Supporting Information

Pd-catalyzed intramolecular aerobic oxidative C-H amination of 2-aryl-3-(arylamino)quinazolinones: synthesis of fluorescent indazolo[3,2-*b*]quinazolinones

Weiguang Yang, Jiuxi Chen,* Xiaobo Huang, Jinchang Ding, Miaochang Liu and Huayue Wu*

College of Chemistry & Materials Engineering, Wenzhou University, Wenzhou 325035, P. R. China

Email: jiuxichen@wzu.edu.cn; huayuewu@wzu.edu.cn

Table of Contents

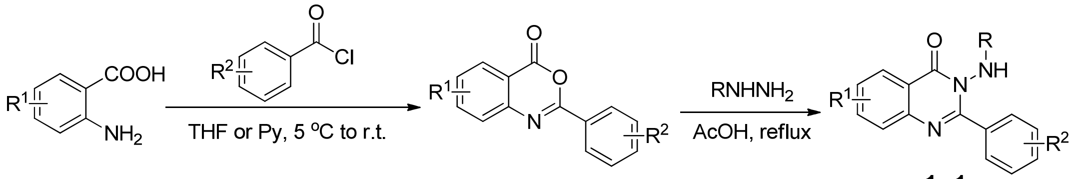
1. General Information

Chemicals were received from commercial sources without further purification or prepared by literature methods. Melting points are uncorrected and recorded on Digital Melting Point Apparatus WRS-1B. ^{1}H NMR and ^{13}C NMR spectra were measured on a 500 MHz Bruker spectrometer, using DMSO-d_6 or $CDCl_3$ as the solvent with tetramethylsilane (TMS) as the internal standard at room temperature. Chemical shifts are given in δ relative to TMS, the coupling constants J are given in Hz. IR spectra were recorded on an AVATAR 370 FI-Infrared Spectrophotometer. High-resolution mass spectra were recorded on an ESI-Q-TOF mass spectrometer. X-ray crystallographic analysis of palladacycle complex **3** was done at the X-ray crystallography facility, Shanghai Institute of Organic Chemistry (SIOC), Chinese Academy of Sciences (CAS).

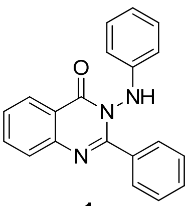
2. Experimental Section

2.1 Preparation of Substrates

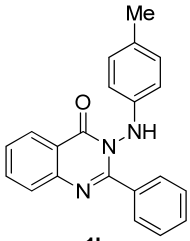
All 2-aryl-3-(arylamino)quinazolinones substrates (**1a**-**1t**) were prepared by literature methods.[1]



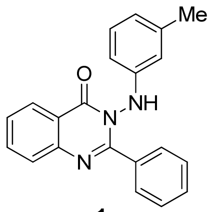
1a-1v



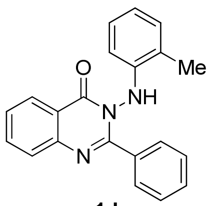
1a



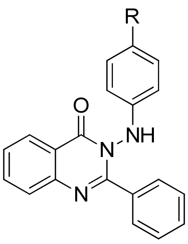
1b



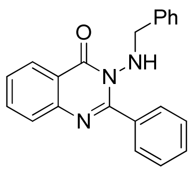
1c



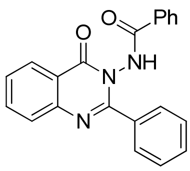
1d



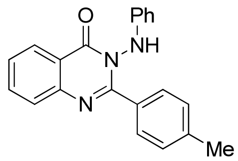
R = F (**1e**), Cl (**1f**), CF_3 (**1g**)



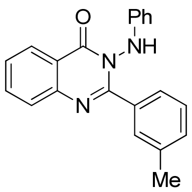
1h



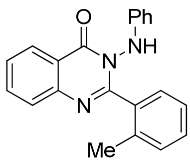
1i



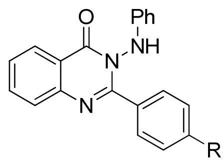
1j



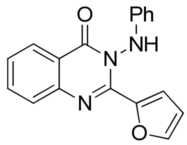
1k



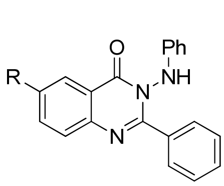
1l



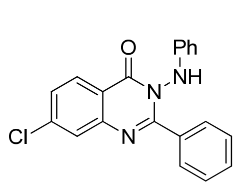
R = CN (**1m**), F (**1n**), Cl (**1o**), Br (**1p**)



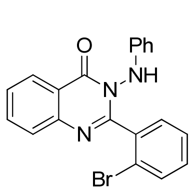
1q



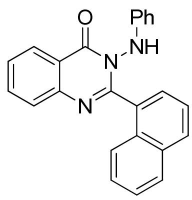
R = Me (**1r**), OMe (**1s**)



1t



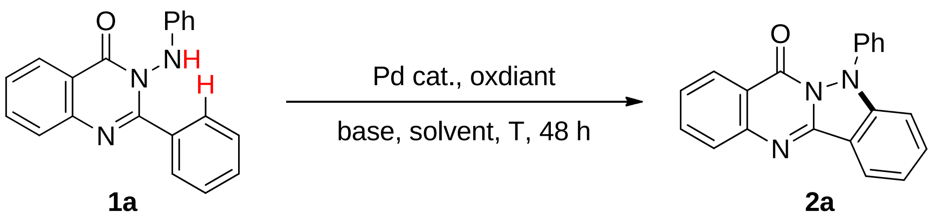
1u



1v

2.2 Optimization of Reaction Conditions

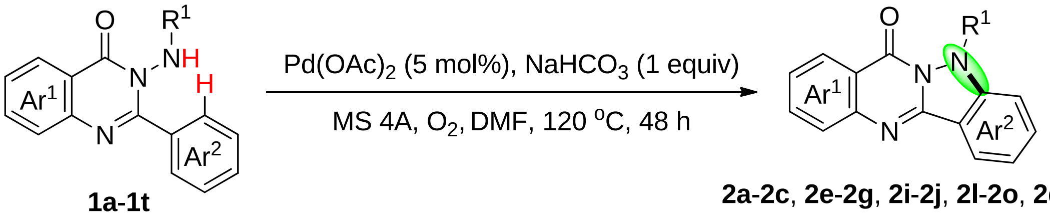
Table S1. Initial Screening of the Reaction Conditions[a]



Entry	Pd catalyst	Oxdiant	Base (*x* equiv)	T (°C)	Solvent	Yield (%)[b]
1	$Pd(OAc)_2$	O_2	Cs_2CO_3 (2)	120	dioxane	trace
2	$Pd(OAc)_2$	O_2	Cs_2CO_3 (2)	120	xylene	24
3	$Pd(OAc)_2$	O_2	Cs_2CO_3 (2)	120	PhCl	14
4	$Pd(OAc)_2$	O_2	Cs_2CO_3 (2)	120	DMA	18
5	$Pd(OAc)_2$	O_2	Cs_2CO_3 (2)	120	DMSO	29
6	$Pd(OAc)_2$	O_2	Cs_2CO_3 (2)	120	DMF	32
7	$Pd(OAc)_2$	O_2	Cs_2CO_3 (2)	80	DMF	13
8	$Pd(OAc)_2$	O_2	Cs_2CO_3 (2)	100	DMF	21
9	$Pd(OAc)_2$	O_2	Cs_2CO_3 (2)	130	DMF	33
10	$Pd(OAc)_2$	O_2	Cs_2CO_3 (1.5)	120	DMF	31
11	$Pd(OAc)_2$	O_2	Cs_2CO_3 (1)	120	DMF	35
12	$Pd(OAc)_2$	O_2	Na_2CO_3 (1)	120	DMF	72
13	$Pd(OAc)_2$	O_2	K_2CO_3 (1)	120	DMF	69
14	$Pd(OAc)_2$	O_2	$NaHCO_3$ (1)	120	DMF	89
15	$Pd(OAc)_2$	O_2	NaOAc (1)	120	DMF	73
16	$Pd(OAc)_2$	O_2	K_3PO_4 (1)	120	DMF	32
17	$Pd(OAc)_2$	O_2	KOH (1)	120	DMF	28
18	$Pd(OAc)_2$	O_2		120	DMF	36
19	$PdCl_2(dppf)$	O_2	$NaHCO_3$ (1)	120	DMF	trace
20	$PdCl_2(dppe)$	O_2	$NaHCO_3$ (1)	120	DMF	32
21	$PdCl_2(MeCN)_2$	O_2	$NaHCO_3$ (1)	120	DMF	45
22	$PdCl_2(NH_3)_4$	O_2	$NaHCO_3$ (1)	120	DMF	30
23	$PdCl_2(cod)$	O_2	$NaHCO_3$ (1)	120	DMF	trace
24	$Pd(OAc)_2$	AgOAc	$NaHCO_3$ (1)	120	DMF	43[c]
25	$Pd(OAc)_2$	$K_2S_2O_8$	$NaHCO_3$ (1)	120	DMF	35[c]
26	$Pd(OAc)_2$	BQ	$NaHCO_3$ (1)	120	DMF	38[c]
27	$Pd(OAc)_2$	$PhI(OAc)_2$	$NaHCO_3$ (1)	120	DMF	41[c]

[a] Reaction Conditions: **1a** (0.2 mmol), Pd catalyst (5 mol%), base (*x* equiv), oxidant, MS 4 A (60 mg), and solvent (5 mL), O_2, 120 °C, 48 h. [b] Isolated yield. [c] 2-Phenylquinazolin-4(3*H*)-one was obtained using 1.5 equiv oxdiant under a N_2 atmosphere.

2.3 Typical Procedure for Pd-Catalyzed Intramolecular C-H Amination

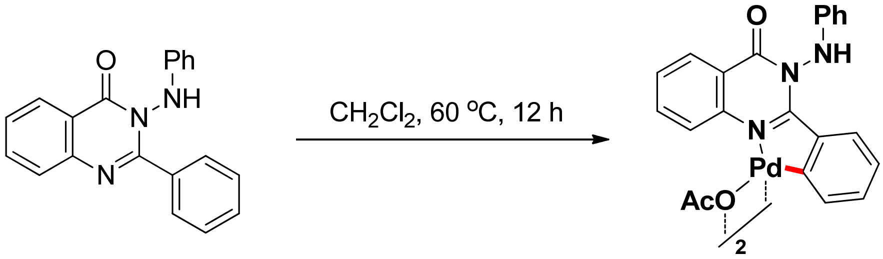


1a-1t

2a-2c, **2e-2g**, **2i-2j**, **2l-2o**, **2q-2t**

In a 50 mL sealed tube, 2-phenyl-3-(phenylamino)quinazolinone (**1a**) (62.7 mg, 0.2 mmol, 1.0 equiv.), $Pd(OAc)_2$ (2.3 mg, 0.01 mmol, 5 mol %), $NaHCO_3$ (16.8 mg, 0.2 mmol 1.0 equiv.) and MS 4Å (60 mg), were dissolved in DMF (5 mL) under an oxygen atmosphere. The reaction mixture was then tightly capped and stirred for 10 minutes at room temperature for proper mixing of the reactants, and then heated at 120 °C with vigorous stirring for 48 hours. The reaction mixture was then cooled to room temperature, diluted with dichloromethane and filtered through a small pad of Celite. The filtrate was concentrated *in vacuo* and purified by a silica gel packed flash chromatography column with petroleum ether/ethyl acetate (5:1) as the eluent to afford the desired product **2a**.

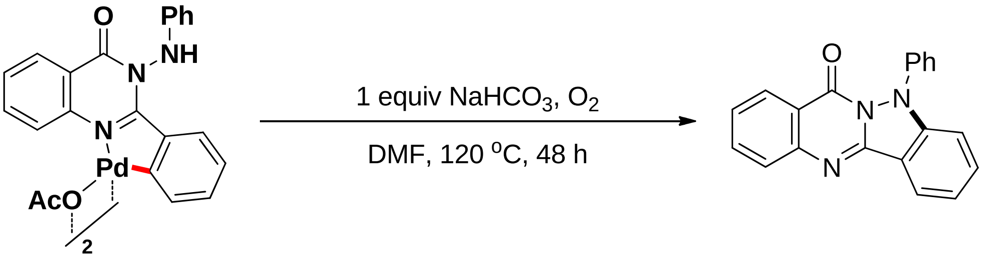
2.4 Procedure for the Preparation of Palladium Complex 3



1a **3**

In a 25 mL sealed tube, 2-phenyl-3-(phenylamino)quinazolinone (**1a**) (62.7 mg, 0.2 mmol, 1.0 equiv.) and $Pd(OAc)_2$ (67.6 mg, 0.3 mmol, 1.5 equiv.) were dissolved in dichloromethane (5 mL) under a N_2 atmosphere. The reaction mixture was then tightly capped and stirred for 10 minutes at room temperature for proper mixing of the reactants, and then heated at 60 °C with vigorous stirring for 12 hours. The reaction mixture was then cooled to room temperature, and filtered through a small pad of Celite. The residue was washed by dichloromethane (3 x 5 mL) and the product was dissolved in dichloromethane. After removing acetone *in vacuo*, the complex **3** was obtained as a black brown amorphous solid (15.3 mg, 16 % yield) after crystallized from ethyl acetate/hexane (1:3). The complex **3** was crystallized from dichloromethane/petroleum ether (1:1) for about a week at room temperature to give a black brown block.

2.5 Intramolecular Amination of Palladium Complex 3



3 2a

In a 25 mL sealed tube, complex **3** (47.8 mg, 0.05 mmol, 1.0 equiv.), $NaHCO_3$ (4.2 mg, 0.05 mmol 1.0 equiv.) and MS 4Å (15 mg) were dissolved in DMF (3 mL) under an oxygen atmosphere. The reaction mixture was then tightly capped and stirred for 10 minutes at room temperature for proper mixing of the reactants, and then heated at 120 °C with vigorous stirring for 48 hours. The reaction mixture was then cooled to room temperature, diluted with dichloromethane and filtered through a small pad of Celite. The filtrate was concentrated *in vacuo* and purified by a silica gel packed flash chromatography column with petroleum ether/ethyl acetate (5:1) as the eluent. The product **2a** was obtained as a white solid amorphous solid (19.9 mg, 64% yield).

3. UV-vis Absorption and Fluorescence

3.1 UV-vis Absorption Spectra of indazolo[3,2-*b*]quinazolinones

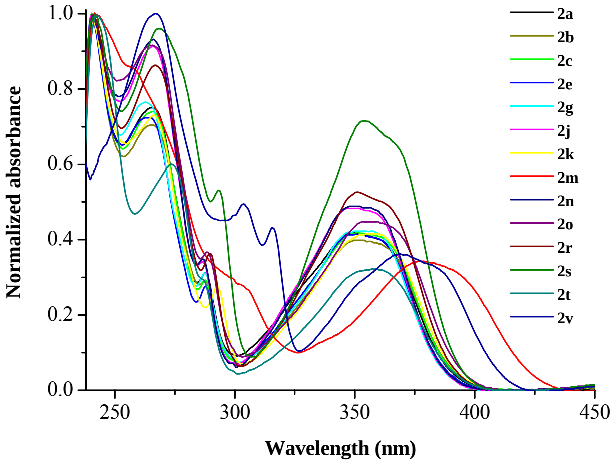


Figure S1 UV-vis absorption spectra of indazolo[3,2-*b*]quinazolinones in $CHCl_3$.

3.2 Fluorescence Spectra of indazolo[3,2-*b*]quinazolinones

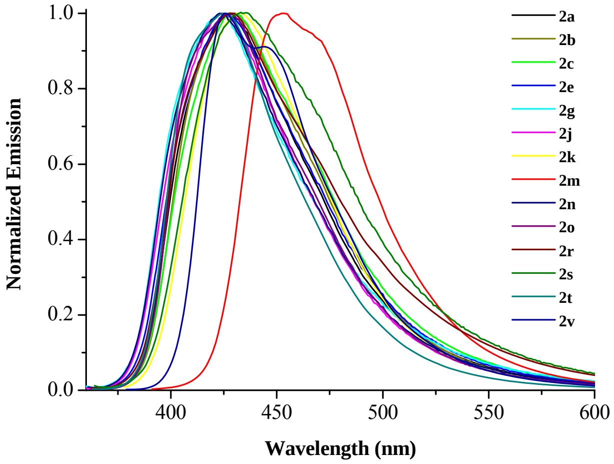


Figure S2 Fluorescence spectra of indazolo[3,2-*b*]quinazolinones in $CHCl_3$.

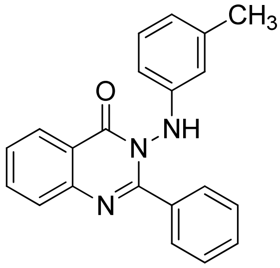
3.3 Photophysical Properties of indazolo[3,2-*b*]quinazolinones

Table S2. Photophysical properties of indazolo[3,2-*b*]quinazolinones in $CHCl_3$.

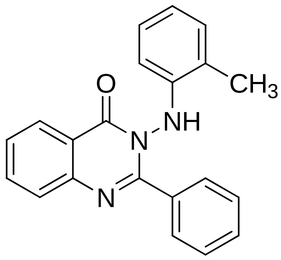
Compound	λ_{abs} (nm)	λ_{em} (nm)	Stoke's shift (nm)	Φ_{PL}
2a	241, 266, 288, 348	427	79	0.070
2b	241, 266, 288, 350	429	79	0.10
2c	241, 266, 288, 351	430	79	0.083
2e	241, 264, 288, 350	426	76	0.066
2g	241, 263, 287, 350	424	74	0.034
2j	240, 267, 287, 348	424	76	0.043
2k	241, 266, 293, 359	433	74	0.13
2m	242, 377	453	76	0.56
2n	241, 266, 287, 349	423	74	0.051
2o	241, 265, 289, 354	428	74	0.11
2r	241, 267, 290, 351	429	78	0.046
2s	242, 269, 293, 353	434	81	0.02
2t	243, 274, 357	426	69	0.089
2v	267, 303, 316, 369	425, 444	75	0.25

4. Analytical Data

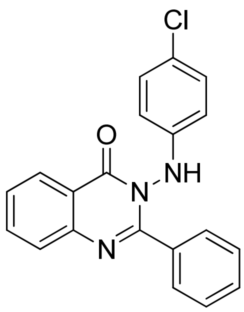
4.1 Analytical Data for Unknown 2-Aryl-3-(arylamino)quinazolinones



3-(m-Toluidino)-2-phenylquinazolin-4(3H)-one ***(1c)***: White solid, mp 132-133 °C. ^{1}H NMR (500 MHz, DMSO-d_6) δ 9.00 (s, 1H), 8.15-8.14 (m, 1H), 7.93-7.90 (m, 1H), 7.80 (d, *J* = 8.0 Hz, 1H), 7.75-7.74 (m, 2H), 7.61-7.58 (m, 1H), 7.47-7.40 (m, 3H), 6.98 (t, *J* = 8.0 Hz, 1H), 6.57 (d, *J* = 7.5 Hz, 1H), 6.44 (s, 1H), 6.34 (d, *J* = 8.0 Hz, 1H), 2.15 (s, 3H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 160.6, 157.5, 147.0, 146.8, 138.2, 134.9, 134.2, 129.7, 128.9, 128.4, 127.7, 127.4, 127.1, 126.2, 121.3, 120.8, 113.0, 109.4, 21.0.

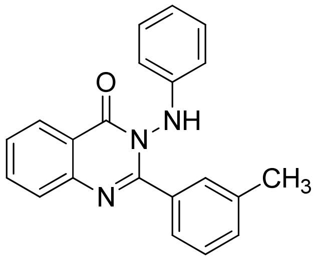


3-(o-Toluidino)-2-phenylquinazolin-4(3H)-one ***(1d)***: White solid, mp 142-143 °C. ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.50 (s, 1H), 8.17-8.15 (m, 1H), 7.94-7.91 (m, 1H), 7.83-7.81 (m, 3H), 7.62-7.59 (m, 1H), 7.46-7.39 (m, 3H), 7.02 (d, *J* = 7.0 Hz, 1H), 6.89 (t, *J* = 8.0, Hz, 1H), 6.68 (t, *J* = 7.5, Hz, 1H), 6.19 (d, *J* = 8.0 Hz, 1H), 2.17 (s, 3H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 160.4, 157.4, 146.8, 144.4, 135.0, 134.0, 130.2, 129.8, 129.1, 127.7, 127.4, 127.2, 126.6, 126.3, 122.4, 121.1, 119.9, 110.5, 17.1.

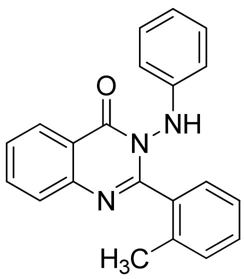


3-(4-Chlorophenylamino)-2-phenylquinazolin-4(3H)-one ***(1f)***: White solid, mp

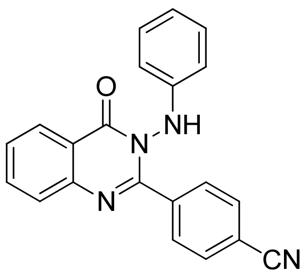
211-212 °C. ^{1}H NMR (500 MHz, DMSO-d_6) δ 9.25 (s, 1H), 8.16-8.14 (m, 1H), 7.94-7.91 (m, 1H), 7.80 (d, *J* = 8.0 Hz, 1H), 7.72-7.70 (m, 2H), 7.62-7.58 (m, 1H), 7.48-7.40 (m, 3H), 7.16-7.13 (m, 2H), 6.65-6.62 (m, 2H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 160.4, 157.3, 146.7, 146.0, 135.6, 135.0, 134.1, 129.8, 128.8, 127.7, 127.5, 127.2, 126.3, 123.4, 121.2, 114.0.



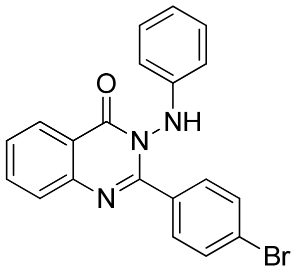
3-(Phenylamino)-2-m-tolylquinazolin-4(3H)-one ***(1k)***: White solid, mp 128-129 °C. ^{1}H NMR (500 MHz, DMSO-d_6) δ 9.08 (s, 1H), 8.14 (dd, *J* = 8.5, 1.0Hz, 1H), 7.93-7.90 (m, 1H), 7.80 (d, *J* = 8.5 Hz, 1H), 7.60-7.56 (m, 1H), 7.56 (s, 1H), 7.53 (d, *J* = 7.0 Hz, 1H), 7.30-7.25 (m, 2H), 7.12 (t, *J* = 8.0 Hz, 2H), 6.76 (t, *J* = 7.5 Hz, 1H), 6.57 (d, *J* = 8.0 Hz, 2H), 2.31 (s, 3H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 160.6, 157.6, 147.0, 146.8, 136.7, 134.9, 134.2, 130.3, 129.4, 128.9, 127.7, 127.3, 127.0, 126.2, 126.0, 121.2, 119.9, 112.3, 20.9.



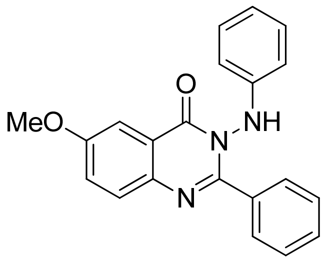
3-(pPhenylamino)-2-o-tolylquinazolin-4(3H)-one ***(1l)***: mp 136-137 °C. ^{1}H NMR (500 MHz, DMSO-d_6) δ 9.20 (s, 1H), 8.18-8.16 (m, 1H), 7.94-7.90 (m, 1H), 7.78 (d, *J* = 8.0 Hz, 1H), 7.62-7.59 (m, 1H), 7.42 (d, *J* = 7.5 Hz, 1H), 7.31-7.24 (m, 2H), 7.16-7.13 (m, 1H), 7.11-7.08 (m, 2H), 6.74 (t, *J* = 8.0 Hz, 1H), 6.59 (d, *J* = 8.0 Hz, 2H), 2.28 (s, 3H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 160.3, 158.0, 146.9, 146.8, 135.5, 134.9, 134.7, 139.4, 128.9, 128.8, 127.6, 127.2, 126.2, 126.0, 124.9, 121.4, 120.0, 112.5, 19.1.



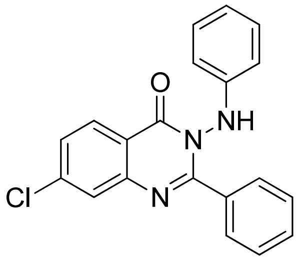
4-(4-Oxo-3-(phenylamino)-3,4-dihydroquinazolin-2-yl)benzonitrile (***1m***): White solid, mp 220-221 ºC. [1]H NMR (500 MHz, DMSO-d_6) δ 9.10 (s, 1H), 8.16 (d, *J* = 8.0 Hz, 1H), 7.96-7.92 (m, 5H), 7.83 (d, *J* = 8.0 Hz, 1H), 7.63 (t, *J* = 8.0 Hz, 1H), 7.12 (t, *J* = 8.0 Hz, 2H), 6.78 (t, *J* = 7.5 Hz, 1H), 6.63 (d, *J* = 8.0 Hz, 2H); [13]C NMR (125 MHz, DMSO-d_6) δ 160.3, 156.0, 146.7, 146.6, 138.6, 135.0, 131.5, 129.7, 129.0, 127.8, 127.6, 126.3, 121.5, 120.2, 118.3, 112.5, 112.3.



2-(4-Bromophenyl)-3-(phenylamino)quinazolin-4(3H)-one (***1p***): White solid, mp 199-200 ºC. [1]H NMR (500 MHz, DMSO-d_6) δ 9.11 (s, 1H), 8.16-8.14 (m, 1H), 7.94-7.91 (m, 1H), 7.81 (d, *J* = 7.5 Hz, 1H), 7.72-7.70 (m, 2H), 7.64-7.59 (m, 3H), 7.13-7.10 (m, 2H), 6.77 (t, *J* = 7.5Hz, 1H), 6.60 (d, *J* = 7.5Hz, 2H); [13]C NMR (125 MHz, DMSO-d_6) δ 160.4, 156.4, 146.8, 146.7, 135.0, 133.4, 131.0, 130.6, 129.0, 127.7, 127.3, 126.3, 123.5, 121.4, 120.1, 112.4.

