Supporting Information

Ruthenium-catalyzed reaction of diazoquinones with arylamines to synthesize diarylamines

Junxin Rao,[a] Xiaoyu Ren,[b] Xin Zhu,[a] Zhen Guo,*[b] Chengming Wang,*[a] Cong-Ying Zhou*[a]

[a] College of Chemistry and Materials Science, Guangdong Provincial Key Laboratory of Functional Supramolecular Coordination Materials and Applications, Jinan University, Guangzhou 510632, China.

[b] College of Materials Science & Engineering, Key Laboratory of Interface Science and Engineering in Advanced Materials, Ministry of Education, Taiyuan University of Technology, Shanxi 030024, China.

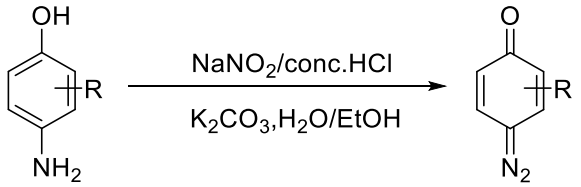
Contents

1. Experimental Section

1.1 General Information

All commercial reagents were used as provided without further purification. The diazoquinones were prepared according to the literature.[1] Arylamines were purchased or prepared according to the literature.[2] The reactions were monitored by thin layer chromatography (TLC) on silica gel GF254 coated 0.2 mm plates (Branch of Qingdao Haiyang Chemical plant). The product spots were visualized with UV and iodine (I_2). Flash column chromatography were performed using silica gel (200-300 mesh, Branch of Qingdao Haiyang Chemical plant) and a gradient solvent system (EtOAc/*n*-hexane as eluent). ^{1}H and ^{13}C NMR spectra were recorded on either a Bruker Avance 300 or Ascend 600 spectrometer. Chemical shifts (δ) were measured with tetramethylsilane (TMS) as internal reference. High Resolution Mass Spectrometry (HR-MS) data were obtained on AB SCIEX TripleTOF 5600+ mass spectrometer.

1.2 General Procedure for the Preparation of Diazoquinones



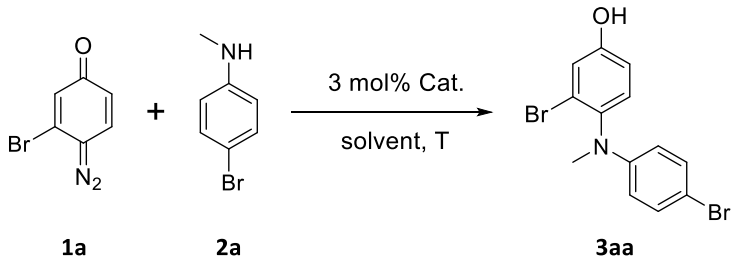
1

Caution: *Many of diazoquinones are sensitive to heat, light, shock and metal catalysts. They decompose slowly at room temperature and under air. Therefore, precaution should be taken in preparation, storage and use.*

Aminophenols (10 mmol, 1.0 equiv.) were dissolved in EtOH (40 mL) and cooled to 0 °C, and then HCl (8.4 mL, 12 N, 10 equiv.) was added slowly to the solution. This mixture was stirred at this temperature for 10 min, then an ice-cold solution of $NaNO_2$ (2.1 g, 3.0 equiv. in 4 mL H_2O) was added dropwise over 10 minutes. The resulting mixture was stirred for 2 h at 0 °C, and diluted with cold CH_2Cl_2 (150 mL) followed by addition of 10 g of ice. Then the mixture was stirred vigorously while a cold solution of K_2CO_3 (9.2 g, 6.7 equiv. in 9 mL H_2O) was added slowly. The organic layers were then separated and the aqueous layer was then extracted with CH_2Cl_2 (50 mL). The combined organic layer was then washed with brine (50 mL), and dried over Na_2SO_4. Evaporation in vacuo resulted in a solid. All of the diazo quinones were kept at -20 °C under dark conditions and used without further purification unless otherwise stated.

1.3 General procedure for the cross-coupling reaction of diazoquinones with arylamines to synthesize diarylamines

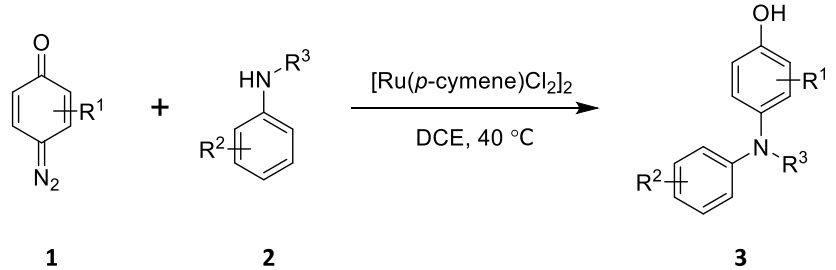
(1) General Procedure for the reaction condition screening



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

Diazoquinone **1a** (59.7 mg, 0.3 mmol, 1.0 equiv.) were added to a flame-dried 10 mL Schlenk tube with a magnetic stir bar. The tube was sealed, evacuated and flushed with argon three times. Then commercial anhydrous solvent (1.0 mL, noted in Table 1) was added. The mixture was stirred for 1 minute followed by adding 4-bromo-N-methylaniline **2a** (167.4 mg, 0.9 mmol, 3.0 equiv.), catalyst (3 mol%) and 1.0 mL solvent. The reaction mixture was then stirred for the indicated temperature and time in Table 1. Upon completion, the reaction solution was concentrated by vacuum and the residue was purified by flash column chromatography on silica gel to give the corresponding product.

(2) General procedure for the [Ru(*p*-cymene)Cl_2]$_2$-catalyzed cross-coupling reaction of diazoquinones with arylamines to synthesize diarylamines

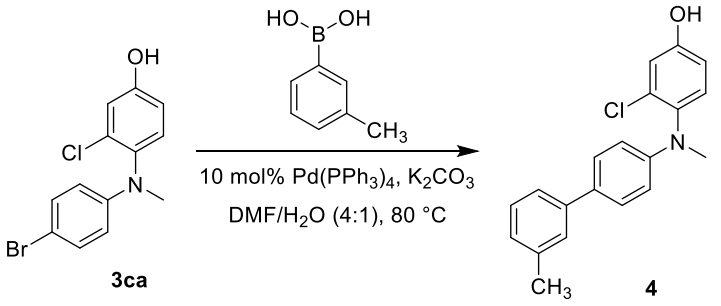


1 **2** **3**

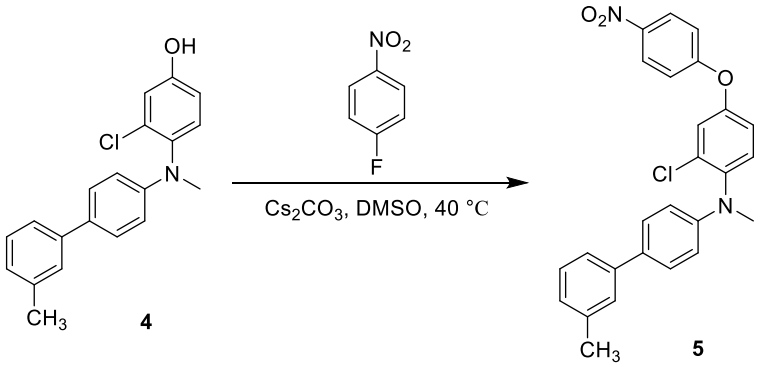
Diazoquinone (0.3 mmol, 1.0 equiv.) were added to a flame-dried 10 mL Schlenk tube with a magnetic stir bar. The tube was sealed, evacuated and flushed with argon three times. Then commercial anhydrous DCE (1.0 mL) was added. The mixture was stirred for 1 minute followed by adding arylamines (0.9 mmol, 3.0 equiv. see in Table 2), [Ru(*p*-cymene)Cl_2]$_2$ (3 mol%, 5.5 mg) and 1.0 mL DCE. The reaction mixture was then stirred at 40 °C until the complete consumption of diazoquinone as monitored by TLC analysis. Upon completion, the reaction solution was concentrated by vacuum and the

residue was purified by flash column chromatography on silica gel to give the corresponding product.

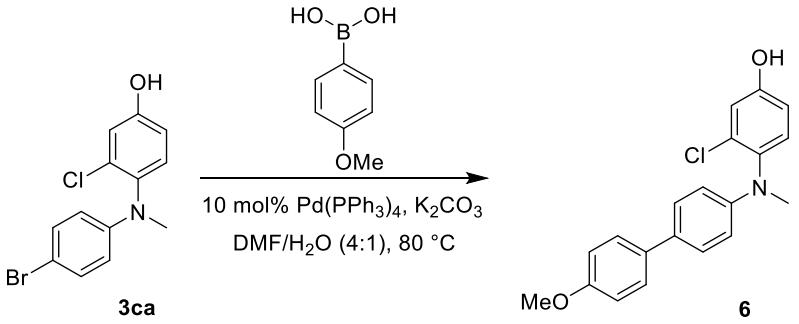
1.4 Modular synthesis of complex diarylamine derivatives



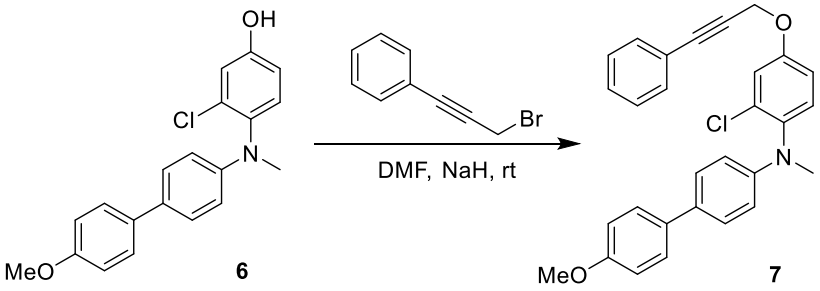
To a solution of the compound **3ca** (62.6 mg, 0.2 mmol), 4-methoxyphenylboronic acid 7(32.6 mg, 0.24 mmol), K_2CO_3 (83.0 mg, 0.6 mmol) in DMF/H_2O (4:1, 8 mL) was added $Pd(PPh_3)_4$ (23.2 mg, 0.02 mmol) and N_2 was bubbled through the mixture for 2 min. The mixture was stirred at 80 °C for 4h, then cooled to room temperature. The reaction mixture was diluted with water (25 mL), and then extracted with EtOAc (3 × 30 mL). The combined organic layer was washed with water, dried over anhydrous Na_2SO_4. The filtrate was concentrated by vacuum and the residue was purified by flash column chromatography on silica gel to give compound **4** in 82% yield (53.2 mg).



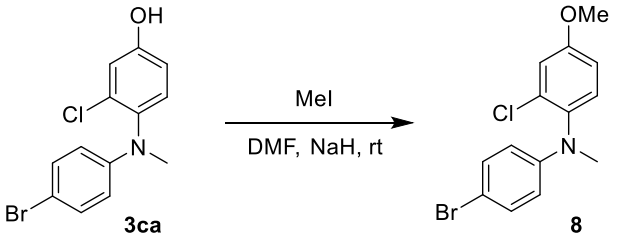
In a 10 mL oven-dried Schlenk tube equipped with a magnetic stirring bar, **4** (32.4 mg, 0.1 mmol), 1-fluoro-4-nitrobenzene (28.2 mg, 0.2 mmol), Cs_2CO_3 (32.6 mg, 0.1 mmol), and DMSO (1.0 mL) were vigorously stirred at 40 °C for 5 h. Then, the reaction mixture was cooled to room temperature, and water was added (5 mL) and extracted with EtOAc (3 × 5 mL). The combined organic phases were dried over anhydrous Na_2SO_4 and filtered. The filtrate was concentrated by vacuum and the residue was purified by flash column chromatography on silica gel to give compound **5** in 90% yield (40.0 mg).



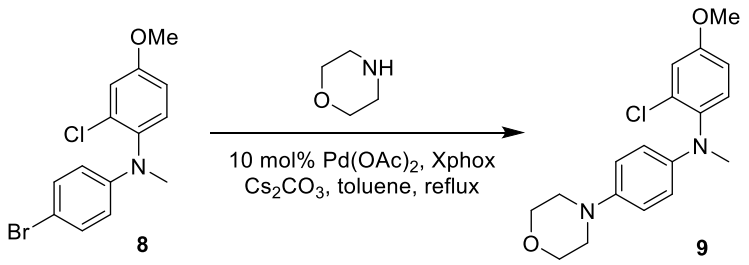
To a solution of the compound **3ca** (62.6 mg, 0.2 mmol), 4-methoxyphenylboronic acid 7(36.4 mg, 0.24 mmol), K_2CO_3 (83.0 mg, 0.6 mmol) in DMF/H_2O (4:1, 8 mL) was added $Pd(PPh_3)_4$ (23.2 mg, 0.02 mmol) and N_2 was bubbled through the mixture for 2 min. The mixture was stirred at 80 °C for 4 h, then cooled to room temperature. The reaction mixture was diluted with water (25 mL), and then extracted with EtOAc (3 × 30 mL). The combined organic layer was washed with water, dried over anhydrous Na_2SO_4 and filtered. The filtrate was concentrated by vacuum and the residue was purified by flash column chromatography on silica gel to give compound **6** in 81% yield (55.0 mg).



To a solution of **6** (34.0 mg, 0.1 mmol) in DMF (1 mL) was added NaH (4.0 mg, 60% in mineral oil, 0.1 mmol) at 0 °C. After stirring at room temperature for 10 min, (3-bromo-1-propynyl) benzene (23.4 mg, 0.12 mmol) was added to the reaction mixture. After stirring at room temperature for 4 h, the reaction was quenched with H_2O (1.5 mL) and extracted with ether (3 × 1.5 mL). The combined organic layers were washed with brine, dried over Na_2SO_4 and filtered. The filtrate was concentrated by vacuum and the residue was purified by flash column chromatography on silica gel to give compound **7** in 92% yield (41.8 mg).



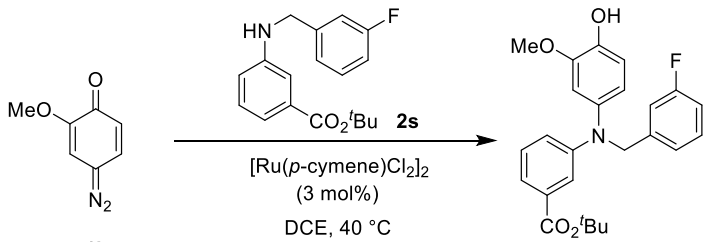
Compound **3ca** (62.4 mg, 0.2 mmol) was added to a suspension of NaH (40.0 mg, 60% in mineral oil, 1.0 mmol) in DMF (3 mL). Iodomethane (141.8 mg, 1.0 mmol) was then added and the reaction mixture was stirred at room temperature and monitored by TLC. When reaction was complete, a solution of saturated NH_4Cl (20 mL) was slowly added and the aqueous phase was extracted with $CHCl_3$ (2 × 30 mL). The combined organic layers were washed with water (10 × 30 mL), dried over anhydrous Na_2SO_4 and filtered. The filtrate was concentrated by vacuum and the residue was purified by flash column chromatography on silica gel to give compound **8** in 90% yield (58.8 mg).



8 **9**

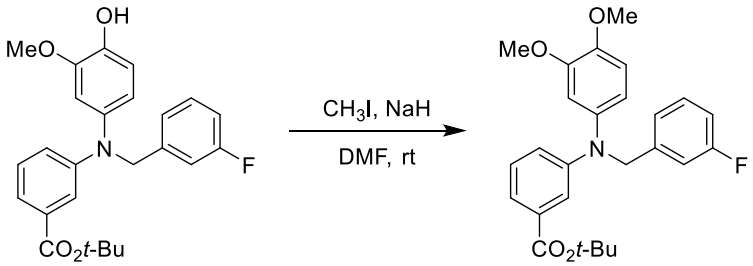
In a sealed tube was combined **8** (32.7 mg, 0.1 mmol), morpholine (11.3 mg, 0.13 mmol), $Pd(OAc)_2$ (2.2 mg, 0.01 mmol), Xphox (4.8 mg, 0.01 mmol), Cs_2CO_3 (32.6 mg, 0.1 mmol) and toluene (1 mL). This mixture was then degassed with N_2 for 10 min and subsequently heated at 116 °C for 16 h. The mixture was then cooled to rt and filtered through a plug of celite. The plug of celite was washing thoroughly with EtOAc. The filtrate was concentrated by vacuum and the residue was purified by flash column chromatography on silica gel to give compound **9** in 74% yield (24.6 mg).

1.5 Synthesis of an anti-inflammatory compound



1j **10**

Diazoquinone **1j** (30.0 mg, 0.2 mmol) were added to a flame-dried 10 mL Schlenk tube with a magnetic stir bar. The tube was sealed, evacuated and flushed with argon three times. Then commercial anhydrous DCE (1.0 mL) was added. The mixture was stirred for 1 minute followed by adding aniline **2s** (180.8 mg, 0.6 mmol), $[Ru(p\text{-cymene})Cl_2]_2$ (3 mol%, 5.5 mg) and 1.0 mL DCE. The reaction mixture was then stirred at 40 °C until the complete consumption of diazoquinone **1j** as monitored by TLC analysis. Upon completion, the reaction solution was concentrated by vacuum and the residue was purified by flash column chromatography on silica gel to give compound XX in 76% yield (64.4 mg).

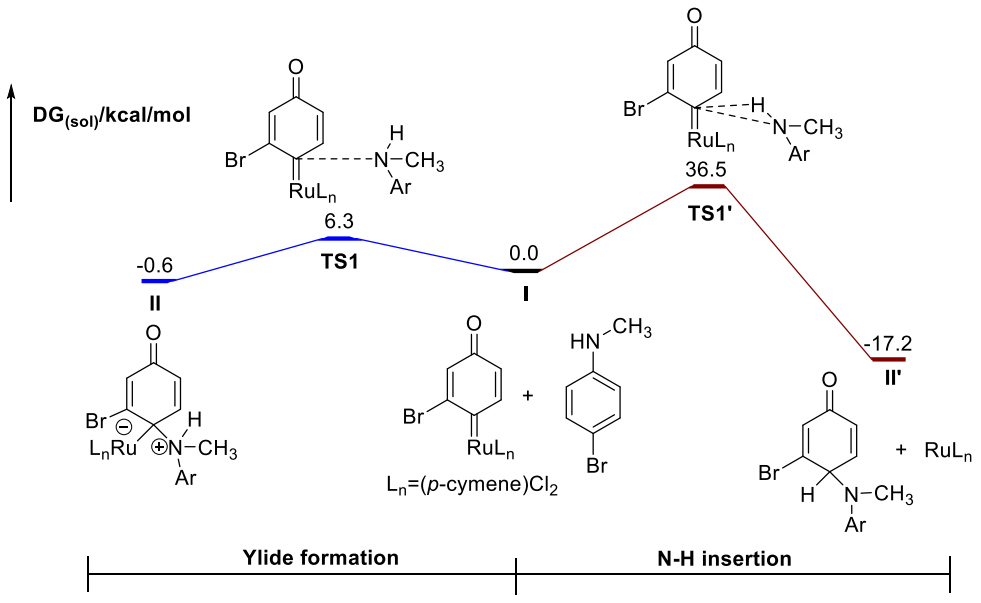


10 **11**

The **12** (42.3 mg, 0.1 mmol) was added to a suspension of NaH (20.0 mg, 60% in mineral oil, 0.5 mmol) in DMF (3 mL). The alkylating reagent (70.9 mg, 0.5 mmol) was then added and the reaction mixture was stirred at room temperature and monitored by TLC. When reaction was complete, a solution of saturated NH_4Cl (10 mL) was slowly added and the aqueous phase was extracted with $CHCl_3$ (2 × 15 mL). The combined organic layers were washed with water (10 × 15 mL), dried over anhydrous Na_2SO_4 and filtered. The filtrate was concentrated by vacuum and the residue was purified by flash column chromatography on silica gel to give compound **11** in 96% yield (42.0 mg).

1.6 Computational details

All calculations were performed with a Gaussian 09 program package. Geometry optimizations and vibrational frequency calculations were carried out at the B3LYP/6−31G(d) level in the gas phase with the effective core potential (ECP) type basis set SDD for Ru atom. The nature of all stationary points (local minima or transition states) was confirmed by the number of imaginary frequencies. Intrinsic reaction coordination (IRC) calculations were used to verify the connections among the transition states and their reactants and products.



The Cartesian coordinates of all stationary points at B3LYP/6–31G(d) level of theory.

I

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No imaginary frequencies
Sum of electronic and thermal Free Energies= -2063.276279 (Hartree/Particle)

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H	2.753751000	-0.940133000	2.113170000
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H	-2.449817000	1.612837000	-2.119536000
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H	-0.606407000	1.889277000	-0.795585000
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One Frequency = -146.45 cm^{-1}
Sum of electronic and thermal Free Energies= - -2063.266219 (Hartree/Particle)

II

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Cl	-0.639481520	-1.360251200	3.825691000
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C	-5.924943520	-1.271626200	2.632469000
C	-7.176837520	-1.070666200	3.215548000
C	-7.259487520	-0.842511200	4.586888000
C	-6.123694520	-0.846315200	5.393770000
C	-4.874527520	-1.049792200	4.804936000
H	-5.859056520	-1.417837200	1.561259000
H	-8.068859520	-1.070390200	2.599985000
H	-6.201636520	-0.673876200	6.460901000
H	-3.979379520	-1.024908200	5.419561000
Br	-9.006007520	-0.474815200	5.385786000
N	-3.439852520	-1.329330200	2.808533000

H	-2.710430520	-1.422785200	3.550912000
C	-3.251241520	-2.589910200	2.020077000
H	-4.015728520	-2.687298200	1.256757000
H	-2.262423520	-2.549404200	1.573484000
H	-3.312847520	-3.421165200	2.725655000

No imaginary frequencies
Sum of electronic and thermal Free Energies= -2063.277255(Hartree/Particle)

TS1’

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C	-2.708336000	-0.008200000	1.807892000
C	-2.572266000	-1.410659000	1.589781000
C	-3.396355000	-2.081448000	0.657652000
C	-4.410725000	-1.313748000	-0.013520000
C	-4.530291000	0.065422000	0.204644000
H	-2.042139000	0.478750000	2.507683000
H	-1.795848000	-1.958164000	2.111114000
H	-5.016896000	-1.789810000	-0.777186000
H	-5.225234000	0.626468000	-0.406352000
C	-3.261101000	-3.554151000	0.388591000
H	-2.385839000	-3.970604000	0.895064000
H	-4.151604000	-4.084224000	0.747726000
H	-3.159732000	-3.730823000	-0.686764000
C	-3.799082000	2.259142000	1.427572000
H	-4.058110000	2.308039000	2.497148000
C	-2.464486000	3.005593000	1.233542000
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H	-1.650085000	2.562877000	1.815630000
H	-2.177008000	2.987357000	0.179188000
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H	-5.899054000	2.488599000	0.829615000
H	-4.991939000	3.999225000	0.957698000
H	-4.715793000	2.930839000	-0.429569000
Ru	-2.384472000	-0.339421000	-0.416433000
Cl	-2.059796000	-1.780494000	-2.311171000
Cl	-2.851947000	1.451560000	-2.009518000
C	0.016044000	0.861200000	-1.774950000
C	-0.293551000	0.201351000	-0.500953000
C	0.468246000	0.764614000	0.616213000
C	1.165811000	1.913091000	0.574904000
C	1.307299000	2.654549000	-0.702456000
C	0.722978000	2.011285000	-1.882713000

H	-0.380505000	0.372667000	-2.657363000
H	1.687321000	2.324685000	1.431223000
H	0.876605000	2.503964000	-2.837708000
O	1.940589000	3.708157000	-0.748577000
Br	0.611574000	-0.261774000	2.316676000
C	2.377970000	-1.487493000	-0.641242000
C	3.161764000	-1.851130000	0.492800000
C	4.422999000	-1.314801000	0.683860000
C	4.917009000	-0.379233000	-0.235930000
C	4.185142000	0.008194000	-1.360010000
C	2.934049000	-0.552470000	-1.565647000
H	2.772937000	-2.555661000	1.217998000
H	5.019191000	-1.600904000	1.543227000
H	4.592116000	0.725320000	-2.063571000
H	2.357949000	-0.306378000	-2.448262000
Br	6.676782000	0.389922000	0.060815000
N	1.144497000	-1.973930000	-0.943872000
C	0.580666000	-3.044057000	-0.142754000
H	0.620932000	-2.882599000	0.943718000
H	-0.455680000	-3.180452000	-0.456613000
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H	0.027951000	-0.937096000	-0.683342000

One Frequency = -639.82 cm^{-1}
Sum of electronic and thermal Free Energies= -2063.218067 (Hartree/Particle)

II'

C	-2.725206000	1.277617000	1.484032000
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C	-3.623702000	1.981612000	0.643009000
H	-2.375467000	-0.717777000	2.303035000
H	-4.517510000	-1.696734000	1.635817000
H	-5.431909000	1.900680000	-0.564254000
H	-3.348970000	2.947711000	0.239340000
C	-6.495164000	-0.571393000	0.066572000
H	-7.315143000	-0.435305000	0.782735000
H	-6.789861000	-0.123248000	-0.886392000
H	-6.343945000	-1.641240000	-0.098838000
C	-1.398095000	1.866858000	1.957176000
H	-1.556851000	2.110040000	3.020216000

C	-0.236139000	0.857932000	1.878496000
H	0.684723000	1.329288000	2.235953000
H	-0.409720000	-0.033247000	2.487658000
H	-0.074755000	0.540552000	0.846316000
C	-1.022366000	3.166010000	1.227091000
H	-1.750383000	3.966048000	1.403545000
H	-0.050777000	3.523808000	1.581550000
H	-0.945376000	2.993318000	0.148586000
Ru	-3.221588000	0.055170000	-0.350885000
Cl	-3.728038000	-1.675748000	-1.838309000
Cl	-1.424556000	0.732966000	-1.695681000
C	0.977078000	-2.660594000	-1.555751000
C	2.326518000	-2.677473000	-0.863526000
C	2.180280000	-2.502321000	0.632175000
C	1.014353000	-2.422451000	1.278855000
C	-0.271385000	-2.481583000	0.542406000
C	-0.203800000	-2.601388000	-0.924035000
H	1.031260000	-2.700083000	-2.640753000
H	0.948230000	-2.324611000	2.356518000
H	-1.148804000	-2.582079000	-1.457323000
O	-1.336115000	-2.421468000	1.158202000
Br	3.853458000	-2.464248000	1.647218000
C	3.277489000	-0.409392000	-1.181598000
C	4.456955000	0.306162000	-0.909115000
C	4.416257000	1.667829000	-0.601001000
C	3.188523000	2.316898000	-0.557369000
C	2.005934000	1.640933000	-0.836185000
C	2.056049000	0.285987000	-1.148248000
H	5.418604000	-0.193552000	-0.907192000
H	5.334073000	2.202577000	-0.382191000
H	1.048703000	2.147511000	-0.834092000
H	1.127736000	-0.213856000	-1.390767000
Br	3.113996000	4.224599000	-0.089808000
N	3.303174000	-1.786447000	-1.502102000
C	4.576981000	-2.384988000	-1.879564000
H	5.271082000	-2.526910000	-1.037116000
H	4.391158000	-3.360996000	-2.338157000
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H	2.720337000	-3.695220000	-1.005217000

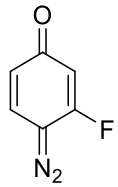
No imaginary frequencies

Sum of electronic and thermal Free Energies= -2063.30366 (Hartree/Particle)

2. Characterization Data of Compounds

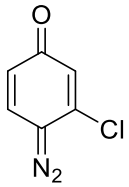
2.1 Characterization data of diazoquinones

4-diazo-3-fluorocyclohexa-2,5-dien-1-one (1b)



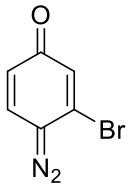
yellow solid, 85% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.34 (t, *J* = 9.3 Hz, 1H), 6.29 (d, *J* = 9.8 Hz, 1H), 6.19 (d, *J* = 14.3 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 183.2, 183.0, 163.0, 159.5, 126.5, 125.5, 109.9, 109.8. ^{19}F NMR (282 MHz, CDCl3) δ -110.43. HR-MS (ESI): Calcd for $C_6H_3FN_2ONa^+$ $[M+Na]^+$: 161.0121; found: 161.0132.

3-chloro-4-diazocyclohexa-2,5-dien-1-one (1c)[1]



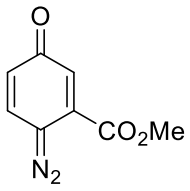
yellow solid, 90% yield. ^{1}H NMR(300 MHz, $CDCl_3$) δ 7.45 (d, *J* = 9.8 Hz, 1H), 6.61 (d, *J* = 1.9 Hz, 1H), 6.43 (dd, *J* = 9.8, 1.9 Hz, 1H). ^{13}C NMR(75 MHz, $CDCl_3$) δ 181.1, 135.0, 129.6, 126.6, 125.9, 85.3.

3-bromo-4-diazocyclohexa-2,5-dien-1-one (1a) [1]



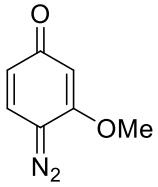
yellow solid, 85% yield. ^{1}H NMR(300 MHz, $CDCl_3$) δ 7.41 (d, *J* = 9.7 Hz, 1H), 6.77 (s, 1H), 6.42 (d, *J* = 9.8 Hz, 1H). ^{13}C NMR(75 MHz, $CDCl_3$) δ 180.9, 130.2, 130.1, 126.0, 123.1, 80.7.

Methyl 6-diazo-3-oxocyclohexa-1,4-diene-1-carboxylate (1d) [1]



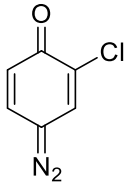
yellow solid, 84% yield. ^{1}H NMR (300 MHz, DMSO) δ 7.91 (d, *J* = 9.7 Hz, 1H), 6.70 (s, 1H), 6.34 (d, *J* = 9.7 Hz, 1H), 3.84 (s, 3H). ^{13}C NMR (75 MHz, DMSO) δ 180.5, 164.0, 134.9, 131.8, 127.9, 126.6, 75.7, 53.6.

4-diazo-3-methoxycyclohexa-2,5-dien-1-one (1e)



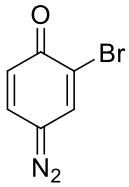
brown solid, 80% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.19 (d, *J* = 9.7 Hz, 1H), 6.19 (d, *J* = 10.6 Hz, 1H), 5.92 (s, 1H), 3.88 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 183.2, 161.4, 126.9, 123.4, 103.9, 56.4. HR-MS (ESI): Calcd for $C_7H_6N_2O_2Na^+$ $[M+Na]^+$: 173.0321; found: 173.0327.

2-chloro-4-diazocyclohexa-2,5-dien-1-one (1f) [1]



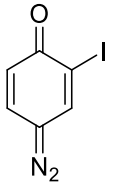
black solid, 68% yield. ^{1}H NMR(300 MHz, $CDCl_3$) δ 7.68 (d, *J* = 2.7 Hz, 1H), 7.48 (d, *J* = 9.7 Hz, 1H), 6.51 (d, *J* = 9.7 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 176.1, 129.7, 129.3, 127.3, 125.8, 74.9.

2-bromo-4-diazocyclohexa-2,5-dien-1-one (1g)



black solid, 66% yield.^{1}H NMR (300 MHz, $CDCl_3$) δ 7.85 (d, *J* = 2.7 Hz, 1H), 7.44 (dd, *J* = 9.7, 2.7 Hz, 1H), 6.51 (d, *J* = 9.7 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 176.2, 130.5, 129.5, 125.3, 120.5, 75.2. HR-MS (ESI): Calcd for $C_6H_3BrN_2ONa^+$ $[M+Na]^+$: 220.9321; found: 220.9330.

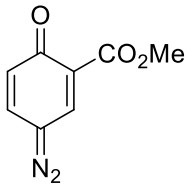
4-diazo-2-iodocyclohexa-2,5-dien-1-one (1h)



black solid, 70% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.09 (s, 1H), 7.46 (d, *J* = 12.4 Hz, 1H), 6.46 (d, *J* = 9.6 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 177.3, 136. 8, 129.8,

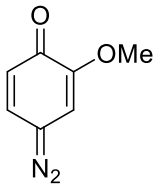
123.1, 108.3, 99.3. HR-MS (ESI): Calcd for $C_6H_3IN_2ONa^+$ $[M+Na]^+$: 268.9182; found: 268.9186.

methyl 3-diazo-6-oxocyclohexa-1,4-diene-1-carboxylate (1i)[3]



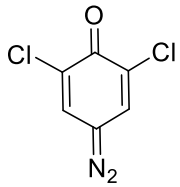
yellow solid, 80% yield. ^{1}H NMR (300 MHz, DMSO) δ 8.48 (d, *J* = 3.0 Hz, 1H), 7.74 (dd, *J* = 9.8, 3.0 Hz, 1H), 6.25 (d, *J* = 9.8 Hz, 1H), 3.70 (s, 3H). ^{13}C NMR (75 MHz, DMSO) δ 177.3, 165.5, 138.5, 131.3, 127.7, 124.8, 78.1, 52.0.

4-diazo-2-methoxycyclohexa-2,5-dien-1-one (1j)



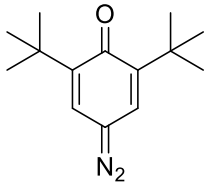
black solid, 60% yield.^{1}H NMR (300 MHz, $CDCl_3$) δ 7.41 (dd, *J* = 9.5, 2.7 Hz, 1H), 6.54 (d, *J* = 2.6 Hz, 1H), 6.45 (d, *J* = 9.5 Hz, 1H), 3.81 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 176.2, 152.1, 129.3, 125. 2, 101.5, 55.7. HR-MS (ESI): Calcd for $C_7H_6N_2O_2Na^+$ $[M+Na]^+$: 173.0321; found: 173.0328.

2,6-dichloro-4-diazocyclohexa-2,5-dien-1-one (1k)[1]



brown solid, 60% yield. ^{1}H NMR (300 MHz, DMSO) δ 8.27 (s, 2H). ^{13}C NMR (75 M Hz, DMSO) δ 169.1, 130.0, 125.0, 78.5.

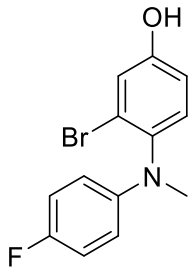
2,6-di-tert-butyl-4-diazocyclohexa-2,5-dien-1-one (1l)[3]



red solid, 50% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.18 (s, 2H), 1.33 (s, 18H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 181.1, 146.8, 130.1, 122.4, 71.0, 36.0, 29.1.

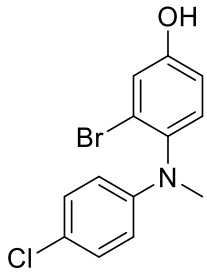
2.2 Characterization Data of Diarylamines

3-bromo-4-((4-fluorophenyl)(methyl)amino)phenol (3ab)



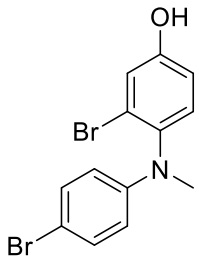
Eluent for flash column chromatography: petroleum ether/ethyl acetate = 10/1. yellow oil, 68.4 mg, 77% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.17 (d, *J* = 2.8 Hz, 1H), 7.10 (d, *J* = 8.6 Hz, 1H), 6.89 (t, *J* = 8.8 Hz, 2H), 6.82 (dd, *J* = 8.6, 2.8 Hz, 1H), 6.55 – 6.38 (m, 2H), 5.31 (s, 1H), 3.17 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.5, 145.5, 140.1, 131.0, 124.8, 120.6, 116.2, 115.5, 115.2, 113.9, 113.8, 39.4. ^{19}F NMR (282 MHz, Chloroform-d) δ -128.61. HR-MS (ESI): Calcd for $C_{13}H_{10}BrFNO^-$ [M-H]$^-$: 293.9935; found: 293.9935.

3-bromo-4-((4-chlorophenyl)(methyl)amino)phenol (3ac)



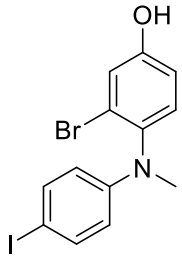
Eluent for flash column chromatography: petroleum ether/ethyl acetate = 10/1. yellow oil, 88.2 mg, 94% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.19 (d, *J* = 2.8 Hz, 1H), 7.16 – 7.07 (m, 3H), 6.85 (dd, *J* = 8.6, 2.8 Hz, 1H), 6.46 (d, *J* = 9.0 Hz, 2H), 3.18 (s, 3H).^{13}C NMR (75 MHz, $CDCl_3$) δ 154. 8, 147.5, 139.3, 131.2, 128.8, 124.8 122.0, 120.7, 116.3, 113.9, 39.2. HR-MS (ESI): Calcd for $C_{13}H_{10}BrClNO^-$ [M-H]$^-$: 309.9640; found: 309.9644.

3-bromo-4-((4-bromophenyl)(methyl)amino)phenol (3aa)



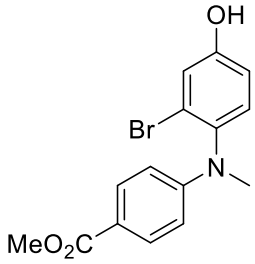
Eluent for flash column chromatography: petroleum ether/ethyl acetate = 10/1. yellow oil, 91.0 mg, 85% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.26 (d, *J* = 8.9 Hz, 2H), 7.19 (d, *J* = 2.7 Hz, 1H), 7.11 (d, *J* = 8.6 Hz, 1H), 6.85 (dd, *J* = 8.6, 2.7 Hz, 1H), 6.41 (d, *J* = 8.9 Hz, 2H), 5.95 (s, 1H), 3.18 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.0, 147.9, 139.0, 131.7, 131.2, 124.8, 120.7, 116.3, 114.4, 109.3, 39.1. HR-MS (ESI): Calcd for $C_{13}H_{10}Br_2NO^-$ $[M-H]^-$: 353.9135; found: 353.9123.

3-bromo-4-((4-iodophenyl)(methyl)amino)phenol (3ad)



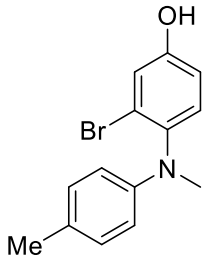
Eluent for flash column chromatography: petroleum ether/ethyl acetate = 10/1. yellow oil, 114.0 mg, 94% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.42 (d, *J* = 9.0 Hz, 2H), 7.19 (d, *J* = 2.8 Hz, 1H), 7.09 (d, *J* = 8.6 Hz, 1H), 6.85 (dd, *J* = 8.6, 2.8 Hz, 1H), 6.31 (d, *J* = 9.0 Hz, 2H), 3.17 (s, 3H).^{13}C NMR (75 MHz, $CDCl_3$) δ 155.1, 148.5, 138.8, 137.5, 131.2, 124.8, 120.7, 116.4, 115.0, 78.4, 39.0. HR-MS (ESI): Calcd for $C_{13}H_{10}BrINO^-$ $[M-H]^-$: 401.8996; found: 401.8997.

methyl 4-((2-bromo-4-hydroxyphenyl)(methyl)amino)benzoate (3ae)



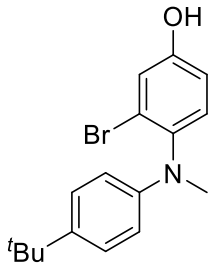
Eluent for flash column chromatography: petroleum ether/ethyl acetate = 5/1. yellow solid, 88.8 mg, 88% yield. ^{1}H NMR (300 MHz, DMSO) δ 10.12 (s, 1H), 7.74 (d, *J* = 9.0 Hz, 2H), 7.24 – 7.13 (m, 2H), 6.89 (dd, *J* = 8.6, 2.7 Hz, 1H), 6.47 (d, *J* = 8.8 Hz, 2H), 3.75 (s, 3H), 3.19 (s, 3H). ^{13}C NMR (75 MHz, DMSO) δ 166.7, 157.9, 152.8, 136.3, 131.6, 131.2, 123.9, 120.4, 117.5, 117.1, 111.8, 51.8, 39.5. HR-MS (ESI): Calcd for $C_{15}H_{13}BrNO_3^-$ [M-H]$^-$: 334.0084; found: 334.0092.

3-bromo-4-(methyl(p-tolyl)amino)phenol (3af)



Eluent for flash column chromatography: petroleum ether/ethyl acetate = 10/1. yellow oil, 55.2 mg, 63% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.17 (d, *J* = 2.8 Hz, 1H), 7.10 (d, *J* = 8.6 Hz, 1H), 6.99 (d, *J* = 8.3 Hz, 2H), 6.81 (dd, *J* = 8.6, 2.8 Hz, 1H), 6.50 – 6.42 (m, 2H), 5.25 (s, 1H), 3.17 (s, 3H), 2.24 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.4, 146.8, 140.2, 131.1, 129.5, 126.4, 125.0, 120.5, 116.0, 113.0, 39.1, 29.7. HR-MS (ESI): Calcd for $C_{14}H_{13}BrNO^-$ [M-H]$^-$: 290.0186; found: 290.0187.

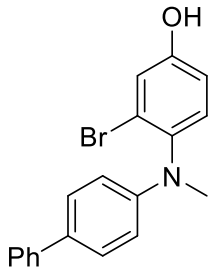
3-bromo-4-((4-(tert-butyl)phenyl)(methyl)amino)phenol (3ag)



Eluent for flash column chromatography: petroleum ether/ethyl acetate = 10/1. yellow oil, 61.2 mg, 61% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.20 (d, *J* = 9.0 Hz, 2H), 7.13 – 7.05 (m, 2H), 6.81 (dd, *J* = 8.6, 2.8 Hz, 1H), 6.49 (d, *J* = 8.8 Hz, 2H), 3.17 (s, 3H), 1.27 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.7, 146.6, 139.8, 131.1, 125.7, 123.7,

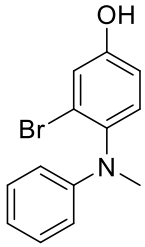
120.4, 118.8, 116.1, 114.3, 112.5, 39.0, 33.8, 31.5. HR-MS (ESI): Calcd for $C_{17}H_{19}BrNO^-$ $[M-H]^-$: 332.0656; found: 332.0653.

4-([1,1'-biphenyl]-4-yl(methyl)amino)-3-bromophenol (3ah)



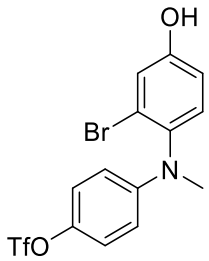
Eluent for flash column chromatography: petroleum ether/ethyl acetate = 10/1. yellow oil, 64.8 mg, 61% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.58 – 7.51 (m, 2H), 7.46 (d, *J* = 8.8 Hz, 2H), 7.39 (t, *J* = 7.6 Hz, 2H), 7.28 (s, 1H), 7.22 – 7.13 (m, 2H), 6.85 (dd, *J* = 8.6, 2.8 Hz, 1H), 6.62 (d, *J* = 8.8 Hz, 2H), 5.43 (s, 1H), 3.25 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.8, 148.3, 141.2, 139.5, 131.2, 130.0, 128.6, 127.6, 126.4, 126.1, 125.0, 120.6, 116.2, 113.0, 39.1. HR-MS (ESI): Calcd for $C_{19}H_{15}BrNO^-$ $[M-H]^-$: 352.0343; found: 352.0340.

