

Supplementary Information

Nanoporous Aluminosilicate Catalyzed Friedel-Crafts Alkylation Reactions of Indoles with Aldehydes and Acetals

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General Experimental Details

Benzaldehyde dimethyl acetal and cyclohexanone diethyl acetal were purchased from commercial suppliers and used without further purification. All acetals were synthesised using reported procedures. Flash chromatography was carried out using Merck Kieselgel 60 H silica or Matrex silica 60. Analytical thin layer chromatography (TLC) was carried out using aluminium-backed plates coated with Merck Kieselgel 60 GF254 that were visualized under UV light (at 254 and/or 360 nm) or using potassium permanganate solution (1% in water) followed by charring. Infra-red (IR) spectra were recorded between 4000-600 cm^{-1} as neat oils or solids and are reported in cm^{-1} . Nuclear magnetic resonance (NMR) spectra were recorded at either 400 or 270 MHz in CDCl_3 at 25 °C and are reported in ppm; J values are recorded in Hz and multiplicities are expressed by the usual conventions. Low-resolution mass spectra (MS) were determined using the ionization technique stated. High resolution mass spectra (HRMS) were obtained courtesy of the EPSRC Mass Spectrometry Service, Swansea University using the ionization method specified. Removal of solvent refers to evaporation at reduced pressure using a rotary evaporator followed by the removal of trace volatiles using a vacuum pump. Specific surface areas were obtained by the BET method at liquid nitrogen temperatures using a Micromeritics Gemini or a Quantachrome Autosorb-1 automated gas sorption instrument. Samples were degassed at 120 °C under a flow of helium for 2 hours prior to analysis. Pore sizes were obtained using a Quantachrome Autosorb-1 automated gas sorption instrument. Samples were degassed at room temperature under a stream of helium for 3 hours prior to analysis. Pore sizes were calculated from the desorption branch of the isotherm by the BJH $Dv(d)$ method. Elemental compositions were obtained with a JOEL scanning electron microscope fitted with an EDX detector using a 20 KeV accelerating voltage.

Typical Procedure for the Synthesis of Acetals using Indium Triflate

Indium triflate (5.8 mg, 1 mol%) was added to a mixture of 4-nitrobenzaldehyde (157 mg, 1.04 mmol) and trimethyl orthoformate (220 mg, 2.08 mmol) in dichloromethane (15 mL) and the reaction mixture was stirred at room temperature for 5 minutes. The mixture was then passed through a short plug of neutral alumina which was washed with additional dichloromethane (2 x 5 mL) and the solvent removed under reduced pressure to give *4-nitrobenzaldehyde dimethyl acetal*¹ as a colorless oil; ν_{max} (film)/ cm^{-1} (neat) 2937, 2833, 1520, 1340, 1205, 1052, 853, 745 and 712; ^1H NMR (CDCl_3 ; 400 MHz) δ = 8.15 (2H, d, J = 9 Hz), 7.57 (2H, d, J = 9 Hz), 5.40 (1H, s), 3.27 (6H, s); ^{13}C NMR (CDCl_3 ; 100 MHz) δ = 148.4, 145.5, 128.2, 123.8, 102.0, 53.1; MS (EI) m/z 197; HRMS (ES) calculated for $\text{C}_9\text{H}_{11}\text{NO}_4$ ($\text{M} + \text{NH}_4$)⁺ 215.1026, found ($\text{M} + \text{NH}_4$)⁺ 215.1023.