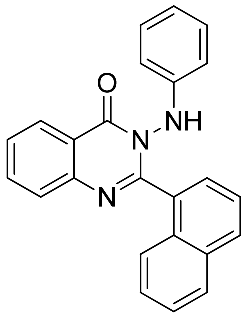


6-Methoxy-2-phenyl-3-(phenylamino)quinazolin-4(3H)-one (***1s***): White solid, mp 178-180 ºC. [1]H NMR (500 MHz, DMSO-d_6) δ 9.10 (s, 1H), 7.76-7.72 (m, 3H), 7.52-7.51 (m, 2H), 7.45-7.38 (m, 3H), 7.11 (t, *J* = 8.0 Hz, 2H), 6.75 (t, *J* = 7.5Hz, 1H), 6.56 (d, *J* = 8.0 Hz, 2H), 2.50 (s, 3H); [13]C NMR (125 MHz, DMSO-d_6) δ 160.3, 158.0, 155.2, 147.0, 141.3, 134.2, 129.5, 129.4, 128.9, 128.9, 127.4, 124.4, 122.2, 119.9, 112.3, 106.2, 55.7.



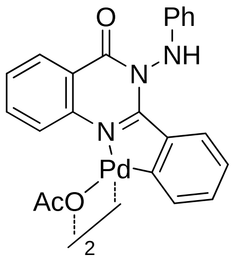
7-Chloro-2-phenyl-3-(phenylamino)quinazolin-4(3H)-one (***1t***): White solid, mp

143-144 °C. ^{1}H NMR (500 MHz, DMSO-d_6) δ 9.10 (s, 1H), 8.14 (d, J = 8.5 Hz, 1H), 7.88 (d, J = 2.0 Hz, 1H), 7.75-7.73 (m, 2H), 7.64-7.62 (m, 1H), 7.48-7.40 (m, 3H), 7.12 (t, J = 8.0 Hz, 2H), 6.76 (t, J = 8.0 Hz, 1H), 6.60 (d, J = 8.0 Hz, 2H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 160.0, 159.0, 147.8, 146.8, 139.6, 133.9, 130.0, 129.0, 128.9, 128.3, 127.5, 127.4, 126.8, 120.1, 120.0, 112.4.



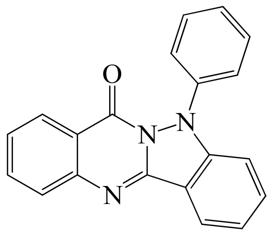
*2-(Naphthalen-1-yl)-3-(phenylamino)quinazolin-4(3H)-one (**1v**)*: White solid, mp 216-217 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.37 (d, J = 8.0 Hz, 1H), 7.94-7.85 (m, 4H), 7.67 (s, 1H), 7.64 (d, J = 7.0 Hz, 1H), 7.60-7.57 (m, 1H), 7.53-7.48 (m, 2H), 7.43 (t, J = 8.0 Hz, 1H), 7.12-7.09 (m, 2H), 6.87-6.85 (m, 2H), 6.57 (d, J = 8.0 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.6, 157.0, 147.4, 146.2, 135.2, 133.4, 132.0, 131.1, 130.2, 129.2, 128.8, 128.3, 127.6, 127.2, 127.1, 126.5, 126.3, 125.0, 124.5, 122.5, 121.8, 114.4.

4.2 Analytical Data for Palladium Complex 3

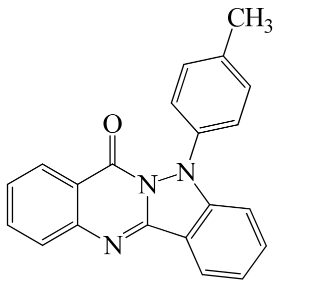


*Palladium complex **3***: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.21 (d, *J* = 8.5 Hz, 1H), 8.06 (d, *J* = 8.0 Hz, 1H), 7.91 (d, *J* = 7.5 Hz, 1H), 7.69-7.66 (m, 1H), 7.40 (t, *J* = 7.5 Hz, 1H), 7.29-7.28 (m, 2H), 7.08 (s, 1H), 7.04 (t, *J* = 7.5 Hz, 1H), 6.85 (t, *J* = 7.5 Hz, 1H), 6.79 (d, *J* = 7.5 Hz, 2H), 6.58 (d, *J* = 8.0 Hz, 1H), 6.44 (t, *J* = 7.0 Hz, 1H), 2.13 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 180.9, 162.2, 159.9, 153.0, 145.7, 145.2, 138.9, 134.4, 131.5, 130.6, 130.3, 130.0, 127.3, 126.5, 126.3, 124.6, 123.9, 119.3, 115.2, 24.8.

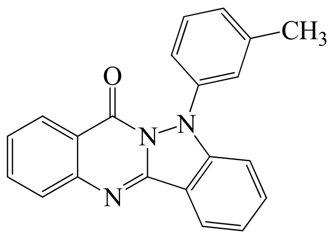
4.3 Analytical Data for All Products



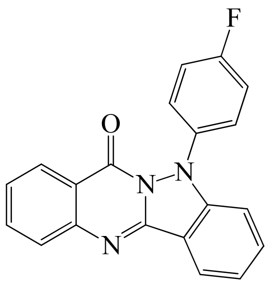
*5-Phenylindazolo[3,2-b]quinazolin-7(5H)-one (**2a**)*: White solid (55.4 mg, 89%), mp 230-231 °C (lit.[2] 238-239 °C). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.34-8.32 (m, 1H), 8.29 (d, *J* = 8.0 Hz, 1H), 7.9 (d, *J* = 8.5 Hz, 1H), 7.83-7.80 (m, 1H), 7.63-7.60 (m, 1H), 7.50-7.35 (m, 7H), 7.21 (d, *J* = 8.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.5, 149.2, 148.8, 148.3, 141.9, 134.1, 133.5, 129.6, 128.7, 127.1, 126.8, 125.5, 124.7, 124.4, 123.4, 119.9, 118.9, 112.5.



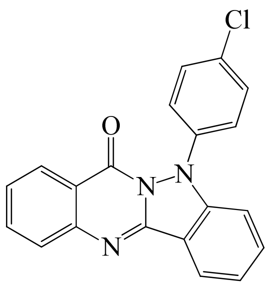
*5-p-Tolylindazolo[3,2-b]quinazolin-7(5H)-one (**2b**)*: White solid (59.8 mg, 92%), White solid, mp 184-185 °C (lit.[3] 184-185 °C). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.34-8.32 (m, 1H), 8.28 (d, *J* = 7.5 Hz, 1H), 7.91 (d, *J* = 8.0 Hz, 1H), 7.83-7.79 (m, 1H), 7.63-7.59 (m, 1H), 7.47-7.39 (m, 2H), 7.28-7.24 (m, 4H), 7.18 (d, *J* = 8.0 Hz, 1H), 2.40 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.5, 149.4, 148.7, 148.3, 139.3, 138.8, 134.1, 135.5, 130.3, 127.0, 126.8, 125.4, 124.7, 124.3, 123.3, 119.9, 118.8, 112.5, 21.4.



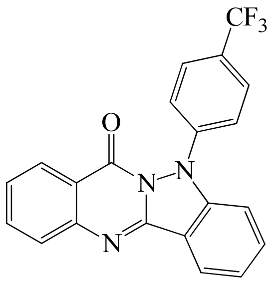
*5-m-Tolylindazolo[3,2-b]quinazolin-7(5H)-one (**2c**)*: White solid (58.5 mg, 90%), White solid, mp 221-223 °C (lit.[3] 241-242 °C). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.35-8.33 (m, 1H), 8.29 (d, *J* = 8.0 Hz, 1H), 7.92 (d, *J* = 8.0 Hz, 1H), 7.84-7.80 (m, 1H), 7.64-7.60 (m, 1H), 7.48-7.34 (m, 3H), 7.22-7.16 (m, 3H), 7.14 (s, 1H), 2.38 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.5, 149.3, 148.8, 148.4, 141.9, 139.8, 134.1, 133.5, 129.6, 129.4, 127.1, 126.8, 125.5, 125.0, 124.4, 123.3, 121.7, 119.9, 118.9, 112.6, 21.6.



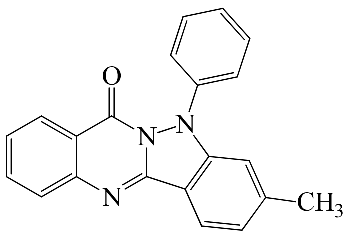
5-(4-Fluorophenyl)indazolo[3,2-b]quinazolin-7(5H)-one ***(2e)***: Pale-green solid (56.6 mg, 86%), mp 197-198 °C (lit.[4] no report). ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.25 (d, J = 7.5 Hz, 1H), 8.17 (d, J = 8.0 Hz, 1H), 7.92-7.88 (m, 2H), 7.77-7.74 (m, 1H), 7.57-7.49 (m, 4H), 7.33-7.30 (m, 3H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 161.2 (d, $^1J_{C\text{-}F}$ = 243.7 Hz, 1C), 155.3, 148.4, 148.2, 147.6, 137.9, 134.0, 133.8, 126.9, 126.5 (d, $^3J_{C\text{-}F}$ = 8.7 Hz, 1C), 125.9, 125.3, 124.6, 122.9, 119.4, 118.3, 116.0 (d, $^2J_{C\text{-}F}$ = 22.5 Hz, 1C), 112.3.



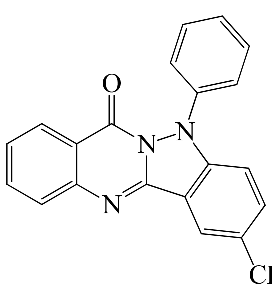
5-(4-Chlorophenyl)indazolo[3,2-b]quinazolin-7(5H)-one ***(2f)***: Pale-yellow solid (51.8 mg, 75%), mp 240-242 °C (lit.[2] 236-237 °C). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.34-8.30 (m, 2H), 7.92 (d, J = 8.0 Hz, 1H), 7.85-7.82 (m, 1H), 7.66-7.63 (m, 1H), 7.50-7.43 (m, 4H), 7.32-7.31 (m, 2H), 7.18 (d, J = 8.5 Hz, 1H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 155.2, 148.2, 148.0, 147.6, 140.5, 134.0, 133.8, 132.2, 129.2, 126.9, 125.9, 125.8, 125.4, 124.8, 123.0, 119.4, 118.5, 112.3.



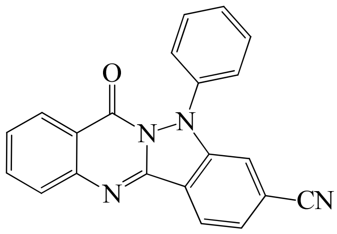
5-(4-(Trifluoromethyl)phenyl)indazolo[3,2-b]quinazolin-7(5H)-one (***2g***): White solid (59.1 mg, 78%), mp 214-215 °C (lit.[3] 210-212 °C). ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.27 (d, J = 8.0 Hz, 1H), 8.19 (d, J = 8.0 Hz, 1H), 7.94-7.90 (m, 2H), 7.86 (d, J = 8.5 Hz, 2H), 7.79-7.74 (m, 3H), 7.57-7.52 (m, 2H), 7.49 (d, J = 8.0 Hz, 1H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 155.3, 148.2, 147.7, 147.4, 144.9, 134.2, 133.9, 127.9 (q, $^2J_{C-F}$ = 32.5 Hz, 1C), 126.9, 126.4 (q, $^3J_{C-F}$ = 3.8 Hz, 1C), 126.0, 125.5, 125.1, 124.3, 123.9 (q, $^1J_{C-F}$ = 270.0 Hz, 1C), 123.1, 119.4, 118.6, 112.2.



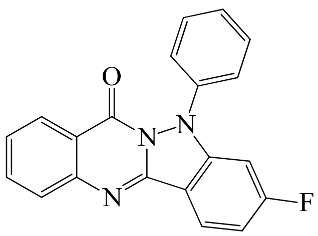
3-Methyl-5-phenylindazolo[3,2-b]quinazolin-7(5H)-one (***2j***): White solid (49.4 mg, 76%), mp 254-255 °C (lit.[3] 248-250 °C). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.32 (d, J = 8.0Hz, 1H), 8.16 (d, J = 8.0 Hz, 1H), 7.89 (d, J = 8.5 Hz, 1H), 7.82-7.79 (m, 1H), 7.50-7.42 (m, 4H), 7.35 (d, J = 7.5 Hz, 2H), 7.24 (d, J = 8.0 Hz, 1H), 6.99 (s, 1H), 2.46 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.6, 149.7, 148.9, 148.4, 145.0, 142.1, 134.1, 129.6, 128.6, 127.0, 126.8, 126.2, 125.3, 124.7, 123.0, 119.8, 116.5, 112.4, 22.6.



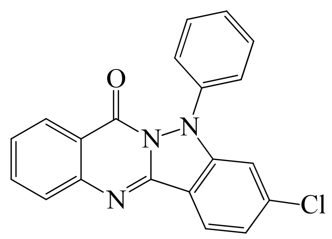
2-Methyl-5-phenylindazolo[3,2-b]quinazolin-7(5H)-one (***2k***): White solid (50.7 mg, 78%), mp 234-236 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.34-7.80 (m, 1H), 8.09 (s, 1H), 7.90 (d, J = 8.0 Hz, 1H), 7.83-7.80 (m, 1H), 7.48-7.33 (m, 7H), 7.11 (d, J = 8.0 Hz, 1H), 2.51 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.5, 148.8, 148.5, 147.7, 142.3, 135.0, 134.1, 129.6, 129.2, 128.5, 127.1, 126.8, 125.4, 124.5, 122.9, 119.9, 119.1, 112.4, 21.2. IR (KBr): 3057, 2923, 2856, 1672, 1630, 1483, 1266, 1016 cm^{-1}. HRMS (ESI) calcd for $C_{21}H_{15}N_3O$ $[M+H]^+$: 326.1288, found 326.1294.



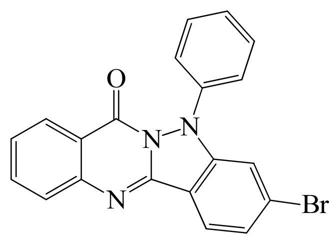
7-Oxo-5-phenyl-5,7-dihydroindazolo[3,2-b]quinazoline-3-carbonitrile ***(2m)***: Green solid (34.9 mg, 52%), mp 212-213 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.39 (d, J = 8.5 Hz, 1H), 8.34 (d, J = 8.0 Hz, 1H), 7.93 (d, J = 8.5 Hz, 1H), 7.88-7.85 (m, 1H), 7.66 (d, J = 8.0 Hz, 1H), 7.55-7.48 (m, 5H), 7.38-7.37 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.1, 148.4, 148.2, 146.5, 140.7, 134.5, 130.0, 129.5, 127.5, 127.2, 126.9, 126.5, 124.8, 124.5, 122.5, 120.2, 117.9, 116.5, 29.8. IR (KBr): 3046, 2920, 2852, 2228, 1691, 1596, 1460, 1277, 997 cm^{-1}. HRMS (ESI) calcd for $C_{21}H_{12}N_4O$ $[M+H]^+$: 337.1084, found 337.1076.



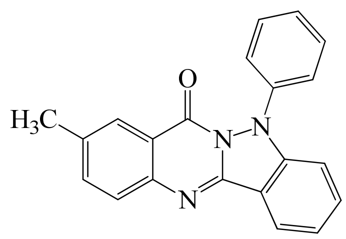
3-Fluoro-5-phenylindazolo[3,2-b]quinazolin-7(5H)-one ***(2n)***: . Pale-green solid (48.0 mg, 73%), mp 216-217 °C (lit.[2] 211-212 °C). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.32-8.25 (m, 2H), 7.89 (d, J = 8.0 Hz, 1H), 7.84-7.80 (m, 1H), 7.52-7.43 (m, 4H), 7.37-7.35 (m, 2H), 7.16-7.11 (m, 1H), 6.88-6.86 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.2 (d, $^1J_{C\text{-}F}$ = 252.5 Hz, 1C), 156.2, 150.2 (d, $^3J_{C\text{-}F}$ = 12.5 Hz, 1C), 148.6, 147.4, 141.2, 134.2, 129.7, 128.9, 126.7 (d, $^3J_{C\text{-}F}$ = 7.5 Hz, 1C), 125.5, 124.6, 119.5, 114.9, 113.3, 113.0, 99.5 (d, $^2J_{C\text{-}F}$ = 27.5 Hz, 1C), 99.4 (d, $^2J_{C\text{-}F}$ = 28.7 Hz, 1C).



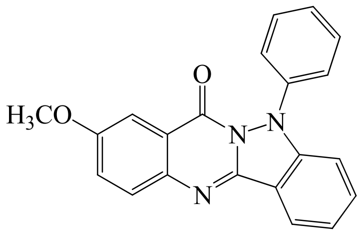
3-Chloro-5-phenylindazolo[3,2-b]quinazolin-7(5H)-one (***2o***): White solid (51.8 mg, 75%), mp 212-213 °C (lit.[3] 255-256 °C). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.33-8.31 (m, 1H), 8.21 (d, *J* = 8.5 Hz, 1H), 7.89 (d, *J* = 8.0 Hz, 1H), 7.84-7.83 (m, 1H), 7.52-7.45 (m, 4H), 7.40-7.35 (m, 3H), 7.18 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.3, 149.6, 148.6, 147.4, 141.2, 139.9, 134.3, 129.8, 129.1, 127.1, 126.8, 125.7, 125.3, 124.7, 124.4, 119.8, 117.4, 112.6.



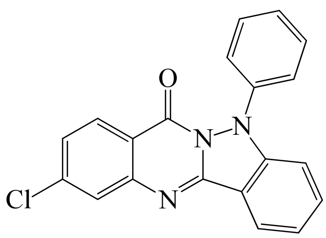
3-Bromo-5-phenylindazolo[3,2-b]quinazolin-7(5H)-one (***2p***): Pale-yellow solid (48.2 mg, 62%), mp 212-213 °C (lit.[3] 244-246 °C). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.34-8.32 (m, 1H), 8.29 (d, *J* = 7.5 Hz, 1H), 7.91 (d, *J* = 8.5 Hz, 1H), 7.83-7.80 (m, 1H), 7.63-7.60 (m, 1H), 7.50-7.36 (m, 7H), 7.21 (d, *J* = 8.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.5, 149.2, 148.8, 148.3, 142.0, 134.1, 133.5, 129.7, 128.7, 127.1, 126.8, 125.5, 124.7, 124.5, 123.4, 119.9, 119.0, 112.5.



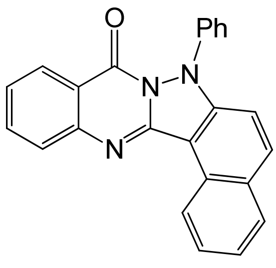
9-Methyl-5-phenylindazolo[3,2-b]quinazolin-7(5H)-one (***2r***): White solid (51.4 mg, 79%), mp 241-242 °C (lit.[3] 236-238 °C). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.27 (d, *J* = 7.5 Hz, 1H), 8.11 (s, 1H), 7.82 (d, *J* = 8.5 Hz, 1H), 7.65-7.59 (m, 2H), 7.49-7.34 (m, 6H), 7.22-7.20 (m, 1H), 2.50 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.4, 149.2, 147.8, 146.8, 142.1, 135.8, 135.7, 133.3, 129.6, 128.6, 126.9, 126.1, 124.5, 124.4, 123.2, 119.7, 119.1, 112.5, 21.5.



9-Methoxy-5-phenylindazolo[3,2-b]quinazolin-7(5H)-one (**2s**): Pale-green solid (58.0 mg, 85%), mp 222-224 °C. [1]H NMR (500 MHz, $CDCl_3$) δ 8.25 (d, *J* = 8.0 Hz, 1H), 7.84 (d, *J* = 9.0 Hz, 1H), 7.68 (d, *J* = 2.5 Hz, 1H), 7.60-7.57 (m, 1H), 7.49-7.35 (m, 7H), 7.20-7.18 (m, 1H), 3.89 (s, 3H); [13]C NMR (125 MHz, $CDCl_3$) 157.6, 156.2, 148.9, 146.6, 143.5, 142.1, 133.0, 129.6, 128.7, 128.6, 125.0, 124.7, 124.4, 123.0, 120.6, 119.1, 112.5, 105.6, 55.9. IR (KBr): 3015, 2939, 2825, 1673, 1625, 1484, 1272, 1022 cm^{-1}. HRMS (ESI) calcd for $C_{21}H_{15}N_3O_2$ $[M+H]^+$: 342.1237, found 342.1242.



10-Chloro-5-phenylindazolo[3,2-b]quinazolin-7(5H)-one (**2t**): Pale-yellow solid (50.4 mg, 92%), mp 204-205 °C (lit.[2] 208-209 °C). [1]H NMR (500 MHz, DMSO-d_6) δ 8.24 (d, *J* = 8.0 Hz, 1H), 8.15 (d, *J* = 8.5 Hz, 1H), 7.94 (d, *J* = 2.0 Hz, 1H), 7.79-7.75 (m, 1H), 7.55-7.40 (m, 7H), 7.36 (d, *J* = 8.5 Hz, 1H); [13]C NMR (125 MHz, DMSO-d_6) δ 154.8, 149.3, 148.9, 148.4, 141.3, 138.6, 134.2, 129.3, 128.0, 127.9, 125.8, 125.4, 124.7, 123.9, 123.1, 118.2, 118.0, 112.3.

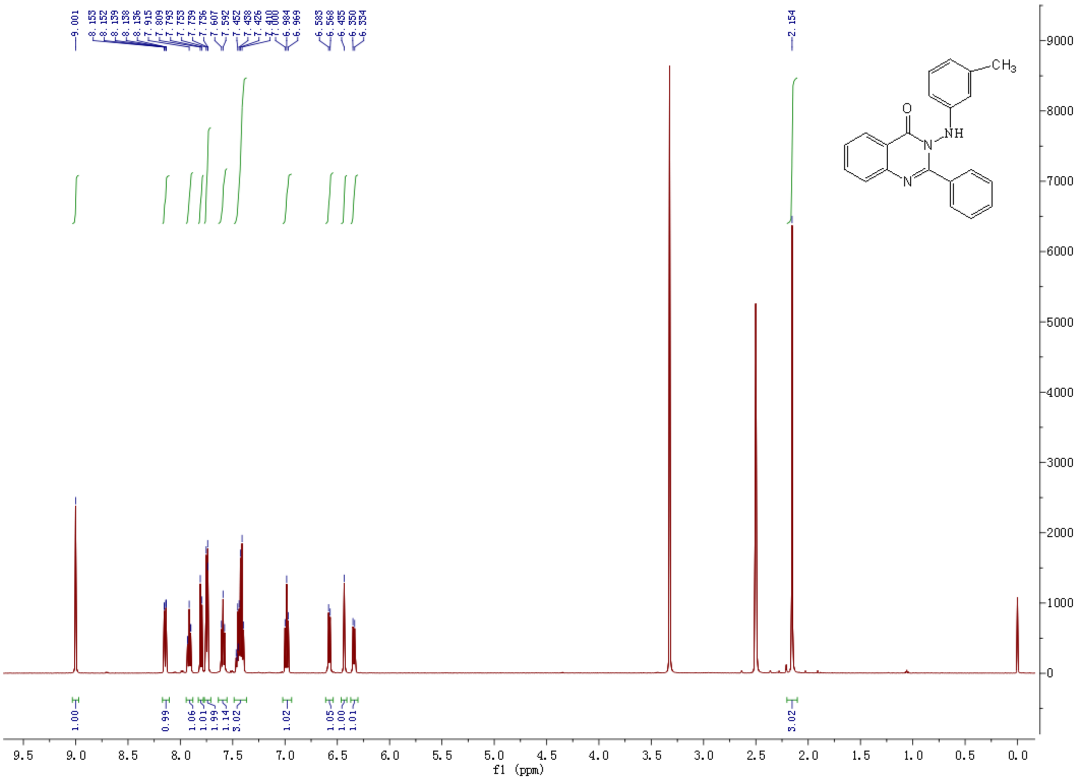


5-(Naphthalen-1-yl)indazolo[3,2-b]quinazolin-7(5H)-one (**2v**): Yellow solid (52.0 mg, 72%), mp 234-236 °C. [1]H NMR (500 MHz, $CDCl_3$) δ 9.56 (d, *J* = 8.0 Hz, 1H), 8.34 (d, *J* = 8.0 Hz, 1H), 8.03-8.00 (m, 2H), 7.96 (d, *J* = 8.0 Hz, 1H), 7.88-7.81 (m, 2H), 7.63-7.60 (m, 1H), 7.52-7.49 (m, 2H), 7.46-7.41 (m, 4H), 7.27 (d, *J* = 9.0 Hz, 1H);

^{13}C NMR (125 MHz, $CDCl_3$) δ 156.7, 149.4, 149.0, 148.4, 141.1, 135.0, 133.9, 130.6, 129.7, 129.4, 129.0, 128.9, 128.8, 127.5, 126.7, 126.0, 125.4, 125.0, 124.6, 119.1, 111.5, 111.1. IR (KBr): 3036, 2921, 2847, 1669, 1593, 1461, 1282, 1011 cm^{-1}. HRMS (ESI) calcd for $C_{24}H_{15}N_3O$ $[M+H]^+$: 362.1288, found 362.1279.