3-bromo-4-(methyl(phenyl)amino)phenol (3ai)



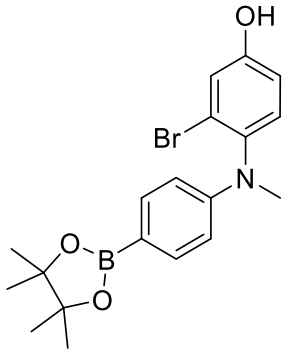
Eluent for flash column chromatography: petroleum ether/ethyl acetate = 10/1. yellow oil, 35.9 mg, 43% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.25 – 7.15 (m, 3H), 7.13 (d, *J* = 8.6 Hz, 1H), 6.83 (dd, *J* = 8.6, 2.8 Hz, 1H), 6.75 (t, *J* = 7.3 Hz, 1H), 6.64 – 6.49 (m, 2H), 5.57 (s, 1H), 3.20 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.6, 148. 9, 139.7, 131.3, 129.0, 125.0, 120.6, 117.2, 116.2, 112.8, 39.0. HR-MS (ESI): Calcd for $C_{13}H_{11}BrNO^-$ $[M-H]^-$: 276.0030; found: 276.0028.

4-((2-bromo-4-hydroxyphenyl)(methyl)amino)phenyl trifluoromethanesulfonate (3aj)



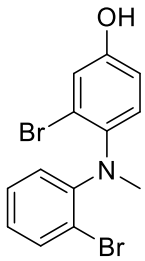
Eluent for flash column chromatography: petroleum ether/ethyl acetate = 10/1. yellow oil, 112.5 mg, 88% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.19 (d, *J* = 2.8 Hz, 1H), 7.11 (d, *J* = 8.6 Hz, 1H), 7.09 – 7.02 (m, 2H), 6.85 (dd, *J* = 8.6, 2.8 Hz, 1H), 6.52 – 6.44 (m, 2H), 5.33 (s, 1H), 3.20 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.5, 148.6, 140.8, 138.4, 131.1, 124.7, 122.2, 121.7, 120.8, 116.4, 113.0, 39.2. HR-MS (ESI): Calcd for $C_{14}H_{10}BrF_3NO_4S^-$ [M-H]$^-$: 423.9471; found: 423.9477.

3-bromo-4-(methyl(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)amino)phenol (3ak)



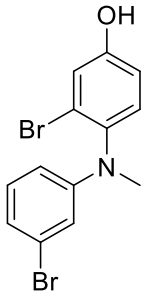
Eluent for flash column chromatography: petroleum ether/ethyl acetate = 10/1. yellow oil, 95.8 mg, 79% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.6 Hz, 2H), 7.37 (s, 1H), 7.20 (d, *J* = 2.8 Hz, 1H), 7.05 (d, *J* = 8.6 Hz, 1H), 6.85 (dd, *J* = 8.6, 2.8 Hz, 1H), 6.46 (d, *J* = 8.7 Hz, 2H), 3.23 (s, 3H), 1.38 (s, 12H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.7, 151.5, 138.1, 136.2, 131.2, 124.8, 120.8, 116.2, 111.7, 83.8, 38.8, 24.8. HR-MS (ESI): Calcd for $C_{19}H_{22}BBrNO_3^-$ [M-H]$^-$: 402.0882; found: 402.0884.

3-bromo-4-((2-bromophenyl)(methyl)amino)phenol (3al)



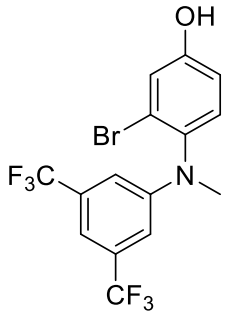
Eluent for flash column chromatography: petroleum ether/ethyl acetate = 10/1. yellow oil, 92.1 mg, 86% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.52 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.29 – 7.22 (m, 1H), 7.12 (d, *J* = 2.8 Hz, 1H), 7.05 (d, *J* = 8.1 Hz, 1H), 6.94 – 6.86 (m, 1H), 6.81 (d, *J* = 8.6 Hz, 1H), 6.71 (dd, *J* = 8.7, 2.8 Hz, 1H), 3.18 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 152.5, 148.8, 142.3, 134.4, 128.0, 125.4, 124.1, 122.6, 121.8, 121.0, 119.1, 115.1, 41.6. HR-MS (ESI): Calcd for $C_{13}H_{10}Br_2NO^-$ $[M-H]^-$: 353.9135; found: 353.9130.

3-bromo-4-((3-bromophenyl)(methyl)amino)phenol (3am)



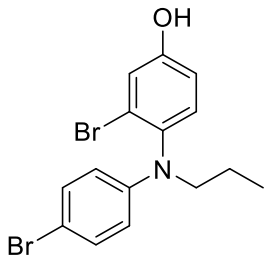
Eluent for flash column chromatography: petroleum ether/ethyl acetate = 10/1. yellow oil, 90.0 mg, 84% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.19 (d, *J* = 2.8 Hz, 1H), 7.11 (d, *J* = 8.6 Hz, 1H), 7.02 (t, *J* = 8.1 Hz, 1H), 6.85 (dd, *J* = 8.6, 2.7 Hz, 2H), 6.68 (t, *J* = 2.0 Hz, 1H), 6.42 (dd, *J* = 8.3, 1.9 Hz, 1H), 3.18 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.1, 150.1, 138.7, 131.2, 130.2, 124.8, 123.3, 120.8, 119.9, 116.4, 115.3, 111.4, 39.1. HR-MS (ESI): Calcd for $C_{13}H_{10}Br_2NO^-$ $[M-H]^-$: 353.9135; found: 353.9134.

4-((3,5-bis(trifluoromethyl)phenyl)(methyl)amino)-3-bromophenol (3an)



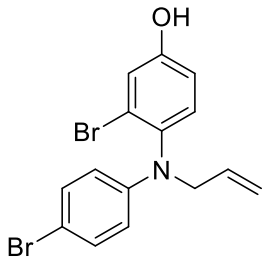
Eluent for flash column chromatography: petroleum ether/ethyl acetate = 10/1. yellow oil, 91.9 mg, 74% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.22 (d, *J* = 2.8 Hz, 1H), 7.18 (s, 1H), 7.12 (d, *J* = 8.6 Hz, 1H), 6.89 (dd, *J* = 8.6, 2.8 Hz, 1H), 6.83 (s, 2H), 5.42 (s, 1H),3.27 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.5, 149.4, 137.6, 132.4, 132.0, 131.0, 124.5, 121.0, 116.6, 111.7, 110.1, 39.2. ^{19}F NMR (282 MHz, Chloroform-d) δ -128.63. HR-MS (ESI): Calcd for $C_{15}H_{19}BrF_6NO^-$ [M-H]$^-$: 411.9777; found: 411.9777.

3-bromo-4-((4-bromophenyl)(propyl)amino)phenol (3ao)



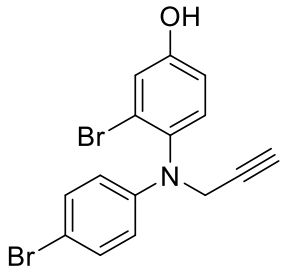
Eluent for flash column chromatography: petroleum ether/ethyl acetate = 10/1. yellow oil, 73.9 mg, 64% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.25 – 7.16 (m, 3H), 7.10 (d, *J* = 8.5 Hz, 1H), 6.85 (dd, *J* = 8.6, 2.8 Hz, 1H), 6.36 (d, *J* = 9.1 Hz, 2H), 5.41 (s, 1H), 3.55 – 3.37 (m, 2H), 1.66 (dq, *J* = 15.0, 7.4 Hz, 2H), 0.94 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.8, 147.4, 137.6, 132.4, 131.7, 125.6, 120.8, 116.1, 114.3, 108.8, 53.5, 20.6, 11.5. HR-MS (ESI): Calcd for $C_{15}H_{14}Br_2NO^-$ [M-H]$^-$: 381.9448; found: 381.9441.

4-(allyl(4-bromophenyl)amino)-3-bromophenol (3ap)



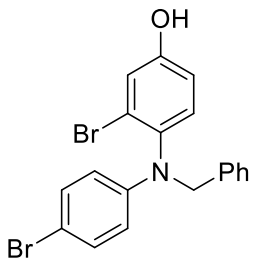
Eluent for flash column chromatography: petroleum ether/ethyl acetate = 10/1. yellow oil, 100.0 mg, 87% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.25 – 7.18 (m, 3H), 7.11 (d, *J* = 8.5 Hz, 1H), 6.83 (dd, *J* = 8.6, 2.8 Hz, 1H), 6.44 – 6.31 (m, 2H), 5.94 (ddt, *J* = 17.2, 10.5, 5.3 Hz, 1H), 5.35 – 5.13 (m, 3H), 4.14 (d, *J* = 5.3 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.1, 147.2, 137.6, 133.7, 132.3, 131.6, 125.3, 120.8, 117.1, 116.1, 114.8, 109.3, 54.6. HR-MS (ESI): Calcd for $C_{15}H_{12}Br_2NO^-$ $[M-H]^-$: 379.9291; found: 379.9292.

3-bromo-4-((4-bromophenyl)(prop-2-yn-1-yl)amino)phenol (3aq)



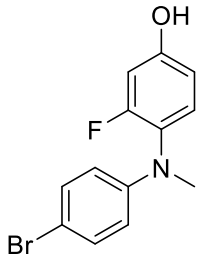
Eluent for flash column chromatography: petroleum ether/ethyl acetate = 10/1. yellow oil, 80.0 mg, 70% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.31 (d, *J* = 2.2 Hz, 2H), 7.26 (d, *J* = 8.7 Hz, 1H), 7.22 (d, *J* = 2.8 Hz, 1H), 6.86 (dd, *J* = 8.6, 2.8 Hz, 1H), 6.60 – 6.51 (m, 2H), 4.26 (d, *J* = 2.3 Hz, 2H), 2.28 (t, *J* = 2.4 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.3, 146.3, 137.5, 131.7, 127.8, 124.9, 120.4, 116.2, 115.7, 110.6, 79.2, 72.7, 40.9. HR-MS (ESI): Calcd for $C_{15}H_{10}Br_2NO^-$ $[M-H]^-$: 377.9135; found: 377.9134.

4-(benzyl(4-bromophenyl)amino)-3-bromophenol (3ar)



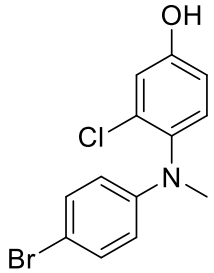
Eluent for flash column chromatography: petroleum ether/ethyl acetate = 15/1. yellow oil, 91.0 mg, 70% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.38 – 7.27 (m, 4H), 7.24 (t, *J* = 3.4 Hz, 1H), 7.21 – 7.11 (m, 4H), 6.77 (dd, *J* = 8.6, 2.8 Hz, 1H), 6.44 – 6.32 (m, 2H), 5.61 (s, 1H), 4.77 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.1, 147.5, 138.1, 138.0, 132.3, 131.7, 128.6, 127.1, 127.0, 125.1, 121.0, 116.0, 115.0, 109.7, 56.1. HR-MS (ESI): Calcd for $C_{19}H_{14}Br_2NO^-$ [M-H]$^-$: 429.9448; found: 429.9444.

4-((4-bromophenyl)(methyl)amino)-3-fluorophenol (3ba)



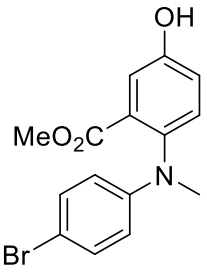
Eluent for flash column chromatography: petroleum ether/ethyl acetate = 10/1. yellow oil, 72.0 mg, 81% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.32 – 7.24 (m, 2H), 7.17 – 7.07 (m, 1H), 6.75 – 6.63 (m, 2H), 6.60 – 6.49 (m, 2H), 5.71 (s, 1H), 3.22 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.1, 157.8, 155.1, 148.3, 131.6, 130.3, 128.0, 114.9, 112.0, 109.7, 104.9, 104.6, 39.7. ^{19}F NMR (282 MHz, Chloroform-d) δ -118.50. HR-MS (ESI): Calcd for $C_{13}H_{10}BrFNO^-$ [M-H]$^-$: 293.9935; found: 293.9936.

4-((4-bromophenyl)(methyl)amino)-3-chlorophenol (3ca)



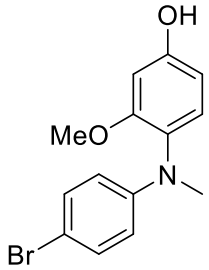
Eluent for flash column chromatography: petroleum ether/ethyl acetate = 10/1. yellow oil, 71.3 mg, 76% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.25 (d, *J* = 8.8 Hz, 2H), 7.11 (d, *J* = 8.6 Hz, 1H), 7.00 (d, *J* = 2.8 Hz, 1H), 6.79 (dd, *J* = 8.6, 2.8 Hz, 1H), 6.42 (d, *J* = 8.8 Hz, 2H), 5.65 (s, 1H), 3.18 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.9, 148.0, 137.5, 134.5, 131.7, 131.2, 117.7, 115.6, 114.4, 109.3, 39.1. HR-MS (ESI): Calcd for $C_{13}H_{10}BrClNO^-$ [M-H]$^-$: 309.9640; found: 309.9642.

methyl 2-((4-bromophenyl)(methyl)amino)-5-hydroxybenzoate (3da)



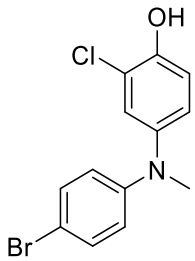
Eluent for flash column chromatography: petroleum ether/ethyl acetate = 10/1. yellow oil, 78.7 mg, 78% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.36 (d, *J* = 2.9 Hz, 1H), 7.23 – 7.16 (m, 2H), 7.12 (d, *J* = 8.6 Hz, 1H), 7.04 (dd, *J* = 8.6, 3.0 Hz, 1H), 6.38 (d, *J* = 9.1 Hz, 2H), 3.66 (s, 3H), 3.18 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.8, 154.0, 148.6, 140.3, 131.8, 131.5, 130.6, 120.8, 118.0, 114.4, 108.9, 52.4, 40.2. HR-MS (ESI): Calcd for $C_{15}H_{13}BrNO_3^-$ [M-H]$^-$: 334.0084; found: 334.0084.

4-((4-bromophenyl)(methyl)amino)-3-methoxyphenol (3ea)



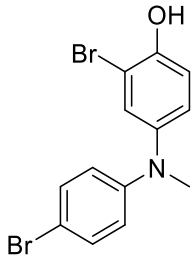
Eluent for flash column chromatography: petroleum ether/ethyl acetate = 10/1. yellow oil, 69.3 mg, 75% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.24 – 7.17 (m, 2H), 7.00 (d, *J* = 8.4 Hz, 1H), 6.50 (d, *J* = 2.6 Hz, 1H), 6.48 – 6.38 (m, 3H), 5.13 (s, 1H), 3.72 (s, 3H), 3.14 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.1, 155.3, 148.8, 131.4, 130.0, 129.1, 114.5, 108.7, 107.4, 100.6, 55.7, 39.4. HR-MS (ESI): Calcd for $C_{14}H_{13}BrNO_2^-$ [M-H]$^-$: 306.0135; found: 306.0140.

4-((4-bromophenyl)(methyl)amino)-2-chlorophenol (3fa)



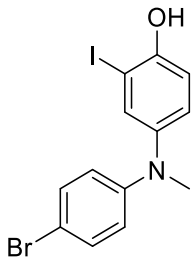
Eluent for flash column chromatography: petroleum ether/ethyl acetate = 10/1. yellow oil, 60.0 mg, 64% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.29 (d, *J* = 9.0 Hz, 2H), 7.11 (d, *J* = 1.8 Hz, 1H), 7.03 – 6.93 (m, 2H), 6.68 (d, *J* = 8.9 Hz, 2H), 5.47 (s, 1H), 3.21 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 148.2, 142.3, 136.4, 131.8, 125.1, 120.3, 118.1, 117.0, 111.4, 40.6. HR-MS (ESI): Calcd for $C_{13}H_{10}BrClNO^-$ [M-H]$^-$: 309.9640; found: 309.9635.

2-bromo-4-((4-bromophenyl)(methyl)amino)phenol (3ga)



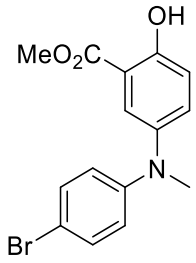
Eluent for flash column chromatography: petroleum ether/ethyl acetate = 10/1. yellow oil, 55.7 mg, 52% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.31 – 7.29 (m, 1H), 7.28 (d, *J* = 2.2 Hz, 1H), 7.24 (t, *J* = 1.4 Hz, 1H), 7.00 (d, *J* = 1.4 Hz, 2H), 6.70 – 6.63 (m, 2H), 5.44 (s, 1H), 3.21 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 148.3, 131.8, 128.0, 125.8, 120.1, 119.8, 118.0, 116.7, 111.4, 110.4, 40.6. HR-MS (ESI): Calcd for $C_{13}H_{10}Br_2NO^-$ [M-H]$^-$: 353.9135; found: 353.9132.

4-((4-bromophenyl)(methyl)amino)-2-iodophenol (3ha)



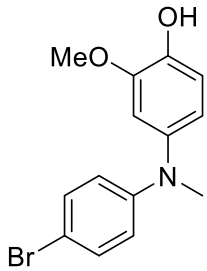
Eluent for flash column chromatography: petroleum ether/ethyl acetate = 10/1. yellow oil, 67.9 mg, 56% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.43 (d, *J* = 2.4 Hz, 1H), 7.28 (d, *J* = 8.9 Hz, 2H), 7.08 – 6.93 (m, 2H), 6.66 (d, *J* = 8.9 Hz, 2H), 5.30 (s, 1H), 3.20 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 151.9, 148.3, 142.8, 134.3, 131.8, 127.0, 117.7, 115.5, 111.2, 85.7, 40.6. HR-MS (ESI): Calcd for $C_{13}H_{10}BrINO^-$ [M-H]$^-$: 401.8996; found: 401.8995.

methyl 5-((4-bromophenyl)(methyl)amino)-2-hydroxybenzoate (3ia)



Eluent for flash column chromatography: petroleum ether/ethyl acetate = 5/1. yellow oil, 58.5 mg, 58% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.68 (s, 1H), 7.65 (d, *J* = 2.7 Hz, 1H), 7.30 (dd, *J* = 9.3, 2.5 Hz, 3H), 7.01 (d, *J* = 8.8 Hz, 1H), 6.64 (d, *J* = 9.0 Hz, 2H), 3.95 (s, 3H), 3.25 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.1, 158. 8, 148.5, 140.1, 133.8, 131.8, 126.2, 119.0, 117.1, 113.0, 110.7, 52.4, 40.5. HR-MS (ESI): Calcd for $C_{15}H_{13}BrNO_3^-$ [M-H]$^-$: 334.0084; found: 334.0079.

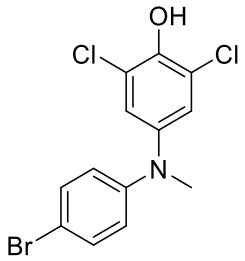
4-((4-bromophenyl)(methyl)amino)-2-methoxyphenol (3ja)



Eluent for flash column chromatography: petroleum ether/ethyl acetate = 5/1. yellow oil, 57.3 mg, 62% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.24 (d, *J* = 2.2 Hz, 2H), 6.95 – 6.87 (m, 1H), 6.72 – 6.64 (m, 2H), 6.64 – 6.57 (m, 2H), 5.49 (s, 1H), 3.83 (s, 3H), 3.22 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 148.8, 147.1, 143.2, 141.2, 131.6, 118.8,

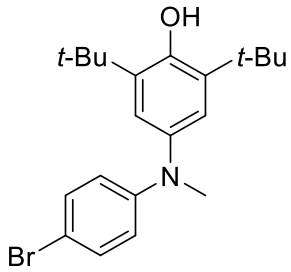
116.5, 115.0, 109.0, 100.0, 56.0, 40.6. HR-MS (ESI): Calcd for $C_{14}H_{13}BrNO_2^-$ [M-H]$^-$: 306.0135; found: 306.0127.

4-((4-bromophenyl)(methyl)amino)-2,6-dichlorophenol (3ka)



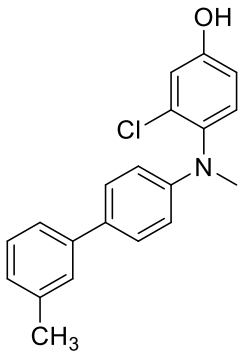
Eluent for flash column chromatography: petroleum ether/ethyl acetate = 10/1. yellow oil, 56.2 mg, 54% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.38 – 7.32 (m, 2H), 6.98 (s, 2H), 6.81 – 6.73 (m, 2H), 3.21 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 147.6, 143.8, 142.2, 132.2, 131.9, 122.6, 121.5, 120.2, 114.4, 113.3, 40.6. HR-MS (ESI): Calcd for $C_{13}H_9BrCl_2NO^-$ [M-H]$^-$: 343.9243; found: 343.9243.

4-((4-bromophenyl)(methyl)amino)-2,6-di-tert-butylphenol (3la)



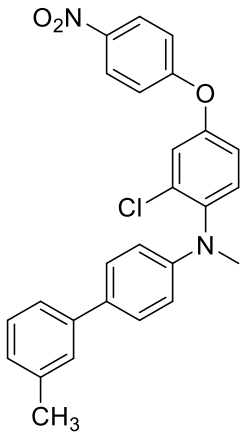
Eluent for flash column chromatography: petroleum ether/ethyl acetate = 30/1. yellow oil, 113.6 mg, 97% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.25 – 7.21 (m, 2H), 6.96 (s, 2H), 6.61 – 6.54 (m, 2H), 5.13 (s, 1H), 3.23 (s, 3H), 1.42 (s, 18H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 151.3, 148.9, 140.0, 137.3, 131.5, 122.9, 115.6, 40.6, 34.5, 30.3. HR-MS (ESI): Calcd for $C_{21}H_{27}BrNO^-$ [M-H]$^-$: 388.1282; found: 388.1284.

3-chloro-4-(methyl(3'-methyl-[1,1'-biphenyl]-4-yl)amino)phenol (4)



Eluent for flash column chromatography: petroleum ether/ethyl acetate = 10/1. yellow oil, 53.2 mg, 82% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.48 – 7.39 (m, 2H), 7.37 – 7.24 (m, 3H), 7.17 (d, *J* = 8.6 Hz, 1H), 7.08 (d, *J* = 7.4 Hz, 1H), 7.01 (d, *J* = 2.8 Hz, 1H), 6.79 (dd, *J* = 8.6, 2.9 Hz, 1H), 6.67 – 6.59 (m, 2H), 5.35 (s, 1H), 3.25 (s, 3H), 2.40 (s, 3H).^{13}C NMR (75 MHz, $CDCl_3$) δ 154.7, 148.3, 141.2, 138.1, 137.9, 134.6, 131.2, 130.2, 128.5, 127.6, 127.2, 126.9, 123.5, 117.5, 115.4, 113.0, 39.1, 21.6. HR-MS (ESI): Calcd for $C_{20}H_{17}ClNO^-$ [M-H]$^-$: 322.1004; found: 322.1008.

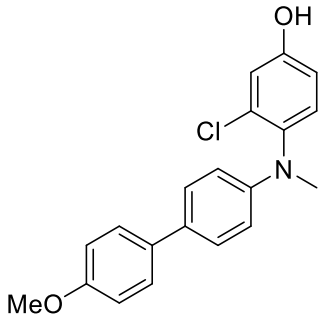
N-(2-chloro-4-(4-nitrophenoxy)phenyl)-N,3'-dimethyl-[1,1'-biphenyl]-4-amine (5)



Eluent for flash column chromatography: petroleum ether/ethyl acetate = 50/1. yellow oil, 40.0 mg, 90% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.31 – 8.22 (m, 2H), 7.51 – 7.43 (m, 2H), 7.40 – 7.33 (m, 3H), 7.30 (d, *J* = 7.3 Hz, 1H), 7.27 (s, 1H), 7.16 – 7.08 (m, 3H), 7.05 (dd, *J* = 8.7, 2.8 Hz, 1H), 6.74 – 6.66 (m, 2H), 3.32 (s, 3H), 2.41 (s, 3H).^{13}C NMR (75 MHz, $CDCl_3$) δ 162.4, 153.3, 147.8, 143.3, 142.4, 141.0, 138.2, 135.0, 131.5,

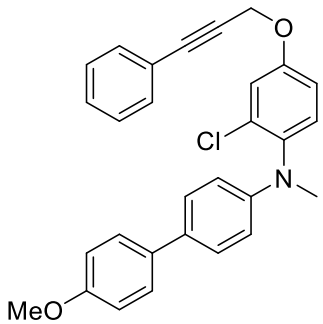
131.2, 128.6, 127.7, 127.2, 127.1, 126.1, 123.5, 122.6, 120.0, 117.7, 113.8, 39.2, 21.6. HR-MS (ESI): Calcd for $C_{26}H_{22}ClN_2O_3^+$ $[M+H]^+$: 445.1313; found: 445.1321.

3-chloro-4-((4'-methoxy-[1,1'-biphenyl]-4-yl)(methyl)amino)phenol (6)



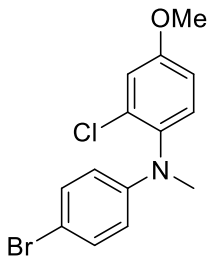
Eluent for flash column chromatography: petroleum ether/ethyl acetate = 15/1. yellow oil, 55.0 mg, 81% yield.^{1}H NMR (300 MHz, DMSO) δ 9.93 (s, 1H), 7.35 (dd, *J* = 9.3, 2.4 Hz, 2H), 7.28 (d, *J* = 8.8 Hz, 2H), 7.06 (d, *J* = 8.6 Hz, 1H), 6.87 – 6.81 (m, 3H), 6.72 (dd, *J* = 8.6, 2.7 Hz, 1H), 6.40 (d, *J* = 8.8 Hz, 2H), 3.64 (s, 3H), 3.05 (s, 3H). ^{13}C NMR (75 MHz, DMSO) δ 157.7, 156.6, 147.6, 135.4, 132.9, 132.6, 131.0, 128.3, 126.5, 126.4, 116.5, 115.7, 114.0, 112.6, 54.9, 38.8. HR-MS (ESI): Calcd for $C_{20}H_{17}ClNO_2^-$ $[M-H]^-$: 338.0953; found: 338.0954.

N-(2-chloro-4-((3-phenylprop-2-yn-1-yl)oxy)phenyl)-4'-methoxy-N-methyl-[1,1'-biphenyl]-4-amine (7)



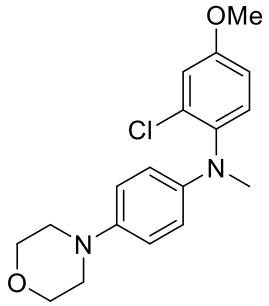
Eluent for flash column chromatography: petroleum ether/ethyl acetate = 50/1. yellow oil, 41.8 mg, 92% yield. ^{1}H NMR (300 MHz, DMSO) δ 7.50 – 7.44 (m, 4H), 7.41 (dq, *J* = 6.7, 4.0, 3.3 Hz, 5H), 7.36 – 7.29 (m, 2H), 7.13 (dd, *J* = 8.8, 2.9 Hz, 1H), 6.95 (d, *J* = 8.8 Hz, 2H), 6.53 (d, *J* = 8.8 Hz, 2H), 5.11 (s, 2H), 3.75 (s, 3H), 3.18 (s, 3H). ^{13}C NMR (75 MHz, DMSO) δ 158.4, 156. 7, 148.0, 138.3, 136.3, 133.8, 133.1, 132.0, 131.6, 129.7, 129.3, 127.2, 127.2, 121.8, 117.1, 116.2, 114.7, 113.5, 87.3, 84.9, 57.2, 55.5, 39.4. HR-MS (ESI): Calcd for $C_{29}H_{25}ClNO_2^+$ $[M+H]^+$: 454.1568; found: 454.1558.

N-(4-bromophenyl)-2-chloro-4-methoxy-N-methylaniline (8)



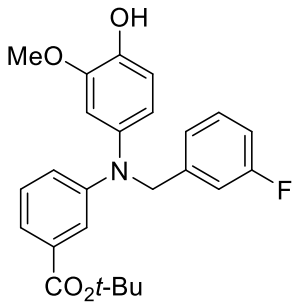
Eluent for flash column chromatography: petroleum ether/ethyl acetate = 50/1. yellow oil, 58.8 mg, 90% yield.^{1}H NMR (300 MHz, $CDCl_3$) δ 7.25 (d, *J* = 8.9 Hz, 2H), 7.16 (d, *J* = 8.7 Hz, 1H), 7.04 (d, *J* = 2.8 Hz, 1H), 6.85 (dd, *J* = 8.7, 2.9 Hz, 1H), 6.41 (d, *J* = 9.0 Hz, 2H), 3.83 (s, 3H), 3.19 (s, 3H).^{13}C NMR (75 MHz, $CDCl_3$) δ 158.64, 148.01, 137.37, 134.53, 131.62, 130.91, 115.85, 114.36, 114.31, 109.25, 55.75, 39.07. HR-MS (ESI): Calcd for $C_{14}H_{14}BrClNO^+$ $[M+H]^+$: 325.9942; found: 325.9943.

2-chloro-4-methoxy-N-methyl-N-(4-morpholinophenyl)aniline (9)



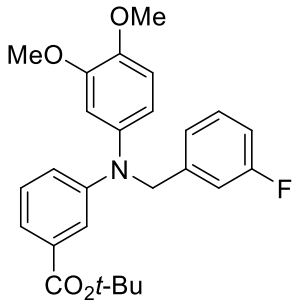
Eluent for flash column chromatography: petroleum ether/ethyl acetate = 10/1. colorless oil, 24.6 mg, 74% yield.^{1}H NMR (300 MHz, $CDCl_3$) δ 7.15 (d, *J* = 8.8 Hz, 1H), 7.02 (d, *J* = 2.9 Hz, 1H), 6.82 (dd, *J* = 8.1, 3.5 Hz, 3H), 6.55 (d, *J* = 8.8 Hz, 2H), 3.89 – 3.83 (m, 4H), 3.81 (s, 3H), 3.18 (s, 3H), 3.11 – 2.93 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.0, 143.9, 143.2, 138.8, 134.2, 130.5, 117.9, 115.7, 114.2, 114.1, 67.1, 55.7, 51.1, 39.3. HR-MS (ESI): Calcd for $C_{18}H_{22}ClN_2O_2^+$ $[M+H]^+$: 333.1364; found: 333.1368.

tert-butyl 3-((3-fluorobenzyl)(4-hydroxy-3-methoxyphenyl)amino)benzoate (10)



Eluent for flash column chromatography: petroleum ether/ethyl acetate = 50/1. yellow oil, 64.4 mg, 76% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.45 – 7.41 (m, 1H), 7.41 – 7.36 (m, 1H), 7.32 – 7.23 (m, 1H), 7.20 – 7.10 (m, 2H), 7.07 (d, *J* = 9.8 Hz, 1H), 6.97 – 6.84 (m, 3H), 6.80 – 6.70 (m, 2H), 5.64 (s, 1H), 4.91 (s, 2H), 3.80 (s, 3H), 1.54 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.0, 164. 8, 161.5, 148.7, 147.2, 143.3, 141.8, 140.0, 132.8, 130.2, 128.8, 122.3, 119.5, 119.0, 115.9, 115.2, 114.0, 113.8, 113.8, 113.5, 109.3, 80.8, 56.6, 56.0, 28.2. ^{19}F NMR (282 MHz, Chloroform-d) δ -112.88. HR-MS (ESI): Calcd for $C_{25}H_{25}FNO_4^-$ [M-H]$^-$: 422.1773; found: 422.1779.

tert-butyl 3-((3,4-dimethoxyphenyl)(3-fluorobenzyl)amino)benzoate (11)



Eluent for flash column chromatography: petroleum ether/ethyl acetate = 50/1. yellow oil, 42.0 mg, 96% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.45 (d, *J* = 1.9 Hz, 1H), 7.39 (d, *J* = 7.7 Hz, 1H), 7.31 – 7.25 (m, 1H), 7.21 – 7.10 (m, 2H), 7.06 (d, *J* = 9.7 Hz, 1H), 6.92 (t, *J* = 6.4 Hz, 2H), 6.84 (d, *J* = 8.4 Hz, 1H), 6.80 – 6.71 (m, 2H), 4.92 (s, 2H), 3.87 (s, 3H), 3.78 (s, 3H), 1.53 (s, 9H).^{13}C NMR (75 MHz, $CDCl_3$) δ 166.0, 149.8, 148.5, 146.5, 141.8, 140.8, 132.9, 130.2, 130.1, 128.8, 122.3, 120.0, 119.7, 117.5, 116.4, 114.0, 113.8, 113.5, 112.0, 109.5, 80.8, 56.5, 56.1, 56.0, 28.1. ^{19}F NMR (376 MHz,

Chloroform-d) δ -112.84. HR-MS (ESI): Calcd for $C_{26}H_{29}FNO_4^+$ $[M+H]^+$: 438.2075; found: 438.2081.

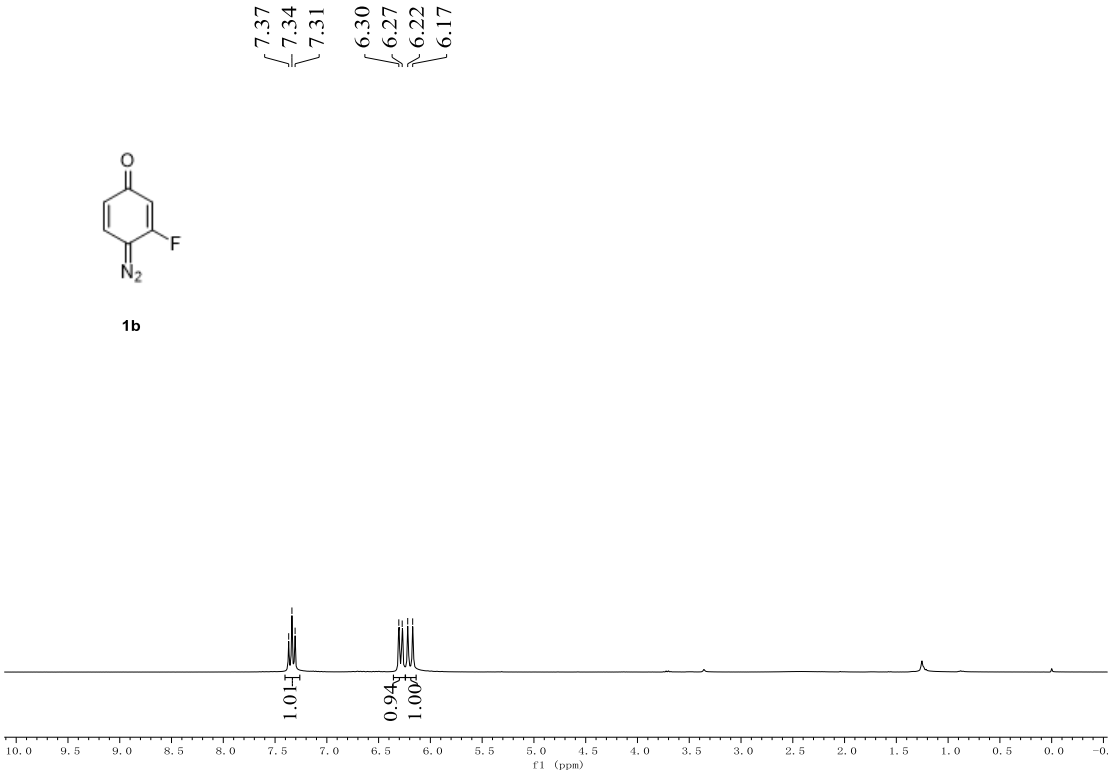
3. References

1. S. Yan, J. Rao, C.-Y. Zhou, Chemoselective Rearrangement Reactions of Sulfur Ylide Derived from Diazoquinones and Allyl/Propargyl Sulfides. *Org. Lett.* 2020, **22**, 9091-9096.
2. J. Jiao, F. Xiao, C. Wang, Z. Zhang, Iodine-Promoted Metal-Free Cyclization and O/S Exchange of Acrylamides with Thiuram: One-Step Synthesis of Quinolino-2-thiones. *J. Org. Chem.* 2022, **87**, 4965–4970.
3. K. Wu, B. Cao, C.-Y. Zhou, C.-M. Che, Rh^{II}-Catalyzed Intermolecular C−H Arylation of Aromatics with Diazo Quinones. *Chem. Eur. J.* 2018, **24**, 4815-4819.

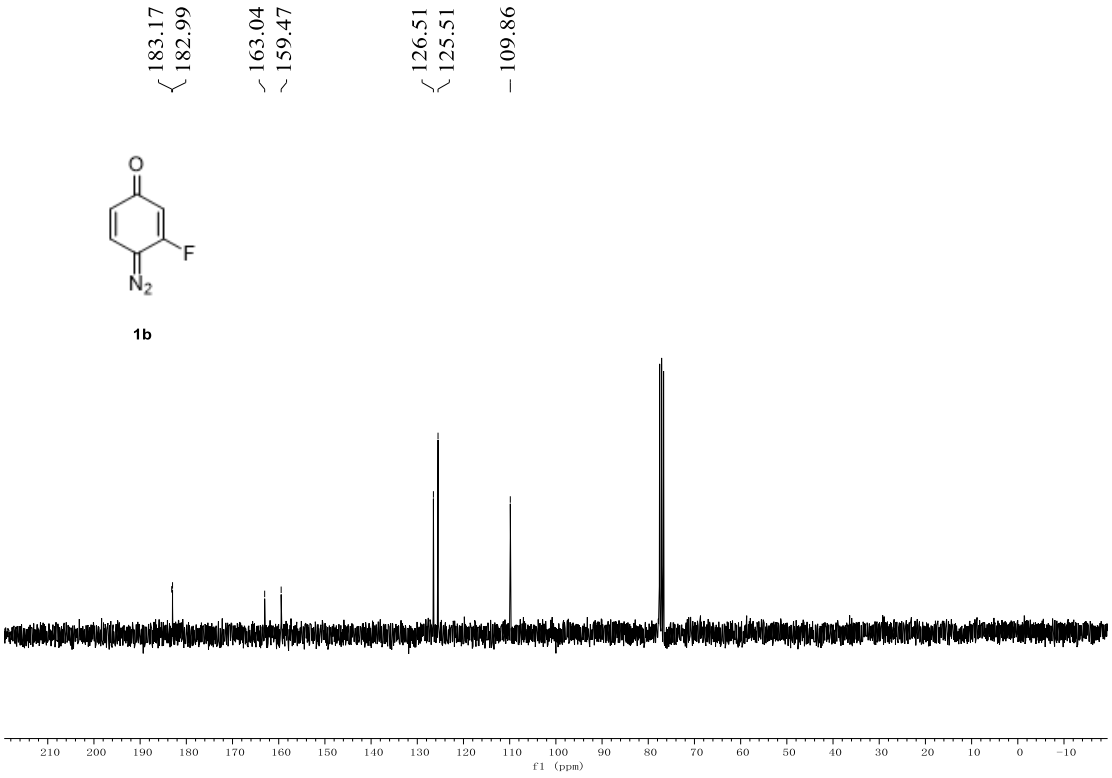
4. NMR Spectra of Compounds

NMR Spectrum for Diazoquinones

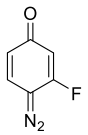
^{1}H NMR (300 MHz, $CDCl_3$)



^{13}C NMR (75 MHz, $CDCl_3$)

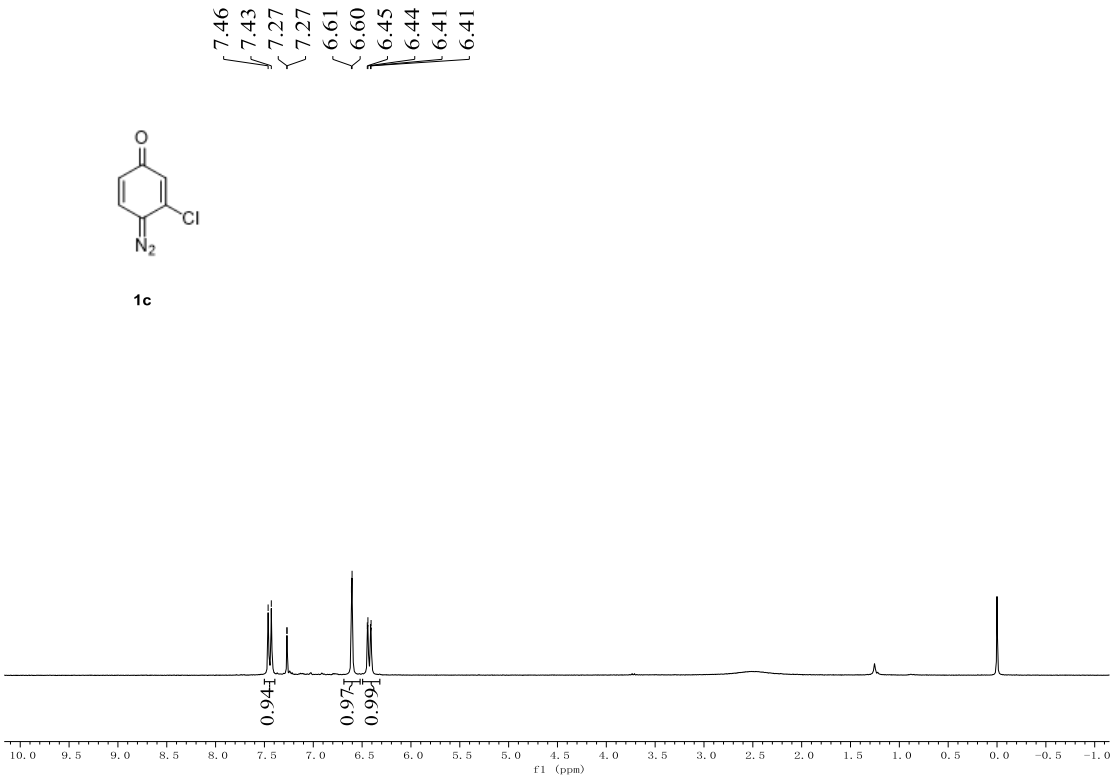


19F NMR (282 MHz, CDCl3)

