

# Novel DABCO based ionic liquids: green and efficient catalysts with dual catalytic roles for aqueous Knoevenagel condensation

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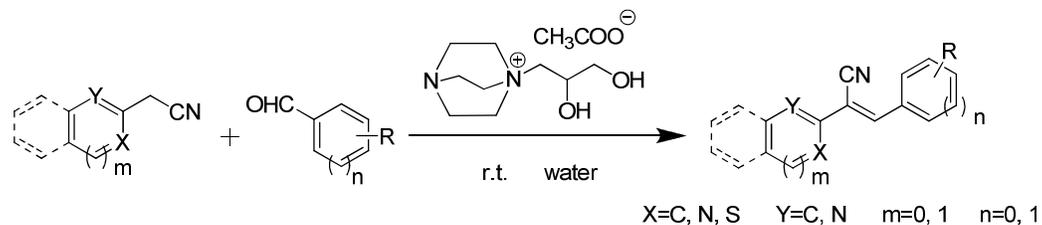
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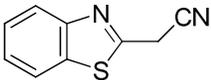
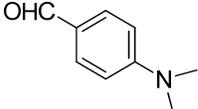
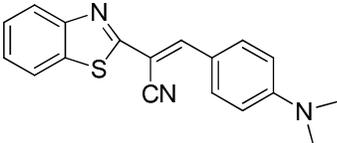
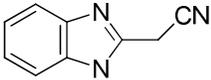
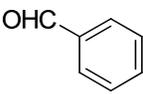
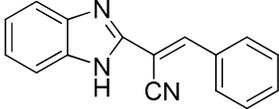
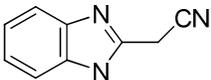
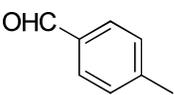
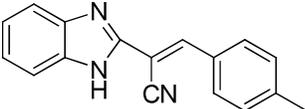
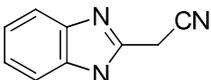
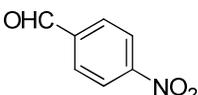
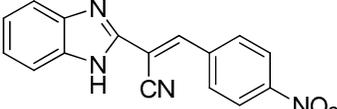
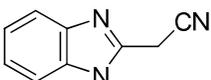
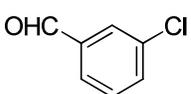
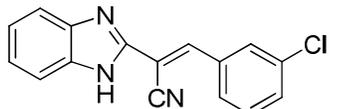
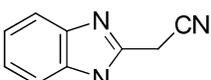
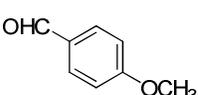
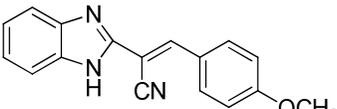
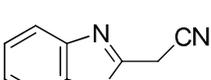
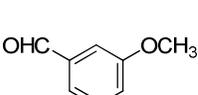
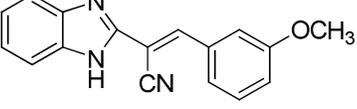
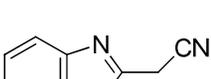
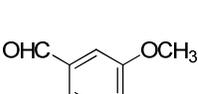
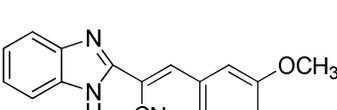
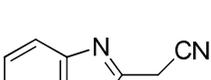
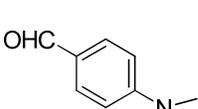
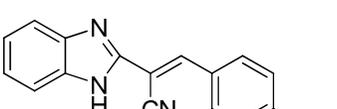
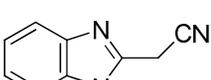
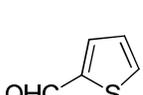
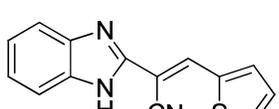
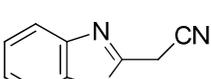
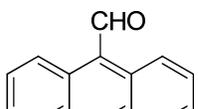
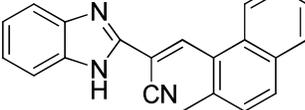
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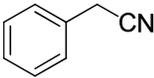
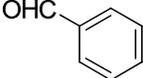
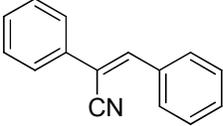
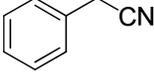
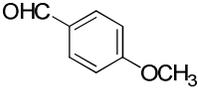
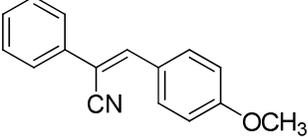
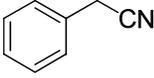
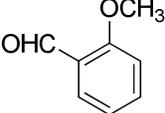
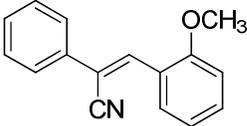
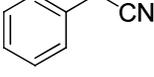
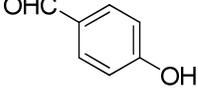
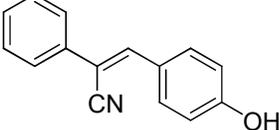
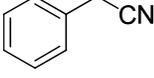
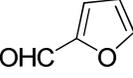
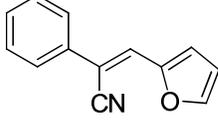
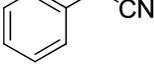
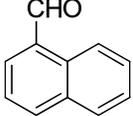
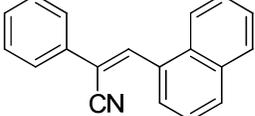
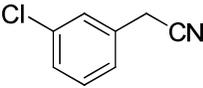
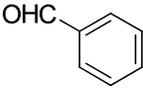
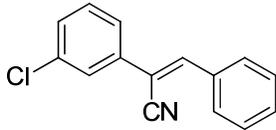
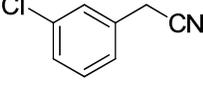
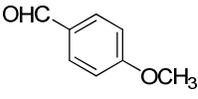
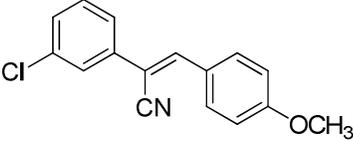
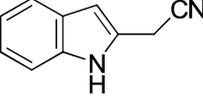
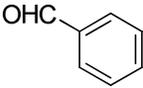
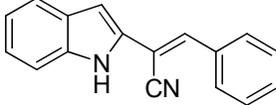
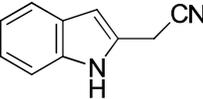
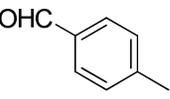
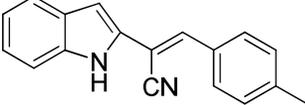
E-mail address: [slxu@tju.edu.cn](mailto:slxu@tju.edu.cn) (S. Xu)