5. NMR Spectra

5.1 NMR Spectra for Unknown 2-Aryl-3-(arylamino)quinazolinones



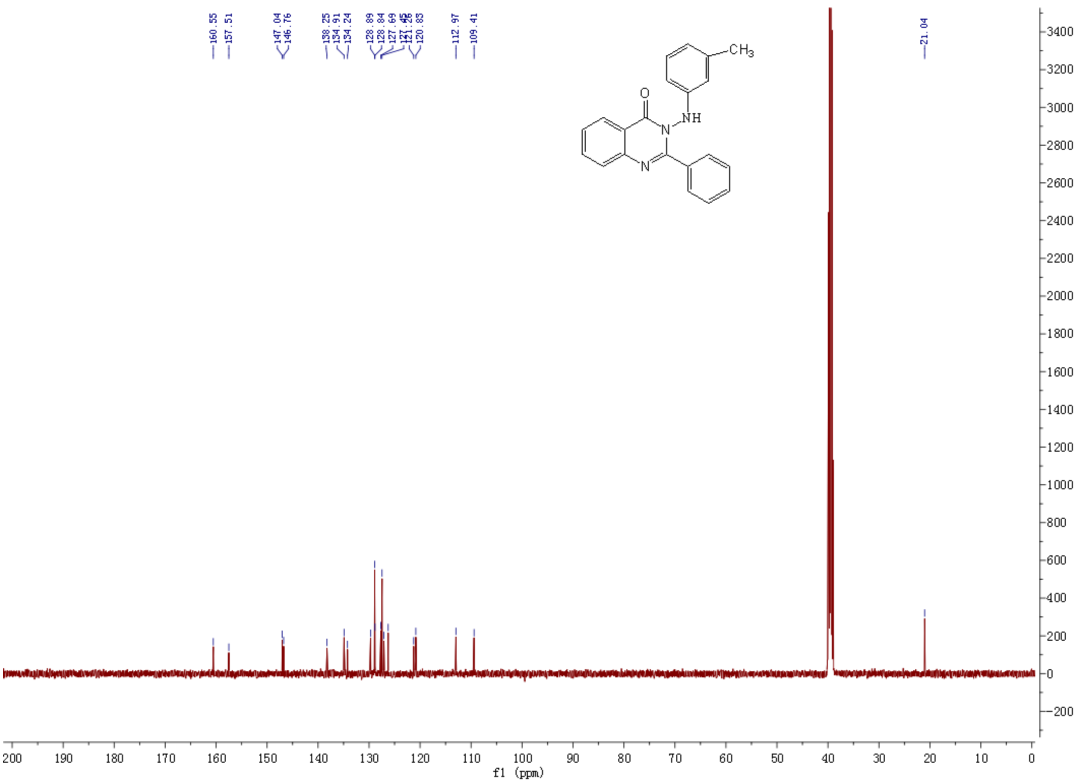
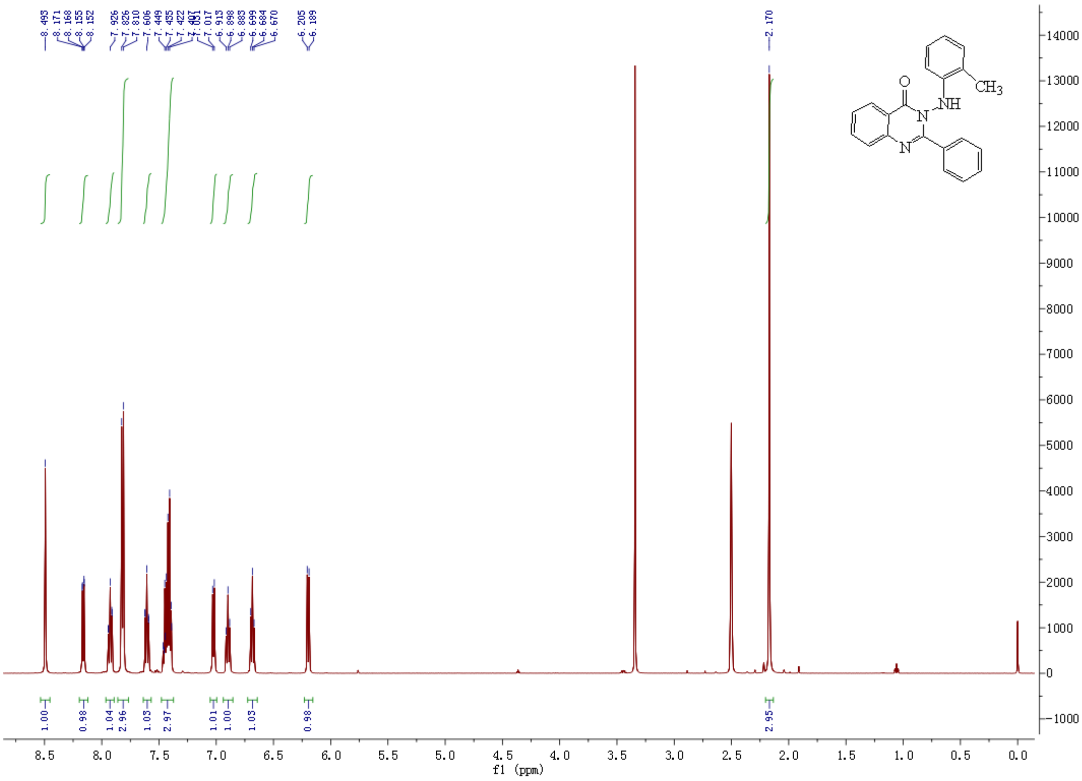


Figure S3. ^{1}H NMR of **1c** (500 MHz, DMSO-d_6) and ^{13}C NMR of **1c** (125 MHz, DMSO-d_6).



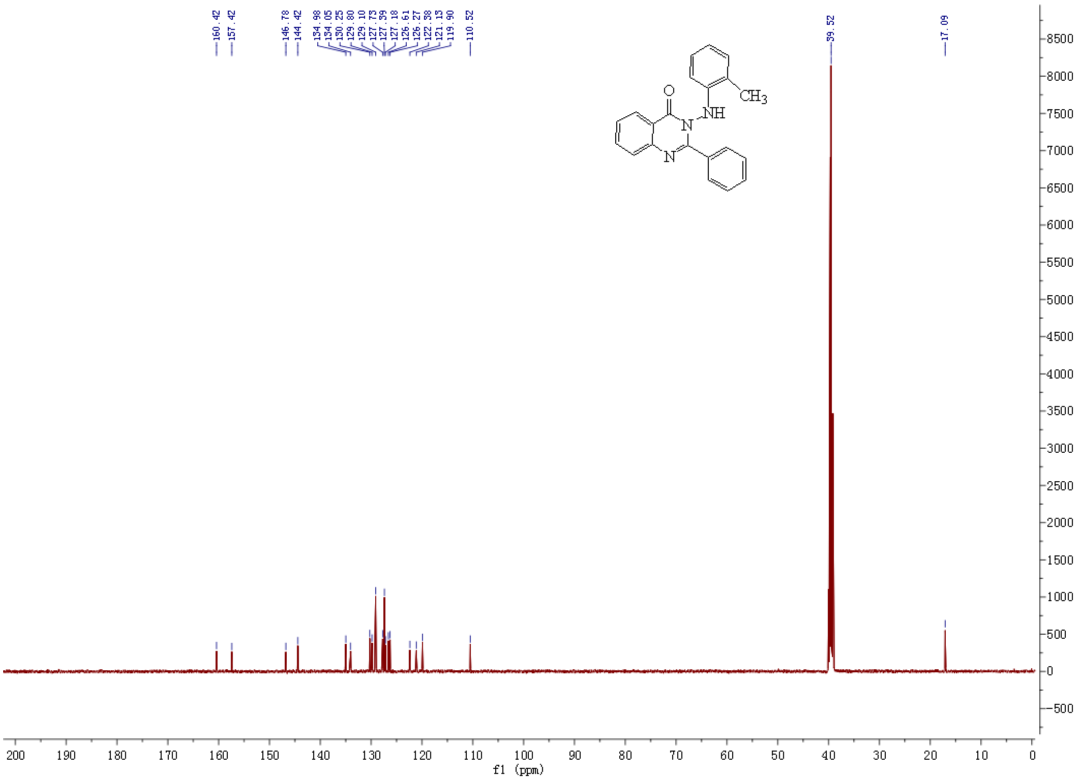
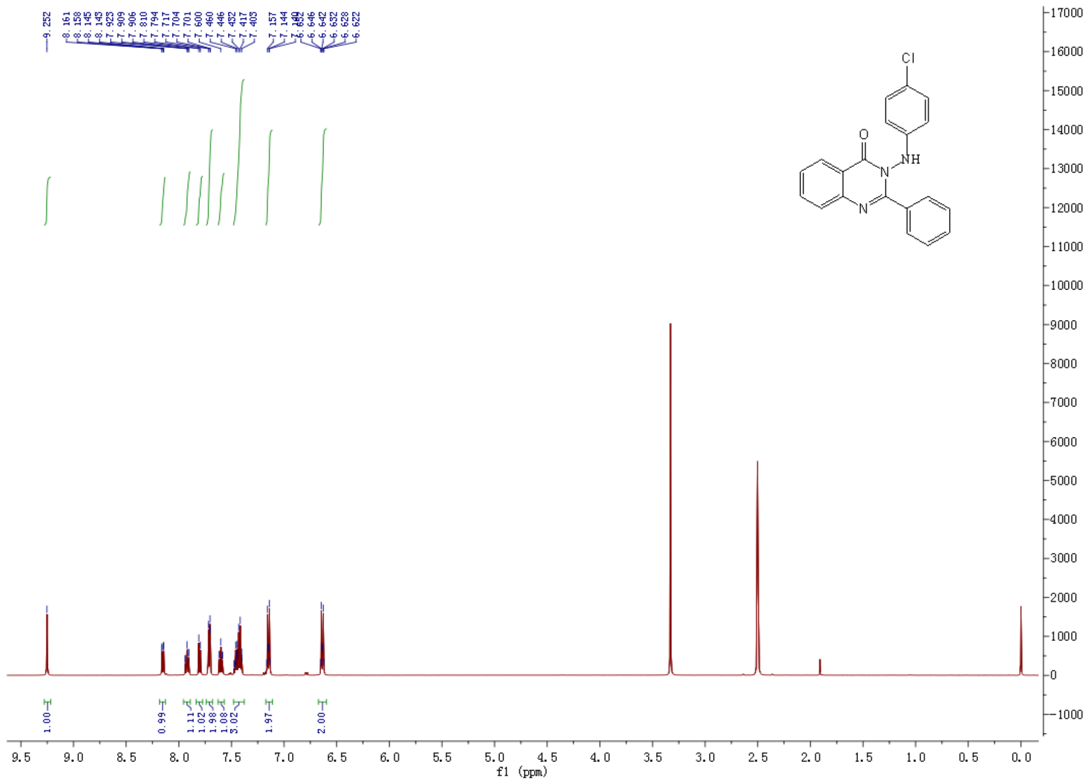


Figure S4. [1]H NMR of **1d** (500 MHz, DMSO-d_6) and [13]C NMR of **1d** (125 MHz, DMSO-d_6).



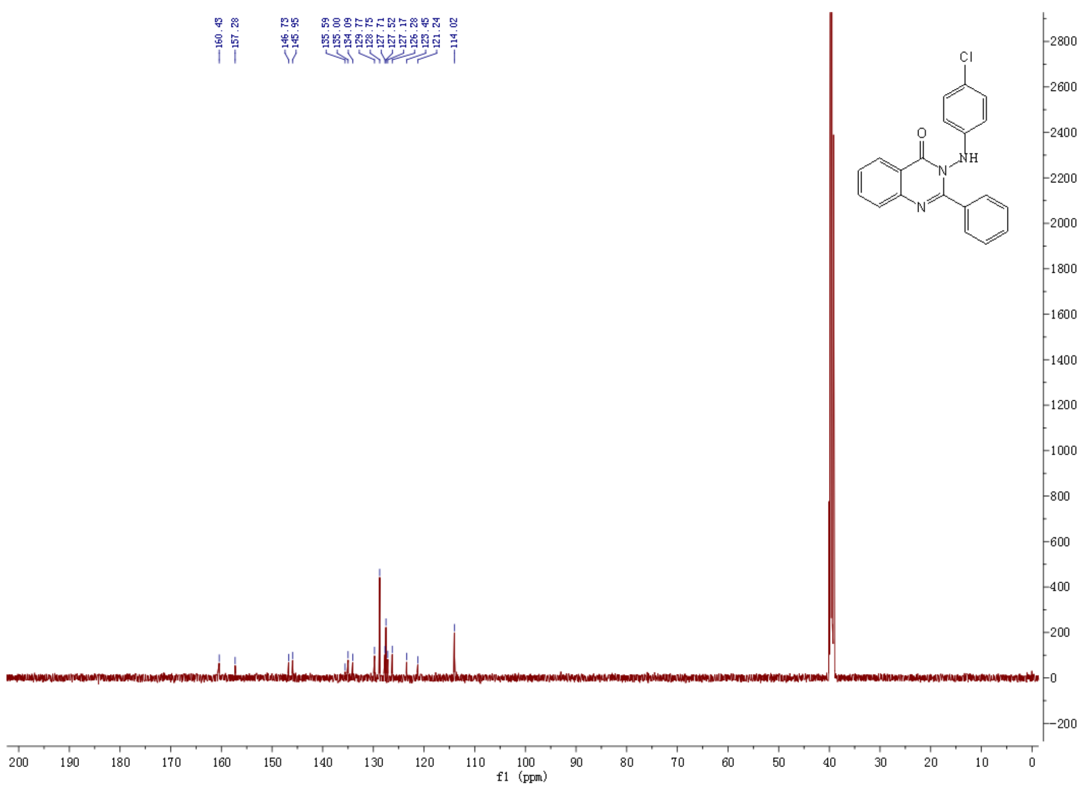


Figure S5. [1]H NMR of **1f** (500 MHz, DMSO-d_6) and [13]C NMR of **1f** (125 MHz, DMSO-d_6).

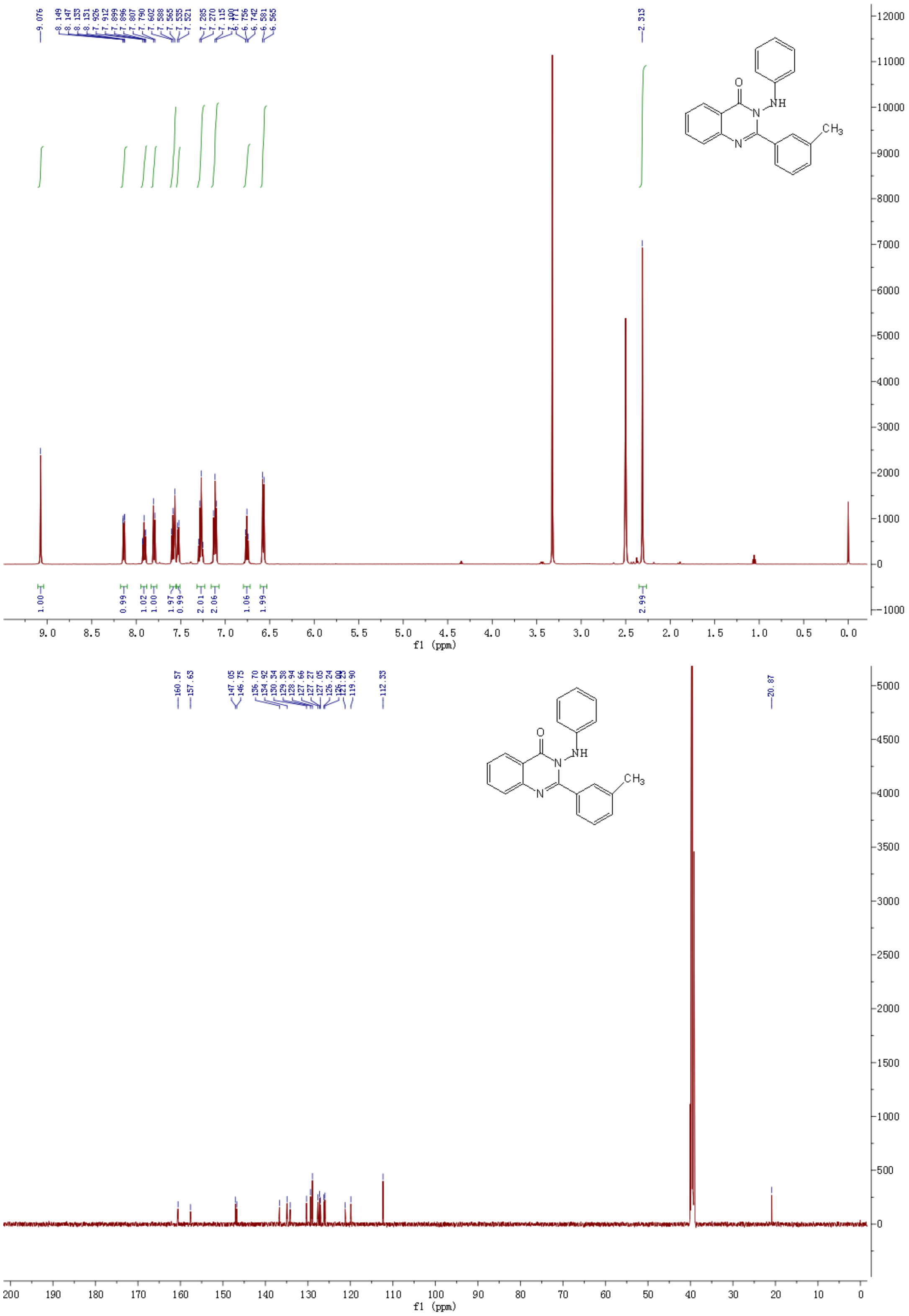
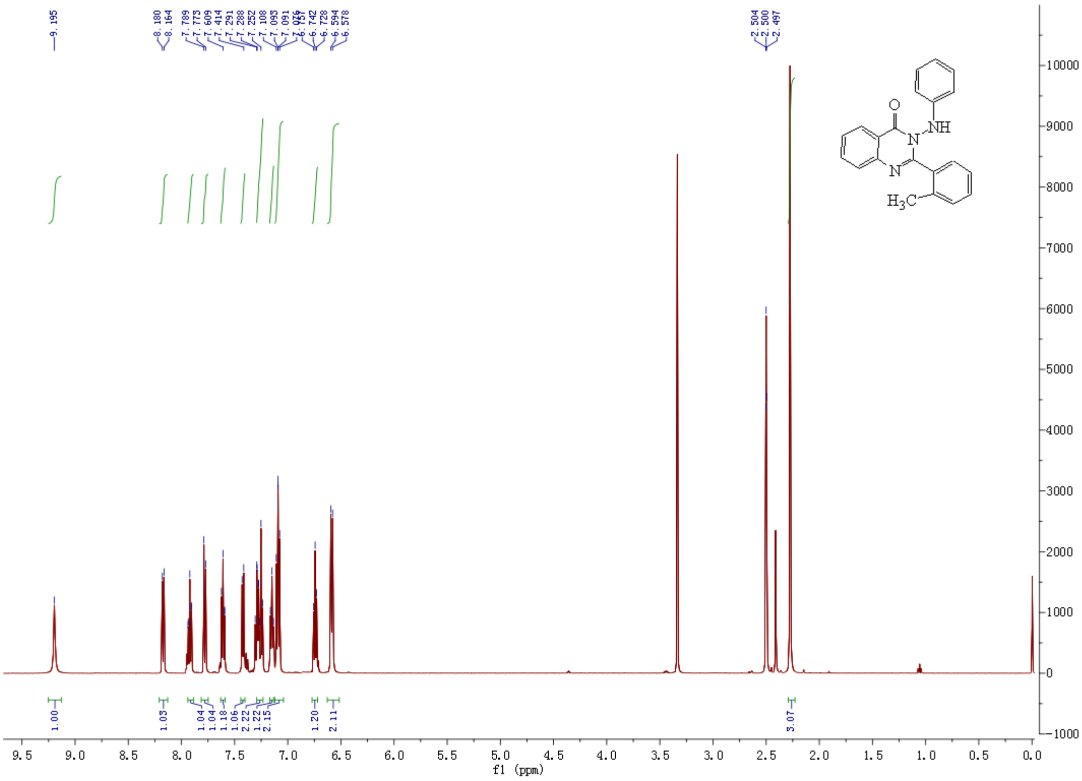


Figure S6. [1]H NMR of **1k** (500 MHz, DMSO-d_6) and [13]C NMR of **1k** (125 MHz, DMSO-d_6).



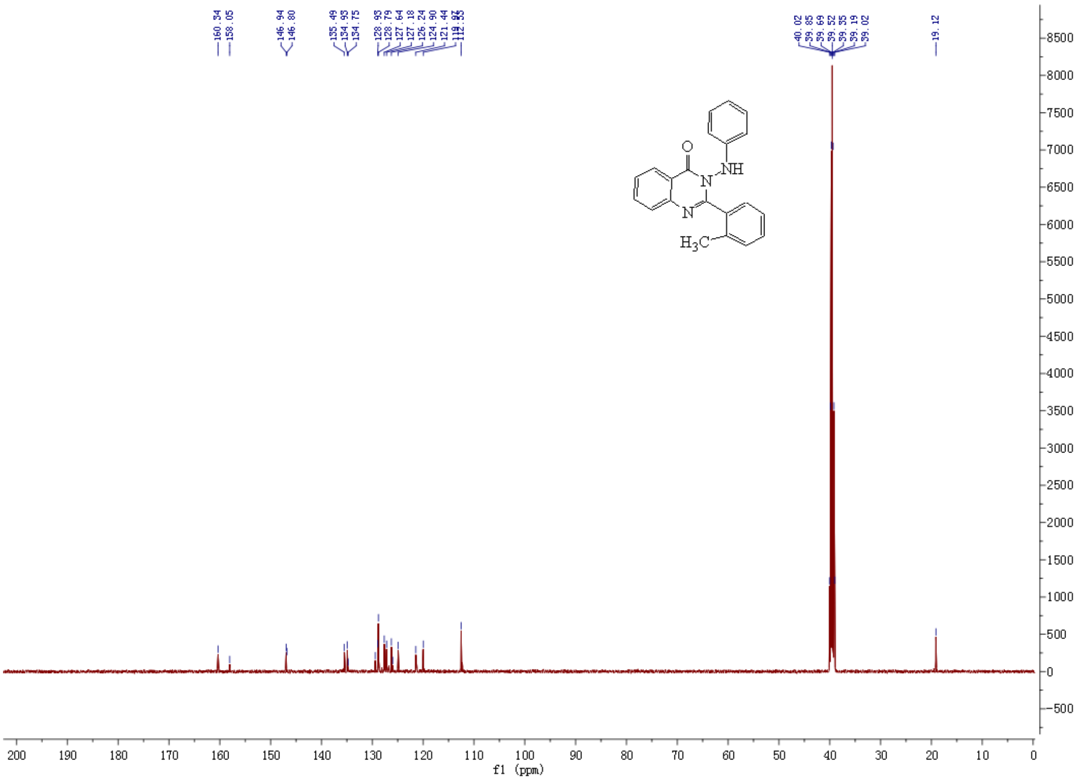
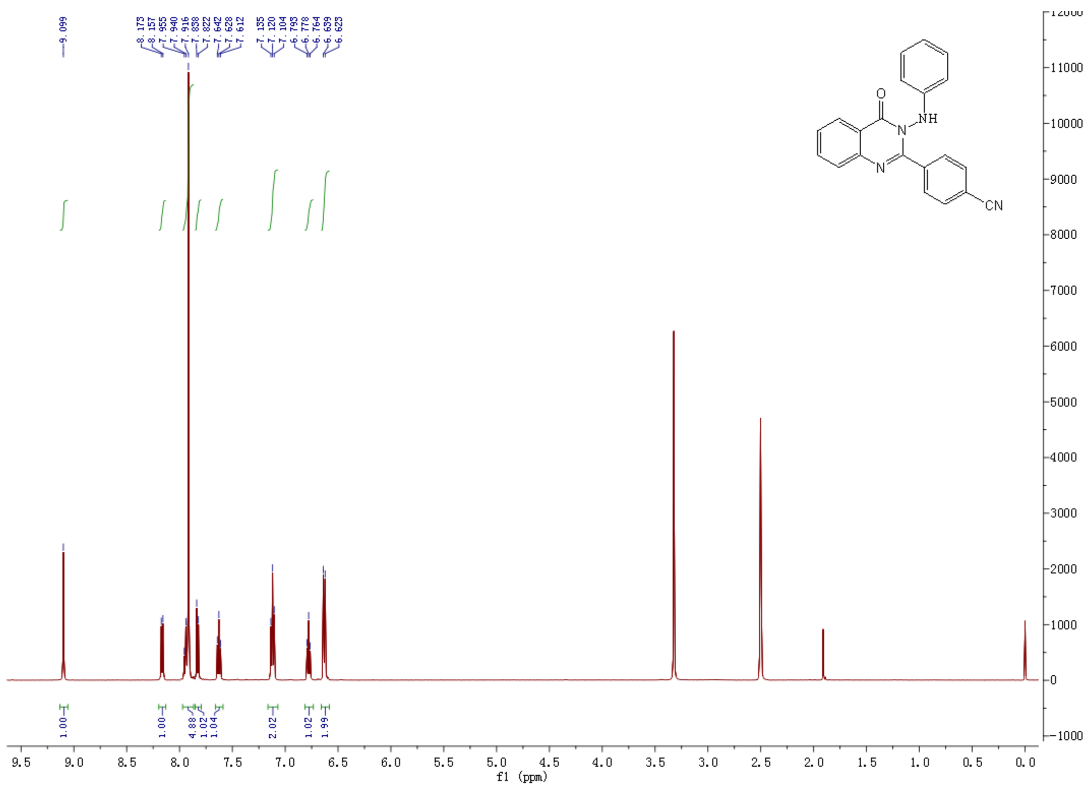


Figure S7. ^{1}H NMR of **1l** (500 MHz, DMSO-d_6) and ^{13}C NMR of **1l** (125 MHz, DMSO-d_6).



