Supplementary Information

Metal-free regioselective nitration of quinoxalin-2(1*H*)-ones with *tert*-butyl nitrite

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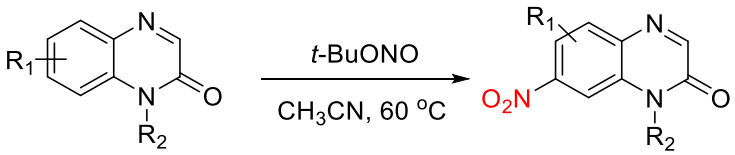
1. General information

All reagents were obtained commercially and used without further purification. Column chromatography was performed on silica gel (200-300 mesh). The reported yields are the actual isolated yields of pure products. ^{1}H NMR spectra were obtained in $CDCl_3$ or DMSO-d_6 at 400 MHz (Bruker AVANCE III 400) or 500 MHz (Bruker Ascend 500). ^{13}C NMR spectra were obtained at 101 MHz or 126 MHz. The chemical shifts (δ) were expressed in ppm and coupling constants (J) were in Hz. High-resolution mass spectra (HRMS) were obtained on a mass spectrometer by the ESI method.

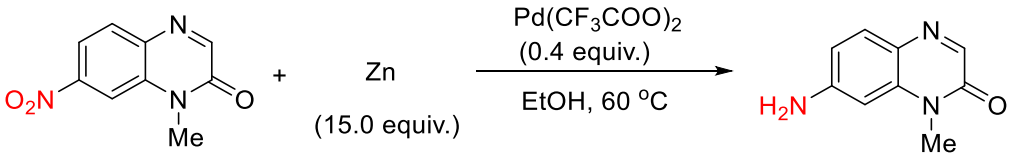
2. General procedure for the coupling of quinoxalin-2(1*H*)-ones with *t*-BuONO



1 **2**

In a 10 mL reaction tube with magnetic stir bar, *t*-BuONO (1.2 mmol) was added to the solution of quinoxalin-2(1*H*)-ones **1** (0.4 mmol) in MeCN (4.0 mL). The mixture was stirred at 60 °C for 6-24 h. Upon completion as indicated by TLC, the solution was concentrated under reduced pressure. The residue was purified by flash column chromatography over silica gel using a mixture of petroleum ether and ethyl acetate as eluent to give the desired product **2**.

3. Synthesis of 7-amino-1-methylquinoxalin-2(1*H*)-one

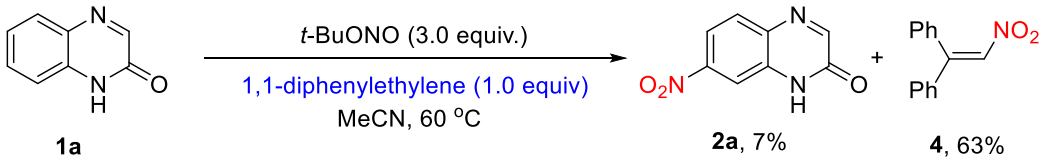


2b **3b**, 74%

To a stirred mixture of the 1-methyl-7-nitroquinoxalin-2(1*H*)-one **2b** (0.1 mmol) in EtOH (2.0 mL) was added Zn (1.5 mmol, 15. 0 equiv) and $Pd(CF_3COO)_2$ (0.04 mmol, 0.4 equiv). The mixture was stirred at 60 °C. Upon completion as monitored by TLC, the mixture was filtered and evaporated under reduced pressure. The residue was

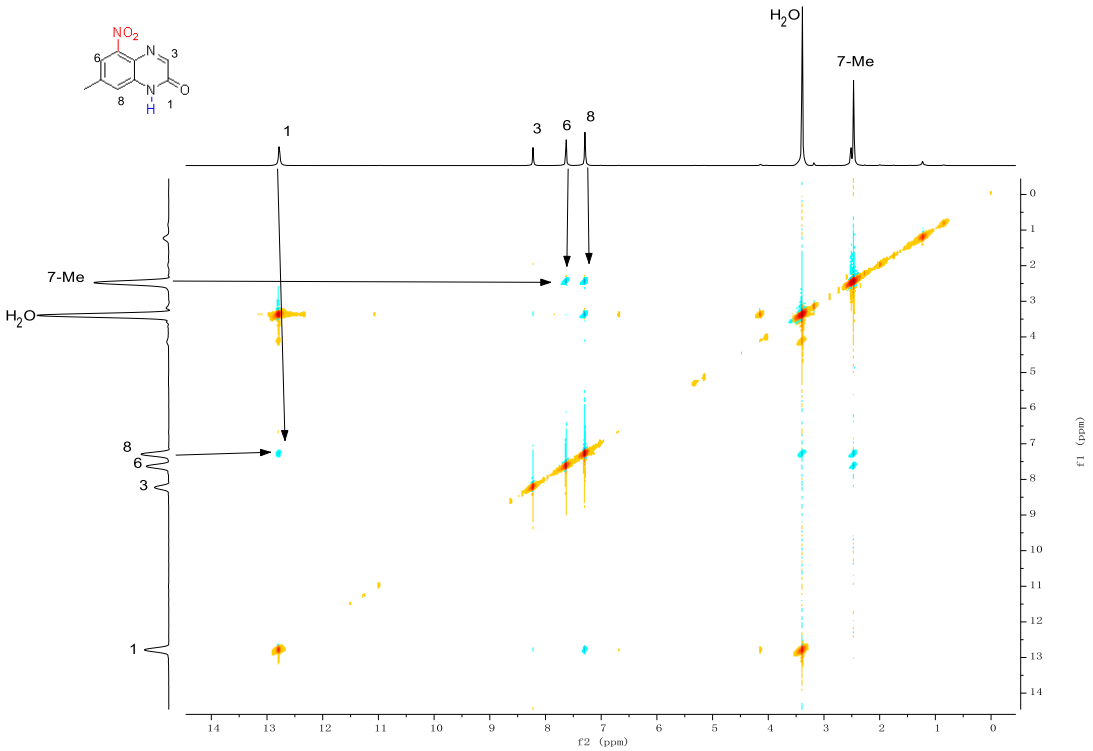
purified by flash column chromatography over silica gel using petroleum ether/ethyl acetate as eluent to afford the desired product **3b**.

4. Control experiments

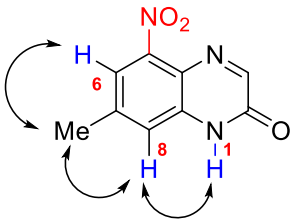


In a 10 mL reaction tube with magnetic stir bar, *t*-BuONO (1.2 mmol) was added to the solution of quinoxalin-2(1*H*)-ones **1a** (0.4 mmol) and 1,1-diphenylethylene (0.4 mmol) in MeCN (4.0 mL). The mixture was stirred at 60 °C for 6 h. Then the reaction mixture was concentrated under reduced pressure and purified by flash column chromatography over silica gel using a mixture of petroleum ether and ethyl acetate as eluent.

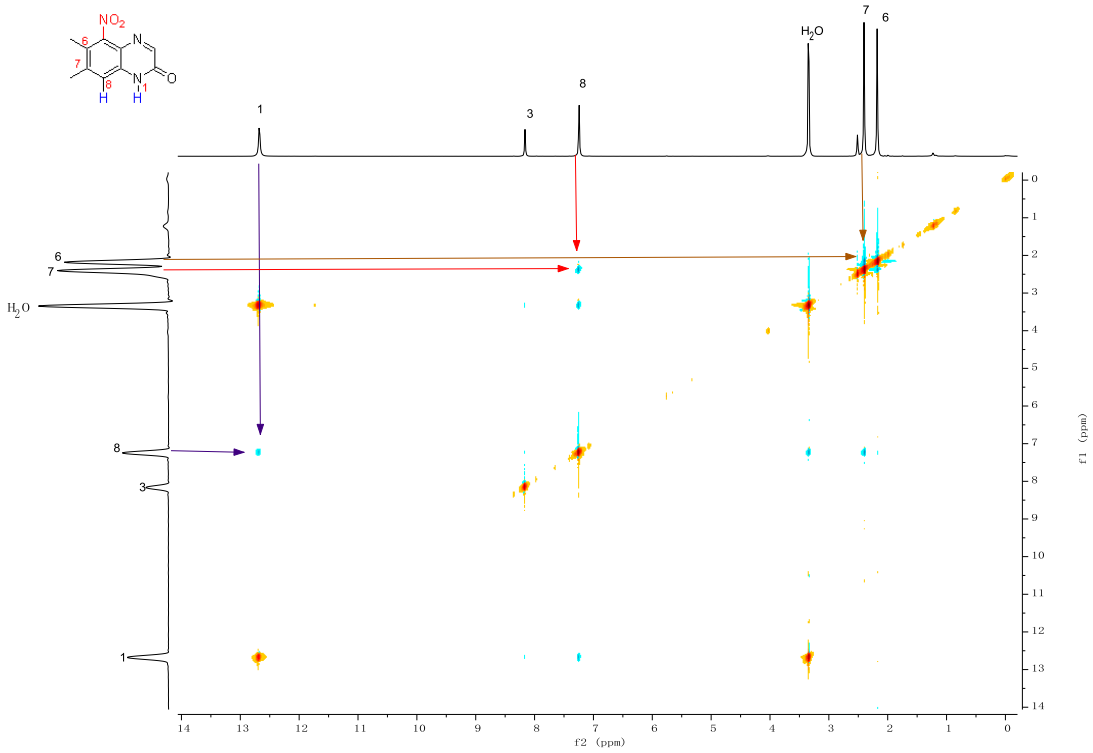
5. Validation of the structures of compounds 2u and 2v



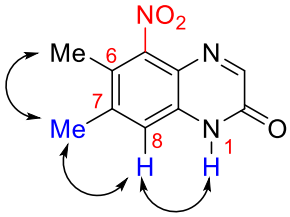
NOESY NMR spectrum of **2u** in DMSO-*d*6.



From the NOESY NMR spectrum of **2u**, correlation peaks between 7-Me (δ_H 2.45, s) and 6-H (δ_H 7.61, s), 7-Me (δ_H 2.45, s) and 8-H (δ_H 7.28, s), 8-H (δ_H 7.28, s) and N-H (δ_H 12.67, s) were observed, which gave evidence that the nitro group was located at C5 position of phenyl ring.



NOESY NMR spectrum of **2v** in DMSO-*d*6.



From the NOESY NMR spectrum of **2v**, correlation peaks between 7-Me (δ_H 2.39, s) and 6-Me (δ_H 2.17, s), 7-Me (δ_H 2.39, s) and 8-H (δ_H 7.24, s), 8-H (δ_H 7.24, s) and N-H (δ_H 12.69, s) were observed, which gave evidence that the nitro group was located at C5 position of phenyl ring.

6. Single crystal X-ray structure of compound 2aa

X-ray crystallographic data for compound **2aa** (CCDC: 2120757)

Crystal Data for $C_{17}H_{14}BrN_3O_3$ (*M* =388.22 g/mol): monoclinic, space group $P2_1/c$ (no. 14), *a* = 21.4559(18) Å, *b* = 8.8913(8) Å, *c* = 17.8312(16) Å, *β* = 102.210(9)°, *V* = 3324.7(5) Å^3, *Z* = 8, *T* = 292.99(10) K, μ(Mo Kα) = 2.493 mm^{-1}, *Dcalc* = 1.551 g/cm^3, 17453 reflections measured (4.668° ≤ 2Θ ≤ 50°), 5861 unique (R_{int} = 0.0614, R_{sigma} = 0.0952) which were used in all calculations. The final R_1 was 0.0554 (I > 2σ(I)) and wR_2 was 0.1249 (all data).

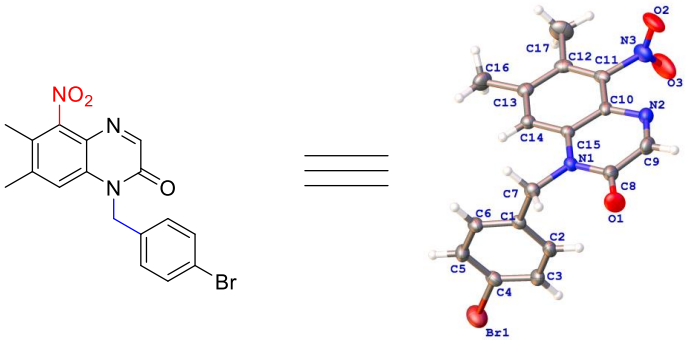


Table 1 Crystal data and structure refinement for 2aa.

Identification code	**2aa**
Empirical formula	$C_{17}H_{14}BrN_3O_3$
Formula weight	388.22
Temperature/K	292.99(10)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	21.4559(18)
b/Å	8.8913(8)
c/Å	17.8312(16)
α/°	90
β/°	102.210(9)
γ/°	90
Volume/Å^3	3324.7(5)
Z	8
ρ_{calc}g/cm^3	1.551
μ/mm^{-1}	2.493
F(000)	1568.0
Crystal size/mm^3	0.14 × 0.12 × 0.11
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	4.668 to 50
Index ranges	$-25 \leq h \leq 23$, $-9 \leq k \leq 10$, $-19 \leq l \leq 21$
Reflections collected	17453
Independent reflections	5861 [R_{int} = 0.0614, R_{sigma} = 0.0952]
Data/restraints/parameters	5861/0/438
Goodness-of-fit on F^2	1.018
Final R indexes [I>=2σ (I)]	R_1 = 0.0554, wR_2 = 0.0981
Final R indexes [all data]	R_1 = 0.1298, wR_2 = 0.1249
Largest diff. peak/hole / e Å^{-3}	0.49/-0.42

Table 2 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for 2aa. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
Br1	3057.4(3)	9425.5(7)	3821.4(4)	78.2(2)
O1	140.3(18)	4039(4)	2690.0(17)	71.9(11)
O2	611(2)	533(4)	5998(2)	84.2(12)
O3	1597(2)	616(4)	5942(3)	106.2(16)
N1	489.4(15)	4925(4)	3911.4(17)	34.8(8)
N2	616.4(17)	1921(4)	4400(2)	45.8(10)
N3	1079(2)	1184(5)	5892(2)	58.6(12)
C1	1072(2)	7218(5)	3667(2)	33.7(10)
C2	1538(2)	6492(5)	3368(2)	46.5(12)
C3	2127(2)	7149(5)	3405(2)	49.3(12)
C4	2238(2)	8534(5)	3740(2)	46.2(12)
C5	1779(2)	9296(5)	4026(2)	49.7(12)
C6	1195(2)	8615(5)	3985(2)	45.6(12)
C7	436(2)	6494(5)	3641(2)	41.5(11)
C8	331(2)	3785(5)	3380(3)	45.8(12)
C9	403(2)	2271(5)	3696(3)	51.0(13)
C10	782.5(19)	3101(5)	4909(2)	33.3(10)
C11	1019.2(19)	2798(5)	5683(2)	36.2(11)
C12	1192.3(19)	3874(5)	6245(2)	40.7(11)
C13	1121(2)	5385(5)	6003(2)	40.2(11)
C14	891.0(19)	5723(5)	5239(2)	37.1(11)
C15	725.9(18)	4602(4)	4688(2)	30.1(10)
C16	1312(2)	6638(5)	6575(2)	61.6(15)
C17	1438(3)	3471(6)	7078(2)	72.5(17)
Br2	3377.0(4)	9211.5(8)	7024.1(4)	100.4(3)
O4	1974.1(17)	3236(4)	4024(2)	68.4(10)
O5	4569(2)	1796(6)	2875(2)	116.4(18)
O6	4850(2)	4100(7)	3086(3)	120.1(19)
N4	2993.3(19)	3035(4)	4725(2)	50.1(10)
N5	3409(2)	3261(4)	3335(2)	53.6(11)
N6	4655(2)	2916(8)	3265(3)	77.4(15)
C18	2899(2)	4545(6)	5854(3)	52.7(13)
C19	3297(3)	4676(7)	6575(3)	70.7(16)
C20	3432(3)	6025(8)	6926(3)	71.9(17)
C21	3174(3)	7323(7)	6550(3)	65.5(16)

C22	2771(2)	7240(6)	5840(3)	64.1(15)
C23	2647(2)	5855(6)	5501(3)	54.4(13)
C24	2771(2)	3053(6)	5452(3)	60.1(14)
C25	2547(3)	3197(5)	4048(3)	53.9(13)
C26	2818(3)	3356(5)	3370(3)	58.3(14)
C27	3832(2)	2996(5)	4029(2)	46.3(12)
C28	3646(2)	2901(5)	4732(2)	47.6(12)
C29	4110(2)	2649(6)	5393(2)	58.2(14)
C30	4742(3)	2488(7)	5370(3)	68.6(16)
C31	4941(2)	2602(6)	4664(3)	68.0(16)
C32	4476(2)	2838(6)	4024(2)	54.2(13)
C33	5631(3)	2448(9)	4629(3)	113(3)
C34	5220(3)	2202(8)	6106(3)	108(3)

Table 3 Anisotropic Displacement Parameters ($Å^2×10^3$) for 2aa. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Br1	52.5(4)	66.6(5)	118.3(5)	1.4(3)	24.6(3)	-10.2(3)
O1	95(3)	74(3)	40.0(19)	-2.3(17)	-2.5(19)	-15(2)
O2	79(3)	56(3)	128(3)	30(2)	45(3)	-7(2)
O3	73(3)	67(3)	185(4)	54(3)	42(3)	31(2)
N1	32(2)	32(2)	40(2)	1.8(17)	7.7(16)	-2.2(17)
N2	49(3)	38(2)	53(2)	-3.7(19)	18(2)	-1.2(19)
N3	55(3)	48(3)	74(3)	20(2)	16(2)	11(3)
C1	29(3)	34(3)	37(2)	6(2)	4(2)	2(2)
C2	60(4)	33(3)	48(3)	0(2)	14(2)	-2(3)
C3	58(4)	36(3)	58(3)	2(2)	22(3)	9(3)
C4	44(3)	41(3)	55(3)	11(2)	13(2)	-1(2)
C5	55(3)	36(3)	61(3)	-10(2)	19(3)	-4(3)
C6	43(3)	39(3)	60(3)	2(2)	22(2)	1(2)
C7	42(3)	42(3)	40(2)	5(2)	6(2)	4(2)
C8	53(3)	40(3)	46(3)	-5(2)	14(2)	-9(2)
C9	54(3)	48(3)	52(3)	-19(2)	14(3)	-9(3)
C10	28(2)	31(3)	44(2)	-3(2)	14(2)	-2(2)
C11	24(2)	41(3)	46(3)	14(2)	12(2)	8(2)
C12	25(3)	58(3)	41(2)	7(2)	11(2)	0(2)
C13	31(3)	49(3)	42(3)	-2(2)	13(2)	-1(2)
C14	36(3)	39(3)	38(2)	1(2)	10(2)	-1(2)

C15	25(2)	32(3)	33(2)	2.8(19)	6.5(19)	-2.4(19)
C16	71(4)	70(4)	43(3)	-17(2)	12(3)	-13(3)
C17	73(4)	88(4)	46(3)	17(3)	-10(3)	-4(3)
Br2	104.2(6)	112.0(6)	87.3(5)	-39.8(4)	25.2(4)	-18.7(4)
O4	43(2)	62(3)	100(3)	3.2(19)	14(2)	0.9(19)
O5	138(5)	147(5)	74(3)	-25(3)	46(3)	8(4)
O6	122(4)	149(5)	106(3)	35(3)	61(3)	-11(4)
N4	45(3)	54(3)	54(2)	0.7(19)	17(2)	-2(2)
N5	53(3)	59(3)	51(2)	3.1(19)	15(2)	-3(2)
N6	67(4)	117(5)	56(3)	8(3)	29(3)	6(3)
C18	37(3)	76(4)	51(3)	5(3)	21(2)	1(3)
C19	65(4)	100(5)	49(3)	14(3)	16(3)	14(3)
C20	66(4)	107(5)	40(3)	-8(3)	7(3)	4(4)
C21	51(4)	98(5)	53(3)	-19(3)	24(3)	-3(3)
C22	61(4)	72(4)	59(3)	-8(3)	13(3)	8(3)
C23	37(3)	77(4)	49(3)	-7(3)	9(2)	5(3)
C24	45(3)	72(4)	69(3)	13(3)	26(3)	1(3)
C25	49(4)	40(3)	72(4)	-2(2)	13(3)	-4(3)
C26	66(4)	50(3)	54(3)	-4(2)	3(3)	-4(3)
C27	39(3)	52(3)	45(3)	-1(2)	2(2)	-1(2)
C28	41(3)	52(3)	50(3)	-4(2)	12(3)	2(2)
C29	53(4)	86(4)	38(3)	4(2)	15(3)	6(3)
C30	42(4)	111(5)	51(3)	5(3)	6(3)	12(3)
C31	42(3)	108(5)	56(3)	4(3)	14(3)	3(3)
C32	41(3)	78(4)	46(3)	2(2)	15(3)	0(3)
C33	44(4)	213(9)	87(4)	13(5)	25(3)	26(4)
C34	66(5)	202(8)	56(3)	11(4)	10(3)	30(5)

Table 4 Bond Lengths for 2aa.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Br1	C4	1.905(5)	Br2	C21	1.889(5)
O1	C8	1.232(5)	O4	C25	1.221(5)
O2	N3	1.209(5)	O5	N6	1.206(6)
O3	N3	1.207(5)	O6	N6	1.201(6)
N1	C7	1.473(5)	N4	C24	1.472(5)
N1	C8	1.380(5)	N4	C25	1.381(6)
N1	C15	1.400(5)	N4	C28	1.404(6)
N2	C9	1.280(5)	N5	C26	1.286(6)
N2	C10	1.384(5)	N5	C27	1.391(5)
N3	C11	1.482(6)	N6	C32	1.485(6)
C1	C2	1.387(6)	C18	C19	1.390(6)
C1	C6	1.368(6)	C18	C23	1.378(6)
C1	C7	1.500(6)	C18	C24	1.505(6)
C2	C3	1.382(6)	C19	C20	1.356(7)
C3	C4	1.367(6)	C20	C21	1.390(7)
C4	C5	1.378(6)	C21	C22	1.376(6)
C5	C6	1.381(6)	C22	C23	1.373(6)
C8	C9	1.455(6)	C25	C26	1.455(7)
C10	C11	1.391(5)	C27	C28	1.396(6)
C10	C15	1.390(5)	C27	C32	1.389(6)
C11	C12	1.379(6)	C28	C29	1.390(6)
C12	C13	1.410(6)	C29	C30	1.372(7)
C12	C17	1.509(5)	C30	C31	1.415(7)
C13	C14	1.380(5)	C30	C34	1.507(6)
C13	C16	1.507(6)	C31	C32	1.365(6)
C14	C15	1.392(5)	C31	C33	1.501(7)

Table 5 Bond Angles for 2aa.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C8	N1	C7	118.7(3)	C25	N4	C24	118.4(4)
C8	N1	C15	120.9(4)	C25	N4	C28	121.5(4)
C15	N1	C7	120.3(3)	C28	N4	C24	120.1(4)
C9	N2	C10	116.7(4)	C26	N5	C27	115.7(4)
O2	N3	C11	118.2(4)	O5	N6	C32	116.7(6)
O3	N3	O2	124.8(5)	O6	N6	O5	126.2(5)
O3	N3	C11	117.0(4)	O6	N6	C32	117.1(6)
C2	C1	C7	120.8(4)	C19	C18	C24	121.9(5)
C6	C1	C2	119.4(4)	C23	C18	C19	117.1(5)
C6	C1	C7	119.8(4)	C23	C18	C24	120.9(4)
C3	C2	C1	120.7(4)	C20	C19	C18	122.1(5)
C4	C3	C2	118.4(4)	C19	C20	C21	119.2(5)
C3	C4	Br1	118.8(4)	C20	C21	Br2	119.4(4)
C3	C4	C5	122.1(4)	C22	C21	Br2	120.0(5)
C5	C4	Br1	119.1(4)	C22	C21	C20	120.6(5)
C4	C5	C6	118.4(4)	C23	C22	C21	118.5(5)
C1	C6	C5	120.9(4)	C22	C23	C18	122.5(5)
N1	C7	C1	112.9(3)	N4	C24	C18	111.6(4)
O1	C8	N1	122.2(4)	O4	C25	N4	122.7(5)
O1	C8	C9	122.8(4)	O4	C25	C26	123.0(5)
N1	C8	C9	115.0(4)	N4	C25	C26	114.3(5)
N2	C9	C8	126.2(4)	N5	C26	C25	127.2(5)
N2	C10	C11	119.6(4)	N5	C27	C28	123.5(4)
N2	C10	C15	123.1(4)	C32	C27	N5	118.3(4)
C11	C10	C15	117.3(4)	C32	C27	C28	118.2(4)
C10	C11	N3	115.5(4)	C27	C28	N4	117.5(4)
C12	C11	N3	119.5(4)	C29	C28	N4	123.7(4)
C12	C11	C10	124.9(4)	C29	C28	C27	118.8(4)
C11	C12	C13	116.3(4)	C30	C29	C28	121.7(4)
C11	C12	C17	122.4(4)	C29	C30	C31	120.4(4)
C13	C12	C17	121.3(4)	C29	C30	C34	119.1(5)
C12	C13	C16	120.0(4)	C31	C30	C34	120.5(5)
C14	C13	C12	120.2(4)	C30	C31	C33	121.1(5)
C14	C13	C16	119.8(4)	C32	C31	C30	116.7(5)
C13	C14	C15	121.7(4)	C32	C31	C33	122.2(5)
C10	C15	N1	118.0(3)	C27	C32	N6	116.8(4)
C10	C15	C14	119.5(3)	C31	C32	N6	119.0(5)
C14	C15	N1	122.5(4)	C31	C32	C27	124.2(4)

Table 6 Torsion Angles for 2aa.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
Br1	C4	C5	C6	-177.9(3)	Br2	C21	C22	C23	178.1(4)
O1	C8	C9	N2	177.7(5)	O4	C25	C26	N5	-176.6(5)
O2	N3	C11	C10	-83.0(5)	O5	N6	C32	C27	-79.3(7)
O2	N3	C11	C12	96.7(5)	O5	N6	C32	C31	99.8(6)
O3	N3	C11	C10	96.9(5)	O6	N6	C32	C27	97.9(6)
O3	N3	C11	C12	-83.4(6)	O6	N6	C32	C31	-82.9(7)
N1	C8	C9	N2	-2.7(7)	N4	C25	C26	N5	5.0(7)
N2	C10	C11	N3	0.7(6)	N4	C28	C29	C30	178.4(5)
N2	C10	C11	C12	-179.1(4)	N5	C27	C28	N4	2.0(7)
N2	C10	C15	N1	0.0(6)	N5	C27	C28	C29	-179.3(4)
N2	C10	C15	C14	178.7(4)	N5	C27	C32	N6	-2.0(7)
N3	C11	C12	C13	-180.0(4)	N5	C27	C32	C31	178.8(5)
N3	C11	C12	C17	-0.6(6)	C18	C19	C20	C21	-0.9(8)
C1	C2	C3	C4	-0.4(6)	C19	C18	C23	C22	-0.8(7)
C2	C1	C6	C5	-1.4(6)	C19	C18	C24	N4	-118.1(5)
C2	C1	C7	N1	48.3(5)	C19	C20	C21	Br2	-178.5(4)
C2	C3	C4	Br1	178.2(3)	C19	C20	C21	C22	1.9(8)
C2	C3	C4	C5	-1.2(6)	C20	C21	C22	C23	-2.2(8)
C3	C4	C5	C6	1.4(7)	C21	C22	C23	C18	1.7(8)
C4	C5	C6	C1	-0.1(7)	C23	C18	C19	C20	0.4(8)
C6	C1	C2	C3	1.6(6)	C23	C18	C24	N4	58.8(6)
C6	C1	C7	N1	-132.2(4)	C24	N4	C25	O4	-5.8(7)
C7	N1	C8	O1	-0.9(6)	C24	N4	C25	C26	172.6(4)
C7	N1	C8	C9	179.5(4)	C24	N4	C28	C27	-175.6(4)
C7	N1	C15	C10	-178.3(3)	C24	N4	C28	C29	5.8(7)
C7	N1	C15	C14	3.1(6)	C24	C18	C19	C20	177.4(5)
C7	C1	C2	C3	-178.8(4)	C24	C18	C23	C22	-177.8(4)
C7	C1	C6	C5	179.1(4)	C25	N4	C24	C18	-102.1(5)
C8	N1	C7	C1	-107.2(4)	C25	N4	C28	C27	2.5(6)
C8	N1	C15	C10	-1.5(6)	C25	N4	C28	C29	-176.1(4)
C8	N1	C15	C14	179.9(4)	C26	N5	C27	C28	-2.7(7)
C9	N2	C10	C11	-179.8(4)	C26	N5	C27	C32	178.1(4)
C9	N2	C10	C15	0.1(6)	C27	N5	C26	C25	-1.0(7)
C10	N2	C9	C8	1.3(7)	C27	C28	C29	C30	-0.2(8)
C10	C11	C12	C13	-0.2(6)	C28	N4	C24	C18	76.0(5)

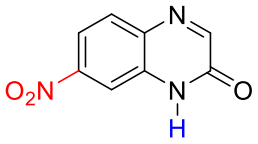
C10	C11	C12	C17	179.2(4)	C28	N4	C25	O4	176.0(4)
C11	C10	C15	N1	179.9(4)	C28	N4	C25	C26	-5.5(6)
C11	C10	C15	C14	-1.4(6)	C28	C27	C32	N6	178.8(5)
C11	C12	C13	C14	-0.1(6)	C28	C27	C32	C31	-0.3(8)
C11	C12	C13	C16	-178.7(4)	C28	C29	C30	C31	1.1(9)
C12	C13	C14	C15	-0.3(6)	C28	C29	C30	C34	-179.4(5)
C13	C14	C15	N1	179.8(4)	C29	C30	C31	C32	-1.5(9)
C13	C14	C15	C10	1.2(6)	C29	C30	C31	C33	179.2(6)
C15	N1	C7	C1	69.7(5)	C30	C31	C32	N6	-178.0(5)
C15	N1	C8	O1	-177.8(4)	C30	C31	C32	C27	1.2(8)
C15	N1	C8	C9	2.6(6)	C32	C27	C28	N4	-178.8(4)
C15	C10	C11	N3	-179.2(4)	C32	C27	C28	C29	-0.2(7)
C15	C10	C11	C12	1.0(6)	C33	C31	C32	N6	1.3(9)
C16	C13	C14	C15	178.2(4)	C33	C31	C32	C27	-179.6(5)
C17	C12	C13	C14	-179.5(4)	C34	C30	C31	C32	179.0(5)
C17	C12	C13	C16	1.9(6)	C34	C30	C31	C33	-0.3(9)

Table 7 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 2aa.

