

SUPPORTING INFORMATION

Polystyrene-immobilized DABCO as a highly efficient and recyclable organocatalyst for Knoevenagel condensation

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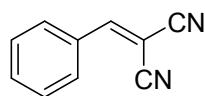
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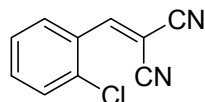
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Spectroscopic Data for Compounds 6



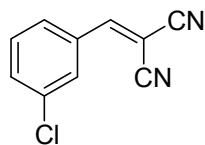
2-(Phenylmethylene)malononitrile (6a)¹

White solid (153 mg, yield > 99%), mp. 83-84°C. ¹H NMR (400MHz, CDCl₃) δ: 7.57 (t, J = 8.0Hz, 2H), 7.67 (t, J = 7.2Hz, 2H), 7.82 (s, 1H), 7.94 (d, J = 7.6Hz, 2H). ¹³C NMR (100MHz, CDCl₃) δ: 83.34, 112.38, 113.48, 129.29, 130.10, 131.88, 141.18, 158.35.



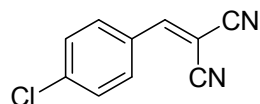
2-(2-chlorobenzylidene)malononitrile (6b)¹

White solid (187 mg, yield 99%), m.p. 94°C. ¹H NMR (400MHz, CDCl₃) δ: 7.43-7.48 (m, 1H), 7.53-7.59 (m, 2H), 8.18 (d, J = 8.0Hz, 1H), 8.28 (s, 1H). ¹³C NMR (100MHz, CDCl₃) δ: 85.78, 111.94, 113.25, 127.82, 129.06, 129.52, 130.73, 135.08, 136.36, 156.10.



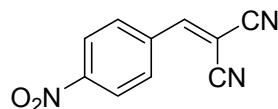
2-(3-chlorobenzylidene)malononitrile (6c)²

White solid (187 mg, yield 99%), m.p. 113-115°C. ¹H NMR (400MHz, CDCl₃) δ: 7.50 (t, J = 8.4Hz, 1H), 7.59-7.61 (m, 1H), 7.74(s, 1H), 7.83-7.85 (m, 2H). ¹³C NMR (100MHz, CDCl₃) δ: 84.69, 112.06, 113.23, 128.37, 130.46, 130.92, 132.32, 134.39, 135.82, 158.25.



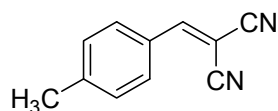
2-(4-chlorobenzylidene)malononitrile (6d)¹

White solid (187 mg, yield 99%), m.p. 164-165°C. ¹H NMR (400MHz, CDCl₃) δ: 7.52 (d, J = 8.4, 2H), 7.75 (s, 1H), 7.86 (d, J = 8.8, 2H). ¹³C NMR (100MHz, CDCl₃) δ: 83.34, 112.38, 113.48, 129.29, 130.10, 131.88, 141.18, 158.35.



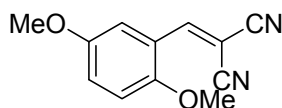
2-(4-nitrobenzylidene)malononitrile (6e)¹

Yellow solid (197 mg, yield 99%), m.p. 161-162°C. ¹H NMR (400MHz, CDCl₃) δ: 7.92 (s, 1H), 8.11 (d, J = 8.8Hz, 2H), 8.42 (d, J = 8.4Hz, 2H). ¹³C NMR (100MHz, CDCl₃) δ: 87.54, 111.63, 112.66, 124.67, 131.35, 135.82, 150.37, 156.93.



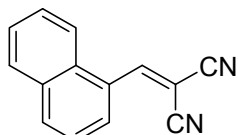
2-(p-tolyl) malononitrile (6f)³

White solid (165 mg, yield 98%), m.p. 133-134°C. ¹H NMR (400MHz, CDCl₃) δ: 2.46 (s, 3H), 7.34 (d, J = 8.4Hz, 2H), 7.73 (s, 1H), 7.81 (d, J = 8.4Hz, 2H). ¹³C NMR (100MHz, CDCl₃) δ: 22.06, 81.18, 112.91, 114.06, 128.48, 130.41, 130.96, 146.44, 159.83.