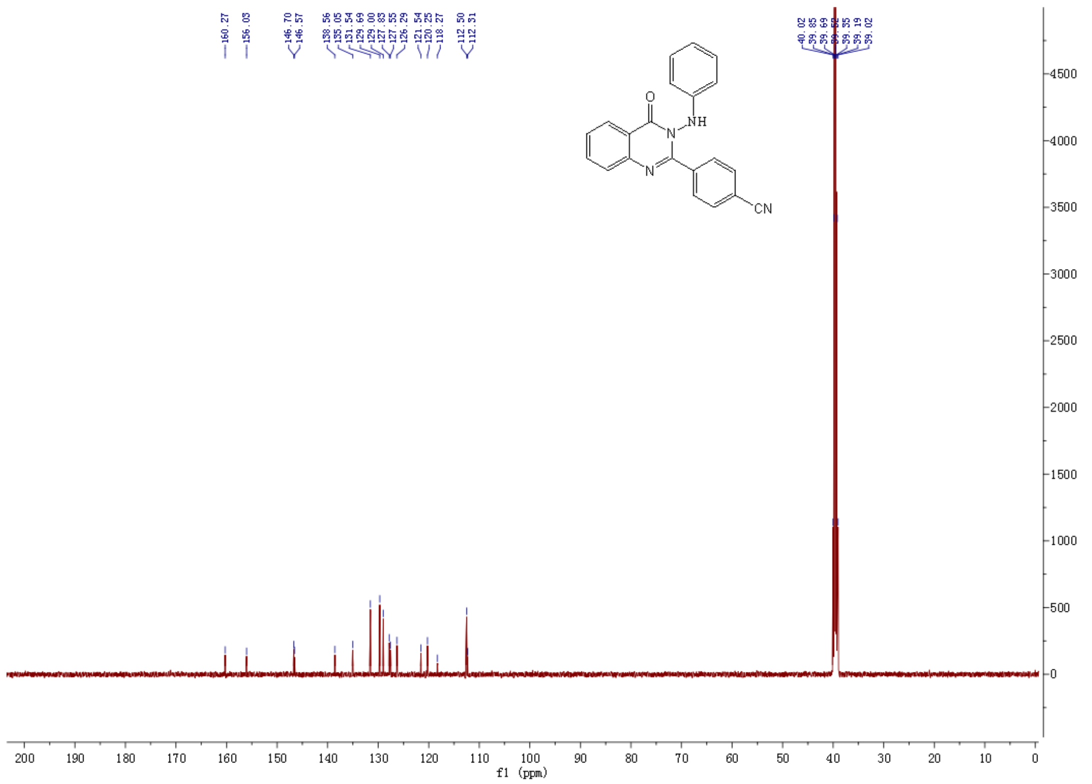
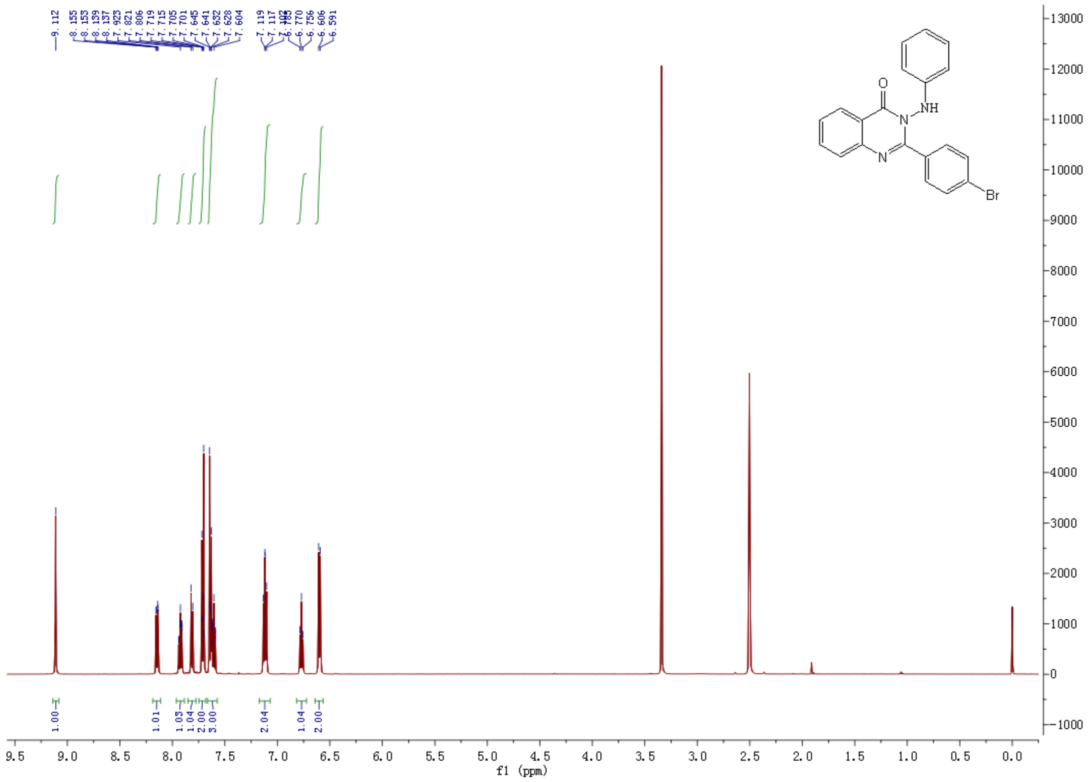


Figure S8. ¹H NMR of **1m** (500 MHz, DMSO-d_6) and ¹³C NMR of **1m** (125 MHz, DMSO-d_6).



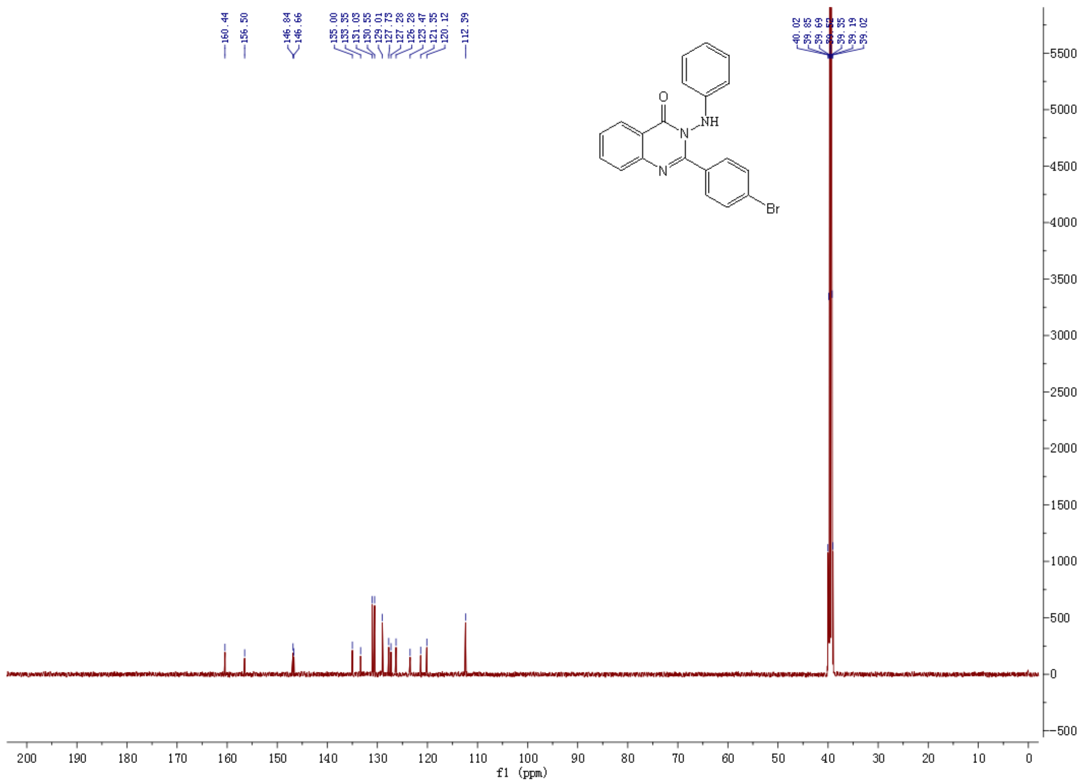
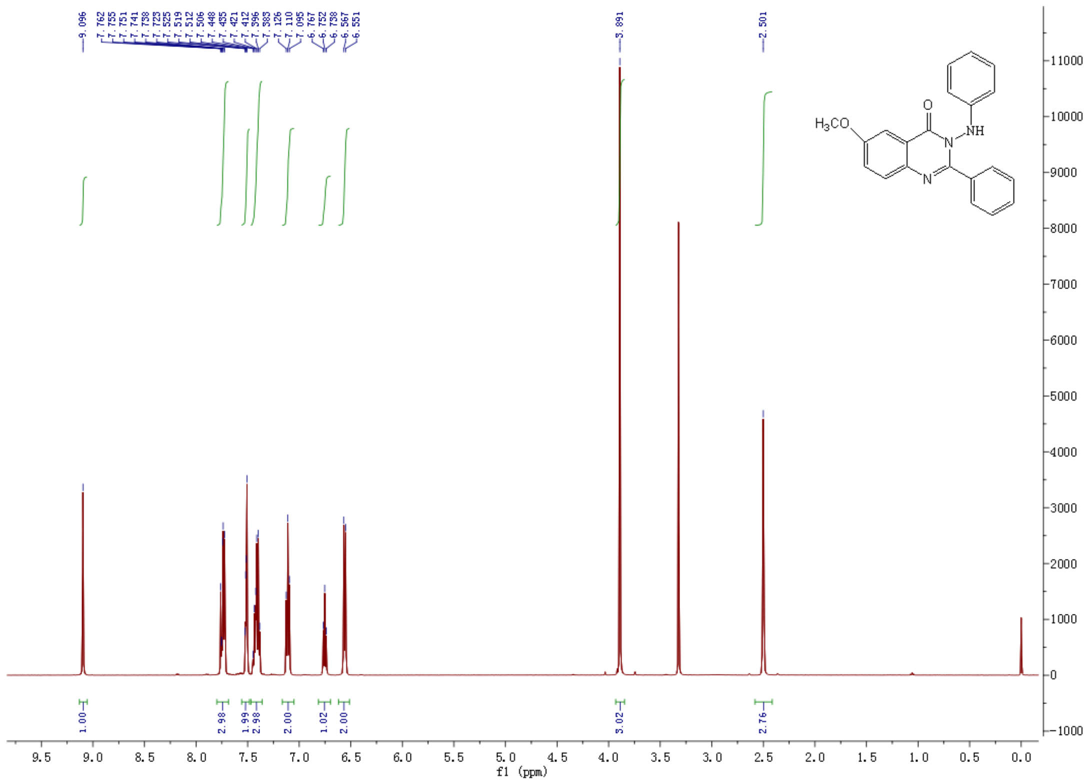


Figure S9. ^{1}H NMR of **1p** (500 MHz, DMSO-d_6) and ^{13}C NMR of **1p** (125 MHz, DMSO-d_6).



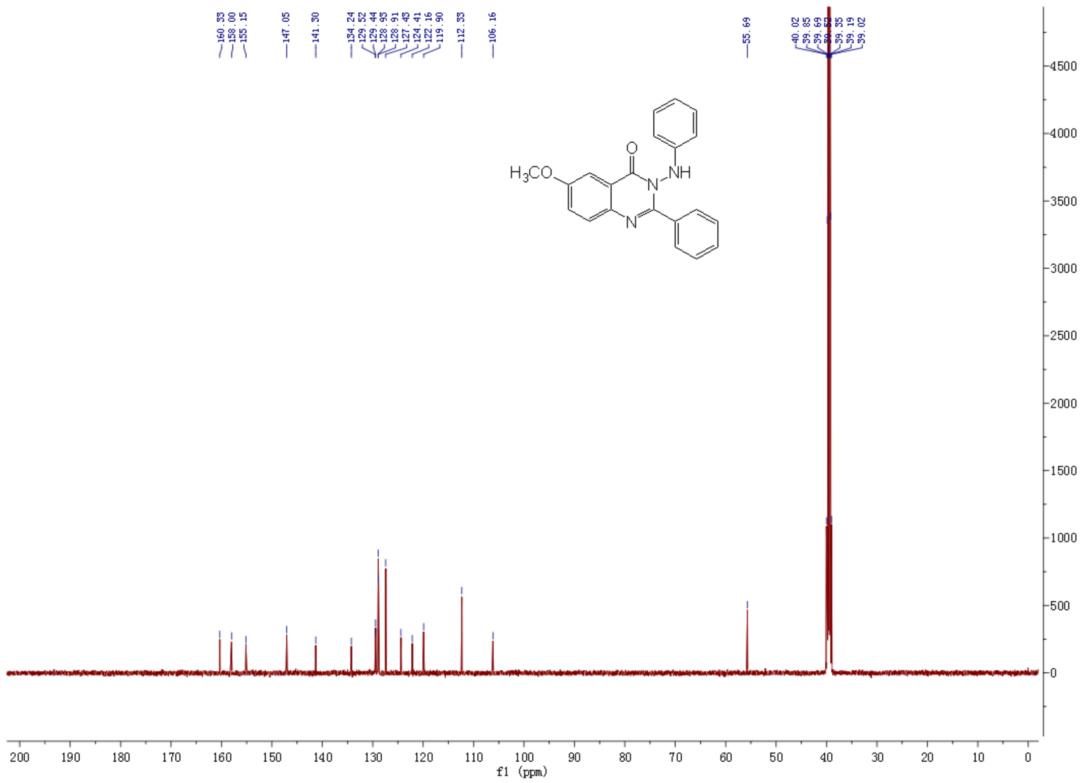


Figure S10. [1]H NMR of **1s** (500 MHz, DMSO-d_6) and [13]C NMR of **1s** (125 MHz, DMSO-d_6).

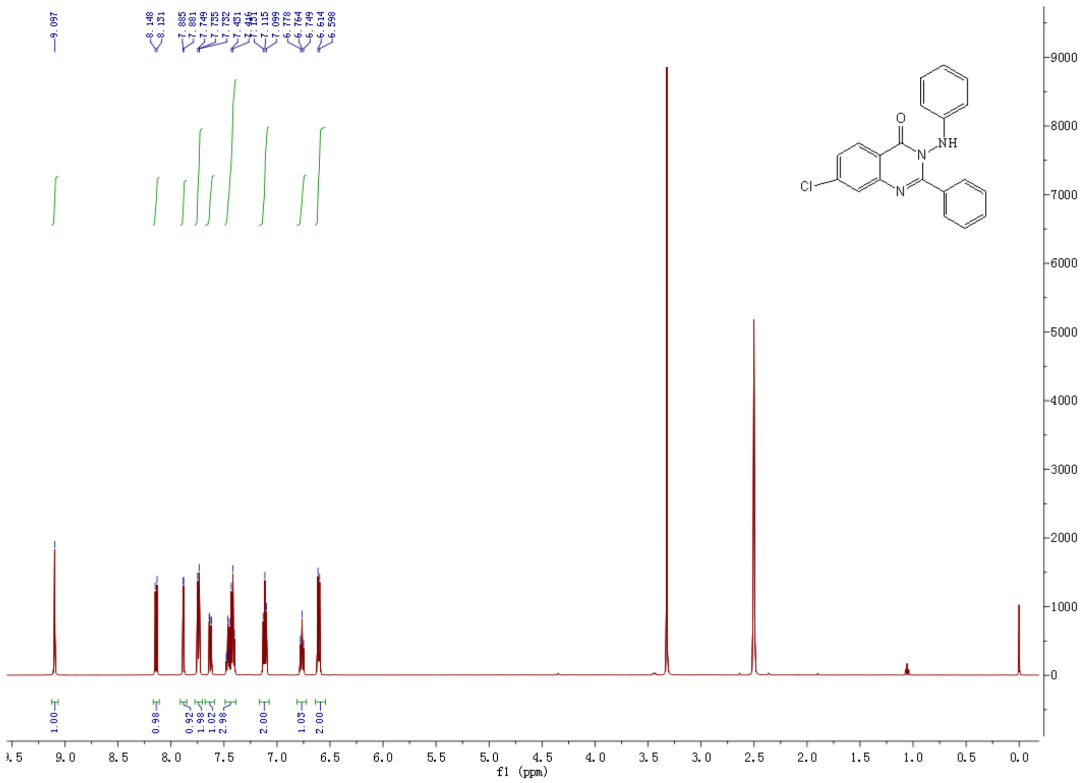
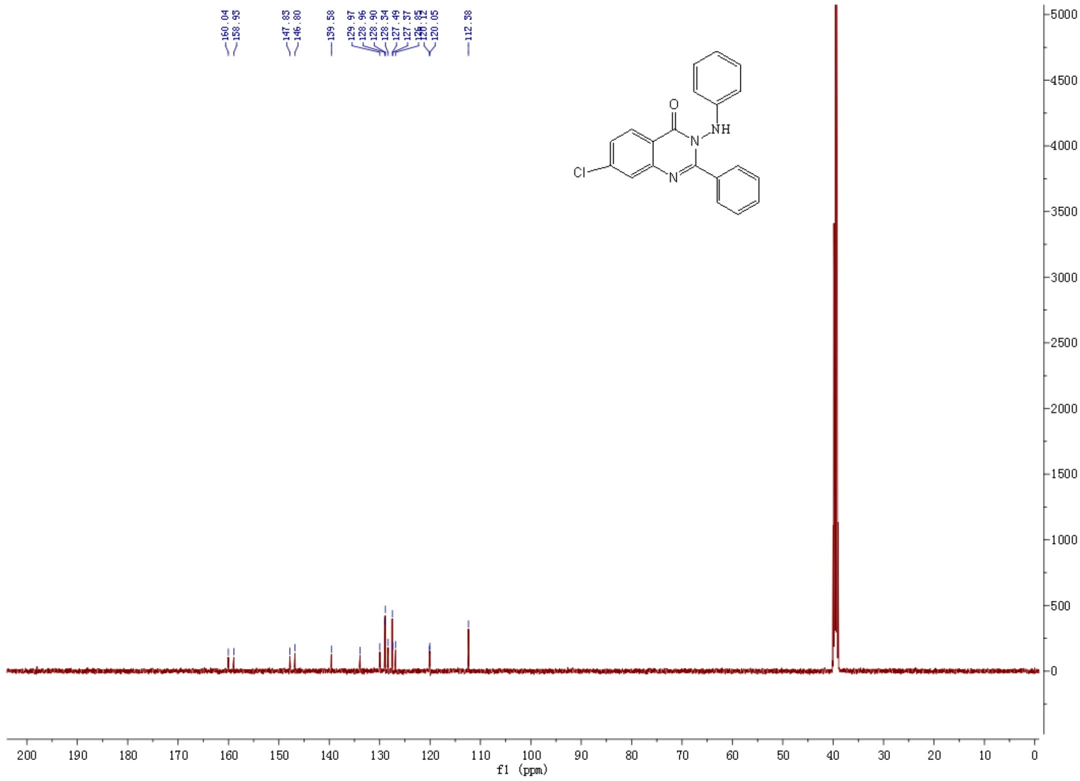
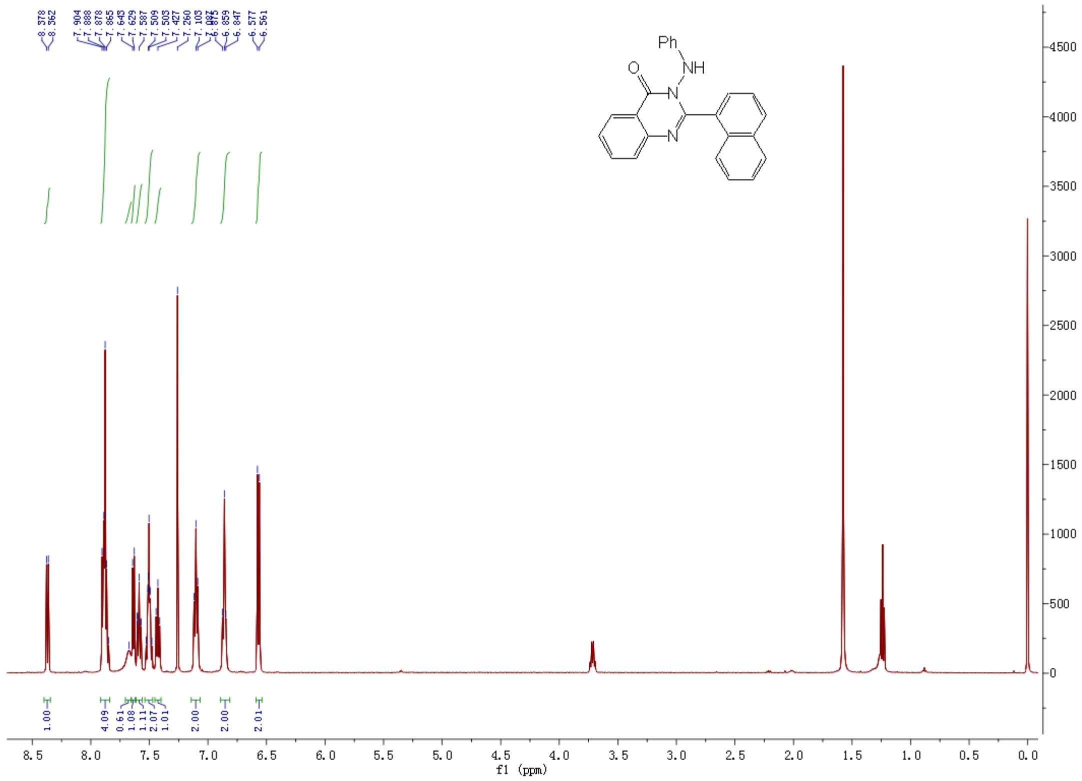



Figure S11. ^{1}H NMR of **1t** (500 MHz, DMSO-d_6) and ^{13}C NMR of **1t** (125 MHz, DMSO-d_6).



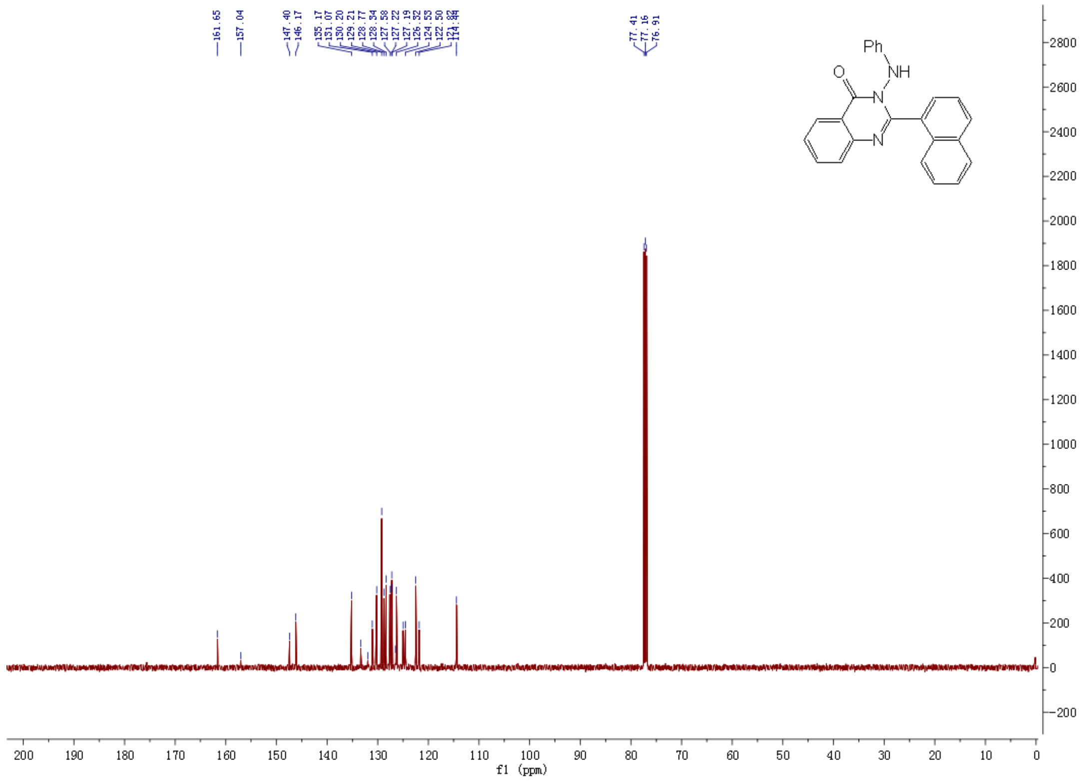
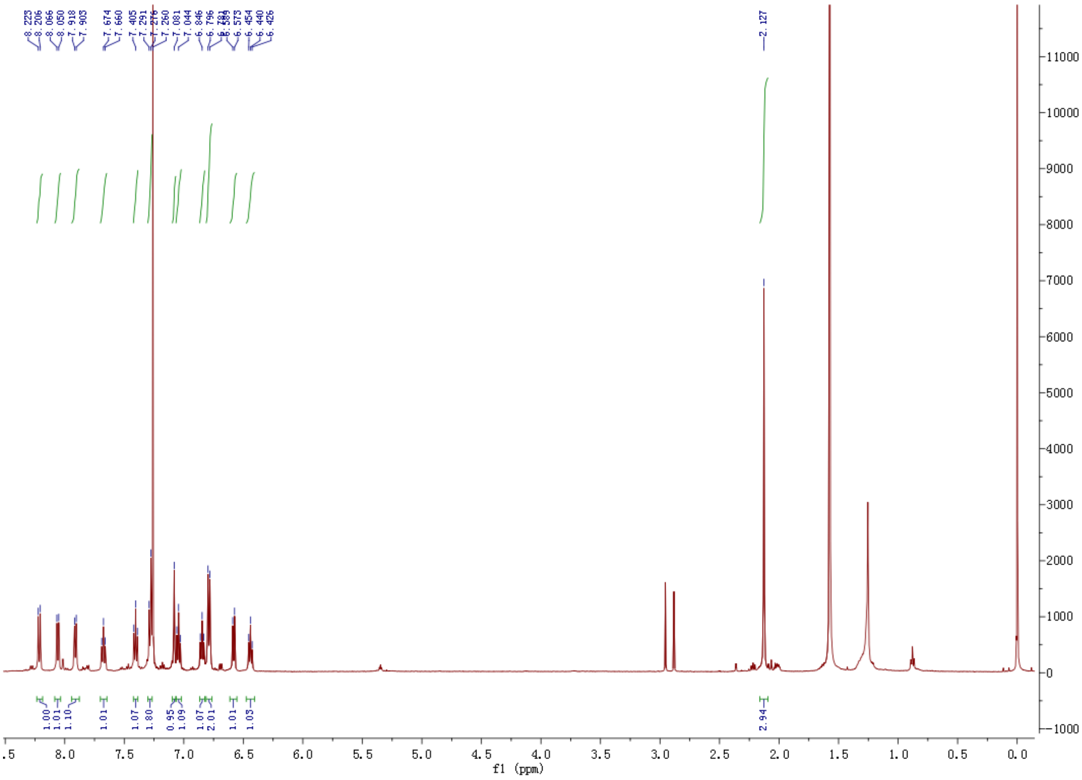


Figure S12. [1]H NMR of **1v** (500 MHz, $CDCl_3$) and [13]C NMR of **1v** (125 MHz, $CDCl_3$).