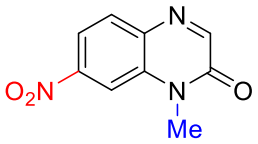
Atom	*x*	*y*	*z*	U(eq)
H2	1452.39	5552.41	3140.01	56
H3	2440.32	6661.43	3207.34	59
H5	1861.7	10247.19	4241.1	60
H6	880.55	9112.51	4176.02	55
H7A	206.52	7072.11	3956.28	50
H7B	190.78	6519.74	3117.74	50
H9	282.57	1481.71	3353.4	61
H14	844.87	6725.89	5089.12	45
H16A	1764.5	6608.68	6769.39	92
H16B	1096.57	6514.66	6991.45	92
H16C	1195.83	7587.29	6328.78	92
H17A	1405.43	2404.43	7142.52	109
H17B	1189.4	3981.06	7388.11	109
H17C	1876.37	3772.4	7232.2	109
H19	3475.55	3810.95	6824.92	85
H20	3695.1	6081.64	7411.97	86
H22	2585.32	8103.54	5594.79	77
H23	2384.33	5797.67	5015.38	65

H24A	2986.33	2264.67	5785.37	72
H24B	2317.11	2847.04	5349.39	72
H26	2531.21	3547.92	2910.61	70
H29	3988.83	2587.9	5862.82	70
H33A	5676.45	2570.74	4108.46	170
H33B	5781.78	1470.39	4810.96	170
H33C	5875.62	3205.54	4945.21	170
H34A	5009.43	2234.8	6529.63	162
H34B	5546.16	2958.68	6172.04	162
H34C	5409.45	1228.58	6083.82	162

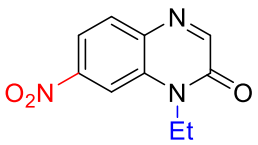
7. Characterization data of products



7-nitroquinoxalin-2(1*H*)-one (2a)[1]**:** Yellow solid; (30.2 mg, 79% yield); m.p. 266.1-266.6 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.72 (s, 1H), 8.33 (s, 1H), 8.10-8.01 (m, 2H), 7.98 (d, J = 8.7 Hz, 1H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 155.6, 154.5, 147.6, 135.3, 132.4, 130.2, 117.5, 111.2. **ESI-MS:** calcd for $C_8H_6N_3O_3$ $[M + H]^+$: 192.0403, found: 192.0404.



1-methyl-7-nitroquinoxalin-2(1*H*)-one (2b)[2]: Brown solid; (50.1 mg, 61% yield); m.p. 173.3-174.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (s, 1H), 8.23 (d, J = 2.2 Hz, 1H), 8.18 (dd, J = 8.7, 2.3 Hz, 1H), 8.04 (d, J = 8.7 Hz, 1H), 3.76 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.5, 153.8, 148.6, 136.6, 133.9, 131.8, 118.4, 109.9, 29.4. **ESI-MS:** calcd for $C_9H_8N_3O_3$ $[M + H]^+$: 206.0559, found: 206.0560.

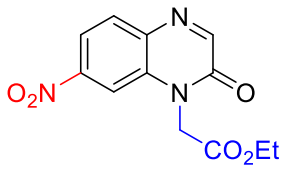


1-ethyl-7-nitroquinoxalin-2(1*H*)-one (2c): Brown solid; (58.9 mg, 67% yield); m.p. 155.8-156.7 °C; ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.41 (s, 1H), 8.34 (d, J = 2.3 Hz, 1H), 8.15 (dd, J = 8.7, 2.3 Hz, 1H), 8.07 (d, J = 8.7 Hz, 1H), 4.31 (q, J = 7.2 Hz, 2H), 1.26 (t, J = 7.2 Hz, 3H); ^{13}C NMR (126 MHz, DMSO-d_6) δ 153.9, 153.7, 148.3, 136.4, 132.6, 131.3, 117.7, 110.2, 36.9, 12.2. **ESI-MS:** calcd for $C_{10}H_{10}N_3O_3$ $[M + H]^+$: 220.0716, found:

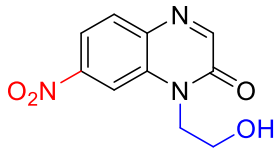
[1] H. Zhu, R. Mishra, L. Yuan, S. F. Abdul Salam, J. Liu, G. Gray, A. D. Sterling, M. Wunderlich, J. Landero-Figueroa, J. T. Garrett and E. J. Merino, *ChemMedChem*, 2019, **14**, 1933.

[2] A. Carrer, J.-D. Brion, S. Messaoudi and M. Alami, *Org. Lett.* 2013, **15**, 5606.

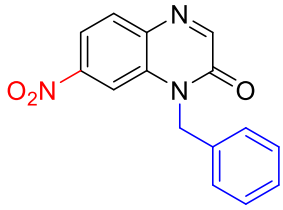
220.0717.



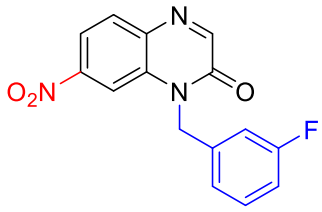
ethyl 2-(7-nitro-2-oxoquinoxalin-1(2*H*)-yl)acetate (2d): Brown solid; (66.5 mg, 60% yield); m.p. 146.6-148.0 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.46 (s, 1H), 8.19 (dd, *J* = 8.7, 1.5 Hz, 1H), 8.06 (d, *J* = 8.7 Hz, 1H), 7.99 (d, *J* = 2.1 Hz, 1H), 5.05 (s, 2H), 4.30 (q, *J* = 7.1 Hz, 2H), 1.33 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.4, 153.9, 153.5, 148.6, 136.7, 133.1, 132.2, 118.7, 109.5, 62.8, 43.5, 14.2. **ESI-MS:** calcd for $C_{12}H_{11}N_3O_5Na$ $[M + Na]^+$: 300.0591, found: 300.0591.



1-(2-hydroxyethyl)-7-nitroquinoxalin-2(1*H*)-one (2e): Brown solid; (33.9 mg, 36% yield); m.p. 179.6-180.1 °C; ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.51 (s, 1H), 8.42 (s, 1H), 8.12 (dd, *J* = 8.7, 1.9 Hz, 1H), 8.03 (d, *J* = 8.8 Hz, 1H), 4.97 (t, *J* = 5.8 Hz, 1H), 4.35 (t, *J* = 5.6 Hz, 2H), 3.74 (q, *J* = 5.6 Hz, 2H); ^{13}C NMR (126 MHz, DMSO-d_6) δ 154.1, 153.9, 147.8, 136.1, 133.9, 130.9, 117.5, 111.4, 58.0, 44.6. **ESI-MS:** calcd for $C_{10}H_9N_3O_4Na$ $[M + Na]^+$: 258.0485, found: 258.0484.

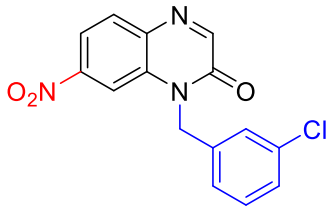


1-benzyl-7-nitroquinoxalin-2(1*H*)-one (2f): Brown solid; (56.3 mg, 50% yield); m.p. 163.6-164.4 °C; ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.54 (s, 1H), 8.20 (s, 1H), 8.13 (d, *J* = 8.8 Hz, 1H), 8.08 (d, *J* = 8.7 Hz, 1H), 7.37-7.31 (m, 5H), 5.56 (s, 2H); ^{13}C NMR (126 MHz, DMSO-d_6) δ 154.3, 154.2, 147.8, 136.5, 135.2, 132.9, 131.2, 128.9, 127.6, 126.9, 118.0, 110.7, 44.9. **ESI-MS:** calcd for $C_{15}H_{12}N_3O_3$ $[M + H]^+$: 282.0873, found: 282.0872.

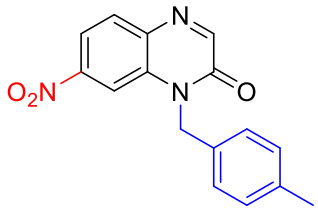


1-(3-fluorobenzyl)-7-nitroquinoxalin-2(1*H*)-one (2g): Red solid; (63.4 mg, 53% yield); m.p. 169.6-169.8 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.52 (s, 1H), 8.15 (d, *J* = 11.1 Hz, 2H), 8.05 (d, *J* = 8.6 Hz, 1H), 7.34 (dd, *J* = 14.1, 7.6 Hz, 1H), 7.12 (d, *J* = 7.7 Hz, 1H), 6.99 (dd, *J* = 18.5, 9.2 Hz, 2H), 5.50 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.4 (d, *J* = 248.1 Hz), 154.5, 153.8, 148.6, 136.9, 136.6 (d, *J* = 7.3 Hz), 132.9, 132.1, 131.1 (d, *J* = 8.4 Hz), 122.9 (d, *J* = 2.8 Hz), 118.6, 115.7 (d, *J* = 21.1 Hz), 114.3 (d, *J* = 22.3 Hz), 110.4, 45.6 (d, *J* = 1.5 Hz). **ESI-MS:** calcd for

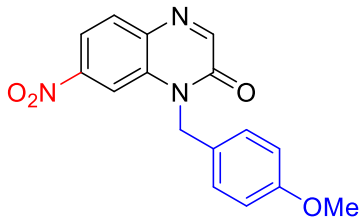
$C_{15}H_{11}FN_3O_3$ [M + H]$^+$: 300.0778, found: 300.0779.



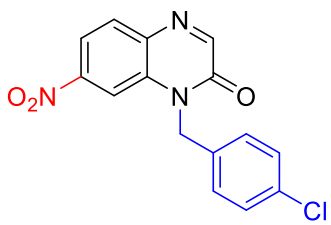
1-(3-chlorobenzyl)-7-nitroquinoxalin-2(1*H*)-one (2h): Brown solid; (51.8 mg, 41% yield); m.p. 123.9-124.7 °C; ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.53 (s, 1H), 8.18 (d, *J* = 1.6 Hz, 1H), 8.13 (dd, *J* = 8.8, 2.1 Hz, 1H), 8.08 (d, *J* = 8.7 Hz, 1H), 7.47 (s, 1H), 7.40 – 7.32 (m, 2H), 7.30 (d, *J* = 7.2 Hz, 1H), 5.56 (s, 2H); ^{13}C NMR (126 MHz, DMSO-d_6) δ 154.4, 154.3, 147.9, 137.8, 136.5, 133.5, 132.9, 131.2, 130.7, 127.7, 126.9, 125.5, 118.1, 110.5, 44.4. **ESI-MS:** calcd for $C_{15}H_{10}ClN_3O_3$ [M + H]$^+$: 316.0484, found: 316.0496.



1-(4-methylbenzyl)-7-nitroquinoxalin-2(1*H*)-one (2i): Brown solid; (72.1 mg, 61% yield); m.p. 156.9-157.8 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.50 (s, 1H), 8.26 (d, *J* = 2.1 Hz, 1H), 8.11 (dd, *J* = 8.7, 2.1 Hz, 1H), 8.01 (d, *J* = 8.7 Hz, 1H), 7.22 (d, *J* = 8.0 Hz, 2H), 7.15 (d, *J* = 7.9 Hz, 2H), 5.47 (s, 2H), 2.31 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 154.7, 153.9, 148.5, 138.4, 136.9, 133.1, 131.9, 131.2, 130.1, 127.4, 118.3, 110.7, 45.9, 21.2. **ESI-MS:** calcd for $C_{16}H_{13}N_3O_3Na$ [M + Na]$^+$: 318.0849, found: 318.0850.

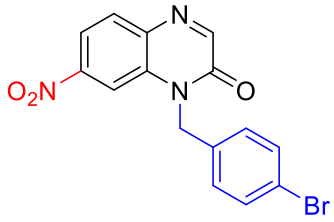


1-(4-methoxybenzyl)-7-nitroquinoxalin-2(1*H*)-one (2j): Brown solid; (56.0 mg, 45% yield); m.p. 134.5-135.9 °C; ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.53 (s, 1H), 8.25 (d, *J* = 2.2 Hz, 1H), 8.12 (dd, *J* = 8.8, 2.2 Hz, 1H), 8.07 (d, *J* = 8.7 Hz, 1H), 7.29 (d, *J* = 8.7 Hz, 2H), 6.90 (d, *J* = 8.7 Hz, 2H), 5.49 (s, 2H), 3.71 (s, 3H); ^{13}C NMR (126 MHz, DMSO-d_6) δ 158.7, 154.3, 154.3, 147.8, 136.4, 132.8, 131.2, 128.4, 127.0, 117.9, 114.3, 110.8, 55.1, 44.3. **ESI-MS:** calcd for $C_{16}H_{13}N_3O_4Na$ [M + Na]$^+$: 334.0798, found: 334.0798.

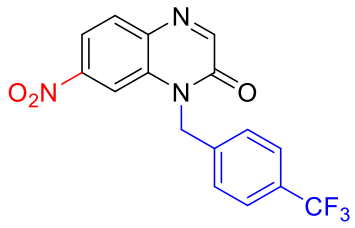


1-(4-chlorobenzyl)-7-nitroquinoxalin-2(1*H*)-one (2k): Red solid; (74.5 mg, 59% yield); m.p. 149.1-150.0 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.49 (s, 1H), 8.16 (d, *J* = 2.2 Hz, 1H), 8.13 (dd, *J* = 8.7, 2.2 Hz, 1H), 8.03 (d, *J* = 8.7 Hz,

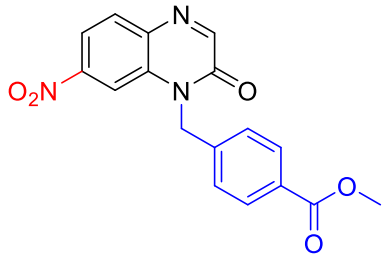
1H), 7.33-7.30 (m, 2H), 7.27-7.24 (m, 2H), 5.46 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 154.5, 153.8, 148.5, 136.9, 134.6, 132.9, 132.7, 132.1, 129.7, 128.8, 118.5, 110.4, 45.5. **ESI-MS:** calcd for $C_{15}H_{11}ClN_3O_3$ $[M + H]^+$: 316.0484, found: 316.0481.



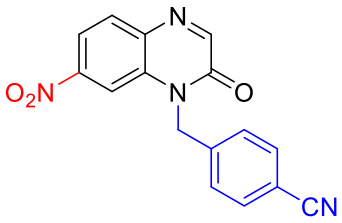
1-(4-bromobenzyl)-7-nitroquinoxalin-2(1*H*)-one (2l): Brown solid; (86.4 mg, 60% yield); m.p. 177.1-177.4 ºC; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.51 (s, 1H), 8.18-8.12 (m, 2H), 8.04 (d, *J* = 8.7 Hz, 1H), 7.48 (d, *J* = 8.4 Hz, 2H), 7.20 (d, *J* = 8.3 Hz, 2H), 5.46 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 154.5, 153.8, 148.5, 136.9, 133.2, 132.9, 132.6, 132.1, 129.1, 122.6, 118.5, 110.3, 45.6. **ESI-MS:** calcd for $C_{15}H_{11}BrN_3O_3$ $[M + H]^+$: 359.9978, found: 359.9979.



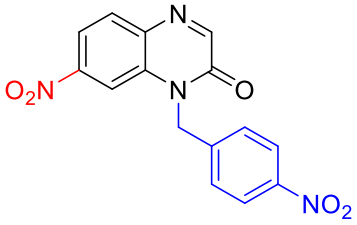
7-nitro-1-(4-(trifluoromethyl)benzyl)quinoxalin-2(1*H*)-one (2m): Yellow solid (86.6 mg, 62% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.53 (s, 1H), 8.15 (d, *J* = 8.1 Hz, 2H), 8.06 (d, *J* = 8.5 Hz, 1H), 7.62 (d, *J* = 8.0 Hz, 2H), 7.43 (d, *J* = 8.0 Hz, 2H), 5.56 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 154.5, 153.8, 148.6, 138.2, 136.9, 132.9, 132.2, 130.9 (q, *J* = 33.5 Hz), 127.7, 126.5 (q, *J* = 3.5 Hz), 123.9 (q, *J* = 272.7 Hz), 118.7, 110.2, 45.7; ^{19}F NMR (471 MHz, Chloroform-*d*) δ -62.78. **ESI-MS:** calcd for $C_{16}H_{11}F_3N_3O_3$ $[M + H]^+$: 350.0747, found: 350.0750.



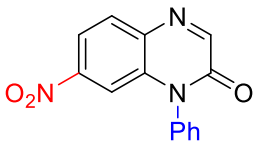
methyl 4-((7-nitro-2-oxoquinoxalin-1(2*H*)-yl)methyl)benzoate (2n): Yellow solid (78.7 mg, 58% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.53 (s, 1H), 8.14 (d, *J* = 9.5 Hz, 2H), 8.05 (d, *J* = 4.9 Hz, 1H), 8.02 (d, *J* = 8.0 Hz, 2H), 7.36 (d, *J* = 7.9 Hz, 2H), 5.56 (s, 2H), 3.89 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.5, 154.5, 153.8, 148.6, 139.1, 136.9, 132.9, 132.1, 130.7, 130.5, 127.2, 118.6, 110.4, 52.4, 45.9. **ESI-MS:** calcd for $C_{17}H_{14}N_3O_5$ $[M + H]^+$: 340.0931, found: 350.0936.



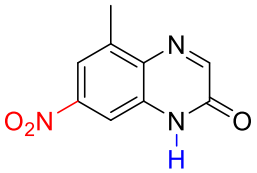
4-((7-nitro-2-oxoquinoxalin-1(2*H*)-yl) methyl) benzonitrile (2o): Yellow solid (73.5 mg, 60% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.53 (s, 1H), 8.17 (d, *J* = 8.7 Hz, 1H), 8.08 (d, *J* = 8.4 Hz, 2H), 7.67 (d, *J* = 7.9 Hz, 2H), 7.42 (d, *J* = 7.9 Hz, 2H), 5.56 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 154.4, 153.7, 148.6, 139.4, 136.9, 133.3, 132.8, 132.3, 128.0, 118.8, 118.2, 112.8, 110.0, 45.7. **ESI-MS:** calcd for $C_{16}H_{11}N_4O_3$ $[M + H]^+$: 307.0827, found: 307.0834.



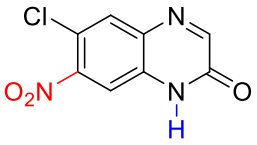
7-nitro-1-(4-nitrobenzyl)quinoxalin-2(1*H*)-one (2p): Yellow solid (65.3 mg, 50% yield). ^{1}H NMR (500 MHz, DMSO) δ 8.56 (s, 1H), 8.19 (d, *J* = 8.4 Hz, 2H), 8.15 (d, *J* = 9.4 Hz, 2H), 8.11 (d, *J* = 8.5 Hz, 1H), 7.61 (d, *J* = 8.3 Hz, 2H), 5.71 (s, 2H); ^{13}C NMR (126 MHz, DMSO) δ 154.3, 154.2, 148.0, 147.0, 143.0, 136.5, 132.9, 131.3, 128.1, 123.9, 118.2, 110.4, 44.6. **ESI-MS:** calcd for $C_{15}H_{11}N_4O_5$ $[M + H]^+$: 327.0723, found: 327.0730.



7-nitro-1-phenylquinoxalin-2(1*H*)-one (2q): Yellow solid (73.8 mg, 69% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.51 (s, 1H), 8.14 (d, *J* = 8.7 Hz, 1H), 8.07 (d, *J* = 8.7 Hz, 1H), 7.71 – 7.61 (m, 3H), 7.59 (s, 1H), 7.31 (d, *J* = 7.5 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 154.4, 154.2, 148.5, 136.3, 134.6, 134.2, 131.5, 131.0, 130.6, 128.1, 118.5, 111.5. **ESI-MS:** calcd for $C_{14}H_{10}N_3O_3$ $[M + H]^+$: 268.0726, found: 268.0727.



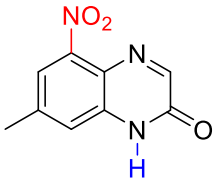
5-methyl-7-nitroquinoxalin-2(1*H*)-one (2r): Brown solid; (34.2 mg, 42% yield); m.p. 220.9-221.5 ºC; ^{1}H NMR (500 MHz, DMSO-d_6) δ 12.67 (s, 1H), 8.34 (s, 1H), 7.96 (s, 1H), 7.92 (s, 1H), 2.64 (s, 3H); ^{13}C NMR (126 MHz, DMSO-d_6) δ 154.5, 154.0, 147.1, 139.5, 133.8, 132.3, 117.9, 108.9, 17.1. **ESI-MS:** calcd for $C_9H_7N_3O_3Na$ $[M + Na]^+$: 228.0379, found: 228.0387.



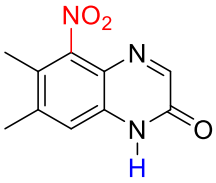
6-chloro-7-nitroquinoxalin-2(1*H*)-one (2s) [3] : Brown solid; (25.3 mg, 28% yield); m.p. 224.6-225.1 ºC; ^{1}H NMR (500 MHz,

[3] K. Aoki, T. Obata, Y. Yamazaki, Y. Mori, H. Hirokawa, J. Koseki, T. Hattori, K. Niitsu, S. Takeda, M. Aburada and K.

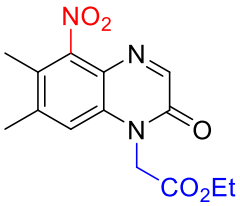
DMSO-d_6) δ 12.76 (s, 1H), 8.35 (s, 1H), 8.18 (s, 1H), 7.89 (s, 1H); ^{13}C NMR (126 MHz, DMSO-d_6) δ 156.3, 154.5, 147.3, 134.1, 131.5, 131.2, 118.3, 113.2. **ESI-MS:** calcd for $C_8H_5ClN_3O_3$ $[M + H]^+$: 226.0014, found: 226.0023.



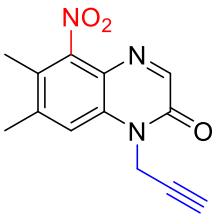
7-methyl-5-nitroquinoxalin-2(1*H*)-one (2u): Yellow solid; (25.4 mg, 31% yield); m.p. 221.4-223.7 °C; ^{1}H NMR (500 MHz, DMSO-d_6) δ 12.75 (s, 1H), 8.21 (s, 1H), 7.61 (s, 1H), 7.28 (s, 1H), 2.45 (s, 3H); ^{13}C NMR (126 MHz, DMSO-d_6) δ 154.7, 153.1, 147.4, 141.8, 133.0, 121.5, 118.6, 117.8, 21.1. **ESI-MS:** calcd for $C_9H_8N_3O_3$ $[M + H]^+$: 206.0560, found: 206.0569.



6,7-dimethyl-5-nitroquinoxalin-2(1*H*)-one (2v): White solid; (42.1 mg, 48% yield); m.p. 229.1-229.6 °C; ^{1}H NMR (500 MHz, DMSO-d_6) δ 12.69 (s, 1H), 8.16 (s, 1H), 7.24 (s, 1H), 2.39 (s, 3H), 2.17 (s, 3H); ^{13}C NMR (126 MHz, DMSO-d_6) δ 154.8, 152.9, 147.8, 142.0, 130.6, 121.9, 121.7, 117.3, 20.3, 13.4. **ESI-MS:** calcd for $C_{10}H_{10}N_3O_3$ $[M + H]^+$: 220.0716, found: 220.0717.



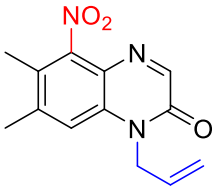
ethyl 2-(6,7-dimethyl-5-nitro-2-oxoquinoxalin-1(2*H*)-yl)acetate (2w): White solid; (67.2 mg, 55% yield); m.p. 206.1-207.8 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.28 (s, 1H), 6.99 (s, 1H), 4.98 (s, 2H), 4.26 (q, *J* = 7.1 Hz, 2H), 2.46 (s, 3H), 2.26 (s, 3H), 1.29 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.6, 154.1, 150.8, 149.7, 142.7, 131.1, 123.6, 123.5, 115.2, 62.6, 43.4, 21.4, 14.2, 13.9. **ESI-MS:** calcd for $C_{14}H_{15}N_3O_5Na$ $[M + Na]^+$: 328.0904, found: 328.0904.



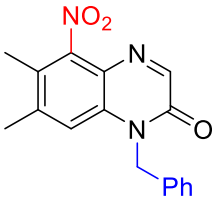
6,7-dimethyl-5-nitro-1-(prop-2-yn-1-yl)quinoxalin-2(1*H*)-one (2x): Yellow solid; (32.4 mg, 63% yield); m.p. 188.1-189.2 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.26 (d, *J* = 2.7 Hz, 1H), 7.39 (s, 1H), 5.02 (d, *J* = 1.9 Hz, 2H), 2.52 (s, 3H), 2.33 (t, *J* = 2.5 Hz, 1H), 2.28 (d, *J* = 1.3 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.5, 150.9, 149.6, 142.7, 130.3, 123.7, 123.6, 116.2, 77.2, 74.1, 31.5, 21.4, 13.9. **ESI-MS:** calcd for $C_{13}H_{12}N_3O_3$ [M +

Miyamoto, *Chem. Pharm. Bull.* 2007, **55**, 255.

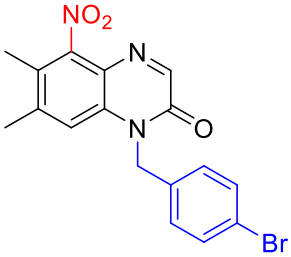
H]$^+$: 258.0872, found: 258.0873.



