# DBU catalyzed cyanoacylation of ketones with acyl cyanides

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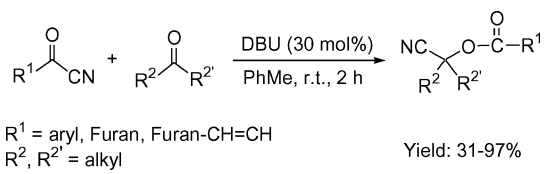
***Received 14th February 2006, Accepted 2nd March 2006***
***First published as an Advance Article on the web 29th March 2006***
**DOI: 10.1039/b602197b**

The reaction of cyclohexanone with benzoyl cyanide catalyzed by amines provides the corresponding *O*-benzoyl cyanohydrin adducts in moderate to good yields under mild conditions. Among the catalysts, DBU was found to be the most effective promoter allowing the reaction to proceed smoothly at room temperature and to give the corresponding *O*-acyl cyanohydrin adducts in higher yields for a variety of substituted cyclohexanones, cyclopentanone, acetone or pentan-3-one and various acyl cyanides.

Quaternary stereocenters are useful structures in pharmaceutical, medicinal and natural products.[1] Cyanohydrins are of synthetic interest as they can be transformed into a number of relevant functional groups such as β-amino alcohols, α-hydroxyacids and α-hydroxyesters, α-sulfonyloxynitriles, α-aminonitriles, α-fluoronitriles, 3-amino-2-alkenoates and substituted azacycloalkenes.[2] The synthesis of cyanohydrins and their *O*-protected derivatives can be accomplished by enzymes,[3] organocatalysts[1,4] and metal complexes.[5–8] Among various cyanide ion sources, trimethylsilyl cyanide is a safer and more easily handled reagent compared to hydrogen cyanide, and various cyanosilylations of aldehydes catalyzed by Lewis acids have already been developed.[9] On the other hand, acyl cyanides are also safer and commercially available reagents.[10] It has already been reported that base catalysts such as potassium carbonate[11] and 1,4-diazabicyclo[2.2.2]octane (DABCO)[12] are required to promote the cyanoacylation of aldehydes. Recently, the direct preparation of cyanohydrin esters by the reaction of aldehydes with acyl cyanides in DMSO using no catalyst has also been reported.[13] Although these reactions are very efficient methods for synthesizing cyanohydrin derivatives of aldehydes, only one example of a $Et_3N$ catalyzed reaction of 4-*tert*-butylcyclohexanone with cyanides has been reported.[14] Herein, we report the cyanoacylation of ketones catalyzed by 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) to give the corresponding cyanohydrin esters in moderate to high yields at room temperature in toluene within 2 h (Scheme 1).

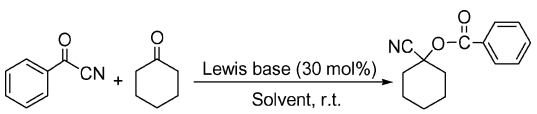



**Scheme 1** Cyanoacylation of ketones with acyl cyanides.

Optimization of the reaction conditions was performed with benzoyl cyanide **1a** and cyclohexenone **2a**. Initially, we examined the effect of the various amino base catalysts such as DBU, DMAP, DABCO, $^{i}Pr_2NEt$, $Et_3N$, pyridine and DBN (30 mol%) in this reaction. The best yield of **3a** was 63% by using DBU as a catalyst in DMF or using DBN as a catalyst in THF at room temperature within 4 h (Table 1, entries 1 to 8). In our next investigation, we examined various solvents such as toluene, THF, DMSO, MeOH, MeCN, and $CH_2Cl_2$ with DBU as a Lewis base catalyst. We found that **3a** was obtained in 96% yield in toluene in the presence of DBU (30 mol%) within 2 h (Table 1, entries 1, and 9 to 14). These are the best reaction conditions for the preparation of **3a**.

