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Use of isopropyl alcohol as a solvent in Ti(O-*i*-Pr)$_4$-catalyzed Knöevenagel reactions

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Abstract—Knöevenagel reactions of aldehydes and ketones with malononitrile, isopropyl cyanoacetate and diisopropyl malonate catalyzed by Ti(O-*i*-Pr)$_4$ proceeded smoothly in *i*-PrOH to give the corresponding reaction products in good to high yield. 3-Substituted coumarins were prepared by the present method.

1. Introduction

The Knöevenagel reaction is a well-known classical reaction as a condensation between carbonyl compounds and activated methylene compounds catalyzed by amines.[1] As activated methylene compounds, alkyl acetoacetates and dialkyl malonates have often been used.

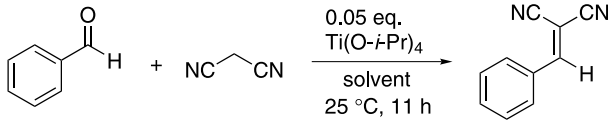
Recently, on the other hand, Knöevenagel reactions catalyzed by Lewis acids have been reported. The Venkataratnam[2] and Sandhu[3,4] groups reported reactions catalyzed by $ZnCl_2$, $BiCl_3$, and CdI_2, respectively. However, all of them required a high temperature (75–100 °C) under solvent-free conditions. Furthermore, the reaction in an ionic liquid was also reported.[5]

We recently reported Ti(O-*i*-Pr)$_4$-promoted Knöevenagel reaction of aldehydes with diketene.[6] During the course of this study, we observed that Ti(O-*i*-Pr)$_4$ promoted the reaction of aldehydes with isopropyl acetoacetate. Therefore, we examined the scope of Ti(O-*i*-Pr)$_4$-promoted Knöevegenal reaction of carbonyl compounds with activated methylene compounds.

2. Results and discussion

We first examined the reaction of benzaldehyde with malononitrile in the presence of Ti(O-*i*-Pr)$_4$ in a variety of solvents (Table 1).

Table 1. Solvent effect in the reaction of benzaldehyde with malononitrile



Entry	Solvent	Product (% yield[a])
1	*i*-PrOH	93
2	CH_3CN	72
3	CH_2Cl_2	66[b]
4	Toluene	24[b]

[a] Isolated yield by fractional recrystallizations unless otherwise noted.
[b] Isolated yield by silica-gel column chromatography.

As shown in Table 1, we found that the reaction using *i*-PrOH as a solvent was accelerated by 0.05 equiv of Ti(O-*i*-Pr)$_4$ to produce 2-(phenylmethylene)malononitrile in 93% yield at 25 °C for 11 h. Under identical conditions, a variety of aldehydes were reacted with malononitrile to afford 2-(arylidene)malononitrile in good to high yield (Table 2, entries 1–9). In the cases of ketones, larger amounts of Ti(O-*i*-Pr)$_4$ were required (0.5–1 equiv) to obtain the products in satisfactory yield (entries 10 and 11).

As for the reaction mechanism, the carboanion of malonate will attack the electrophilic carbonyl carbon coordinated by Ti(O-*i*-Pr)$_4$. The carboanionic character of malononitrile might be enhanced by the alcoholic solvent producing a keteneimine intermediate.[5a] After addition to carbonyl compounds, some kind of an elimination process may occur to produce 2-substituted methylenemalononitrile and to regenerate the Ti species those activate aldehydes.

We then examined the reactions of some aldehydes with

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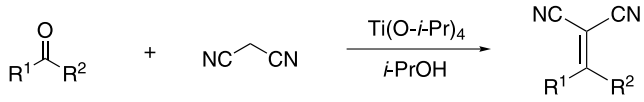
Table 2. Reactions of a variety of aldehydes and ketones with malononitrile promoted by Ti(O-*i*-Pr)$_4$



