Supproting Information

for

WEPA: A reusable waste biomass-originated catalyst for external oxidant/metal-free quinoxalines synthesis *via* tandem condensation-cyclization-oxidation of α-hydroxy ketones

Bandameeda Ramesh Naidu, Katta Venkateswarlu*

Laboratory for Synthetic & Natural Products Chemistry, Department of Chemistry, Yogi Vemana University, Kadapa 516005, India

* Corresponding author.
E-mail address: kvenkat@yogivemanauniversity.ac.in (K. Venkateswarlu)

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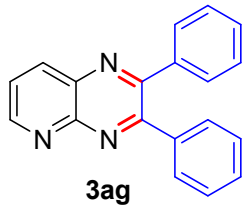
1. Characterization data of quinoxalines

Melting points of quinoxalines

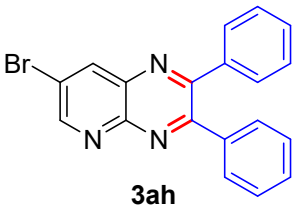
Entry	Quinoxalines (**3**)	Melting point (°C)	
		Present	Reported
1	**3aa**	122–124	126–127[1]
2	**3ab**	124–126	120–121[2]
3	**3ac**	115–117	116–117[1]
4	**3ad**	177–179	170–172[3]
5	**3ee**	120–122	122–123[2]
6	**3af**	145–147	140–142[1]
7	**3ag**	138–140	142–143[4]
8	**3ah**	153–155	149–150[5]
9	**3ai**	152–154	148–150[4]
10	**3aj**	161–163	156–158[6]
11	**3ak**	151–153	147–148[4]
12	**3al**	126–128	122–124[7]
13	**3am**	191–193	187–189[3]
14	**3an**	141–142	134–136[1]
15	**3ao**	104–106	–
16	**3ap**	122–124	122–124[1]
17	**3aq**	117–119	115.5–116.5[8]
18	**3ar**	151–153	152–154[1]
19	**3as**	96–98	–
20	**3at**	91–93	91–92[10]
21	**3au**	70–72	71–72[10]
22	**3av**	88–90	89–90[10]
23	**3aw**	185–187	183–184[10]
24	**3ax**	135–137	132–134[11]
25	**3ay**	261–263	258–260[12]
26	**3az**	328–330	320[12]
27	**3ba**	67–69	67–69[13]
28	**3bb**	109–111	107–112[14]
29	**3bc**	122–124	120–121[15]
30	**3bd**	138–140	140–141[13]
31	**3be**	211–213	209–210[16]

Physical appearance and ^{1}H NMR, ^{13}C NMR and mass spectral data of quinoxalines



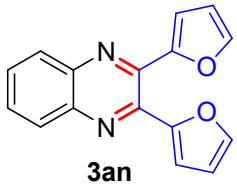
3ag

2,3-Diphenylpyrido[2,3-*b*]pyrazine (3ag).[4] Pale pink solid; Yield: 94% (0.8 h); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 9.17 (dd, *J* = 2.0, 4.0 Hz, 1H), 8.52 (dd, *J* = 2.0, 8.4 Hz, 1H), 7.71 (dd, *J* = 4.4, 8.4 Hz, 1H), 7.65–7.62 (m, 2H), 7.57–7.54 (m, 2H), 7.41–7.30 (m. 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 156.3, 154.7, 154.1, 149.9, 138.6, 138.1, 136.2, 130.3. 129.8, 129.5, 129.3, 128.4, 128.2, 125.2; ESMS: *m*/*z* 284.17 (M+1).



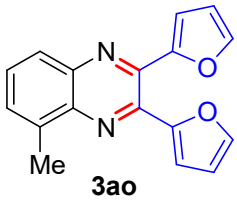
3ah

7-Bromo-2,3-diphenylpyrido[2,3-*b*]pyrazine (3ah).[5] Pale yellow solid; Yield: 90% (0.9 h); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 9.16 (d, *J* = 2.4 Hz, 1H), 8.68 (d, *J* = 2.4 Hz, 1H), 7.63–7.60 (m, 2H), 7.56–7.52 (m, 2H), 7.43–7.30 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 156.5, 155.5, 155.1, 148.3, 139.4, 138.1, 137.8, 136.4, 130.2, 129.9, 129.7, 129.6, 128.5, 128.3, 121.0; ESMS: *m*/*z* 362.27 and 364.23 (1:1) (M+1 and M+3).



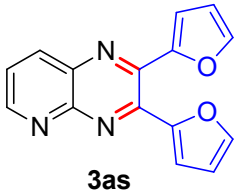
3an

2,3-Di(2-furanyl)quinoxaline (3an).[3] Gold colour solid; Yield: 98% (0.8 h); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.14 (dd, *J* = 3.2, 6.2 Hz, 2H), 7.5 (dd, *J* = 3.2, 6.4 Hz, 2H), 7.63 (d, *J* = 1.6 Hz, 2H), 6.6 (d, *J* = 3.6 Hz, 2H), 6.57 (dd, *J* = 2.0, 3.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 150.8, 144.2, 142.7, 140.7, 130.4, 129.1, 113.0, 111.9; ESMS: *m*/*z* 263.43 (M+1).



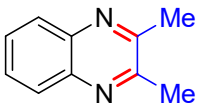
3ao

2,3-Di(2-furanyl)-5-methylquinoxaline (3ao).[1] Cream colour solid; Yield: 96% (0.9 h); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.99–7.96 (m, 2H), 7.66–7.56 (m, 3H), 6.81 (d, *J* = 3.2 Hz, 1H), 6.59–6.53 (m, 3H), 2.82 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 151.7, 151.0, 144.2, 143.8, 142.1, 141.3, 140.8, 139.8, 137.5, 130.2 (2C), 126.9, 112.9, 112.5, 111.9, 111.8, 17.1; ESMS: *m*/*z* 277.31 (M+1).



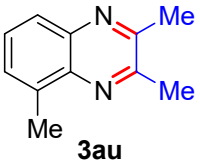
3as

2,3-Di(2-furanyl)pyrido[2,3-*b*]pyrazine (3as). Cream colour solid; Yield: 90% (0.8 h); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 9.12 (dd, *J* = 2.0, 4.4 Hz, 1H), 8.47 (dd, *J* = 2.0, 8.0 Hz, 1H), 7.70 (dd, *J* = 1.0, 3.6 Hz, 1H), 6.75 (dd, *J* = 1.0, 3.6 Hz, 1H), 6.61 (dd, *J* = 2.0, 3.6 Hz, 1H), 6.59 (dd, *J* = 1.6, 3.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 154.4, 150.6, 150.4, 149.2, 145.0, 144.8, 148.7, 143.3, 137.8, 135.8, 125.4, 114.7, 114.0, 112.3, 112.1; ESMS: *m/z* 264.36 (M+1).



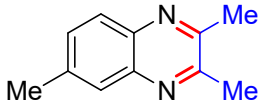
3at

2,3-Dimethylquinoxaline (3at).[2] White solid; Yield: 94% (0.9 h); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.95 (dd, *J* = 3.5, 6.3 Hz, 2H), 7.63 (dd, *J* = 3.5, 6.3 Hz, 2H), 2.78 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 153.5, 141.0, 128.9, 128.3, 23.2; ESMS: *m/z* 159.08 (M+1).



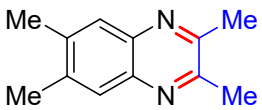
3au

2,3,5-Trimethylquinoxaline (3au).[2] Cream colour solid; Yield: 91% (1 h); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.80 (d, *J* = 8.1 Hz, 1H), 7.53 (t, *J* = 7.4 Hz, 1H), 7.47 (d, *J* = 7.0 Hz, 1H), 2.76 (s, 3H), 2.72 (s, 3H), 2.70 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 152.8, 152.2, 141.1, 140.3, 136.7, 128.8, 128.4, 126.1, 23.4, 23.1, 17.1; ESMS: *m/z* 173.02 (M+1).



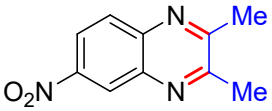
3av

2,3,6-Trimethylquinoxaline (3av).[2] Cream colour solid; Yield: 93% (0.8 h); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.86 (d, *J* = 8.6 Hz, 1H), 7.75 (m, 1H), 7.49 (d, *J* =8.6 Hz, 1H), 2.70 (s, 6H), 2.55 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 153.3, 152.4, 141.1, 139.5, 1392, 131.0, 127.8, 127.3, 23.2, 23.1, 21.7; ESMS: *m/z* 173.15 (M+1).



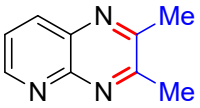
3aw

2,3,6,7-Tetramethylquinoxaline (3aw). White solid; Yield: 92% (0.8 h); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.70 (s, 2H), 2.68 (s, 6H), 2.44 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 152.3, 140.0, 139.0, 127.5, 23.1, 20.3; ESMS: *m/z* 187.37 (M+1).



3ax

2,3-Dimethyl-6-nitroquinoxaline (3ax).[17] Cream colour solid; Yield: 86% (1.1 h); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.9 (d, *J* = 2.5 Hz, 1H), 8.44 (dd, *J* = 2.5, 9.1 Hz, 1H), 8.10 (d, *J* = 9.1 Hz, 1H), 2.80 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 157.3, 156.3, 147.1, 143.7, 139.9, 129.9, 124.9, 122.4, 23.5, 23.3; ESMS: *m*/*z* 202.11 (M–1).

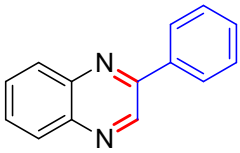


3ay

2,3-Dimethylpyrido[2,3-*b*]pyrazine (3ay).[18] White solid; Yield: 92% (1 h); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 9.05 (dd, *J* = 2.0, 4.4 Hz, 1H), 8.33 (dd, *J* = 2.0, 8.0 Hz, 1H), 7.63 (dd, *J* = 4.4, 8.0 Hz, 1H), 2.82 (s, 3H), 2.78 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 157.3, 155.0, 152.6, 150.2, 137.3, 135.9, 124.3, 23.5, 23.0; ESMS: *m*/*z* 160.02 (M+1).

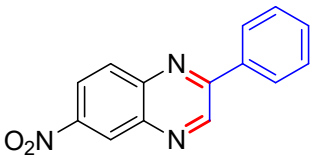
3az

7-Bromo-2,3-dimethylpyrido[2,3-*b*]pyrazine (3az).[12] Light pink solid; Yield: 89% (1.1 h); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 9.05 (d, *J* = 2.8 Hz, 1H), 8.50 (d, *J* = 2.8 Hz, 1H), 2.80 (s, 3H), 2.78 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 157.7, 156.1, 153.7, 148.6, 138.8, 136.2, 119.9, 23.6, 23.1; ESMS: *m*/*z* 338.27 and 340.17 (1:1) (M+1 and M+3).



3ba

2-Phenylquinoxaline (3ba).[19] Pale red solid; Yield: 94% (1.5 h); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 9.32 (s, 1H), 8.23–8.09 (m, 4H), 7.82–7.69 (m, 2H), 7.62–7.49 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 152.0, 143.5, 142.4, 141.7, 136.9, 130.4, 130.3, 129.7 (2C), 129.3, 129.2, 127.7.



3be

6-Nitro-2-phenylquinoxaline (3be).[19] Yellowish solid; Yield: 88% (2.3 h); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 9.5 (s, 1H), 9.03 (d, *J* = 2.5 Hz, 1H), 8.56 (dd, *J* = 2.5, 9.2 Hz, 1H) 8.32-8.24 (m, 3H), 7.72-7.47 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 154.4, 147.5, 145.6, 145.0, 140.4, 135.7, 131.5, 131.3, 129.5, 128.0, 125.8, 123.9.