5.2 NMR Spectra for Palladium Complex 3



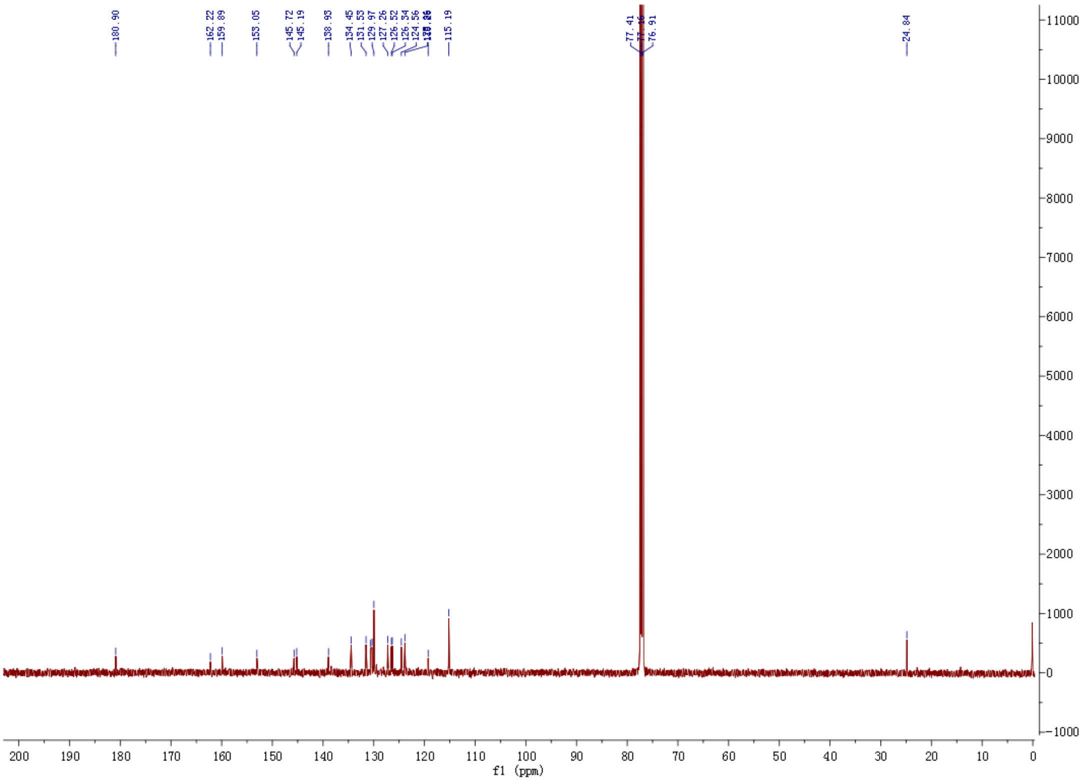
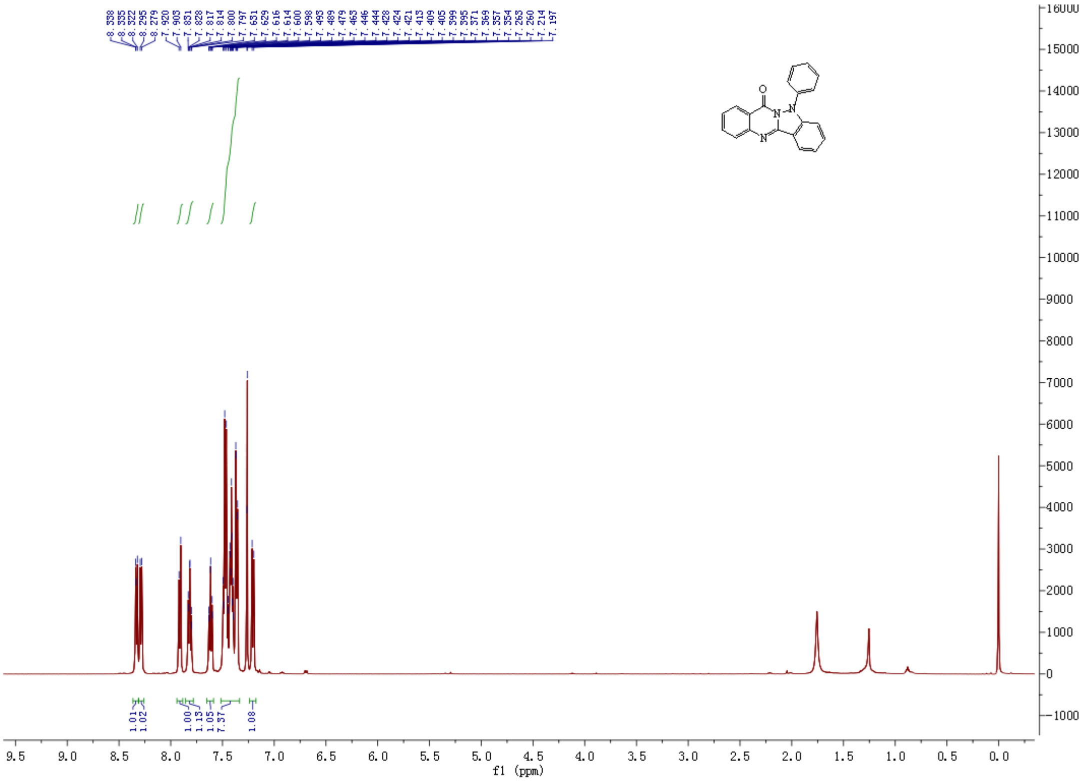


Figure S13. [1]H NMR of **3** (500 MHz, $CDCl_3$) and [13]C NMR of **3** (125 MHz, $CDCl_3$).

5.3 NMR Spectra for All Products



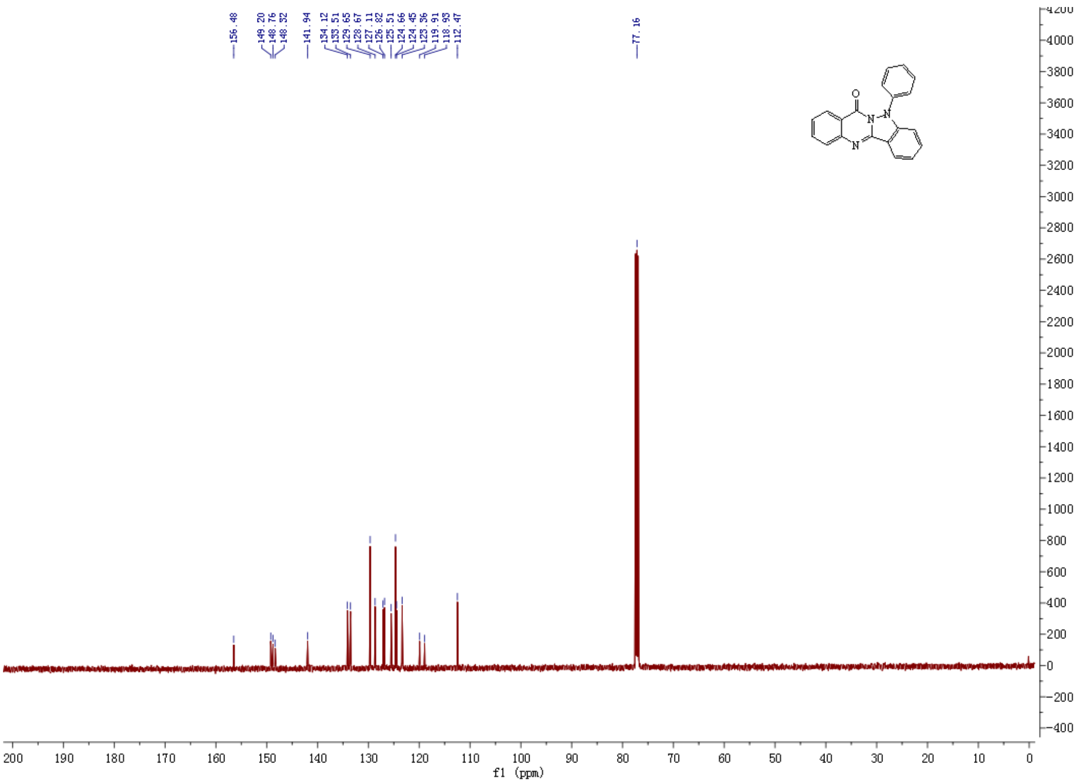
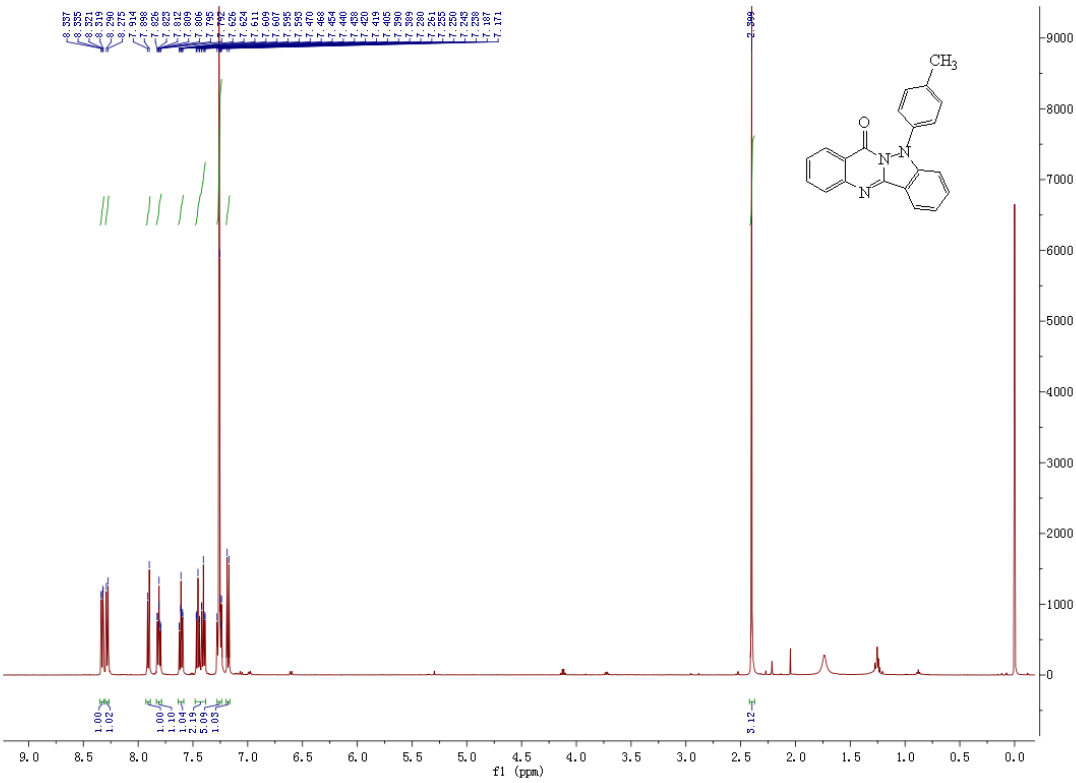


Figure S14. [1]H NMR of **2a** (500 MHz, $CDCl_3$) and [13]C NMR of **2a** (125 MHz, $CDCl_3$).



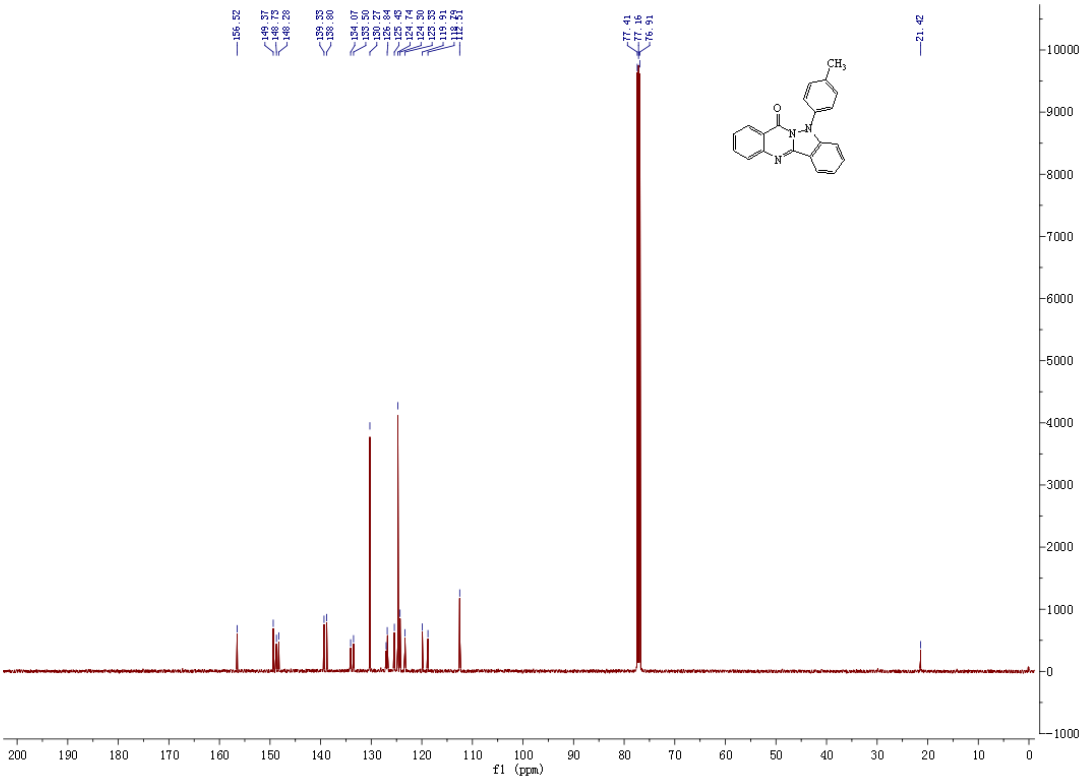


Figure S15. [1]H NMR of **2b** (500 MHz, $CDCl_3$) and [13]C NMR of **2b** (125 MHz, $CDCl_3$).

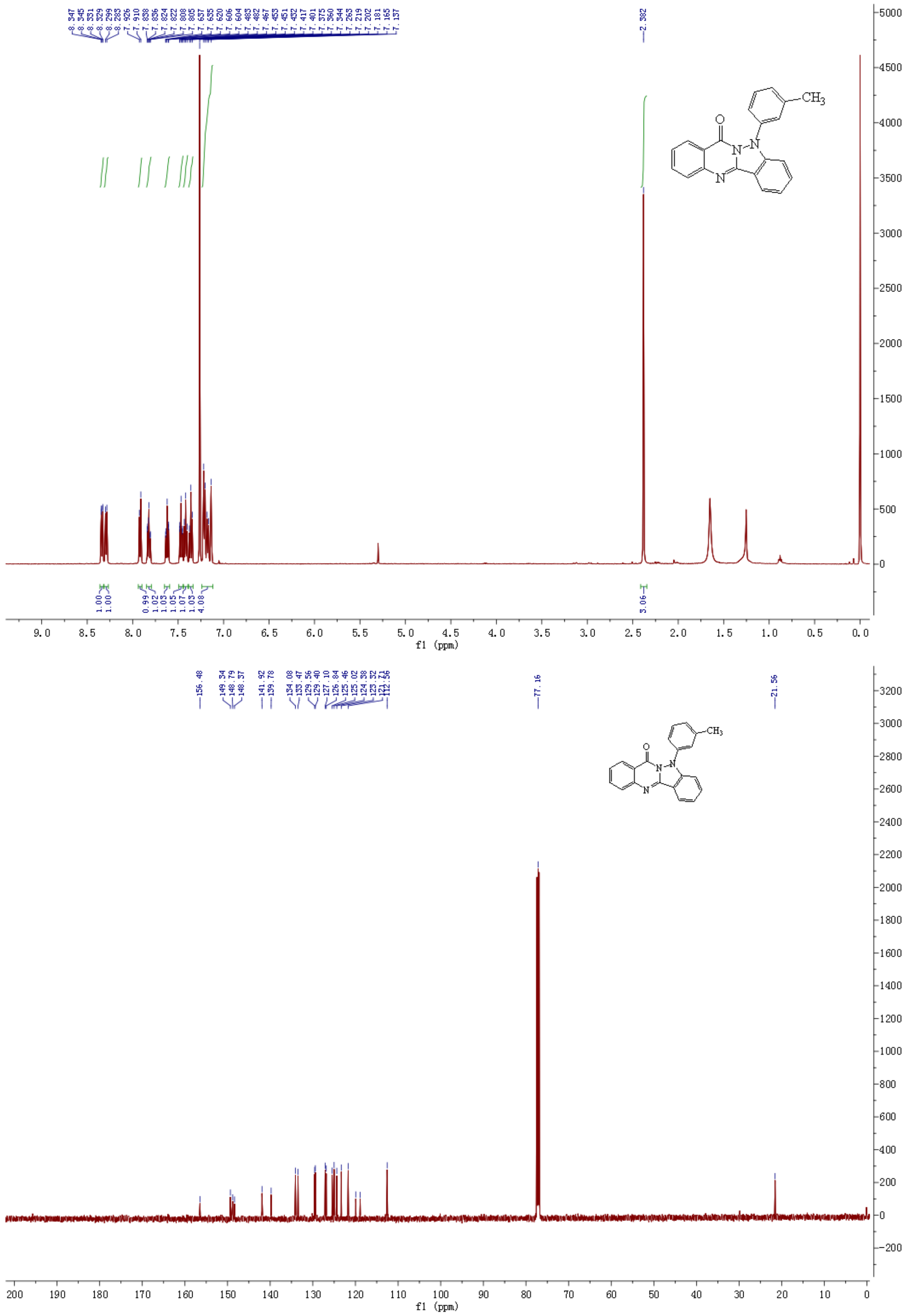


Figure S16. ^{1}H NMR of **2c** (500 MHz, $CDCl_3$) and ^{13}C NMR of **2c** (125 MHz, $CDCl_3$).

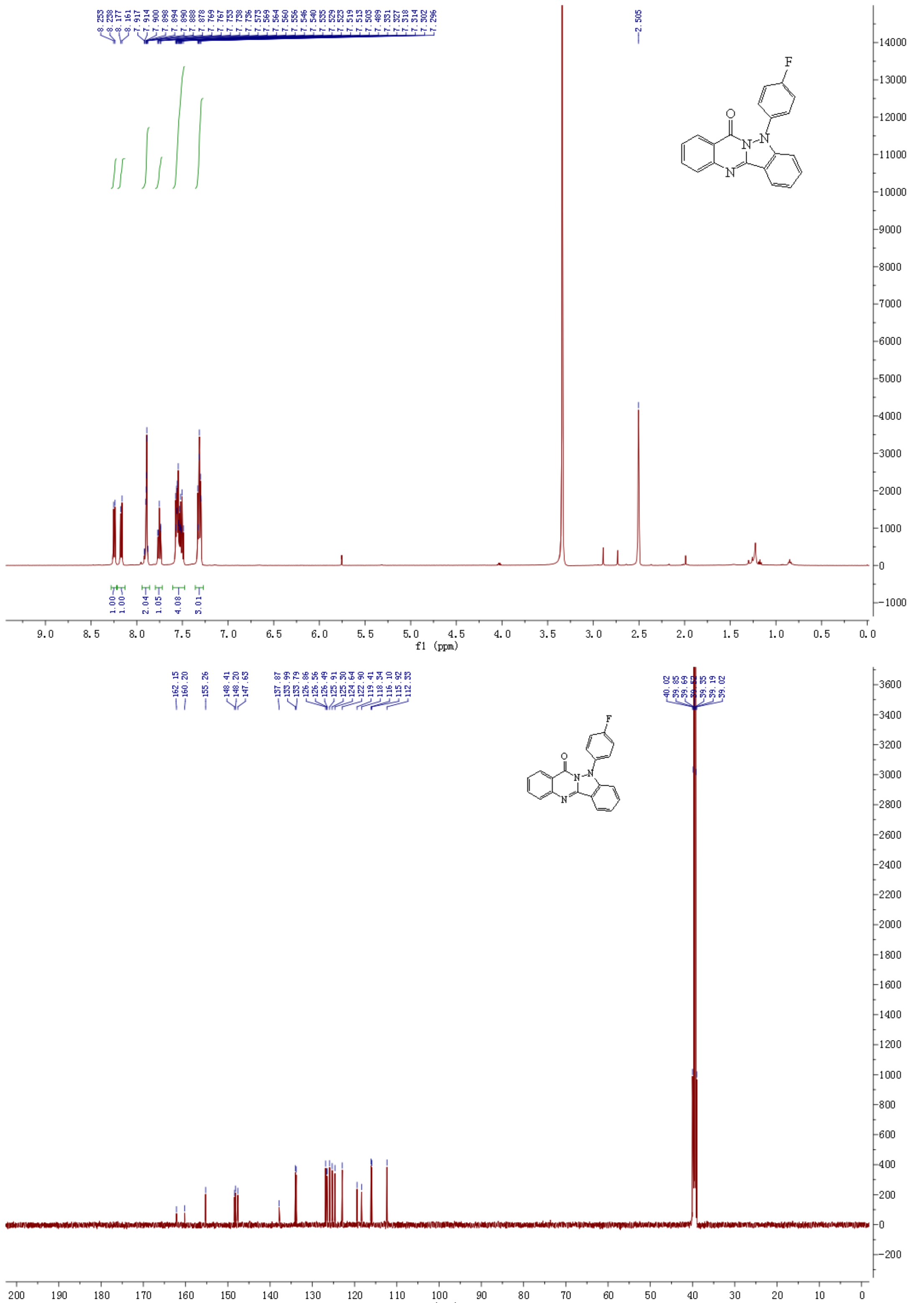
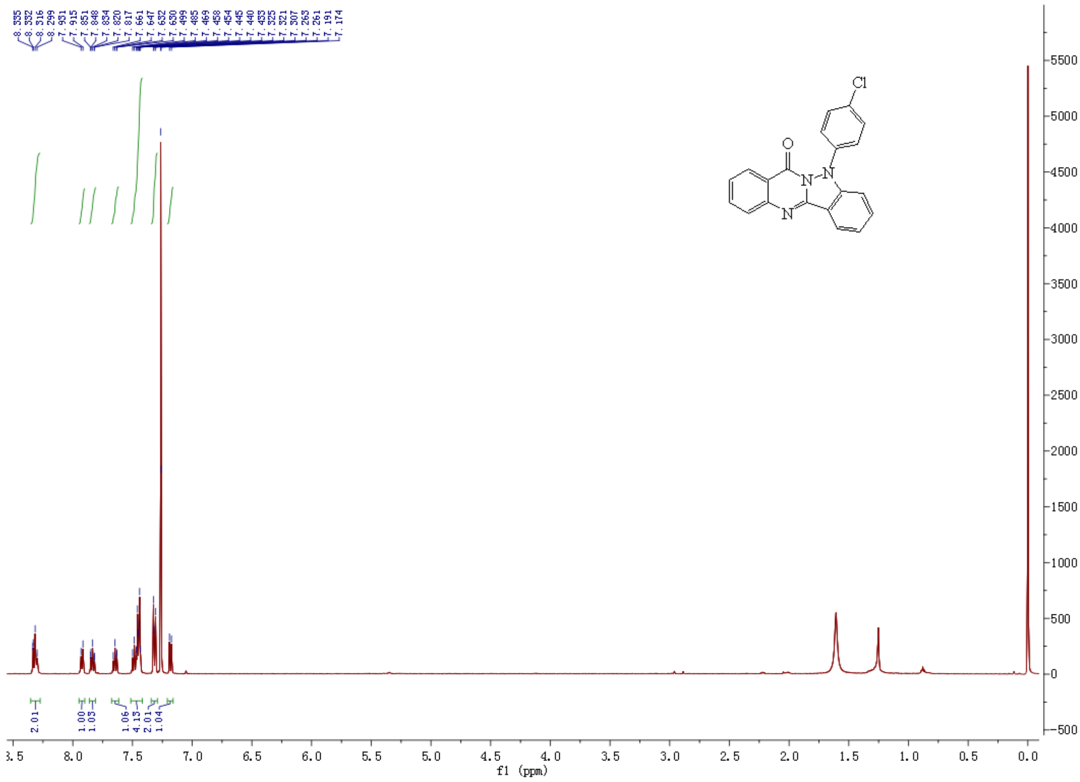


Figure S17. [1]H NMR of **2e** (500 MHz, $CDCl_3$) and [13]C NMR of **2e** (125 MHz, $CDCl_3$).



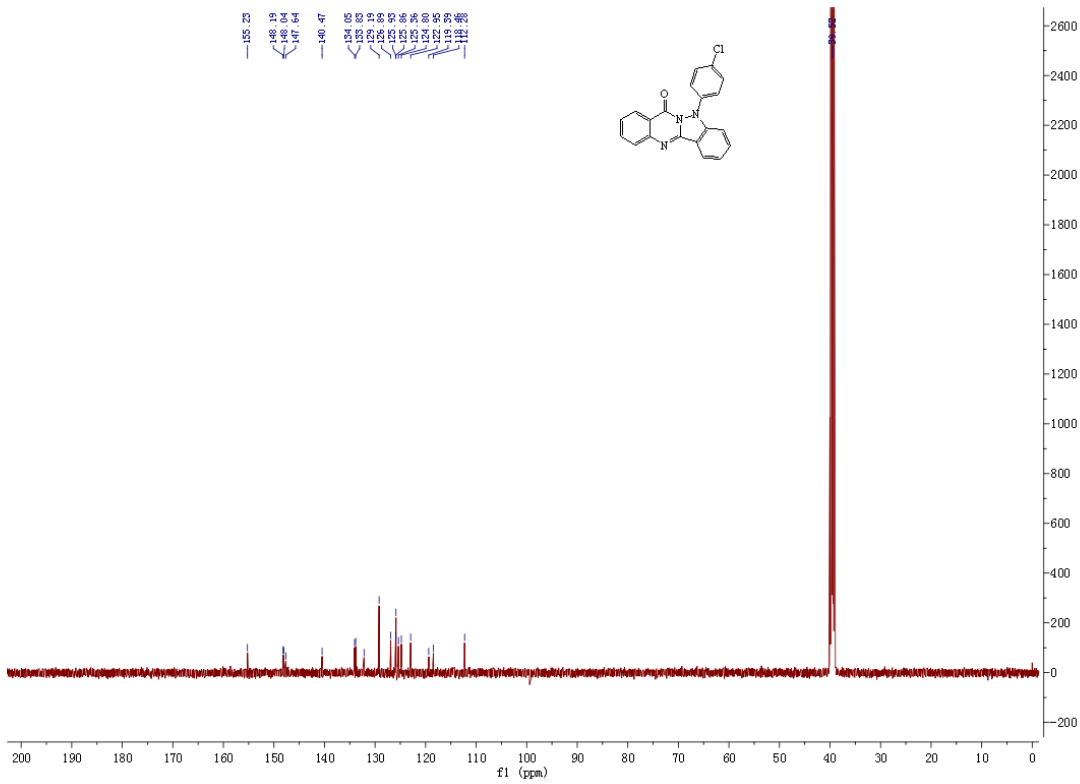
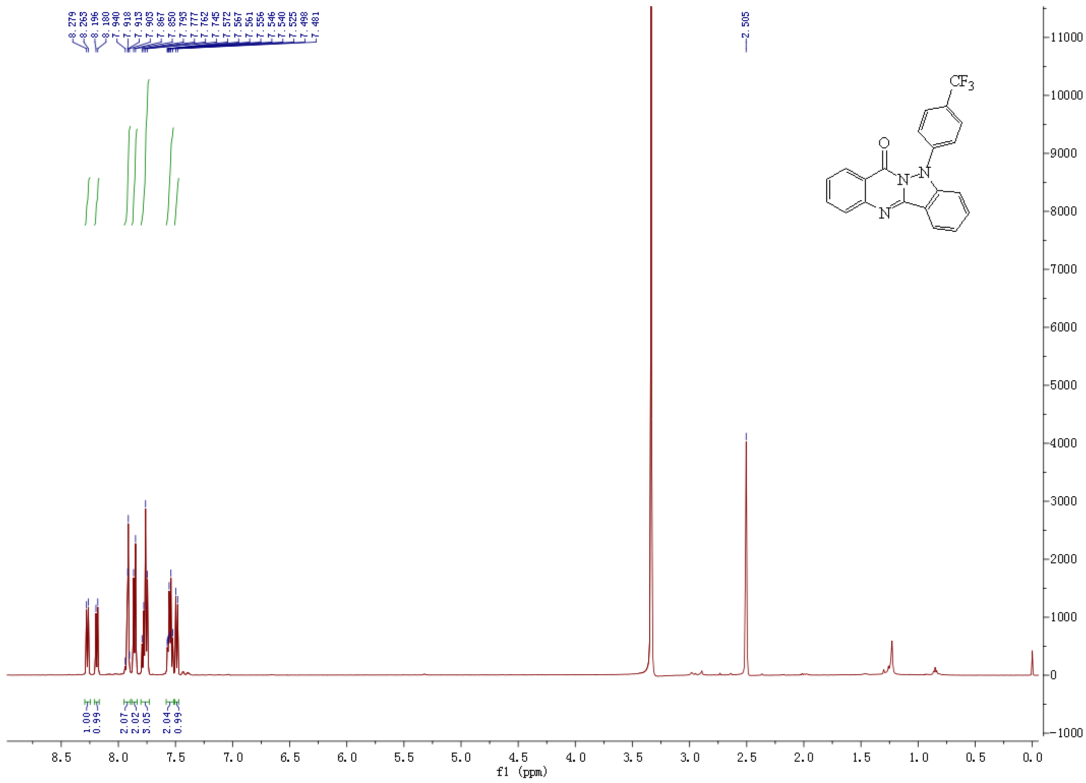


Figure S18. ^{1}H NMR of **2f** (500 MHz, $CDCl_3$) and ^{13}C NMR of **2f** (125 MHz, DMSO-d_6).



