

Supporting Information

Ionic liquids as a shuttle of releasing and capturing hydrogen chloride: a new way to utilize waste HCl generated in organic reactions

Fanzeng Kong^a, Minghao Li^a, Rongxian Bai^{a*}, and Yanlong Gu^{a*}

^aKey Laboratory of Material Chemistry for Energy Conversion and Storage, Ministry of Education, School of Chemistry and Chemical Engineering, Hubei. Key Laboratory of Material Chemistry and Service Failure, Huazhong University of Science and Technology, Wuhan, 430074, China.

*Corresponding authors, E-mail addresses: bairx@126.com (R. Bai); klgyl@hust.edu.cn (Y. Gu)

Table of Contents

Contents	Page
1. Experimental procedures	S2
2. Figure S1-S7	S4
3. Table S1-S4	S10
4. Characterization data	S14

1 Experimental

Chemicals and Equipment. Ethanol absolute (99.7%) and *o*-phenylenediamine (98.5%) were purchased from Sinopharm Chemical Reagents Co., Ltd. Ethyl 2-chloroacetoacetate (98%) and 1-methyl-1H-imidazole (98%) were purchased from Shanghai bidepharmatech Co., Ltd. Benzoyl chloride (99%), glycidyl phenyl ether (99%), 2-chloroacetophenone (99%), epichlorohydrin (99%), L-Carnitine (98%), betaine (96%) and 2-aminopyridine (99%) were manufactured by energy-chemical Factory. All reagents were raw and directly used to experiment. The pH meter with a resolution ratio of 0.01 pH was purchased from Leici Laboratory (China).

1.1 Preparation of ionic liquid.

1-Carboxymethyl-3-methylimidazolium chloride: the target ionic liquid was prepared according to the literature's method.¹ In a typical procedure, 1-methylimidazole (5 mmol) was added to a solution of chloroacetic acid (5 mmol) in anhydrous chloroform (8 mL) at room temperature. The resulting mixture was refluxed at 70 °C for 50 h under a nitrogen atmosphere. The produced solid was filtrated and washed with anhydrous ethanol at least three times. The final product was obtained by drying in vacuo at 60°C for 24 h.

3-(triethylammonio) propane sulfonate: 3-(triethylammonio) propane sulfonate was synthesized based on the literature's method.² In a typical procedure, Triethylamine (5 mmol) and 1,3-propanesultone (5 mmol) were dissolved in ethanol (10 mL) and heated with stirring at 70°C for 12 h. The obtained white precipitate, 3-(triethylammonio) propane sulfonate, was filtered, washed with diethyl ether to remove unreacted reactants. The white solid was obtained by drying in vacuo at 80°C for 12 h.

1.2 Recycle of HCl.

Recycle of the reaction of *o*-phenylenediamine with 2-chloroacetophenone and ring-opening of phenyl glycidyl ether: To a V-type flask containing the 1-[1-(ethoxycarbonyl)-2-oxopropyl]-3-methylimidazolium inner salt (0.75 mmol) solution in toluene (1 mL) was added *o*-phenylenediamine (1.0 mmol), 2-chloroacetophenone (0.5 mmol). The tube reactor equipped with triangular magnetic stirrer was heated at 40°C and monitored by TLC. After the completion of the reaction, reaction mixture was allowed to cool to room temperature and was extracted by n-hexane, which subjected to an isolation with preparative TLC (20 cm × 20 cm) by using eluting solution (PE/EA = 7/3(v/v)). The remaining ionic liquid was washed with toluene (5 mL × 3). Then 0.75 mmol of phenyl glycidyl ether was added into the above tube, which was then heated at 40 °C for 12 hours. After the completion of the reaction, reaction mixture was allowed to cool to room temperature again. The reaction solution was isolated by extraction to calculate the yield of product, and the remaining ionic liquid was used for the next run.

Recycle of the reaction of 2-aminopyridine with 2-chloroacetophenone and ring-opening of phenyl glycidyl ether: To a V-type flask containing 1-[1-(ethoxycarbonyl)-2-oxopropyl]-3-methylimidazolium inner salt (0.5 mmol) solution in anisole (1 mL) was added 2-aminopyridine

(1.0 mmol), 2-chloroacetophenone (0.5 mmol). The tube reactor equipped with triangular magnetic stirrer was heated at 60°C and monitored by TLC. After the completion of the reaction, reaction mixture was allowed to cool to room temperature and extracted by n-hexane, which subjected to an isolation with preparative TLC (20 cm × 20 cm) by using eluting solution (PE/EA = 7/3(v/v)). The remaining ionic liquid was washed with toluene (5 ml × 3). Then 0.5 mmol of phenyl glycidyl ether was added into the above tube, which was heated at 40 °C for 12 hours. After the completion of the reaction, reaction mixture was allowed to cool to room temperature again. The reaction solution was isolated by extraction for calculating the yield of product, and the remaining ionic liquid was used for the next run.

1.3 Characterization

FT-IR spectra were obtained on Bruker Compass VERTEX 70. The UV spectra were obtained with the Shimadzu UV-Vis Spectrophotometer UV-2600i. The reactions were monitored by TLC with Haiyang GF-254 silica gel plates (Qingdao Haiyang chemical industry Co. Ltd, Qingdao, China) using UV light or KMnO₄ as visualizing agents as needed. Flash column chromatography was performed using 200-300 mesh silica gel at increased pressure. ¹H NMR spectra and ¹³C NMR spectra were respectively recorded on Brüker AV-400 spectrometers. Chemical shifts (δ) were expressed in ppm relative to Me₄Si in CDCl₃, and coupling constants (J) were reported in Hz. High-resolution mass spectra (HRMS) were obtained on Brüker Compass Data Analysis 4.0. TGA was recorded on Pyris1 TGA under N₂ environment.

References

- 1 D.Liu, J.Gui, X.Zhu, L.Song and Z.Sun, *Synthetic.Commun.*, 2007,**37**,759–765.
- 2 Z.Y.Yu, M.Y.Chen, J.X.He, D.J.Tao, J.J.Yuan, Y.Y.Peng and Z.B.Song, *Mol.Catal.*, 2017, **434**,134–139.