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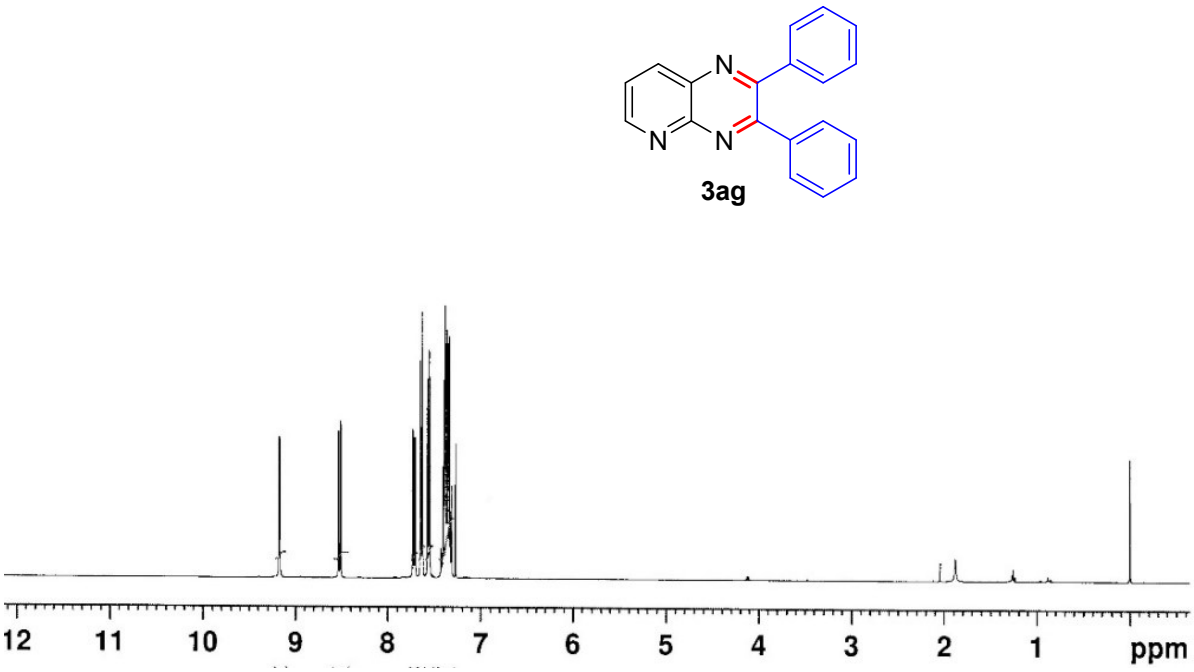
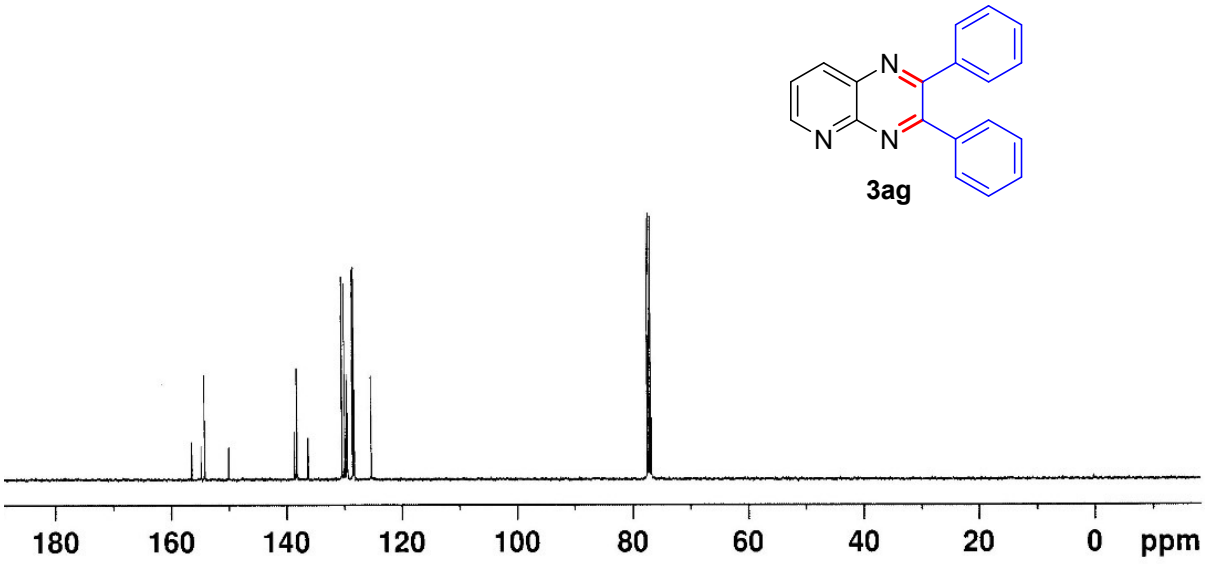
2. Copies of ^{1}H NMR and ^{13}C NMR spectra of quinoxalines

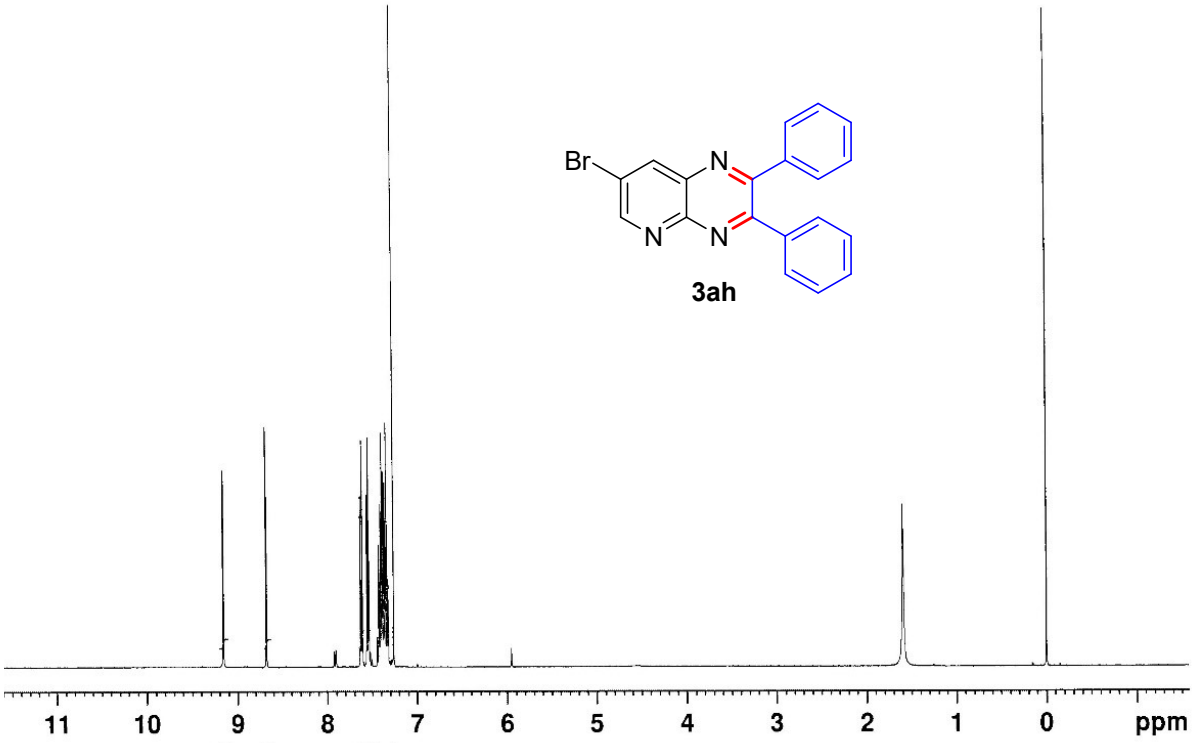
^{1}H NMR spectrum of compound **3ag**:



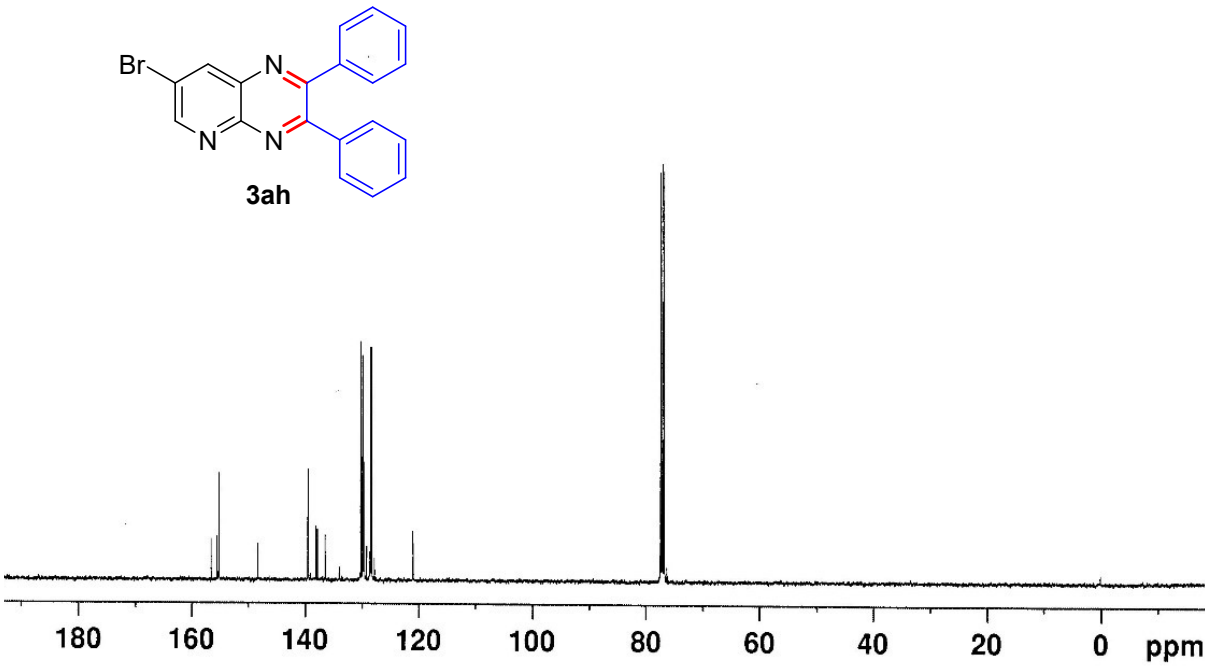
^{13}C NMR spectrum of compound **3ag**:



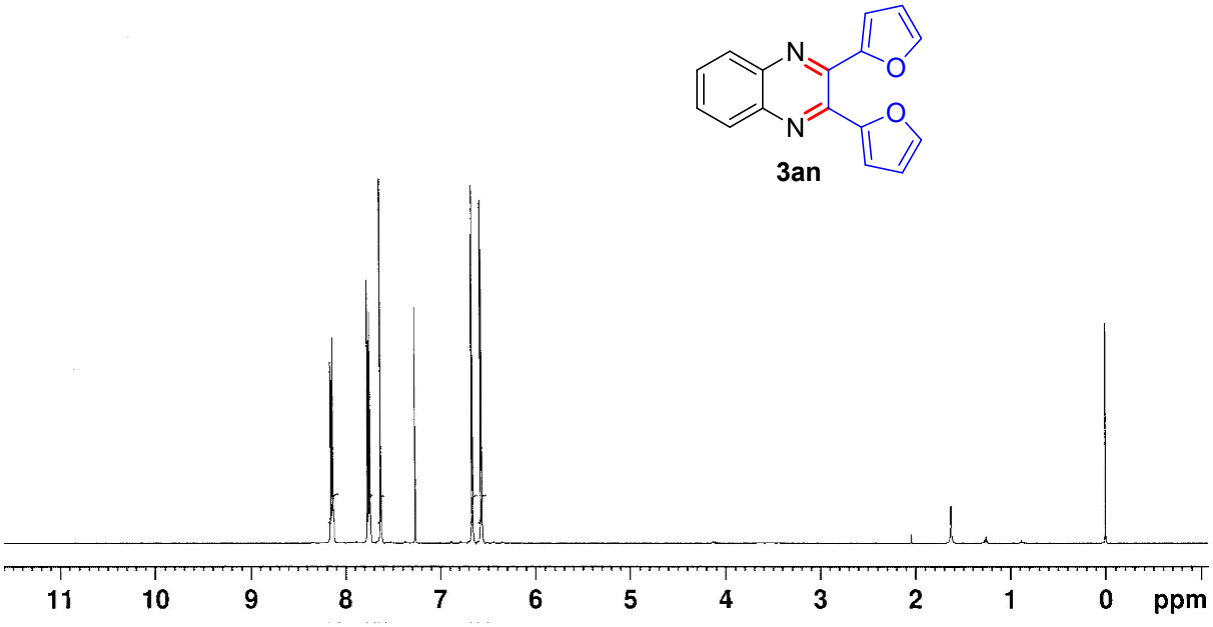
^{1}H NMR spectrum of compound **3ah**:



^{13}C NMR spectrum of compound **3ah**:



^{1}H NMR spectrum of compound **3an**:



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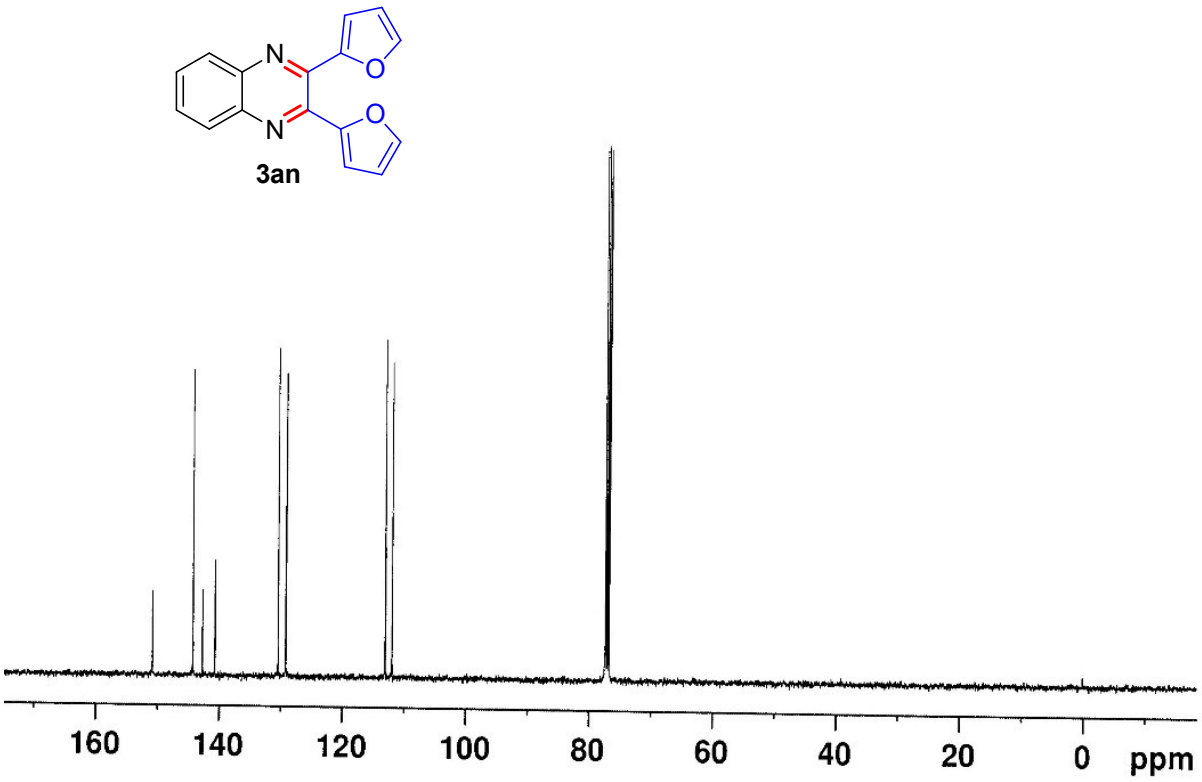
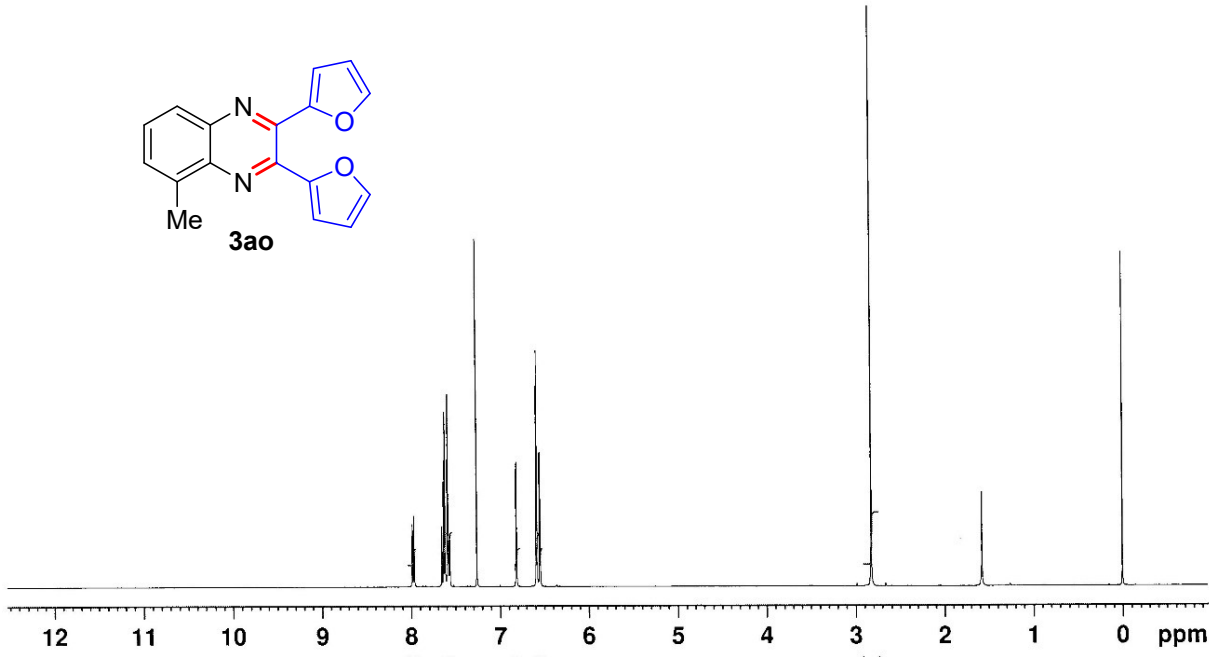
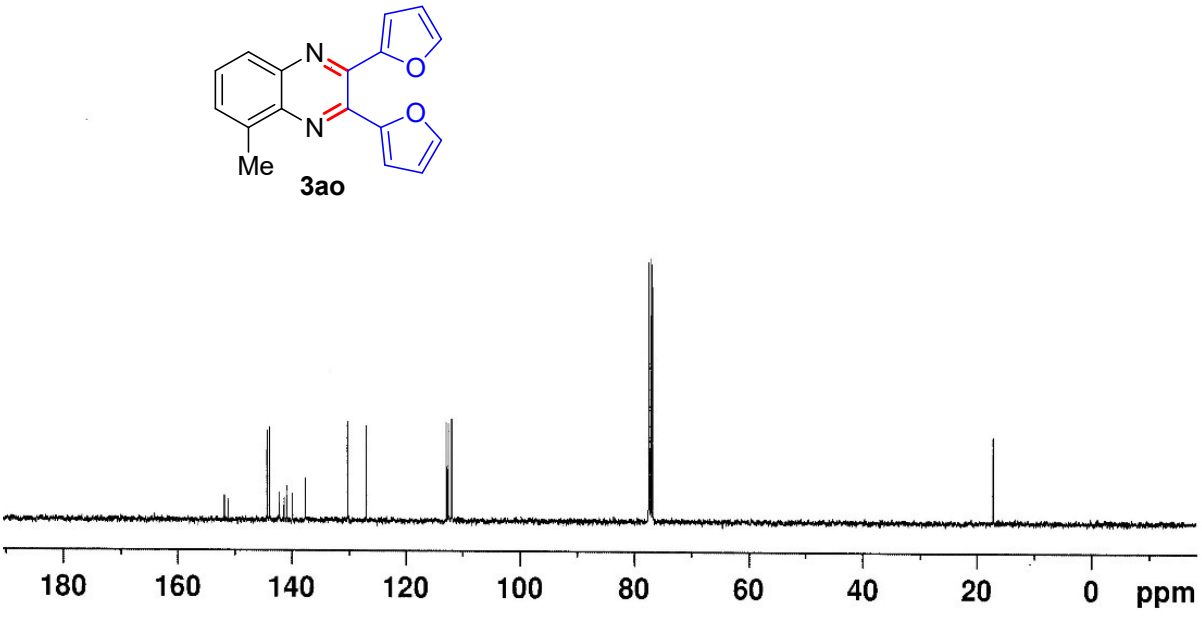


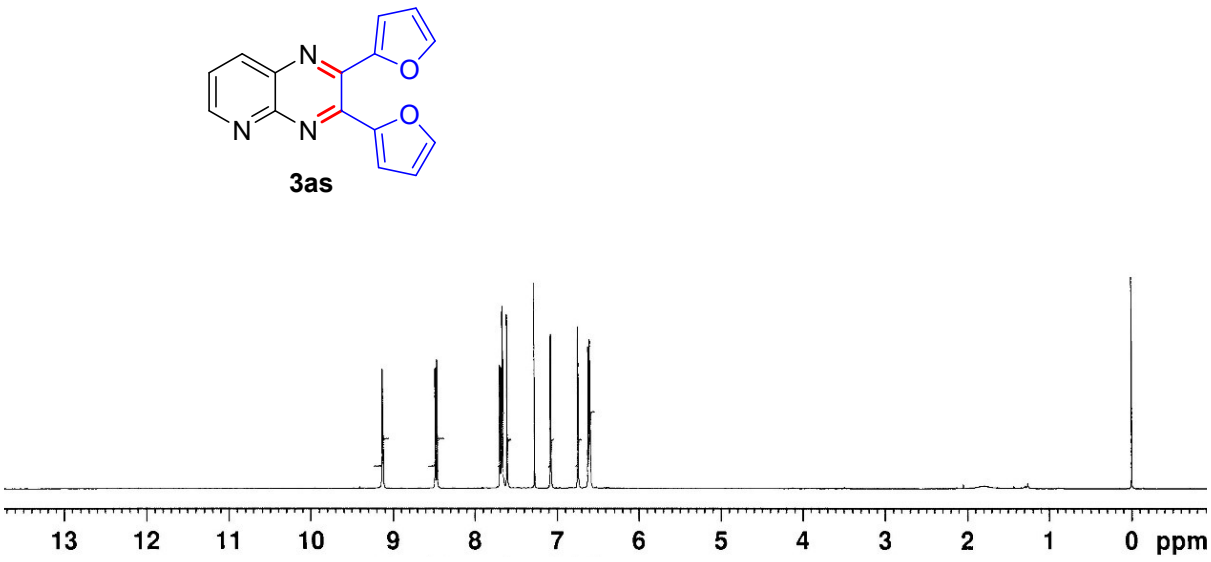
^{1}H NMR spectrum of compound **3ao**:



^{13}C NMR spectrum of compound **3ao**:



^{1}H NMR spectrum of compound **3as**:



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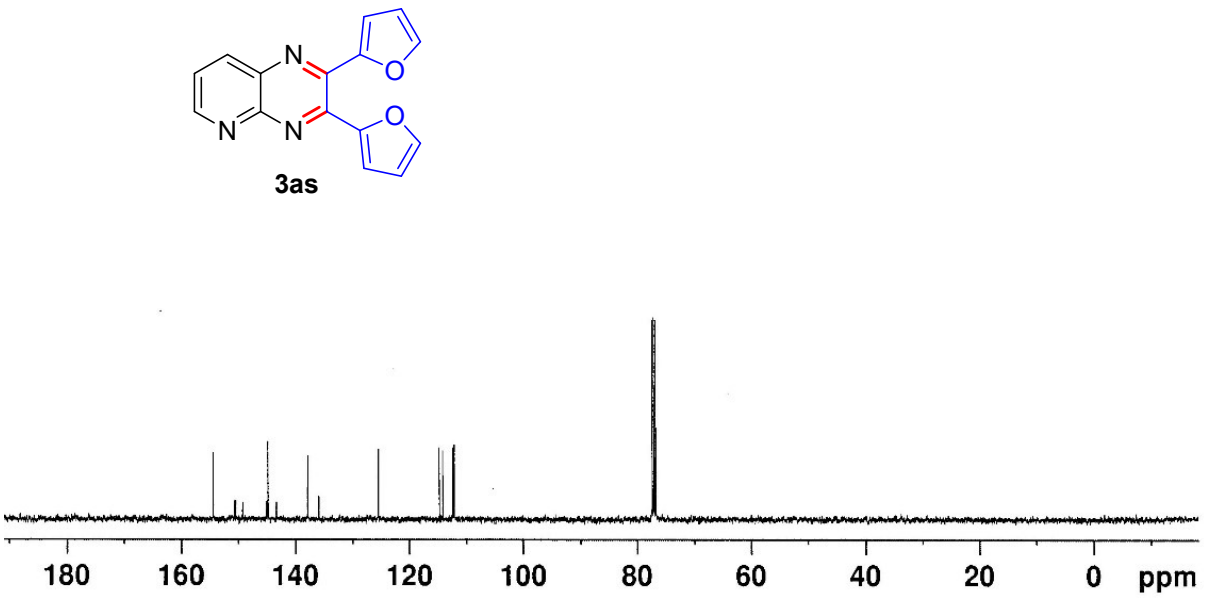
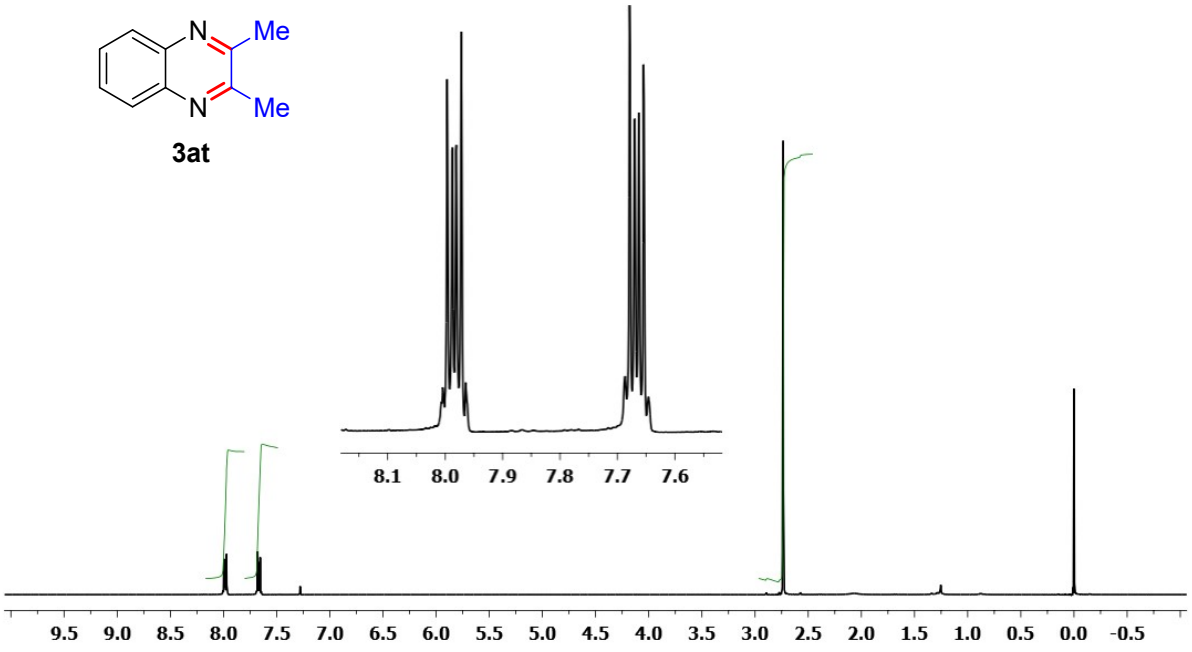
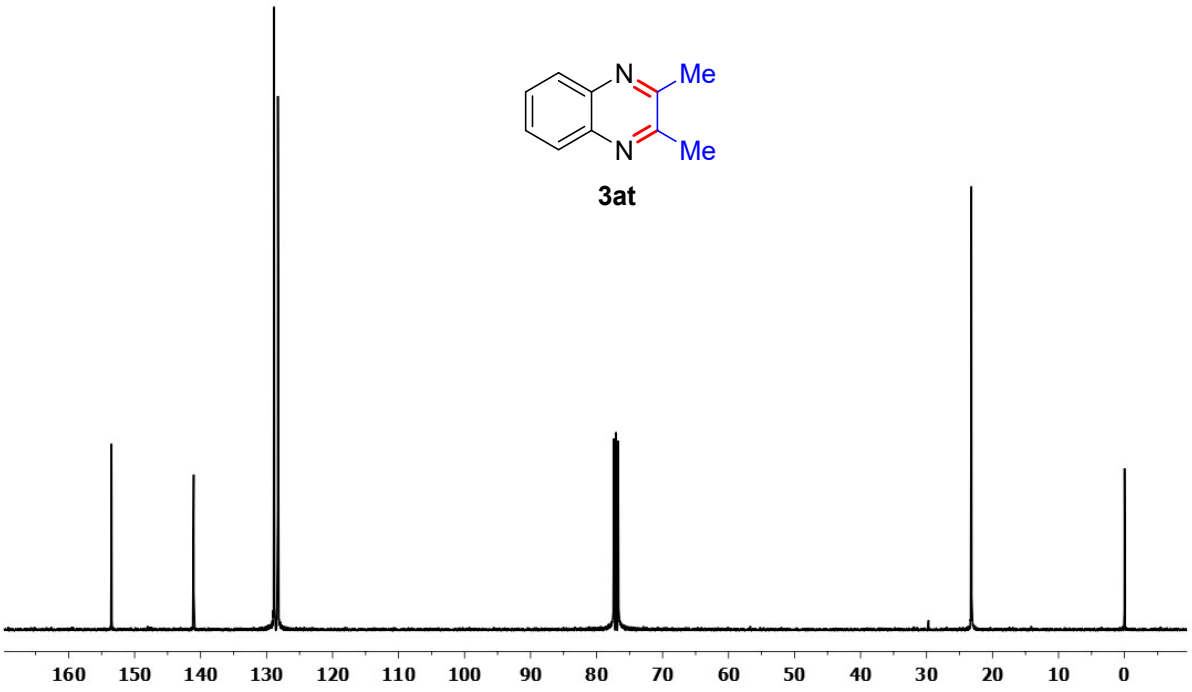


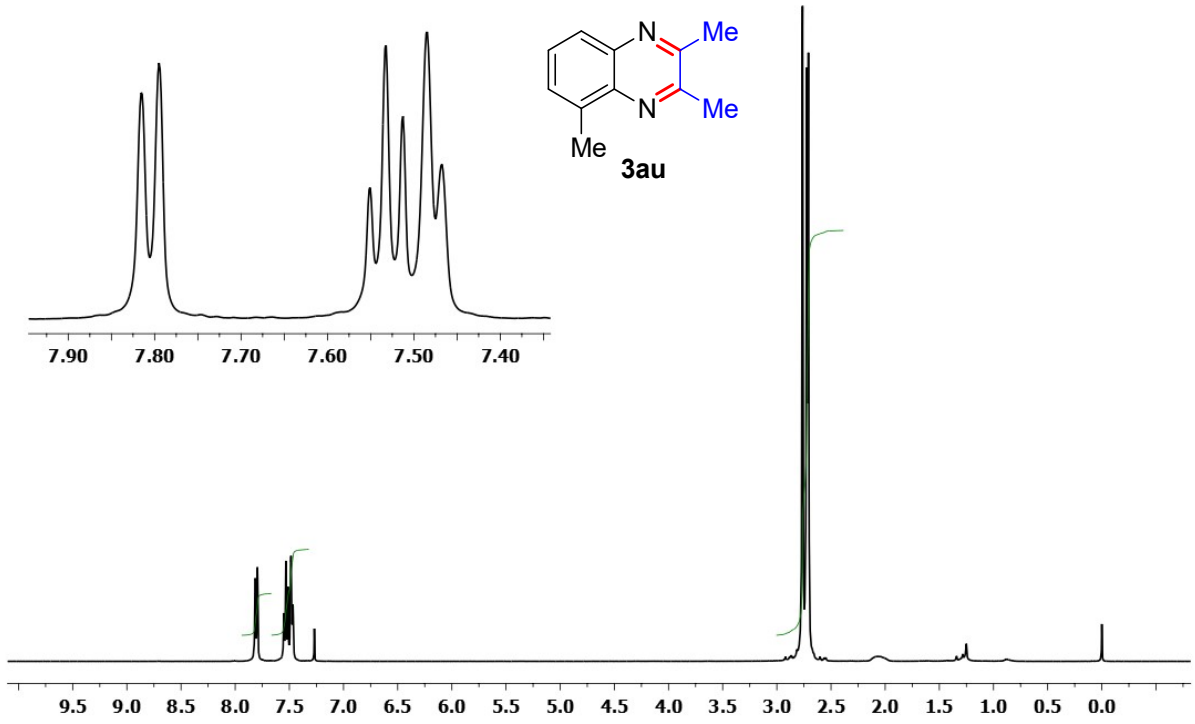
^{1}H NMR spectrum of compound **3at**:



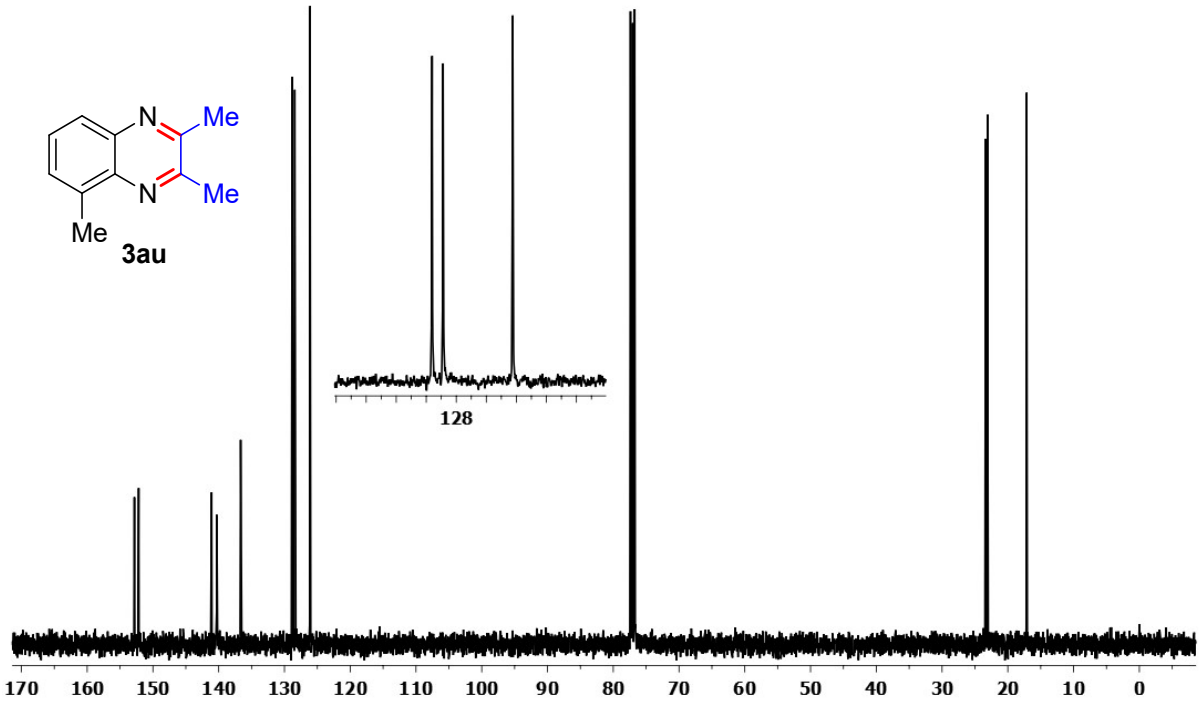
^{13}C NMR spectrum of compound **3at**:



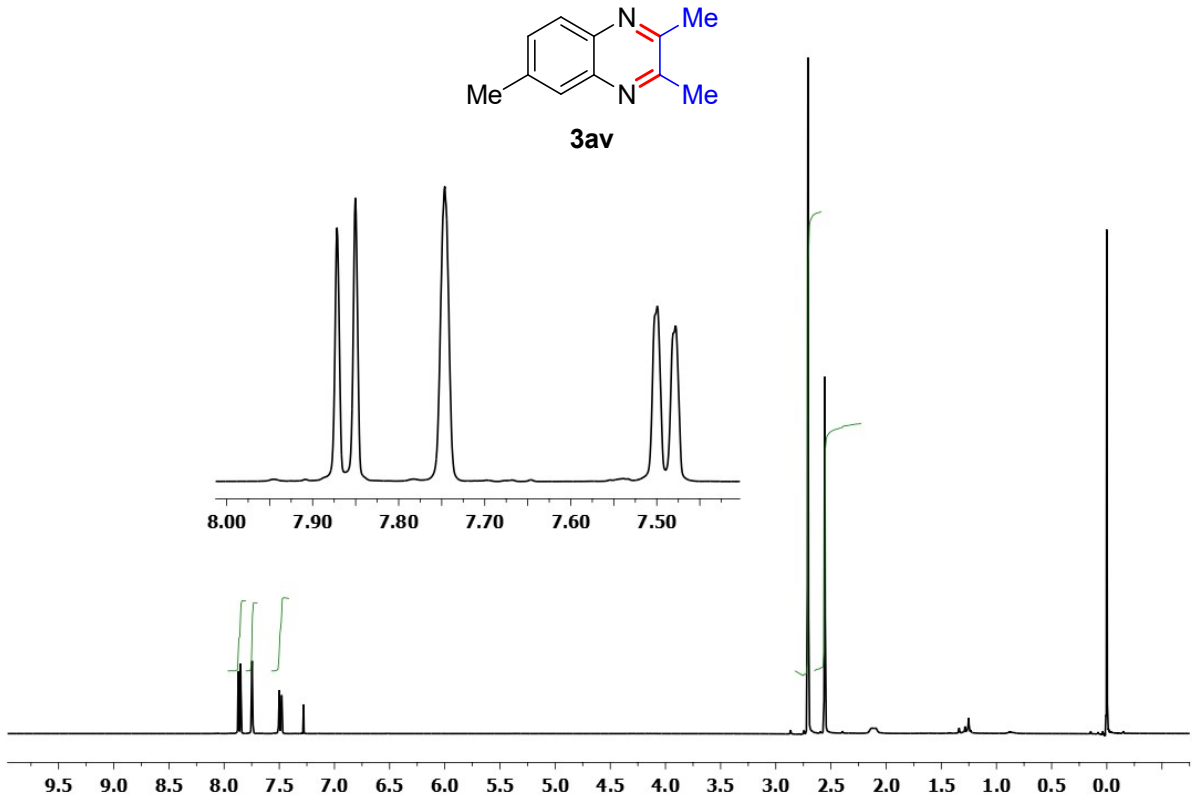
^{1}H NMR spectrum of compound **3au**:



