Supporting Information

Copper-Catalyzed C-O Bond Cleavage and Cyclization: Synthesis of Indazolo[3,2-*b*]quinazolinones

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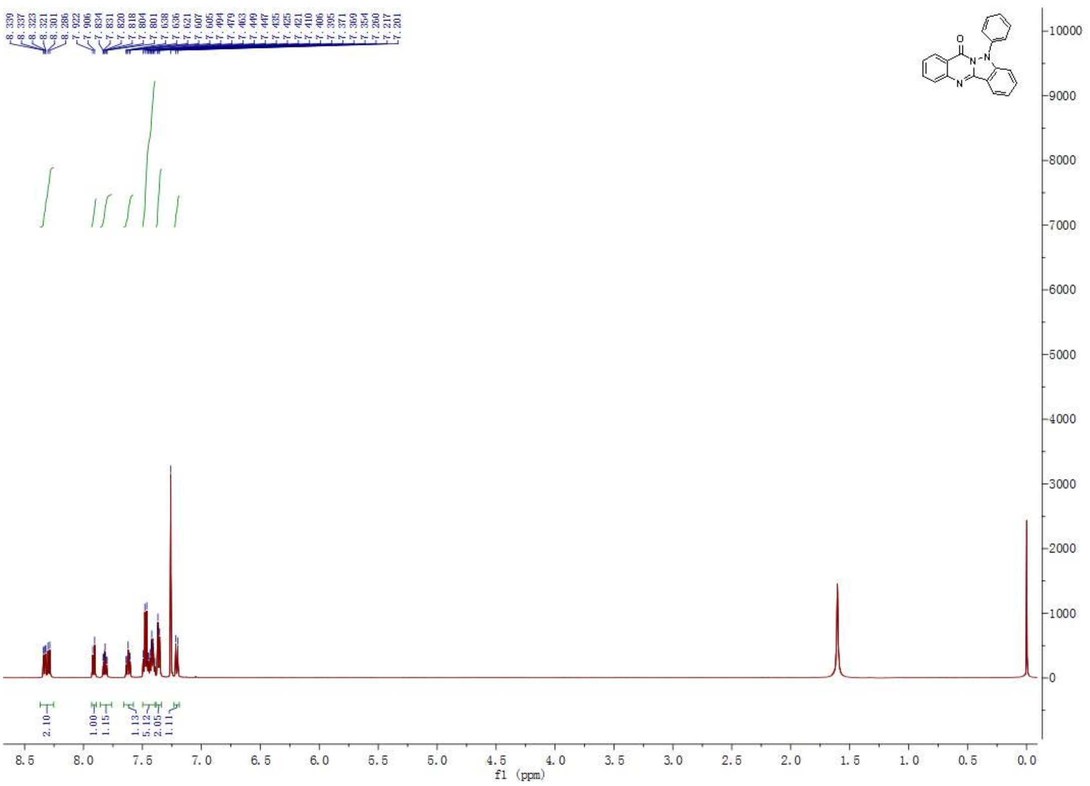
1. NMR Spectra for All Products



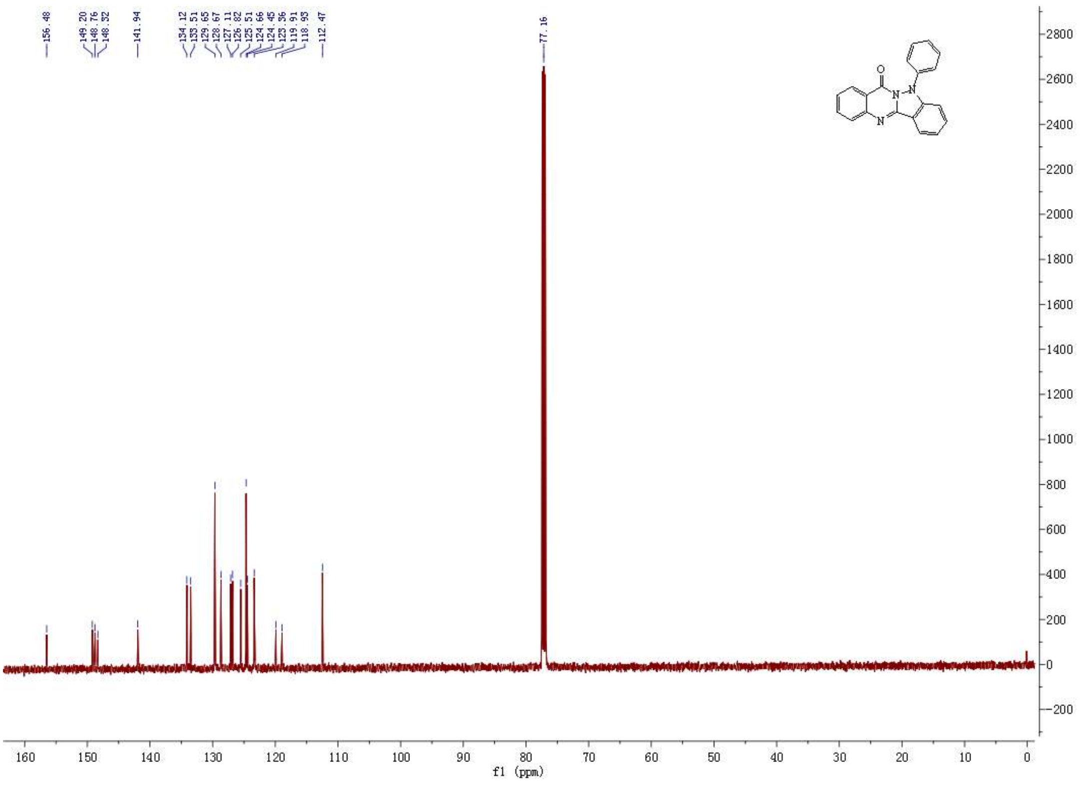
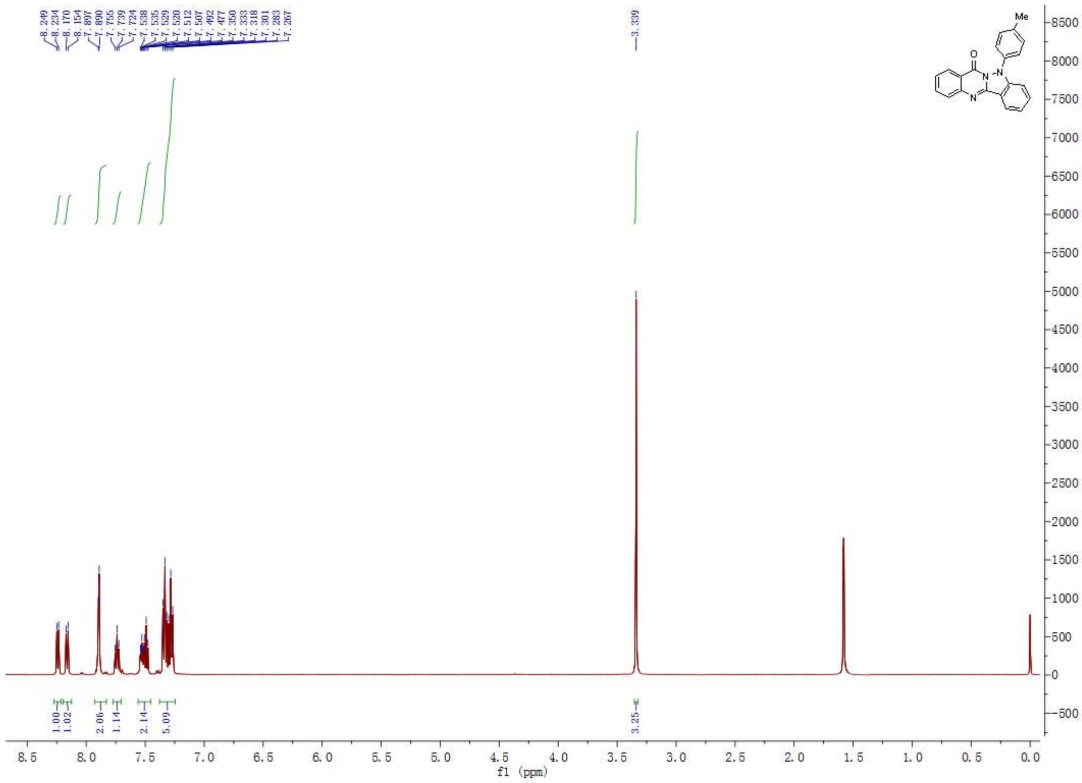


Figure S1. ^{1}H NMR of **2a** (500 MHz, $CDCl_3$) and ^{13}C NMR of **2a** (125 MHz, $CDCl_3$).



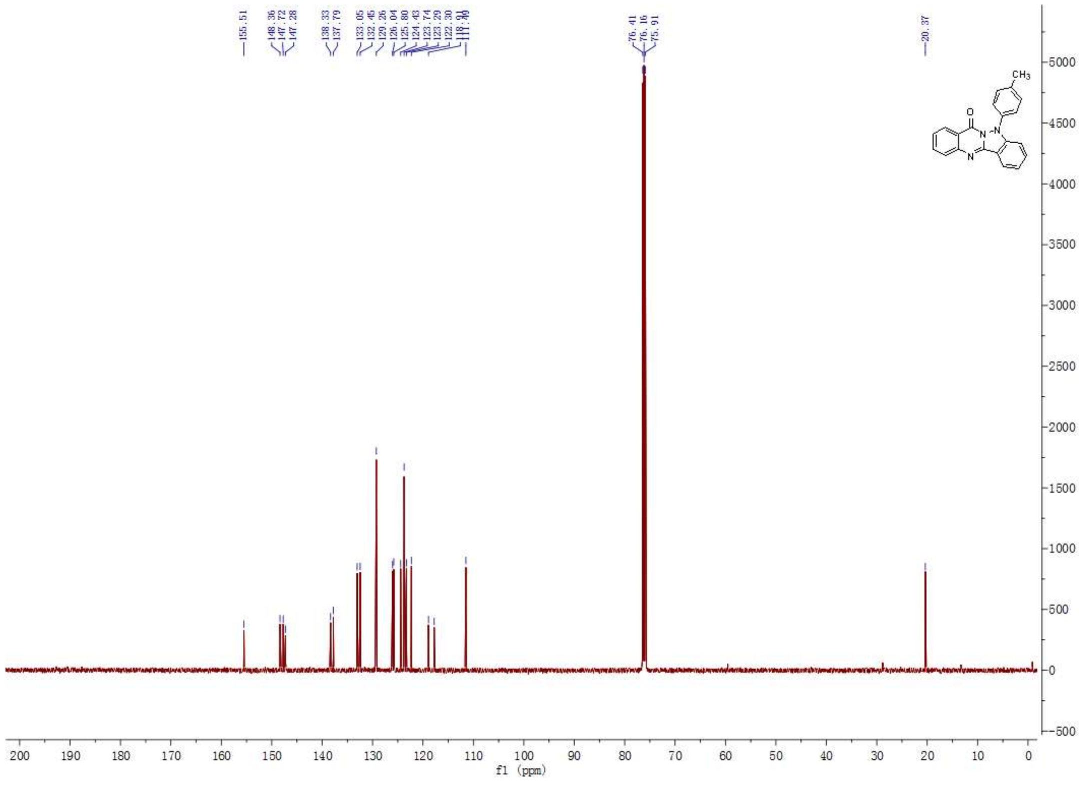
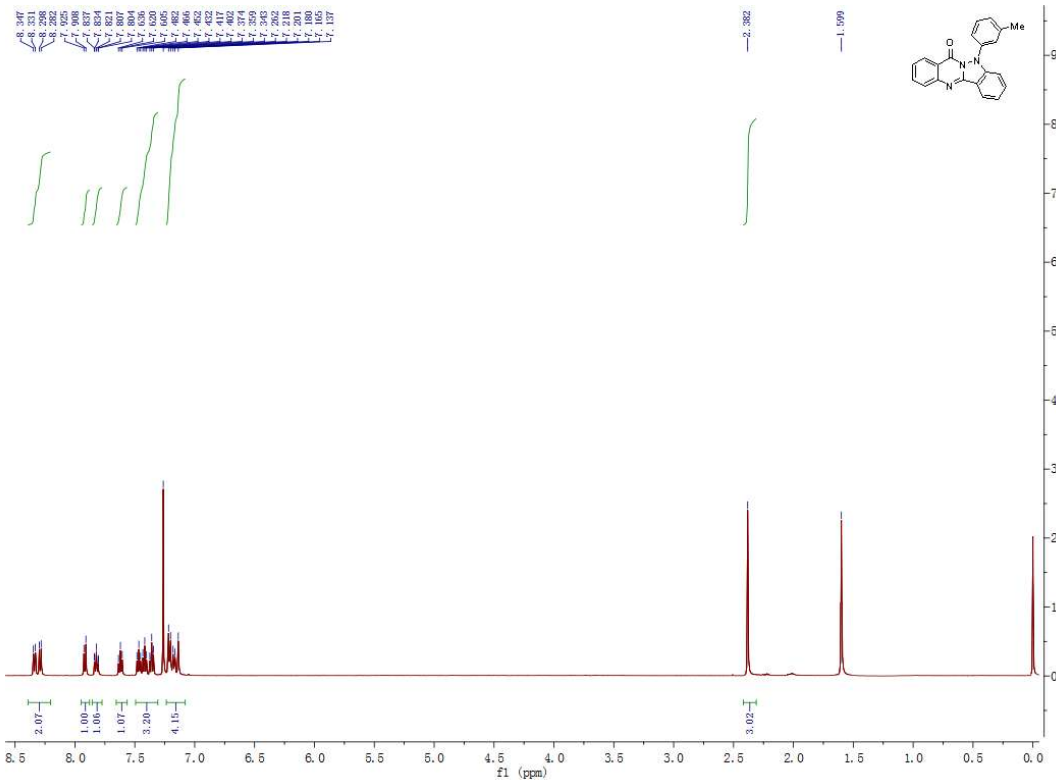


Figure S2. ^{1}H NMR of **2b** (500 MHz, DMSO-d_6) and ^{13}C NMR of **2b** (125 MHz, $CDCl_3$).