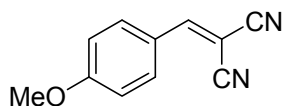
2-(2,5-dimethoxybenzylidene)malononitrile (6g)⁴

White solid (212 mg, yield 99%), m.p. 109-110°C. ¹H NMR (400MHz, CDCl₃) δ: 3.81 (s, 3H), 3.88 (s, 3H), 6.93 (d, J = 9.2Hz, 1H), 7.17 (dd, J₁ = 3.2Hz, J₂ = 9.2Hz, 1H), 7.72 (d, J = 2.8Hz, 1H), 8.28 (s, 1H). ¹³C NMR (100MHz, CDCl₃) δ: 55.88, 56.35, 80.95, 111.17, 112.85, 113.24, 114.38, 120.14, 124.30, 153.47, 153.79, 154.14.



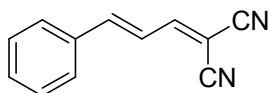
2-(naphthalen-1-yl)methylene)malononitrile (6h)⁵

White solid (202 mg, yield 99%), m.p. 164-165°C. ¹H NMR (400MHz, CDCl₃) δ: 7.62-7.74 (m, 3H), 7.99 (d, J = 8.8Hz, 2H), 8.14 (d, J = 8.4Hz, 1H), 8.30 (d, J = 7.2Hz, 1H), 8.68 (s, 1H). ¹³C NMR (100MHz, CDCl₃) δ: 85.16, 112.54, 113.75, 122.32, 125.41, 127.52, 128.54, 128.60, 129.46, 131.09, 133.55, 134.96, 157.74.



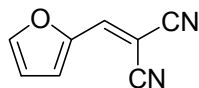
2-(4-methoxybenzylidene)malononitrile (6i)⁶

White solid (182 mg, yield 99%), m.p. 110-112°C. ¹H NMR (400MHz, CDCl₃) δ: 3.95 (s, 3H), 7.04 (d, J = 8.8Hz, 2H), 7.68 (s, 1H), 7.94 (d, J = 8.8Hz, 2H). ¹³C NMR (100MHz, CDCl₃) δ: 55.86, 78.52, 113.41, 114.49, 115.17, 124.04, 133.51, 158.94, 164.87.



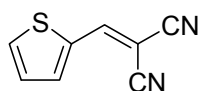
2-(E)-3-phenylallylidene)malononitrile (6j)¹

Yellow solid (179 mg, yield 99%), m.p. 126-127°C. ¹H NMR (400MHz, CDCl₃) δ: 7.27-73.5 (m, 2H), 7.46-7.52 (m, 3H), 7.62-7.66 (m, 3H). ¹³C NMR (100MHz, CDCl₃) δ: 82.94, 111.74, 113.59, 122.29, 129.01, 129.39, 132.17, 133.96, 150.55, 160.17.



2-(furan-2-yl)methylene)malononitrile (6k)⁷

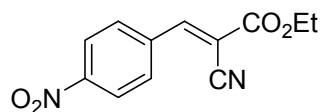
Brown solid (143 mg, yield 99%), m.p. 69-70°C. ¹H NMR (400MHz, CDCl₃) δ: 6.75 (m, J = 2.0Hz, 1H), 7.38 (d, J = 2.4Hz, 1H), 7.55 (s, 1H), 7.84 (s, 1H). ¹³C NMR (100MHz, CDCl₃) δ: 112.65, 113.86, 114.50, 123.28, 143.12, 148.10, 149.63.



2-(thiophen-2-yl)methylene)malononitrile (6l)⁸

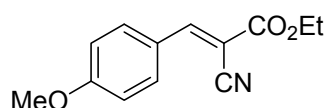
Brown solid (159 mg, yield 99%), m.p. 110-112°C. ¹H NMR (400MHz, CDCl₃) δ: 7.28 (dd, J₁ = 4.0 Hz,

$J_2 = 5.2$ Hz, 1H), 7.82 (d, $J = 4.0$ Hz, 1H), 7.89 (s, 2H). ^{13}C NMR (100MHz, CDCl_3) δ : 78.23, 113.02, 113.86, 129.09, 135.42, 137.04, 138.36, 151.24.



