Bonded- and Discreted- Linqvist Hexatungstate-Based Copper hybrids as Heterogeneous Catalysts for One-pot Synthesis of 2-Phenylquinoxalines *via* 2-Haloanilines with Vinyl Azides or 3-Phenyl-2*H*-azirines

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1. Data of Cu-POMs 1 and Cu-POMs 2

Table S1 Crystal data and structure refinement for compounds **1-2**.

Compound	**1**	**2**	**2c**
Formula	$C_{48}H_{32}Cu_4N_8O_{29}W_6$	$C_{48}H_{37}ClCu_2N_8O_{21}W_6$	$C_{15}H_{12}N_2$
M_r	2542.08	2327.48	220.27
Crystal system	Triclinic	monoclinic	monoclinic
Space group	*P-1*	*C 2/c*	*P 21*
T(K)	298(2)	298(2)	
a (Å)	10.6500(9)	26.174(2)	9.580(2)
b (Å)	12.1479(11)	16.2204(14)	4.8156(10)
c (Å)	13.1931(12)	14.0404(12)	12.595(3)
α (deg)	108.267(3)	90	90
β (deg)	101.159(2)	118.393(4)	103.16(3)
γ (deg)	106.443(3)	5243.9(8)	90
V (Å^3)	1478.0(2)	5243.9(8)	565.8(2)
Z	1	4	2
$D_{calc.}$(mg/cm^{-3})	2.856	2.948	1.293
F(000)	1168	4272	232
$R_1[I>2\sigma(I)]$	0.0567	0.0551	0.0716
$wR_2[I>2\sigma(I)]$	0.1833	0.1587	0.2276
R_1(all data)	0.0677	0.1045	0.0910
wR_2(all data)	0.1910	0.1894	0.2693
GOOF	1.070	1.073	1.139
Highest peak	4.18	1.93	
Deepest hole	-4.10	-3.94	
CCDC No.	1515325	1918834	2008846

Table S2. Selected Bond lengths [Å] and angles [º] for compounds **1-2**

Compound **1**			
W(1)-O(1)	1.701(9)	O(9)-W(2)#1	1.889(9)
W(1)-O(8)#1	1.868(9)	O(1)-W(1)-O(8)#1	103.0(4)
W(1)-O(3)	1.915(9)	O(1)-W(1)-O(3)	102.3(4)
W(1)-O(5)#1	1.956(8)	O(8)#1-W(1)-O(3)	90.2(4)
W(1)-O(2)	1.999(8)	O(1)-W(1)-O(5)#1	101.7(4)
W(1)-O(6)	2.2868(7)	O(8)#1-W(1)-O(5)#1	89.3(4)
W(1)-W(3)#1	3.2283(10)	O(3)-W(1)-O(5)#1	155.5(4)
W(2)-O(4)	1.702(9)	O(1)-W(1)-O(2)	100.7(4)
W(2)-O(9)#1	1.889(9)	O(8)#1-W(1)-O(2)	156.2(4)
W(2)-O(5)	1.926(9)	O(3)-W(1)-O(2)	87.0(4)
W(2)-O(3)	1.935(9)	O(5)#1-W(1)-O(2)	83.6(4)
W(2)-O(7)	1.956(9)	O(1)-W(1)-O(6)	177.8(3)
W(2)-O(6)	2.3144(6)	O(8)#1-W(1)-O(6)	79.1(3)
W(3)-O(10)	1.684(9)	O(3)-W(1)-O(6)	78.3(3)

W(3)-O(7)	1.895(9)	O(5)#1-W(1)-O(6)	77.6(3)
W(3)-O(2)	1.907(8)	O(2)-W(1)-O(6)	77.2(3)
W(3)-O(9)	1.961(8)	O(1)-W(1)-W(3)#1	136.5(3)
W(3)-O(8)	1.964(8)	O(8)#1-W(1)-W(3)#1	33.5(3)
W(3)-O(6)	2.3064(7)	O(3)-W(1)-W(3)#1	84.2(3)
W(3)-W(1)#1	3.2283(10)	O(5)#1-W(1)-W(3)#1	82.0(3)
Cu(1)-O(11)	1.948(9)	O(2)-W(1)-W(3)#1	122.7(3)
Cu(1)-O(12)	1.957(9)	O(6)-W(1)-W(3)#1	45.592(18)
Cu(1)-N(1)	2.026(11)	O(4)-W(2)-O(9)#1	103.8(4)
Cu(1)-N(2)	2.032(11)	O(4)-W(2)-O(5)	102.0(4)
Cu(1)-O(2)	2.467(9)	O(9)#1-W(2)-O(5)	88.6(4)
Cu(2)-O(12)	1.943(9)	O(4)-W(2)-O(3)	103.3(4)
Cu(2)-O(11)	1.953(9)	O(9)#1-W(2)-O(3)	87.9(4)
Cu(2)-N(4)	2.018(11)	O(5)-W(2)-O(3)	154.6(4)
Cu(2)-N(3)	2.035(11)	O(4)-W(2)-O(7)	102.5(4)
Cu(2)-O(1)	2.280(10)	O(9)#1-W(2)-O(7)	153.7(4)
N(1)-C(1)	1.333(18)	O(5)-W(2)-O(7)	87.0(4)
N(1)-C(5)	1.352(18)	O(3)-W(2)-O(7)	85.1(4)
N(2)-C(12)	1.348(18)	O(4)-W(2)-O(6)	178.8(3)
N(2)-C(6)	1.356(18)	O(9)#1-W(2)-O(6)	77.3(3)
N(3)-C(13)	1.340(18)	O(5)-W(2)-O(6)	77.5(2)
N(3)-C(17)	1.371(17)	O(3)-W(2)-O(6)	77.2(2)
N(4)-C(24)	1.344(17)	O(7)-W(2)-O(6)	76.4(3)
N(4)-C(18)	1.356(16)	O(10)-W(3)-O(7)	104.0(4)
O(5)-W(1)#1	1.956(8)	O(10)-W(3)-O(2)	103.9(4)
O(6)-W(1)#1	2.2868(7)	O(7)-W(3)-O(2)	90.5(4)
O(6)-W(3)#1	2.3064(7)	O(10)-W(3)-O(9)	102.0(4)
O(6)-W(2)#1	2.3144(6)	O(7)-W(3)-O(9)	153.8(4)
O(8)-W(1)#1	1.868(9)	O(2)-W(3)-O(9)	86.4(4)
O(10)-W(3)-O(8)	100.7(4)	C(17)-N(3)-Cu(2)	111.9(8)
O(7)-W(3)-O(8)	87.9(4)	C(24)-N(4)-C(18)	118.1(11)
O(2)-W(3)-O(8)	154.9(4)	C(24)-N(4)-Cu(2)	128.1(9)
O(9)-W(3)-O(8)	84.1(4)	C(18)-N(4)-Cu(2)	113.6(8)
O(10)-W(3)-O(6)	177.0(3)	W(1)-O(1)-Cu(2)	131.0(5)
O(7)-W(3)-O(6)	77.7(3)	W(3)-O(2)-W(1)	113.5(4)
O(2)-W(3)-O(6)	78.4(3)	W(3)-O(2)-Cu(1)	120.2(4)
O(9)-W(3)-O(6)	76.2(3)	W(1)-O(2)-Cu(1)	119.6(4)
O(8)-W(3)-O(6)	76.8(3)	W(1)-O(3)-W(2)	114.7(4)
O(10)-W(3)-W(1)#1	132.4(3)	W(2)-O(5)-W(1)#1	114.6(4)
O(7)-W(3)-W(1)#1	81.3(3)	W(1)-O(6)-W(1)#1	180.0
O(2)-W(3)-W(1)#1	123.5(3)	W(1)-O(6)-W(3)	90.69(3)
O(9)-W(3)-W(1)#1	78.8(3)	W(1)#1-O(6)-W(3)	89.31(3)
O(8)-W(3)-W(1)#1	31.7(3)	W(1)-O(6)-W(3)#1	89.31(3)
O(6)-W(3)-W(1)#1	45.097(18)	W(1)#1-O(6)-W(3)#1	90.69(3)

O(11)-Cu(1)-O(12)	83.3(4)	W(3)-O(6)-W(3)#1	180.000(1)
O(11)-Cu(1)-N(1)	95.1(4)	W(1)-O(6)-W(2)	89.59(2)
O(12)-Cu(1)-N(1)	170.6(5)	W(1)#1-O(6)-W(2)	90.41(2)
O(11)-Cu(1)-N(2)	170.6(5)	W(3)-O(6)-W(2)	89.90(2)
O(12)-Cu(1)-N(2)	98.1(4)	W(3)#1-O(6)-W(2)	90.10(2)
N(1)-Cu(1)-N(2)	82.0(4)	W(1)-O(6)-W(2)#1	90.41(2)
O(11)-Cu(1)-O(2)	91.5(4)	W(1)#1-O(6)-W(2)#1	89.59(2)
O(12)-Cu(1)-O(2)	91.5(4)	W(3)-O(6)-W(2)#1	90.10(2)
N(1)-Cu(1)-O(2)	97.8(4)	W(3)#1-O(6)-W(2)#1	89.90(2)
N(2)-Cu(1)-O(2)	97.8(4)	W(2)-O(6)-W(2)#1	180.00(3)
O(12)-Cu(2)-O(11)	83.5(4)	W(3)-O(7)-W(2)	115.9(4)
O(12)-Cu(2)-N(4)	97.6(4)	W(1)#1-O(8)-W(3)	114.8(4)
O(11)-Cu(2)-N(4)	173.4(4)	W(2)#1-O(9)-W(3)	116.3(4)
O(12)-Cu(2)-N(3)	174.8(5)	Cu(1)-O(11)-Cu(2)	96.3(4)
O(11)-Cu(2)-N(3)	96.4(4)	Cu(2)-O(12)-Cu(1)	96.3(4)
N(4)-Cu(2)-N(3)	81.9(4)	N(1)-C(1)-C(2)	120.4(13)
O(12)-Cu(2)-O(1)	94.2(4)	N(1)-C(5)-C(4)	124.3(12)
O(11)-Cu(2)-O(1)	92.6(4)	N(1)-C(5)-C(6)	116.1(12)
N(4)-Cu(2)-O(1)	93.8(4)	N(2)-C(6)-C(7)	123.4(12)
N(3)-Cu(2)-O(1)	91.0(4)	N(2)-C(6)-C(5)	116.9(12)
C(1)-N(1)-C(5)	119.0(12)	N(2)-C(12)-C(11)	120.8(13)
C(1)-N(1)-Cu(1)	128.1(9)	N(3)-C(13)-C(14)	121.7(13)
C(5)-N(1)-Cu(1)	112.8(9)	N(3)-C(17)-C(16)	123.8(12)
C(12)-N(2)-C(6)	119.1(12)	N(3)-C(17)-C(18)	116.7(11)
C(12)-N(2)-Cu(1)	128.8(10)	N(4)-C(18)-C(19)	124.6(12)
C(6)-N(2)-Cu(1)	112.0(8)	N(4)-C(18)-C(17)	115.7(11)
C(13)-N(3)-C(17)	117.6(12)	N(4)-C(24)-C(23)	122.0(12)
C(13)-N(3)-Cu(2)	130.4(10)	C(17)-N(3)-Cu(2)	111.9(8)
O(10)-W(3)-O(8)	100.7(4)	C(24)-N(4)-C(18)	118.1(11)

Symmetry transformations used to generate equivalent atoms: #1 -x+1,-y+1,-z+1

Compound **2**

W1-O1	1.686(12)	O4-W2-O10	88.1(5)
W1-O2	1.902(11)	O7-W2-O2	104.6(5)
W1-O4	1.906(12)	O8-W2-O2	86.2(5)
W1-O3	1.917(10)	O4-W2-O2	152.9(5)
W1-O5	1.928(11)	O10-W2-O2	86.7(4)
W1-O6	2.3096(7)	O7-W2-O6	178.1(7)
W2-O7	1.690(15)	O8-W2-O6	76.3(4)
W2-O8	1.902(14)	O4-W2-O6	76.1(3)
W2-O4	1.913(12)	O10-W2-O6	76.5(4)
W2-O10	1.935(13)	O2-W2-O6	76.8(3)
W2-O2	1.941(12)	O9-W3-O10	103.8(8)
W2-O6	2.3046(8)	O9-W3-O3	104.3(5)

W3-O9	1.688(13)	O10-W3-O3	87.3(5)
W3-O10	1.901(13)	O9-W3-O8	102.7(8)
W3-O3	1.901(11)	O10-W3-O8	153.5(5)
W3-O8	1.907(14)	O3-W3-O8	88.2(5)
W3-O5	1.927(11)	O9-W3-O5	101.7(5)
W3-O6	2.3004(9)	O10-W3-O5	86.6(5)
Cu1-N2	1.967(13)	O3-W3-O5	154.0(5)
Cu1-N4	2.000(13)	O8-W3-O5	86.0(5)
Cu1-N1	2.053(12)	O9-W3-O6	178.2(6)
Cu1-N3	2.069(14)	O10-W3-O6	77.2(4)
Cu1-Cl1	2.551(4)	O3-W3-O6	77.1(3)
O1-W1-O2	101.9(5)	O8-W3-O6	76.3(4)
O1-W1-O4	104.6(5)	O5-W3-O6	76.9(3)
O2-W1-O4	153.5(5)	N2-Cu1-N4	177.0(6)
O1-W1-O3	103.6(5)	N2-Cu1-N1	82.1(5)
O2-W1-O3	87.7(5)	N4-Cu1-N1	99.7(5)
O4-W1-O3	86.2(5)	N2-Cu1-N3	98.8(6)
O1-W1-O5	103.1(5)	N-Cu1-N3	81.7(6)
O2-W1-O5	88.4(5)	N1-Cu1-N3	134.3(5)
O4-W1-O5	85.5(5)	N2-Cu1-Cl1	89.9(4)
O3-W1-O5	153.2(5)	N4-Cu1-Cl1	87.3(4)
O1-W1-O6	179.3(4)	N1-Cu1-Cl1	105.8(3)
O2-W1-O6	77.4(3)	N3-Cu1-Cl1	119.8(4)
O4-W1-O6	76.1(3)	Cu1-Cl1-Cu1	128.6(3)
O3-W1-O6	76.6(3)	C1-N1-C5	117.4(13)
O5-W1-O6	76.6(3)	C1-N1-Cu1	134.0(11)
O7-W2-O8	105.1(9)	C5-N1-Cu1	108.5(10)
O7-W2-O4	102.6(6)	C6-N2-C12	115.2(15)
O8-W2-O4	86.4(5)	C6-N2-Cu1	115.9(11)
O7-W2-O10	102.2(9)	C12-N2-Cu1	128.5(12)
O8-W2-O10	152.7(5)	C13-N3-C17	117.6(15)
C13-N3-Cu1	131.6(13)	W2- O6- W2	180.0
C17-N3-Cu1	110.7(11)	W3-O6-W1	89.62(3)
C24-N4-C18	118.3(15)	W3-O6-W1	90.38(3)
C24-N4-Cu1	128.4(12)	W2-O6-W1	89.86(3)
C18-N4-Cu1	113.0(11)	W2-O6-W1	90.14(3)
W1-O2-W2	116.0(5)	W3-O6-W1	90.38(3)
W3-O3- W1	116.6(5)	W3-O6-W1	89.62(3)
W1-O4-W2	117.6(6)	W2-O6-W1	90.14(3)
W3-O5-W1	116.1(5)	W2-O6-W1	89.86(3)
W3-O6-W3	180.0	W1-O6-W1	180.0
W3-O6-W2	89.98(3)	W2-O8-W3	117.5(6)
N1-C5-C4	120.4(14)	W3-O9-H9	109.5
C7-C6-N2	126.3(17)	W2-O6-W2	180.0

N2-C6-C5	114.0(14)	W3-O10-W2	116.2(6)
N3-C13-C14	120.9(19)	N1-C5-C6	119.3(13)
N3-C17-C16	125.4(18)	N4-C18-C17	117.2(14)
N3-C17-C18	117.2(14)	N4-C18-C19	120.7(17)

Table S3. Bond valance sum calculations for compound **1-2.**

1	**W site**	W1	W2	W3
	BVS	6.03	6.05	6.11
	assigned O.S.	6	6	6
	Cu site	Cu1	Cu2	
	BVS	1.72	1.82	
	assigned O.S.	2	2	
	O site	O11		
	BVS	2.06		
	assigned O.S.	2		
2	**W site**	W1	W2	W3
	BVS	6.26	6.14	6.30
	assigned O.S.	6	6	6
	Cu site	Cu1		
	BVS	1.41		
	assigned O.S.	1		

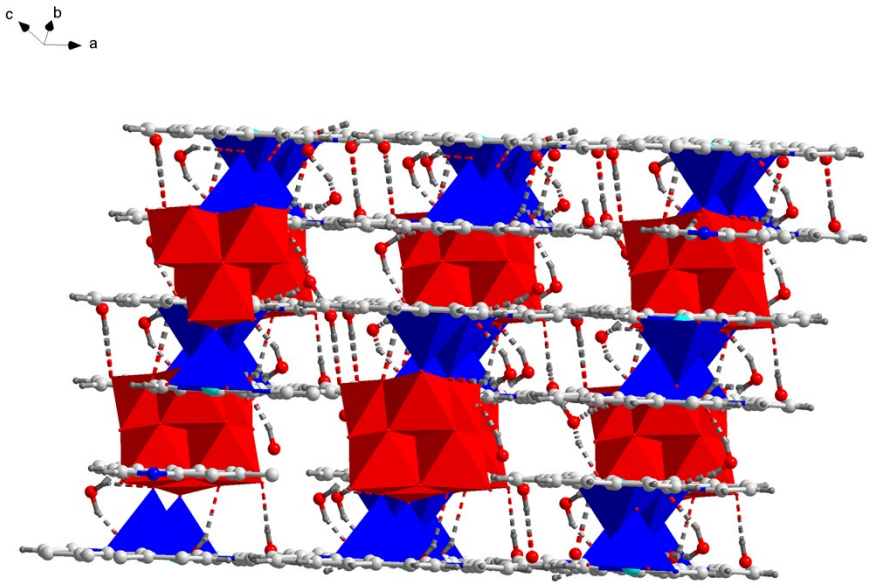


Fig. S1 The supramolecular structure of compound 1.