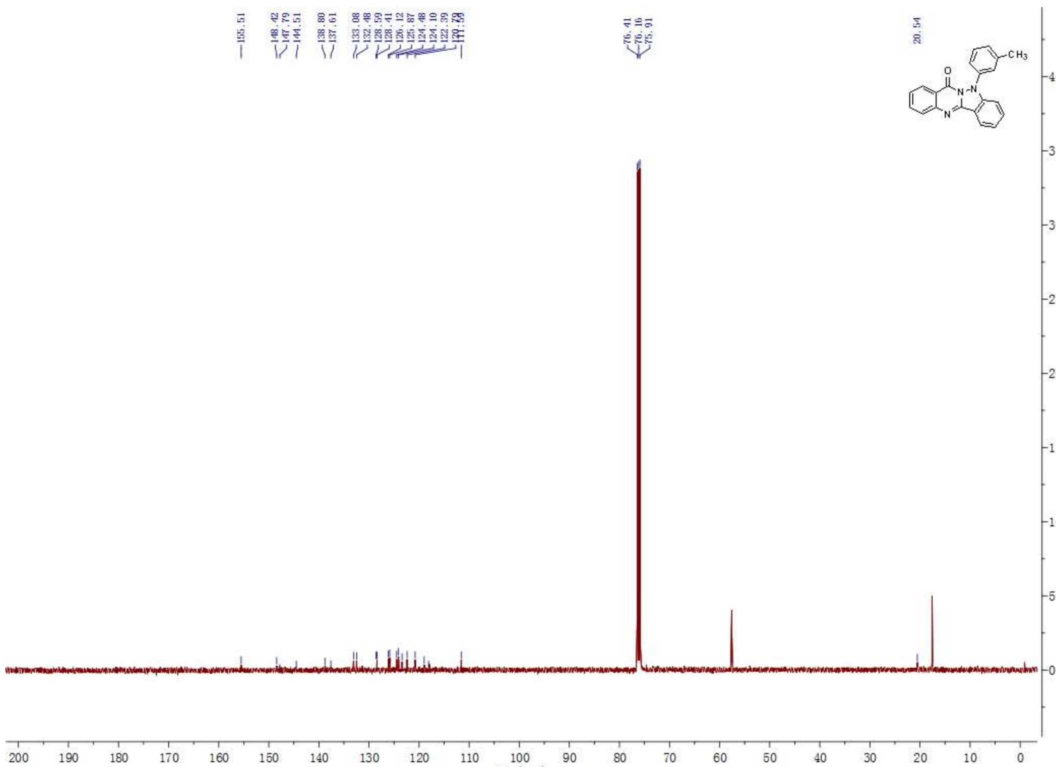
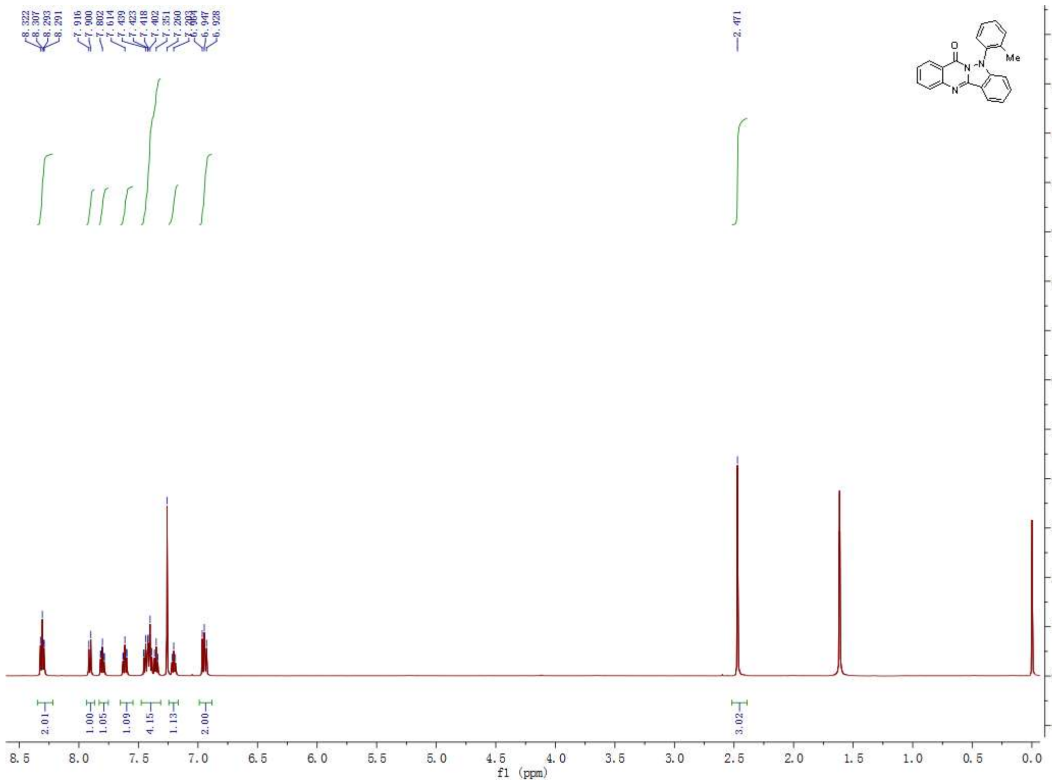


Figure S3. ^{1}H NMR of **2c** (500 MHz, $CDCl_3$) and ^{13}C NMR of **2c** (125 MHz, $CDCl_3$).



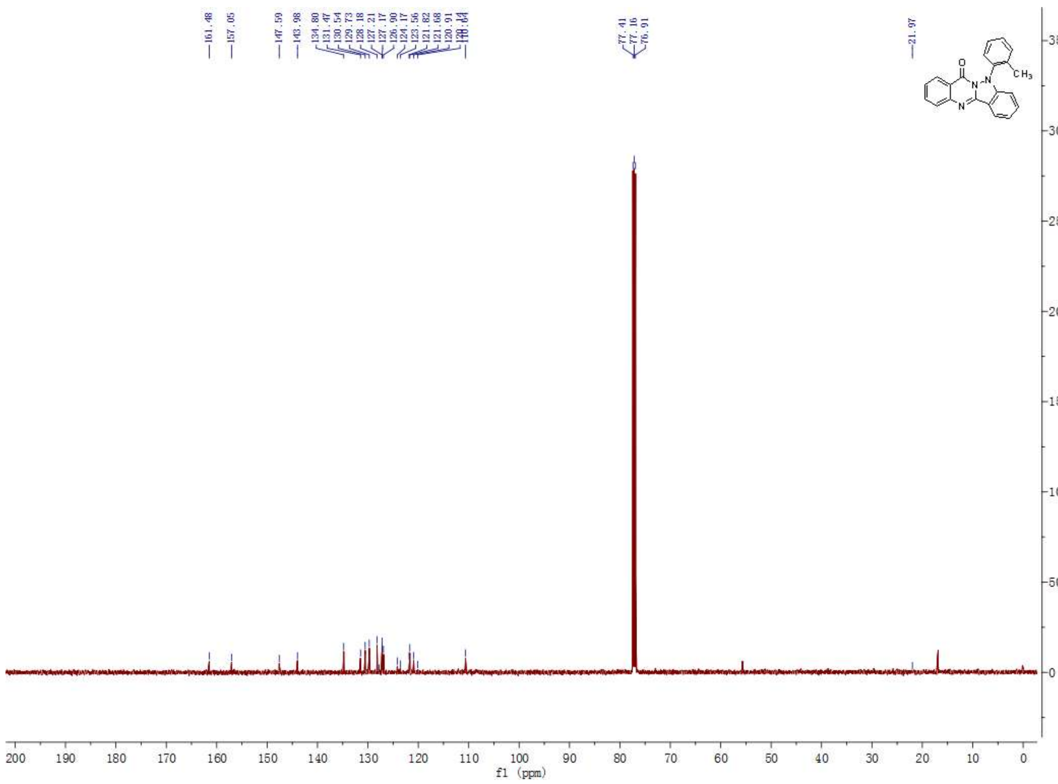
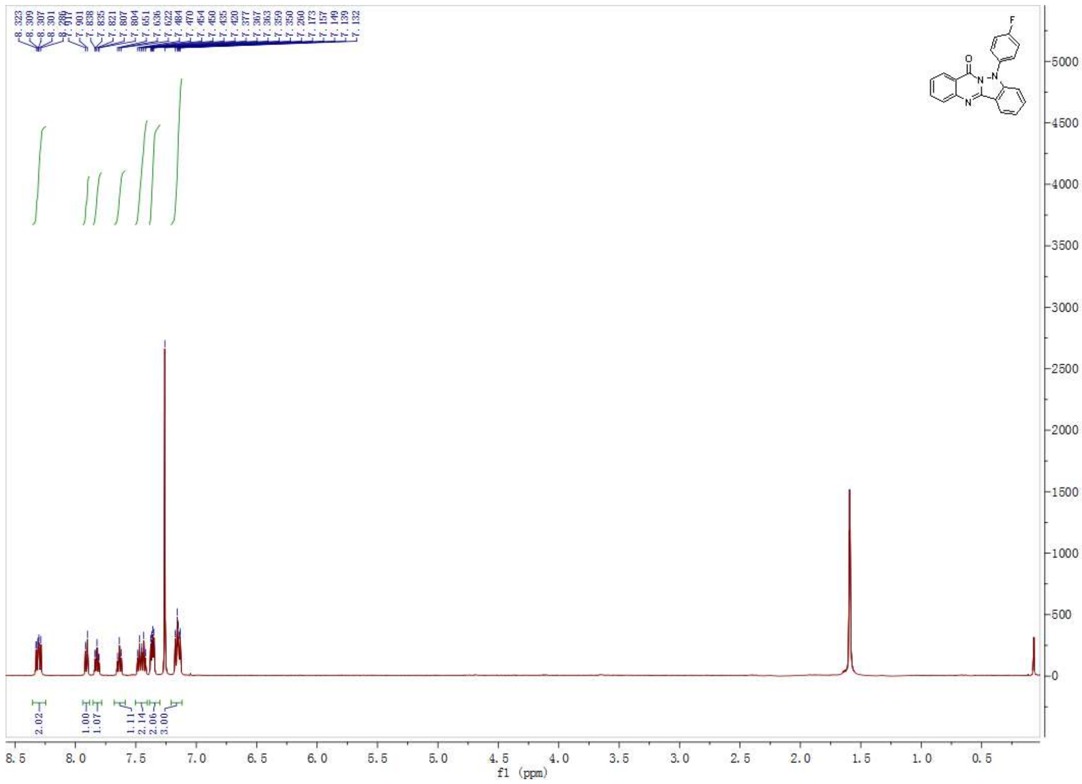


Figure S4. ^{1}H NMR of **2d** (500 MHz, $CDCl_3$) and ^{13}C NMR of **2d** (125 MHz, $CDCl_3$).



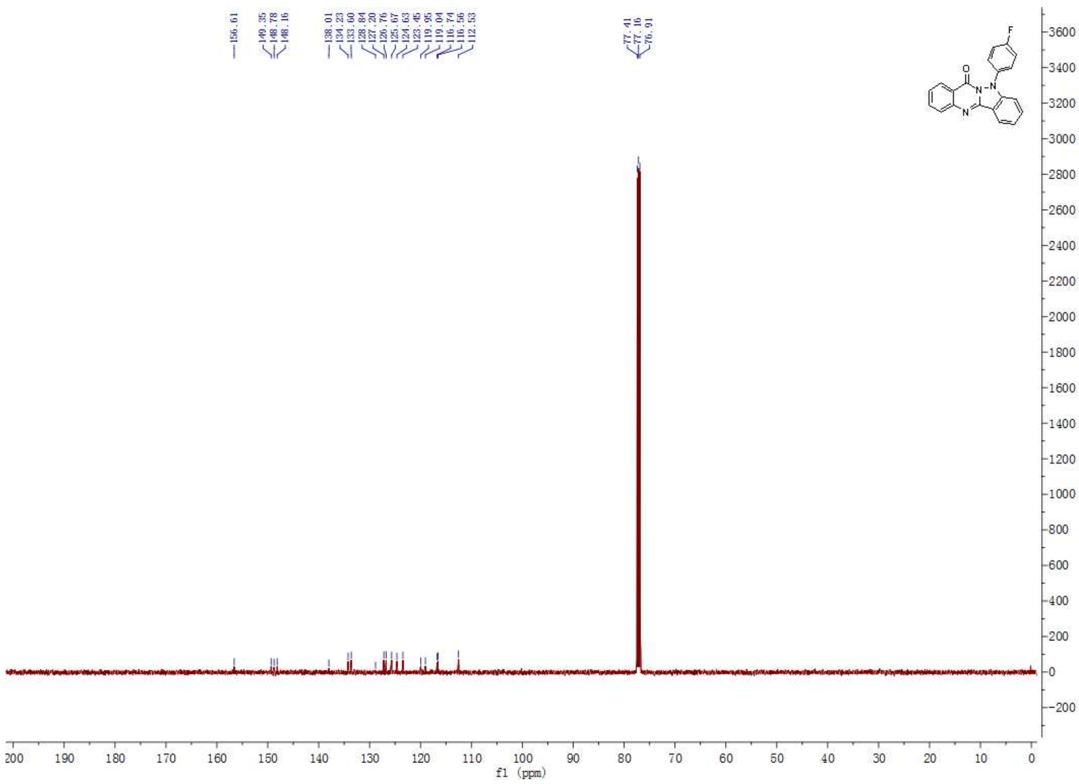
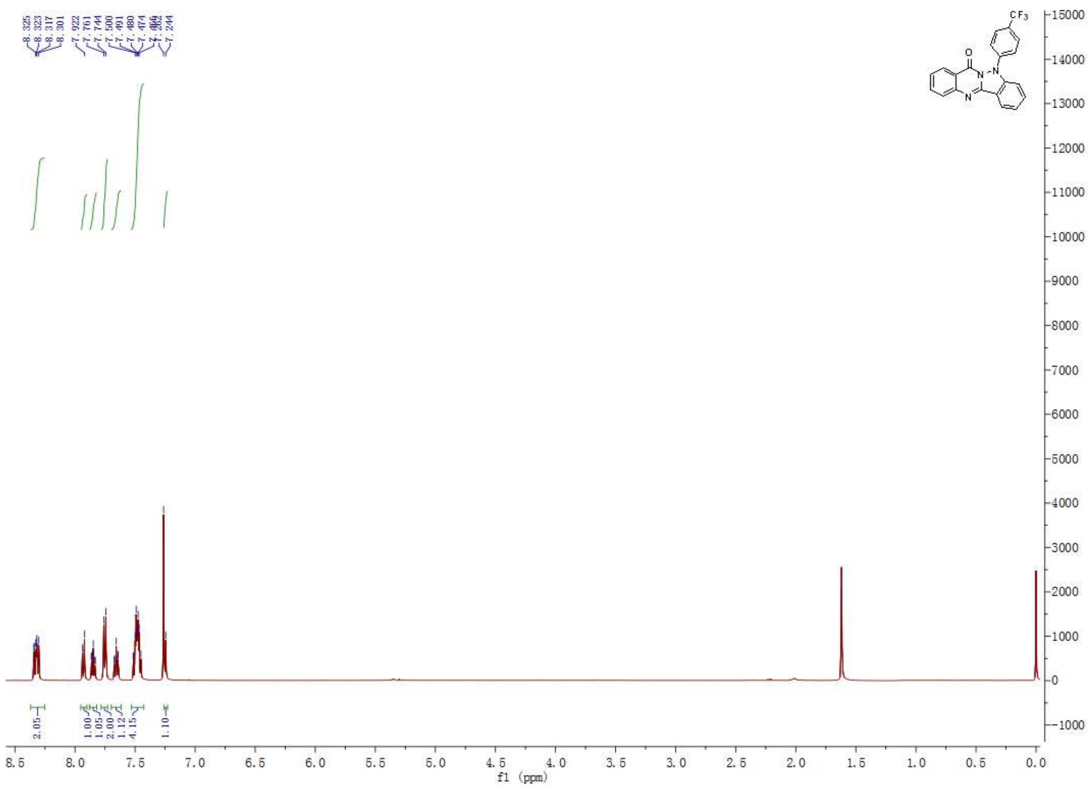


