Eco-friendly mono-1,4-hydrocyanation of diarenyl ketones using potassium hexacyanoferrate(II) as a cyanide source

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A selective mono-1,4-hydrocyanation of 10 diarenyl ketones using potassium hexacyanoferrate(II) as an eco-friendly cyanide source, potassium hydroxide as a catalyst, and benzoyl chloride as a promoter has been achieved. This protocol has the advantages of a non-toxic cyanide source, a heavy metal-free catalyst, selectivity, very good yields and a simple work-up procedure.

Keywords: mono-1,4-hydrocyanation, diarenyl ketone, potassium hexacyanoferrate(II), *in situ* HCN generation

The conjugate hydrocyanation of α,β-unsaturated ketones is an important C–C bond forming reaction in synthetic organic chemistry, which can produce significant β-cyano ketones. β-Cyano ketones are valuable synthons for synthetic organic chemistry.[1,2] Therefore many different methods for the conjugate hydrocyanation of α,β-unsaturated ketones have been reported, which mainly use HCN,[3] KCN,[4] and Et_2AlCN[5] as cyanide sources. However, these cyanide sources are strongly toxic chemicals. Recently it has been reported that conjugate hydrocyanation of α,β-unsaturated ketones could be conducted using trimethylsilyl cyanide[6–8] and acetone cyanohydrin[9,10] as cyanide sources. However, trimethylsilyl cyanide is very sensitive to moisture, and acetone cyanohydrin is unstable and both can easily release toxic hydrogen cyanide when heated. Therefore, there is a need to explore eco-friendly cyanating agents for hydrocyanation reactions.

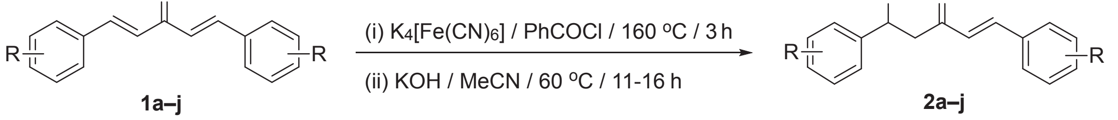
Potassium hexacyanoferrate(II), $K_4[Fe(CN)_6]$, is non-toxic and is used in the food industry for metal precipitation. In addition, it has been described as an anti-agglutinating auxiliary for table salt. $K_4[Fe(CN)_6]$ is a by-product of the coal chemical industry and is commercially available on a ton scale, and is even cheaper than KCN. Recently, $K_4[Fe(CN)_6]$ has been used as a cyanide source for some substitution reactions to synthesise benzonitriles,[11–13] aroyl cyanides,[14] benzyl cyanides,[15] and arylsulfonyl cyanides.[16] Our current research focused on the cyanation of unsaturated compounds including C=O,[17–20] C=N[21–26] and/or C=C[27–29] by nucleophilic addition reactions using $K_4[Fe(CN)_6]$ as an eco-friendly cyanide source. As an extension of this work, we here report an efficient method for the selective (conjugate) mono-1,4-hydrocyanation of unsaturated compounds bearing one C=O and two C=C bonds, a series of diarenyl ketones, using $K_4[Fe(CN)_6]$ as a selective 1,4-nucleophilic addition reagent and an eco-friendly cyanide source. To the best of our knowledge, no previous reports of conjugate mono-1,4-hydrocyanation of diarenyl ketones have been made.

Results and discussion

For the optimisation of the mono-1,4-hydrocyanation of diarenyl ketones using $K_4[Fe(CN)_6]$ as an eco-friendly cyanide source we used as model substrate, 1,5-diphenylpenta-1,4-dien-3-one **1a** (Scheme 1, R = H). Because $K_4[Fe(CN)_6]$ is a very stable complex, it is difficult to release cyanide ions in general conditions. In our previous work, it was found that benzoyl chloride is an efficient promoter to activate cyanide ions through the formation of benzoyl cyanide as an intermediate, which could be isolated and identified from the reaction system.[20] Therefore, the hydrocyanation of **1a** with $K_4[Fe(CN)_6]$ was attempted using benzoyl chloride as a promoter, in the expectation that the reaction might afford the mono-1,4-hydrocyanation product **2a** (Scheme 1, R = H) in the presence of appropriate catalysts and solvents. Indeed, this was the case, and it was also found that only 0.2 equiv. of $K_4[Fe(CN)_6]$ was required for 1 equiv. of **1a**, which indicated that six CN^- of $K_4[Fe(CN)_6]$ could be fully utilised in this reaction. In addition, no other side reactions such as 1,2-addition or di-1,4-hydrocyanation were observed, even using an excess of $K_4[Fe(CN)_6]$, which indicated the high chemoselectivity of the reaction.