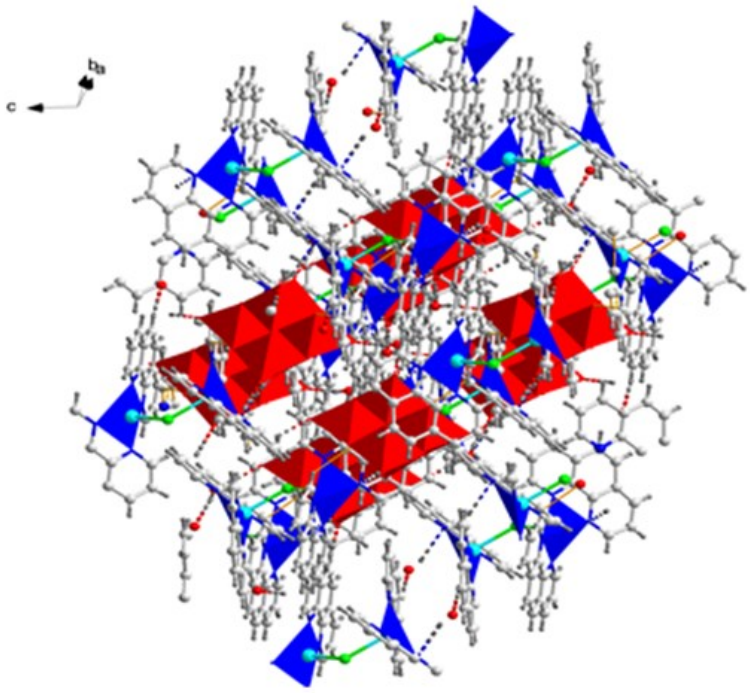


Fig. S2 The supramolecular structure of compound 2

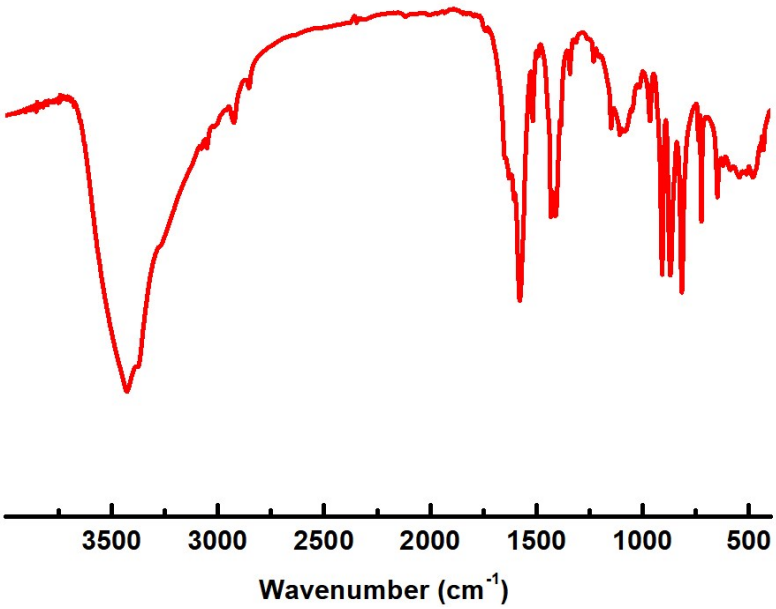


Fig. S3. The FT-IR spectra of compound **1**.

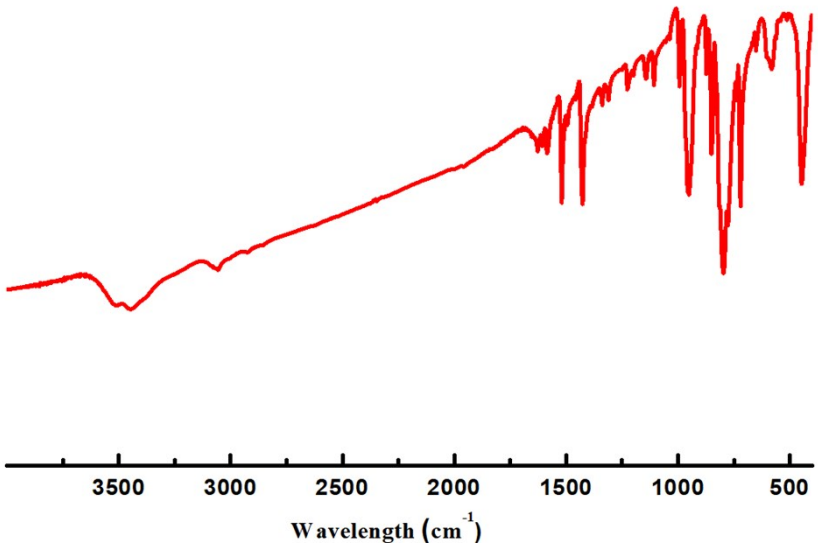


Figure S4. The FT-IR spectra of compound **2**.

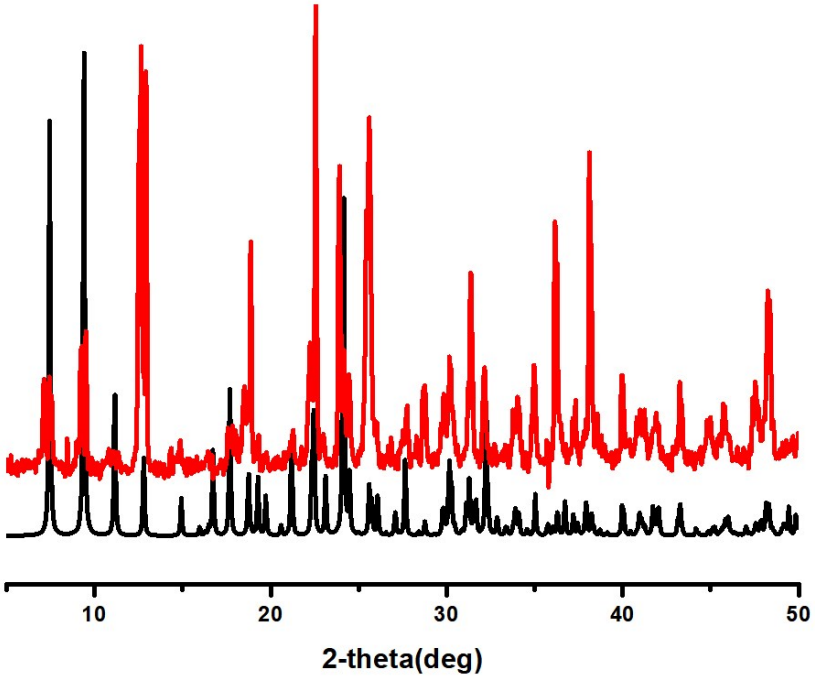


Fig. S5. The simulated (black) and experimental (red) PXRD patterns of compound **1**. Simulation based on the SXRD data.

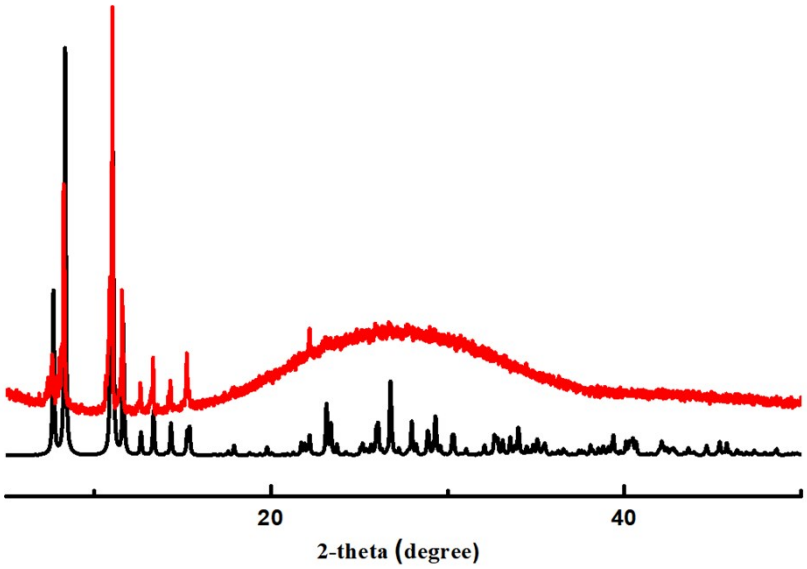


Fig. S6. The simulated (black) and experimental (red) PXRD patterns of compound **2**. Simulation based on the SXRD data.

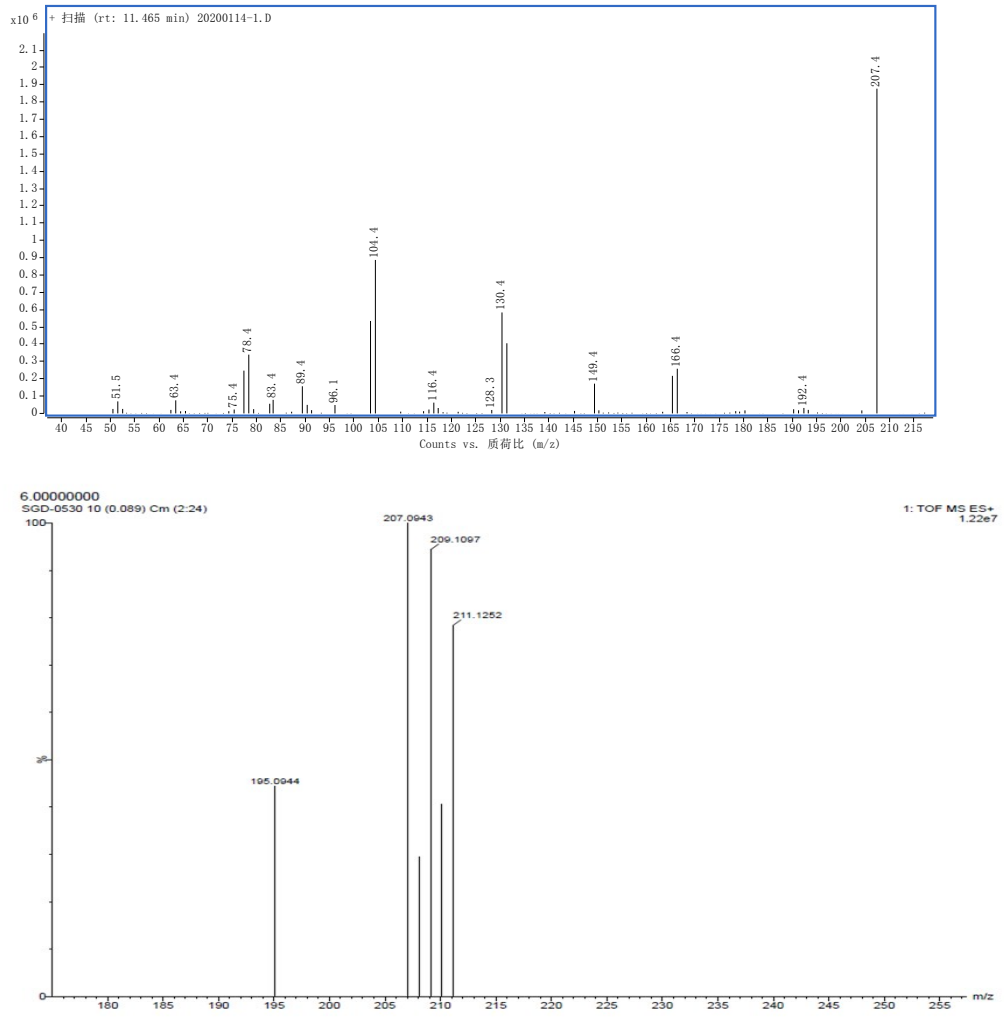


Fig. S7. The Gc-Ms and HPLC-Ms data of intermediates 3-phenyl-1,2-dihydroquinoxaline **1c**

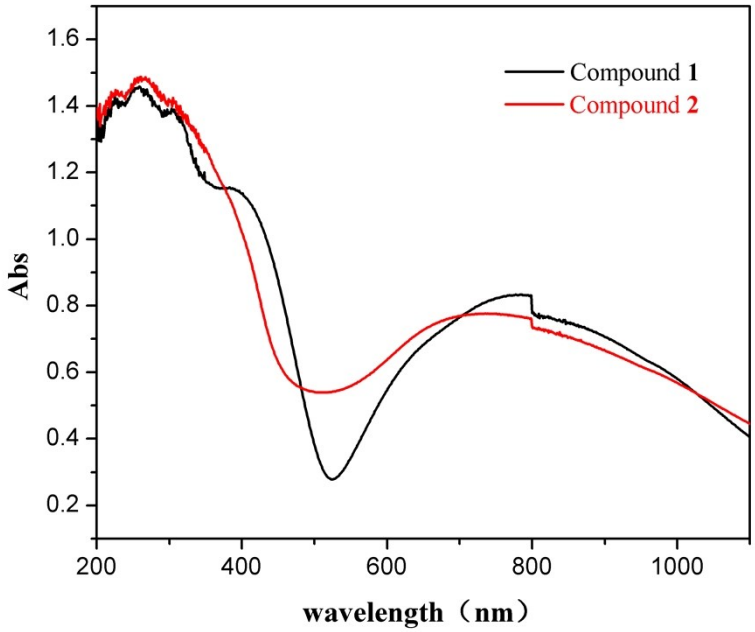
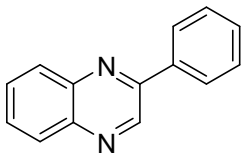


Fig. S8. The Electronic absorption spectra of compounds **1** and **2**

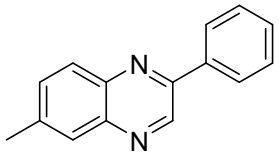
S9. Atomic absorption analysis of product solution after reaction

The detection limit of the inductivelyvcoupledvplasma (ICP) analyzer (ICP-6000) is 1 mg/L and the analysis results of copper and tungsate ions are both below the detection limit.