**1. Table S1.** Knoevenagel condensation reactions of aromatic/ heteroaromatic aldehydes and  $\alpha$ -aromatic (heteroaromatic or polyaromatic)-substituted methylene compounds catalyzed by [DABCO-PDO][OAc]<sup>[a]</sup>



Entry	Methylene compound	Aldehyde	Time	Product	Yield (%) <sup>[b]</sup>
1			10min		92
2			1min		95
3			3min		91
4			3min		90
5			5min		93
6			5min		92
7			10min		91
8			3min		91

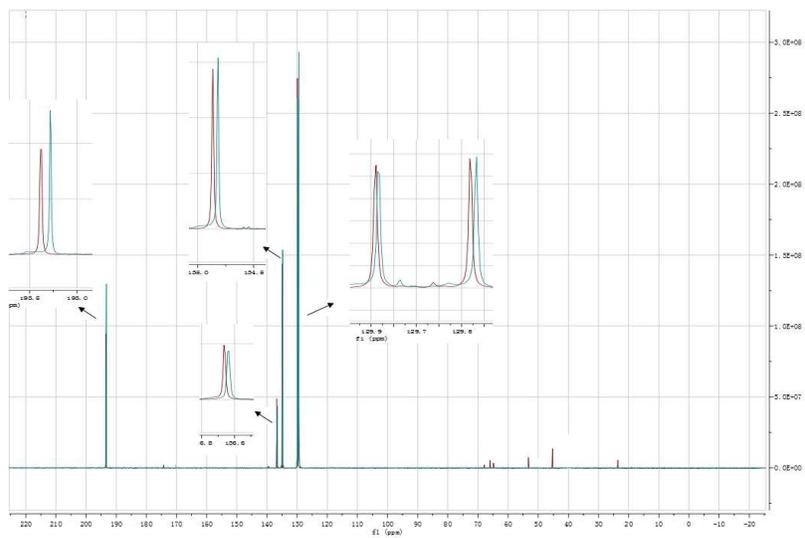
9			10min		86
10			5min		90
11			10min		92
12			1min		95
13			3min		92
14			3min		93
15			5min		91
16			10min		90
17			10min		87
18			10min		86
19			10min		92