In addition, it was also found that catalysts played a critical role in the reaction. Various bases were used as catalysts to examine the reaction of **1a** with $K_4[Fe(CN)_6]$ using benzoyl chloride as a promoter and the results are shown in Table 1. No reactions were observed using sodium carbonate or potassium carbonate as catalysts, even after 24 h, but *N,N*-dimethylaminopyridine (DMAP), 1,4-diazabicyclooctane (DABCO) or Et_3N as catalysts gave the product in low yield after heating at 60 °C for 12 h (entries 1–3). However, the reaction proceeded in very good yield under the same conditions in the presence of NaOH or KOH, the latter giving the mono-1,4-hydrocyanation product in slightly higher yield (entries 4 and 5).

The solvent also has a significant effect on the reaction, as shown in Table 2. For example, although there was no reaction



Scheme 1 Mono-1,4-hydrocyanation of diarenyl ketones **1a**–**j** using $K_4[Fe(CN)_6]$ as a cyanide source.

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Table 1 The effect of various bases on the yield of mono-1,4-cyanation of 1,5-diphenylpenta-1,4-dien-3-one **1a** using $K_4[Fe(CN)_6]$ as a cyanide source (Scheme 1)[a]

Entry	Catalyst	Yield/%[b]
1	DMAP	12
2	DABCO	25
3	Et_3N	36
4	NaOH	81
5	KOH	84

[a] Reaction conditions: (i) $K_4[Fe(CN)_6]$ (0.4 mmol)/PhCOCl (2 mmol)/160 °C/3 h; (ii) cooled, then **1a** (1.5 mmol) and base (0.4 mmol) in MeCN (5 mL) were added and stirred at 60 °C for 12 h.
[b] Isolated yield.

Table 2 The effect of solvents on the yield of mono-1,4-hydrocyanation of 1,5-diphenylpenta-1,4-dien-3-one **1a** using $K_4[Fe(CN)_6]$ as a cyanide source (Scheme 1)[a]

Entry	Solvent	Yield/%[b]
1	CH_2Cl_2	33
2	THF	42
3	DMF	45
4	MeOH	68
5	EtOH	74
6	MeCN	84

[a] Reaction conditions: (i) $K_4[Fe(CN)_6]$ (0.4 mmol)/PhCOCl (2 mmol)/160 °C/3 h; (ii) cooled, then **1a** (1.5 mmol) and KOH (0.4 mmol) in solvent (5 mL) were added and stirred at reflux or at 60 °C for 12 h.
[b] Isolated yield.

Table 3 Yields/reaction times of the mono-1,4-hydrocyanation of 1,5-diarylpenta-1,4-dien-3-ones **1a**–**j** using $K_4[Fe(CN)_6]$ as a cyanide source (Scheme 1)[a]

Entry	Compd	R	Reaction time/h	Yield/%[b]
1	**2a**	H	12	84
2	**2b**	2-Me	12	83
3	**2c**	4-Me	13	81
4	**2d**	4-MeO	16	76
5	**2e**	2,3-OCH_2O	11	73
6	**2f**	2-Cl	13	70
7	**2g**	4-Cl	13	81
8	**2h**	4-Br	12	76
9	**2i**	4-NO_2	15	70
10	**2j**	2-furyl[c]	13	78

[a] Reaction conditions: (i) $K_4[Fe(CN)_6]$ (0.4 mmol)/PhCOCl (2 mmol)/160 °C/3 h; (ii) cooled, then **1a**–**j** (1.5 mmol) and KOH (0.4 mmol) in MeCN (5 mL) were added and stirred at 60 °C for 11–16 h.
[b] Isolated yield.
[c] This substituent replaces RC_6H_4.

