

4-(N,N-Dimethylamino)pyridine Hydrochloride as a Recyclable Catalyst for Acylation of Inert Alcohols: Substrate Scope and Reaction Mechanism

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Table of Content

1. Instruments	s2
2. Preparation of DMAP·HCl	s2
3. ¹ H NMR and ¹³ C NMR spectra of DMAP·HCl	s2
4. General procedure for the DMAP·HCl-catalysed acylation	s3–s4
5. Analytical data of products in Tables 1, 2, 3 and 4 (Tables s1, s2 and s3)....	s6–s13
6. Recyclability of DMAP·HCl	s13–s14
7. The GC details of the reaction with or without TBAC.....	s14–s16
8. Isolation of <i>N</i> -acetylated DMAP chloride	s17
9. Reaction details of table 5	s17–s20
10. NMR spectra of products in Tables 1, 2, 3 and 4 (Tables s1, s2 and s3)...	s21–s46

1. Instruments

^1H NMR and ^{13}C NMR spectra were obtained at 400 MHz using a Bruker AC-P 400 spectrometer in CDCl_3 or $\text{DMSO}-d_6$ solution with tetramethylsilane as the internal standard. Chemical shift values (δ) are given in parts per million. HRMS data were obtained on an FTICR-MS instrument (Ionspec 7.0T). Gas chromatograms were obtained at SHIMADZU GC-2014 FID detector. The melting points were determined on an X-4 binocular microscope melting point apparatus (Beijing Tech Instruments Co., Beijing, China) and are uncorrected.

2. Preparation of DMAP·HCl

The 100 mL round bottomed flask was charged with 30 mL toluene and 5.0 g (40.9 mmol) 4-(*N,N*-dimethylamino)-pyridine (DMAP), and dry HCl (gas) was blown. White solid was formed immediately. After stirring 1 h at room temperature, the product was collected by filtering. After drying in vacuum, white solid was obtained in 6.28 g, yield 96.9%, mp 220–221 °C. ^1H NMR (400 MHz, CDCl_3) δ 15.45 (br, 1H), 8.14 (t, $J = 6.8$ Hz, 2H), 6.78 (d, $J = 6.8$ Hz, 2H), 3.27 (s, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ 138.6, 106.8, 40.3.

3. ^1H NMR and ^{13}C NMR of DMAP·HCl

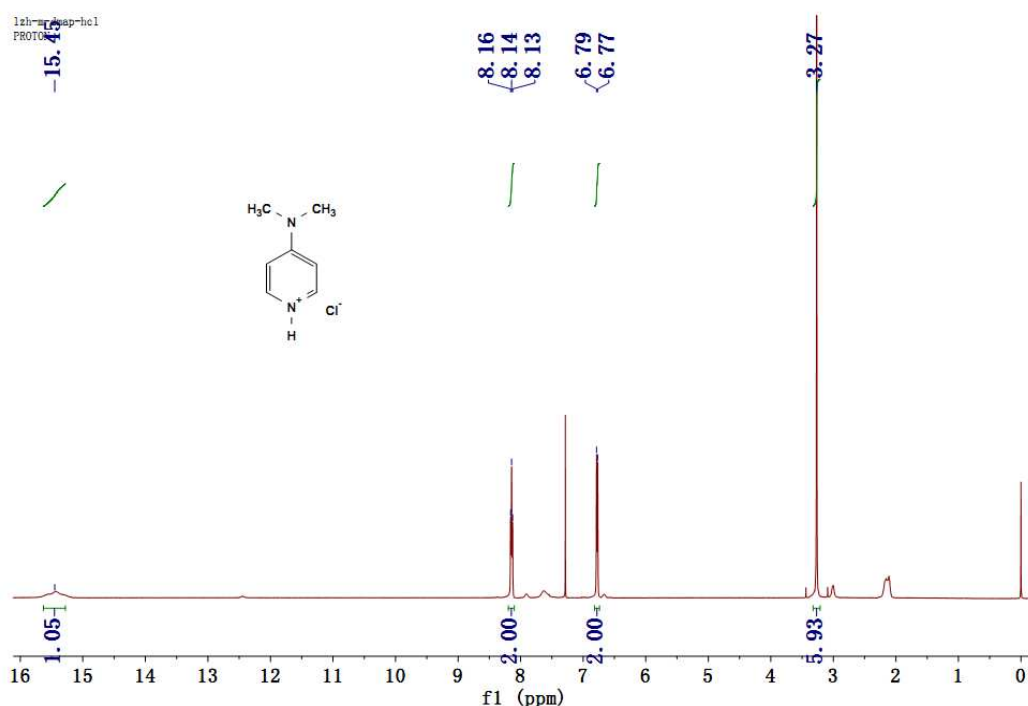


Figure S1. ^1H NMR spectrum of DMAP·HCl (400 MHz, CDCl_3)

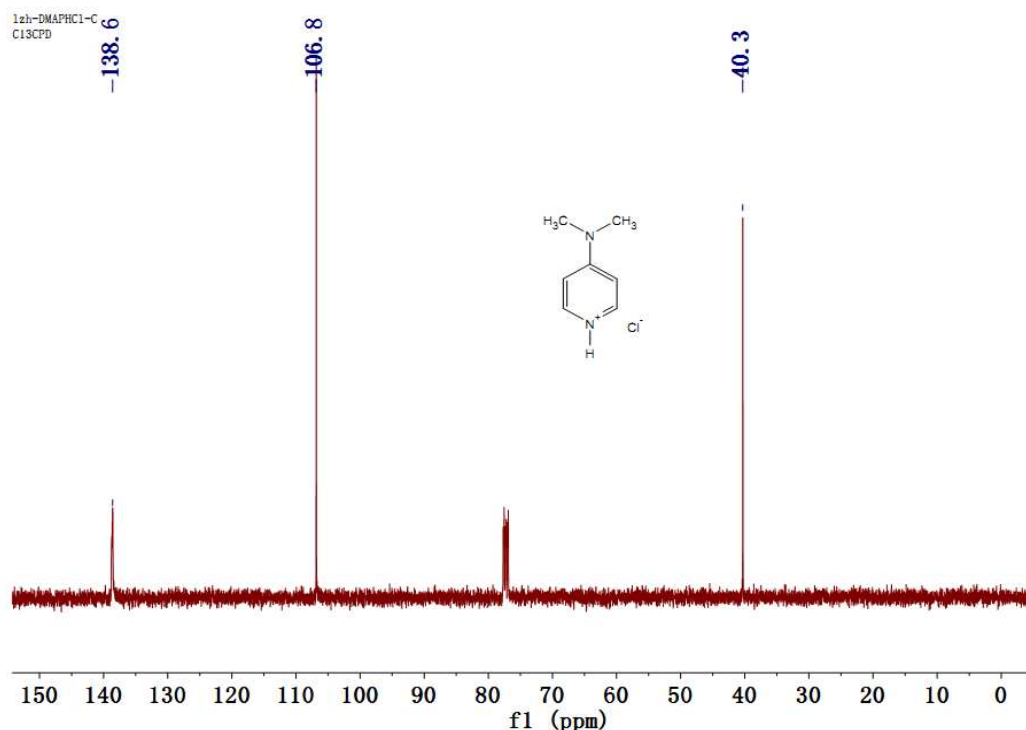
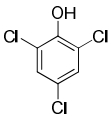
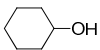

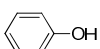
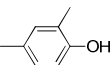
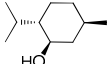

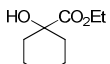
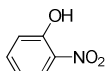
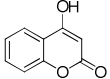
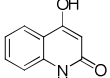
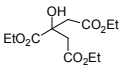



Figure S2. ^{13}C NMR spectrum of DMAP·HCl (100 MHz, CDCl_3)

4. General procedure for the DMAP·HCl-catalyzed acylation

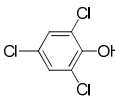

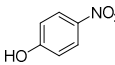







The alcohol (10.0 mmol) and the acylation reagent (11.0 mmol) were mixed in a 10 mL round-bottom flask with a calcium chloride tube at the top of condenser (for solid substrates, 50 mL round-bottom flask was used, and 30 mL toluene was used as solvent). After 5.0 mol% of DMAP·HCl (0.5 mmol) was added, the reaction mixture was stirred at required temperature. After a couple of hours the mixture was allowed to cool to room temperature, and then 20 mL hexane was added. DMAP·HCl was precipitated and then recovered by filtration, which could be used for the next run. The filtrate was evaporated to afford the crude product, which was purified by the flash column chromatography. The isolated yields are given in table 1, table 2, table 3 and table 4 (also in table s1, s2 and s3). For each contrast experiment (control reaction without DMAP·HCl), both of the product and material were separated by column chromatography, and the conversion was calculated based on the material recovered.



