Base promoted cascade approach for the preparation of reduced Knoevenagel adducts using Hantzsch esters as reducing agent in water

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General Methods: All starting materials were of the commercially available (analytical grade) and used without further purification. All the solvents are used after redistillation. Reactions were monitored by thin layer chromatography using silica gel HSGF254 plates. Flash chromatography was performed using silica gel HG/T2354-92. Melting points were measured with SGW X-4 melting point apparatus. 1H NMR (300, 400 or 600 MHz) spectra were recorded in CDCl3. 1H NMR chemical shifts are reported in ppm ( ) relative to tetramethylsilane (TMS) with the solvent resonance employed as the internal standard (CDCl3, δ = 7.26 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, q = quartet, m = multiplet), coupling constants (Hz) and integration. 13C NMR chemical shifts are reported in ppm from tetramethylsilane (TMS) with the solvent resonance as the internal standard (CDCl3, δ = 77.0ppm). Chemical yields refer to pure isolated substances. All products were prepared according to the general procedure. All the products are known compounds and their 1H NMR data (For 3ba-3bm and 3ca-3cn, the spectra data are the products synthesized in the presence of DEAE) matched the literature data.1-8

General experimental procedures for preparing reduced Knoevenagel adducts of malononitrile: The mixture of aldehydes (0.2 mmol), malononitrile(0.24 mmol) and Hantzsch esters (0.24 mmol) in water (2.0 mL) was stirred at 100 °C for 12 h. After the reaction mixtures were cooled to room temperature, the crude solution was extracted with ethyl acetate (3 x 5 mL). The combined organic layers were washed with brine and dried over anhydrous Na2SO4. After removal of solvents under reduced pressure, the residue was purified through column chromatograph on silica gel to give the pure products.
General experimental procedures for preparing reduced Knoevenagel adducts of ethyl 2-cyanoacetate: The mixture of aldehydes (0.2 mmol), ethyl 2-cyanoacetate (0.24 mmol), DEAE or K$_2$CO$_3$ (0.02 mmol) and Hantzsch esters (0.24 mmol) in water (2.0 mL) was stirred at 100 °C for 12 h. After the reaction mixtures were cooled to room temperature, the crude solution was extracted with ethyl acetate (3 x 5 mL). The combined organic layers were washed with brine and dried over anhydrous Na$_2$SO$_4$. After removal of solvents under reduced pressure, the residue was purified through column chromatograph on silica gel to give the pure products.

General experimental procedures for preparing reduced Knoevenagel adducts of 2-(4-nitrophenyl)-acetonitrile: The mixture of aldehydes (0.2 mmol), 2-(4-nitrophenyl) acetonitrile (0.24 mmol), DEAE or K$_2$CO$_3$ (0.2 mmol) and Hantzsch esters (0.24 mmol) in water (2.0 mL) was stirred at 100 °C for 12 h. After the reaction mixtures were cooled to room temperature, the crude solution was extracted with ethyl acetate (3 x 5 mL). The combined organic layers were washed with brine and dried over anhydrous Na$_2$SO$_4$. After removal of solvents under reduced pressure, the residue was purified through column chromatograph on silica gel to give the pure products.

The gram-scale synthesis of 3-(naphthalen-2-yl)-2-(4-nitrophenyl)propanenitrile: The mixture of 2-naphthaldehyde (1.00 g, 6.41 mmol), 2-(4-nitrophenyl) acetonitrile (1.25 g, 7.69 mmol), DEAE (169.5 ul, 1.28 mmol) and Hantzsch esters (1.94 g, 7.69 mmol) in water (10.0 mL) was stirred at 100 °C for 12 h. After the reaction mixtures were cooled to room temperature, the crude product was separated by filtration. The pure product was obtained through column chromatograph on silica gel.

2-benzylmalononitrile (3aa): The crude mixture was purified by column chromatography using Petroleum ether /EtOAc (15/1) to yield 3aa as white solid with 88% yield. $^1$HNMR (400 MHz, CDCl$_3$): 3.29 (d, J = 6.92 Hz, 2H), 3.96 (t, J = 6.96 Hz, 1H), 7.32-7.42 (m, 5H).

