Supplementary Material (ESI) for Green Chemistry

ELECTRONIC SUPPORTING INFORMATION (ESI)

Versatile Co(II)-heterogeneously catalysed C-heteroatom forming reactions

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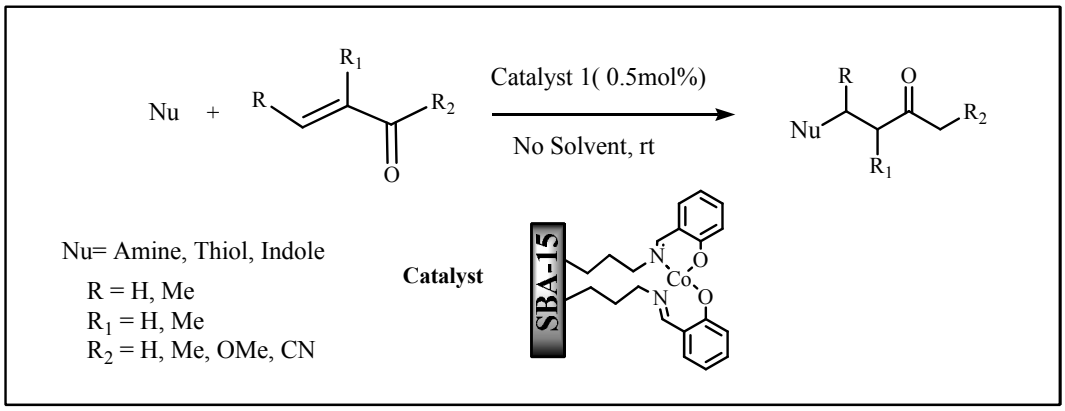

Scheme 1. Michael addition of thiols, indoles and amines to α,β-unsaturated using a supported cobalt(II)/SBA-15 catalyst under solventless conditions.

Preparation of the supported catalyst

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-NH_2) 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 H_2O. The resulting mixture was stirred at 40°C for 20 h and then reacted at 90°C 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°C. Final material has been denoted as Co/SBA-15 in both text and ESI.