20			30min		93
21			40min		93
22			30min		92
23			60min		84
24			30min		91
25			40min		94
26			40min		88
27			40min		91
28			60min		94
29			60min		91

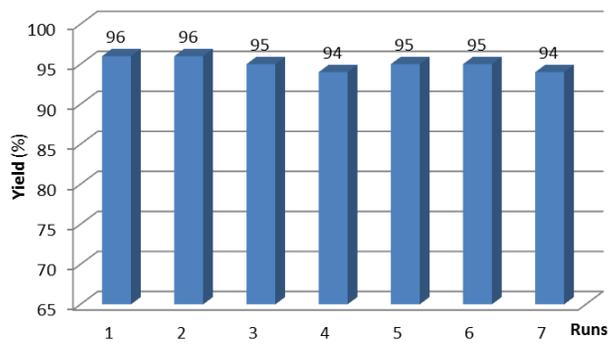
[a] Reaction conditions: aromatic/ heteroaromatic aldehydes (1.0mmol),  $\alpha$ -aromatic (heteroaromatic or polyaromatic)-substituted methylene compounds (1.0mmol), catalyst (15 mol %), water (2ml), room temperature.

[b] Isolated yield based on aldehydes.

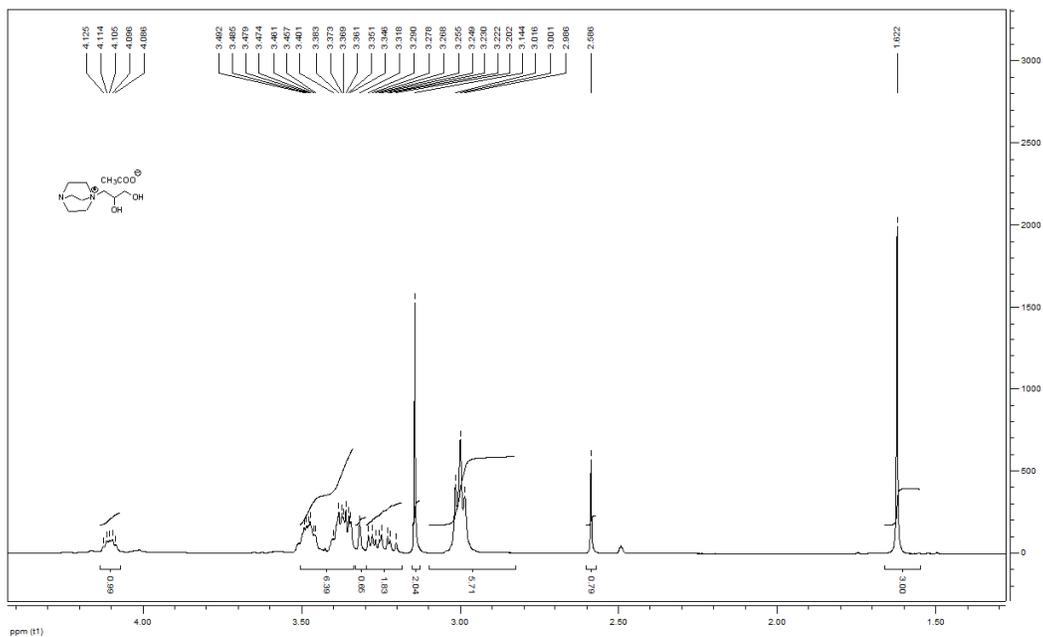
2. **Fig. S1**  $^{13}\text{C}$  NMR spectrum overlay of benzaldehyde and benzaldehyde-[DABCO-PDO][OAc] mixture