2-(4-methylbenzyl)malononitrile (3ab): The crude mixture was purified by column chromatography using Petroleum ether /EtOAc (15/1) to yield
3ab white solid with 86% yield. $^1$H NMR (400 MHz, CDCl$_3$): 2.39 (s, 3H), 3.27 (d, J = 6.92 Hz, 2H), 3.90 (t, J = 6.92 Hz, 1H), 7.23-7.29 (m, 4H).

2-(4-methoxybenzyl)malononitrile (3ac): the crude mixture was purified by column chromatography using Petroleum ether / EtOAc (10/1) to yield 3ac as white solid with 77% yield. Mp.: 88-89°C. $^1$H NMR (400 MHz, CDCl$_3$) : 3.26(d, J = 6.84 Hz, 2H), 3.84(s, 3H), 3.89(t, J = 6.80 Hz, 1H), 6.95(d, J = 8.64 Hz, 2H), 7.28(d, J = 8.68 Hz, 2H).

2-(4-fluorobenzyl)malononitrile (3ad): the crude mixture was purified by column chromatography using Petroleum ether / EtOAc (10/1) to yield 3ad as white solid with 87% yield. Mp.: 120-121°C. $^1$H NMR (400 MHz, CDCl$_3$) : 3.29 (d, J = 6.76 Hz, 2H), 3.93 (t, J = 6.84 Hz, 1H), 7.13 (t, J = 8.64 Hz, 2H), 7.32-7.36 (m, 2H).

2-(4-chlorobenzyl)malononitrile (3ae): the crude mixture was purified by column chromatography using Petroleum ether / EtOAc (10/1) to yield 3ae as white solid with 77% yield. Mp.: 97°C. $^1$H NMR (400 MHz, CDCl$_3$) : 3.29 (d, J = 6.76 Hz, 2H), 3.94 (t, J = 6.80 Hz, 1H), 7.29 (d, J = 8.64 Hz, 2H), 7.42 (d, J = 8.44 Hz, 2H).

2-(4-bromobenzyl)malononitrile (3af): The crude mixture was purified by column chromatography using Petroleum ether / EtOAc (15/1) to yield 3af as white solid with 94% yield. $^1$HNMR (400 MHz, CDCl$_3$): 3.27 (d, J = 6.76 Hz, 2H), 3.93 (t, J = 6.72 Hz, 1H), 7.23 (d, J = 8.32 Hz, 2H), 7.57 (d, J = 8.44 Hz, 2H).

4-(2,2-dicyanoethyl)benzonitrile (3ag): the crude mixture was purified by column chromatography using Petroleum ether / EtOAc (10/1) to yield 3ag as light yellow solid with 85% yield. Mp.: 113-114°C. $^1$H NMR (400 MHz, CDCl$_3$) δ 3.38(d, J = 6.68 Hz, 2H), 4.05(t, J = 6.68 Hz, 1H), 7.50(d, J = 8.20 Hz, 2H), 7.75(d, J = 8.24 Hz, 2H).
2-(4-nitrobenzyl)malononitrile (3ah): the crude mixture was purified by column chromatography using Petroleum ether / EtOAc (10/1) to yield 3ah as light yellow solid with 87% yield. Mp.: 148-150°C. $^1$H NMR (400 MHz, CDCl$_3$) δ 3.44(d, $J = 6.60$ Hz, 2H), 4.06(t, $J = 6.64$ Hz, 1H), 7.58(d, $J = 8.64$ Hz, 2H), 8.32(d, $J = 8.64$ Hz, 2H).

2-(2-nitrobenzyl)malononitrile (3ai): the crude mixture was purified by column chromatography using Petroleum ether / EtOAc (10/1) to yield 3ai as light yellow solid with 62% yield. Mp.: 148-150°C. $^1$H NMR (400 MHz, CDCl$_3$) δ 3.61(d, $J = 7.76$ Hz, 2H), 4.48(t, $J = 7.80$ Hz, 1H), 7.51-7.69(m, 2H), 7.74-7.78(m, 1H).