Typical Procedure for the Synthesis of Acetals using Nanoporous Aluminosilicate AS-(13)

Benzaldehyde (106 mg, 1 mmol) was dissolved in methanol (10 mL) at room temperature. The AS-(13) catalyst (50 mg) was added and the reaction mixture stirred at room temperature for 3 hours. Upon completion of the reaction, the catalyst was removed by filtration through a Celite plug, which was washed with dichloromethane (2 x 5 mL), and the combined solvents removed to give *benzaldehyde dimethyl acetal*¹ as a clear oil; ν_{max} (film)/ cm^{-1} (neat) 2937, 2830, 1454,

1353, 1102, 1050, 743 and 698; ^1H NMR (CDCl_3 ; 400 MHz) $\delta = 7.52\text{--}7.33$ (5H, m), 5.43 (1H, s), 3.37 (6H, s); ^{13}C NMR (CDCl_3 ; 100 MHz) $\delta = 138.5, 128.9, 128.6, 127.1, 103.5, 53.0$; MS (EI) m/z 152; HRMS (EI) calculated for $\text{C}_9\text{H}_{11}\text{O}_2$ ($\text{M} - \text{H}$) $^+$ 151.0754, found ($\text{M} - \text{H}$) $^+$ 151.0756.

Benzaldehyde diethyl acetal:² ν_{max} (film)/ cm^{-1} (neat) 1705, 1205, 1050 and 700; ^1H NMR (CDCl_3 ; 400 MHz) $\delta = 7.45\text{--}7.20$ (5H, m), 5.42 (1H, s), 3.49 (4H, m), 1.15 (6H, t, $J = 7$ Hz); ^{13}C NMR (CDCl_3 ; 100 MHz) $\delta = 139.5, 128.7, 128.6, 127.1, 102.0, 61.4, 15.6$; MS (EI) m/z 180; HRMS (EI) calculated for $\text{C}_{11}\text{H}_{16}\text{O}_2$ (M) $^+$ 180.1145, found (M) $^+$ 180.1145.

4-Methoxybenzaldehyde dimethyl acetal:¹ ν_{max} (film)/ cm^{-1} (neat) 1614, 1512, 1247, 1098 and 822; ^1H NMR (CDCl_3 ; 400 MHz) $\delta = 7.30$ (2H, d, $J = 9$ Hz), 6.82 (2H, d, $J = 9$ Hz), 5.30 (1H, s), 3.73 (3H, s), 3.24 (6H, s); ^{13}C NMR (CDCl_3 ; 100 MHz) $\delta = 160.1, 130.7, 128.4, 114.8, 114.0, 55.7, 53.0$; MS (EI) m/z 182; HRMS (EI) calculated for $\text{C}_{10}\text{H}_{14}\text{O}_3$ (M) $^+$ 182.0937, found (M) $^+$ 182.0935.

4-Methylbenzaldehyde dimethyl acetal:³ ν_{max} (film)/ cm^{-1} (neat) 1618, 1445, 1343, 1207, 1103, 1054 and 807; ^1H NMR (CDCl_3 ; 400 MHz) $\delta = 7.20$ (2H, d, $J = 8$ Hz), 7.00 (2H, d, $J = 8$ Hz), 5.20 (1H, s), 3.15 (6H, s), 2.20 (3H, s); MS (EI) m/z 166.

4-Bromobenzaldehyde dimethyl acetal:⁴ ν_{max} (film)/ cm^{-1} (neat) 1728, 1636, 1591, 1351, 1275, 1205, 1101, 1055 and 805; ^1H NMR (CDCl_3 ; 400 MHz) $\delta = 7.40$ (2H, d, $J = 8$ Hz), 7.20 (2H, d, $J = 8$ Hz), 5.35 (1H, s), 3.20 (6H, s); MS (EI) m/z 232.

Data for bisindolylalkanes

Bis(3-indolyl)-4-nitrophenylmethane:⁶ orange solid; m.p. 221–224°C; ν_{max} (film)/ cm^{-1} 3455, 1592, 1506, 1457, 1344, 1094, 854; ^1H NMR (CDCl_3 ; 400 MHz) $\delta = 8.20$ (2H, d, $J = 9$ Hz), 8.05 (2H, br s), 7.55 (2H, d, $J = 9$ Hz), 7.45–7.35 (4H, m), 7.25–7.20 (2H, m), 7.05–6.95 (2H, m), 6.60 (2H, s), 5.95 (1H, s); ^{13}C NMR (CDCl_3 ; 67 MHz) $\delta = 151.8, 146.5, 136.7, 129.5, 126.6, 123.6, 122.3, 119.6, 119.5, 118.1, 111.2, 40.2$.