Figure S5. ^{1}H NMR of **2e**(500 MHz, $CDCl_3$) and ^{13}C NMR of **2e** (125 MHz, $CDCl_3$).



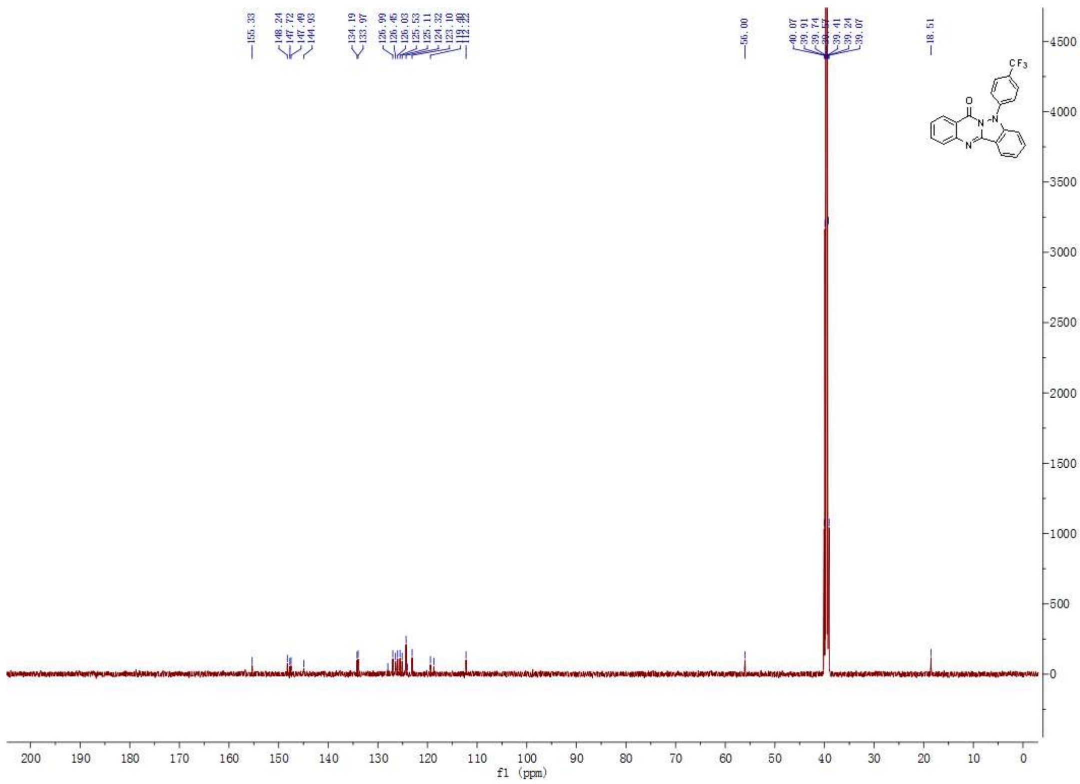
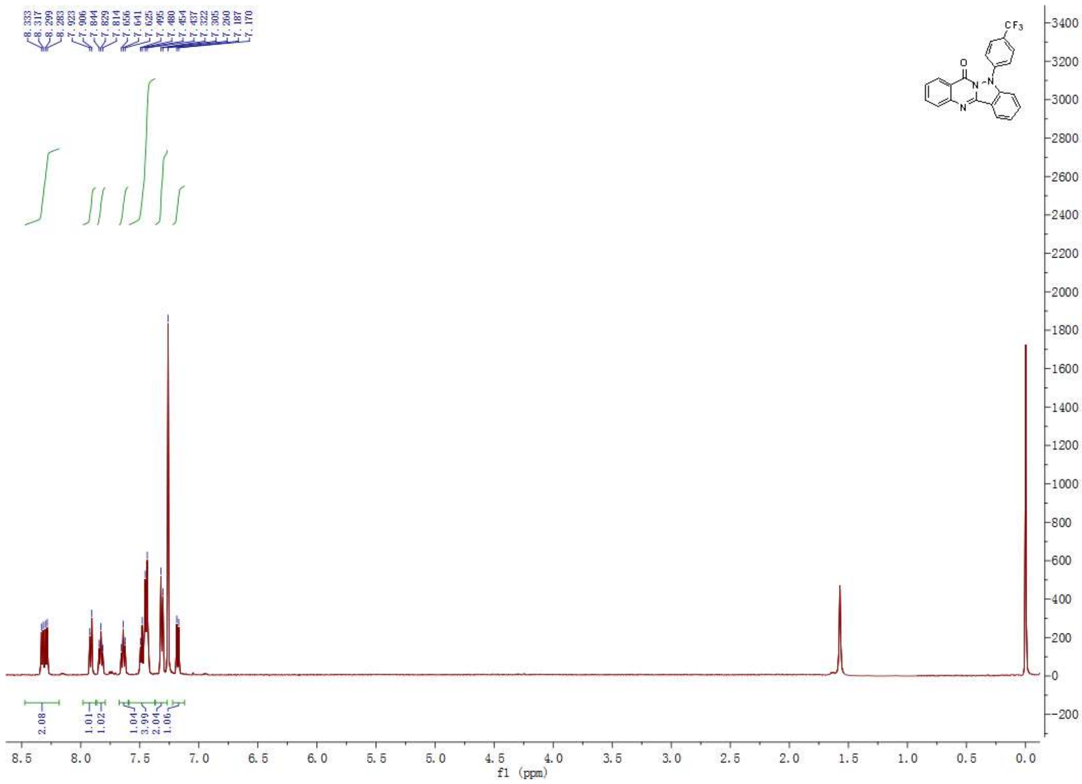


Figure S6. ^{1}H NMR of **2f** (500 MHz, DMSO-d_6) and ^{13}C NMR of **2f** (125 MHz, DMSO-d_6).



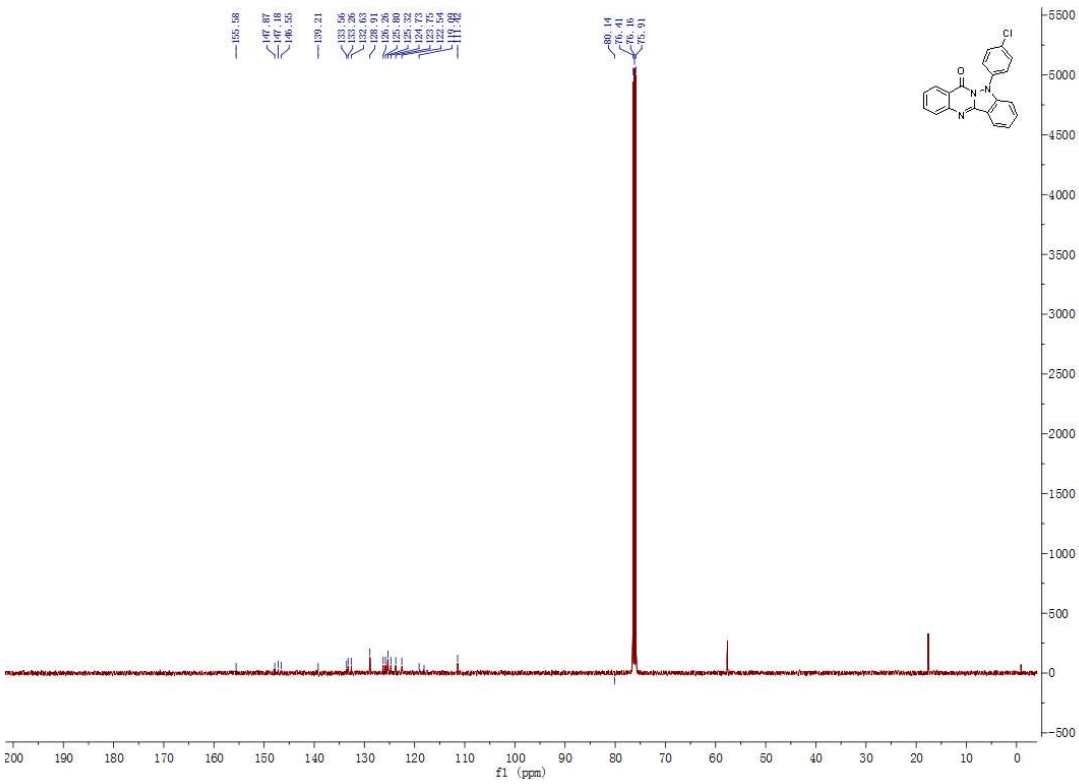
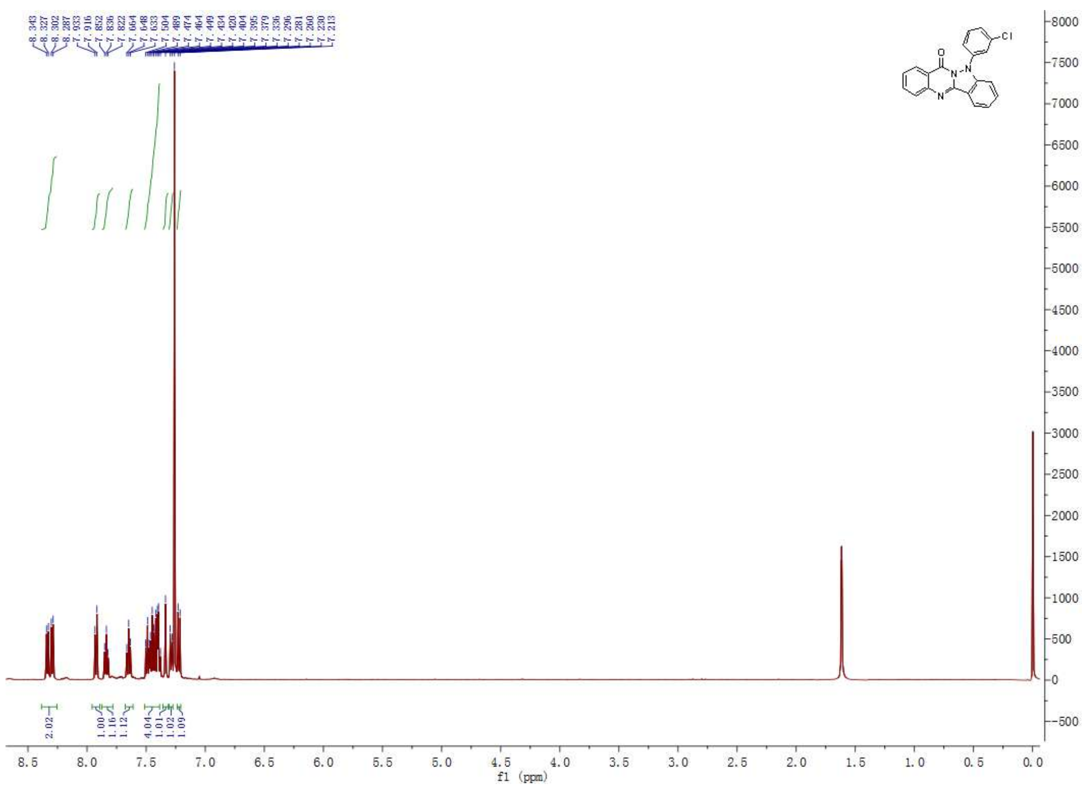


Figure S7. ^1H NMR of **2g**(500 MHz, $CDCl_3$) and ^{13}C NMR of **2g**(125 MHz, $CDCl_3$).



