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Supporting Information

Electrochemical oxidative cross-coupling of tetrahydroquinolines and azoles

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Contents

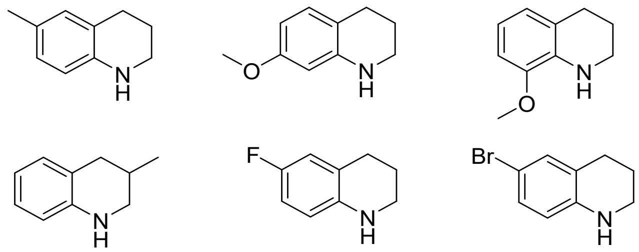
1. General methods

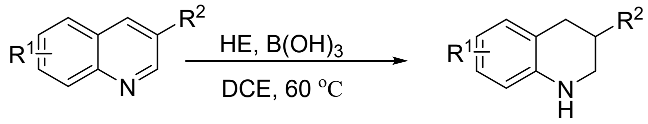
Unless otherwise noted, all reagents were purchased from commercial suppliers and used without further purification. Reactions were monitored by thin-layer chromatography (TLC) with Haiyang GF 254 silica gel plates (Qingdao Haiyang chemical industry Co Ltd, Qingdao, China) using UV light and vanillic aldehyde or phosphomolybdic acid as visualizing agents. Flash column chromatography was performed using 200-300 mesh silica gel at increased pressure. ^{1}H NMR spectra, ^{19}F NMR spectra and ^{13}C NMR spectra were respectively recorded on 600 MHz, 565 MHz, 400 MHz, 151 MHz and 101 MHz NMR spectrometers. Chemical shifts (δ) were expressed in ppm with TMS as the internal standard, and coupling constants (J) were reported in Hz. High-resolution mass spectra were obtained by using ESI ionization sources (quadrupole time-of-flight mass spectrometer, Bruker Impact II, Bremen, Germany). Cyclic voltammograms were obtained on a CHI 700E potentiostat (CH Instruments, Inc.).

Abbreviations: THF = tetrahydrofuran, HFIP = 1,1,1,3,3,3-hexafluoropropan-2-ol, MeOH = methanol, DMA = *N*,*N*-dimethylaniline, DMF = *N*,*N*-dimethylformamide, CYH = cyclohexane, DMSO = dimethyl sulfoxide, EA = ethyl acetate, DCE = dichloroethane, DCM = dichloromethane, MeCN = acetonitrile, TEMPO = 2,2,6,6-tetramethylpiperidinooxy, ACT = 4-ACETAMIDO-TEMPO, FC = ferrocene, TAPA = triphenylamine, ABN = 9-azabicyclo[3.3.1]nonane N-oxyl, DABCO = triethylenediamine

2. Experimental procedures

2.1. General procedure for the preparation of tetrahydroquinolines 1[1]

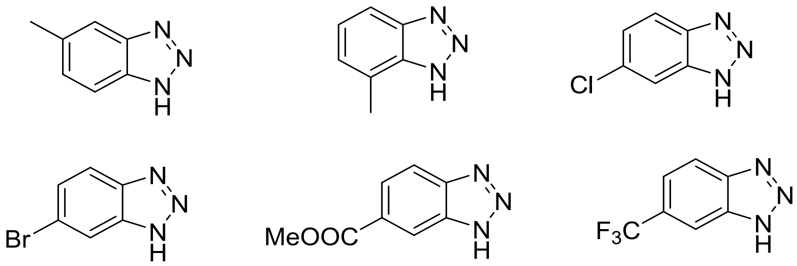


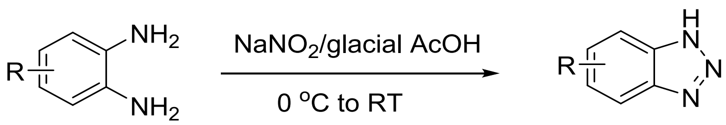


1

In a 50 mL round-bottomed flask, quinoline (5 mmol), Hantzsch ester (2.5 equiv), $B(OH)_3$ (15 mol%) and dichloroethane (20 mL) were charged. The reaction mixture was stirred at 60 °C (in a preheated oil bath). After completion of the reaction (detected by TLC), the reaction mixture was cooled to RT, extracted with EtOAc and washed with H_2O. The combined organic layers were dried over anhydrous Na_2SO_4 and evaporated in vacuo. The residue was purified by flash chromatography on silica gel using petroleum ether/ethyl acetate as the eluent to give desired product **1**.

2.2. General procedure for the preparation of benzotriazoles 2[2]

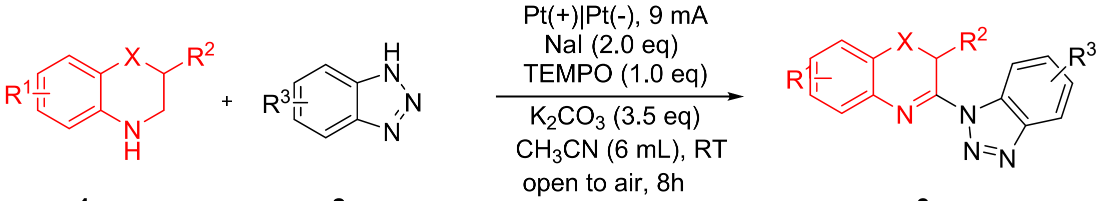




2

1,2-Phenylenediamine derivative (3.26 mmol) was dissolved in a mixture of 0.45 mL of glacial acetic acid and 1.2 mL of water and cooled to 4 °C. A solution of sodium nitrite (0.26 g, 3.76 mmol) in 1 mL of water was added. The reaction temperature rose to 50 °C for 30 min, and then was allowed to reach RT. and stirred at this temperature for 12 h. The mixture was cooled to 0 °C for 1 h. Produced precipitate was collected by suction filtration, and washed with water, and dried to provide substituted benzotriazoles **2**.

2.3. General procedure for the electrochemical synthesis of dihydroquinoline-azole derivatives 3



1 **2** **3**

(X = C, O)

Substrate **1** (0.3 mmol, 1 equiv.), substrate **2** (0.6 mmol, 2 equiv.), NaI (0.6 mmol, 2 equiv.), TEMPO (0.3 mmol, 1 equiv.), K_2CO_3 (1.05 mmol, 3.5 equiv.) and CH_3CN (6 mL) were added to a three-necked flask (10 mL) equipped with a magnetic stirring bar. Two platinum plates (1 cm x 1 cm x 0.2 mm each) were used as anode and cathode respectively (the electrodes were immersed 1 cm in the reaction solution). The reaction mixture was stirred and electrolyzed at a constant current of 9 mA at RT. After reaction completion (monitored by TLC), solvent (CH_3CN) was removed, the crude reaction mixture was purified by flash column chromatography on silica gel with petroleum ether/ethyl acetate as the eluent to obtain the target product **3**. (**Note:** Some products **3** may undergo decomposition in deuterated chloroform).

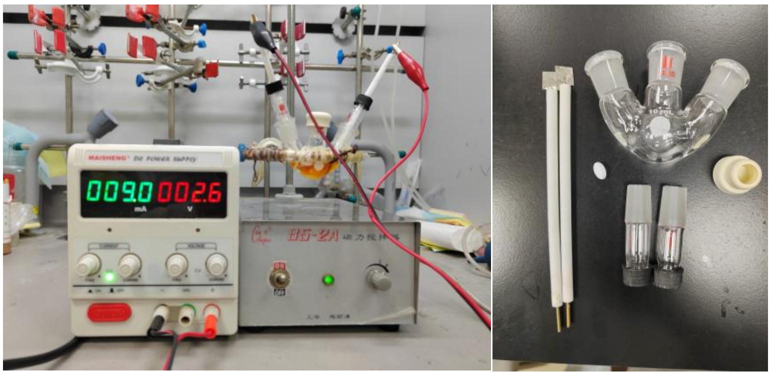
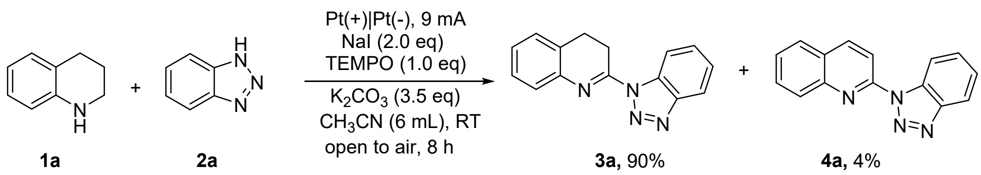


Figure S1 Electrochemical setup used.

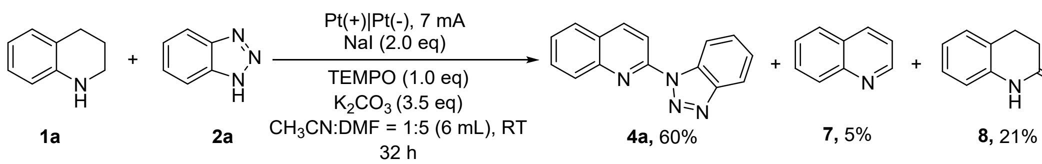
The experimental setup consisted of two platinum sheet electrodes (1 cm x 1 cm x 0.2 mm each), a three-necked flask (10 mL), an adjustable DC regulated power supply (MS-150V 100 mA), a magnetic stirrer, The reaction system is not sealed.

2.4. By-products

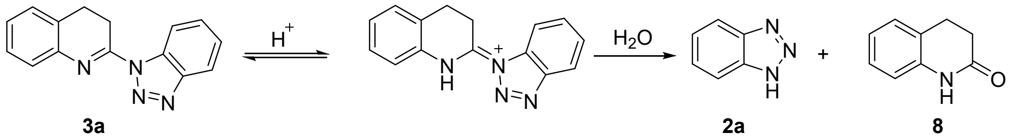
In some cases (but not all) depicted in Figure 1, both products **3** and **4** were obtained, with **3** being the major product and **4** the minor product. Taking the model reaction as an example: under the standard conditions depicted in Scheme 1, the reaction was conducted for 8 h, and after silica gel column chromatography separation, dihydroquinazoline-imidazole derivative **3a** (90% yield) and further oxidized product quinazoline-imidazole derivative **4a** (4% yield) were obtained.



Under the standard reaction conditions depicted in Scheme 2, after 32 h of reaction, no dihydroquinazoline-imidazole derivative **3a** was observed, and the reaction generated quinazoline derivative **4a** (60% yield), with the main by-products being quinazoline **7** (5% yield) and dihydroquinazolin-4-one **8** (21% yield).

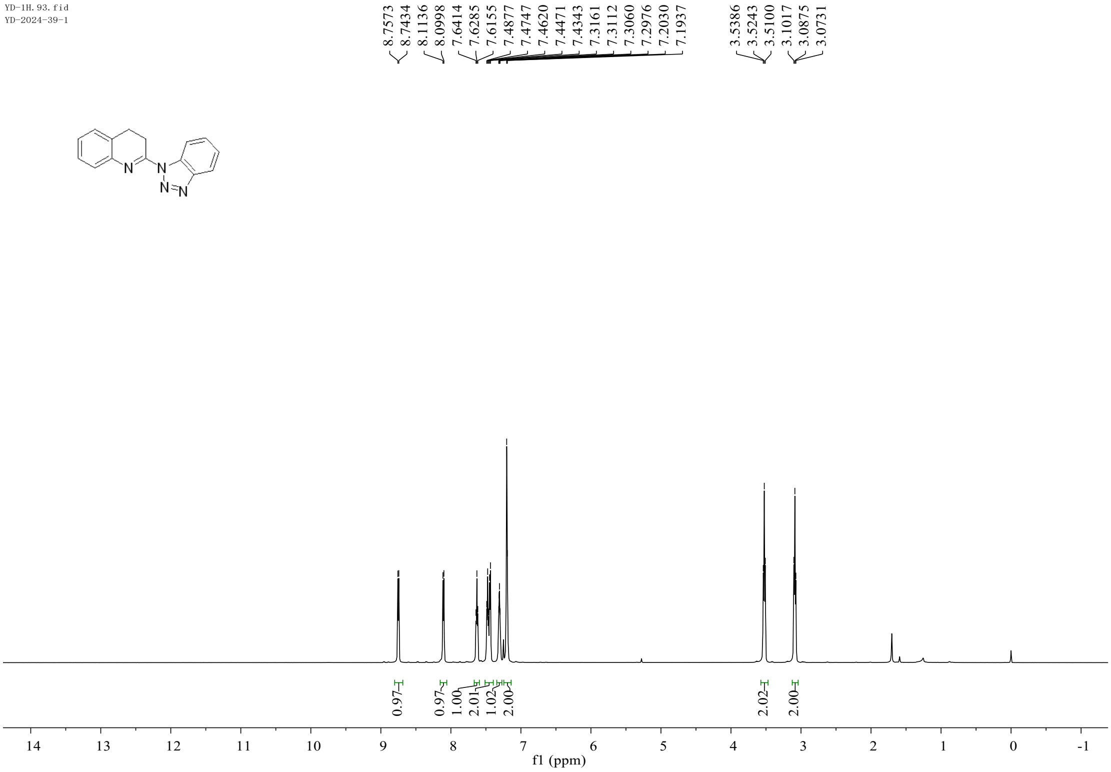


Some products **3** may undergo decomposition in deuterated chloroform. Taking product **3a** as an example, possible path way is shown as following:



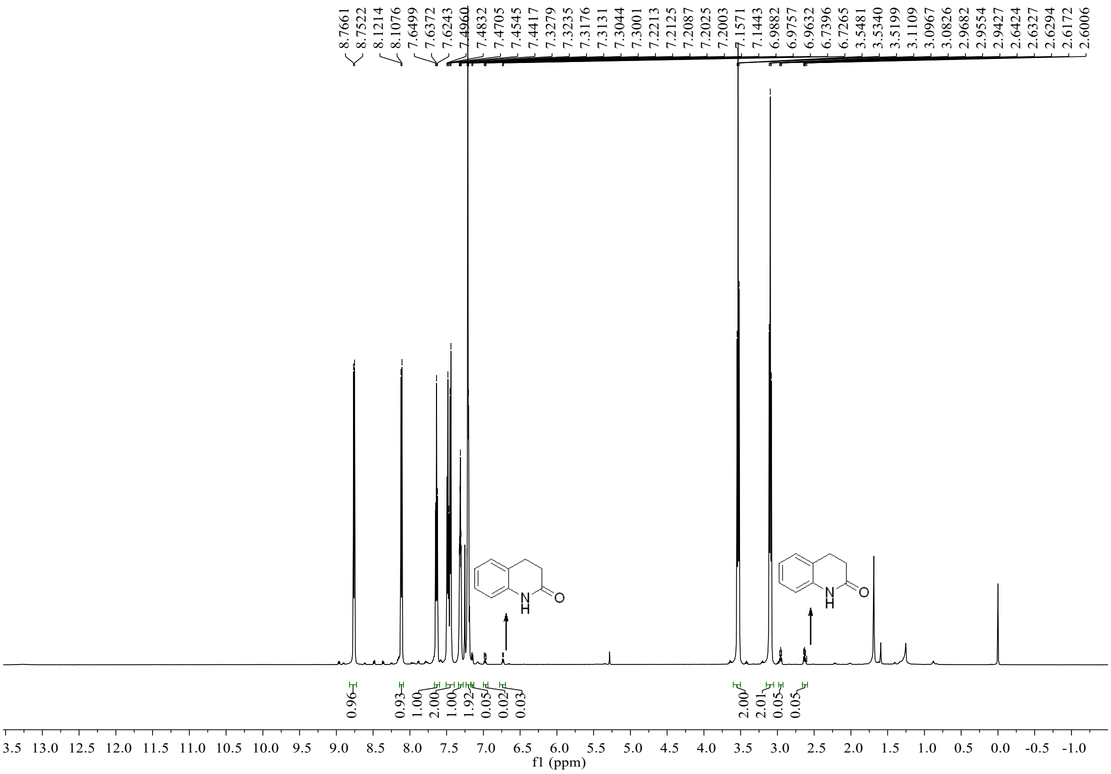
We conducted ^{1}H-NMR analysis of product **3a** at different time intervals in deuterated chloroform and observed that the extent of decomposition increased with prolonged exposure.

^{1}H-NMR Spectrum (600 MHz, $CDCl_3$) of 3a:



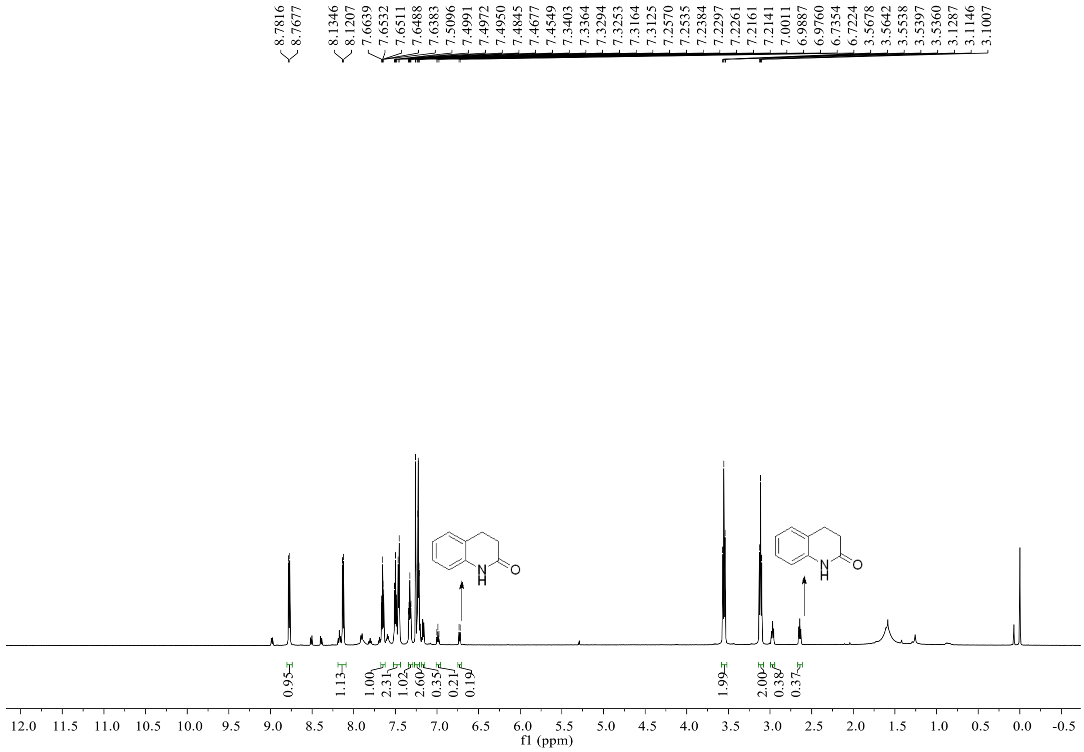
After one day：

^{1}H-NMR Spectrum (600 MHz, $CDCl_3$) of 3a:

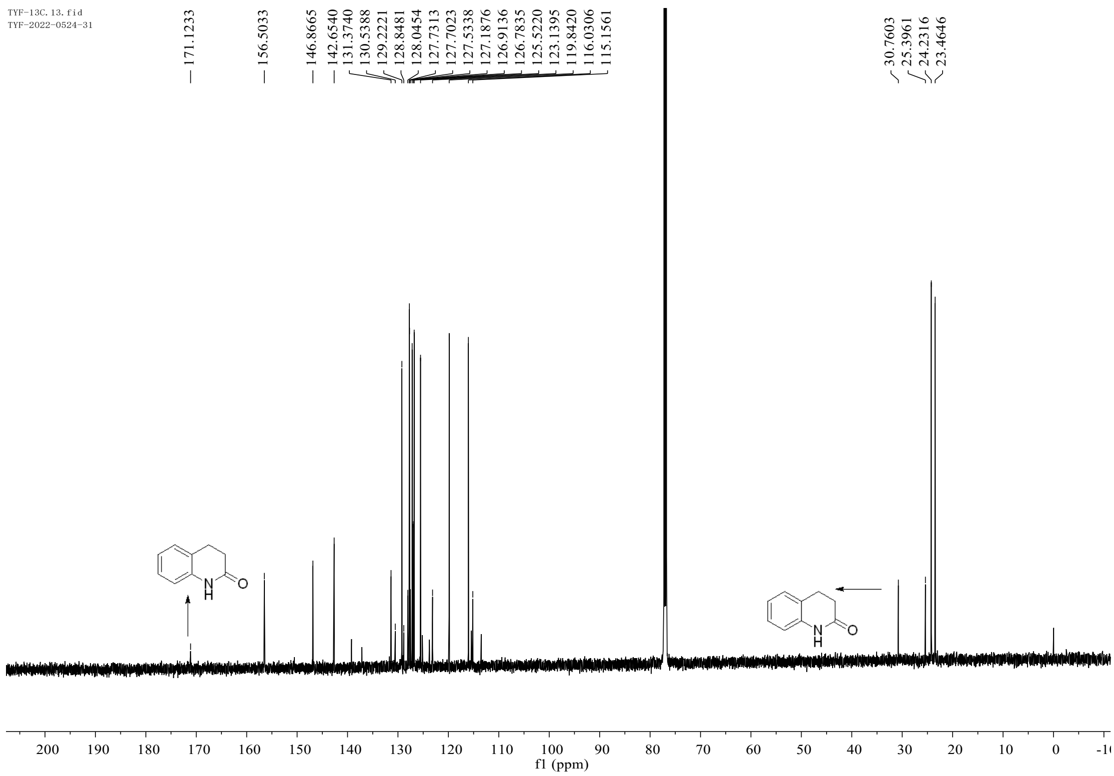


After five days:

¹H-NMR Spectrum (600 MHz, $CDCl_3$) of 3a



¹³C-NMR Spectrum (151 MHz, $CDCl_3$) of 3a



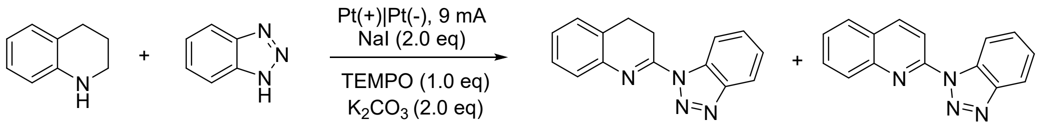
quinoline (8)[3] : R_f = 0.25 (Petroleum ether/EtOAc, 5:1). Colorless liquid. ¹H NMR (600 MHz, Chloroform-d) δ 8.88 (dd, J = 4.3, 1.7 Hz, 1H), 8.13 – 8.09 (m, 1H), 8.05 (dd, J = 8.3, 1.8 Hz, 1H), 7.73 (dd, J = 8.2, 1.5 Hz, 1H), 7.65 – 7.67 (m, 1H), 7.46 – 7.49 (m, 1H), 7.30 (dd, J = 8.3, 4.2 Hz, 1H). ^{13}C NMR (151 MHz, Chloroform-d) δ 150.3, 148.2, 135.9, 129.4, 129.3, 128.2, 127.7, 126.4, 121.0.

3,4-dihydroquinolin-2(1H)-one (9) [3] : R_f = 0.25 (Petroleum ether/EtOAc, 5:1). White solid. ^{1}H NMR (600 MHz, Chloroform-d) δ 9.60 (s, 1H), 7.19 – 7.11 (m, 2H), 7.01 – 6.95 (m, 1H), 6.87 (d, J = 7.8 Hz, 1H), 2.96 (t, J = 7.6 Hz, 2H), 2.64 (dd, J = 8.6, 6.7 Hz, 2H). ^{13}C NMR (151 MHz, Chloroform-d) δ 137.4, 127.8, 127.5, 123.6, 123.0, 115.7, 30.7, 25.3.

3. Optimization of reaction conditions

3.1. Reaction condition optimization for synthesizing dihydroquinoline-azole derivatives

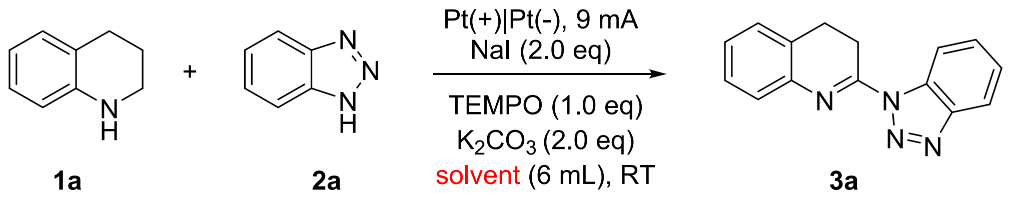
Table S1. Solvent screening [a]



Entry	Solvent	**3a** Yield (%) [b]	**4a** Yield (%) [b]
1	THF	N.D.	Trace
2	Acetone	N.D.	N.D.
3	MeOH	N.D.	Trace
4	DMSO	N.D.	26
5	DMA	Trace	17
6	EA	N.D.	13
7	DCE	N.D.	N.D.
8	CYH	N.D.	N.D.
9	DMF	18	25
10	**CH_3CN**	**60**	**Trace**

[a] Reaction conditions: A mixture of **1a** (0.3 mmol, 1 *equiv*), **2a** (0.6 mmol, 2.0 *equiv*), NaI (0.6 mmol, 2.0 *equiv*), TEMPO (0.3 mmol, 1.0 *equiv*) and K_2CO_3 (0.6 mmol, 2.0 *equiv*) in a solvent (6 mL) under a constant current of 9 mA (Pt anode: 1 cm x 1 cm x 0.2 mm; Pt cathode: 1 cm x 1 cm x 0.2 mm) in an undivided cell at RT for 8 h. [b] Isolated yield.

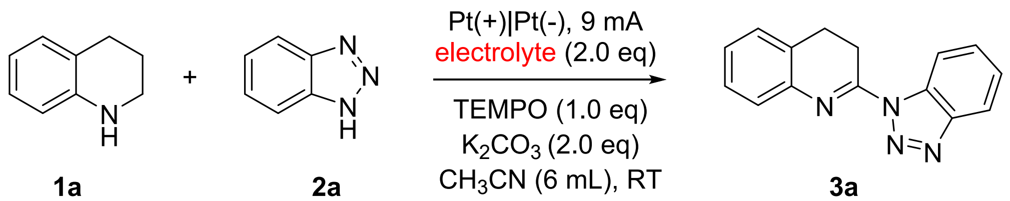
Table S2. Screening of mixed solvents [a]



Entry	Solvent	Yield (%) [b]
1	**CH_3CN**	**60**
2	CH_3CN:DMF = 5:1	7
3	CH_3CN:DMF = 1:1	36
4	CH_3CN:DMF = 1:5	14
5	CH_3CN:HFIP = 5:1	N.D.
6	CH_3CN:HFIP = 2:1	N.D.
7	CH_3CN:HFIP = 1:1	N.D.
8	CH_3CN:HFIP = 1:5	N.D.

[a] Reaction conditions: A mixture of **1a** (0.3 mmol, 1 *equiv*), **2a** (0.6 mmol, 2.0 *equiv*), NaI (0.6 mmol, 2.0 *equiv*), TEMPO (0.3 mmol, 1.0 *equiv*) and K_2CO_3 (0.6 mmol, 2.0 *equiv*) in a solvent (6 mL) under a constant current of 9 mA (Pt anode: 1 cm x 1 cm x 0.2 mm; Pt cathode: 1 cm x 1 cm x 0.2 mm) in an undivided cell at RT for 8 h. [b] Isolated yield.

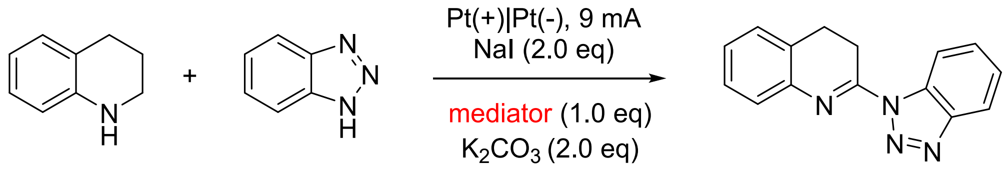
Table S3. Electrolyte screening



Entry	Electrolyte	Yield (%) [b]
1	--	Oveload
2	**NaI**	**60**
3	KI	7
4	NH_4I	Trace
5	$^nBu_4NI$	9
6	$^nBu_4NBr$	17
7	$^nBu_4NOAc$	10
8	$^nBu_4NPF_6$	Trace
9	$^nBu_4NClO_4$	9
10	$^nBu_4NBF_4$	Trace
11	$NaBF_4$	Trace
12	$^nBu_4NCF_3SO_3$	Trace
13	$LiClO_4$	12
14	LiOAc	N.D.

[a] Reaction conditions: A mixture of **1a** (0.3 mmol, 1 *equiv*), **2a** (0.6 mmol, 2.0 *equiv*), electrolyte (0.6 mmol, 2.0 *equiv*), TEMPO (0.3 mmol, 1.0 *equiv*) and K_2CO_3 (0.6 mmol, 2.0 *equiv*) in CH_3CN (6 mL) under a constant current of 9 mA (Pt anode: 1 cm x 1 cm x 0.2 mm; Pt cathode: 1 cm x 1 cm x 0.2 mm) in an undivided cell at RT for 8 h. [b] Isolated yield.

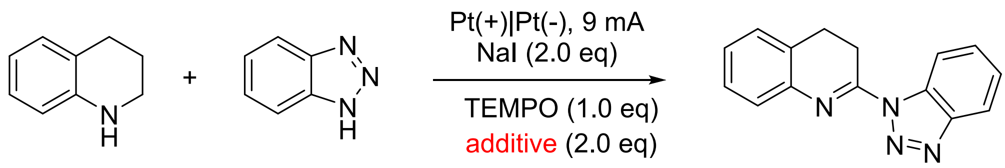
Table S4. Mediator screening [a]



Entry	Mediator	Yield (%) [b]
1	--	Trace
2	**TEMPO**	**60**
3	ACT	27
4	FC	8
5	TAPA	15
6	NaBr	Trace
7	^{n}Bu$_4$NBr	26
8	ABN	15
9	DABCO	Trace

[a] Reaction conditions: A mixture of **1a** (0.3 mmol, 1 *equiv*), **2a** (0.6 mmol, 2.0 *equiv*), NaI (0.6 mmol, 2.0 *equiv*), mediator (0.3 mmol, 1.0 *equiv*) and K_2CO_3 (0.6 mmol, 2.0 *equiv*) in CH_3CN (6 mL) under a constant current of 9 mA (Pt anode: 1 cm x 1 cm x 0.2 mm; Pt cathode: 1 cm x 1 cm x 0.2 mm) in an undivided cell at RT for 8 h. [b] Isolated yield.

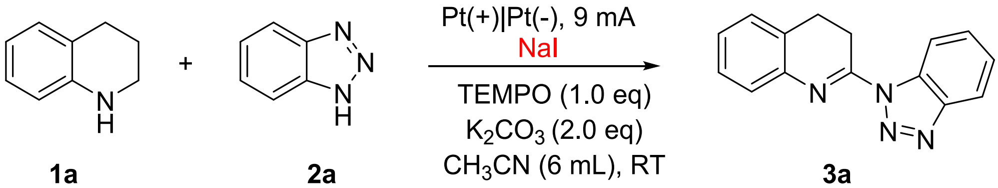
Table S5. Additive screening [a]



Entry	Additive	Yield (%) [b]
1	--	23
2	**K_2CO_3**	**60**
3	Na_2CO_3	9
4	Cs_2CO_3	22
5	$KHCO_3$	17
6	K_3PO_4	8
7	KOH	44
8	NaOH	26
9	^{t}BuOK	24
10	KF	40
11	CsF	47
12	DBU	19
13	DABCO	Trace
14	2,6-Dimethylpyridine	10

[a] Reaction conditions: A mixture of **1a** (0.3 mmol, 1 *equiv*), **2a** (0.6 mmol, 2.0 *equiv*), NaI (0.6 mmol, 2.0 *equiv*), TEMPO (0.3 mmol, 1.0 *equiv*) and additive (0.6 mmol, 2.0 *equiv*) in CH_3CN (6 mL) under a constant current of 9 mA (Pt anode: 1 cm x 1 cm x 0.2 mm; Pt cathode: 1 cm x 1 cm x 0.2 mm) in an undivided cell at RT for 8 h. [b] Isolated yield.

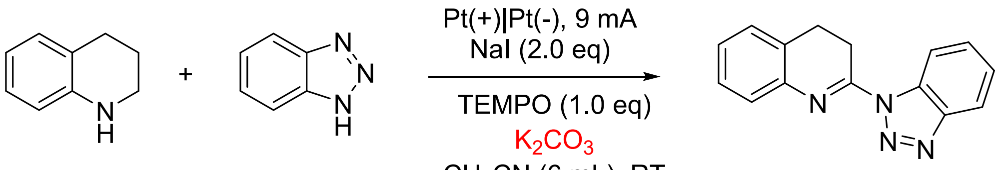
Table S6. Screening of the amount of NaI [a]



Entry	Amount of NaI (*equiv*)	Yield (%) [b]
1	1.0	22
2	1.5	24
3	**2.0**	**60**
4	2.5	55

[a] Reaction conditions: A mixture of **1a** (0.3 mmol, 1 *equiv*), **2a** (0.6 mmol, 2.0 *equiv*), NaI (x mmol), TEMPO (0.3 mmol, 1.0 *equiv*) and K_2CO_3 (0.6 mmol, 2.0 *equiv*) in CH_3CN (6 mL) under a constant current of 9 mA (Pt anode: 1 cm x 1 cm x 0.2 mm; Pt cathode: 1 cm x 1 cm x 0.2 mm) in an undivided cell at RT for 8 h. [b] Isolated yield.