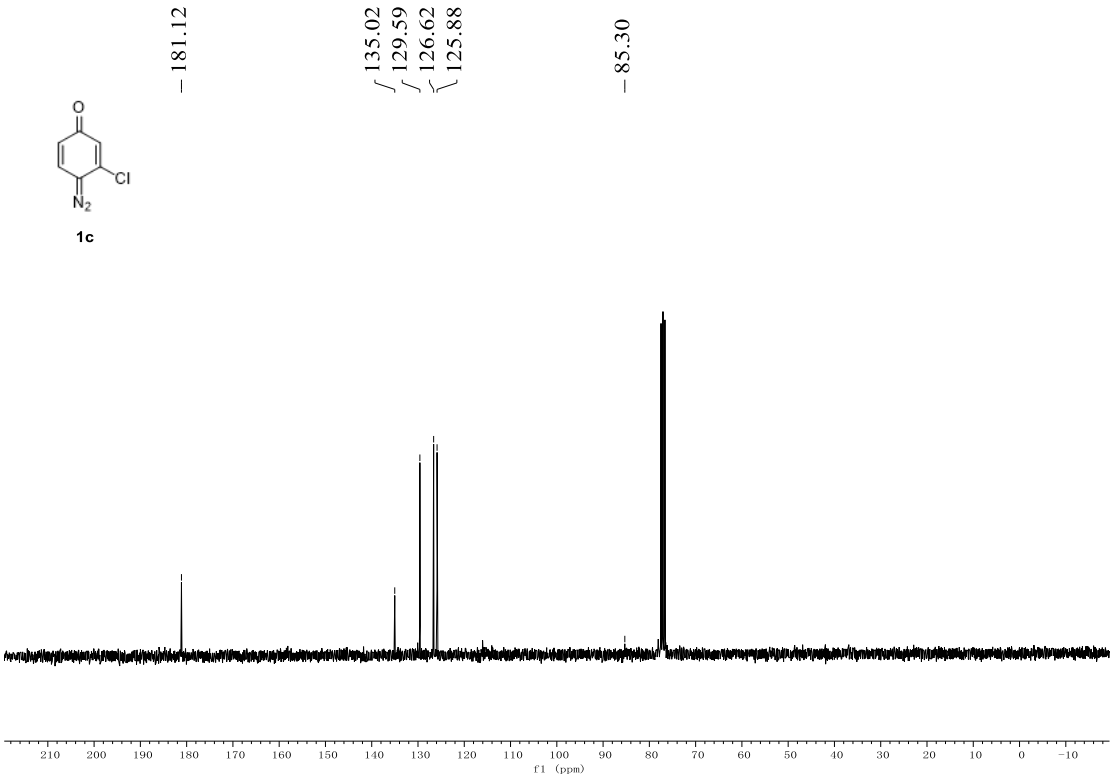


1b

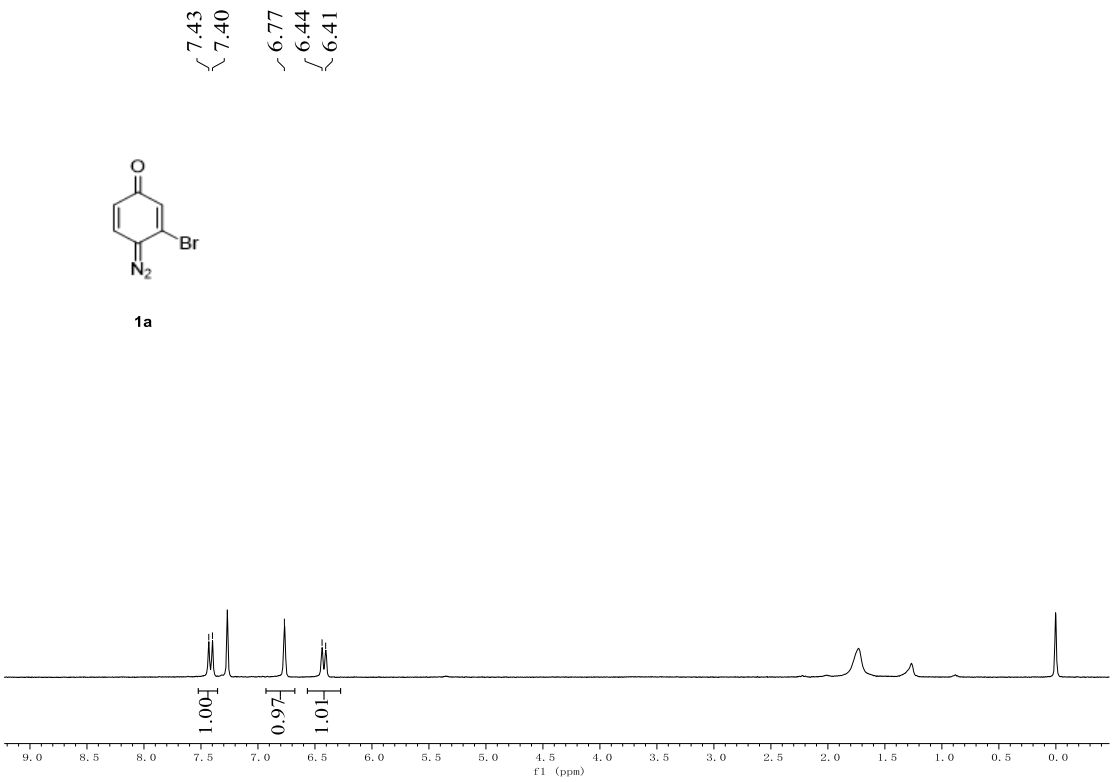
^{1}H NMR (300 MHz, $CDCl_3$)



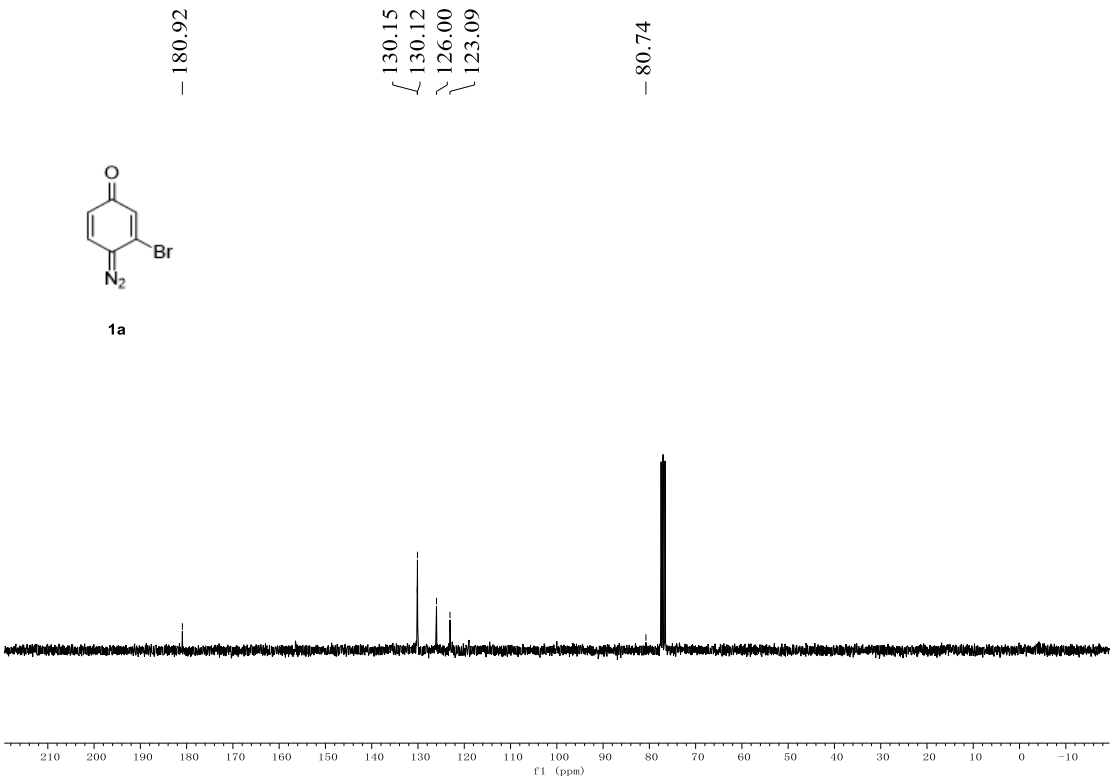
^{13}C NMR (75 MHz, $CDCl_3$)



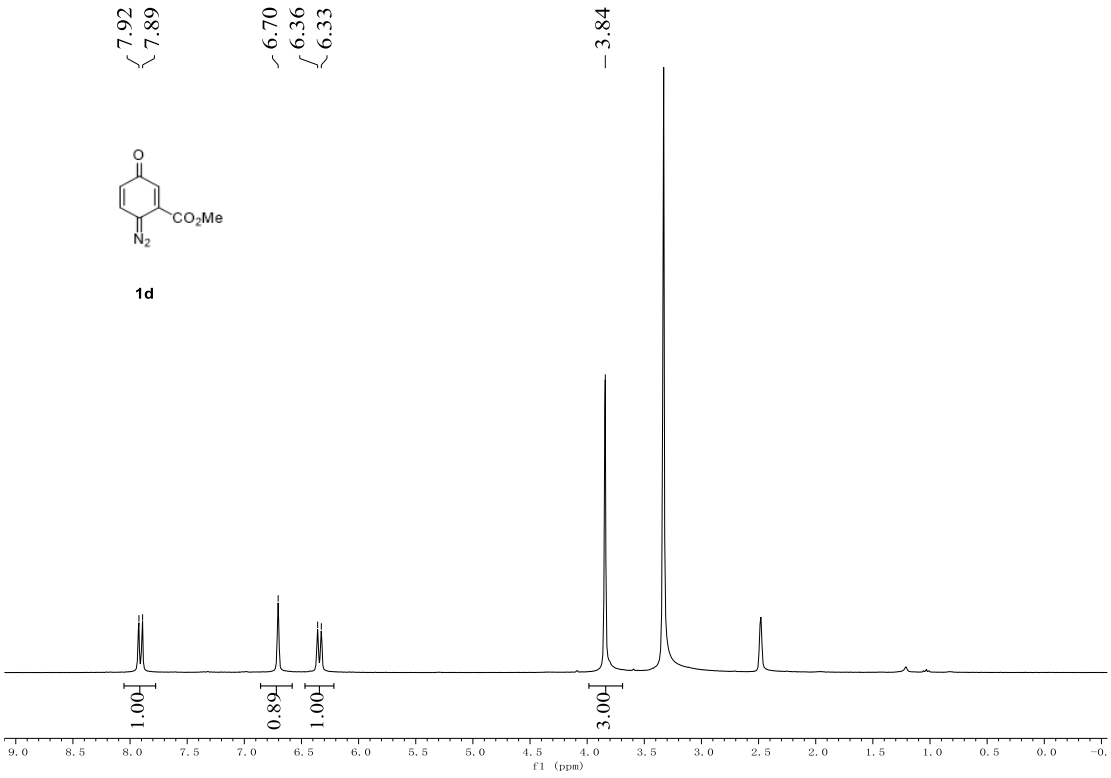
^{1}H NMR (300 MHz, $CDCl_3$)



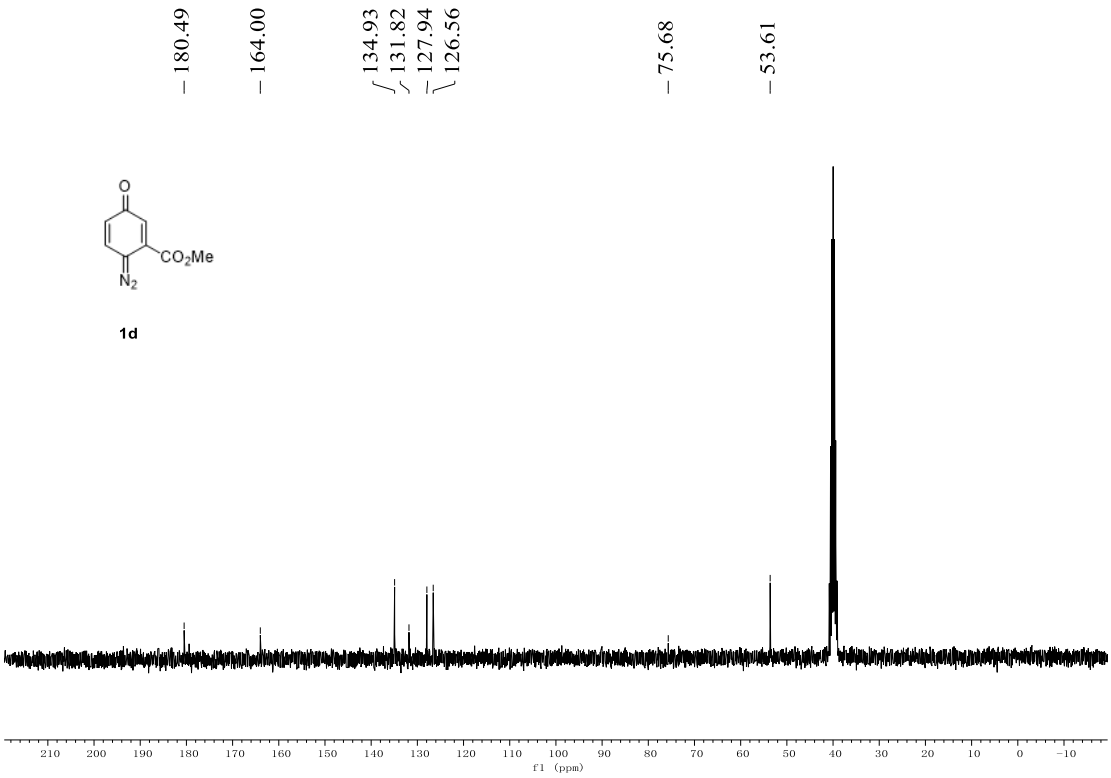
^{13}C NMR (75 MHz, $CDCl_3$)



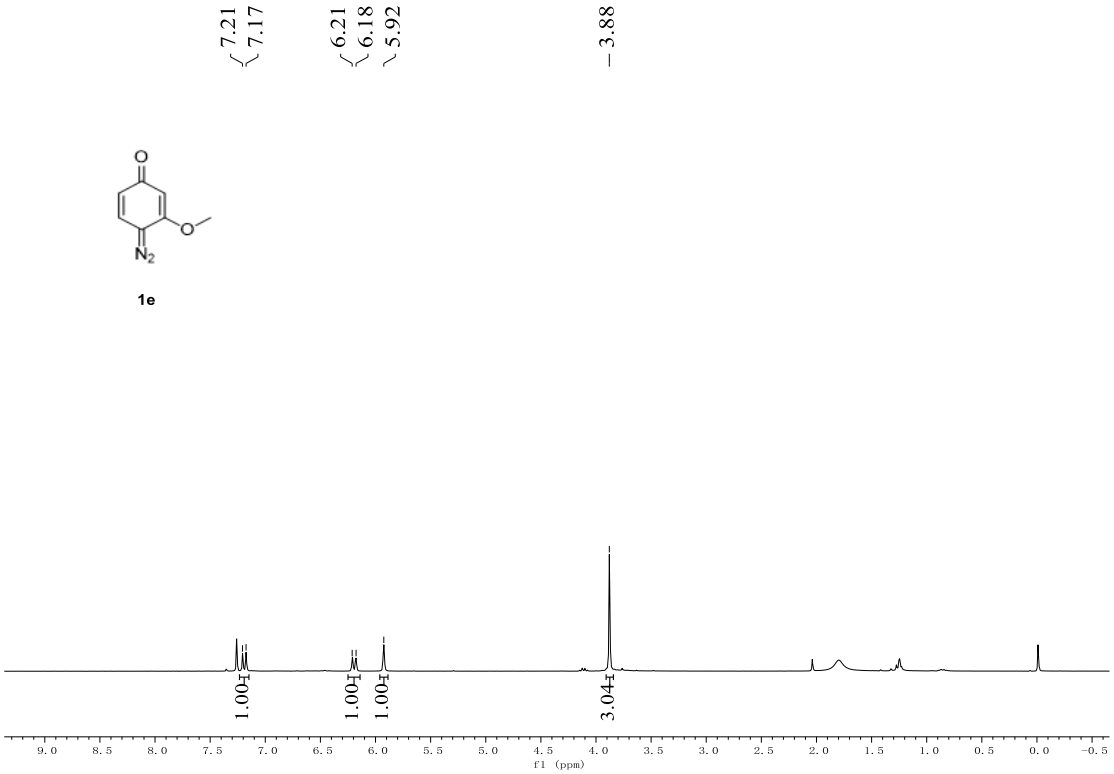
^{1}H NMR (300 MHz, DMSO)



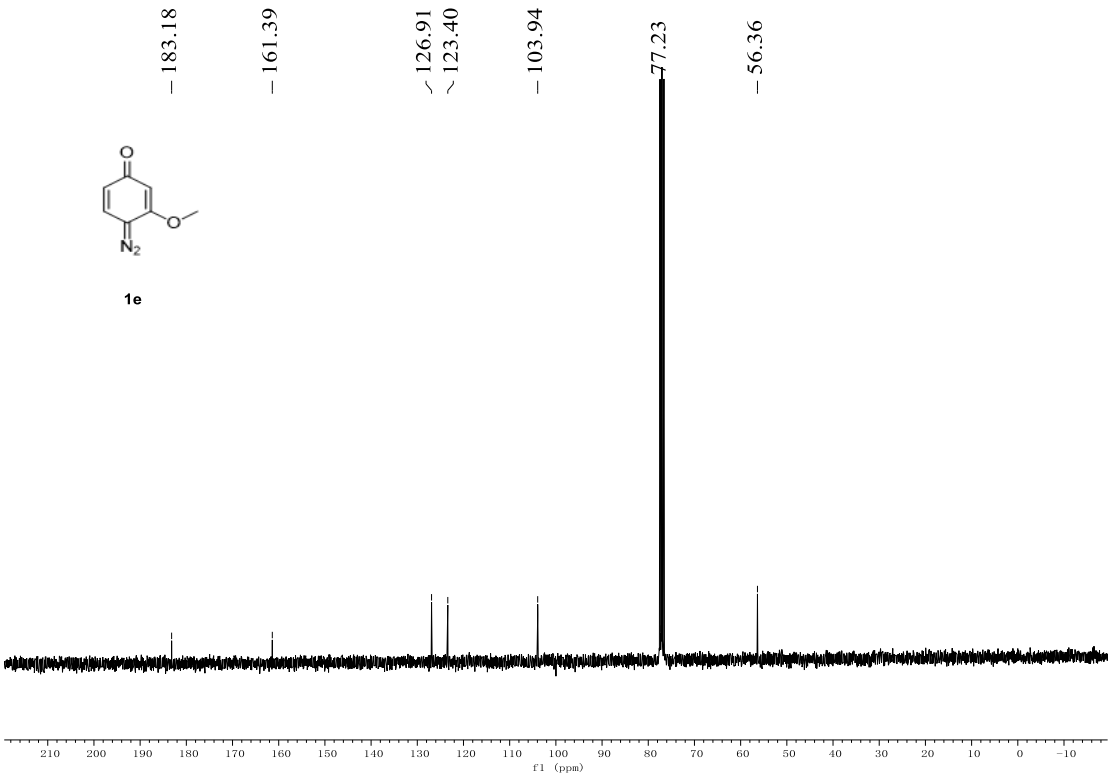
^{13}C NMR (75 MHz, DMSO)



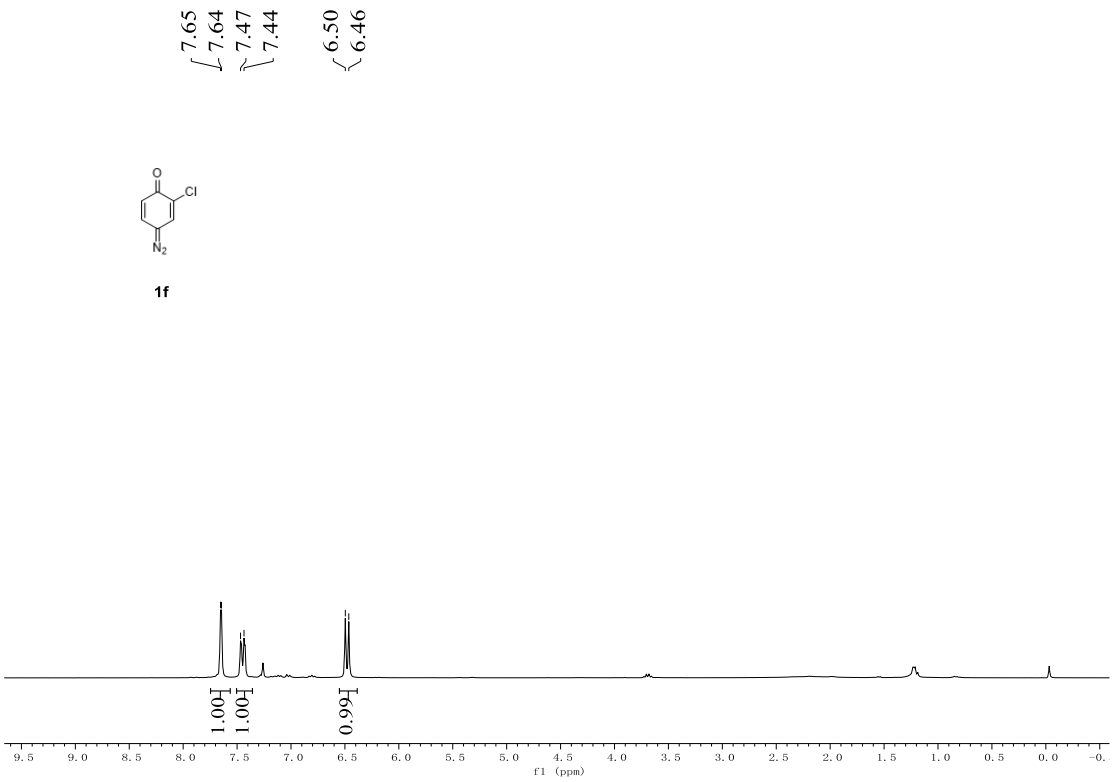
^{1}H NMR (300 MHz, $CDCl_3$)



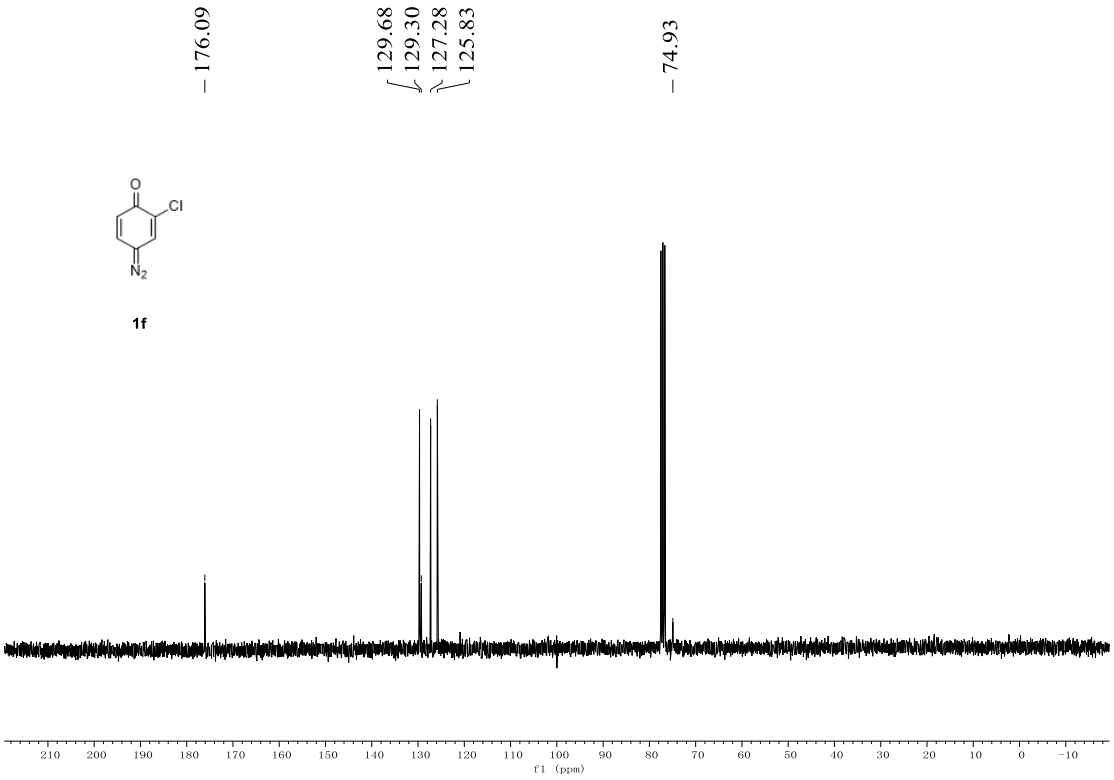
^{13}C NMR (75 MHz, $CDCl_3$)



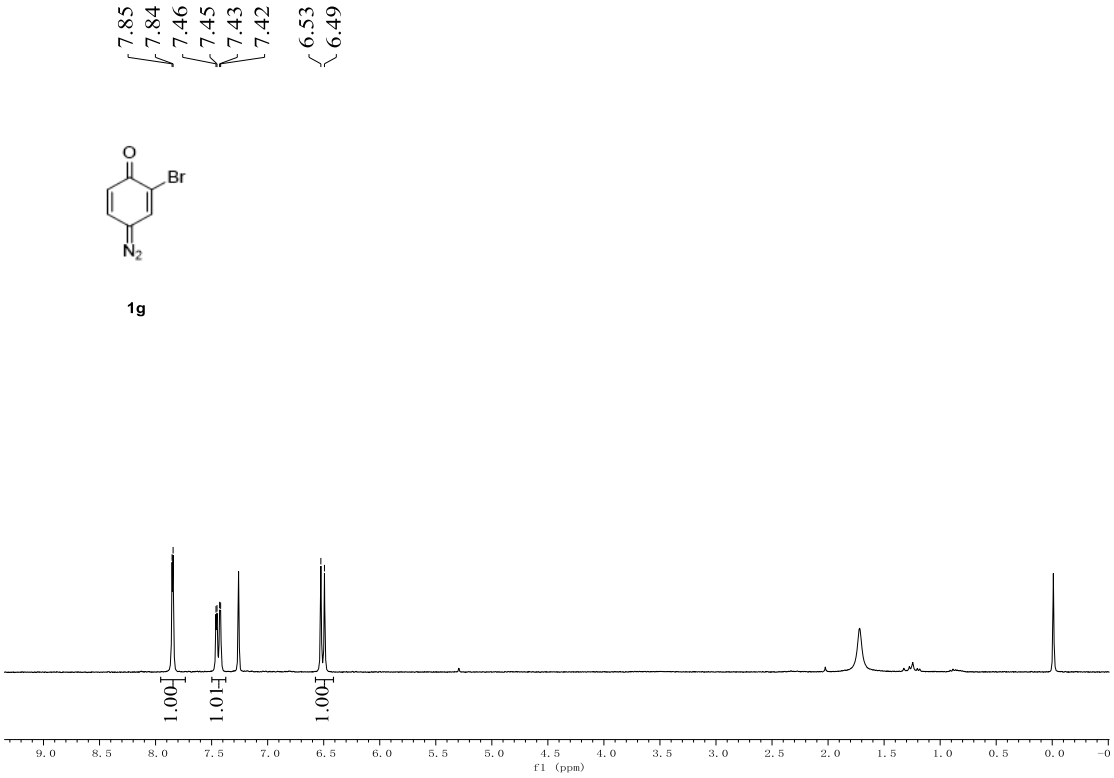
^{1}H NMR (300 MHz, $CDCl_3$)



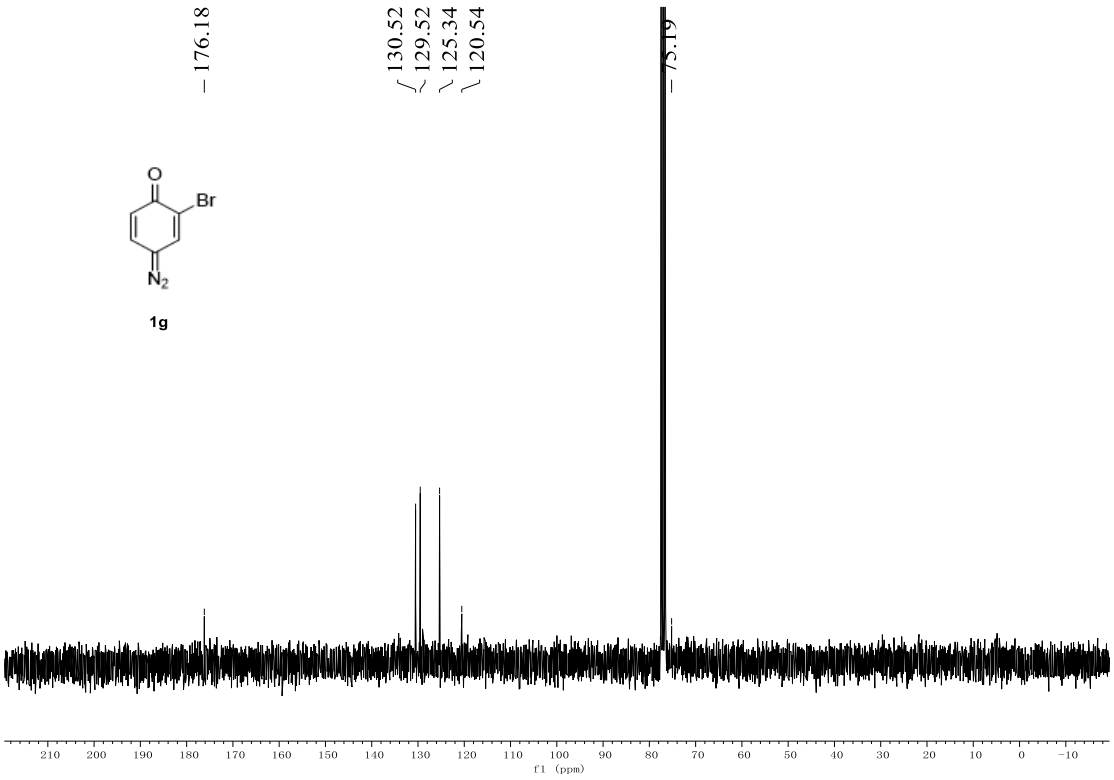
^{13}C NMR (75 MHz, $CDCl_3$)



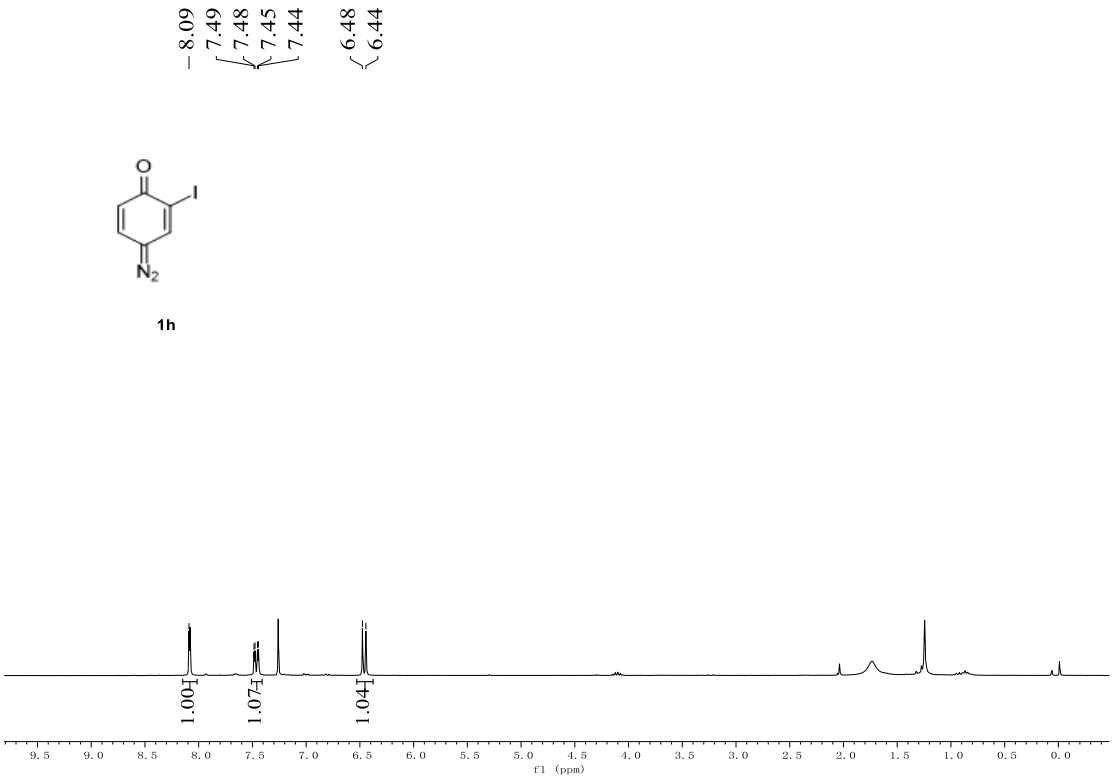
^{1}H NMR (300 MHz, $CDCl_3$)



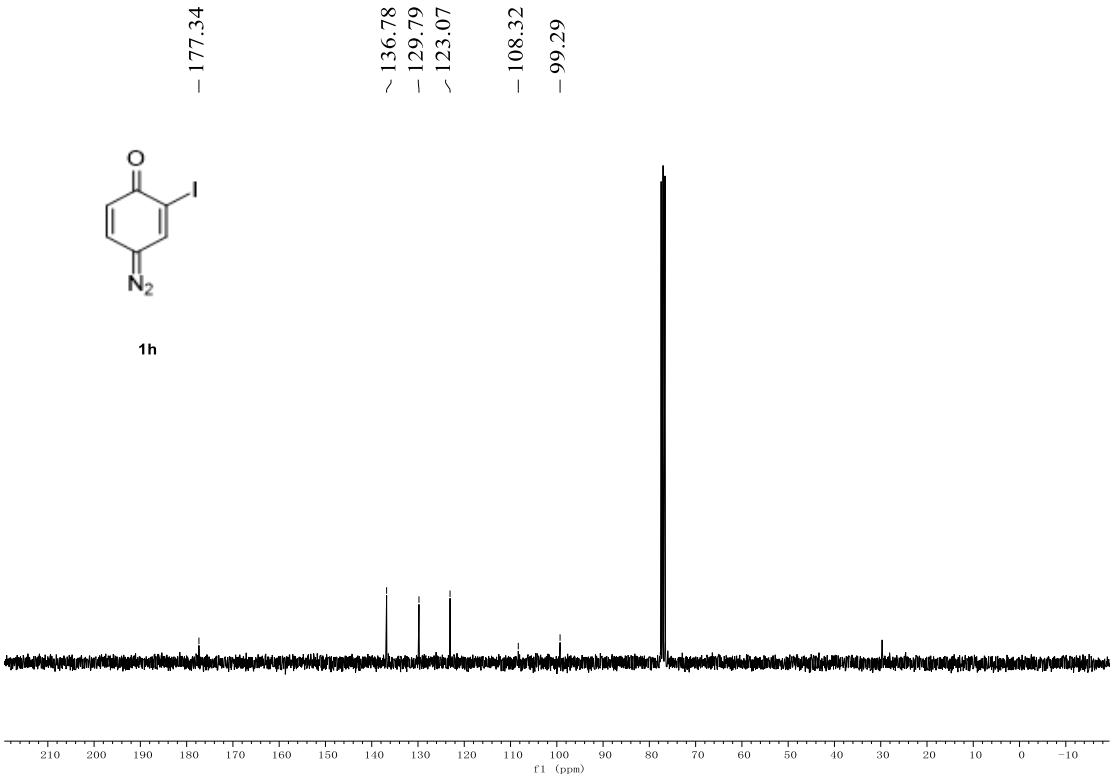
^{13}C NMR (75 MHz, $CDCl_3$)



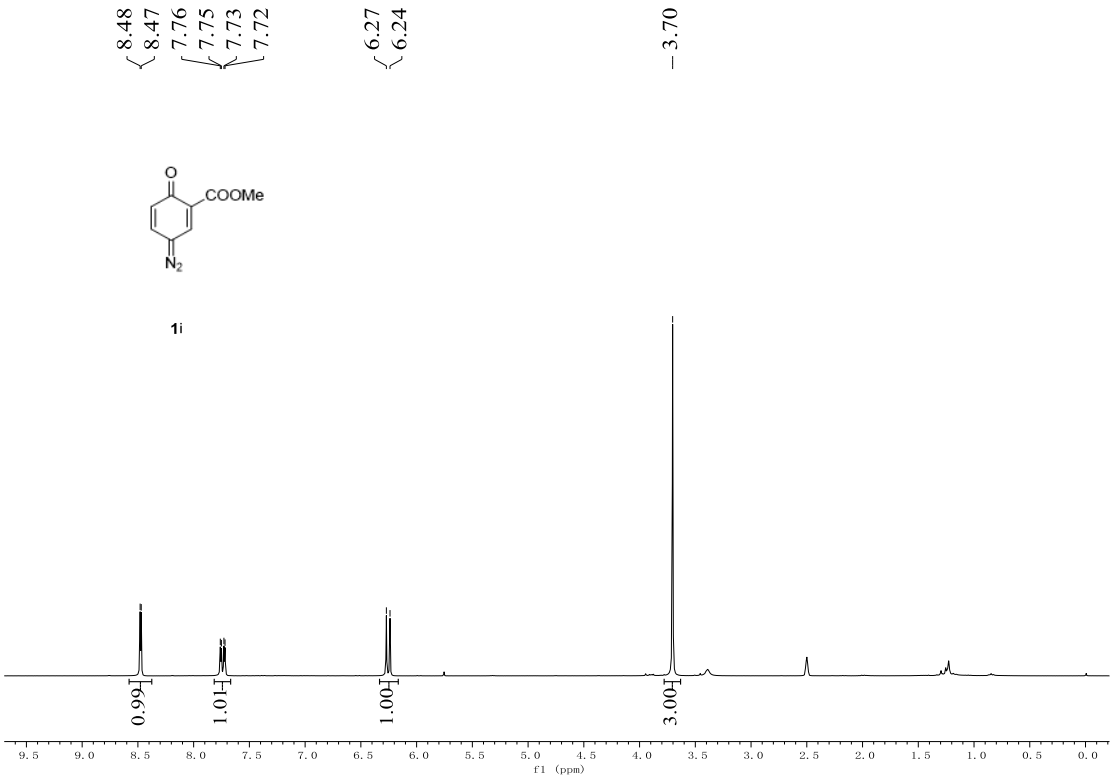
^{1}H NMR (300 MHz, $CDCl_3$)



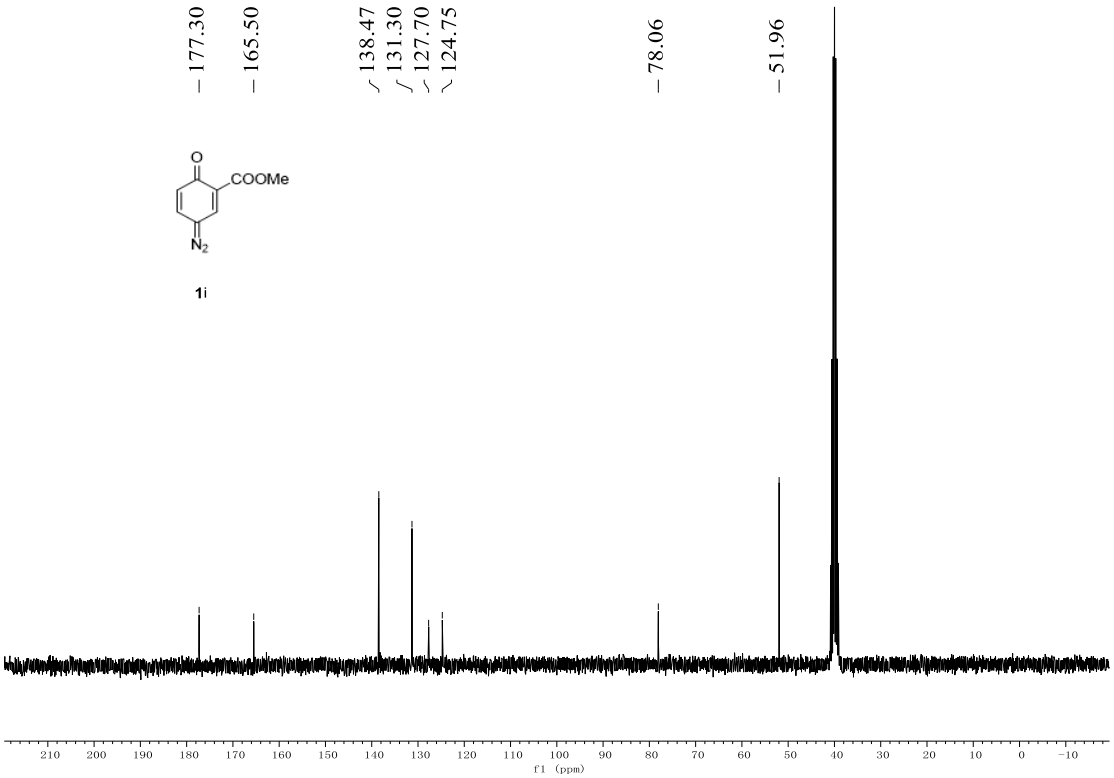
^{13}C NMR (75 MHz, $CDCl_3$)



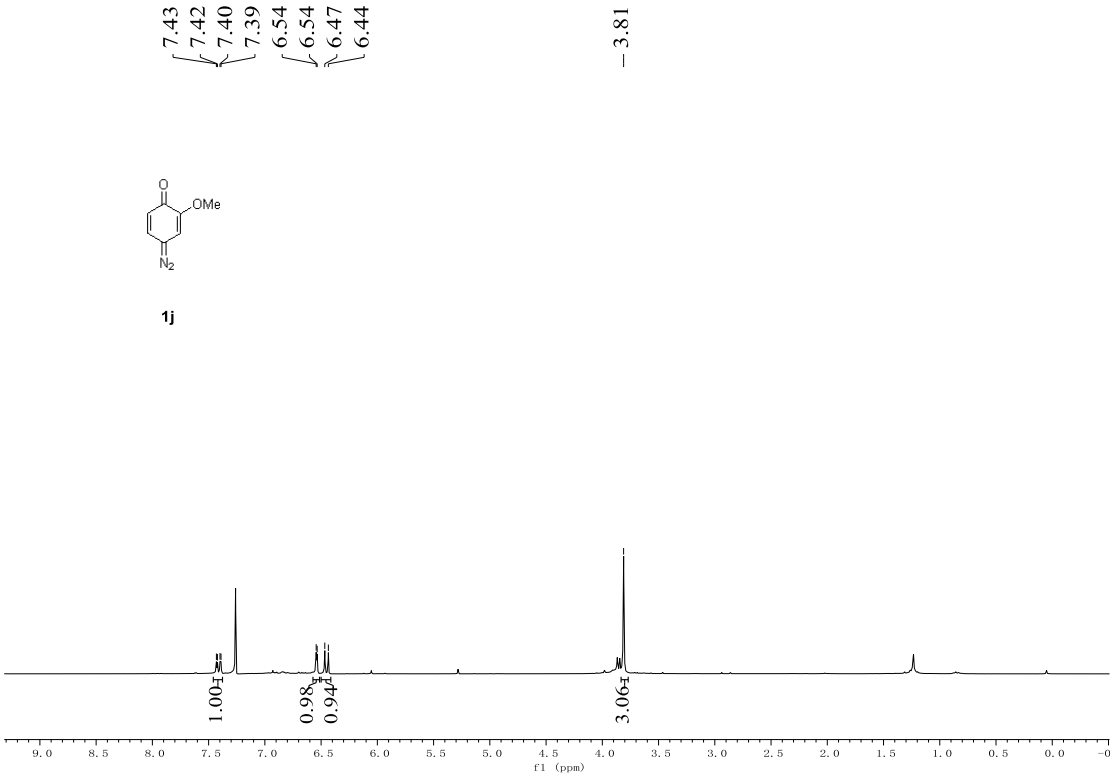
^{1}H NMR (300 MHz, DMSO)