Under these optimized conditions, various substituted acyl cyanides were examined in this reaction. The results are summarized in Table 2. In most cases, cyanoacylation proceeded smoothly to give the corresponding **3** in moderate to excellent yields. Electron-donating substituents on the benzene ring of **1** produced the corresponding **3** in higher yields at room temperature under identical conditions (Table 2, entries 2 to 4). Electron-withdrawing substituents such as the nitro group on the benzene

**Table 1** Cyanobenzoylation of cyclohexanone with benzoyl cyanide in the presence of various solvents and bases[a,b]




1a 2a 3a

| Entry | Lewis base | Solvent | Time/h | **3a**[c] (%) |
|---|---|---|---|---|
| 1 | DBU | DMF | 4 | 63 |
| 2 | DMAP | DMF | 9 | 25 |
| 3 | DABCO | DMF | 9 | 30 |
| 4 | $^{i}Pr_2NEt$ | DMF | 9 | 31 |
| 5 | $Et_3N$ | PhMe | 19 | 51 |
| 6 | Pyridine | DMF | 24 | NR[d] |
| 7 | DBN | PhMe | 2 | 50 |
| 8 | DBN | THF | 2 | 63 |
| 9 | DBU | DMSO | 4 | 30 |
| 10 | DBU | MeOH | 24 | NR[d] |
| 11 | DBU | MeCN | 4 | 94 |
| 12 | DBU | THF | 4 | 96 |
| 13 | DBU | $CH_2Cl_2$ | 2 | 90 |
| 14 | DBU | PhMe | 2 | 96 |

[a] All reactions were carried out using benzoyl cyanide **1a** (0.5 mmol), cyclohexanone **2a** (1.0 mmol), and Lewis base (0.15 mmol) in solvent (0.5 mL, 1.0 M) at room temperature. [b] DBU: 1,8-diazabicyclo[5.4.0]undec-7-ene, DMAP: 4-dimethylaminopyridine, DABCO: 1,4-diazabicyclo[2.2.2]octane, DBN: 1,5-diazabicyclo[4.3.0]-5-nonene, DMF: *N*,*N*-dimethyl formamide, DMSO: dimethyl sulfone, THF: tetrahydrofuran. [c] Isolated yields. [d] No reaction took place.

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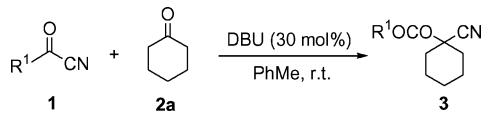
**Table 2** Cyanoacylation of cyclohexanone with acyl cyanides[a]




1 2a 3

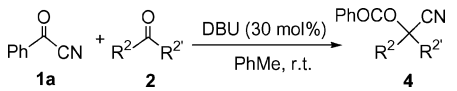
| Entry | $R^1$(**1**) | Time/h | **3** (%)[b] |
|---|---|---|---|
| 1 | $C_6H_5$ (**1a**) | 2 | **3a**, 96 |
| 2 | 4-$ClC_6H_4$ (**1b**) | 2 | **3b**, 70 |
| 3 | 3,5-$Me_2C_6H_3$ (**1c**) | 2 | **3c**, 89 |
| 4 | 3,4,5-$(MeO)_3C_6H_2$ (**1d**) | 2 | **3d**, 97 |
| 5 | 4-$NO_2C_6H_4$ (**1e**) | 2 | **3e**, 31 |
| 6 | 2-$BrC_6H_4$ (**1f**) | 2 | **3f**, 52 |
| 7 | Furan (**1g**) | 2 | **3g**, 89 |
| 8 | Furan–CH=CH (**1h**) | 2 | **3h**, 51 |

[a] All reactions were carried out using acyl cyanides (0.5 mmol), cyclohexanone (1.0 mmol), DBU (0.15 mmol) in PhMe (0.5 mL) at room temperature for 2 h. [b] Isolated yields.

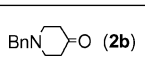
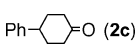
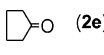
ring of **1e** retarded the reaction to give the corresponding **3e** in a lower yield (31%) under identical conditions (Table 2, entry 5). For *ortho*-substituted acyl cyanide (**1f**), the corresponding **3f** was obtained in a lower yield (52%) as well, presumably due to the steric effect (Table 2, entry 6). The reaction of furan-2-carbonyl cyanide (**1g**) with **2a** produced the corresponding **3g** in 89% yield under the standard conditions (Table 2, entry 7). Alkyl substrates such as 3-furan-2-ylacryloyl cyanide (**1h**) also reacted smoothly with **2a** to give the corresponding **3h** in 51% yield under identical conditions (Table 2, entry 8).