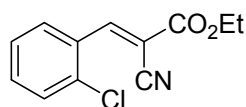
(E)-ethyl 2-cyano-3-(4-nitrophenyl)acrylate (6n)⁹

Yellow solid (244 mg, yield 99%), m.p. 172-173 °C. ^1H NMR (400MHz, CDCl_3) δ : 1.42 (t, $J = 6.8$ Hz, 3H), 4.43 (q, $J_1 = 7.2$ Hz, $J_2 = 14.4$ Hz, 2H), 8.14 (d, $J = 8.8$ Hz, 2H), 8.31 (s, 1H), 8.35 (d, $J = 8.8$ Hz). ^{13}C NMR (100MHz, CDCl_3) δ : 14.12, 63.36, 107.37, 114.56, 124.34, 131.54, 136.92, 149.71, 151.76, 161.42.



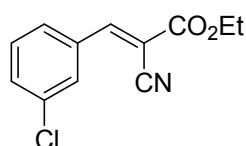
(E)-ethyl 2-cyano-3-(4-methoxyphenyl)acrylate (6o)⁹

White solid (224 mg, yield 97%), m.p. 79-80 °C. ^1H NMR (400MHz, CDCl_3) δ : 1.39 (t, $J = 7.2$ Hz, 3H), 3.89 (s, 3H), 4.36 (q, $J_1 = 7.2$ Hz, $J_2 = 14.4$ Hz, 2H), 6.99 (d, $J = 8.8$ Hz, 2H), 8.00 (d, $J = 8.8$ Hz, 2H), 8.17 (s, 1H). ^{13}C NMR (100MHz, CDCl_3) δ : 14.21, 55.64, 62.44, 99.32, 114.77, 116.25, 124.36, 133.65, 154.40, 163.13, 163.78.



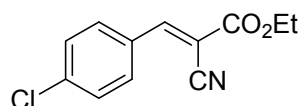
(E)-ethyl 3-(2-chlorophenyl)-2-cyanoacrylate (6p)³

White solid (233 mg, yield 99%), m.p. 51-52 °C. ^1H NMR (400MHz, CDCl_3) δ : 1.41 (t, $J = 7.2$ Hz, 3H), 4.41 (q, $J_1 = 7.2$ Hz, $J_2 = 14.4$ Hz, 2H), 7.40 (t, $J = 7.2$ Hz, 1H), 7.45-7.51 (m, 2H), 8.23 (d, $J = 8.0$ Hz, 1H), 8.68 (s, 1H). ^{13}C NMR (100MHz, CDCl_3) δ : 14.14, 62.96, 106.16, 114.82, 127.48, 129.85, 130.34, 133.71, 136.42, 151.14, 161.80.



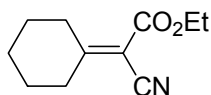
(E)-ethyl 3-(3-chlorophenyl)-2-cyanoacrylate (6q)¹⁰

White solid (233 mg, yield 99%), m.p. 100-101 °C. ^1H NMR (400MHz, CDCl_3) δ : 1.40 (t, $J = 7.2$ Hz, 3H), 4.39 (q, $J_1 = 6.8$ Hz, $J_2 = 14.0$ Hz, 2H), 7.45 (t, $J = 8.0$ Hz, 1H), 7.53 (d, $J = 8.4$ Hz, 1H), 7.90-7.93 (m, 2H), 8.18 (s, 1H). ^{13}C NMR (100MHz, CDCl_3) δ : 14.15, 63.00, 104.67, 114.96, 128.65, 130.56, 130.84, 133.07, 135.36, 153.23, 162.01.



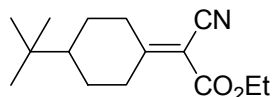
(E)-ethyl 3-(4-chlorophenyl)-2-cyanoacrylate (6r)⁹

White solid (233 mg, yield 99%), m.p. 91-92 °C. ^1H NMR (400MHz, CDCl_3) δ : 1.40 (t, $J = 7.2$ Hz, 3H), 4.39 (q, $J_1 = 7.2$ Hz, $J_2 = 14.4$ Hz, 2H), 7.48 (d, $J = 8.4$ Hz, 2H), 7.94 (d, $J = 8.8$ Hz, 2H), 8.20 (s, 1H). ^{13}C NMR (100MHz, CDCl_3) δ : 14.16, 62.90, 103.48, 115.29, 129.69, 129.88, 132.22, 139.61, 153.42, 162.25.