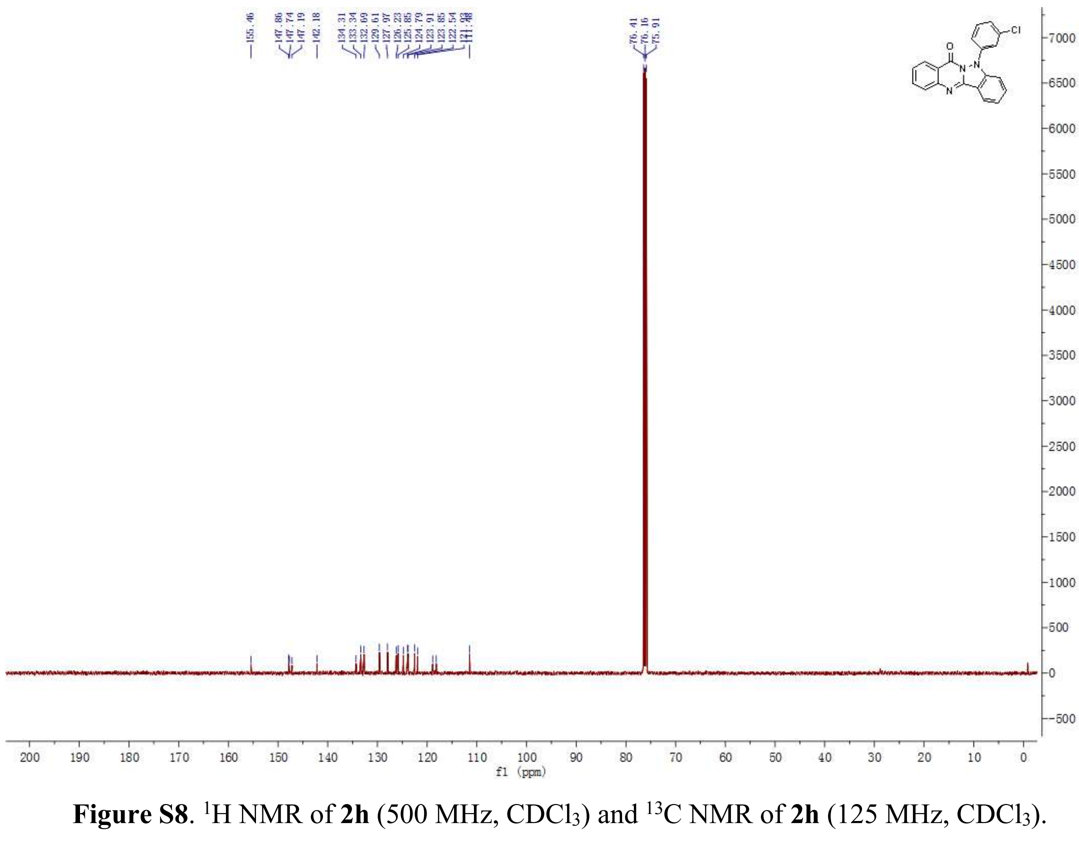
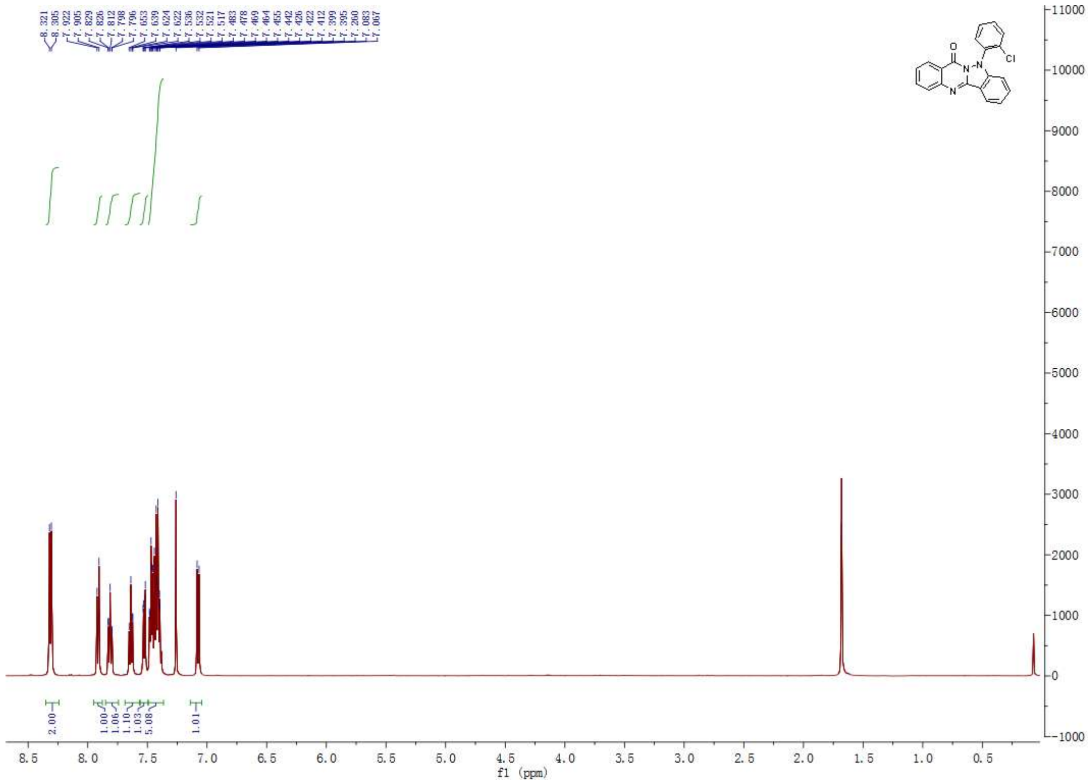


Figure S8. ^{1}H NMR of **2h** (500 MHz, $CDCl_3$) and ^{13}C NMR of **2h** (125 MHz, $CDCl_3$).



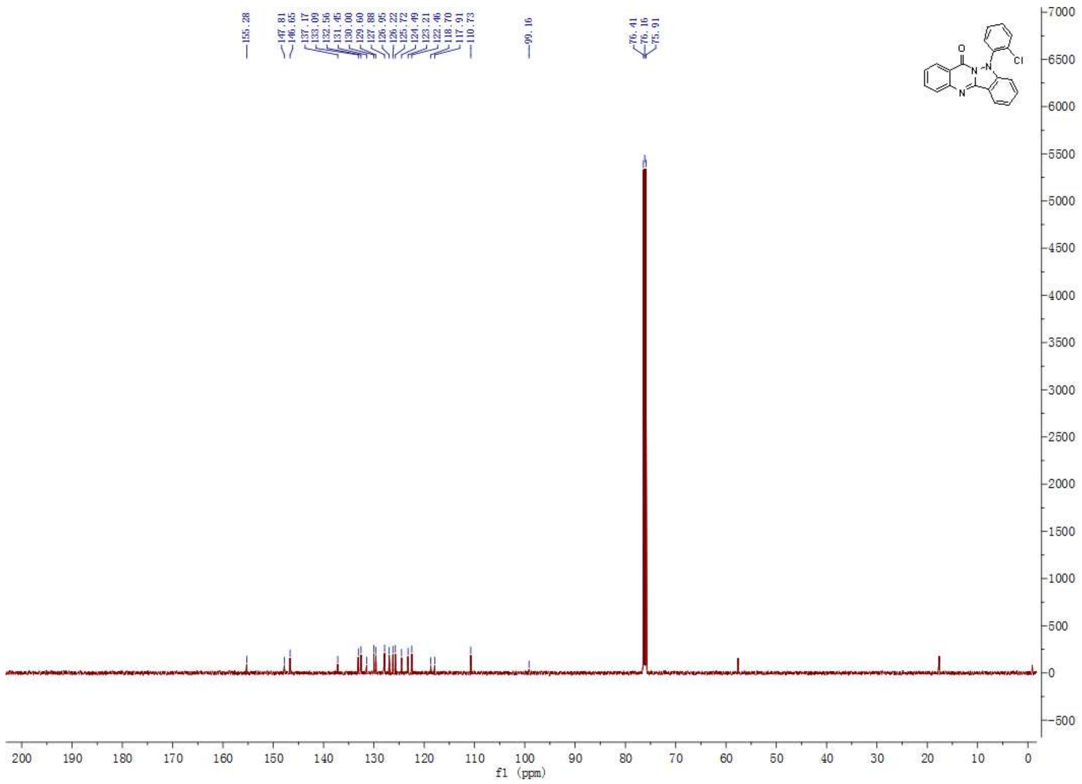
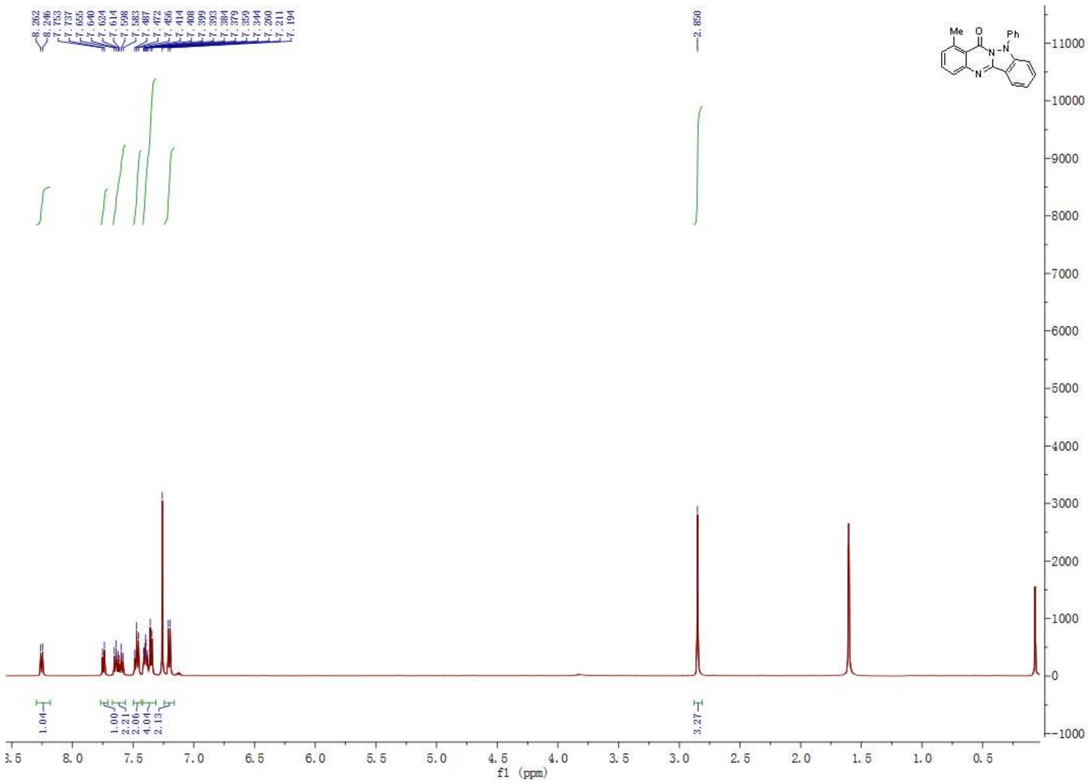


Figure S9. [1]H NMR of **2i** (500 MHz, $CDCl_3$) and [13]C NMR of **2i**(125 MHz, $CDCl_3$).