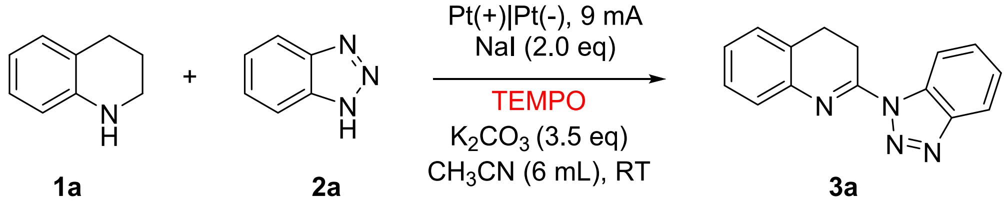
Table S7. Screening of the amount of K_2CO_3 [a]



Entry	Amount of K_2CO_3 (*equiv*)	Yield (%) [b]
1	0	23
2	1	25
3	2	60
4	3	63
5	**3.5**	**90**
6	4.0	75

[a] Reaction conditions: A mixture of **1a** (0.3 mmol, 1 *equiv*), **2a** (0.6 mmol, 2.0 *equiv*), NaI (0.6 mmol, 2.0 *equiv*), TEMPO (0.3 mmol, 1.0 *equiv*) and K_2CO_3 (x mmol) in CH_3CN (6 mL) under a constant current of 9 mA (Pt anode: 1 cm x 1 cm x 0.2 mm; Pt cathode: 1 cm x 1 cm x 0.2 mm) in an undivided cell at RT for 8 h. [b] Isolated yield.

Table S8. Screening of the amount of TEMPO [a]

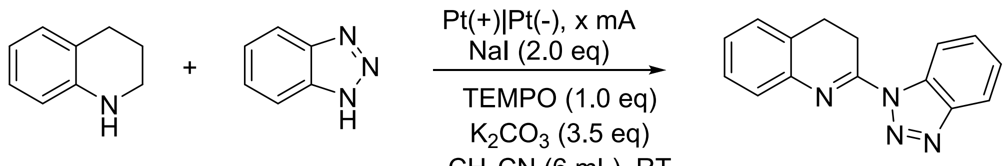


1a 2a 3a

Entry	Amount of TEMPO (*equiv*)	Yield (%) [b]
1	0	Trace
2	0.25	28
3	0.5	65
4	0.75	71
5	**1.0**	**90**
6	1.5	78

[a] Reaction conditions: A mixture of **1a** (0.3 mmol, 1 *equiv*), **2a** (0.6 mmol, 2.0 *equiv*), NaI (0.6 mmol, 2.0 *equiv*), TEMPO (x mmol) and K_2CO_3 (1.05 mmol, 3.5 *equiv*) in CH_3CN (6 mL) under a constant current of 9 mA (Pt anode: 1 cm x 1 cm x 0.2 mm; Pt cathode: 1 cm x 1 cm x 0.2 mm; Pt cathode : 1 cm x 1 cm x 0.2 mm) in an undivided cell at RT for 8 h. [b] Isolated yield.

Table S9. Current screening [a]

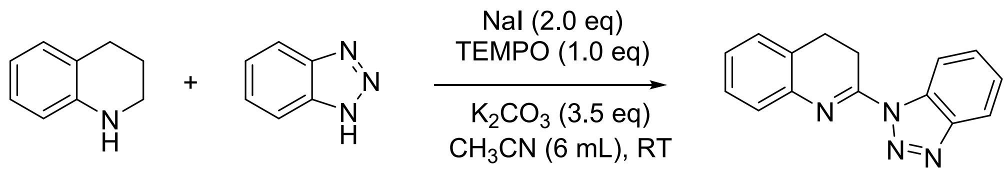


1a 2a 3a

Entry	Current (mA)	Time (h)	Yield (%) [b]
1	3	13	29
2	6	9.5	57
3	**9**	**8**	**90**
4	12	6	85
5	14	5.5	85

[a] Reaction conditions: A mixture of **1a** (0.3 mmol, 1 *equiv*), **2a** (0.6 mmol, 2.0 *equiv*), NaI (0.6 mmol, 2.0 *equiv*), TEMPO (0.3 mmol, 1.0 *equiv*) and K_2CO_3 (1.05 mmol, 3.5 *equiv*) in CH_3CN (6 mL) under a constant current (Pt anode: 1 cm x 1cm x 0.2 mm; Pt cathode: 1 cm x 1 cm x 0.2 mm) in an undivided cell at RT. [b] Isolated yield.

Table S10. Electrode material screening [a]



1a 2a 3a

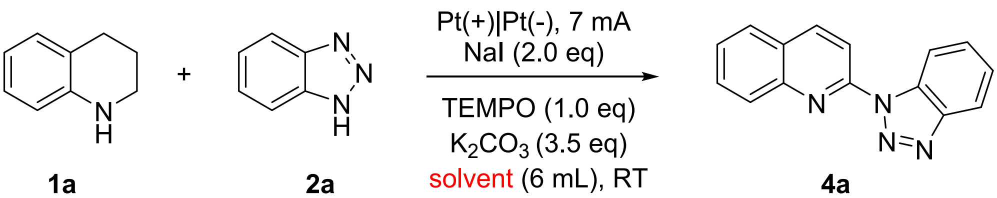
Entry	Electrode material	Yield (%) [b]
1	C(+) || Pt(-)	70

2	C(+) || C(-)	Carbon electrode corrosion
3	**Pt(+) || Pt(-)**	**90**
4	Pt(+) || C(-)	Carbon electrode corrosion

[a] Reaction conditions: A mixture of **1a** (0.3 mmol, 1 *equiv*), **2a** (0.6 mmol, 2.0 *equiv*), NaI (0.6 mmol, 2.0 *equiv*), TEMPO (0.3 mmol, 1.0 *equiv*) and K_2CO_3 (1.05 mmol, 3.5 *equiv*) in CH_3CN (6 mL) under a constant current of 9 mA (x anode, x cathode) in an undivided cell at RT for 8 h. [b] Isolated yield.

3.2. Reaction condition optimization for synthesizing of quinoline-azole derivatives

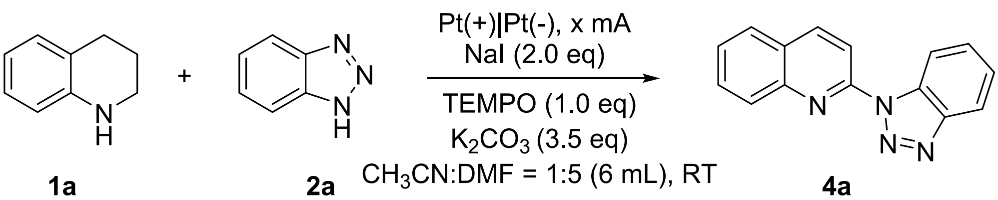
Table S11. Solvent screening [a]



Entry	Solvent	Yield (%) [b]
1	DMF	28
2	CH_3CN	51
3	CH_3CN:DMF = 5:1	Trace
4	CH_3CN:DMF = 1:1	42
5	**CH_3CN:DMF = 1:5**	**60**
6	CH_3CN:DMF = 1:2	55

[a'] Reaction conditions: A mixture of **1a** (0.3 mmol, 1 *equiv*), **2a** (0.6 mmol, 2 *equiv*), NaI (0.6 mmol, 2 *equiv*), TEMPO (0.3 mmol, 1 *equiv*) and K_2CO_3 (1.05 mmol, 3.5 *equiv*) in solvent (6 mL) under a constant current of 7 mA (Pt anode: 1 cm x 1cm x 0.2 mm; Pt cathode: 1 cm x 1 cm x 0.2 mm) in an undivided cell at RT for 32 h. [b] Isolated yield.

Table S12. Current screening [a]



Entry	Current (mA)	Time (h)	Yield (%) [b]
1	**7**	**32**	**60**
2	9	28	53
3	11	22	48
4	13	18	45

[a], Reaction conditions: A mixture of **1a** (0.3 mmol, 1 *equiv*), **2a** (0.6 mmol, 2 *equiv*), NaI (0.6 mmol, 2 *equiv*), TEMPO (0.3 mmol, 1 *equiv*) and K_2CO_3 (1.05 mmol, 3.5 *equiv*) in CH_3CN:DMF = 1:5 (6 mL) under a constant current of x mA (Pt anode: 1 cm x 1cm x 0.2 mm; Pt cathode: 1 cm x 1 cm x 0.2 mm) in an undivided cell at RT. [b] Isolated yield.

4. Mechanistic investigation

4.1. Cyclic voltammetry experiments

The electrochemical measurement was performed by a computer-controlled electrochemical analyzer. Cyclic voltammetry performed in a three-electrode cell was carried out in a three-electrode battery (volume 15 mL; CH_3CN as solvent, $^{n}Bu_4NClO_4$ 0.05 M as supporting electrolyte, 2 mM concentration of test compound), and glassy carbon (diameter 3 mm) as working electrode, platinum wire as auxiliary electrode, Ag/AgCl (3 M KCl) as reference electrode. The scanning speed was 100 mV·s^{-1}. For tetrahydroquinoline (**1a**), benzotriazole (**2a**), NaI, and TEMPO, the oxidation potential range studied was 0.0 V to +3.0 V, relative to Ag/AgCl (3 M KCl). The oxidation potential of 1,2,3,4-tetrahydroquinoline (**1a**), 1*H*-benzo[*d*][1,2,3] triazole (**2a**), NaI and TEMPO was determined as: 1,2,3,4-tetrahydroquinoline (**1a**) (E_{ox} = + 0.58 V vs. Ag/AgCl in CH_3CN); NaI (E_{ox} = + 0.23 V *vs* Ag/AgCl in CH_3CN); TEMPO (E_{ox} = + 0.53 V *vs* Ag/AgCl in CH_3CN). Benzotriazole (**2a**) had no oxidation potential peak in the tested range.

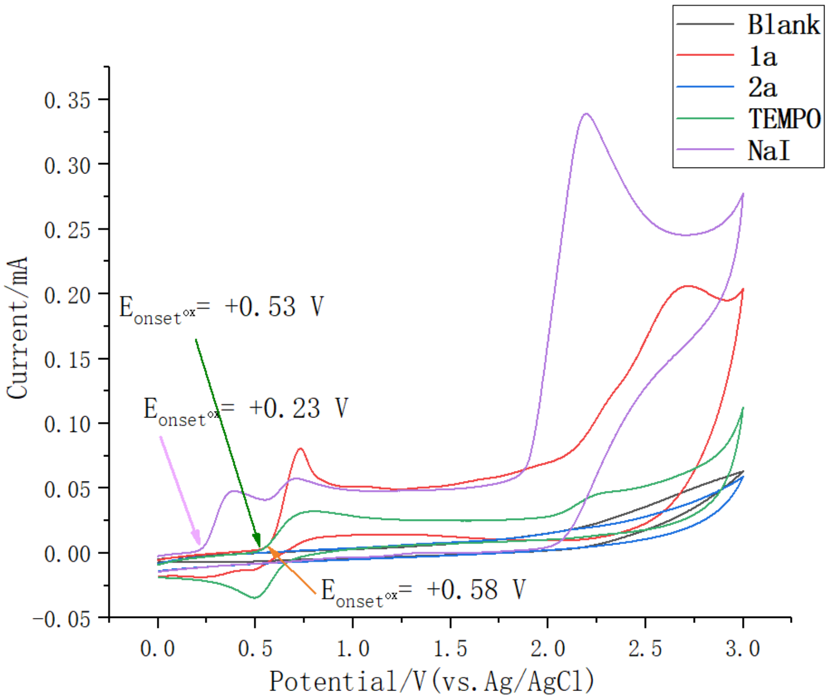
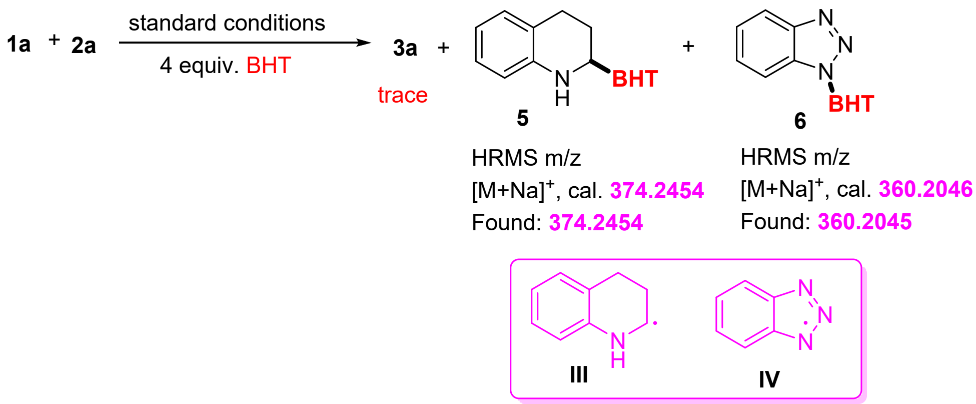


Figure S2. Cyclic voltammetry of NaI, TEMPO, **1a** and **2a** in CH_3CN and blank.

4.2. Radical trapping experiments

Under standard conditions, BHT (4.0 *equiv* to **1a**) was added to the model reaction system at the beginning of the reaction. After 4 h, a small amount of reaction mixture was taken out for high-resolution mass spectrometry (HRMS) measurement. From TLC, only trace amount of product **3a** was observed.



Scheme S1. Radical trapping experiments.

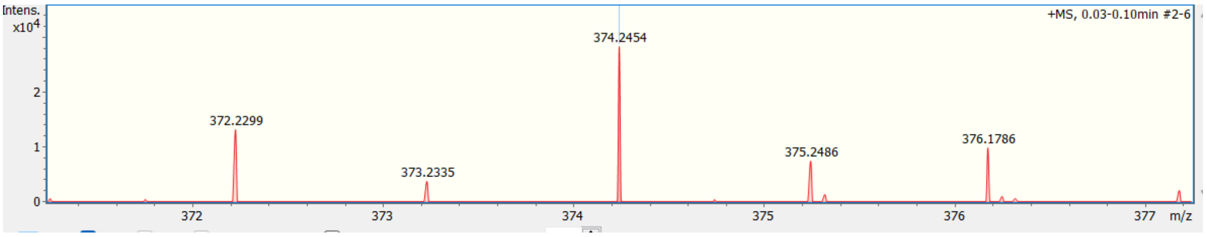


Figure S3. Mass spectrometry (HRMS) data of the radical trapping experiments (with BHT).

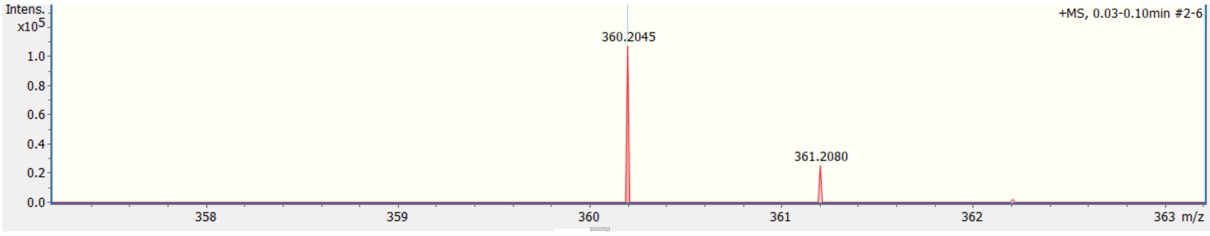
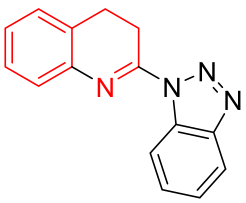
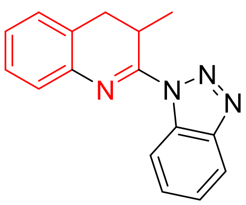


Figure S4. Mass spectrometry (HRMS) data of the radical trapping experiments (with BHT).

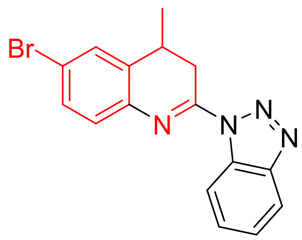
5. Characterization data of the products



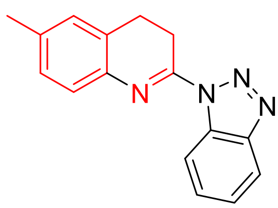
2-(1*H*-benzo[*d*][1,2,3]triazol-1-yl)-3,4-dihydroquinoline (3a): R_f = 0.25 (Petroleum ether/EtOAc, 5:1). 63.9 mg, 90% yield. White solid. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.73 (d, *J* = 8.3 Hz, 1H), 8.09 (d, *J* = 8.3 Hz, 1H), 7.61 (t, *J* = 7.7 Hz, 1H), 7.46 (t, *J* = 7.6 Hz, 1H), 7.42 (d, *J* = 7.7 Hz, 1H), 7.29 (dt, *J* = 8.0, 4.3 Hz, 1H), 7.18 (d, *J* = 4.6 Hz, 2H), 3.50 (t, *J* = 8.5 Hz, 2H), 3.07 (t, *J* = 8.5 Hz, 2H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 156.4, 146.8, 142.6, 131.3, 129.2, 127.7, 127.2, 127.1, 126.9, 126.7, 125.5, 119.8, 116.0, 24.1, 23.4. HRMS (ESI): m/z: calcd for $C_{15}H_{12}N_4Na$ $(M+Na)^+$ 271.0954; found 271.0956



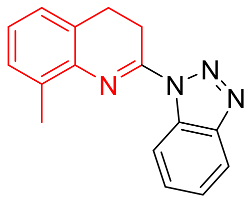
2-(1*H*-benzo[*d*][1,2,3]triazol-1-yl)-3-methyl-3,4-dihydroquinoline (3b): R_f = 0.25 (Petroleum ether/EtOAc, 5:1). 24.1 mg, 32% yield. White solid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.78 (d, *J* = 8.3 Hz, 1H), 8.13 (d, *J* = 8.2 Hz, 1H), 7.65 (t, *J* = 7.6 Hz, 1H), 7.48 (dd, *J* = 17.0, 7.7 Hz, 2H), 7.37 – 7.29 (m, 1H), 7.22 (d, *J* = 11.4 Hz, 2H), 4.21 (p, *J* = 7.0 Hz, 1H), 3.37 (dd, *J* = 16.1, 7.0 Hz, 1H), 2.82 (d, *J* = 16.2 Hz, 1H), 1.27 (d, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 160.5, 146.8, 141.8, 131.5, 129.3, 128.7, 127.7, 127.4, 126.5, 125.6, 125.5, 119.9, 116.2, 32.0, 28.3, 16.3. HRMS (ESI): m/z: calcd for $C_{16}H_{14}N_4Na$ $(M+Na)^+$ 285.1111; found 285.1111



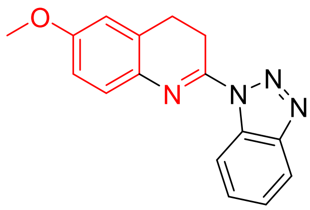
2-(1*H*-benzo[*d*][1,2,3]triazol-1-yl)-6-bromo-4-methyl-3,4-dihydroquinoline (3c): R_f = 0.25 (Petroleum ether/EtOAc, 5:1). 67.0 mg, 70% yield. White solid. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.72 (d, *J* = 8.3 Hz, 1H), 8.12 (d, *J* = 8.3 Hz, 1H), 7.65 (t, *J* = 7.7 Hz, 1H), 7.50 (t, *J* = 7.7 Hz, 1H), 7.46 – 7.39 (m, 2H), 7.33 (d, *J* = 8.2 Hz, 1H), 3.53 (dd, *J* = 17.2, 7.1 Hz, 1H), 3.39 (dd, *J* = 17.2, 7.7 Hz, 1H), 3.24 (q, *J* = 7.2 Hz, 1H), 1.37 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 156.2, 146.9, 141.0, 134.4, 131.2, 130.7, 129.3, 129.2, 128.4, 125.7, 120.6, 119.9, 115.9, 30.7, 29.4, 19.8. HRMS (ESI): m/z: calcd for $C_{16}H_{13}BrN_4Na$ $(M+Na)^+$ 363.0216; found 363.0216



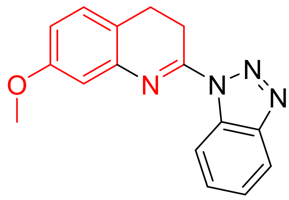
2-(1*H*-benzo[*d*][1,2,3]triazol-1-yl)-6-methyl-3,4-dihydroquinoline (3d): R_f = 0.25 (Petroleum ether/EtOAc, 5:1). 66.0 mg, 89% yield. White solid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.76 (d, *J* = 8.3 Hz, 1H), 8.11 (d, *J* = 8.3 Hz, 1H), 7.63 (dd, *J* = 8.3, 7.0, 1.1 Hz, 1H), 7.48 (dd, *J* = 8.2, 7.0, 1.1 Hz, 1H), 7.34 (d, *J* = 7.9 Hz, 1H), 7.12 (dd, *J* = 7.9, 2.0 Hz, 1H), 7.03 (d, J = 2.0 Hz, 1H), 3.52 (t, J = 8.5 Hz, 2H), 3.06 (t, J = 8.5 Hz, 2H), 2.37 (s, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 155.7, 146.8, 140.2, 137.1, 131.4, 129.1, 128.4, 128.2, 126.7, 126.6, 125.4, 119.7, 116.0, 24.2, 23.5, 21.2. HRMS (ESI): m/z: calcd for $C_{16}H_{14}N_4Na$ $(M+Na)^+$ 285.1111; found 285.1111



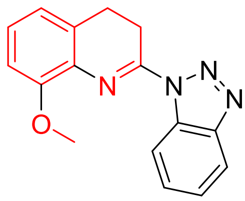
2-(1*H*-benzo[*d*][1,2,3]triazol-1-yl)-8-methyl-3,4-dihydroquinoline (3e): R_f = 0.25 (Petroleum ether/EtOAc, 5:1). 70.0 mg, 93% yield. White solid. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.70 (d, J = 8.3 Hz, 1H), 8.11 (d, J = 8.3 Hz, 1H), 7.64 (t, J = 7.6 Hz, 1H), 7.47 (t, J = 7.6 Hz, 1H), 7.17 (d, J = 7.4 Hz, 1H), 7.09 (t, J = 7.4 Hz, 1H), 7.04 (d, J = 7.2 Hz, 1H), 3.49 (t, J = 8.4 Hz, 2H), 3.05 (t, J = 8.4 Hz, 2H), 2.56 (s, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 155.2, 146.8, 140.9, 134.7, 131.2, 129.3, 126.8, 126.7, 125.9, 125.5, 125.3, 119.9, 115.7, 24.6, 23.2, 18.3. HRMS (ESI): m/z: calcd for $C_{16}H_{14}N_4Na$ $(M+Na)^+$ 285.1111; found 285.1110



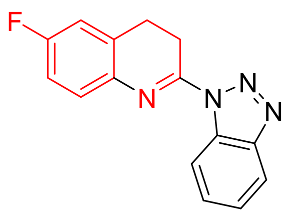
2-(1*H*-benzo[*d*][1,2,3]triazol-1-yl)-6-methoxy-3,4-dihydroquinoline (3f): R_f = 0.25 (Petroleum ether/EtOAc, 5:1). 44.8 mg, 56% yield. White solid. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.79 – 8.69 (m, 1H), 8.16 – 8.05 (m, 1H), 7.62 (dd, J = 8.2, 7.0, 1.1 Hz, 1H), 7.47 (dd, J = 8.2, 7.0, 1.1 Hz, 1H), 7.38 (d, J = 8.5 Hz, 1H), 6.84 (dd, J = 8.5, 2.8 Hz, 1H), 6.80 – 6.72 (m, 1H), 3.84 (s, 3H), 3.51 (t, J = 8.6 Hz, 2H), 3.08 (t, J = 8.4 Hz, 2H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 158.6, 154.4, 146.7, 136.1, 131.2, 129.0, 128.3, 127.8, 125.4, 119.7, 115.9, 113.5, 112.3, 55.5, 24.7, 23.2. HRMS (ESI): m/z: calcd for $C_{16}H_{14}N_4ONa$ $(M+Na)^+$ 301.1060; found 301.1059



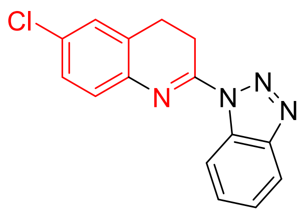
2-(1*H*-benzo[*d*][1,2,3]triazol-1-yl)-7-methoxy-3,4-dihydroquinoline (3g): R_f = 0.25 (Petroleum ether/EtOAc, 5:1). 73.6 mg, 92% yield. White solid. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.76 (d, *J* = 8.3 Hz, 1H), 8.12 (d, *J* = 8.3 Hz, 1H), 7.69 – 7.63 (m, 1H), 7.54 – 7.44 (m, 1H), 7.12 (d, *J* = 8.2 Hz, 1H), 7.03 (d, *J* = 2.7 Hz, 1H), 6.78 (dd, *J* = 8.1, 2.6 Hz, 1H), 3.87 (s, 3H), 3.53 (t, *J* = 8.4 Hz, 2H), 3.04 (t, *J* = 8.5 Hz, 2H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 159.3, 157.0, 146.8, 143.5, 131.3, 129.2, 128.1, 125.5, 119.8, 118.9, 116.0, 113.0, 112.0, 55.5, 23.8, 23.4. HRMS (ESI): m/z: calcd for $C_{16}H_{14}N_4ONa$ $(M+Na)^+$ 301.1060; found 301.1059



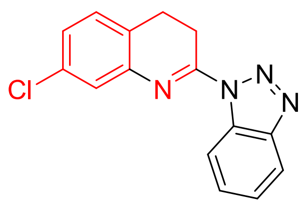
2-(1*H*-benzo[*d*][1,2,3]triazol-1-yl)-8-methoxy-3,4-dihydroquinoline (3h): R_f = 0.25 (Petroleum ether/EtOAc, 5:1). 73.6 mg, 92% yield. White solid. ^{1}H NMR (600 MHz, DMSO-*d*$_6$) δ 8.93 – 8.86 (m, 1H), 8.42 – 8.34 (m, 1H), 7.92 (dd, *J* = 8.3, 7.0, 1.1 Hz, 1H), 7.75 (dd, *J* = 8.2, 7.0, 1.1 Hz, 1H), 7.57 – 7.52 (m, 1H), 7.05 (d, *J* = 7.3 Hz, 2H), 3.96 (s, 3H), 3.62 (t, *J* = 8.5 Hz, 2H), 3.24 (t, *J* = 8.5 Hz, 2H). ^{13}C NMR (151 MHz, DMSO-*d*$_6$) δ 158.7, 155.2, 146.5, 136.0, 131.1, 129.9, 129.2, 128.0, 126.2, 120.0, 116.1, 113.9, 112.8, 55.8, 24.2, 23.2. HRMS (ESI): m/z: calcd for $C_{16}H_{14}N_4ONa$ $(M+Na)^+$ 301.1060; found 301.1059



2-(1*H*-benzo[*d*][1,2,3]triazol-1-yl)-6-fluoro-3,4-dihydroquinoline (3i): R_f = 0.25 (Petroleum ether/EtOAc, 5:1). 68.0 mg, 92% yield. White solid. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.72 (dd, *J* = 8.3, 1.2 Hz, 1H), 8.12 (dd, *J* = 8.4, 1.2 Hz, 1H), 7.64 (dd, *J* = 8.3, 7.0, 1.1 Hz, 1H), 7.49 (dd, *J* = 8.3, 7.0, 1.2 Hz, 1H), 7.41 (dd, *J* = 8.6, 5.4 Hz, 1H), 7.00 (dt, *J* = 8.8, 4.4 Hz, 1H), 6.94 (dd, *J* = 8.6, 2.8 Hz, 1H), 3.53 (t, *J* = 8.5 Hz, 2H), 3.09 (t, *J* = 8.5 Hz, 2H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 161.4 (d, *J* = 247.2 Hz), 155.8, 146.8, 138.8, 131.2, 129.2, 128.1 (d, *J* = 8.6 Hz), 125.59, 119.9, 115.8, 114.7 (d, *J* = 23.1 Hz), 114.3, 114.2 (d, *J* = 22.2 Hz), 24.4, 22.9. ^{19}F NMR (565 MHz, Chloroform-d) δ -114.85. HRMS (ESI): m/z: calcd for $C_{15}H_{11}FN_4Na$ $(M+Na)^+$ 289.0860; found 289.0859

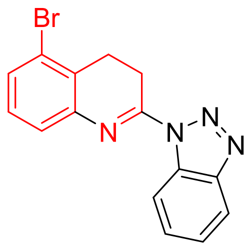


2-(1*H*-benzo[*d*][1,2,3]triazol-1-yl)-6-chloro-3,4-dihydroquinoline (3j): R_f = 0.25 (Petroleum ether/EtOAc, 5:1). 76.0 mg, 94% yield. White solid. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.69 (d, *J* = 8.3 Hz, 1H), 8.10 (d, *J* = 8.3 Hz, 1H), 7.62 (t, *J* = 7.7 Hz, 1H), 7.48 (t, *J* = 7.7 Hz, 1H), 7.35 (d, *J* = 8.3 Hz, 1H), 7.29 – 7.23 (m, 1H), 7.18 (s, 1H), 3.55 – 3.46 (m, 2H), 3.06 (t, *J* = 8.5 Hz, 2H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 156.6, 146.8, 141.1, 132.2, 131.2, 129.3, 128.5, 127.8, 127.7, 125.6, 119.9, 115.9, 24.1, 23.0. HRMS (ESI): m/z: calcd for $C_{15}H_{11}ClN_4Na$ $(M+Na)^+$ 305.0564; found 305.0563

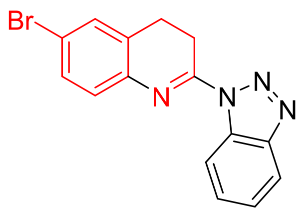


2-(1*H*-benzo[*d*][1,2,3]triazol-1-yl)-7-chloro-3,4-dihydroquinoline (3k): R_f = 0.25 (Petroleum ether/EtOAc, 5:1). 62.3 mg, 77% yield. White solid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.73 (d, *J* = 8.3 Hz, 1H), 8.13 (d, *J* = 8.3 Hz, 1H), 7.66 (t, *J* = 7.7 Hz, 1H), 7.59 – 7.43 (m, 2H), 7.21 – 7.14 (m, 2H), 3.56 (t, *J* = 8.4 Hz, 2H), 3.08 (t, *J* = 8.4 Hz, 2H). ^{13}C

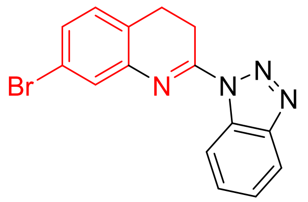
NMR (151 MHz, Chloroform-*d*) δ 157.5, 146.8, 143.8, 133.0, 131.2, 129.5, 128.6, 126.9, 126.6, 125.7, 125.2, 119.9, 115.9, 23.6, 23.3. HRMS (ESI): m/z: calcd for $C_{15}H_{11}ClN_4Na$ $(M+Na)^+$ 305.0564; found 305.0564



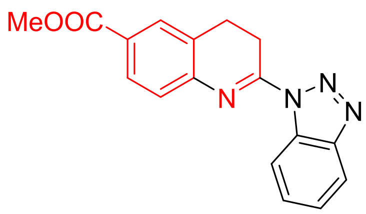
2-(1*H*-benzo[*d*][1,2,3]triazol-1-yl)-5-bromo-3,4-dihydroquinoline (3l): R_f = 0.25 (Petroleum ether/EtOAc, 5:1). 50.0 mg, 54% yield. White solid. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.72 (d, *J* = 8.3 Hz, 0.80H), 8.13 (d, *J* = 8.3 Hz, 0.80H), 7.65 (t, *J* = 7.7 Hz, H), 7.50 (t, *J* = 7.6 Hz, 1H), 7.45 (d, *J* = 8.0 Hz, 1H), 7.41 (d, *J* = 7.7 Hz, 1H), 7.19 (t, *J* = 7.9 Hz, 1H), 3.57 (t, *J* = 8.6 Hz, 2H), 3.19 (t, *J* = 8.6 Hz, 2H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 156.9, 146.8, 144.0, 131.2, 131.0, 129.4, 128.5, 126.9, 126.1, 125.7, 123.7, 119.9, 115.9, 24.2, 23.2. HRMS (ESI): m/z: calcd for $C_{15}H_{11}BrN_4Na$ $(M+Na)^+$ 349.0059; found 349.0055



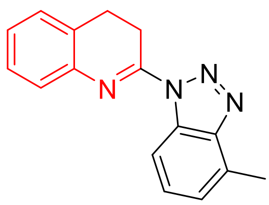
2-(1*H*-benzo[*d*][1,2,3]triazol-1-yl)-6-bromo-3,4-dihydroquinoline (3m): R_f = 0.25 (Petroleum ether/EtOAc, 5:1). 87.1 mg, 91% yield. White solid. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.68 (d, *J* = 8.3 Hz, 1H), 8.10 (d, *J* = 8.3 Hz, 1H), 7.63 (q, *J* = 8.5, 7.7 Hz, 1H), 7.47 (t, *J* = 7.7 Hz, 1H), 7.41 (dd, *J* = 8.3, 2.3 Hz, 1H), 7.33 (d, *J* = 2.5 Hz, 1H), 7.28 (d, *J* = 8.2 Hz, 1H), 3.50 (t, *J* = 8.5 Hz, 2H), 3.06 (t, *J* = 8.5 Hz, 2H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 156.6, 146.8, 141.6, 131.2, 130.7, 130.6, 129.3, 128.9, 128.1, 125.6, 120.2, 119.9, 115.9, 23.9, 23.0. HRMS (ESI): m/z: calcd for $C_{15}H_{11}BrN_4Na$ $(M+Na)^+$ 349.0059; found 349.0053