2. Data of the products

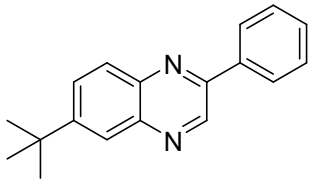


2-phenylquinoxaline (**1c**). Yield 84% (83%, 3-phenyl-2H-azirine **1d** was used); white solid; Mp: 67-69 ºC; ^{1}H NMR (500M Hz, $CDCl_3$/TMS): δ 9.33 (s, 1H), 8.21-8.10 (m, 4H), 7.80-7.75 (m, 2H), 7.59-7.52 (m, 3H). ^{13}C NMR (125M Hz, $CDCl_3$/TMS): 151.97, 143.33, 142.41, 141.50, 136.80, 130.49, 130.36, 129.75, 129.72, 129.29, 129.14, 127.68. HRMS (ESI): *m/z* calcd for $C_{14}H_{11}N_2$ $[M+H]^+$: 207.0917, found: 207.0911.

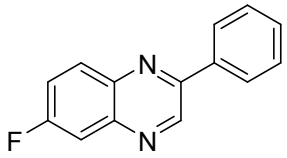


6-methyl-2-phenylquinoxaline (**2c**). Yield 82%; light yellow solid, Mp: 120-123 ºC;

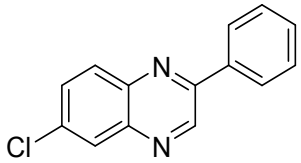
^{1}H NMR (400M Hz, $CDCl_3$/TMS): δ 9.29 (s, 1H), 8.18 (d, *J* = 8.0 Hz, 2H), 8.05 (d, *J* = 8.0 Hz, 1H), 7.89 (s, 1H), 7.63-7.51 (m, 4H), 2.62 (s, 3H). ^{13}C NMR (100M Hz, $CDCl_3$/TMS): 151.17, 143.36, 141.77, 140.89, 140.22, 137.08, 132.70, 130.06, 129.25, 129.22, 128.09, 127.54, 21.95. HRMS (ESI): *m/z* calcd for $C_{15}H_{13}N_2$ $[M+H]^+$: 221.1073, found: 221.1064.



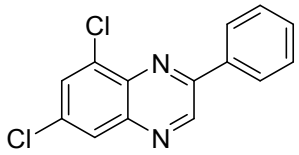
6-(*tert*-butyl)-2-phenylquinoxaline (**3c**). Yield 82%; yellow solid, Mp: 88-90 ºC; ^{1}H NMR (500M Hz, $CDCl_3$/TMS): δ 9.30 (s, 1H), 8.18 (d, *J*=7.5 Hz, 2H), 8.12-8.09 (m, 2H), 7.90 (d, *J*=9.0 Hz, 1H), 7.59-7.51 (m, 3H), 1.47 (s, 9H). ^{13}C NMR (125M Hz, $CDCl_3$/TMS): 153.55, 151.53, 142.90, 141.15, 140.90, 136.95, 130.22, 129.65, 129.30, 129,04, 127.61, 124.16, 35.44, 31.22. HRMS (ESI): *m/z* calcd for $C_{18}H_{19}N_2$ $[M+H]^+$: 263.1543, found: 263.1550.



6-fluoro-2-phenylquinoxaline (**4c**). Yield 78%; light yellow solid, Mp: 96-98 ºC; ^{1}H NMR (400M Hz, $CDCl_3$/TMS): δ 9.33 (s, 1H), 8.19-8.15 (m, 3H), 7.76 (dd, J_1=2.0 Hz, J_2=8.0 Hz, 1H), 7.59-7.52 (m, 4H). ^{13}C NMR (100M Hz, $CDCl_3$/TMS): 162.64 (d, *J*=1000 Hz), 151.42, 144.20, 142.34 (d, *J*=52 Hz), 139.65, 136.64, 131.79 (d, *J*=40 Hz), 130.39, 129.33, 127.56, 120.81 (d, *J*=104 Hz), 112.84 (d, *J*=88 Hz). HRMS (ESI): *m/z* calcd for $C_{14}H_{10}FN_2$ $[M+H]^+$: 225.0823, found: 225.0820.

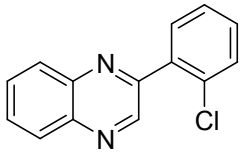


6-chloro-2-phenylquinoxaline (**5c**). Yield 79%, yellow solid, Mp: 140-141 ºC; ^{1}H NMR (400M Hz, $CDCl_3$/TMS): δ 9.33 (s, 1H), 8.20-8.08 (m, 4H), 7.73 (d, *J* = 8.0 Hz, 1H), 7.58-7.56 (m, 3H). ^{13}C NMR (100M Hz, $CDCl_3$/TMS): 152.11, 144.29, 141.98, 141.01, 136.53, 135.41, 131.47, 130.99, 130.58, 129.37, 128.23, 127.67. HRMS (ESI): *m/z* calcd for $C_{14}H_{10}ClN_2$ $[M+H]^+$: 241.0527, found: 241.0529.

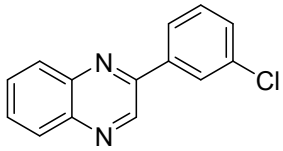


5,7-dichloro-2-phenylquinoxaline (**6c**). Yield 75%, light yellow solid, Mp: 185-187 ºC; ^{1}H NMR (400M Hz, $CDCl_3$/TMS): δ 9.39 (s, 1H), 8.28 (d, *J* = 8.0 Hz, 2H), 8.05 (d, *J* = 2.0 Hz, 1H), 7.87 (d, *J* = 2.0 Hz, 1H), 7.61-7.55 (m, 3H). ^{13}C NMR (100M Hz, $CDCl_3$/TMS): 152.02, 144.68, 143.65, 142.47, 137.97, 136.03, 134.72, 131.09, 131.01, 129.44, 127.86, 127.37. HRMS (ESI): *m/z* calcd for $C_{14}H_9Cl_2N_2$ $[M+H]^+$:

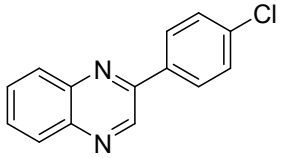
275.0137, found: 275.0129.



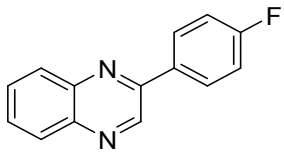
2-(2-chlorophenyl)quinoxaline (**7c**). Yield 71%, yellow solid; Mp: 133-135 ºC; ^{1}H NMR (400M Hz, $CDCl_3$/TMS)*:* δ 9.21 (s, 1H), 8.19-8.17 (m, 2H), 7.83-7.80 (m, 2H), 7.74 (d, *J* = 8.0 Hz, 1H), 7.56 (d, *J* = 8.0 Hz, 1H), 7.47-7.45 (m, 2H). ^{13}C NMR (100M Hz, $CDCl_3$/TMS): 152.56, 146.19, 142.48, 141.38, 136.67, 132.79, 132.13, 131.00, 130.47, 130.44, 130.35, 129.79, 129.34, 127.64. HRMS (ESI): *m/z* calcd for $C_{14}H_{10}ClN_2$ $[M+H]^+$: 241.0527, found: 241.0536.



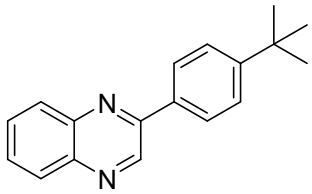
2-(3-chlorophenyl)quinoxaline (**8c**). Yield 79%, light yellow solid, Mp: 128-130 ºC; ^{1}H NMR (400M Hz, $CDCl_3$/TMS)*:* δ 9.29 (s, 1H), 8.23 (s, 1H), 8.18-8.14 (m, 2H), 8.06 (t, *J* = 6.0 Hz, 1H), 7.83-7.76 (m, 2H), 7.50-7.49 (m, 2H). ^{13}C NMR (100M Hz, $CDCl_3$/TMS): 150.53, 142.76, 142.44, 141.65, 138.61, 135.56, 130.76, 130.51, 130.40, 130.23, 129.84, 129.14, 127.84, 125.66. HRMS (ESI): *m/z* calcd for $C_{14}H_{10}ClN_2$ $[M+H]^+$: 241.0527, found: 241.0520.



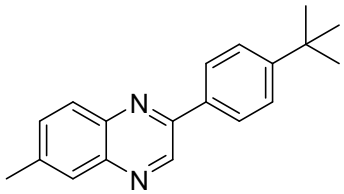
3-(4-chlorophenyl)quinoxaline (**9c**). Yield 80%, light yellow solid, Mp: 132-134 ºC; ^{1}H NMR (500M Hz, $CDCl_3$/TMS)*:* δ 9.31 (s, 1H), 8.15-8.17 (m, 4H), 7.76-7.83 (m, 2H), 7.55 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR (125M Hz, $CDCl_3$/TMS): 150.7, 142.52, 142.37, 141.19, 136.83, 35.06, 130.79, 130.13, 129.68, 129.54, 28.96, 128.89. HRMS (ESI): *m/z* calcd for $C_{14}H_{10}ClN_2$ $[M+H]^+$: 241.0527, found: 241.0522.



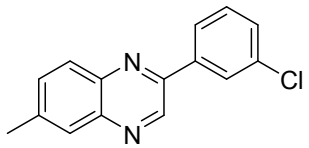
2-(4-fluorophenyl)quinoxaline (**10c**). Yield 83%, light yellow solid, Mp: 120-122 ºC; ^{1}H NMR (400M Hz, $CDCl_3$/TMS): δ 9.30 (s, 1H), 8.23-8.19 (m, 2H), 8.13 (t, *J* = 8.0 Hz, 2H), 7.81-7.74 (m, 2H), 7.26 (t, *J* =8.0 Hz, 2H). ^{13}C NMR (100M Hz, $CDCl_3$/TMS): 164.37 (d, *J* = 996 Hz), 150.84, 143.02, 142.31, 141.62, 133.06 (d, *J* = 12 Hz), 130.50, 129.68, 129.65, 129.56, 129.26, 116.33 (d, *J* = 84 Hz). HRMS (ESI): *m/z* calcd for $C_{14}H_{10}FN_2$ $[M+H]^+$: 225.0823, found: 225.0810.



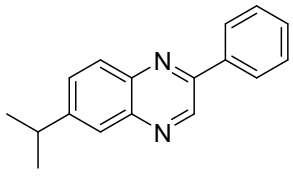
2-(4-(*tert*-buty)phenyl)quinoxaline (**11c**). Yield 81%, brown oil; ^{1}H NMR (400M Hz, $CDCl_3$/TMS): δ 9.32 (s, 1H), 8.16-8.10 (m, 4H), 7.79-7.71(m, 2H), 7.59 (d, *J* = 8.0 Hz, 2H) 1.39 (s, 9H). ^{13}C NMR (100M Hz, $CDCl_3$/TMS): δ 153.75, 152.02, 143.51, 142.53, 141.62, 134.16, 130.29, 129.73, 129.42, 129.24, 127.45, 126.29, 35.01, 31.38. HRMS (ESI): m/z calcd for$C_{18}H_{19}N_2$ [M+H]+: 263.1543, found: 263.1552.



2-(4-(*tert*-butyl)phenyl)-6-methylquinoxaline (**12c**). Yield 82% (80%, 3-(4-(tert-butyl)phenyl)-2*H*-azirine **3d** was used), yellow solid, Mp: 115-116 ºC; ^{1}H NMR (400M Hz, $CDCl_3$/TMS): δ 9.27 (s, 1H), 8.11 (d, *J*=8.0 Hz, 2H), 8.03 (d, *J*=8.0 Hz, 1H), 7.88 (s, 1H), 7.61-7.57 (m, 3H), 2.61 (s, 3H), 1.39 (s, 9H). ^{13}C NMR (100M Hz, $CDCl_3$/TMS): 153.49, 151.26, 143.42, 141.67, 140.98, 139.98, 134.33, 132.62, 129.25, 128.11, 127.31, 126.25, 35.00, 31.40, 21.96. HRMS (ESI): *m/z* calcd for $C_{19}H_{21}N_2$ [M+H]$^{+}$: 277.1699, found: 277.1690.



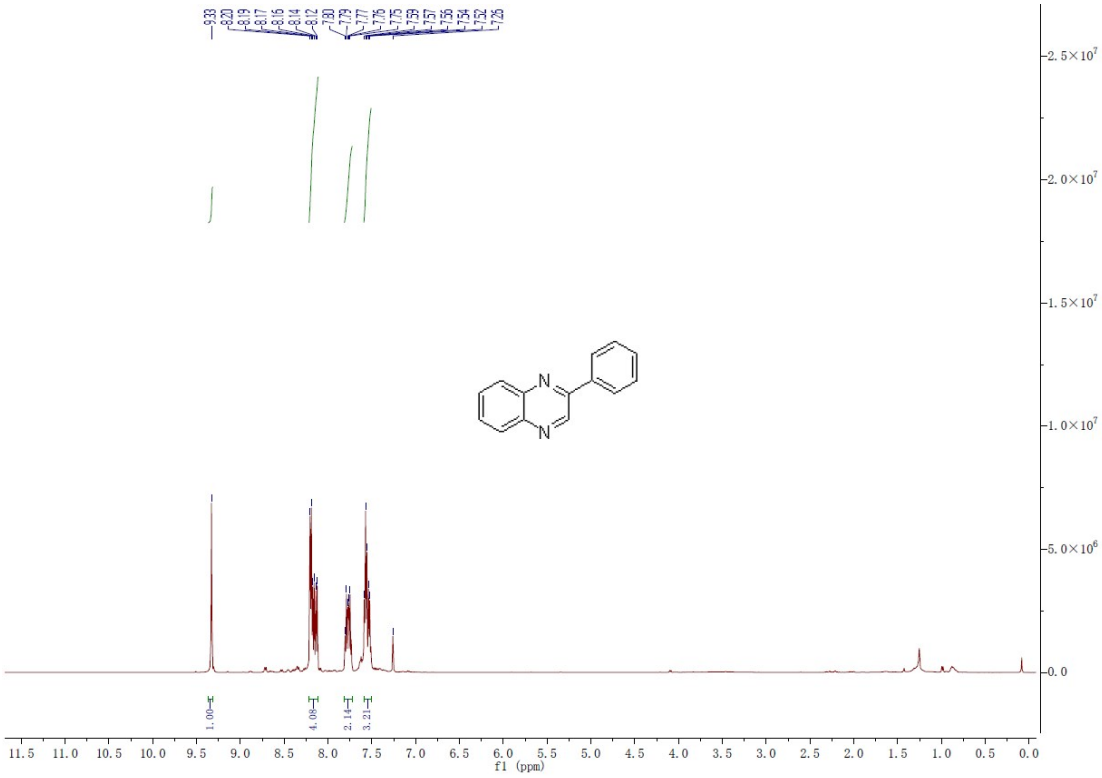
2-(3-chlorophenyl)-6-methylquinoxaline (**13c**). Yield 80%, light yellow solid, Mp: 121-122 ºC; ^{1}H NMR (400M Hz, $CDCl_3$/TMS): δ 9.16 (s, 1H), 8.06 (d, *J*=8.0 Hz, 1H), 7.93(s, 1H), 7.73-7.71 (m, 1H), 7.64 (d, *J*=8.0 Hz, 1H), 7.56-7.54 (m, 1H), 7.46-7.44 (m, 2H), 2.63 (s, 3H). ^{13}C NMR (100M Hz, $CDCl_3$/TMS): 151.60, 146.17, 141.54, 140.90, 139.13, 136.80, 132.74, 132.69, 132.05, 130.77, 130.36, 129.24, 128.18, 127.55, 22.01. HRMS (ESI): *m/z* calcd for $C_{15}H_{12}ClN_2$ [M+H]$^{+}$: 255.0684, found: 255.0688.