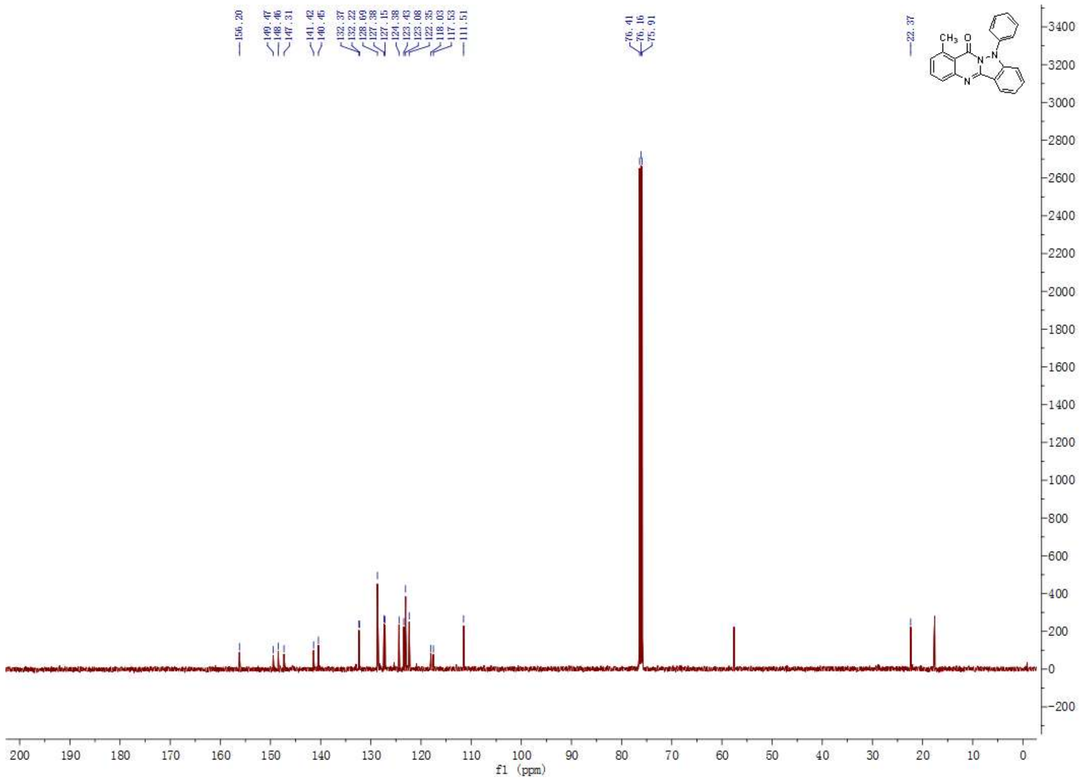
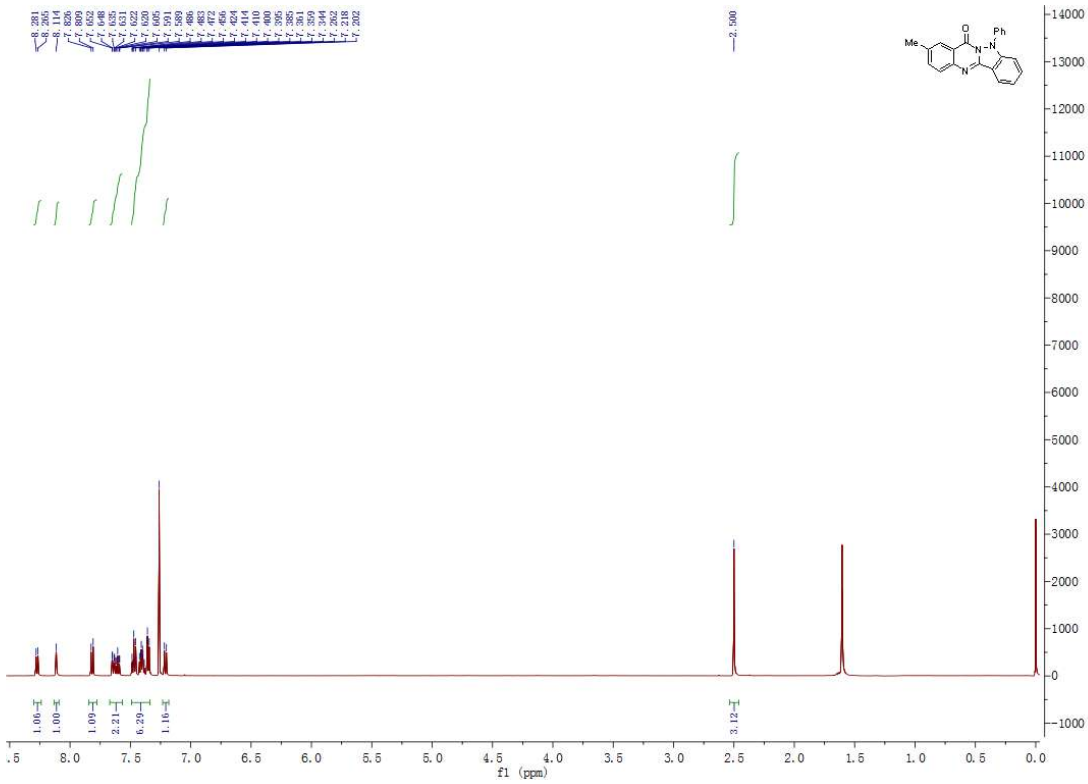


Figure S10. ^{1}H NMR of **2j** (500 MHz, $CDCl_3$) and ^{13}C NMR of **2j** (125 MHz, $CDCl_3$).



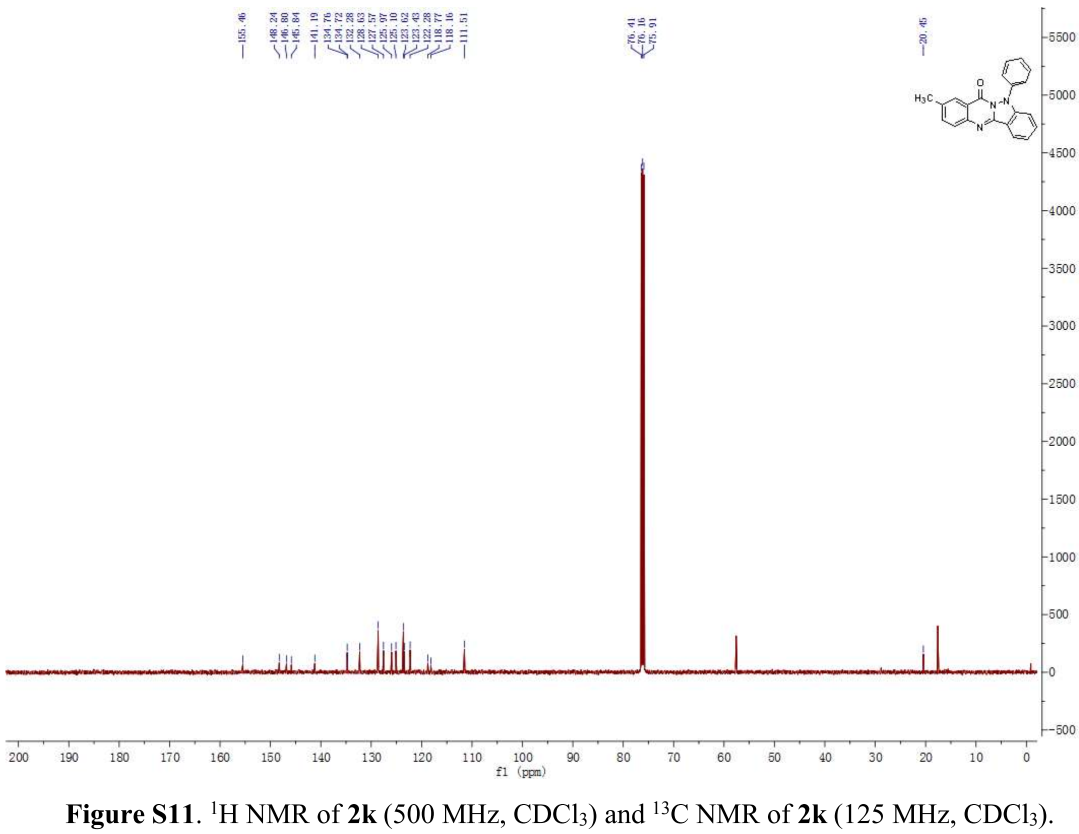
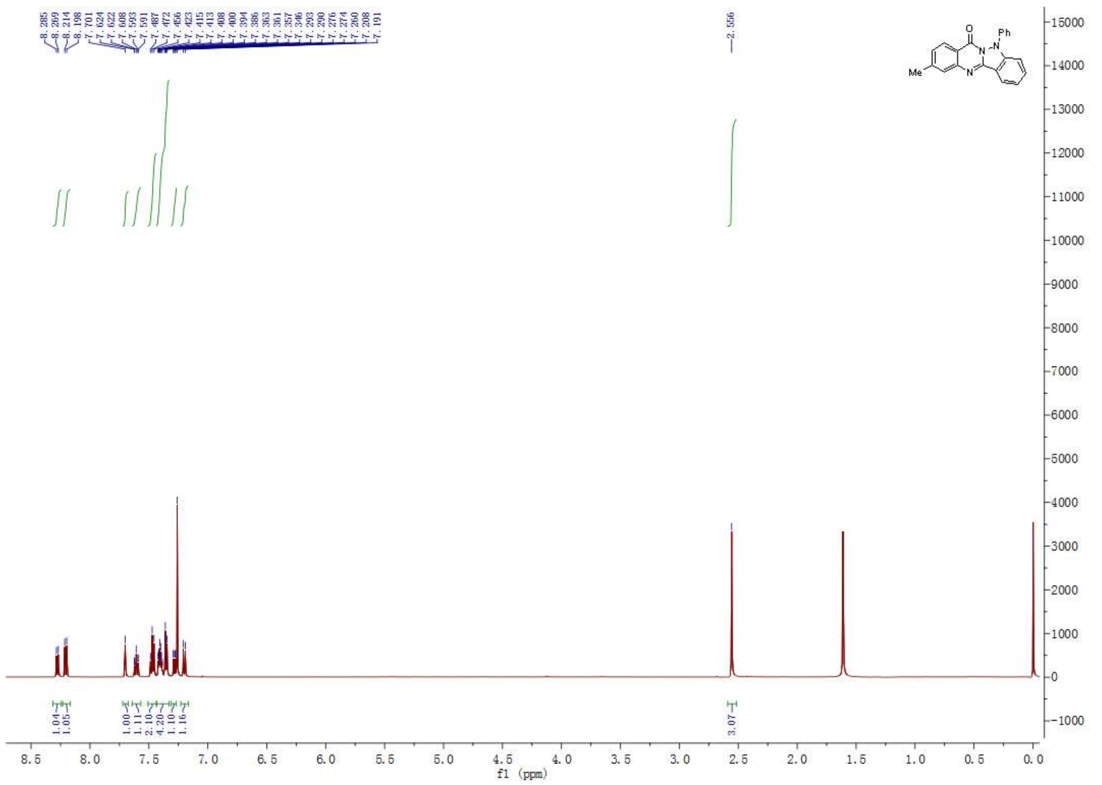


Figure S11. ^{1}H NMR of **2k** (500 MHz, $CDCl_3$) and ^{13}C NMR of **2k** (125 MHz, $CDCl_3$).



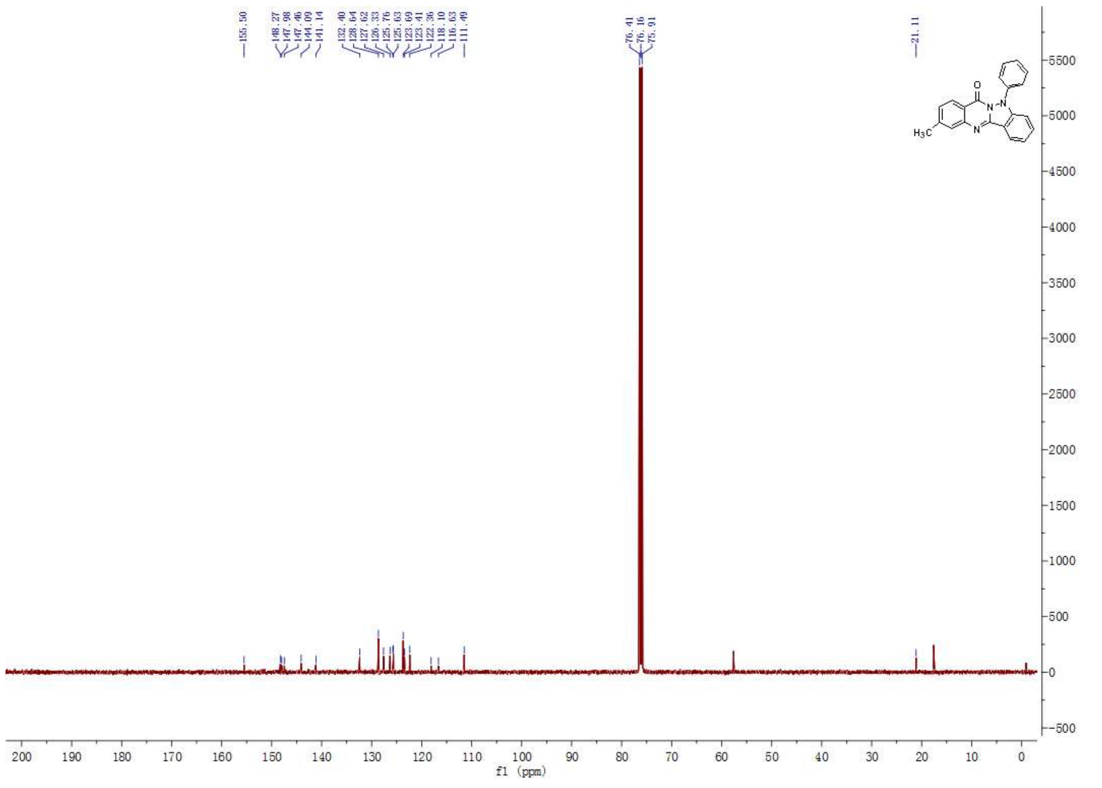
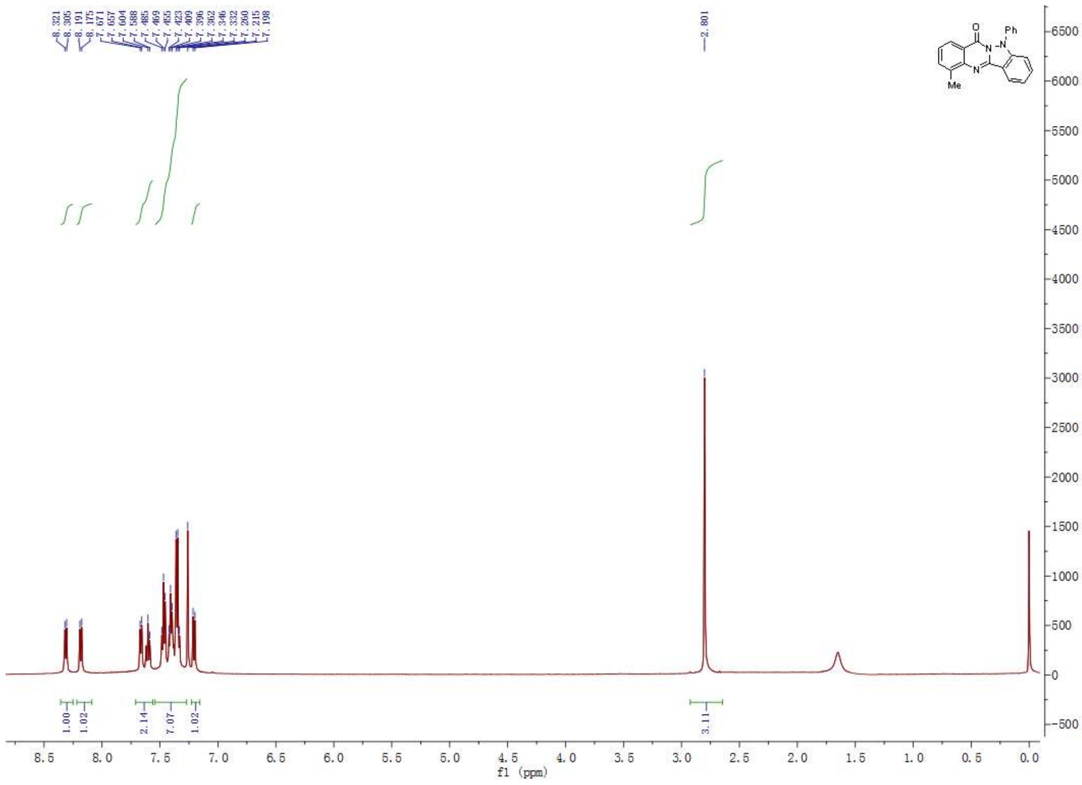


Figure S12. ^{1}H NMR of **2l** (500 MHz, $CDCl_3$) and ^{13}C NMR of **2l** (125 MHz, $CDCl_3$).