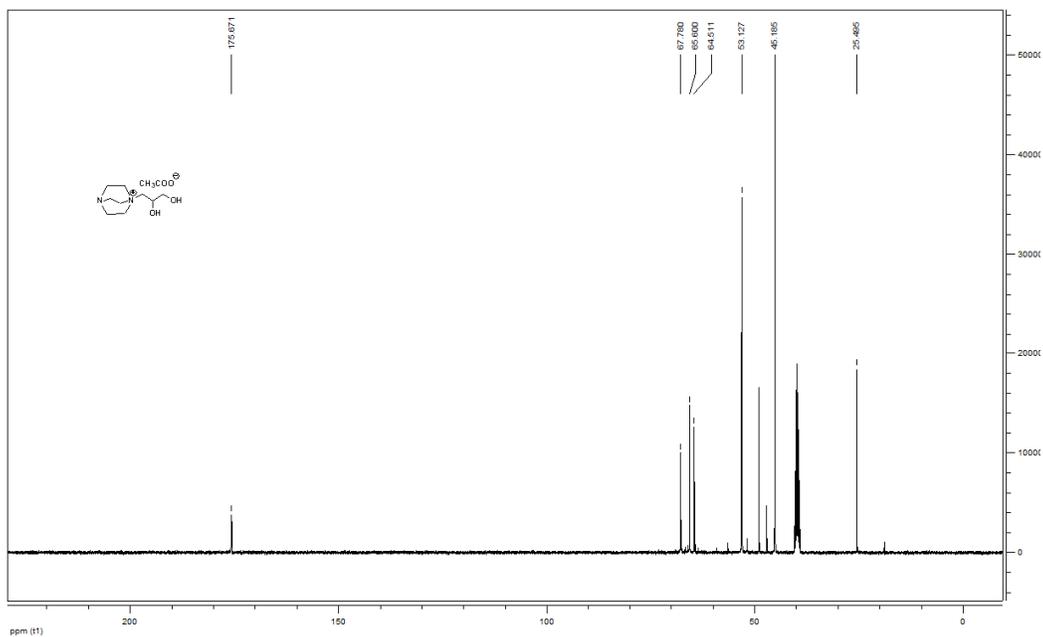
3. **Fig. S2** Reusability of IL [DABCO-PDO][OAc]



4. Spectra data and copies of  $^1\text{H}$  and  $^{13}\text{C}$  NMR of the novel ionic liquids  
[DABCO-PDO][OAc]

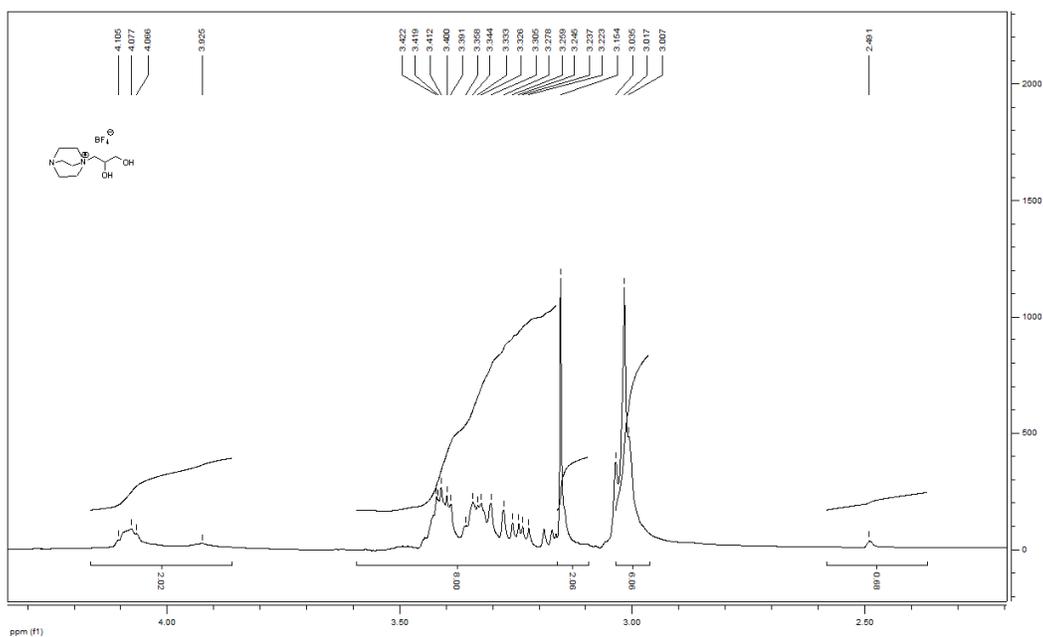


$^1\text{H}$  NMR (400 MHz, DMSO):  $\delta$  1.62(s, 3H), 2.59(s, 1H), 3.0(t, 6H,  $J=6\text{Hz}$ ), 3.14(s, 2H), 3.20-3.29(m, 2H), 3.32(s, 1H), 3.35-3.49(m, 6H)