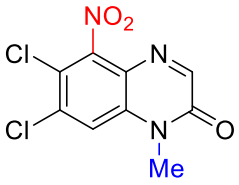
1-allyl-6,7-dimethyl-5-nitroquinoxalin-2(1*H*)-one (2y): Yellow solid; (39.4 mg, 38% yield); m.p. 175.7-176.2 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.27 (s, 1H), 7.19 (s, 1H), 5.95-5.87 (m, 1H), 5.29 (d, *J* = 10.4 Hz, 1H), 5.13 (d, *J* = 17.3 Hz, 1H), 4.87 (d, *J* = 3.6 Hz, 2H), 2.47 (s, 3H), 2.26 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 154.3, 151.1, 149.6, 142.3, 131.1, 130.0, 123.7, 123.3, 118.5, 116.2, 44.3, 21.4, 13.9. **ESI-MS:** calcd for $C_{13}H_{14}N_3O_3$ [M + H]$^+$: 260.1029, found: 260.1020.



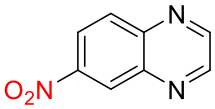
1-benzyl-6,7-dimethyl-5-nitroquinoxalin-2(1*H*)-one (2z): Yellow solid; (90.3 mg, 73% yield); m.p. 181.6-182.0 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.34 (s, 1H), 7.35-7.27 (m, 3H), 7.21 (d, *J* = 7.3 Hz, 2H), 7.17 (s, 1H), 5.46 (s, 2H), 2.37 (s, 3H), 2.22 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 154.8, 151.2, 149.6, 142.4, 134.5, 131.2, 129.3, 128.2, 126.8, 123.8, 123.3, 116.4, 45.8, 21.4, 13.9. **ESI-MS:** calcd for $C_{17}H_{16}N_3O_3$ [M + H]$^+$: 310.1185, found: 310.1186.



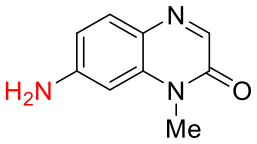
1-(4-bromobenzyl)-6,7-dimethyl-5-nitroquinoxalin-2(1*H*)-one (2aa): White solid; (108.9 mg, 70% yield); m.p. 185.6-187.1 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.34 (s, 1H), 7.46 (d, *J* = 8.3 Hz, 2H), 7.09 (m, 3H), 5.40 (s, 2H), 2.38 (s, 3H), 2.23 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 154.7, 151.1, 149.7, 142.6, 133.5, 132.4, 131.0, 128.6, 123.8, 123.6, 122.2, 116.1, 45.3, 21.5, 13.9. **ESI-MS:** calcd for $C_{17}H_{15}BrN_3O_3$ [M + H]$^+$: 388.0292, found: 388.0298.



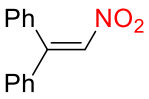
6,7-dichloro-1-methyl-5-nitroquinoxalin-2(1*H*)-one (2ab): Brown solid; (10.5 mg, 10% yield); m.p. 198.5-199.2 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.32 (s, 1H), 7.57 (s, 1H), 3.69 (s, 3H); ^{13}C NMR (126 MHz, DMSO-*d*$_6$) δ 154.2, 154.0, 146.9, 134.3, 134.1, 124.1, 118.4, 116.1, 29.5. **ESI-MS:** calcd for $C_9H_6Cl_2N_3O_3$ [M + H]$^+$: 273.9781, found: 273.9789.



6-nitroquinoxaline (2ac)[4]: White solid; (23.1 mg, 33% yield); m.p. 169.6-170.8 ºC; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.03-9.01 (m, 3H), 8.55 (dd, *J* = 9.2, 2.0 Hz, 1H), 8.28 (d, *J* = 9.2 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 148.1, 147.8, 147.2, 145.5, 142.1, 131.5, 126.1, 123.6. **ESI-MS:** calcd for $C_8H_6N_3O_2$ $[M + H]^+$: 176.0455, found: 176.0459.



7-amino-1-methylquinoxalin-2(1*H*)-one (3b): Yellow solid (13.0 mg, 74% yield). ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.74 (s, 1H), 7.44 (d, *J* = 8.7 Hz, 1H), 6.62 (dd, *J* = 8.7, 2.1 Hz, 1H), 6.49 (d, *J* = 2.1 Hz, 1H), 6.12 (s, 2H), 3.47 (s, 3H); ^{13}C NMR (126 MHz, DMSO-d_6) δ 155.1, 152.1, 141.3, 135.4, 130.9, 125.2, 111.4, 95.6, 28.2. ESI-MS: calcd for $C_9H_{10}N_3O$ $[M + H]^+$: 176.0819, found: 176.0825.



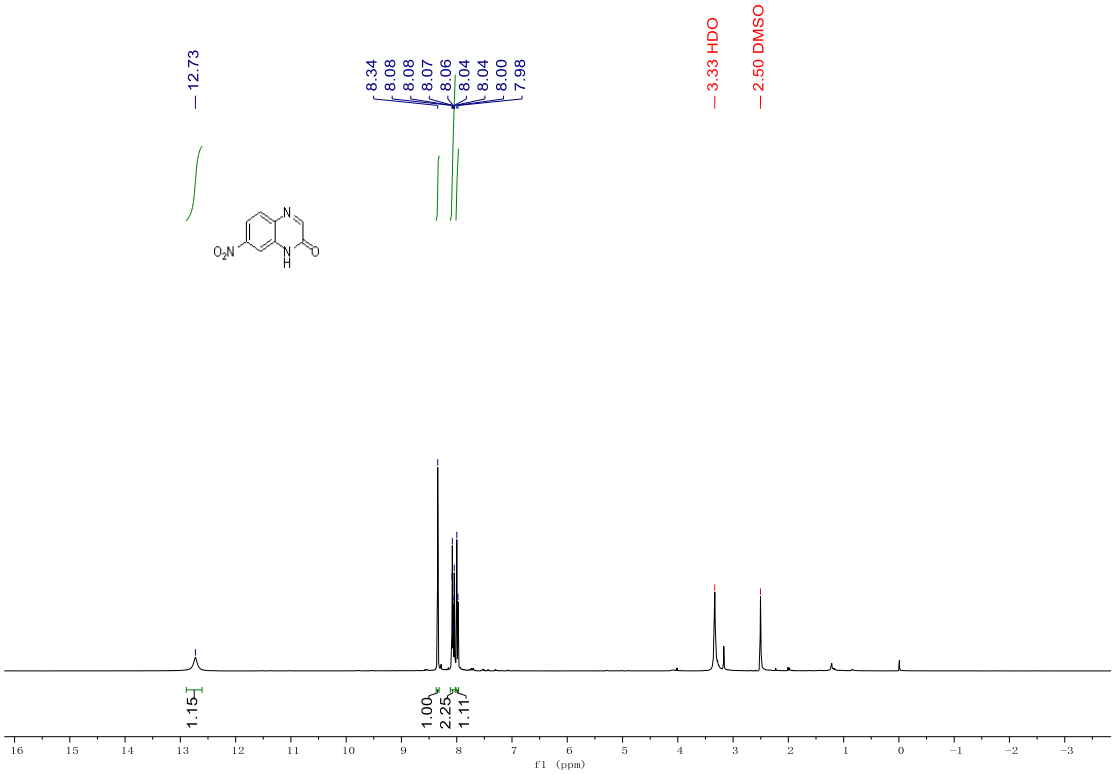
(2-nitroethene-1,1-diyl)dibenzene (4)[5]: Yellow solid (56.7 mg, 63% yield) ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.49-7.44 (m, 5H), 7.39 (t, *J* = 7.6 Hz, 2H), 7.29 (d, *J* = 7.3 Hz, 2H), 7.23 (d, *J* = 6.0 Hz, 2H); ^{13}C NMR (126 MHz, Chloroform-*d*) δ 150.6, 137.2, 135.7, 134.5, 131.0, 129.5, 129.0, 129.0, 128.9, 128.6.

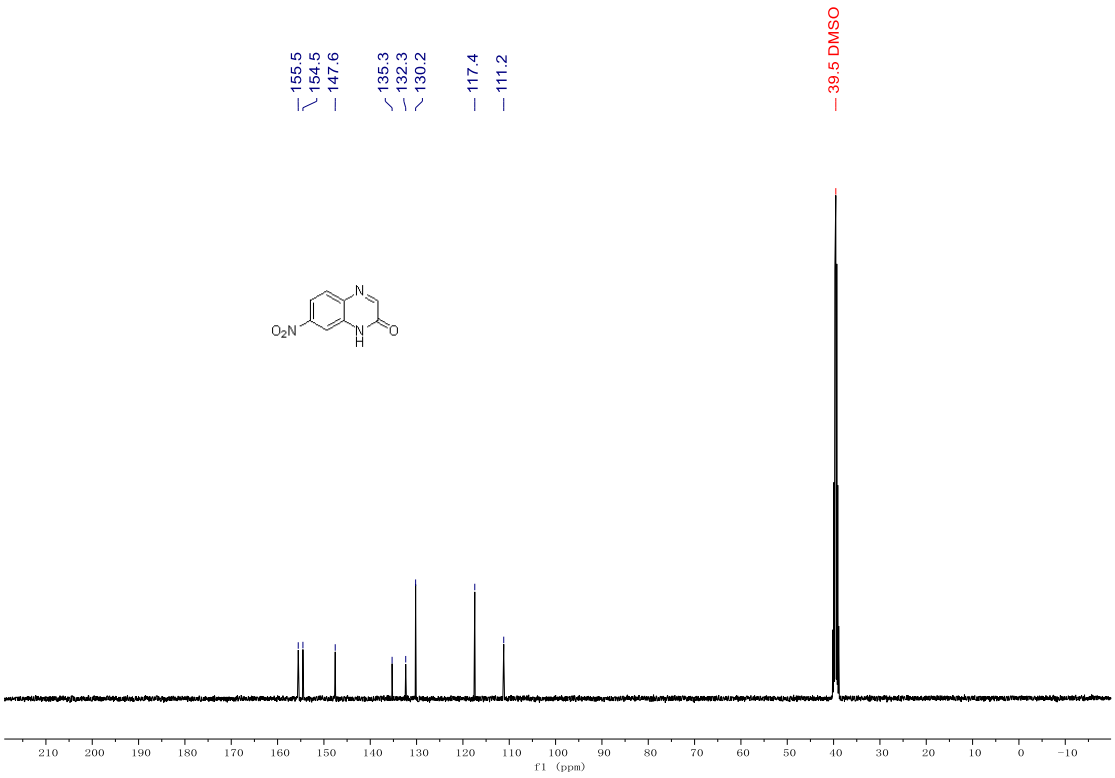
[4] S. T. Hazeldine, L. Polin, J. Kushner, J. Paluch, K. White, M. Edelstein, E. Palomino, T. H. Corbett and J. P. Horwitz, *J. Med. Chem.* 2001, **44**, 1758.

[5] X. Guan, H. Zhu, Y. Zhao and T. G. Driver, *Eur. J. Org. Chem.*, 2020, **2020**, 57.

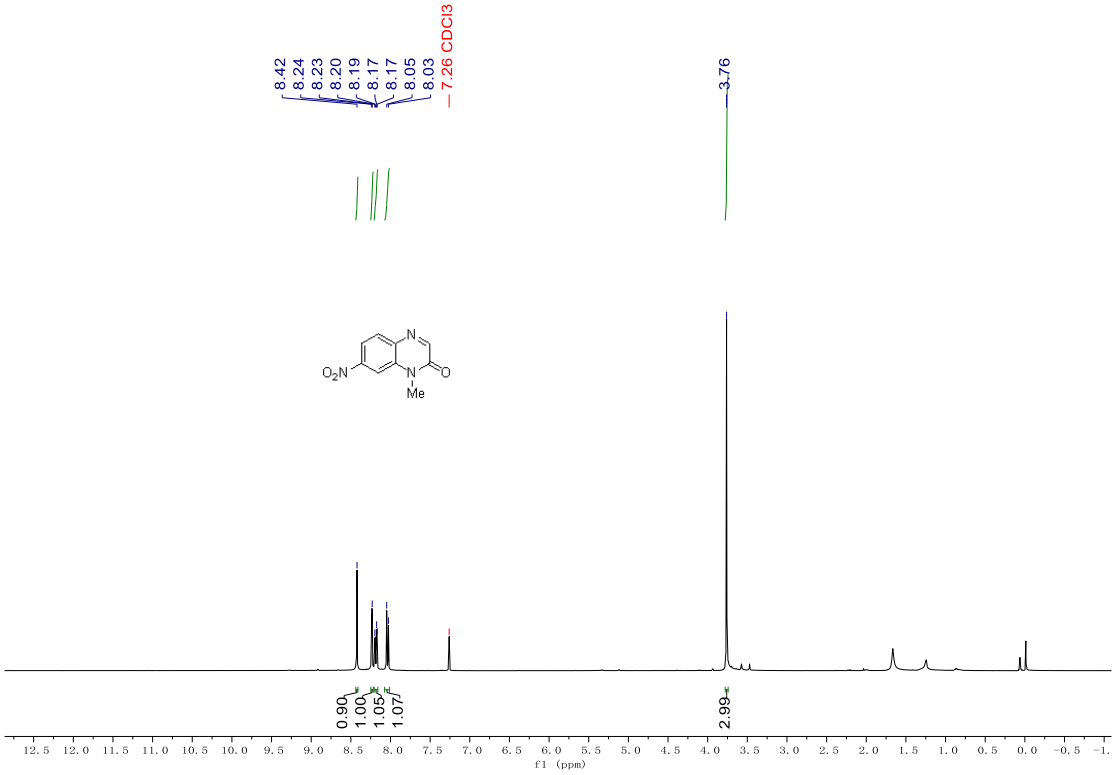
8. NMR spectra of products

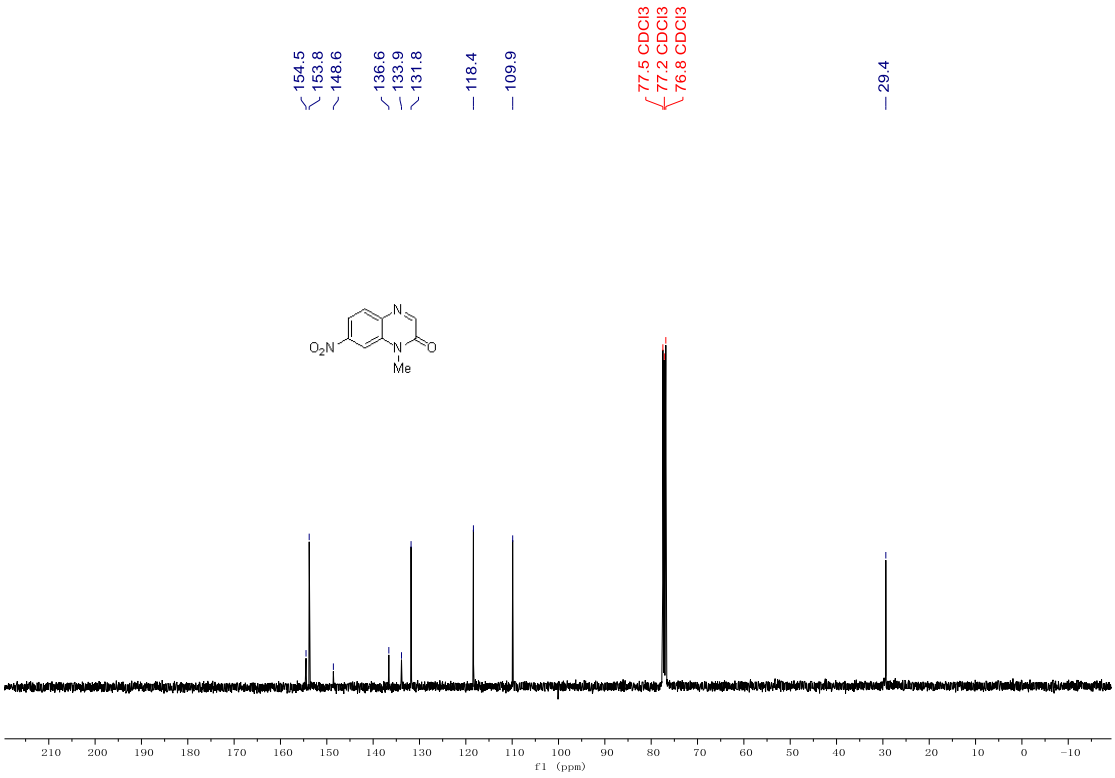
7-nitroquinoxalin-2(1*H*)-one (2a)



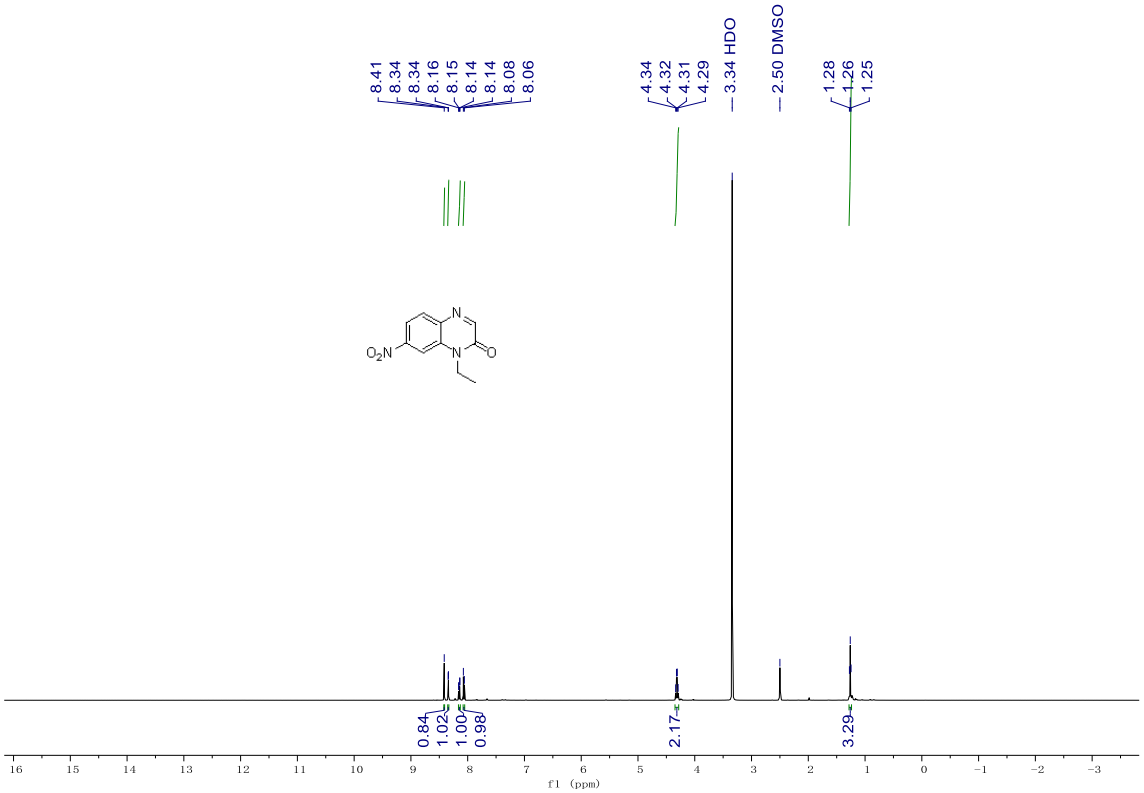


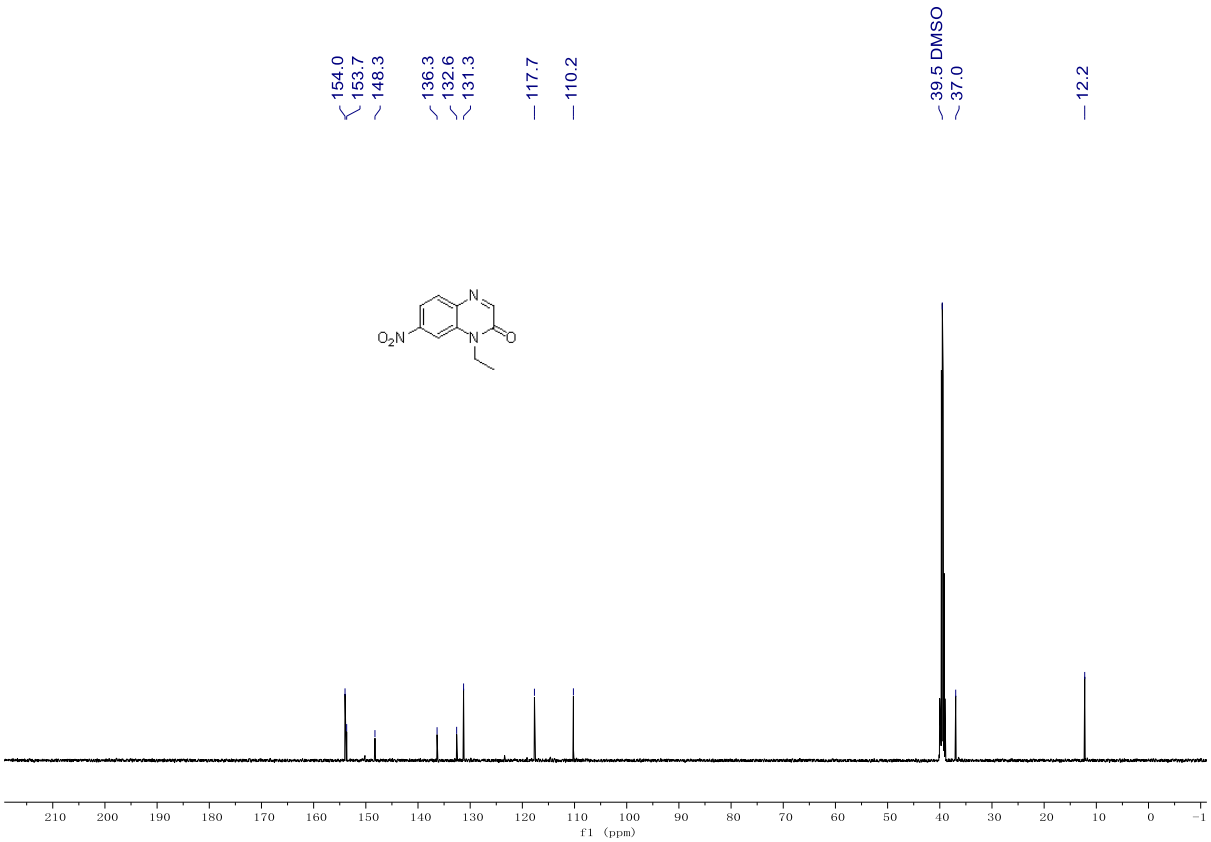
1-methyl-7-nitroquinoxalin-2(1*H*)-one (2b)



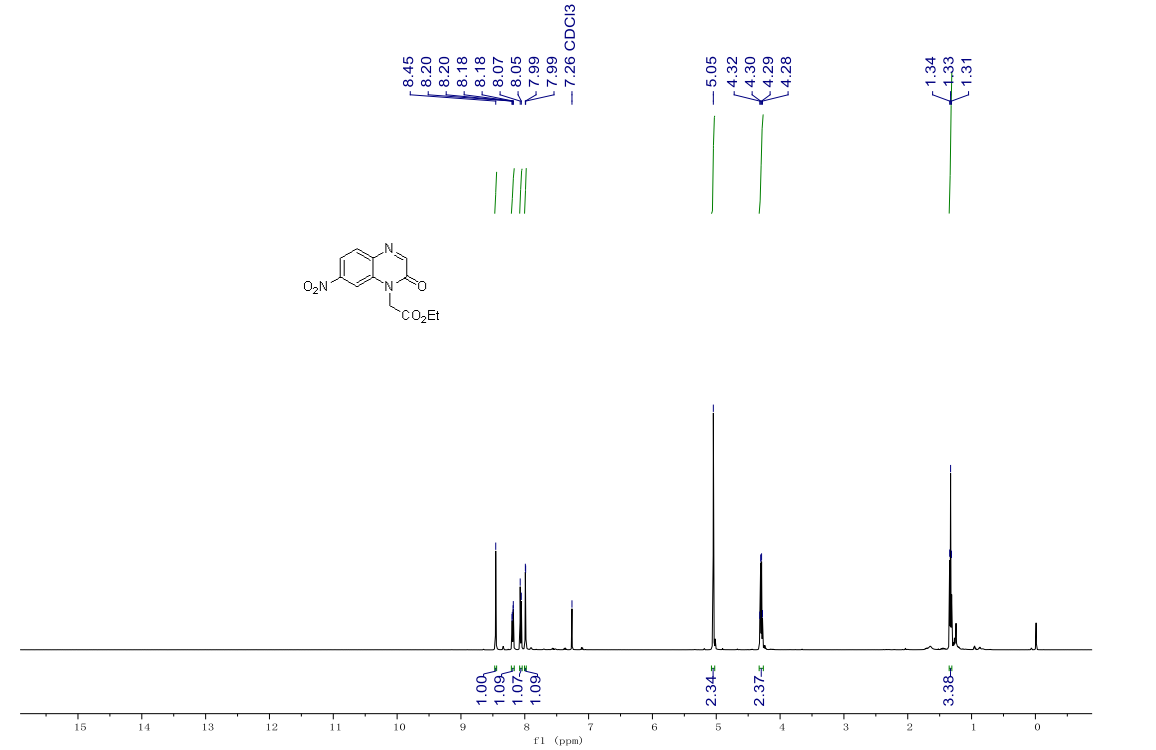


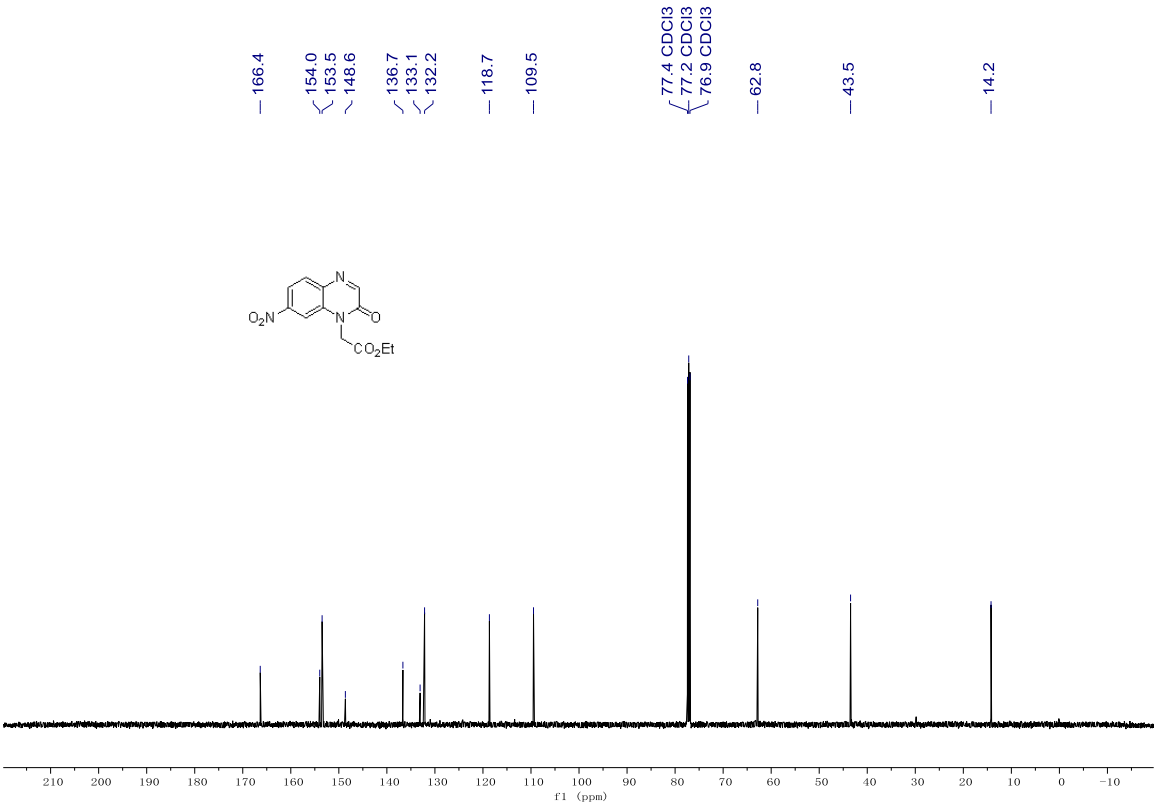
1-ethyl-7-nitroquinoxalin-2(1*H*)-one (2c)