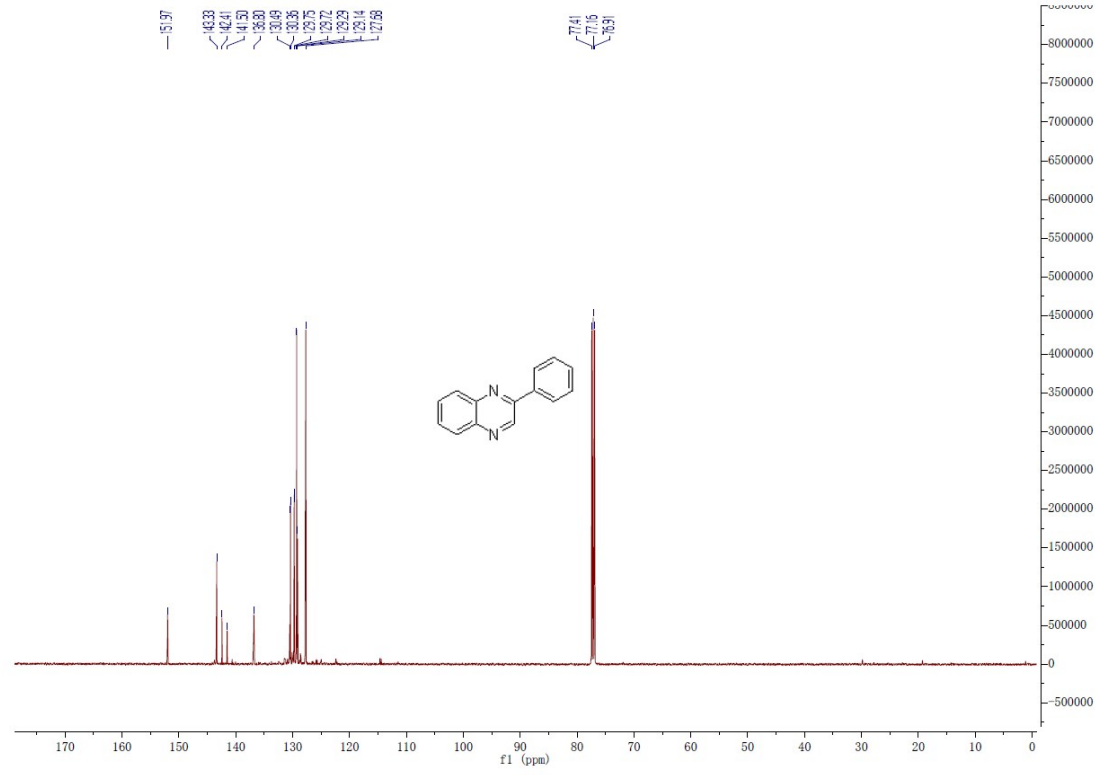


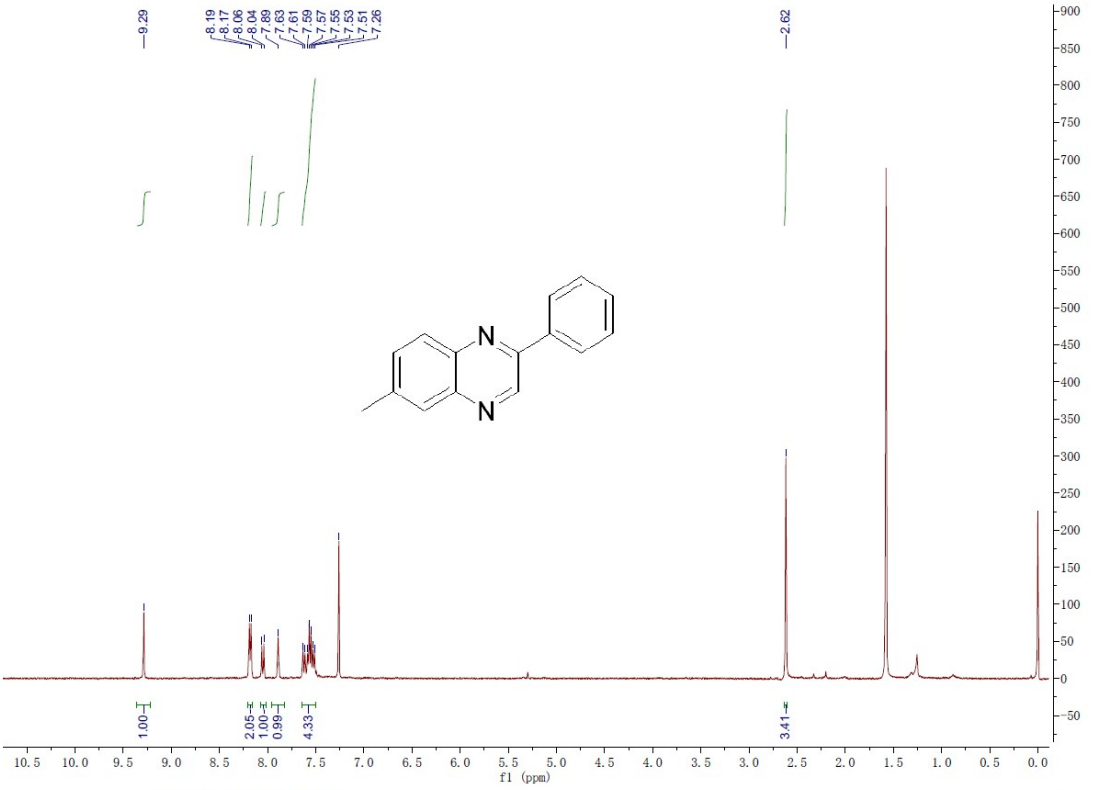
6-isopropyl-2-phenylquinoxaline (**14c**). Yield 85%, light yellow solid, Mp: 69-72 ºC; ^{1}H NMR (400M Hz, $CDCl_3$/TMS): δ 9.29 (s, 1H), 8.18 (d, *J*=8.0 Hz, 1H), 8.09 (d, *J*=8.0 Hz,1H), 7.93 (s, 1H), 7.70 (d-d, J_1= 4.0 Hz, J_2= 8.0 Hz, 1H), 7.58-7.49 (m, 3H), 3.20-3.13 (m, 1H), 1.39 (d, *J*=8.0 Hz, 6H). ^{13}C NMR (100M Hz, $CDCl_3$/TMS): 151.34, 150.99, 143.33, 141.92, 141.23, 137.18, 130.49, 130.07, 129.45, 129.24, 127.59, 125.37, 34.24, 23.86. HRMS (ESI): *m/z* calcd for $C_{17}H_{17}N_2$ [M+H]$^{+}$:

249.1386, found: 249.1388.