1a—1k

Entry	R^1	R^2	Ti(O-*i*-Pr)$_4$/equiv	Conditions		Product (% yield[a])
				Temperature/°C	Time/h	
1	Ph	H	0.05	25	11	93 (**1a**)
2	*p*-ClC_6H_4	H	0.05	22	12	97 (**1b**)
3	*p*-$MeOC_6H_4$	H	0.05	21	12	92 (**1c**)
4	*p*-BrC_6H_4	H	0.05	21	13	98 (**1d**)
5	*c*-C_6H_{11}	H	0.05	20	25	92[b] (**1e**)
6	$Ph(CH_2)_2$	H	0.05	20	3	74[b] (**1f**)
7	(*E*)-PhCH=CH	H	0.05	22	11	64 (**1g**)
8	$CH_3(CH_2)_2$	H	0.05	20	12	63[b] (**1h**)
9	*t*-Bu	H	0.05	20	24	60[b] (**1i**)
10	Ph	Me	1.0	70	18	61[b] (**1j**)
11	Ph	Ph	1.0	70	52	86 (**1k**)

[a] Isolated yield by fractional recrystallizations unless otherwise noted.
[b] Isolated yield by silica-gel column chromatography.

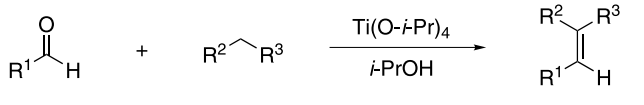
isopropyl cyanoacetate and diisopropyl malonate with the aid of Ti(O-*i*-Pr)$_4$ in *i*-PrOH (Table 3). The reactions of isopropyl cyanoacetate and diisopropyl malonate with aldehydes were carried out with the aid of 0.2–1.0 equiv of Ti(O-*i*-Pr)$_4$ in *i*-PrOH.

While 0.05 equiv of Ti(O-*i*-Pr)$_4$ was enough for the reaction of aldehydes with malononitrile, it was found that 0.2 equiv and 1 equiv of Ti(O-*i*-Pr)$_4$ were necessary in the cases of isopropyl cyanoacetate and diisopropyl malonate, respectively, for the completion of the reaction, probably due to the lower reactivity of activated methylene compounds. In the cases of entry 1 and 2, only (*E*)-isomers (**2a** and **2b**) were obtained, that was consistent with the results of the reported methods.[2,3,5]

We applied our method to the synthesis coumarin derivatives. Coumarins (2*H*-1-benzopyran-2-one) are important compounds found in natural and artificial compounds such as perfume, agricultural and pharmaceutical products. So far, there have been many reports for the synthesis of coumarin frameworks. There are fundamentally two methods, one is the so-called Pechmann condensation, that is, acid-mediated condensation of phenol with β-ketoesters to produce coumarins.[7] In these reactions, strong acids such as H_2SO_4 and $AlCl_3$ have been used. The other method is the Knöevenagel reaction between salicylaldehydes and dialkyl malonate. For example, solvent-free synthesis,[8] Montmorillonite KSF-catalyzed synthesis[9] and a solid-phase synthesis[10] for substituted coumarin-3-carboxylic acids derivatives have been recently reported.

We first examined the reaction of salicylaldehyde with malononitrile in the presence of 0.1 equiv of Ti(O-*i*-Pr)$_4$ in *i*-PrOH (Scheme 1). The reaction proceeded smoothly at room temperature to afford 3-cyanocoumarin (**4**) in 70% yield. The introduction of isopropyl carboxylate to the 3-position of coumarin was performed by using isopropyl cyanoacetate in the presence of 1 equiv of Ti(O-*i*-Pr)$_4$ in *i*-PrOH to give 3-isopropoxycarbonylcoumarin (**5**). The reaction of diisopropyl malonate was so sluggish that the yield of **5** was only moderate (37%). It should be mentioned that the reaction of salicylaldehyde with diketene in the

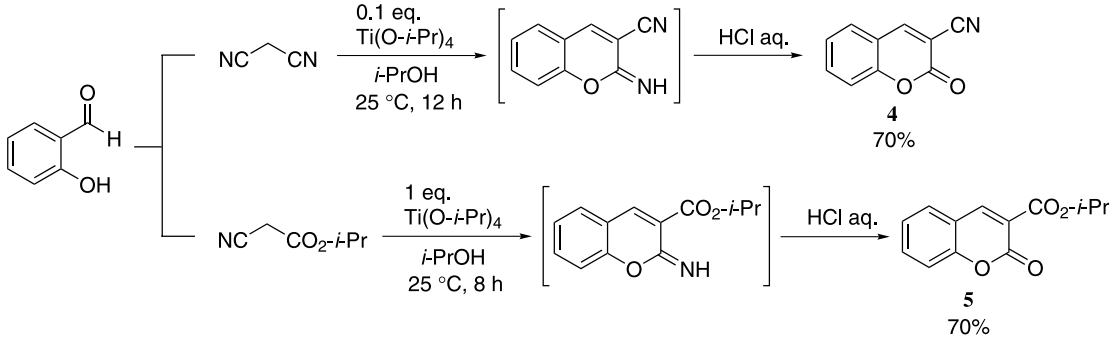
Table 3. Reactions of some aldehydes with isopropyl cyanoacetate and diisopropyl malonate promoted by Ti(O-*i*-Pr)$_4$