2-(3-nitrobenzyl)malononitrile (3aj): the crude mixture was purified by column chromatography using Petroleum ether / EtOAc (10/1) to yield 3aj as light yellow solid with 68% yield. Mp.: 126-128°C. $^1$H NMR (400 MHz, CDCl$_3$) δ 3.46(d, $J = 6.76$ Hz, 2H), 4.06(t, $J = 6.76$ Hz, 1H), 7.65-7.76(m, 2H).

2-(naphthalen-2-ylmethyl)malononitrile (3ak): The crude mixture was purified by column chromatography using Petroleum ether / EtOAc (15/1) to yield 3ak as white solid with 77% yield. $^1$HNMR (400 MHz, CDCl$_3$): 3.82 (d, $J = 7.60$ Hz, 2H), 4.10 (t, $J = 7.68$ Hz, 1H), 7.50 - 7.67 (m, 4H), 7.88 - 7.98 (m, 3H).

2-(furan-2-ylmethyl)malononitrile (3al): The crude mixture was purified by column chromatography using Petroleum ether / EtOAc (10/1) to yield 3al as white solid with 68% yield. $^1$HNMR (400 MHz, CDCl$_3$): 3.40 (d, $J = 7.0$ Hz, 2H), 4.07 (t, $J = 7.04$ Hz, 1H), 6.41 (d, $J = 1.56$ Hz, 2H), 7.45 (s, 1H).
2-propylmalononitrile (3am): The crude mixture was purified by column chromatography using Petroleum ether /EtOAc (10/1) to yield 3am as brown solid with 45% yield. $^1$H NMR (400 MHz, CDCl$_3$): 1.06 (t, $J = 7.36$ Hz, 3H), 1.62 - 1.72 (m, 2H), 2.02 - 2.07 (m, 2H), 3.75 (t, $J = 6.88$ Hz, 1H).

ethyl 2-cyano-3-phenylpropanoate (3ba): The crude mixture was purified by column chromatography using Petroleum ether /Dichloromethane (3/1) to yield 3ba as colorless oil (92% and 90% yield respectively). $^1$H NMR (400 MHz, CDCl$_3$): 1.29 (t, $J = 7.20$ Hz, 3H), 3.19 - 3.33 (m, 2H), 3.72-3.75 (m, 1H), 4.27 (q, $J = 7.20$ Hz, 2H), 7.29-7.37 (m, 5H).

ethyl 2-cyano-3-p-tolylpropanoate (3bb): The crude mixture was purified by column chromatography using Petroleum ether /Dichloromethane (3/1) to yield 3bb as colorless oil (85% and 83% yield respectively). $^1$H NMR (400 MHz, CDCl$_3$): 1.30 (t, $J = 7.16$ Hz, 3H), 2.36 (s, 3H), 3.15 - 3.29 (m, 2H), 3.72 (dd, $J = 5.84$, 8.40 Hz, 1H), 4.24 - 4.30 (m, 2H), 7.15-7.20 (m, 4H).

ethyl 2-cyano-3-(4-methoxyphenyl)propanoate (3bc): The crude mixture was purified by column chromatography using Petroleum ether /Dichloromethane (3/1) to yield 3bc as colorless oil (83% and 88% yield respectively). $^1$H NMR (400 MHz, CDCl$_3$): 1.29(t, $J = 7.16$ Hz, 3H), 3.13-3.26(m, 2H), 3.70(dd, $J = 5.84$, 8.24 Hz, 1H), 3.82(s, 3H), 4.25(q, $J = 7.16$ Hz, 2H), 6.89(d, $J = 8.60$Hz, 2H), 7.20-7.23(m, 2H).

ethyl 2-cyano-3-(4-fluorophenyl)propanoate (3bd): The crude mixture was purified by column chromatography using Petroleum ether /Dichloromethane (3/1) to yield 3bd as colorless oil (90% and 91% yield respectively). $^1$H NMR (400 MHz, CDCl$_3$): 1.29(t, $J = 7.12$ Hz, 3H), 3.17-3.29(m, 2H), 3.72(dd, $J = 5.80$, 8.12 Hz, 1H), 4.19-4.37(m, 2H), 7.05(t, $J = 8.60$ Hz, 2H), 7.19-7.33(m, 2H).
ethyl 3-(4-chlorophenyl)-2-cyanopropanoate (3be): The crude mixture was purified by column chromatography using Petroleum ether / Dichloromethane (3/1) to yield 3be as colorless oil (85% and 80% yield respectively). \(^1\)H NMR (400 MHz, CDCl\(_3\)): 1.30(t, \(J = 7.16\) Hz, 3H), 3.17-3.29(m, 2H), 3.61-3.87(m, 1H), 4.26(q, \(J = 7.10\) Hz, 2H), 7.24(d, \(J = 8.36\) Hz, 2H), 7.34(d, \(J = 8.40\) Hz, 2H).