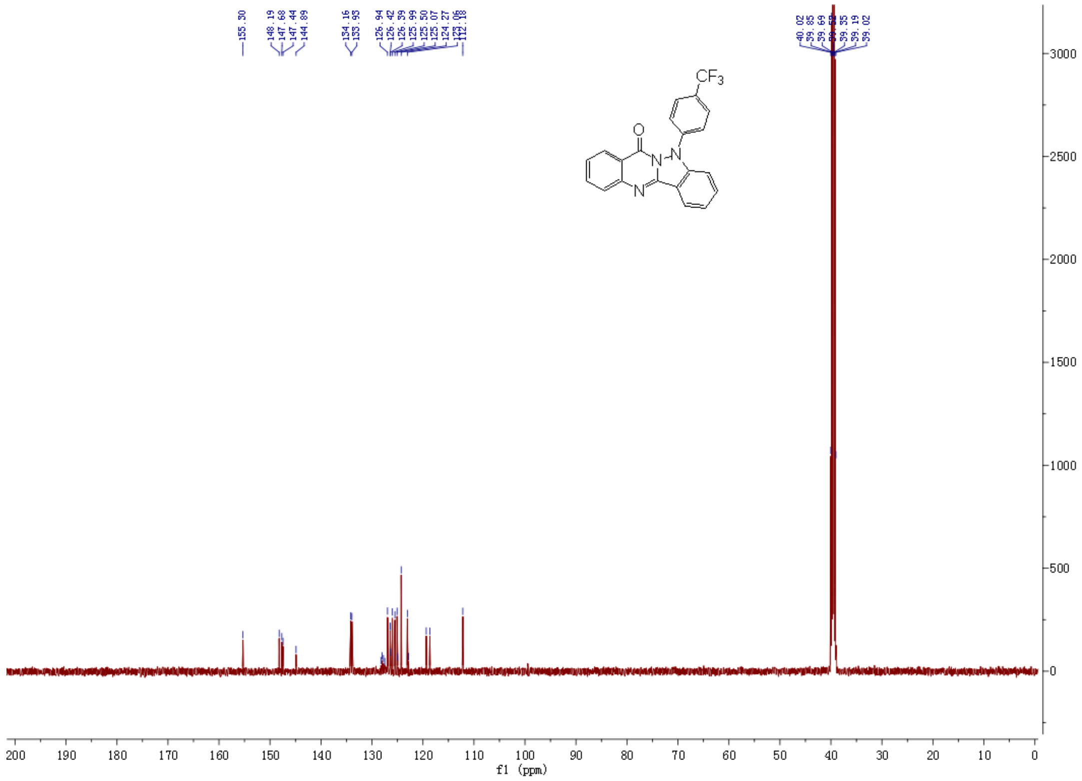
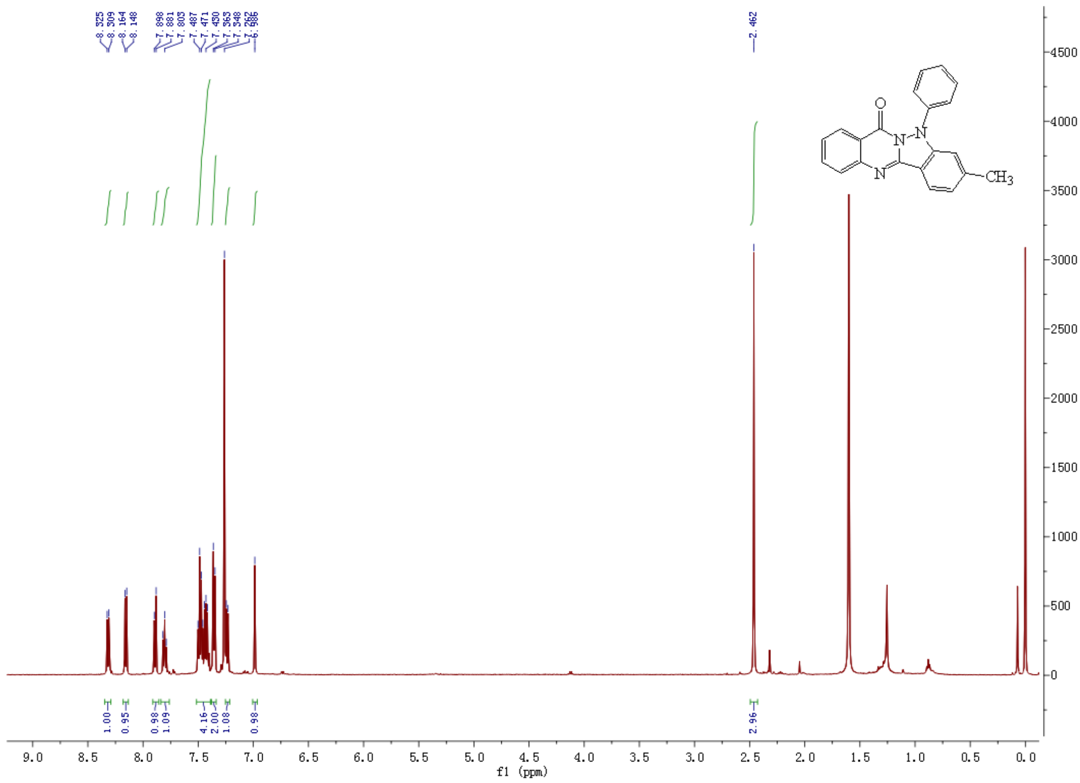


Figure S19. ^{1}H NMR of **2g** (500 MHz, DMSO-d_6) and ^{13}C NMR of **2g** (125 MHz, DMSO-d_6).



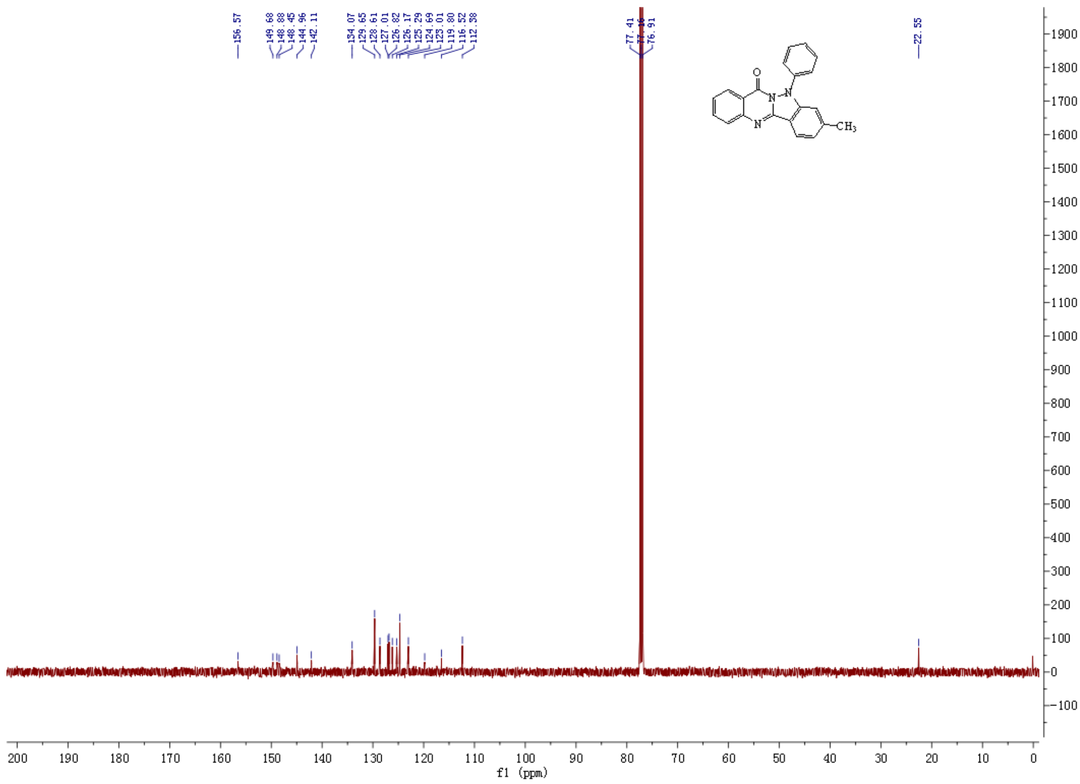
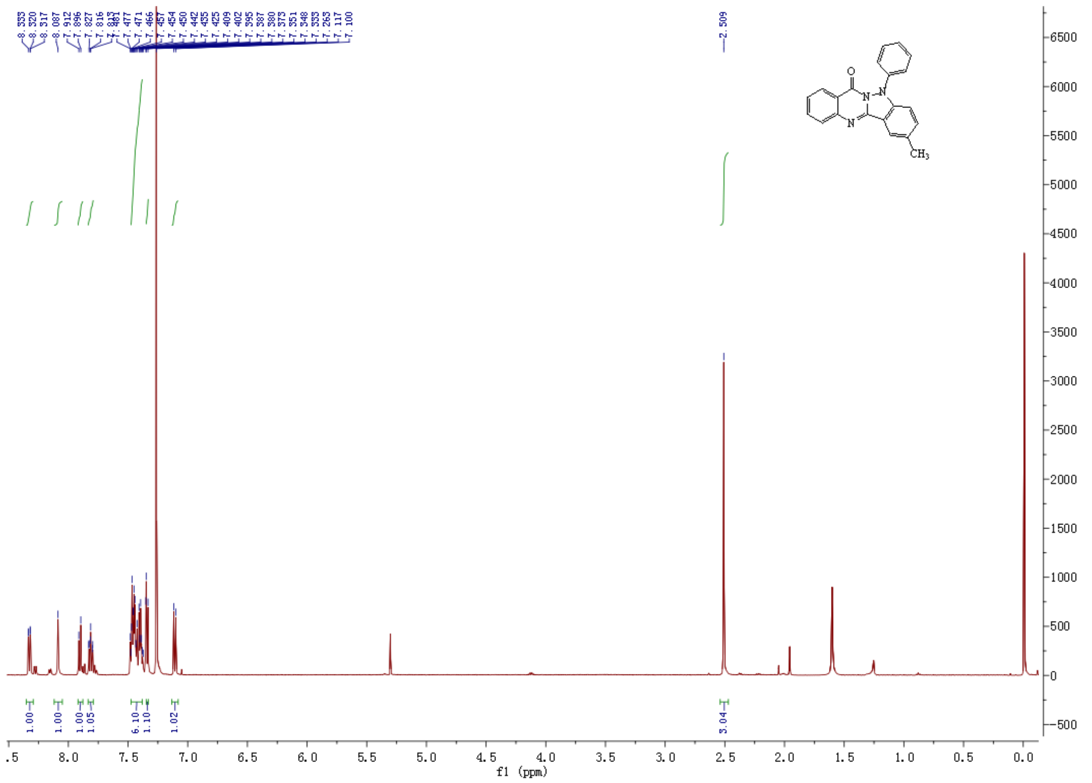


Figure S20. ^{1}H NMR of **2j** (500 MHz, $CDCl_3$) and ^{13}C NMR of **2j** (125 MHz, $CDCl_3$).



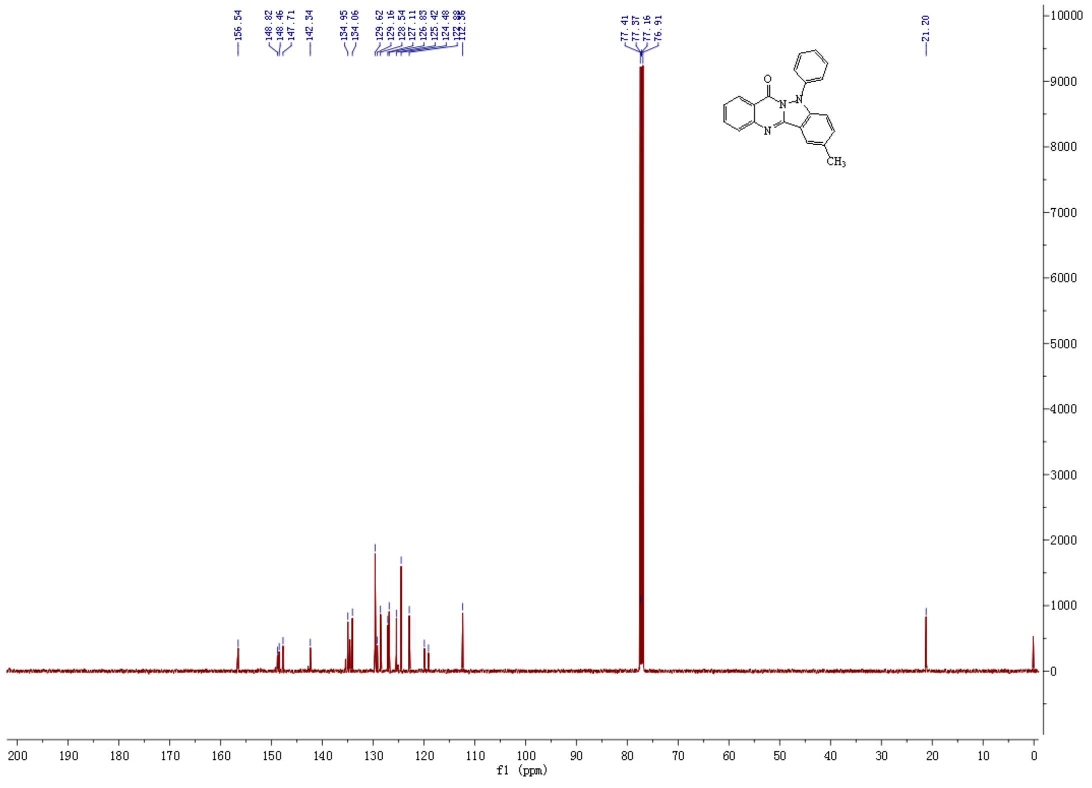


Figure S21. [1]H NMR of **2k** (500 MHz, $CDCl_3$) and [13]C NMR of **2k** (125 MHz, $CDCl_3$).

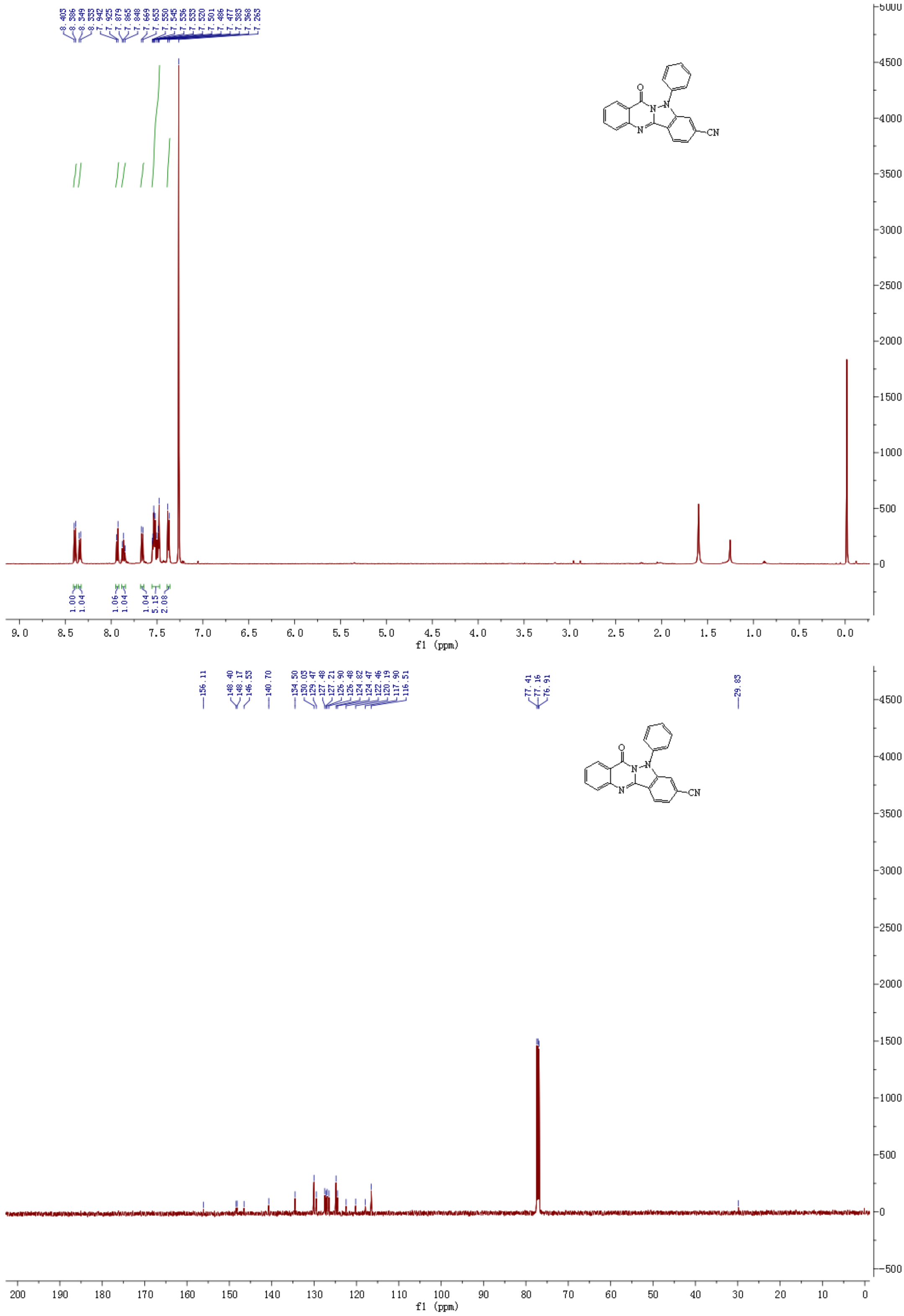


Figure S22. ^{1}H NMR of **2m** (500 MHz, $CDCl_3$) and ^{13}C NMR of **2m** (125 MHz, $CDCl_3$).

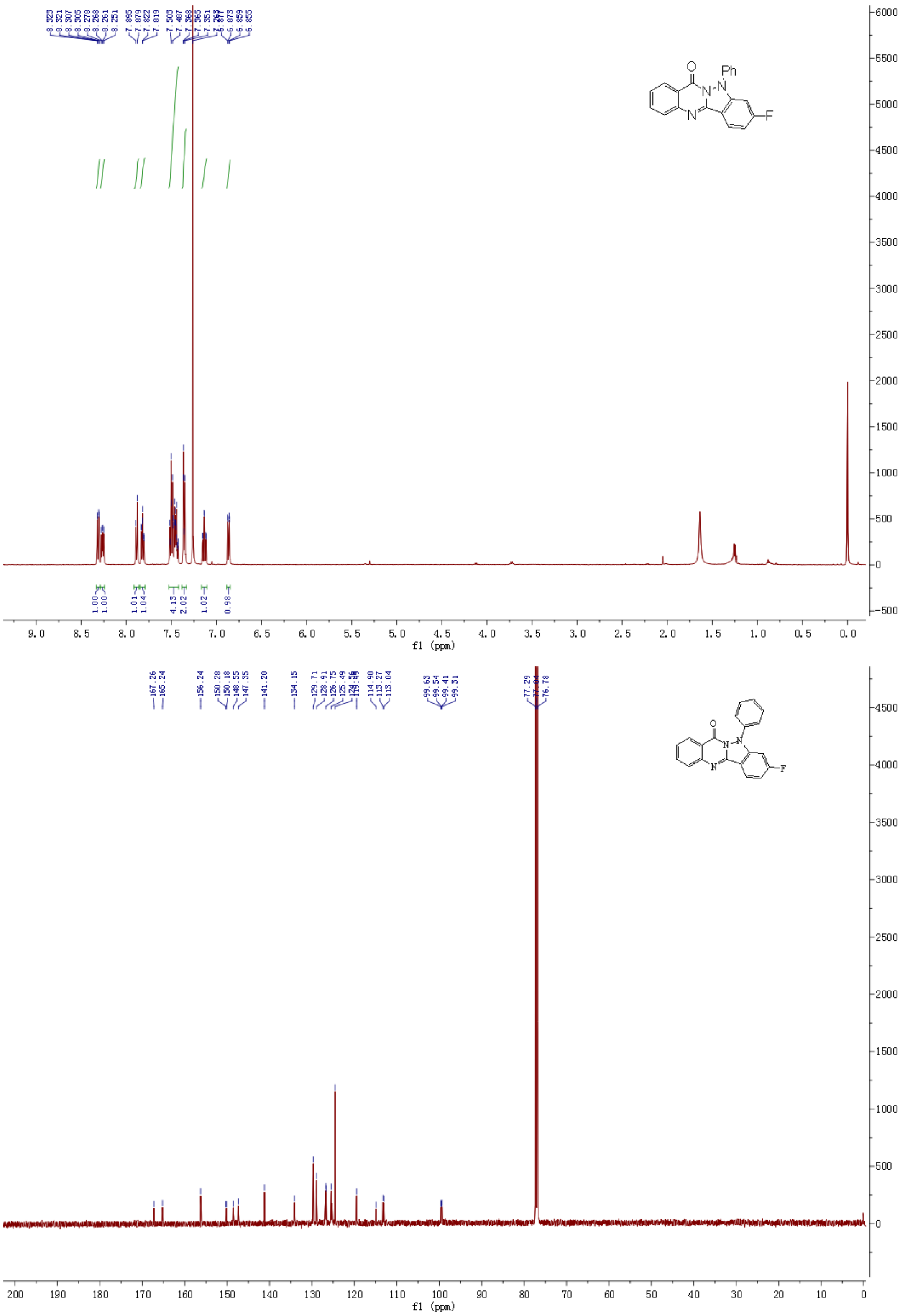
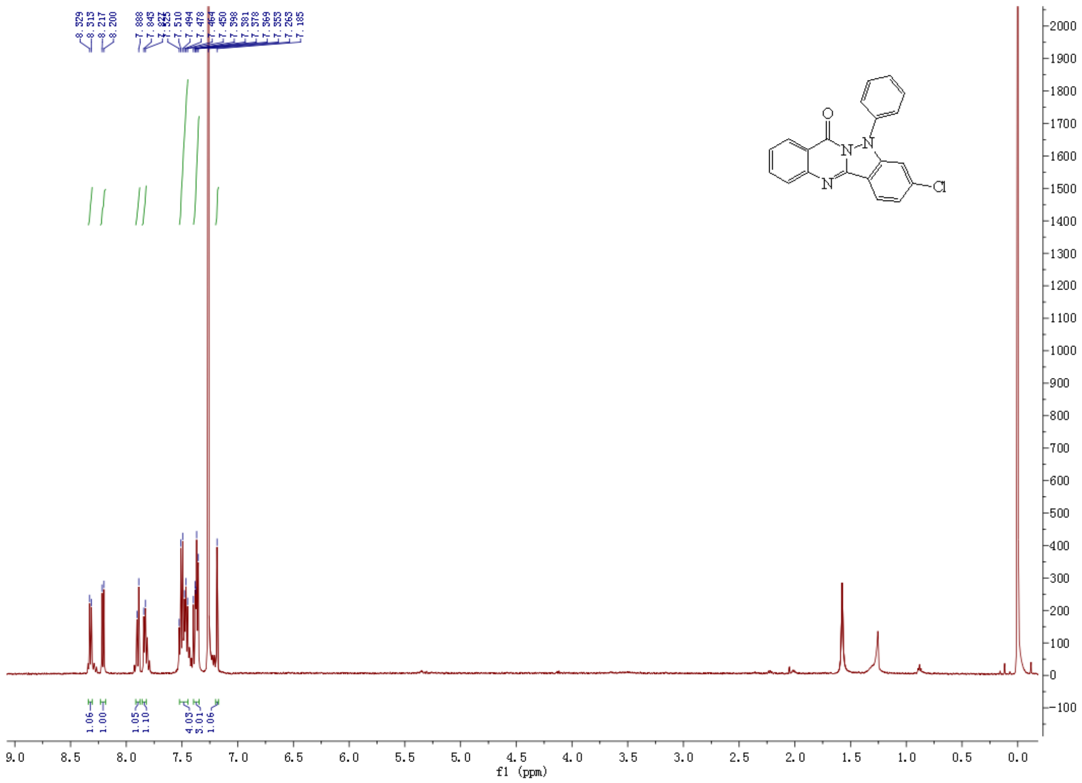


Figure S23. [1]H NMR of **2n** (500 MHz, $CDCl_3$) and [13]C NMR of **2n** (125 MHz, $CDCl_3$).