Bis(3-indolyl)-4-methoxyphenylmethane:⁶ yellow solid; m.p. 190–192°C; ν_{max} (film)/ cm^{-1} 3392, 1610, 1509, 1455, 1335, 1244, 1172, 1092, 1010, 734; ^1H NMR (CDCl_3 ; 270 MHz) $\delta = 7.80$ (2H, br s), 7.30–7.40 (4H, m), 7.10–7.30 (4H, m), 6.95–7.05 (2H, m), 6.75–6.85 (2H, m), 6.60 (2H, m), 5.80 (1H, s), 3.80 (3H, s); ^{13}C NMR (CDCl_3 ; 67 MHz) $\delta = 157.8, 136.7, 136.2, 129.5, 127.0, 123.5, 121.9, 120.0, 119.9, 119.2, 113.5, 110.9, 55.19, 39.30$.

Bis(3-indolyl)-4-methylphenylmethane:⁷ orange solid; m.p. 95–97°C; ν_{max} (film)/ cm^{-1} 3478, 1511, 1456, 1337, 1091, 911, 750; ^1H NMR (CDCl_3 ; 400 MHz) $\delta = 7.70$ (2H, br s), 7.20 (2H, d, $J = 9$ Hz), 7.25–6.85 (10H, m), 6.67 (2H, m), 5.75 (1H, s), 2.25 (3H, s); $\delta = 140.9, 136.6, 135.5, 128.9, 128.5, 127.0, 123.5, 121.8, 119.9, 119.8, 119.1, 110.9, 39.7, 21.1$.

Bis(3-indolyl)-4-bromophenylmethane:⁸ red solid; m.p. 108–111°C; ν_{max} (film)/ cm^{-1} 3460, 1698, 1455, 1336, 1092, 904, 750; ^1H NMR (CDCl_3 ; 400 MHz) $\delta = 7.80$ (2H, br s), 7.35–7.05 (6H, m),

6.95–7.05 (2H, m), 6.65 (2H, s), 5.70 (1H, s); ^{13}C NMR (CDCl_3 ; 100 MHz) δ = 143.3, 136.7, 131.3, 130.5, 126.9, 123.8, 122.1, 119.9, 119.8, 119.3, 118.9, 111.3, 39.7.

1,1-Bis(3-indolyl)cyclohexane:⁷ yellow solid; m.p. 114–117°C; ν_{max} (film)/ cm^{-1} 3477, 1456, 1336, 1100, 908, 734; ^1H NMR (CDCl_3 ; 400 MHz) δ = 7.80 (2H, br s), 7.50 (2H, d, J = 8Hz), 7.20 (2H, d, J = 8Hz), 7.15 (2H, t, J = 8Hz), 7.05–7.0 (2H, m), 6.90 (2H, t, J = 8Hz), 2.55–2.45 (4H, m), 1.75–1.60 (6H, m); ^{13}C NMR (CDCl_3 ; 100 MHz) δ = 136.9, 126.6, 123.5, 121.9, 121.4, 121.2, 122.1, 118.6, 111.3, 39.7, 36.8, 26.6, 22.9.

Bis(5-bromo-3-indolyl)phenylmethane:⁷ red solid; m.p. 240–243°C; ν_{max} (film)/ cm^{-1} 3464, 1596, 1420, 1096, 895, 704; ^1H NMR (CDCl_3 ; 270 MHz) δ = 8.10 (2H, br s), 7.50 (2H, s), 7.30–7.10 (9H, m), 6.60 (2H, s), 5.70 (1H, s); ^{13}C NMR (CDCl_3 ; 67 MHz) δ = 143.0, 135.3, 128.6, 128.5, 128.4, 126.5, 125.0, 124.7, 122.3, 119.1, 112.7, 112.5, 39.9; MS (EI) m/z 477.

