Supplementary Material (ESI) for Green Chemistry

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ELECTRONIC SUPPORTING INFORMATION (ESI)

Efficient Co(II) heterogeneously catalysed synthesis of α-aminonitriles at room temperature via Strecker-type reactions

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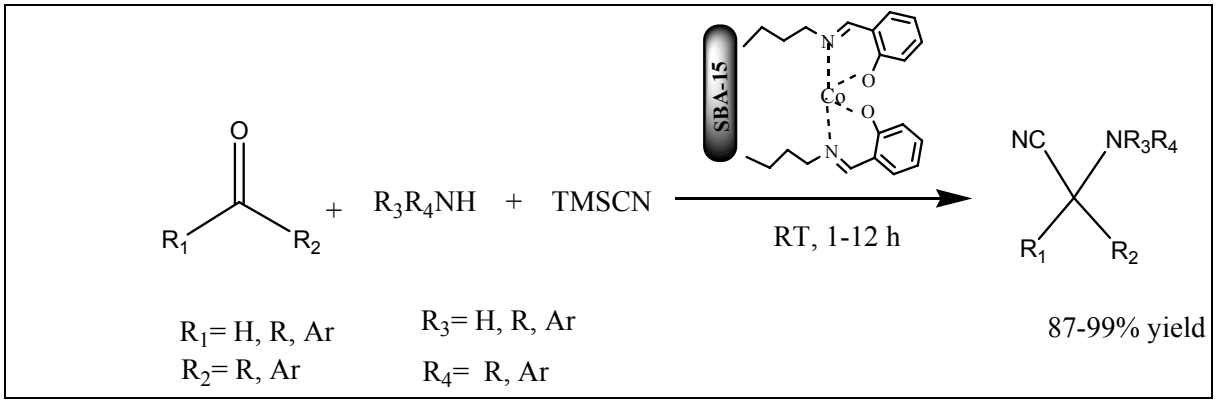

Scheme1. Three-component Strecker reaction of various aldehydes, ketones, and amines using a supported cobalt(II)/SBA-15 catalyst under solventless conditions.

Preparation of SBA-15-NH_2

Co-condensed amino-SBA-15 silicas were synthesized according to the procedure described by Wang et al. (Wang, X.; Lin, K. S. K.; Chan, J. C. C.; Cheng, S. *J. Phys. Chem. B* **2005**, *109*, 1763). Aminopropyl-functionalized SBA-15 materials (denoted as SBA-NH2) were prepared by a one-pot synthesis method. Pluronic 123 (4 g) was dissolved in 125 g of 2.0 M HCl solution at room temperature. After TEOS was added, the resultant solution was equilibrated at 40 °C for prehydrolysis, and then APTES was slowly added into the solution. The molar composition of the mixture was 0.9 TEOS: *0.1* APTES: 6.1 HCl: 0.017 P123:165 H2O. The resulting mixture was stirred at 40 °C for 20 h and then reacted at 90 °C under static condition for 24 h. The solid product was recovered by filtration and dried at room-temperature overnight. The template was removed from the material by refluxing in excess ethanol for 24 h. Finally, the material was filtered, washed several times with water and ethanol, and dried at 50 °C.

Preparation of SBA-15 cobalt(II) catalyst:

Salicylaldehyde (2 mmol, 0.244 g) was added to excess absolute MeOH, to which Aminopropyl-functionalized SBA-15 materials (2.35 g, loading of NH_2 group is 0.85 mmol/g) was then added. The solution became yellow due to imine formation. After 6 h, cobalt(II) acetate, $Co(OAc)_2{\cdot}2H_2O$ (1 mmol, 0.248 g), was added to the solution, and the mixture was stirred for a further 24 h to allow the new ligands to complex the cobalt and a color change from pink to olive green was observed. The final product was washed with MeOH and water until the washings were colorless. Further drying of the solid product was carried out in an oven at 80°C for 8 h.

The loading achieved is about 0.3 mmolg-1, as determined from the 11.5% loss in mass between 200 and 600^{o}C.

General procedure for the Strecker reaction of aldehydes, Ketimines, and ketiminum salts using Co/SBA-15 catalyst: To the mixture of aldehyde (1 mmol), amine (1 mmol), and catalyst Co/SBA-15 **(**34 mg; ~1mol% Co/SBA-15) in sealed tube, trimethylsilyl cyanide (1.1 mmol) was added and the mixture was stirred at room temperature and the appropriate time as indicated in Table 2. The reaction was monitored by TLC. After the completion of the reaction, the reaction mixture was diluted with ethyl acetate and filtrated to obtain the crude product. In some cases the crude product was purified by column chromatography on silica gel to afford the pure related α-amino nitrile in good to excellent yields (Table 2, 3).