2. Figure S1-S6

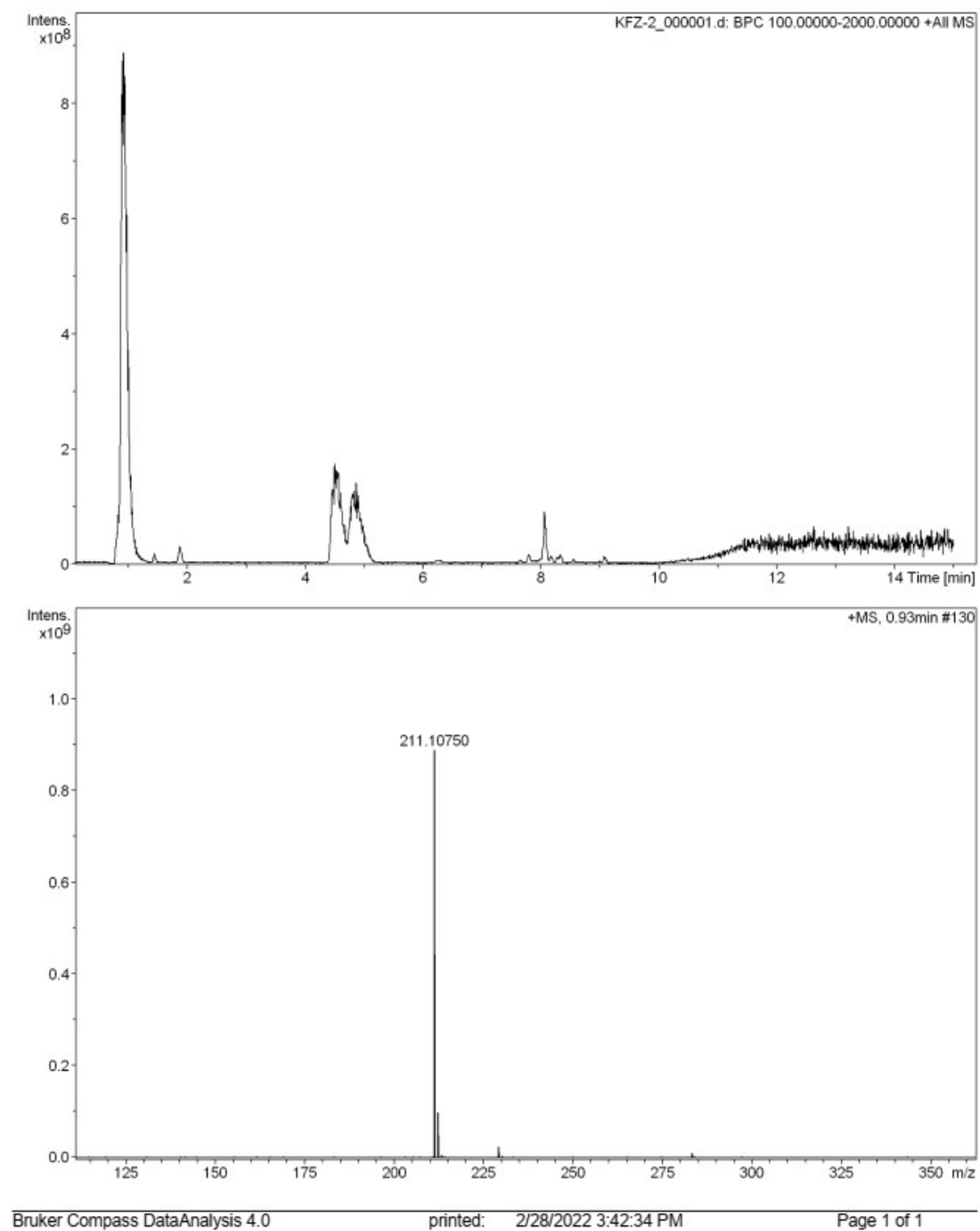


Fig.S1 LC-MS profile of 1,3-(CO)₂IL-HCl

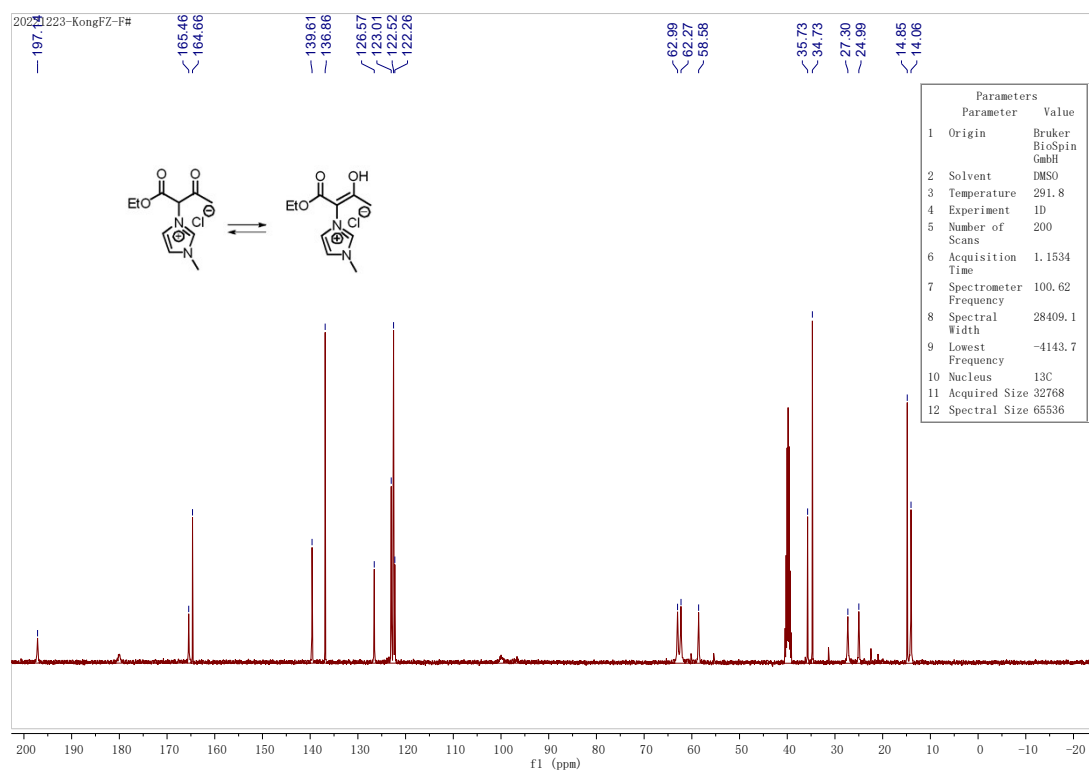
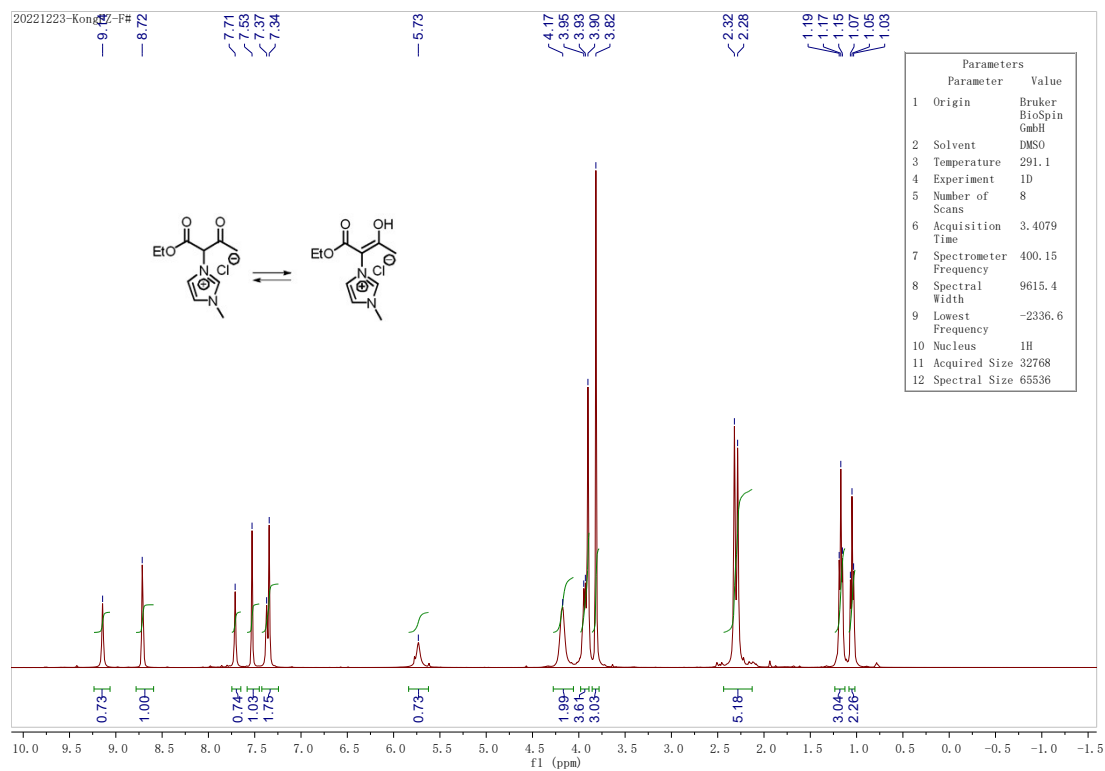