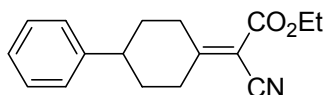
Ethyl 2-cyano-2-cyclohexylideneacetate (8a)⁹

Colourless liquid (174 mg, yield 90%). ¹H NMR (400MHz, CDCl₃) δ: 1.34 (t, J = 7.2Hz, 3H), 1.64-1.82 (m, 6H), 2.66 (t, J = 6.4Hz, 2H), 2.98 (t, J = 6.4Hz, 2H), 4.27 (q, J₁ = 7.2Hz, J₂ = 14Hz, 2H). NMR (100MHz, CDCl₃) δ: 14.08, 25.64, 28.26, 28.59, 31.57, 36.91, 61.71, 102.01, 115.63, 162.01, 180.07.



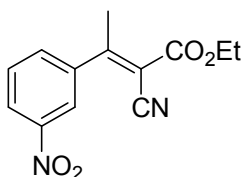
Ethyl 2-(4-tert-butylcyclohexylidene)-2-cyanoacetate (8b)¹¹

Pale solid (232 mg, yield 93%), m.p. 44-45 °C. ¹H NMR (400MHz, CDCl₃) δ: 0.92 (s, 9H), 1.34 (t, J = 7.2Hz, 3H), 1.42-1.50 (m, 3H), 2.06-2.10 (m, 3H), 2.29-2.38 (m, 3H), 4.27 (t, J₁ = 7.2Hz, J₂ = 14.4Hz, 2H). ¹³C NMR (100MHz, CDCl₃) δ: 14.09, 27.46, 29.12, 32.46, 36.68, 41.32, 46.69, 61.69, 101.78, 115.63, 162.01, 180.16.



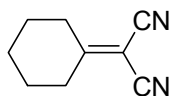
Ethyl 2-cyano-2-(4-phenylcyclohexylidene)acetate (8c)¹²

Pale solid (240 mg, yield 89%), m.p. 71-72 °C. ¹H NMR (400MHz, CDCl₃) δ: 1.35 (t, J = 7.2Hz, 3H), 1.64-1.81 (m, 2H), 2.19-2.25 (m, 3H), 2.46-2.51 (m, 1H), 2.84-2.92 (m, 1H), 3.18-3.22 (m, 1H), 4.29 (q, J₁ = 7.2Hz, J₂ = 14.4Hz, 2H), 7.18-7.23 (m, 3H), 7.30 (t, J = 7.2Hz, 2H). ¹³C NMR (100MHz, CDCl₃) δ: 14.12, 31.13, 34.91, 36.57, 43.39, 61.89, 102.75, 115.55, 126.61, 126.72, 128.62, 144.57, 161.93, 178.30.



Ethyl 2-cyano-3-(3-nitrophenyl)but-2-enoate (8d)¹³

Yellow solid (169 mg, yield 65%), m.p. 94-95 °C. ¹H NMR (400MHz, CDCl₃) δ: 1.33 (t, J = 7.2Hz, 3H), 2.70 (s, 3H), 4.28 (q, J₁ = 7.2Hz, J₂ = 14.4Hz, 2H), 7.70 (t, J = 7.6Hz, 1H), 8.30 (d, J = 8.0Hz, 1H), 8.43 (d, J = 8.4Hz, 1H), 8.78 (s, 1H). ¹³C NMR (100MHz, CDCl₃) δ: 13.98, 24.77, 26.76, 63.02, 113.11, 123.24, 127.43, 129.95, 133.81, 138.23, 162.95, 195.72.



2-cyclohexylidenemalononitrile (8e)⁷

Colourless liquid (145 mg, yield 99%). ¹H NMR (400MHz, CDCl₃) δ: 1.69-1.87 (m, 6H), 2.64-2.66 (m, 4H). ¹³C NMR (100MHz, CDCl₃) δ: 24.99, 27.96, 31.19, 34.75, 82.37, 111.74, 185.31.

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Spectra of compounds (¹H NMR, ¹³C NMR)