3. Copies of NMR spectra of products



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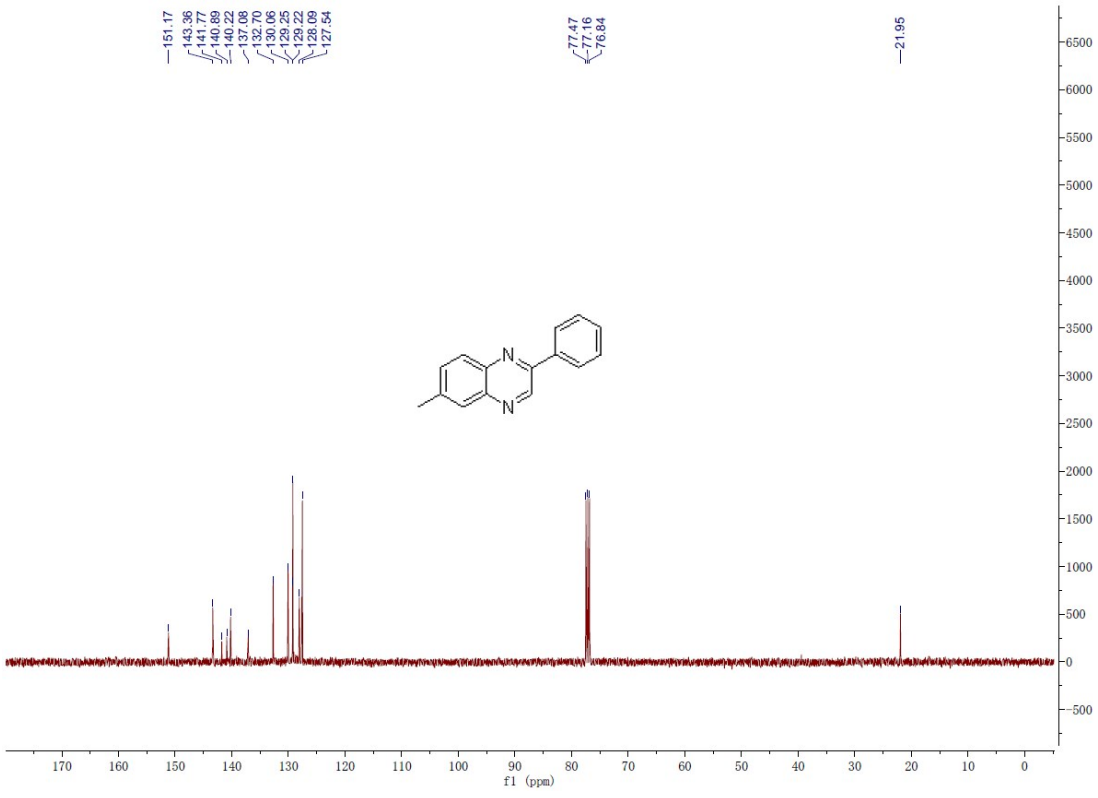
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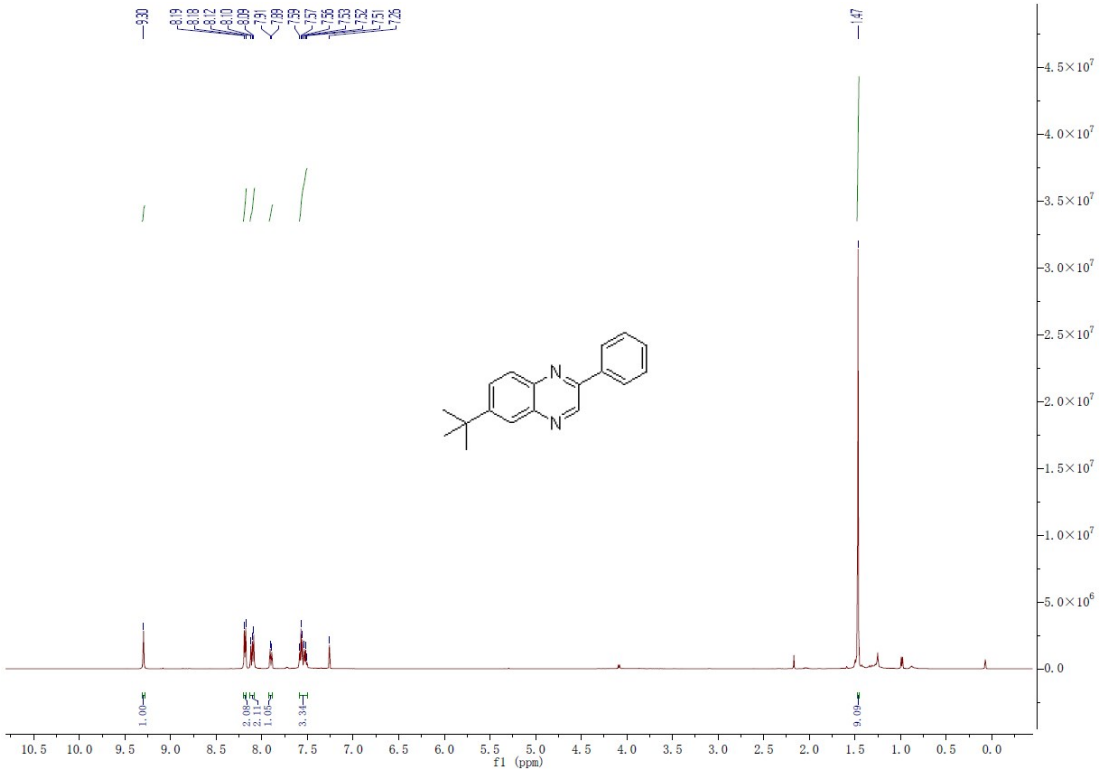
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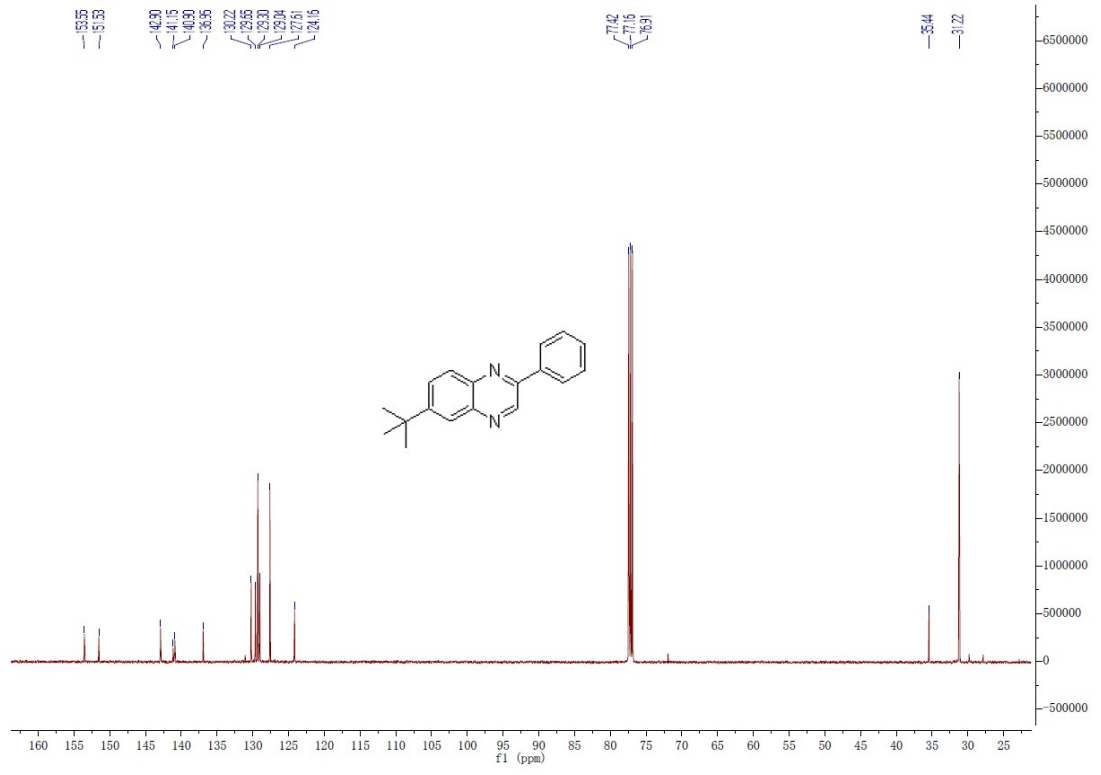
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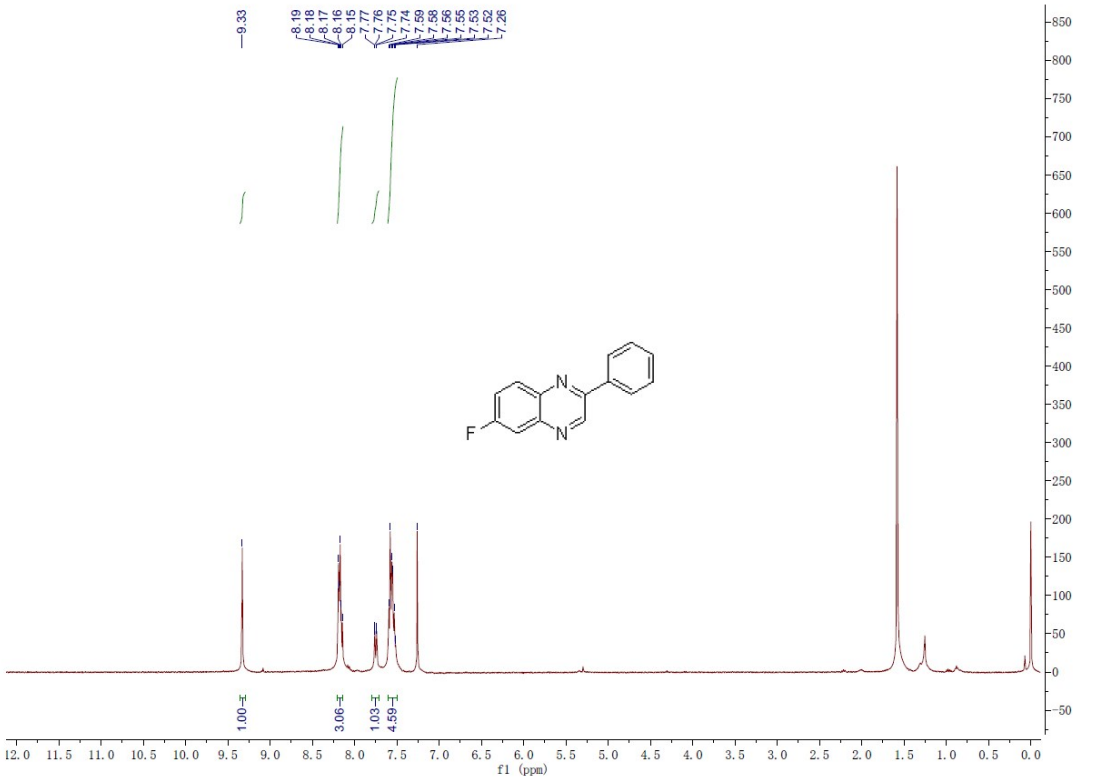
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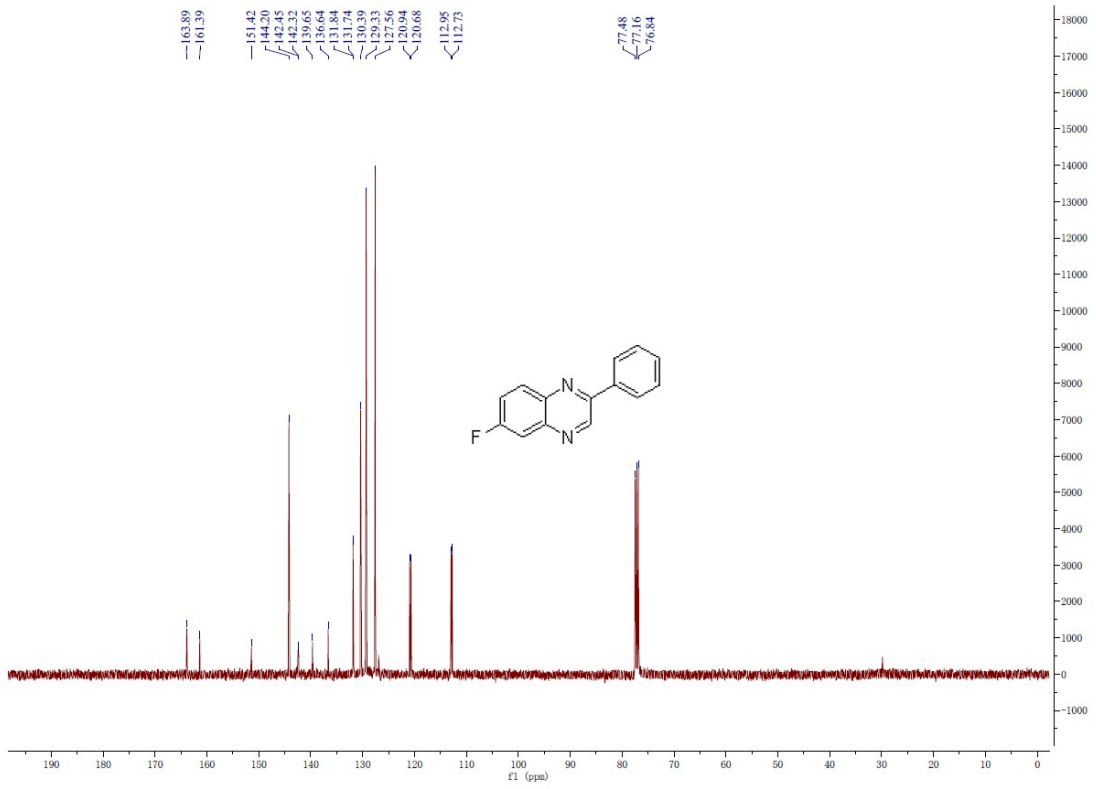
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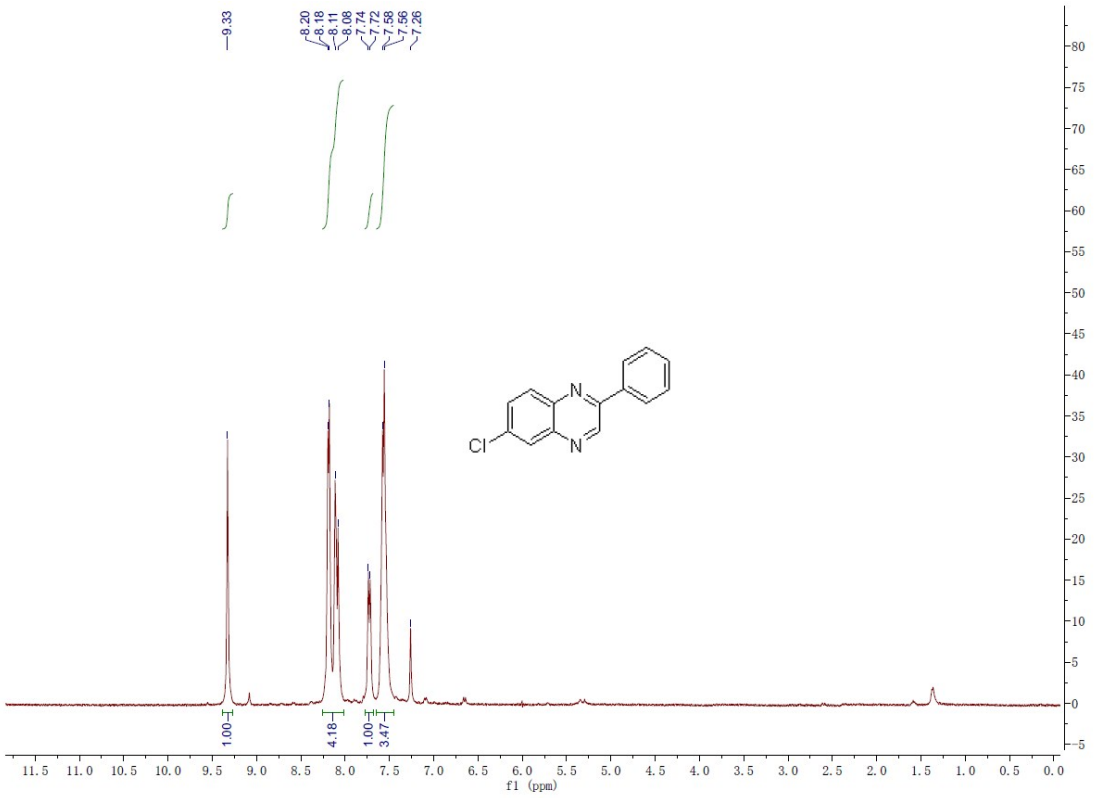
f1 (ppm)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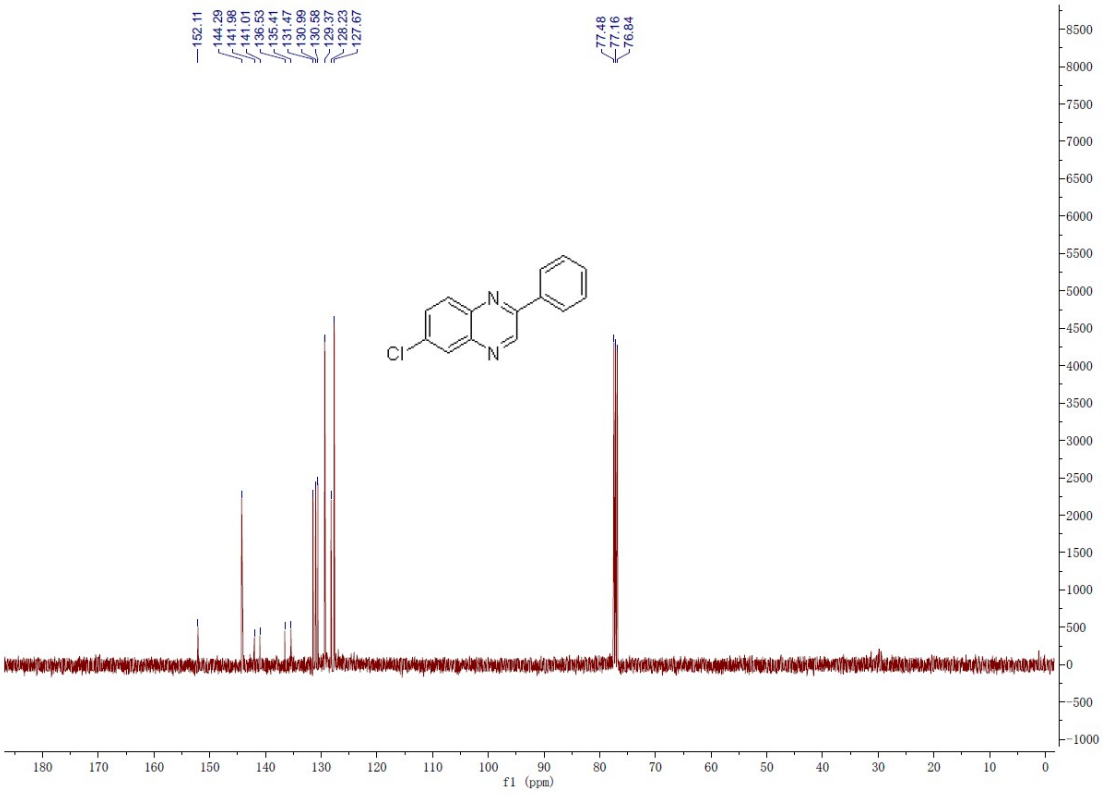
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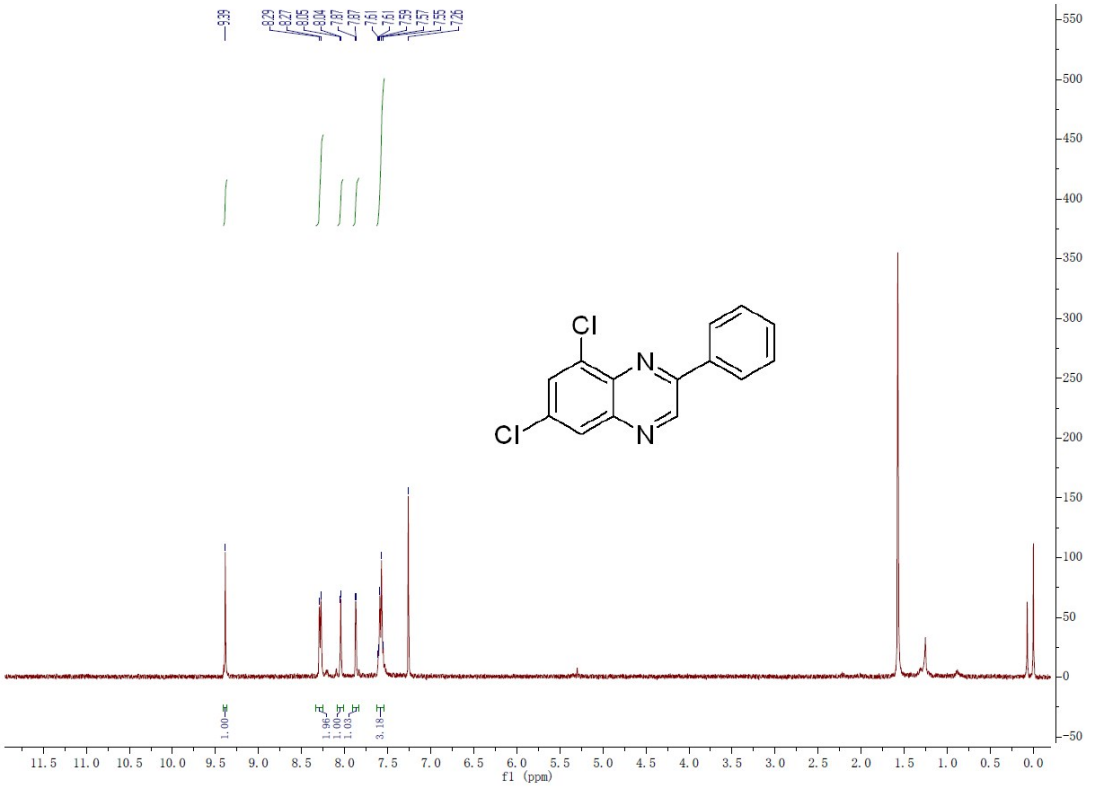
f1 (ppm)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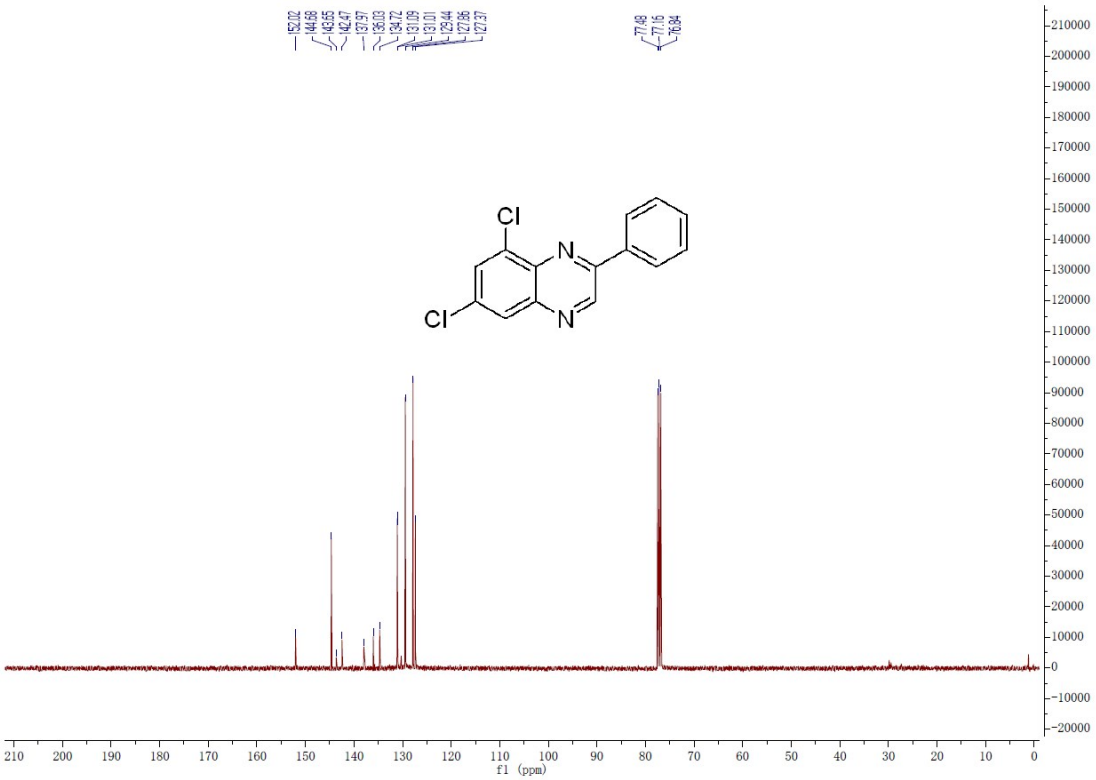
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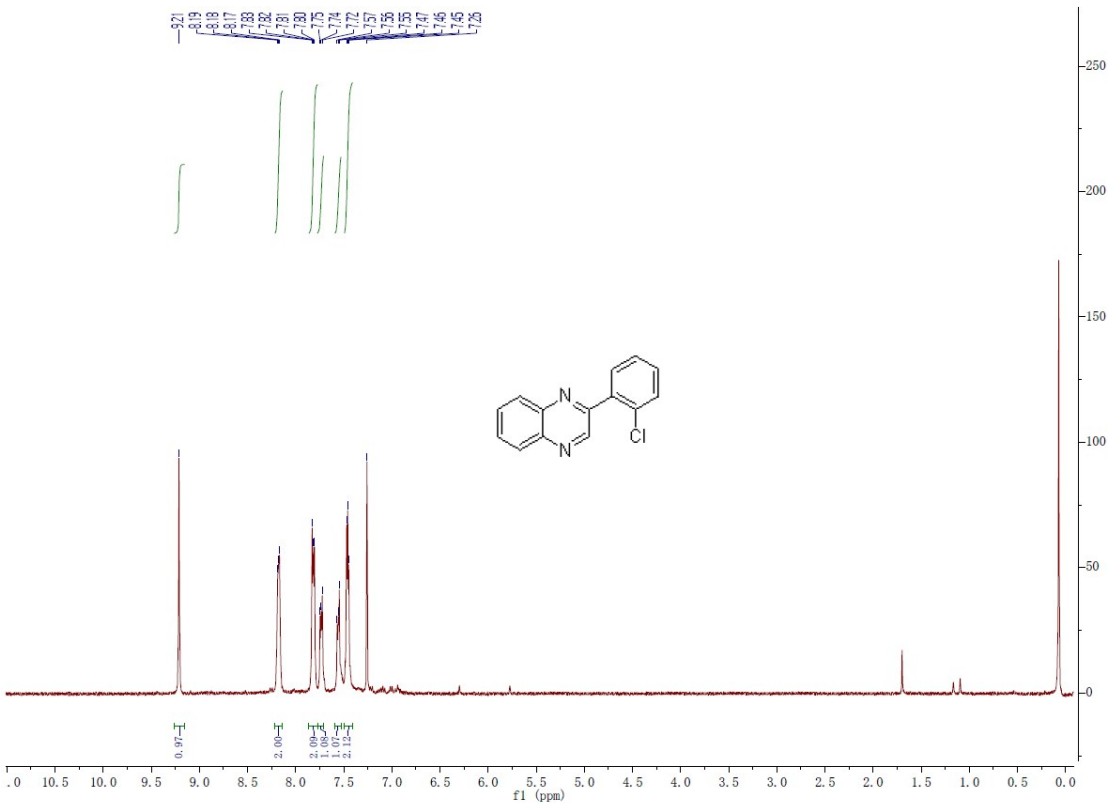
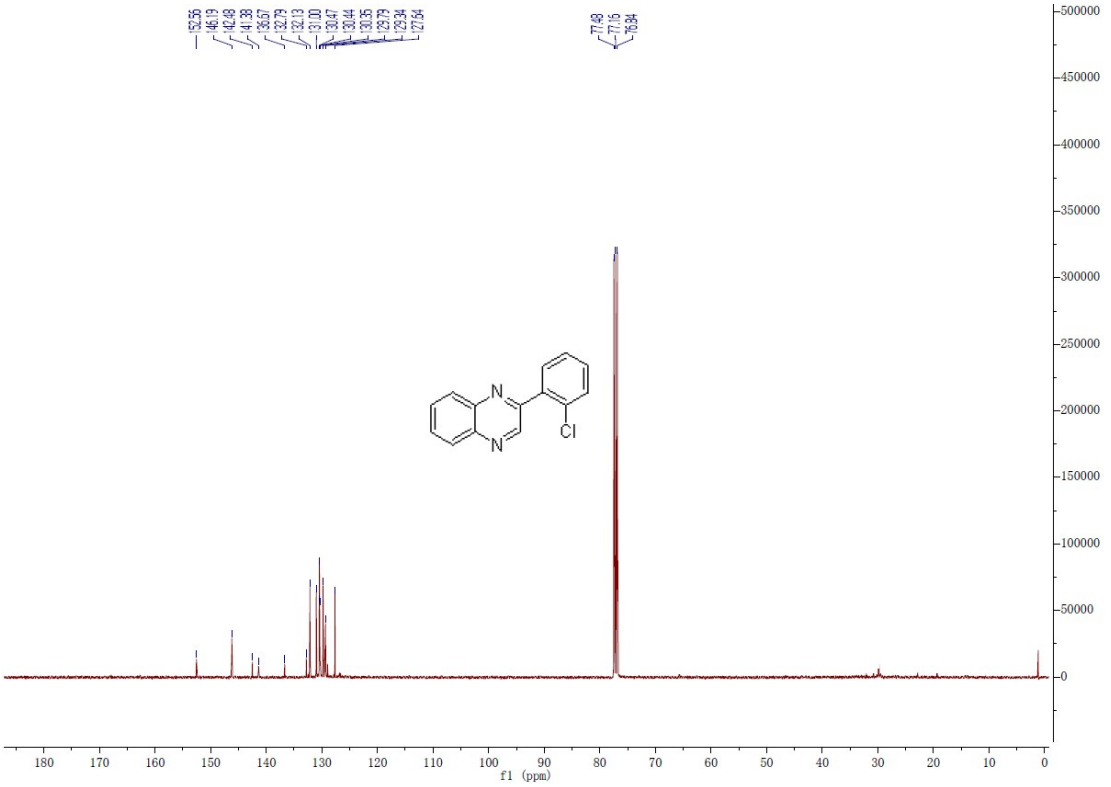
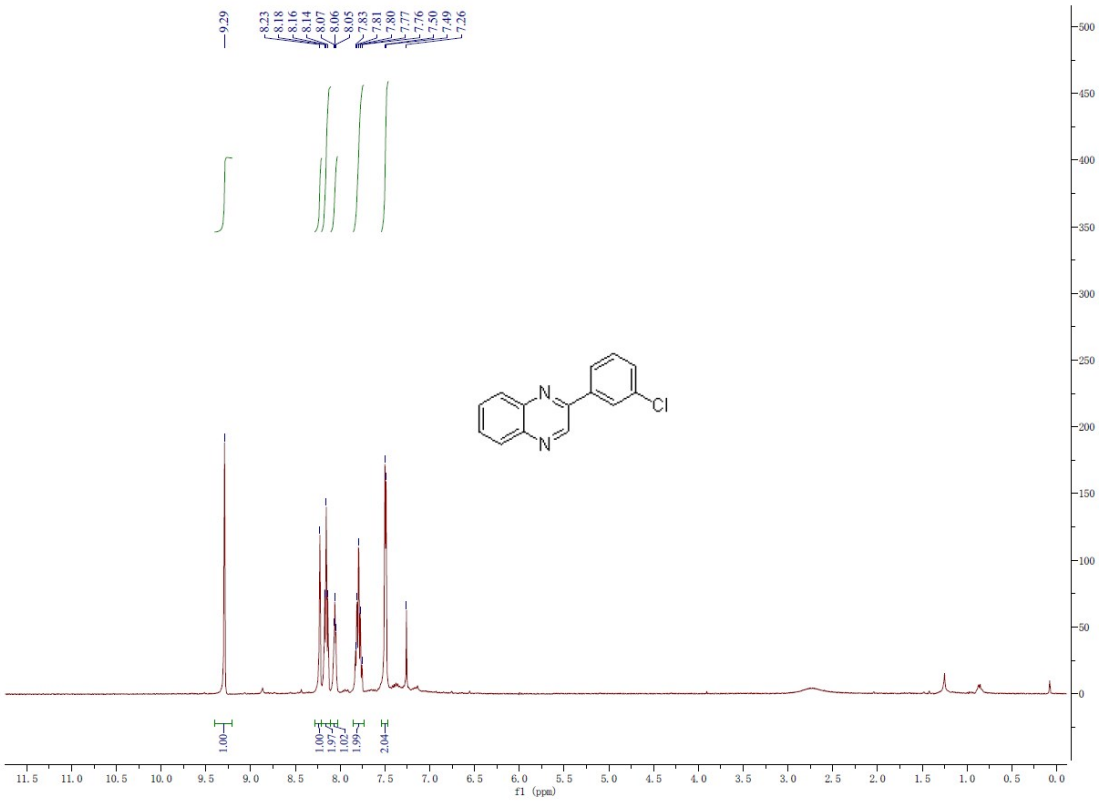
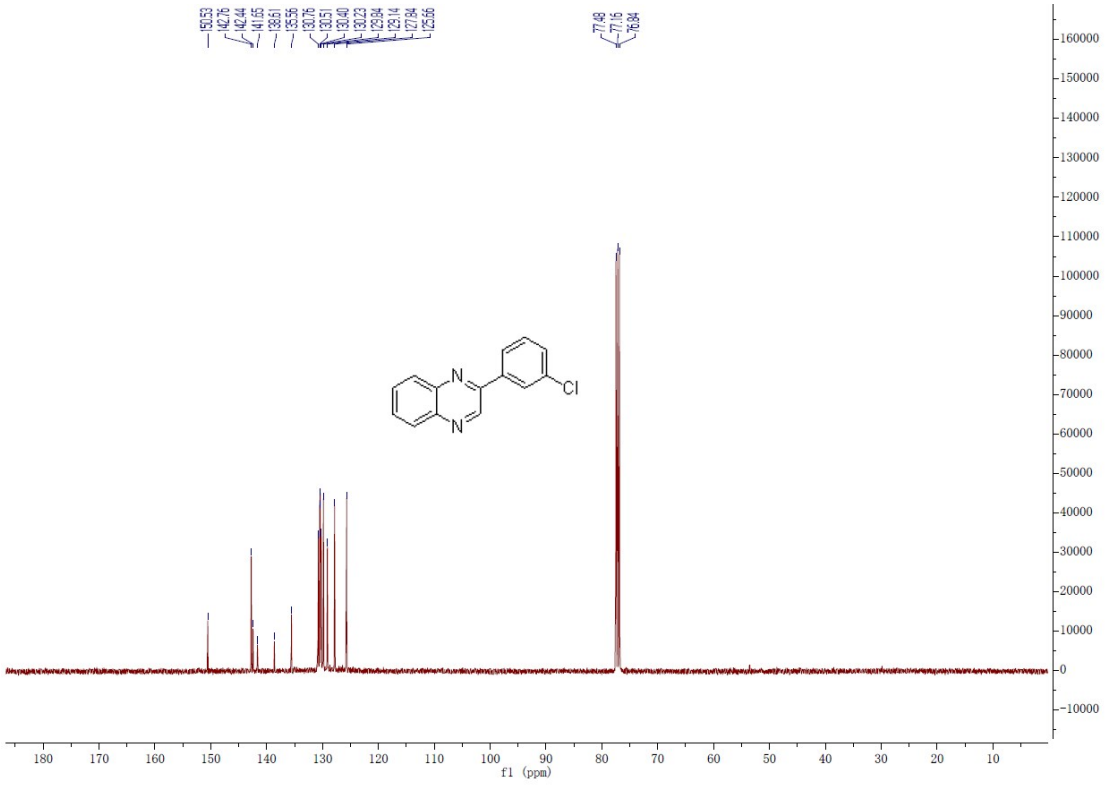
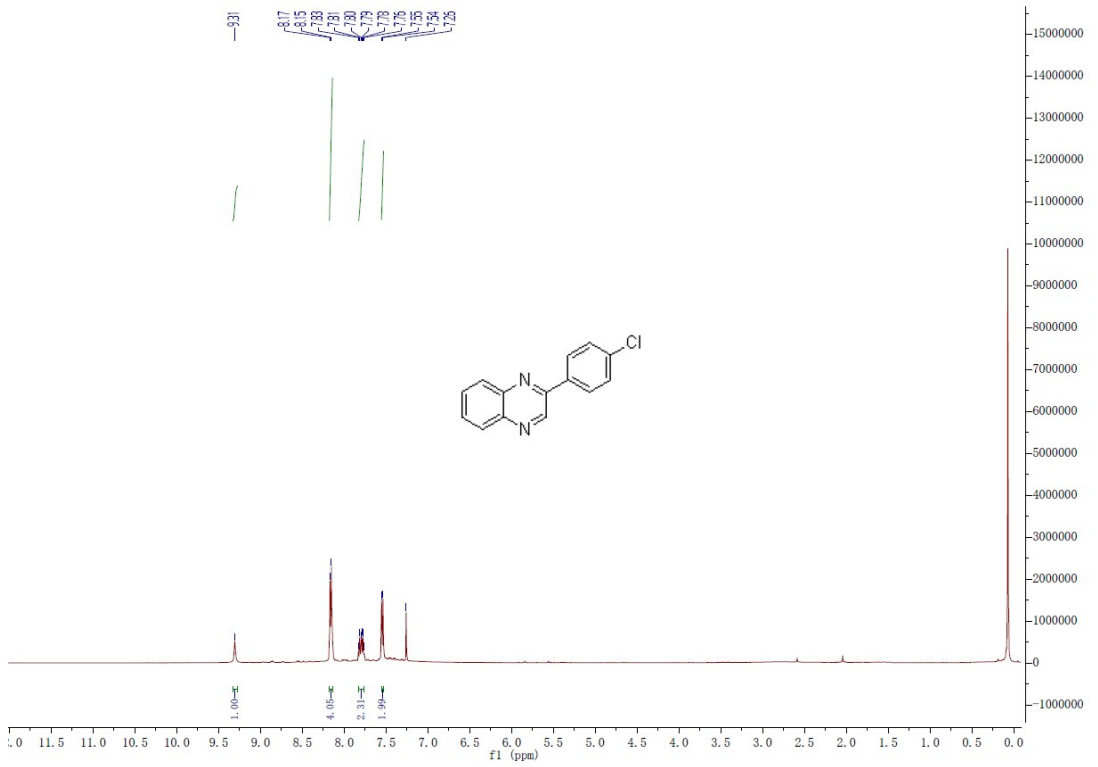
76.84
Cl
N
Cl
N
f1 (ppm)