Table s1. DMAP·HCl-Catalyzed Acylation of Alcohols and Phenols with Acid Anhydrides under Base-Free Condition^a

entry	substrate ^a	acylating agent	T (°C)	time (h)	yield (%)
a			110	1	98
b		Ac ₂ O	60	8	98
c			25	78	98
d		(PhCO) ₂ O	110	1.2	96
e			60	10	97
1		Ac ₂ O		6	98
2		(PhCO) ₂ O	25	8	97
3		Ac ₂ O		6	98
4		(PhCO) ₂ O		8	98
5		Ac ₂ O		10	99
6		(PhCO) ₂ O	25	15	99
7		Ac ₂ O		8	99
8		(PhCO) ₂ O		10	97
9		Ac ₂ O		4	98
10		(PhCO) ₂ O		6	98
11		Ac ₂ O	60	6	97
12		(PhCO) ₂ O		9	98
13		Ac ₂ O		8	98
14		(PhCO) ₂ O		12	97
15		Ac ₂ O	60	4	98
16		(PhCO) ₂ O		8	96
17		Ac ₂ O	60	4	99
18		(PhCO) ₂ O		5	98
19		Ac ₂ O	60	6	96
20		(PhCO) ₂ O		8	94
21		Ac ₂ O		8	90
22		(PhCO) ₂ O	110 ^a	28	88
23		Ac ₂ O		4	97
24		(PhCO) ₂ O		8	93

^aThe reactions in the absence of DMAP·HCl had no obvious conversion monitored by TLC.

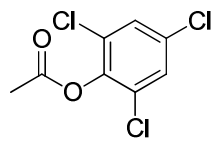
Table s2. DMAP·HCl-Catalyzed Acylation of Alcohols and Phenols with Acyl Chloride under Base-Free Condition.

Entry	substrate	acylating agent	cat.	time (h)	conv. (%)	yield (%)
1		PhCOCl	Y	8	98	97
1 ^c			N	8	20	----
2		<i>t</i> BuCOCl	Y	6	>99	95
2 ^c			N	6	30	----
3		PhCOCl	Y	6	>99	97.9
3 ^c			N	6	40	----
4		<i>t</i> BuCOCl	Y	18	>99	96.4
4 ^c			N	18	<20	----
5		PhCOCl	Y	6	>99	98
5 ^c			N	6	40	----
6		<i>t</i> BuCOCl	Y	8	>99	99
6 ^c			N	8	40	-----
7		PhCOCl	Y	2	>99	93
7 ^c			N	2	30	----
8		<i>t</i> BuCOCl	Y	8	>99	99
8 ^c			N	8	40	----
9		PhCOCl	Y	4	99	94
9 ^c			N	4	67	----
10		<i>t</i> BuCOCl	Y	2	99	95
10 ^c			N	2	56	----
11		PhCOCl	Y	2	>99	94.2
11 ^c			N	2	28	----
12		<i>t</i> BuCOCl	Y	2	>99	95
12 ^c			N	2	32	----
13		PhCOCl	Y	6	>99	96
13 ^c			N	6	<5	----
14		<i>t</i> BuCOCl	Y	5	>99	97
14 ^c			N	5	<5	----
15		PhCOCl	Y	1	>99	96
15 ^c			N	1	<15	----
16		<i>t</i> BuCOCl	Y	1.25	>99	98
16 ^c			N	1.25	<10	----
17		PhCOCl	Y	2.5	>99	96
17 ^c			N	2.5	<5	----
18		<i>t</i> BuCOCl	Y	4	>99	93
18 ^c			N	4	<5	----
19		PhCOCl	Y	0.25	>99	94
19 ^c			N	0.25	60	----
20		<i>t</i> BuCOCl	Y	0.13	>99	94
20 ^c			N	0.13	50	----

21		PhCOCl	Y	2	>99	94
21 ^c			N	2	<50	----

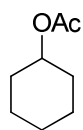
5. Analytical data of products

All of the products from Tables S1, S2 and S3 were tested by ¹H NMR. ¹³C NMR and HRMS were also given for new products.



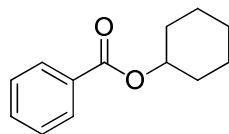
(product for Table S1, entries a, b, c; Table 1, entries 3-7)

White crystal, mp 49–50 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.38 (s, 2H), 2.39 (s, 3H).



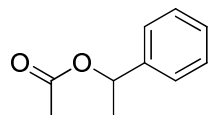
(product for Table S1 and Table 2, entry 1)

Colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 4.83–4.63 (m, 1H), 2.04 (s, 3H), 1.90–1.83 (m, 2H), 1.77–1.67 (m, 2H), 1.58–1.50 (m, 1H), 1.46–1.29 (m, 4H), 1.28–1.19 (m, 1H).



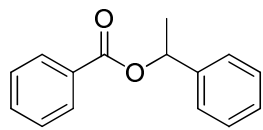
(product for Table S1 and Table 2, entry 2)

Colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 8.08 (d, *J* = 7.2 Hz, 2H), 7.58 (t, *J* = 7.2 Hz, 1H), 7.47 (t, *J* = 7.6 Hz, 2H), 5.07 (ddd, *J* = 12.4, 8.4, 3.6 Hz, 1H), 2.02–1.94 (m, 2H), 1.86–1.78 (m, 2H), 1.66–1.56 (m, 3H), 1.53–1.34 (m, 3H).



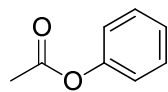
(product for Table S1 and Table 2, entry 3)

Colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.40–7.33 (m, 4H), 7.32–7.27 (m, 1H), 5.88 (q, *J* = 6.4 Hz, 1H), 2.08 (s, 3H), 1.54 (d, *J* = 6.4 Hz, 3H).



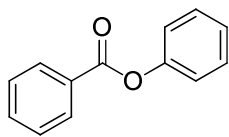
(product for Table S1 and Table 2, entry 4)

Colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 8.08 (d, *J* = 7.2 Hz, 2H), 7.56 (t, *J* = 7.2 Hz, 1H), 7.44 (t, *J* = 7.6 Hz, 4H), 7.37 (t, *J* = 7.6 Hz, 2H), 7.30 (t, *J* = 7.2 Hz, 1H), 6.14 (q, *J* = 6.8 Hz, 1H), 1.68 (d, *J* = 6.8 Hz, 3H).



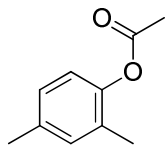
(product for Table S1 and Table 2, entry 5)

Colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 7.38 (t, $J = 8.0$ Hz, 2H), 7.23 (t, $J = 7.2$ Hz, 1H), 7.08 (d, $J = 7.6$ Hz, 2H), 2.30 (s, 3H).



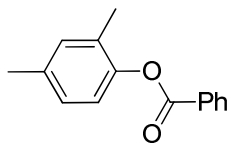
(product for Table S1 and Table 2, entry 6)

White solid, mp 71–72 °C. ^1H NMR (400 MHz, CDCl_3) δ 8.21 (dd, $J = 8.4, 7.6$ Hz, 2H), 7.63 (dd, $J = 11.6, 4.4$ Hz, 1H), 7.51 (t, $J = 7.6$ Hz, 2H), 7.43 (dd, $J = 8.0, 7.6$ Hz, 2H), 7.31–7.25 (m, 1H), 7.22 (dd, $J = 8.4, 1.0$ Hz, 2H).