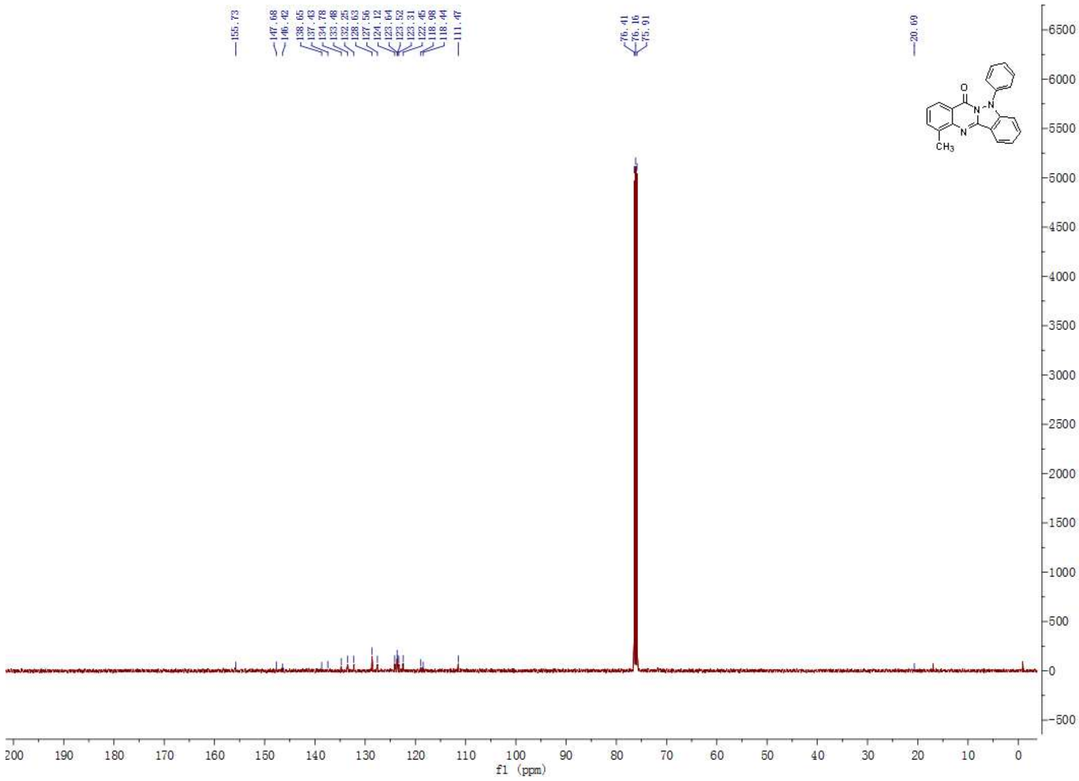
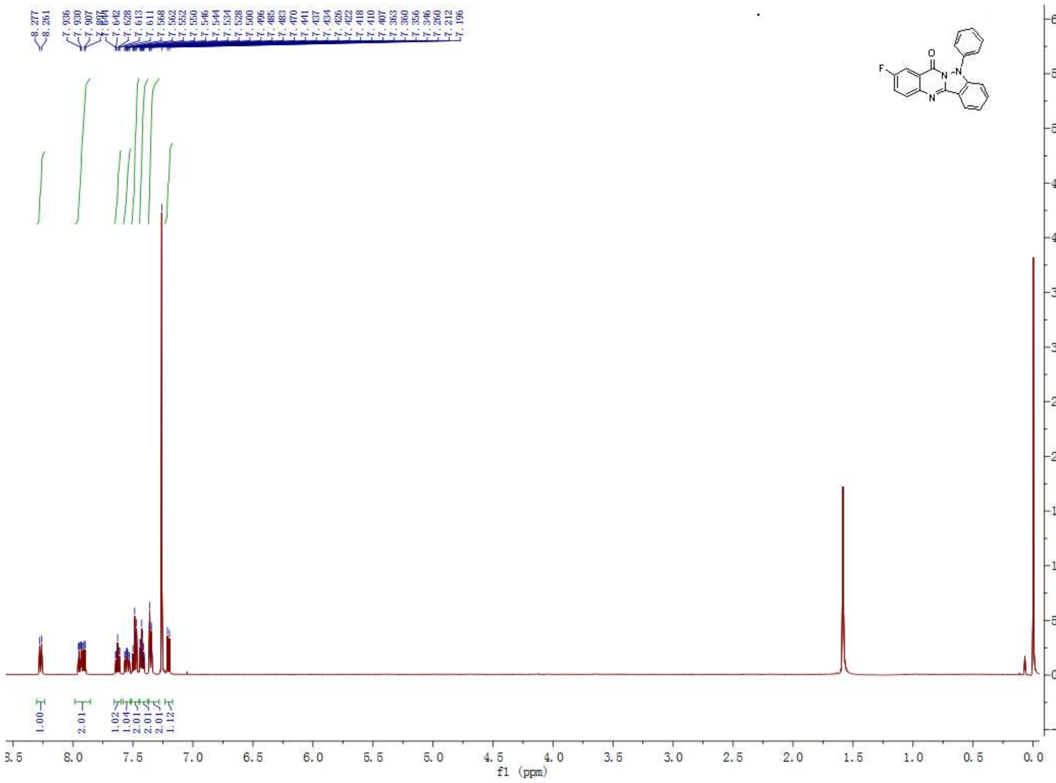


Figure S13 ^{1}H NMR of 2m (500 MHz, $CDCl_3$) and ^{13}C NMR of 2m (125 MHz, $CDCl_3$)..



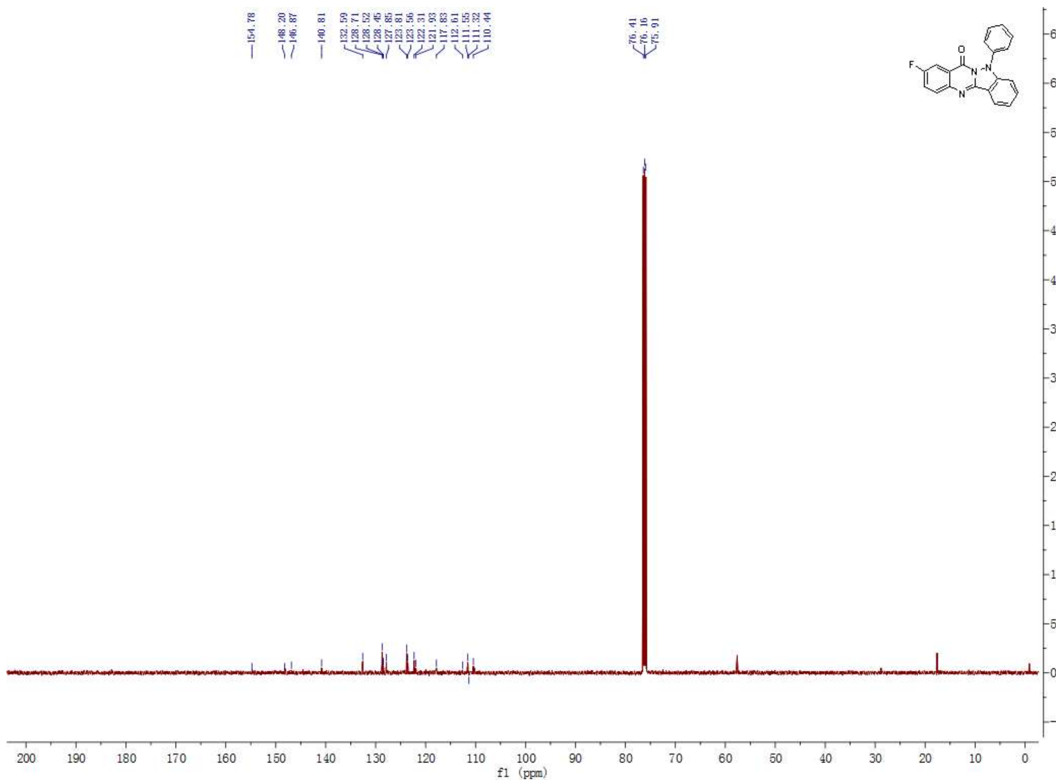
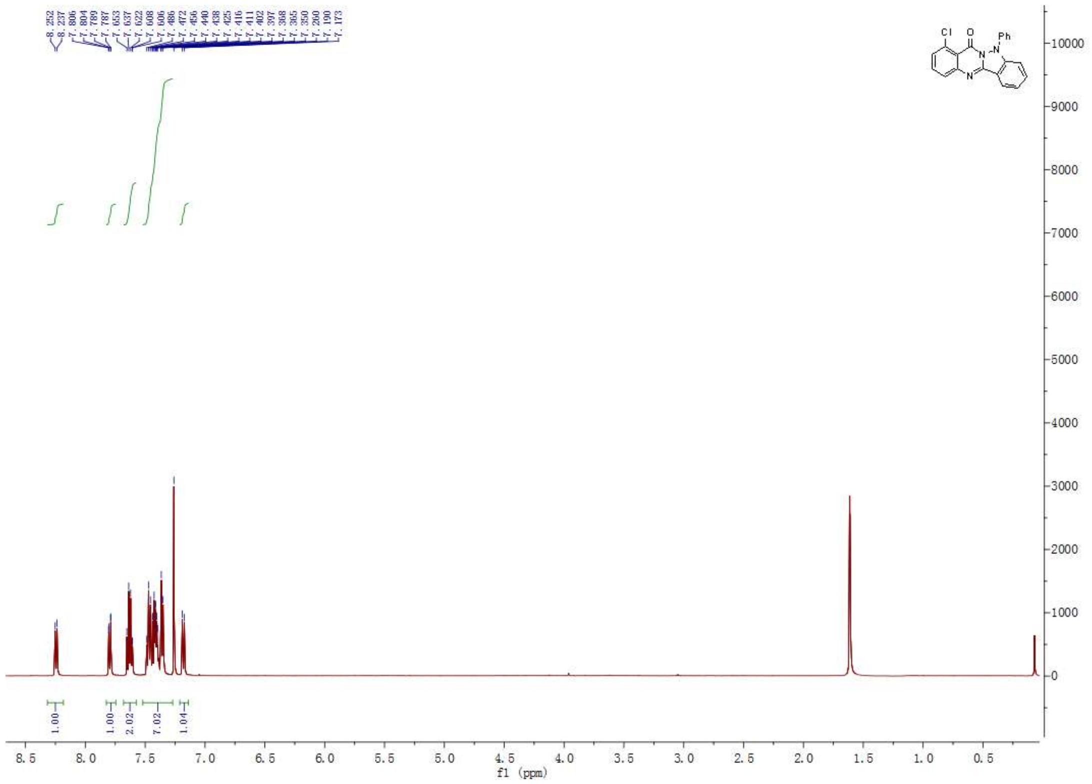


Figure S14. ^{1}H NMR of **2n** (500 MHz, $CDCl_3$) and ^{13}C NMR of **2n** (125 MHz, $CDCl_3$).