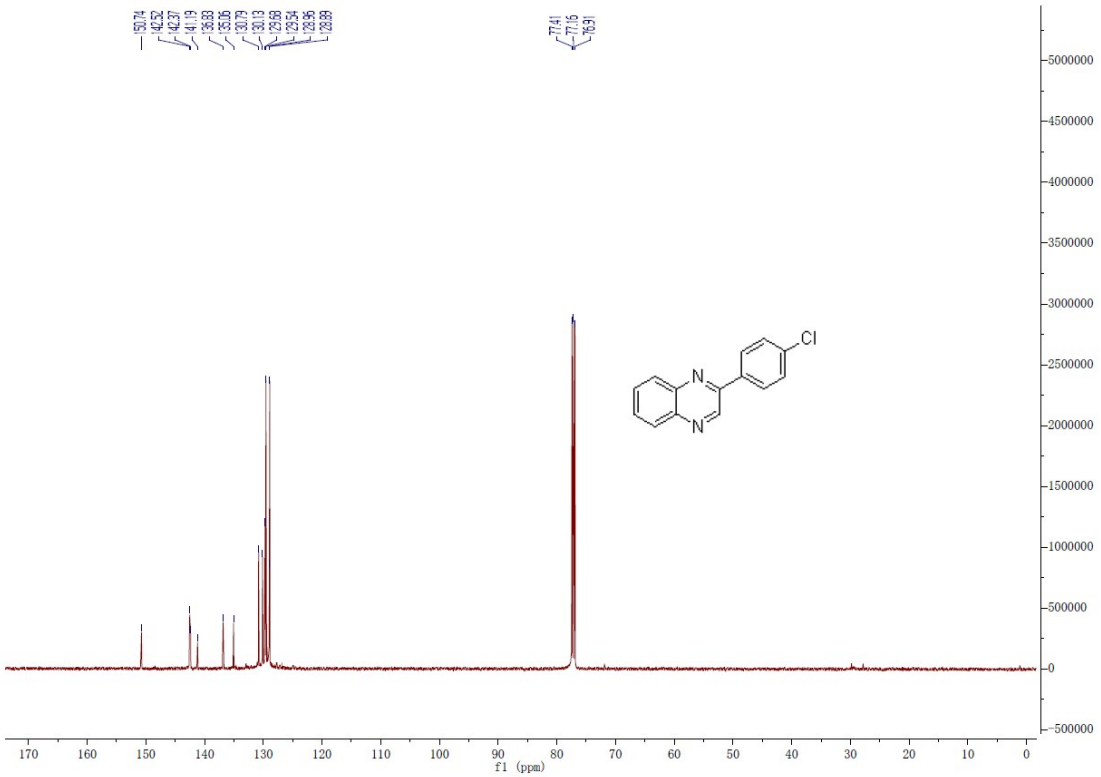

9.21
8.19
8.18
8.17
7.83
7.82
7.81
7.80
7.75
7.74
7.72
7.57
7.56
7.55
7.47
7.45
7.25
N
N
Cl
f1 (ppm)