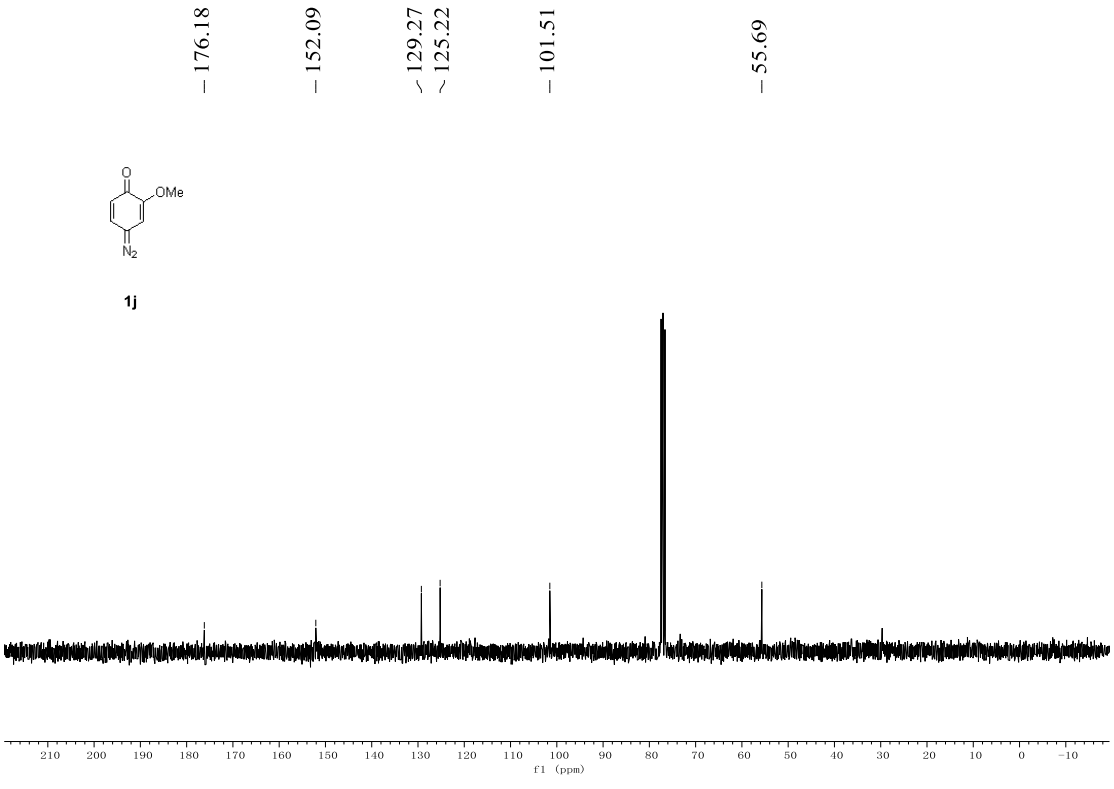
^{13}C NMR (75 MHz, DMSO)



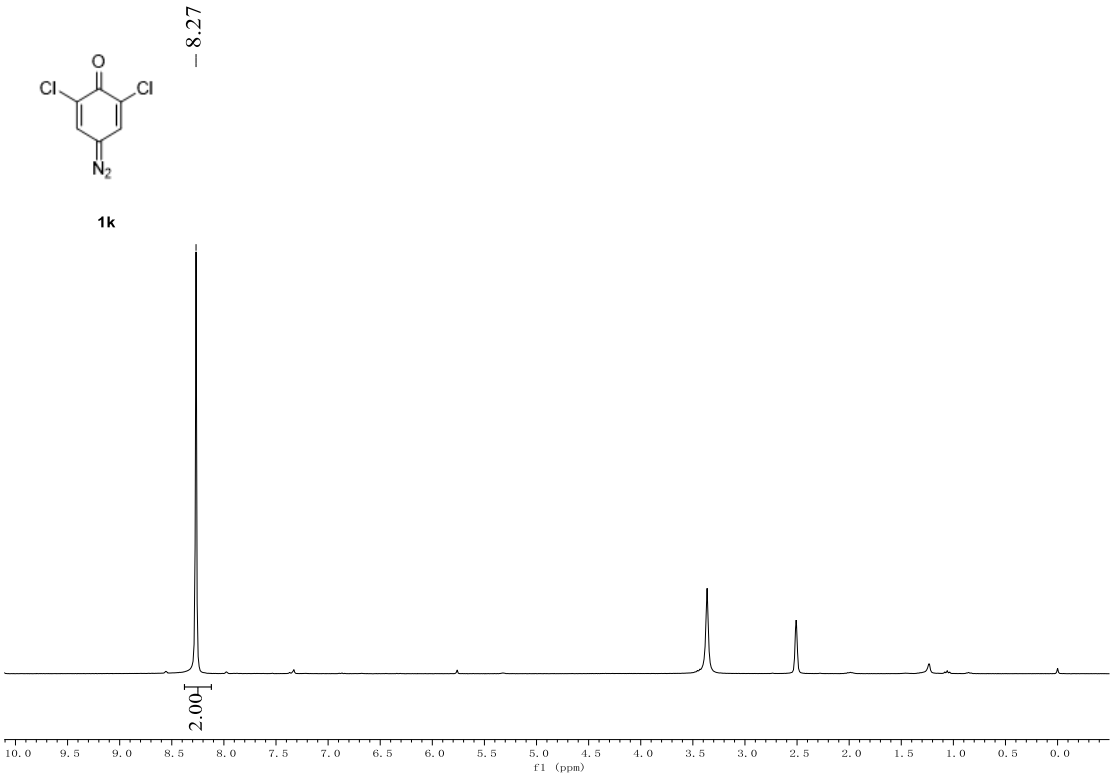
^{1}H NMR (300 MHz, $CDCl_3$)



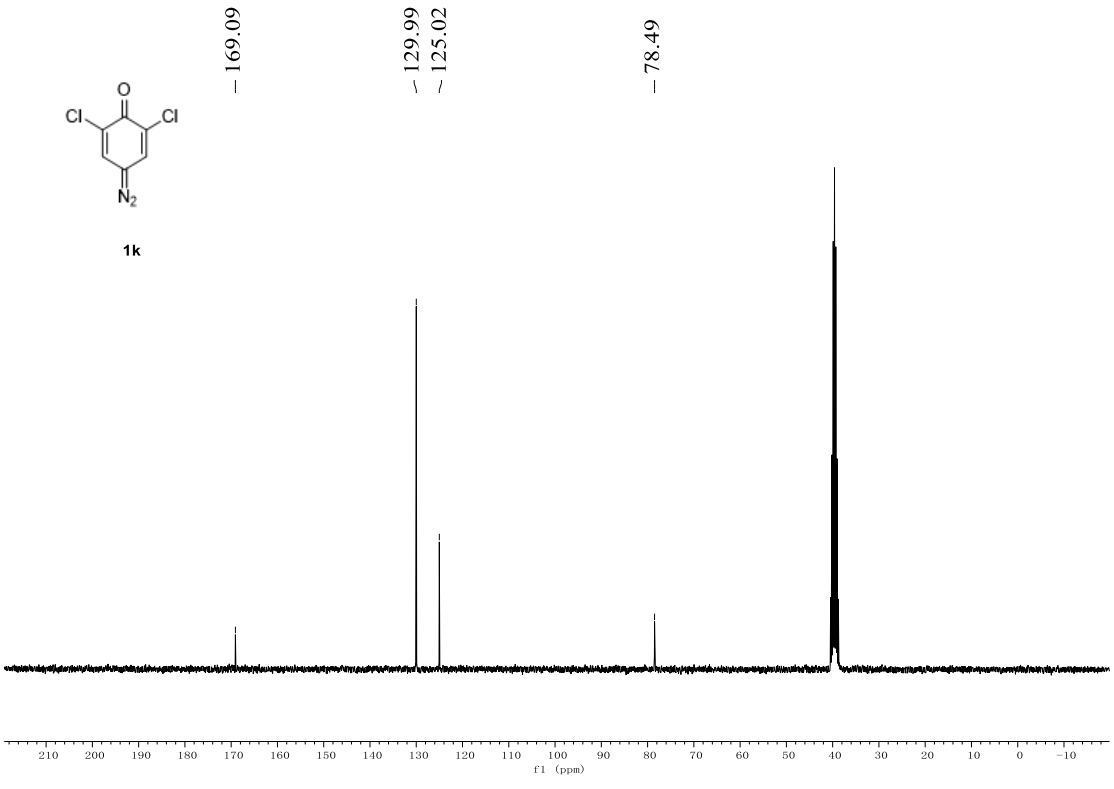
^{13}C NMR (75 MHz, $CDCl_3$)



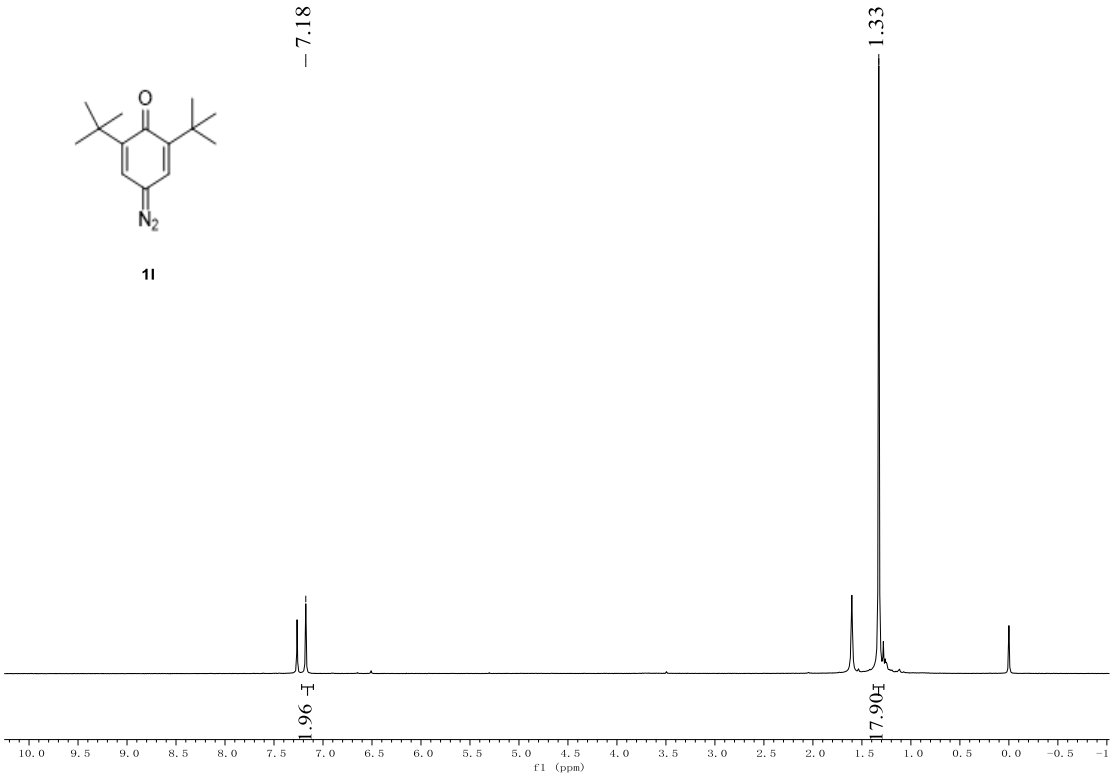
^{1}H NMR (300 MHz, DMSO)



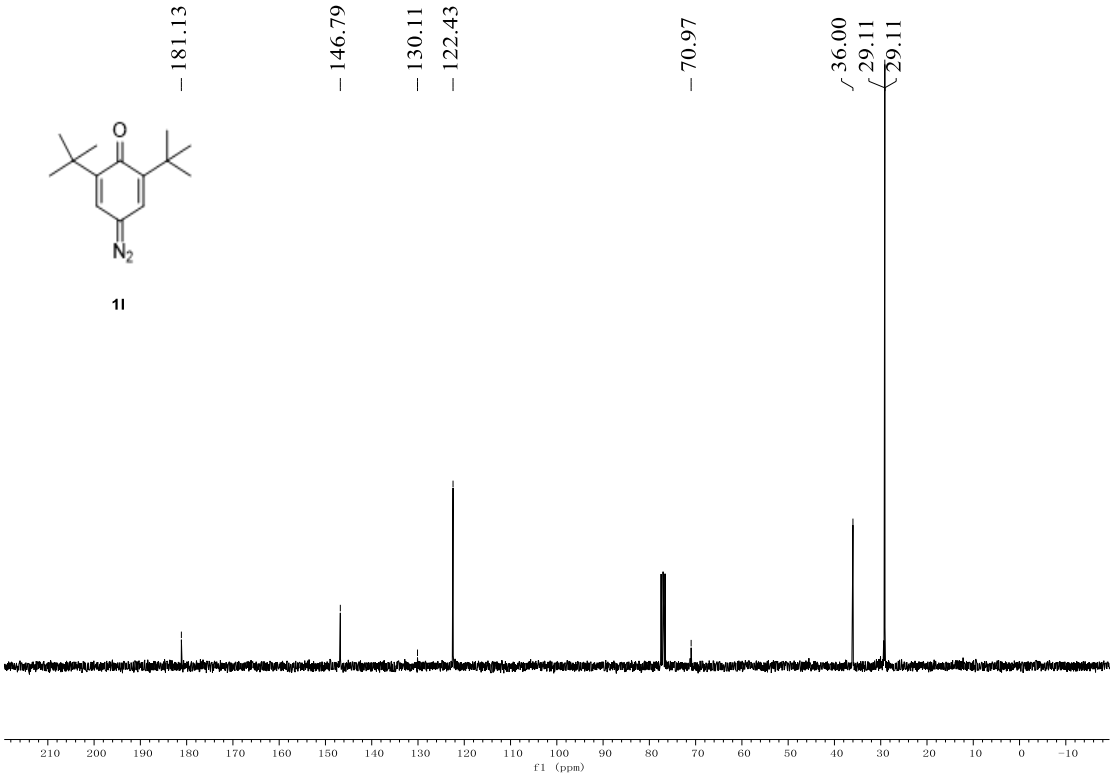
^{13}C NMR (75 MHz, DMSO)



^{1}H NMR (300 MHz, $CDCl_3$)

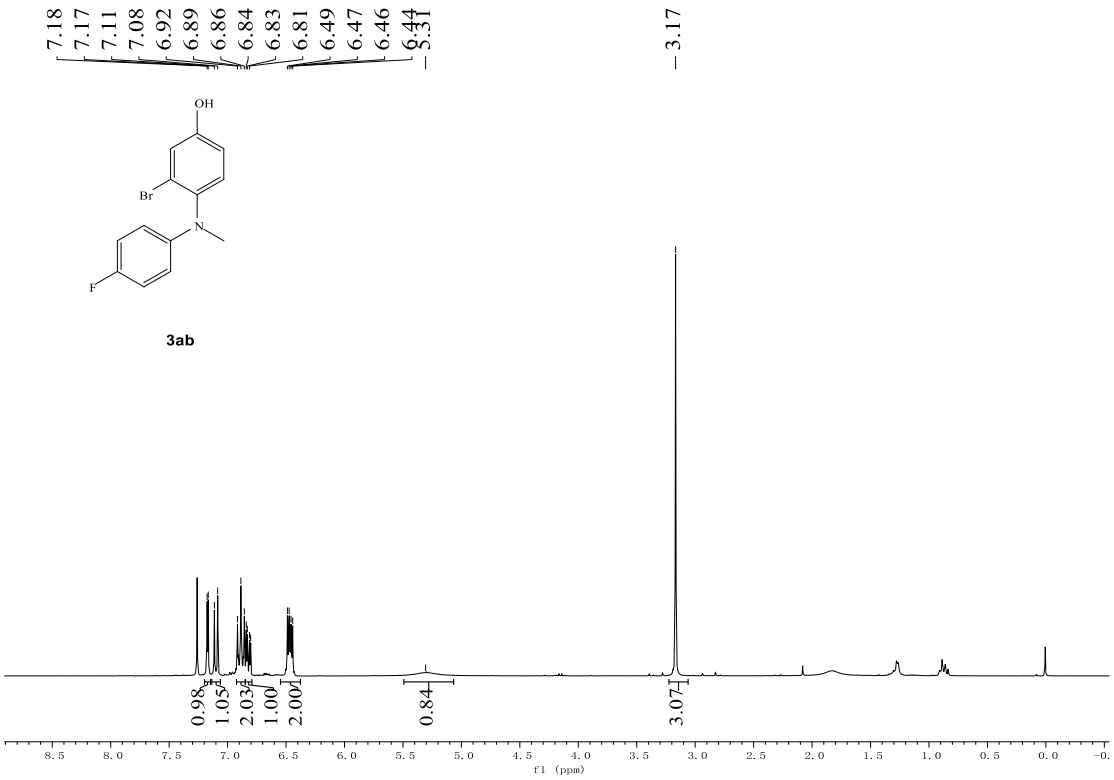


^{13}C NMR (75 MHz, $CDCl_3$)

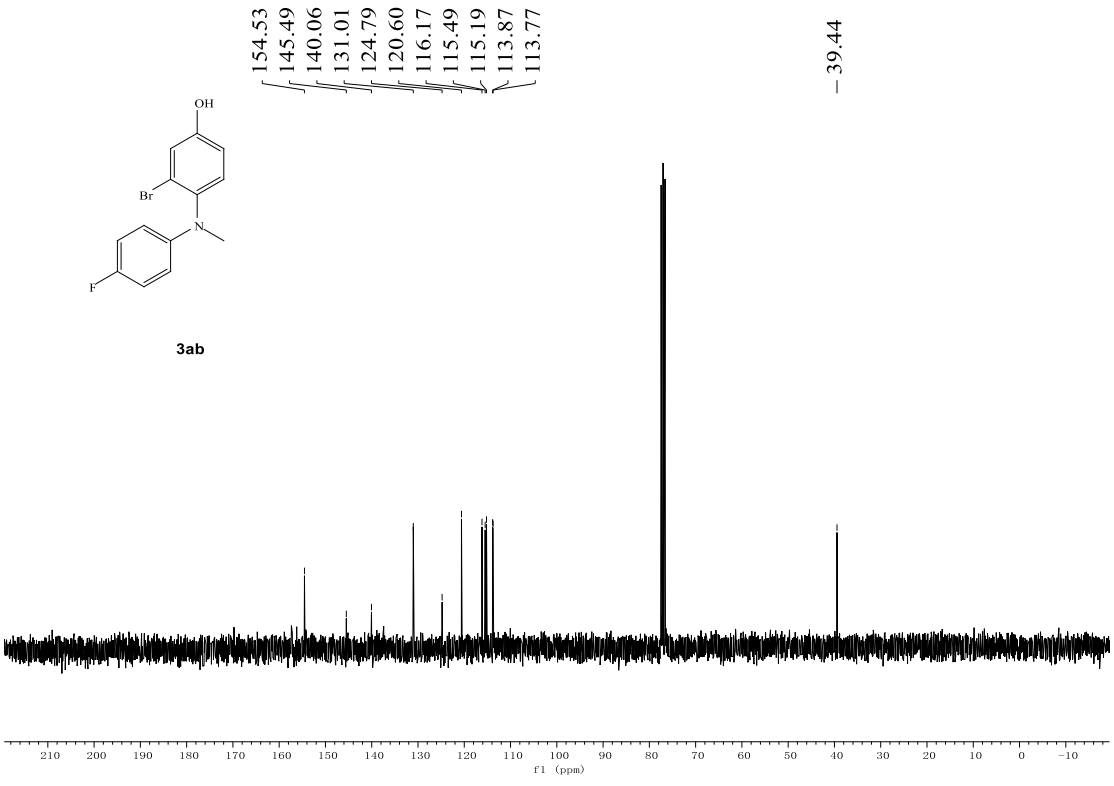


NMR Spectrum for Products

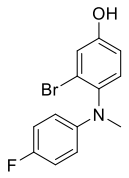
^{1}H NMR (300 MHz, $CDCl_3$)



^{13}C NMR (75 MHz, $CDCl_3$)

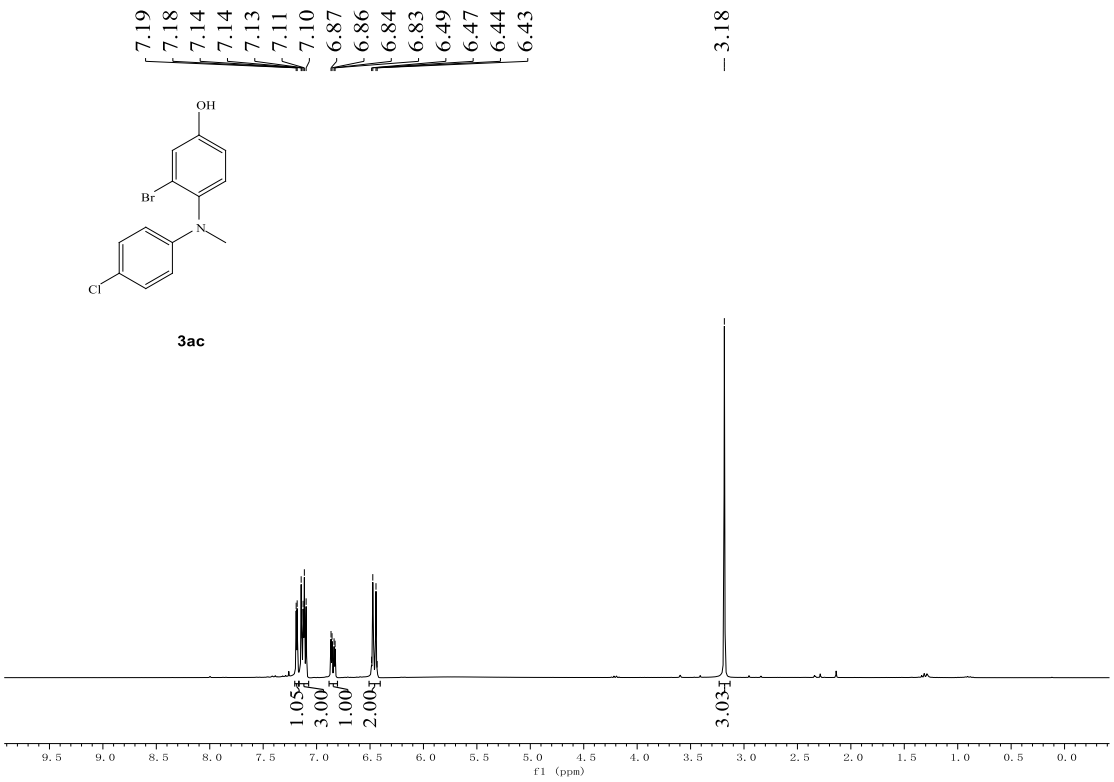


19F NMR (282 MHz, $CDCl_3$)

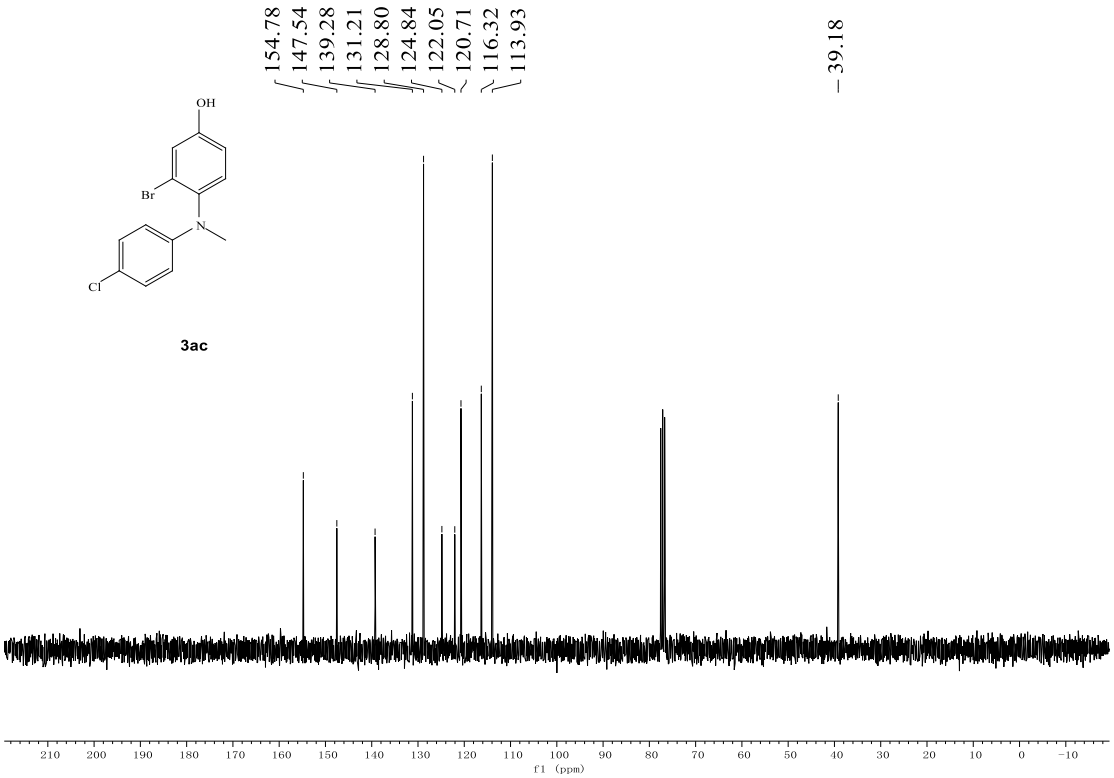


3ab

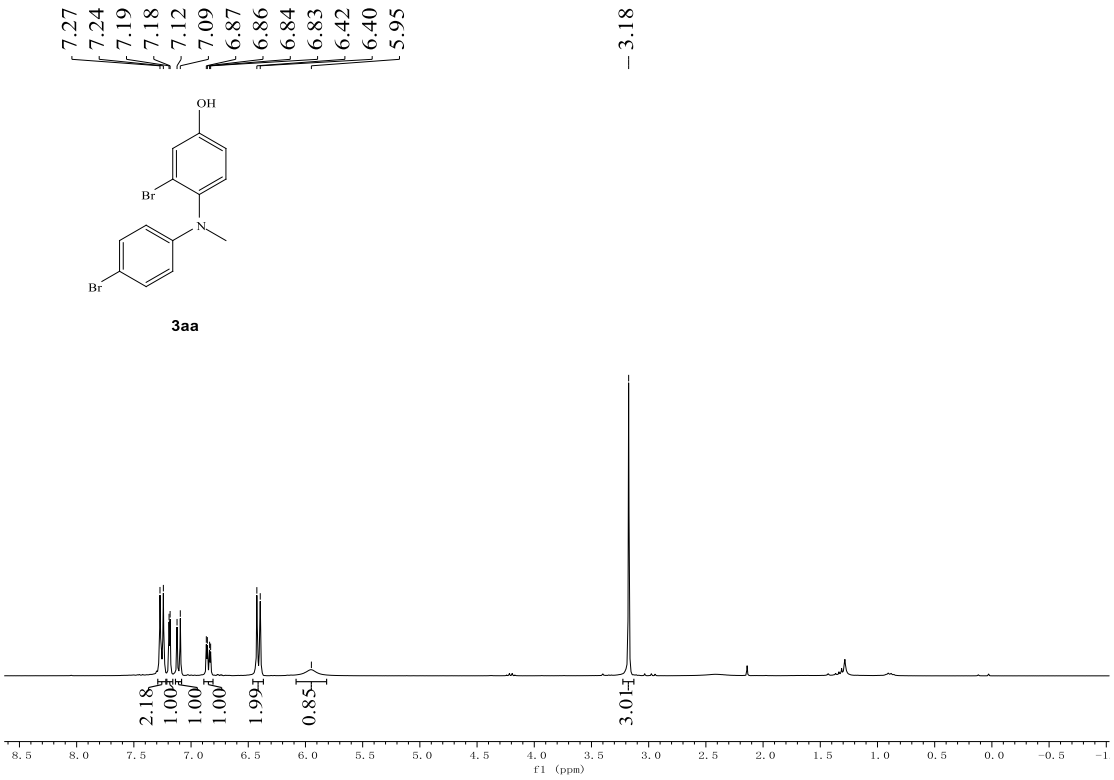
^{1}H NMR (300 MHz, $CDCl_3$)



^{13}C NMR (75 MHz, $CDCl_3$)

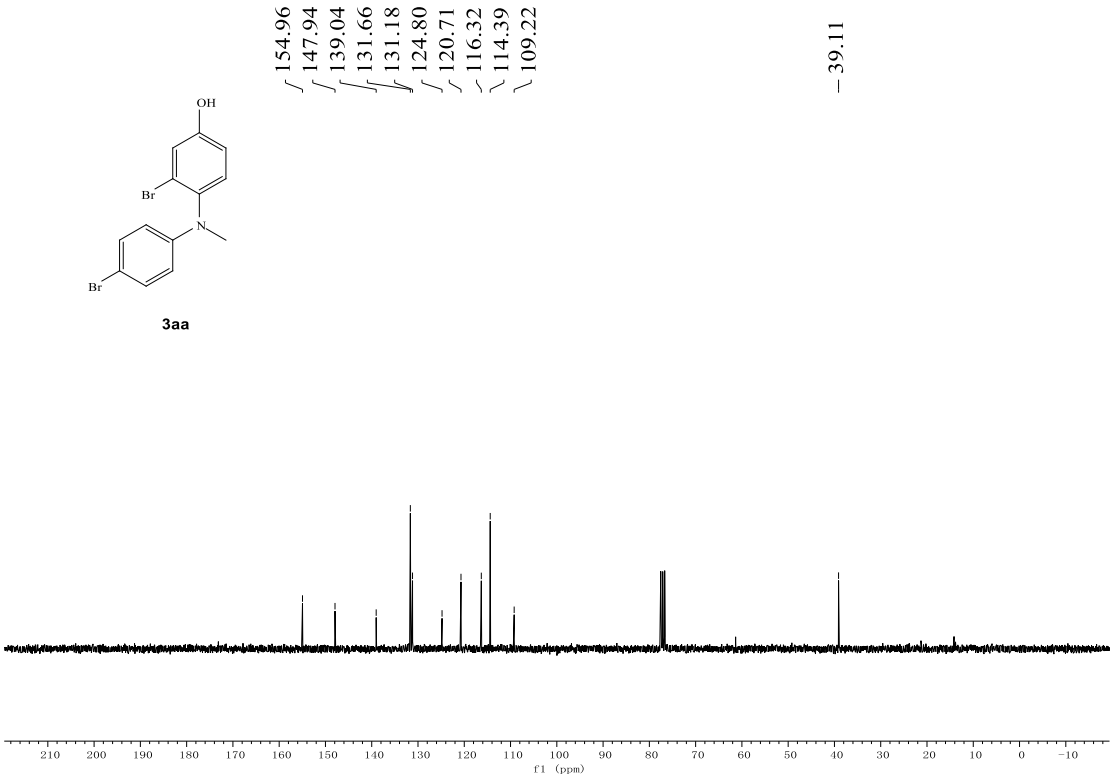


^{1}H NMR (300 MHz, $CDCl_3$)



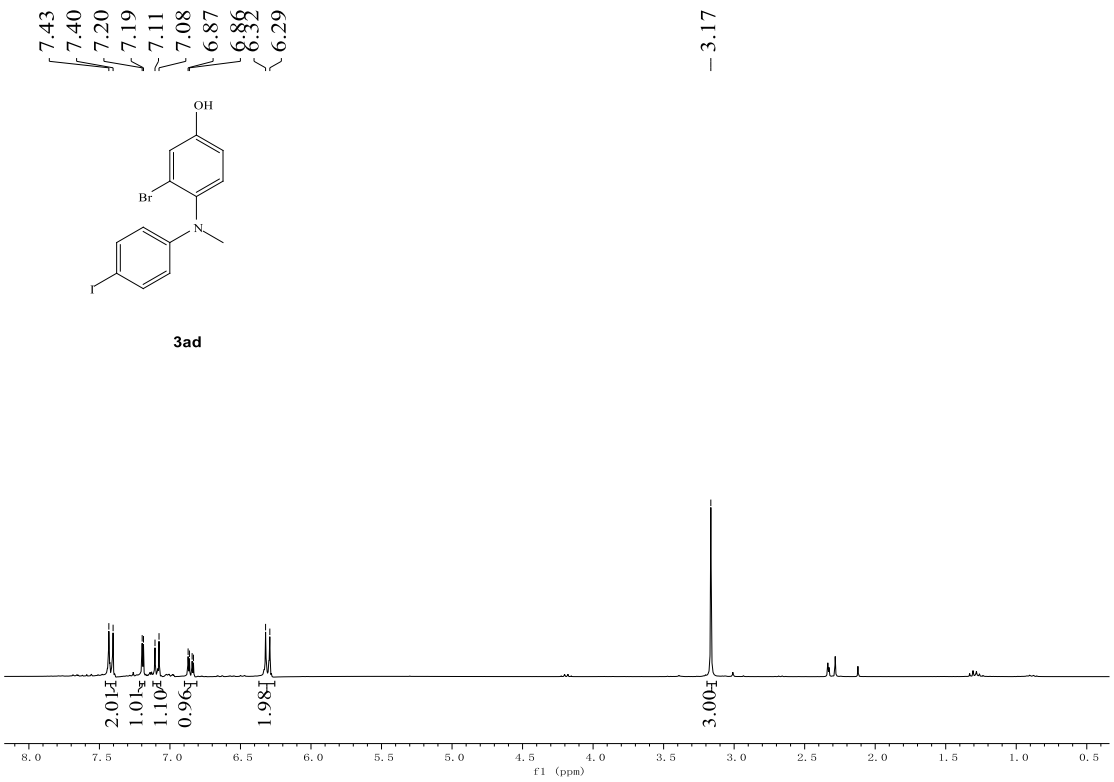
3aa

^{13}C NMR (75 MHz, $CDCl_3$)

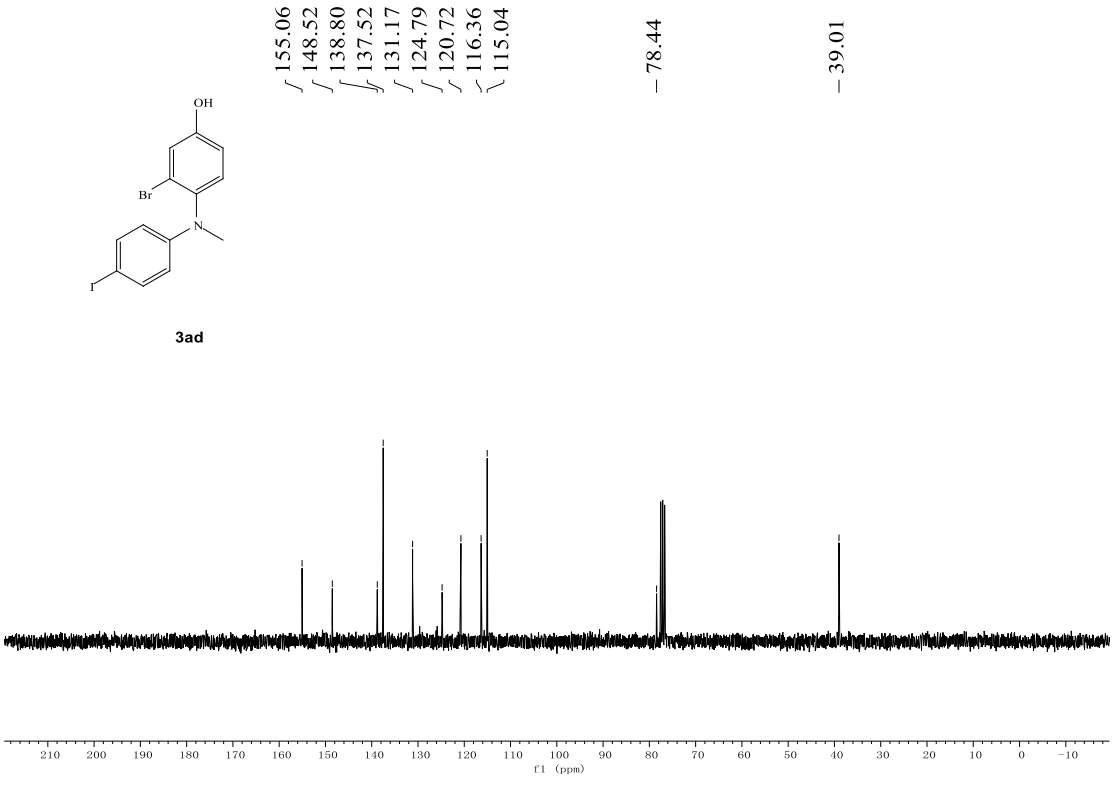


3aa

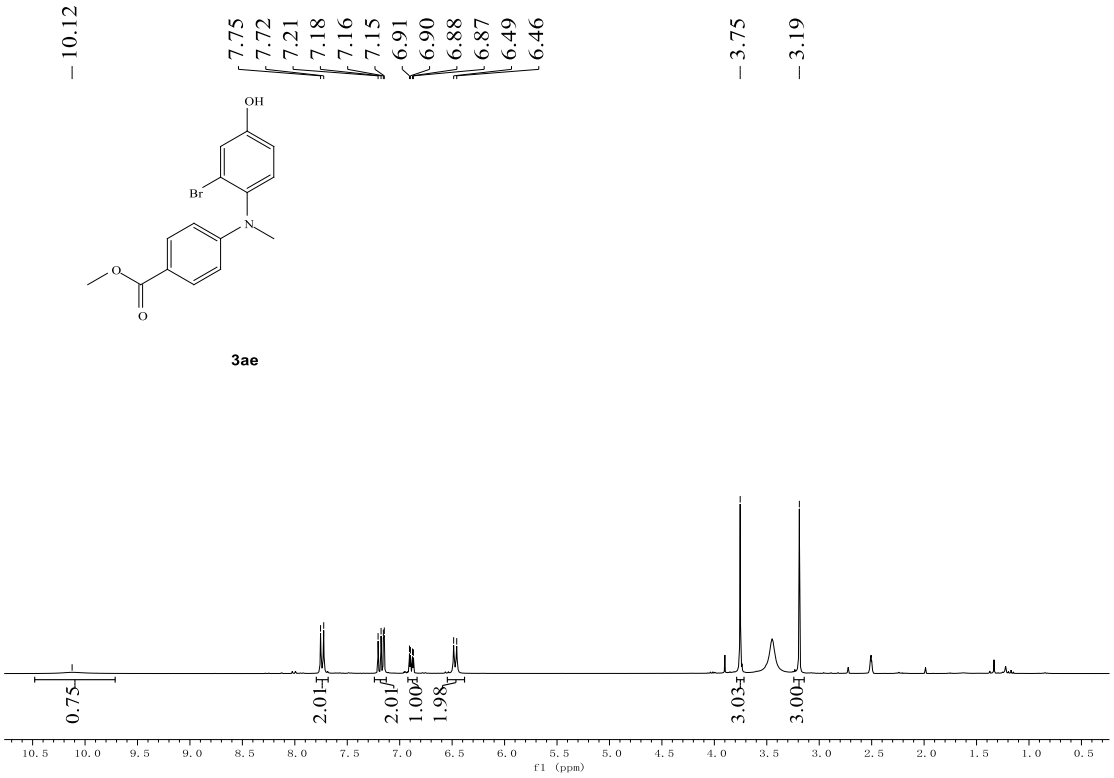
^{1}H NMR (300 MHz, $CDCl_3$)



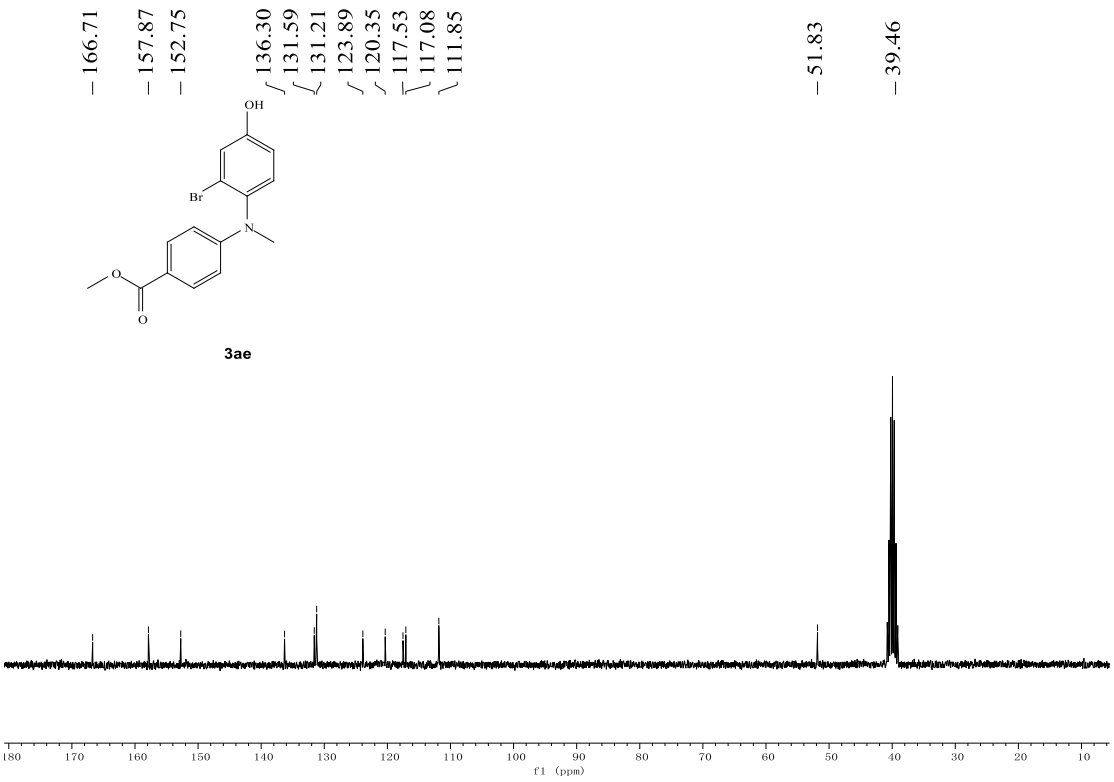
^{13}C NMR (75 MHz, $CDCl_3$)