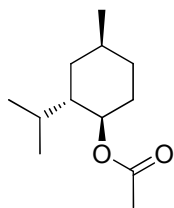
(product for Table S1 and Table 2, entry 7)

Colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 7.03 (s, 1H), 7.02–6.97 (m, 1H), 6.87 (d, $J = 8.0$ Hz, 1H), 2.30 (s, 6H), 2.14 (s, 3H).



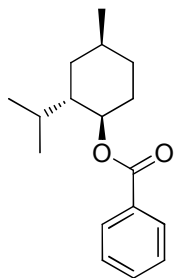
(product for Table S1 and Table 2, entry 8)

Colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 8.22 (d, $J = 8.0$ Hz, 2H), 7.64 (t, $J = 7.6$ Hz, 1H), 7.52 (t, $J = 7.6$ Hz, 2H), 7.09 (s, 1H), 7.05 (t, $J = 8.4$ Hz, 1H), 7.01 (d, $J = 8.0$ Hz, 1H), 2.34 (s, 3H), 2.19 (s, 3H).



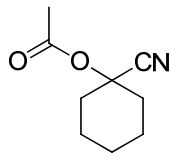
(product for Table S1 and Table 2, entry 9)

Colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 4.67 (td, $J = 10.8, 4.4$ Hz, 1H), 2.04 (s, 3H), 2.02–1.95 (m, 1H), 1.92–1.81 (m, 1H), 1.73–1.62 (m, 2H), 1.54–1.42 (m, 1H), 1.40–1.32 (m, 1H), 1.12–1.03 (m, 1H), 1.01–0.94 (m, 1H), 0.84–0.90 (m, 1H), 0.92–0.87 (m, 6H), 0.76 (d, $J = 7.2$ Hz, 3H).



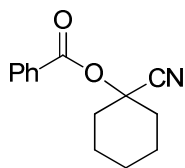
(product for Table S1 and Table 2, entry 10)

White crystal, mp 49–50 °C. ^1H NMR (400 MHz, CDCl_3) δ 8.10–8.00 (m, 2H), 7.55 (t, $J = 7.2$ Hz, 1H), 7.44 (t, $J = 7.6$ Hz, 2H), 4.93 (td, $J = 10.8, 4.4$ Hz, 1H), 2.17–2.10 (m, 1H), 2.02–1.92 (m, 1H), 1.77–1.69 (m, 2H), 1.62–1.52 (m, 2H), 1.19–1.05 (m, 2H), 0.96–0.90 (m, 7H), 0.79 (d, $J = 6.8$ Hz, 3H).



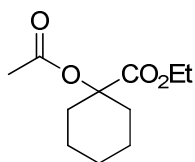
(product for Table S1 and Table 2, entry 11; Table 4 and Table S3, entry 13)

Colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 2.33–2.25 (m, 2H), 2.11 (s, 3H), 1.88–1.79 (m, 2H), 1.77–1.71 (m, 2H), 1.69–1.61 (m, 3H), 1.41–1.29 (m, 1H).



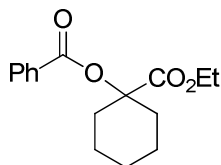
(product for Table S1 and Table 2, entry 12; Table S2 and Table 3, entry 9; Table S3 and Table 4, entries 14 and 16)

White crystal, mp 75–76 °C. ^1H NMR (400 MHz, CDCl_3) δ 8.06 (d, $J = 7.6$ Hz, 2H), 7.63 (t, $J = 7.6$ Hz, 1H), 7.49 (t, $J = 7.6$ Hz, 2H), 2.48–2.34 (m, 2H), 2.13–2.01 (m, 2H), 1.88–1.72 (m, 4H), 1.69–1.63 (m, 1H), 1.52–1.40 (m, 1H).



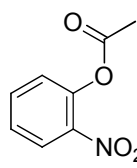
(product for Table S1 and Table 2, entry 13)

Colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 4.17 (q, $J = 7.2$ Hz, 2H), 2.13 (d, $J = 12.8$ Hz, 2H), 2.10 (s, 3H), 1.83–1.73 (m, 2H), 1.70–1.59 (m, 3H), 1.58–1.48 (m, 2H), 1.37–1.30 (m, 1H), 1.25 (t, $J = 7.2$ Hz, 3H).



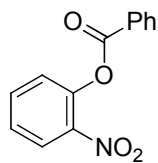
(product for Table S1 and Table 2, entry 14; Table S2 and Table 3, entry 11)

Colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 8.09 (d, $J = 7.2$ Hz, 2H), 7.60 (t, $J = 7.2$ Hz, 1H), 7.48 (t, $J = 7.6$ Hz, 2H), 4.23 (q, $J = 7.2$ Hz, 2H), 2.34 (d, $J = 14.4$ Hz, 2H), 1.95–1.86 (m, 2H), 1.77–1.60 (m, 5H), 1.43–1.32 (m, 1H), 1.25 (t, $J = 7.2$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 172.7, 165.1, 133.1, 130.3, 129.7, 128.4, 80.3, 61.1, 32.2, 25.1, 21.4, 14.1. HRMS (ESI) m/z Calcd. for $\text{C}_{16}\text{H}_{21}\text{O}_4$ $[\text{M}+\text{H}]^+$: 277.1434, found: 277.1435.



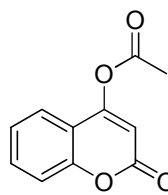
(product for Table S1 and Table 2, entry 15; Table S3 and Table 4, entry 2)

Faint yellow oil. ^1H NMR (400 MHz, CDCl_3) δ 8.10 (dd, $J = 8.0, 1.6$ Hz, 1H), 7.66 (td, $J = 8.0, 1.6$ Hz, 1H), 7.28 (td, $J = 8.0, 1.2$ Hz, 1H), 7.25 (dd, $J = 8.0, 1.2$ Hz, 1H), 2.38 (s, 3H).



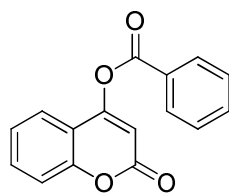
(product for Table S1 and Table 2, entry 16; Table S2 and Table 3, entry 3; Table S3 and Table 4, entries 3 and 6)

Faint yellow oil. ^1H NMR (400 MHz, CDCl_3) δ 8.25–8.18 (m, 2H), 8.16 (dd, $J = 8.0, 1.6$ Hz, 1H), 7.75–7.66 (m, 2H), 7.54 (t, $J = 7.6$ Hz, 2H), 7.48–7.43 (m, 1H), 7.43–7.37 (m, 1H).



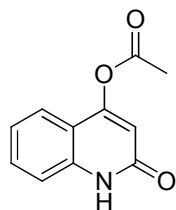
(product for Table S1 and Table 2, entry 17; Table S3 and Table 4, entry 9)

White solid, mp 108–110 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.66 (dd, $J = 8.0, 1.2$ Hz, 1H), 7.61 (td, $J = 8.0, 1.6$ Hz, 1H), 7.39 (d, $J = 8.4$ Hz, 1H), 7.34 (td, $J = 7.6, 0.8$ Hz, 1H), 6.55 (s, 1H), 2.48 (s, 3H). HRMS (ESI) m/z Calcd. for $\text{C}_{11}\text{H}_8\text{NaO}_4$ $[\text{M}+\text{Na}]^+$: 227.0315, found: 227.0317.



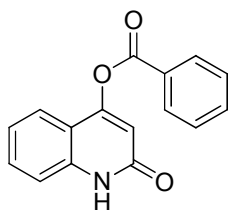
(product for Table S1 and Table 2, entry 18; Table S2 and Table 3, entry 15; Table S3 and Table 4, entries 10 and 12)

White solid, mp 128–130 °C. ^1H NMR (400 MHz, CDCl_3) δ 8.30–8.25 (m, 2H), 7.80–7.72 (m, 2H), 7.67–7.58 (m, 3H), 7.46–7.41 (m, 1H), 7.37–7.32 (m, 1H), 6.66 (s, 1H).