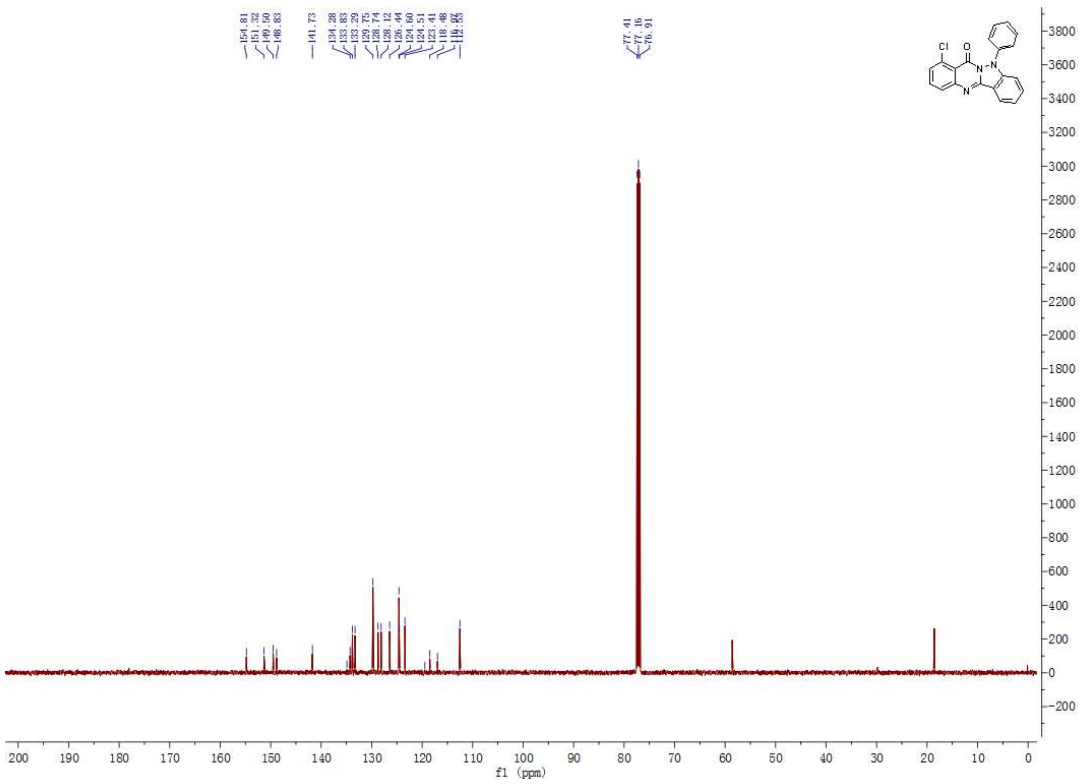
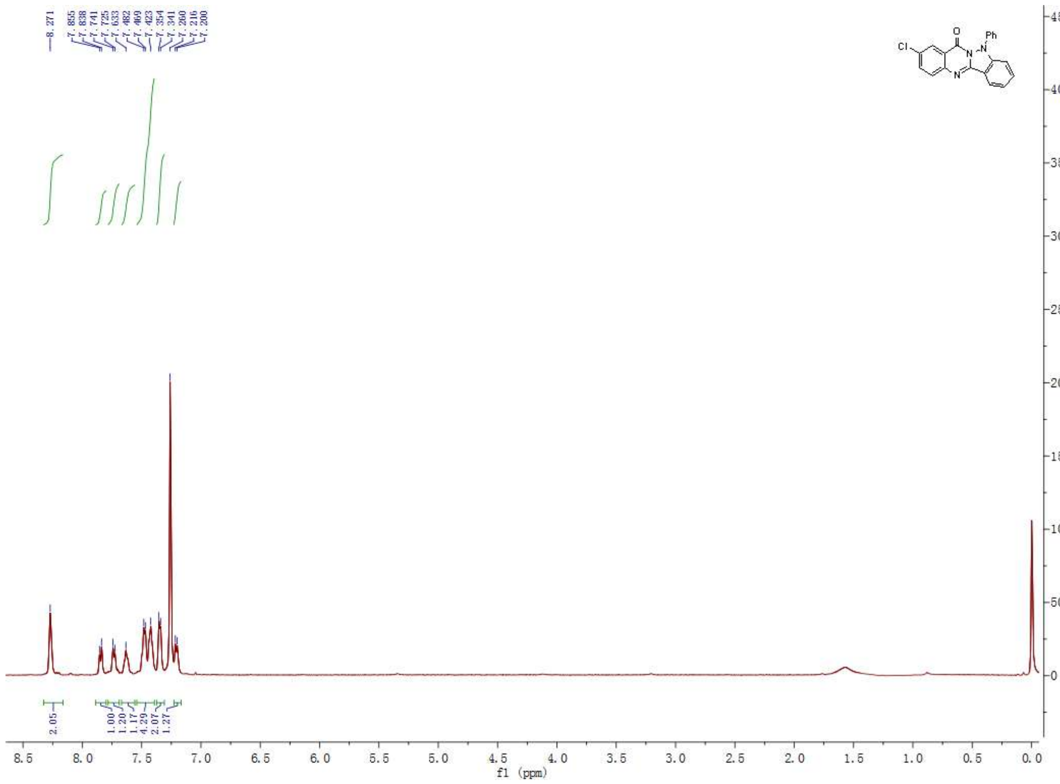


Figure S15. ^{1}H NMR of **2o** (500 MHz, $CDCl_3$) and ^{13}C NMR of **2o** (125 MHz, $CDCl_3$).



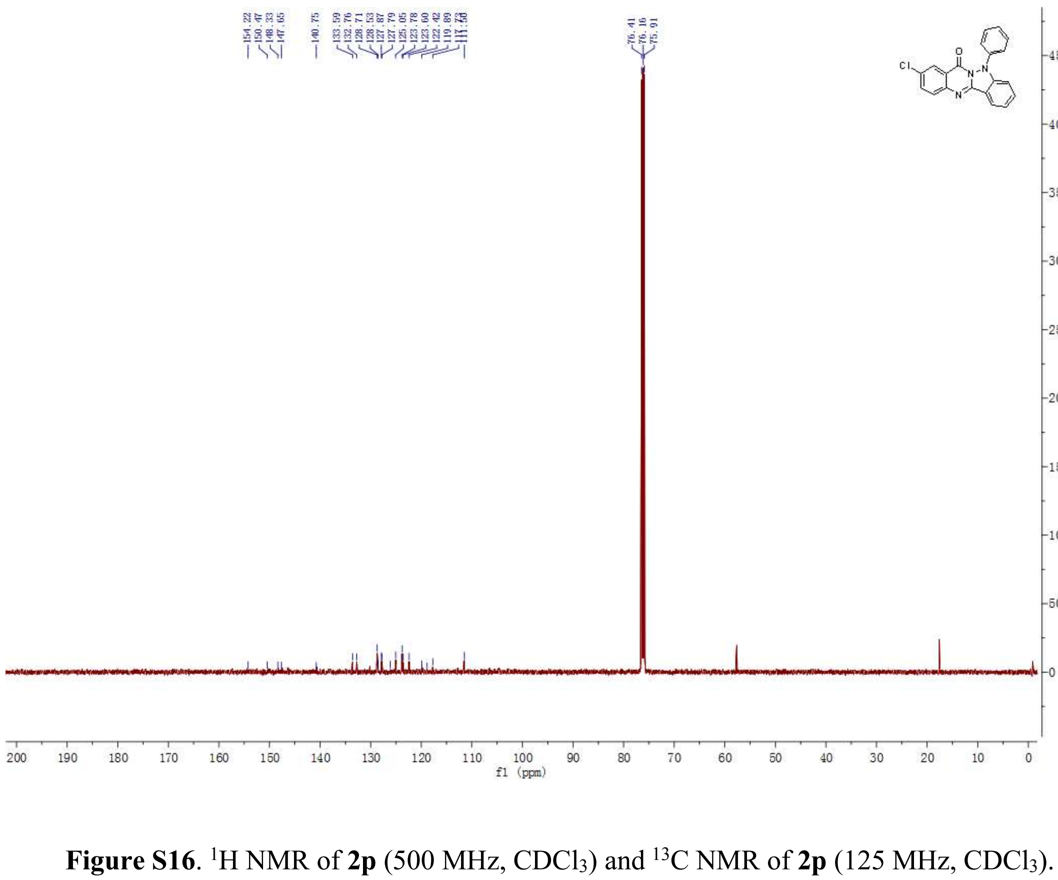
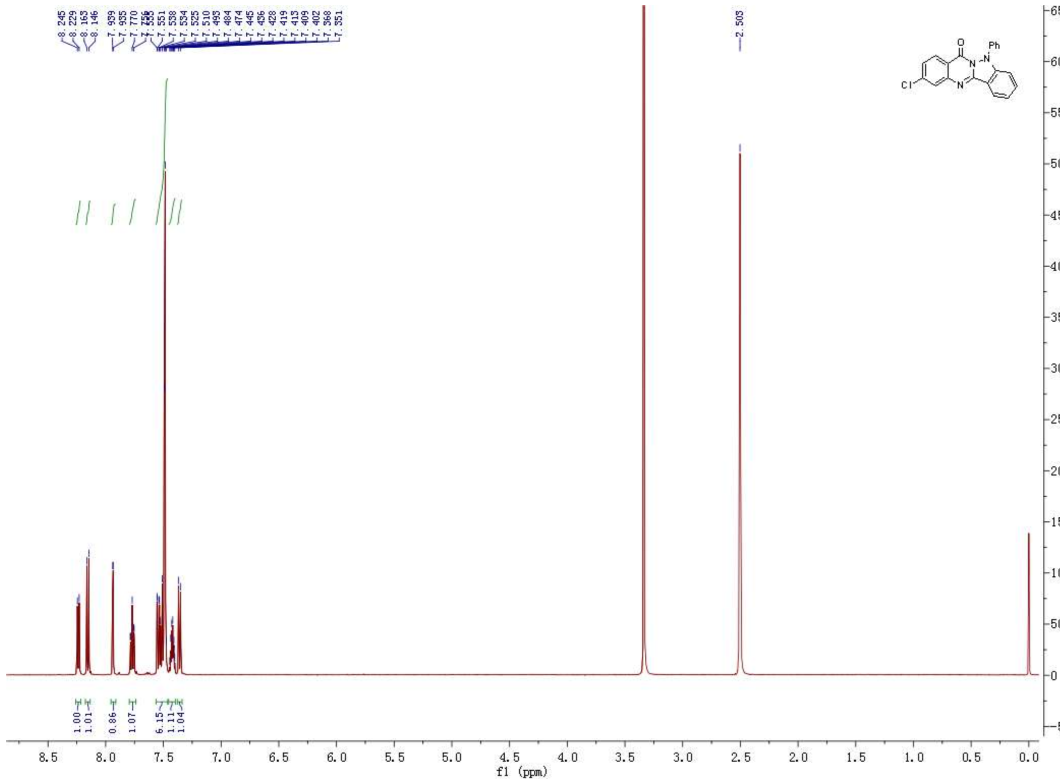


Figure S16. [1]H NMR of **2p** (500 MHz, $CDCl_3$) and [13]C NMR of **2p** (125 MHz, $CDCl_3$).



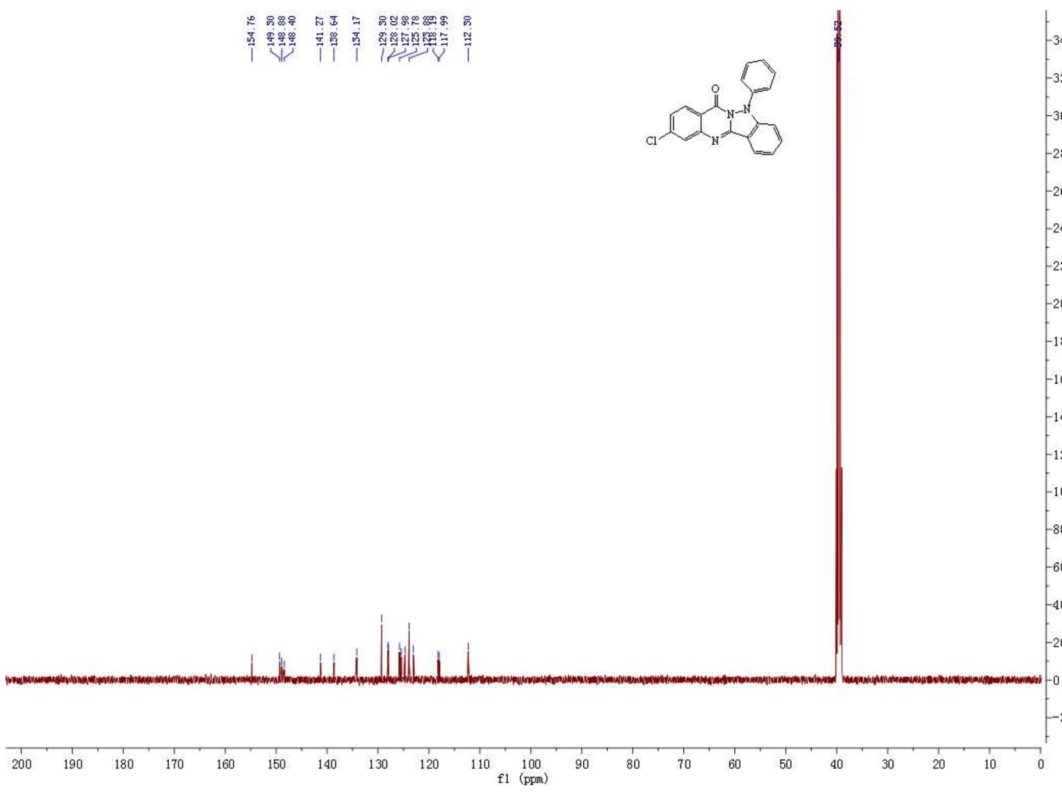


Figure S17. ^{1}H NMR of **2q** (500 MHz, $CDCl_3$) and ^{13}C NMR of **2q** (125 MHz, DMSO-d_6).

2. X-ray Crystallographic Data for Product 2a

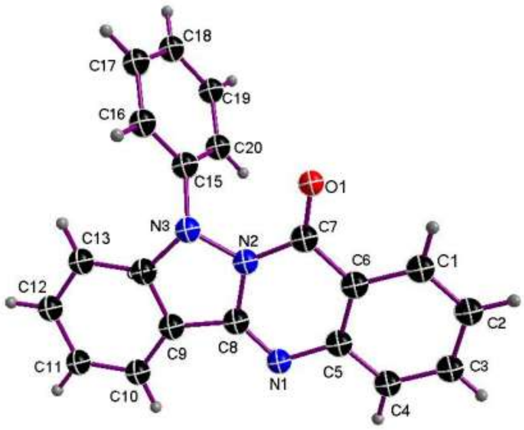


Figure S18 X-ray crystal structure of **2a**.

Table 1. Crystal data and structure refinement for 1.