Fig. S2 NMR spectra of 1,3-(CO)₂IL-HCl

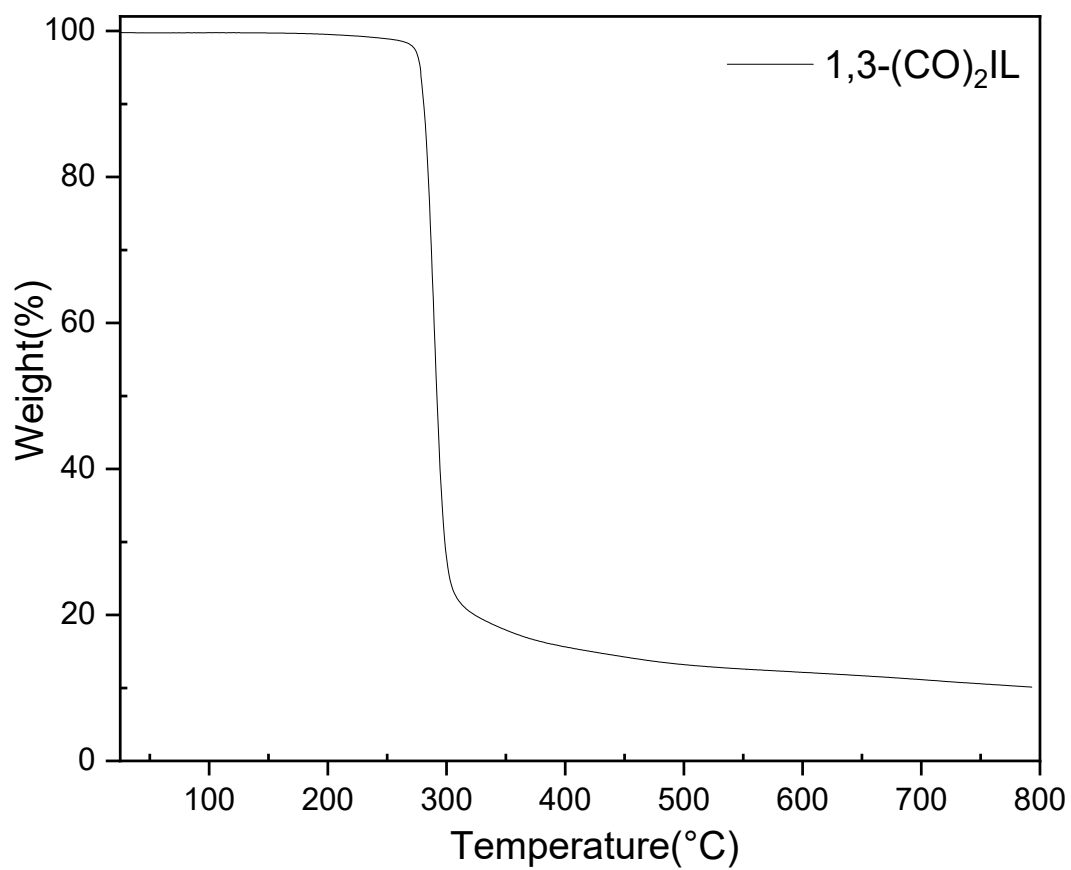


Fig. S3 TG curve of 1,3-(CO)₂IL

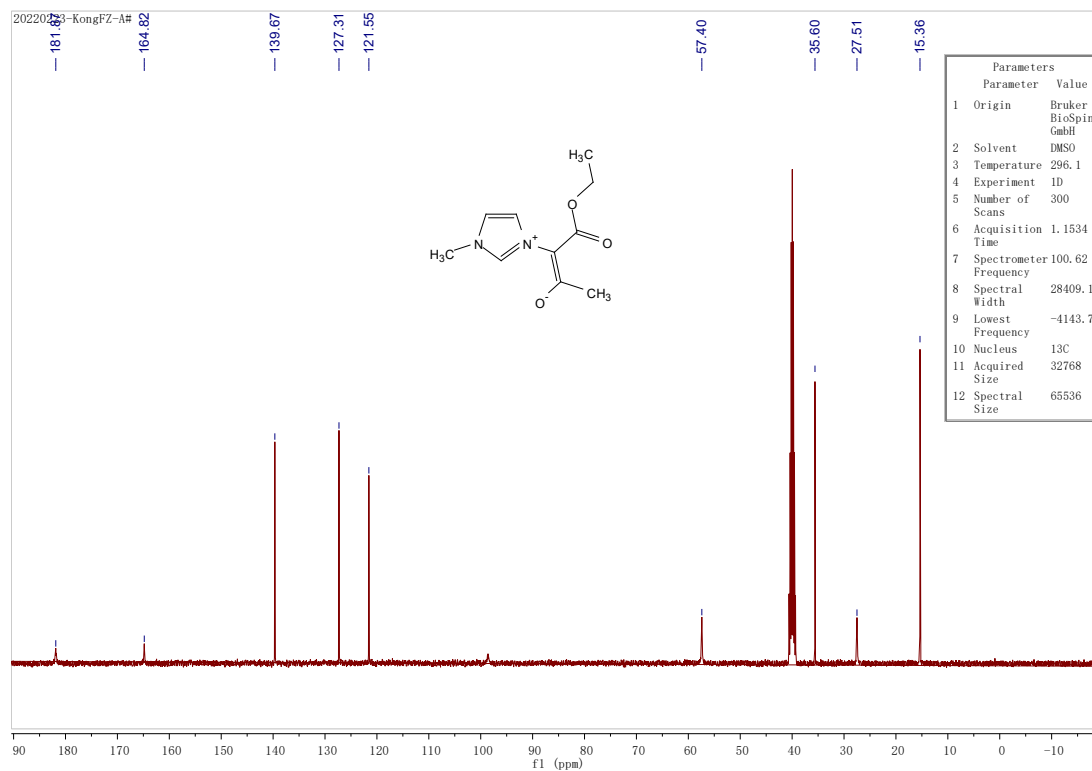
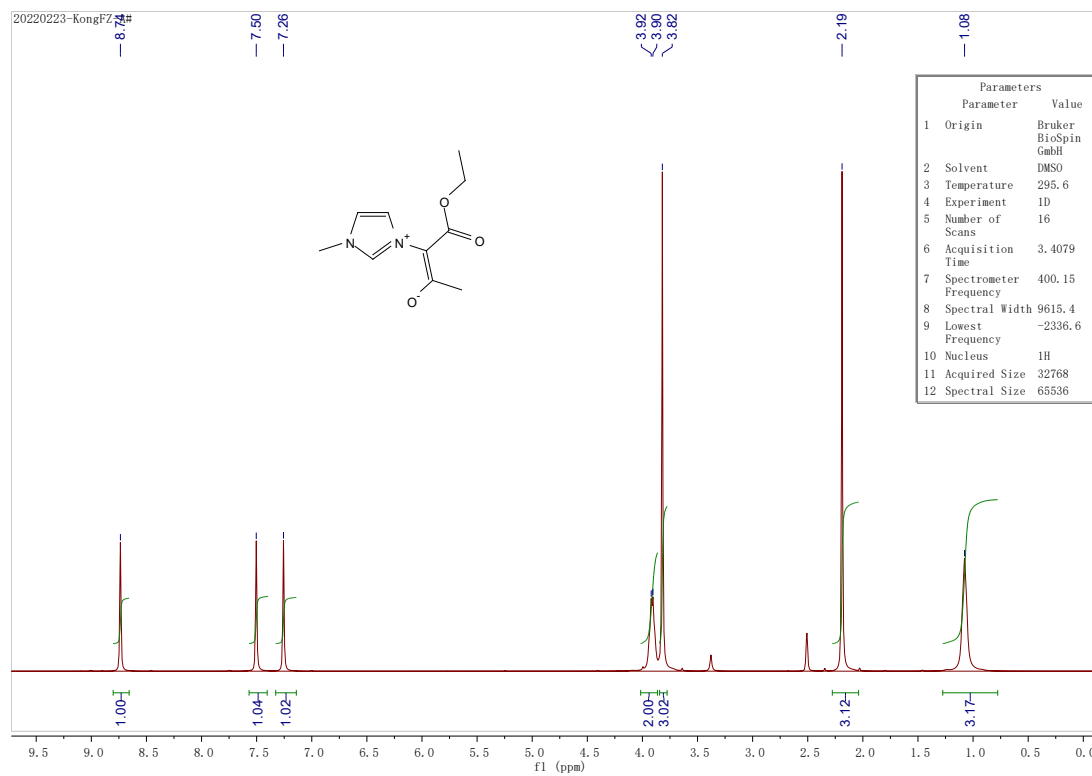