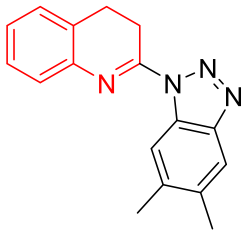
2-(1*H*-benzo[*d*][1,2,3]triazol-1-yl)-7-bromo-3,4-dihydroquinoline (3n): R_f = 0.25 (Petroleum ether/EtOAc, 5:1). 80.0 mg, 86% yield. White solid. ^1H NMR (600 MHz, Chloroform-*d*) δ 8.66 (d, *J* = 8.3 Hz, 1H), 8.08 (d, *J* = 8.5 Hz, 1H), 7.62 (t, *J* = 7.6 Hz, 1H), 7.57 (d, *J* = 2.2 Hz, 1H), 7.47 (t, *J* = 7.7 Hz, 1H), 7.29 (dd, *J* = 8.0, 2.1 Hz, 1H), 7.05 (d, *J* = 7.9 Hz, 1H), 3.50 (t, *J* = 8.5 Hz, 2H), 3.01 (t, *J* = 8.5 Hz, 2H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 157.4, 146.8, 143.9, 131.1, 129.7, 129.5, 129.4, 128.9, 125.7, 125.7, 120.6, 119.9, 115.9, 23.6, 23.2. HRMS (ESI): m/z: calcd for $C_{15}H_{11}BrN_4Na$ $(M+Na)^+$ 349.0059; found 349.0046



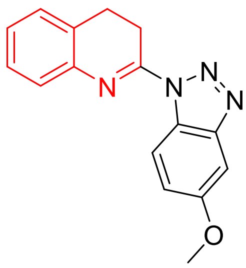
Methyl-2-(1*H*-benzo[*d*][1,2,3]triazol-1-yl)-3,4-dihydroquinoline-6-carboxylate (3o): R_f = 0.25 (Petroleum ether/EtOAc, 5:1). 40.0 mg, 46% yield. White solid. ^1H NMR (600 MHz, Chloroform-*d*) δ 8.75 (d, *J* = 8.3 Hz, 1H), 8.13 (d, *J* = 8.3 Hz, 1H), 8.00 (dd, *J* = 8.1, 1.9 Hz, 1H), 7.92 (d, *J* = 2.1 Hz, 1H), 7.71 – 7.64 (m, 1H), 7.53 – 7.46 (m, 2H), 3.94 (s, 3H), 3.59 (t, *J* = 8.4 Hz, 2H), 3.15 (t, *J* = 8.5 Hz, 2H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 166.7, 166.3, 159.7, 146.7, 146.6, 131.1, 130.4, 129.2, 128.3, 128.1, 126.8, 126.5, 120.2, 116.3, 52.5, 23.4, 23.2. HRMS (ESI): m/z: calcd for $C_{17}H_{14}N_4O_2Na$ $(M+Na)^+$ 329.1009; found 329.1008



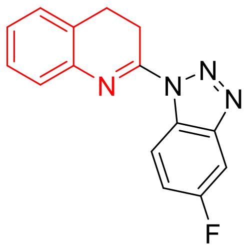
2-(4-methyl-1*H*-benzo[*d*][1,2,3]triazol-1-yl)-3,4-dihydroquinoline (3p): R_f = 0.25 (Petroleum ether/EtOAc, 5:1). 60.0 mg, 85% yield. White solid. ^1H NMR (600 MHz, Chloroform-*d*) δ 8.55 (d, *J* = 8.3 Hz, 1H), 7.51 (t, *J* = 7.7 Hz, 1H), 7.44 (d, *J* = 7.7 Hz, 1H), 7.30 (td, J = 7.7, 7.1, 2.4 Hz, 1H), 7.26 – 7.22 (m, 1H), 7.22 – 7.15 (m, 2H), 3.52 (t, J = 8.4 Hz, 2H), 3.08 (t, J = 8.5 Hz, 2H), 2.84 (s, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 156.5, 146.6, 142.7, 131.2, 130.7, 129.2, 127.7, 127.6, 127.0, 126.9, 126.7, 125.6, 113.2, 24.2, 23.4, 16.6. HRMS (ESI): m/z: calcd for $C_{16}H_{14}N_4Na$ $(M+Na)^+$ 285.1111; found 2285.1110



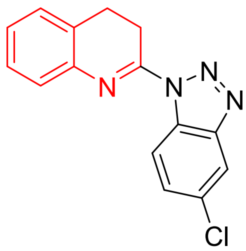
2-(5,6-dimethyl-1*H*-benzo[*d*][1,2,3]triazol-1-yl)-3,4-dihydroquinoline (3q): R_f = 0.25 (Petroleum ether/EtOAc, 5:1). 60.0 mg, 75% yield. White solid. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.48 (s, 1H), 7.83 (s, 1H), 7.46 (d, J = 7.7 Hz, 1H), 7.34 – 7.27 (m, 1H), 7.23 – 7.16 (m, 2H), 3.50 (t, J = 8.4 Hz, 2H), 3.07 (t, J = 8.5 Hz, 2H), 2.49 (s, 3H), 2.43 (s, 3H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 157.3, 145.7, 142.7, 140.2, 135.8, 130.0, 128.2, 127.9, 127.7, 127.4, 126.8, 119.1, 115.5, 23.7, 23.3, 21.1, 20.3. HRMS (ESI): m/z: calcd for $C_{17}H_{16}N_4Na$ $(M+Na)^+$ 299.1267; found 299.1269



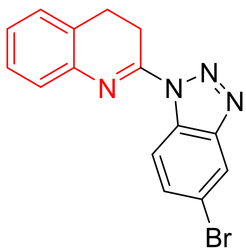
2-(5-methoxy-1*H*-benzo[*d*][1,2,3]triazol-1-yl)-3,4-dihydroquinoline (3r): R_f = 0.25 (Petroleum ether/EtOAc, 5:1). 35.0 mg, 44% yield. White solid. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.20 (d, J = 2.4 Hz, 1H), 7.96 (d, J = 9.0 Hz, 1H), 7.42 (d, J = 7.7 Hz, 1H), 7.32 (dd, J = 7.2, 2.1 Hz, 1H), 7.25 – 7.19 (m, 2H), 7.11 (dd, J = 9.0, 2.4, 0.9 Hz, 1H), 3.98 (d, J = 0.9 Hz, 3H), 3.56 – 3.50 (m, 2H), 3.10 (t, J = 8.4 Hz, 2H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 161.2, 156.8, 142.6, 142.0, 132.7, 127.7, 127.6, 127.1, 126.9, 126.6, 120.4, 117.2, 96.8, 55.8, 24.2, 23.4. HRMS (ESI): m/z: calcd for $C_{16}H_{14}N_4ONa$ $(M+Na)^+$ 3301.1060; found 301.1060



2-(5-fluoro-1*H*-benzo[*d*][1,2,3]triazol-1-yl)-3,4-dihydroquinoline (3s): R_f = 0.25 (Petroleum ether/EtOAc, 5:1). 39.0 mg, 53% yield. White solid. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.45 (dd, *J* = 8.6, 2.4 Hz, 1H), 8.07 (dd, *J* = 9.0, 4.7 Hz, 1H), 7.45 (d, *J* = 7.7 Hz, 1H), 7.33 (td, *J* = 8.0, 6.6, 3.6 Hz, 1H), 7.28 – 7.25 (m, 1H), 7.24 – 7.20 (m, 2H), 3.52 (t, *J* = 8.5 Hz, 2H), 3.11 (t, *J* = 8.5 Hz, 2H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 163.2 (d, *J* = 249.3 Hz), 156.3, 143.5, 139.4, 142.3, 127.8, 127.7, 127.3, 126.8 (d, *J* = 2.3 Hz), 121.2, 121.1, 115.2 (d, *J* = 26.8 Hz), 102.2 (d, *J* = 29.3 Hz), 24.1, 23.3. ^{19}F NMR (565 MHz, Chloroform-d) δ -109.49. HRMS (ESI): m/z: calcd for $C_{15}H_{11}FN_4Na$ $(M+Na)^+$ 289.0860; found 289.0859

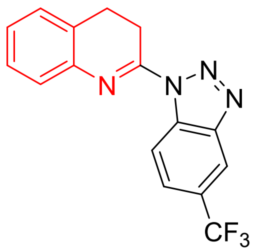


2-(5-chloro-1*H*-benzo[*d*][1,2,3]triazol-1-yl)-3,4-dihydroquinoline (3t): R_f = 0.25 (Petroleum ether/EtOAc, 5:1). 38.3 mg, 47% yield. White solid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.80 (s, 1H), 8.04 (d, *J* = 9.1 Hz, 1H), 7.48 (t, *J* = 7.3 Hz, 2H), 7.37 – 7.30 (m, 1H), 7.23 (d, *J* = 4.3 Hz, 2H), 3.53 (t, *J* = 8.5 Hz, 2H), 3.12 (t, *J* = 8.5 Hz, 2H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 156.2, 145.3, 142.3, 135.6, 131.8, 127.8, 127.7, 127.4, 126.9, 126.8, 126.6, 120.6, 115.9, 24.1, 23.3. HRMS (ESI): m/z: calcd for $C_{15}H_{11}ClN_4Na$ $(M+Na)^+$ 305.0564; found 305.0566

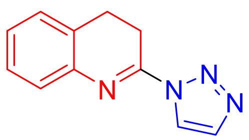


2-(5-bromo-1*H*-benzo[*d*][1,2,3]triazol-1-yl)-3,4-dihydroquinoline (3u): R_f = 0.25

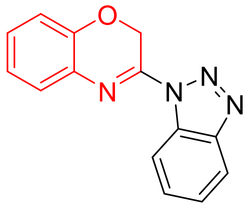
(Petroleum ether/EtOAc, 5:1). 32.0 mg, 35% yield. White solid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.96 (d, *J* = 1.8 Hz, 1H), 7.97 (d, *J* = 8.7 Hz, 1H), 7.60 (dd, *J* = 8.8, 1.9 Hz, 1H), 7.48 (d, *J* = 7.7 Hz, 1H), 7.33 (dd, *J* = 8.0, 4.3 Hz, 1H), 7.23 (d, *J* = 4.5 Hz, 2H), 3.52 (t, *J* = 8.5 Hz, 2H), 3.11 (t, *J* = 8.5 Hz, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 156.1, 145.6, 142.3, 132.1, 129.2, 127.8, 127.7, 127.4, 126.9, 126.8, 123.7, 120.8, 118.9, 24.1, 23.3. HRMS (ESI): m/z: calcd for $C_{15}H_{11}BrN_4Na$ $(M+Na)^+$ 349.0059; found 349.0057



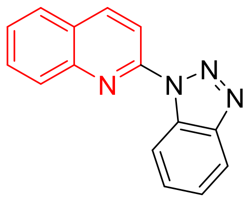
2-(1*H*-benzo[*d*][1,2,3]triazol-1-yl)-5-(trifluoromethyl)-3,4-dihydroquinoline (3v): R_f = 0.25 (Petroleum ether/EtOAc, 5:1). 28.4 mg, 30% yield. White solid. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 9.12 (s, 1H), 8.25 (d, *J* = 8.6 Hz, 1H), 7.74 (dd, *J* = 8.7, 1.7 Hz, 1H), 7.49 (d, *J* = 7.7 Hz, 1H), 7.38 – 7.32 (m, 1H), 7.26 – 7.24 (m, 2H), 3.56 (t, *J* = 8.5 Hz, 2H), 3.14 (t, *J* = 8.5 Hz, 2H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 156.1, 147.9, 142.1, 131.2 (q, *J* = 32.5 Hz), 130.7, 127.9, 127.8, 127.7, 127.0, 126.8, 123.9 (q, *J* = 271.8 Hz), 122.4 (q, *J* = 3.6 Hz), 120.7, 114.3 (q, *J* = 4.7 Hz), 24.1, 23.4. ^{19}F NMR (565 MHz, Chloroform-d) δ -61.62. HRMS (ESI): m/z: calcd for $C_{16}H_{11}F_3N_4Na$ $(M+Na)^+$ 339.0828; found 339.0831



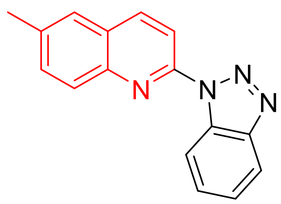
2-(1*H*-1,2,3-triazol-1-yl)-3,4-dihydroquinoline (3w): R_f = 0.25 (Petroleum ether/EtOAc, 5:1). 19.1 mg, 32% yield. White solid. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.62 (d, *J* = 1.2 Hz, 1H), 7.82 (d, *J* = 1.3 Hz, 1H), 7.35 (d, *J* = 7.7 Hz, 1H), 7.30 (dd, *J* = 7.8, 6.1, 2.8 Hz, 1H), 7.24 – 7.20 (m, 2H), 3.41 (t, *J* = 8.5 Hz, 2H), 3.06 (t, *J* = 8.5 Hz, 2H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 154.2, 141.9, 139.7, 137.1, 134.2, 127.8, 126.9, 120.7, 112.8, 24.0, 22.8. HRMS (ESI): m/z: calcd for $C_{11}H_{10}N_4Na$ $(M+Na)^+$ 221.0798; found 221.0797



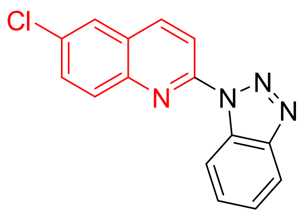
3-(1*H*-benzo[*d*][1,2,3]triazol-1-yl)-2*H*-benzo[*b*][1,4]oxazine (3x): R_f = 0.25 (Petroleum ether/EtOAc, 5:1). 60.0 mg, 83% yield. White solid. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.65 (d, *J* = 8.3 Hz, 1H), 8.14 (d, *J* = 8.3 Hz, 1H), 7.68 (t, *J* = 7.7 Hz, 1H), 7.52 (t, *J* = 7.7 Hz, 1H), 7.43 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.19 (td, *J* = 7.7, 1.6 Hz, 1H), 7.06 (td, *J* = 7.6, 1.4 Hz, 1H), 6.99 (dd, *J* = 8.0, 1.5 Hz, 1H), 5.58 (s, 2H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 149.1, 146.4, 146.0, 131.5, 130.9, 129.7, 128.8, 127.3, 126.0, 122.7, 120.1, 116.0, 115.3, 61.1. HRMS (ESI): m/z: calcd for $C_{14}H_{10}N_4ONa$ $(M+Na)^+$ 273.0747; found 273.0747



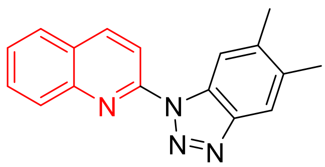
2-(1*H*-benzo[*d*][1,2,3]triazol-1-yl)quinoline (4a)[4]: R_f = 0.25 (Petroleum ether/EtOAc, 5:1). 42.6 mg, 60% yield. White solid. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.97 (d, *J* = 8.3 Hz, 1H), 8.50 (d, *J* = 8.8 Hz, 1H), 8.38 (d, *J* = 8.8 Hz, 1H), 8.18 – 8.14 (m, 2H), 7.90 (d, *J* = 8.1 Hz, 1H), 7.80 (m, *J* = 8.4, 6.8, 1.5 Hz, 1H), 7.69 (t, *J* = 7.7 Hz, 1H), 7.59 (t, *J* = 7.5 Hz, 1H), 7.51 (t, *J* = 7.6 Hz, 1H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 150.4, 146.9, 146.5, 139.1, 131.6, 130.5, 128.9, 128.8, 127.7, 127.0, 126.6, 125.1, 119.8, 115.4, 113.4.



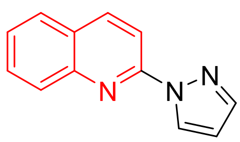
2-(1*H*-benzo[*d*][1,2,3]triazol-1-yl)-6-methylquinoline (4b)[4]: R_f = 0.25 (Petroleum ether/EtOAc, 5:1). 36.0 mg, 49% yield. White solid. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.96 (d, *J* = 8.3 Hz, 1H), 8.45 (dd, *J* = 8.7, 2.3 Hz, 1H), 8.29 (d, *J* = 8.7 Hz, 1H), 8.16 (d, *J* = 8.3 Hz, 1H), 8.06 (d, $J = 8.4$ Hz, 1H), 7.67 (d, $J = 8.0$ Hz, 2H), 7.63 (d, $J = 8.7$ Hz, 1H), 7.50 (t, $J = 7.6$ Hz, 1H), 2.58 (s, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 149.9, 146.9, 145.0, 138.5, 136.7, 132.7, 131.6, 128.9, 128.5, 127.1, 126.7, 125.1, 119.8, 115.4, 113.4, 21.6.



2-(1*H*-benzo[*d*][1,2,3]triazol-1-yl)-6-chloroquinoline (4c)[4]: $R_f = 0.25$ (Petroleum ether/EtOAc, 5:1). 42.0 mg, 52% yield. White solid. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.89 (d, $J = 8.3$ Hz, 1H), 8.50 (d, $J = 8.9$ Hz, 1H), 8.26 (d, $J = 8.9$ Hz, 1H), 8.15 (d, $J = 8.3$ Hz, 1H), 8.07 (d, $J = 8.9$ Hz, 1H), 7.85 (d, $J = 2.3$ Hz, 1H), 7.71 (dd, $J = 8.9, 2.3$ Hz, 1H), 7.69 – 7.63 (m, 1H), 7.53 – 7.45 (m, 1H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 150.6, 146.9, 144.9, 138.2, 132.3, 131.5, 131.4, 130.3, 129.1, 127.6, 126.5, 125.3, 119.9, 115.3, 114.3.



2-(5,6-dimethyl-1*H*-benzo[*d*][1,2,3]triazol-1-yl)quinoline (4d)[5]: $R_f = 0.25$ (Petroleum ether/EtOAc, 5:1). 32.9 mg, 40% yield. White solid. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.71 (s, 1H), 8.48 (d, $J = 8.9$ Hz, 1H), 8.37 (d, $J = 8.9$ Hz, 1H), 8.20 (d, $J = 8.4$ Hz, 1H), 7.90 (d, $J = 7.3$ Hz, 2H), 7.80 (dd, $J = 8.3, 6.8, 1.5$ Hz, 1H), 7.59 (t, $J = 7.6$ Hz, 1H), 2.55 (s, 3H), 2.47 (s, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 150.1, 146.6, 143.0, 141.7, 139.4, 139.10, 130.6, 130.4, 128.8, 127.8, 127.0, 126.5, 119.0, 114.8, 113.6, 21.1, 20.5.



(1*H*-pyrazol-1-yl)quinoline (4e)[5]: $R_f = 0.25$ (Petroleum ether/EtOAc, 5:1). 40.0 mg, 67% yield. White solid. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.39 (s, 0.34H), 8.78 (d, $J = 2.6$ Hz, 1H), 8.20 (q, J = 8.8 Hz, 2H), 7.99 (d, J = 8.4 Hz, 1H), 7.77 (d, J = 7.8 Hz, 2H), 7.68 (t, J = 7.6 Hz, 1H), 7.46 (t, J = 7.5 Hz, 1H), 6.50 (t, J = 2.2 Hz, 1H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 150.2, 146.6, 142.3, 139.0, 130.3, 128.5, 127.7, 127.4, 127.0, 125.9, 112.3, 108.2.

6. References

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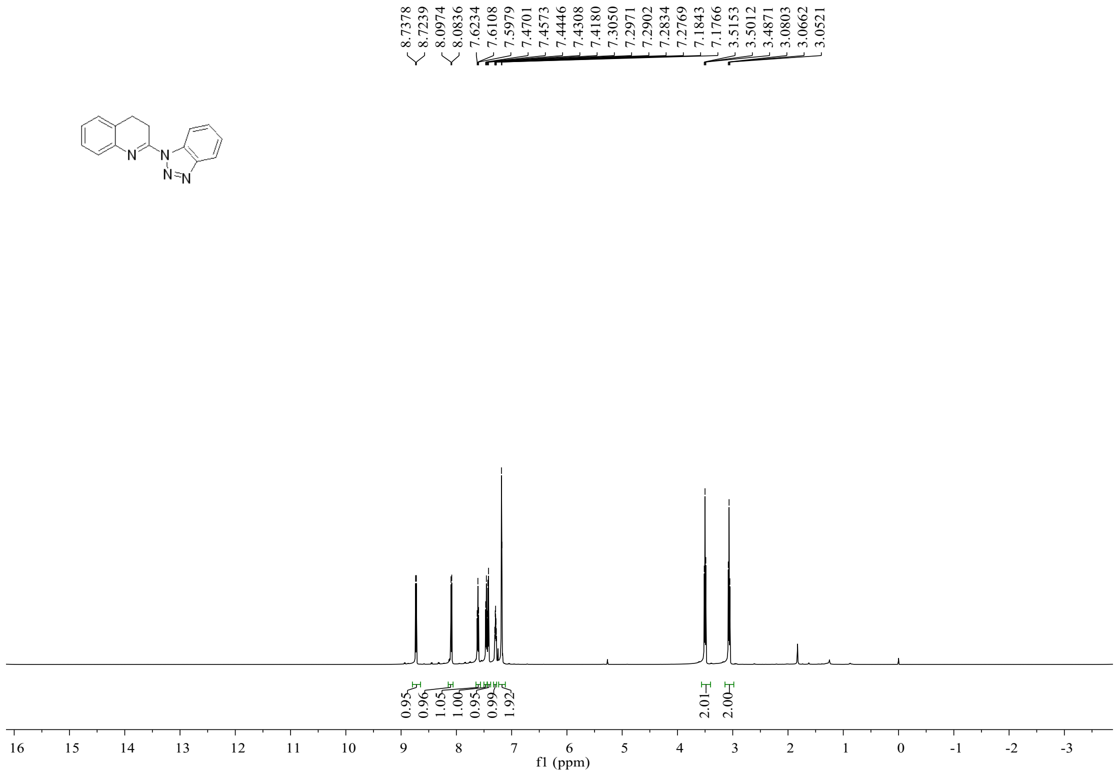
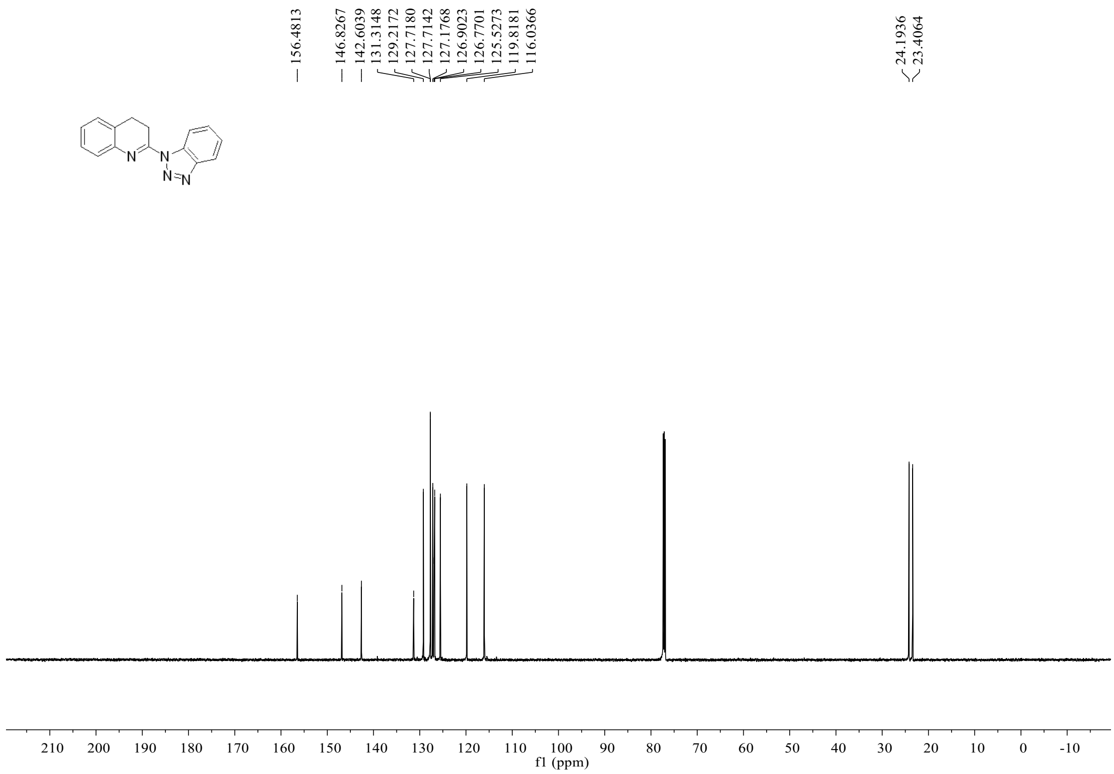
7. NMR Spectra of Products

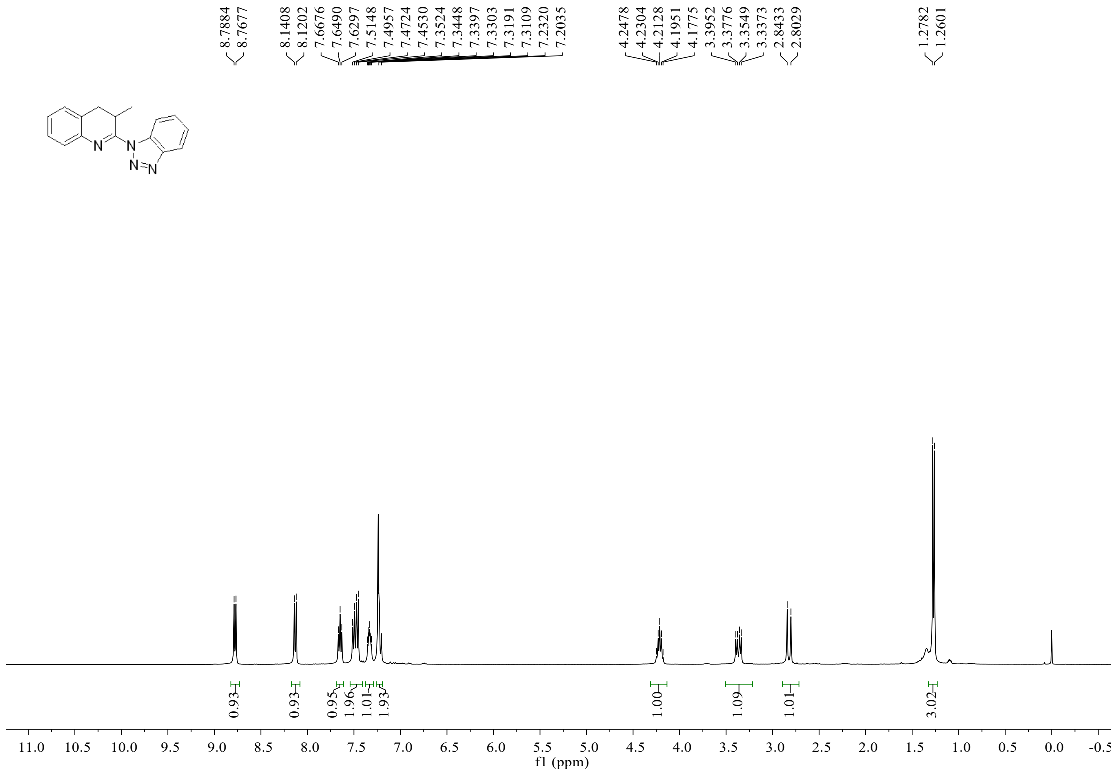
^{1}H-NMR Spectrum (600 MHz, $CDCl_3$) of 3a



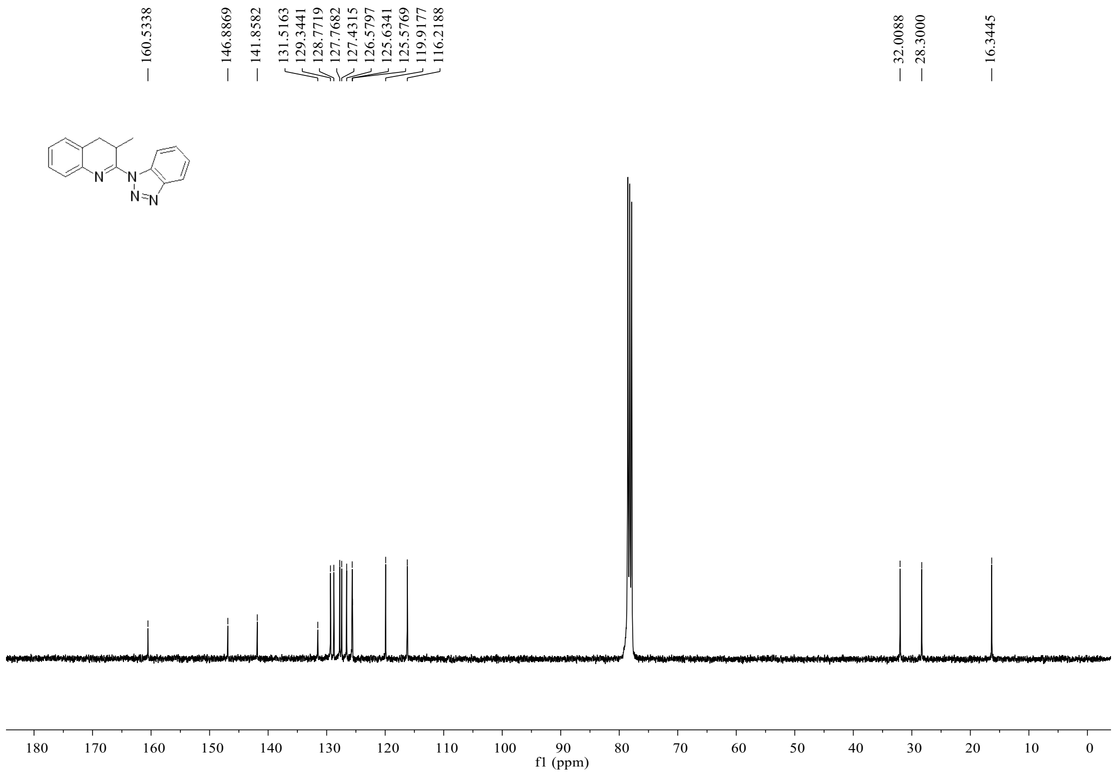
^{13}C-NMR Spectrum (151 MHz, $CDCl_3$) of 3a



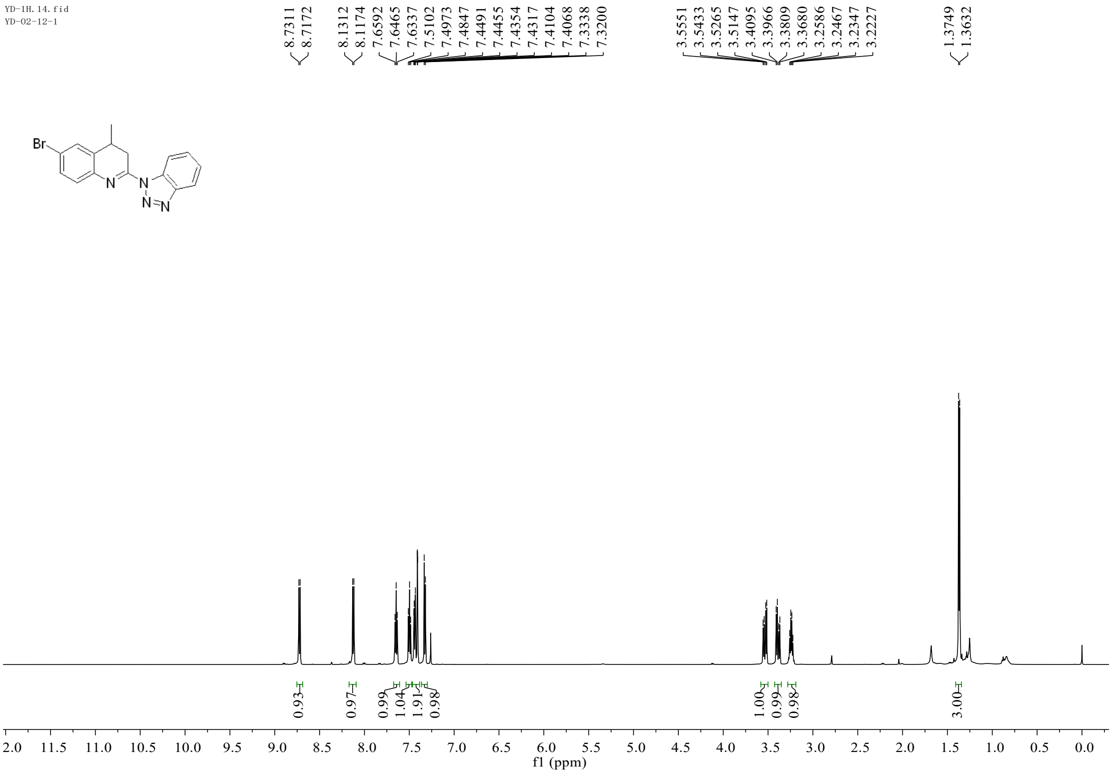
^{1}H-NMR Spectrum (400MHz, $CDCl_3$) of 3b