ethyl 3-(4-bromophenyl)-2-cyanopropanoate (3bf): The crude mixture was purified by column chromatography using Petroleum ether / Dichloromethane (3/1) to yield 3bf as colorless oil (92% and 91% yield respectively). \(^1\)HNMR (400 MHz, CDCl\(_3\)): 1.30 (t, \(J = 7.12\) Hz, 3H), 3.15 - 3.27 (m, 2H), 3.73 (dd, \(J = 5.88, 8.00\) Hz, 1H), 4.27 (q, \(J = 7.12\) Hz, 2H), 7.18 (d, \(J = 8.24\) Hz, 2H), 7.49 (d, \(J = 8.24\) Hz, 2H).

ethyl 2-cyano-3-(4-cyanophenyl)propanoate (3bg): the crude mixture was purified by column chromatography using Petroleum ether / Dichloromethane (3/1) to yield 3bg as white solid (88% and 82% yield respectively). Mp.: 71 - 72°C. \(^1\)H NMR (400 MHz, CDCl\(_3\)): 1.30(t, \(J = 7.16\) Hz, 3H), 3.26-3.38(m, 2H), 3.75-3.80(m, 1H), 4.28(q, \(J = 7.12\) Hz, 2H), 7.44(d, \(J = 8.16\) Hz, 2H), 7.68(d, \(J = 8.20\) Hz, 2H).

ethyl 2-cyano-3-(2-nitrophenyl)propanoate (3bi): the crude mixture was purified by column chromatography using Petroleum ether / EtOAc (10/1) to yield 3bi as yellow solid (75% and 72% yield respectively). Mp.: 58°C. \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta 1.34(t, J = 7.12 \text{ Hz}, 3\text{H}), 3.31(dd, J = 9.84, 13.52 \text{ Hz}, 1\text{H}), 3.73(dd, J = 5.76, 13.52 \text{ Hz}, 1\text{H}), 4.15(dd, J = 5.76, 9.88 \text{ Hz}, 1\text{H}), 4.28-4.34(m, 2\text{H}), 7.53-7.58(m, 2\text{H}), 7.65-7.74(m, 1\text{H}), 8.10-8.12(m, 1\text{H}).

ethyl 2-cyano-3-(3-nitrophenyl)propanoate (3bj): the crude mixture was purified by column chromatography using Petroleum ether / EtOAc (10/1) to yield 3bj as light yellow solid (90% and 83% yield respectively). Mp.: 60°C. \(^1\)H NMR (400 MHz, CDCl\(_3\)): 1.31(t, \(J = 7.12\) Hz, 3H), 3.32-3.44(m, 2H), 3.84(dd, \(J = 5.92, 8.00\) Hz, 2H).
Hz, 1H), 4.29(q, J = 7.16 Hz, 2H), 7.58(t, J = 7.92 Hz, 1H), 7.69(d, J = 7.64 Hz, 1H), 8.12-8.29(m, 2H).

**ethyl 2-cyano-3-(naphthalen-2-yl)propanoate (3bk):** The crude mixture was purified by column chromatography using Petroleum ether / Dichloromethane (3/1) to yield 3bk as colorless oil (80% and 82% yield respectively). $^1$HNMR (400 MHz, CDCl$_3$): 1.30 (t, J = 7.16 Hz, 3H), 3.57 (dd, J = 10.80, 15.40 Hz, 2H), 3.91 - 3.93 (m, 1H), 4.28 (q, J = 7.08 Hz, 2H), 7.46-7.62 (m, 4H), 7.85 (d, J = 7.76 Hz, 1H), 7.93 (d, J = 7.92 Hz, 1H), 7.98 (d, J = 8.32 Hz, 1H).