Fig. S4 NMR spectra of 1,3-(CO)₂IL

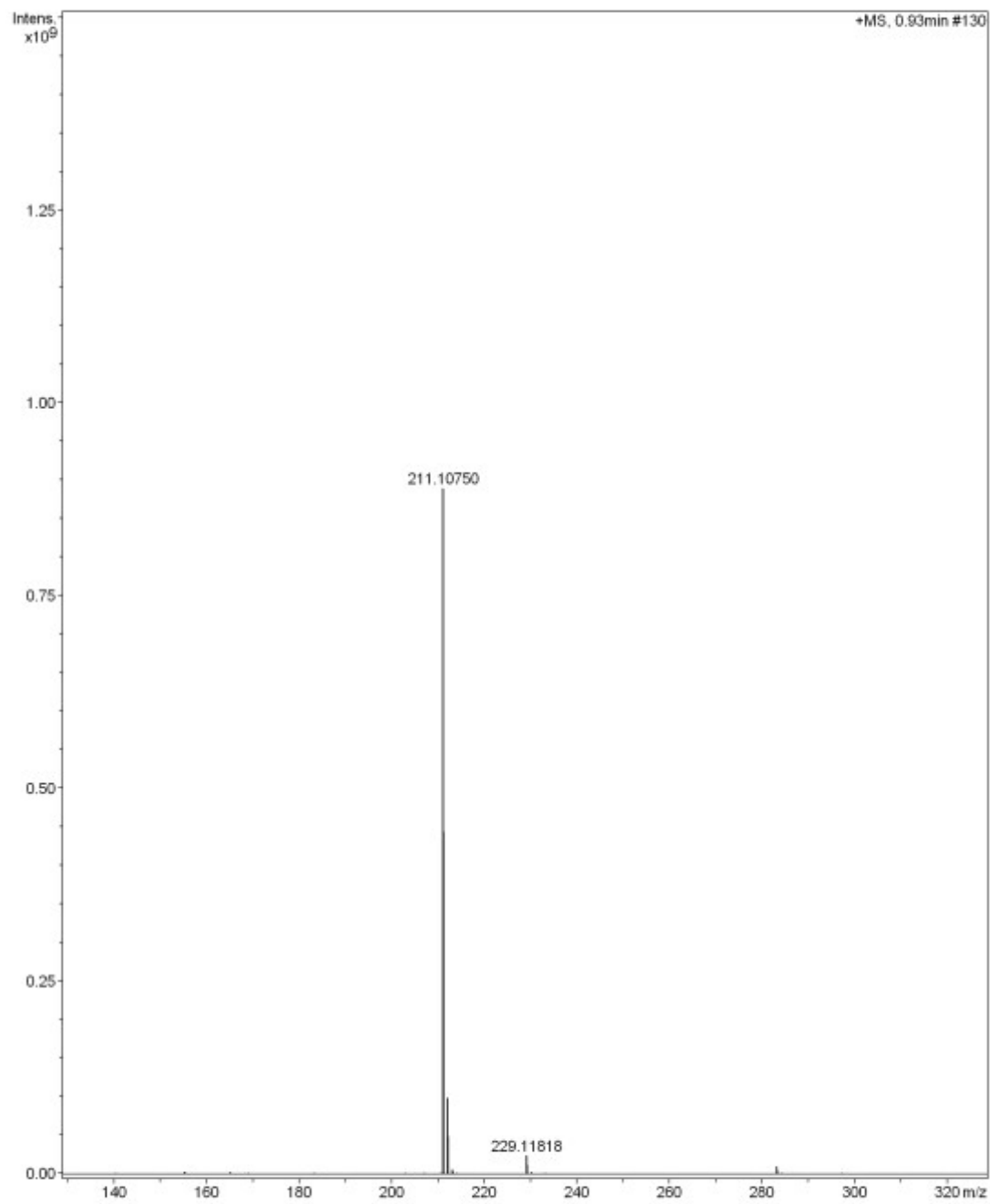


Fig. S5 HRMS profile of 1,3-(CO)₂IL

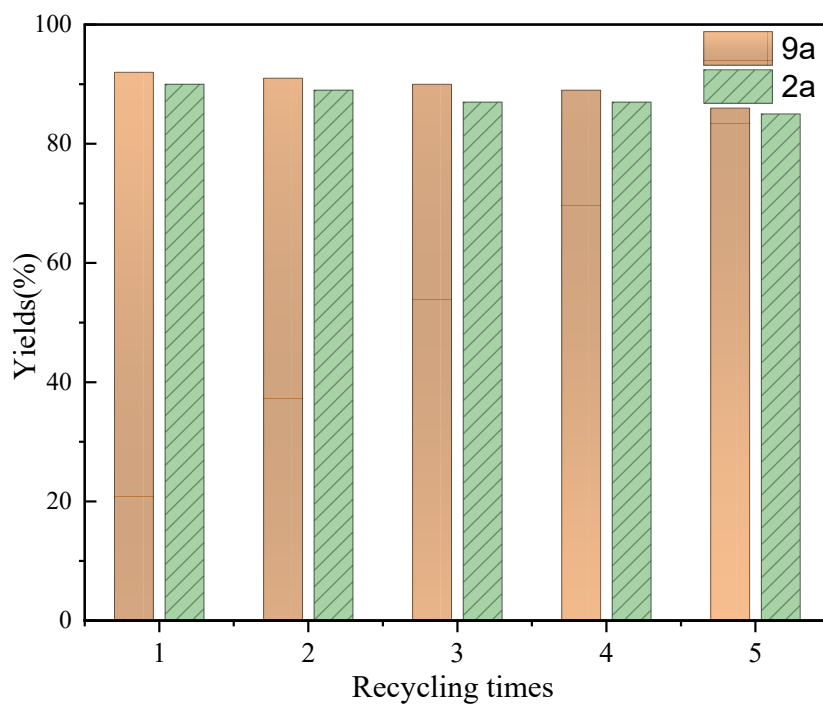


Fig. S6 Recycle of HCl based on the reaction of *o*-phenylenediamine and 2-chloroacetophenone and ring-opening of phenyl glycidyl ether.

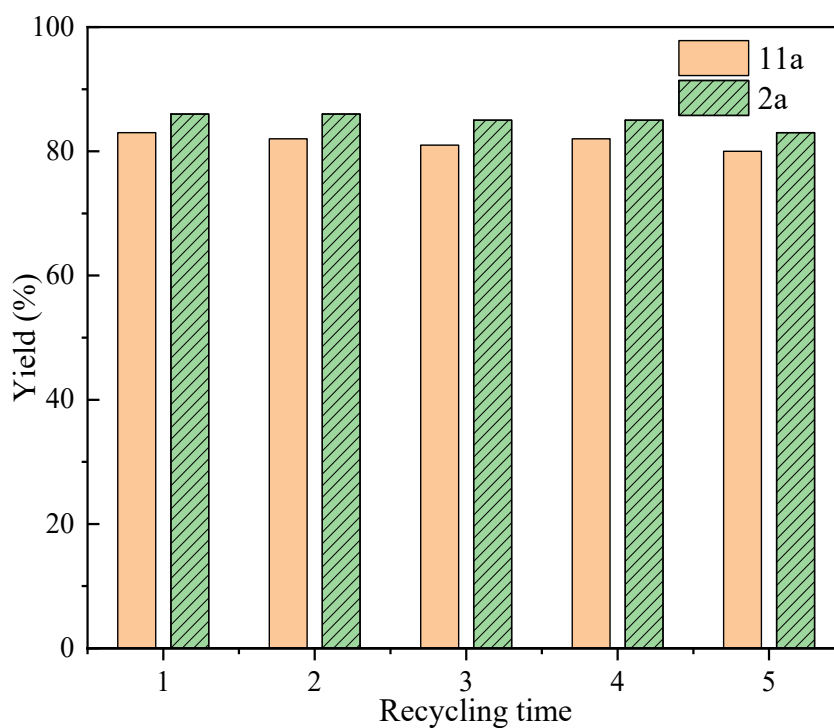


Fig. S7 Recycle of HCl based on the reaction of 2-aminopyridine and 2-chloroacetophenone and ring-opening of phenyl glycidyl ether.

3. Table S1-S4

Table S1. pK_a at different UV wavelengths in H₂O

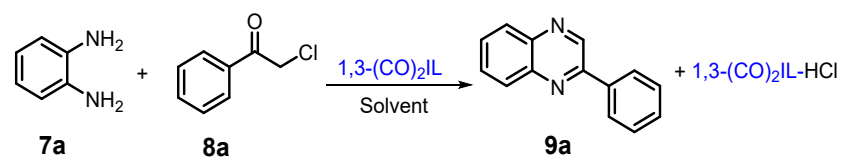
H ₂ O							
Wavelength /nm	H ₂ SO ₄ /A _{HL}	NaOH/A _L - A	(A- A _L ⁻) (B- / _(A_{HL}-A))	(A-A _L -)/ (A _{HL} -A)	Lg (A-A _L -)/ (A _{HL} -A)	pK_a	
pH	1.02	12.83	4.70				
251	0.232	0.856	0.518	1.18182	1.18182	0.07255	4.77255
252	0.224	0.906	0.543	1.13793	1.13793	0.05612	4.75612
253	0.215	0.959	0.567	1.11364	1.11364	0.04674	4.74674
254	0.205	1.010	0.590	1.09091	1.09091	0.03779	4.73779
255	0.195	1.057	0.611	1.07212	1.07212	0.03024	4.73024
256	0.185	1.104	0.632	1.05593	1.05593	0.02363	4.72363
257	0.173	1.147	0.650	1.04193	1.04193	0.01784	4.71784
258	0.163	1.184	0.666	1.02982	1.02982	0.01276	4.71276
259	0.152	1.217	0.679	1.02087	1.02087	0.00897	4.70897
260	0.141	1.245	0.689	1.01460	1.01460	0.00629	4.70629
261	0.130	1.268	0.696	1.01060	1.01060	0.00458	4.70458
262	0.119	1.284	0.700	1.00516	1.00516	0.00224	4.70224
263	0.109	1.293	0.700	1.00338	1.00338	0.00147	4.70147
264	0.099	1.296	0.696	1.00503	1.00503	0.00218	4.70218
265	0.091	1.290	0.689	1.00502	1.00502	0.00217	4.70217
266	0.082	1.277	0.677	1.00840	1.00840	0.00363	4.70363
267	0.074	1.257	0.661	1.01533	1.01533	0.00661	4.70661
268	0.067	1.230	0.643	1.01910	1.01910	0.00822	4.70822
269	0.061	1.195	0.620	1.02862	1.02862	0.01226	4.71226
270	0.055	1.154	0.595	1.03519	1.03519	0.01502	4.71502
271	0.050	1.107	0.566	1.04845	1.04845	0.02055	4.72055
272	0.046	1.056	0.535	1.06544	1.06544	0.02753	4.72753
273	0.043	1.000	0.503	1.08043	1.08043	0.03360	4.73360
274	0.040	0.941	0.467	1.11007	1.11007	0.04535	4.74535
275	0.037	0.878	0.431	1.13452	1.13452	0.05481	4.75481
276	0.035	0.813	0.394	1.16713	1.16713	0.06712	4.76712
277	0.033	0.750	0.359	1.19939	1.19939	0.07896	4.77896
278	0.032	0.685	0.323	1.24399	1.24399	0.09482	4.79482
279	0.030	0.625	0.289	1.29730	1.29730	0.11304	4.81304
280	0.029	0.568	0.257	1.36404	1.36404	0.13483	4.83483