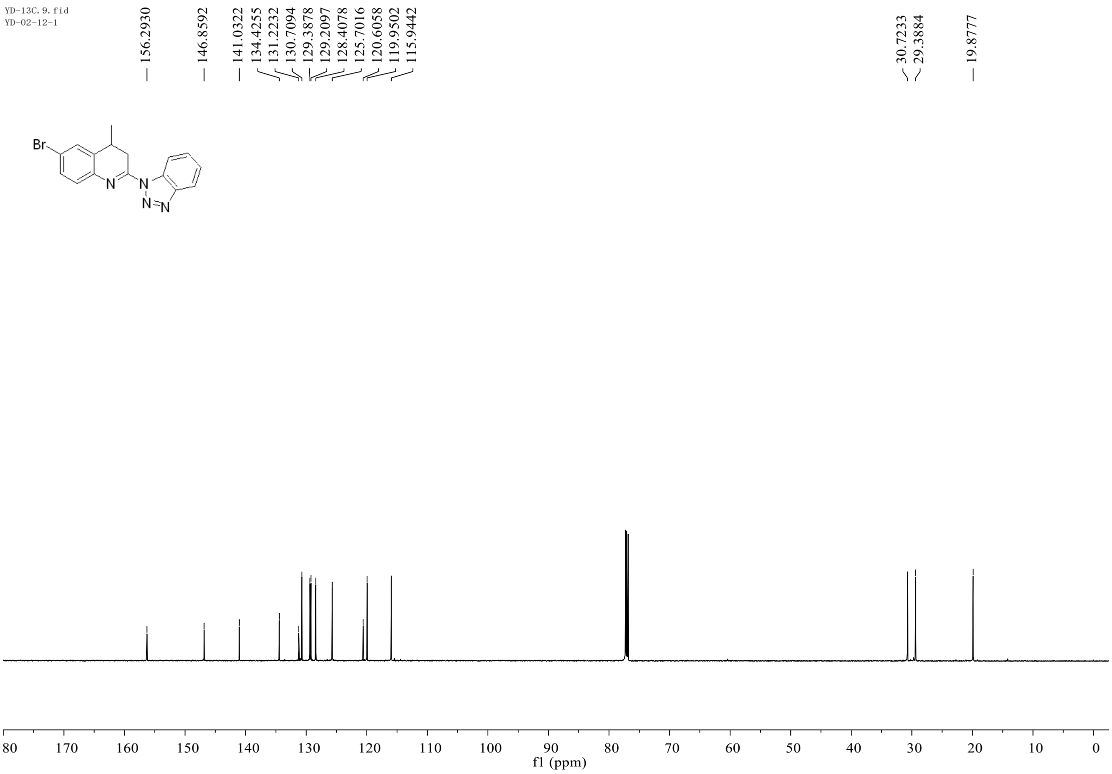
^{13}C-NMR Spectrum (101MHz, $CDCl_3$) of 3b



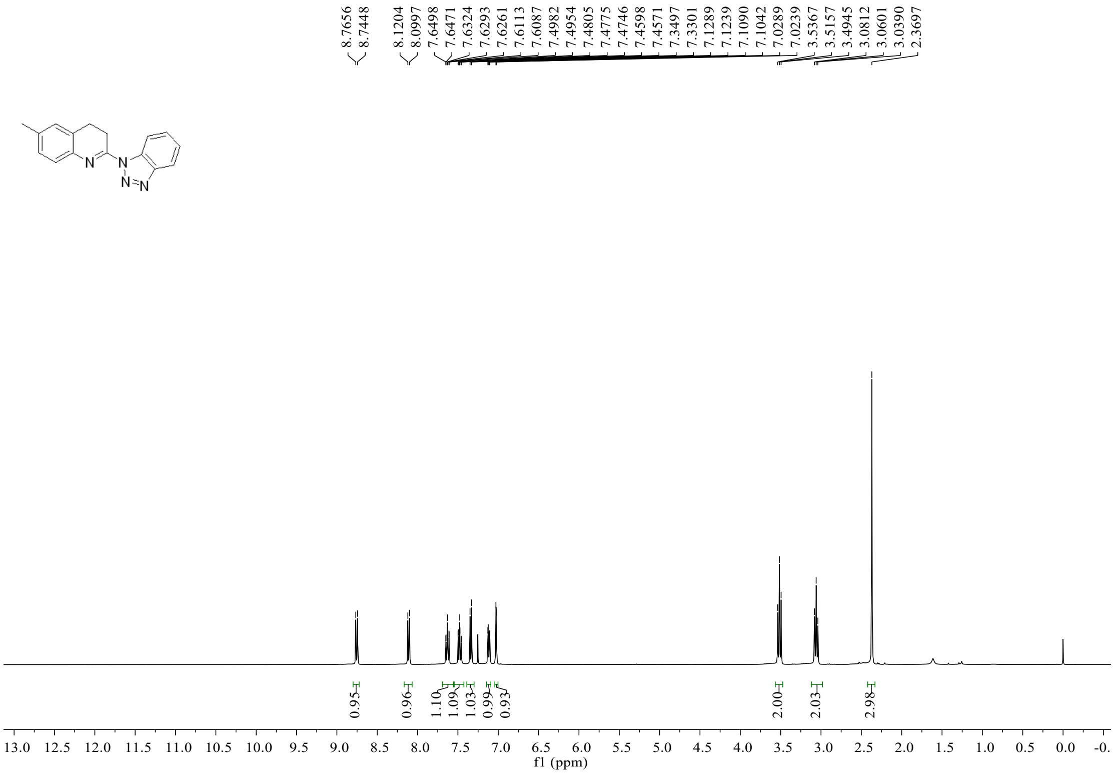
[1]H-NMR Spectrum (600 MHz, $CDCl_3$) of 3c



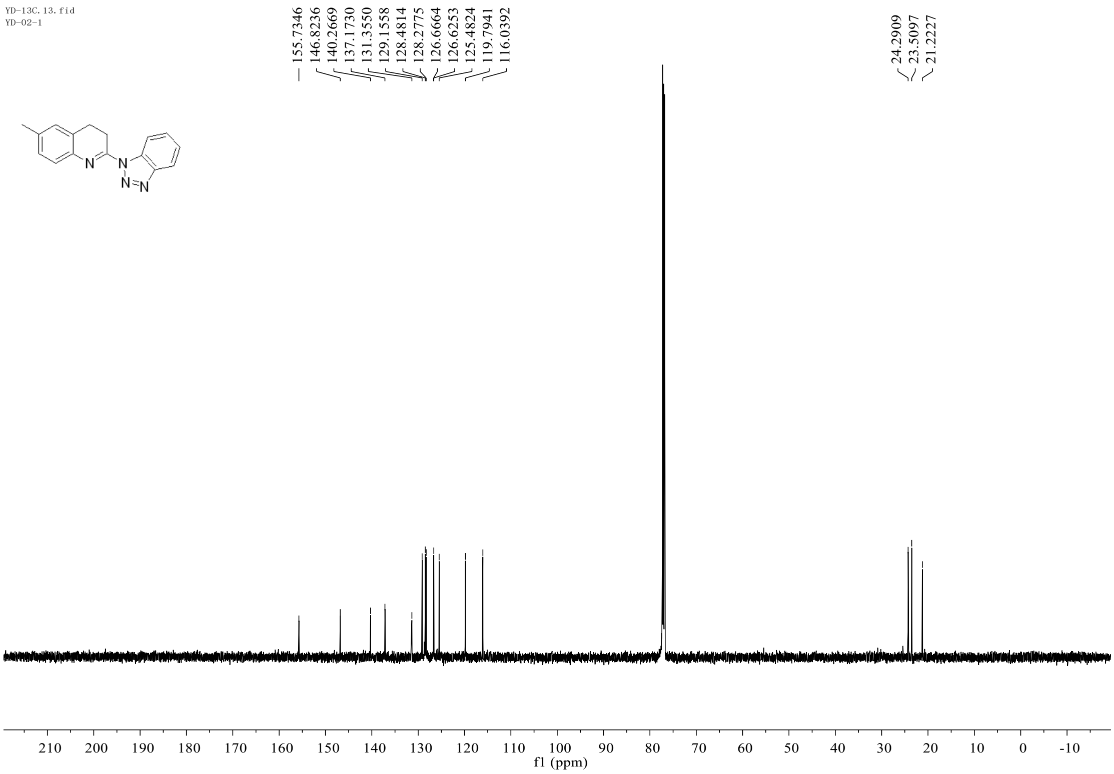
[13]C-NMR Spectrum (151 MHz, $CDCl_3$) of 3c



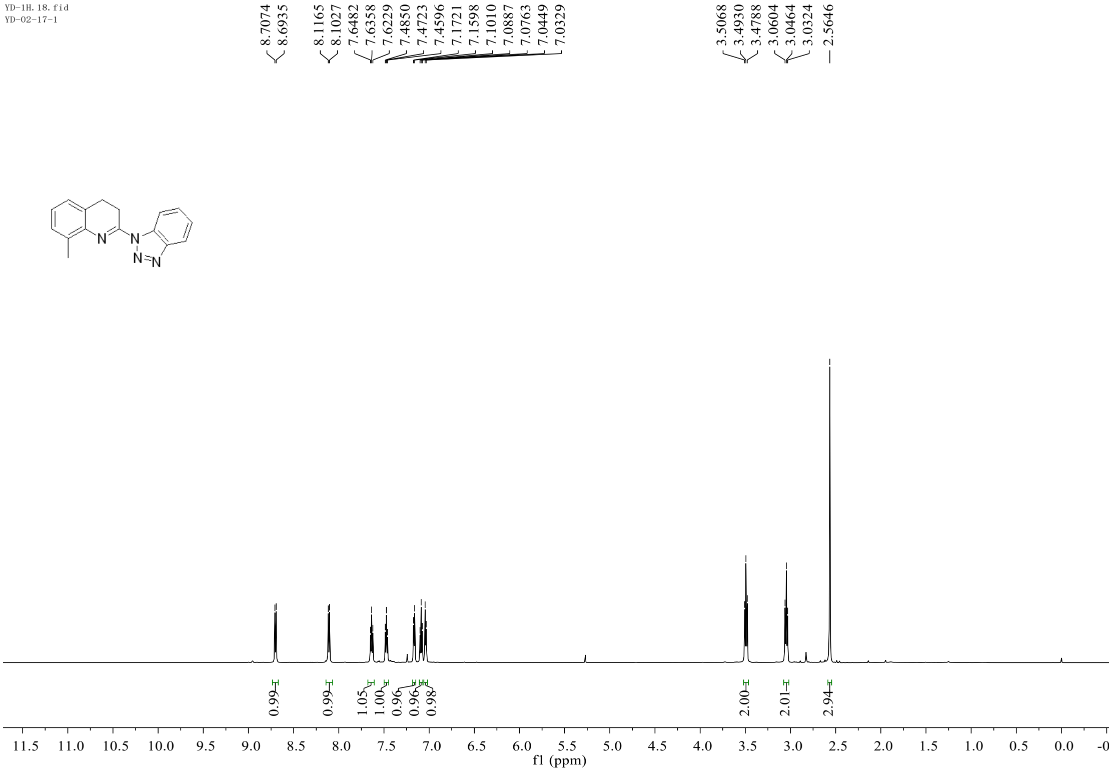
[1]H-NMR Spectrum (400MHz, $CDCl_3$) of 3d



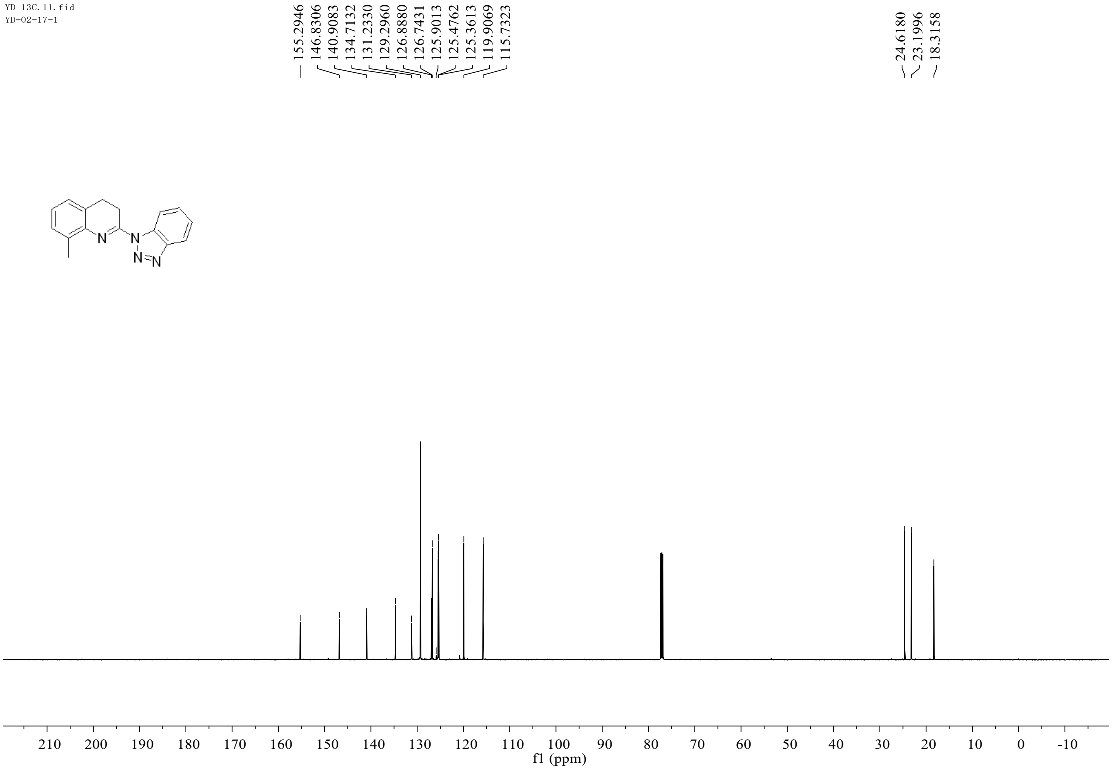
[13]C-NMR Spectrum (151MHz, $CDCl_3$) of 3d



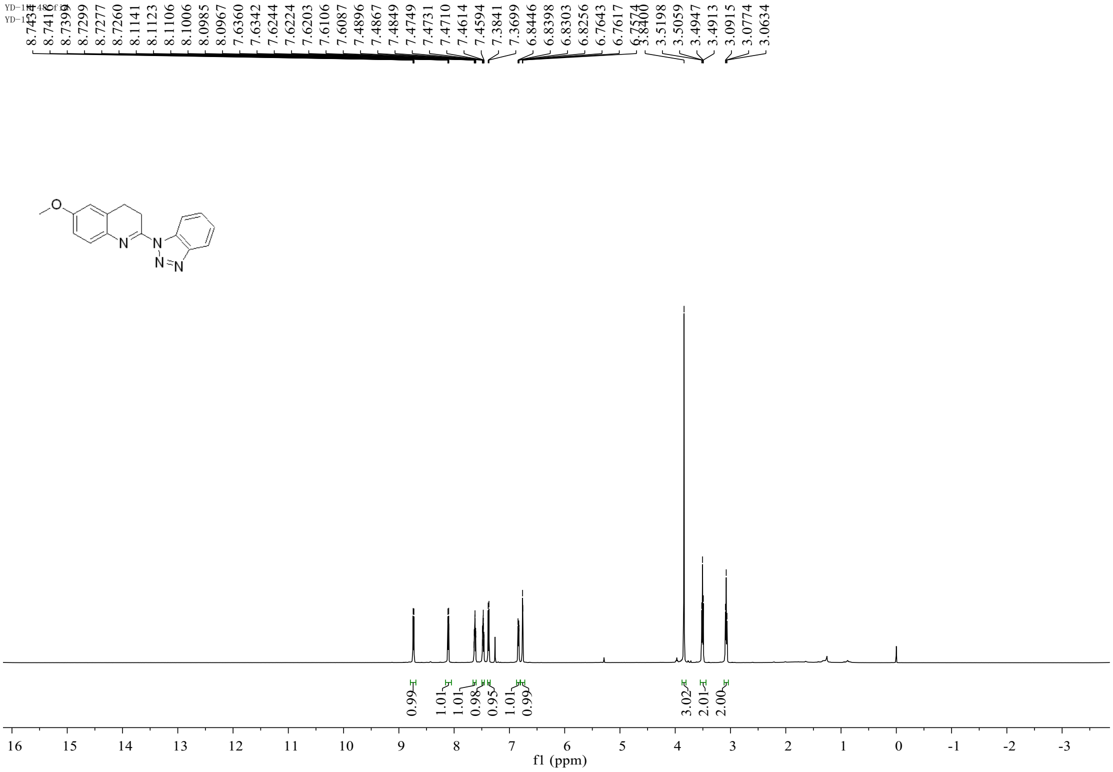
^{1}H-NMR Spectrum (600 MHz, $CDCl_3$) of 3e



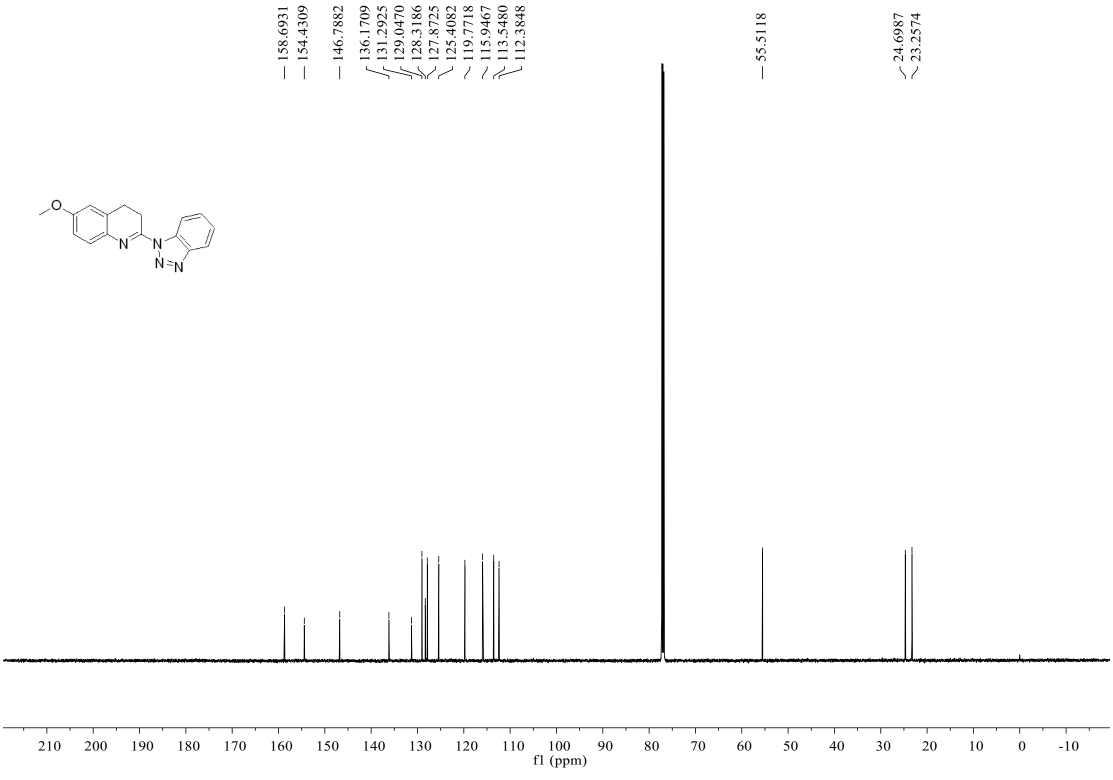
^{13}C-NMR Spectrum (151 MHz, $CDCl_3$) of 3e



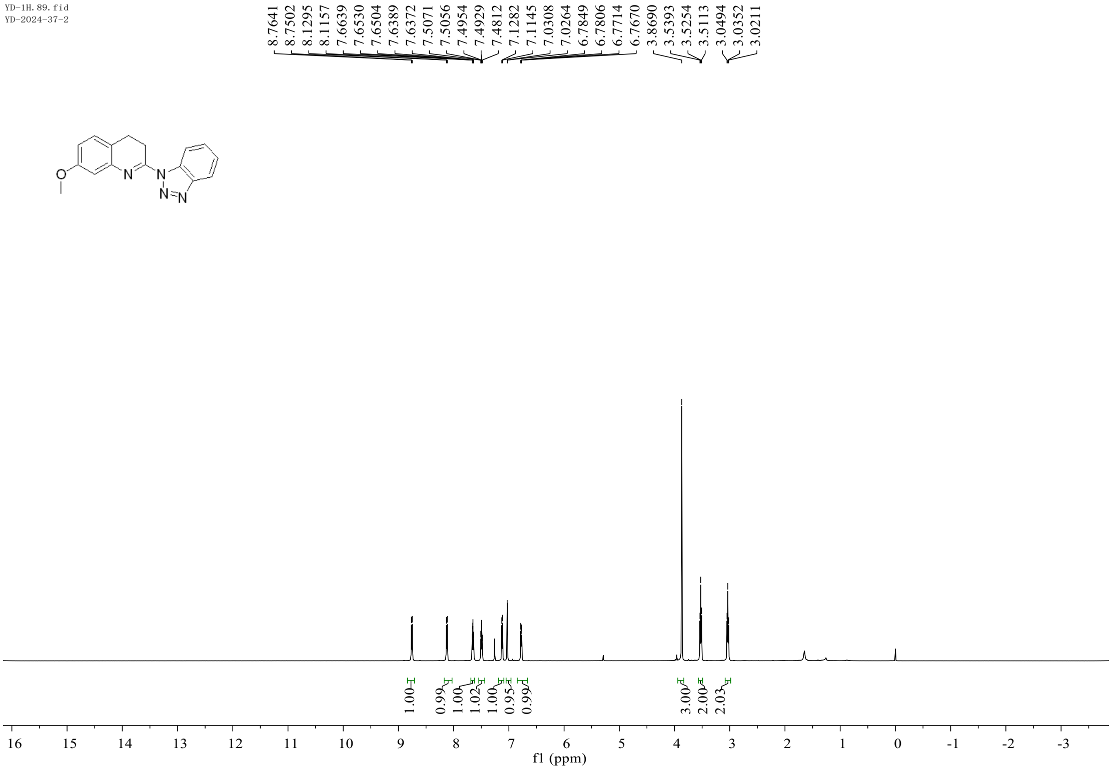
^{1}H-NMR Spectrum (400MHz, $CDCl_3$) of 3f



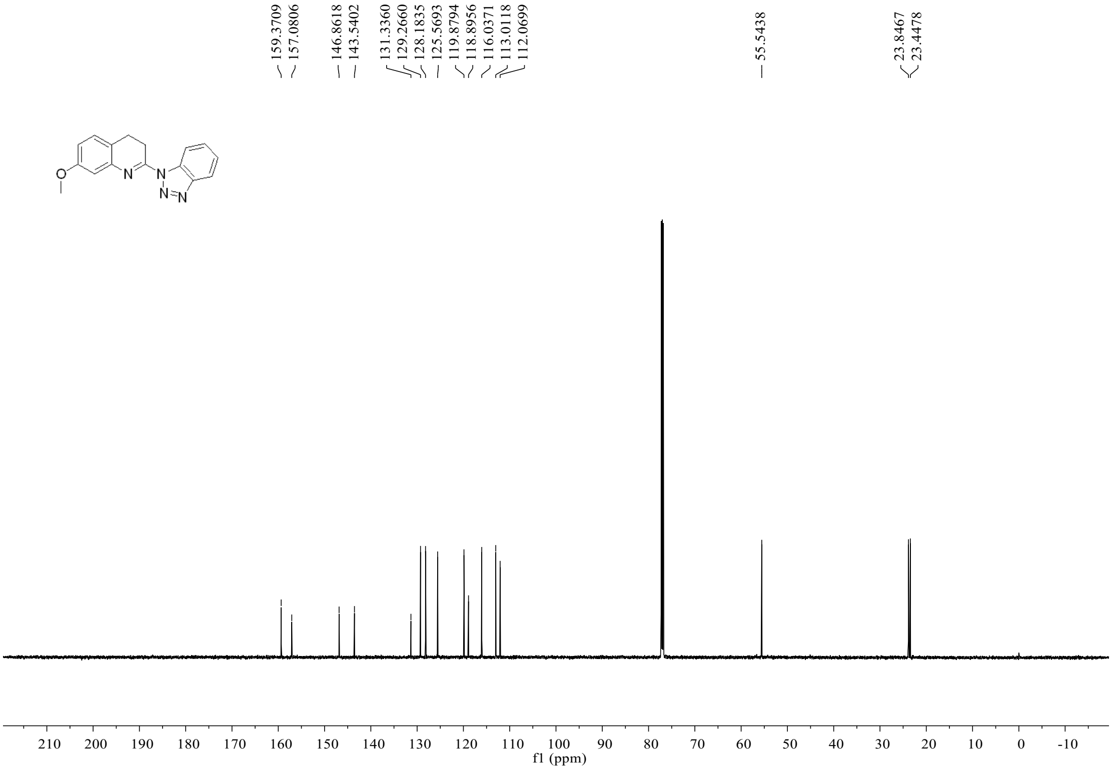
^{13}C-NMR Spectrum (101MHz, $CDCl_3$) of 3f



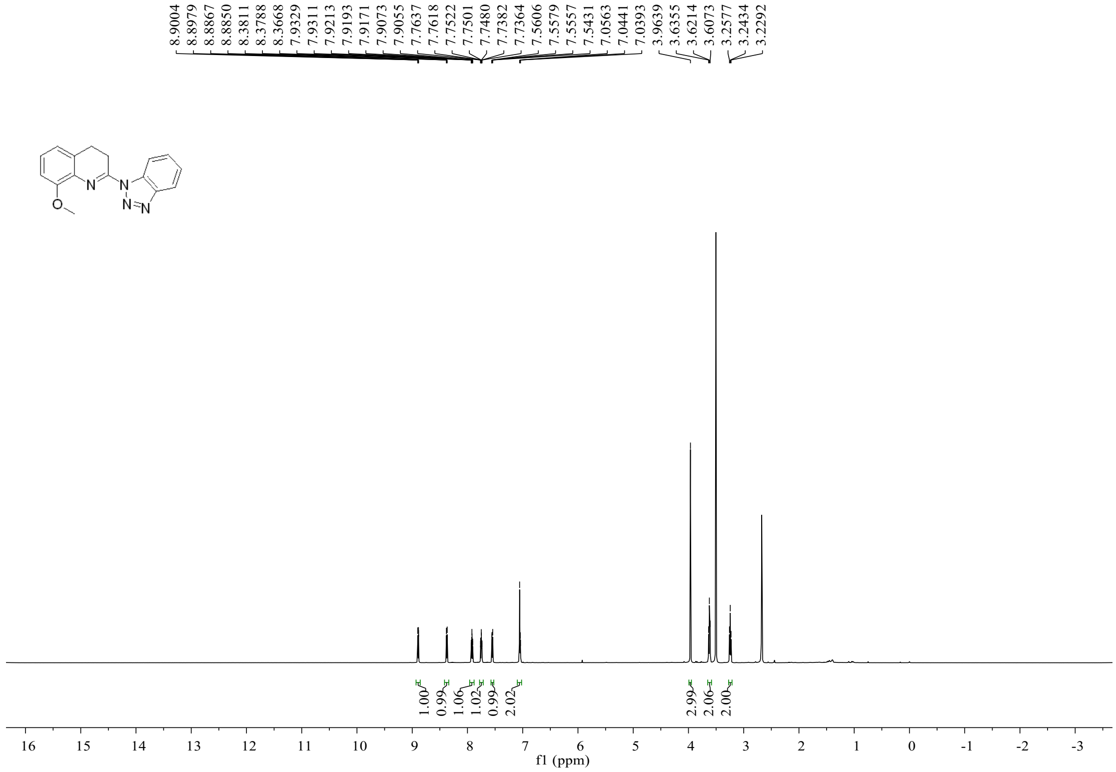
¹H-NMR Spectrum (600 MHz, $CDCl_3$) of 3g



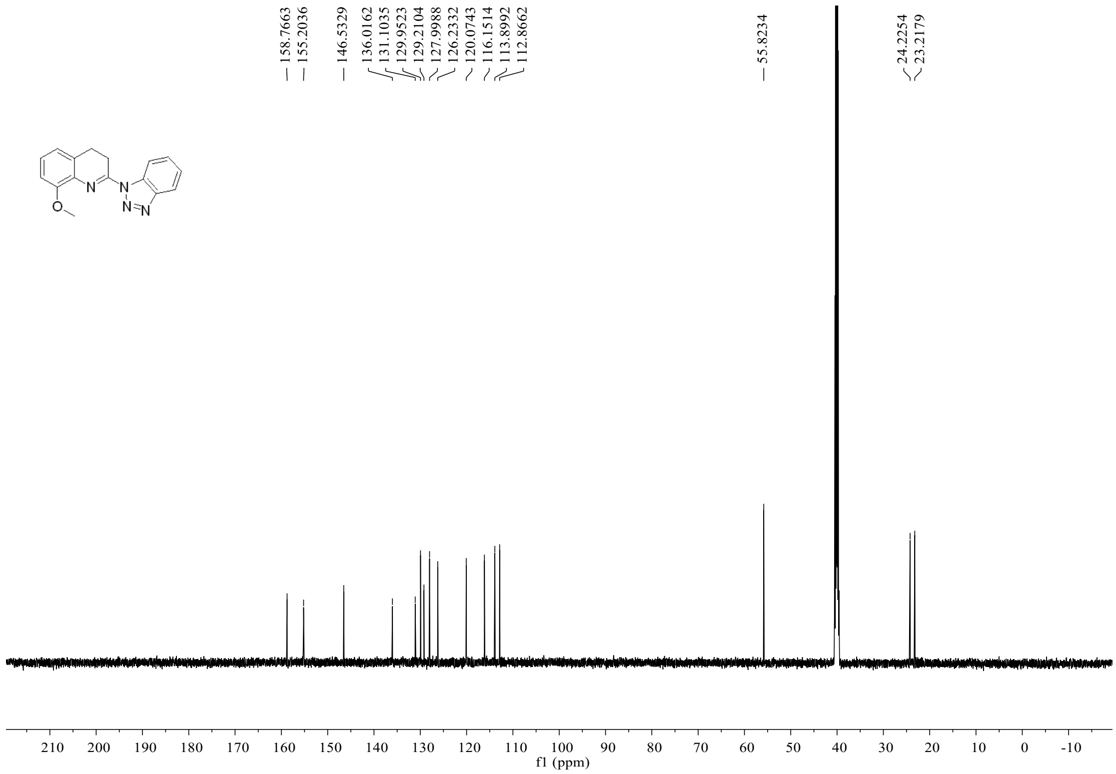
¹³C-NMR Spectrum (151 MHz, $CDCl_3$) of 3g