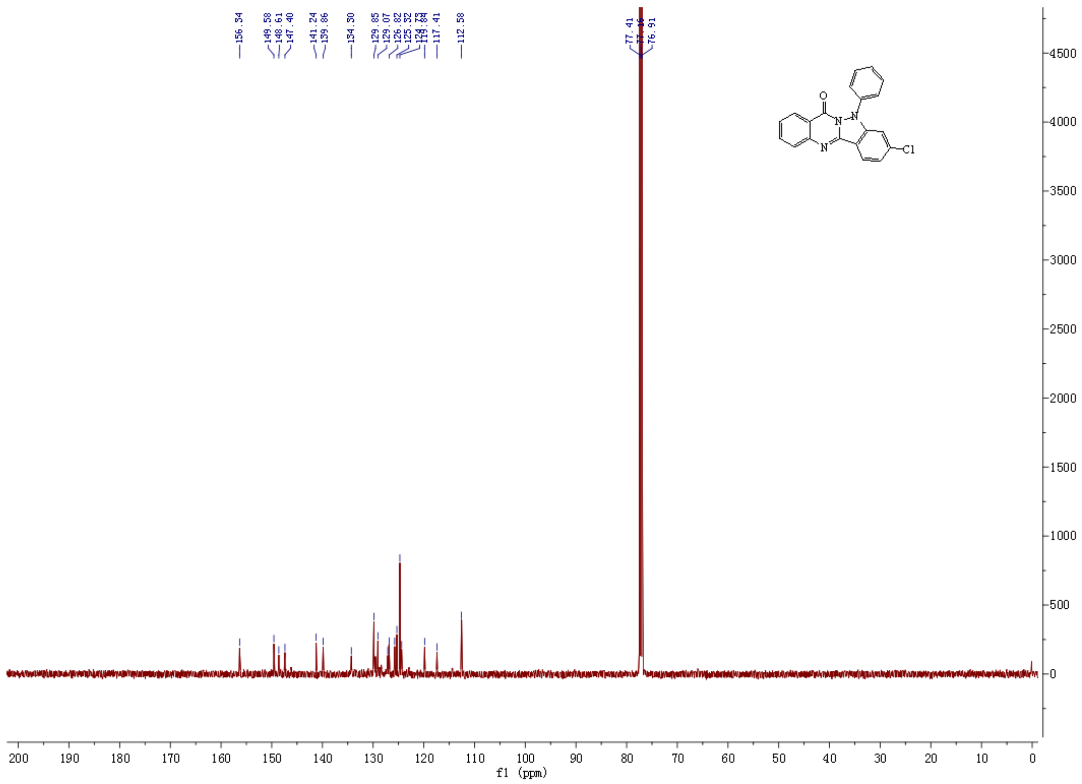
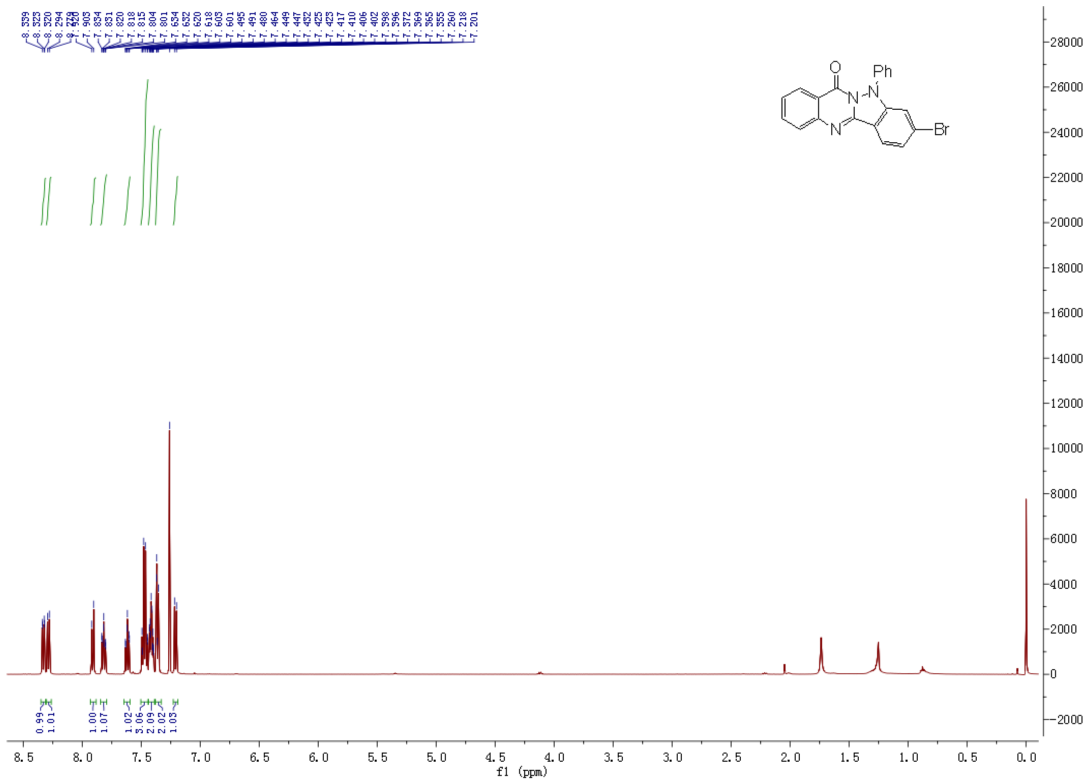


Figure S24. ^{1}H NMR of **2o** (500 MHz, $CDCl_3$) and ^{13}C NMR of **2o** (125 MHz, $CDCl_3$).



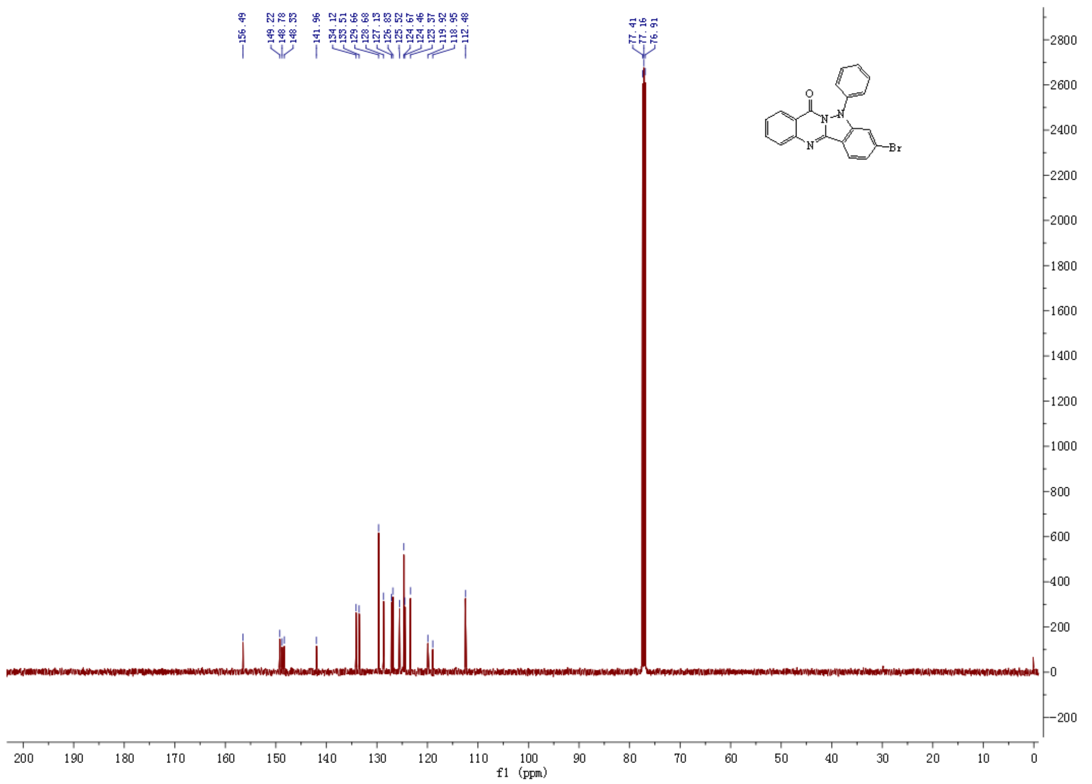
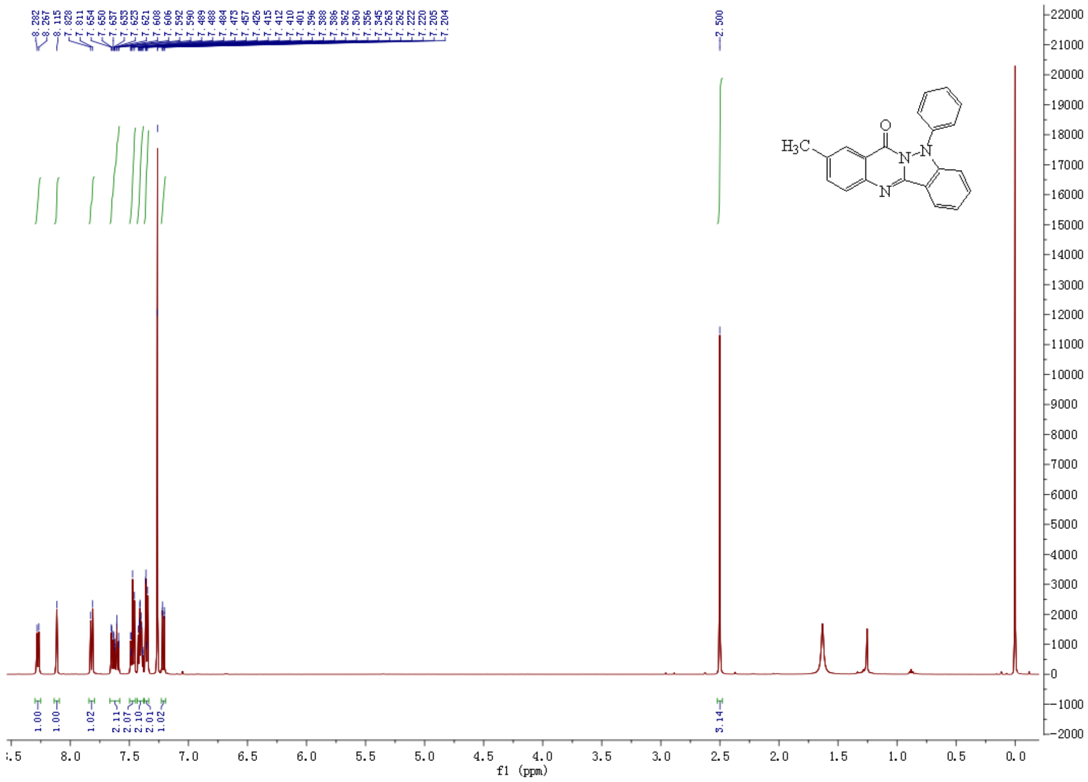


Figure S25. ^{1}H NMR of **2p** (500 MHz, $CDCl_3$) and ^{13}C NMR of **2p** (125 MHz, $CDCl_3$).



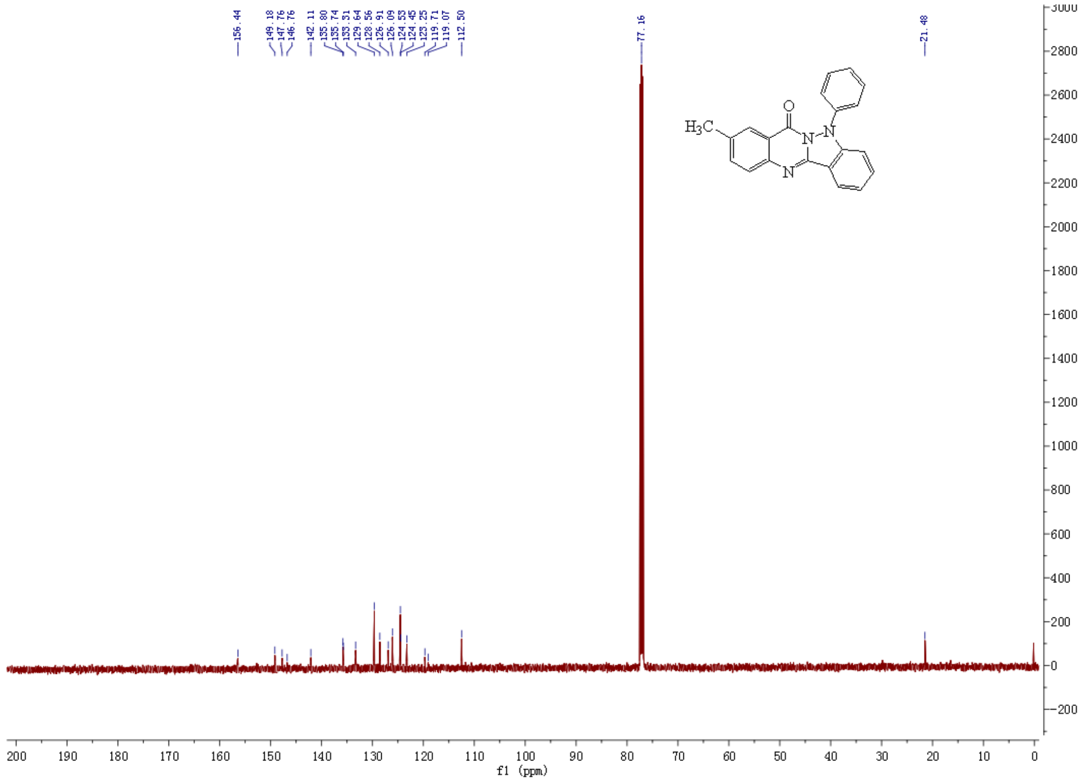
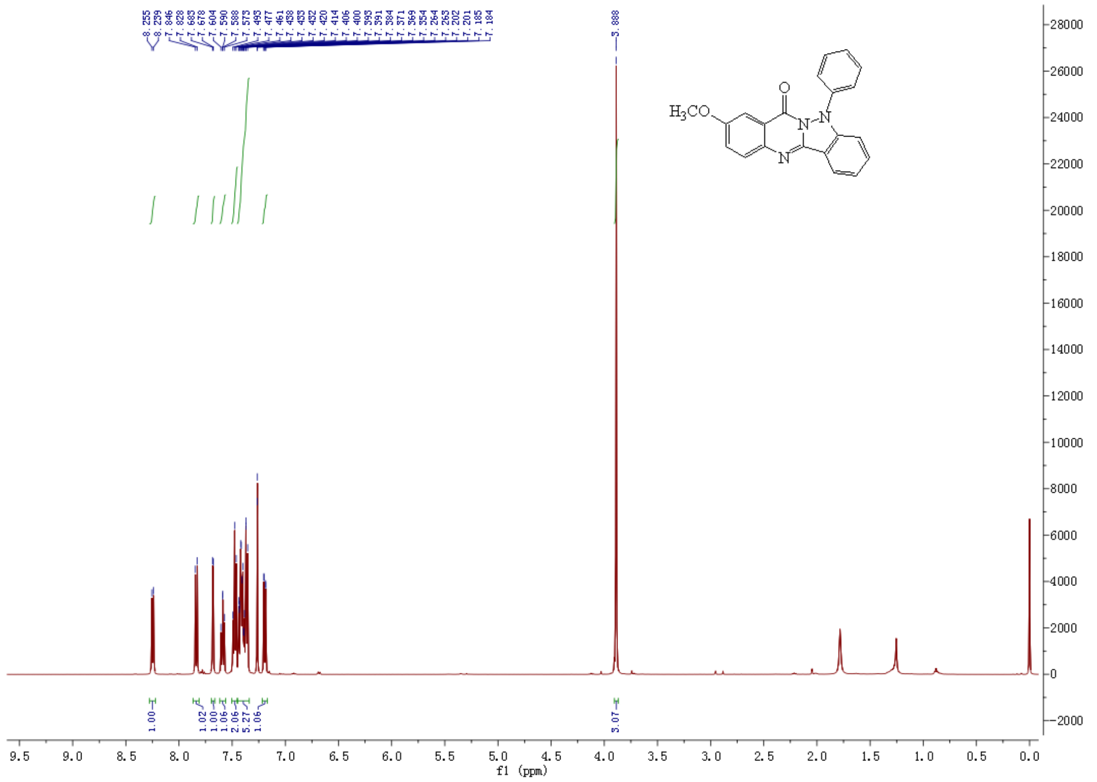


Figure S26. [1]H NMR of **2r** (500 MHz, $CDCl_3$) and [13]C NMR of **2r** (125 MHz, $CDCl_3$).



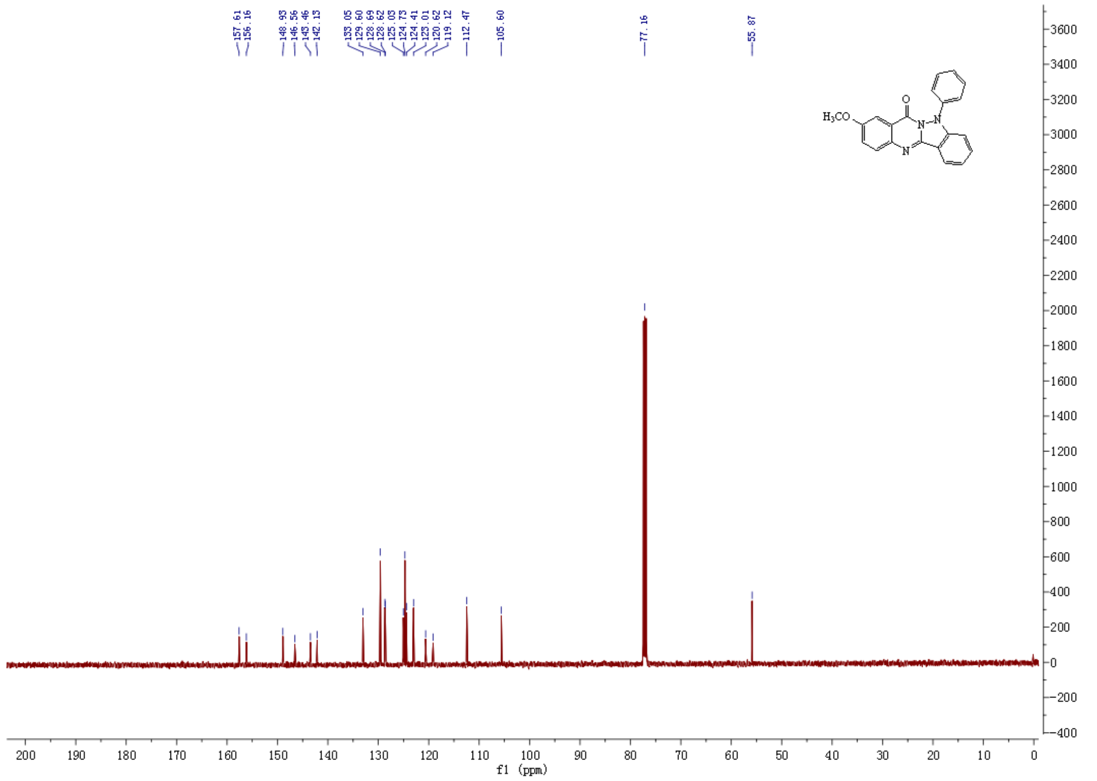
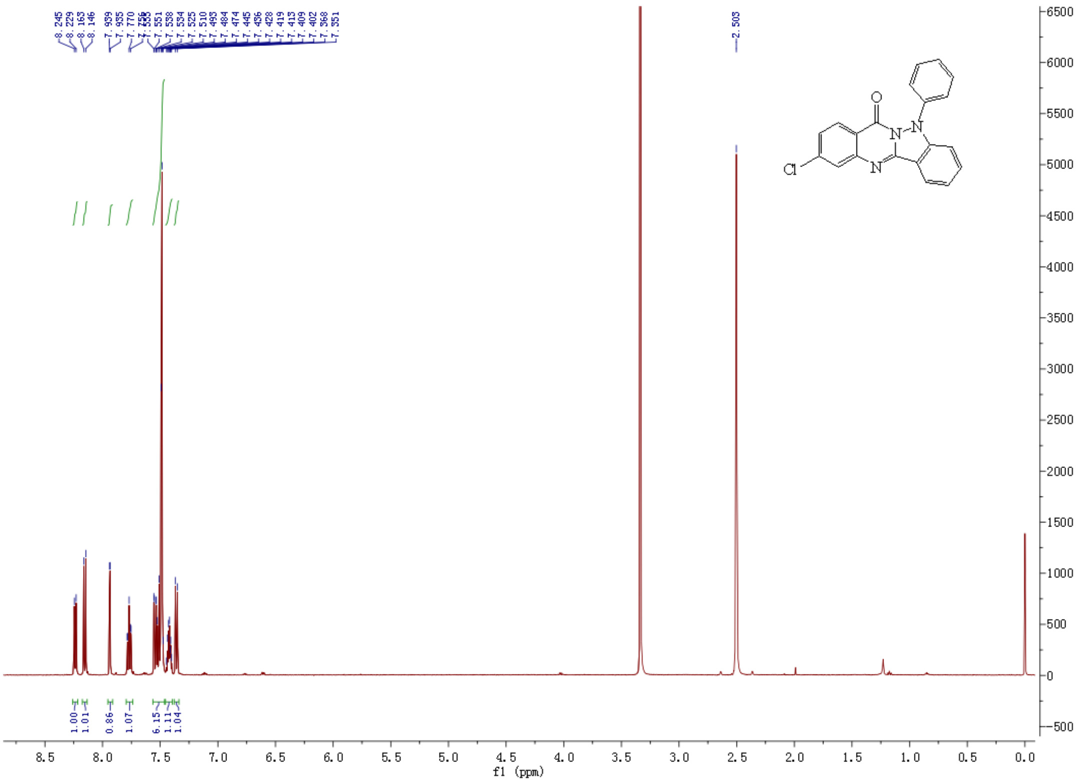


Figure S27. ^{1}H NMR of **2s** (500 MHz, $CDCl_3$) and ^{13}C NMR of **2s** (125 MHz, $CDCl_3$).



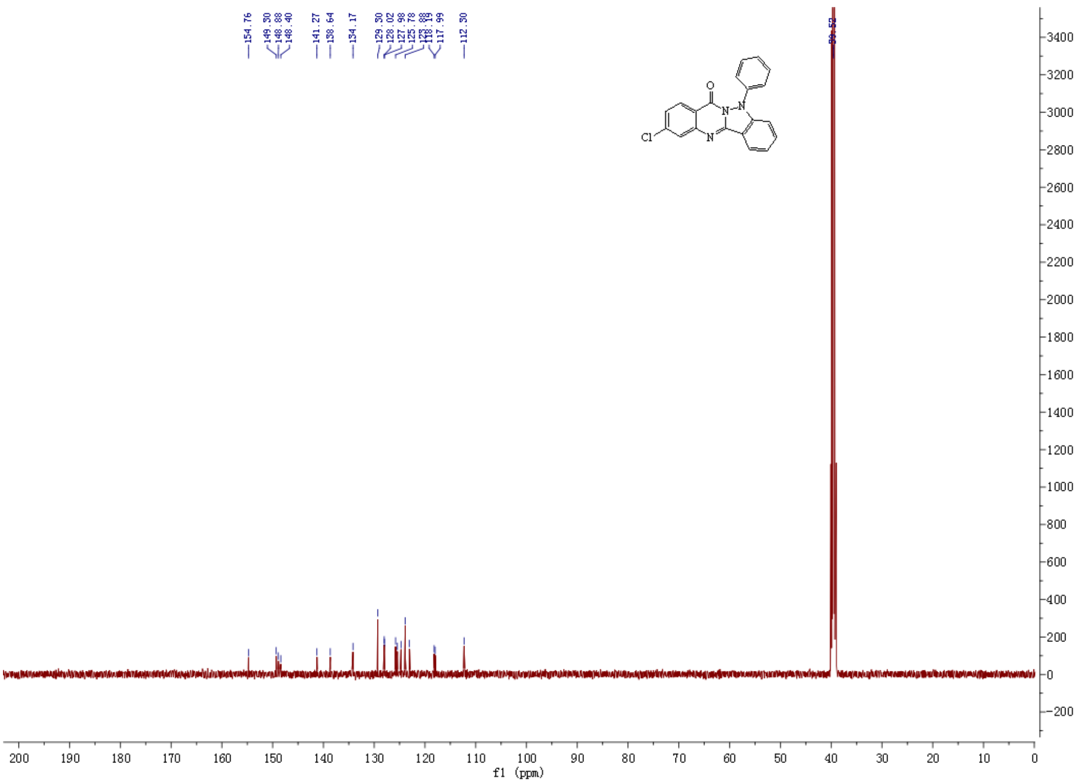
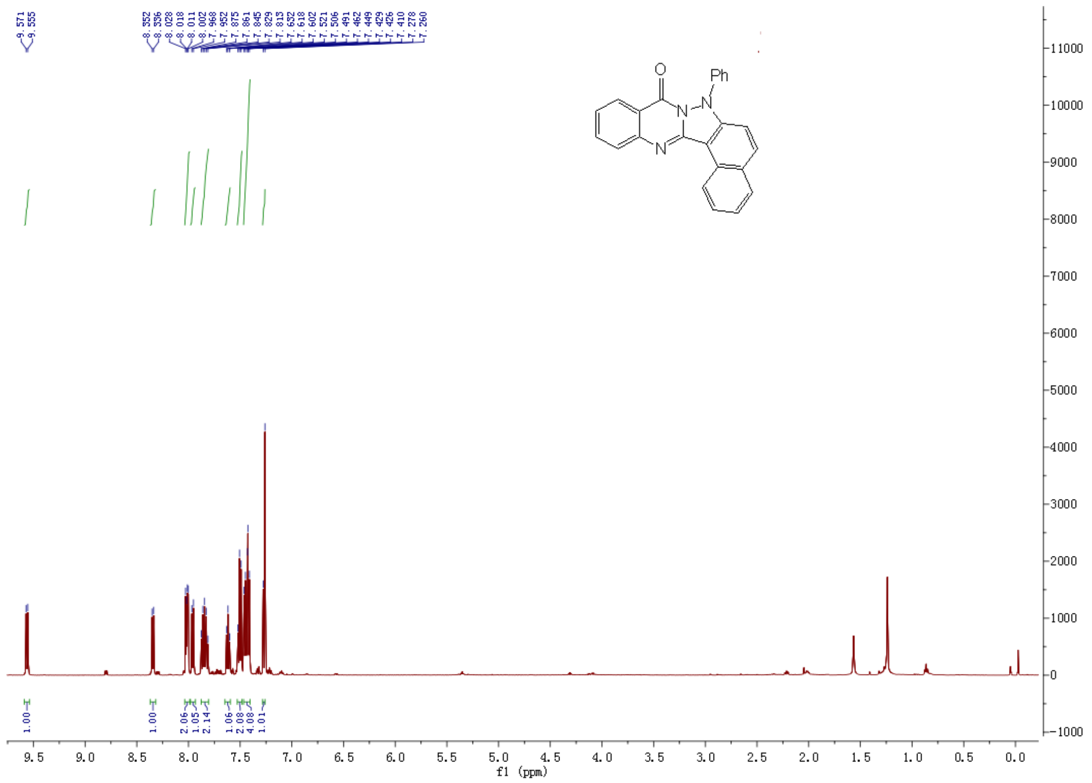


Figure S28. [1]H NMR of **2t** (500 MHz, DMSO-d_6) and [13]C NMR of **2t** (125 MHz, DMSO-d_6).