$$pK_a = 4.73$$

Table S2. pK_a at different UV wavelengths in DMSO

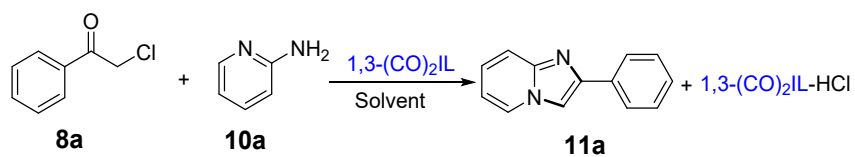
DMSO							
Wavelength /nm	H ₂ SO ₄ / A _{HL}	A _L -	H ₂ O/A	(A- A _L -)/ (B- (A _{HL} -A)	(A-A _L -)/ (A _{HL} -A)	Lg (A-A _L -)/ (A _{HL} -A)	pK_a
pH	1.80	9.08	6.51				
260	0.408	1.602	0.675	3.47191	3.47191	0.54057	7.05057
261	0.366	1.730	0.663	3.59259	3.59259	0.55541	7.06541
262	0.344	1.809	0.660	3.63608	3.63608	0.56063	7.07063
263	0.320	1.837	0.643	3.69659	3.69659	0.56780	7.07780
264	0.288	1.882	0.636	3.58046	3.58046	0.55394	7.06394
265	0.262	1.872	0.604	3.70760	3.70760	0.56909	7.07909
266	0.240	1.862	0.585	3.70145	3.70145	0.56837	7.07837
267	0.218	1.828	0.563	3.66667	3.66667	0.56427	7.07427
268	0.196	1.752	0.537	3.56305	3.56305	0.55182	7.06182
269	0.177	1.696	0.506	3.61702	3.61702	0.55835	7.06835
270	0.160	1.629	0.476	3.64873	3.64873	0.56214	7.07214
271	0.150	1.556	0.450	3.68667	3.68667	0.56663	7.07663
272	0.129	1.464	0.416	3.65157	3.65157	0.56248	7.07248
273	0.118	1.370	0.388	3.63704	3.63704	0.56075	7.07075
274	0.108	1.276	0.359	3.65339	3.65339	0.56270	7.07270
275	0.100	1.178	0.329	3.70742	3.70742	0.56907	7.07907
276	0.088	1.076	0.300	3.66038	3.66038	0.56353	7.07353
277	0.080	0.980	0.273	3.66321	3.66321	0.56386	7.07386
278	0.073	0.897	0.252	3.60335	3.60335	0.55671	7.06671
279	0.068	0.818	0.227	3.71698	3.71698	0.57019	7.08019
280	0.066	0.739	0.211	3.64138	3.64138	0.56127	7.07127
281	0.058	0.667	0.188	3.68462	3.68462	0.56639	7.07639
282	0.054	0.604	0.171	3.70085	3.70085	0.56830	7.07830
283	0.051	0.544	0.156	3.69524	3.69524	0.56764	7.07764
284	0.044	0.491	0.139	3.70526	3.70526	0.56882	7.07882
285	0.045	0.449	0.128	3.86747	3.86747	0.58743	7.09743
286	0.040	0.400	0.117	3.67532	3.67532	0.56530	7.07530
287	0.037	0.362	0.104	3.85075	3.85075	0.58554	7.09555
288	0.040	0.332	0.100	3.86667	3.86667	0.58734	7.09734
289	0.031	0.293	0.085	3.85185	3.85185	0.58567	7.09567
290	0.029	0.270	0.076	4.12766	4.12766	0.61570	7.12570

$$pK_a = 7.07$$

Table S3. Optimization of reaction conditions of *o*-phenylenediamine and chloroacetophenone ^{a,b}

Entry	Solvent	Temperature (°C)	Yield (%)
1	-	40	68
2	C ₂ H ₅ OH	40	59
3	CH ₃ CN	40	67
4	Butyl acetate	40	66
5	1,4-Dioxane	40	45
6	Toluene	40	55
7	Toluene	r.t.	43
8	Toluene	40	48
9 ^c	Toluene	60	44
10 ^d	Toluene	40	92
11 ^d	Toluene	60	90
12 ^e	Toluene	40	83
13 ^f	Toluene	40	91

^aReaction conditions: **7a** (0.3 mmol), **8a** (0.3 mmol), 1,3-(CO)₂ILs (0.45 mmol), Solvent (1.0 mL), 40°C, 12 h; ^b Isolated yields; ^c 1,3-(CO)₂ILs (0.3 mmol); ^d **7a** (0.6 mmol); ^e **7a** (0.45 mmol); ^f14 h.

Table S4. Optimization of reaction conditions of aminopyridine and chloroacetophenone ^{a,b}

Entry	Solvent	1,3-(CO) ₂ IL (equiv.)	Temperature (°C)	Yield (%)
1	-	1.0	40°C	45
2	CH ₃ OH	1.0	40°C	47
3	CH ₃ CH ₂ OH	1.0	40°C	64
4	Butyl acetate	1.0	40°C	49
5	Anisole	1.0	40°C	63
6	Toluene	1.0	40°C	56
7	Anisole	1.5	60°C	71
8	Anisole	2.0	60°C	70
9	Anisole	1.0	60°C	61
10 ^c	Anisole	1.0	60°C	73
11 ^d	Anisole	1.0	60°C	83
12 ^e	Anisole	1.0	60°C	82

^aReaction conditions: **8a** (0.3 mmol), **10a** (0.3 mmol), solvent (1 mL), 10 h; ^bisolate yield; ^c **8a** (0.45 mmol); ^d **10a** (0.6 mmol); ^e 12 h.

4 Characterization data

1-[1-(ethoxycarbonyl)-2-oxopropyl]-3-methylimidazolium inner salt: ^1H NMR (400 MHz, DMSO- d_6) δ 8.74 (s, 1H), 7.50 (s, 1H), 7.26 (s, 1H), 3.91 (d, J = 8.0 Hz, 2H), 3.82 (s, 3H), 2.19 (s, 3H), 1.08 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, DMSO- d_6) δ 181.88, 164.82, 139.67, 127.31, 121.56, 98.83, 57.40, 35.60, 27.51, 15.36. HRMS (ESI): Calculated for $\text{C}_{10}\text{H}_{15}\text{O}_3\text{N}_2$, $[\text{M}+\text{H}]^+$: 211.1077; found :211.1075.

1-Carboxymethyl-3-methylimidazolium chloride: ^1H NMR (400 MHz, DMSO) δ 9.39 (s, 1H), 7.82 (d, J = 9.7 Hz, 2H), 5.26 (s, 2H), 3.92 (s, 3H). ^{13}C NMR (100 MHz, DMSO) δ 168.44, 138.13, 124.14, 123.60, 50.19, 36.34.

3-(triethylammonio) propane sulfonate: ^1H NMR (400 MHz, MeOD) δ 3.50 – 3.41 (m, 2H), 3.34 (q, J = 7.3 Hz, 6H), 2.88 (t, J = 6.6 Hz, 2H), 2.13 (dq, J = 13.5, 6.9 Hz, 2H), 1.32 (t, J = 7.5 Hz, 9H). ^{13}C NMR (100 MHz, MeOD) δ 55.30, 55.27, 55.24, 52.56, 52.53, 52.50, 47.46, 47.25, 47.21, 47.04, 17.70, 6.31.

1-chloro-3-phenoxypropan-2-ol : ^1H NMR (400 MHz, CDCl_3) δ 7.29 (t, J = 7.9 Hz, 2H), 6.98 (t, J = 7.3 Hz, 1H), 6.91 (d, J = 8.1 Hz, 2H), 4.20 (p, J = 5.3 Hz, 1H), 4.11 – 4.02 (m, 2H), 3.73 (qd, J = 11.3, 5.4 Hz, 2H), 2.83 (s, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 158.21, 129.62, 121.48, 114.58, 69.91, 68.43, 45.99.

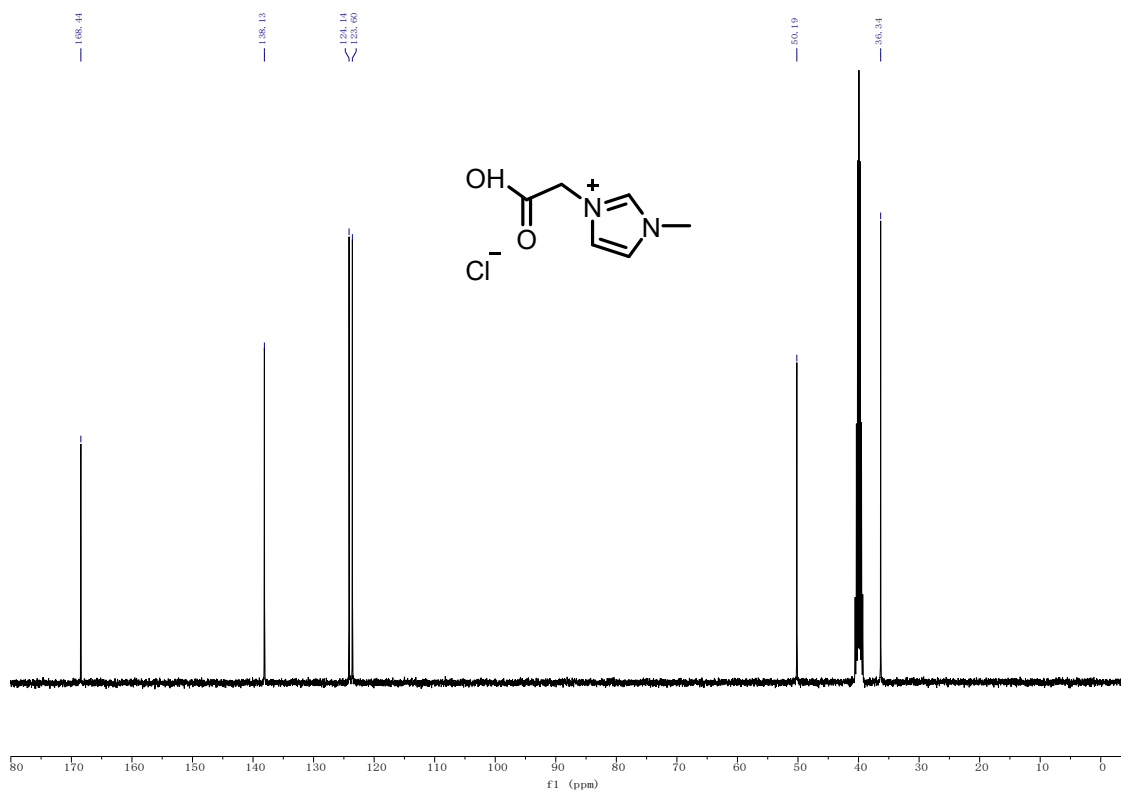
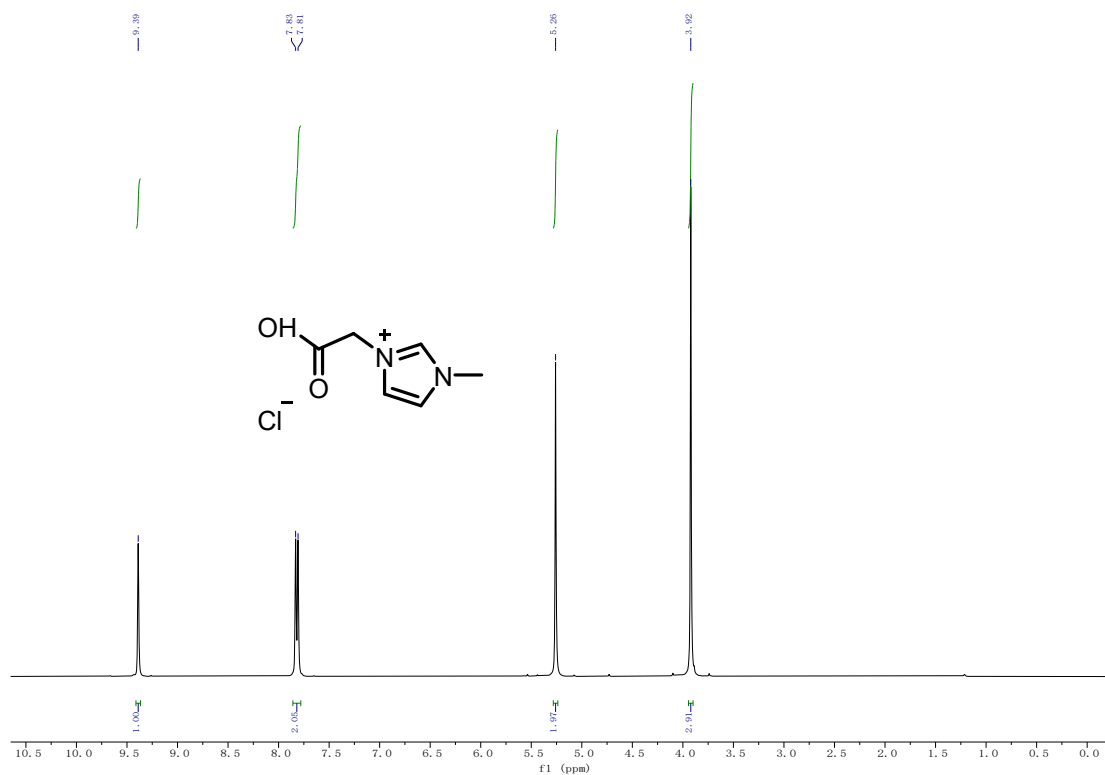
1,3-Dichloro-2-propanol: ^1H NMR (400 MHz, CDCl_3) δ 4.08 (p, J = 5.3 Hz, 1H), 3.70 (d, J = 5.3 Hz, 4H), 2.73 – 2.61 (m, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 70.86, 45.77.