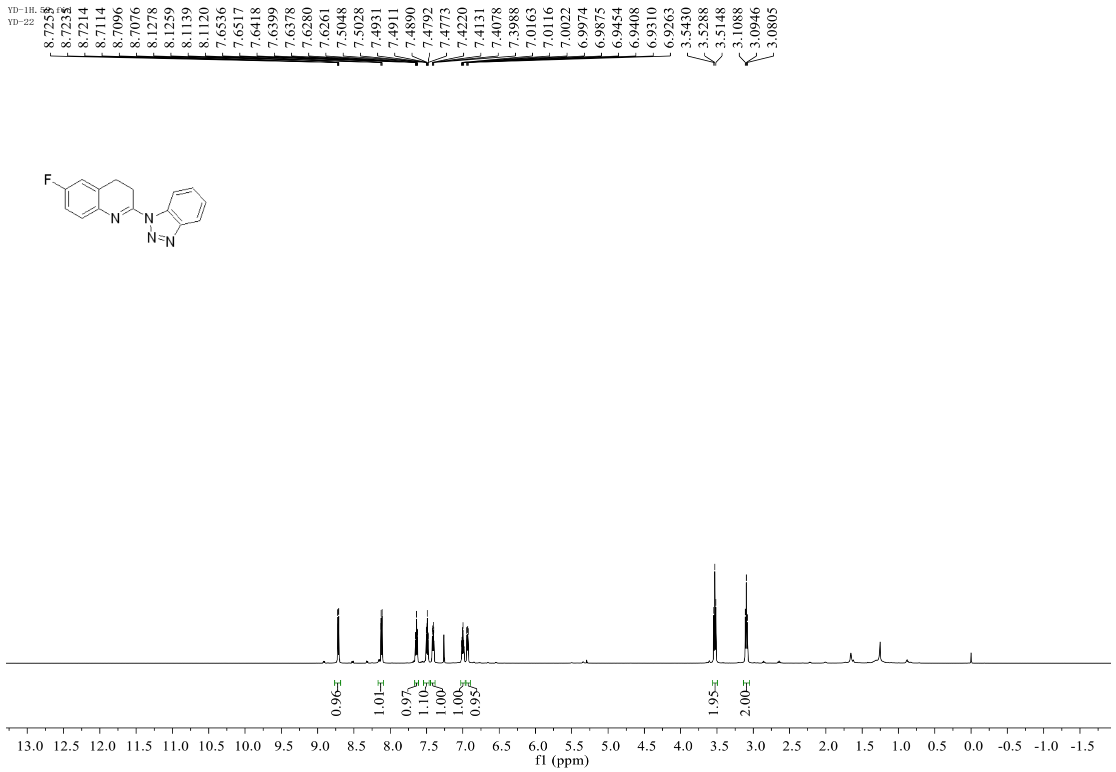
[1]H-NMR Spectrum (600MHz, DMSO) of 3h



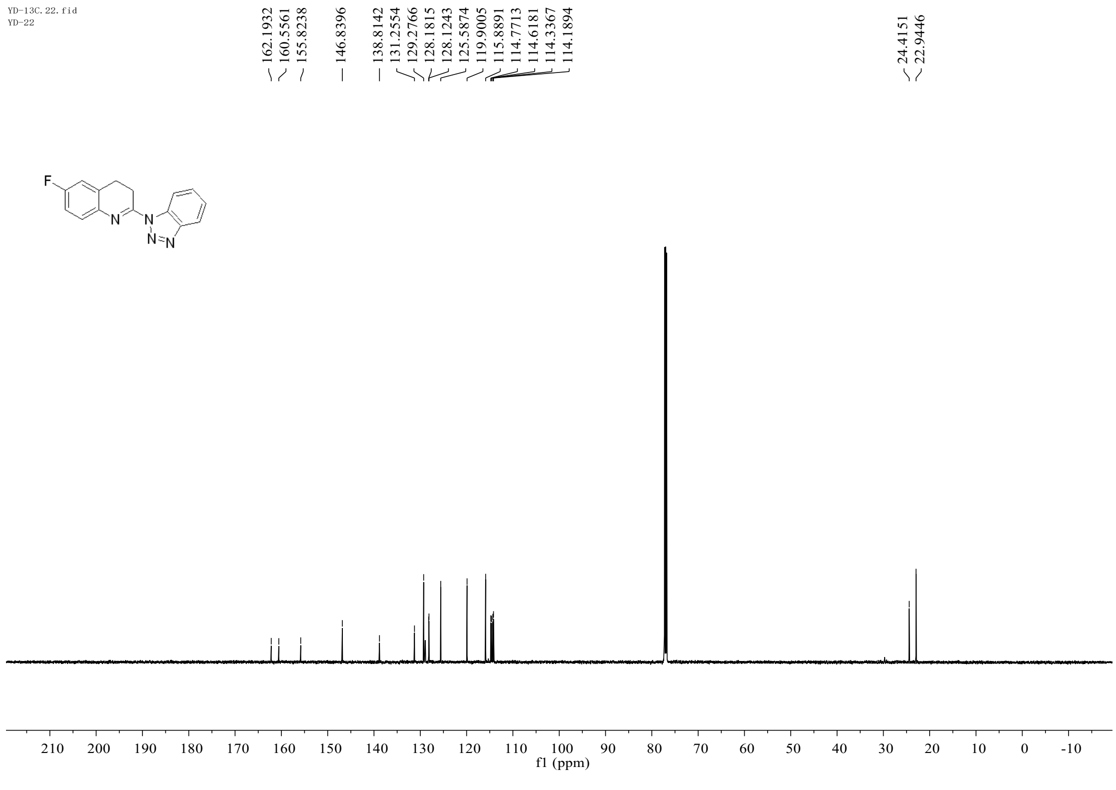
[13]C-NMR Spectrum (151MHz, DMSO) of 3h



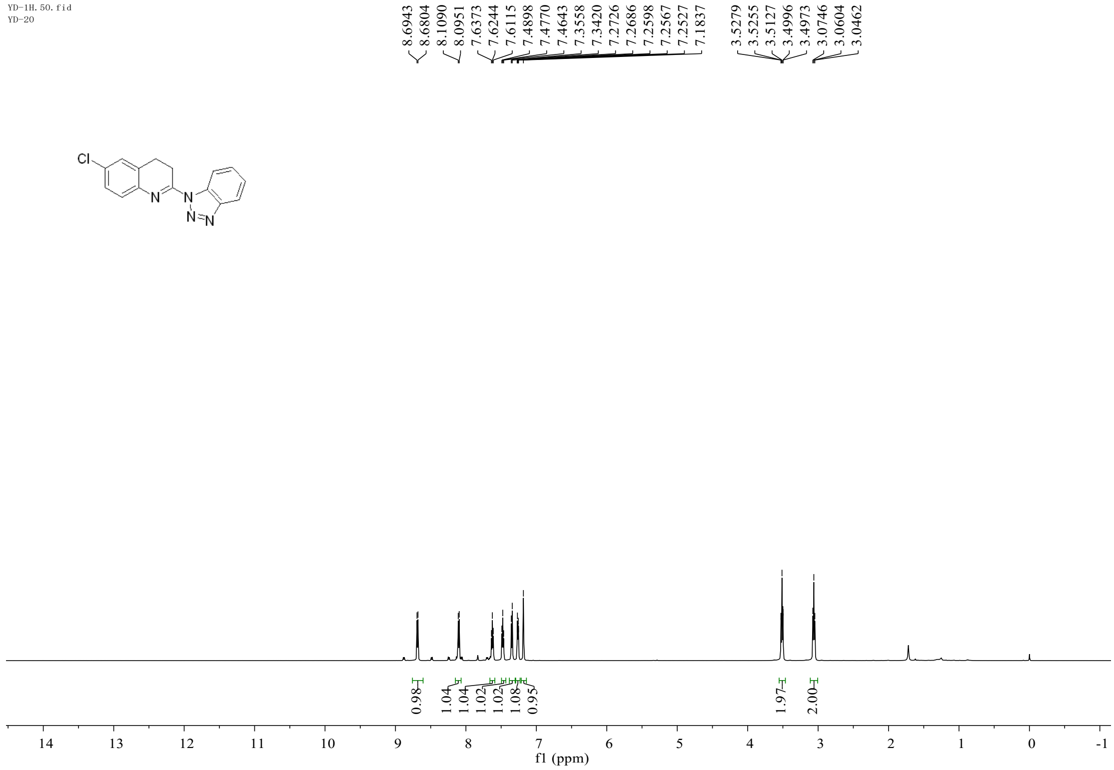
^{1}H-NMR Spectrum (600 MHz, $CDCl_3$) of 3i



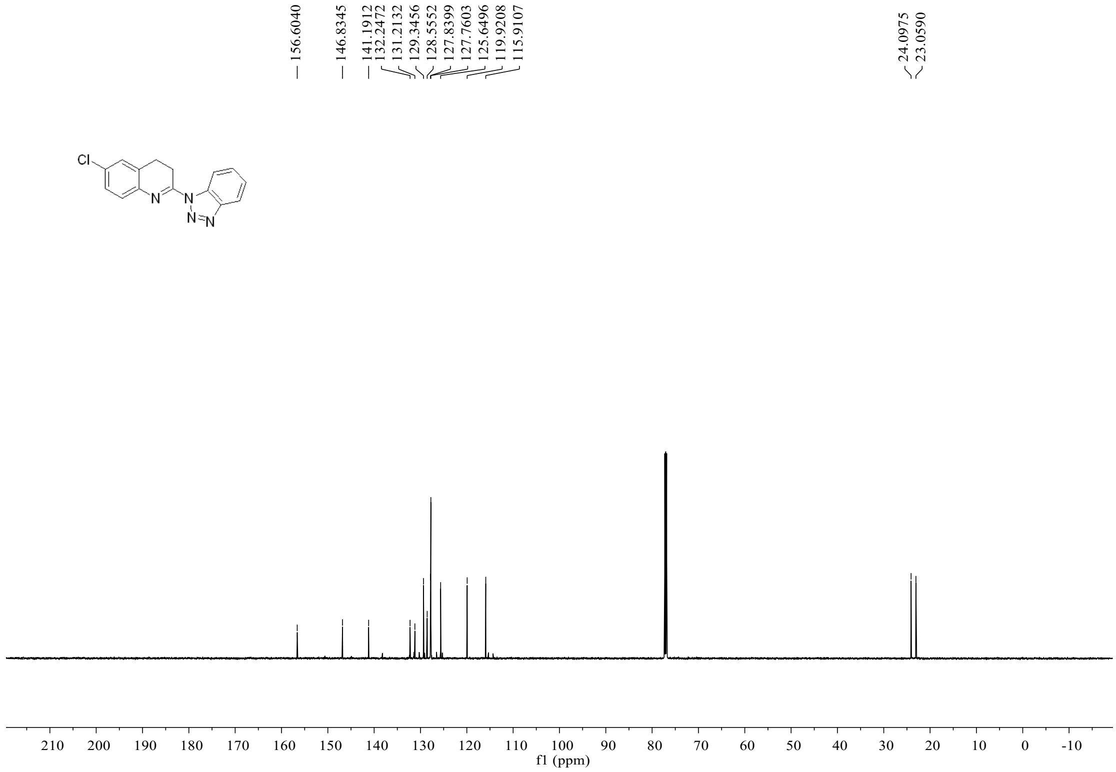
^{13}C-NMR Spectrum (151 MHz, $CDCl_3$) of 3i



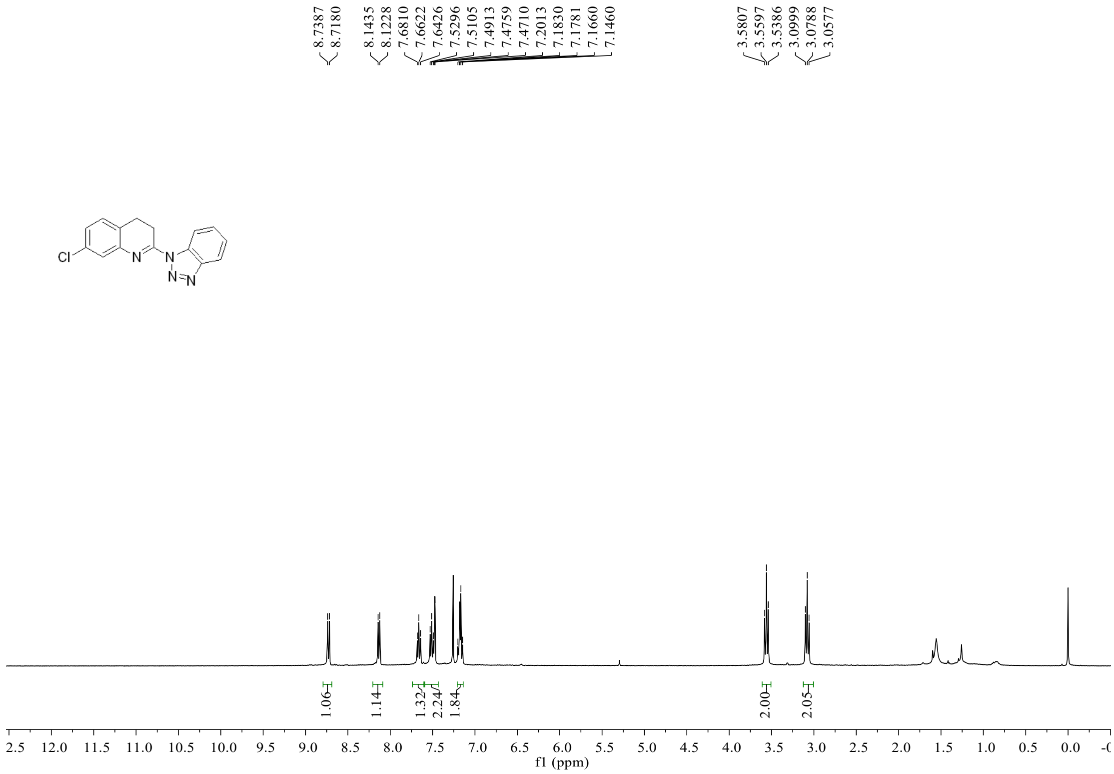
^{1}H-NMR Spectrum (600 MHz, $CDCl_3$) of 3j



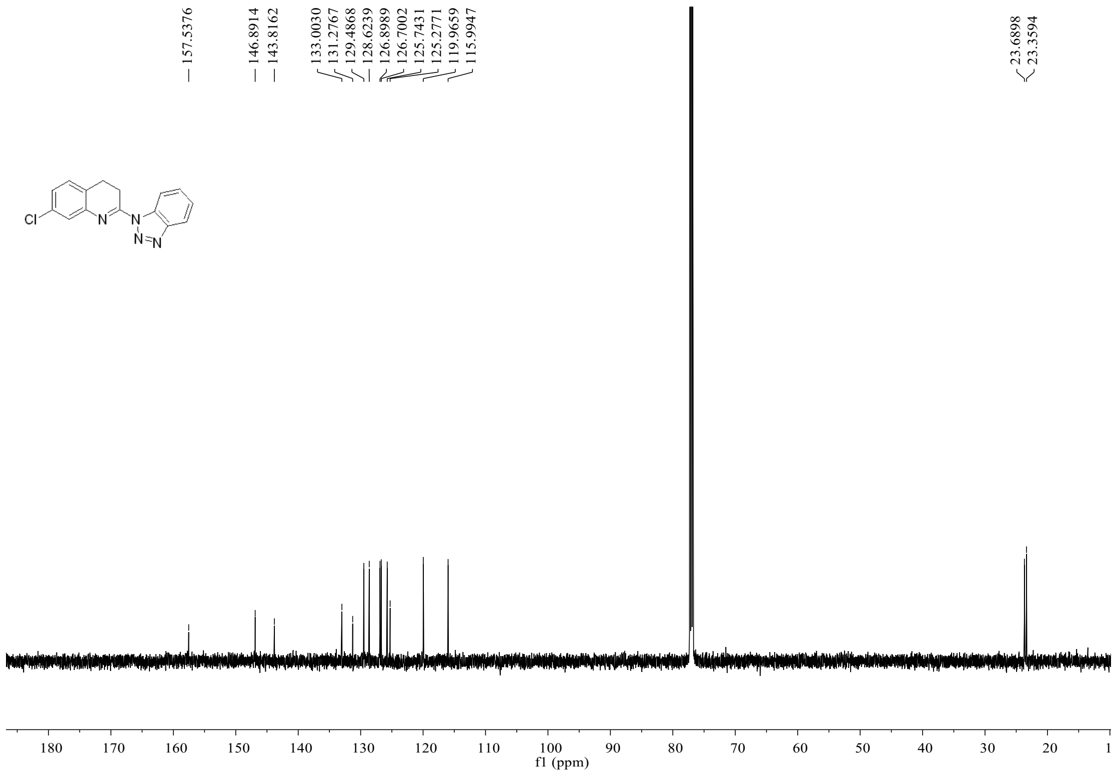
^{13}C-NMR Spectrum (151 MHz, $CDCl_3$) of 3j



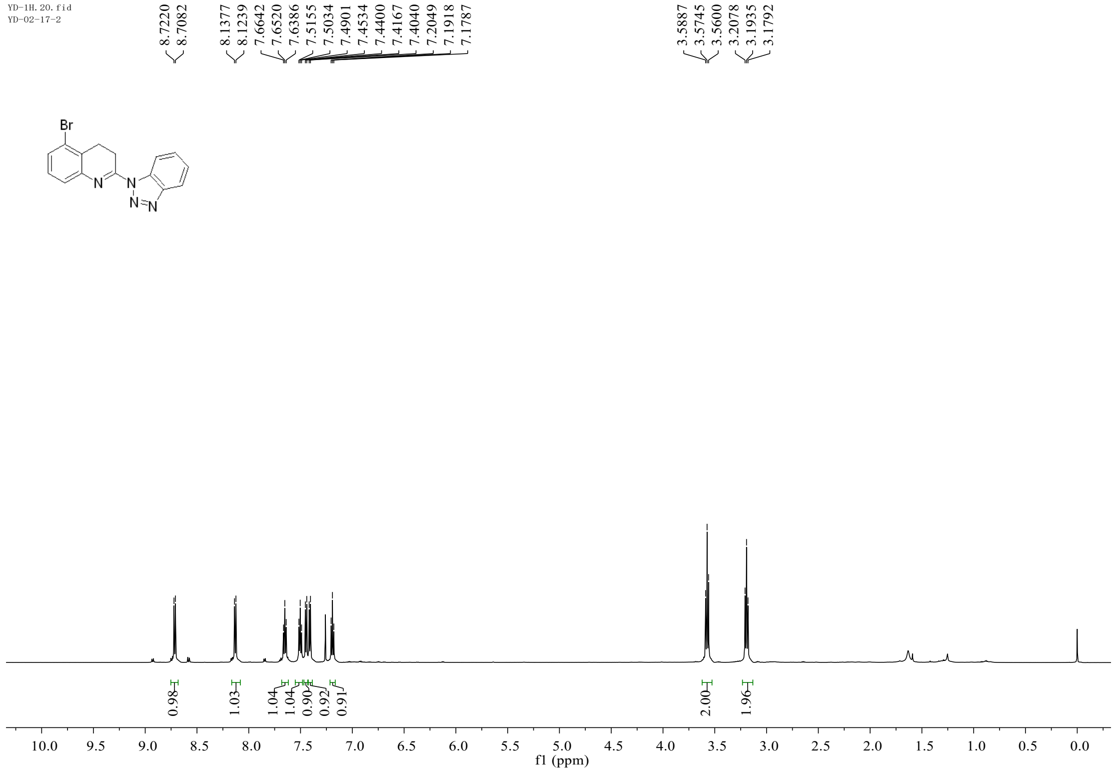
^{1}H-NMR Spectrum (400MHz, $CDCl_3$) of 3k



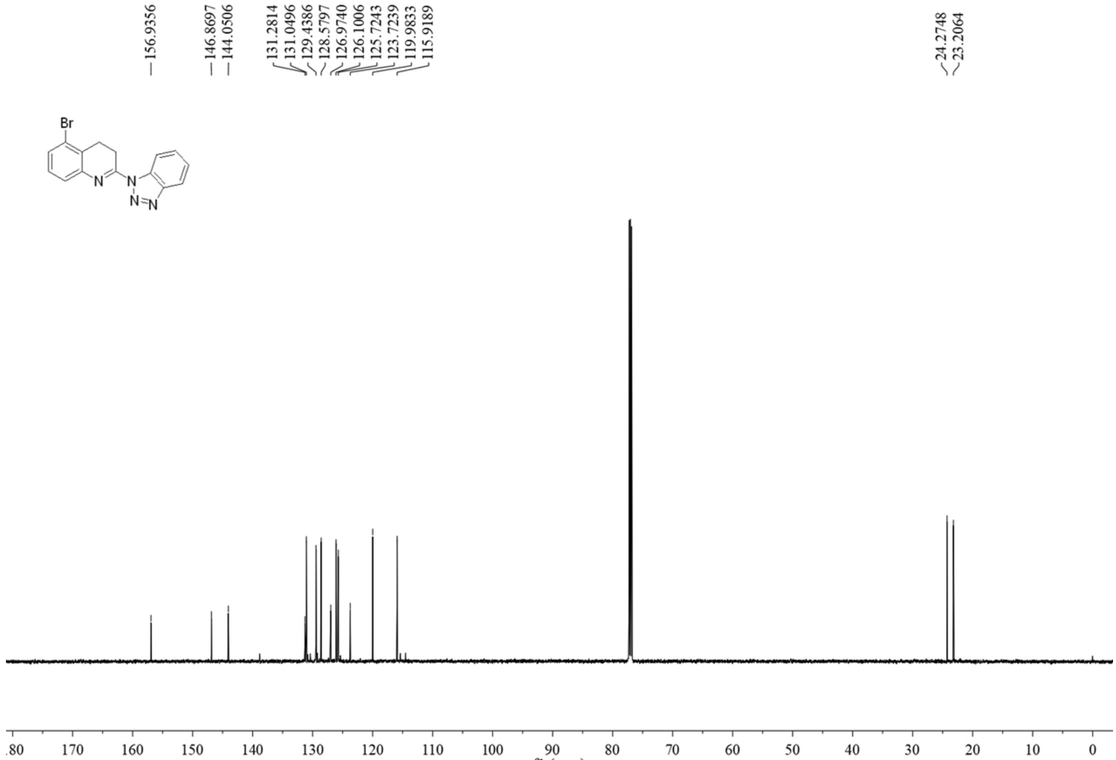
^{13}C-NMR Spectrum (151MHz, $CDCl_3$) of 3k



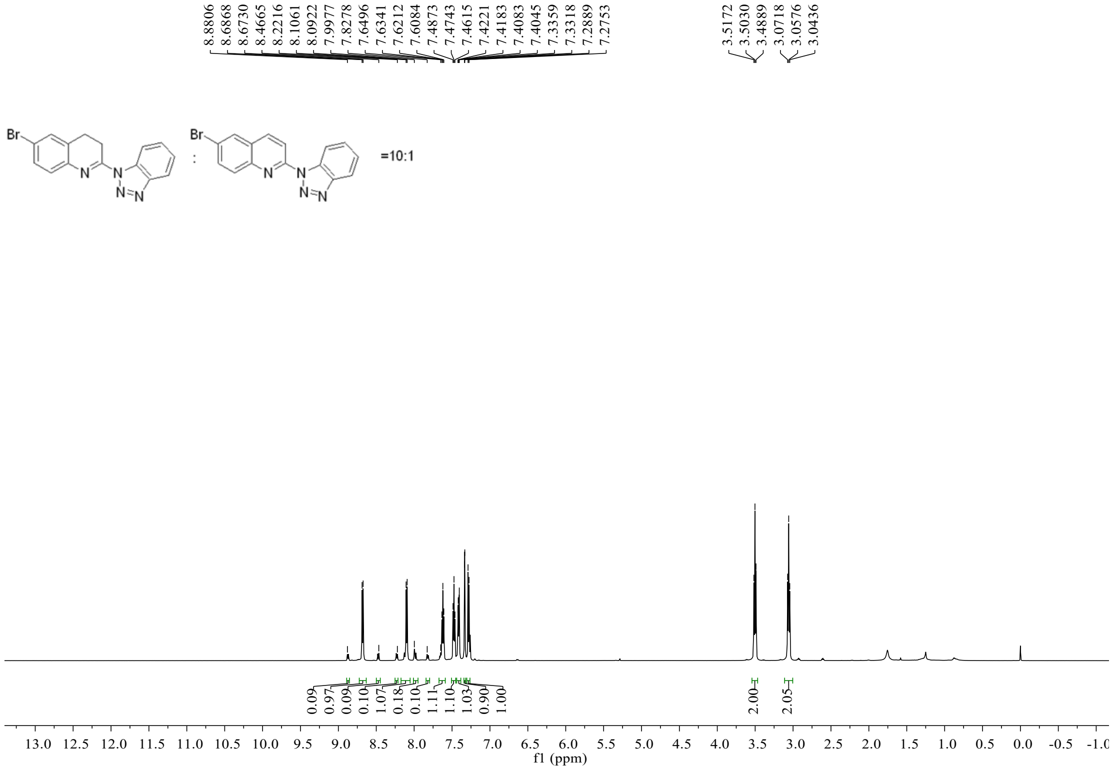
^{1}H-NMR Spectrum (600 MHz, $CDCl_3$) of 3l



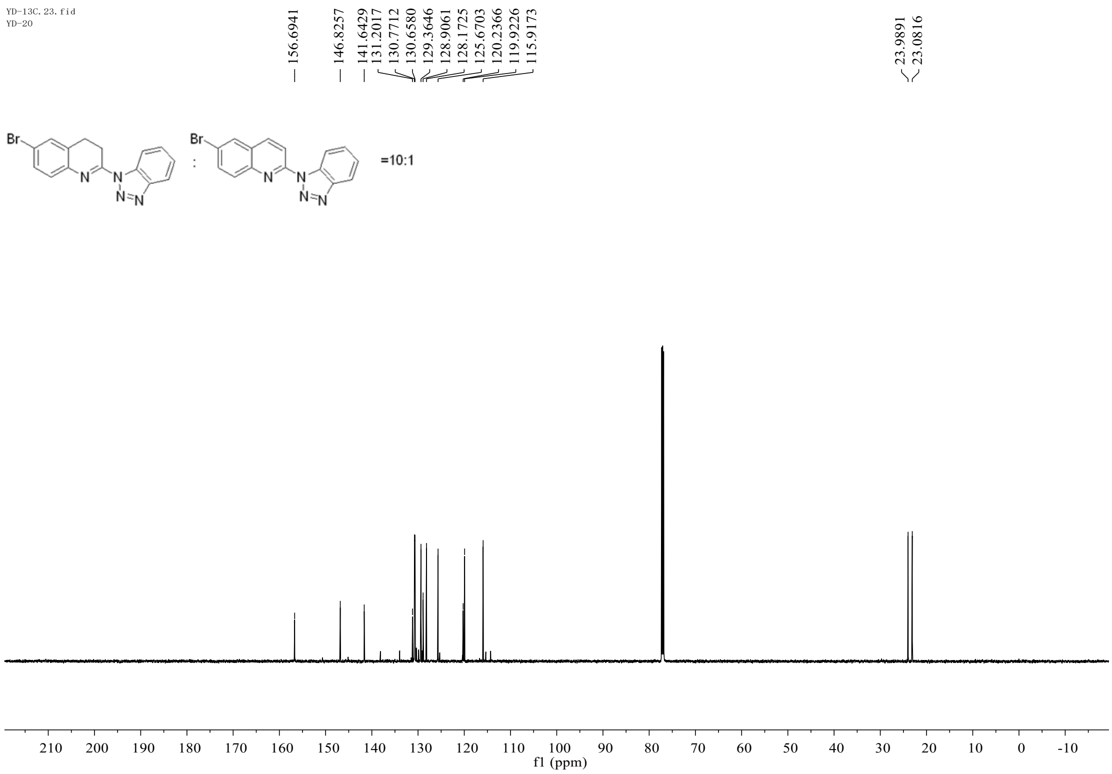
^{13}C-NMR Spectrum (151 MHz, $CDCl_3$) of 3l



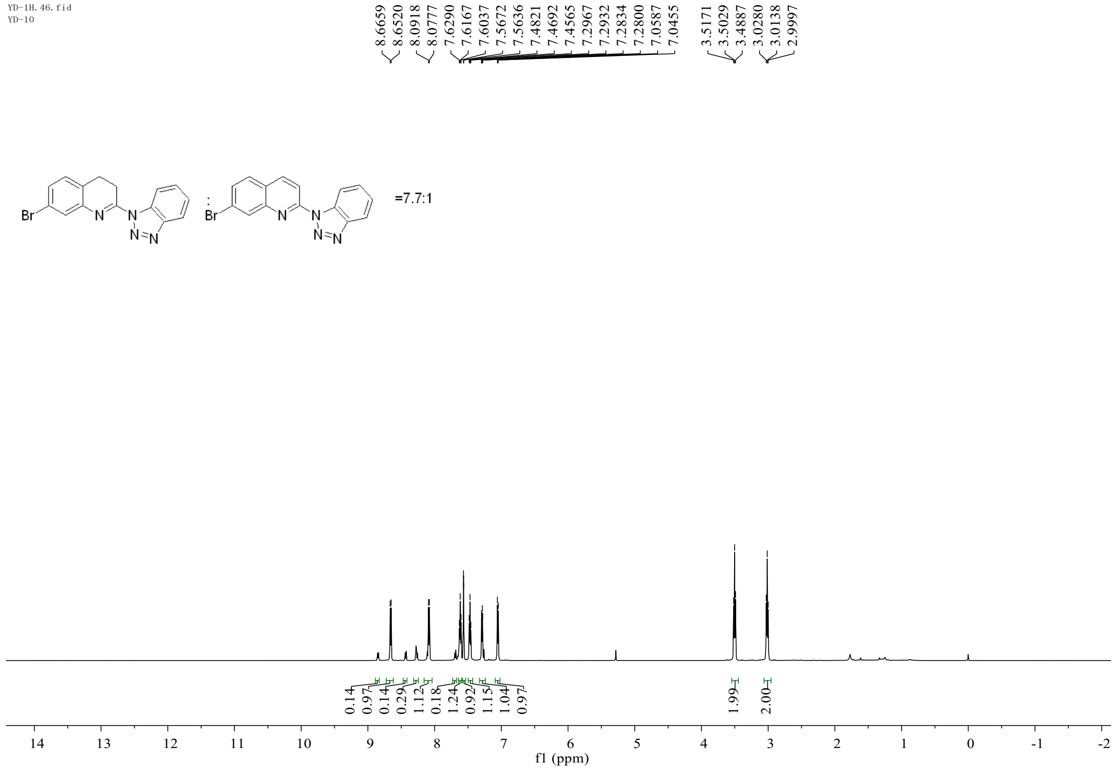
[1]H-NMR Spectrum (600 MHz, $CDCl_3$) of 3m



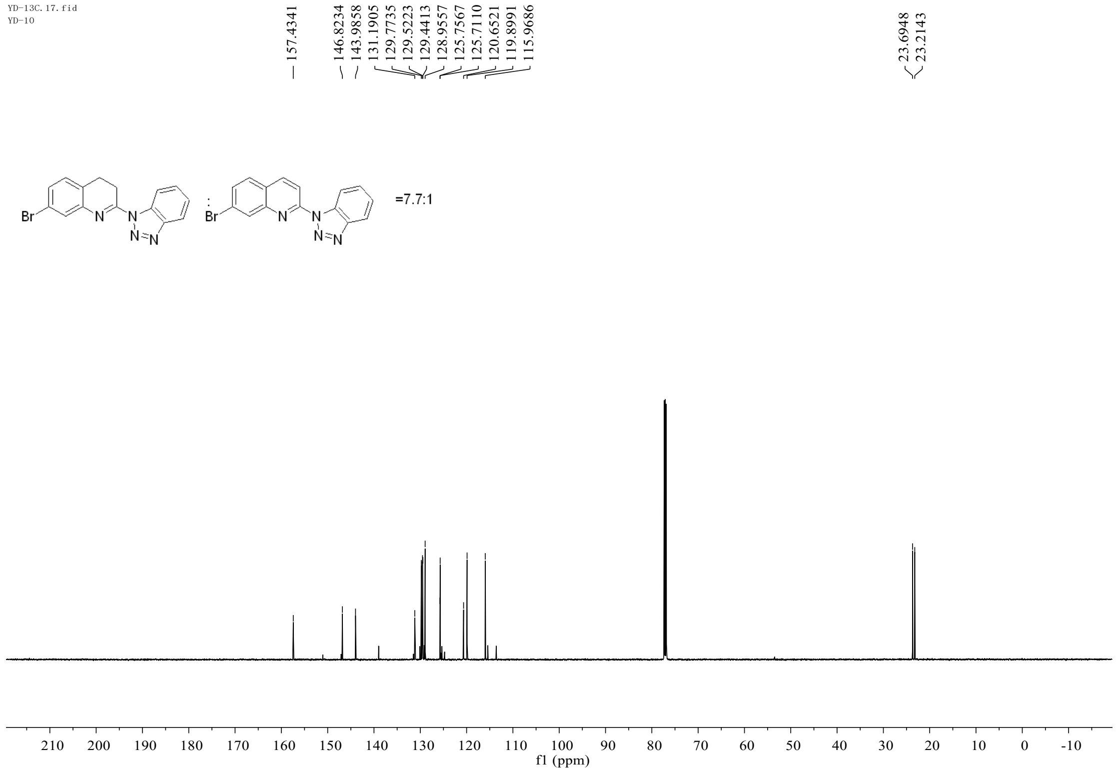
[13]C-NMR Spectrum (151 MHz, $CDCl_3$) of 3m



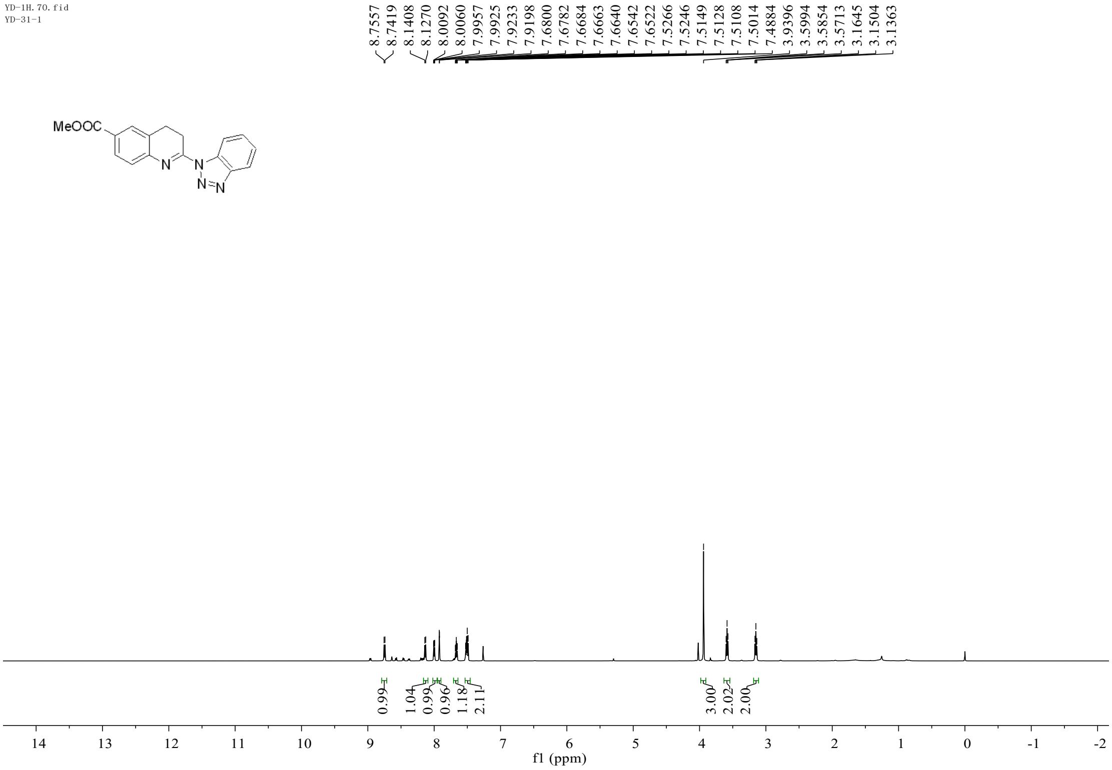
^{1}H-NMR Spectrum (600MHz, $CDCl_3$) of 3n