General procedure for the Strecker reaction of Ketimines and ketiminum salts using Co/SBA-15 catalyst: To the mixture of **Ketimine or ketiminum salt** (1 mmol) and catalyst Co/SBA-15 (34 mg; ~1mol% Co/SBA-15) in sealed tube, trimethylsilyl cyanide (1.2 mmol) was added at 40 °C and the mixture was stirred at appropriate time as indicated in Table 3. The reaction was monitored by TLC. After the completion of the reaction, the reaction mixture was diluted with ethyl acetate and filtrated to obtain the crude product. In some cases the crude product was purified by column chromatography on silica gel to afford the pure related α-amino nitrile in good to excellent yields (Table 4).

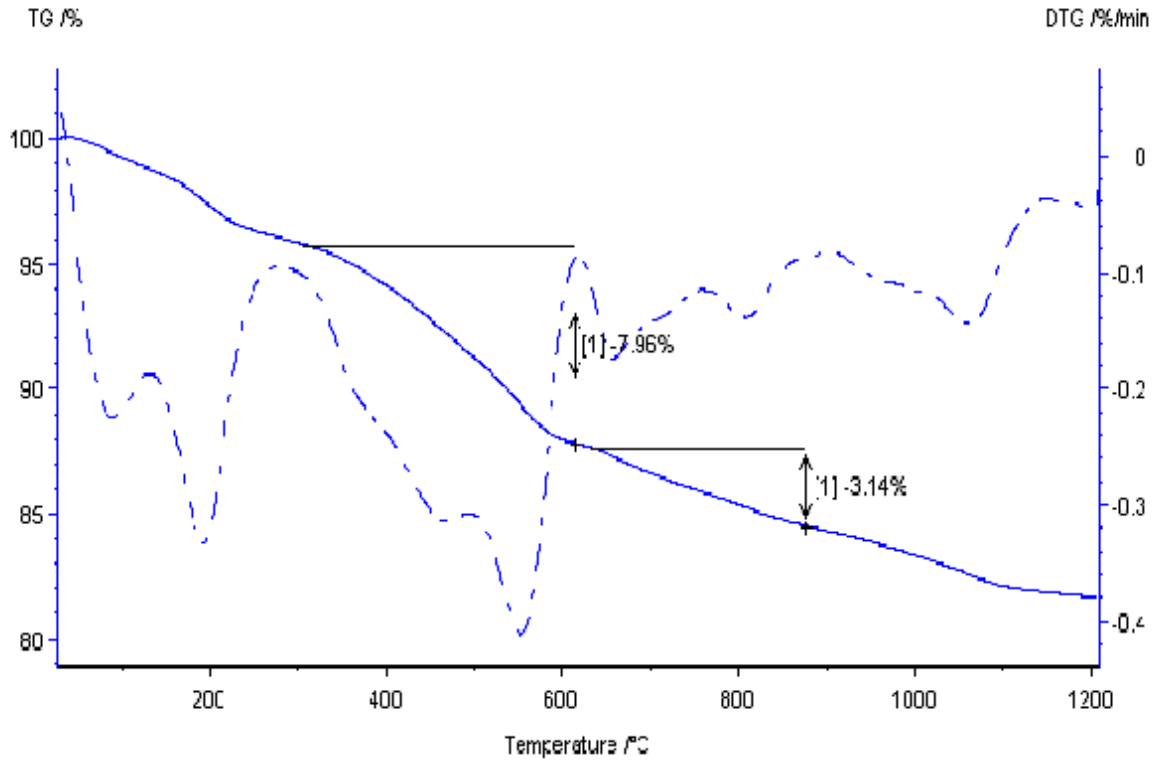

Figure 1S. TGA of Co/SBA-15 catalyst

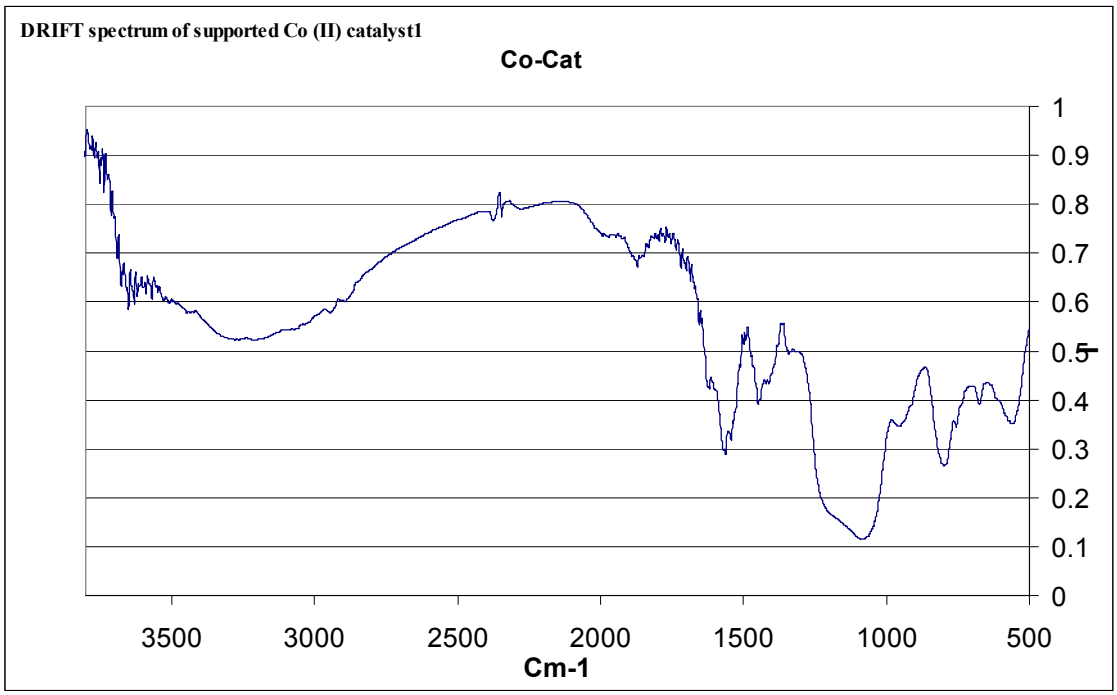

Figure 2S. DRIFT spectrum of Co/SBA-15 catalyst

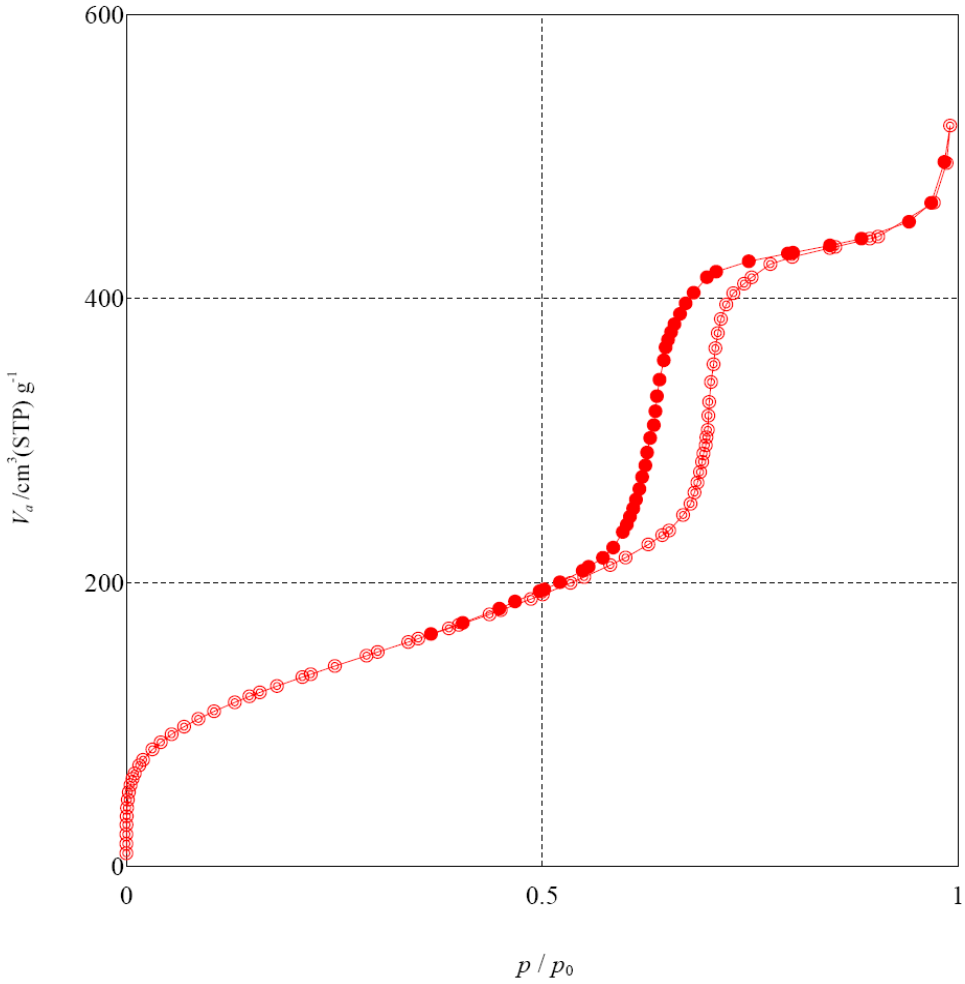

Figure 3S. Isotherm profile of the Co/SBA-15 catalyst.