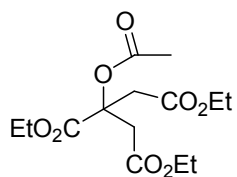
(product for Table S1 and Table 2, entry 19)

White solid, mp >260 °C. ^1H NMR (400 MHz, $\text{DMSO}-d_6$) δ 11.93 (s, 1H), 7.67 (d, $J = 8.0$ Hz, 1H), 7.59 (t, $J = 7.6$ Hz, 1H), 7.39 (d, $J = 8.4$ Hz, 1H), 7.23 (t, $J = 7.6$ Hz, 1H), 6.41 (s, 1H), 2.44 (s, 3H). HRMS (ESI) m/z Calcd. for $\text{C}_{11}\text{H}_9\text{NO}_3\text{Na}$ $[\text{M}+\text{Na}]^+$: 226.0475, found: 226.0475.



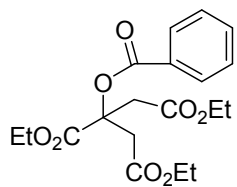
(product for Table S1 and Table 2, entry 20; Table S2 and Table 3, entry 17)

White solid, mpt 234–236°C. ^1H NMR (400 MHz, $\text{DMSO}-d_6$) δ 11.99 (s, 1H), 8.24 (d, $J = 7.2$ Hz, 2H), 7.83 (t, $J = 7.6$ Hz, 1H), 7.71–7.57 (m, 4H), 7.42 (d, $J = 8.0$ Hz, 1H), 7.23 (t, $J = 7.2$ Hz, 1H), 6.63 (s, 1H).



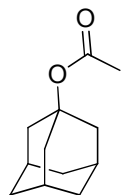
(product for Table S1 and Table 2, entry 21)

Colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 4.25 (q, $J = 7.2$ Hz, 2 H), 4.17 (q, $J = 7.2$ Hz, 4 H), 3.26 (dd, $J = 40.0, 16.0$ Hz, 4 H), 2.10 (s, 3 H), 1.33–1.25 (m, 9 H). ^{13}C NMR (100 MHz, CDCl_3) δ 170.0, 169.9, 169.4, 78.7, 62.6, 61.3, 39.3, 21.5, 14.7, 14.4.



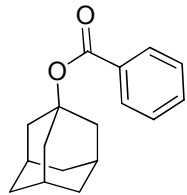
(product for Table S1 and Table 2, entry 22)

Colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 8.07–7.99 (m, 2H), 7.61 (t, $J = 7.6$ Hz, 1H), 7.47 (t, $J = 7.6$ Hz, 2H), 4.30 (q, $J = 7.2$ Hz, 2H), 4.19–4.05 (m, 4H), 1.31 (t, $J = 7.2$ Hz, 3H), 1.21 (t, $J = 7.2$ Hz, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ 169.4, 168.9, 164.9, 133.5, 130.2, 129.9, 128.4, 78.6, 62.2, 60.9, 39.0, 14.0, 13.9.



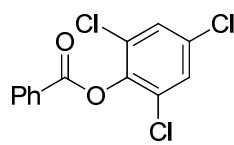
(product for Table S1 and Table 2, entry 23)

Colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 2.16 (s, 3H), 2.11 (s, 3H), 2.10 (s, 3H), 1.97 (s, 3H), 1.66 (s, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ 169.1, 79.2, 40.3, 35.2, 29.8, 21.6.



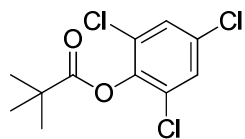
(product for Table S1 and Table 2, entry 24; Table S2 and Table 3, entry 13)

Colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 8.02–7.96 (m, 2H), 7.52 (t, $J = 7.6$ Hz, 1H), 7.41 (t, $J = 7.6$ Hz, 2H), 2.26 (s, 6H), 2.22 (s, 3H), 1.79–1.67 (m, 6H).



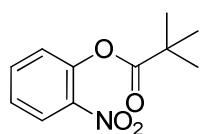
(product for Table S1, d and e; Table S2, entry 1; Table 3 entry 1)

White crystal, mp 70–71 °C. ^1H NMR (400 MHz, CDCl_3) δ 8.24 (d, J = 7.2 Hz, 2H), 7.69 (t, J = 7.2 Hz, 1H), 7.55 (t, J = 7.6 Hz, 2H), 7.43 (s, 2H).



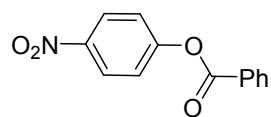
(product for Table S2 and Table 3, entry 2)

White solid, mp 60–61 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.36 (s, 2H), 1.41 (s, 9H).



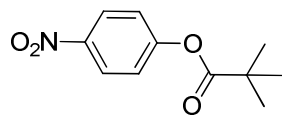
(product for Table S2 and Table 3, entry 4; Table S3 and Table 4, entry 5)

Faint yellow oil. ^1H NMR (400 MHz, CDCl_3) δ 8.08 (dd, J = 8.0, 1.6 Hz, 1H), 7.64 (td, J = 8.0, 1.6 Hz, 1H), 7.38 (td, J = 8.0, 0.8 Hz, 1H), 7.19 (dd, J = 8.1, 0.8 Hz, 1H), 1.39 (s, 9H).



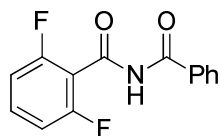
(product for Table S2 and Table 3, entry 5)

White crystal, mp 145–146 °C. ^1H NMR (400 MHz, CDCl_3) δ 8.37 (d, J = 9.2 Hz, 2H), 8.24 (d, J = 8.0 Hz, 2H), 7.72 (t, J = 8.0 Hz, 1H), 7.58 (t, J = 8.0 Hz, 2H), 7.46 (d, J = 9.2 Hz, 2H).



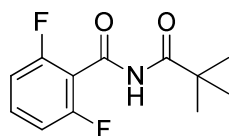
(product for Table S2 and Table 3, entry 6)

White crystal, mp 95–96 °C. ^1H NMR (400 MHz, CDCl_3) δ 8.27 (d, J = 9.2 Hz, 2H), 7.25 (d, J = 9.2 Hz, 2H), 1.38 (s, 9H).



(product for Table S2 and Table 3, entry 7; Table S3 and Table 4, entry 8)

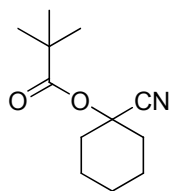
White needle-like crystal, mp 137–139 °C. ^1H NMR (400 MHz, CDCl_3) δ 9.04 (s, 1H), 7.90–7.85 (m, 2H), 7.66–7.61 (m, 1H), 7.55–7.49 (m, 2H), 7.48–7.41 (m, 1H), 6.99 (t, J = 8.4 Hz, 2H).



(product for Table S2 and Table 3, entry 8; Table S3 and Table 4, entry 7))

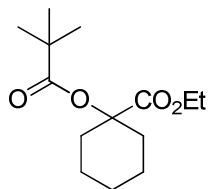
White needle-like crystal, mp 159–160 °C. ^1H NMR (400 MHz, CDCl_3) δ 8.55 (s, 1H), 7.45–7.37 (m, 1H), 6.95 (t, J = 8.0 Hz, 2H), 1.27 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3) δ 176.3, 162.3, 160.7 (d), 158.2,

132.0 (t), 111.8 (d), 40.1, 26.8. HRMS (ESI) m/z Calcd. for $C_{12}H_{14}F_2NO_2$ $[M+H]^+$: 242.0987, found: 242.0987.



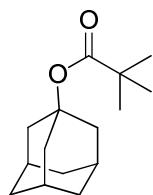
(product for Table S2 and Table 3, entry 10 ; Table S3 and Table 4, entry 15)

Colorless oil. 1H NMR (400 MHz, $CDCl_3$) δ 2.29–2.17 (m, 2H), 2.04–1.89 (m, 2H), 1.79–1.66 (m, 4H), 1.64–1.53 (m, 1H), 1.49–1.37 (m, 1H), 1.26 (s, 9H).