Identification code	1
Empirical formula	C20 H13 N3 O
Formula weight	311.33
Temperature	100(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, P 21/c
Unit cell dimensions	a = 10.5528(10) A alpha = 90 deg.
	b = 18.8340(17) A beta = 110.027(2) deg.
	c = 8.0510(8) A gamma = 90 deg.
Volume	1503.4(2) A^3
Z, Calculated density	4, 1.376 Mg/m^3
Absorption coefficient	0.088 mm^-1
F(000)	648
Crystal size	0.31 x 0.25 x 0.22 mm
Theta range for data collection	2.05 to 25.99 deg.
Limiting indices	-13<=h<=13, -23<=k<=23, -9<=l<=9
Reflections collected / unique	11852 / 2942 [R(int) = 0.0208]
Completeness to theta = 25.99	99.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9810 and 0.9733
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2942 / 0 / 217
Goodness-of-fit on F^2	1.054
Final R indices [I>2sigma(I)]	R1 = 0.0349, wR2 = 0.0969
R indices (all data)	R1 = 0.0389, wR2 = 0.0996
Largest diff. peak and hole	0.198 and -0.270 e.A^-3

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic

displacement parameters (A^2 x 10^3) for 1.
U(eq) is defined as one third of the trace of the orthogonalized
Uij tensor.

	x	y	z	U(eq)
O(1)	4668(1)	3016(1)	6847(1)	24(1)
N(1)	1723(1)	2149(1)	8543(1)	21(1)
N(2)	3687(1)	2073(1)	7726(1)	19(1)
N(3)	4435(1)	1541(1)	7244(1)	21(1)
C(1)	2813(1)	3951(1)	7688(2)	26(1)
C(2)	1888(1)	4362(1)	8108(2)	30(1)
C(3)	935(1)	4037(1)	8714(2)	29(1)
C(4)	896(1)	3312(1)	8868(2)	25(1)
C(5)	1826(1)	2879(1)	8427(2)	21(1)
C(6)	2807(1)	3209(1)	7867(2)	20(1)
C(7)	3807(1)	2792(1)	7414(2)	20(1)
C(8)	2641(1)	1782(1)	8187(1)	19(1)
C(9)	2794(1)	1023(1)	8120(2)	21(1)
C(10)	2066(1)	459(1)	8476(2)	26(1)
C(11)	2505(1)	-224(1)	8340(2)	29(1)
C(12)	3638(1)	-343(1)	7849(2)	29(1)
C(13)	4348(1)	212(1)	7456(2)	25(1)
C(14)	3902(1)	898(1)	7597(2)	21(1)
C(15)	5878(1)	1625(1)	7762(2)	22(1)
C(16)	6486(1)	1363(1)	6611(2)	30(1)
C(17)	7881(2)	1392(1)	7102(2)	38(1)
C(18)	8650(1)	1692(1)	8697(2)	37(1)
C(19)	8021(1)	1971(1)	9809(2)	31(1)
C(20)	6629(1)	1935(1)	9358(2)	24(1)

Table 3. Bond lengths [A] and angles [deg] for 1.

O(1)-C(7)	1.2234(14)
N(1)-C(8)	1.2983(15)
N(1)-C(5)	1.3864(16)
N(2)-C(7)	1.3912(15)
N(2)-C(8)	1.3913(14)

N(2)-N(3)	1.4096(13)
N(3)-C(14)	1.4040(15)
N(3)-C(15)	1.4430(15)
C(1)-C(2)	1.3766(18)
C(1)-C(6)	1.4043(17)
C(1)-H(1)	0.9300
C(2)-C(3)	1.4002(19)
C(2)-H(2)	0.9300
C(3)-C(4)	1.3738(18)
C(3)-H(3)	0.9300
C(4)-C(5)	1.4103(16)
C(4)-H(4)	0.9300
C(5)-C(6)	1.4080(16)
C(6)-C(7)	1.4588(16)
C(8)-C(9)	1.4416(16)
C(9)-C(14)	1.3925(16)
C(9)-C(10)	1.3980(16)
C(10)-C(11)	1.3830(18)
C(10)-H(10)	0.9300
C(11)-C(12)	1.3995(19)
C(11)-H(11)	0.9300
C(12)-C(13)	1.3846(18)
C(12)-H(12)	0.9300
C(13)-C(14)	1.3936(16)
C(13)-H(13)	0.9300
C(15)-C(20)	1.3865(18)
C(15)-C(16)	1.3867(17)
C(16)-C(17)	1.388(2)
C(16)-H(16)	0.9300

C(17)-C(18)	1.383(2)
C(17)-H(17)	0.9300
C(18)-C(19)	1.388(2)
C(18)-H(18)	0.9300
C(19)-C(20)	1.3890(17)
C(19)-H(19)	0.9300
C(20)-H(20)	0.9300
C(8)-N(1)-C(5)	115.55(10)
C(7)-N(2)-C(8)	124.12(9)
C(7)-N(2)-N(3)	123.18(9)
C(8)-N(2)-N(3)	111.38(9)
C(14)-N(3)-N(2)	104.84(9)
C(14)-N(3)-C(15)	119.45(9)
N(2)-N(3)-C(15)	118.51(9)
C(2)-C(1)-C(6)	120.42(12)
C(2)-C(1)-H(1)	119.8
C(6)-C(1)-H(1)	119.8
C(1)-C(2)-C(3)	119.57(12)
C(1)-C(2)-H(2)	120.2
C(3)-C(2)-H(2)	120.2
C(4)-C(3)-C(2)	120.93(11)
C(4)-C(3)-H(3)	119.5
C(2)-C(3)-H(3)	119.5
C(3)-C(4)-C(5)	120.43(12)
C(3)-C(4)-H(4)	119.8
C(5)-C(4)-H(4)	119.8
N(1)-C(5)-C(6)	122.86(10)
N(1)-C(5)-C(4)	118.63(10)
C(6)-C(5)-C(4)	118.51(11)

C(1)-C(6)-C(5)	120.10(11)
C(1)-C(6)-C(7)	118.76(11)
C(5)-C(6)-C(7)	121.12(11)
O(1)-C(7)-N(2)	121.95(10)
O(1)-C(7)-C(6)	126.90(11)
N(2)-C(7)-C(6)	111.15(10)
N(1)-C(8)-N(2)	124.74(11)
N(1)-C(8)-C(9)	129.54(10)
N(2)-C(8)-C(9)	105.69(9)
C(14)-C(9)-C(10)	120.72(11)
C(14)-C(9)-C(8)	107.20(10)
C(10)-C(9)-C(8)	132.08(11)
C(11)-C(10)-C(9)	117.91(12)
C(11)-C(10)-H(10)	121.0
C(9)-C(10)-H(10)	121.0
C(10)-C(11)-C(12)	120.92(12)
C(10)-C(11)-H(11)	119.5
C(12)-C(11)-H(11)	119.5
C(13)-C(12)-C(11)	121.61(12)
C(13)-C(12)-H(12)	119.2
C(11)-C(12)-H(12)	119.2
C(12)-C(13)-C(14)	117.27(11)
C(12)-C(13)-H(13)	121.4
C(14)-C(13)-H(13)	121.4
C(9)-C(14)-C(13)	121.55(11)
C(9)-C(14)-N(3)	110.56(10)
C(13)-C(14)-N(3)	127.89(11)
C(20)-C(15)-C(16)	121.38(12)
C(20)-C(15)-N(3)	121.75(10)

C(16)-C(15)-N(3)	116.86(11)
C(15)-C(16)-C(17)	118.94(13)
C(15)-C(16)-H(16)	120.5
C(17)-C(16)-H(16)	120.5
C(18)-C(17)-C(16)	120.56(12)
C(18)-C(17)-H(17)	119.7
C(16)-C(17)-H(17)	119.7
C(17)-C(18)-C(19)	119.71(12)
C(17)-C(18)-H(18)	120.1
C(19)-C(18)-H(18)	120.1
C(18)-C(19)-C(20)	120.62(13)
C(18)-C(19)-H(19)	119.7
C(20)-C(19)-H(19)	119.7
C(15)-C(20)-C(19)	118.75(12)
C(15)-C(20)-H(20)	120.6
C(19)-C(20)-H(20)	120.6

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for 1.

The anisotropic displacement factor exponent takes the form:

-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
O(1)	23(1)	23(1)	29(1)	5(1)	12(1)	-1(1)
N(1)	19(1)	22(1)	23(1)	0(1)	7(1)	-1(1)
N(2)	18(1)	17(1)	21(1)	0(1)	8(1)	1(1)
N(3)	22(1)	17(1)	24(1)	-1(1)	10(1)	2(1)
C(1)	25(1)	22(1)	27(1)	1(1)	5(1)	-1(1)

C(2)	32(1)	20(1)	33(1)	-2(1)	4(1)	4(1)
C(3)	25(1)	29(1)	28(1)	-5(1)	5(1)	8(1)
C(4)	20(1)	30(1)	24(1)	-3(1)	5(1)	2(1)
C(5)	18(1)	22(1)	19(1)	-1(1)	3(1)	1(1)
C(6)	19(1)	21(1)	19(1)	0(1)	3(1)	1(1)
C(7)	19(1)	19(1)	19(1)	2(1)	4(1)	-1(1)
C(8)	18(1)	21(1)	18(1)	0(1)	4(1)	-2(1)
C(9)	20(1)	20(1)	20(1)	0(1)	4(1)	-2(1)
C(10)	22(1)	24(1)	28(1)	2(1)	6(1)	-5(1)
C(11)	29(1)	21(1)	32(1)	2(1)	5(1)	-7(1)
C(12)	33(1)	18(1)	31(1)	-1(1)	4(1)	1(1)
C(13)	26(1)	22(1)	27(1)	-2(1)	7(1)	2(1)
C(14)	21(1)	20(1)	19(1)	0(1)	4(1)	-2(1)
C(15)	22(1)	17(1)	30(1)	5(1)	13(1)	3(1)
C(16)	38(1)	22(1)	38(1)	0(1)	24(1)	1(1)
C(17)	42(1)	22(1)	66(1)	3(1)	40(1)	4(1)
C(18)	23(1)	21(1)	74(1)	8(1)	25(1)	2(1)
C(19)	23(1)	22(1)	47(1)	5(1)	9(1)	1(1)
C(20)	22(1)	20(1)	30(1)	4(1)	11(1)	3(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for 1.

	x	y	z	U(eq)
H(1)	3447	4165	7283	31
H(2)	1896	4853	7989	36
H(3)	320	4316	9017	34
H(4)	253	3104	9265	30
H(10)	1311	539	8795	31
H(11)	2041	-608	8577	35

H(12)	3920	-807	7785	35
H(13)	5091	130	7112	30
H(16)	5968	1170	5527	36
H(17)	8302	1209	6351	45
H(18)	9584	1706	9023	45
H(19)	8537	2185	10866	38
H(20)	6209	2115	10112	28

Table 6. Torsion angles [deg] for 1.

C(7)-N(2)-N(3)-C(14)	-173.27(10)
C(8)-N(2)-N(3)-C(14)	-5.94(11)
C(7)-N(2)-N(3)-C(15)	50.45(14)
C(8)-N(2)-N(3)-C(15)	-142.22(10)
C(6)-C(1)-C(2)-C(3)	-0.10(18)
C(1)-C(2)-C(3)-C(4)	-1.09(18)
C(2)-C(3)-C(4)-C(5)	0.42(18)
C(8)-N(1)-C(5)-C(6)	3.41(15)
C(8)-N(1)-C(5)-C(4)	-177.37(10)
C(3)-C(4)-C(5)-N(1)	-177.84(11)
C(3)-C(4)-C(5)-C(6)	1.41(17)
C(2)-C(1)-C(6)-C(5)	1.95(17)
C(2)-C(1)-C(6)-C(7)	-179.79(11)
N(1)-C(5)-C(6)-C(1)	176.64(10)
C(4)-C(5)-C(6)-C(1)	-2.58(16)
N(1)-C(5)-C(6)-C(7)	-1.58(16)
C(4)-C(5)-C(6)-C(7)	179.21(10)
C(8)-N(2)-C(7)-O(1)	-172.82(10)
N(3)-N(2)-C(7)-O(1)	-7.10(16)

C(8)-N(2)-C(7)-C(6)	7.81(14)
N(3)-N(2)-C(7)-C(6)	173.52(9)
C(1)-C(6)-C(7)-O(1)	-1.42(17)
C(5)-C(6)-C(7)-O(1)	176.82(11)
C(1)-C(6)-C(7)-N(2)	177.92(10)
C(5)-C(6)-C(7)-N(2)	-3.85(14)
C(5)-N(1)-C(8)-N(2)	0.50(16)
C(5)-N(1)-C(8)-C(9)	-177.36(11)
C(7)-N(2)-C(8)-N(1)	-6.74(17)
N(3)-N(2)-C(8)-N(1)	-173.93(10)
C(7)-N(2)-C(8)-C(9)	171.54(10)
N(3)-N(2)-C(8)-C(9)	4.35(12)
N(1)-C(8)-C(9)-C(14)	177.21(11)
N(2)-C(8)-C(9)-C(14)	-0.96(12)
N(1)-C(8)-C(9)-C(10)	-3.1(2)
N(2)-C(8)-C(9)-C(10)	178.71(12)
C(14)-C(9)-C(10)-C(11)	1.75(17)
C(8)-C(9)-C(10)-C(11)	-177.88(12)
C(9)-C(10)-C(11)-C(12)	-0.40(18)
C(10)-C(11)-C(12)-C(13)	-1.0(2)
C(11)-C(12)-C(13)-C(14)	1.01(18)
C(10)-C(9)-C(14)-C(13)	-1.77(18)
C(8)-C(9)-C(14)-C(13)	177.95(10)
C(10)-C(9)-C(14)-N(3)	177.54(10)
C(8)-C(9)-C(14)-N(3)	-2.74(13)
C(12)-C(13)-C(14)-C(9)	0.36(18)
C(12)-C(13)-C(14)-N(3)	-178.82(11)
N(2)-N(3)-C(14)-C(9)	5.24(12)
C(15)-N(3)-C(14)-C(9)	141.02(10)

N(2)-N(3)-C(14)-C(13)	-175.50(11)
C(15)-N(3)-C(14)-C(13)	-39.72(17)
C(14)-N(3)-C(15)-C(20)	-94.51(13)
N(2)-N(3)-C(15)-C(20)	35.39(15)
C(14)-N(3)-C(15)-C(16)	83.73(13)
N(2)-N(3)-C(15)-C(16)	-146.37(10)
C(20)-C(15)-C(16)-C(17)	2.13(18)
N(3)-C(15)-C(16)-C(17)	-176.11(11)
C(15)-C(16)-C(17)-C(18)	-1.36(19)
C(16)-C(17)-C(18)-C(19)	-0.6(2)
C(17)-C(18)-C(19)-C(20)	1.8(2)
C(16)-C(15)-C(20)-C(19)	-0.92(18)
N(3)-C(15)-C(20)-C(19)	177.24(10)
C(18)-C(19)-C(20)-C(15)	-1.08(18)

Symmetry transformations used to generate equivalent atoms:

Table 7. Hydrogen bonds for 1 [A and deg.].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)