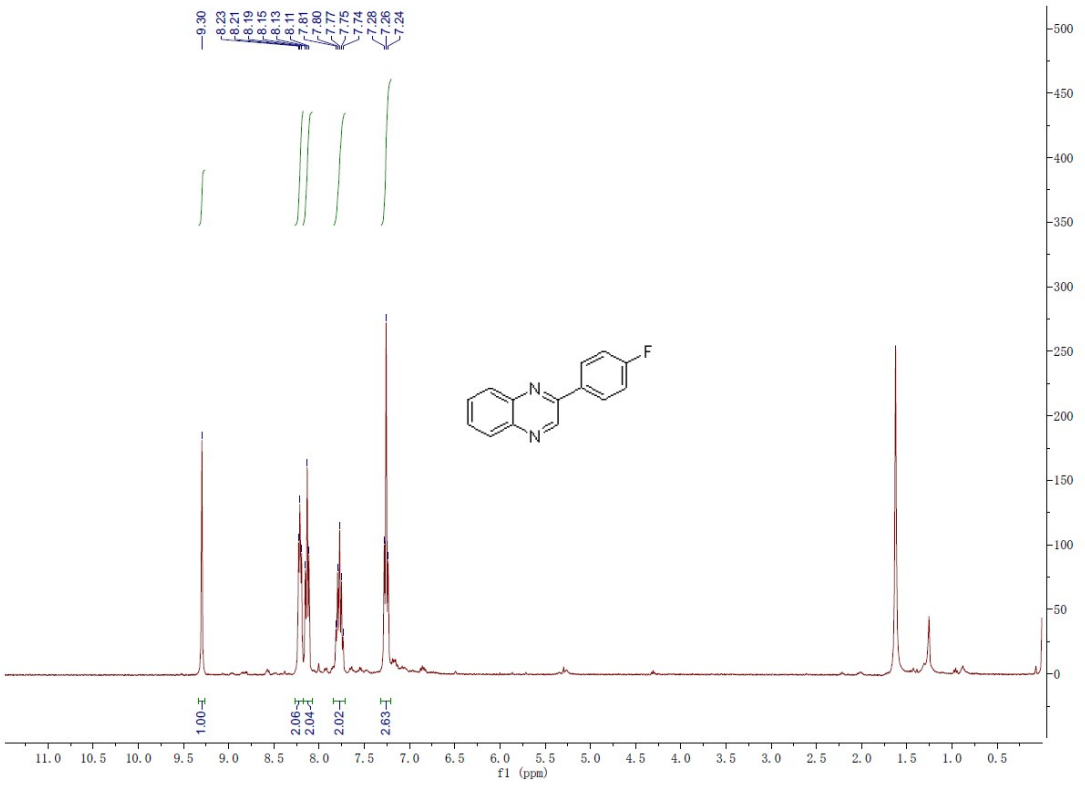

152.26
146.19
142.68
141.38
136.67
132.79
132.13
131.00
130.47
130.44
130.35
129.79
129.34
127.54
77.48
77.15
76.84
N
N
Cl
f1 (ppm)

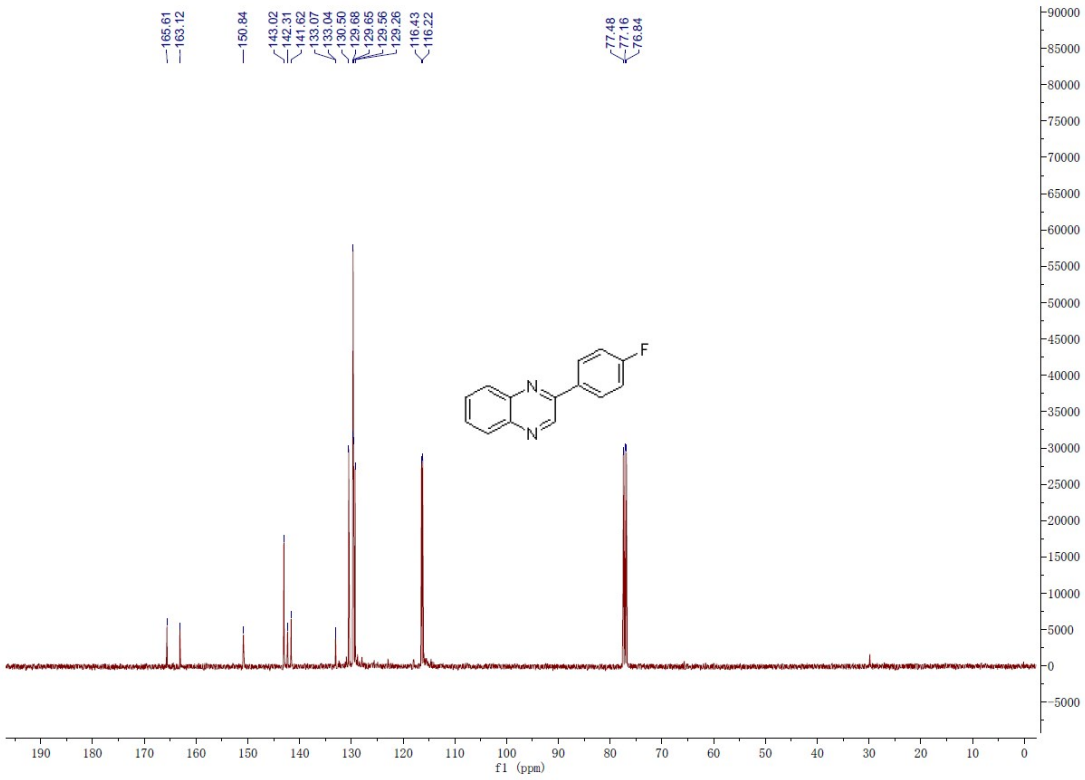

9.29
8.23
8.18
8.16
8.14
8.07
8.06
8.05
7.83
7.81
7.80
7.77
7.76
7.50
7.49
7.26
N
N
Cl
1.00
1.00
1.97
1.02
1.99
2.04
f1 (ppm)

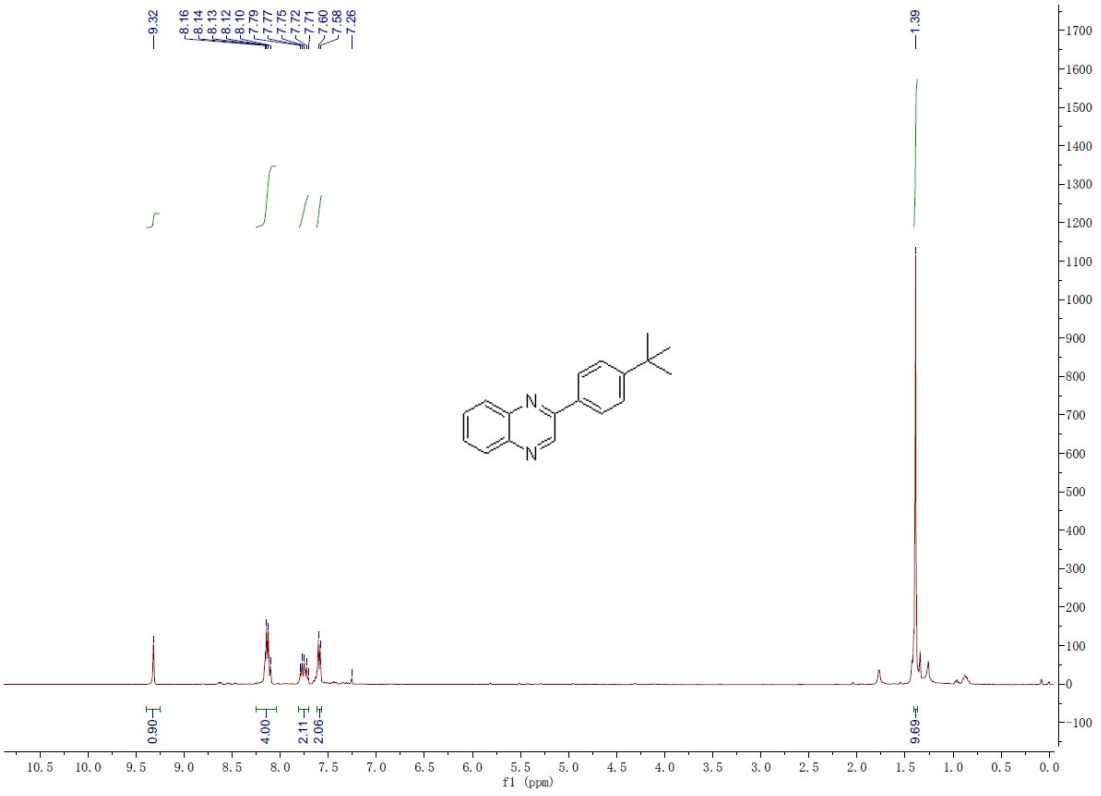

150.53
142.76
142.44
141.65
138.61
135.56
130.76
130.51
130.40
130.23
129.94
129.14
127.94
125.66
77.48
77.16
76.84
N
N
Cl
f1 (ppm)

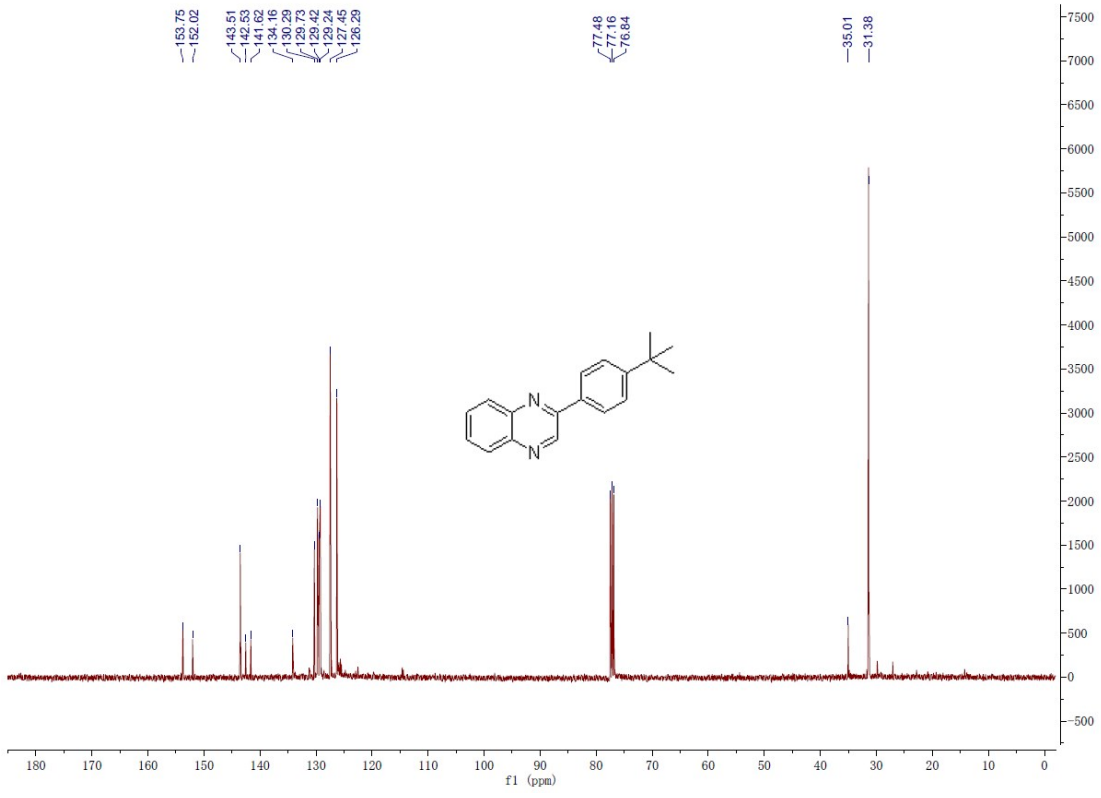

9.31
8.17
8.15
7.33
7.31
7.30
7.79
7.78
7.75
7.55
7.54
7.26
Cl
N
N
1.00
4.05
2.31
1.99
f1 (ppm)

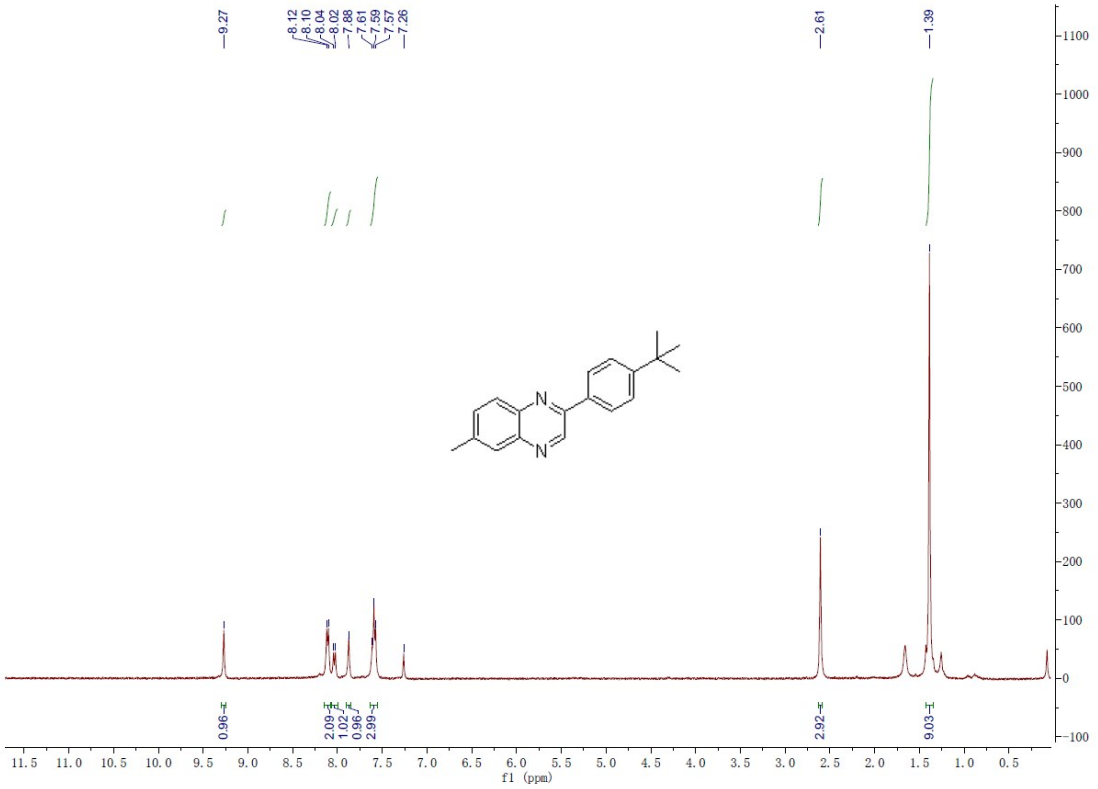

150.74
142.52
142.37
141.19
136.83
135.06
130.79
130.13
129.68
129.54
128.95
128.89
77.41
77.16
76.91
Cl
N
N
f1 (ppm)