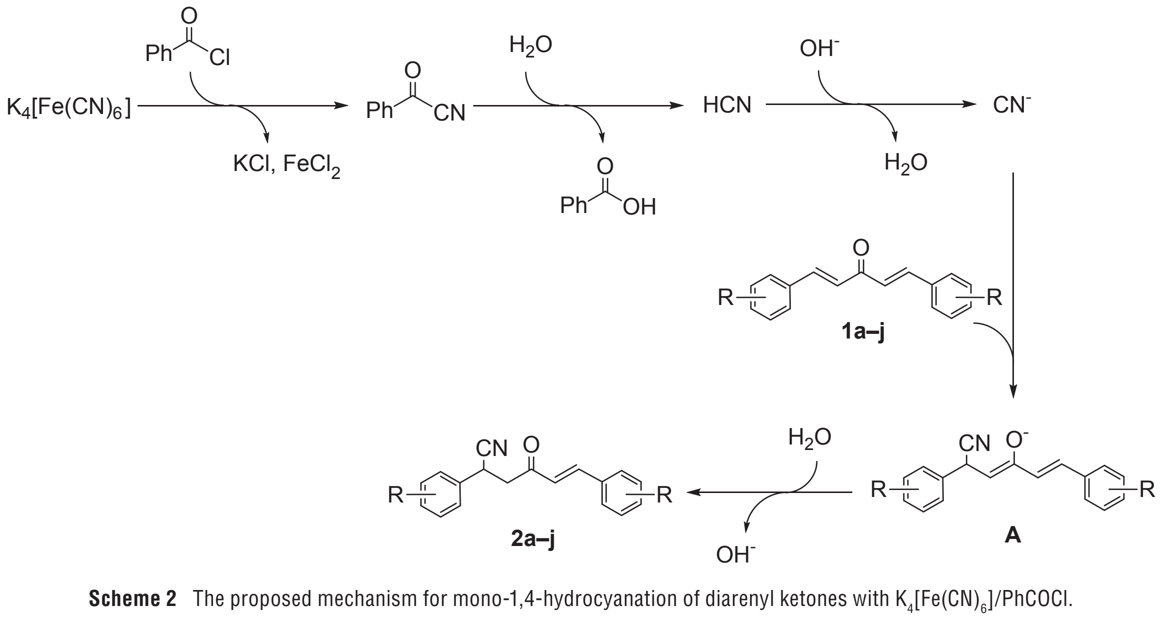
in toluene, in CH_2Cl_2, THF or DMF low yields were obtained (entries 1–3). However, reaction in MeOH, EtOH or MeCN gave the desired product in good to high yield (entries 4–6), the latter giving the best yield.

Mono-1,4-hydrocyanations of various diarenyl ketones with $K_4[Fe(CN)_6]$ were then examined using benzoyl chloride as a promoter and potassium hydroxide as a catalyst in MeCN the results are shown in Table 3. Diarenyl ketones bearing electron-donating groups on their aromatic rings, such as methyl and methoxy, or electron-withdrawing groups, such as chloro, bromo or nitro, all gave 1,4-addition products smoothly in high yield. The substitutents on the diarenyl ketones clearly have no obvious effect on the yield of products. Di(furan-2-ylethenyl) ketone also gave a monohydrocyanation product in good (78%) yield.

A plausible mechanism for the mono-1,4-hydrocyanation of diarenyl ketones **1a**–**j** with $K_4[Fe(CN)_6]$ is shown in Scheme 2. $K_4[Fe(CN)_6]$ first reacts with benzoyl chloride to form benzoyl cyanide. Then benzoyl cyanide is attacked by water in undried MeCN to produce hydrogen cyanide *in situ*, which is converted into cyanide ion in the presence of potassium hydroxide. The cyanide ion then reacts with the diarenyl ketone by 1,4-addition to form an intermediate enolate **A**, which is quenched by water to produce the final monohydrocyanation products **2a**–**j**.

Experimental

IR spectra were recorded using KBr pellets on an Alpha Centauri FTIR spectrophotometer. NMR spectra were obtained on a Mercury-400BB spectrometer (^{1}H NMR at 400 MHz, ^{13}C NMR at 100 MHz) in $CDCl_3$ using Me_4Si as internal standard. Elemental analyses were performed on a Vario El Elemental Analysis instrument. Melting points were determined in an electrothermal melting point apparatus. Potassium hexacyanoferrate(II) was dried at 80 °C under vacuum for 24 h and finely powdered prior to use. Diarenyl ketones were prepared according to literature method.[30]



Scheme 2 The proposed mechanism for mono-1,4-hydrocyanation of diarenyl ketones with $K_4[Fe(CN)_6]$/PhCOCl.