**ethyl 2-cyano-3-(furan-2-yl)propanoate (3bl):** The crude mixture was purified by column chromatography using Petroleum ether / Dichloromethane (3/1) to yield 3bl as colorless oil (68% and 65% yield respectively). $^1$HNMR (400 MHz, CDCl$_3$): 1.33 (t, J = 7.12 Hz, 3H), 3.26 - 3.38 (m, 2H), 3.85 (dd, J = 6.20, 7.84 Hz, 1H), 4.30 (q, J = 7.12, 2H), 6.27 (d, J = 3.08 Hz, 1H), 6.35 (t, J = 2.84 Hz, 1H), 7.39 (s, 1H).

**ethyl 2-cyanopentanoate (3bm):** The crude mixture was purified by column chromatography using Petroleum ether / Dichloromethane (3/1) to yield 3bm as colorless oil (45% and 40% yield respectively). $^1$HNMR (400 MHz, CDCl$_3$): 1.02 (t, J = 7.00 Hz, 3H), 1.35 (t, J = 7.12 Hz, 3H), 1.56 - 1.59 (m, 2H), 1.97 (q, J = 8.04 Hz, 2H), 3.52 (t, J = 6.84 Hz, 1H), 4.30 (q, J = 7.16 Hz, 2H).

**2-(4-nitrophenyl)-3-phenylpropanenitrile (3ca):** The crude mixture was purified by column chromatography using Petroleum ether /EtOAc (10/1) to yield 3ca as yellow solid (91% and 89% yield respectively). $^1$HNMR (600 MHz, CDCl$_3$): 3.10 (dd, J = 6.72, 13.62 Hz, 1H), 3.20 (dd, J = 7.68, 13.68 Hz, 1H), 4.07 (t, J = 7.14 Hz, 1H), 7.01 - 7.02 (m, 2H), 7.22 (d, J = 5.70 Hz, 3H), 7.32 (d, J = 8.22 Hz, 2H), 8.13 (d, J = 8.16 Hz, 2H).
2-(4-Nitro-phenyl)-5-phenyl-pentanenitrile (3cb): The crude mixture was purified by column chromatography using Petroleum ether/EtOAc (10/1) to yield 3cb as white solid (75% and 82% yield respectively). $^{1}$HNMR (400 MHz, CDCl$_3$): 2.35 (s, 3H), 3.15 (dd, J = 6.76, 13.64 Hz, 1H), 3.24 (dd, J = 7.56, 13.64 Hz, 1H), 4.14 (t, J = 7.52 Hz, 1H), 6.98 (d, J = 7.92 Hz, 2H), 7.10 (d, J = 7.84 Hz, 2H), 7.42 (d, J = 8.64 Hz, 2H), 8.22 (d, J = 8.72 Hz, 2H).

3-(4-methoxyphenyl)-2-(4-nitrophenyl)propanenitrile (3cc): The crude mixture was purified by column chromatography using Petroleum ether/EtOAc (10/1) to yield 3cc as yellow oil (85% and 85% yield respectively). $^{1}$HNMR (600 MHz, CDCl$_3$): 3.10 - 3.20 (m, 2H), 3.78 (s, 3H), 4.10 (t, J = 7.20 Hz, 1H), 6.80 (d, J = 8.46 Hz, 2H), 6.97 (d, J = 8.40 Hz, 2H), 7.37 (d, J = 8.58 Hz, 2H), 8.19 (d, J = 8.58 Hz, 2H).

3-(4-fluorophenyl)-2-(4-nitrophenyl)propanenitrile (3cd): The crude mixture was purified by column chromatography using Petroleum ether/EtOAc (10/1) to yield 3cd as white solid (85% and 87% yield respectively). $^{1}$HNMR (400 MHz, CDCl$_3$): 3.16 - 3.25 (m, 2H), 4.16 (t, J = 6.96 Hz, 1H), 6.99 - 7.09 (m, 2H), 7.42 (d, J = 8.44 Hz, 2H), 8.24 (d, J = 8.36 Hz, 2H).