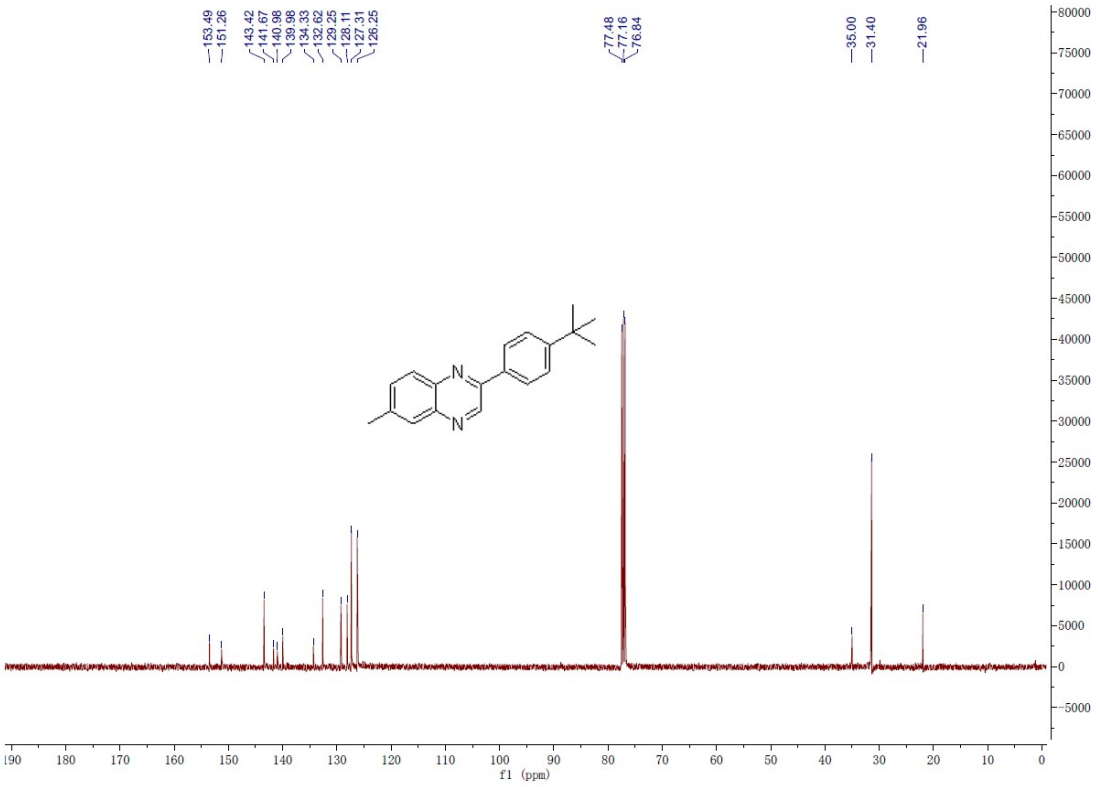

9.30
8.23
8.21
8.19
8.15
8.13
8.11
7.81
7.80
7.77
7.75
7.74
7.28
7.26
7.24
F
N
N
1.00
2.06
2.04
2.02
2.63
f1 (ppm)

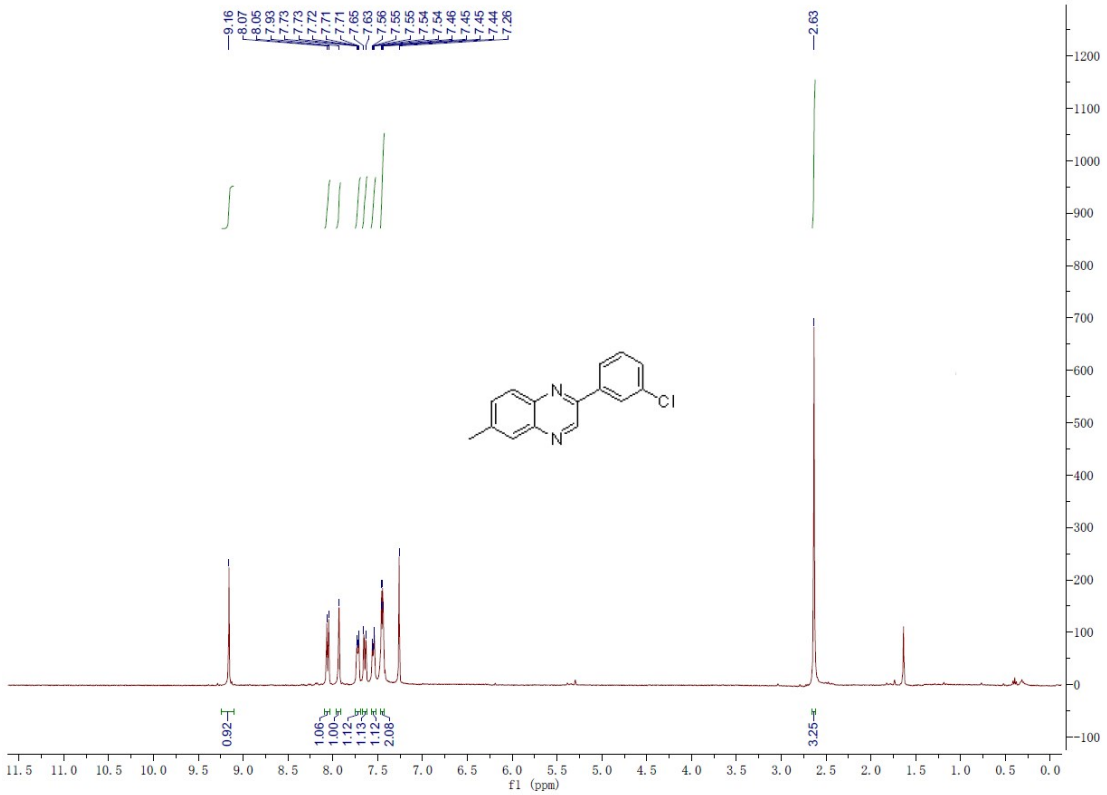

165.61
163.12
150.84
143.02
142.31
141.62
133.07
133.04
130.50
129.68
129.65
129.56
129.28
116.43
116.22
77.48
77.16
76.84
F
N
N
f1 (ppm)

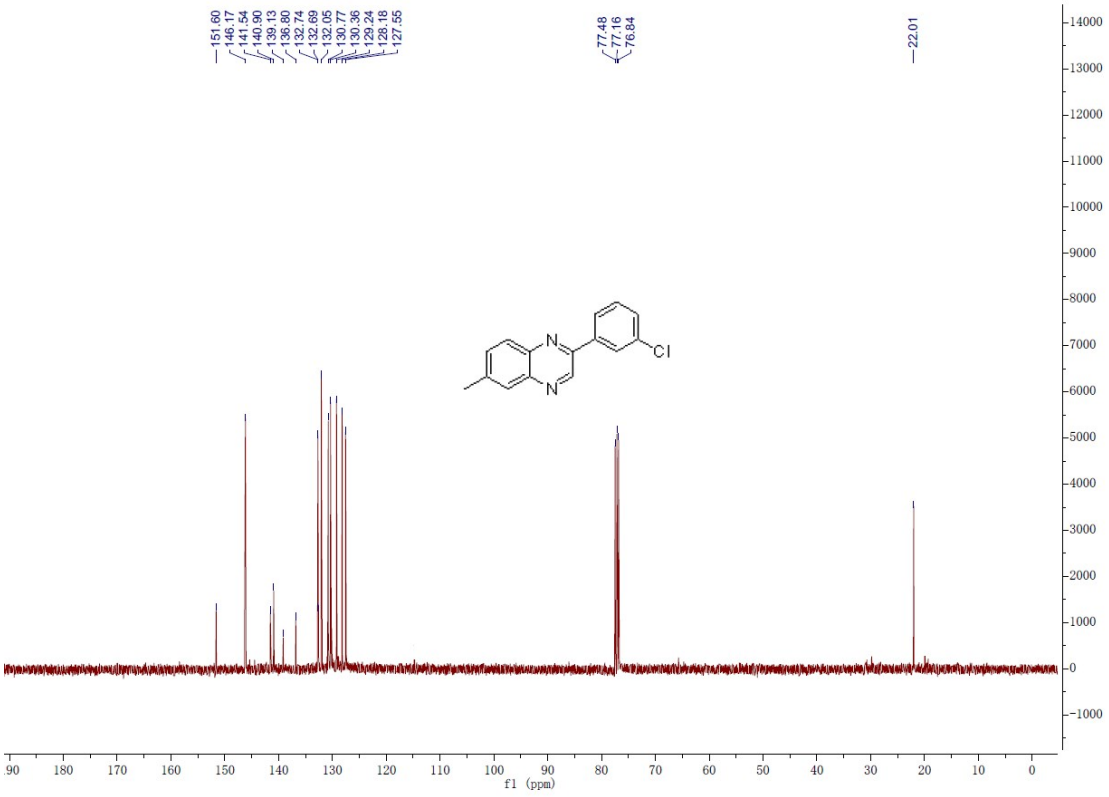

9.32
8.16
8.14
8.13
8.12
8.10
7.79
7.77
7.75
7.72
7.71
7.60
7.58
7.26
1.39
0.90
4.00
2.11
2.06
9.69
f1 (ppm)

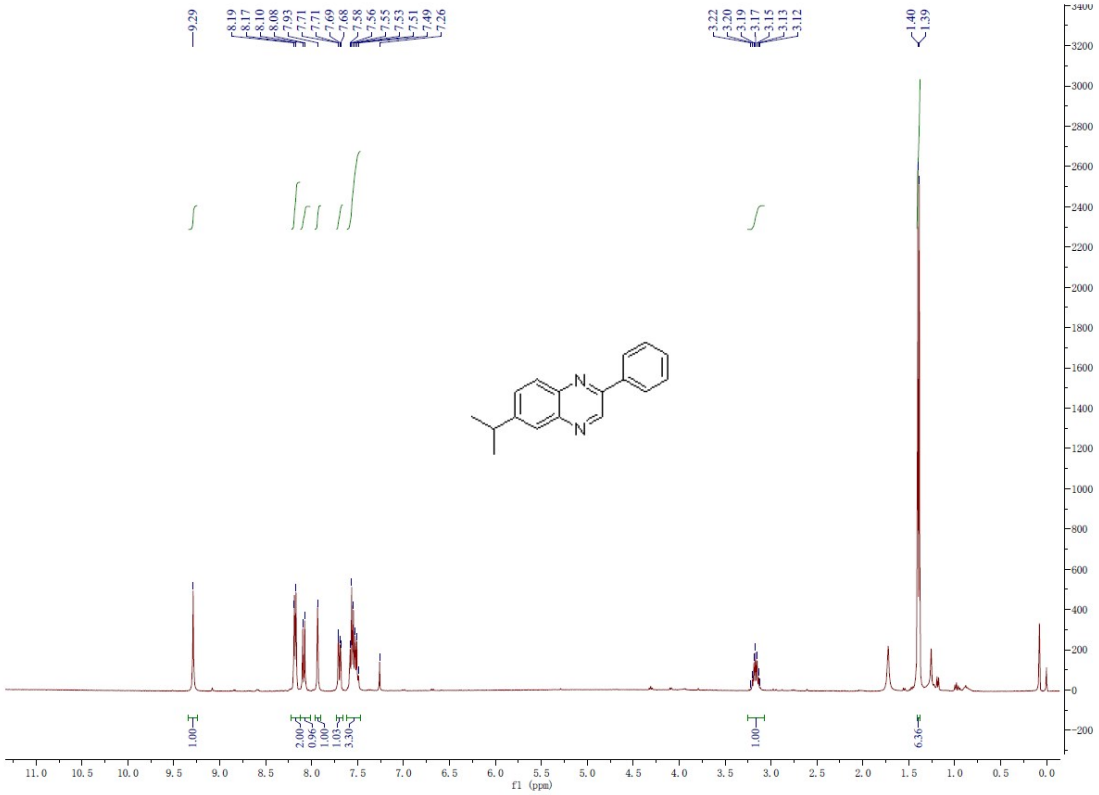

153.75
152.02
143.51
142.53
141.62
134.16
130.29
129.73
129.42
129.24
127.45
126.29
77.48
77.16
76.84
35.01
31.38
f1 (ppm)

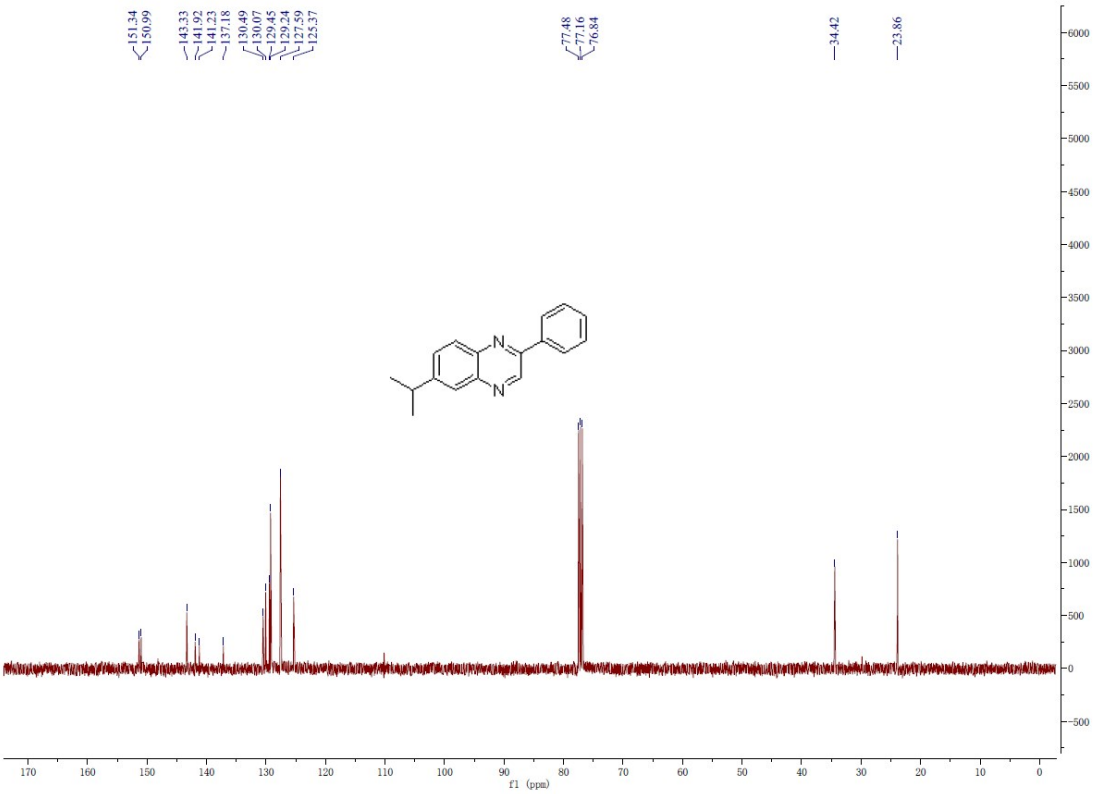

9.27
8.12
8.10
8.04
8.02
7.88
7.61
7.59
7.57
7.26
2.61
1.39
0.96
2.09
1.02
0.96
2.99
2.92
9.03
f1 (ppm)


153.49
151.26
143.42
141.67
140.98
139.98
134.33
132.62
129.25
128.11
127.31
126.25
77.48
77.16
76.84
35.00
31.40
21.96
f1 (ppm)


9.16
8.07
8.05
7.93
7.73
7.73
7.72
7.71
7.71
7.65
7.63
7.56
7.55
7.55
7.54
7.54
7.46
7.45
7.45
7.44
7.26
2.63
Cl
N
N
0.92
1.06
1.00
1.12
1.13
1.12
2.08
3.25
f1 (ppm)


151.60
146.17
141.54
140.90
139.13
136.80
132.74
132.69
132.05
130.77
130.36
129.24
128.18
127.55
77.48
77.16
76.84
22.01
Cl
N
N
f1 (ppm)


9.29
8.19
8.17
8.10
8.08
7.93
7.71
7.71
7.69
7.68
7.58
7.56
7.55
7.53
7.51
7.49
7.26
3.22
3.20
3.19
3.17
3.15
3.13
3.12
1.40
1.39
1.00
2.00
0.96
1.00
1.03
3.30
1.00
6.36
f1 (ppm)


151.34
150.99
143.33
141.92
141.23
137.18
130.49
130.07
129.45
129.24
127.59
125.37
77.48
77.16
76.84
34.42
23.86
f1 (ppm)