H), 2.09 (s, 3H), 2.07 – 2.02 (m, 1H), 1.70 – 1.63 (m, 1H), 1.50 – 1.41 (m, 2H), 1.19 – 1.14 (m, 2H), 0.74 (t, *J* = 7.3 Hz, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 205.2, 180.9, 176.7, 154.8, 138.3, 136.5, 132.6, 131.6, 130.5, 129.6, 129.3, 128.8, 128.6, 128.6, 127.5, 125.6, 123.3, 120.9, 73.9, 60.4, 29.5, 28.7, 22.0, 20.9, 13.6; HRMS (ESI) calculated for [C₂₉H₂₇NNaO] [M+Na]⁺: 428.1985, found: 428.1995.

14. (1*R*,5*R*)-2-butyl-2'-phenyl-5-(*m*-tolyl)spiro[cyclopentane-1,3'-indol]-2-en-4-one (**3n**)

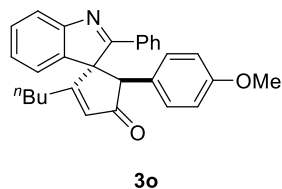


The general procedure was followed using **1n** (96.2 mg, 0.4 mmol, 2.0 equiv.) and **2a** (38.9 mg, 0.2 mmol, 1.0 equiv.), Cu(OTf)₂ (7.3 mg, 10 mol%), 3,4,7,8-tetramethyl-1,10-phenanthroline (7.1 mg, 15 mol%) and 4 mL DCM by **GP-1**, TLC (*R_f* = 0.3, PE/EA = 10:1). After purification by column chromatography (PE/EA = 50:1 to 20:1), **3n** (dr = 3.6:1, 67.0 mg, 83%) was obtained as yellow oil: Two diastereoisomers are hard to be separated by column chromatography on silica gel. ¹H NMR (500 MHz, CDCl₃) δ [8.06 (d, *J* = 7.2 Hz, 1.8H), 7.75 – 7.72 (m, 0.1H), 7.40 – 7.37 (m, 0.1H)], [7.57 – 7.48 (m, 3.6H), 7.36 – 7.30 (m, 0.4H)], 7.18 (q, *J* = 7.4 Hz, 1H), [7.15 – 7.11 (m, 0.1H), 7.01 (t, *J* = 7.5 Hz, 0.9H)], 6.92 – 6.78 (m, 2H), [6.75 (d, *J* = 7.7 Hz, 0.9H), 6.72 – 6.69 (m, 0.1H)], [6.62 (s, 0.1H), 6.59 (s, 0.9H)], [6.55 (s, 1H), 6.29 (s, 0.1H)], [6.50 (d, *J* = 7.7 Hz, 0.9H), 6.22 (d, *J* = 7.7 Hz, 0.1H)], [4.49 (s, 0.9H), 4.39 (s, 0.1H)], [2.08 (s, 2.7H), 1.91 (s, 0.3H)], 2.03 (d, *J* = 9.4 Hz, 1H), 1.71 – 1.64 (m, 1H), 1.52 – 1.39 (m, 2H), 1.17 (q, *J* = 7.9 Hz, 2H), [0.80 – 0.77 (m, 0.3H), 0.74 (t, *J* = 7.4 Hz, 2.7H)]; ¹³C NMR (125 MHz, CDCl₃) δ 205.2, 181.0, 176.7, 154.8, 138.2, 137.3, 133.6, 132.6, 131.6, 129.7, 129.4, 129.4, 128.8, 127.7, 127.7, 127.5, 125.7, 125.4, 123.4, 120.8, 73.9, 60.4,

29.5, 28.7, 22.0, 21.2, 13.6; **HRMS** (ESI) calculated for $[C_{29}H_{27}NNaO] [M+Na]^+$: 428.1985, found: 428.1996.

15. **(1*R*,5*R*)-2-butyl-5-(4-methoxyphenyl)-2'-phenylspiro[cyclopentane-1,3'-indol]-2-en-4-one**

(3o)



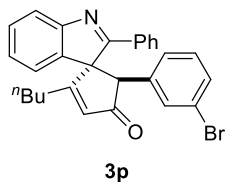
The general procedure was followed using **1o** (107.8 mg, 0.4 mmol, 2.0 equiv.) and **2a** (36.0 mg, 0.2 mmol, 1.0 equiv.), Cu(OTf)₂ (7.3 mg, 10 mol%), 3,4,7,8-tetramethyl-1,10-phenanthroline (7.0 mg, 15 mol%) and 4 mL DCM by **GP-1**, TLC (R_f = 0.3, PE/EA = 10:1). After purification

by column chromatography (PE/EA = 60:1 to 30:1), **3o** (dr = 6.0:1, 57.2 mg, 73%) was obtained as yellow oil: Two diastereoisomers are hard to be separated by column chromatography on silica gel.

¹H NMR (600 MHz, CDCl₃) δ [8.07 – 8.04 (m, 1.8H), 7.75 – 7.72 (m, 0.1H), 7.50 – 7.47 (m, 0.1H)], [7.56 – 7.50 (m, 3.6H), 7.40 – 7.35 (m, 0.4H)], [7.33 – 7.30 (m, 0.1H), 7.22 – 7.19 (m, 0.9H), 7.05 – 7.02 (m, 1H), [7.19 – 7.15 (m, 0.1H), 6.88 (d, J = 7.3, 0.9H)], [6.64 (d, J = 8.7 Hz, 1.8H), 6.39 (d, J = 8.7 Hz, 0.2H)], [6.61 (s, 0.1H), 6.58 (s, 0.9H)], [6.51 (d, J = 8.7 Hz, 1.8H), 6.36 (d, J = 8.7 Hz, 0.2H)], [4.50 (s, 0.9H), 4.40 (s, 0.1H)], 3.60 (s, 3H), 2.10 – 2.03 (m, 1H), 1.70 – 1.65 (m, 1H), 1.50 – 1.40 (m, 2H), 1.20 – 1.14 (m, 2H), [0.79 – 0.77 (m, 0.3H), 0.74 (t, J = 7.3 Hz, 2.7H)]; **¹³C NMR (150 MHz, CDCl₃)** δ 205.2, 180.8, 176.7, 158.3, 154.8, 138.3, 132.5, 131.6, 129.8, 129.5, 129.4, 128.9, 127.4, 125.7, 125.6, 123.2, 120.9, 113.3, 74.0, 60.2, 55.0, 29.6, 28.7, 22.0, 13.6; **HRMS** (ESI) calculated for $[C_{29}H_{27}NNaO_2] [M+Na]^+$: 444.1934, found: 444.1945.

16. **(1*R*,5*R*)-5-(3-bromophenyl)-2-butyl-2'-phenylspiro[cyclopentane-1,3'-indol]-2-en-4-one**

(3p)



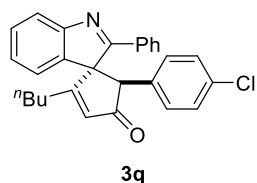
The general procedure was followed using **1p** (122.1 mg, 0.4 mmol, 2.0 equiv.) and **2a** (37.1 mg, 0.2 mmol, 1.0 equiv.), Cu(OTf)₂ (7.3 mg, 10 mol%), 3,4,7,8-tetramethyl-1,10-phenanthroline (7.1 mg, 15 mol%) and 4 mL DCM by **GP-1**, TLC (R_f = 0.3, PE/EA = 10:1). After purification by column

chromatography (PE/EA = 50:1 to 20:1), **3p** (dr = 6.3:1, 67.6 mg, 75%) was obtained as yellow oil:

Two diastereoisomers are hard to be separated by column chromatography on silica gel. **¹H NMR (600 MHz, CDCl₃)** δ [8.08 – 8.03 (m, 1.8H), 7.75 (d, J = 7.7 Hz, 0.1H), 7.50 (d, J = 7.7 Hz, 0.1H)], [7.59 – 7.52 (m, 3.6H), 7.36 – 7.30 (m, 0.4H)], [7.40 – 7.36 (m, 0.1H), 7.24 – 7.21 (m, 0.9H)], [7.21

– 7.18 (m, 0.2H), 7.09 – 7.07 (m, 0.8H)], 7.07 – 7.02 (m, 1H), [6.94 (t, J = 1.9 Hz, 0.9H), 6.66 (t, J = 1.9 Hz, 0.1H)], 6.85 (d, J = 7.1 Hz, 1H), [6.83 (t, J = 7.9 Hz, 0.9H), 6.71 (t, J = 7.9 Hz, 0.1H)], [6.60 (d, J = 7.9 Hz, 0.9H), 6.35 (d, J = 7.9 Hz, 0.1H)], [6.63 (t, J = 1.6 Hz, 0.1H), 6.59 (t, J = 1.6 Hz, 0.9H)], [4.47 (s, 0.9H), 4.37 (s, 0.1H)], 2.10 – 2.04 (m, 1H), 1.71 – 1.65 (m, 1H), 1.52 – 1.40 (m, 2H), 1.22 – 1.14 (m, 2H), [0.78 (t, J = 7.3 Hz, 0.3H), 0.74 (t, J = 7.3 Hz, 2.7H)]; ^{13}C NMR (125 MHz, CDCl_3) δ 204.1, 181.2, 176.3, 154.7, 137.8, 135.9, 132.3, 131.8, 131.6, 130.2, 129.5, 129.5, 129.4, 129.2, 127.4, 127.3, 125.7, 123.1, 121.8, 121.1, 73.6, 59.7, 29.5, 28.7, 22.0, 13.6; HRMS (ESI) calculated for $[\text{C}_{28}\text{H}_{24}\text{BrNNaO}]$ $[\text{M}+\text{Na}]^+$: 492.0933, found: 492.0930.

17. **(1*R*,5*R*)-2-butyl-5-(4-chlorophenyl)-2'-phenylspiro[cyclopentane-1,3'-indol]-2-en-4-one (3q)**

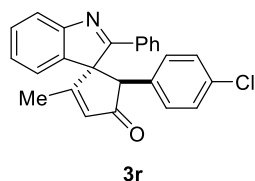


The general procedure was followed using **1q** (103.4 mg, 0.4 mmol, 2.0 equiv.) and **2a** (37.1 mg, 0.2 mmol, 1.0 equiv.), $\text{Cu}(\text{OTf})_2$ (7.3 mg, 10 mol%), 3,4,7,8-tetramethyl-1,10-phenanthroline (7.1 mg, 15 mol%) and 4 mL DCM by **GP-1**, TLC (R_f = 0.3, PE/EA = 10:1). After purification by

column chromatography (PE/EA = 60:1 to 30:1), **3q** (dr = 8.4:1, 81.5 mg, 82%) was obtained as yellow oil: Two diastereoisomers are hard to be separated by column chromatography on silica gel.

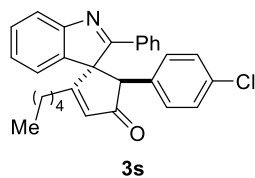
^1H NMR (600 MHz, CDCl_3) δ [8.07 – 8.04 (m, 1.8H), 7.76 – 7.74 (m, 0.1H), 7.50 – 7.49 (m, 0.1H)], [7.58 – 7.51 (m, 3.6H), 7.40 – 7.35 (m, 0.4H)], 7.25 – 7.21 (m, 1H), 7.04 (t, J = 7.5 Hz, 1H), [6.95 (d, J = 8.5 Hz, 1.8H), 6.79 (d, J = 8.5 Hz, 0.2H)], 6.85 (d, J = 7.5 Hz, 1H), [6.66 (d, J = 8.5 Hz, 1.8H), 6.40 (d, J = 8.5 Hz, 0.2H)], [6.62 (s, 0.1H), 6.58 (s, 0.9H)], [4.49 (s, 0.9H), 4.38 (s, 0.1H)], 2.10 – 2.04 (m, 1H), 1.71 – 1.65 (m, 1H), 1.50 – 1.39 (m, 2H), 1.19 – 1.14 (m, 2H), [0.79 – 0.77 (m, 0.3H), 0.74 (t, J = 7.3 Hz, 2.7H)]; ^{13}C NMR (125 MHz, CDCl_3) δ 204.3, 181.1, 176.4, 154.7, 137.9, 132.9, 132.3, 132.1, 131.8, 130.0, 129.4, 129.4, 129.2, 128.1, 127.4, 125.8, 123.0, 121.1, 73.6, 59.8, 29.5, 28.7, 22.0, 13.6; HRMS (ESI) calculated for $[\text{C}_{28}\text{H}_{24}\text{ClNNaO}]$ $[\text{M}+\text{Na}]^+$: 448.1439, found: 448.1437.

18. **(1*R*,5*R*)-5-(4-chlorophenyl)-2-methyl-2'-phenylspiro[cyclopentane-1,3'-indol]-2-en-4-one (3r)**



The general procedure was followed using **1r** (94.8 mg, 0.4 mmol, 2.0 equiv.) and **2a** (38.1 mg, 0.2 mmol, 1.0 equiv.), Cu(OTf)₂ (7.3 mg, 10 mol%), 3,4,7,8-tetramethyl-1,10-phenanthroline (7.1 mg, 15 mol%) and 4 mL DCM by **GP-1**, TLC (*R_f* = 0.3, PE/EA = 10:1). After purification by column chromatography (PE/EA = 50:1 to 20:1), **3r** (dr = 4.0:1, 63.4 mg, 84%) was obtained as yellow oil: Two diastereoisomers are hard to be separated by column chromatography on silica gel. **¹H NMR (600 MHz, CDCl₃)** δ [8.06 (d, *J* = 6.5 Hz, 1.8H), 7.76 – 7.74 (m, 0.1H), 7.51 – 7.49 (m, 0.1H), [7.58 – 7.52 (m, 3.6H), 7.38 – 7.29 (m, 0.4H)], 7.23 (t, *J* = 7.6 Hz, 1H), 7.05 (t, *J* = 7.5 Hz, 1H), [6.95 (d, *J* = 8.5 Hz, 1.8H), 6.79 (d, *J* = 8.5 Hz, 0.2H)], [7.19 – 7.17 (m, 0.1H), 6.86 (d, *J* = 7.4 Hz, 0.9H)], [6.67 (d, *J* = 8.4 Hz, 1.8H), 6.41 (d, *J* = 8.4 Hz, 0.2H)], [6.60 (s, 0.1H), 6.56 (s, 0.9H)], [4.49 (s, 0.9H), 4.39 (s, 0.1H)], [1.75 (s, 2.7H), 1.68 (s, 0.3H)]; **¹³C NMR (125 MHz, CDCl₃)** δ 204.4, 176.5, 176.3, 154.8, 137.5, 132.9, 132.3, 132.2, 131.8, 131.4, 123.0, 129.5, 129.2, 128.1, 127.4, 125.9, 123.0, 121.1, 73.6, 60.0, [29.7, 15.9]; **HRMS (ESI)** calculated for [C₂₅H₁₈ClNNaO]⁺: 406.0969, found: 406.0966.

19. (1S,5R)-5-(4-chlorophenyl)-2-ethyl-2,2,2-trimethyl-2'-phenyl-2λ⁷-spiro[cyclopentane-1,3'-indol]-2-en-4-one (3s**)**

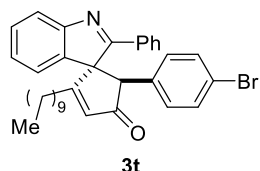


The general procedure was followed using **1s** (116.3 mg, 0.4 mmol, 2.0 equiv.) and **2a** (39.0 mg, 0.2 mmol, 1.0 equiv.), Cu(OTf)₂ (7.2 mg, 10 mol%), 3,4,7,8-tetramethyl-1,10-phenanthroline (7.1 mg, 15 mol%) and 4 mL DCM by **GP-1**, TLC (*R_f* = 0.4, PE/EA = 10:1). After purification by column chromatography (PE/EA = 50:1 to 20:1), **3s** (dr = 7.2:1, 59.0 mg, 62%) was obtained as yellow oil: Two diastereoisomers are hard to be separated by column chromatography on silica gel. **¹H NMR (600 MHz, CDCl₃)** δ [8.07 – 8.04(m, 1.8H), 7.75 (d, *J* = 7.7 Hz, 0.1H), 7.50 (d, *J* = 7.6 Hz, 0.1H)] [7.56 – 7.50 (m, 3.6H), 7.40 – 7.36 (m, 0.4H)], [7.34 – 7.30 (m, 0.1H), 7.25 – 7.21 (m, 0.9H),] 7.04 (t, *J* = 6.9 Hz, 1H), [6.95 (d, *J* = 8.1 Hz, 1.8H), 6.79 (d, *J* = 8.2 Hz, 0.2H)], [7.18 (d, *J* = 7.6 Hz, 0.1H), 6.85 (d, *J* = 7.5 Hz, 0.9H)], [6.66 (d, *J* = 8.1 Hz, 1.8H), 6.40 (d, *J* = 8.2 Hz, 0.2H)], [6.62 (s, 0.1H), 6.59 (s, 0.9H)], [4.49 (s, 0.9H), 4.39 (s, 0.1H)], 2.10 – 2.03 (m, 1H), 1.70 – 1.64 (m, 1H), 1.51 – 1.42 (m, 2H), 1.14 – 1.12 (s, 4H), 0.76 (s, 3H); **¹³C NMR (150 MHz, CDCl₃)** δ 204.4, 181.1, 176.4, 154.6, 137.9, 132.9, 132.2, 132.1, 131.8, 130.0, 129.4, 129.1, 128.0, 127.4, 125.8,

123.0, 121.1, 73.6, 59.8, 30.9, 29.7, 26.2, 22.1, 13.7; **HRMS** (ESI) calculated for $[C_{29}H_{26}ClNNaO]$ $[M+Na]^+$: 462.1595, found: 462.1593.

20. **(1*S*,5*R*)-5-(4-bromophenyl)-2-ethyl-2,2,2,2,2,2-octamethyl-2'-phenyl-2*λ*¹²-**

spiro[cyclopentane-1,3'-indol]-2-en-4-one (3t)



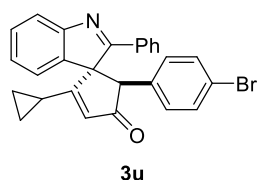
The general procedure was followed using **1t** (138.5 mg, 0.4 mmol, 2.0 equiv.) and **2a** (40.5 mg, 0.2 mmol, 1.0 equiv.), $Cu(OTf)_2$ (7.3 mg, 10 mol%), 3,4,7,8-tetramethyl-1,10-phenanthroline (7.1 mg, 15 mol%) and 4 mL DCM by **GP-1**, TLC (R_f = 0.4, PE/EA = 10:1). After purification by

column chromatography (PE/EA = 50:1 to 20:1), **3t** (dr = 12:1, 92.8 mg, 82%) was obtained as yellow oil: Two diastereoisomers are hard to be separated by column chromatography on silica gel.

¹H NMR (500 MHz, $CDCl_3$) δ [8.05 (d, J = 6.2 Hz, 1.8H), 7.76 – 7.73 (m, 0.1H), 7.51 – 7.48 (m, 0.1H)], [7.57 – 7.51 (m, 3.6H), 7.40 – 7.35 (m, 0.4H)], [7.23 (t, J = 7.1 Hz, 0.9H), 7.40 – 7.30 (m, 0.1H)], [7.10 (d, J = 8.4 Hz, 1.8H), 6.94 (d J = 8.4 Hz, 0.2H)], 7.04 (t, J = 7.4 Hz, 1H), [7.18 (d, J = 7.5 Hz, 0.1H), 6.85 (d, J = 7.5 Hz, 0.9H)], [6.61 (d, J = 8.4 Hz, 1.8H), 6.34 (d, J = 8.4 Hz, 0.2H)], 6.58 (s, 1H), [4.47 (s, 0.9H), 4.37 (s, 0.1H)], 2.10 – 2.03 (m, 1H), 1.70 – 1.64 (m, 1H), 1.50 – 1.40 (m, 2H), 1.27 – 1.23 (m, 2H), 1.21 – 1.18 (m, 4H), 1.16 – 1.09 (m, 8H), 0.86 (t, J = 7.1 Hz, 3H); **¹³C NMR (125 MHz, $CDCl_3$)** δ 204.2, 181.1, 176.4, 154.7, 137.9, 132.7, 132.3, 131.7, 131.0, 130.4, 129.4, 129.2, 127.4, 125.8, 123.0, 121.2, 121.1, 73.5, 59.9, 31.8, 29.8, 29.4, 29.3, 29.2, 29.0, 28.8, 26.6, 22.6, 14.0; **HRMS** (ESI) calculated for $[C_{34}H_{36}BrNNaO]$ $[M+Na]^+$: 576.1872, found: 576.1866.

21. **(1*R*,5*R*)-5-(4-bromophenyl)-2-cyclopropyl-2'-phenylspiro[cyclopentane-1,3'-indol]-2-en-**

4-one (3u)

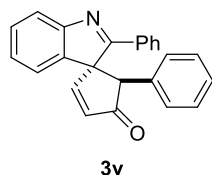


The general procedure was followed using **1u** (117.7 mg, 0.4 mmol, 2.0 equiv.) and **2a** (39.7 mg, 0.2 mmol, 1.0 equiv.), $Cu(OTf)_2$ (7.3 mg, 10 mol%), 3,4,7,8-tetramethyl-1,10-phenanthroline (7.1 mg, 15 mol%) and 4 mL DCM by **GP-1**, TLC (R_f = 0.3, PE/EA = 10:1). After purification by

column chromatography (PE/EA = 50:1 to 20:1), **3u** (dr = 1.7:1, 73.6 mg, 79%) was obtained as yellow soild: Two diastereoisomers are hard to be separated by column chromatography on silica gel. **¹H NMR (600 MHz, $CDCl_3$)** δ [8.10 (d, J = 7.6 Hz, 1.70H), 7.76 – 7.74 (m, 0.15H), 7.51 –

7.49 (m, 0.15H), [7.59 – 7.52 (m, 3.55H), 7.40 – 7.36 (m, 0.45H)], [7.34 – 1.31 (m, 0.15H), 7.24 (t, $J = 7.6$ Hz, 0.85H)], [7.2 – 7.16 (m, 0.15H), 6.88 (d, $J = 7.5$ Hz, 0.85H)], [7.10 (d, $J = 8.1$ Hz, 1.70H), 6.94 (d, $J = 8.1$ Hz, 0.30H)], 7.06 (t, $J = 7.5$ Hz, 1H), [6.60 (d, $J = 8.1$ Hz, 1.70H), 6.34 (d, $J = 8.1$ Hz, 0.30H)], 6.17 (d, $J = 6.7$ Hz, 1H), [4.45 (s, 0.85H), 4.36 (s, 0.15H)], 1.04 – 1.00 (m, 1H), 0.91 – 0.81 (m, 4H); ^{13}C NMR (125 MHz, CDCl_3) δ [204.4, 203.7], [185.5, 184.2], [177.1, 176.7], [154.8, 141.9], [137.9, 134.8], [133.0, 132.8], 132.4, 131.7, [131.0, 130.7], [130.5, 130.4], [129.8, 129.4], [129.3, 129.2], 128.1, [127.7, 127.1], [125.9, 124.5], [123.4, 121.6], [122.9, 121.4], [121.1, 121.0], [74.0, 73.6], [59.6, 59.5], [14.2, 13.9], [13.6, 13.5], [11.7, 11.6]; m.p. = 136.7 – 147.8 °C; HRMS (ESI) calculated for $[\text{C}_{27}\text{H}_{20}\text{BrNNaO}] [\text{M}+\text{Na}]^+$: 476.0620, found: 476.0617.

22. (1*S*,5*R*)-2',5-diphenylspiro[cyclopentane-1,3'-indol]-2-en-4-one (3v)



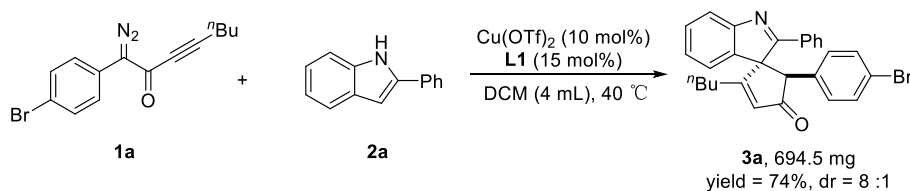
The general procedure was followed using **1v** (68.2 mg, 0.4 mmol, 2.0 equiv.) and **2a** (38.2 mg, 0.2 mmol, 1.0 equiv.), $\text{Cu}(\text{OTf})_2$ (7.3 mg, 10 mol%), 3,4,7,8-tetramethyl-1,10-phenanthroline (7.1 mg, 15 mol%) and 4 mL DCM by **GP-1**,

TLC (R_f = 0.4, PE/EA = 10:1). After purification by column chromatography

(PE/EA = 50:1 to 20:1), **3v** (dr = 2.3:1, 23.1 mg, 35%) was obtained as pale yellow oil: Two diastereoisomers are hard to be separated by column chromatography on silica gel. ^1H NMR (500 MHz, CDCl_3) δ [8.12 – 8.09 (m, 1.50H), 7.75 – 7.73 (m, 0.25H), 7.58 – 7.56 (m, 0.25H)], [7.64 (d, $J = 5.6$ Hz, 0.75H), 7.29 – 7.27 (m, 0.25H)], [7.55 – 7.49 (m, 3.00H), 7.39 – 7.33 (m, 1.00H)], [7.21 – 7.12 (m, 1.25H), 7.05 – 6.91 (m, 3.75H)], 6.87 – 6.84 (m, 1.00H), [6.83 – 6.82 (m, 0.25H), 6.81 (d, $J = 5.4$ Hz, 0.75H)], [6.73 (d, $J = 5.9$ Hz, 1.50H), 6.49 – 6.47 (m, 0.50H)], [4.47 (s, 0.75H), 4.39 (s, 0.25H)]; ^{13}C NMR (125 MHz, CDCl_3) δ 205.6, 176.8, [162.4, 161.8], 154.6, [136.9, 135.8], 134.2, 133.6, 132.8, [131.6, 130.3], [129.5, 129.3], 129.0, [128.7, 128.1], [128.0, 127.9], [127.8, 127.6], [127.2, 127.1], [126.9, 125.6], [124.2, 121.6], [121.5, 121.0], [71.4, 71.0], 59.3; HRMS (ESI) calculated for $[\text{C}_{24}\text{H}_{17}\text{NNaO}] [\text{M}+\text{Na}]^+$: 358.1202, found: 358.1205.

6. Gram scale preparation of 3a and synthetic application

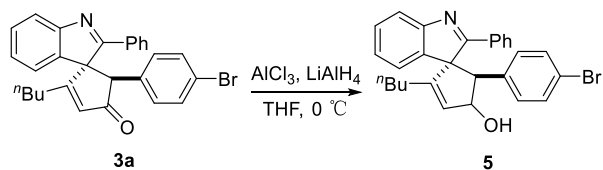
6.1 Gram scale preparation of spirocyclic 3a



In a dried glass tube, a mixture of Cu(OTf)_2 (72.8 mg, 10 mol%), 3,4,7,8-tetramethyl-1,10-phenanthroline (70.2 mg, 15 mol%) in DCM (20 mL) was stirred at room temperature for 15 mins. Subsequently, indole **2a** (2.0 mmol, 1.0 equiv.) was added to the reaction mixture at room temperature, and diazo compounds **1a** (4.0 mmol, 2.0 equiv.) was dissolved in 20 mL DCM and added to the reaction mixture. Then the resulting mixture was continually stirred at 40 °C for 2 h and **2a** was consumed completely determined by TLC analysis. The dr of the product was calculated by crude ^1H NMR. The mixture was concentrated under reduced pressure and the residue was purified by column chromatography on silica gel (PE/EA = 60:1 to 30:1) to afford the desired product **3a**.

6.2 Synthetic application

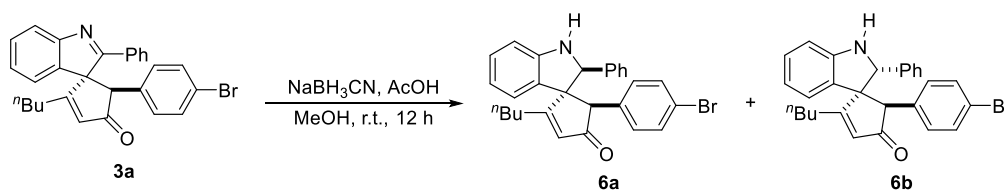
1) 5-(4-bromophenyl)-2-butyl-2'-phenylspiro[cyclopentane-1,3'-indol]-2-en-4-ol (**5**)



In a dried reaction tube, **3a** (70.4 mg, 0.15 mmol, 1.0 equiv.) and AlCl_3 (30 mg, 0.22 mmol, 1.5 equiv.) were dissolved with THF (2.0 mL), then LiAlH_4 (0.3 mL, 0.3 mmol, 2.0 equiv.) was slowly dropped at 0 °C and stirred for 15 mins. After the reaction was complete (monitored by TLC), the crude reaction mixture was filtered with Celite and washed with EA. The solvent was removed under reduced pressure. Then the residue was purified by silica gel column chromatography (PE/EA = 30:1 to 10:1) to afford the desired product **5** (dr = 5.7:1, 27.1 mg, 38%; 29.5 mg, 42%) as a yellow oil. ^1H NMR

(**500 MHz, CDCl₃**) δ [8.00 – 7.93 (m, 1.70H), 7.44 – 7.40 (m, 0.30H)], [7.73 – 7.70 (m, 0.85H), 7.66 – 7.64 (m, 0.15H)], 7.53 (d, J = 7.7 Hz, 1H), [7.51 – 7.45 (m, 2.55H), 7.39 – 7.35 (m, 0.45H)], 7.34 – 7.30 (m, 1H), [7.25 – 7.21 (m, 0.85H), 6.97 – 6.93 (m, 0.15)], [7.10 (d, J = 8.6 Hz, 0.3H), 7.05 (d, J = 8.6 Hz, 1.7H)], 6.64 (t, J = 9.5 Hz, 2H), [6.30 (d, J = 2.3 Hz, 0.15H), 6.23 (d, J = 2.3 Hz, 0.85H), 5.15 (s, 1H), 3.98 (d, J = 5.5 Hz, 1H), [2.20 (d, J = 3.7 Hz, 0.85H), 2.03 – 2.04 (m, 0.15H)], [1.88 – 1.80 (m, 0.85H), 1.74 – 1.68 (m, 0.15H)], 1.49 – 1.42 (m, 1H), 1.42 – 1.29 (m, 2H), 1.20 – 1.12 (m, 2H), [0.82 (t, J = 7.3 Hz, 0.45H), 0.74 (t, J = 7.3 Hz, 2.55H)]; **¹³C NMR (125 MHz, CDCl₃)** δ 179.1, 154.8, 153.6, 139.2, 134.6, 133.5, 131.4, 130.9, [130.7, 130.7], 130.5, 128.9, [128.6, 128.5], [128.2, 128.2], 127.8, [125.6, 121.63], [125.5, 121.3], 121.1, 120.7, 76.5, 76.0, [57.5, 56.9], [29.2, 29.1], [27.7, 27.3], [22.4, 22.2], [13.8, 13.8]; **HRMS (ESI)** calculated for [C₂₈H₂₇BrNO] [M+H]⁺: 472.1271, found: 472.1280. **¹H NMR (500 MHz, CDCl₃)** δ 8.23 – 8.20 (m, 2H), 7.55 – 7.51 (m, 3H), 7.44 (d, J = 7.7 Hz, 1H), 7.23 – 7.19 (m, 1H), 7.13 – 7.04 (m, 4H), 6.62 (d, J = 8.6 Hz, 2H), 6.11 (d, J = 1.7 Hz, 1H), 5.71 (s, 1H), 4.04 (d, J = 8.1 Hz, 1H), 2.28 (d, J = 5.8 Hz, 1H), 1.90 – 1.83 (m, 1H), 1.42 – 1.36 (m, 1H), 1.35 – 1.26 (m, 2H), 1.18 – 1.11 (m, 2H), 0.72 (t, J = 7.3 Hz, 3H); **¹³C NMR (125 MHz, CDCl₃)** δ 177.7, 154.2, 148.9, 139.6, 134.4, 133.0, 131.1, 130.8, 129.4, 129.2, 129.1, 128.5, 128.2, 125.4, 122.9, 120.9, 120.8, 78.4, 75.9, 62.7, 29.0, 28.0, 22.2, 13.7; **HRMS (ESI)** calculated for [C₂₈H₂₇BrNO] [M+H]⁺: 472.1271, found: 472.1277.

2) **5-(4-bromophenyl)-2-butyl-2'-phenylspiro[cyclopentane-1,3'-indolin]-2-en-4-one (6)**



To a dried reaction tube containing compound **3a** (90.0 mg, 0.20 mmol, 1.0 equiv.) in MeOH (2 mL) at RT was added NaBH₃CN (50.3 mg, 0.40 mmol, 2.0 equiv.), and AcOH (28.8 mg, 0.24 mmol, 1.2 equiv.). After 48 h, the reaction was quenched with saturated aqueous NaHCO₃ (10 mL), extracted successively with EA (3×10 mL), and the combined organics washed with brine (10 mL), dried by Na₂SO₄. The solvent was removed under reduced pressure. Then the residue was purified by silica gel column chromatography (PE/EA = 50:1 to 20:1) to afford the desired yellow solid product **6a**.

(51.5 mg, 57%) and yellow oil product **6b** (11.7 mg, 13%): Two diastereoisomers can be separated by column chromatography on silica gel. **¹H NMR (500 MHz, CDCl₃)** δ 7.41 (d, *J* = 5.0 Hz, 4H), 7.36 – 7.32 (m, 1H), 7.07 (d, *J* = 8.2 Hz, 2H), 6.95 – 6.90 (m, 1H), 6.58 (d, *J* = 8.1 Hz, 3H), 6.49 (t, *J* = 7.4 Hz, 1H), 6.41 (d, *J* = 9.5 Hz, 2H), 5.32 (s, 1H), 4.14 (s, 1H), 3.56 (s, 1H), 2.70 – 2.58 (m, 1H), 2.52 – 2.45 (m, 1H), 1.82 – 1.73 (m, 2H), 1.47 (q, *J* = 7.4 Hz, 2H), 0.98 (t, *J* = 7.3 Hz, 3H); **¹³C NMR (125 MHz, CDCl₃)** δ 206.9, 180.9, 150.1, 137.4, 136.3, 132.3, 131.5, 130.4, 129.1, 128.9, 128.6, 128.3, 126.8, 125.2, 120.3, 119.0, 109.8, 70.3, 67.8, 57.5, 30.4, 29.5, 22.6, 13.9; m.p. = 125.7 - 126.3 °C; **HRMS (ESI)** calculated for [C₂₈H₂₆BrNNaO] [M+Na]⁺: 494.1090, found: 494.1086. **¹H NMR (500 MHz, CDCl₃)** δ 7.35 – 7.28 (m, 5H), 7.27 – 7.25 (m, 2H), 7.00 (t, *J* = 7.7 Hz, 1H), 6.84 (d, *J* = 8.5 Hz, 2H), 6.72 (d, *J* = 7.8 Hz, 1H), 6.42 (t, *J* = 7.5 Hz, 1H), 6.11 (s, 1H), 6.09 (d, *J* = 7.5 Hz, 1H), 5.07 (s, 1H), 4.26 (s, 1H), 4.14 (s, 1H), 1.75 – 1.68 (m, 1H), 1.40 – 1.33 (m, 1H), 1.28 – 1.20 (m, 2H), 1.02 – 0.95 (m, 2H), 0.66 (t, *J* = 6.9 Hz, 3H); **¹³C NMR (125 MHz, CDCl₃)** δ 207.0, 184.2, 151.1, 139.4, 136.6, 131.2, 131.1, 130.6, 128.7, 128.6, 128.3, 126.8, 126.6, 126.1, 121.0, 118.9, 109.3, 74.7, 68.6, 65.1, 30.5, 29.3, 22.2, 13.6; **MALDI-MS** calculated for [C₂₈H₂₇BrNO] [M+H]⁺: 472.1276, found: 472.0580.

7. The studies of biological activity

Antibacterial activity of compounds **3**, **5** and **6a** against *Xanthomonas oryzae* pv. *oryzae* (*Xoo*) and *Xanthomonas axonopodis* pv. *citri* (*Xac*):

Antibacterial activities of the title compounds against *Xoo* and *Xac* were evaluated by using the turbidimeter test. Thiodiazole-copper was used as the positive controls. The compound was dissolved in 150.0 μL of dimethylformamide and diluted with 0.1% (V/V) Tween-20 to prepare the solutions on a concentration of 100 $\mu\text{g/mL}$. 1.0 mL of the above solution was added to the non-toxic nutrient broth (NB: 1.5 g of beef extract, 2.5 g of peptone, 0.5 g of yeast powder, 5.0 g of glucose and 500 mL of distilled water, pH = 7.0 ~ 7.2) liquid medium in a 4.0 mL tube. Then, 40.0 μL of NB solution containing *Xanthomonas oryzae* pv. *oryzae* (*Xoo*) or *Xanthomonas axonopodis* pv. *citri* (*Xac*) was added to 5.0 mL of the NB solution containing the test compound. The inoculated test tube was incubated at $(28 \pm 1)^\circ\text{C}$ under continuous shaking at 200 rpm for 24 h. The culture growth was monitored by measuring the optical density at 595 nm (OD_{595}) and expressed as corrected turbidity. The relative inhibitory rate was calculated as follows:

$$I(\%) = (C_{\text{tur}} - T_{\text{tur}}) / C_{\text{tur}} \times 100\%$$

C_{tur} : the corrected turbidity value of bacterial growth on untreated NB;

T_{tur} : the corrected turbidity value of bacterial growth on treated NB;

I : The relative inhibitory rate.^[4]

Supplementary Table 3. Inhibition rate of compound **3**, **5** and **6a** against *Xoo* and *Xac* at (100 $\mu\text{g/mL}$). ^[a]

compounds	<i>Xoo</i> inhibition rate [%]	<i>Xac</i> inhibition rate [%]
3a	50.05 \pm 2.68	7.37 \pm 3.81
3b	29.58 \pm 1.95	43.49 \pm 5.03
3c	24.34 \pm 1.54	45.04 \pm 3.35
3d	54.41 \pm 5.65	5.42 \pm 2.28
3e	13.28 \pm 1.94	68.54 \pm 1.26
3f	56.50 \pm 2.28	23.49 \pm 3.89
3g	21.42 \pm 4.48	46.13 \pm 3.06

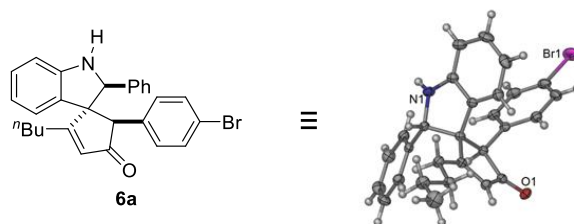
3h	64.68±2.88	42.40±2.0
3i	3.82±3.35	48.15±3.32
3k	0	41.21±0.59
3l	71.68±1.27	67.38±2.52
3m	23.27±2.58	19.74±1.87
3n	50.82±1.23	25.67±2.99
3o	65.08±1.65	0
3p	41.31±0.58	65.29±1.26
3q	71.77±0.22	78.45±0.44
3r	56.64±0.77	54.87±1.27
3s	33.22±0.57	52.70±2.27
3t	62.07±0.38	76.06±1.27
3u	44.22±2.71	58.93±2.05
3v	63.63±2.52	0
5	76.72±0.70	78.73±2.46
6a	29.43±0.46	33.84±1.02
BT^[b]	53.29±1.30	53.72±2.11
TC^[b]	49.88±1.36	49.60±1.97

^[a] All data were average data of three replicates; ^[b] Commercial bactericide was used as the positive control, **BT** = Bismethiazol, **TC** = Thiodiazole-copper.