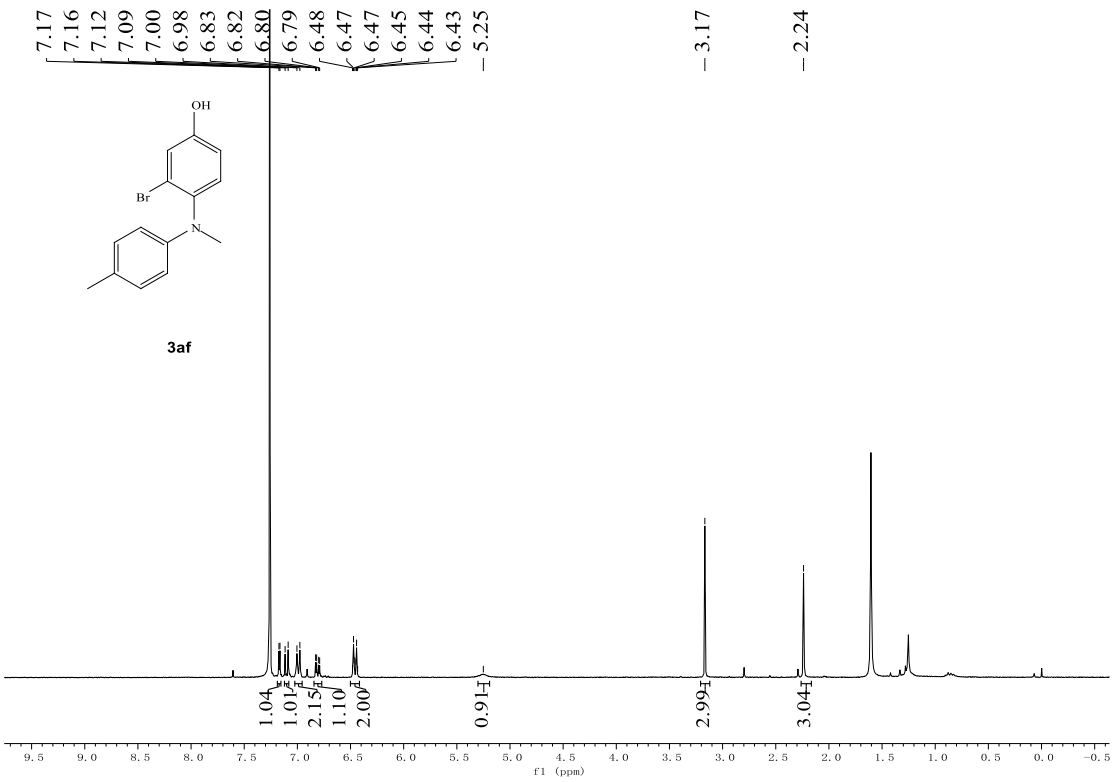
^{1}H NMR (300 MHz, DMSO)



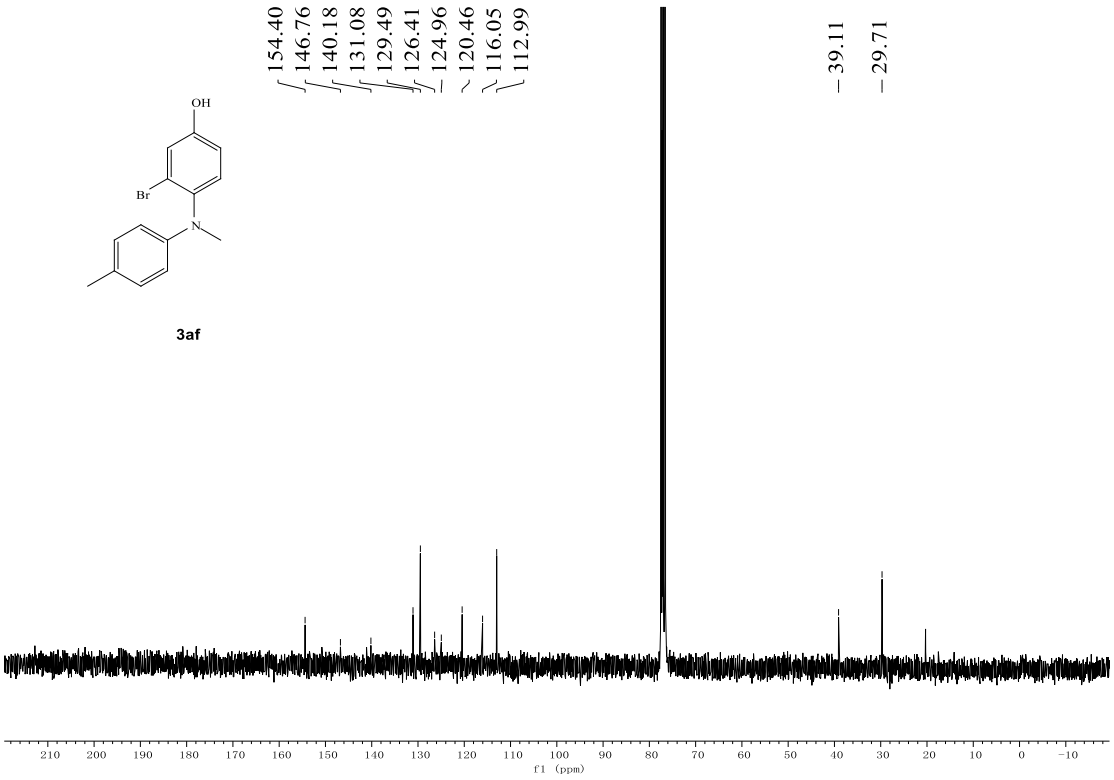
^{13}C NMR (75 MHz, DMSO)



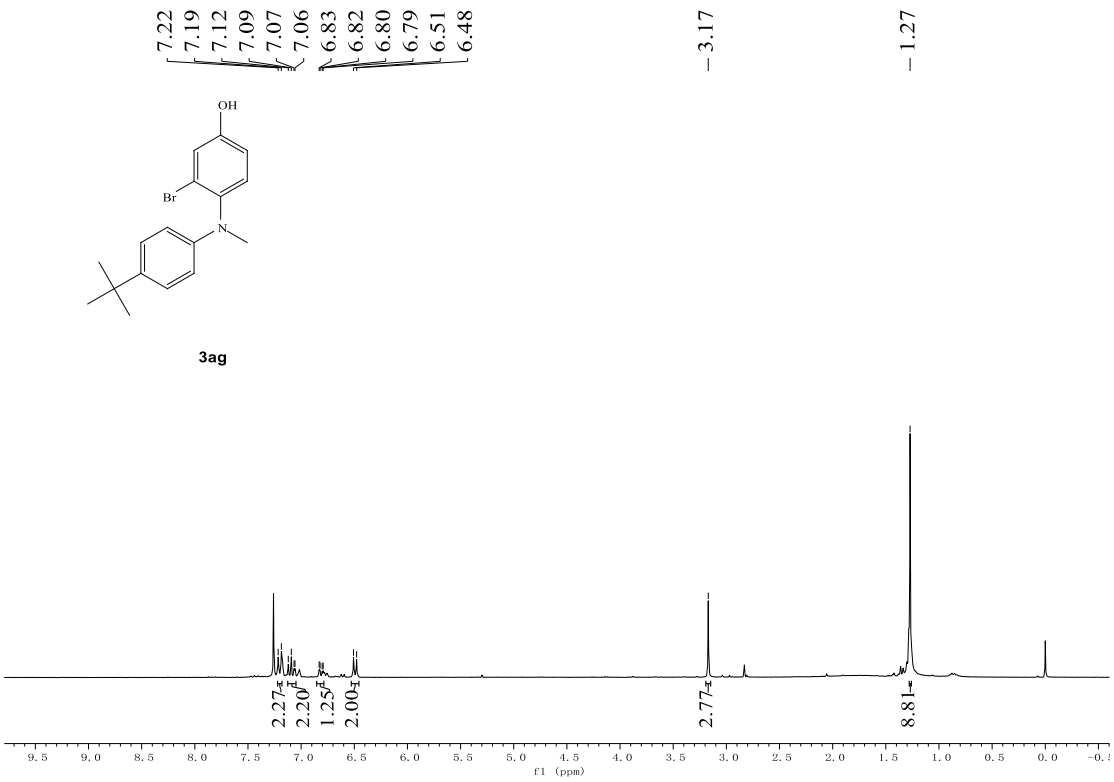
^{1}H NMR (300 MHz, $CDCl_3$)



^{13}C NMR (75 MHz, $CDCl_3$)

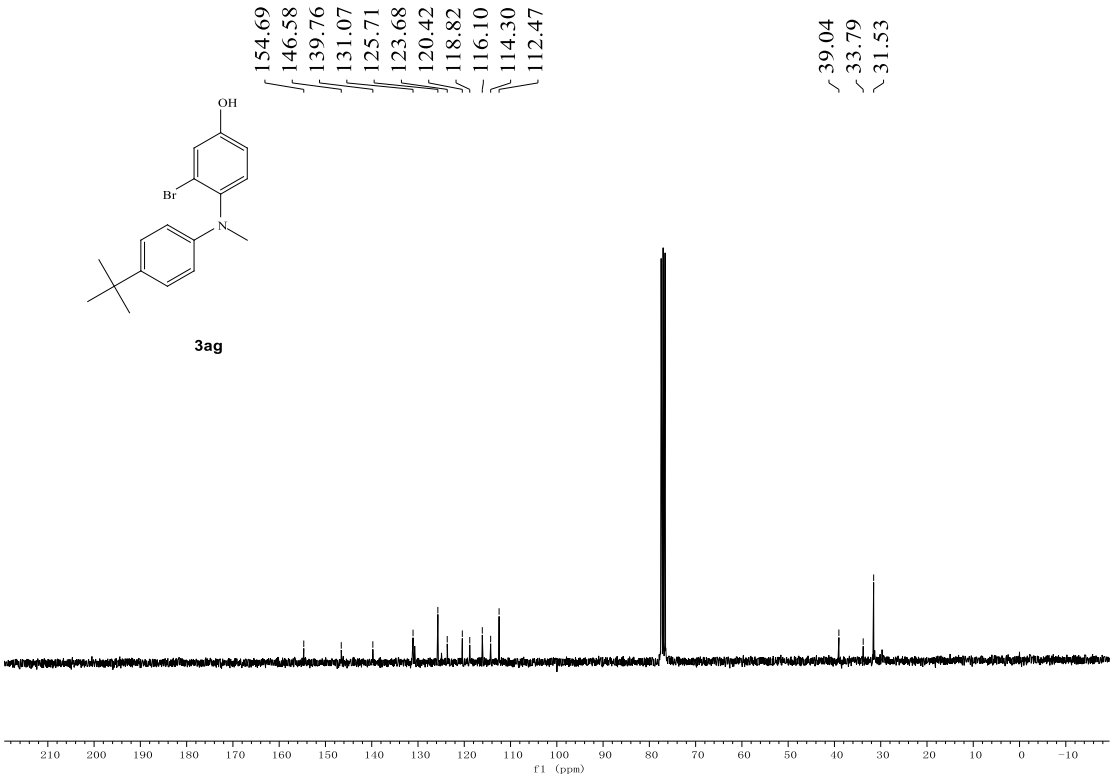


^{1}H NMR (300 MHz, $CDCl_3$)



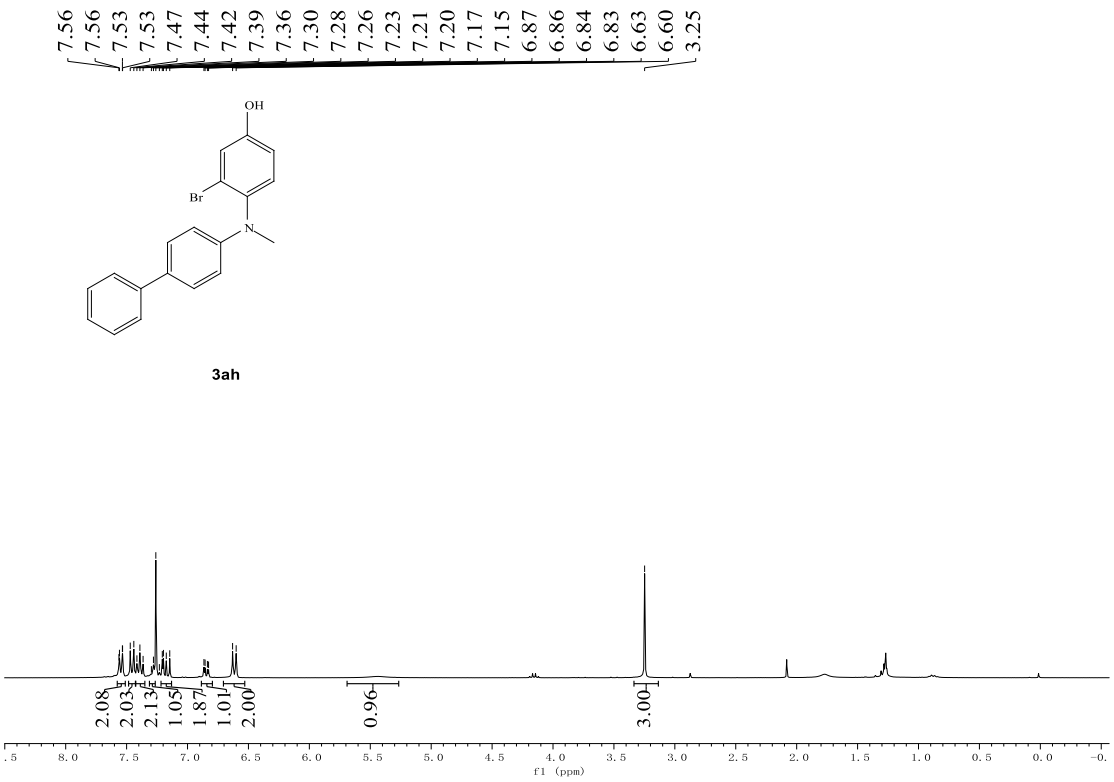
3ag

^{13}C NMR (75 MHz, $CDCl_3$)

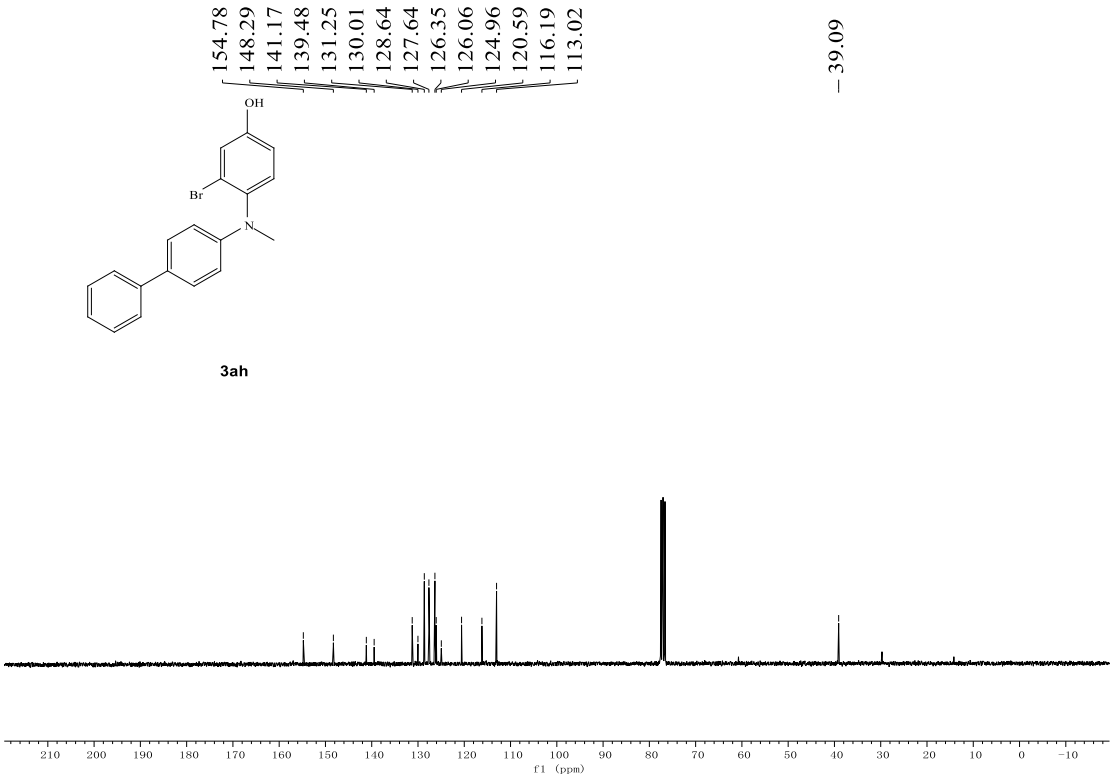


3ag

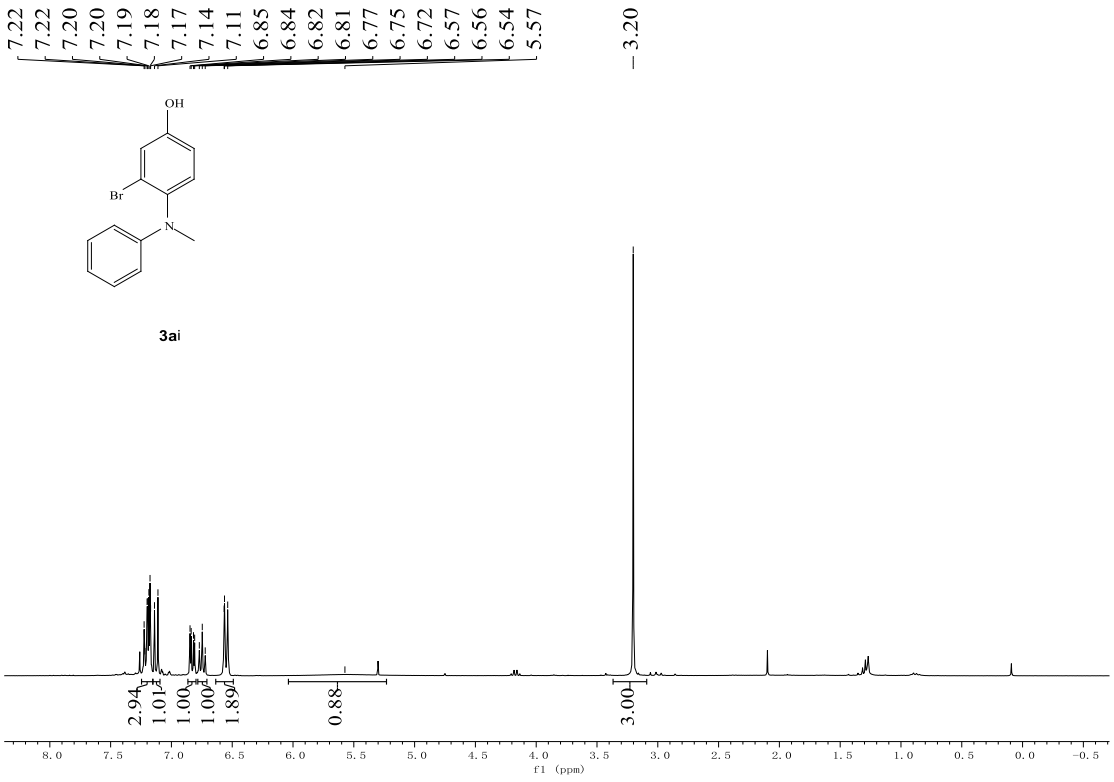
^{1}H NMR (300 MHz, $CDCl_3$)



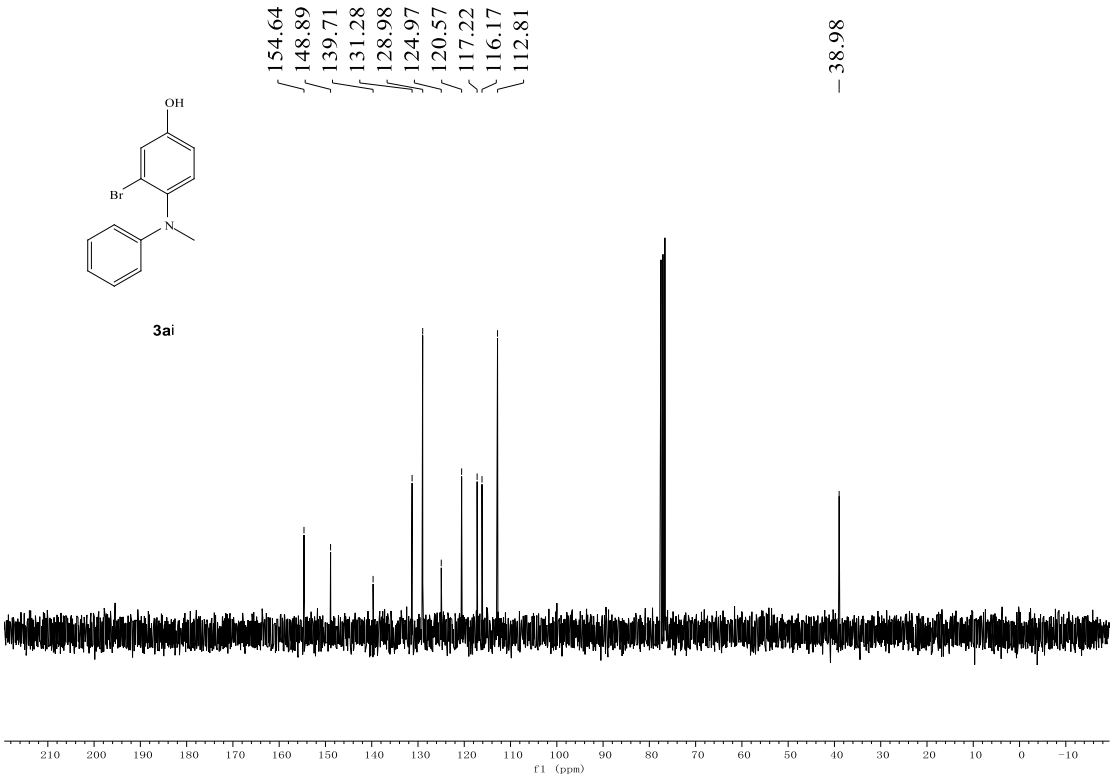
^{13}C NMR (75 MHz, $CDCl_3$)



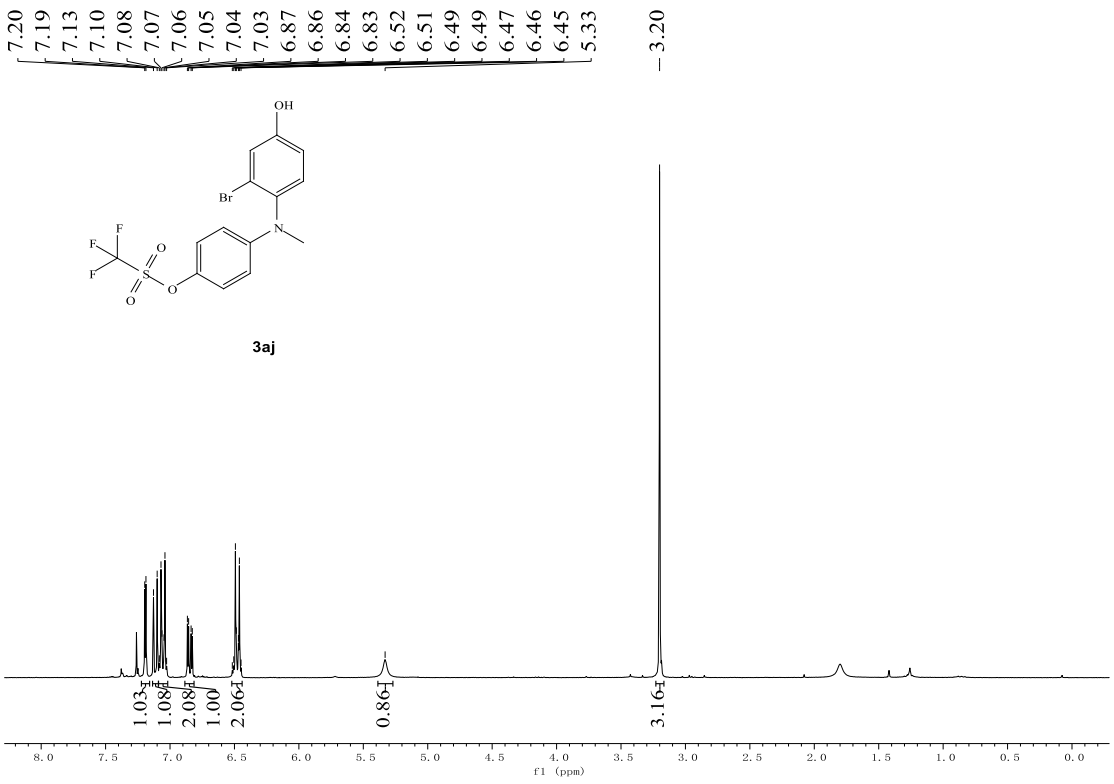
^{1}H NMR (300 MHz, $CDCl_3$)



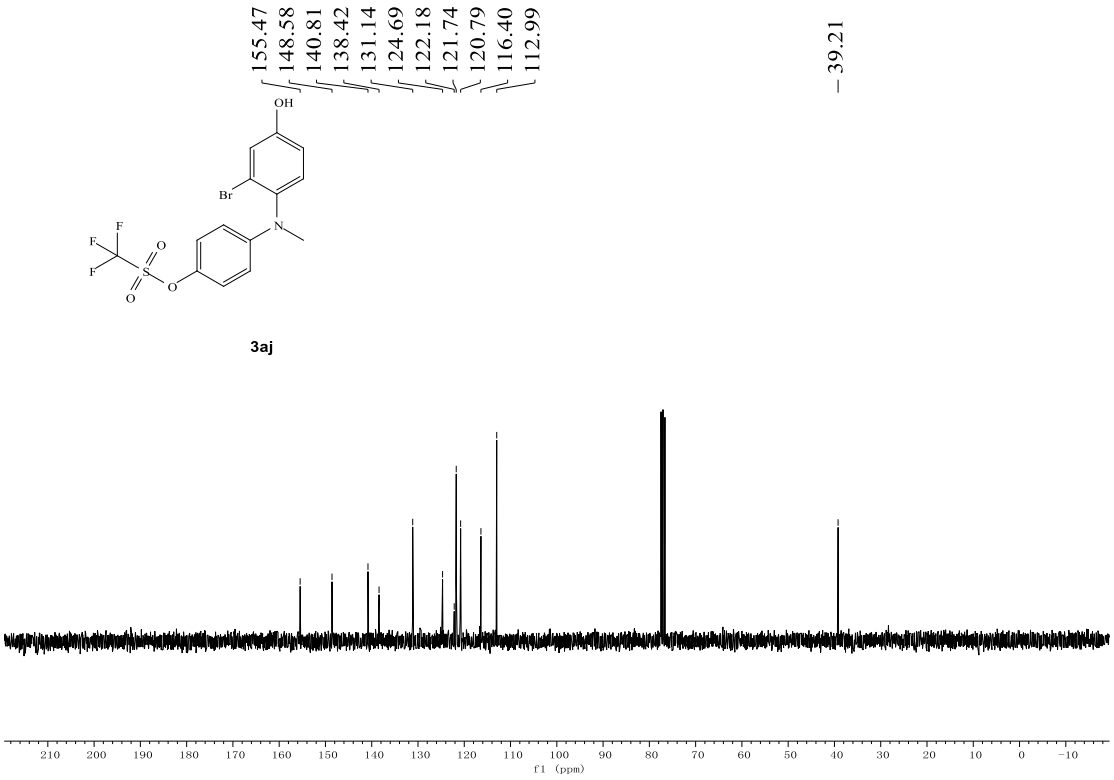
^{13}C NMR (75 MHz, $CDCl_3$)



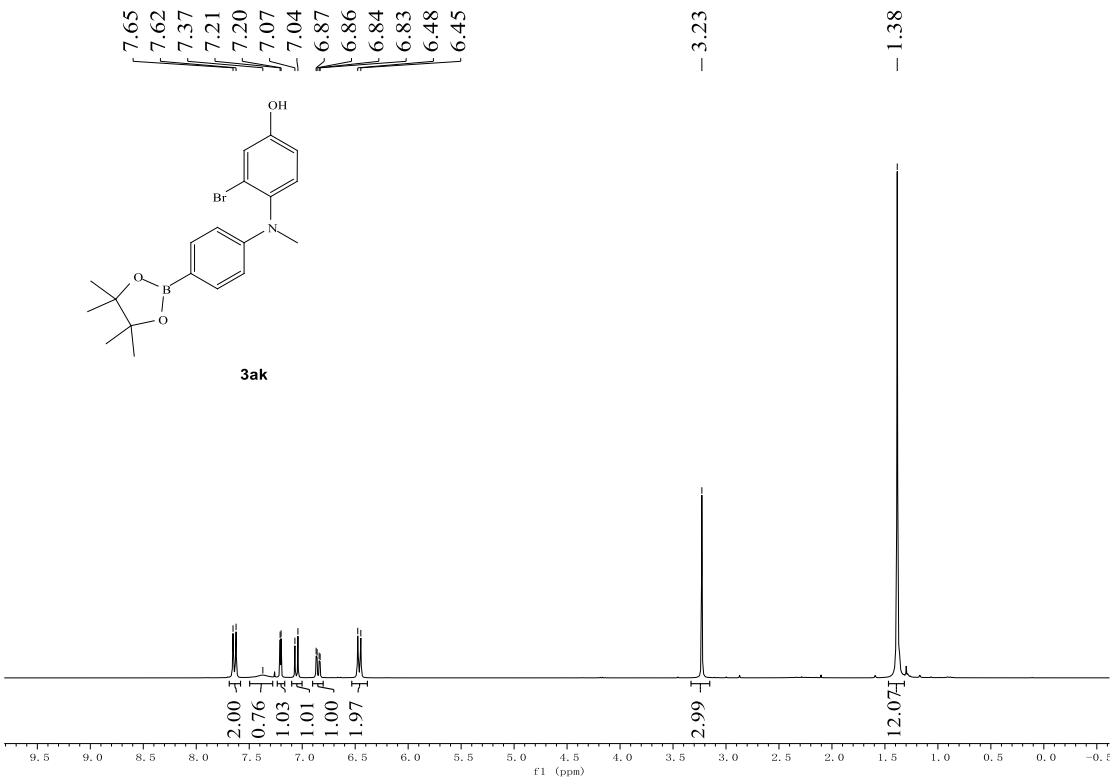
^{1}H NMR (300 MHz, $CDCl_3$)



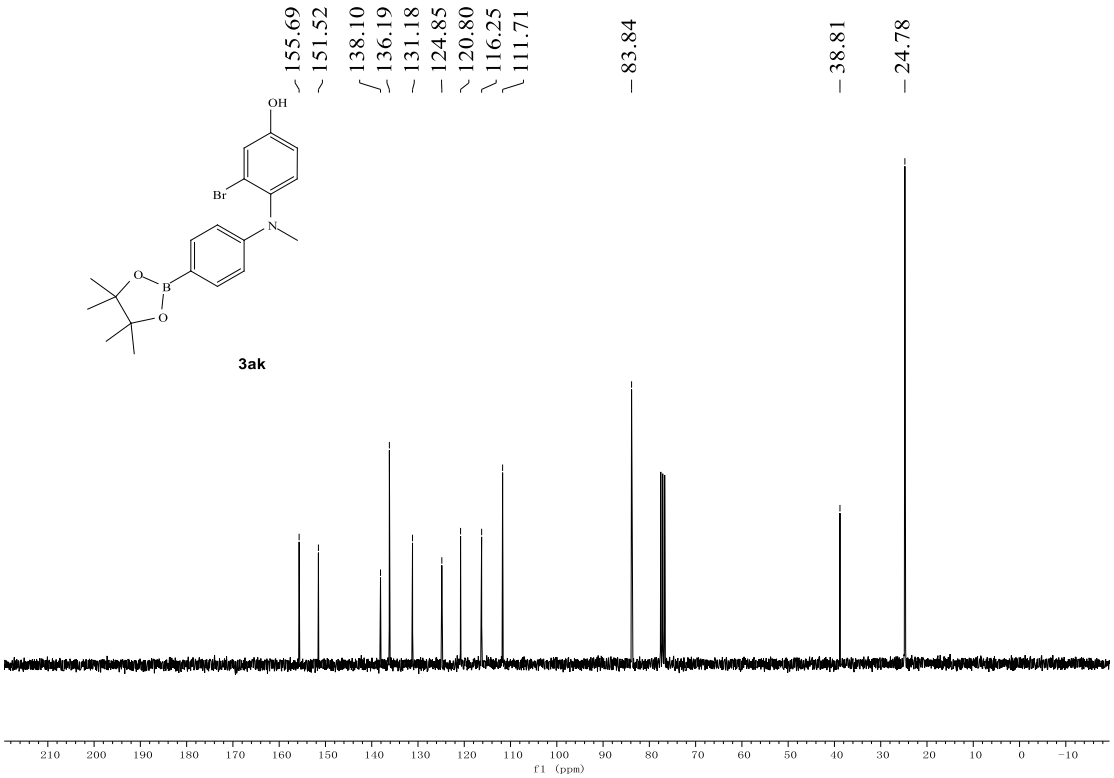
^{13}C NMR (75 MHz, $CDCl_3$)



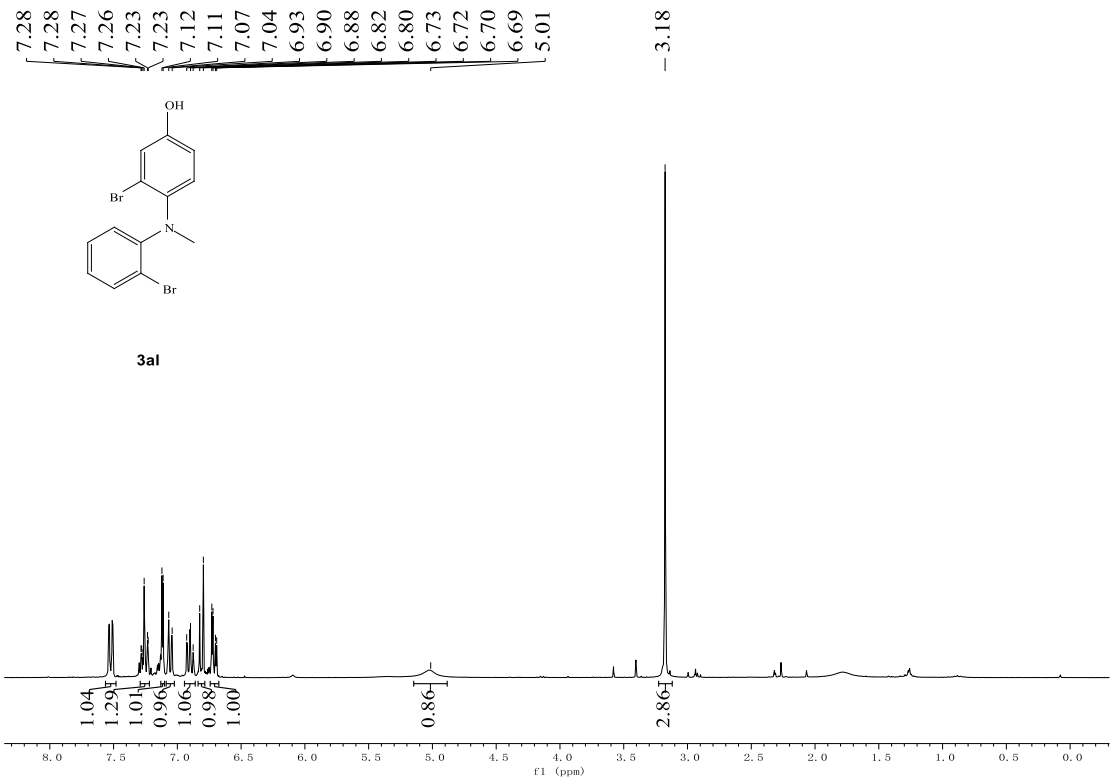
^{1}H NMR (300 MHz, $CDCl_3$)



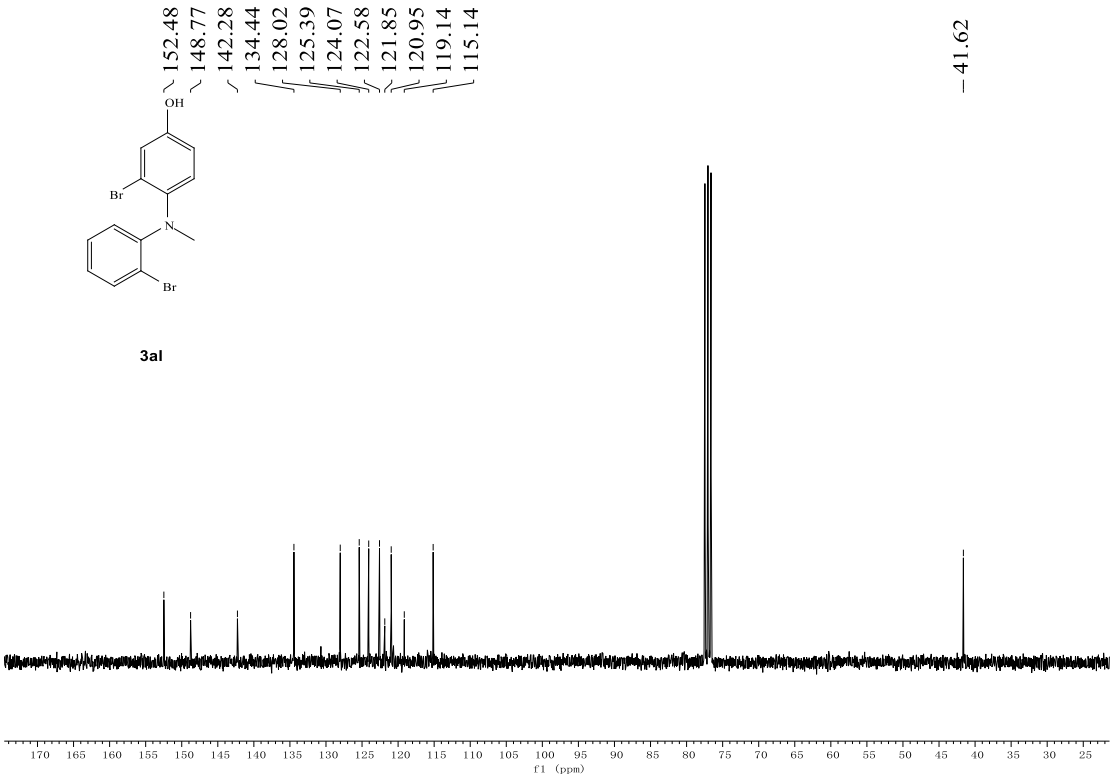
^{13}C NMR (75 MHz, $CDCl_3$)



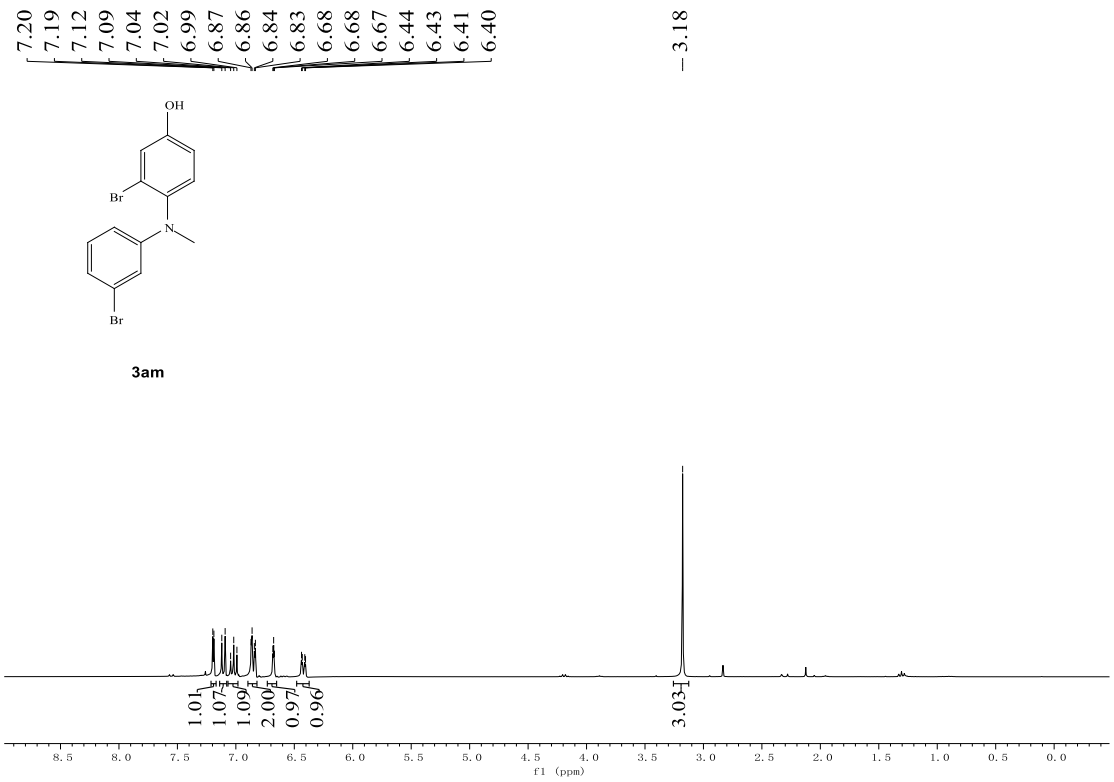
^{1}H NMR (300 MHz, $CDCl_3$)



^{13}C NMR (75 MHz, $CDCl_3$)

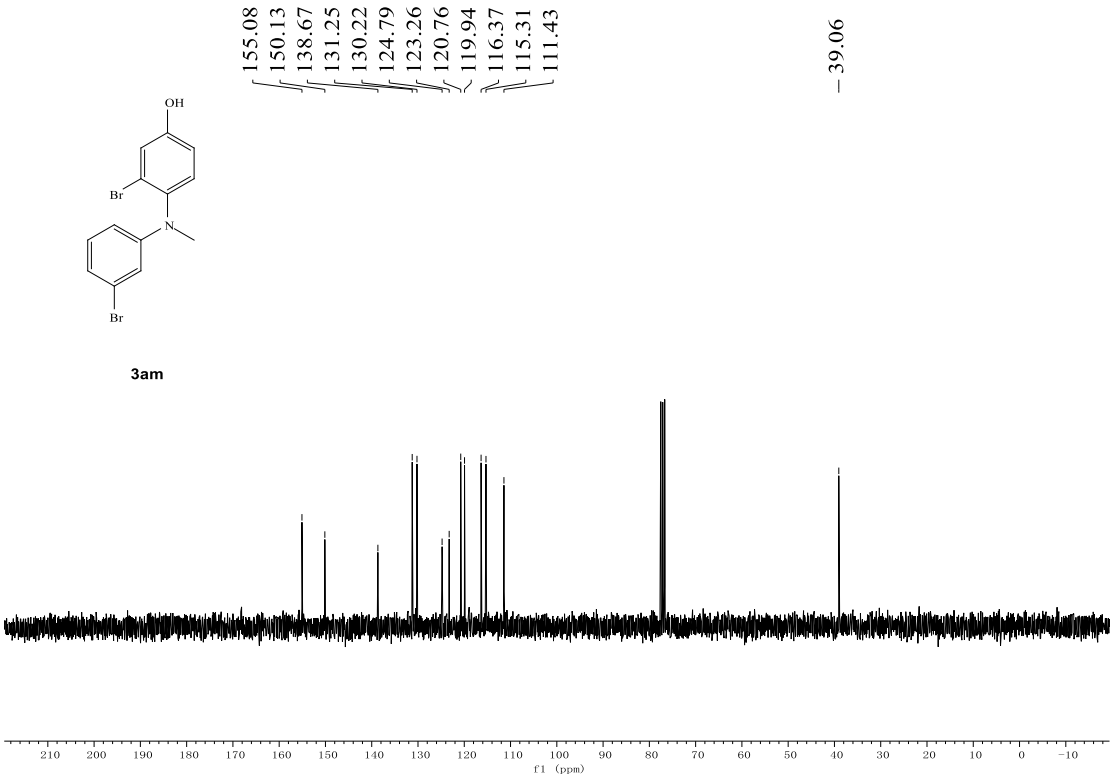


^{1}H NMR (300 MHz, $CDCl_3$)