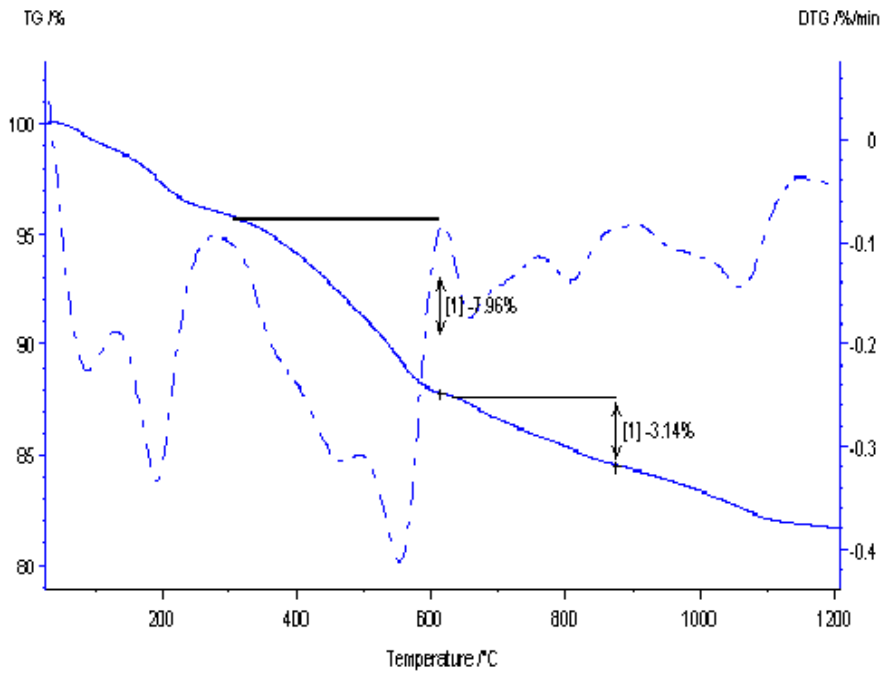

Figure 1S. TGA of Co/SBA-15 catalyst

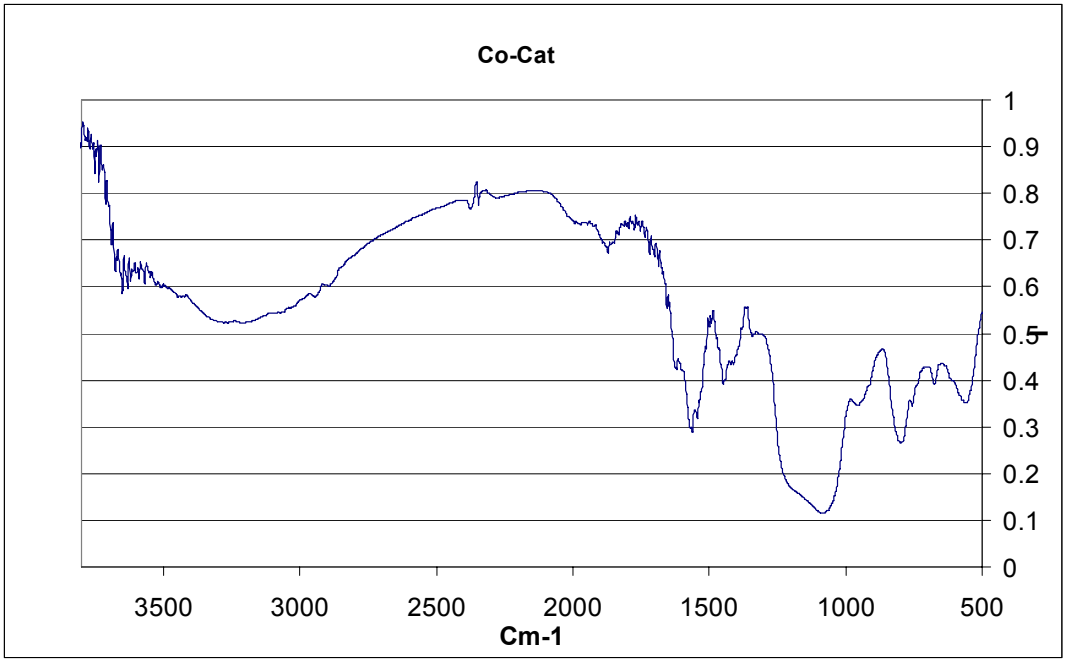

Figure 2S. DRIFT spectrum of Co/SBA-15 catalyst

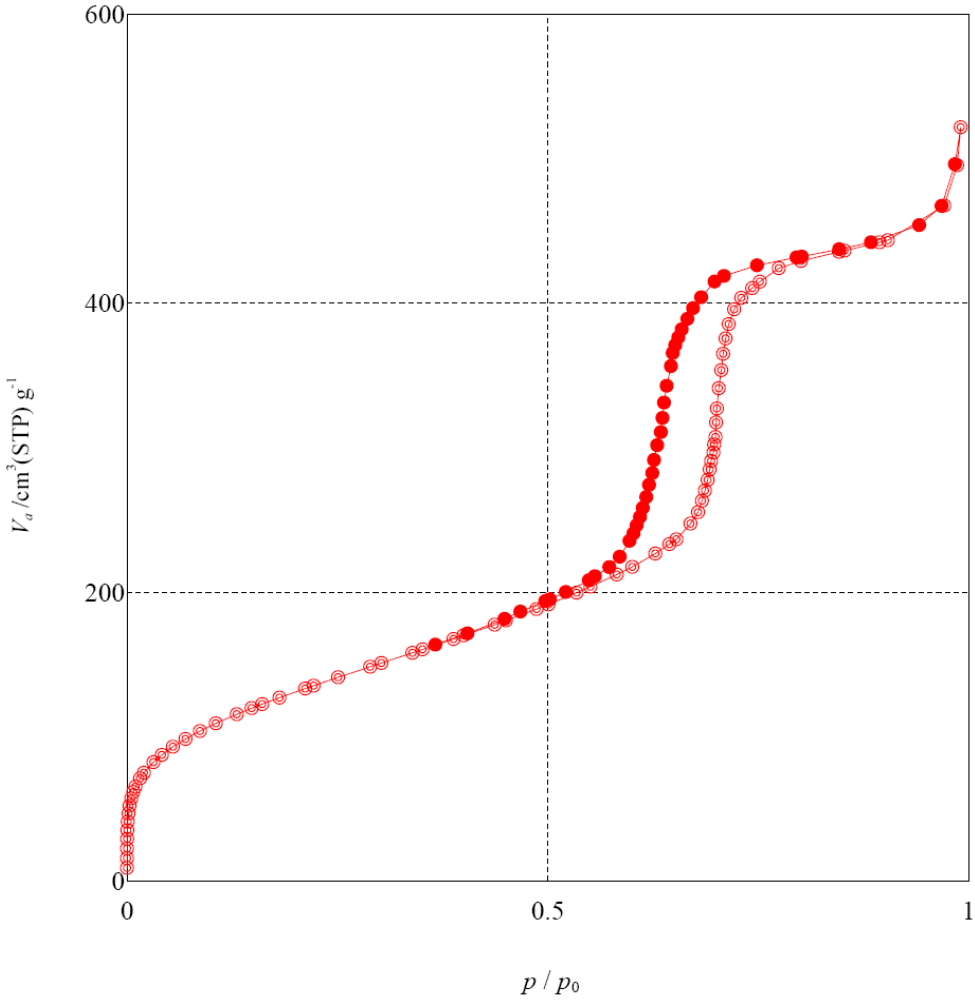

Figure 3S. Isotherm profile of the Co/SBA-15 catalyst.

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, NMR, and MS spectra. Results are included as follows:

4-(3-Indolyl)-2-butanone.white solid, mp 93-95 ^{0}C; ^{1}H NMR ($CDCl_3$): δ, 2.18 (s, 3H), 2.98 (t, *J* = 7.5 Hz, 2H), 3.10 (t, *J* = 7.5Hz, 2H), 7.01 (m, 1H), 7.11-8.00 (m, 5H). IR (KBr): υ, 3315.2, 2908.3, 1702.6, 1474.5, 1461.5, 736.4 cm^{-1}.

4-(3-*N*-Methylindolyl))-2-butanone. Oil; ^{1}H NMR ($CDCl_3$): δ,2.19 (s, 3H), 2.87 (t, *J*=7.4 Hz, 2H), 3.09 (t, *J*=7.4Hz, 