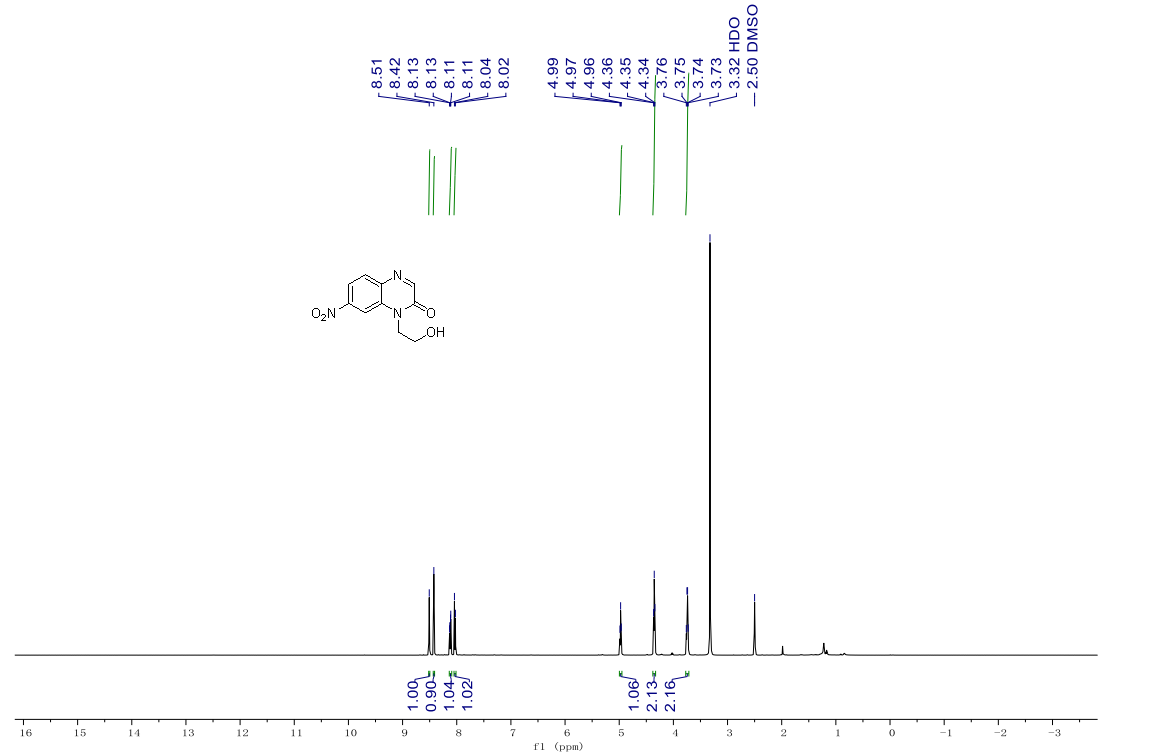


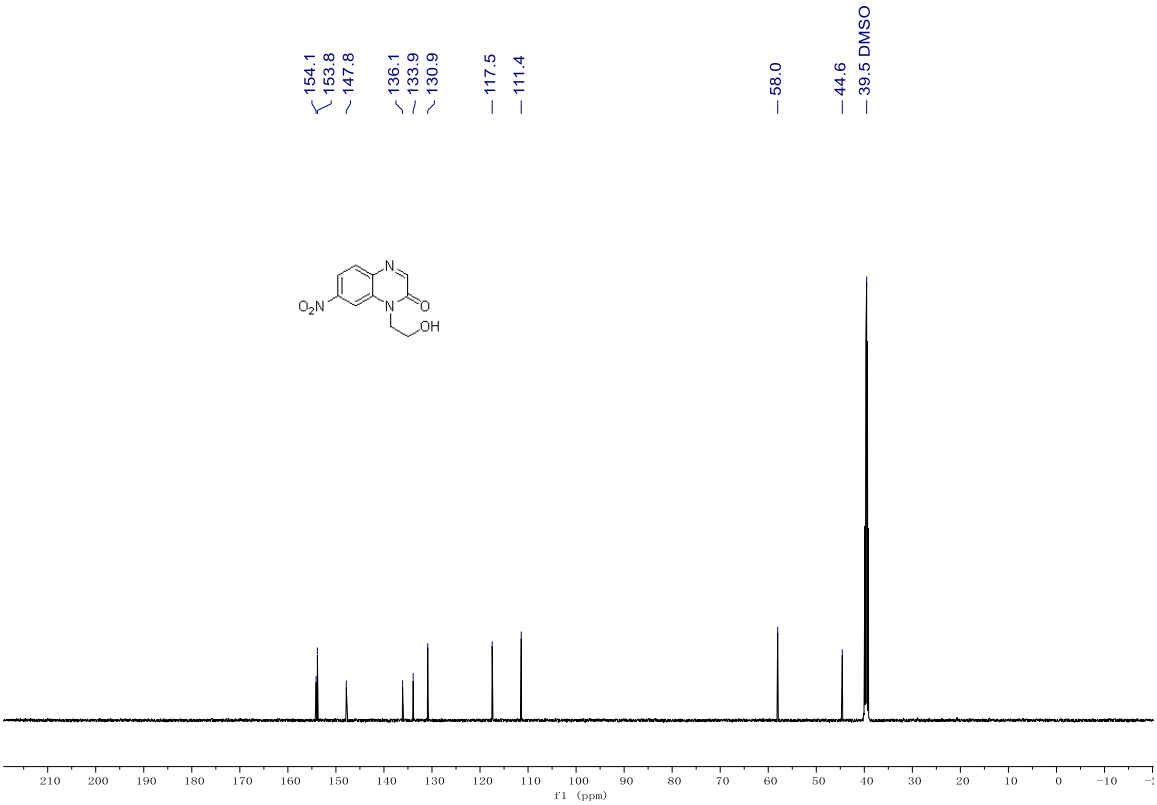
ethyl 2-(7-nitro-2-oxoquinoxalin-1(2*H*)-yl)acetate (2d)



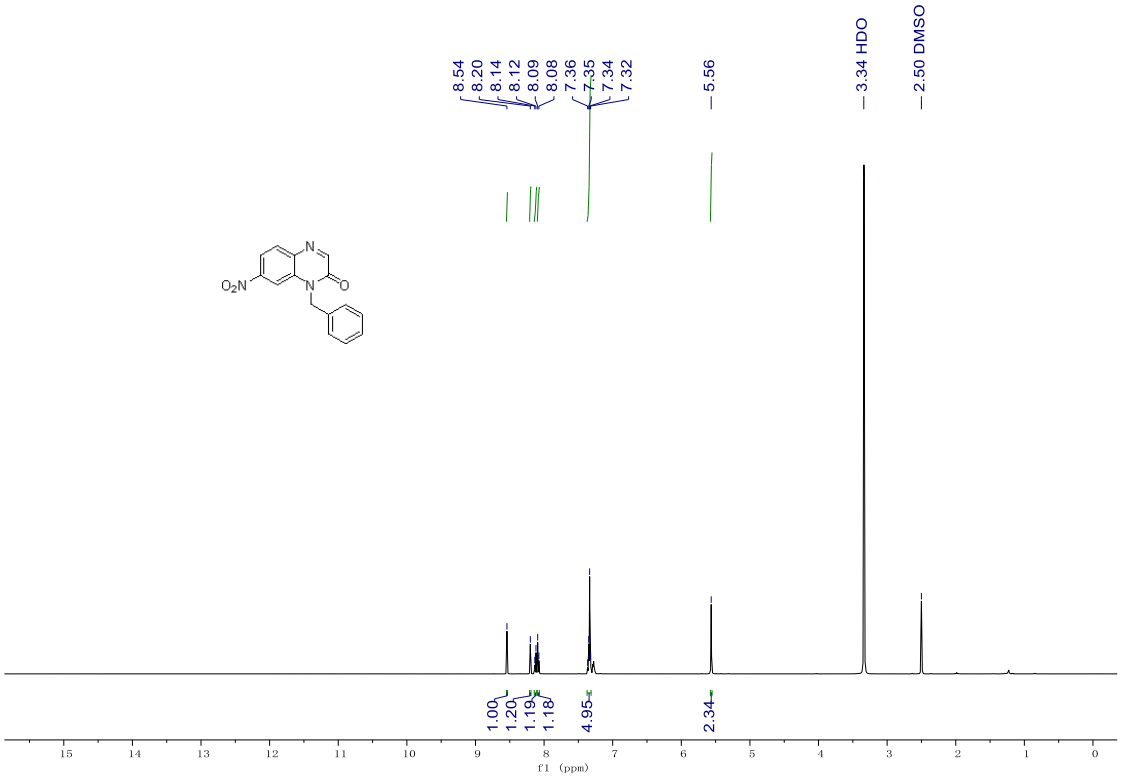


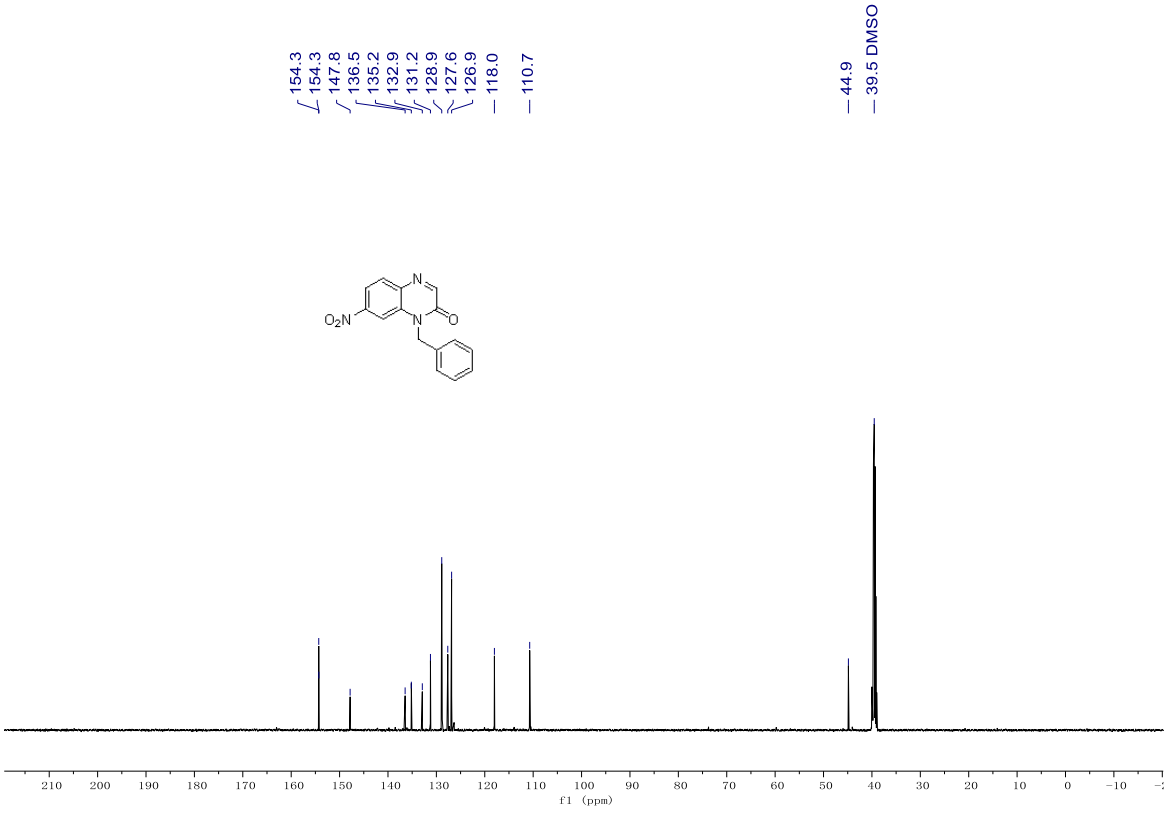
1-(2-hydroxyethyl)-7-nitroquinoxalin-2(1*H*)-one (2e)



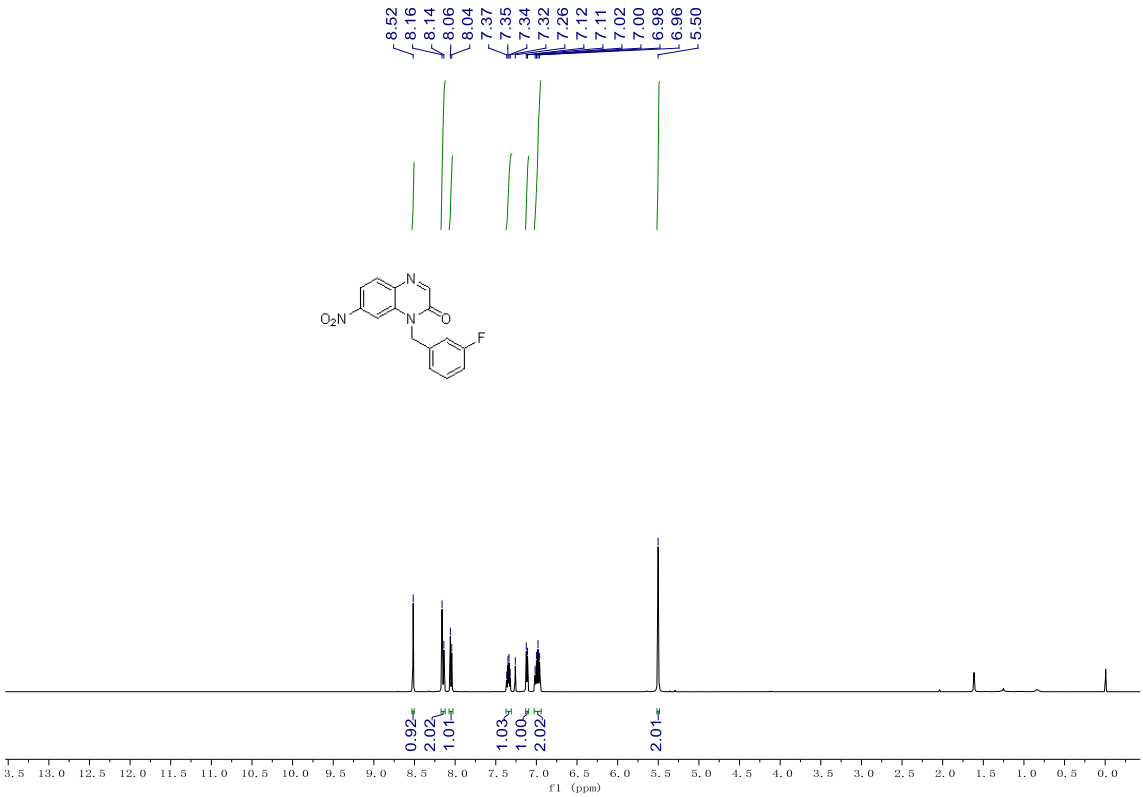


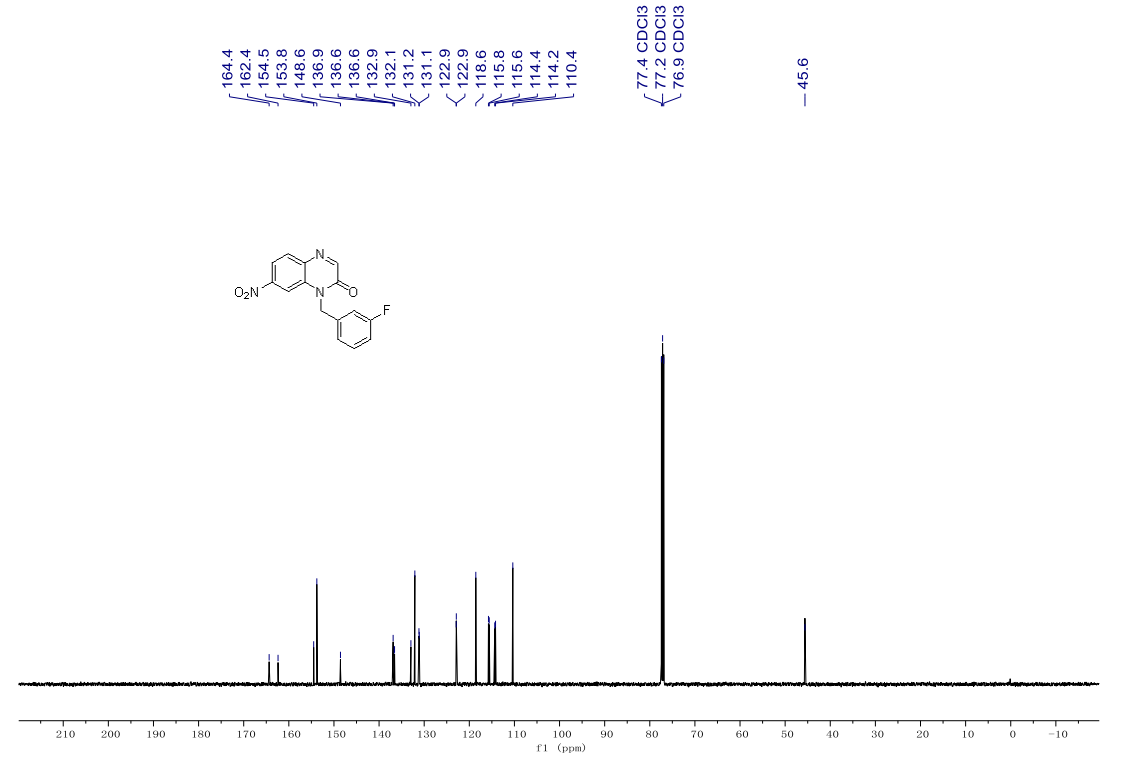
1-benzyl-7-nitroquinoxalin-2(1*H*)-one (2f)



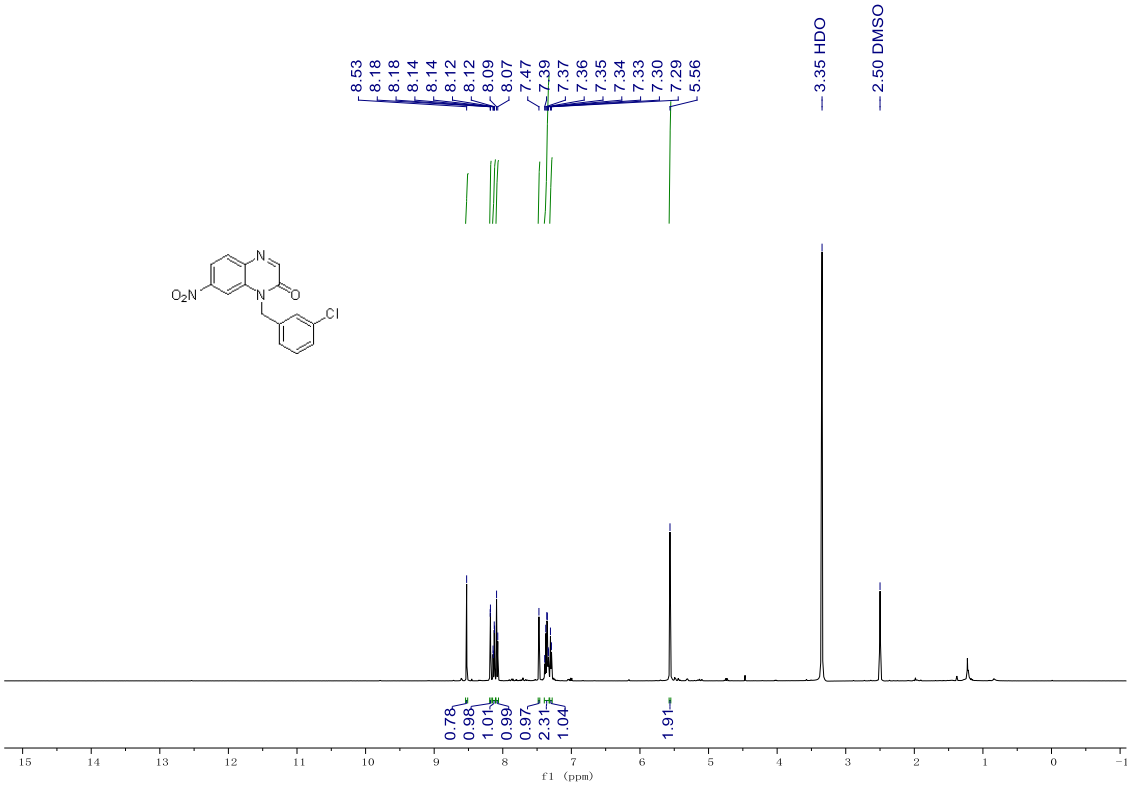


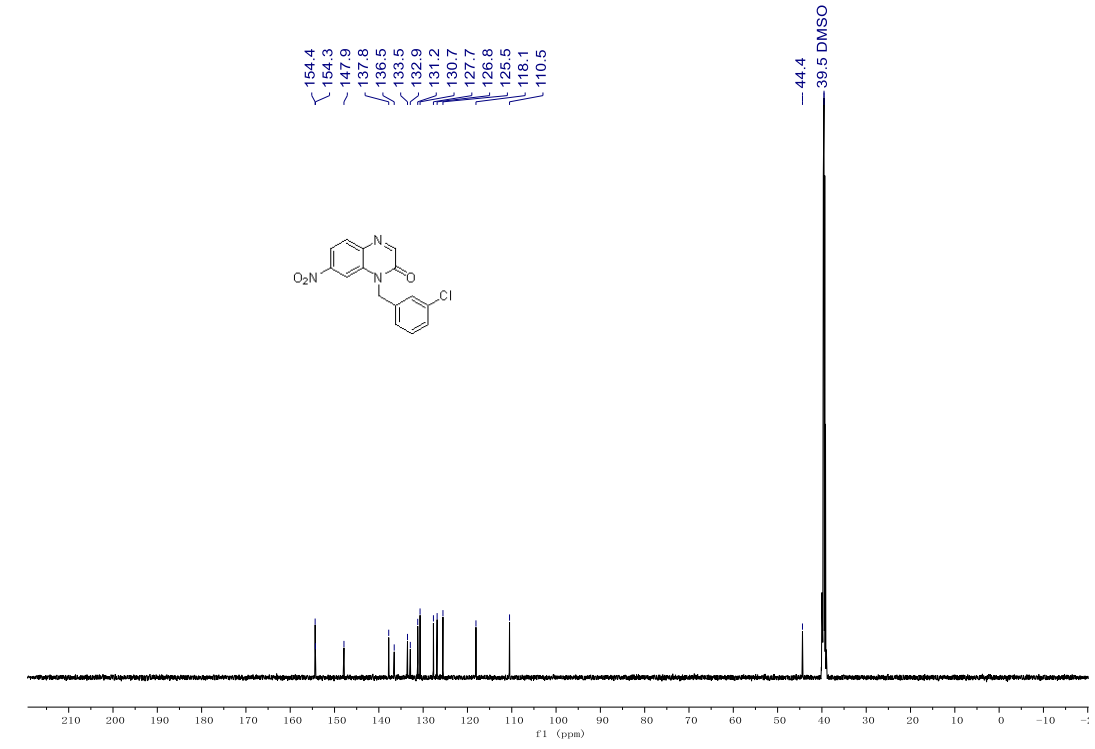
1-(3-fluorobenzyl)-7-nitroquinoxalin-2(1*H*)-one (2g)



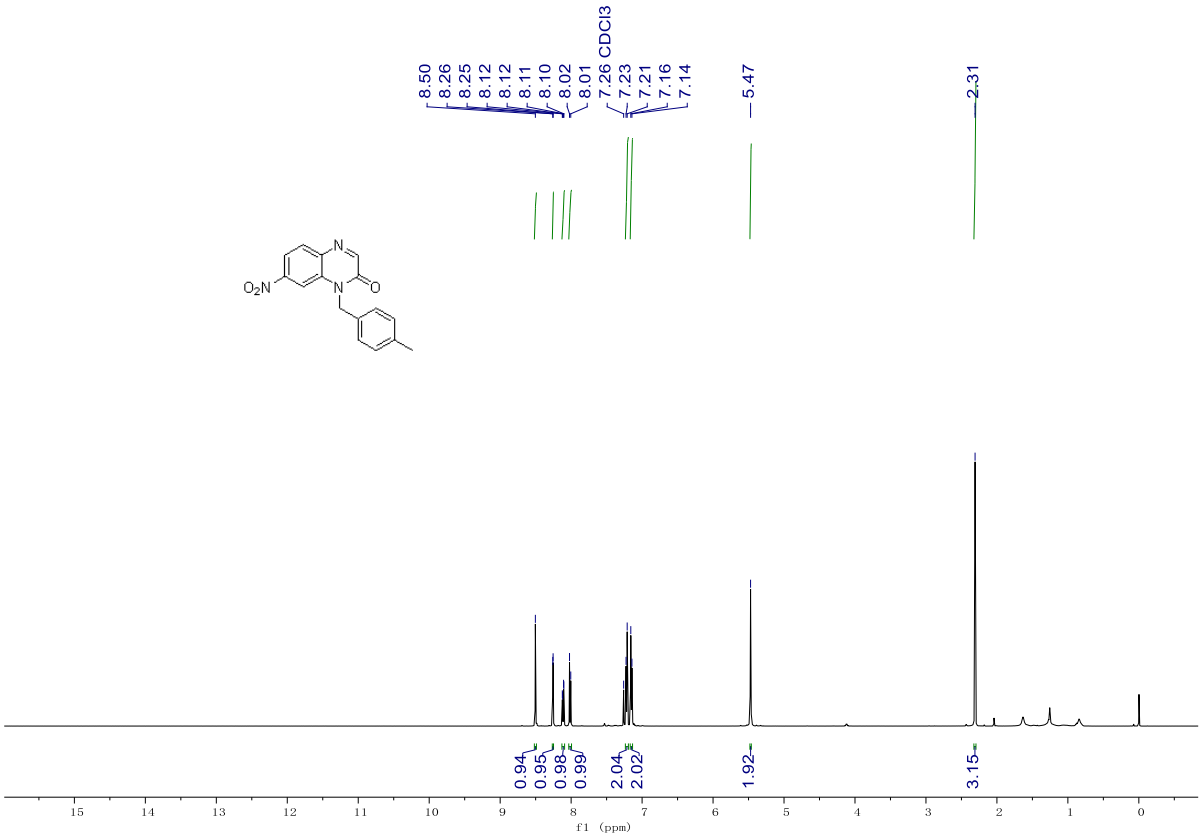


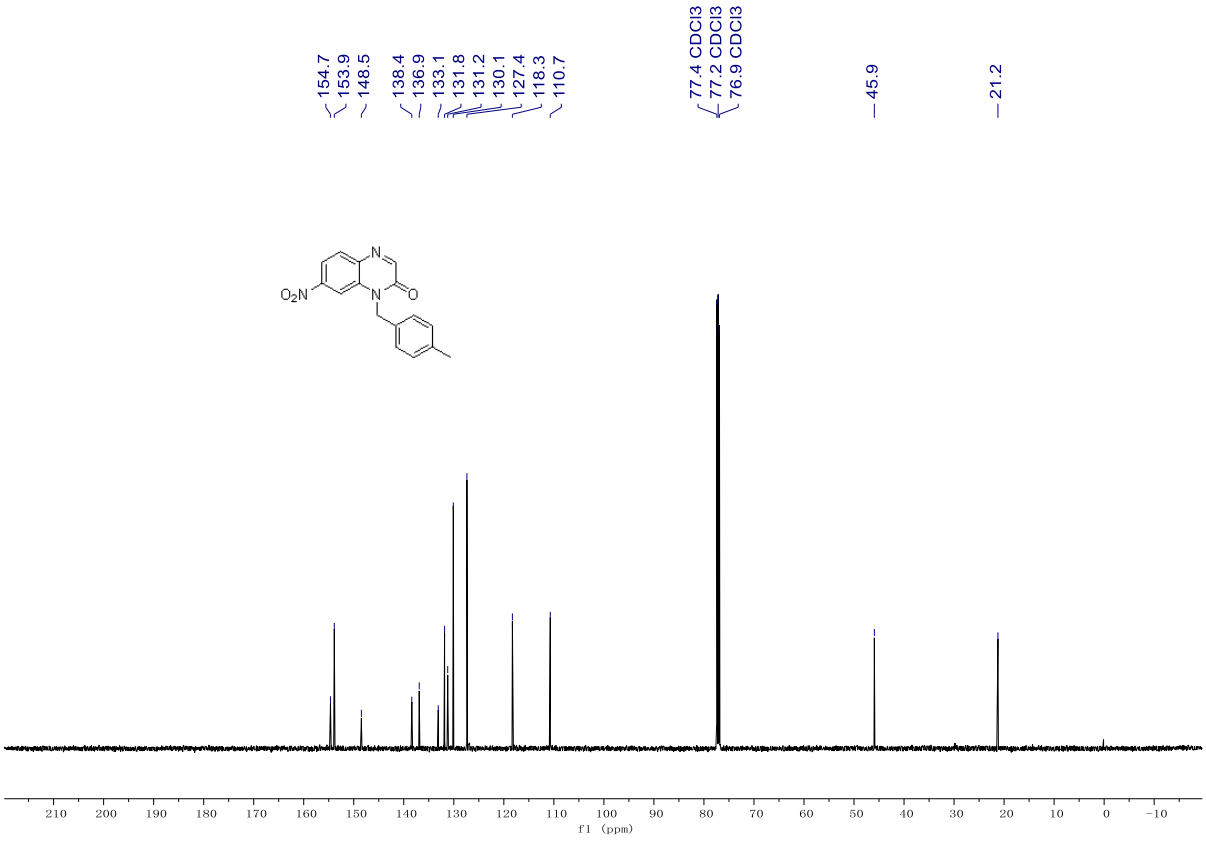
1-(3-chlorobenzyl)-7-nitroquinoxalin-2(1*H*)-one (2h)