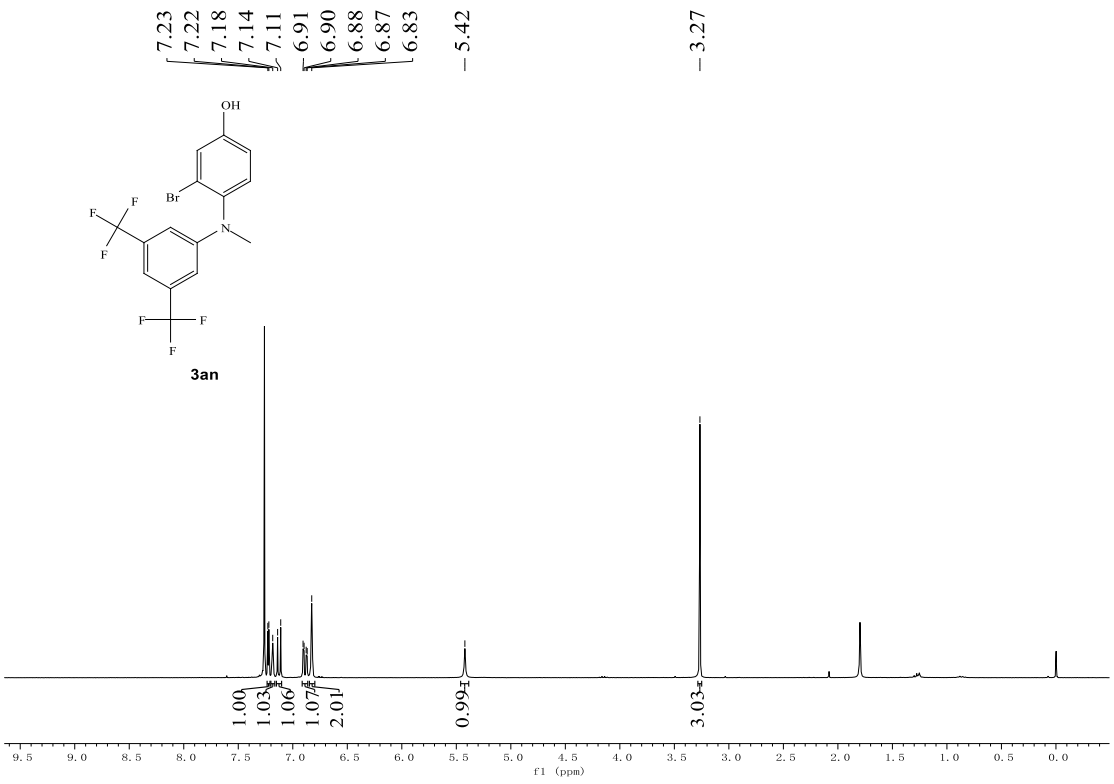
3am

^{13}C NMR (75 MHz, $CDCl_3$)

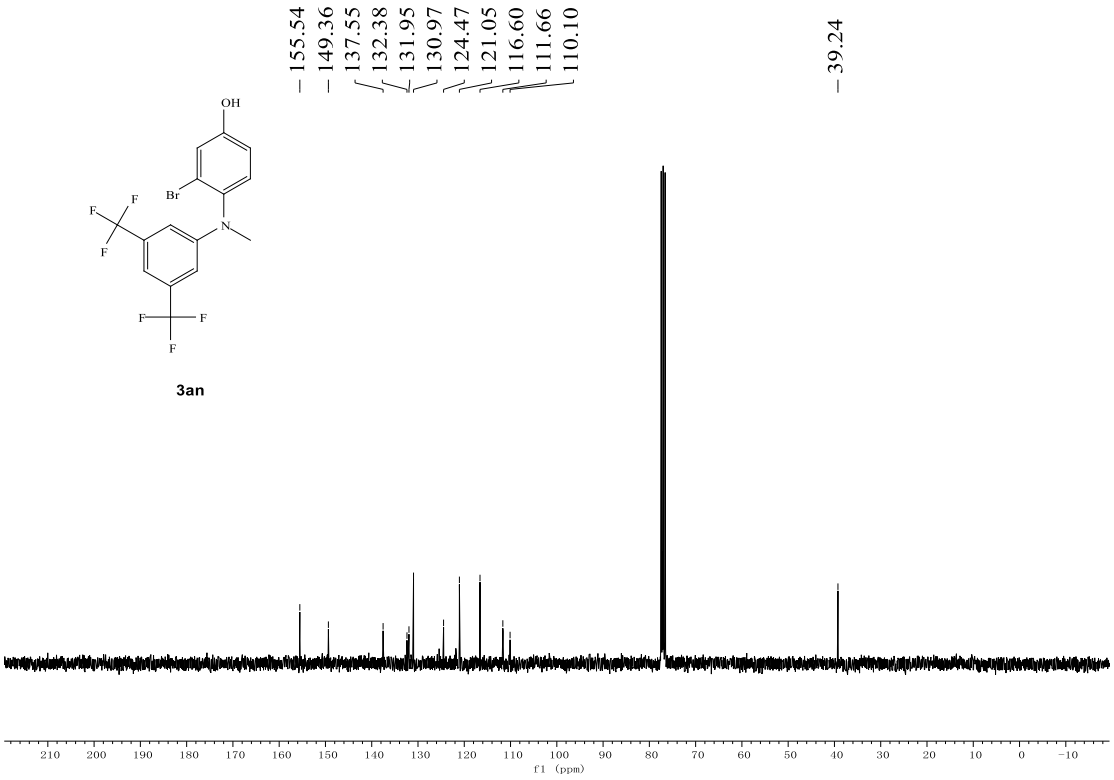


3am

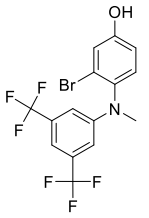
^{1}H NMR (300 MHz, $CDCl_3$)



^{13}C NMR (75 MHz, $CDCl_3$)

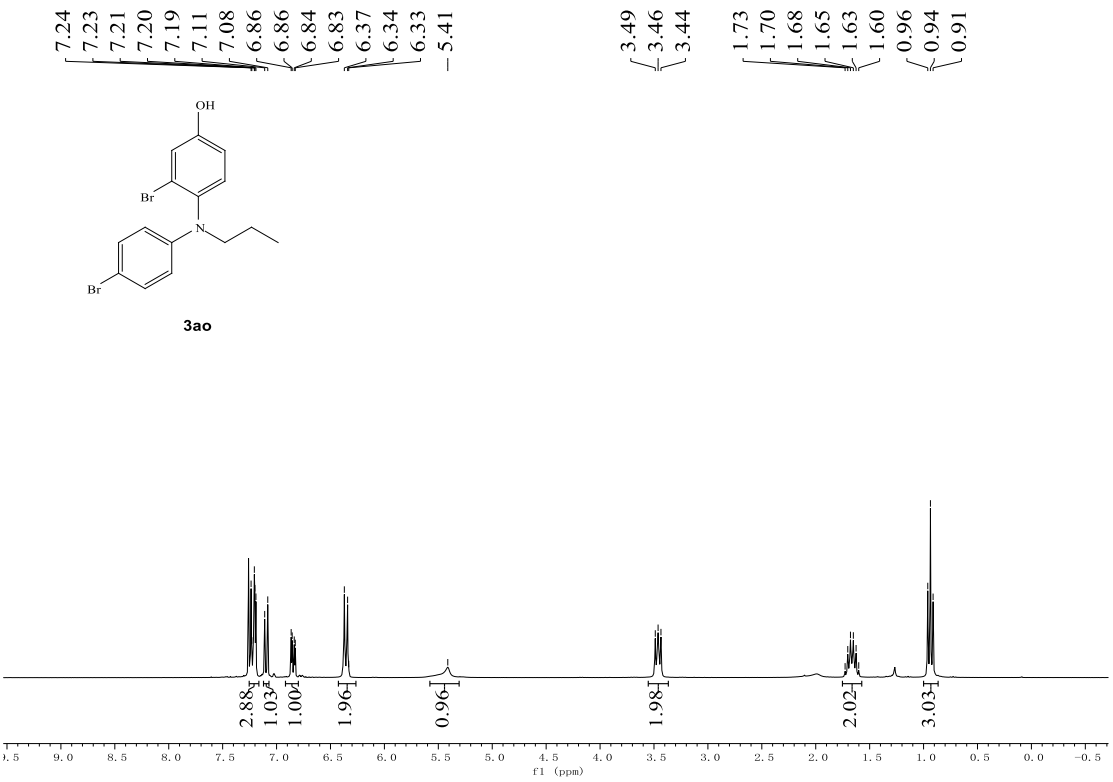


^{19}F NMR (282 MHz, $CDCl_3$)



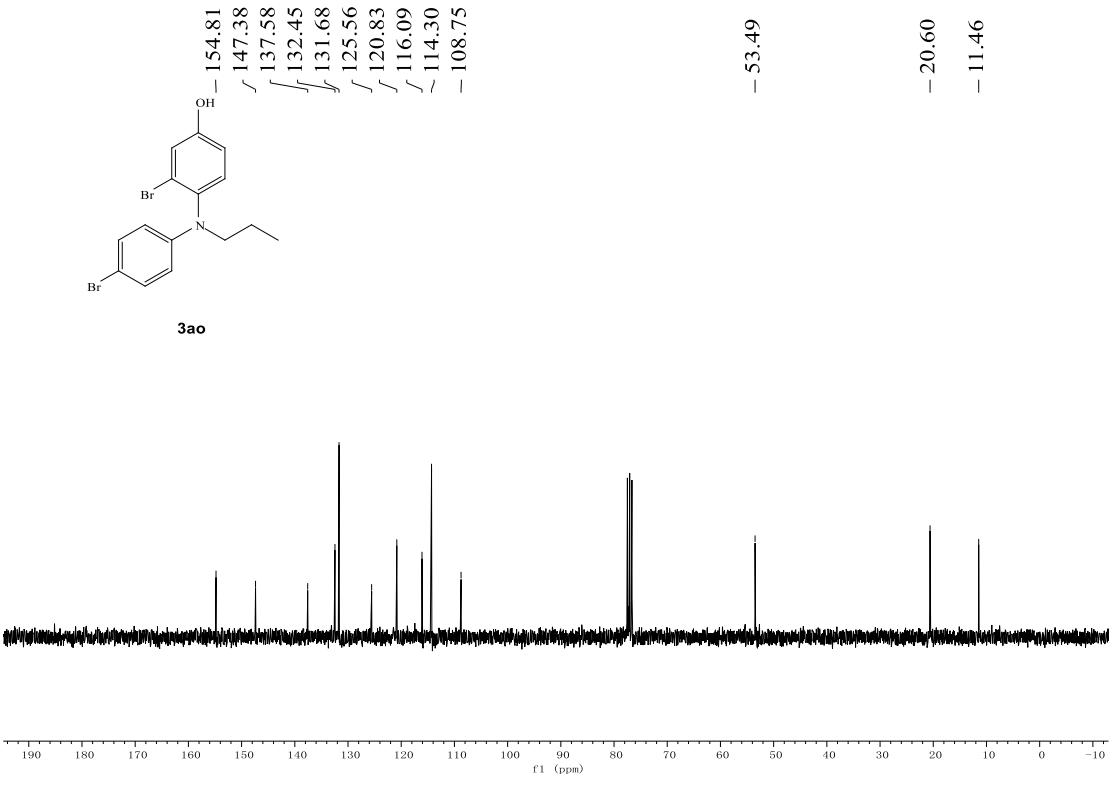
3an

^{1}H NMR (300 MHz, $CDCl_3$)



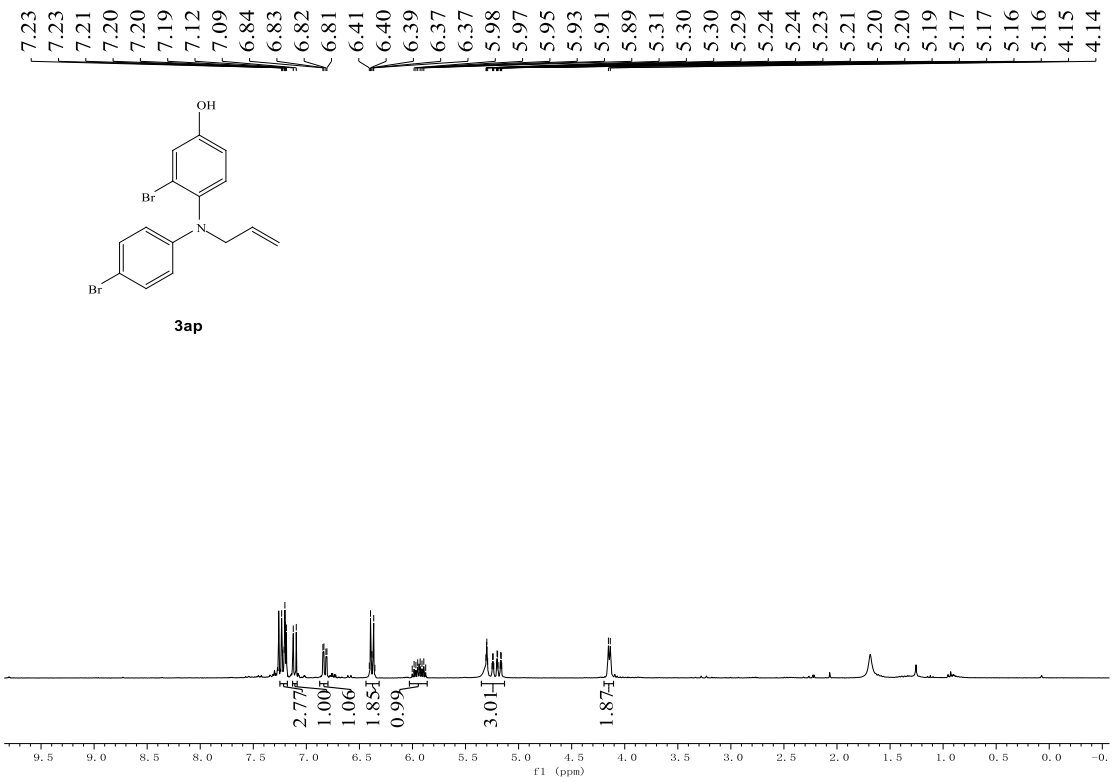
3ao

^{13}C NMR (75 MHz, $CDCl_3$)

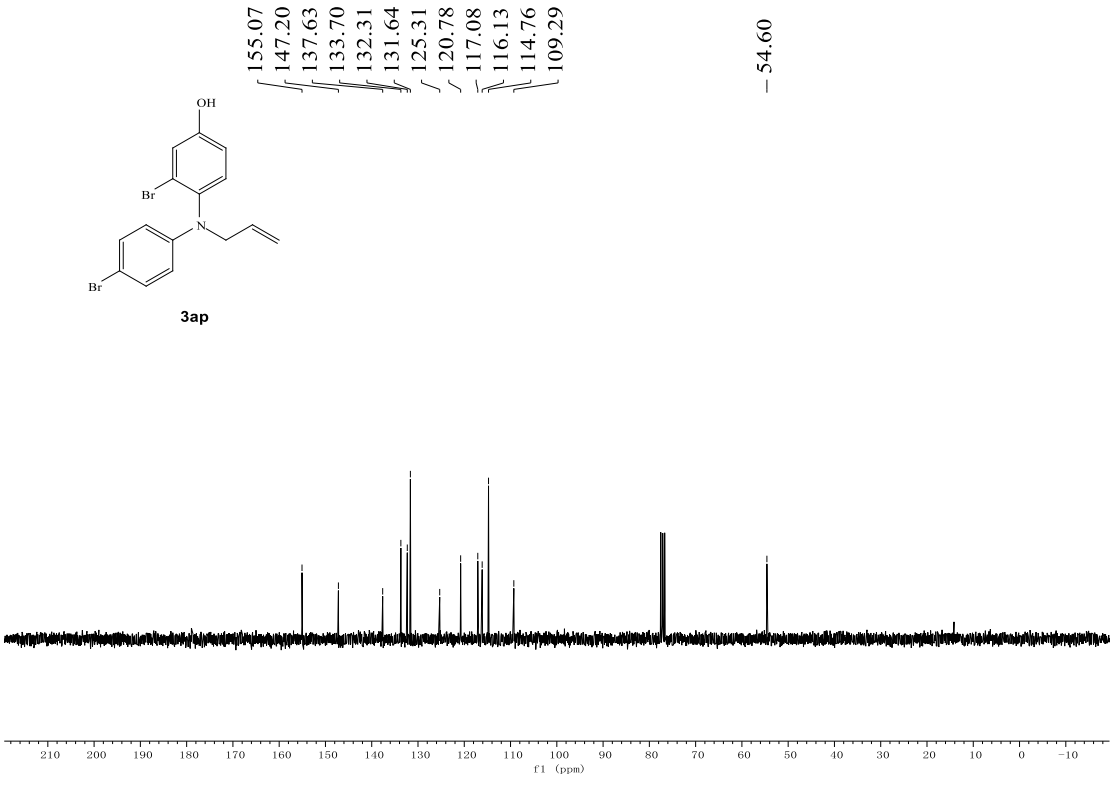


3ao

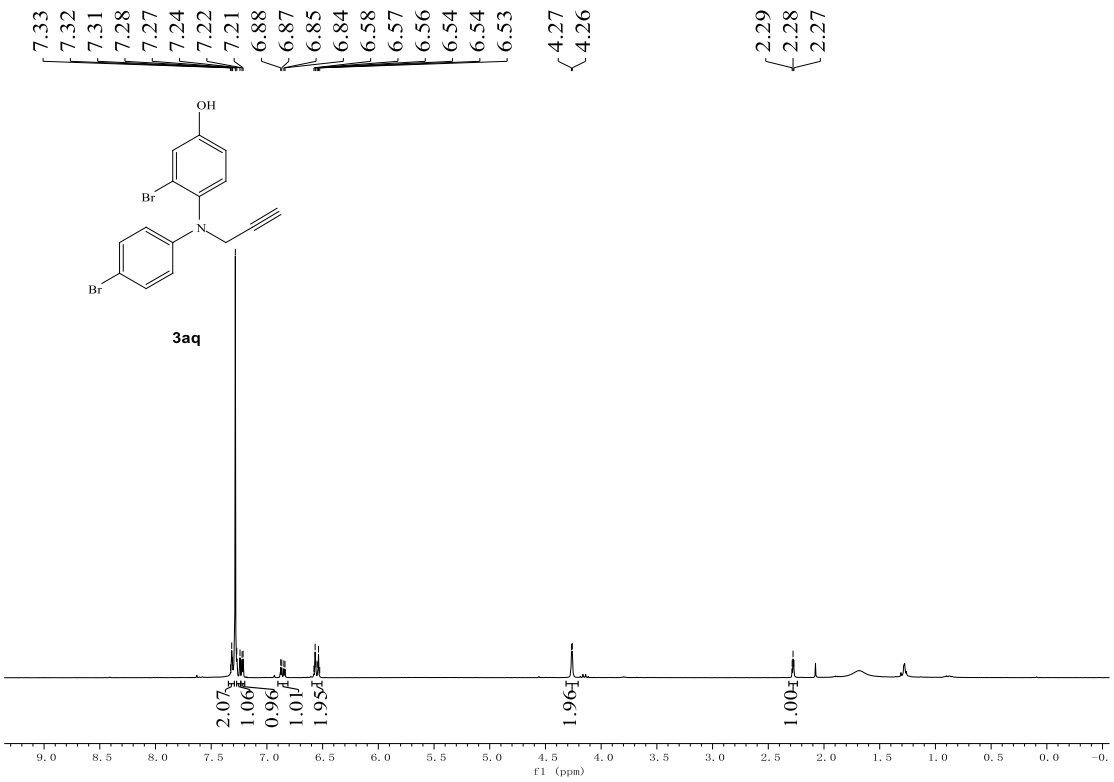
^{1}H NMR (300 MHz, $CDCl_3$)



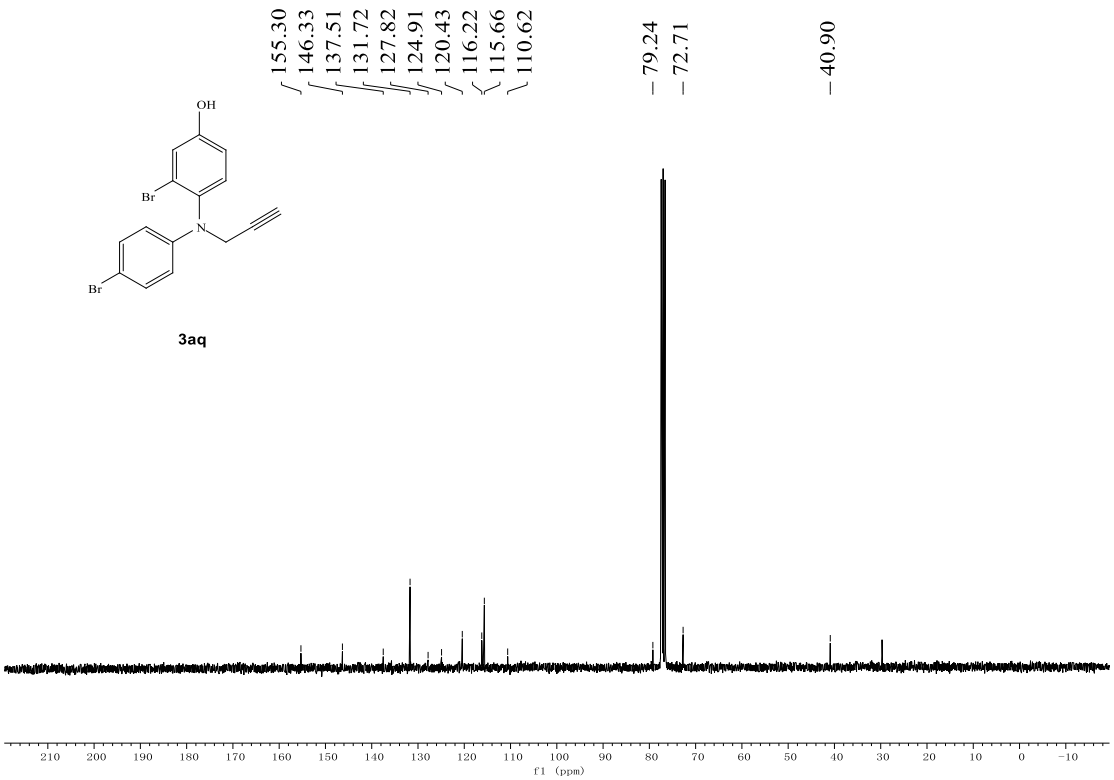
^{13}C NMR (75 MHz, $CDCl_3$)



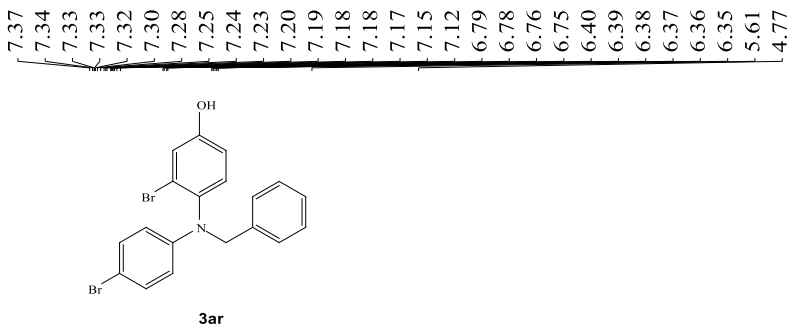
^{1}H NMR (300 MHz, $CDCl_3$)



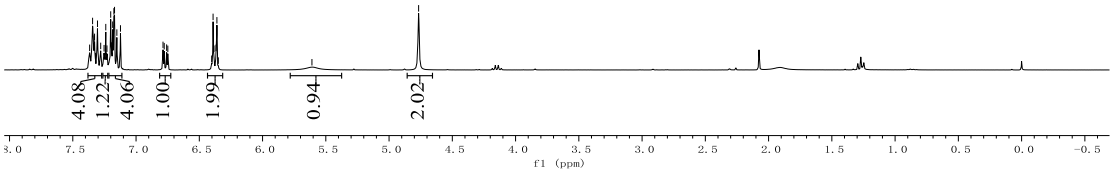
^{13}C NMR (75 MHz, $CDCl_3$)



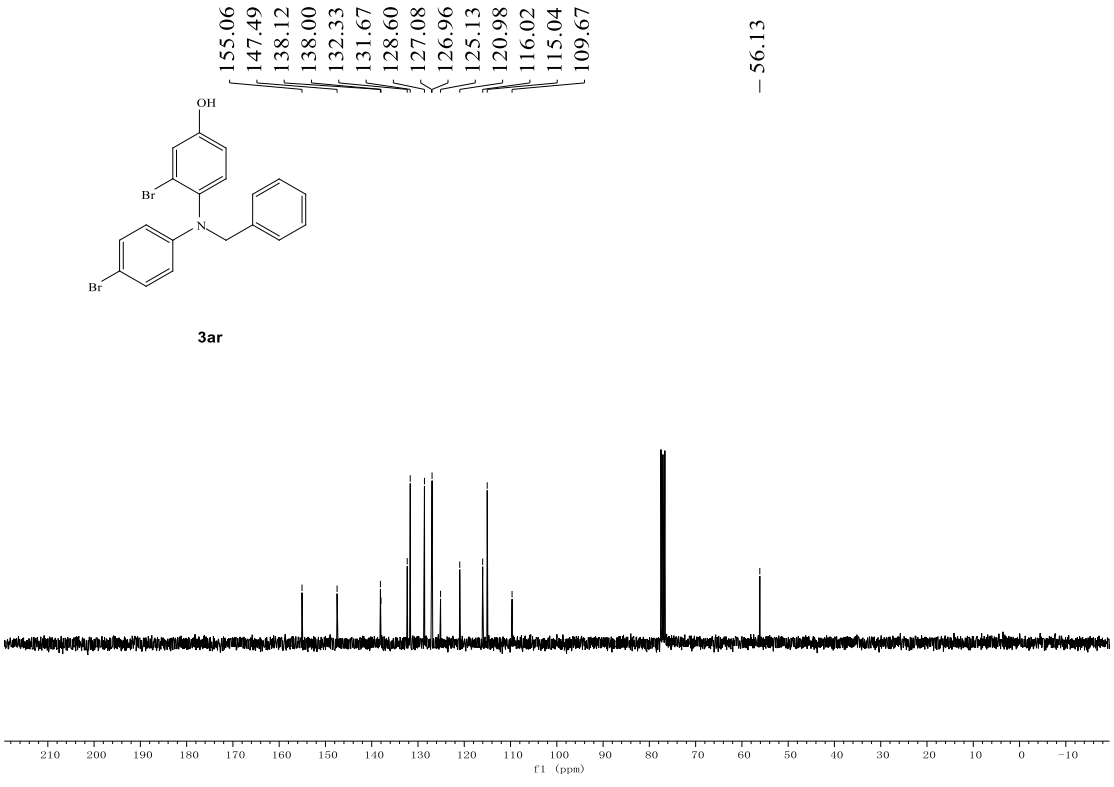
^{1}H NMR (300 MHz, $CDCl_3$)



3ar

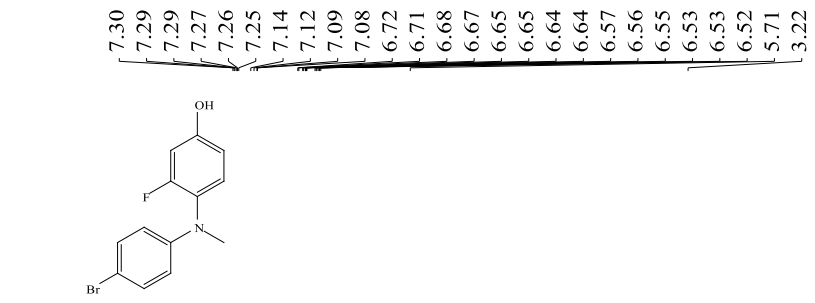


^{13}C NMR (75 MHz, $CDCl_3$)

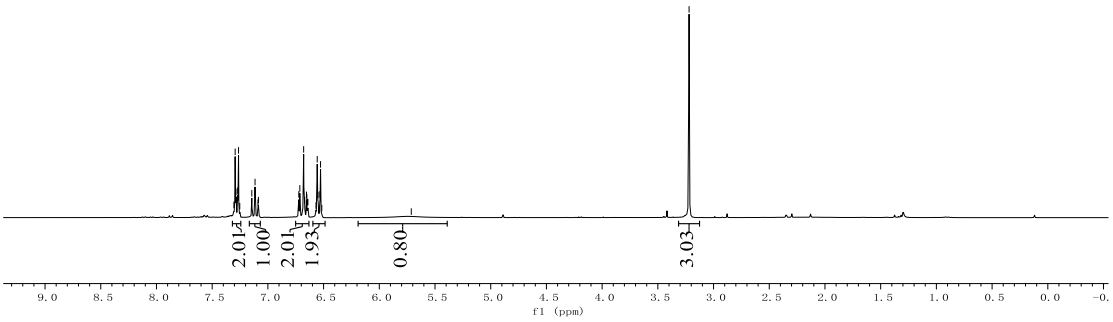


3ar

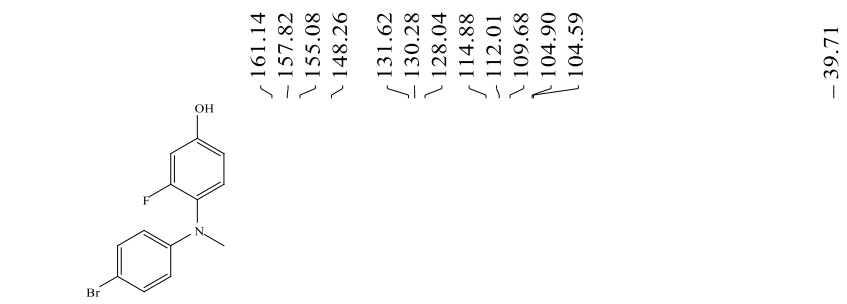
^{1}H NMR (300 MHz, $CDCl_3$)



3ba



^{13}C NMR (75 MHz, $CDCl_3$)



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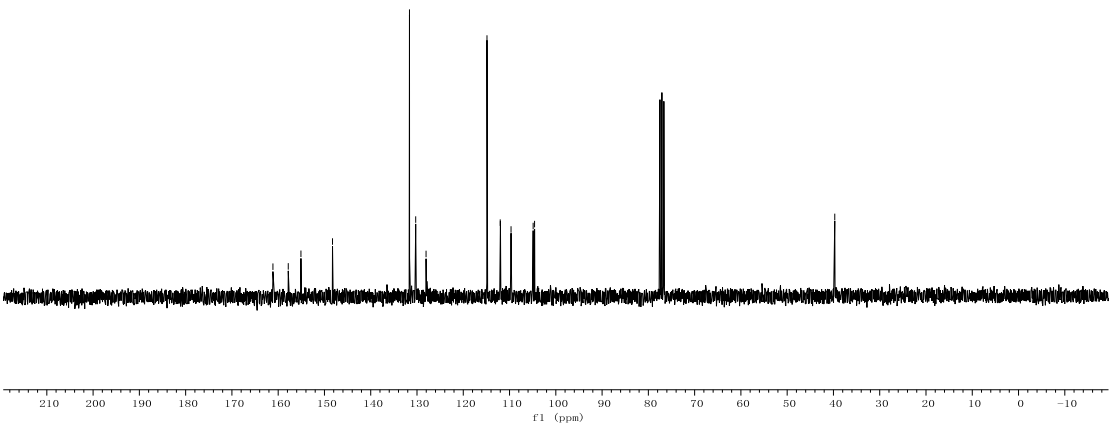
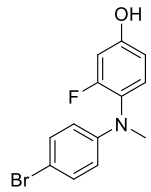
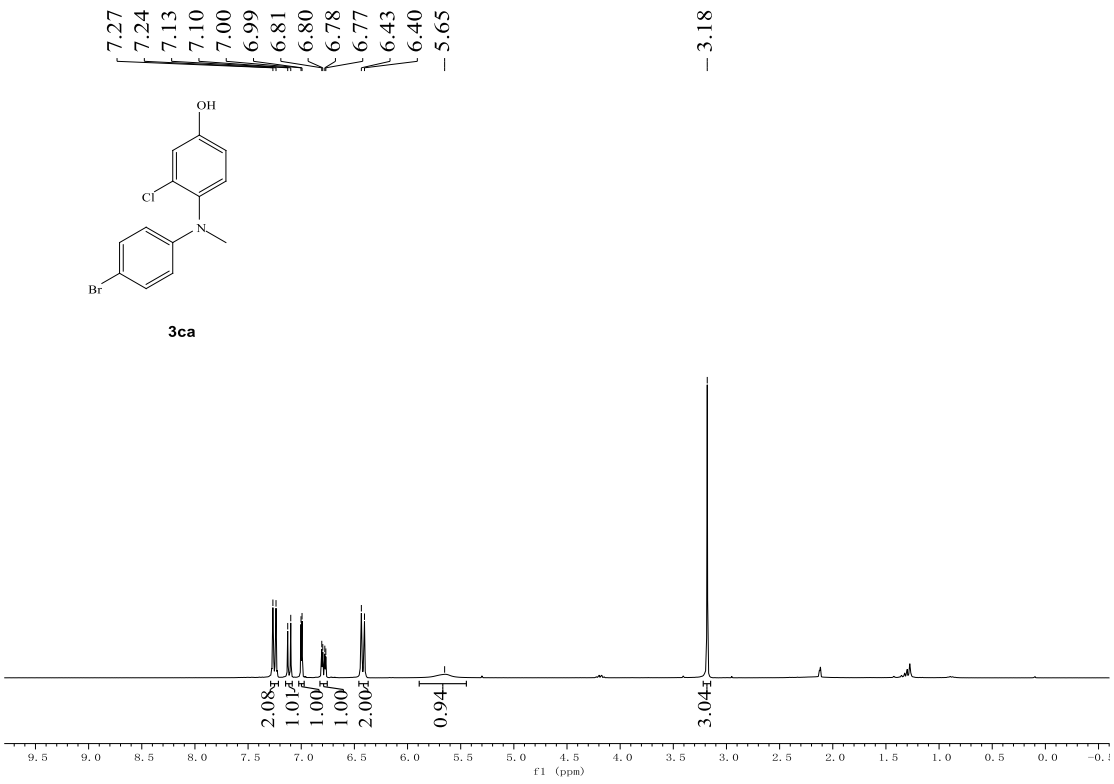


^{19}F NMR (282 MHz, $CDCl_3$)



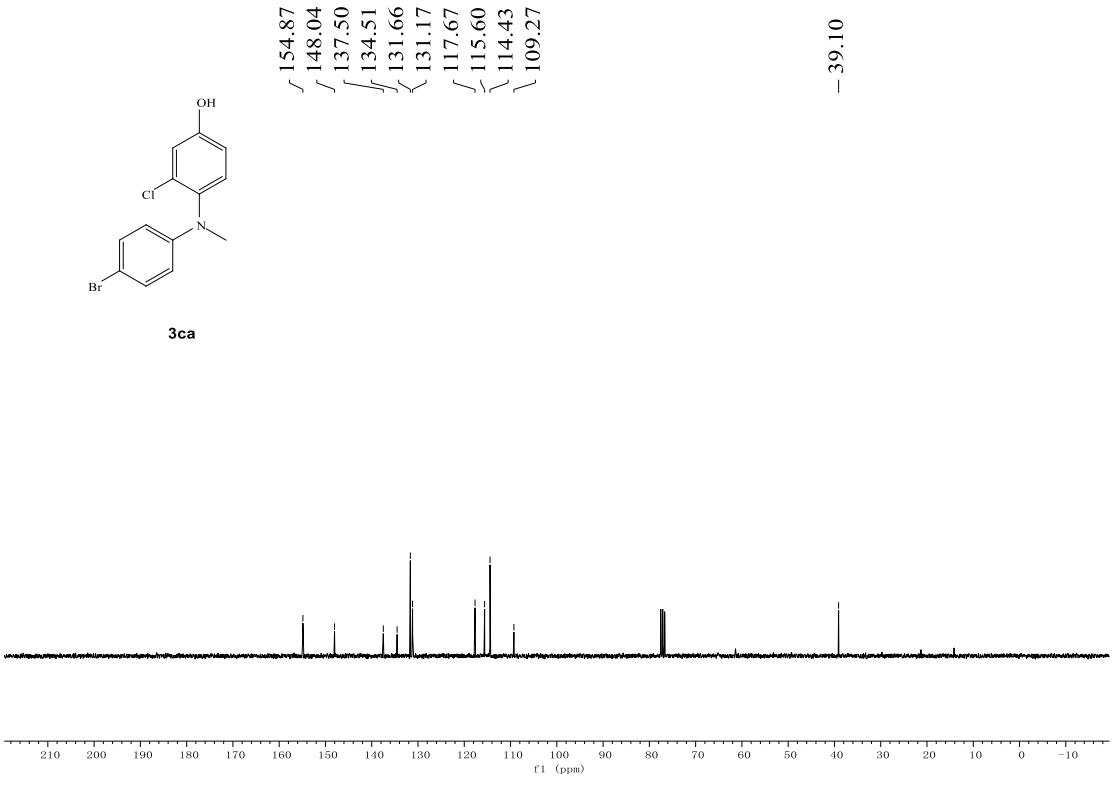
3ba

^{1}H NMR (300 MHz, $CDCl_3$)



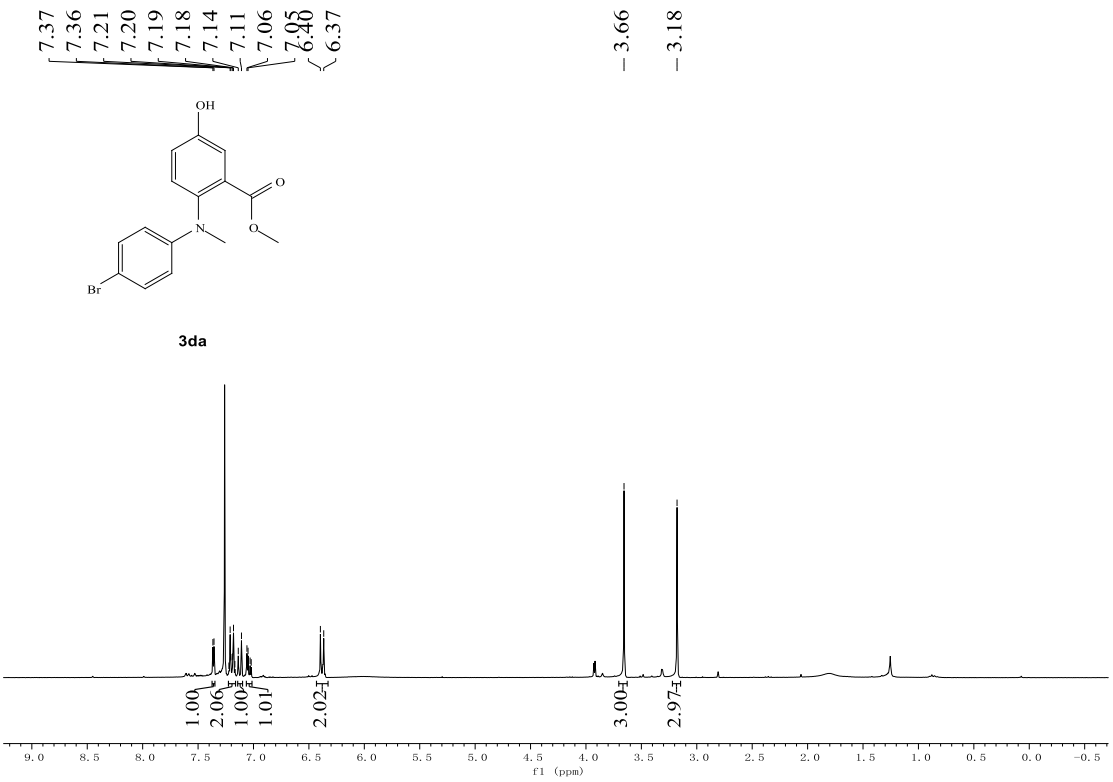
3ca

^{13}C NMR (75 MHz, $CDCl_3$)

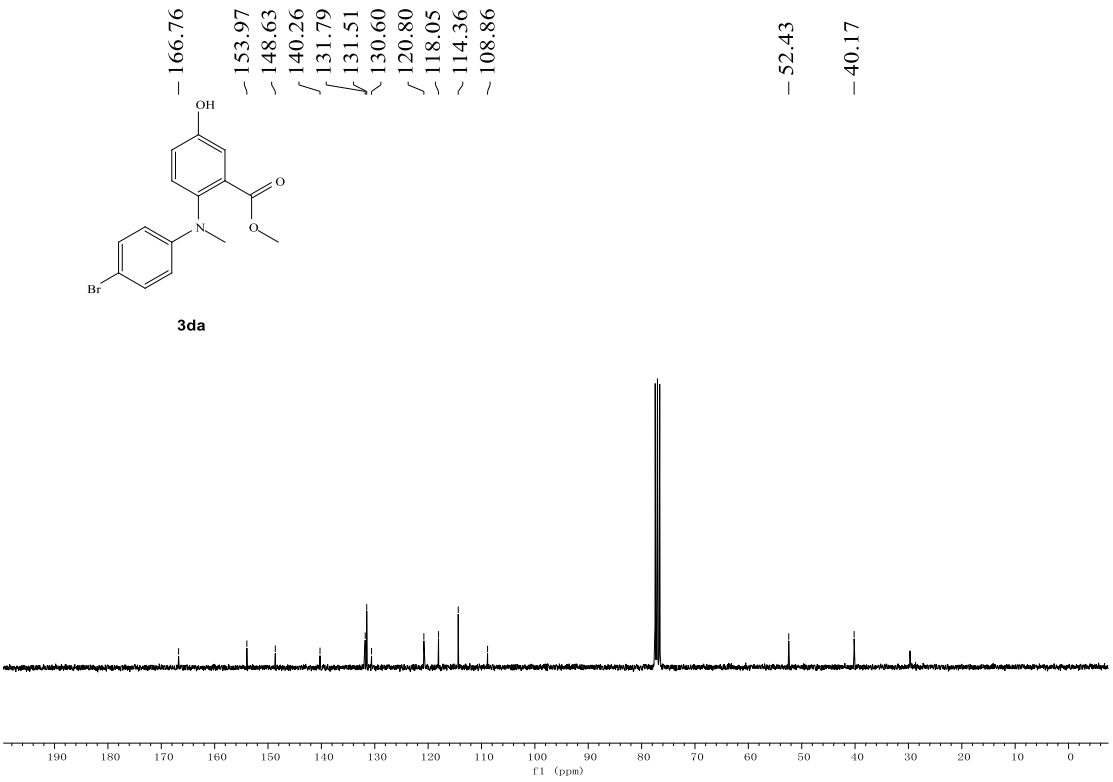


3ca

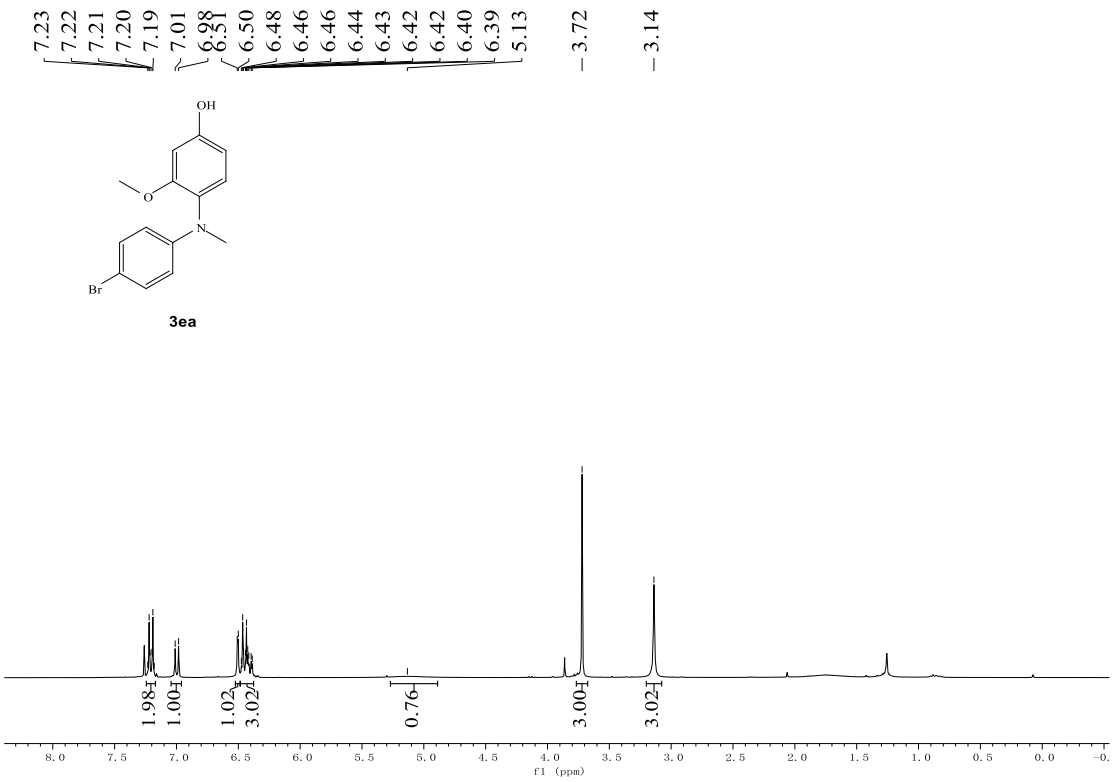
^{1}H NMR (300 MHz, $CDCl_3$)