Next, in order to compare the reactivity of ketones in this reaction, we attempted the reaction of benzoyl cyanide with various ketones under the standard conditions. The results are summarized in Table 3. 1-Benzyl-4-piperidone (**2b**) reacted smoothly with benzoyl cyanide **1a** to give the corresponding product **4a** in 84% yield (Table 3, entry 1). By using substituted

**Table 3** Cyanobenzoylation of ketones with benzoyl cyanide[a]



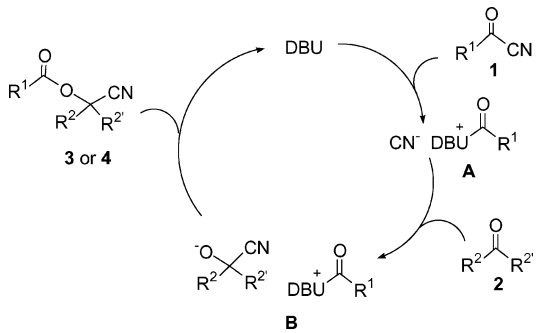

1a 2 4

| Entry | Ketone (**2**) | Time/h | **4** (%)[b] |
|---|---|---|---|
| 1 |  (**2b**) | 2 | **4a**, 84 |
| 2 |  (**2c**) | 2 | **4b**, 92 |
| 3 |  (**2d**) | 2 | **4c**, 92 |
| 4 |  (**2e**) | 2 | **4d**, 57 |
| 5 |  (**2f**) | 2 | **4e**, 68 |
| 6 |  (**2g**) | 2 | **4f**, 44 |

[a] All reactions were carried out using benzoyl cyanide (0.5 mmol), ketone (1.0 mmol), DBU (0.15 mmol) in PhMe (0.5 mL) at room temperature for 2 h. [b] Isolated yields.

cyclohexanones **2c** and **2d**, the corresponding products **4b** and **4c** were formed in high yields under the standard conditions (Table 3, entries 2 and 3). Additionally, cyclopentanone **2e**, acetone **2f** and pentan-3-one **2g** were also examined in this reaction to give the corresponding products **4d–4f** in moderate yields, respectively (Table 3, entries 4 to 6).

A plausible mechanism, similar to that proposed by Deng and Tian[4] for the asymmetric cyanation of ethyl cyanoformate to ketones, is shown in Scheme 2. We suppose that benzoyl cyanide is activated by a nucleophilic attack by DBU to form the corresponding intermediate **A**, which reacts with the ketone to give the cyanoalkoxide intermediate **B**. Then, intramolecular nucleophilic attack of the cyanoalkoxide on the carbonyl group in intermediate **B** produces the final *O*-acyl cyanohydrin ester **3** or **4** and regenerates the DBU catalyst.




**Scheme 2** Proposed DBU catalyzed cyanoacylation of ketones with acyl cyanides.

As a conclusion, in this paper, we disclosed an efficient catalytic system for the cyanoacylation of ketones with acyl cyanides catalyzed by the organocatalyst DBU. These reactions take place smoothly at room temperature in toluene to give the corresponding *O*-acyl cyanohydrin esters **3** or **4** in moderate to high yields within 2 h. Efforts are under way to elucidate the catalytic asymmetric version of this reaction.

## Experimental

### General remarks

MPs were obtained with a Yanagimoto micro melting point apparatus and are uncorrected. $^1$H NMR and $^{13}$C NMR spectra were recorded for a solution in $CDCl_3$ with tetramethylsilane (TMS) as an internal standard. *J* values are in Hz. Mass spectra were recorded with a HP-5989 instrument and HRMS was measured on a Finnigan $MA^+$ mass spectrometer. The solid compounds reported in this paper gave satisfactory CHN microanalyses with a Carlo-Erba 1106 analyzer. Commercially obtained reagents were used without further purification. All reactions were monitored by TLC with Huanghai $GF_{254}$ silica gel coated plates. Flash column chromatography was carried out using 200–300 mesh silica gel at increased pressure. Reaction experiments were performed under ambient atmosphere. The starting materials **1b–1h**[15] were synthesized according to the previous literature.

**General reaction procedure**

A mixture of benzoyl cyanide (65.5 mg, 0.5 mmol), cyclohexanone (104 μL, 1.0 mmol), base (0.15 mmol) and solvent (0.5 mL) was stirred under ambient atmosphere at room temperature for the required time indicated in the Tables 1–3. After the reaction the solution was concentrated under reduced pressure and the residue was purified by flash chromatography on silica gel (eluent: EtOAc–petroleum ether = 1 : 20) to afford the pure products **3** or **4**.