Final products obtained isolated and subsequently purified by column chromatography on silica-gel, eluting with ethyl acetate/light petroleum. All compounds were characterized by their IR and NMR. Some results are included as follows:

Table 2 (Entry 1): ^{1}H-NMR (500 MHz, $CDCl_3$, 25 ºC, TMS): δ = 7.54-7.56 (m, 2H), 7.37-7.43 (m, 3H), 5.07 (s, 1H), 2.65-2.73 (m, 4H), 1.86-1.89 (m, 4H).

Table 2 (Entry 3): ^{1}H-NMR (500 MHz, $CDCl_3$, 25 ºC, TMS): δ = 8.19-8.20 (m, 1H), 7.70-7.73(m, 1H), 7.45-7.50 (m, 1H), 4.82(s, 1H) ,3.47-3.50 (t, 4H, J= Hz), 1.76-1.86 (t, 4H); ^{13}C-

NMR(125 MHz,$CDCl_3$, 25 ºC, TMS): δ = 148.2, 139.0, 133.5, 129.9, 124.7, 122.6, 117.1, 66.1, 49.8, 46.8, 26.7, 24.7.

Table 3 (Entry 2): ^{1}H-NMR (500 MHz, $CDCl_3$, 25 ºC, TMS): δ = 8.25-8.27 (d, 2H, J=6.8 Hz), 7.54-7.56 (d, 2H, J=6.8 Hz), 4.45 (s, 1H), 3.72 (m, 2H), 3.96 (m,2H), 1.54 (m, 4H), 1.25-1.26 (m, 2H)); ^{13}C-NMR(125 MHz,$CDCl_3$, 25 ºC, TMS): δ = 134.7, 129.1, 128.0, 114.2, 59.6, 50.5, 30.1, 23.9.