8. References

1. a) H. Wang, J. R. Denton, H. M. L. Davies, *Org. Lett.* **2011**, *13*, 4316–4319; b) X. Liu, M. Li, K. Dong, S. Peng, L. Liu, *Org. Lett.* **2022**, *24*, 2175–2180; c) X. Liu, Z. Tang, Z. Li, L. Xu, L. Liu, *Nat. Commun.* **2021**, *12*, 7298. c) X. Ji, C. Shen, Y. Ni, Z.-Y. Si, Y. Wang, X. Zhi, Y. Zhao, H. Peng and L. Liu, *Angew. Chem. Int. Ed.* **2024**, e202400805 (3 of 8).
2. J. Zhao, Y. Zhang, and K. Cheng, *J. Org. Chem.* **2008**, *73*, 7428–7431.
3. a) Á. González-Gómez, G. Domínguez, and J. Pérez-Castells, *Eur. J. Org. Chem.* **2009**, 5057–5062; b) S. S. K. Boominathan, G. C. Senadi, J. K. Vandavasi, J. Y.-F. Chen, and J.-J. Wang, *Chem. Eur. J.* **2015**, *21*, 3193–3197; c) Z. Chen, X.-X. Shi, D.-Q. Ge, Z.-Z. Jiang, Q.-Q. Jin, H.-J. Jiang, J.-S. Wu, *Chinese Chemical Letters* **2017**, *28*, 231–234; d) Y. Jiang and S. Youn, *Org. Lett.* **2014**, *16*, 3720–3723.
4. Y. Chen, T. Li, Z. Jin, Y. R. Chi, *J. Agric. Food Chem.* **2022**, *70*, 6050–6058.

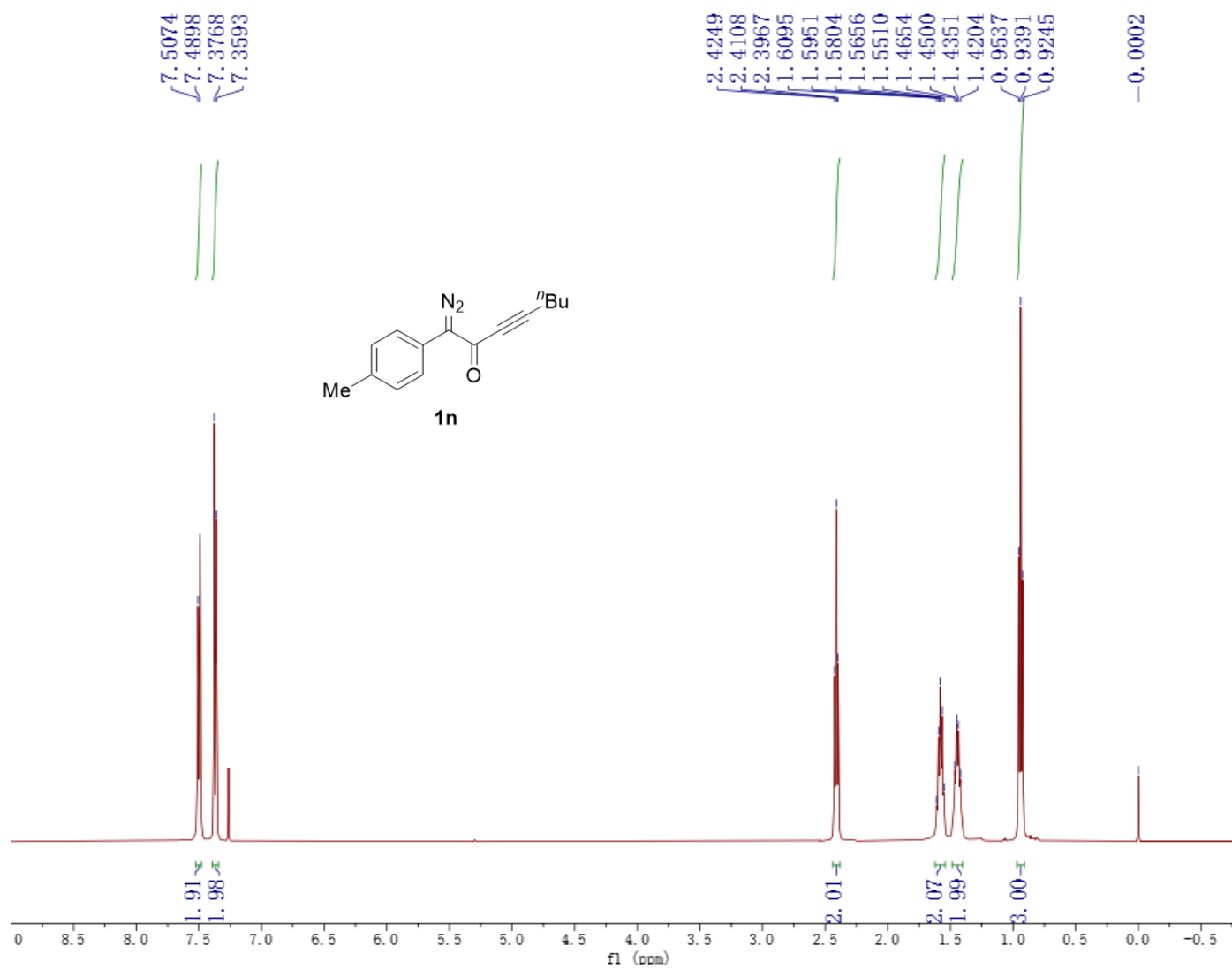
9. X-ray Crystal data for 6a

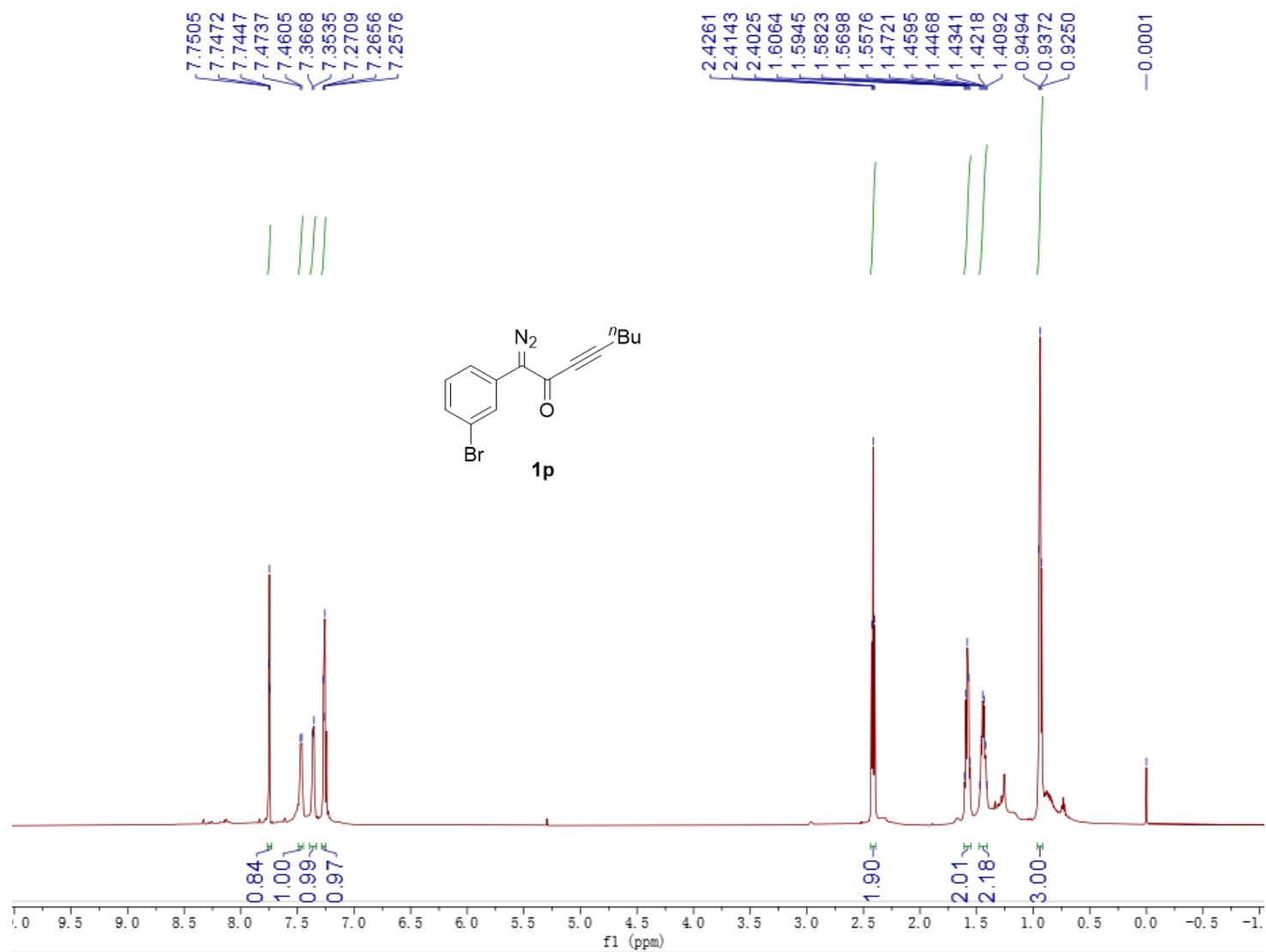


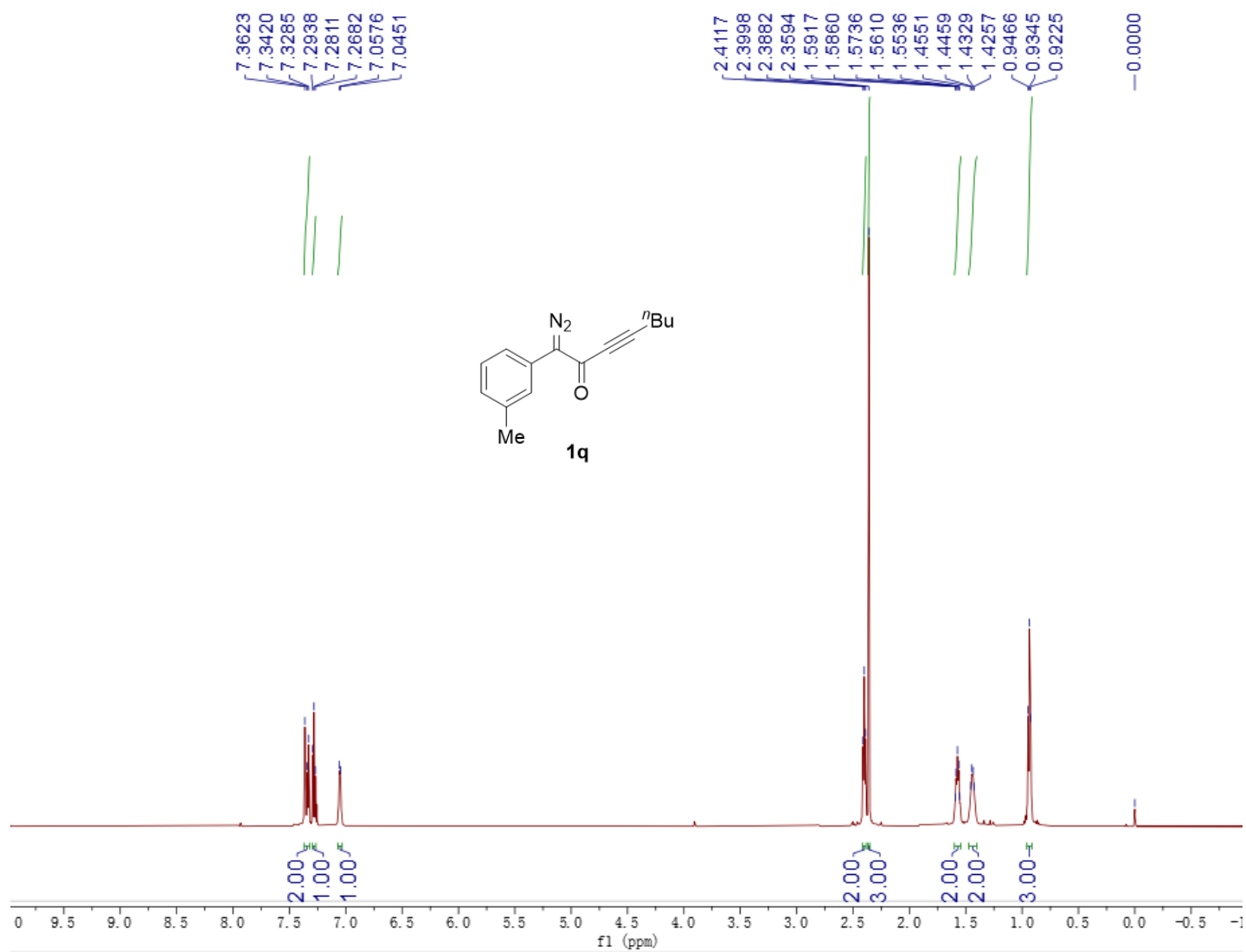
Crystal data and structure refinement for exp_4174_auto.

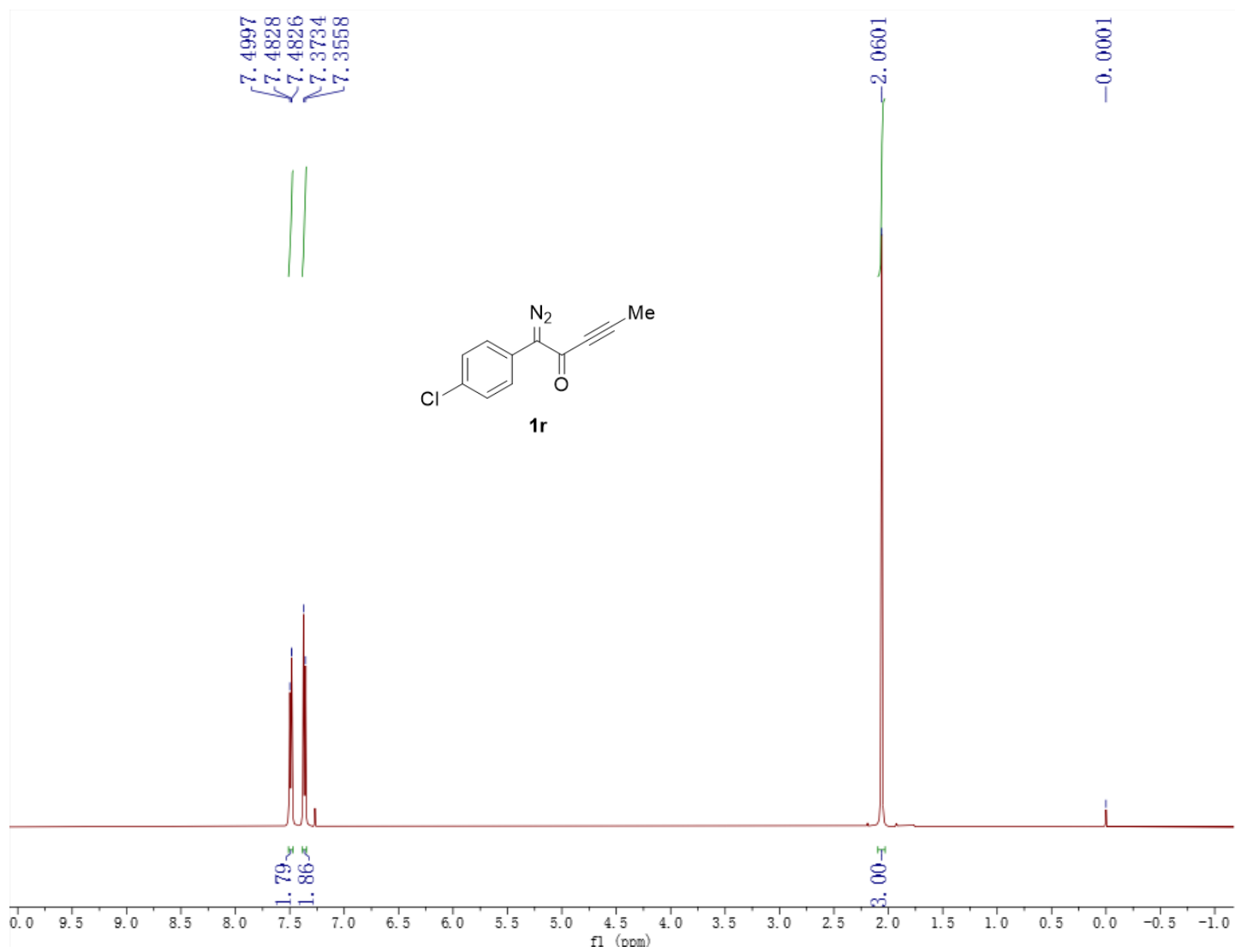
Identification code	exp_4174_auto
Empirical formula	C ₂₈ H ₂₆ BrNO
Formula weight	472.41
Temperature/K	169.99(10)
Crystal system	orthorhombic
Space group	P2 ₁ 2 ₁ 2 ₁
a/Å	15.45840(10)
b/Å	15.99770(10)
c/Å	18.87770(10)
α/°	90
β/°	90
γ/°	90
Volume/Å ³	4668.43(5)
Z	8
ρ _{calc} /cm ³	1.344
μ/mm ⁻¹	2.538
F(000)	1952.0
Crystal size/mm ³	0.26 × 0.22 × 0.18
Radiation	Cu Kα (λ = 1.54184)
2θ range for data collection/°	7.244 to 134.15
Index ranges	-18 ≤ h ≤ 18, -19 ≤ k ≤ 19, -22 ≤ l ≤ 22
Reflections collected	133994
Independent reflections	8340 [R _{int} = 0.0567, R _{sigma} = 0.0191]
Data/restraints/parameters	8340/0/561
Goodness-of-fit on F ²	1.042
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0230, wR ₂ = 0.0596
Final R indexes [all data]	R ₁ = 0.0236, wR ₂ = 0.0600
Largest diff. peak/hole / e Å ⁻³	0.33/-0.48
Flack parameter	-0.020(4)

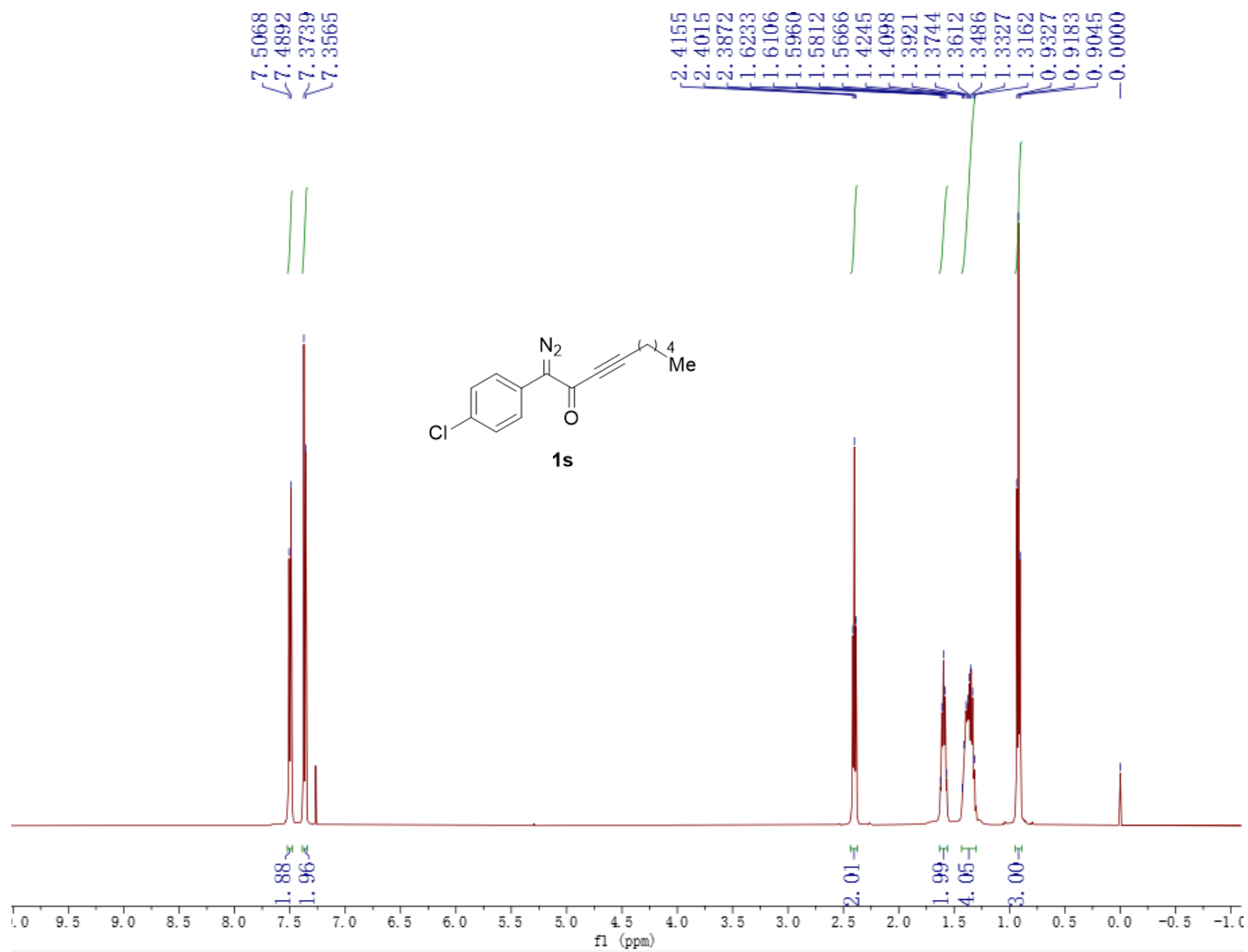
10. NMR and HRMS spectra of new compounds