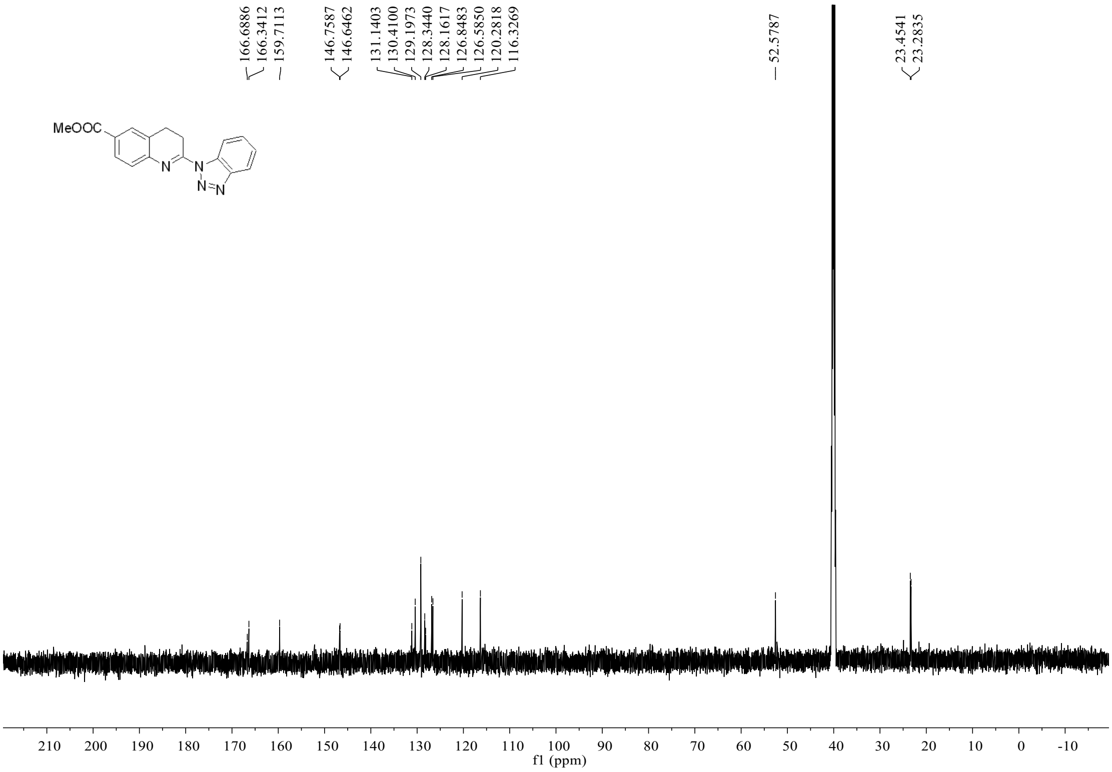
^{13}C-NMR Spectrum (151 MHz, $CDCl_3$) of 3n



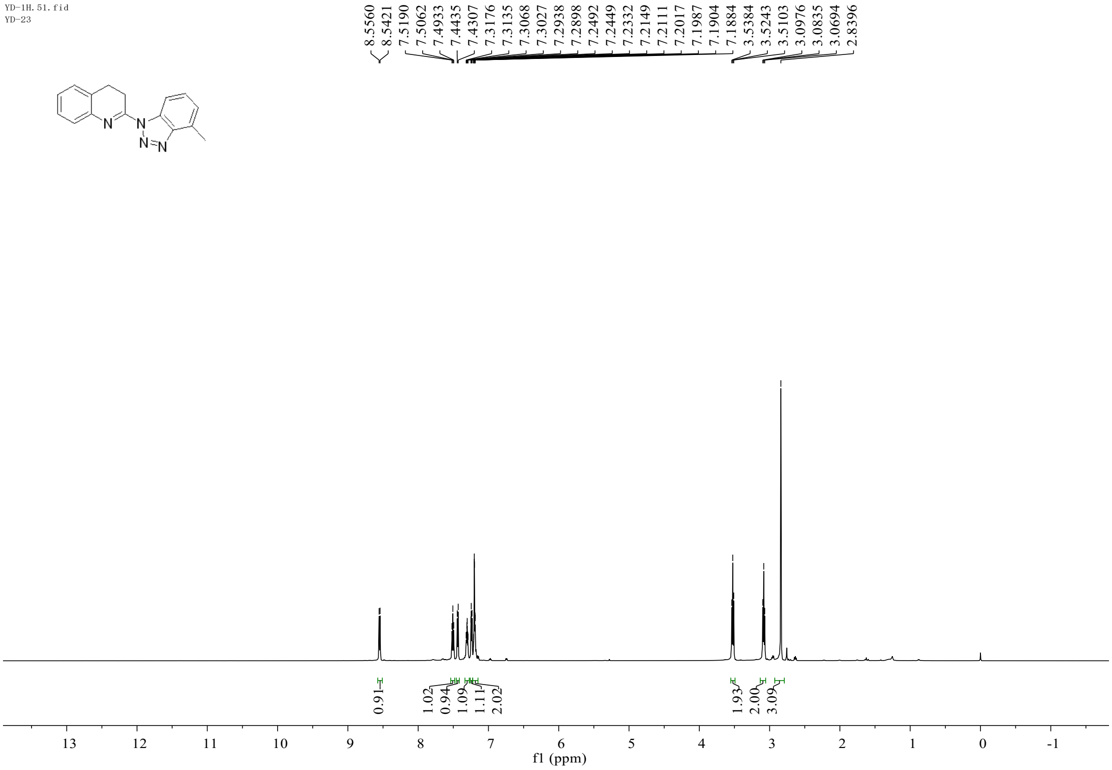
[1]H-NMR Spectrum (400MHz, $CDCl_3$) of 3o



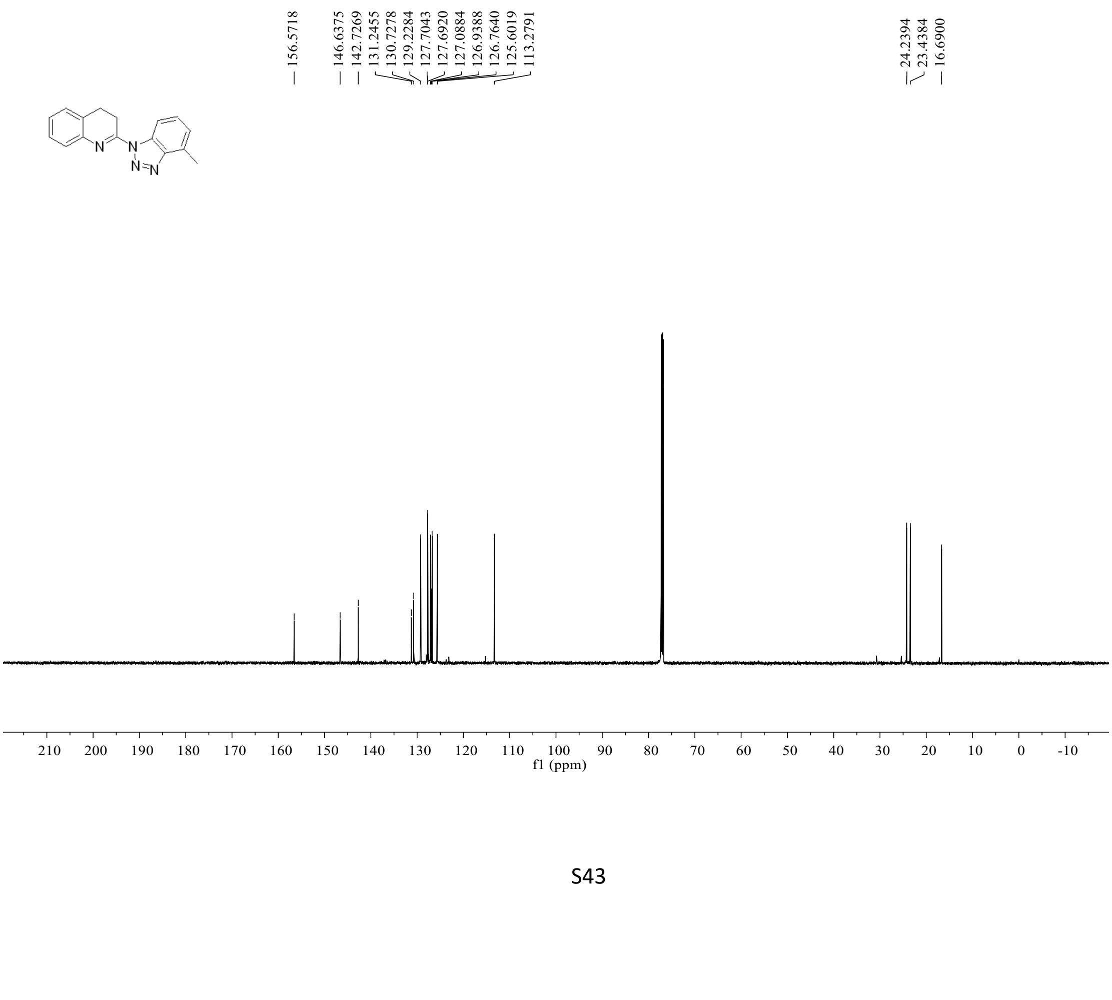
[13]C-NMR Spectrum (101MHz, $CDCl_3$) of 3o



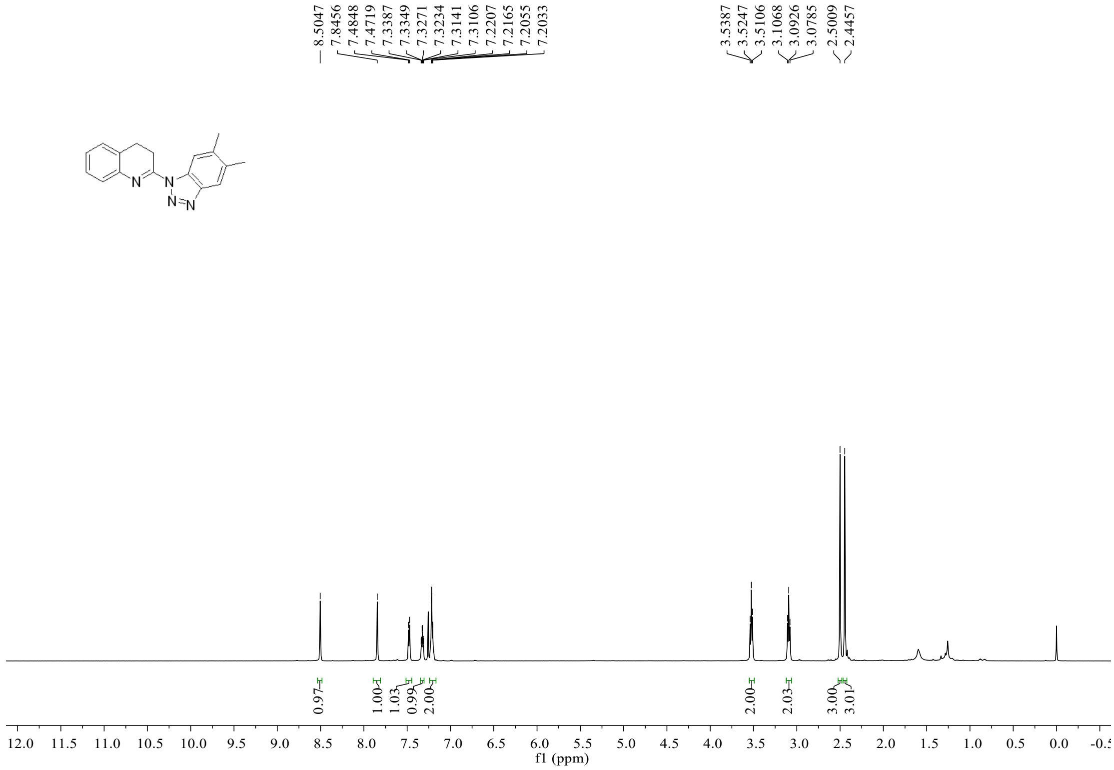
[1]H-NMR Spectrum (400MHz, $CDCl_3$) of 3p



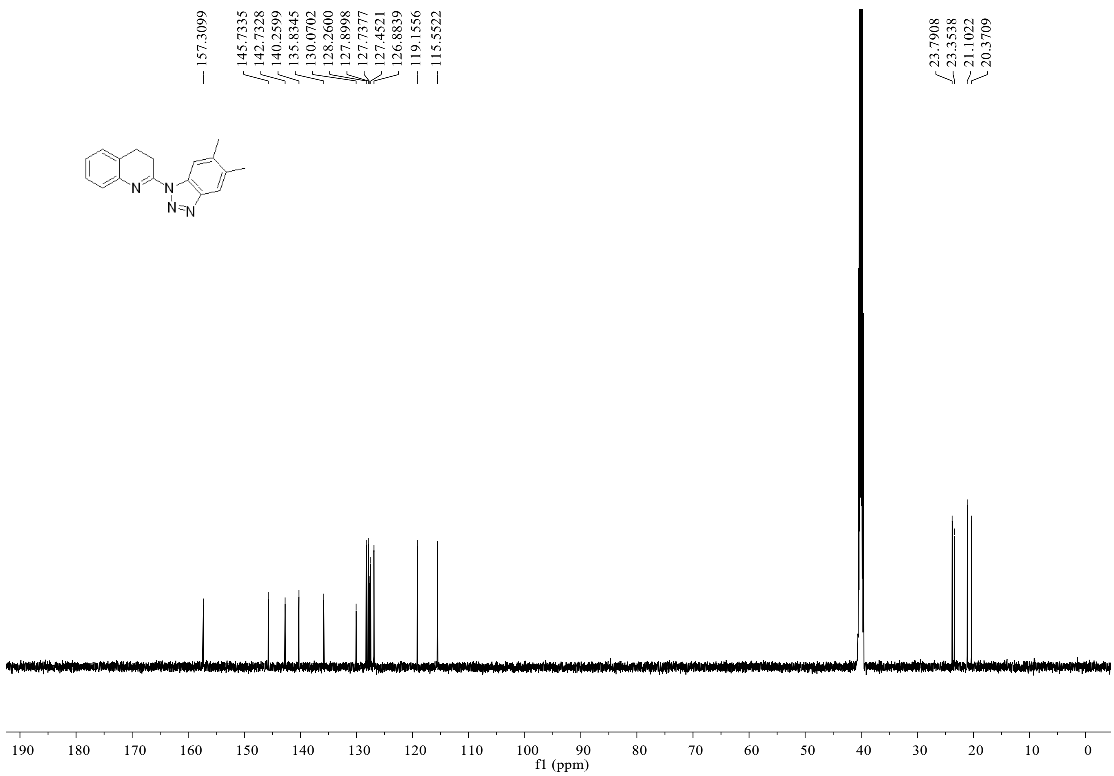
[13]C-NMR Spectrum (101MHz, $CDCl_3$) of 3p



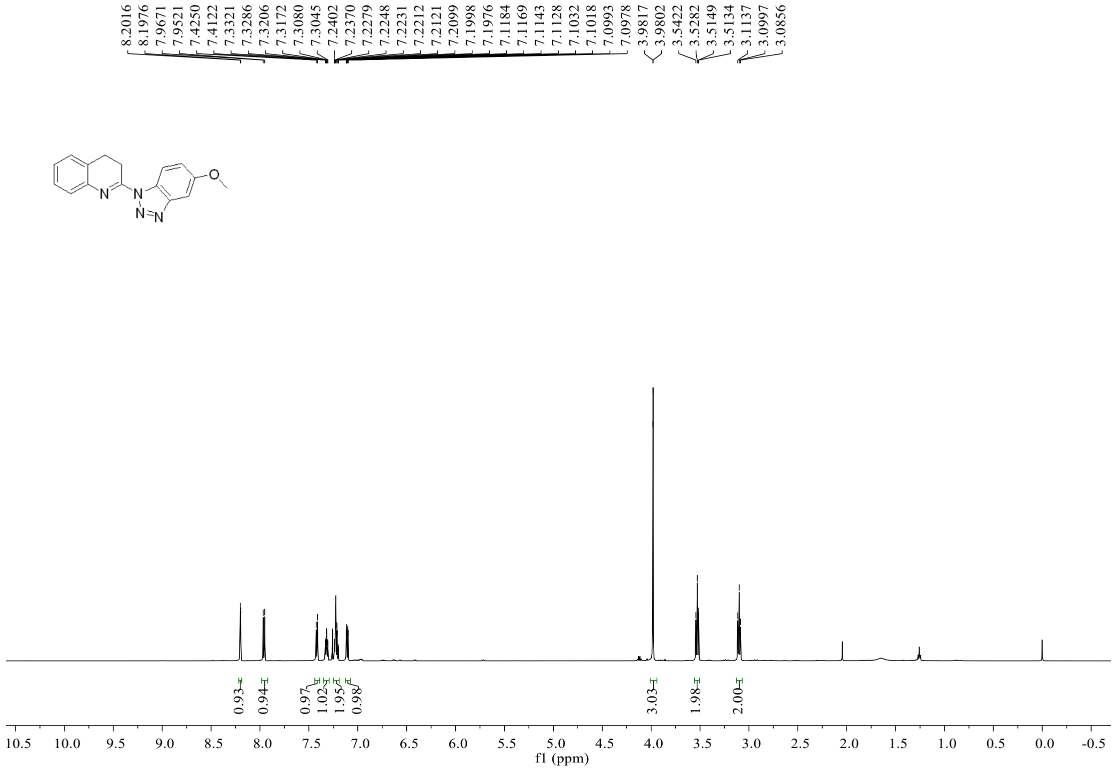
[1]H-NMR Spectrum (600MHz, $CDCl_3$) of 3q



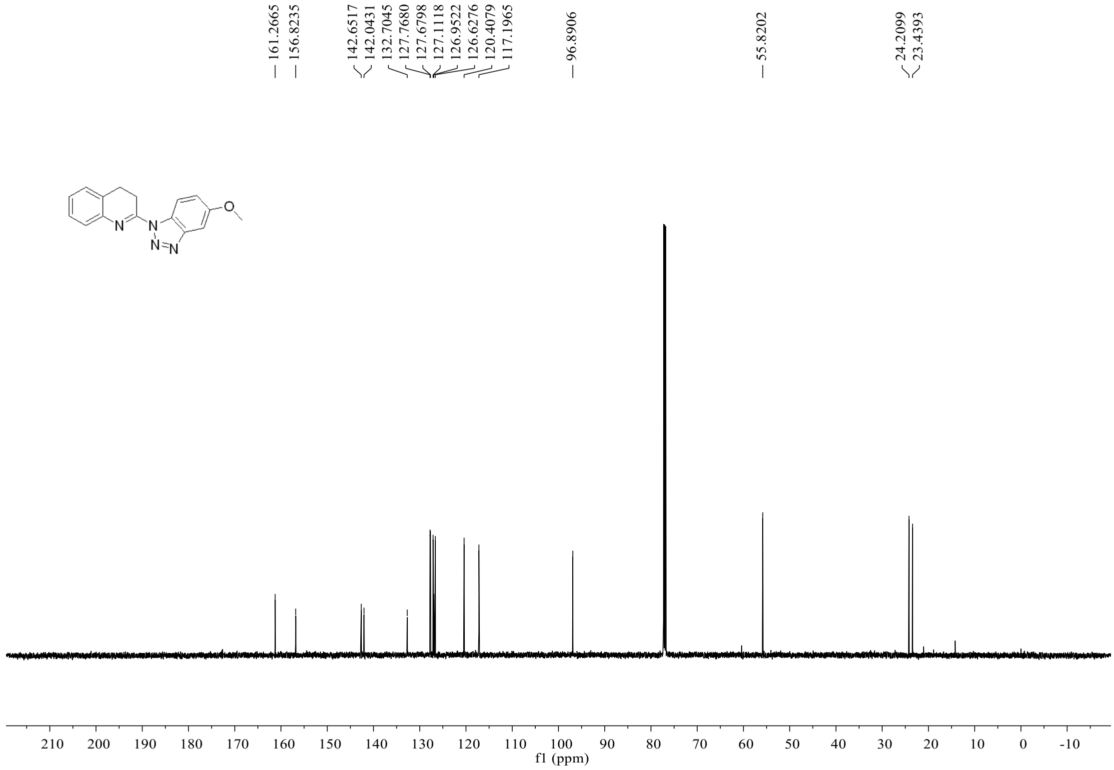
[13]C-NMR Spectrum (151MHz, DMSO) of 3q



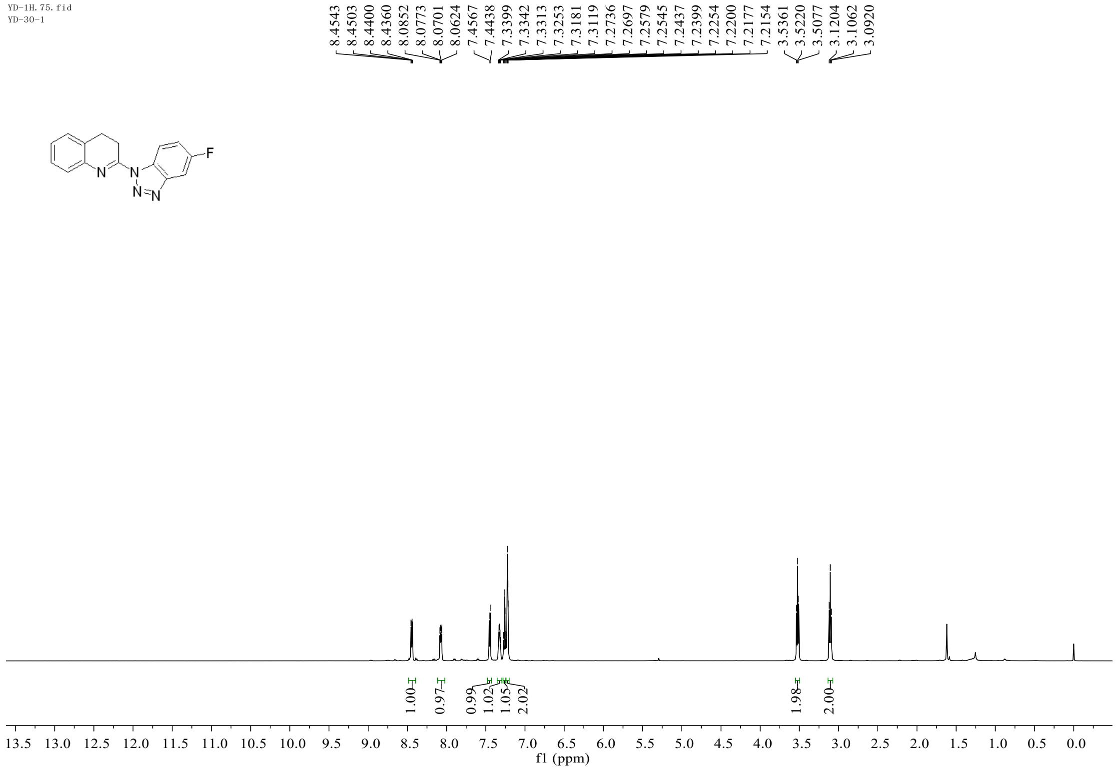
^{1}H-NMR Spectrum (600 MHz, $CDCl_3$) of 3r



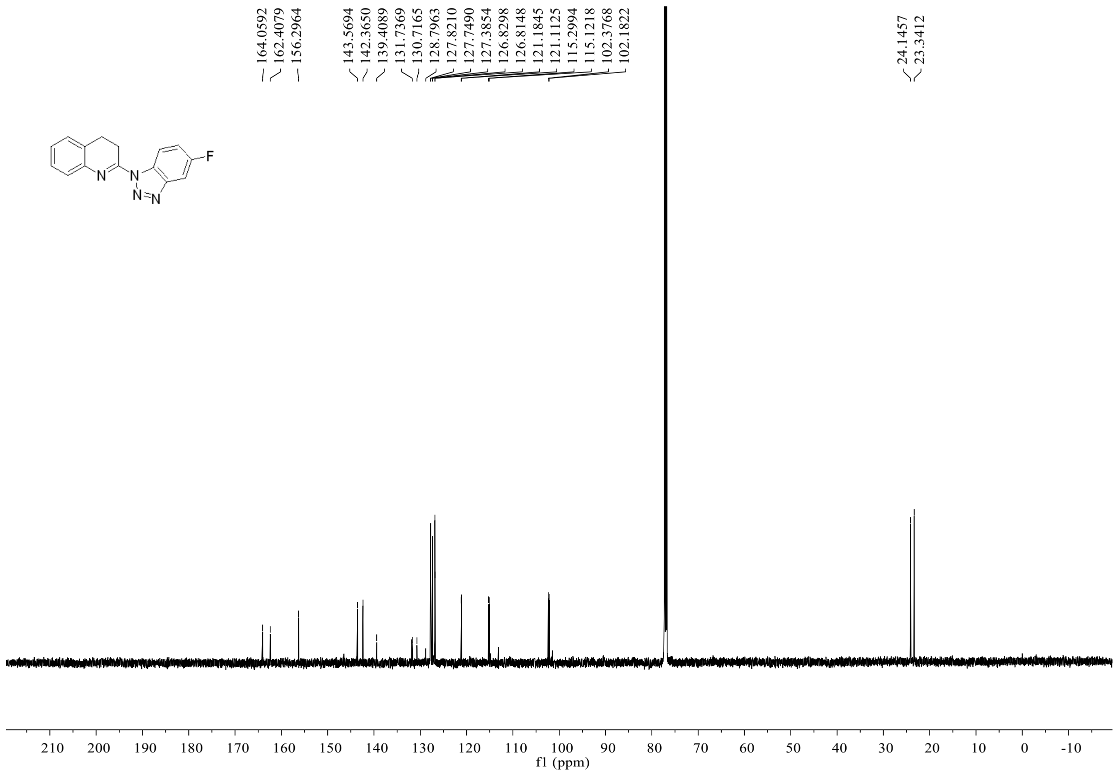
^{13}C-NMR Spectrum (151 MHz, $CDCl_3$) of 3r



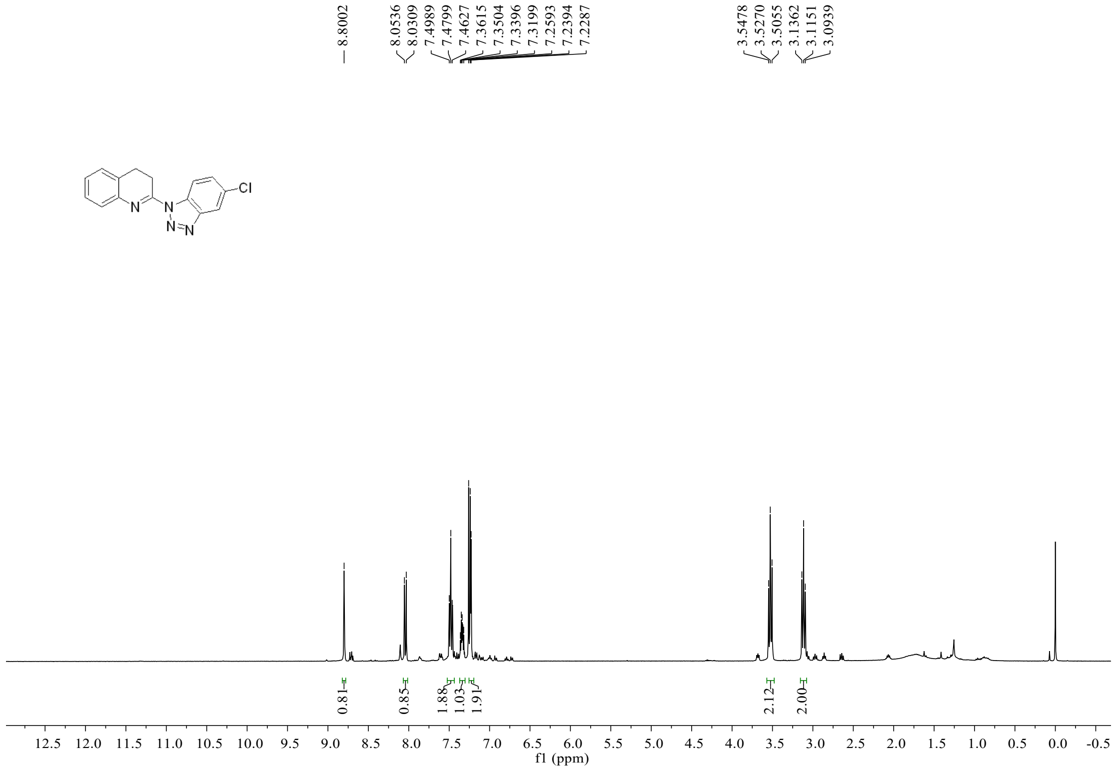
^{1}H-NMR Spectrum (600MHz, $CDCl_3$) of 3s



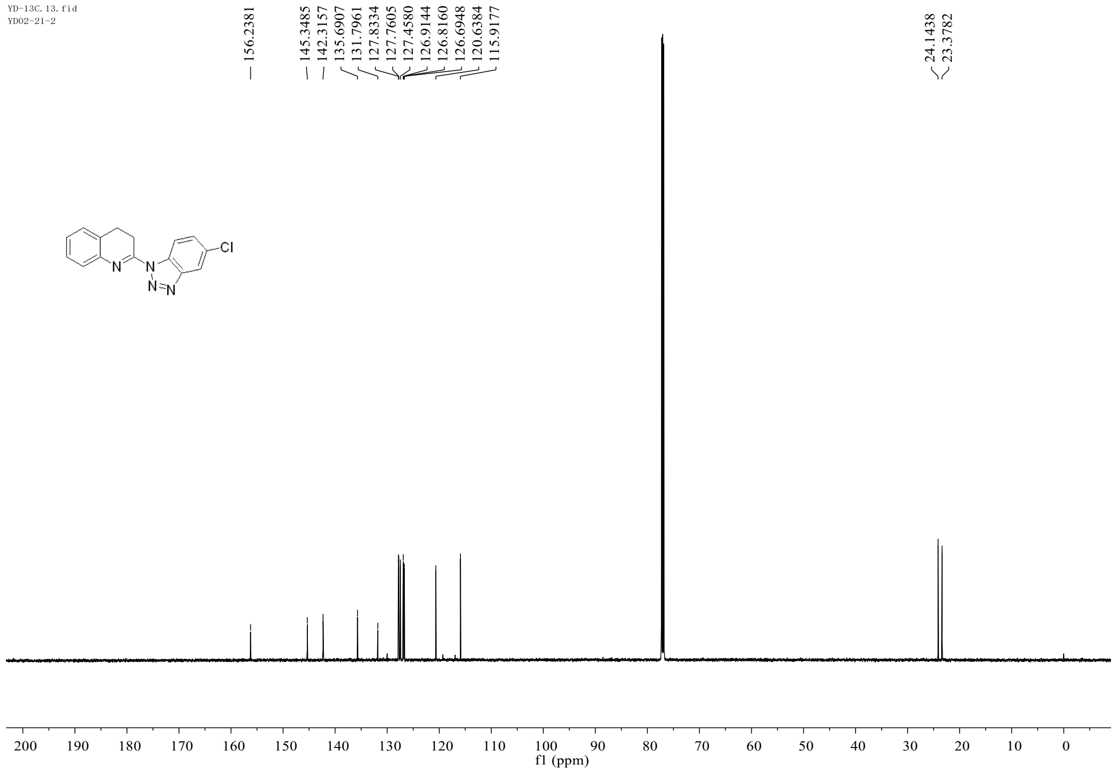
^{13}C-NMR Spectrum (151MHz, $CDCl_3$) of 3s