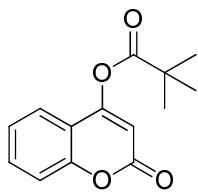
(product for Table S2 and Table 3, entry 12)

Colorless oil. 1H NMR (400 MHz, $CDCl_3$) δ 4.15 (q, $J = 7.2$ Hz, 2H), 2.16 (d, $J = 12.8$ Hz, 2H), 1.80–1.70 (m, 2H), 1.70–1.61 (m, 3H), 1.57–1.44 (m, 2H), 1.34–1.25 (m, 1H), 1.24 (s, 9H), 1.23 (t, $J = 7.2$ Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.1, 171.9, 78.4, 60.0, 38.0, 31.2, 26.3, 24.3, 20.5, 13.2.



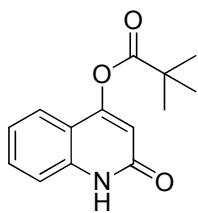
(product for Table S2 and Table 3, entry 14)

Colorless oil. 1H NMR (400 MHz, $CDCl_3$) δ 2.15 (s, 3H), 2.09 (s, 3H), 2.08 (s, 3H), 1.66 (s, 6H), 1.14 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.6, 78.4, 40.2, 38.2, 35.3, 29.8, 26.2.



(product for Table S2 and Table 3, entry 16; Table S3 and Table 4, entry 11)

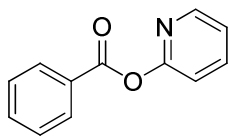
White solid, mp 115–116 °C. 1H NMR (400 MHz, $CDCl_3$) δ 7.63–7.56 (m, 2H), 7.38 (d, $J = 8.4$ Hz, 1H), 7.35–7.28 (m, 1H), 6.48 (s, 1H), 1.45 (s, 9H).



(product for Table S2 and Table 3, entry 18)

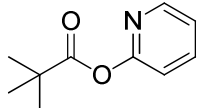
White solid, mp 219–221 °C. 1H NMR (400 MHz, $CDCl_3$) δ 12.65 (s, 1H), 7.55 (d, $J = 8.0$ Hz, 1H), 7.51–7.46 (m, 1H), 7.42 (d, $J = 8.0$ Hz, 1H), 7.19–7.14 (m, 1H), 6.55 (s, 1H), 1.39 (s, 9H). ^{13}C NMR (100

MHz, CDCl₃) δ 175.0, 165.4, 157.4, 138.8, 131.5, 122.8, 122.1, 116.7, 115.9, 111.1, 39.8, 27.2. HRMS (ESI) m/z Calcd. for C₁₄H₁₆NO₃ [M+H]⁺: 246.1125. Found: 246.1128.



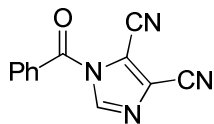
(product for Table S2 and Table 3, entry 19)

Colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 8.48 (dd, J = 4.8, 1.6 Hz, 1H), 8.26–8.21 (m, 2H), 7.86 (td, J = 7.8, 2.0 Hz, 1H), 7.65 (t, J = 7.5 Hz, 1H), 7.51 (d, J = 7.6 Hz, 2H), 7.28 (td, J = 7.2, 4.8 Hz, 1H), 7.23 (d, J = 8.1 Hz, 1H).



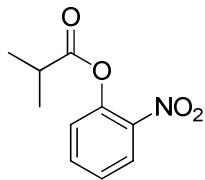
(product for Table S2 and Table 3, entry 20)

Colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 8.42 (dd, J = 4.8, 1.6 Hz, 1H), 7.79 (td, J = 8.0, 2.0 Hz, 1H), 7.22 (dd, J = 7.2, 4.8 Hz, 1H), 7.04 (d, J = 8.0 Hz, 1H), 1.39 (s, 9H).



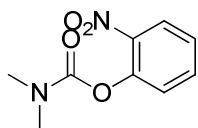
(product for Table S2 and Table 3, entry 21)

White solid, mp 89–91 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.10 (s, 1H), 7.89–7.82 (m, 3H), 7.71–7.65 (m, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 141.6, 136.1, 134.7, 130.6, 129.8, 126.1, 111.6, 110.6, 107.1.



(product for Table S3 and Table 4, entry 1)

Faint yellow oil. ¹H NMR (400 MHz, CDCl₃) δ 8.09 (d, J = 8.0 Hz, 1H), 7.65 (t, J = 8.0 Hz, 1H), 7.40 (t, J = 8.0 Hz, 1H), 7.23 (d, J = 8.0 Hz, 1H), 2.96–2.83 (m, 1H), 1.36 (d, J = 7.2 Hz, 6H).



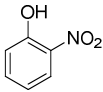
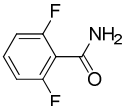
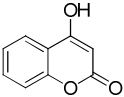

(product for Table S3 and Table 4, entry 4)

Colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 8.06 (dd, J = 8.0, 1.6 Hz, 1H), 7.63 (td, J = 8.0, 1.6 Hz, 1H), 7.35 (td, J = 8.0, 1.2 Hz, 1H), 7.31 (dd, J = 8.0, 1.2 Hz, 1H), 3.15 (s, 3H), 3.04 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 152.4, 144.0, 141.1, 133.5, 124.9, 124.5, 35.9, 35.6. HRMS (ESI) m/z Calcd. for C₉H₁₀N₂O₄Na [M+Na]⁺: 233.0533, found: 233.0529.

6. Recyclability of DMAP·HCl

The reactions were carried out as the procedures reported above.

Table s3. Assessment of DMAP·HCl as a Recyclable Catalyst in the Acylation of Various Substrates under Base-Free Conditions^a.

entry	substrate ^b	acylating agent	T (°C)	time (h)	yield (%) ^c of each run										M ^d (mg)
					1	2	3	4	5	6	7	8	9	10	
1		(i-PrCO) ₂ O	60	4	98	98	93	95	97	97	92	94	93	94	67.1
2		Ac ₂ O		4	98	97	99	98	96	94	97	93	95	96	65.5
3		(PhCO) ₂ O		7~9	96	96	94	95	92	89	94	96	92		62.6
4		Me ₂ NCOCl		10	97	95	96	93	93	97	89	89			70.0
5		t-BuCOCl		18~20	98	96	97	97	98	95	94	94	95	93	64.8
6		PhCOCl		6~8	96	94	92	93	90	92	94	93			65.2
7		t-BuCOCl	110	6~9	99	98	92	93	93	91	92	94	90		61.6
8		PhCOCl		2~3	93	93	94	90	91	91	94	90	90		63.7
9		Ac ₂ O	60	4~5	99	97	97	99	98	98	96	95	94		68.8
10		(PhCO) ₂ O		5~6	98	96	93	95	97	96	94	93	90		62.9
11		t-BuCOCl		4~5	98	95	93	97	97	95	92	94	92		67.2
12		PhCOCl		5~6	96	96	90	95	94	93	94	89	89		66.2
13		Ac ₂ O	60	6~7	98	97	99	98	96	94	97	93	95	96	69.0
14		(PhCO) ₂ O		8~10	97	94	92	93	92	92	94	82			62.8
15		t-BuCOCl		4	95	96	94	91	94	92	92	89	89	91	60.9
16		PhCOCl		2	94	92	91	93	89	92	89	91	89	90	58.9

^a The reaction of each substrate (10.0 mmol) with the acylating reagent (11.0 mmol) was conducted with DMAP·HCl (79.0 mg, 5 mol %) in 20 mL toluene unless otherwise noted. ^b For 1-cyanocyclohexanol, no solvent was used. ^c Isolated yield. ^d The weight of DMAP·HCl recovered after each cycle.