**Benzoic acid 1-cyanocyclohexyl ester (3a) (a known compound)[16].** A white solid: 110 mg, 96% yield. $^1$H NMR ($CDCl_3$, 300 MHz, TMS): $\delta$ 1.40–1.83 (m, 6H, $3CH_2$), 2.01–2.10 (m, 2H, $CH_2$), 2.35–2.43 (m, 2H, $CH_2$), 7.50 (dd, $J$ = 7.2, 8.4 Hz, 2H, Ar), 7.60 (t, $J$ = 7.5 Hz, 1H, Ar), 8.03 (d, $J$ = 8.1 Hz, 2H, Ar). $^{13}$C NMR ($CDCl_3$, 75 MHz): $\delta$ 21.8, 24.3, 34.9, 72.7, 118.5, 128.4, 129.0, 129.5, 133.5, 164.0. MS (EI) $m/e$: 230 ($M^+$ + 1, 6.13), 105 (100), 77 (31.39), 51 (18.85). Anal. calcd for $C_{14}H_{15}NO_2$: C, 73.34%; H, 6.59%; N, 6.11%; found: C, 73.57%; H, 6.59%; N, 5.95%.

**4-Chlorobenzoic acid 1-cyanocyclohexyl ester (3b).** A white solid: 92 mg, 70% yield. Mp: 78–80 °C. IR ($CH_2Cl_2$) $\nu$ 2942, 2864, 1730, 1594, 1402, 1274, 1253 cm$^{-1}$. $^1$H NMR ($CDCl_3$, 300 MHz, TMS): $\delta$ 1.37–1.83 (m, 6H, $3CH_2$), 1.99–2.08 (m, 2H, $CH_2$), 2.38–2.42 (m, 2H, $CH_2$), 7.44 (d, $J$ = 8.7 Hz, 2H, Ar), 7.96 (d, $J$ = 8.7 Hz, 2H, Ar). $^{13}$C NMR ($CDCl_3$, 75 MHz): $\delta$ 21.9, 24.4, 35.0, 73.1, 118.3, 127.5, 128.8, 131.0, 140.1, 163.3. MS (EI) $m/e$: 263 ($M^+$, 0.24), 156 (57.65), 139 (100), 107 (49.76). Anal. calcd for $C_{14}H_{14}ClNO_2$: C, 63.76%; H, 5.35%; N, 5.31%; found: C, 63.90%; H, 5.34%; N, 5.17%.

**3,5-Dimethylbenzoic acid 1-cyanocyclohexyl ester (3c).** A white solid: 114 mg, 89% yield. Mp: 83–85 °C. IR ($CH_2Cl_2$) $\nu$ 2941, 1728, 1312, 1112 cm$^{-1}$. $^1$H NMR ($CDCl_3$, 300 MHz, TMS): $\delta$ 1.40–1.83 (m, 6H, $3CH_2$), 2.00–2.09 (m, 2H, $CH_2$), 2.37–2.43 (m, 2H, $CH_2$), 2.39 (s, 6H, $2CH_3$), 7.23 (s, 1H, Ar), 7.63 (s, 2H, Ar). $^{13}$C NMR ($CDCl_3$, 75 MHz): $\delta$ 20.9, 21.8, 24.3, 34.9, 72.5, 118.5, 127.2, 128.8, 135.1, 138.0, 164.3. MS (EI) $m/e$: 257 ($M^+$, 5.00), 150 (66.05), 133 (100), 105 (44.90). Anal. calcd for $C_{16}H_{19}NO_2$: C, 74.68%; H, 7.44%; N, 5.44%; found: C, 74.47%; H, 7.29%; N, 5.20%.

**3,4,5-Trimethoxybenzoic acid 1-cyanocyclohexyl ester (3d).** A white solid: 154 mg, 97% yield. Mp: 82–84 °C. IR ($CH_2Cl_2$) $\nu$ 2941, 1725, 1416, 1336, 1218, 1128 cm$^{-1}$. $^1$H NMR ($CDCl_3$, 300 MHz, TMS): $\delta$ 1.40–1.83 (m, 6H, $3CH_2$), 2.00–2.09 (m, 2H, $CH_2$), 2.37–2.43 (m, 2H, $CH_2$), 3.91 (s, 6H, $2CH_3$), 3.92 (s, 3H, $CH_3$), 7.23 (s, 2H, Ar). $^{13}$C NMR ($CDCl_3$, 75 MHz): $\delta$ 21.8, 24.1, 34.8, 55.9, 60.5, 72.7, 106.6, 118.2, 123.7, 142.5, 152.6, 163.6. MS (EI) $m/e$: 319 ($M^+$, 64.34), 212 (100), 197 (70.93), 93 (20.07), 81 (17.66). Anal. calcd for $C_{17}H_{21}NO_5$: C, 63.94%; H, 6.63%; N, 4.39%; found: C, 63.76%; H, 6.52%; N, 4.16%.