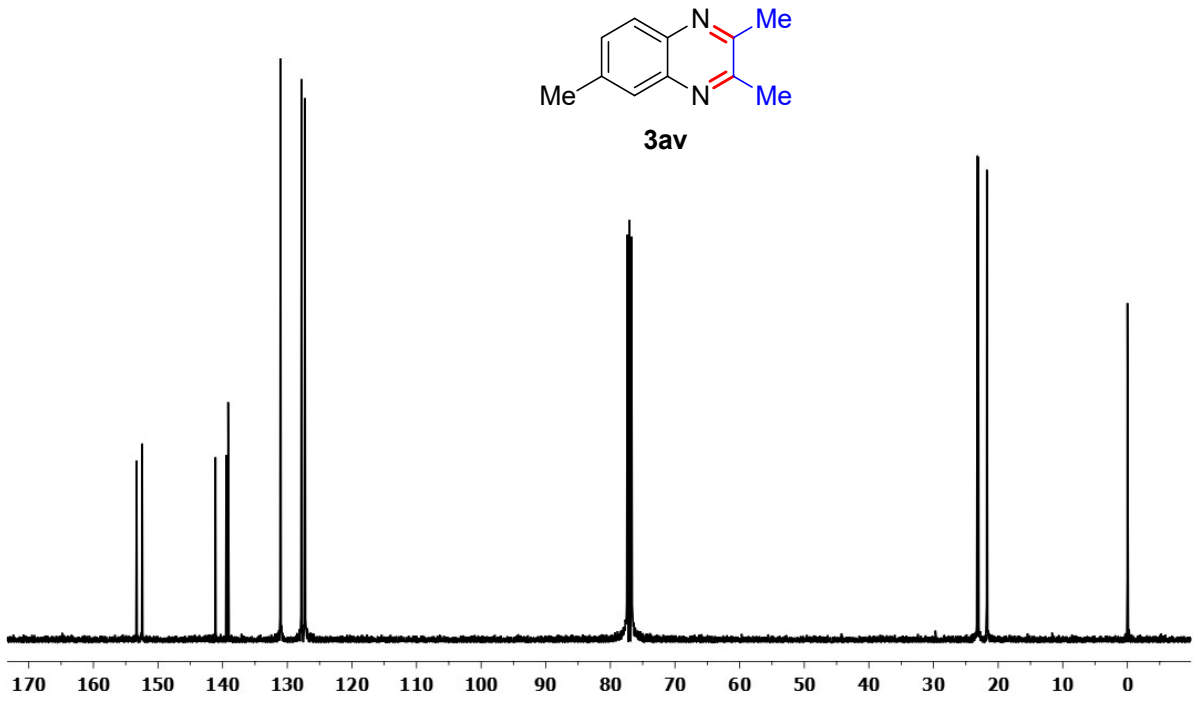
^{13}C NMR spectrum of compound **3au**:



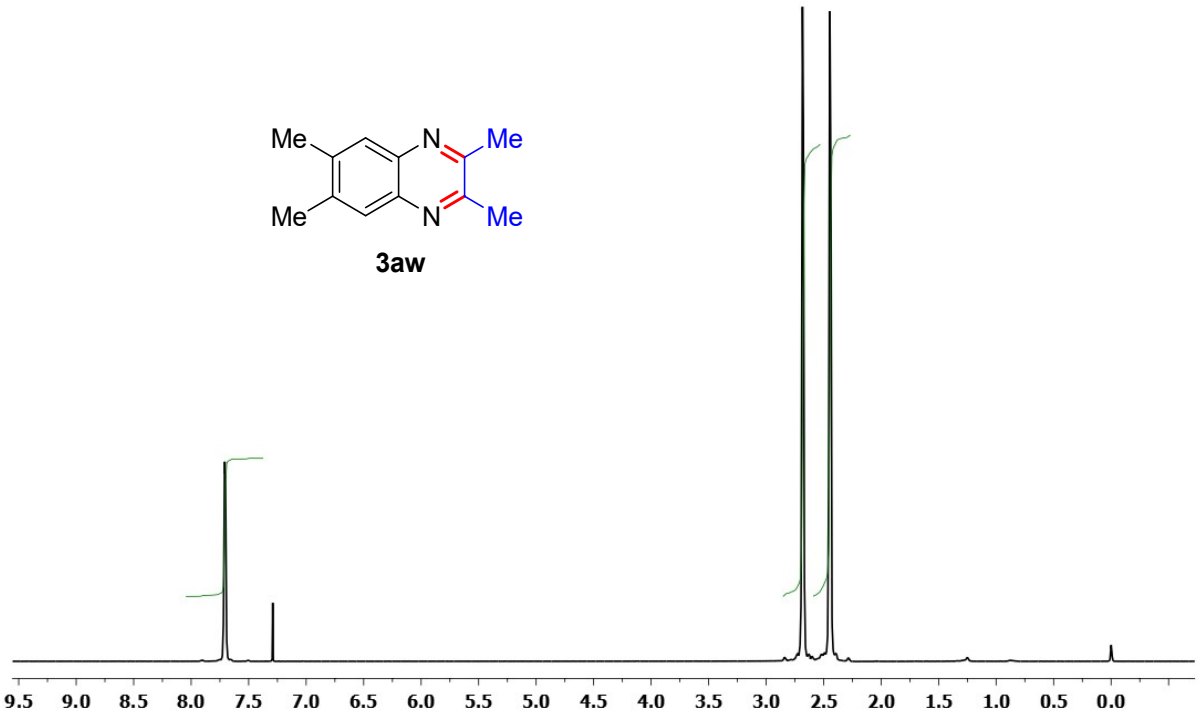
^{1}H NMR spectrum of compound **3av**:



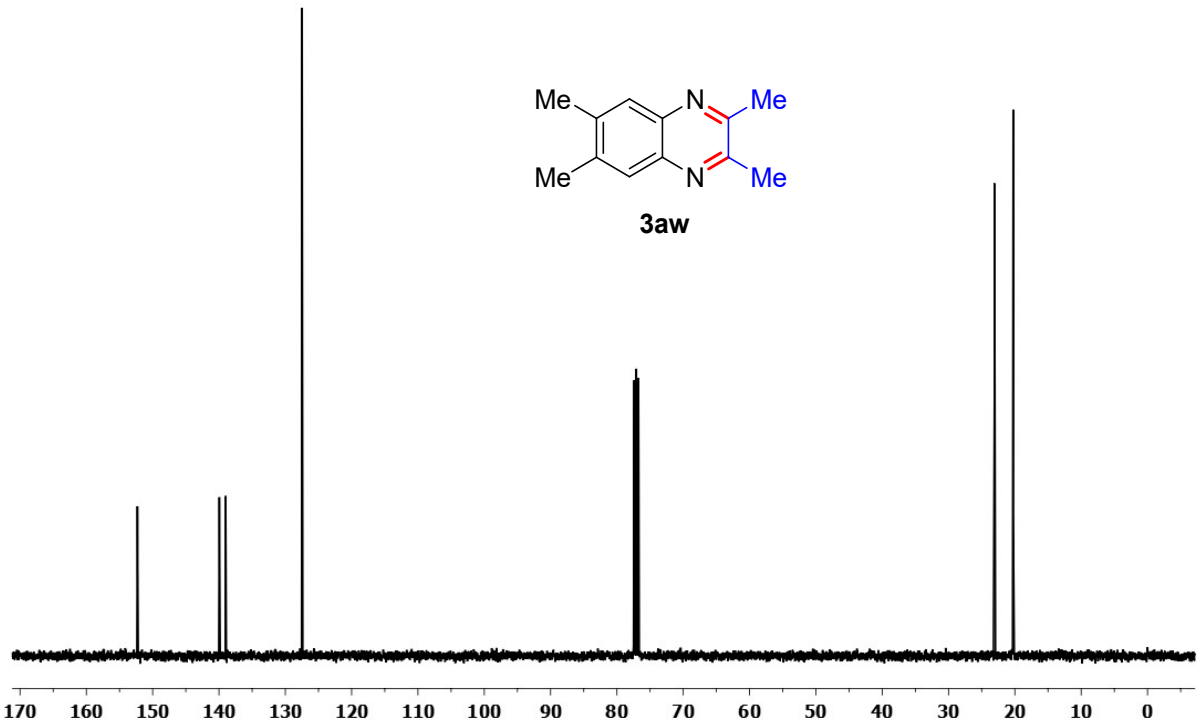
^{13}C NMR spectrum of compound **3av**:



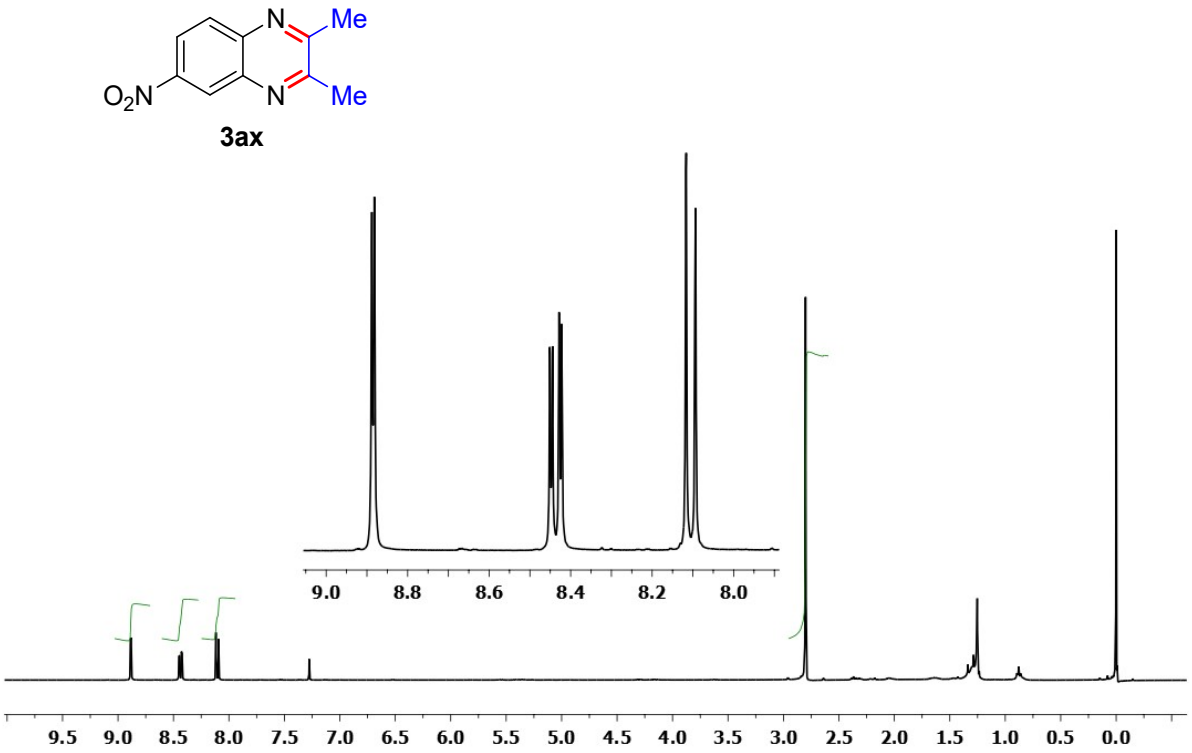
^{1}H NMR spectrum of compound **3aw**:



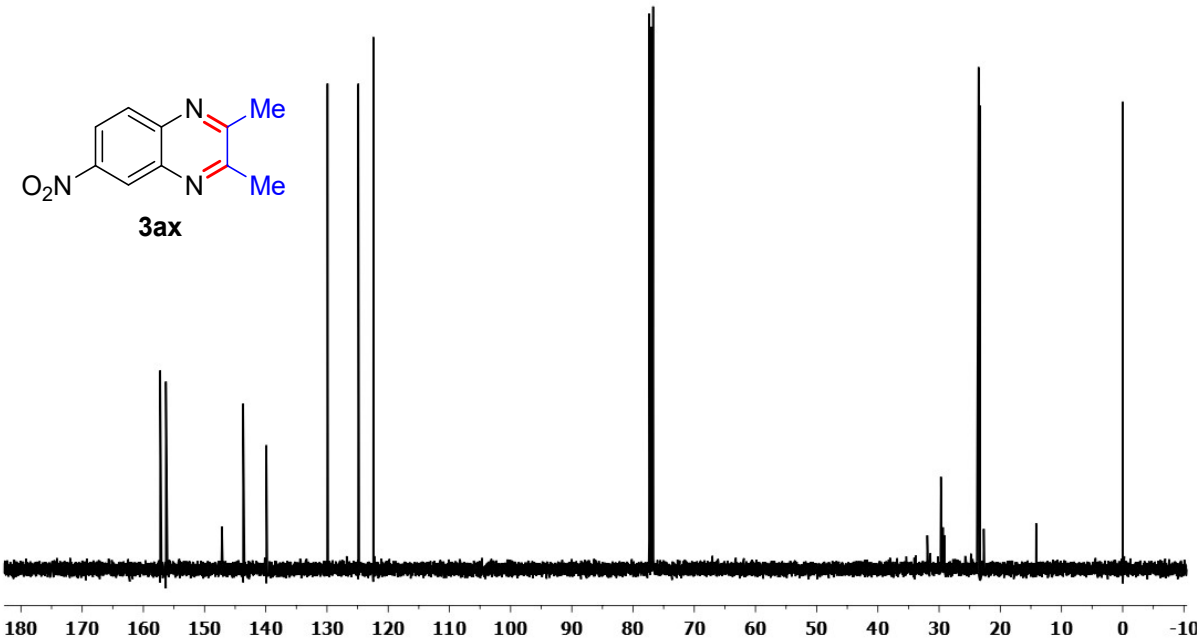
^{13}C NMR spectrum of compound **3aw**:



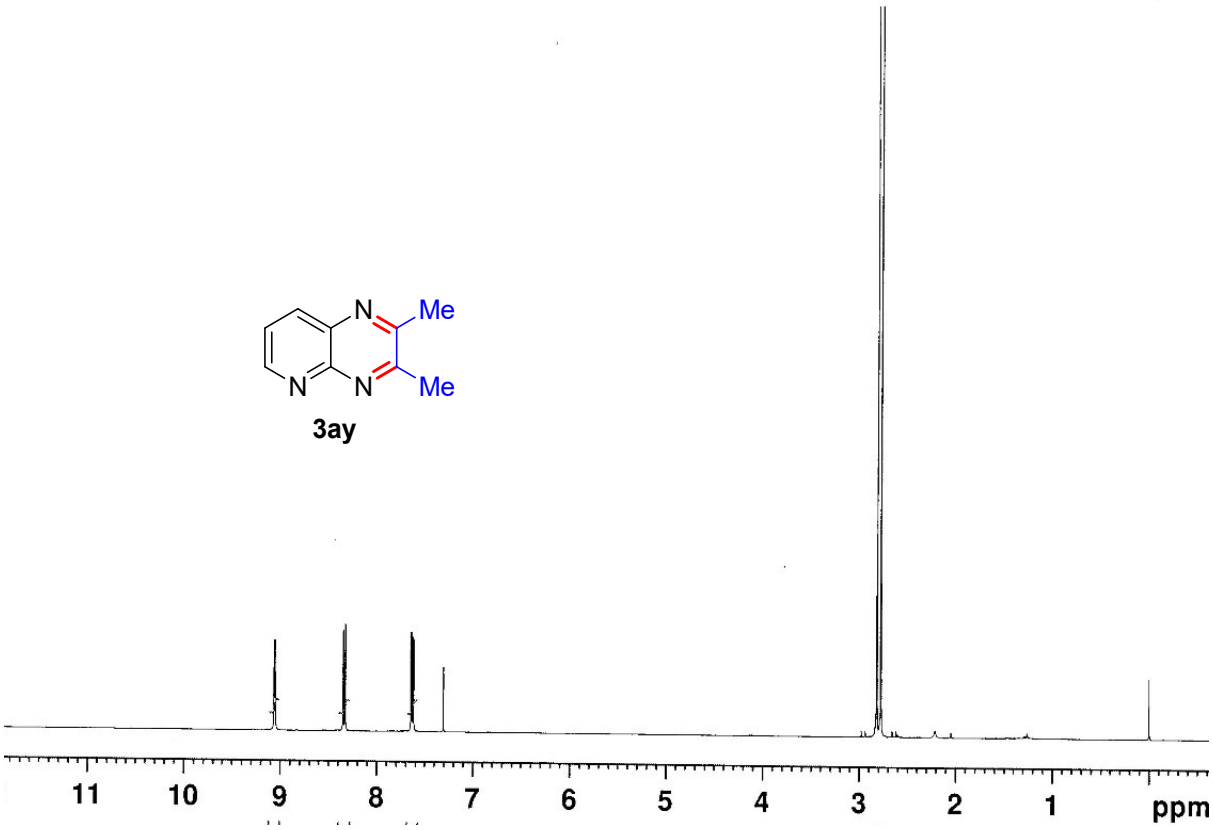
^{1}H NMR spectrum of compound **3ax**:



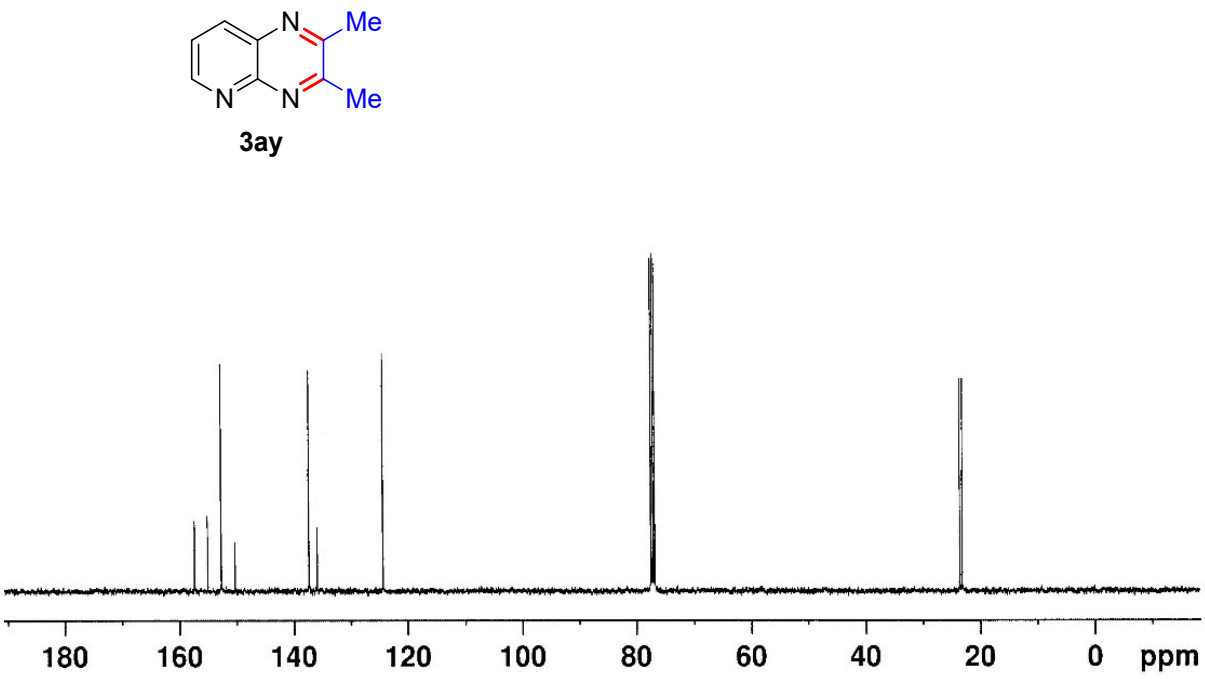
^{13}C NMR spectrum of compound **3ax**:



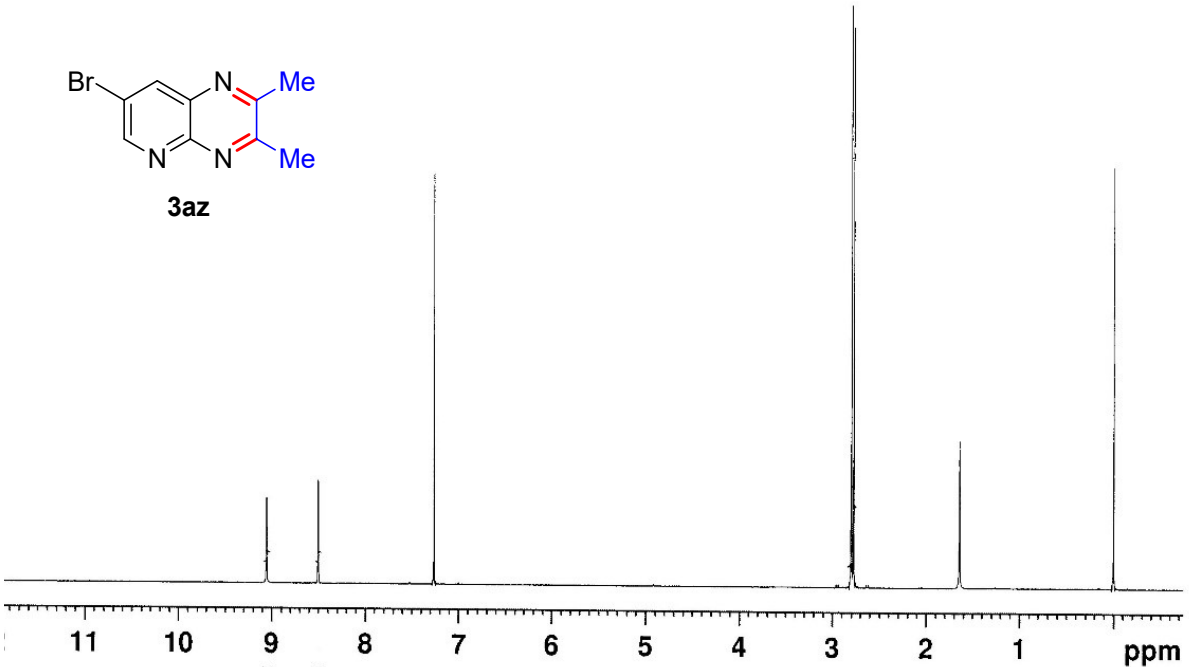
^{1}H NMR spectrum of compound **3ay**:



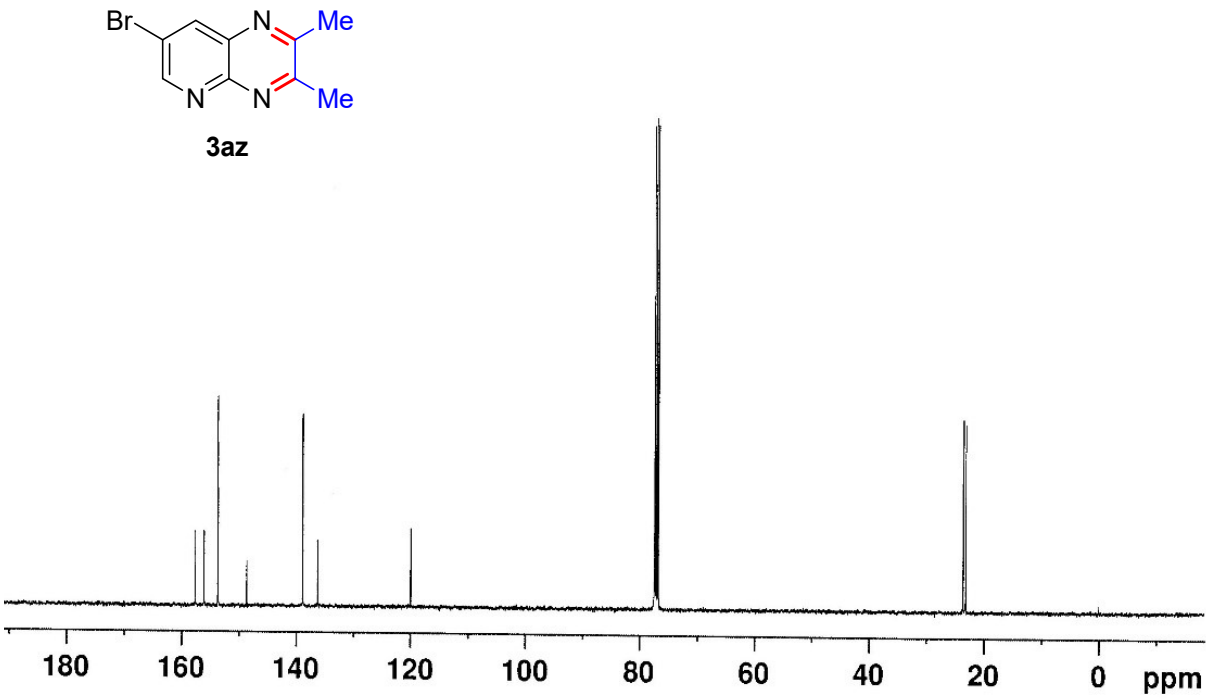
^{13}C NMR spectrum of compound **3ay**:



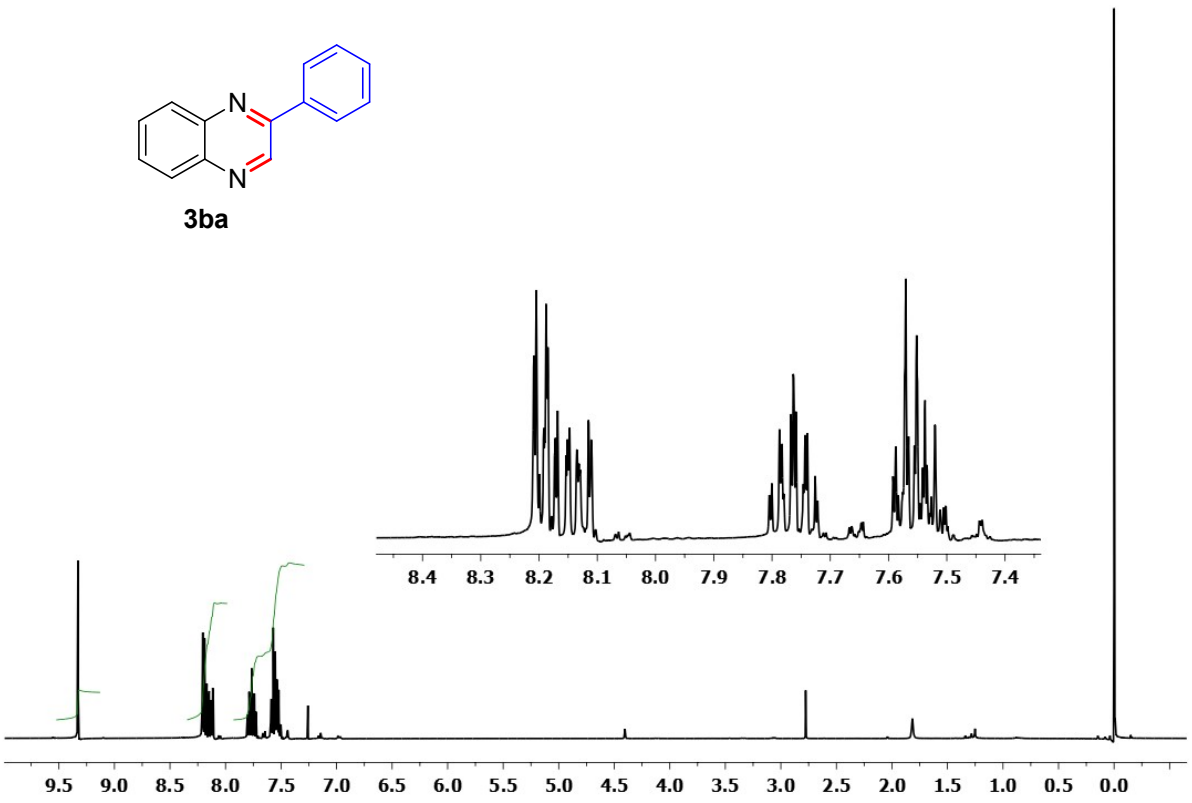
^{1}H NMR spectrum of compound **3az**:



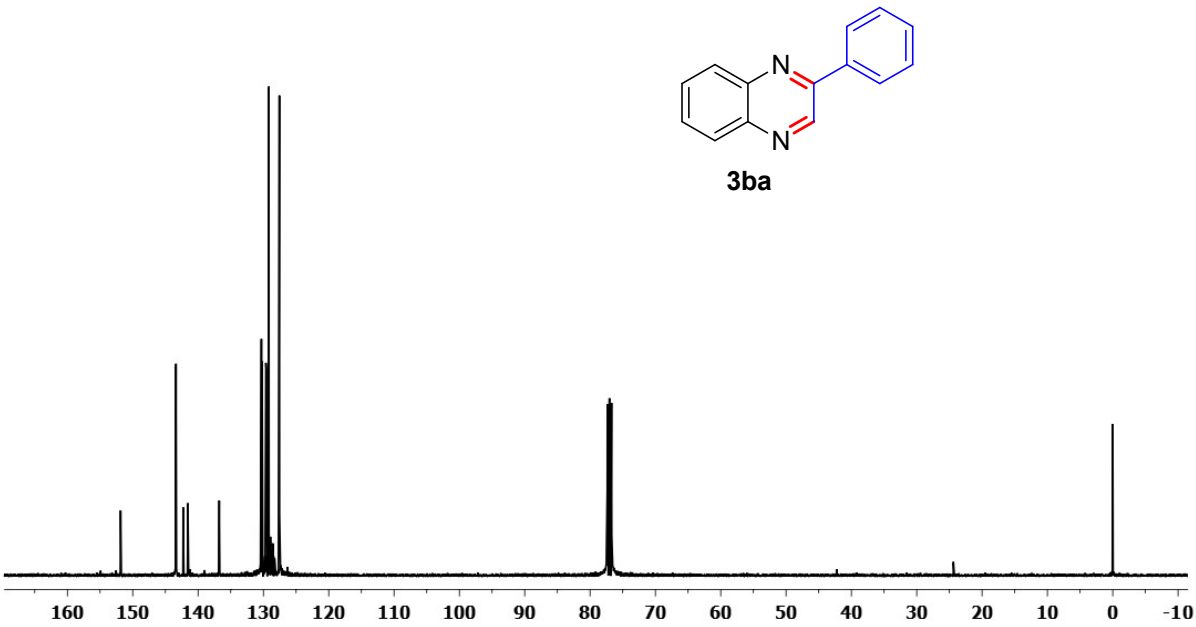
^{13}C NMR spectrum of compound **3az**:



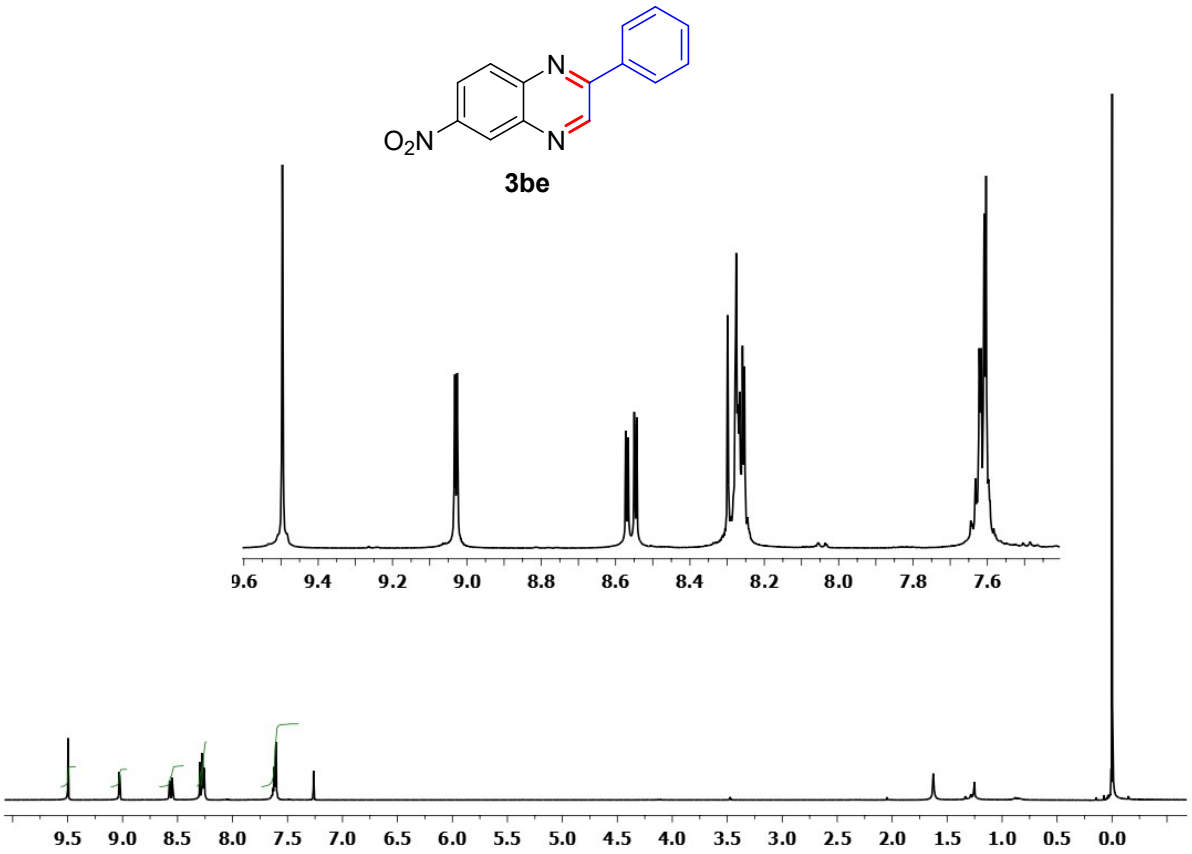
^{1}H NMR spectrum of compound **3ba**:



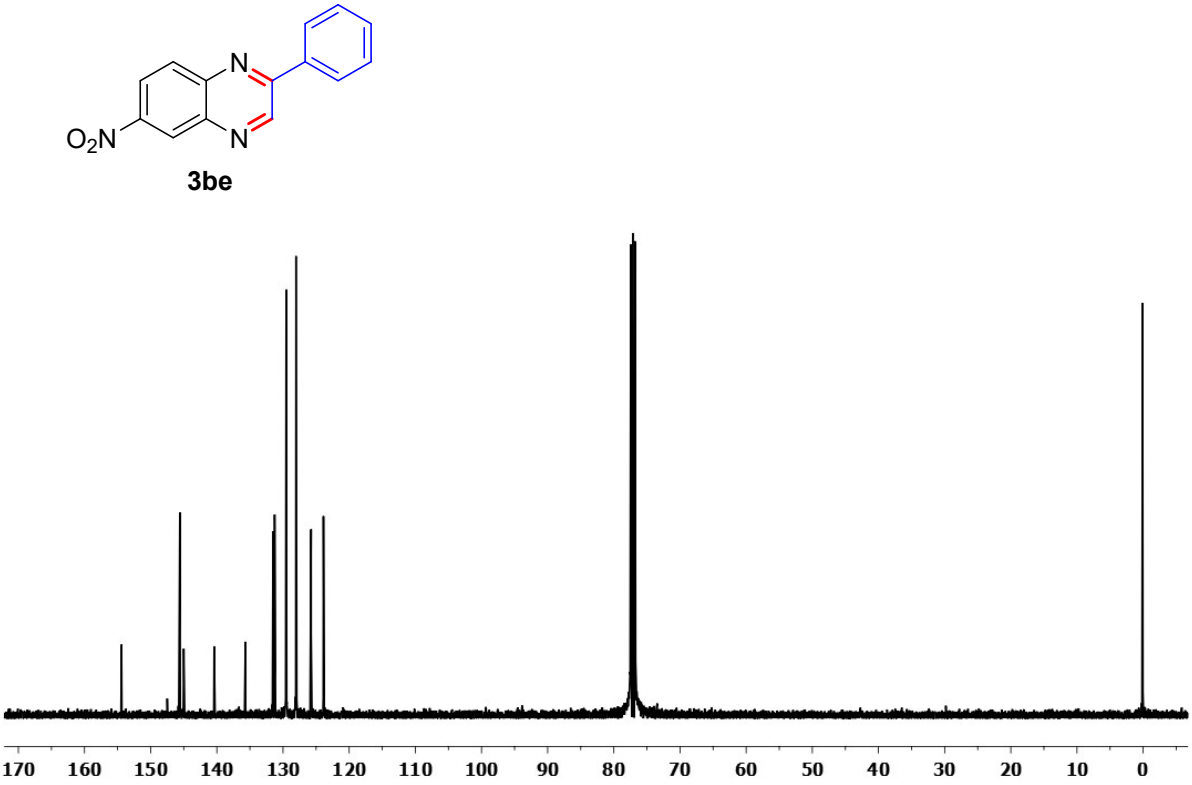
^{13}C NMR spectrum of compound **3ba**:



^{1}H NMR spectrum of compound **3be**:



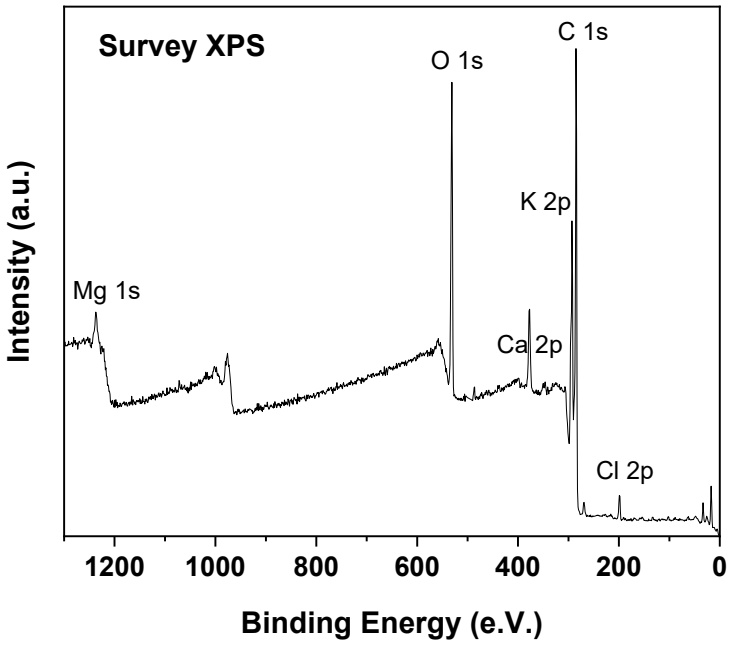
^{13}C NMR spectrum of compound **3be**:



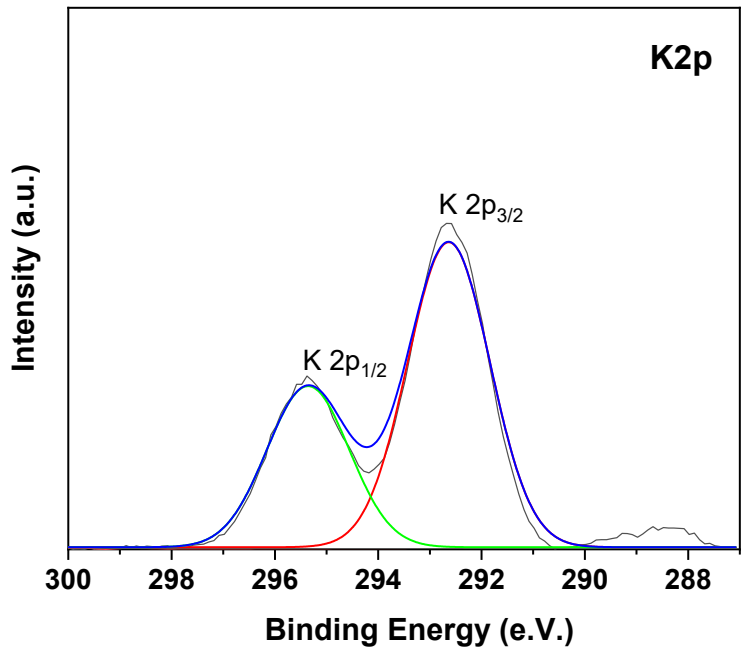
3. XPS Analysis of WEPA

The XPS analysis of WEPA was showed the presence of K, Mg, Ca, C, O, Cl in WEPA.[1]

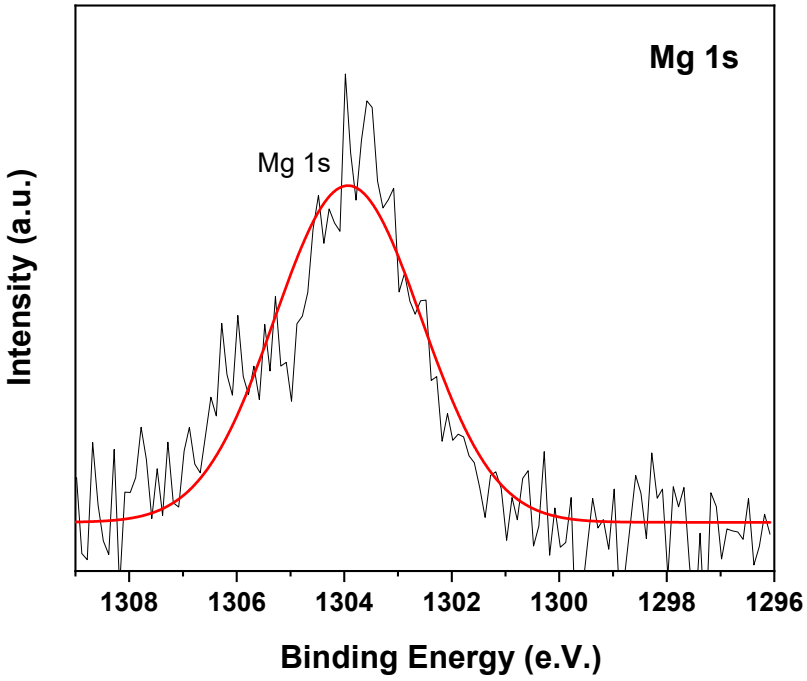
Survey spectrum



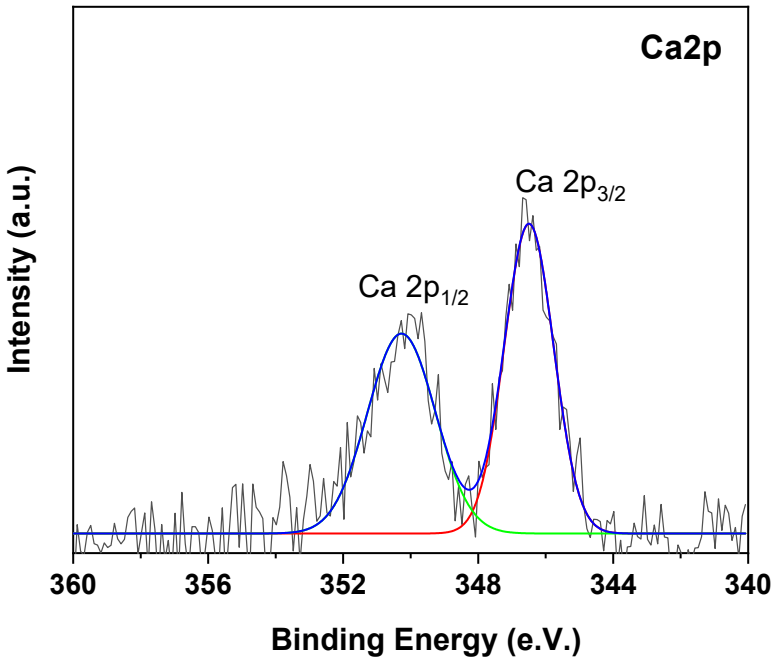
K 2p



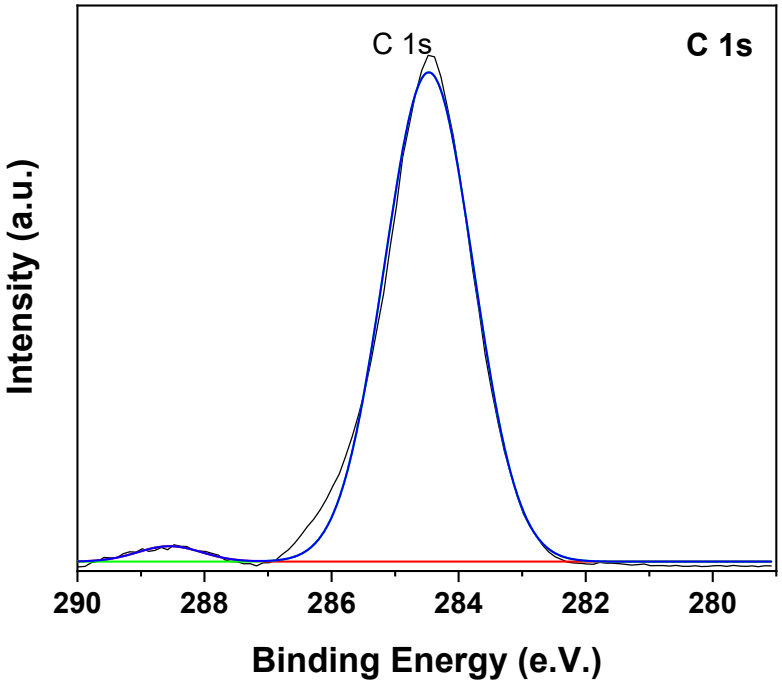
Mg 1s


Mg 1s
Mg 1s
Intensity (a.u.)
1308
1306
1304
1302
1300
1298
1296
Binding Energy (e.V.)

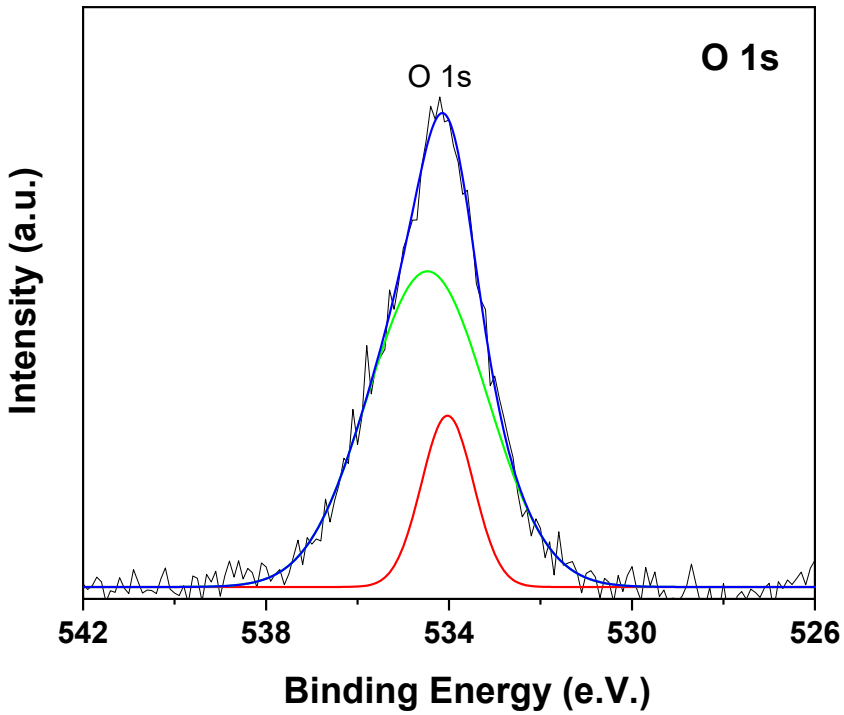
Ca 2p


Ca2p
Ca 2p3/2
Ca 2p1/2
Intensity (a.u.)
360
356
352
348
344
340
Binding Energy (e.V.)

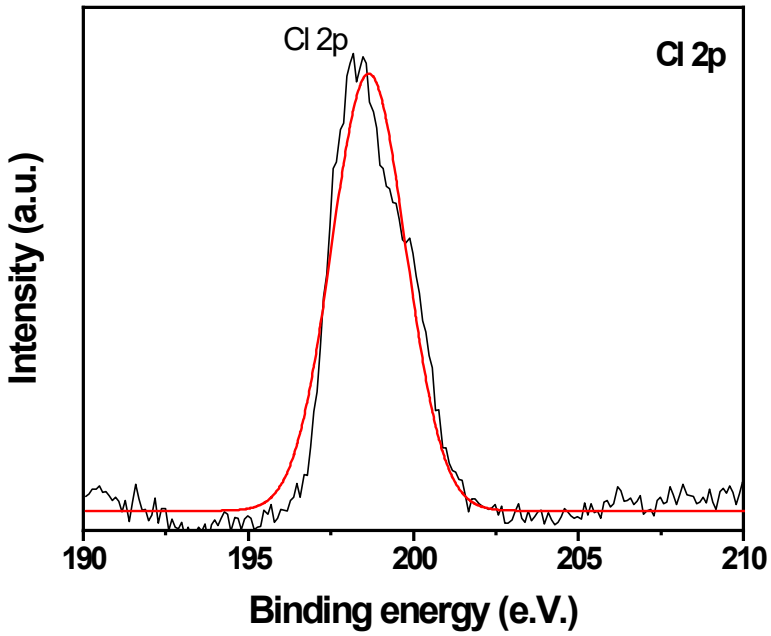
C 1s


C 1s
C 1s
Intensity (a.u.)
290
288
286
284
282
280
Binding Energy (e.V.)

O 1s


O 1s
O 1s
Intensity (a.u.)
542
538
534
530
526
Binding Energy (e.V.)

Cl 2p



Reference

1 J. Lakshmidevi, R. M. Appa, B. R. Naidu, S. S. Prasad, L. S. Sarma, K. Venkateswarlu, *Chem. Commun.*, 2018, **54**, 12333–12336.

4. XRF analysis of WEPA.

The X-ray fluorescence (XRF) data of WEPA is showed in the following table which indicates the presence of large quantity of K_2O and chlorides in WEPA. It also showed the presence of minor quantities of Na_2O, SO_3, MgO, CaO, Al_2O_3 and SiO_2 along with very minor quantities of other metallic/non-metallic species.[1,2]

Table XRF data of WEPA[a].

Entry	Compound	Reference 1	Reference 2	Unit
1	K_2O	66.513	64.309	%
2	Cl	19.393	23.504	%
3	SiO_2	1.926	1.577	%
4	MgO	1.895	1.599	%
5	Na_2O	2.197	2.629	%
6	Fe_2O_3	0.152	936 (ppm)	%
7	ZnO	71.8	35.3 (Zn)	ppm
8	CaO	2.112	1.545	%
9	SrO	0.132	-	%
10	SO_3	3.892	4.331	%
11	P_2O_5	576.4	757.1	ppm
12	Al_2O_3	0.236	0.131	%
13	Cu	193.6	70.8	ppm
14	Br	0.136	0.159	%
15	Cr_2O_3	11.4	-	ppm
16	MnO	51.2	-	ppm
17	TiO_2	19.2	-	ppm
18	Y	6.5	5.9	ppm
19	Rb	-	251.3	ppm
20	Bi	-	38.4	ppm
21	Ni	-	65.1	ppm

[a]This data is based on semi-quantitative analysis.

References

1 R. M. Appa, J. Lakshmidevi, B. R. Naidu, K. Venkateswarlu, *Mol. Catal.*, 2021, **501**, 111366.

2 B. R. Naidu, J. Lakshmidevi, B. S. S. Naidu, K. Venkateswarlu, *Mol. Catal.*, 2021, **511**, 111719.