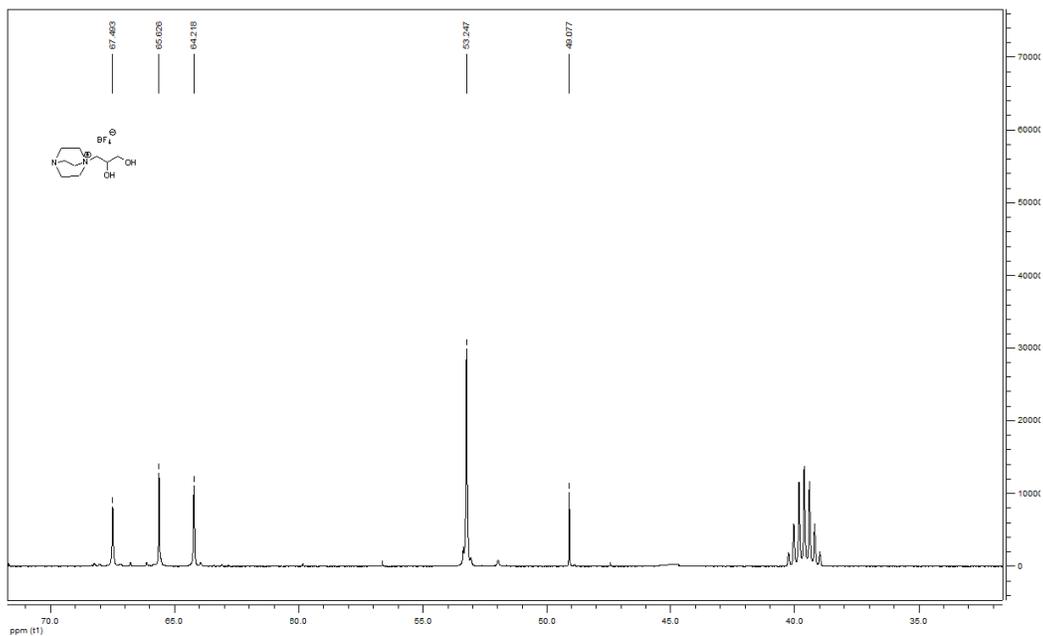


$^{13}\text{C}$  NMR (100 MHz, DMSO):  $\delta$  25.5, 45.2, 53.1, 64.5, 65.6, 67.8, 175.7

[DABCO-PDO][BF<sub>4</sub>]