3-(4-chlorophenyl)-2-(4-nitrophenyl)propanenitrile (3ce): The crude mixture was purified by column chromatography using Petroleum ether/EtOAc (10/1) to yield 3ce as white solid (88% and 90% yield respectively). $^{1}$HNMR (400 MHz, CDCl$_3$): 3.16 - 3.25 (m, 2H), 4.16 (t, J = 7.04 Hz, 1H), 7.04 (d, J = 8.36 Hz, 2H), 7.29 (d, J = 8.68 Hz, 2H), 7.43 (d, J = 8.68 Hz, 2H), 8.24 (d, J = 8.72 Hz, 2H).

3-(4-bromophenyl)-2-(4-nitrophenyl)propanenitrile (3cf): The crude mixture was purified by column chromatography using
Petroleum ether /EtOAc (10/1) to yield 3cf as red solid (95% and 92% yield respectively).

1HNMR (400 MHz, CDCl3): 3.18 - 3.21 (m, 2H), 4.16 (t, J = 6.96 Hz, 1H), 6.98 (d, J = 8.32 Hz, 2H), 7.42 - 7.46 (m, 4H), 8.24 (d, J = 8.68 Hz, 2H).

4-(2-cyano-2-(4-nitrophenyl)ethyl)benzonitrile (3cg): The crude mixture was purified by column chromatography using Petroleum ether /EtOAc (10/1) to yield 3cg as yellow solid (78% and 75% yield respectively). 1HNMR (400 MHz, CDCl3): 3.30 (d, J = 7.08 Hz, 2H), 4.23 (t, J = 7.04 Hz, 1H), 7.25 (d, J = 8.12 Hz, 2H), 7.45 (d, J = 8.64 Hz, 2H), 7.63 (d, J = 8.12 Hz, 2H), 8.26 (d, J = 8.64 Hz, 2H).

2,3-bis(4-nitrophenyl)propanenitrile (3ch): The crude mixture was purified by column chromatography using Petroleum ether /EtOAc (10/1) to yield 3ch as yellow solid (86% and 84% yield respectively).

1HNMR (400 MHz, CDCl3): 3.35 (d, J = 7.08 Hz, 2H), 4.26 (t, J = 7.04 Hz, 1H), 7.32 (d, J = 8.52 Hz, 2H), 7.47 (d, J = 8.60 Hz, 2H), 8.21 (d, J = 8.48 Hz, 2H), 8.28 (d, J = 8.60 Hz, 2H).

3-(2-nitrophenyl)-2-(4-nitrophenyl)propanenitrile (3ci): The crude mixture was purified by column chromatography using Petroleum ether /EtOAc (10/1) to yield 3ci as yellow solid (80% and 82% yield respectively). HNMR (600 MHz, CDCl3): 3.25 (t, J = 10.74 Hz, 1H), 3.58 (dd, J = 8.40, 13.32 Hz, 1H), 4.54 (t, J = 10.56 Hz, 1H), 7.48 (d, J = 7.62 Hz, 1H), 7.55 (t, J = 8.16 Hz, 1H), 7.66 – 7.71 (m, 3H), 8.12 (d, J = 8.16 Hz, 1H), 8.29 (d, J = 8.58 Hz, 2H).

3-(3-nitrophenyl)-2-(4-nitrophenyl)propanenitrile (3cj): The crude mixture was purified by column chromatography using Petroleum ether /EtOAc (10/1) to yield 3cj as white solid (83% and 84% yield respectively). 1HNMR (400 MHz, CDCl3): 3.36 (d, J = 7.28 Hz, 2H), 4.27 (t, J = 7.24 Hz, 1H), 7.50 - 7.58 (m, 4H), 8.05 (s, 1H), 8.20 (d, J = 7.92 Hz, 1H), 8.28 (d, J = 8.56 Hz, 2H).
3-(naphthalen-2-yl)-2-(4-nitrophenyl)propanenitrile (3ck):
The crude mixture was purified by column chromatography using Petroleum ether /EtOAc (10/1) to yield 3ck as yellow solid in 97% yield (89% and 87% yield respectively). $^1$HNMR (400 MHz, CDCl$_3$): 3.57 - 3.62 (m, 1H), 3.74 - 3.8114 (m, 1H), 4.33 (t, J = 7.64 Hz, 1H), 7.21 (d, J = 6.92 Hz, 1H), 7.38 - 7.43 (m, 3H), 7.55 - 7.61 (m, 2H), 7.83 - 7.95 (m, 3H), 8.21 (d, J = 8.64 Hz, 2H).