2a, **2b**, **3a**, **3b**

Entry	R^1	R^2	R^3	Ti(O-*i*-Pr)$_4$/equiv	Conditions		Product (% yield[a])
					Temperature/°C	Time/h	
1	Ph	CN	CO_2-*i*-Pr	0.2	70	25	78[b] (**2a**)
2	(*E*)-PhCH=CH	CN	CO_2-*i*-Pr	0.2	70	24	63[b,c] (**2b**)
3	Ph	CO_2-*i*-Pr	CO_2-*i*-Pr	1.0	22	50	93 (**3a**)
4	*c*-C_6H_{11}	CO_2-*i*-Pr	CO_2-*i*-Pr	1.0	20	51	97 (**3b**)

[a] Isolated yield by silica-gel column chromatography unless otherwise noted.
[b] Only (*E*)-isomer was obtained (determined by NOE experiments).
[c] Isolated yield by fractional recrystallizations.



Scheme 1.

presence of 2 equiv of Ti(O-*i*-Pr)$_4$ at 25 °C proceeded smoothly to produce 3-acetylcoumarin in 76% yield in CH_2Cl_2 and 59% yield in *i*-PrOH, respectively.

The present method has the following characteristic features: (1) Ti(O-*i*-Pr)$_4$-catalyzed Knöevegenal reaction of aldehydes and ketones is performed in non-toxic *i*-PrOH. (2) In the case of aldehydes, only a catalytic amount (0.05 equiv) of Ti(O-*i*-Pr)$_4$ was required for smooth reaction. (3) Coumarin derivatives are synthesized when salicylaldehyde is used.

3. Experimental

3.1. General procedure for Ti(O-*i*-Pr)$_4$-promoted Knöevenagel reaction

Malononitrile (330 mg, 5 mmol) and *i*-PrOH (Wako dehydrated grade) 6 mL were placed in a Schlenk tube under argon atmosphere. To this solution, aldehydes (5 mmol) then Ti(O-*i*-Pr)$_4$ 0.08 mL (0.025 mmol) were added and stirred at room temperature (20–25 °C) for 3–25 h. After confirmation of the completion of the reaction, the reaction mixture was poured into 1 N HCl and vigorously stirred at 0 °C for 0.5 h. It was extracted by ethyl acetate and the extract was washed with sodium bicarbonate and brine solution. The organic layer was dried with anhydrous sodium sulfate and evaporated. Purification of the residues by recrystallization or silica-gel column chromatography afforded Knöevenagel reaction products.

3.1.1. 2-(Phenylmethylene)malononitrile (1a). R_f=0.56 (3:1 hexane–ethyl acetate); mp 84–85 °C (lit.[11] 83 °C); IR (KBr, ν_{max} (cm^{-1})): 2223 (CN), 1591 (C=C); ^{1}H NMR: δ 7.91 (d, 2H, J=7.2 Hz), 7.78 (s, 1H), 7.64 (t, 1H, J=7.2 Hz), 7.55 (t, 2H, J=7.2 Hz); ^{13}C NMR: δ 160.1, 134.6, 131.0, 130.7, 129.6, 113.8, 112.7, 82.6; MS *m*/*z* (relative intensity): 154 (M$^+$, 100%), 127 (94%), 103 (70%), 76 (23%).

3.1.2. 2-[(4-Chlorophenyl)methylene]malononitrile (1b). R_f=0.54 (3:1 hexane–ethyl acetate); mp 167–168 °C (lit.[2] 165 °C); IR (KBr, ν_{max} (cm^{-1})): 2228 (CN), 1584 (C=C); ^{1}H NMR: δ 7.85 (d, 2H, J=8.4 Hz), 7.73 (s, 1H), 7.52 (d, 2H, J=8.4 Hz); ^{13}C NMR: δ 158.2, 141.2, 131.8, 130.1, 129.3, 113.4, 112.3, 83.4; MS *m*/*z* (relative intensity): 190 (^{37}Cl-M$^+$, 26%), 188 (^{35}Cl-M$^+$, 75%), 161 (29%), 153 (100%), 137 (22%), 126 (19%), 100 (12%), 75 (21%).