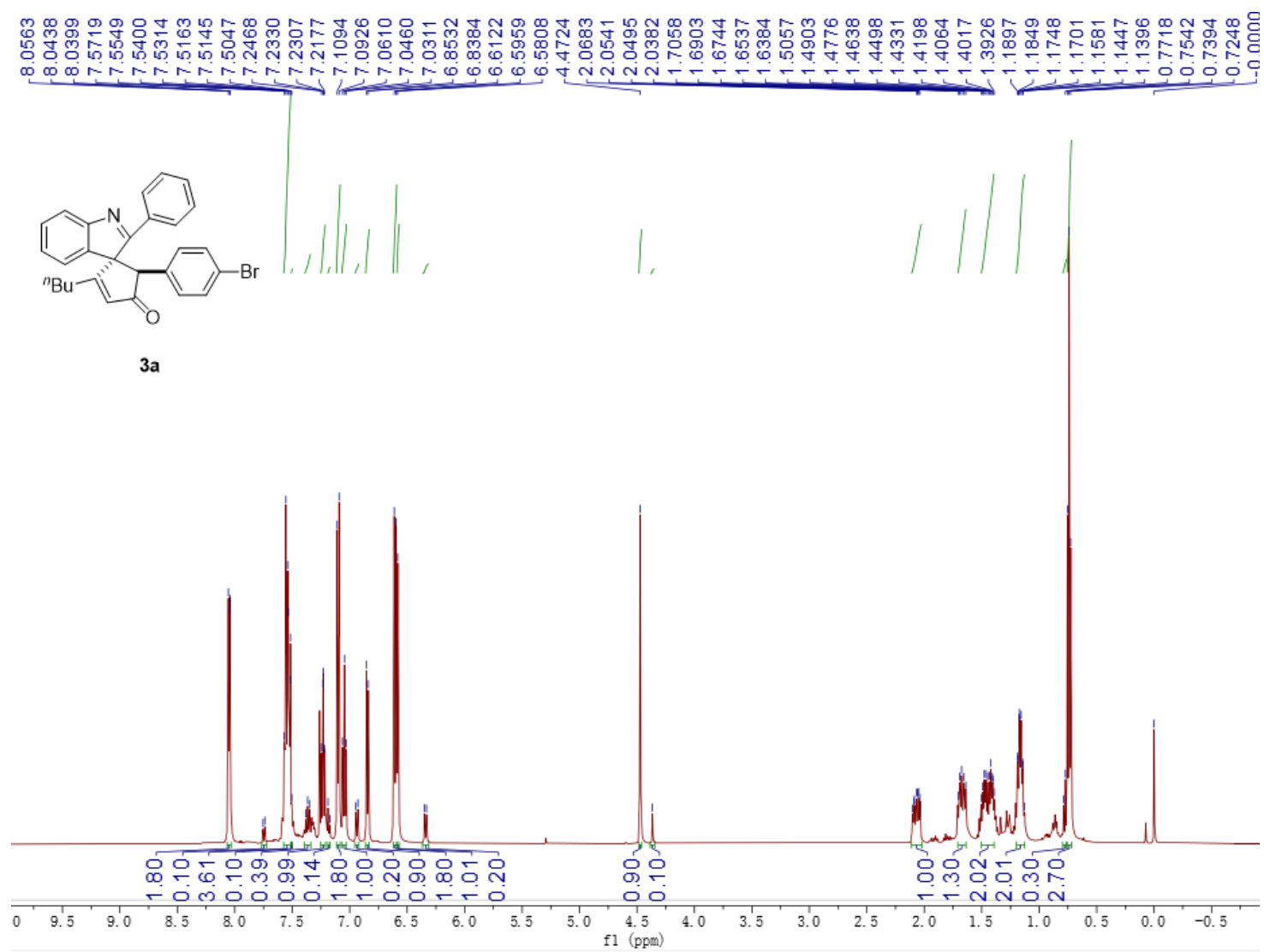


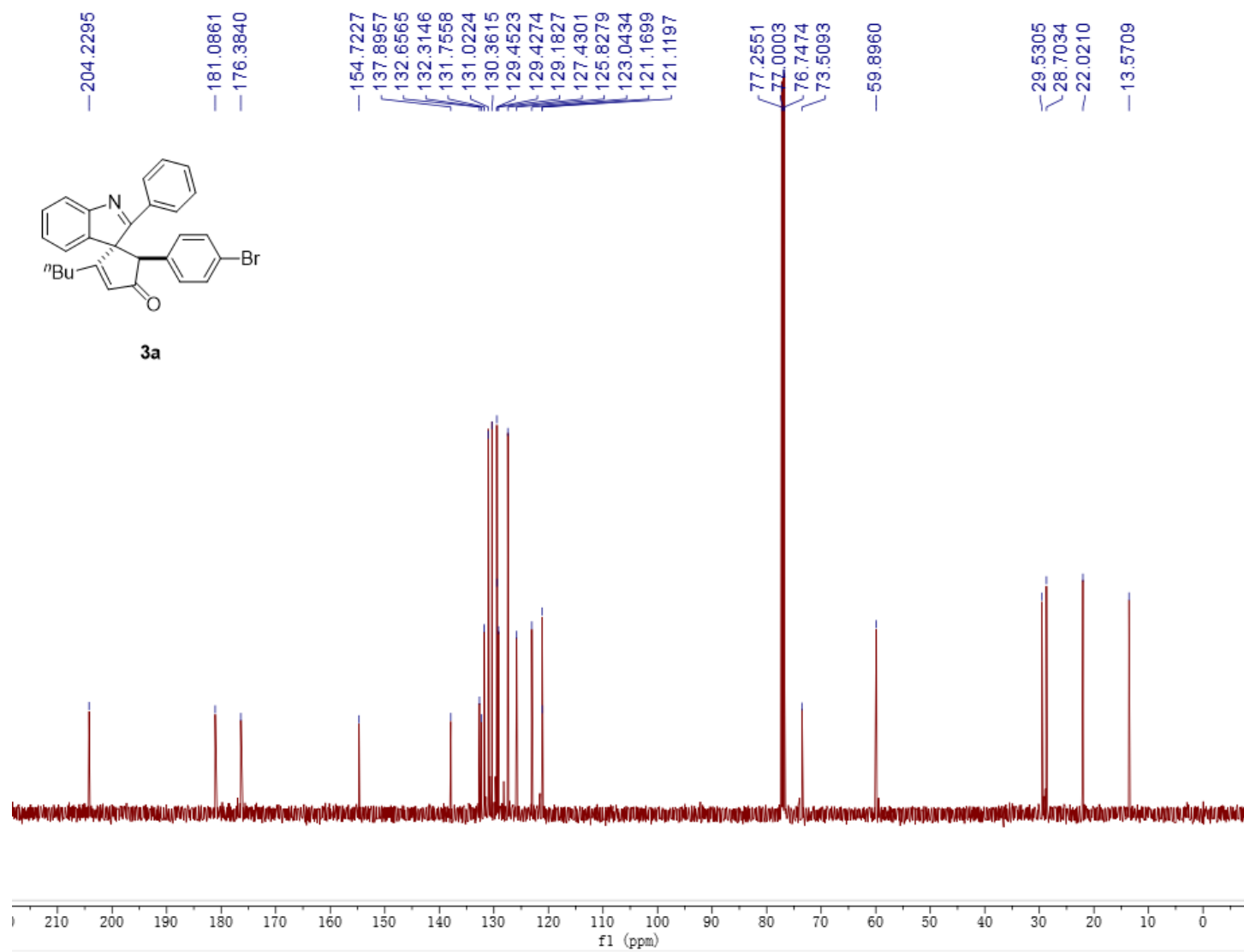


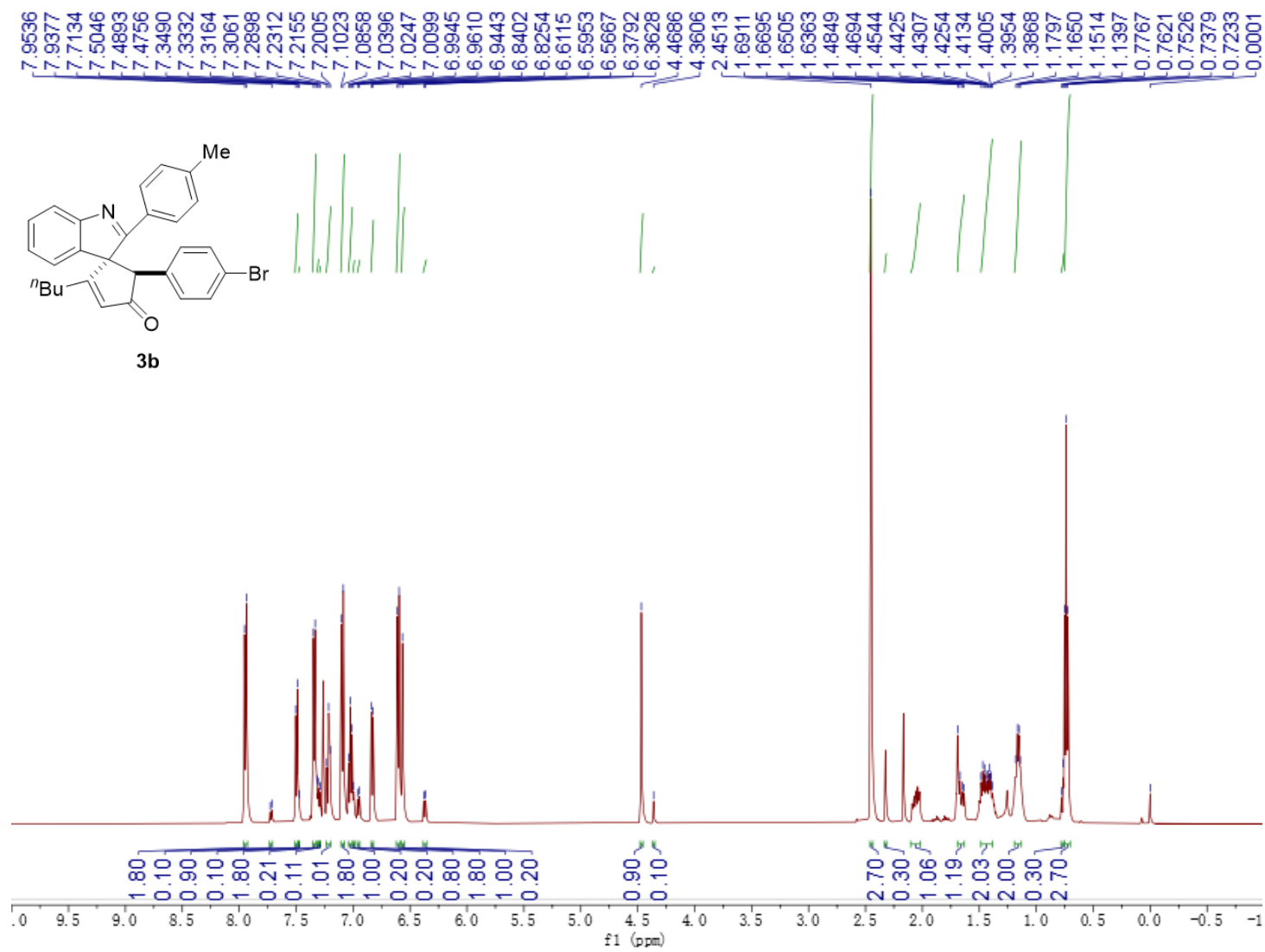


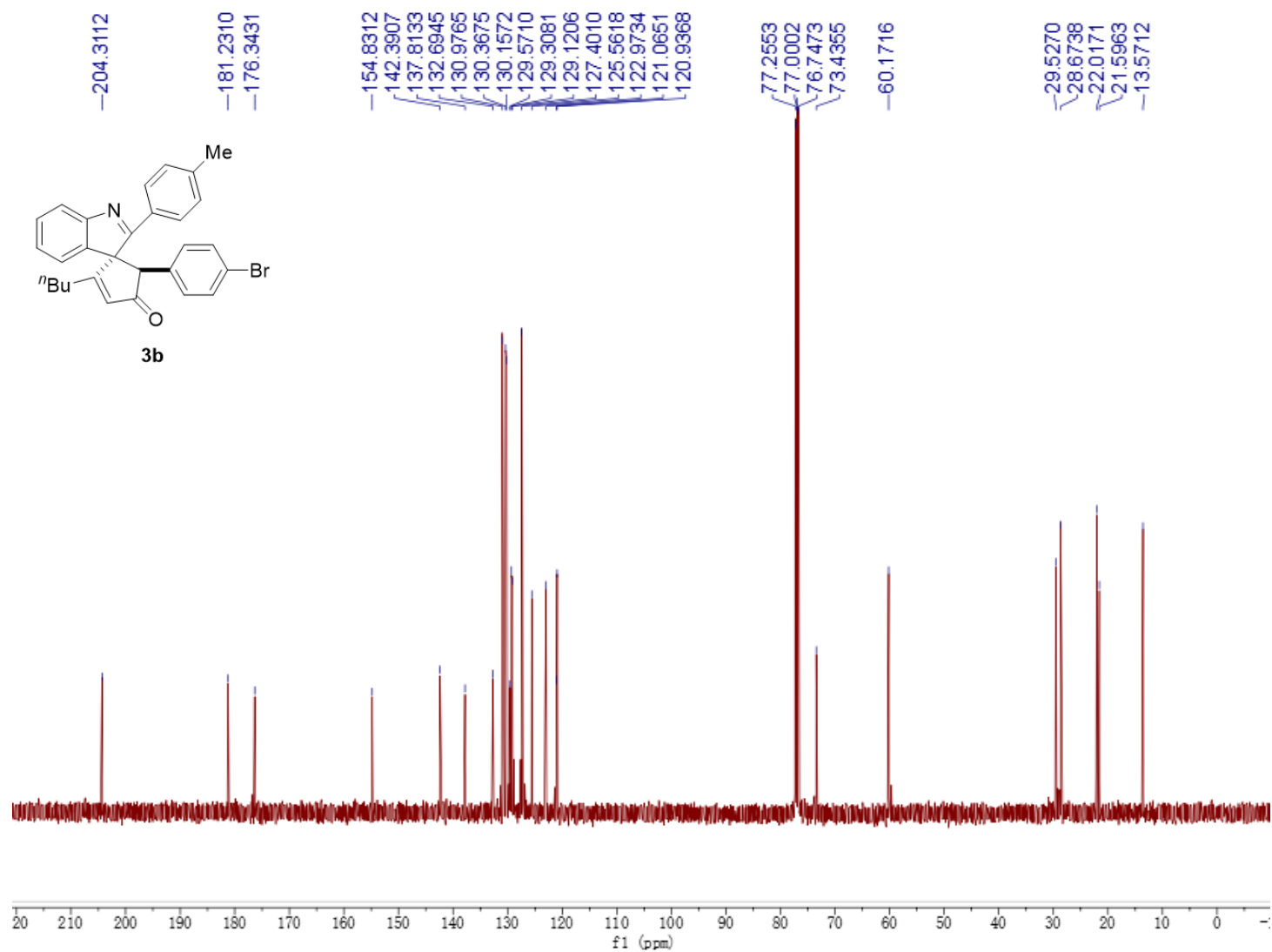


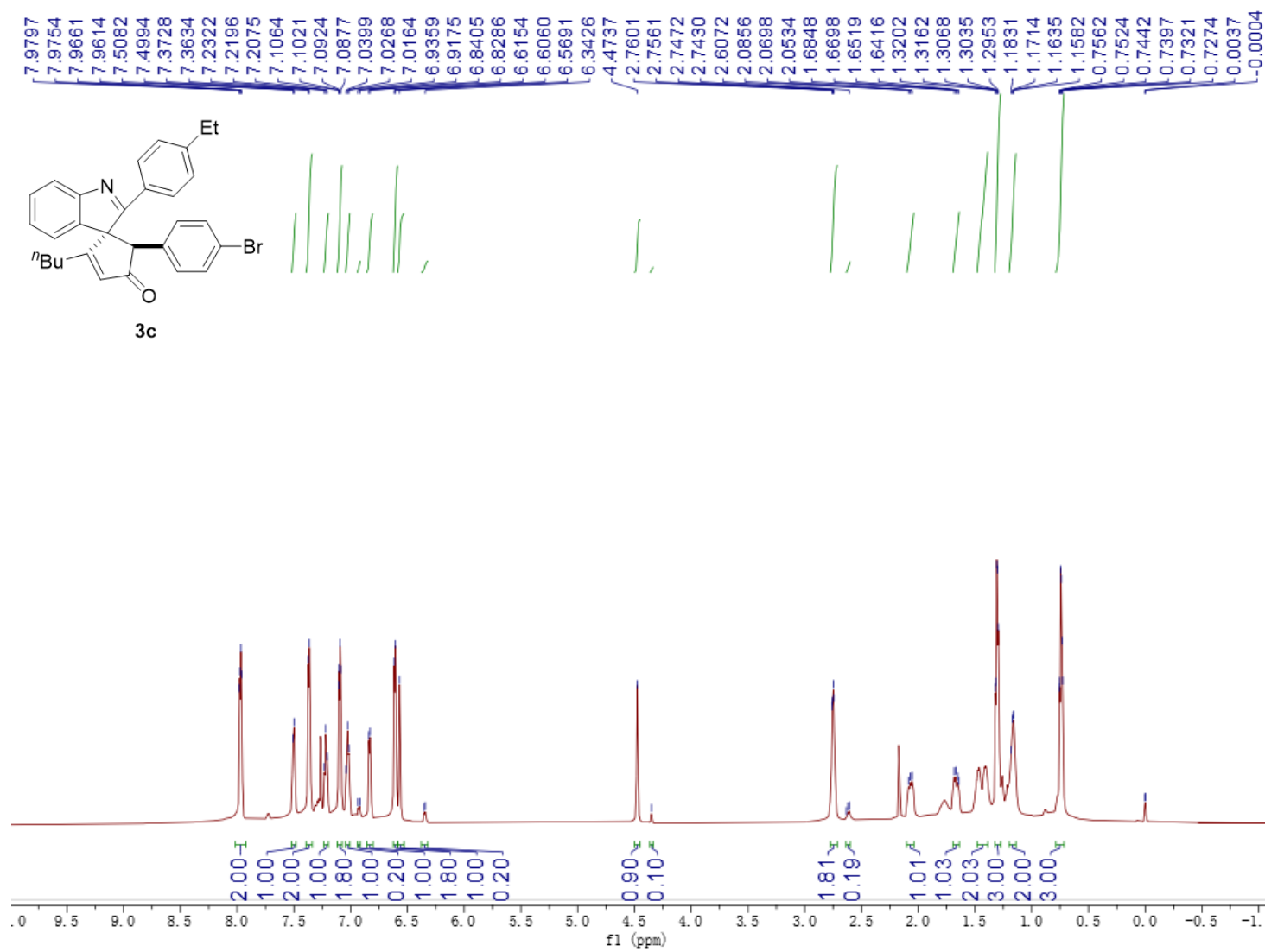


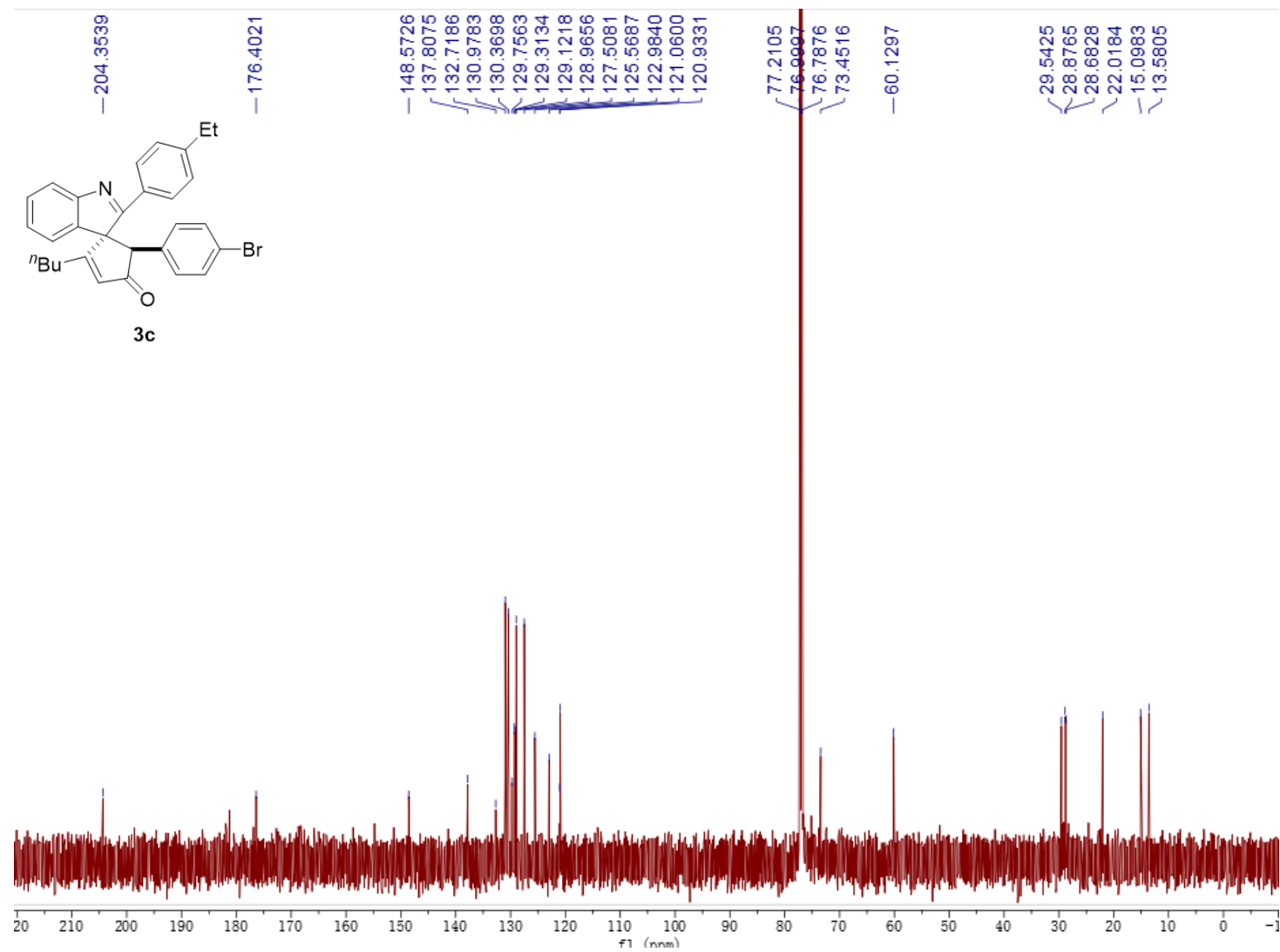


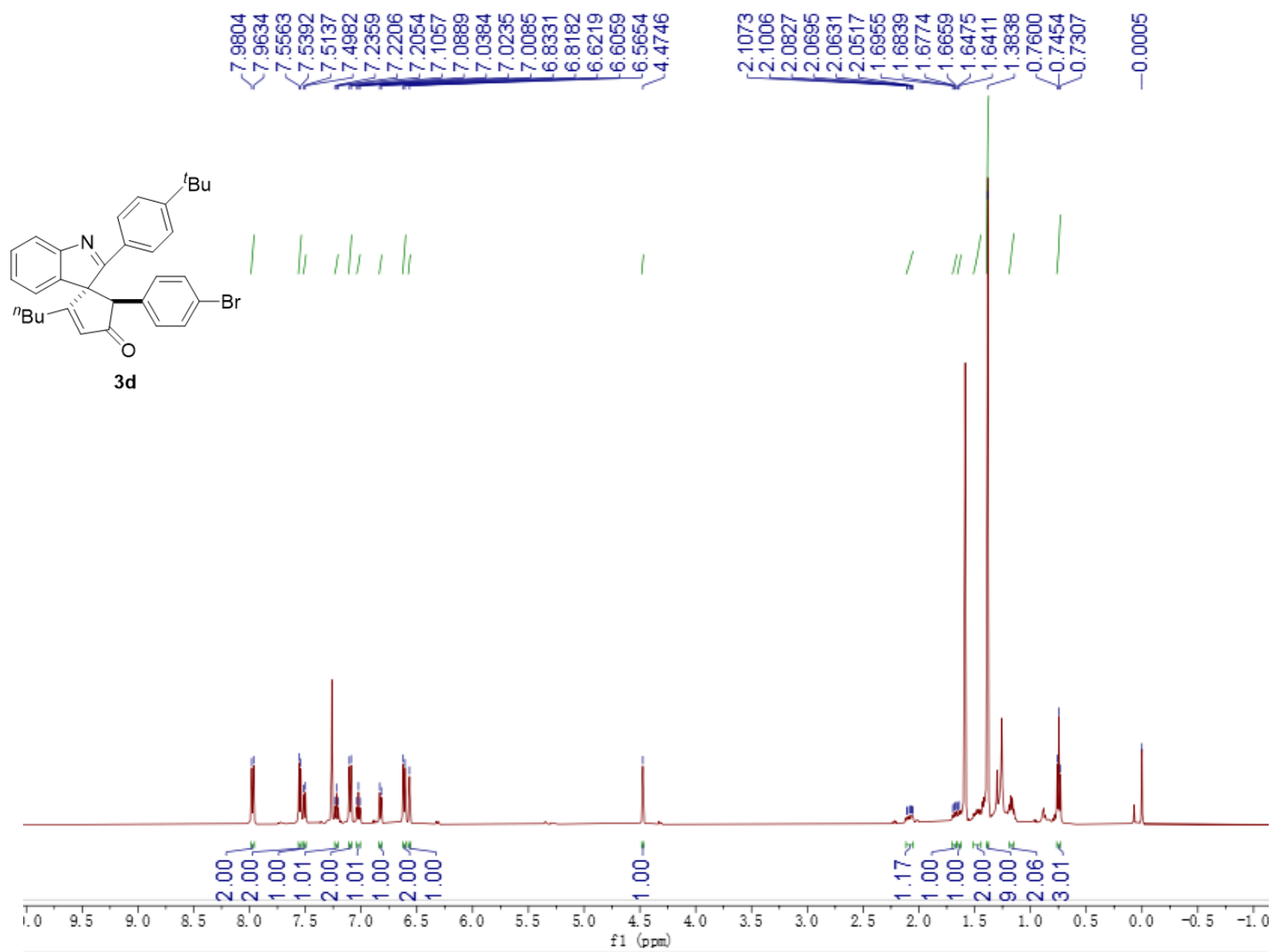


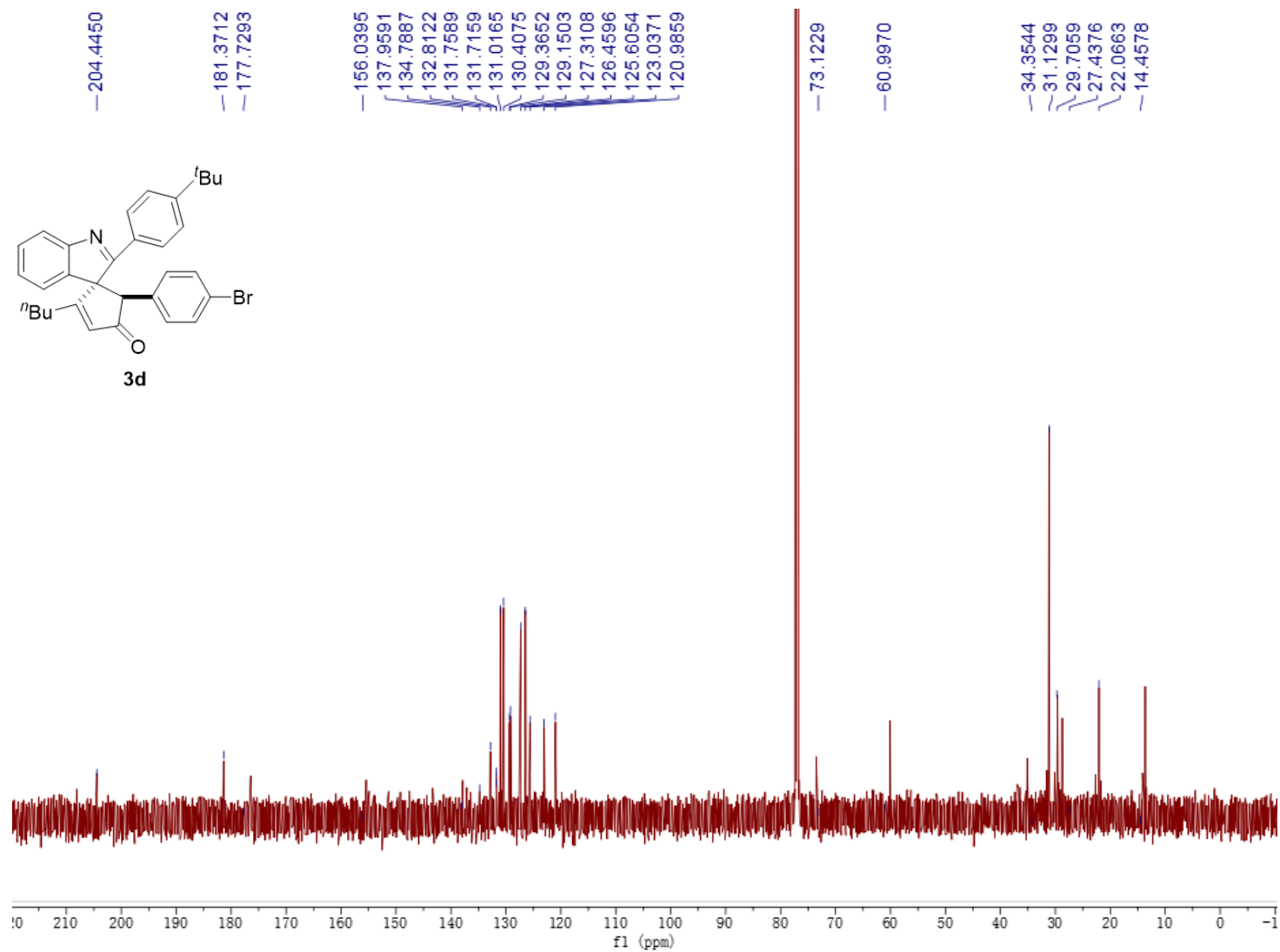


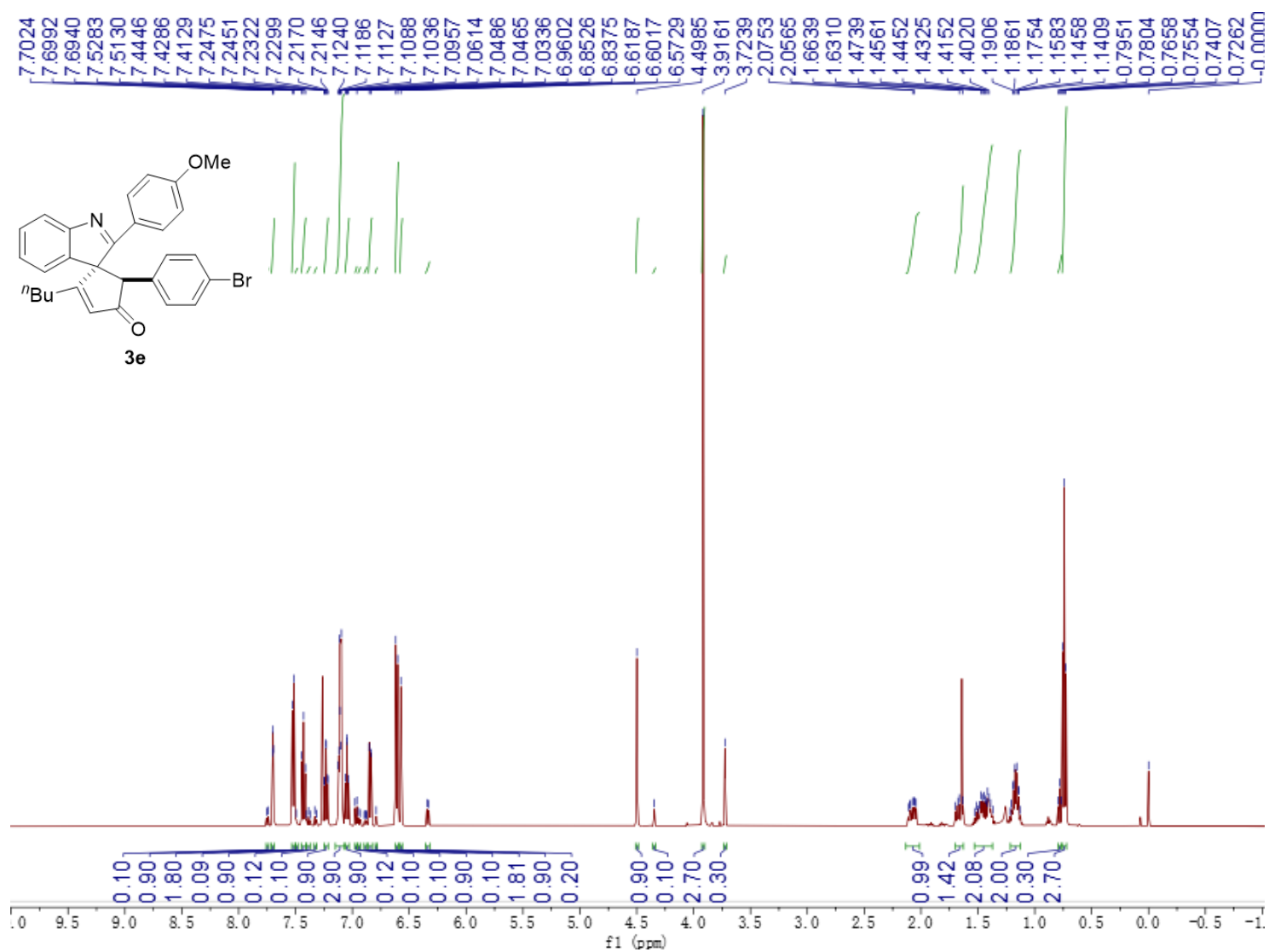


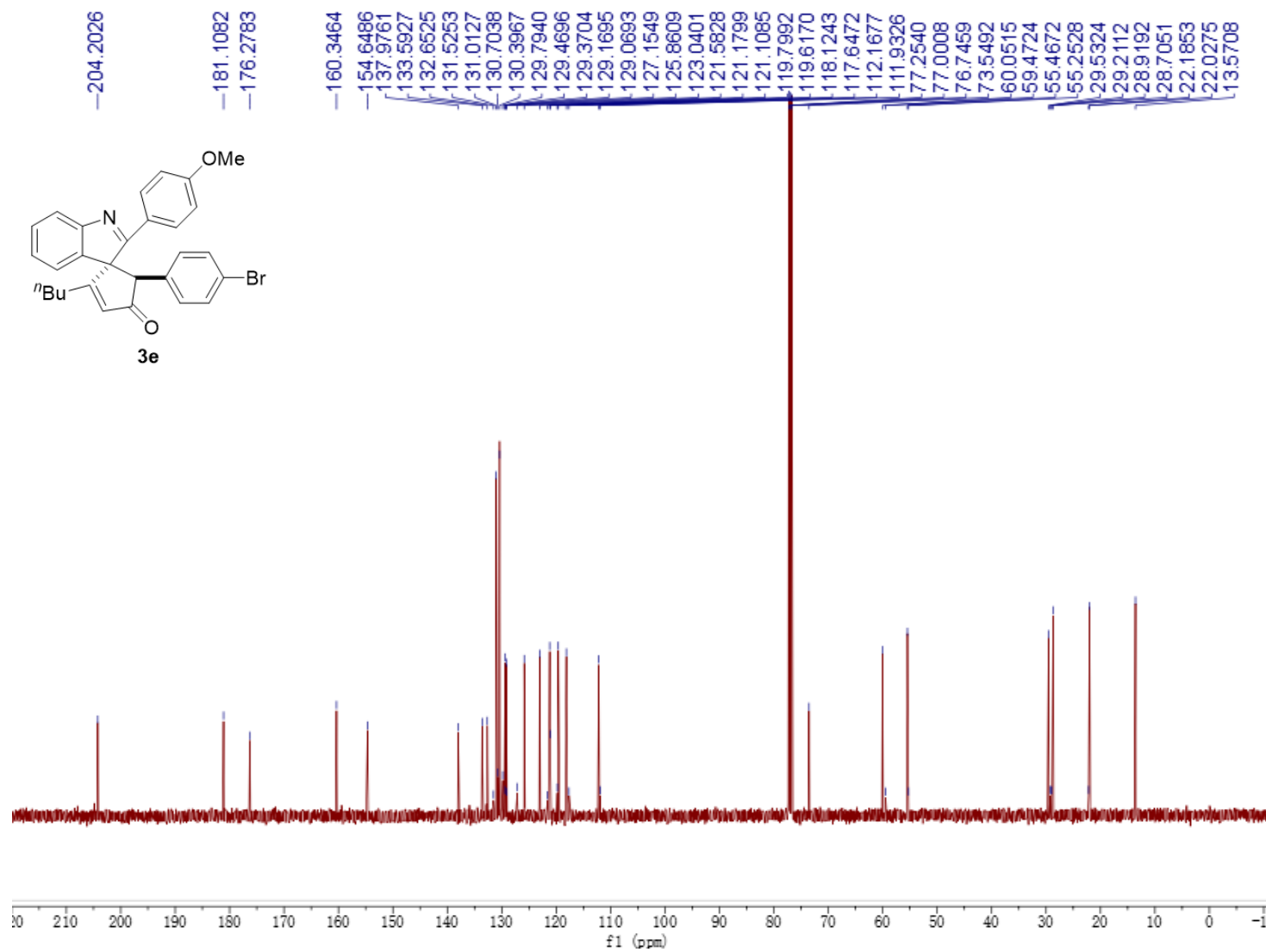


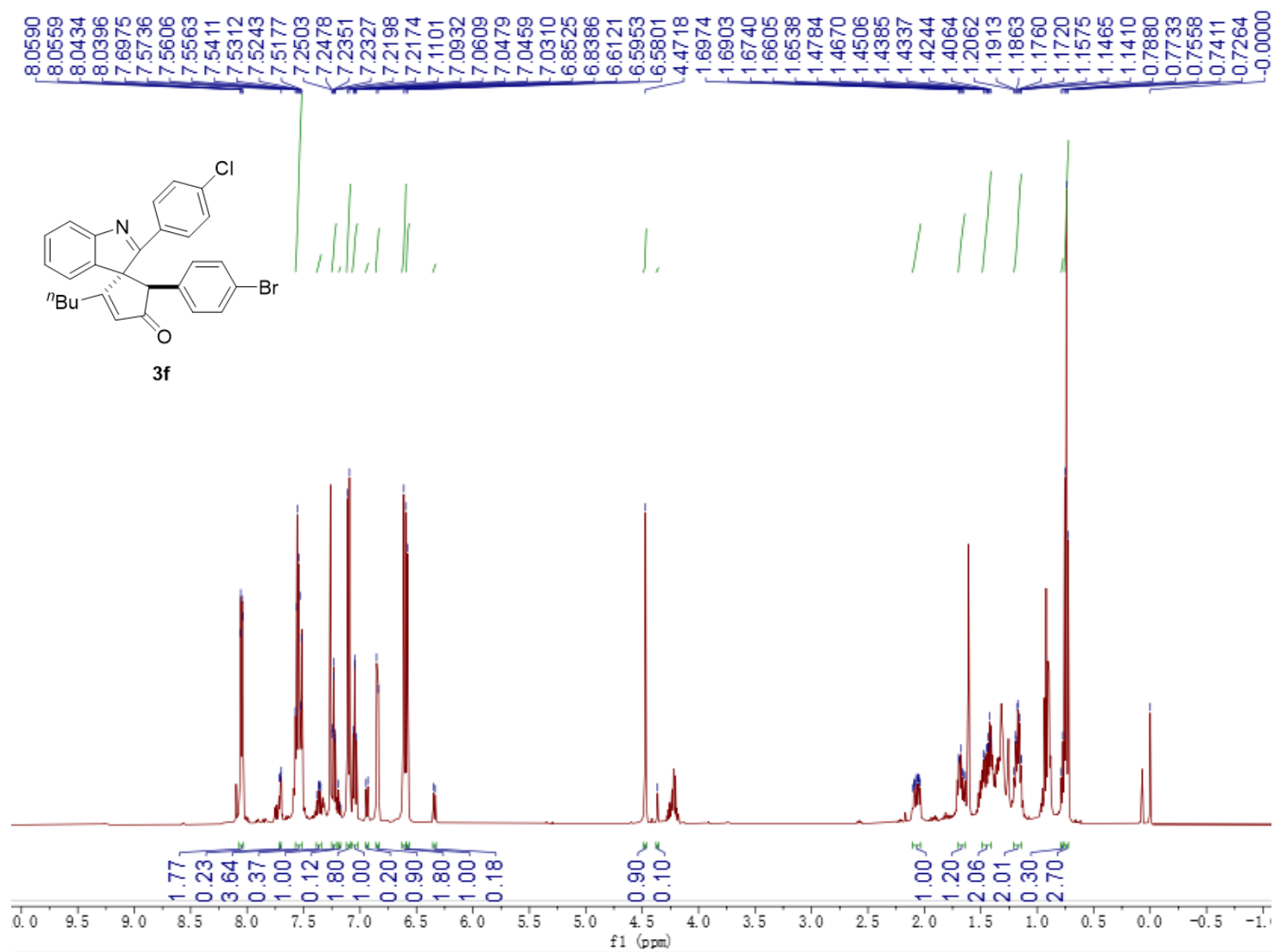