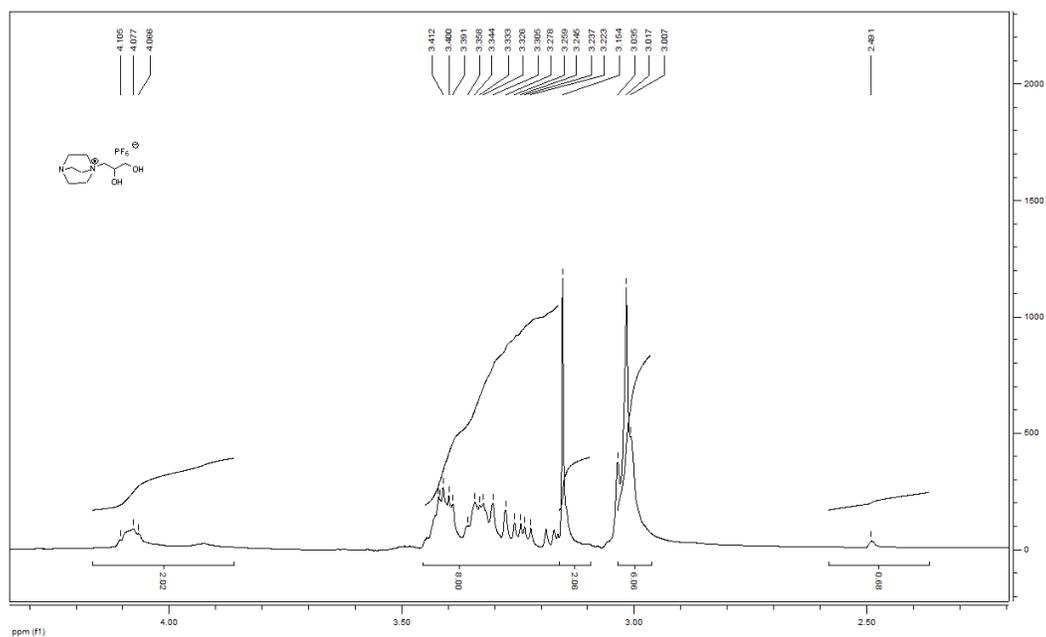


<sup>1</sup>H NMR (400 MHz, DMSO):  $\delta$  2.49(s, 1H), 3.01(m, 6H), 3.15(s, 2H), 3.22-3.42(m, 8H), 3.92-4.11(m, 2H)

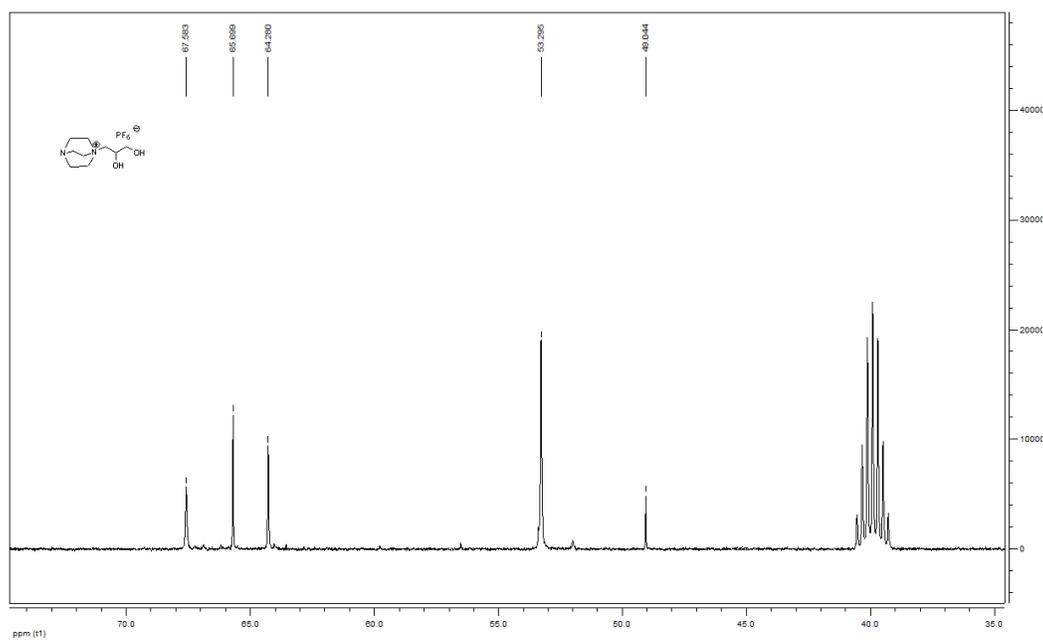


<sup>13</sup>C NMR (100 MHz, DMSO):  $\delta$  49.1, 53.2, 64.2, 65.6, 67.5

[DABCO-PDO][PF<sub>6</sub>]