7. The GC details of the reaction with or without tetrabutylammonium chloride (TBAC).

Gas chromatography: SHIMADZU GC-2014, FID detector

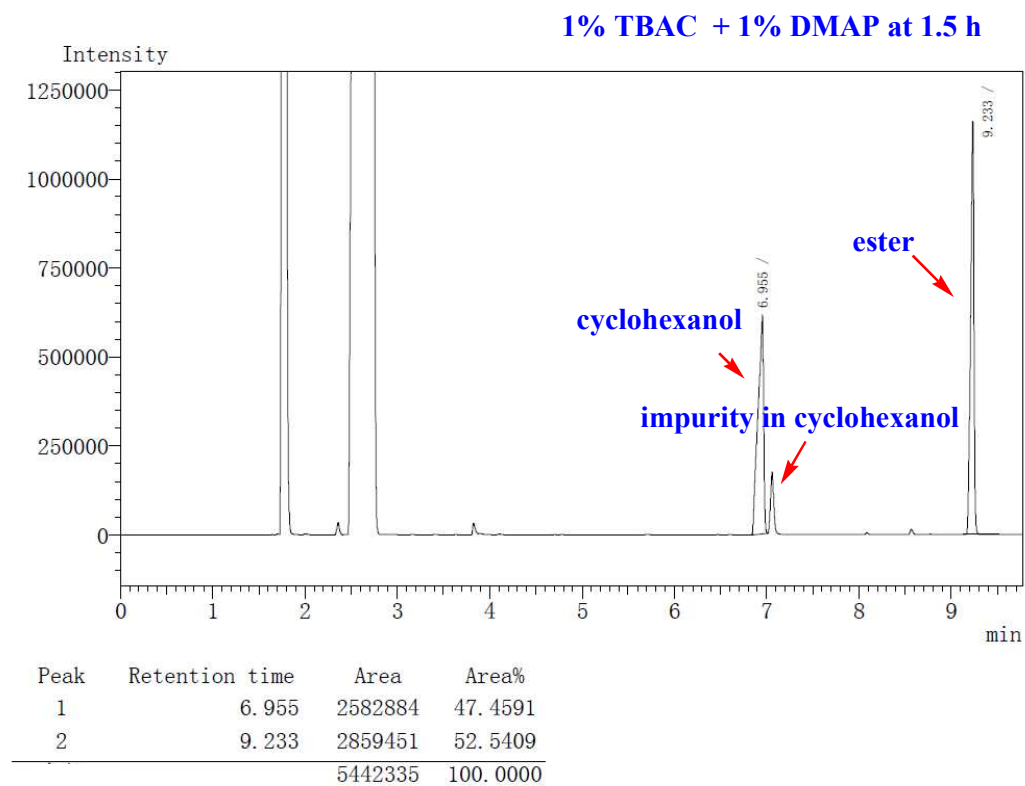
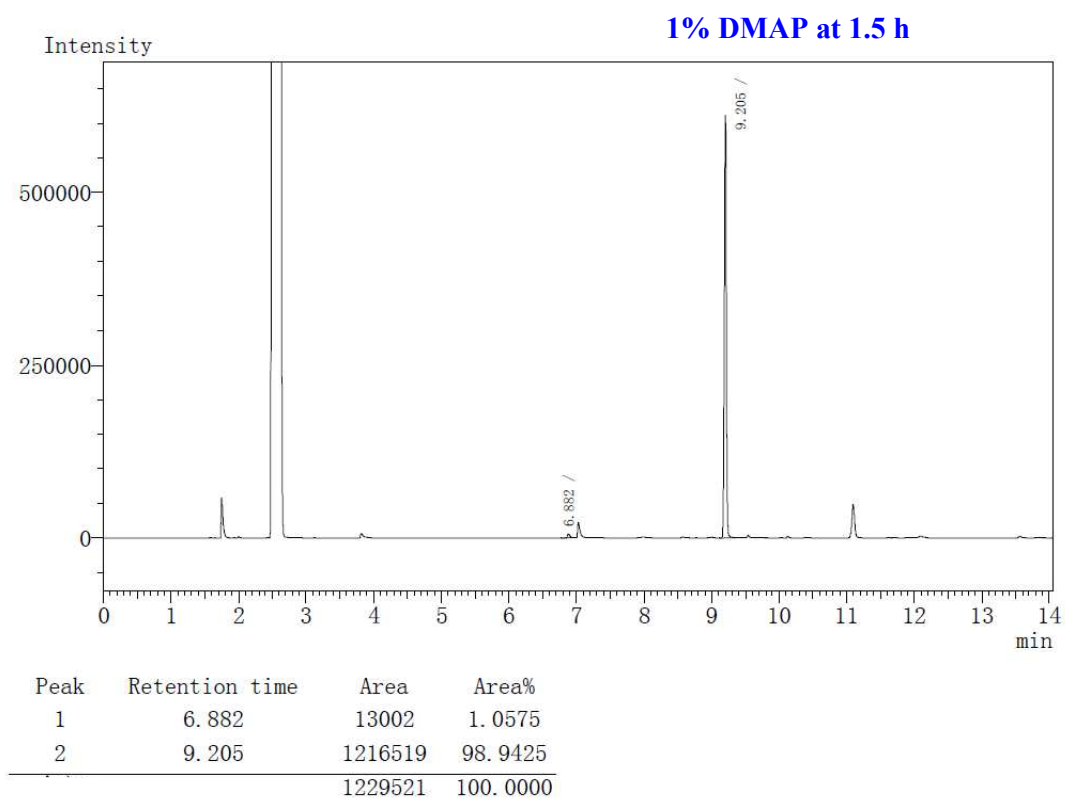
Chromatographic column: RTX-5 30m*0.25mm

Chromatographic condition: Column temperature was kept at 40 °C for three minutes, heated up 15 °C/min until 250 °C, and kept at this temperature for further three minutes.

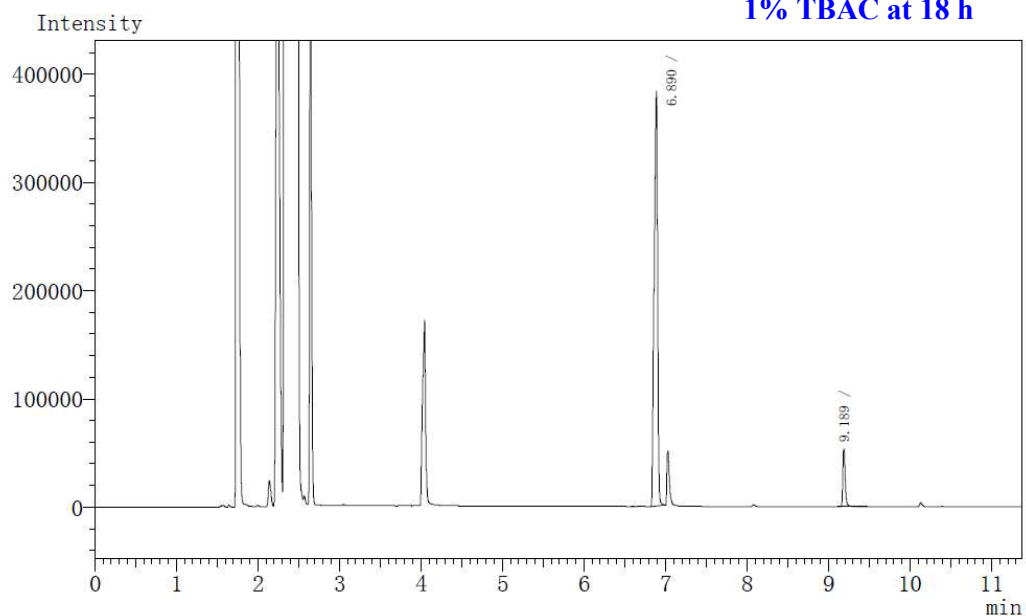
Sample size: 1µl.