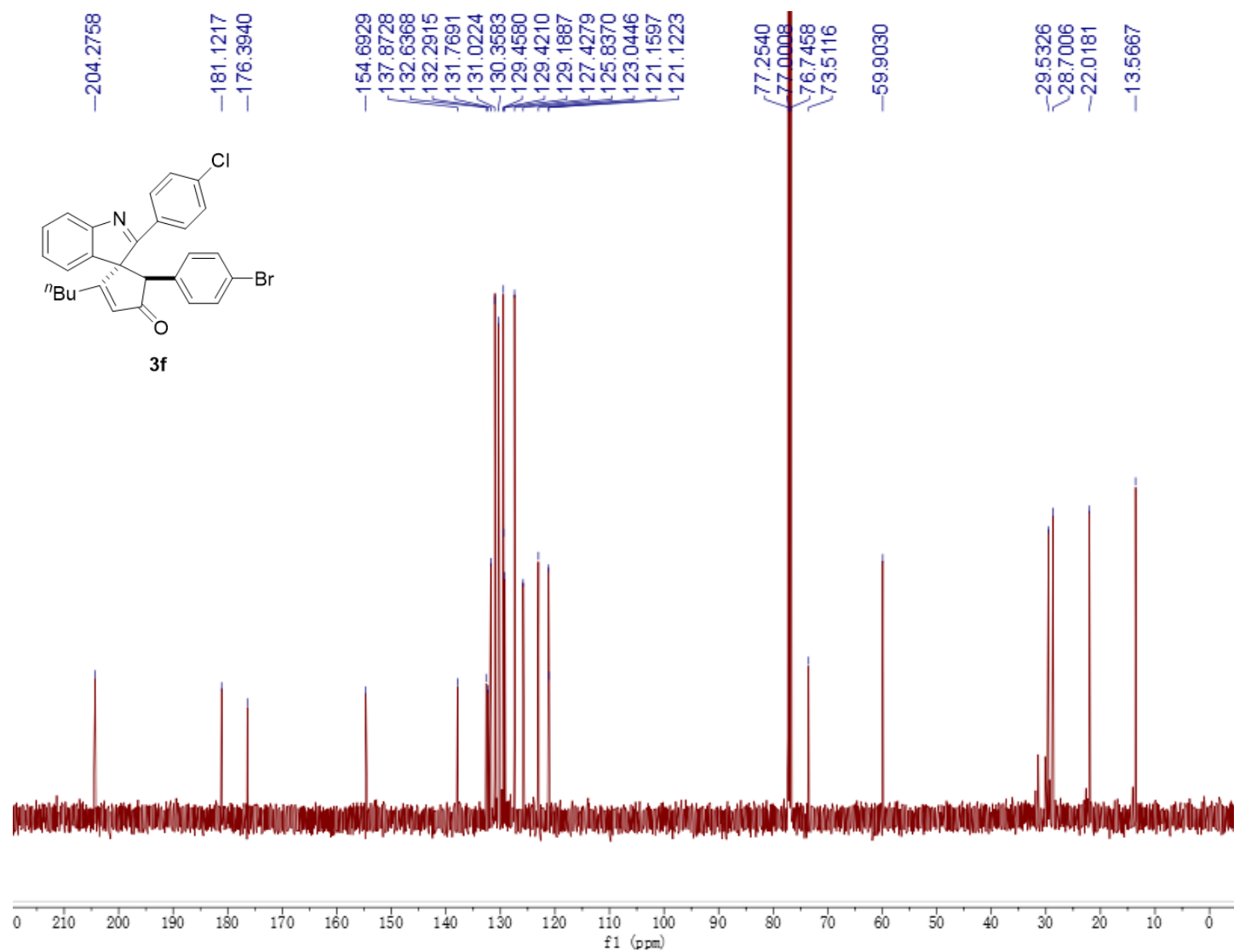


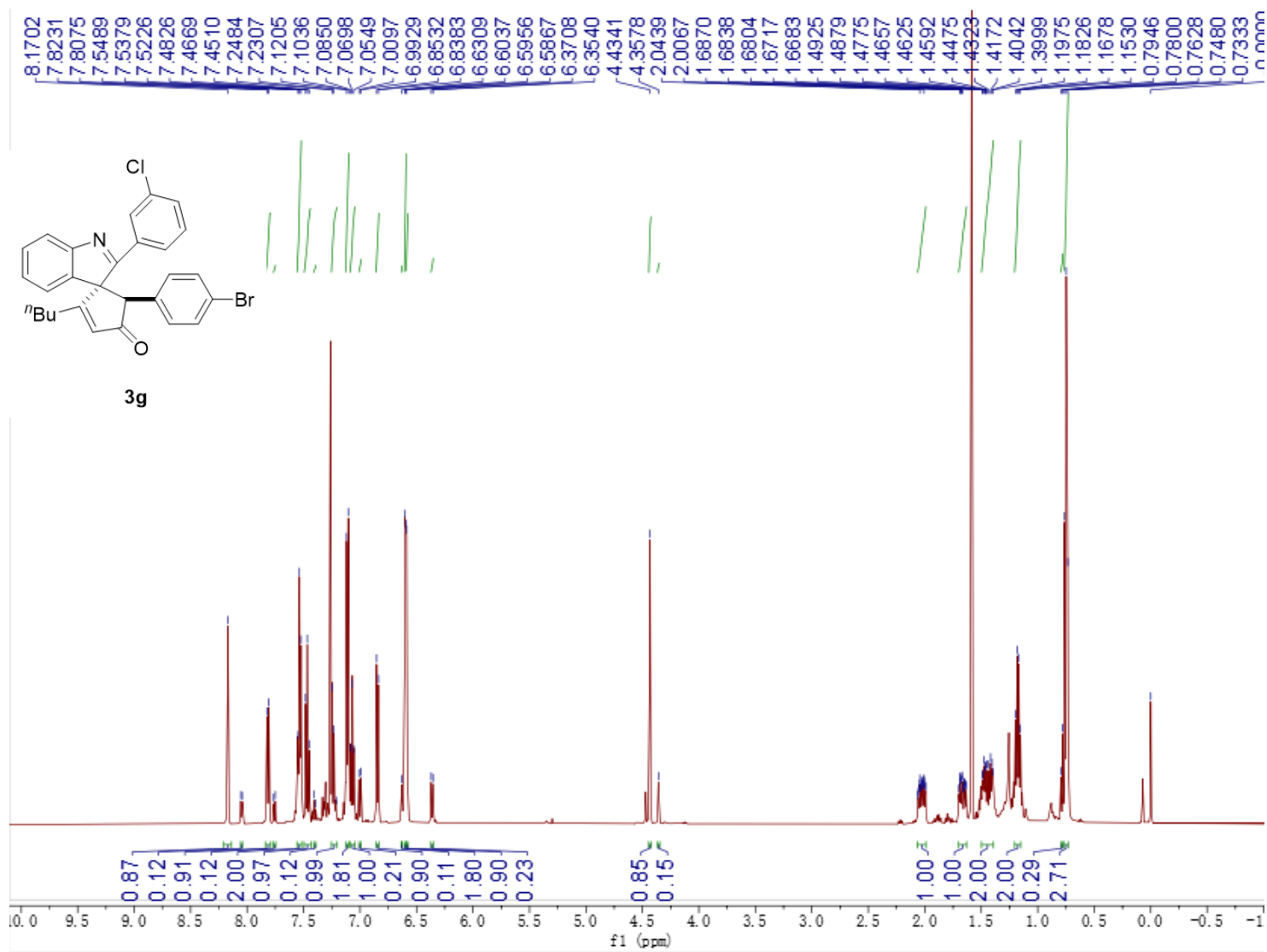


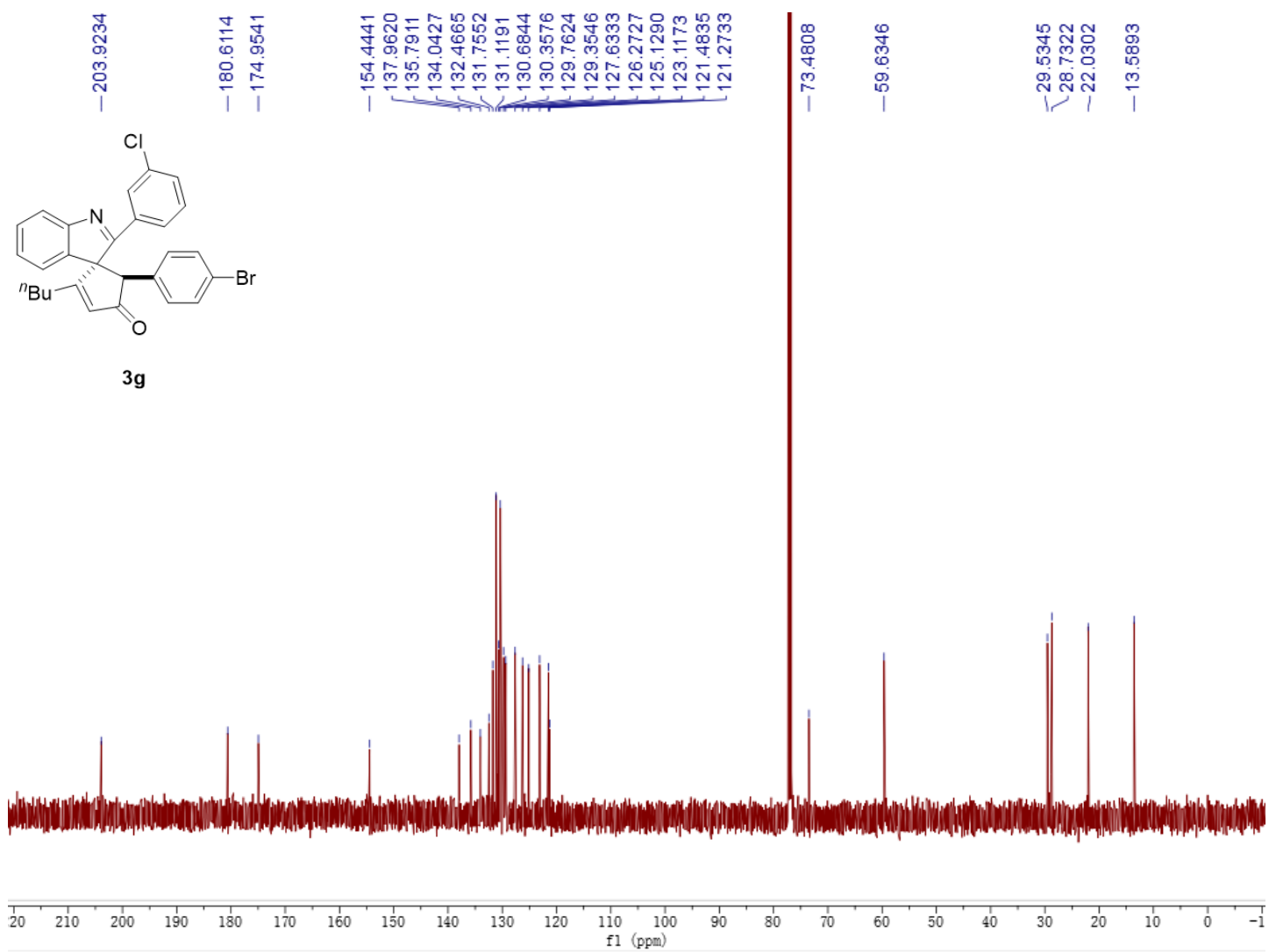


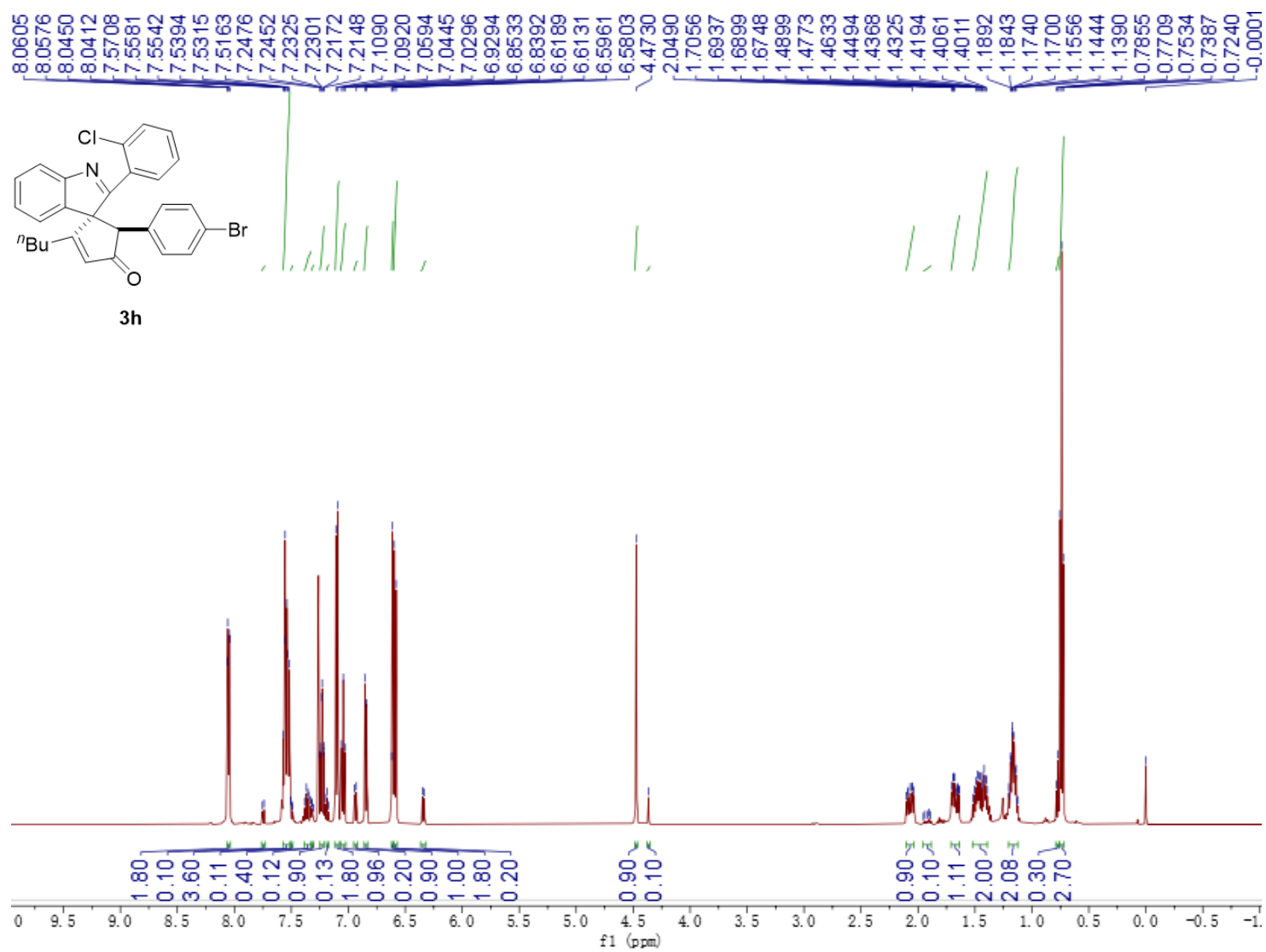


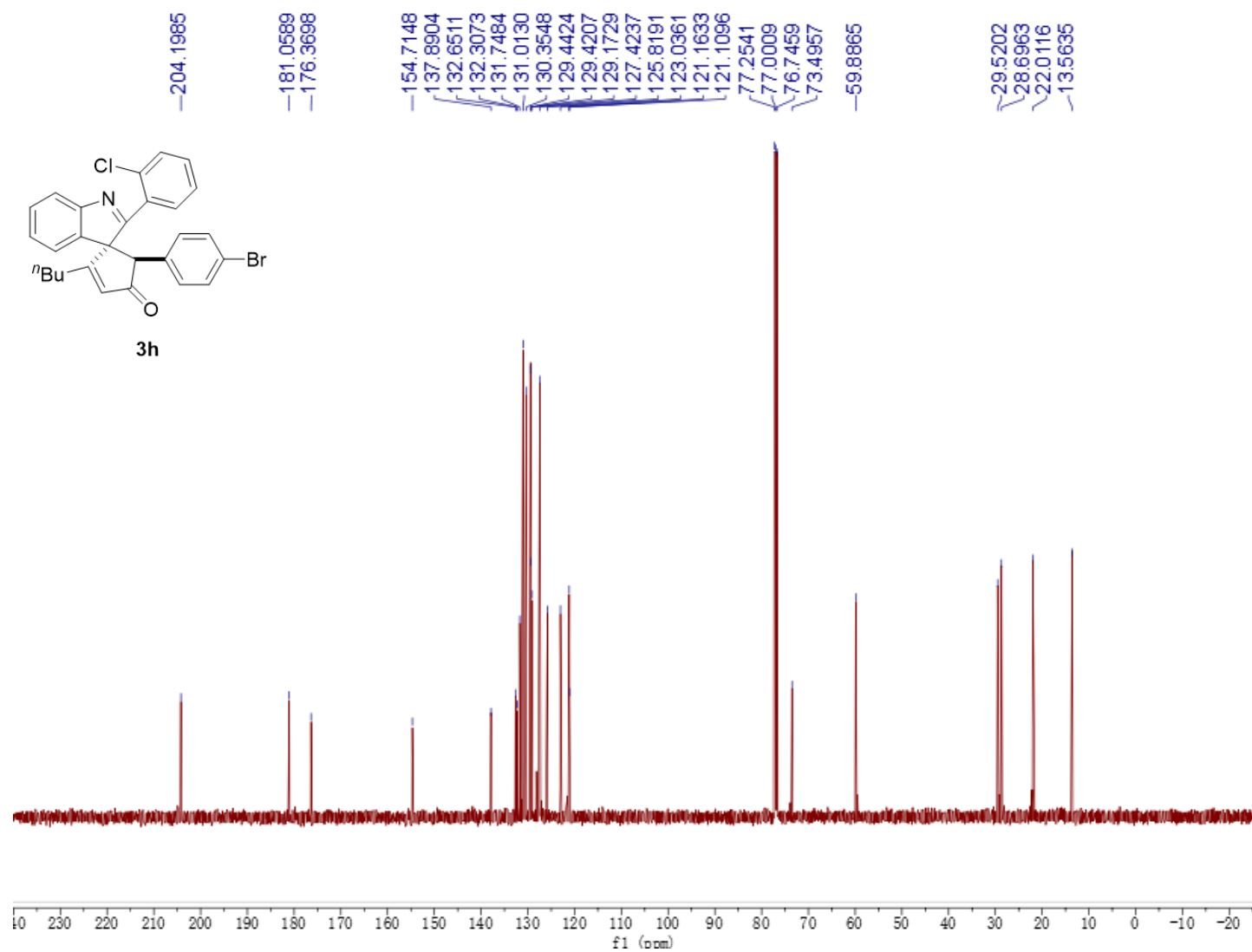


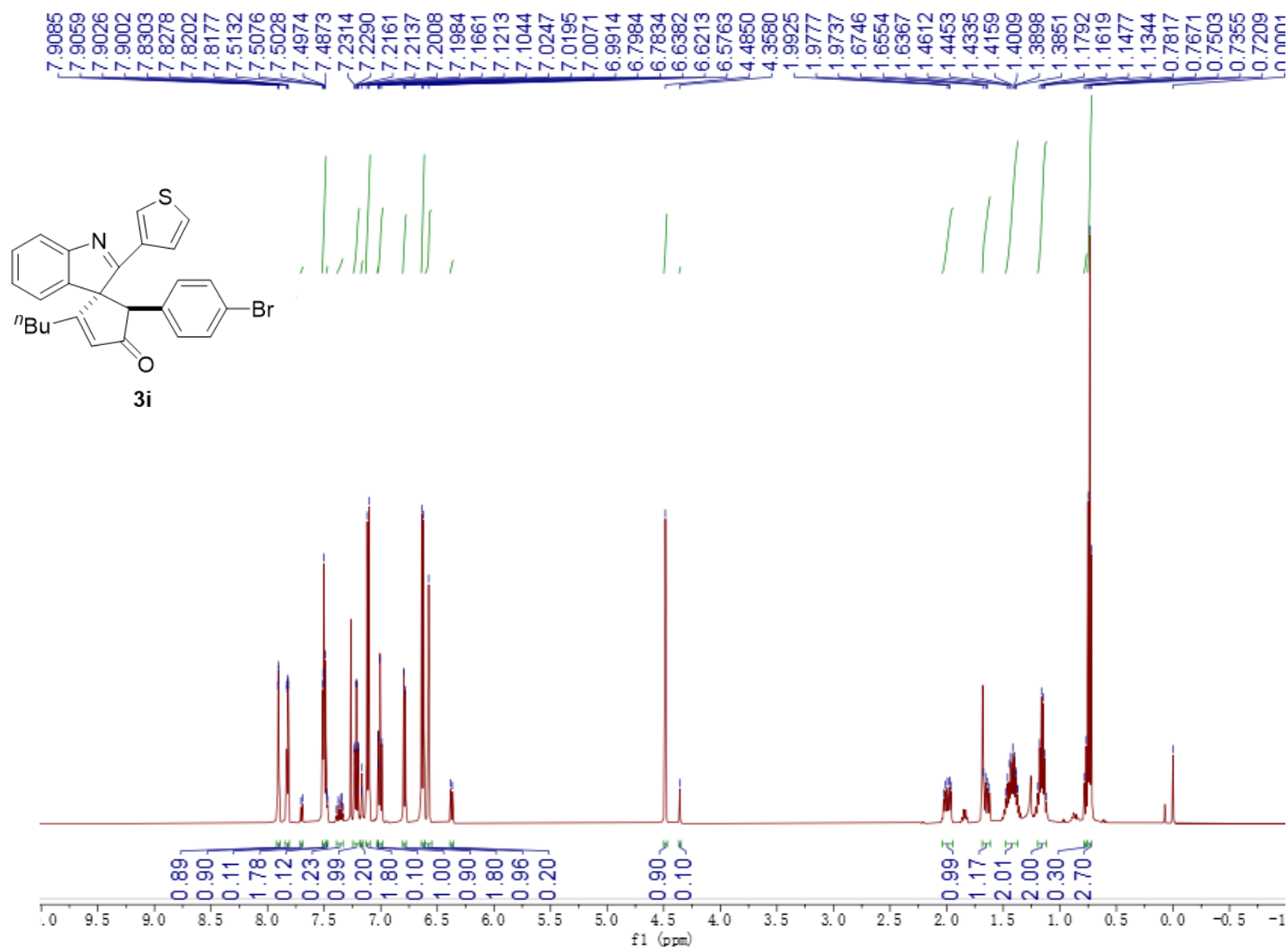


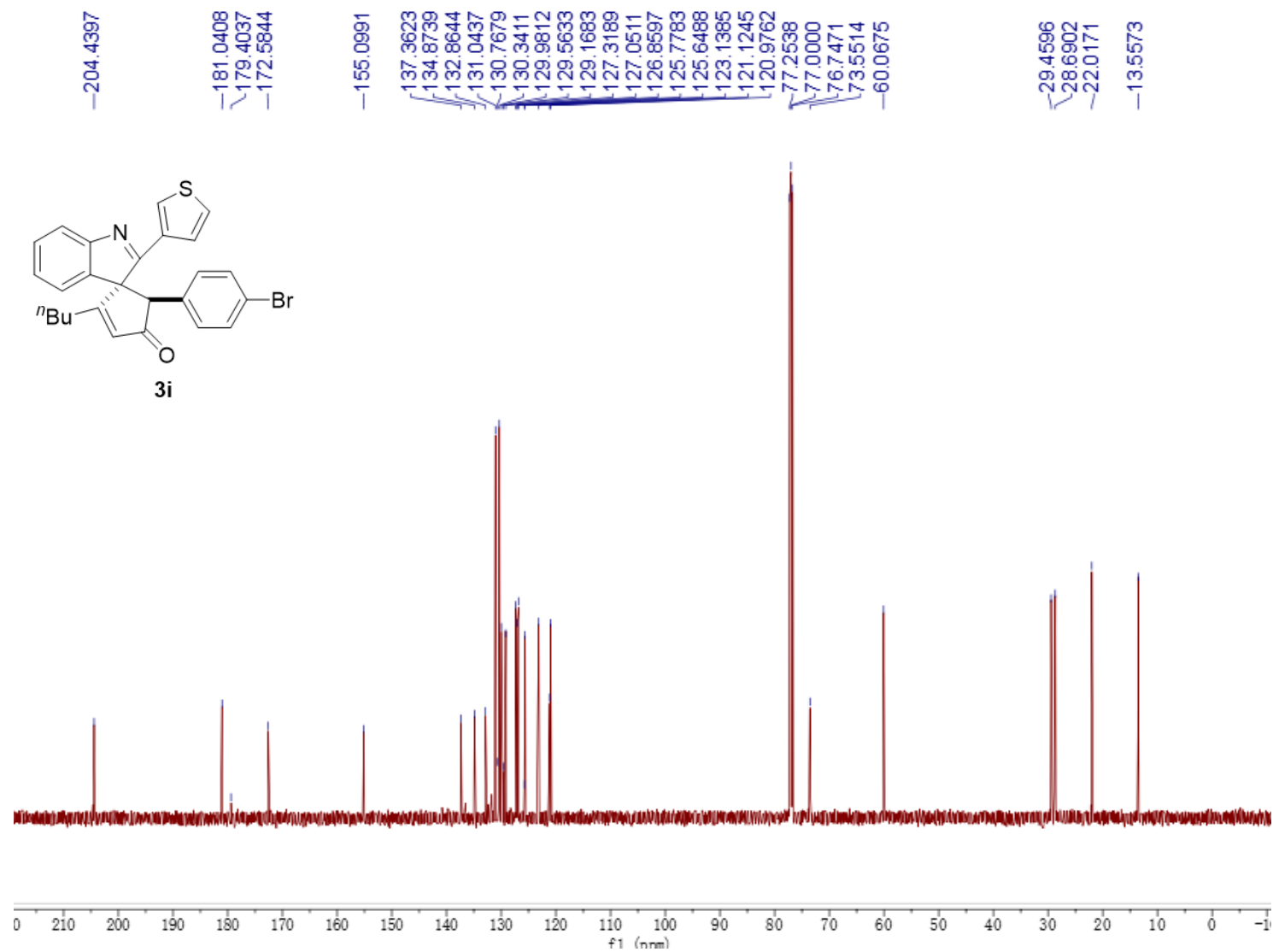


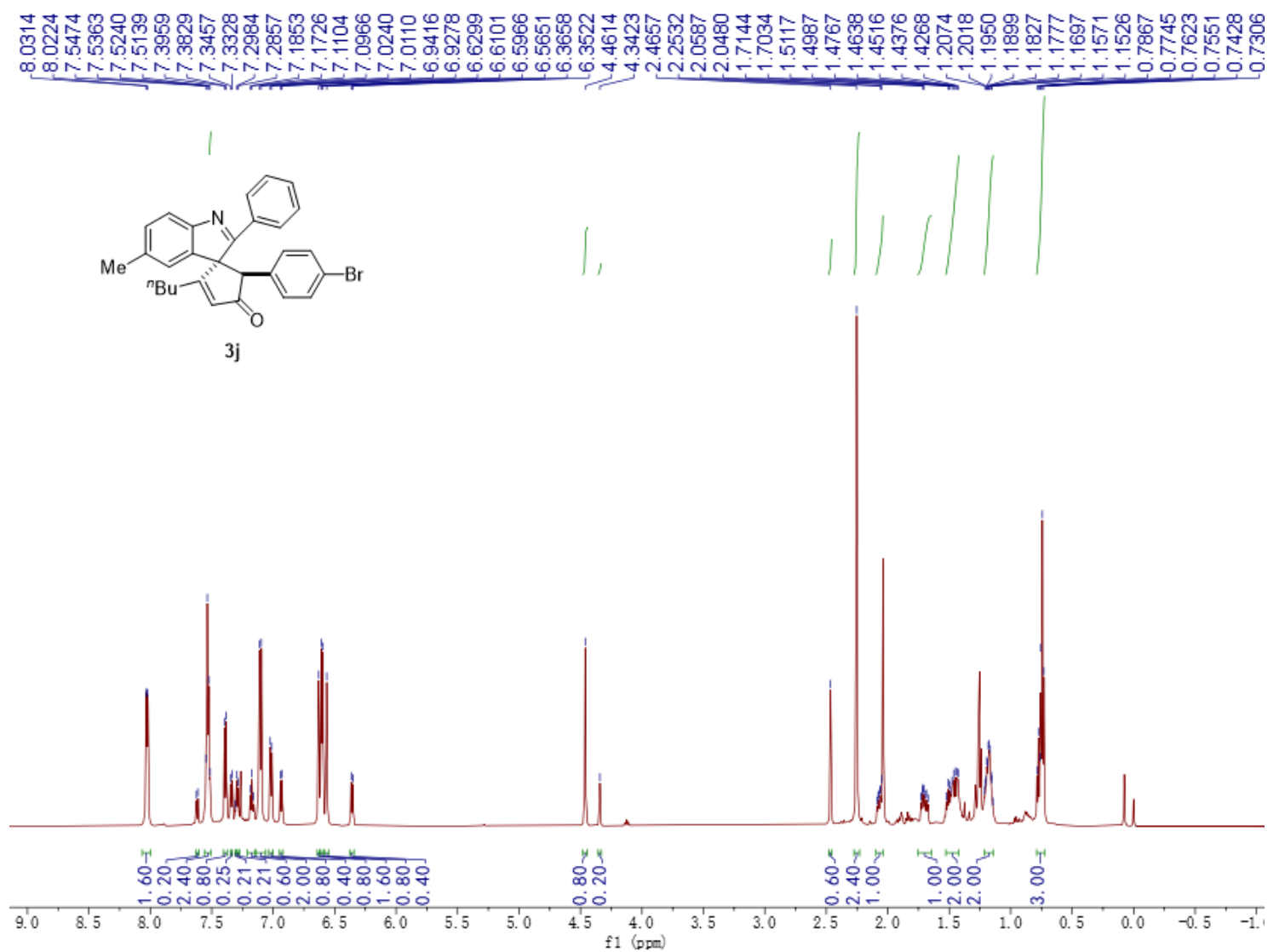


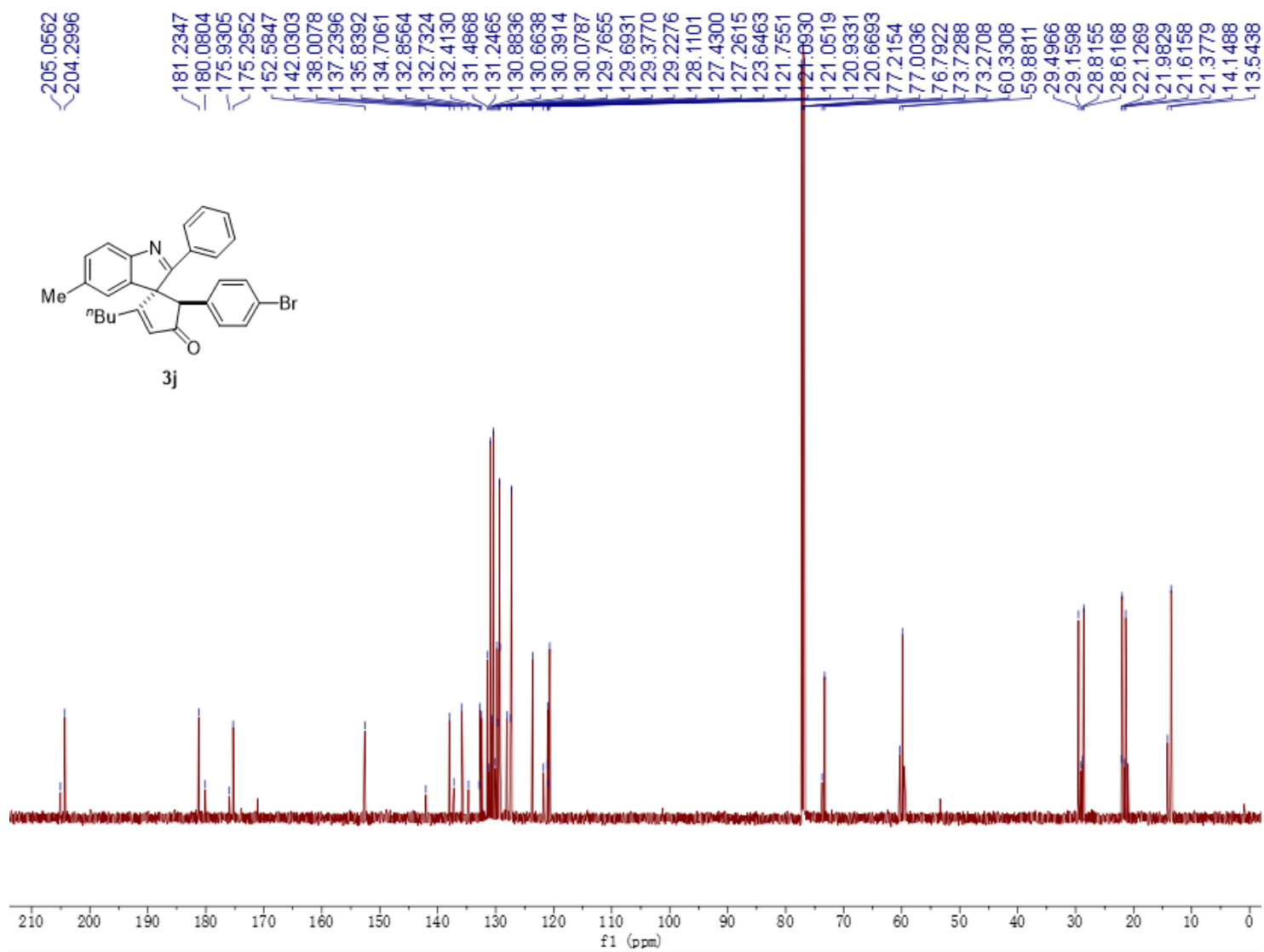


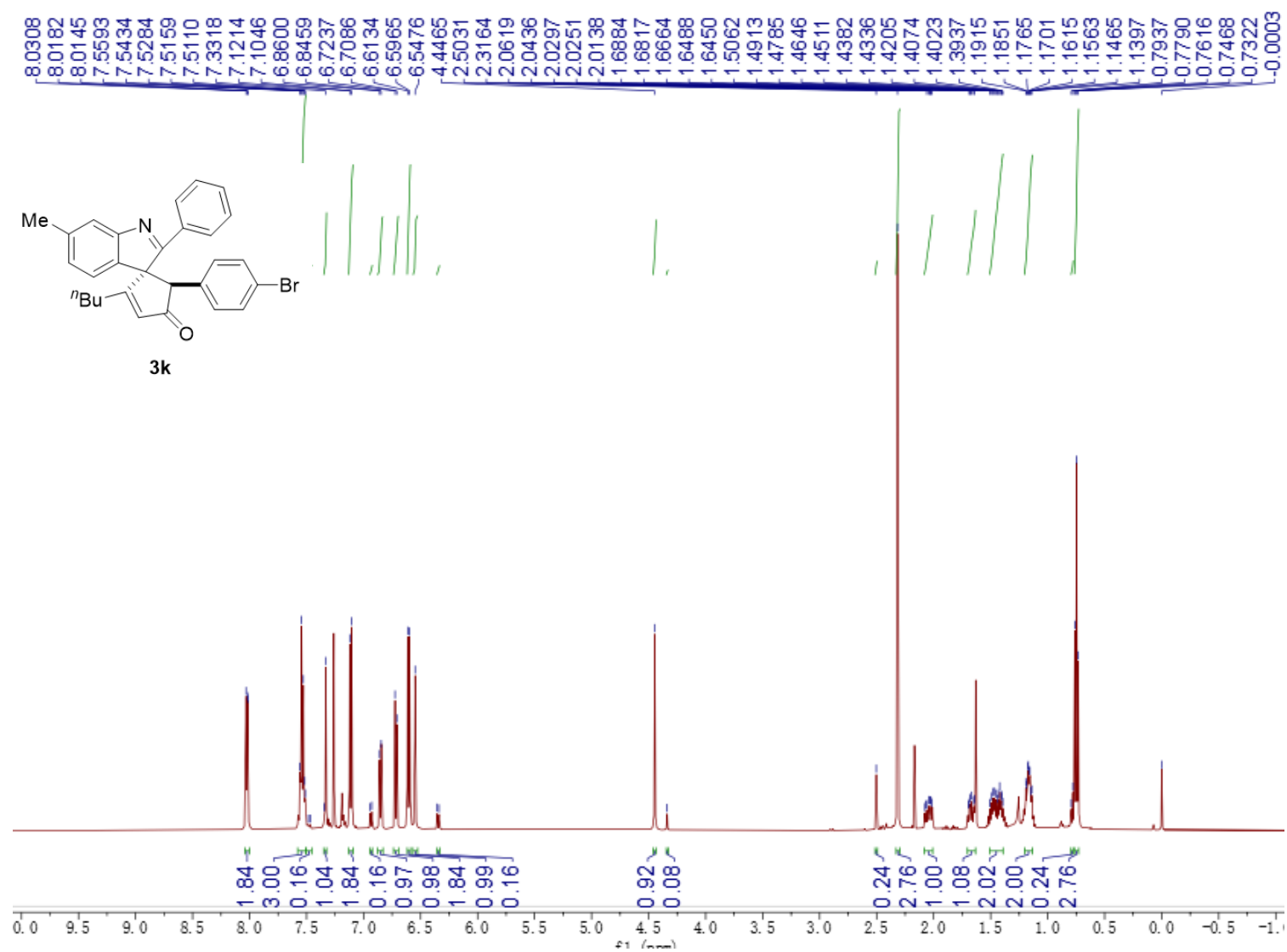


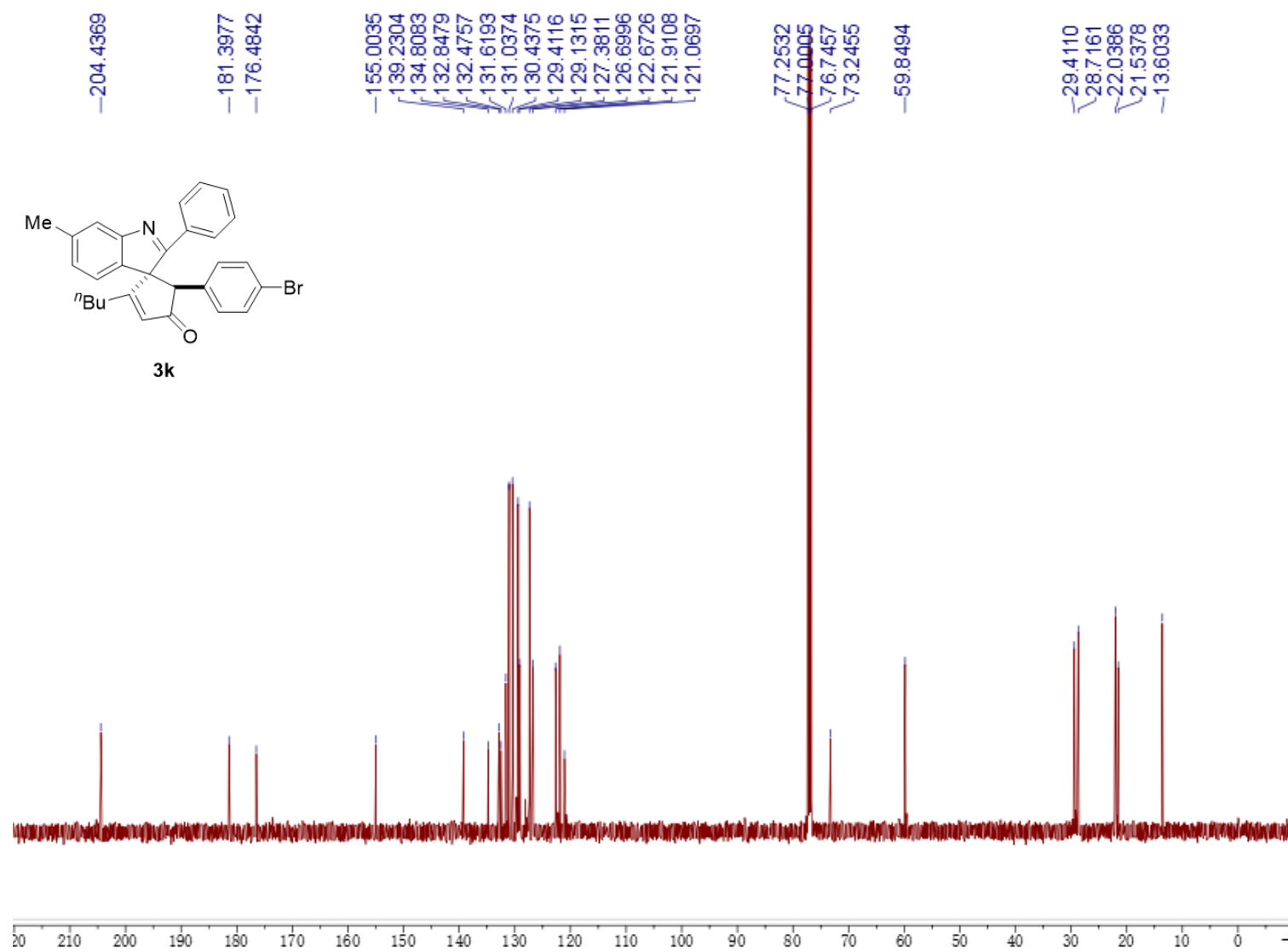