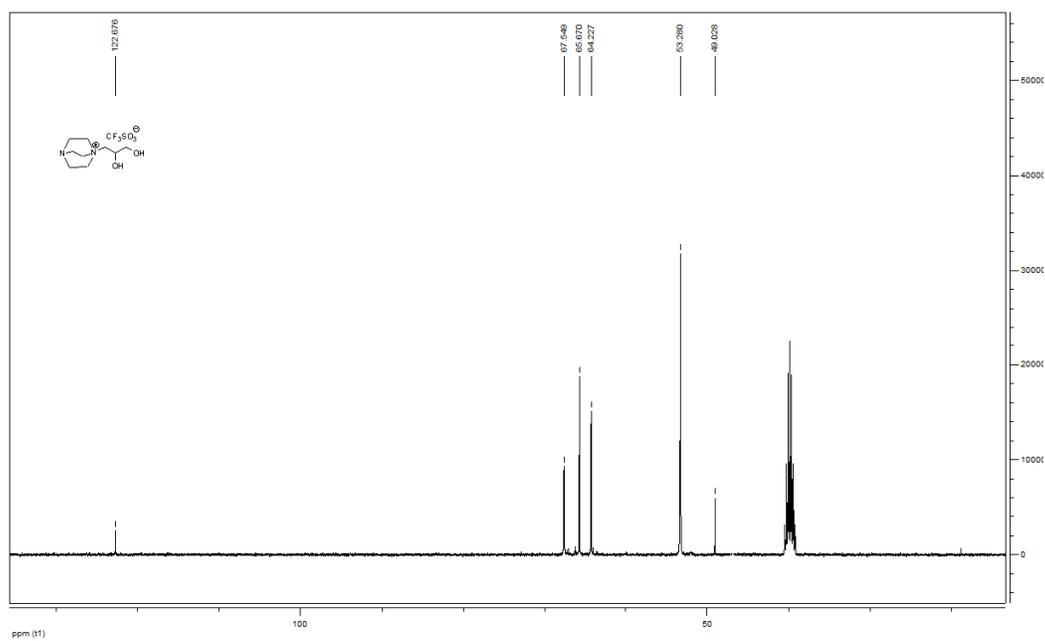
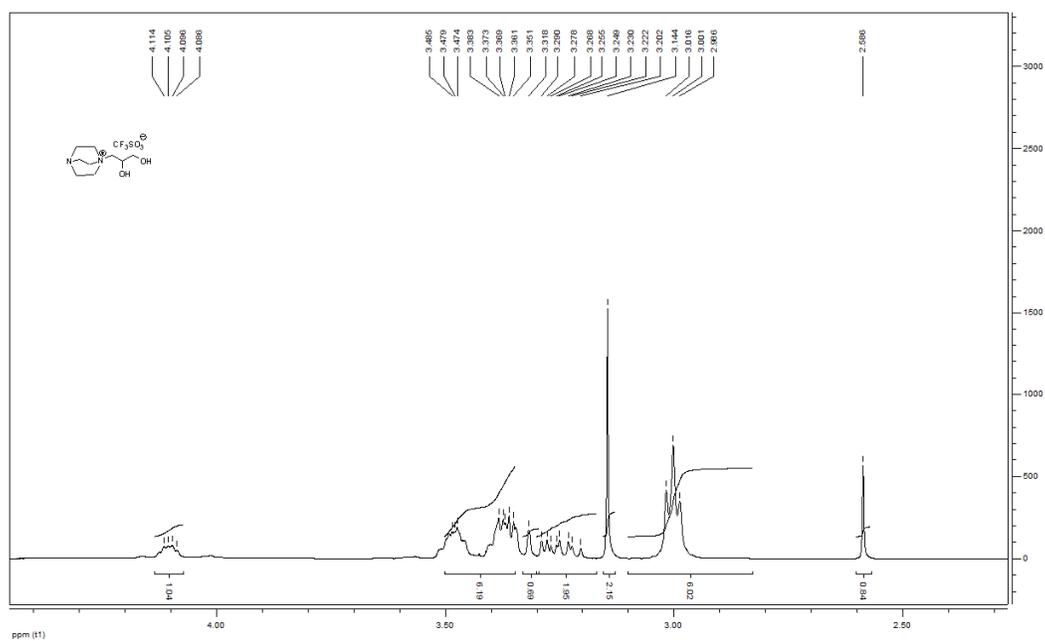


<sup>1</sup>H NMR (400 MHz, DMSO): δ 2.49(s, 1H), 3.01-3.04(m, 6H), 3.15(s, 2H), 3.22-3.41(m, 8H), 4.01-4.11(m, 2H)



<sup>13</sup>C NMR (100 MHz, DMSO): δ 49.0, 53.3, 64.3, 65., 67.6

[DABCO-PDO][CH<sub>3</sub>SO<sub>3</sub>]



5. Spectra data for the representative condensation products:

**2-(benzothiazol-2-yl)-3-phenylacrylonitrile (model reaction)**

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.45(m, 1H), 7.52-7.54(m, 4H), 7.91(d, 1H, *J*=6.4Hz), 8.03(m, 2H), 8.09(d, 1H, *J*=6.4Hz), 8.26(s, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 105.8, 116.7, 121.9, 123.8, 126.2, 127.2, 129.5, 130.6, 132.5, 135.2, 147.1, 153.8, 163.0