3.1.3. 2-[(4-Methoxyphenyl)methylene]malononitrile (1c). R_f=0.47 (2:1 hexane–ethyl acetate); mp 116–118 °C (lit.[2] 119 °C); IR (KBr, ν_{max} (cm^{-1})): 2225 (CN), 1560 (C=C); ^{1}H NMR: δ 7.91 (d, 2H, J=8.8 Hz), 7.65 (s, 1H,), 7.01 (d, 2H, J=8.8 Hz), 3.92 (s, 3H); ^{13}C NMR: δ 164.8, 158.8, 133.4, 124.0, 115.1, 114.4, 113.3, 78.7, 55.8; MS *m*/*z* (relative intensity): 184 (M$^+$, 100%), 169 (13%), 141 (28%), 114 (45%).

3.1.4. 2-[(4-Bromophenyl)methylene]malononitrile (1d). R_f=0.61 (3:1 hexane–ethyl acetate); mp 165–166 °C (lit.[11] 164 °C); IR (KBr, ν_{max} (cm^{-1})): 2225 (CN), 1558 (C=C); ^{1}H NMR: δ 7.77 (d, 2H, J=8.2 Hz), 7.72 (s, 1H), 7.69 (d, 2H, J=8.2 Hz); ^{13}C NMR: δ 158.4, 133.0, 131.8, 130.0, 129.6, 113.4, 112.3, 83.5; MS *m*/*z* (relative intensity): 235 (^{81}Br-M$^+$, 11%), 234 (88%), 233 (^{79}Br-M$^+$, 13%), 232 (89%), 153 (100%), 126 (79%), 100 (34%).

3.1.5. 2-(Cyclohexylmethylene)malononitrile (1e). R_f=0.54 (4:1 hexane–ethyl acetate); IR (KBr, ν_{max} (cm^{-1})): 2235 (CN), 1608 (C=C); ^{1}H NMR: δ 7.15 (d, 1H, J=10.4 Hz), 2.78–2.68 (m, 1H), 1.83–1.71 (m, 4H), 1.43–1.18 (m, 6H); ^{13}C NMR: δ 173.6, 112.2, 110.6, 87.8, 42.1, 30.9, 25.1, 24.6; MS *m*/*z* (relative intensity): 160 (M$^+$, 3%), 159 (9%), 145 (11%), 132 (14%), 118 (7%), 105 (18%), 82 (19%), 67 (52%), 56 (78%), 41 (100%). Anal. Calcd for $C_{10}H_{12}N_2$: C, 74.97; H, 7.55; N, 17.48. Found: C, 74.89; H, 7.59; N, 17.32.

3.1.6. 2-(3-Phenylpropylidene)malononitrile (1f). R_f=0.54 (3:1 hexane–ethyl acetate); IR (KBr, ν_{max} (cm^{-1})): 2236 (CN), 1601 (C=C); ^{1}H NMR: δ 7.34 (t, 2H, J=7.2 Hz), 7.30–7.27 (m, 2H), 7.17 (d, 2H, J=7.2 Hz), 2.96–2.86 (m, 4H); ^{13}C NMR: δ 168.3, 138.2, 136.9, 129.0, 128.3, 127.1, 114.9, 112.0, 110.4, 90.5, 34.2, 33.5; MS *m*/*z* (relative intensity): 182 (M$^+$, 40%), 91 (100%), 77 (25%), 65 (100%), 51 (59%). Anal. Calcd for $C_{12}H_{10}N_2$: C, 79.10; H, 5.53; N, 15.37. Found: C, 79.10; H, 5.56; N, 15.22.

3.1.7. 2-[(*E*)-3-Phenyl-2-propenylidene]malononitrile (1g). R_f=0.53 (3:1 hexane–ethyl acetate); mp 126–128 °C (lit.[12] 126 °C); IR (KBr, ν_{max} (cm^{-1})): 2224 (CN), 1609 (C=C), 1560 (C=C); ^{1}H NMR: δ 7.61–7.59 (m, 3H), 7.48–7.42 (m, 3H), 7.27 (d, 2H, J=10.4 Hz); ^{13}C NMR: δ 159.9, 150.3, 134.0, 132.1, 129.3, 128.9, 122.3, 113.5, 111.6; MS *m*/*z* (relative intensity): 180 (M$^+$, 99%), 179 (41%), 153 (100%), 115 (97%), 51 (40%).