ethyl benzoate: ^1H NMR (400 MHz, CDCl_3) δ 8.05 (d, J = 6.9 Hz, 2H), 7.59 – 7.50 (m, 1H), 7.44 (t, J = 7.7 Hz, 2H), 4.38 (q, J = 7.0 Hz, 2H), 1.40 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 166.65, 132.80, 130.52, 129.54, 128.31, 60.96, 14.34.

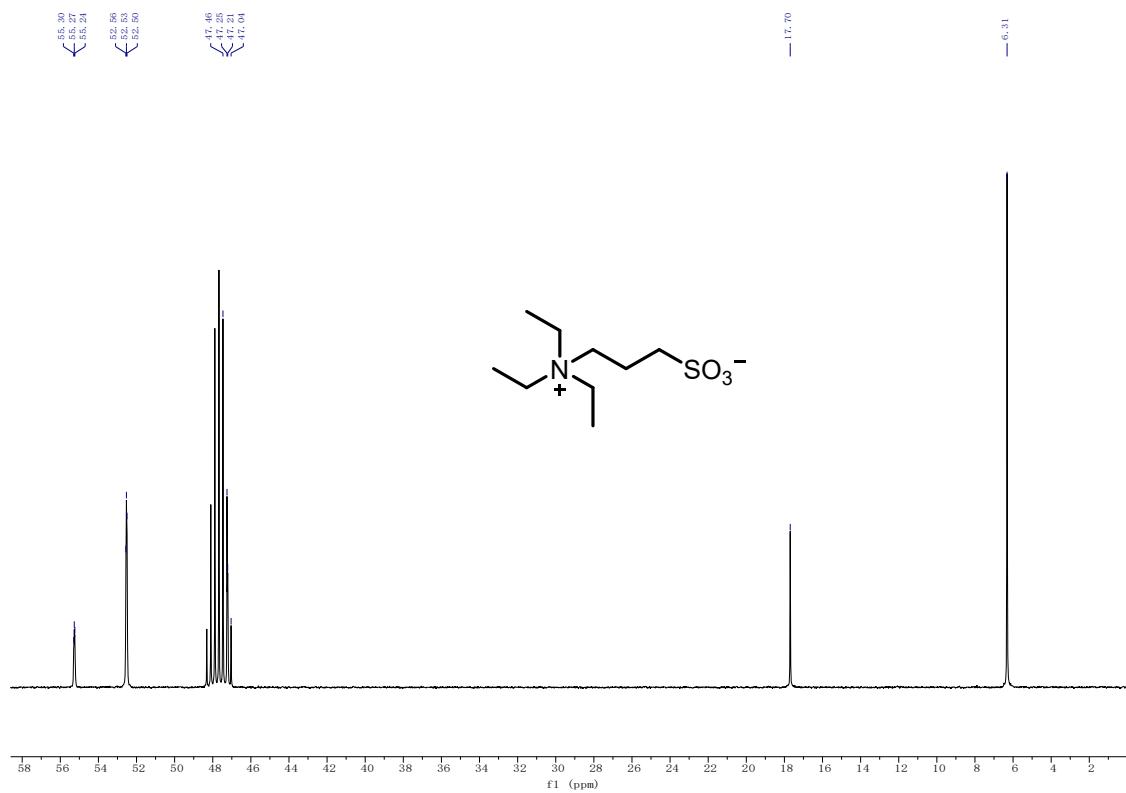
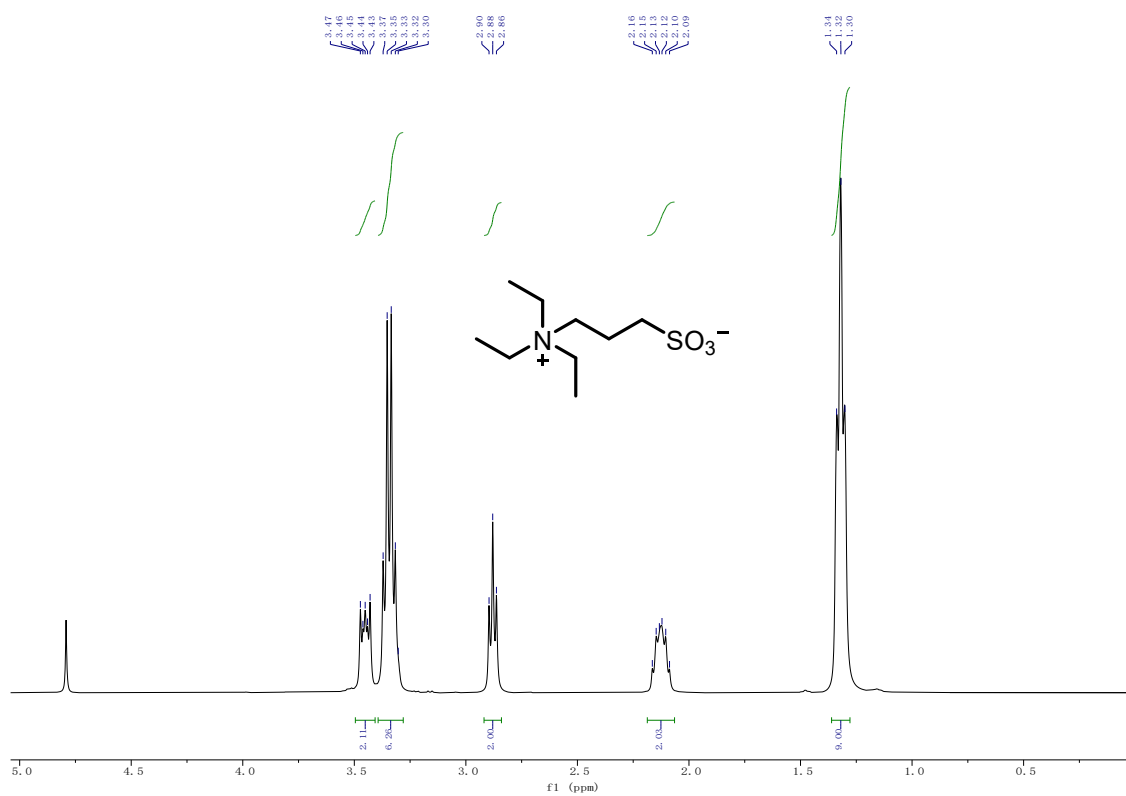
2-Phenylquinoline: ^1H NMR (400 MHz, DMSO- d_6) δ 9.33 (s, 1H), 8.29 – 8.05 (m, 4H), 7.77 (p, J = 7.0 Hz, 2H), 7.56 (dt, J = 12.6, 6.9 Hz, 3H). ^{13}C NMR (100 MHz, DMSO- d_6) δ 147.14, 138.65, 137.58, 136.86, 132.06, 125.57, 125.47, 124.90, 124.82, 124.44, 124.40, 122.83.