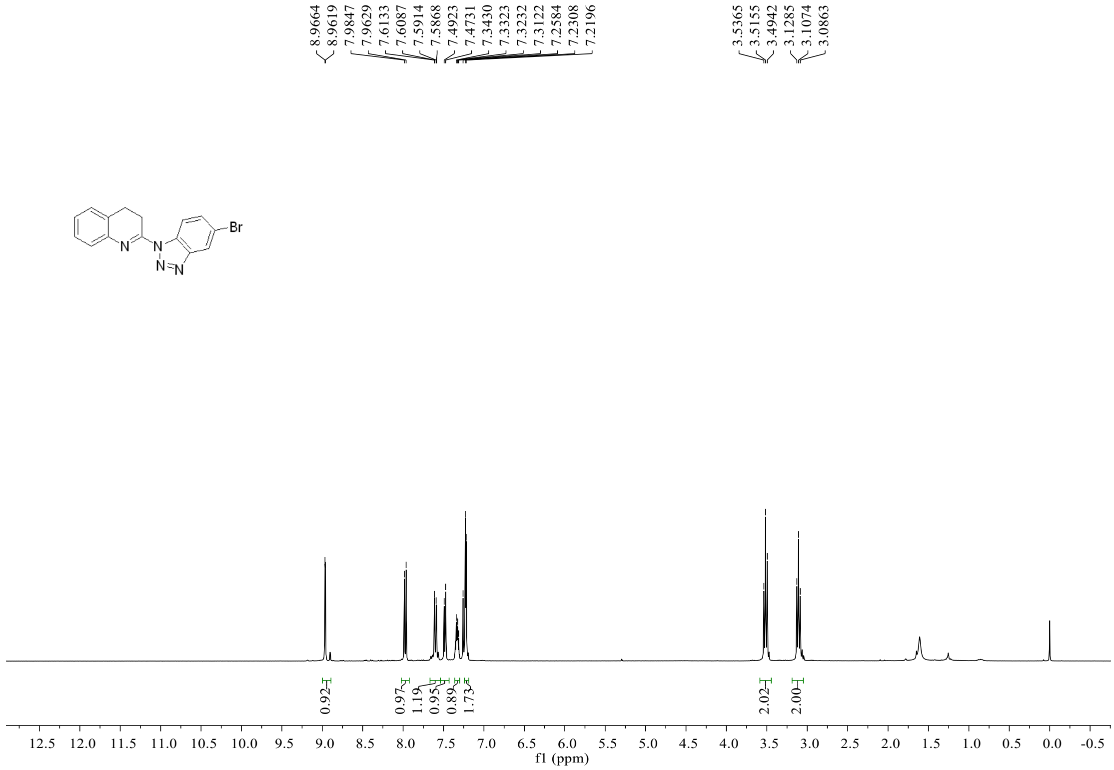
[1]H-NMR Spectrum (400MHz, $CDCl_3$) of 3t



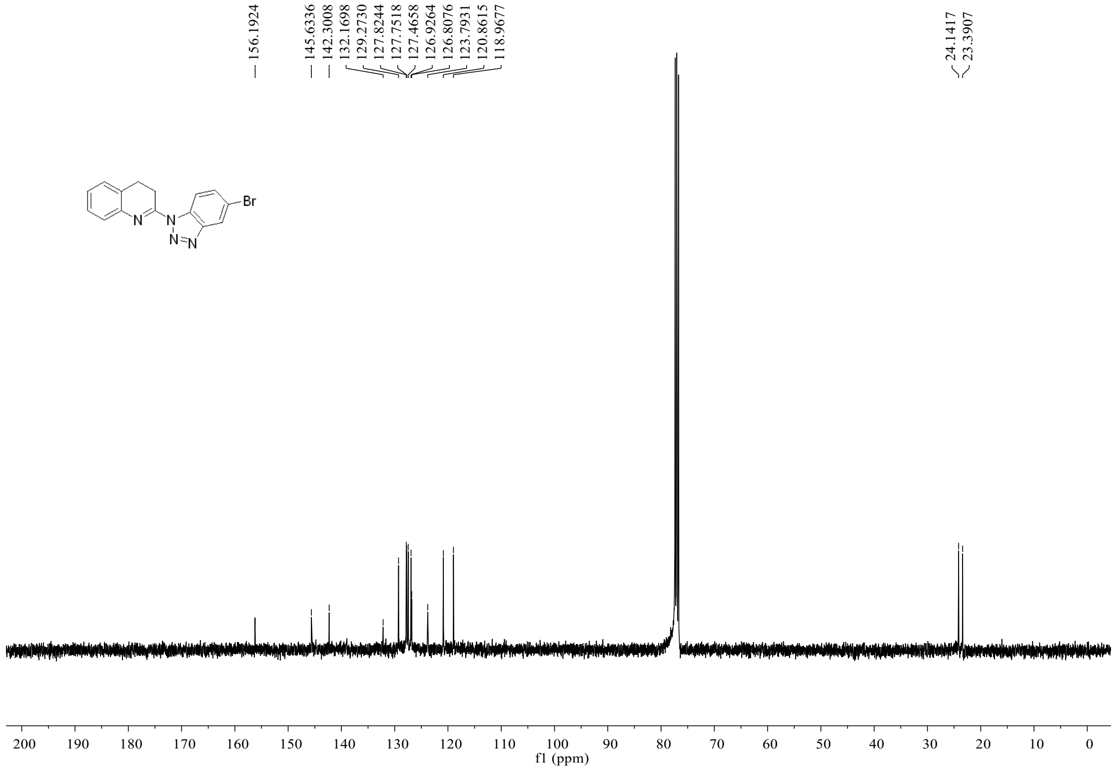
[13]C-NMR Spectrum (101MHz, $CDCl_3$) of 3t



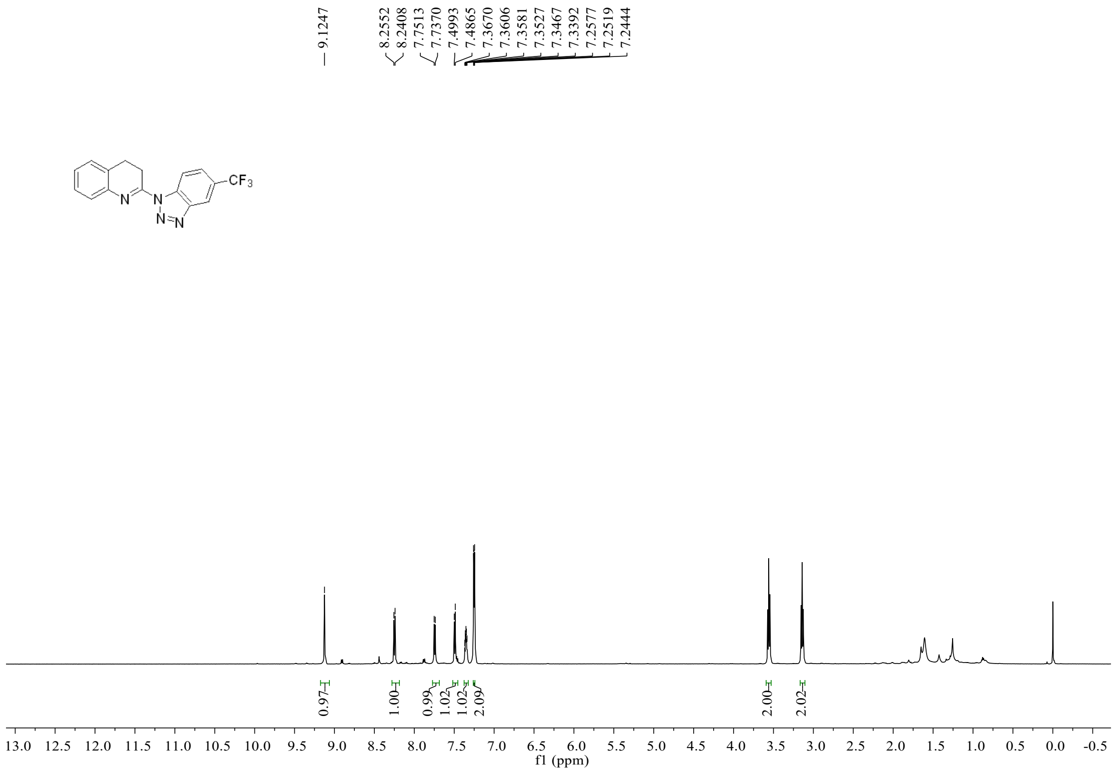
^{1}H-NMR Spectrum (400MHz, $CDCl_3$) of 3u



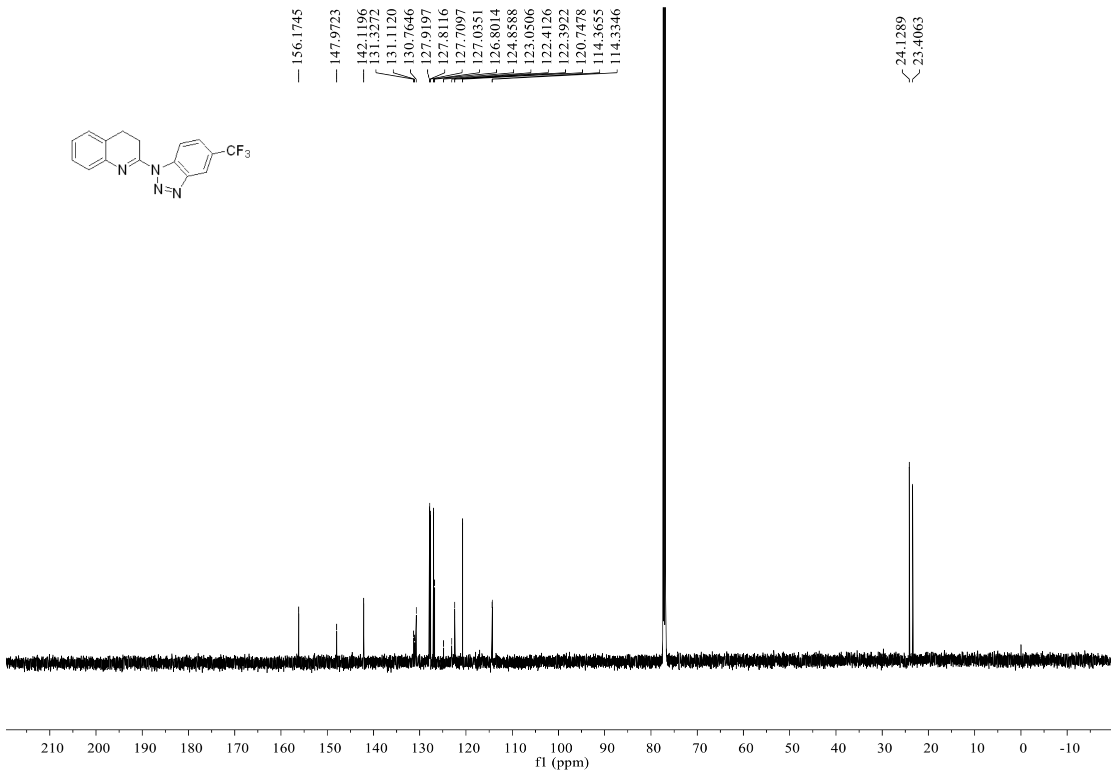
^{13}C-NMR Spectrum (101MHz, $CDCl_3$) of 3u



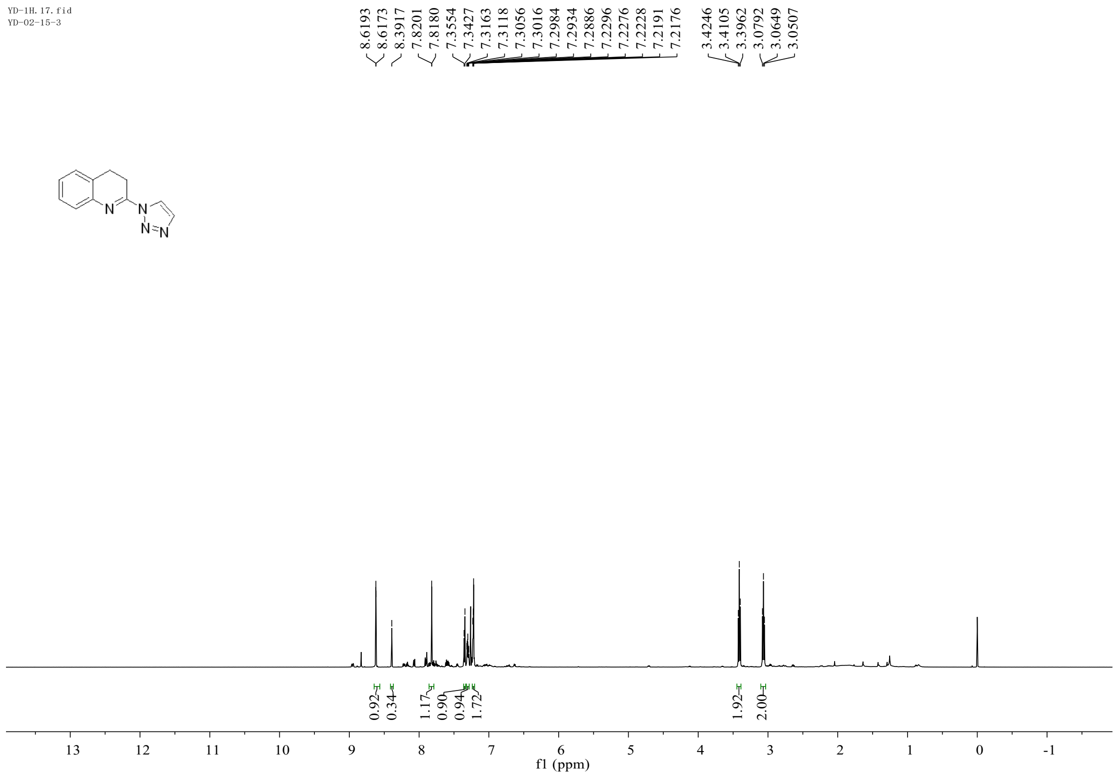
[1]H-NMR Spectrum (600 MHz, $CDCl_3$) of 3v



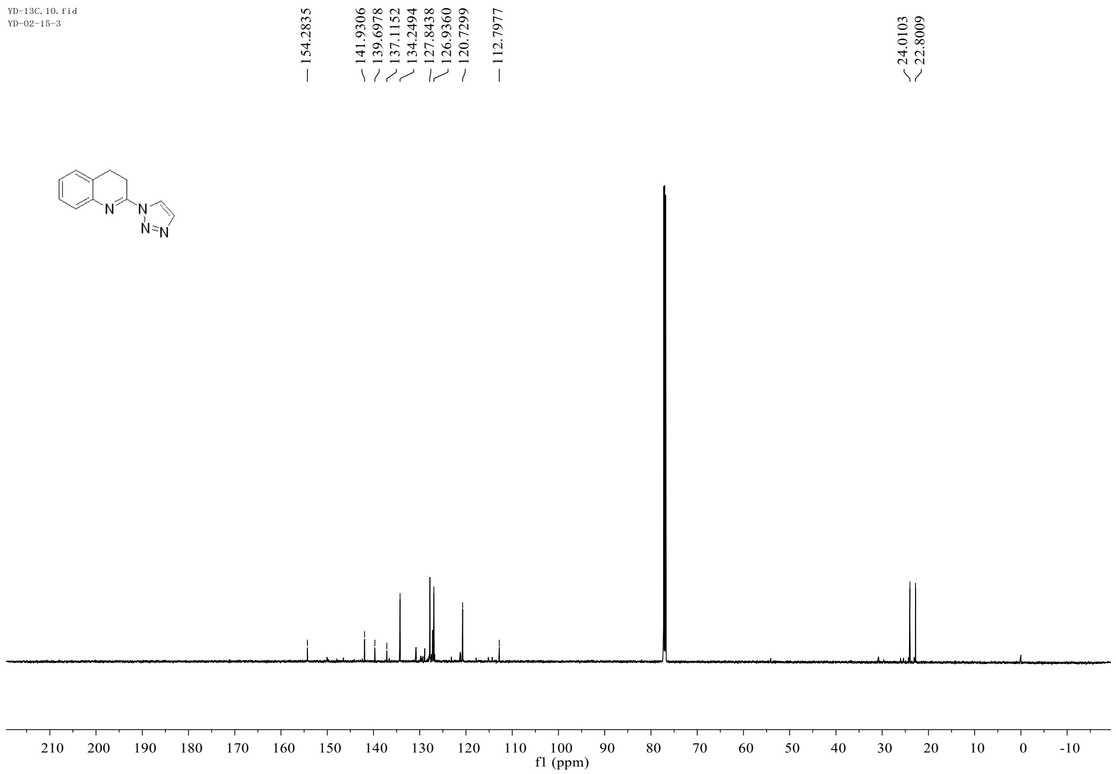
[13]C-NMR Spectrum (151 MHz, $CDCl_3$) of 3v



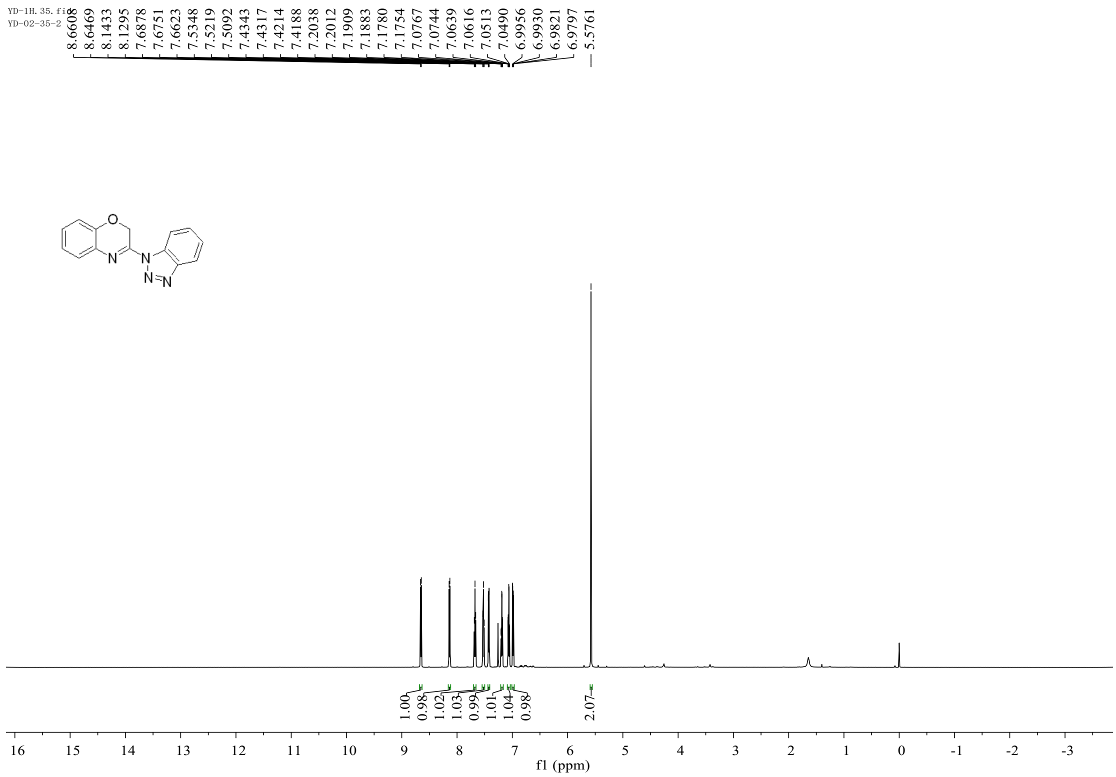
^{1}H-NMR Spectrum (600 MHz, $CDCl_3$) of 3w



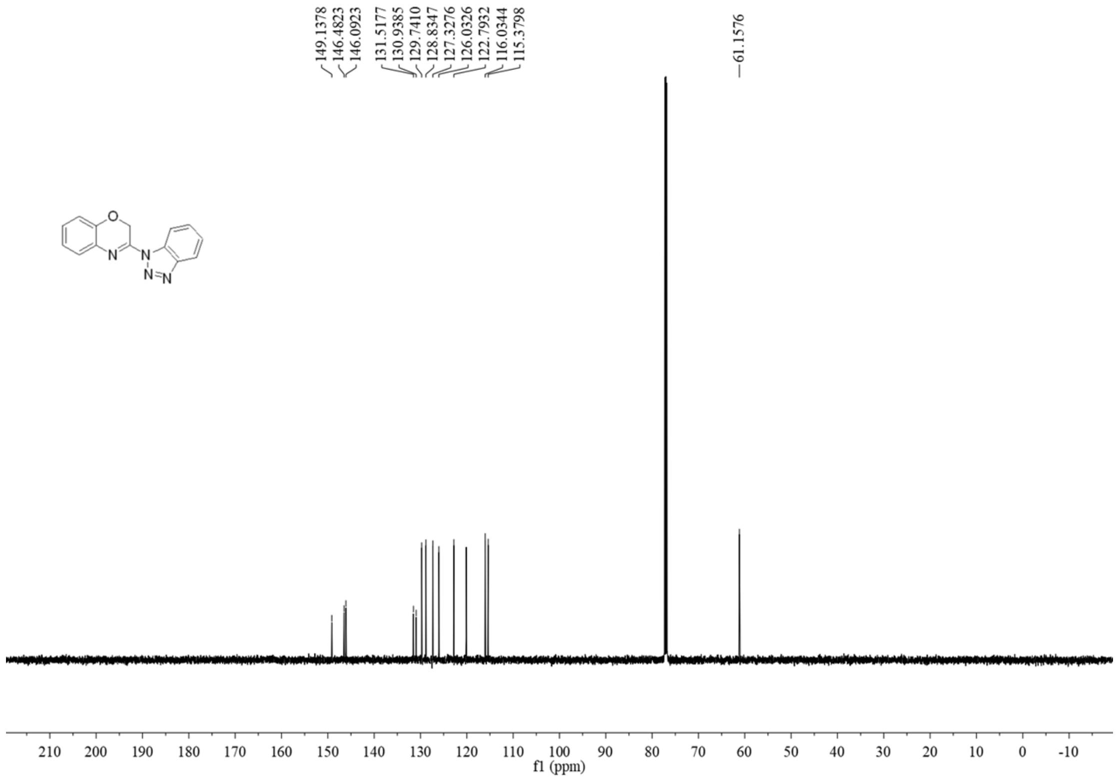
^{13}C-NMR Spectrum (151 MHz, $CDCl_3$) of 3w



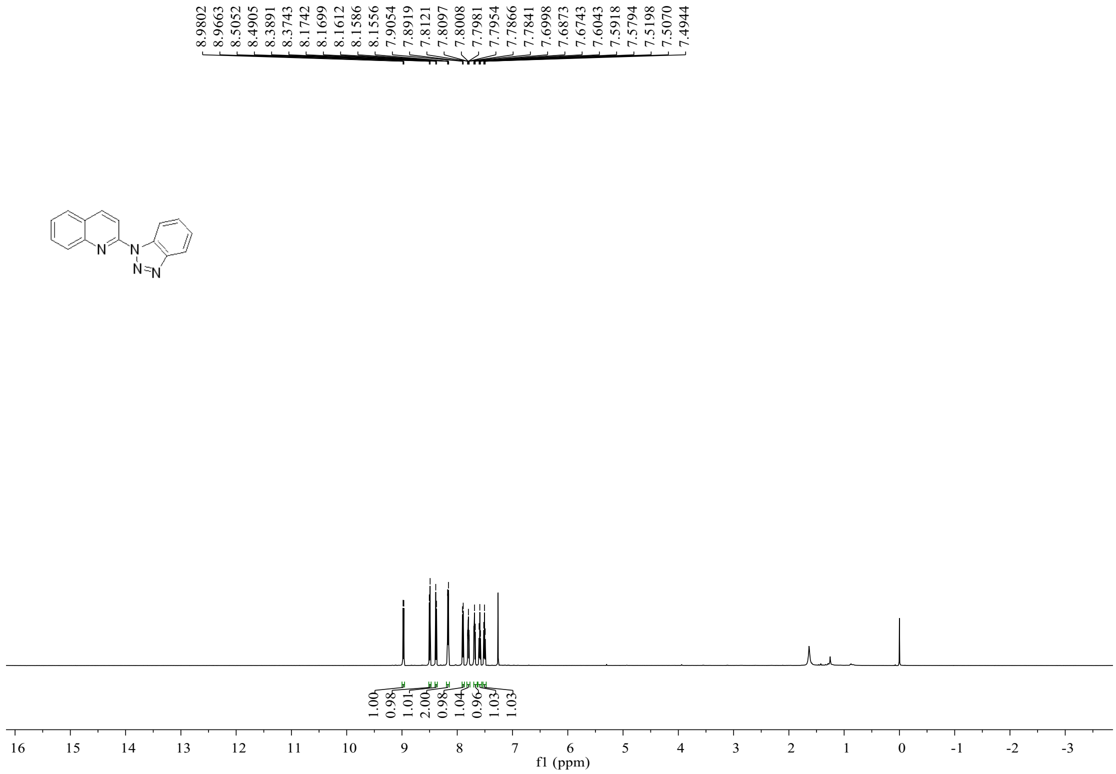
[1]H-NMR Spectrum (400MHz, $CDCl_3$) of 3x



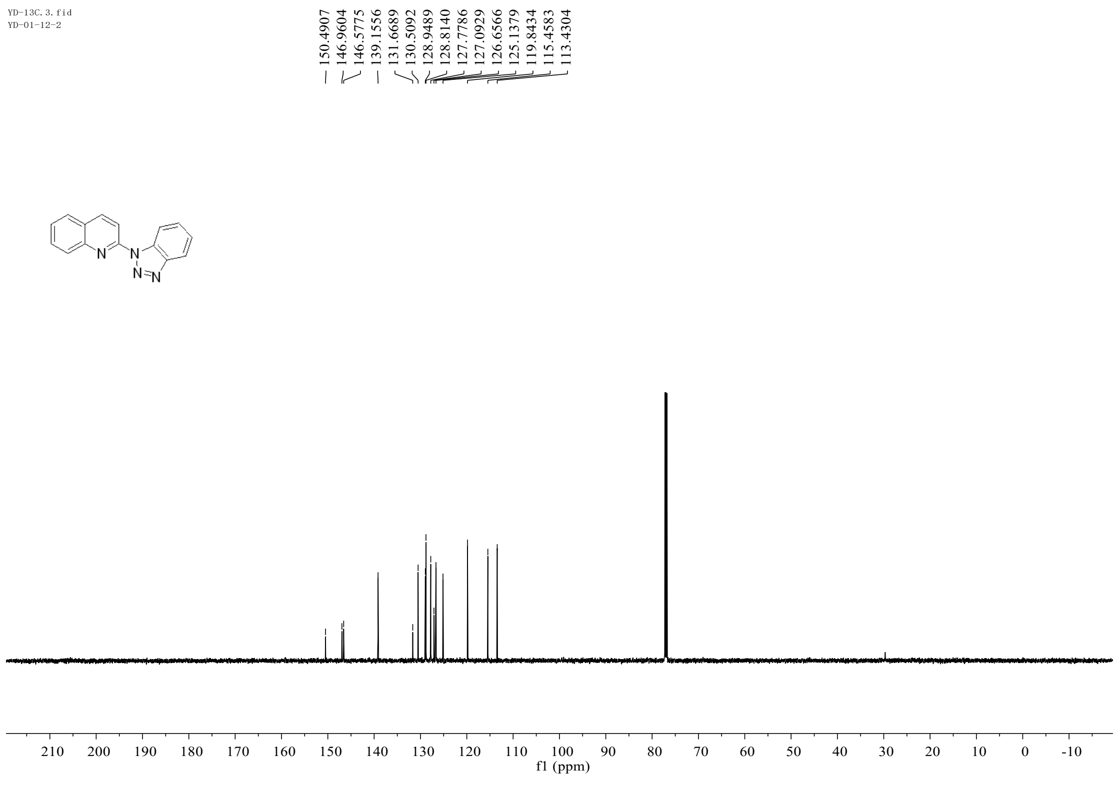
[13]C-NMR Spectrum (151 MHz, $CDCl_3$) of 3x



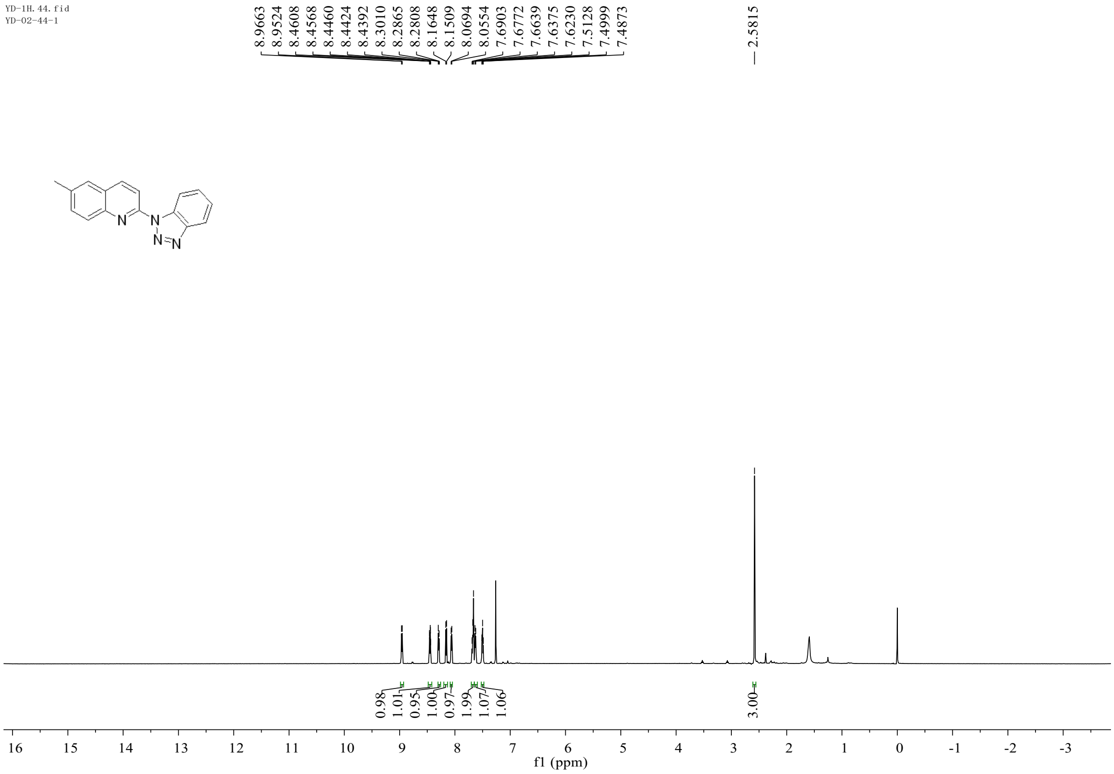
[1]H-NMR Spectrum (600 MHz, $CDCl_3$) of 4a



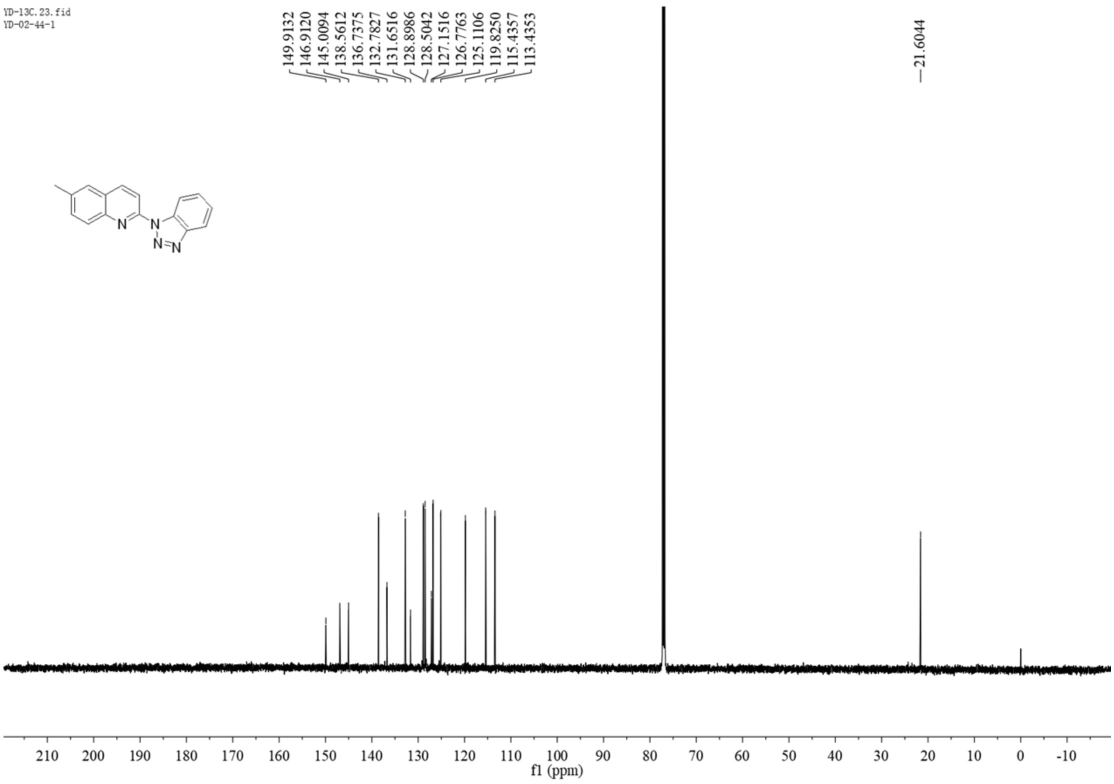
[13]C-NMR Spectrum (151 MHz, $CDCl_3$) of 4a