**4-Nitrobenzoic acid 1-cyanocyclohexyl ester (3e).** A white solid: 42 mg, 31% yield. Mp: 104–106 °C. IR ($CH_2Cl_2$) $\nu$ 2946, 1730, 1527, 1350, 1290, 718 cm$^{-1}$. $^1$H NMR ($CDCl_3$, 300 MHz, TMS): $\delta$ 1.66–1.86 (m, 6H, $3CH_2$), 2.00–2.09 (m, 2H, $CH_2$), 2.41–2.48 (m, 2H, $CH_2$), 8.19 (d, $J$ = 8.7 Hz, 2H, Ar), 8.31 (d, $J$ = 9.3 Hz, 2H, Ar). $^{13}$C NMR ($CDCl_3$, 75 MHz): $\delta$ 22.1, 24.4, 35.0, 74.1, 118.0, 123.7, 130.9, 134.5, 150.8, 162.4. MS (EI) $m/e$: 275 ($M^+$ + 1, 1.07), 150 (71.63), 107 (100), 81 (39.75), 56 (51.53). Anal. calcd for $C_{14}H_{14}N_2O_4$: C, 61.31%; H, 5.14%; N, 10.21%; found: C, 61.40%; H, 5.12%; N, 10.16%.

**2-Bromobenzoic acid 1-cyanocyclohexyl ester (3f).** A colorless oil: 80 mg, 52% yield. IR ($CH_2Cl_2$) $\nu$ 2941, 2864, 1743, 1433, 1292, 1244, 1028 cm$^{-1}$. $^1$H NMR ($CDCl_3$, 300 MHz, TMS): $\delta$ 1.41–1.88 (m, 6H, $3CH_2$), 2.00–2.09 (m, 2H, $CH_2$), 2.41–2.45 (m, 2H, $CH_2$), 7.36–7.40 (m, 2H, Ar), 7.66–7.69 (m, 1H, Ar), 7.79–7.82 (m, 1H, Ar). $^{13}$C NMR ($CDCl_3$, 75 MHz): $\delta$ 22.0, 24.4, 35.0, 73.9, 118.2, 121.7, 127.2, 131.0, 131.5, 133.1, 134.4, 163.8. MS (EI) $m/e$: 308 ($M^+$, 1.38), 200 (56.77), 185 (100), 183 (78.29), 107 (48.23). HRMS (MALDI) for $C_{14}H_{14}NO_2BrNa^+$: 330.0104; found: 330.0100.

**Furan-3-carboxylic acid 1-cyanocyclohexyl ester (3g).** A white solid: 97 mg, 89% yield. Mp: 75–77 °C. IR ($CH_2Cl_2$) $\nu$ 2942, 2865, 1737, 1471, 1302, 1015 cm$^{-1}$. $^1$H NMR ($CDCl_3$, 300 MHz, TMS): $\delta$ 1.20–1.78 (m, 6H, $3CH_2$), 1.92–2.01 (m, 2H, $CH_2$), 2.29–2.37 (m, 2H, $CH_2$), 6.50 (dd, $J$ = 1.8, 3.6 Hz, 1H, Fu), 7.19 (d, $J$ = 3.6 Hz, 1H, Fu), 7.58 (d, $J$ = 2.4 Hz, 1H, Fu). $^{13}$C NMR ($CDCl_3$, 75 MHz): $\delta$ 21.8, 24.2, 35.0, 73.1, 112.0, 118.1, 119.1, 143.2, 147.0, 156.0. MS (EI) $m/e$: 219 ($M^+$, 0.54), 112 (66.92), 107 (100), 95 (65.98). Anal. calcd for $C_{12}H_{13}NO_3$: C, 65.74%; H, 5.98%; N, 6.39%; found: C, 65.93%; H, 6.23%; N, 6.16%.