Table 3 (Entry 3): ^{1}H-NMR (500 MHz, $CDCl_3$, 25 ºC, TMS): δ = 8.50 (s, 1H), 8.26-8.28 (m, 1H), 7.94-7.96 (m, 1H), 7.62-7.65 (m, 1H), 4.92(s, 1H) ,2.55-2.57 (m, 4H), 1.65-1.70 (m, 4H), 1.54-1.56 (m, 2H); ^{13}C-NMR(125 MHz,$CDCl_3$, 25 ºC, TMS): δ = 133.9, 130.2, 124.3, 114.9, 62.8, 26.1, 24.1.

Table 3 (Entry 4): ^{1}H-NMR (500 MHz, $CDCl_3$, 25 ºC, TMS): δ = 7.30-7.34 (m, 2H), 7.22-7.25 (m, 3H), 3.36-3.39 (t, 1H, J=7.9 Hz), 2. 85 (m, 1H), 2.79 (m, 1H), 2.67(m, 2H), 2.40 (m, 2H), 2.10-2.40(m, 2H), 1.65-1.70 (m, 4H), 1.54-1.56 (m, 2H); ^{13}C-NMR(125 MHz,$CDCl_3$, 25 ºC, TMS): δ = 140.4, 129.0, 128.7, 126.8, 117.4, 57.8, 51.3, 32.9, 32.2, 26.3, 24.6.

Table 3 (Entry 5): ^{1}H-NMR (500 MHz, $CDCl_3$, 25 ºC, TMS): δ = 7.86-7.91 (m, 3H), 7.54-7.55 (m, 2H), 4.99 (s, 1H), 2.57-2.59 (m, 4H), 1.62-1.68 (m, 4H), 1.51-1.53 (t, 2H, J= 5.6 Hz).