Mono-1,4-hydrocyanation of diarenyl ketones **1a**–**j***; general procedure*

A mixture of potassium hexacyanoferrate(II) (0.4 mmol) and benzoyl chloride (2 mmol) was heated at 160 °C for 3 h. Then the reaction system was cooled to room temperature and diarenyl ketone **1a**–**j** (1.5 mmol), potassium hydroxide (0.4 mmol) and acetonitrile (5 mL) were added. The mixture was stirred at 60 °C for the appropriate time indicated in Table 3. After completion of the reaction (monitored by TLC), the resulting mixture was filtered and the filtrate was concentrated and subjected to column chromatography using petroleum ether and ethyl acetate (V/V = 10 : 1) as eluent to give pure product.

(E)-4-Oxo-2,6-diphenylhex-5-enenitrile (**2a**): White solid; m.p. 120–122 °C (EtOAc); IR (ν_{max}): 1680 (C=O), 2244 (CN) cm^{-1}; ^{1}H NMR: δ 3.14 (dd, *J* = 6.4, 17.6 Hz, 1H, CHCH_aHCO), 3.35 (dd, *J* = 7.6, 17.6 Hz, 1H, CHCHH_bCO), 4.43 (dd, *J* = 6.4, 7.6 Hz, 1H, ArC*H*CH$_2$), 6.64 (d, *J* = 16.0 Hz, 1H, COC*H*=CHAr), 7.19–7.36 (m, 8H, ArH), 7.44–7.46 (m, 2H, ArH), 7.50 (d, *J* = 16.0 Hz, 1H, COCH=C*H*Ar); ^{13}C NMR: δ 31.7, 46.0, 120.5, 124.9, 127.4, 128.3, 128.4, 128.9, 129.2, 130.9, 133.8, 135.2, 144.2, 194.4. Anal. calcd for $C_{18}H_{15}NO$: C, 82.73; H, 5.79; N, 5.36; found: C, 82.67; H, 5.81; N, 5.35%.

(E)-4-Oxo-2,6-di(2-tolyl)hex-5-enenitrile (**2b**): White solid, m.p. 8688 °C (EtOAc); IR (ν_{max}): 1658 (C=O), 2237 (CN) cm^{-1}; ^{1}H NMR: δ 2.33 (s, 3H, CH$_3$), 2.36 (s, 3H, CH$_3$), 3.05 (dd, *J* = 8.8, 17.6 Hz, 1H, CHCH_aHCO), 3.34 (dd, *J* = 8.8, 17.6 Hz, 1H, CHCH_bHCO), 4.55 (dd, *J* = 4.8, 9.6 Hz, 1H, ArC*H*CH$_2$), 6.59 (d, *J* = 16.0 Hz, 1H, COC*H*=CHAr), 7.13–7.24 (m, 6H, ArH), 7.39–7.48 (m, 2H, ArH), 7.83 (d, *J* = 16.0 Hz, 1H, COCH=C*H*Ar); ^{13}C NMR: δ 19.2, 19.8, 28.6, 44.9, 120.7, 125.6, 126.4, 126.5, 126.9, 127.4, 128.4, 130.7, 130.9, 131.2, 132.8, 133.3, 135.3, 138.3, 141.7, 194.5. Anal. calcd for $C_{20}H_{19}NO$: C, 83.01; H, 6.62; N, 4.84; found: C, 82.95; H, 6.61; N, 4.86%.

(E)-4-Oxo-2,6-di(4-tolyl)hex-5-enenitrile (**2c**): White solid, m.p. 140–142 °C (EtOAc); IR (ν_{max}): 1680 (C=O), 2244 (CN) cm^{-1}; ^{1}H NMR: δ 2.28 (s, 3H, CH$_3$), 2.31 (s, 3H, CH$_3$), 3.11 (dd, *J* = 6.4, 17.2 Hz, 1H, CHCH_aHCO), 3.32 (dd, *J* = 8.0, 17.6 Hz, 1H, CHCH_bHCO), 4.39 (dd, *J* = 6.8, 7.6 Hz, ArC*H*CH$_2$), 6.60 (d, *J* = 16.4 Hz, 1H, COC*H*=CHAr), 7.19–7.36 (m, 8H, ArH), 7.47 (d, *J* = 16.4, 1H, COCH=C*H*Ar); ^{13}C NMR: δ 21.1, 21.5, 31.4, 46.0, 120.8, 124.0, 127.3, 128.5, 129.7, 129.8, 131.1, 132.2, 138.2, 141.7, 144.3, 194.5. Anal. calcd for $C_{20}H_{19}NO$: C, 83.01; H, 6.62; N, 4.84; found: C, 83.09; H, 6.64; N, 4.83%.