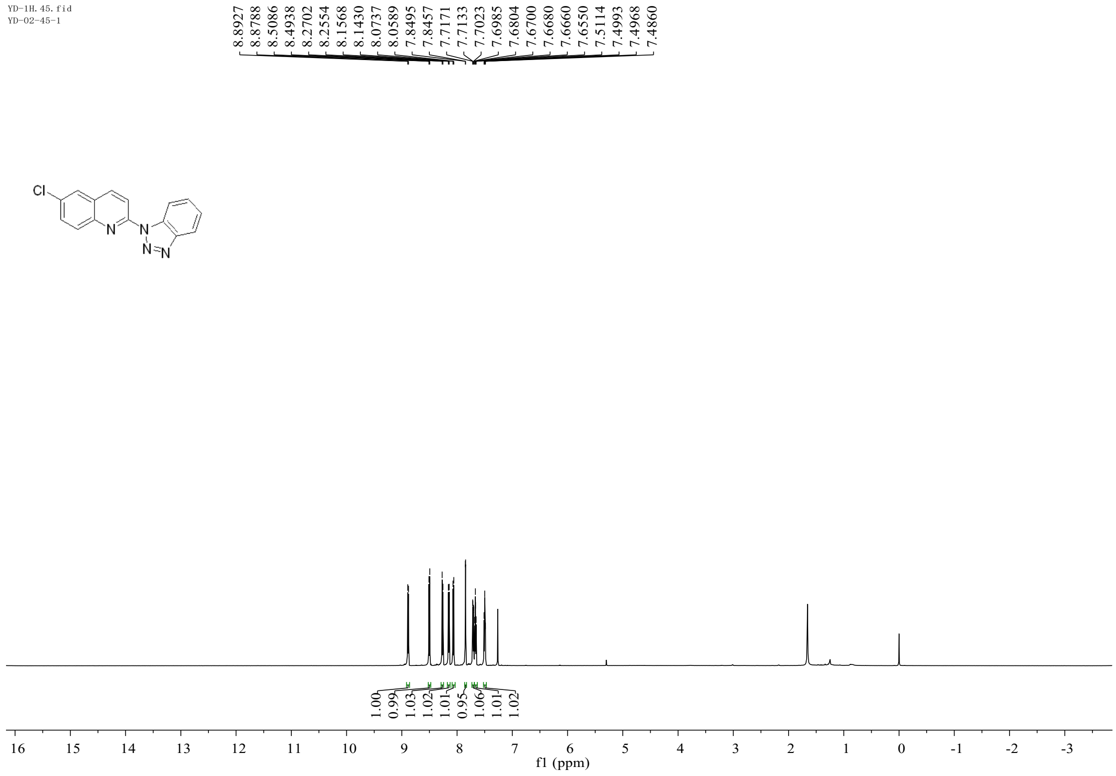
[1]H-NMR Spectrum (600 MHz, $CDCl_3$) of 4b



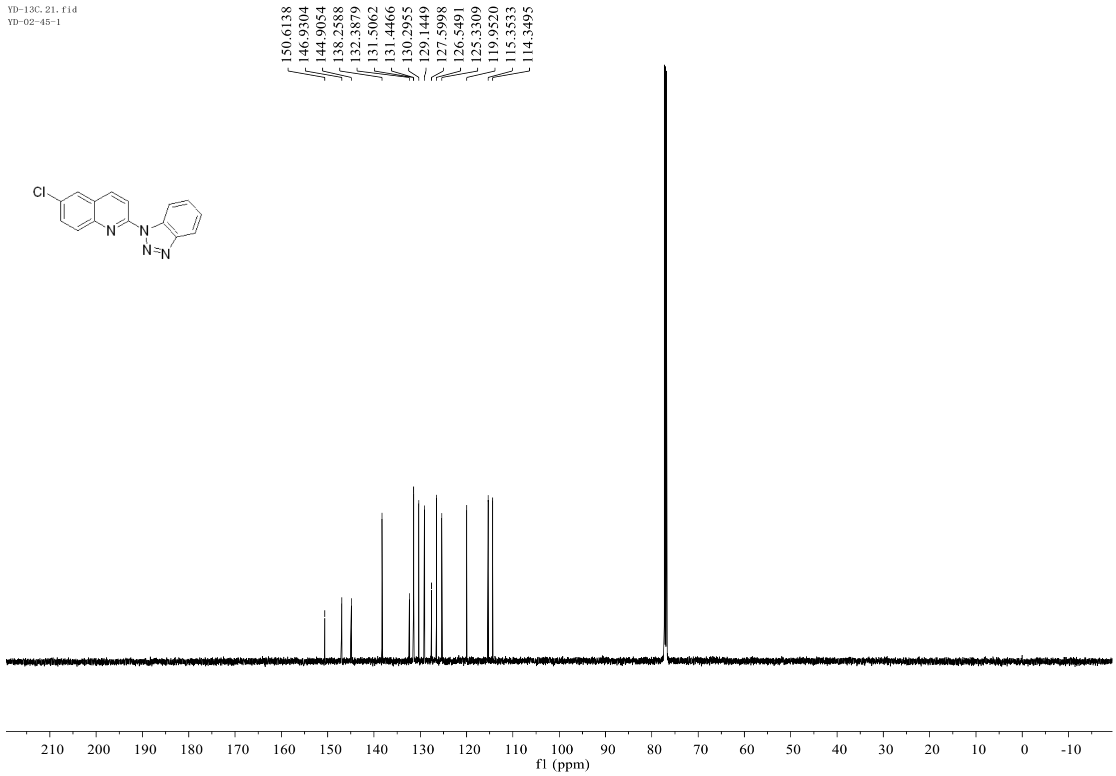
[13]C-NMR Spectrum (151 MHz, $CDCl_3$) of 4b



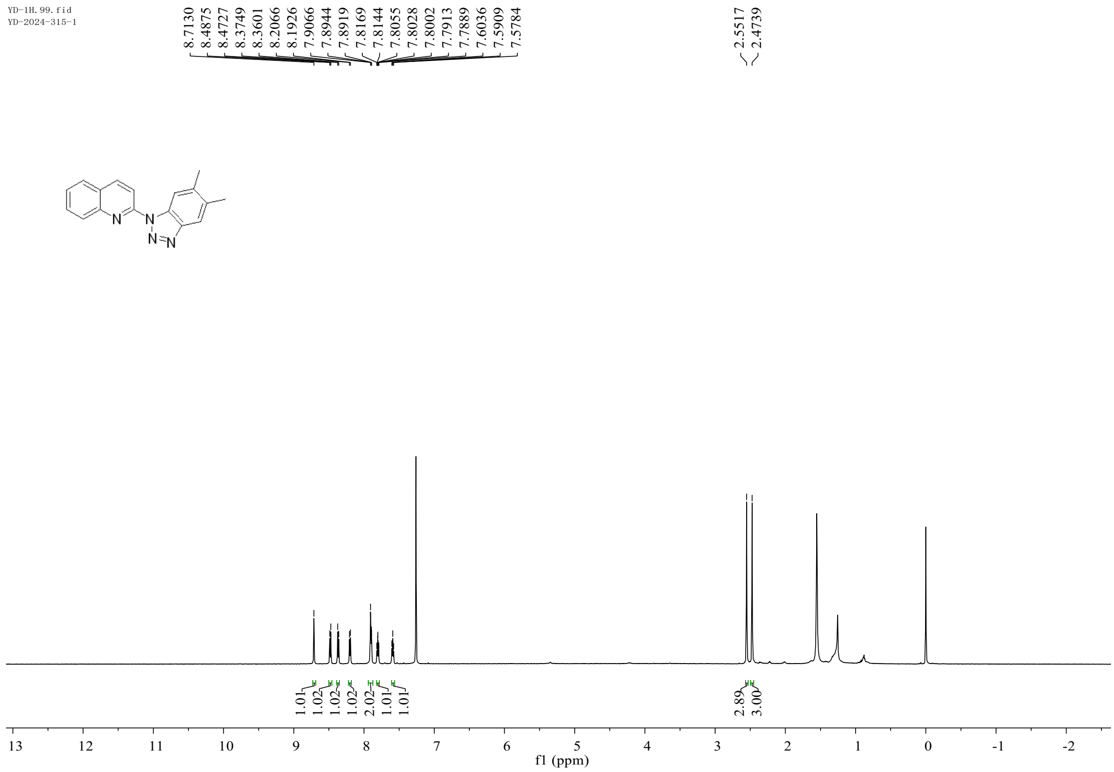
^{1}H-NMR Spectrum (600 MHz, $CDCl_3$) of 4c



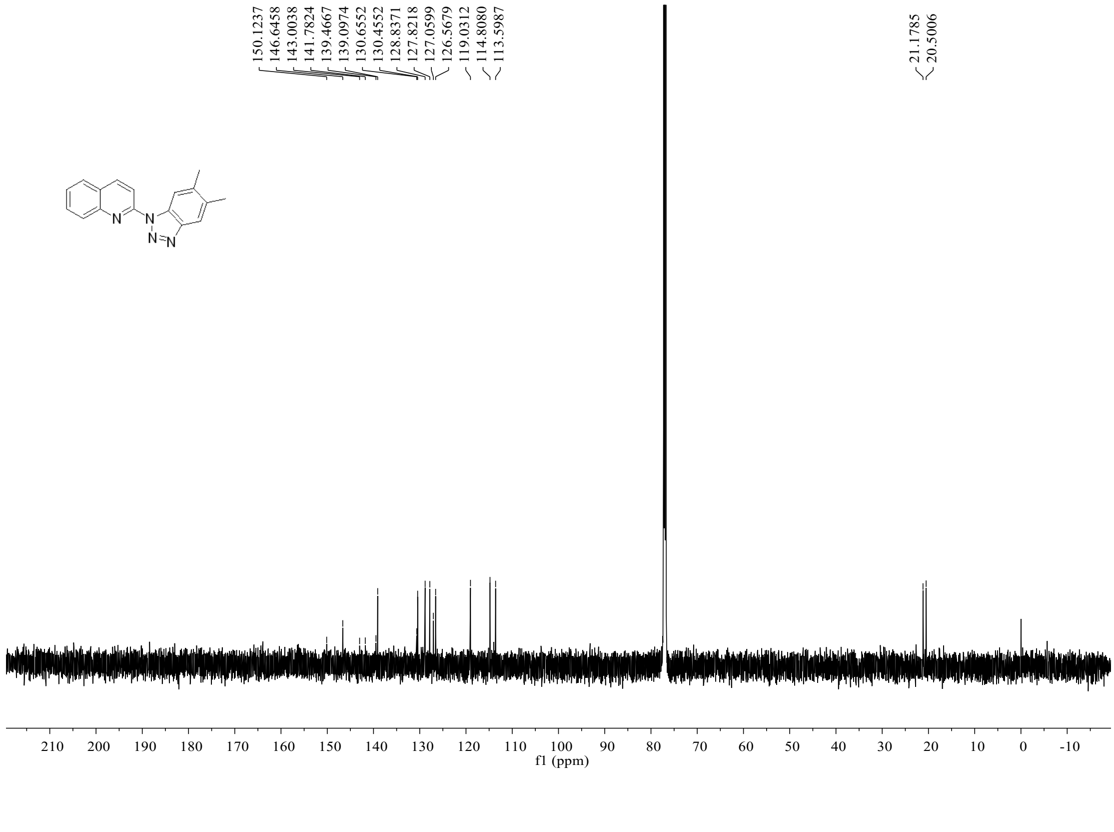
^{13}C-NMR Spectrum (151 MHz, $CDCl_3$) of 4c



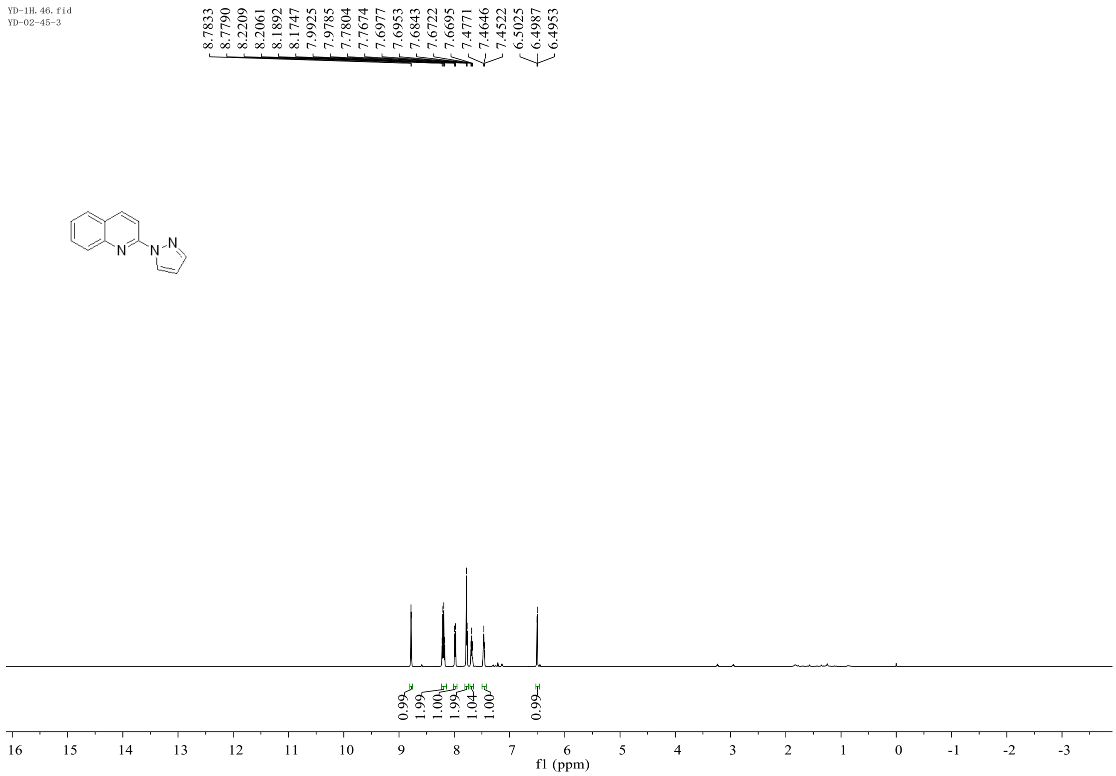
^{1}H-NMR Spectrum (600 MHz, $CDCl_3$) of 4d



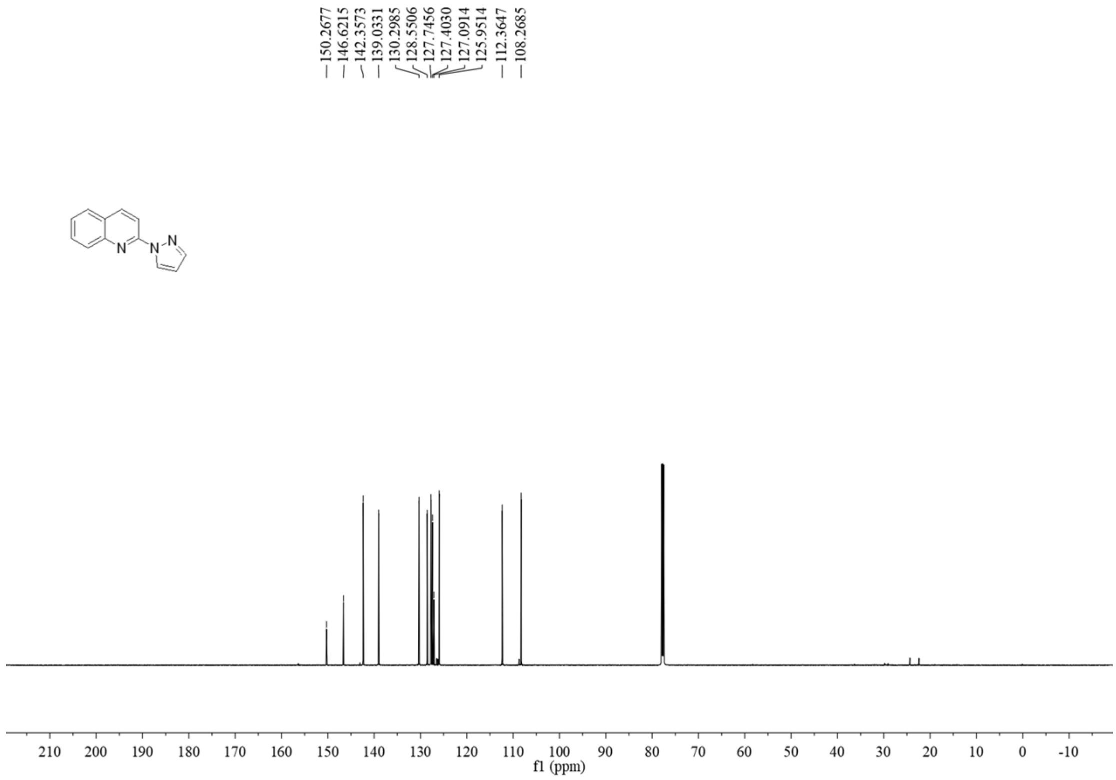
^{13}C-NMR Spectrum (151 MHz, $CDCl_3$) of 4d



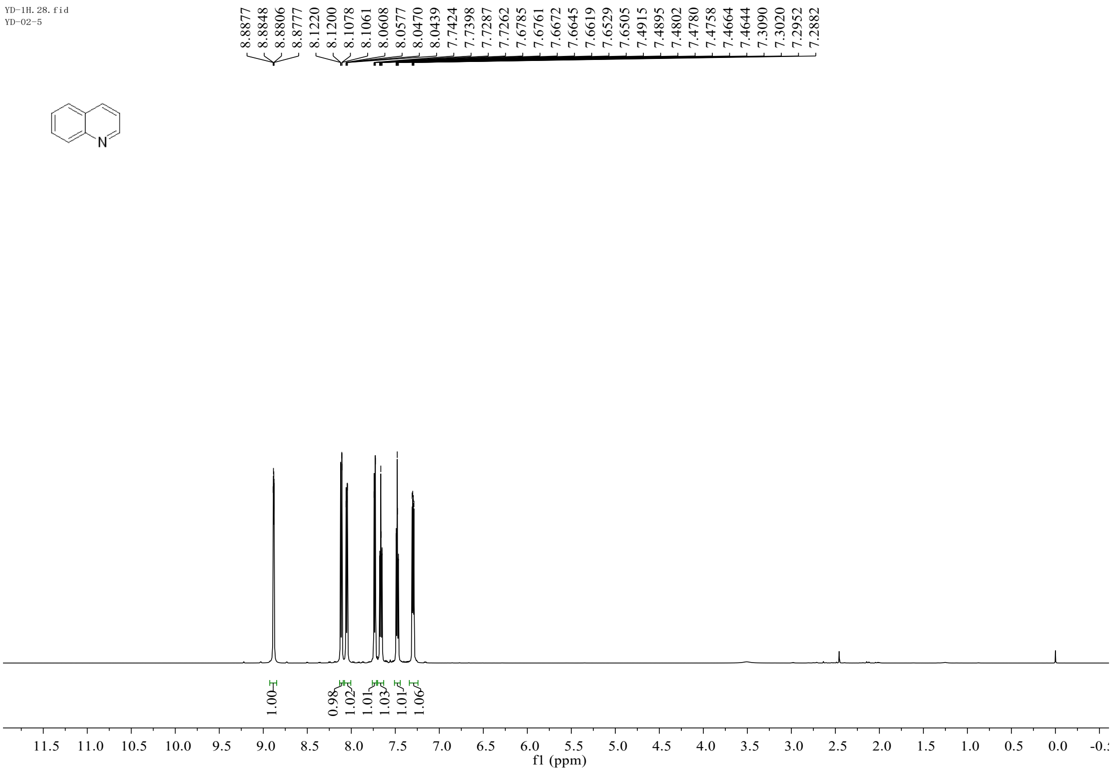
^{1}H-NMR Spectrum (600 MHz, $CDCl_3$) of 4e



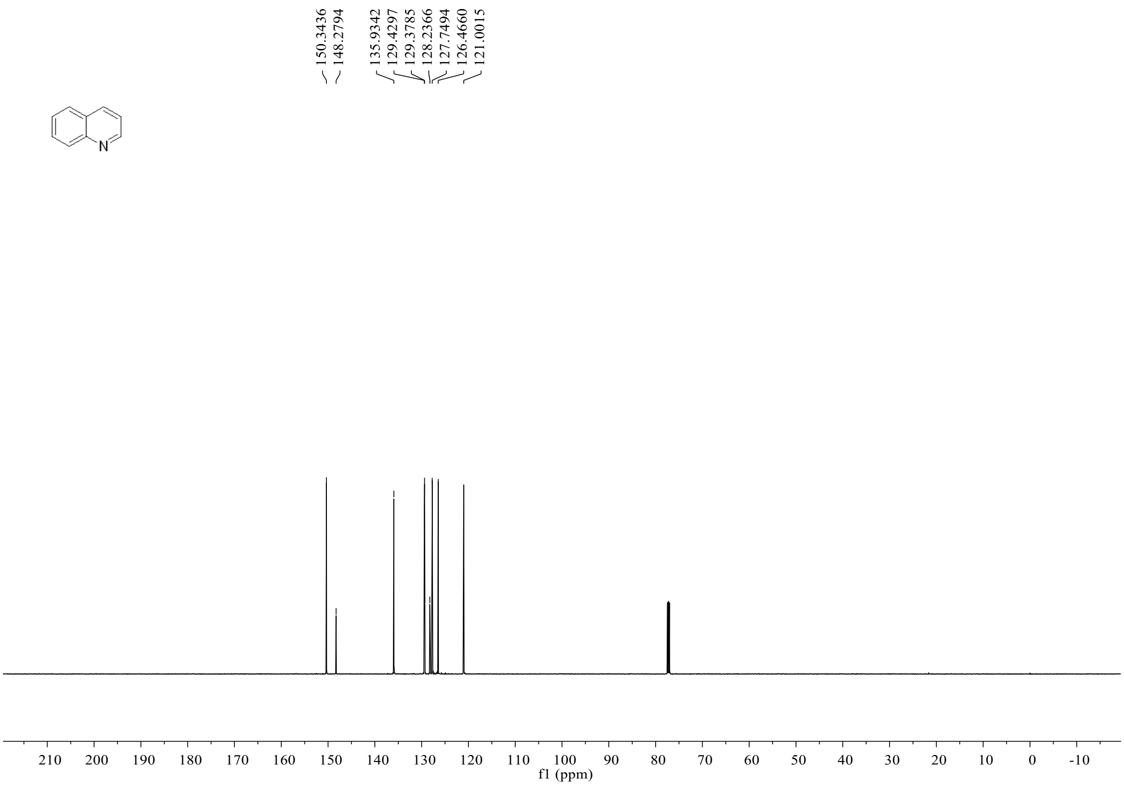
^{13}C-NMR Spectrum (151 MHz, $CDCl_3$) of 4e



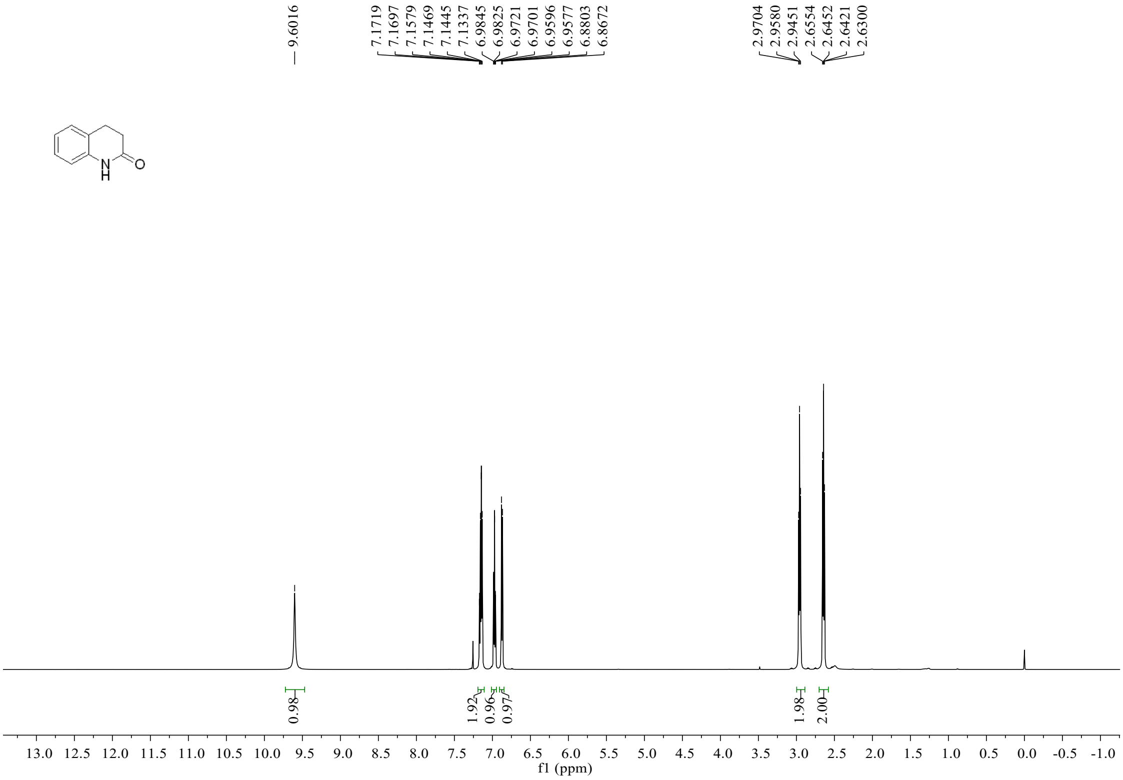
[1]H-NMR Spectrum (600 MHz, $CDCl_3$) of 8



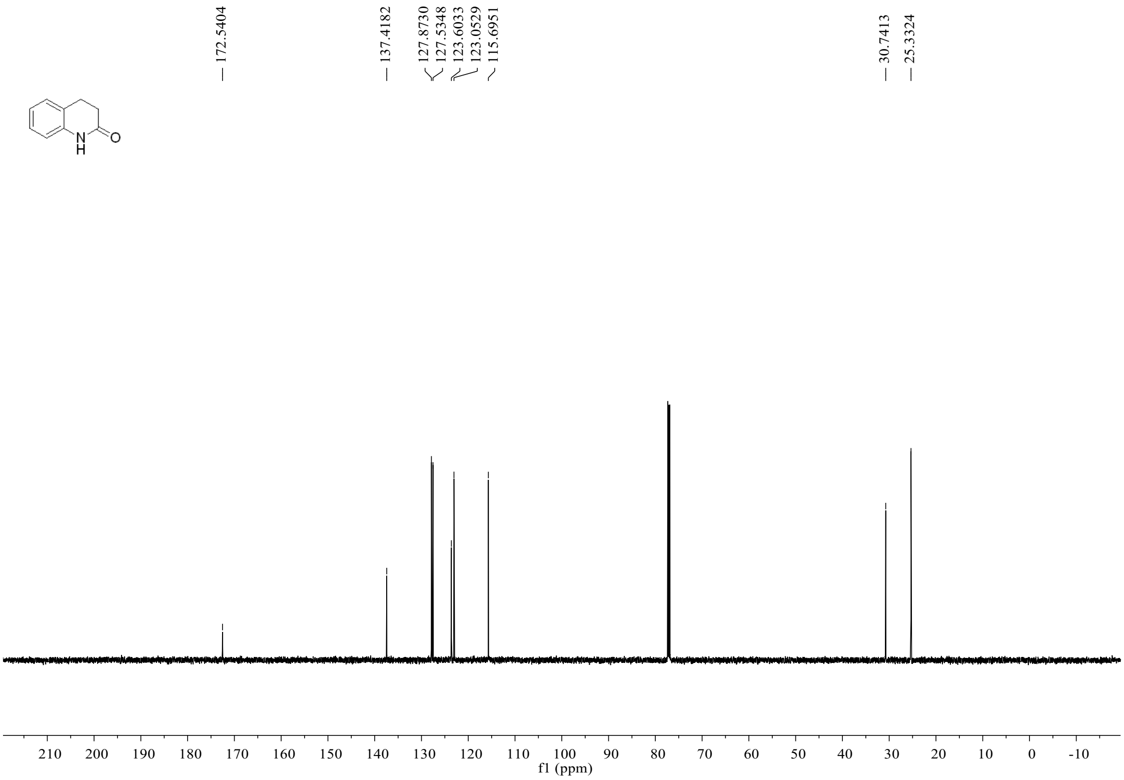
[13]C-NMR Spectrum (151 MHz, $CDCl_3$) of 8



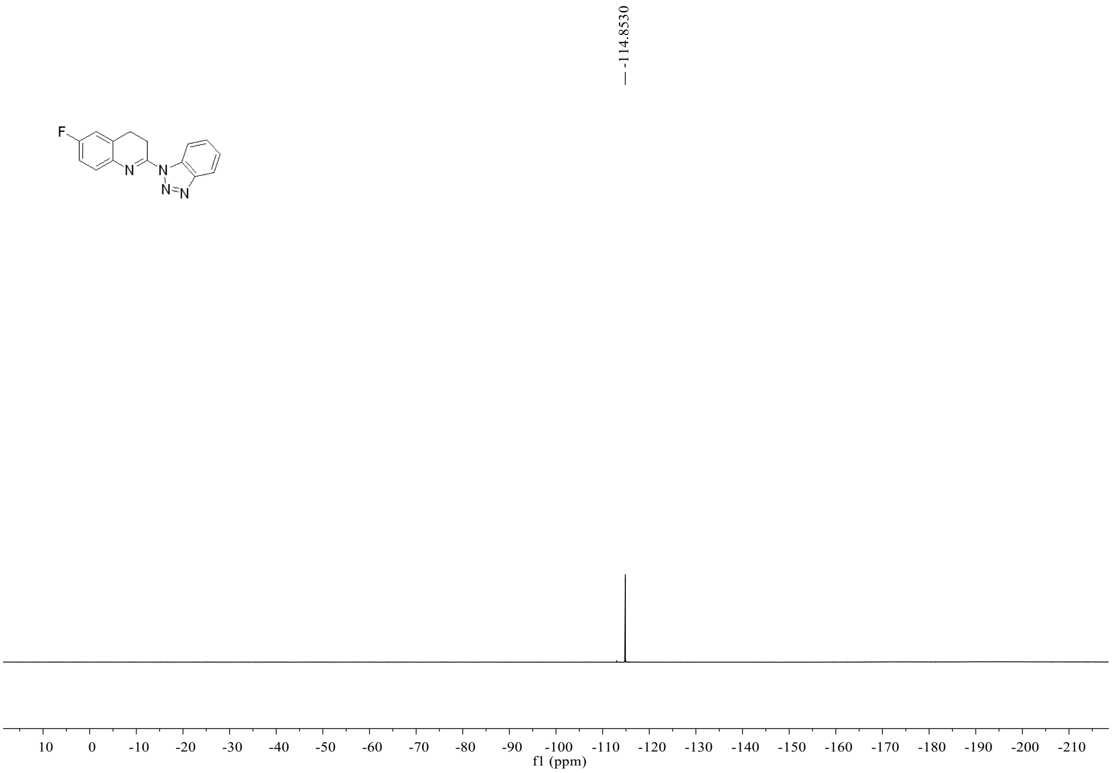
[1]H-NMR Spectrum (600 MHz, $CDCl_3$) of 9



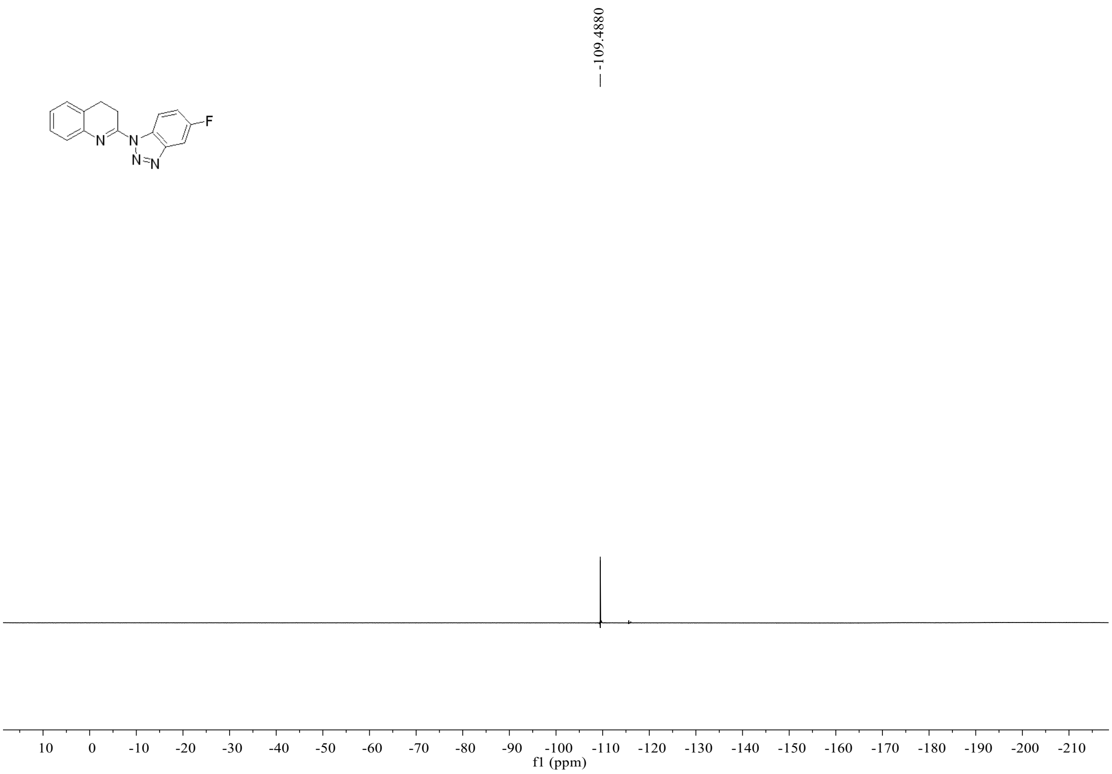
[13]C-NMR Spectrum (151 MHz, $CDCl_3$) of 9



^{19}F-NMR Spectrum (565 MHz, $CDCl_3$) of 3i



^{19}F-NMR Spectrum (565 MHz, $CDCl_3$) of 3s



[19]F-NMR Spectrum (565 MHz, $CDCl_3$) of 3w