**3-Furan-2-ylacrylic acid 1-cyanocyclohexyl ester (3h).** A white solid: 62 mg, 51% yield. Mp: 125–127 °C. IR ($CH_2Cl_2$) $\nu$ 2944, 1722, 1637, 1482, 1139 cm$^{-1}$. $^1$H NMR ($CDCl_3$, 300 MHz, TMS): $\delta$ 1.36–1.80 (m, 6H, $3CH_2$), 1.89–1.98 (m, 2H, $CH_2$), 2.31–2.36 (m, 2H, $CH_2$), 6.28 (d, $J$ = 15.6 Hz, 1H, CH), 6.49 (d, $J$ = 3.3 Hz, 1H, Fu), 6.66 (d, $J$ = 3.3 Hz, 1H, Fu), 7.46 (d, $J$ = 15.9 Hz, 1H, CH), 7.50 (s, 1H, Fu). $^{13}$C NMR ($CDCl_3$, 75 MHz): $\delta$ 21.9, 24.4, 35.0, 72.4, 112.4, 114.2, 115.8, 118.6, 132.4, 145.2, 150.4, 164.6. MS (EI) $m/e$: 245 ($M^+$, 15.84), 138 (62.67), 121 (100), 65 (48.86). Anal. calcd for $C_{14}H_{15}NO_3$: C, 68.56%; H, 6.16%; N, 5.71%; found: C, 68.54%; H, 6.10%; N, 5.52%.

**Benzoic acid 1-benzyl-4-cyanopiperidin-4-yl ester (4a).** A light yellow oil: 135 mg, 84% yield. IR ($CH_2Cl_2$) $\nu$ 2948, 2812, 2771, 1723, 1601, 1452, 1253, 1177 cm$^{-1}$. $^1$H NMR ($CDCl_3$, 300 MHz, TMS): $\delta$ 2.46 (t, $J$ = 5.7 Hz, 4H, $2CH_2$), 2.76 (t, $J$ = 6.0 Hz, 4H, $2CH_2$), 3.56 (s, 2H, $CH_2$), 7.27–7.36 (m, 5H, Ar), 7.48 (dd, $J$ = 7.8, 7.5 Hz, 2H, Ar), 7.62 (t, $J$ = 7.5 Hz, 1H, Ar), 8.02 (d, $J$ = 8.1 Hz, 2H, Ar). $^{13}$C NMR ($CDCl_3$, 75 MHz): $\delta$ 34.5, 41.0, 62.2, 70.9, 118.0, 127.1, 128.1, 128.4, 128.7, 128.8, 129.6, 133.6, 137.6, 164.0. MS (EI) $m/e$: 320 ($M^+$, 3.02), 198 (10.23), 107 (36.08), 91 (100), 77 (12.42). HRMS (MALDI) for $C_{20}H_{21}N_2O_2^+$: 321.1602; found: 321.1598.

**Benzoic acid 1-cyano-4-phenylcyclohexyl ester (4b).** A white solid: 141 mg, 92% yield. Mp: 146–148 °C. IR ($CH_2Cl_2$) $\nu$ 2949, 1728, 1451, 1278, 719 cm$^{-1}$. $^1$H NMR ($CDCl_3$, 300 MHz, TMS): $\delta$ 1.90–2.12 (m, 6H, $3CH_2$), 2.50–2.55 (m, 1H, CH), 2.80–2.84 (m, 2H, $CH_2$), 7.21–7.37 (m, 5H, Ar), 7.48 (dd, $J$ = 7.8, 8.1 Hz, 2H, Ar), 7.62 (t, $J$ = 7.8 Hz, 1H, Ar), 8.05 (d, $J$ = 8.4 Hz, 2H, Ar). $^{13}$C NMR ($CDCl_3$, 75 MHz): $\delta$ 30.1, 33.7, 35.2, 73.4, 117.8, 126.4, 126.5, 126.6, 128.3, 128.4, 129.6, 133.5, 144.4, 164.1. MS (EI) $m/e$: 305 ($M^+$, 0.24), 183 (37.42), 117 (21.07), 104 (100), 77 (36.35). Anal. calcd for $C_{20}H_{19}NO_2$: C, 78.66%; H, 6.27%; N, 4.59%; found: C, 78.83%; H, 6.25%; N, 4.33%.