(E)-2,6-Bis(4-methoxyphenyl)-4-oxohex-5-enenitrile (**2d**): Oil; IR (ν_{max}): 1683 (C=O), 2246 (CN) cm^{-1}; ^{1}H NMR: δ 3.16 (dd, *J* = 6.4, 17.2 Hz, 1H, CHCH_aHCO), 3.37 (dd, *J* = 8.0, 17.6 Hz, 1H, CHCH_bHCO), 3.76 (s, 3H, OCH$_3$), 3.79 (s, 3H, OCH$_3$), 4.45 (dd, *J* = 6.8, 7.6 Hz, ArC*H*CH$_2$), 6.66 (d, *J* = 16.4 Hz, 1H, COC*H*=CHAr), 7.21–7.38 (m, 8H, ArH), 7.54 (d, *J* = 16.4, 1H, COCH=C*H*Ar); ^{13}C NMR: δ 31.6, 46.3, 55.6, 55.9, 120.9, 124.2, 127.5, 128.7, 129.8, 129.9, 131.2, 132.4, 138.3, 141.9, 144.4, 194.6. Anal. calcd for $C_{20}H_{19}NO_3$: C, 74.75; H, 5.96; N, 4.36; found: C, 74.81; H, 5.95; N, 4.35%.

*(E)-2,6-Di(benzo[*d*][1,3]dioxol-5-yl)-4-oxohex-5-enenitrile* (**2e**): Oil; IR (ν_{max}): 1658 (C=O), 2244 (CN) cm^{-1}; ^{1}H NMR: δ 3.17 (dd, *J* = 8.0, 16.0 Hz, 1H, CHCH_aHCO), 3.37 (dd, *J* = 8.0, 16.0 Hz, 1H, CHCH_bHCO), 4.45 (dd, *J* = 4.8, 9.6 Hz, 1H, ArC*H*CH$_2$), 6.00 (s, 2H, CH$_2$), 6.05 (s, 2H, CH$_2$), 6.56 (d, *J* = 16.0 Hz, 1H, COC*H*=CHAr), 6.83–7.06 (m, 6H, ArH), 7.51 (d, *J* = 16.0, 1H, COCH=C*H*Ar); ^{13}C NMR: δ 31.5, 46.2, 101.5, 101.8, 106.5, 107.9, 108.8, 120.7, 121.0, 123.0, 125.5, 128.3, 128.8, 144.2, 147.6, 148.3, 148.5, 150.4, 193.2. Anal. calcd for $C_{20}H_{15}NO_5$: C, 68.76; H, 4.33; N, 4.01; found: C, 68.65; H, 4.32; N, 4.02%.

(E)-2,6-Bis(2-chlorophenyl)-4-oxohex-5-enenitrile (**2f**): Oil; IR (ν_{max}): 1661 (C=O), 2242 (CN) cm^{-1}; ^{1}H NMR: δ 3.02 (dd, *J* = 6.0, 16.0 Hz, 1H, CHCH_aHCO), 3.24 (dd, *J* = 6.0, 16.0 Hz, 1H, CHCH_bHCO), 4.27 (dd, *J* = 7.6, 8.0 Hz, 1H, ArC*H*CH$_2$), 6.52 (d, *J* = 16.0 Hz, 1H, COC*H*=CHAr), 7.05–7.35 (m, 8H, ArH), 7.34 (d, *J* = 16.0, 1H, COCH=C*H*Ar); ^{13}C NMR: δ 28.9, 44.9, 120.9, 125.7, 126.6, 126.7, 127.2, 127.6, 128.7, 130.8, 130.9, 131.5, 132.9, 133.6, 135.7, 138.6, 141.9, 194.7. Anal. calcd for $C_{18}H_{13}Cl_2NO$: C, 65.47; H, 3.97; N, 4.24; found: C, 65.56; H, 3.96; N, 4.25%.