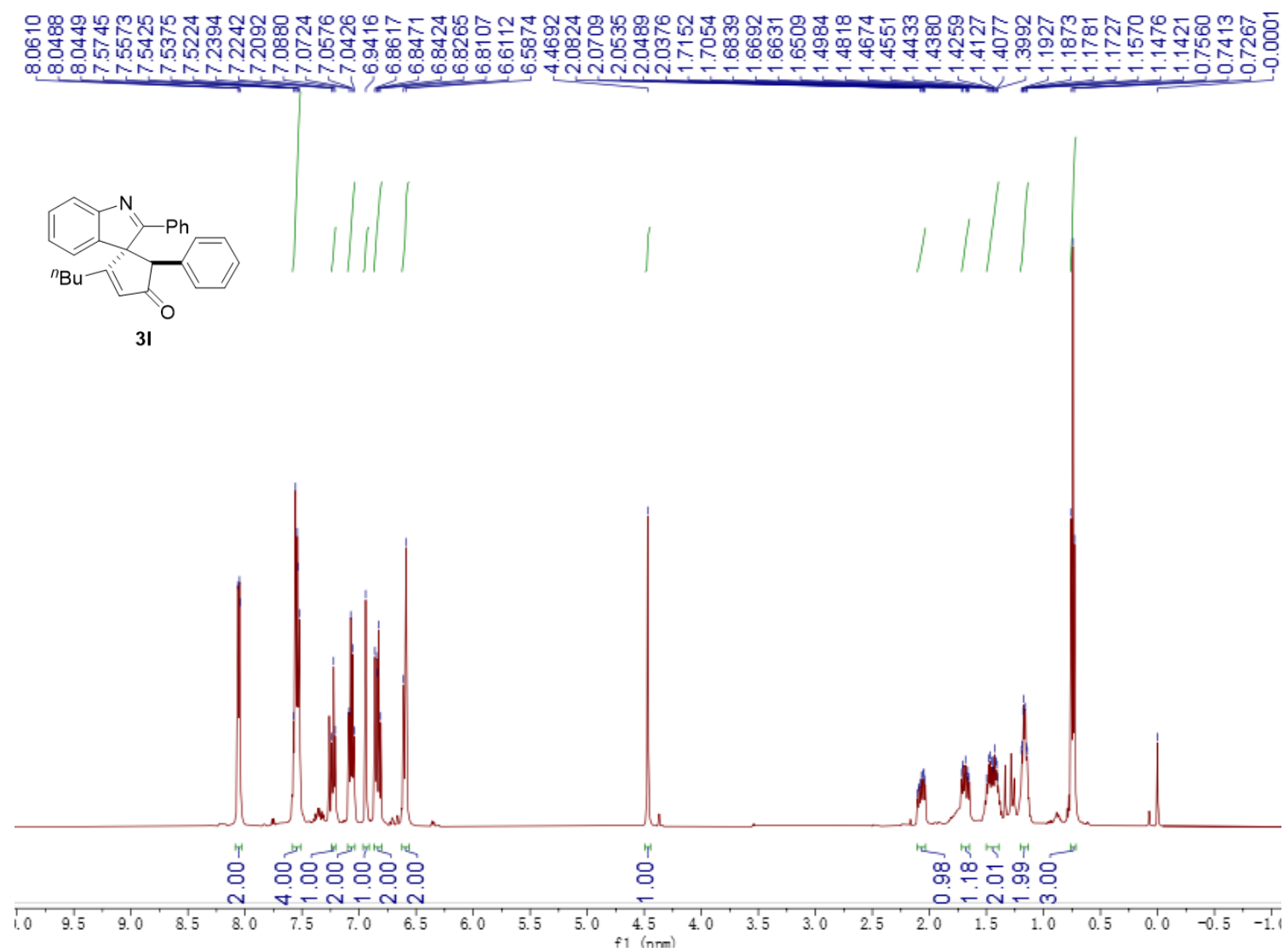


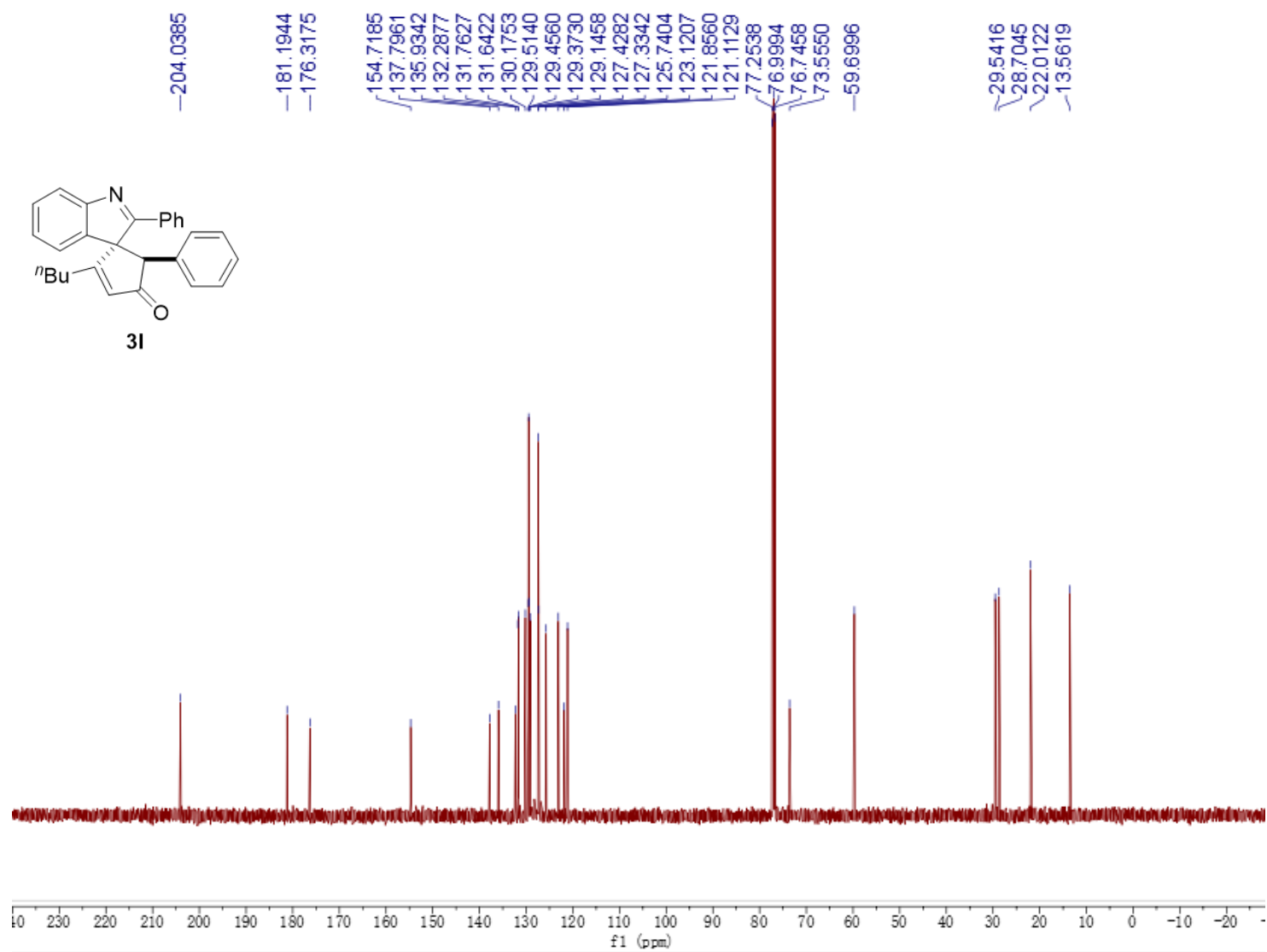


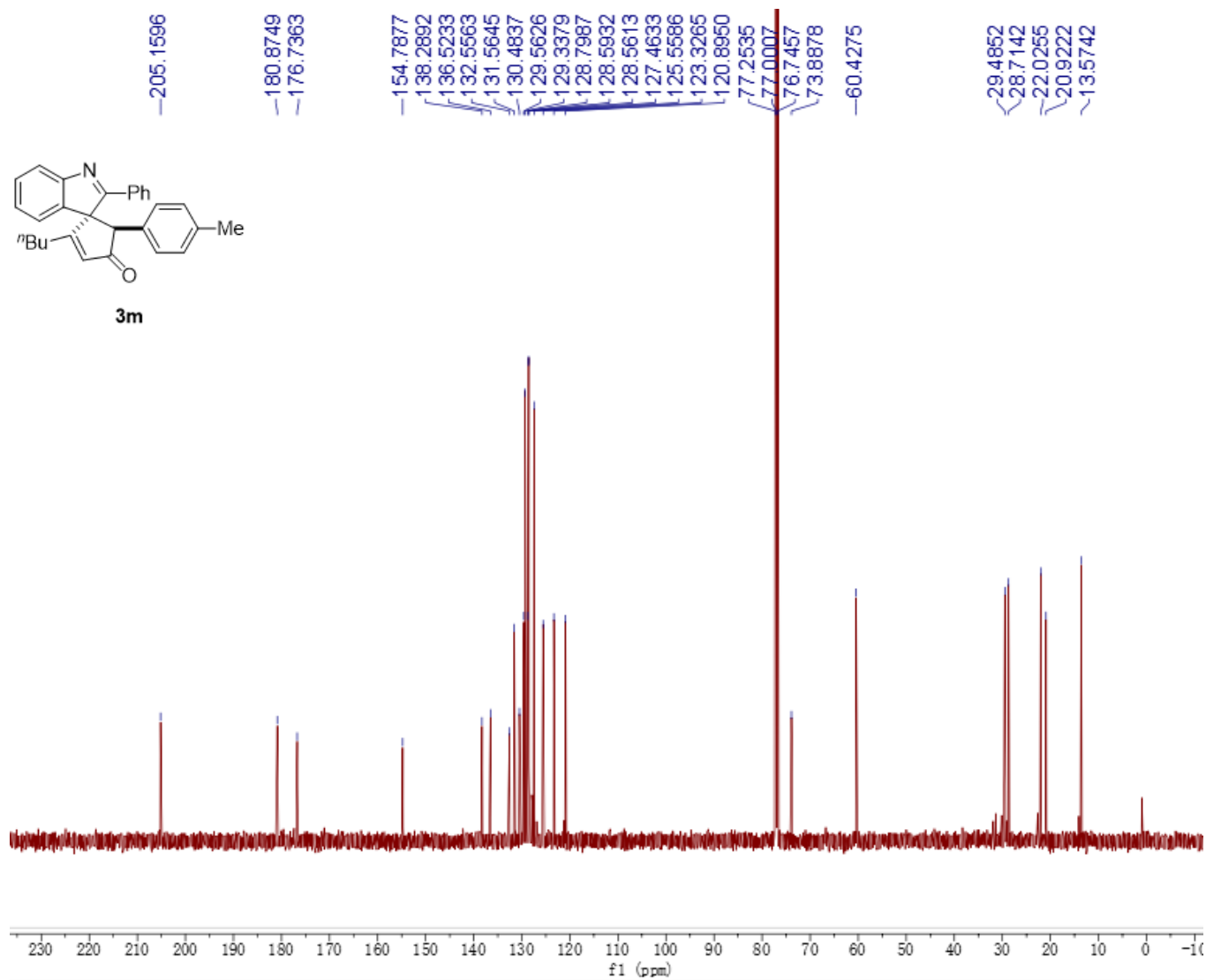


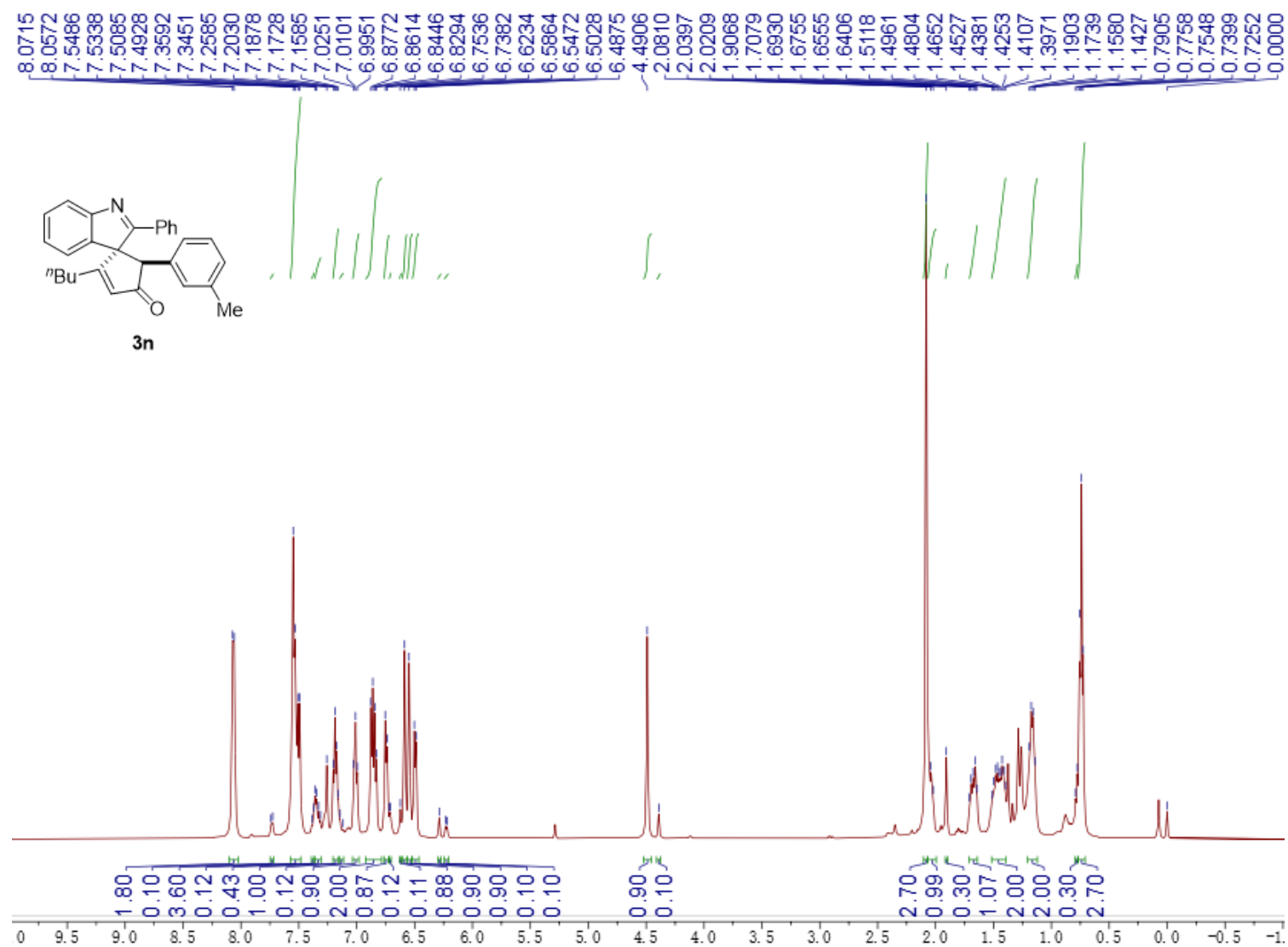


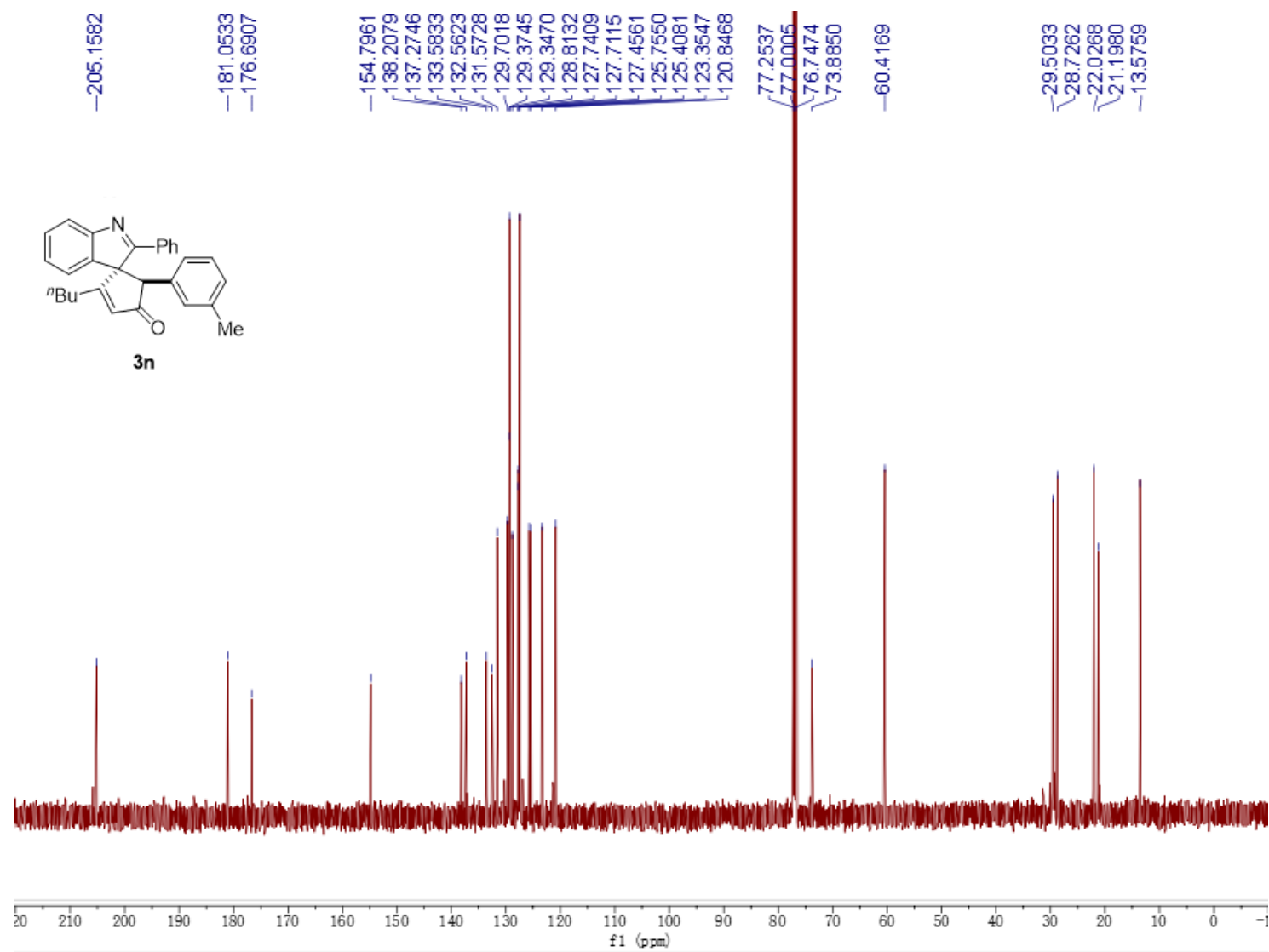


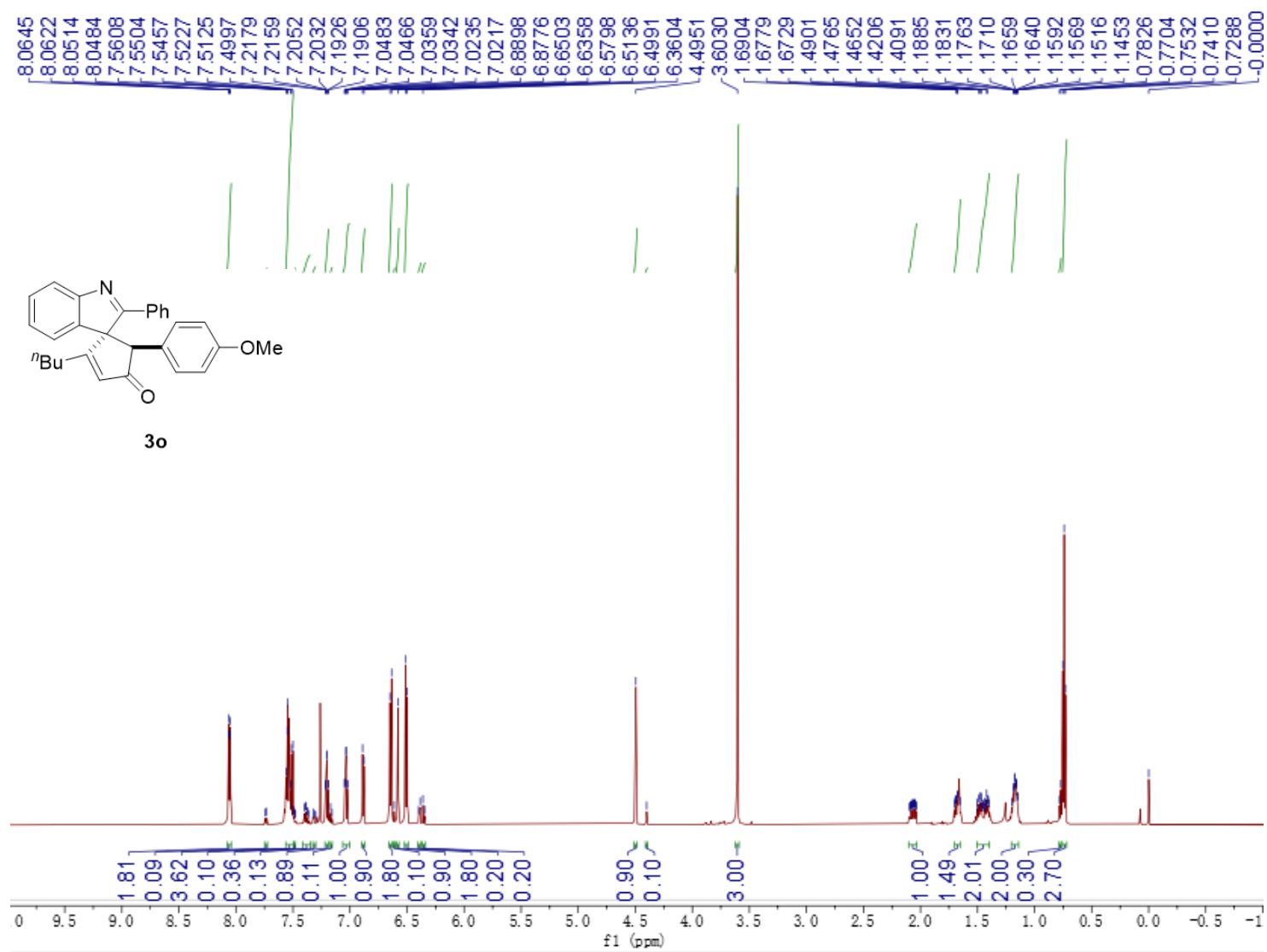


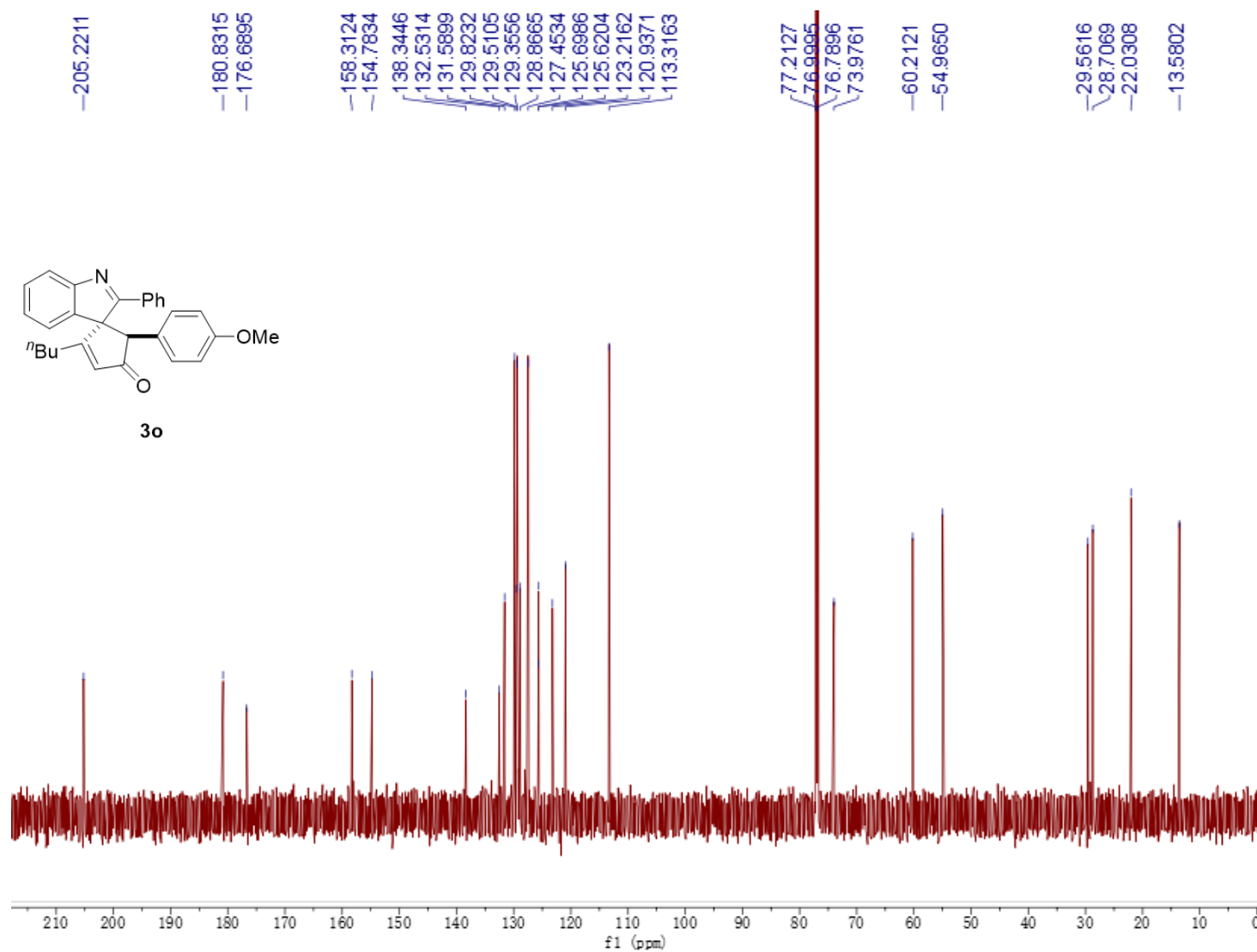


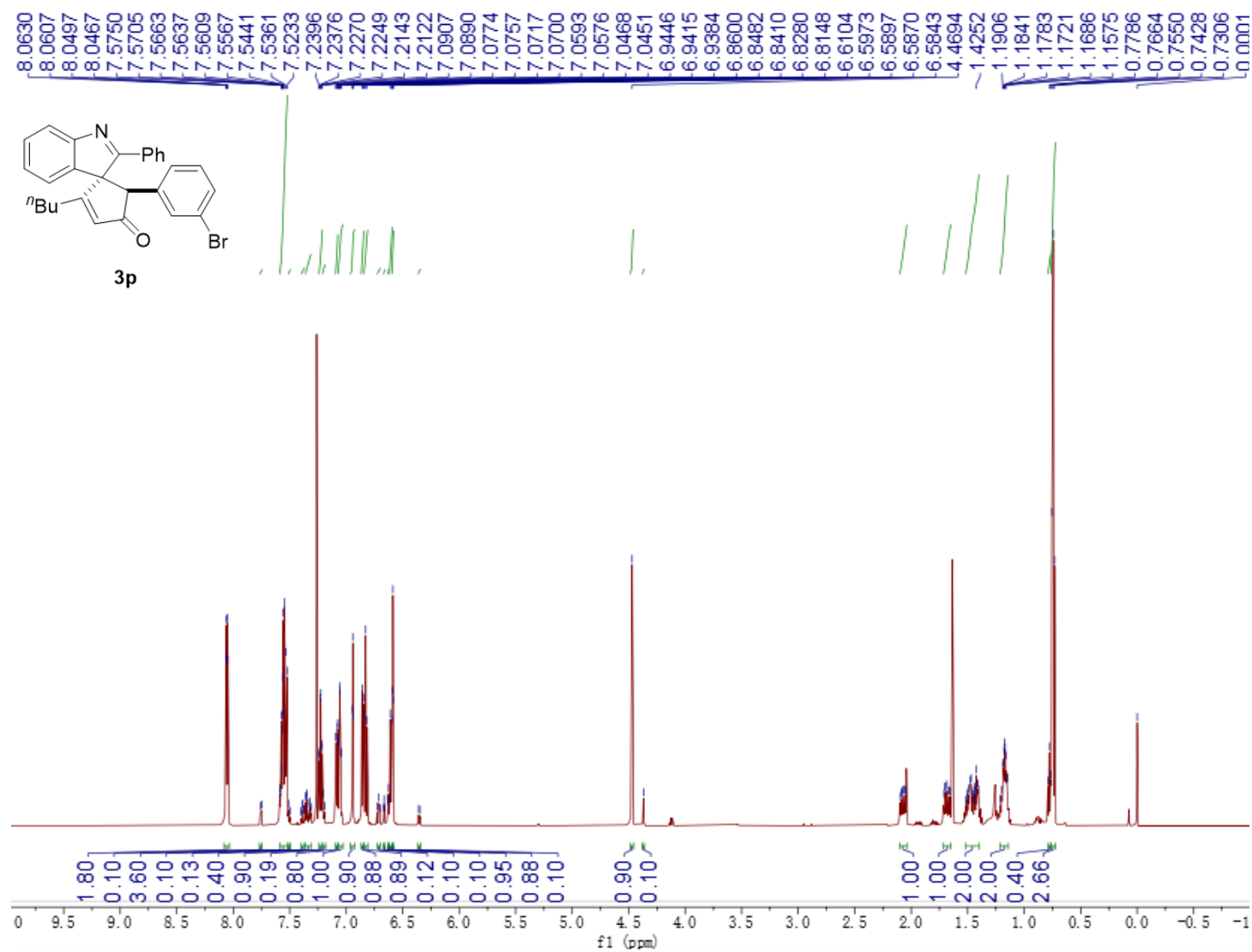


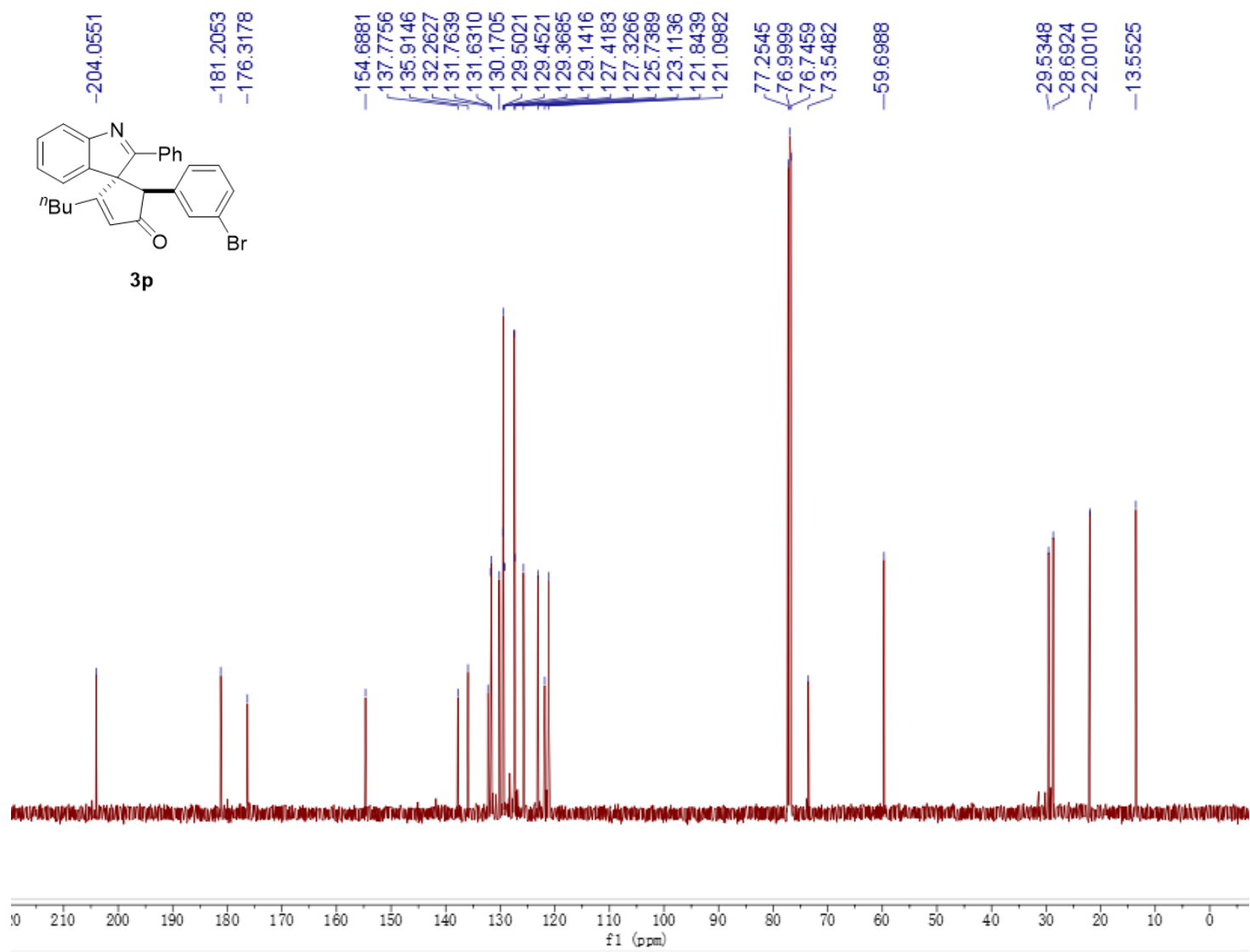


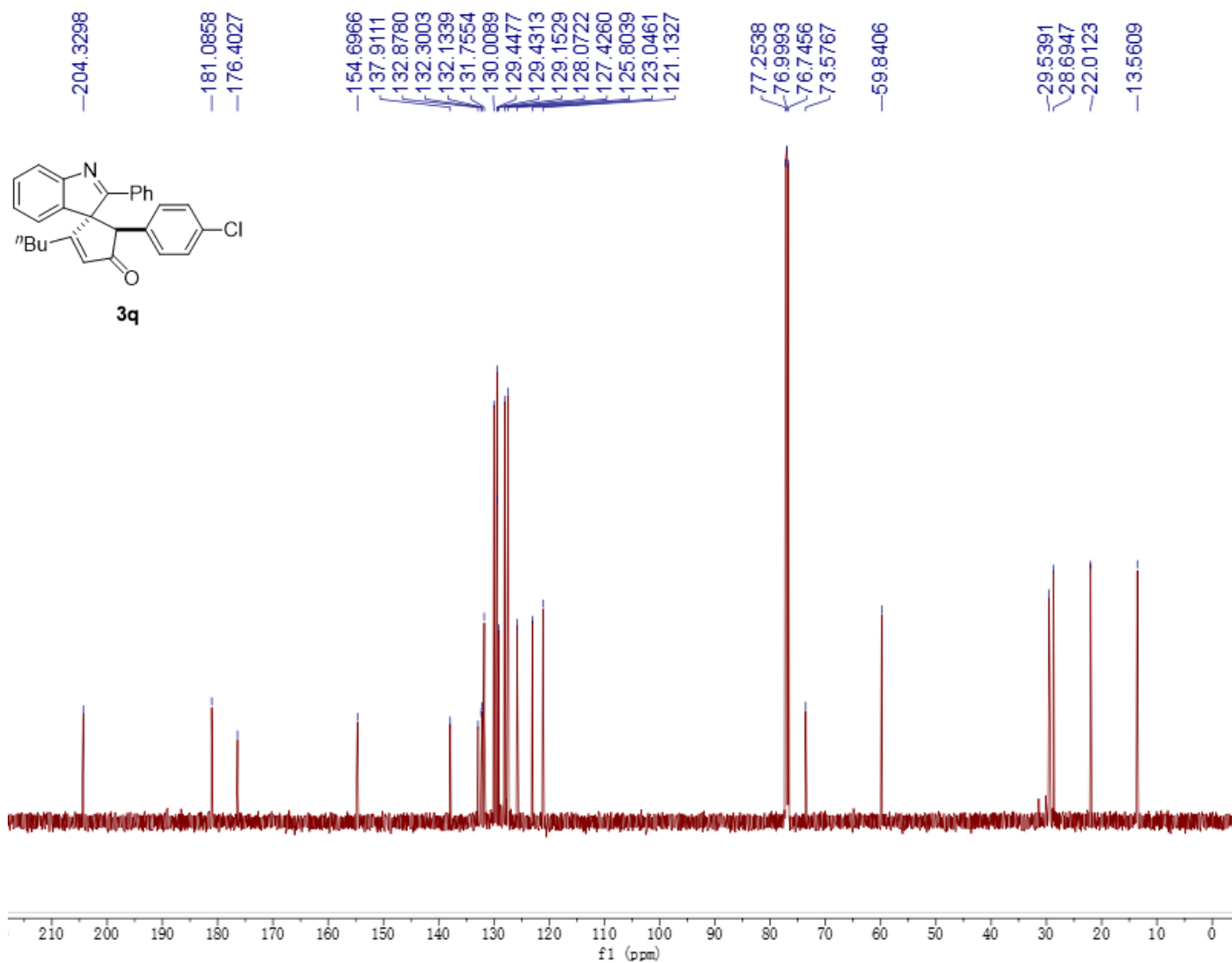


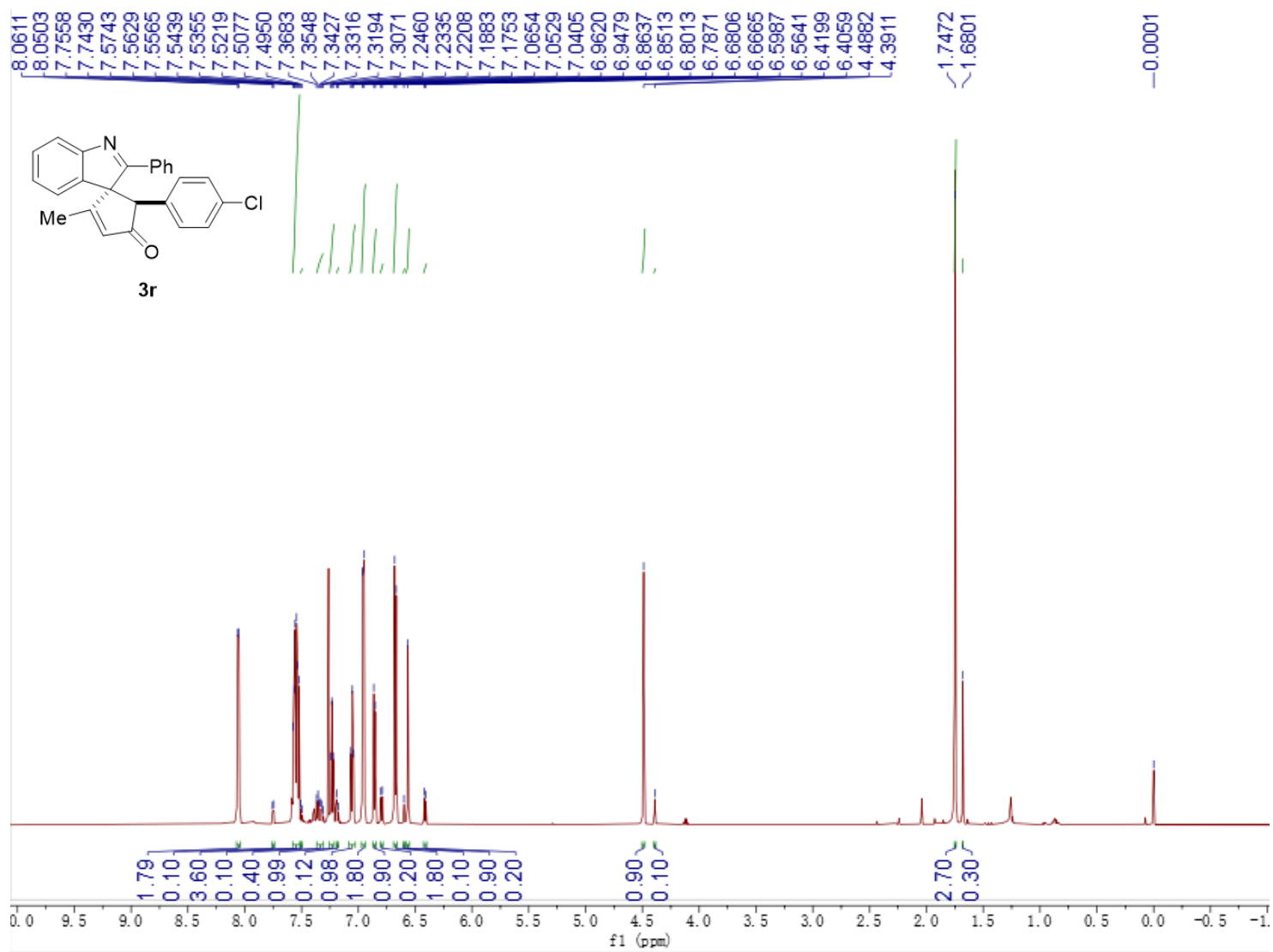