2H), 3.79 (s, 3H), 6.88 (s, 1H), 7.15 (td, *J*=7.3, 0.4Hz, 1H), 7.26 (td, *J*=7.4, 0.4Hz, 1H), 7.31 (dd, *J*= 8.6, 0.4Hz, 1H), 7.61 (dd, *J*=8.1, 0.4Hz, 1H).

4-Thiophenyl-2-butanone. Oil; ^{1}H NMR ($CDCl_3$): δ, 2.18 (s, 3H), 2.77 (t, *J* = 7.3, 2H), 3.17 (t, *J* = 7.3 Hz, 2H), 7.18-7.38 (m, 5H).

4-(4-Methoxythiophenyl)-2-butanone. Yellow oil, ^{1}H NMR ($CDCl_3$): δ, 2.17 (s, 3H), 2.59 (t, *J* = 7.4 Hz, 2H), 2.91 (t, *J* = 7.4 Hz, 2H), 3.67 (s, 3H), 6.76 (dm, *J* = 10.2 Hz, 2H), 7.21 (dm, *J* = 10.2 Hz, 2H). ^{13}C NMR ($CDCl_3$): δ, 29.5, 29.6, 42.8, 54.9, 114.2, 114.3, 125.1, 128.7, 133.1, 133.4, 206.4. MS: 210 (M^{+}), 153, 140, 125, 108, 96, 71, 43 (100). IR (KBr): υ, 3056.4, 2943.6, 1716.5, 1593.8, 1247.8, 1183.2, 1033.9, 746.5 cm^{-1}.