2-Phenylimidazo[1,2-a]pyridine: ^1H NMR (400 MHz, CDCl_3) δ 8.11 (d, J = 6.7 Hz, 1H), 8.01 – 7.92 (m, 2H), 7.86 (s, 1H), 7.64 (d, J = 9.1 Hz, 1H), 7.44 (t, J = 7.6 Hz, 2H), 7.33 (t, J = 7.4 Hz, 1H), 7.22 – 7.11 (m, 1H), 6.77 (t, J = 6.8 Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 145.75, 145.67, 133.76, 128.74, 127.98, 126.05, 125.61, 124.66, 117.50, 112.41, 108.16.

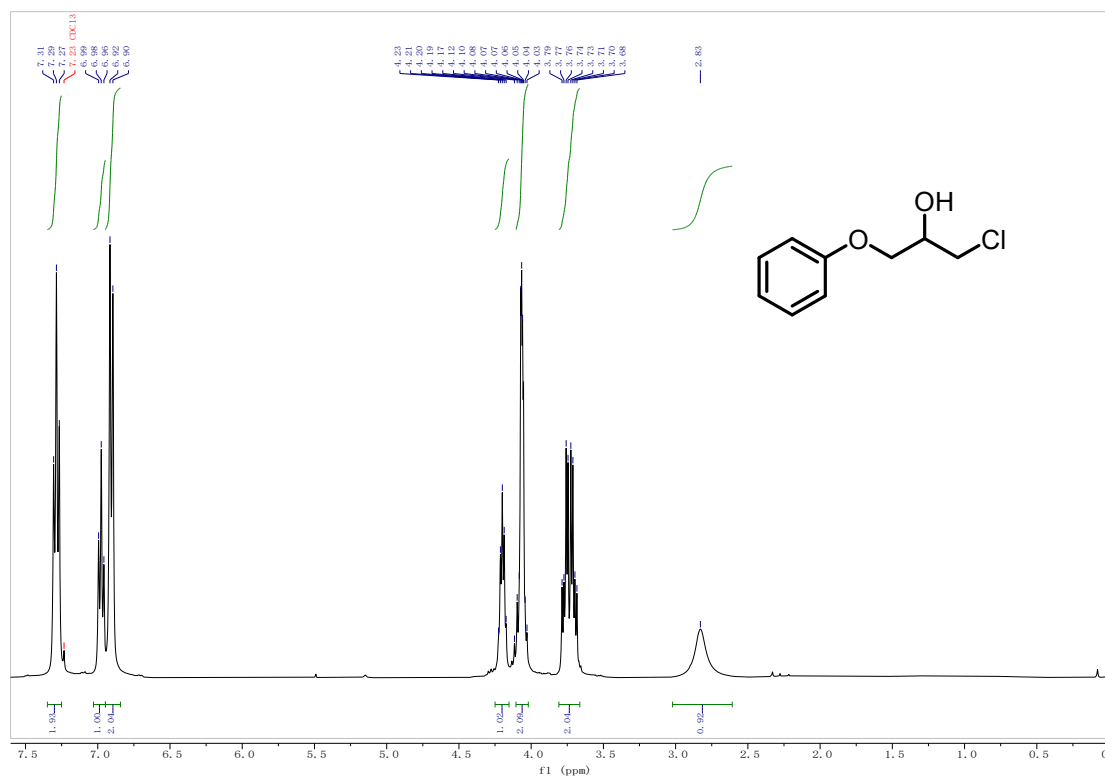
¹H NMR and ¹³C NMR of 1-Carboxymethyl-3-methylimidazolium chloride



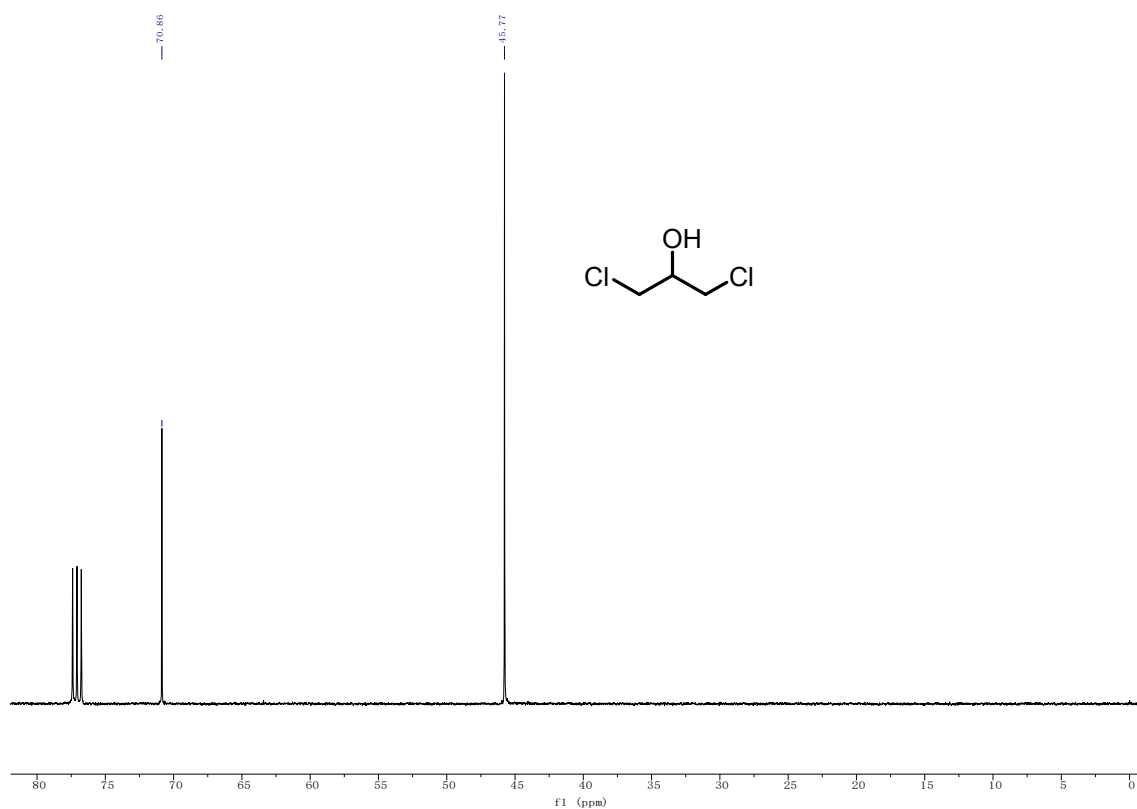
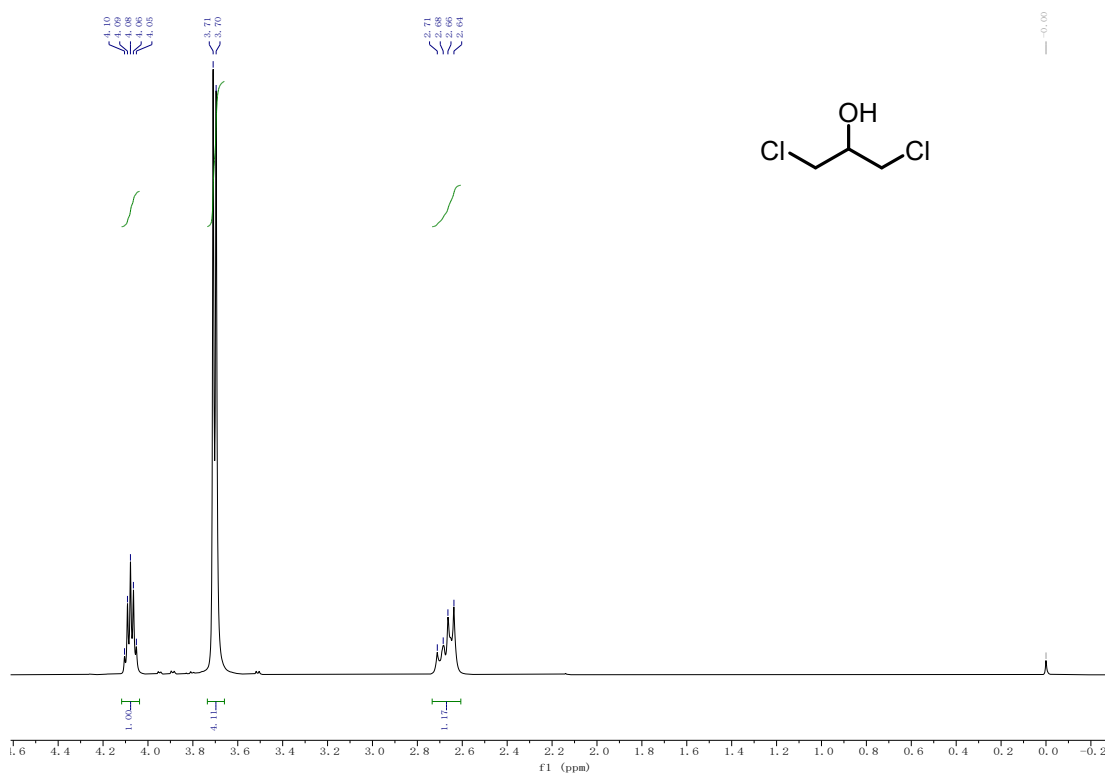
^1H NMR and ^{13}C NMR of 3-(triethylammonio) propane sulfonate