Control mode: pressure (100KPa), total flow (53.4ml/min), column flow (0.99ml/min).

entry	DMAP	additive	time	conv. ^b
1	1%	none	1.5h	98.9
2	1%	1% TBAC	1.5 h	52.5
3	none	1% TBAC	18 h	9.2
4	none	none	18 h	10.8

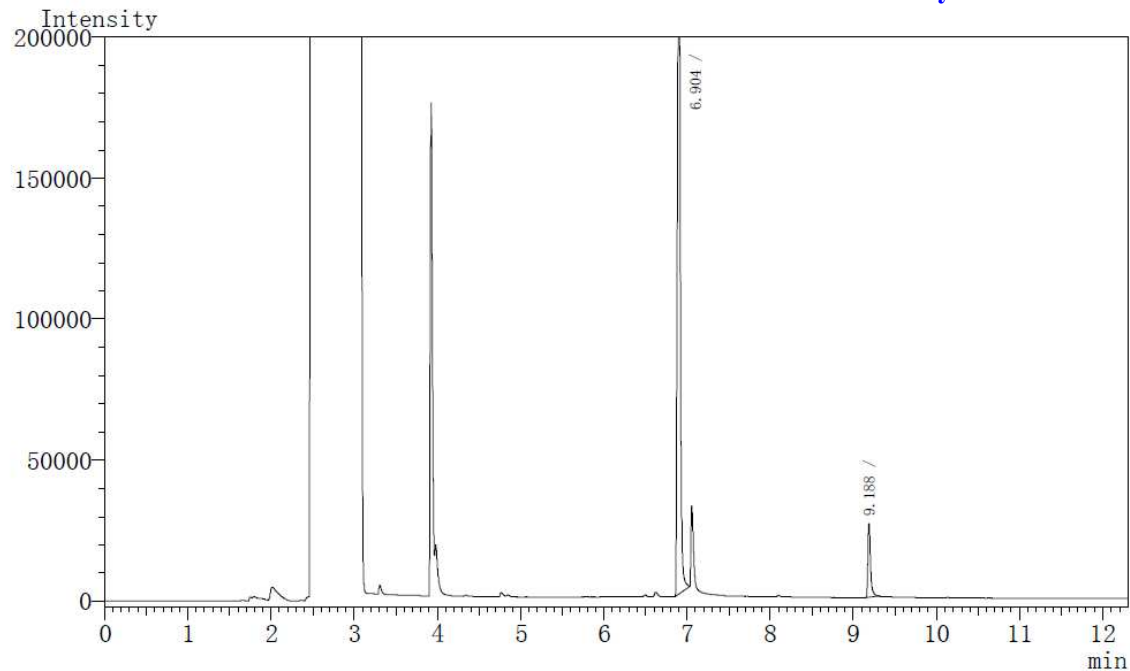


1% TBAC at 18 h



Peak	Retention time	Area	Area%
1	6.890	1106620	91.1581
2	9.189	107337	8.8419
		1213957	100.0000

no catalyst



peak	Retention time	area	area%
1	6.904	602488	91.3051
2	9.188	57374	8.6949
		659862	100.0000

8. Isolation of *N*-acetylated DMAP chloride (**IIa**)

To a solution of DMAP (0.2 g) in toluene (20 mL) was added Ac₂O (0.2 g). To the colorless transparent solution was then added TBAC in toluene, and a turbid suspension was formed immediately. The solid was filtered carefully, dried under vacuum and determined by ¹H NMR (Figure S4) to be *N*-acetylated DMAP chloride accompanied with DMAP·HCl (formed by hydrolysis of *N*-acetylated DMAP chloride). To confirm this structure, the solid was mixed with phenol in toluene, and corresponding ester was detected by TLC.

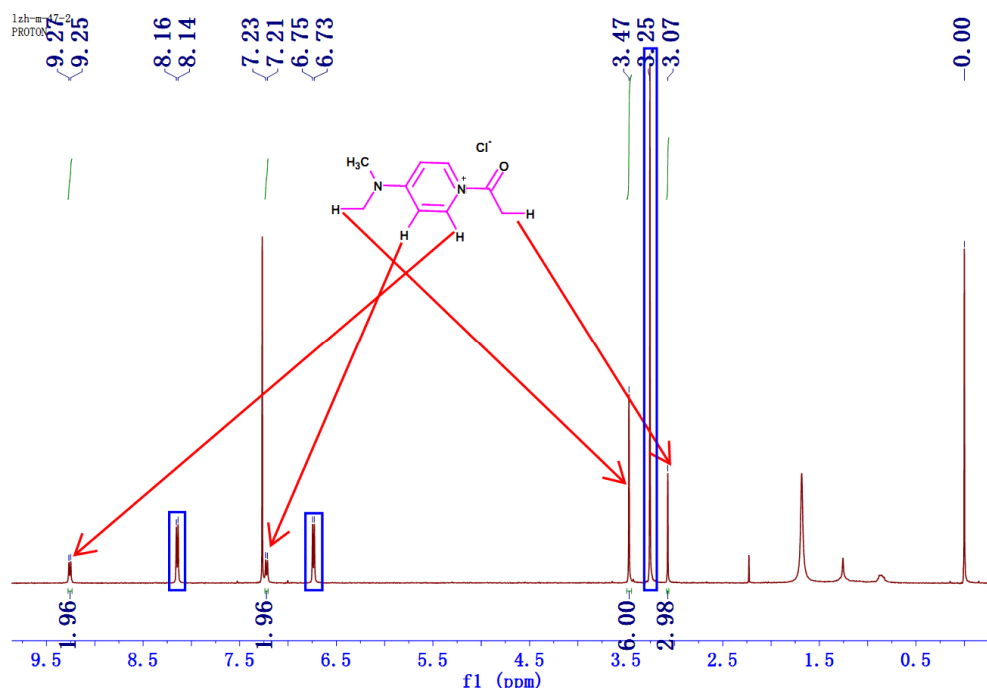
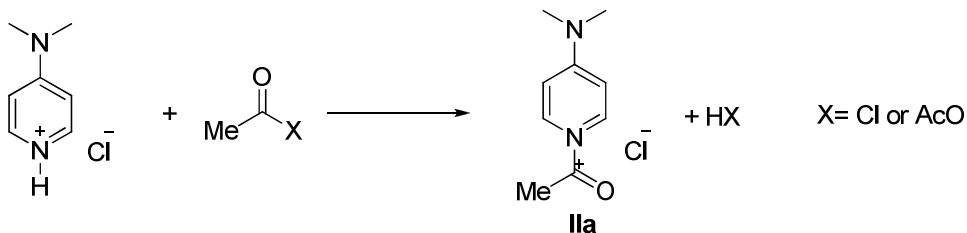


Figure S3. The new intermediate formed after TBAC was added. The signals lined out in blue rectangles belong to DMAP·HCl.

9. Reaction details of table 5.



entry	DMAP analogue	acylating reagent	solvent	T (°C)	phenomenon
1	DMAP	AcCl	CDCl ₃	rt	Intermediate IIa was formed immediately.
2	DMAP·HCl	AcCl	CDCl ₃	rt	No reaction happened even after several days.
3	DMAP·HCl+ 10 equiv HCl	Ac ₂ O	CHCl ₃	rt	Intermediate IIa was isolated after 24 h.
4	DMAP·HCl	AcCl	PhMe	110	Intermediate IIa was isolated within 30 min.

Entry 1: 5 mg DMAP and 5 mg AcCl was dissolved in 0.5 mL CDCl₃, and the mixture was tested by ¹H NMR. The spectrum is shown in Figure S4.

Entry 2: 5 mg DMAP and 10 mg AcCl was dissolved in 0.5 mL CDCl₃, and the mixture was tested by ¹H NMR, The spectrum is shown in Figure S5.

Entry 3: 50 mg DMAP·HCl was dissolved in 0.5 mL CHCl₃, 20mg HCl was blown into this solution, and then 50 mg Ac₂O was added. The mixture was kept 24h at room temperature. And then 5 mL hexane was added, the white solid was filtrated, dried in vacuum and tested by ¹H NMR. The spectrum is shown in Figure S6.

Entry 4: Acetylchloride was added to the DMAP·HCl solution in toluene, and the mixture was heated to reflux for half an hour. Itermediate **IIa** was isolated (with a little DMAP·HCl) and tested by ¹H NMR. The spectrum is shown in Figure S7.

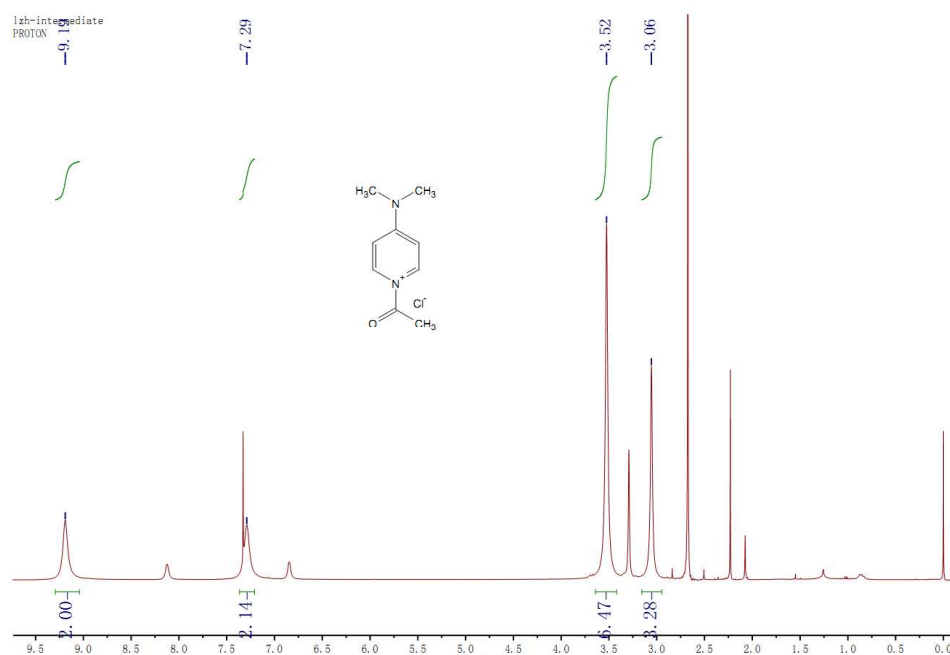


Figure S4. ¹H NMR of intermediate **IIa**.

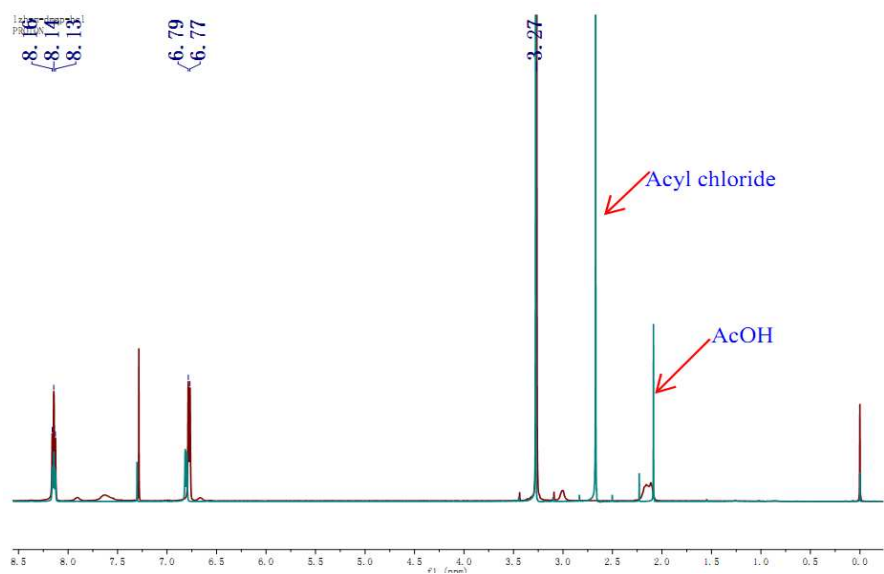


Figure S5. No reaction occurred while mixing acetylchloride and DMAP·HCl. Red line, signals of DMAP·HCl. Blue line, signals of the mixture of DMAP·HCl and acetylchloride.

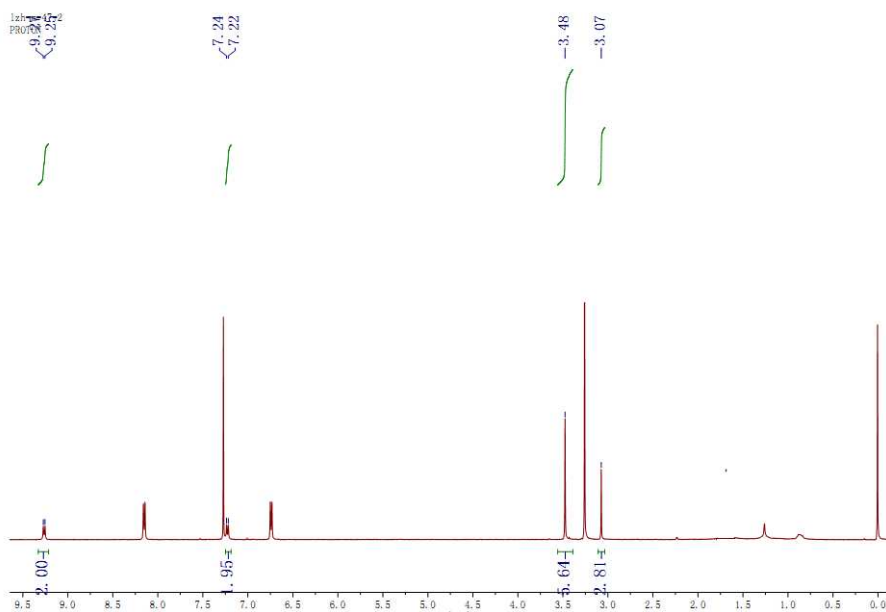
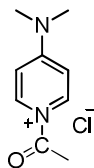


Figure S6. Intermediate **IIa** formed from DMAP·HCl and Ac₂O at room temperature.



¹H NMR (400 MHz, CDCl₃) δ 9.18 (d, *J* = 4.4 Hz, 2H), 7.32 (d, *J* = 6.8 Hz, 2H), 3.53 (s, 6H), 3.05 (s, 3H).

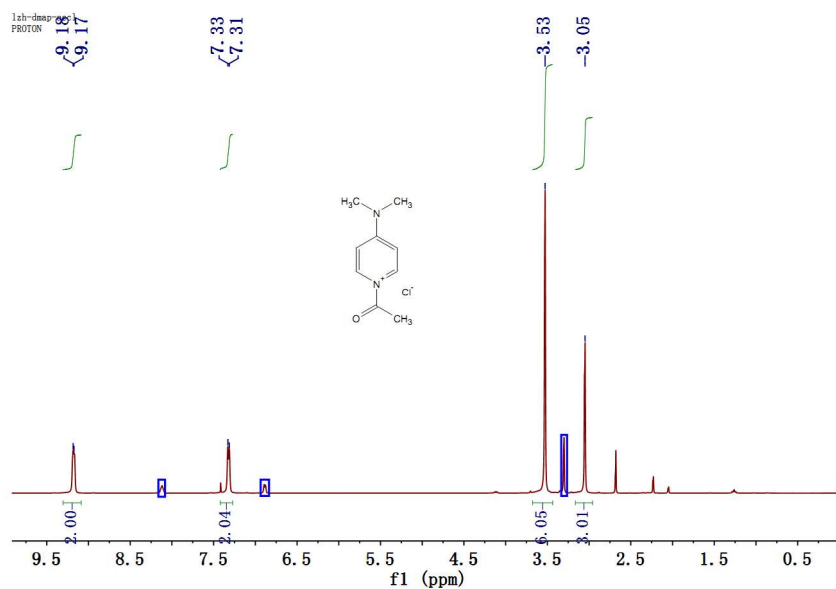


Figure S7. Intermediate **IIa** formed from DMAP·HCl and AcCl in refluxing toluene. The signal sectioned out in blue rectangles belong to DMAP·HCl (formed by hydroxylation of intermediate **IIa**).

10. NMR spectra of products in Tables 1, 2, 3 and 4 (Tables s1, s2 and s3).