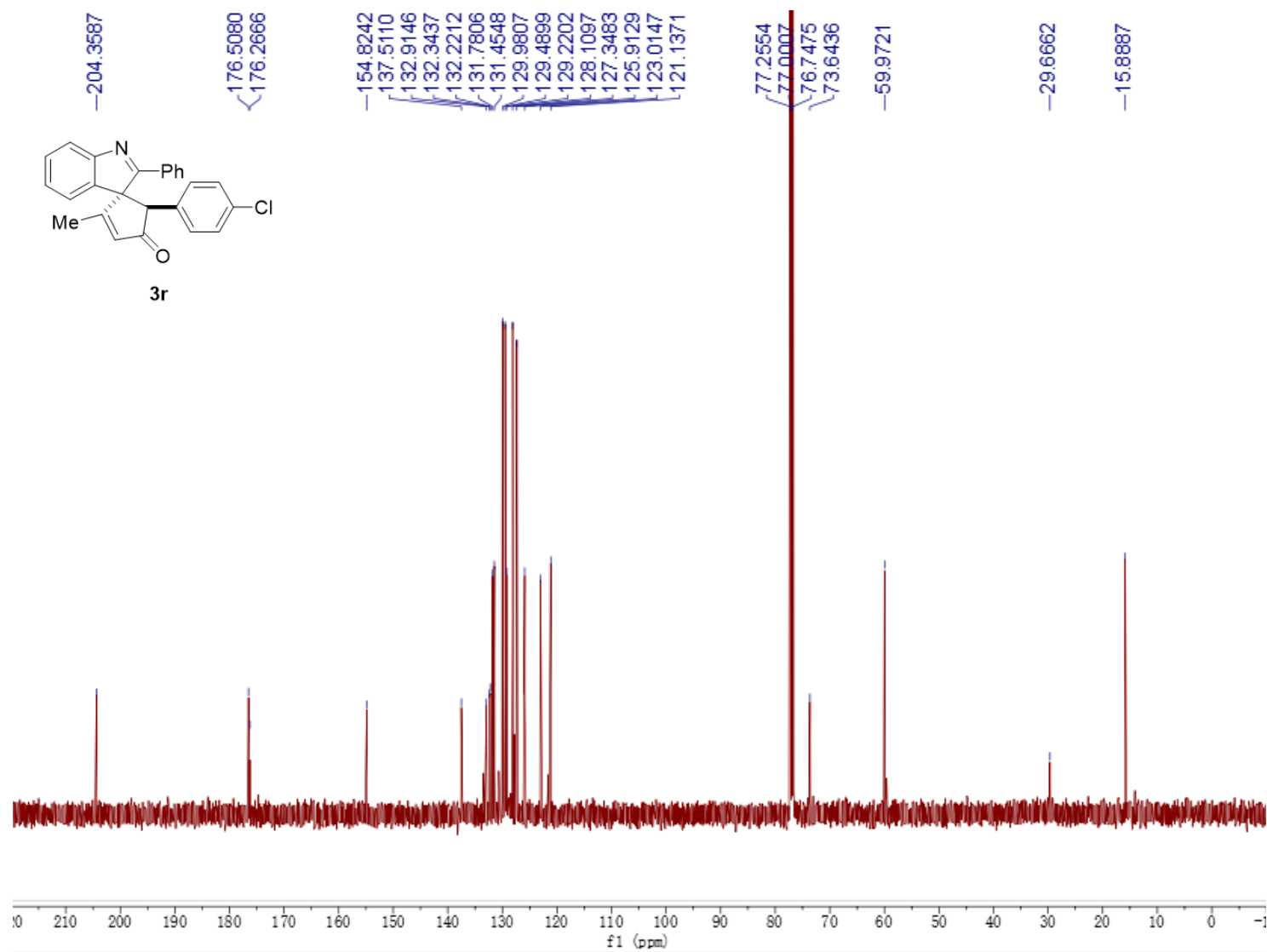


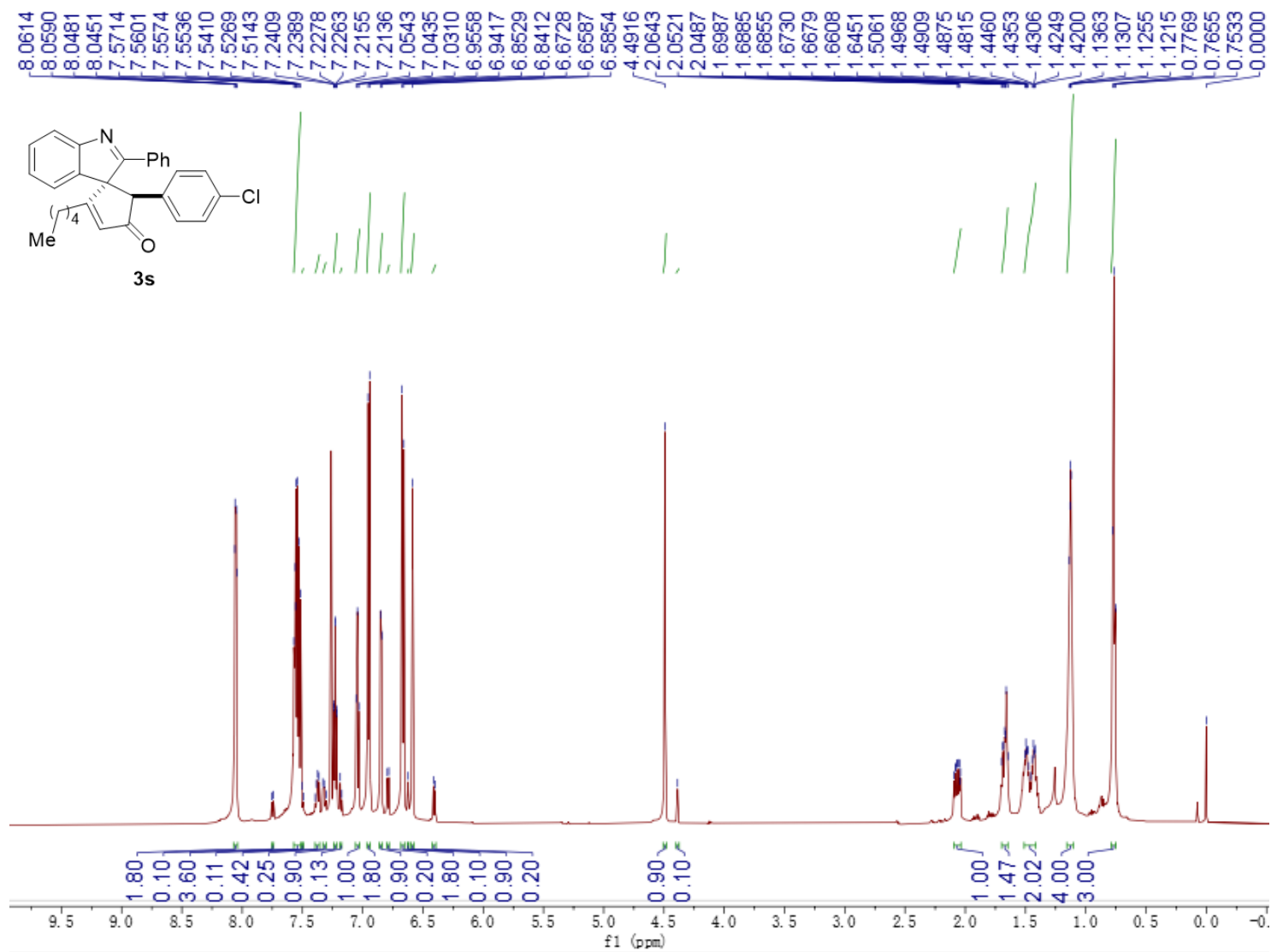


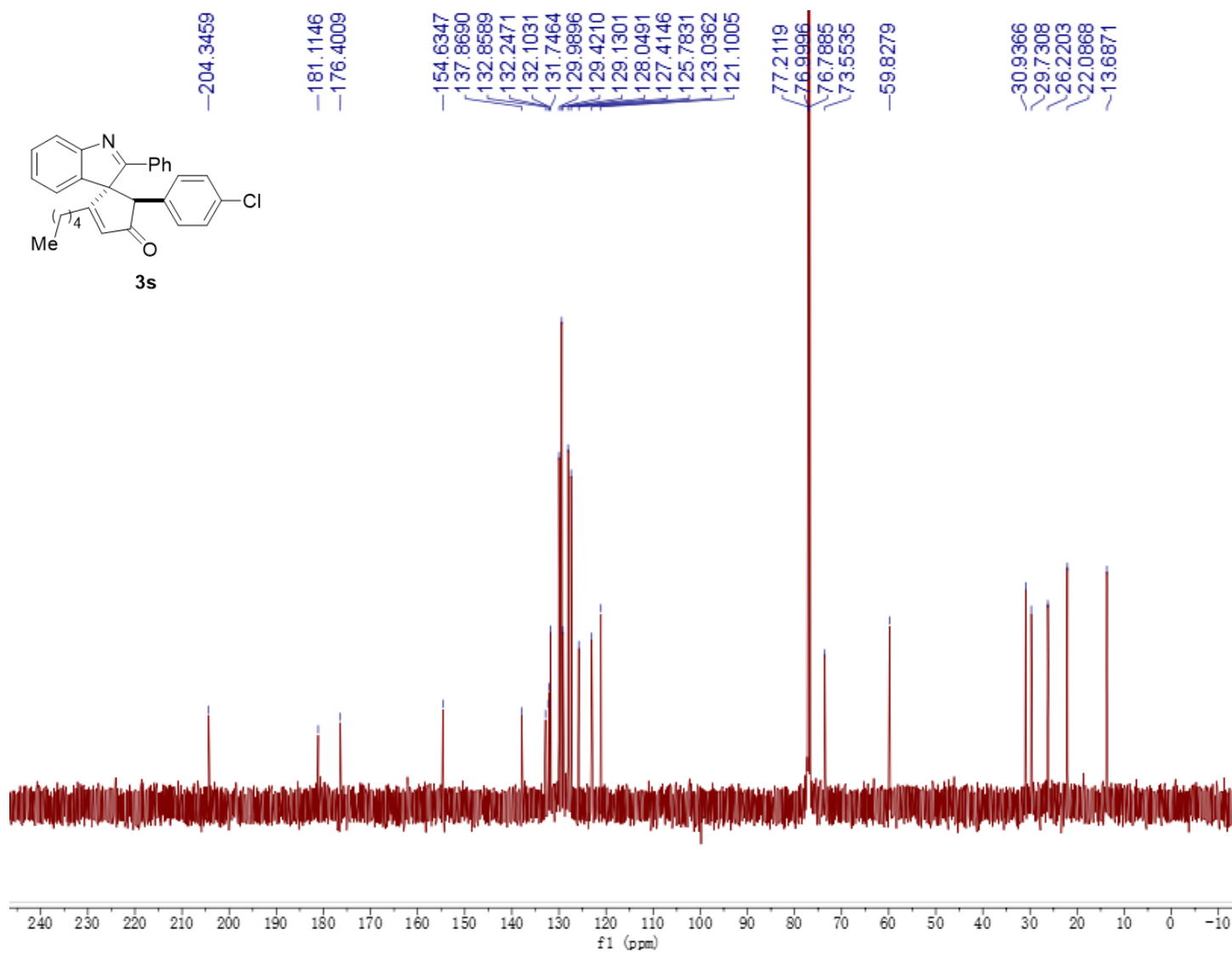


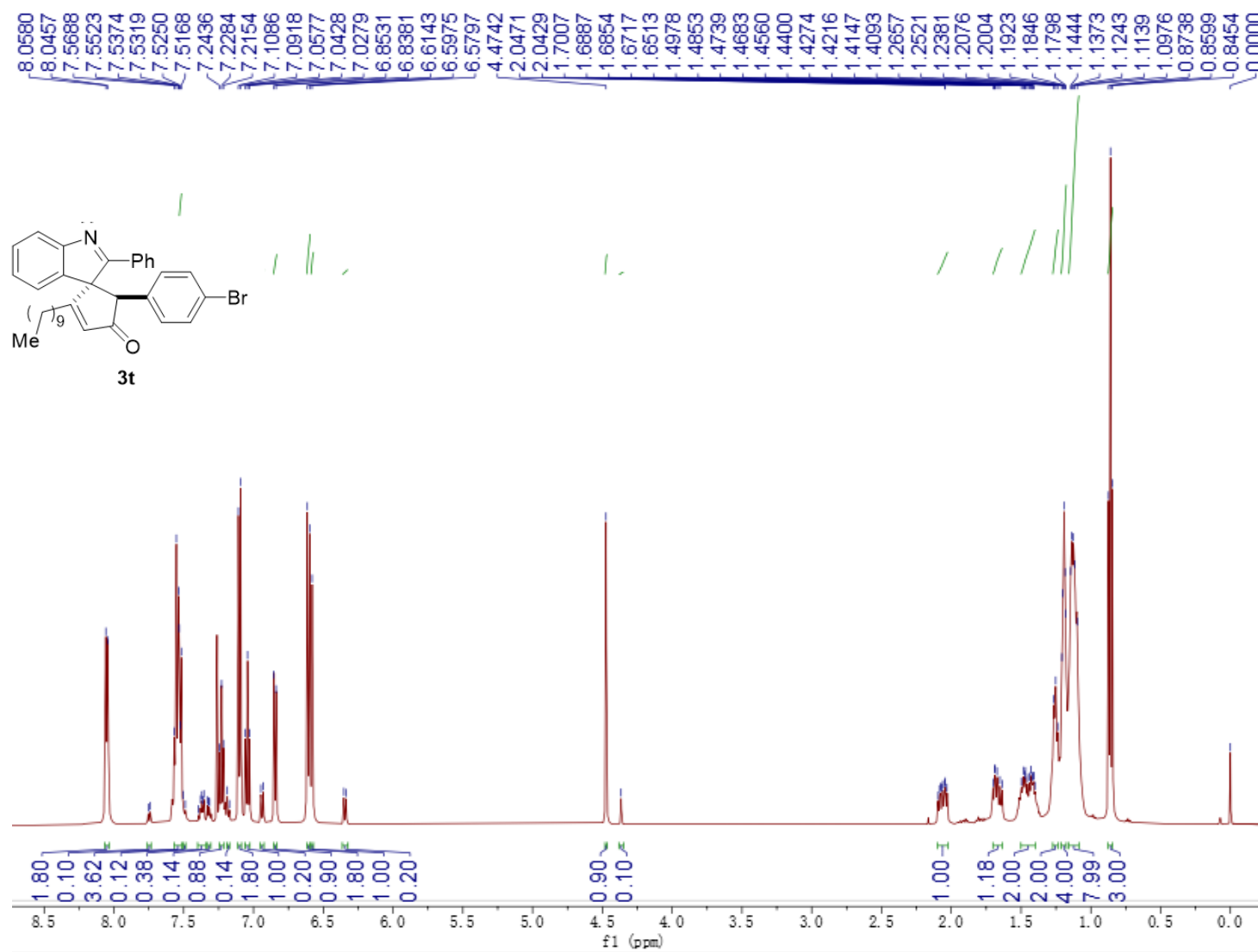


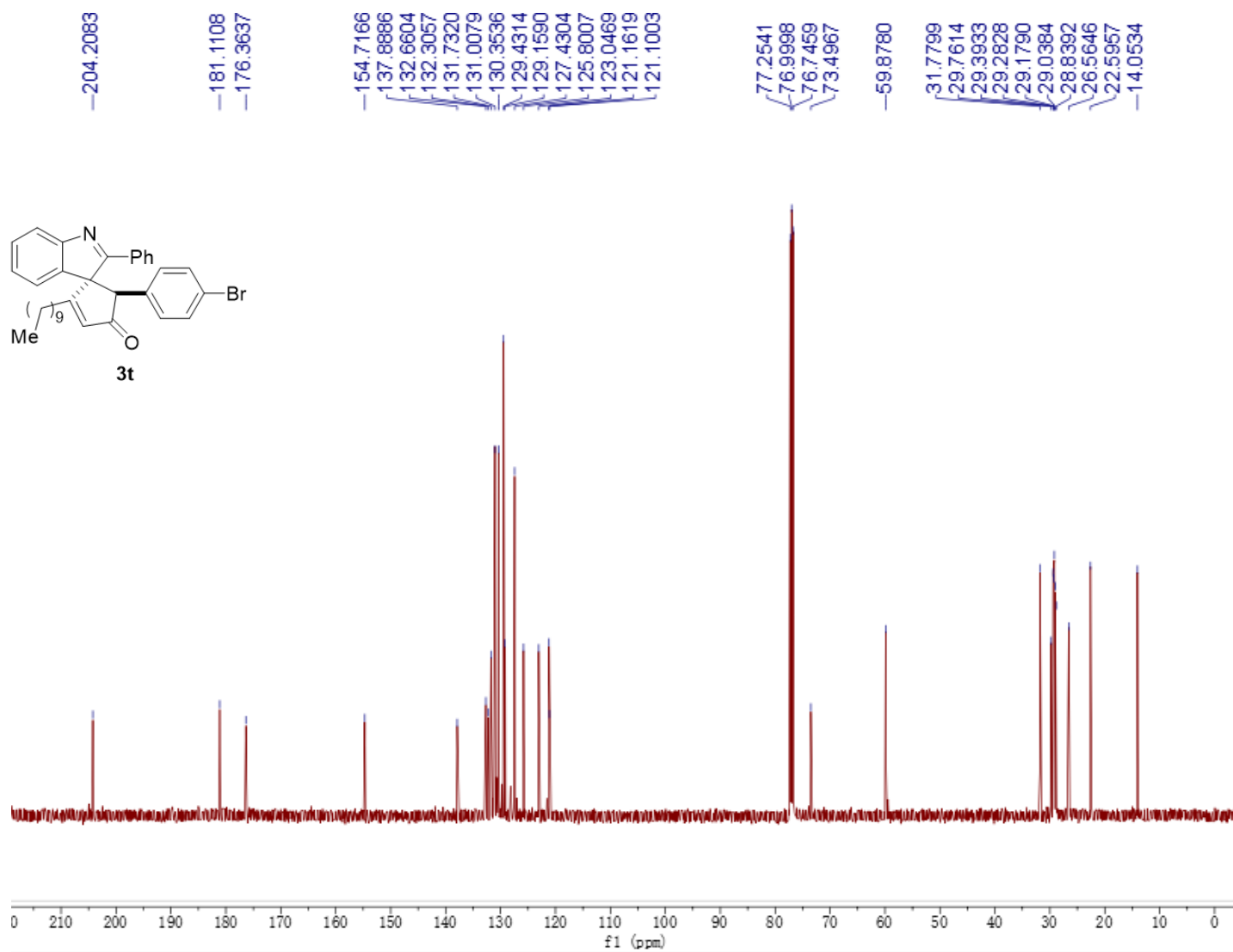


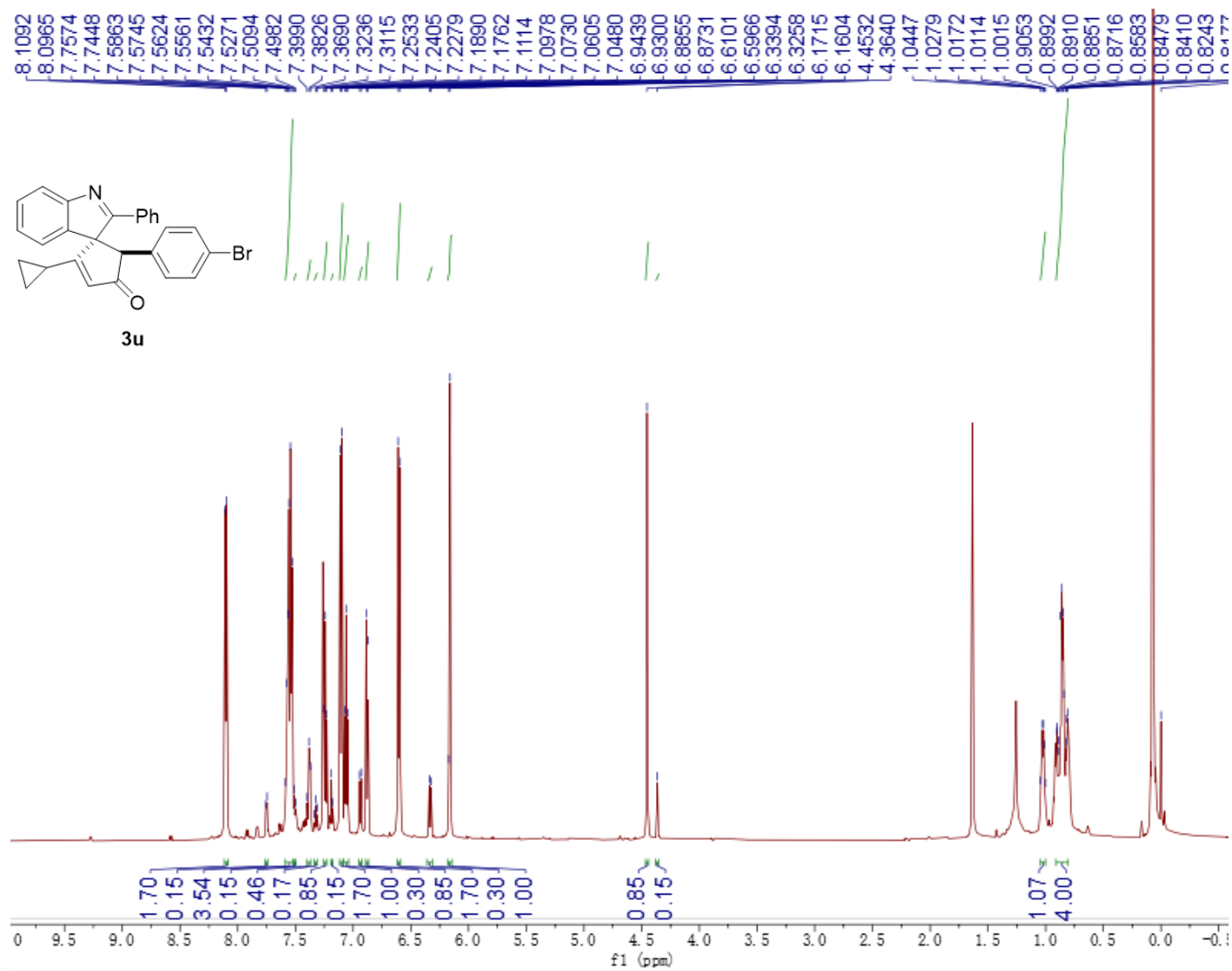


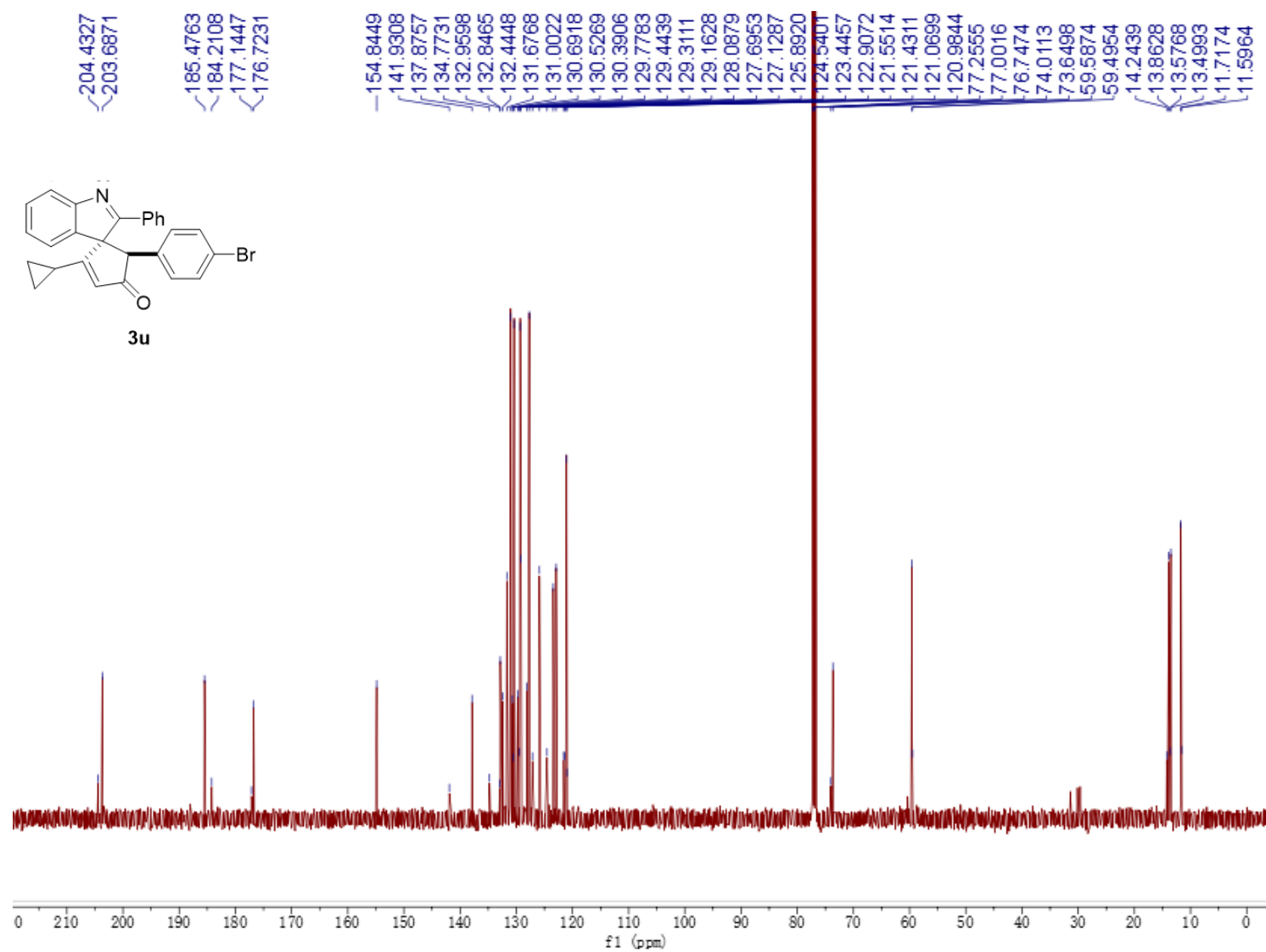


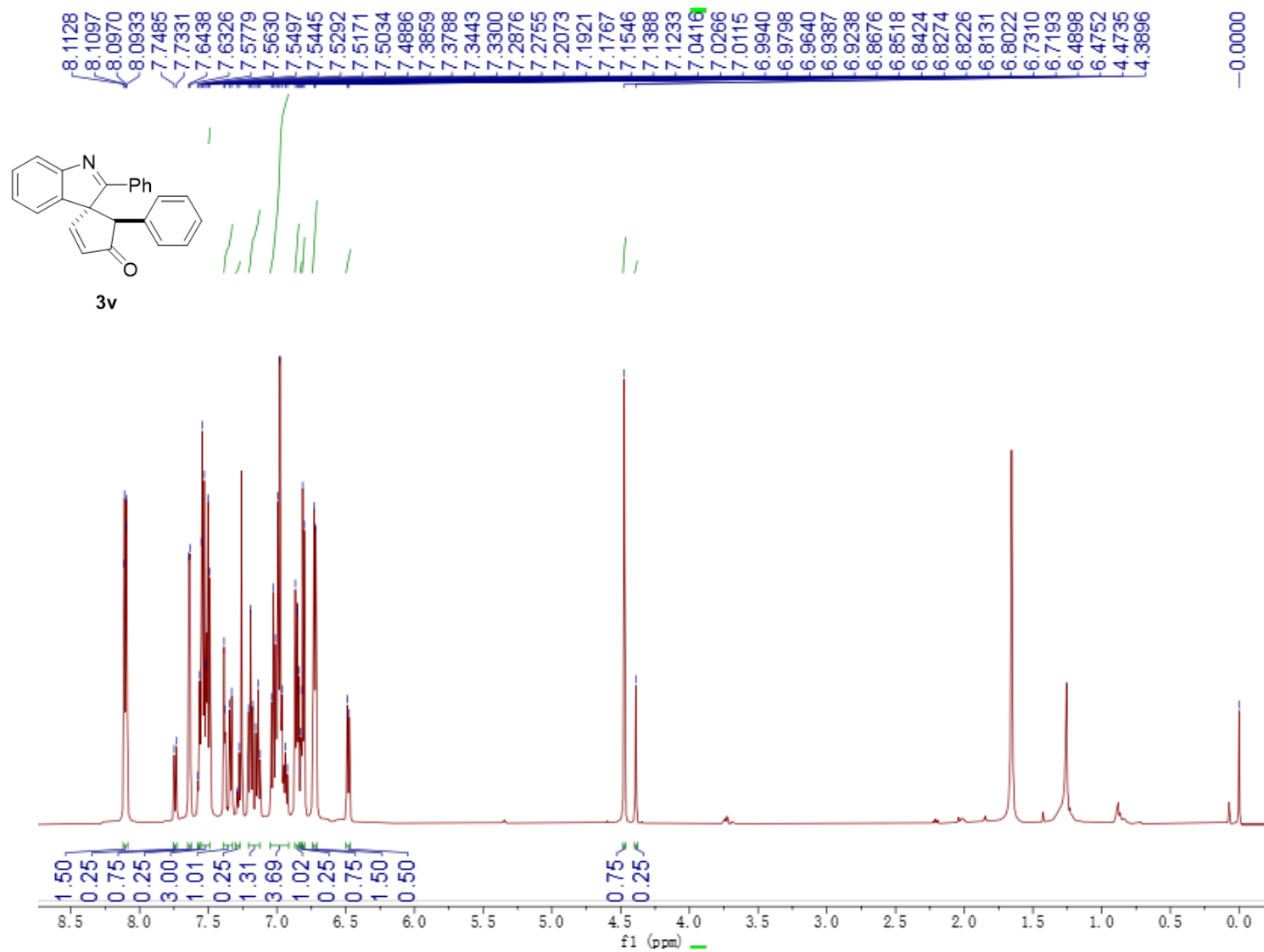


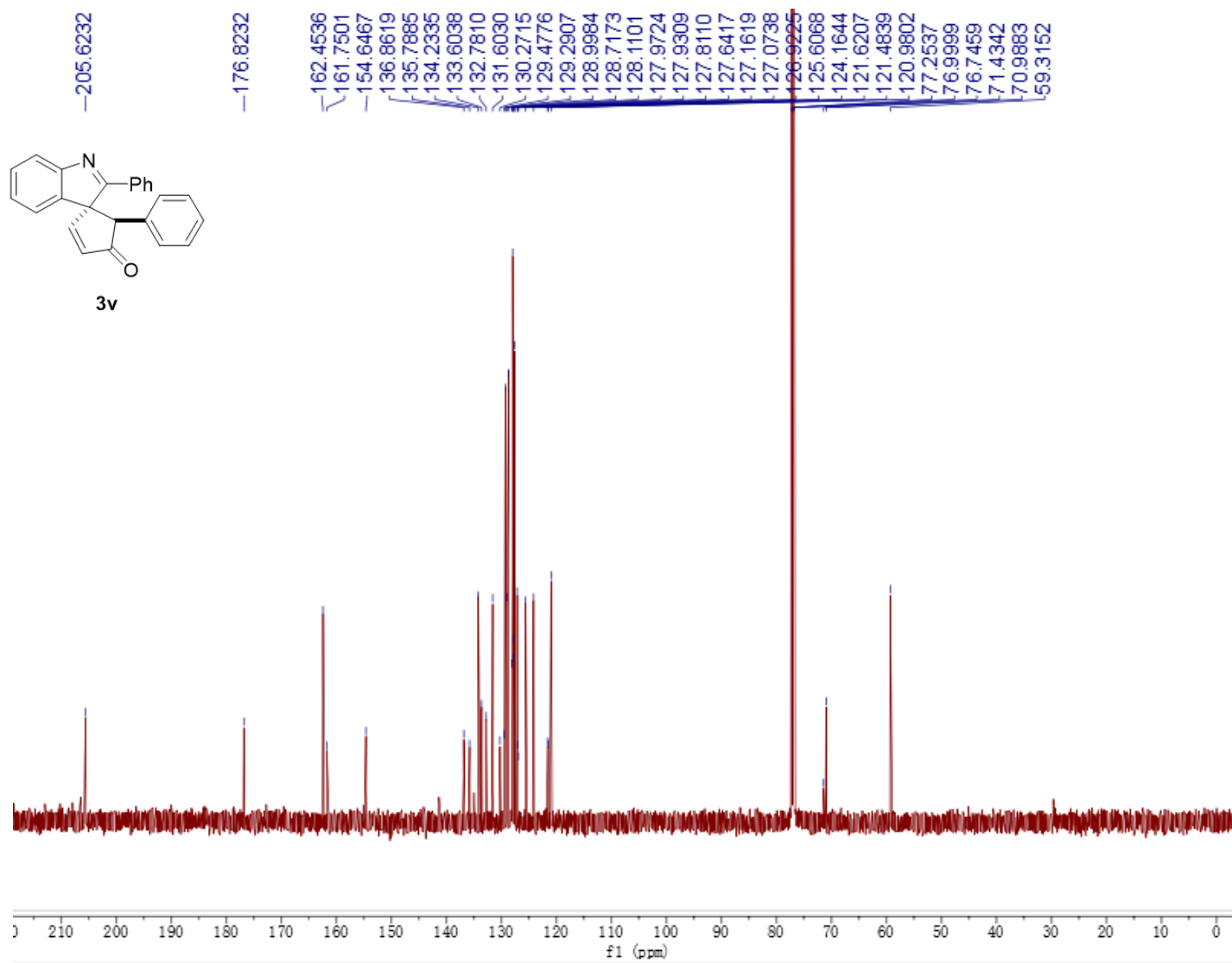


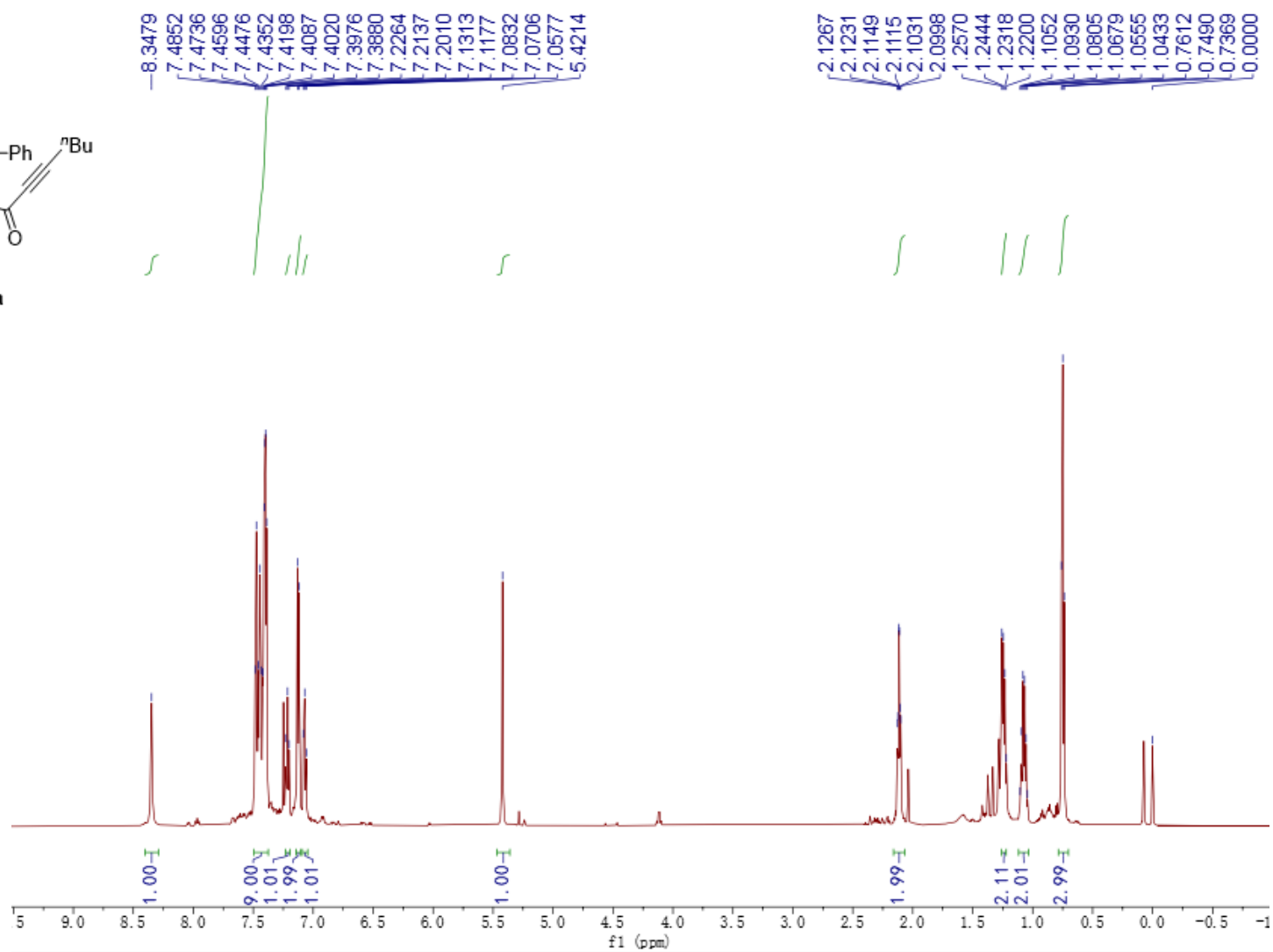
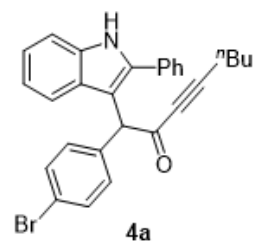