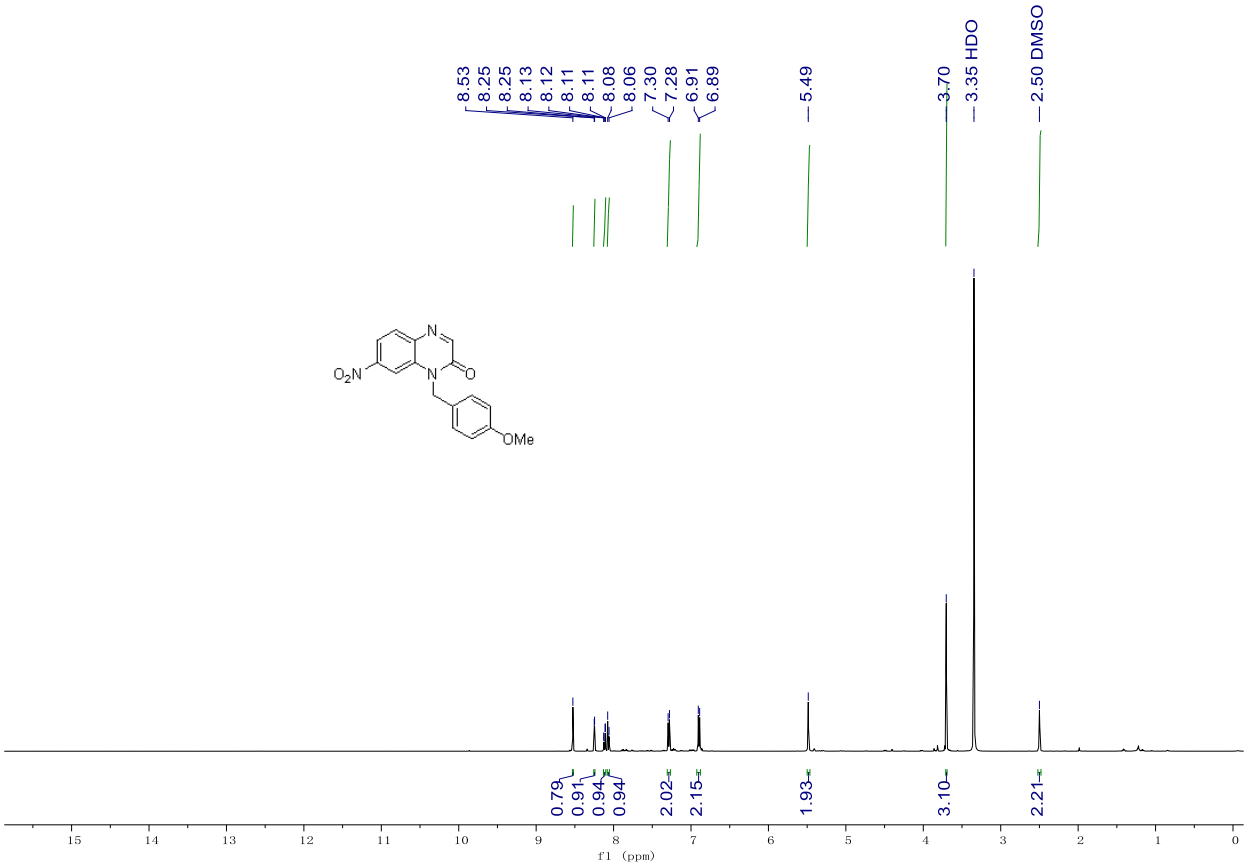


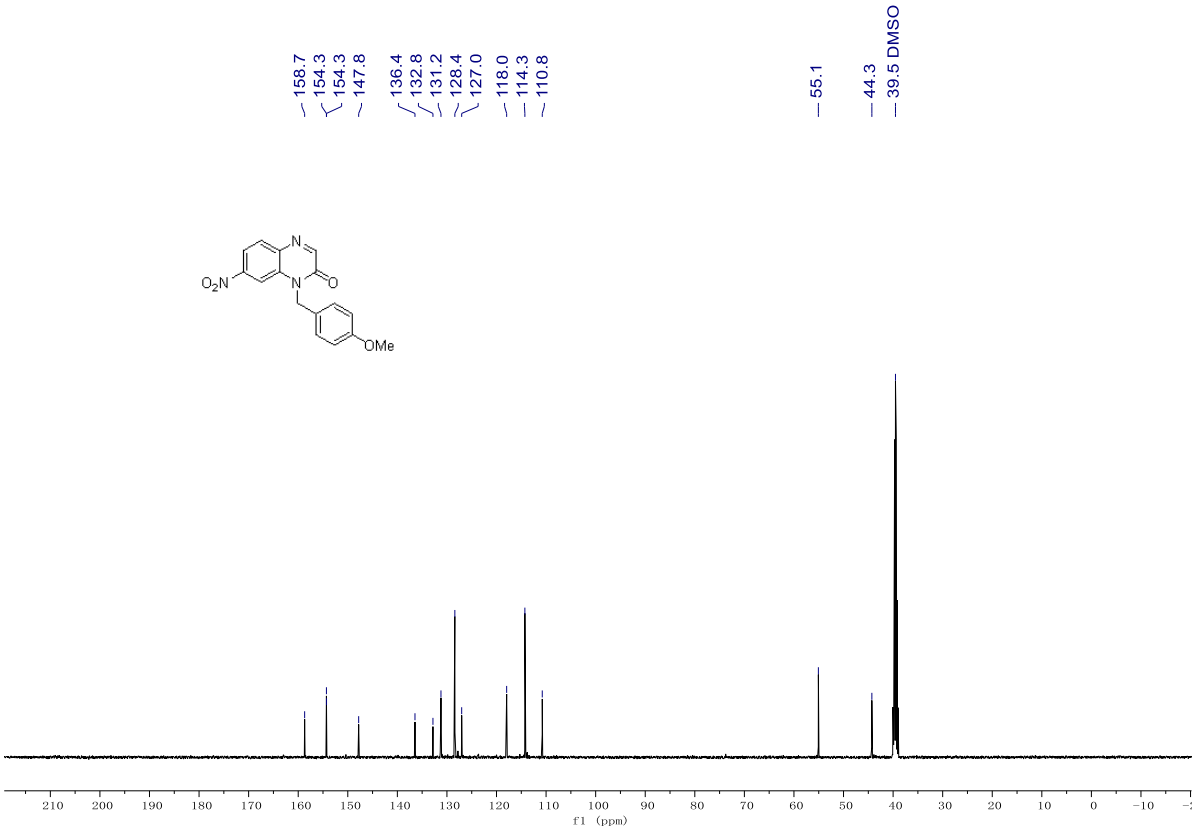
1-(4-methylbenzyl)-7-nitroquinoxalin-2(1*H*)-one (2i)



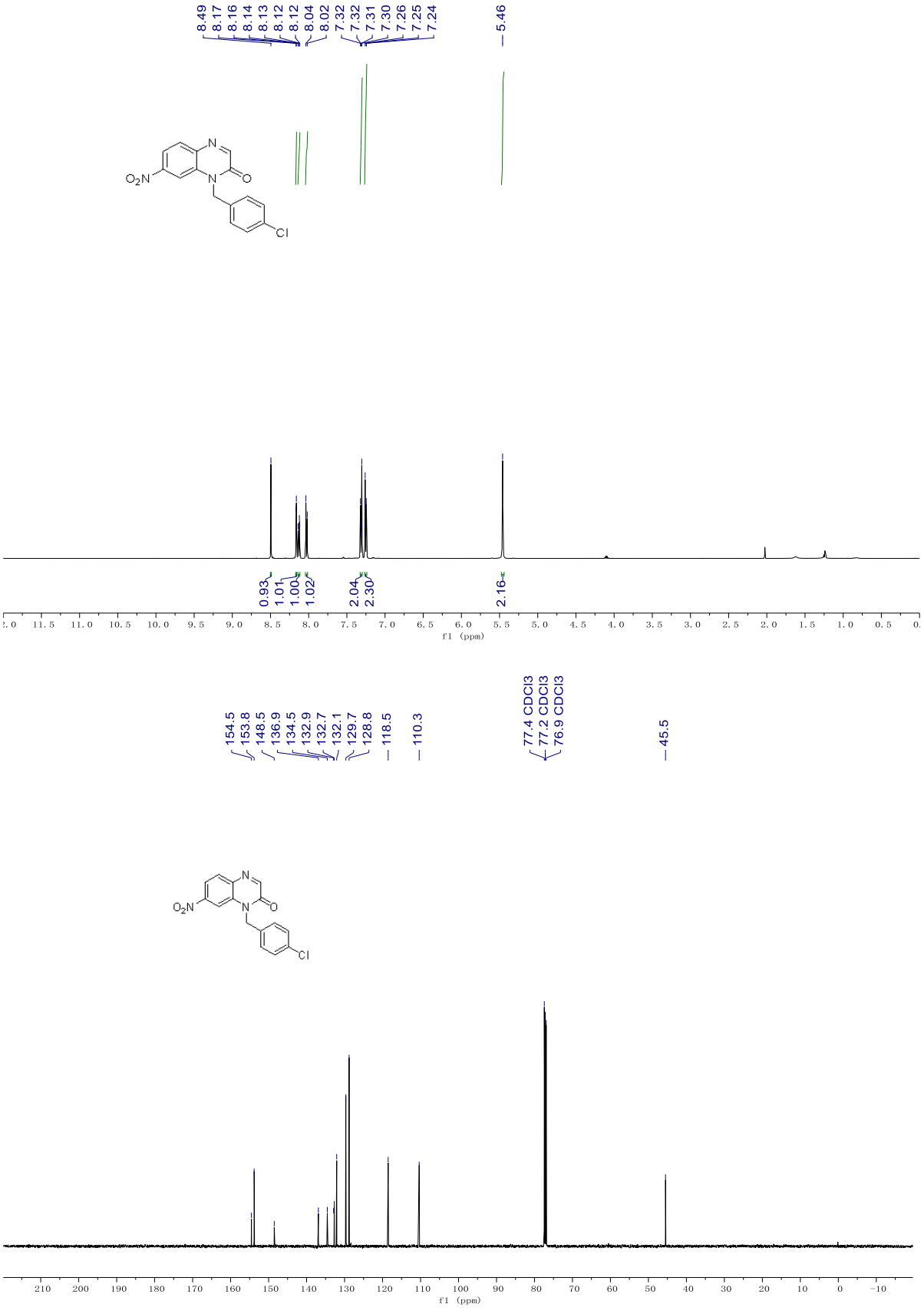


1-(4-methoxybenzyl)-7-nitroquinoxalin-2(1*H*)-one (2j)

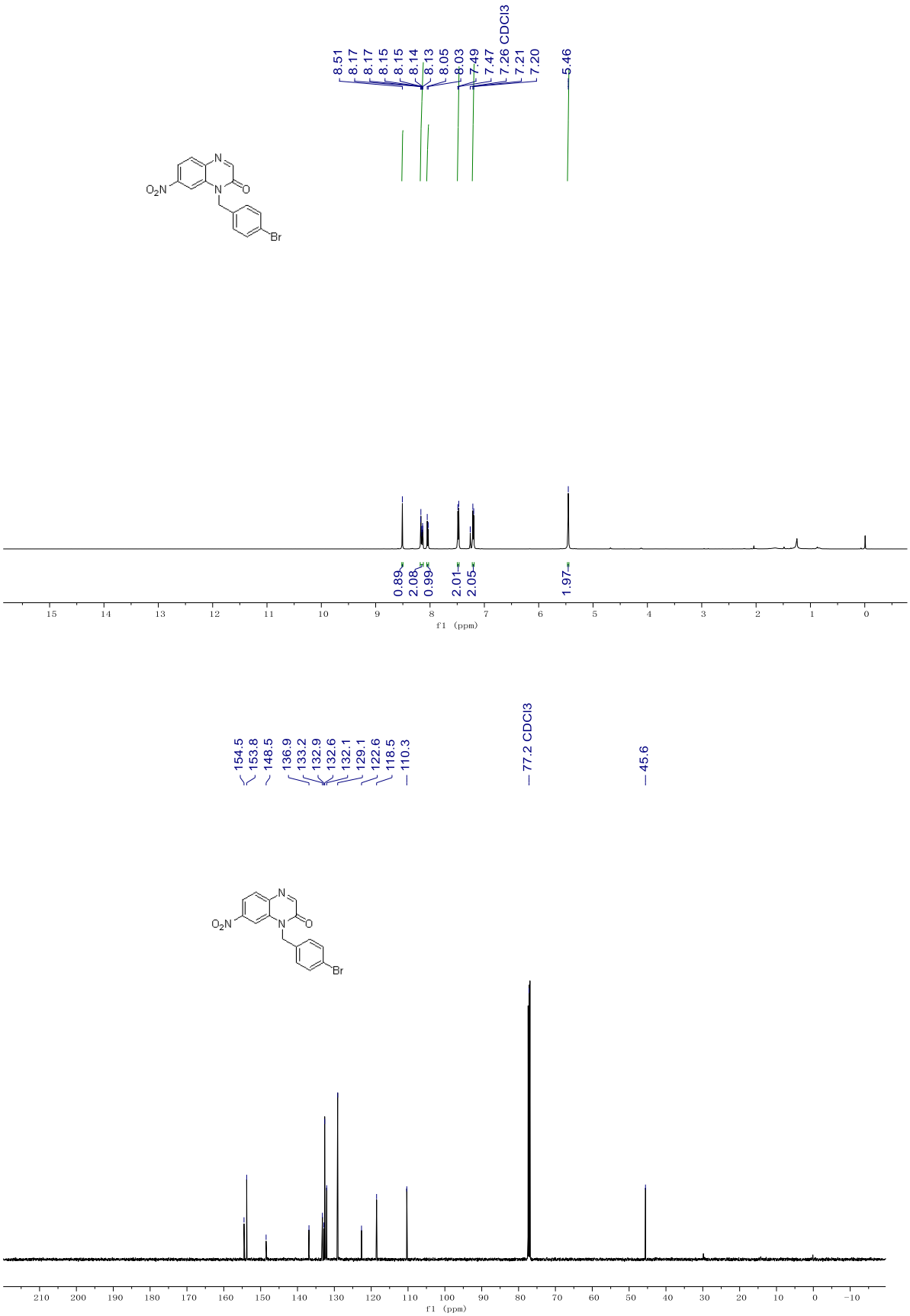




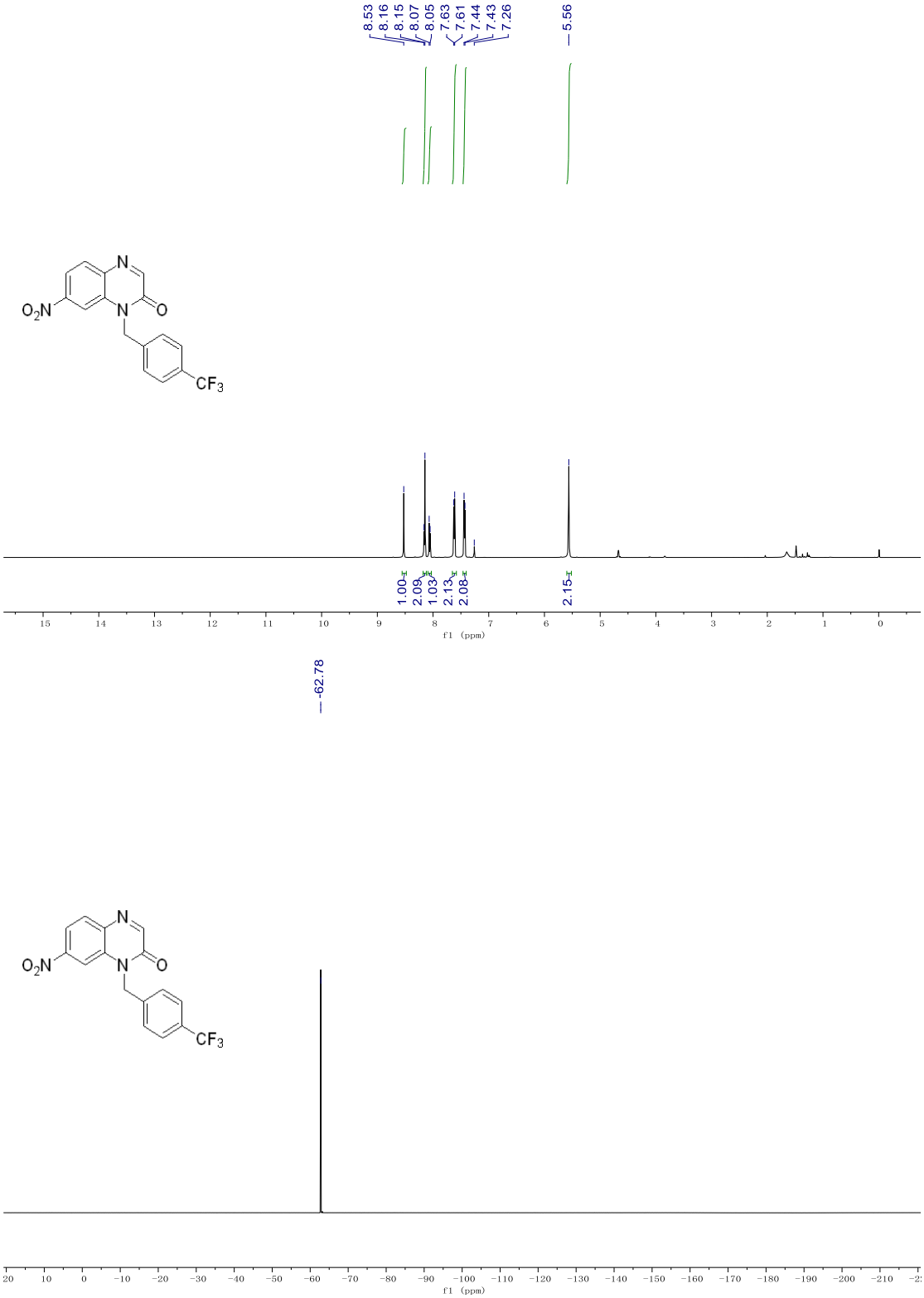
1-(4-chlorobenzyl)-7-nitroquinoxalin-2(1*H*)-one (2k)

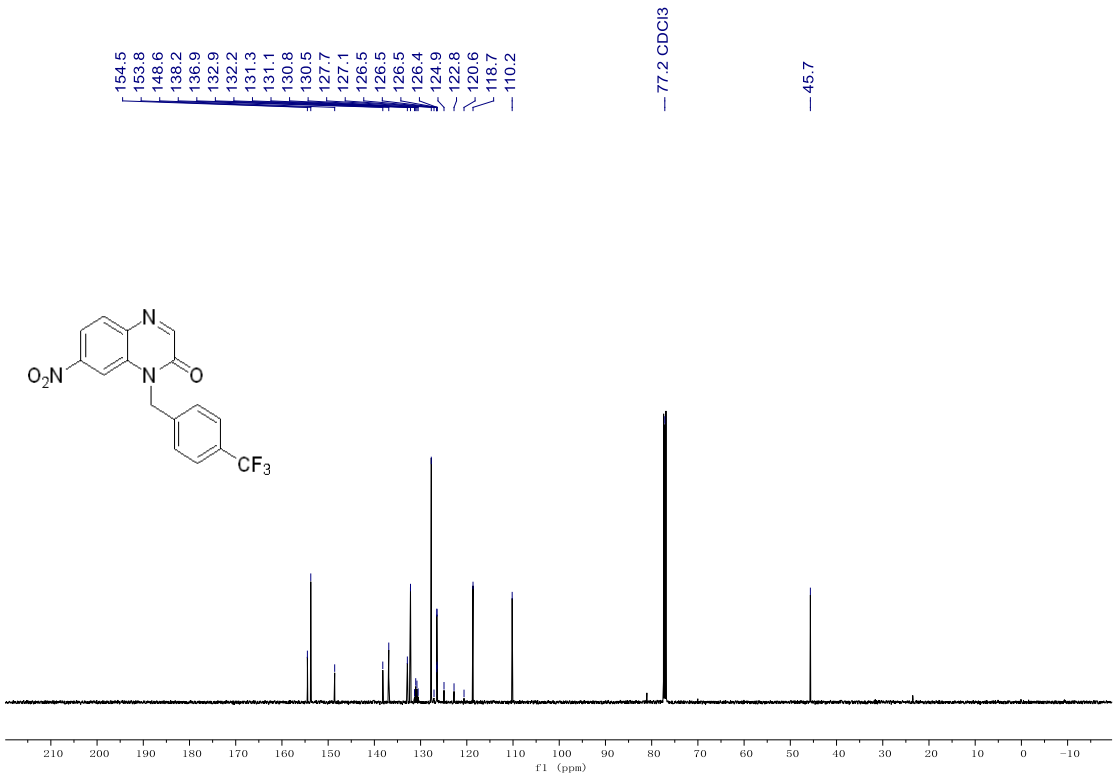


1-(4-bromobenzyl)-7-nitroquinoxalin-2(1*H*)-one (2l)

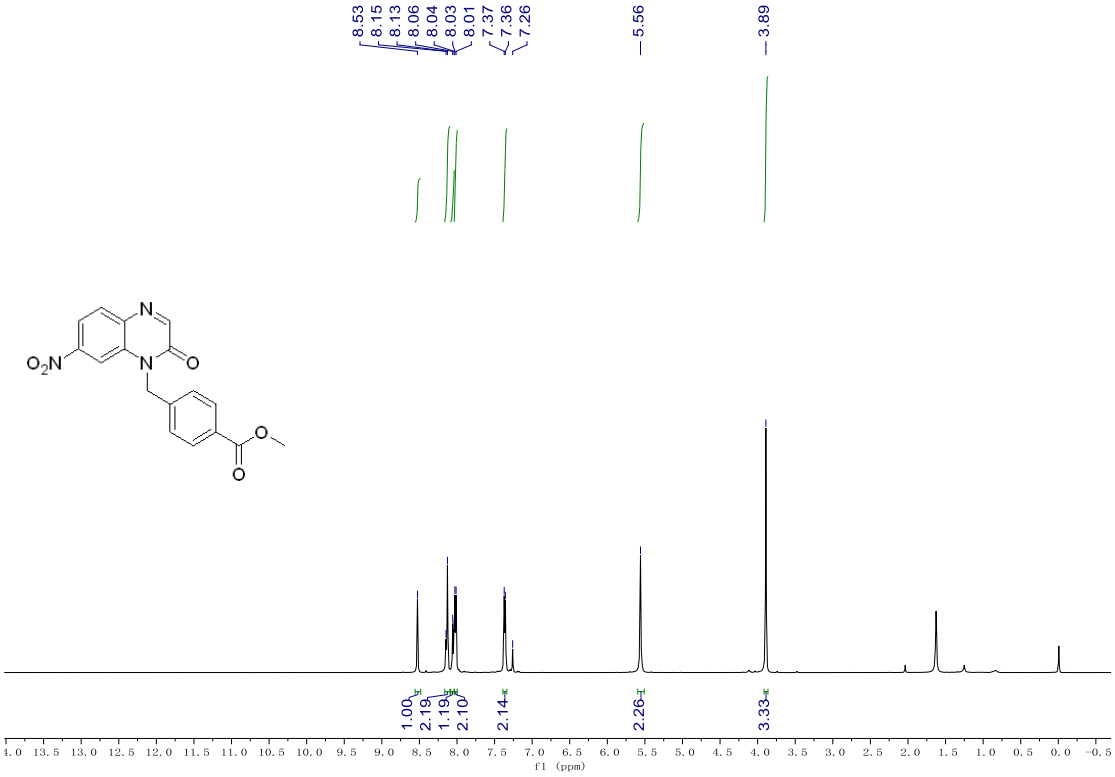


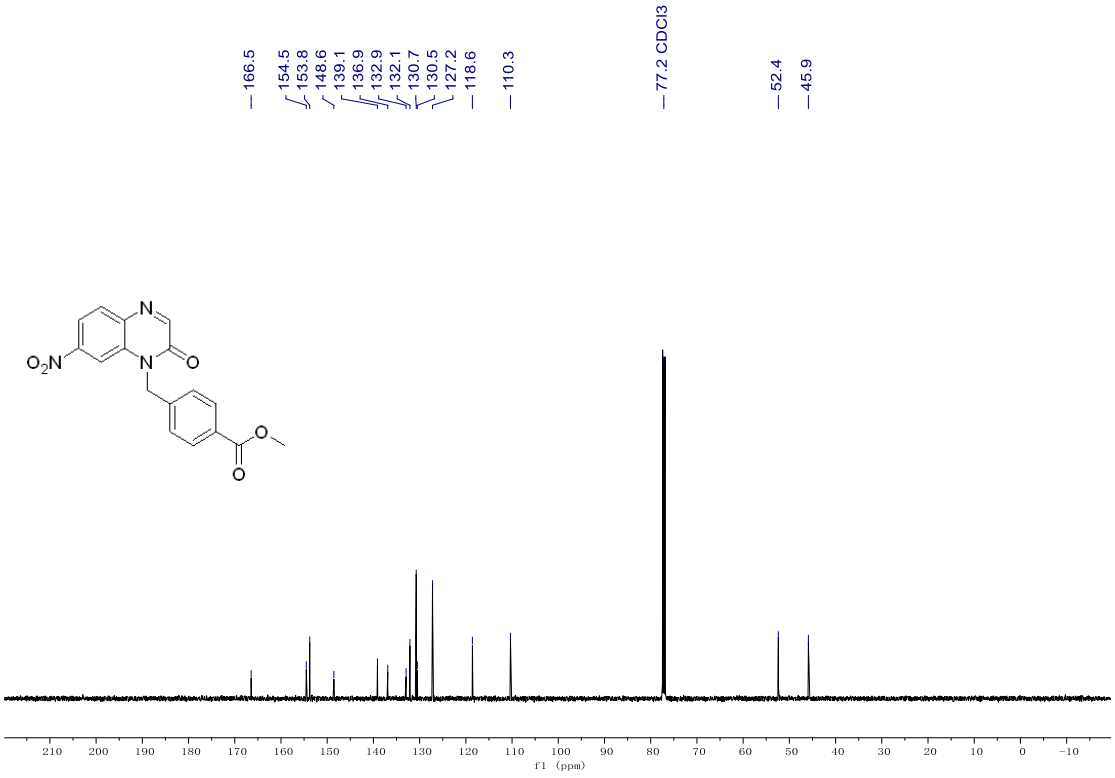
7-nitro-1-(4-(trifluoromethyl)benzyl)quinoxalin-2(1*H*)-one (2m)



