

Supporting Information  
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# Nitrile synthesis through catalyzed cascades involving acid–nitrile exchange

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NMR spectra were recorded on an Avance 400 spectrometer, using  $\text{CDCl}_3$  solvent as reference and/or internal deuterium lock. Two-dimensional NMR spectroscopy [ $^1\text{H}$ - $^1\text{H}$  COSY spectra,  $^1\text{H}$ - $^{13}\text{C}$  COSY spectra (HSQC) and long-range  $^1\text{H}$ - $^{13}\text{C}$  COSY spectra (HMBC)], were carried out to determine the correlation between  $^1\text{H}$  and  $^{13}\text{C}$ . The chemical shifts for all NMR spectra are expressed in parts per million to high frequency of TMS reference. Coupling constants (J) are quoted in Hz and are recorded to the nearest 0.1 Hz. The IR spectra were obtained using ATR accessories. High-resolution (HR) mass spectra were performed on a GC/MS system spectrometer. TLC was carried out using precoated plates of silica gel 60F254.

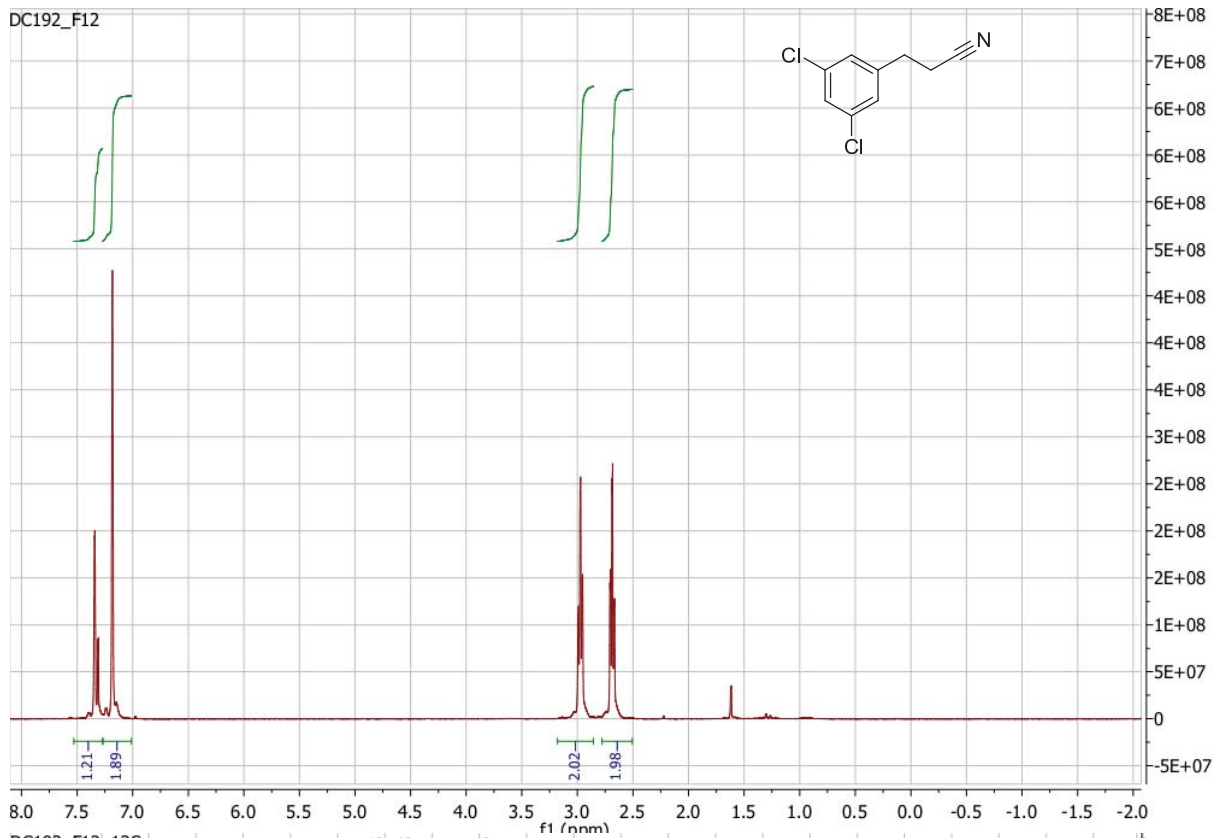
## General procedure for 2b and 2e:

In a glass tube, the dinitrile (3.0 mmol, 1.0 equiv.) is added to a mixture of acid (3.0 mmol) and aluminum trichloride (0.06 mmol, 0.02 equiv.). The tube is then sealed (with a screw cap) and the mixture is allowed to stir at 200 °C for 5 h. After completion, the crude reaction mixture is diluted with 10 mL of ethanol, 3 g of silica are then added to this crude material to make a solid deposit after evaporation of the ethanol. A silica gel column chromatography finally afforded the pure nitrile together with the cyclic imide.

**3-(3,5-dichlorophenyl)propanenitrile 2b:** white solid MP = 44 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.29 (s, 1H), 7.13 (s, 2H), 2.91 (t,  $J$  = 7.2 Hz, 2H), 2.63 (t,  $J$  = 7.2 Hz, 2H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  141.0, 134.9, 127.2, 126.7, 118.3, 30.5, 18.5. IR (thin film) 2247, 2217, 1590, 1566, 1431, 1101,  $\text{cm}^{-1}$ . HRMS (EI)  $m/z$  calcd for  $\text{C}_9\text{H}_7\text{Cl}_2\text{N}$ : 198.9956, found 198.9958.

**(E)-3-(3-methoxyphenyl)acrylonitrile 2e:** yellow oil.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.38-7.30 (m, 2H), 7.05-6.95 (m, 3H), 5.87 (d,  $J = 16.8$  Hz, 1H), 3.83 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  159.9, 150.5, 134.7, 130.1, 119.9, 118.0, 116.8, 112.4, 96.6, 55.3. IR (thin film) 2215, 1619, 1597, 1577, 1488, 1455, 1431, 1275, 1244, 1157, 1036  $\text{cm}^{-1}$ . HRMS (EI)  $m/z$  calcd for  $\text{C}_{10}\text{H}_9\text{NO}$ : 159.0684, found 159.0686.

DC192\_F12



DC192\_F12\_13C