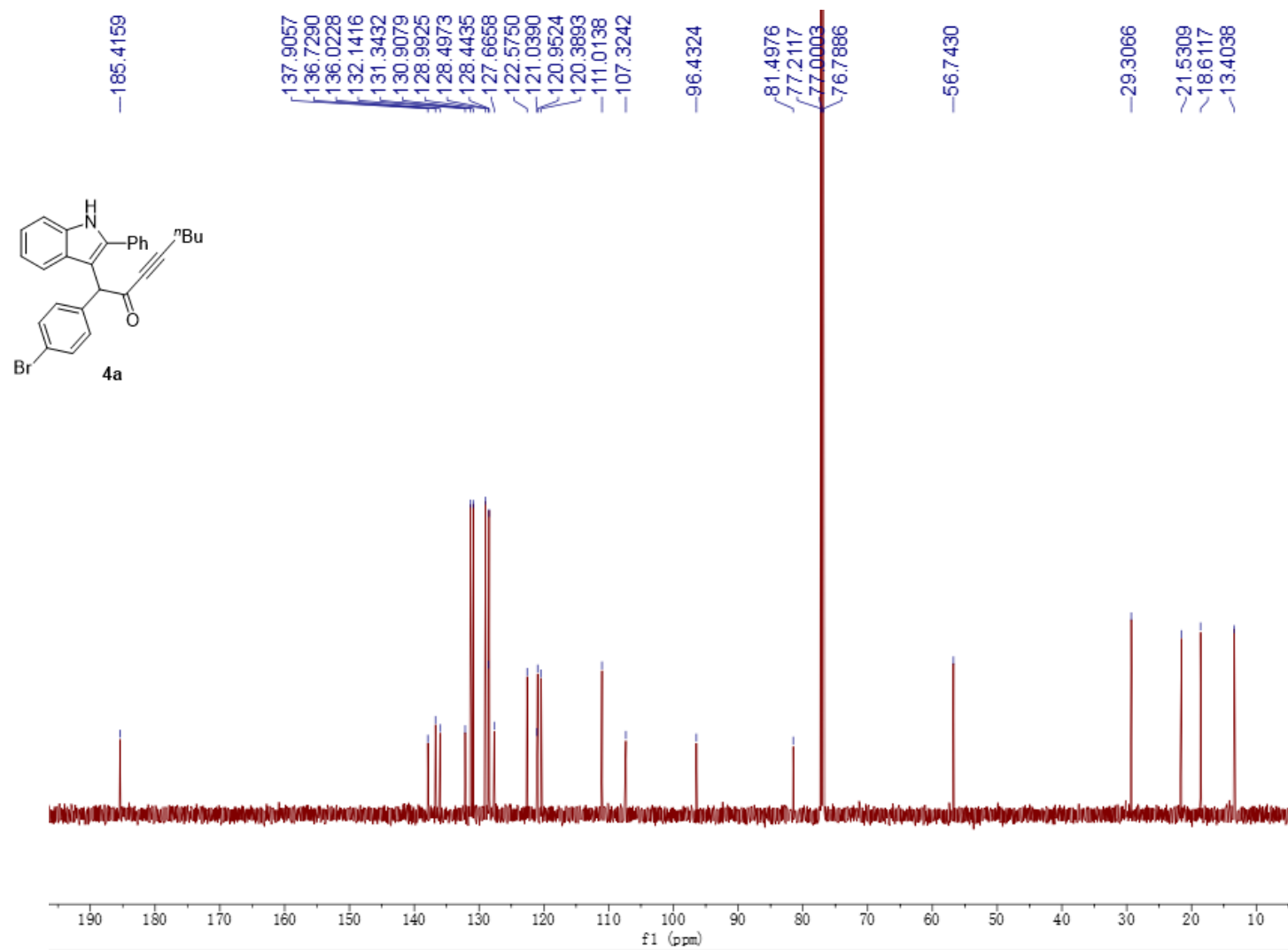


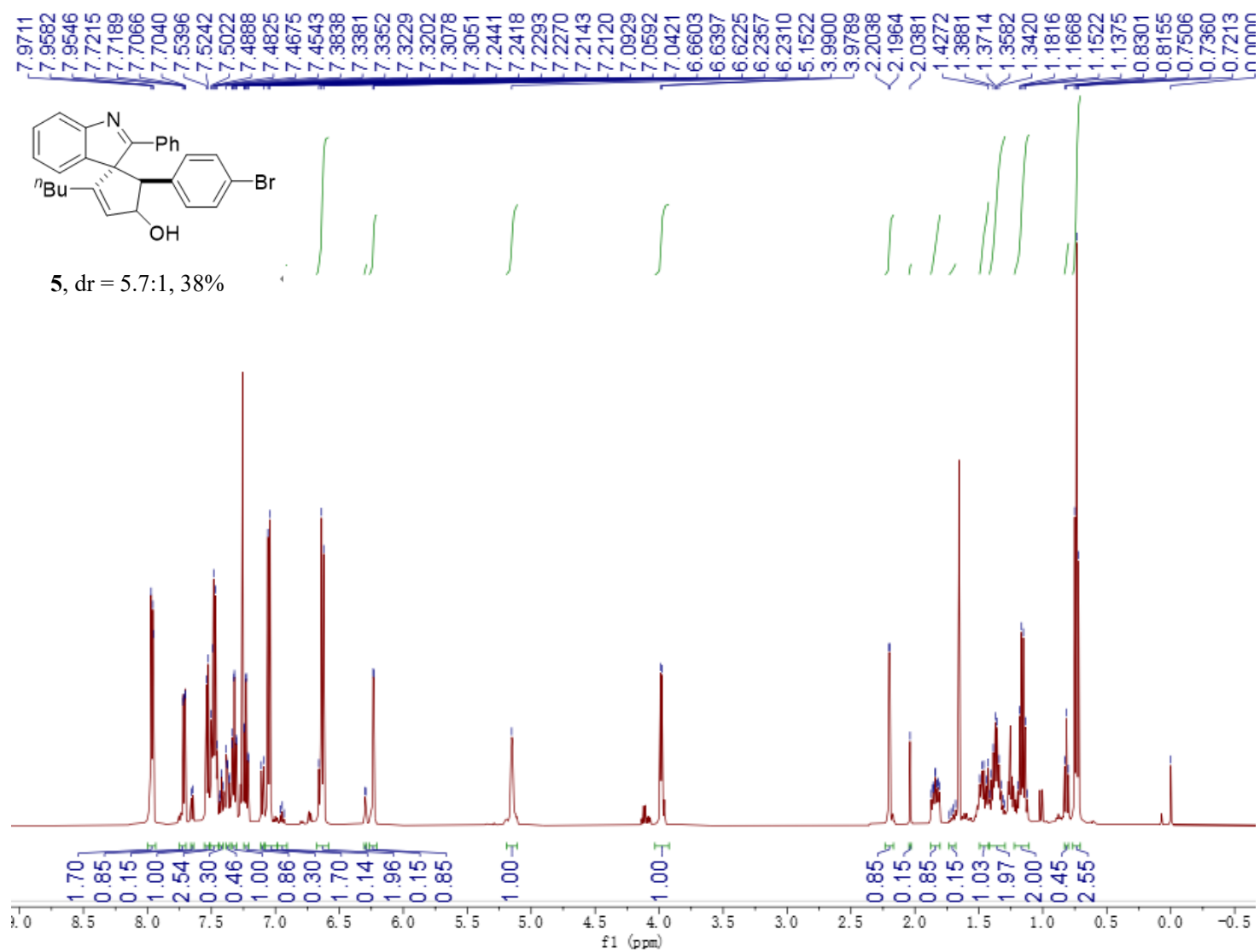


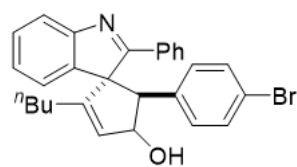




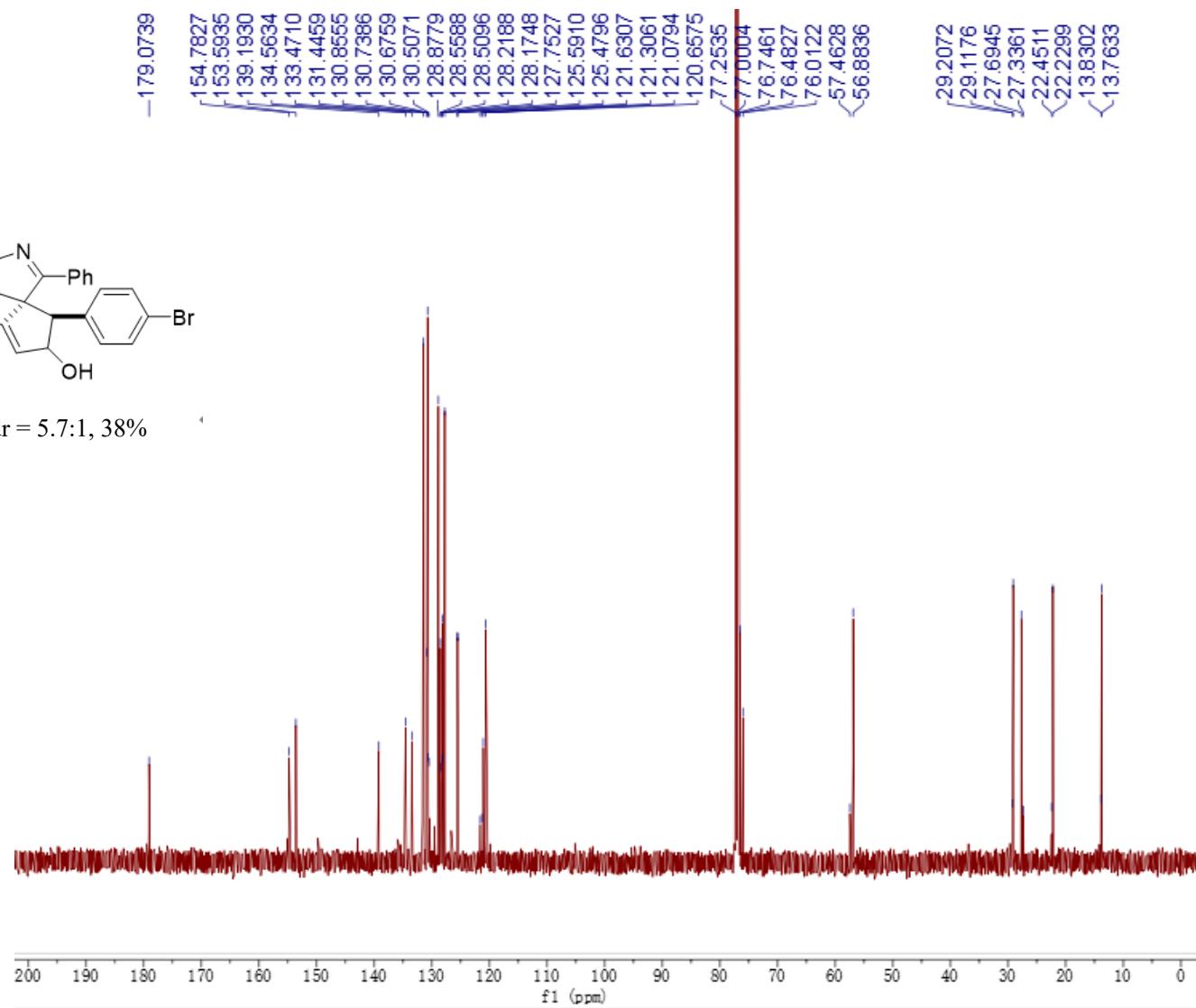


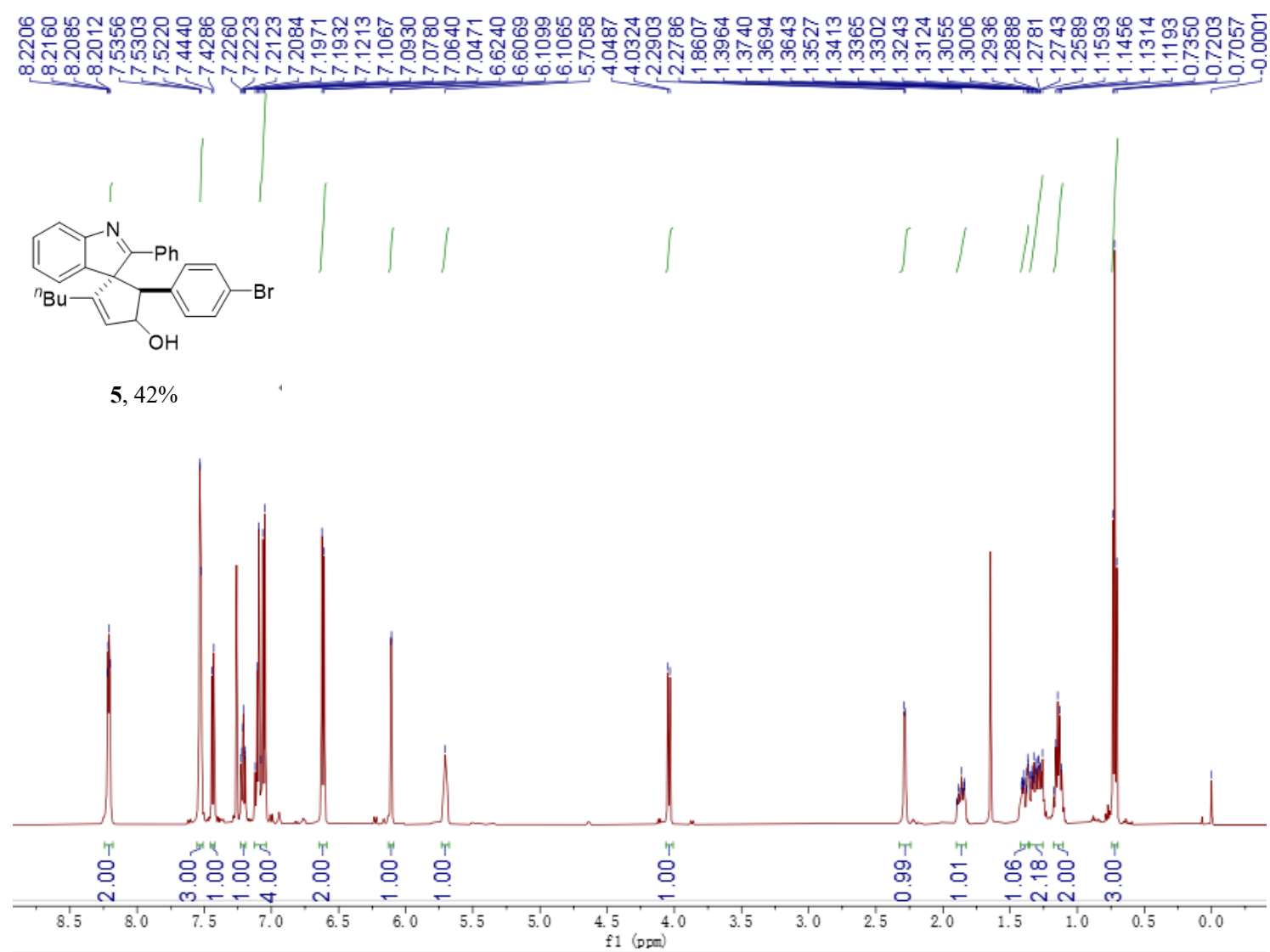


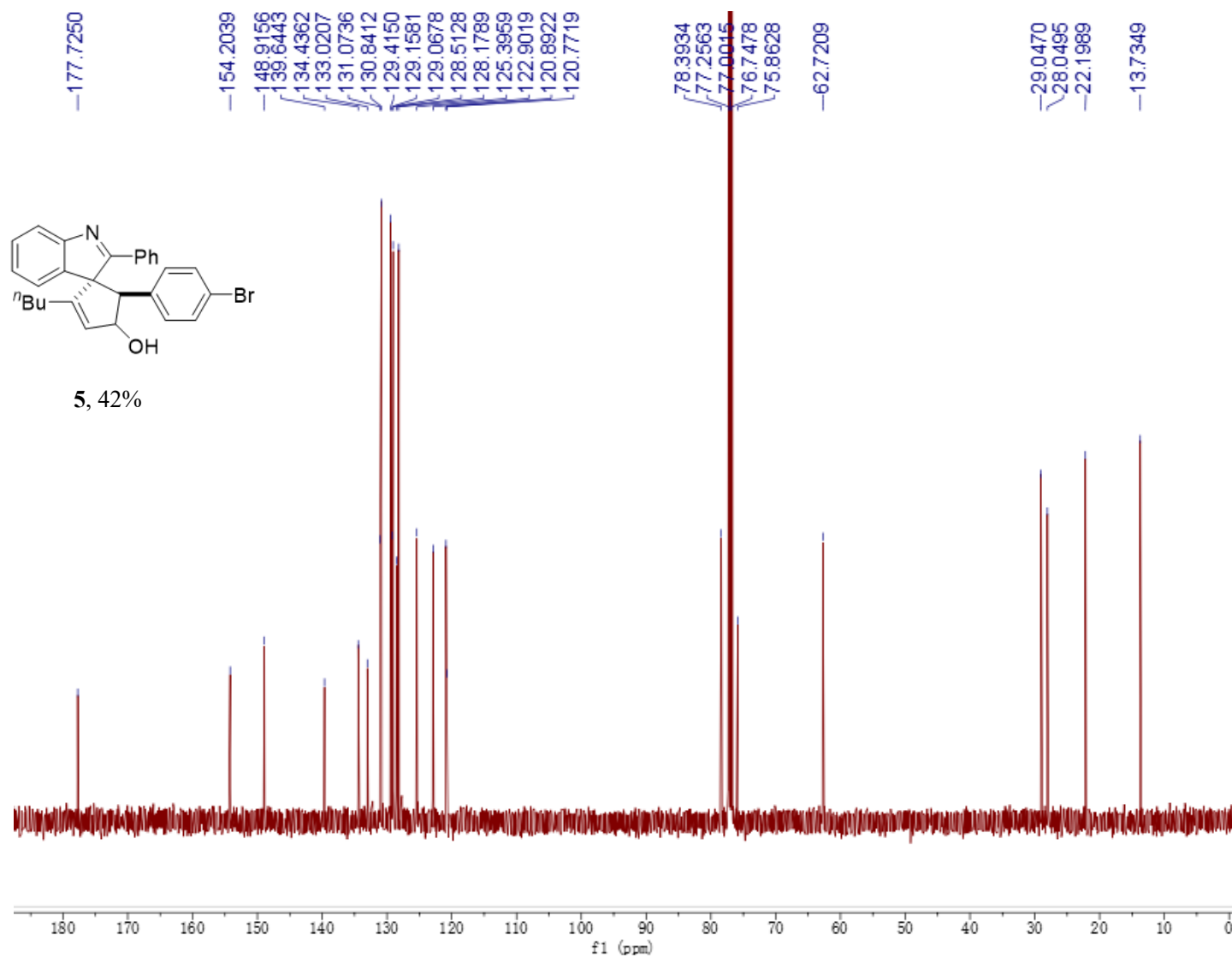


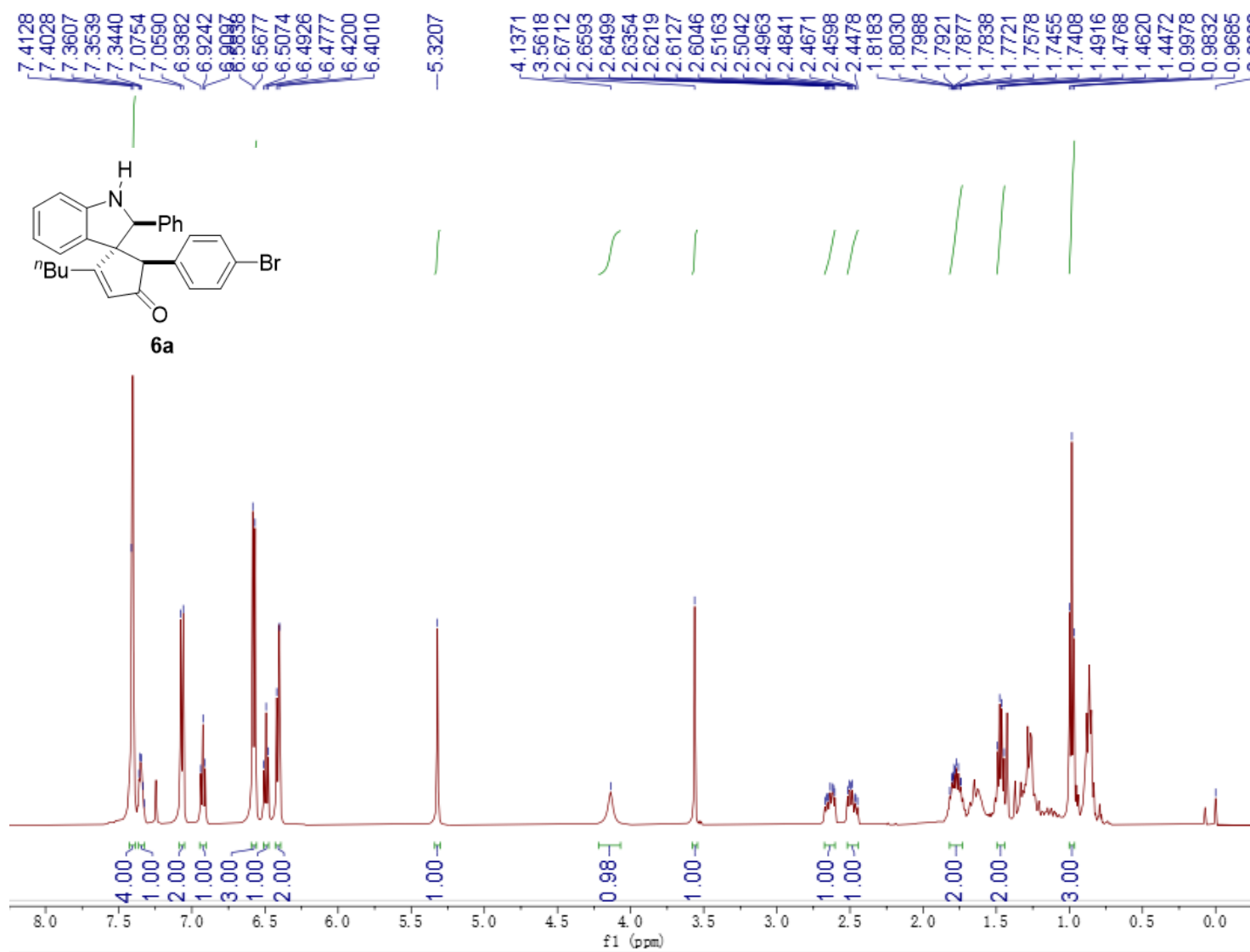


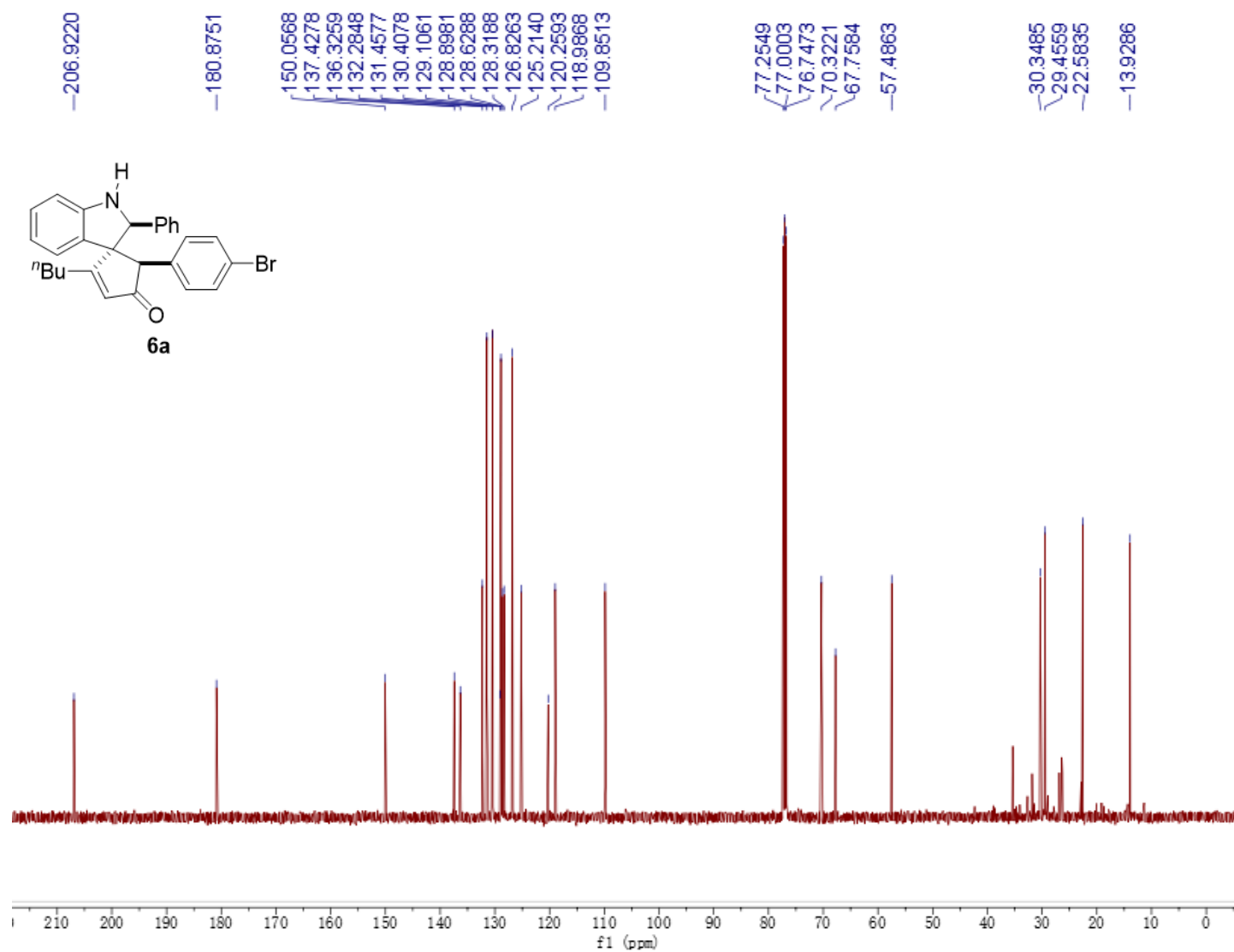
5, dr = 5.7:1, 38%

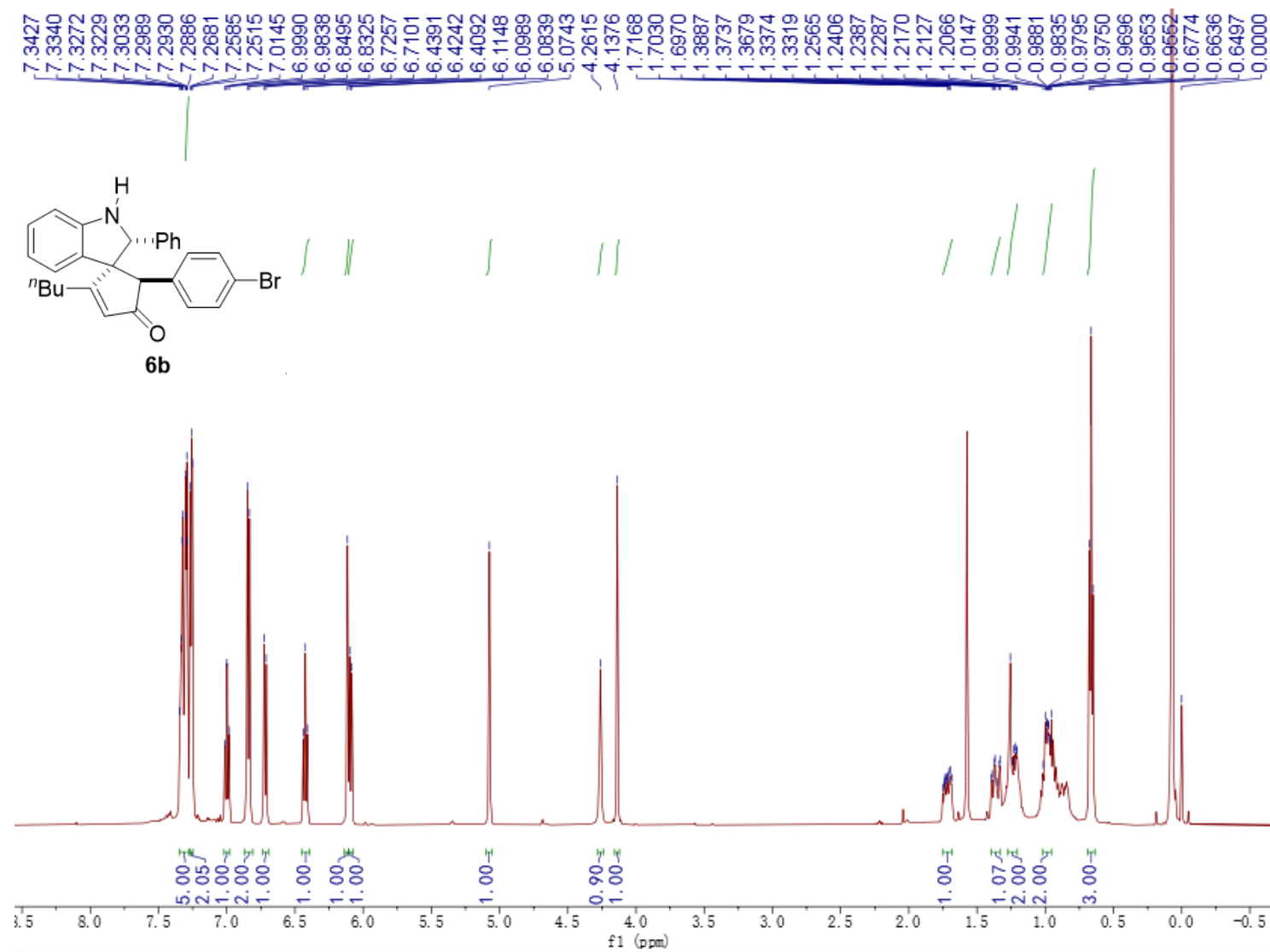


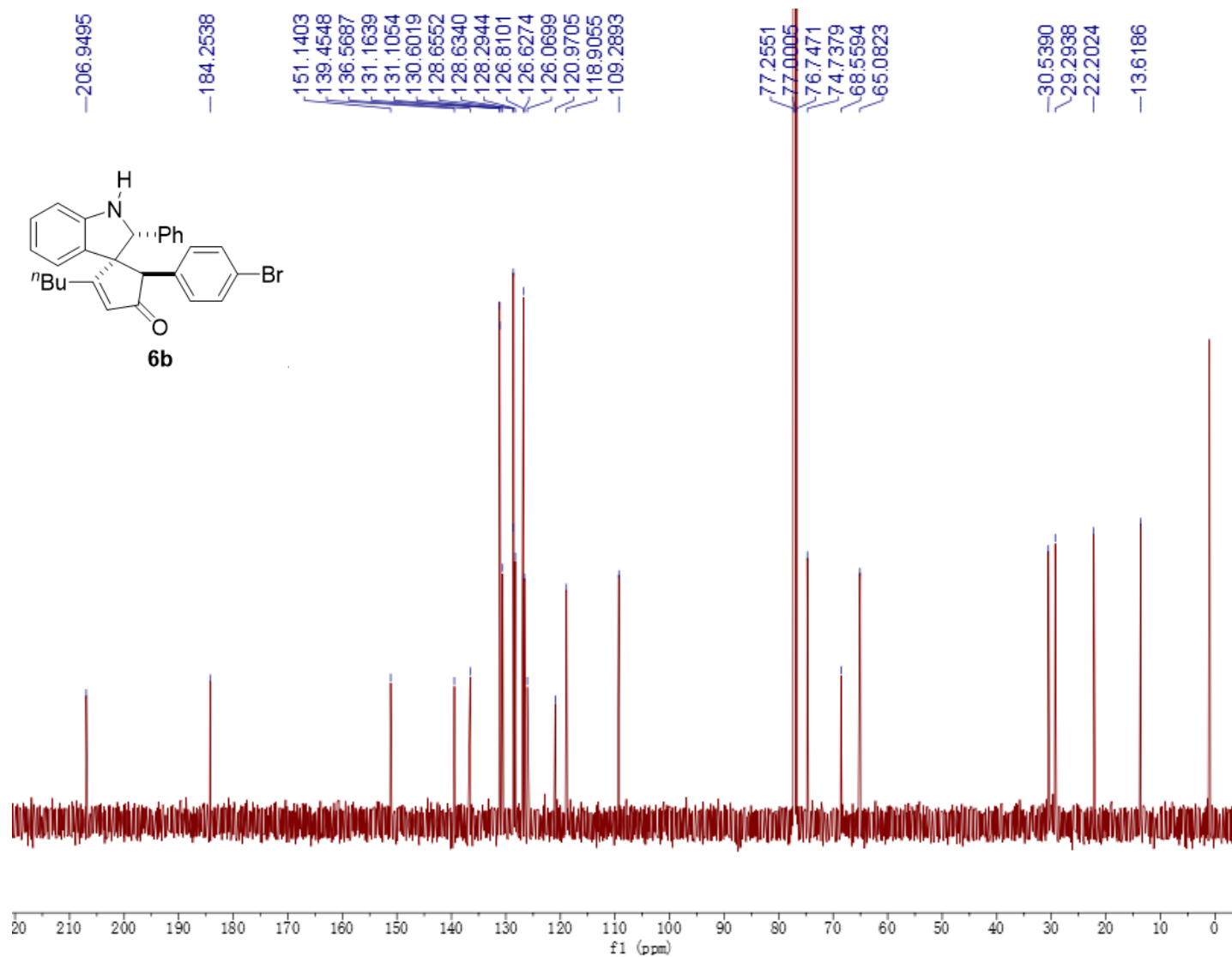












Mass Spectrum List Report

Analysis Info

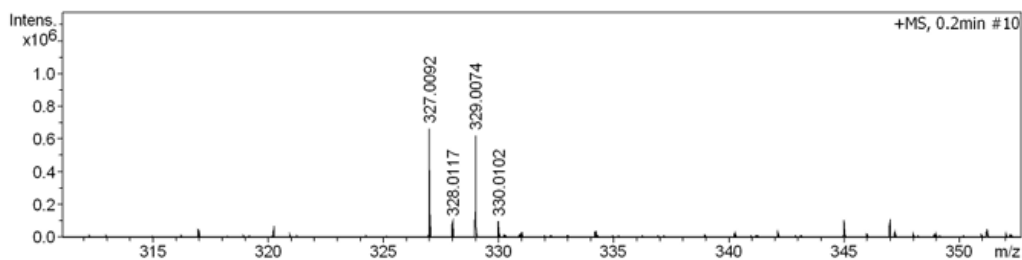
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 Method Tune_pos_low_LC with calibration_2min_20210727.m
 Sample Name ZYT-1P
 Comment

Acquisition Date 4/15/2024 2:08:18 PM

Operator ECNU-Chem
 Instrument maXis impact 282001.00122

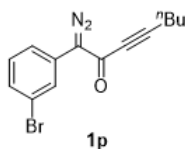
Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.5 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	6.0 l/min
Scan End	1350 m/z	Set Collision Cell RF	700.0 Vpp	Set Divert Valve	Waste



#	m/z	Res.	S/N	I	I %	FWHM
1	327.0092	24441	1105.8	665604	100.0	0.0134
2	328.0117	19755	165.2	99588	15.0	0.0166
3	329.0074	23641	1028.5	621032	93.3	0.0139
4	330.0102	18484	163.1	98852	14.9	0.0179

Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	Score	rdb	e ⁻	Conf	N-Rule
327.0092	1	C14H13BrN2NaO	327.0103	3.4	28.8	1	100.00	8.5	even	ok



Mass Spectrum List Report

Analysis Info

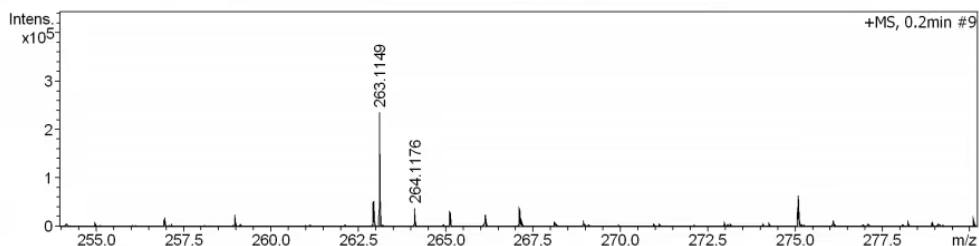
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 Sample Name ZYT-1Q
 Comment

Acquisition Date 4/15/2024 2:11:27 PM

Operator ECNU-Chem
 Instrument maXis impact 282001.00122

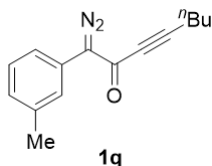
Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.5 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	6.0 l/min
Scan End	1350 m/z	Set Collision Cell RF	700.0 Vpp	Set Divert Valve	Waste



#	m/z	Res.	S/N	I	I %	FWHM
1	263.1149	20070	568.9	234456	100.0	0.0131
2	264.1176	17340	91.5	37860	16.1	0.0152

Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	Score	rdb	e ⁻	Conf	N-Rule
263.1149	1	C ₁₅ H ₁₆ N ₂ NaO	263.1155	2.4	10.9	1	100.00	8.5	even	ok



Mass Spectrum List Report

Analysis Info

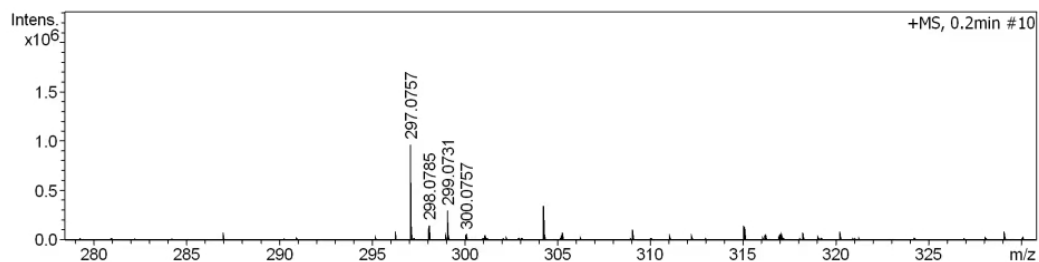
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 Method Tune_pos_low_LC with calibration_2min_20210727.m
 Sample Name ZYT-1S
 Comment

Acquisition Date 4/15/2024 2:21:03 PM

Operator ECNU-Chem
 Instrument maXis impact 282001.00122

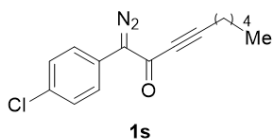
Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.5 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	6.0 l/min
Scan End	1350 m/z	Set Collision Cell RF	700.0 Vpp	Set Divert Valve	Waste



#	m/z	Res.	S/N	I	I %	FWHM
1	297.0757	25902	1706.3	967064	100.0	0.0115
2	298.0785	17807	254.1	144488	14.9	0.0167
3	299.0731	19988	523.0	298488	30.9	0.0150
4	300.0757	15967	89.9	51472	5.3	0.0188

Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	Score	rdb	e ⁻	Conf	N-Rule
297.0757	1	C15H15ClN2NaO	297.0765	2.8	15.9	1	100.00	8.5	even	ok



Mass Spectrum List Report

Analysis Info

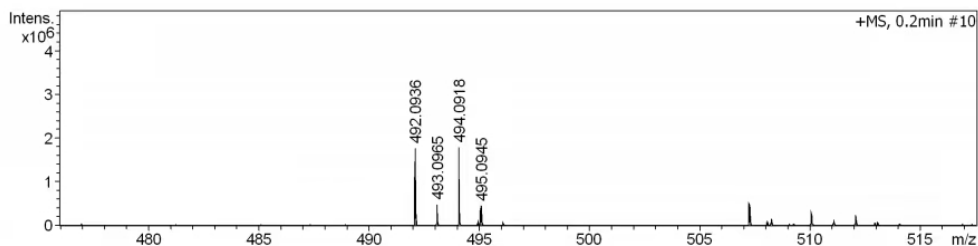
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 Comment

Acquisition Date 4/9/2024 7:05:56 PM

Operator ECNU-Chem
 Instrument maXis impact 282001.00122

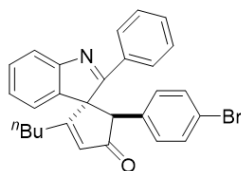
Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.5 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	6.0 l/min
Scan End	1350 m/z	Set Collision Cell RF	700.0 Vpp	Set Divert Valve	Waste



#	m/z	Res.	S/N	I	I %	FWHM
1	492.0936	31703	1309.3	1762344	99.0	0.0155
2	493.0965	24267	356.8	482284	27.1	0.0203
3	494.0918	31874	1313.0	1780364	100.0	0.0155
4	495.0945	23697	334.9	455532	25.6	0.0209

Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	Score	rdb	e ⁻ Conf	N-Rule
492.0936	1	C ₂₈ H ₂₄ BrNNaO	492.0933	-0.4	22.8	1	100.00	16.5 even	ok



3a

Mass Spectrum List Report

Analysis Info

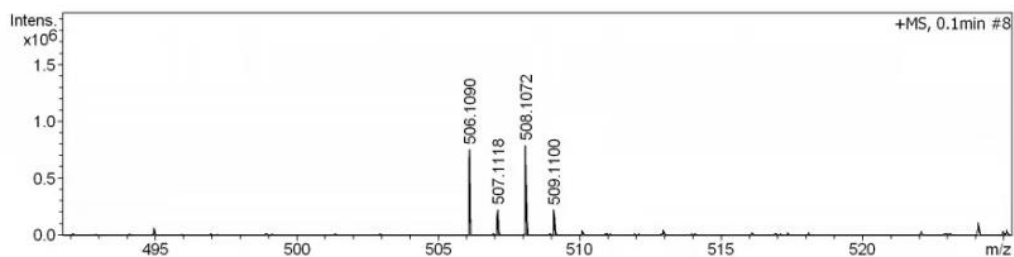
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 Method Tune_pos_low_LC with calibration_2min_20210727.m
 Sample Name ZYT-2-141
 Comment

Acquisition Date 4/9/2024 7:09:06 PM

Operator ECNU-Chem
 Instrument maXis impact 282001.00122

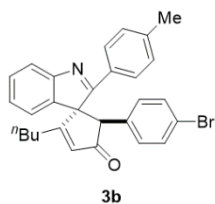
Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.5 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	6.0 l/min
Scan End	1350 m/z	Set Collision Cell RF	700.0 Vpp	Set Divert Valve	Waste



#	m/z	Res.	S/N	I	I %	FWHM
1	506.1090	26247	510.1	752428	95.4	0.0193
2	507.1118	19372	153.5	227036	28.8	0.0262
3	508.1072	27441	531.9	788492	100.0	0.0185
4	509.1100	20470	148.5	220800	28.0	0.0249

Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	Score	rdb	e ⁻	Conf	N-Rule
506.1090	1	C ₂₉ H ₂₆ BrNNaO	506.1090	-0.0	18.3	1	100.00	16.5	even	ok



Mass Spectrum List Report

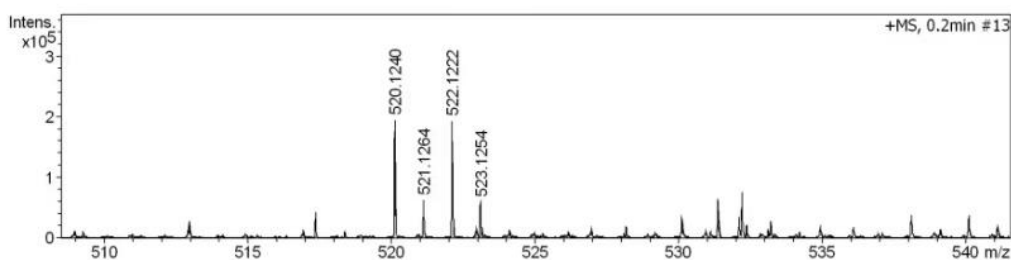
Analysis Info

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 Sample Name ZYT-2-149
 Comment

Acquisition Date 4/9/2024 7:12:14 PM
 Operator ECNU-Chem
 Instrument maXis impact 282001.00122

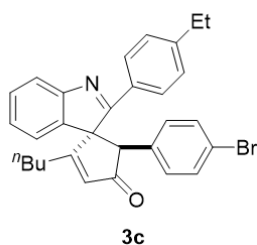
Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.5 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	6.0 l/min
Scan End	1350 m/z	Set Collision Cell RF	700.0 Vpp	Set Divert Valve	Waste



#	m/z	Res.	S/N	I	I %	FWHM
1	520.1240	19287	154.6	194608	100.0	0.0270
2	521.1264	16317	50.0	63032	32.4	0.0319
3	522.1222	19526	152.2	192572	99.0	0.0267
4	523.1254	16680	47.1	59692	30.7	0.0314

Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	Score	rdb	e ⁻ Conf	N-Rule
520.1240	1	C30H28BrNNaO	520.1246	1.3	14.1	1	100.00	16.5	even ok



Mass Spectrum List Report

Analysis Info

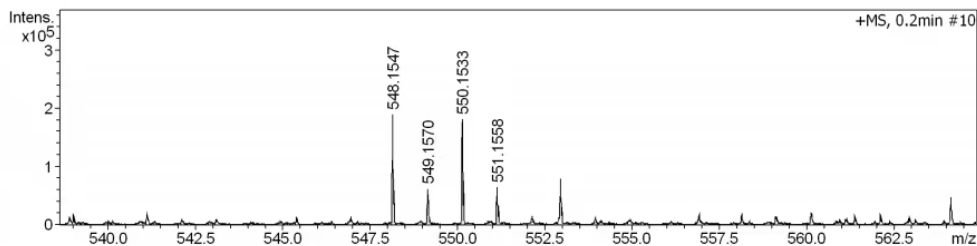
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 Sample Name ZYT-2-170
 Comment

Acquisition Date 4/9/2024 7:15:21 PM

Operator ECNU-Chem
 Instrument maXis impact 282001.00122

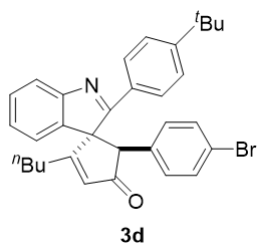
Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.5 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	6.0 l/min
Scan End	1350 m/z	Set Collision Cell RF	700.0 Vpp	Set Divert Valve	Waste



#	m/z	Res.	S/N	I	I%	FWHM
1	548.1547	20108	112.3	188692	100.0	0.0273
2	549.1570	16593	37.1	62408	33.1	0.0331
3	550.1533	18794	107.1	181016	95.9	0.0293
4	551.1558	18135	38.0	64484	34.2	0.0304

Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	Score	rdb	e ⁻	Conf	N-Rule
548.1547	1	C32H32BrNNaO	548.1559	2.3	23.1	1	100.00	16.5	even	ok



Mass Spectrum List Report

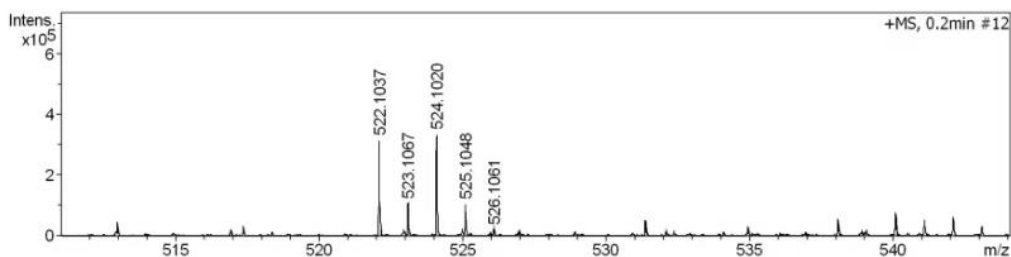
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 Sample Name ZYT-2-143
 Comment

Acquisition Date 4/9/2024 7:18:28 PM
 Operator ECNU-Chem
 Instrument maXis impact 282001.00122

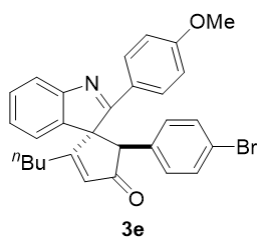
Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.5 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	6.0 l/min
Scan End	1350 m/z	Set Collision Cell RF	700.0 Vpp	Set Divert Valve	Waste



#	m/z	Res.	S/N	I	I %	FWHM
1	522.1037	20294	236.7	314532	94.2	0.0257
2	523.1067	18445	79.6	106048	31.8	0.0284
3	524.1020	20692	250.0	333792	100.0	0.0253
4	525.1048	17280	78.6	105068	31.5	0.0304
5	526.1061	13367	14.9	19984	6.0	0.0394

Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	Score	rdb	e ⁻	Conf	N-Rule
522.1037	1	C29H26BrNNaO2	522.1039	0.5	13.9	1	100.00	16.5	even	ok



Mass Spectrum List Report

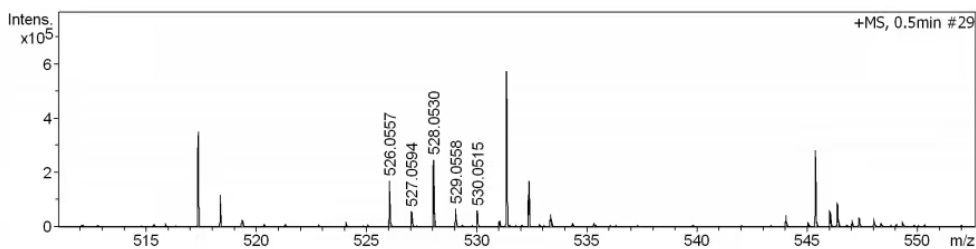
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 Sample Name ZYT-2-131
 Comment