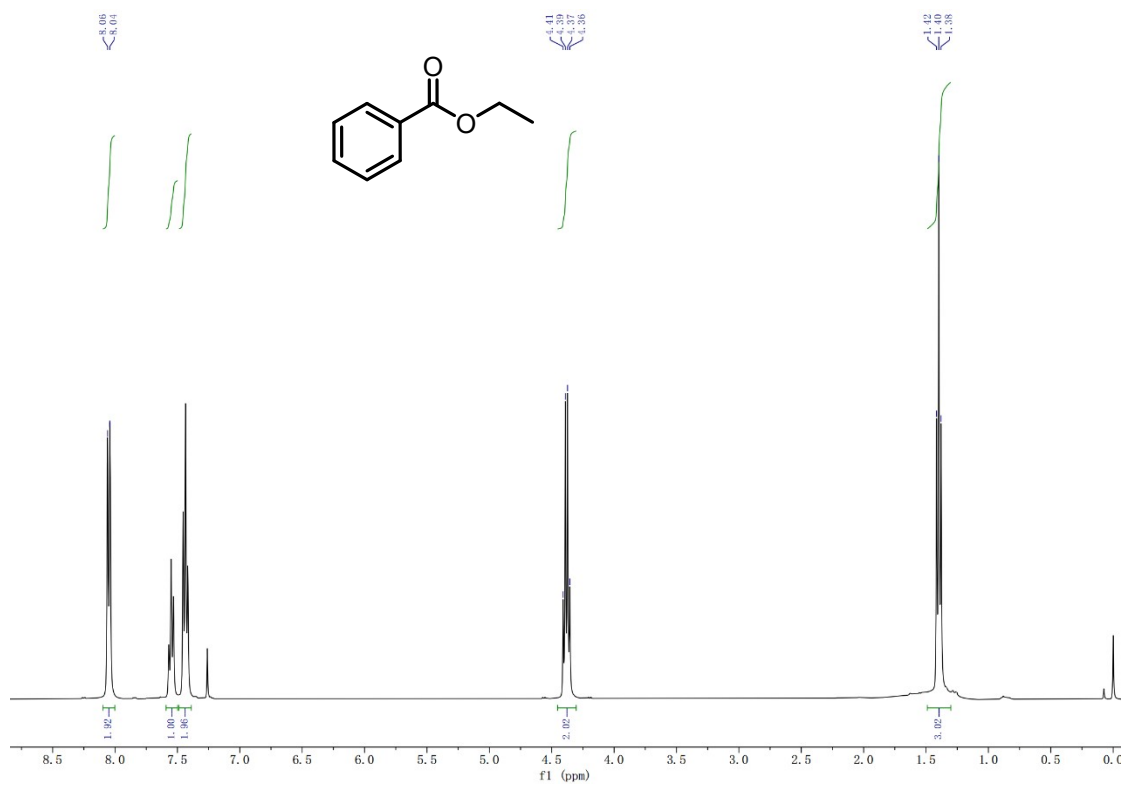
^1H NMR and ^{13}C NMR of 1-chloro-3-phenoxypropan-2-ol



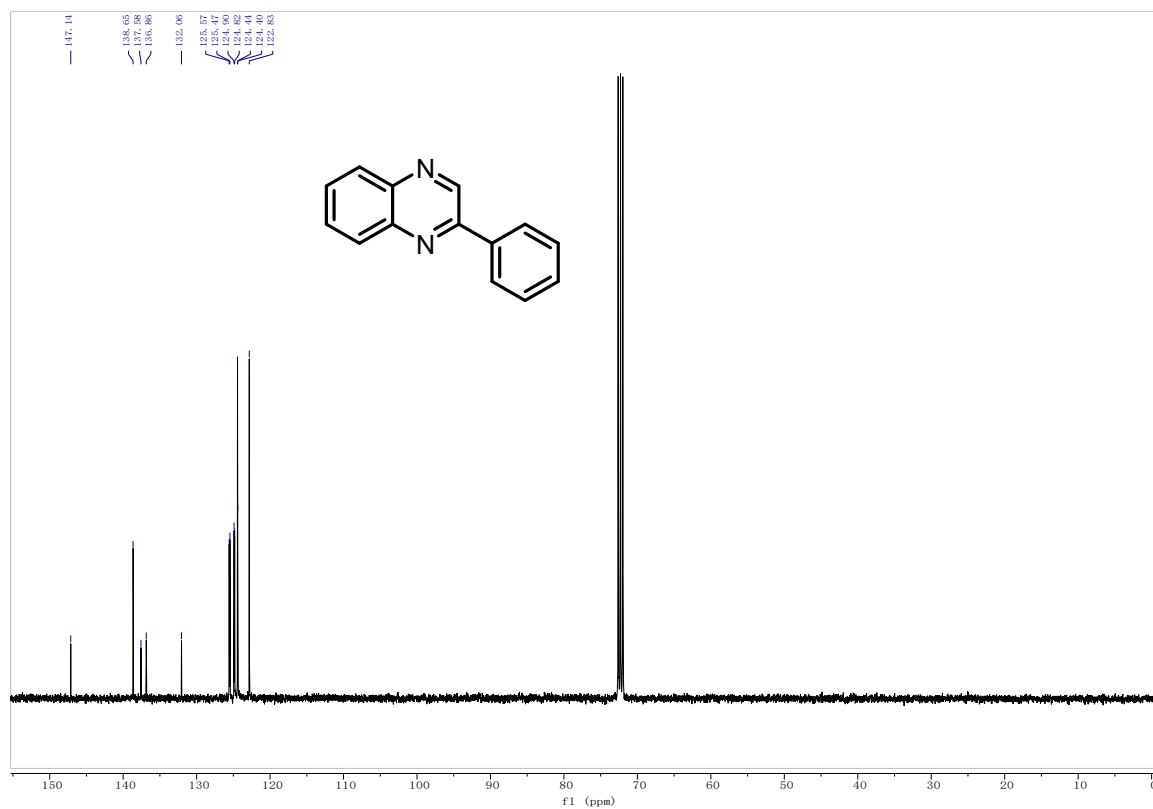
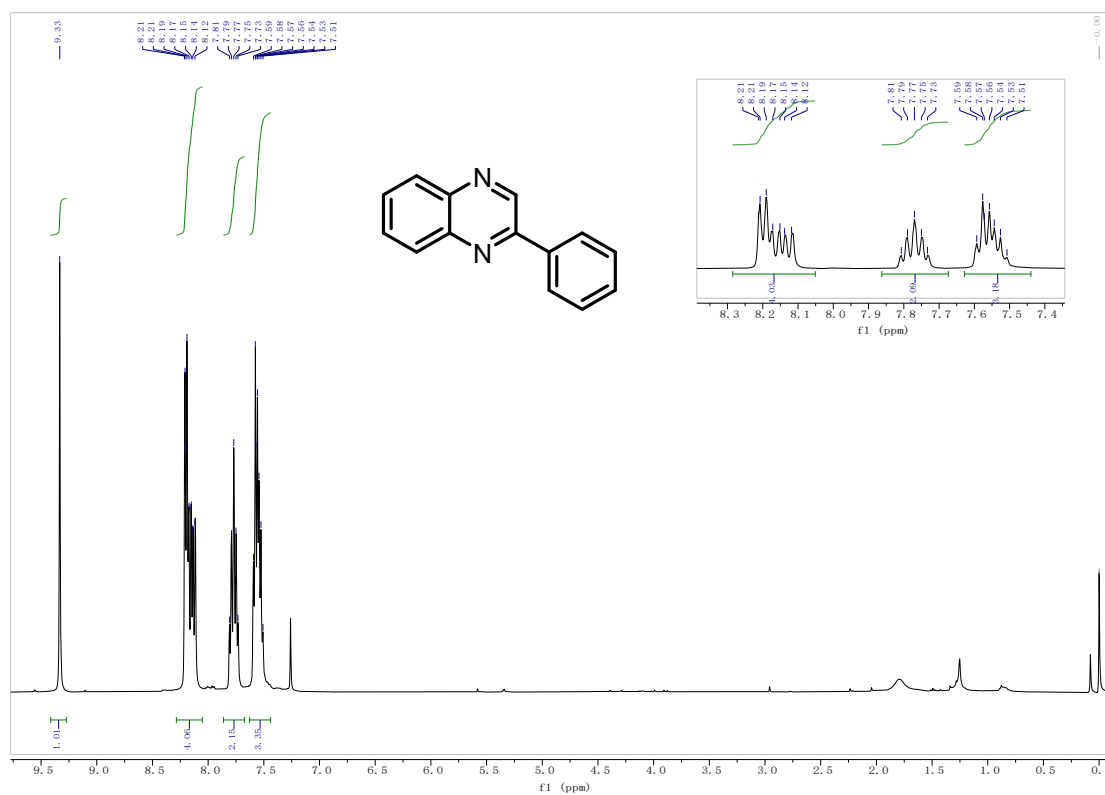
^1H NMR and ^{13}C NMR of 1,3-Dichloro-2-propanol:



^1H NMR and ^{13}C NMR of ethyl benzoate:



^1H NMR and ^{13}C NMR of 2-Phenylquinoline



^1H NMR and ^{13}C NMR of 2-Phenylimidazo[1,2-a]pyridine:

