Supplementary Material (ESI) for Chemical Communications

Supplementary Material for:

Balancing supramolecular reagents for reliable formation of co-crystals

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Experimental

Synthesis

Synthesis of 4-(1*H*-1-pyrazolylmethyl)benzonitrile
To a round-bottomed flask, pyrazole (1.5g, 22.1mmol) and THF (80ml) were added. To this solution, NaOH pellets (8.82g, 221mmol) were added and the reaction was stirred at room temperature. After two hrs, α-Bromo-4-tolunitrile (4.32g, 22.1mmol) in THF (80ml) was added and the reaction mixture stirred at room temperature overnight. On completion, water was added to dissolve any excess NaOH. The organic layer was separated, dried over $MgSO_4$ and the solvent removed under vacuum to yield a white solid (3.358g, 83.3%). Mp: 71-73°C. ^{1}H NMR (δ_H; 400MHz, $CDCl_3$): 5.392 (s, 2H), 6.339 (t, *J* = 2.2Hz, 1H), 7.234-7.254 (d, *J* = 8Hz, 2H), 7.442-7.448 (d, *J* = 2.4Hz, 1H), 7.581-7.586 (d, *J* = 2Hz, 1H), 7.615-7.636 (d, *J* = 8.4Hz, 2H); IR (KBr): 3111, 2939, 2223, 1619, 1500, 1447, 1387, 1275, 1076, 1036, 950, 824, and 744 cm^{-1}.

Synthesis of 4-(1*H*-1-pyrazolylmethyl)benzamide, **1**
To a round-bottomed flask, 4-(1H-1-pyrazolylmethyl)benzonitrile (2.858g, 15.60mmol) and 85% H_2SO_4 (12ml) were added. The mixture was heated to 80°C and stirred. After four hours, the solution was poured slowly over ice. The resulting brown solution was adjusted to basic pH using 5M NaOH. The aqueous solution was washed with $CHCl_3$ and the organic extracts were separated, dried over $MgSO_4$ and reduced to a white solid (2.627g, 83.7%). Mp: 154-156°C. ^{1}H NMR, (δ_H; 400MHz, $CDCl_3$): 5.400 (s, 2H), 5.570 (s, 1H), 6.020 (s, 1H), 6.330 (t, *J* = 4 Hz, *J* = 2 Hz, 1H), 7.260-7.280 (d, *J* = 8Hz, 2H), 7.430-7.436 (d, *J* = 2.4Hz, 1H), 7.586-7.590 (d, *J* = 1.6Hz, 1H), 7.779-7.800 (d, *J* = 4.4Hz, 2H); IR (KBr): 3370, 3171, 3018, 2925, 1659, 1407, 1301, 1142, 923, and 758 cm^{-1}.