3-(furan-2-yl)-2-(4-nitrophenyl)propanenitrile (3cl):
The crude mixture was purified by column chromatography using Petroleum ether /EtOAc (10/1) to yield 3ci as white solid (88% and 87% yield respectively). $^1$HNMR (400 MHz, CDCl$_3$): 3.21 (dd, J = 7.12, 14.88 Hz, 1H), 3.36 (dd, J = 7.44, 14.88 Hz, 1H), 4.31 (t, J = 7.28 Hz, 1H), 6.11 (d, J = 3.16 Hz, 1H), 6.31 (t, J = 3.00 Hz, 1H), 7.37 (d, J = 1.32 Hz, 1H), 7.45 (d, J = 8.40 Hz, 2H), 8.22 (d, J = 8.40 Hz, 2H).

2-(4-nitrophenyl)-5-phenylpent-4-enenitrile (3cm):
The crude mixture was purified by column chromatography using Petroleum ether /EtOAc (10/1) to yield 3cm as yellow solid (75% and 72% yield respectively). $^1$HNMR (400 MHz, CDCl$_3$): 2.87 (t, J = 7.28 Hz, 2H), 4.09 (t, J = 6.96 Hz, 1H), 6.11 - 6.19 (m, 1H), 6.52 (d, J = 15.72 Hz, 1H), 7.26 - 7.35 (m, 5H), 7.58 (d, J = 8.64 Hz, 2H), 8.30 (d, J = 8.72 Hz, 2H);

2-(4-nitrophenyl)pentanenitrile (3cn):
The crude mixture was purified by column chromatography using Petroleum ether /EtOAc (10/1) to yield 3cn as yellow oil (50% and 53% yield respectively); $^1$HNMR (400 MHz, CDCl$_3$): 1.01 (t, J = 7.36 Hz, 3H), 1.54 – 1.58 (m, 2H), 1.86 - 2.00 (m, 2H), 3.95 (t, J = 6.28 Hz, 1H), 7.55 (d, J = 8.60 Hz, 2H), 8.28 (d, J = 8.72 Hz, 2H).

References
$^1$H and $^{13}$C NMR Spectra:

The $^1$H NMR Spectra of 3aa

The $^1$H NMR Spectra of 3ab
The $^1$H NMR Spectra of 3ac

The $^1$H NMR Spectra of 3ad
The $^1$H NMR Spectra of 3ae

The $^1$H NMR Spectra of 3af
The $^1$H NMR Spectra of 3ag

The $^1$H NMR Spectra of 3ah
The $^1$H NMR Spectra of 3ai
The $^1$H NMR Spectra of 3aj

The $^1$H NMR Spectra of 3ak

The $^1$H NMR Spectra of 3al
The $^1$H NMR Spectra of 3am

The $^1$H NMR Spectra of 3ba
The $^1$H NMR Spectra of 3bb
The $^1$H NMR Spectra of 3bc

The $^1$H NMR Spectra of 3bd

The $^1$H NMR Spectra of 3be
The $^1$H NMR Spectra of 3bf
The $^1$H NMR Spectra of 3bi

The $^1$H NMR Spectra of 3bj
The $^1$H NMR Spectra of 3bk

The $^1$H NMR Spectra of 3bl
The $^1$H NMR Spectra of 3bm

The $^1$H NMR Spectra of 3ca
The $^1$H NMR Spectra of 3cb

The $^1$H NMR Spectra of 3cc
The $^1$H NMR Spectra of 3cd

The $^1$H NMR Spectra of 3ce
The $^1$H NMR Spectra of 3cf

The $^1$H NMR Spectra of 3cg
The $^1$H NMR Spectra of 3ch

The $^1$H NMR Spectra of 3ci
The $^1$H NMR Spectra of 3cj
The $^1$H NMR Spectra of 3ck

The $^1$H NMR Spectra of 3cl

The $^1$H NMR Spectra of 3cm
The $^1$H NMR Spectra of 3cn