Table 3 (Entry 7): ^{1}H-NMR (500 MHz, $CDCl_3$, 25 ºC, TMS): δ = 7.55-7.56 (m, 2H), 7.38-7.45 (m, 3H), 5.32 (s, 1H), 3.70-3.78 (m, 4H), 2.60-2.62 (t, 4H, J= 4.4Hz); ^{13}C-NMR(125 MHz,$CDCl_3$, 25 ºC, TMS): δ = 133.0, 129.5, 129.3, 128.4, 115.5, 67.0, 62.8, 50.4.

Table 3 (Entry 9): ^{1}H-NMR (500 MHz, $CDCl_3$, 25 ºC, TMS): δ = 8.25-8.27 (m, 2H), 7.72-7.74(d, 1H, J= 7.7Hz), 7.60-7.63 (m, 1H), 4.92(s, 1H) ,3.70-3.72 (t, 4H, J=4.8 Hz), 3.21-3.23 (t, 4H, J=4.8 Hz); ^{13}C-NMR(125 MHz,$CDCl_3$, 25 ºC, TMS): δ = 148.5, 137.3, 133.5, 130.3, 125.0, 122.7, 114.5, 67.1, 66.0, 43.1.

Table 3 (Entry 11): ^{1}H-NMR (500 MHz, $CDCl_3$, 25 ºC, TMS): δ = 7.37-7.51 (m, 9H), 4.39(m, 1H), 4.25-4.29 (m, 1H), 1.63-1.65 (m, 1H), 1.42-1.44 (d, 3H, J=6.5 Hz); ^{13}C-NMR(125 MHz,$CDCl_3$, 25 ºC, TMS): δ = 144.1, 135.3, 134.2, 131.3, 129.4, 129.2, 128.9, 128.3, 127.2, 127.1, 118.9, 57.3, 52.2, 25.2.

Table 3 (Entry 12): ^{1}H-NMR (500 MHz, $CDCl_3$, 25 ºC, TMS): δ = 8.36-8.38 (d, 2H, J=8.3 Hz), 8.21-8.23 (d, 2H, J=8.3 Hz), 4.02-4.05 (m, 1H), 2.20 (s, 2H), 1.75-1.81(m, 2H), 1.38-1.40 (d, 3H, J=5.7Hz), 0.94-0.98(m, 3H); ^{13}C-NMR (125 MHz,$CDCl_3$, 25 ºC, TMS): δ = 138.3, 128.9, 126.3, 124.4, 113.2, 66.8, 66.6, 31.2, 31.1, 21.8, 11.2.

Table 4 (Entry 1): ^{13}C-NMR (125 MHz, CDCl3, 25 ºC, TMS): δ = 119.9, 68.6, 61.9, 48.0, 46.1, 42.4, 34.5, 27.4, 26.7, 25.4, 24.7, 23.0, 22.7, 22.4.

Table 4 (Entry 3): ^{13}C-NMR (125 MHz, CDCl3, 25 ºC, TMS): δ = 122.5, 57.6, 44.0, 42.4, 38.3, 36.5, 27.4, 25.5, 24.9, 22.9, 22.8.

Table 4 (Entry 5): ^{13}C-NMR (125 MHz, CDCl3, 25 ºC, TMS): δ = 116.9, 57.8, 22.8, 31.3, 2.3.

Table 4 (Entry 7): ^{1}H-NMR (500 MHz, $CDCl_3$, 25 ºC, TMS): δ = 7.65-7.67 (d, 2H, J=7.3Hz), 7.42-7.44 (m, 2H), 7.36-7.39 (m, 1H), 6.94-6.95 (d, 2H, J=8.3Hz), 6.47-6.48 (d, 2H, J=8.3Hz), 2.25 (s, 3H) ,1.97 (s, 3H); ^{13}C-NMR(125 MHz,$CDCl_3$, 25 ºC, TMS): δ = 130.0, 129.6, 128.9, 125.4, 116.8, 57.8, 33.7, 20.9.

Table 4 (Entry 11): ^{1}H-NMR (500 MHz, $CDCl_3$, 25 ºC, TMS): δ = 7.07-7.09 (d, 2H, J=8.4Hz), 6.86-6.87 (d, 2H, J=8.4Hz), 3.74 (brs, 1H), 2.33 (s, 3H), 1.99-2.02 (m, 1H), 1.88-1.91 (m, 1H), 1.62 (s, 3H), 1.18-1.21 (t, 3H, J= 7.5 Hz); ^{13}C-NMR(125 MHz,$CDCl_3$, 25 ºC, TMS): δ = 141.5, 131.1, 130.2,130.1, 121.6, 119.9, 115.6, 54.5, 34.0, 25.5, 21.0, 9.0.