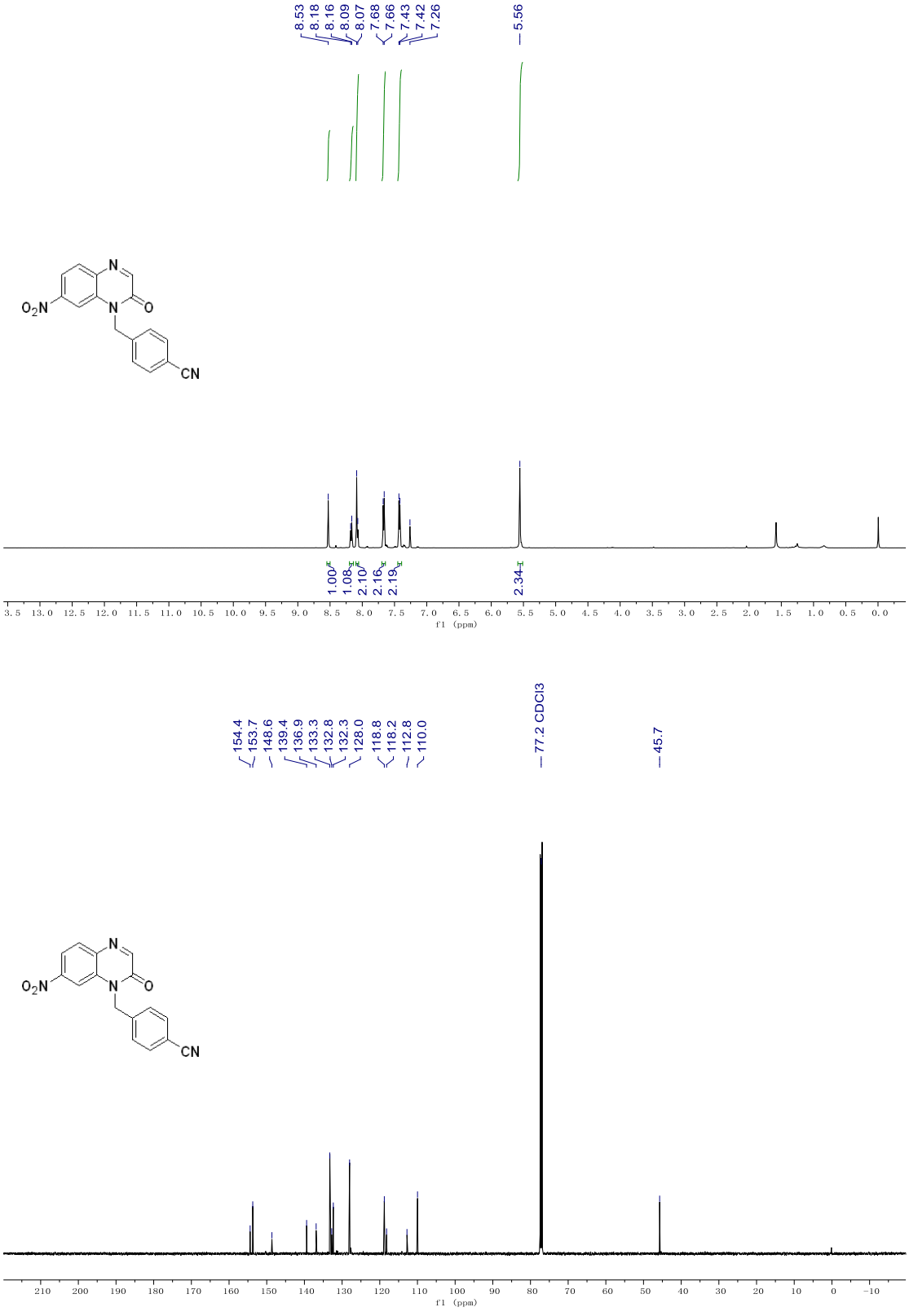

154.5
153.8
148.6
138.2
136.9
132.9
132.2
131.3
131.1
130.8
130.5
127.7
127.1
126.5
126.5
126.5
126.4
124.9
122.8
120.6
118.7
110.2
77.2 CDCl3
45.7
O2N
N
N
O
CF3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

methyl 4-((7-nitro-2-oxoquinoxalin-1(2*H*)-yl)methyl)benzoate (2n)

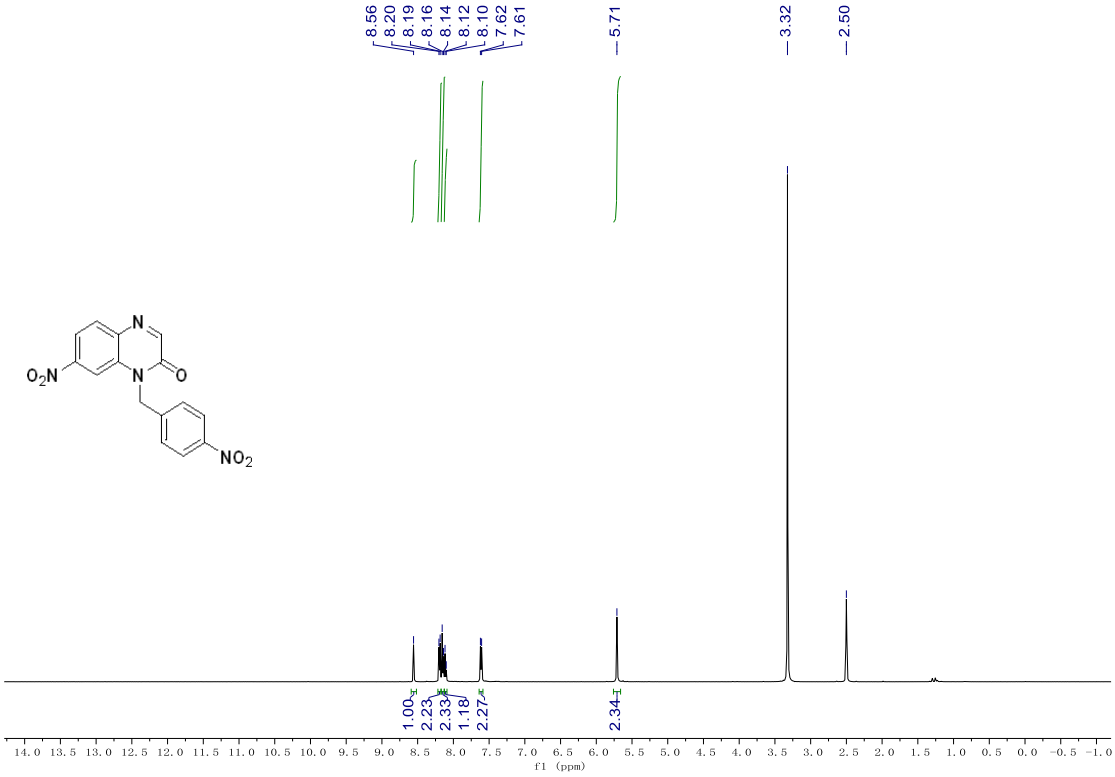


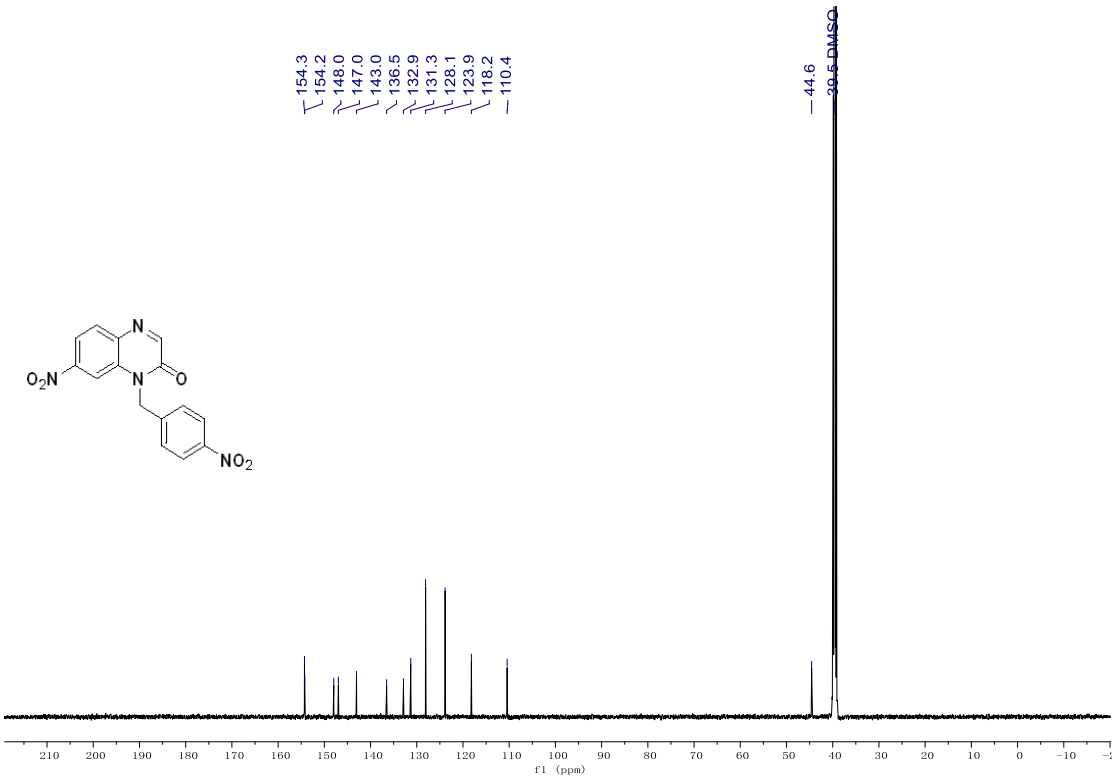


4-((7-nitro-2-oxoquinoxalin-1(2*H*)-yl)methyl)benzonitrile (2o)

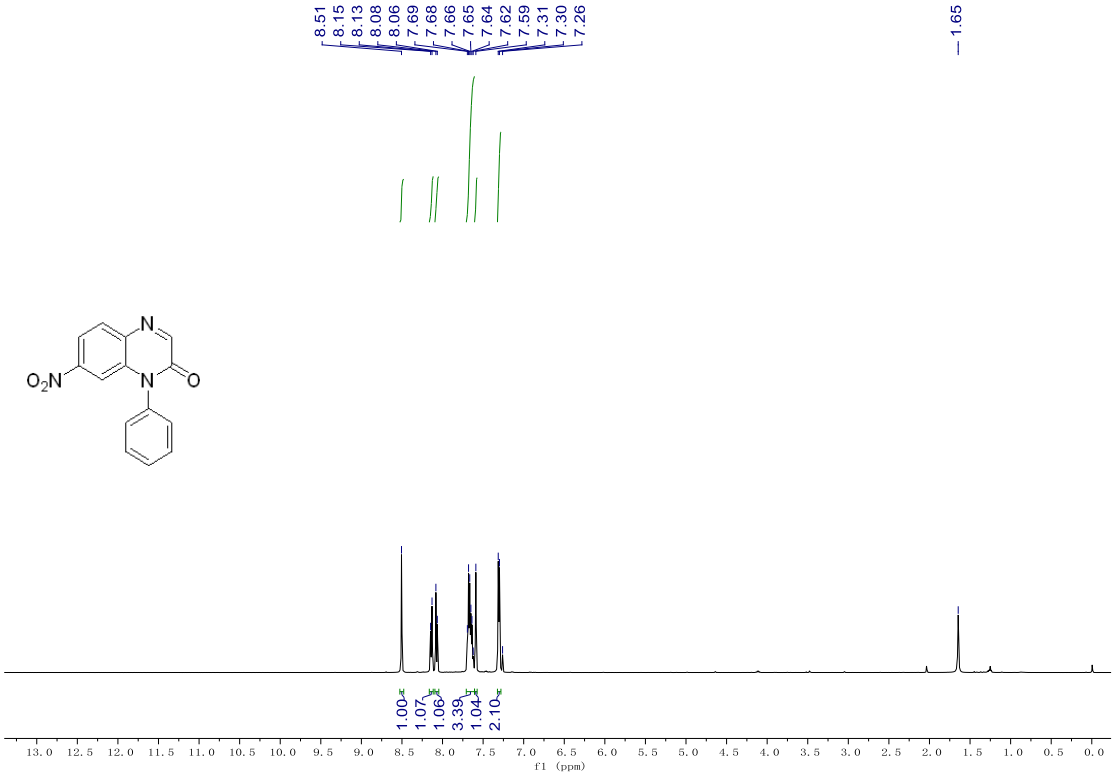


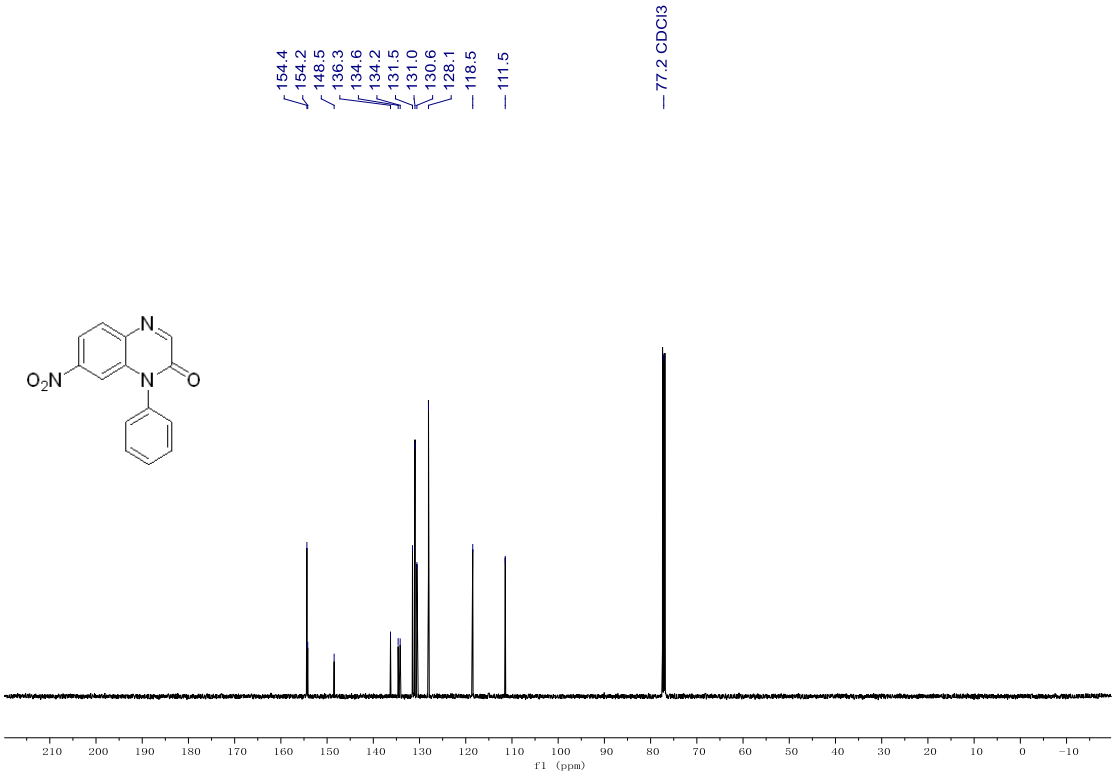
7-nitro-1-(4-nitrobenzyl)quinoxalin-2(1*H*)-one (2p)



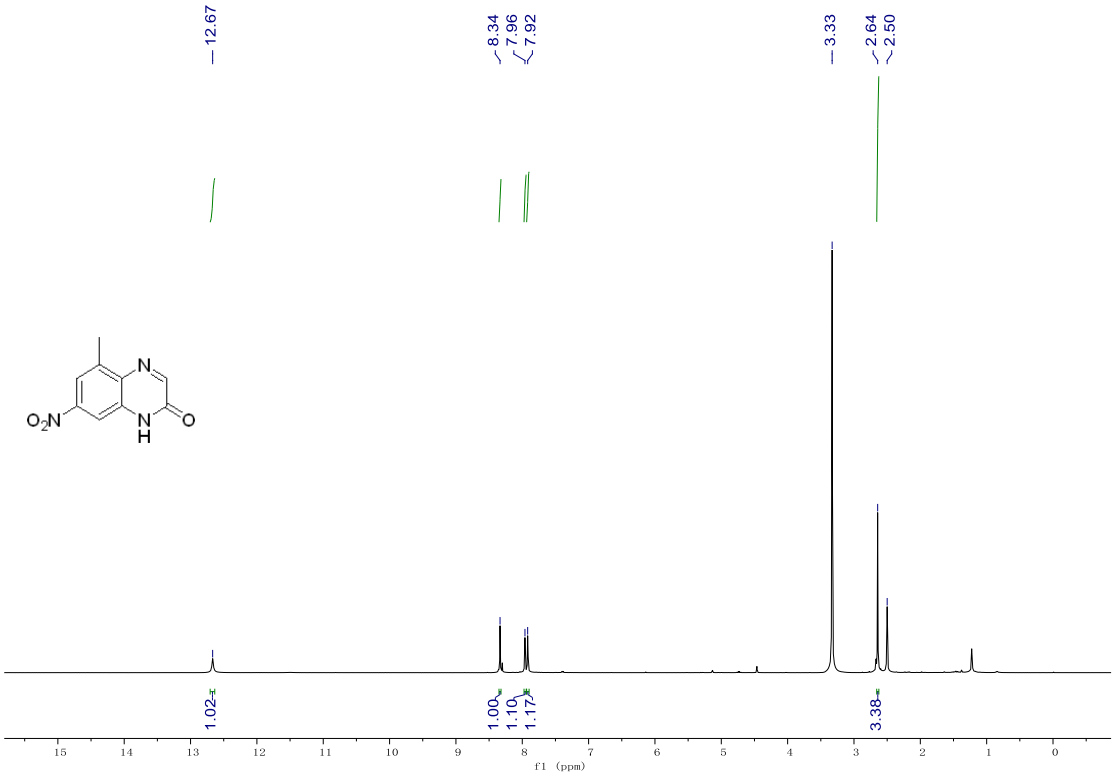


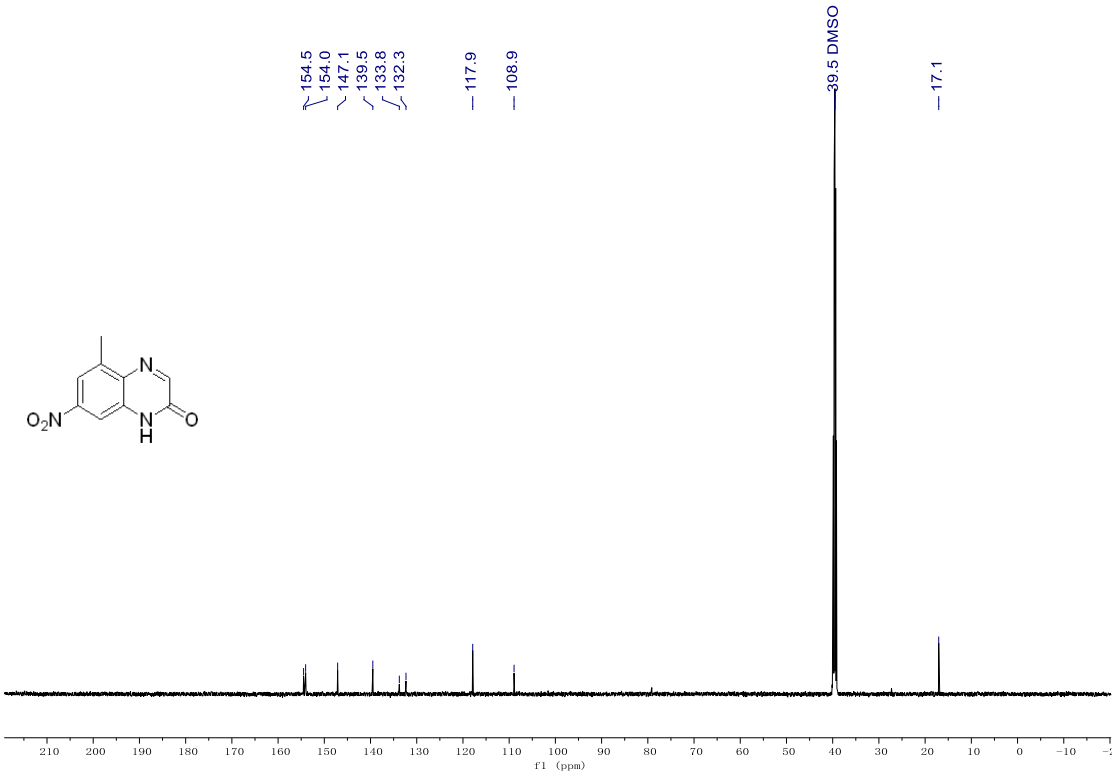
7-nitro-1-phenylquinoxalin-2(1*H*)-one (2q)



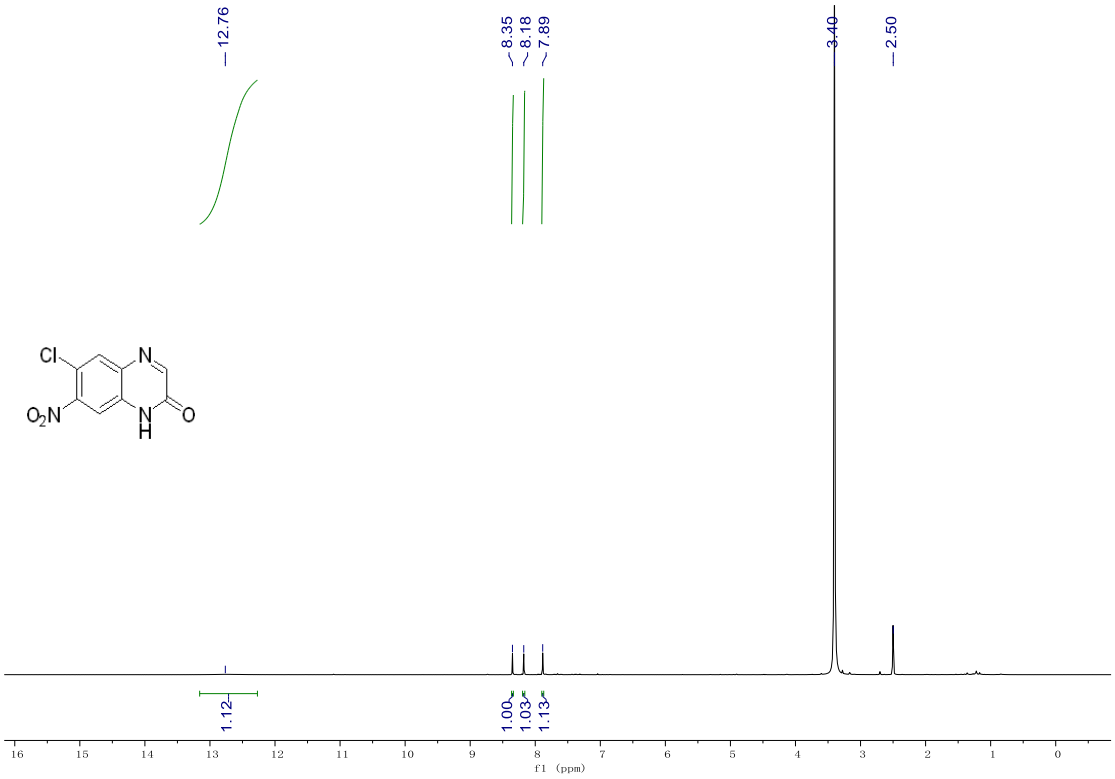


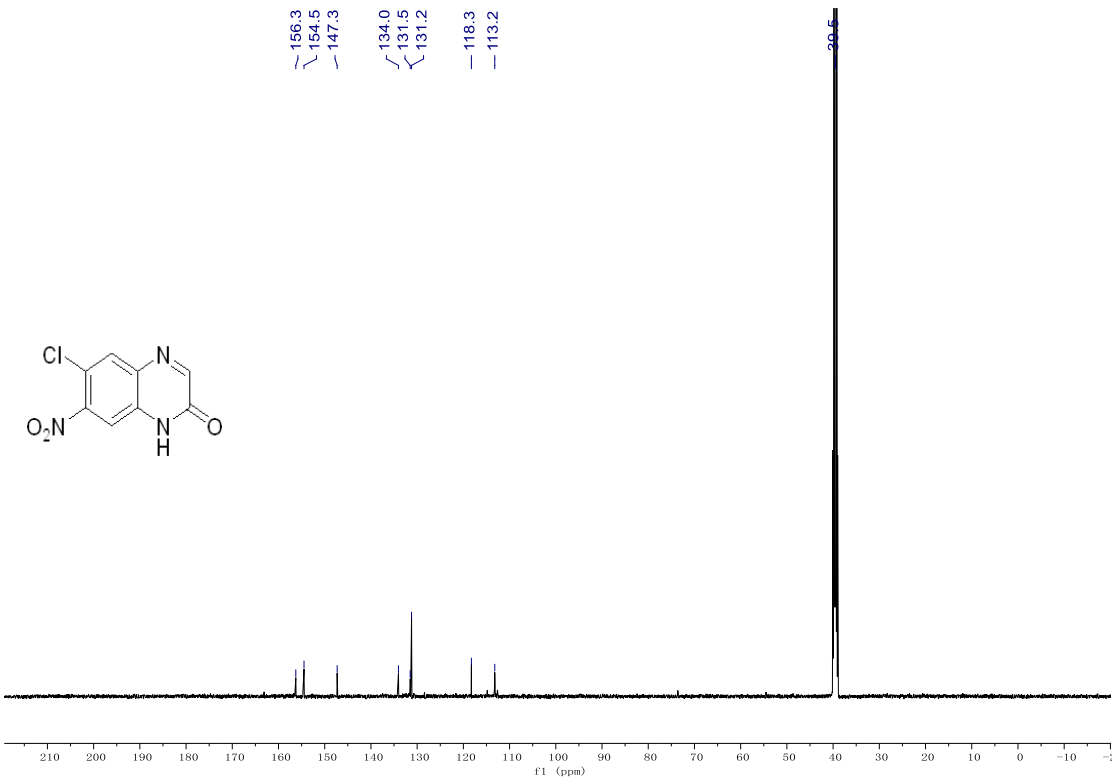
5-methyl-7-nitroquinoxalin-2(1*H*)-one (2r)