(E)-2,6-Bis(4-chlorophenyl)-4-oxohex-5-enenitrile (**2g**): White solid, m.p. 104–106 °C (EtOAc); IR (ν_{max}): 1656 (C=O), 2235 (CN) cm^{-1}; ^{1}H NMR: δ 3.00 (dd, *J* = 6.0 16.0 Hz, 1H, CHCH_aHCO), 3.21 (dd, *J* = 6.0, 16.0 Hz, 1H, CHCH_bHCO), 4.29 (dd, *J* = 7.6, 8.0 Hz, 1H, ArC*H*CH$_2$), 6.50 (d, *J* = 16.0 Hz, 1H, COC*H*=CHAr), 7.047.32 (m, 8H, ArH), 7.36 (d, *J* = 16.0 Hz, 1H, COCH=C*H*Ar); ^{13}C NMR: δ 31.5, 44.2, 120.3, 124.8, 127.2, 127.8, 128.1, 128.5, 128.9, 133.6, 134.9, 135.3, 145.1, 194.3. Anal. calcd for $C_{18}H_{13}Cl_2NO$: C, 65.47; H, 3.97; N, 4.24; found: C, 65.39; H, 3.97; N, 4.23%.

(E)-2,6-Bis(4-bromophenyl)-4-oxohex-5-enenitrile (**2h**): Oil; IR (ν_{max}): 1653 (C=O), 2231 (CN) cm^{-1}; ^{1}H NMR: δ 2.98 (dd, *J* = 6.0 16.0 Hz, 1H, CHCH_aHCO), 3.19 (dd, *J* = 6.0, 16.0 Hz, 1H, CHCH_bHCO), 4.28 (dd, *J* = 7.6, 8.0 Hz, 1H, ArC*H*CH$_2$), 6.49 (d, *J* = 16.0 Hz, 1H, COC*H*=CHAr), 7.02–7.30 (m, 8H, ArH), 7.33 (d, *J* = 16.0 Hz, 1H, COCH=C*H*Ar); ^{13}C NMR: δ 31.3, 44.1, 120.1, 124.5, 127.0, 127.5, 127.9, 128.2, 128.6, 133.2, 134.5, 135.1, 145.0, 194.2. Anal. calcd for $C_{18}H_{13}Br_2NO$: C, 51.58; H, 3.13; N, 3.34; found: C, 51.66; H, 3.12; N, 3.35%.

(E)-2,6-Bis(4-nitrophenyl)-4-oxohex-5-enenitrile (**2i**): Oil; IR (ν_{max}): 1658 (C=O), 2251 (CN) cm^{-1}; ^{1}H NMR: δ 3.05 (dd, *J* = 7.6, 16.0 Hz, 1H, CHCH_aHCO), 3.36 (dd, *J* = 7.6, 16.0 Hz, 1H, CHCH_bHCO), 4.33 (dd, *J* = 7.6, 8.0 Hz, 1H, ArC*H*CH$_2$), 6.58 (d, *J* = 16.0 Hz, 1H, COC*H*=CHAr), 7.37–7.40 (m, 2H, ArH), 7.42 (d, *J* = 16.0 Hz, 1H, COCH=C*H*Ar), 8.01–8.26 (m, 6H, ArH); ^{13}C NMR: δ 31.8, 44.6, 120.7, 125.1, 127.6, 127.9, 128.3, 128.8, 128.9, 133.8, 135.0, 135.8, 150.7, 194.6. Anal. calcd for $C_{18}H_{13}N_3O_5$: C, 61.54; H, 3.73; N, 11.96; found: C, 61.60; H, 3.72; N, 11.92%.

(E)-2,6-Bis(furan-2-yl)-4-oxohex-5-enenitrile (**2j**): Oil; IR (ν_{max}): 1678 (C=O), 2247 (CN) cm^{-1}; ^{1}H NMR: δ 3.17 (dd, *J* = 6.4, 17.6 Hz, 1H, CHCH_aHCO), 3.36 (dd, *J* = 7.6, 17.6 Hz, 1H, CHCHH_bCO), 4.46 (dd, *J* = 6.4, 7.6 Hz, 1H, ArC*H*CH$_2$), 6.34–6.81 (m, 3H, FuH), 6.68 (d, *J* = 16.0 Hz, 1H, COC*H*=CHFu), 7.45–7.62 (m, 2H, FuH), 7.53 (d, *J* = 16.0 Hz, 1H, COCH=C*H*Fu), 8.13 (d, *J* = 6.8 Hz, 1H, FuH); ^{13}C NMR: δ 31.9, 46.4, 106.3, 109.8, 110.2, 112.9, 113.2, 120.4, 129.5, 132.2, 141.5, 143.2, 154.6, 194.9. Anal. calcd for $C_{14}H_{11}NO_3$: C, 69.70; H, 4.60; N, 5.81; found: C, 69.64; H, 4.61; N, 5.83%.

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