Catalyst Recycling Studies

The mesoporous catalyst AS-(13) (25 mg) was added to a stirred solution of benzaldehyde dimethyl acetal (76 mg, 0.5 mmol) and indole (117 mg, 1.0 mmol) in acetonitrile (10 mL). The reaction mixture was then heated to 60 °C and stirred for 2 hours. Upon completion of the reaction, the catalyst was isolated by filtration and washed with warm acetonitrile (2 x 5 ml) and dried at 100 °C prior to re-use. Product conversions were determined by ^1H NMR analysis of the crude reaction mixtures.

Entry	Number of cycles	Conversion (%) ^a
1	0	91
2	1	90
3	2	88

^[a] Determined by ^1H NMR analysis of the crude reaction mixture.

Figure 1: Representative BET Isotherm Data for AS-(13), AS-(56) and AS-(111)

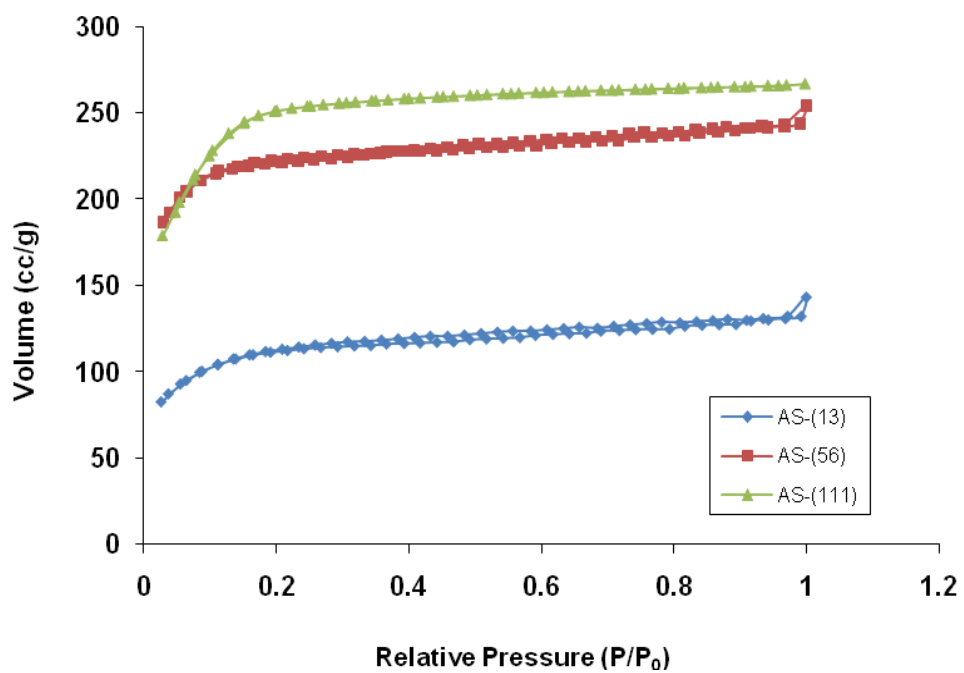


Figure 2: Pore size distribution of aluminosilicate catalysts

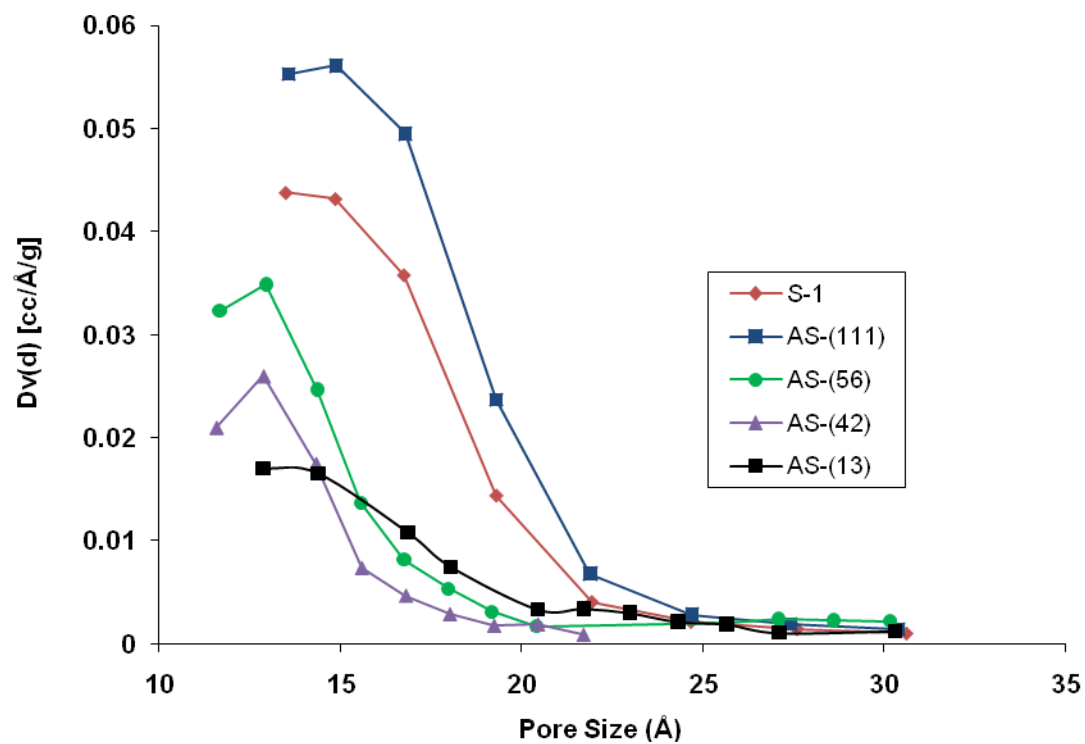


Figure 3a: ^{27}Al MAS NMR AS-(13)

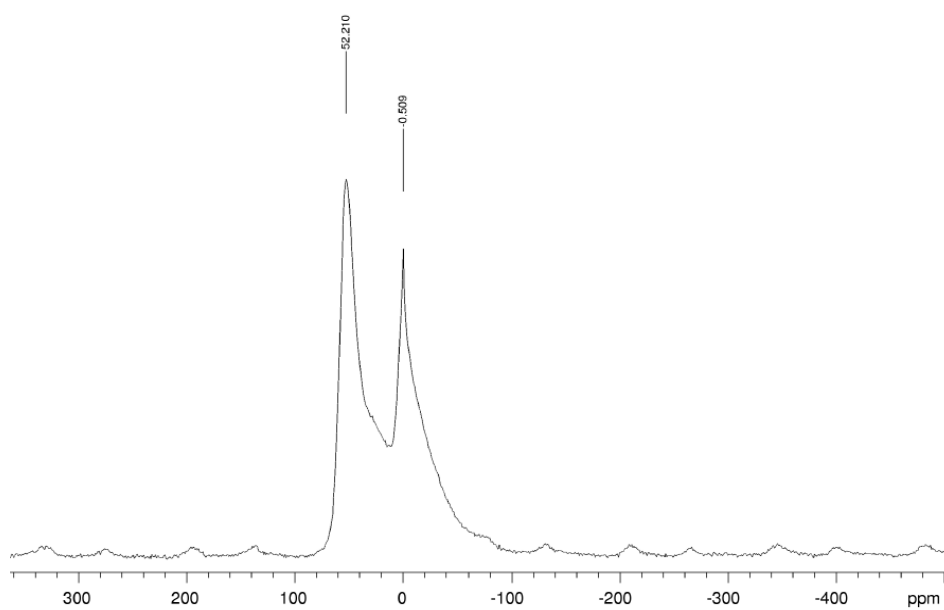


Figure 3b: ^{28}Si MAS NMR AS-(13)