3.1.8. 2-(Butylidene)malononitrile (1h). R_f=0.54 (3:1 hexane–ethyl acetate); IR (KBr, ν_{max} (cm^{-1})): 2239 (CN), 1607 (C=C); ^1H NMR: δ 7.33 (t, 1H, J=7.6 Hz), 2.58 (q, 2H, J=7.6 Hz), 1.62 (sextet, 2H, J=7.6 Hz), 1.02 (t, 3H, J=7.6 Hz); ^{13}C NMR: δ 169.4, 112.1, 90.2, 34.6, 21.1, 19.6, 13.5; MS m/z (relative intensity): 120 (M^+, 19%), 119 (21%), 105 (31%), 92 (33%), 79 (28%), 67 (46%), 55 (59%), 42 (100%), 41 (73%). Anal. Calcd for $C_7H_8N_2$: C, 69.97; H, 6.71; N, 23.32. Found: C, 69.93; H, 6.65; N, 23.23.

3.1.9. 2-(2,2-Dimethylpropylidene)malononitrile (1i). R_f=0.53 (3:1 hexane–ethyl acetate); mp 64–65 °C; IR (KBr, ν_{max} (cm^{-1})): 2233 (CN), 1606 (C=C); ^1H NMR: δ 7.26 (s, 1H), 1.32 (s, 9H); ^{13}C NMR: δ 177.4, 113.1, 111.1, 86.9, 37.0, 28.5; MS m/z (relative intensity): 133 (M^+-1, 8%), 119 (29%), 92 (63%), 73 (38%), 65 (53%), 57 (35%), 42 (100%). Anal. Calcd for $C_8H_{10}N_2$: C, 71.61; H, 7.51; N, 20.88. Found: C, 71.40; H, 7.47; N, 20.76.

3.1.10. 2-(1-Phenylethylidene)malononitrile (1j). R_f=0.42 (3:1 hexane–ethyl acetate); mp 94–96 °C (lit.[13] 92 °C); IR (KBr, ν_{max} (cm^{-1})): 2228 (CN), 1585 (C=C); ^1H NMR: δ 7.58–7.48 (m, 5H), 2.64 (s, 3H); ^{13}C NMR: δ 175.4, 135.9, 132.2, 129.1, 127.3, 112.7, 84.7, 24.2; MS m/z (relative intensity): 168 (M^+, 100%), 141 (64%), 140 (67%), 128 (58%), 114 (37%), 103 (30%), 77 (33%), 51 (49%).

3.1.11. 2-(Diphenylmethylene)malononitrile (1k). R_f=0.51 (3:1 hexane–ethyl acetate); mp 143–144 °C (lit.[14] 138 °C); IR (KBr, ν_{max} (cm^{-1})): 2223 (CN), 1530 (C=C); ^1H NMR: δ 7.58 (t, 2H, J=7.2 Hz), 7.51–7.42 (m, 8H); ^{13}C NMR: δ 175.0, 136.1, 132.7, 130.4, 128.9, 113.9, 81.7; MS m/z (relative intensity): 230 (M^+, 96%), 229 (75%), 203 (64%), 165 (100%), 88 (29%).

3.1.12. Isopropyl (*E*)-2-cyano-3-phenyl-2-propenoate (2a). R_f=0.63 (3:1 hexane–ethyl acetate); mp 76–79 °C; IR (KBr, ν_{max} (cm^{-1})): 2219 (CN), 1717 (C=O), 1607 (C=C); ^1H NMR: δ 8.24 (s, 1H), 7.99 (d, 2H, J=6.8 Hz), 7.58–7.48 (m, 3H), 5.26–5.16 (m, 1H), 1.38 (d, 6H, J=6.4 Hz); ^{13}C NMR: δ 161.9, 154.7, 133.1, 131.5, 130.9, 129.2, 115.4, 103.5, 70.7, 21.7; MS m/z (relative intensity): 215 (M^+, 32%), 173 (100%), 172 (100%), 156 (85%), 129 (78%), 128 (63%), 102 (58%), 101 (33%), 77 (57%), 43 (88%). Anal. Calcd for $C_{10}H_6N_2$: C, 72.54; H, 6.09; N, 6.51. Found: C, 72.52; H, 6.11; N, 6.46.