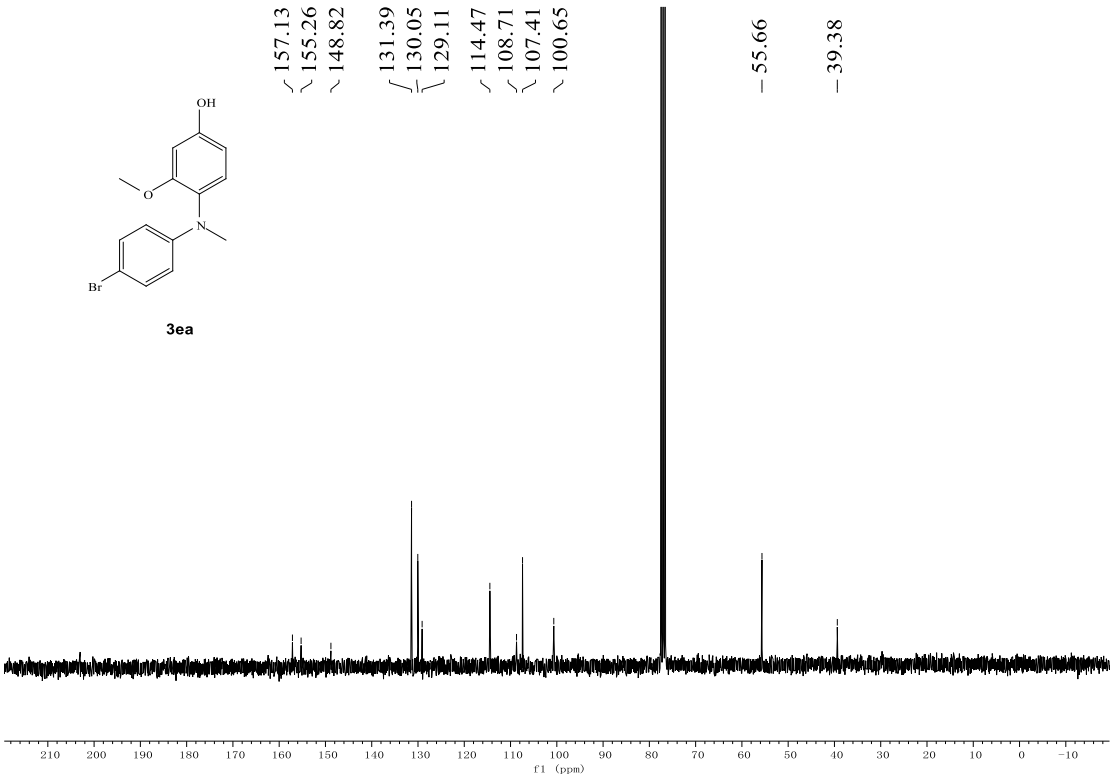
^{13}C NMR (75 MHz, $CDCl_3$)



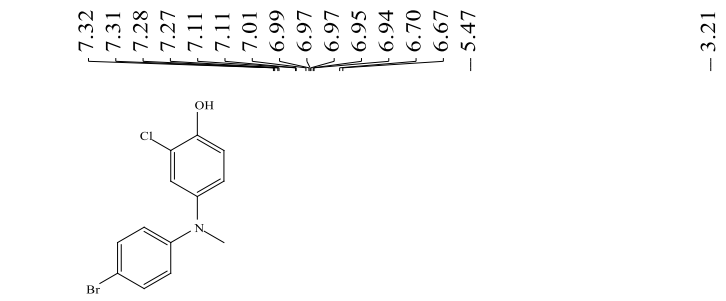
^{1}H NMR (300 MHz, $CDCl_3$)



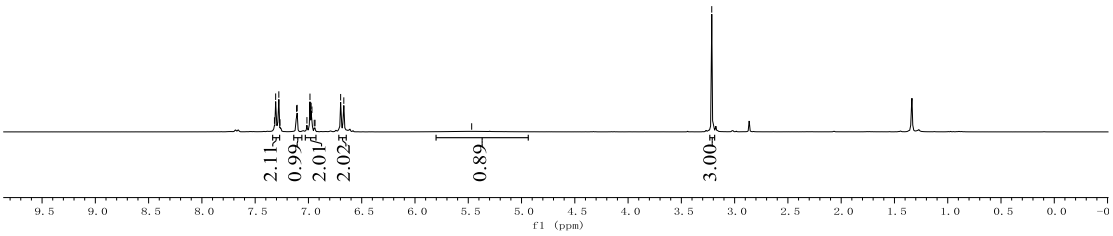
^{13}C NMR (75 MHz, $CDCl_3$)



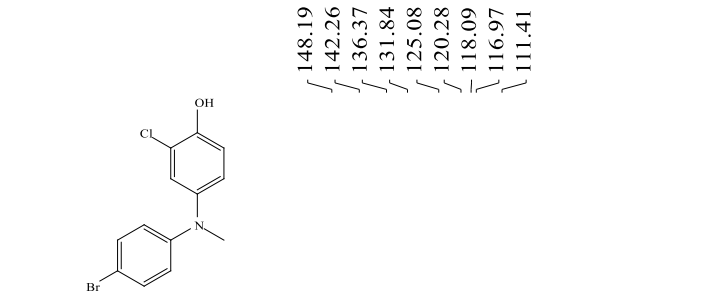
^{1}H NMR (300 MHz, $CDCl_3$)



3fa



^{13}C NMR (75 MHz, $CDCl_3$)



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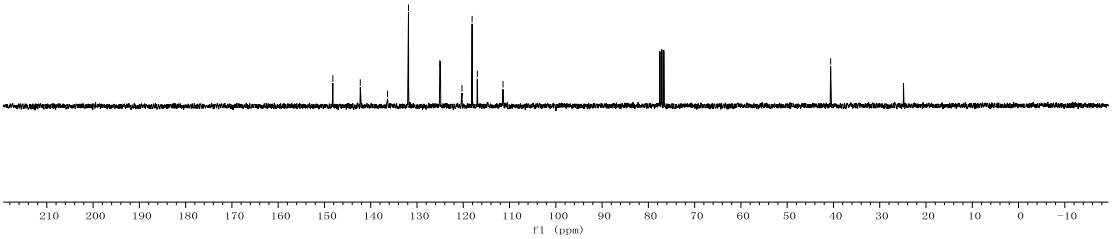
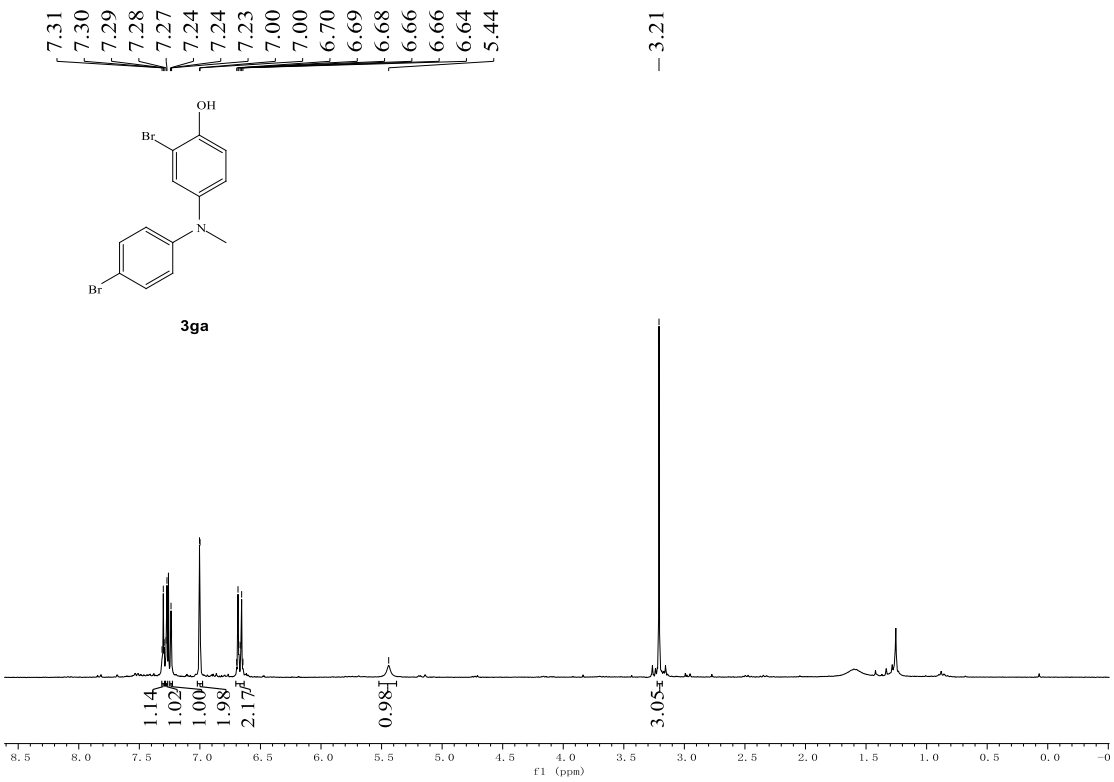
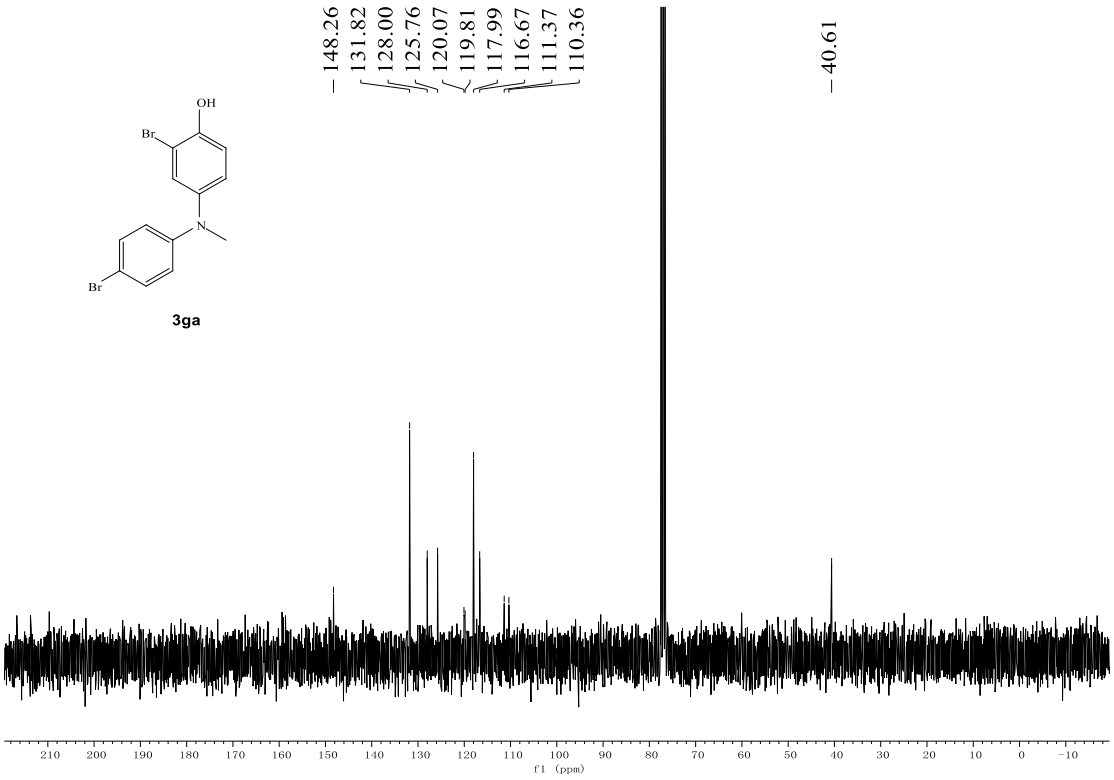


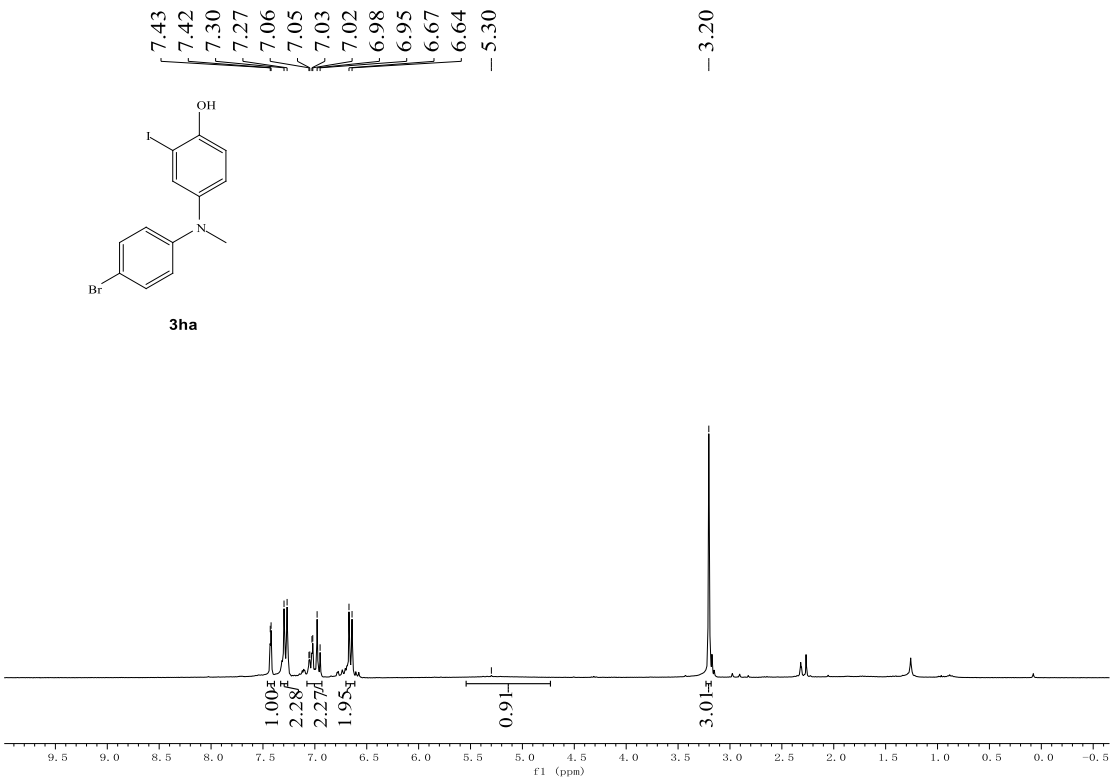
^{1}H NMR (300 MHz, $CDCl_3$)



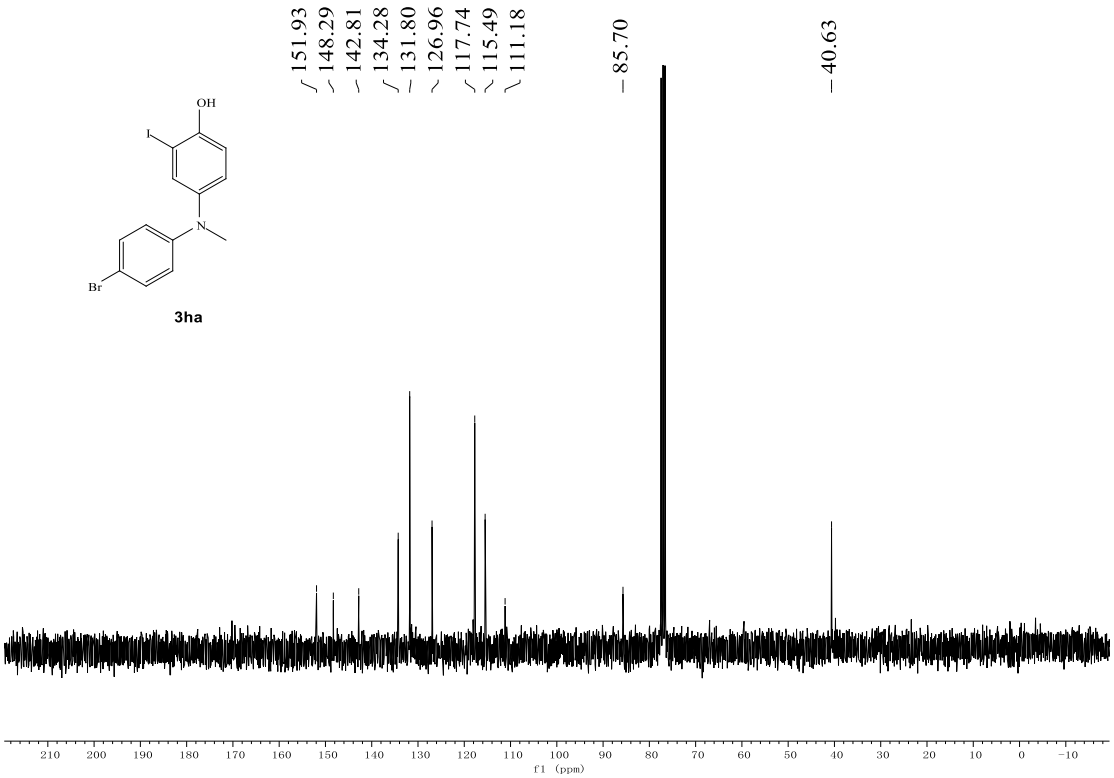
^{13}C NMR (75 MHz, $CDCl_3$)



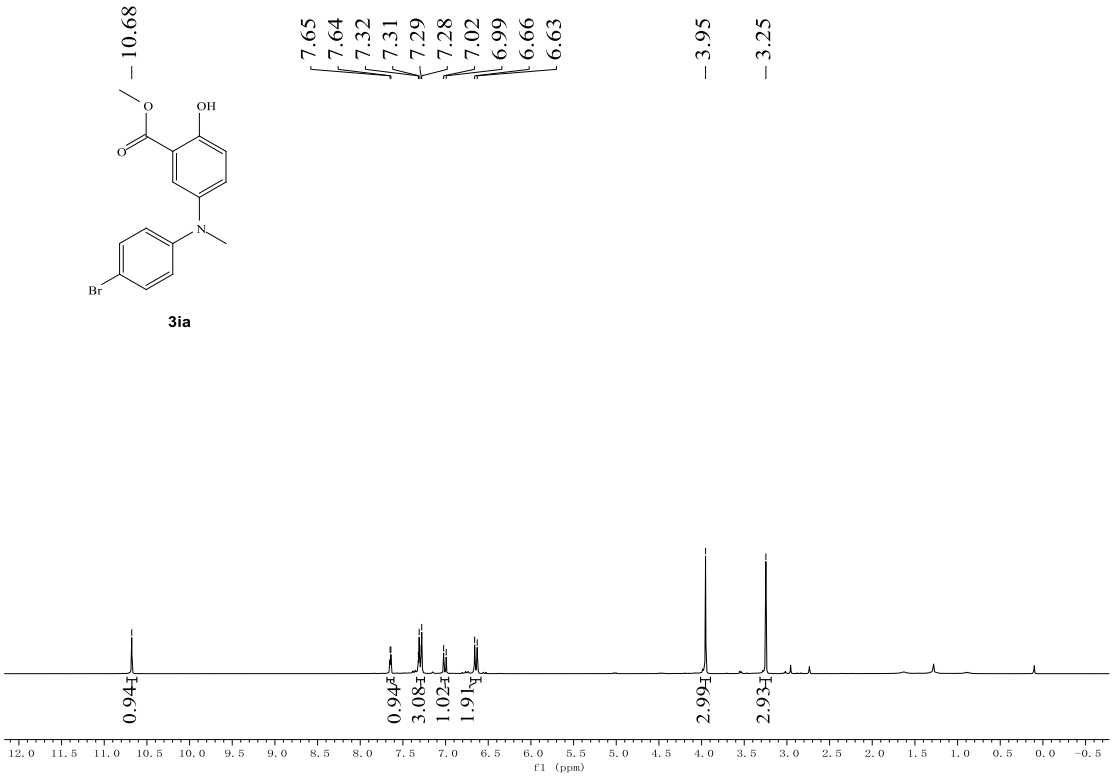
^{1}H NMR (300 MHz, $CDCl_3$)



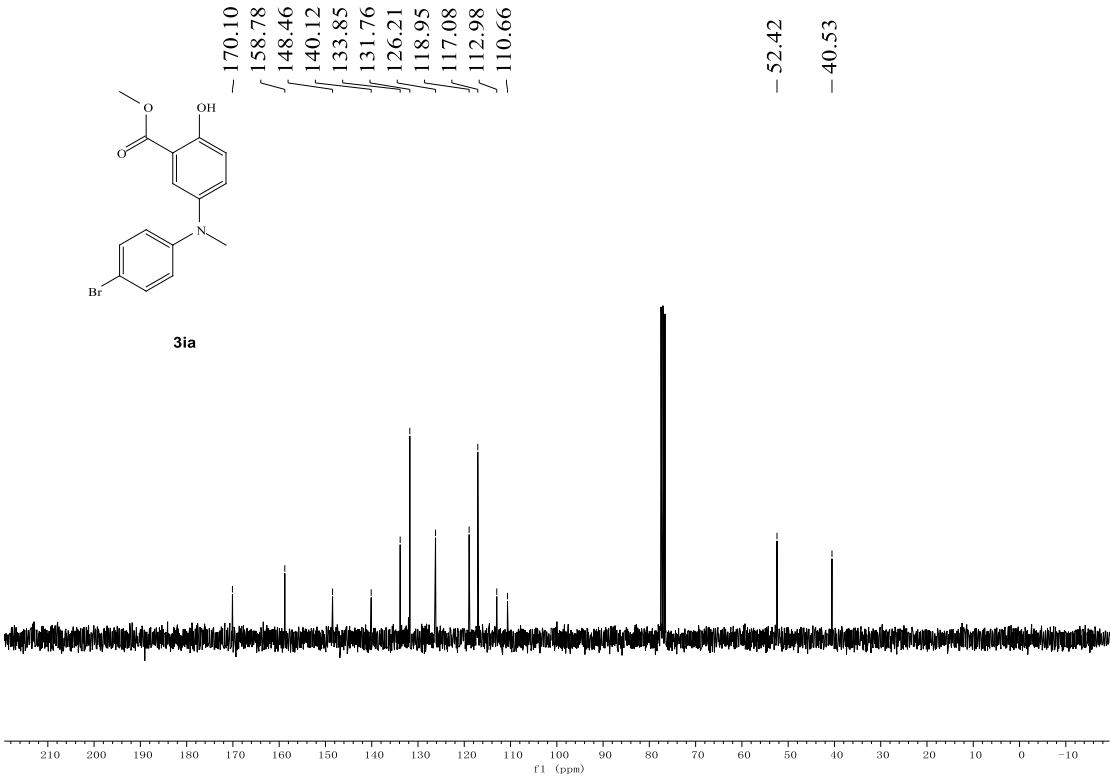
^{13}C NMR (75 MHz, $CDCl_3$)



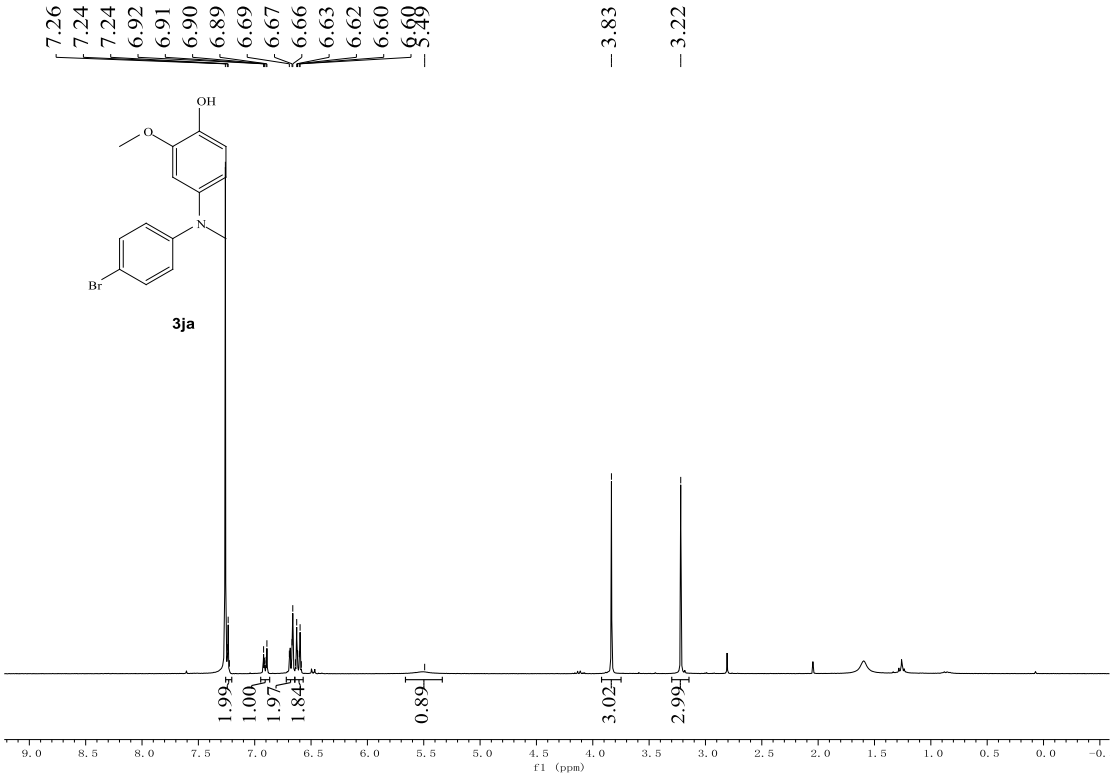
^{1}H NMR (300 MHz, $CDCl_3$)



^{13}C NMR (75 MHz, $CDCl_3$)



^{1}H NMR (300 MHz, $CDCl_3$)



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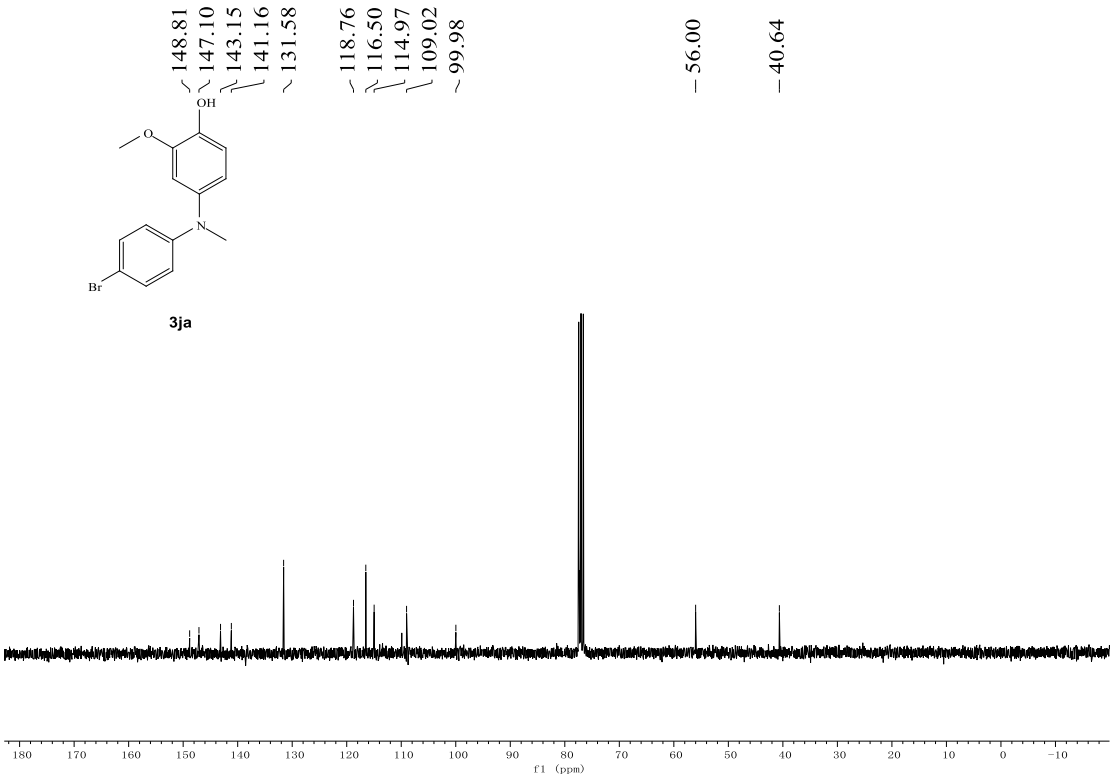
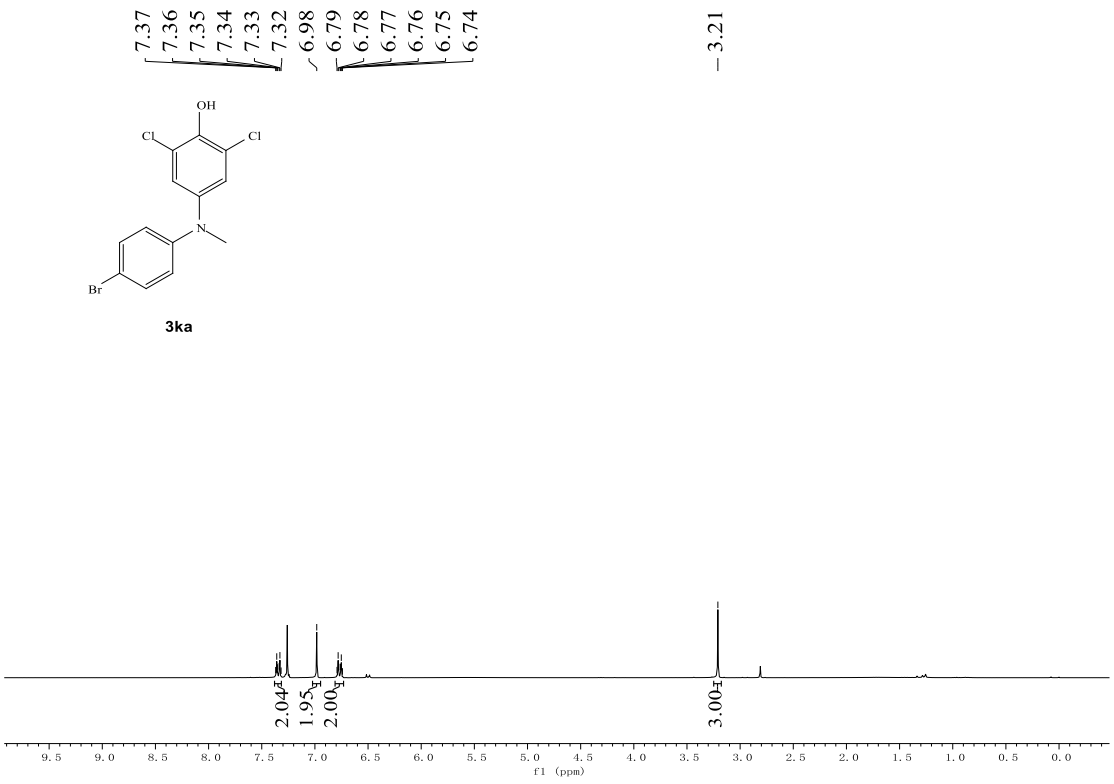
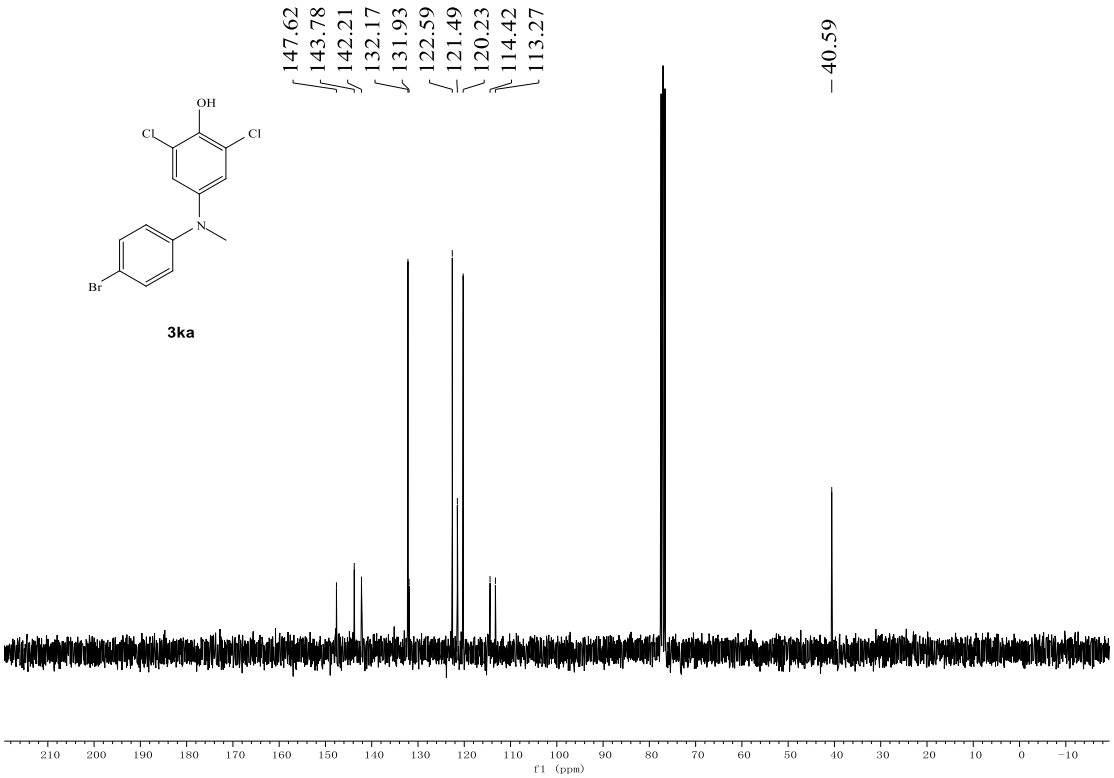


^{1}H NMR (300 MHz, $CDCl_3$)



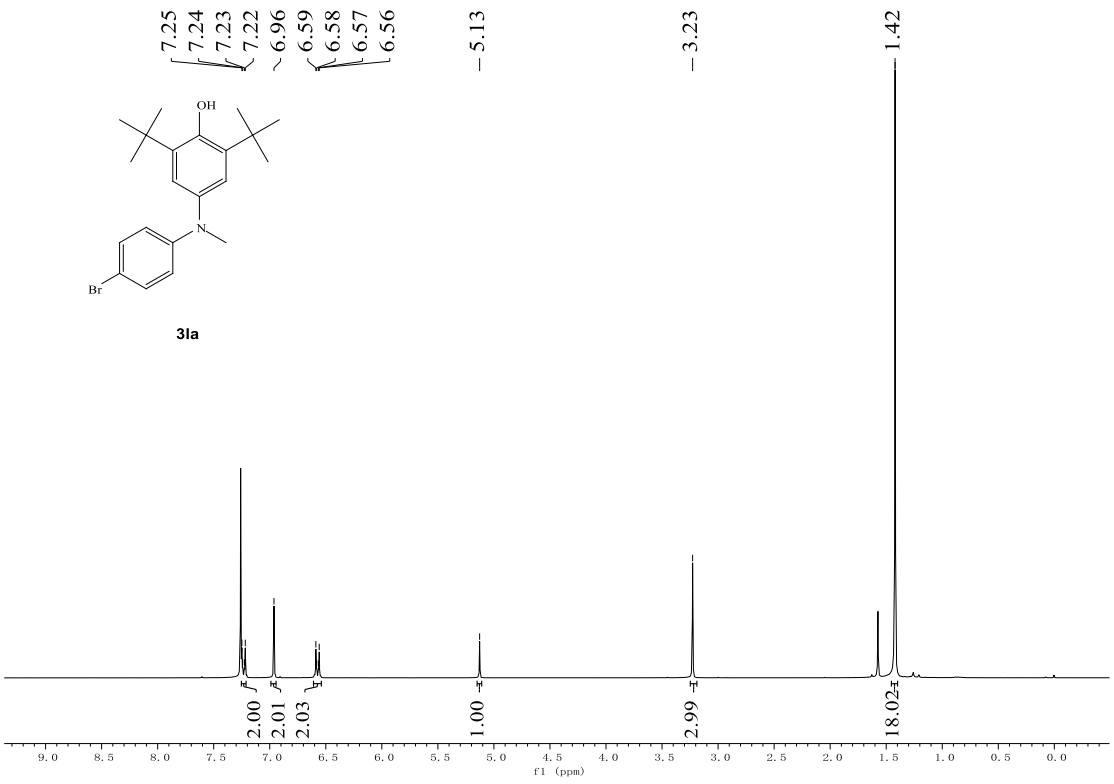
3ka

^{13}C NMR (75 MHz, $CDCl_3$)



3ka

^{1}H NMR (300 MHz, $CDCl_3$)



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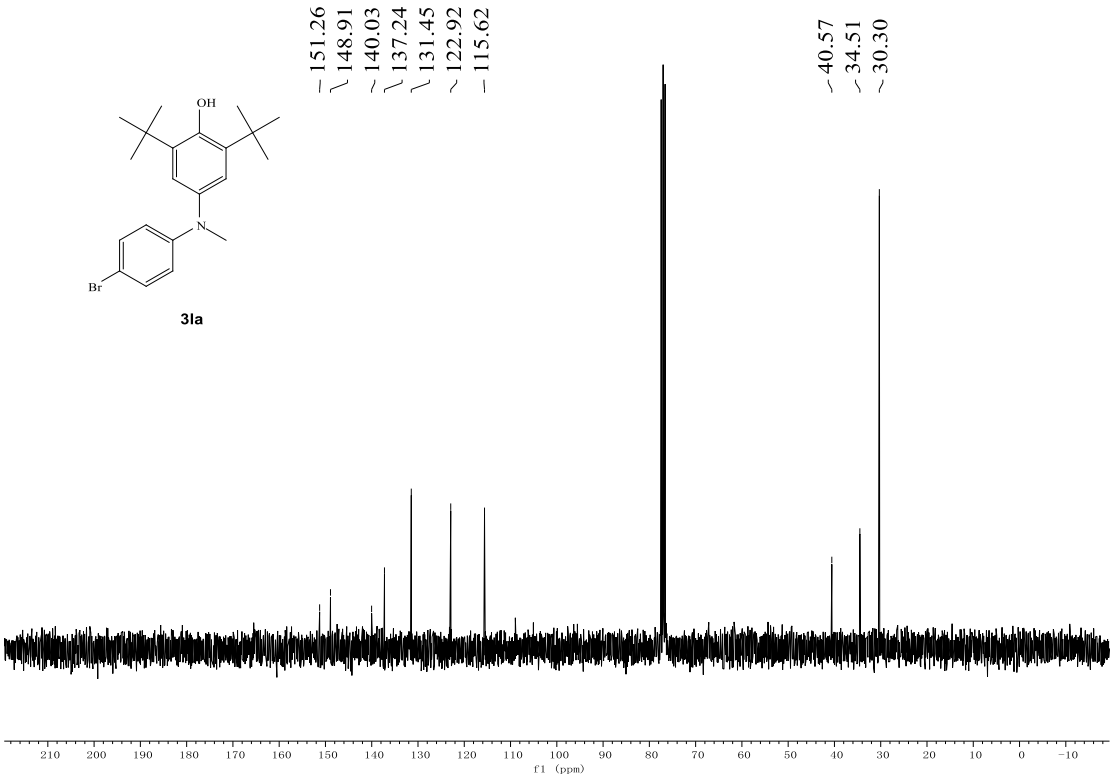
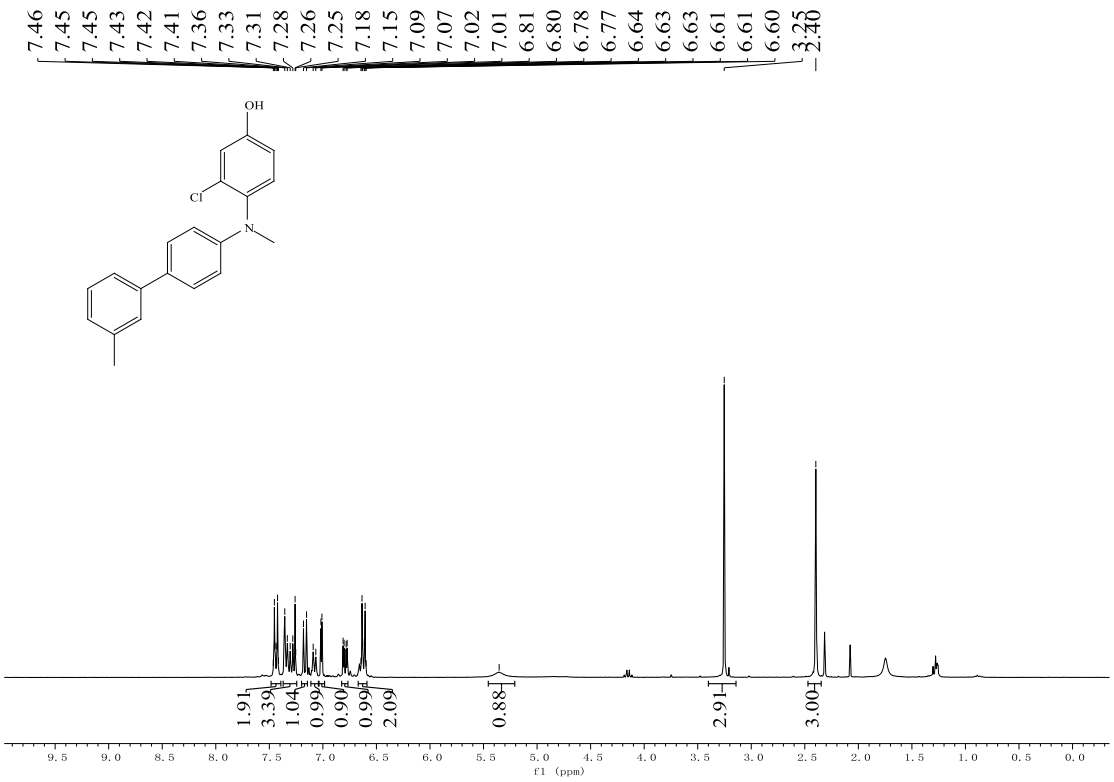