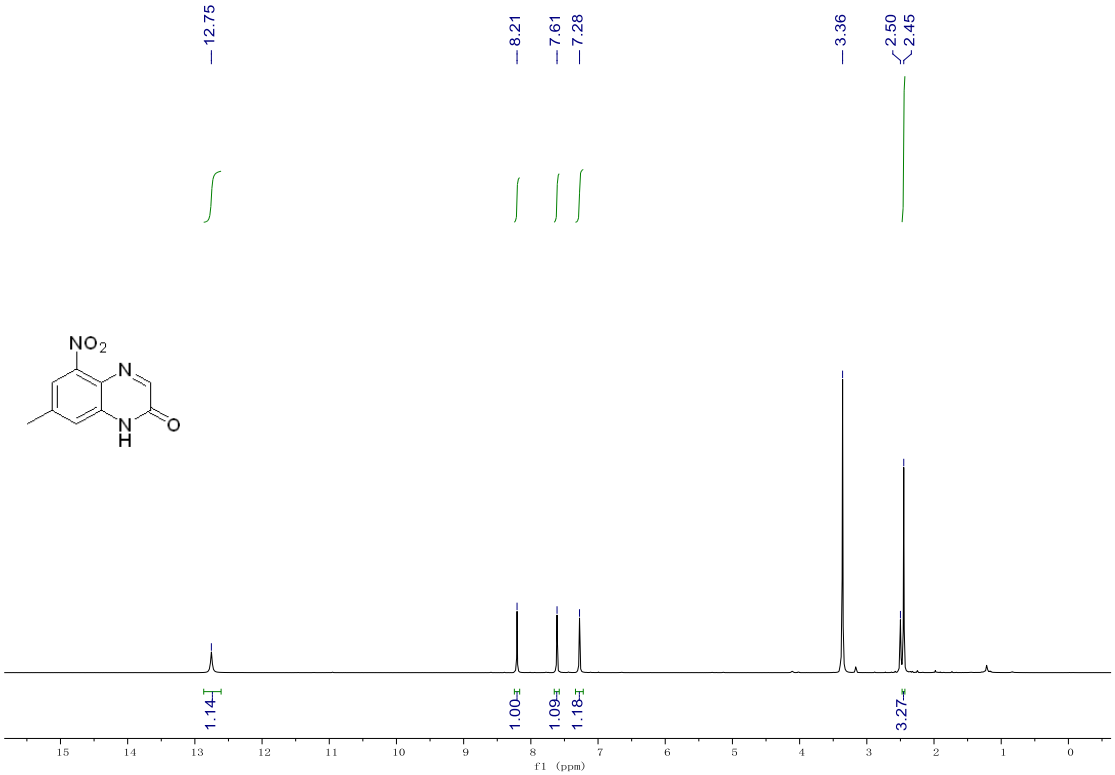


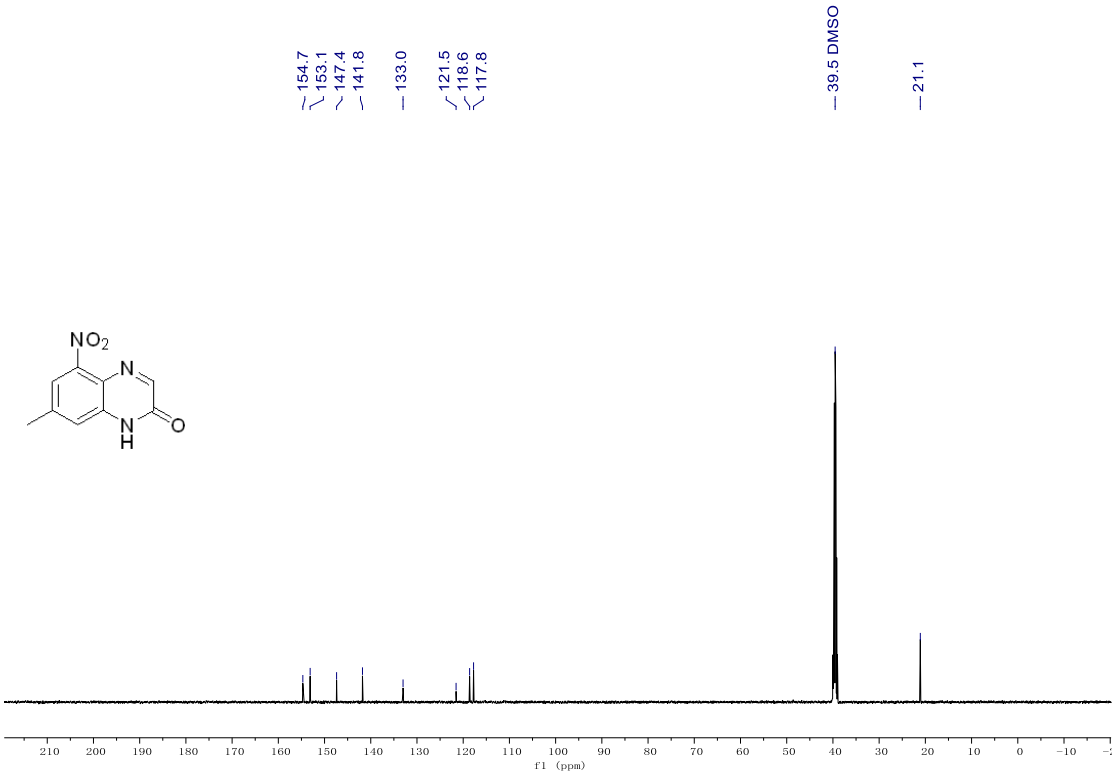
6-chloro-7-nitroquinoxalin-2(1*H*)-one (2s)



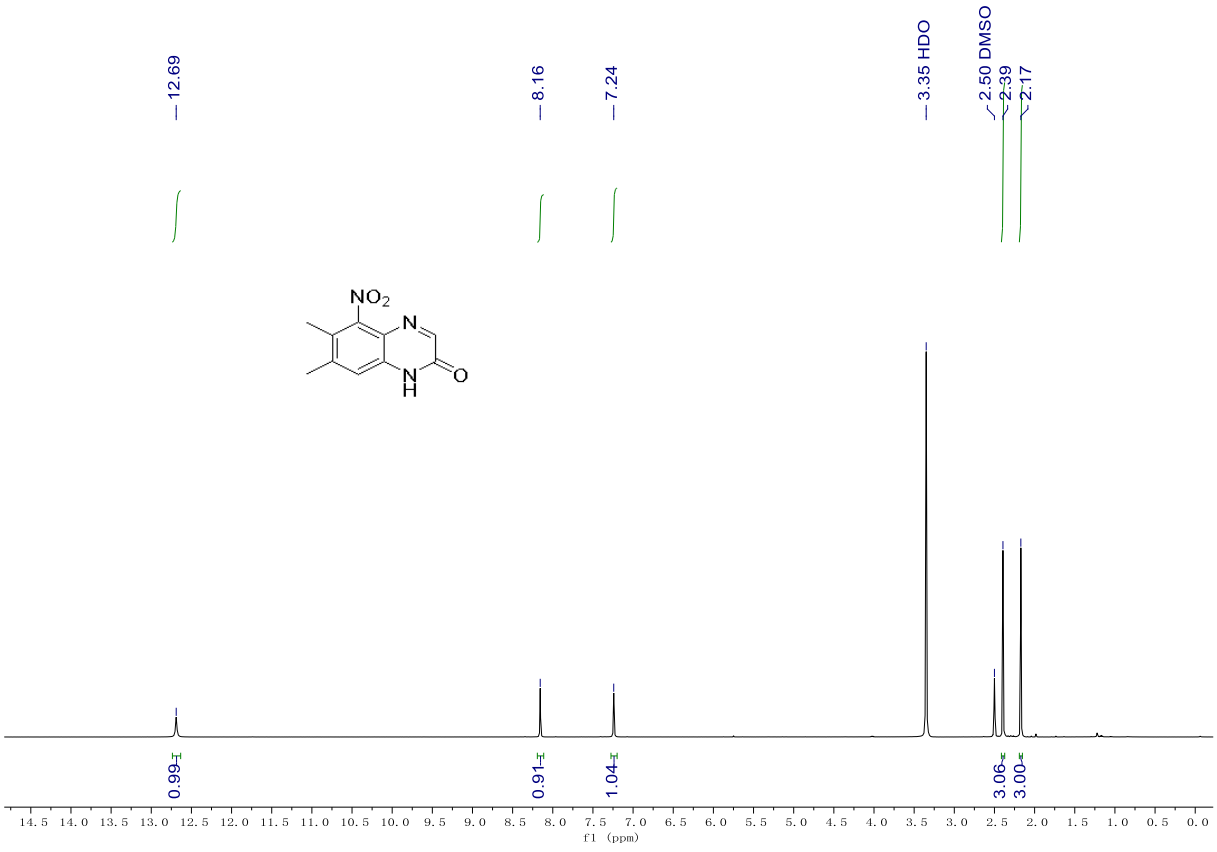


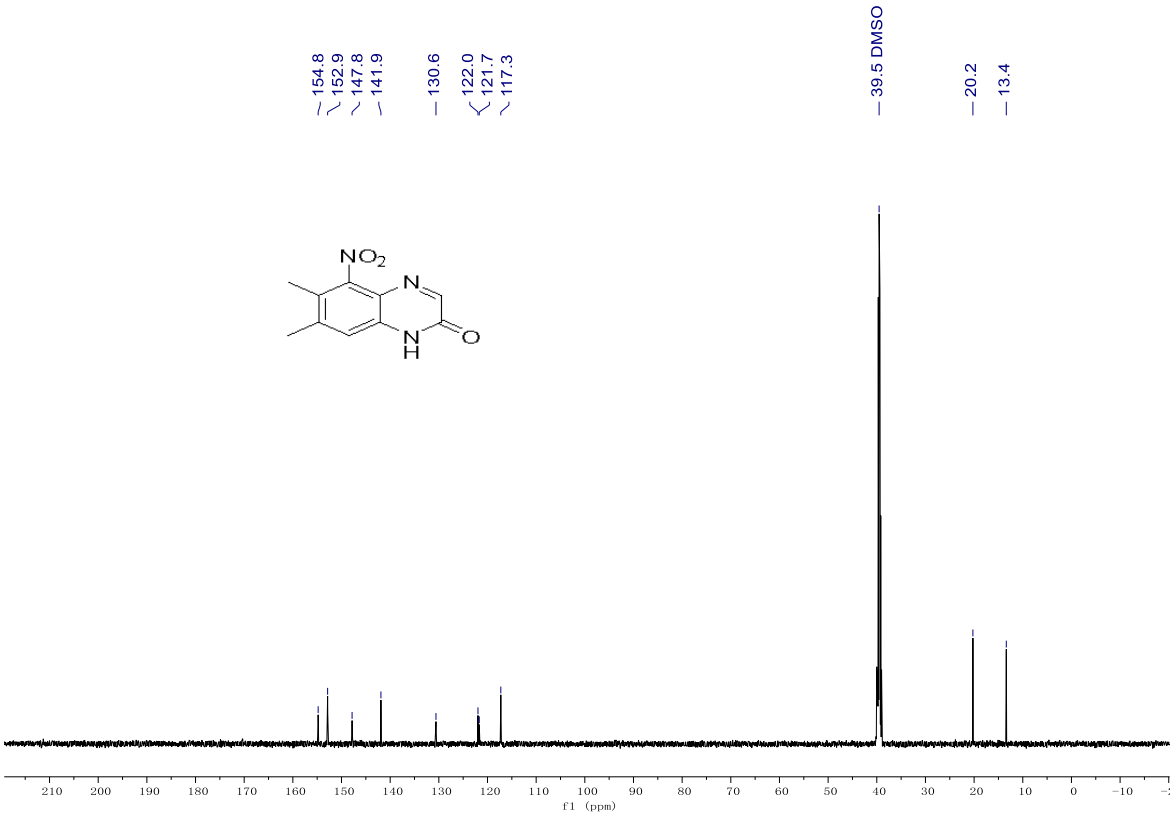
7-methyl-5-nitroquinoxalin-2(1*H*)-one (2u)



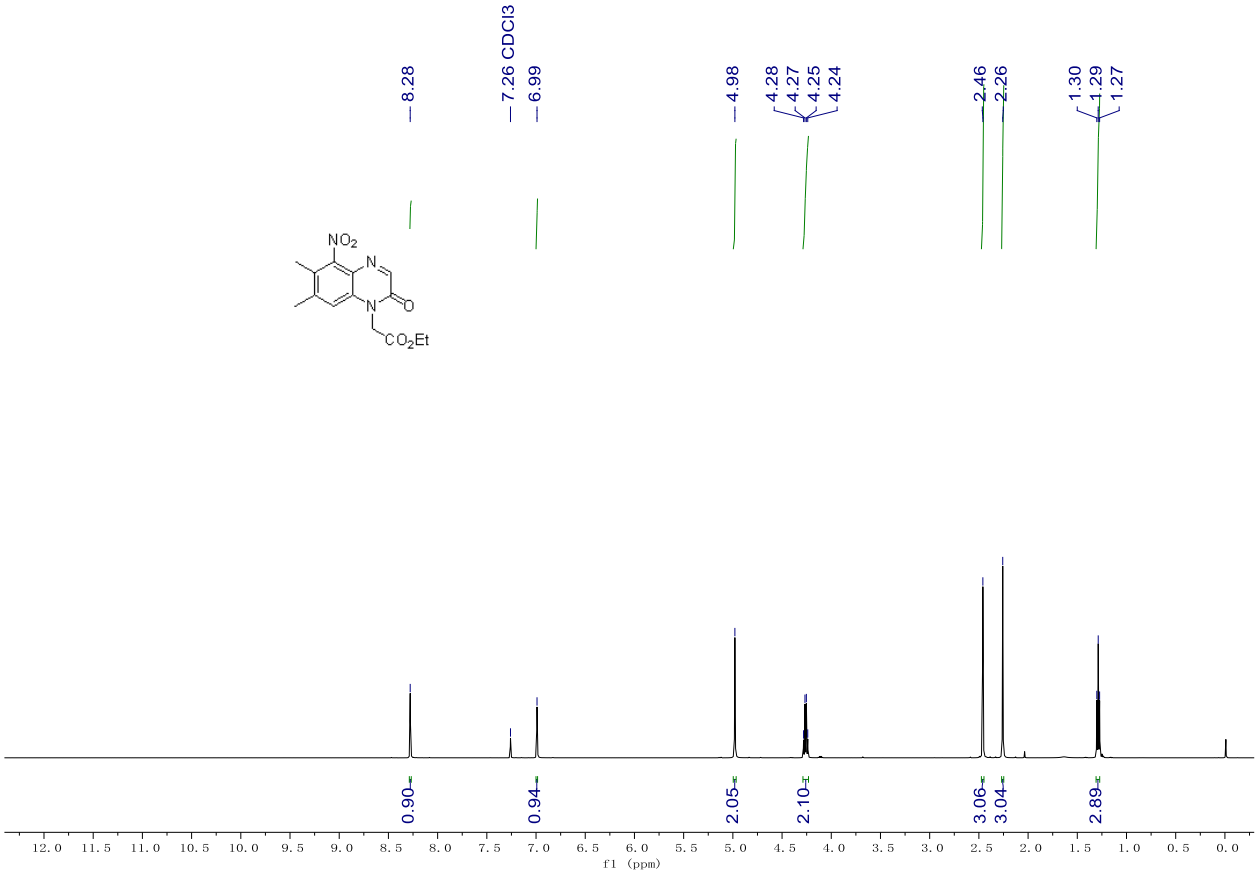


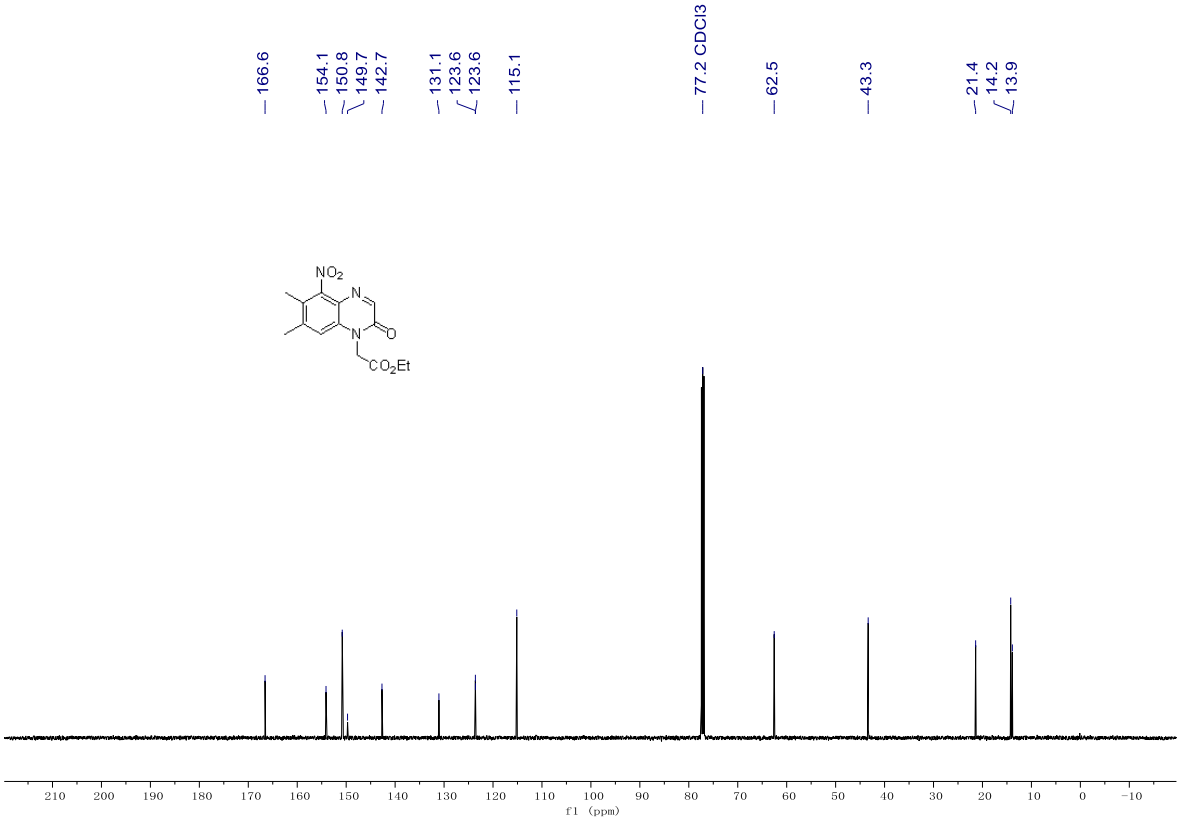
6,7-dimethyl-5-nitroquinoxalin-2(1*H*)-one (2v)



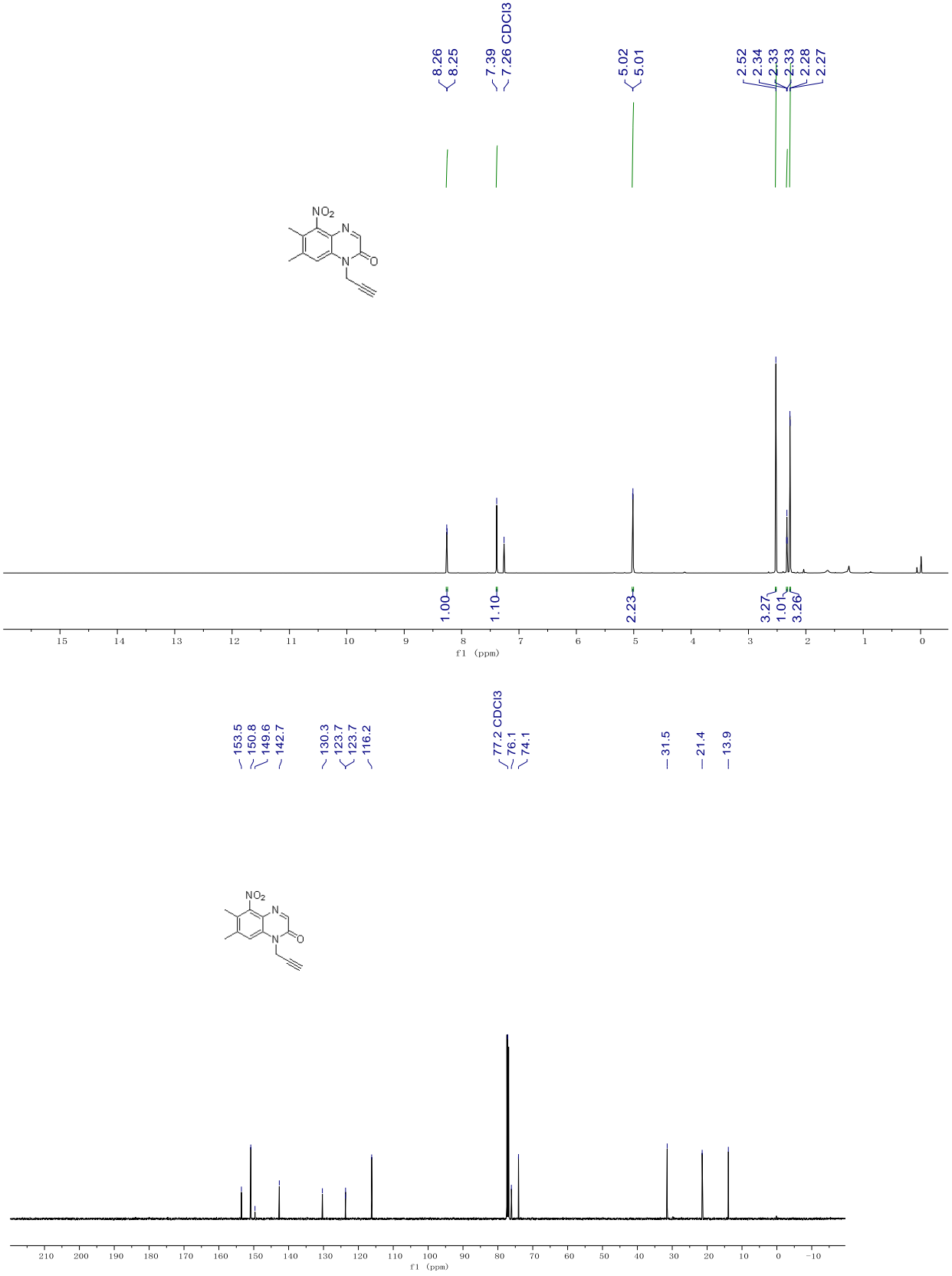


ethyl 2-(6,7-dimethyl-5-nitro-2-oxoquinoxalin-1(2*H*)-yl)acetate (2w)

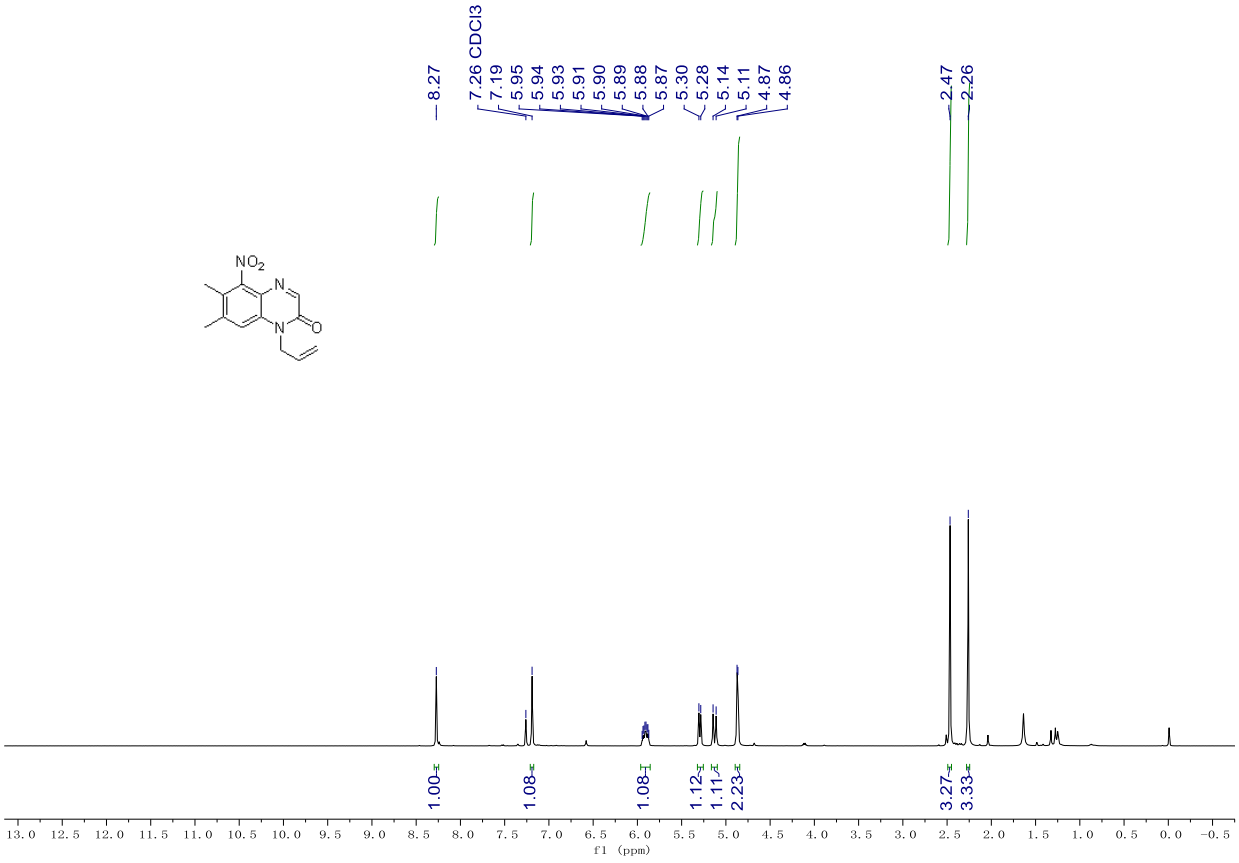


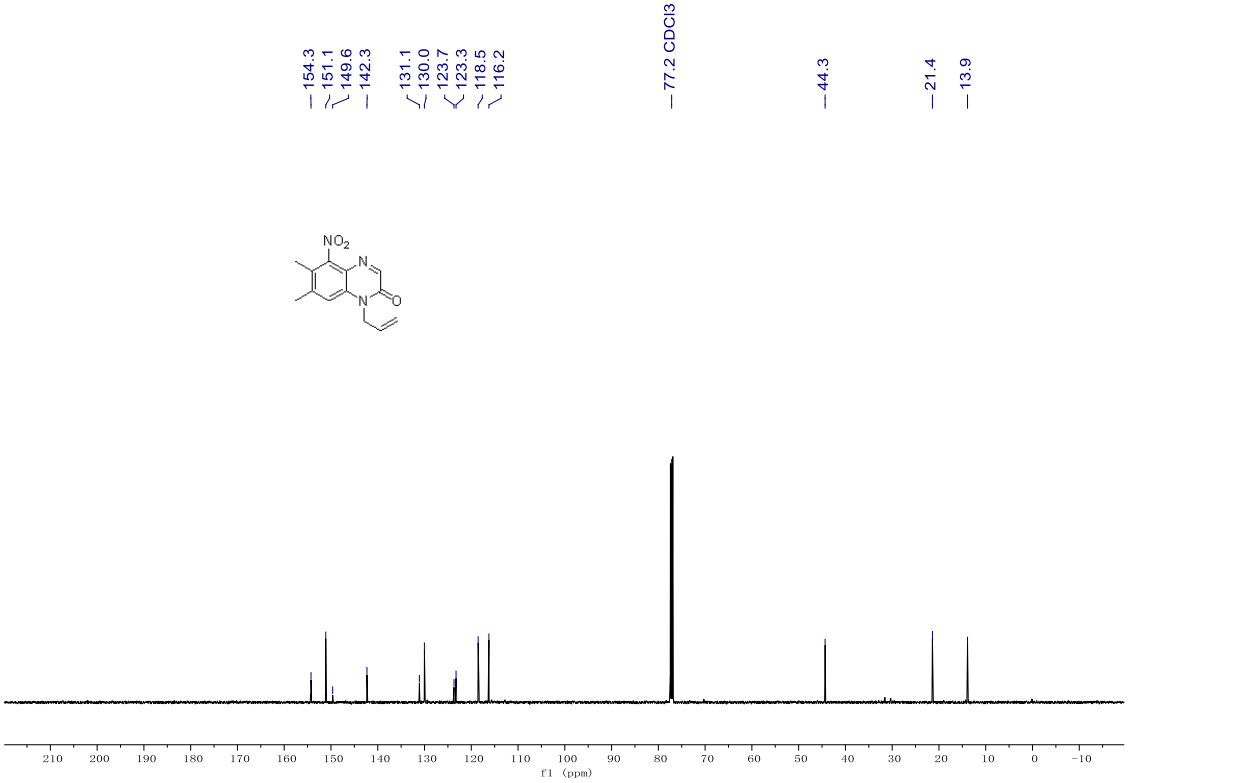


6,7-dimethyl-5-nitro-1-(prop-2-yn-1-yl)quinoxalin-2(1*H*)-one (2x)