3.1.13. Isopropyl (2*E*,4*E*)-2-cyano-5-phenyl-2,4-pentadienoate (2b). R_f=0.69 (3:1 hexane–ethyl acetate); mp 104–106 °C; IR (KBr, ν_{max} (cm^{-1})): 2220 (CN), 1712 (C=O), 1612 (C=C), 1582 (C=C); ^1H NMR: δ 8.00 (dd, 1H, J=8.0, 2.4 Hz), 7.59 (dd, 2H, J=6.8, 2.4 Hz), 7.44–7.42 (m, 3H), 7.28 (d, 1H, J=8.0 Hz), 7.27 (d, 1H, J=2.4 Hz), 5.22–5.12 (m, 1H), 1.35 (d, 6H, J=6.0 Hz); ^{13}C NMR: δ 161.8, 155.1, 148.5, 134.7, 131.1, 129.1, 128.5, 123.1, 114.6, 105.2, 70.3, 21.7; MS m/z (relative intensity): 241 (M^+, 20%), 199 (74%), 182 (27%), 171 (58%), 155 (64%), 154 (100%), 127 (64%), 115 (55%), 77 (33%), 43 (69%). Anal. Calcd for $C_{10}H_6N_2$: C, 74.67; H, 6.27; N, 5.81. Found: C, 74.51; H, 6.28; N, 5.75.

3.1.14. Diisopropyl 2-(phenylmethylene)malonate (3a). R_f=0.41 (7:1 hexane–ethyl acetate); IR (KBr, ν_{max} (cm^{-1})): 1724 (C=O), 1631 (C=C); ^1H NMR: δ 7.69 (s, 1H), 7.48 (dd, 2H, J=6.8, 2.4 Hz), 7.41–7.34 (m, 3H), 5.29–5.21 (m, 1H), 5.19–5.11 (m, 1H), 1.31 (d, 6H, J=6.4 Hz), 1.29 (d, 6H, J=6.4 Hz); ^{13}C NMR: δ 166.3, 163.7, 141.4, 133.0, 130.4, 129.5, 128.7, 127.1, 69.3, 69.2, 21.8, 21.5; MS m/z (relative intensity): 276 (M^+, 9%), 217 (20%), 175 (66%), 174 (100%), 158 (27%), 146 (29%), 130 (24%), 102 (28%), 43 (98%). Anal. Calcd for $C_{10}H_6N_2$: C, 69.54; H, 7.30. Found: C, 69.54; H, 7.31.

3.1.15. Diisopropyl 2-(cyclohexylmethylene)malonate (3b). R_f=0.54 (6:1 hexane–ethyl acetate); IR (KBr, ν_{max} (cm^{-1})): 1718 (C=O), 1646 (C=C); ^1H NMR: δ 6.73 (d, 1H, J=10.8 Hz), 5.24–5.14 (m, 1H), 5.13–5.03 (m, 1H), 2.42–2.33 (m, 1H), 1.74–1.66 (m, 4H), 1.31 (d, 6H, J=6.4 Hz), 1.27 (d, 6H, J=6.8 Hz), 1.23–1.10 (m, 6H); ^{13}C NMR: δ 165.4, 163.8, 152.5, 127.6, 68.7, 68.6, 38.9, 31.7, 25.6, 25.2, 21.7; MS m/z (relative intensity): 180 (49%), 163 (55%), 162 (100%), 95 (33%), 43 (89%), 41 (72%). Anal. Calcd for $C_{10}H_6N_2$: C, 68.06; H, 9.28. Found: C, 68.13; H, 9.37.