**1-Cyano-2-methylcyclohexyl benzoate (4c).** A white solid: 112 mg, 92% yield. Mp: 84–86 °C. IR ($CH_2Cl_2$) $\nu$ 2937, 1731, 1453, 1278, 1068 cm$^{-1}$. $^1$H NMR ($CDCl_3$, 300 MHz, TMS): $\delta$ 1.24 (d, $J$ = 6.9 Hz, 3H, $CH_3$), 1.29–1.86 (m, 7H, $4CH_2$), 2.08–2.15 (m,

1H, $CH_2$), 2.91–2.96 (m, 1H, CH), 7.45 (dd, $J = 7.8$, 7.8 Hz, 2H, Ar), 7.59 (t, $J = 8.1$ Hz, 1H, Ar), 8.01 (d, $J = 7.2$ Hz, 2H, Ar). $^{13}$C NMR ($CDCl_3$, 75 MHz): $\delta$ 16.3, 22.9, 24.4, 31.0, 34.3, 40.2, 78.5, 116.5, 128.4, 129.2, 129.6, 133.5, 164.2. MS (EI) *m/e*: 244 ($M^+ + 1$, 11.22), 105 (100), 77 (15.23). Anal. calcd for $C_{15}H_{17}NO_2$: C, 74.05%; H, 7.04%; N, 5.76%; found: C, 73.90%; H, 7.03%; N, 5.55%.

**Benzoic acid 1-cyanocyclopentyl ester (4d) (a known compound)[17].** A light yellow solid: 61 mg, 57% yield. $^1$H NMR ($CDCl_3$, 300 MHz, TMS): $\delta$ 1.87–1.96 (m, 4H, $2CH_2$), 2.38–2.50 (m, 4H, $2CH_2$), 7.46 (dd, $J = 7.8$, 7.8 Hz, 2H, Ar), 7.61 (t, $J = 8.1$ Hz, 1H, Ar), 8.01 (d, $J = 7.8$ Hz, 2H, Ar). $^{13}$C NMR ($CDCl_3$, 75 MHz): $\delta$ 23.3, 39.0, 76.7, 119.3, 128.5, 128.8, 129.6, 133.6, 164.6. MS (EI) *m/e*: 215 ($M^+$, 0.61), 105 (100), 77 (18.48), 51 (12.85). Anal. calcd for $C_{13}H_{13}NO_2$: C, 72.54%; H, 6.09%; N, 6.51%; found: C, 72.56%; H, 5.95%; N, 6.58%.

**Benzoic acid cyanodimethylmethyl ester (4e) (a known compound)[18].** A yellow solid, 64 mg, 68% yield. $^1$H NMR ($CDCl_3$, 300 MHz, TMS): $\delta$ 1.89 (s, 6H, $2CH_3$), 7.47 (dd, $J = 7.5$, 8.1 Hz, 2H, Ar), 7.61 (t, $J = 7.5$ Hz, 1H, Ar), 8.02 (d, $J = 8.4$ Hz, 2H, Ar). $^{13}$C NMR ($CDCl_3$, 75 MHz): $\delta$ 26.8, 68.7, 119.3, 128.4, 128.9, 129.6, 133.6, 164.3. MS (EI) *m/e*: 189 ($M^+$, 2.53), 122 (47.55), 105 (100), 77 (35.31), 51 (25.48).

**Benzoic acid 1-cyano-1-ethylpropyl ester (4f) (a known compound)[19].** A light yellow oil: 47 mg, 44% yield. $^1$H NMR ($CDCl_3$, 300 MHz, TMS): $\delta$ 1.14 (t, $J = 7.5$ Hz, 6H, $2CH_3$), 2.12–2.29 (m, 4H, $2CH_2$), 7.47 (dd, $J = 8.4$, 6.9 Hz, 2H, Ar), 7.61 (t, $J = 7.5$ Hz, 1H, Ar), 8.02 (d, $J = 7.8$ Hz, 2H, Ar). $^{13}$C NMR ($CDCl_3$, 75 MHz): $\delta$ 8.0, 29.5, 77.1, 118.1, 128.5, 129.1, 129.6, 133.6, 164.3. MS (ESI) *m/e*: 218 ($M^+ + 1$).

## Acknowledgements

We thank the State Key Project of Basic Research (Project 973) (No. G2000048007), Shanghai Municipal Committee of Science and Technology (04JC14083), Chinese Academy of Sciences (KGCX2-210-01), and the National Natural Science Foundation of China for financial support (20025206, 203900502 and 20272069).

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