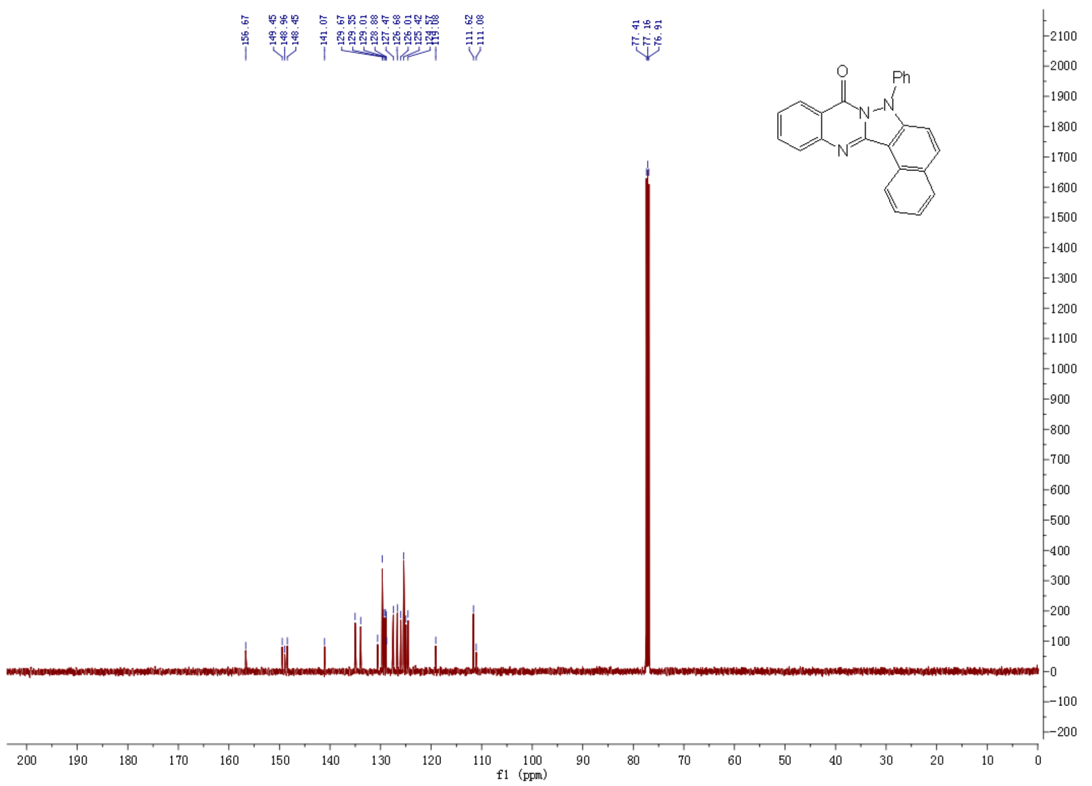


Figure S29. ^{1}H NMR of **2v** (500 MHz, $CDCl_3$) and ^{13}C NMR of **2v** (125 MHz, $CDCl_3$).

6. X-ray Crystallographic Data for Palladium Complex 3

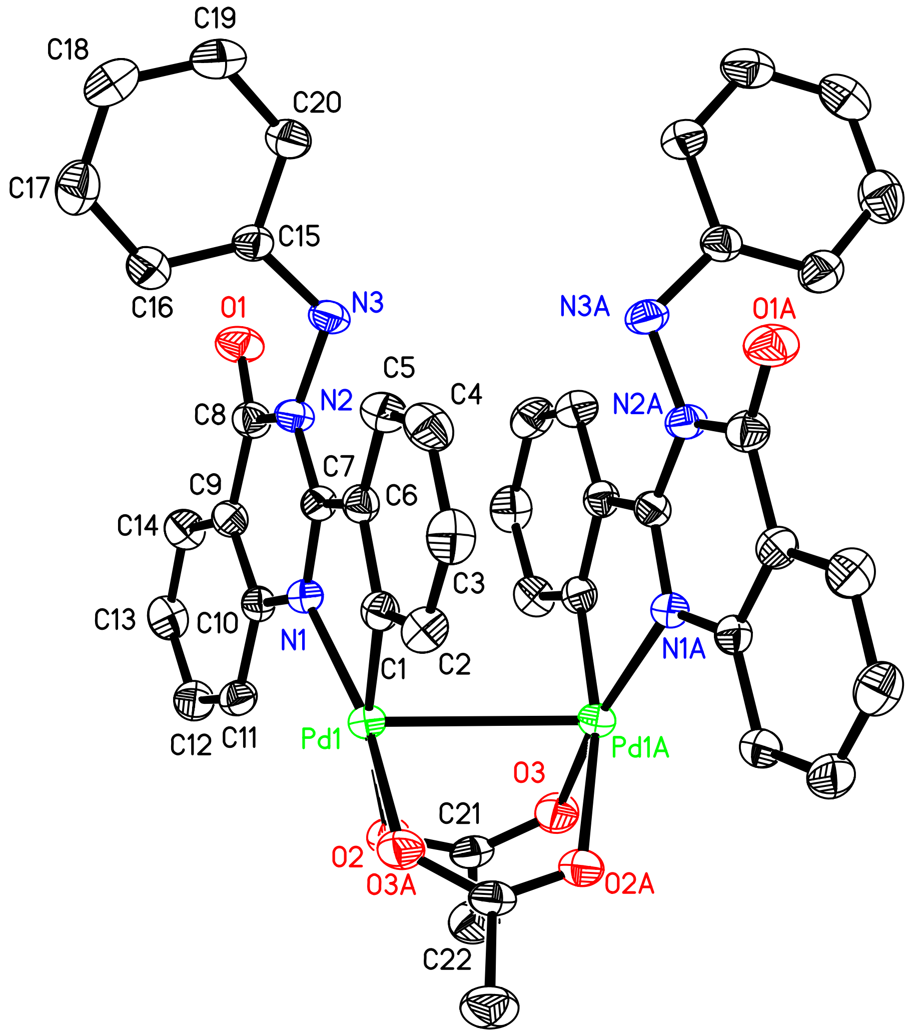


Table 1. Crystal data and structure refinement for cd214390.

Identification code	cd214390	
Empirical formula	C44 H34 N6 O6 Pd2	
Formula weight	955.57	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C 2/c	
Unit cell dimensions	a = 15.4148(17) Å	α= 90°.
	b = 18.670(2) Å	β= 120.833(2)°.
	c = 15.0377(17) Å	γ = 90°.
Volume	3716.1(7) Å^3	
Z	4	
Density (calculated)	1.708 Mg/m^3	
Absorption coefficient	1.029 mm^{-1}	
F(000)	1920	
Crystal size	0.187 x 0.145 x 0.112 mm^3	
Theta range for data collection	2.182 to 25.992°.	
Index ranges	-18<=h<=11, -20<=k<=22, -15<=l<=18	
Reflections collected	11139	
Independent reflections	3656 [R(int) = 0.0259]	
Completeness to theta = 25.242°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7457 and 0.6643	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3656 / 0 / 267	
Goodness-of-fit on F^2	1.082	
Final R indices [I>2sigma(I)]	R1 = 0.0276, wR2 = 0.0740	
R indices (all data)	R1 = 0.0312, wR2 = 0.0767	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.477 and -0.382 e.Å^{-3}	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3)
for cd214390. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Pd(1)	10032(1)	10558(1)	6548(1)	38(1)
N(1)	9134(1)	9760(1)	5572(1)	36(1)
N(2)	8905(2)	8520(1)	5361(2)	40(1)
N(3)	9212(2)	7838(1)	5814(2)	44(1)
O(1)	7434(2)	8026(1)	4120(2)	57(1)
O(2)	8981(2)	11443(1)	6221(1)	51(1)
O(3)	8872(1)	11302(1)	7640(2)	52(1)
C(1)	10962(2)	9758(1)	7105(2)	38(1)
C(2)	11943(2)	9821(2)	7930(2)	49(1)
C(3)	12504(2)	9212(2)	8394(2)	55(1)
C(4)	12113(2)	8544(2)	8032(2)	53(1)
C(5)	11140(2)	8465(1)	7215(2)	49(1)
C(6)	10540(2)	9076(1)	6738(2)	38(1)
C(7)	9492(2)	9108(1)	5870(2)	37(1)
C(8)	7925(2)	8563(1)	4484(2)	43(1)
C(9)	7597(2)	9282(1)	4120(2)	41(1)
C(10)	8196(2)	9865(1)	4687(2)	37(1)
C(11)	7850(2)	10561(1)	4328(2)	45(1)
C(12)	6923(2)	10653(2)	3438(2)	52(1)
C(13)	6335(2)	10072(2)	2880(2)	54(1)
C(14)	6669(2)	9396(1)	3217(2)	51(1)
C(15)	9552(2)	7344(1)	5340(2)	41(1)
C(16)	9758(2)	7522(2)	4582(2)	56(1)
C(17)	10141(2)	7005(2)	4214(3)	66(1)
C(18)	10339(2)	6327(2)	4605(3)	64(1)
C(19)	10140(2)	6151(2)	5360(2)	62(1)
C(20)	9743(2)	6652(1)	5734(2)	52(1)
C(21)	8647(2)	11599(1)	6795(2)	44(1)
C(22)	7875(2)	12196(2)	6464(3)	67(1)

Table 3. Bond lengths [Å] and angles [°] for cd214390.

Pd(1)-C(1)	1.938(2)
Pd(1)-O(3)#1	2.0397(18)
Pd(1)-N(1)	2.0509(19)
Pd(1)-O(2)	2.1858(18)
Pd(1)-Pd(1)#1	2.9137(5)
N(1)-C(7)	1.317(3)
N(1)-C(10)	1.388(3)
N(2)-C(7)	1.378(3)
N(2)-N(3)	1.407(3)
N(2)-C(8)	1.409(3)
N(3)-C(15)	1.419(3)
N(3)-H(3A)	0.79(3)
O(1)-C(8)	1.206(3)
O(2)-C(21)	1.246(3)
O(3)-C(21)	1.261(3)
O(3)-Pd(1)#1	2.0397(17)
C(1)-C(2)	1.385(3)
C(1)-C(6)	1.409(3)
C(2)-C(3)	1.381(4)
C(2)-H(2)	0.9300
C(3)-C(4)	1.370(4)
C(3)-H(3)	0.9300
C(4)-C(5)	1.376(4)
C(4)-H(4)	0.9300
C(5)-C(6)	1.410(3)
C(5)-H(5)	0.9300
C(6)-C(7)	1.468(3)
C(8)-C(9)	1.440(4)
C(9)-C(14)	1.394(4)
C(9)-C(10)	1.398(3)
C(10)-C(11)	1.404(3)
C(11)-C(12)	1.379(4)
C(11)-H(11)	0.9300
C(12)-C(13)	1.385(4)
C(12)-H(12)	0.9300
C(13)-C(14)	1.360(4)

C(13)-H(13)	0.9300
C(14)-H(14)	0.9300
C(15)-C(16)	1.371(4)
C(15)-C(20)	1.389(4)
C(16)-C(17)	1.386(4)
C(16)-H(16)	0.9300
C(17)-C(18)	1.362(5)
C(17)-H(17)	0.9300
C(18)-C(19)	1.360(5)
C(18)-H(18)	0.9300
C(19)-C(20)	1.385(4)
C(19)-H(19)	0.9300
C(20)-H(20)	0.9300
C(21)-C(22)	1.515(4)
C(22)-H(22A)	0.9600
C(22)-H(22B)	0.9600
C(22)-H(22C)	0.9600
C(1)-Pd(1)-O(3)#1	93.61(10)
C(1)-Pd(1)-N(1)	80.10(9)
O(3)#1-Pd(1)-N(1)	166.18(8)
C(1)-Pd(1)-O(2)	168.07(8)
O(3)#1-Pd(1)-O(2)	84.91(8)
N(1)-Pd(1)-O(2)	103.75(8)
C(1)-Pd(1)-Pd(1)#1	88.02(7)
O(3)#1-Pd(1)-Pd(1)#1	81.20(6)
N(1)-Pd(1)-Pd(1)#1	110.65(5)
O(2)-Pd(1)-Pd(1)#1	80.05(5)
C(7)-N(1)-C(10)	120.3(2)
C(7)-N(1)-Pd(1)	114.62(15)
C(10)-N(1)-Pd(1)	124.97(15)
C(7)-N(2)-N(3)	119.4(2)
C(7)-N(2)-C(8)	123.9(2)
N(3)-N(2)-C(8)	115.98(19)
N(2)-N(3)-C(15)	117.7(2)
N(2)-N(3)-H(3A)	107(2)
C(15)-N(3)-H(3A)	111(2)
C(21)-O(2)-Pd(1)	122.85(16)

C(21)-O(3)-Pd(1)#1	128.14(17)
C(2)-C(1)-C(6)	120.0(2)
C(2)-C(1)-Pd(1)	123.3(2)
C(6)-C(1)-Pd(1)	115.92(17)
C(3)-C(2)-C(1)	119.8(3)
C(3)-C(2)-H(2)	120.1
C(1)-C(2)-H(2)	120.1
C(4)-C(3)-C(2)	120.9(3)
C(4)-C(3)-H(3)	119.5
C(2)-C(3)-H(3)	119.5
C(3)-C(4)-C(5)	120.6(3)
C(3)-C(4)-H(4)	119.7
C(5)-C(4)-H(4)	119.7
C(4)-C(5)-C(6)	119.9(3)
C(4)-C(5)-H(5)	120.1
C(6)-C(5)-H(5)	120.1
C(1)-C(6)-C(5)	118.8(2)
C(1)-C(6)-C(7)	112.8(2)
C(5)-C(6)-C(7)	128.4(2)
N(1)-C(7)-N(2)	120.4(2)
N(1)-C(7)-C(6)	114.8(2)
N(2)-C(7)-C(6)	124.8(2)
O(1)-C(8)-N(2)	119.9(2)
O(1)-C(8)-C(9)	125.9(2)
N(2)-C(8)-C(9)	114.1(2)
C(14)-C(9)-C(10)	120.2(2)
C(14)-C(9)-C(8)	119.8(2)
C(10)-C(9)-C(8)	120.0(2)
N(1)-C(10)-C(9)	120.9(2)
N(1)-C(10)-C(11)	120.2(2)
C(9)-C(10)-C(11)	118.9(2)
C(12)-C(11)-C(10)	119.2(2)
C(12)-C(11)-H(11)	120.4
C(10)-C(11)-H(11)	120.4
C(11)-C(12)-C(13)	121.5(2)
C(11)-C(12)-H(12)	119.3
C(13)-C(12)-H(12)	119.3
C(14)-C(13)-C(12)	119.7(3)

C(14)-C(13)-H(13)	120.2
C(12)-C(13)-H(13)	120.2
C(13)-C(14)-C(9)	120.5(3)
C(13)-C(14)-H(14)	119.7
C(9)-C(14)-H(14)	119.7
C(16)-C(15)-C(20)	119.4(3)
C(16)-C(15)-N(3)	124.2(2)
C(20)-C(15)-N(3)	116.2(2)
C(15)-C(16)-C(17)	119.3(3)
C(15)-C(16)-H(16)	120.3
C(17)-C(16)-H(16)	120.3
C(18)-C(17)-C(16)	121.5(3)
C(18)-C(17)-H(17)	119.2
C(16)-C(17)-H(17)	119.2
C(19)-C(18)-C(17)	119.2(3)
C(19)-C(18)-H(18)	120.4
C(17)-C(18)-H(18)	120.4
C(18)-C(19)-C(20)	120.8(3)
C(18)-C(19)-H(19)	119.6
C(20)-C(19)-H(19)	119.6
C(19)-C(20)-C(15)	119.8(3)
C(19)-C(20)-H(20)	120.1
C(15)-C(20)-H(20)	120.1
O(2)-C(21)-O(3)	126.7(2)
O(2)-C(21)-C(22)	118.6(2)
O(3)-C(21)-C(22)	114.7(3)
C(21)-C(22)-H(22A)	109.5
C(21)-C(22)-H(22B)	109.5
H(22A)-C(22)-H(22B)	109.5
C(21)-C(22)-H(22C)	109.5
H(22A)-C(22)-H(22C)	109.5
H(22B)-C(22)-H(22C)	109.5

Symmetry transformations used to generate equivalent atoms:

#1 -x+2,y,-z+3/2

Table 4. Anisotropic displacement parameters ($Å^2 x 10^3$) for cd214390. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Pd(1)	43(1)	31(1)	39(1)	-2(1)	21(1)	-2(1)
N(1)	40(1)	32(1)	38(1)	-1(1)	20(1)	0(1)
N(2)	44(1)	30(1)	43(1)	2(1)	21(1)	-1(1)
N(3)	52(1)	30(1)	52(1)	4(1)	30(1)	-2(1)
O(1)	54(1)	41(1)	64(1)	-4(1)	22(1)	-15(1)
O(2)	64(1)	37(1)	50(1)	1(1)	26(1)	8(1)
O(3)	54(1)	44(1)	55(1)	5(1)	26(1)	15(1)
C(1)	39(1)	40(1)	43(1)	1(1)	25(1)	2(1)
C(2)	43(1)	51(2)	51(1)	-5(1)	23(1)	0(1)
C(3)	39(1)	70(2)	49(2)	3(1)	18(1)	6(1)
C(4)	47(1)	54(2)	57(2)	16(1)	25(1)	13(1)
C(5)	52(2)	40(1)	54(2)	6(1)	27(1)	4(1)
C(6)	39(1)	38(1)	39(1)	2(1)	23(1)	1(1)
C(7)	42(1)	34(1)	40(1)	-2(1)	24(1)	-1(1)
C(8)	43(1)	41(1)	46(1)	-1(1)	24(1)	-6(1)
C(9)	39(1)	41(1)	42(1)	2(1)	22(1)	-1(1)
C(10)	40(1)	38(1)	36(1)	1(1)	21(1)	1(1)
C(11)	52(2)	37(1)	43(1)	-1(1)	23(1)	4(1)
C(12)	56(2)	49(2)	52(2)	9(1)	27(1)	16(1)
C(13)	41(1)	64(2)	47(1)	9(1)	16(1)	7(1)
C(14)	43(1)	54(2)	48(2)	0(1)	18(1)	-7(1)
C(15)	40(1)	35(1)	43(1)	-2(1)	19(1)	-4(1)
C(16)	66(2)	49(2)	61(2)	5(1)	38(2)	-1(1)
C(17)	69(2)	79(2)	66(2)	-6(2)	44(2)	-2(2)
C(18)	56(2)	59(2)	73(2)	-19(2)	30(2)	2(1)
C(19)	62(2)	41(2)	71(2)	-1(1)	25(2)	5(1)
C(20)	60(2)	41(2)	55(2)	5(1)	28(1)	3(1)
C(21)	43(1)	30(1)	47(1)	-3(1)	14(1)	1(1)
C(22)	64(2)	52(2)	72(2)	8(2)	25(2)	22(2)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for cd214390.

	x	y	z	U(eq)
H(2)	12224	10271	8172	58
H(3)	13157	9256	8959	66
H(4)	12508	8141	8342	64
H(5)	10878	8010	6978	58
H(11)	8242	10956	4685	54
H(12)	6687	11114	3207	63
H(13)	5715	10145	2278	65
H(14)	6276	9006	2841	61
H(16)	9641	7985	4317	67
H(17)	10265	7124	3689	80
H(18)	10607	5989	4358	77
H(19)	10272	5689	5628	75
H(20)	9606	6525	6248	63
H(22A)	7909	12493	5963	101
H(22B)	8016	12478	7057	101
H(22C)	7211	11993	6164	101
H(3A)	8750(20)	7675(15)	5850(20)	43(8)

Table 6. Torsion angles [°] for cd214390.

C(7)-N(2)-N(3)-C(15)	-109.8(2)
C(8)-N(2)-N(3)-C(15)	79.8(3)
C(6)-C(1)-C(2)-C(3)	-0.3(4)
Pd(1)-C(1)-C(2)-C(3)	169.2(2)
C(1)-C(2)-C(3)-C(4)	1.7(4)
C(2)-C(3)-C(4)-C(5)	-1.8(4)
C(3)-C(4)-C(5)-C(6)	0.5(4)
C(2)-C(1)-C(6)-C(5)	-1.0(3)
Pd(1)-C(1)-C(6)-C(5)	-171.17(19)
C(2)-C(1)-C(6)-C(7)	179.3(2)
Pd(1)-C(1)-C(6)-C(7)	9.1(2)
C(4)-C(5)-C(6)-C(1)	0.8(4)
C(4)-C(5)-C(6)-C(7)	-179.5(2)
C(10)-N(1)-C(7)-N(2)	-5.8(3)
Pd(1)-N(1)-C(7)-N(2)	171.37(17)
C(10)-N(1)-C(7)-C(6)	172.55(19)
Pd(1)-N(1)-C(7)-C(6)	-10.2(2)
N(3)-N(2)-C(7)-N(1)	-166.8(2)
C(8)-N(2)-C(7)-N(1)	2.8(3)
N(3)-N(2)-C(7)-C(6)	15.0(3)
C(8)-N(2)-C(7)-C(6)	-175.4(2)
C(1)-C(6)-C(7)-N(1)	1.2(3)
C(5)-C(6)-C(7)-N(1)	-178.6(2)
C(1)-C(6)-C(7)-N(2)	179.5(2)
C(5)-C(6)-C(7)-N(2)	-0.2(4)
C(7)-N(2)-C(8)-O(1)	-175.4(2)
N(3)-N(2)-C(8)-O(1)	-5.5(3)
C(7)-N(2)-C(8)-C(9)	3.2(3)
N(3)-N(2)-C(8)-C(9)	173.0(2)
O(1)-C(8)-C(9)-C(14)	-5.9(4)
N(2)-C(8)-C(9)-C(14)	175.6(2)
O(1)-C(8)-C(9)-C(10)	172.4(2)
N(2)-C(8)-C(9)-C(10)	-6.1(3)
C(7)-N(1)-C(10)-C(9)	2.7(3)
Pd(1)-N(1)-C(10)-C(9)	-174.17(17)
C(7)-N(1)-C(10)-C(11)	-175.1(2)

Pd(1)-N(1)-C(10)-C(11)	8.0(3)
C(14)-C(9)-C(10)-N(1)	-178.2(2)
C(8)-C(9)-C(10)-N(1)	3.5(3)
C(14)-C(9)-C(10)-C(11)	-0.4(4)
C(8)-C(9)-C(10)-C(11)	-178.7(2)
N(1)-C(10)-C(11)-C(12)	179.1(2)
C(9)-C(10)-C(11)-C(12)	1.2(4)
C(10)-C(11)-C(12)-C(13)	-1.3(4)
C(11)-C(12)-C(13)-C(14)	0.6(4)
C(12)-C(13)-C(14)-C(9)	0.2(4)
C(10)-C(9)-C(14)-C(13)	-0.3(4)
C(8)-C(9)-C(14)-C(13)	178.0(3)
N(2)-N(3)-C(15)-C(16)	11.2(4)
N(2)-N(3)-C(15)-C(20)	-173.1(2)
C(20)-C(15)-C(16)-C(17)	0.8(4)
N(3)-C(15)-C(16)-C(17)	176.4(3)
C(15)-C(16)-C(17)-C(18)	-1.5(5)
C(16)-C(17)-C(18)-C(19)	1.1(5)
C(17)-C(18)-C(19)-C(20)	-0.2(5)
C(18)-C(19)-C(20)-C(15)	-0.4(5)
C(16)-C(15)-C(20)-C(19)	0.1(4)
N(3)-C(15)-C(20)-C(19)	-175.8(2)
Pd(1)-O(2)-C(21)-O(3)	2.4(4)
Pd(1)-O(2)-C(21)-C(22)	-176.47(19)
Pd(1)#1-O(3)-C(21)-O(2)	8.2(4)
Pd(1)#1-O(3)-C(21)-C(22)	-172.92(19)

Symmetry transformations used to generate equivalent atoms:

#1 -x+2,y,-z+3/2

Table 7. Hydrogen bonds for cd214390 [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(3)-H(3A)...O(1)#2	0.79(3)	2.27(3)	3.051(3)	167(3)
C(16)-H(16)...O(3)#3	0.93	2.54	3.335(3)	143.1
C(11)-H(11)...O(2)	0.93	2.18	2.961(3)	140.8

Symmetry transformations used to generate equivalent atoms:

#1 -x+2,y,-z+3/2 #2 -x+3/2,-y+3/2,-z+1 #3 x,-y+2,z-1/2

7. References

(1) (a) Kale, A. U.; Kardile, D. P.; Kalyane, N. V.; Patel, M. R.; Patel, H. *Int. J. Pharm Appl. Sci.* 2010, 85; (b) Georgios, R.; Athanasios, K.; George, V. *Tetrahedron* **2011**, *67*, 7805; (c) Manivannan, E.; Chaturvedi, S. C. *Bioorg. Med. Chem.* **2011**, *19*, 4520.

(2) Chen, D.; Dou, G.; Li, Y.; Liu, Y.; Wang, X. *J. Org. Chem.* **2013**, *78*, 5700.

(3) Yang, W.; Ye, L.; Huang, D.; Liu, M.; Ding, J.; Chen, J.; Wu, H. *Tetrahedron* **2013**, *69*, 9852.

(4) Kumar, K. S.; Kumar, P. M.; Rao, V. S.; Jafar, A. A.; Meda, C. L. T.; Kapavarapu, R.; Parsac, K. V. L.; Pal, M. *Org. Biomol. Chem.* **2012**, *10*, 3098.