Acquisition Date 4/12/2024 12:11:23 PM
 Operator ECNU-Chem
 Instrument maXis impact 282001.00122

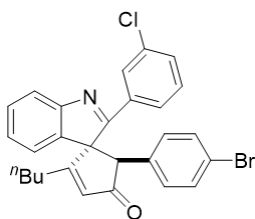
Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.5 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	6.0 l/min
Scan End	1350 m/z	Set Collision Cell RF	700.0 Vpp	Set Divert Valve	Waste



#	m/z	Res.	S/N	I	I%	FWHM
1	526.0557	16977	243.2	170184	68.9	0.0310
2	527.0594	16256	80.5	56348	22.8	0.0324
3	528.0530	20161	352.4	246924	100.0	0.0262
4	529.0558	17413	97.1	68052	27.6	0.0304
5	530.0515	14881	87.3	61168	24.8	0.0356

Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	Score	rdb	e ⁻ Conf	N-Rule
526.0557	1	C28H23BrClNNaO	526.0544	-2.5	26.7	1	100.00	16.5	even ok



3g

Mass Spectrum List Report

Analysis Info

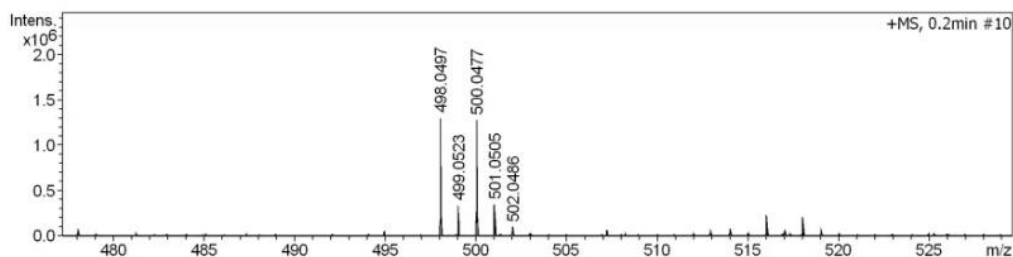
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 Sample Name ZYT-2-145
 Comment

Acquisition Date 4/9/2024 7:31:02 PM

Operator ECNU-Chem
 Instrument maXis impact 282001.00122

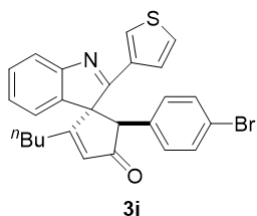
Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.5 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	6.0 l/min
Scan End	1350 m/z	Set Collision Cell RF	700.0 Vpp	Set Divert Valve	Waste



#	m/z	Res.	S/N	I	I %	FWHM
1	498.0497	30943	1180.6	1297468	100.0	0.0161
2	499.0523	22048	305.5	336356	25.9	0.0226
3	500.0477	29032	1155.9	1276856	98.4	0.0172
4	501.0505	22600	316.4	350000	27.0	0.0222
5	502.0486	14700	87.0	96348	7.4	0.0342

Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	Score	rdb	e ⁻	Conf	N-Rule
498.0497	1	C ₂₆ H ₂₂ BrNNaOS	498.0498	0.2	27.1	2	100.00	15.5	even	ok



Mass Spectrum List Report

Analysis Info

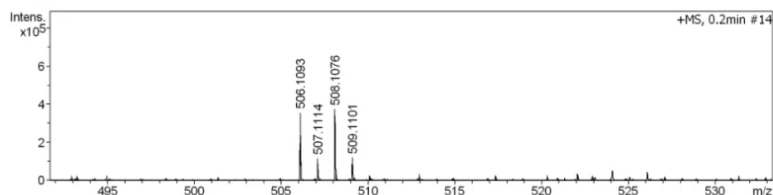
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 Method Tune_pos_low_LC with calibration_2min_20210727.m
 Sample Name ZYT-3-189
 Comment

Acquisition Date 2/24/2025 2:09:36 PM

Operator ECNU-Chem
 Instrument maXis impact 282001.00122

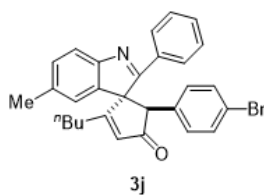
Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.5 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	6.0 l/min
Scan End	1350 m/z	Set Collision Cell RF	700.0 Vpp	Set Divert Valve	Waste



#	m/z	Res.	S/N	I	I %	FWHM
1	506.1093	19417	328.4	355616	95.3	0.0261
2	507.1114	18105	107.4	116176	31.1	0.0280
3	508.1076	19544	344.9	373252	100.0	0.0260
4	509.1101	18244	112.0	121184	32.5	0.0279

Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	Score	rdb	e ⁻	Conf	N-Rule
506.1093	1	C29H26BrNNaO	506.1090	-0.6	11.3	1	100.00	16.5	even	ok



Mass Spectrum List Report

Analysis Info

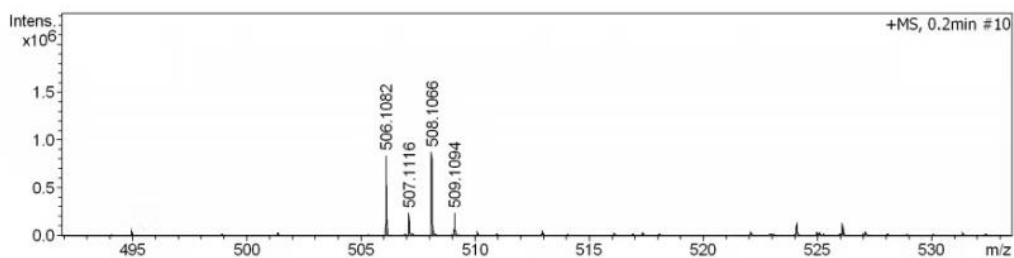
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 Sample Name ZYT-2-147
 Comment

Acquisition Date 4/9/2024 7:37:20 PM

Operator ECNU-Chem
 Instrument maXis impact 282001.00122

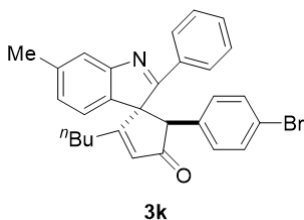
Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.5 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	6.0 l/min
Scan End	1350 m/z	Set Collision Cell RF	700.0 Vpp	Set Divert Valve	Waste



#	m/z	Res.	S/N	I	I %	FWHM
1	506.1082	27500	607.7	837948	95.9	0.0184
2	507.1116	20361	173.6	240120	27.5	0.0249
3	508.1066	27874	629.6	873548	100.0	0.0182
4	509.1094	20593	172.5	239864	27.5	0.0247

Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	Score	rdb	e ⁻ Conf	N-Rule
506.1082	1	C ₂₉ H ₂₆ BrNNaO	506.1090	1.6	22.4	1	100.00	16.5 even	ok



Mass Spectrum List Report

Analysis Info

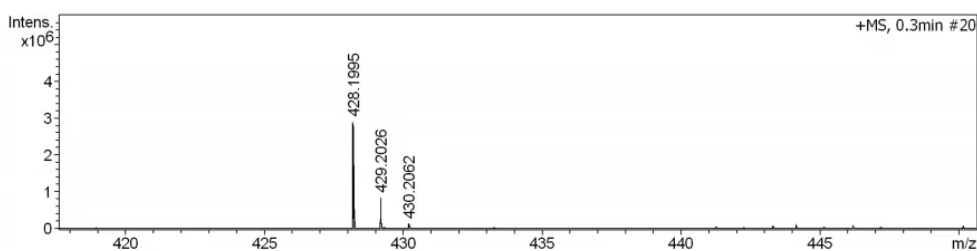
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 Sample Name ZYT-2-165
 Comment

Acquisition Date 4/9/2024 7:43:36 PM

Operator ECNU-Chem
 Instrument maXis impact 282001.00122

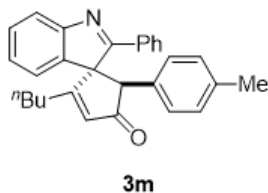
Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.5 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	6.0 l/min
Scan End	1350 m/z	Set Collision Cell RF	700.0 Vpp	Set Divert Valve	Waste



#	m/z	Res.	S/N	I	I %	FWHM
1	428.1995	26325	3586.3	2900816	100.0	0.0163
2	429.2026	23909	1041.7	844356	29.1	0.0180
3	430.2062	16600	160.6	130556	4.5	0.0259

Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	Score	rdb	e ⁻	Conf	N-Rule
428.1995	1	C ₂₉ H ₂₇ NNaO	428.1985	-2.3	15.2	1	100.00	16.5	even	ok



Mass Spectrum List Report

Analysis Info

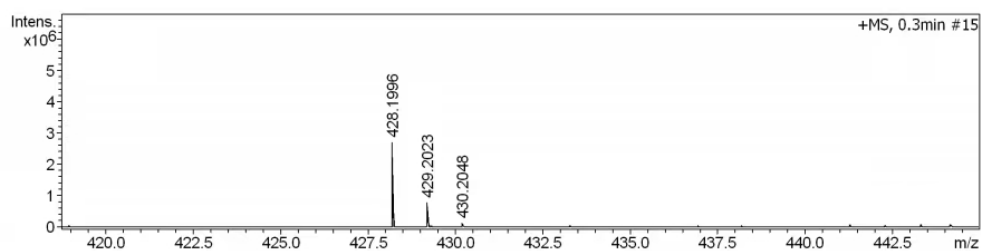
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 Sample Name ZYT-2-189
 Comment

Acquisition Date 4/9/2024 8:25:24 PM

Operator ECNU-Chem
 Instrument maXis impact 282001.00122

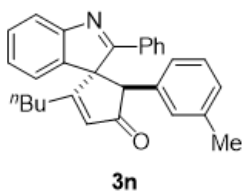
Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.5 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	6.0 l/min
Scan End	1350 m/z	Set Collision Cell RF	700.0 Vpp	Set Divert Valve	Waste



#	m/z	Res.	S/N	I	I%	FWHM
1	428.1996	27638	3232.3	2702328	100.0	0.0155
2	429.2023	25089	921.0	771008	28.5	0.0171
3	430.2048	19409	139.1	116776	4.3	0.0222

Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	Score	rdb	e ⁻	Conf	N-Rule
428.1996	1	C ₂₉ H ₂₇ NNaO	428.1985	-2.7	18.3	1	100.00	16.5	even	ok



Mass Spectrum List Report

Analysis Info

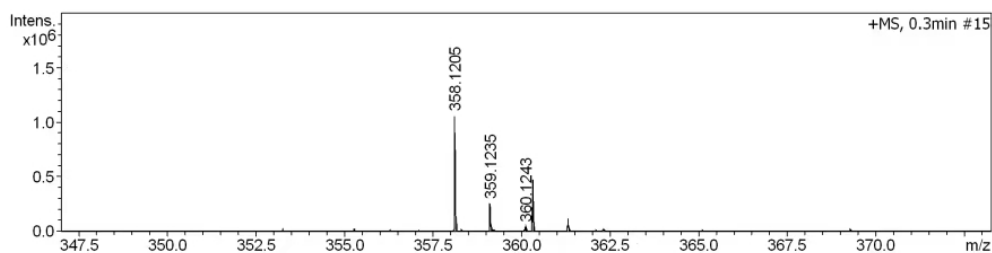
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 Sample Name ZYT-3-11
 Comment

Acquisition Date 4/12/2024 12:20:48 PM

Operator ECNU-Chem
 Instrument maXis impact 282001.00122

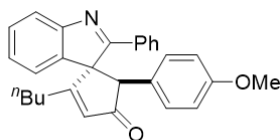
Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.5 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	6.0 l/min
Scan End	1350 m/z	Set Collision Cell RF	700.0 Vpp	Set Divert Valve	Waste



#	m/z	Res.	S/N	I	I %	FWHM
1	358.1205	23625	1465.1	1057560	100.0	0.0152
2	359.1235	18772	352.3	254396	24.1	0.0191
3	360.1243	16862	54.0	39052	3.7	0.0214

Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	Score	rdb	e ⁻ Conf	N-Rule
358.1205	1	C ₂₄ H ₁₇ NNaO	358.1202	-0.6	14.5	1	100.00	16.5 even	ok



3o

Mass Spectrum List Report

Analysis Info

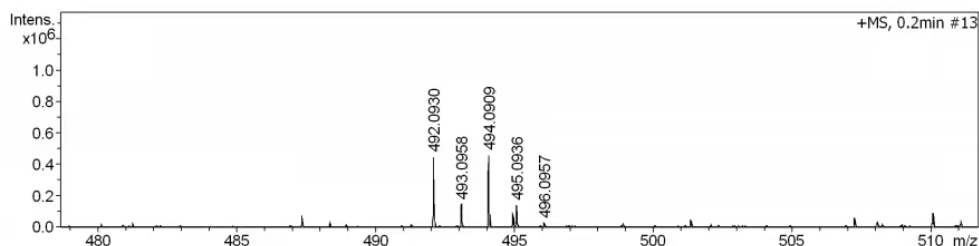
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 Comment

Acquisition Date 4/9/2024 8:22:16 PM

Operator ECNU-Chem
 Instrument maXis impact 282001.00122

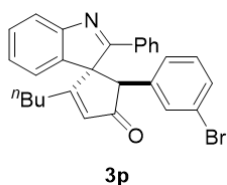
Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.5 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	6.0 l/min
Scan End	1350 m/z	Set Collision Cell RF	700.0 Vpp	Set Divert Valve	Waste



#	m/z	Res.	S/N	I	I%	FWHM
1	492.0930	21405	430.2	445448	97.2	0.0230
2	493.0958	19504	137.8	143056	31.2	0.0253
3	494.0909	22237	440.5	458224	100.0	0.0222
4	495.0936	19160	135.8	141536	30.9	0.0258
5	496.0957	17705	22.6	23644	5.2	0.0280

Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	Score	rdb	e ⁻	Conf	N-Rule
492.0930	1	C28H24BrNNaO	492.0933	0.7	6.4	100.00	16.5	even		ok



Mass Spectrum List Report

Analysis Info

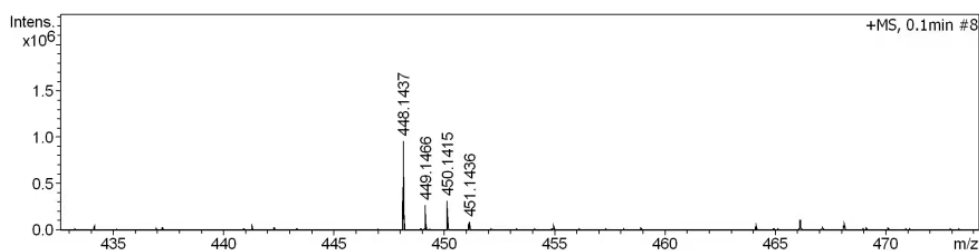
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 Sample Name ZYT-2-164
 Comment

Acquisition Date 4/9/2024 7:40:29 PM

Operator ECNU-Chem
 Instrument maXis impact 282001.00122

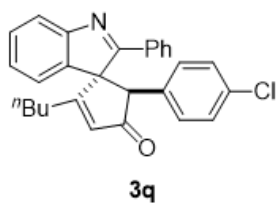
Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.5 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	6.0 l/min
Scan End	1350 m/z	Set Collision Cell RF	700.0 Vpp	Set Divert Valve	Waste



#	m/z	Res.	S/N	I	I %	FWHM
1	448.1437	28836	789.0	956160	100.0	0.0155
2	449.1466	21790	220.7	268332	28.1	0.0206
3	450.1415	21300	258.0	315024	32.9	0.0211
4	451.1436	17374	71.4	87460	9.1	0.0260

Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	Score	rdb	e ⁻ Conf	N-Rule
448.1437	1	C ₂₈ H ₂₄ ClNNaO	448.1439	0.3	22.4	1	100.00	16.5	even ok



Mass Spectrum List Report

Analysis Info

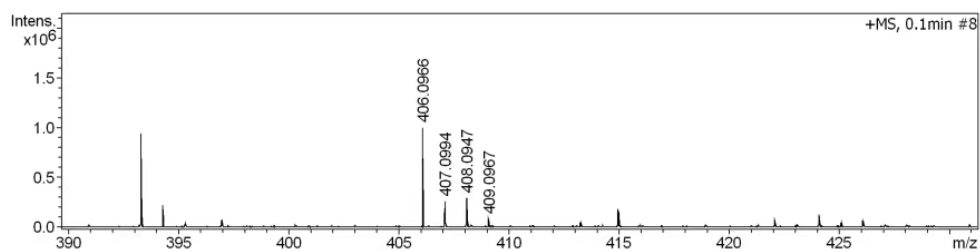
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 Comment

Acquisition Date 4/9/2024 8:28:33 PM

Operator ECNU-Chem
 Instrument maXis impact 282001.00122

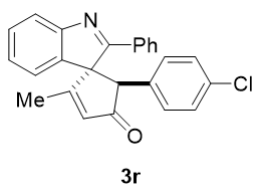
Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.5 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	6.0 l/min
Scan End	1350 m/z	Set Collision Cell RF	700.0 Vpp	Set Divert Valve	Waste



#	m/z	Res.	S/N	I	I %	FWHM
1	406.0966	29402	824.8	997972	100.0	0.0138
2	407.0994	22361	211.6	257320	25.8	0.0182
3	408.0947	19678	237.7	290816	29.1	0.0207
4	409.0967	17176	63.7	78264	7.8	0.0238

Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	Score	rdB	e ⁻	Conf	N-Rule
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Mass Spectrum List Report

Analysis Info

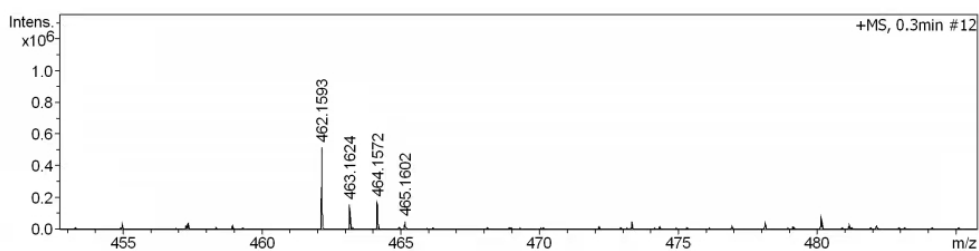
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 Sample Name ZYT-2-167
 Comment

Acquisition Date 4/9/2024 6:50:14 PM

Operator ECNU-Chem
 Instrument maXis impact 282001.00122

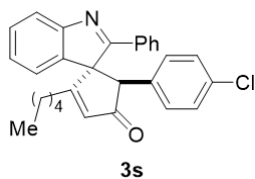
Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.5 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	6.0 l/min
Scan End	1350 m/z	Set Collision Cell RF	700.0 Vpp	Set Divert Valve	Waste



#	m/z	Res.	S/N	I	I %	FWHM
1	462.1593	23458	486.9	513692	100.0	0.0197
2	463.1624	18442	147.6	155920	30.4	0.0251
3	464.1572	17948	165.4	174932	34.1	0.0259
4	465.1602	16572	48.2	51184	10.0	0.0281

Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	Score	rdb	e ⁻	Conf	N-Rule
462.1593	1	C ₂₉ H ₂₆ ClNNaO	462.1595	0.4	16.4	1	100.00	16.5	even	ok



Mass Spectrum List Report

Analysis Info

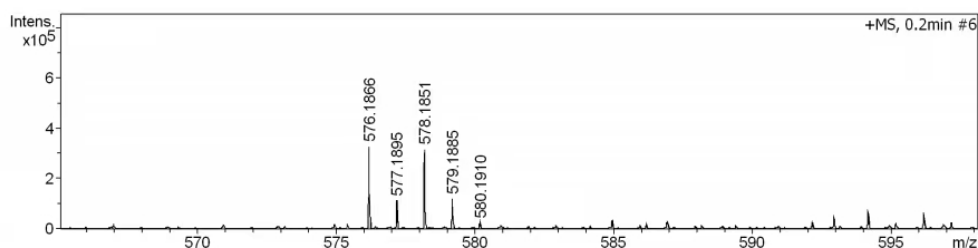
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 Method Tune_pos_low_LC with calibration_2min_20210727.m
 Sample Name ZYT-2-94
 Comment

Acquisition Date 4/9/2024 6:53:22 PM

Operator ECNU-Chem
 Instrument maXis impact 282001.00122

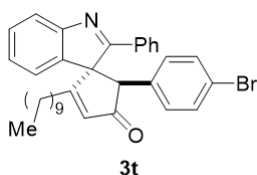
Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.5 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	6.0 l/min
Scan End	1350 m/z	Set Collision Cell RF	700.0 Vpp	Set Divert Valve	Waste



#	m/z	Res.	S/N	I	I %	FWHM
1	576.1866	22042	254.2	327152	100.0	0.0261
2	577.1895	17416	87.0	112384	34.4	0.0331
3	578.1851	21786	243.6	315404	96.4	0.0265
4	579.1885	19008	91.5	118724	36.3	0.0305
5	580.1910	16265	17.6	23000	7.0	0.0357

Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	Score	rdb	e ⁻ Conf	N-Rule
576.1866	1	C34H36BrNNaO	576.1872	1.1	23.7	1	100.00	16.5	even ok



Mass Spectrum List Report

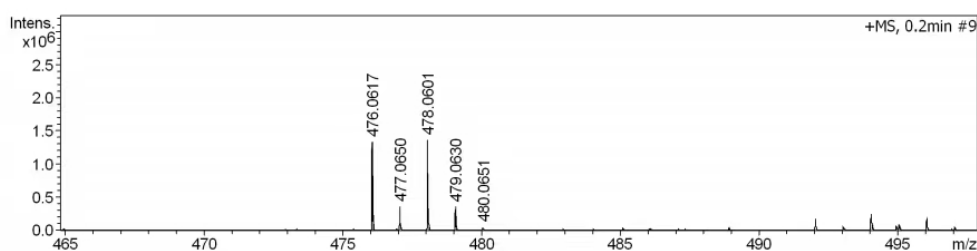
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 Sample Name ZYT-2-73
 Comment

Acquisition Date 4/9/2024 6:56:31 PM
 Operator ECNU-Chem
 Instrument maXis impact 282001.00122

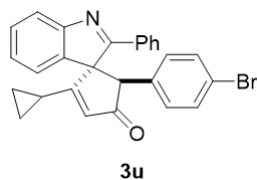
Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.5 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	6.0 l/min
Scan End	1350 m/z	Set Collision Cell RF	700.0 Vpp	Set Divert Valve	Waste



#	m/z	Res.	S/N	I	I %	FWHM
1	476.0617	30643	1074.0	1335940	98.1	0.0155
2	477.0650	22691	287.9	358516	26.3	0.0210
3	478.0601	30480	1091.7	1361860	100.0	0.0157
4	479.0630	21382	283.2	353780	26.0	0.0224
5	480.0651	15560	41.3	51632	3.8	0.0309

Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	Score	rdb	e ⁻	Conf	N-Rule
476.0617	1	C27H20BrNNaO	476.0620	0.6	17.4	100.00	17.5	even		ok



Mass Spectrum List Report

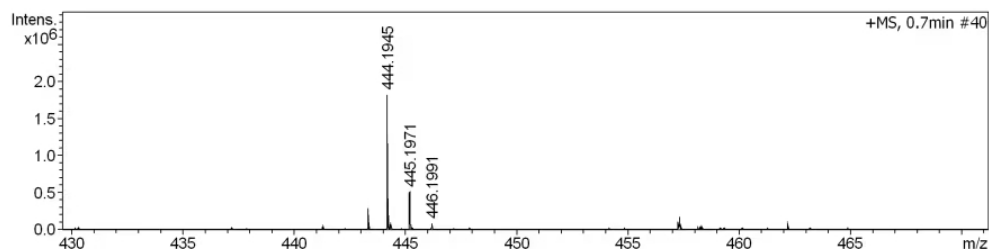
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 Sample Name ZYT-3-6
 Comment

Acquisition Date 4/12/2024 12:23:58 PM
 Operator ECNU-Chem
 Instrument maXis impact 282001.00122

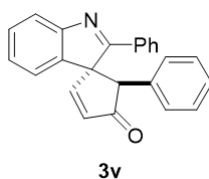
Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.5 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	6.0 l/min
Scan End	1350 m/z	Set Collision Cell RF	700.0 Vpp	Set Divert Valve	Waste



#	m/z	Res.	S/N	I	I %	FWHM
1	444.1945	26524	2367.2	1814104	100.0	0.0167
2	445.1971	21730	665.7	510652	28.1	0.0205
3	446.1991	17436	102.6	78764	4.3	0.0256

Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	Score	rdb	e ⁻	Conf	N-Rule
444.1945	1	C ₂₉ H ₂₇ NNaO ₂	444.1934	-2.4	20.5	1	100.00	16.5	even	ok



Mass Spectrum List Report

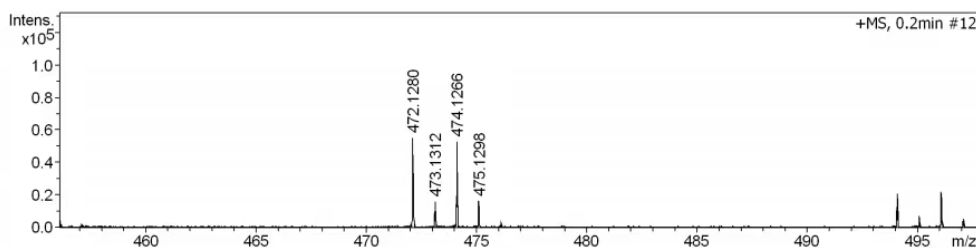
Analysis Info

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 Sample Name ZYT-2-196-1
 Comment

Acquisition Date 1/30/2024 4:02:01 PM
 Operator ECNU-Chem
 Instrument maXis impact 282001.00122

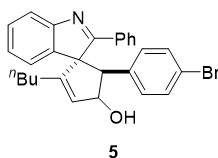
Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.5 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	6.0 l/min
Scan End	1350 m/z	Set Collision Cell RF	700.0 Vpp	Set Divert Valve	Waste



#	m/z	Res.	S/N	I	I %	FWHM
1	472.1280	20475	126.8	54996	100.0	0.0231
2	473.1312	18421	36.6	15884	28.9	0.0257
3	474.1266	18354	121.8	52772	96.0	0.0258
4	475.1298	21660	37.7	16320	29.7	0.0219

Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	Score	rdb	e ⁻	Conf	N-Rule
472.1280	1	C ₂₈ H ₂₇ BrNO	472.1271	-2.0	20.0	1	100.00	15.5	even	ok



Mass Spectrum List Report

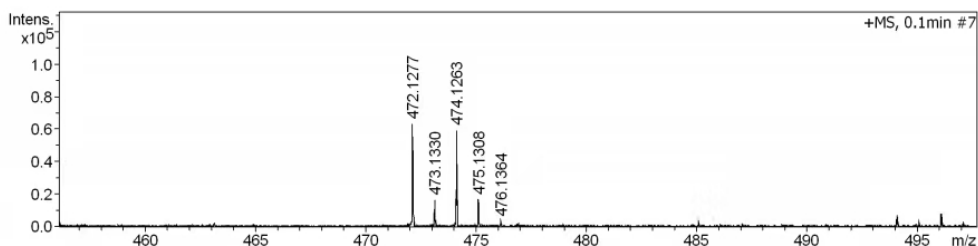
Analysis Info

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 Sample Name ZYT-2-196-2
 Comment

Acquisition Date 1/30/2024 4:05:09 PM
 Operator ECNU-Chem
 Instrument maXis impact 282001.00122

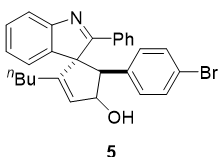
Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.5 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	6.0 l/min
Scan End	1350 m/z	Set Collision Cell RF	700.0 Vpp	Set Divert Valve	Waste



#	m/z	Res.	S/N	I	I%	FWHM
1	472.1277	21284	129.0	63124	100.0	0.0222
2	473.1330	19210	33.9	16560	26.2	0.0246
3	474.1263	18981	121.2	59200	93.8	0.0250
4	475.1308	18063	34.3	16724	26.5	0.0263
5	476.1364	20135	6.4	3100	4.9	0.0236

Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	Score	rdb	e ⁻ Conf	N-Rule
472.1277	1	C ₂₈ H ₂₇ BrNO	472.1271	-1.4	34.8	1	100.00	15.5	even ok



Mass Spectrum List Report

Analysis Info

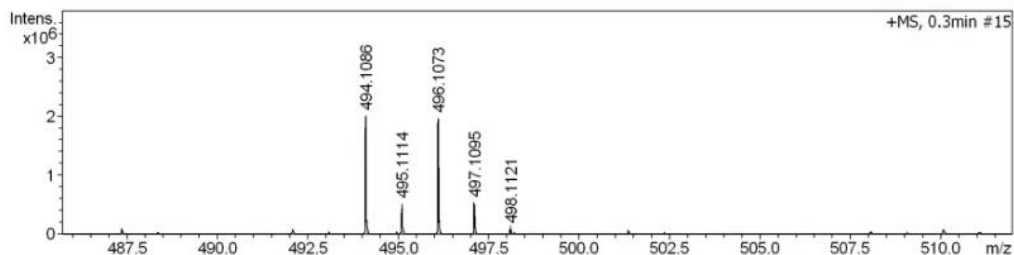
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 Comment

Acquisition Date 4/15/2024 1:58:55 PM

Operator ECNU-Chem
 Instrument maXis impact 282001.00122

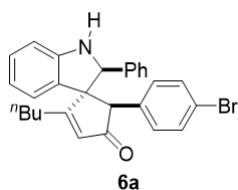
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Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.5 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	6.0 l/min
Scan End	1350 m/z	Set Collision Cell RF	700.0 Vpp	Set Divert Valve	Waste



#	m/z	Res.	S/N	I	I %	FWHM
1	494.1086	27688	2140.2	2010468	100.0	0.0178
2	495.1114	22545	560.5	527296	26.2	0.0220
3	496.1073	28534	2090.2	1970488	98.0	0.0174
4	497.1095	23574	576.1	543904	27.1	0.0211
5	498.1121	18971	95.4	90184	4.5	0.0263

Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	Score	rdB	e ⁻ Conf	N-Rule
494.1086	1	C28H26BrNNaO	494.1090	0.8	23.8	1	100.00	15.5	even ok



Mass Spectrum List Report

Analysis Info

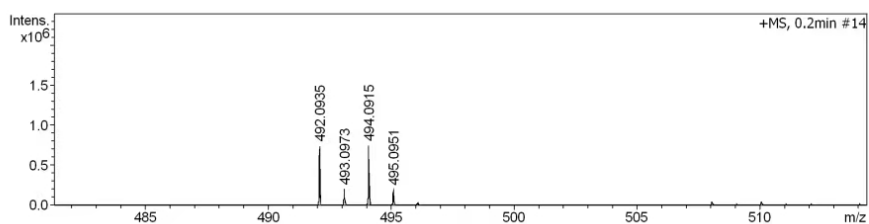
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 Comment

Acquisition Date 6/29/2023 2:36:01 PM

Operator ECNU-Chem
 Instrument maXis impact 282001.00122

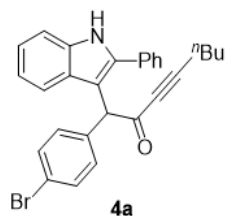
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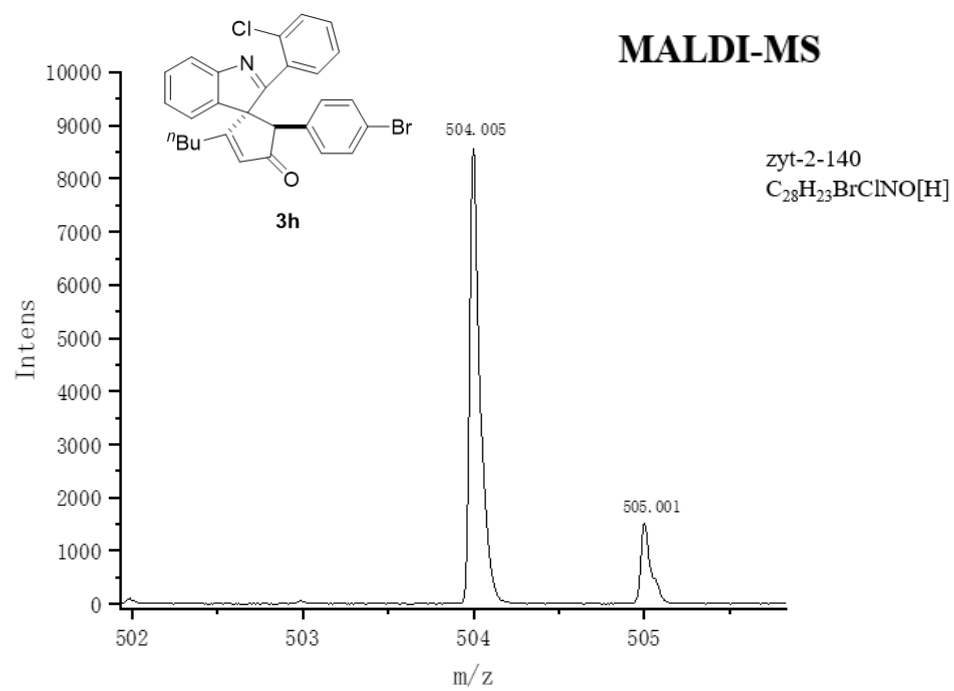
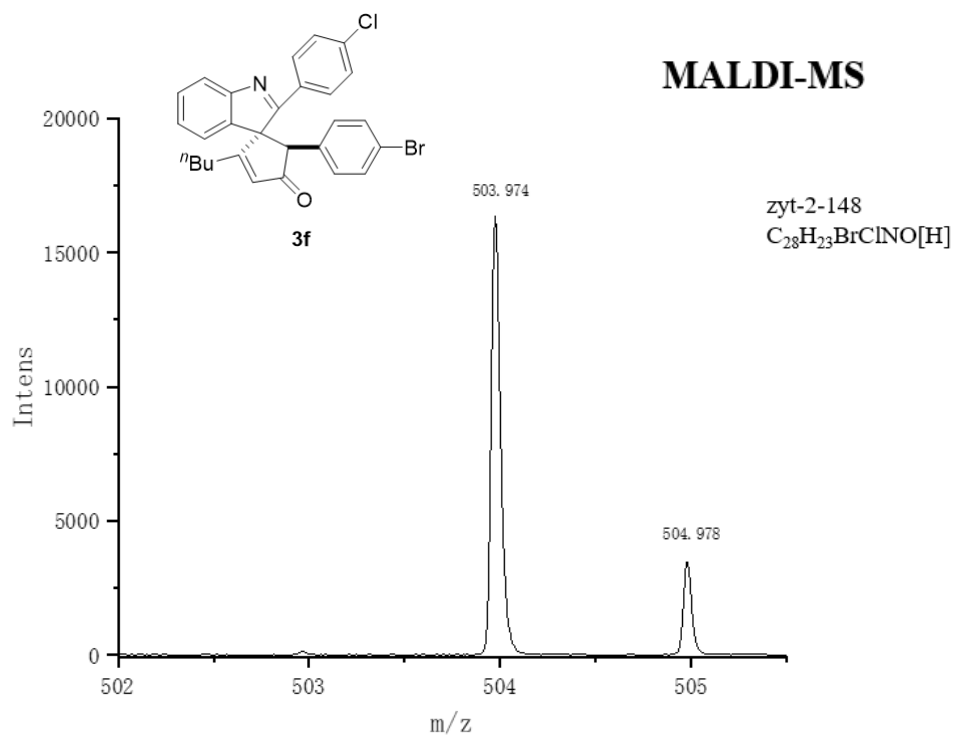
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.5 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	6.0 l/min
Scan End	1350 m/z	Set Collision Cell RF	700.0 Vpp	Set Divert Valve	Waste



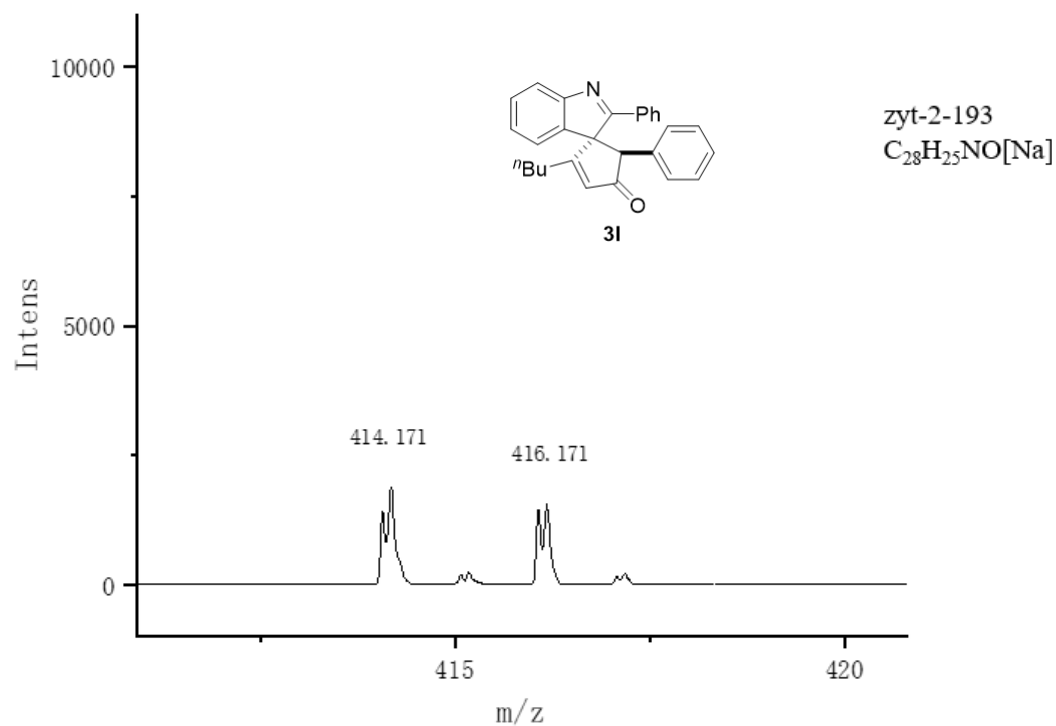
#	m/z	Res.	S/N	I	I %	FWHM
1	492.0935	23279	1628.4	739208	99.4	0.0211
2	493.0973	18370	443.5	201344	27.1	0.0268
3	494.0915	23406	1637.3	743524	100.0	0.0211
4	495.0951	17503	422.2	191644	25.8	0.0283

Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	Score	rdb	e ⁻ Conf	N-Rule
492.0935	1	C28H24BrNNaO	492.0933	-0.3	23.3	1	100.00	16.5 even	ok





MALDI-MS



MALDI-MS