^{1}H NMR (300 MHz, $CDCl_3$)



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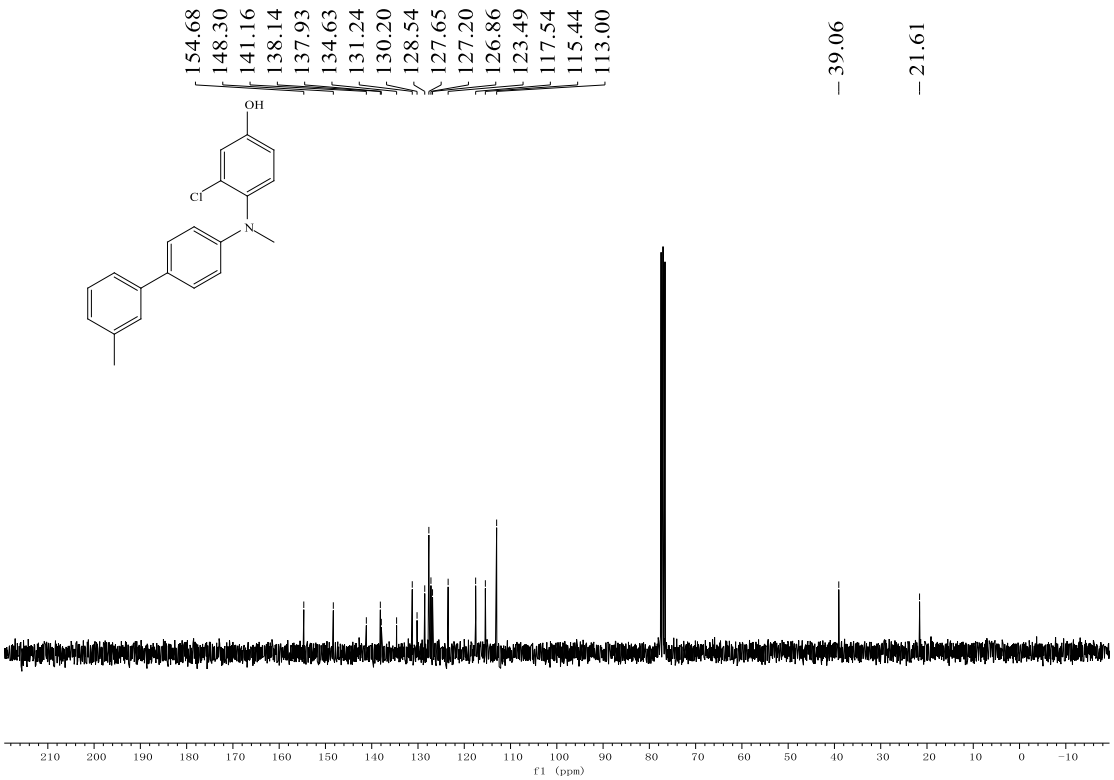
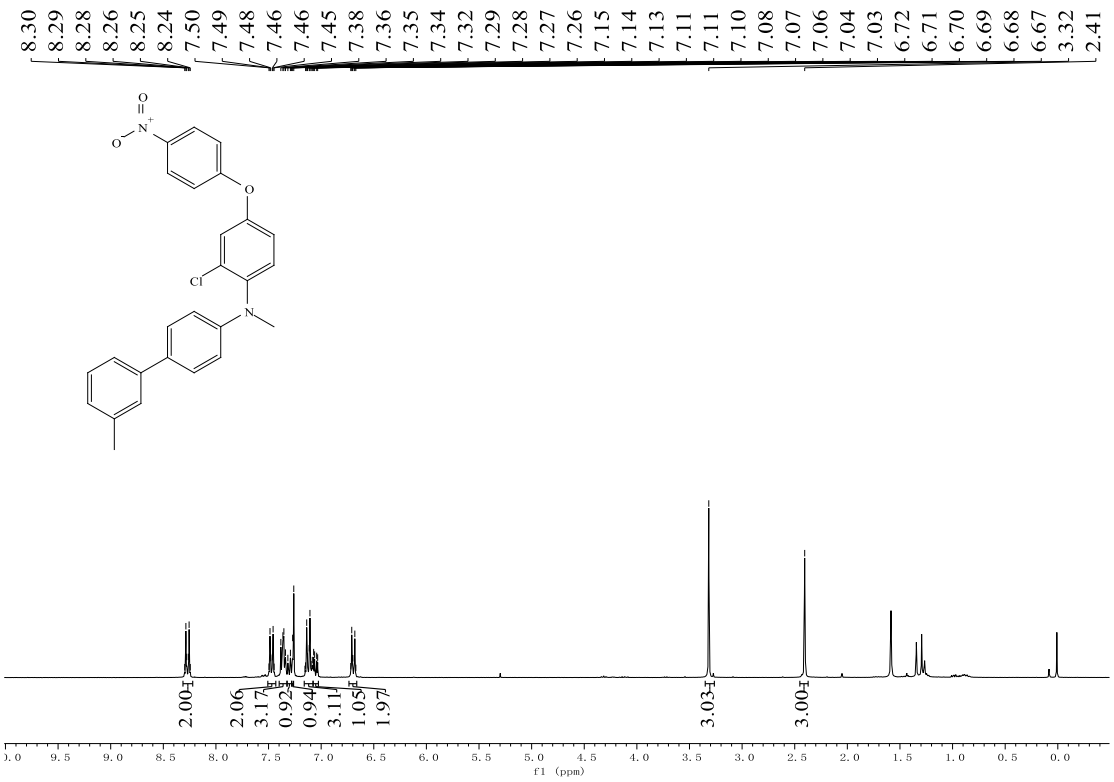
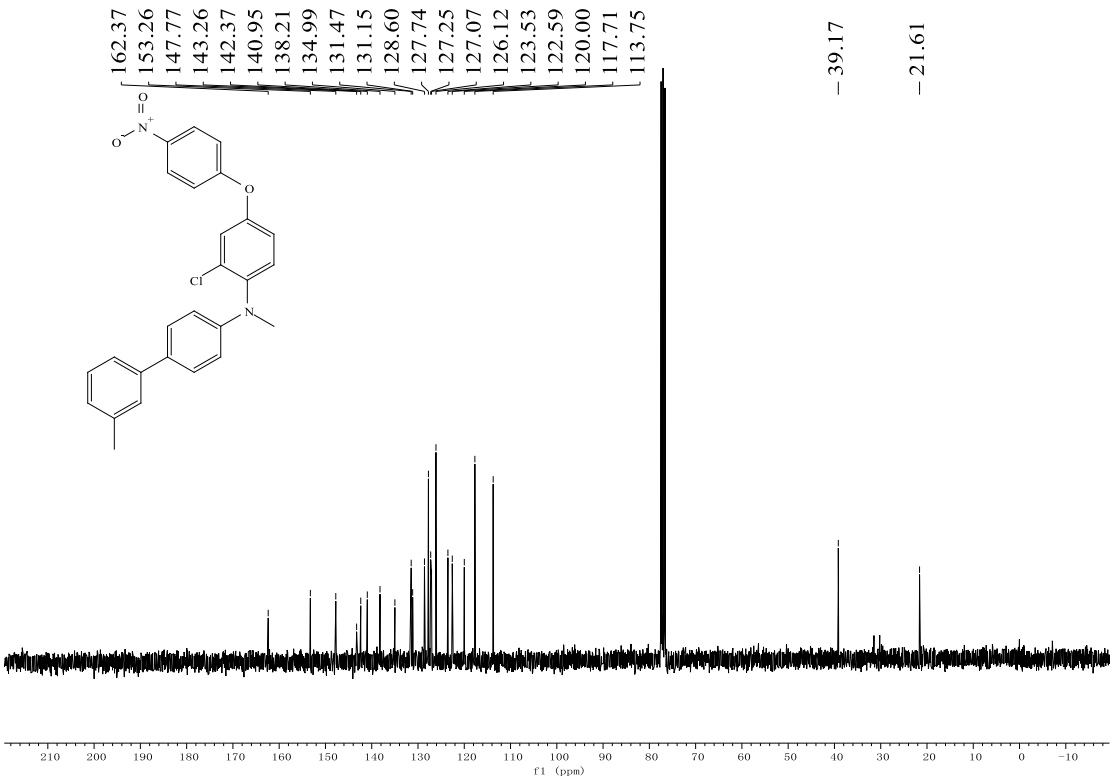


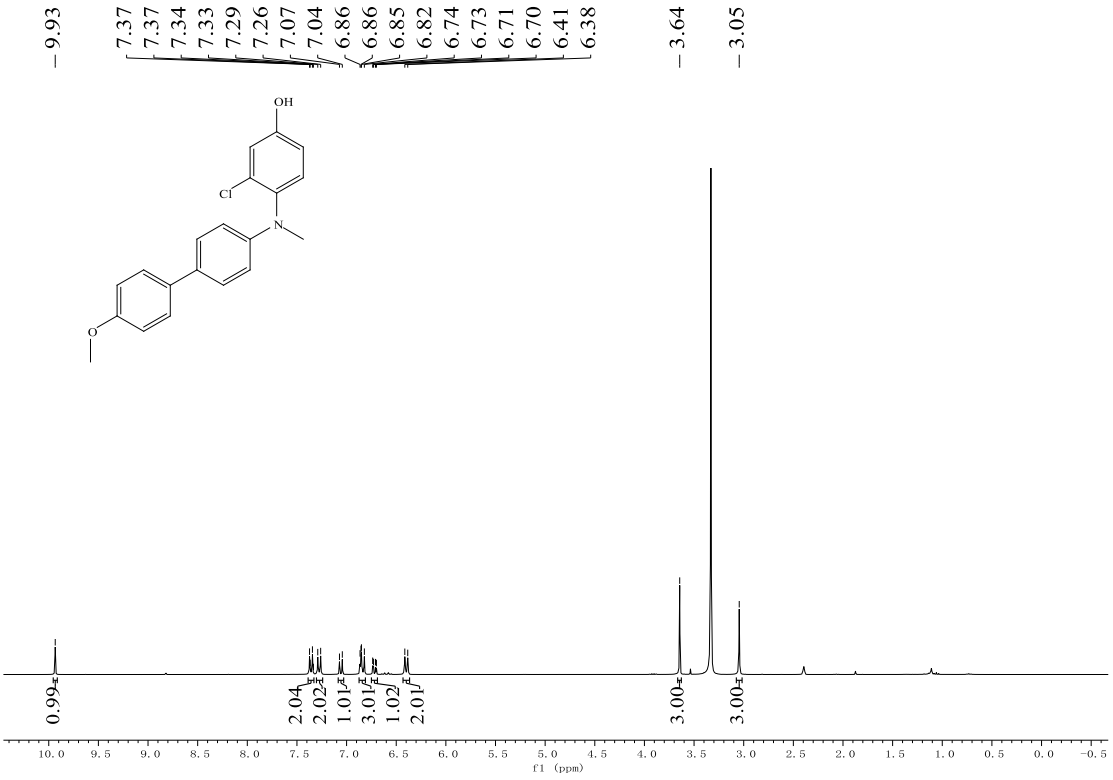
^{1}H NMR (300 MHz, $CDCl_3$)



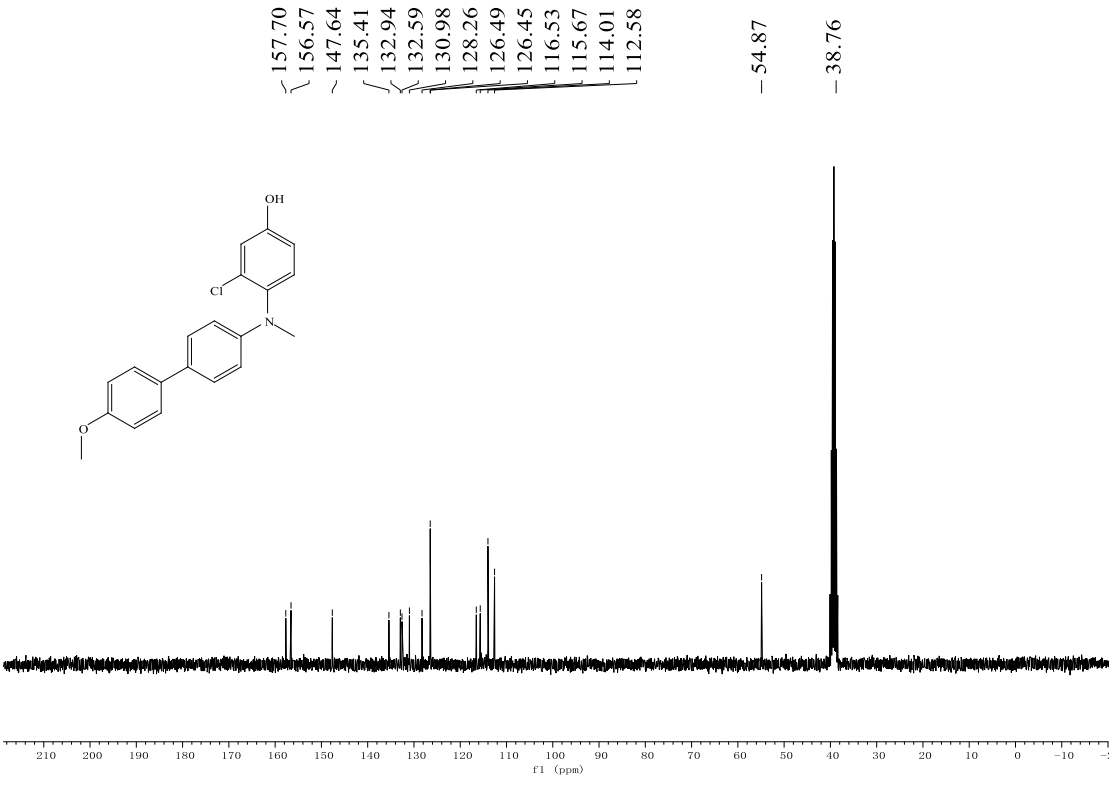
^{13}C NMR (75 MHz, $CDCl_3$)



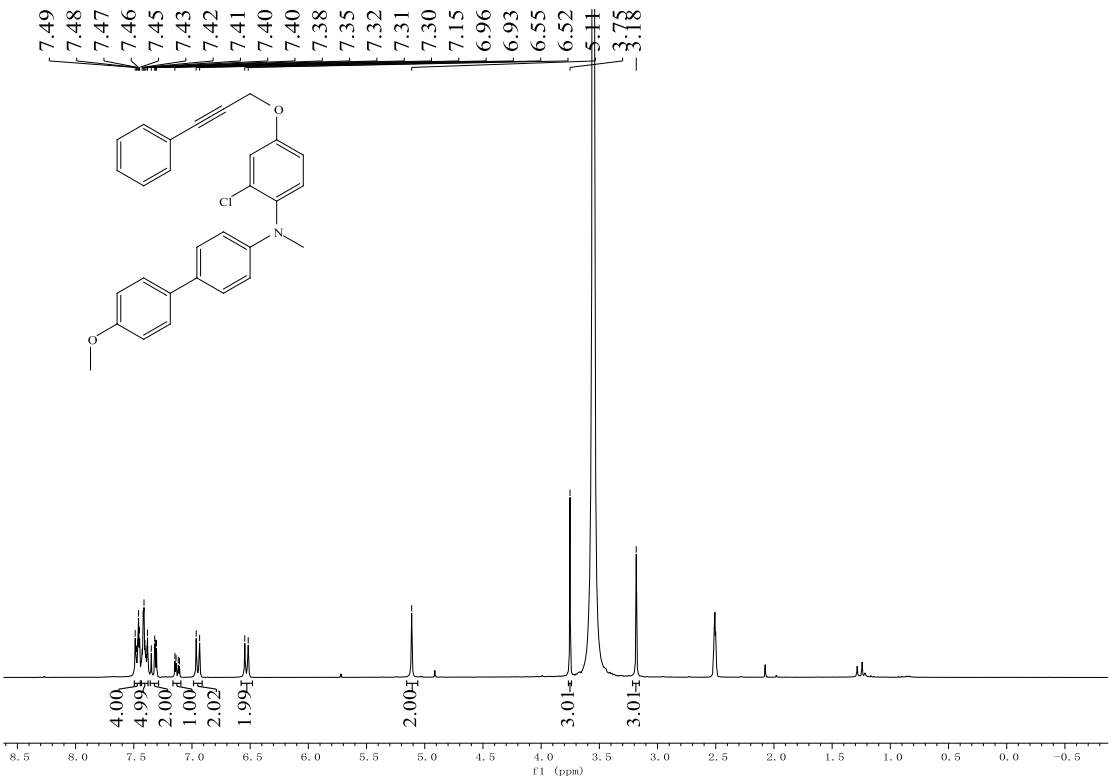
^{1}H NMR (300 MHz, DMSO)



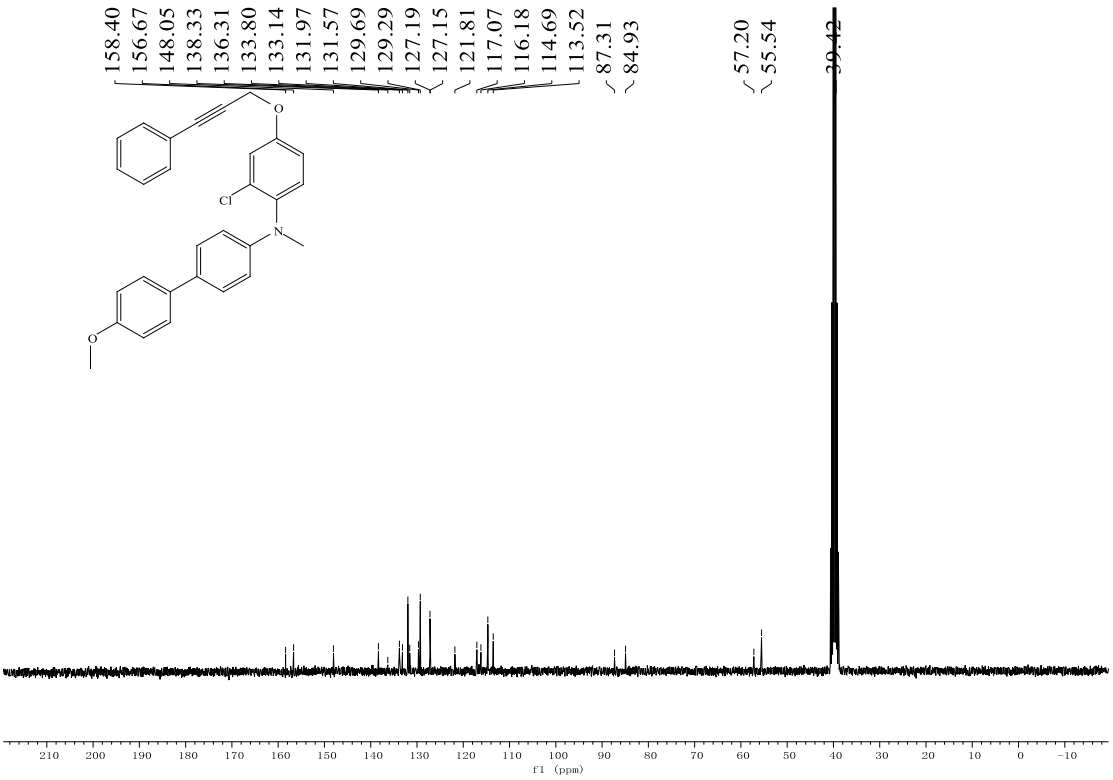
^{13}C NMR (75 MHz, DMSO)



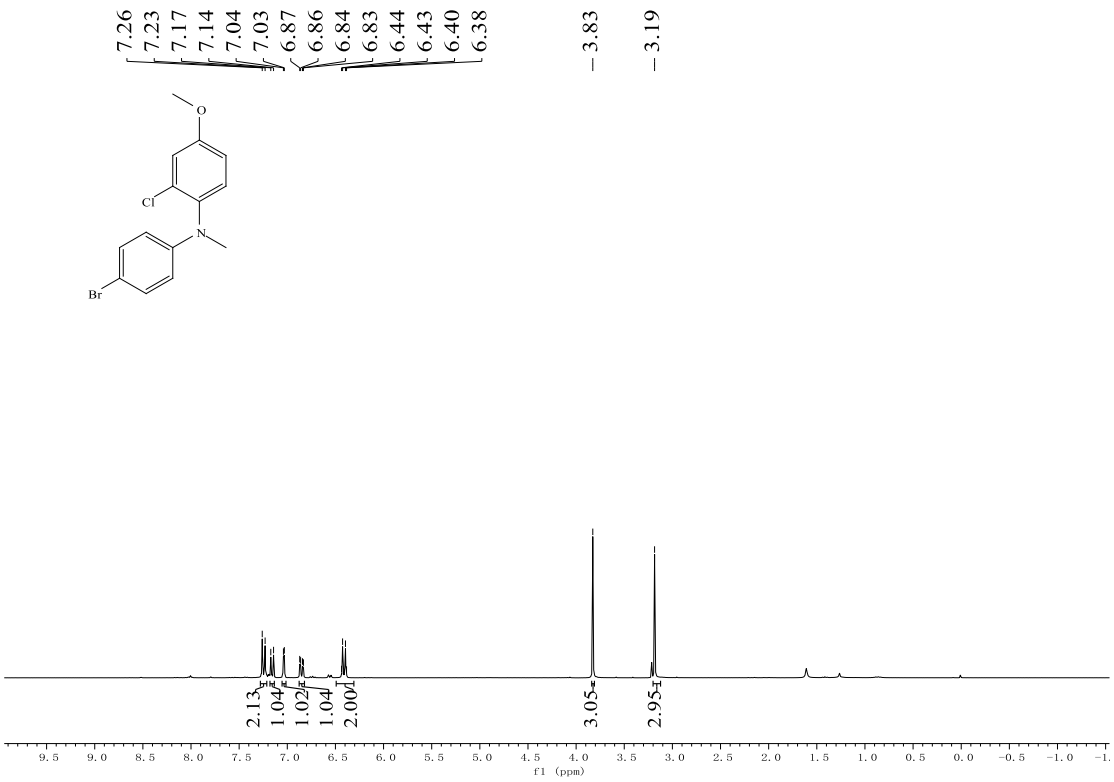
^{1}H NMR (300 MHz, DMSO)



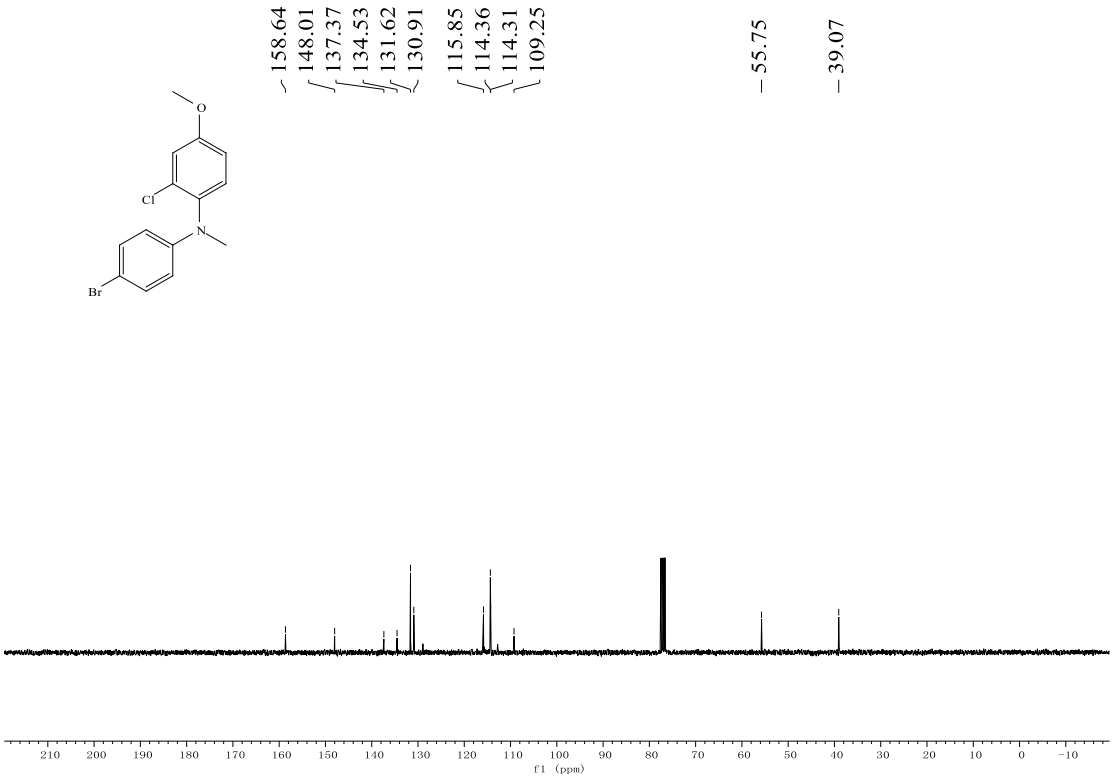
^{13}C NMR (75 MHz, DMSO)



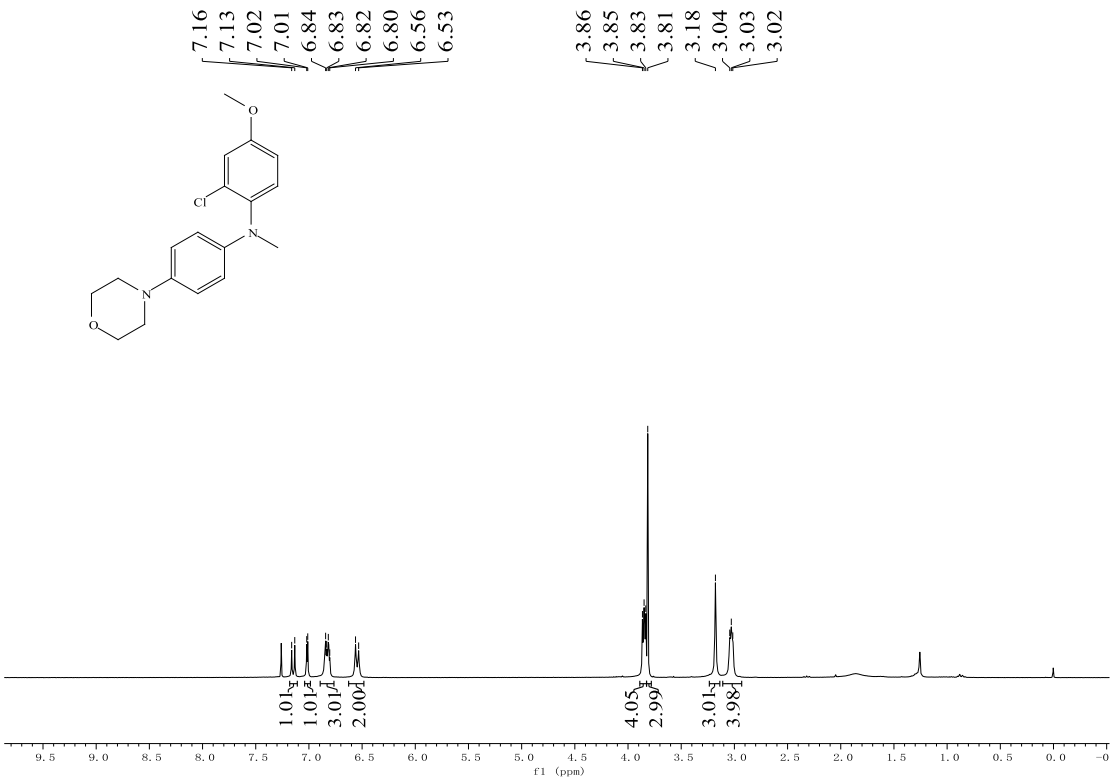
^{1}H NMR (300 MHz, $CDCl_3$)



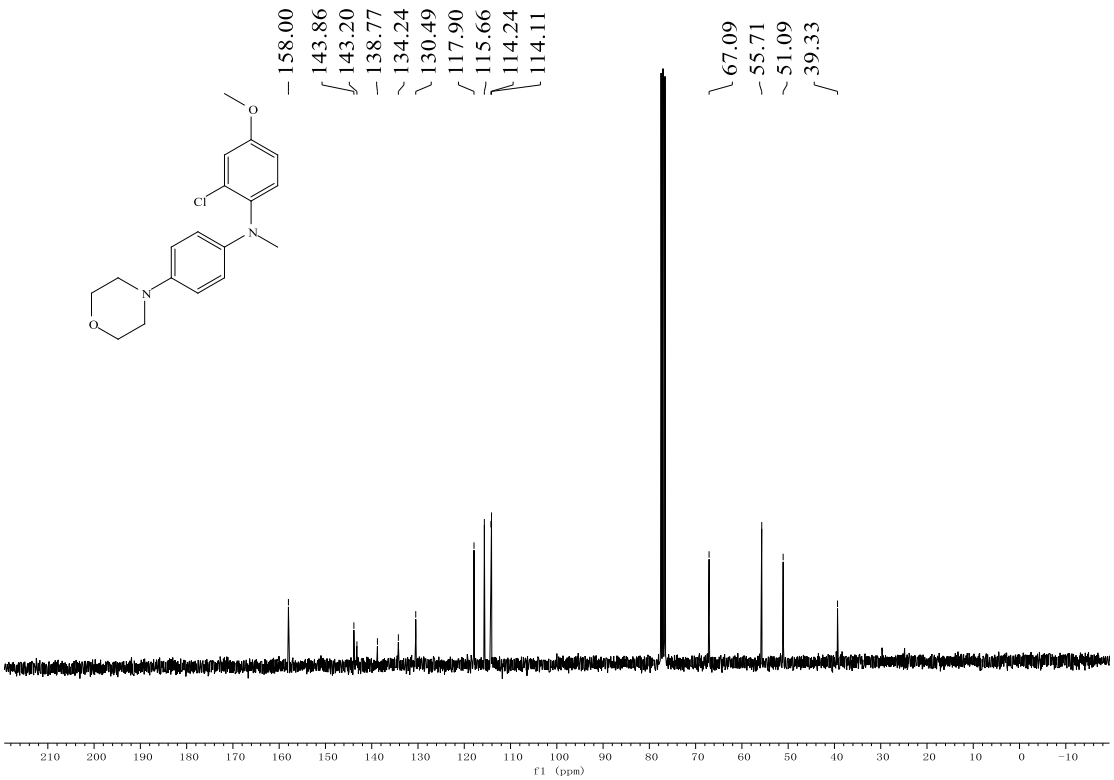
^{13}C NMR (75 MHz, $CDCl_3$)



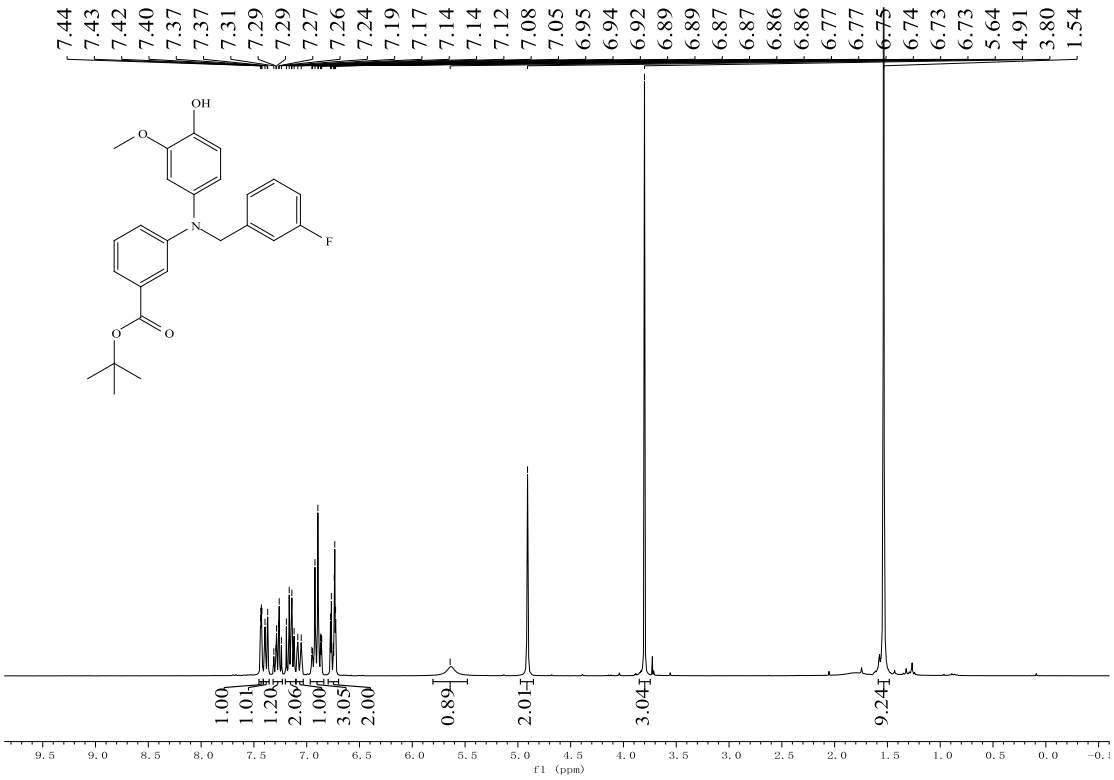
^{1}H NMR (300 MHz, $CDCl_3$)



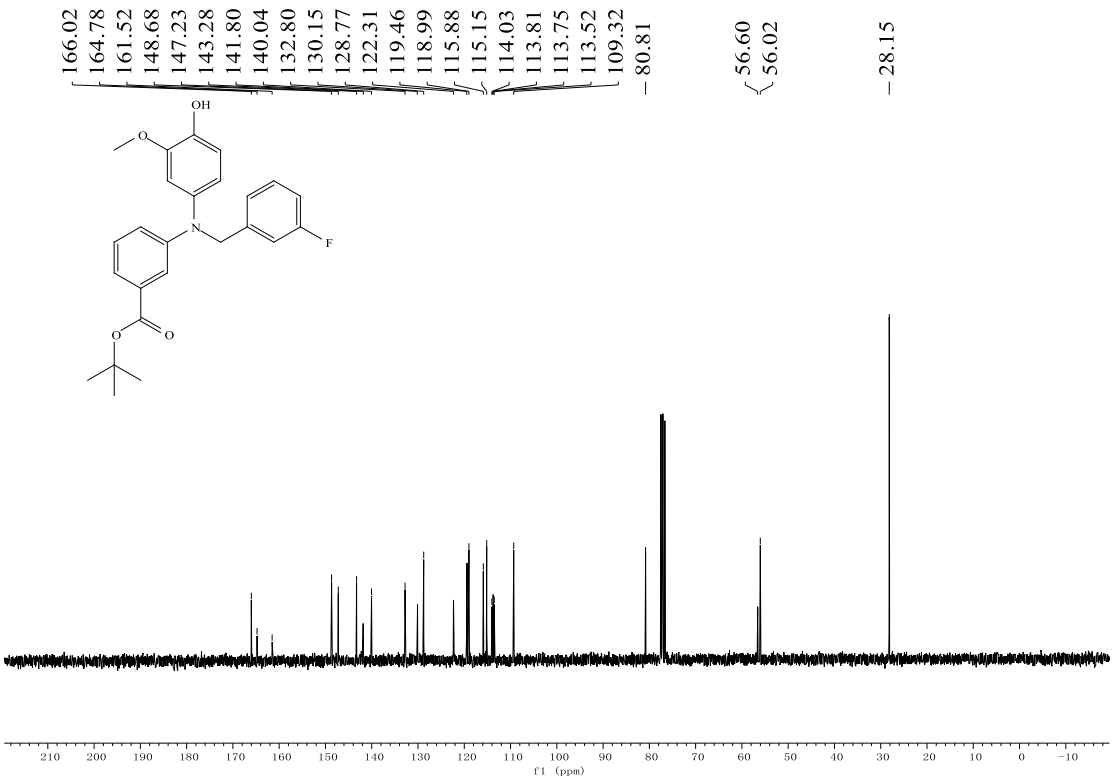
^{13}C NMR (75 MHz, $CDCl_3$)



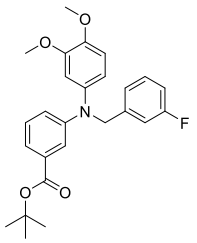
^{1}H NMR (300 MHz, $CDCl_3$)



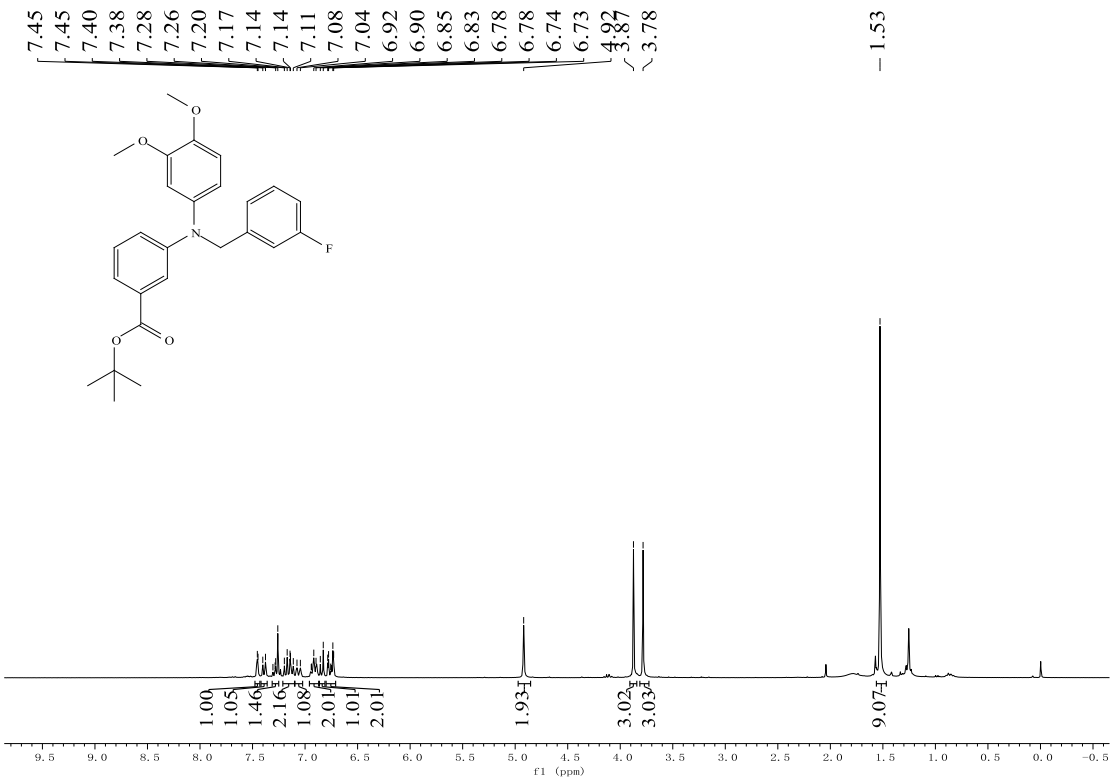
^{13}C NMR (75 MHz, $CDCl_3$)



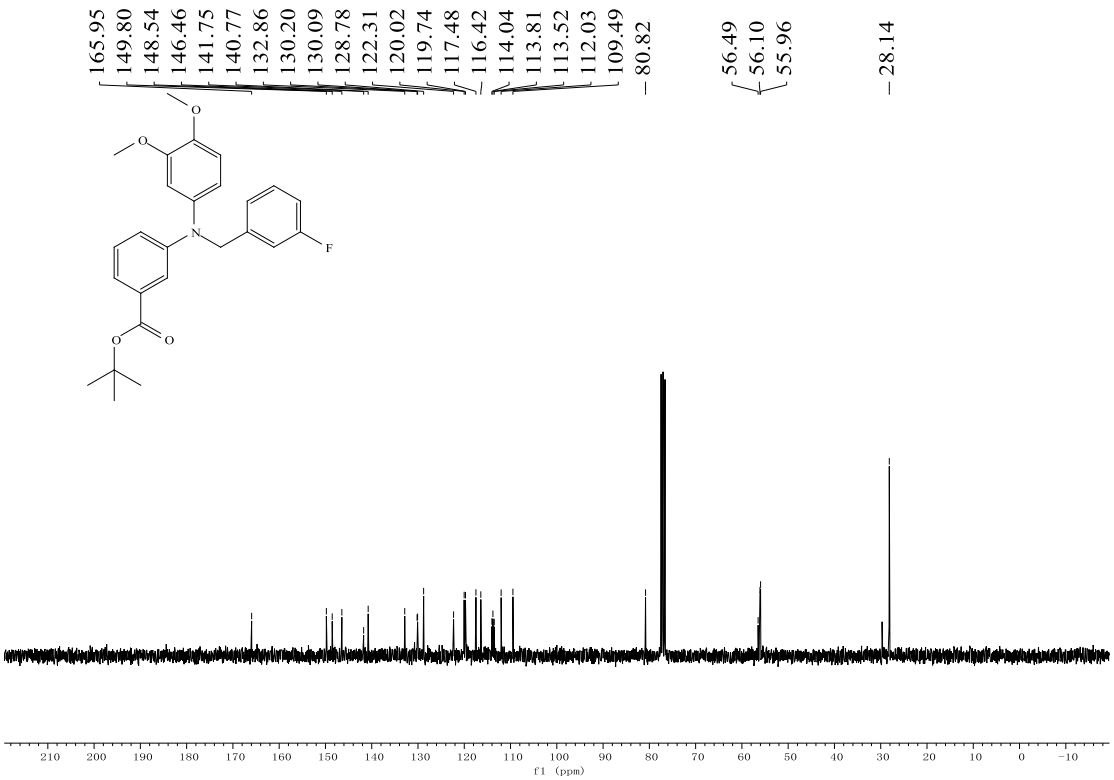
^{19}F NMR (282 MHz, CDCl3)



^{1}H NMR (300 MHz, $CDCl_3$)



^{13}C NMR (75 MHz, $CDCl_3$)



^{19}F NMR (376 MHz, $CDCl_3$)