**2-(benzothiazol-2-yl)-3-(4-methoxyphenyl)acrylonitrile (Table S1, Entry 5)**

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 3.90 (s, 3H), 7.01 (d, 2H, *J*=6.4 Hz), 7.40-7.53 (m, 2H), 7.89 (d, 1H, *J*=6.4 Hz), 8.02-8.07 (m, 3H), 8.18 (s, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 55.8, 102.5, 115.0, 117.3, 121.8, 123.6, 125.4, 125.9, 127.0, 133.0, 135.0, 146.7, 153.8, 163.1, 163.6

**2-(benzothiazol-2-yl)-3-(4-(dimethylamino)phenyl)acrylonitrile (Table S1, Entry 9)**

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 3.13(s, 6H), 6.74(d, 2H, *J*=8.8Hz), 7.38-7.41(m, 1H), 7.49-7.53(m, 1H), 7.88(d, 1H, *J*=7.6Hz), 7.99-8.05(m, 3H), 8.12(s, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 40.0, 97.7, 111.7, 118.2, 120.2, 121.5, 122.9, 125.1, 126.6, 133.1, 134.6, 147.0, 152.9, 153.8, 164.7

**2-(1H-benzoimidazol-2-yl)-3-phenylacrylonitrile (Table S1, Entry 10)**

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.31-7.34(m, 2H), 7.50-7.52(m, 3H), 7.65(s, 2H), 7.98-7.80(m, 2H), 8.51(s, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 111.2, 116.8, 119.7, 123.6, 124.2, 129.3, 130.0, 132.1, 132.7, 146.3, 146.8

**2-(1H-benzoimidazol-2-yl)-3-(3-methoxyphenyl)acrylonitrile (Table S1, Entry 15)**

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 3.89(s, 3H), 7.07-7.09(m, 1H), 7.33-7.44(m, 3H), 7.55-7.59(m, 2H), 7.66(s, 2H), 8.53(s, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 55.5, 105.8, 114.1, 116.5, 119.0, 121.7, 123.4, 123.7, 126.0, 127.0, 130.2, 133.6, 135.0, 146.9, 153.6, 160.0, 162.7

**2-(1H-benzoimidazol-2-yl)-3-(thiophen-2-yl)acrylonitrile (Table S1, Entry 18)**

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.15-7.22(m, 1H), 7.30-7.37(m, 2H), 7.50-7.52(m, 1H), 7.66-7.70(m, 2H), 7.76-7.77(m, 1H), 7.87-7.89(m, 1H), 8.63(s, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 98.1, 115.6, 115.7, 116.7, 123.6, 129.1, 134.5, 136.8, 137.0, 139.3, 147.6

**2-(4-chlorophenyl)-3-phenylacrylonitrile (Table S1, Entry 26)**

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.40(m, 2H), 7.48-7.50(m, 3H), 7.55-7.59(m, 2H), 7.67(s, 1H), 7.90-7.91(m, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 110.5, 117.8, 124.5, 126.2, 129.3, 129.5, 129.7, 130.5, 131.2, 133.5, 135.4, 136.5, 143.6

**2-(1H-indol-2-yl)-3-phenylacrylonitrile (Table S1, Entry 28)**

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.28-7.33 (m, 2H), 7.41-7.49 (m, 4H), 7.60-7.63 (m, 2H), 7.88 (d, 2H,  $J=5.6$  Hz), 8.00 (d, 1H,  $J=6.0$ Hz), 8.58 (s, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  106.5, 112.4, 113.1, 118.9, 120.0, 121.5, 123.6, 124.4, 125.8, 128.9, 129.1, 129.8, 134.9, 137.3, 138.2

**2-(1*H*-indol-2-yl)-3-*p*-tolylacrylonitrile (Table S1, Entry 29)**

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  2.42(s, 3H), 7.26-7.33(m, 4H), 7.45(d, 1H,  $J=6.4$ Hz), 7.57-7.60(m, 2H), 7.79(d, 2H,  $J=6.4$ Hz), 8.00(d, 1H,  $J=6.0$ Hz), 8.46(s, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  21.8, 105.3, 112.3, 113.3, 119.1, 120.0, 121.4, 123.5, 124.4, 125.4, 128.9, 129.8, 132.1, 137.2, 138.5, 140.2