3.1.16. 3-Cyanocoumarin (4). R_f=0.30 (2:1 hexane–ethyl acetate); mp 184–186 °C (lit.[15] 182–184 °C); IR (KBr, ν_{max} (cm^{-1})): 2229 (CN), 1728 (C=O), 1604 (C=C); ^1H NMR: δ 8.28 (s, 1H), 7.73 (t, 1H, J=8.0 Hz), 7.62 (dd, 1H, J=8.0, 1.6 Hz), 7.43 (t, 1H, J=8.0 Hz), 7.42 (t, 1H, J=8.0 Hz); ^{13}C NMR: δ 155.5, 154.0, 136.5, 130.8, 126.5, 118.5, 118.3, 117.9, 115.2, 103.8; MS m/z (relative intensity): 171 (M^+, 100%), 143 (99%), 115 (50%), 88 (27%), 63 (24%), 62 (23%). Anal. Calcd for $C_{10}H_6N_2$: C, 70.18; H, 2.94; N, 8.18. Found: C, 70.30; H, 2.94; N, 8.35.

3.1.17. 3-Isopropoxycarboxycoumarin (5). R_f=0.62 (3:1 hexane–ethyl acetate); mp 89–90 °C (lit.[16] 84–86 °C); IR (KBr, ν_{max} (cm^{-1})): 1750 (C=O), 1606 (C=C); ^1H NMR: δ 8.47 (s, 1H), 7.64 (t, 1H, J=8.0 Hz), 7.61 (dd, 1H, J=8.0, 1.6 Hz), 7.36 (d, 1H, J=8.0 Hz), 7.34 (t, 1H, J=8.0 Hz), 5.32–5.23 (m, 1H), 1.4 (d, 6H, J=6.0 Hz); ^{13}C NMR: δ 162.4, 156.7, 155.1, 148.0, 134.2, 129.4, 124.8, 118.7, 117.9, 116.8, 69.7, 21.8. MS m/z (relative intensity): 232 (M^+, 26%), 174 (35%), 173 (98%), 146 (100%), 118 (41%), 101 (22%), 89 (41%), 43 (49%). Anal. Calcd for $C_{13}H_{12}O_2$: C, 67.23; H, 5.21. Found: C, 67.23; H, 5.12.

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References and notes

1. Jones, G. *Org. React.* **1967**, *15*, 204–599.
2. Rao, P. S.; Venkataratnam, R. V. *Tetrahedron Lett.* **1991**, *32*, 5821–5822.
3. Prajapati, D.; Sandhu, J. S. *Chem. Lett.* **1992**, 1945–1946.

4. Prajapati, D.; Sandhu, J. S. *J. Chem. Soc., Perkin Trans. 1* **1993**, 739–740.
5. (a) Su, C.; Chen, Z. C.; Zheng, Q. G. *Synthesis* **2003**, *4*, 555–559. See also for recently reported Knöevenagel reaction: (b) Bigi, F.; Conforti, M. L.; Maggi, R.; Piccinno, A.; Satori, G. *Green Chem.* **2000**, *2*, 101–103. (c) Amantini, D.; Fringuelli, F.; Piermatti, O.; Pizzo, F.; Vaccaro, L. *Green Chem.* **2001**, *3*, 229–232. (d) Hangarge, R. V.; Sonwane, S. A.; Jarikote, D. V.; Shingare, M. S. *Green Chem.* **2001**, *3*, 310–312.
6. Hayashi, M.; Nakamura, N.; Yamashita, K. *Tetrahedron* **2004**, *60*, 6777–6783.
7. Pechmann, H.; Duisberg, C. *Ber. Dtsch. Chem. Ges.* **1883**, *16*, 2119.
8. Sugino, T.; Tanaka, K. *Chem. Lett.* **2001**, 110–111.
9. Bigi, F.; Chesini, L.; Maggi, R.; Sartori, G. *J. Org. Chem.* **1999**, *64*, 1033–1035.
10. Watson, B. T.; Christiansen, G. E. *Tetrahedron Lett.* **1998**, *39*, 6087–6090.
11. Zabicky, J. *J. Chem. Soc.* **1961**, 683–687.
12. Angeletti, E.; Canepa, C.; Martinetti, G.; Venturello, P. *J. Chem. Soc., Perkin Trans. 1* **1989**, 105–107.
13. Texier-Boullet, F.; Foucaud, A. *Tetrahedron Lett.* **1982**, *23*, 4927–4928.
14. Cruz, P. D. L.; Díez-Barra, E.; Loupy, A.; Langa, F. *Tetrahedron Lett.* **1996**, *37*, 1113–1116.
15. Jose, A. C.; Juan, M. C.; Angel, G.; Luna, D.; Jose, M. M. *J. Org. Chem.* **1984**, *49*, 5195–5197.
16. Kadaba, P. K. *Synthesis* **1972**, 628–630.