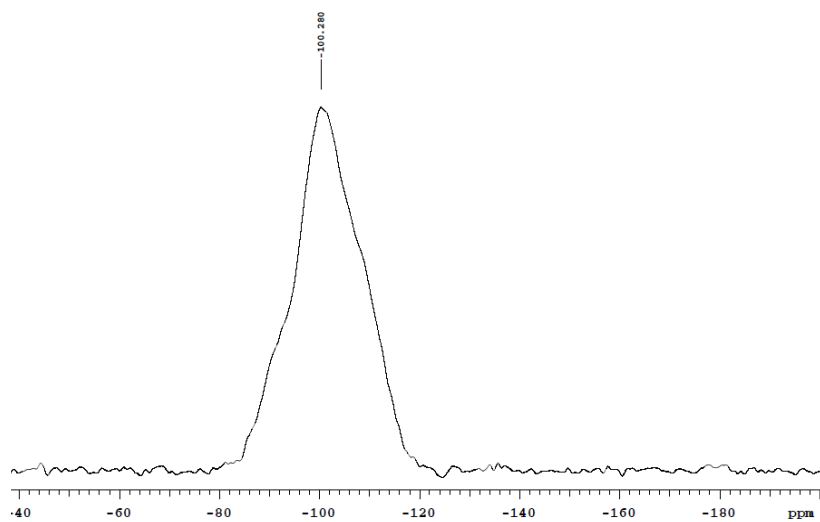
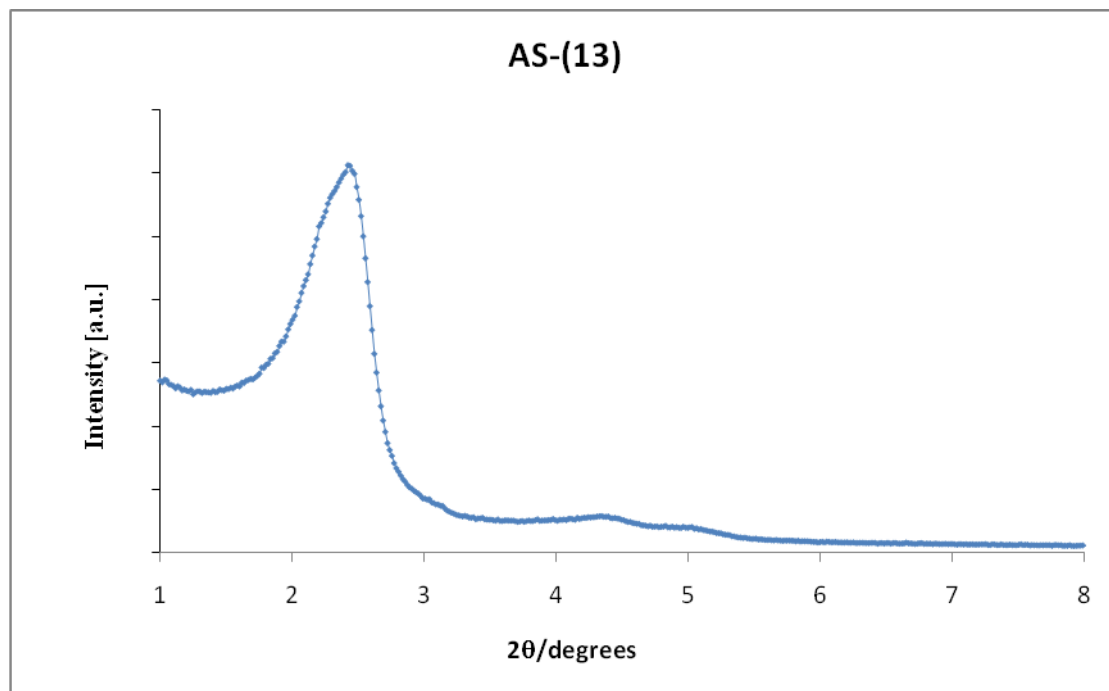


Figure 4: Representative XRD Data for calcined AS-(13)



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