3-Thiophenyl butanal. Oil, ^{1}H NMR ($CDCl_3$): δ, 1.36 (d, *J* = 6.8 Hz, 3H), 2.54-2.60 (ddd, *J* = 17.3, 9.5, 1.5, 1H), 2.66-2.71 (ddd, *J* = 17.2, 9.5, 1.5), 3.69 (m, 1H), 7.25-7.33 (m, 3H), 7.42-7.43 (m, 2H), 9.73 (t, *J* = 1.5 Hz, 1H).

Methyl 3-thiophenylpropionate. Colorless oil; ^{1}H NMR ($CDCl_3$): δ, 2.45 (t, *J* = 7.4 Hz, 2H), 3.03 (t, *J* = 7.4 Hz, 2H), 7.03-7.06 (m, 1H), 7.11-7.14 (m, 2H), 7.27-8.00 (m, 2H). IR (KBr): υ, 3031.5, 2951.3, 1739.1, 1581.2, 1479.1, 1441.2, 1404.2, 1250.8, 1174.5, 1021.1, 772.7 cm^{-1}.

Methyl 3-(4-methoxythiophenyl)propionate. Yellow oil, ^{1}H NMR ($CDCl_3$): δ, 2.48 (t, *J* = 7.3 Hz, 2H), 2.96 (t, *J* = 7.2 Hz, 2H), 3.58 (s, 3H), 3.71 (s, 3H), 6.76 (dm, *J* = 8.8 Hz, 2H), 7.28 (dm, *J* = 8.8 Hz, 2H). ^{13}C NMR ($CDCl_3$): δ 30.9, 34.2, 51.5, 55.1, 114.5, 114.8, 124.9, 126.3, 128.1, 134.0, 174.5. MS: 226 (M^+, 100), 195, 166, 153, 139, 124, 108, 96, 87, 69, 59, 45. IR (KBr): υ, 2954.5, 1737.4, 1599.2, 1497.1, 1439.6, 1247.8, 916.6, 729.2 cm^{-1}.

3-(4-Methoxylthiophenyl)cyclohexanone. Colorless oil; ^{1}H NMR ($CDCl_3$): δ, 1.57-1.58 (m 2H), 2.01-2.02 (m, 2H), 2.22-2.23 (m, 3H), 2.49-2.54 (m, 1H), 3.14 (m, 1H), 6.77 (dm, *J* = 8.3 Hz, 2H), 7.28 (dm, *J* = 8.4 Hz, 2H). ^{13}C NMR ($CDCl_3$): δ, 23.7, 30.9, 40.5, 46.7, 47.4, 55.0, 114.3, 114.5, 122.6, 132.3, 136.1, 159.7, 208.7. MS: 236(M^+), 140 (100), 125, 97, 69, 55, 41. IR (KBr): υ, 2954.1, 1716.7, 1591.9, 1492.3, 1252.3, 1173.7, 734.5 cm^{-1}.

3-(4-Methoxylthiophenyl)cyclopentanone. Colorless Oil; ^{1}H NMR ($CDCl_3$): δ, 2.11-2.45 (m, 6H), 3.65 (m, 1H), 3.68 (s, 3H), 6.73 (dm, *J* = 8.1 Hz, 2H), 7.27 (dm, *J* = 8.2 Hz, 2H). ^{13}C NMR ($CDCl_3$): δ, 28.8, 36.4, 44.3, 44.7, 55.0, 114.2, 114.3, 123.6, 132.9, 134.9, 135.5, 216.2. MS: 222 (M^+), 140 (100), 125, 96, 83, 69, 55, 39. IR (KBr): υ, 3045.3, 2965.6, 1743.7, 1593.4, 1492.5, 1247.9, 734.8 cm^{-1}.

4-(2-Butanthio)-2-butanone: White oil, ^{1}H NMR ($CDCl_3$): δ, 0.72 (t, *J* = 7.3 Hz, 3H), 1.00 (d, *J* = 6.8 Hz, 3H), 1.23-1.37 (m, 2H), 1.91 (s, 3H), 2.41-2.50 (m, 5H). ^{13}C NMR ($CDCl_3$): δ, 11.6, 21.0, 24.2, 29.7, 29.8, 42.4, 44.1, 206.1. IR (KBr): υ, 2961.5, 1717.0, 1463.4, 1369.2, 1230.8, 1161.5, 923.9, 800.0, 738.4 cm^{-1}.