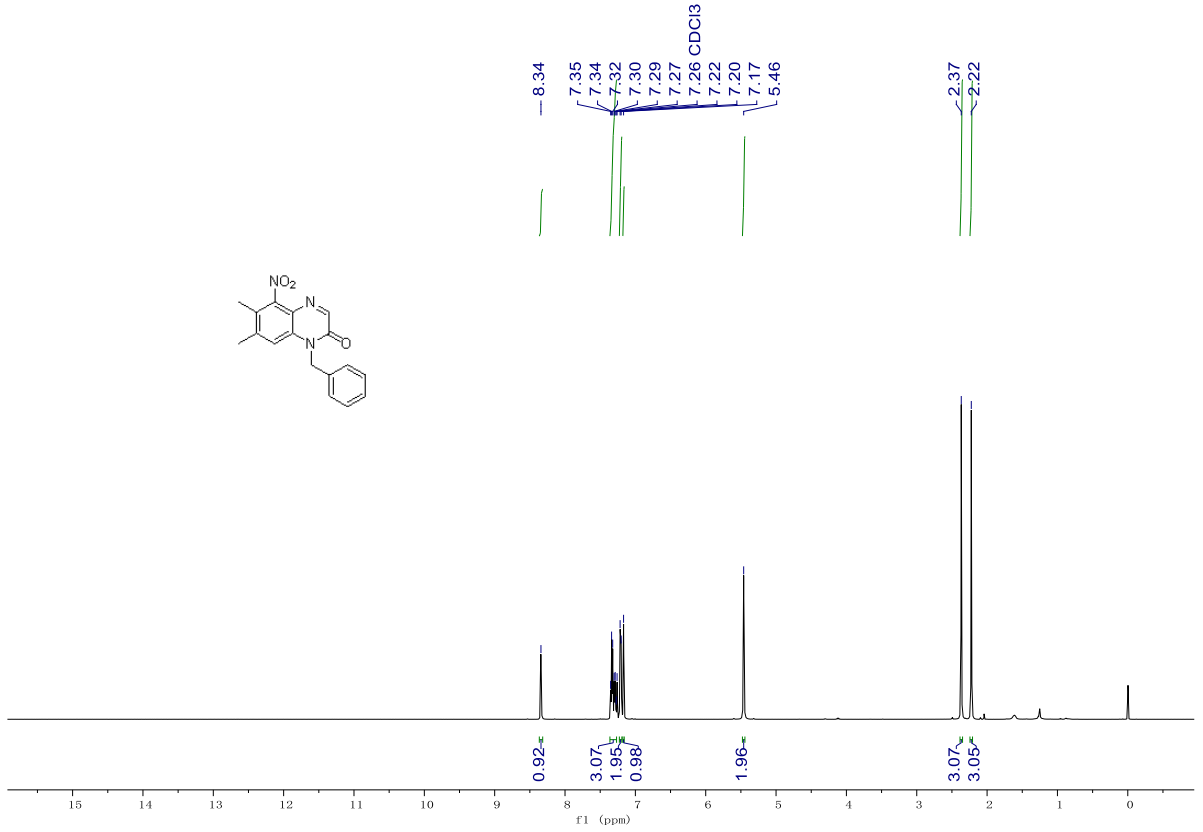


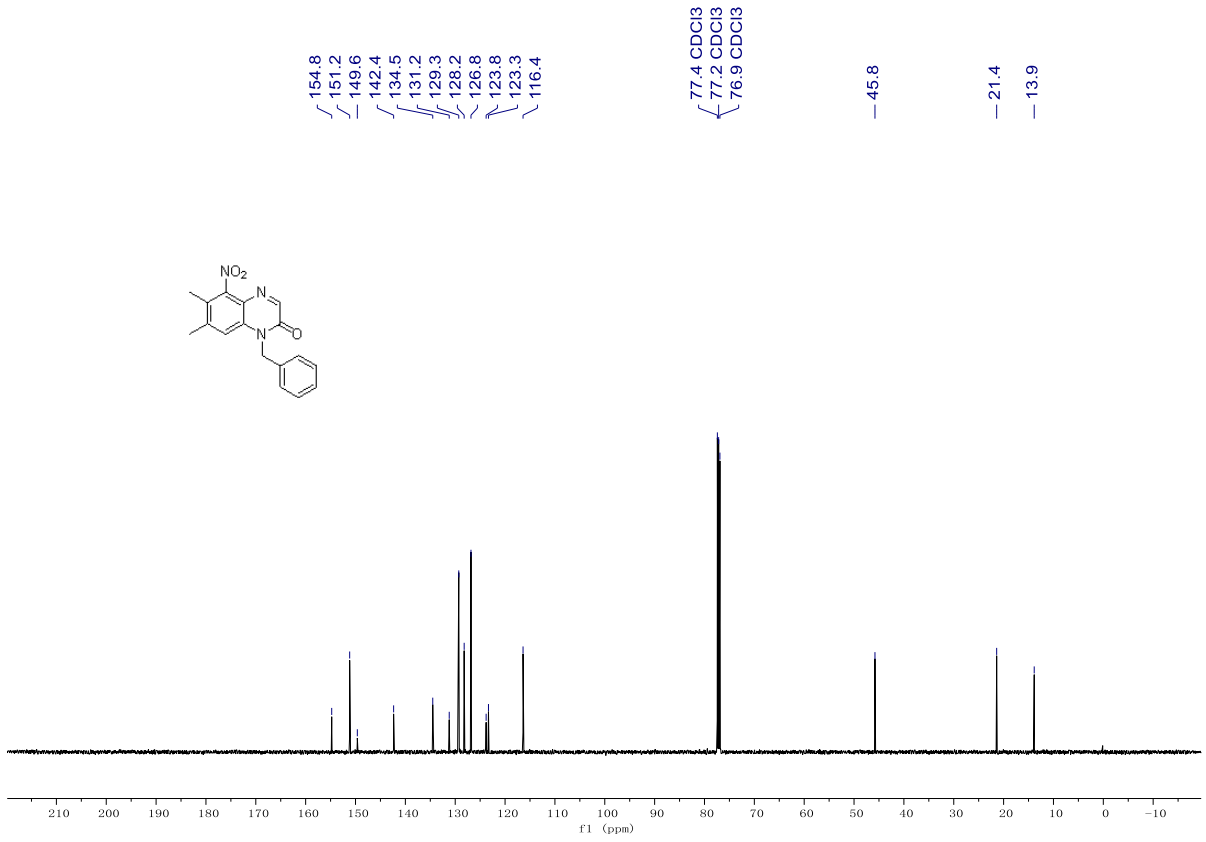
1-allyl-6,7-dimethyl-5-nitroquinoxalin-2(1H)-one (2y)



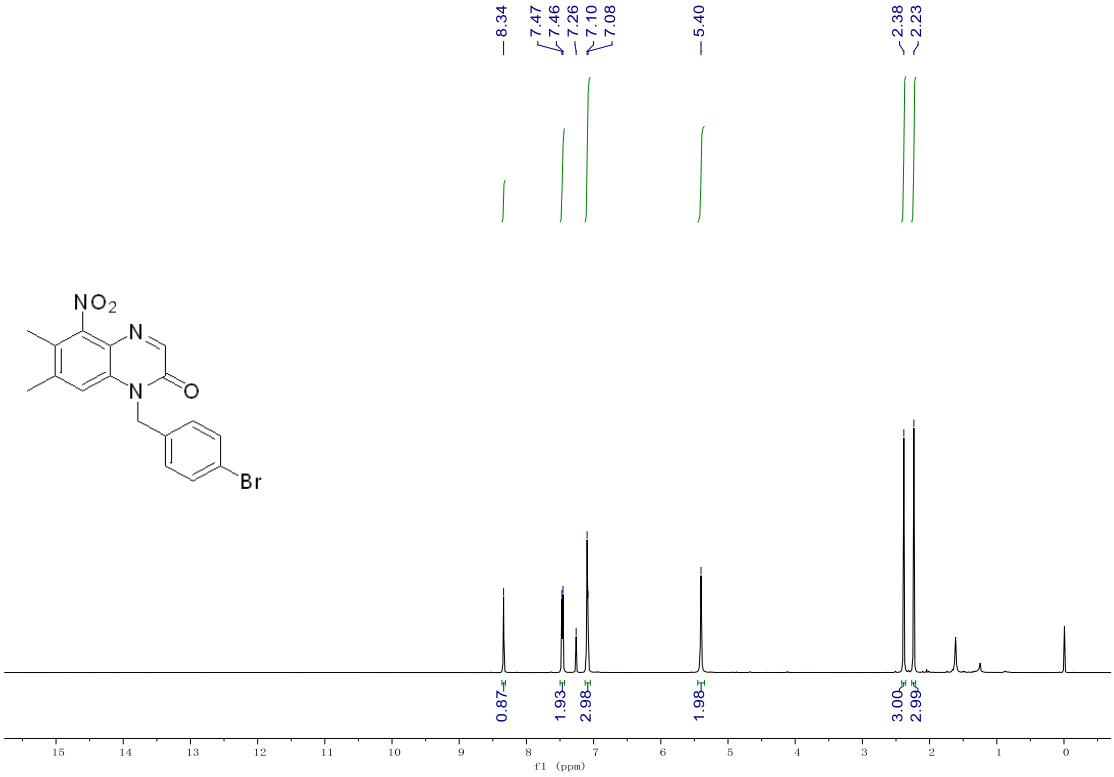


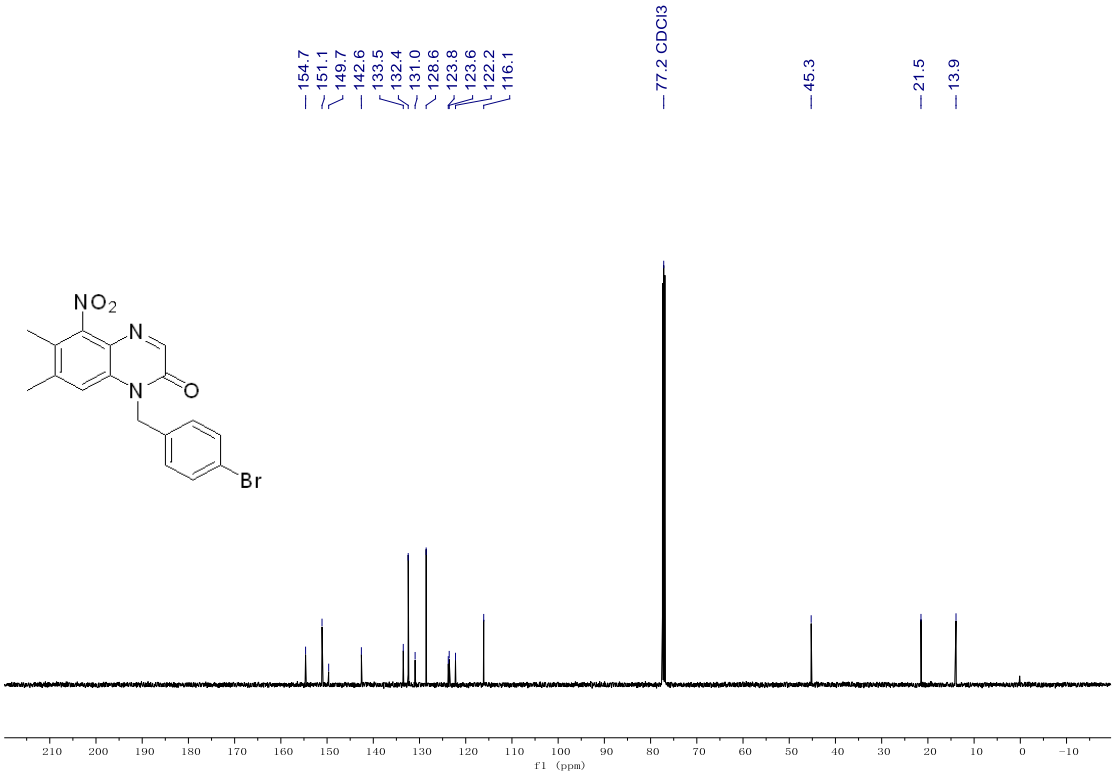
1-benzyl-6,7-dimethyl-5-nitroquinoxalin-2(1*H*)-one (2z)



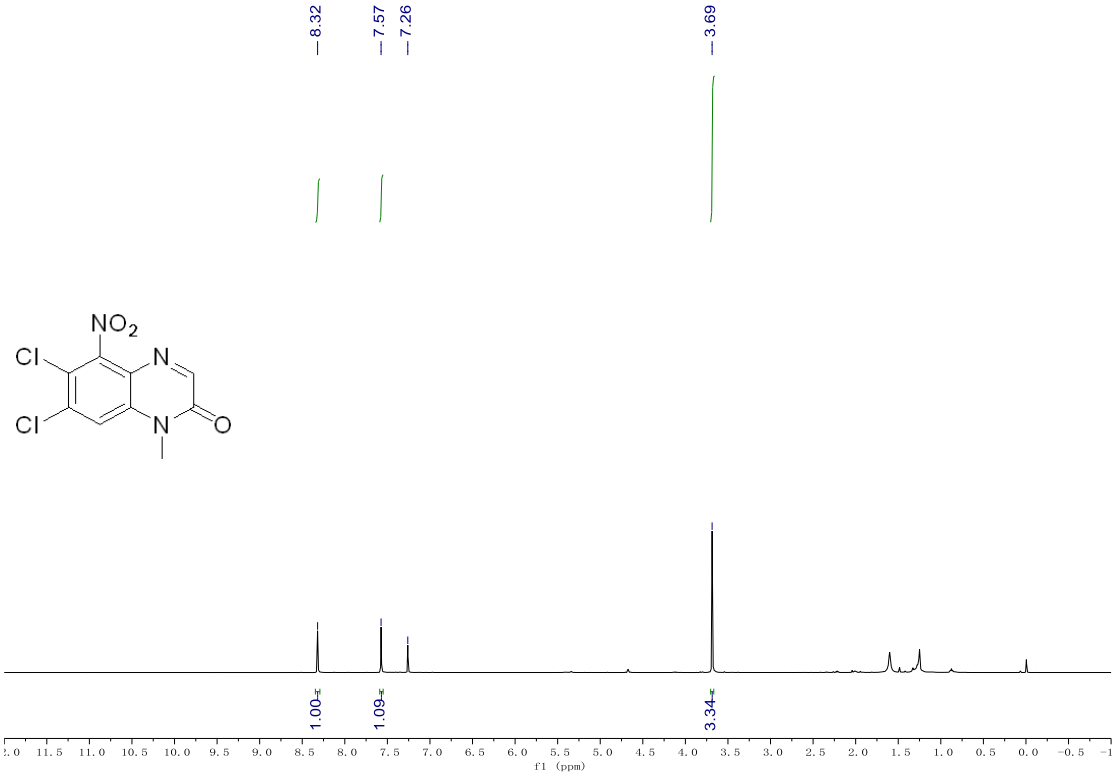


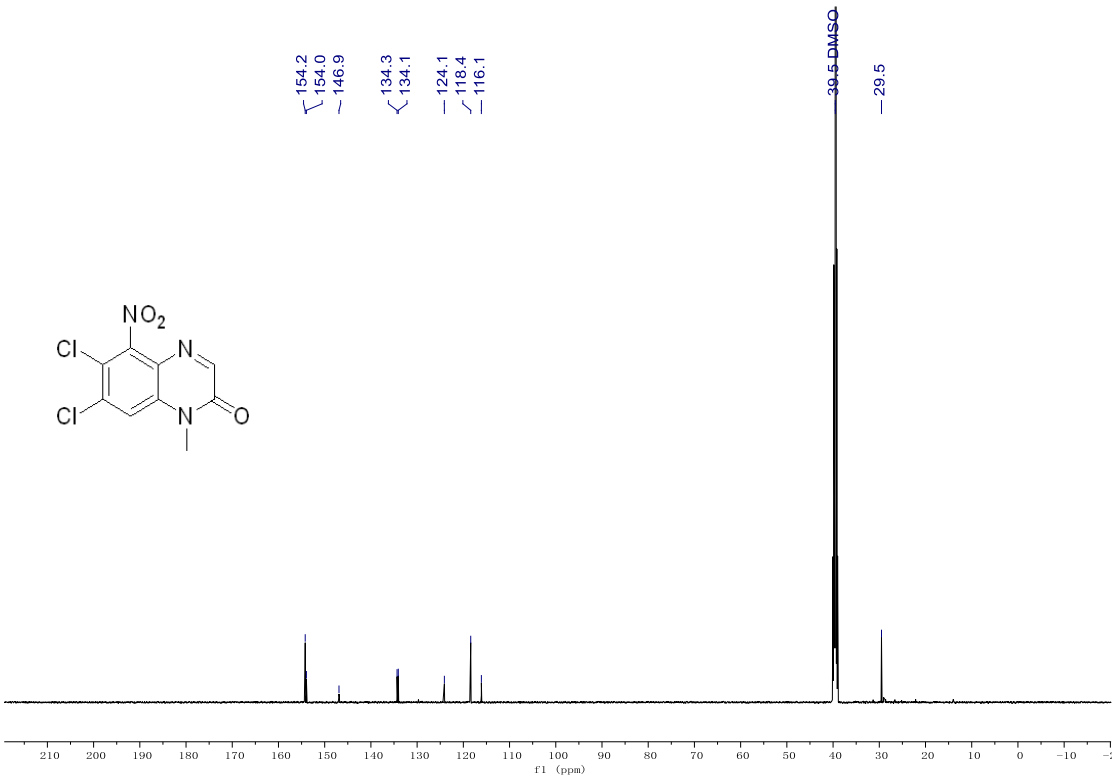
1-(4-bromobenzyl)-6,7-dimethyl-5-nitroquinoxalin-2(1*H*)-one (2aa)



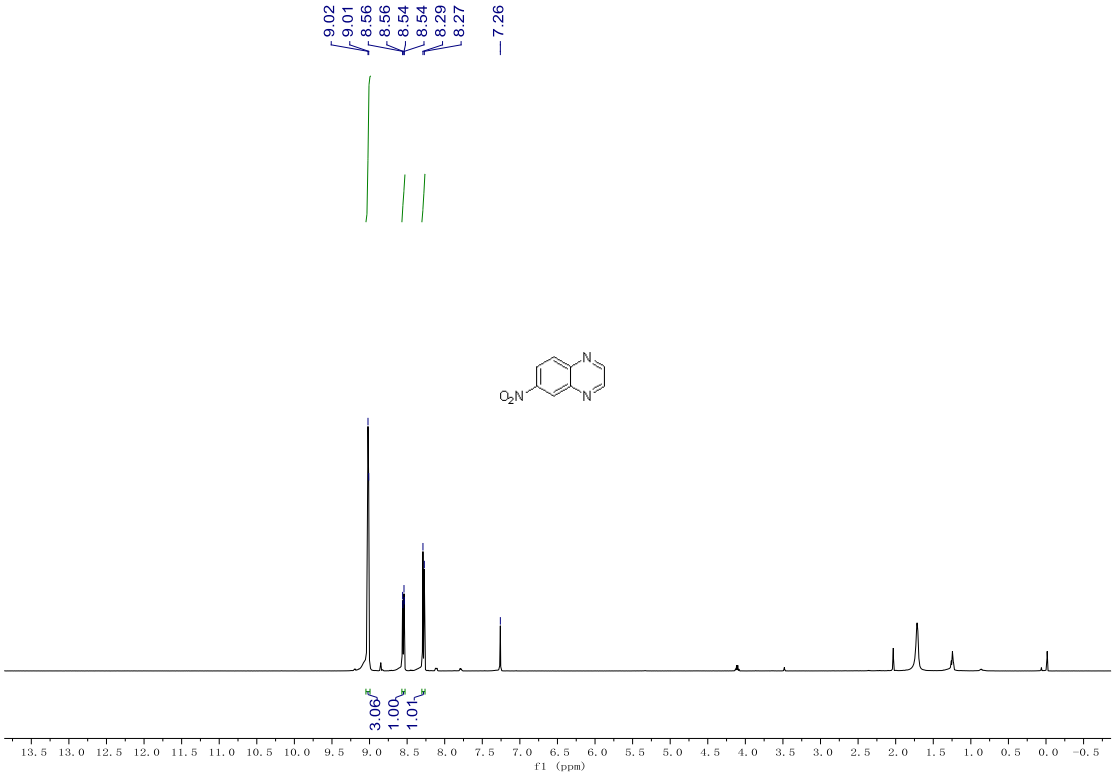


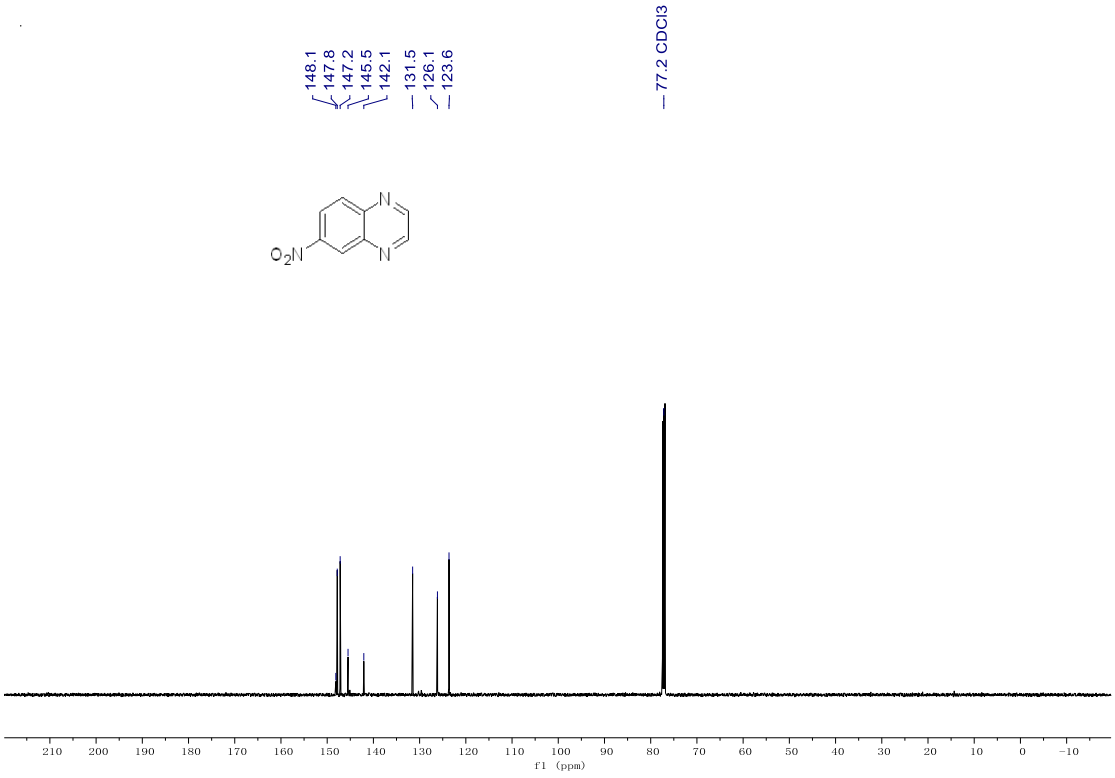
6,7-dichloro-1-methyl-5-nitroquinoxalin-2(1*H*)-one (2ab)



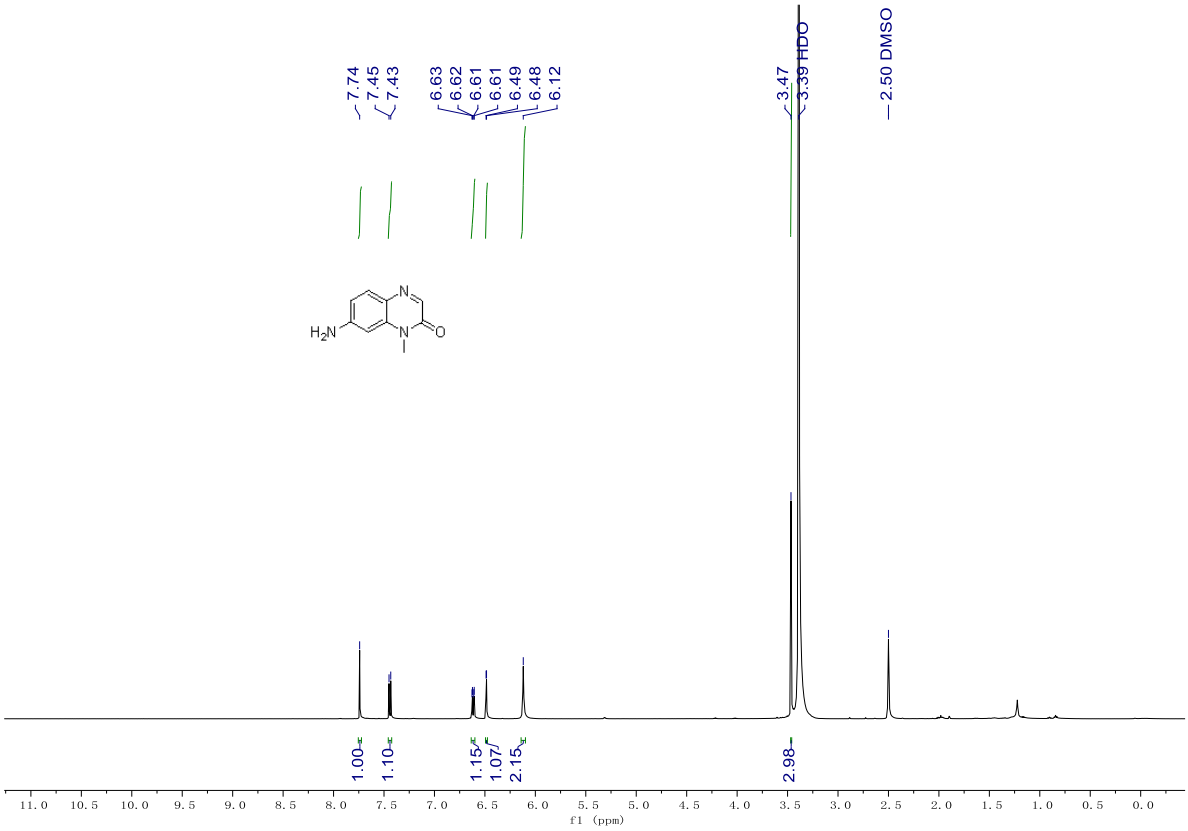


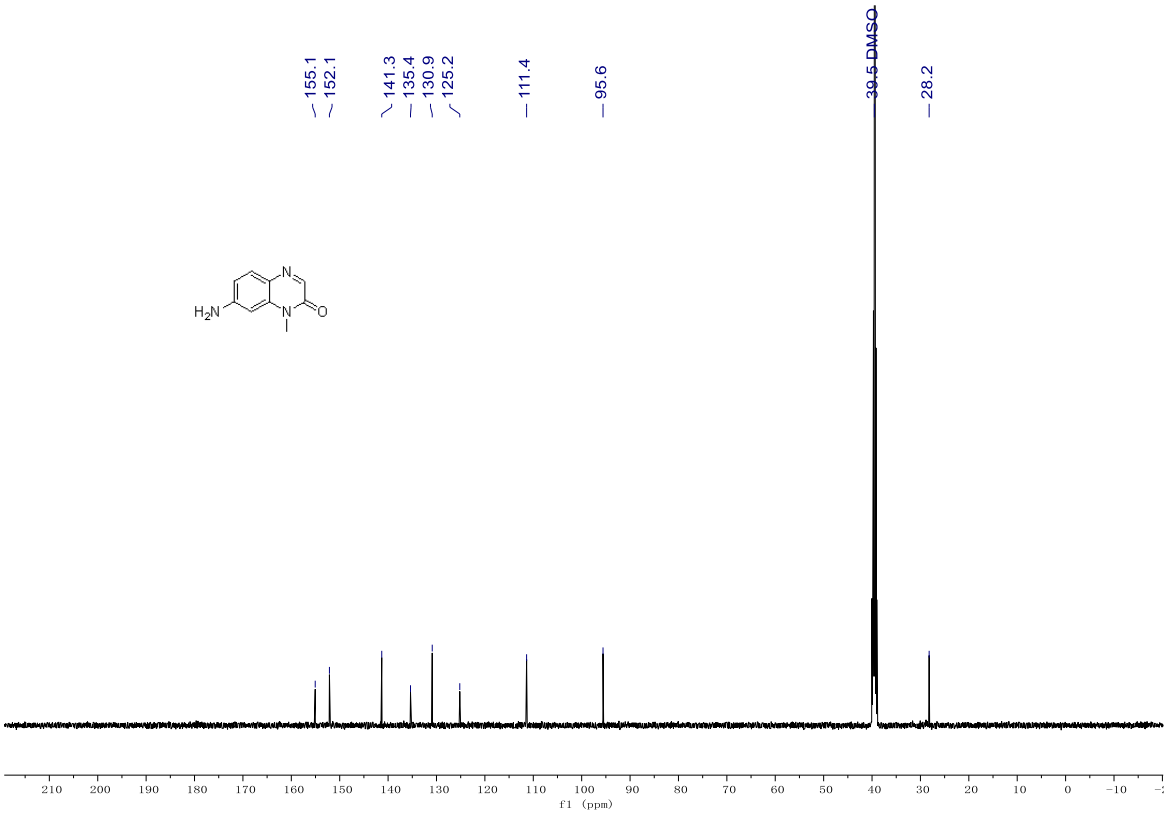
6-nitroquinoxaline (2ac)





7-amino-1-methylquinoxalin-2(1*H*)-one (3b)





(2-nitroethene-1,1-diyl)dibenzene (4)