4-(1-Butanthio)-2-butanone: Brown oil, ^{1}H NMR ($CDCl_3$): δ, 0.79 (t, *J* = 7.3 Hz, 3H), 1.26-1.30 (m, 2H), 1.41-1.45(m, 2H), 2.05 (s, 3H), 2.40 (t, *J* = 7.3 Hz, 3H), 2.59-2.61 (m, 4H). ^{13}C NMR ($CDCl_3$): δ, 11.2, 19.3, 22.2, 26.1, 30.1, 30.3, 44.0, 207.1. IR (KBr): 2962.3, 1718.0, 1465.7, 1368.4, 1231.1, 1163.5, 921.7, 798.8, 736.1 cm^{-1}.

3-(Methyl (phenyl) amino)propanenitrile: Brown oil, ^{1}H NMR ($CDCl_3$): δ, 2.58-2.61(t, *J* = 7.1 Hz, 2H), 3.08 (s, 3H), 3.79-3.82 (t, *J* = 7.1 Hz, 2H), 6.75-7.32 (m, 5H). ^{13}C NMR ($CDCl_3$): ^{13}C NMR ($CDCl_3$): δ, 15.3, 39.2, 49.0, 112.8, 117.9, 118.7, 129.9, 147.8.

Methyl 3-(methyl (phenyl) amino)propanoate: Yellow oil, ^{1}H NMR ($CDCl_3$): δ, 2.60-2.64 (t, *J* = 7.1 Hz, 2H), 2.97 (s, 3H), 3.71-3.76 (m, 5H), 6.78-7.32 (m, 5H). ^{13}C NMR ($CDCl_3$): δ, 31.9, 38.6, 49.1, 520, 112.5, 116.8, 129.9, 149.1, 173.2.

Methyl 3-(4- methoxy phenylamino)propanoate: Brown solid, ^{1}H NMR ($CDCl_3$): δ, 2.61-2.65 (t, *J* = 6.8 Hz, 2H), 3.39-3.43 (t, *J* = 6.8 Hz, 2H), 3.71 (br s, 1H), 3.71 (s, 3H), 6.60-6.62 (d, *J* = 9.4 Hz, 2H), 6.78-6.81 (d, *J* = 9.4 Hz, 2H). ^{13}C NMR ($CDCl_3$): δ, 32.9, 40.2, 51.8, 56.1, 114.3, 114.9, 141.8, 152.7, 173.2. IR (KBr):υ, 3390.1, 3040.2, 2997.8, 2950.6, 2835.5, 1734.9, 1621.2, 1514.8, 1463.0, 1440.2, 1365.8, 1239.5, 1176.8, 1122.0, 1095.1, 1036.5, 825.1 cm^{-1}.

Bis- (2, 4-(3-oxobutyl))pyrrol: ^{1}H NMR ($CDCl_3$): δ, 2.13 (s, 6H), 2.78-2.83 (m, 8H), 5.73 (d, *J* = 2.5 Hz, 2H), 8.70 (br s, 1H). ^{13}C NMR ($CDCl_3$): δ, 23.9, 30.4, 44.3, 105.2, 130.7, 209.6.

Methyl 3-(3-(N-methylindolyl))-propanoate: ^{1}H NMR ($CDCl_3$): δ, 2.71-2.75 (t, *J* = 7.6 Hz, 2H), 3.09-3.13 (t, *J* = 7.6 Hz, 2H), 3.68 (s, 3H), 3.73 (s, 3H), 6.87 (s, 1H), 7.12-7.28 (m, 3H), 7.63 (d, *J* = 7.6 Hz, 1H). ^{13}C NMR ($CDCl_3$):
δ, 20.4, 32.3, 34.8, 51.2, 109.1, 112.9, 118.4, 121.1, 126.0, 127.2, 136.8, 173.3. MS: 217 (M^+), 145, 144 (100), 143, 131, 130, 77. (KBr):υ, 2935.1, 2910.3, 2840.5, 1730.1, 1545.4, 1460.4, 1425.7, 1370.5, 1315.6, 1180.8, 1155.2, 1125.0, 1110.5, 1060.4, 731.1 cm^{-1}.